Electronic Supplementary Material (ESI) for RSC Advances.

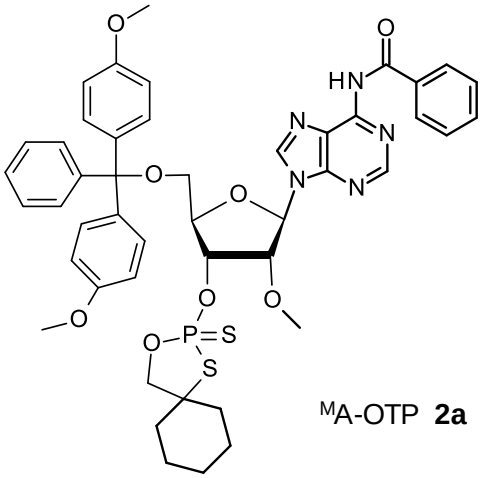
Supporting Information

Synthesis and Hybridizing Properties of P-Stereodefined Chimeric [PS]-{DNA:RNA} and [PS]-{DNA:(2'-OMe)-RNA} Oligomers.

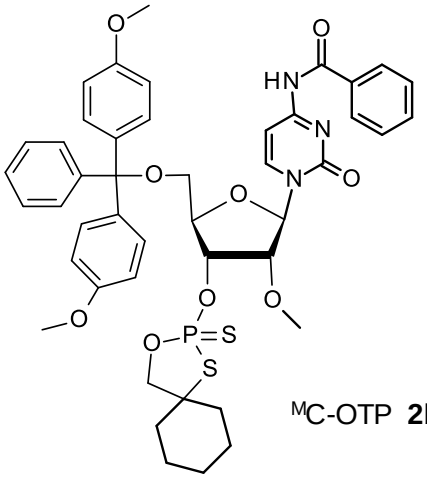
Katarzyna Jastrzębska*, Anna Maciaszek, Rafał Dolot, Agnieszka Tomaszewska-Antczak, Barbara Mikołajczyk and Piotr Guga

Table of contents

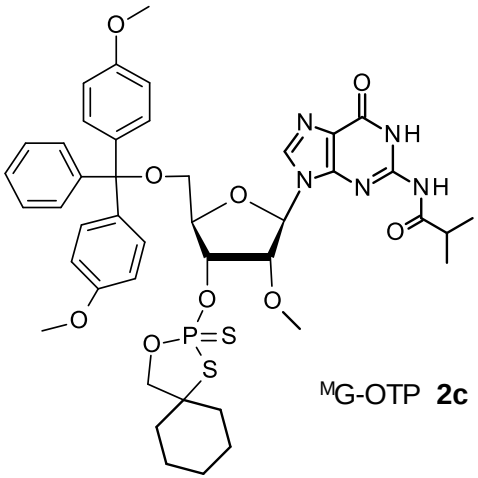
Structures of ^{M}N-OTP monomers



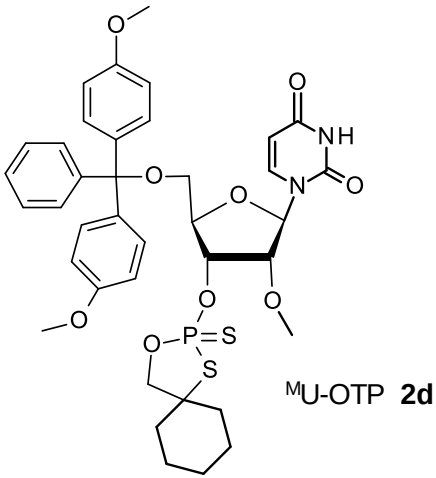
^{M}A-OTP **2a**



^{M}C-OTP **2b**

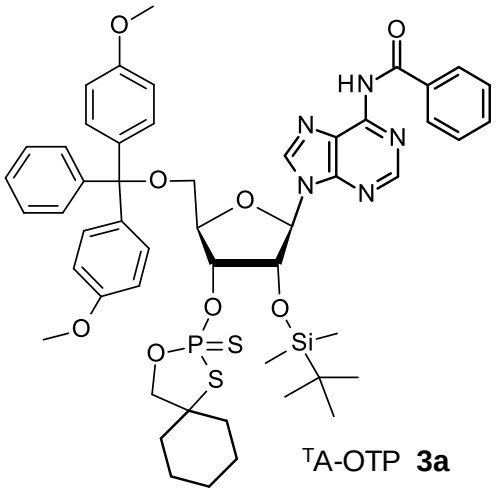


^{M}G-OTP **2c**

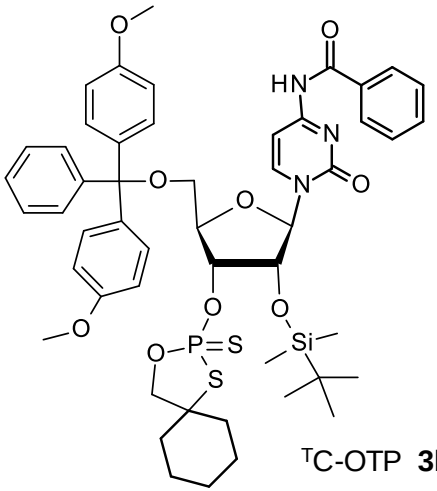


^{M}U-OTP **2d**

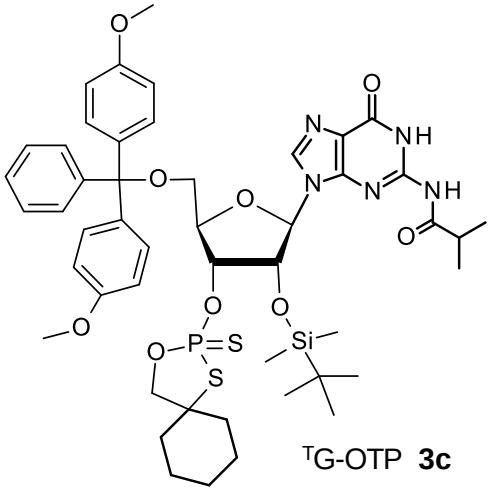
Structures of ^{T}N-OTP monomers



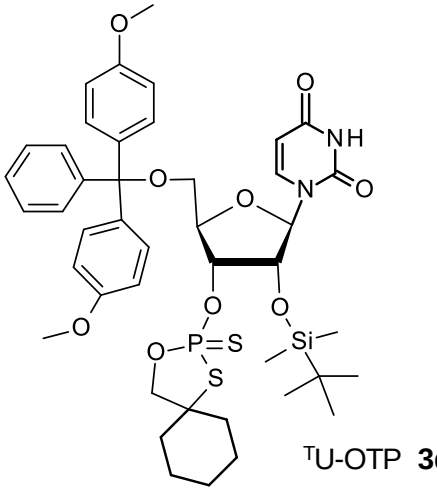
^{T}A-OTP **3a**



^{T}C-OTP **3b**



^{T}G-OTP **3c**



^{T}U-OTP **3d**

Separation of the P-diastereomers of ^{M}N-OTP and ^{T}N-OTP monomers.

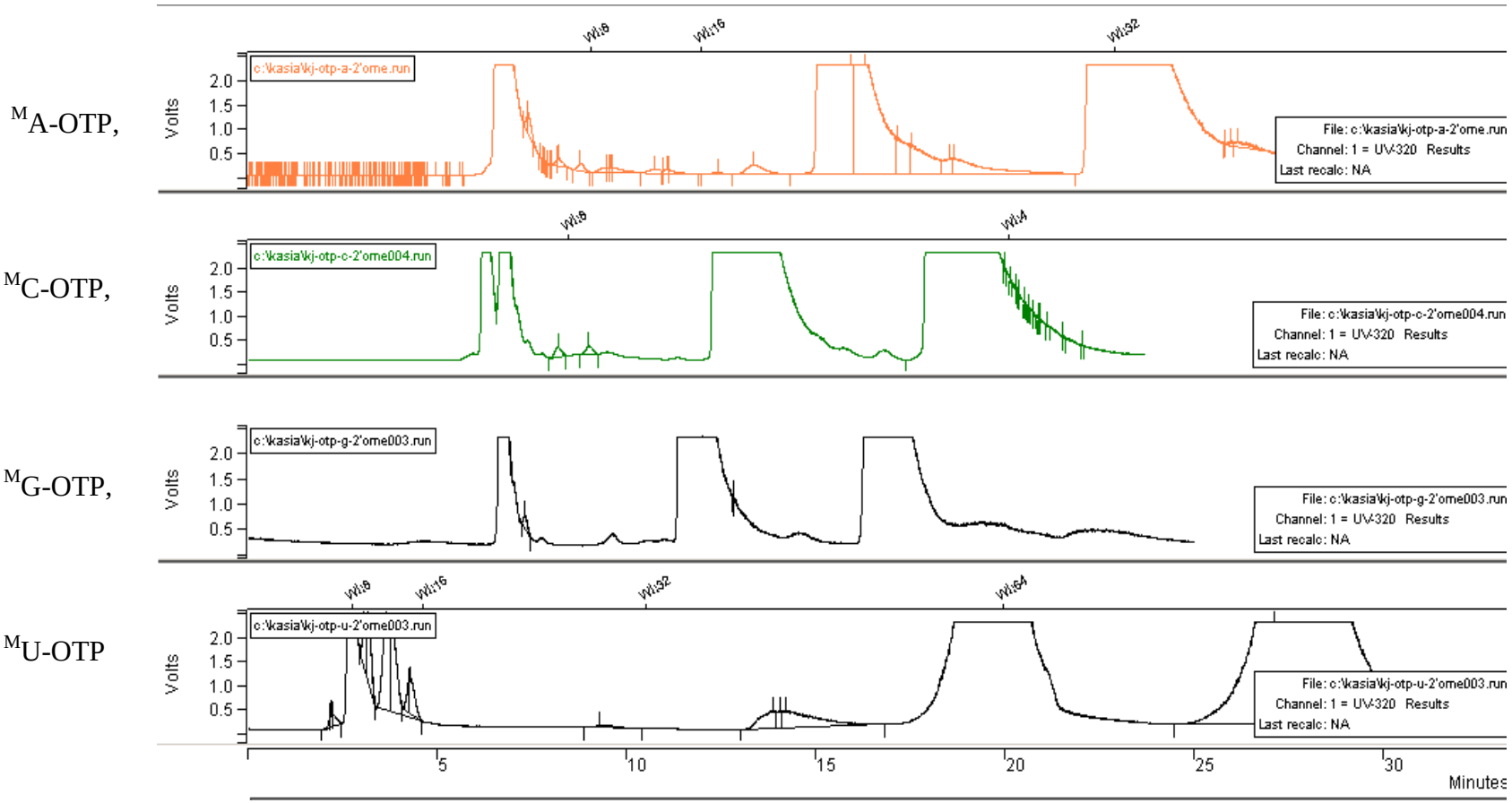


Figure S1a. HPLC profiles recorded for semi-preparative separation of the P-diastereomers of ^{M}A-OTP, ^{M}C-OTP, ^{M}G-OTP, and ^{M}U-OTP. The conditions were determined using a Phenomenex Luna 5 µm Silica column (100Å; 250×10 mm; flow rate 5 mL/min). The UV detector was set at 275 nm. For each run, the column was loaded with 100-150 mg ^{M}N-OTP.

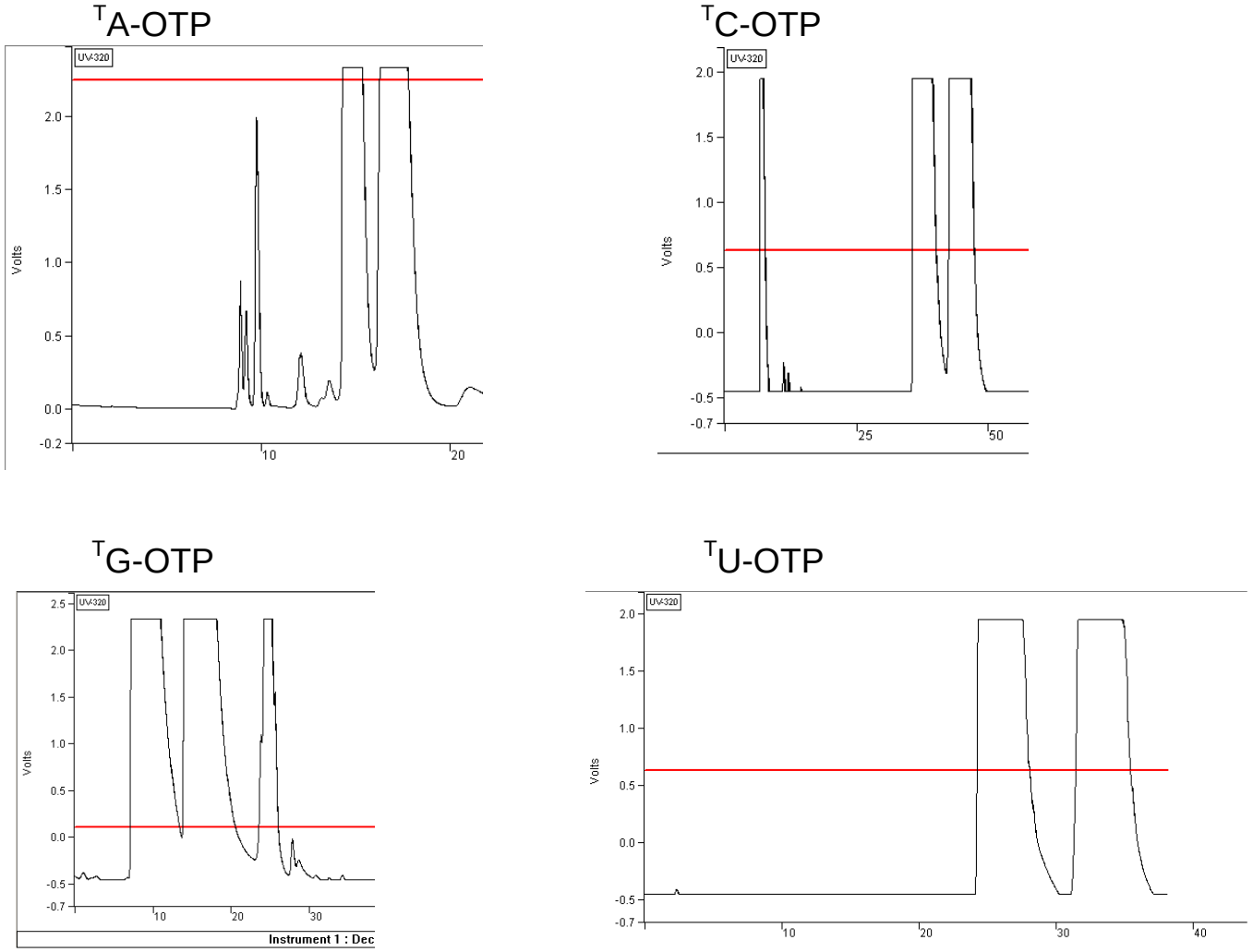


Figure S1b. HPLC profiles recorded for semi-preparative separation of the P-diastereomers of ^{T}A-OTP, ^{T}C-OTP, ^{T}G-OTP, and ^{T}U-OTP. The conditions were determined using a Phenomenex Luna 5 µm Silica column (100Å; 250×10 mm; flow rate 5 mL/min). The UV detector was set at 275 nm. For each run, the column was loaded with 100-150 mg ^{T}N-OTP.

HR MS spectra for separated P-diastereomers of ^{M}N-OTP and ^{T}N-OTP.

Figures S2a-h. HR MS spectra for separated P-diastereomers of ^{M}N-OTP (2a-d) recorded with a SYNAPT G2-Si High Definition Mass Spectrometer (qTOF, Electro Spray Ionization; Waters)

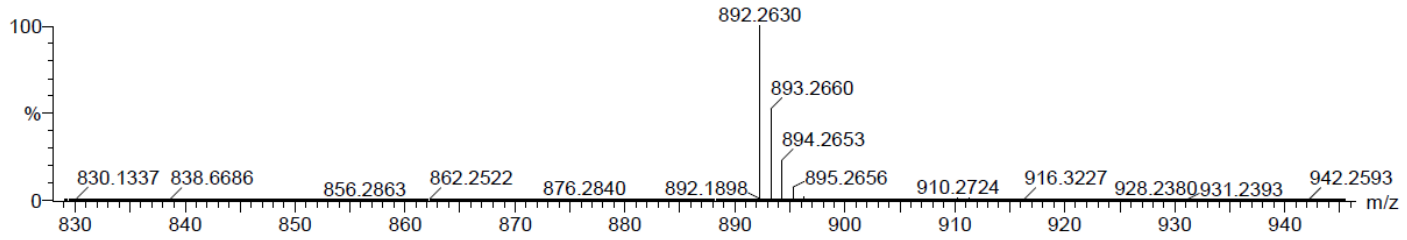
Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 70.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 6

Monoisotopic Mass, Even Electron Ions
59 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-50 H: 0-50 N: 0-5 O: 0-9 P: 1-1 S: 2-2

Jastrzebska
191211_KJ_AfA 35 (0.846) Cm (6:41)

TOF MS ES-
2.75e+007



Minimum:				-1.5				
Maximum:		5.0	5.0	70.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
892.2630	892.2604	2.6	2.9	26.5	2057.8	n/a	n/a	C46 H47 N5 O8 P S2

2a: *fast*-eluting ^{M}A-OTP

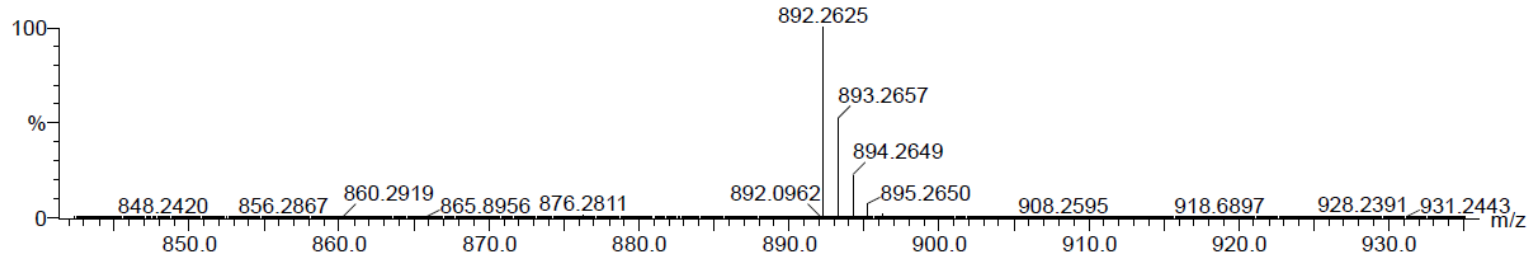
Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 70.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 6

Monoisotopic Mass, Even Electron Ions
59 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-50 H: 0-50 N: 0-5 O: 0-9 P: 1-1 S: 2-2

Jastrzebska
191211_KJ_As_A 17 (0.423) Cm (3:39)

TOF MS ES-
2.05e+007



Minimum:				-1.5				
Maximum:		5.0	5.0	70.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
892.2625	892.2604	2.1	2.4	26.5	1613.8	n/a	n/a	C46 H47 N5 O8 P S2

2b: *slow*-eluting ^{M}A-OTP

Elemental Composition Report

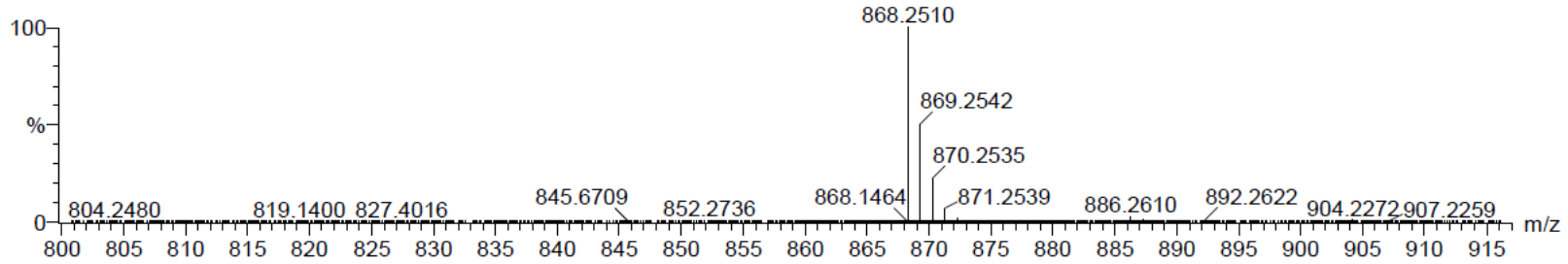
Single Mass Analysis

Tolerance = 5.0 PPM / DBE: min = -1.5, max = 70.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 6

Monoisotopic Mass, Even Electron Ions
83 formula(e) evaluated with 2 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-50 H: 0-50 N: 0-5 O: 0-9 P: 1-1 S: 2-2

Jastrzebska
191211_KJ_Cf_A 3 (0.087) Cm (3:41)

TOF MS ES-
1.74e+007



Minimum:				-1.5				
Maximum:		5.0	5.0	70.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
868.2510	868.2491	1.9	2.2	24.5	1432.4	0.049	95.22	C45 H47 N3 O9 P S2
	868.2532	-2.2	-2.5	28.5	1435.4	3.041	4.78	C50 H47 N O7 P S2

2c: *fast*-eluting ^{M}C-OTP

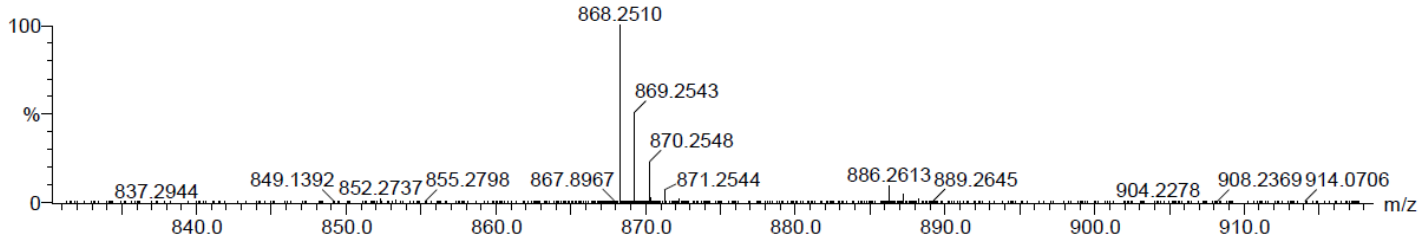
Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 70.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 6

