Supplementary Material (ESI) for Organic & Biomolecular Chemistry

Electronic supplementary information

Poly(vinyl)chloride supported palladium nanoparticles: Catalyst for rapid hydrogenation reactions

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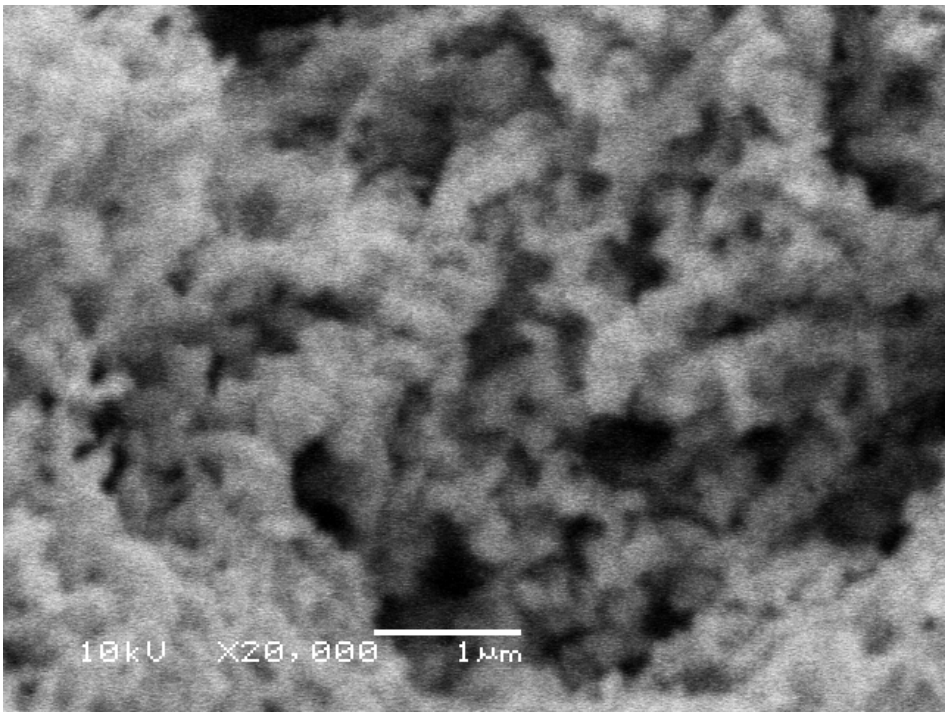
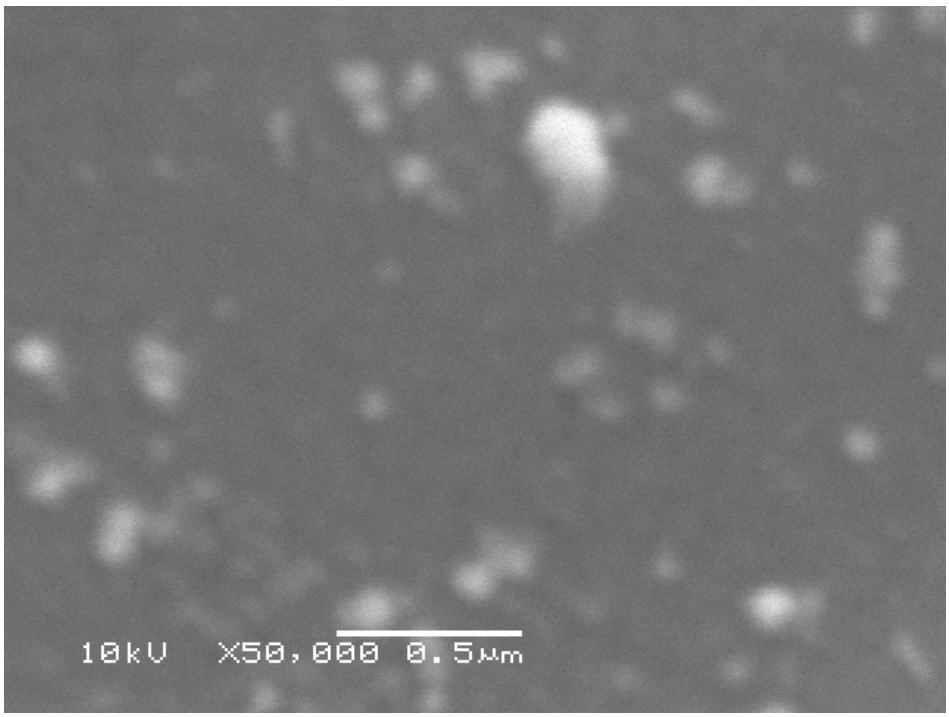
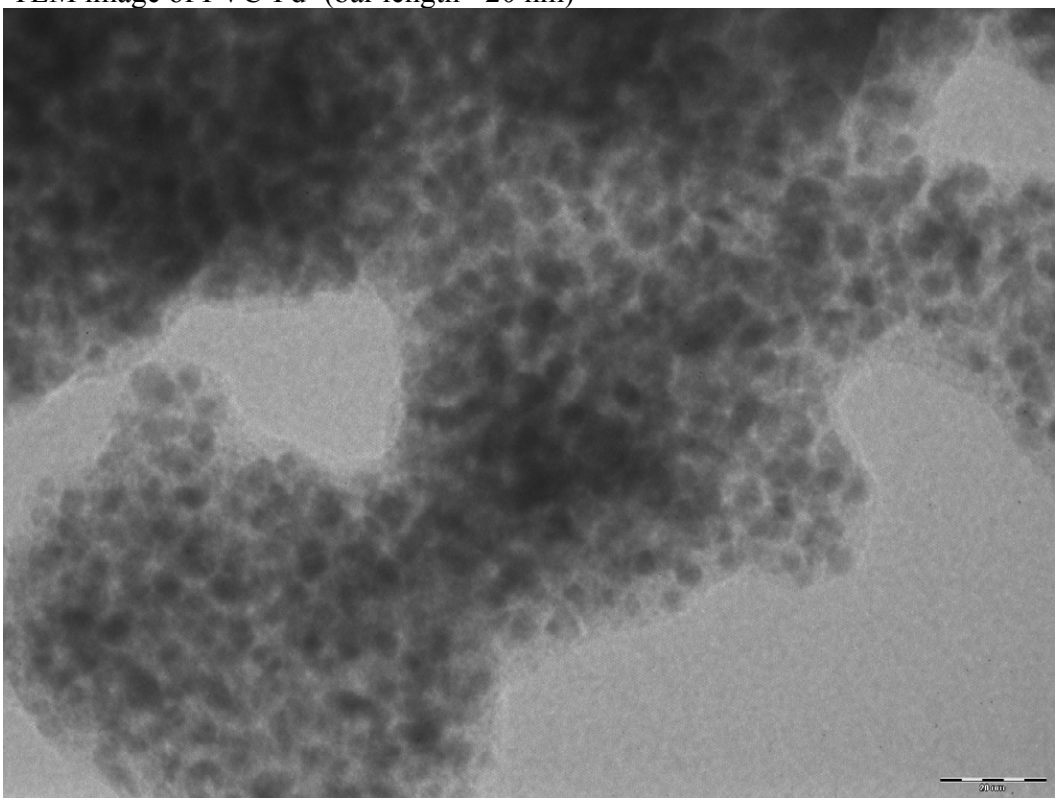
SEM image of PVC-Pd^{0}



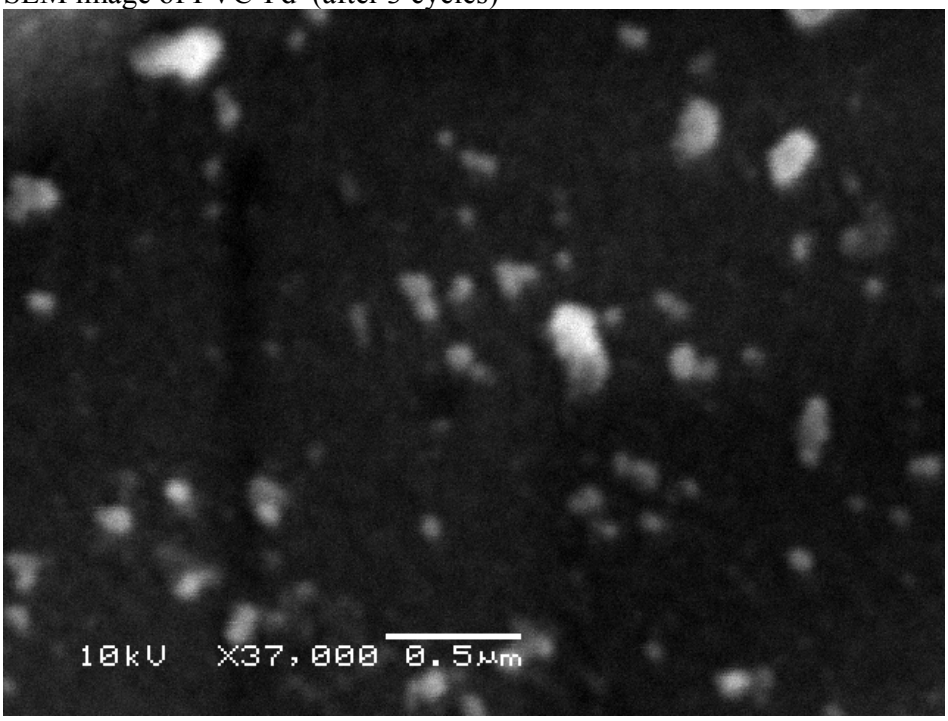
SEM image of PVC-Pd^0



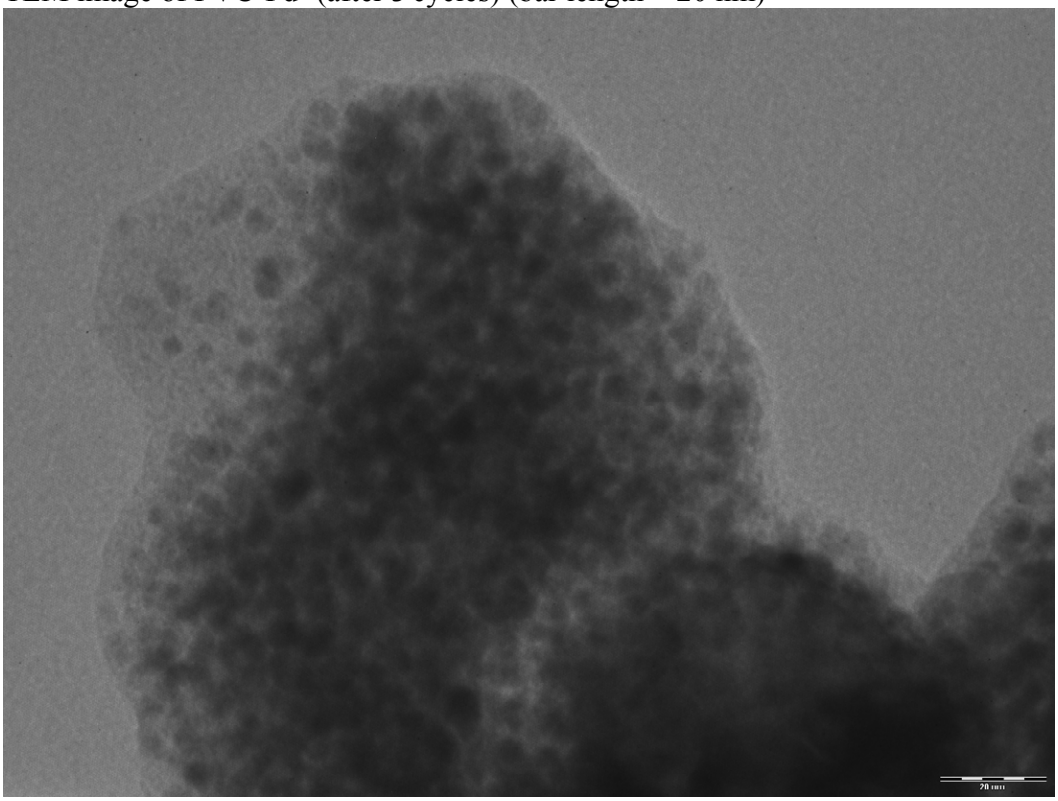
TEM image of PVC-Pd^0 (bar length= 20 nm)



SEM image of PVC-Pd^0 (after 3 cycles)



TEM image of PVC-Pd^0 (after 3 cycles) (bar length = 20 nm)

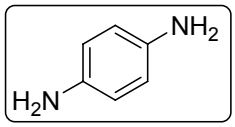


General remarks:

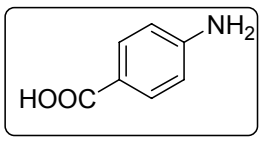
^{1}H NMR and ^{13}C NMR were recorded on a Bruker AMX 400 MHz instrument with tetra methyl silane (TMS) as an internal standard. Mass spectra were recorded on high resolution mass spectra (HRMS) Q-Tof micro mass spectrometer. All the reactions were monitored using TLCs with precoated silica gel plates purchased from Merck. HPLC analyses were made using Agilent 1100 series having G1311A VWD at λ=254 nm or 210 nm, flow 0.5 mL/min, Column: Agilent Eclipse XDB-C18, pore size-5µm, diameter x length = 4.6 x 150 mm; Method: gradient 0.1% TFA water-acetonitrile; acetonitrile 30-70 % in 30 min or 40-90 % in 30 min. IR measurements were made on a Nicolet model impact 400 D FT-IR spectrometer (KBr pellets, 3 cm^{-1} resolution). PVC was puchased from Sigma-Aldrich as grannules and used as such.

