

Organocatalytic Synthesis of Poly(hydroxymethylfuroate) via Ring-Opening Polymerization of 5-Hydroxymethylfurfural-Based Cyclic Oligoesters

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Electronic supplementary information

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Proposed mechanism for the synthesis of $c(\text{HMF})_n$ by NHC oxidative catalysis

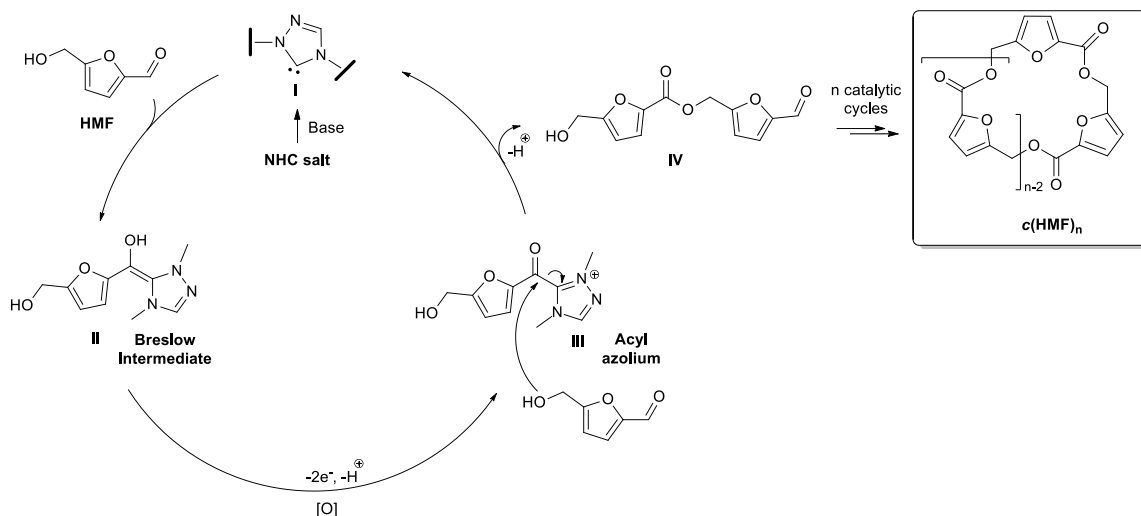
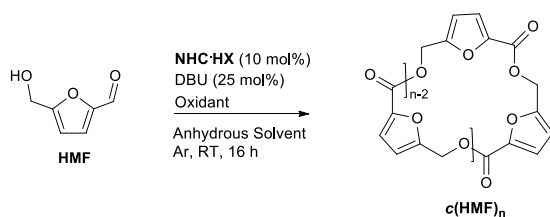
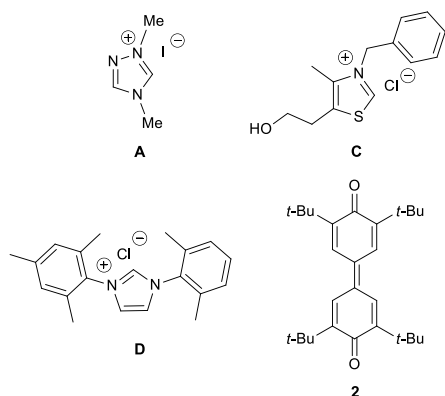


Table S1. Extended optimization study of the NHC-catalyzed synthesis of $c(\text{HMF})_n$.^a

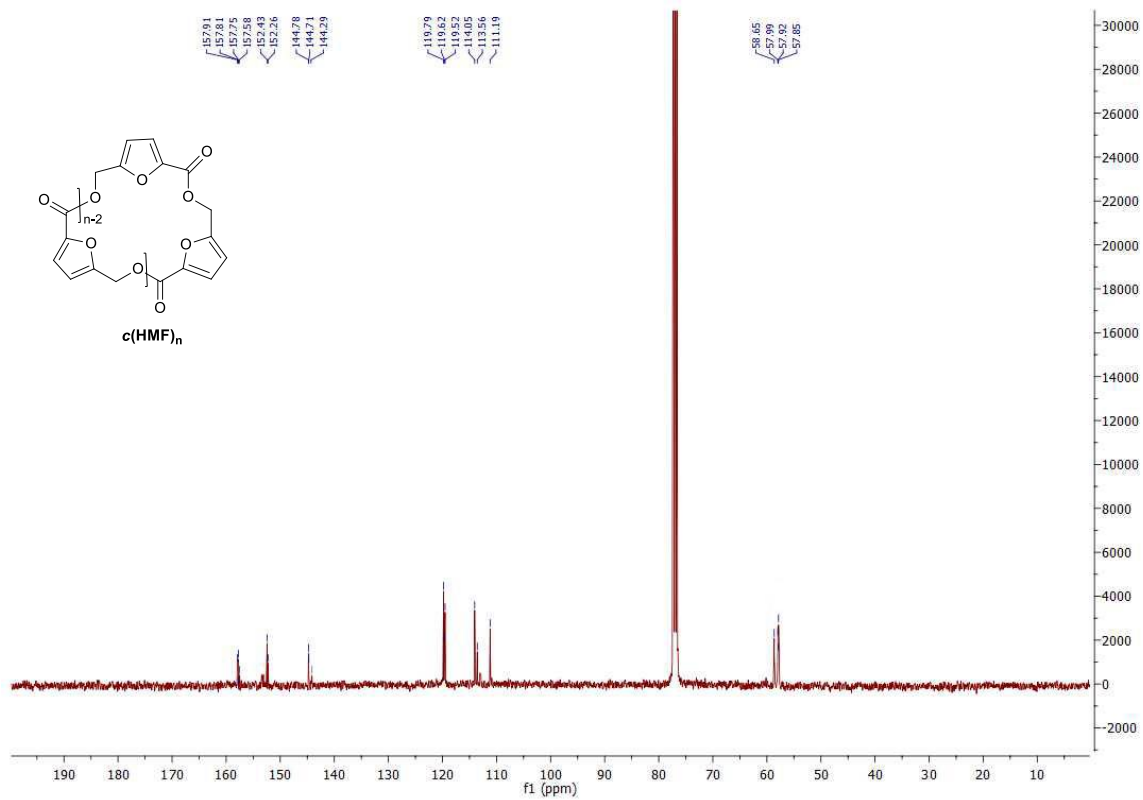
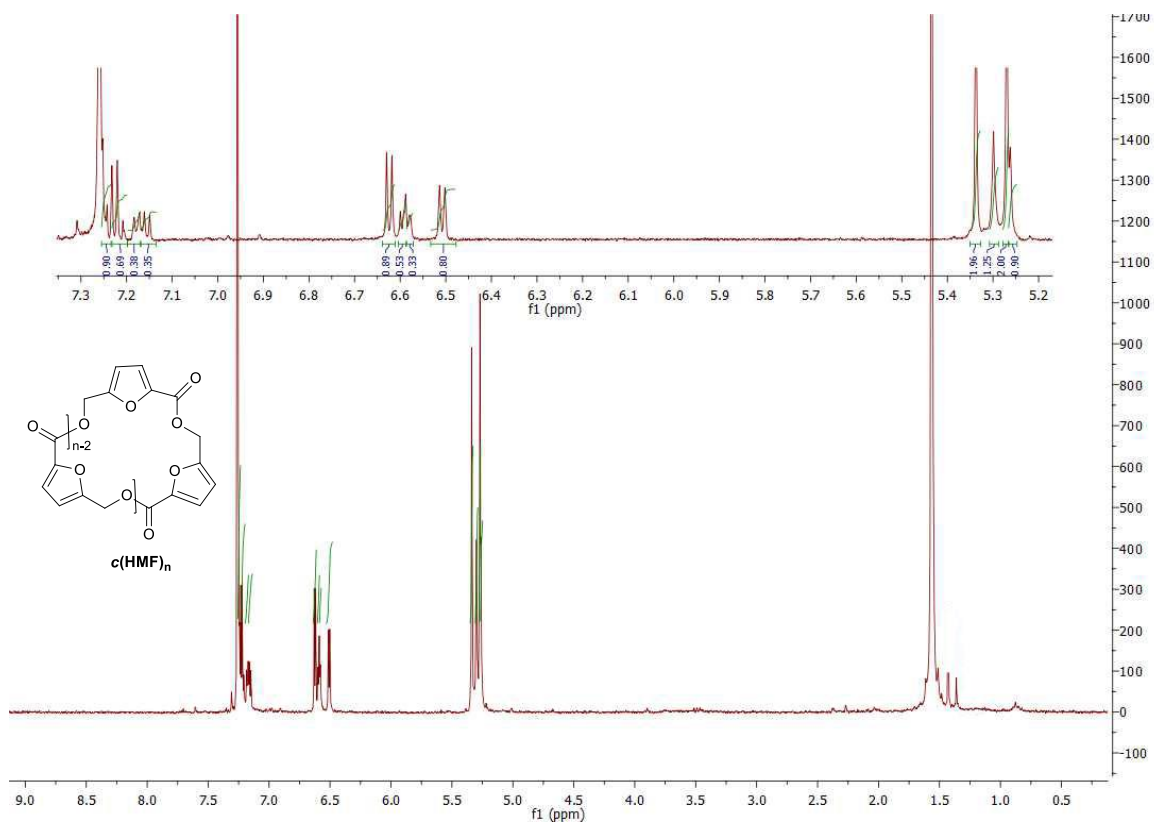


