

Supplementary Information

Properties of 5- and/or 2'-modified 2'-*O*-cyanoethyl uridine residue: 2'-*O*-cyanoethyl-5-propynyl-2-thiouridine as an efficient duplex stabilizing component

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Table S1. MALDI-TOF-Mass for 2'-OMe-(CGUUNXNUUGC) oligonucleotides

X	N	formula	calcd. (exact)	found
U _{OCE}	A	C ₁₁₆ H ₁₅₂ N ₃₇ O ₇₈ P ₁₀ ⁺	3620.6	3621.3
	G	C ₁₁₆ H ₁₅₂ N ₃₇ O ₈₀ P ₁₀ ⁺	3652.6	3653.3
	C	C ₁₁₄ H ₁₅₂ N ₃₃ O ₈₀ P ₁₀ ⁺	3572.6	3573.3
s ² U _{OCE}	A	C ₁₁₆ H ₁₅₂ N ₃₇ O ₇₇ P ₁₀ S ⁺	3636.6	3637.8
	G	C ₁₁₆ H ₁₅₂ N ₃₇ O ₇₉ P ₁₀ S ⁺	3668.6	3669.9
	C	C ₁₁₄ H ₁₅₂ N ₃₃ O ₇₉ P ₁₀ S ⁺	3588.6	3589.6
p ⁵ U _{OCE}	A	C ₁₁₉ H ₁₅₄ N ₃₇ O ₇₈ P ₁₀ ⁺	3658.7	3659.6
	G	C ₁₁₉ H ₁₅₄ N ₃₇ O ₈₀ P ₁₀ ⁺	3690.7	3691.9
	C	C ₁₁₇ H ₁₅₄ N ₃₃ O ₈₀ P ₁₀ ⁺	3610.6	3611.3
p ⁵ s ² U _{OCE}	A	C ₁₁₉ H ₁₅₄ N ₃₇ O ₇₇ P ₁₀ S ⁺	3674.6	3676.5
	G	C ₁₁₉ H ₁₅₄ N ₃₇ O ₇₉ P ₁₀ S ⁺	3706.6	3707.7
	C	C ₁₁₇ H ₁₅₄ N ₃₃ O ₇₉ P ₁₀ S ⁺	3626.6	3627.2

Table S2. MALDI-TOF-Mass for consecutively or discretely modified oligonucleotides, (CGUUXXXUUGC), or (CGXUUXUUXGC)

sequence	formula	calcd. (exact)	found	found (max)
5'- CGUUXXXUUGC -3'	C ₁₂₇ H ₁₅₈ N ₃₃ O ₇₉ P ₁₀ S ₃ ⁺	3814.6	3814.9	3616.8
5'- CGXUUXUUXGC -3'	C ₁₂₇ H ₁₅₈ N ₃₃ O ₇₉ P ₁₀ S ₃ ⁺	3814.6	3814.5	3616.4

Table S3. Pairing energies in different level of theory [kcal mol⁻¹]

