

Supplementary information

Sugar-thioacetamide Backbone in Oligodeoxyribonucleosides for Specific Recognition of Nucleic Acids

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General Experimental Procedure: Melting points of samples were determined in open capillary tubes and are uncorrected. IR spectra were recorded on an infrared Fourier Transform spectrophotometer using Chloroform, Nujol and KBr pellets. Column chromatographic separations were performed using silica gel 60-120 mesh, and 230-400 mesh, solvent systems EtOAc/Pet ether and pure MeOH/DCM. ^1H and ^{13}C were obtained using Bruker AC-200 (200 MHz) and 500 MHz NMR spectrometers. The chemical shifts are reported in delta (δ) values. The optical rotations were recorded in an ADP220 Polarimeter. Mass spectra were obtained either by LCMS and MALDI-TOF mass spectrometry techniques. Oligomers were purified and analyzed by RP HPLC, C18 column and MALDI-TOF mass spectrometry.

3'-[9-fluorenylmethoxycarbonyloxy]-amino-3'-deoxy thymidin -5'-thioacetic acid, 6.

M.p. 147-150 °C. $[\alpha]_{\text{D}}^{20} +16^\circ$ (c 0.5; CH_3OH). IR, $\nu(\text{cm}^{-1})$, (Chloroform)

3326.98, 2927.74, 2358.78, 1704.96, 1677.95, 1529.45, 1463.87.

^1H NMR: (DMSO-d_6 , 200MHz) δ 1.78(s, 3H; 5- CH_3), 2.06-2.28(m, 2H; 2', 2''-H), 3.15-3.38(m, 2H; S- CH_2), 3.4-4.32(m, 6H; 4'-H, 3'-H; 5', 5''-H, - CH_2 Fmoc), 6.06-6.12(t, 1H; 1'-H), 7.27-7.96(m, 10H; 6-H, Fmoc-H), 11.33(s, b, 1H, -NH).

^{13}C (DMSO-d_6 , 200MHz) δ 12.63(CH_3), 34.68(CH_2), 36.41(CH_2), 47.28(CH), 53.75(CH), 62.66(CH_2), 64.39(CH_2), 83.25(CH), 83.83(CH), 110.57(C), 120.67(CH), 125.64(CH), 127.68(CH), 128.25(CH), 136.76(CH), 141.31(C), 144.29(C), 150.94(C=O), 156.44(C=O), 164.48(C=O), 172.04(C=O). Anal Calcd (%) for $\text{C}_{27}\text{H}_{27}\text{N}_3\text{O}_7\text{S}$: C 60.19; H 5.246; N 7.805, S 5.955; Found C 60.79; H 5.02; N 7.46; S 6.03. MS, $\text{M}+\text{Na}^+$, Calculated 560.33; Observed, MALDI-TOF 560.38, LCMS 560.06.

3'-[9-fluorenylmethoxycarbonyloxy]-amino-3'-deoxy 5-methyl cytidine 5'-thioacetic acid, 14 M.p. 160-163 °C. $[\alpha]_{\text{D}}^{20} +18^\circ$ (c 0.5; CH_3OH).

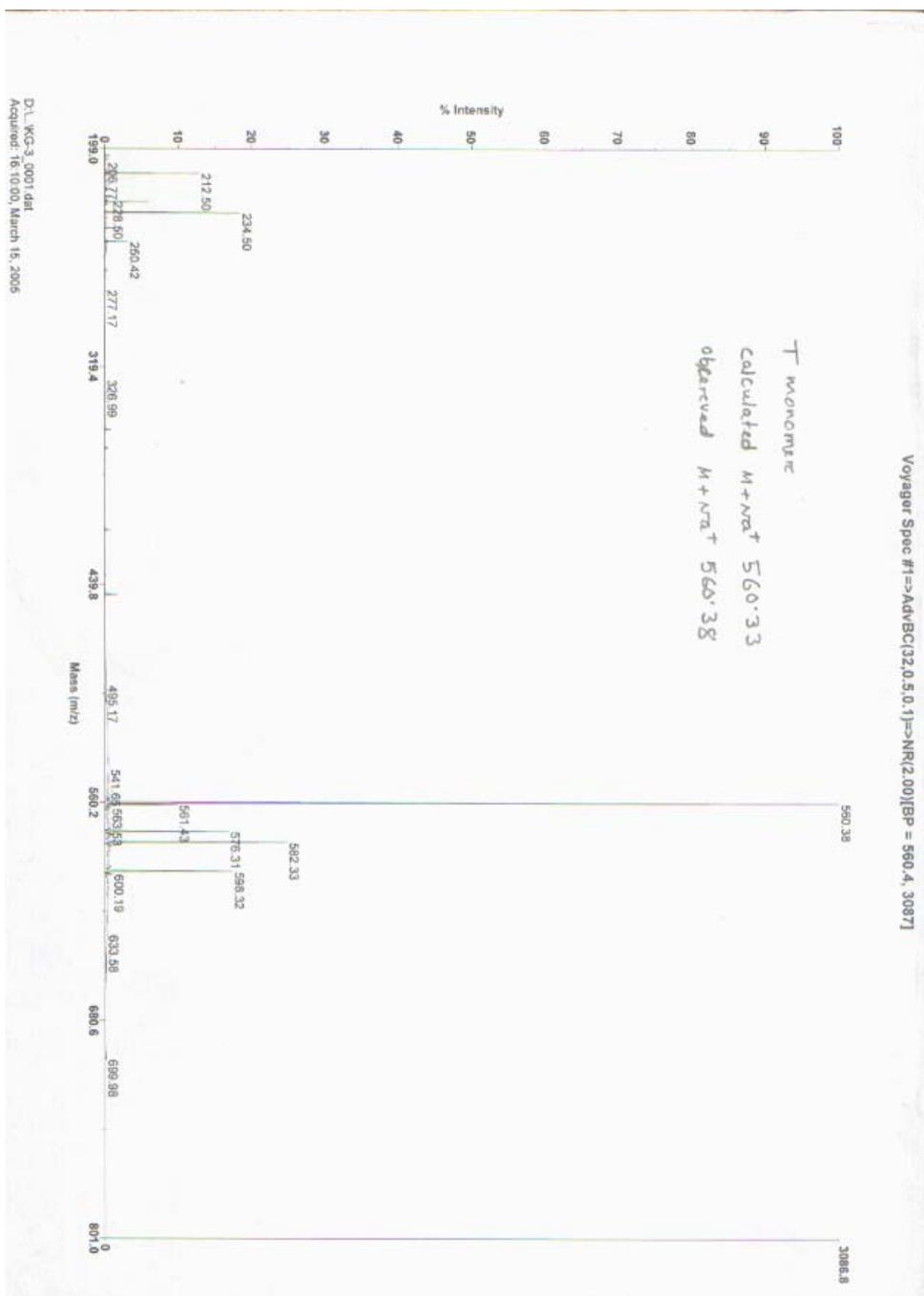
IR, $\nu(\text{cm}^{-1})$, (nujol) 3238.26, 2923.88, 2854.45, 1714.6, 1666.38 (cm^{-1}).

