

Aliphatic amines from waste polyolefins by tandem pyrolysis, hydroformylation, and reductive amination

Houqian Li,¹ Amy C. Cuthbertson,² Ahmad Amer Alamer,¹ Victor S. Cecon,³ Harish Radhakrishnan,⁴ Jiayang Wu,¹ Greg W. Curtzwiler,³ Keith L. Vorst,³ Xianglan Bai,⁴ Clark R. Landis,⁵ Gregg T. Beckham,² George W. Huber^{1,*}

¹ Department of Chemical and Biological Engineering, University of Wisconsin-Madison; Madison, WI 53706, USA

² Renewable Resources and Enabling Sciences Center, National Renewable Energy Laboratory, Golden, CO 80401, USA

³ Polymer and Food Protection Consortium, Department of Food Science and Human Nutrition, Iowa State University, Ames, IA 50011, USA

⁴ Department of Mechanical Engineering, Iowa State University, Ames, IA 50011, USA

⁵ Department of Chemistry, University of Wisconsin-Madison; Madison, WI 53706, USA

*Corresponding author: gwhuber@wisc.edu

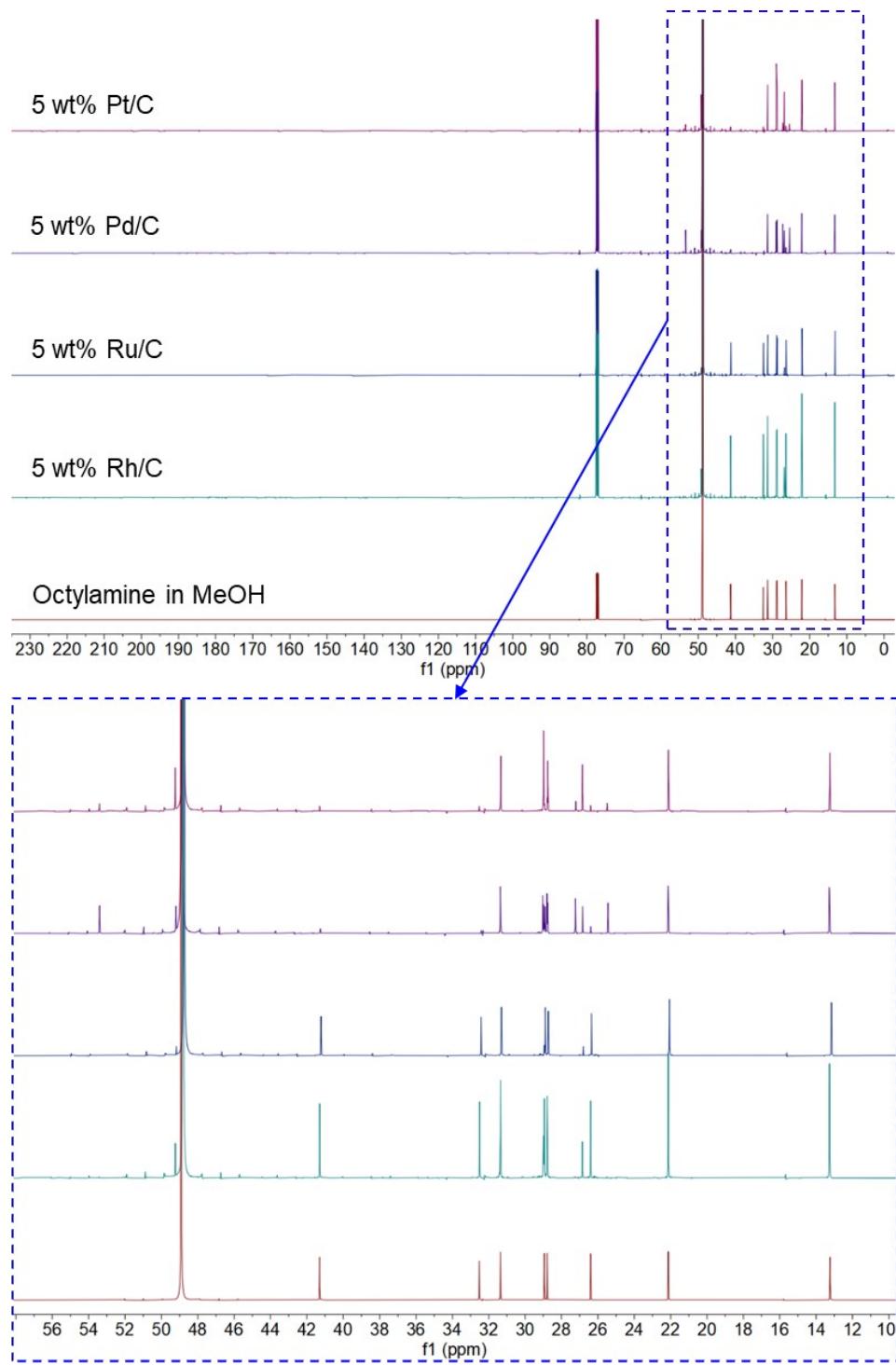


Figure S1. Quantitative ^{13}C NMR spectra were obtained for octanal reductive amination after complete conversion over Pt/C, Pd/C, Rh/C, and Ru/C (all 5 wt% metal). The spectrum of octylamine is included as a reference.

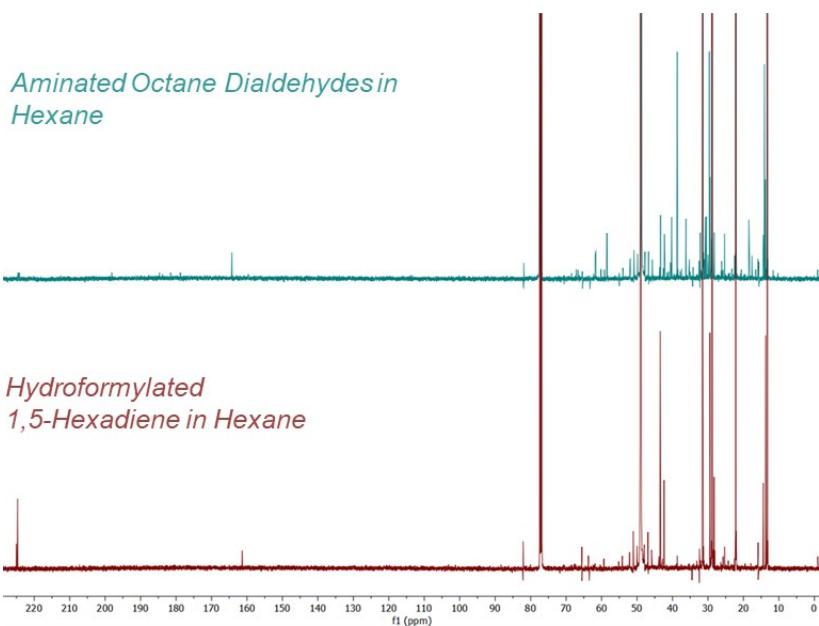
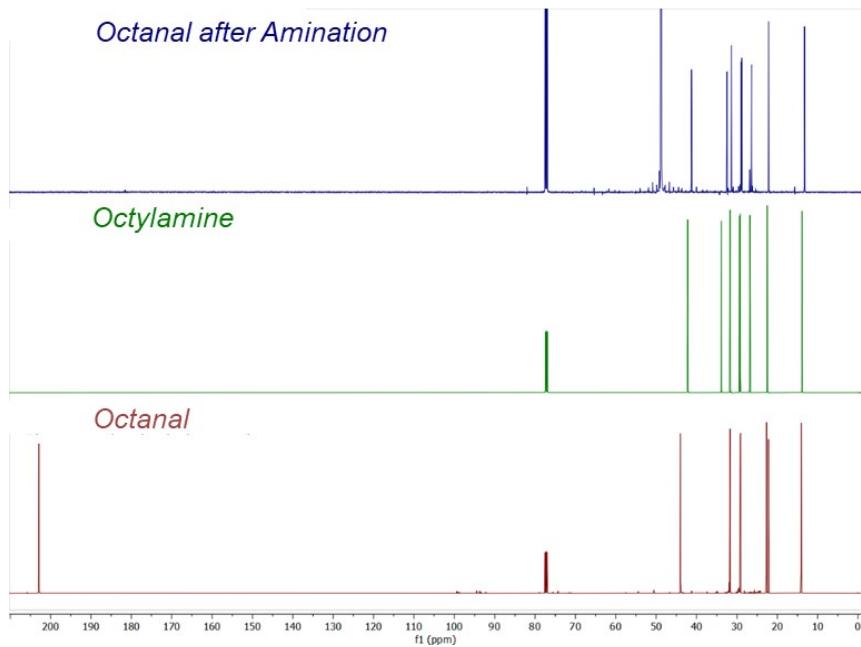


Figure S2. Quantitative ¹³C NMR spectra of model compounds animation catalyzed by 5 wt% Ru/C. Reaction conditions: Batch Reactor, 90 °C, 800 rpm, 40 Bar H₂, 150 min reaction time, 0.43 mol/L aldehydes in 7N NH₃/MeOH solution. Ru/Aldehydes=1/50 (molar ratio). The peak at 50 ppm in “Octanal after Amination” spectrum was resulted from methanol as a solvent in reductive amination.

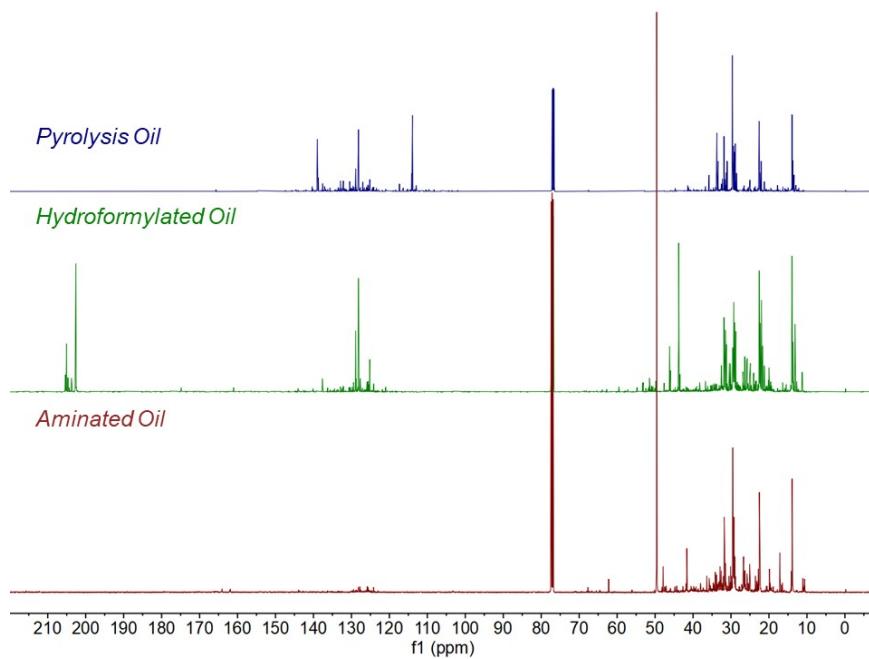


Figure S3. Complete quantitative ^{13}C NMR spectra of pyrolysis oil (A), hydroformylated pyrolysis oil (B), and aminated oil (C). The peaks belonging to aromatic species decreased in the aminated oil, likely as a result of rotary evaporation after the amination reaction.