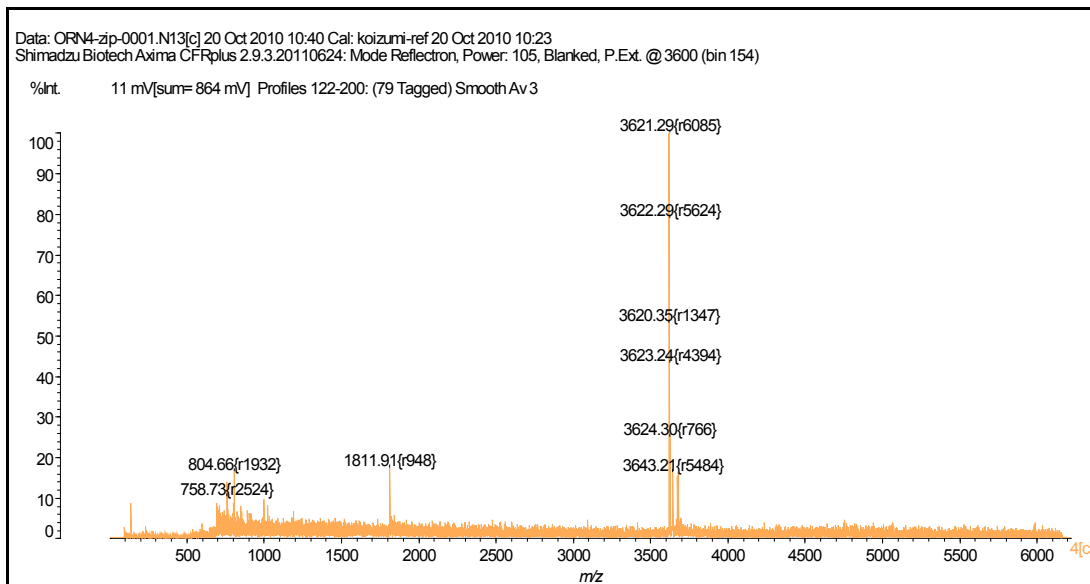
	wB97XD/cc-pVTZ//wB97XD/6-31+G(d)	wB97XD/6-31+G(d)	M06-2X/6-31+G(d)
A-U	-16.4	-15.7	-15.1
A-s ² U	-16.0	-15.6	-14.8
A-m ² U	-16.5	-16.0	-15.0
A-m ² s ² U	-15.9	-15.6	-14.8
A-b ² U	-17.0	-17.3	-16.4
A-b ² s ² U	-16.4	-16.9	-16.1
A-p ² U	-16.7	-16.1	-15.1
A-p ² s ² U	-16.2	-15.7	-15.0
G-U	-16.9	-16.5	-15.8
G-s ² U	-14.3	-13.4	-12.8
G-m ² U	-17.3	-16.9	-16.2
G-m ² s ² U	-14.5	-13.6	-13.1
G-b ² U	-17.2	-17.4	-16.7
G-b ² s ² U	-14.6	-14.4	-13.7
G-p ² U	-16.9	-16.5	-15.8
G-p ² s ² U	-14.2	-13.4	-12.8

Complete Reference for Gaussian 09, Revision C.01*

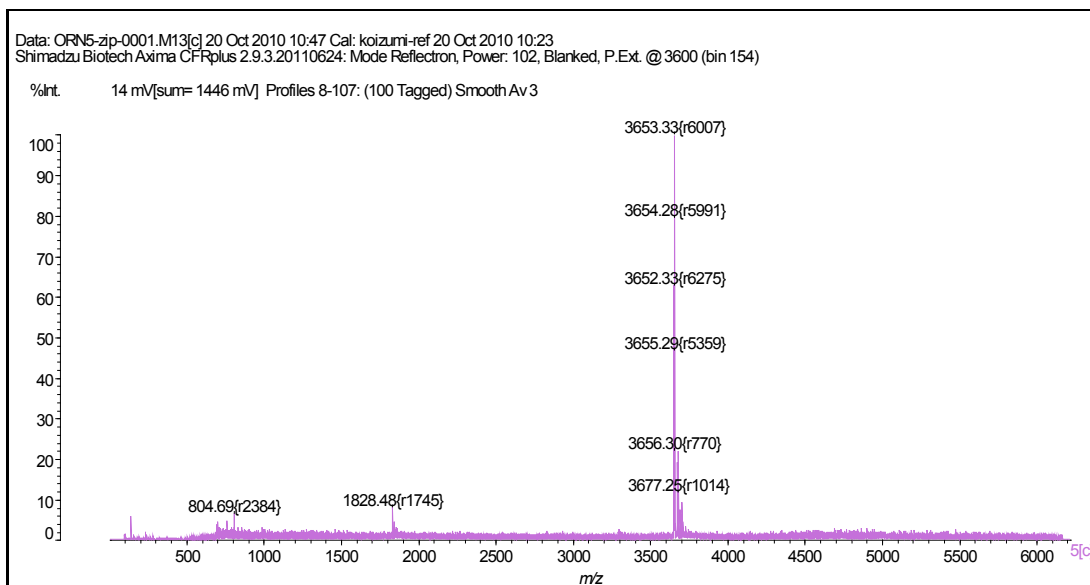
* M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2010.