Monoisotopic Mass, Even Electron Ions
83 formula(e) evaluated with 2 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-50 H: 0-50 N: 0-5 O: 0-9 P: 1-1 S: 2-2

Jastrzebska
191211_KJ_Cs_A 36 (0.863) Cm (36:41)

TOF MS ES-
2.29e+006



Minimum:				-1.5				
Maximum:		5.0	5.0	70.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
868.2510	868.2491	1.9	2.2	24.5	1056.7	0.121	88.60	C45 H47 N3 O9 P S2
	868.2532	-2.2	-2.5	28.5	1058.8	2.171	11.40	C50 H47 N O7 P S2

2d: *slow*-eluting ^{M}C-OTP

Elemental Composition Report **Page 1**

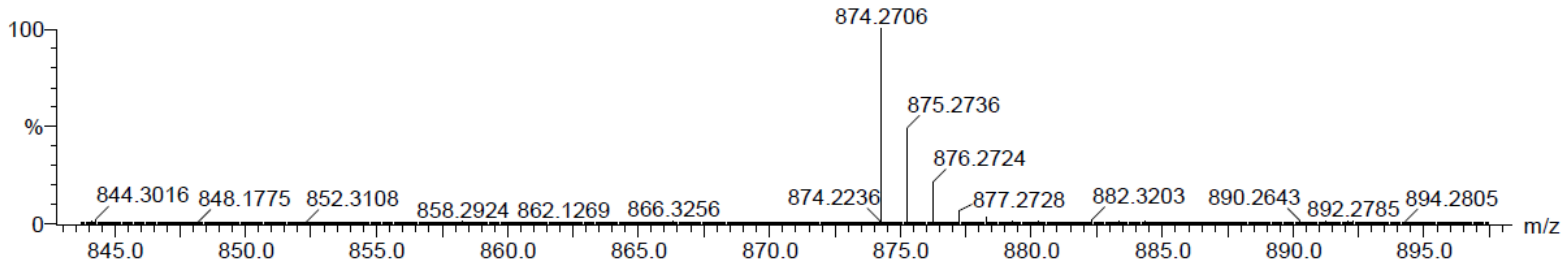
Single Mass Analysis

Tolerance = 5.0 PPM / DBE: min = -1.5, max = 70.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 9

Monoisotopic Mass, Even Electron Ions
147 formula(e) evaluated with 3 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-50 H: 0-55 N: 0-5 O: 0-9 P: 1-1 S: 1-2

Jastrzebska_K
200123_KJ_Gf_ 6 (0.158) Cm (3:41)

1: TOF MS ES-
8.55e+007



Minimum:				-1.5				
Maximum:		5.0	5.0	70.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
874.2706	874.2709	-0.3	-0.3	22.5	4377.3	0.089	91.47	C43 H49 N5 O9 P S2
	874.2676	3.0	3.4	27.5	4382.8	5.610	0.37	C46 H45 N5 O9 P S
	874.2750	-4.4	-5.0	26.5	4379.7	2.506	8.16	C48 H49 N3 O7 P S2

2e: *fast*-eluting ^{M}G-OTP

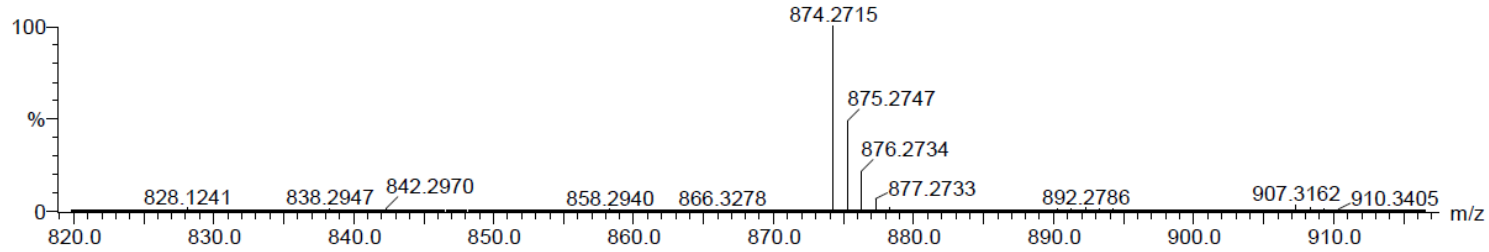
Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 70.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 9

Monoisotopic Mass, Even Electron Ions
147 formula(e) evaluated with 3 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-50 H: 0-55 N: 0-5 O: 0-9 P: 1-1 S: 1-2

Jastrzebska_K
200123_KJ_GS_ 40 (0.970) Cm (35:41)

1: TOF MS ES-
1.30e+007



Minimum:				-1.5				
Maximum:		5.0	5.0	70.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
874.2715	874.2709	0.6	0.7	22.5	3491.9	0.024	97.62	C43 H49 N5 O9 P S2
	874.2750	-3.5	-4.0	26.5	3497.4	5.559	0.39	C48 H49 N3 O7 P S2
	874.2676	3.9	4.5	27.5	3495.8	3.915	1.99	C46 H45 N5 O9 P S

2f: *slow*-eluting ^{M}G-OTP

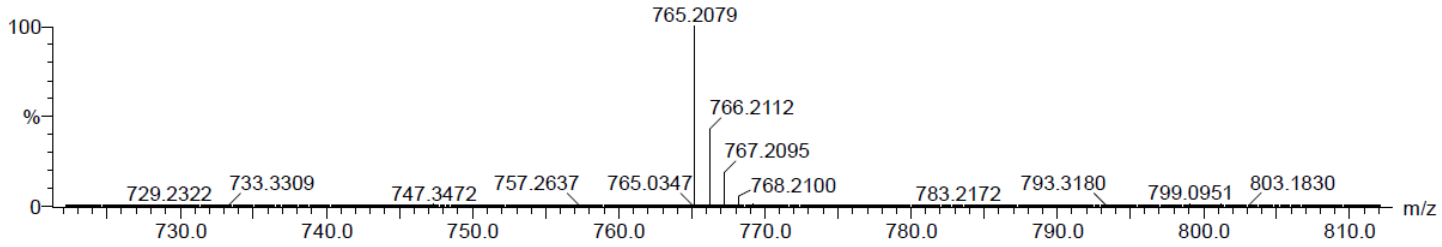
Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 70.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 6

Monoisotopic Mass, Even Electron Ions
230 formula(e) evaluated with 3 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-50 H: 0-50 N: 0-5 O: 0-9 P: 1-1 S: 2-2

Jastrzebska
191211_KJ_Uf_A 4 (0.124) Cm (4:41)

TOF MS ES-
5.36e+007



Minimum:				-1.5				
Maximum:		5.0	5.0	70.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
765.2079	765.2069	1.0	1.3	19.5	1948.5	0.000	99.96	C38 H42 N2 O9 P S2
	765.2051	2.8	3.7	32.5	1958.6	10.099	0.00	C50 H38 O2 P S2
	765.2110	-3.1	-4.1	23.5	1956.4	7.876	0.04	C43 H42 O7 P S2

2g: *fast*-eluting ^{M}U-OTP

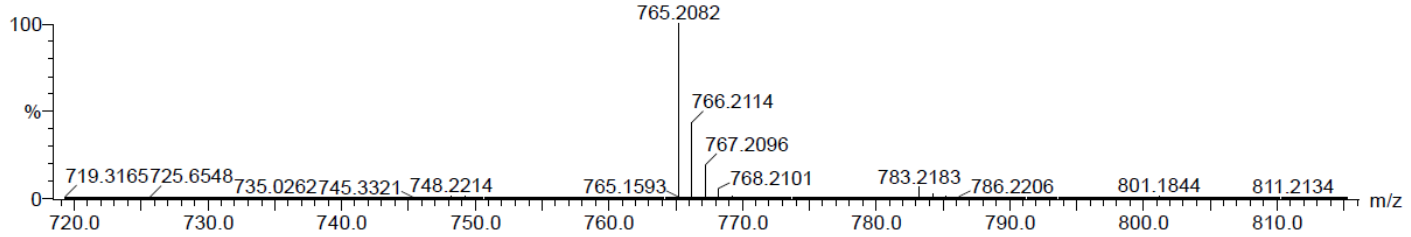
Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 70.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 6

Monoisotopic Mass, Even Electron Ions
230 formula(e) evaluated with 3 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-50 H: 0-50 N: 0-5 O: 0-9 P: 1-1 S: 2-2

Jastrzebska
191211_KJ_Us_A 17 (0.423) Cm (3:41)

TOF MS ES-
1.05e+008



Minimum:				-1.5				
Maximum:		5.0	5.0	70.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
765.2082	765.2069	1.3	1.7	19.5	2610.0	0.000	99.98	C38 H42 N2 O9 P S2
	765.2110	-2.8	-3.7	23.5	2618.4	8.404	0.02	C43 H42 O7 P S2
	765.2051	3.1	4.1	32.5	2621.8	11.735	0.00	C50 H38 O2 P S2

2h: *slow*-eluting ^{M}U-OTP

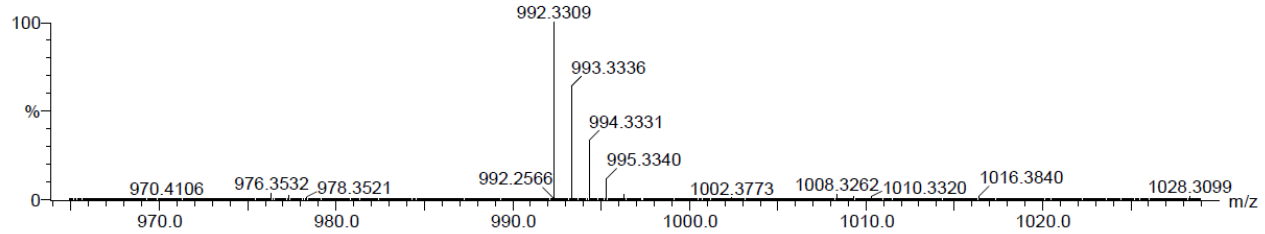
Figure S3a-h. HR MS spectra for separated P-diastereomers of ^{T}N-OTP (3a-d) recorded with a SYNAPT G2-Si High Definition Mass Spectrometer (qTOF, Electro Spray Ionization; Waters)

Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 70.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 9

Monoisotopic Mass, Even Electron Ions
516 formula(e) evaluated with 4 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-60 H: 0-80 N: 0-5 O: 0-11 Si: 1-1 P: 1-1 S: 1-2

200526_KJ_Af_newA 4 (0.124) Cm (4:41) TOF MS ES-
3.55e+006



Minimum:				-1.5				
Maximum:		5.0	5.0	70.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
992.3309	992.3312	-0.3	-0.3	26.5	2504.9	4.702	0.91	C51 H59 N5 O8 Si P S2
	992.3318	-0.9	-0.9	35.5	2501.4	1.251	28.63	C59 H55 N3 O6 Si P S
	992.3278	3.1	3.1	31.5	2500.5	0.356	70.03	C54 H55 N5 O8 Si P S
	992.3352	-4.3	-4.3	30.5	2505.6	5.440	0.43	C56 H59 N3 O6 Si P S2

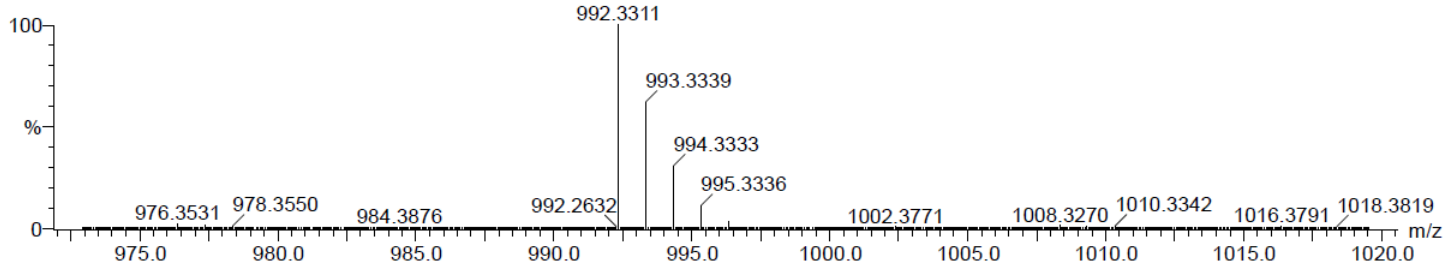
3a: *fast*-eluting ^{T}A-OTP

Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 70.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 9

Monoisotopic Mass, Even Electron Ions
516 formula(e) evaluated with 4 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-60 H: 0-80 N: 0-5 O: 0-11 Si: 1-1 P: 1-1 S: 1-2

200526_KJ_As_new_A 4 (0.124) Cm (3:40) TOF MS ES-
1.89e+007



Minimum:				-1.5				
Maximum:		5.0	5.0	70.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
992.3311	992.3312	-0.1	-0.1	26.5	2974.0	5.985	0.25	C51 H59 N5 O8 Si P S2
	992.3318	-0.7	-0.7	35.5	2970.3	2.276	10.27	C59 H55 N3 O6 Si P S
	992.3278	3.3	3.3	31.5	2968.1	0.112	89.43	C54 H55 N5 O8 Si P S
	992.3352	-4.1	-4.1	30.5	2975.5	7.472	0.06	C56 H59 N3 O6 Si P S2

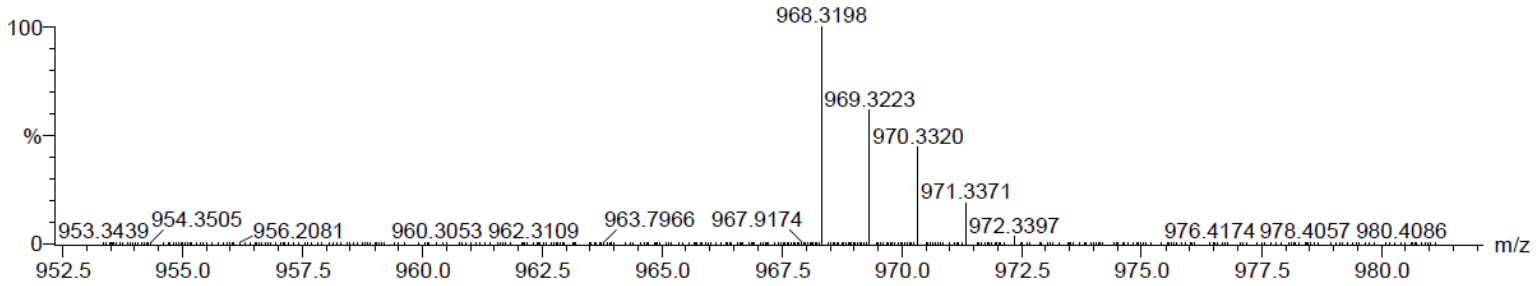
3b: *slow*-eluting ^{T}A-OTP

Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 70.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 9

Monoisotopic Mass, Even Electron Ions
670 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-50 H: 0-65 N: 0-5 O: 0-9 S: 0-2 P: 0-1 Si: 0-1

200429_KJ_CfA 22 (0.547) Cm (7:40) TOF MS ES-
4.22e+006



Minimum:				-1.5				
Maximum:		5.0	5.0	70.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
968.3198	968.3200	-0.2	-0.2	24.5	1275.5	n/a	n/a	C50 H59 N3 O9 S2 P Si

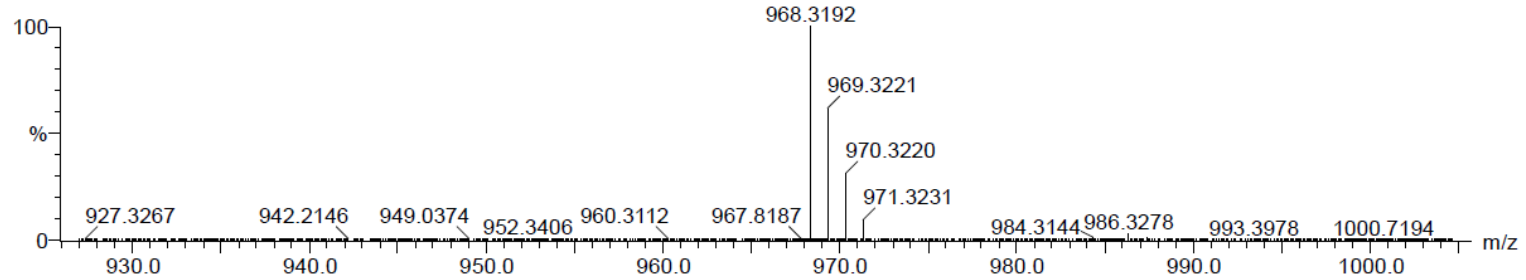
3c: *fast*-eluting ^{T}C-OTP

Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 70.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 9

Monoisotopic Mass, Even Electron Ions
670 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-50 H: 0-65 N: 0-5 O: 0-9 Si: 0-1 P: 0-1 S: 0-2

200429_KJ_CsA 40 (0.970) Cm (6:41) TOF MS ES-
2.87e+006



Minimum:				-1.5				
Maximum:		5.0	5.0	70.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
968.3192	968.3200	-0.8	-0.8	24.5	1157.4	n/a	n/a	C50 H59 N3 O9 Si P S2

3d: *slow*-eluting ^{T}C-OTP

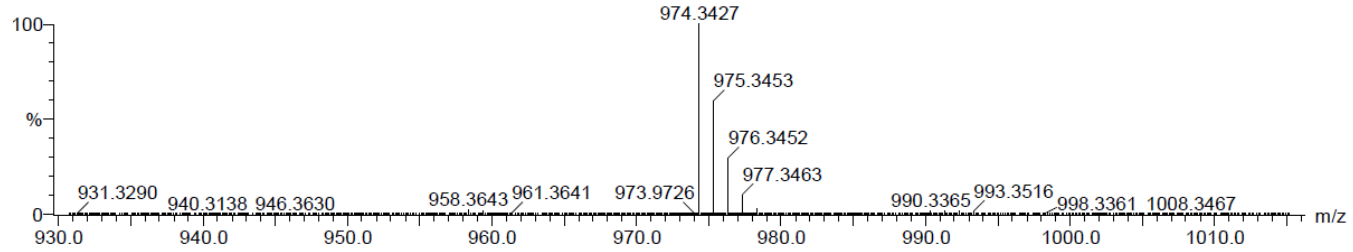
Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 70.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 9

Monoisotopic Mass, Even Electron Ions
666 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-50 H: 0-65 N: 0-5 O: 0-9 Si: 0-1 P: 0-1 S: 0-2

200429_KJ_GfB 20 (0.493) Cm (3:39)

TOF MS ES-
5.51e+007



Minimum:				-1.5				
Maximum:		5.0	5.0	70.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
974.3427	974.3418	0.9	0.9	22.5	1995.9	n/a	n/a	C48 H61 N5 O9 Si P S2

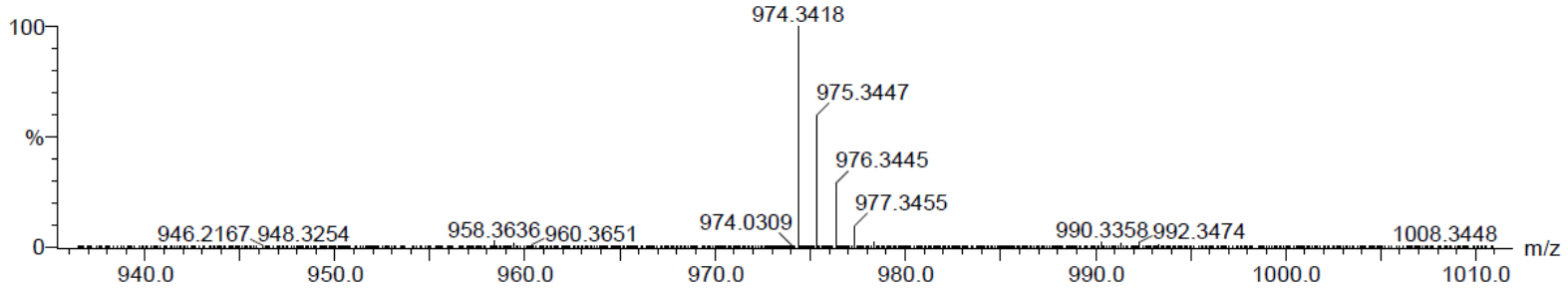
3e: *fast*-eluting ^{T}G-OTP

Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 70.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 9

Monoisotopic Mass, Even Electron Ions
666 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-50 H: 0-65 N: 0-5 O: 0-9 S: 0-2 P: 0-1 Si: 0-1

200429_KJ_GsA 21 (0.510) Cm (7:39) TOF MS ES-
5.29e+007



Minimum:				-1.5				
Maximum:		5.0	5.0	70.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
974.3418	974.3418	0.0	0.0	22.5	1865.0	n/a	n/a	C48 H61 N5 O9 S2 P Si

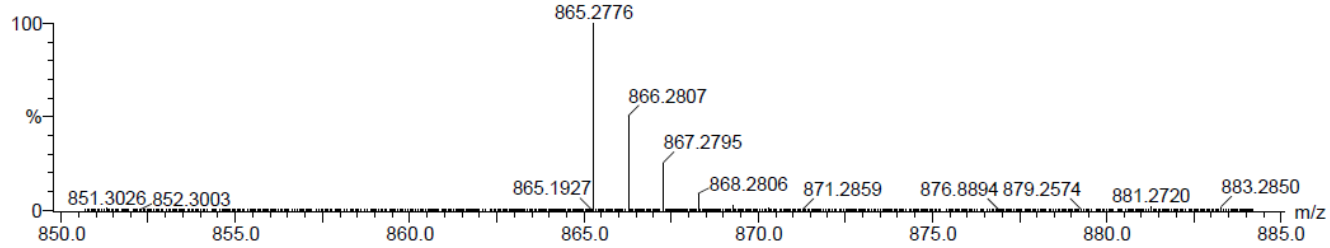
3f: *slow*-eluting ^{T}G-OTP

Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 70.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 9