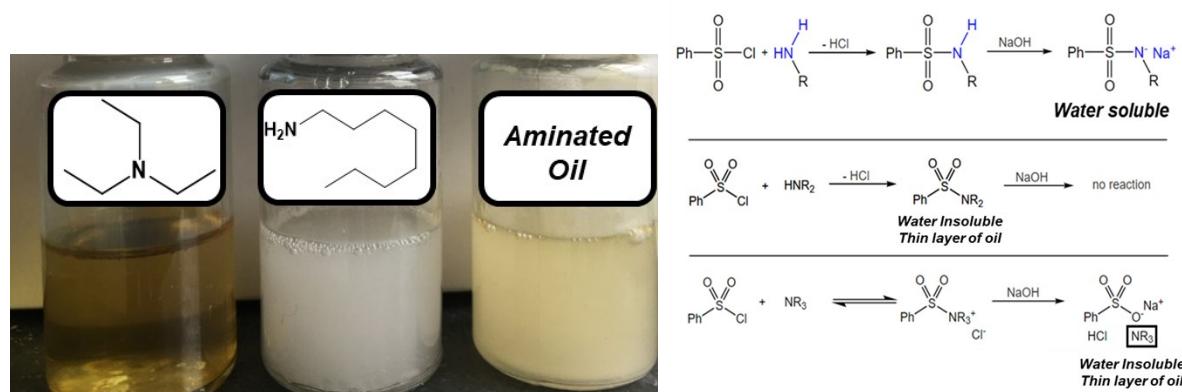
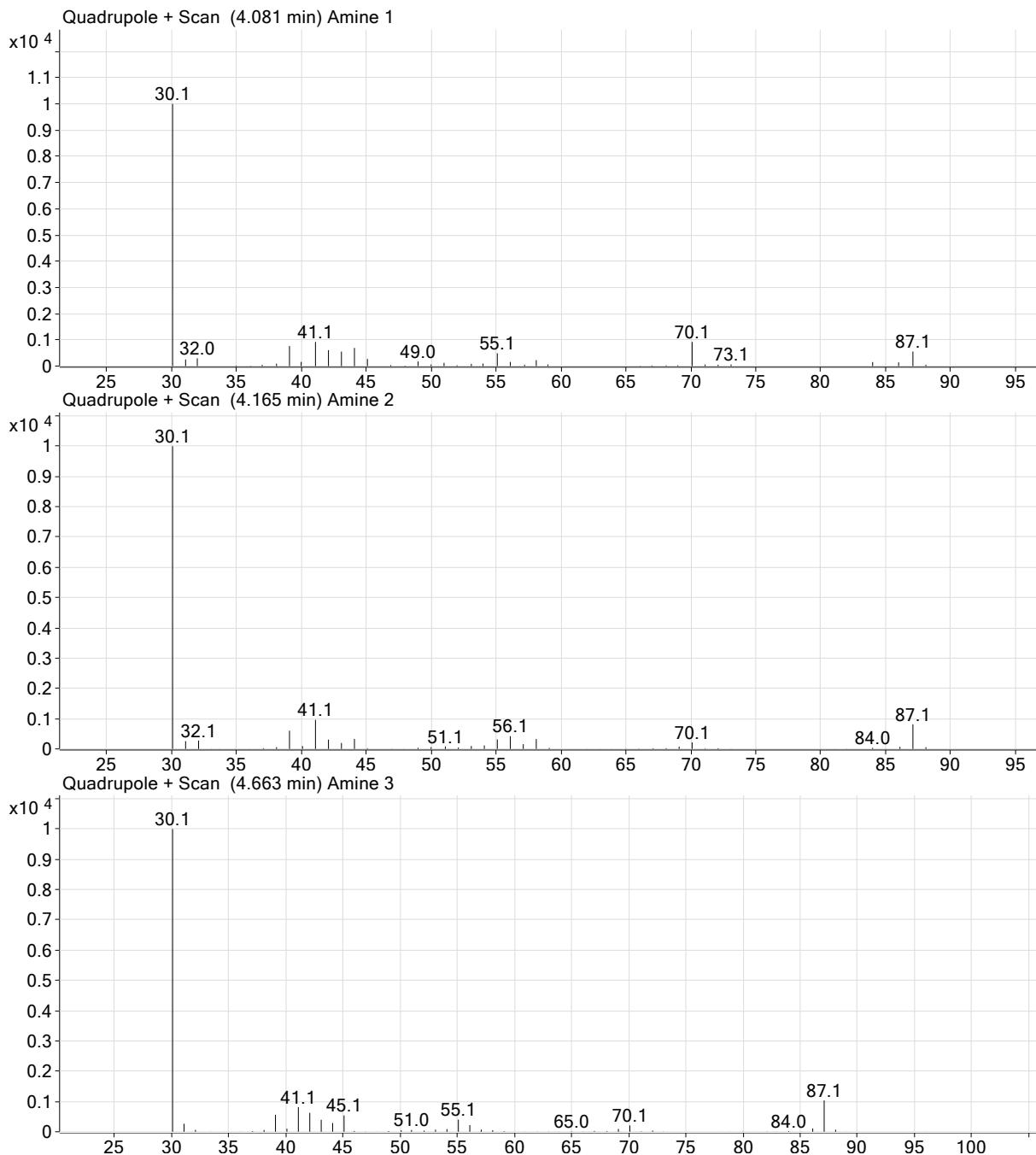
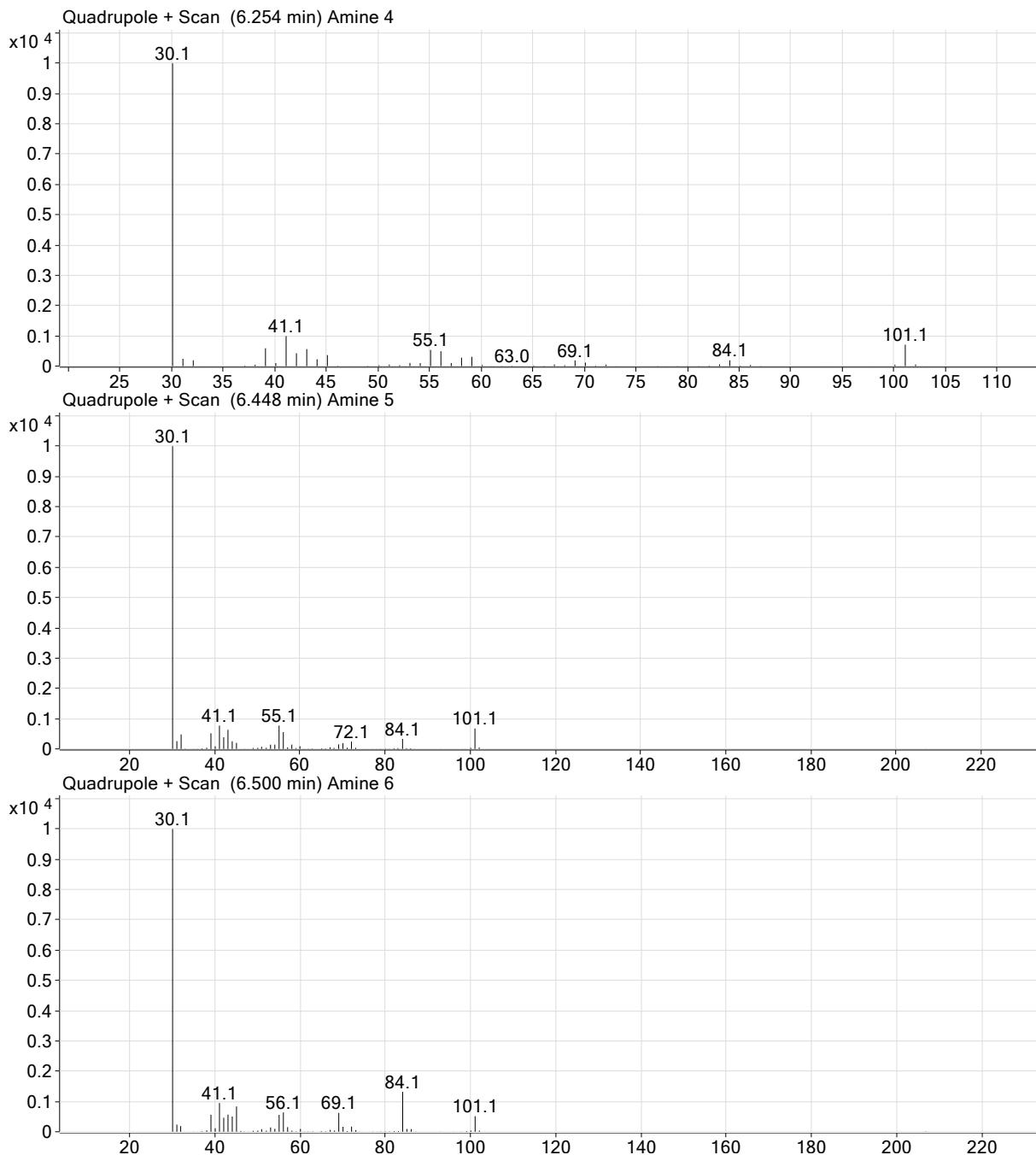
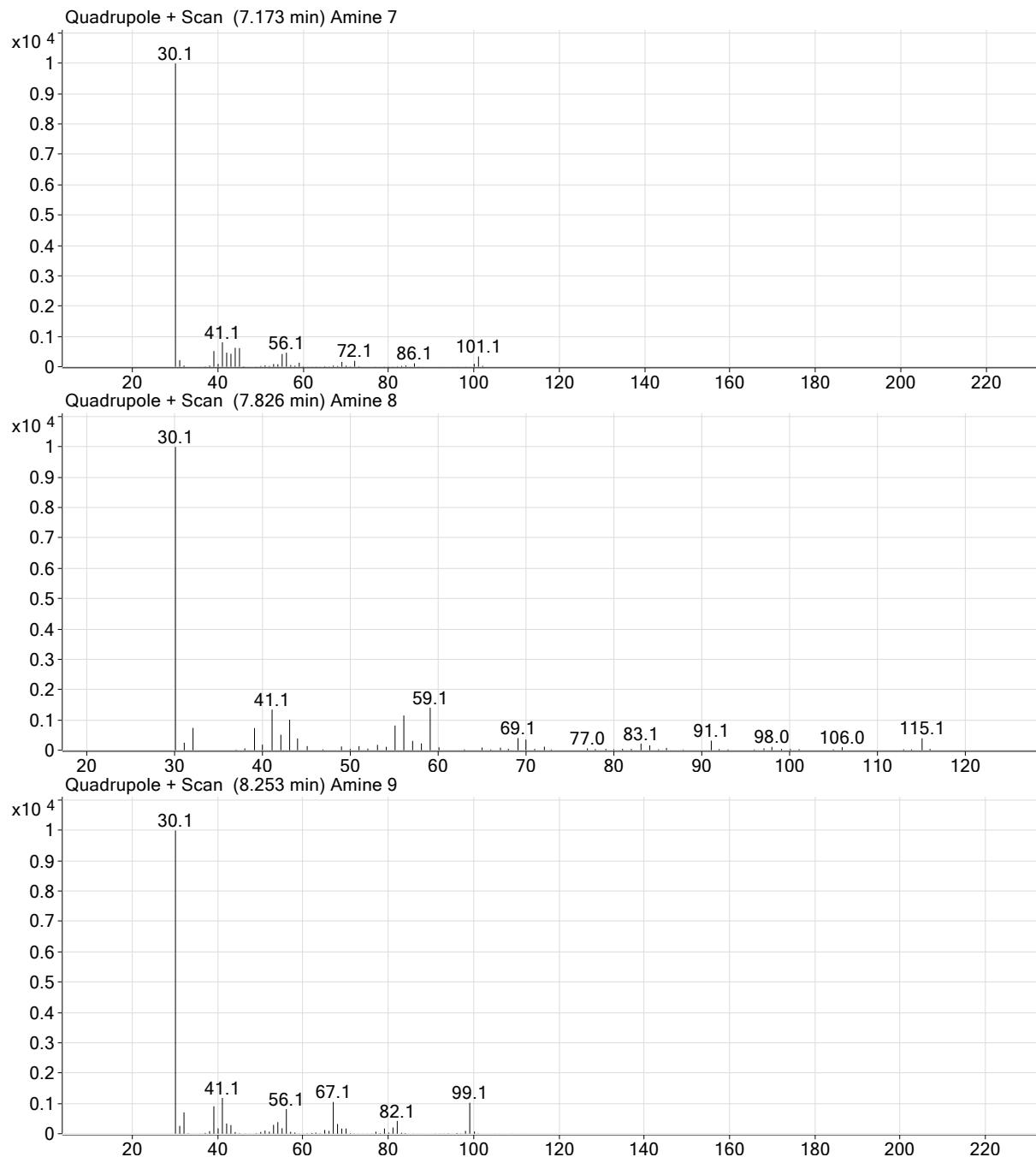
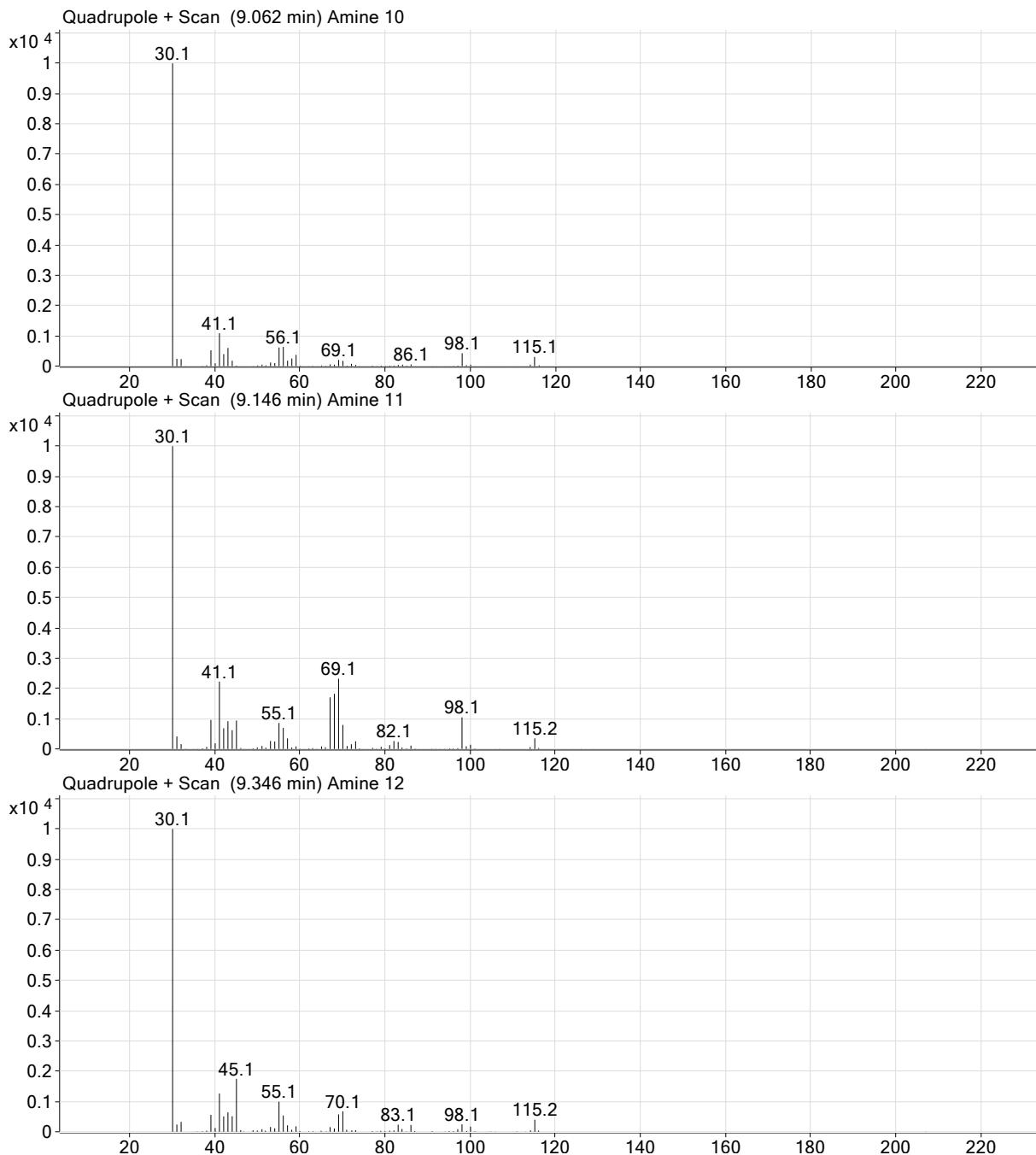


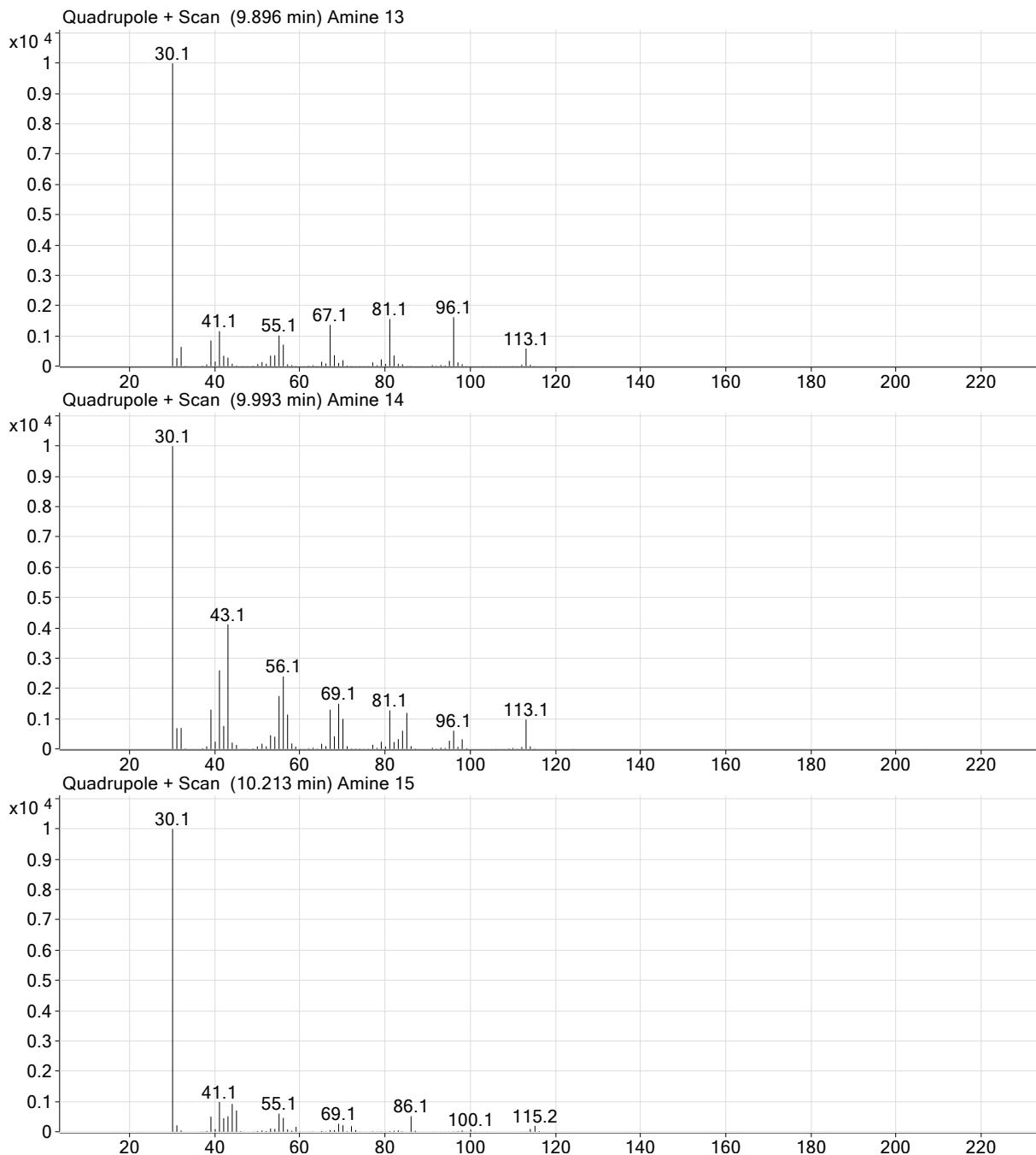
Figure S4. Hinsberg Test of tertiary amine, primary amine and the aminated oil.