Entry	NHCHX	Oxidant (mol%)	Solvent	Conv. (%) ^b	$c(\text{HMF})_n$ (%) ^c
1	C	2 (100)	THF	10	-
2	D	2 (100)	THF	-	-
3 ^d	A	2 (100)	THF	62	43
4 ^e	A	2 (100)	THF	73	51
5	A	2 (100)	Toluene	78	46

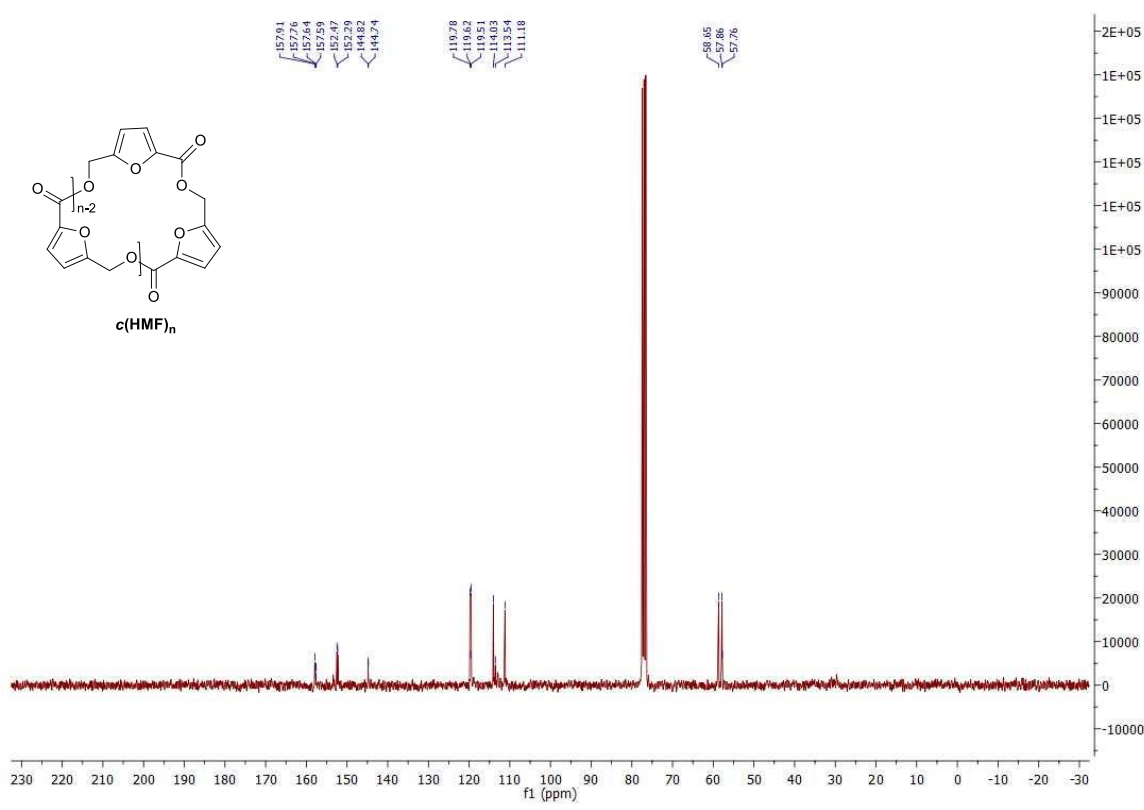
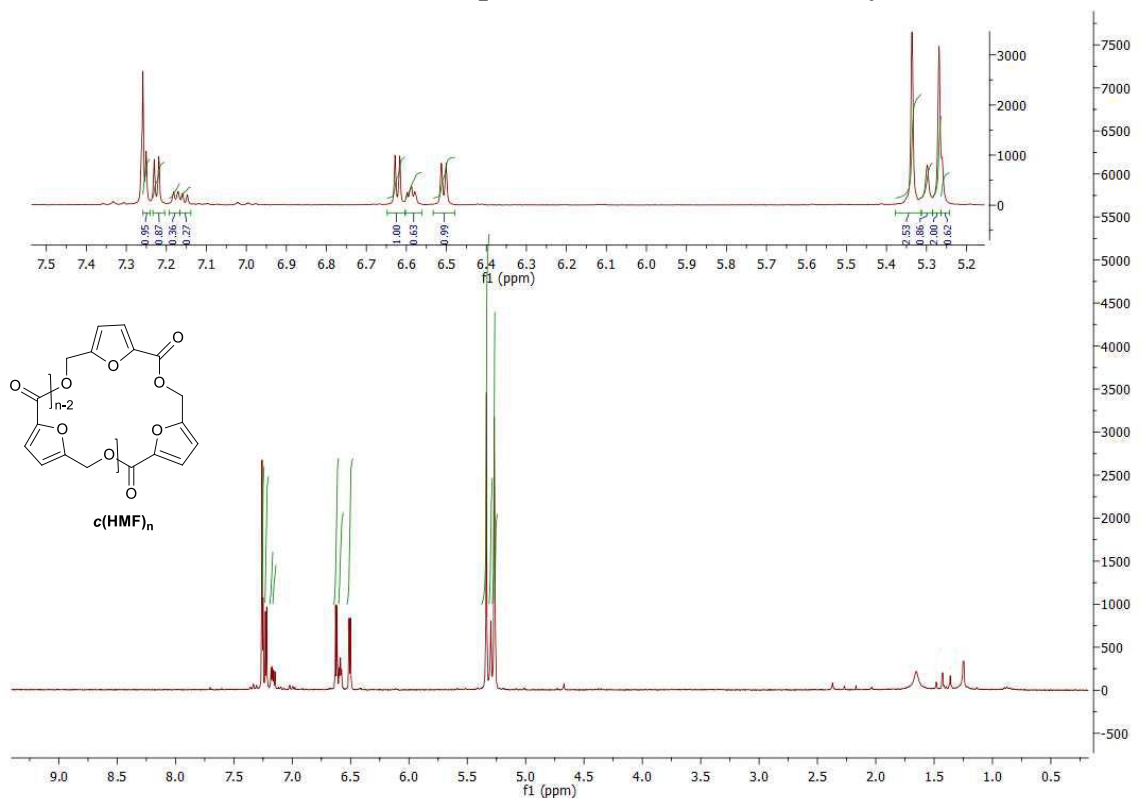
^aHMF (1.60 mmol), anhydrous solvent (120 mL). ^bDetected by ¹H NMR analysis of the crude reaction mixture (durene as internal standard). ^cIsolated yield. ^dReaction time: 8 h. ^e**A** (5 mol%), DBU (15 mol%).



