

Supplemental Information:

Sequencing Biodegradable and Potentially Biobased Polyesteramide of Sebacic Acid and 3-Amino-1-Propanol by MALDI TOF-TOF Tandem Mass Spectrometry

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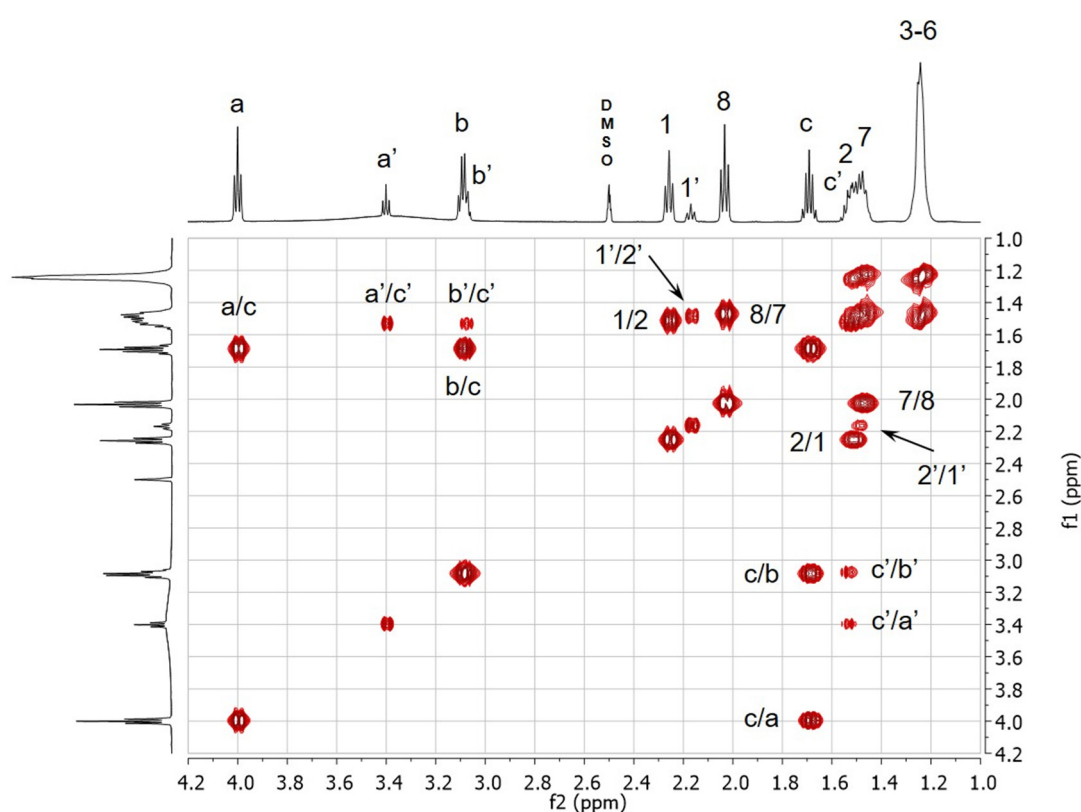


Figure S1. Partial g-COSY spectrum of PEA-Pro in 6d-DMSO at 50 °C showing the 4.2 – 1.0 ppm range.