MALDI-TOF-Mass for 2'-OMe-(CGUUNXNUUGC) oligonucleotides

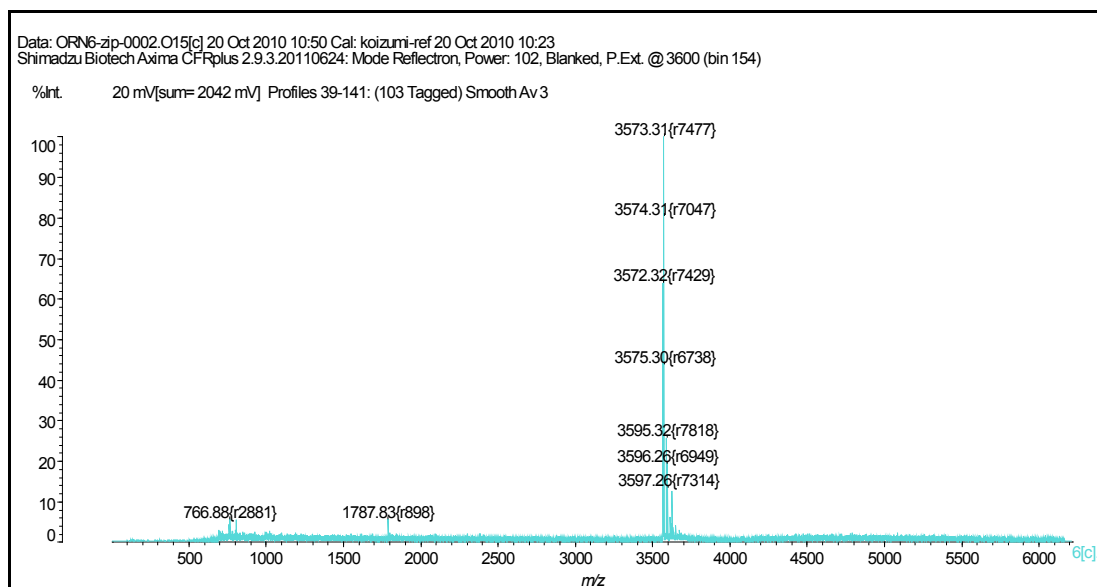
X = U_{OCE}, N = A C₁₁₆H₁₅₂N₃₇O₇₈P₁₀⁺ calcd: 3620.6



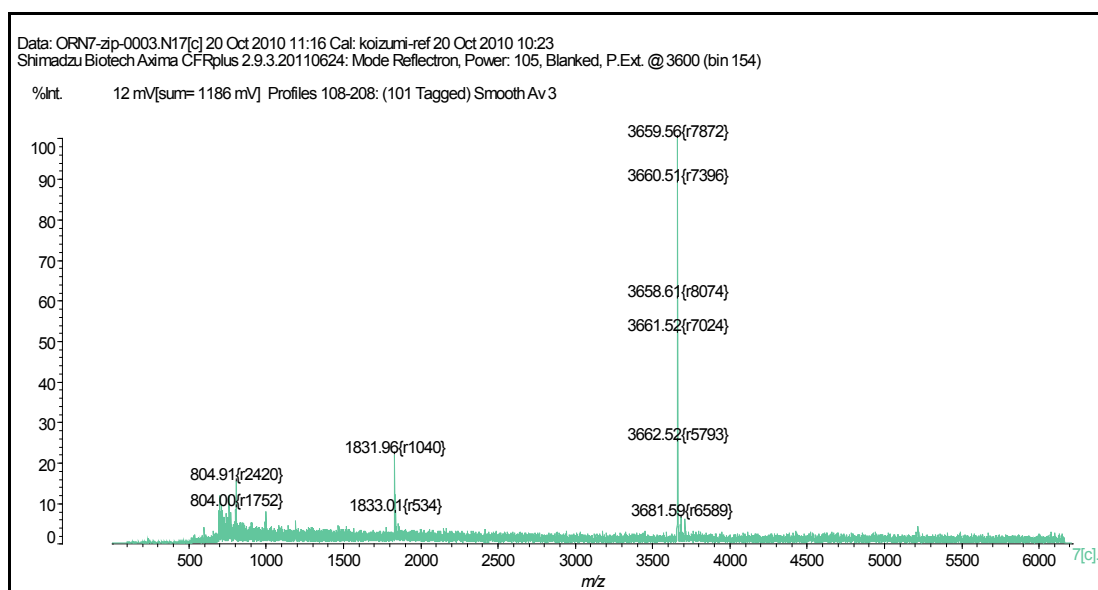
X = U_{OCE}, N = G C₁₁₆H₁₅₂N₃₇O₈₀P₁₀⁺ calcd: 3652.6

