Supporting Information

Energy-Resolved Mass Spectrometry to investigate nucleobase triplexes - a study applied to triplex-forming artificial nucleobase

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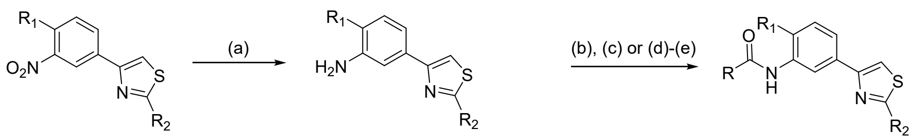
Synthesis

General procedure for the reduction of nitro group. To a suspension of corresponding nitro-aryl (1 eq) and Pd/C – 10% (10% wt.) in methanol (0.01 M), under stirring and at 0°C, was added carefully by portions sodium borohydride (5 eq). The reaction mixture was stirred at 0°C until complete dissolution of sodium borohydride and was then allowed to react at r.t. The crude mixture was filtered through a pad of celite, concentrated under reduced pressure and purified by silica gel column chromatography to afforded corresponding amino product.

General procedure for the amide synthesis. To a solution of the corresponding anilines (1 equiv) under argon in anhydrous pyridine (0.3 M) was added the corresponding acyl chloride or anhydride (1.1 equiv). The reaction mixture was allowed to react at rt until complete conversion of the starting material (approximately 2h), and pyridine was removed under reduced pressure. The crude material was dissolved in 50 mL of ethyl acetate. The aqueous layer was washed twice with 1 M aq HCL solution (50 mL), then washed two times with saturated aq $NaHCO_3$ solution (50 mL) and brine (50 mL) and dried with $MgSO_4$ to afford the corresponding amide

General procedure for the urea synthesis. To a solution of 2-methylbenzo[d]oxazol-5-amine **3** (0.55 mmol, 1 eq.) in anhydrous DCM (0.05 M) was added the corresponding isocyanate (0.66 mmol, 1.2 eq.) and the mixture was stirred for 2 hours at room temperature. The formed precipitate was removed by filtration and washed with DCM (3 × 5 mL) to afford the corresponding urea as light solids.

Scheme 1. Synthetic route to **S** nucleobase analogues $\mathbf{S_{1\text{-}9}}$



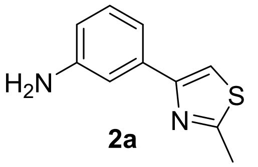
1a R_1 = H; R_2 = CH_3
1b R_1 = H; R_2 = NHAc
1c R_1 = F; R_2 = NHAc

2a R_1 = H; R_2 = CH_3
$\mathbf{S^{*}_{11}}$ R_1 = H; R_2 = NHAc[*J. Med. Chem.* **2016**, 59, 18, 8276]
2c R_1 = F; R_2 = NHAc

$\mathbf{S^{*}_{10}}$ R = CH_3; R_1 = H; R_2 = CH_3
$\mathbf{S_1}$ R = CH_3; R_1 = H; R_2 = NHAc
$\mathbf{S_2}$ R = pentyl; R_1 = H; R_2 = NHAc
$\mathbf{S_3}$ R = hexyl; R_1 = H; R_2 = NHAc[*J. Med. Chem.* **2016**, 59, 18, 8276]
$\mathbf{S_4}$ R = CF_3; R_1 = H; R_2 = NHAc
$\mathbf{S_5}$ R = 2-furyl; R_1 = H; R_2 = NHAc[*J. Med. Chem.* **2016**, 59, 18, 8276]
$\mathbf{S_6}$ R = 2-naphthyl; R_1 = H; R_2 = NHAc[*J. Med. Chem.* **2016**, 59, 18, 8276]
$\mathbf{S_9}$ R = CH_3; R_1 = F; R_2 = NHAc
$\mathbf{S_7}$ R = L-lysine; R_1 = H; R_2 = NHAc[*Chem. Eur. J.* **2014**, 20, 2071]
$\mathbf{S_8}$ R = L-histidine; R_1 = H; R_2 = NHAc[*Chem. Eur. J.* **2014**, 20, 2071]

Reagents and conditions. I) $NaBH_4$, Pd/C (10%), MeOH/DCM (1/1), r.t., overnight. b) corresponding anhydride, pyridine, r.t., 2h (for $\mathbf{S^{*}_{10}}$, $\mathbf{S_4}$, $\mathbf{S_1}$ and $\mathbf{S_9}$); c) corresponding acyl chloride, pyridine, r.t., 2h (for $\mathbf{S_2}$, $\mathbf{S_3}$, $\mathbf{S_6}$, $\mathbf{S_7}$); d) corresponding *N*-Boc protected amino acid, 2-chloro-1-methylpyridinium iodide, Et_3N, CH_2Cl_2, reflux, 3h (for $\mathbf{S_7}$ and $\mathbf{S_8}$); e) 50% TFA, CH_2Cl_2, r.t., 24 h.

2a

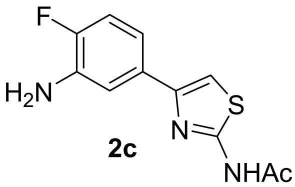


The general procedure for the reduction of nitro group was followed using **1a** (1.1 g, 5.0 mmol), Pd/C and $NaBH_4$ (1.04 g) to afford compound 2a in 76% yield (722 mg).

^{1}H NMR (200 MHz, MeOD-d_4) δ 7.45 (s, 1H), 7.28 – 7.06 (m, 3H), 6.70 (dt, J = 6.5, 2.3 Hz, 1H), 2.70 (s, 3H).

^{13}C NMR (50 MHz, MeOD-d_4) δ 167.9, 156.6, 149.1, 136.4, 130.4, 117.3, 116.4, 114.3, 113.8, 18.8.

2c



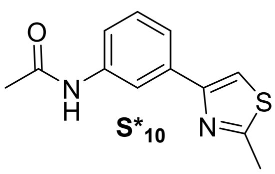
The general procedure for the reduction of nitro group was followed using **1c** (1.4 g, 5.0 mmol), Pd/C and $NaBH_4$ (1.04 g) to afford compound 2a in 54% yield (677 mg).

^{1}H NMR (400 MHz, DMSO) δ 12.21 (s, 1H), 7.34 (s, 1H), 7.29 – 7.23 (m, 1H), 7.01 (dd, J = 5.7, 4.1 Hz, 2H), 5.21 (s, 2H), 2.15 (s, 3H).

^{19}F NMR (377 MHz, DMSO) δ -135.90.

^{13}C NMR (101 MHz, DMSO) δ 168.9, 157.7, 151.6, 149.2, 148.6, 136.4 (d, J = 13.3 Hz), 130.9 (d, J = 3.0 Hz), 115.1 (d, J = 18.8 Hz), 113.6 (d, J = 5.4 Hz), 106.7, 22.5.

S*$_{10}$

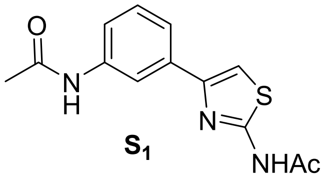


The general procedure for the amide synthesis was followed using **2a** (190 mg, 1.0 mmol, 1 eq.) and Ac_2O (102 µL, 1.1 mmol, 1.1 eq.) to afford **S*$_{10}$** in 72% (167 mg).

^{1}H NMR (200 MHz, MeOD-d_4) δ 8.04 (s, 1H), 7.66 – 7.47 (m, 3H), 7.33 (t, J = 7.9 Hz, 1H), 2.72 (s, 3H), 2.14 (s, 3H).

^{13}C NMR (50 MHz, MeOD-d_4) δ 171.7, 168.2, 155.9, 140.3, 136.3, 130.2, 123.1, 120.8, 119.0, 114.5, 23.9, 18.8.

S_1

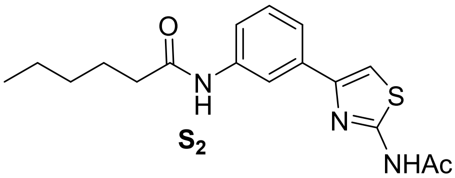


The general procedure for the amide synthesis was followed using **2b** (233 mg, 1.0 mmol, 1 eq.) and Ac_2O (102 µL, 1.1 mmol, 1.1 eq.) to afford **S_1** in 81% (222 mg).

^{1}H NMR (400 MHz, DMSO-d_6) δ 12.27 (s, 1H), 10.00 (s, 1H), 8.22 (s, 1H), 7.54 (d, J = 7.7 Hz, 1H), 7.48 (s, 1H), 7.41 (d, J = 8.1 Hz, 1H), 7.32 (t, J = 7.9 Hz, 1H), 2.16 (s, 3H), 2.06 (s, 3H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 168.7, 168.3, 157.9, 148.7, 139.7, 134.8, 129.0, 120.5, 118.5, 116.6, 107.9, 24.1, 22.5.

S_2

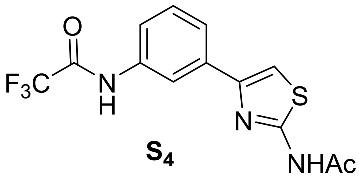


The general procedure for the amide synthesis was followed using **2b** (233 mg, 1.0 mmol, 1 eq.) and hexanoyl chloride (140 µL, 1.1 mmol, 1.1 eq.) to afford **S_2** in 49% (162 mg).

^{1}H NMR (200 MHz, MeOD-d_4) δ 8.14 (t, J = 1.7 Hz, 1H), 7.62 (dt, J = 7.6, 1.4 Hz, 1H), 7.50 – 7.41 (m, 1H), 7.37 – 7.26 (m, 2H), 2.38 (t, J = 7.5 Hz, 2H), 2.22 (s, 3H), 1.80 – 1.63 (m, 2H), 1.41 – 1.34 (m, 4H), 0.94 (t, J = 5.9 Hz, 3H).

^{13}C NMR (50 MHz, MeOD-d_4) δ 174.8, 170.9, 159.4, 150.9, 140.2, 136.6, 130.0, 122.8, 120.7, 118.9, 108.8, 38.0, 32.6, 26.7, 23.5, 22.6, 14.3.

S_4



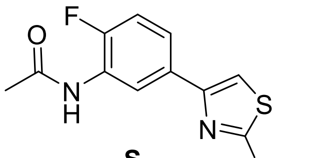
The general procedure for the amide synthesis was followed using **2b** (233 mg, 1.0 mmol, 1 eq.) and trifluoroacetic anhydride (154 µL, 1.1 mmol, 1.1 eq.) to afford **S_4** in 32% (105 mg).

^{1}H NMR (400 MHz, Acetone-d_6) δ 11.15 (s, 1H), 10.29 (s, 1H), 8.38 (t, J = 1.8 Hz, 1H), 7.81 – 7.73 (m, 1H), 7.58 (ddd, J = 8.1, 2.1, 1.0 Hz, 1H), 7.46 – 7.42 (m, 2H), 2.29 (s, 3H).

^{19}F NMR (377 MHz, Acetone-d_6) δ -76.22.

^{13}C NMR (101 MHz, Acetone-d_6) δ 206.2, 159.0 (d, 9.9 Hz), 158.9, 149.6, 137.7, 136.6, 130.2, 124.0, 120.9, 119.4, 108.9, 22.8.

S_9



S_9

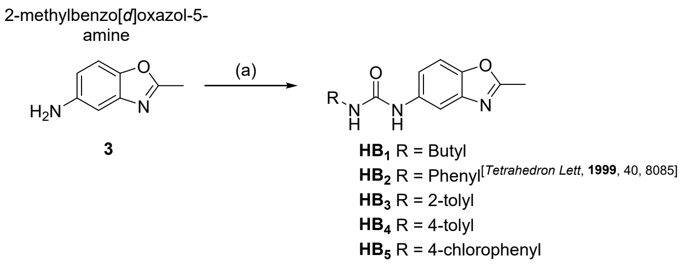
The general procedure for the amide synthesis was followed using **2c** (251 mg, 1.0 mmol, 1 eq.) and Ac_2O (102 μL, 1.1 mmol, 1.1 eq.) to afford **S_9** in 62% (181 mg).

^{1}H NMR (400 MHz, DMSO-d_6) δ 12.29 (s, 1H), 9.77 (s, 1H), 8.45 (d, J = 6.3 Hz, 1H), 7.65 – 7.59 (m, 1H), 7.52 (s, 1H), 7.29 (dd, J = 10.6, 8.7 Hz, 1H), 2.16 (s, 3H), 2.11 (s, 3H).

^{19}F NMR (377 MHz, DMSO-d_6) δ -126.11.

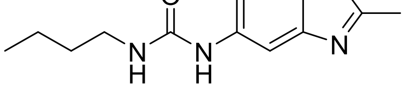
^{13}C NMR (101 MHz, DMSO-d_6) δ 168.7, 168.7, 158.0, 155.9, 154.3, 147.7, 130.7 (d, J = 3.1 Hz), 126.4 (d, J = 12.1 Hz), 122.2 (d, J = 7.6 Hz), 121.6, 115.7 (d, J = 20.2 Hz), 107.8, 23.6, 22.5.

Scheme 2. Synthetic route to **HB** nucleobase analogues **HB_{1-5}**



Reagents and conditions. a) RNCO, DCM, r.t., 2 hours.

HB_1



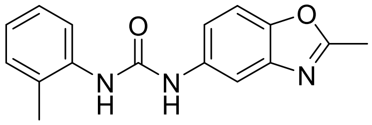
HB_1

The general procedure for the urea synthesis was followed using **3** (80 mg) and butyl isocyanate (59 mg) to afford **HB_1** in 79% yield (105 mg).

[1]H NMR (200 MHz, MeOD-d_4) δ 7.73 (d, *J* = 2.1 Hz, 1H), 7.41 (d, *J* = 8.8 Hz, 1H), 7.21 (dd, *J* = 8.8, 2.1 Hz, 1H), 3.20 (t, *J* = 6.8 Hz, 2H), 2.59 (s, 3H), 1.59 – 1.32 (m, 4H), 0.96 (t, *J* = 7.1 Hz, 3H).

[13]C NMR (50 MHz, MeOD-d_4) δ 166.7, 158.5, 148.0, 142.4, 138.1, 118.3, 111.1, 110.6, 40.6, 33.4, 21.0, 14.1.

HB_3



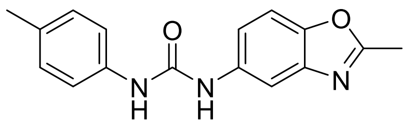
HB_3

The general procedure for the urea synthesis was followed using **3** (80 mg) and o-tolyl isocyanate (82 µL) to afford **HB_3** in 67% yield (101 mg).

[1]H NMR (200 MHz, DMSO-d_6) δ 9.13 (s, 1H), 7.93 (s, 1H), 7.89 (d, *J* = 1.9 Hz, 1H), 7.84 (d, *J* = 8.2 Hz, 1H), 7.55 (d, *J* = 8.7 Hz, 1H), 7.25 (dd, *J* = 8.8, 2.1 Hz, 1H), 7.15 (t, *J* = 7.9 Hz, 2H), 7.00 – 6.88 (m, 1H), 2.58 (s, 3H), 2.25 (s, 3H).

[13]C NMR (50 MHz, DMSO-d_6) δ 164.4, 152.9, 145.7, 141.5, 137.4, 136.6, 130.2, 127.6, 126.2, 122.7, 121.1, 115.6, 110.1, 108.3, 17.9, 14.2.

HB_4



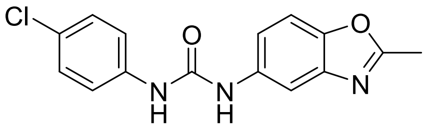
HB_4

The general procedure for the urea synthesis was followed using **3** (80 mg) and o-tolyl isocyanate (82 µL) to afford **HB_4** in 66% yield (100 mg).

[1]H NMR (200 MHz, DMSO-d_6) δ 8.73 (s, 1H), 8.57 (s, 1H), 7.85 (d, *J* = 1.9 Hz, 1H), 7.53 (d, *J* = 8.7 Hz, 1H), 7.34 (d, *J* = 8.4 Hz, 2H), 7.25 (dd, *J* = 8.8, 2.1 Hz, 1H), 7.08 (d, *J* = 8.3 Hz, 1H), 2.58 (s, 3H), 2.24 (s, 3H).

[13]C NMR (50 MHz, DMSO-d_6) δ 164.4, 152.8, 145.8, 141.5, 137.1, 136.5, 130.6, 129.2, 118.3, 115.8, 110.1, 108.5, 20.3, 14.2.

HB_5



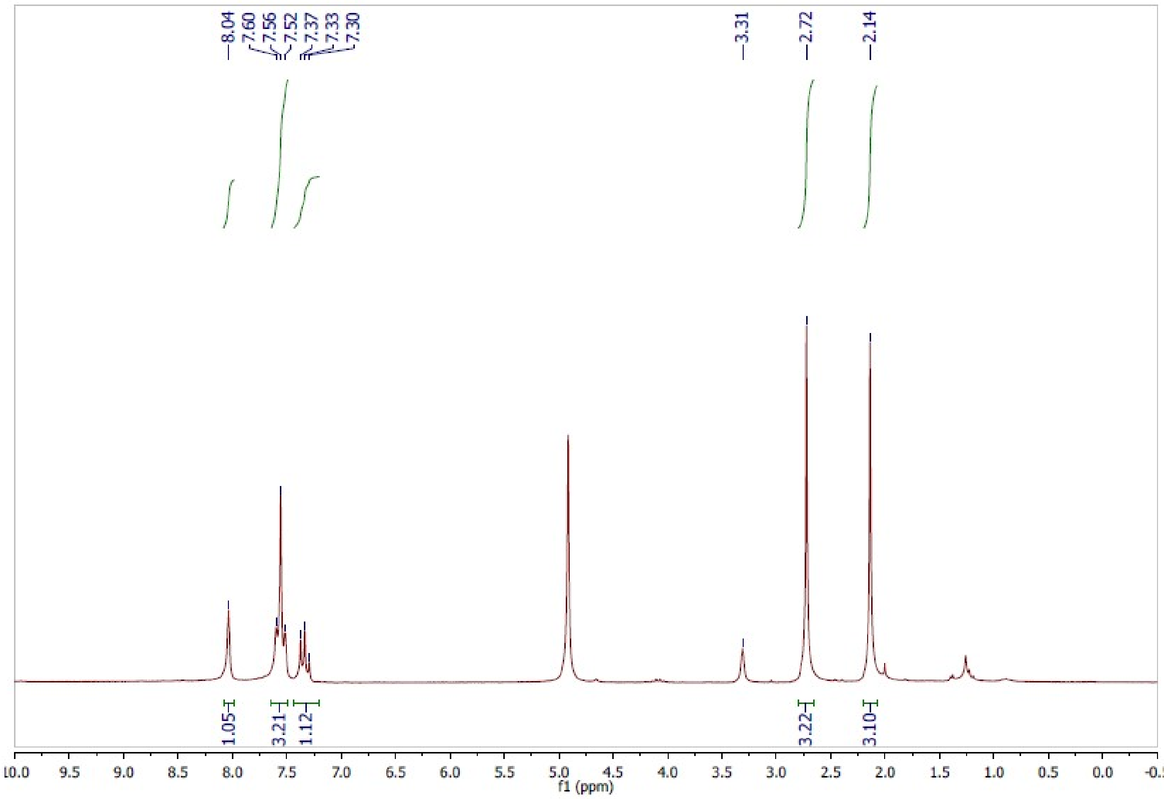
HB_5

The general procedure for the urea synthesis was followed using **3** (80 mg) and o-tolyl isocyanate (100 mg) to afford **HB_5** in 51% yield (76 mg).

^{1}H NMR (200 MHz, DMSO-d_6) δ 8.83 (d, J = 3.9 Hz, 2H), 7.85 (d, J = 1.9 Hz, 1H), 7.58 – 7.42 (m, 3H), 7.35 – 7.19 (m, 3H), 2.58 (s, 3H).

^{13}C NMR (50 MHz, DMSO-d_6) δ 164.5, 152.7, 145.9, 141.5, 138.8, 136.2, 128.6, 125.3, 119.8, 115.9, 110.1, 108.8, 14.2.

S*$_{10}$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7.30
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2.14
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1.12
3.22
3.10
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
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0.5
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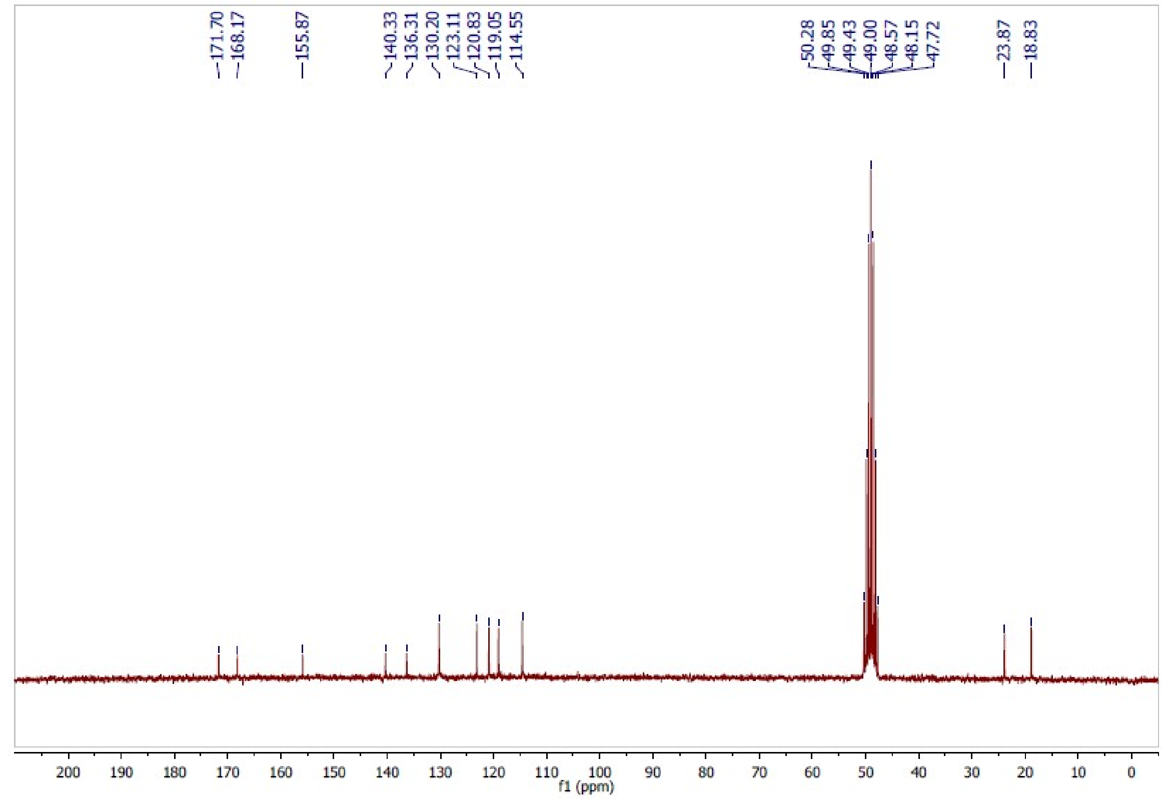
-0.5
f1 (ppm)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49.00
48.57
48.15
47.72
23.87
18.83
200
190
180
170
160
150
140
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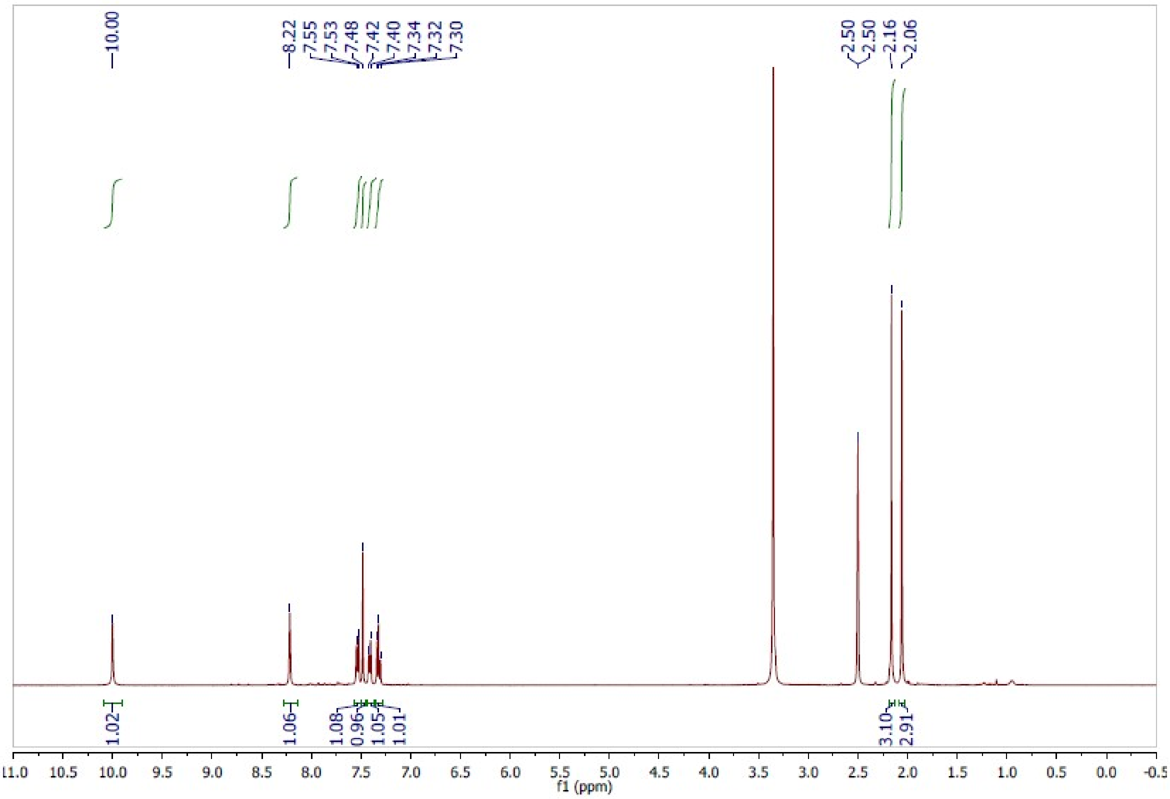
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

