Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Reactive Imidazole Intermediates: Simplified Synthetic Approach to Functional Aliphatic Cyclic Carbonates

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Experimental

Materials and Methods: Vacuum flame-dried flasks were used for all synthetic procedures and all transformations were conducted under N_2-atmosphere. Trimethylolpropane (TMP), Dimethylolpropionic Acid (Bis-MPA) and Trimethylolpropane oxetane (TMPO) were acquired from Perstorp chemicals and used as received. 1,1'-Carbonyldiimidazole (CDI) was purchased from Carbosynth and used as received. HPLC grade Acetone and THF solvents were used for all synthetic transformations. Anhydrous dichloromethane (Merck) was used for all ROP reactions, and the catalyst/initiator stock-solutions were prepared and stored under heat/vacuum activated molecular sieves (3Å) in a N_2-atmosphere prior to polymerization. Silica gel, ultrapure, 40-60 µm, 60Å from Acros organics was used for all synthetic transformations and for silica gel column chromatography. Monomethoxylated PEG (1K) was purchased from Fluka and dried *in-vacuo* prior to use. Acetonide protected TMP[1] and Thiourea[2] was synthesized according to literature procedures. $CDCl_3$ used for NMR was stored under activated molecular sieves (3Å) prior to use. All other chemicals were purchased from Aldrich and used without further purification.

Instrumentation:

MALDI-TOF: THF/HABA/Na^+-matrix was used for sample preparation for MALDI-TOF analysis, concentration 1 mg/ml of sample in THF (20µL Matrix solution/5µL sample/2µL NaTFA (10 mg/ml) solution). The MALDI-TOF MS spectrum acquisitions were conducted on a Bruker UltraFlex MALDI-TOF MS with SCOUT-MTP Ion Source (Bruker Daltonics, Bremen) equipped with a N_2-laser (337nm), a gridless ion source and reflector design. All

spectra were acquired using a reflector-positive method with an acceleration voltage of 25kV and a reflector voltage of 26,3kV. The detector mass range was set to 500-10000 Da in order to exclude high intensity peaks from the lower mass range. The laser intensity was set to the lowest value possible to acquire high resolution spectra. The instrument was calibrated using SpheriCal™ calibrants purchased from Polymer Factory Sweden AB. A THF solution of HABA or DHB (10 mg/mL) doped with sodium trifluoroacetate was used as matrix. The obtained spectra were analyzed with FlexAnalysis Bruker Daltonics version 2.2 and Polytools version 1.0.

HRMS-ESI: HRMS-ESI experiments were performed by direct inlet on a Bruker MicroTOF instrument, using positive ion mode. Capillary voltage set to 4500 V, end plate offset -500 V, nebulizer 0.3 Bar, dry heater 180 °C and dry gas 4.0 l/min. The obtained spectra were analyzed with Bruker Compass Data Analysis 4.0 software.

Size Exclusion Chromatography (SEC): A TOSOH EcoSECHLC-8320GPC system equipped with an EcoSES RI detector and three columns from PSS GmbH was used (PSS PFG 5 µm; Microguard, 100 Å and 300 Å). The mobile phase was DMF with 0.01M LiBr (0.2mL min^{-1}) at 50°C using a conventional calibration method with narrow linear polymethylmethacrylate (PMMA) standards.

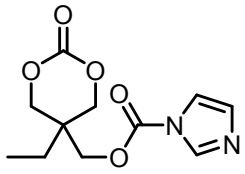
^{1}H NMR and ^{13}C NMR: NMR experiments were performed on a Bruker Avance 400 MHz NMR instrument. Proton NMR spectra were acquired with a spectral window of 20 ppm, an acquisition time of 4 seconds, a relaxation delay of 1 second. ^{13}C NMR spectra were acquired with a spectral window of 240 ppm, an acquisition time of 0.7 seconds, a relaxation delay of 2 seconds. For all NMR experiments, the $CDCl_3$ solvent peak reference was set to 7.26 ppm for ^{1}H-NMR and 77.0 ppm (middle peak) for ^{13}C-NMR.

DSC: Differential scanning calorimetry (DSC) was performed using a Mettler Toledo DSC820. A heating and cooling rate of 10 °C min^{-1} was used. Starting from room temperature (-50 °C), the sample was heated to 100 °C, cooled to −50 °C, and then heated to 100 °C. Analyses regarding midpoint T_g were performed on the second heating scan.

Synthesis of functional carbonates

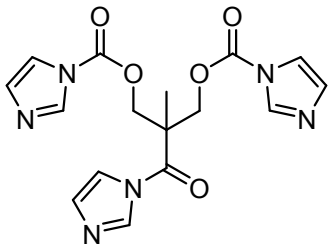
Synthesis of TMP-imidazole-carbonate (1). Trimethylolpropane (TMP) (50 g, 0.37 mol) was dissolved in acetone (900 mL) by stirring at room temperature for 5 minutes (N_2-atm). The flask was put under constant N_2-flow, using a long needle, and equipped with a powder funnel on top of the needle. Then, 1,1'-Carbonyldiimidazole (CDI) (140 g, 0.86 mol) was added in portions by spatula, under a constant N_2-flow, over a period of 1 hour at 20 °C, with high stirring (900 rpm). Each addition was done after the solution had turned homogenous following the previous addition. After complete addition, a white cloudy solution began to form, and stirring was maintained for an additional 1 hour at room temperature. The stirring was then after discontinued and the mixture was allowed to stand for 1 hour at room temperature. A white precipitate was collected by filtration, washed with Et_2O (2x300 ml), transferred to a 1L rb-flask and dried under vacuum vacuo. The product **1** was obtained as a fluffy white powder (61.2 g, 65% yield). ^{1}H NMR ($CDCl_3$) δ ppm: 1.00 (t, 3H, J=7.7Hz, -C**H**$_3$), 1.59 (q, 2H, J=7.7 Hz, -C**H**$_2$-CH_3), 4.29 (d, geminal J=11.1 Hz, 2H, up-C**H**$_1$-OCO-), 4.35 (d, geminal J=11.1 Hz, 2H, down-C**H**$_{1'}$-OCO-), 4.50 (s, 2H, -C**H**$_2$-OCON-), 7.09 (s, 1H, imidazole-**H**), 7.40 (s, 1H, imidazole-**H**), 8.12 (s, 1H, imidazole-**H**). ^{13}C NMR ($CDCl_3$) δ ppm: 7.3, 23.7, 34.9, 66.6, 72.2, 116.9, 131.2, 136.9,

147.6, 148.2. Calculated: $C_{11}H_{14}N_2NaO_5$ $[M+Na]^+$ m/z = 277.07949 Found: HRMS-ESI: $[M+Na]^+$ m/z = 277.08001 Error (ppm): 1.88



(1)

Synthesis of 2,2-(diimidazolemethylol) imidazole propionic acid (DIMIPA) (2b). 2,2-Dimethylolpropionic Acid (Bis-MPA) (50.00 g, 0.37 mol) was dispersed in THF (1.3 L), by stirring at ambient temperature for 10 minutes (N_2-atm). The flask was put under constant N_2-flow, using a long needle, and equipped with a powder funnel on top of the needle. Then, CDI (200.0 g, 1.23 mol) was added in portions by spatula, under a constant N_2-flow, over a period of 1 hour with high stirring (900 rpm). Shortly after complete addition, a white cloudy solution began to form, and stirring was maintained for an additional 1 hour at room temperature. Thereafter, stirring was interrupted and the mixture was allowed to stand for 1 hour at room temperature. The white precipitate was collected by filtration, washed one time with THF:Et_2O (1:1) (300 ml), then with Et_2O (2x300 ml), transferred to a 1L round-bottomed flask and dried in vacuo. The product **2b** was obtained as a fluffy white powder (93.0g, 67% yield). ^1H NMR ($CDCl_3$) δ ppm: 1.72 (s, 3H, -C**H**$_3$), 4.84 (s, 4H, -C**H**$_2$-OCON-), 7.07 (s, 2H, -CH_2-OCON-imidazole-**H**), 7.16 (s, 1H, -C-CON-imidazole-**H**), 7.31 (s, 2H, -CH_2-OCON-imidazole-**H**), 7.60 (s, 1H, -C-CON-imidazole-**H**), 8.05 (s, 2H, -CH_2-OCON-imidazole-**H**), 8.34 (s, 1H, -C-CON-imidazole-**H**). ^{13}C NMR ($CDCl_3$) δ ppm: 18.1, 48.8, 68.1, 116.6, 116.8, 131.3, 131.5, 136.7, 136.9, 147.8, 168.6. Calculated: $C_{16}H_{17}N_6O_5$ $[M+H]^+$ m/z = 373.12549 Found: HRMS-ESI: $[M+Na]^+$ m/z = 373.12455 Error (ppm): 2.54



(2b)

General procedure for synthesis of functionalized TMP-carbonates (3a-e)

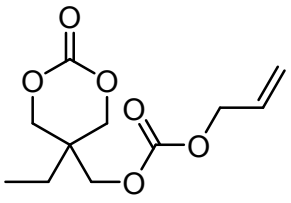
A 250 ml round-bottomed flask (flame dried), with a stir bar, was charged with **1** (10.0g, 39.3 mmol), and acetone (150 ml). Then, the appropriate alcohol (32 mmol) was added under stirring at room temperature (N_2-atm). CsF (100 mg, 0.66 mmol) was then after added and the resulting mixture was allowed to stir for the specified time and temperature under N_2-atm. Subsequently, the formed clear solution was diluted by addition of Et_2O (100 ml), filtered through a plug of silica, and then eluted by additional Et_2O (300 ml). The filtrate was concentrated on a rotary evaporator and the crude product was purified by silica gel column chromatography using Heptane:EtOAc (1:1) as the eluent unless otherwise noted. The isolated cyclic carbonate products were characterized by their ^{1}H- and ^{13}C-NMR (See Figure S1-S14) spectra as well as HRMS(ESI) for new compounds. The reported isolated yields were all based on the parent alcohol.

General procedure for synthesis of functionalized bis-MPA- carbonates (4a-e)

A 250 ml round-bottomed flask (flame dried), with a stir bar, was charged with **DIMIPA** (**2b**) (10.0g, 26.9 mmol), and acetone (150 ml). Then, the appropriate alcohol (24.2 mmol) was added under stirring at room temperature (N_2-atm). The resulting mixture was allowed to stir for the allotted time at 50°C under N_2-atm. To the formed clear solution SiO_2 (10.0g) and triethylamine (1.0g, 9.88 mmol) were added and the resulting mixture was allowed to stir for 4 hours at 50°C, where the reaction progress was monitored by ^{1}H-

NMR once every hour. After complete substitution, the reaction mixture was diluted by addition of Et_2O (100 ml), filtered through a plug of silica, and eluted by additional Et_2O (300 ml). The filtrate was concentrated on a rotary evaporator and the crude product was purified by silica gel column chromatography using Heptane:EtOAc (1:1) as the eluent. The fractions containing the products were combined and concentrated *in-vacuo*. The isolated cyclic carbonate products were characterized by their ^{1}H- and ^{13}C-NMR spectra (See Figure S15-S24) as well as HRMS(ESI) for new compounds. The reported isolated yields were all based on the parent alcohol.

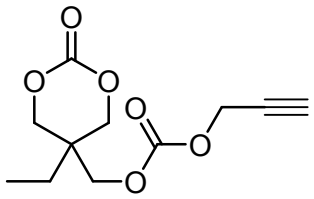
Synthesis of allyl-TMP-carbonate (3a). Synthesis was carried out according to the general procedure above at 20°C for 16 hours. The product was purified by column chromatography using EtOAc/Heptane 1/1, and obtained **3a** as a transparent viscous oil (5.99 g, 78% yield). The ^{1}H- and ^{13}C-NMR spectra were in well correspondence with literature values.[3] ^{1}H NMR ($CDCl_3$) δ ppm: 0.94 (t, 3H, J=7.8 Hz, -C**H**$_3$), 1.56 (q, 2H, J=7.8 Hz, -C**H**$_2$-CH_3), 4.19 (m, 4H, -C-C**H**-OCO_2-, C-C**H**$_2$-OCO_2 pendant), 4.31 (d, 2H, geminal J=11.1 Hz, -C-C**H**-OCO2-), 4.64 (d, 2H, J=6.0 Hz, -O-C**H**$_2$-CH=CH_2), 5.30 (d, 1H, J=10.4 Hz, cis -O-CH_2-CH=C**H**$_2$), 5.36 (d, 1H, J=17.2 Hz, trans -O-CH_2-CH=C**H**$_2$), 5.92 (ddt, 1H, J=17.2 Hz, 10.4 Hz, 6.0 Hz, -O-CH_2-C**H**=CH_2). ^{13}C NMR ($CDCl_3$) δ ppm: 7.2, 23.1, 34.9, 65.5, 68.9, 72.0, 119.5, 131.0, 147.8, 154.4.



(3a)

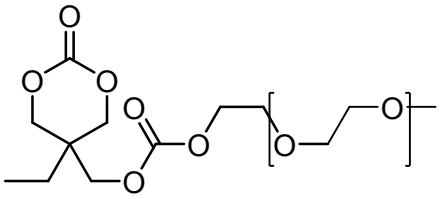
Synthesis of propargyl-TMP-carbonate (3b). Synthesis was carried out according to the general procedure above at 20°C for 16 hours. The product was purified by column

chromatography in EtOAc/Heptane 1/1 and obtained **3b** as a white solid (6.73 g, 84% yield). ^{1}H NMR ($CDCl_3$) δ ppm: 0.95 (t, 3H, J=7.7 Hz, -C**H**$_3$), 1.57 (q, 2H, J=7.7 Hz, -C**H**$_2$-CH_3), 2.56 (t, J=2.5 Hz, 1H, -O-CH_2-C≡C**H**), 4.20 (m, 4H, -C-C**H**-OCO_2-, C-C**H**$_2$-OCO_2 pendant), 4.31 (d, 2H, geminal J=11.1 Hz, -C-C**H**-OCO2-), 4.75 (d, 2H, J=2.5 Hz, -O-C**H**$_2$-C≡CH). ^{13}C NMR ($CDCl_3$) δ ppm: 7.2, 23.1, 34.9, 55.8, 65.9, 71.9, 76.2, 76.4, 147.7, 154.0. Calculated: $C_{11}H_{14}NaO_6$ $[M+Na]^+$ m/z = 265.06826 Found: HRMS-ESI: $[M+Na]^+$ m/z = 265.06909 Error (ppm): 3.15.



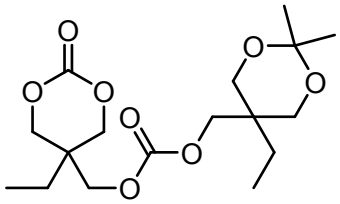
(3b)

Synthesis of MeOPEG-TMP-carbonate (3c). Synthesis was carried out according to the general procedure above, using MeOPEG-OH (M_n=1 kDa, Đ=1.03) (10 g, 10.0 mmol), **1** (4.00 g, 15.7 mmol) and CsF (50 mg, 0.33 mmol) in acetone (80 ml) at 20 °C for 20 hours. The silica filtration was performed without prior dilution with Et_2O, and was then eluted by addition of extra acetone (400 ml). After concentrating the filtrate on a rotary evaporator, the product was purified by precipitation of a concentrated acetone solution into stirring Et_2O (1L). The white precipitate was collected by filtration and washed several times with Et_2O, then dried *in-vacuo* to give **3c** as a white solid (8.60 g, 69% yield). ^{1}H NMR ($CDCl_3$) δ ppm: 0.93 (br, 3H, -CH_2-C**H**$_3$), 1.55 (br, 2H, -C**H**$_2$-CH_3), 3.36 (s, 3H, -PEG-OC**H**$_3$), 3.62 (br, 90H, -O-C**H**$_2$-C**H**$_2$-O-), 4.16 (m, 4H, -C-C**H**-OCO_2-, -C-C**H**$_2$-OCO_2- pendant), 4.30 (m, 4H, -C-C**H**-OCO_2-, -O-CH_2-C**H**$_2$-OCO_2- PEG carbonate end). ^{13}C NMR ($CDCl_3$) δ ppm: 7.0, 22.8, 34.7, 58.8, 65.2, 67.3, 68.5, 70.3, 71.7, 71.8, 147.6, 154.4. MALDI-TOF (See Fig. S37). SEC(DMF): M_n = 1.46 kDa, Đ = 1.26 (using PEG calibration instead of PMMA).



(3c)

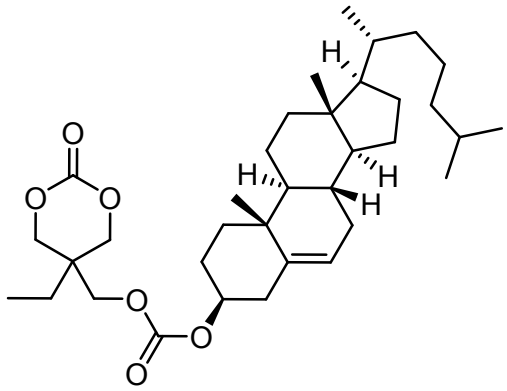
Synthesis of acetonide-TMP-carbonate (3d). Synthesis was carried out according to the general procedure above, using acetonide protected TMP (1.00 g, 5.74 mmol), **1** (2.19 g, 8.61 mmol) and CsF (174 mg, 1.14 mmol) in acetone (50 ml) at 20°C for 20 hours. The product was purified by column chromatography in EtOAc/Heptane 30/70 and obtained **3d** as transparent viscous oil, which solidified upon standing (1.20 g, 58% yield). ^{1}H NMR ($CDCl_3$) δ ppm: 0.84 (t, J=7.6 Hz, acetal part -CH_2-C**H**$_3$), 0.96 (t, 3H, J=7.6 Hz, carbonate part -CH_2-C**H**$_3$), 1.32 (q, 2H, J=7.6 Hz, acetal part -C**H**$_2$-CH_3), 1.39 (s, 3H, C**H**$_3$-C-O-), 1.42 (s, 3H, C**H**$_3$-C-O-), 1.57 (q, J=7.6 Hz, 2H, carbonate part -C**H**$_2$-CH_3), 3.66 (s, 4H, C-C**H**$_2$-O-), 4.17 (s, 2H, acetonide part -OCO_2-C**H**$_2$-C-), 4.19 (d, 2H, geminal J= 11.2 Hz, -C-C**H**-OCO_2-), 4.32 (m, 4H, -C-C**H**-OCO_2-, carbonate part -OCO_2-C**H**$_2$-C-), 4.75 (d, 2H, J=2.5 Hz,). ^{13}C NMR ($CDCl_3$) δ ppm: 7.2, 23.1, 34.9, 55.8, 65.9, 71.9, 76.2, 76.4, 147.7, 154.0. Calculated: $C_{17}H_{28}NaO_8$ $[M+Na]^+$ m/z = 383.16764 Found: HRMS-ESI: $[M+Na]^+$ m/z = 383.16780 Error (ppm): 0.42.



(3d)

Synthesis of cholesterol-TMP-carbonate (3e). Synthesis was carried out according to the general procedure above using cholesterol (3.0 g, 7.76 mmol), **1** (4.0 g, 15.73 mmol) in acetone (50 ml) at 50 °C for 24 hours, with the addition of CsF (100 mg, 0.66 mmol). After silica filtration, the product was purified by column chromatography using

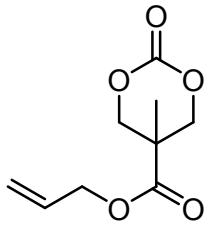
EtOAc/Heptane 1/2 to obtain **3e** as a white solid (3.60 g, 81 % yield). ^{1}H NMR ($CDCl_3$) δ ppm: 0.66 (s, 3H, -C-C**H**$_3$), 0.83-2.10 (m, 43H, cholesterol backbone, carbonate -C**H**$_2$-C**H**$_3$), 2.39 (m, 2H, -OCO_2-CH-C**H**$_2$-CR=CHR), 4.14 (s, 2H, -OCO_2-C**H**$_2$-C-), 4.18 (d, 2H, geminal J=10.9 Hz, -C-C**H**-OCO_2-), 4.31 (d, 2H, geminal J=10.9 Hz, -C-C**H**-OCO_2-), 4.47 (m, 1H, -OCO_2-CH-C**H**$_2$-), 5.39 (s, 1H, -CH=C-). ^{13}C NMR ($CDCl_3$) δ ppm: 7.2, 11.8, 18.7, 19.2, 21.0, 22.5, 22.8, 23.1, 23.8, 24.2, 27.6, 28.0, 28.2, 31.7, 31.8, 34.9, 35.7, 36.1, 36.5, 36.8, 37.9, 39,5, 39.6, 42.2, 49.9, 56.1, 56.6, 65.1, 72.0, 78.6, 123.1, 139.0, 147.8, 154.0. Calculated: $C_{35}H_{56}NaO_6$ $[M+Na]^+$ m/z = 595.39691 Found: HRMS-ESI: $[M+Na]^+$ m/z = 595.39894 Error (ppm): 3.40.