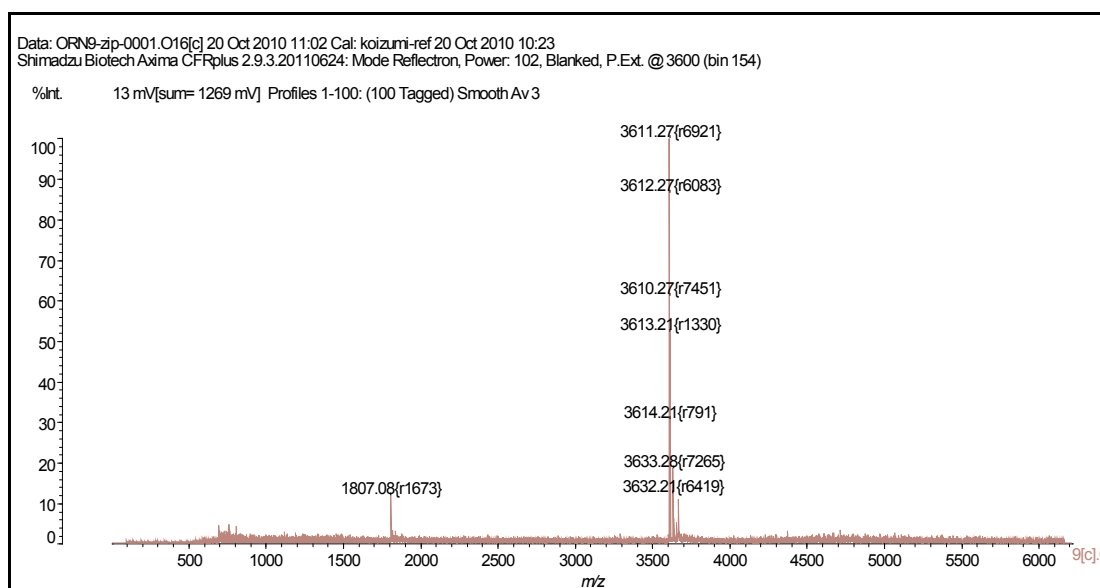
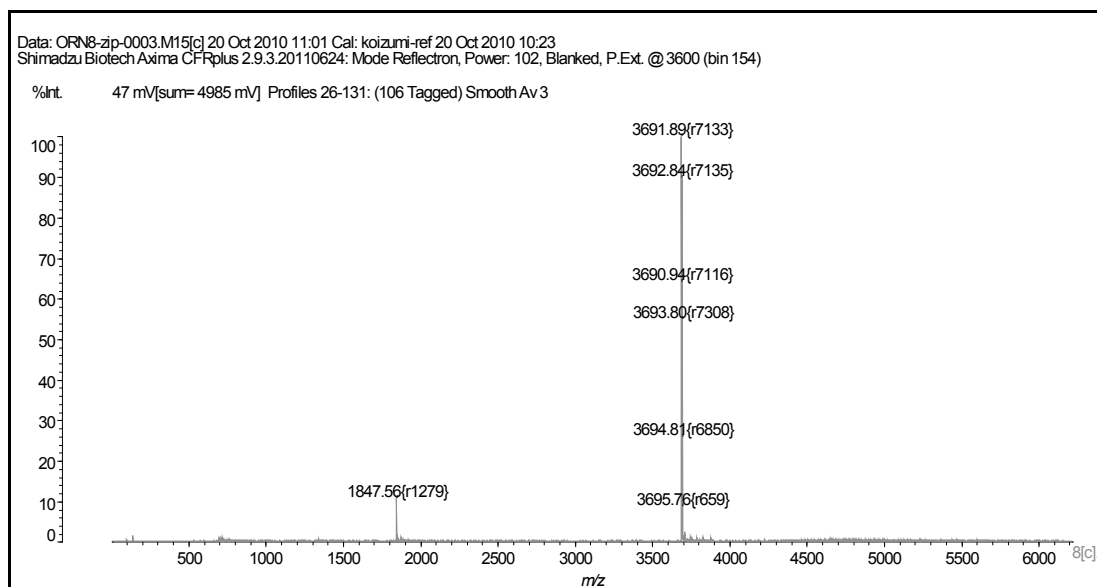


$X = \text{U}_{\text{OCE}}, N = \text{C}$ $\text{C}_{114}\text{H}_{152}\text{N}_{33}\text{O}_{80}\text{P}_{10}^{+}$ calcd: 3572.6



$X = \text{p}^5\text{U}_{\text{OCE}}, N = \text{A}$ $\text{C}_{119}\text{H}_{154}\text{N}_{37}\text{O}_{78}\text{P}_{10}^{+}$ calcd: 3658.7





