

Exploring the Versatility of Novel Furan-Based α,ω -Diene Carbonate Monomers: Synthesis, (Co-)Polymerization, and Comparative Study

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Experimental Section

Materials and methods

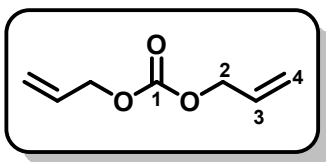
All reagents and solvents were purchased from Merck and used without further purification. Reactions were conducted in either a silicon bath or in Drysyn at the required temperature, measured with a thermocouple. Reactions were monitored by TLC on an aluminium strip coated with silica gel 60 F254 from Merck, revealed under UV light (254 nm) and in the presence of permanganate staining solution. ^1H NMR spectra of some monomers were obtained using a Bruker 400 MHz spectrometer in CDCl_3 , and were calibrated using the residual signal of CDCl_3 at 7.26 ppm. ^{13}C NMR spectra were recorded on a Bruker Fourier 400 (101 MHz) in CDCl_3 . Chromatographic purification was conducted using approximately 20 cm of silica. Polymerization was carried out under inert conditions using standard Schlenk techniques on a dual manifold line and a high-vacuum line. All ruthenium catalysts were purchased from Sigma-Aldrich (Merck), including Grubbs catalyst first generation (C_1), Grubbs catalyst second generation (C_2), dichloro[1,3-bis(2-methylphenyl)-2-imidazolidinylidene] (benzylidene) (tricyclohexylphosphine) ruthenium (II) (Grubbs catalyst M205) (C_3), Hoveyda–Grubbs catalyst second generation (C_4), dichloro[1,3-bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene][[5-[(dimethylamino)sulfonyl]-2-(1-methylethoxy-O)phenyl]methylene-C] ruthenium(II) (Zhan catalyst-1B) (C_5), dichloro[1,3-bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene][[2-(1-methylacetoxy)phenyl]methylene} ruthenium(II) (Grubbs catalyst) M510 (C_6), and Grubbs catalyst third generation (C_7). All ruthenium catalysts used for the polymerization experiments were stored in an air-dried container at 2 °C.

Polymers were analysed by ^1H NMR in CDCl_3 using a Bruker Fourier 300 (300 MHz) and were calibrated using the residual signal of CDCl_3 at 7.26 ppm. ^{13}C NMR spectra were recorded on a Bruker Fourier 300 (75 MHz) in CDCl_3 and calibrated using the solvent peak at 77.16 ppm. Additionally, 2D experiments were conducted, including ^1H - ^1H COSY, ^1H - ^{13}C HMBC, and ^1H - ^{13}C HSQC spectra, to assign the peaks. Size-exclusion chromatography (SEC) was performed on an Agilent Technologies 1260 Infinity Series liquid chromatography system with an internal differential refractive index detector and two PLgel columns (5 μm MIXED-D 300 x 7.5 mm) using HPLC grade THF as the mobile phase at a flow rate of 1.0 mL/min at 50 $^\circ\text{C}$. Calibration was done with polystyrene standards from Agilent Technologies. Thermogravimetric Analysis (TGA) was carried out with a TGA Q500 (TA Instruments); 5 to 10 mg of dried sample was equilibrated at 50 $^\circ\text{C}$ for 5 min and flushed with highly pure nitrogen gas. All experiments were performed with a heating rate of 10 $^\circ\text{C}/\text{min}$ up to 600 $^\circ\text{C}$. The reported values of $T_{\text{d}5\%}$ represent the temperature at which 5% of the product mass is lost. Differential Scanning Calorimetry (DSC) was performed with a DSC Q20 (TA Instruments); 8 to 14 mg of sample were placed in a sealed pan, flushed with highly pure nitrogen gas and subjected to a heat-cool-heat cycle at 10 $^\circ\text{C}/\text{min}$ in a temperature range of -70 $^\circ\text{C}$ to 150 $^\circ\text{C}$. Three heat/cool cycles were done for each sample, and the T_g values recorded were from the third cycle.

Monomer synthesis

The monomers were prepared adapting a previously published procedure used to synthesize several dialkyl carbonates.³

Synthesis of diallyl carbonate

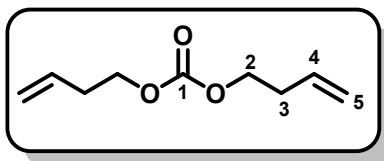


Diallyl carbonate was obtained as a clear liquid from the reaction mixture using fractional distillation ($T(\text{ext}) = 105\text{--}110\text{ }^\circ\text{C}$, $T(\text{vapour}) = 85\text{--}90\text{ }^\circ\text{C}$, $p = 60\text{ mbar}$). With a final yield of 59%.

$^1\text{H NMR}$ (300 MHz CDCl_3) δ (ppm) 5.94 (1H, s, H_3); 5.37 (1H, s, H_4); 5.27 (1H, s, H_4); 4.64 (2H, s, H_2).

$^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ (ppm) 154.8 (C_1); 131.6 (C_3); 118.9 (C_4); 68.5 (C_2).

Synthesis of di(but-3-en-1-yl) carbonate

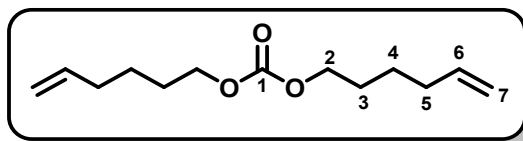


Di(but-3-en-1-yl) carbonate was obtained as clear liquid after filtration in acidic silica followed by fractional distillation under vacuum ($T(\text{ext}) = 40\text{--}50\text{ }^\circ\text{C}$, $T(\text{vapour}) = 25\text{ }^\circ\text{C}$, $p = 60\text{ mbar}$) with a final yield of 74%.

$^1\text{H NMR}$ (300 MHz CDCl_3) δ (ppm) 5.79 (1H, s, H_4); 5.11 (2H, d, $J = 14.1\text{ Hz}$, H_5); 4.18 (2H, s, H_2); 2.43 (2H, s, H_3).

$^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ (ppm) 155.2 (C_1); 133.5 (C_4); 117.6 (C_5); 66.9 (C_2); 33.1 (C_3).

Synthesis of di(hex-5-en-1-yl) carbonate

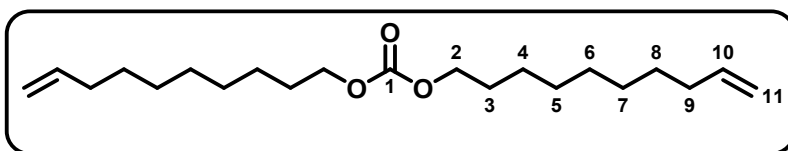


Di(hex-5-en-1-yl) carbonate was obtained as clear liquid after filtration in acidic silica followed by fractional distillation under vacuum ($T(\text{ext}) = 55\text{-}65\text{ }^\circ\text{C}$, $T(\text{vapour}) = 36\text{ - }40\text{ }^\circ\text{C}$, $p = 60\text{ mbar}$) with a final yield of 68%.

$^1\text{H NMR}$ (300 MHz CDCl_3) δ (ppm) 5.78 (1H, ddt, $J = 16.9, 10.2, 6.6\text{ Hz}$, H_6); 5.08 – 4.88 (2H, m, H_7); 4.12 (2H, t, $J = 6.6\text{ Hz}$, H_2); 2.13 – 1.99 (2H, m, H_5); 1.81 – 1.56 (2H, m, H_3); 1.55 – 1.40 (2H, m, H_4).

$^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ (ppm) 155.4 (C1); 138.2 (C6); 114.9 (C7); 67.8 (C2); 33.2 (C5); 28.1 (C4); 24.9 (C3).

Synthesis of di(dec-9-en-1-yl) carbonate

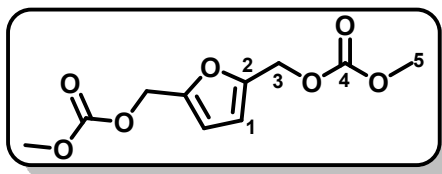


Di(dec-9-en-1-yl) carbonate was obtained as clear liquid after filtration in acidic silica followed by fractional distillation under vacuum ($T(\text{ext}) = 110\text{ - }140\text{ }^\circ\text{C}$, $T(\text{vapour}) = 86\text{ - }95\text{ }^\circ\text{C}$, $p = 60\text{ mbar}$) with a final yield of 70%.

$^1\text{H NMR}$ (300 MHz, CDCl_3) δ (ppm) 5.81 (1H, ddt, $J = 16.9, 10.2, 6.7\text{ Hz}$, H_{10}); 5.05 – 4.87 (2H, m, H_{11}); 4.13 (2H, t, $J = 6.7\text{ Hz}$, H_2); 2.11 – 1.96 (2H, m, H_9); 1.76 – 1.57 (2H, m, H_3); 1.32 (11H, t, $J = 4.6\text{ Hz}$, H_{4-8}).

¹³C NMR (75 MHz, CDCl₃) δ (ppm) 155.4 (C₁); 139.1 (C₁₀); 114.1 (C₁₁); 68.0 (C₂); 33.8 (C₉); 29.3 (C₆); 29.2 (C₇); 29.0 (C₈); 28.9 (C₅); 28.7 (C₃); 25.7 (C₄).

Synthesis of furan-2,5-diylbis(methylene) dimethyl bis(carbonate) (DCMF)



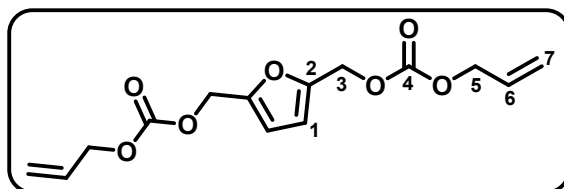
In a two-necked round bottom flask a mixture of (1.00 g, 1.00 g, 7.80 mmol, 1.00 eq. mol) of BHMf was mixed with dimethyl carbonate (DMC) (7.03 g, 78.00 mmol, 10 eq. mol) and (0.01 g, 0.08 mmol, 0.01 eq. mol) of TBD as a basic catalyst. The flask was coupled with a Dean-Stark apparatus and N₂ flow. The reaction mixture was stirred vigorously and heated to 95 °C. The reaction progress was monitored by TLC. After 1 hour and 30 minutes, the reaction was stopped and the mixture was cooled at room temperature. The crude was filtered under vacuum with a gooch packed with acidic silica and washed with dichloromethane. The product was concentrated under reduced pressure obtaining a pale yellow solid (1.59 g) with an isolated yield of 85%.

Characterization was coherent with previously published data.⁴

¹H NMR (400 MHz, CDCl₃): δ (ppm) 6.45 (1H, s, H₁), 5.11 (2H, s, H₃), 3.82 (3H, s, H₅).

¹³C NMR (100 MHz, CDCl₃): δ (ppm) 155.4 (C₄), 149.7 (C₂), 112.1 (C₁), 61.2 (C₃), 55.0 (C₅).

Synthesis of diallyl (furan-2,5-diylbis(methylene)) bis(carbonate) (All- BACF)



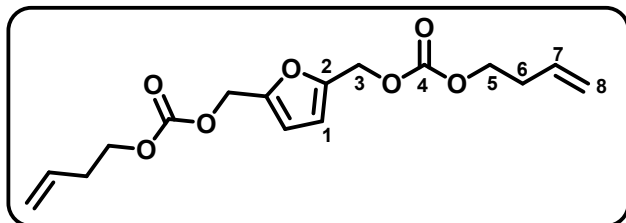
A mixture of (1.00 g, 7.80 mmol, 1.00 eq. mol) of BHMf, diallyl carbonate (11.10 g, 78.08 mmol, 10.00 eq. mol), and TBD (0.01 g, 0.08 mmol, 0.01 eq. mol) was placed in a two-necked round bottom flask equipped with a Dean-Stark apparatus, a magnetic stirrer, and N₂ flow. The flask was heated to 95 °C. Once the temperature was reached, it was maintained for 1 hour and 30 minutes. The reaction progress was monitored by TLC on an aluminium strip coated with silica gel, using dichloromethane as an eluent phase revealed in the presence of potassium permanganate staining solution.

Afterward, the reaction mixture was filtered over acidic silica and washed with dichloromethane. The solvent is then evaporated using a rotary evaporator, followed by vacuum distillation (T(ext) = 50 °C, T(vapour) = 32 °C, p = 60 mbar) recovering 77% of the excess carbonate used in the reaction. The pure product was isolated as a light yellow liquid (1.92 g) with a yield of 83%. Characterization was in accordance with previously published data.⁴

¹H NMR (300 MHz, CDCl₃) δ (ppm) 6.42 (1H, s, H₁); 5.92 (1H, ddt, J = 17.2, 10.4, 5.8 Hz, H₆); 5.41 – 5.20 (2H, m, H₇); 5.09 (2H, s, H₃); 4.63 (2H, dt, J = 5.8, 1.4 Hz, H₅).

¹³C NMR (75 MHz, CDCl₃) δ (ppm) 154.6 (C₄); 149.7 (C₂); 131.4 (C₆); 119.0 (C₇); 112.1 (C₁); 68.7 (C₅); 61.2 (C₃).

Synthesis of di(but-3-en-1-yl) (furan-2,5-diylbis(methylene)) bis(carbonate) (*But-BACF*)



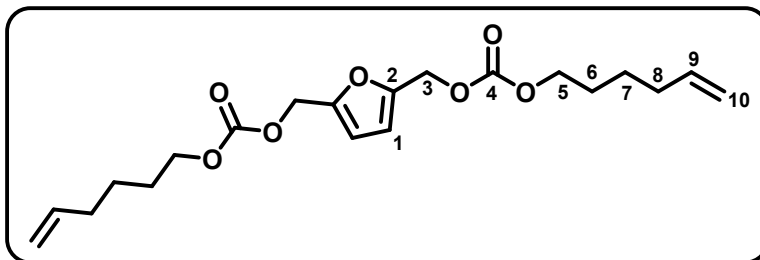
In a typical reaction BHMf (1.00 g, 7.80 mmol, 1.00 eq. mol), di(but-3-en-1-yl) carbonate (6.64 g, 39.00 mmol, 5.00 eq. mol), and TBD (0.03 g, 0.39 mmol, 0.05 eq. mol) were added to a 2-necked 25 ml round bottom flask. The reaction was kept for 2 hours at 110 °C with a Dean-Stark apparatus, magnetic stirrer, and N₂ flow. The reaction progress was monitored by TLC on an aluminium strip coated with silica gel, using dichloromethane as an eluent phase revealed in the presence of potassium permanganate staining solution.

Afterward, the reaction mixture was filtered over acidic silica and washed with dichloromethane. The solvent was then evaporated using a rotary evaporator, followed by vacuum distillation (T(ext) = 116 °C, T(vapour) = 95 °C, p = 60 mbar) recovering 74% of the excess carbonate used in the reaction. The pure product was recovered in the form of a yellowish liquid (1.90 g) in 75% yield.

¹H NMR (300 MHz, CDCl₃) δ (ppm) 6.42 (1H, d, *J* = 0.7 Hz, H₁); 5.88 – 5.70 (1H, m, H₇); 5.18 – 5.02 (4H, m, H_{8,3}); 4.20 (2H, td, *J* = 6.8, 0.5 Hz, H₅); 2.49 – 2.35 (2H, m, H₆).

¹³C NMR (75 MHz, CDCl₃) δ (ppm) 154.8 (C₄); 149.7 (C₂); 133.3 (C₇); 117.7 (C₈); 112.1 (C₁); 67.3 (C₅); 61.1 (C₃); 33.0 (C₆).

Synthesis of furan-2,5-diylbis(methylene) di(hex-5-en-1-yl) bis(carbonate) (*Hex-BACF*)



In a typical reaction BHMF (1.00 g, 7.80 mmol, 1.00 eq. mol), di(hex-5-en-1-yl) carbonate (17.65 g, 78.00 mmol, 10.00 mol. eq.), and TBD (0.20 g, 1.56 mmol, 0.20 eq. mol) were added to a 2-necked 25 ml round bottom flask. The reaction was kept for 3 hours at 140 °C with a Dean-Stark apparatus, magnetic stirrer, and inert gas flow. The reaction progress was monitored by TLC on an aluminium strip coated with silica gel, using dichloromethane as an eluent phase revealed in the presence of potassium permanganate staining solution.

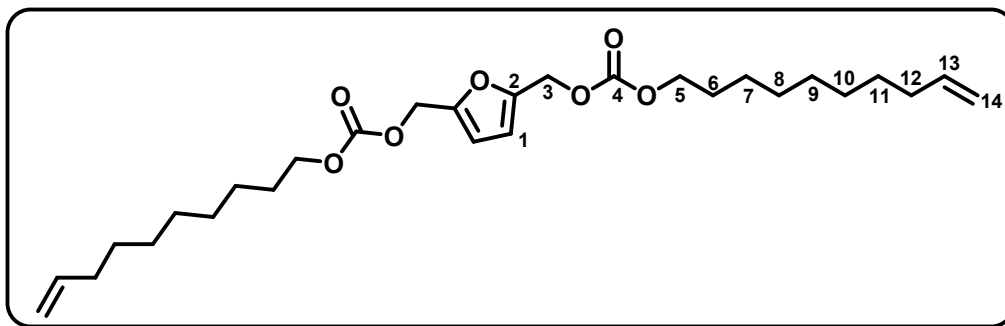
The mixture was filtered using a gooch packed with acid silica and washed with dichloromethane to remove TBD. Then, the mixture was evaporated and dried under vacuum to obtain the crude product as a yellow liquid. The weight of the reaction crude was measured and then analysed using proton NMR to determine conversion and selectivity.

Reaction product was isolated by silica gel chromatographic column using gradient-elution (Hexane:EtOAc from 98:2 to 9:1) as a yellowish liquid (1.80 g) with a yield of 61%.

¹H NMR (300 MHz, CDCl₃) δ (ppm) 6.25 (1H, s, H₁); 5.79 (1H, ddt, *J* = 16.9, 10.2, 6.6 Hz, H₉); 4.95 (2H, m, H₁₀); 4.41 (2H, s, H₃); 3.47 (2H, t, *J* = 6.5 Hz, H₅); 2.05 (H₂, qt, *J* = 6.9, 1.5 Hz, H₈); 1.60 (H₂, m, H₆); 1.45 (H₂, m, H₇).

¹³C NMR (75 MHz, CDCl₃) δ (ppm) 152.3 (C₄); 138.7 (C₂); 114.5 (C₉); 114.5 (C₁₀); 109.6 (C₁); 70.2 (C₅); 64.9 (C₃); 33.5 (C₈); 29.1 (C₇); 25.4 (C₆).

Synthesis of di(dec-9-en-1-yl) (furan-2,5-diylbis(methylene)) bis(carbonate) (*Dec-BACF*)



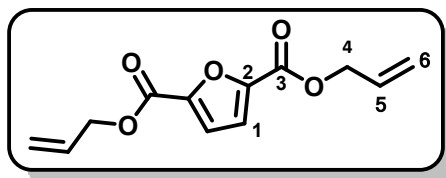
In a typical reaction BHMf (0.22 g, 1.70 mmol, 1.00 eq. mol), di(dec-9-en-1-yl) carbonate (3.00 g, 8.86 mmol, 5.00 mol. eq.), and TBD (0.02 g, 0.14 mmol, 0.05 eq. mol) were added to a 2-necked 25 ml round bottom flask. The reaction was kept for 3 hours at 140 °C with a Dean-Stark apparatus, magnetic stirrer, and N₂ flow. The reaction progress was monitored by TLC on an aluminium strip coated with silica gel, using dichloromethane as an eluent phase revealed in the presence of potassium permanganate staining solution. The mixture was filtered using a gooch with acid silica and washed with dichloromethane to remove TBD.

Then, the mixture was evaporated and dried under vacuum to obtain the crude product as a yellow liquid. Reaction product was isolated by silica gel chromatographic column via gradient elution (Hexane:EtOAc from 98:2 to 9:1) as a yellowish liquid (0.37 g) with a yield of 44%.

¹H NMR (300 MHz, CDCl₃) δ (ppm) 6.41 (1H, s, H₁); 5.80 (1H, ddt, J = 16.9, 10.2, 6.7 Hz, H₁₃); 5.06 (2H, s, H₃); 5.03 – 4.88 (2H, m, H₁₄); 4.14 (2H, t, J = 6.7 Hz, H₅); 2.03 (2H, tdd, J = 6.6, 5.3, 1.4 Hz, H₁₂); 1.72 – 1.58 (2H, m, H₆); 1.45 – 1.16 (10H, m, H₇-H₁₁).

¹³C NMR (75 MHz, CDCl₃) δ (ppm) 154.9 (C₄); 149.8 (C₂); 139.1 (C₁₃); 114.2 (C₁₄); 112.0 (C₁); 68.5 (C₅), 61.0 (C₃); 33.7 (C₁₂); 29.3 (C₉); 29.1 (C₁₀); 29.0 (C₁₁); 28.9 (C₆); 28.6 (C₈); 25.6 (C₇).

Synthesis of diallyl furan-2,5-dicarboxylate (*All-FDE*)

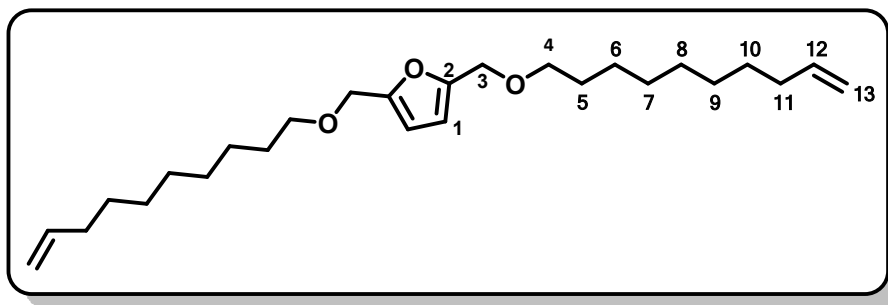


All-FDE was prepared using a previously published procedure.²

¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.26 (2H, s, H₁), 6.04 (2H, m, H₅), 5.44 (2H, dt, J = 17.2, 1.6 Hz, H₆), 5.34 (2H, dq, J = 10.4, 1.5 Hz, H₆), 4.86 (4H, dq, 4.85, J = 5.9, 1.6 Hz, H₄).

¹³C NMR (101 MHz, CDCl₃) δ (ppm) 157.7 (C₃), 146.8 (C₂), 131.5 (C₅), 119.2 (C₁), 118.6 (C₆), 66.1 (C₄).

Synthesis of 2,5-bis((dec-9-en-1-yloxy)methyl)furan (*Dec-BDMF*)

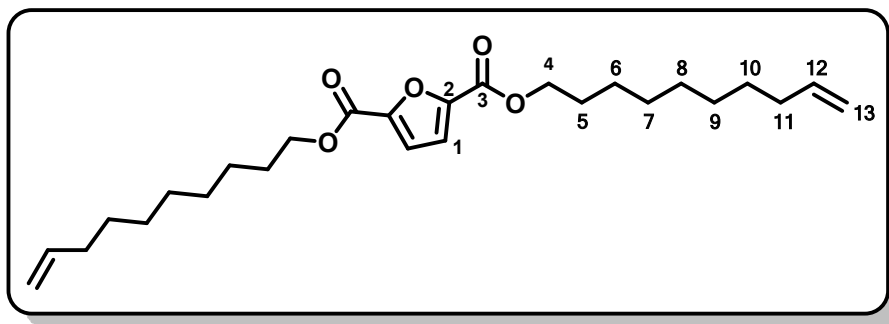


Dec-BDMF was prepared using a previously published procedure.¹

¹H-NMR (400 MHz, CDCl₃) δ (ppm) 6.27 (1H, s, H₁); 5.88 – 5.78 (1H, m, H₁₂); 5.03 – 4.93 (2H, m, H₁₃); 4.44 (2H, s, H₃); 3.48 (2H, t, J = 6.7, 0.9 Hz, H₄); 2.08 – 2.03 (2H, t, J = 6.9 Hz, H₁₁); 1.64 – 1.56 (2H, m, J = 6.9 Hz, H₅); 1.39 – 1.29 (10H, m, J = 6.9 Hz, H_{6,7,8,9,10}).

¹³C-NMR (100 MHz, CDCl₃) δ (ppm) 152.3 (C₂); 139.2 (C₁₂); 114.1 (C₁₃); 109.6 (C₁); 70.5 (C₃); 64.9 (C₄); 33.8 (C₁₁); 29.6 (C₅); 29.4 (C₈); 29.1 (C₉); 28.9 (C₁₀); 26.1 (C₇), 25.7 (C₆).

Synthesis of di(dec-9-en-1-yl) furan-2,5-dicarboxylate (*Dec-FDE*)



Dec-FDE was prepared using a previously published procedure.²

¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.21 (1H, s, H₁); 5.83 (1H, m, H₁₂); 5.01 (1H, d, H₁₃); 4.95 (1H, d, H₁₃); 4.35 (2H, t, J = 6.9 Hz, H₄); 2.06 (2H, m, H₁₁); 1.78 (2H, m, H₅); 1.37 (10H, m, H_{6,7,8,9,10}).

¹³C NMR (101 MHz, CDCl₃) δ (ppm) 158.2 (C₃); 147.0 (C₂); 139.2 (C₁₂); 118.2 (C₁); 114.2 (C₁₃); 65.7 (C₄); 33.8 (C₁₁); 29.3 (C₅); 29.2 (C₈); 29.0 (C₉); 28.9 (C₁₀); 28.6 (C₇); 25.8 (C₆).

Table S1. Optimization of furan-based α,ω -diene carbonate monomers.