Monoisotopic Mass, Even Electron Ions
1249 formula(e) evaluated with 5 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-50 H: 0-556 N: 0-3 O: 0-9 S: 0-2 P: 0-1 Si: 0-1

200429_KJ_UfA 20 (0.493) Cm (5:40) TOF MS ES-
2.04e+007



Minimum:				-1.5				
Maximum:		5.0	5.0	70.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
865.2776	865.2778	-0.2	-0.2	19.5	2679.7	5.793	0.30	C43 H54 N2 O9 S2 P Si
	865.2801	-2.5	-2.9	28.5	2685.8	11.868	0.00	C50 H49 N2 O6 S2 Si
	865.2746	3.0	3.5	24.5	2674.0	0.058	94.37	C47 H50 N2 O8 S2 P
	865.2744	3.2	3.7	24.5	2676.9	2.933	5.32	C46 H50 N2 O9 S P Si
	865.2818	-4.2	-4.9	23.5	2683.8	9.892	0.01	C48 H54 O7 S2 P Si

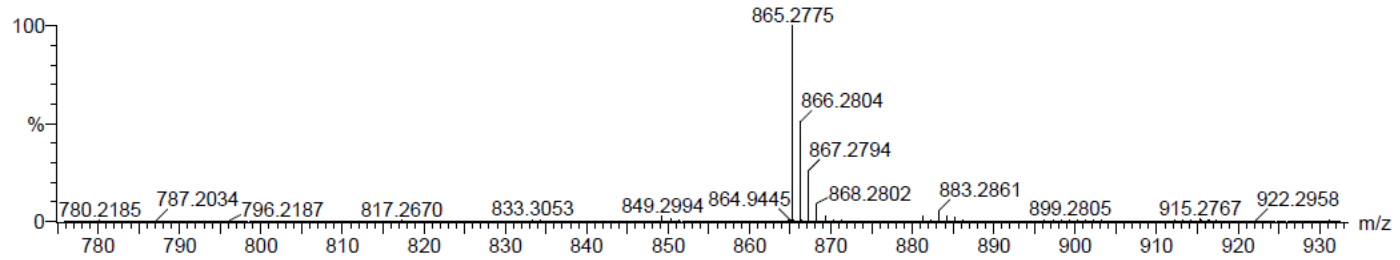
3g: *fast*-eluting ^{T}U-OTP

Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 70.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 9

Monoisotopic Mass, Even Electron Ions
1042 formula(e) evaluated with 6 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-50 H: 0-65 N: 0-5 O: 0-9 Si: 0-1 P: 0-1 S: 0-2

200429_KJ_UsA 38 (0.916) Cm (6:39) TOF MS ES-
2.38e+007

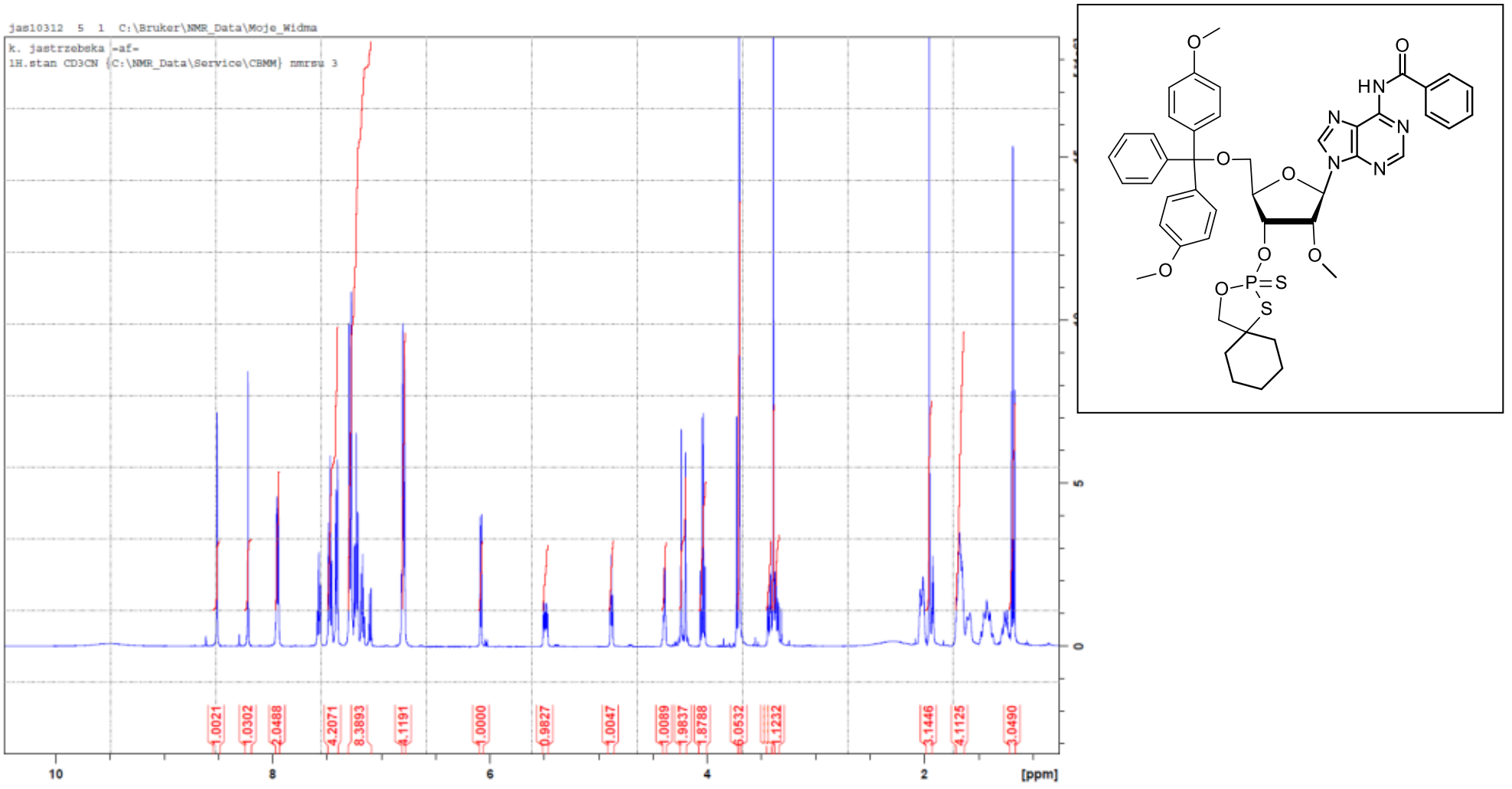


Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
Minimum:				-1.5				
Maximum:		5.0	5.0	70.0				
865.2775	865.2778	-0.3	-0.3	19.5	2672.4	2.614	7.32	C43 H54 N2 O9 Si P S2
	865.2761	1.4	1.6	24.5	2675.9	6.134	0.22	C45 H49 N4 O8 Si S2
	865.2801	-2.6	-3.0	28.5	2679.9	10.121	0.00	C50 H49 N2 O6 Si S2
	865.2746	2.9	3.4	24.5	2669.9	0.110	89.56	C47 H50 N2 O8 P S2
	865.2744	3.1	3.6	24.5	2673.4	3.555	2.86	C46 H50 N2 O9 Si P S
	865.2818	-4.3	-5.0	23.5	2677.7	7.859	0.04	C48 H54 O7 Si P S2

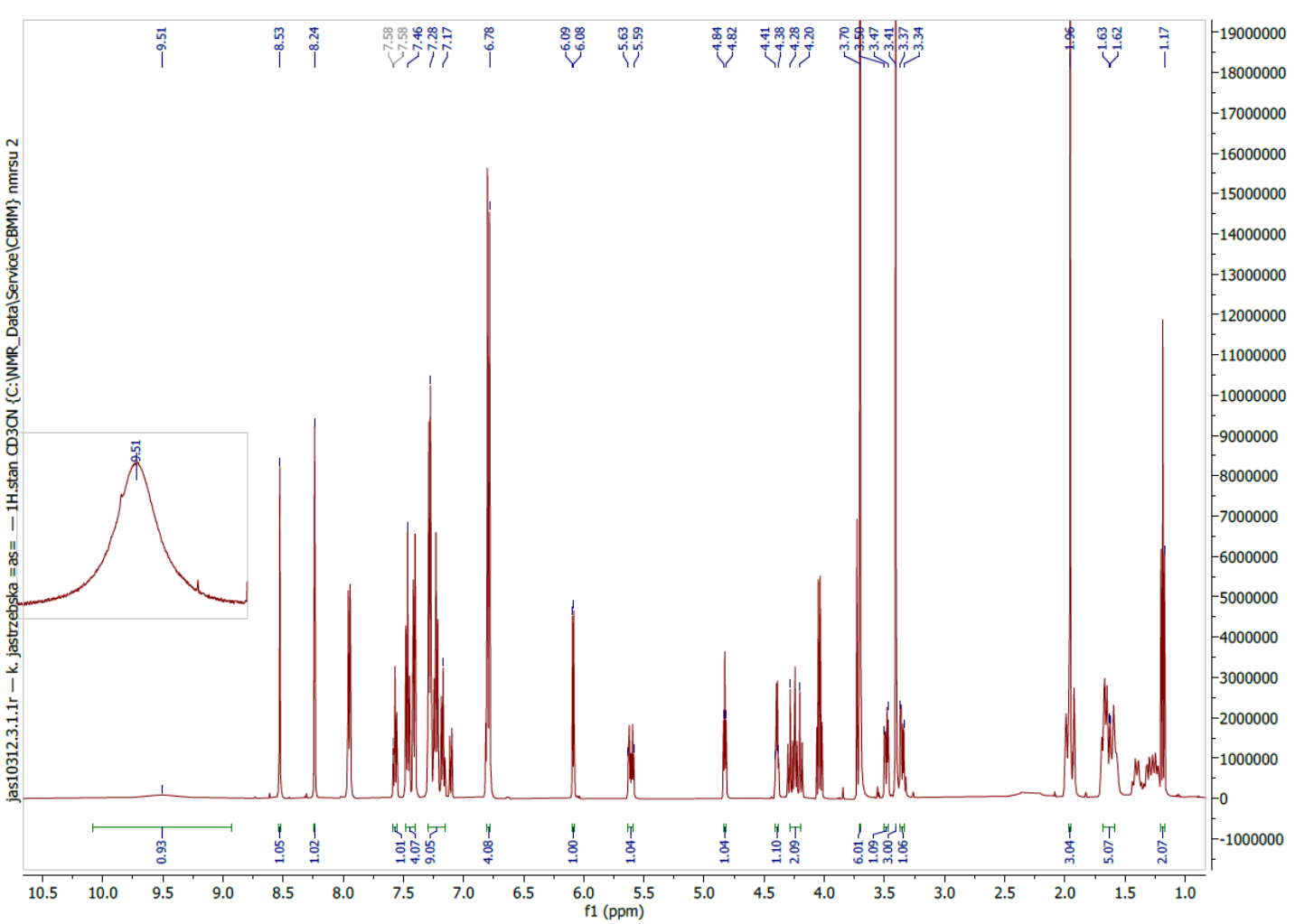
3h: *slow*-eluting ^{T}U-OTP

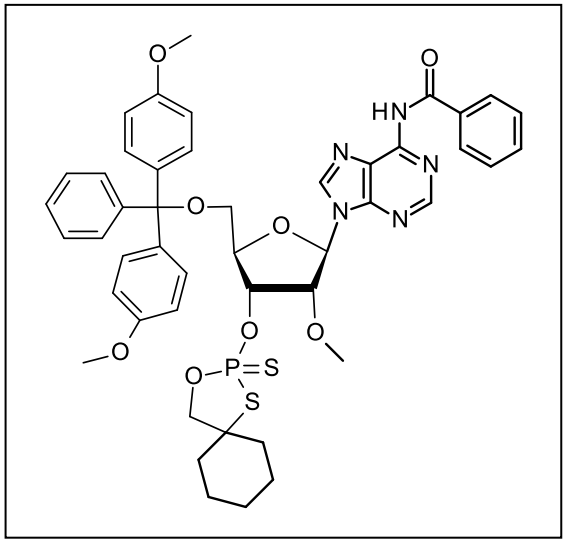
^{1}H NMR spectra for separated P-diastereomers of ^{M}N-OTP and ^{T}N-OTP monomers.

Figure S4. ^{1}H NMR spectra for separated P-diastereomers of ^{M}N-OTP and ^{T}N-OTP monomers, recorded with a Bruker AV-500 spectrometer (500 MHz)

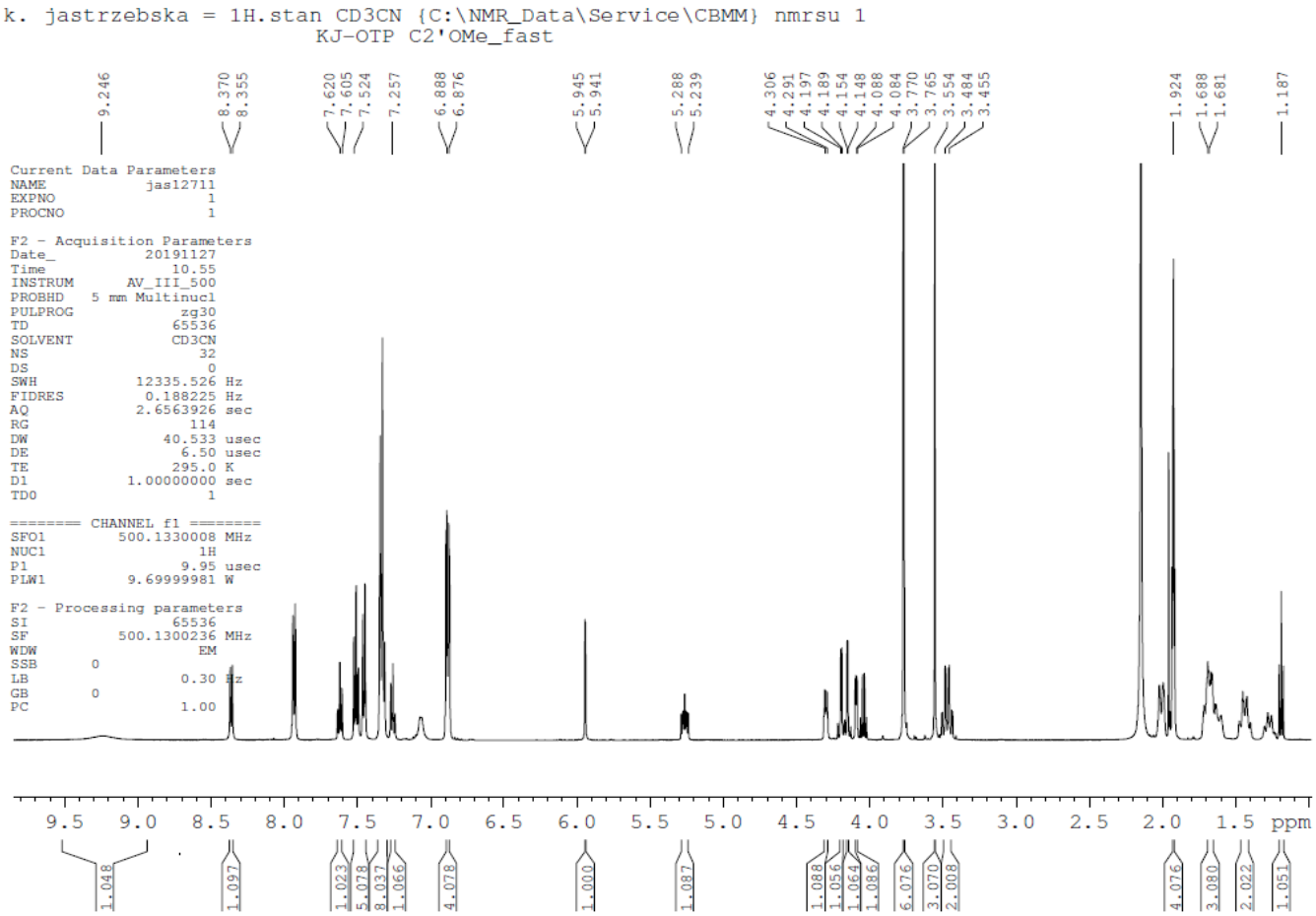


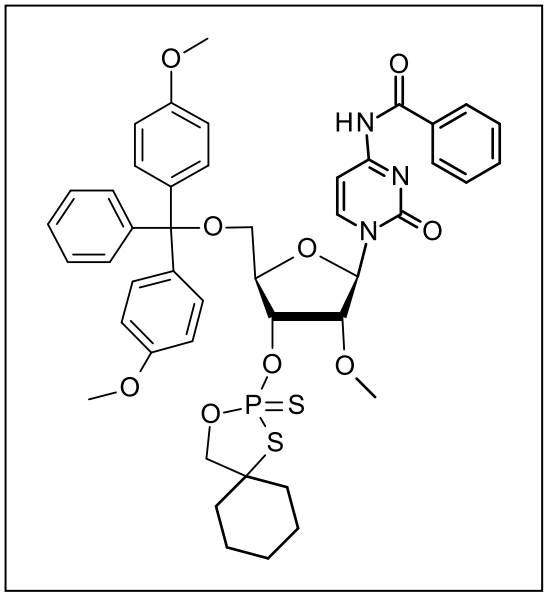
Fast-eluting ^{M}A-OTP in CD_3CN; δ (ppm)
^{1}H NMR: 9.50 (1H, NHCO), 8.51 (1H, C8-H), 8.23 (1H, C2-H), 7.58-6.79 (18H, DMT, Bz), 6.09-6.08 (1H, C1'-H), 5.51-5.47 (1H, C3'-H), 4.89-4.87 (1H, C2'-H), 4.40-4.39 (1H, C4'-H), 4.24-4.20 (2H, P-O-CH_2C-S), 3.71 (6H, 2xOCH_3), 3.39 (3H, 2'OCH_3), 3.45-3.34 (2H, 5'CH_2), 1.96-1.17 (10H, -$(CH_2)_5$-*„spiro"*)



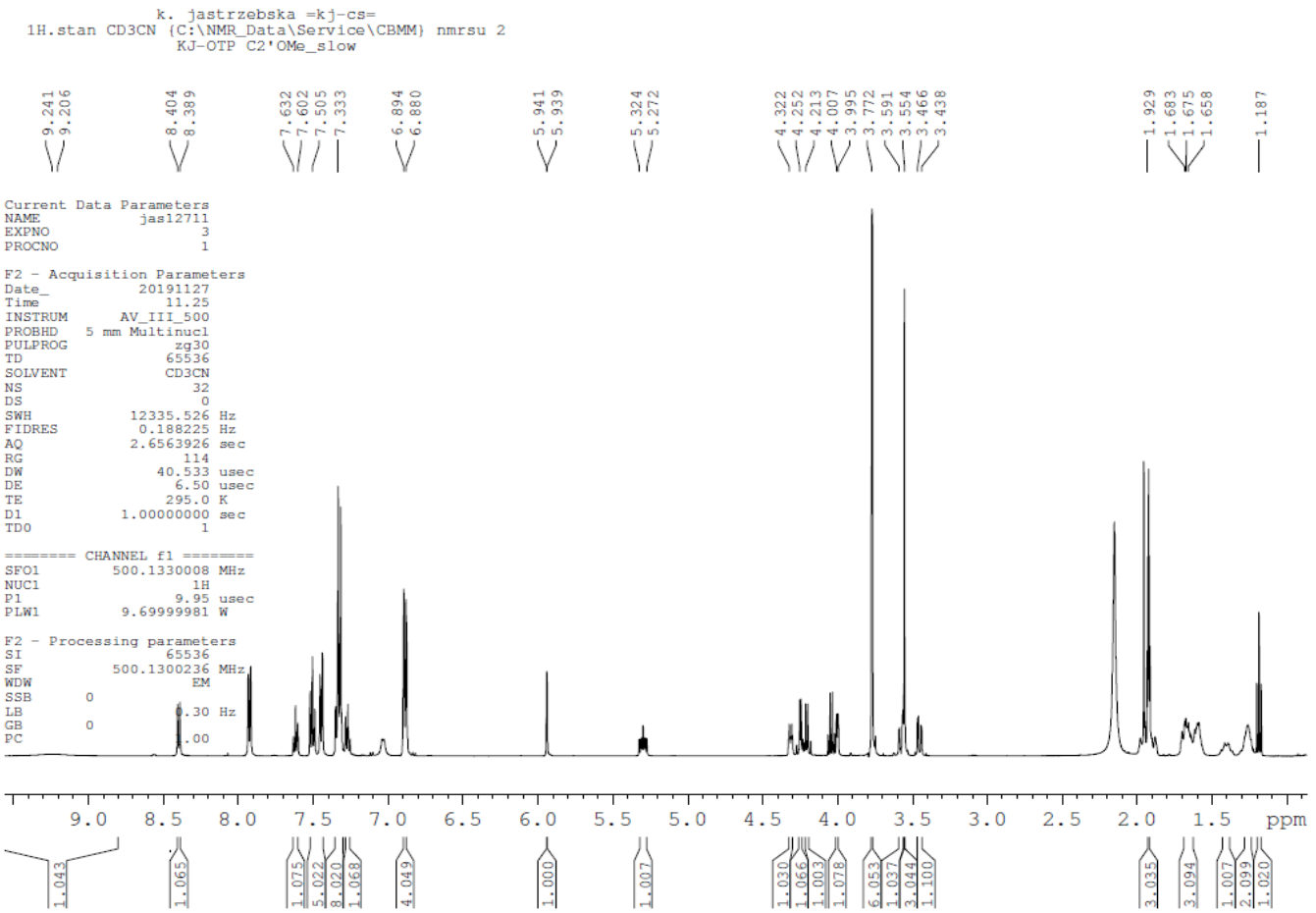


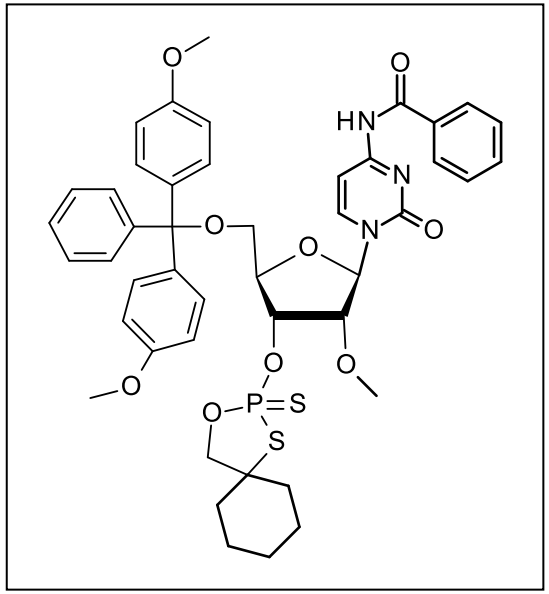
Slow-eluting ^{M}A-OTP in CD_3CN; δ (ppm)
^{1}H NMR: 9.51 (1H, NHCO), 8.53 (1H, C8-H), 8.24 (1H, C2-H), 7.59-6.78 (18H, DMT, Bz), 6.09-6.08 (1H, C1'-H), 5.63-5.59 (1H, C3'-H), 4.84-4.82 (1H, C2'-H), 4.41-4.38 (1H, C4'-H), 4.28-4.20 (2H, P-O-CH_2C-S), 3.70 (6H, 2xOCH3), 3.41 (3H, 2'OCH_3), 3.50-3.34 (2H, 5'CH_2), 1.96-1.17 (10H, -$(CH_2)_5$-*„spiro"*)