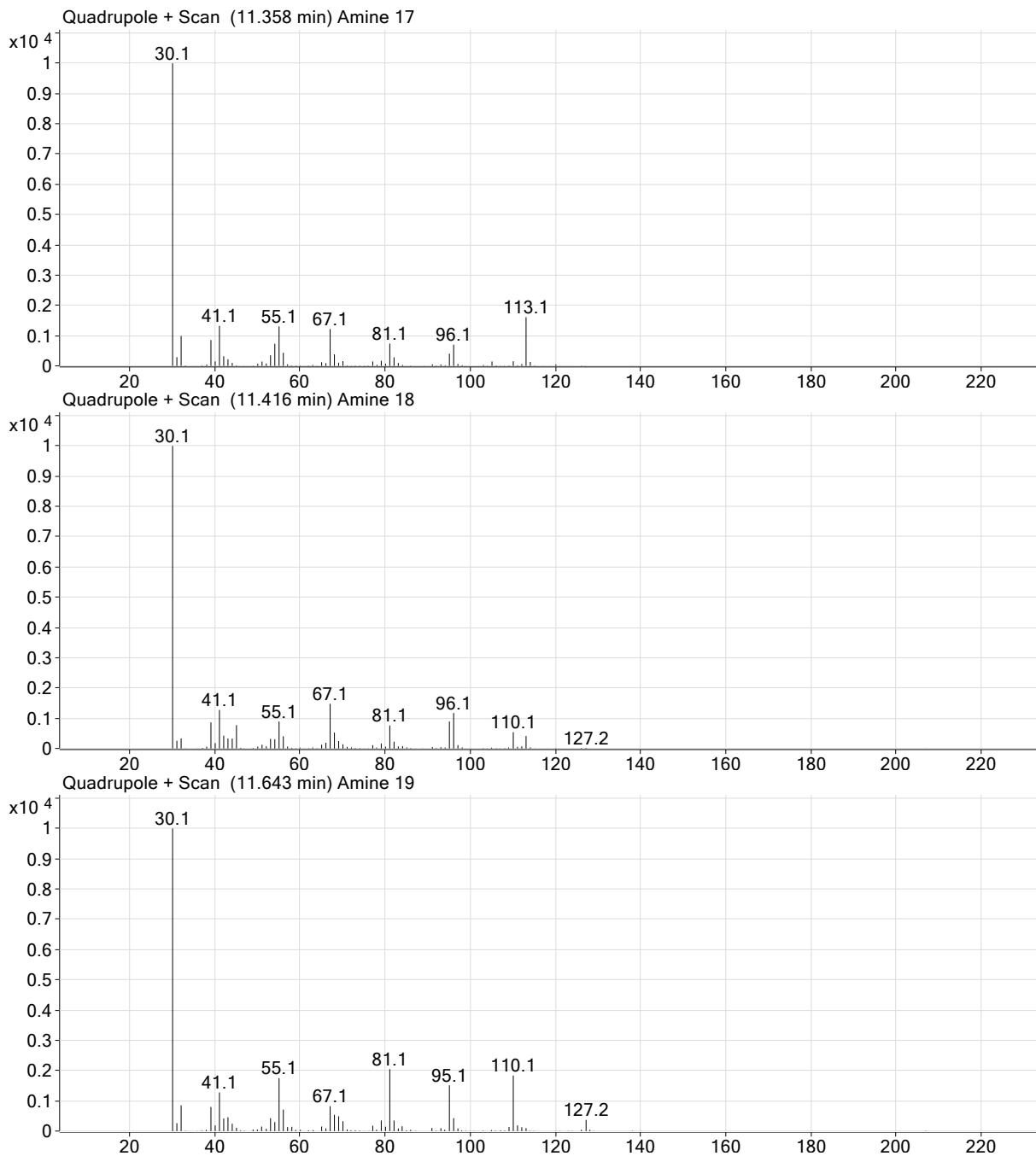


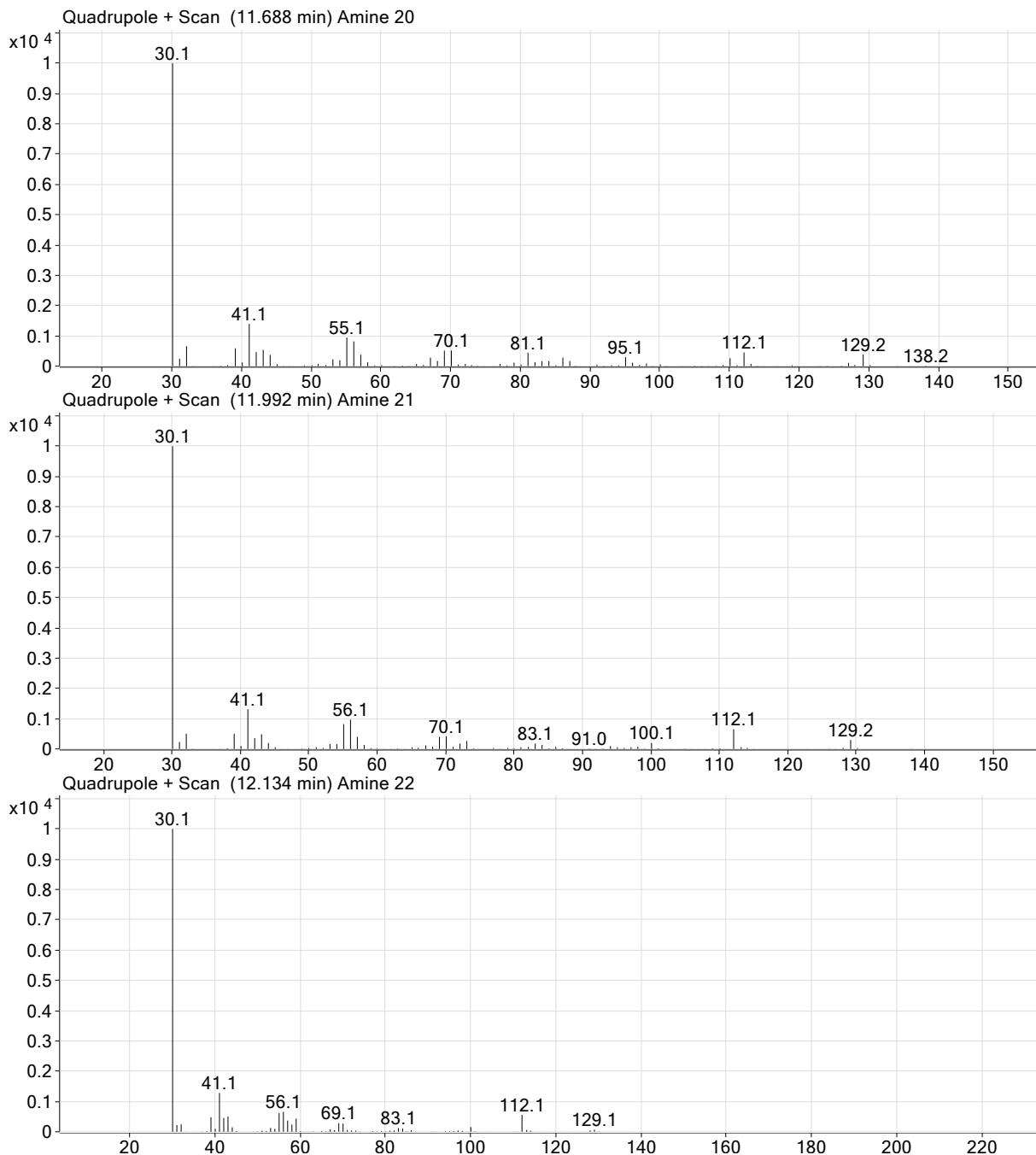


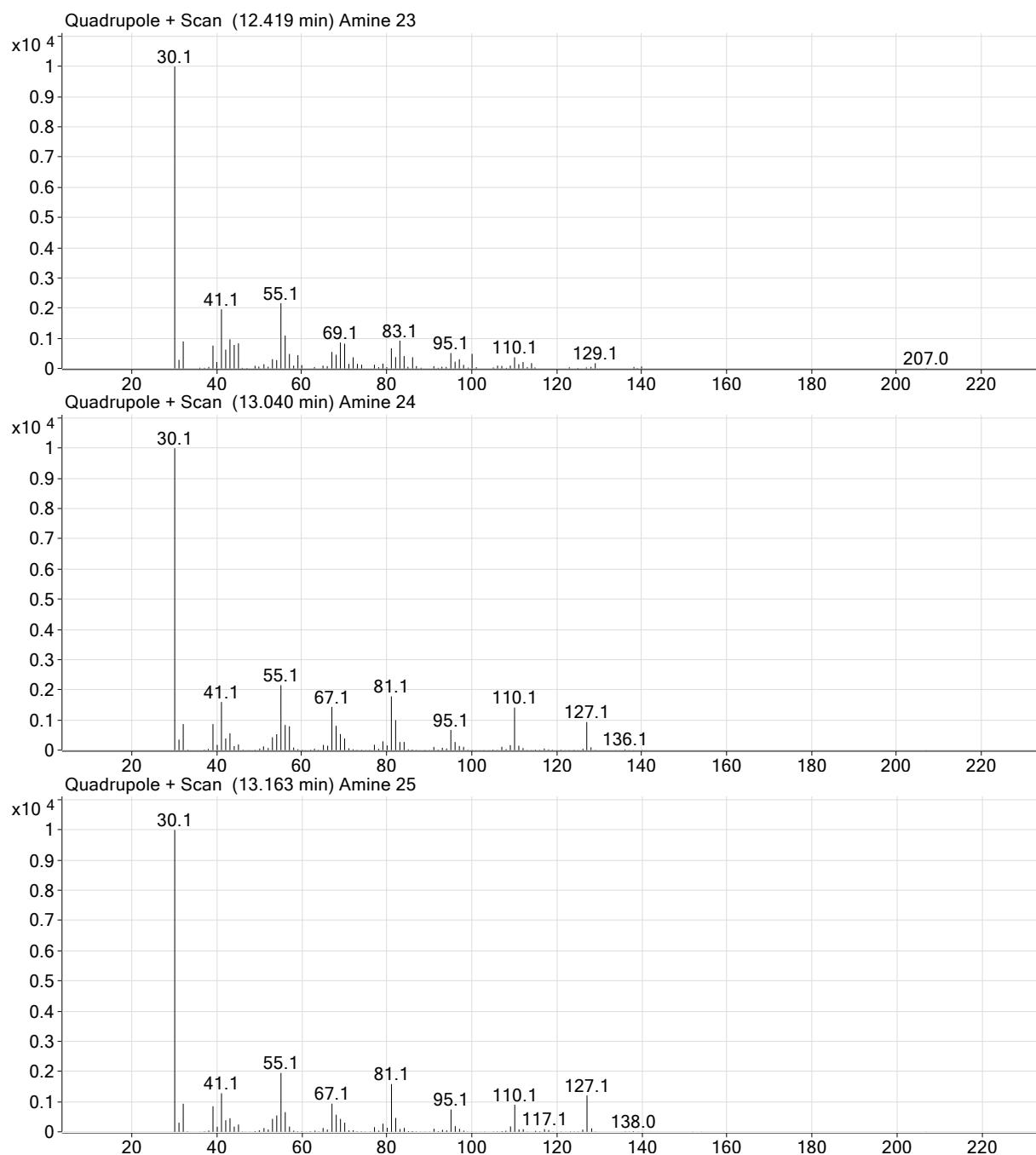


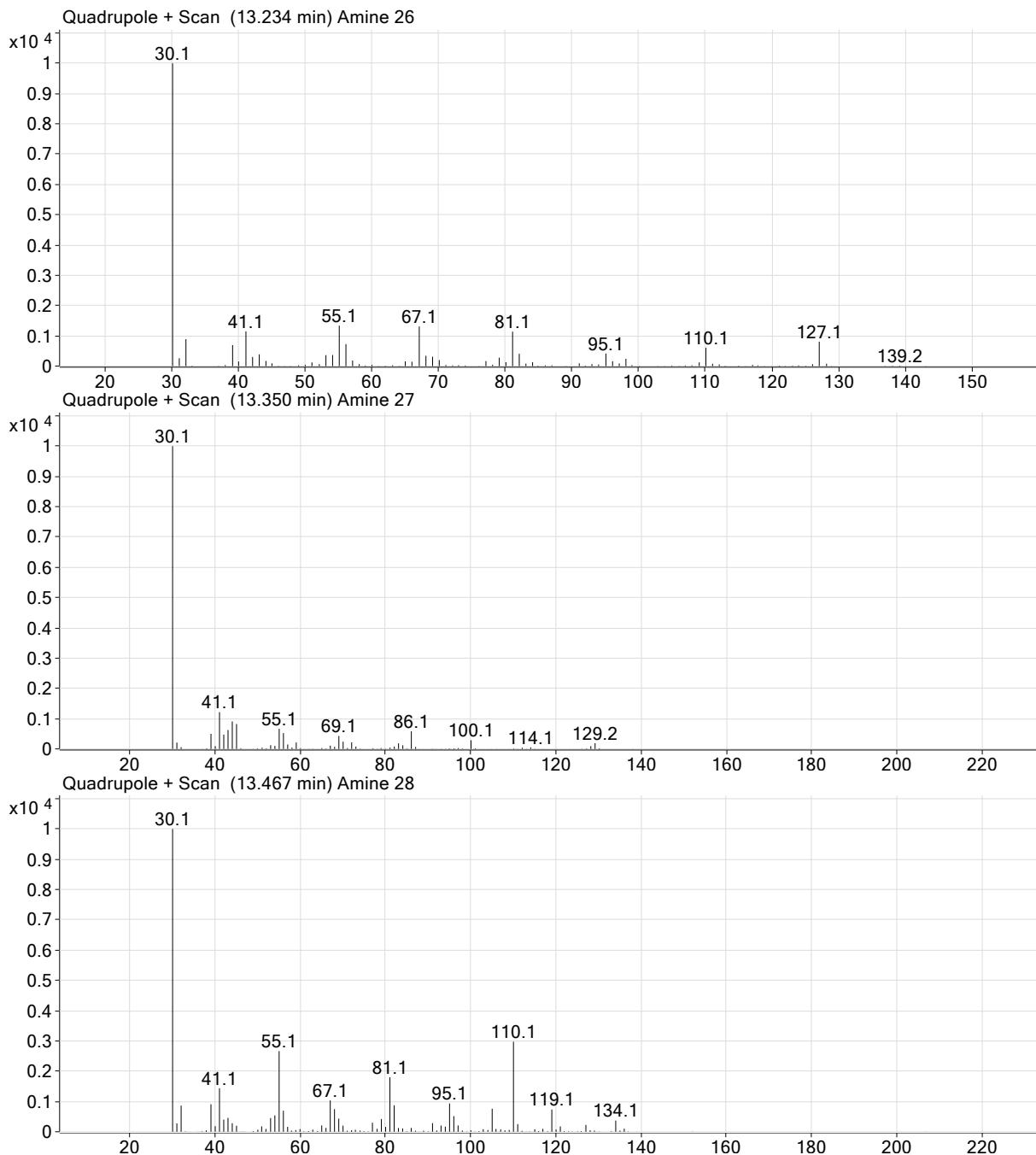


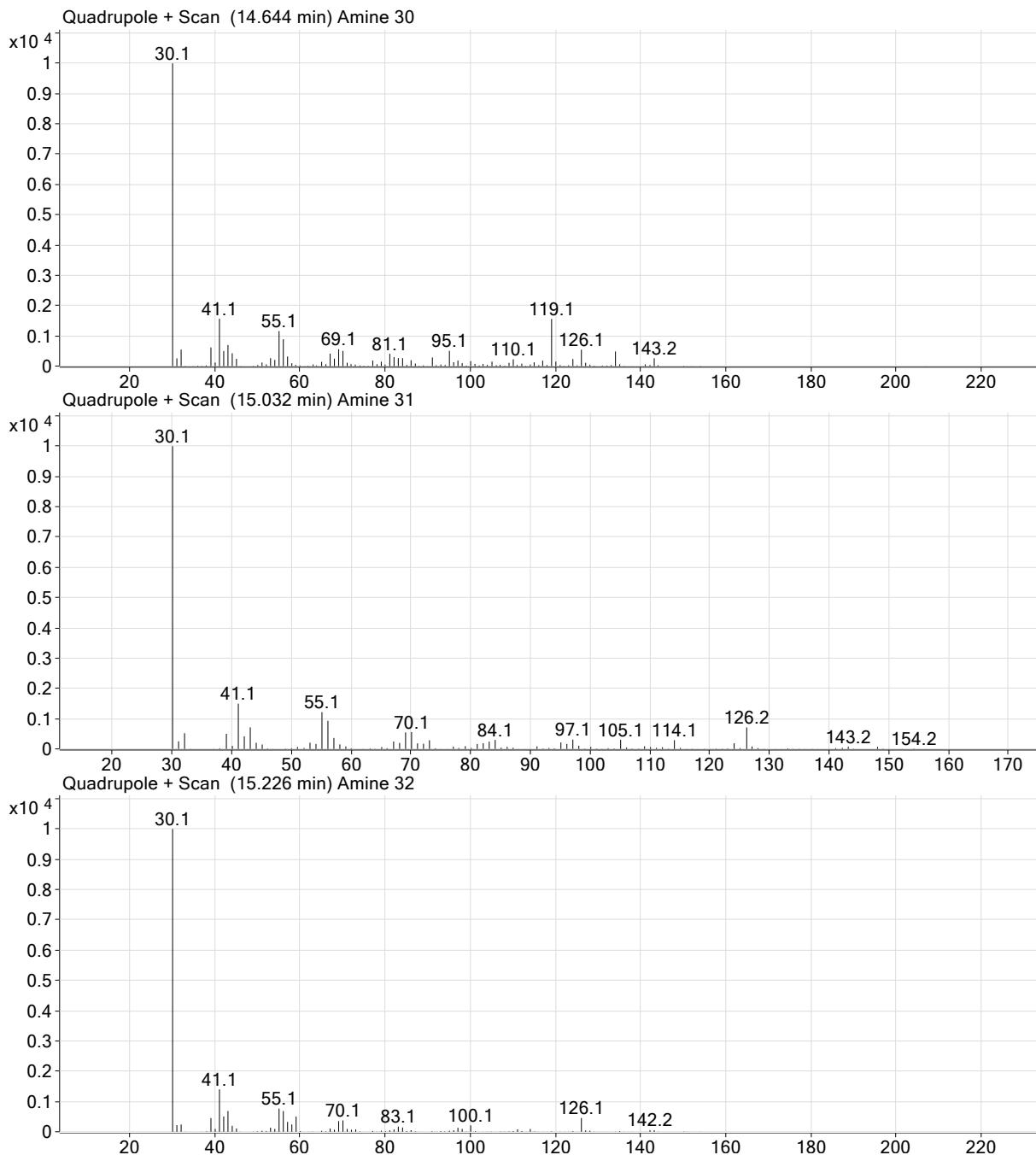


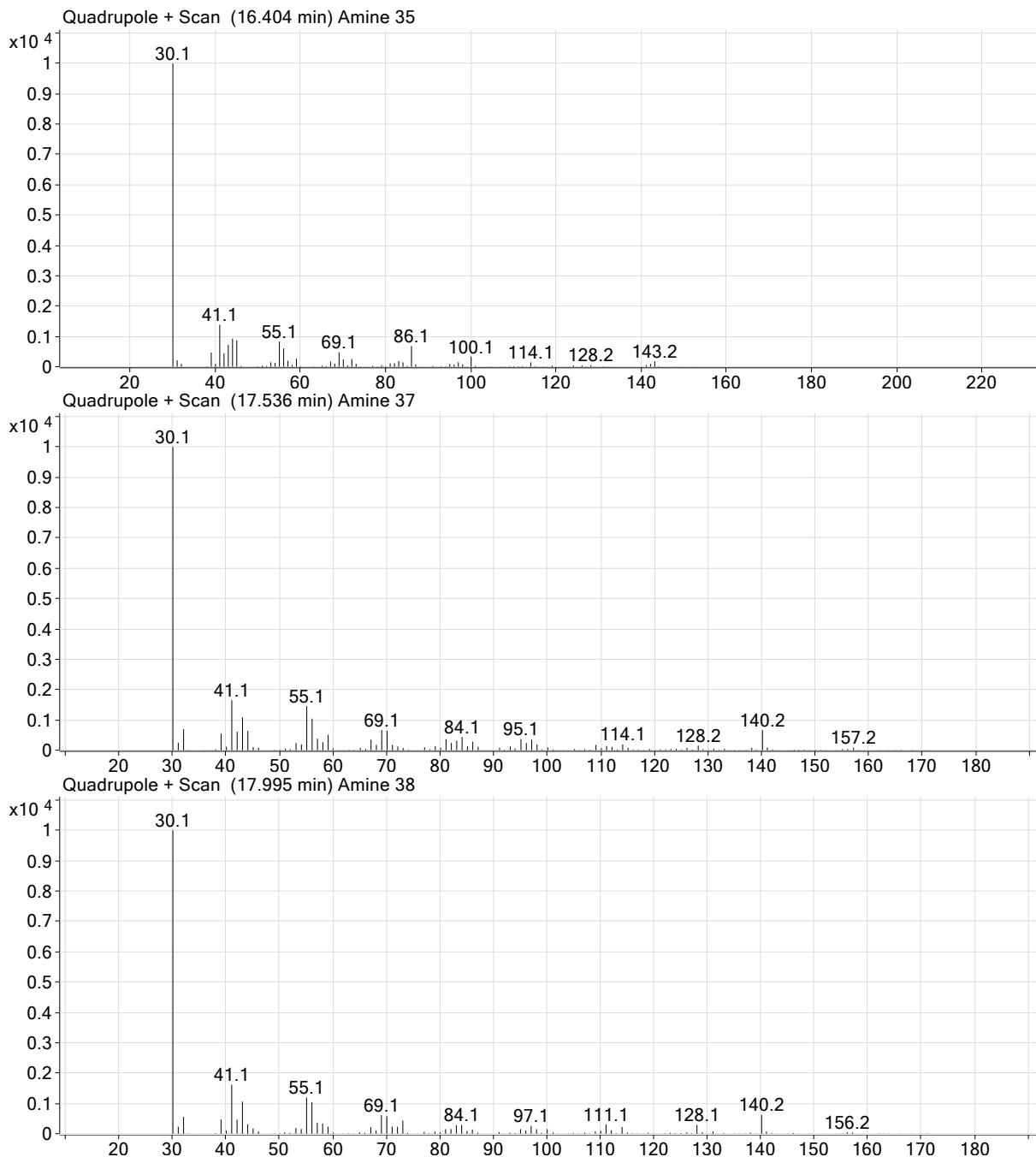


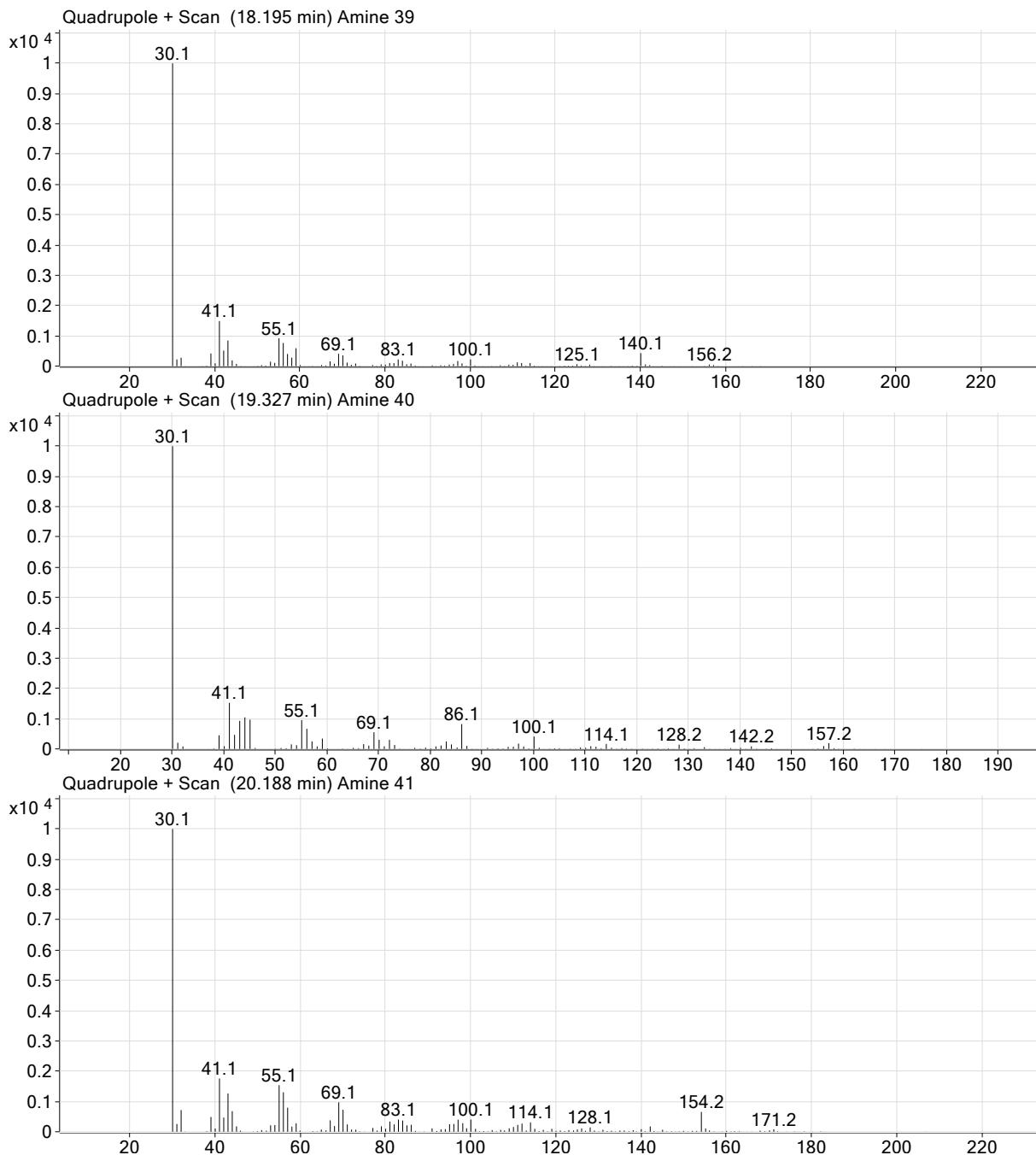


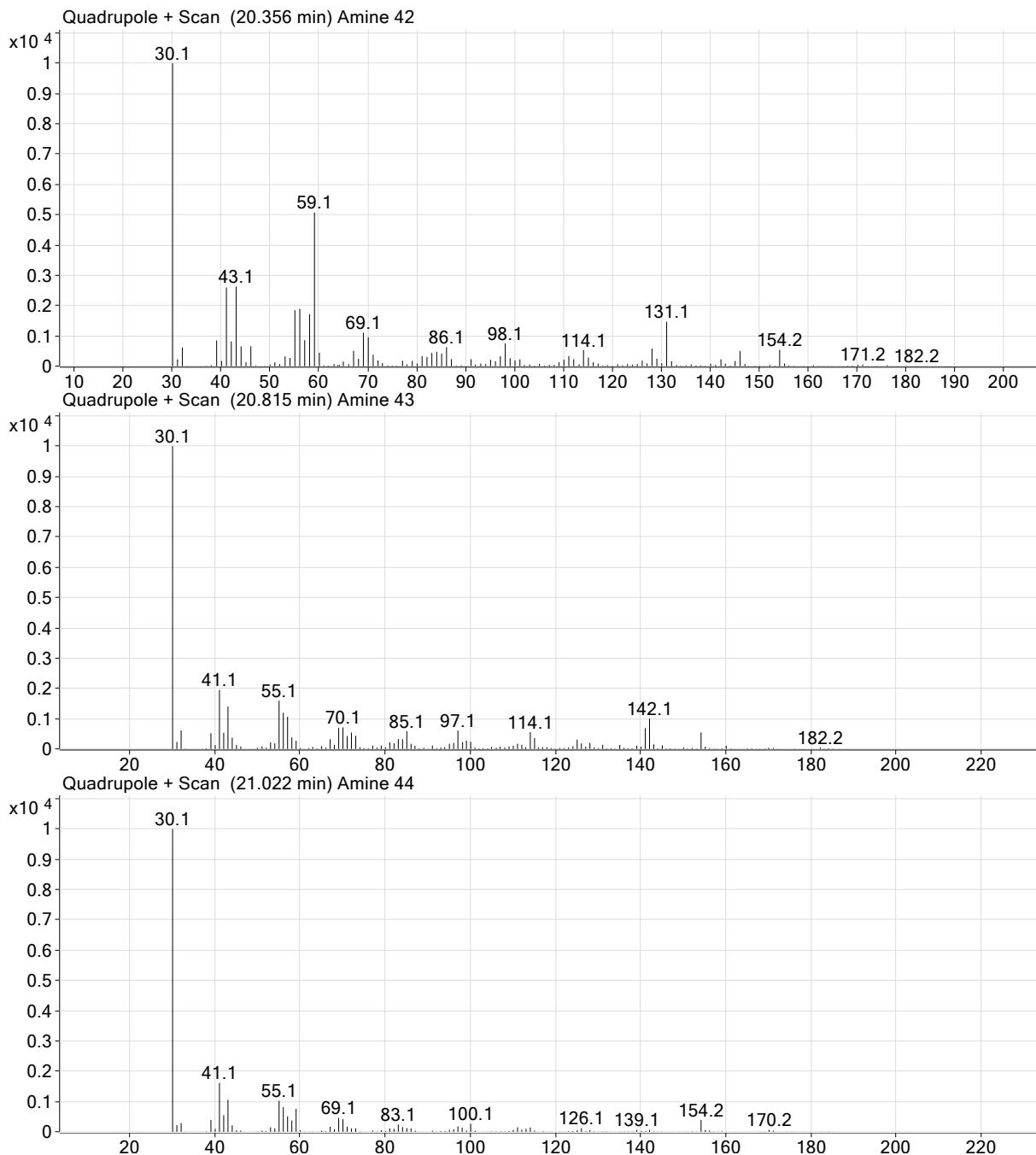


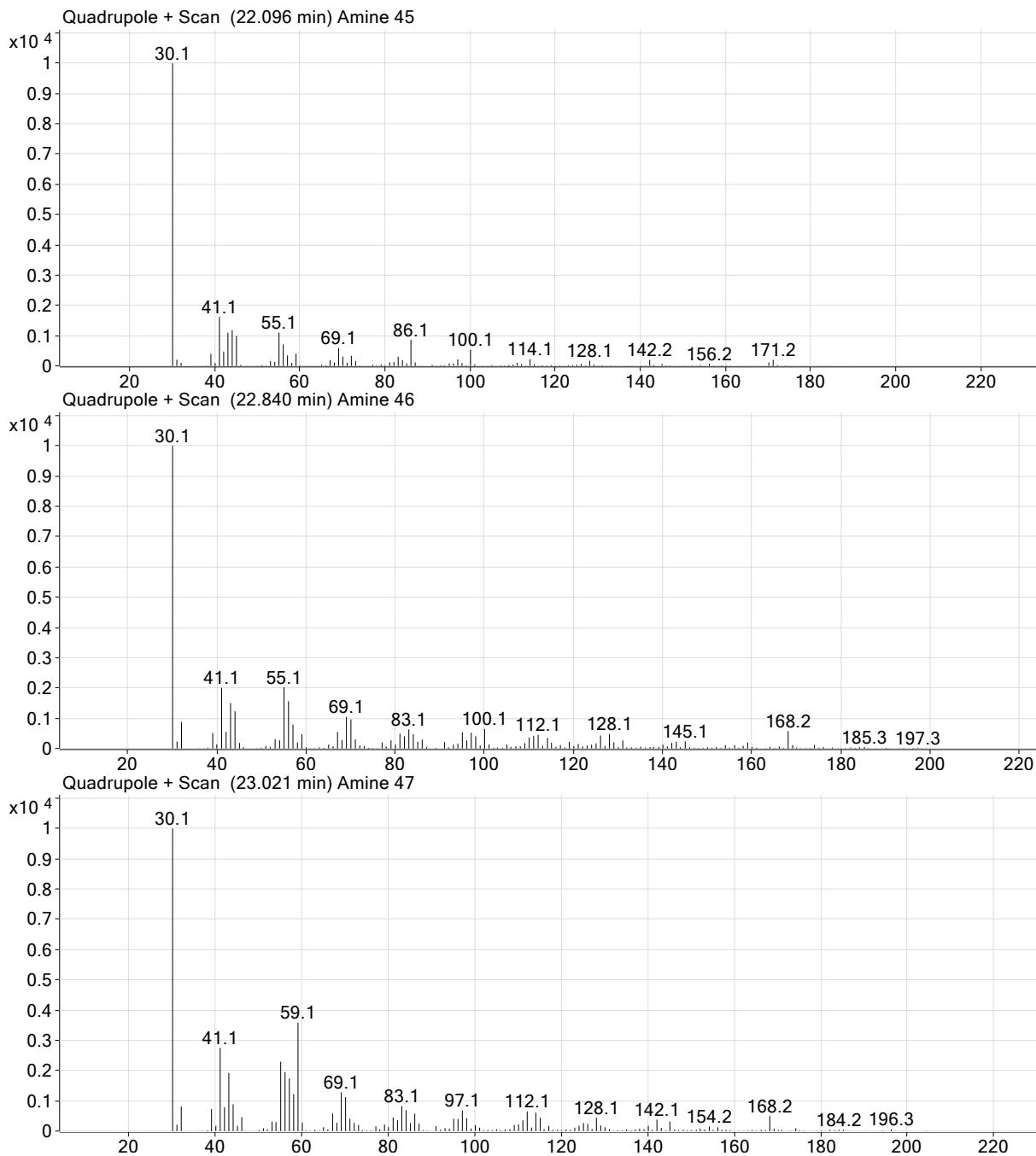


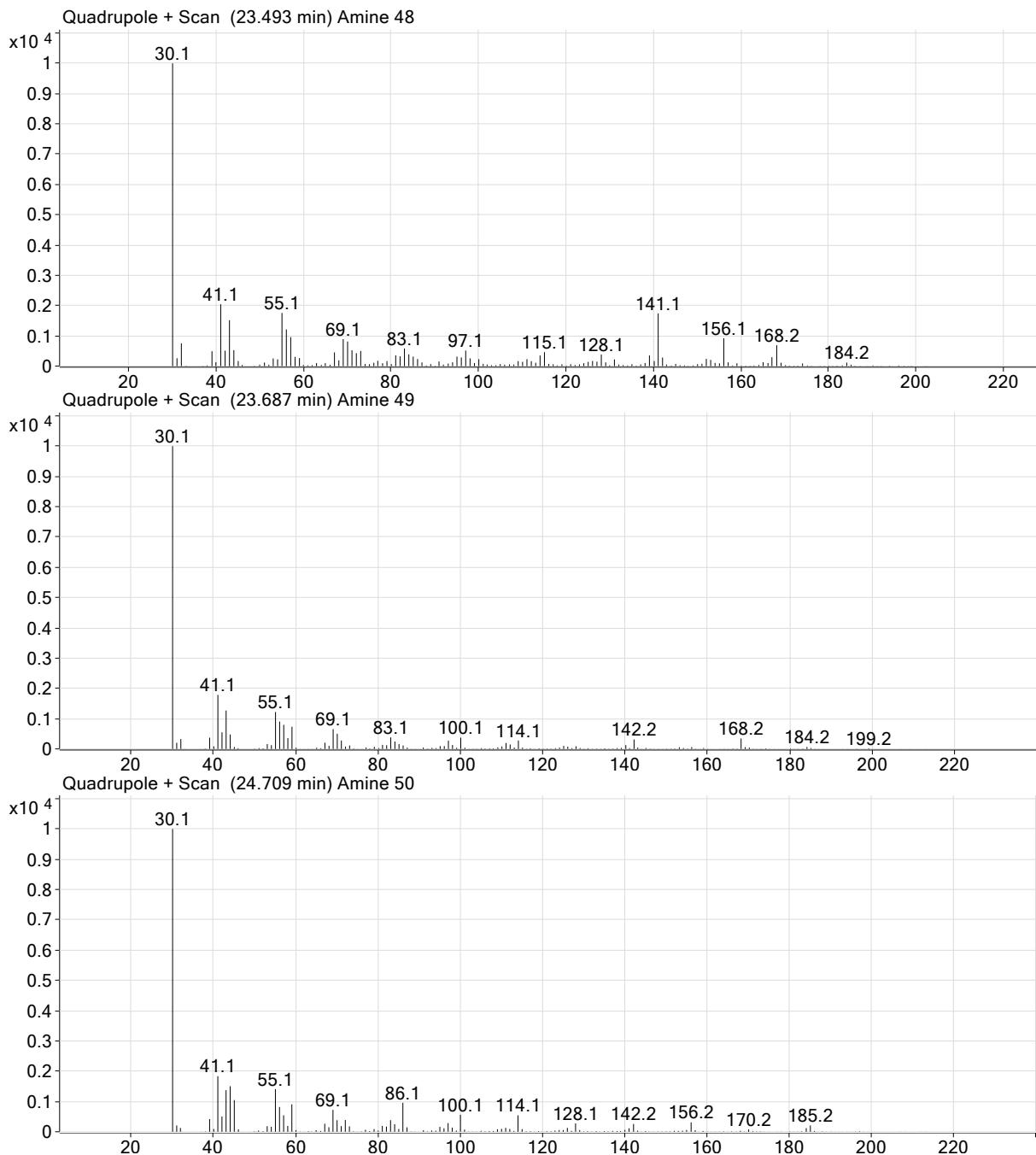


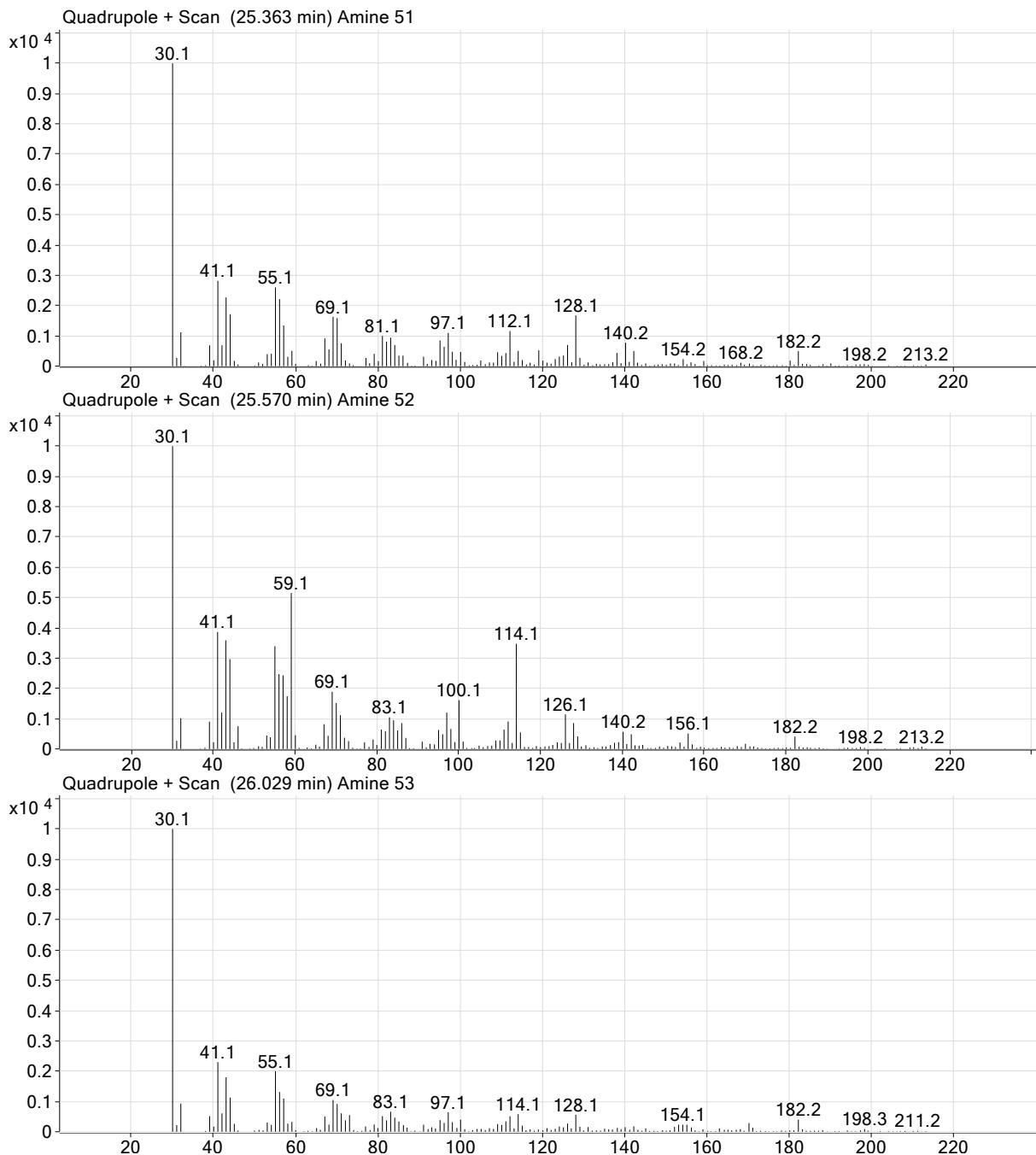


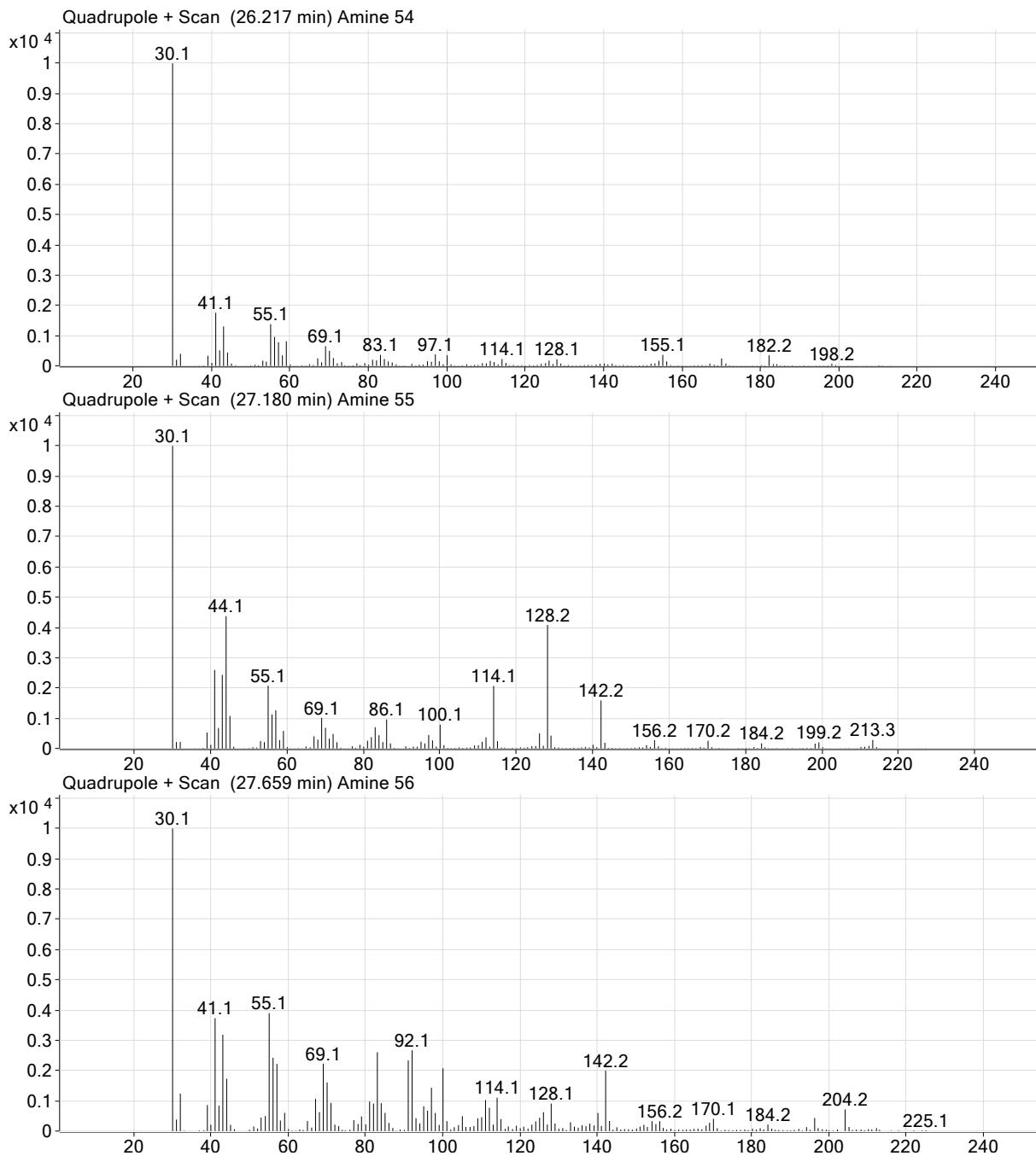


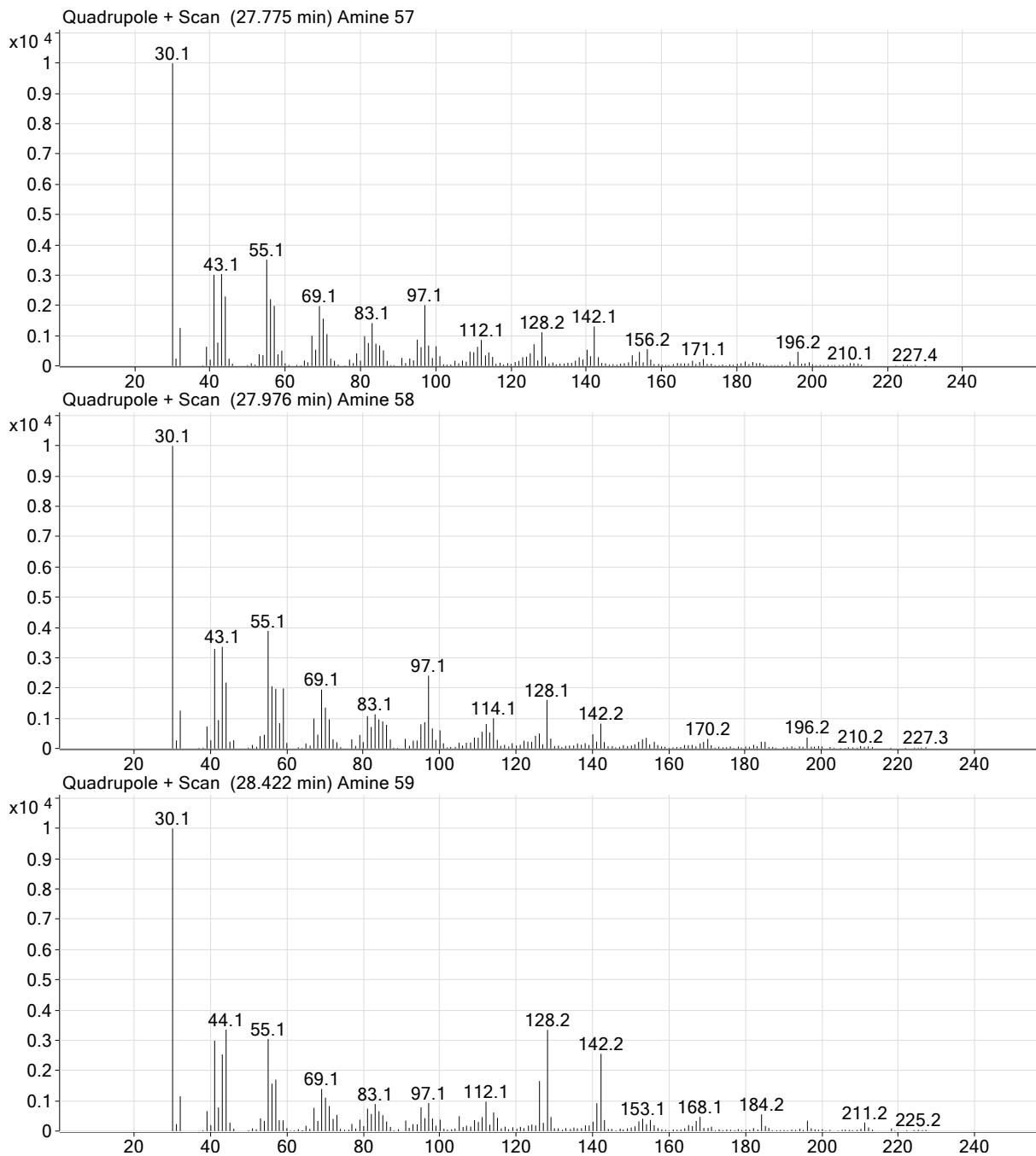


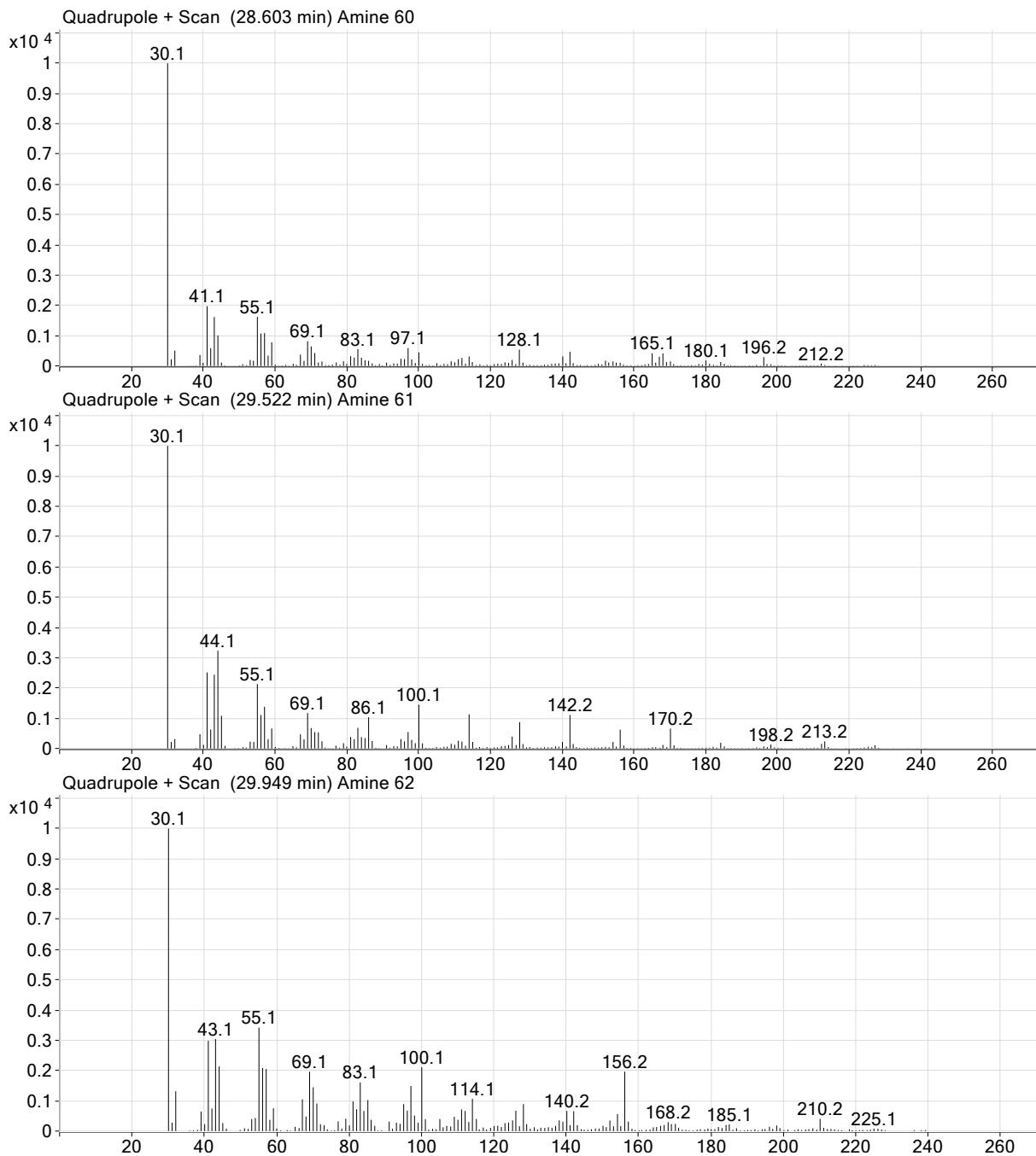


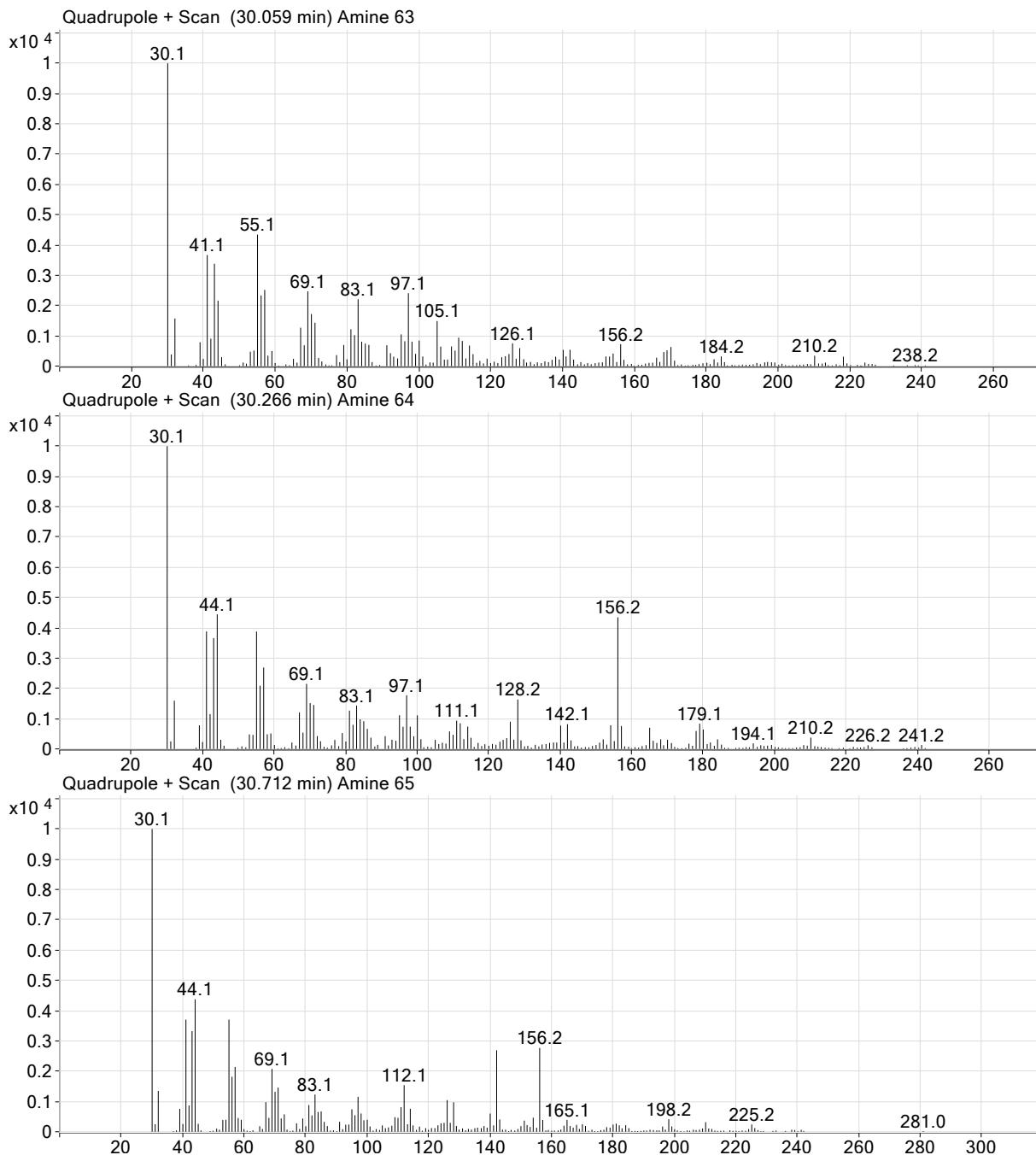


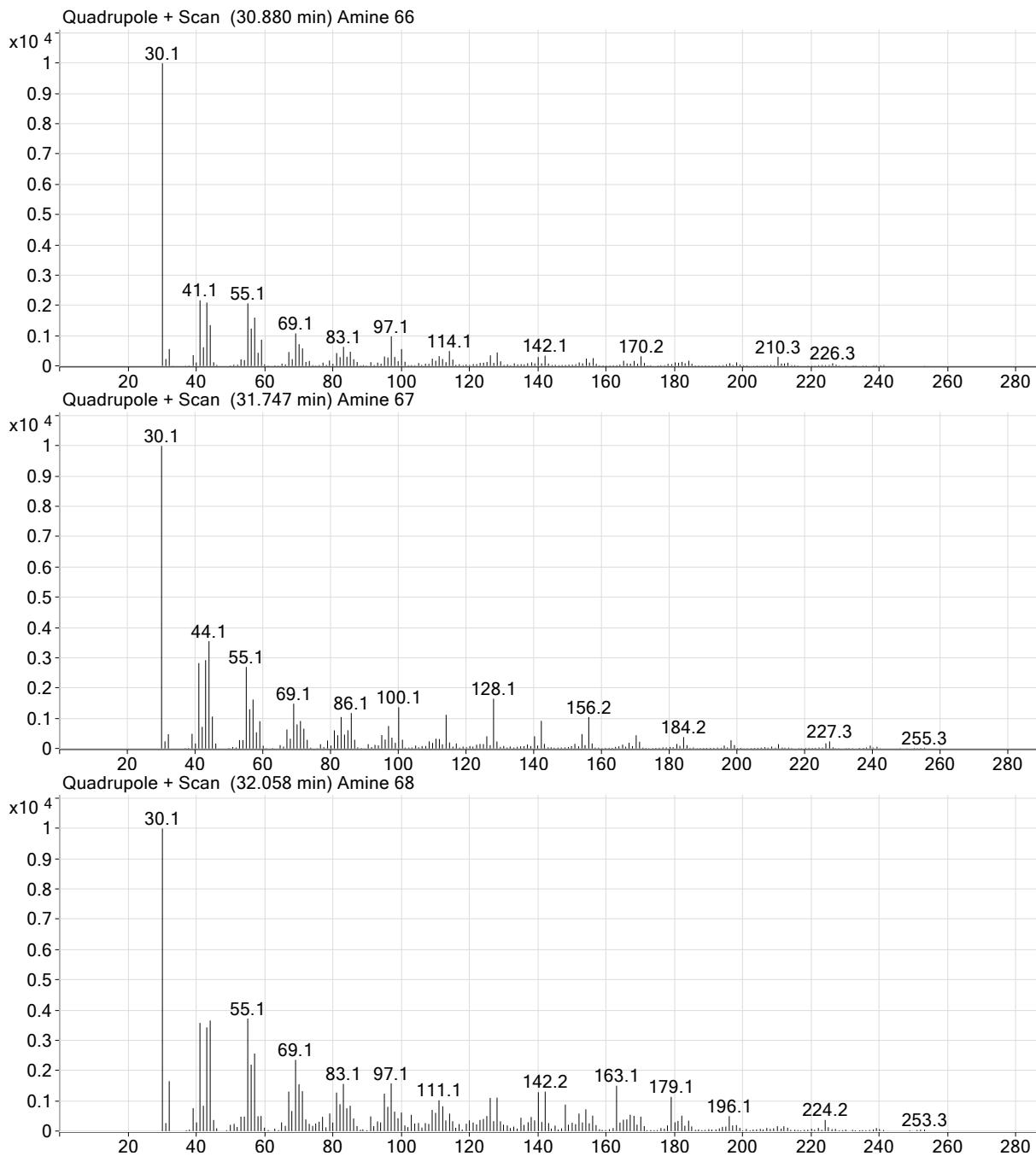


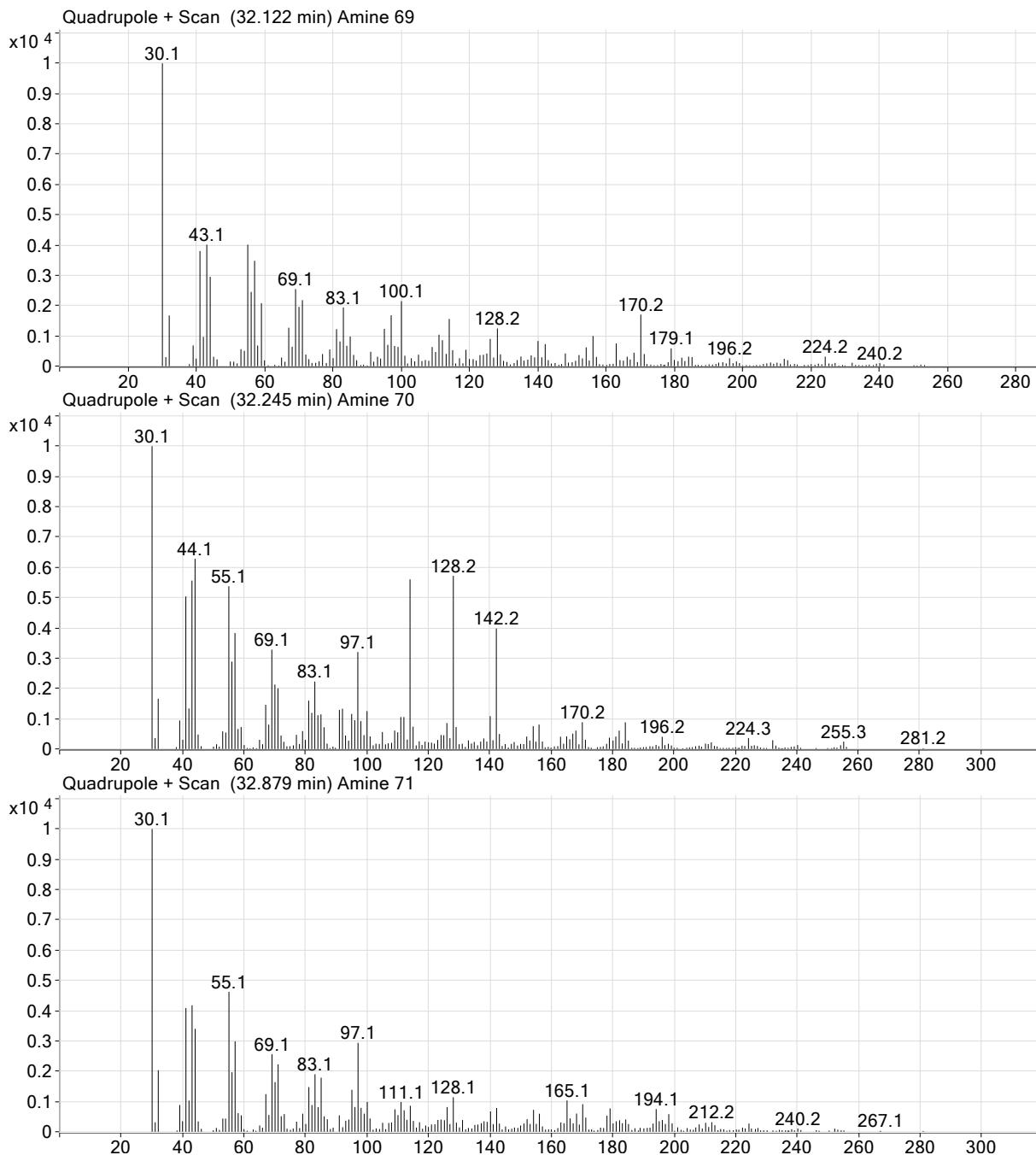


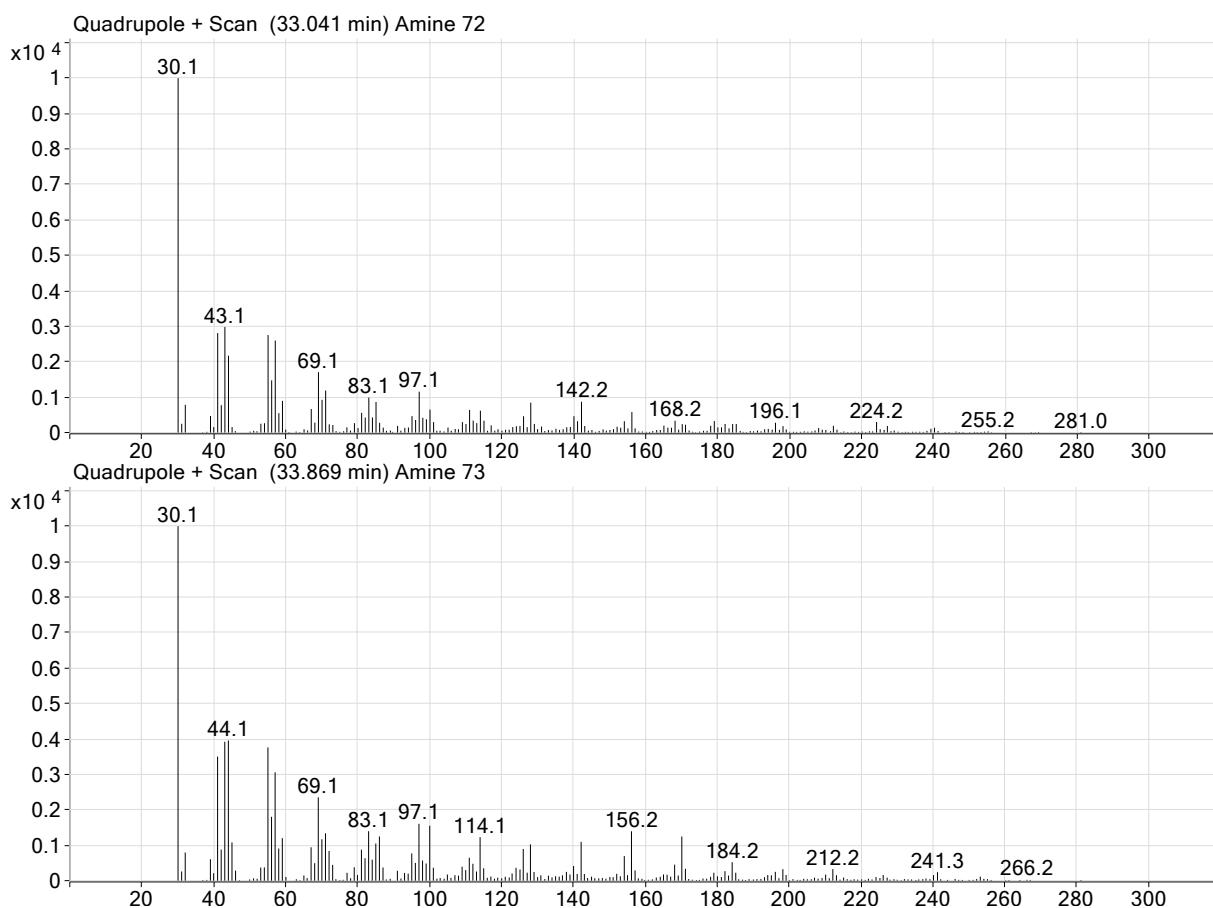












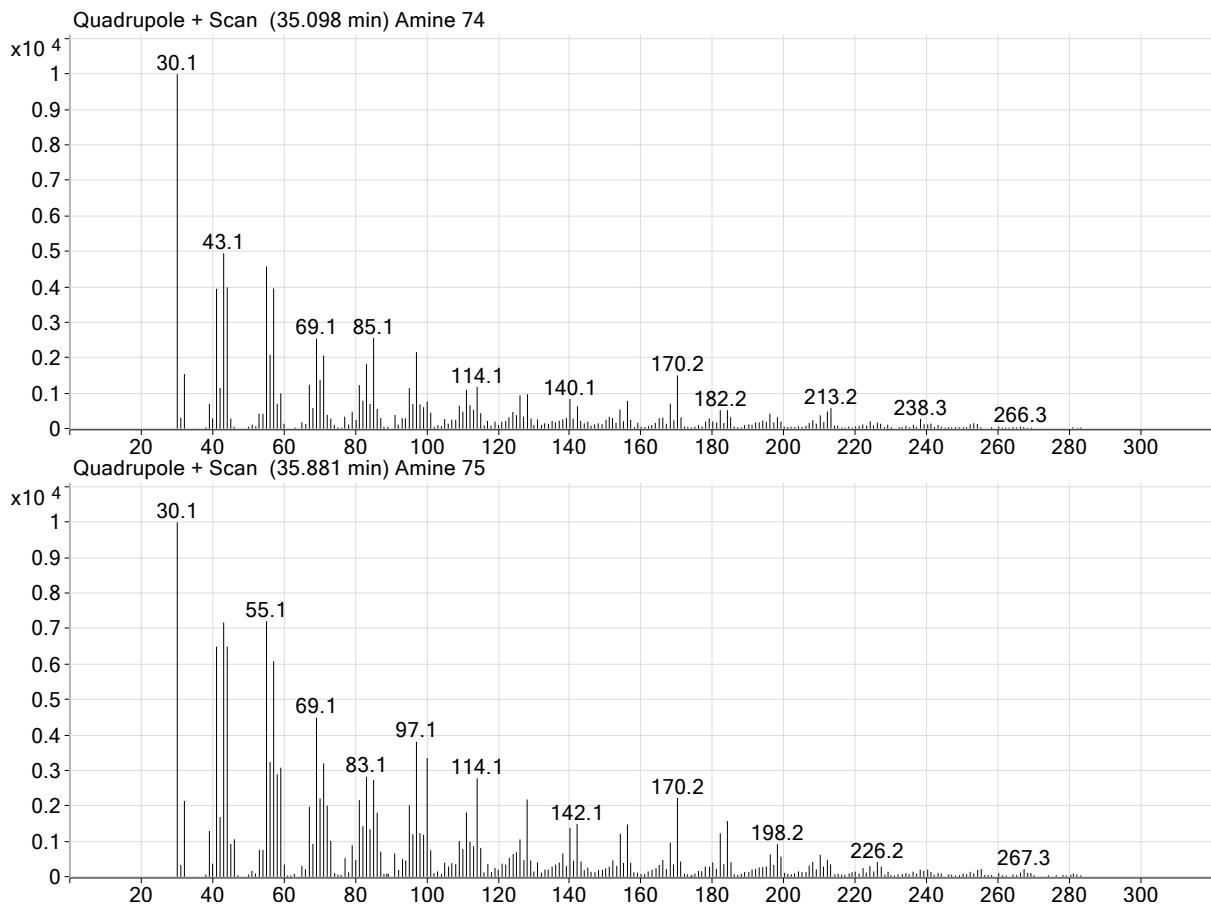


Figure S5. Library matching and reference mass spectra for the gas chromatography mass spectrometry with a polyarc flame ionization detection (GC-MS/Polyarc-FID) of the aminated oil generated from post-consumer recycled (PCR) HDPE by pyrolysis, hydroformylation, reductive amination, and rotary evaporation.

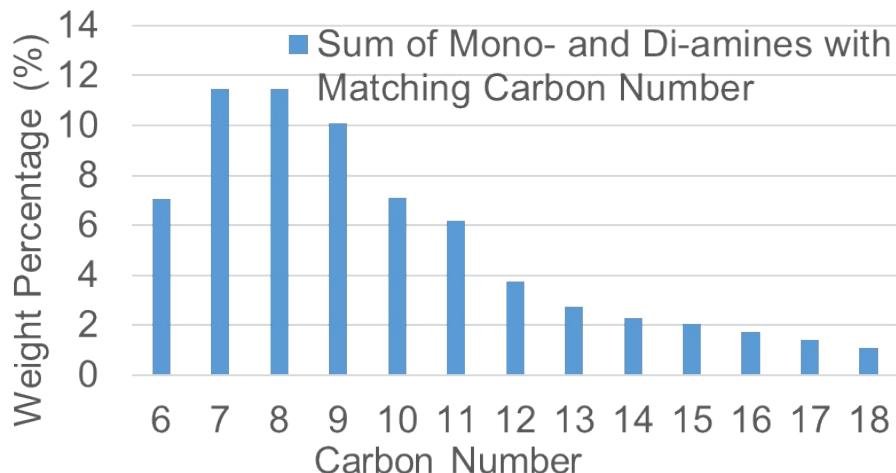


Figure S6. Theoretical carbon distribution of the sum of monoamines and diamines in the aminated oil based on the mono- and di-olefins in the pyrolysis oil.

Table S1. Karl Fischer titration of the aminated oil after rotary evaporation. The measured 6.3 wt% H₂O indicates a 9.4 wt% H₂O in the aminated oil after excluding the weight of CH₃OH.

	H ₂ O %
1st measurement	6.3
2nd measurement	6.3
3rd measurement	6.4

Table S2. Detailed information on the high-resolution liquid chromatography mass spectrometry (HRLC-MS) chromatogram of the aminated oil.

Adducts	Formula	Mass Error (ppm)	Isotope Similarity	m/z [M+H]	Retention time (min)	Manually Centered	m/z minus H