(x = 1, 2, 4 and 8)

<i>All</i> -BACF x = 1	<i>Hex</i> -BACF x = 4	<i>All</i> -MACF x = 1	<i>Hex</i> -MACF x = 4
<i>But</i> -BACF x = 2	<i>Dec</i> -BACF x = 8	<i>But</i> -MACF x = 2	<i>Dec</i> -MACF x = 8

#	BHMF (g)	DAC	DAC (eq. mol)	Cat. (% mol)	T (°C)	t (h)	Selectivity ^a		Yield (%) ^b
							x-BACF (%)	x-MACF (%)	
1	1.00	<i>All</i> -Carbonate	5.00	1.00	95	2	<i>All</i> -BACF (74)	<i>All</i> -MACF (26)	60 ^c
2	1.00	<i>All</i> -Carbonate	10.00	1.00	95	2	<i>All</i> -BACF (100)	-	83
3	0.50	<i>But</i> -Carbonate	10.00	1.00	110	2	<i>But</i> -BACF (34)	<i>But</i> -MACF (64)	15 ^d
4	0.50	<i>But</i> -Carbonate	10.00	5.00	110	2	<i>But</i> -BACF (100)	-	76
5	0.50	<i>But</i> -Carbonate	10.00	10.00	110	2	<i>But</i> -BACF (100)	-	75
6	0.50	<i>But</i> -Carbonate	2.50	5.00	110	2	<i>But</i> -BACF (100)	-	54
7	0.50	<i>But</i> -Carbonate	5.00	5.00	110	2	<i>But</i> -BACF (100)	-	79
8	0.50	<i>But</i> -Carbonate	10.00	5.00	110	2	<i>But</i> -BACF (100)	-	76
9	0.20	<i>Hex</i> -Carbonate	5.00	5.00	120	4	<i>Hex</i> -BACF (45)	<i>Hex</i> -MACF (55)	16 ^c
10	0.20	<i>Hex</i> -Carbonate	5.00	5.00	140	3	<i>Hex</i> -BACF (55)	<i>Hex</i> -MACF (45)	19 ^c
11	0.20	<i>Hex</i> -Carbonate	5.00	5.00	140	3	<i>Hex</i> -BACF (55)	<i>Hex</i> -MACF (45)	19 ^c
12	0.20	<i>Hex</i> -Carbonate	5.00	10.00	140	3	<i>Hex</i> -BACF (100)	-	29 ^c
13	0.20	<i>Hex</i> -Carbonate	5.00	20.00	140	3	<i>Hex</i> -BACF (100)	-	44 ^c
14	0.20	<i>Hex</i> -Carbonate	5.00	50.00	140	2.5	<i>Hex</i> -BACF (100)	-	41 ^c
15	0.20	<i>Hex</i> -Carbonate	5.00	20.00	140	3	<i>Hex</i> -BACF (100)	-	44 ^c
16	0.20	<i>Hex</i> -Carbonate	10.00	20.00	140	3	<i>Hex</i> -BACF (100)	-	69 ^c
17	0.20	<i>Dec</i> -Carbonate	5.00	5.00	110	2	<i>Dec</i> -BACF (100)	-	14 ^c
18	0.20	<i>Dec</i> -Carbonate	5.00	5.00	140	3	<i>Dec</i> -BACF (100)	-	44 ^c

Reaction conditions: BHMF and an excess of Diene-carbonate (DAC) is reacted in the presence of TBD at a certain temperature. The reaction was monitored by TLC until it reached full conversion; ^a Selectivity was calculated using ¹H NMR, where x-BACF stands for a generic bis(alkylcarbonate)furans and x-MACF for mono(alkylcarbonate)furans; thus for specific monomers *All* = Allyl, *But* = Butenyl, *Hex* = Hexenyl, *Dec* = Decenyl. ^b Reported isolated yield. ^c Product isolated via column chromatography. ^d Yield calculated using ¹H NMR.

Table S2. Gram-scale furan-based α,ω -diene carbonate monomers.

#	BHMF (g)	DAC	DAC (eq. mol)	Cat. (% mol)	T (°C)	t (h)	Selectivity ^a		Yield ^b (%)
							x-BACF	x-MACF	
1	1.00	<i>All</i> -Carbonate	10.00	1.00	95	2	<i>All</i> -BACF (100)	-	83
2	0.50	<i>But</i> -Carbonate	5.00	5.00	110	2	<i>But</i> -BACF (100)	-	79
3	1.00	<i>But</i> -Carbonate	5.00	5.00	110	2	<i>But</i> -BACF (100)	-	75
4	0.50	<i>Hex</i> -Carbonate	10.00	20.00	140	3	<i>Hex</i> -BACF (100)	-	74 ^c
5	1.00	<i>Hex</i> -Carbonate	10.00	20.00	140	3	<i>Hex</i> -BACF (100)	-	61 ^c

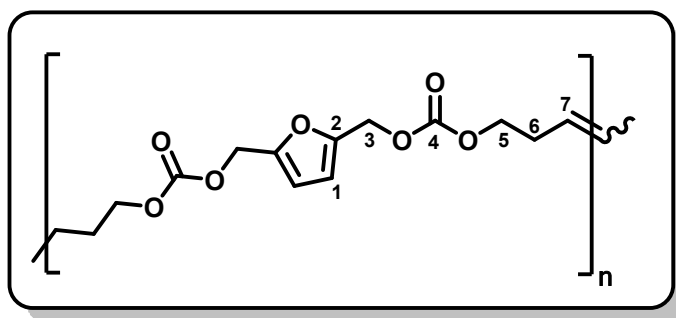
Reaction conditions: BHMF and an excess of carbonate is reacted in the presence of TBD at a certain temperature. The reaction was monitored by TLC until it reached full conversion. ^a Selectivity was calculated using ¹H NMR. ^b Reported isolated yield. ^c Product isolated via column chromatography.

Homo-Polymer synthesis

Solvent free ADMET polymerisation of homopolymers general procedure: In a 25 mL Schleck flask, the chosen monomer (0.10 g) was combined with p-benzoquinone (3.00 eq. mol relative to the catalyst). The flask underwent 3 cycles of 15 minutes vacuum followed by N₂ purging. Upon completion of the purge, the appropriate catalyst amount was introduced along with a magnetic stirrer. The flask was then positioned in a pre-heated Drysyn at 80 °C and subjected to vacuum (25 mbar). To monitor reaction progress, samples were taken at various time points, dissolved in CDCl₃, and examined via ¹H NMR. The reaction was terminated using an ethyl vinyl ether/THF solution (1:9) for 1 hour. Subsequently, the crude product was precipitated in cold methanol. The precipitated product was separated based on the formed polymer's state.

For low molecular weight, sticky polymers, a minimal amount of a low boiling point solvent (acetone or CH₂Cl₂) was utilized to recover the product. Solid polymers were filtered and washed with cold methanol. Both polymer types were then dried under vacuum for 24 hours.

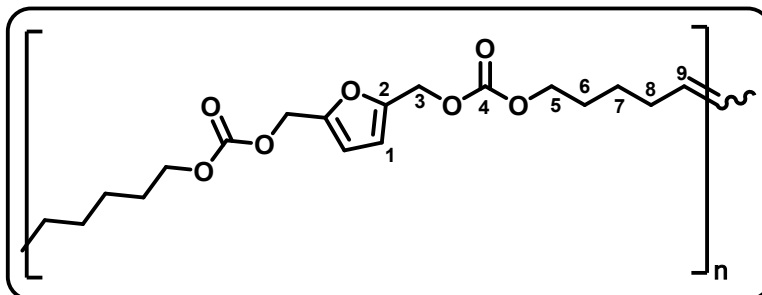
But-BACF derived homo-polymer (P(*But*-BACF))



¹H NMR (300 MHz, CDCl₃) δ (ppm) 6.41 (1H, s, H₁); 5.50 (1H, td, J = 3.8, 1.9 Hz, H₇); 5.07 (2H, s, H₃); 4.14 (2H, t, J = 6.8 Hz, H₅); 2.38 (2H, dt, J = 16.2, 6.1 Hz, H₆).

^{13}C NMR (75 MHz, CDCl_3) δ (ppm) 154.8 (C_4); 149.7 (C_2); 128.1 (C_7); 112.1 (C_1); 67.5 (C_5); 61.1 (C_3); 31.9 (C_6).

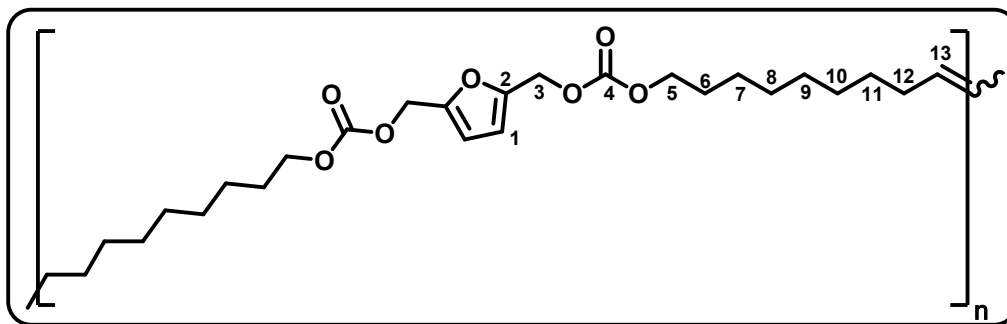
Hex-BACF derived homo-polymer (P(Hex-BACF))



^1H NMR (300 MHz, CDCl_3) δ (ppm) 6.17 (1H, d, $J = 0.9$ Hz, H_1); 5.39 – 5.19 (1H, m, H_9), 4.33 (2H, s, H_3); 3.38 (2H, t, $J = 6.6$ Hz, H_5); 1.92 (2H, dq, $J = 18.7, 6.7, 6.1$ Hz, H_8); 1.51 (2H, ddd, $J = 14.9, 8.8, 4.4$ Hz, H_6); 1.37 – 1.20 (2H, m, H_7).

^{13}C NMR (75 MHz, CDCl_3) δ (ppm) 152.3 (C_4); 130.3 (C_2); 129.5 (C_9); 109.6 (C_1); 70.3 (C_5); 64.9 (C_3); 32.3 (C_8); 29.1 (C_6); 26.0 (C_7).

Dec-BACF derived homo-polymer (P(Dec-BACF))



^1H NMR (300 MHz, CDCl_3) δ (ppm) 6.34 (1H, s, H_1); 5.40 – 5.21 (1H, m, H_{13}); 5.00 (2H, s, H_3); 4.07 (2H, t, $J = 6.7$ Hz, H_5); 1.88 (2H, d, $J = 6.2$ Hz, H_{12}); 1.71 – 1.42 (2H, m, H_6); 1.23 (10H, d, $J = 9.4$ Hz, H_{7-11}).

¹³C NMR (75 MHz, CDCl₃) δ (ppm) 154.9 (C₄); 149.8 (C₂); 130.3 (C₁₃); 112.0 (C₁); 68.5 (C₅); 61.0 (C₃); 32.6 (C₁₂); 29.6 (C₁₁); 29.3 (C₁₀); 29.2 (C₉); 29.1 (C₈); 28.6 (C₆); 25.6 (C₇).

Table S3- Catalyst loading for the homo-polymerization of *But*-BACF via ADMET Polymerization.

#	Catalyst	Cat. (%mol)	Conv. ^a (%)	M _n ^b (Kda)	\mathcal{D} ^c	T _{d5%} ^d (°C)	T _g ^e (°C)
1	C4	0.50	100	4.4	1.6	175	-34
2		1.00	100	13.0	1.4	159	-8
3		2.00	100	6.3	1.9	162	-17
4		10.00	100	3.9	1.4	132	-24

Reaction conditions: 100 mg of *But*-BACF was added to a Schlenk flask in the presence of second-generation Hoveyda–Grubbs catalyst (C4) and 1,4-benzoquinone (3.00 eq. mol compared to catalyst) at 80 °C under 25 mbar of vacuum for 24 hours; ^a Conversion was calculated through ¹H NMR; ^b Determined by SEC in THF (10 mM LiBr) at 50 °C; ^c \mathcal{D} = dispersity; ^d TGA degradation temperatures at which 5% mass loss (T_{d5%}) was observed under nitrogen; ^e Glass transition temperature (T_g) determined by DSC, temperature ramp 10 °C min⁻¹.

Table S4- Homo-polymerization results of different furan-based α,ω -diene monomers.

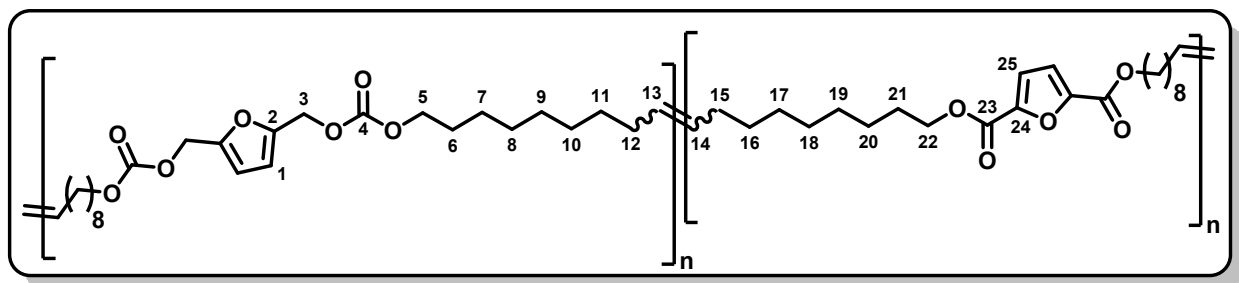
#	Monomer	Catalyst (%mol)	T (°C)	t (h)	Conv. ^a (%)	Yield ^b (%)	M _n ^c (Kda)	\mathcal{D} ^d	T _{d5%} ^e (°C)	T _g ^f (°C)	T _c ^g (°C)	T _m ^h (°C)	Ref.
1	<i>Dec</i> -BDMF	C4 (1.00)	80	2	100	-	9.5	1.8	257	-53	4.2	21	¹
2	<i>Dec</i> -FDE	C4 (1.00)	80	0.5	100	86	26.4	2.48	257	-31	-	70	²
3	<i>Dec</i> -BACF	C4 (1.00)	80	0.5	100	85	19.0	2.3	244	-36	-20	0	This work

Reaction conditions: Monomer was added to a Schlenk flask in the presence of second-generation Hoveyda–Grubbs catalyst (C4) and 1,4-benzoquinone (3.00 eq. mol compared to catalyst) at 80 °C under 25 mbar of vacuum until it reached full conversion; ^a Conversion was calculated through ¹H NMR; ^b Isolated yield after purification and drying, yield = (isolated mass/theoretical mass) × 100. ^c Determined by SEC in THF (10 mM LiBr) at 50 °C; ^d \mathcal{D} = dispersity; ^e TGA degradation temperatures at which 5% mass loss (T_{d5%}) was observed under nitrogen; ^f Glass transition temperature (T_g) determined by DSC, temperature ramp 10 °C min⁻¹; ^g T_c was determined by DSC and it stands for crystallization temperature; ^h T_m was determined by DSC and it stands for melting temperature.

Co-Polymer synthesis

Solvent free ADMET polymerisation of co-polymers general procedure: Two distinct monomers were combined in a 1:1 molar ratio, totalling 0.40 mmol. Subsequently, 1.29 mg of *p*-benzoquinone (3.00 molar equivalents relative to the catalyst) was introduced. The mixture underwent purging through 3 cycles of 15-minute vacuum followed by N₂. Upon completion of the purge, the appropriate quantity of C4 (2.50 mg, 1.00% mol) was added, along with a magnetic stirrer. The flask was then placed in a pre-heated Drysyn set at 80 °C and subjected to vacuum (25 mbar). To monitor reaction progress, samples were extracted at various time intervals, dissolved in CDCl₃, and examined via ¹H NMR. The reaction was terminated using a solution of Ethyl Vinyl Ether/THF (1:9) for 1 hour. The resulting crude product was precipitated in cold methanol. The final purified polymer was isolated following the same procedure as described for solvent-free polymerization.

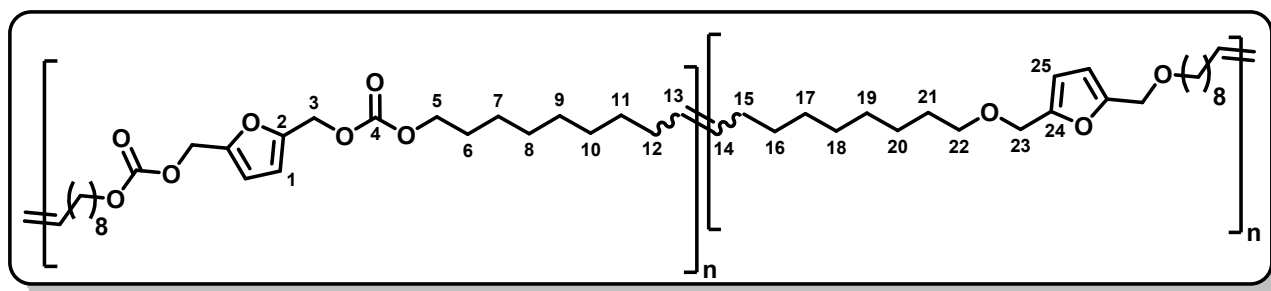
P(*Dec*-BACF: *Dec*-FDE) (1:1) co-polymer



¹H NMR (300 MHz, CDCl₃) δ (ppm) 7.11 (1H, s, H₂₅); 6.34 (1H, s, H₁); 5.35 – 5.22 (2H, m, H_{13,14}); 5.00 (2H, s, H₃); 4.25 (2H, t, *J* = 6.8 Hz, H₂₂); 4.07 (2H, t, *J* = 6.8 Hz, H₅); 1.89 (4H, s, H_{12,15}); 1.76 – 1.48 (4H, m, H_{6,21}); 1.36 – 1.18 (20H, m, H_{7-11,16-20}).

^{13}C NMR (75 MHz, CDCl_3) δ (ppm) 158.2 (C_{23}); 154.9 (C_4); 149.8 (C_{24}); 147.0 (C_1); 130.3 - 129.8 ($\text{C}_{13, 14}$); 118.2 (C_{25}); 112.0 (C_1); 68.5 (C_5); 65.7 (C_3); 61.1 (C_{22}); 32.6 (C_{12-15}); 29.7 - 29.1 ($\text{C}_{9,10, 17, 18}$); 28.6- 27.2 ($\text{C}_{8,19}$); 25.8 (C_7); 25.7 (C_{20}).

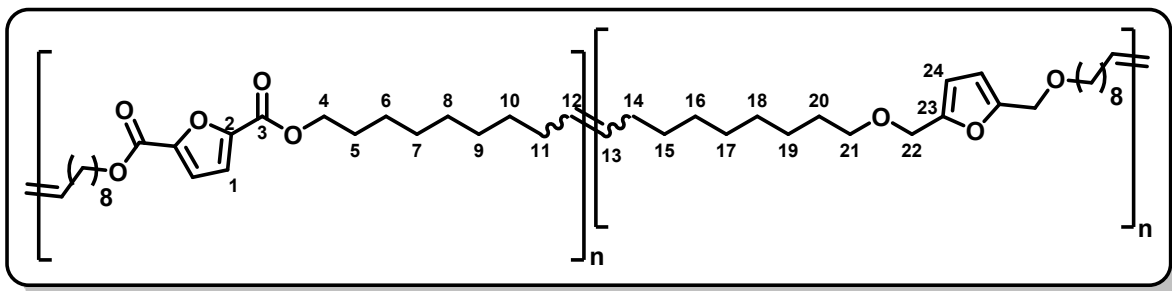
P(Dec-BDMF: Dec-BACF) (1:1) co-polymer



^1H NMR (300 MHz, CDCl_3) δ (ppm) 6.34 (1H, s, H_1); 6.17 (1H, s, H_{25}); 5.38 – 5.21 (2H, m, H_{13-14}); 5.00 (2H, s, H_3); 4.34 (2H, s, H_{23}); 4.07 (2H, t, $J = 6.7$ Hz, H_5); 3.38 (2H, t, $J = 6.7$ Hz, H_{22}); 1.88 (4H, d, $J = 7.4$ Hz, H_{12-16}); 1.65 – 1.51 (4H, m, $\text{H}_{6, 21}$); 1.21 (20H, s, $\text{H}_{7-11; 16-20}$).

^{13}C NMR (75 MHz, CDCl_3) δ (ppm) 154.9 (C_4); 152.3 (C_{24}); 149.8 (C_1); 130.3 ($\text{C}_{13, 14}$); 112.0/109.7 ($\text{C}_{1, 25}$); 70.5 (C_{23}); 68.5 (C_5); 64.9 (C_3); 32.6 ($\text{C}_{12, 15}$); 29.6 - 28.6 ($\text{C}_{8-10, 17-19}$); 26.1 (C_6); 25.7 (C_7).

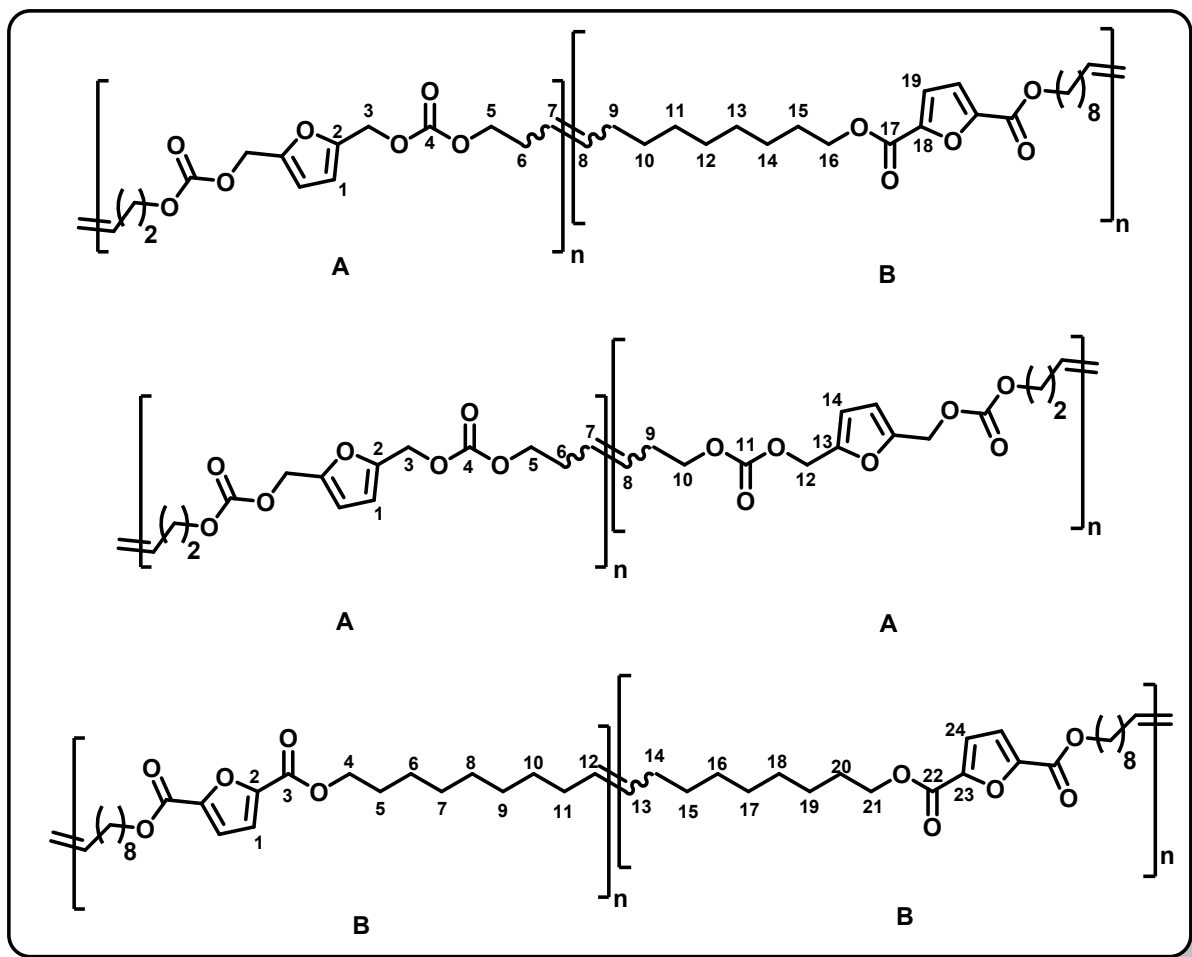
P(Dec-BDMF: Dec-FDE) (1:1) co-polymer



^1H NMR (300 MHz, CDCl_3) δ (ppm) 7.18 (1H, s, H_1); 6.24 (1H, s, H_{24}); 5.43 – 5.29 (2H, m, H_{12-13}); 4.41 (2H, s, H_{22}); 4.32 (2H, t, $J = 6.8$ Hz, H_4); 3.45 (2H, t, $J = 6.7$ Hz, H_{21}); 1.98 (4H, d, $J = 17.4$ Hz, $\text{H}_{11, 14}$); 1.75 (2H, t, $J = 7.2$ Hz, H_5); 1.56 (4H, dd, $J = 13.7, 6.6$ Hz, $\text{H}_{6, 20}$); 1.40 – 1.18 (20H, m, $\text{H}_{6-10, \text{H}_{15-19}}$).

^{13}C NMR (75 MHz, CDCl_3) δ (ppm) 158.2 (C_3); 152.3 (C_{23}); 147.0 (C_2); 130.3 ($\text{C}_{12, 13}$); 118.2 (C_1); 109.6 (C_{24}); 70.5 (C_{22}); 65.7 (C_{21}); 64.9 (C_4); 32.6 ($\text{C}_{11, 14}$); 29.6 (C_5); 29.6 (C_{15}); 29.4 (C_{10}); 29.4 - 29.1 ($\text{C}_{8,9,16, 17}$); 28.6 (C_{20}); 26.1 (C_{19}); 25.8 (C_6).

P(Dec-FDE: But-BACF) (1:1) co-polymer



¹H NMR (300 MHz, CDCl₃) δ (ppm) 7.11 (1H, s, H₁₉); 6.34 (1H, s, H₁); 5.54 – 5.37 (1H, m, H₇); 5.37 – 5.20 (1H, m, H₈); 5.00 (2H s, H₃); 4.25 (2H, t, *J* = 6.8 Hz, H₁₆); 4.13 – 3.96 (2H, m, H₅); 2.44 – 2.16 (2H, m, H₆); 1.90 (2H, d, *J* = 6.7 Hz, H₉); 1.69 (2H, q, *J* = 7.0 Hz, H₁₅); 1.53 (2H, s, H₁₄); 1.25 (8H, d, *J* = 16.2 Hz, H₁₀₋₁₃).

¹³C NMR (75 MHz, CDCl₃) δ (ppm) 158.2 (C₁₇); 154.8 (C₄); 149.7 (C₁₈); 147.0 (C₂); 134.0 (C_{8(AB)}); 130.3 (C_{7(AB)}); 128.1 (C_{12, 13 (BB)}); 124.3 (C_{7, 8 (AA)}); 118.2 (C₁₉), 112.1 (C₁), 67.5 (C₅); 65.7 (C₃); 61.1 (C₁₆); 32.6 (C₉); 31.9 (C₁₅); 29.6 - 28.6 (C₁₀₋₁₃); 25.8 (C₁₄).