^1H NMR: ($\text{CDCl}_3+\text{CD}_3\text{OD}$, 200MHz) δ 2.08(s, 3H; 5-Me), 2.26-2.55(m, 2H; 2', 2''-H), 3.2(m, 2H; - CH_2 , Fmoc), 3.22-3.44(m, 2H; - SCH_2), 3.7-4.39(m, 4H; 4'-H, 5', 5''-H, 3'-H), 6.09(s, 1H; 1'-H), 7.29-8.07(m, 10H; 6-H, Fmoc-H). ^{13}C (DMSO-d_6)

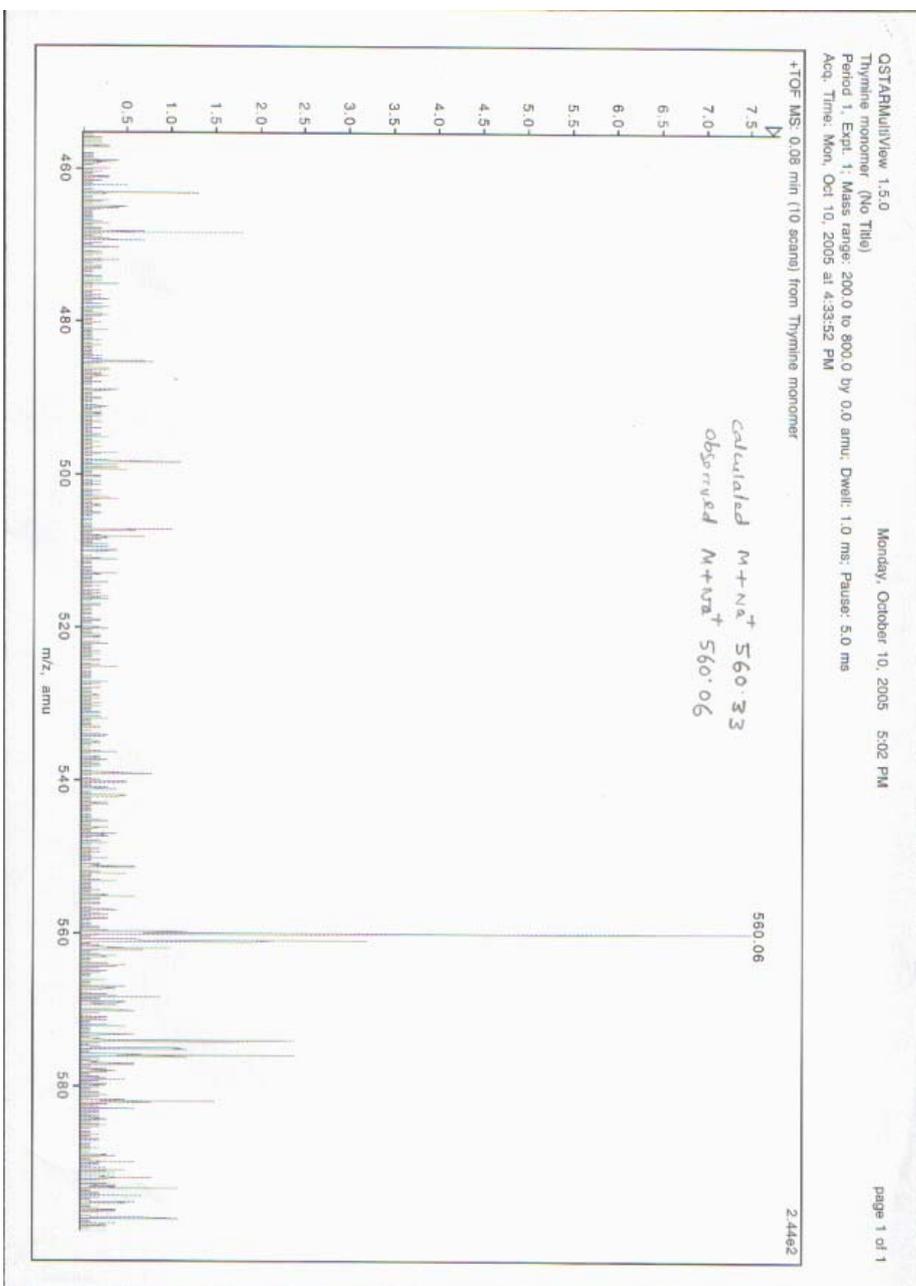
13.4(CH_3), 34.07(CH_2), 35.97(CH_2), 46.67(CH), 53.9(CH), 62.78(CH_2), 66.06(CH_2), 83.94(CH), 83.97(CH), 110.71(C), 120.74(CH), 125.69(CH), 127.9(CH), 128.45(CH), 137.02(CH), 141.9(C), 144.53(C), 151.2(C), 156.49(C=O), 166.23(C=O), 172.32(C=O).

MS, M ; $\text{M}+\text{Na}^+$ Calculated 536.60, 559.39; Observed MALDI-TOF, 559.43; LCMS 537.06