M+H	C8H17N	4.92	99.2	128.1440	15.298		127.1362
M+H	C8H17N	4.93	99.4	128.1440	16.617		127.1362
M+H	C8H17N	4.94	98.2	128.1440	12.356		127.1362
M+H	C8H19N	4.00	98.5	130.1595	3.235		129.1517
M+H	C9H19N	4.99	96.2	142.1597	3.185		141.1519
M+H	C9H21N	2.80	98.1	144.1754	4.690	Y	143.1676
M+H	C9H21N	2.10	98.8	144.1755	5.597	Y	143.1677
M+H	C10H21N	4.31	98.5	156.1753	5.324		155.1675
M+H	C10H21N	4.54	99.5	156.1754	5.955		155.1676
M+H	C10H21N	4.55	99.1	156.1754	4.862		155.1676
M+H	C10H21N	4.97	98.4	156.1754	4.605		155.1676
M+H	C9H19NO	5.96	99.4	158.1549	13.092		157.1471
M+H	C9H19NO	3.20	98.8	158.1550	12.150	Y	157.1472
M+H	C10H23N	3.70	98.5	158.1909	2.652		157.1831
M+H	C10H23N	4.45	98.9	158.1910	7.308		157.1832
M+H	C10H23N	4.54	99.1	158.1910	2.105		157.1832
M+H	C10H23N	4.98	99.0	158.1911	7.085		157.1833
M+H	C10H23N	1.90	99.8	158.1912	8.010	Y	157.1834
M+H	C10H23N	2.50	98.8	158.1913	6.674	Y	157.1835
M+H	C10H19NO	4.37	89.1	170.1547	12.920		169.1469
M+H	C11H23N	3.02	93.5	170.1908	2.088		169.1830
M+H	C11H23N	3.30	93.7	170.1909	16.651		169.1831
M+H	C11H23N	3.45	98.9	170.1909	7.736		169.1831
M+H	C11H23N	3.56	98.2	170.1909	2.618		169.1831
M+H	C11H23N	3.88	99.1	170.1910	7.052		169.1832
M+H	C11H23N	3.91	98.6	170.1910	7.325		169.1832
M+H	C11H23N	3.92	94.3	170.1910	8.334		169.1832
M+H	C11H23N	3.96	94.3	170.1910	17.832		169.1832

M+H	C11H23N	4.30	92.5	170.1911	15.386		169.1833
M+H	C11H23N	4.44	99.0	170.1911	7.959		169.1833
M+H	C10H21NO	4.35	97.8	172.1703	15.146		171.1625
M+H	C10H21NO	4.74	97.5	172.1704	14.614		171.1626
M+H	C10H21NO	4.94	99.9	172.1704	15.950		171.1626
M+H	C11H25N	3.47	99.1	172.2066	4.312		171.1988
M+H	C11H25N	4.27	99.2	172.2067	3.886		171.1989
M+H	C11H25N	4.48	99.6	172.2067	4.656		171.1989
M+H	C11H25N	3.50	99.7	172.2071	10.132	Y	171.1993
M+H	C11H25N	4.60	99.2	172.2073	9.309	Y	171.1995
