

Supplementary Material

Boron clusters as enhancers of RNase H activity in the smart strategy of gene silencing by antisense oligonucleotides

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Figure S2. Spectral analysis of 8-(5-azido-3-oxa-pentoxo)-3-iron-bis(1,2-dicarbollide) [Fe(C₂B₉H₁₁)₂]⁻ (azido derivative of FESAN).

Figure S3. Spectral analysis of 1-(3-azidopropyl)-1,2-dicarba-*closo*-dodecaborane (1,2-DCDDB, [C₂B₁₀H₁₂]) (azido derivative of 1,2-dicarba-*closo*-dodecaborate).

Figure S4. Spectral analysis of the bis-tetrabutylammonium-(4-azidobutoxy)-undecahydro-*closo*-dodecaborate (DDB, [B₁₂H₁₂]²⁻) (azido derivative of *closo*-dodecaborate).

Figure S1. Analytical RP HPLC profiles and MALDI-TOF or ESI-Q-TOF mass spectra of **1** - **4**, P1a - P1e, P2a-P2c, 1a₁ – 1a₃, 1b₁, 1c₁, 1d₁, 1e₁, 2a₁, 2b₁, 2c₁.

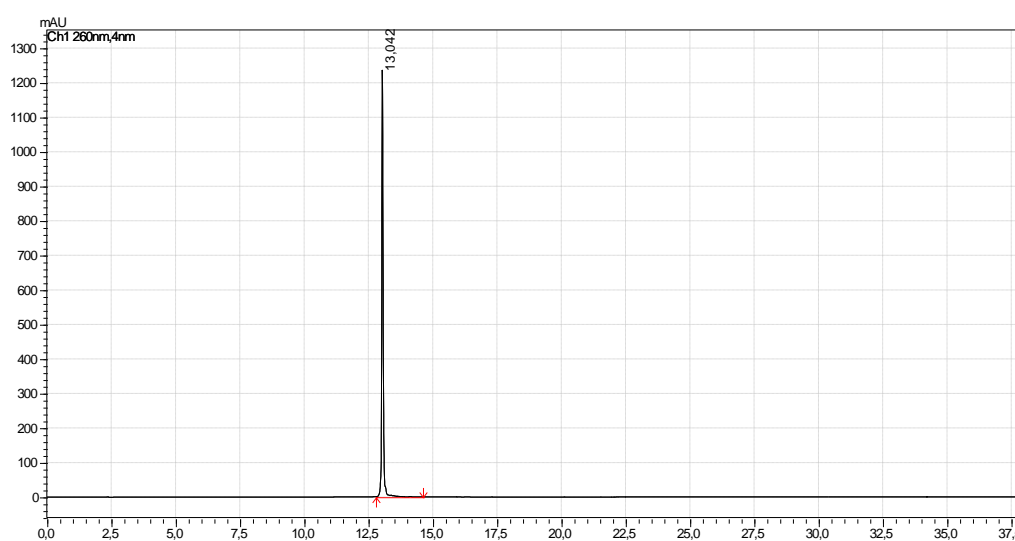
RP-HPLC conditions were as follow: the buffer A (0.1 M CH₃COONH₄) and the buffer B (100% CH₃CN). The buffer B gradient:

B1: 0→2 min 0%; 2→25 min 0-48%; 25→30 min 48-60%; 30→35 min 60-0%; 35→38 min 0%

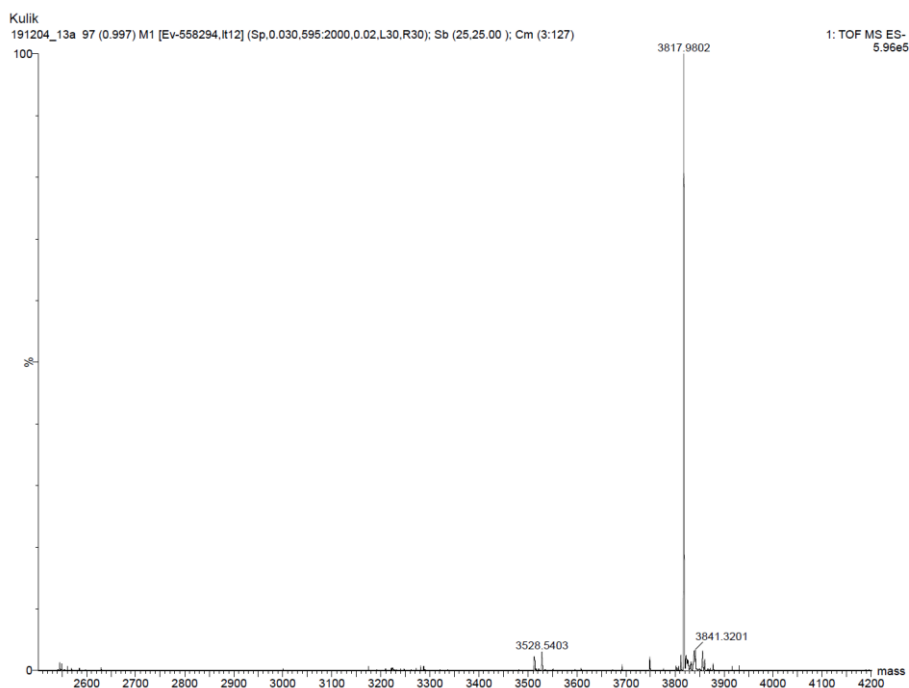
B2: 0→2 min 0%; 2→25 min 0-45%; 25→28 min 48-60%; 28→30 min 60-0%; 30→33 min 0%.

RP-HPLC conditions for **3** and **4** were as follow: the buffer A (0.1 M CH₃COONH₄) and the buffer B (0.1 M CH₃COONH₄ / 40%CH₃CN). The buffer B3 gradient: 0→3 min 0%; 3→23 min 0-100%; 23→27 min 100%; 27→30 min 100-0%; 30→32 min 0%.

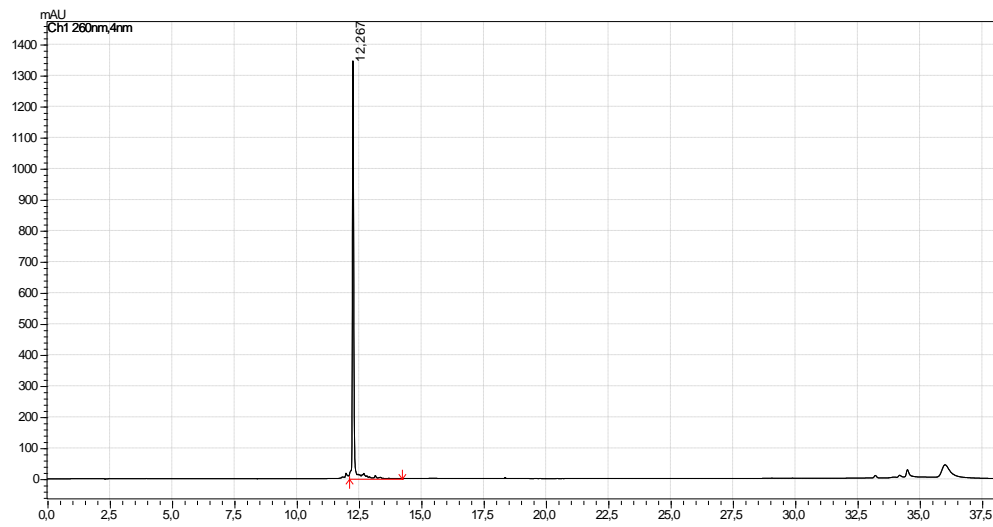
1: 5'-d(TTT CTT TTC CTC C)-3'



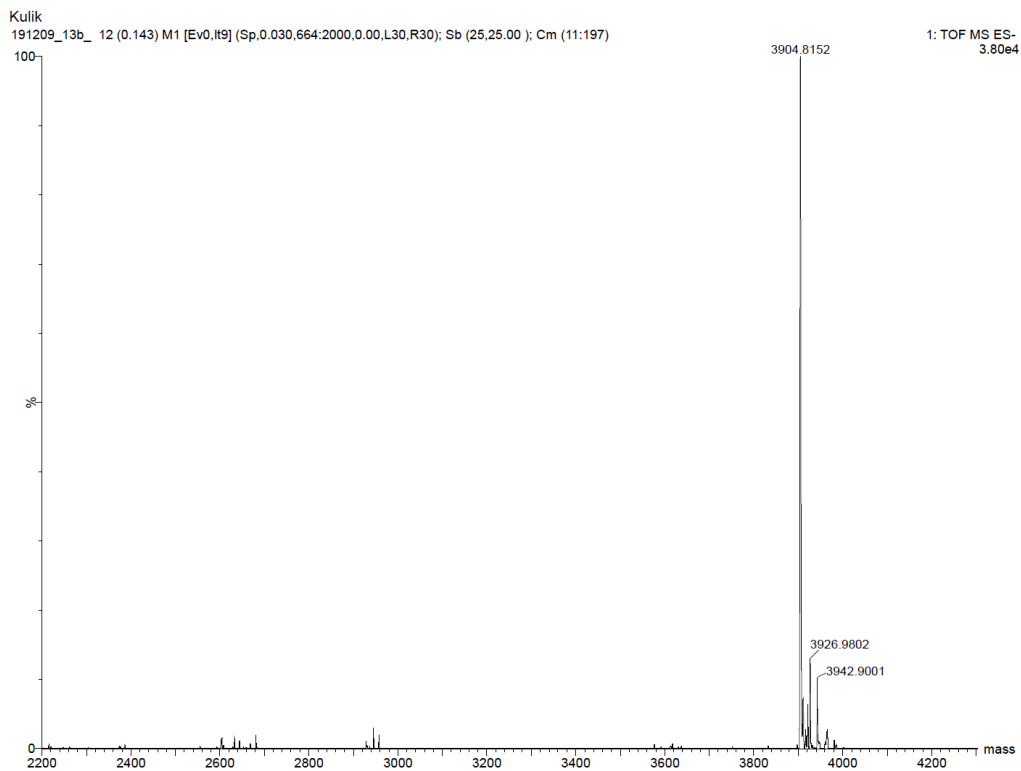
ESI-Q-TOF



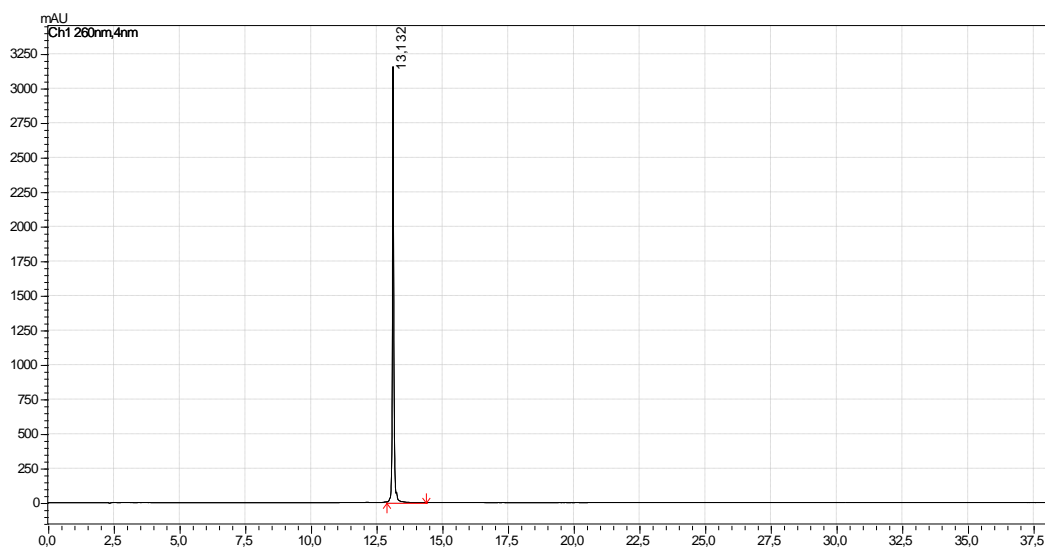
2: 5'-d(CTC CAG AGC CCG A)-3'



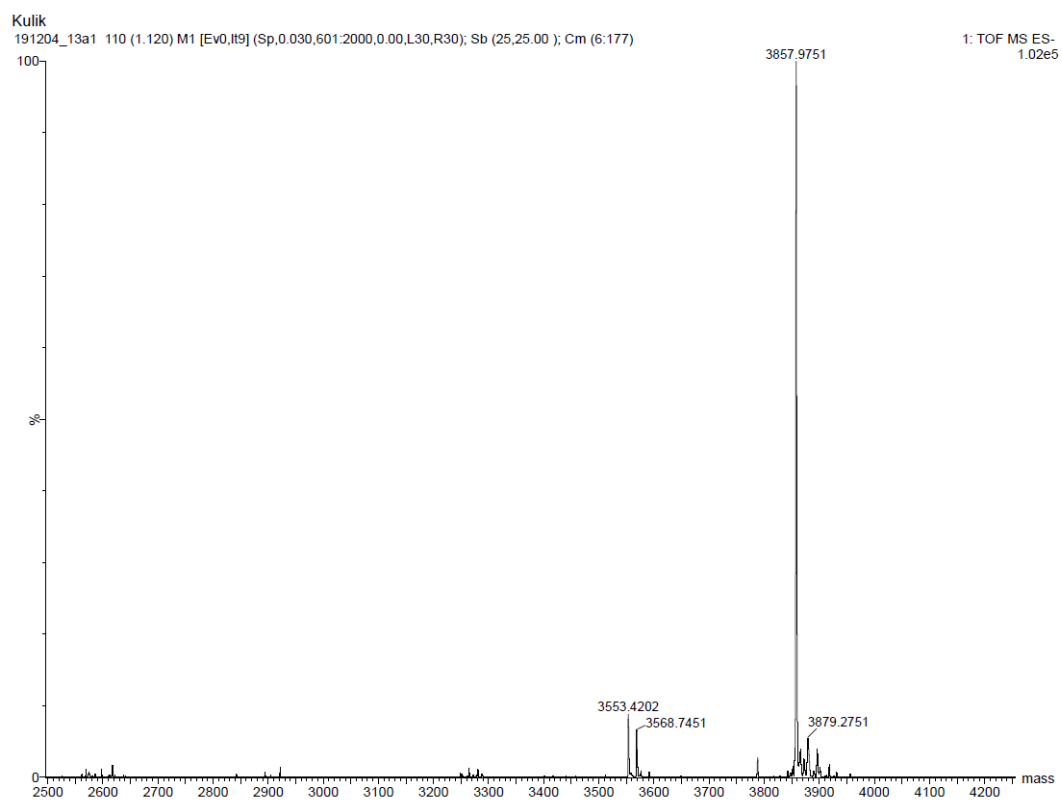
ESI-Q-TOF



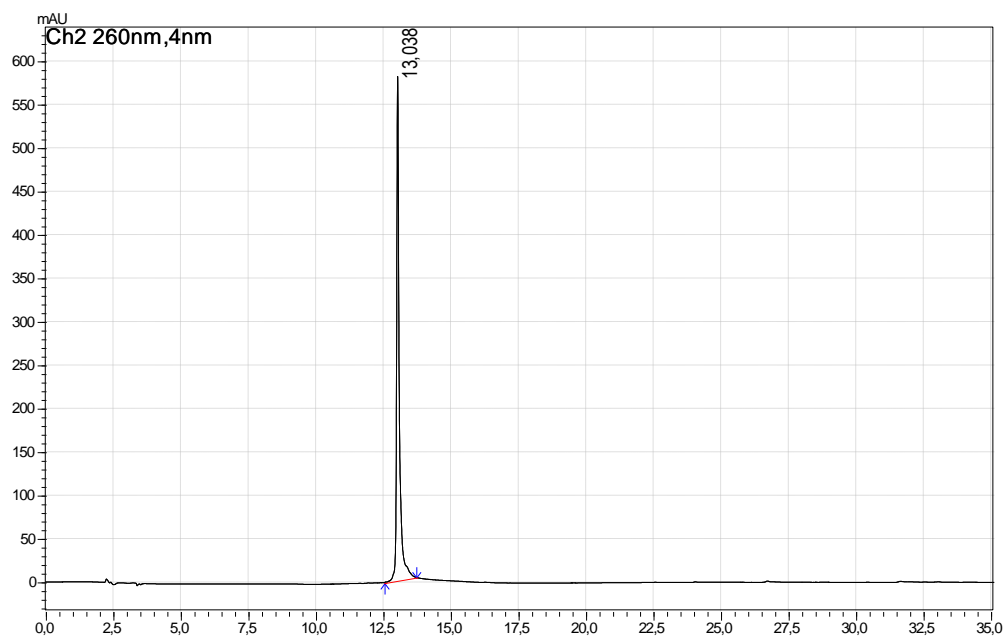
P1a: 5'-d(U_{Pr}TT CTT TTC CTC C)-3'