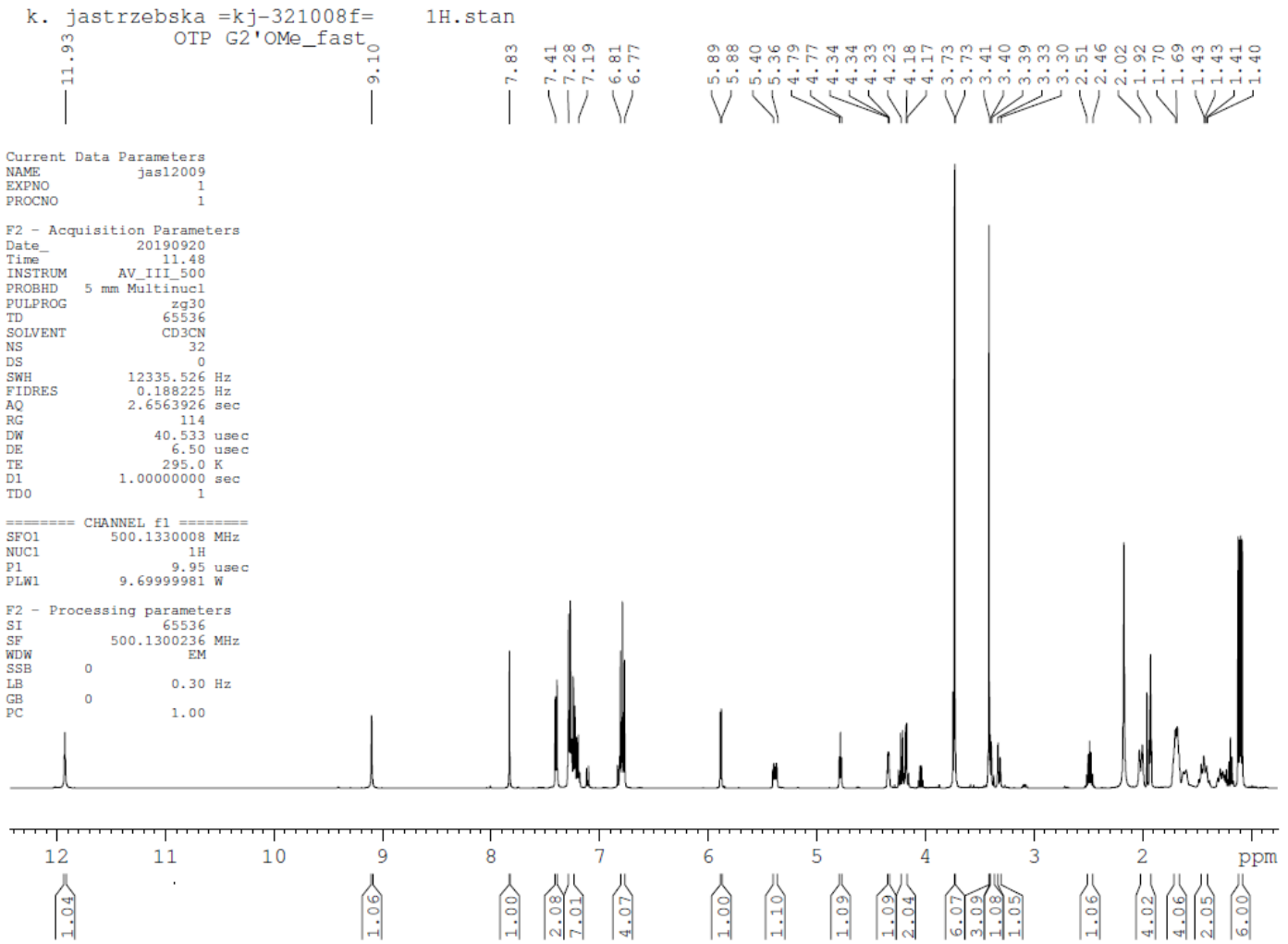


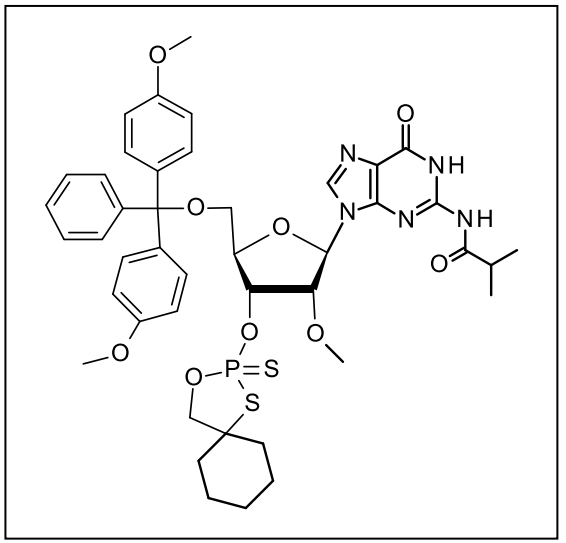
Fast-eluting ^{M}C-OTP in CD_3CN; δ (ppm)
^{1}H NMR: 9.25 (1H, NHCO), 8.37-8.35 (1H, C6-H), 7.62-7.60 (1H, C5-H), 7,52-6,88 (18H, DMT, Bz), 5,94 (1H, C1'-H), 5,29-5,24 (1H, C3'-H), 4,30-4.29 (1H, C2'-H), 4.20-4.19 (1H, C4'-H), 4,15-4.08 (2H, P-O-CH_2C-S), 3,77 (6H, 2xOCH_3), 3.55 (3H, 2'OCH_3), 3,48-3.46 (2H, 5'CH_2), 1,92-1,19 (10H, -$(CH2)_5$- *„spiro"*)



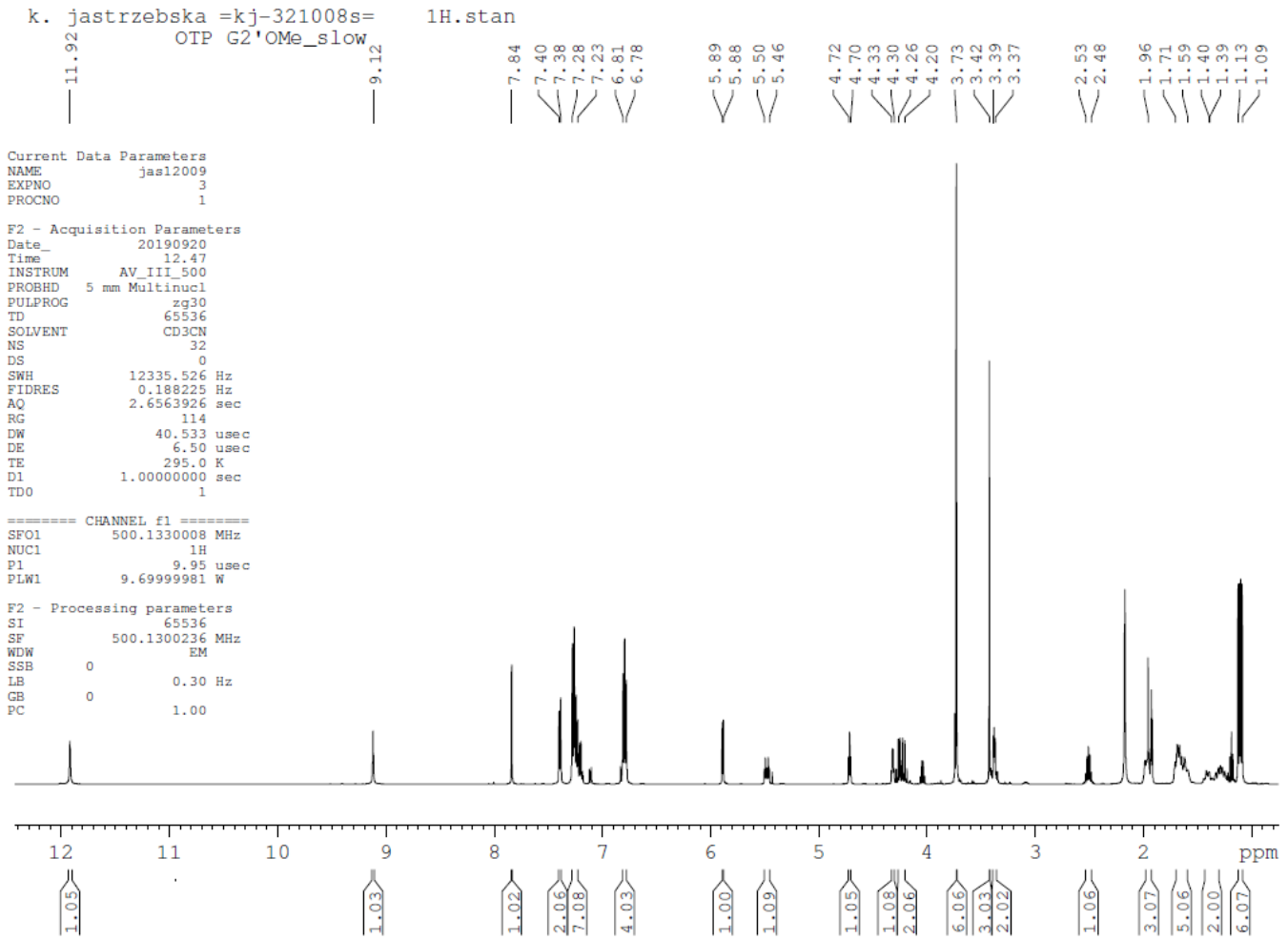


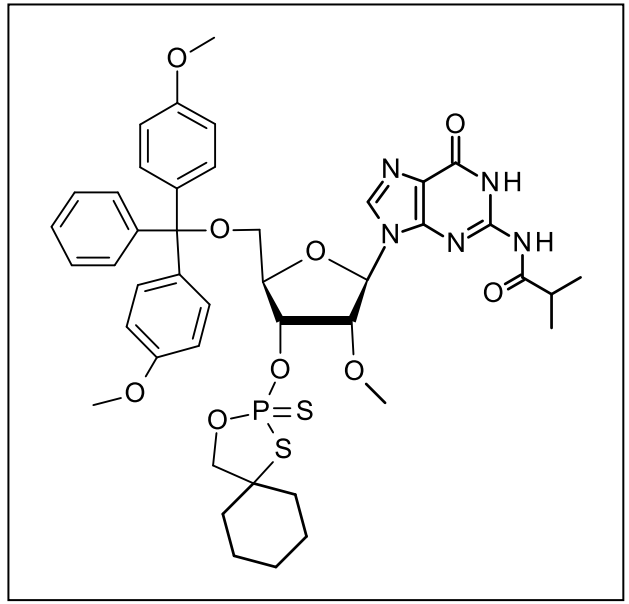
Slow-eluting ^{M}C-OTP in CD_3CN; δ (ppm)
^{1}H NMR: 9.24 (1H, NHCO), 8.40-8.39 (1H, C6-H), 7.63-7.60 (1H, C5-H), 7,50-6,88 (18H, DMT, Bz), 5,94 (1H, C1'-H), 5,32-5,27 (1H, C3'-H), 4,32-4.30 (1H, C2'-H), 4.26-4.25 (1H, C4'-H), 4,21-3.99 (2H, P-O-CH_2C-S), 3,77 (6H, 2xOCH_3), 3.55 (3H, 2'OCH_3), 3,59-3.44 (2H, 5'CH_2), 1,93-1,19 (10H, -$(CH_2)_5$- *„spiro"*)



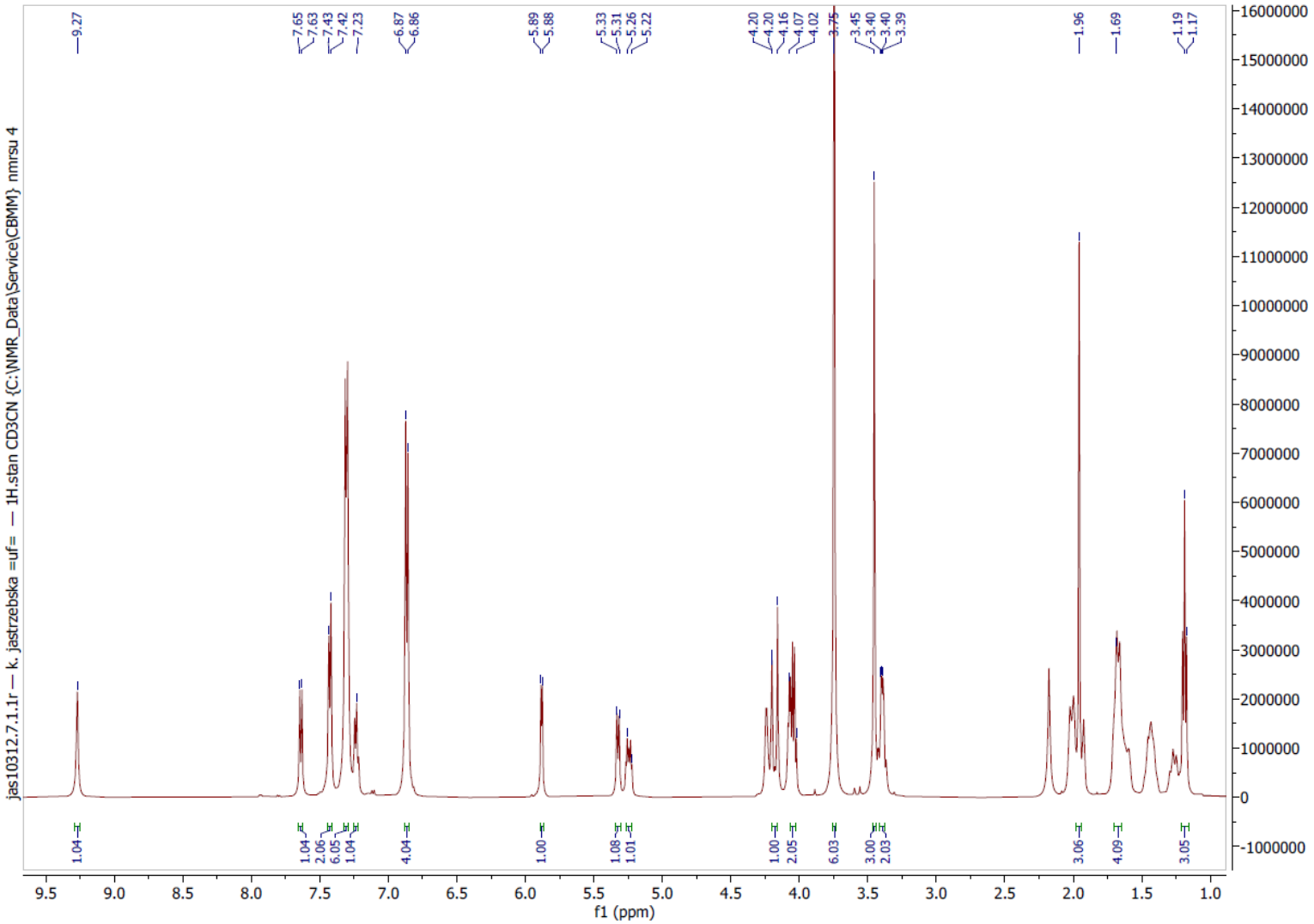


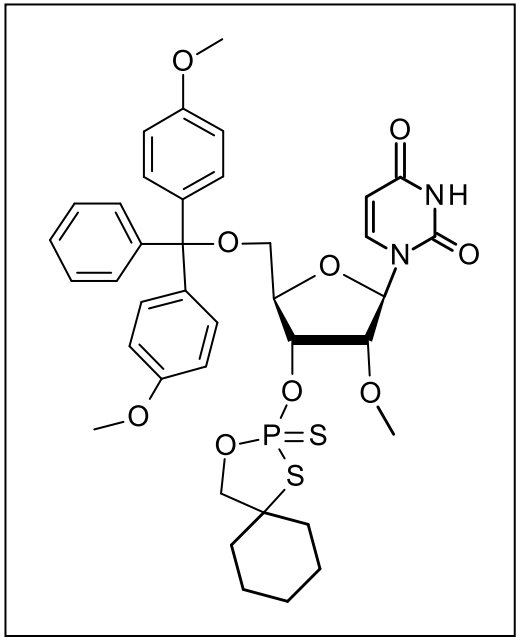
Fast-eluting ^{M}G-OTP in CD_3CN; δ (ppm)
^{1}H NMR: 11.93 (1H, N1-H), 9.10 (1H, N2-H), 7.83 (1H, C8-H), 7.40-6.77 (13H, DMT), 5.88-5.87 (1H, C1'-H), 5.40-5.36 (1H, C3'-H), 4.79-4.77 (1H, C2'-H), 4.34-4.33 (1H, C4'-H), 4.22-4.17 (2H, P-O-CH_2C-S), 3.73 (6H, 2xOCH_3), 3.41 (3H, 2'OCH_3), 3.40-3.30 (2H, C5'CH_2), 2.51-2.46 (1H, CH, iBu), 2.02-1.40 (10H, -$(CH_2)_5$- *„spiro"*), 1.12-1.08 (6H, 2xCH_3, iBu)



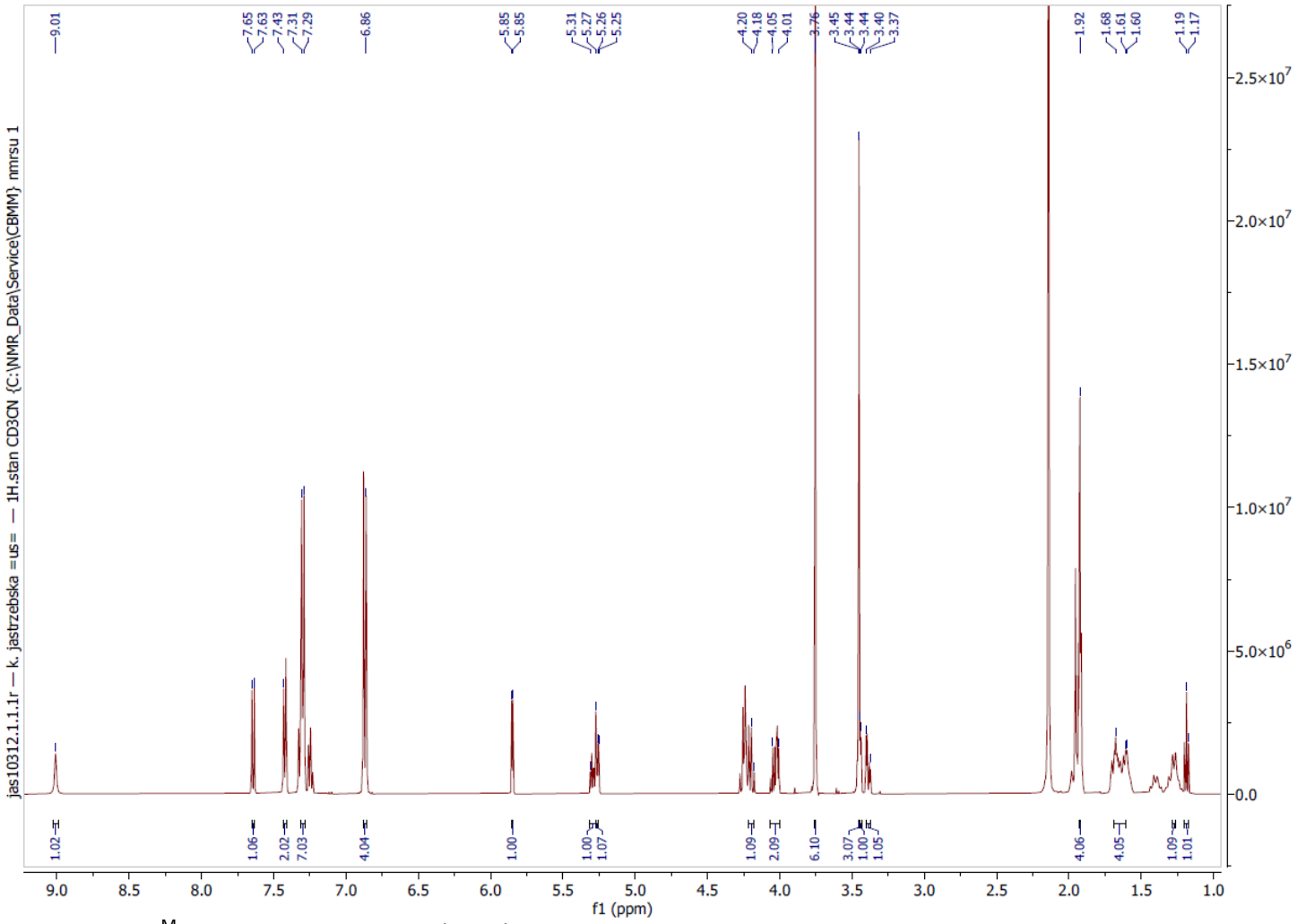


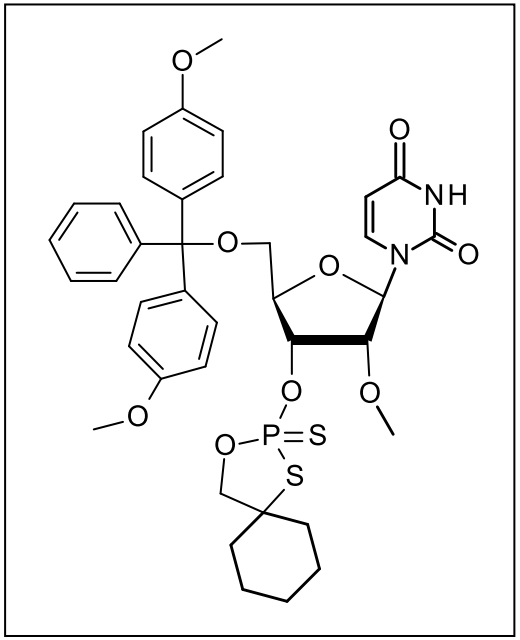
Slow-eluting ^{M}G-OTP in CD_3CN; δ (ppm)
^{1}H NMR: 11.92 (1H, N1-H), 9.12 (1H, N2-H), 7.84 (1H, C8-H), 7.40-6.78 (13H, DMT), 5.89-5.88 (1H, C1'-H), 5.50-5.46 (1H, C3'-H), 4.72-4.70 (1H, C2'-H), 4.32-4.30 (1H, C4'-H), 4.26-4.20 (2H, P-O-CH_2C-S), 3.73 (6H, 2xOCH_3), 3.42 (3H, 2'OCH_3), 3.39-3.37 (2H, C5'CH_2), 2.53-2.48 (1H, CH, iBu), 1.96-1.36 (10H, -$(CH_2)_5$- *„spiro"*), 1.12-1.09 (6H, 2xCH_3, iBu)