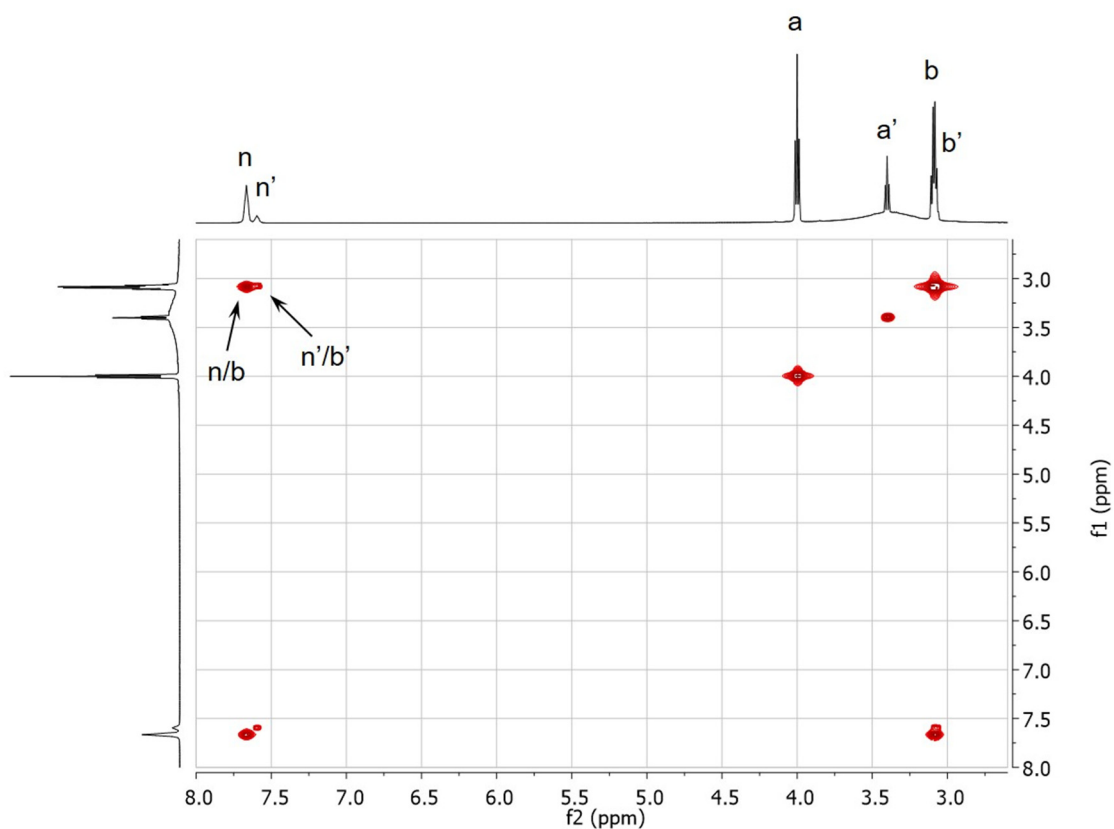


Figure S2. Partial g-COSY spectrum of PEA-Pro in 6d-DMSO at 50°C showing the 8.0 – 2.6 ppm range.

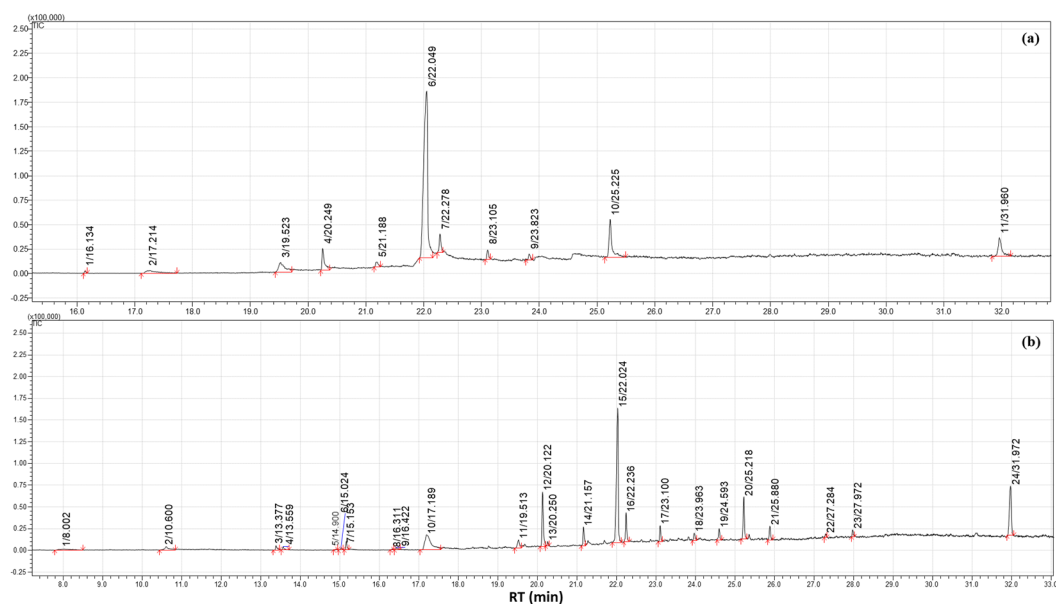
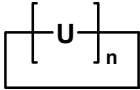