^1H NMR and ^{13}C NMR spectra

Diallyl carbonate

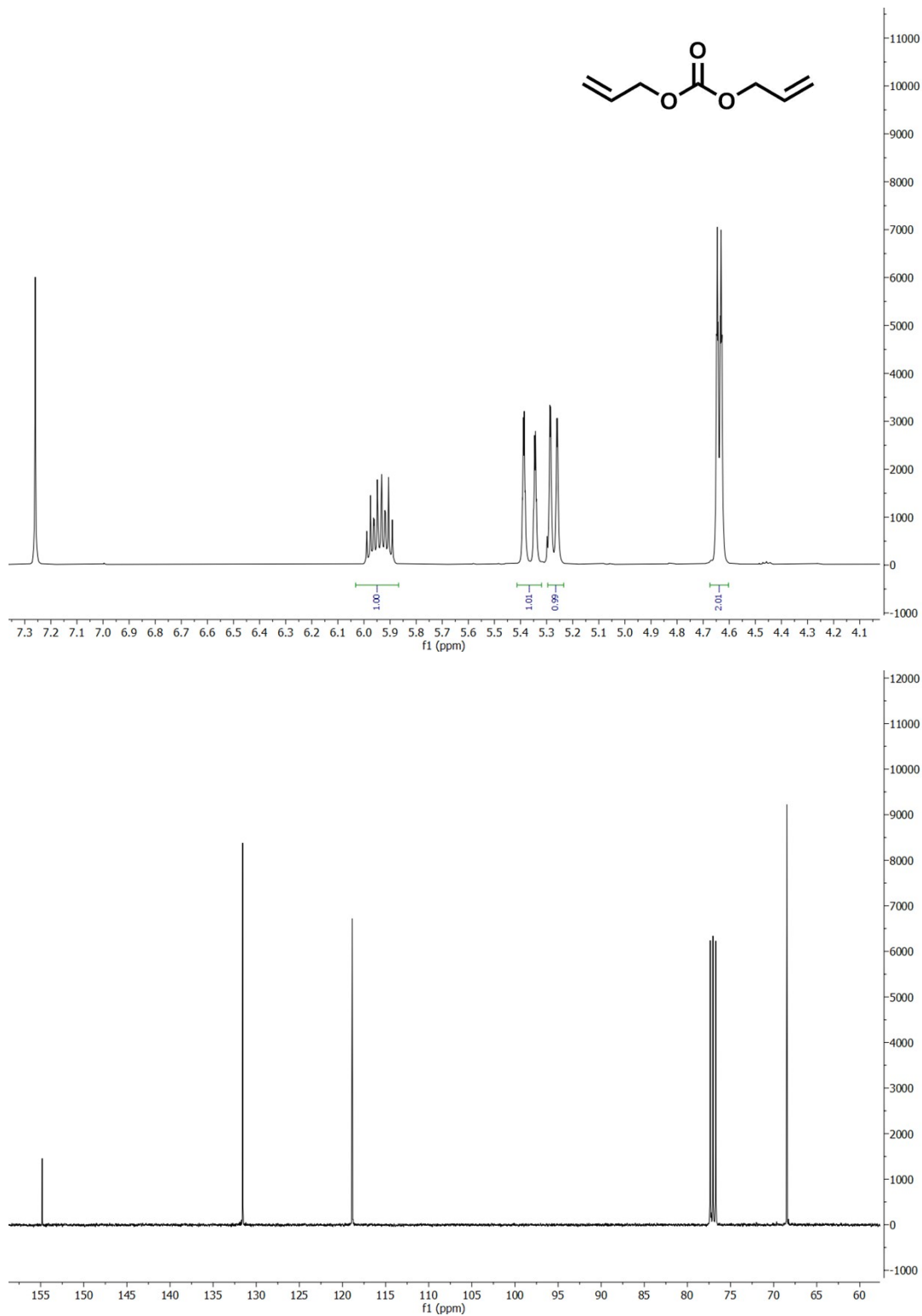


Figure S1- (top) ^1H NMR spectra of *All*-Carbonate in CDCl_3 ; (bottom) ^{13}C NMR spectra of *All*-Carbonate in CDCl_3 .

Di(but-3-en-1-yl) carbonate

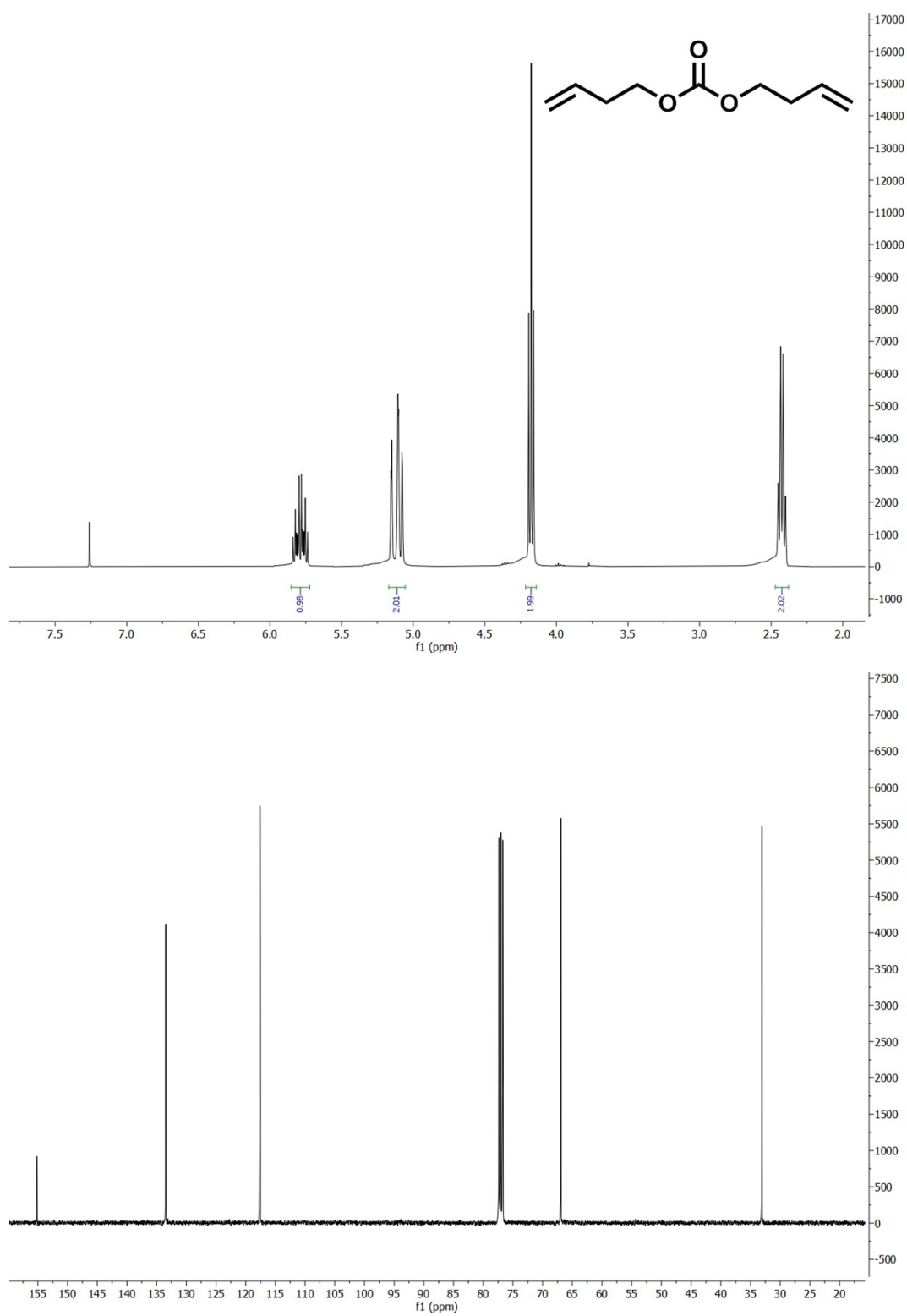


Figure S2- (top) ¹H NMR spectra of *But*-Carbonate in CDCl₃; (bottom) ¹³C NMR spectra of *But*-Carbonate in CDCl₃.

Di(hex-5-en-1-yl) carbonate

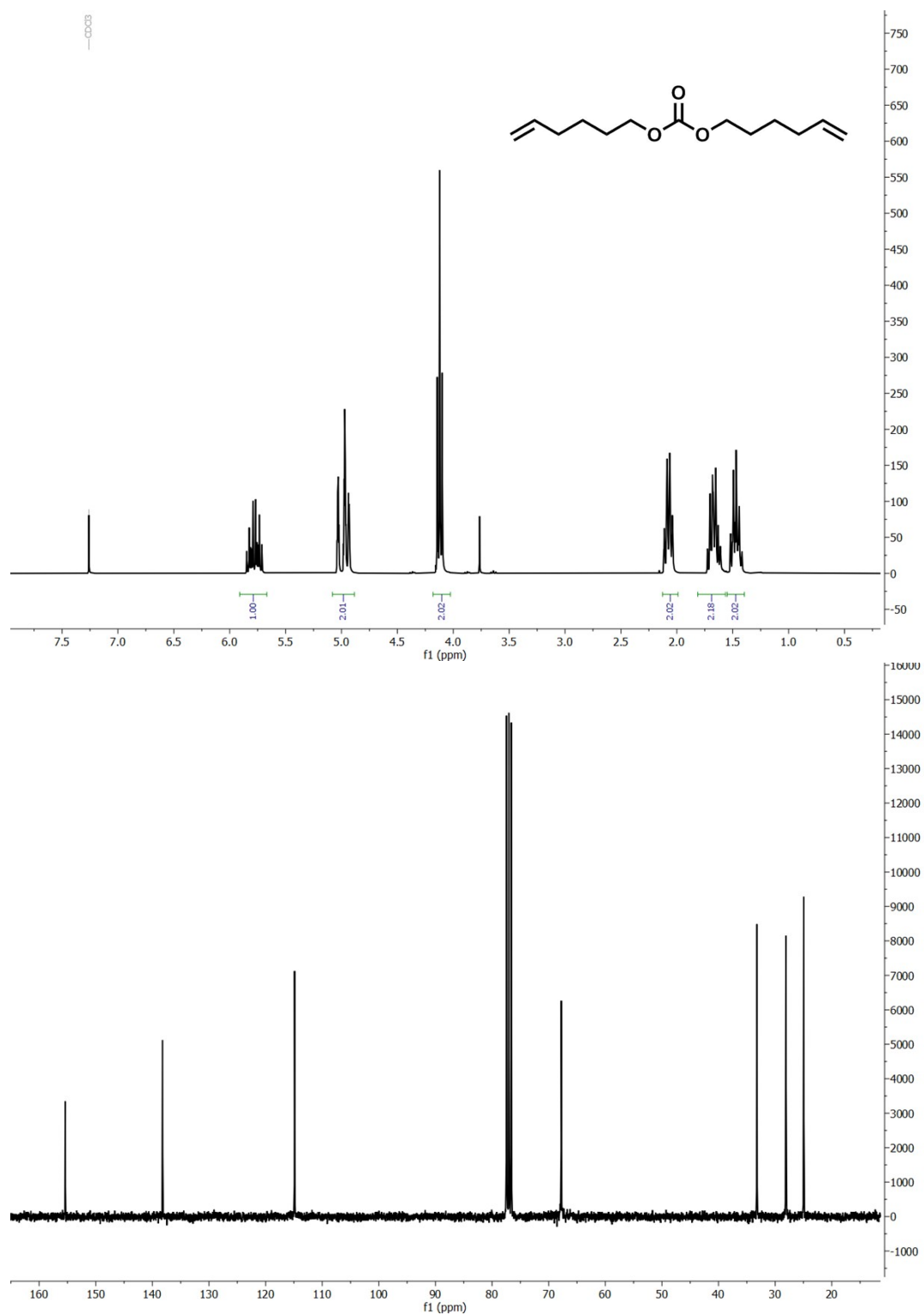


Figure S3- (top) ¹H NMR spectra of Hex-Carbonate in CDCl₃; (bottom) ¹³C NMR spectra of Hex-Carbonate in CDCl₃.

Di(dec-9-en-1-yl) carbonate

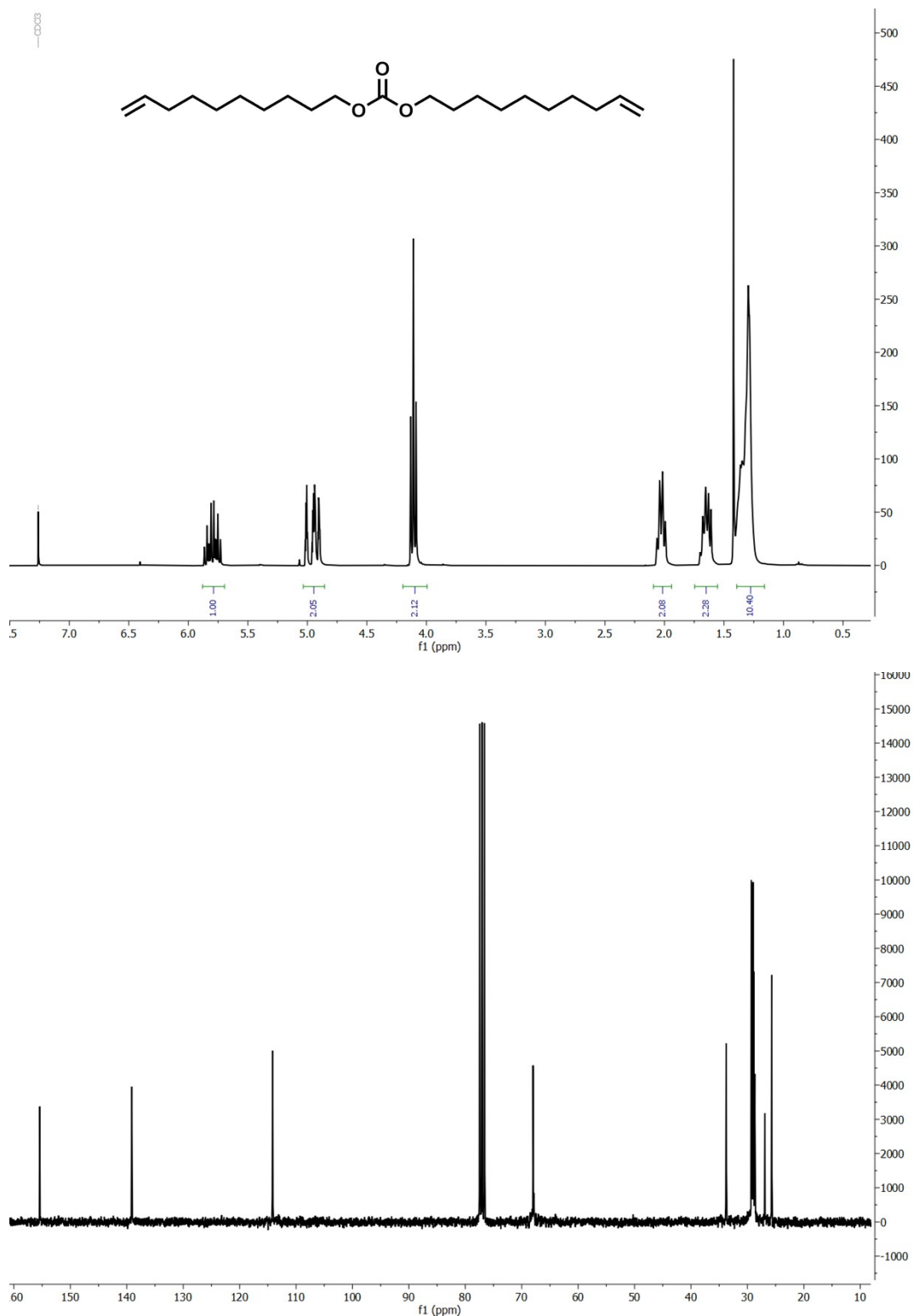


Figure S4- (top) ¹H NMR spectra of *Dec*-Carbonate in CDCl₃; (bottom) ¹³C NMR spectra of *Dec*-Carbonate in CDCl₃.

Diallyl (furan-2,5-diylbis(methylene)) bis(carbonate) (*A//*-BACF)

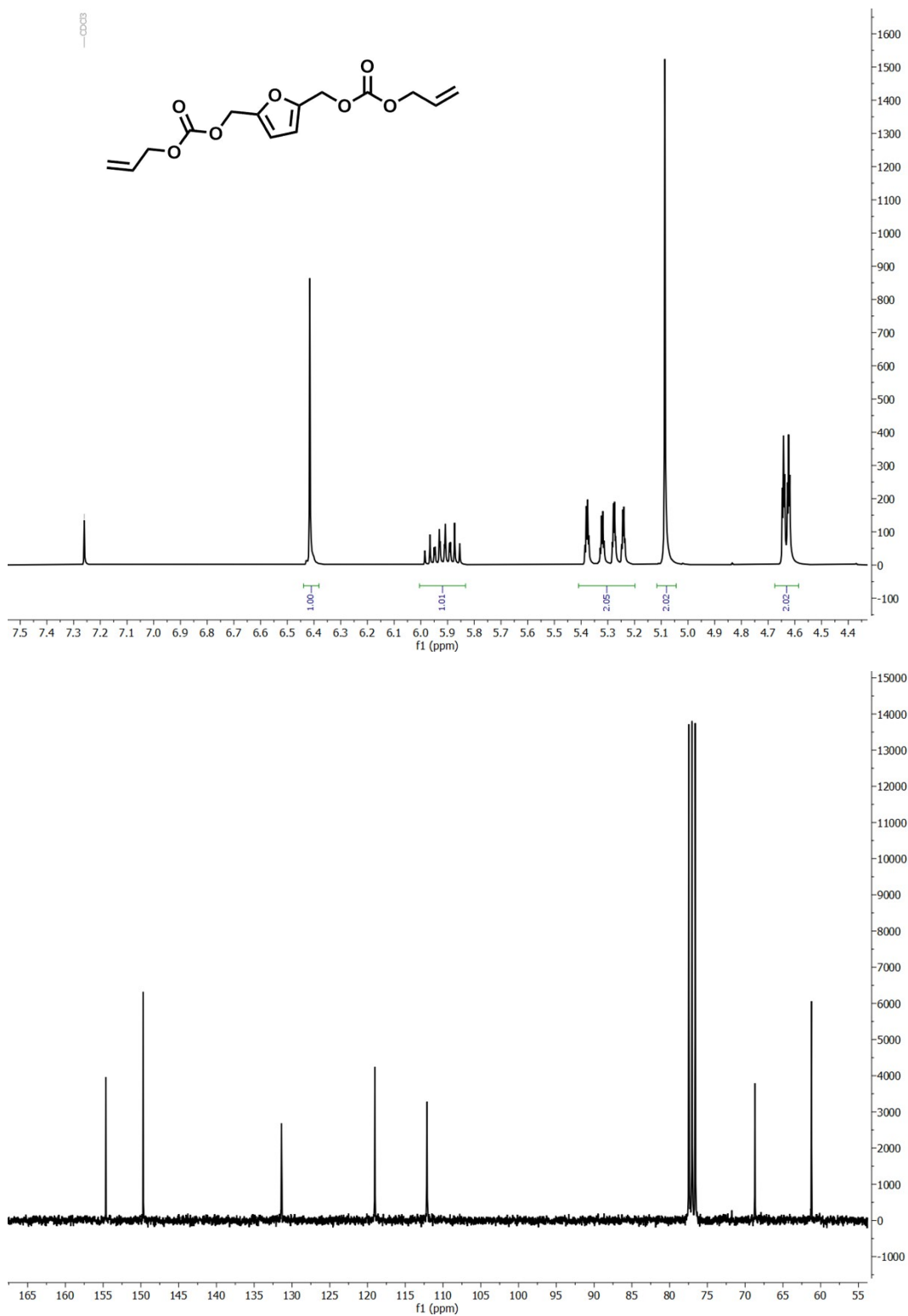


Figure S5- (top) ¹H NMR spectra of *A//*-BACF in CDCl₃; (bottom) ¹³C NMR spectra of *A//*-BACF in CDCl₃.

Di(but-3-en-1-yl) (furan-2,5-diylbis(methylene)) bis(carbonate) (*But-BACF*)

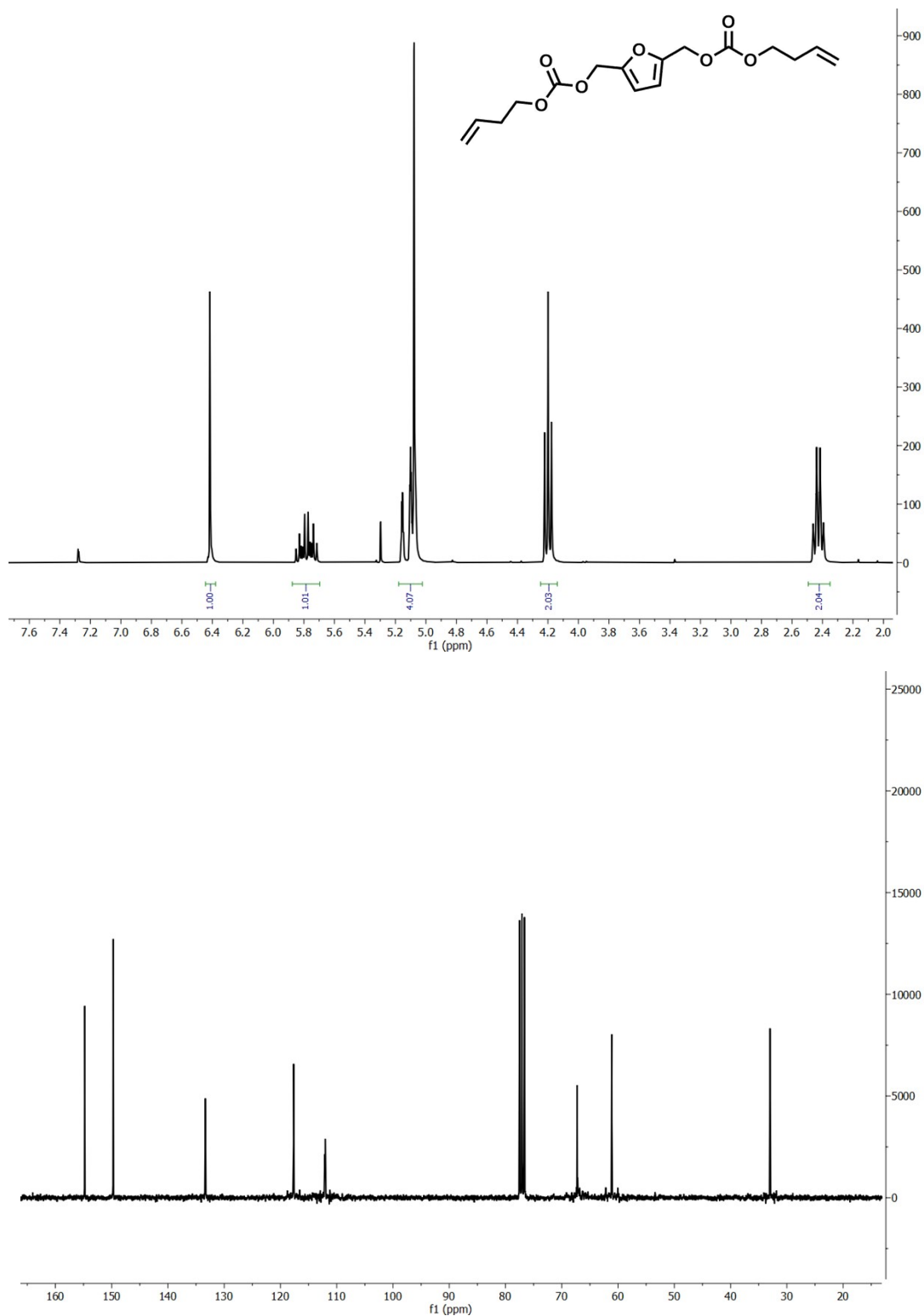


Figure S6- (top) ¹H NMR spectra of *But-BACF* in CDCl₃; (bottom) ¹³C NMR spectra of *But-BACF* in CDCl₃.

Furan-2,5-diylbis(methylene) di(hex-5-en-1-yl) bis(carbonate) (*Hex-BACF*)

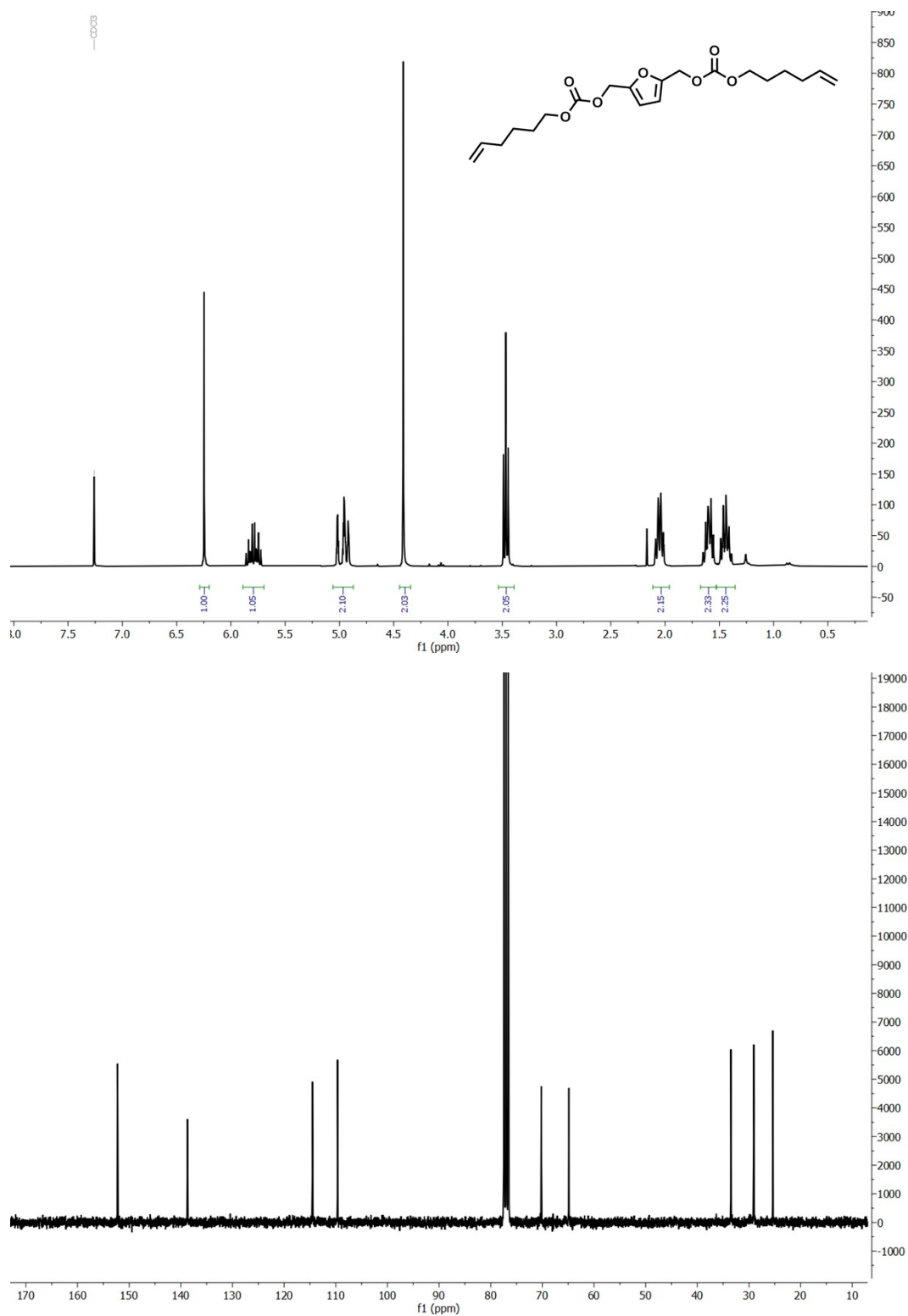


Figure S7- (top) ¹H NMR spectra of *Hex-BACF* in CDCl₃; (bottom) ¹³C NMR spectra of *Hex-BACF* in CDCl₃.