ICP-OES data were obtained from Shiva Analyticals (India) Ltd., Bangalore 562114, India using Perkin Elmer OPTIMA 5300DV. In brief, known quantity of sample was weighed into a beaker, digested in aquaregia, cooled and made up to a known volume. The instrument was calibrated with NIST traceable standard and aspirated the sample solution by ICP-OES.

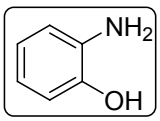
Characterization data for selected compounds:



Benzene-1,4-diamine (Table 1, entry 1): Solid, m.p. 137-139 ^{o}C (reported: 138-143); ^{1}H NMR (DMSO-d_6, 400 MHz) δ: 3.72 (4H, br), 6.21 (4H, d, J = 5.4 Hz); ^{13}C NMR (DMSO-d_6, 200 MHz) δ: 121.2, 137.6. ESI-MS Calcd for $C_6H_8N_2$: 108.06; found: 109.20 $(M+H)^+$.

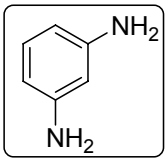


4-aminobenzoic acid (Table 1, entry 2): Solid, m.p. 190-192 ^{o}C (reported: 187-189 ^{o}C); ^{1}H NMR (DMSO-d_6, 400 MHz) δ: 3.21 (2H, s), 6.57 (2H, d, J = 5.8 Hz), 7.12 (2H, d, J = 4. 4 Hz), 10.31 (1H, s); ^{13}C NMR (DMSO-d_6, 200 MHz) δ: 119.3, 126.2, 133.6, 141.5, 171.0; HR-MS Calcd for $C_7H_7NaNO_2$: 160.0374; found: 160.0377 $[M+Na]^+$.

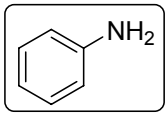


2-amiophenol (Table 1, entry 3): Solid, m.p. 170-173 ^{o}C (170-175 ^{o}C); ^{1}H NMR (DMSO-d_6, 400 MHz) δ: 3.23 (2H, s), 4.72 (1H, s), 6.31-6-72 (4H, m); ^{13}C NMR (DMSO-d_6, 200 MHz) δ: 117.2, 119.3, 123.4, 125.9, 132.1, 143.0; ES-MS Calcd for C_6H_7NO: 109.05, found: 110.12 (M+H).

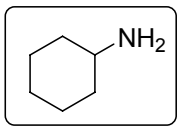
Benzene-1,3-diamine (Table 1, entry 4): Solid, m.p. 64-65 ^{o}C (reported 64-66 ^{o}C); ^{1}H NMR (DMSO-d_6, 400 MHz) δ: 4.11 (4H, s), 5.61 (1H, s), 5.97-6.14 (3H, m); ^{13}C NMR (DMSO-d_6, 200 MHz) δ: 106.7, 110.1, 132.2, 144.9.



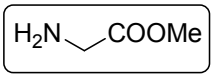
Aniline (Table 1, entry 5): Liquid. ESI-MS Calcd for C_6H_7N: 93.13; found 94.0 $(M+H)^+$.



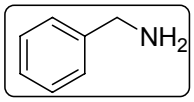
Cyclohexylamine (Table 1, entry 6): Liquid; Completion of reaction was confirmed through IR analysis.



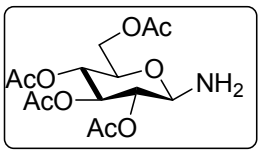
Methyl-2-aminoacetate (Table 1, entry 7): Gum. ^{1}H NMR (DMSO-d_6, 400 MHz) δ: 3.65 (3H, s), 3.92 (2H, m), 6.11 (2H, br); ^{13}C NMR (200 MHz, DMSO-d_6) δ: 40.2, 51.6, 169.2; HR-MS Calcd for $C_3H_7NNaO_2$: 112.0374; found: 112.0360 $[M+Na]^+$.



Benzylamine (Table 1, entry 8): Liquid, ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 3.66 (2H, m), 6.21 (2H, br), 7.01-7.21 (5H, m); ^{13}C NMR ($CDCl_3$, 200 MHz) δ: 52.0, 125.5, 127.9, 128.4, 139.3.

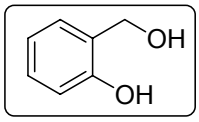


(2,3,4,6-tetra-*O*-acetyl-*β*-D-glucopyranosyl-1-amine (Table 1, entry 9): Gum; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 2.01-2.46 (12H, 4s), 4.12 (1H, m), 4.62 (1H, q), 4.99 (2H, d, J = 4.6 Hz), 5.50 (1H, t, J = 3.3 Hz), 5.73 (2H, m); HR-MS Calcd for $C_{14}H_{21}NNaO_9$: 370.1114; found: 370.1127 $[M+Na]^+$.

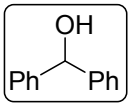


Benzylalcohol (Table 1, entry 10): Liquid; Quantitative disappearance of aldehyde signal (1722 cm^{-1}) confirmed the completion of reaction.

2-(hydroxymethyl)phenol (Table 1, entry 11): Solid, m.p. 81-84 ^{o}C (reported: 81-83 ^{o}C); ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 4.62 (2H, s), 5.13-5.24 (2H, br), 6.65-7.13 (4H, m); ^{13}C NMR ($CDCl_3$, 200 MHz) δ: 55.3, 120.3, 126.2, 128.1, 129.3, 129.8, 151.5; ES-MS Calcd for $C_7H_8O_2$: 124.05; found 125.1 $(M+H)^+$.

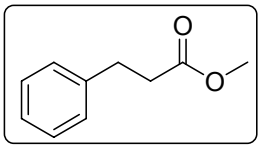


3-methylbutan-1-ol (Table 1, entry 12): Liquid; Complete disappearance of the aldehyde signal (1731 cm^{-1}) was confirmed as the end point of the reaction.



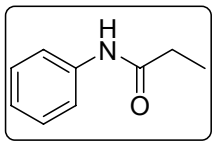
Diphenylmethanol (Table 1, entry 13): ES-MS Calcd for $C_{13}H_{12}O$:184.23; found: 185.12 $(M+H)^+$; ^{13}C NMR ($CDCl_3$, 200 MHz) δ: 75.2, 128.3, 128.9, 129.1.

Methyl 3-phenylpropanoate (Table 1, entry 14): Solid; m.p. 142-145 ^oC; ^1H NMR ($CDCl_3$, 400 MHz) δ: 2.45-2.66 (4H, m), 3.67 (3H, s), 7.11-7.44 (5H, m); ^{13}C NMR ($CDCl_3$, 200 MHz) δ: 29.2, 36.3, 52.3, 123.2, 127.6, 128.1, 139.2, 172.5; HR-MS Calcd for $C_{10}H_{12}NaO_2$: 187.0735; found 187.0754 $[M+Na]^+$.

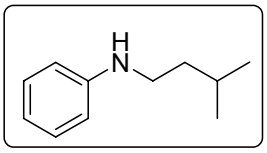


***N*-propanol** (Table 1, entry 15): Liquid; Complete disappearance of alkyne signal (2121 cm^{-1}) in the IR spectrum was confirmed as the end point.

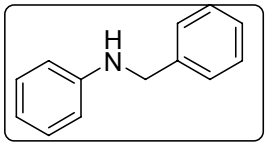
***N*-phenylpropionamide** (Table 1, entry 16): Solid; m.p. 123-126 ^oC; ^1H NMR ($CDCl_3$, 400 MHz) δ: 1.21 (3H, t, J = 3.3 Hz), 2.25 (2H, q), 6.22 (1H, br), 7.21-7.54 (5H, m); ^{13}C NMR ($CDCl_3$, 200 MHz) δ: 15.1, 28.6, 124.8, 127.7, 128.5, 138.6, 173.4; HR-MS Calcd for $C_9H_{11}NaNO$: 172.0738; found: 172.0728 $[M+Na]^+$.



***N*-Isopentylbenzeneamine** (Table 1, entry 17) ^1H NMR ($CDCl_3$, 400 MHz) δ: 1.01 (6H, d, J = 4.8 Hz), 1.53 (2H, m), 1.78 (1H, m), 3.51 (2H, m), 6.41-6.62 (5H, m); ^{13}C NMR ($CDCl_3$, 200 MHz): 21.6, 24.8, 41.1, 43.4, 112,9, 119.8, 132.0, 139.9; HR-MS Calcd for $C_{11}H_{17}NNa$: 186.1259; found: 186.1269 $[M+Na^+]$.



***N*-benzylbenzenamine** (Table 1, entry 18): ^1H NMR ($CDCl_3$, 400 MHz) δ: 4.16 (2H, d), 5.42 (1H, br), 6.61-6.83 (10 H, m); ^{13}C NMR ($CDCl_3$, 200 MHz): δ 46.2, 113.1, 118.5, 125.5, 127.6, 127.9, 128.8, 139.8, 141.0; HR-MS Calcd for $C_{13}H_{13}NNa$: 206.0946; found: 206.0955 $[M+Na^+]$.



Physical data for the products listed in Table 2 of the MS

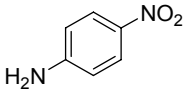
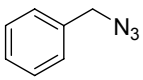
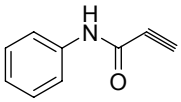
Entry	Product	m.p.(^oC)		HPLC
		Reported	Obtained	Purity
1	H-Phe-OH	270-275	272-276	99%
2	H-Lys(Boc)OH	250 (dec)	249 (dec)	97%
3	Fmoc-Pro-OH	117-118	115-116	98%

4	Fmoc-Leu-OH	152-156	155-158	100%
5	Boc-Asp-OH	116-118	114-117	95%
6	Boc-His-OH	195	197-198	92%
7	Boc-Tyr-OH	133-135	133-134	100%
8	Boc-Thr-OMe	----	Gum	91%
9	H-Glu-OH	205	205-207	100%
10	Ala(Oxa)	----	122-126	94%

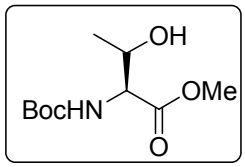
Recycling efficiency of PVC-Pd^0

Substrate	**Reduction efficieny (isolated yield, duration in min)**			
	Fresh catalyst	**Catalyst recovered after 1st cycle**	**Catalyst recovered afer 2nd cycle**	**Catalyst recovered afer 3rd cycle**
Benzaldehyde	100%, 30 min	100%, 30 min	98%, 35 min	92%, 40 min
O-nitrophenol	95%, 35 min	94%, 35 min	95%, 40 min	90%, 40 min

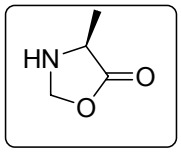
Issultrative examples for comparision of efficiency of PVC-Pd^0 over Pd/C

Substrate	**Reduction yield, duration**	
	With PVC-Pd^0	**With Pd/C**
	99%, 35 min	100%, 2.0 h
	96%, 35 min	97%, 2.5 h
	94%, 60 min	82%, 4.2 h
Z-Phe-OH	100%, 30 min	95%, 2.5 h
Z-Glu(OBzl)OH	98%, 80 min	78%, 4.1 h
Z-Ala-Asp(OBzl)-Ser-Gly-OH	78%, 110 min	65%, 5.2 h

Boc-Thr-OMe (Table 2, entry 8) Gum; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 1.19 (3H, d, *J* = 5.2 Hz), 1.27 (9H, s), 3.41 (1H, m), 3.57 (3H, s), 4.21 (1H, m); ^{13}C NMR ($CDCl_3$, 200 MHz): δ 18.3, 27.9, 53.3, 58.2, 65.9, 80.6, 155.3, 172.0; ESI-MS: Calc for $C_{10}H_{19}NO_5$: 233.2; found: 234.5 $[M+H]^+$.