S_1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7.30
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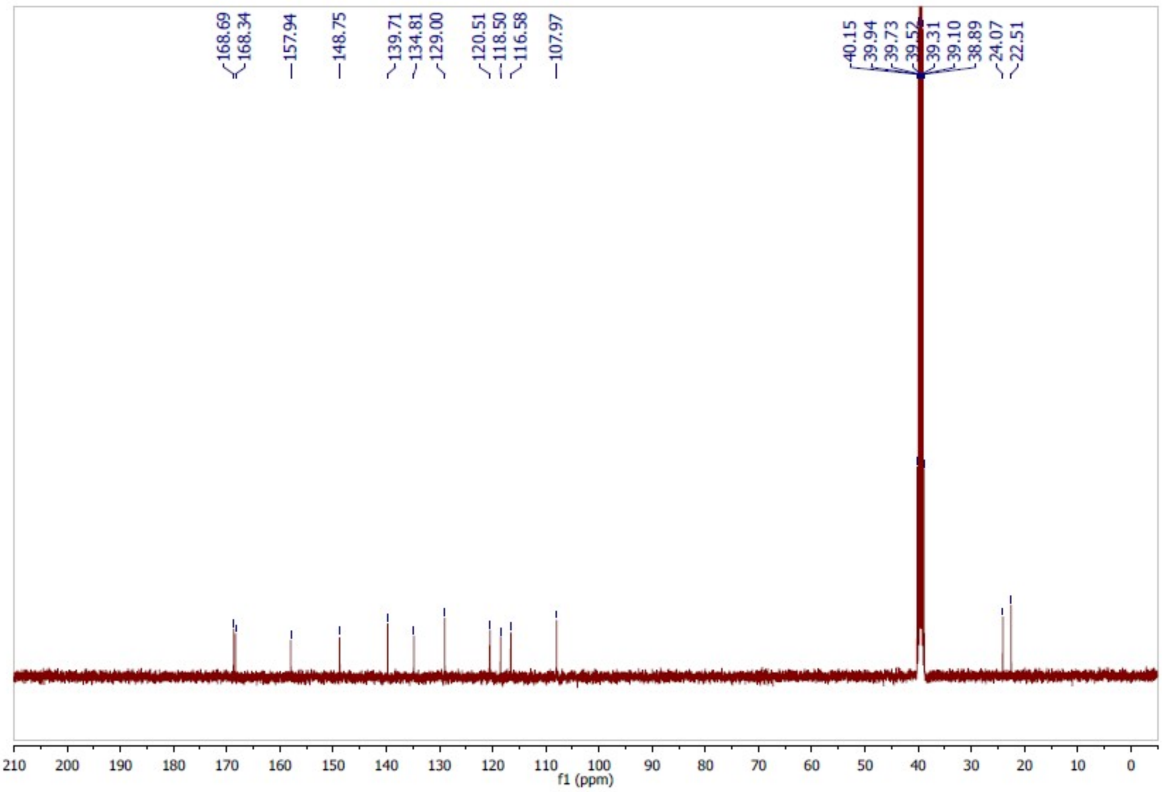
1.02
1.06
1.08
0.96
1.05
1.01
3.10
2.91
f1 (ppm)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39.52
39.31
39.10
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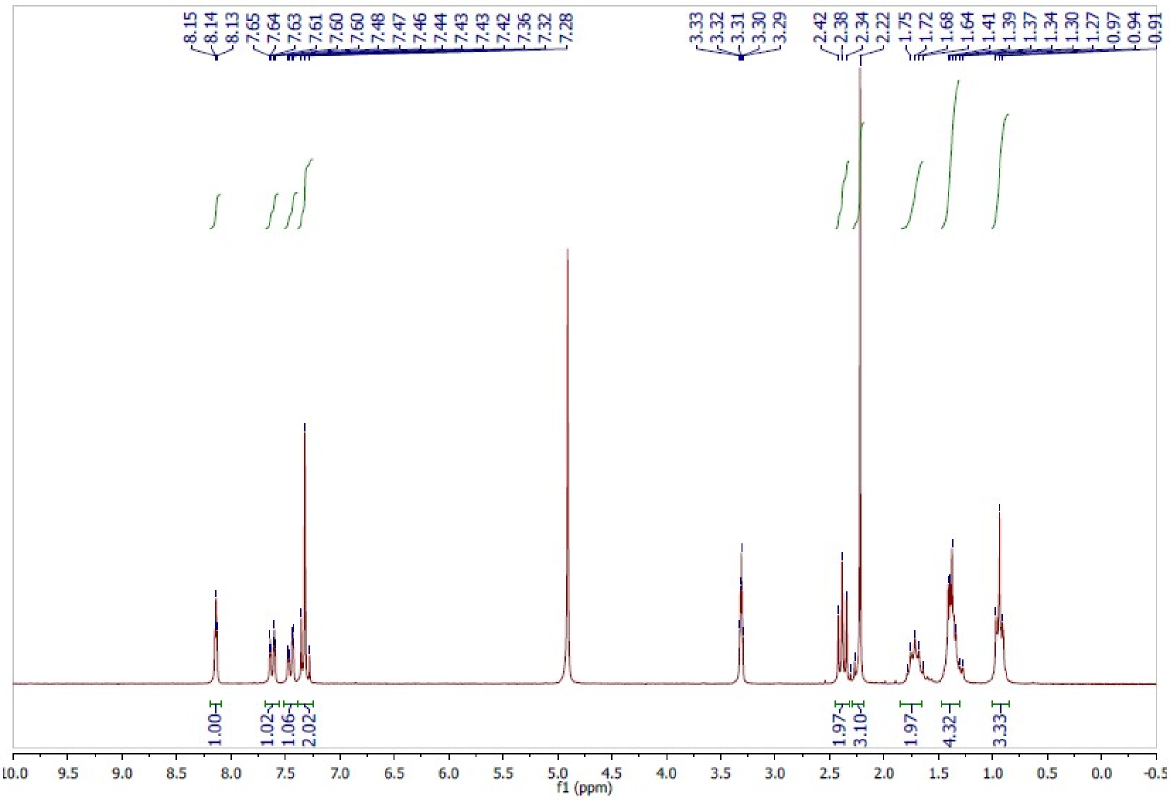
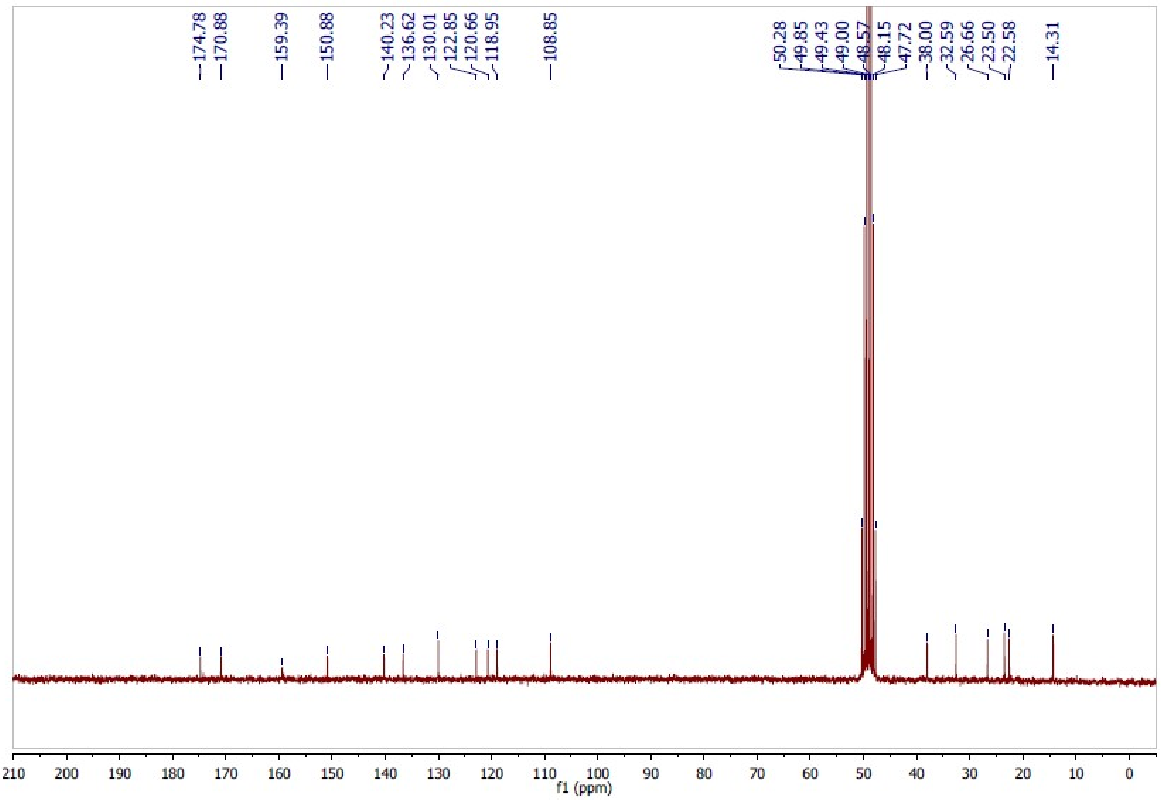
24.07
22.51
f1 (ppm)

S2

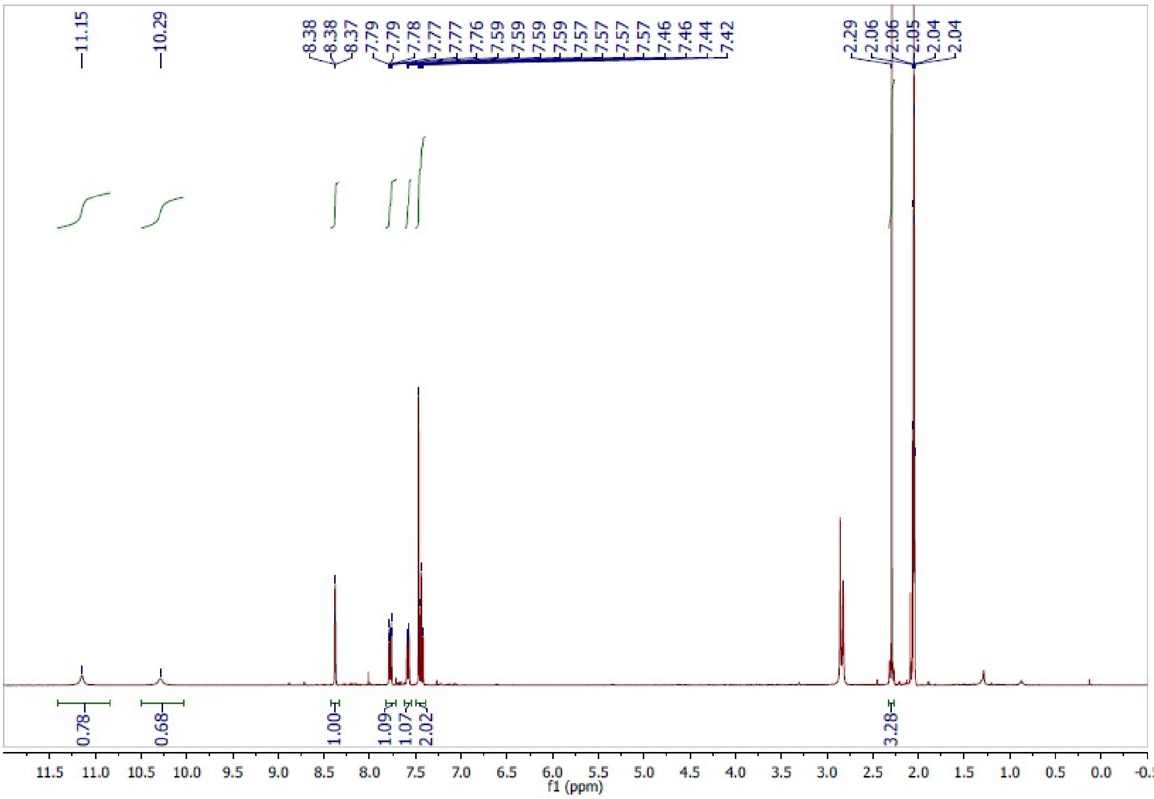


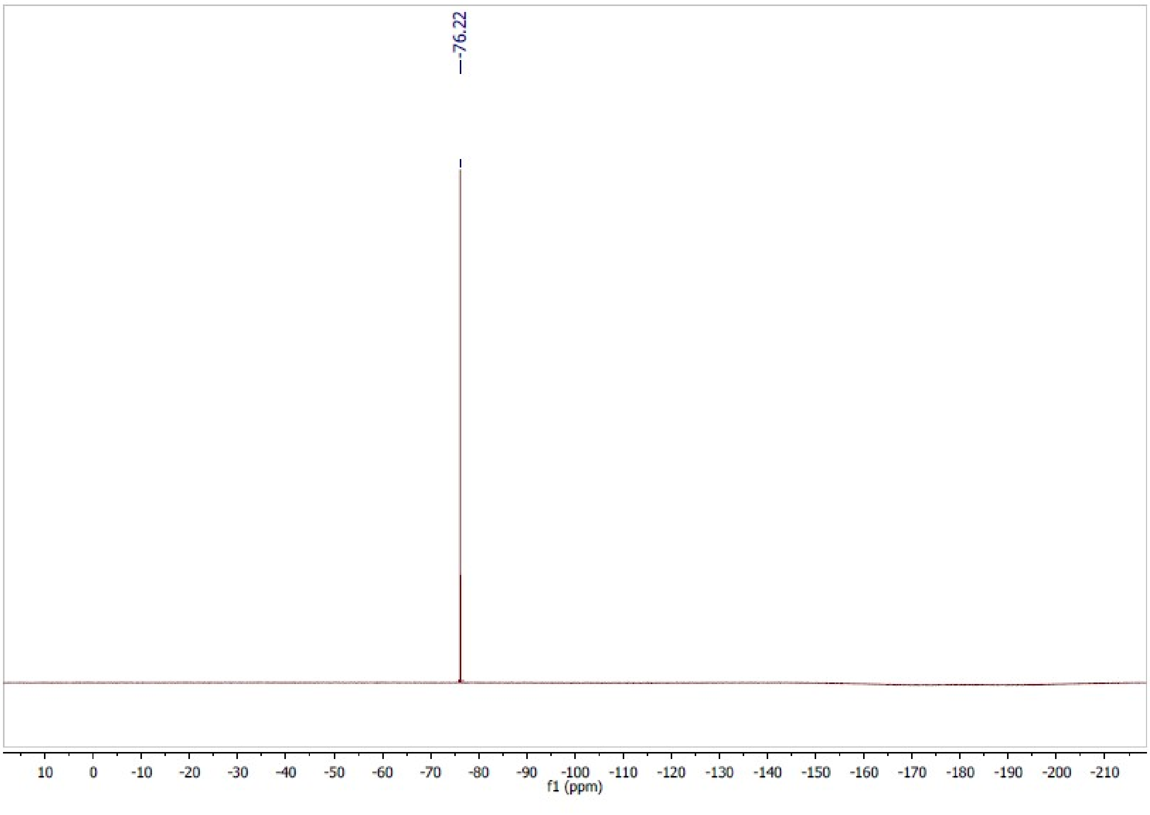
8.15 8.14 8.13 7.65 7.64 7.63 7.61 7.60 7.48 7.47 7.46 7.44 7.43 7.43 7.42 7.36 7.32 7.28
3.33 3.32 3.31 3.30 3.29
2.42 2.38 2.34 2.22 1.75 1.72 1.68 1.64 1.41 1.39 1.37 1.34 1.30 1.27 0.97 0.94 0.91
1.00 1.02 1.06 2.02 1.97 3.10 1.97 4.32 3.33
f1 (ppm)

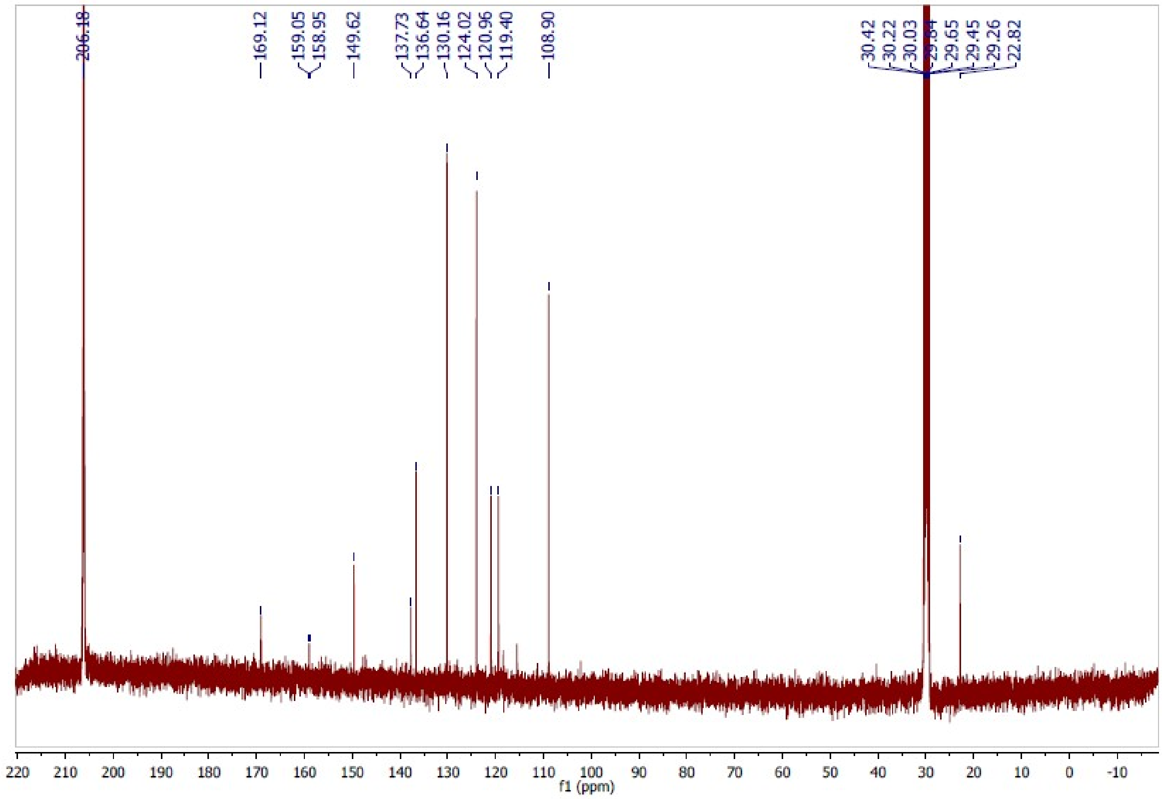


174.78 170.88 159.39 150.88 140.23 136.62 130.01 122.85 120.66 118.95 108.85
50.28 49.85 49.43 49.00 48.57 48.15 47.72 38.00 32.59 26.66 23.50 22.58 14.31
f1 (ppm)

S_4







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159.05
158.95
149.62
137.73
136.64
130.16
124.02
120.96
119.40
108.90
30.42
30.22
30.03
29.84
29.65
29.45
29.26
22.82
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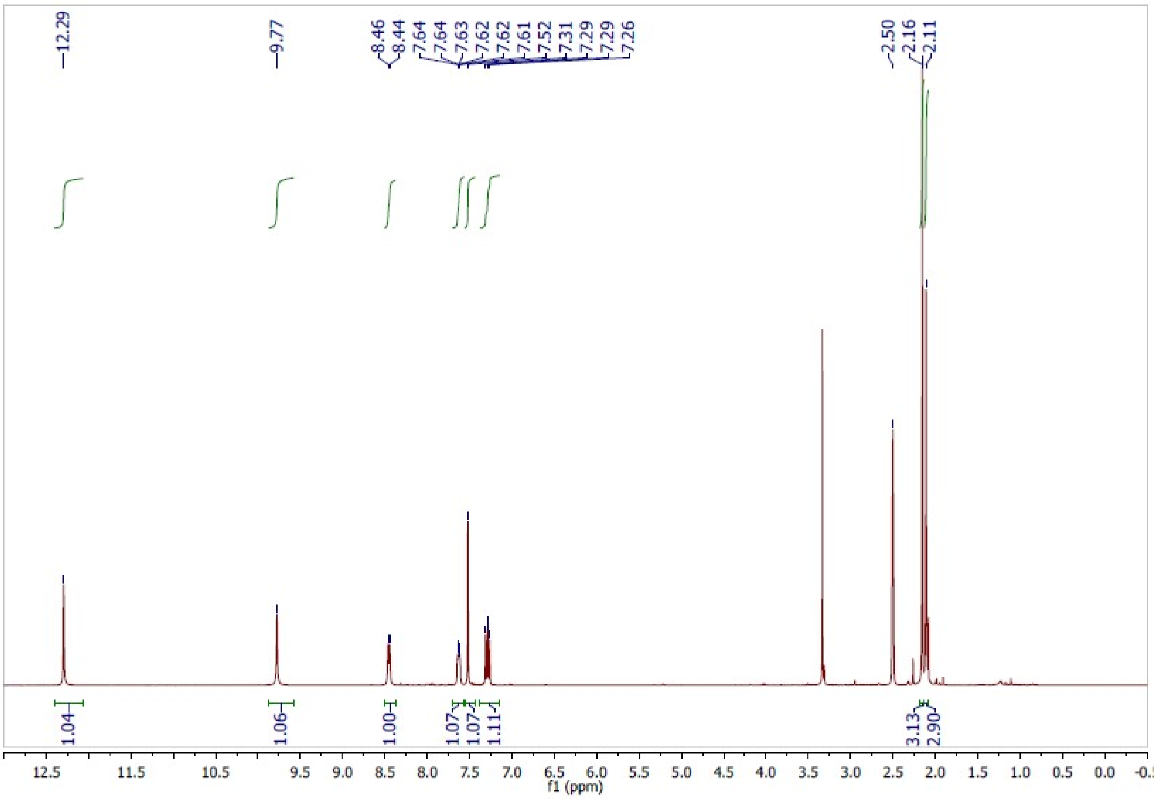
f1 (ppm)