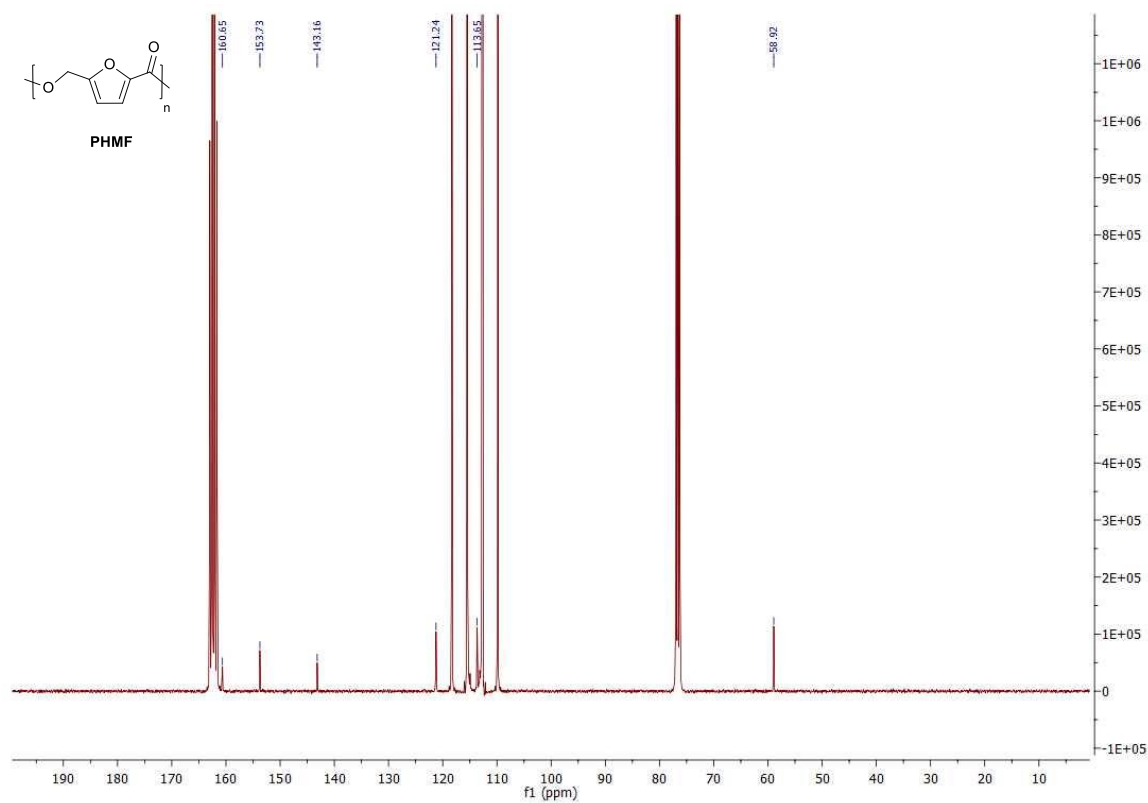
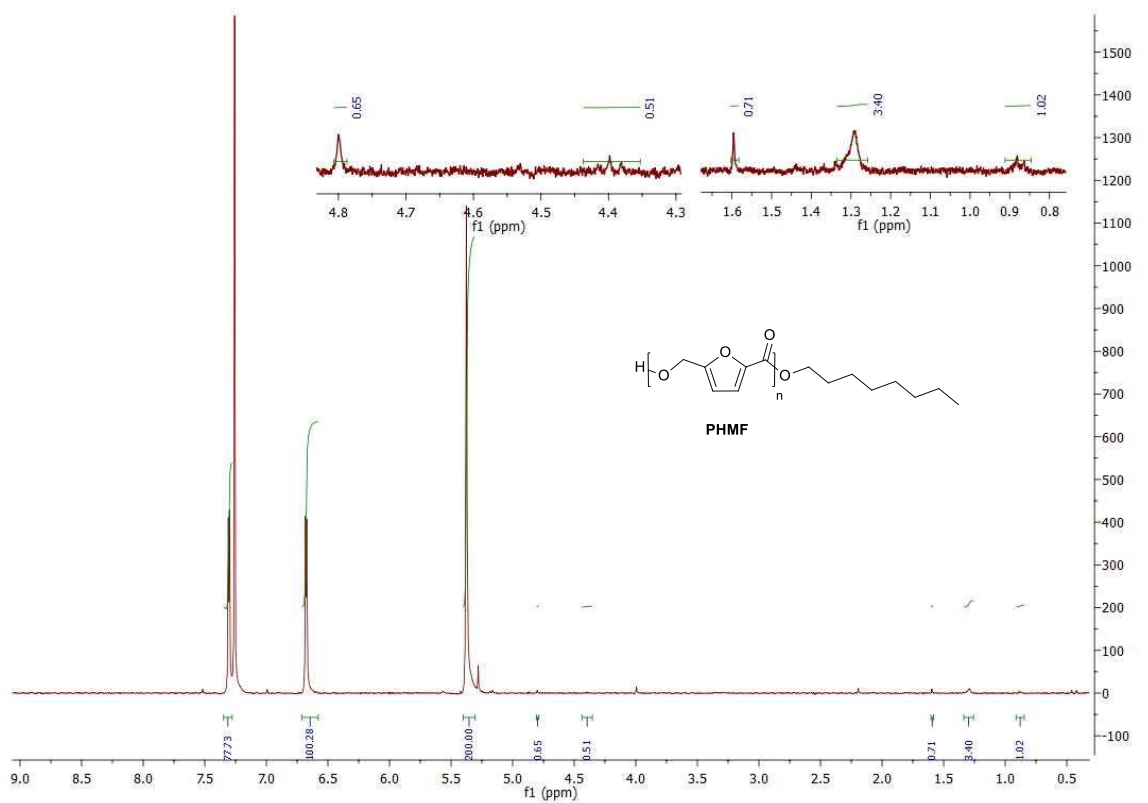
^1H (300 MHz) and ^{13}C (101 MHz) spectra (CDCl_3) of $c(\text{HMF})_n$ synthesized from HMFCFA