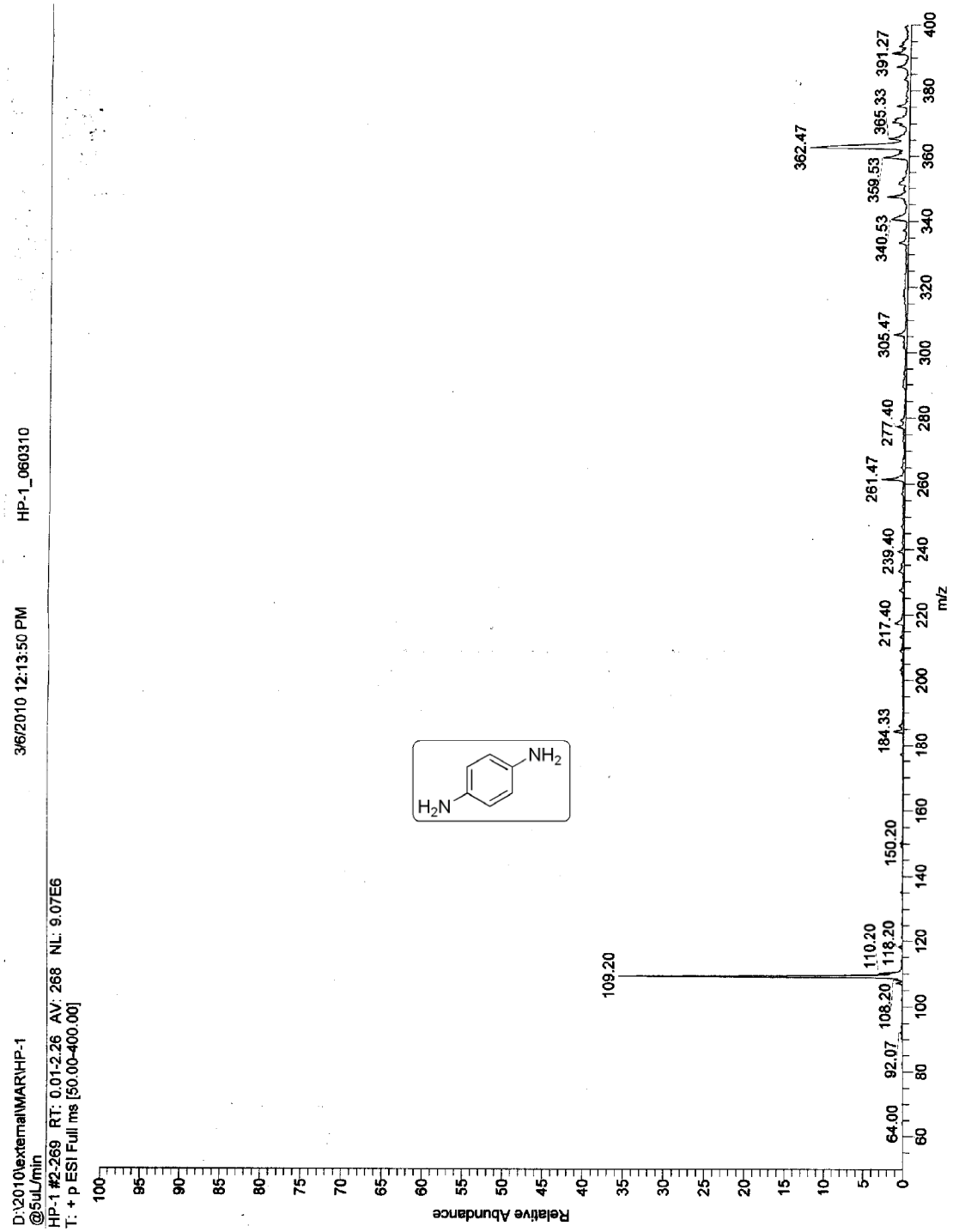
Ala(Oxa) (Table 2, entry 10): Solid; m.p. 122-126 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 1.65 (3H, d, *J* = 5.6 Hz), 3.57 (1H, m), 4.89 (2H, s); ^{13}C NMR ($CDCl_3$, 200 MHz): δ 16.9, 62.6, 79.3, 176.3; HR-MS Calcd for $C_4H_8NO_2$: 102.0555; found 102.0575 $[M+H]^+$.



Fmoc-MeLeu-MeLeu-OH (Table 3, entry 1): Solid; m.p. 116-119 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 0.93 (6H, d, *J* = 5.63 Hz), 1.01 (6H, d, *J* = 4.8 Hz), 1.65-1.72 (4H, m), 1.79-1.83 (2H, m), 3.07 (6H, s), 3.92 (2H, m), 4.11 (1H, t, *J* = 3.2 Hz), 4.27 (2H, d, *J* = 5.5 Hz), 6.92-7.34 (8H, m), 11.01 (1H, s); HR-MS Calcd for $C_{28}H_{38}N_2NaO_5$: 517.2678; found: 517.2689 $[M+Na]^+$.

Fmoc-MeLeu-Val-MeLeu-Ala-OH (Table 3, entry 2): ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 0.78-0.96 (18H, m), 1.33 (3H, d, *J* = 6.6 Hz), 1.45 (1H, m), 1.65 (4H, m), 1.87 (2H, m), 3.11 (6H, s), 3.77-3.82 (4H, m), 4.13-4.24 (3H, m), 6.47 (2H, br), 7.10-7.44 (8H, m), 10.56 (1H. s); ESI-MS: Cacld for $C_{37}H_{52}N_4O_7$: 664.3; found 687.2 $[M+Na^+]$.