Figure S3. Total ion current (TIC) trace of pyrolysis products of PEA-Pro at (a) 350 °C and (b) 400 °C.

Table S1. Structure assignments of product ions appearing in the MALDI-TOF/TOF-MS/MS spectra of the PEA-Pro sample (precursor ions at m/z 1189.8, 1228.8, 1246.8 and 1303.9).

Structure	n	[M+Na ⁺]	[M+H ⁺]
$\text{HO}-\left[\text{U}\right]_n-\text{CO}(\text{CH}_2)_8\text{COOH}$	4	1189.78	
	3	948.61	
	2	707.44	/
	1	466.27	
	0	225.10	
$\text{H}_2\text{C}=\text{CHCH}_2\text{NH}-\left[\text{U}\right]_n-\text{CO}(\text{CH}_2)_8\text{COOH}$	4	1228.83	
	3	987.66	
	2	746.48	/
	1	505.32	
	0	264.18	
	5	1228.83	
	4	987.66	
	3	746.48	
	2	505.32	
	1	264.18	242.18
$\text{CH}_2=\text{CHCO}-\left[\text{U}\right]_n-\text{OH}$	4	1059.83	
	3	818.50	
	2	577.37	/
$\text{HCO}-\left[\text{U}\right]_n-\text{OCH}=\text{CH}_2$	1	336.21	
	0	95.04	
$\text{CH}_2=\text{CHCH}_2\text{CO}-\left[\text{U}\right]_n-\text{OH}$	3	832.52	
	2	591.35	
	1	350.18	/
$\text{HCO}-\left[\text{U}\right]_n-\text{OCH}_2\text{CH}=\text{CH}_2$	0	109.01	
$\text{CH}_3\text{CO}-\left[\text{U}\right]_n-\text{OCH}=\text{CH}_2$			
$\text{CH}_2=\text{CH}(\text{CH}_2)_2\text{CO}-\left[\text{U}\right]_n-\text{OH}$	3	846.82	
	2	605.63	
	1	364.34	/
$\text{CH}_2=\text{CHCO}-\left[\text{U}\right]_n-\text{OCH}_2\text{CH}_3$	0	123.09	
$\text{CH}_2=\text{CHCH}_2\text{NH}-\left[\text{U}\right]_n-\text{H}$	4	1044.63	1022.62
	3	803.52	781.48
	2	562.38	540.40
	1	321.22	299.23
	0	80.59	58.04
$\text{CH}_2=\text{CH}_2\text{CO}-\left[\text{U}\right]_n-\text{O}(\text{CH}_2)_3\text{NHCO}(\text{CH}_2)_4\text{CH}_3$	2	744.47	
	1	503.30	/
	0	262.13	
$\text{HOCO}(\text{CH}_2)_8\text{CO}-\left[\text{U}\right]_n-\text{NH}_2$	1	465.30	/
	0	224.15	
$\text{HO}-\left[\text{U}\right]_n-\text{H}$	3	1005.68	
	2	764.50	/
	1	523.34	
	0	282.17	
	4	1172.80	
$\text{CH}_2=\text{CH}(\text{CH}_2)_4\text{CO}-\left[\text{U}\right]_n-\text{O}(\text{CH}_2)_3\text{NH}_2$	3	931.74	
	2	690.53	/
	1	449.33	
	0	208.10	
$\text{CH}_2=\text{CH}(\text{CH}_2)_3\text{CO}-\left[\text{U}\right]_n-\text{O}(\text{CH}_2)_3\text{NH}_2$			
$\text{CH}_3(\text{CH}_2)_4\text{CO}-\left[\text{U}\right]_n-\text{NH}(\text{CH}_2)_2\text{CHO}$	3	917.60	
	2	676.49	/
	1	435.32	
$\text{CH}_2=\text{CHCH}_2\text{CO}-\left[\text{U}\right]_n-\text{O}(\text{CH}_2)_3\text{NHCHO}$	0	194.09	