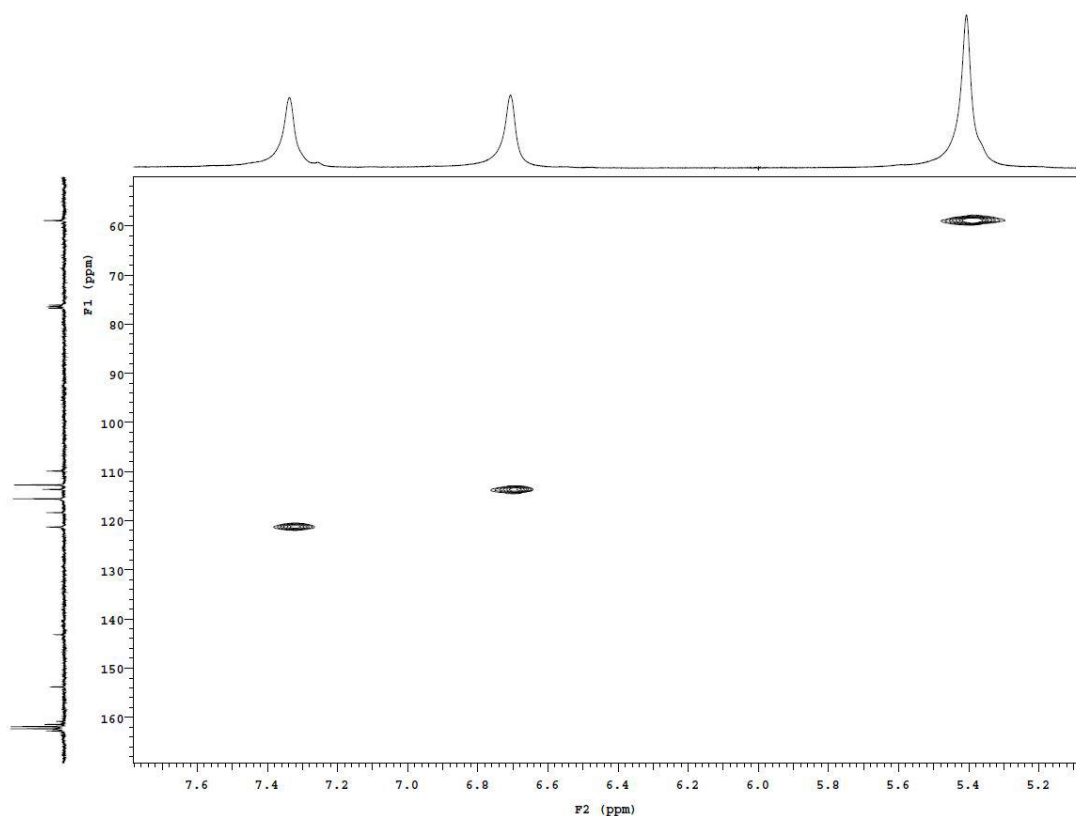
^1H (300 MHz) and ^{13}C (101 MHz) spectra (CDCl_3) of $c(\text{HMF})_n$ synthesized from HMF



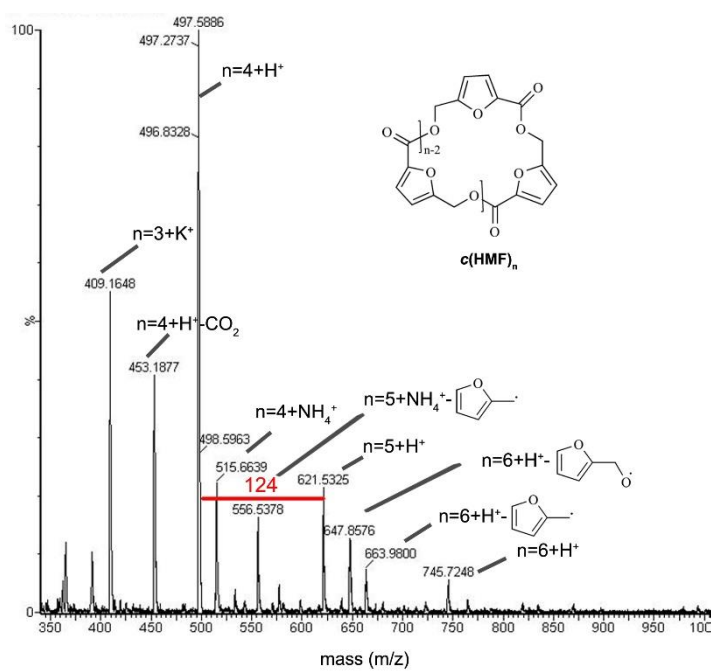
^1H (300 MHz) and ^{13}C (101 MHz) spectra (CDCl_3 : TFA = 1:1) of model PHMF $_E6$



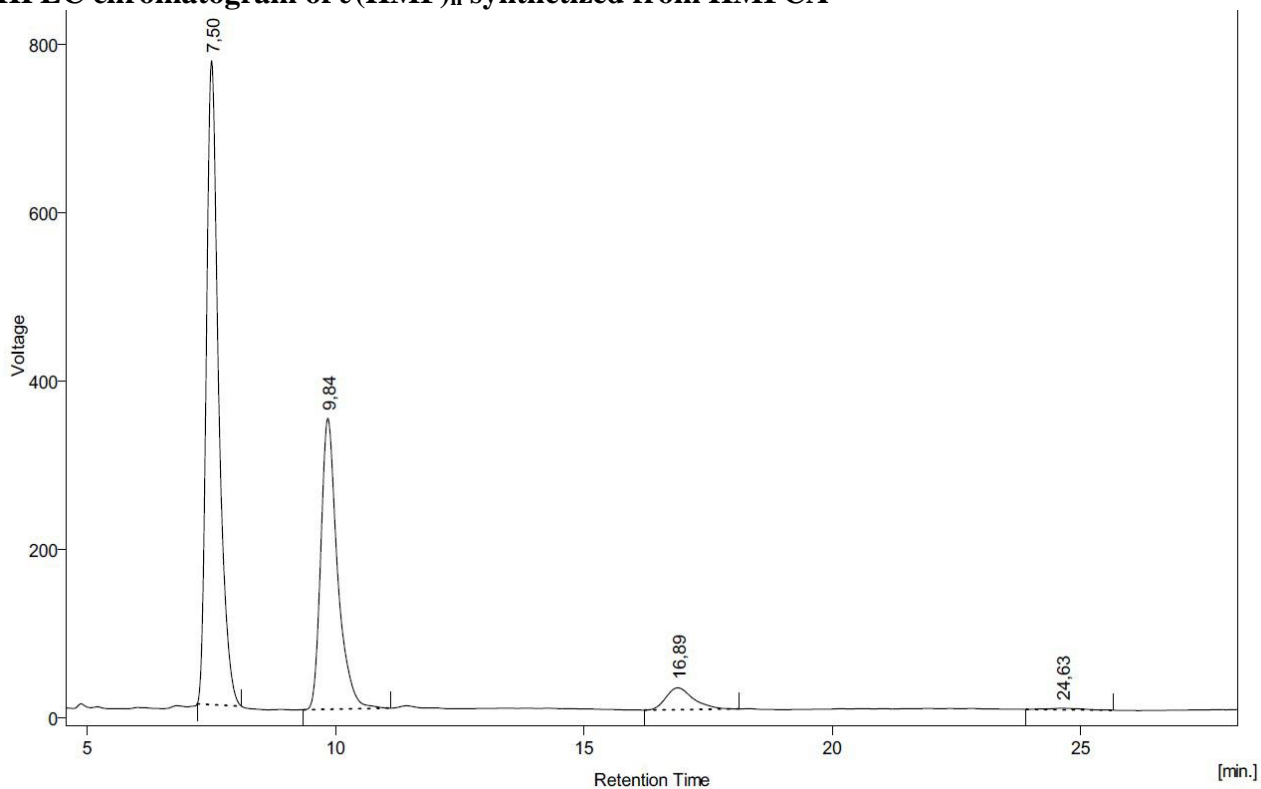
2D ^1H - ^{13}C HMQC correlation spectroscopy (CDCl_3 : TFA = 1:1) of model PHMF $_{\text{E}6}$