M+H	C9H20N2O	3.88	96.5	173.1655	11.843		172.1577
M+H	C12H21N	2.20	94.2	180.1752	1.575	Y	179.1674
M+H	C12H23N	4.11	94.4	182.1911	2.449		181.1833
M+H	C12H23N	1.10	98.8	182.1911	7.274	Y	181.1833
M+H	C12H23N	1.10	99.1	182.1911	7.821	Y	181.1833
M+H	C12H23N	2.20	97.0	182.1913	2.601		181.1835
M+H	C11H21NO	0.00	93.7	184.1701	15.487	Y	183.1623
M+H	C11H21NO	3.80	97.3	184.1708	15.794	Y	183.1630
M+H	C12H25N	4.85	94.8	184.2069	4.929		183.1991
M+H	C12H25N	2.20	98.2	184.2069	3.748	Y	183.1991
M+H	C12H25N	1.60	96.6	184.2069	4.433	Y	183.1991
M+H	C12H25N	1.60	97.5	184.2069	4.177	Y	183.1991
M+H	C12H25N	2.70	98.8	184.2070	3.954	Y	183.1992
M+H	C12H25N	3.30	98.6	184.2071	9.583	Y	183.1993
M+H	C12H25N	3.30	97.5	184.2071	10.062	Y	183.1993
M+H	C12H25N	2.70	98.9	184.2071	4.605	Y	183.1993
M+H	C11H23NO	3.20	97.8	186.1864	17.799	Y	185.1786
M+H	C11H23NO	4.30	100.0	186.1868	18.517	Y	185.1790
M+H	C12H27N	2.70	98.4	186.2226	5.563	Y	185.2148
M+H	C12H27N	3.20	99.5	186.2228	11.259	Y	185.2150
M+H	C12H27N	4.30	99.6	186.2230	6.299		185.2152
M+H	C12H27N	4.30	99.5	186.2230	6.657		185.2152
M+H	C12H27N	4.30	99.3	186.2230	7.035	Y	185.2152
M+H	C12H27N	4.80	99.7	186.2231	5.989	Y	185.2153
M+H	C12H27N	3.80	99.6	186.2237	11.995	Y	185.2159
M+H	C10H22N2O	5.72	98.3	187.1816	14.512		186.1738
M+H	C11H25NO	4.59	98.6	188.2018	3.131		187.1940
M+H	C11H25NO	4.30	98.0	188.2019	2.892	Y	187.1941
M+H	C11H25NO	3.70	98.8	188.2021	3.441	Y	187.1943
M+H	C13H18O	3.19	95.0	191.1436	23.650		190.1358
M+H	C13H23N	3.52	97.9	194.1910	2.156		193.1832
M+H	C13H23N	3.70	96.2	194.1910	2.824		193.1832
M+H	C13H25N	2.49	98.6	196.2065	4.808		195.1987

M+H	C13H25N	2.54	96.9	196.2065	4.143		195.1987
M+H	C13H25N	2.71	92.8	196.2065	3.475		195.1987
M+H	C13H25N	2.92	94.1	196.2065	4.366		195.1987
M+H	C13H25N	3.01	96.7	196.2066	9.636		195.1988
M+H	C13H25N	3.21	97.1	196.2066	3.920		195.1988