Structure	n	[M+Na ⁺]	[M+H ⁺]
$\text{CH}_2=\text{CHCO}-\left[\text{U}\right]_n-\text{O}(\text{CH}_2)_3\text{NHCOCH}_3$	3	903.59	
$\text{CH}_2=\text{CH}(\text{CH}_2)_2\text{CO}-\left[\text{U}\right]_n-\text{O}(\text{CH}_2)_3\text{NH}_2$	2	662.42	/
	1	421.30	
	0	180.10	
$\text{CH}_2=\text{CHCH}_2\text{CO}-\left[\text{U}\right]_n-\text{O}(\text{CH}_2)_3\text{NH}_2$	3	889.74	/
	2	648.40	
	1	407.29	
$\text{CH}_3(\text{CH}_2)_2\text{CO}-\left[\text{U}\right]_n-\text{NH}(\text{CH}_2)\text{CHO}$	0	166.09	
$\text{CH}_2=\text{CHCO}-\left[\text{U}\right]_n-\text{O}(\text{CH}_2)_3\text{NH}_2$	4	1116.73	/
	3	875.61	
	2	634.49	
$\text{CH}_3(\text{CH}_2)_5\text{CO}-\left[\text{U}\right]_n-\text{NH}_2$	1	393.28	/
	0	152.06	
$\text{HOCO}(\text{CH}_2)_8\text{CO}-\left[\text{U}\right]_n-\text{NH}(\text{CH}_2)_2\text{CHO}$	3	1003.76	
	2	762.51	/
$\text{CH}_3\text{CH}_2\text{O}-\left[\text{U}\right]_n-\text{CO}(\text{CH}_2)_8\text{CONHCH}_2\text{CH}_3$	1	521.36	
	0	280.17	
$\text{CH}_2=\text{CHCH}_2\text{NH}-\left[\text{U}\right]_n-\text{CO}(\text{CH}_2)_8\text{CONHC}$	3	1026.91	/
	2	785.69	
	1	544.36	
	0	303.19	/
$\text{CH}_2=\text{CH}(\text{CH}_2)_4\text{CO}-\left[\text{U}\right]_n-\text{NHCH}_2\text{CH}=\text{CH}_2$	3	913.62	
	2	672.45	
$\text{CH}_2=\text{CH}(\text{CH}_2)_5\text{CO}-\left[\text{U}\right]_n-\text{NHCH}=\text{CH}_2$	1	431.28	/
	0	190.11	
	4	1089.80	
$\text{CH}_2=\text{CHCH}_2\text{CO}-\left[\text{U}\right]_n-\text{NHCH}=\text{CH}_2$	3	857.68	/
	2	616.40	
$\text{CH}_2=\text{CHCO}-\left[\text{U}\right]_n-\text{NHCH}_2\text{CH}=\text{CH}_2$	1	375.27	
	0	134.08	/
	4	1060.79	
$\text{H}-\left[\text{U}\right]_n-\text{NH}(\text{CH}_2)\text{CHO}$	3	819.59	
	2	578.44	/
	1	337.25	
	0	96.47	
$\text{CH}_2=\text{CH}(\text{CH}_2)_6\text{CO}-\left[\text{U}\right]_n-\text{NH}_2$			/
$\text{CH}_3(\text{CH}_2)_5\text{CO}-\left[\text{U}\right]_n-\text{NHCH}=\text{CH}_2$	2	660.54	
	1	419.30	
$\text{CH}_3(\text{CH}_2)_4\text{CO}-\left[\text{U}\right]_n-\text{NHCH}_2\text{CH}=\text{CH}_2$	0	178.11	
$\text{CH}_2=\text{CH}(\text{CH}_2)_2\text{CO}-\left[\text{U}\right]_n-\text{NH}(\text{CH}_2)\text{CHO}$			/
$\text{CH}_2=\text{CH}(\text{CH}_2)_4\text{CO}-\left[\text{U}\right]_n-\text{NH}_2$			
$\text{CH}_2=\text{CHCO}-\left[\text{U}\right]_n-\text{NH}(\text{CH}_2)_2\text{CHO}$	2	632.42	
	1	391.25	/
$\text{CH}_3(\text{CH}_2)_2\text{CO}-\left[\text{U}\right]_n-\text{NHCH}_2\text{CH}=\text{CH}_2$	0	150.08	
$\text{CH}_3(\text{CH}_2)_3\text{CO}-\left[\text{U}\right]_n-\text{NHCH}=\text{CH}_2$			
$\text{CH}_2=\text{CH}(\text{CH}_2)_2\text{CO}-\left[\text{U}\right]_n-\text{NH}_2$	2	604.39	/
	1	363.22	
	0	122.05	