ESI-MS of $c(\text{HMF})_n$ with peak assignments

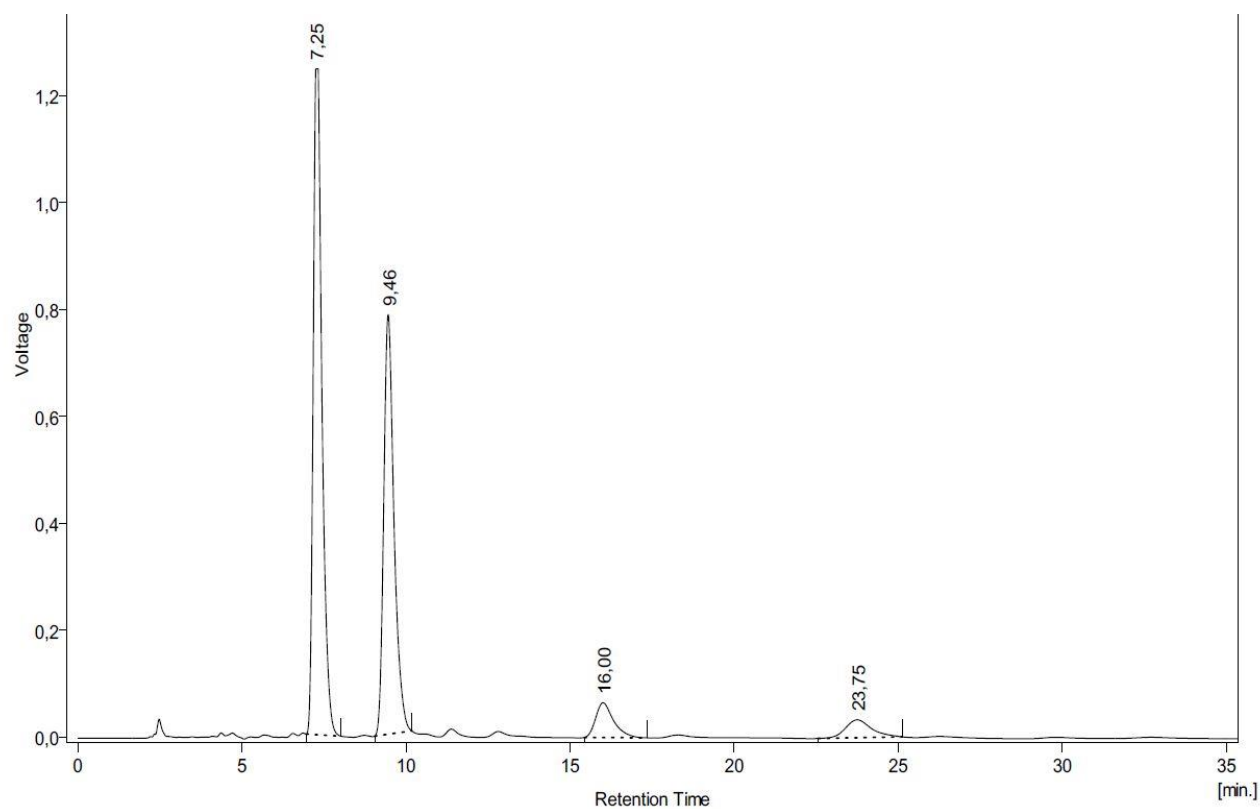


HPLC chromatogram of $c(\text{HMF})_n$ synthesized from HMFCA



HPLC chromatogram. Prep Nova-Pak HR SILICA column (60 Å, 6 μm, 3.9 x 300 mm), *n*-hexane/dioxane 70/30 (v/v), 1.0 mL/min, 254 nm. $n=3$, $t_r = 9.84$ min; $n=4$, $t_r = 7.50$ min; $n=5$, $t_r = 16.89$ min; $n=6$, $t_r = 24.63$ min.

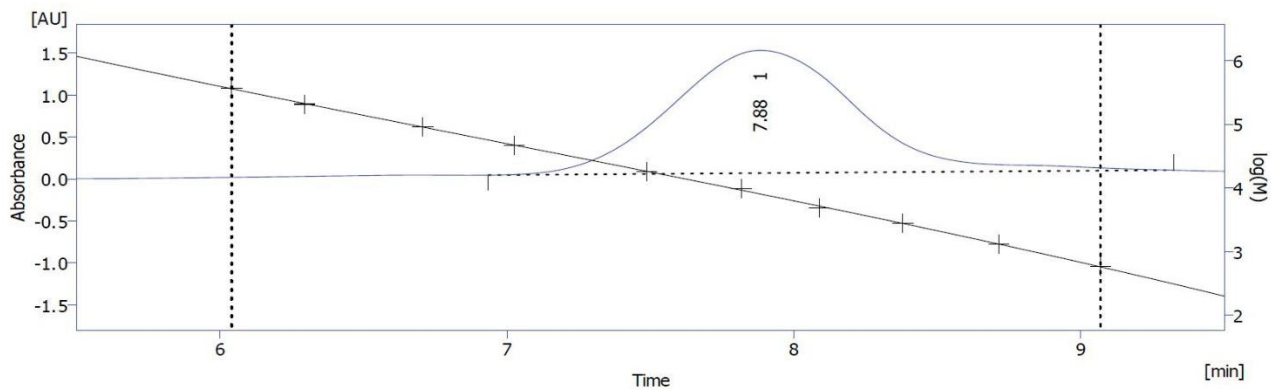
HPLC chromatogram of $c(\text{HMF})_n$ synthesized from HMF



HPLC chromatogram. Prep Nova-Pak HR SILICA column (60 Å, 6 μm, 3.9 x 300 mm), *n*-hexane/dioxane 70/30 (v/v), 1.0 mL/min, 254 nm. *n* = 3, t_r = 9.46 min; *n* = 4, t_r = 7.25 min; *n* = 5, t_r = 16.00 min; *n* = 6, t_r = 23.75 min.

GPC chromatograms of PHMF

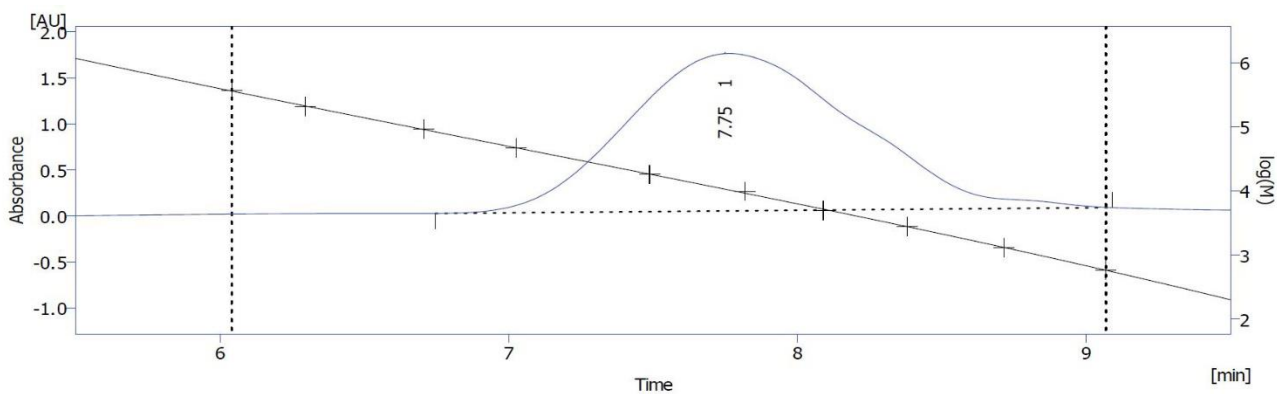
PHMF_{E1}



Equation: $Y = -0.01168 \cdot X^3 + 0.24637 \cdot X^2 - 2.61818 \cdot X + 14.957$
 Correlation Factor: 0.9998978

	Max. RT	Start RT	End RT	Mp	Mn	Mw	PD	Area [mAU.s]	Area [%]
1	7.88	6.93	9.32	8034	5608	9116	1.6255	65536.59	100.00