(3e)

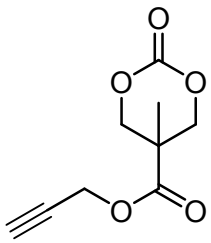
Synthesis of allyl-Bis-MPA-carbonate (4a). Synthesis was carried out according to the general procedure above, using allyl alcohol (1.83 g, 31.44 mmol) and CsF (100 mg, 0.66 mmol) together with **BIMIPA 2b** (10.0 g, 26.9 mmol), and acetone (150 ml) at 20°C for 16 hours. Then, was added SiO_2 (10.0g), and triethylamine (1.0 g, 9.88 mmol) and the resulting mixture was allowed stirred for 4 hours at 50°C. After silica filtration, the product was purified by column chromatography in EtOAc/Heptane 1/1 obtaining **4a** as a fluffy white powder (2.50 g, 50 % yield). The ^{1}H- and ^{13}C-NMR spectras were in well correspondence with literature values.[4] ^{1}H NMR ($CDCl_3$) δ ppm: 1.32 (s, 3H, C**H**$_3$), 4.20 (d, geminal J=10.8 Hz, 2H, C-C**H**-OCO), 4.69 (m, 4H, C-C**H**-OCO and CH_2=CH-C**H**$_2$-O),

5.28 (d, 1H, J=10.4 Hz, cis C**H**$_2$=CH-CH$_2$-O), 5.32 (d, 1H, J=17.2 Hz, trans C**H**$_2$=CH-CH$_2$-O), 5.92 (m, 1H, CH$_2$=C**H**-CH$_2$-O). ^{13}C NMR ($CDCl_3$) δ ppm: 17.5, 40.2, 66.6, 72.9, 119.4, 130.9, 147.4, 170.7.



(4a)

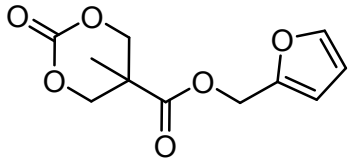
Synthesis of propargyl-Bis-MPA-carbonate (4b). Synthesis was carried out according to the general procedure above, using propargyl alcohol (1.83 g, 32.63 mmol) together with **BIMIPA 2b** (10.0g, 26.9 mmol), and acetone (150 ml) for 16 hours at 50°C. Then, was added SiO_2 (10.0 g), and triethylamine (1.0g, 9.88 mmol) and the resulting mixture was allowed stirred for 4 hours at 50°C. After silica filtration, the product was purified by column chromatography in EtOAc/Heptane 1/1 yielding **4b** as a fluffy white powder (6.73 g, 85 % yield). The ^{1}H- and ^{13}C-NMR spectras were in well correspondence with literature values.[4] ^{1}H NMR ($CDCl_3$) δ ppm: 1.33 (s, 3H, C**H**$_3$), 2.52 (t, J=2.5 Hz, 1H, C**H**≡C-), 4.21 (d, geminal J=10.8 Hz, 2H, C-C**H**-OCO), 4.69 (d, 2H, geminal J=10.8 Hz, C-C**H**-OCO), 4.77 (m, 1H, CH≡C-C**H**$_2$-O). ^{13}C NMR ($CDCl_3$) δ ppm: 17.3, 40.2, 53.4, 72.7, 75.9, 147.2, 170.3.



(4b)

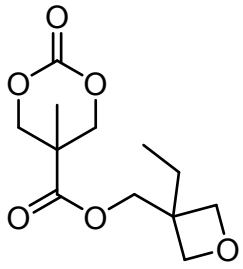
Synthesis of furfuryl-Bis-MPA-carbonate (4c). Synthesis was carried out according to the general procedure above, using furfuryl alcohol (2.37 g, 24.17 mmol) together with

BIMIPA 2b (10.0g, 26.9 mmol), and acetone (150 ml) at 50°C for 16 hours. Then, was added SiO_2 (10.0g), and triethylamine (1.0g, 9.88 mmol) and the resulting mixture was allowed stirred for 4 hours at 50°C. After silica filtration, the product was purified by column chromatography in EtOAc/Heptane 1/1 yielding **4c** as a faint yellow solid (3.73 g, 64 % yield). ^{1}H NMR ($CDCl_3$) δ ppm: 1.30 (s, 3H, C**H**$_3$), 4.18 (d, geminal J=10.8 Hz, 2H, C-C**H**-OCO), 4.67 (d, 2H, geminal J=10.8 Hz, C-C**H**-OCO), 5.16 (s, 1H, furane-C**H**$_2$-O), 6.36 (s, 1H, furfuryl-**H**), 6.42 (s, 1H, furfuryl-**H**), 7.42 (s, 1H, furfuryl-**H**). ^{13}C NMR ($CDCl_3$) δ ppm: 17.4, 40.2, 59.4, 72.8, 110.6, 111.3, 143.6, 147.3, 148.2, 170.7. Calculated: $C_{11}H_{12}NaO_6$ $[M+Na]^+$ m/z = 263.05261 Found: HRMS-ESI: $[M+Na]^+$ m/z = 263.05281 Error (ppm): 0.76.



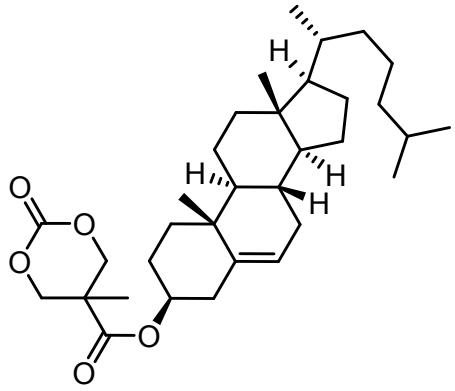
(4c)

Synthesis of oxetane-Bis-MPA-carbonate (4d). Synthesis was carried out according to the general procedure above, using TMPO (2.27 g, 19.54 mmol) and together with **BIMIPA 2b** (11.0 g, 26.9 mmol), acetone (150 ml) and CsF (100 mg, 0.66 mmol) at 50°C for 47 hours. Then, was added SiO_2 (10.0 g), and triethylamine (1.0 g, 9.88 mmol) and the resulting mixture was allowed stirred for 4 hours at 50°C. After silica filtration, the product was purified by column chromatography in EtOAc/Heptane 1/1 yielding **4d** as a transparent oil that solidified upon standing (2.37 g, 47 % yield). ^{1}H NMR ($CDCl_3$) δ ppm: 0.92(t, *J* = 7.5Hz, 3H, -CH_2-C**H**$_3$), 1.36(s, 3H, C-C**H**$_3$), 1.75(q, *J* = 7.5Hz, 2H, -C**H**$_2$-CH_3), 4.22(d, *J* = 10.9Hz, 2H, geminal C-C**H**-OCO), 4.36(s, 2H, -C**H**$_2$-O-CO-), 4.45(s, 4H, -C**H**$_2$-O-C**H**$_2$-), 4.72(d, *J* = 10.9Hz, 2H, geminal C-C**H**-OCO). ^{13}C NMR ($CDCl_3$) δ ppm: 8.00, 17.3, 26.7, 40.3, 42.6, 67.7, 72.8, 77.4, 147.2, 171.1. Calculated: $C_{12}H_{18}NaO_6$ $[M+Na]^+$ m/z = 281.09956 Found: HRMS-ESI: $[M+Na]^+$ m/z = 281.09930 Error (ppm): 0.93.



(4d)

Synthesisof cholesterol-bis-MPA-carbonate (4e). Synthesis was carried out according to the general procedure above, using cholesterol (3.18 g, 8.23 mmol), **BIMIPA 2b** (3.50 g, 9.40 mmol) and CsF (100 mg, 0.66 mmol) in THF (50 ml) at 50°C temperature for 16 hours. Then, was added SiO_2 (3.5 g), (no NEt_3 was added), and the resulting mixture was allowed stirred for 36 hours at 50°C. After silica filtration, the product was purified by column chromatography (two times) using EtOAc/Heptane 1/2 yielding **4e** as a white solid (2.80 g, 34 % yield). ^{1}H NMR ($CDCl_3$) δ ppm: 0.67 (s, 3H, -C-C**H**3), 0.85 (d, J=1.8 Hz, 3H, -CH-C**H**3), 0.87(s, 3H, -CH-C**H**3), 0.91 (d, J=6.5 Hz, C**H**3-CH), 0.93-1.69 (m, 30H), 1.76-1.91 (m, 4H), 1.93-2.07 (m, 2H), 2.33 (m, 2H), 4.18 (d, 2H, J=10.9 Hz), 4.67 (d, 2H, J=10.9 Hz,), 4.71 (m, 1H), 5.38 (s, 1H). ^{13}C NMR ($CDCl_3$) δ ppm: 11.8, 17.4, 18.6, 19.2, 21.0, 22.5, 22.8, 23.8, 24.2, 27.4, 27.9, 28.1, 31.7, 31.8, 35.7, 36.1, 36.5, 36.7, 37.7, 39,4, 39.6, 40.1, 42.2, 49.9, 56.0, 56.6, 73.0, 75.9, 123.2, 138.9, 147.5, 170.4. Calculated: $C_{33}H_{52}NaO_5$ $[M+Na]^+$ m/z = 551.37070 Found: HRMS-ESI: $[M+Na]^+$ m/z = 551.37094 Error (ppm): 0.45.



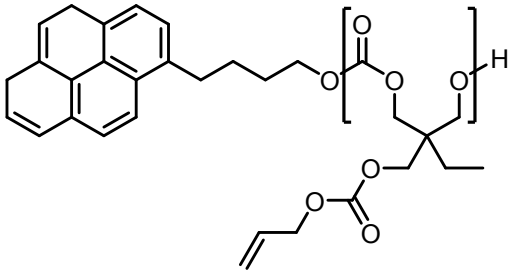
(4e)

General procedure for ROP reactions of carbonates

A vacuum flame-dried vial (3ml) with a stir bar, was charged with cyclic carbonate monomer (0.15 mmol), and was then put under vacuum at 20°C and was back-filled three times with N_2-1atm over 16h, where after the vial was put under N_2-atm. A stock-solution of DBU:TU (1:1) (0.0075 mmol, 5 mol%) and pyrenebutanol initiator (0.003 mmol), was added by syringe (N_2-atm). The reaction mixture was stirred for the specified times at 20°C. Thereafter, the reaction was quenched by addition of a solution (0.1 ml CH_2Cl_2 with acetic acid 10 mg), stirring for 15 minutes at 20°C, where after the mixture was concentrated in vacuum. A crude aliquot was analyzed to measure monomer conversion by ^{1}H-NMR($CDCl_3$), and SEC(DMF) to measure molecular number weight (M_n) and Đ. The crude polymer was purified by precipitating a concentrated CH_2Cl_2 solution into a stirring methanol solution (50 ml). The precipitated polymer was collected by decantation of the methanol solution, followed by washing two times with additional methanol (2x5ml), and then dried *in-vacuo*. The resulting polycarbonates were characterized by their ^{1}H-NMR spectra (See Figure S15-S33), SEC(DMF) for molecular weight analysis and DSC for thermal behavior. NMR-molcular weights were obtained by integration of relevant polymer peaks against the pyrene end-group (9H) (7.83-8.28 ppm).

Synthesis of poly(allyl-TMP-carbonate), p3a. The polymerization was carried out according to the general procedure, (20°C, 6h). The polymer product was collected as transparent sticky solid. ^{1}H NMR ($CDCl_3$) δ ppm: 0.90 (br, 3H, -C**H**$_3$), 1.52 (br, 2H, -C**H**$_2$CH$_3$), 4.11 (br, 6H, -O-C**H**$_2$- (chain+pendant), 4.61 (br, 2H, -CH$_2$=CH-C**H**$_2$O-), 5.27 (d, 1H, J=10.4 Hz, cis-C**H**$_2$=CH-CH$_2$O-), 5.35 (d, 1H, J=17.2 Hz, trans-C**H**$_2$=CH-CH$_2$O-), 5.93 (m, 1H, CH$_2$=C**H**-CH$_2$O-), 7.84-8.29 (m, 0.21H (9H), Pyrene-endgroup). M_n(theo)=10.3

kDa, M_n(NMR)= 10.8 kDa, M_n SEC(DMF) = 3.4 kDa, Đ = 1.7. DSC: glass transition temperature T_g=-12 °C.



(p3a)

Synthesis of poly(propargyl-TMP-carbonate), p3b. The polymerization was carried out according to the general procedure, (20°C, 6h). The polymer product was collected as a transparent sticky solid. ^{1}H NMR ($CDCl_3$) δ ppm: 0.90 (br, 3H, -C**H**$_3$), 1.52 (br, 2H, -C**H**$_2$CH$_3$), 2.56 (br, 1H, -≡C**H**), 4.13 (br, 6H, -O-C**H**$_2$- (chain+pendant), 4.72 (br, 2H, CH≡CH-C**H**$_2$O-), 7.84-8.30 (m, 0.18H (9H), Pyrene-endgroup). M_n(theo)=10.9 kDa, M_n(NMR)= 11.2 kDa, M_n SEC(DMF) = 3.7 kDa, Đ = 1.94. DSC: glass transition temperature T_g= +7 °C.

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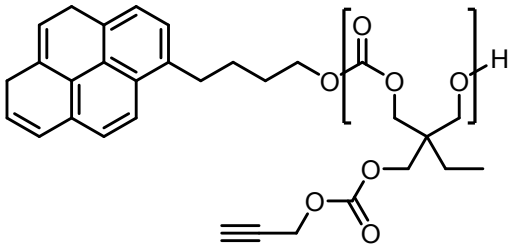
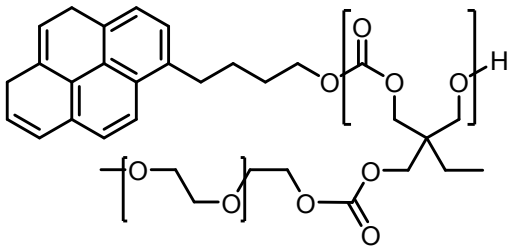


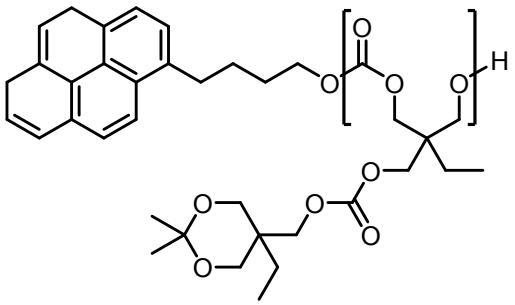
(p3b)

Synthesis of poly(MeOPEG-TMP-carbonate), p3c. The polymerization was carried out according to the general procedure, (20°C, 6h). The polymer product was collected as a white sticky solid, with some residual monomer (%) still left in the material, which inhibited full NMR characterization (See Fig. S29). M_n(theo)=7.8 kDa, M_n(NMR)= 9.9 kDa, SEC(DMF) = multimodal(average excluding monomer peak): M_n = 6.60 kDa, Đ = 1.28.



(p3c)

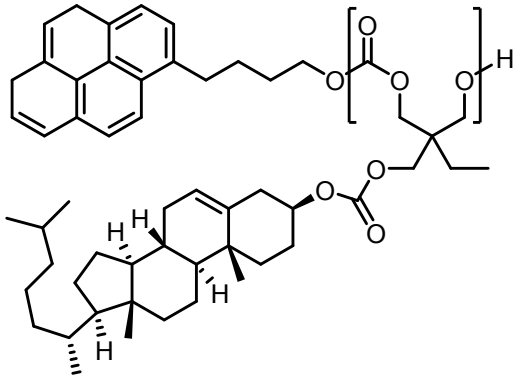
Synthesis of poly(TMP-acetonide**-carbonate), p3d.** The polymerization was carried out according to the general procedure, (20°C, 6h). The polymer product was collected as a white sticky solid. ^{1}H NMR ($CDCl_3$) δ ppm: 0.84 (br, 3H, (acetonide-part)CH_2-C**H**$_3$), 0.91 (br, 3H, CH_2-C**H**$_3$), 1.34 (br, 2H, (acetonide-part)-C**H**$_2$$CH_3$), 1.39 (br, 3H, O-C-C**H**$_3$), 1.42 (br, 3H, O-C-C**H**$_3$), 1.53 (br, 2H, -C**H**$_2$$CH_3$), 3.66 (br, 4H, C-O-C**H**$_2$-C), 4.11 (br, 6H, -O-C**H**$_2$- (chain+pendant), 4.28 (br, 2H, C-C**H**$_2$O-), 7.84-8.30 (m, 0.23H (9H), Pyrene-endgroup). M_n(theo)=11.8 kDa, M_n(NMR)= 13.0 kDa, M_n SEC(DMF) = 4.4 kDa, Đ = 1.29.



(p3d)

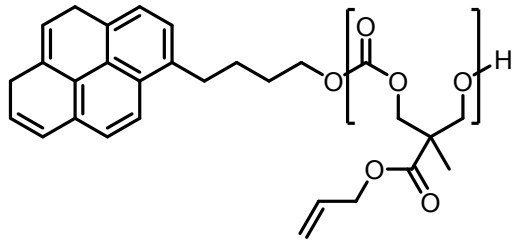
Synthesis of poly(cholesterol-TMP-carbonate), p3e. The polymerization was carried out according to the general procedure, (20°C, 6h). The polymer product was collected as a white sticky "gelly" solid, with some residual monomer (%) still left in the material, which inhibited full NMR characterization (See Fig. S29). This is probably due to the high tendency for cholesterol to form weakly bonded aggregates in solution. Although an NMR molecular weight could be calculated: M_n(theo)=11.7 kDa, M_n(NMR)= 4.8 kDa. The

polymer was poorly soluble in DMF and aggregated in other organic solvents, which inhibited any reasonable SEC analysis.



(p3e)

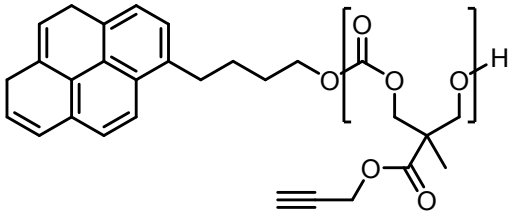
Synthesis of poly(allyl-bis-MPA-carbonate), p4a. The polymerization was carried out according to the general procedure, (20°C, 2h). The polymer product was collected as a white sticky solid. ^{1}H NMR ($CDCl_3$) δ ppm: 1.26 (br, 3H, -C**H**$_3$), 4.30 (br, 4H, -C**H**$_2$-O-CO_2-), 4.62 (br, 2H, CH_2=CH-C**H**$_2$O-), 5.23 (d, 1H, J=10.5 Hz, cis-C**H**$_2$=CH-CH_2O-), 5.30 (d, 1H, J=17.1 Hz, trans-C**H**$_2$=CH-CH_2O-), 5.93 (m, 1H, CH_2=C**H**-CH_2O-), 7.84-8.30 (m, 0.16H (9H), Pyrene-endgroup). M_n(theo)=9.0 kDa, M_n(NMR)= 4.8 kDa, M_n SEC(DMF) = 5.8 kDa, Đ = 1.30. DSC: glass transition temperature T_g= -12 °C.



(p4a)

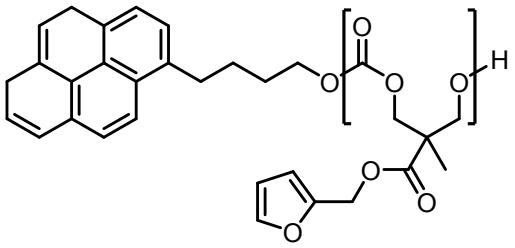
Synthesis of poly(propargyl-bis-MPA-carbonate), p4b. The polymerization was carried out according to the general procedure, (20°C, 2h). The polymer product was collected as a white sticky solid. ^{1}H NMR ($CDCl_3$) δ ppm: 1.28 (br, 3H, -C**H**$_3$), 2.53 (br, 1H, -≡C**H),** 4.30 (br, 4H, -C**H**$_2$-O-CO_2-), 4.67 (br, 2H, CH≡CH-C**H**$_2$O-), 7.83-8.28 (m,

0.17H (9H), Pyrene-endgroup). M_n(theo)=10.0 kDa, M_n(NMR)= 10.8 kDa, M_n SEC(DMF) = 10.5 kDa, Đ = 1.36. DSC: glass transition temperature T_g= +9 °C.



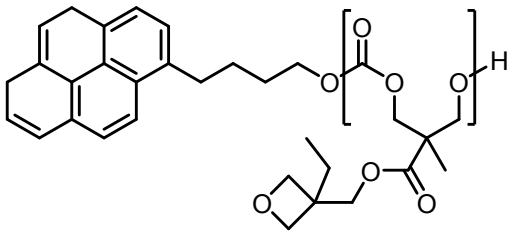
(p4b)

Synthesis of poly(furfuryl-bis-MPA-carbonate), p4c. The polymerization was carried out according to the general procedure, (20°C, 2h). The polymer product was collected as a faint yellow sticky solid. ^{1}H NMR ($CDCl_3$) δ ppm: 1.22 (br, 3H, -C**H**$_3$), 4.26 (br, 4H, -C**H**$_2$-O-CO_2-), 5.09 (br, 2H, -C**H**$_2$OCO-), 6.34 (br, 1H, furfuryl-H), 6.39 (br, 1H, furfuryl-H), 7.40 (br, 1H, furfuryl-H), 7.84-8.28 (m, 0.17H (9H), Pyrene-endgroup). M_n(theo)=11.3 kDa, M_n(NMR)= 11.8 kDa, M_n SEC(DMF) = 4.5 kDa, Đ = 1.40.



(p4c)

Synthesis of poly(oxetane-bis-MPA-carbonate), p4d. The polymerization was carried out according to the general procedure, (20°C, 2h). The polymer product was collected as a white sticky solid. ^{1}H NMR ($CDCl_3$) δ ppm: 0.90, (br, 3H, -CH_2C**H**$_3$), 1.29 (br, 3H, -C**H**$_3$), 1.74 (br, 2H, -C**H**$_2$$CH_3$), 4.28 (br, 6H, -C**H**$_2$-O-$CO_2$-and -C**H**$_2$OCO-), 4.41 (br, 4H, -C**H**$_2$OC**H**$_2$-), 6.34 (br, 1H, furfuryl-H), 6.39 (br, 1H, furfuryl-H), 7.40 (br, 1H, furfuryl-H), 7.84-8.28 (m, 0.32H (9H), Pyrene-endgroup). M_n(theo)=13.1 kDa, M_n(NMR)= 8.3 kDa, M_n SEC(DMF) = 7.7 kDa, Đ = 1.27. DSC: glass transition temperature T_g= +4.0 °C.