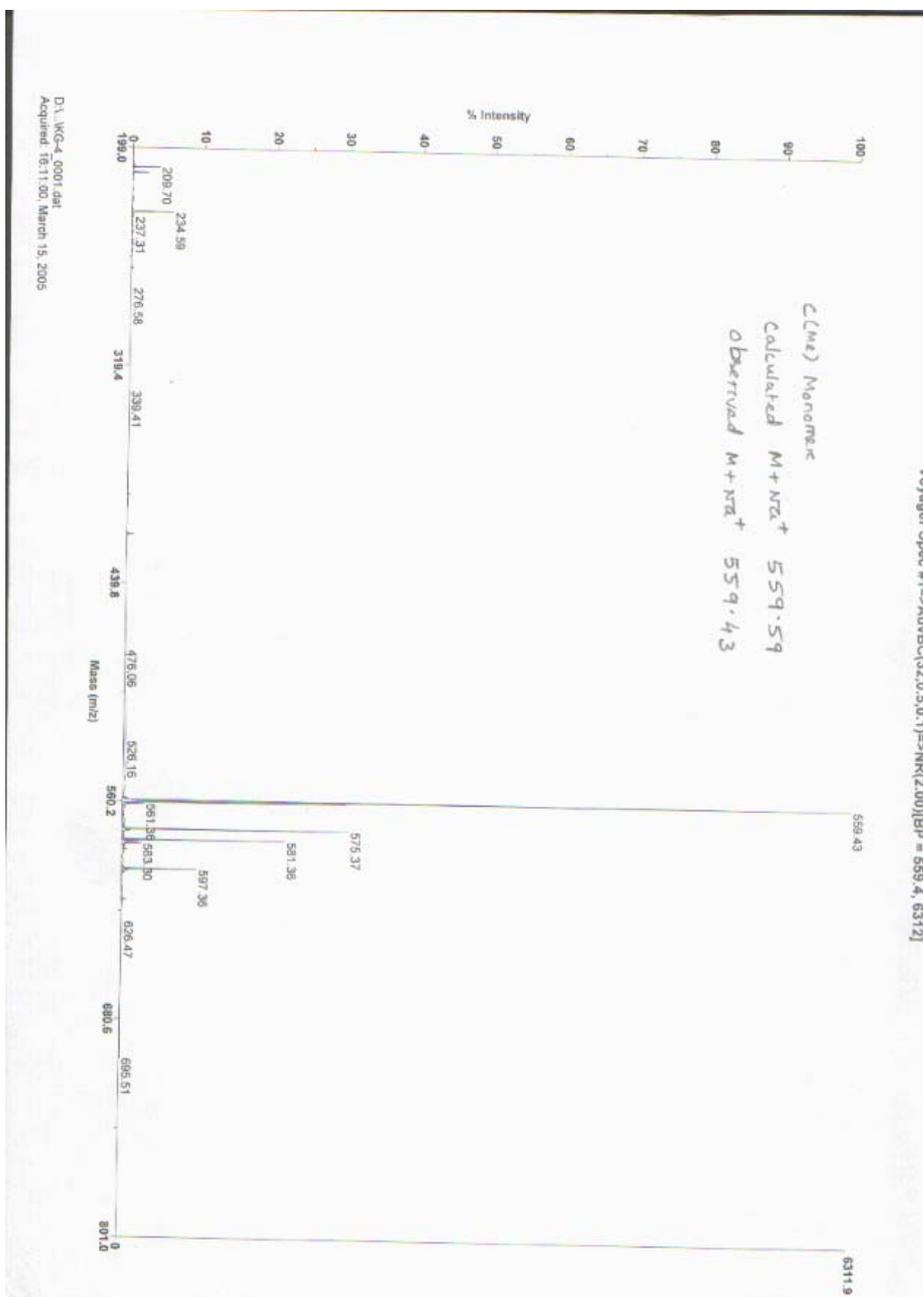
MALDI-TOF mass of compound **6**



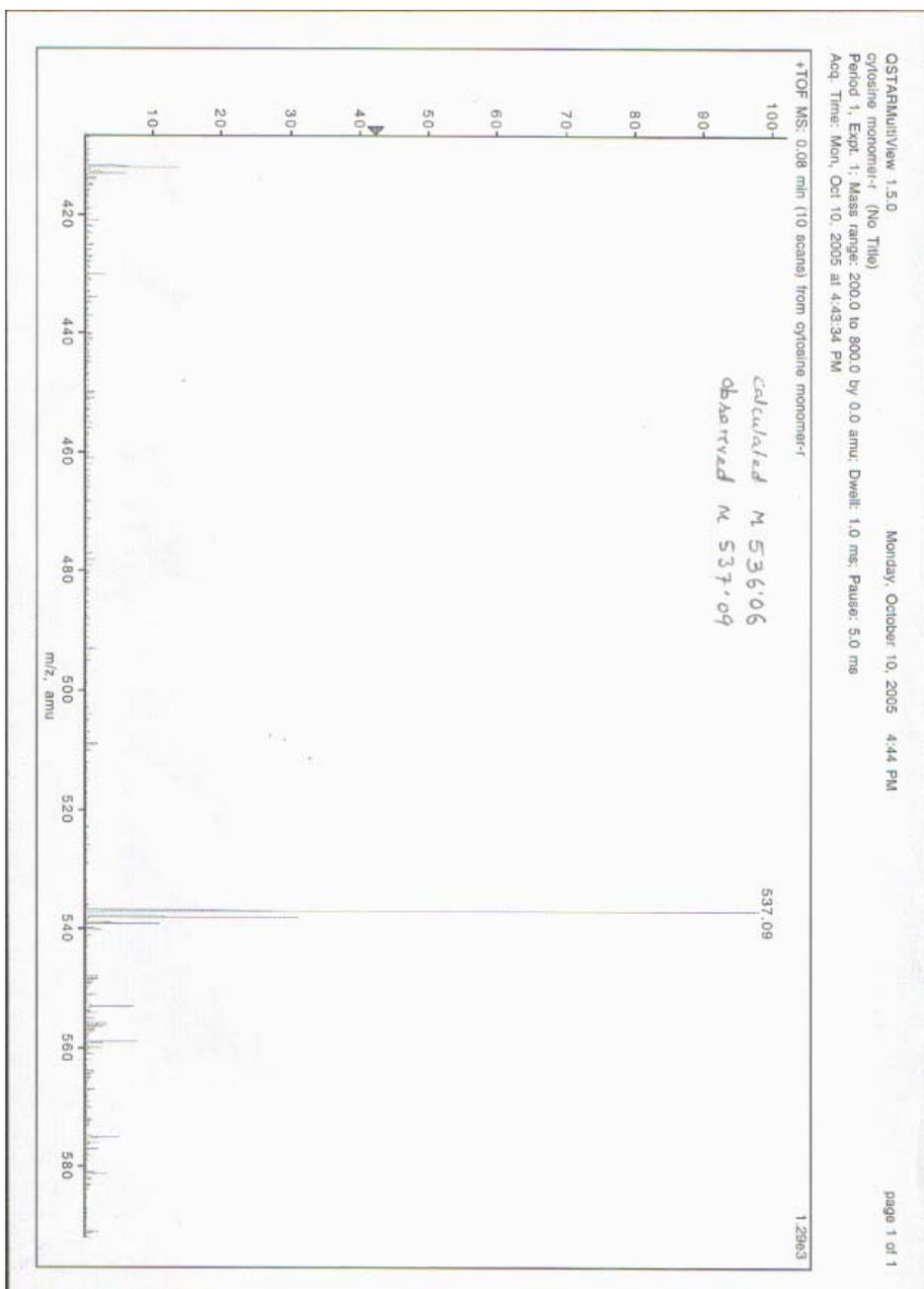
LCMS of compound **6**



MALDI-TOF of compound **14**

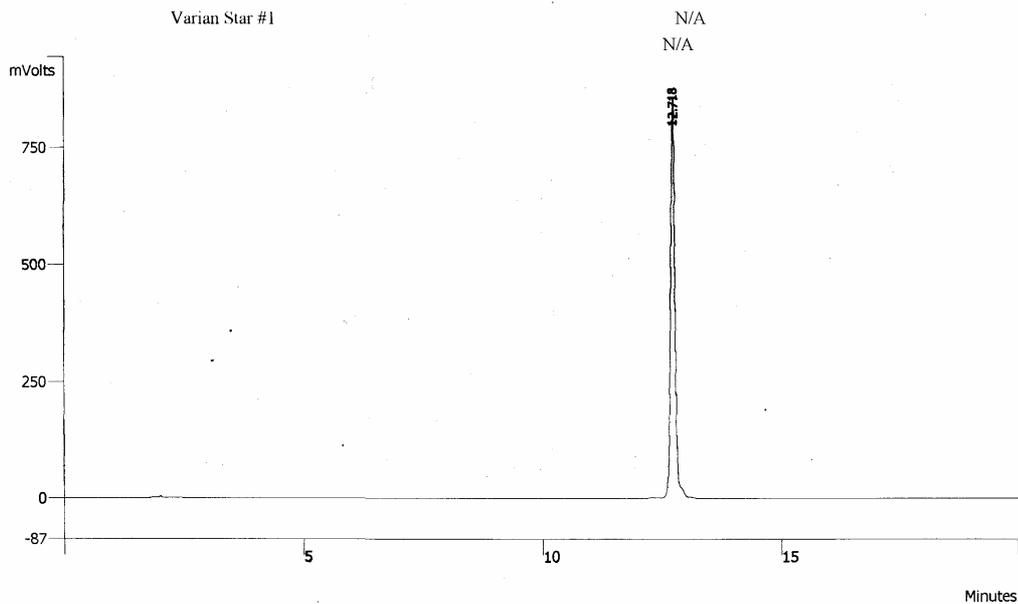


LCMS of compound **14**



HPLC profile of TANA15

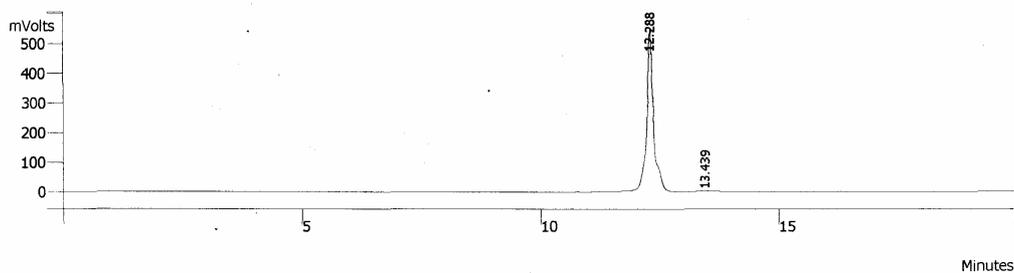
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Channel: A = A 1.0 RESULTS Calculation Method: c:\star\method 1.mth
Sample ID: K 1 Instrument (Calc): Varian Star #1
Operator (Inj): SSK/MVM Peak Measurement: Peak Area
Injection Date: 11/21/05 03:45:25 PM Calculation Type: Percent
Injection Method: c:\star\method 1.mth
Run Time (min): 20.002



Peak No	Ret. Time (min)	Width 1/2 (sec)	Peak Area (counts)	Result (%)
1	12.718	6.0	5465171	100.0000
			5465171	100.0000