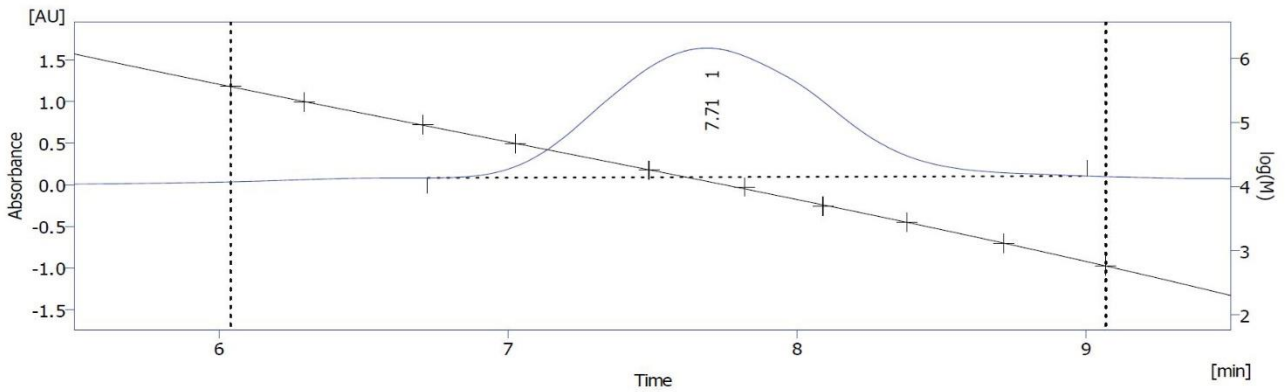
PHMF_{E2}



Equation: $Y = -0.01168 \cdot X^3 + 0.24637 \cdot X^2 - 2.61818 \cdot X + 14.957$
 Correlation Factor: 0.9998978

	Max. RT	Start RT	End RT	Mp	Mn	Mw	PD	Area [mAU.s]	Area [%]
1	7.75	6.75	9.09	10618	6576	11494	1.7479	93479.16	100.00

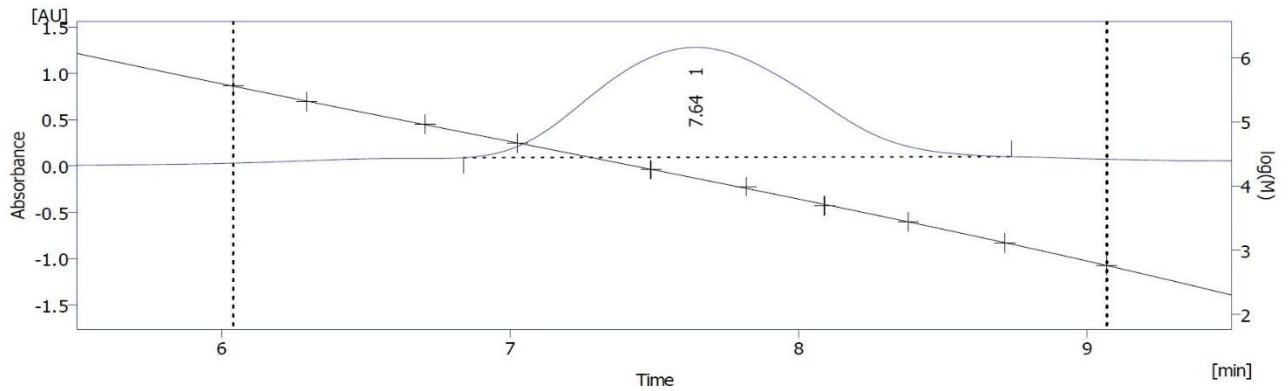
PHMF_{E3}



Equation: $Y = -0.01168 \cdot X^3 + 0.24637 \cdot X^2 - 2.61818 \cdot X + 14.957$
 Correlation Factor: 0.9998978

	Max. RT	Start RT	End RT	Mp	Mn	Mw	PD	Area [mAU.s]	Area [%]
1	7.71	6.72	9.00	11600	8414	13734	1.6324	80976.62	100.00

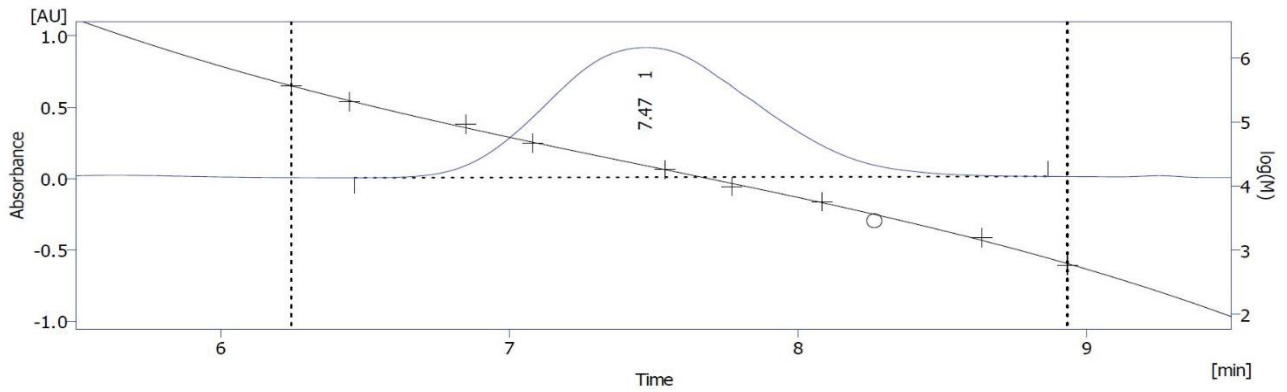
PHMF_{E4}



Equation: $Y = -0.01168 \cdot X^3 + 0.24637 \cdot X^2 - 2.61818 \cdot X + 14.957$
 Correlation Factor: 0.9998978

	Max. RT	Start RT	End RT	Mp	Mn	Mw	PD	Area [mAU.s]	Area [%]
1	7.64	6.84	8.74	13207	9941	15020	1.5108	59394.51	100.00

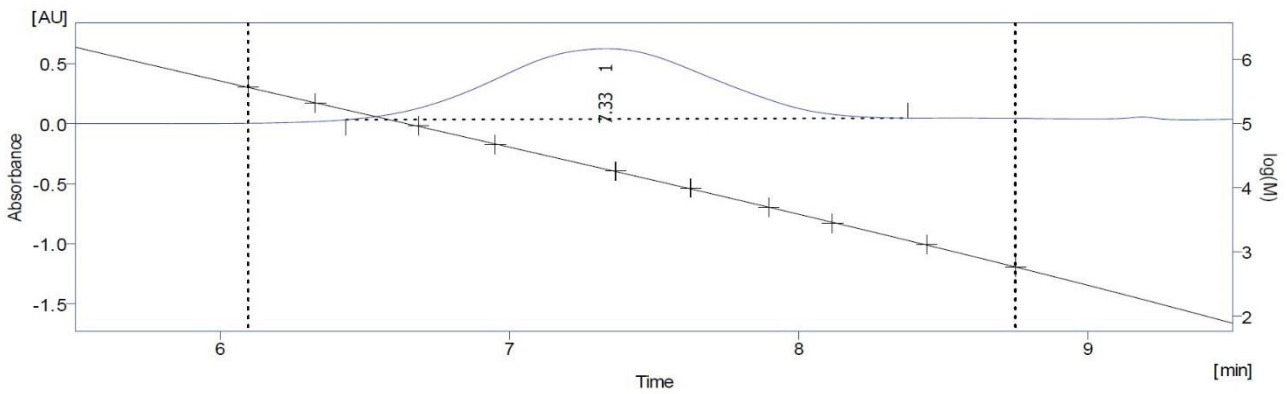
PHMF_{E5}



Equation: $Y = -0.05872 \cdot X^3 + 1.31866 \cdot X^2 - 10.79522 \cdot X + 35.85374$
 Correlation Factor: 0.9994252