S9



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7.62
7.61
7.52
7.31
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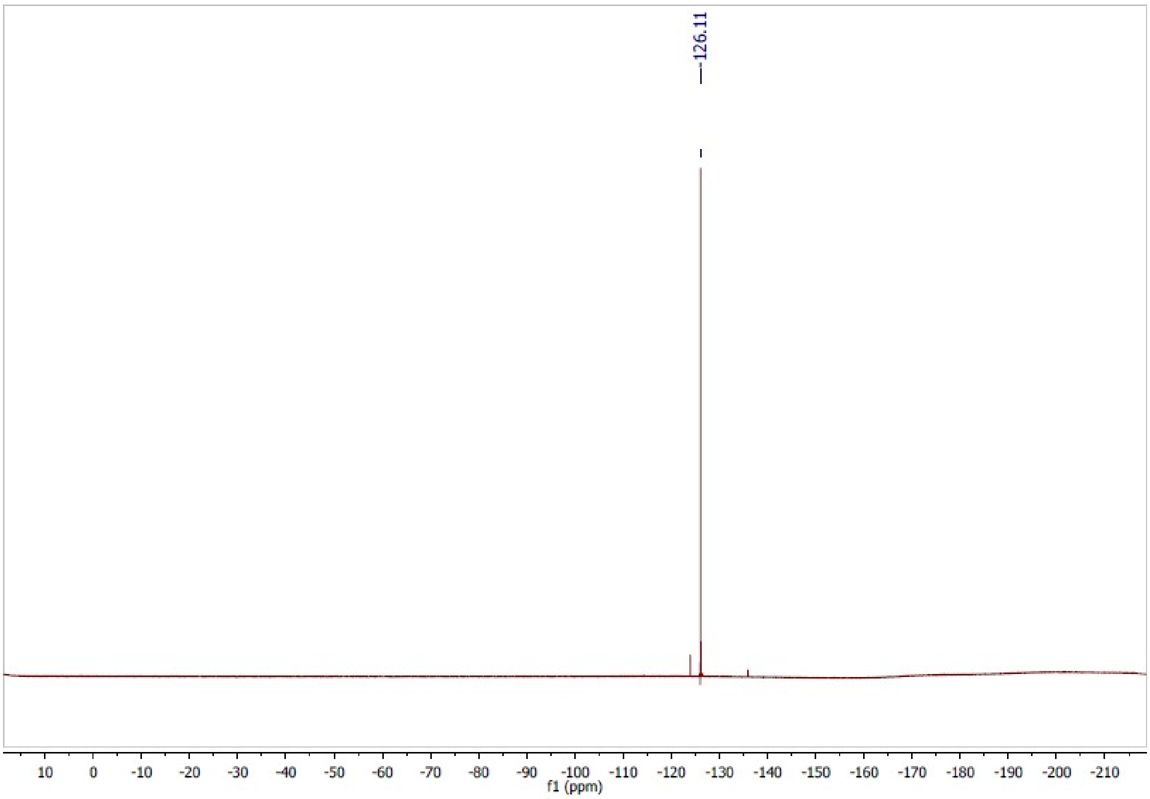
7.29
7.26
2.50
2.16
2.11
1.04
1.06
1.00
1.07
1.07
1.11
3.13
2.90
12.5 11.5 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)



-126.11
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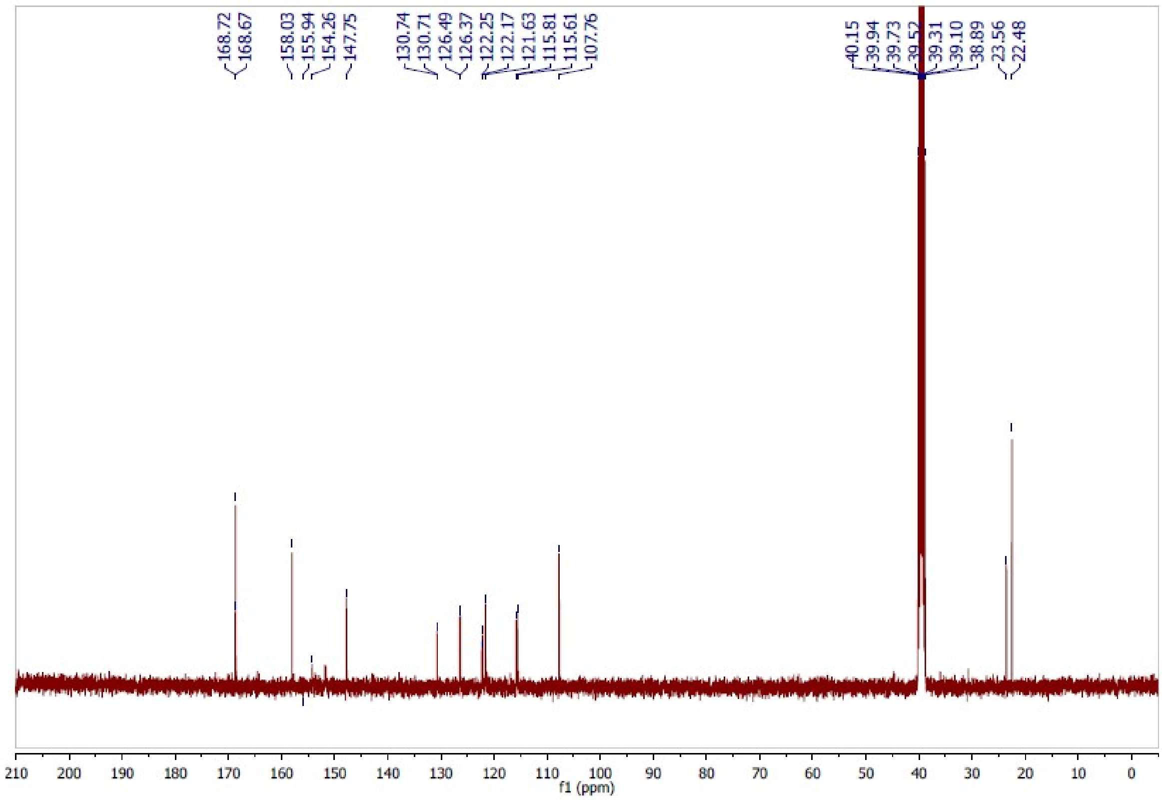
f1 (ppm)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155.94
154.26
147.75
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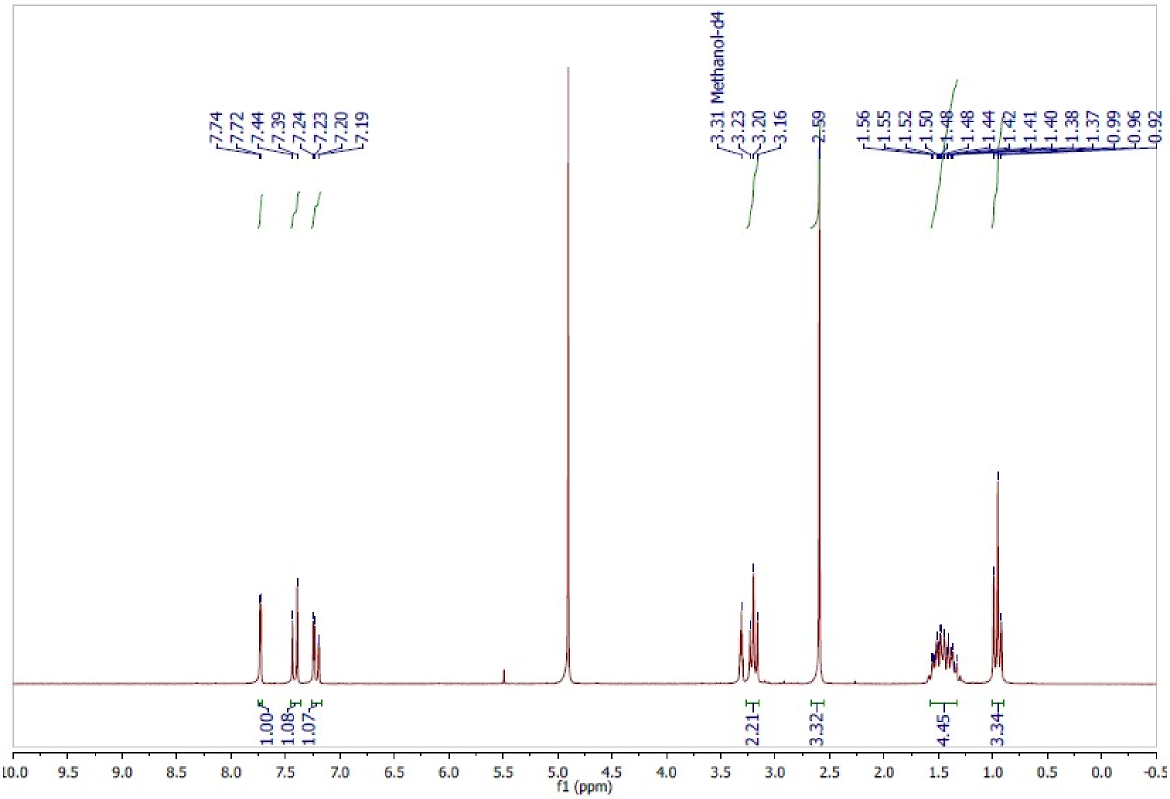
130.71
126.49
126.37
122.25
122.17
121.63
115.81
115.61
107.76
40.15
39.94
39.73
39.52
39.31
39.10
38.89
23.56
22.48
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

HB_1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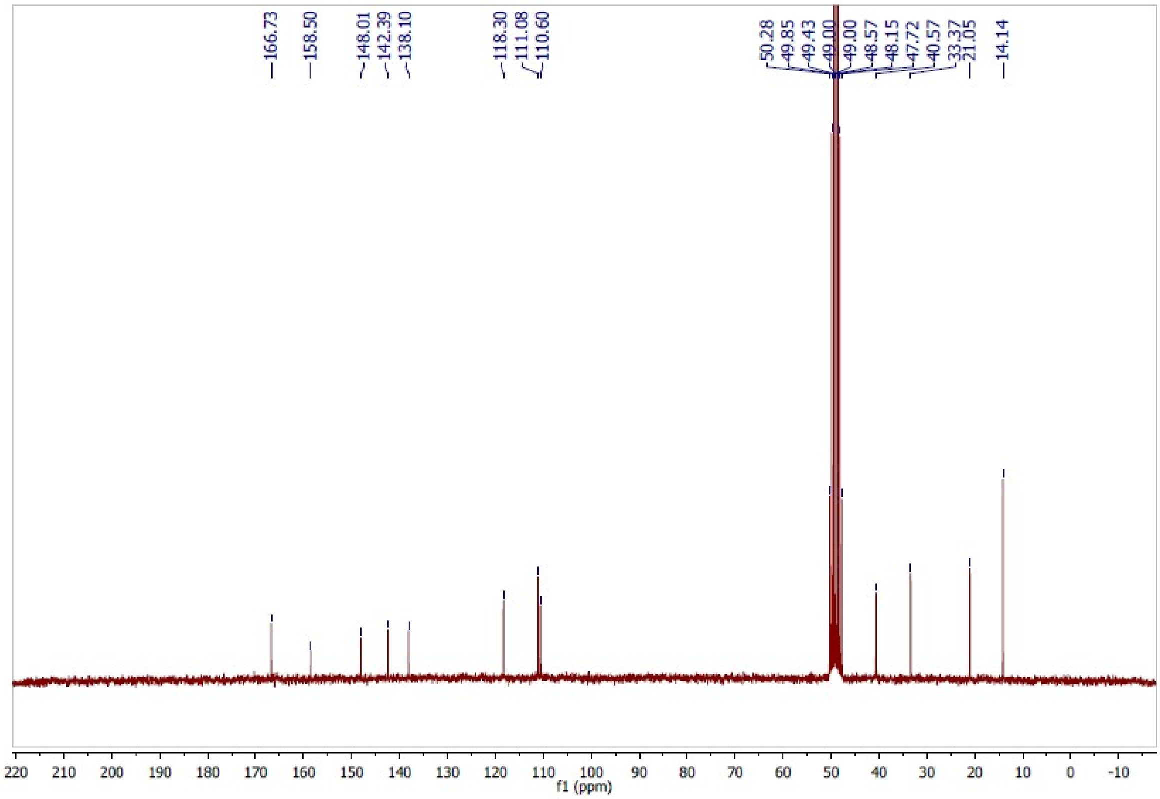
7.72
7.44
7.39
7.24
7.23
7.20
7.19
3.31 Methanol-d4
3.23
3.20
3.16
2.59
1.56
1.55
1.52
1.50
1.48
1.44
1.42
1.41
1.40
1.38
1.37
0.99
0.96
0.92
1.00
1.08
1.07
2.21
3.32
4.45
3.34
f1 (ppm)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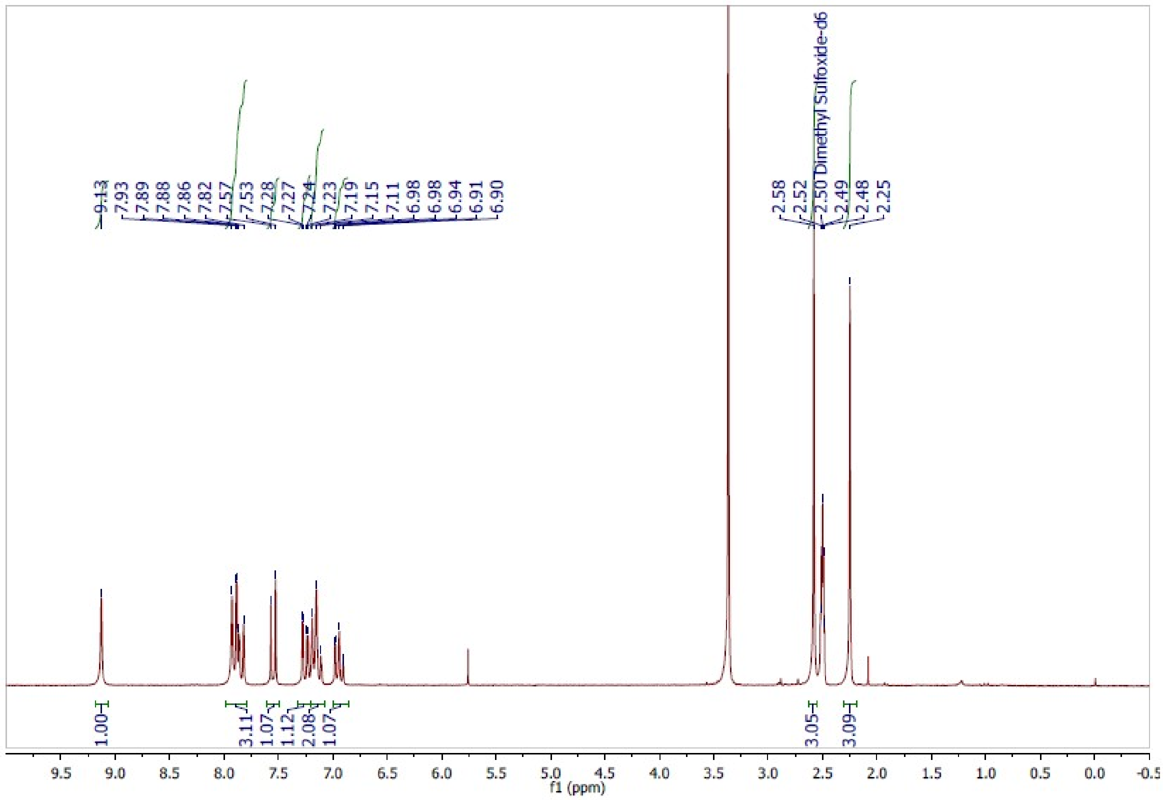
158.50
148.01
142.39
138.10
118.30
111.08
110.60
50.28
49.85
49.43
49.00
49.00
48.57
48.15
47.72
40.57
33.37
21.05
14.14
f1 (ppm)

HB$_3$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7.88
7.86
7.82
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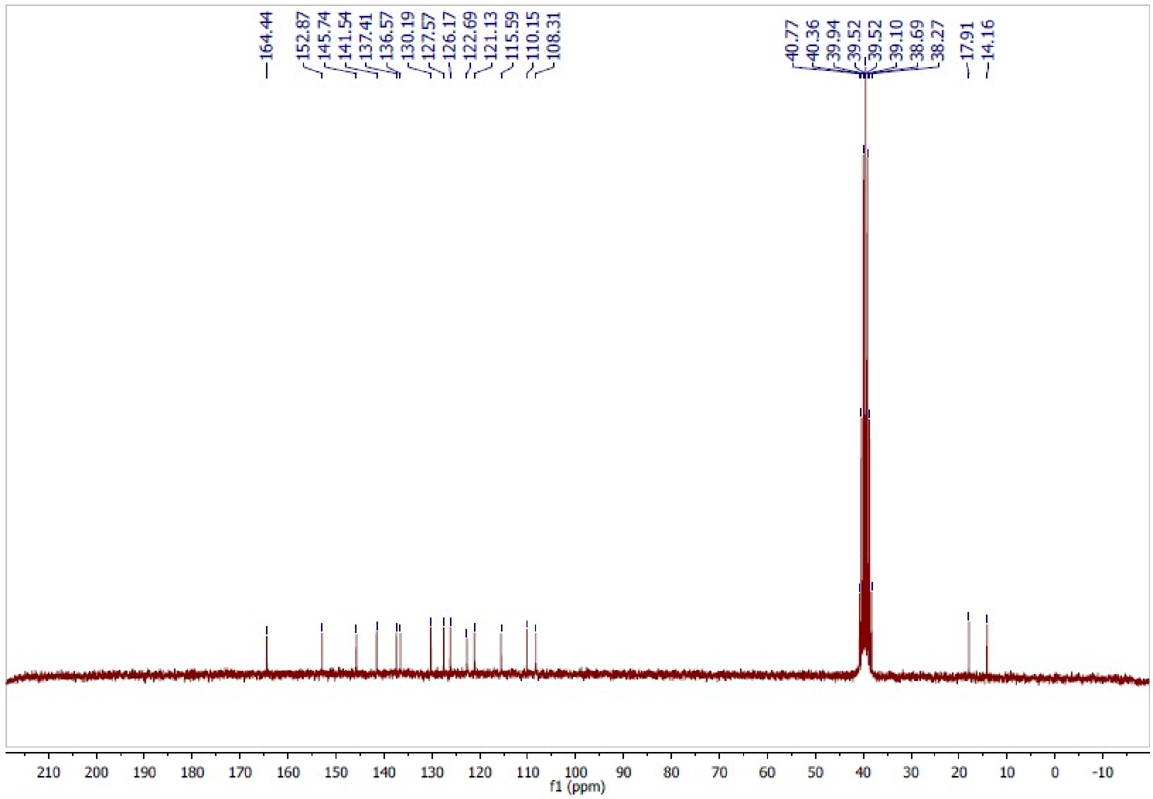
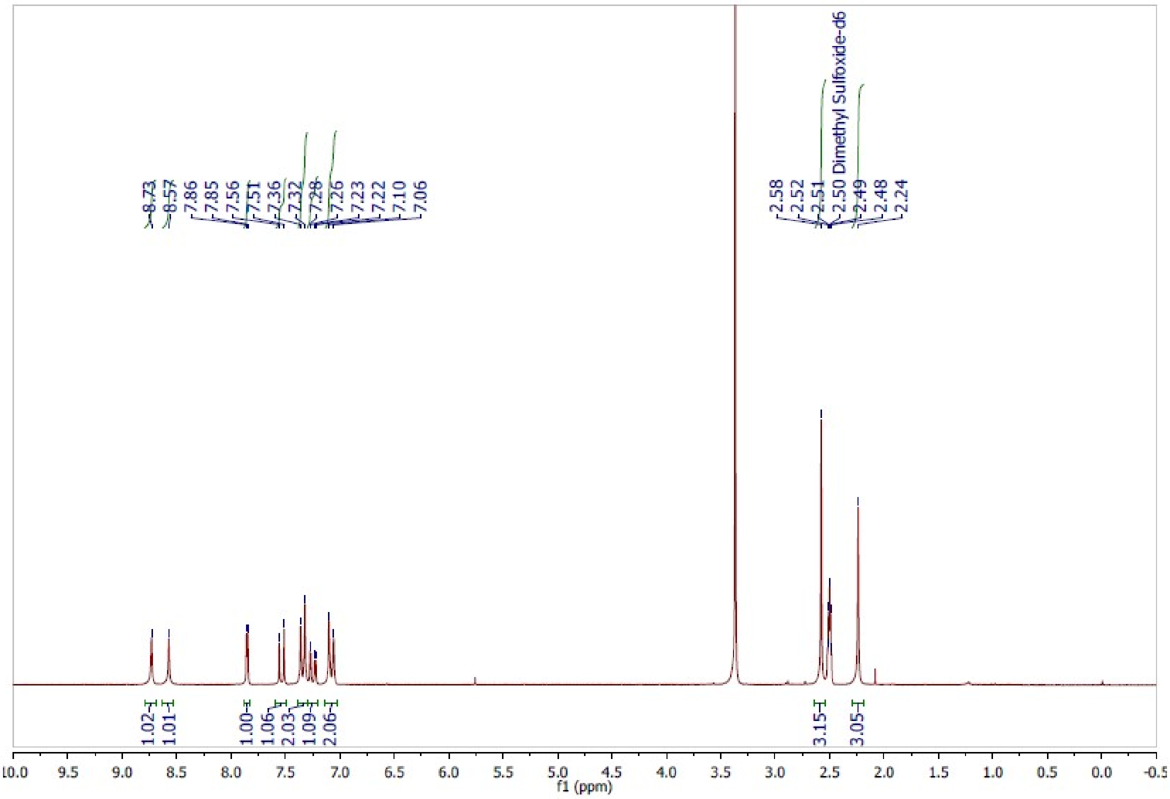
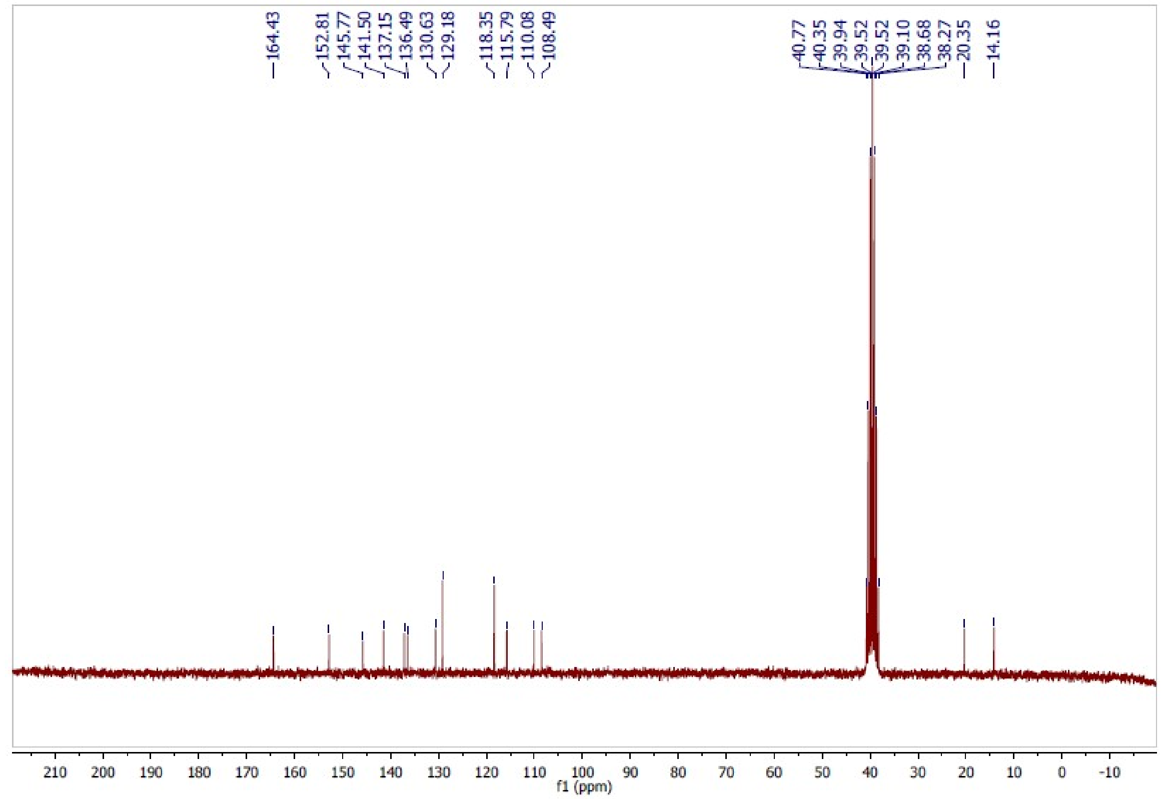
7.53
7.28
7.27
7.24
7.23
7.19
7.15
7.11
6.98
6.98
6.94
6.91
6.90
2.58
2.52
2.50 Dimethyl Sulfoxide-d6
2.49
2.48
2.25
1.00
3.11
1.07
1.12
2.08
1.07
3.05
3.09
f1 (ppm)