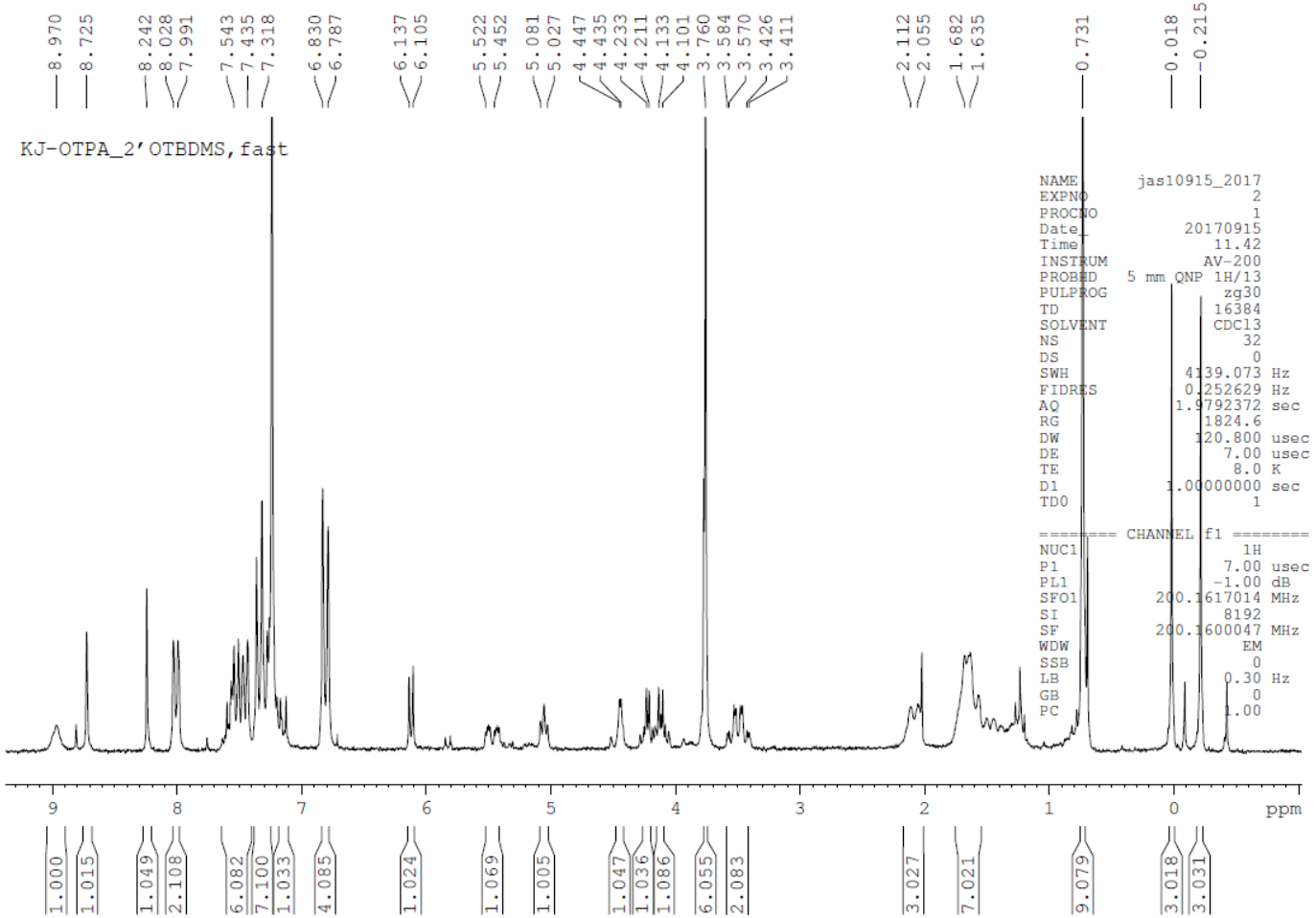


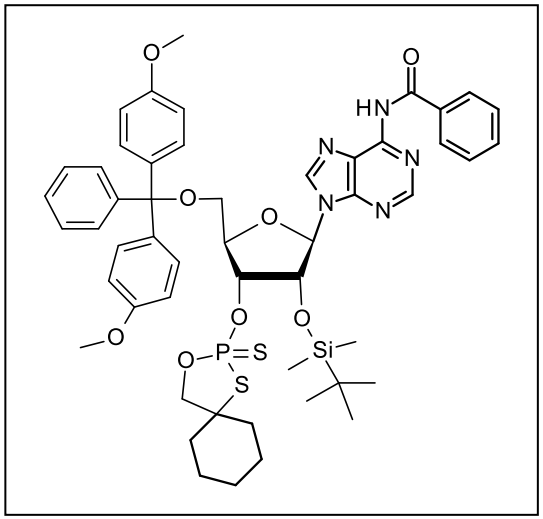
Fast-eluting ^{M}U-OTP in CD_3CN; δ (ppm)
^{1}H NMR: 9.27 (1H, N3-H), 7,65-7.63 (1H, C6-H), 7,43-6,86 (13H, DMT), 5,89-5.88 (1H, C1'-H), 5,33-5.31 (1H, C3'-H), 4,26-4.22 (1H, C2'-H), 4.20-4.16 (1H, C4'-H), 4.07-4.02 (2H, P-O-CH_2C-S), 3.75 (6H, 2xOCH_3), 3.45 (3H, 2'OCH_3), 3.40-3.39 (2H, 5'CH_2), 1.96-1.17 (10H, -$(CH_2)_5$-*„spiro"*)



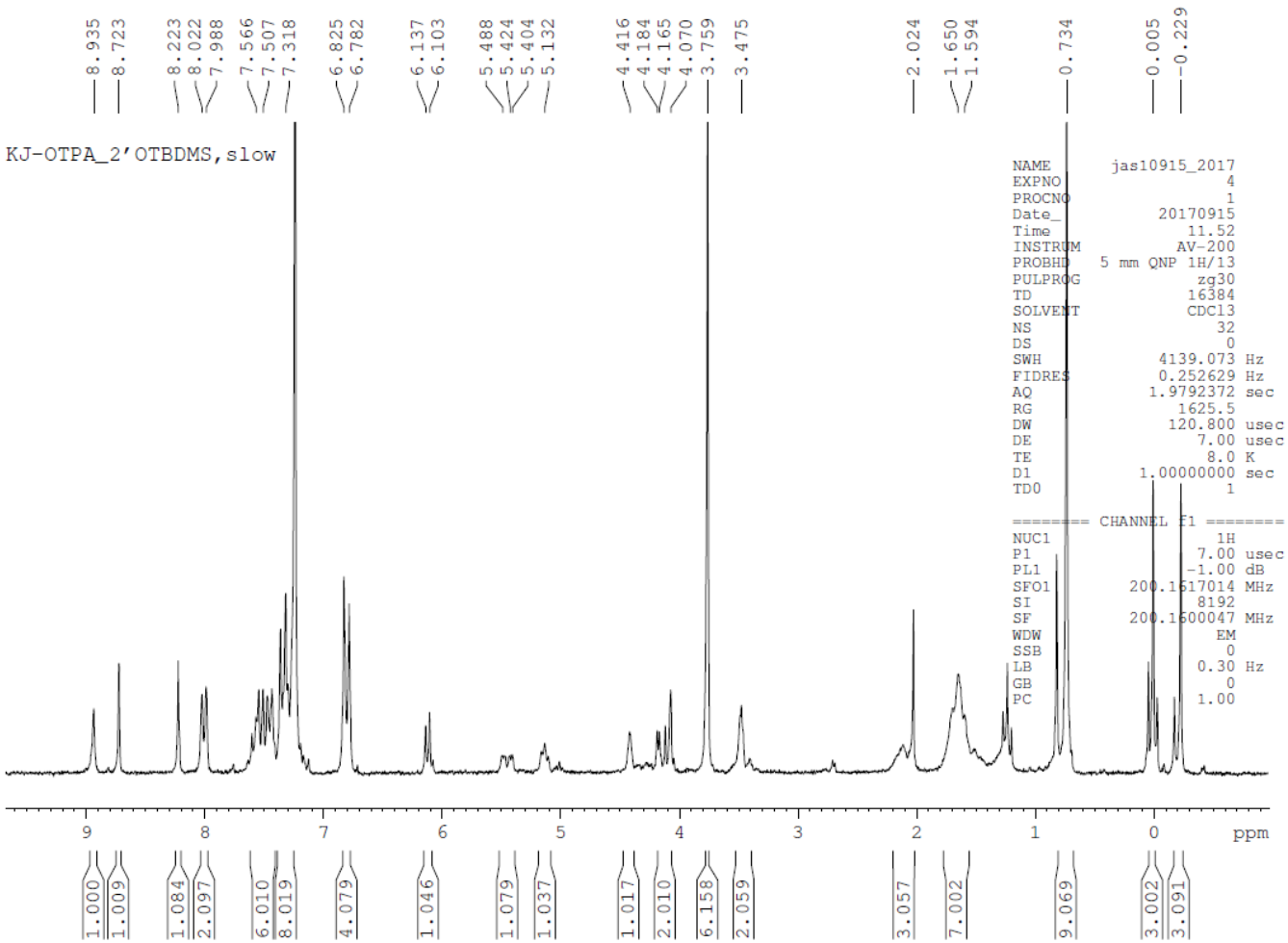


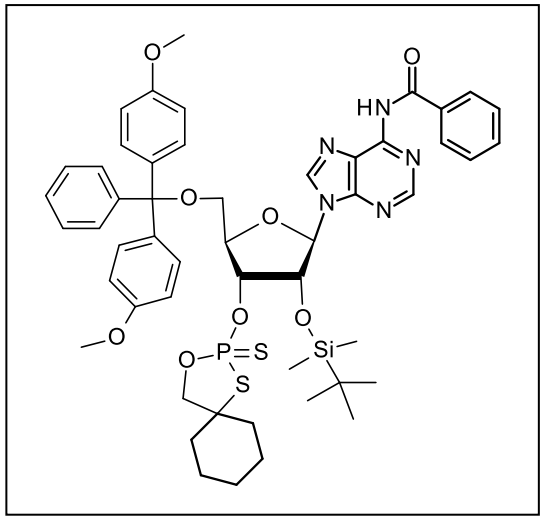
Slow-eluting ^{M}U-OTP in CD_3CN*;* δ (ppm)
^{1}H NMR: 9.01 (1H, N3-H), 7,65-7.63 (1H, C6-H), 7,43-6,86 (13H, DMT), 5,85 (1H, C1'-H), 5,31-5.28 (1H, C3'-H), 4,27-4.25 (1H, C2'-H), 4.20-4.18 (1H, C4'-H), 4.05-4.01 (2H, P-O-CH_2C-S), 3.76 (6H, 2xOCH_3), 3.45 (3H, 2'OCH_3), 3.44-3.37 (2H, 5'CH_2), 1.92-1.17 (10H, -$(CH_2)_5$-*„spiro"*)



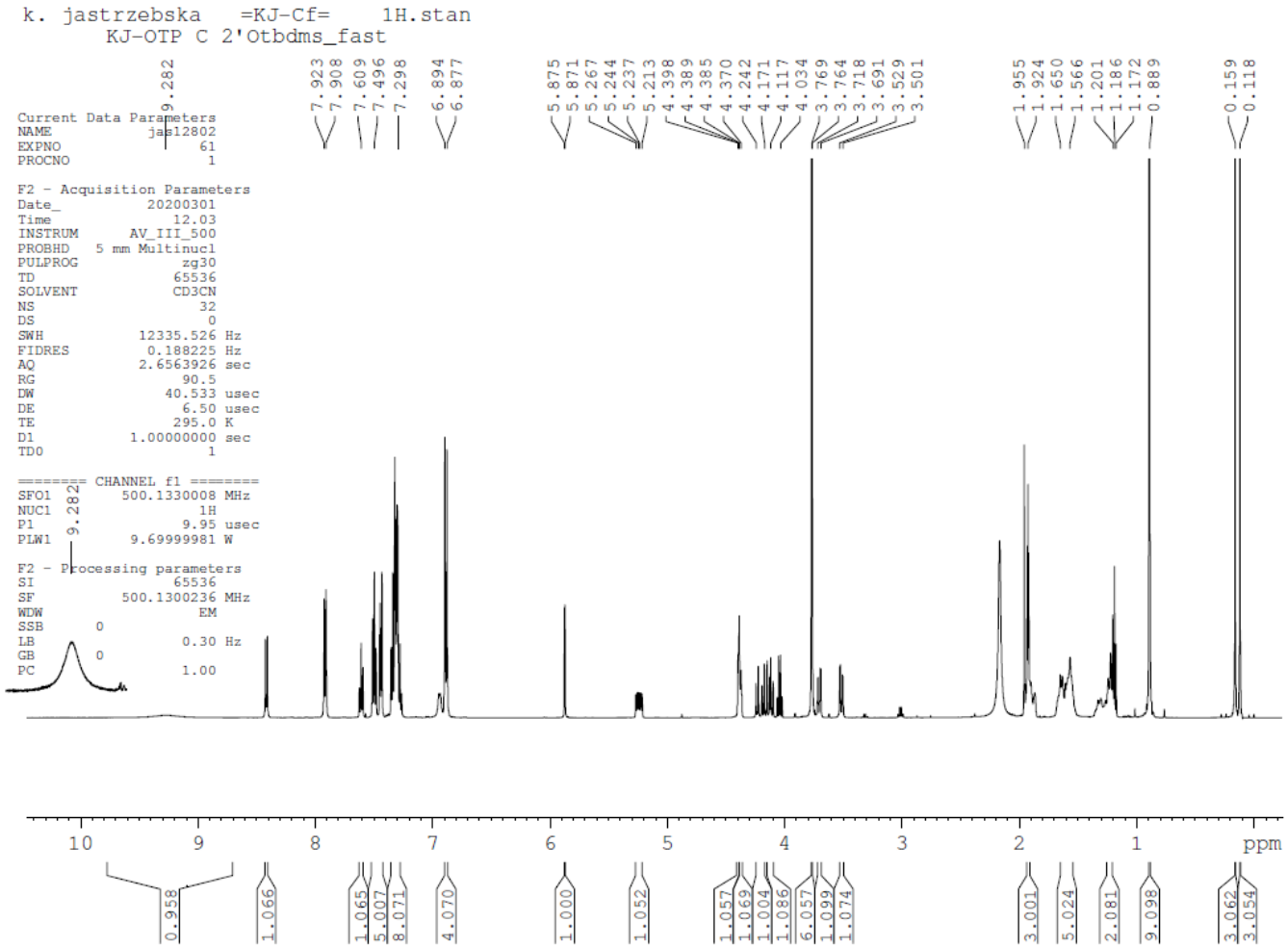


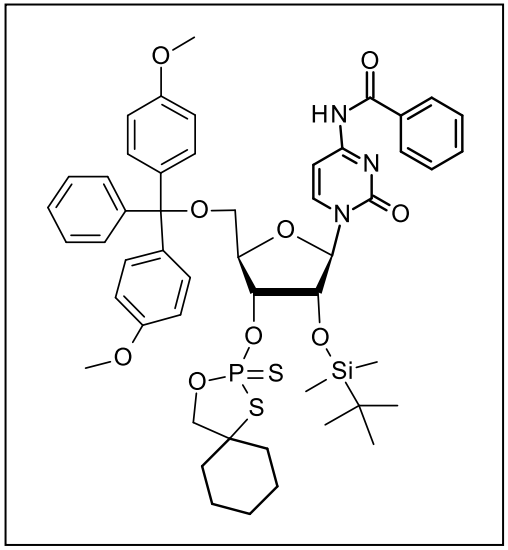
Fast-eluting ^{T}A-OTP in CD_3CN; δ (ppm)
^{1}H NMR: 8.97 (1H, NHCO), 8.73 (1H, C8-H), 8.24 (1H, C2-H), 7.54-6.79 (18H, DMT, Bz), 6.14-6.11 (1H, C1'-H), 5.52-5.45 (1H, C3'-H), 5.08-5.03 (1H, C2'-H), 4.45-4.44 (1H, C4'-H), 4.23-4.10 (2H, P-O-CH_2C-S), 3.76 (6H, 2xOCH_3), 3.58-3.41 (2H, 5'CH_2), 2.11-1.63 (10H, -$(CH_2)_5$-*„spiro"*), 0.73 (9H, 3xCH_3, tert-Butyl), 0.02 (6H, 2xCH_3, -$(CH_3)_2$Si)



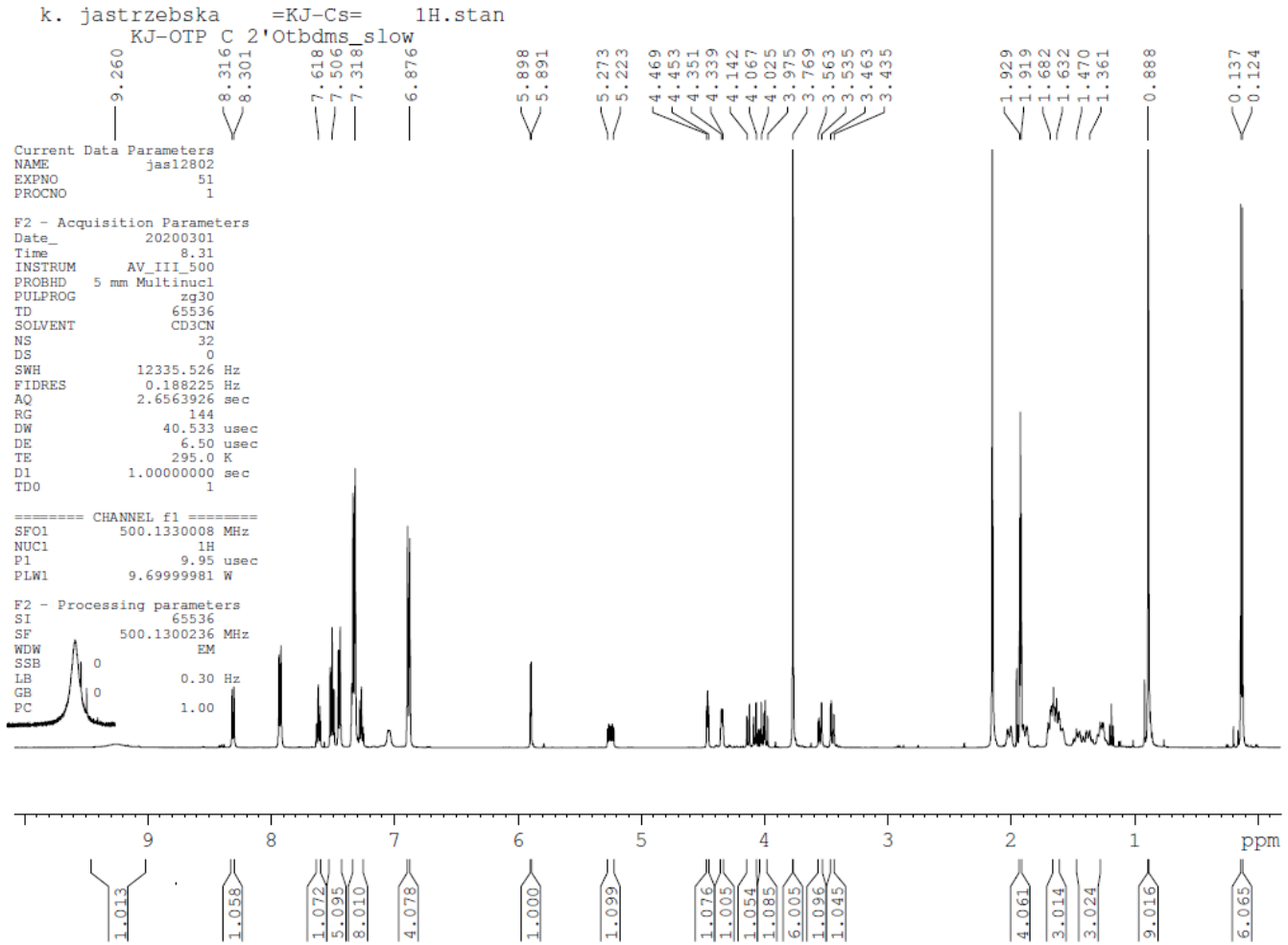


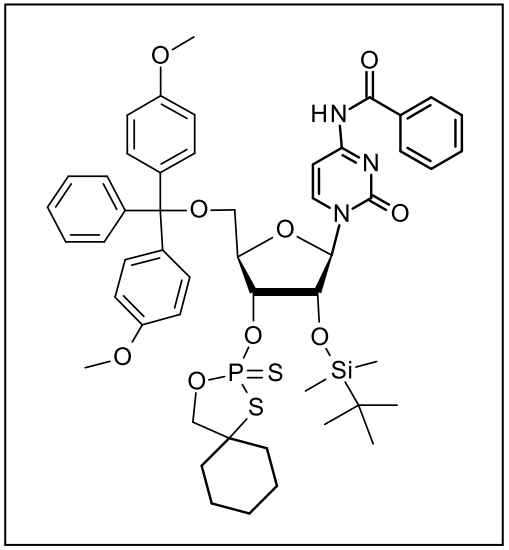
Slow-eluting ^{T}A-OTP in CD_3CN; δ (ppm)
^{1}H NMR: 8.94 (1H, NHCO), 8.72 (1H, C8-H), 8.22 (1H, C2-H), 7.57-6.78 (18H, DMT, Bz), 6.13-6.10 (1H, C1'-H), 5.49-5.40 (1H, C3'-H), 5.13 (1H, C2'-H), 4.42 (1H, C4'-H), 4.18-4.07 (2H, P-O-CH_2C-S), 3.76 (6H, 2xOCH_3), 3.47-3.45 (2H, 5'CH_2), 2.02-1.59 (10H, -$(CH_2)_5$-*„spiro"*), 0.73 (9H, 3xCH_3, tert-Butyl), 0.02 (6H, 2xCH_3, -$(CH_3)_2$Si)