	Max. RT	Start RT	End RT	Mp	Mn	Mw	PD	Area [mAU.s]	Area [%]
1	7.47	6.46	8.87	20846	14403	23360	1.6219	45662.46	100.00

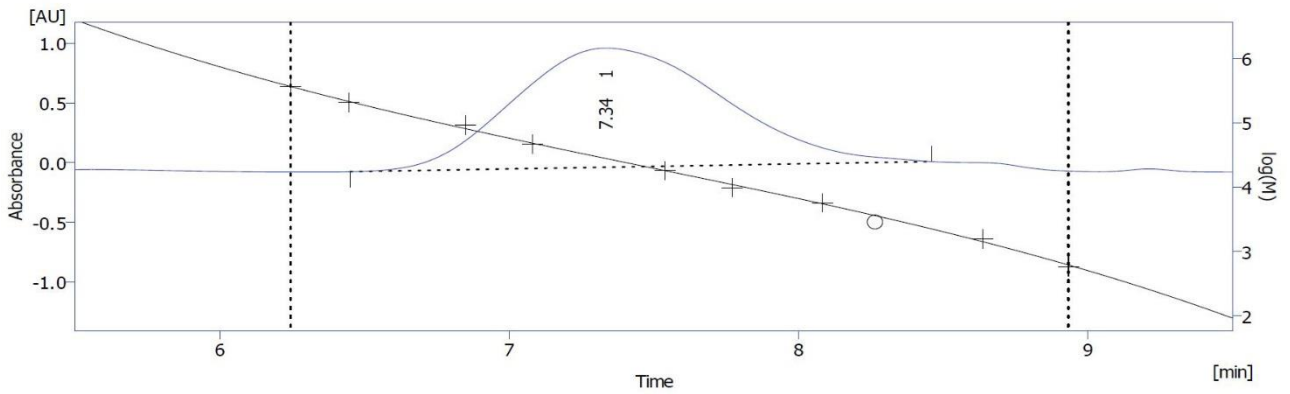
PHMF_{E5}(NHC)



Equation: $Y = -0.00786 \cdot X^3 + 0.15792 \cdot X^2 - 2.08513 \cdot X + 14.18193$
 Correlation Factor: 0.9999535

	Max. RT	Start RT	End RT	Flow Rate Correction	Mp	Mn	Mw	PD	Area [mAU.s]	Area [%]
1	7.33	6.43	8.38	1.0000	19346	14275	25772	1.8053	30389.66	100.00

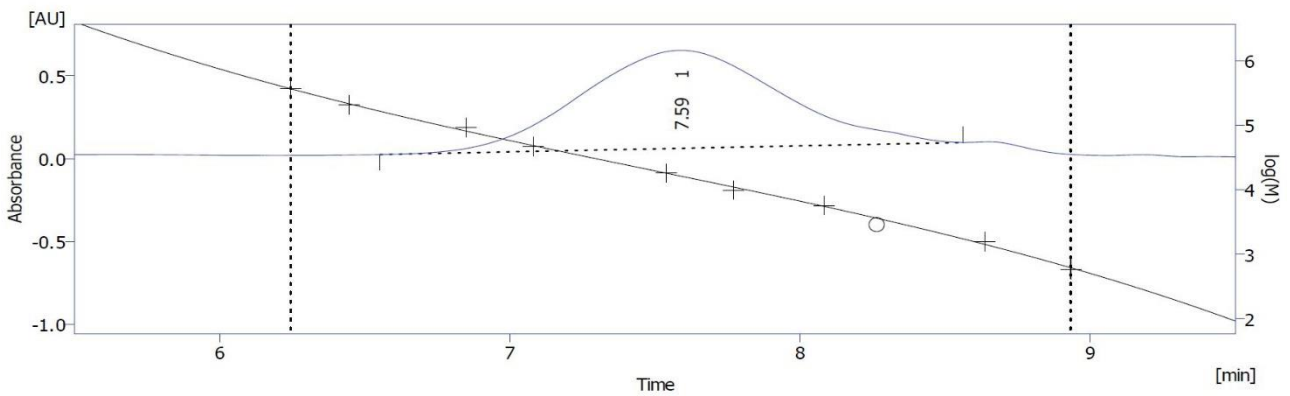
PHMF_{E6}



Equation: $Y = -0.05872 \cdot X^3 + 1.31866 \cdot X^2 - 10.79522 \cdot X + 35.85374$
 Correlation Factor: 0.9994252

	Max. RT	Start RT	End RT	Mp	Mn	Mw	PD	Area [mAU.s]	Area [%]
1	7.34	6.45	8.46	27799	18746	29825	1.5910	49917.10	100.00

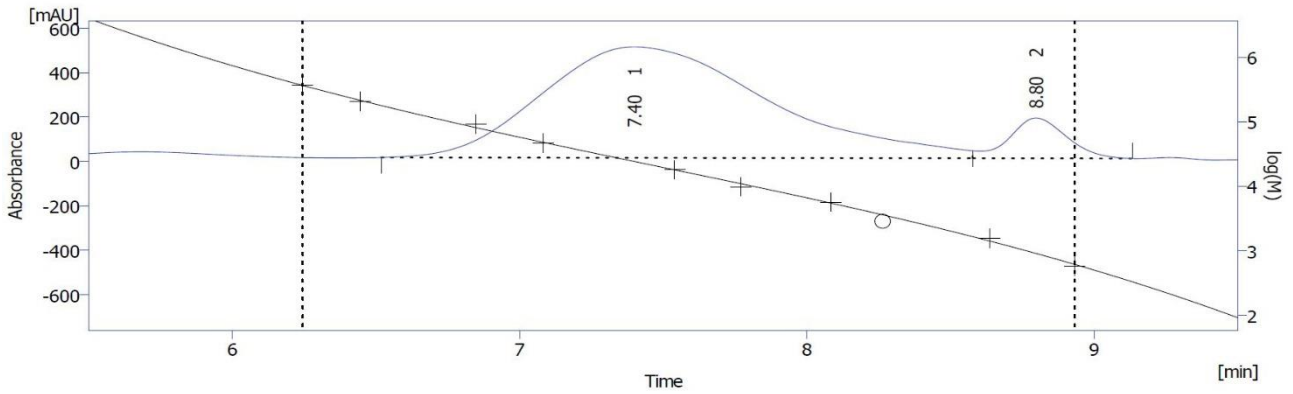
PHMF_{E7}



Equation: $Y = -0.05872 \cdot X^3 + 1.31866 \cdot X^2 - 10.79522 \cdot X + 35.85374$
 Correlation Factor: 0.9994252

	Max. RT	Start RT	End RT	Mp	Mn	Mw	PD	Area [mAU.s]	Area [%]
1	7.59	6.55	8.56	16058	12492	19560	1.5659	28168.48	100.00

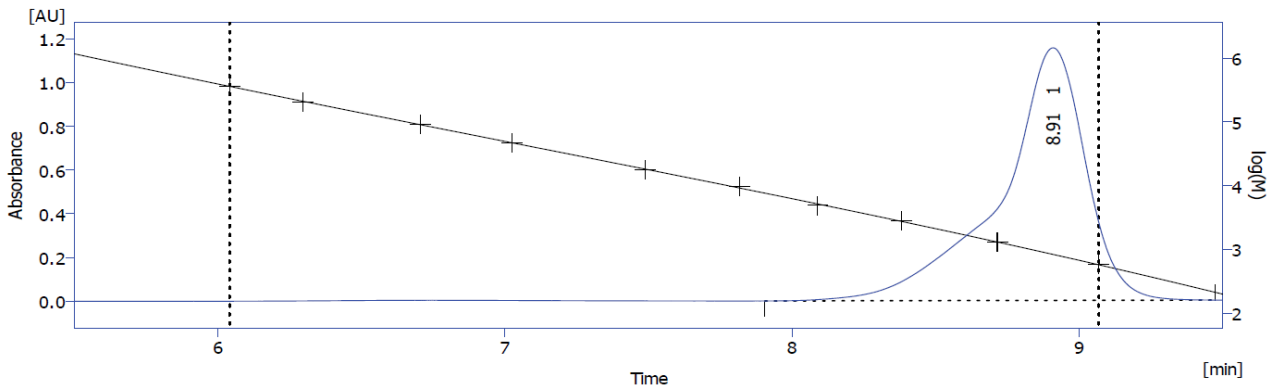
PHMF_{E8}



Equation: $Y = -0.05872 \cdot X^3 + 1.31866 \cdot X^2 - 10.79522 \cdot X + 35.85374$
 Correlation Factor: 0.9994252