Structure	n	[M+Na ⁺]	[M+H ⁺]
$\text{CH}_3\text{CO}-\left[\text{U}\right]_n-\text{NHCH}_2\text{CH}=\text{CH}_2$			
$\text{CH}_2=\text{CHCH}_2\text{CO}-\left[\text{U}\right]_n-\text{NH}_2$			
$\text{CH}_3\text{CO}-\left[\text{U}\right]_n-\text{NHCH}=\text{CH}_2$	2	590.37	
	1	349.20	/
	0	108.03	
$\text{HCO}-\left[\text{U}\right]_n-\text{NHCH}_2\text{CH}=\text{CH}_2$			
$\text{HCO}(\text{CH}_2)_8\text{CO}-\left[\text{U}\right]_n-\text{NHCH}_2\text{CH}=\text{CH}_2$	2	730.54	
	1	489.38	/
	0	248.16	
$\text{H}_2\text{NCO}(\text{CH}_2)_8\text{CO}-\left[\text{U}\right]_n-\text{NHCH}_2\text{CH}=\text{CH}_2$	2	745.63	
	1	504.33	/
	0	263.19	
	3	989.68	
$\text{HOCO}(\text{CH}_2)_8\text{CO}-\left[\text{U}\right]_n-\text{NH}(\text{CH}_2)_2\text{CH}_3$	2	748.51	/
	1	507.29	
	0	266.16	
$\text{NH}_2\text{CO}(\text{CH}_2)_8\text{CO}-\left[\text{U}\right]_n-\text{O}(\text{CH}_2)_3\text{NH}_2$	3	1004.78	
	2	763.58	/
$\text{CH}_3\text{CH}_2\text{O}-\left[\text{U}\right]_n-\text{CO}(\text{CH}_2)_8\text{COOCH}_2\text{CH}_3$	1	522.39	
	0	281.25	
$\text{CH}_2=\text{CH}(\text{CH}_2)_6\text{CO}-\left[\text{U}\right]_n-\text{OH}$			
	3	902.57	
$\text{CH}_2=\text{CH}(\text{CH}_2)_4\text{CO}-\left[\text{U}\right]_n-\text{OCH}_2\text{CH}_3$	2	661.49	/
	1	420.45	
	0	179.19	
$\text{CH}_3(\text{CH}_2)_4\text{CO}-\left[\text{U}\right]_n-\text{OCH}_2\text{CH}=\text{CH}_2$			
$\text{CH}_2=\text{CH}(\text{CH}_2)_5\text{CO}-\left[\text{U}\right]_n-\text{OH}$			
$\text{CH}_3(\text{CH}_2)_3\text{CO}-\left[\text{U}\right]_n-\text{OCH}_2\text{CH}=\text{CH}_2$	2	647.42	
	1	406.25	/
	0	165.11	
$\text{CH}_3(\text{CH}_2)_4\text{CO}-\left[\text{U}\right]_n-\text{OCH}=\text{CH}_2$			
$\text{CH}_2=\text{CH}(\text{CH}_2)_3\text{CO}-\left[\text{U}\right]_n-\text{NH}_2$	2	618.49	
	1	377.23	/
	0	136.06	
$\text{CH}_2=\text{CH}(\text{CH}_2)_4\text{CO}-\left[\text{U}\right]_n-\text{OH}$			
$\text{CH}_2=\text{CH}(\text{CH}_2)_2\text{CO}-\left[\text{U}\right]_n-\text{OCH}_2\text{CH}_3$	4	1115.74	
	3	874.57	
	2	633.40	/
$\text{CH}_3(\text{CH}_2)_3\text{CO}-\left[\text{U}\right]_n-\text{OCH}=\text{CH}_2$	1	392.23	
	0	151.06	
$\text{CH}_3(\text{CH}_2)_2\text{CO}-\left[\text{U}\right]_n-\text{OCH}_2\text{CH}=\text{CH}_2$			
$\text{CH}_2=\text{CH}(\text{CH}_2)_3\text{CO}-\left[\text{U}\right]_n-\text{OH}$			
$\text{CH}_2=\text{CHCH}_2\text{CO}-\left[\text{U}\right]_n-\text{OCH}_2\text{CH}_3$	2	619.49	
	1	378.26	/
	0	137.07	
$\text{CH}_3(\text{CH}_2)_2\text{CO}-\left[\text{U}\right]_n-\text{OCH}=\text{CH}_2$			