HPLC profile of TANA16

Data File:	c:\star\data\gogai\k6.run	Operator (Calc):	SSK/MVM
Channel:	A = A 1.0 RESULTS	Calc Date:	12/23/05 04:18:37 PM
Sample ID:	K6	Times Calculated:	1
Operator (Inj):	SSK/MVM	Calculation Method:	c:\star\method 1.mth
Injection Date:	12/23/05 03:58:33 PM	Instrument (Calc):	Varian Star #1
Injection Method:	c:\star\method 1.mth	Run Mode:	Analysis
Run Time (min):	20.002	Peak Measurement:	Peak Area
Workstation:		Calculation Type:	Percent
Instrument (Inj):	Varian Star #1	Calibration Level:	N/A
		Verification Tolerance:	N/A

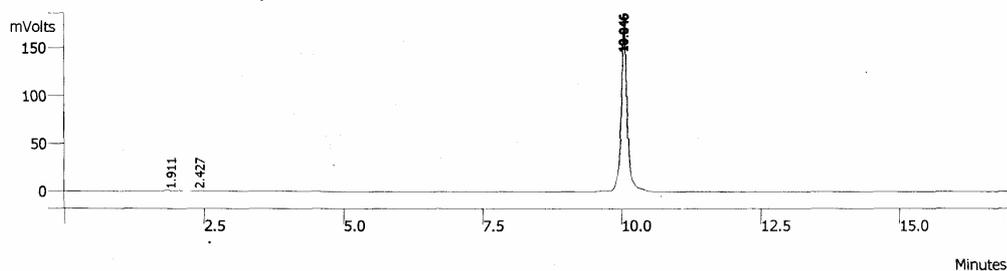


Peak No	Ret. Time (min)	Width 1/2 (sec)	Peak Area (counts)	Result (%)
1	12.288	7.5	5647819	98.7647
2	13.439	0.0	70642	1.2353
			5718461	100.0000

HPLC profile of TANA17

Data File: c:\star\data\gogai\tt7.run
Channel: A = A 1.0 RESULTS
Sample ID: TT7
Operator (Inj): SSK/MVM
Injection Date: 05/19/05 02:06:26 PM
Injection Method: c:\star\method 1.mth
Run Time (min): 17.002
Workstation:
Instrument (Inj): Varian Star #1

Operator (Calc): SSK/MVM
Calc Date: 05/19/05 02:23:28 PM
Times Calculated: 1
Calculation Method: c:\star\method 1.mth
Instrument (Calc): Varian Star #1
Run Mode: Analysis
Peak Measurement: Peak Area
Calculation Type: Percent
Calibration Level: N/A
Verification Tolerance: N/A

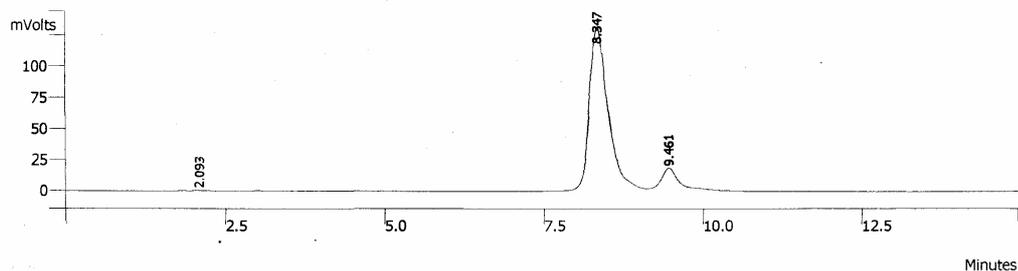


Peak No	Ret. Time (min)	Width 1/2 (sec)	Peak Area (counts)	Result (%)
1	1.911	12.3	15652	1.1294
2	2.427	0.0	9796	0.7069
3	10.046	6.6	1360423	98.1638
			1385871	100.0001

HPLC profile of TANA18

Data File: c:\star\data\gogai\t4 + t3.run
Channel: A = A 1.0 RESULTS
Sample ID: T4 + T3
Operator (Inj): SSK/MVM
Injection Date: 05/19/05 01:33:04 PM
Injection Method: c:\star\method 1.mth
Run Time (min): 15.002
Workstation:
Instrument (Inj): Varian Star #1

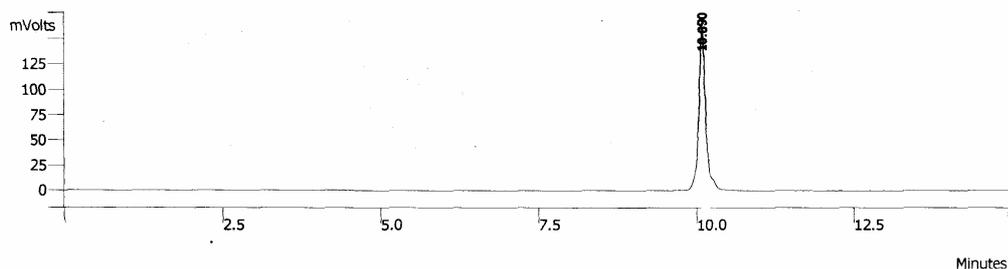
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Calc Date: 05/19/05 01:48:04 PM
Times Calculated: 1
Calculation Method: c:\star\method 1.mth
Instrument (Calc): Varian Star #1
Run Mode: Analysis
Peak Measurement: Peak Area
Calculation Type: Percent
Calibration Level: N/A
Verification Tolerance: N/A



Peak No	Ret. Time (min)	Width 1/2 (sec)	Peak Area (counts)	Result (%)
1	2.093	5.8	12115	0.3805
2	8.347	18.4	2755717	86.5504
3	9.461	15.8	416112	13.0691
			3183944	100.0000

HPLC profile of TANA19

Data File:	c:\star\data\gogai\tt4.run	Operator (Calc):	SSK/MVM
Channel:	A = A 1.0 RESULTS	Calc Date:	05/19/05 02:53:13 PM
Sample ID:	tt4	Times Calculated:	1
Operator (Inj):	SSK/MVM	Calculation Method:	c:\star\method 1.mth
Injection Date:	05/19/05 02:38:13 PM	Instrument (Calc):	Varian Star #1
Injection Method:	c:\star\method 1.mth	Run Mode:	Analysis
Run Time (min):	15.002	Peak Measurement:	Peak Area
Workstation:		Calculation Type:	Percent
Instrument (Inj):	Varian Star #1	Calibration Level:	N/A
		Verification Tolerance:	N/A



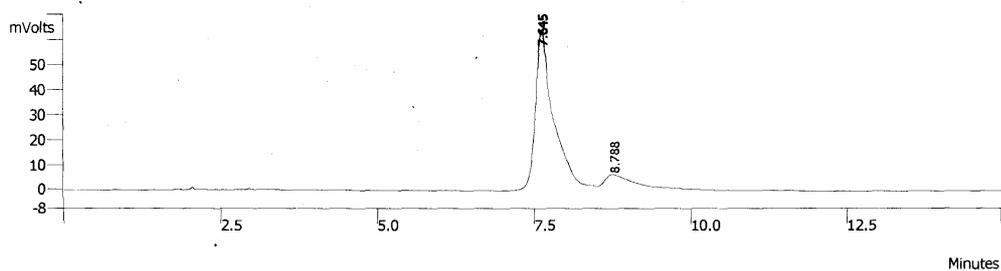
Peak No	Ret. Time (min)	Width 1/2 (sec)	Peak Area (counts)	Result (%)
1	10.090	7.6	1265286	100.0000
			1265286	100.0000

Supplementary Material (ESI) for Chemical Communications
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HPLC profile of aeg PNA 20