H-Leu-Phe-Gly-Gly-Arg-OMe (Table 3, entry 6): ^{1}H NMR (DMSO, d_6, 400 MHz) δ: 0.91 (6H, d, *J* = 6.2 Hz), 1.53-1.65 (4H, m), 1.76 (2H, m), 1.83 (1H, m), 2.11 (2H, br), 2.40 (2H, m), 2.78 (2H, d, *J* = 5.2 Hz), 3.51-3.57 (2H, m), 3.75 (3H, s), 4.11-4.23 (4H, m), 4.45 (1H, m), 6.53-6.78 (5H, br), 7.12 (5H, m), 9.37 (2H, br); ^{13}C NMR (DMSO, d_6, 200 MHz): 19.6, 21.1, 24.6, 28.3, 35.2, 37.8, 42.3, 44.6, 45.6, 51.6, 54.0, 55.3, 55.6, 126.9, 127.2, 128.2, 139.4, 156.3, 169.6, 170.6, 172.3, 173.3, 174.1; HRMS Calcd for $C_{26}H_{42}N_8NaO_6$: 585.3125; found: 585.3135 $[M+Na]^+$.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HP-1_060310
Relative Abundance
m/z
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H2N
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110.20
118.20
108.20
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64.00
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277.40
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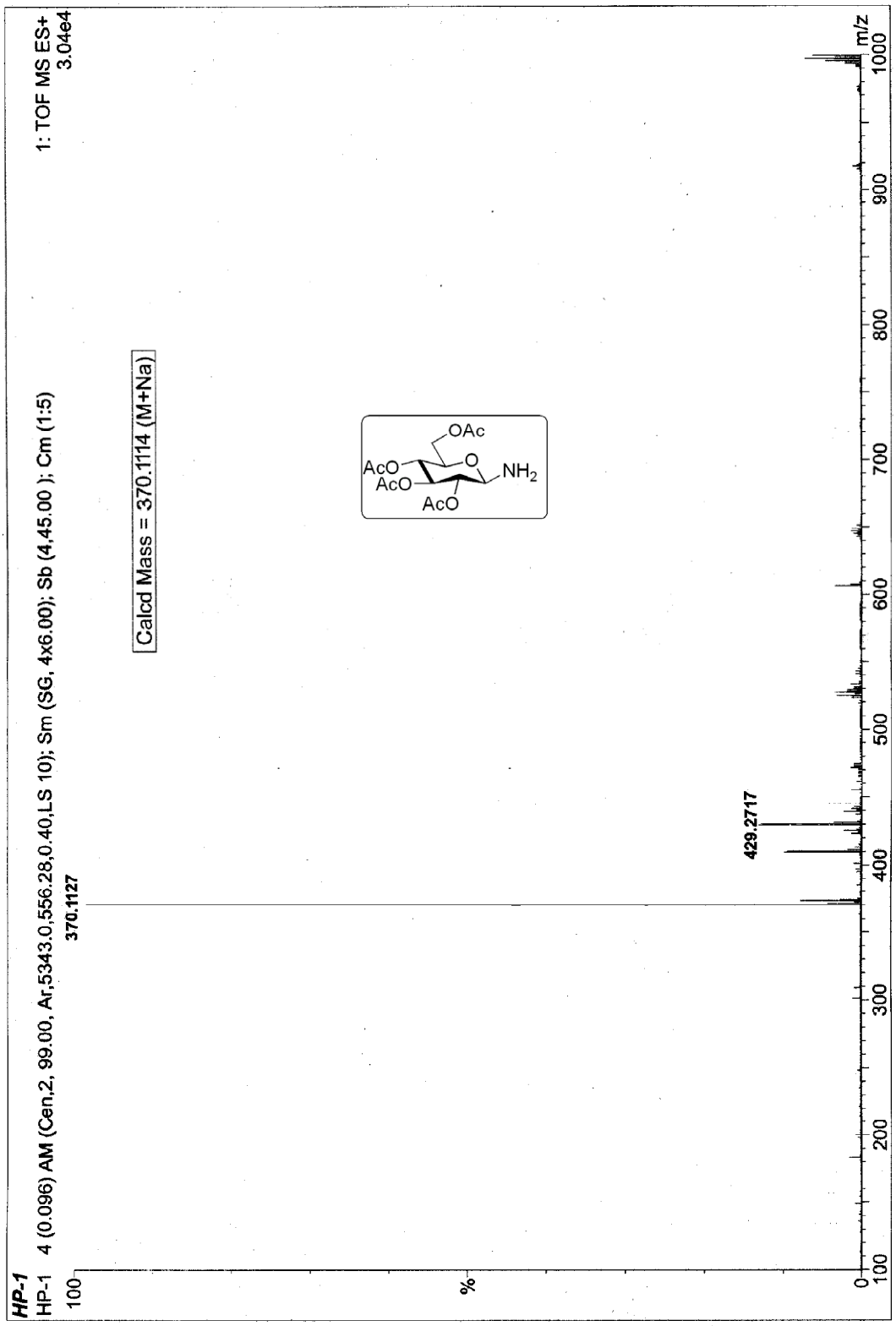
359.53
362.47
365.33
391.27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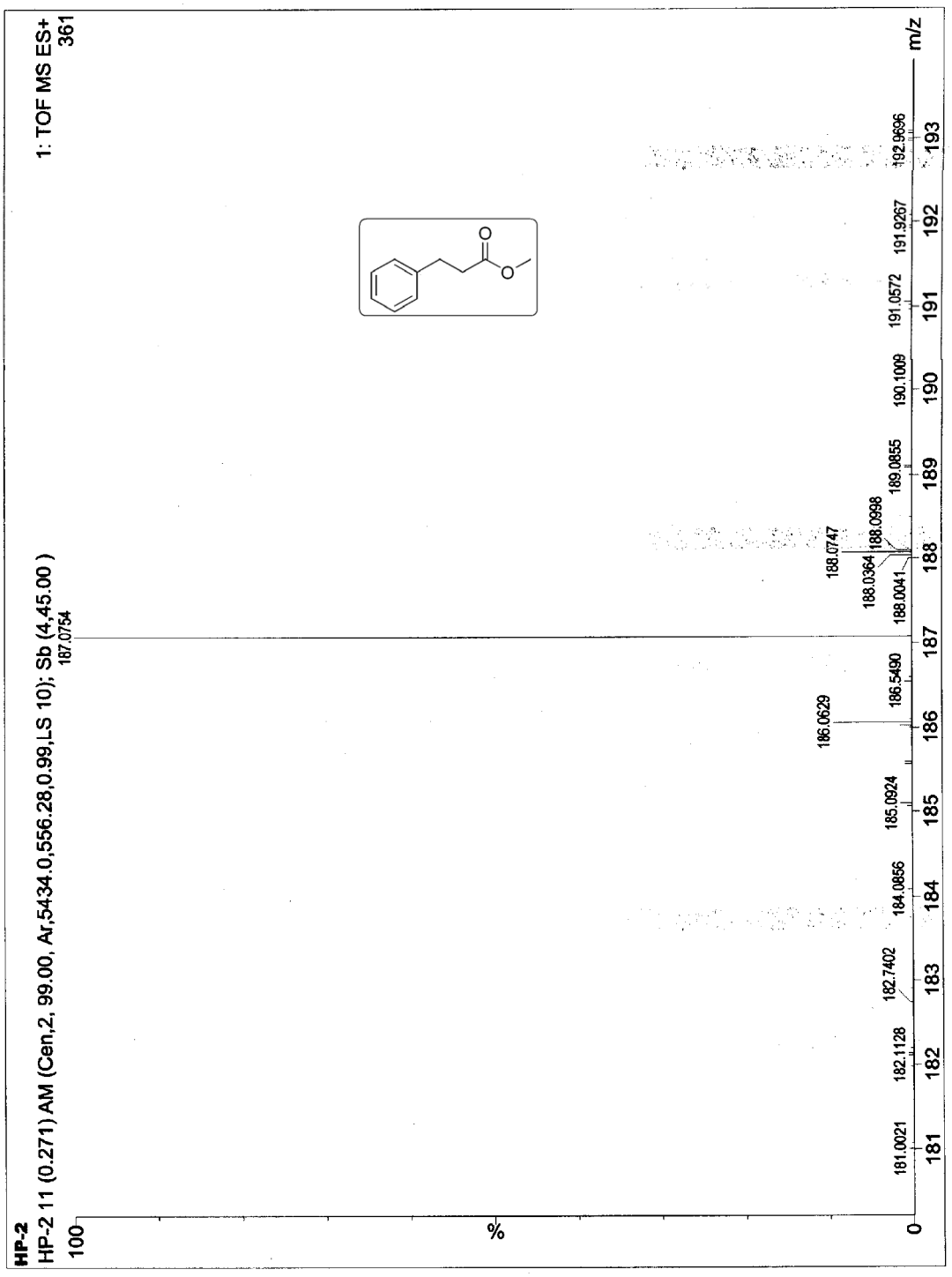
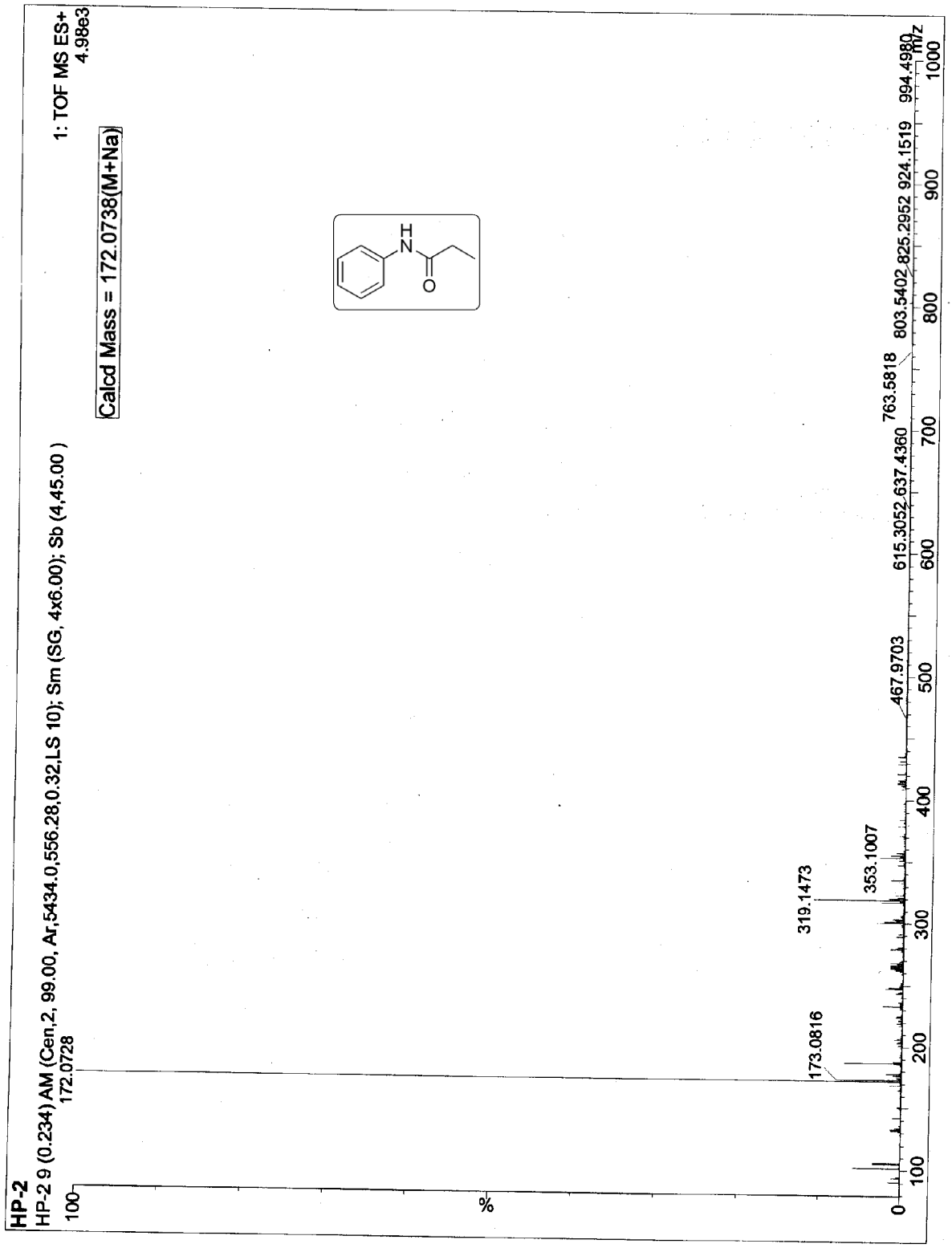
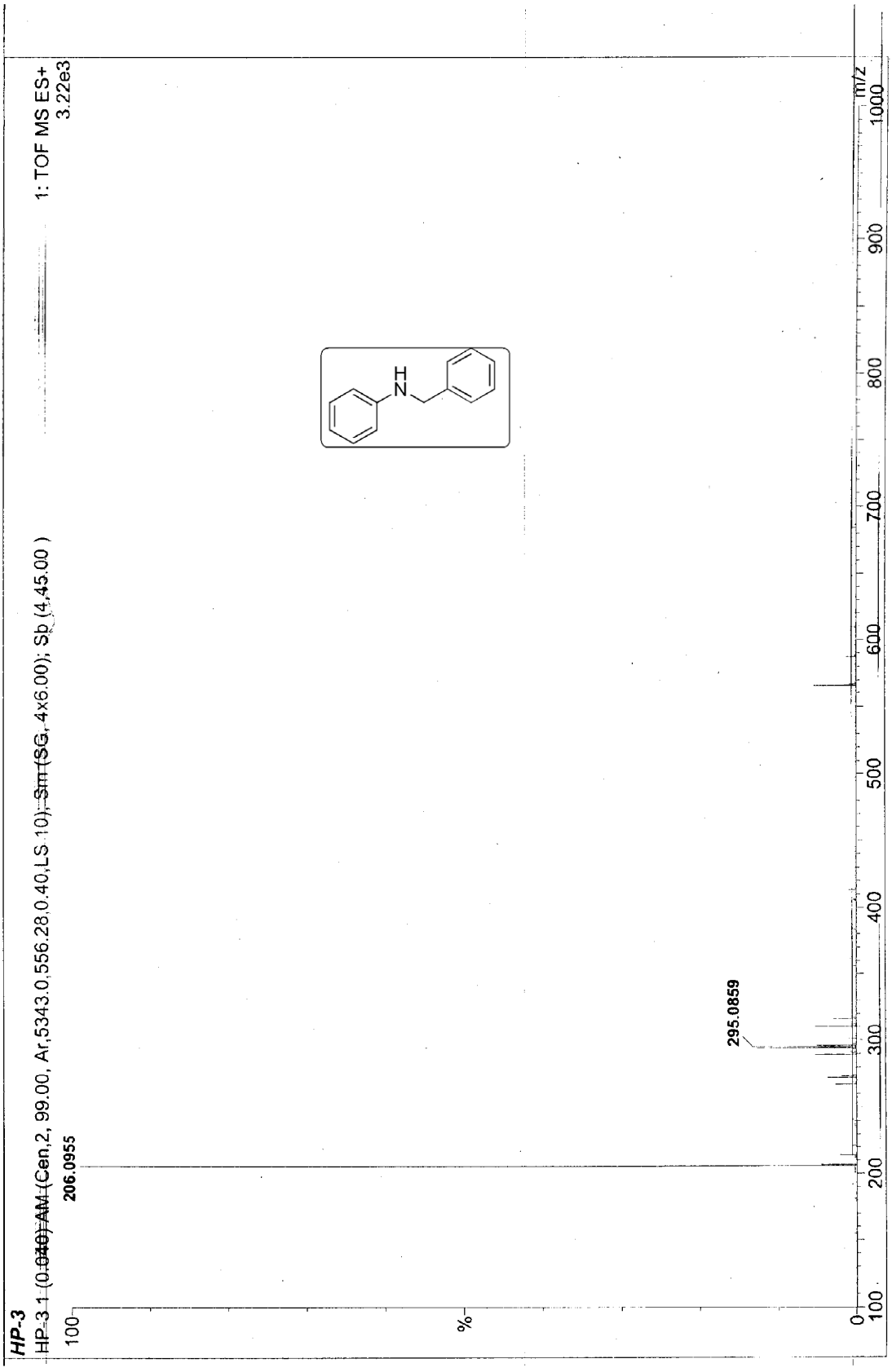
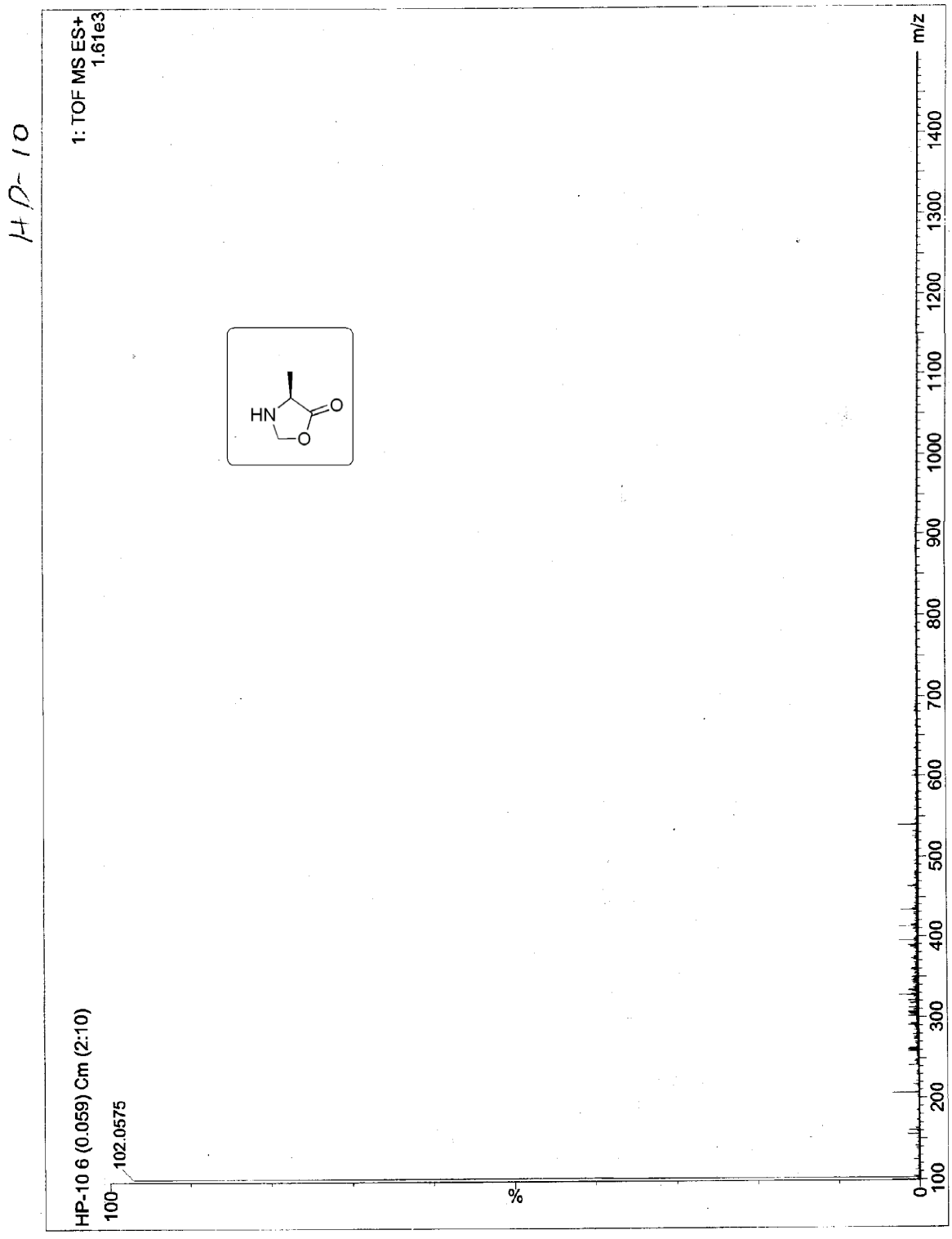
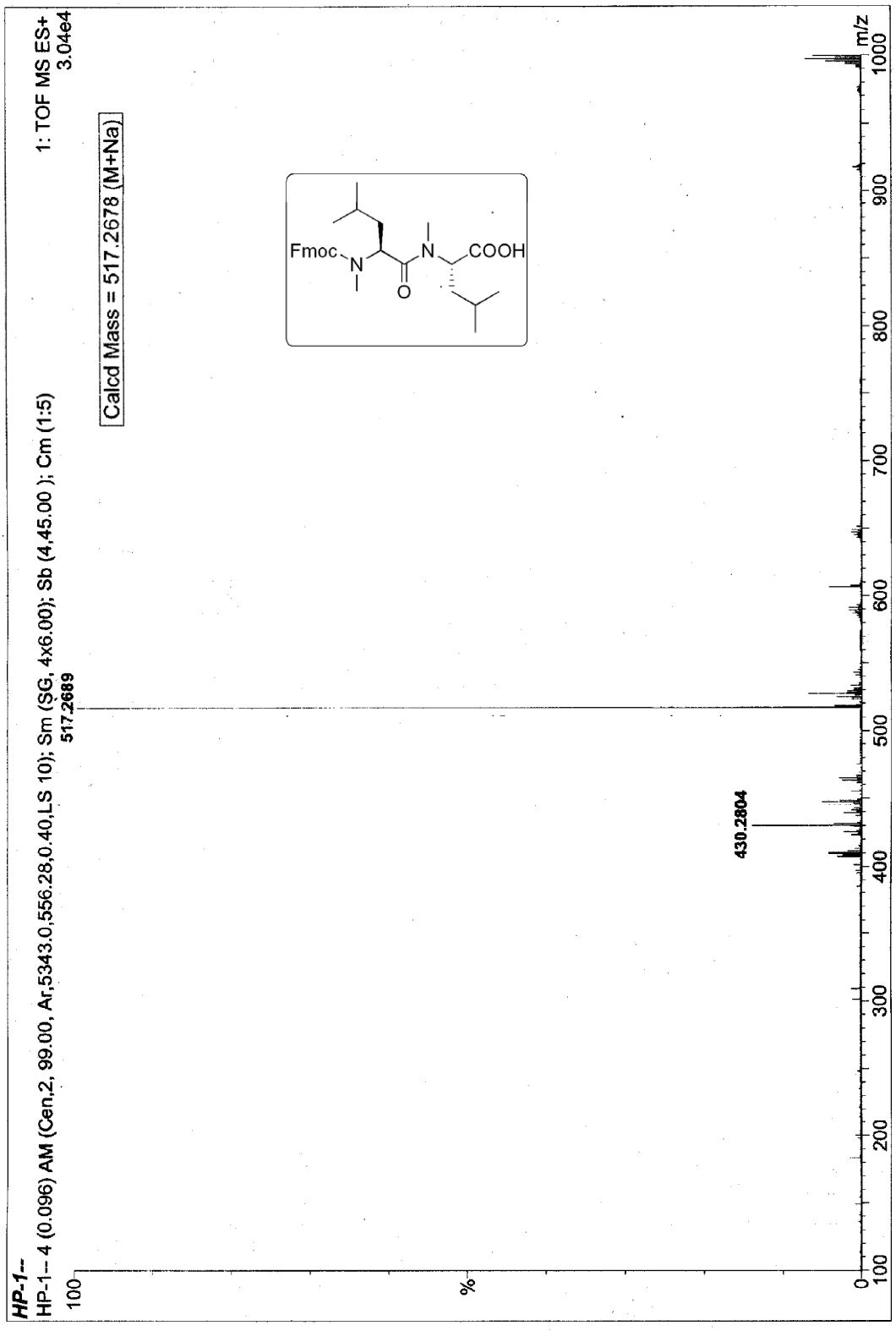
370.1127
429.2717
Calcd Mass = 370.1114 (M+Na)
OAc
AcO
AcO
AcO
O
NH2
%
m/z
100
0
100
200
300
400
500
600
700
800
900
1000