164.44
152.87
145.74
141.54
137.41
136.57
130.19
127.57
126.17
122.69
121.13
115.59
110.15
108.31
40.77
40.36
39.94
39.52
39.52
39.10
38.69
38.27
17.91
14.16
f1 (ppm)

HB_4



8.73
8.57
7.86
7.85
7.56
7.51
7.36
7.32
7.28
7.26
7.23
7.22
7.10
7.06
2.58
2.52
2.51
2.50 Dimethyl Sulfoxide-d6
2.49
2.48
2.24
1.02
1.01
1.00
1.06
2.03
1.09
2.06
3.15
3.05
f1 (ppm)



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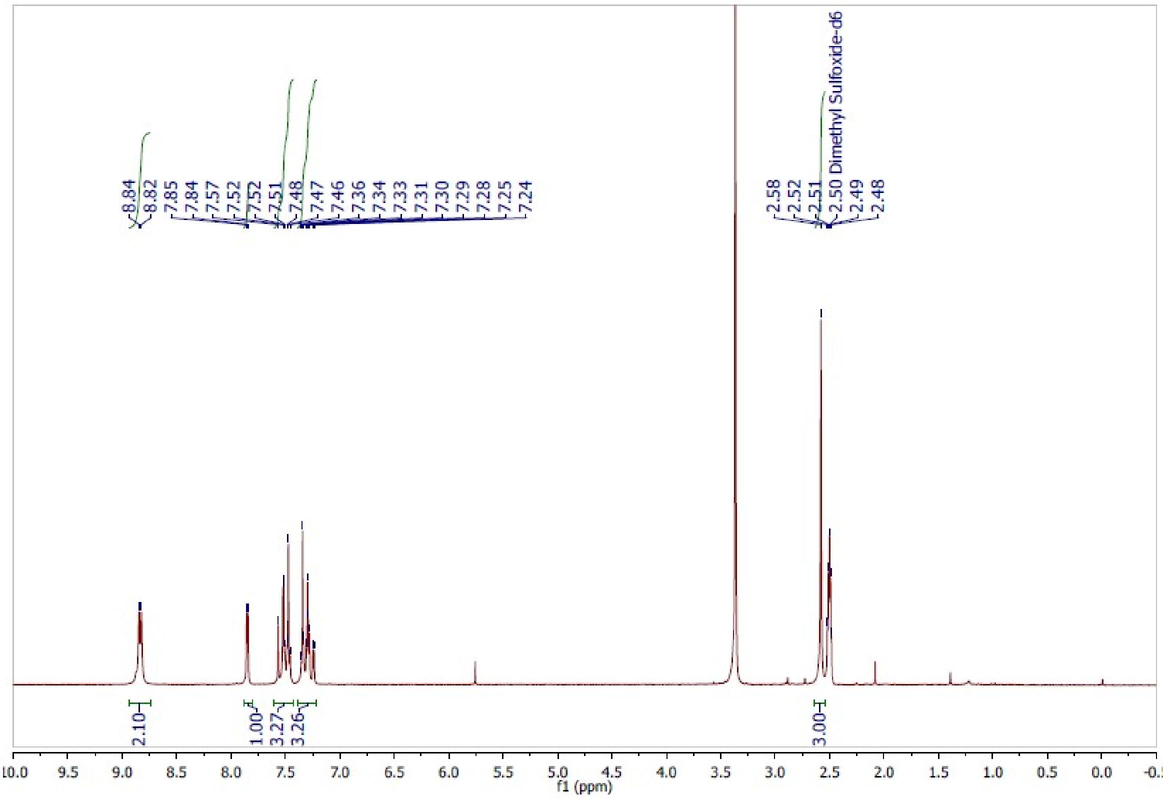
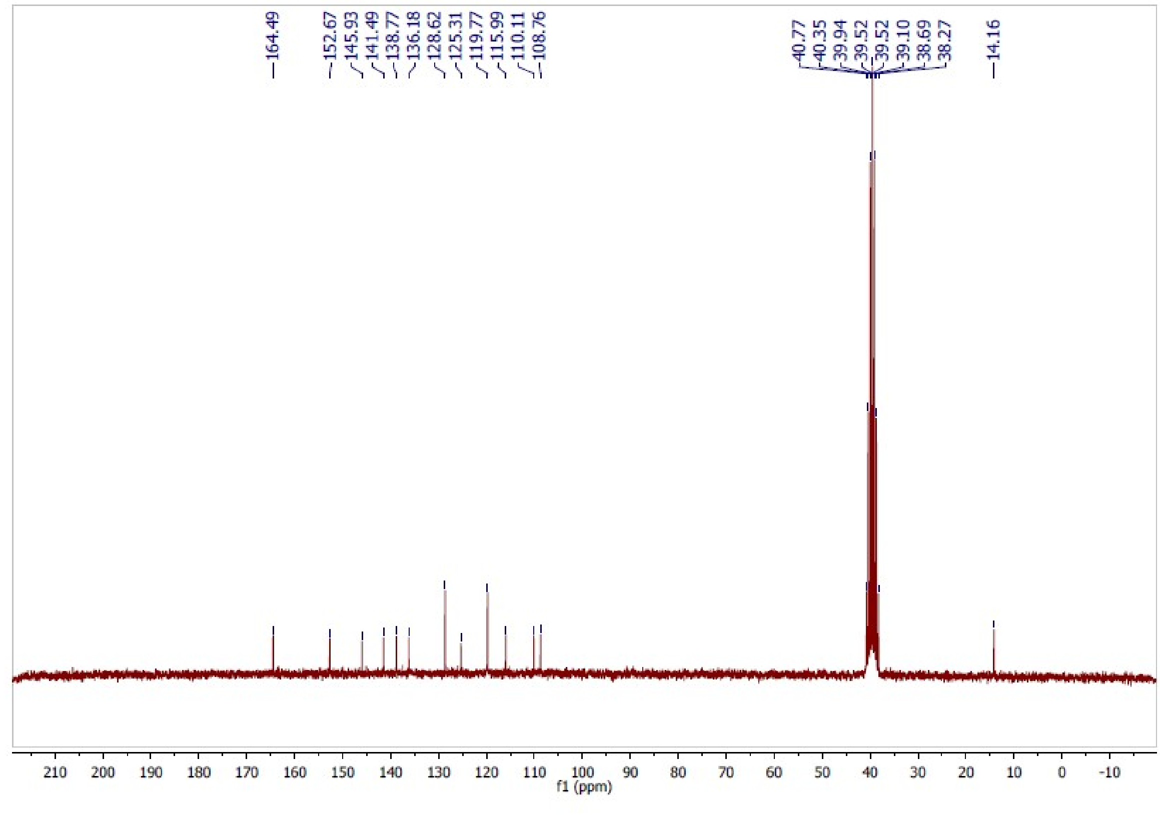
145.77
141.50
137.15
136.49
130.63
129.18
118.35
115.79
110.08
108.49
40.77
40.35
39.94
39.52
39.52
39.10
38.68
38.27
20.35
14.16
f1 (ppm)

HB_5

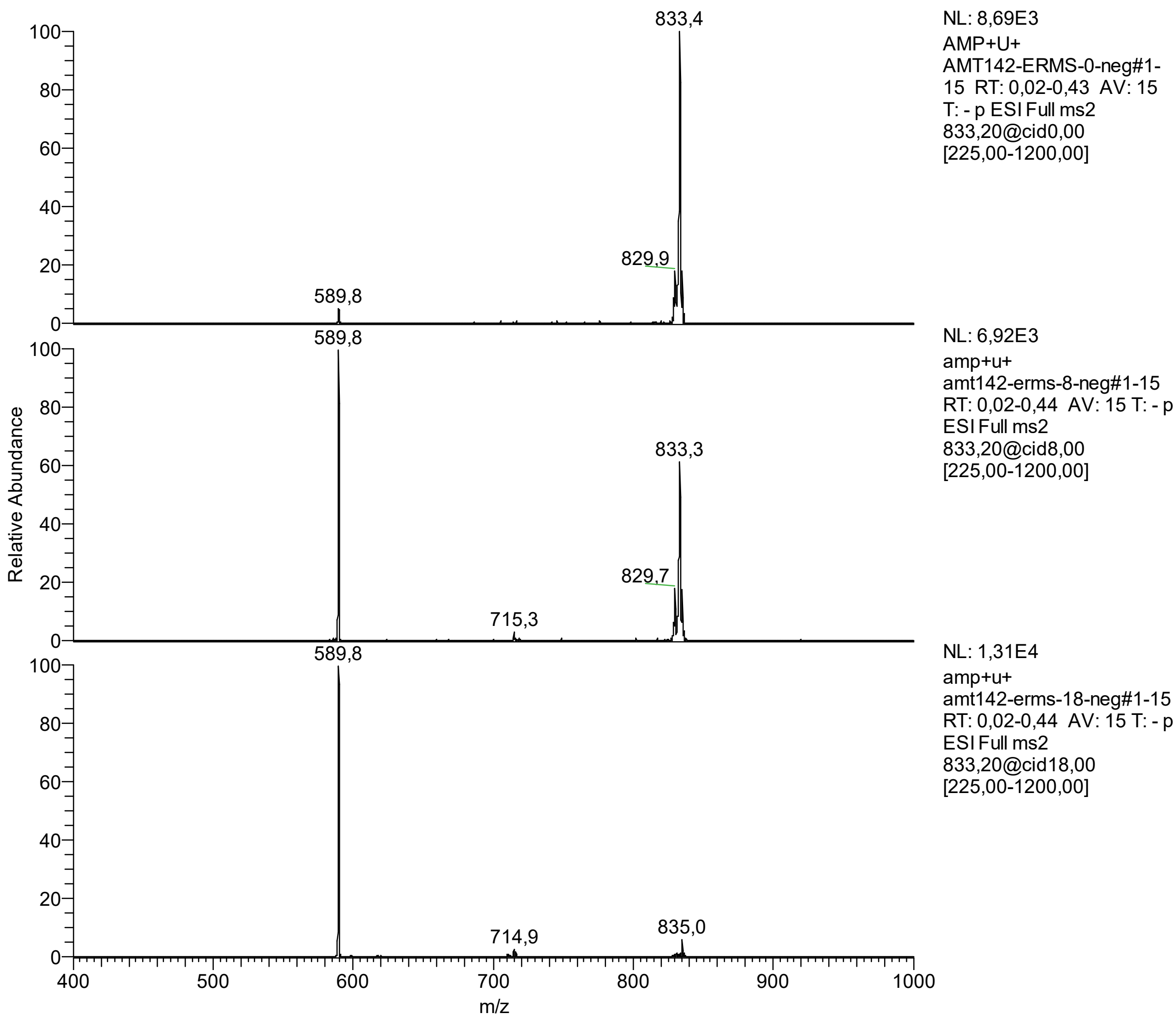


8.84
8.82
7.85
7.84
7.57
7.52
7.52
7.51
7.48
7.47
7.46
7.36
7.34
7.33
7.31
7.30
7.29
7.28
7.25
7.24
2.58
2.52
2.51
2.50 Dimethyl Sulfoxide-d6
2.49
2.48
2.10
1.00
3.27
3.26
3.00
f1 (ppm)

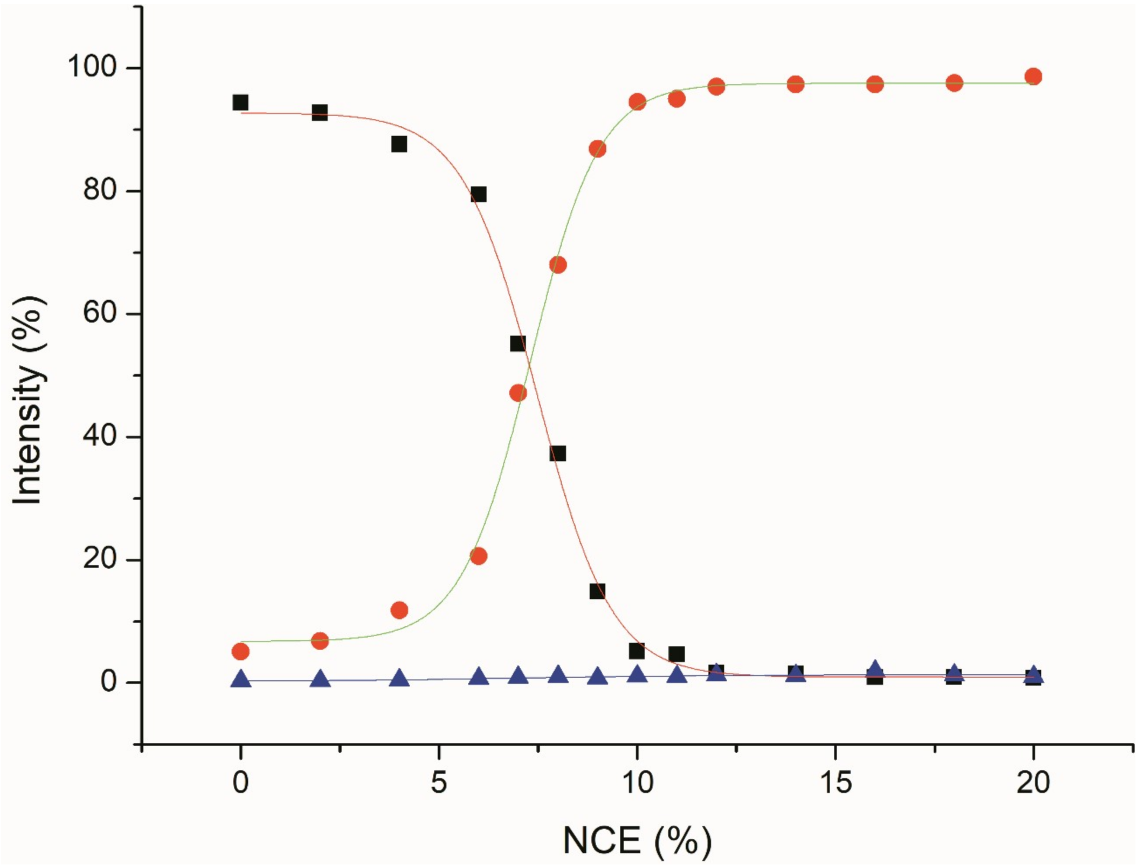


164.49
152.67
145.93
141.49
138.77
136.18
128.62
125.31
119.77
115.99
110.11
108.76
40.77
40.35
39.94
39.52
39.52
39.10
38.69
38.27
14.16
f1 (ppm)

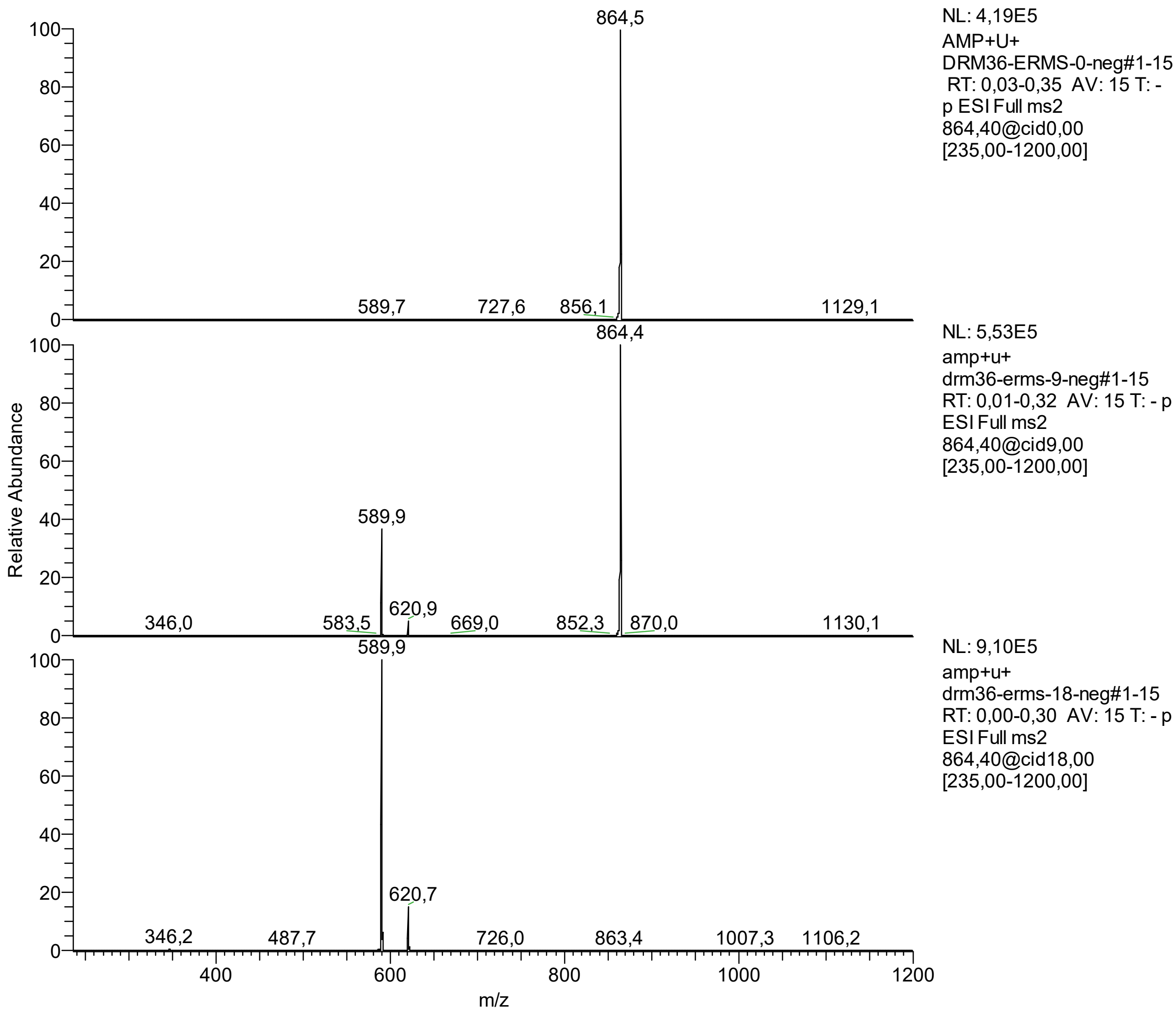
Triplex breakdown curves



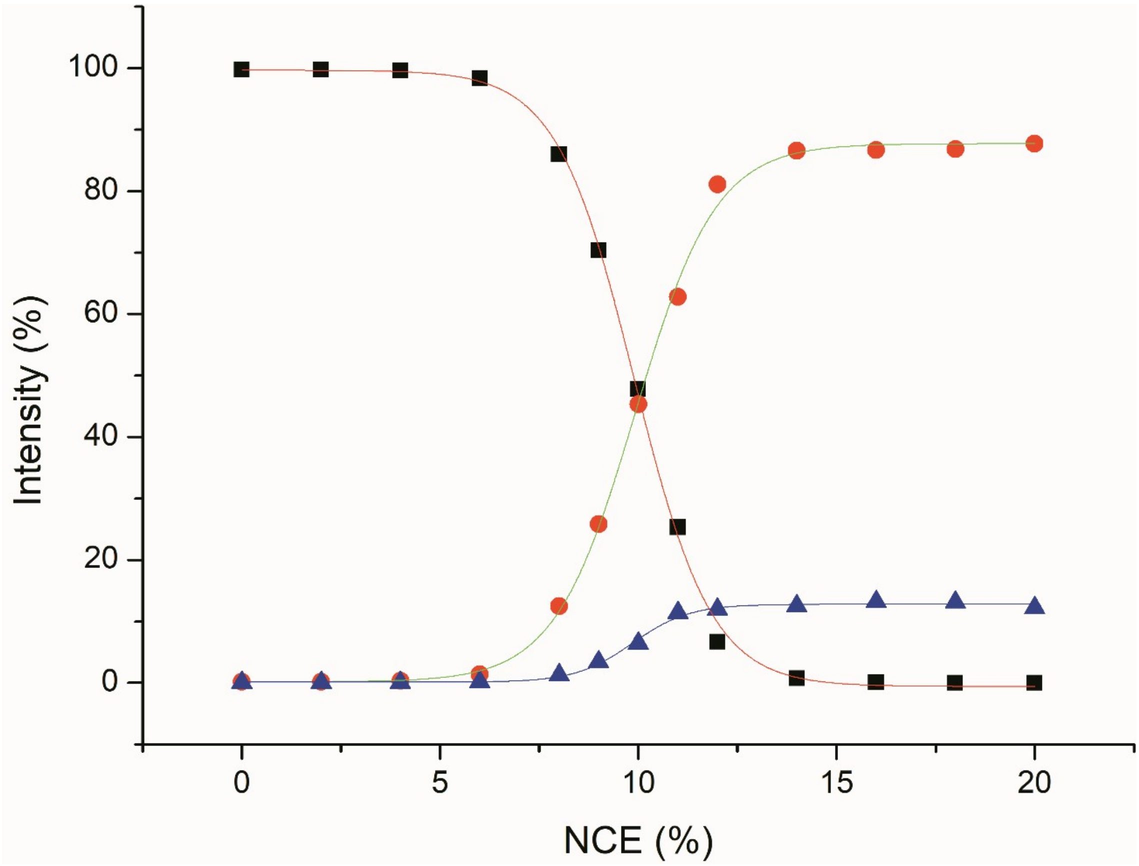
Representative CID of [**U**+ APO_3^-+ U] triplet