(p4d)

Cytotoxicity test

To evaluate the potential of polycarbonates in biomedical applications, the precursors, monomers and polymers of TMP and bis-MPA carbonates were tested for cytotoxicity according to ISO10993-5 procedures[5,6]. Human dermal fibroblasts (hDF), were cultured in complete growth medium, CGM, containing Dulbecco's modified eagle medium, DMEM/F12, with 10% fetal bovine serum (FBS), penicillin (100 U/ml) and streptomycin (100 µg/ml) in an incubator at 37 °C and 5% CO_2 in a humidified atmosphere. The cells were harvested with trypsin-EDTA and cell density was determined with hemocytometer. All reagents for cell culturing are purchased from Thermo Scientific™ HyClone™. The precursors **1** and **2**, monomers **3a** and **3b** and polymers **3a-e**, **4a-e** were dissolved in appropriate solvents and 0.1mg of material was coated on the surface of a sterile cell culture coverslip (Nunc™ Thermanox®) and the solvent were allowed to evaporate. Each coverslip was extracted in 0.5ml CGM in a 24-well tissue culture plate for 24 hours at 37 °C and 5% CO_2 to let the potential toxins to diffuse from the material to the CGM. The extract medium were used to culture hDF in a density of 10^5 cell/ml in 48 well tissue culture plate for 24 hours at 37 °C and 5% CO_2. The CGM extract of the cell culture slide were used as negative control and cell culture with addition of 0.1% Triton X-100 in CGM were used as positive control. Samples were run in triplicate. The viability of hDF

evaluated with AlamarBlue Assay® (Life Technology) according to the instruction from the manufacturer. The metabolic activity of cells, indicated by fluorescent intensity was measured with a plate reader (Tecan Infinite® M200 Pro) with excitation at 560nm and emission at 590nm. Cell growth was also recorded with an inverted optical microscopy after culturing for 24 hours at 37 °C and 5% CO_2.

In direct contact tests, the hDF cells were seeded directly on the coverslips coated with polycarbonates **3a-e** and **4a-e**. The cell viability was evaluated with AlamarBlue Assay and cell growth was recorded with an inverted optical microscopy after culturing for 24 hours at 37 °C and 5% CO_2.

References:

[1] R. Vestberg, A. M. Piekarski, E. D. Pressly, K. Y. Van Berkel, M. Malkoch, J. Gerbac, N. Ueno, C. J. Hawker, *J Polym Sci Pol Chem* **2009**, *47*, 1237-1258.

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[4] D. P. Sanders, K. Fukushima, D. J. Coady, A. Nelson, M. Fujiwara, M. Yasumoto, J. L. Hedrick, *J Am Chem Soc* **2010**, *132*, 14724-14726.

[5] ISO 10993-5: Biological evaluation of medical devices - Part 5: Tests for in vitro cytotoxicity, 2009

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^{1}H NMR and ^{13}C NMR characterization of 1,2,3a-e,4a-e,p3a-e,p4a-d