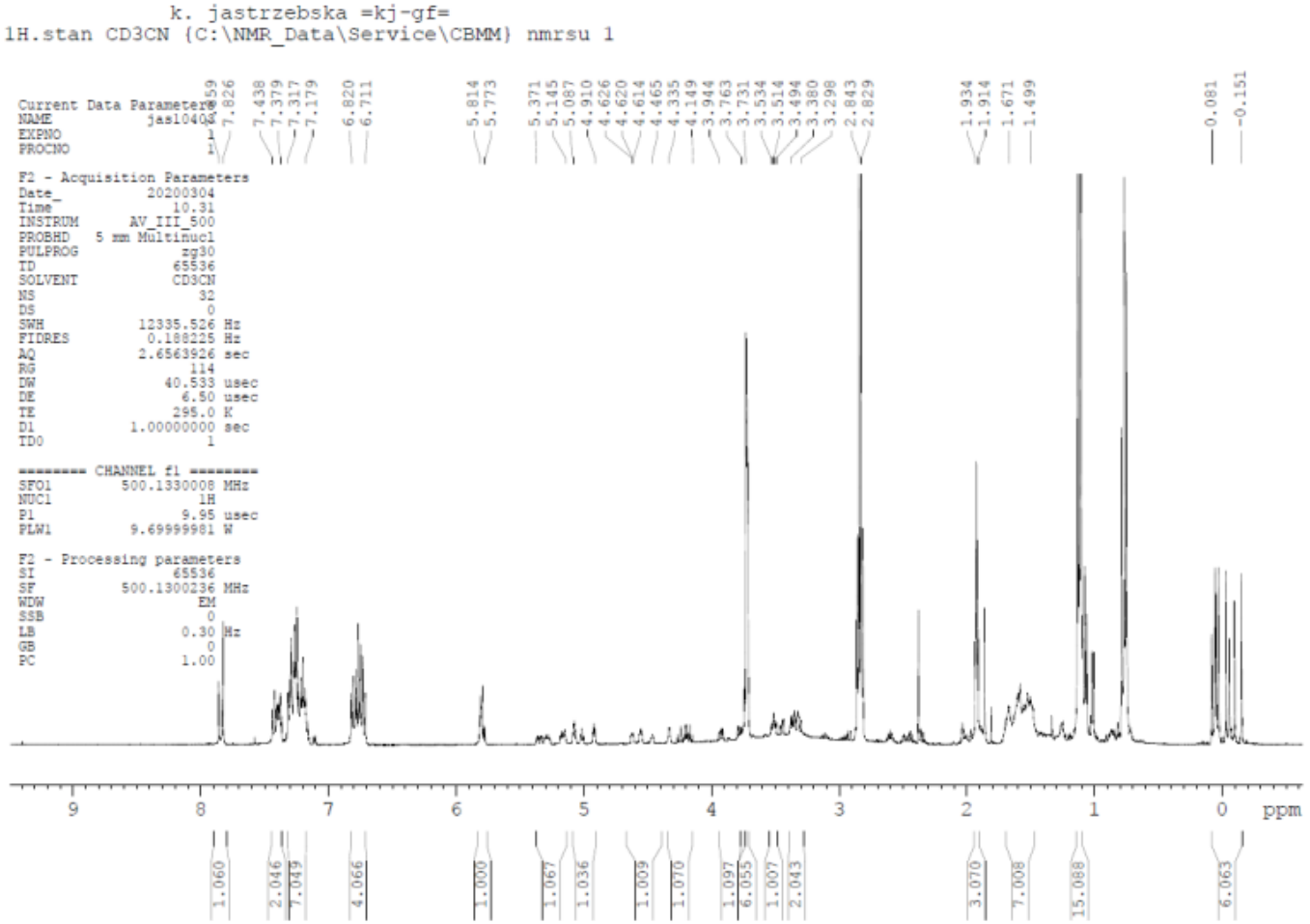


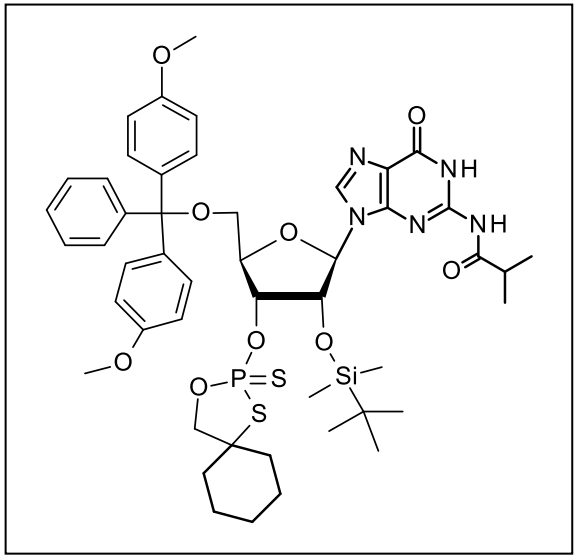
Fast-eluting ^{T}C-OTP in CD_3CN; δ (ppm)
^{1}H NMR: 9.28 (1H, NHCO), 8.50-8.45 (1H, C6-H), 7.61 (1H, C5-H), 7,52-6,88 (18H, DMT, Bz), 5,87 (1H, C1'-H), 5,27-5,21 (1H, C3'-H), 4,40-4.38 (2H, C2'-H, C4'-H), 4,24-4.03 (2H, P-O-CH_2C-S), 3,77 (6H, 2xOCH_3), 3,76-3.50 (2H, 5'CH_2), 1,95-1,17 (10H, -$(CH_2)_5$- *„spiro"*), 0.89 (9H, 3xCH_3, tert-Butyl), 0.15-0.12 (6H, 2xCH_3, -$(CH_3)_2$Si)



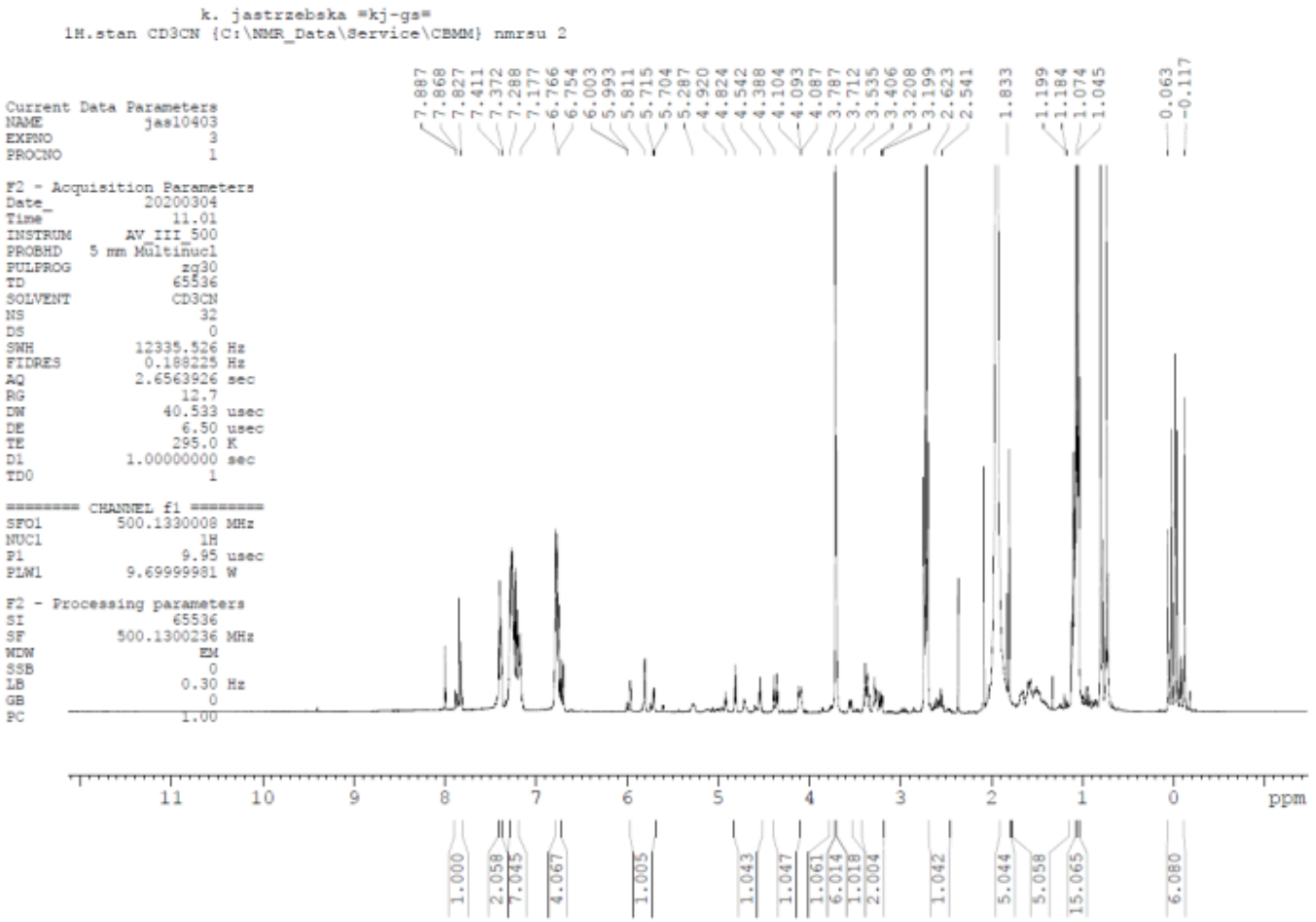


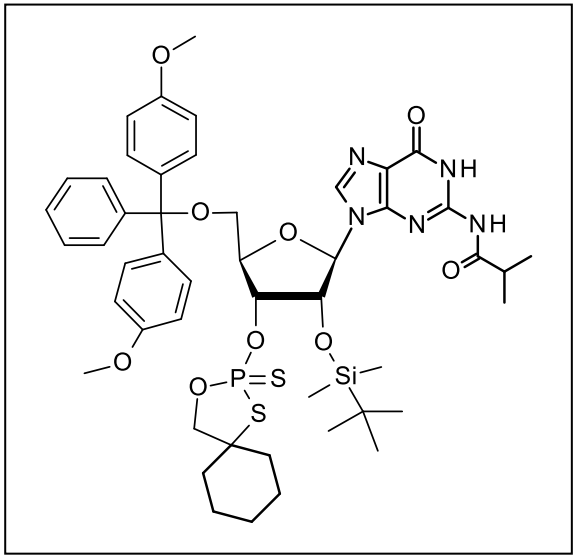
Slow-eluting ^{T}C-OTP in CD_3CN; δ (ppm)
^{1}H NMR: 9.26 (1H, NHCO), 8.32-8.30 (1H, C6-H), 7.61 (1H, C5-H), 7.62-6.88 (18H, DMT, Bz), 5.90-5.89 (1H, C1'-H), 5.27-5,22 (1H, C3'-H), 4.47-4.45 (1H, C2'-H), 4.35-4.34 (1H, C4'-H), 4.14-3.98 (2H, P-O-CH_2C-S), 3,77 (6H, 2xOCH3), 3,56-3.44 (2H, 5'CH_2), 1,91-1,36 (10H, -$(CH_2)_5$- *„spiro"*), 0.89 (9H, 3xCH_3, tert-Butyl), 0.13-0.12 (6H, 2xCH_3, -$(CH_3)_2$Si)



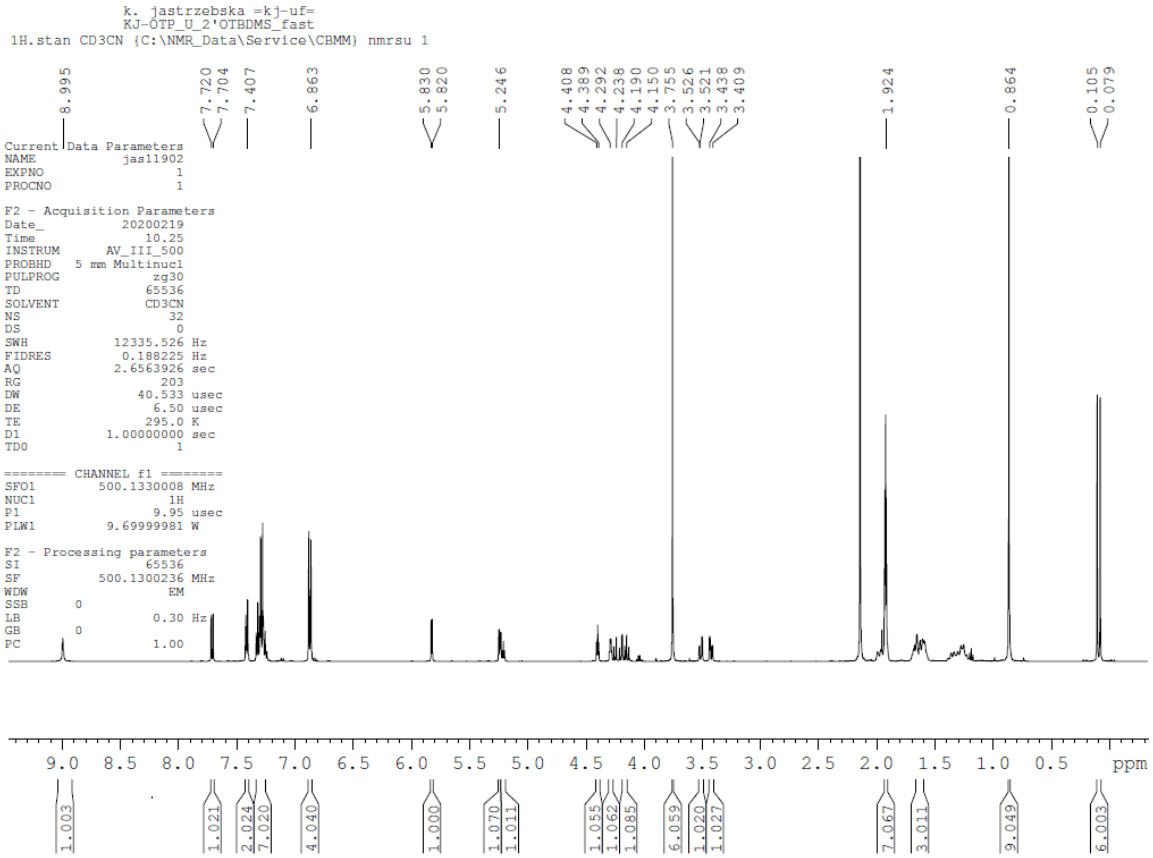


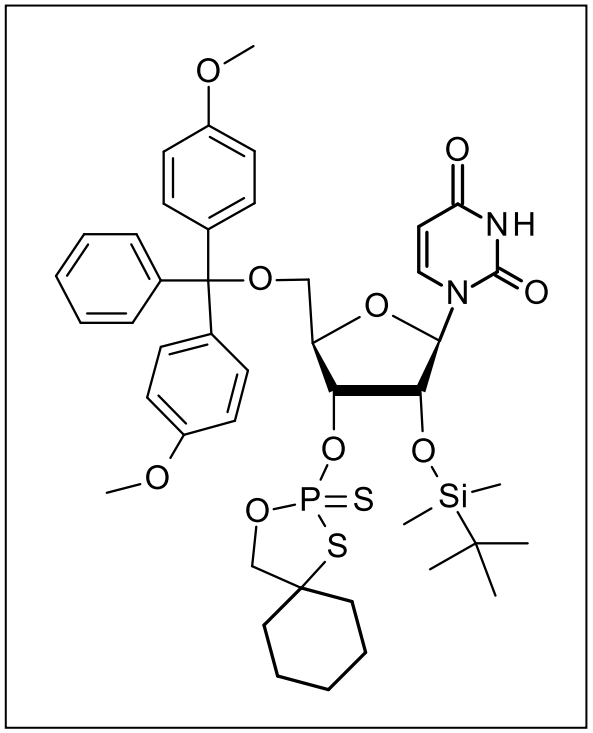
Fast-eluting ^{T}G-OTP in CD_3CN; δ (ppm)
^{1}H NMR: (1H, N1-H), (1H, N2-H), 7.86-7.82 (1H, C8-H), 7.44-6.71 (13H, DMT), 5.81-5.77 (1H, C1'-H), 5.37-5.14 (1H, C3'-H), 5.09-4.91 (1H, C2'-H), 4.62-4.47 (1H, C4'-H), 4.34-3.76 (2H, P-O-CH_2C-S), 3.73 (6H, 2xOCH_3), 3.53-3.49 (1H, CH, iBu), 3.38-3.30 (2H, C5'CH_2), 1.93-1.50 (10H, -$(CH_2)_5$- *„spiro"*), 1.13-1.10 (15H, 5xCH_3, iBu; tert-Butyl), 0.08- (-0.15) (6H, 2xCH_3, -$(CH_3)_2$Si





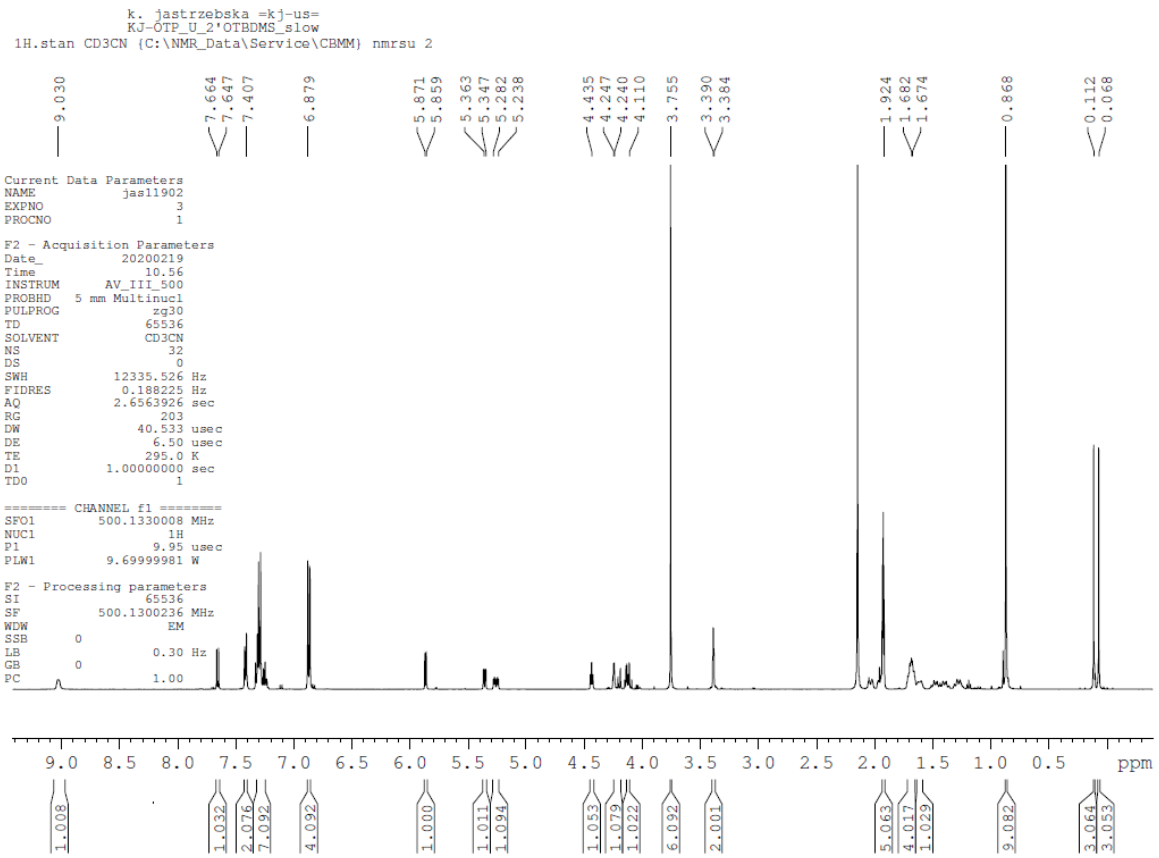
Slow-eluting ^{T}G-OTP in CD_3CN; δ (ppm)
^{1}H NMR: (1H, N1-H), (1H, N2-H), 7.88-7.82 (1H, C8-H), 7.41-6.75 (13H, DMT), 6.00-5.70 (1H, C1'-H), 5.30-4.92 (1H, C3'-H), 4.82-4.54(1H, C2'-H), 4.39-4.10 (1H, C4'-H), (2H, P-O-CH2C-S), 3.71 (6H, 2xOCH3), 3.40-3.20 (2H, C5'CH2), 2.62-2.54 (1H, CH, iBu), 1.83-1.18 (10H, -(CH2)5- *„spiro"*), 1.07-1.04 (15H, 5xCH3, iBu; tert-Butyl), 0.06-(-0.11) (6H, 2xCH3, -(CH3)2Si)