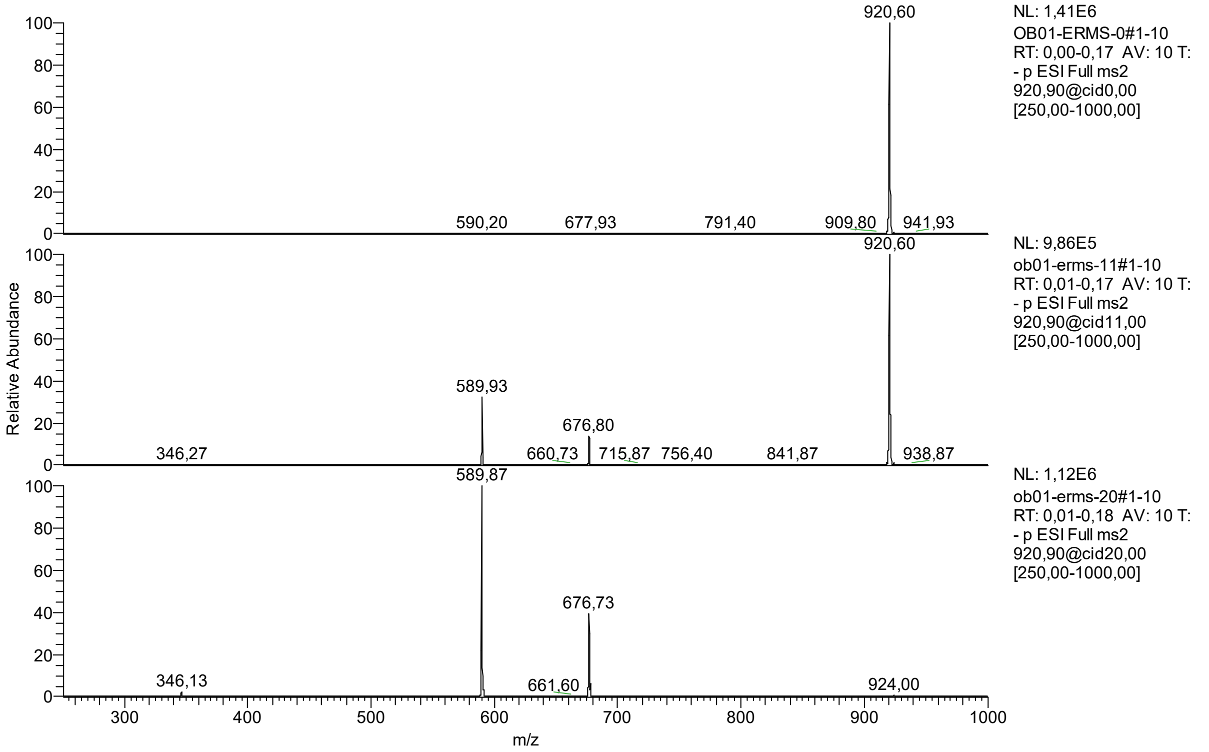
Model	Boltzmann		
Equation	y = A2 + (A1-A2)/(1 + exp((x-x0)/dx))		
Reduced Chi-Sqr	4,27556	3,36064	0,05443
Adj. R-Square	0,99721	0,99778	0,66863
		Value	Standard Error
B	A1	92,75528	1,28446
B	A2	0,9702	0,87713
B	x0	7,47546	0,06878
B	dx	0,93968	0,06094
D	A1	6,75512	1,13003
D	A2	97,57041	0,75126
D	x0	7,29534	0,05812
D	dx	0,86776	0,05175
F	A1	0,26377	0,33727
F	A2	1,31846	0,15361
F	x0	6,94872	2,18196
F	dx	2,45992	1,95694



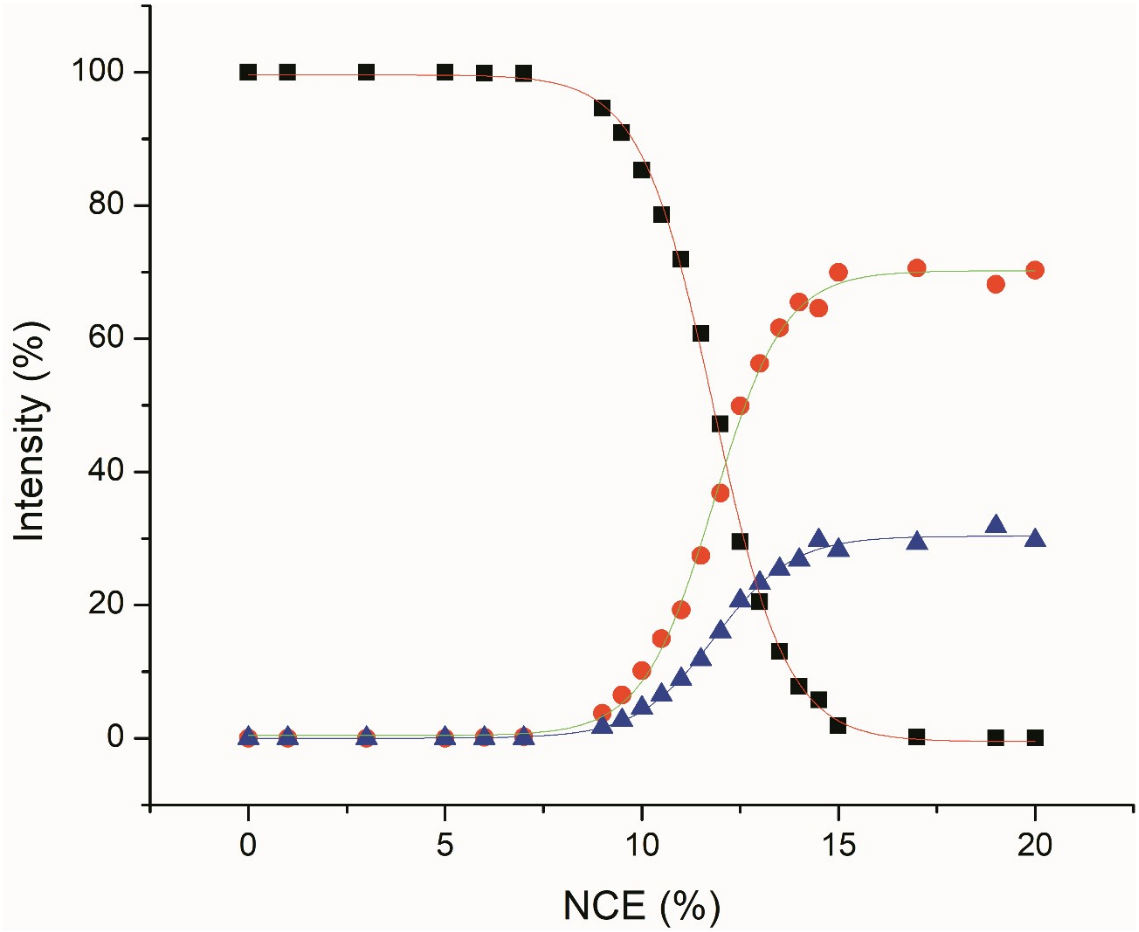
Representative CID of [$\mathbf{S_1}$ + APO_3^-+ U] triplet



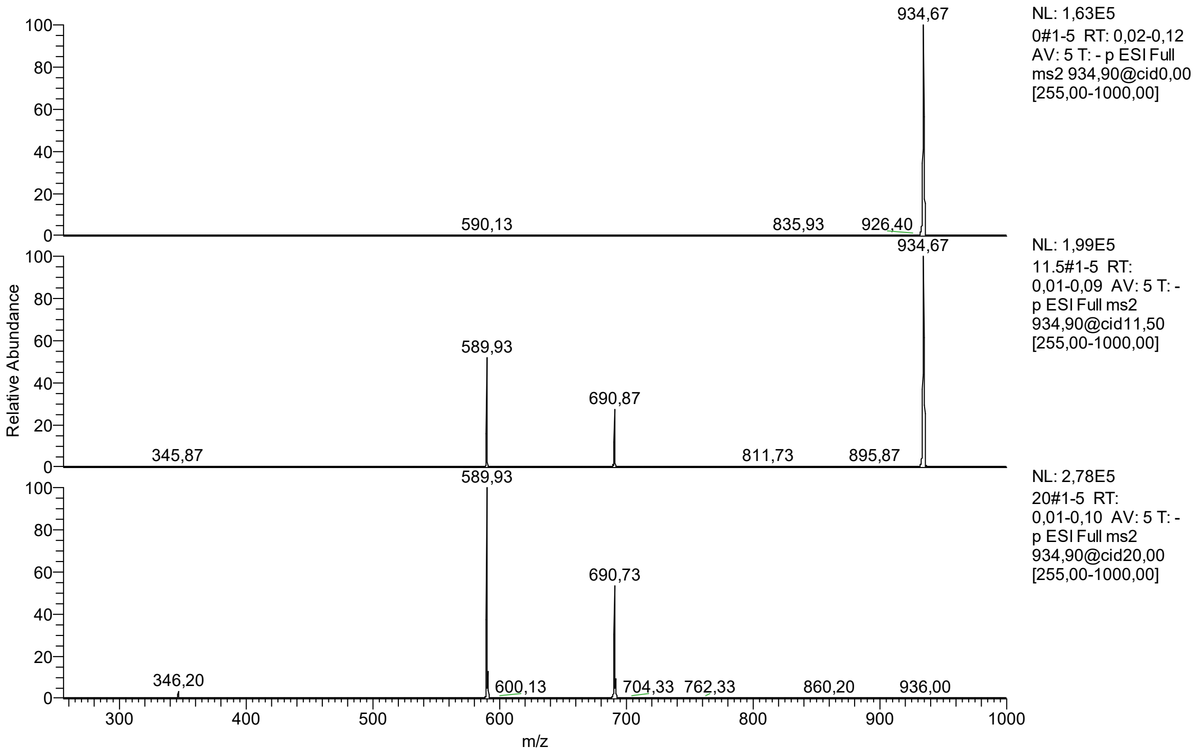
Model	Boltzmann		
Equation	y = A2 + (A1-A2)/(1 + exp((x-x0)/dx))		
Reduced Chi-Sqr	1,73667	2,26911	0,21584
Adj. R-Square	0,99913	0,99849	0,99375
		Value	Standard Error
B	A1	99,68878	0,68521
B	A2	-0,57177	0,67635
B	x0	9,89211	0,04065
B	dx	0,97679	0,036
D	A1	0,1824	0,78928
D	A2	87,75405	0,78198
D	x0	9,92282	0,05478
D	dx	1,01607	0,04887
F	A1	0,13577	0,22839
F	A2	12,82165	0,22361
F	x0	9,85412	0,09132
F	dx	0,71913	0,07836



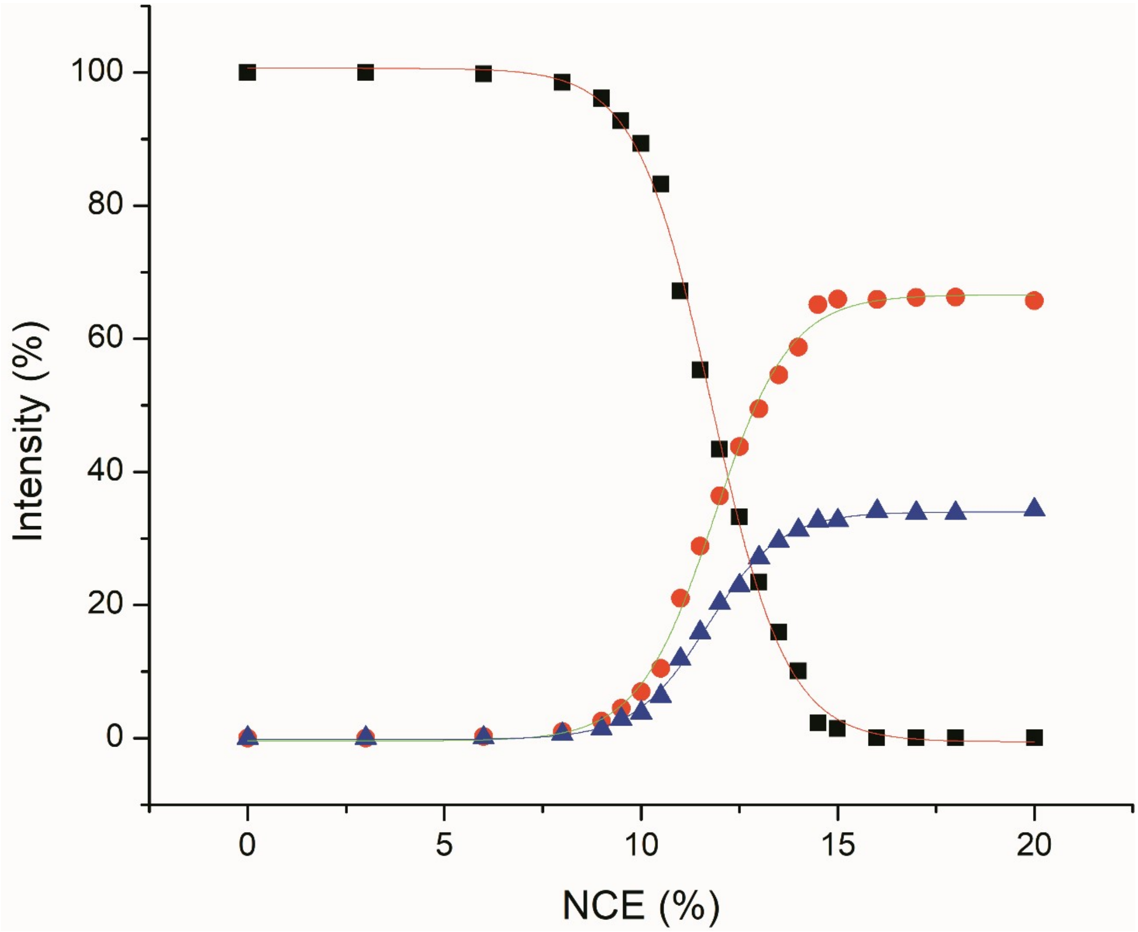
Representative CID of [S2 + APO3-+ U] triplet



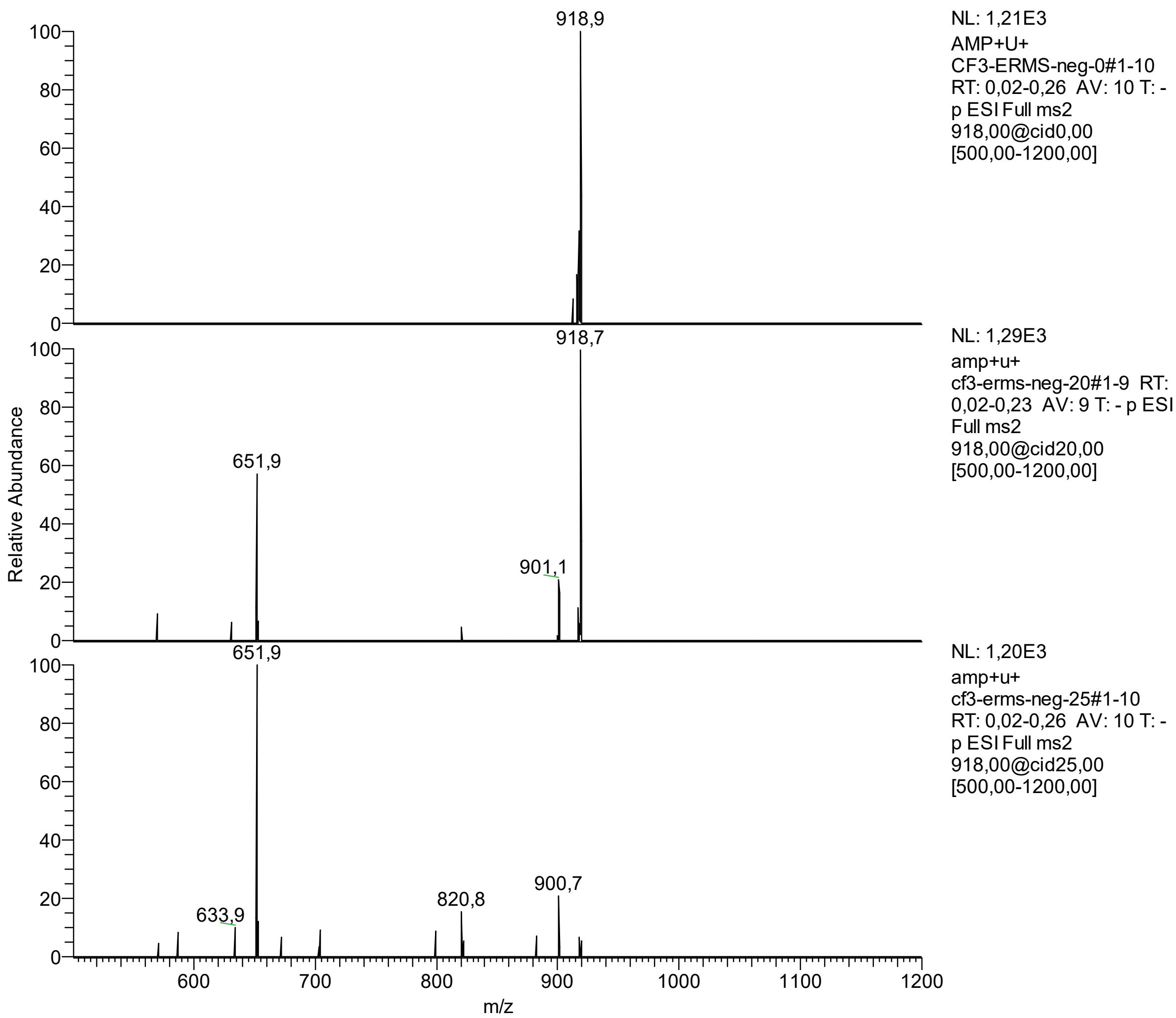
Model	Boltzmann		
Equation	y = A2 + (A1-A2)/(1 + exp((x-x0)/dx))		
Reduced Chi-Sqr	1,91489	1,91096	0,43801
Adj. R-Square	0,99891	0,9978	0,99722
		Value	Standard Error
B	A1	99,61841	0,54178
B	A2	-0,52863	0,6928
B	x0	11,82777	0,03173
B	dx	0,92434	0,02676
C	A1	0,38641	0,53784
C	A2	70,1979	0,68255
C	x0	11,81867	0,04433
C	dx	0,8966	0,03744
D	A1	-0,00129	0,2629
D	A2	30,35893	0,34249
D	x0	11,85458	0,05314
D	dx	0,99145	0,04471



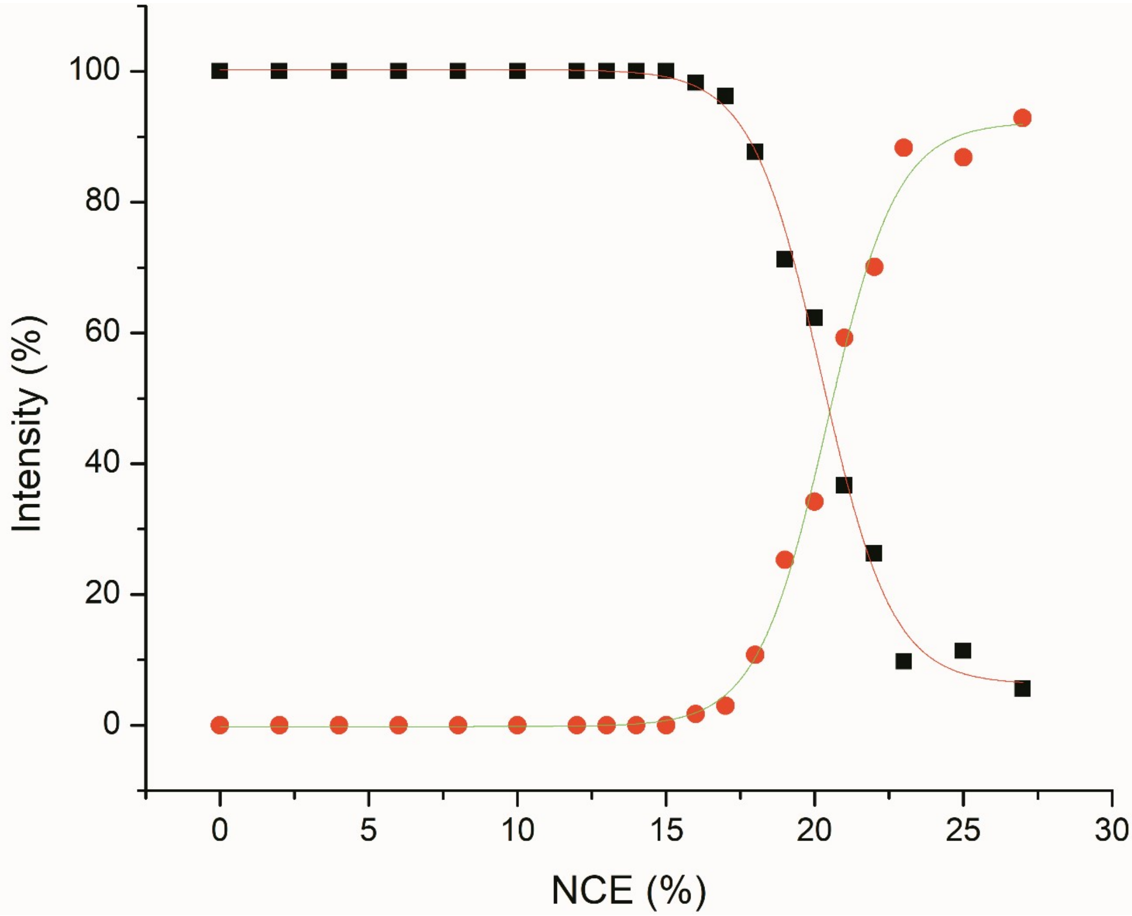
Representative CID of [S3 + APO3-+ U] triplet



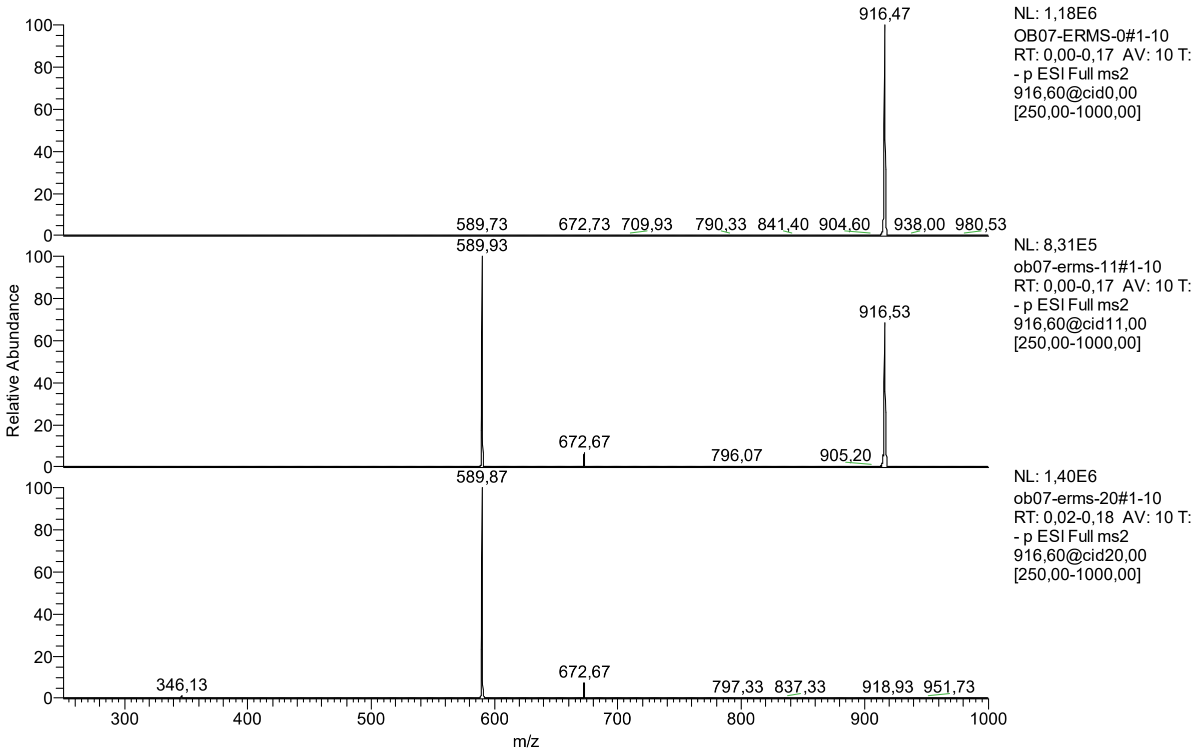
Model	Boltzmann		
Equation	y = A2 + (A1-A2)/(1 + exp((x-x0)/dx))		
Reduced Chi-Sqr	3,15301	1,93038	0,30175
Adj. R-Square	0,9982	0,99749	0,99851
		Value	Standard Error
B	A1	100,64843	0,8648
B	A2	-0,58688	0,83186
B	x0	11,79567	0,04205
B	dx	0,95347	0,03621
C	A1	-0,42988	0,67428
C	A2	66,6039	0,65923
C	x0	11,85217	0,05011
C	dx	0,96232	0,04317
D	A1	-0,20739	0,26885
D	A2	33,98733	0,25059
D	x0	11,68793	0,03774
D	dx	0,93189	0,03249