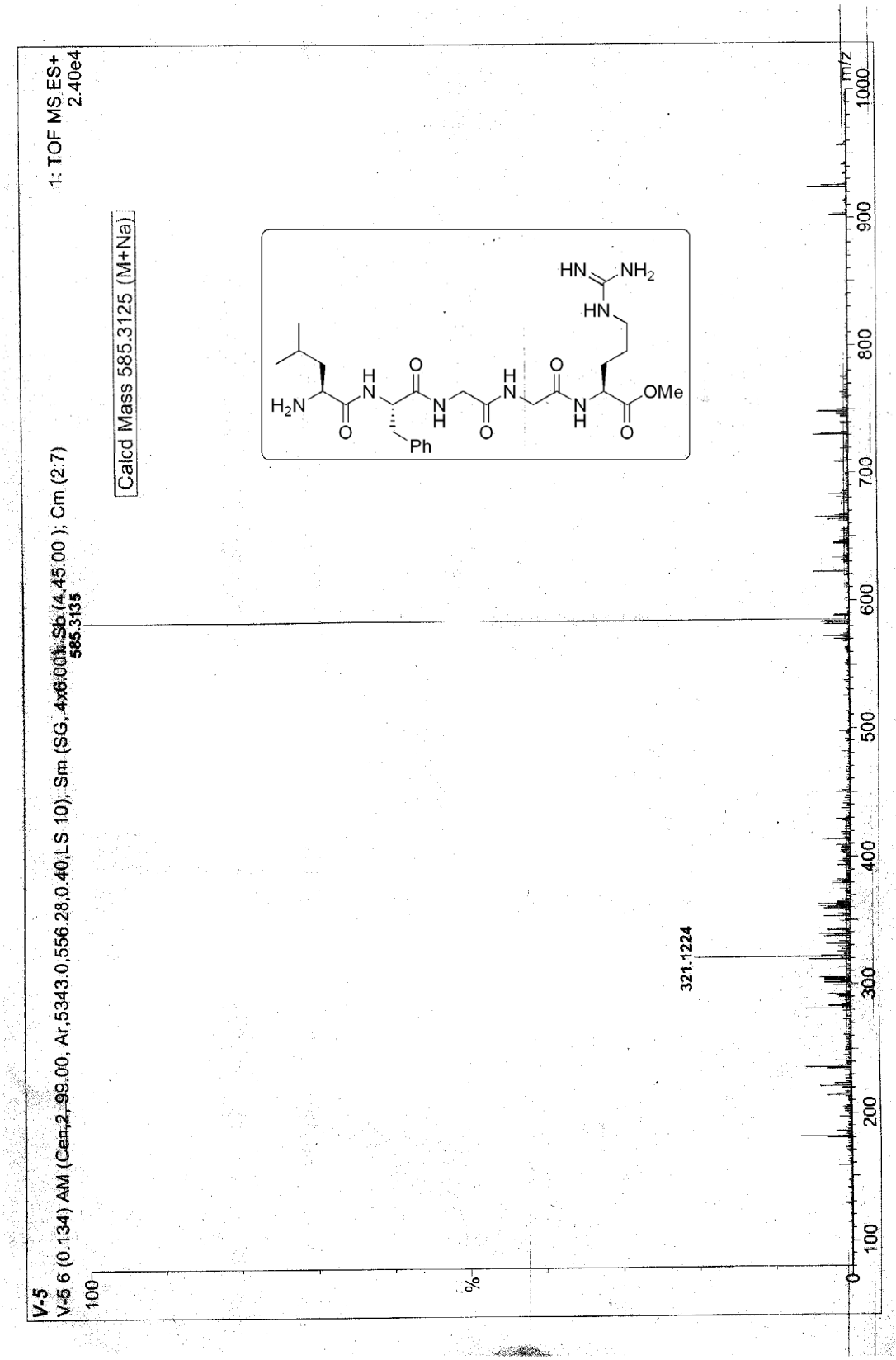

HP-2
HP-2 11 (0.271) AM (Cen,2, 99.00, Ar,5434.0,556.28,0.99,LS 10); Sb (4,45.00)
1: TOF MS ES+
361
187.0754
188.0747
186.0629
188.0364
188.0998
188.0041
186.5490
189.0855
185.0924
190.1009
184.0856
191.0572
182.7402
191.9267
182.1128
192.9696
181.0021
100
%
0
m/z
181
182
183
184
185
186
187
188
189
190
191
192
193

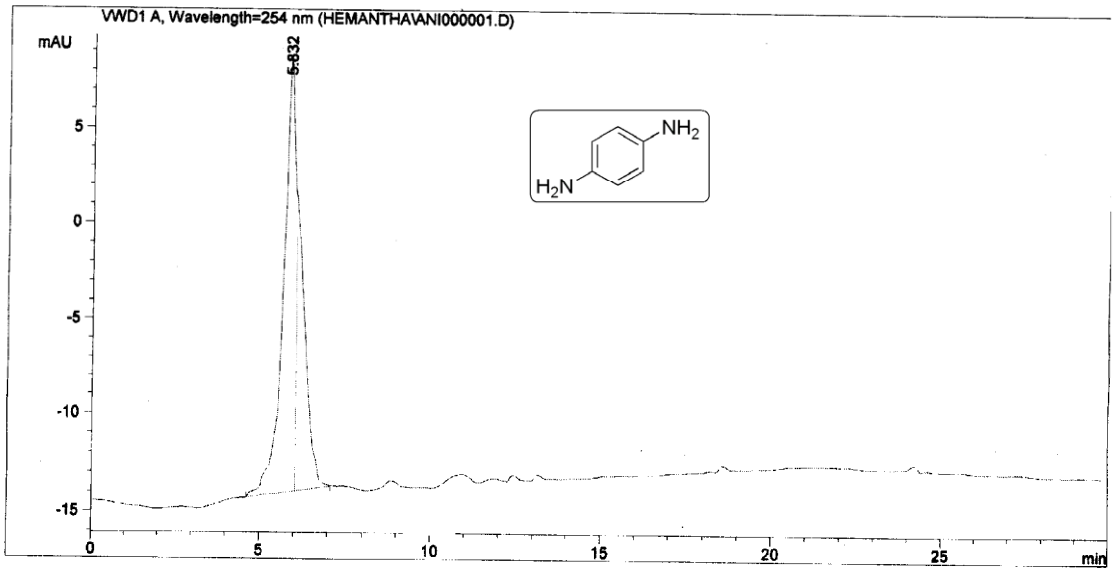

HP-2
HP-2 9 (0.234) AM (Cen,2, 99.00, Ar,5434.0,556.28,0.32,LS 10); Sm (SG, 4x6.00); Sb (4,45.00)
1: TOF MS ES+
4.98e3
Calcd Mass = 172.0738(M+Na)
H
N
O
172.0728
173.0816
319.1473
353.1007
467.9703
615.3052
637.4360
763.5818
803.5402
825.2952
924.1519
994.4980
100
%
0
100
200
300
400
500
600
700
800
900
1000
m/z

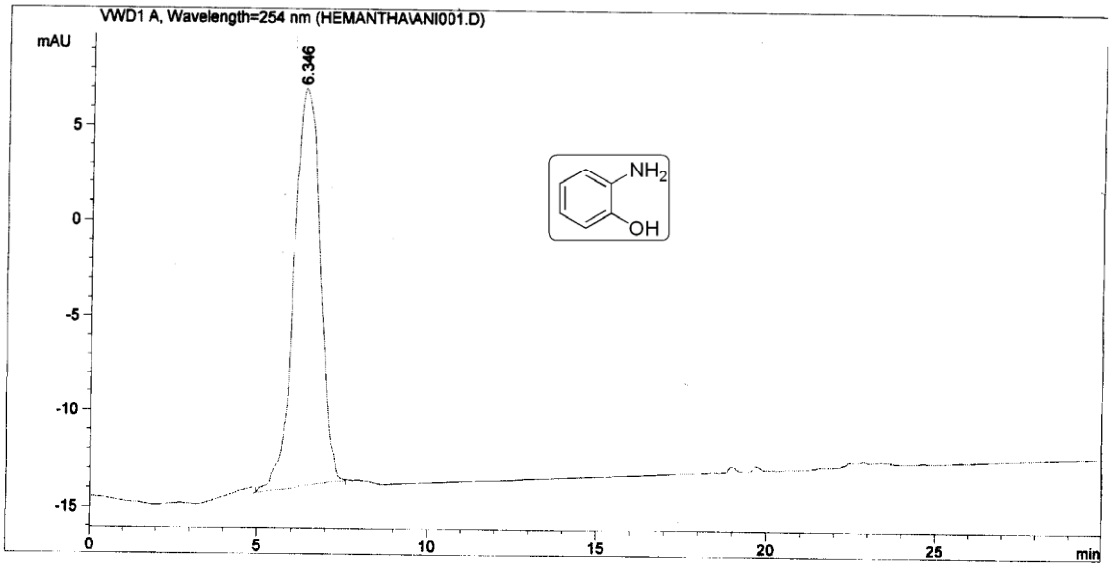

HP-3
HP-3 1 (0.040) AM (Cen,2, 99.00, Ar,5343.0,556.28,0.40,LS 10); Sm (SG, 4x6.00); Sb (4,45.00)
1: TOF MS ES+
3.22e3
206.0955
295.0859
%
m/z
100
0
100
200
300
400
500
600
700
800
900
1000