Di(dec-9-en-1-yl) (furan-2,5-diylbis(methylene)) bis(carbonate) (*Dec-BACF*)

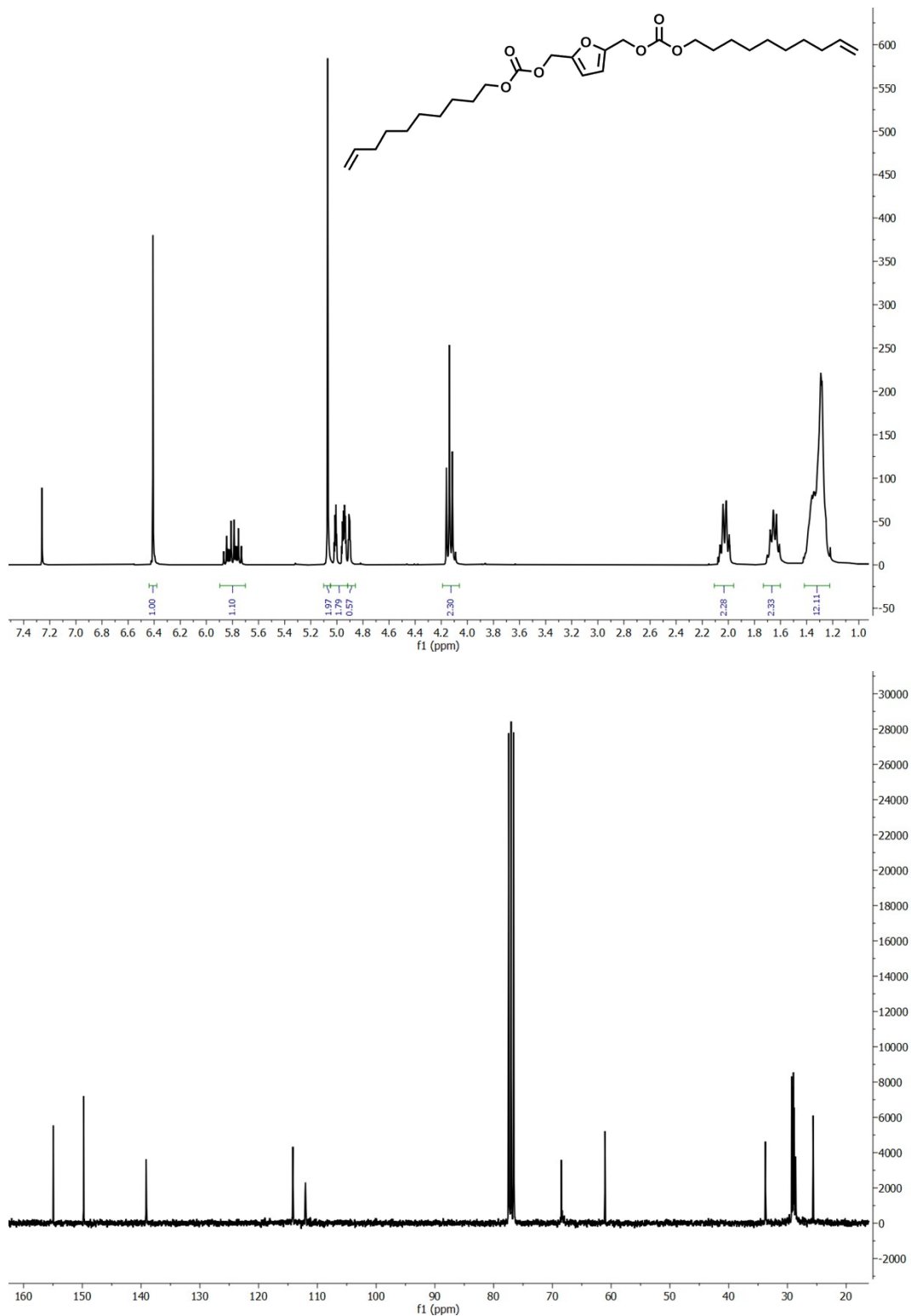


Figure S8- (top) ¹H NMR spectra of *Dec-BACF* in CDCl₃; (bottom) ¹³C NMR spectra of *Dec-BACF* in CDCl₃.

But-BACF derived homo-polymer (P(But-BACF))

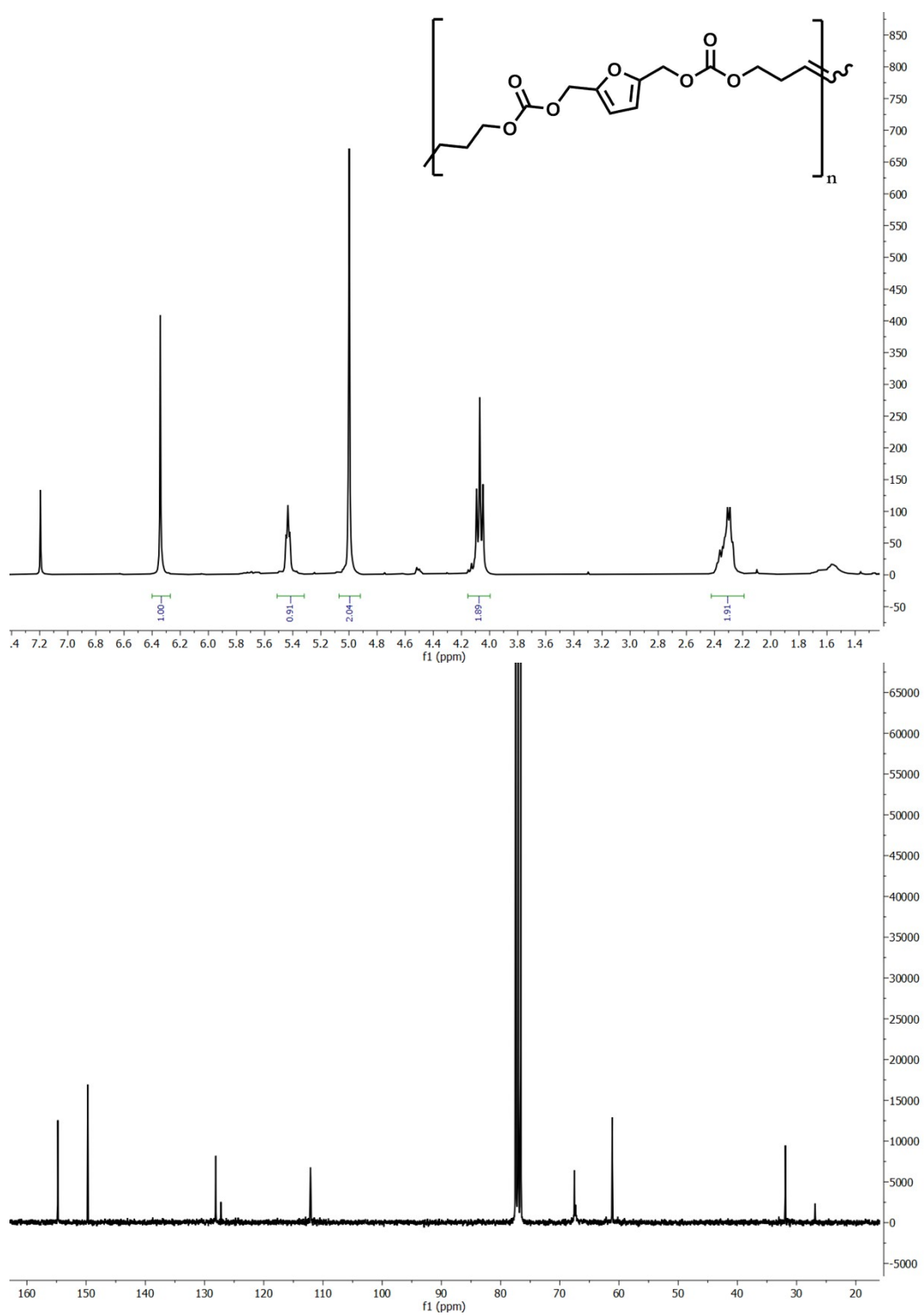


Figure S9- (top) ¹H NMR spectra of P(But-BACF) in CDCl₃; (bottom) ¹³C NMR spectra of P(But-BACF) in CDCl₃.

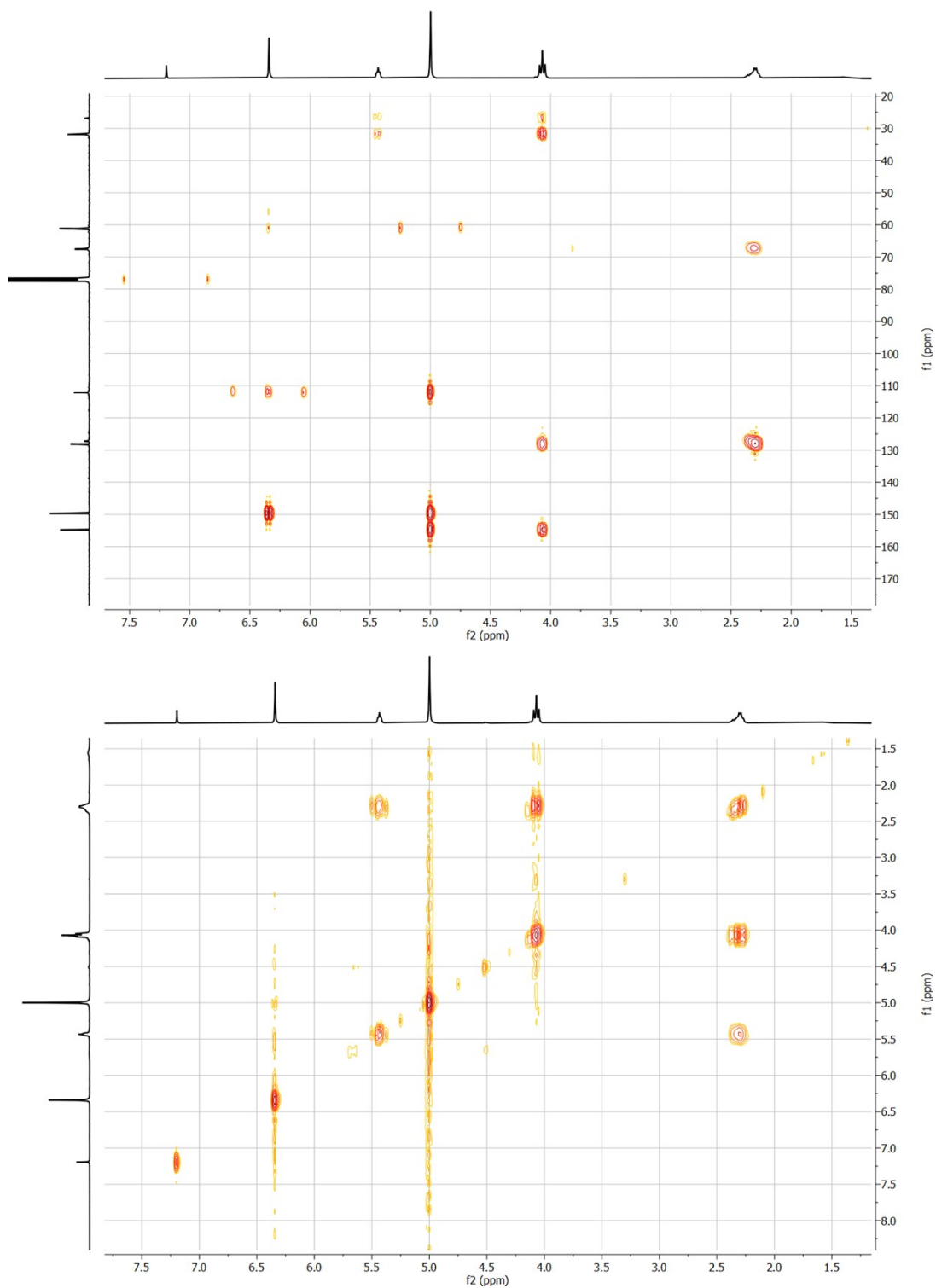


Figure S10- (top) 2D ¹H, ¹³C-HSQC spectra of P(*But*-BACF) in CDCl₃; (bottom) 2D ¹H-¹H COSY spectra of P(*But*-BACF) in CDCl₃.

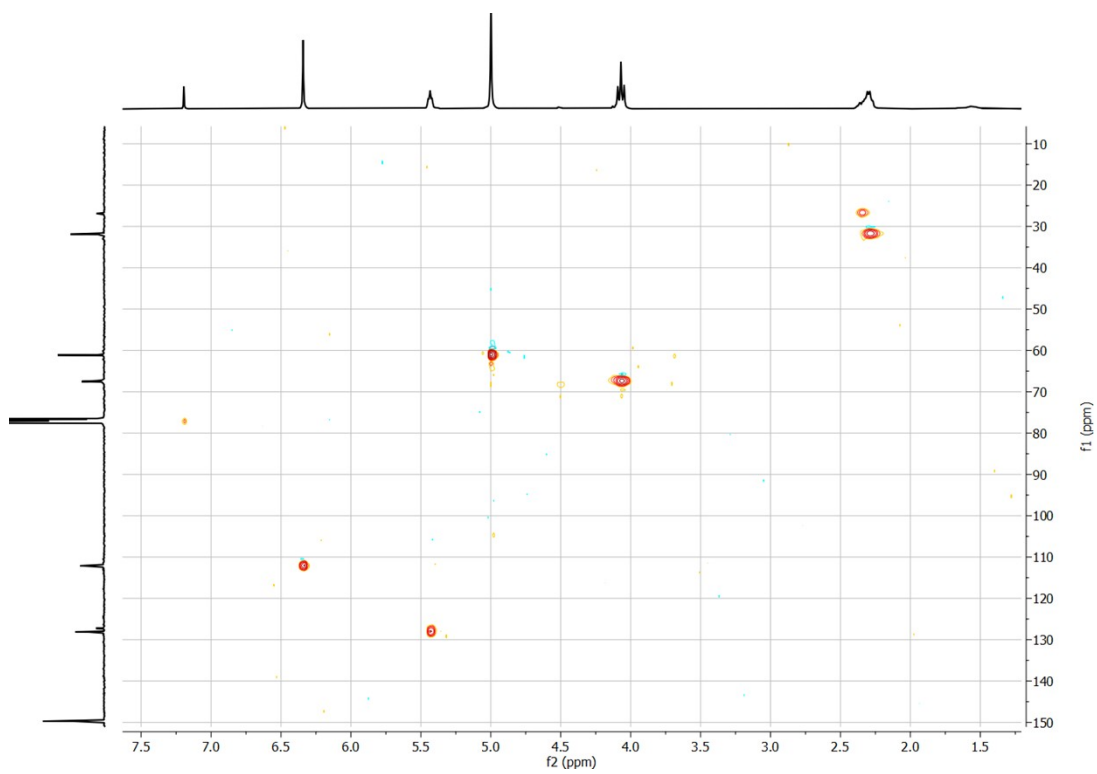


Figure S11- 2D ^1H , ^{13}C -HMQC spectra of P(*But*-BACF) in CDCl_3 .

Hex-BACF derived homo-polymer (P(*Hex*-BACF))

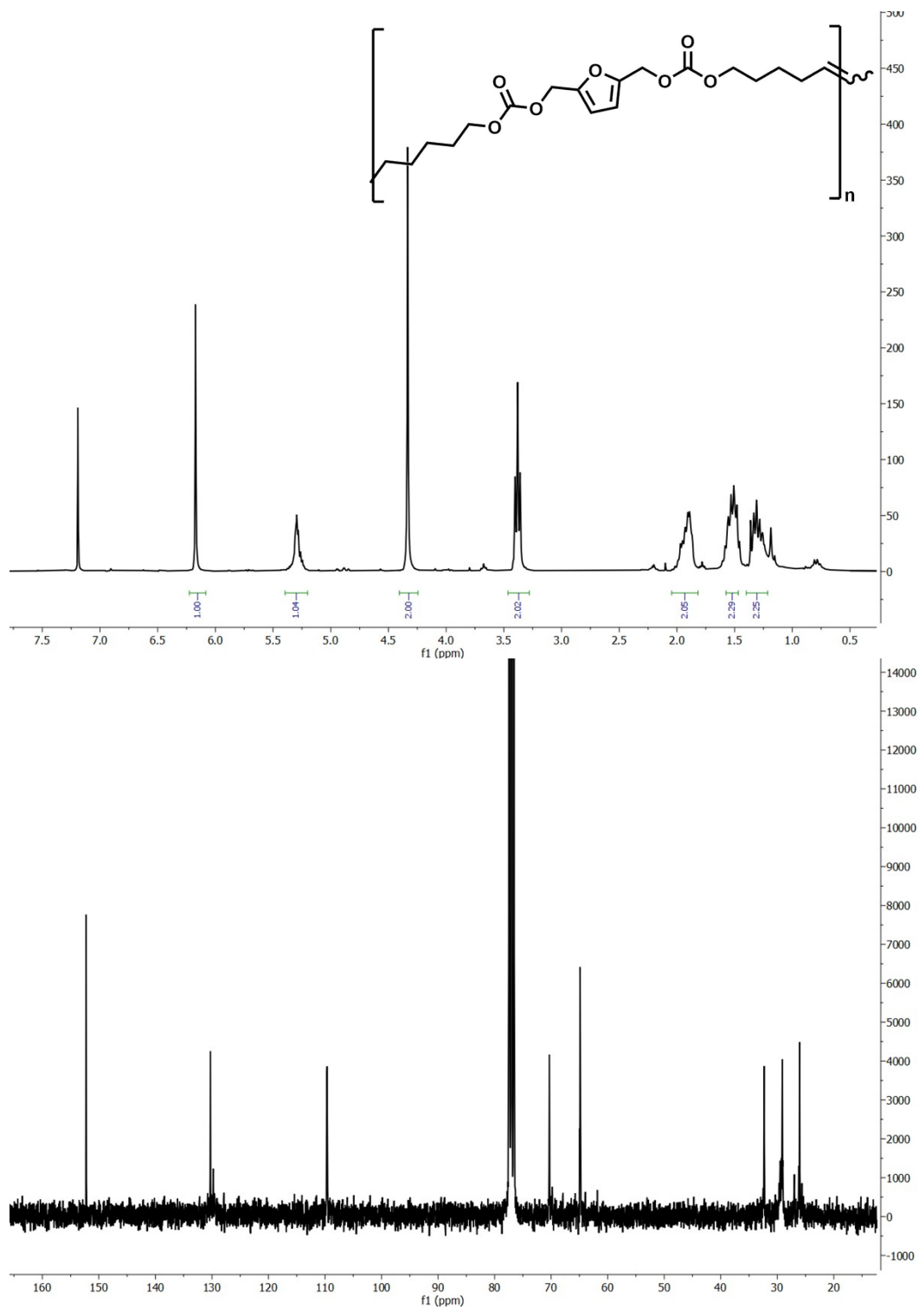


Figure S12- (top) ¹H NMR spectra of P(Hex-BACF) in CDCl₃; (bottom) ¹³C NMR spectra of P(Hex-BACF) in CDCl₃.

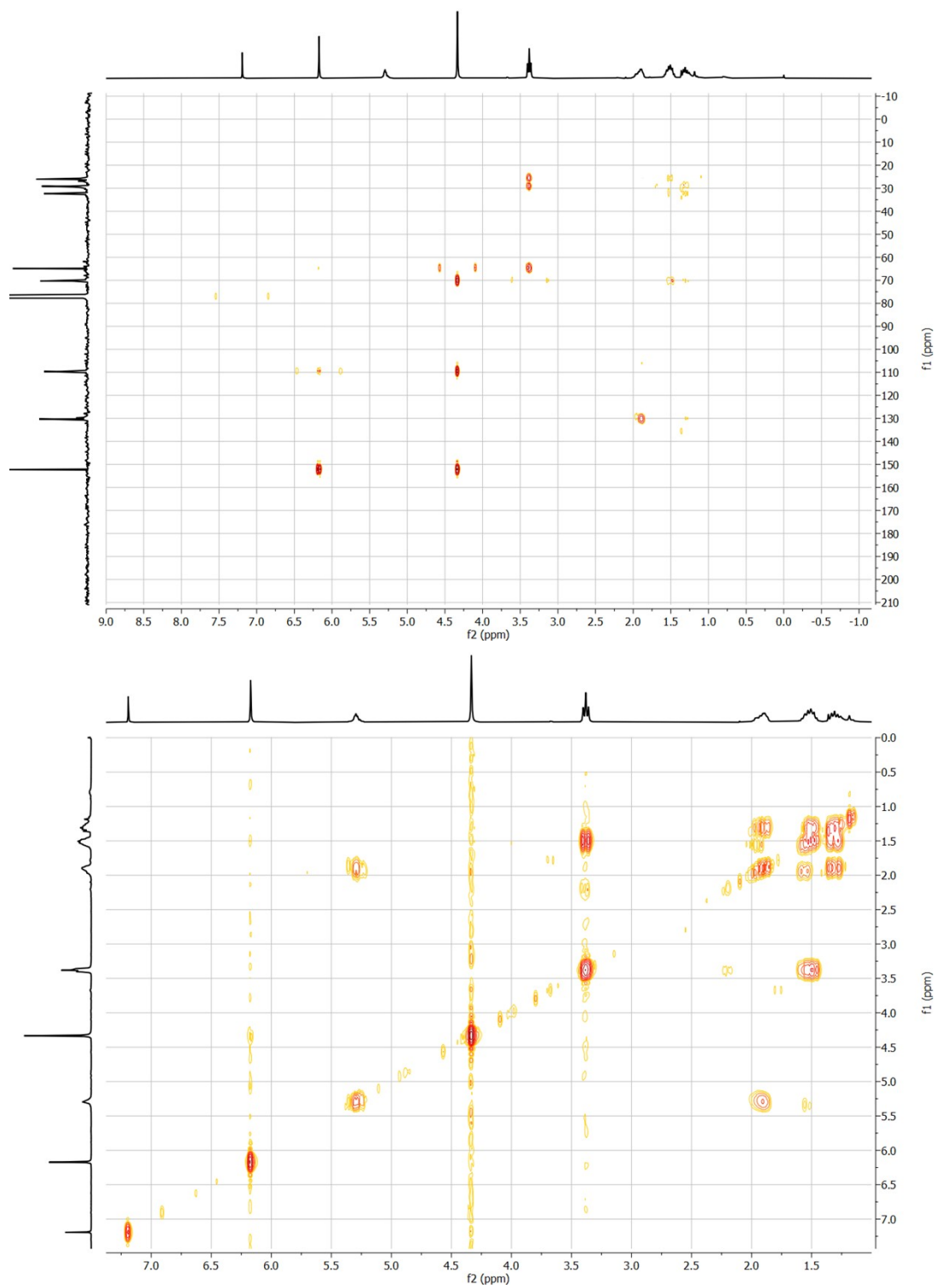


Figure S13- (top) 2D ¹H,¹³C-HSQC spectra of P(Hex-BACF) in CDCl₃; (bottom) 2D ¹H-¹H COSY spectra of P(Hex-BACF) in CDCl₃.

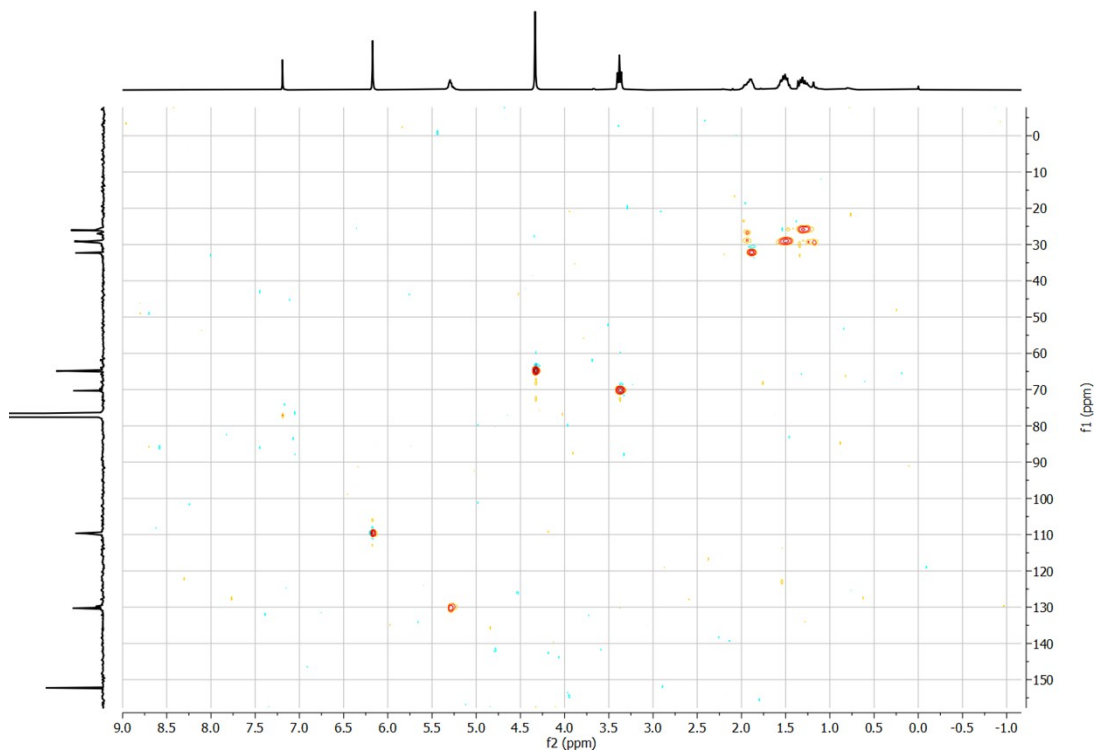


Figure S14- 2D ^1H , ^{13}C -HMQC spectra of P(Hex-BACF) in CDCl_3 .