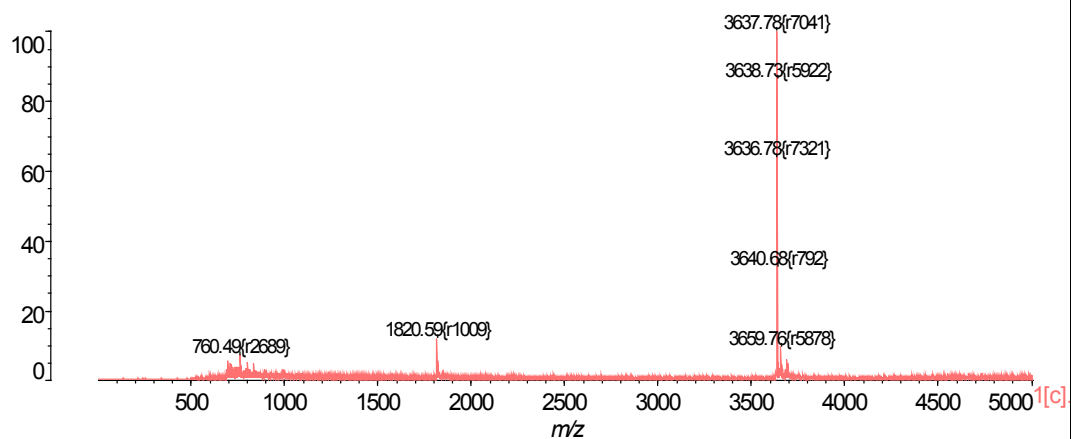
$X = s^2U_{OCE}$, $N = A$ $C_{116}H_{152}N_{37}O_{77}P_{10}S^+$ calcd: 3636.6

1-AsUA

Data: 1-AsUA-0002.B15[c] 19 Nov 2010 11:24 Cal: koizumi-ref 19 Nov 2010 10:41

Shimadzu Biotech Axima CFRplus 2.8.4.20081127: Mode Reflectron, Power: 108, Blanked, P.Ext. @ 3700 (bin 157)

%Int. 20 mV[sum= 2480 mV] Profiles 92-214 Smooth Av 3



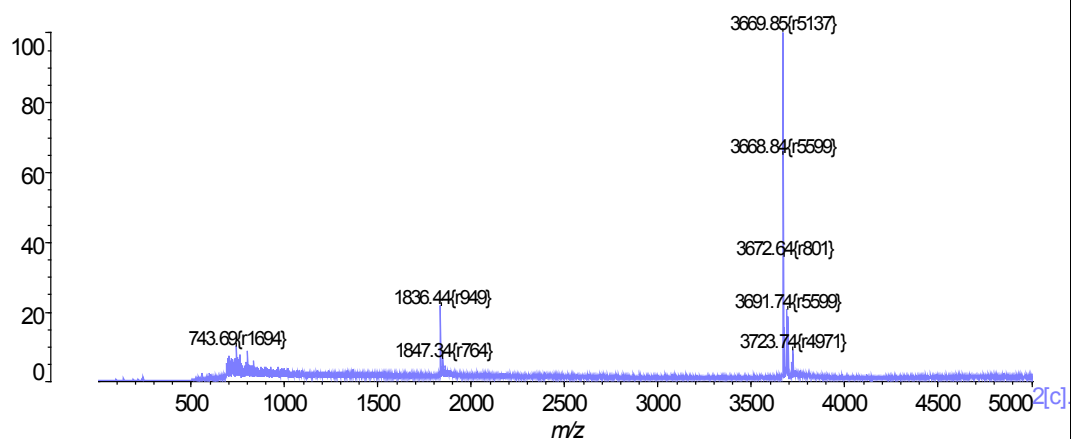
$X = s^2U_{OCE}$, $N = G$ $C_{116}H_{152}N_{37}O_{79}P_{10}S^+$ calcd: 3668.6