ESI-Q-TOF

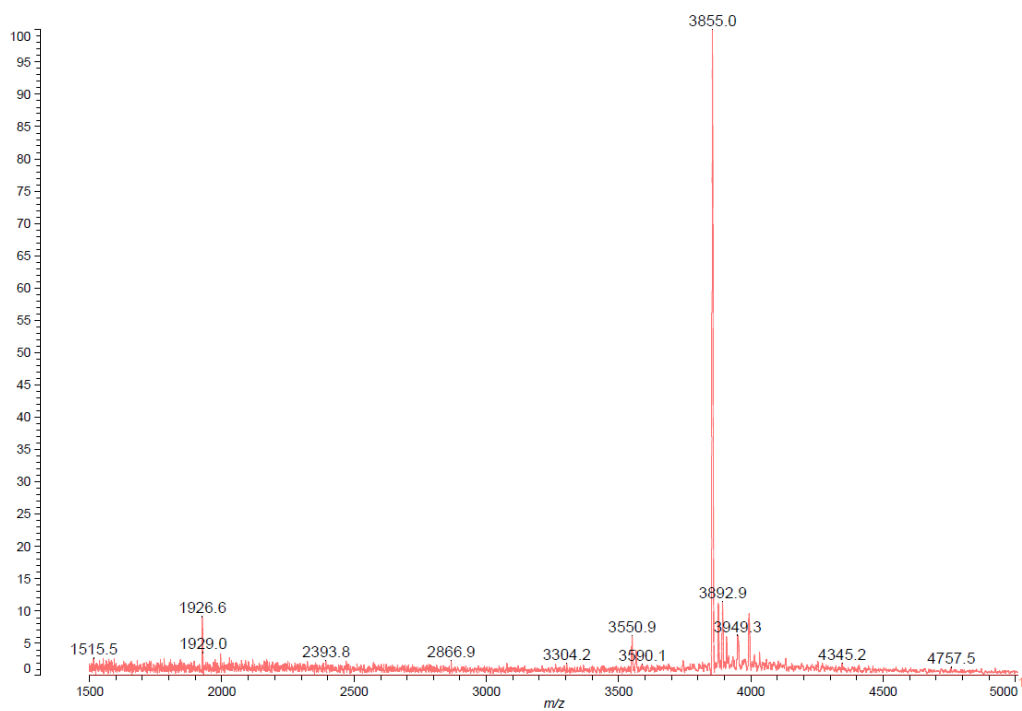


P1b: 5'-d(TT**U**_{Pr} CTT TTC CTC C)-3'

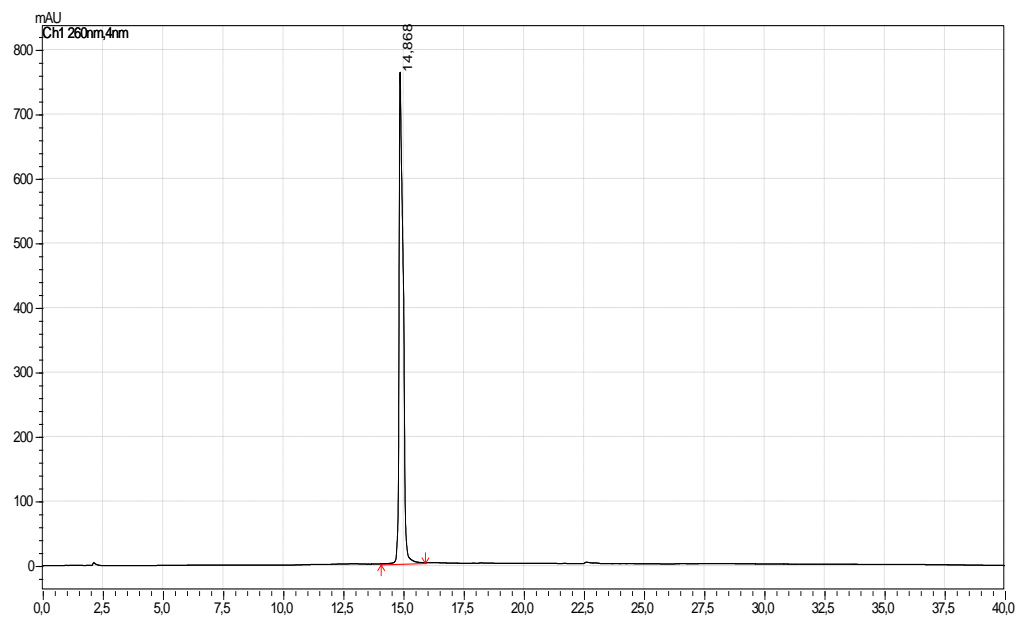


MALDI-TOF

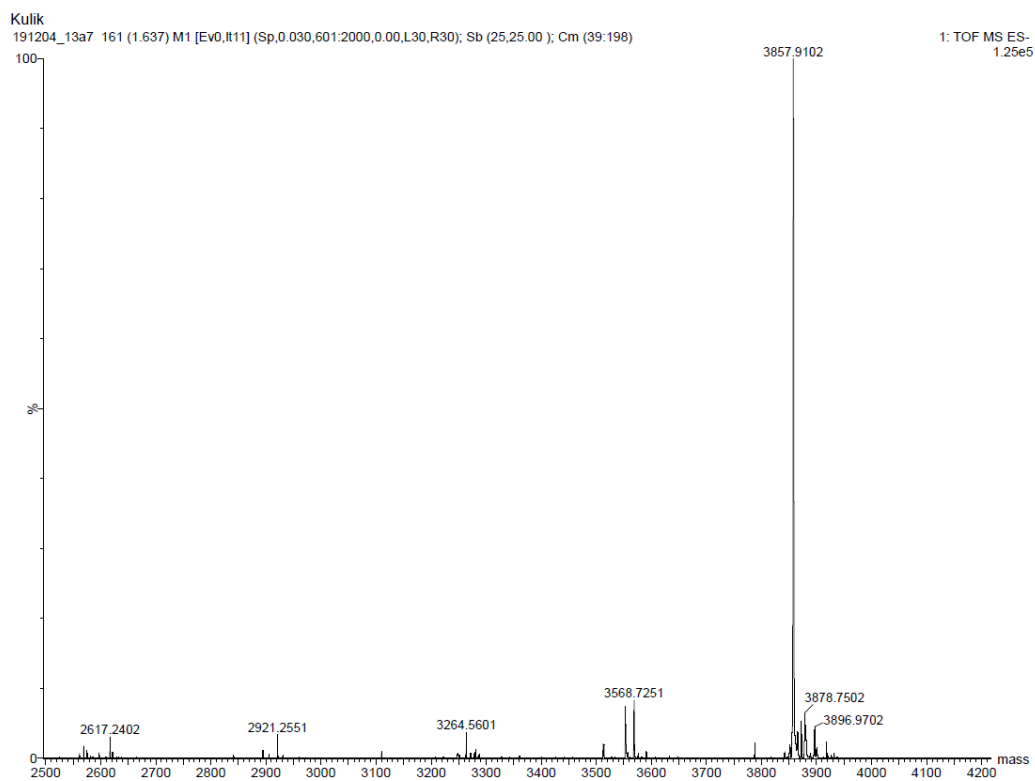
Ebenryter-Olbinska K, 13a3, linear neg
HPA 50 mg/mL H₂O/ACN 1:1 v/v, AC 50 mg/mL H₂O/ACN 1:1 v/v; HPA/AC 8:1
Data: hg770002.D2[c] 13 Mar 2019 15:11 Cal: HPA_T5_T124 31 Oct 2018 15:37
Shimadzu Biotech Axima Performance 2.9.1.20100121: Mode Linear_neg_2018, Power: 104, Blanked, P.Ext. @ 2800 (bin 76)
%Int. 13 mV[sum= 1411 mV] Profiles 1-107 Smooth Gauss 15-Baseline 60



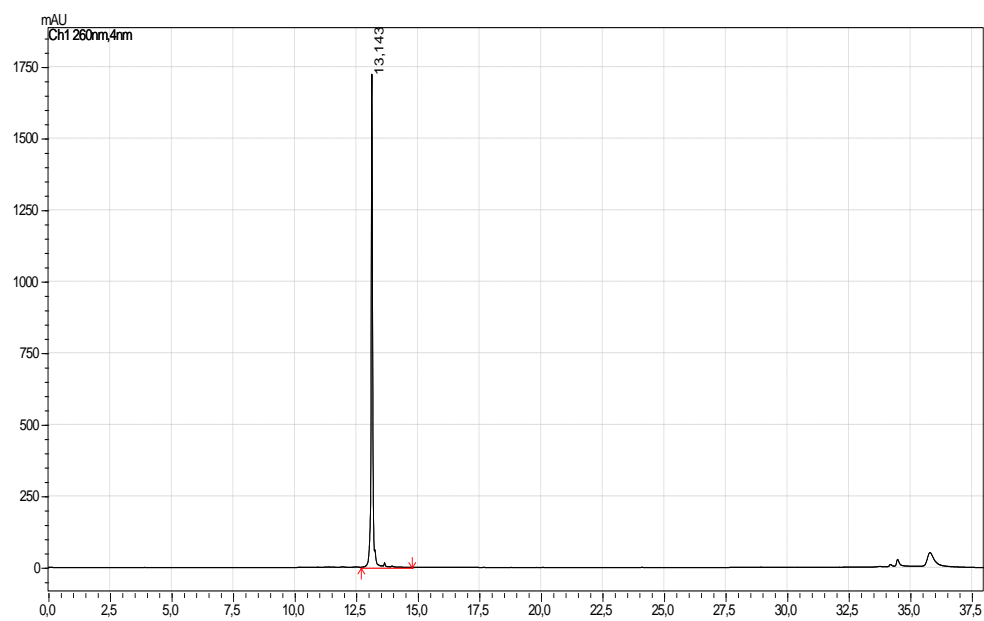
P1c: 5'-d(TTT CTT U_{Pr}TC CTC C)-3'



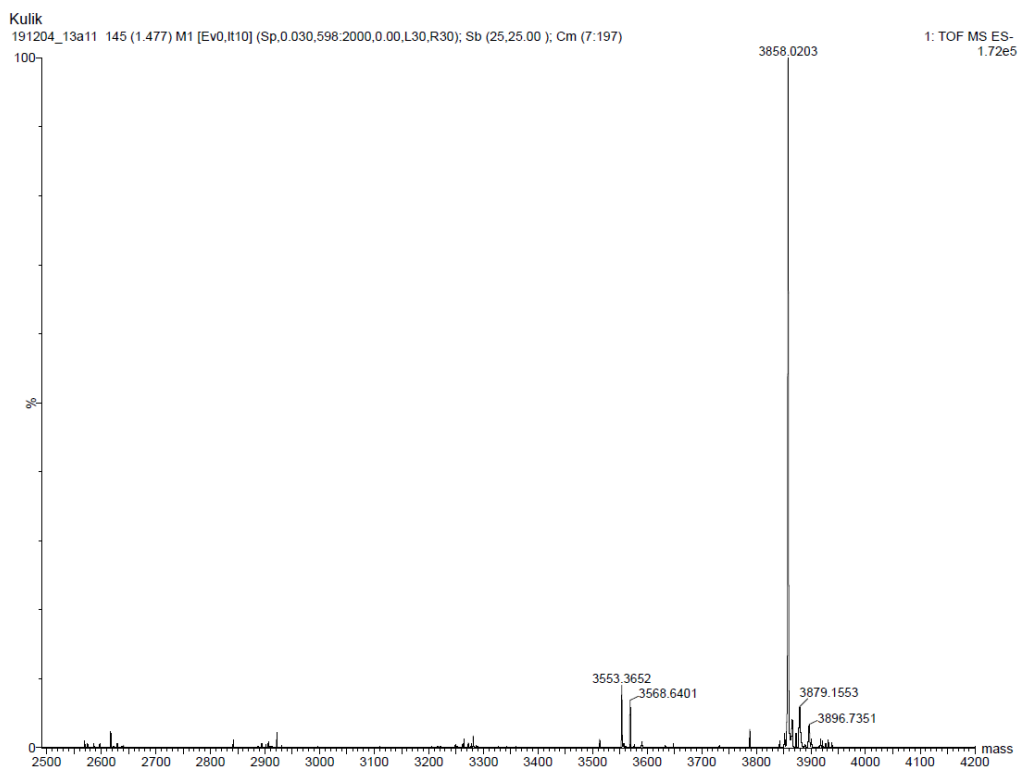
ESI-Q-TOF



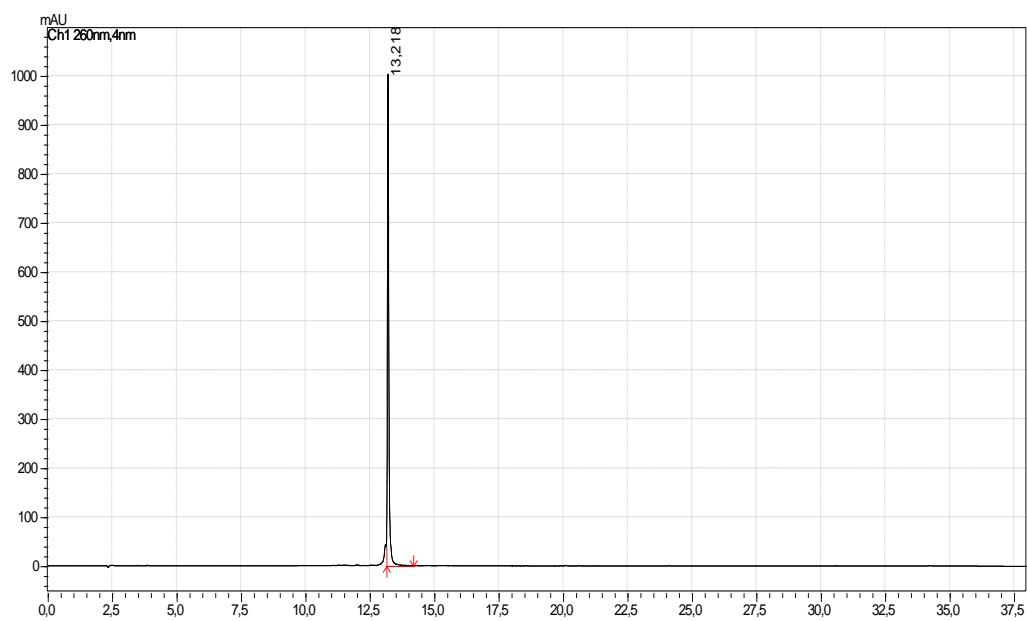
P1d: 5'-d(TTT CTT TTC C_{U_{Pr}}C C)-3'