M+H	C12H23NO	3.38	78.1	198.1859	17.694		197.1781
M+H	C12H23NO	3.87	76.3	198.1860	18.379		197.1782
M+H	C13H27N	3.12	95.8	198.2222	5.270		197.2144
M+H	C13H27N	3.53	98.4	198.2223	11.209		197.2145
M+H	C13H27N	3.64	96.0	198.2223	11.381		197.2145
M+H	C13H27N	3.67	94.7	198.2223	11.911		197.2145
M+H	C13H27N	3.74	97.0	198.2224	7.153		197.2146
M+H	C13H27N	3.85	99.3	198.2224	5.732		197.2146
M+H	C13H27N	4.12	98.7	198.2224	6.930		197.2146
M+H	C13H27N	4.15	99.0	198.2224	6.367		197.2146
M+H	C13H27N	4.18	98.4	198.2225	6.144		197.2147
M+H	C13H27N	4.20	98.6	198.2225	6.572		197.2147
M+H	C12H25NO	3.31	99.4	200.2015	20.896		199.1937
M+H	C12H25NO	3.47	99.6	200.2016	20.211		199.1938
M+H	C12H25NO	3.57	97.9	200.2016	19.644		199.1938
M+H	C13H29N	3.81	99.4	200.2380	12.990		199.2302
M+H	C13H29N	3.88	99.1	200.2381	9.191		199.2303
M+H	C13H29N	3.92	99.0	200.2381	8.266		199.2303
M+H	C13H29N	4.09	99.0	200.2381	8.590		199.2303
M+H	C13H29N	1.50	95.9	200.2381	8.830	Y	199.2303
M+H	C13H29N	4.14	99.4	200.2381	13.638		199.2303
M+H	C12H27NO	2.20	98.7	202.2170	4.673		201.2092
M+H	C12H27NO	2.54	98.9	202.2171	5.324		201.2093
M+H	C12H27NO	2.60	97.5	202.2171	4.366		201.2093
M+H	C12H27NO	3.06	98.1	202.2172	4.980		201.2094
M+H	C13H21NO	4.75	79.5	208.1706	11.894		207.1628
M+H	C14H25N	3.18	89.7	208.2066	3.168		207.1988
M+H	C14H25N	3.34	97.0	208.2067	3.765		207.1989
M+H	C14H25N	3.34	98.4	208.2067	4.845		207.1989
M+H	C12H16O3	4.50	98.2	209.1183	15.214	Y	208.1105
M+H	C14H27N	3.33	90.3	210.2223	5.425		209.2145
M+H	C14H27N	3.78	92.1	210.2224	6.350		209.2146
M+H	C14H27N	3.82	95.7	210.2224	11.209		209.2146
M+H	C14H27N	3.91	95.3	210.2224	5.921		209.2146
M+H	C14H27N	4.05	94.2	210.2225	6.589		209.2147
M+H	C14H27N	4.14	97.5	210.2225	6.110		209.2147
M+H	C14H27N	4.21	93.4	210.2225	5.665		209.2147
M+H	C14H29N	4.35	78.2	212.2382	13.571		211.2304