Dec-BACF derived homo-polymer (P(Dec-BACF))

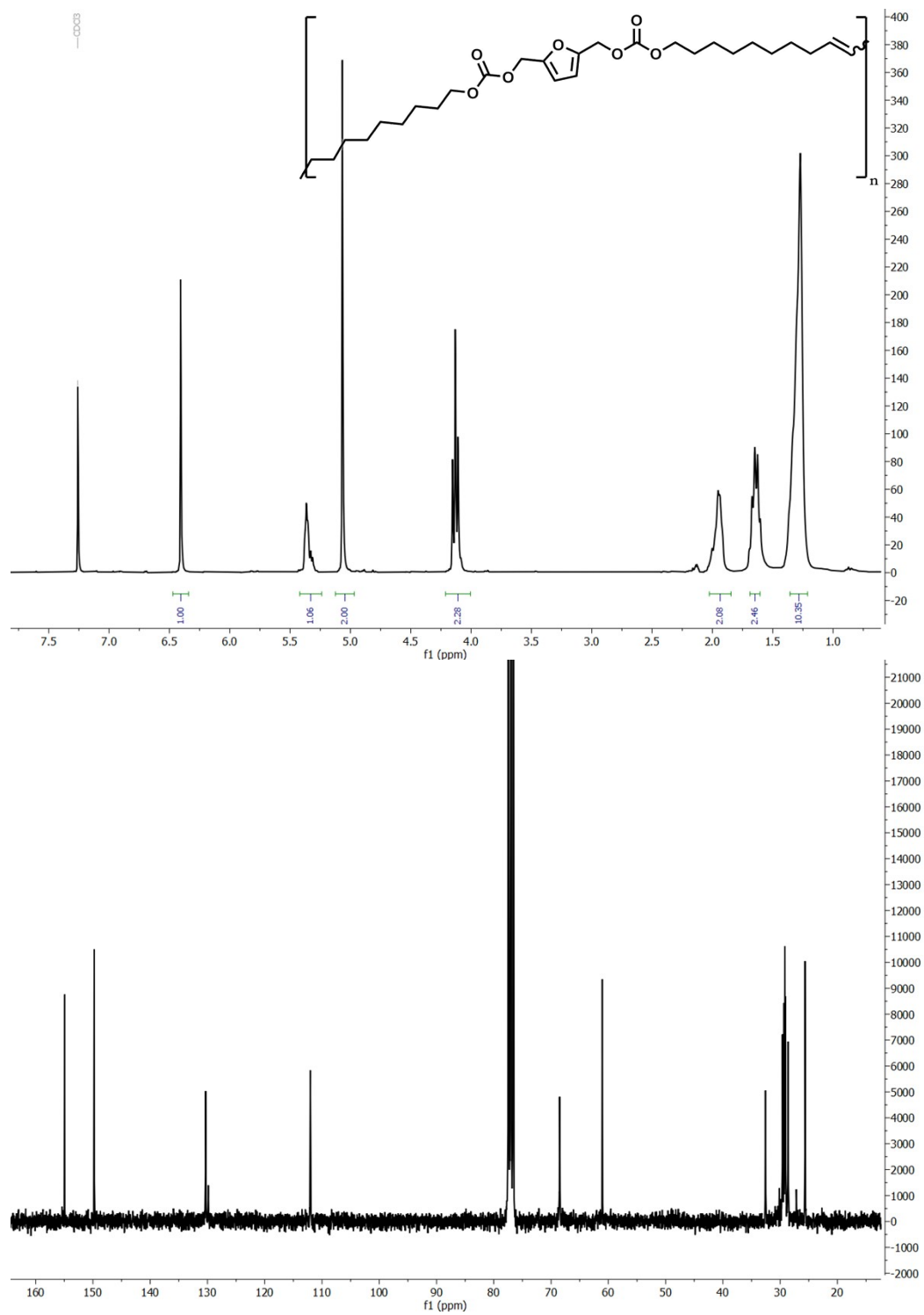


Figure S15- (top) ^1H NMR spectra of P(Dec-BACF) in CDCl_3 ; (bottom) ^{13}C NMR spectra of P(Dec-BACF) in CDCl_3 .

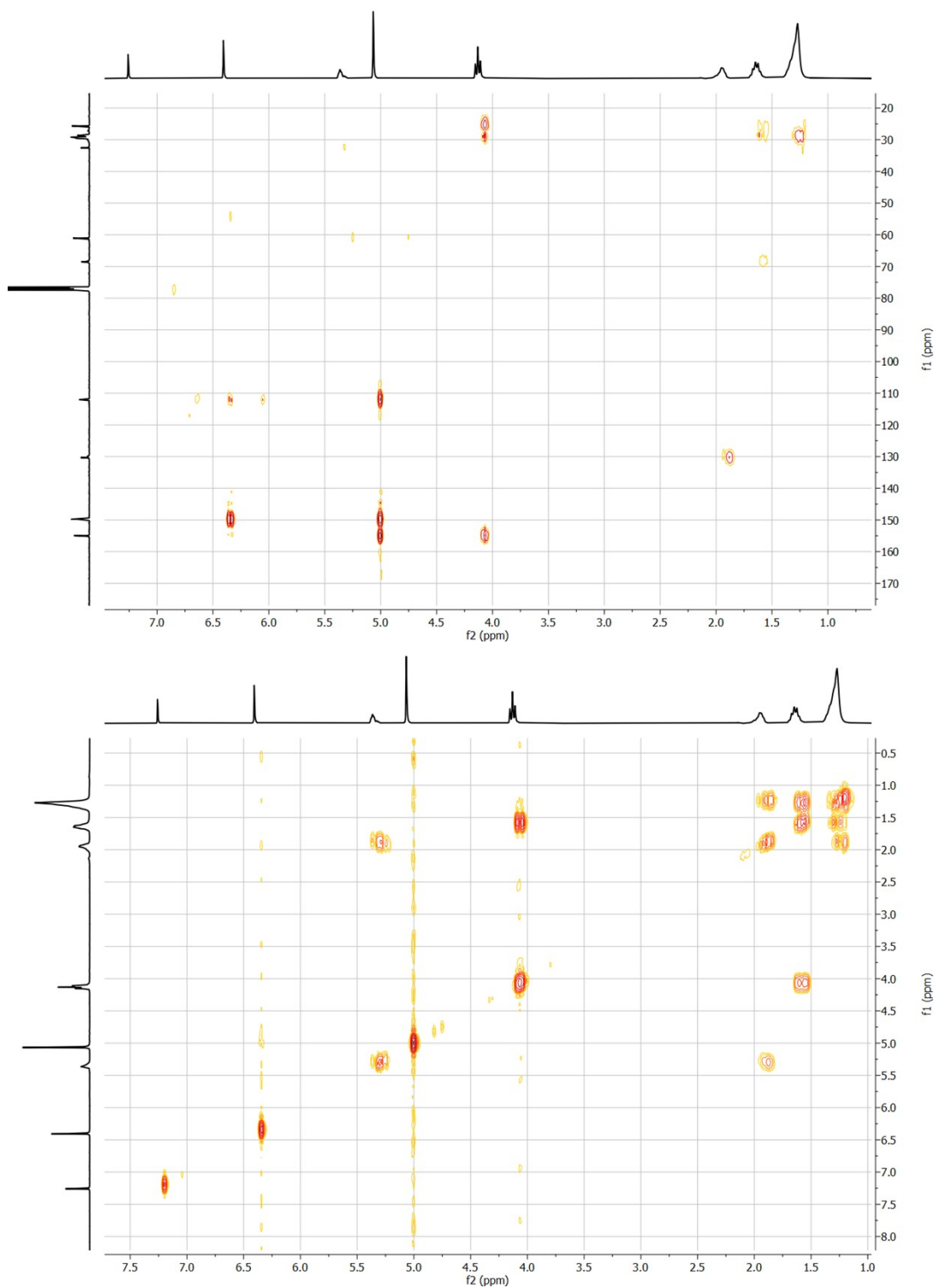


Figure S16- (top) 2D ¹H, ¹³C-HSQC spectra of P(Dec-BACF) in CDCl₃; (bottom) 2D ¹H-¹H COSY spectra of P(Dec-BACF) in CDCl₃.

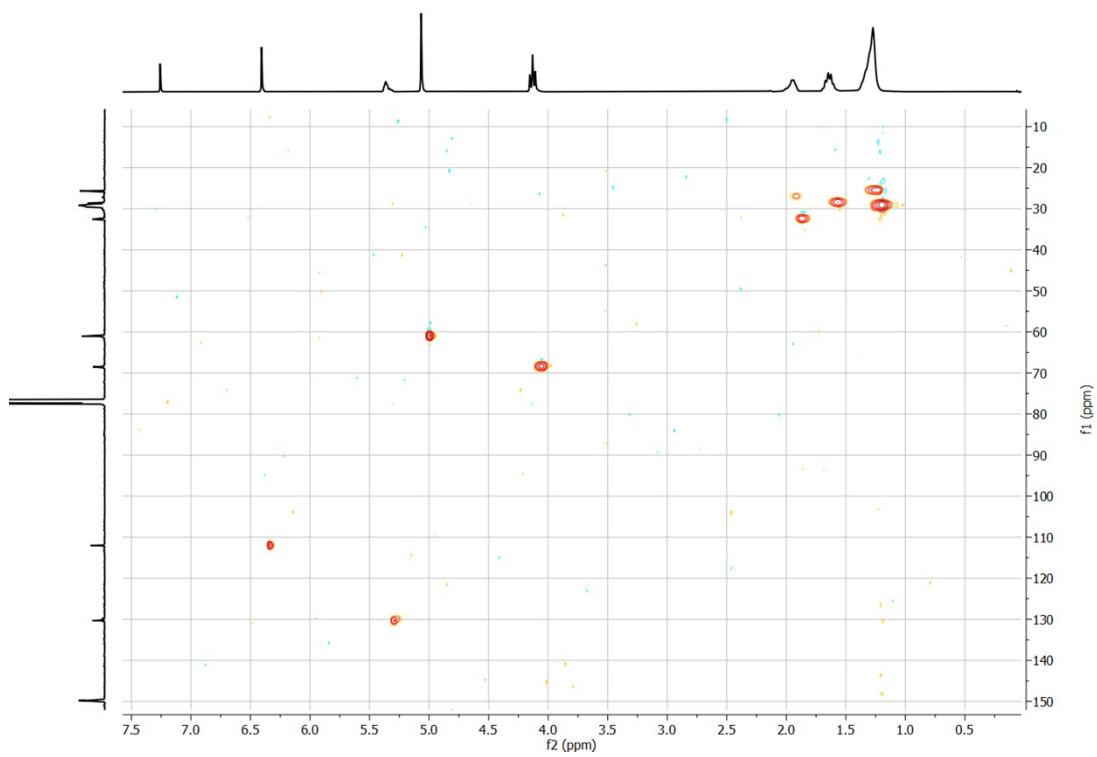


Figure S17- 2D ^1H , ^{13}C -HMQC spectra of P(Dec-BACF) in CDCl_3 .

Synthesis of P(Dec-BACF: Dec-FDE) (1:1) co-polymer

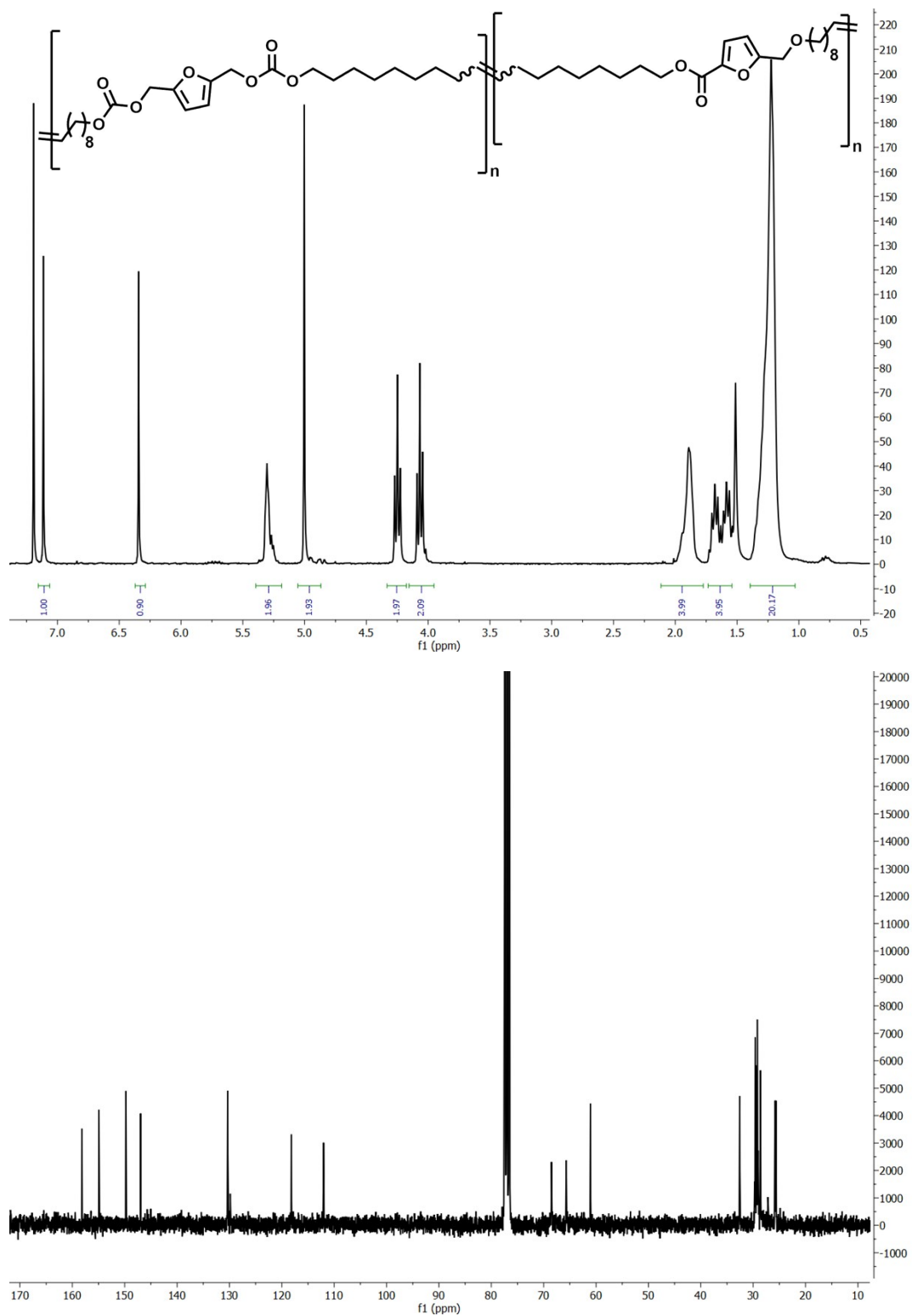


Figure S18- (top) ^1H NMR spectra of P(Dec-BACF: Dec-FDE) in CDCl_3 ; (bottom) ^{13}C NMR spectra of P(Dec-BACF: Dec-FDE) in CDCl_3 .

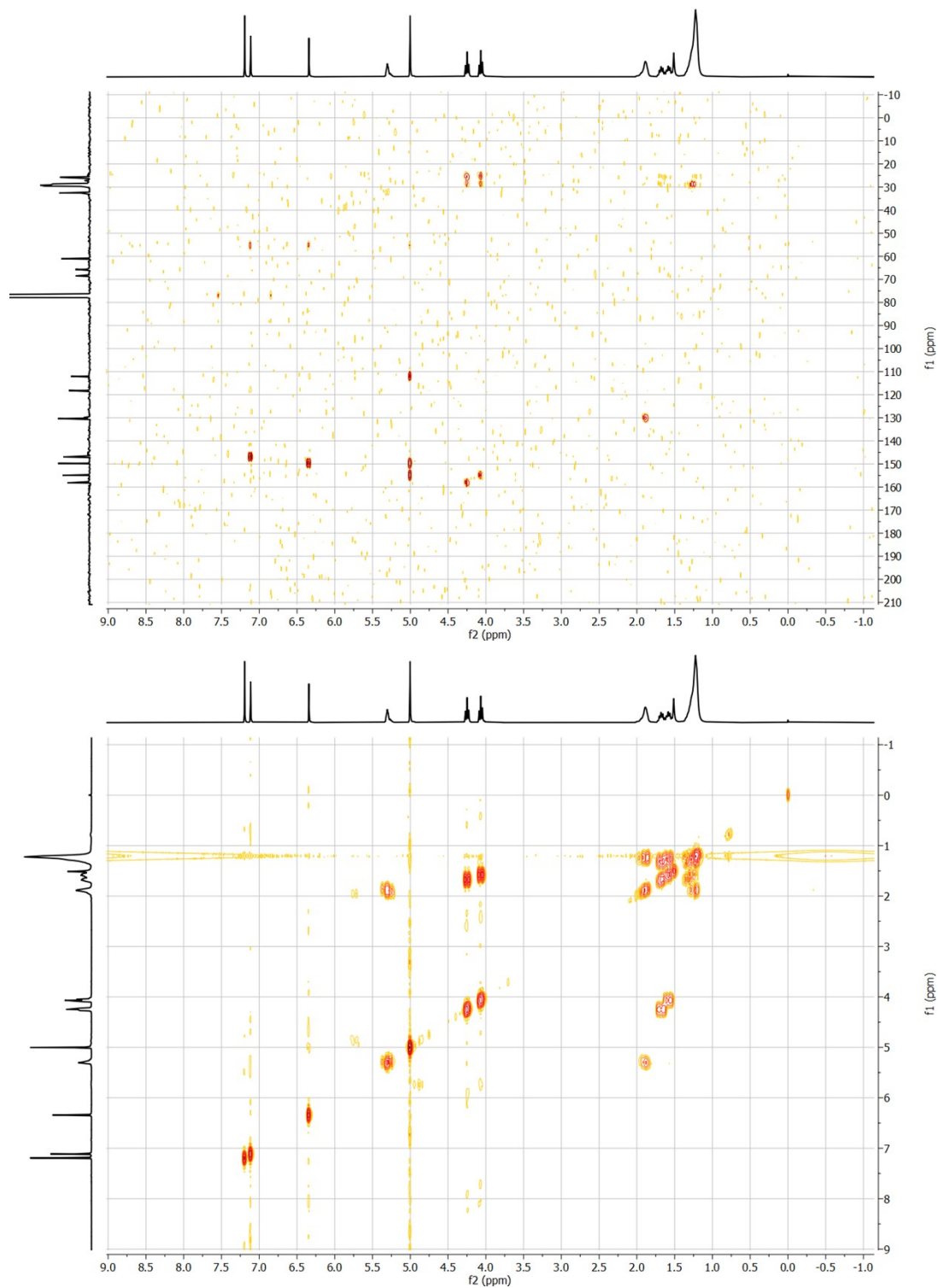


Figure S19- (top) 2D ¹H, ¹³C-HSQC spectra of P(Dec-BACF: Dec-FDE) in CDCl₃; (bottom) 2D ¹H-¹H COSY spectra of P(Dec-BACF: Dec-FDE) in CDCl₃.

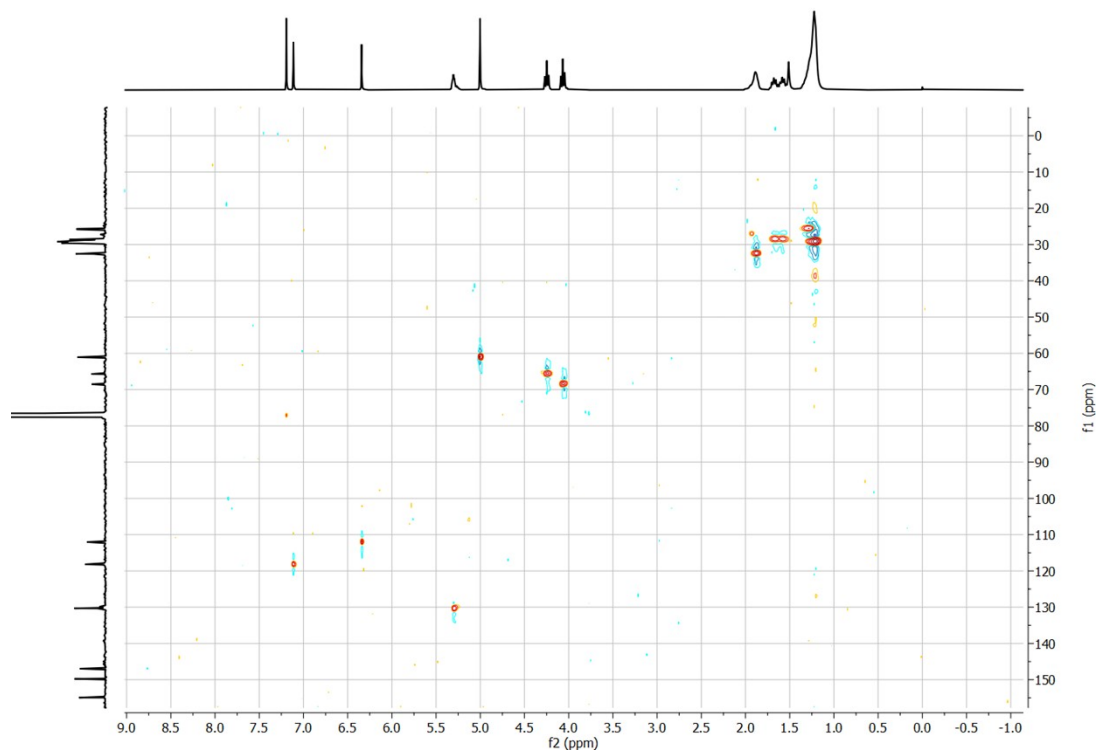


Figure S20- 2D ^1H , ^{13}C -HMQC spectra of P(Dec-BACF: Dec-FDE) in CDCl_3 .

Synthesis of P(Dec-BDMF: Dec-BACF) (1:1) co-polymer

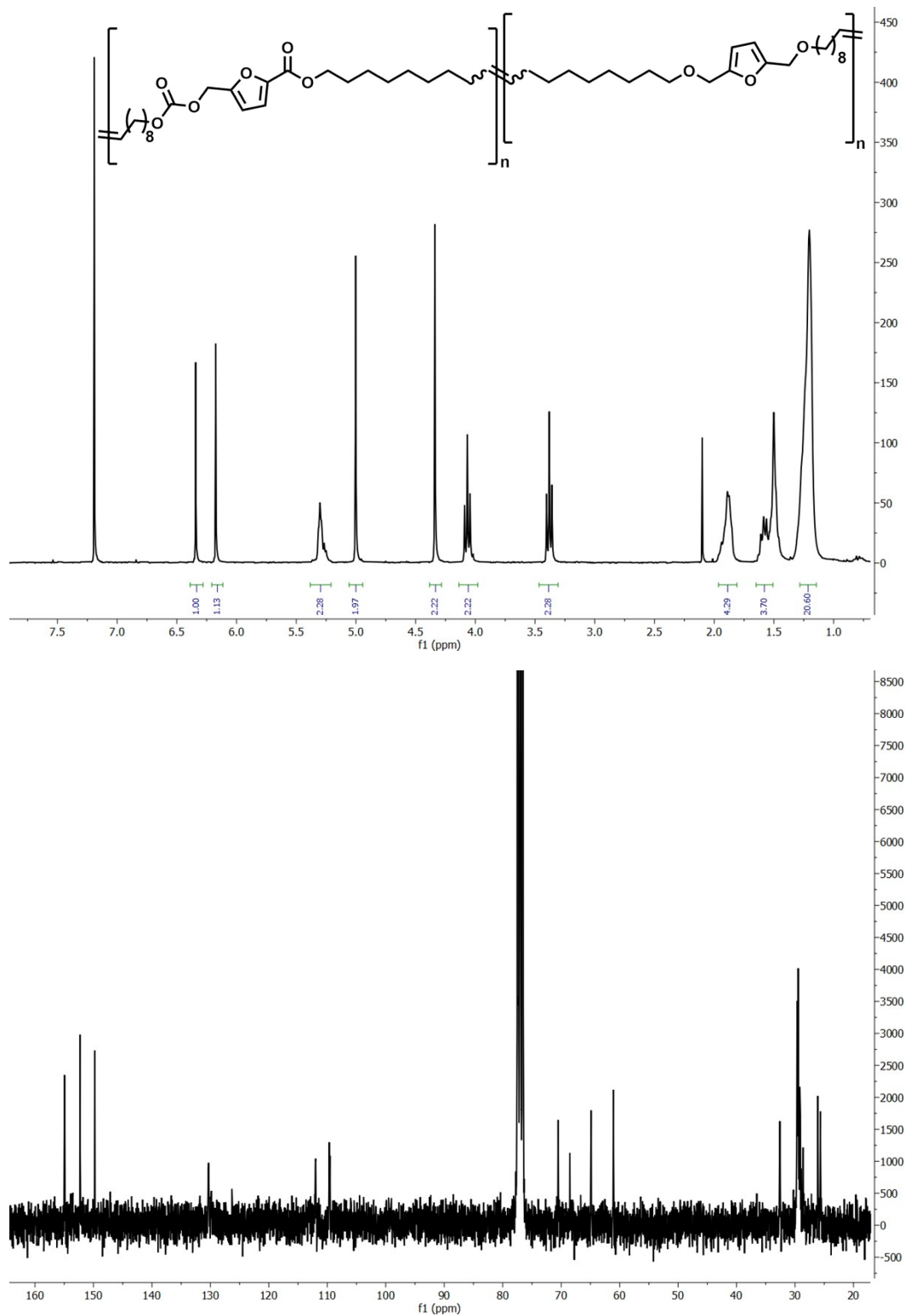


Figure S21- (top) ^1H NMR spectra of P(Dec-BDMF: Dec-BACF) in CDCl_3 ; (bottom) ^{13}C NMR spectra of P(Dec-BDMF: Dec-BACF) in CDCl_3 .