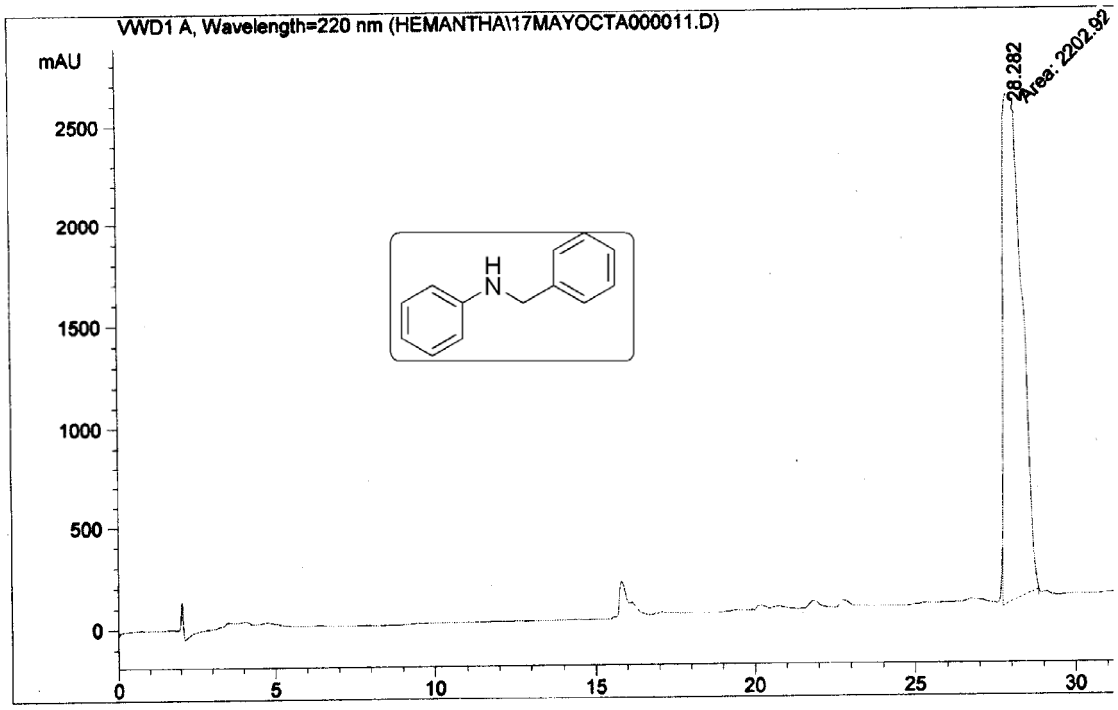

HP-10
1: TOF MS ES+
1.61e3
HP-10 6 (0.059) Cm (2:10)
100
102.0575
%
m/z
HN
O
O
0
100
200
300
400
500
600
700
800
900
1000
1100
1200
1300
1400

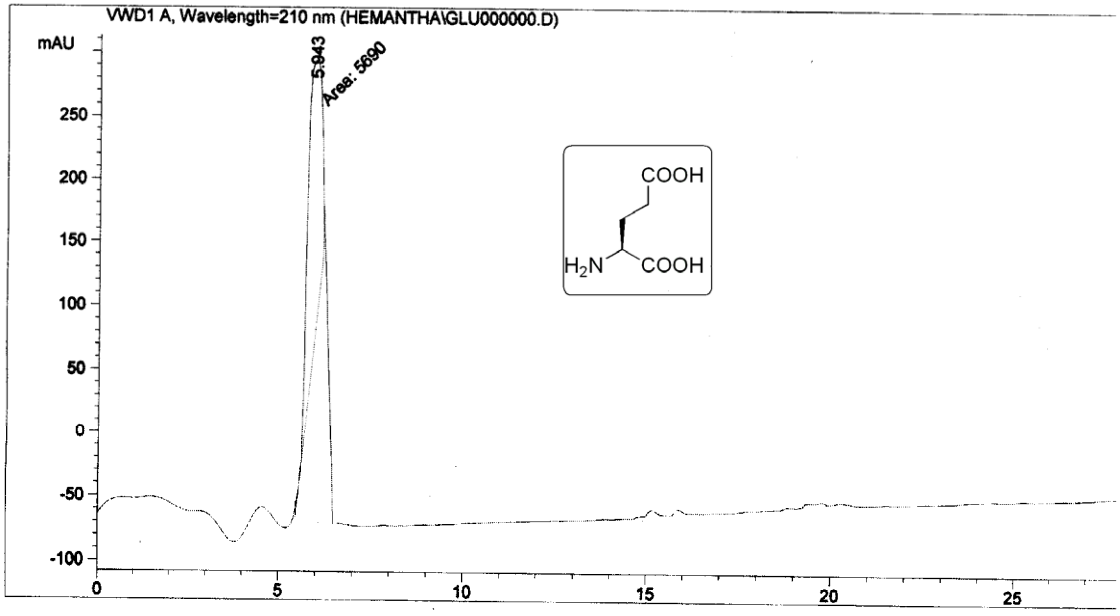

HP-1--
HP-1-- 4 (0.096) AM (Cen,2, 99.00, Ar,5343.0,556.28,0.40,LS 10); Sm (SG, 4x6.00); Sb (4,45.00); Cm (1:5)
1: TOF MS ES+
3.04e4
Calcd Mass = 517.2678 (M+Na)
517.2689
430.2804
Fmoc
N
N
COOH
O
100
%
0
100
200
300
400
500
600
700
800
900
1000
m/z

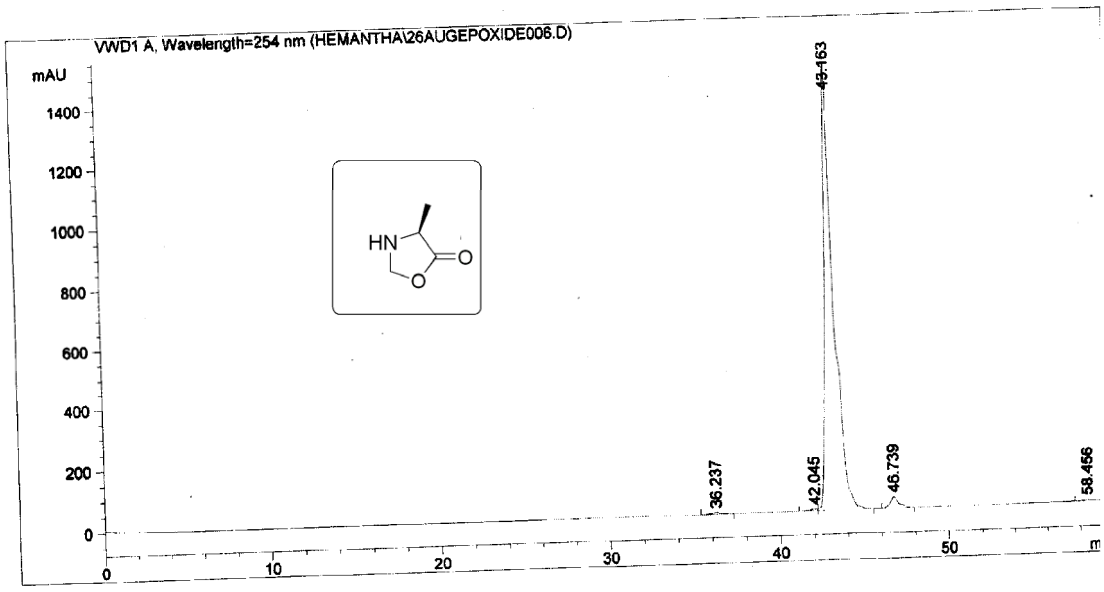

V-5
V-5 6 (0.134) AM (Cen,2, 99.00, Ar,5343.0,556.28,0.40,LS 10); Sm (SG, 4x6.00); Sb (4,45.00); Cm (2:7)
1: TOF MS ES+
2.40e4
Calcd Mass 585.3125 (M+Na)
585.3135
321.1224
100
%
0
100
200
300
400
500
600
700
800
900
1000
m/z
HN
NH2
HN
H2N
O
H
N
Ph
OMe

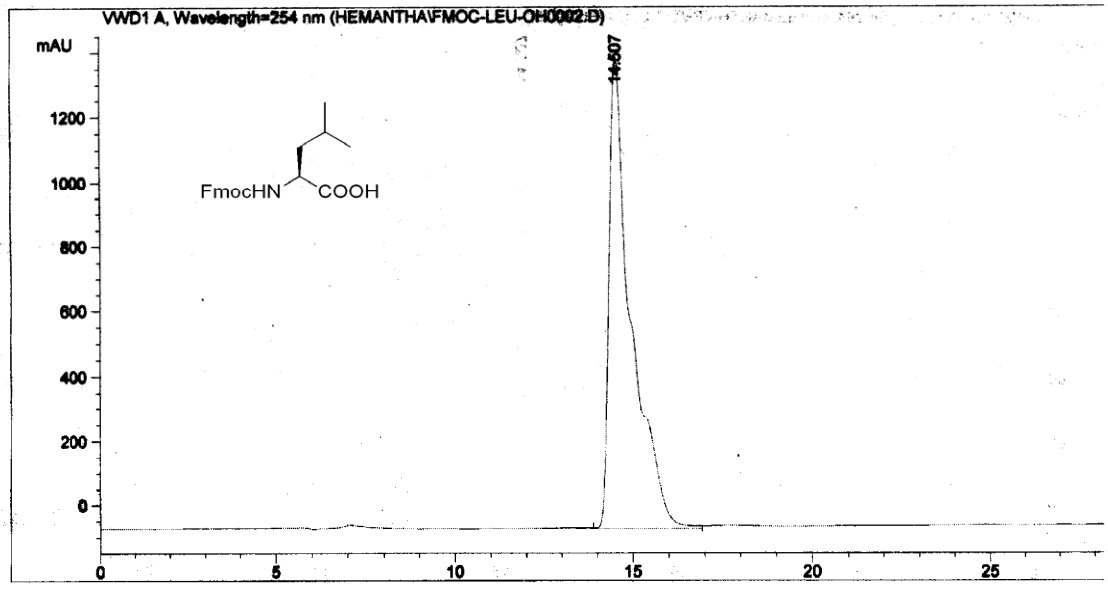

VWD1 A, Wavelength=254 nm (HEMANTHA\ANI000001.D)
mAU
5.832
5
0
-5
-10
-15
0
5
10
15
20
25
min
NH2
H2N