M+H	C14H29N	4.46	94.0	212.2382	7.548		211.2304
M+H	C14H29N	4.93	97.8	212.2383	12.869		211.2305
M+H	C14H29N	3.80	98.8	212.2384	9.242	Y	211.2306
M+H	C14H29N	5.60	98.4	212.2385	8.678		211.2307
M+H	C14H29N	3.80	98.5	212.2386	7.993	Y	211.2308
M+H	C14H29N	3.80	98.5	212.2386	8.455	Y	211.2308
M+H	C14H29N	3.80	97.8	212.2386	8.917	Y	211.2308
M+H	C13H27NO	4.86	96.5	214.2176	21.854		213.2098
M+H	C13H27NO	2.30	93.0	214.2176	6.539	Y	213.2098
M+H	C13H27NO	1.90	98.4	214.2177	22.503	Y	213.2099
M+H	C13H27NO	3.70	99.3	214.2180	23.120	Y	213.2102
M+H	C14H31N	1.40	97.4	214.2538	9.910	Y	213.2460
M+H	C14H31N	1.40	99.9	214.2538	14.067	Y	213.2460
M+H	C14H31N	5.23	99.4	214.2540	13.638		213.2462
M+H	C14H31N	3.30	95.1	214.2542	10.645	Y	213.2464
M+H	C14H31N	3.70	98.7	214.2543	10.389	Y	213.2465
M+H	C14H31N	3.70	99.1	214.2543	11.226	Y	213.2465
M+H	C14H31N	6.49	99.4	214.2543	15.146		213.2465
M+H	C14H31N	4.20	99.5	214.2544	14.529	Y	213.2466
M+H	C12H26N2O	4.60	95.9	215.2131	19.132	Y	214.2053
M+H	C13H29NO	4.47	98.2	216.2332	6.195		215.2254
M+H	C13H29NO	4.55	98.2	216.2332	6.846		215.2254
M+H	C13H29NO	2.30	98.3	216.2332	7.187	Y	215.2254
M+H	C13H29NO	3.20	98.3	216.2334	6.522	Y	215.2256
M+H	C15H22O	4.05	84.7	219.1752	22.333		218.1674
M+H	C15H27N	3.99	94.9	222.2225	7.136		221.2147
M+H	C15H27N	4.67	98.7	222.2227	5.442		221.2149
M+H	C15H27N	4.99	96.4	222.2227	6.539		221.2149
M+H	C15H27N	5.31	92.8	222.2228	5.921		221.2150
M+H	C15H26O	4.06	94.4	223.2065	24.969		222.1987
M+H	C15H29N	3.80	94.0	224.2381	9.481		223.2303
M+H	C15H29N	4.28	92.4	224.2382	12.801		223.2304
M+H	C15H29N	4.52	89.4	224.2383	7.666		223.2305
M+H	C15H29N	4.61	91.7	224.2383	8.934		223.2305
M+H	C15H29N	4.80	92.2	224.2383	8.128		223.2305
M+H	C13H23NO2	3.10	96.0	226.1813	11.894	Y	225.1735
M+H	C15H31N	4.74	87.7	226.2540	14.478		225.2462
M+H	C15H31N	3.10	95.5	226.2542	10.780	Y	225.2464
M+H	C15H31N	3.10	97.9	226.2542	10.935	Y	225.2464
M+H	C15H31N	5.68	98.6	226.2542	10.558		225.2464
M+H	C15H31N	3.50	98.6	226.2543	11.313	Y	225.2465
M+H	C15H21N	4.00	96.8	226.2544	9.755	Y	225.2466
M+H	C15H31N	4.40	96.0	226.2545	9.977	Y	225.2467

M+H	C14H29NO	3.70	94.8	228.2330	21.682		227.2252
M+H	C14H29NO	3.97	96.4	228.2331	23.974		227.2253
M+H	C14H29NO	4.53	96.3	228.2332	24.692		227.2254
M+H	C14H29NO	4.57	93.9	228.2332	8.506		227.2254
M+H	C14H29NO	3.10	98.4	228.2335	25.293	Y	227.2257
M+H	C15H33N	-3.10	92.8	228.2684	12.407	Y	227.2606
M+H	C15H33N	3.29	99.1	228.2693	16.547		227.2615
M+H	C15H33N	3.76	99.1	228.2694	15.966		227.2616
M+H	C15H33N	3.77	98.8	228.2694	12.953		227.2616
M+H	C15H33N	3.79	99.9	228.2694	15.093		227.2616
M+H	C15H33N	3.99	98.5	228.2695	12.271		227.2617
M+H	C15H33N	4.15	99.5	228.2695	15.538		227.2617
M+H	C15H32N	3.90		228.2700	11.809	Y	227.2622
M+H	C14H12O3	4.95	96.8	229.0870	18.362		228.0792
M+H	C14H31NO	2.51	96.7	230.2484	8.300		229.2406
M+H	C14H31NO	3.00	90.5	230.2485	13.469		229.2407
M+H	C14H31NO	3.44	97.6	230.2486	7.993		229.2408
M+H	C14H31NO	3.63	97.6	230.2487	10.490		229.2409
M+H	C14H31NO	3.82	94.2	230.2487	10.284		229.2409
M+H	C14H31NO	4.01	98.2	230.2488	8.641		229.2410
M+H	C14H31NO	4.41	97.2	230.2489	8.951		229.2411
M+H	C14H31NO	5.47	97.6	230.2491	12.373		229.2413
M+H	C15H22O2	3.41	95.1	235.1701	21.099		234.1623
M+H	C16H29N	2.69	90.9	236.2379	8.145		235.2301
M+H	C16H29N	2.79	90.9	236.2379	8.796		235.2301
M+H	C16H29N	2.90	91.1	236.2380	7.666		235.2302
M+H	C16H29N	3.29	82.3	236.2381	9.397		235.2303
M+H	C16H31N	2.32	86.4	238.2535	14.427		237.2457
M+H	C16H31N	2.65	89.9	238.2536	10.115		237.2458
M+H	C15H29NO	4.25	98.0	240.2332	14.684		239.2254
M+H	C16H33N	2.79	89.4	240.2692	15.916		239.2614
M+H	C16H33N	3.64	98.4	240.2694	13.125		239.2616
M+H	C16H33N	3.90	96.8	240.2695	12.305		239.2617
M+H	C16H33N	3.90	98.7	240.2695	12.663		239.2617
M+H	C16H33N	2.50		240.2697	11.944	Y	239.2619
M+H	C16H34N	2.90		240.2698	12.150		239.2620
M+H	C16H34N	2.90	96.8	240.2698	12.407	Y	239.2620
M+H	C15H31NO	2.65	96.1	242.2485	26.457		241.2407
M+H	C15H31NO	2.91	79.6	242.2485	23.325		241.2407
M+H	C15H31NO	2.91	97.3	242.2485	26.062		241.2407
M+H	C15H31NO	3.00	95.2	242.2486	23.805		241.2408
M+H	C15H31NO	3.30	93.4	242.2486	10.028		241.2408
M+H	C15H31NO	3.32	99.3	242.2486	27.432		241.2408

M+H	C15H31NO	3.44	97.9	242.2487	26.849		241.2409
M+H	C15H31NO	2.90	95.8	242.2496	10.662	Y	241.2418
M+H	C16H35N	3.57	98.1	242.2851	13.503		241.2773
M+H	C16H35N	3.63	99.4	242.2851	16.395		241.2773
M+H	C16H35N	3.70	98.7	242.2851	16.719		241.2773
M+H	C16H35N	1.70	96.7	242.2852	13.743		241.2774
M+H	C16H35N	4.35	98.9	242.2853	16.908		241.2775
M+H	C16H35N	4.38	98.9	242.2853	17.319		241.2775
M+H	C16H35N	4.40	98.7	242.2853	14.546		241.2775
M+H	C16H35N	4.45	97.7	242.2853	13.948		241.2775
M+H	C16H35N	4.66	98.8	242.2854	17.900		241.2776
M+H	C15H33NO	2.68	97.9	244.2641	10.524		243.2563
M+H	C15H33NO	3.07	96.8	244.2642	10.251		243.2564
M+H	C15H33NO	3.60	97.2	244.2644	9.498		243.2566
M+H	C15H33NO	3.97	96.0	244.2645	9.636		243.2567
M+H	C17H29N	3.39	87.6	248.2381	11.124		247.2303
M+H	C14H20N2O2	4.64	96.7	249.1609	9.157		248.1531
M+H	C14H20N2O2	4.40	97.6	249.1614	9.977	Y	248.1536
M+H	C17H31N	3.50	88.6	250.2538	10.868		249.2460
M+H	C17H30O	2.61	96.8	251.2376	29.450		250.2298
M+H	C17H34N	1.60	92.4	252.2683	12.407	Y	251.2605
M+H	C17H33N	3.17	85.1	252.2694	15.811		251.2616
M+H	C17H33N	1.60		252.2695	12.150		251.2617
M+H	C17H33N	4.36	90.2	252.2697	12.373		251.2619
M+H	C17H35N	4.55	92.7	254.2854	17.266		253.2776
M+H	C17H35N	5.84	98.0	254.2857	14.323		253.2779
M+H	C16H33NO	4.26	93.1	256.2646	11.792		255.2568
M+H	C16H33NO	4.82	96.5	256.2647	28.954		255.2569
M+H	C16H33NO	3.90	97.0	256.2648	29.538	Y	255.2570
M+H	C16H33NO	3.90	98.6	256.2648	28.151	Y	255.2570
M+H	C17H37N	3.10	99.5	256.3013	18.224	Y	255.2935
M+H	C17H37N	3.50	98.2	256.3013	15.059	Y	255.2935
M+H	C17H37N	3.50	98.2	256.3013	15.420	Y	255.2935
M+H	C17H37N	3.10	98.3	256.3013	18.021	Y	255.2935
M+H	C17H37N	3.90	99.3	256.3014	17.660	Y	255.2936
M+H	C17H37N	4.30	98.8	256.3015	16.000	Y	255.2937
M+H	C17H37N	4.70	99.0	256.3016	19.219	Y	255.2938
M+H	C16H35NO	3.94	97.1	258.2802	11.978		257.2724
M+H	C16H35NO	4.19	87.8	258.2802	16.479		257.2724
M+H	C16H35NO	4.32	94.2	258.2803	13.726		257.2725
M+H	C16H35NO	4.33	94.5	258.2803	11.141		257.2725
M+H	C16H35NO	4.63	95.5	258.2803	11.398		257.2725
M+H	C16H35NO	4.89	95.7	258.2804	11.722		257.2726

M+H	C18H31N	4.81	90.1	262.2542	13.571		261.2464
M+H	C15H22N2O2	4.77	98.1	263.1767	12.646		262.1689
M+H	C15H22N2O2	4.87	97.8	263.1767	11.843		262.1689
M+H	C15H21NO3	3.40	92.6	264.1608	16.787	Y	263.1530
M+H	C18H33N	3.79	79.2	264.2696	13.230		263.2618
M+H	C18H33N	3.87	87.2	264.2696	12.714		263.2618
M+H	C16H24O3	4.99	97.1	265.1811	21.169		264.1733
M+H	C18H35N	3.17	81.1	266.2851	16.857		265.2773
M+H	C18H35N	4.55	89.2	266.2854	13.726		265.2776
M+H	C18H34O	2.43	81.9	267.2689	32.753		266.2611
M+H	C17H33NO	4.98	97.2	268.2648	18.021		267.2570
M+H	C18H37N	3.56	96.9	268.3008	16.240		267.2930
M+H	C18H37N	3.83	94.9	268.3009	18.585		267.2931
M+H	C18H37N	3.97	94.2	268.3009	15.504		267.2931
M+H	C18H37N	4.09	98.2	268.3010	15.710		267.2932
M+H	C17H35NO	2.40	93.5	270.2798	30.648		269.2720
M+H	C17H35NO	3.02	89.2	270.2800	30.442		269.2722
M+H	C17H35NO	3.08	97.5	270.2800	31.640		269.2722
M+H	C17H35NO	3.09	95.8	270.2800	30.084		269.2722
M+H	C17H35NO	3.37	95.8	270.2800	31.043		269.2722
M+H	C18H39N	3.11	97.4	270.3164	16.378		269.3086
M+H	C18H39N	3.74	98.9	270.3165	17.353		269.3087
M+H	C18H39N	4.41	97.9	270.3167	16.823		269.3089
M+H	C18H39N	4.56	98.7	270.3168	19.303		269.3090
M+H	C18H39N	4.64	98.6	270.3168	20.484		269.3090
M+H	C18H39N	4.68	99.2	270.3168	18.858		269.3090
M+H	C18H39N	4.75	99.2	270.3168	19.509		269.3090
M+H	C18H39N	4.82	98.9	270.3168	19.938		269.3090
M+H	C18H10N2O	3.30	96.5	271.0875	16.257		270.0797
M+H	C17H37NO	2.92	98.1	272.2956	15.110		271.2878
M+H	C17H37NO	4.73	97.6	272.2961	16.601		271.2883
M+H	C19H33N	2.39	83.9	276.2692	12.271		275.2614
M+H	C19H33N	3.25	88.9	276.2695	15.248		275.2617
M+H	C16H24N2O2	2.92	97.7	277.1919	14.306		276.1841
M+H	C16H23NO3	3.34	94.9	278.1760	19.287		277.1682
M+H	C16H23NO3	3.40	93.2	278.1760	18.602		277.1682
M+H	C16H23NO3	3.88	99.4	278.1761	19.799		277.1683
M+H	C19H35N	1.90	83.1	278.2848	14.853		277.2770
M+H	C19H35N	2.00	84.9	278.2848	14.374		277.2770
M+H	C19H37N	1.89	87.4	280.3004	15.453		279.2926
M+H	C18H32O2	4.16	93.3	281.2487	20.090		280.2409
M+H	C18H35NO	3.40	91.2	282.2801	29.160		281.2723
M+H	C18H35NO	3.59	76.4	282.2802	26.558		281.2724

M+H	C18H35NO	4.42	93.9	282.2804	21.733		281.2726
M+H	C19H39N	2.86	96.1	282.3163	17.626		281.3085
M+H	C19H39N	2.87	93.3	282.3163	16.908		281.3085
M+H	C19H39N	3.05	96.5	282.3164	19.867		281.3086
M+H	C19H39N	3.26	98.0	282.3164	17.130		281.3086
M+H	C18H37NO	3.17	97.7	284.2957	32.291		283.2879
M+H	C18H37NO	3.30	97.5	284.2957	33.712		283.2879
M+H	C18H37NO	3.44	86.0	284.2958	32.719		283.2880
M+H	C18H37NO	3.48	92.4	284.2958	33.114		283.2880
M+H	C19H41N	2.86	97.1	284.3320	17.711		283.3242
M+H	C19H41N	2.97	98.2	284.3320	20.758		283.3242
M+H	C19H41N	3.12	99.4	284.3321	18.979		283.3243
M+H	C19H41N	3.59	99.0	284.3322	21.784		283.3244
M+H	C19H41N	3.74	96.5	284.3322	18.021		283.3244
M+H	C19H41N	3.74	98.4	284.3322	21.186		283.3244
M+H	C19H41N	3.76	97.5	284.3322	20.535		283.3244
M+H	C19H41N	3.86	98.7	284.3323	20.039		283.3245
M+H	C19H41N	4.19	98.2	284.3324	18.517		283.3246
M+H	C19H12N2O	4.43	96.3	285.1035	18.875		284.0957
M+H	C18H39NO	1.93	96.4	286.3110	15.899		285.3032
M+H	C18H39NO	1.95	94.3	286.3110	16.530		285.3032
M+H	C18H39NO	2.73	95.7	286.3112	14.391		285.3034
M+H	C18H39NO	3.26	96.6	286.3114	14.597		285.3036
M+H	C20H35N	2.80	84.6	290.2850	14.117		289.2772
M+H	C17H26N2O2	3.97	95.3	291.2079	17.232		290.2001
M+H	C17H25NO3	3.72	88.4	292.1918	21.510		291.1840
M+H	C20H39N	3.05	87.4	294.3164	16.823		293.3086
M+H	C20H41N	3.29	93.1	296.3321	21.135		295.3243
M+H	C20H41N	3.82	92.3	296.3323	18.447		295.3245
M+H	C20H41N	4.07	96.6	296.3324	18.943		295.3246
M+H	C19H39NO	2.02	92.5	298.3110	34.754		297.3032
M+H	C19H39NO	3.22	98.0	298.3114	35.783		297.3036
M+H	C19H39NO	3.47	97.0	298.3115	35.183		297.3037
M+H	C19H39NO	3.52	90.1	298.3115	34.515		297.3037
M+H	C19H39NO	3.54	97.7	298.3115	33.985		297.3037
M+H	C20H43N	4.54	97.3	298.3482	21.767		297.3404
M+H	C20H43N	4.64	96.8	298.3482	18.926		297.3404
M+H	C19H41NO	0.86	93.0	300.3263	14.924		299.3185
M+H	C19H41NO	1.40	94.5	300.3265	15.093		299.3187
M+H	C19H41NO	2.64	92.2	300.3269	16.753		299.3191
M+H	C19H41NO	3.31	92.2	300.3271	15.811		299.3193
M+H	C19H41NO	3.57	92.5	300.3272	15.625		299.3194
M+H	C19H41NO	4.00	96.2	300.3281	19.030	Y	299.3203