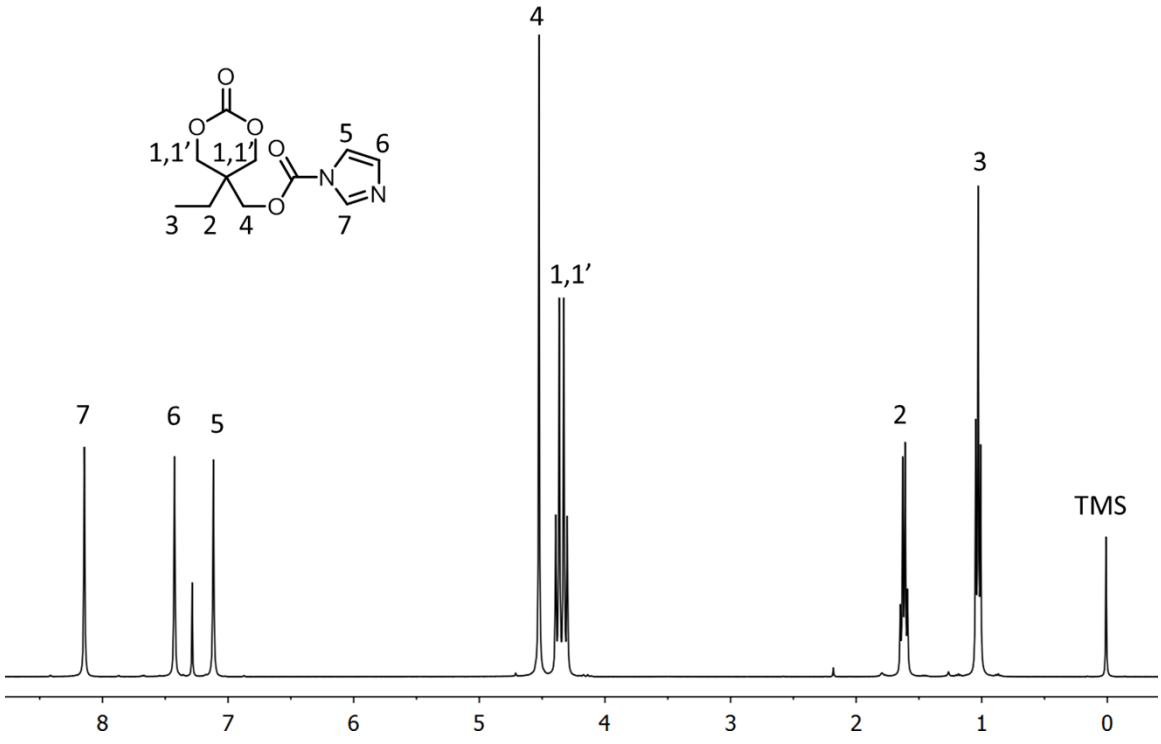


Figure S1. ^{1}H-NMR of imidazole-TMP-carbonate **1**

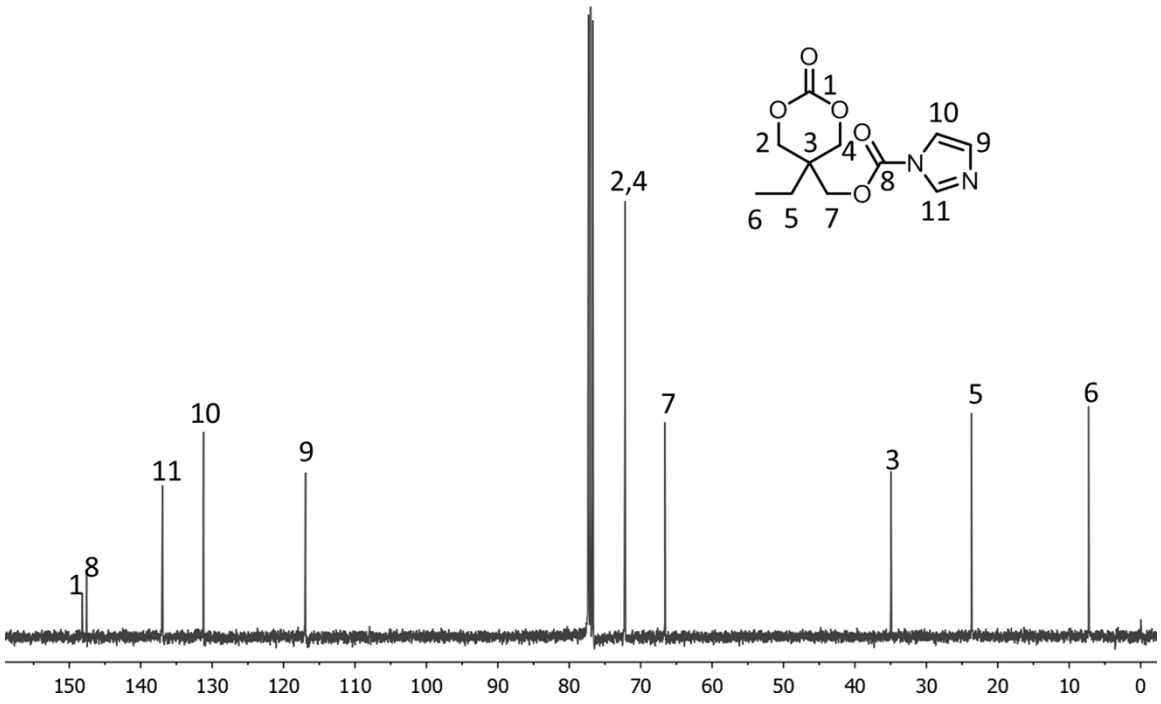


Figure S2. ^{13}C-NMR of imidazole-TMP-carbonate **1**

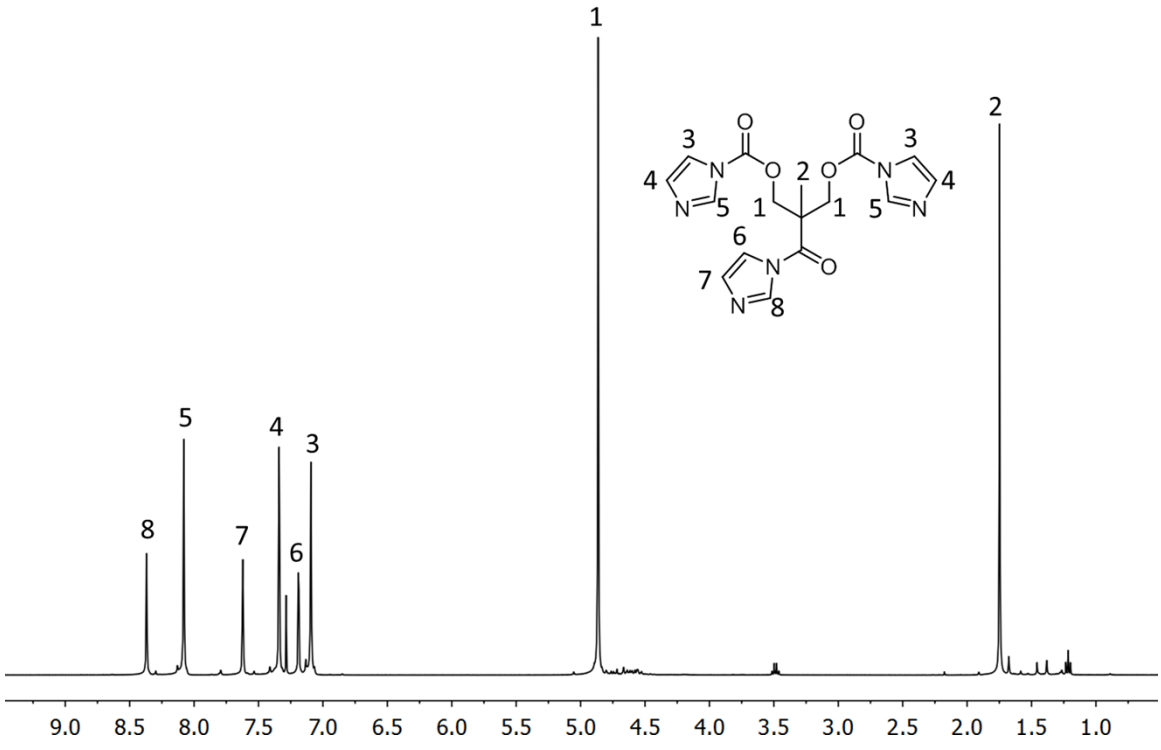


Figure S3. ^{1}H-NMR of BIMIPA- **2**

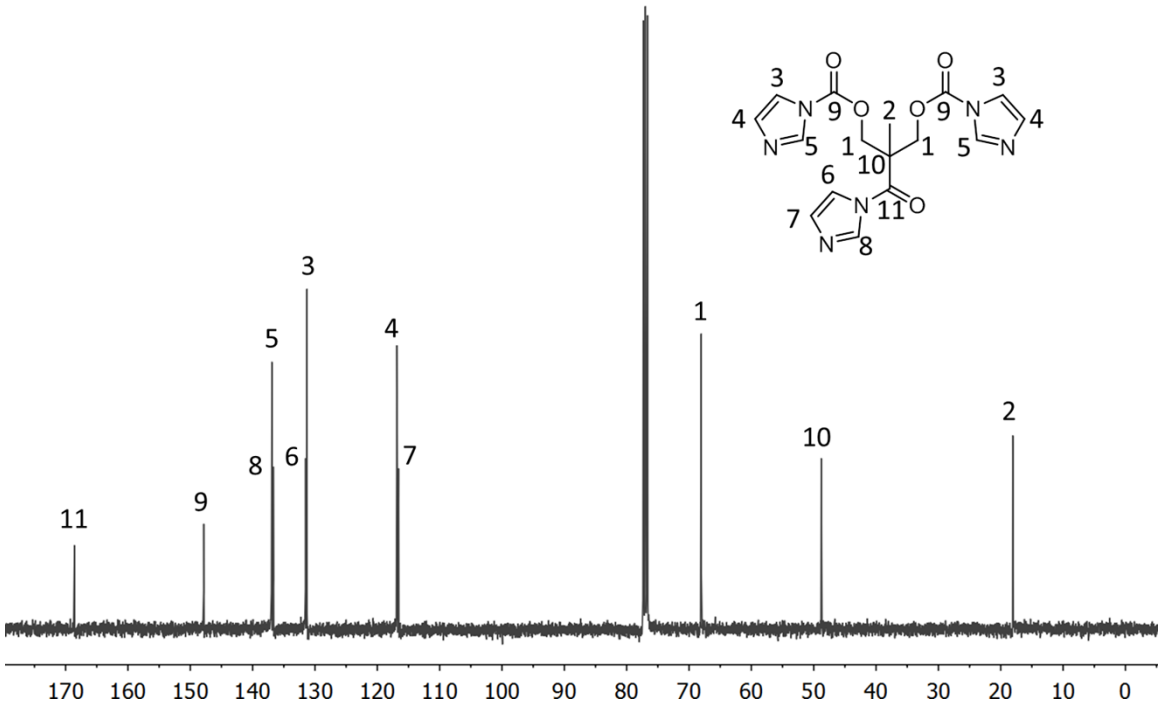


Figure S4. ^{13}C-NMR of BIMIPA **2**

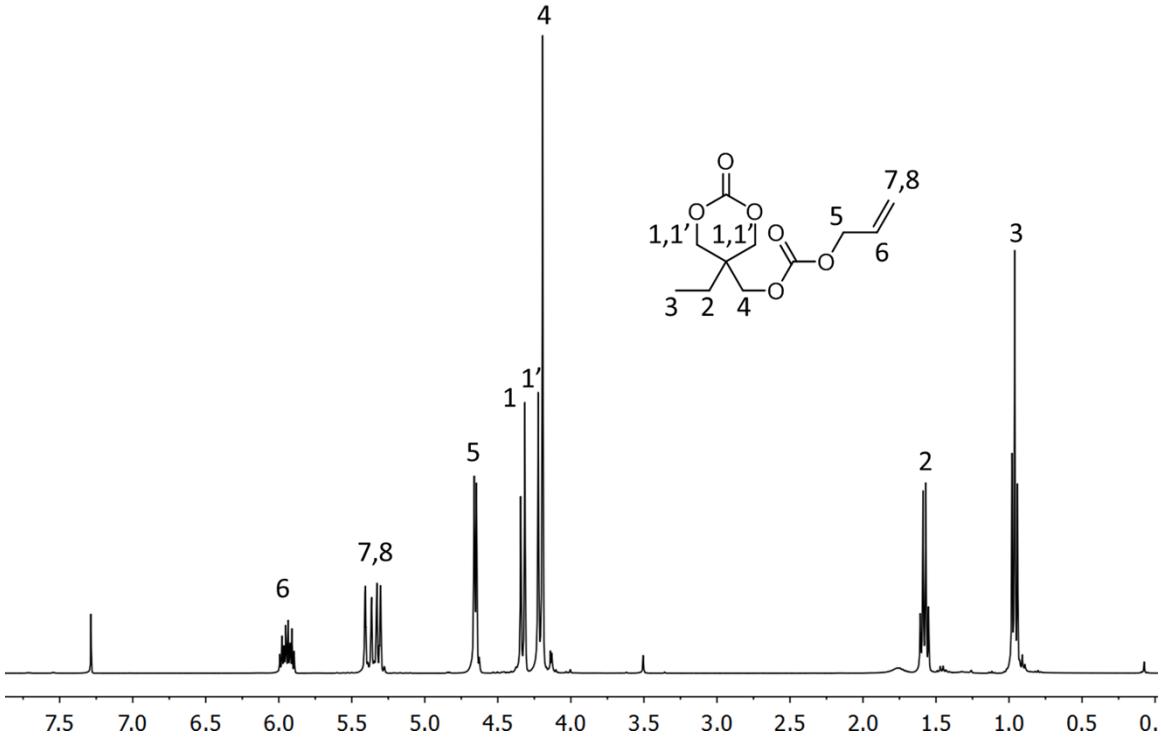


Figure S5. [1]H-NMR of allyl-TMP-carbonate **3a**

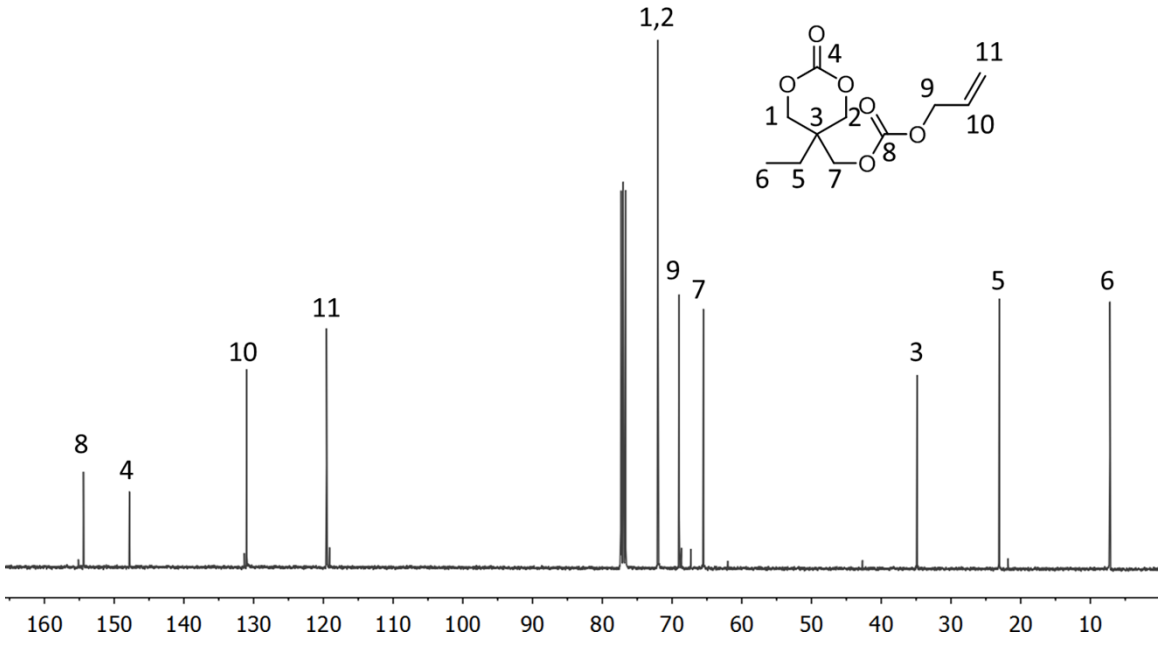


Figure S6. ^{13}C-NMR of allyl-TMP-carbonate **3a**

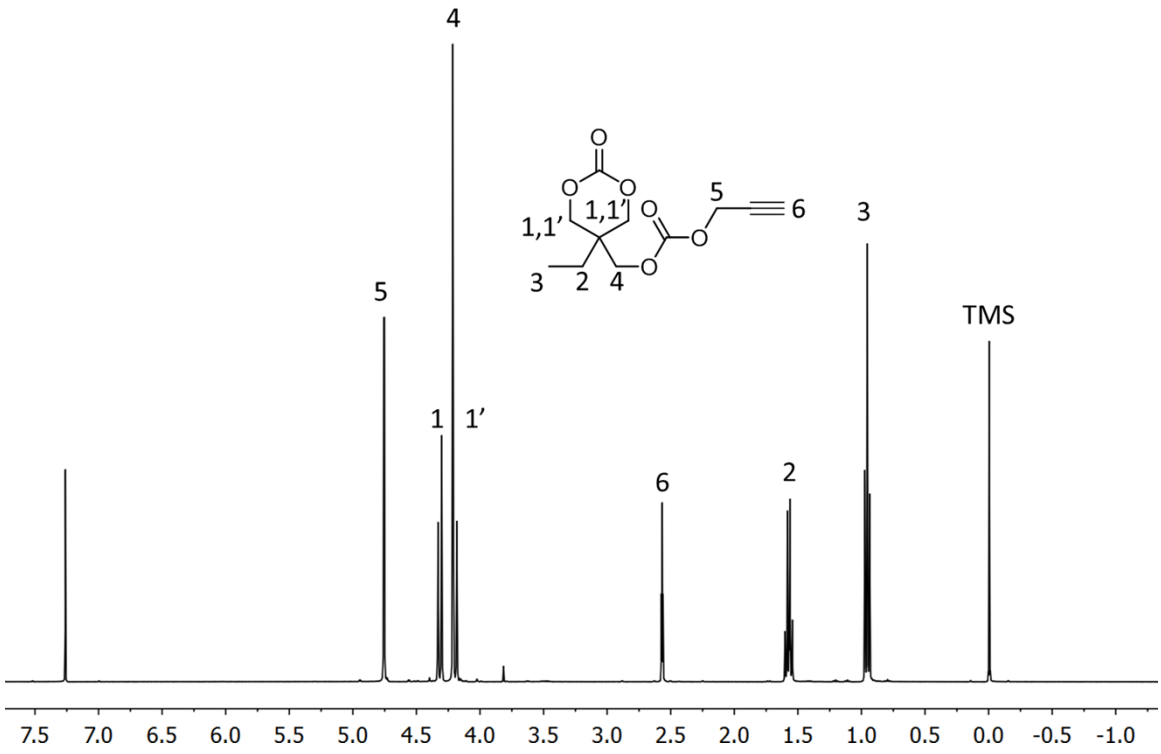


Figure S7. ^{1}H-NMR of propargyl-TMP-carbonate **3b**

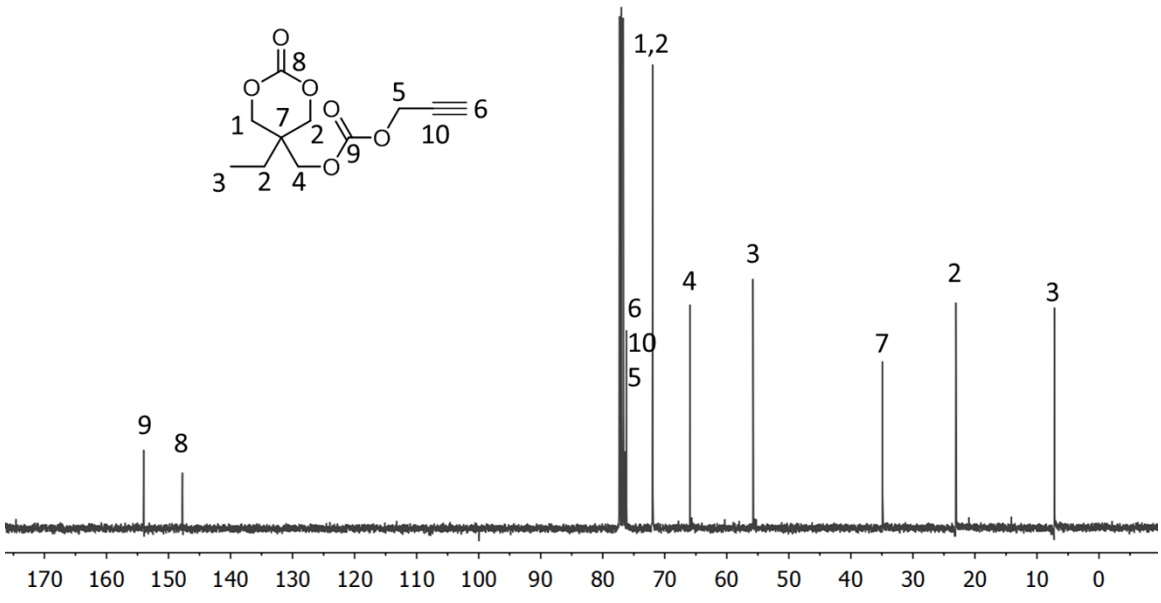


Figure S8. ^{13}C-NMR of propargyl-TMP-carbonate **3b**

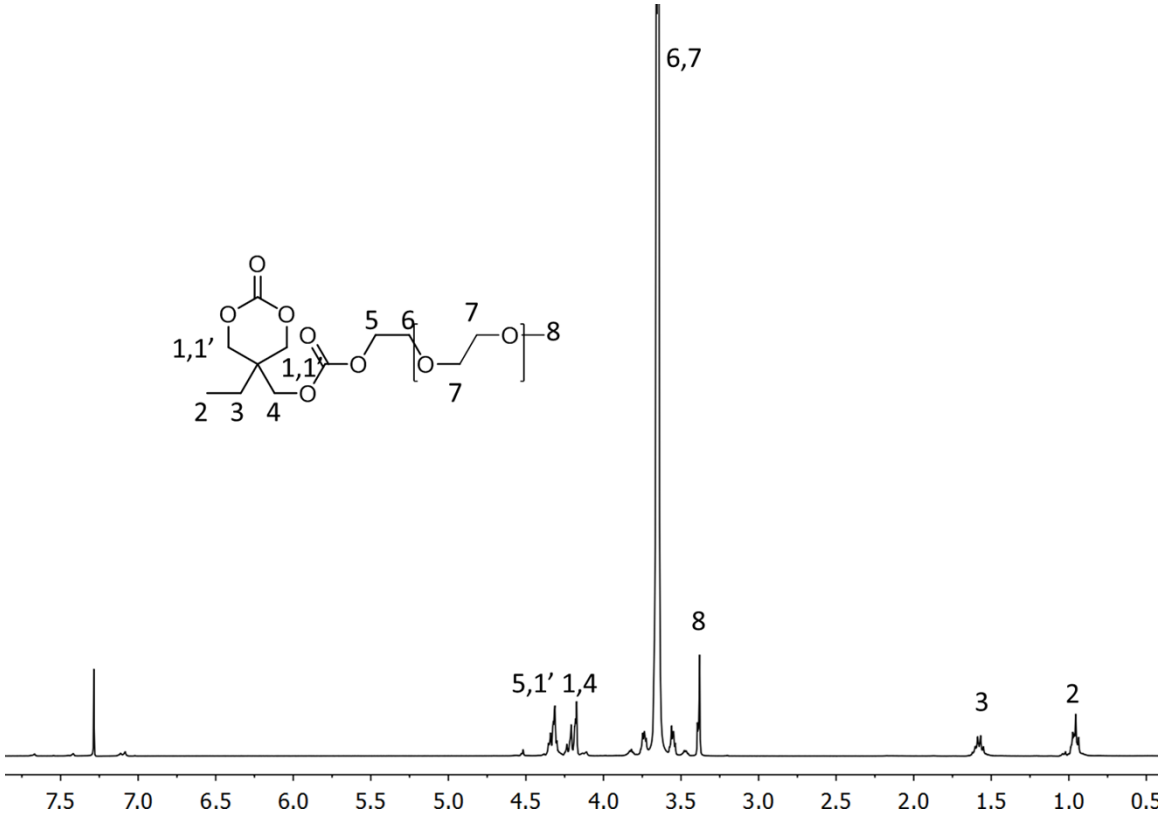


Figure S9. ^{1}H-NMR of PEG-TMP-carbonate **3c**

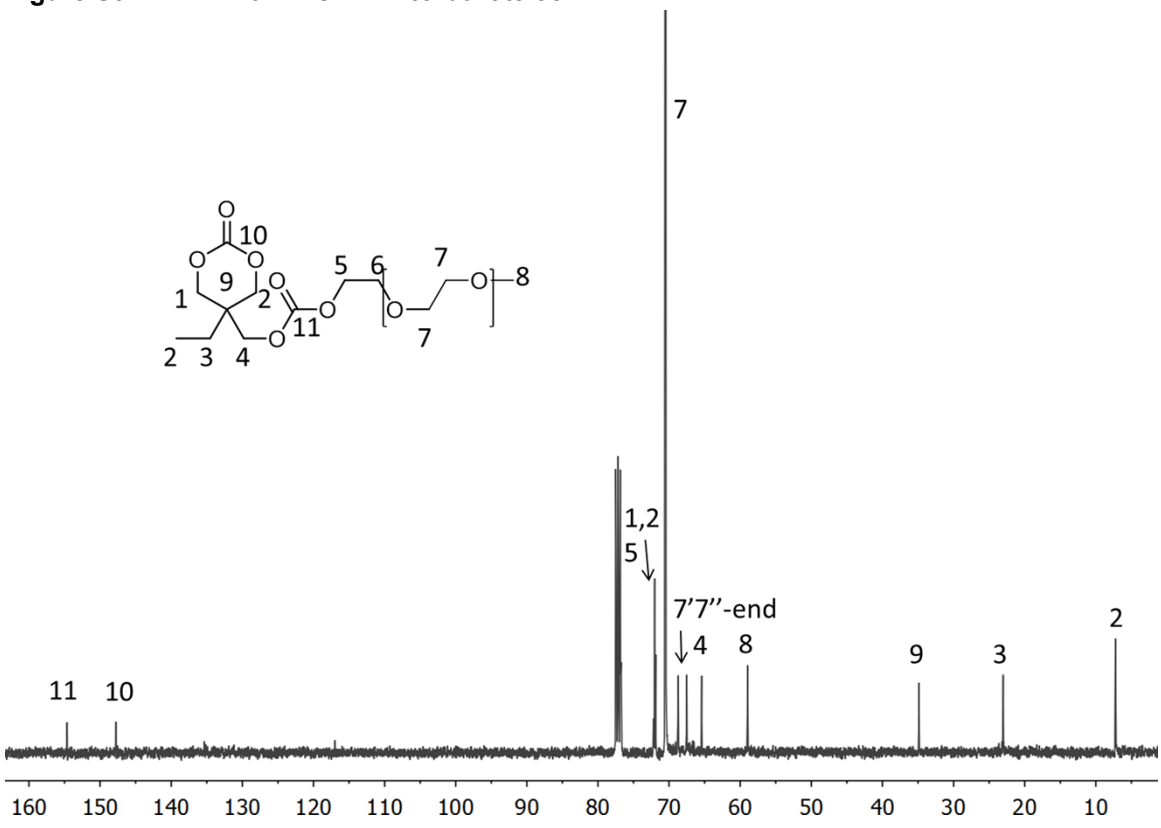


Figure S10. ^{13}C-NMR of PEG-TMP-carbonate **3c**

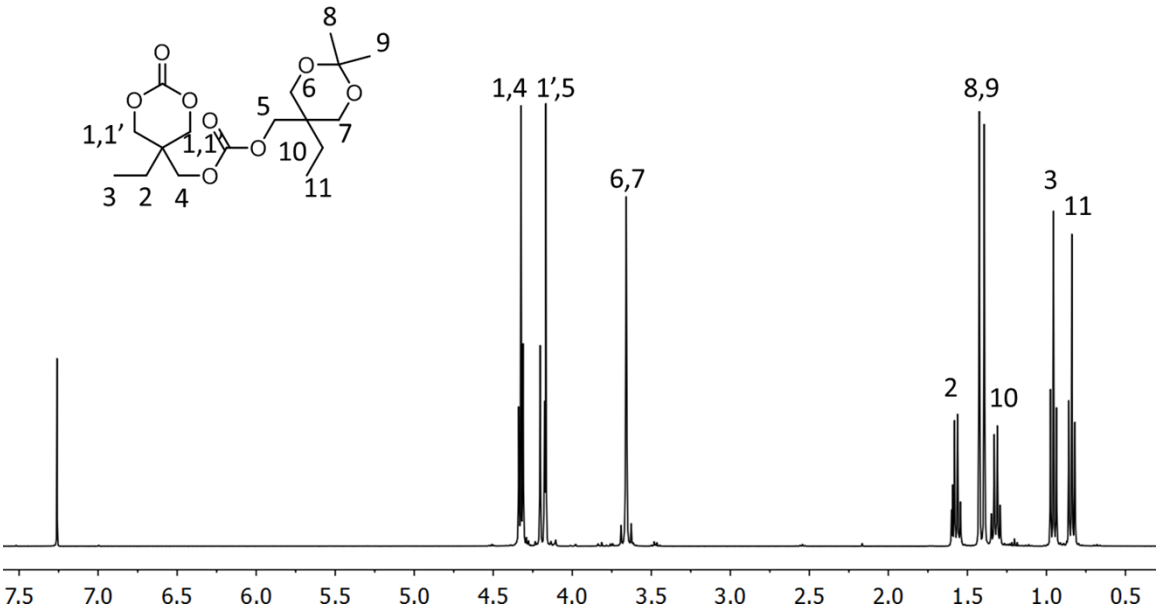


Figure S11. ^{1}H-NMR of acetonide-TMP-carbonate **3d**