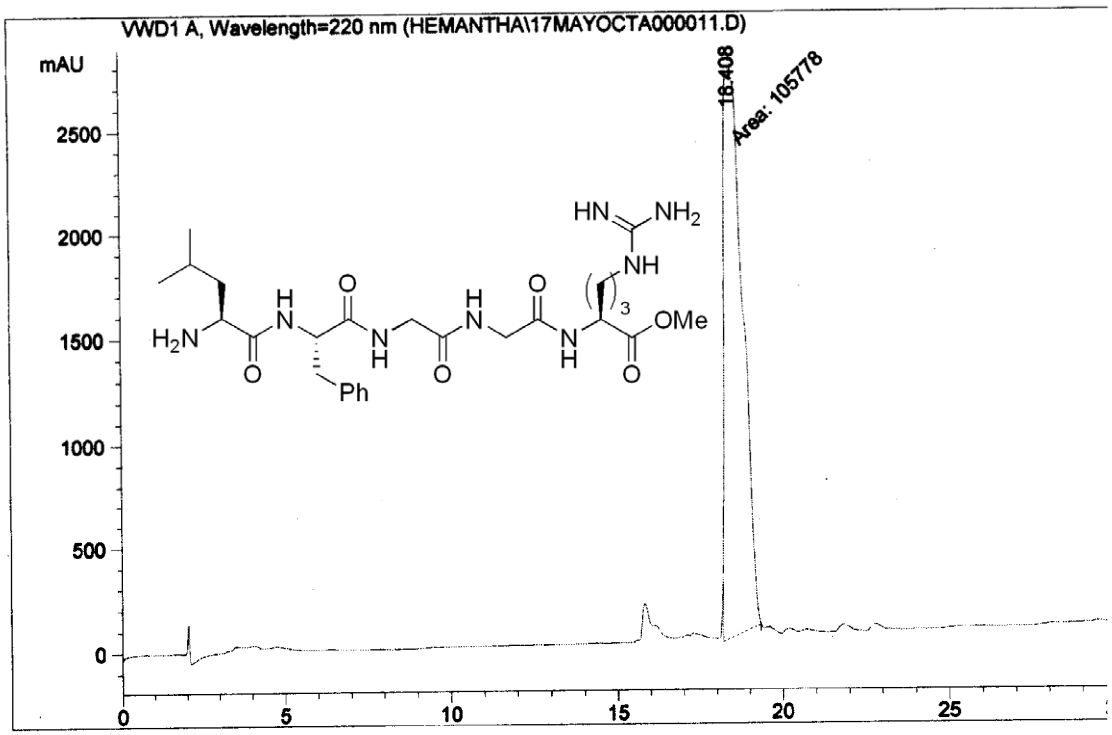

VWD1 A, Wavelength=254 nm (HEMANTHA\ANI001.D)
mAU
6.346
5
0
-5
-10
-15
0
5
10
15
20
25
min
NH2
OH

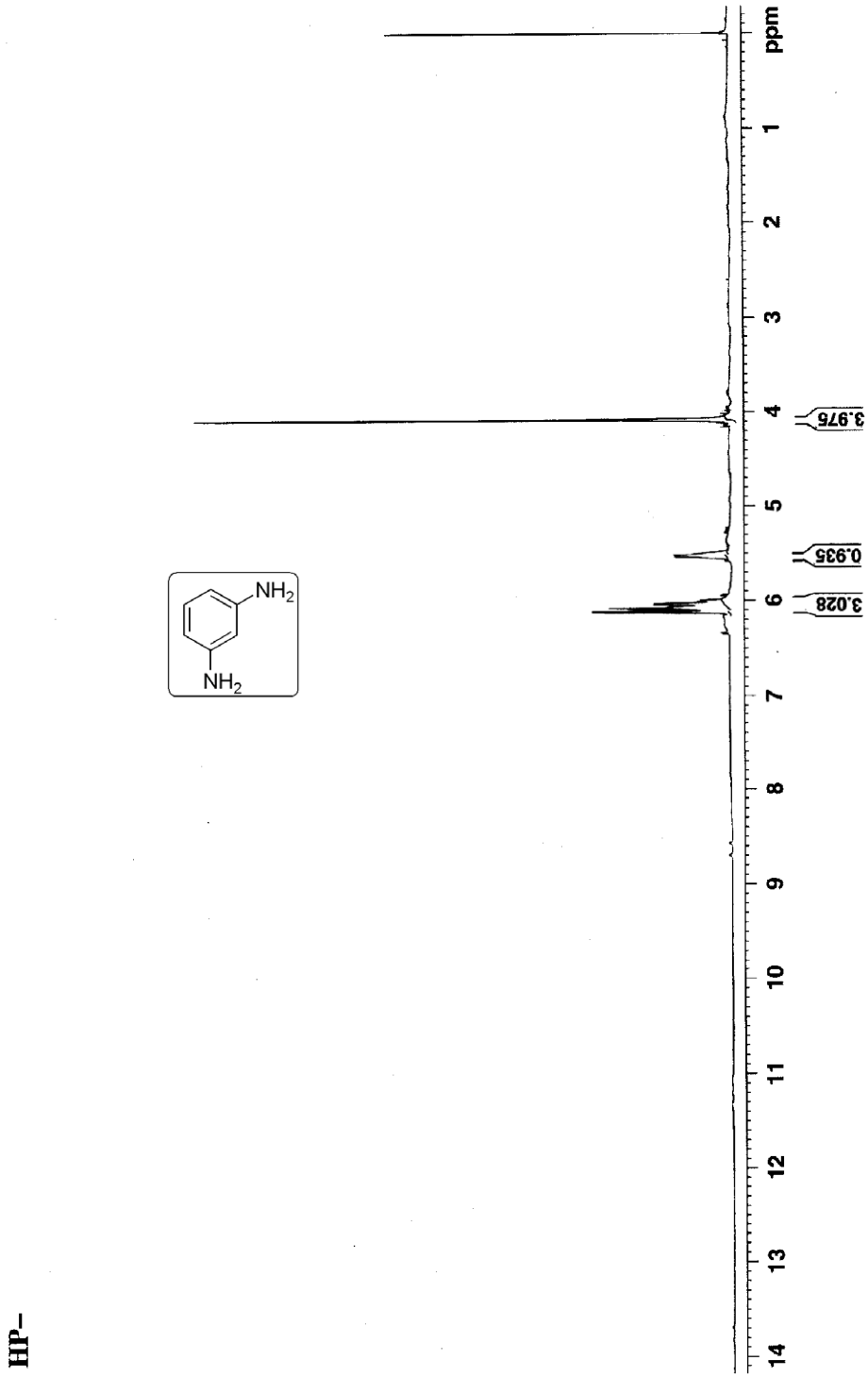

VWD1 A, Wavelength=220 nm (HEMANTHA\17MAYOCTA000011.D)
mAU
2500
2000
1500
1000
500
0
0
5
10
15
20
25
30
28.282
Area: 2202.92
H
N

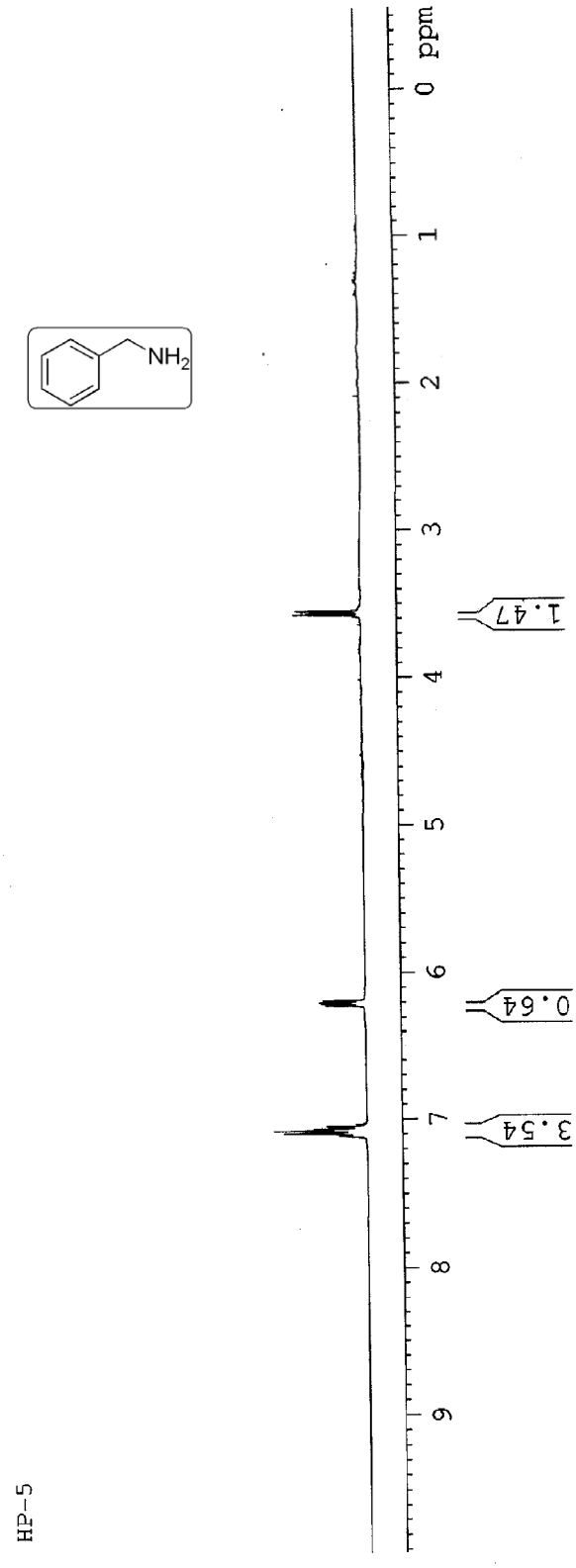

VWD1 A, Wavelength=210 nm (HEMANTHA\GLU000000.D)
mAU
250
200
150
100
50
0
-50
-100
0
5
10
15
20
25
5.943
Area: 5690
COOH
H2N
COOH

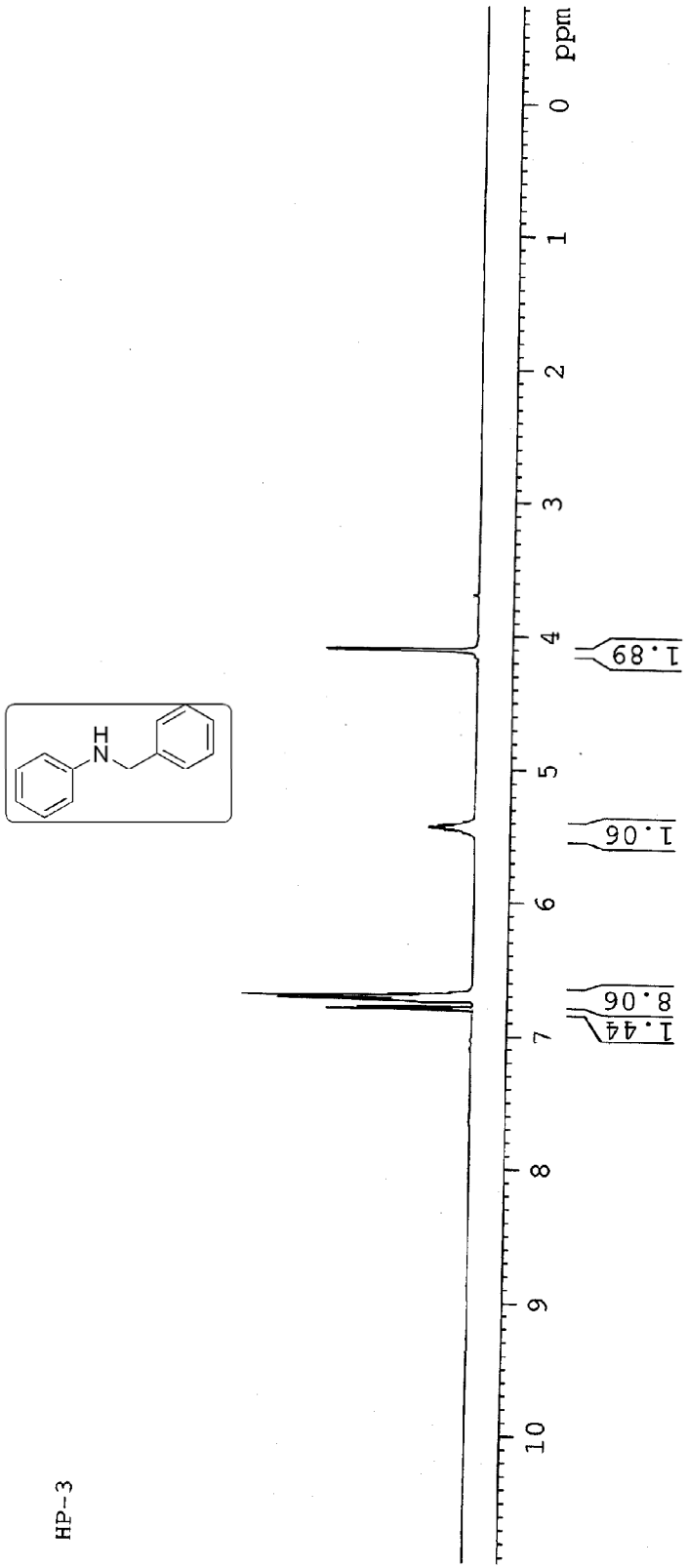

VWD1 A, Wavelength=254 nm (HEMANTHA\26AUGEPOXIDE006.D)
mAU
1400
1200
1000
800
600
400
200
0
HN
O
O
36.237
42.045
43.163
45.739
58.456
0
10
20
30
40
50