M+H	C21H37N	3.30	84.7	304.3009	16.513		303.2931
M+H	C18H28N2O2	3.58	93.8	305.2234	19.253		304.2156
M+H	C22H11NO	3.30	94.5	306.0929	23.650	Y	305.0851
M+H	C21H39N	1.81	80.0	306.3161	17.302		305.3083
M+H	C21H41N	2.82	86.4	308.3320	18.568		307.3242
M+H	C20H39NO	3.13	83.7	310.3114	32.942		309.3036
M+H	C21H43N	2.26	90.3	310.3475	19.475		309.3397
M+H	C21H43N	2.95	94.3	310.3477	22.401		309.3399
M+H	C21H43N	3.04	97.6	310.3478	20.211		309.3400
M+H	C20H41NO	2.17	91.4	312.3268	35.901		311.3190
M+H	C20H41NO	3.88	91.8	312.3273	16.874		311.3195
M+H	C21H45N	3.56	97.5	312.3636	24.453		311.3558
M+H	C21H45N	4.01	97.6	312.3637	23.292		311.3559
M+H	C21H45N	4.30	96.9	312.3638	20.417		311.3560
M+H	C21H45N	4.39	97.3	312.3638	23.771		311.3560
M+H	C21H45N	4.41	96.5	312.3639	22.999		311.3561
M+H	C21H45N	4.70	98.4	312.3639	22.350		311.3561
M+H	C21H45N	4.70	99.0	312.3639	20.775		311.3561
M+H	C20H12N2O2	4.97	97.5	313.0987	18.875		312.0909
M+H	C20H43NO	0.45	94.1	314.3419	16.479		313.3341
M+H	C20H43NO	2.05	93.8	314.3424	17.968		313.3346
M+H	C20H43NO	2.36	91.2	314.3425	17.009		313.3347
M+H	C20H43NO	4.89	97.7	314.3433	20.177		313.3355
M+H	C22H39N	0.54	80.5	318.3157	17.215		317.3079
M+H	C22H39N	2.64	91.1	318.3164	19.422		317.3086
M+H	C22H39N	3.32	96.9	318.3166	19.661		317.3088
M+H	C19H30N2O2	2.16	91.2	319.2387	21.220		318.2309
M+H	C22H41N	0.46	78.9	320.3313	18.619		319.3235
M+H	C22H40O	1.79	94.1	321.3158	32.993		320.3080
M+H	C21H39NO	4.04	87.1	322.3117	14.117		321.3039
M+H	C22H43N	0.81	80.8	322.3471	19.715		321.3393
M+H	C22H45N	1.24	94.9	324.3629	21.443		323.3551
M+H	C22H45N	2.22	90.7	324.3632	20.484		323.3554
M+H	C22H47N	1.97	96.9	326.3788	25.806		325.3710
M+H	C22H47N	2.18	96.8	326.3788	21.476		325.3710
M+H	C22H47N	2.22	98.0	326.3788	23.531		325.3710
M+H	C22H47N	2.40	98.2	326.3789	25.087		325.3711
M+H	C22H47N	2.63	98.6	326.3790	22.195		325.3712
M+H	C22H47N	2.89	98.4	326.3791	21.922		325.3713
M+H	C21H45NO	-4.17	93.8	328.3560	17.266		327.3482
M+H	C21H45NO	-0.37	95.3	328.3573	17.643		327.3495
M+H	C21H45NO	1.10	93.0	328.3578	18.156		327.3500
M+H	C21H45NO	1.40	92.2	328.3579	19.148		327.3501

M+H	C21H45NO	4.22	95.5	328.3588	21.304		327.3510
M+H	C23H41N	-4.15	75.8	332.3298	18.740		331.3220
M+H	C23H41N	2.62	89.6	332.3320	19.182		331.3242
M+H	C23H41N	2.65	92.6	332.3321	21.048		331.3243
M+H	C23H43N	-4.42	75.5	334.3454	19.901		333.3376
M+H	C22H41NO	3.36	83.4	336.3272	15.538		335.3194
M+H	C23H45N	0.63	79.4	336.3627	20.825		335.3549
M+H	C22H43NO	3.22	97.7	338.3428	32.993		337.3350
M+H	C23H47N	2.44	92.6	338.3789	21.699		337.3711
M+H	C23H49N	2.36	95.8	340.3946	26.440		339.3868
M+H	C23H49N	2.50	91.7	340.3946	23.565		339.3868
M+H	C23H49N	2.84	96.9	340.3947	24.692		339.3869
M+H	C23H49N	3.15	96.1	340.3948	22.573		339.3870
M+H	C23H49N	3.97	98.0	340.3951	22.965		339.3873
M+H	C23H20N2O	3.44	96.6	341.1660	27.672		340.1582
M+H	C21H40O3	3.16	99.5	341.3061	32.753		340.2983
M+H	C22H47NO	-3.41	92.9	342.3719	18.791		341.3641
M+H	C22H47NO	1.95	90.3	342.3737	19.287		341.3659
M+H	C22H47NO	2.10	90.5	342.3738	20.279		341.3660
M+H	C24H38O	-7.23	92.8	343.2971	14.684		342.2893
M+H	C19H38N2O3	4.52	96.7	343.2971	14.684		342.2893
M+H	C24H43N	-1.91	76.6	346.3462	19.938		345.3384
M+H	C24H43N	3.12	95.5	346.3479	22.469		345.3401
M+H	C21H33NO3	4.57	88.1	348.2549	28.286		347.2471
M+H	C24H45N	-1.20	75.0	348.3621	21.152		347.3543
M+H	C23H43NO	4.27	85.4	350.3432	17.215		349.3354
M+H	C24H47N	0.07	77.6	350.3782	21.905		349.3704
M+H	C24H49N	2.99	92.0	352.3948	22.624		351.3870
M+H	C24H23N3	-4.99	94.3	354.1947	31.727		353.1869
M+H	C24H51N	-0.76	96.5	354.4092	23.292		353.4014
M+H	C24H51N	2.08	98.8	354.4102	25.890		353.4024
M+H	C24H51N	2.21	98.0	354.4102	27.844		353.4024
M+H	C24H51N	2.96	96.3	354.4105	24.027		353.4027
M+H	C23H49NO	-2.63	93.9	356.3878	19.867		355.3800
M+H	C23H49NO	1.47	92.5	356.3892	21.338		355.3814
M+H	C23H49NO	1.76	92.1	356.3893	20.417		355.3815
M+H	C22H33NO3	1.84	93.1	360.2540	28.562		359.2462
M+H	C25H45N	2.20	94.6	360.3633	23.838		359.3555
M+H	C22H35NO3	1.33	91.9	362.2695	29.673		361.2617
M+H	C22H35NO3	1.85	89.8	362.2696	30.017		361.2618
M+H	C24H45NO	3.12	84.9	364.3585	18.072		363.3507
M+H	C25H49N	-0.92	75.2	364.3934	22.982		363.3856
M+H	C25H53N	0.68	88.0	368.4253	29.281		367.4175

M+H	C25H53N	0.83	94.7	368.4254	27.125		367.4176
M+H	C25H53N	1.28	98.3	368.4255	25.155		367.4177
M+H	C24H20N2O2	2.64	96.5	369.1607	27.672		368.1529
M+H	C25H24N2O	1.66	92.4	369.1968	31.727		368.1890
M+H	C24H51NO	-0.24	90.5	370.4043	21.578		369.3965
M+H	C24H51NO	0.64	91.1	370.4046	22.367		369.3968
M+H	C21H42N2O3	4.64	88.9	371.3285	18.021		370.3207
M+H	C23H35NO3	1.34	89.4	374.2695	30.203		373.2617
M+H	C26H47N	0.84	86.5	374.3784	22.212		373.3706
M+H	C26H47N	0.98	90.9	374.3785	25.276		373.3707
M+H	C23H37NO3	1.27	93.6	376.2851	31.727		375.2773
M+H	C23H37NO3	1.54	90.1	376.2852	31.333		375.2774
M+H	C26H53N	0.75	91.7	380.4254	24.915		379.4176
M+H	C26H55N	0.91	92.0	382.4411	26.285		381.4333
M+H	C26H55N	1.28	92.2	382.4412	28.357		381.4334
M+H	C25H53NO	-3.12	93.5	384.4188	22.212		383.4110
M+H	C24H39NO3	1.96	86.8	390.3010	33.404		389.2932
M+H	C24H39NO3	4.02	75.7	390.3018	33.010		389.2940
M+H	C27H55N	1.21	90.8	394.4412	26.045		393.4334
M+H	C27H57N	0.63	93.7	396.4566	26.885		395.4488
M+H	C27H57N	1.14	88.9	396.4568	29.639		395.4490
M+H	C27H57N	1.95	95.1	396.4571	27.415		395.4493
M+H	C26H24N2O2	3.93	96.5	397.1926	31.727		396.1848
M+H	C27H28N2O	-2.66	94.4	397.2264	35.662		396.2186
M+H	C25H43NO3	-3.97	95.3	406.3300	32.993		405.3222
M+H	C28H57N	0.16	90.6	408.4564	26.953		407.4486
M+H	C28H59N	0.53	95.8	410.4722	28.340		409.4644
M+H	C29H59N	-0.53	90.0	422.4718	28.083		421.4640
M+H	C29H61N	-0.43	95.2	424.4875	29.450		423.4797
M+H	C28H28N2O2	1.52	94.4	425.2230	35.662		424.2152
M+H	C28H28N2O2	1.66	95.7	425.2231	28.765		424.2153
M+H	C31H36O	9.58	88.9	425.2880	29.760		424.2802
M+H	C26H51NO3	-0.87	95.5	426.3938	35.166		425.3860
M+H	C30H61N	-2.49	82.0	436.4866	29.075		435.4788
M+H	C30H63N	-0.27	95.5	438.5032	30.051		437.4954
M+H	C31H65N	-0.20	94.7	452.5189	31.110		451.5111
M+H	C30H32N2O2	2.63	92.6	453.2548	32.753		452.2470
M+H	C32H67N	-0.82	94.4	466.5342	32.804		465.5264
M+H	C33H69N	-1.30	94.0	480.5497	33.354		479.5419
M+H	C36H75N	-0.73	91.1	522.5968	35.456		521.5890
M+H	C46H54	-4.96	85.7	607.4268	31.711		606.4190
M+H	C41H54N2O2	1.67	89.3	607.4268	31.711		606.4190

Table S3. Detailed information on the GC-MS/Polyarc-FID chromatogram of the aminated oil.

Compound	Library ID #	RT	Estimated parent mass	Library Match	Match %	Conc. mg/L	Estimated Carbon #
Amine 1	1	4.081	87	1-Butanamine, 3-methyl-	92	855	5
Amine 2	2	4.165	87	S-(-)-2-Methylbutylamine	96	2962	5
Amine 3	3	4.663	87	1-Pantanamine	92	4934	5
Amine 9	9	8.253	99	4-Methyl-pent-3-enylamine	82	6000	6
Amine 4	4	6.254	101	2-Ethylbutylamine	93	9079	6
Amine 5	5	6.448	101	2-Ethylbutylamine	97	1617	6
Amine 6	6	6.5	101	2-Ethylbutylamine	89	1751	6
Amine 7	7	7.173	101	1-Hexanamine	93	11173	6
Amine 13	13	9.896	113	Cyclohexanemethylamine	91	9579	7
Amine 14	14	9.993	113	octane, 1-azido	83	3061	7
Amine 8	8	7.826	115			564	6
Amine 10	10	9.062	115	1-heptanamine	89	16613	7
Amine 11	11	9.146	115	3-Methylhexan-1-amine	85	1149	7
Amine 12	12	9.346	115	3-Methylhexan-1-amine	91	825	7
Amine 15	15	10.213	115	1-Heptanamine	96	15928	7
Amine 17	16	11.358	120	Cyclohexanemethylamine	76	5817	7
Amine 18	17	11.416	127	Cyclohexanemethylamine	83	2982	8
Amine 19	18	11.643	127	2,2-dimethyl-4-enylamine	86	741	8
Amine 16	63	10.931	129			5241	8
Amine 20	19	11.688	129	1-Hexanamine, 2-ethyl-	83	1002	8
Amine 21	20	11.992	129	1-Hexanamine, 2-ethyl-	95	2531	8
Amine 22	21	12.134	129	1-Hexanamine, 2-ethyl-	92	6521	8
Amine 27	26	13.35	129	1-Octanamine	91	9023	8
Amine 28	27	13.467	134	2,2-dimethylhex-4-enylamine	80	1438	8
Amine 24	23	13.04	136	2-Decen-1-ol, (Z)-	84	2840	9
Amine 25	24	13.163	138	2,2-dimethylhex-4-enylamine	77	1626	9
Amine 26	25	13.234	139	2,2-dimethylhex-4-enylamine	80	806	9
Amine 23	22	12.419	140	18-Nonadecen-1-amine	81	441	9
Amine 32	30	15.226	142	1-Decanamine	83	4876	9
Amine 30	28	14.644	143	Unknown		3005	9
Amine 35	31	16.404	143	1-Decanamine	83	6294	9
Amine 29	64	14.567	154			1592	10
Amine 31	29	15.032	154	1-Decanamine	75	2018	10
Amine 33	65	15.517	154			722	10
Amine 39	34	18.195	156	1-Decanamine	84	3672	10
Amine 40	35	19.327	157	1-Decanamine	89	4590	10
Amine 38	33	17.995	162	1-Decanamine	77	1719	10
Amine 34	66	15.854	166			399	10
Amine 37	32	17.568	166	1-Decanamine	79	1190	11

Amine 36	67	17.432	168			732	11
Amine 44	39	21.022	170	1-Tridecanamine	82	3547	11
Amine 45	40	22.096	171	1-Undecanamine	87	4868	11
Amine 41	36	20.188	178	DL-Leucine, N-glycyl	78	1767	12
Amine 42	37	20.356	182	1-Undecanamine	38	1289	12
Amine 43	38	20.815	182	1-Tridecanamine	80	1916	12
Amine 47	42	23.021	196	Elaidamide	78	935	13
Amine 48	43	23.493	196	Unknown		829	13
Amine 46	41	22.84	197	DL-Leucine, N-glycyl	80	446	13
Amine 50	45	24.709	197	1-Tridecanamine	86	2753	13
Amine 49	44	23.687	199	1-Tridecanamine	82	2515	13
Amine 54	47	26.217	210	1-Tridecanamine	80	1378	14
Amine 53	46	26.029	211	1-Tridecanamine	83	433	14
Amine 51	68	25.363	213			453	14
Amine 52	69	25.57	213			772	14
Amine 55	48	27.18	213	1-Tridecanamine	84	2889	14
Amine 56	49	27.659	225	Unknown		797	15
Amine 59	52	28.422	225	Unknown		569	15
Amine 57	50	27.775	227	Unknown		405	15
Amine 58	51	27.976	227	Unknown		747	15
Amine 60	53	28.603	227	Unknown		980	15
Amine 61	54	29.522	227	1-Tridecanamine	82	2043	15
Amine 63	71	30.059	238			283	16
Amine 62	70	29.949	239			282	16
Amine 64	72	30.266	241			224	16
Amine 65	55	30.712	241	Unknown		398	16
Amine 66	56	30.88	241	Unknown		1093	16
Amine 69	74	32.122	252			96	17
Amine 71	58	32.879	252	Unknown		113	17
Amine 68	73	32.058	253			108	17
Amine 67	57	31.793	255	Unknown		1225	17
Amine 70	75	32.245	255			234	17
Amine 73	60	33.869	266	Unknown		792	18
Amine 75	62	35.881	267	Unknown		533	18
Amine 72	59	33.041	269	Unknown		638	18
Amine 74	61	35.15	269	Unknown		342	18

Table S4. CHN(O)S analysis of aminated oil, aminated oil after excluding methanol (MeOH), and aminated oil after excluding both MeOH and H₂O.

Sample	CHNO(S) Analysis			
	C	H	N	O
	%	%	%	%
Aminated Oil	63.7	10.9	5.0	20.4
Aminated Oil without MeOH	74.8	10.2	7.2	7.9
Aminated Oil without MeOH & H ₂ O	81.0	11.1	7.8	0.1

Table S5. The boiling points of selected chemicals in the aminated oil. The data were obtained using Aspen Plus 12.

Corresponding Final Products	Boiling Point of Final Products (°C)
Methanol	65
Pentane	36
Hexylamine	131
1,7-heptanediamine	214
Hexane	69
Heptylamine	157
1,8-Octanediamine	238
Heptane	98
Octylamine	180
1, 9-Nonanediamine	255
Octane	126
Nonylamine	202
1,10-Diaminodecane	269
Nonane	151
Decylamine	259
1,11-Diaminodecane	288
Decane	174
Undecylamine	242
1,12-Diaminododecane	303
Dodecylamine	259

Table S6. Economic analysis of the proposed route to produce amines from waste polyolefins. The prices of the chemicals were obtained from the resources cited in the main text and listed below:

<https://www.recyclingmarkets.net>

<https://pubs.usgs.gov/periodicals/mcs2022/mcs2022-nitrogen.pdf>

<https://www.energy.gov/eere/fuelcells/hydrogen-shot>

Feedstock				Products					Potential Profit
Feedstocks	\$/ton	Input	Output Value	Products	\$/ton	ratio	Output	Output Value	
HDPE	125	1.00	125.0	Aromatic	780	14.5	0.2	131.2	
CO	150	0.19	28.5	Paraffins	610	20.9	0.2	147.9	
NH ₃	510	0.09	45.9	Monoamines	2000	29.8	0.3	691.4	
H ₂	1000	0.02	20.0	Diamines	3500	10.0	0.1	406.0	
				Gas	600	9.0	0.1	62.6	
				Solid			2.0	0.0	
Sum		1.30	219.4				86.2		1439.2
								1219.8	

Table S7. Estimated cost of the processes.

	CAPEX (\$MM) ^a	Scale (kton/yr) ^a	CAPEX at 100 ton/yr (\$MM)
Pyrolysis	38.10	36.50	69.75
Hydroformylation	32.00	214.10	20.27
Hydrogenation	22.50	21.30	56.91
Pyo oil Separation	6.60	500.00	2.51
Products Separation	3.90	120.00	3.50

^a: Li, H., Wu, J., Jiang, Z., Ma, J., Zavala, V. M., Landis, C. R., ... and Huber, G. W. (2023). Hydroformylation of pyrolysis oils to aldehydes and alcohols from polyolefin waste. *Science*, 381(6658), 660-666.

The sixth scaling rule was used to account for economies of scale when evaluating CAPEX of facilities:

$$\alpha^t = \bar{\alpha}^t \cdot \left(\frac{\xi^t}{\bar{\xi}^t} \right)^\beta$$

Here, α represents CAPEX of technology t at a scale ξ . $\bar{\xi}$ is the CAPEX of such technology at base case scale $\bar{\alpha}$, and β is the scaling factor, which assumed to be 0.6 in this work