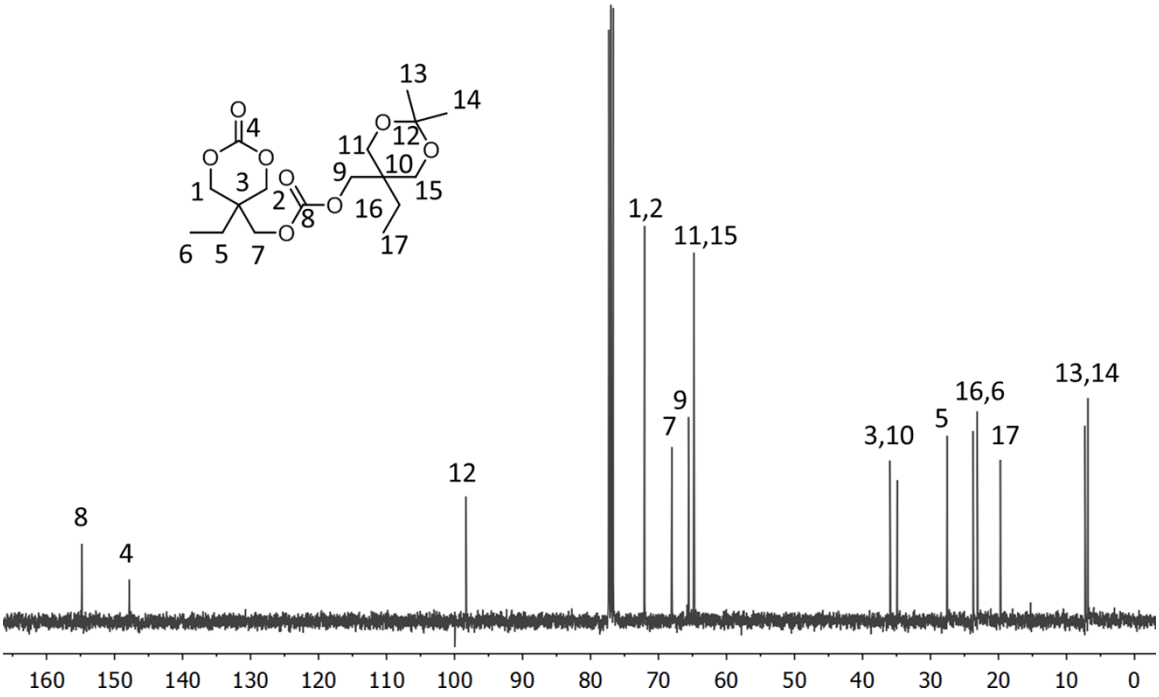


Figure S12. ^{13}C-NMR of acetonide-TMP-carbonate **3d**

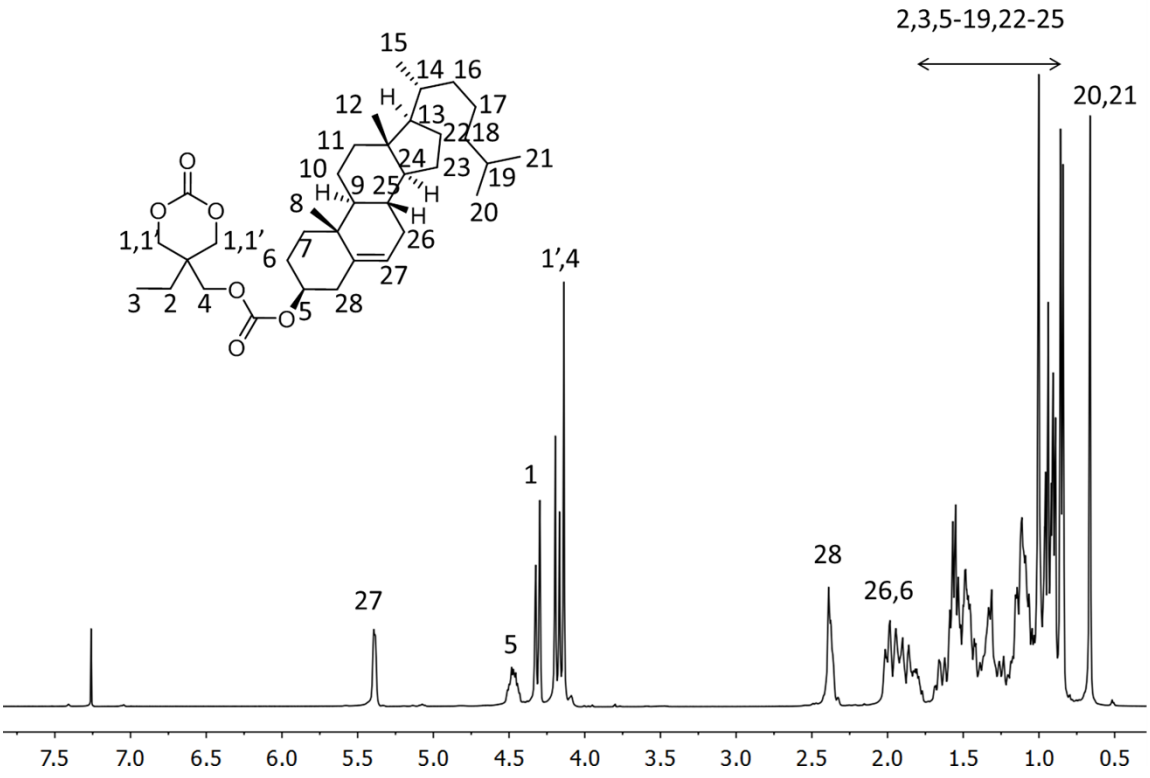


Figure S13. ^{1}H-NMR of cholesterol-TMP-carbonate **3e**

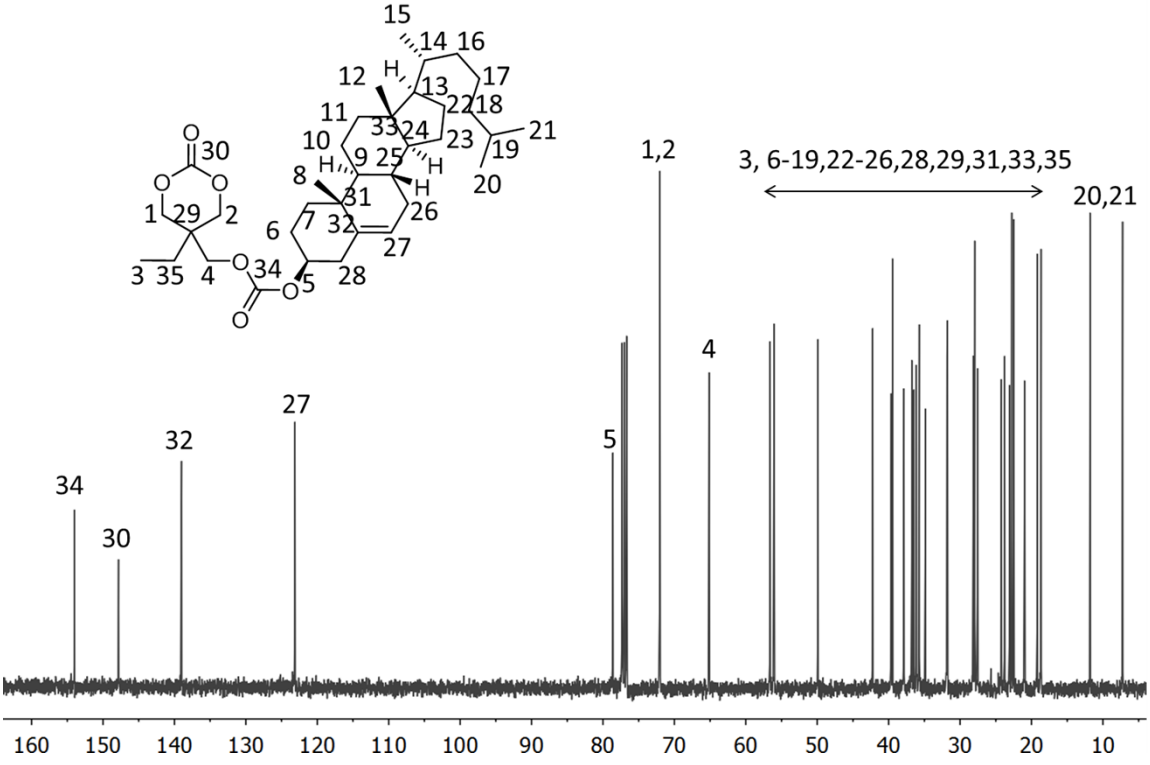


Figure S14. ^{13}C-NMR of cholesterol-TMP-carbonate **3e**

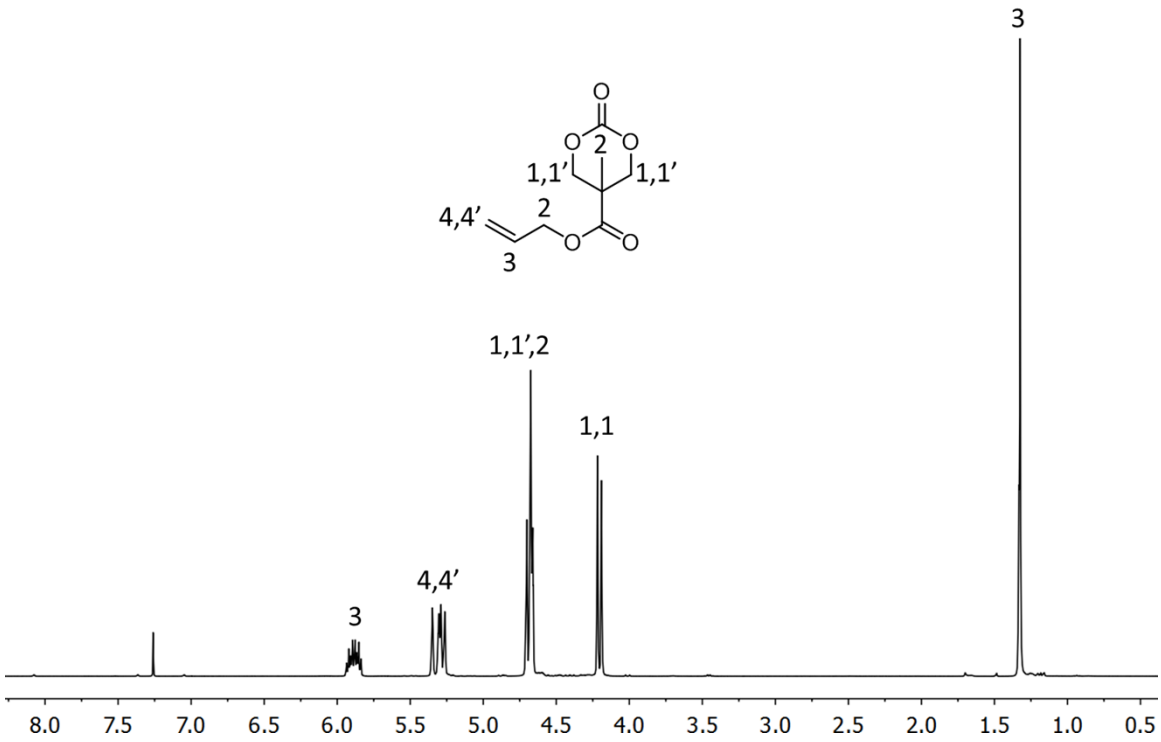


Figure S15. ^{1}H-NMR of allyl-bis-MPA-carbonate **4a**

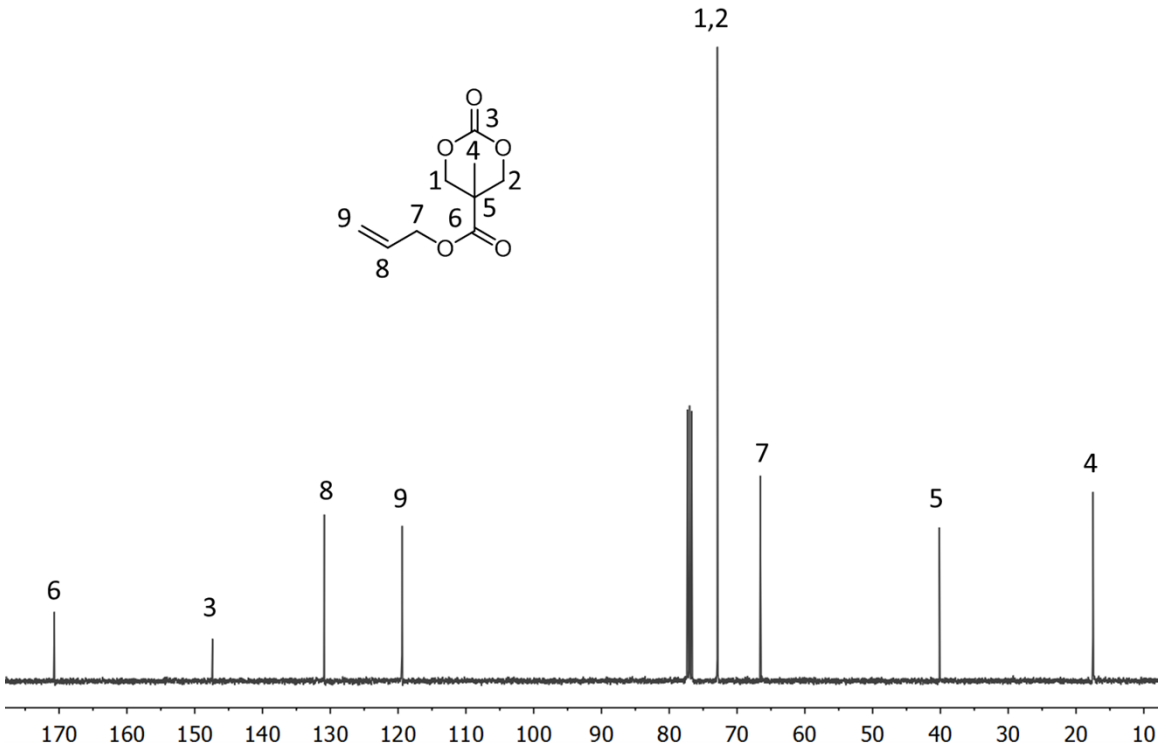


Figure S16. ^{13}C-NMR of allyl- bis-MPA-carbonate **4a**

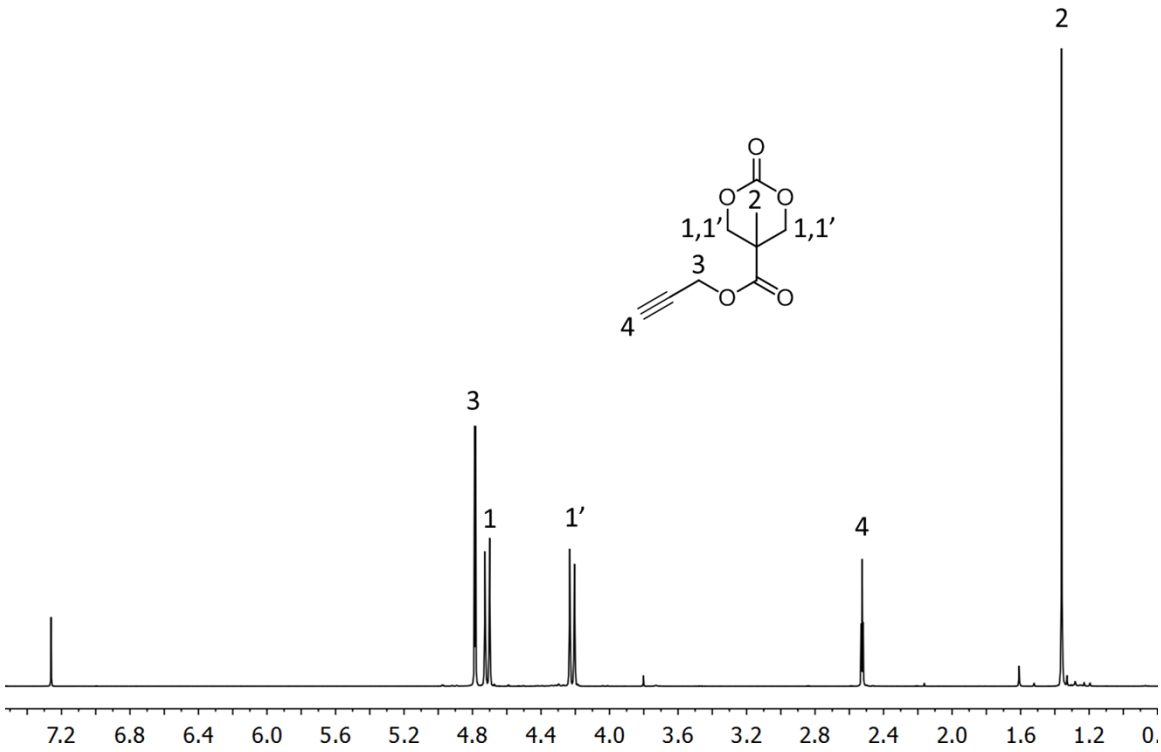


Figure S17. ^{1}H-NMR of propargyl- bisMPA-carbonate **4b**

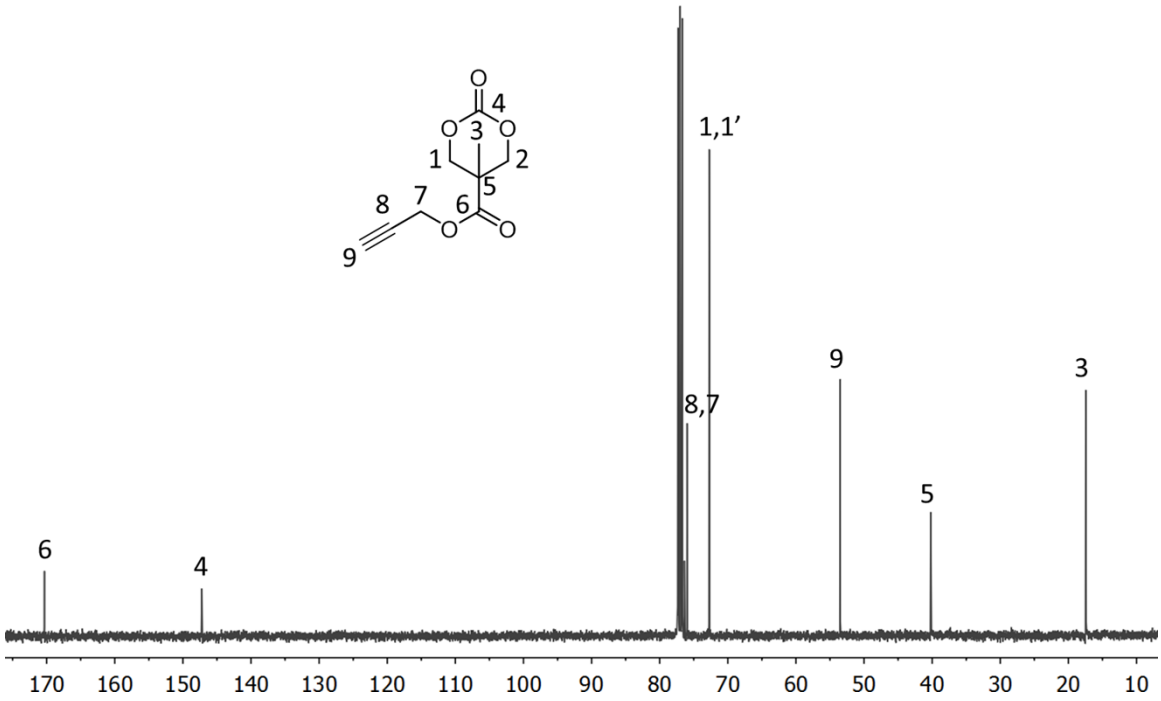


Figure S18. ^{13}C-NMR of propargyl- bisMPA-carbonate **4b**

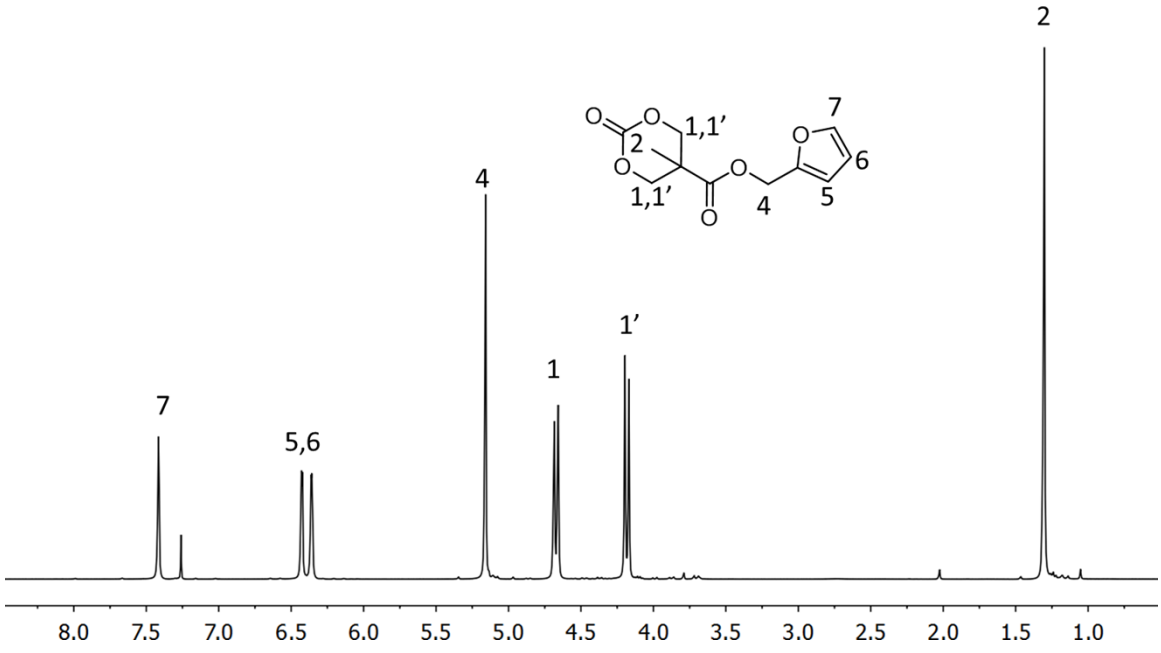


Figure S19. ^{1}H-NMR furfuryl- of bisMPA-carbonate **4c**

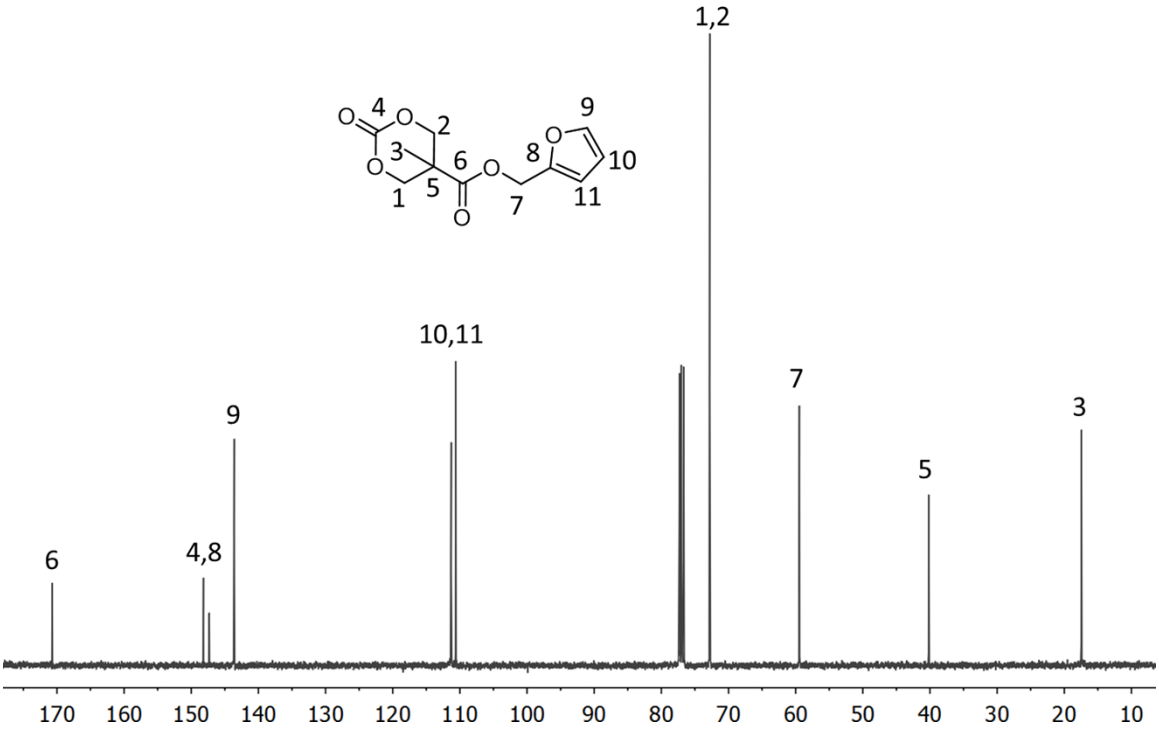


Figure S20. ^{13}C-NMR furfuryl- of bisMPA-carbonate **4c**

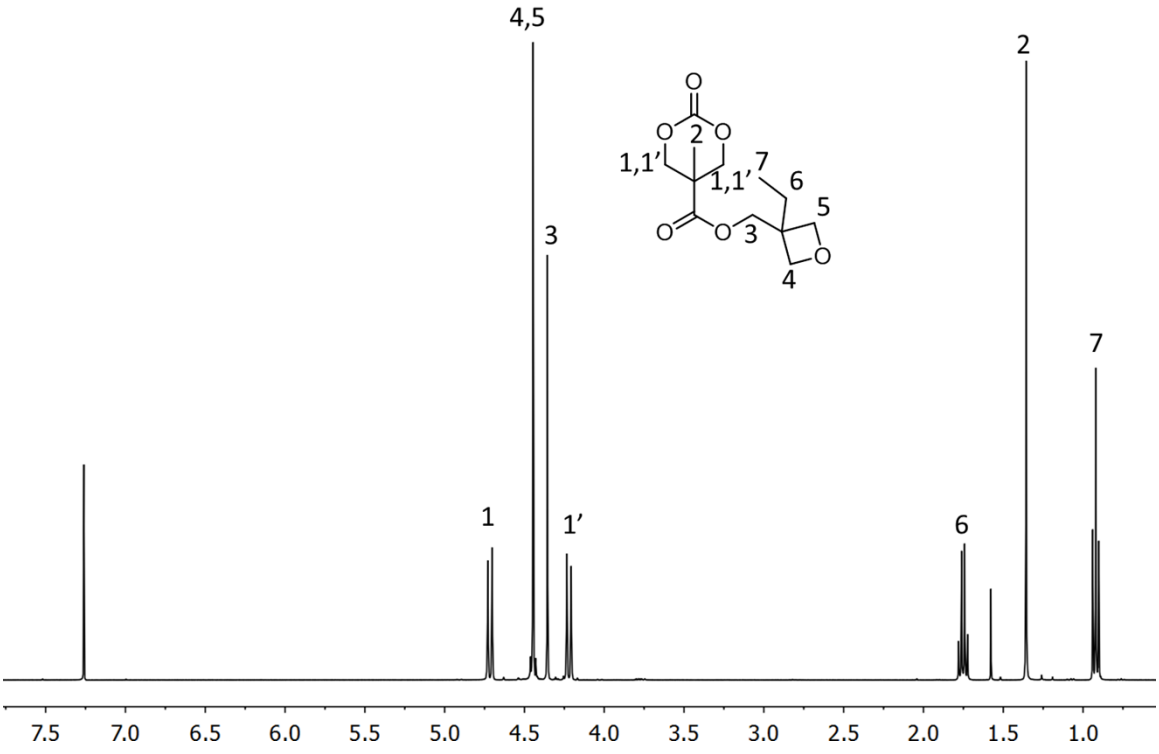


Figure S21. ^{1}H-NMR of oxetane- bis-MPA-carbonate **4d**

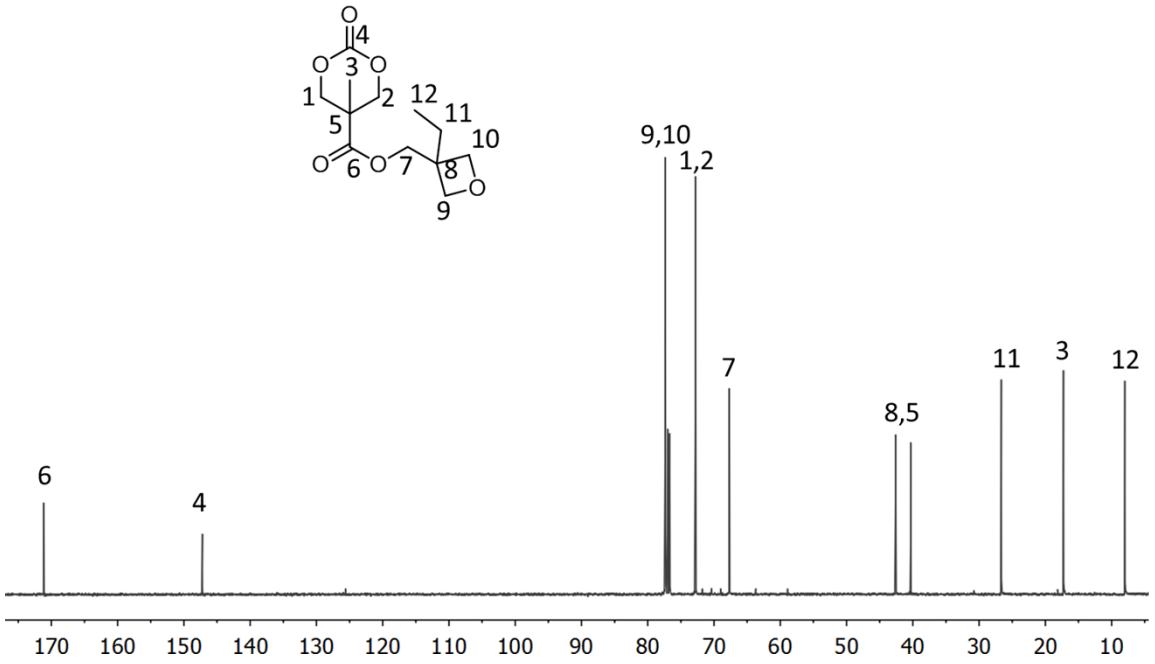