Structure	n	[M+Na ⁺]	[M+H ⁺]
$\text{HOCO}(\text{CH}_2)_8\text{CO}-\left[\text{U}\right]_n-\text{NHCH}=\text{CH}_2$			
$\text{CH}_2=\text{CH}(\text{CH}_2)_6\text{CO}-\left[\text{U}\right]_n-\text{O}(\text{CH}_2)_3\text{NHCO}$	2	772.71	
	1	531.44	/
	0	290.22	
	3	1029.69	
$\text{CH}_2=\text{CH}(\text{CH}_2)_3\text{CO}-\left[\text{U}\right]_n-\text{O}(\text{CH}_2)_3\text{NHCO}$	2	788.52	/
	1	547.35	
	0	306.18	
$\text{CH}_3(\text{CH}_2)_5\text{CO}-\left[\text{U}\right]_n-\text{O}(\text{CH}_2)_3\text{NHCO}(\text{CH}_2)_3\text{NHCO}$	3	1031.11	
$\text{HOCH}=\text{CHCH}_2\text{NH}-\left[\text{U}\right]_n-\text{CO}(\text{CH}_2)_8\text{CO}$	2	790.67	/
	1	549.38	
$\text{HO}(\text{CH}_2)_3\text{NH}-\left[\text{U}\right]_n-\text{CO}(\text{CH}_2)_8\text{COOCH}=\text{CH}_2$	0	308.21	
	3	802.51	
$\text{CH}_2=\text{CHCO}-\left[\text{U}\right]_n-\text{H}$	2	561.34	/
	1	320.17	
	0	79.00	
	3	930.63	
$\text{CH}_2=\text{CH}(\text{CH}_2)_6\text{CO}-\left[\text{U}\right]_n-\text{OCH}_2\text{CH}_3$	2	689.46	/
	1	448.31	
	0	207.14	

* U = -NH(CH₂)₃OCO(CH₂)₈CO- or -O(CH₂)₃NHCO(CH₂)₈CO-.