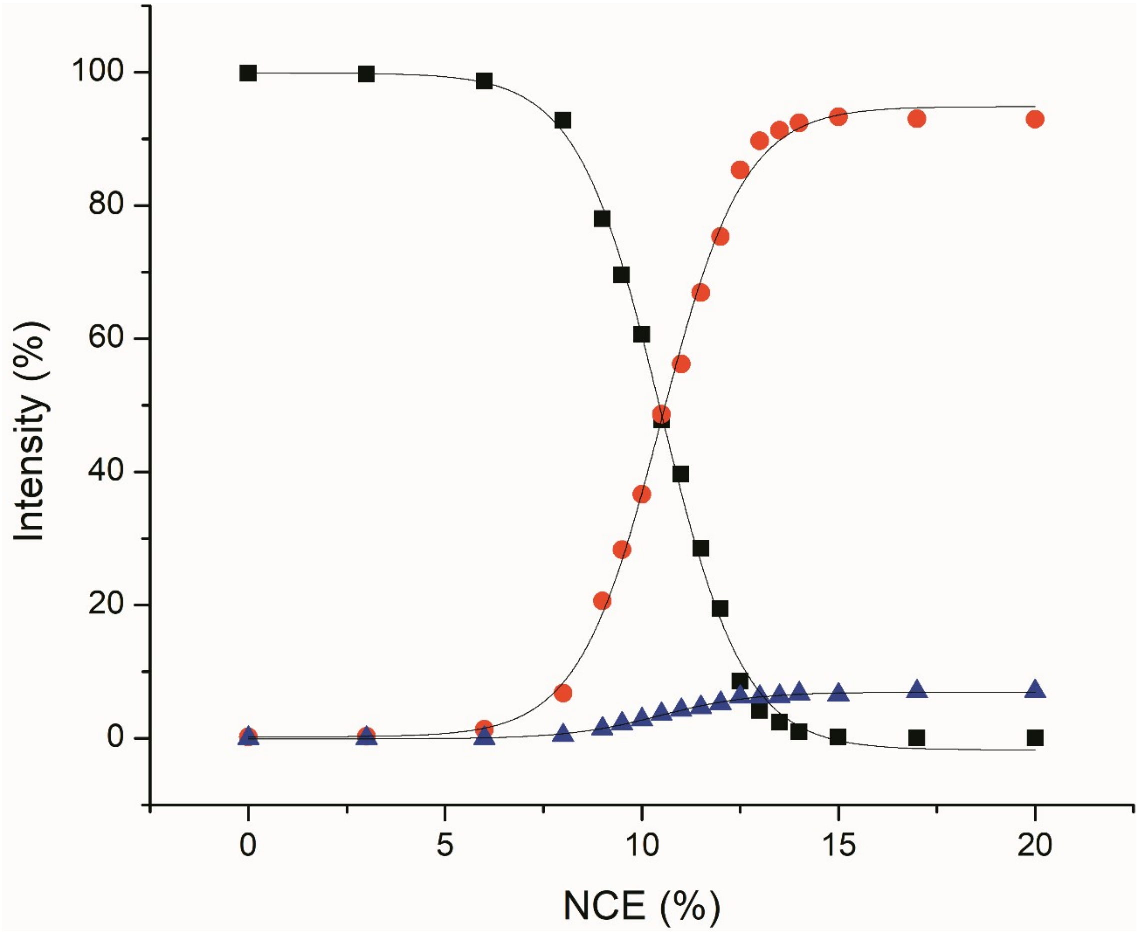
Representative CID of [S4 + APO3-+ U] triplet



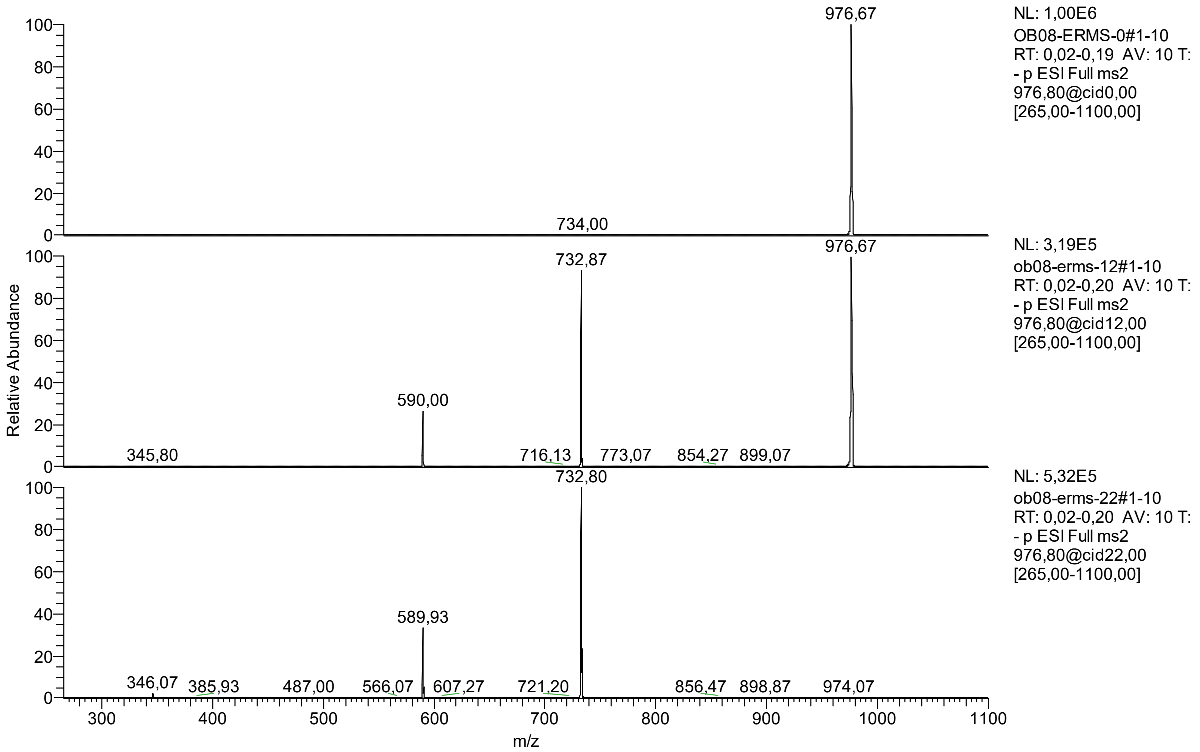
Model	Boltzmann		
Equation	y = A2 + (A1-A2)/(1 + exp((x-x0)/dx))		
Reduced Chi-Sqr	5,68181	5,62034	
Adj. R-Square	0,9956	0,99539	
		Value	Standard Error
triplex	A1	100,25678	0,74624
triplex	A2	6,26368	1,75805
triplex	x0	20,23381	0,09427
triplex	dx	1,18522	0,07861
m/z	A1	-0,18417	0,73526
m/z	A2	92,23059	1,78425
m/z	x0	20,40608	0,09547
m/z	dx	1,17667	0,07951



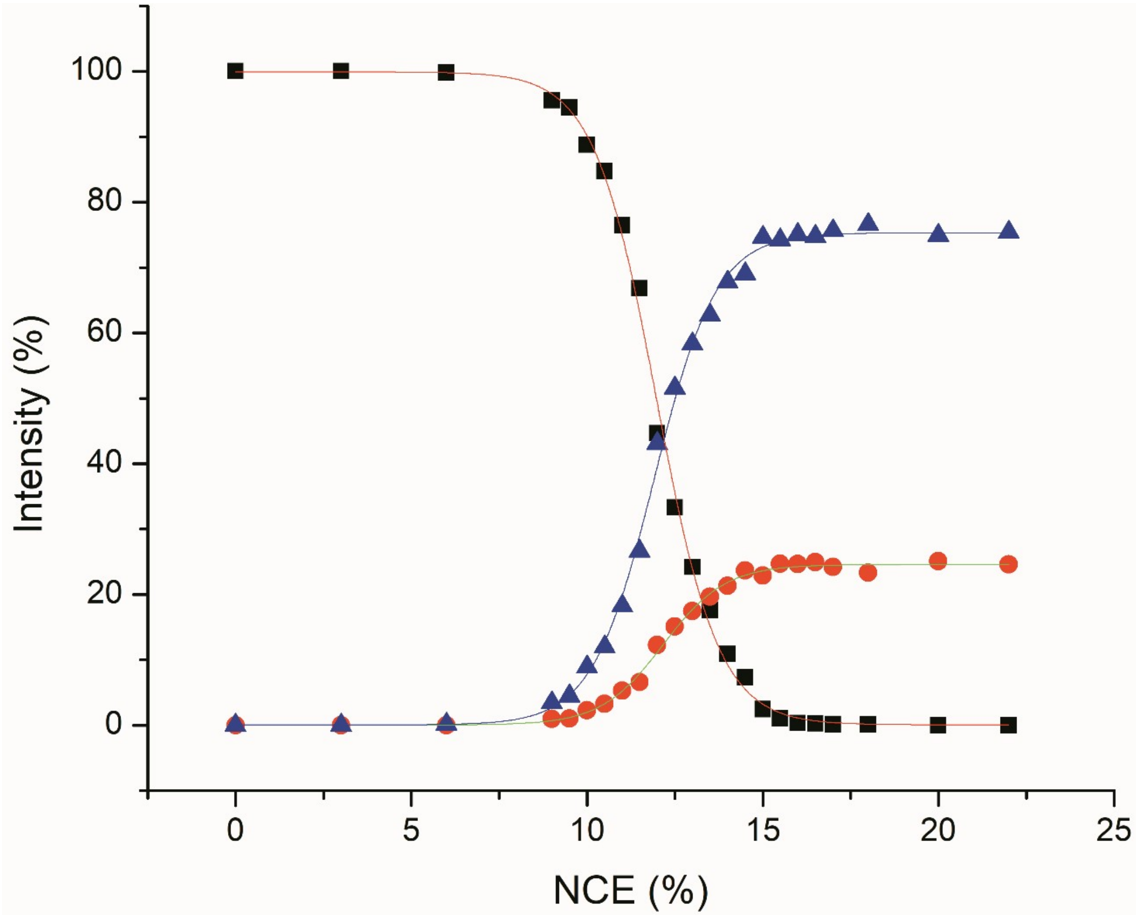
Representative CID of [S5 + APO3-+ U] triplet



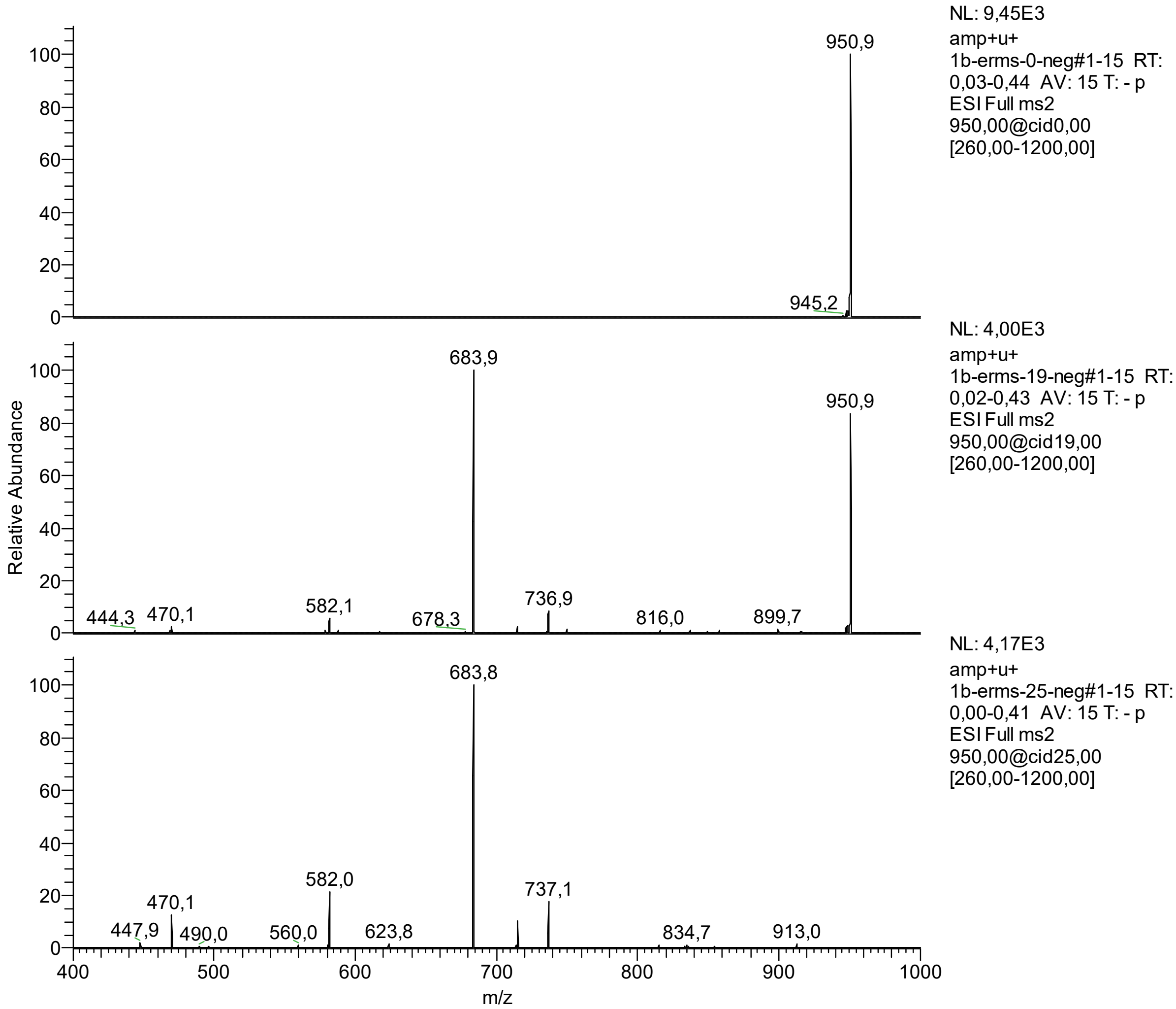
Model	Boltzmann		
Equation	y = A2 + (A1-A2)/(1 + exp((x-x0)/dx))		
Reduced Chi-Sqr	3,44159	3,23755	0,02924
Adj. R-Square	0,99781	0,99763	0,99589
		Value	Standard Error
B	A1	99,89932	1,0731
B	A2	-1,76869	0,98024
B	x0	10,48388	0,05025
B	dx	1,05948	0,04475
C	A1	0,19679	1,03848
C	A2	94,86484	0,94709
C	x0	10,48567	0,05199
C	dx	1,05186	0,04627
D	A1	-0,09662	0,10221
D	A2	6,92298	0,09594
D	x0	10,47094	0,07418
D	dx	1,17709	0,06667



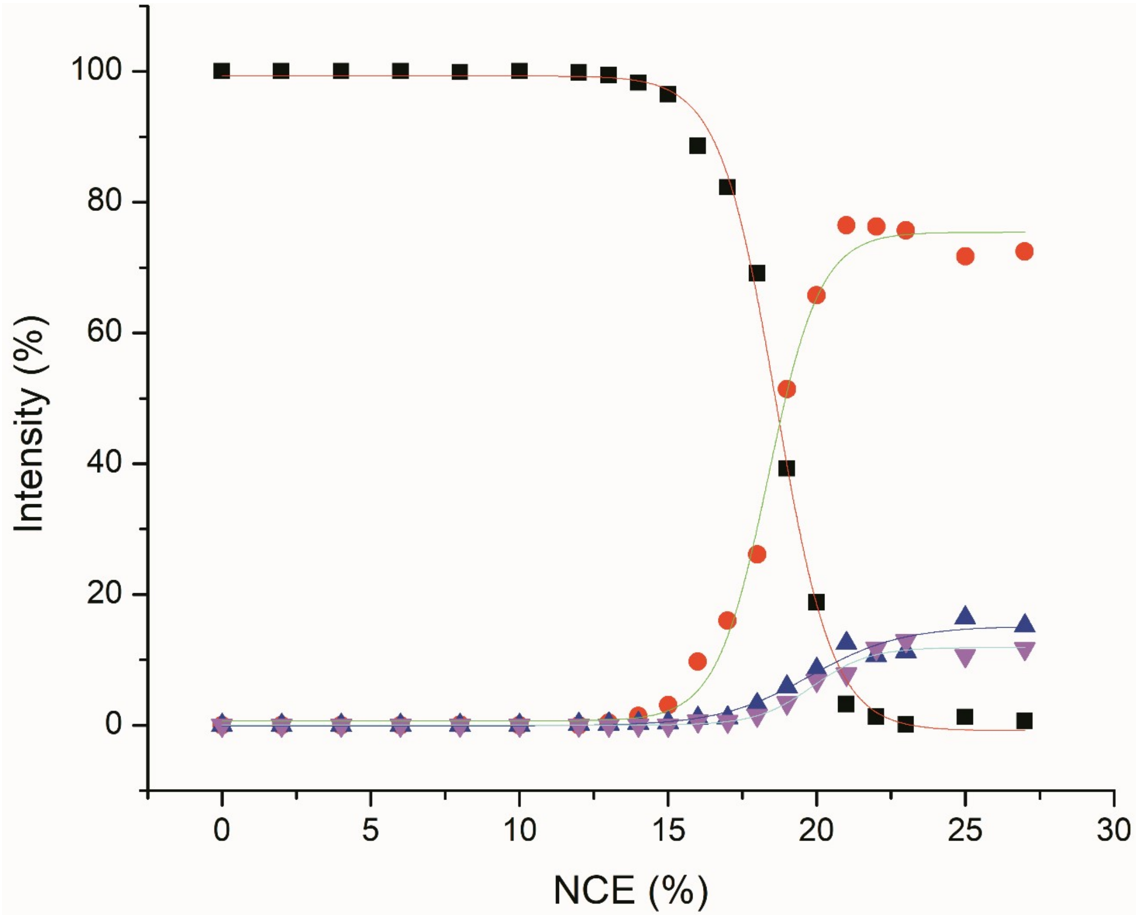
Representative CID of [S6 + APO3-+ U] triplet.



Model	Boltzmann		
Equation	y = A2 + (A1-A2)/(1 + exp((x-x0)/dx))		
Reduced Chi-Sqr	3,16585	0,4025	2,20543
Adj. R-Square	0,99819	0,99624	0,99777
		Value	Standard Error
B	A1	99,90802	0,89367
B	A2	0,08647	0,67255
B	x0	11,97249	0,0395
B	dx	0,88626	0,03383
C	A1	0,05302	0,31025
C	A2	24,58547	0,24587
C	x0	12,16442	0,05706
C	dx	0,88443	0,04917
D	A1	0,06554	0,75055
D	A2	75,30992	0,5554
D	x0	11,91039	0,04356
D	dx	0,88106	0,03724

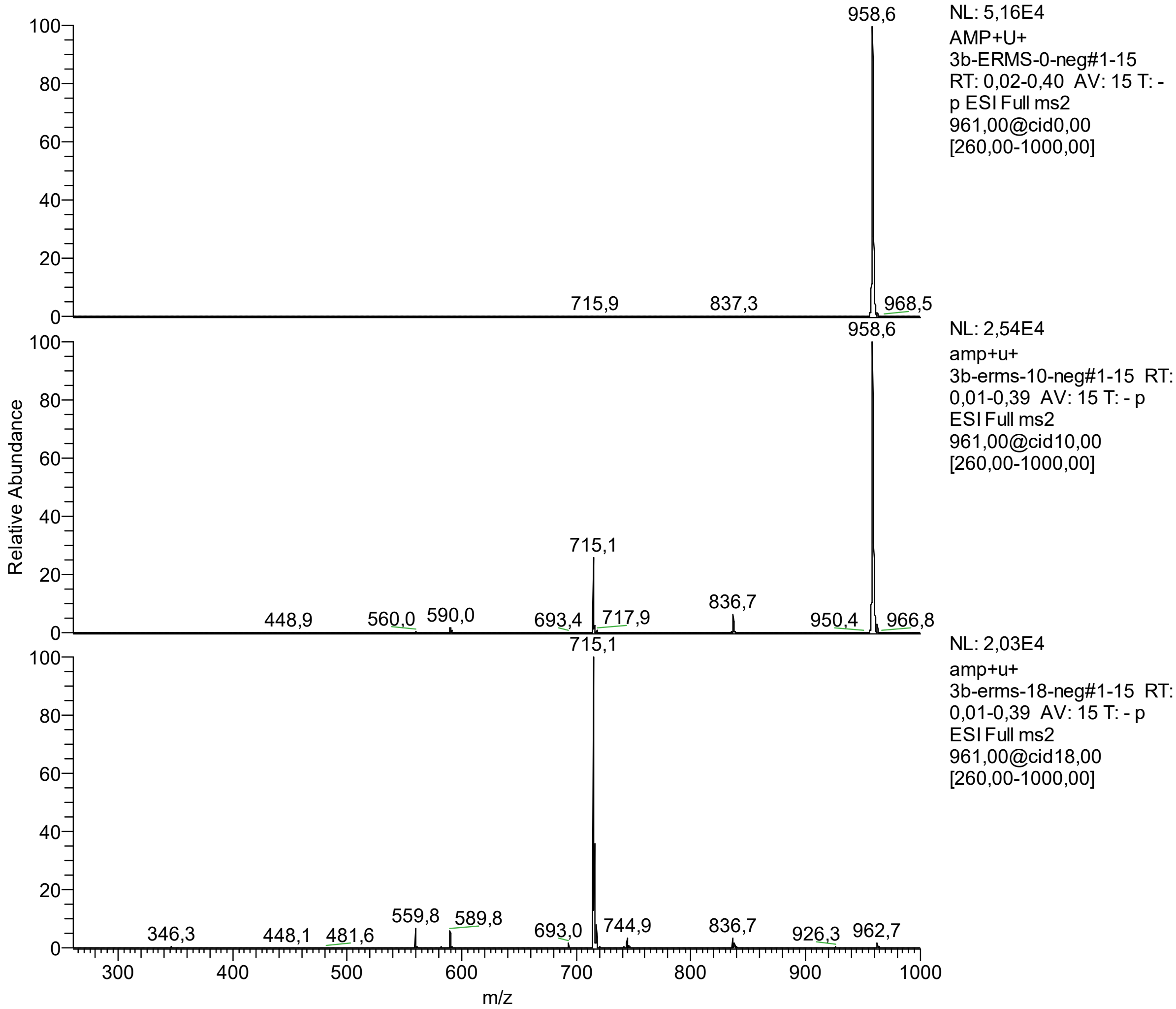


Representative CID of [S7 + APO3-+ U] triplet

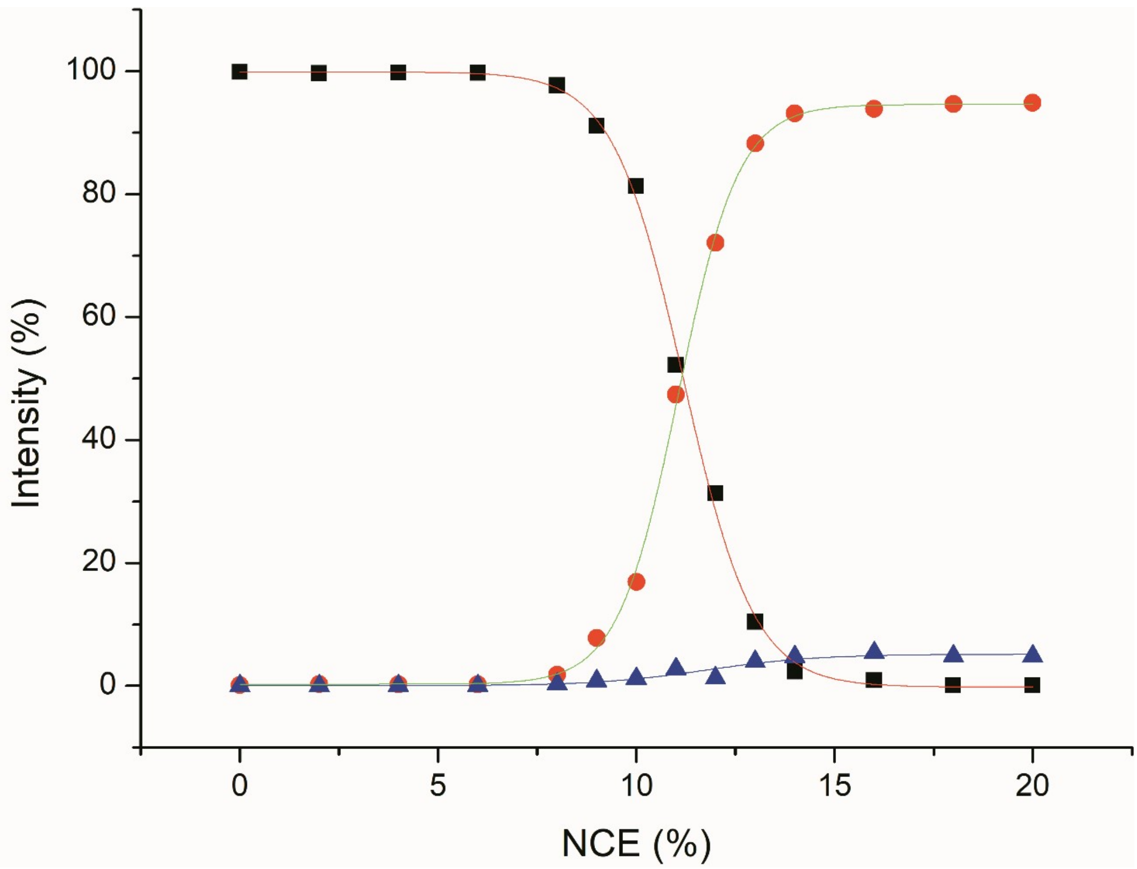


Model	Boltzmann			
Equation	y = A2 + (A1-A2)/(1 + exp((x-x0)/dx))			
Reduced Chi-Sqr	4,03282	5,87795	1,02292	0,42936
Adj. R-Square	0,99786	0,99464	0,96964	0,98178
		Value	Standard Error	
Triplex	A1	99,3073	0,64911	
Triplex	A2	-0,80011	1,07561	
Triplex	x0	18,6342	0,05874	
Triplex	dx	0,95096	0,05063	
D	A1	0,68597	0,78232	
D	A2	75,40231	1,21719	
D	x0	18,36869	0,08874	
D	dx	0,87366	0,07673	
F	A1	-0,08628	0,34752	
F	A2	15,18762	0,81947	
F	x0	19,77328	0,31049	
F	dx	1,53529	0,25761	
H	A1	0,03798	0,1994	
H	A2	11,91487	0,41218	
H	x0	19,86257	0,1666	