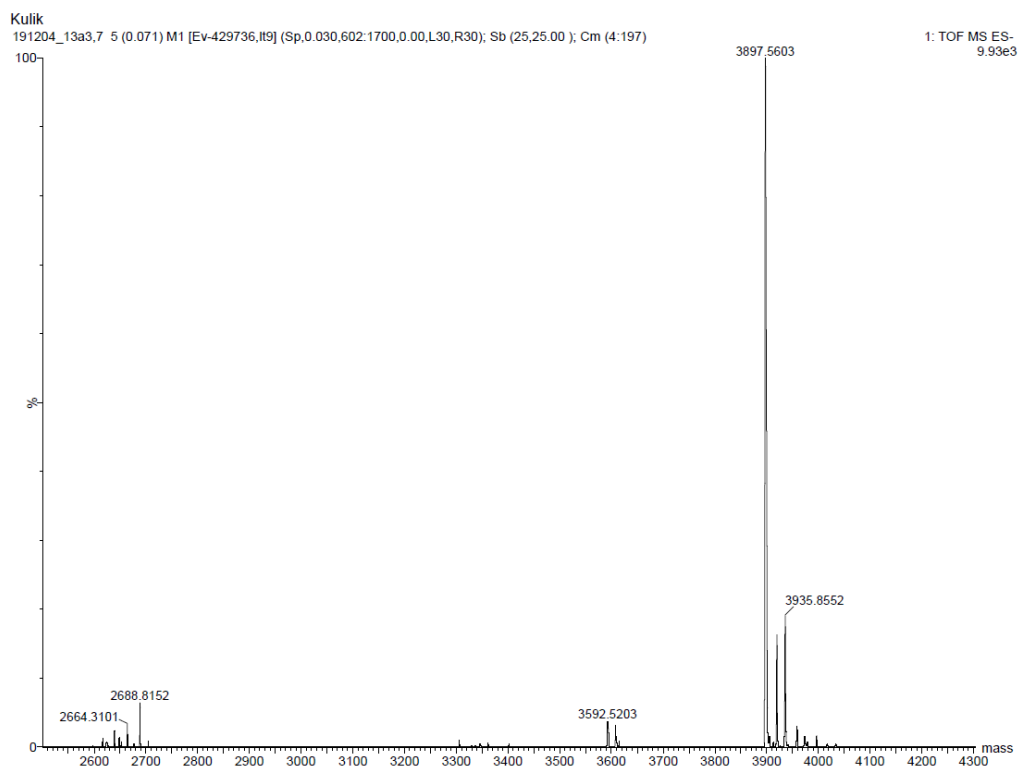
ESI-Q-TOF



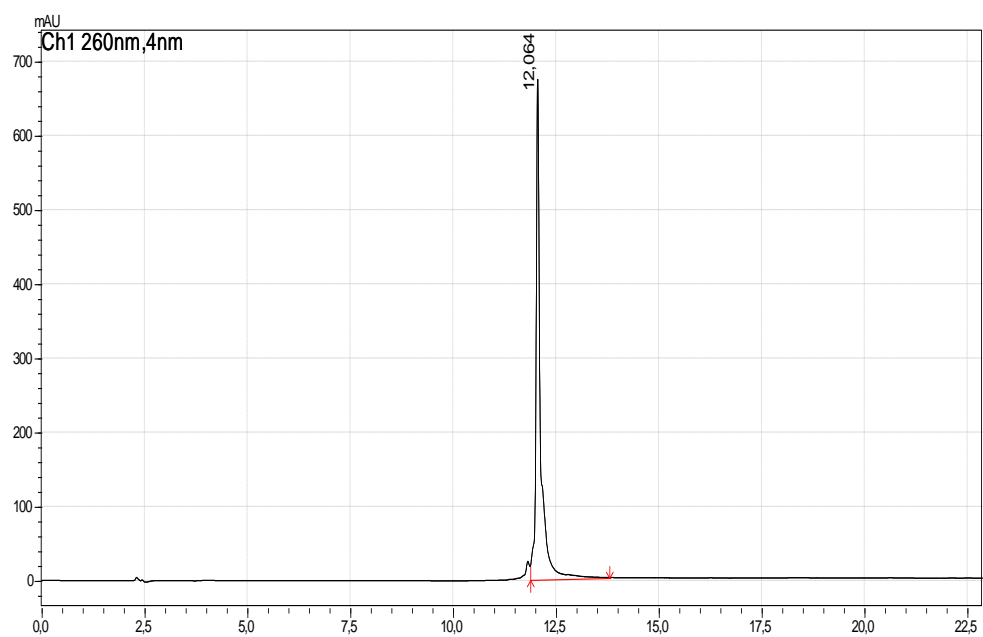
P1e: 5'-d(TT_{U_{Pr}} CTT _{U_{Pr}} TC CTC C)-3'



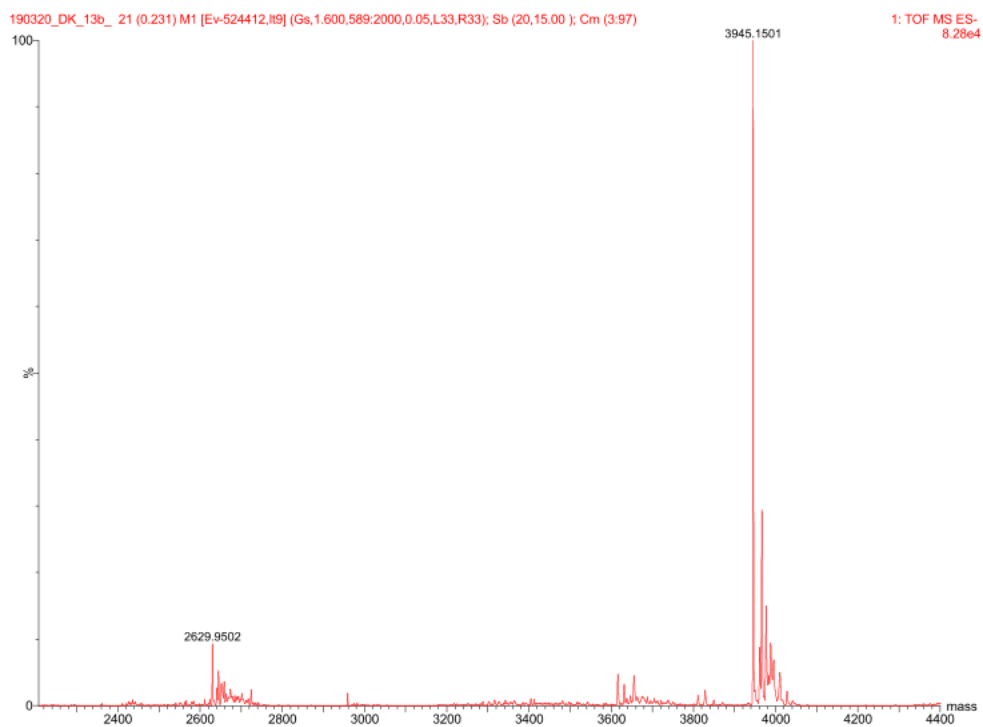
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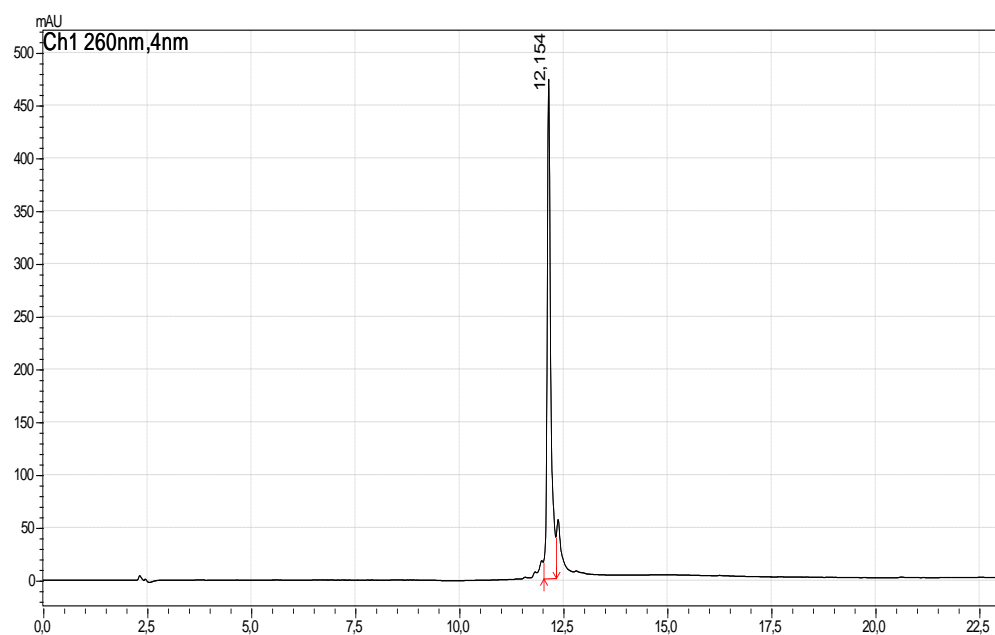
P2a: 5'-d(CU_{Pr}C CAG AGC CCG A)-3'



ESI-Q-TOF

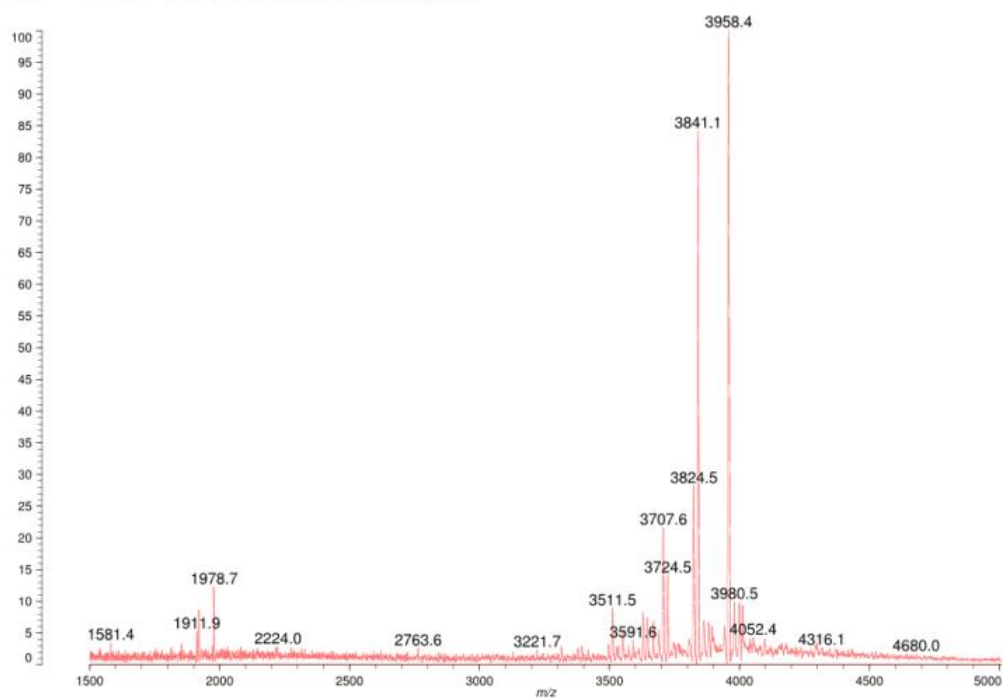


P2b: 5'-d(CTC CAG AGC C_{U_{Pr}}G A)-3'

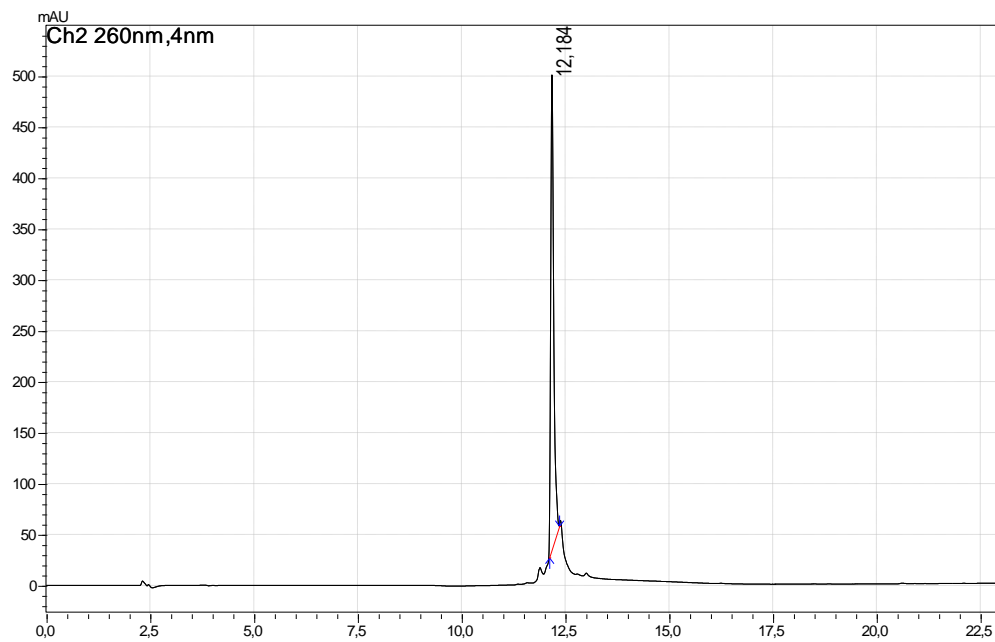


MALDI-TOF

Ebenryter-Olbinska,K, 13b11, linear neg
HPA 50 mg/mL H₂O/ACN 1:1 v/v, AC 50 mg/mL H₂O/ACN 1:1 v/v; HPA/AC 8:1
Data: hg790001.D8[c] 13 Mar 2019 15:22 Cal: HPA_T5_T124 31 Oct 2018 15:37
Shimadzu Biotech Axima Performance 2.9.1.20100121: Mode Linear_neg_2018, Power: 115, Blanked, P.Ext. @ 2800 (bin 76)
%Int. 24 mV[sum= 4825 mV] Profiles 1-200 Smooth Gauss 15-Baseline 60

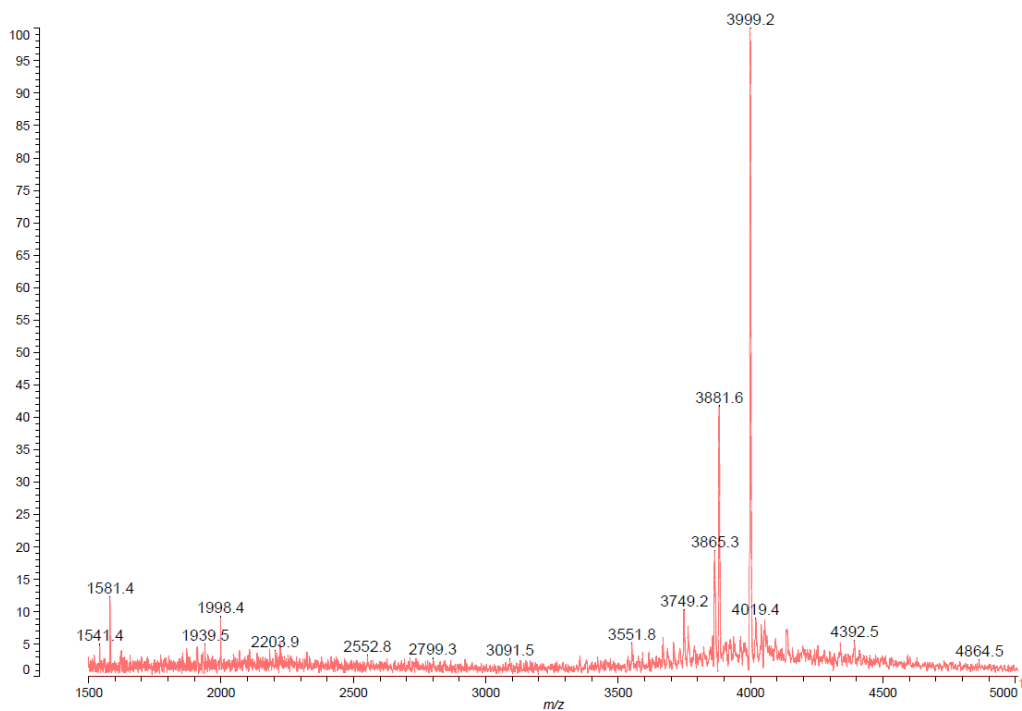


P2c: 5'-d(CU_{Pr}C CAG AGC CU_{Pr}G A)-3'