Table S2. Structure assignment of the degradation products derived from the pyrolysis of the PEA-pro at 350 and 400 °C.

RT (min)	Possible structure (Mol Wt)	Ion EI ^a (m/z)	A% ^b 350 °C	A% ^b 400 °C
8.002	CH ₃ (CH ₂) ₄ COOH* (116)	73	/	1.31
10.600	CH ₃ (CH ₂) ₇ COOH* (158)	129	/	1.99
13.377	CH ₃ (CH ₂) ₄ CONHCH ₂ CH=CH ₂ * (155)	140	/	0.96
13.559	CH ₃ (CH ₂) ₅ CONHCH ₂ CH=CH ₂ * (169)	126	/	0.63
14.900	unidentified	99	/	0.07
15.024	CH ₃ (CH ₂) ₆ CONHCH ₂ CH=CH ₂ (183)	112	/	0.43
15.154	unidentified	168	/	1.33
16.134	unidentified	177	0.28	/
16.311	unidentified	112	/	0.15
16.422	unidentified	112	/	0.45
17.214/ 17.189	HOCO(CH ₂) ₈ COOH (202)	138	2.96	12.15
19.522/ 19.513	NC(CH ₂) ₈ CN (164)	164	5.92	2.54
20.122	NC(CH ₂) ₈ CONHCH ₂ CH=CH ₂ (222)	221	/	9.69
20.249	CH ₃ (CH ₂) ₆ CONHCH ₂ CH=CH ₂ (183)	183	5.30	0.55
21.188/ 21.158	NC(CH ₂) ₈ CONHCH=CH ₂ (208)	207	1.28	3.43

RT (min)	Possible structure (Mol Wt)	Ion EI ^a (<i>m/z</i>)	A% ^b 350 °C	A% ^b 400 °C
22.049/ 22.024	$\left[\text{U} \right]_n$ or HOCO(CH ₂) ₈ CONHCH ₂ CH=CH ₂ (241)	241	61.83	30.49
22.278/ 22.236	$\left[\text{U} \right]_n$ or HOCO(CH ₂) ₈ CONHCH ₂ CH=CH ₂ (241)	241	3.22	4.76
23.100	CH ₂ =CHCH ₂ OCO(CH ₂) ₈ CONHCH ₂ CH=CH ₂ (281)	281	/	2.43
23.104	unidentified	182	1.52	/
23.822	CH ₃ CH ₂ OCO(CH ₂) ₈ CONHCH ₂ CH=CH ₂ (269)	269	0.91	/
23.963	unidentified	281	/	1.61
24.593	CH ₂ =CHCH ₂ NHCO(CH ₂) ₈ CONH(CH ₂) ₃ OH (298)	281	/	2.03
25.225/ 25.218	CH ₃ (CH ₂) ₂ NH(CH ₂) ₃ OCO(CH ₂) ₈ CN (282) or CH ₂ =CHCH ₂ OCO(CH ₂) ₈ CONHCH ₂ CH=CH ₂ or CH ₂ =CHCH ₂ COO(CH ₂) ₃ NHCO(CH ₂) ₆ CH=CH ₂ (281)	265	10.47	6.73
25.880	CH ₃ (CH ₂) ₂ O(CH ₂) ₃ NHCO(CH ₂) ₈ CN (282)	281	/	2.36
27.284	unidentified	429	/	0.59
27.972	unidentified	429	/	1.05
31.960	unidentified	429	6.31	/
31.972	unidentified	429	/	12.27

a: Molecular ion or major fragment; b: Area %.