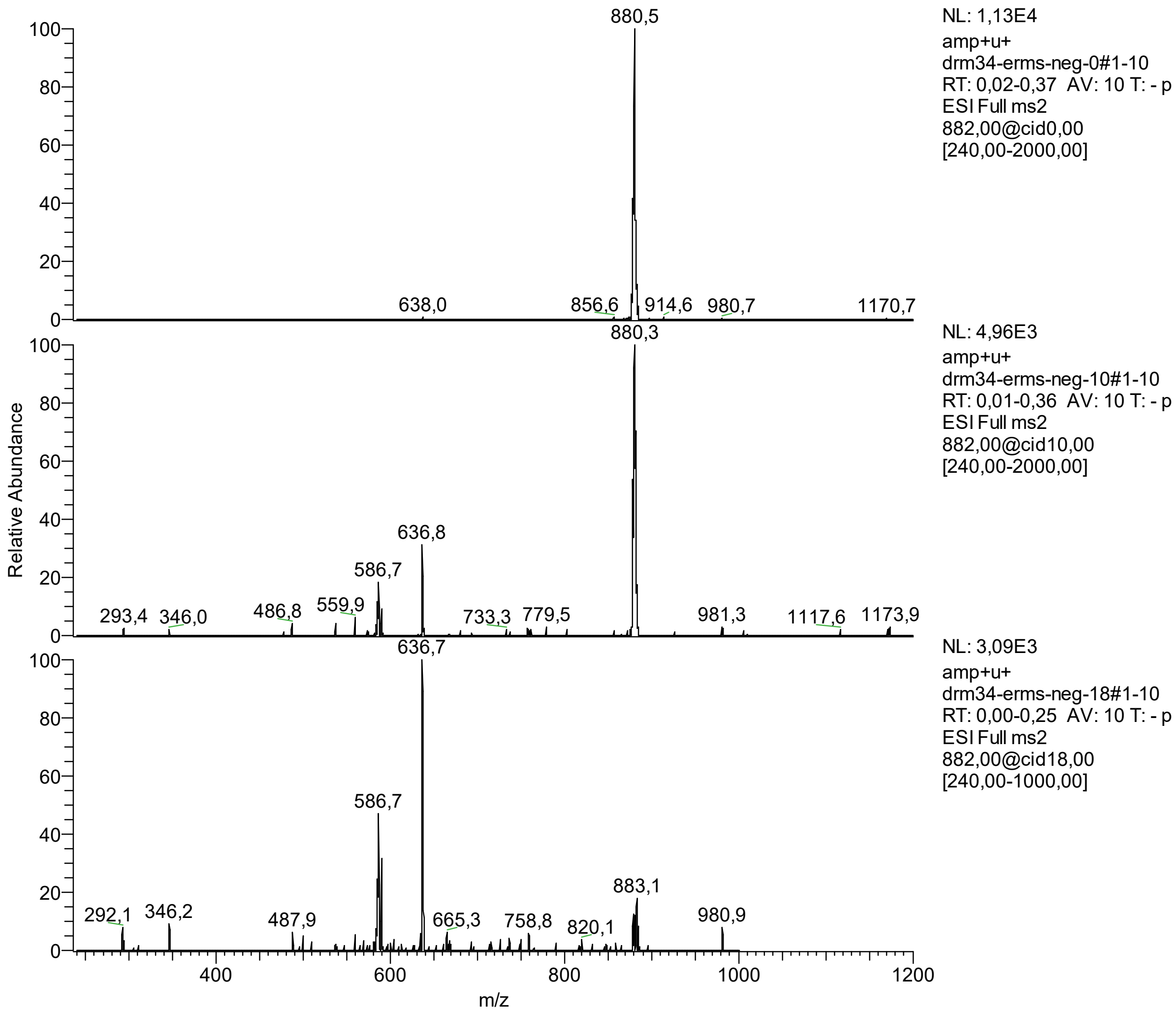
H	dx	0,94311	0,14108



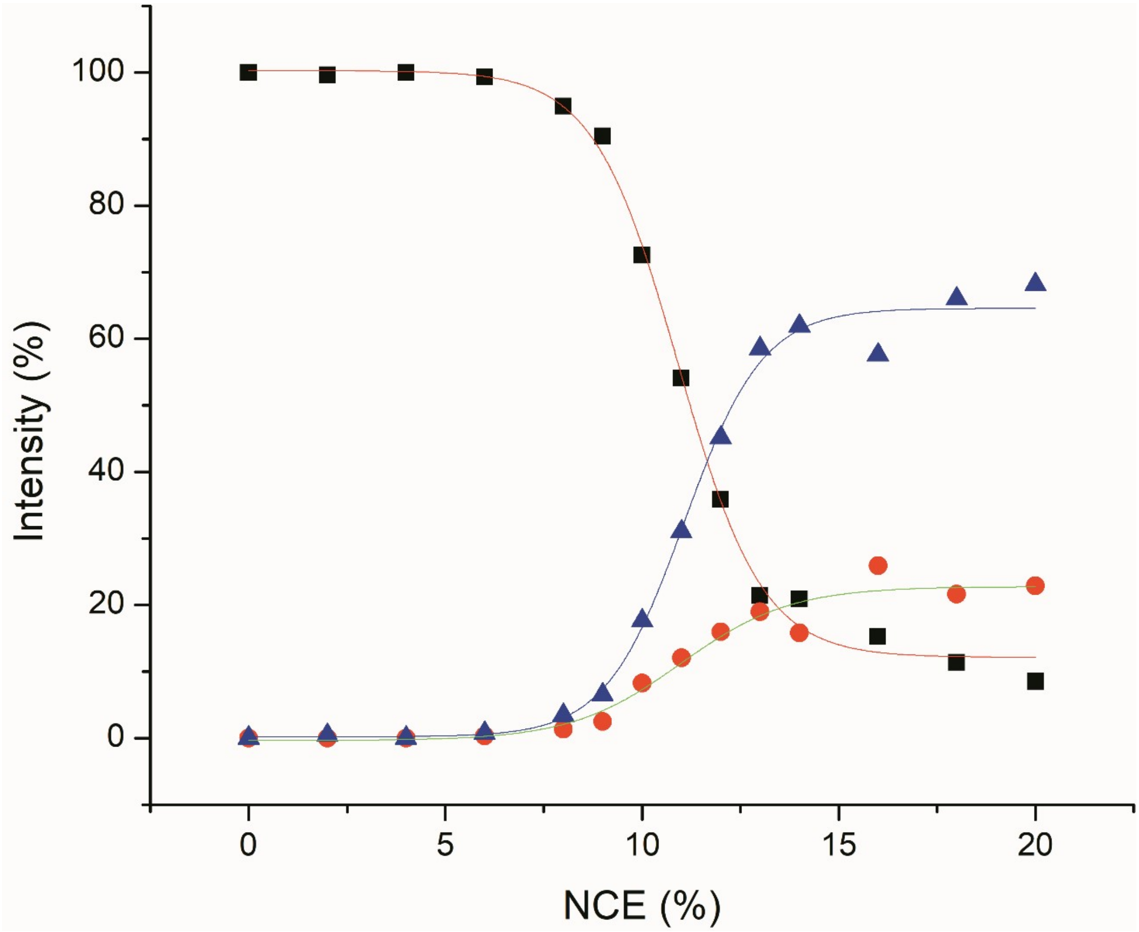
Representative CID of [S8 + APO3-+ U] triplet



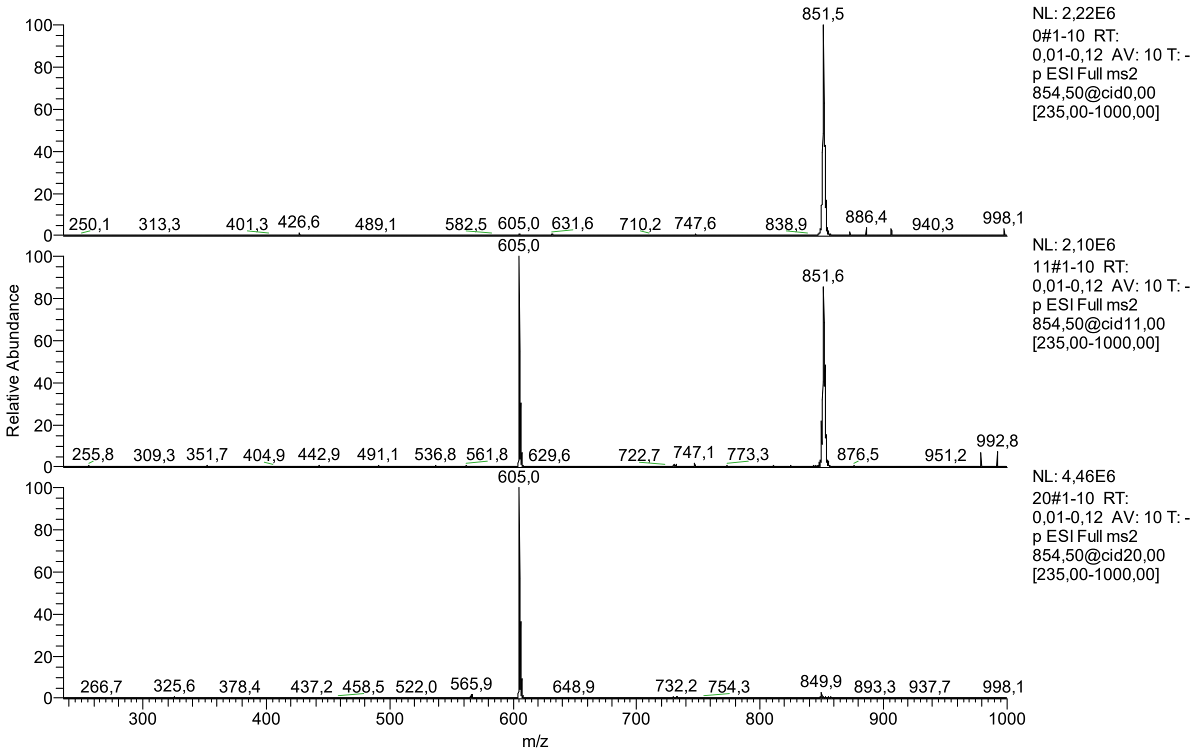
Model	Boltzmann		
Equation	y = A2 + (A1-A2)/(1 + exp((x-x0)/dx))		
Reduced Chi-Sqr	2,65593	1,29627	0,38003
Adj. R-Square	0,99868	0,99931	0,91888
		Value	Standard Error
B	A1	99,90062	0,75464
B	A2	-0,17584	0,88309
B	x0	11,18948	0,04715
B	dx	0,88574	0,04029
D	A1	0,29312	0,51472
D	A2	94,63211	0,58367
D	x0	11,05905	0,03125
D	dx	0,76011	0,02686
F	A1	0,02751	0,31363
F	A2	5,17161	0,41854
F	x0	11,77622	0,50431
F	dx	1,3924	0,44846



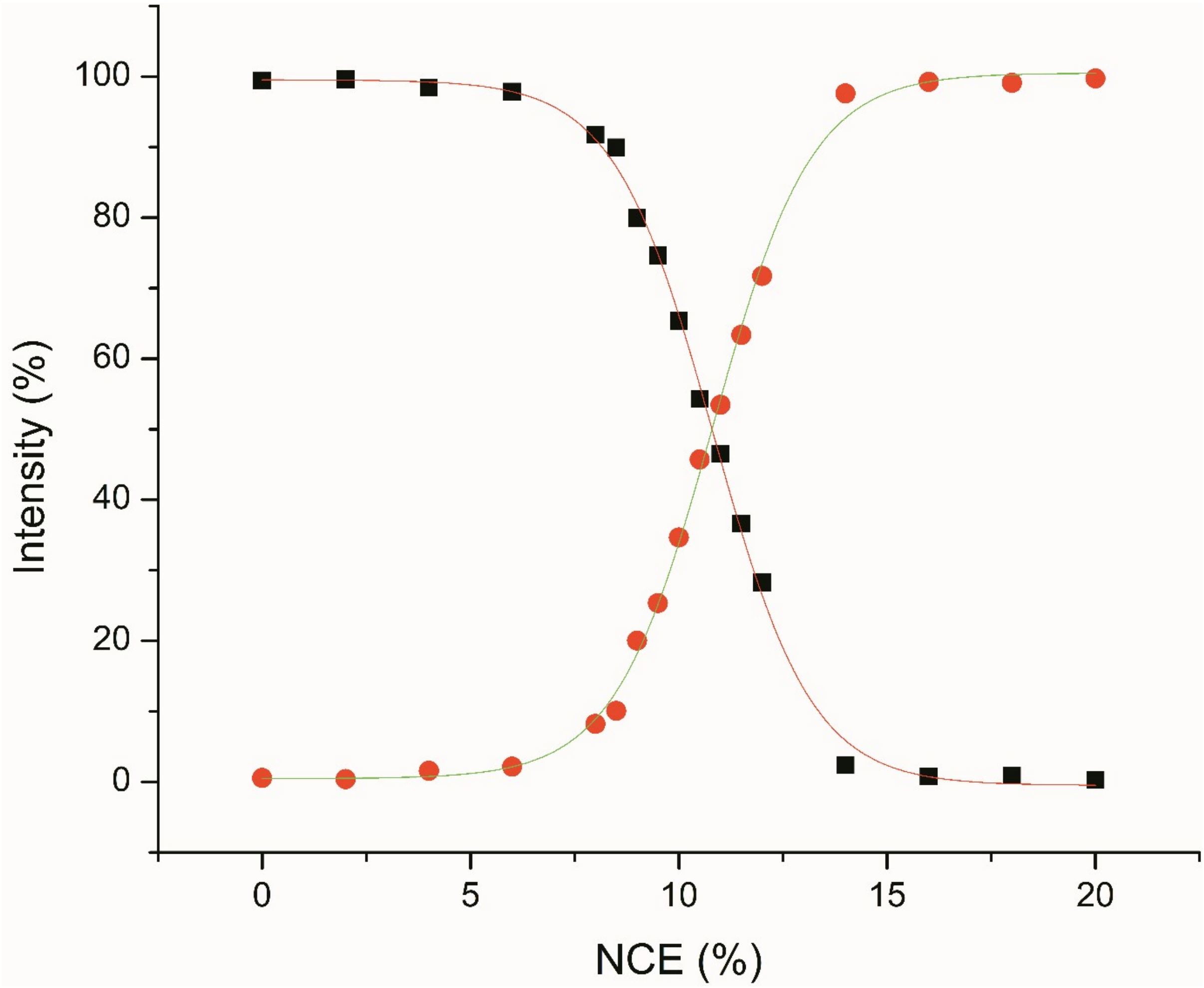
Representative CID of [S9 + APO3-+ U] triplet



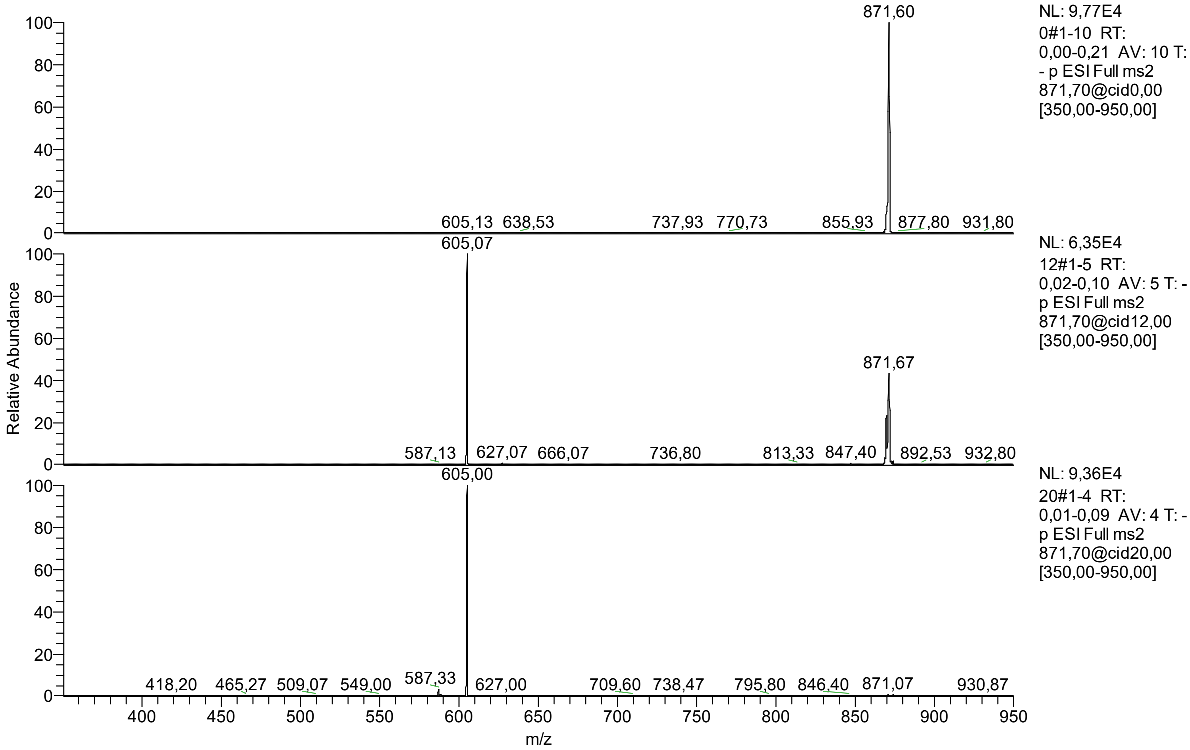
Model	Boltzmann		
Equation	y = A2 + (A1-A2)/(1 + exp((x-x0)/dx))		
Reduced Chi-Sqr	5,00387	4,20009	6,64543
Adj. R-Square	0,99662	0,95575	0,99178
		Value	Standard Error
triplex	A1	100,28684	1,1085
triplex	A2	12,12818	1,25339
triplex	x0	10,91634	0,0846
triplex	dx	1,06925	0,07252
UA	A1	-0,37136	1,09885
UA	A2	22,75499	1,28789
UA	x0	10,98052	0,3676
UA	dx	1,39078	0,32437
F	A1	0,17853	1,24123
F	A2	64,58008	1,43203
F	x0	11,06789	0,12675
F	dx	0,99878	0,10832



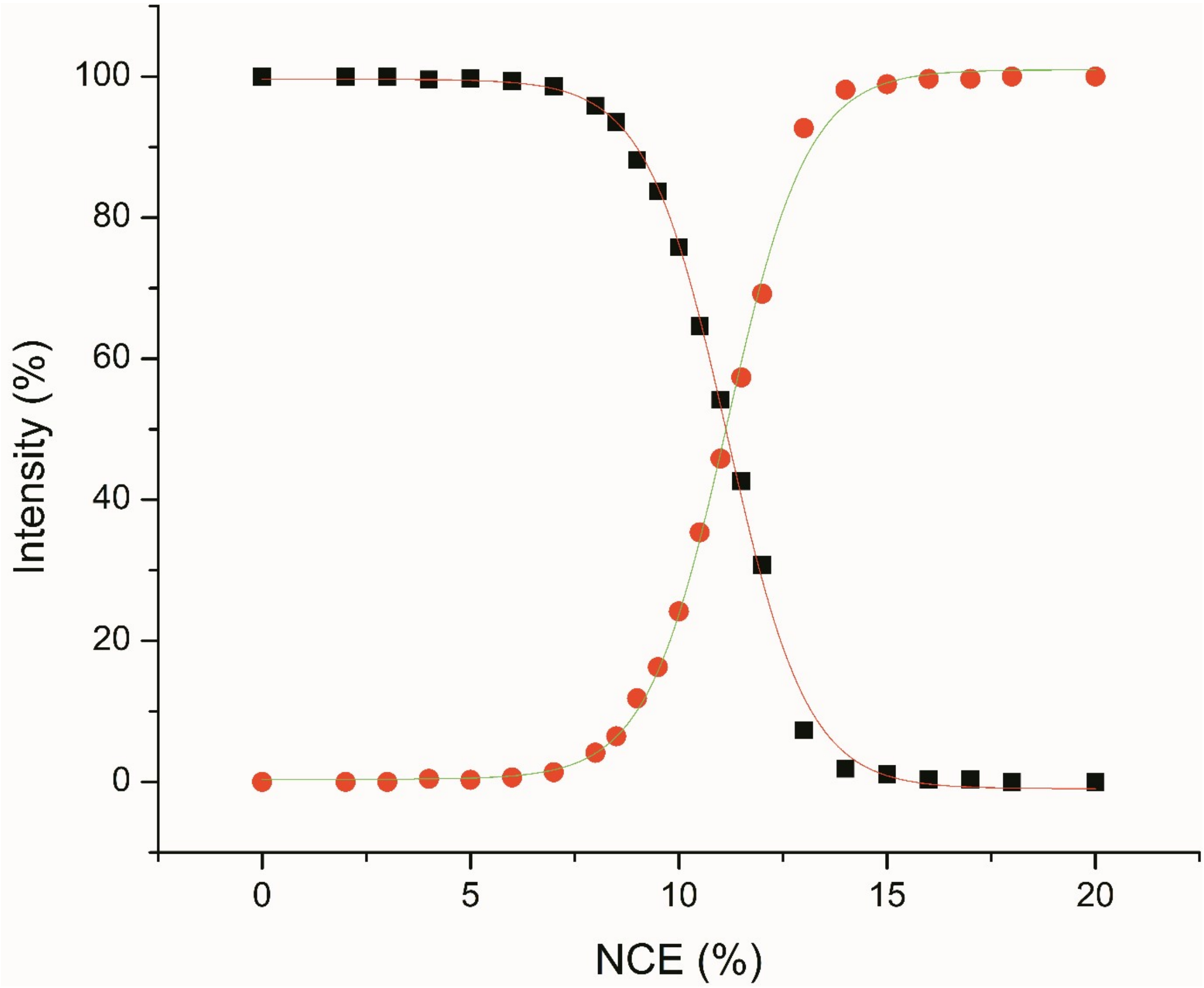
Representative CID of [HB1 + CPO3-+ G] triplet