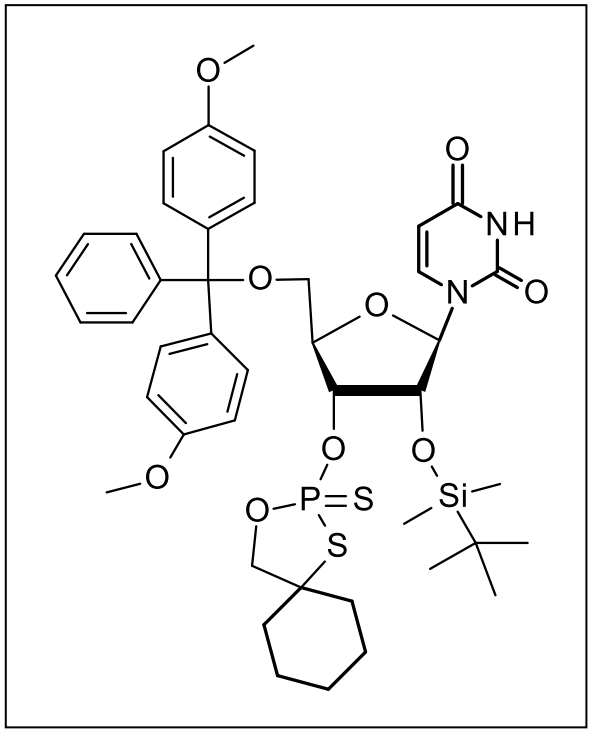




Fast-eluting ^{T}U-OTP in CD_3CN; δ (ppm)

^{1}H NMR: 8.99 (1H, N3-H), 7,72-7.70 (1H, C6-H), 7,40-6,86 (13H, DMT), 5,83-5.82 (1H, C1'-H), 5,25-5.23 (2H, C3'-H, C2'-H), 4.41-4.39 (1H, C4'-H), 4.38-4.15 (2H, P-O-CH_2C-S), 3.76 (6H, 2xOCH_3), 3.53-3.41 (2H, 5'CH_2), 1.93-1.51 (10H, -$(CH_2)_5$-*„spiro"*), 0.86 (9H, 3xCH_3, tert-Butyl), 0.10-0.08 (6H, 2xCH_3, -$(CH_3)_2$Si)



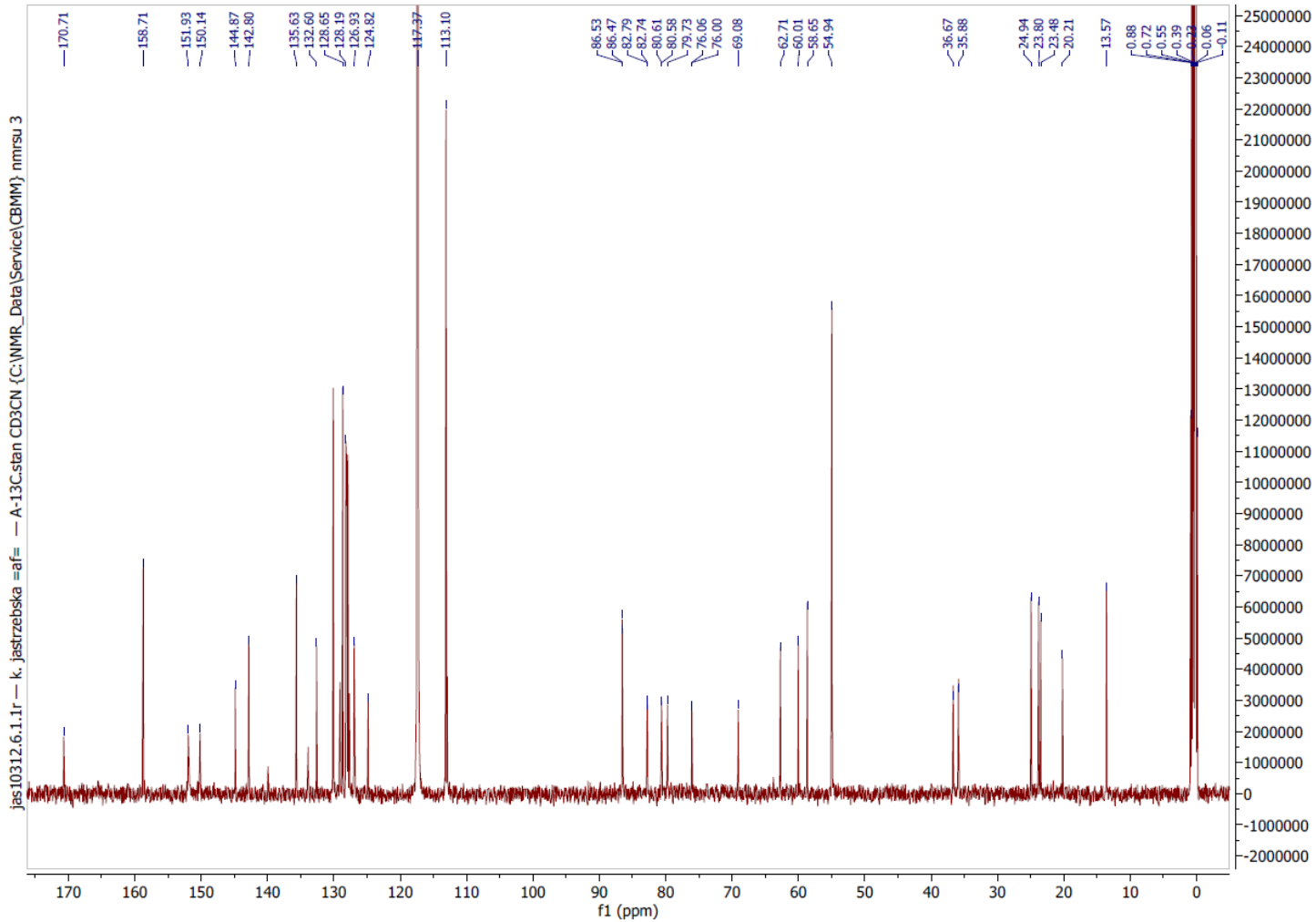


Slow-eluting ^{T}U-OTP in CD_3CN; δ (ppm)

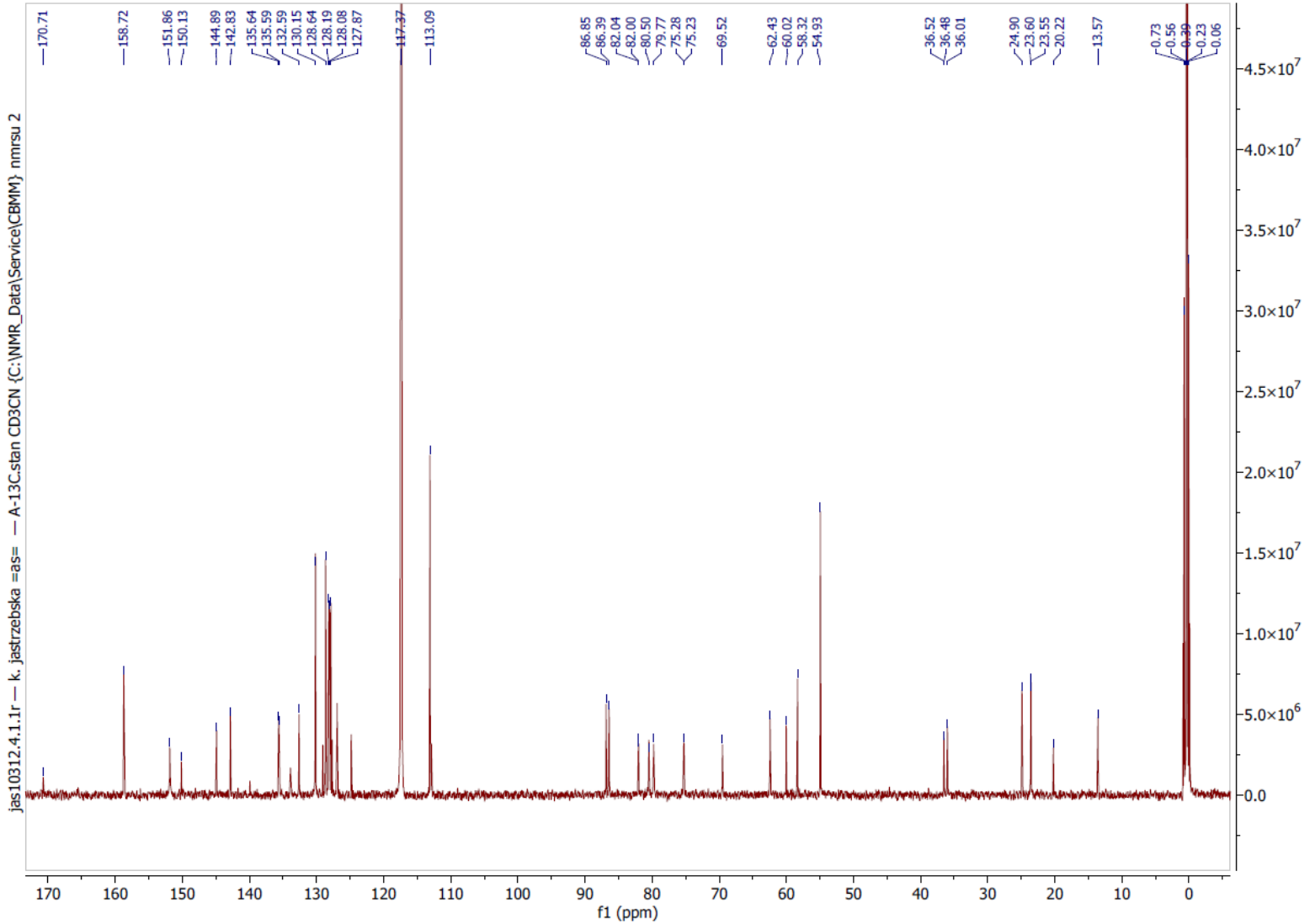
^{1}H NMR: 9.03 (1H, N3-H), 7.66-7.65 (1H, C6-H), 7.41-6.88 (13H, DMT), 5.88-5.86 (1H, C1'-H), 5.36-5.35 (1H, C3'-H), 5.28-5.24 (1H, C2'-H), 4.44-4.42 (1H, C4'-H), 4.25-4.11 (2H, P-O-CH_2C-S), 3.76 (6H, 2xOCH_3), 3.39-3.38 (2H, 5'CH_2), 1.92-1.67 (10H, -$(CH_2)_5$-*„spiro"*), 0.87 (9H, 3xCH_3, tert-Butyl), 0.11-0.07 (6H, 2xCH_3, -$(CH_3)_2$Si)

^{13}C NMR spectra for separated P-diastereomers of ^{M}N-OTP and ^{T}N-OTP monomers

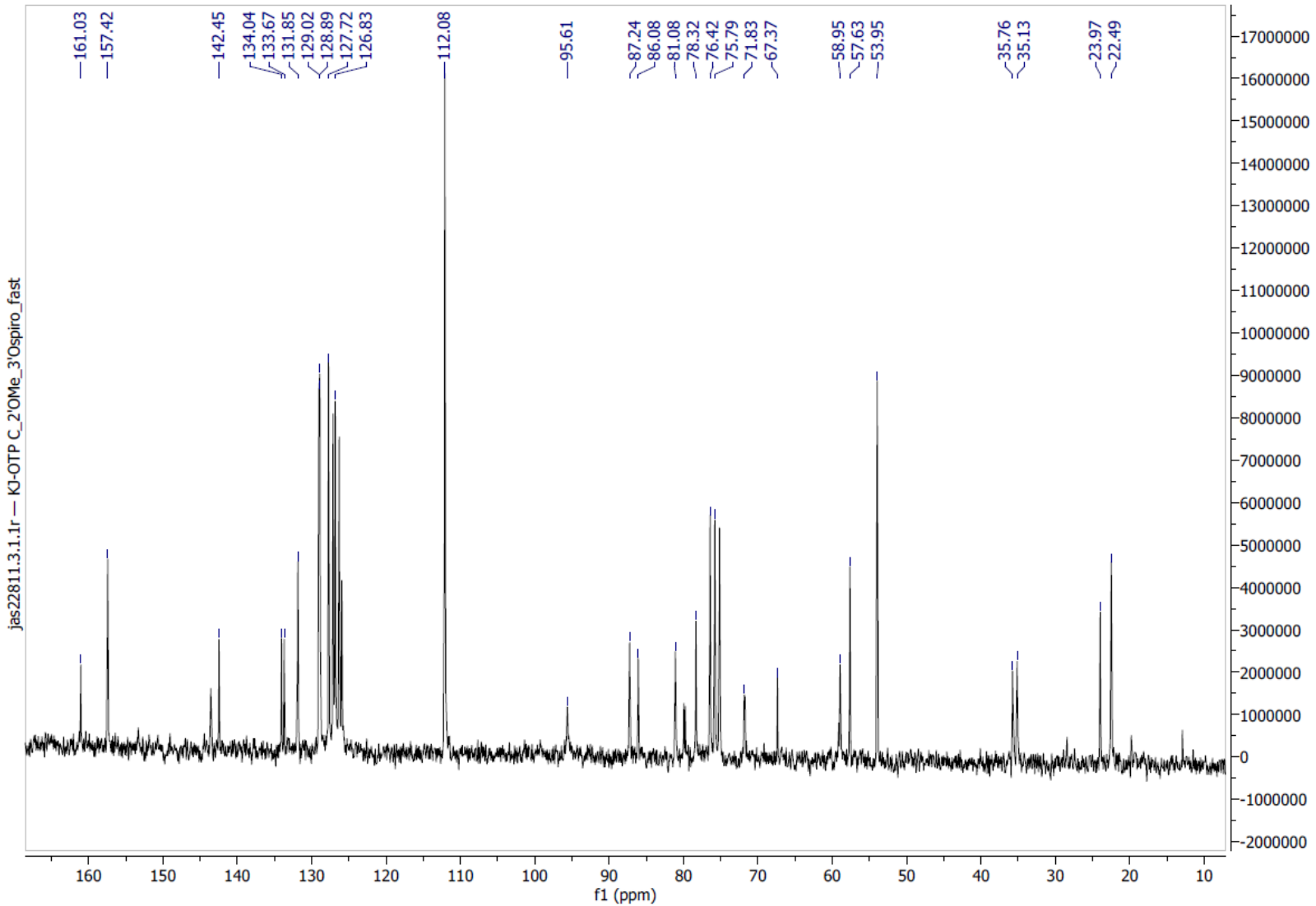
Figure S5. ^{13}C NMR spectra for separated P-diastereomers of ^{M}N-OTP and ^{T}N-OTP monomers.



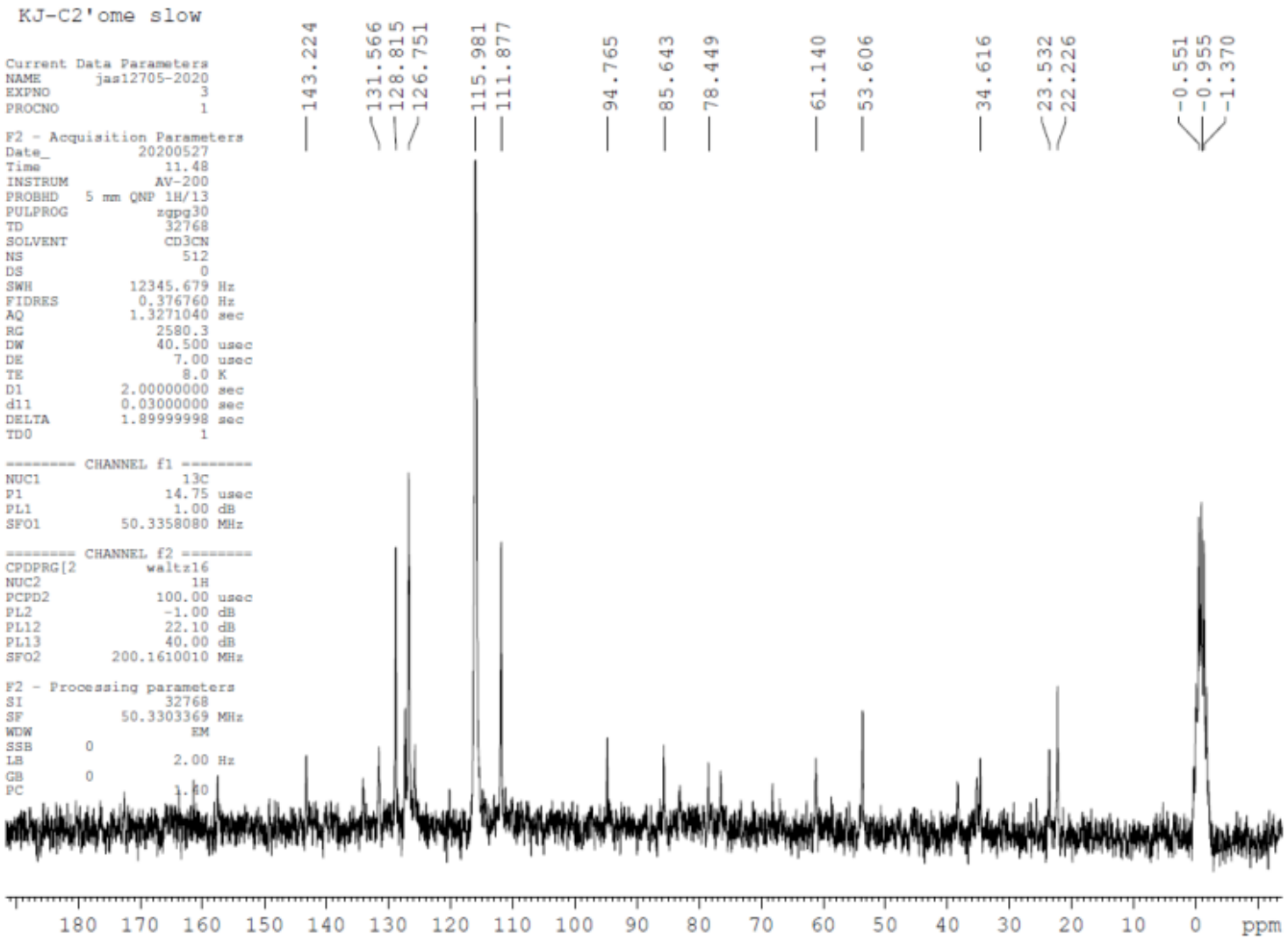
Fast-eluting ^{M}A-OTP; δ (ppm, CD_3CN): 170.71, 158.71, 151.93, 150.14, 144.87, 142.80, 135.63, 132.60, 128.65, 128.19, 126.93, 124.82, 117.37, 113.10, 86.53, 86.47, 82.79, 82.74, 80.61, 80.58, 79.73, 76.06, 76.00, 69.08, 62.71, 60.01, 58.65, 54.94, 36.67, 35.88, 24.94, 23.80, 23.48, 20.21, 13.57.



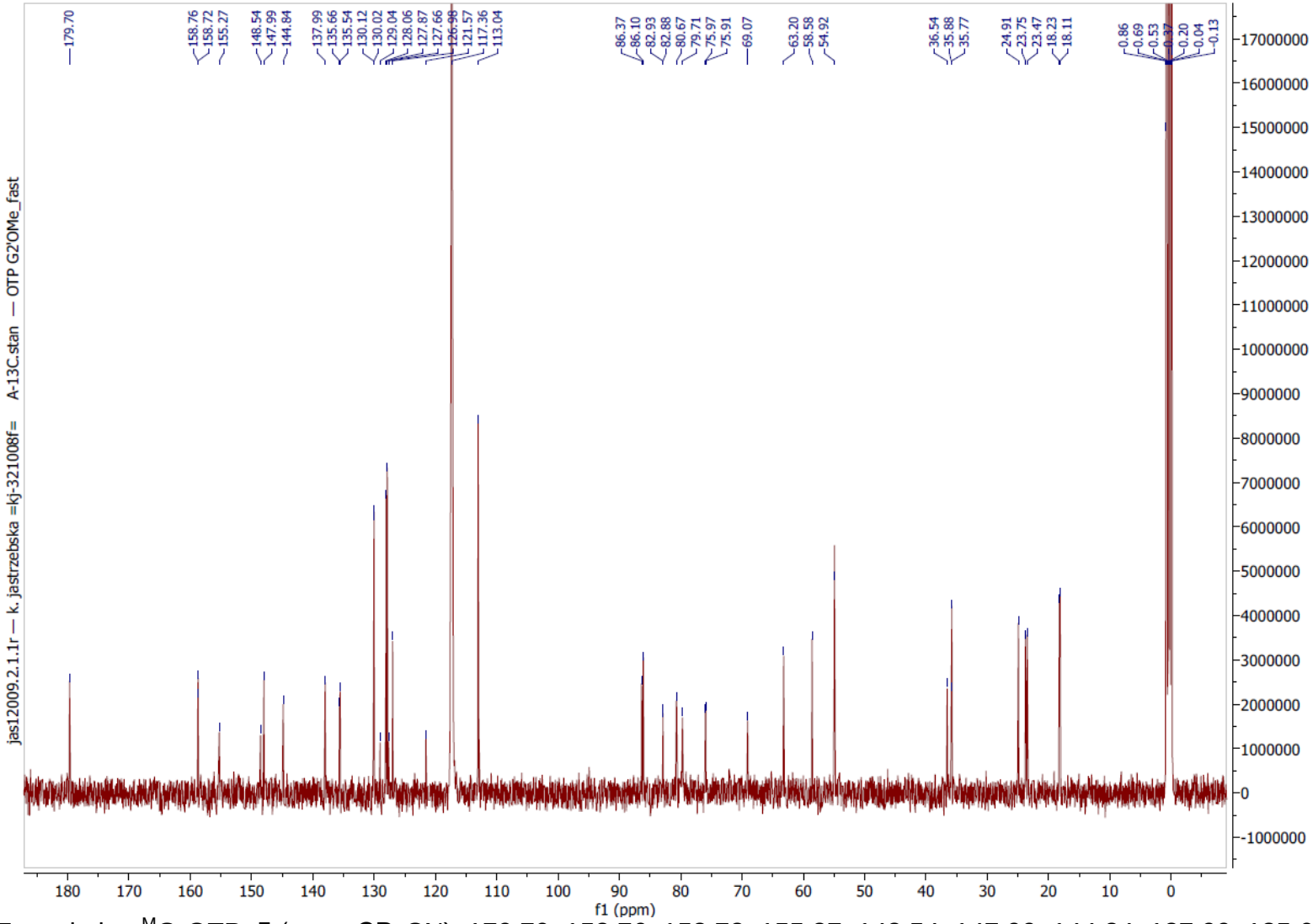
Slow-eluting ^{M}A-OTP; δ (ppm, CD_3CN): 170.71, 158.72, 151.86, 150.13, 144.89, 142.83, 135.59, 130.15, 128.64, 128.19, 128.08, 127.87, 117.37, 113.09, 86.85, 86.39, 82.04, 82.00, 80.50, 79.77, 75.28, 75.23, 69.52, 62.43, 60.02, 58.32, 54.93, 36.52, 36.48, 36.01, 24.90, 23.60, 23.55, 20.22, 13.57.