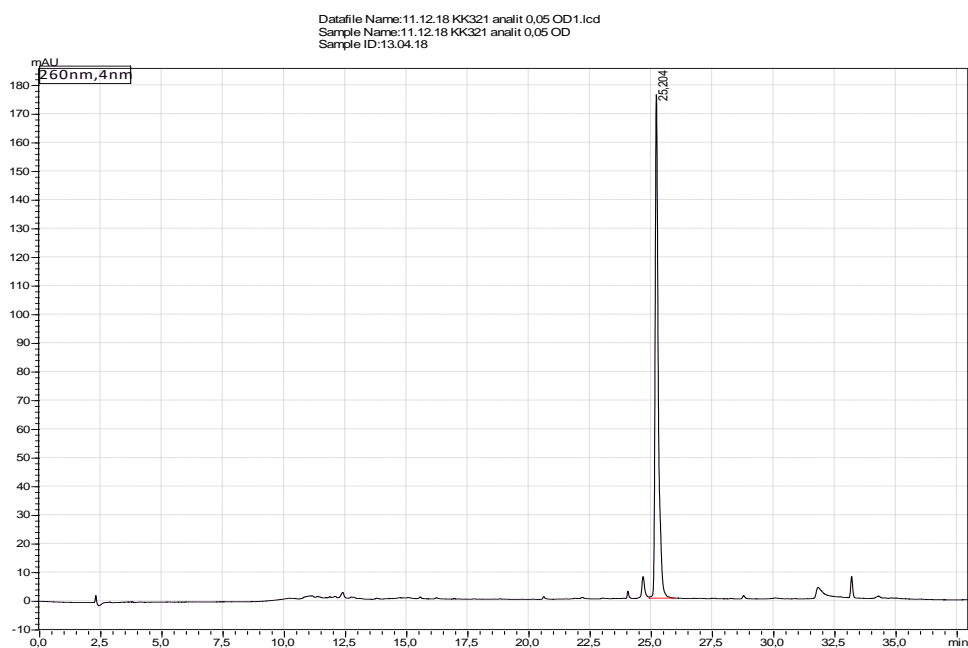


MALDI-TOF

Ebenryter-Olbinska.K, 13b2,11, linear neg
HPA 50 mg/mL H₂O/ACN 1:1 v/v, AC 50 mg/mL H₂O/ACN 1:1 v/v; HPA/AC 8:1
Data: hg780004.D6[c] 13 Mar 2019 15:20 Cal: HPA_T5_T124 31 Oct 2018 15:37
Shimadzu Biotech Axima Performance 2.9.1.20100T21: Mode Linear_neg_2018, Power: 109, Blanked, P.Ext. @ 2800 (bin 76)
%Int. 12 mV[sum= 1475 mV] Profiles 1-128 Smooth Gauss 15-Baseline 60

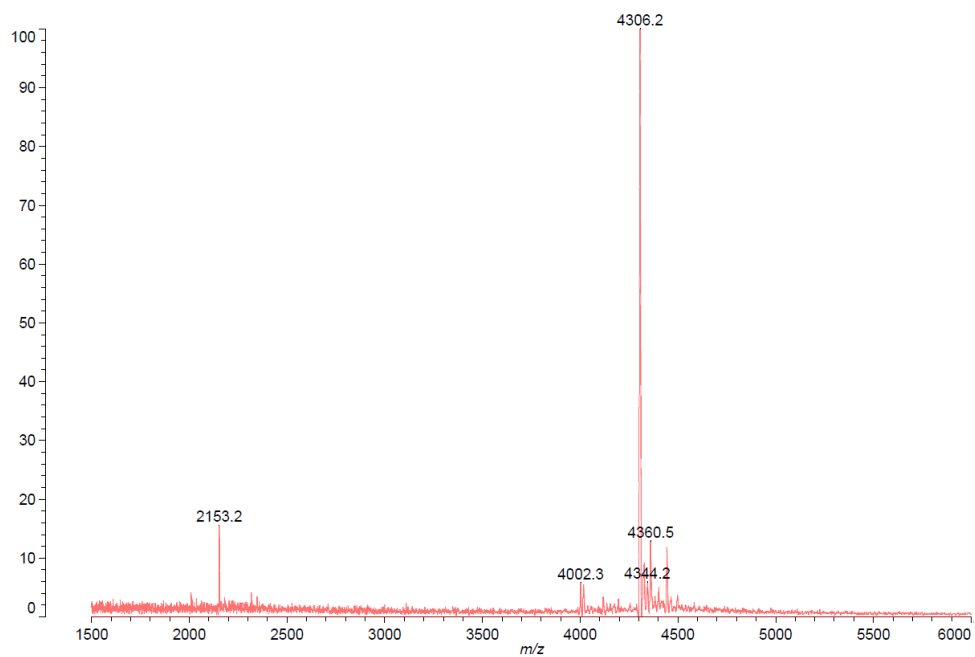


1a: 5'-d(U_{B1}TT CTT TTC CTC C)-3'

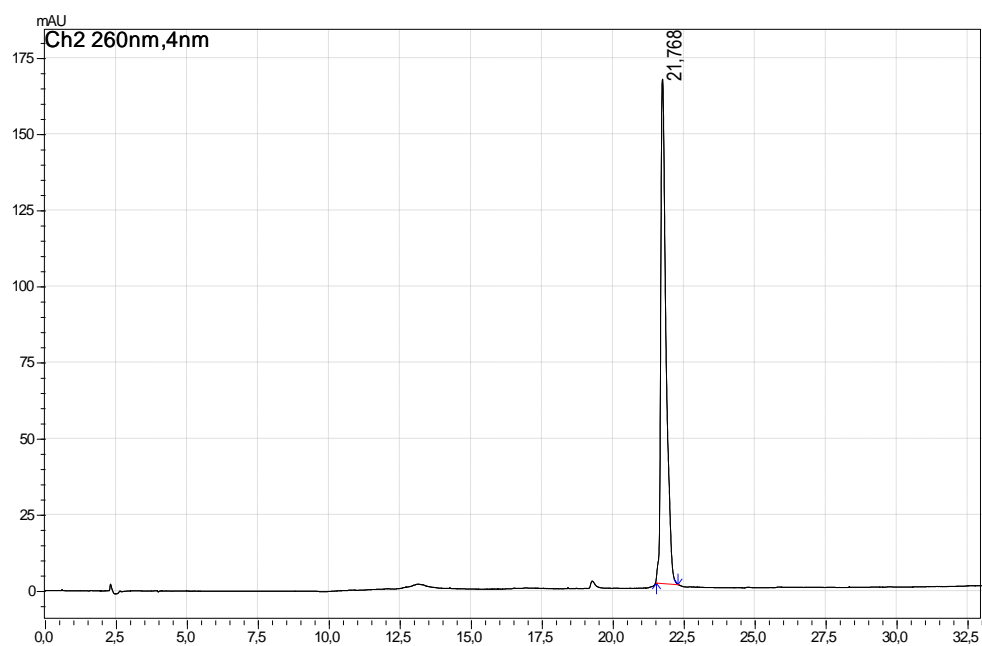


MALDI-TOF

Kulik K, KK-321, linear neg
HPA 50 mg/mL H₂O/ACN 1:1 v/v, AC 50 mg/mL H₂O/ACN 1:1 v/v; HPA/AC 8:1
Data: he280003.L11[c] 3 Dec 2018 15:03 Cal: HPA_T5_T18 31 Oct 2018 15:33
Shimadzu Biotech Axima Performance 2.9.1.20100121: Mode Linear_neg_2018, Power: 118, Blanked, P.Ext. @ 3800 (bin 88)
%Int. 33 mV[sum= 6576 mV] Profiles 1-200 Smooth Av 20 -Baseline 60



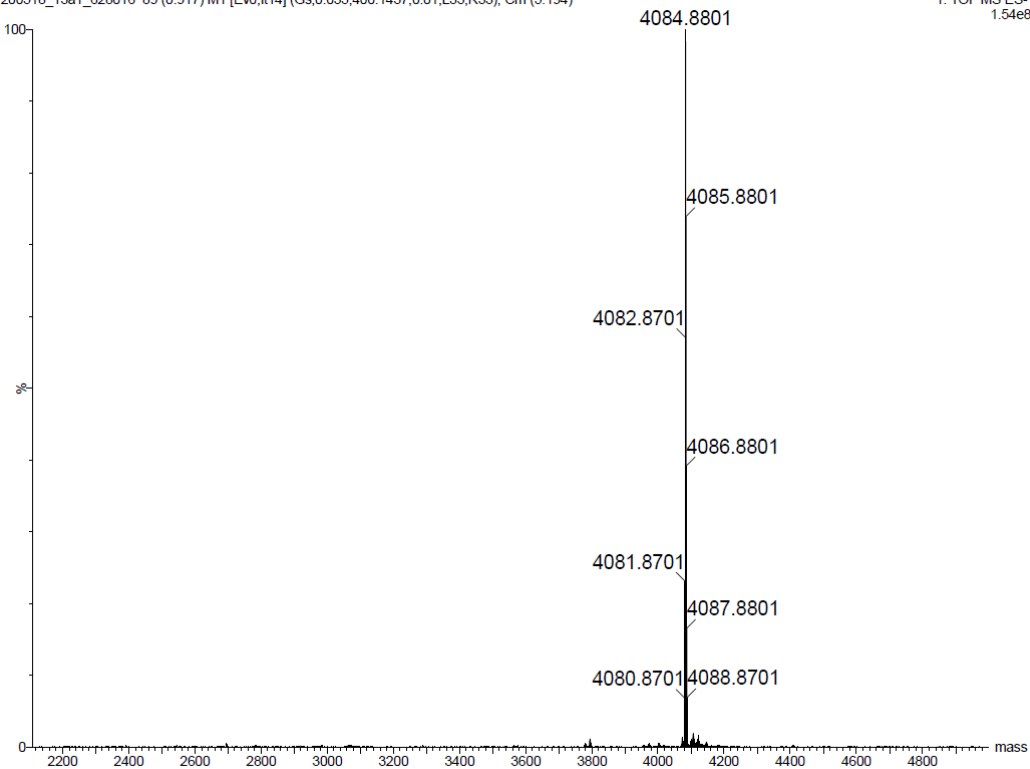
1a2: 5'-d(**U**_{B2}TT CTT TTC CTC C)-3' (B2 RP-HPLC program)



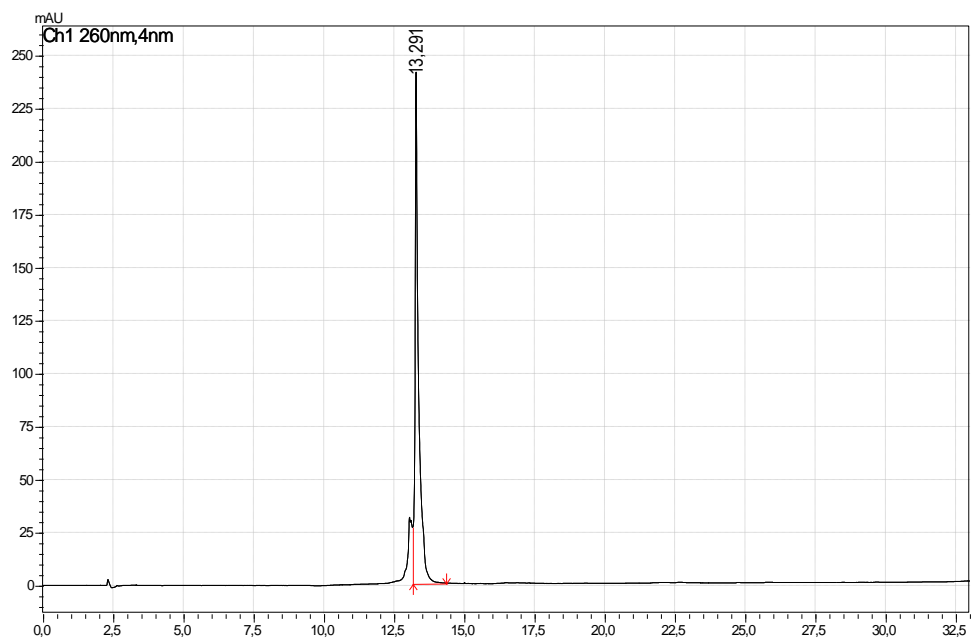
ESI-Q-TOF

200518_13a1_628016 89 (0.917) M1 [Ev0,It14] (Gs,0.035,400:1437,0.01,L33,R33); Cm (5:194)

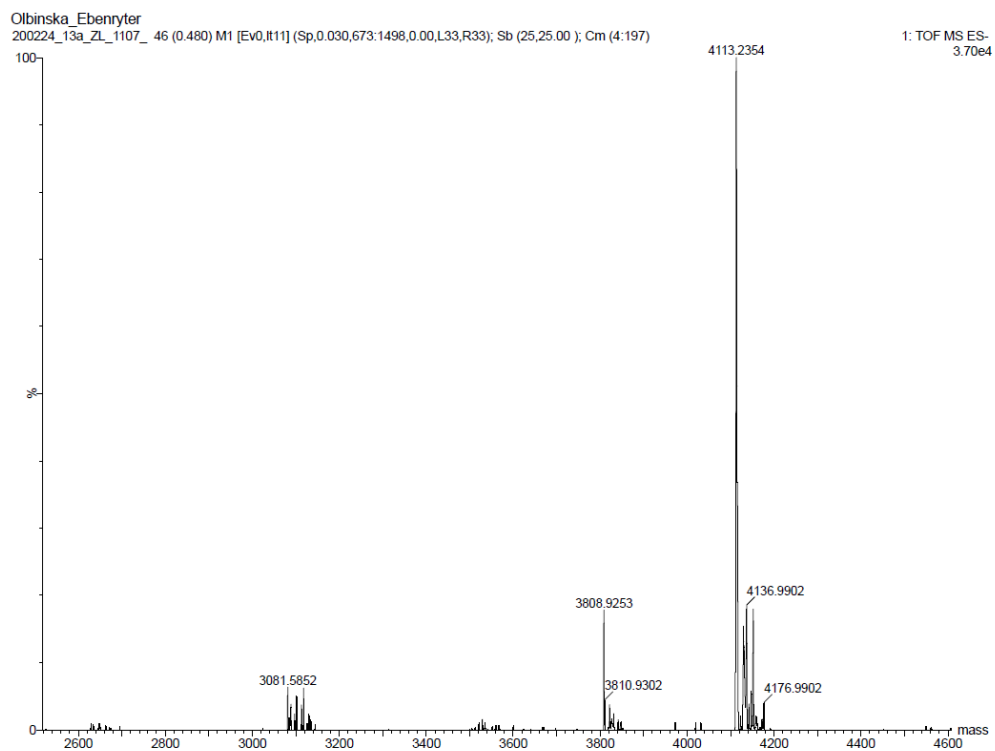
1: TOF MS ES-
1.54e8



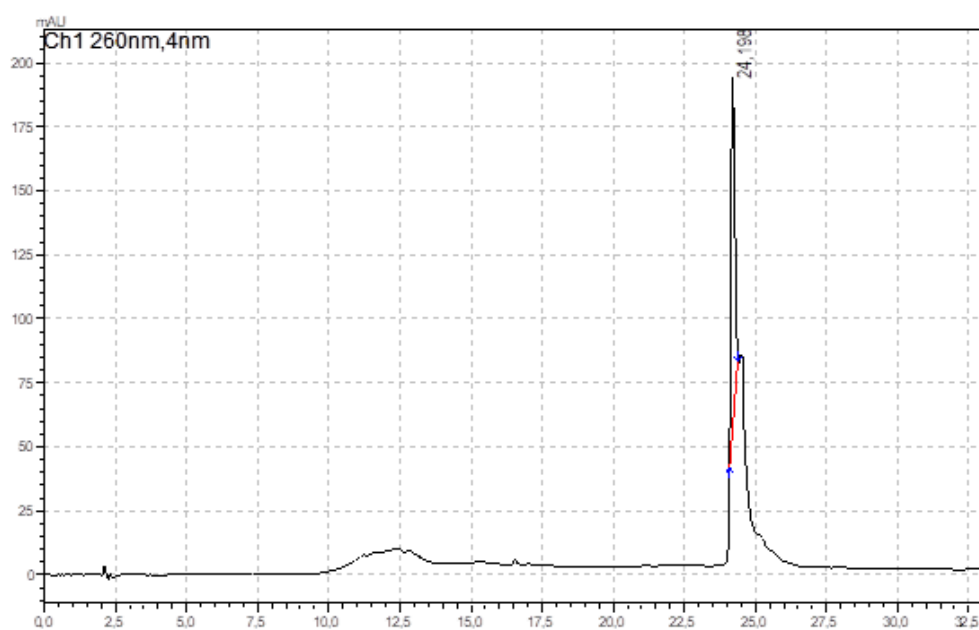
1a3: 5'-d(U_{B3}TT CTT TTC CTC C)-3' (B2 RP-HPLC program)