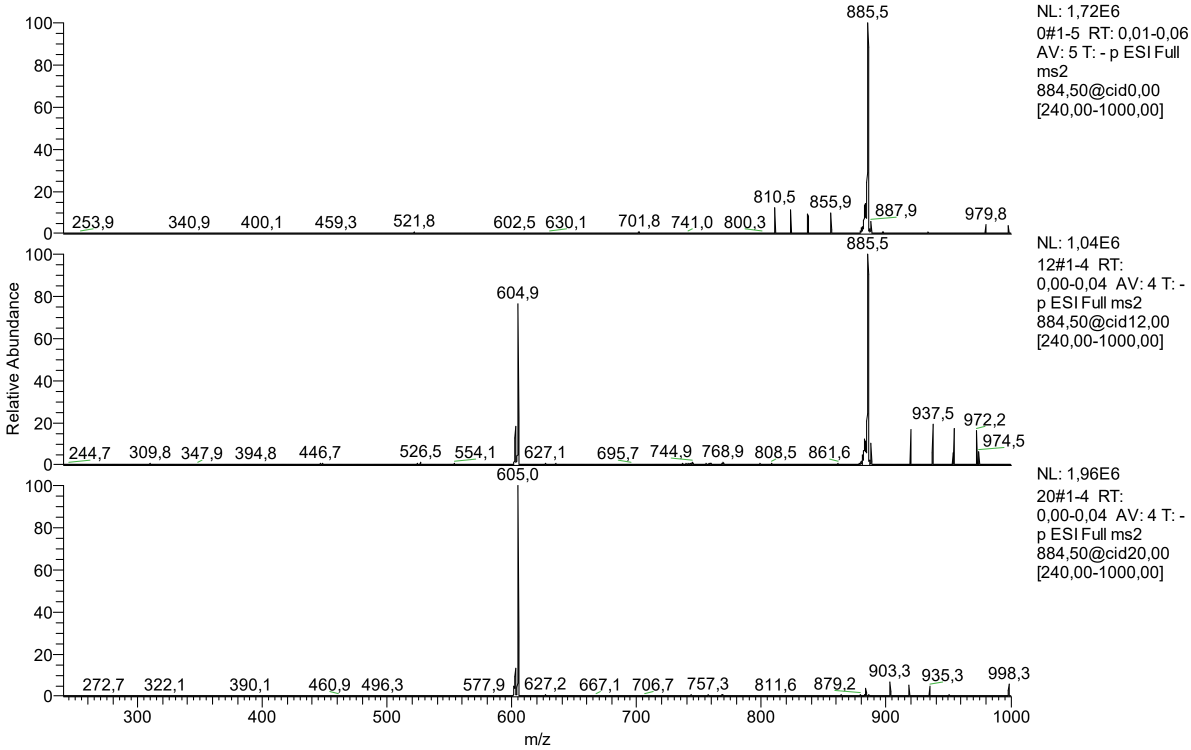
Model	Boltzmann		
Equation	y = A2 + (A1-A2)/(1 + exp((x-x0)/dx))		
Reduced Chi-Sqr	2,75827	2,75827	
Adj. R-Square	0,99817	0,99817	
		Value	Standard Error
B	A1	99,54149	0,84965
B	A2	-0,50245	0,94452
B	x0	10,81938	0,04958
B	dx	1,18421	0,04717
C	A1	0,45851	0,84965
C	A2	100,50245	0,94452
C	x0	10,81938	0,04958
C	dx	1,18421	0,04717



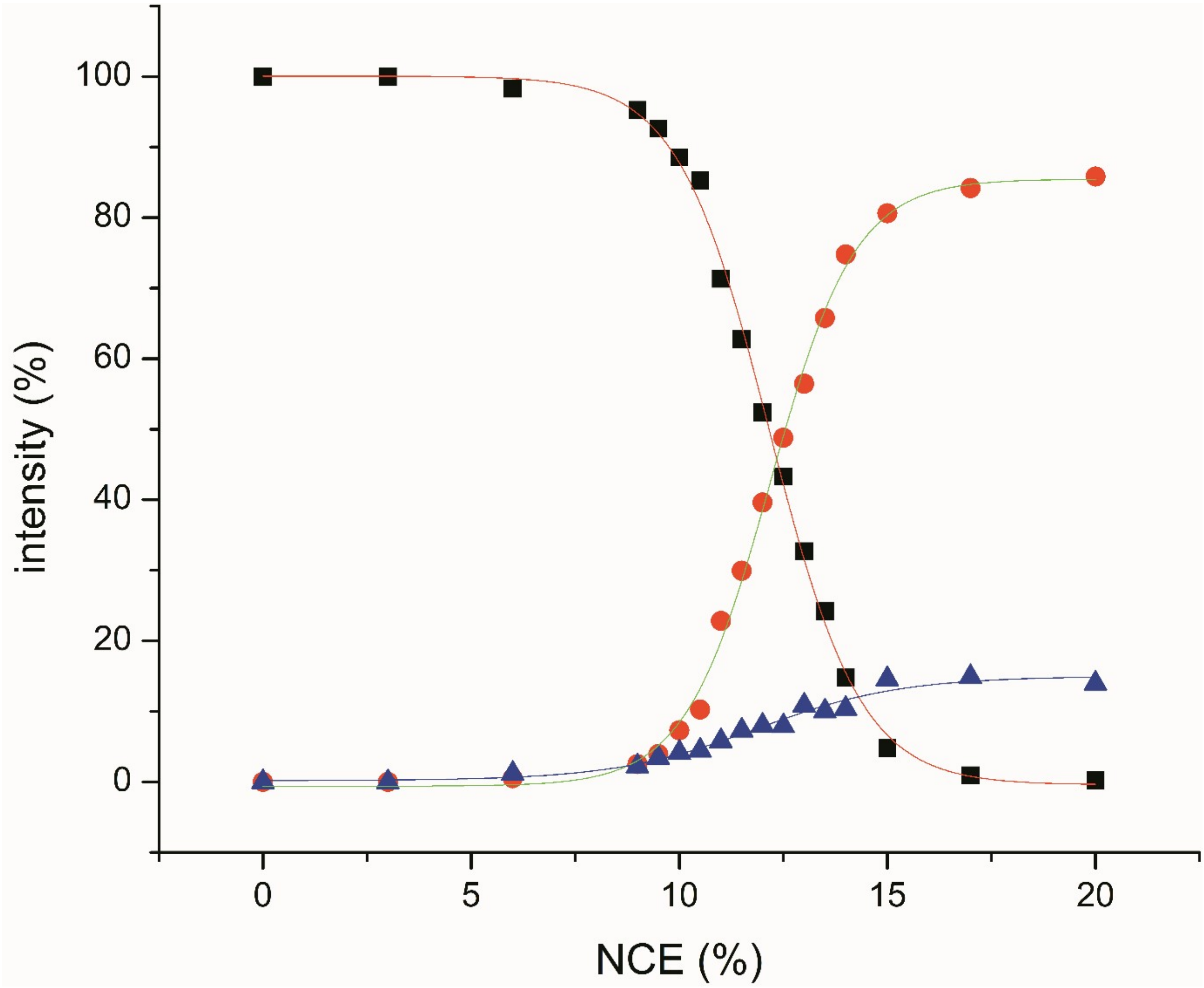
Representative CID of [HB2 + CPO3-+ G] triplet



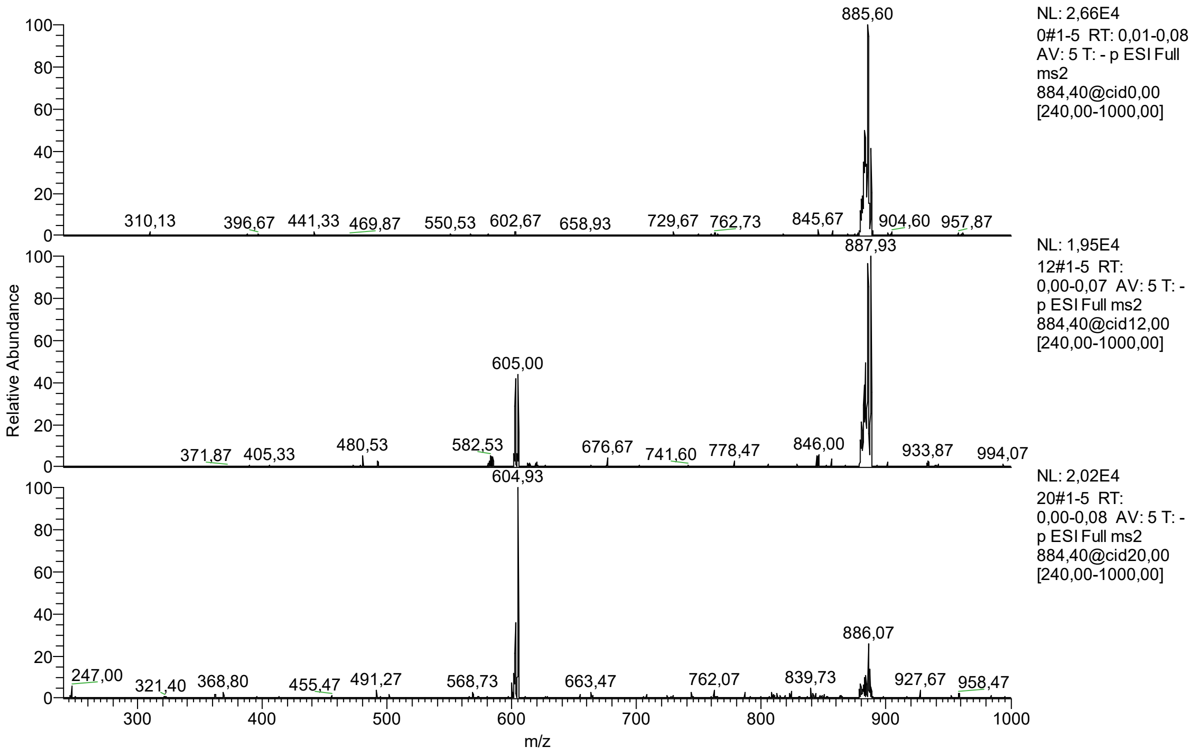
Model	Boltzmann		
Equation	y = A2 + (A1-A2)/(1 + exp((x-x0)/dx))		
Reduced Chi-Sqr	2,40393	2,40393	
Adj. R-Square	0,99868	0,99868	
		Value	Standard Error
B	A1	99,6328	0,57412
B	A2	-0,96603	0,69762
B	x0	11,15538	0,03599
B	dx	0,96596	0,0332
C	A1	0,3672	0,57412
C	A2	100,96603	0,69762
C	x0	11,15538	0,03599
C	dx	0,96596	0,0332



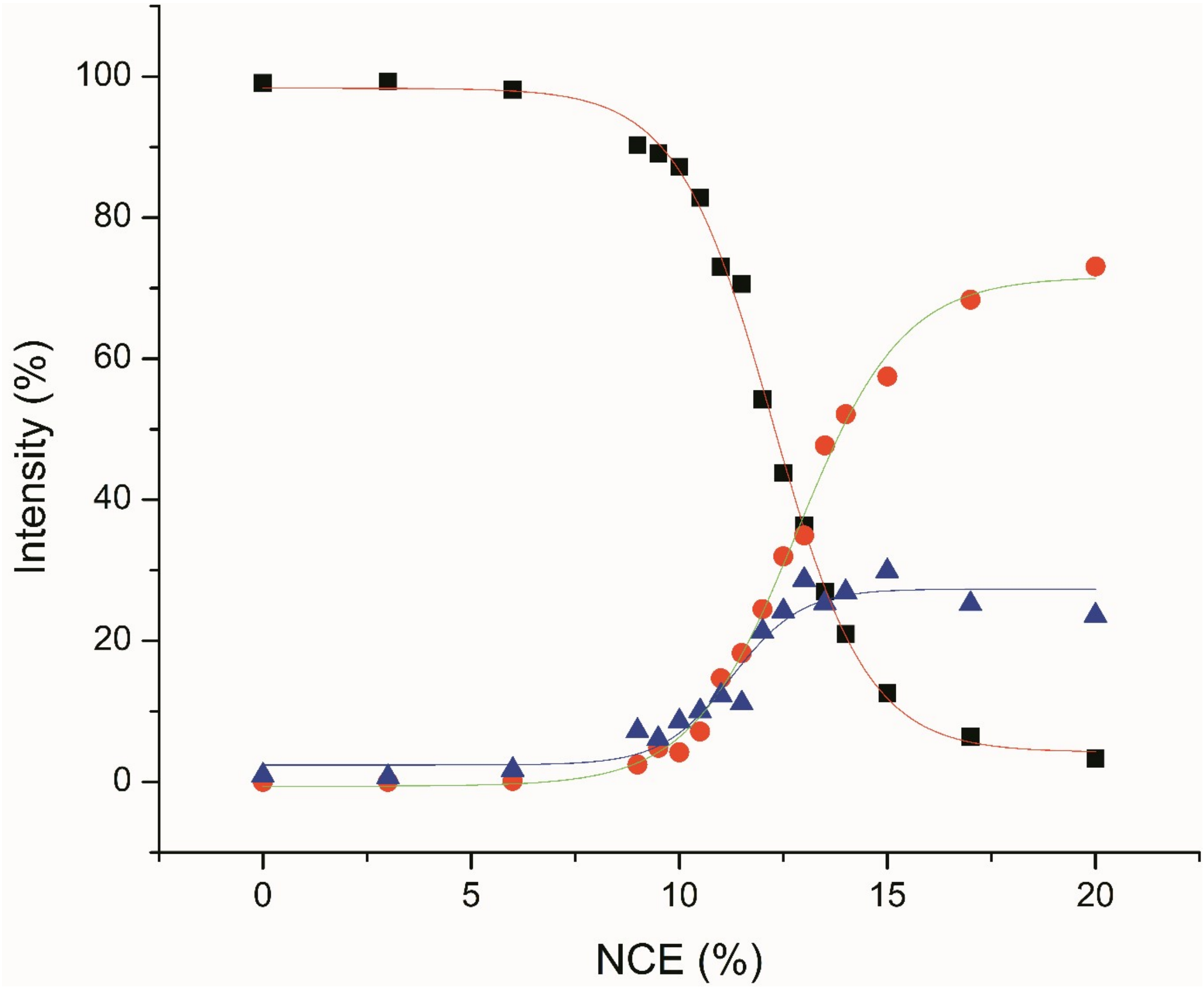
Representative CID of [HB3 + CPO3-+ G] triplet



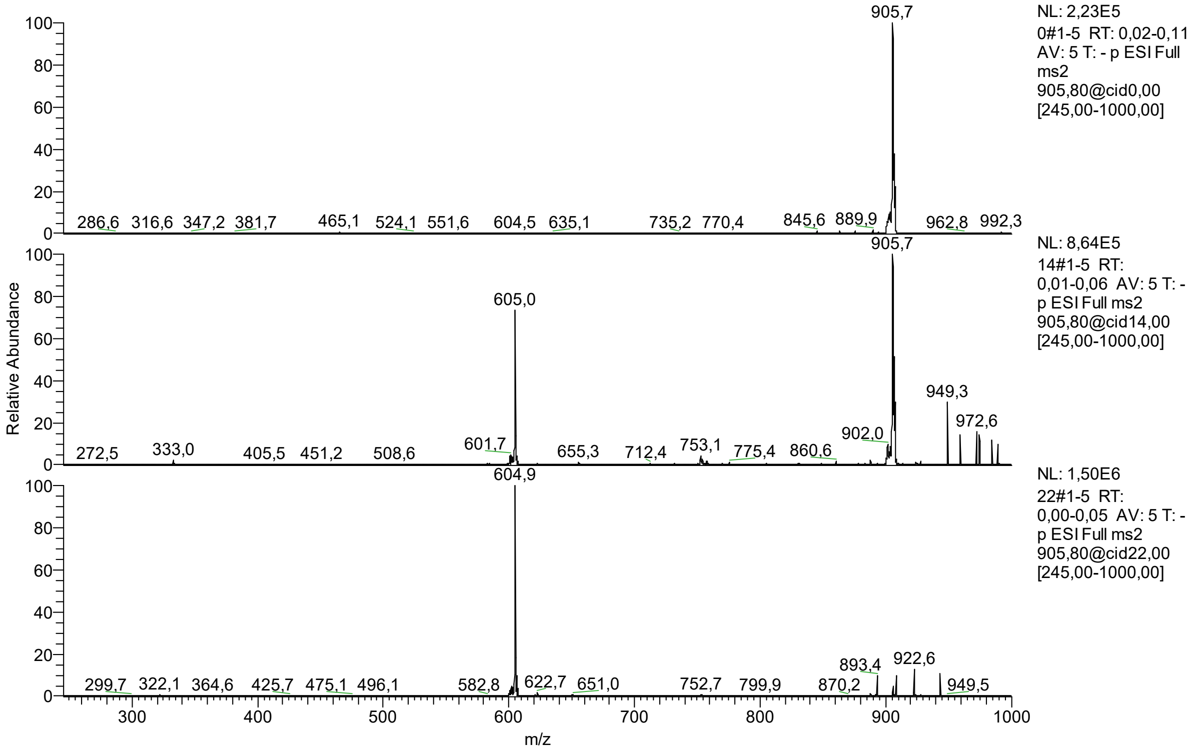
Model	Boltzmann		
Equation	y = A2 + (A1-A2)/(1 + exp((x-x0)/dx))		
Reduced Chi-Sqr	2,81673	2,72473	0,69269
Adj. R-Square	0,99803	0,99751	0,97149
		Value	Standard Error
B	A1	100,07733	0,89472
B	A2	-0,42085	1,14961
B	x0	12,16348	0,05
B	dx	1,09748	0,042
C	A1	-0,60418	0,85554
C	A2	85,47509	1,09855
C	x0	12,18518	0,05351
C	dx	1,01966	0,04505
D	A1	0,18431	0,53218
D	A2	14,97871	0,71861
D	x0	11,87765	0,27129
D	dx	1,72958	0,24068



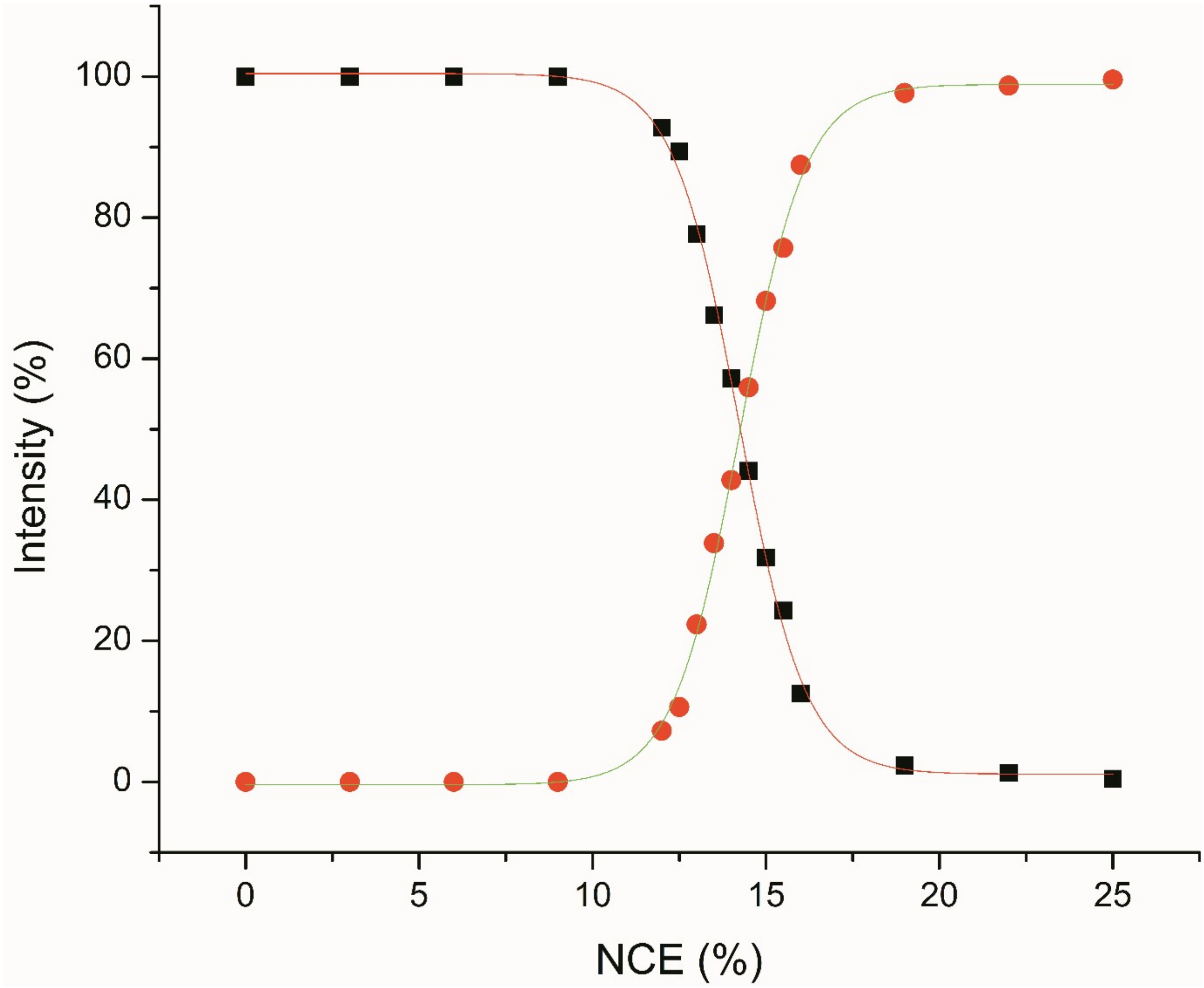
Representative CID of [HB4 + CPO3-+ G] triplet



Model	Boltzmann		
Equation	y = A2 + (A1-A2)/(1 + exp((x-x0)/dx))		
Reduced Chi-Sqr	3,68022	3,49479	7,57601
Adj. R-Square	0,997	0,99458	0,93131
		Value	Standard Error
B	A1	98,35538	1,03012
B	A2	4,20597	1,34907
B	x0	12,23021	0,06348
B	dx	1,14126	0,05347
C	A1	-0,6092	0,98709
C	A2	71,61115	1,49099
C	x0	12,83243	0,09158
C	dx	1,26502	0,07954
D	A1	2,40469	1,48941
D	A2	27,35844	1,4577
D	x0	11,25928	0,25337
D	dx	0,83605	0,21293



Representative CID of [**HB₅** + CPO_3^-+ G] triplet



Model	Boltzmann		
Equation	y = A2 + (A1-A2)/(1 + exp((x-x0)/dx))		
Reduced Chi-Sqr	2,51803	2,51803	
Adj. R-Square	0,99838	0,99838	
		Value	Standard Error
B	A1	100,42859	0,77595
B	A2	1,09018	0,9154
B	x0	14,23032	0,04005
B	dx	0,95505	0,03376
C	A1	-0,42859	0,77595
C	A2	98,90982	0,9154
C	x0	14,23032	0,04005
C	dx	0,95505	0,03376