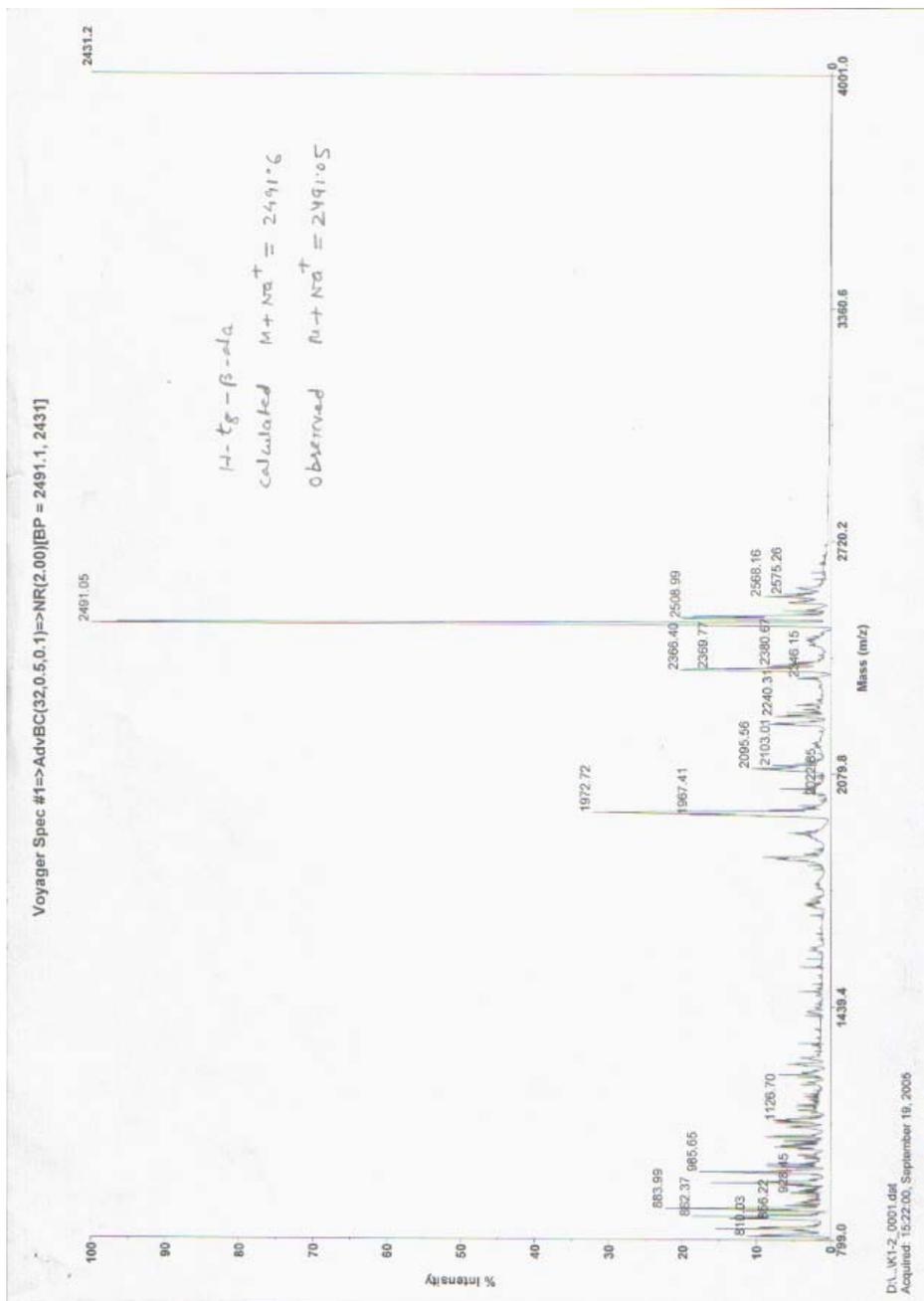
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Sample ID: T8
Operator (Inj): SSK/MVM
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Injection Method: c:\star\method 1.mth
Run Time (min): 15.002
Workstation:
Instrument (Inj): Varian Star #1

Operator (Calc): SSK/MVM
Calc Date: 05/19/05 12:50:30 PM
Times Calculated: 1
Calculation Method: c:\star\method 1.mth
Instrument (Calc): Varian Star #1
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Peak Measurement: Peak Area
Calculation Type: Percent
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Verification Tolerance: N/A

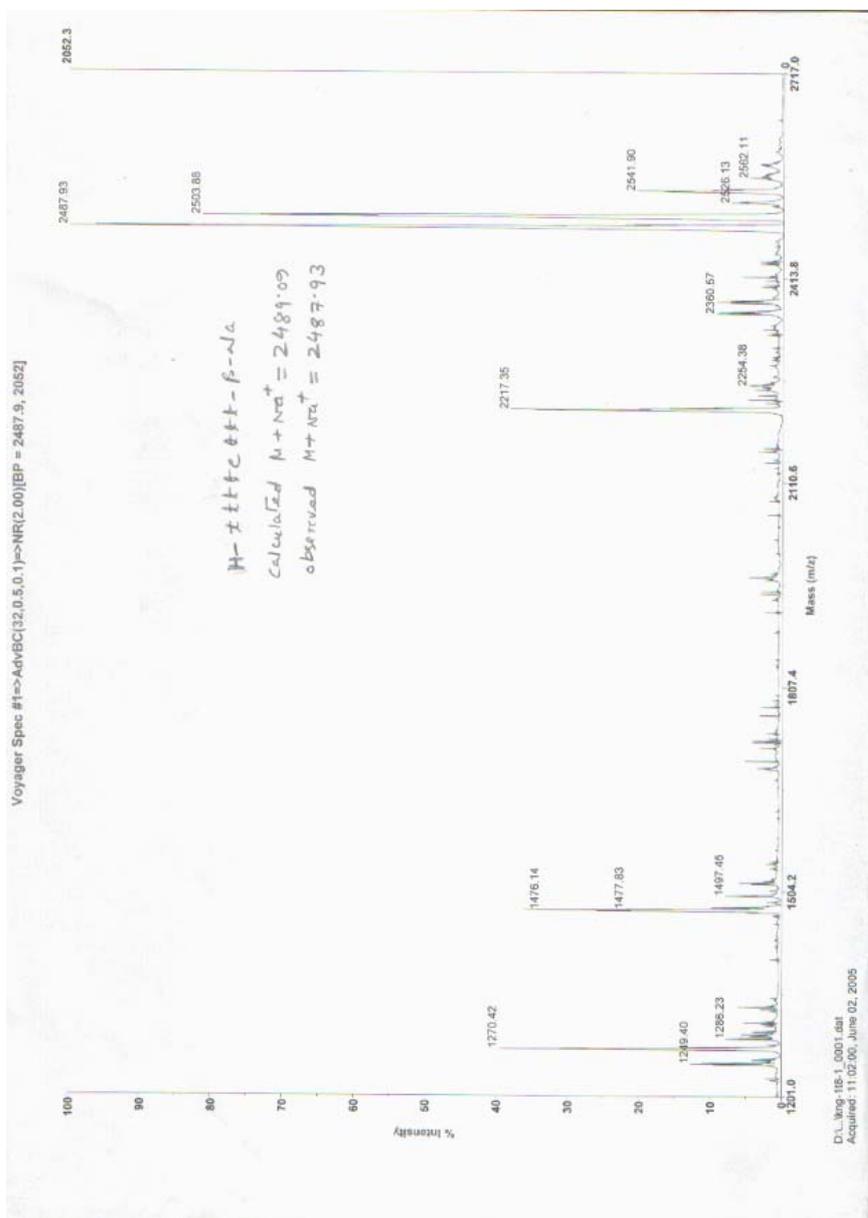


Peak No	Ret. Time (min)	Width 1/2 (sec)	Peak Area (counts)	Result (%)
1	7.645	16.5	1320725	83.1217
2	8.788	29.9	268181	16.8783
			1588906	100.0000