	Max. RT	Start RT	End RT	Mp	Mn	Mw	PD	Area [mAU.s]	Area [%]
1	7.40	6.52	8.58	24155	13192	24732	1.8748	27363.35	91.56
2	8.80	8.58	9.13	908	858	925	1.0775	2521.55	8.44

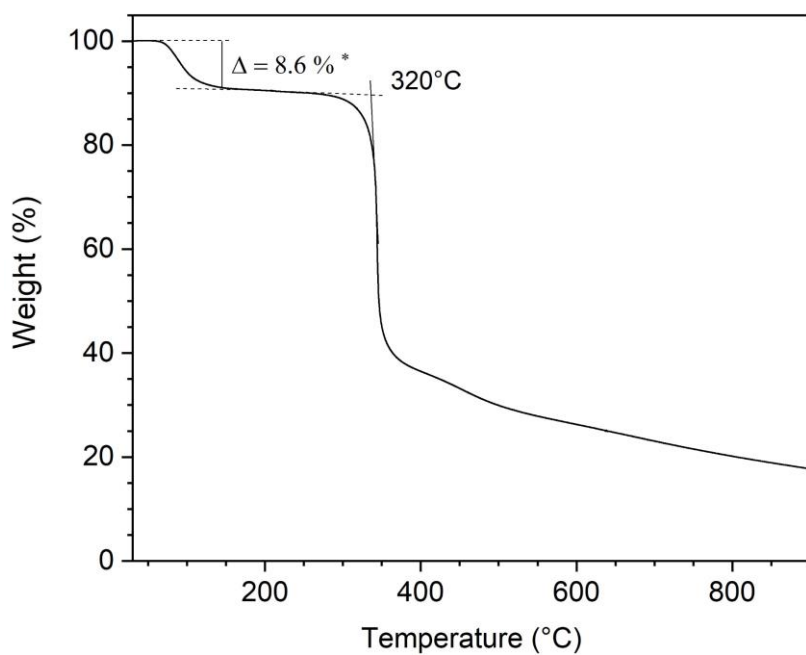
c(HMF)_n



Result Table (cal20201022_mix - Narrow - DS37dildilbis-29_10_2020_15_18_42 - UVD2.1L: UV_signal)
 Equation: $Y = -0.01168 \cdot X^3 + 0.24637 \cdot X^2 - 2.61818 \cdot X + 14.957$
 Correlation Factor: 0.9998978

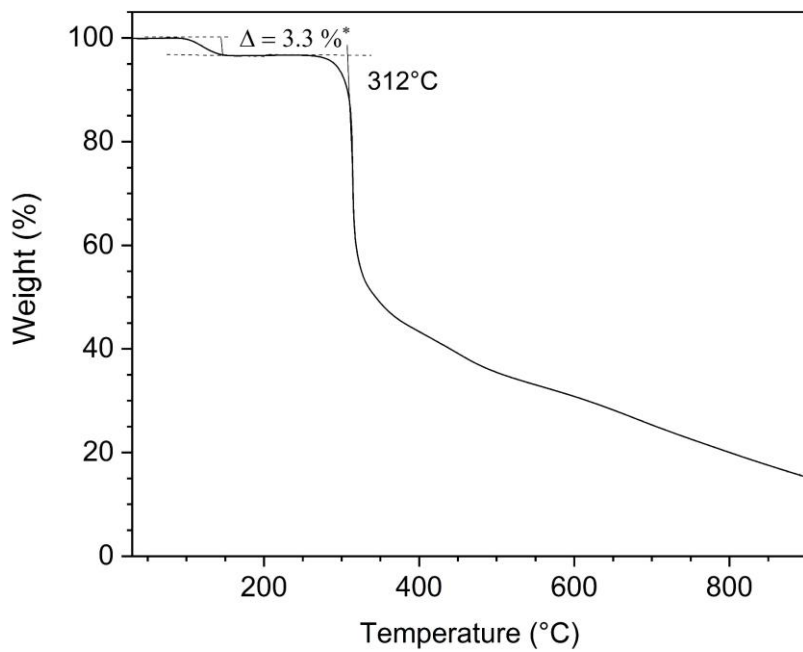
	Max. RT	Start RT	End RT	Mp	Mn	Mw	PD	Area [mAU.s]	Area [%]
1	8.91	7.91	9.47	838	927	1117	1.2055	23758.15	100.00

TGA of $c(\text{HMF})_n$ in nitrogen atmosphere at $10^\circ\text{C}/\text{min}$ as scan rate



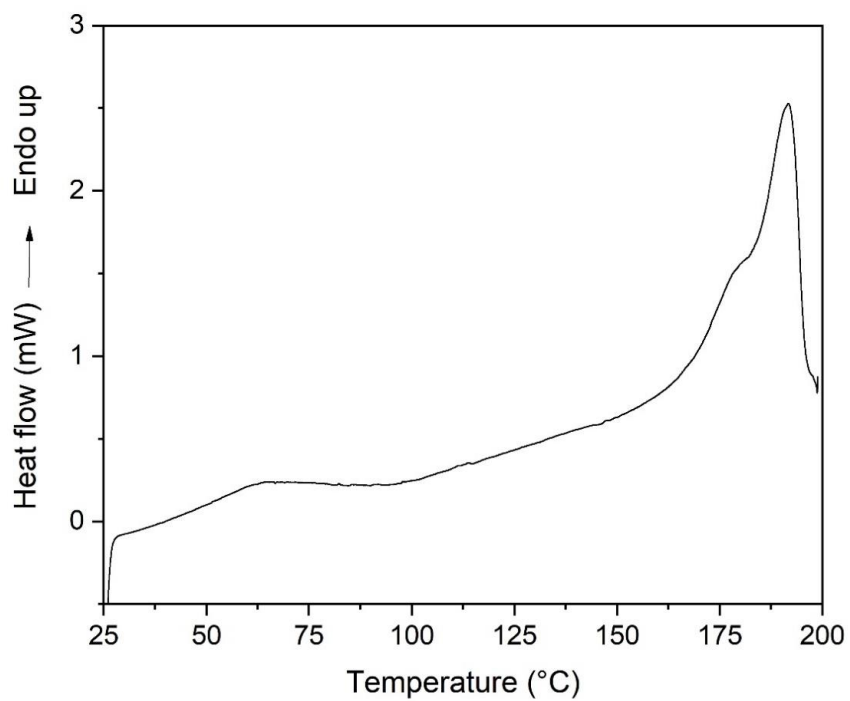
*residual Heptane/EtOAc

TGA of PHMF_{E5} in nitrogen atmosphere at $10^\circ\text{C}/\text{min}$ as scan rate



*residual EtOAc

DSC of PHMF_{E5} previously analyzed by DSC up to 220°C, solubilized with HFIP, dried and analyzed again in nitrogen atmosphere at 10°C/min as scan rate



Picture of PHMF_{E5}



XRD of PHMF_{E5} after solubilization in HFIP and subsequent drying