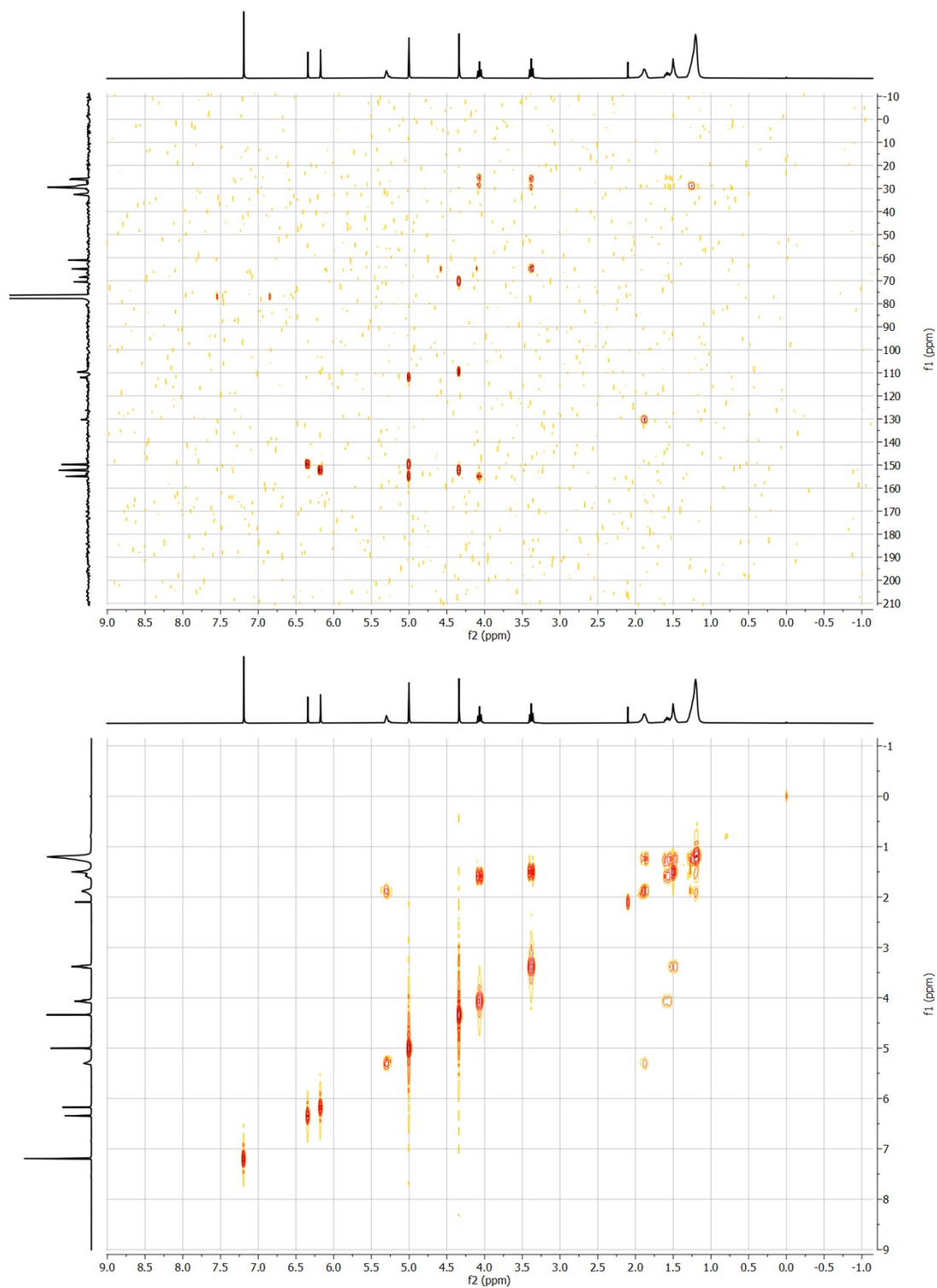


Figure S22- (top) 2D ^1H , ^{13}C -HSQC spectra of P(*Dec*-BDMF: *Dec*-BACF) in CDCl_3 ; (bottom) 2D ^1H - ^1H COSY spectra of P(*Dec*-BDMF: *Dec*-BACF) in CDCl_3 .

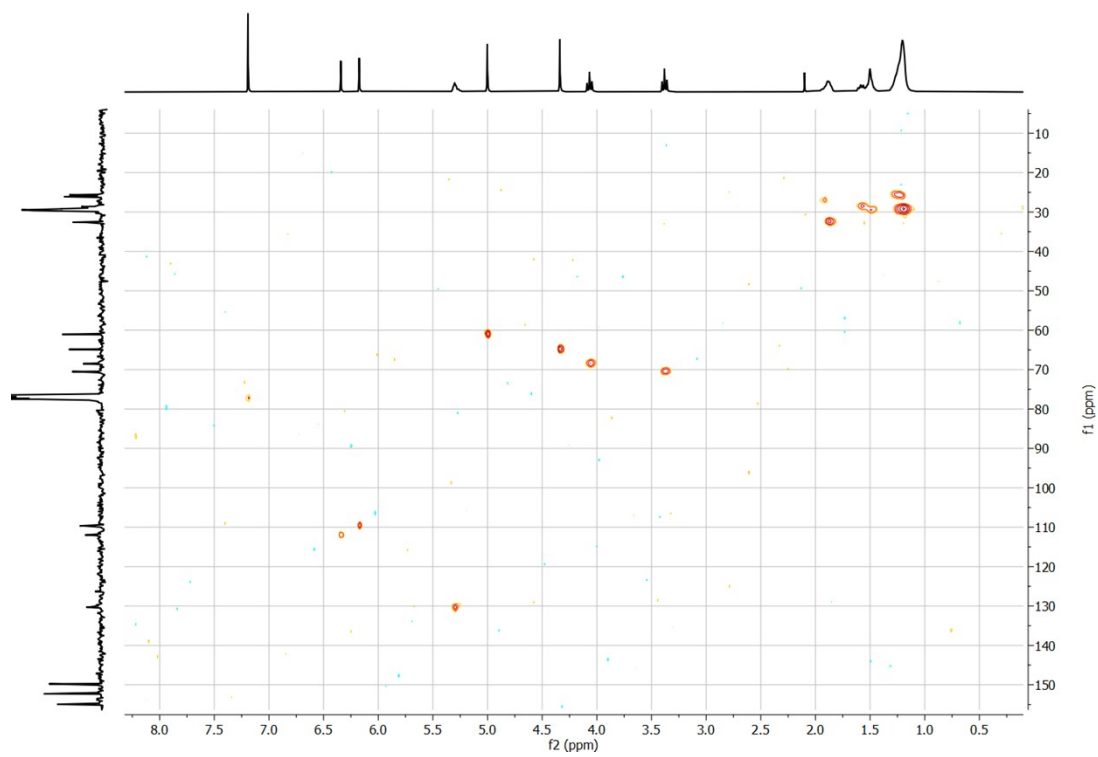


Figure S23- 2D ^1H , ^{13}C -HMQC spectra of P(*Dec*-BDMF: *Dec*-BACF) in CDCl_3 .

Synthesis of P(Dec-BDMF: Dec-FDE) (1:1) co-polymer

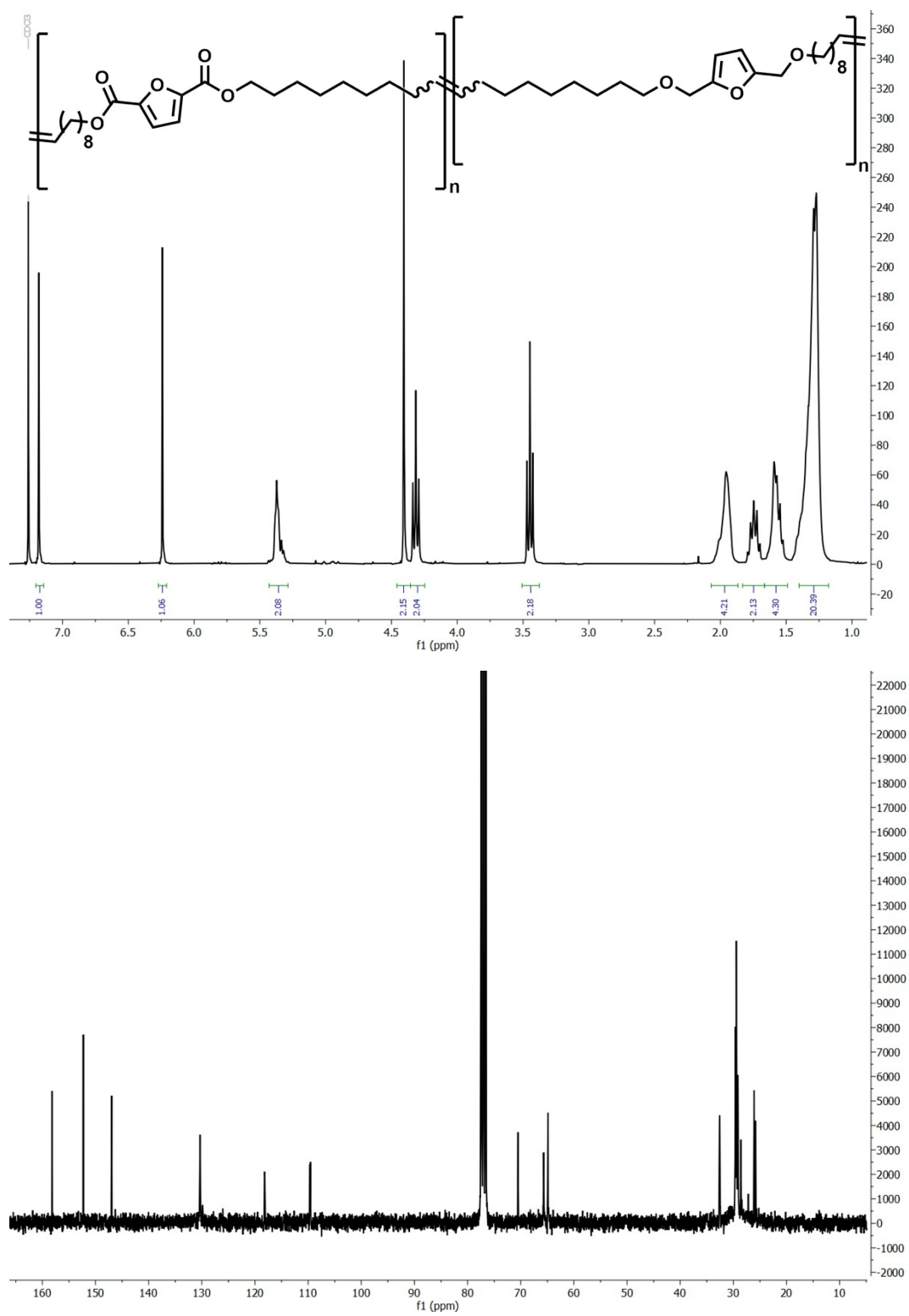


Figure S24- (top) ^1H NMR spectra of P(Dec-BDMF: Dec-FDE) in CDCl_3 ; (bottom) ^{13}C NMR spectra of P(Dec-BDMF: Dec-FDE) in CDCl_3 .

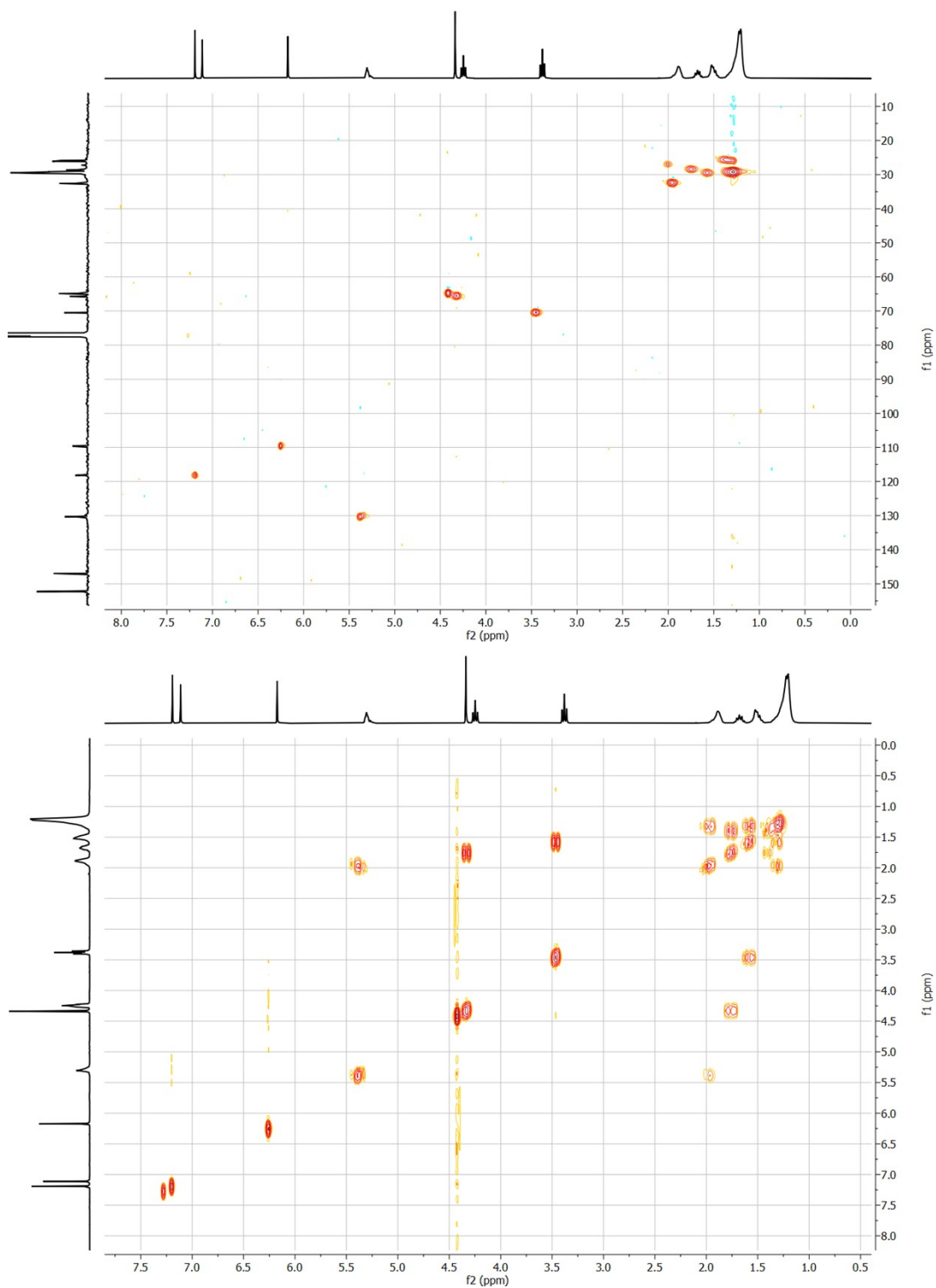


Figure S25- (top) 2D ¹H,¹³C-HSQC spectra of P(Dec-BDMF: Dec-FDE) in CDCl₃; (bottom) 2D ¹H-¹H COSY spectra of P(Dec-BDMF: Dec-FDE) in CDCl₃.

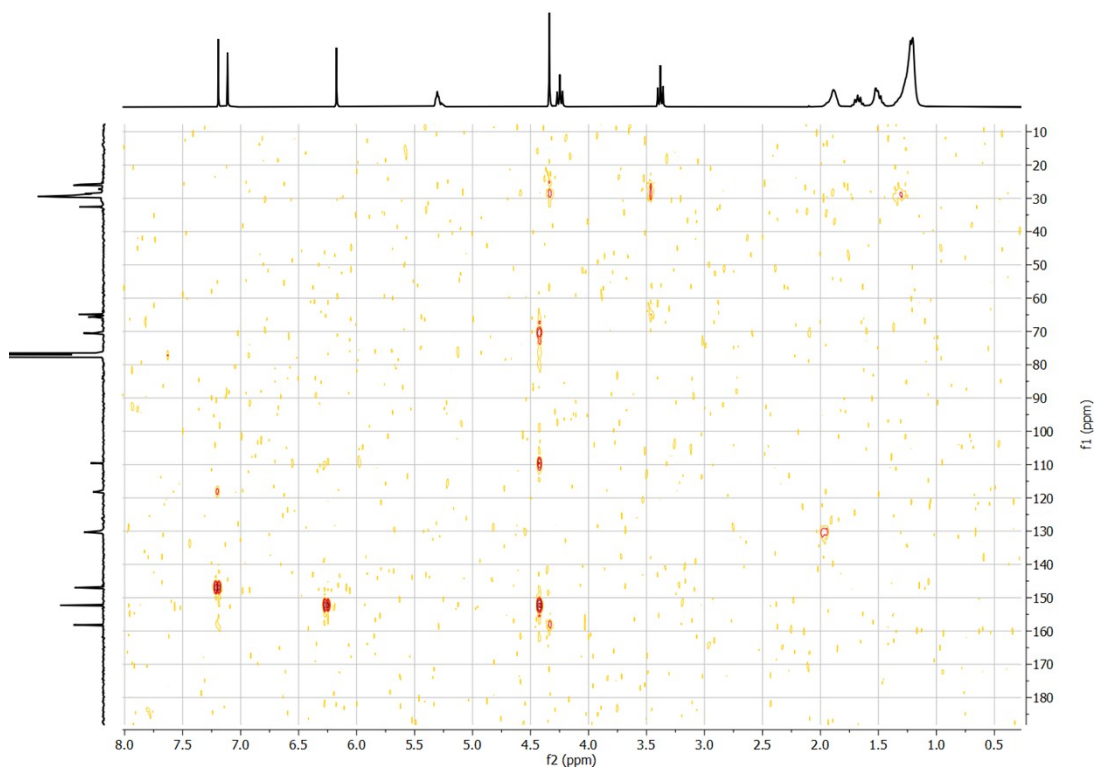


Figure S26- 2D ^1H , ^{13}C -HMQC spectra of P(*Dec*-BDMF: *Dec*-FDE) in CDCl_3 .

Synthesis of P(*Dec*-FDE: *But*-BACF) (1:1) co-polymer

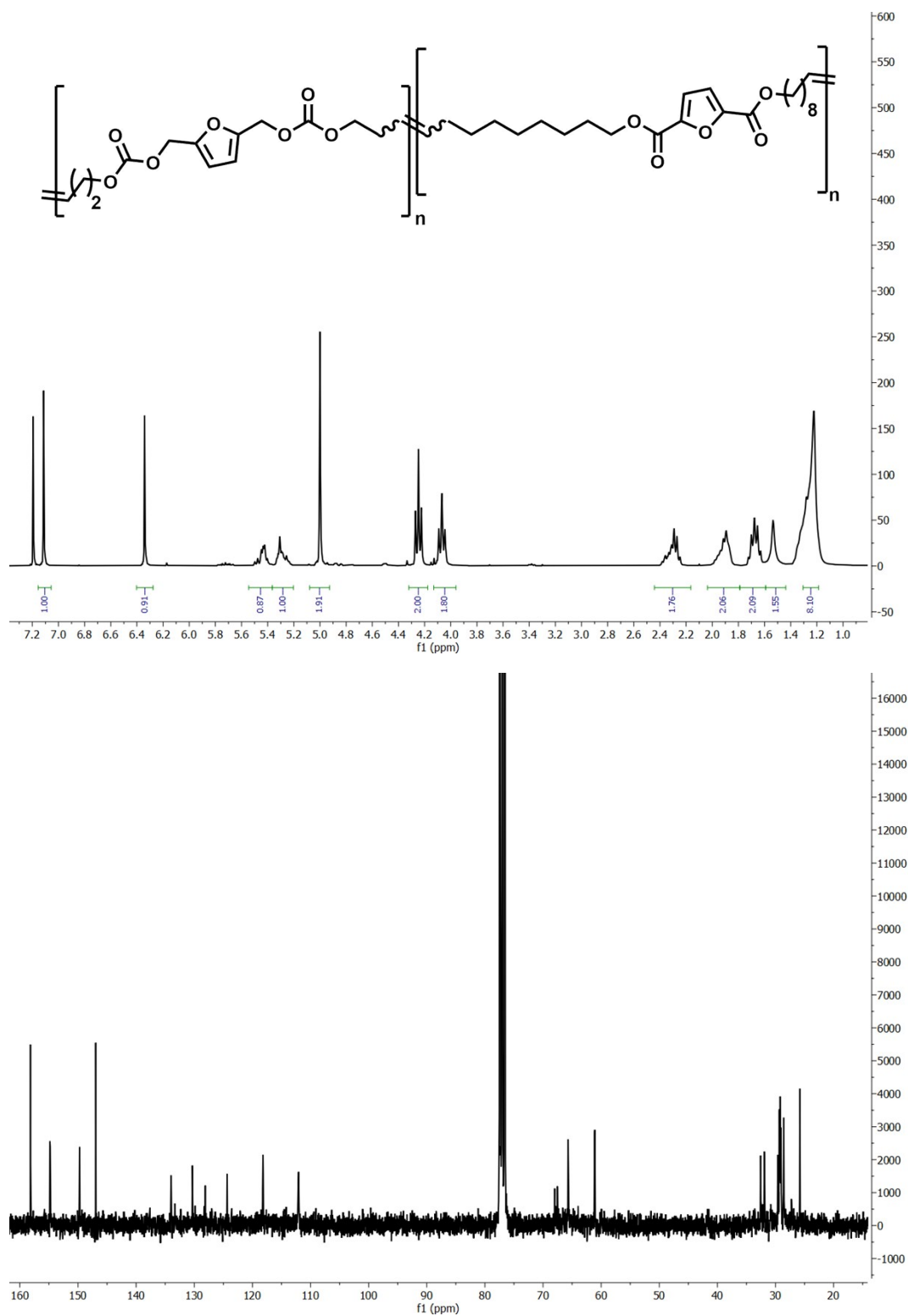


Figure S27- (top) ^1H NMR spectra of P(*Dec*-FDE: *But*-BACF) in CDCl_3 ; (bottom) ^{13}C NMR spectra of P(*Dec*-FDE: *But*-BACF) in CDCl_3 .

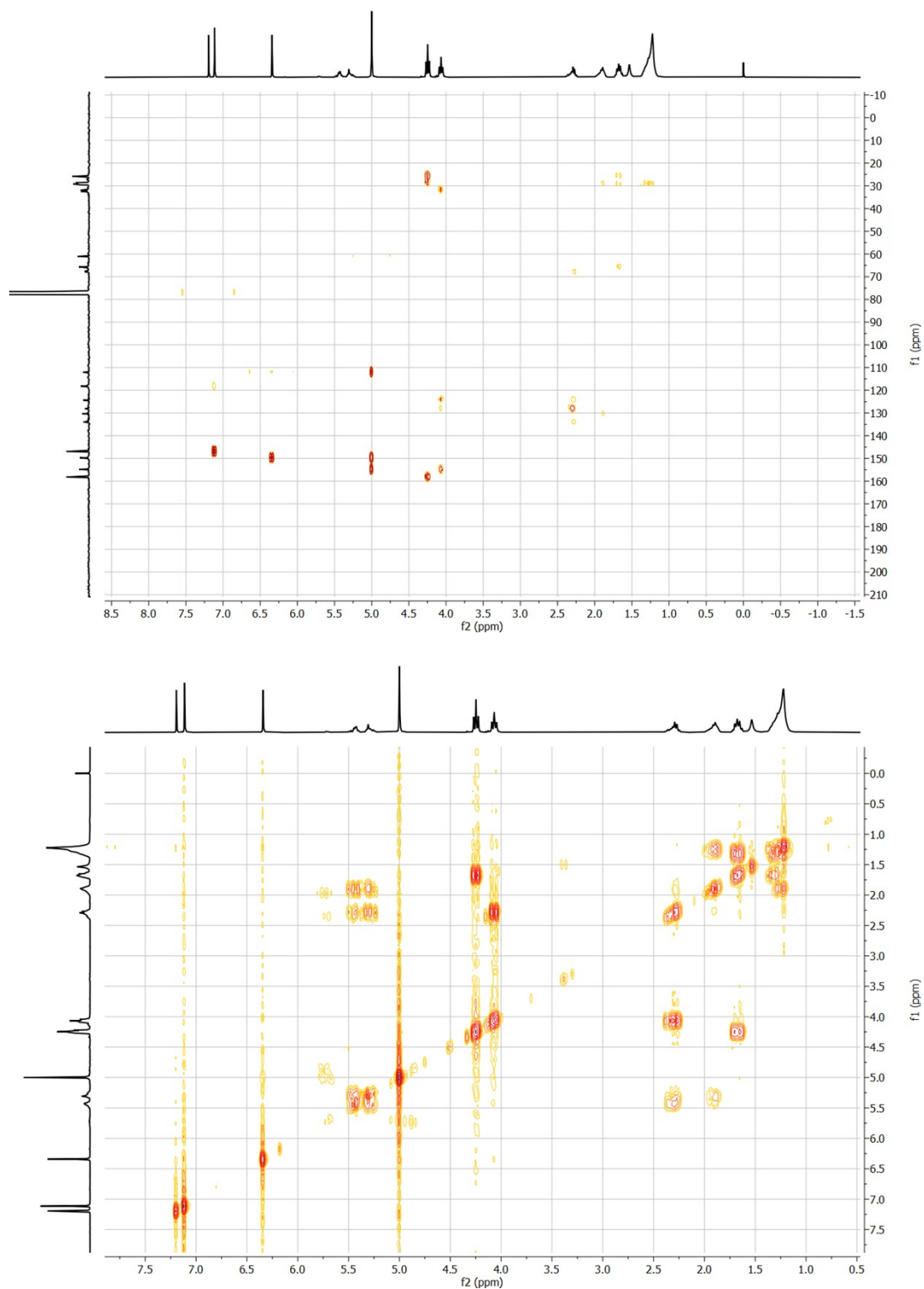


Figure S28- (top) 2D ^1H , ^{13}C -HSQC spectra of P(*Dec*-FDE: *But*-BACF) in CDCl_3 ; (bottom) 2D ^1H - ^1H COSY spectra of P(*Dec*-FDE: *But*-BACF) in CDCl_3 .