Figure S22. ^{13}C-NMR of oxetane- bisMPA-carbonate **4d**

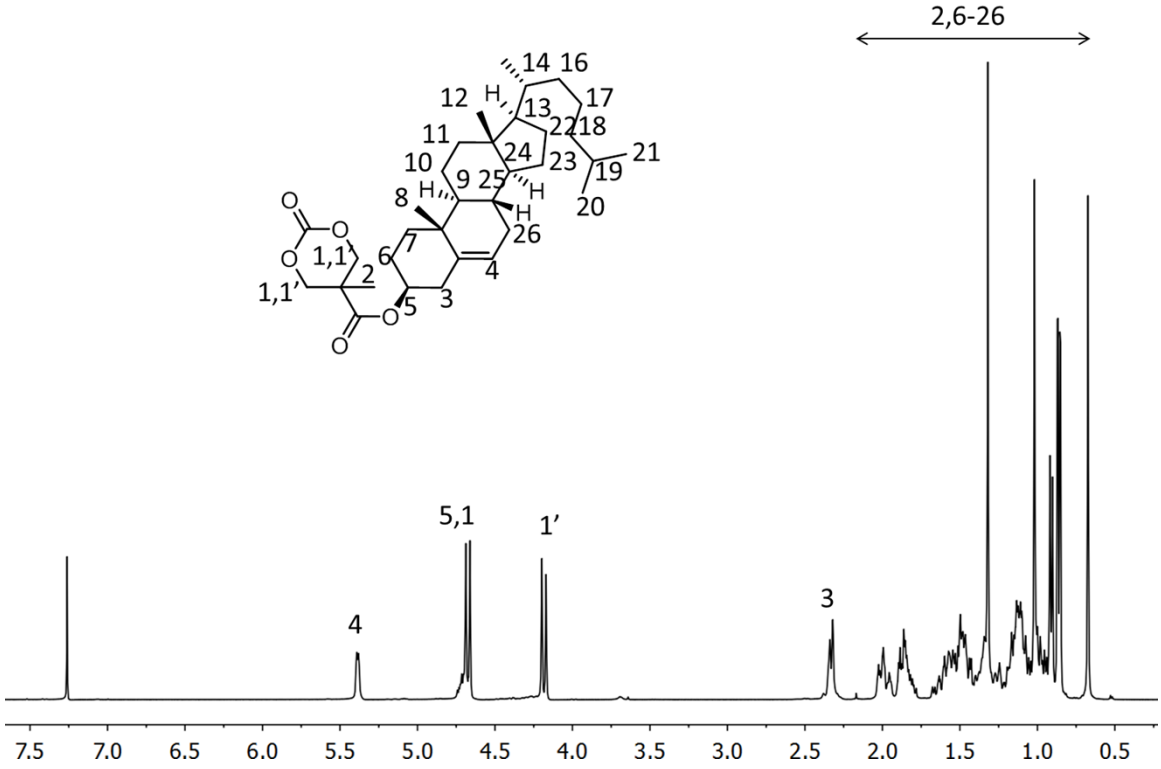


Figure S23. ^{1}H-NMR of cholesterol- bis-MPA-carbonate **4e**

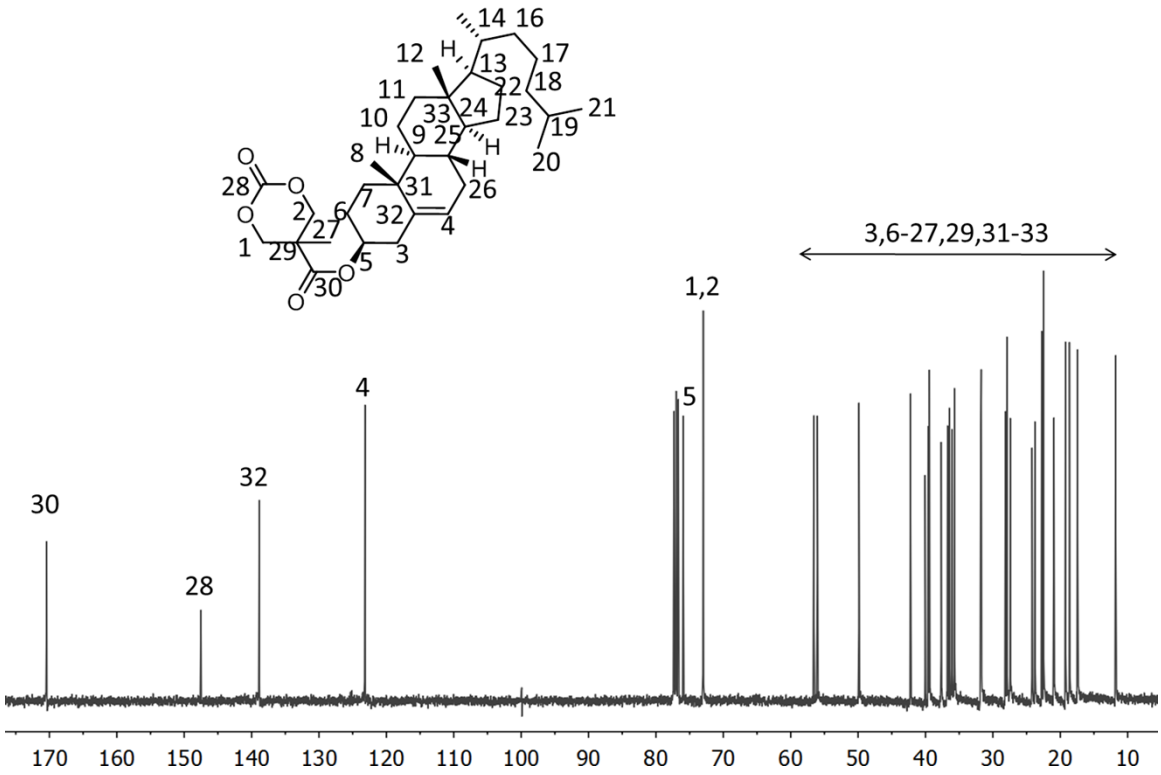


Figure S24. ^{13}C-NMR cholesterol- of bisMPA-carbonate **4e**

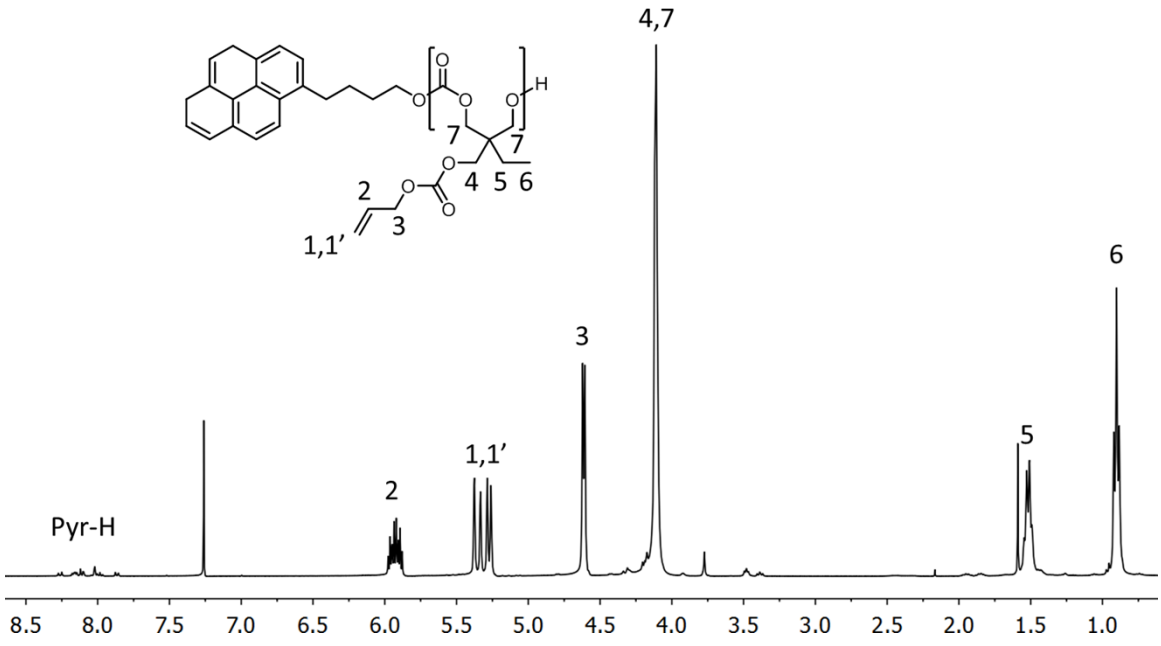


Figure S25. [1]H-NMR of poly(allyl-TMP-carbonate) **p3a** Mn(SEC)**=** 3.4 kDa, Đ=1.7

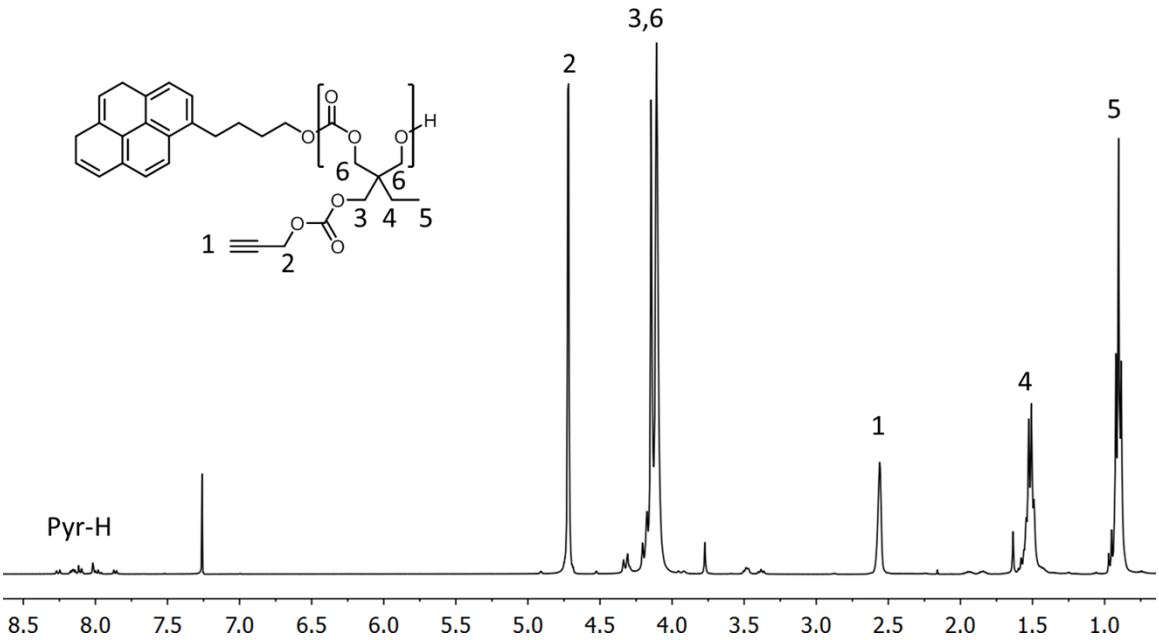


Figure S26. [1]H-NMR of poly(propargyl-TMP-carbonate) **p3b** Mn(SEC)**=**3.7 kDa, Đ=1.94

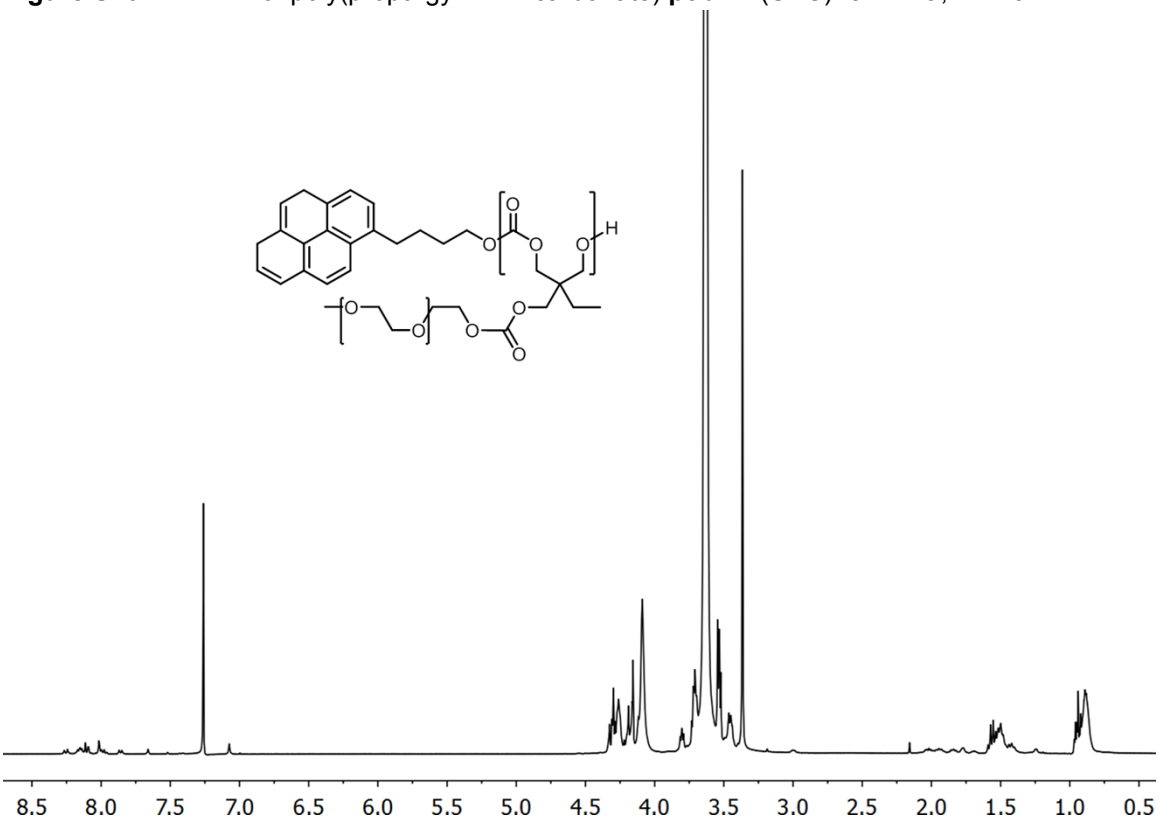


Figure S27. ^{1}H-NMR of poly(PEG-TMP-carbonate) **p3c** Mn(SEC)**=** 6.6 kDa, Đ=1.28

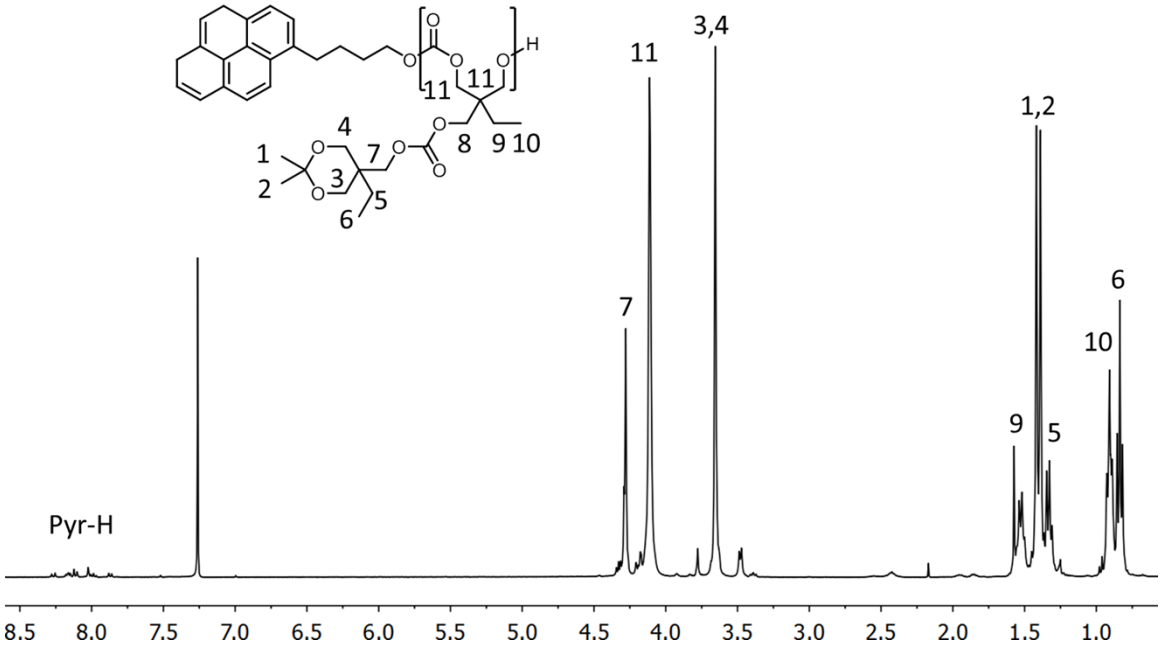


Figure S28. ^{1}H-NMR of poly(acetonide-TMP-carbonate) **p3d** Mn(SEC)**=**4,4 kDa, Đ=1.29

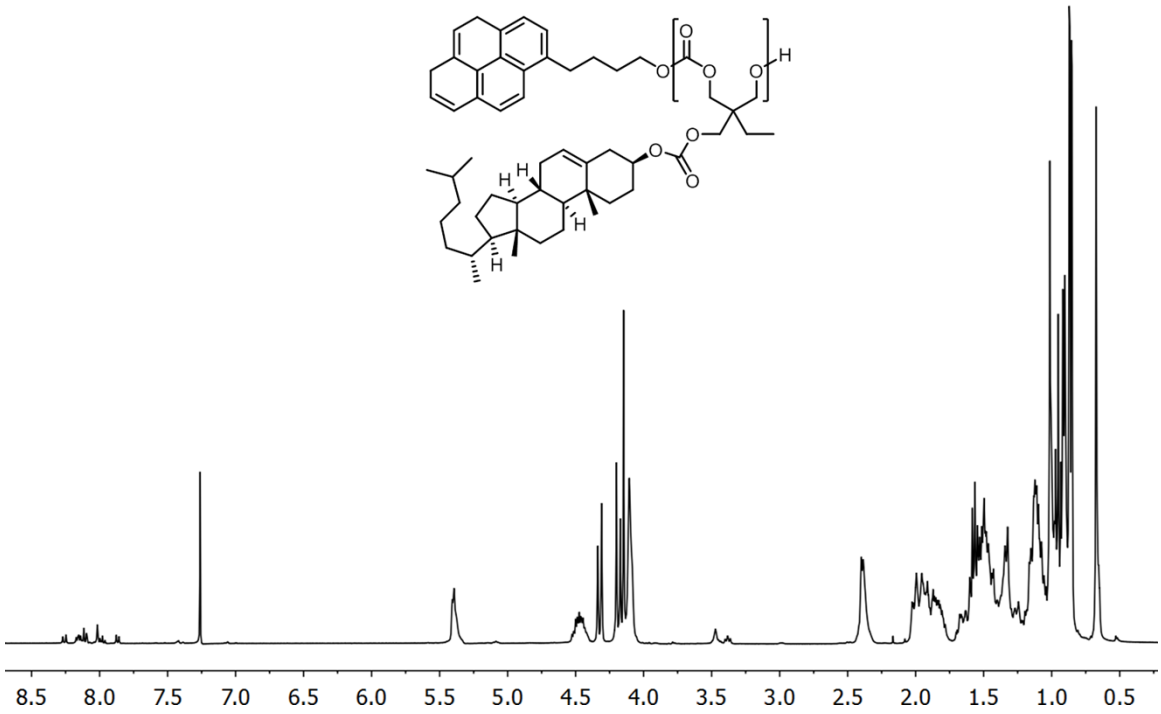


Figure S29. ^{1}H-NMR of poly(cholesterol-TMP-carbonate) p3e

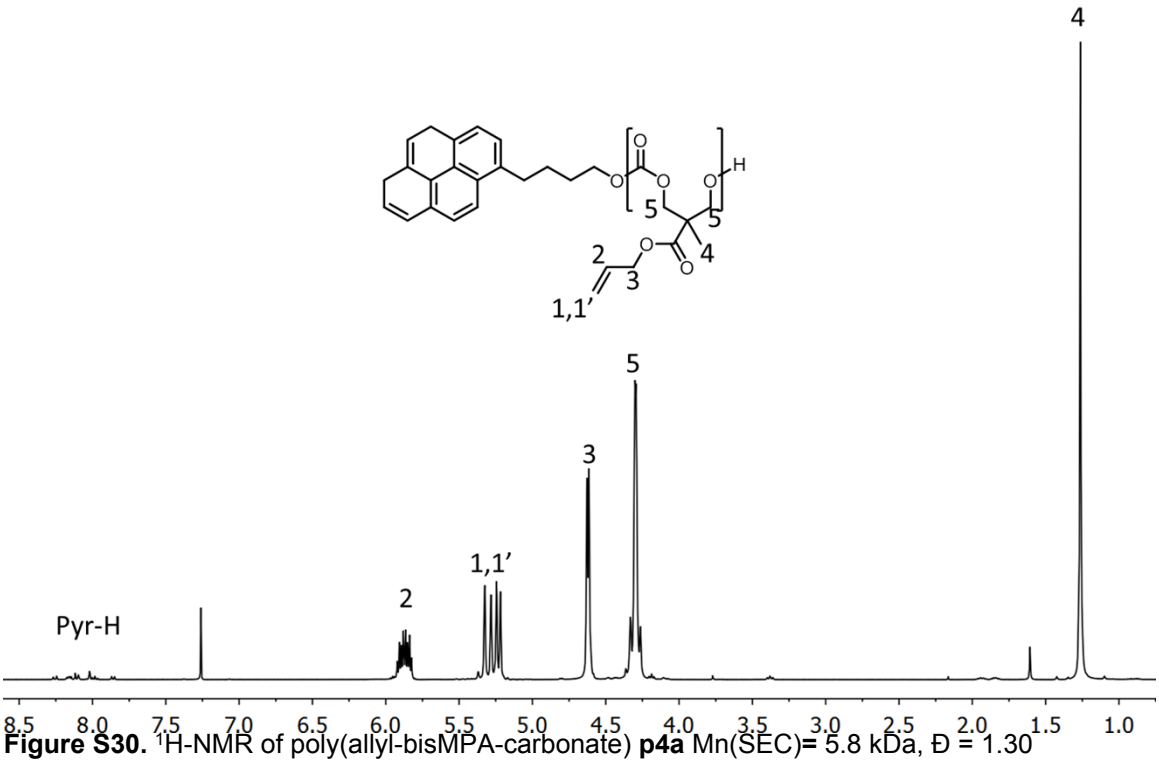


Figure S30. ^{1}H-NMR of poly(allyl-bisMPA-carbonate) **p4a** Mn(SEC)= 5.8 kDa, Đ = 1.30