2-GsUG

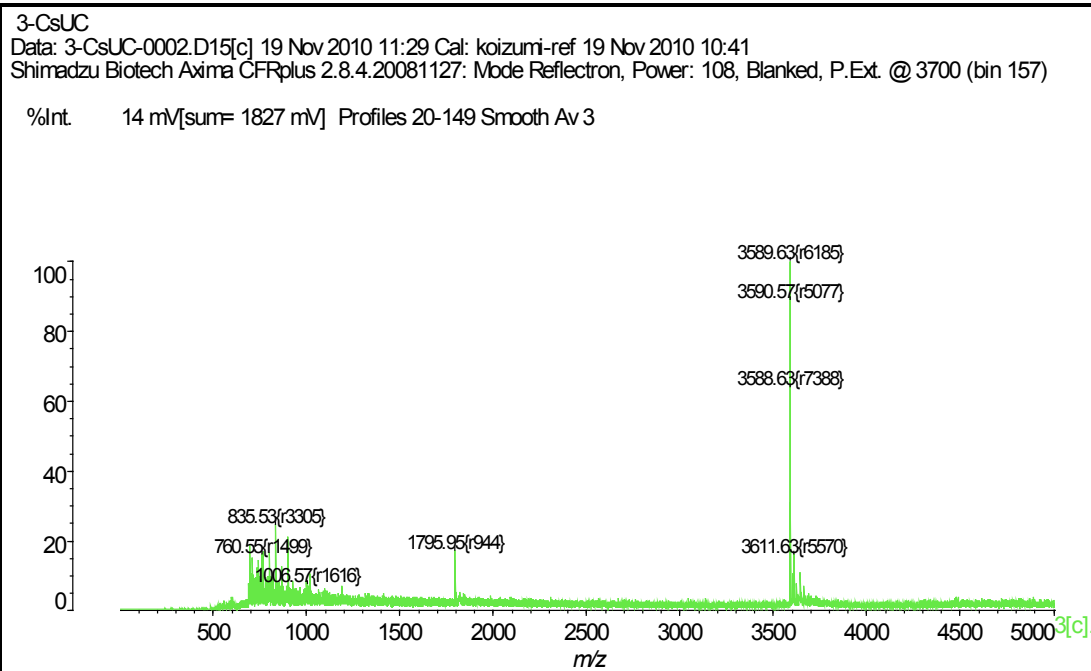
Data: 2-GsUG-0004.C15[c] 19 Nov 2010 11:21 Cal: koizumi-ref 19 Nov 2010 10:41

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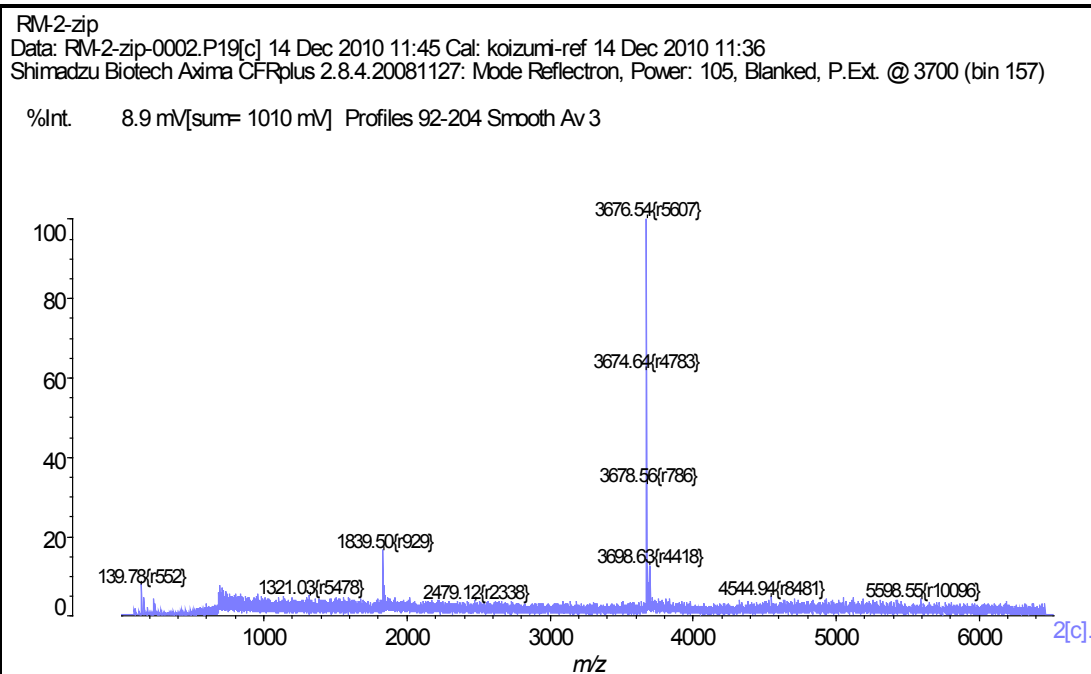
%Int. 42 mV[sum= 4196 mV] Profiles 1-100 Smooth Av 3