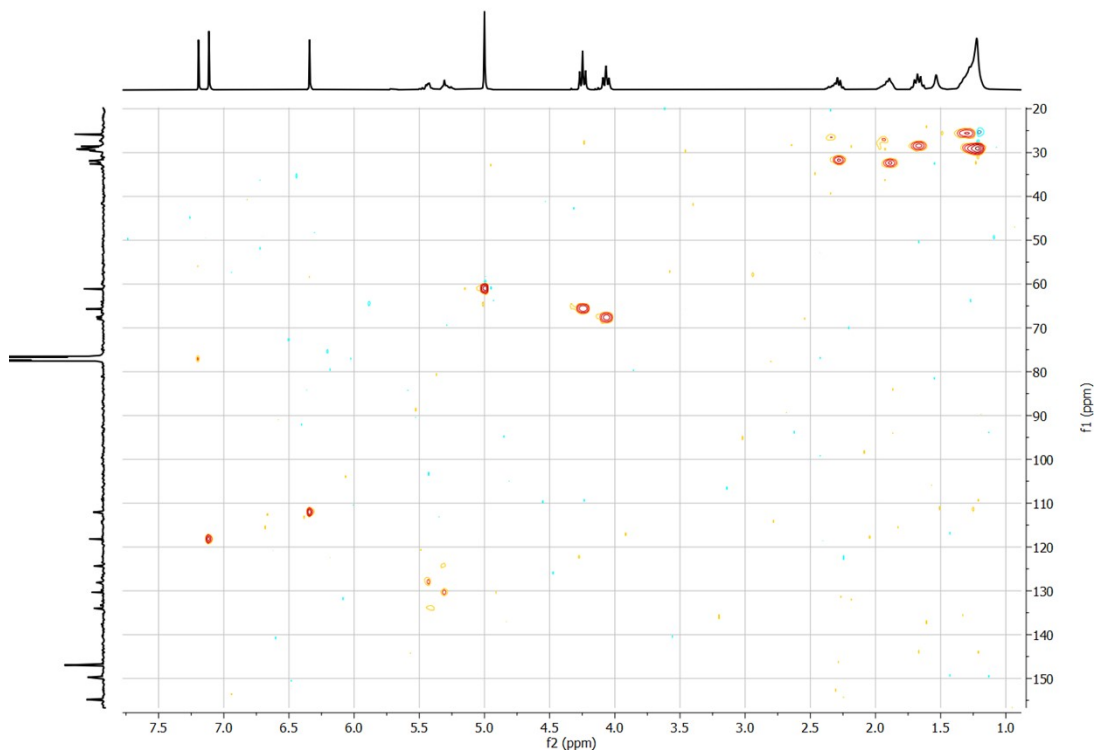


Figure S29- 2D ^1H , ^{13}C -HMQC spectra of P(Dec-FDE: But-BACF) in CDCl_3 .

DSC Thermograms

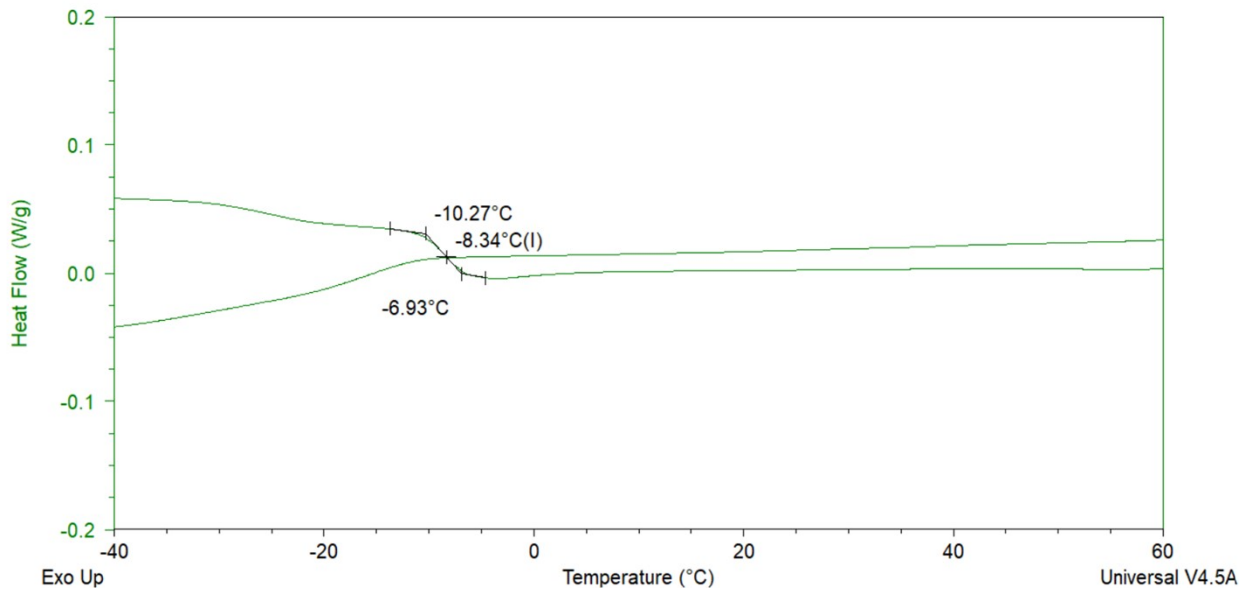


Figure S30- DSC thermogram (3rd heat cycle) of P(*But*-BACF).

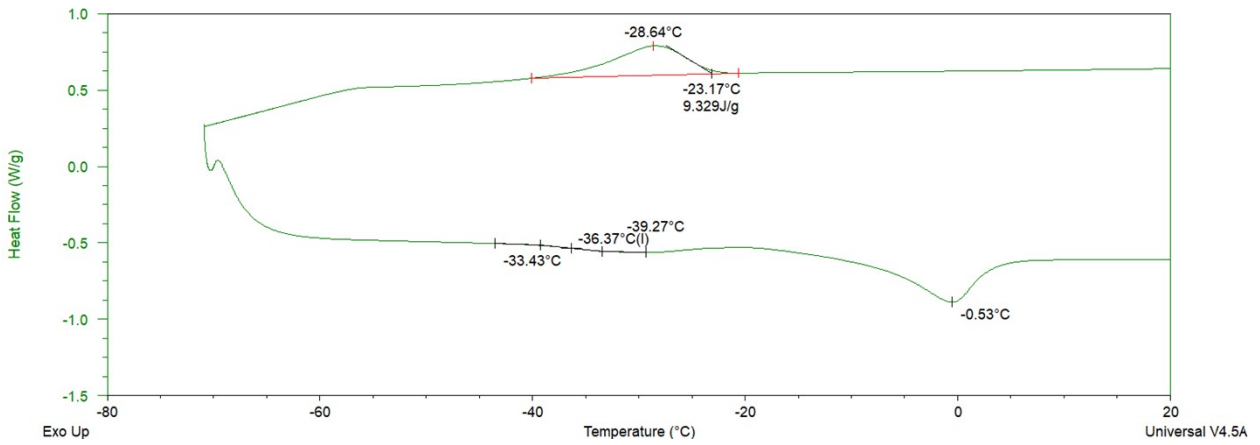


Figure S31- DSC thermogram (3rd heat cycle) of P(*Dec*-BACF).

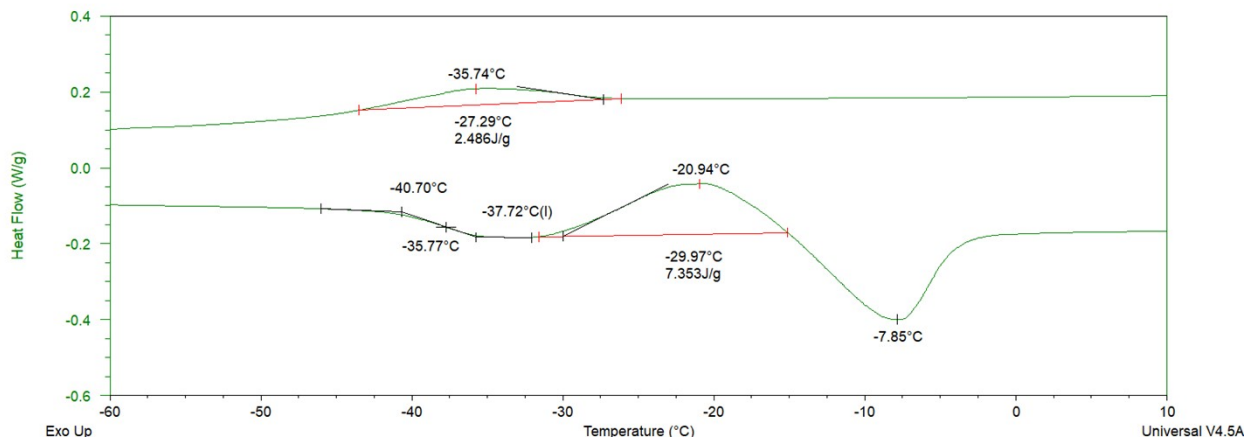


Figure S32- DSC thermogram (3rd heat cycle) of P(Dec-BACF: Dec-FDE).

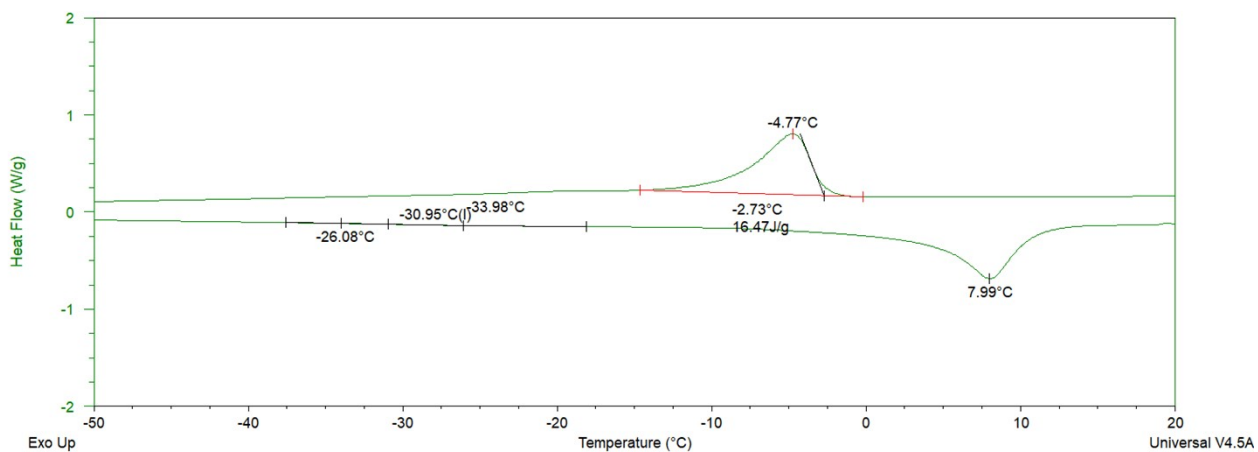


Figure S33- DSC thermogram (3rd heat cycle) of P(Dec-BDMF: Dec-BACF).

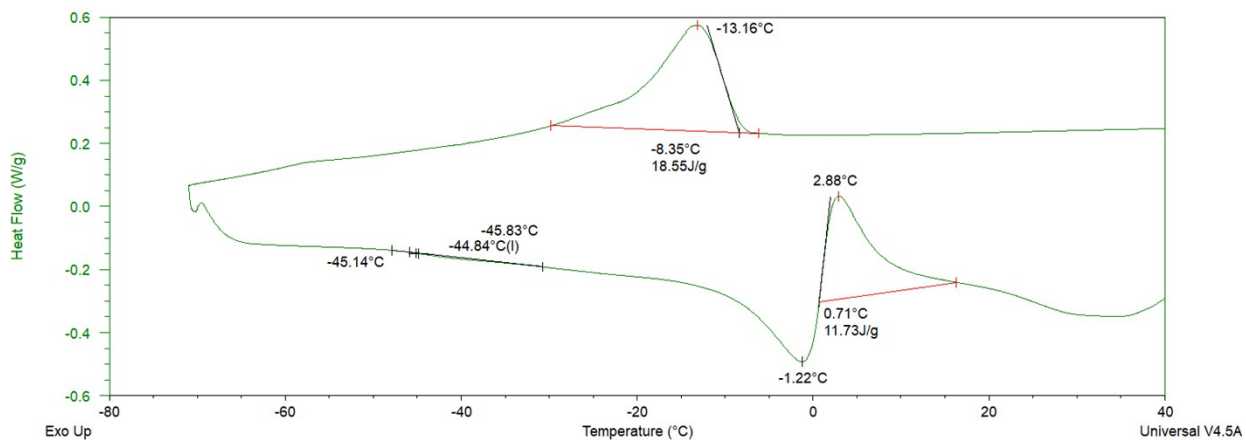


Figure S34- DSC thermogram (3rd heat cycle) of P(Dec-BDMF: Dec-FDE).

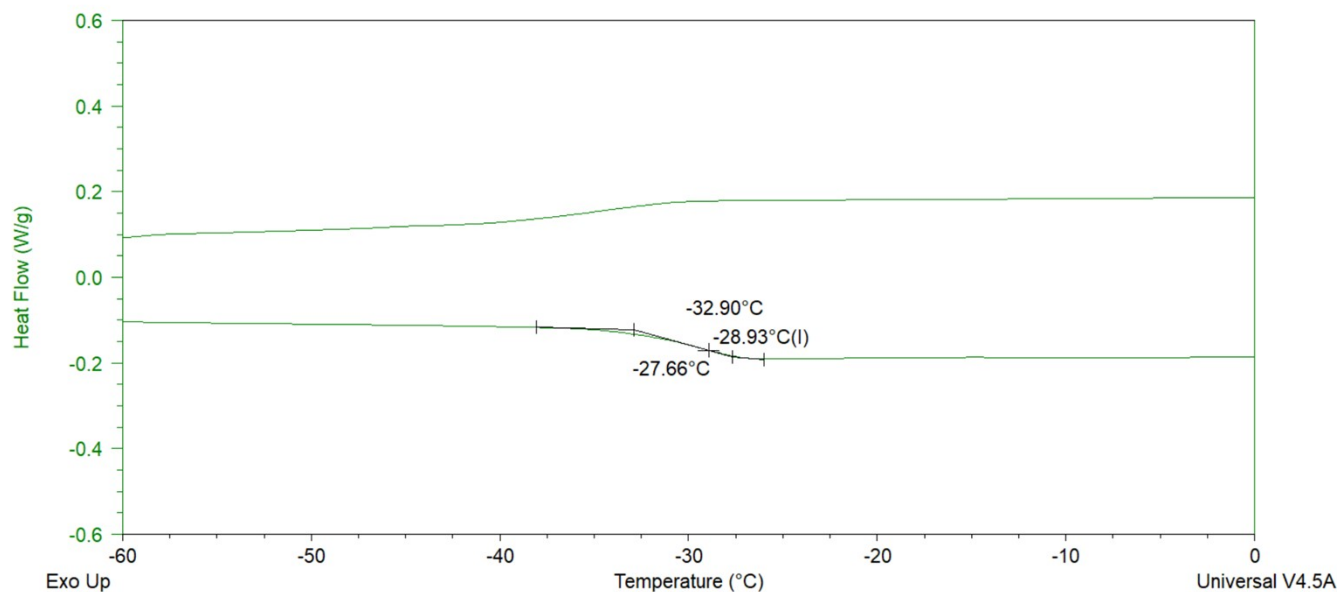


Figure S35- DSC thermogram (3rd heat cycle) of P(Dec-FDE: But-BACF).

TGA analysis

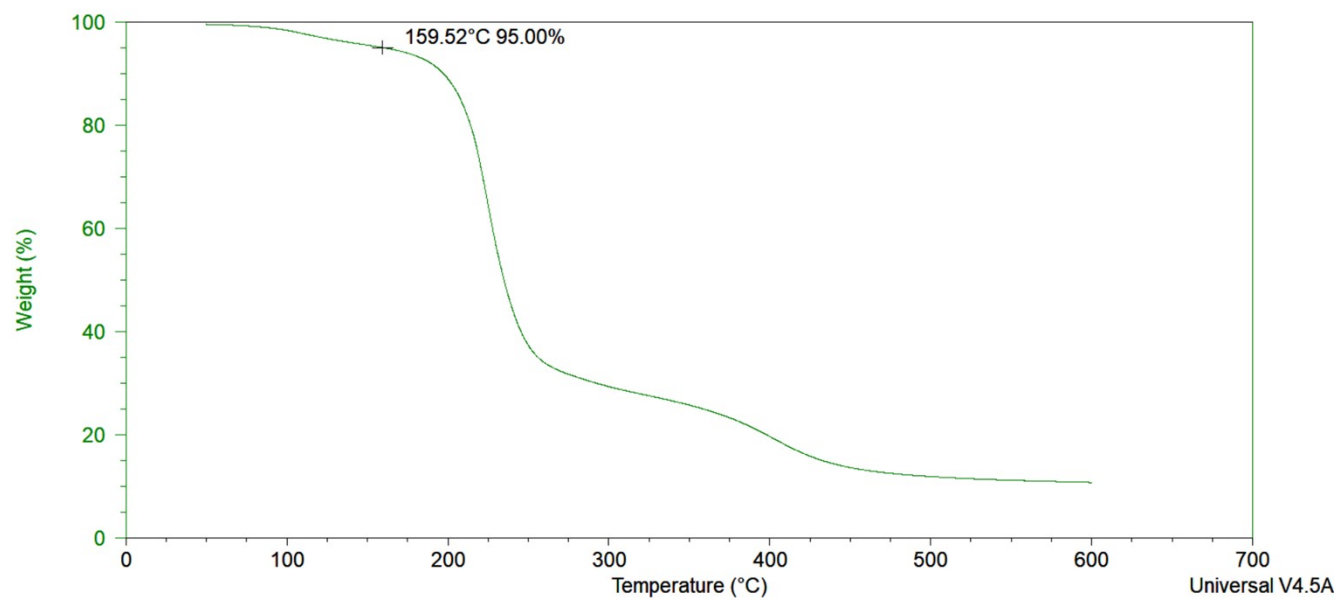


Figure S36- TGA thermogram P(But-BACF).

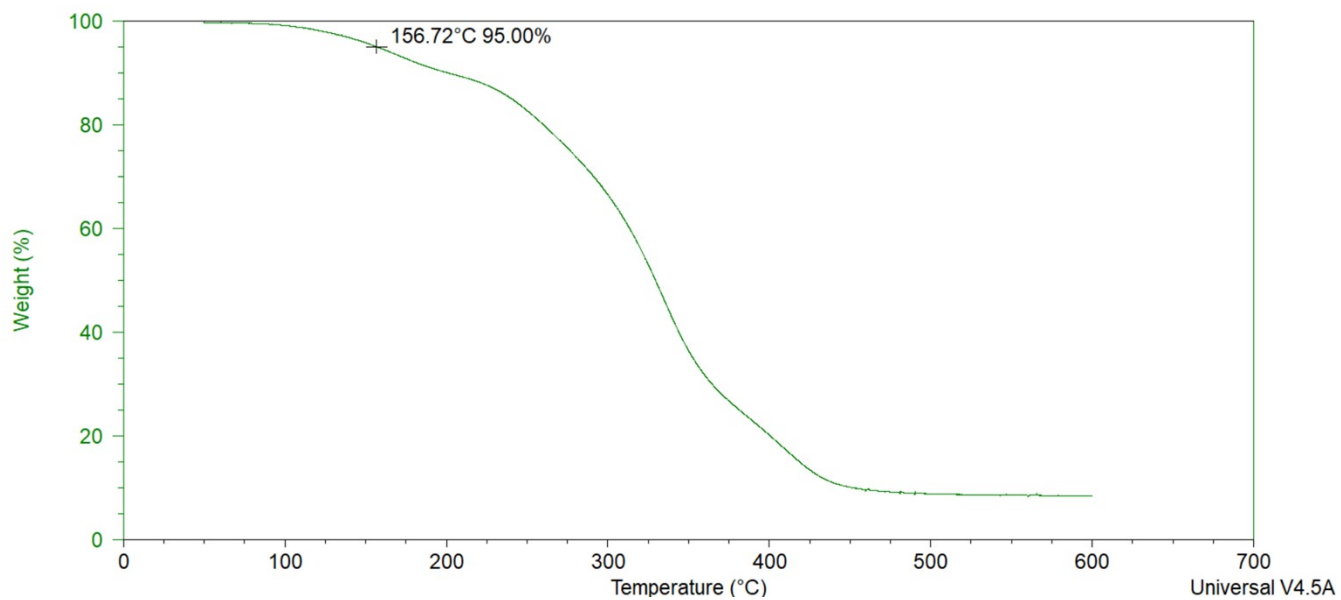


Figure S37- TGA thermogram P(Hex-BACF).

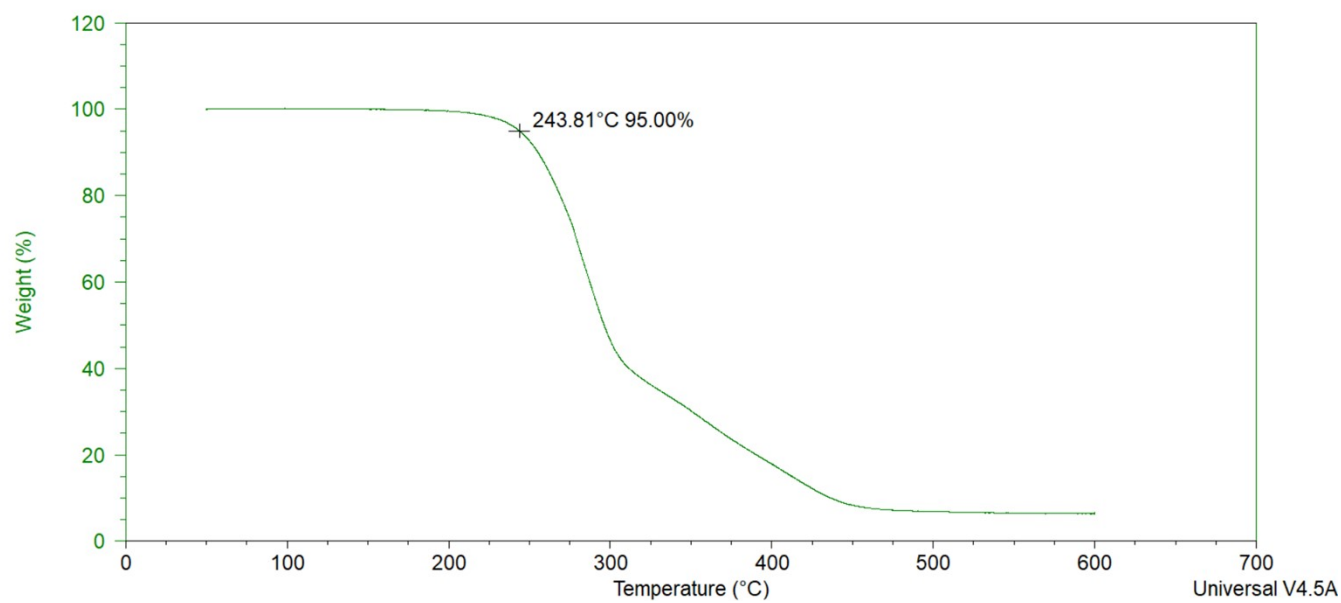


Figure S38- TGA thermogram P(Dec-BACF).

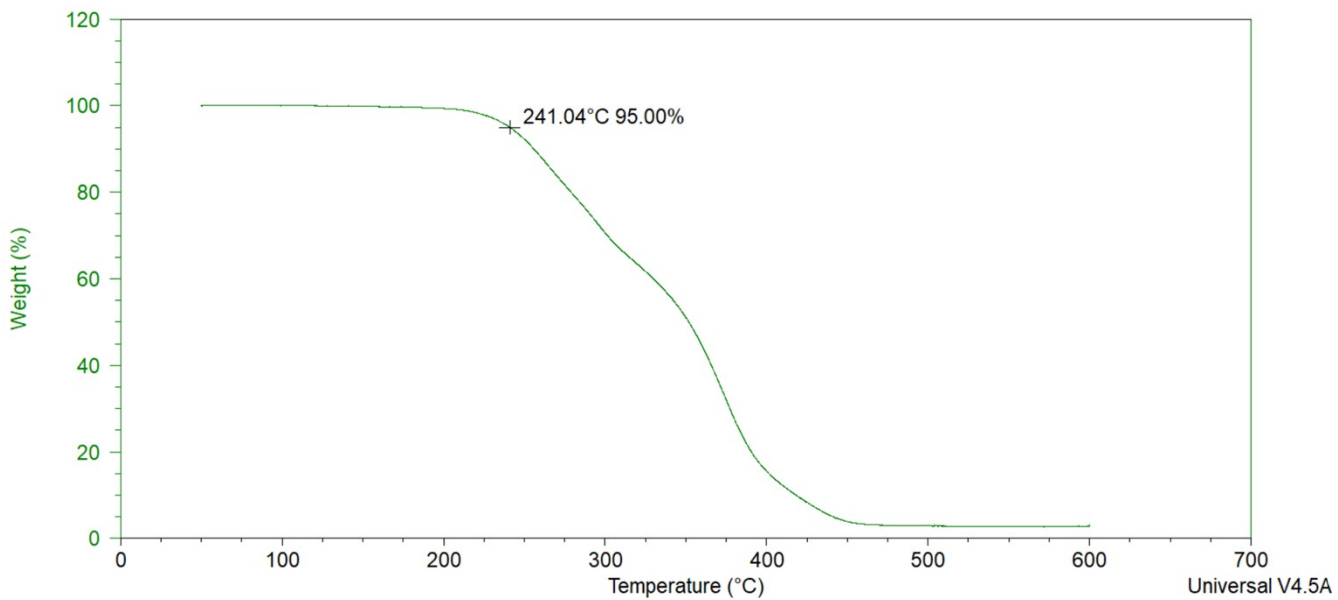


Figure S39- TGA thermogram P(Dec-BACF: Dec-FDE).