ESI-Q-TOF



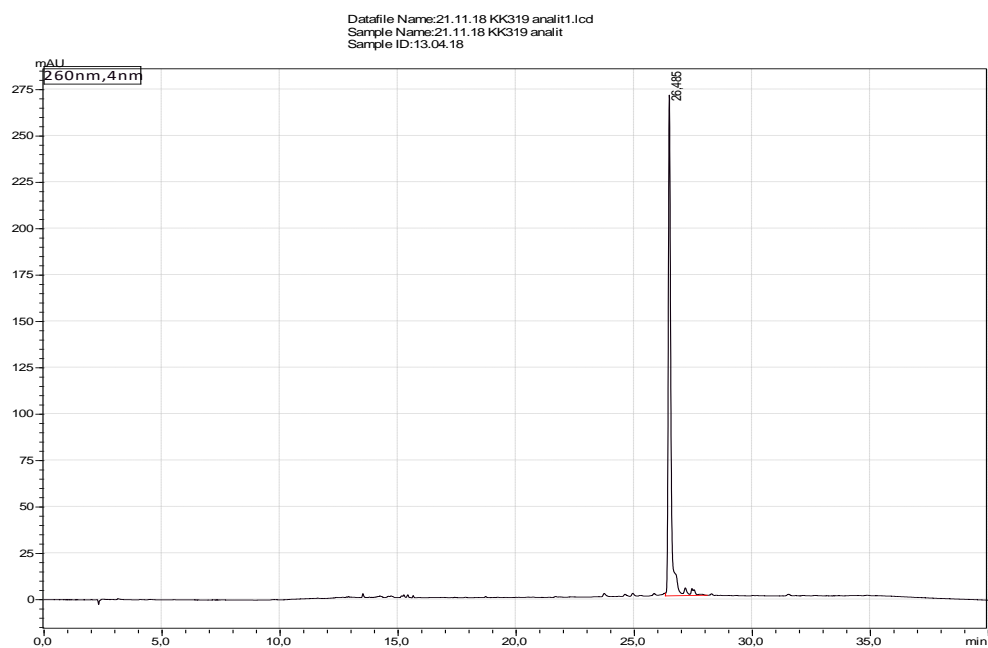
1b1: 5'-d(TT U_{B1} CTT TTC CTC C)-3' (B2 RP-HPLC program)



ESI-Q-TOF



1c1 : 5'-d(TTT CTT **U_{B1}**TC CTC C)-3'

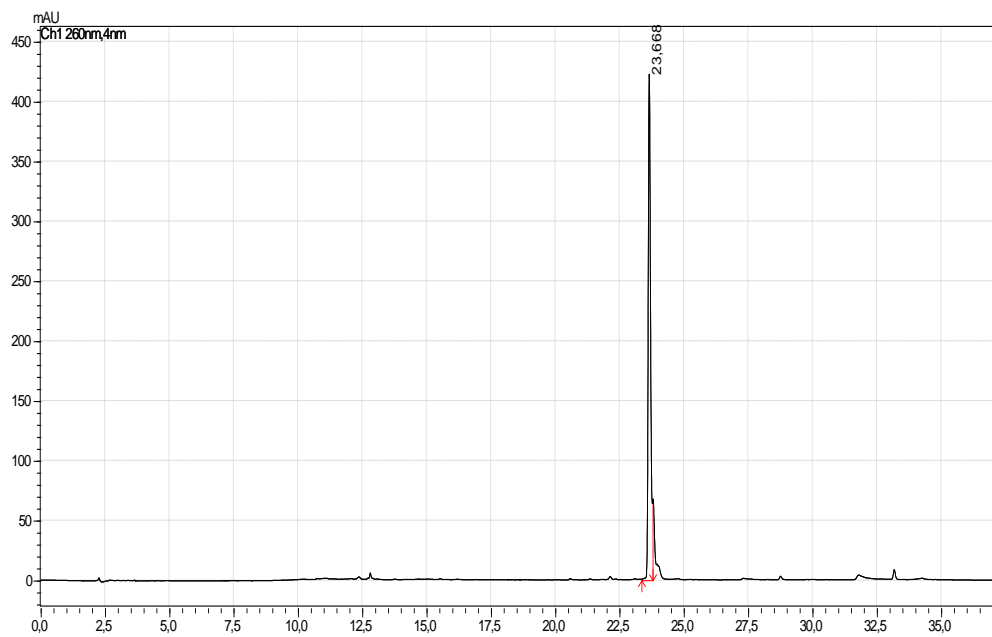


MALDI-TOF

Kulik K, KK319, linear neg
HPA 50 mg/mL H₂O/ACN 1:1 v/v, AC 50 mg/mL H₂O/ACN 1:1 v/v, HPA/AC 8:1
Data: he050001.D15[c] 19 Nov 2018 14:51 Cal: HPA T5 T18 31 Oct 2018 15:33
Shimadzu Biotech Axima Performance 2.9.1 20100121 Mode Linear_neg 2018, Power: 112, Blanked, P.Ext. @ 3500 (bin 85)
%Int. 15mV [sum=2915mV] Profiles 1-200 Smooth Gauss 15 -Baseline 60

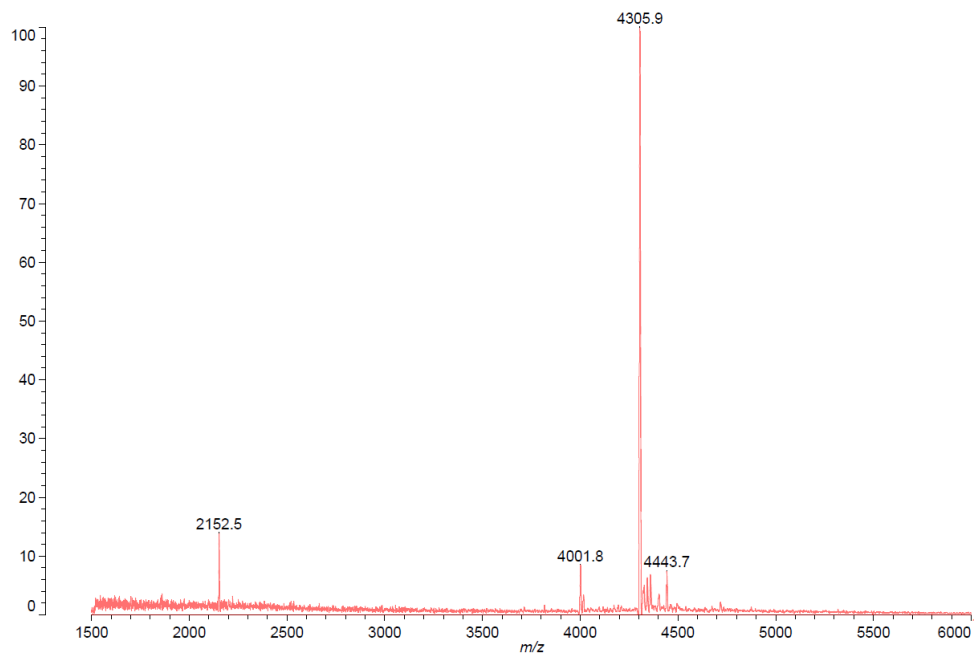


1d1: 5'-d(TTT CTT TTC C**U_{B1}**C C)-3'

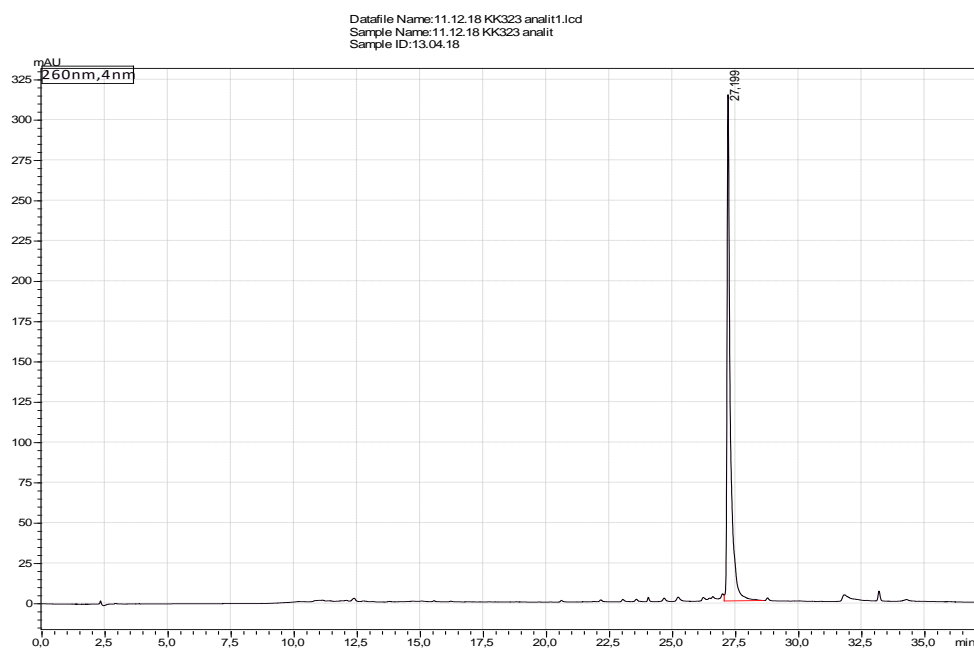


MALDI-TOF

Kulik K, KK-324, linear neg
HPA 50 mg/mL H₂O/ACN 1:1 v/v, AC 50 mg/mL H₂O/ACN 1:1 v/v; HPA/AC 8:1
Data: he290002.L13[c] 3 Dec 2018 15:08 Cal: HPA_T5_T18 31 Oct 2018 15:33
Shimadzu Biotech Axima Performance 2.9.1.20100121: Mode Linear_neg_2018, Power: 112, Blanked, P.Ext. @ 3500 (bin 85)
%Int. 65 mV[sum= 9830 mV] Profiles 1-152 Smooth Av 20 -Baseline 60

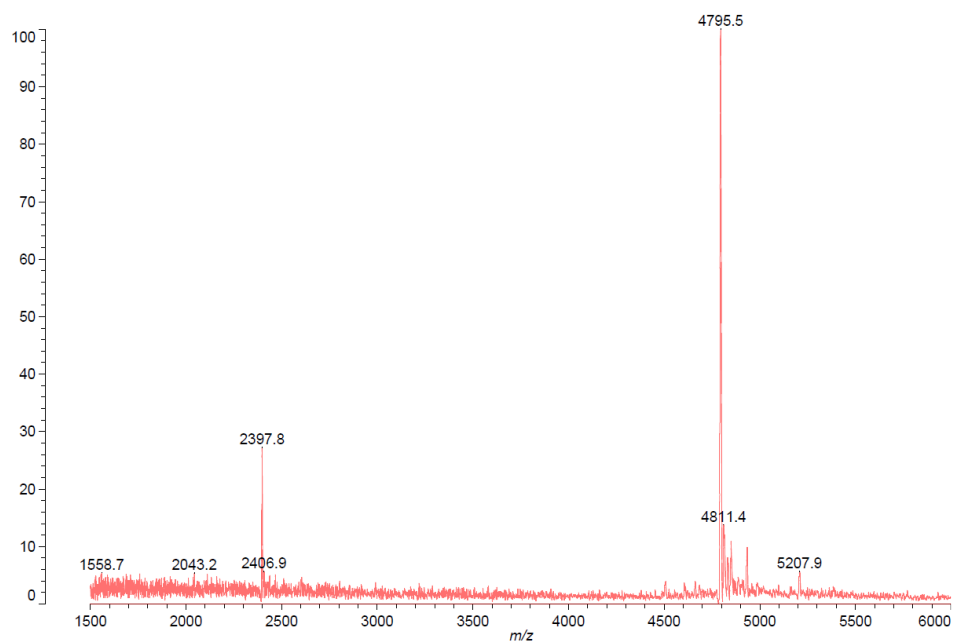


1e: 5'-d(TT**U_{B1}** CTT **U_{B1}**TC CTC C)-3'

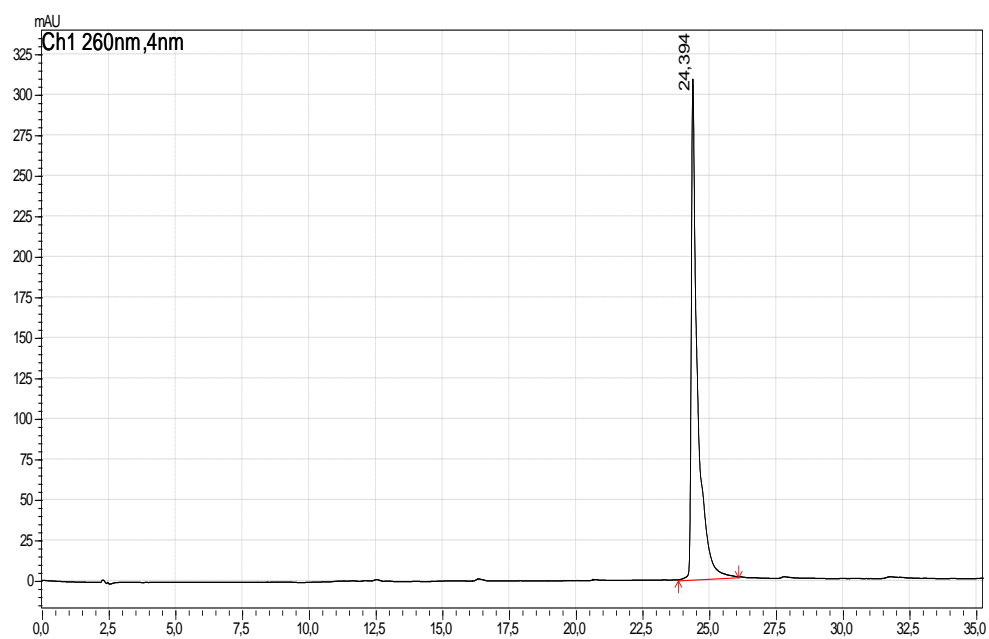


MALDI-TOF

Kulik K, KK-323, linear neg
HPA 50 mg/mL H₂O/ACN 1:1 v/v, AC 50 mg/mL H₂O/ACN 1:1 v/v; HPA/AC 8:1
Data: he310002.L17[c] 3 Dec 2018 15:16 Cal: HPA_T5_T18 31 Oct 2018 15:33
Shimadzu Biotech Axima Performance 2.9.1.20100121: Mode Linear_neg_2018, Power: 113, Blanked, P.Ext. @ 3500 (bin 85)
%Int. 21 mV[sum= 3053 mV] Profiles 1-142 Smooth Av 20 -Baseline 60

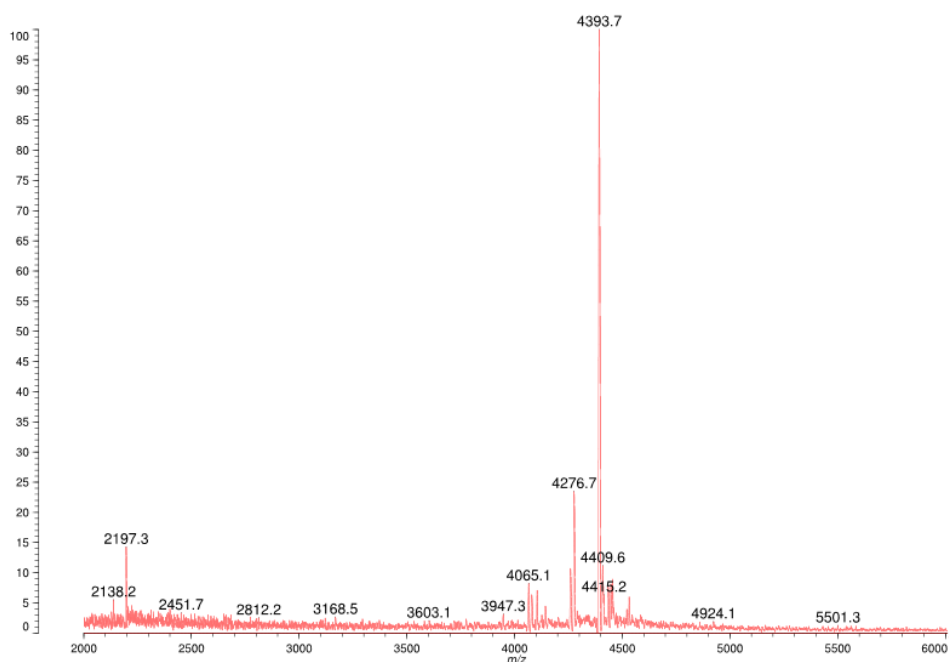


2a: 5'-d(C**U**_{B1}C CAG AGC CCGA)-3'