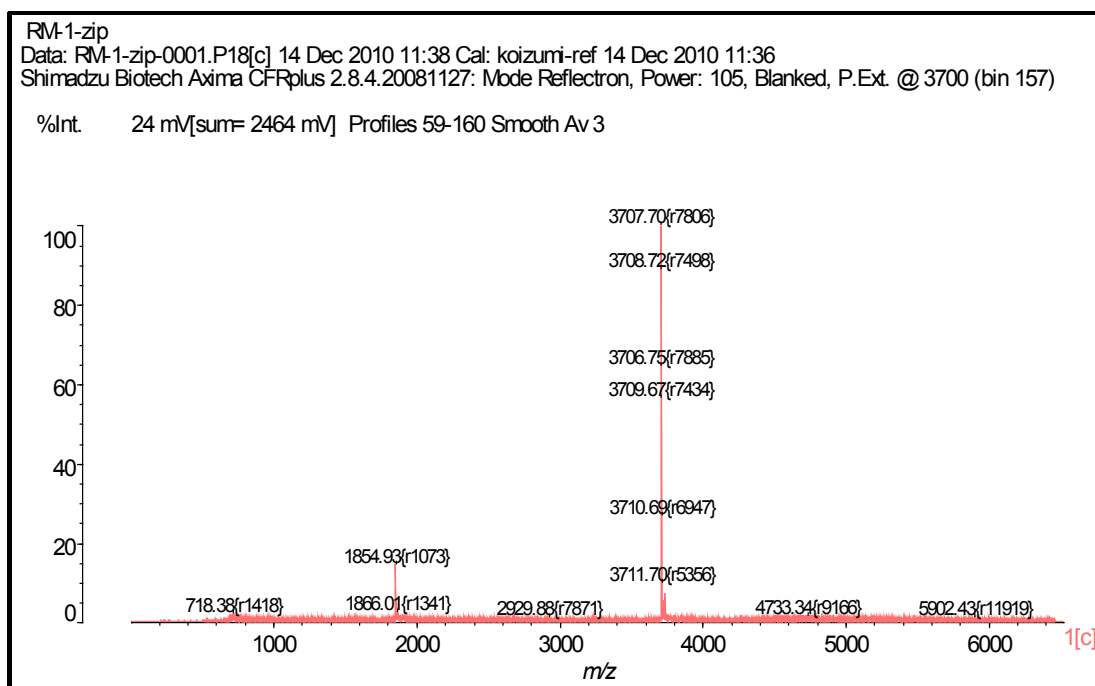
$X = s^2U_{OCE}, N = C$ $C_{114}H_{152}N_{33}O_{79}P_{10}S^+$ calcd: 3588.6



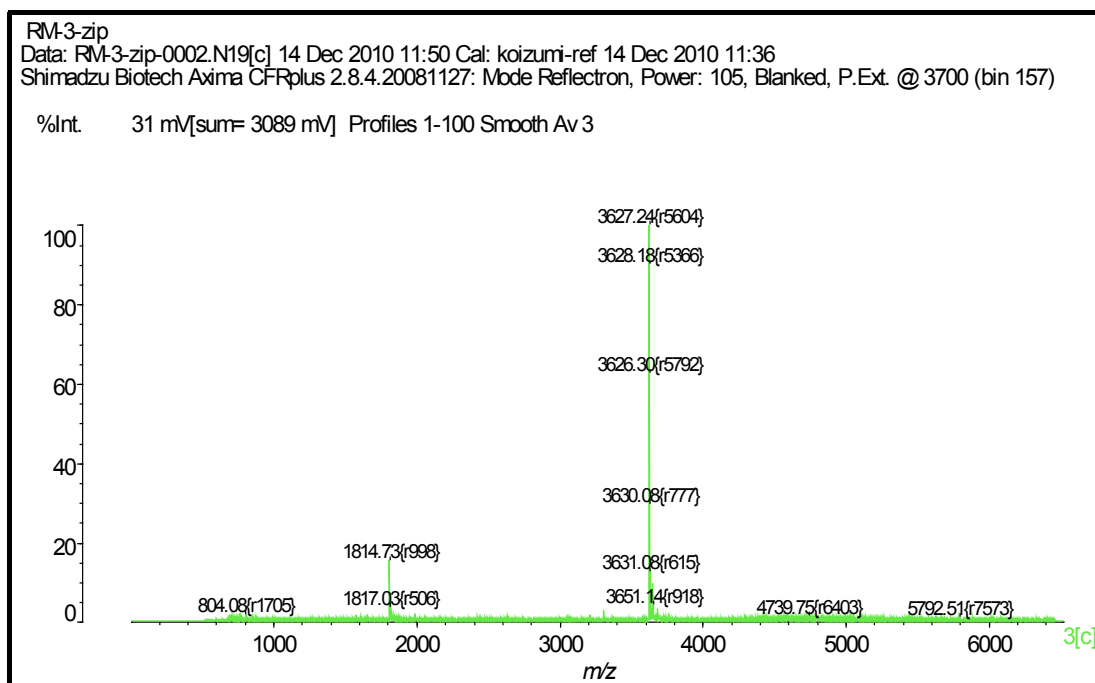
$X = p^5s^2U_{OCE}, N = A$ $C_{119}H_{154}N_{37}O_{77}P_{10}S^+$ calcd: 3674.6