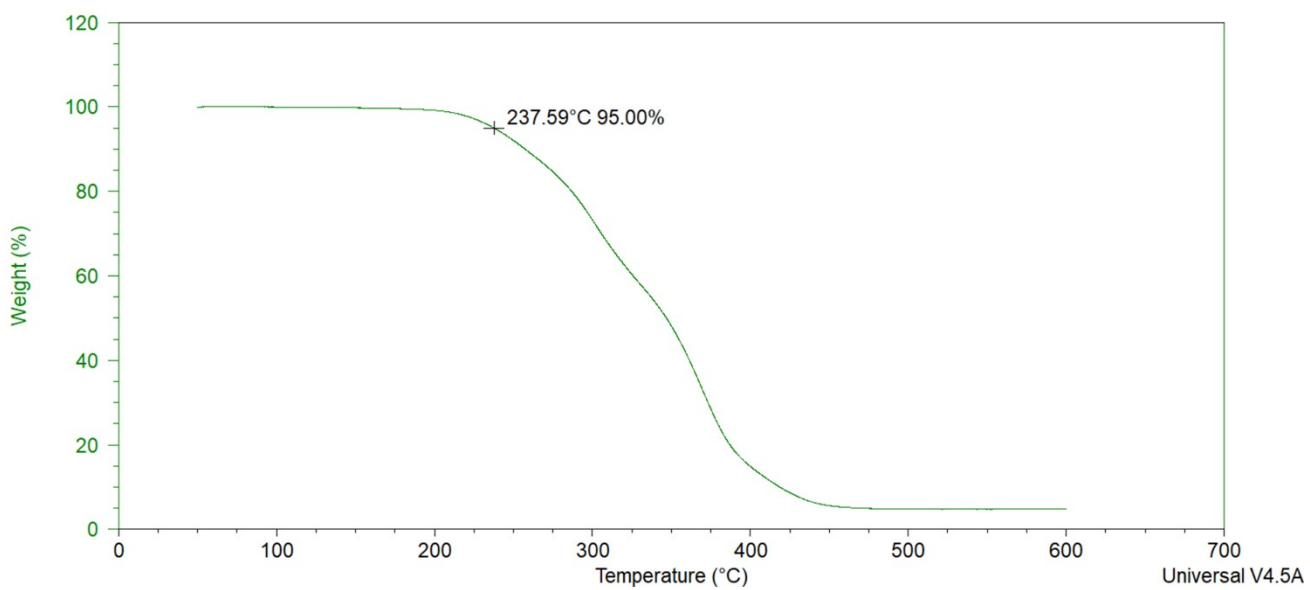


Figure S40- TGA thermogram P(Dec-BDMF: Dec-BACF).

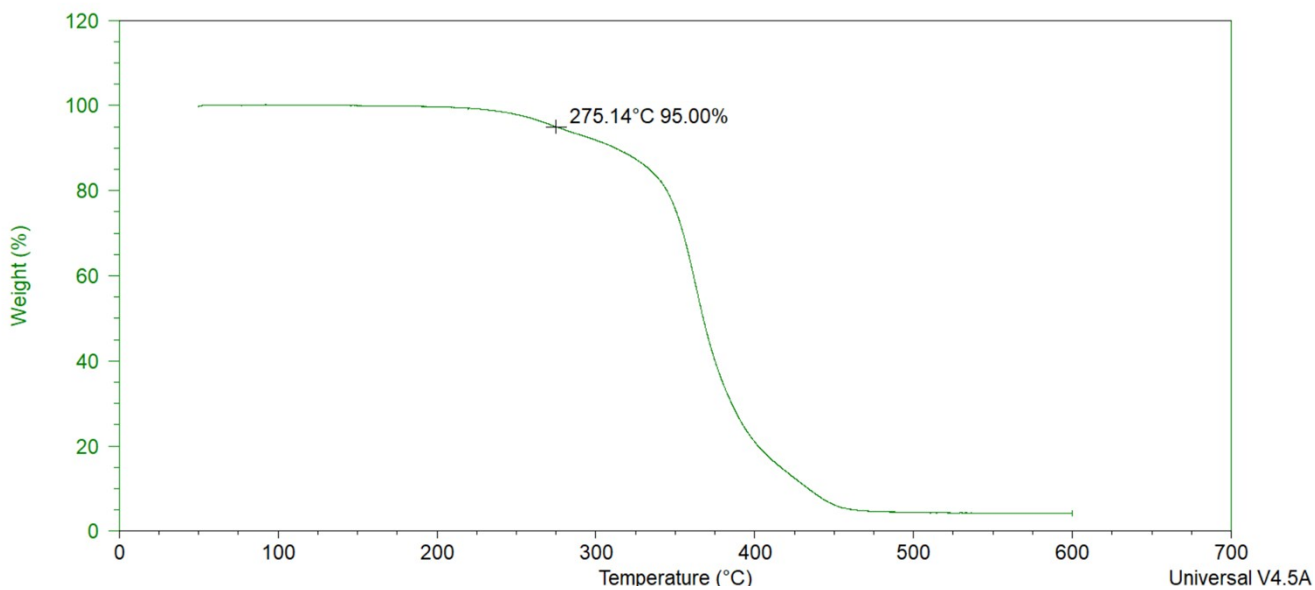


Figure S41- TGA thermogram P(Dec-BDMF: Dec-FDE).

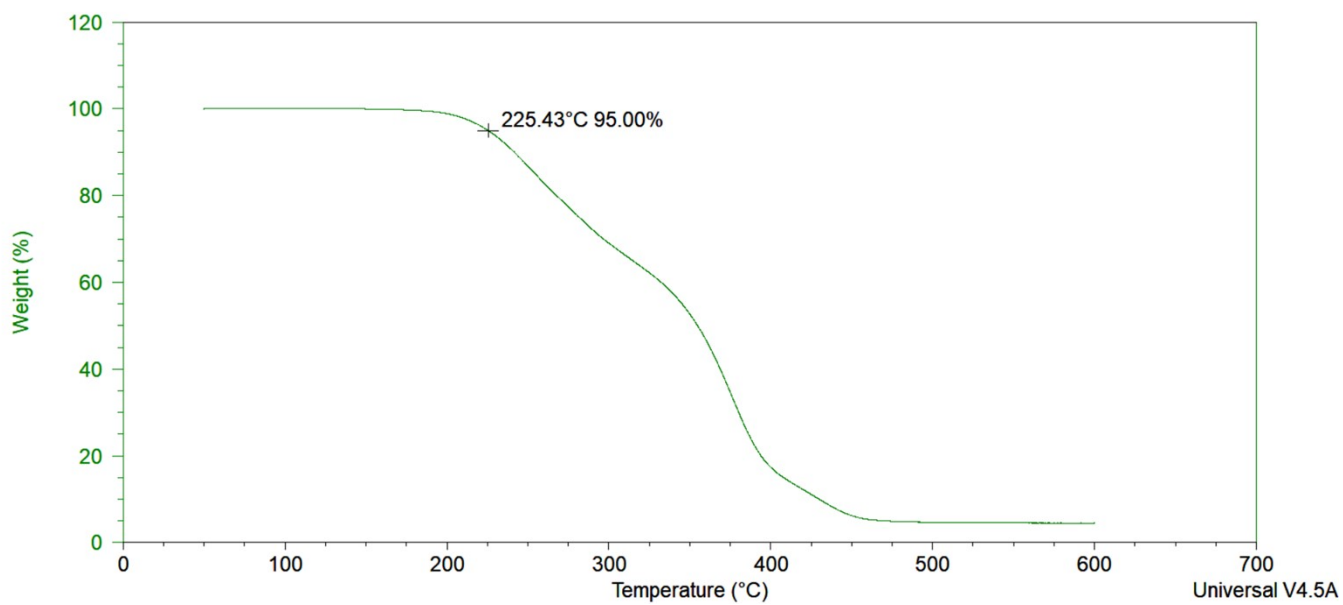


Figure S42- TGA thermogram P(Dec-FDE: But-BACF).

SEC analysis

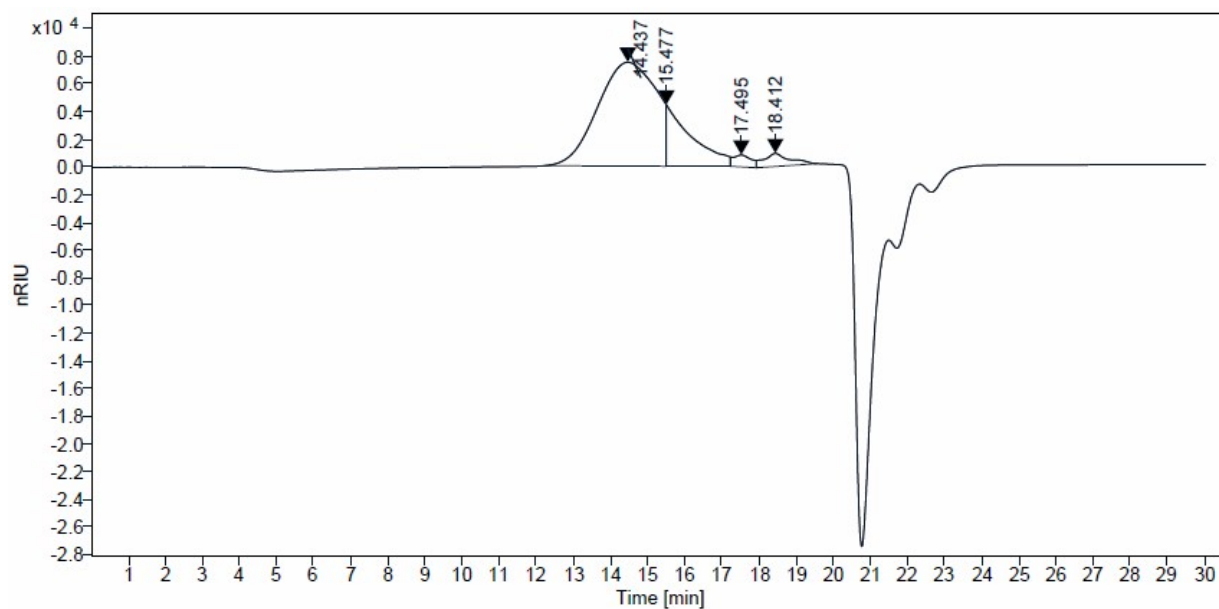


Figure S43- SEC trace of P(But-BACF).

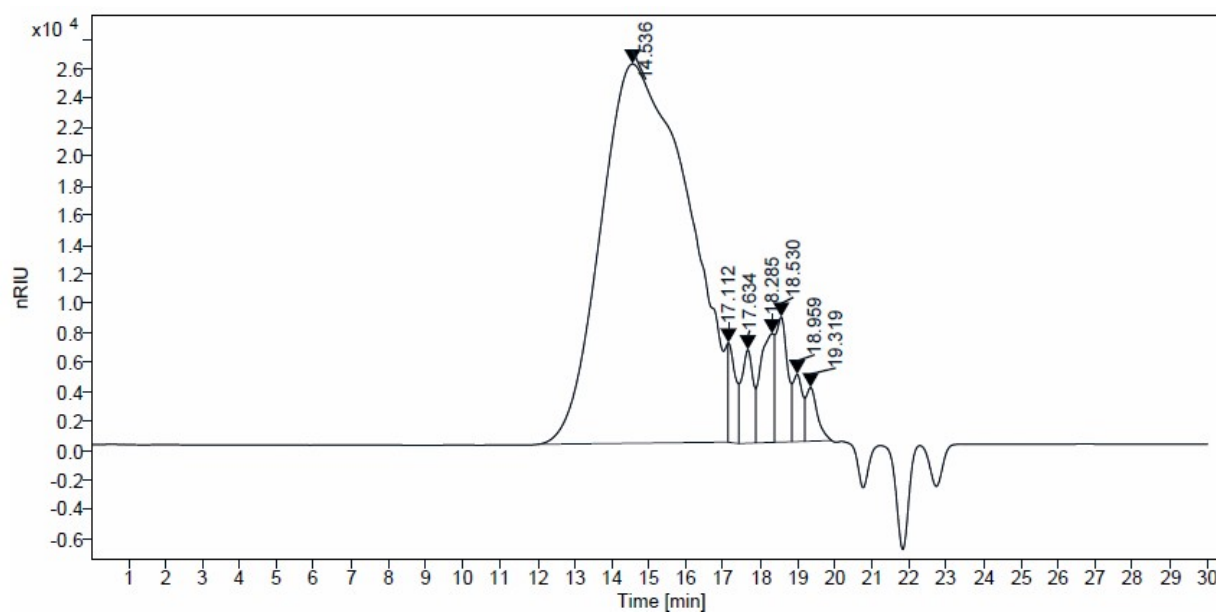


Figure S44- SEC trace of P(Hex-BACF).

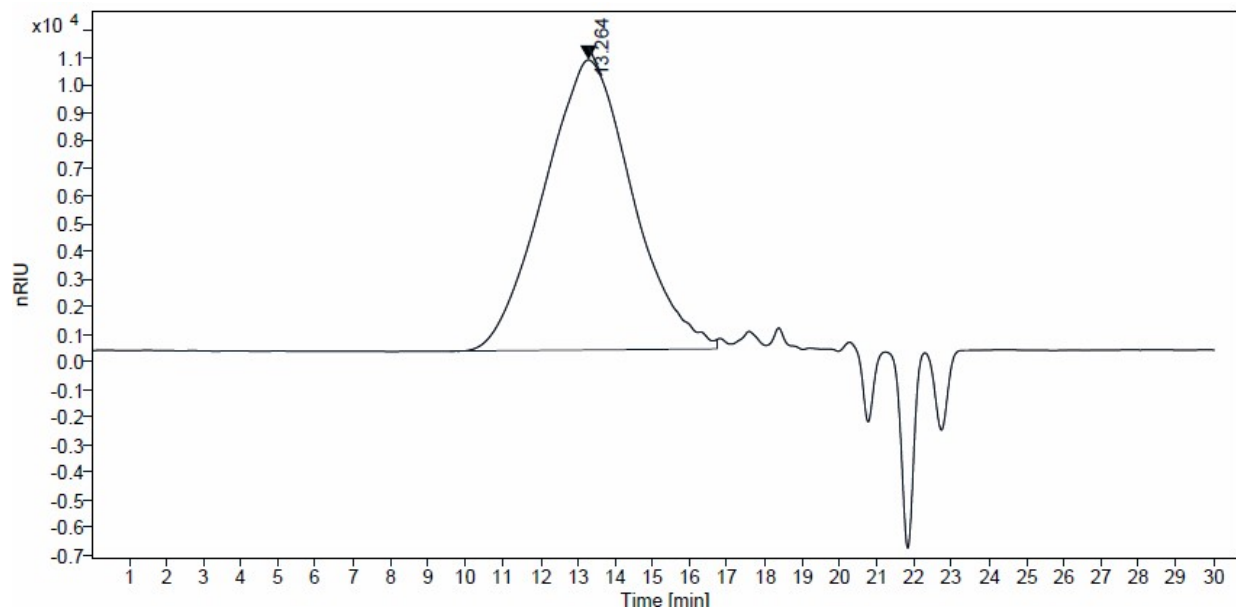


Figure S45- SEC trace of P(Dec-BACF).

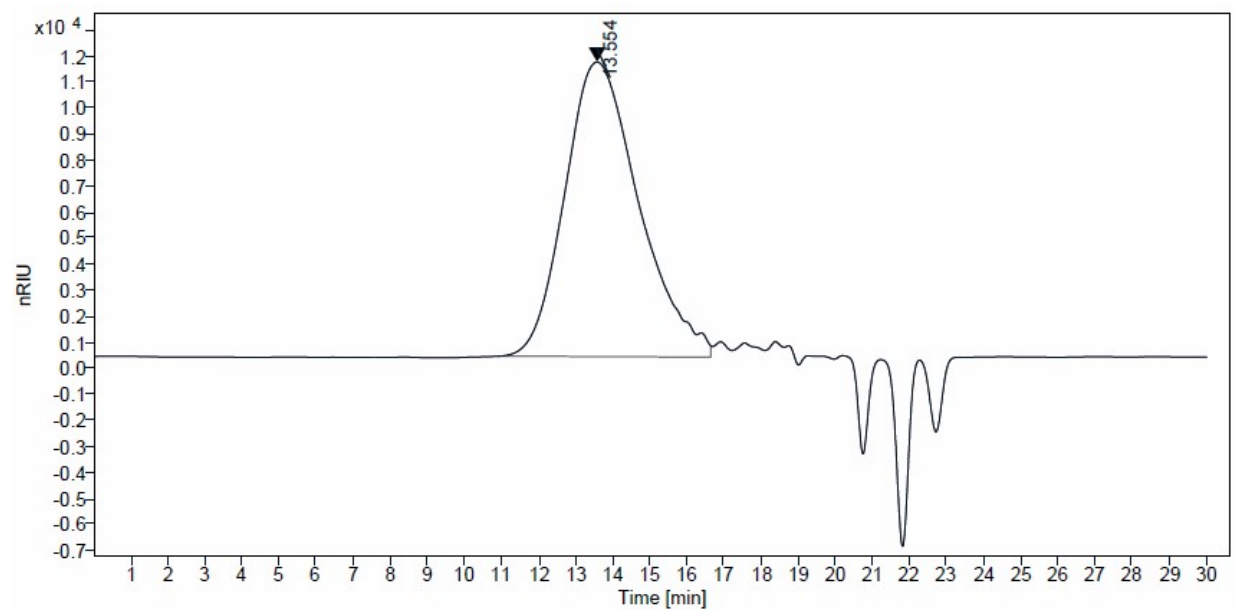


Figure S46- SEC trace of P(Dec-BACF: Dec-FDE).

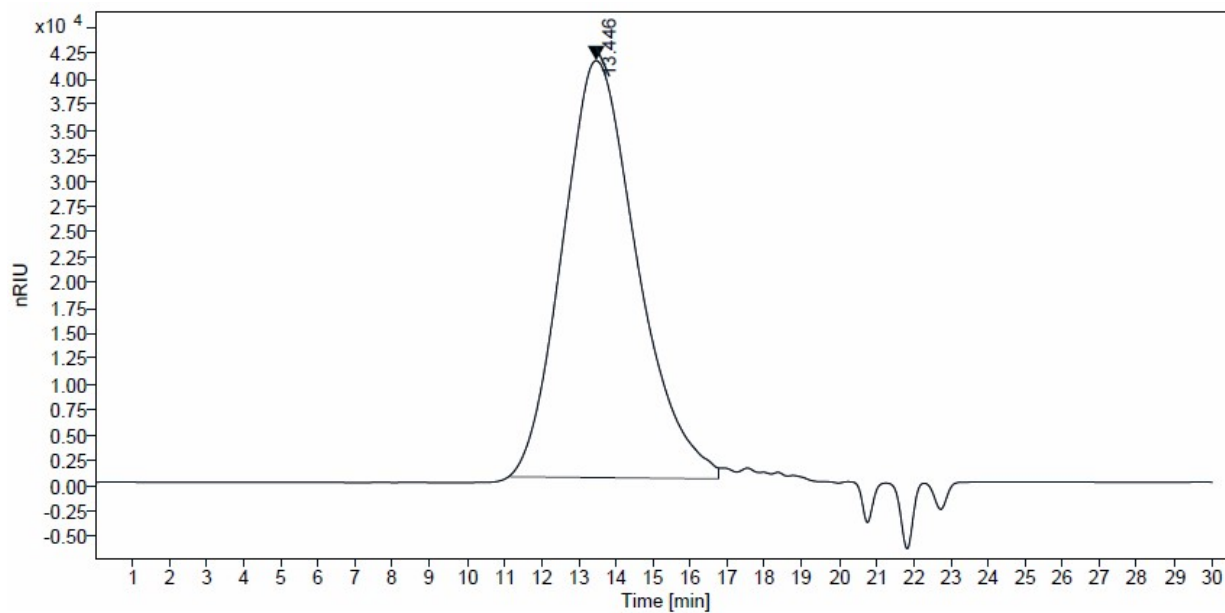


Figure S47- SEC trace of P(Dec-BDMF: Dec-BACF).

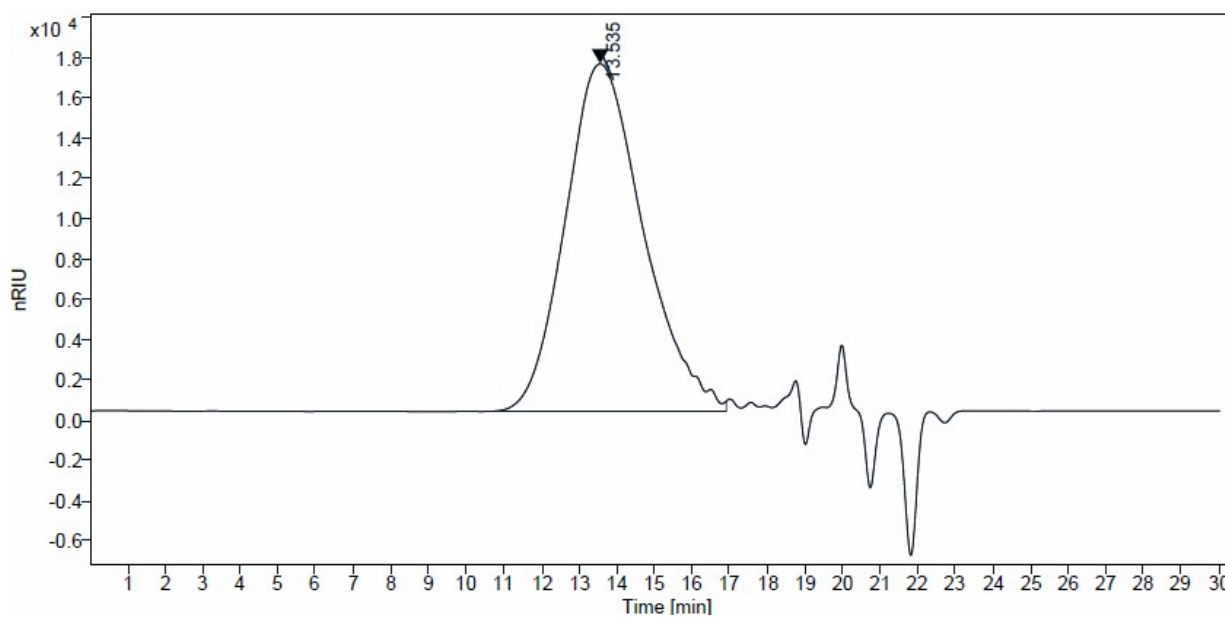


Figure S48- SEC trace of P(Dec-BDMF: Dec-FDE).

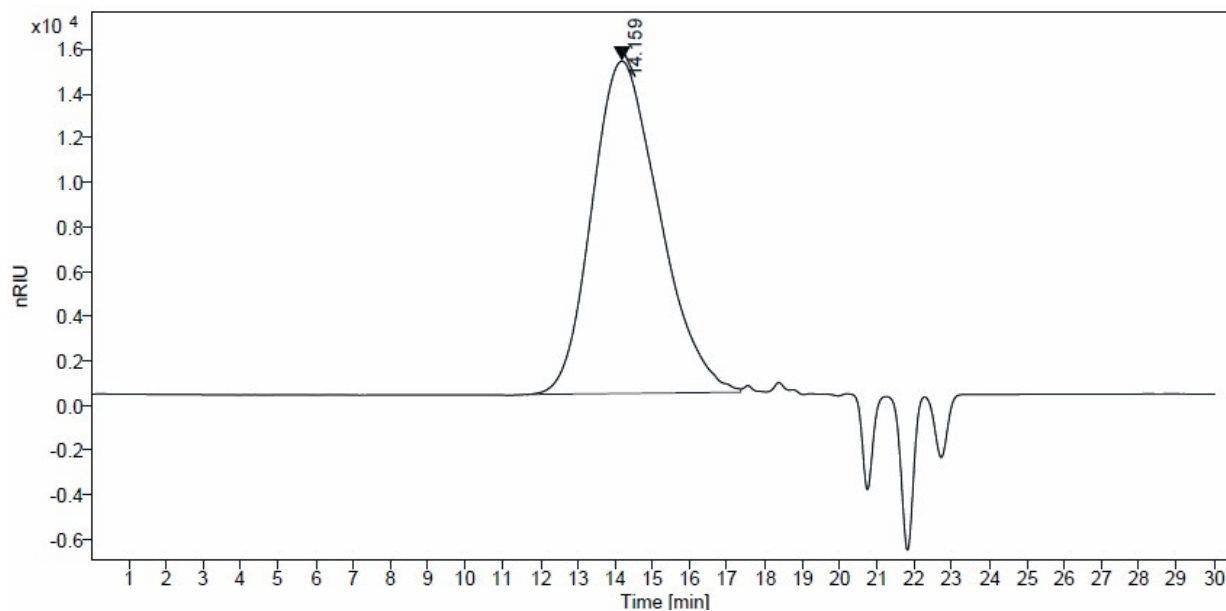


Figure S49- SEC trace of P(Dec-FDE: But-BACF).

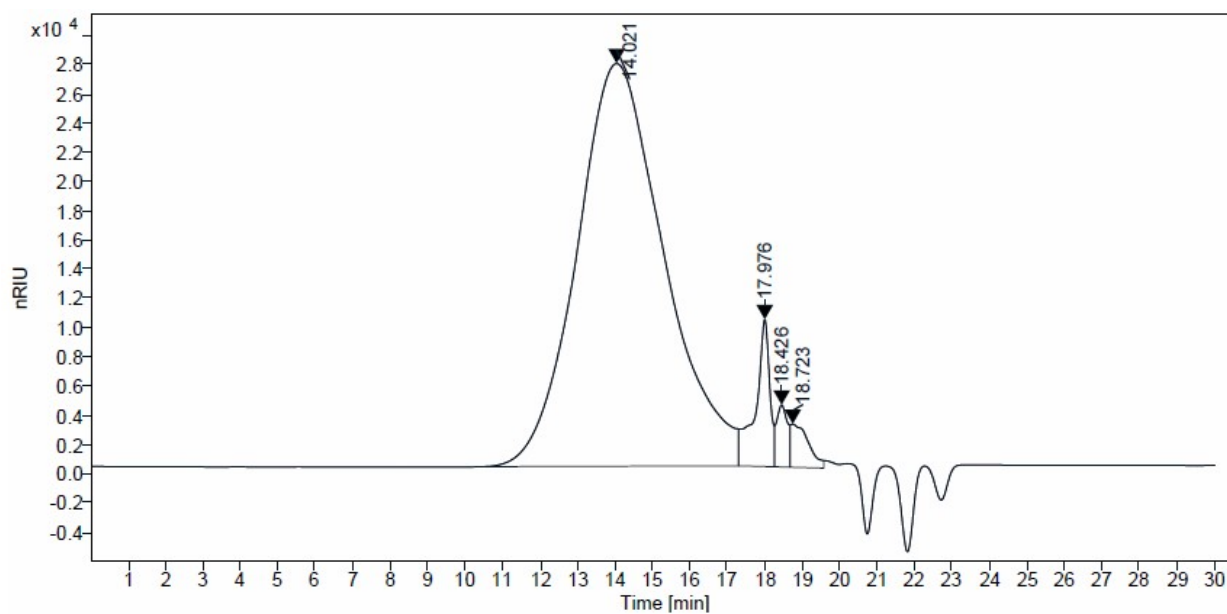


Figure S50- SEC trace of P(Dec-BDMF: But-BACF).

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- (2) B. Chícharo, S. Fadlallah, F. Allais, F. Aricò, *ChemSusChem* 2024, **17**, e202301311.
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- (4) A. G. Sathicq, M. Annatelli, I. Abdullah, G. Romanelli, F. Aricò, *Sustain. Chem. Pharm.* 2021, **19**.