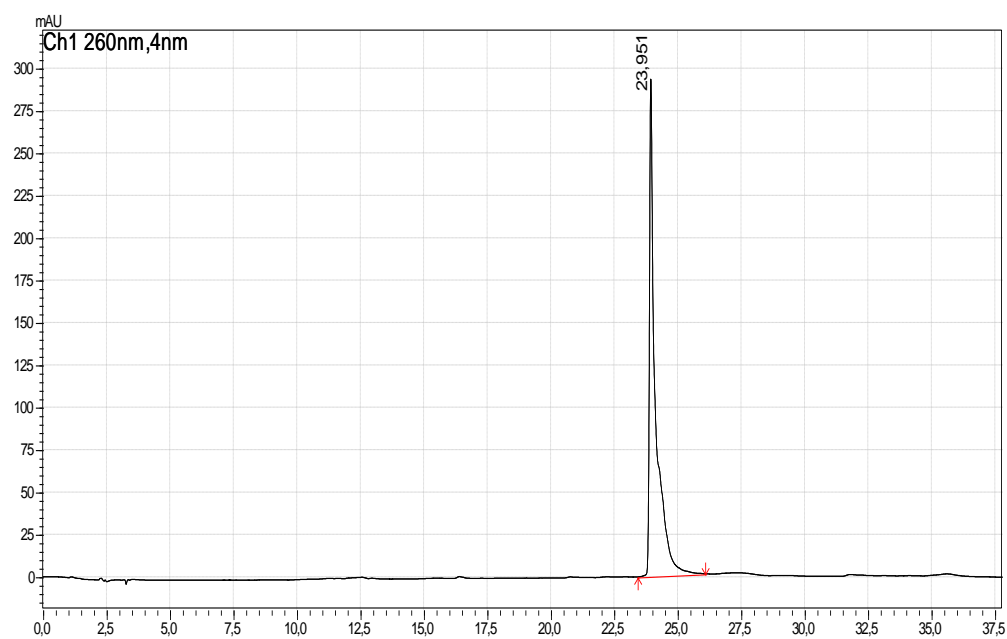


MALDI-TOF

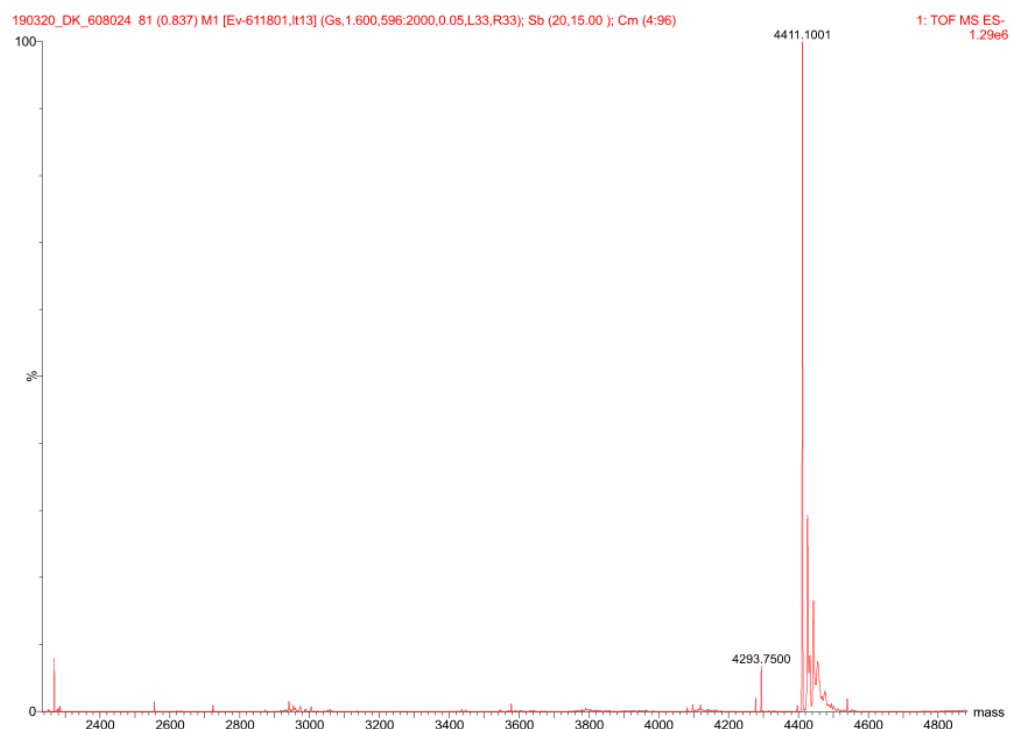
Ebenryter-Olbinska.K. 608022. linear neg
HPA 50 mg/mL H₂O/ACN 1:1 v/v, AC 50 mg/mL H₂O/ACN 1:1 v/v; HPA/AC 8:1
Data: hg86003.N13[c] 18 Mar 2019 12:27 Cal: HPA_T5_T18 31 Oct 2018 15:33
Shimadzu Biotech Axima Performance 2.9.1.20100121: Mode Linear_neg_2018, Power: 113, Blanked, P.Ext. @ 3800 (bin 88)
%Int. 21 mV[sum= 1933 mV] Profiles 1-90 Smooth Gauss 15 -Baseline 60



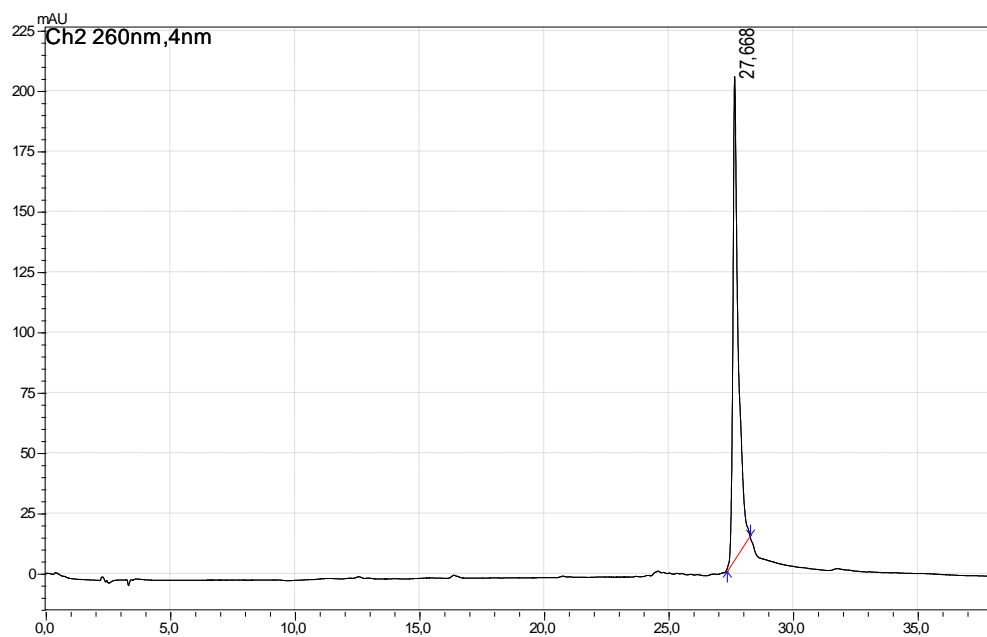
2b1: 5'-d(CTC CAG AGC CU_{B1}GA)-3'



ESI-Q-TOF

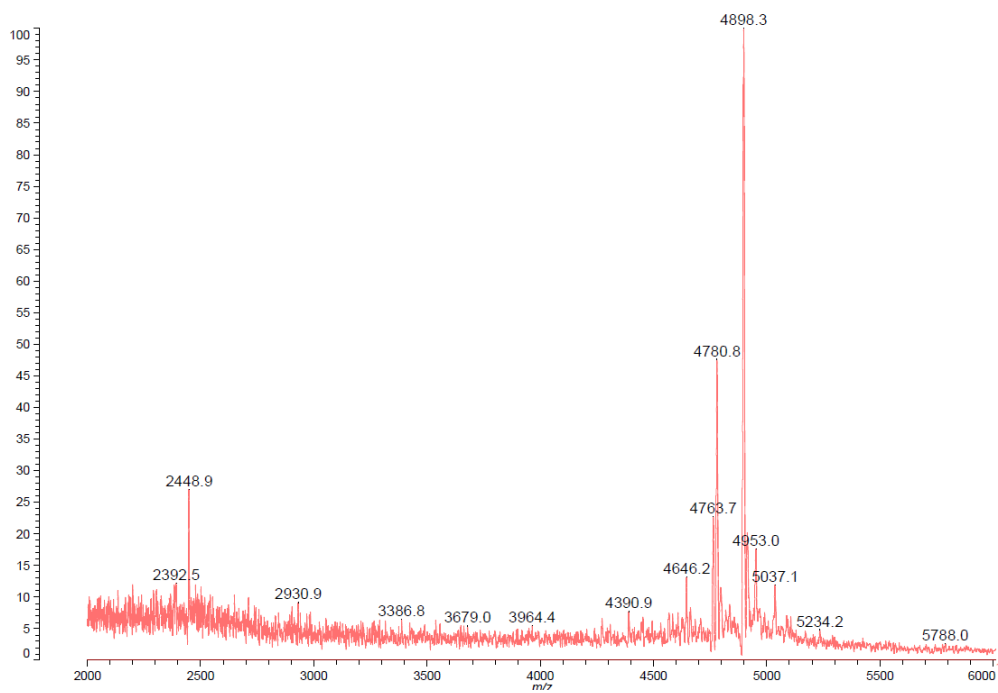


2c: 5'-d(C_{U_{B1}}C CAG AGC C_{U_{B1}}GA)-3'

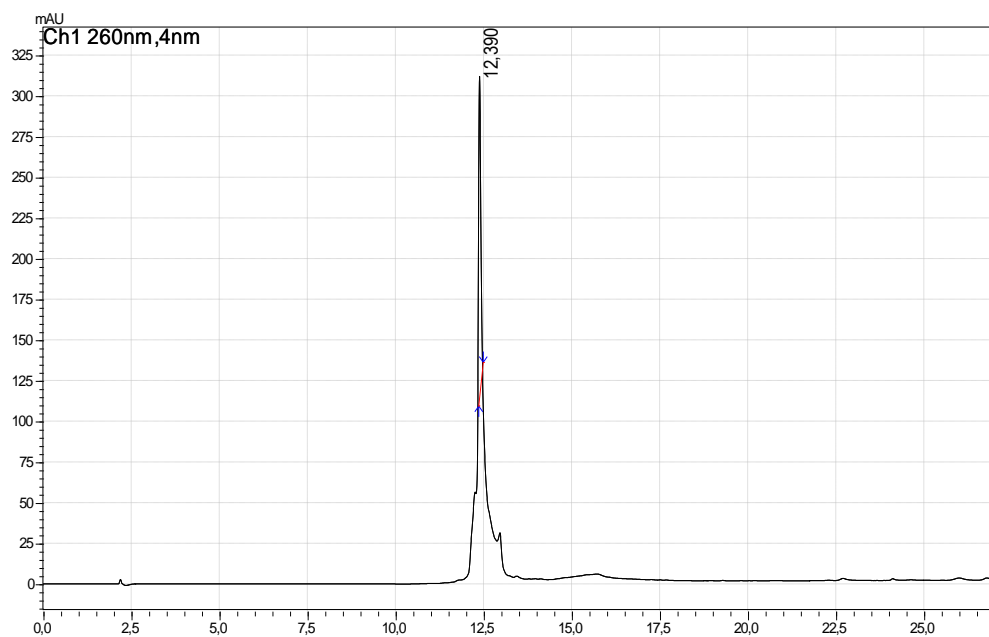


MALDI-TOF

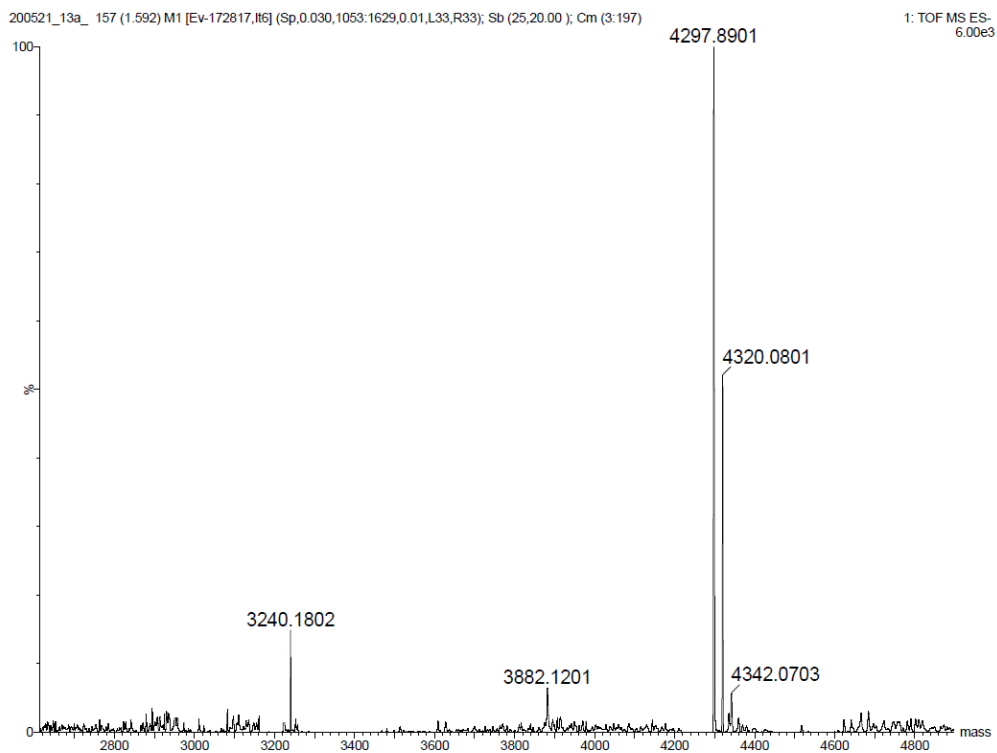
Ebenryter-Olbinska.K, 608023, linear neg
HPA 50 mg/mL H₂O/ACN 1:1 v/v, AC 50 mg/mL H₂O/ACN 1:1 v/v; HPA/AC 8:1
Data: hg870003.N16[c] 18 Mar 2019 12:31 Cal: HPA_T5_T24 31 Oct 2018 15:41
Shimadzu Biotech Axima Performance 2.9.1.20100121; Mode Linear_neg_2018, Power: 116, Blanked, P.Ext. @ 3800 (bin 88)
%Int. 5.5 mV[sum= 1045 mV] Profiles 1-191 Smooth Gauss 20 -Baseline 55



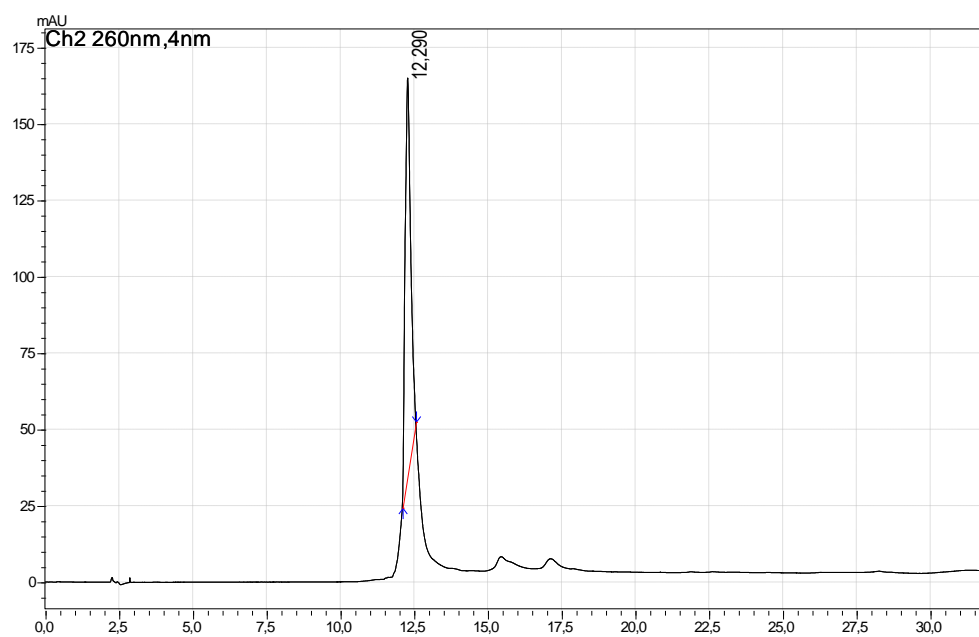
3: 5'-(GGG GGA AAA GAA A)-3' (B3 RP-HPLC program)