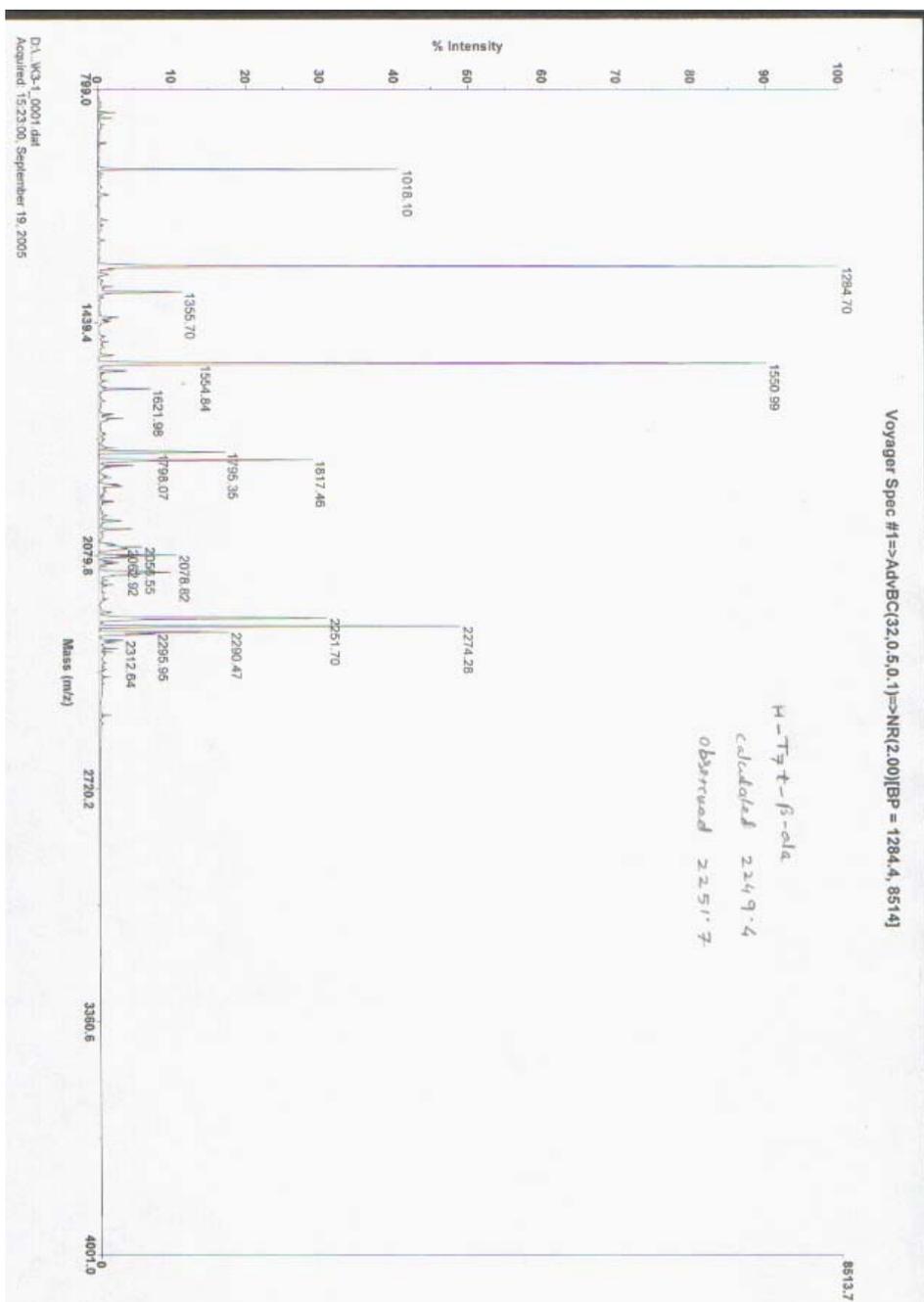
MALDI-TOF mass of TANA15



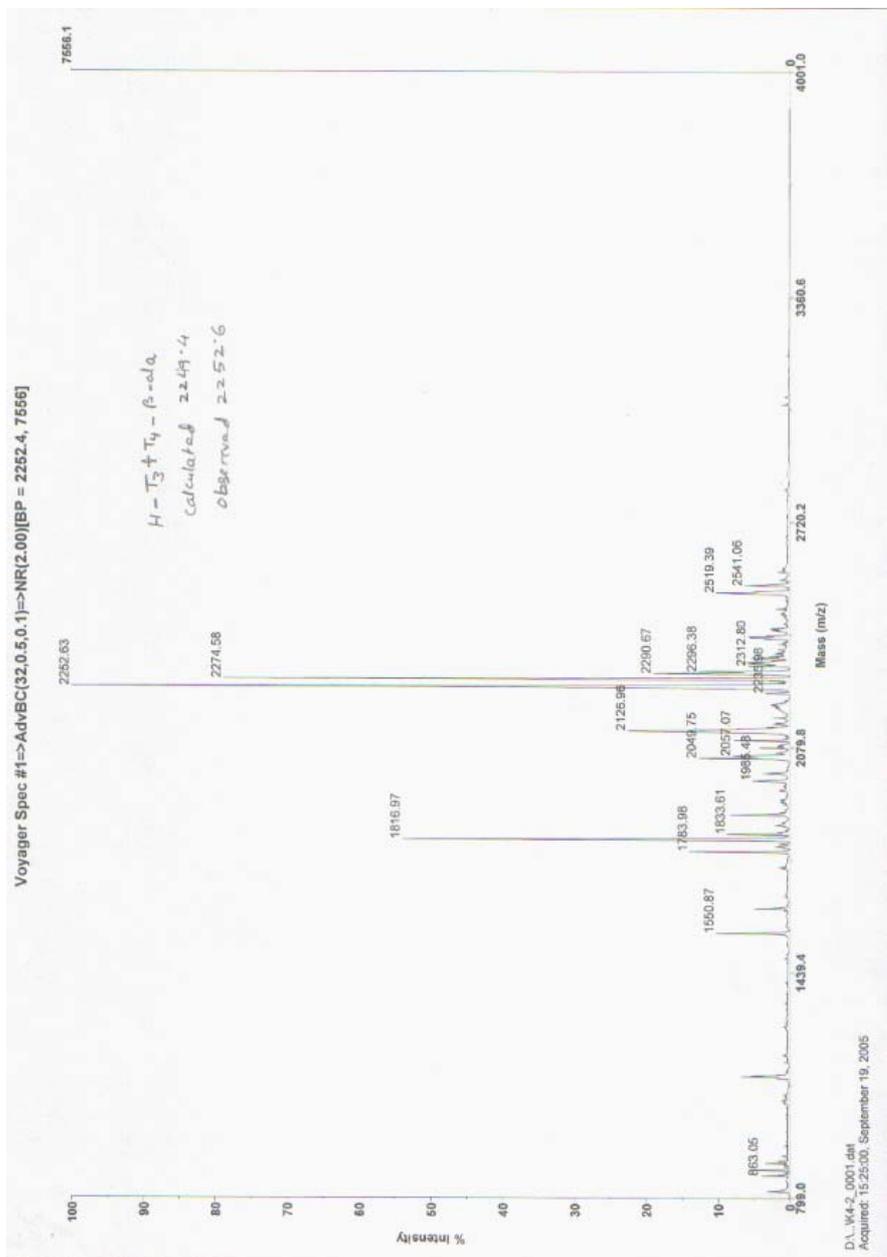
MALDI-TOF mass of TANA16



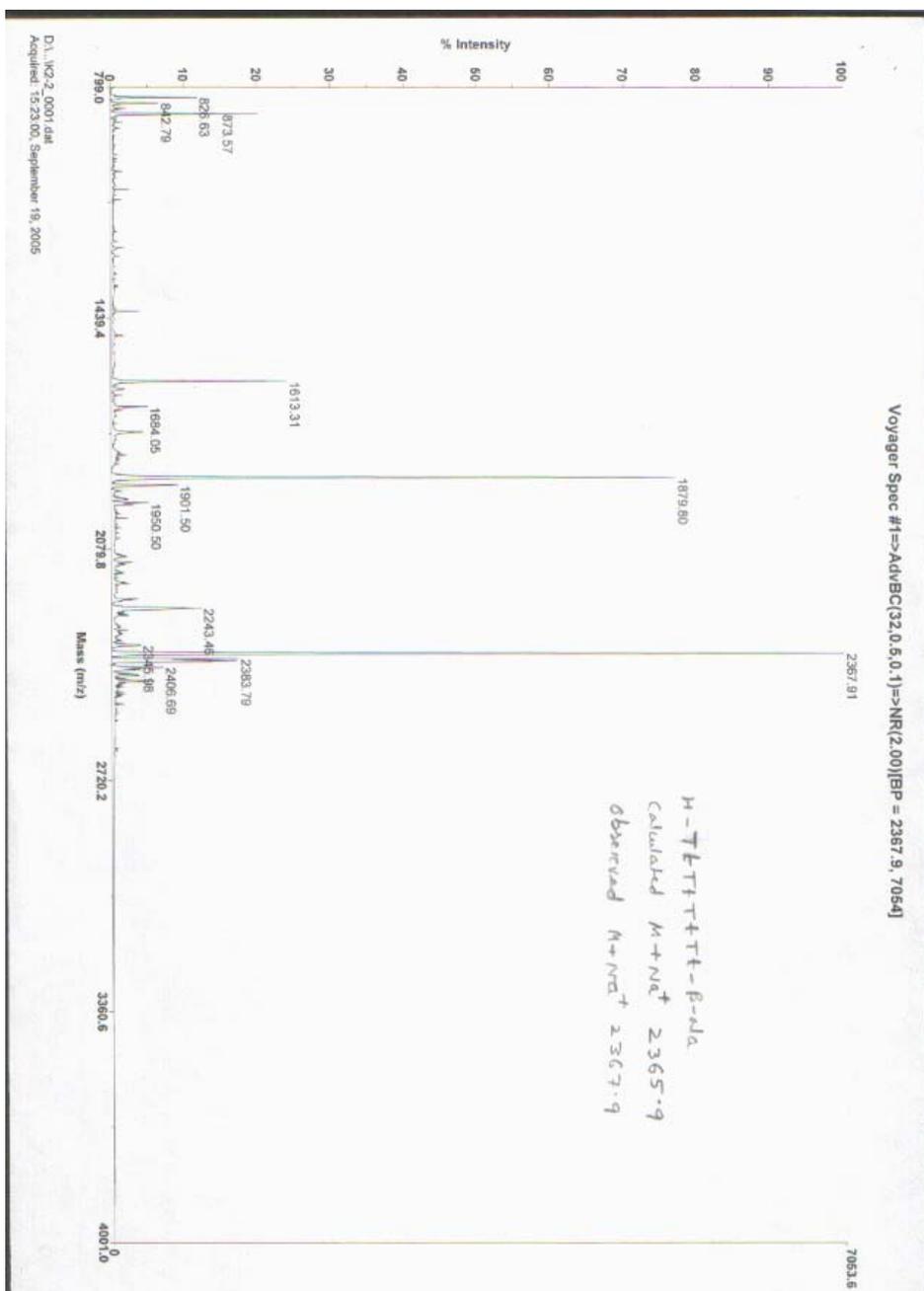
MALDI-TOF of TANA17



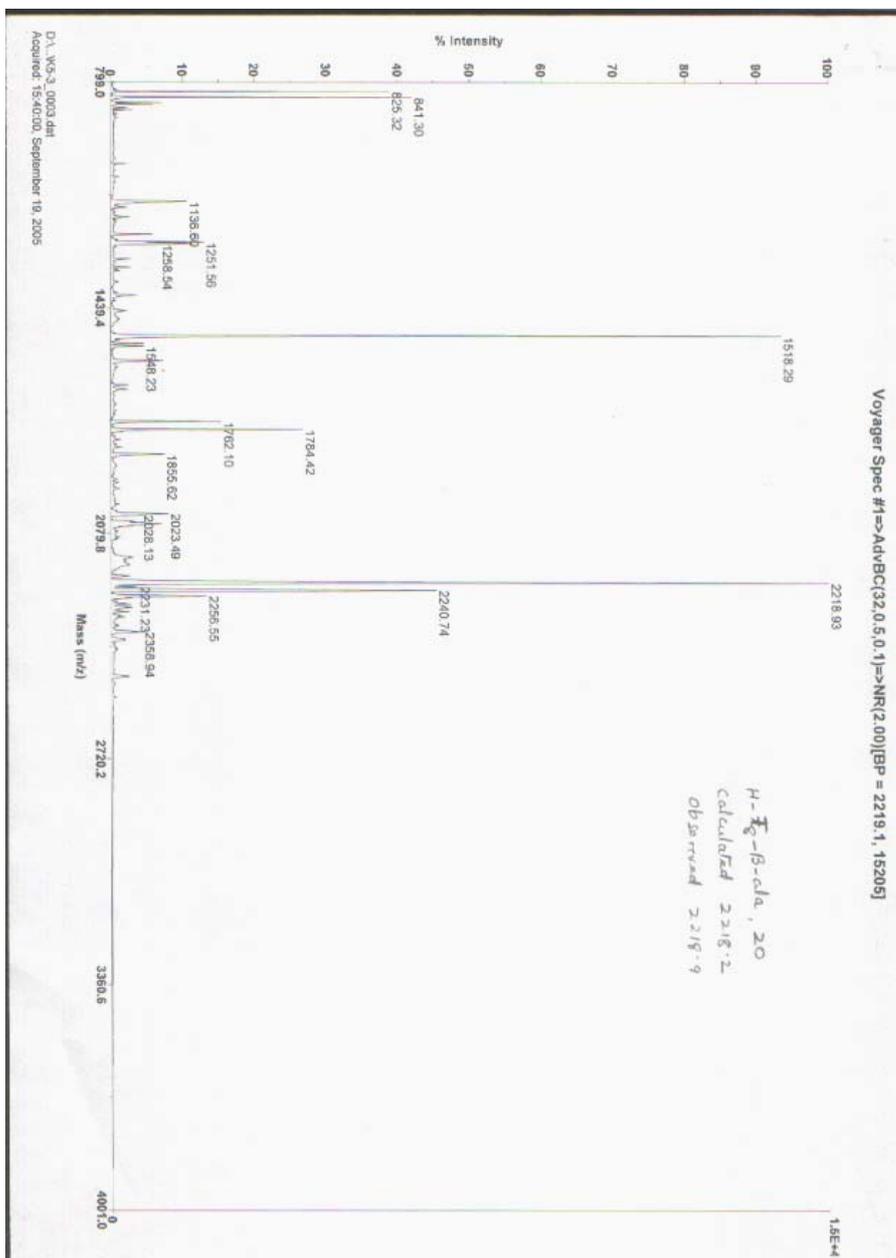
MALDI-TOF mass of TANA18



MALDI-TOF mass of TANA19



MALDI-TOF mass of **aeg PNA 20**



UV-*T_m* measurements: The complementary DNA and RNA oligomers were synthesized on an Applied Biosystems DNA Synthesizer. The concentration was calculated on the basis of absorbance from the molar extinction coefficients of the corresponding nucleobases. The complexes were prepared in 10 mM sodium phosphate buffer, pH 7.4 containing NaCl (10 mM) and were annealed by keeping the samples at 90°C for 5 minutes followed by slow cooling to room temperature. Absorbance versus temperature profiles were obtained by monitoring at 260 nm with Perkin-Elmer Lambda 35 spectrophotometer scanning from 10 to 85°C at a ramp rate of 0.2/0.5°C per minute. The data were processed using Microcal Origin 6.0 and *T_m* values derived from the derivative curves.