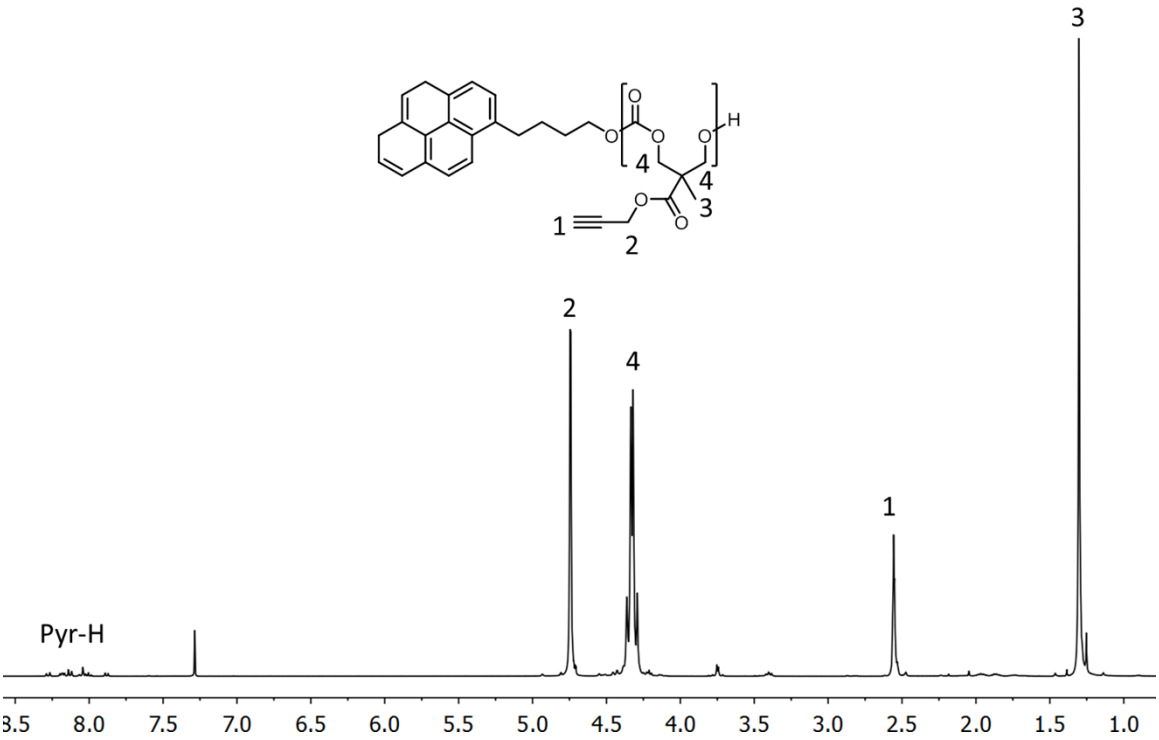


Figure S31. ^{1}H-NMR of poly(propargyl-bisMPA-carbonate) Mn(SEC)**=** 10.5 kDa, Đ=1.36

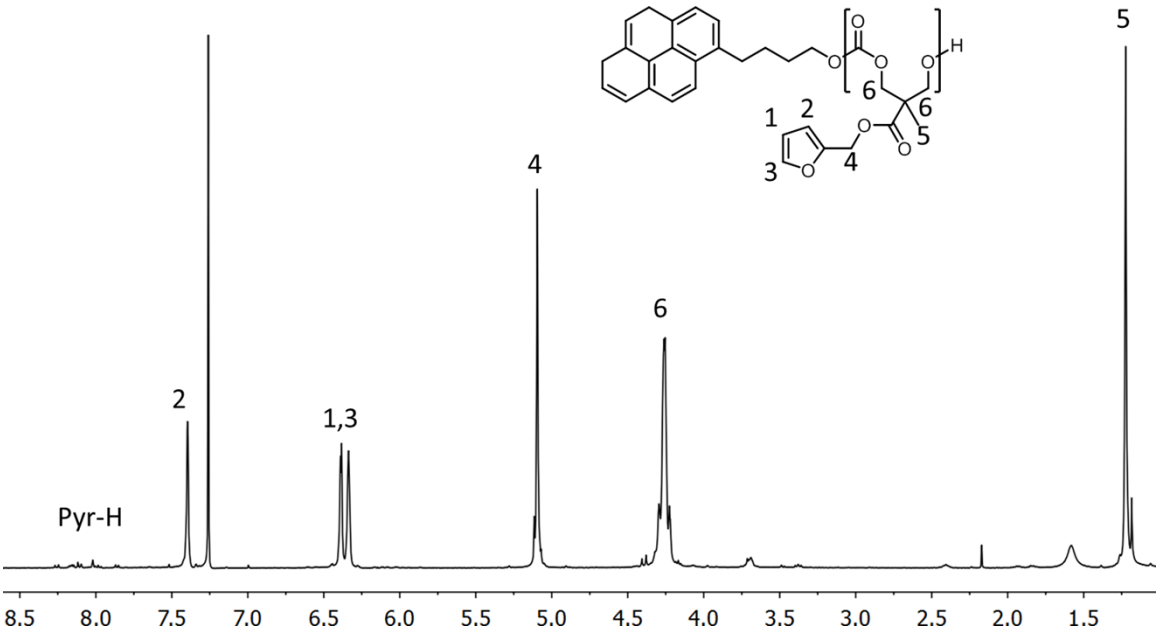


Figure S32. ^{1}H-NMR of poly(furfuryl-bisMPA-carbonate) **p4c** Mn(SEC)**=**4.5 kDa, Đ= 1.40

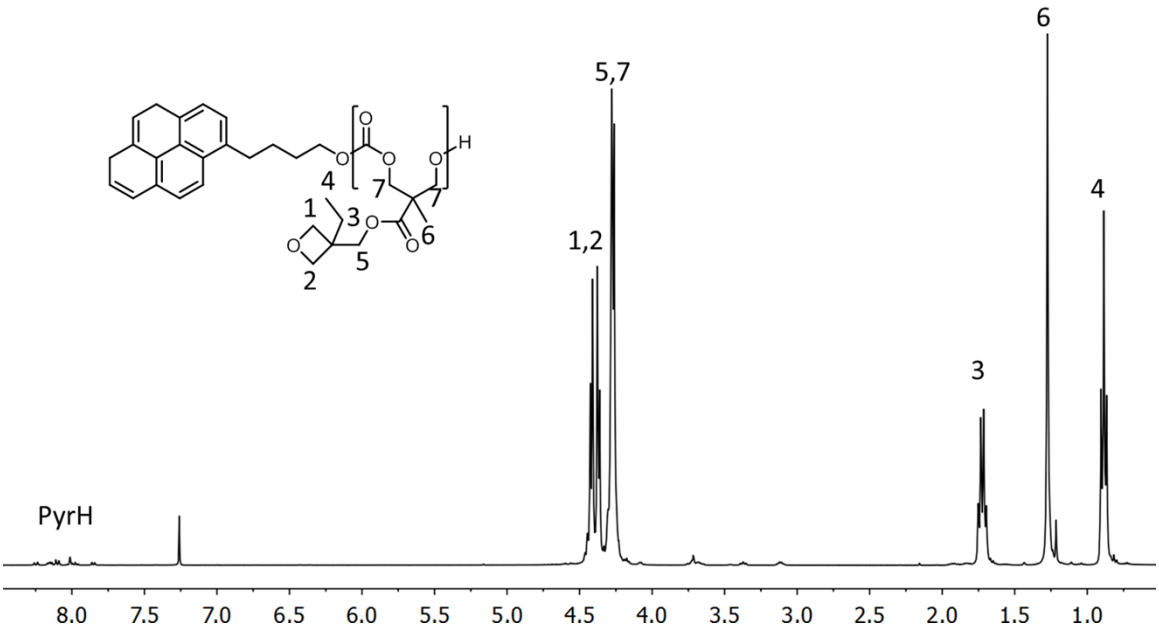


Figure S33. ^{1}H-NMR of poly(oxetane-bisMPA-carbonate) **p4d** Mn(SEC)**=** 7.7 kDa, Đ = 1.27

SEC characterization

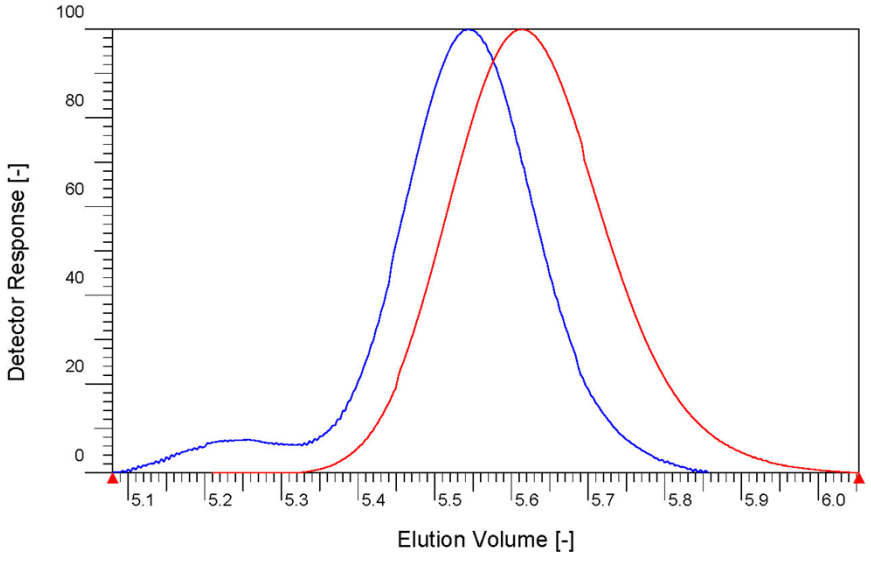


Figure S34. Overlay of SEC curves of MeOPEGOH (red) and TMP-PEG-carbonate **3c** (blue). Physical interactions between two monomer units are present

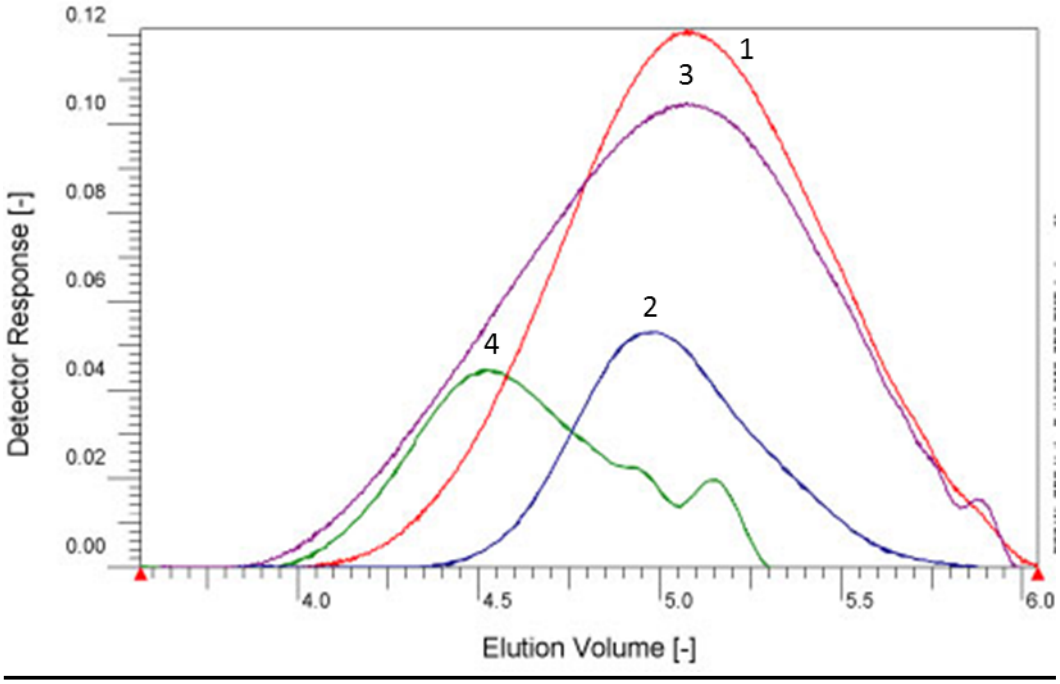


Figure S35. SEC traces of poly-TMP-carbonates: red**1** = poly-TMP-allyl-carbonate pTAC M_n = 3.4 kDa, Đ = 1.7, blue**2** = poly-TMP-propargyl-carbonate pTTC M_n = 3.7 kDa, Đ = 1.94. , purple**3** = poly-TMP-acetonide-carbonate M_n = 4.4 kDa, Đ = 1.29, green**4** = poly-TMP-MeOPEG-carbonate M_n = 6.60 kDa, Đ = 1.33.

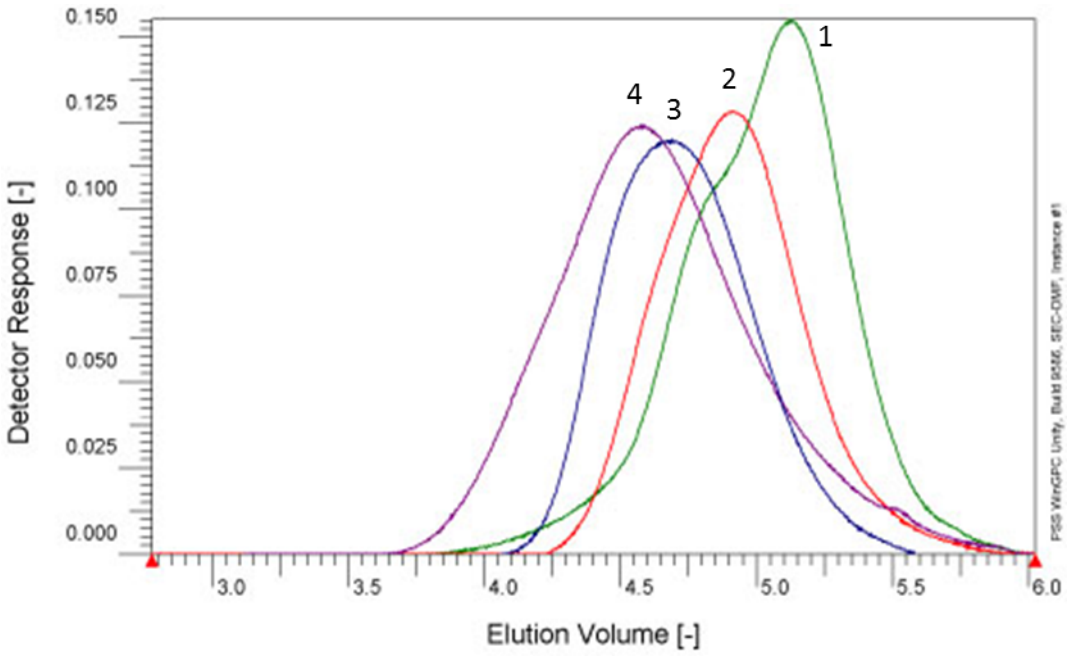


Figure S36. SEC traces of poly-bisMPA-carbonates. Green**1** = poly-bisMPA-allyl-carbonate pBAC M_n = 5.8 kDa, Đ = 1.30; red**2** = poly-bisMPA-furfuryl-carbonate M_n = 4.5 kDa, Đ = 1.40; blue**3** = poly-bisMPA-oxetane-carbonate M_n = 7.7 kDa, Đ = 1.27; purple**4** = poly-bisMPA-propargyl-carbonate. M_n = 10.5 kDa, Đ = 1.36;

MALDI characterization

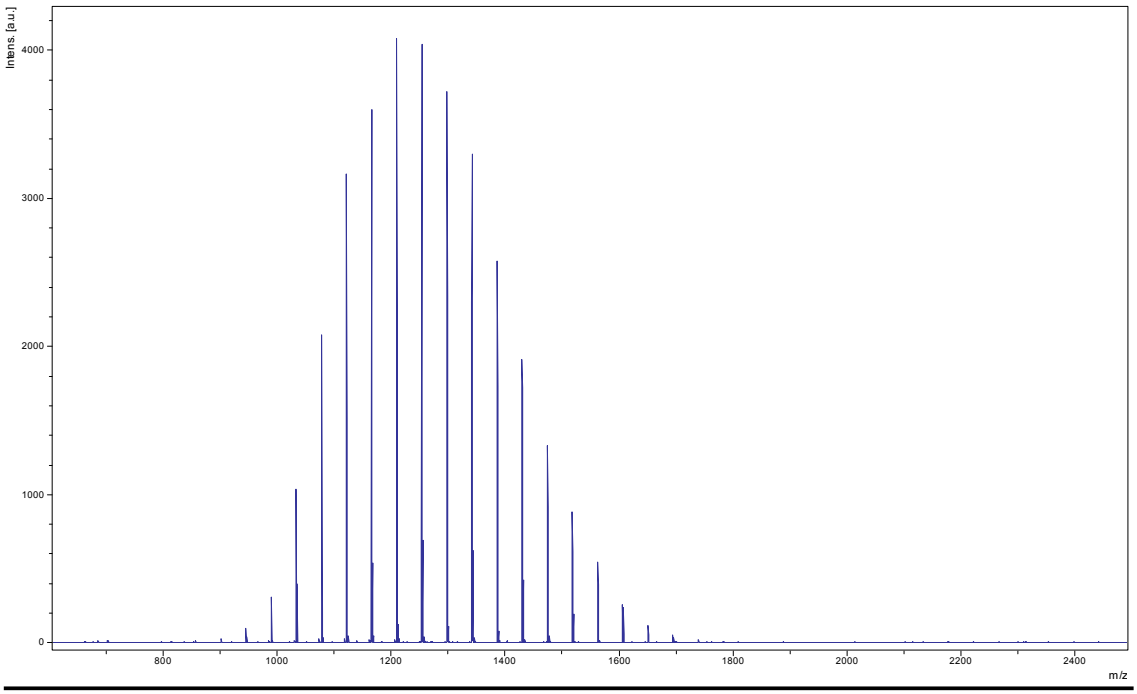


Figure S37. MALDI TOF spectra of PEG- TMP-carbonate **3c**.

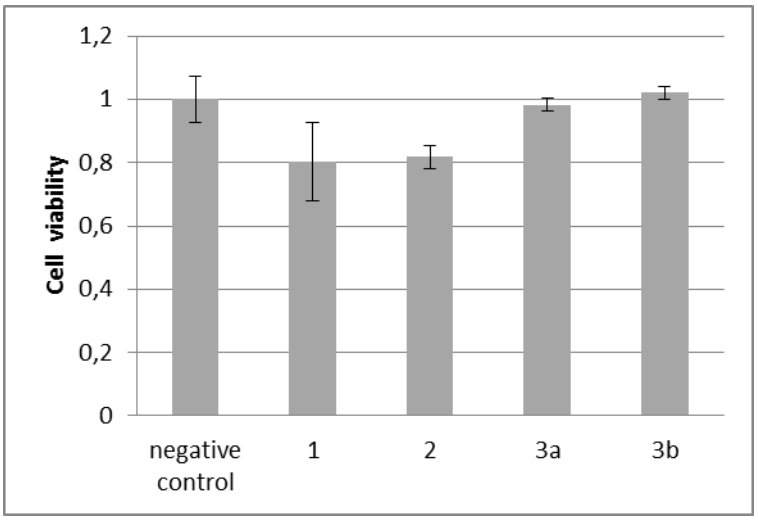


Figure S38. Cell viability after eluting tests of imidazole-TMP-carbonate **1**, BIMIPA **2**, allyl-TMP-carbonate **3a** and propargyl-TMP-carbonate **3b**.

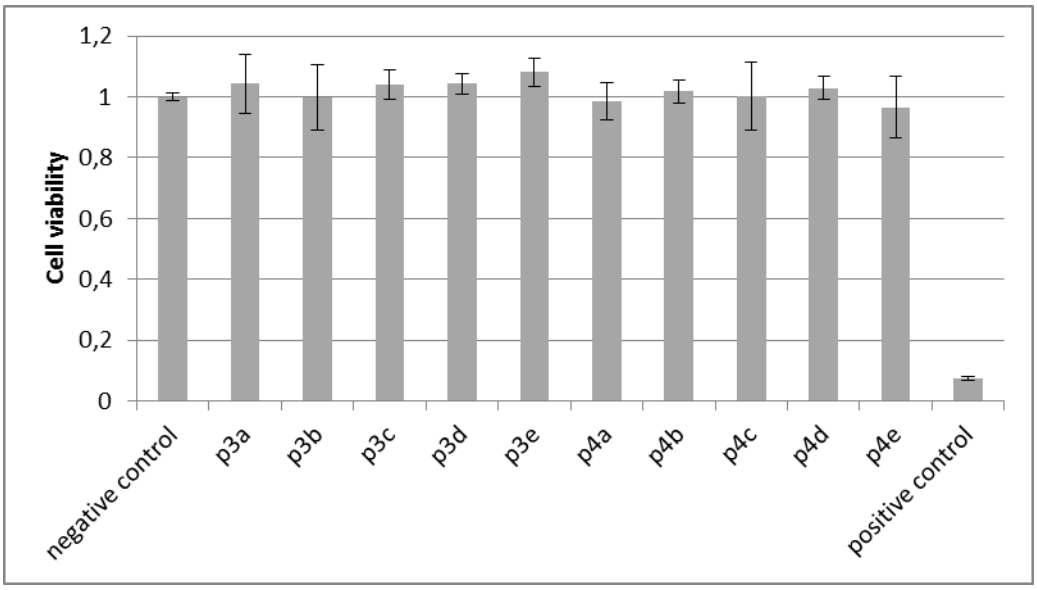


Figure S39. Cell viability after eluting tests of polycarbonates **3a-e** and **4a-e**.