$X = p^5 s^2 U_{OCE}, N = G$ $C_{119}H_{154}N_{33}O_{79}P_{10}S^+$ calcd: 3706.6



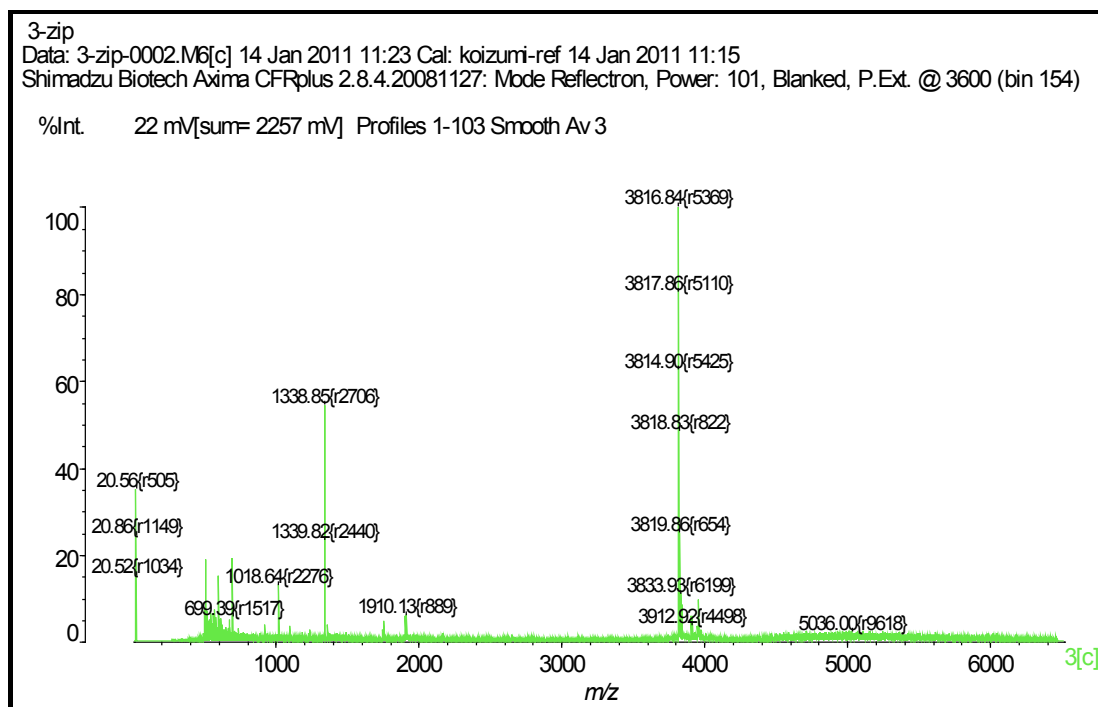
$X = p^5 s^2 U_{OCE}, N = C$ $C_{117}H_{154}N_{33}O_{79}P_{10}S^+$ calcd: 3626.6



**MALDI-TOF-Mass for consecutively or discretely modified oligonucleotides, (CGUXXXXUUGC),
or (CGXUUXUUXGC)**

5'-CGUU p⁵s²U_{OCE} p⁵s²U_{OCE} p⁵s²U_{OCE} UUGC

C₁₂₇H₁₅₈N₃₃O₇₉P₁₀S₃⁺ calcd: 3814.6



5'-CG p⁵s²U_{OCE} UU p⁵s²U_{OCE} UU p⁵s²U_{OCE} GC

C₁₂₇H₁₅₈N₃₃O₇₉P₁₀S₃⁺ calcd: 3814.6