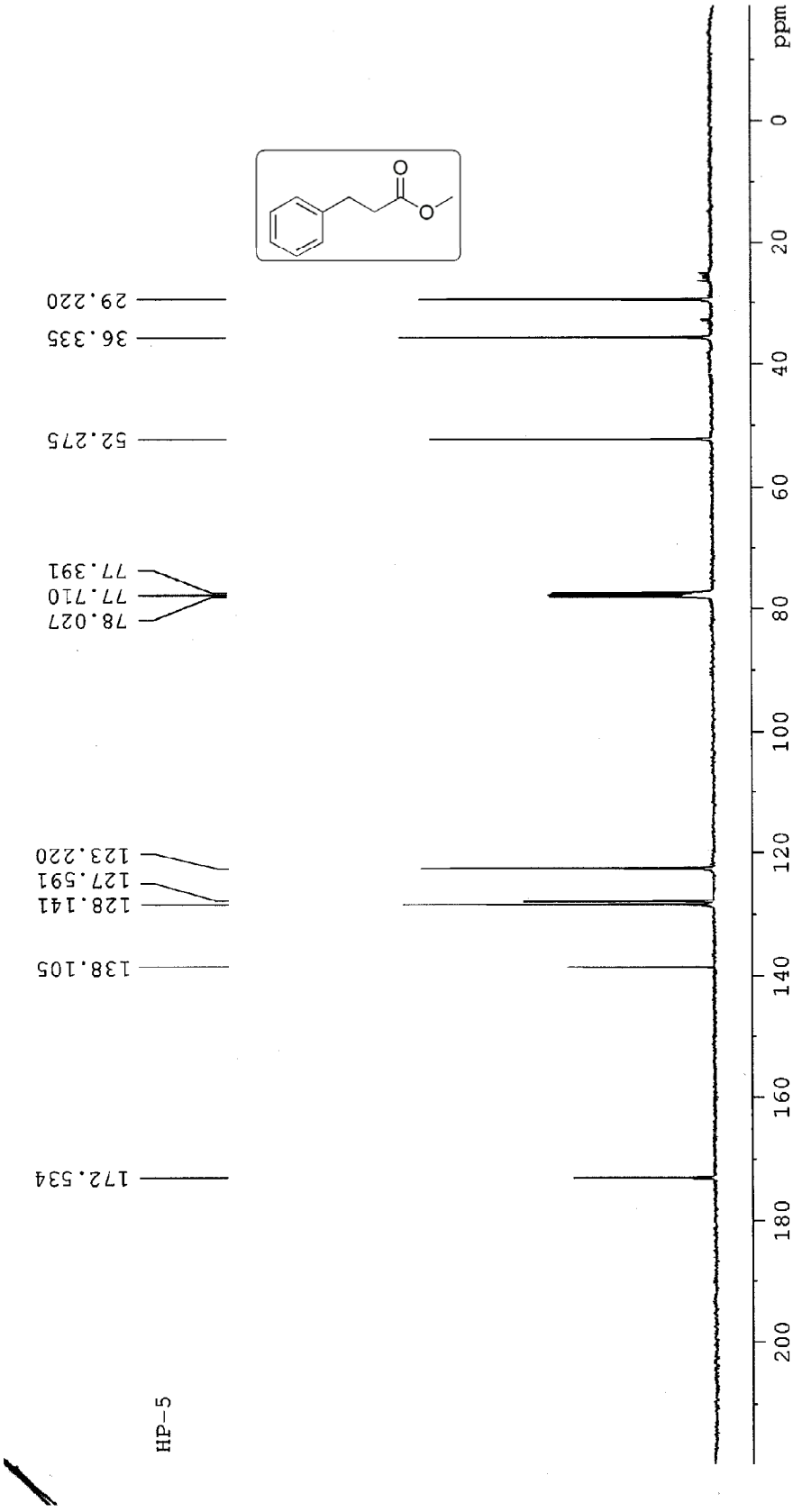

VWD1 A, Wavelength=254 nm (HEMANTHA\FMOC-LEU-OH0002.D)
mAU
1200
1000
800
600
400
200
0
FmocHN
COOH
14.507
0
5
10
15
20
25

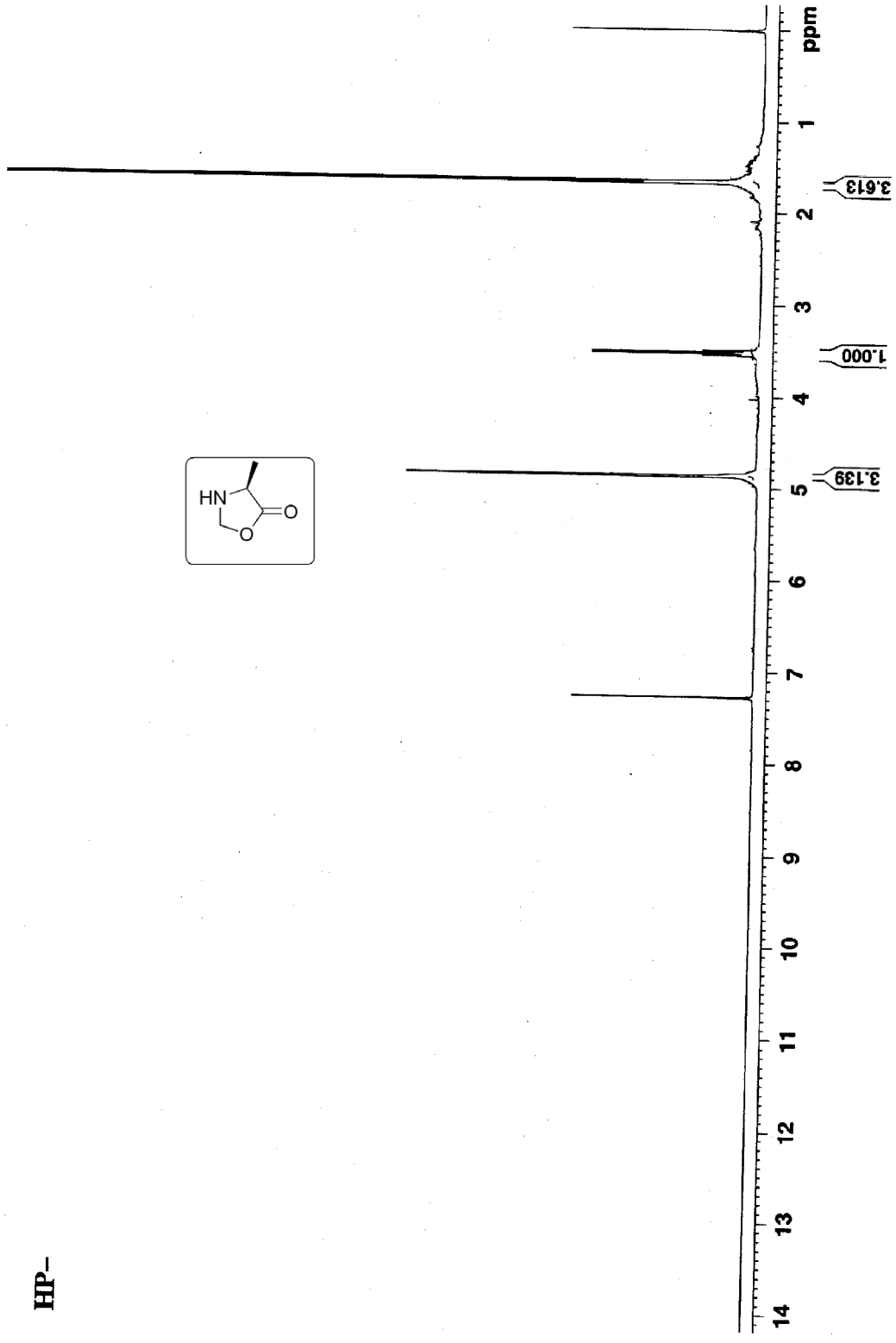

VWD1 A, Wavelength=220 nm (HEMANTHA\17MAYOCTA000011.D)
mAU
2500
2000
1500
1000
500
0
0
5
10
15
20
25
16.408
Area: 105778
HN
NH2
NH
3
OMe
H2N
Ph

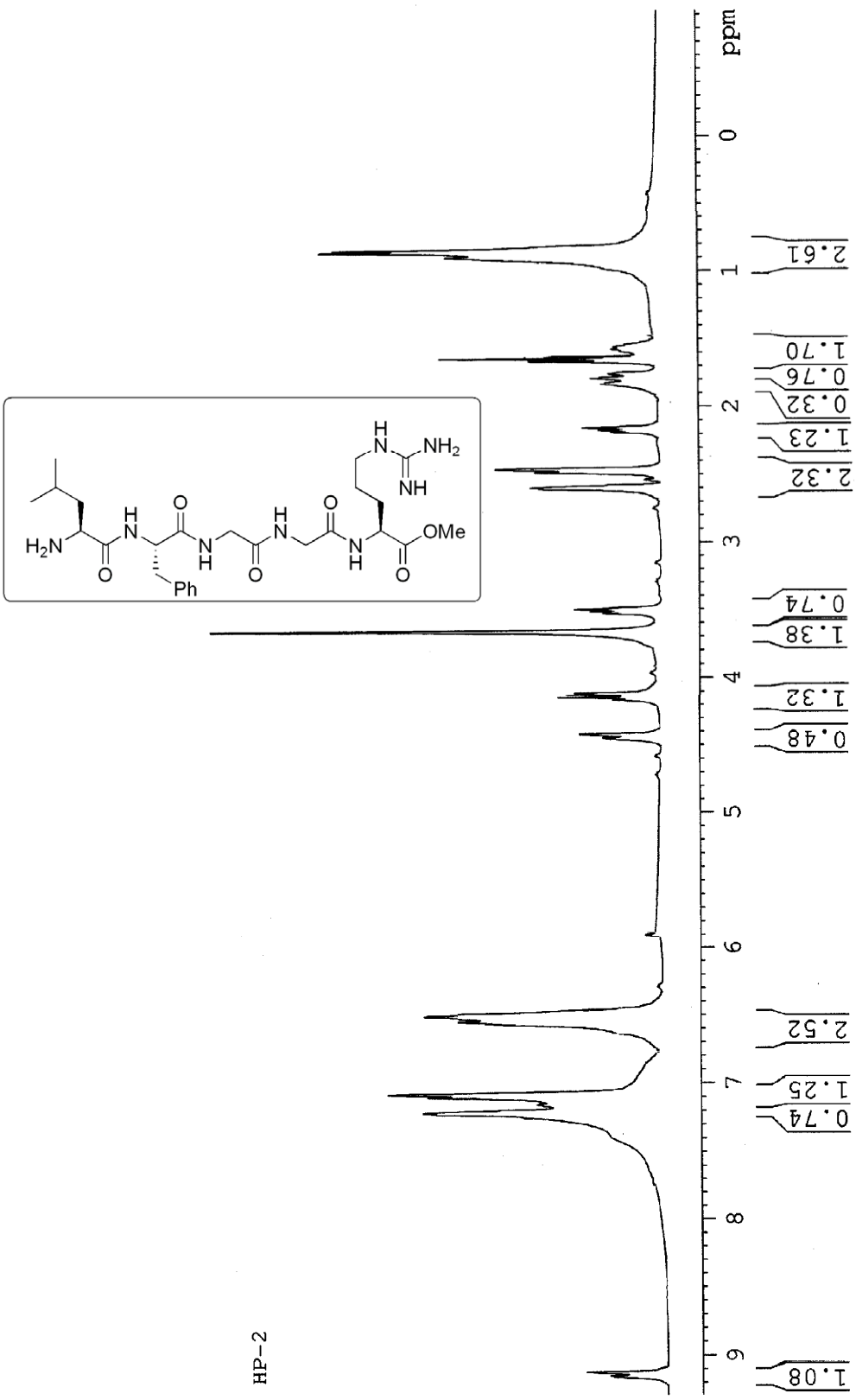

HP-
NH2
NH2
3.976
0.935
3.028
ppm
1
2
3
4
5
6
7
8
9
10
11
12
13
14


NH2
ppm
0
1
2
3
4
5
6
7
8
9
1.47
0.64
3.54
HP-5


HP-3
ppm
0
1
2
3
4
5
6
7
8
9
10
1.89
1.06
8.06
1.44


ppm
0
20
40
60
80
100
120
140
160
180
200
O
O
29.220
36.335
52.275
77.391
77.710
78.027
123.220
127.591
128.141
138.105
172.534
HP-5


HP-
ppm
3.613
1.000
3.139
HN
O
O


HP-2
ppm
0
1
2
3
4
5
6
7
8
9
2.61
1.70
0.76
0.32
1.23
2.32
0.74
1.38
1.32
0.48
2.52
1.25
0.74
1.08
H2N
O
H
N
O
Ph
N
H
O
H
N
O
N
H
O
H
N
NH2
NH
OMe
O