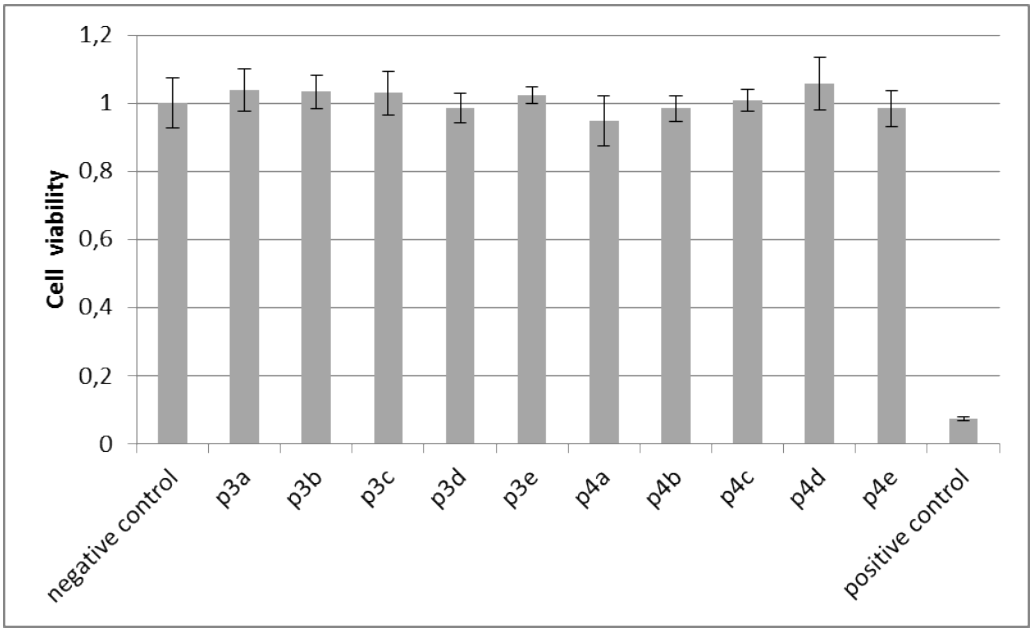
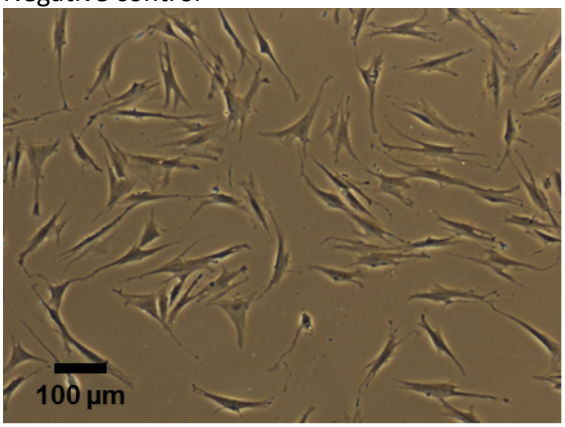
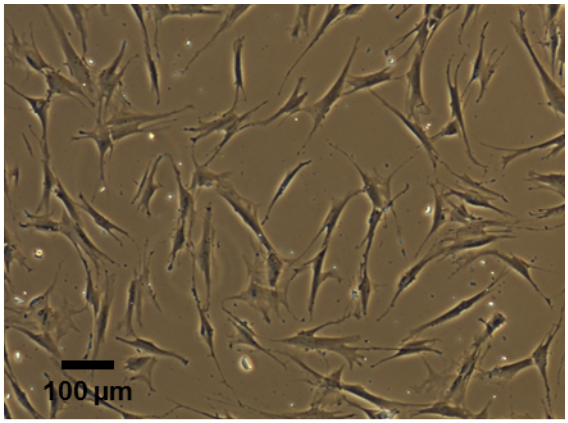


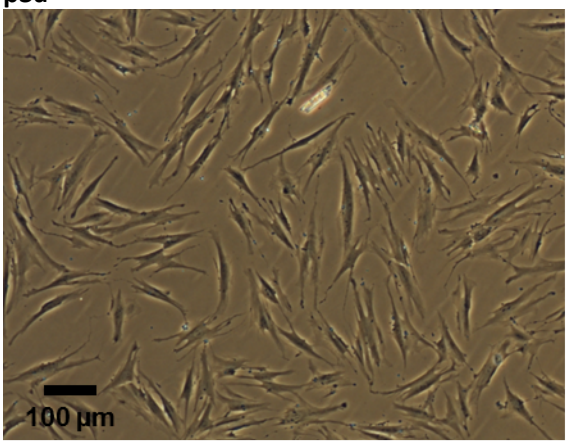
Figure S40. Cell viability after direct contact tests with polycarbonates **3a-e** and **4a-e**.

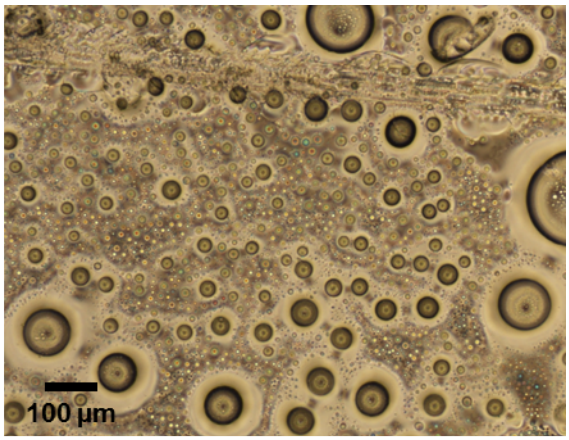
Negative control



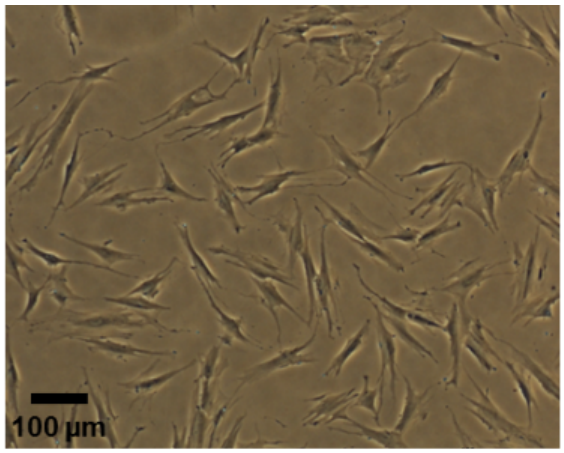


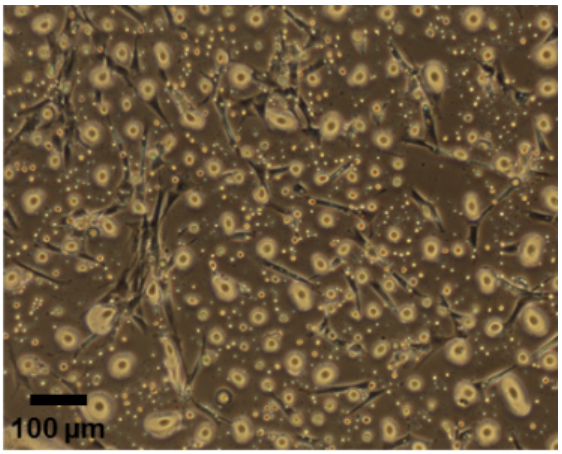
p3a



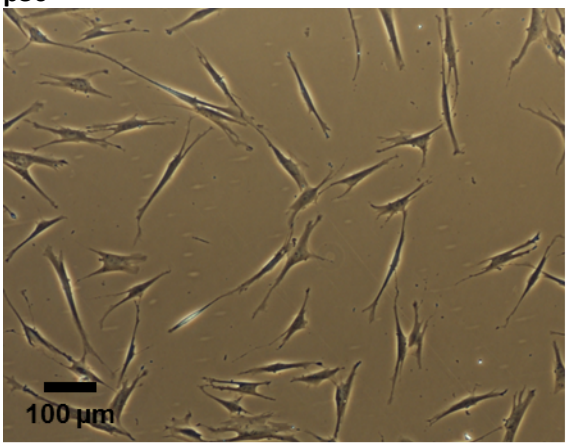


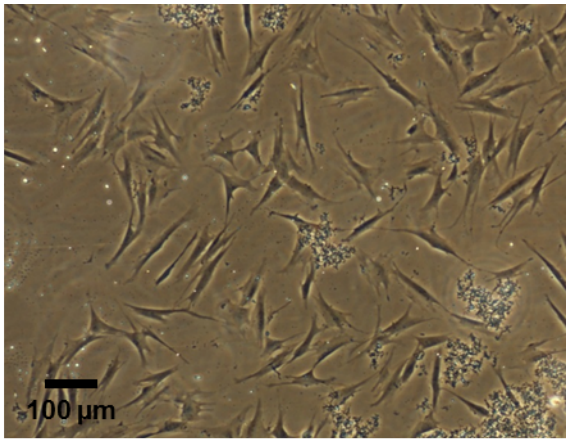
p3b



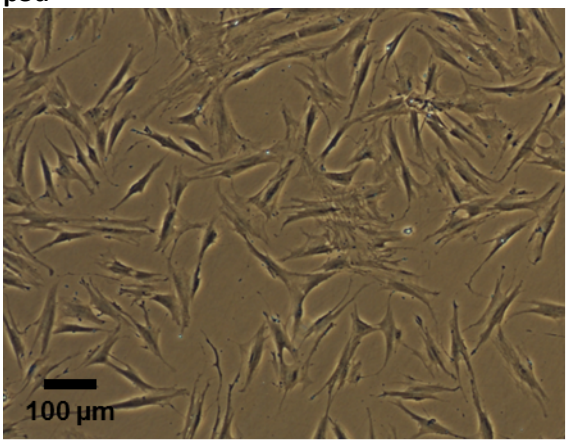


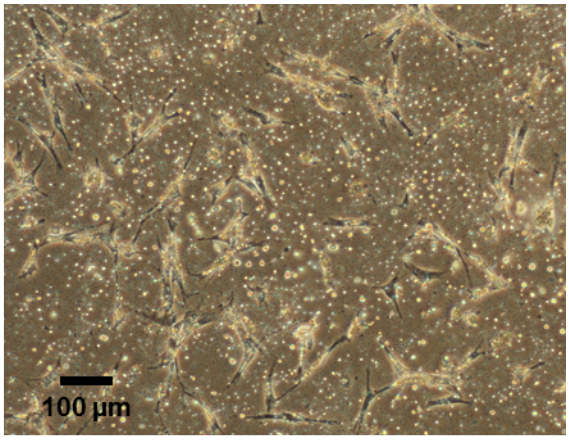
p3c



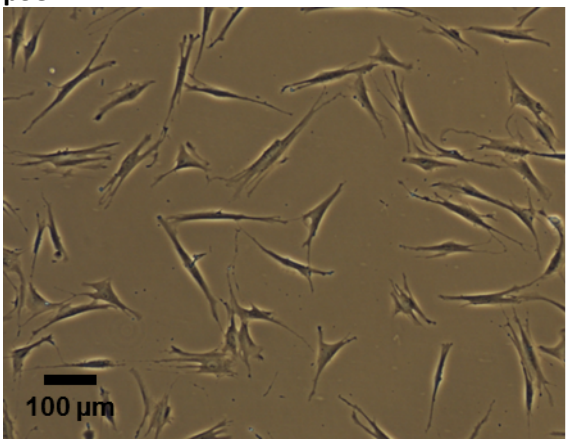


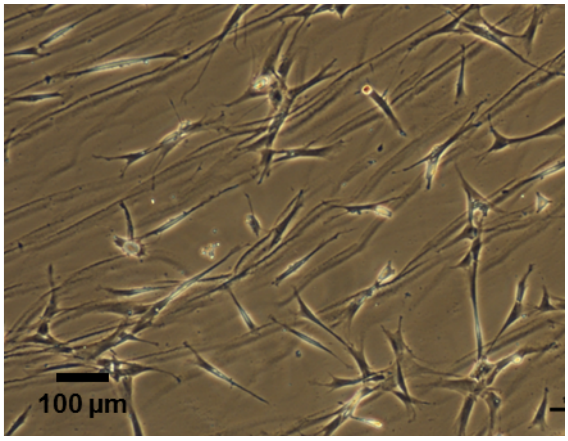
p3d



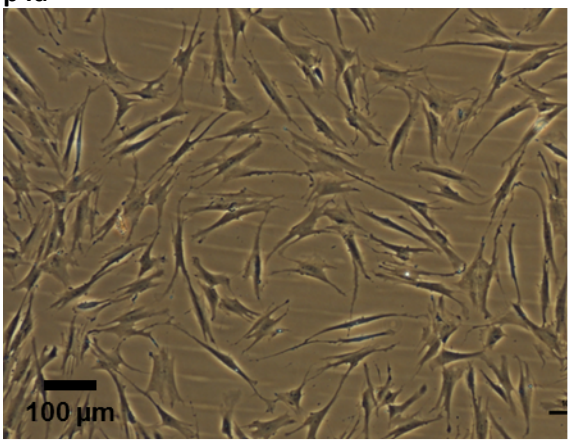


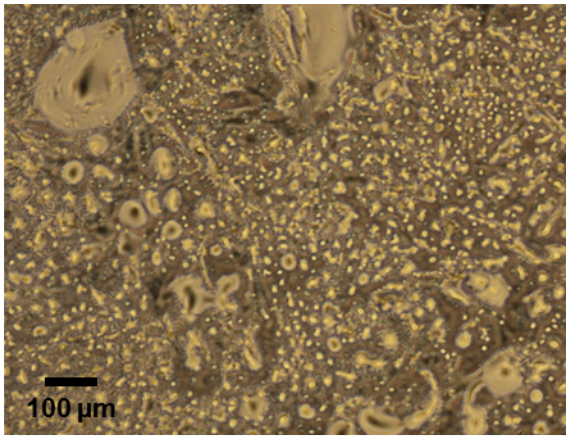
p3e



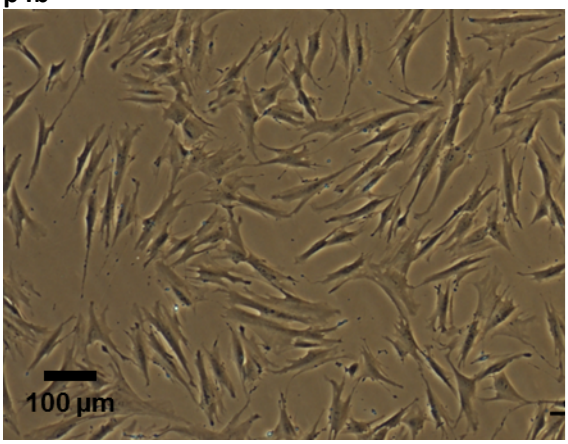


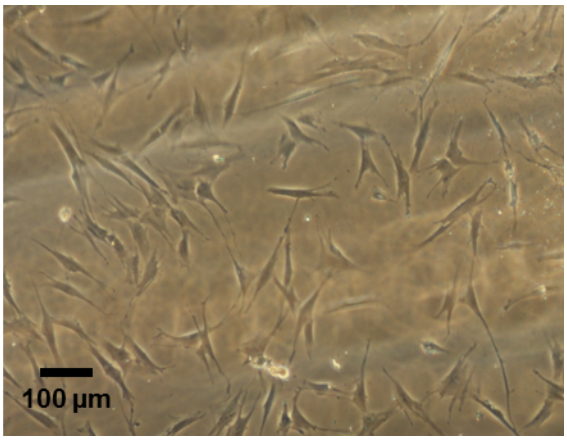
p4a



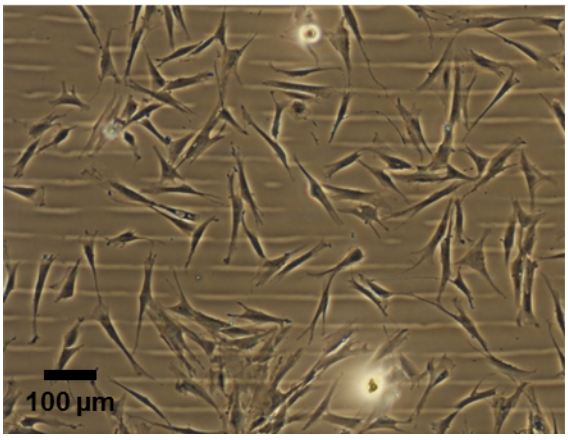


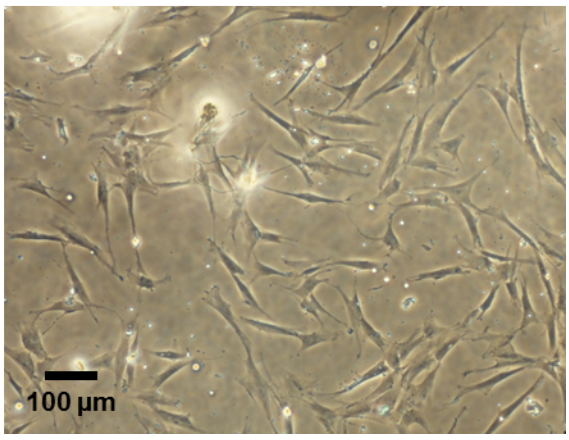
p4b



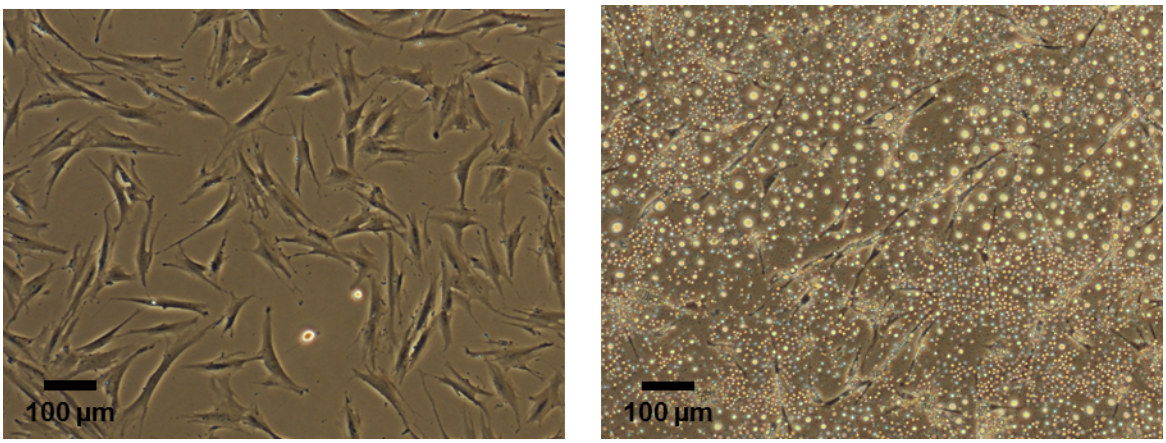


p4c





p4d



p4e

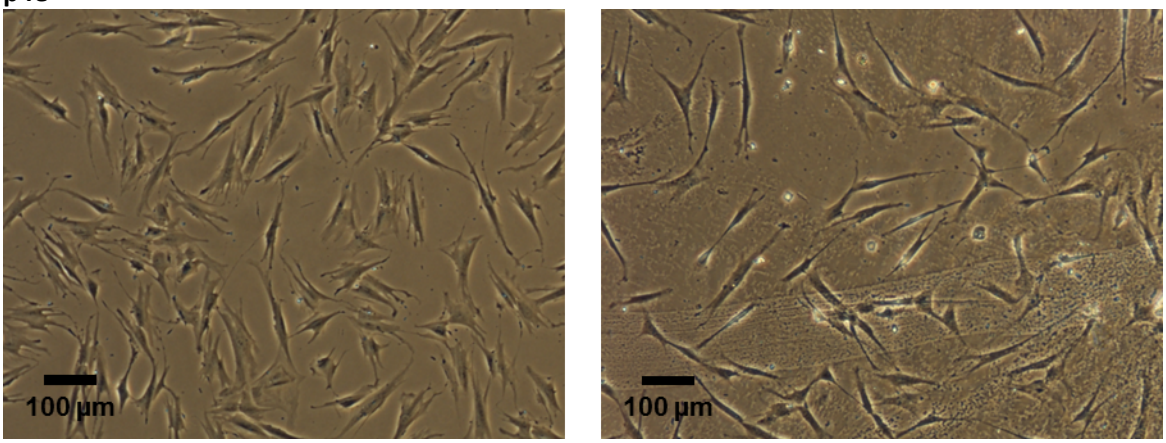


Figure S41. Cell growth in eluting tests (left) and direct contact tests (right) of polycarbonates **3a-e** and **4a-e**.