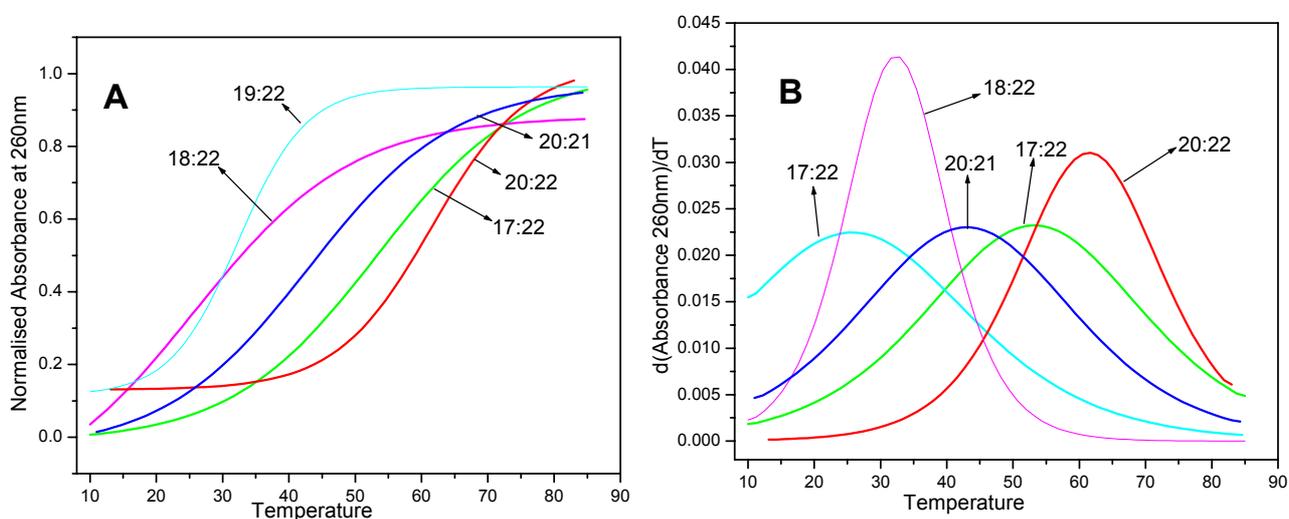


Fig A. Melting curve of TANA 17, 18, 19 & *aegPNA20* with RNA 22 B. Corresponding derivative curve.

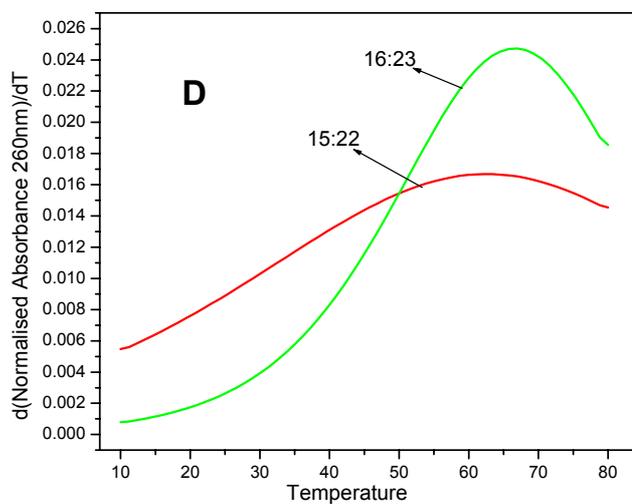
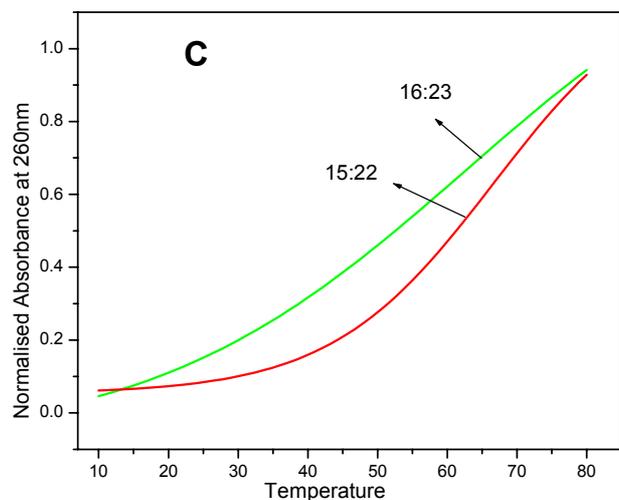


Fig: **C.** Melting curve of **TANA15 and 16** with **RNA22 and 23**, 10mM phosphate buffer (pH= 5.5) and 10 mM NaCl concentration. **B.** Corresponding derivative curve

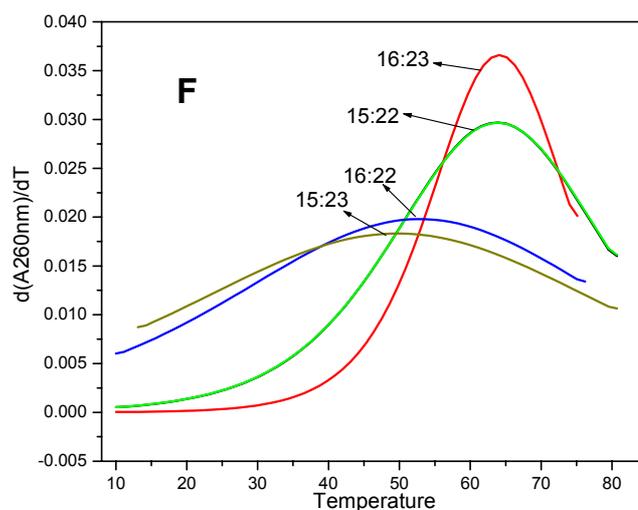
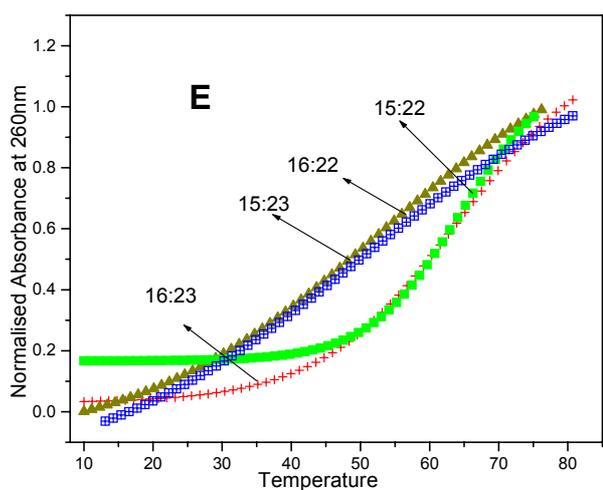


Fig: **E** UV-melting curve of **TANA 15 & 16**, **DNA 24** with complementary **RNA 22 and 23** **F.** Corresponding derivative curves.

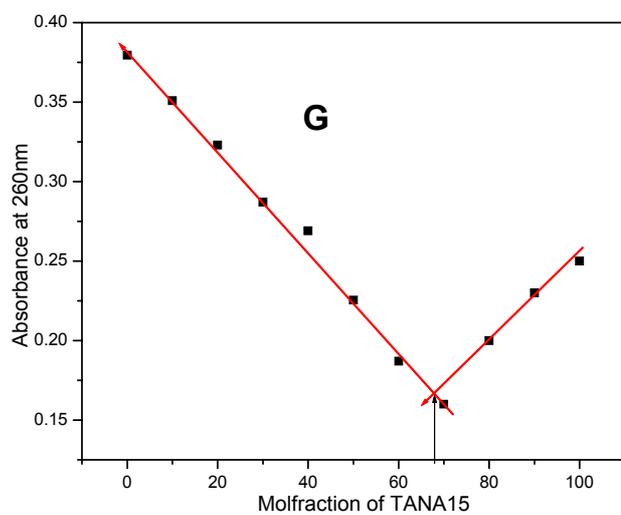


Fig: **G** UV-Jobs Plot of **TANA15** with **RNA22**