ESI-Q-TOF



4: 5'-(UCG GGC UCU GGU G)-3' (B3 RP-HPLC program)



ESI-Q-TOF

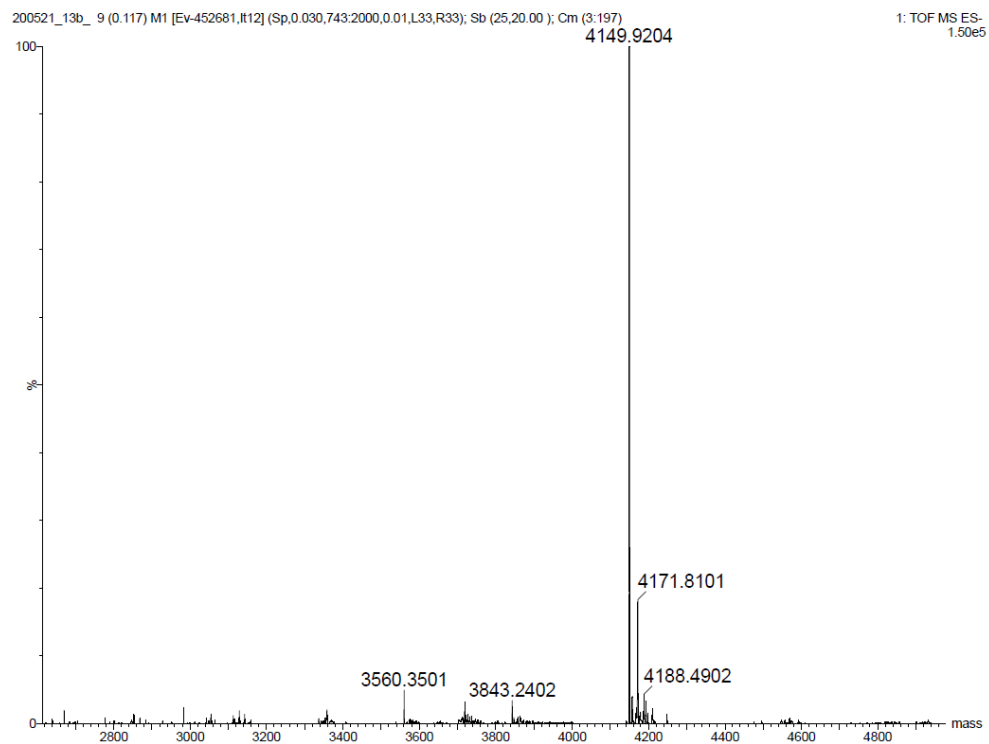
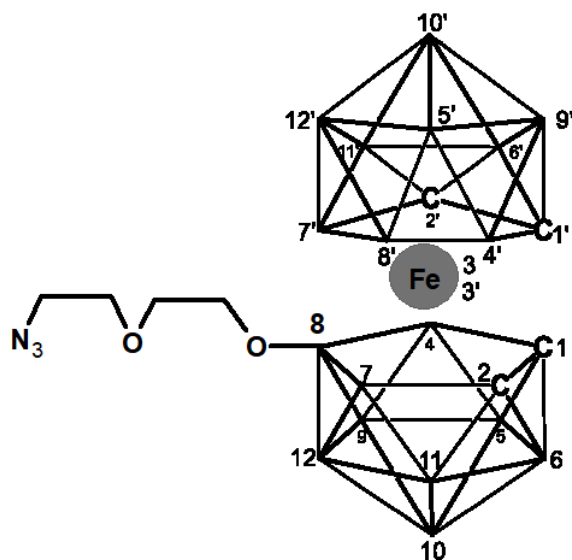
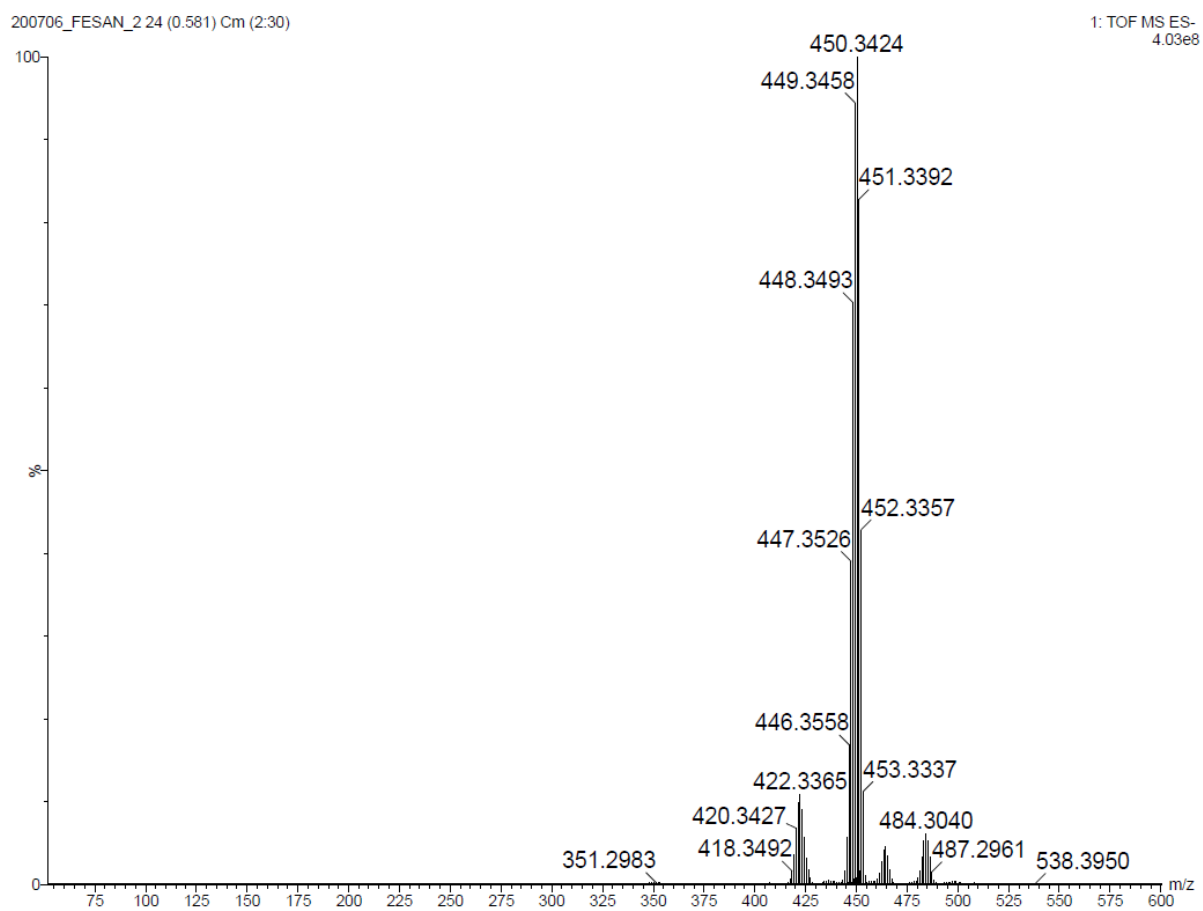


Figure S2. Spectral analysis of 8-(5-azido-3-oxa-pentoxy)-3-iron-bis(1,2-dicarbollide) $[\text{Fe}(\text{C}_2\text{B}_9\text{H}_{11})_2]^-$ (azido derivative of FESAN).



ESI-Q-TOF MS



IR

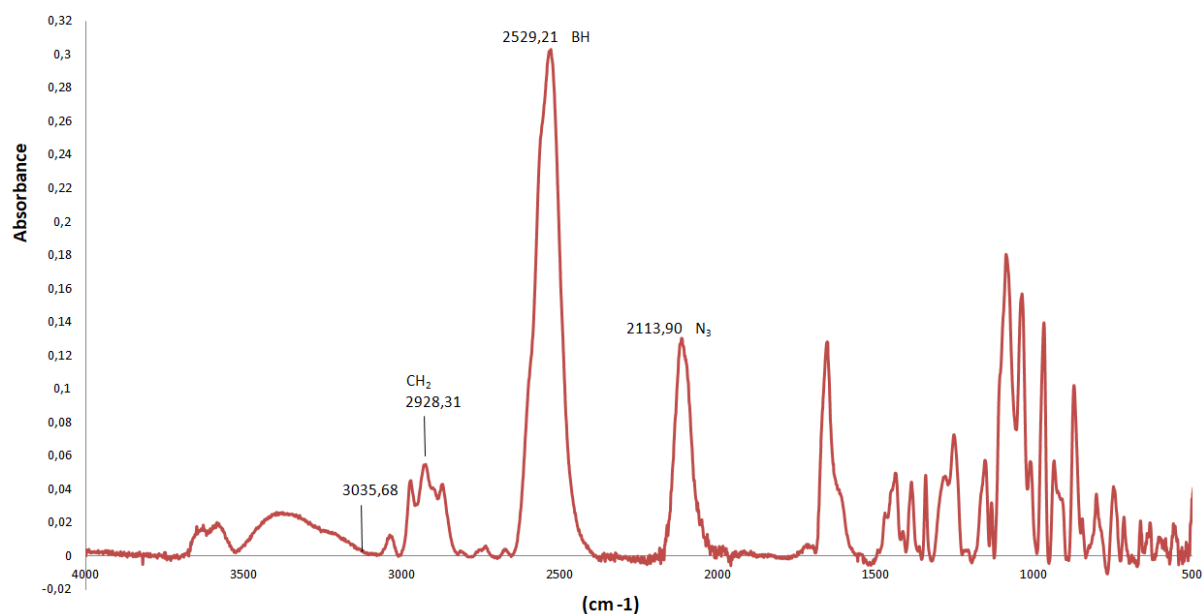
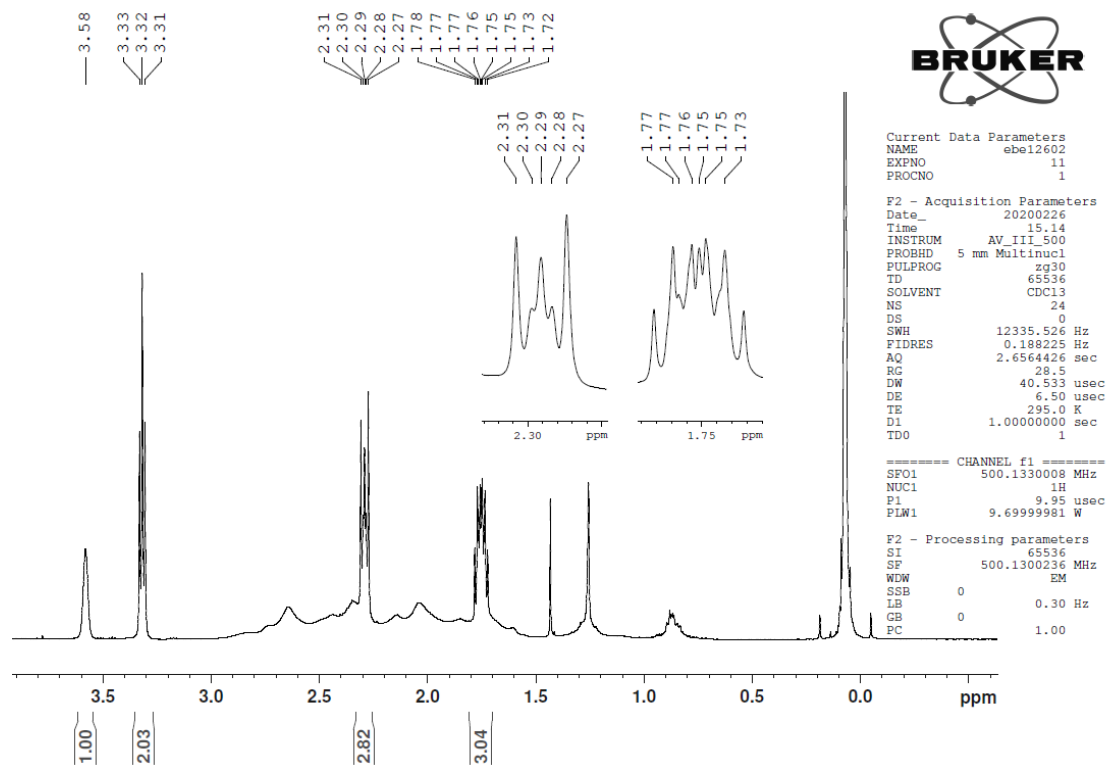
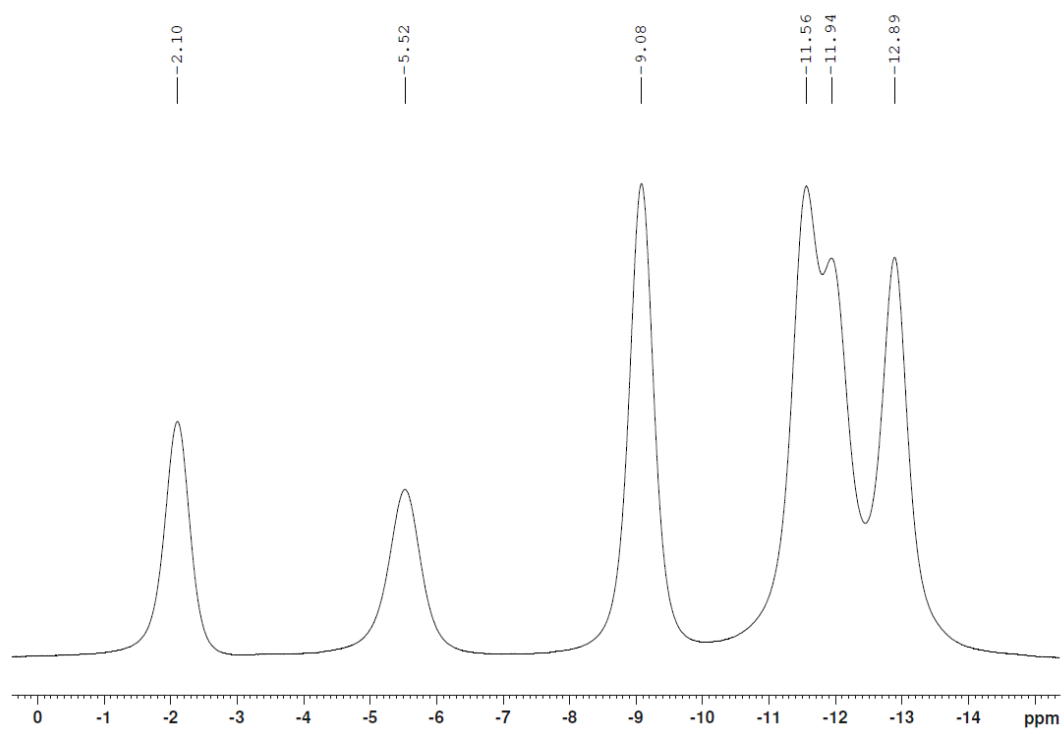


Figure S3. Spectral analysis of 1-(3-azidopropyl)-1,2-dicarba-*closo*-dodecaborane (1,2-DCDDDB, [C₂B₁₀H₁₂]) (azido derivative of 1,2-dicarba-*closo*-dodecaborate).

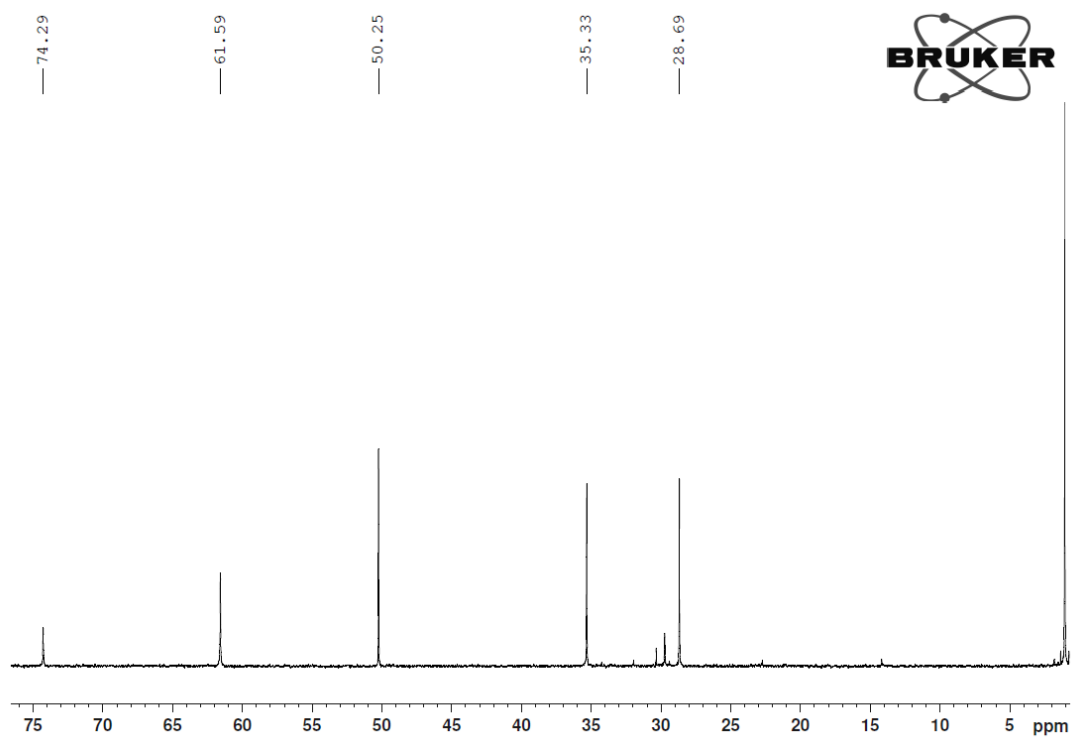
¹H NMR



^{11}B NMR



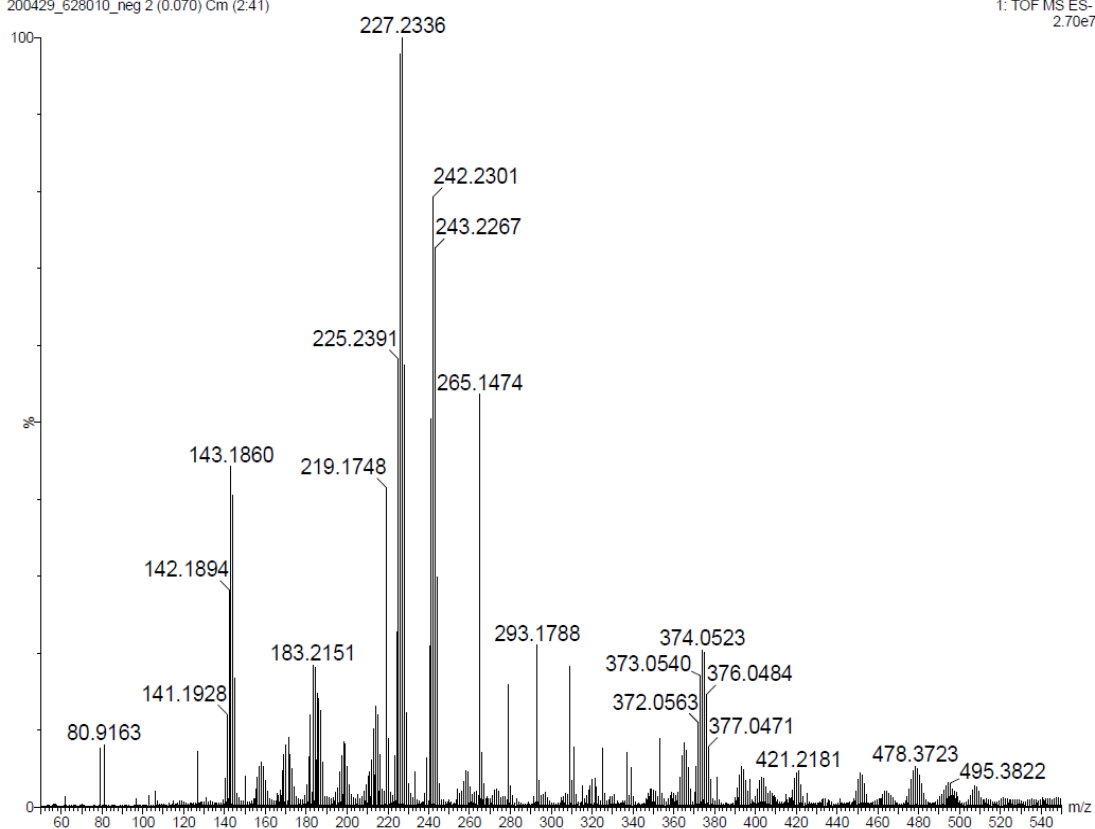
^{13}C NMR



ESI-Q-TOF

200429_628010_neg 2 (0.070) Cm (2:41)

1: TOF MS ES-
2.70e7



IR

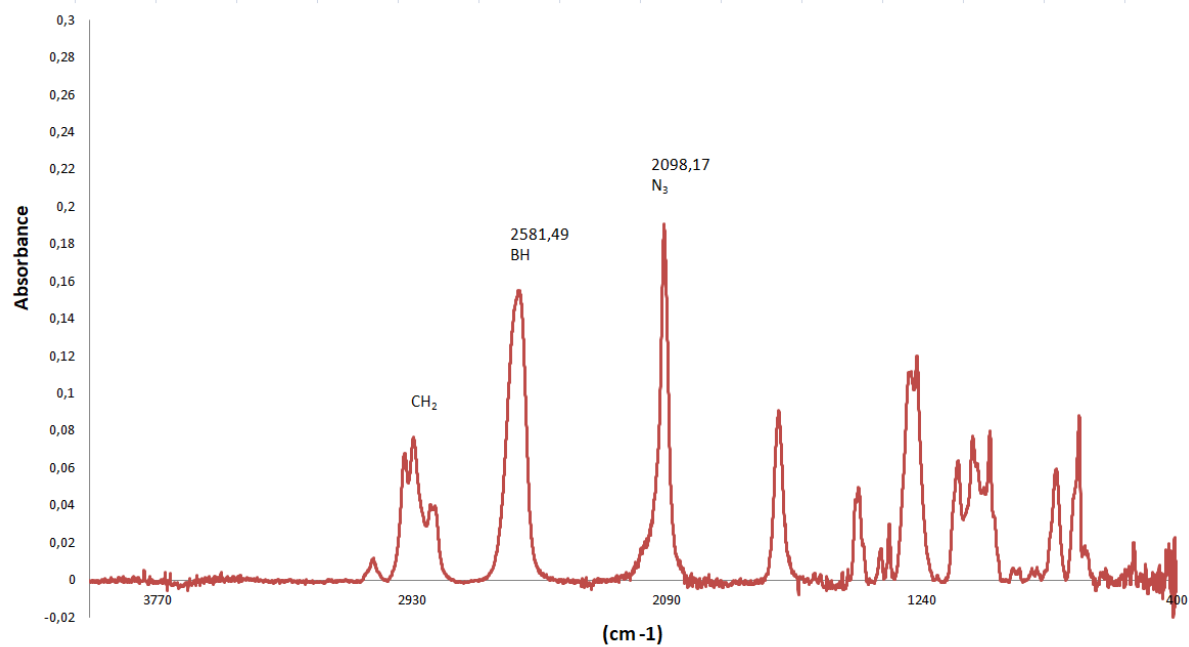
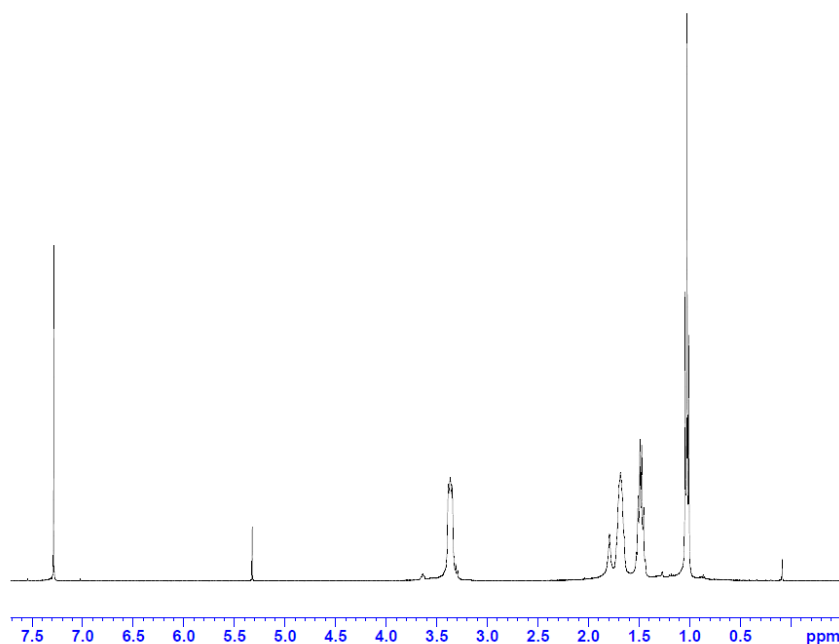


Figure S4. Spectral analysis of the bis-tetrabutylammonium-(4-azidobutoxy)-undecahydro-*closo*-dodecaborate (DDB, $[B_{12}H_{12}]^{2-}$) (azido derivative of *closo*-dodecaborate).

1H NMR

1H.stan
1H CDCl3 {D:\NMR_Data\CBMM\Zespol_08} Zespol_08 51



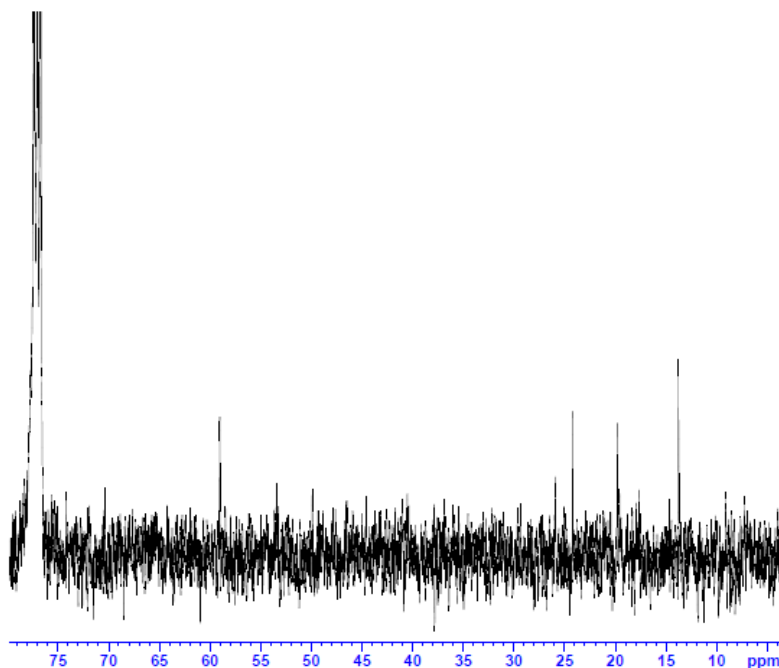
Current Data Parameters
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EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20211123
Time 12.16 h
INSTRUM Avance
PROBHD Z163739_0262 (zg30)
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 24
DS 2
SWH 8196.722 Hz
FIDRES 0.250144 Hz
AQ 3.8976959 sec
RG 101
DW 61.000 usec
DE 13.89 usec
TE 292.8 K
D1 1.00000000 sec
TD0 1
SFO1 400.1524709 MHz
NUC1 1H
P0 2.67 usec
P1 8.00 usec
PLW1 22.01300049 W

F2 - Processing parameters
SI 65536
SF 400.1500000 MHz
WMW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

^{13}C NMR

13C.stan
13C{1H} CDCl3 {D:\NMR_Data\CBMM\Zespol_08} Zespol_08 52



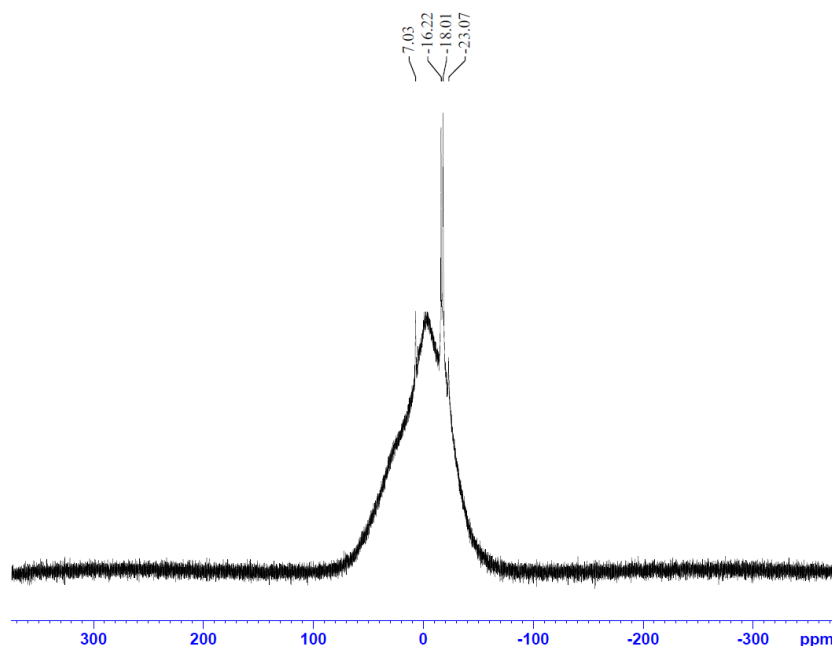
Current Data Parameters
NAME keo_dodecaN3 CH2Cl2
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20211123
Time 12.53 h
INSTRUM Avance
PROBHD Z163739_0262 (zgpg30)
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 256
DS 2
SWH 25906.736 Hz
FIDRES 0.790611 Hz
AQ 1.2648448 sec
RG 101
DW 19.300 usec
DE 6.50 usec
TE 293.9 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
SFO1 100.6298717 MHz
NUC1 13C
P0 2.67 usec
P1 8.00 usec
PLW1 93.92400360 W
SFO2 400.1516006 MHz
NUC2 1H
CPDPRG2 waltz65
PCPD2 90.00 usec
PLW2 22.01300049 W
PLW12 0.17393000 W
PLW13 0.08748700 W

F2 - Processing parameters
SI 32768
SF 100.6177975 MHz
WMW EM
SSB 0
LB 2.00 Hz
GB 0
PC 1.40

^{11}B NMR

11B{1H} - kw. borny / D2O = (+)19.5 ppm
 11B{1H} CDC13 {D:\NMR_Data\CBMM\Zespol_08} Zespol_08 52



Current Data Parameters
 NAME ebe_dodecaN3 11B
 EXFNO 1
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20211124
 Time 13.08 h
 INSTRUM Avance
 PROBHD Z163739_0262 (zggg
 FULPROG zgpg
 TD 65536
 SOLVENT CDC13
 NS 64
 DS 0
 SWH 96153.844 Hz
 FIDRES 2.934382 Hz
 AQ 0.3407872 sec
 RG 101
 DW 5.200 usec
 DE 6.50 usec
 TE 294.0 K
 D1 0.25000000 sec
 D11 0.03000000 sec
 TD0 1
 SFO1 128.3840220 MHz
 NUCL1 11B
 P1 10.00 usec
 PLW1 41.05799866 W
 SFO2 400.1524005 MHz
 NUCL2 1H
 CPDPRG2 waltz16
 PCPD2 90.00 usec
 PLW2 22.01300049 W
 PLW12 0.17393000 W
 PLW13 0.08748700 W

F2 - Processing parameters
 SI 32768
 SF 128.3840220 MHz
 WDW EM
 SSB 0
 LB 2.00 Hz
 GB 0
 PC 1.40

IR