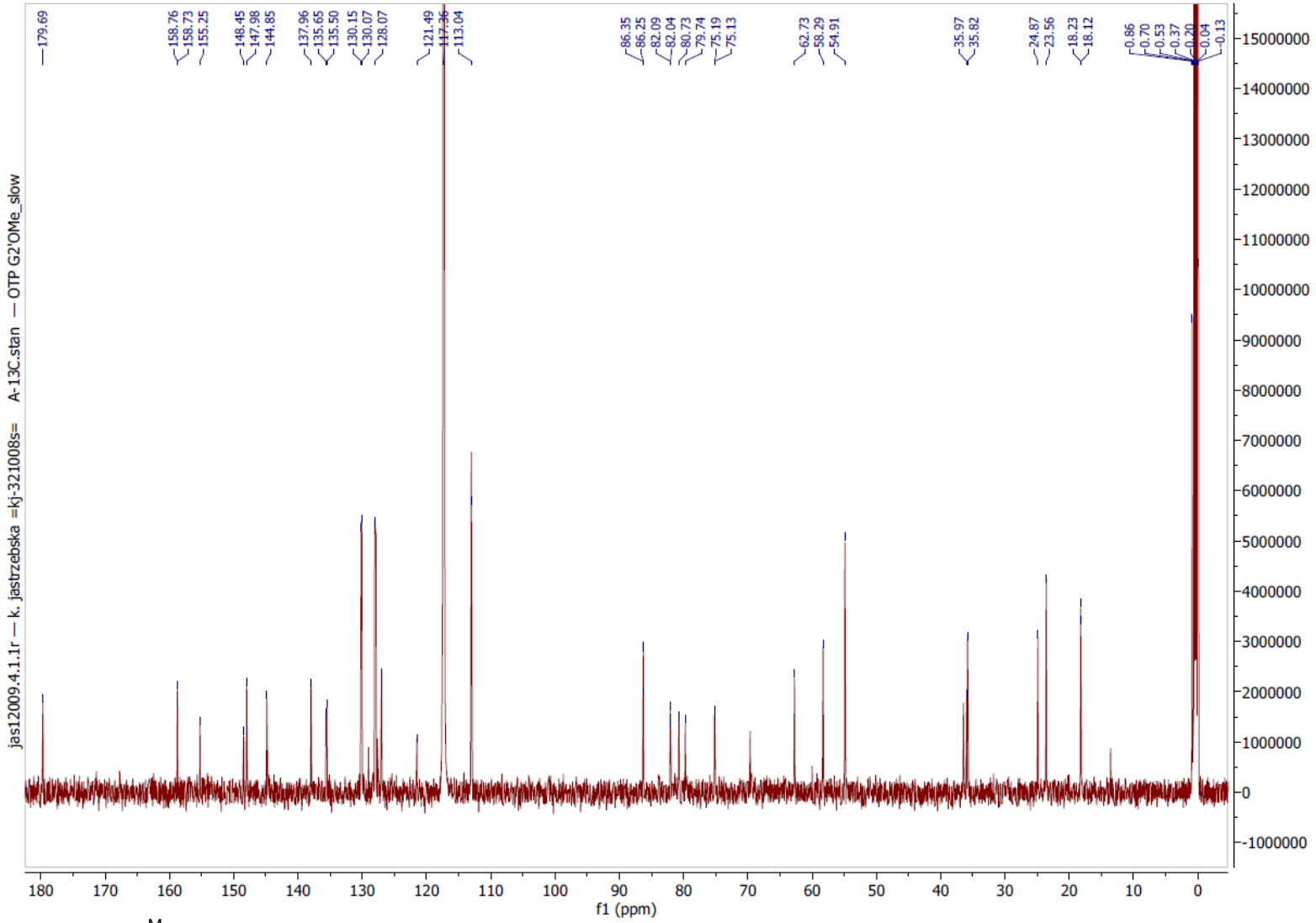
Fast-eluting ^{M}C-OTP; δ (ppm, CD_3CN): 161.03, 157.42, 142.45, 134.04, 133.67, 131.85, 129.02, 128.89, 127.72, 126.83, 112.08, 95.61, 87.24, 86.08, 81.08, 78.32, 76.42, 75.79, 71.83, 67.37, 58.95, 57.63, 53.95, 35.76, 35.13, 23.97, 22.49.



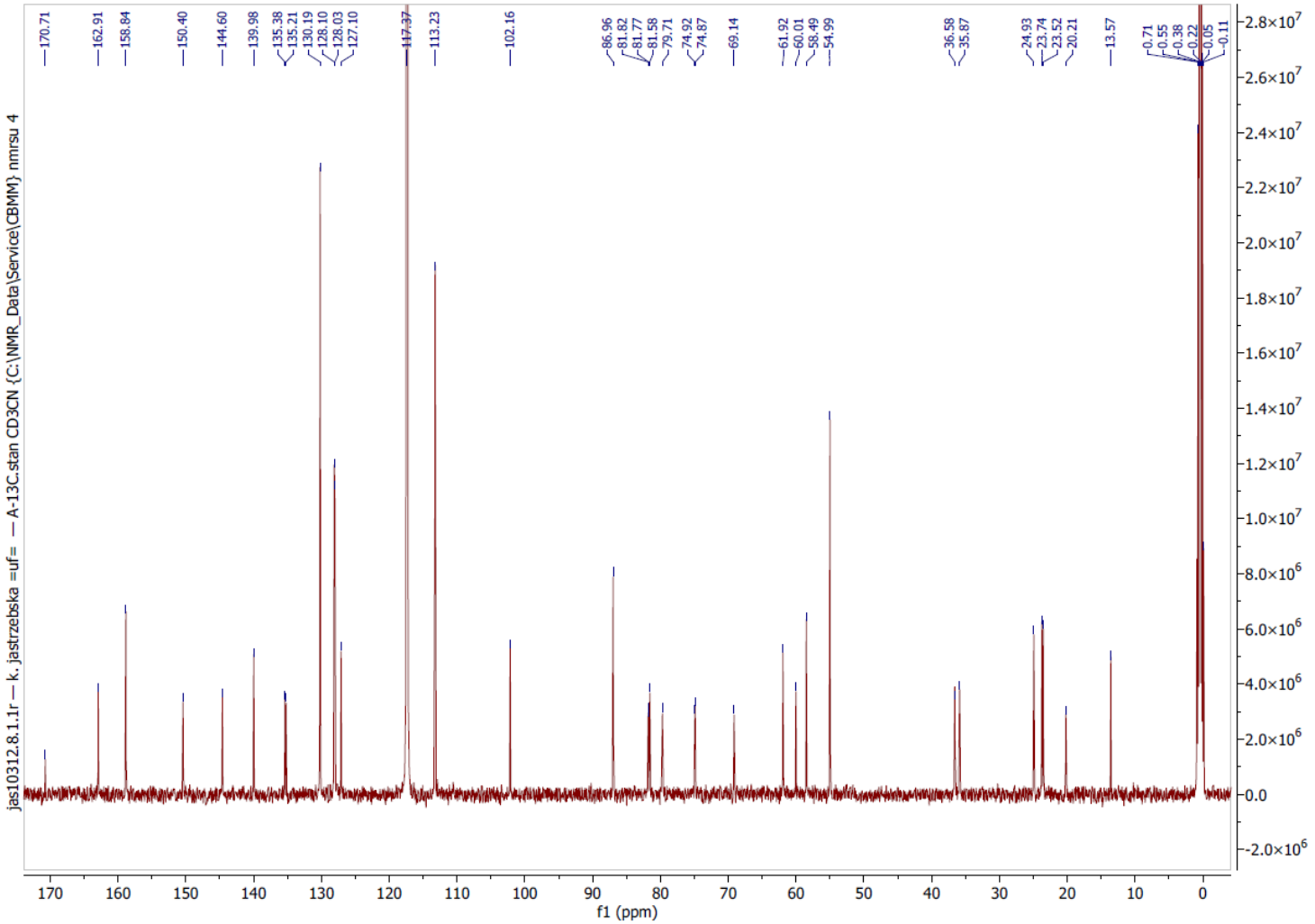
Slow-eluting ^{M}C-OTP; *;* δ (ppm, CD_3CN): 161.22, 157.75, 143.22, 133.40, 132.87, 131.57, 128.82, 128.12, 127.32, 126.75, 115.98, 111.88, 94.77, 85.64, 83.23, 78.45, 77.21, 67.75, 66.32, 61.14, 53.61, 35.77, 34.62, 23.53, 22.23.



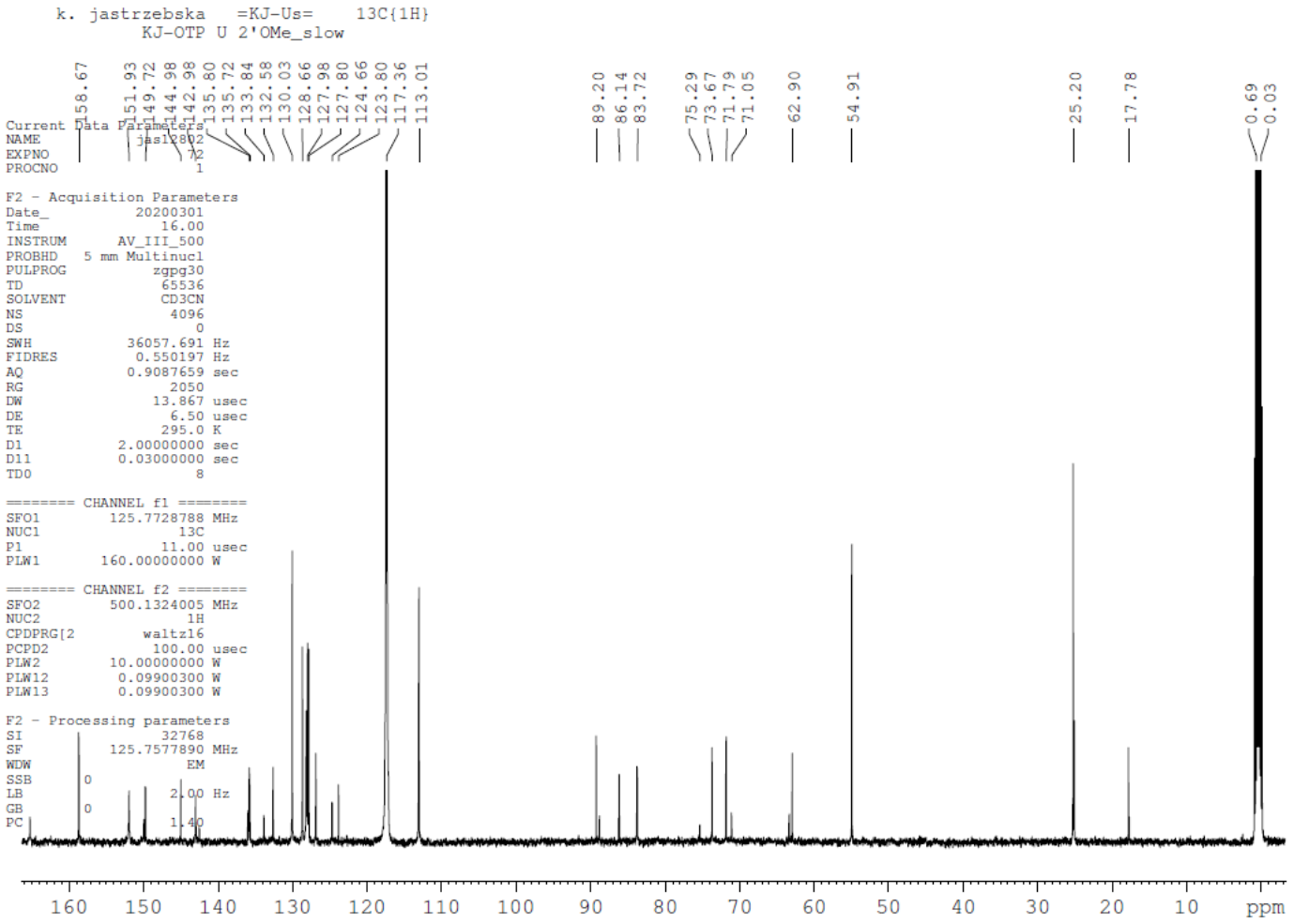
Fast-eluting ^{M}G-OTP; δ (ppm, CD_3CN): 179.70, 158.76, 158.72, 155.27, 148.54, 147.99, 144.84, 137.99, 135.66, 135.54, 130.12, 130.02, 129.04, 128.06, 127.87, 127.66, 126.98, 121.57, 117.36, 113.04, 86.37, 86.10, 82.93, 82.88, 80.67, 79.71, 75.97, 75.91, 69.07, 63.20, 58.58, 54.92, 36.54, 35.88, 35.77, 24.91, 23.75, 23.47, 18.23, 18.11.



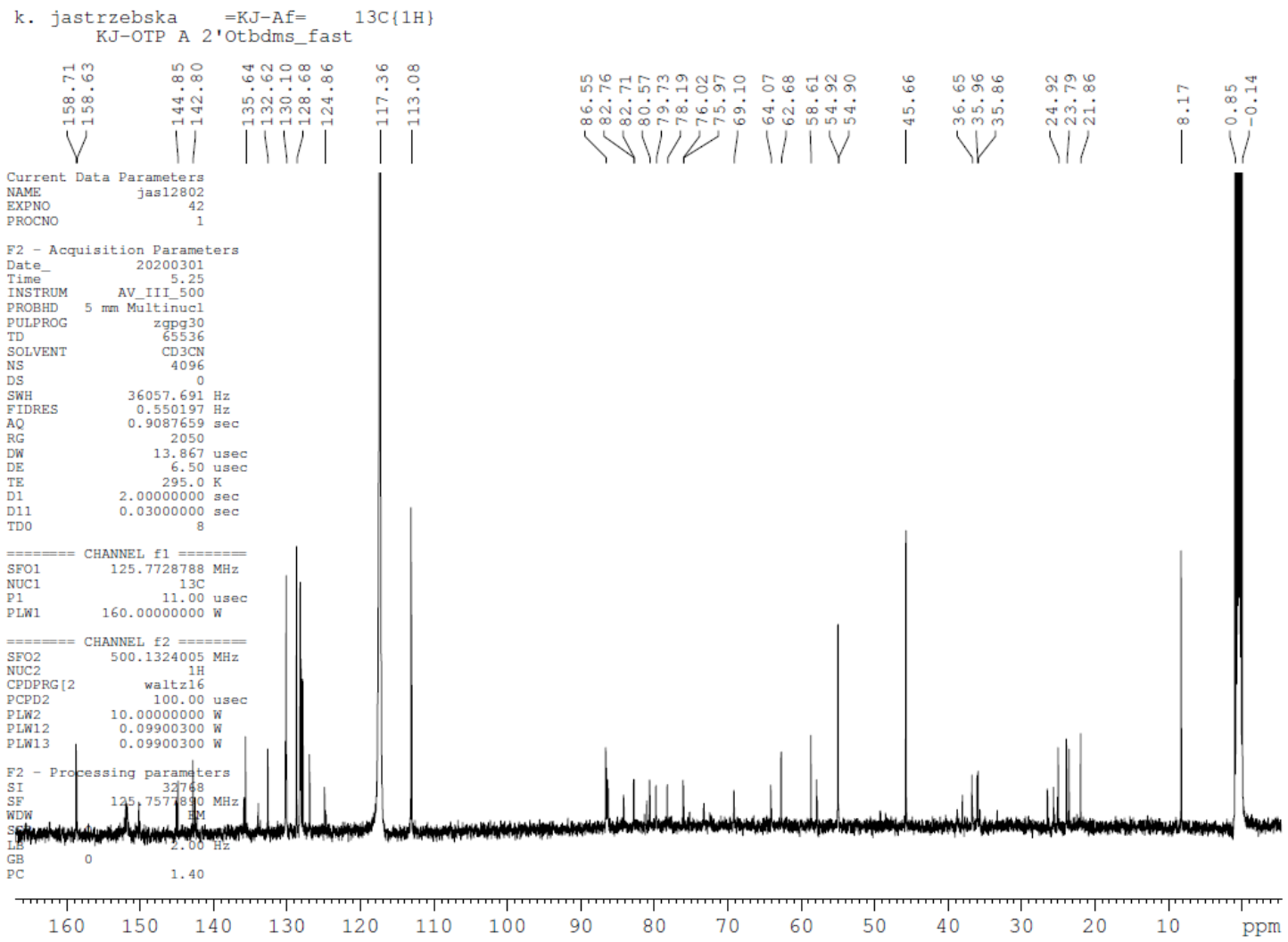
Slow-eluting ^{M}G-OTP; δ (ppm, CD_3CN): 179.69, 158.76, 158.73, 155.25, 148.45, 147.98, 144.85, 137.96, 135.55, 135.50, 130.15, 130.07, 128.07, 121.49, 117.36, 113.04, 86.35, 86.25, 82.09, 82.04, 80.73, 79.74, 75.19, 75.13, 62.73, 58.29, 54.91, 35.97, 35.82, 24.87, 23.56, 18.23, 18.12.



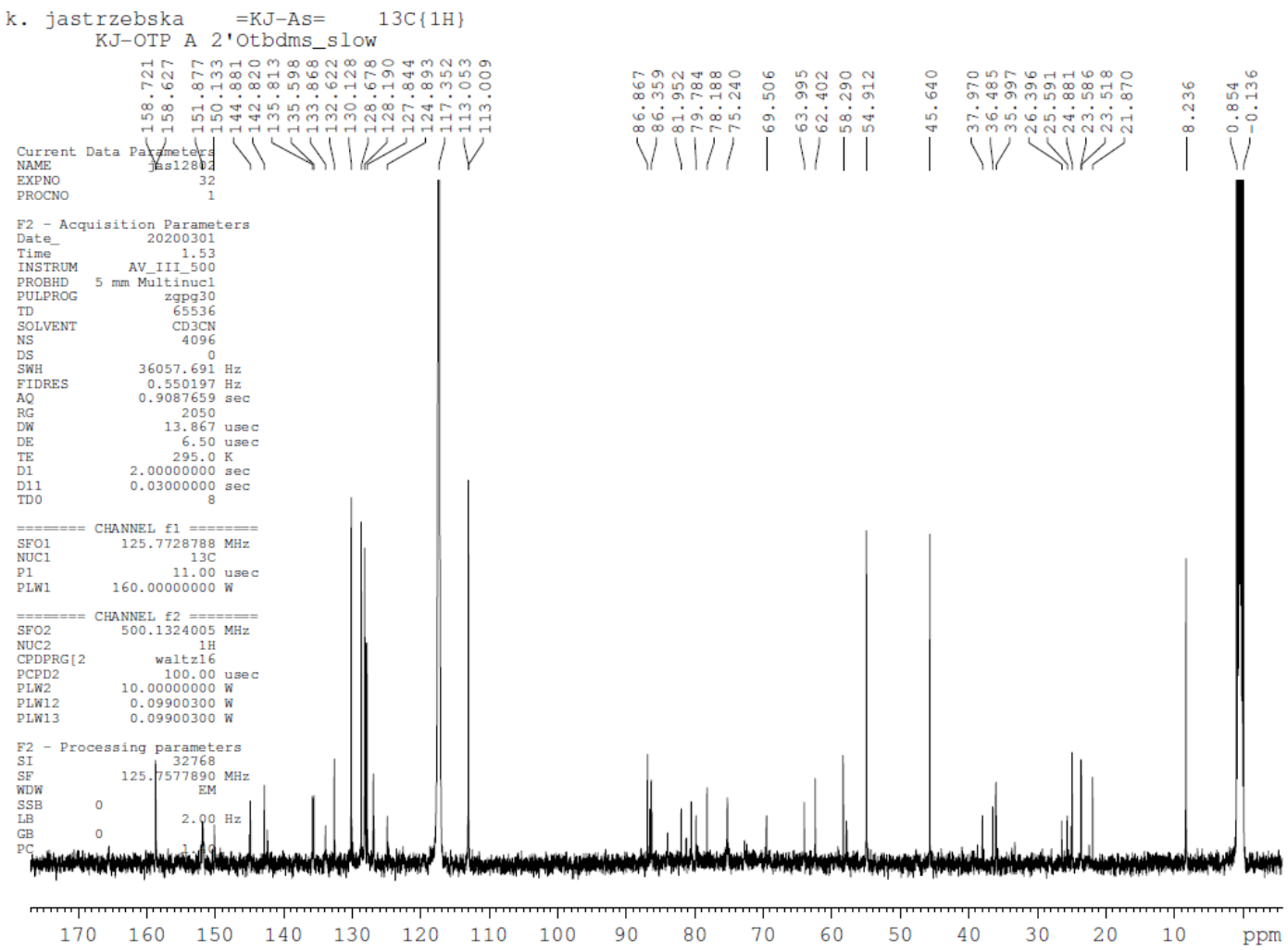
Fast-eluting ^{M}U-OTP; δ (ppm, CD_3CN): 170.71, 162.91, 158.84, 150.40, 144.60, 139.98, 135.38, 135.21, 130.19, 128.10, 128.03, 127.10, 117.37, 113.23, 102.16, 86.96, 81.82, 81.77, 81.58, 79.71, 74.92, 74.87, 69.14, 61.92, 60.01, 58.49, 54.99, 36.58, 35.87, 24.93, 23.74, 23.52, 20.21, 13.57.



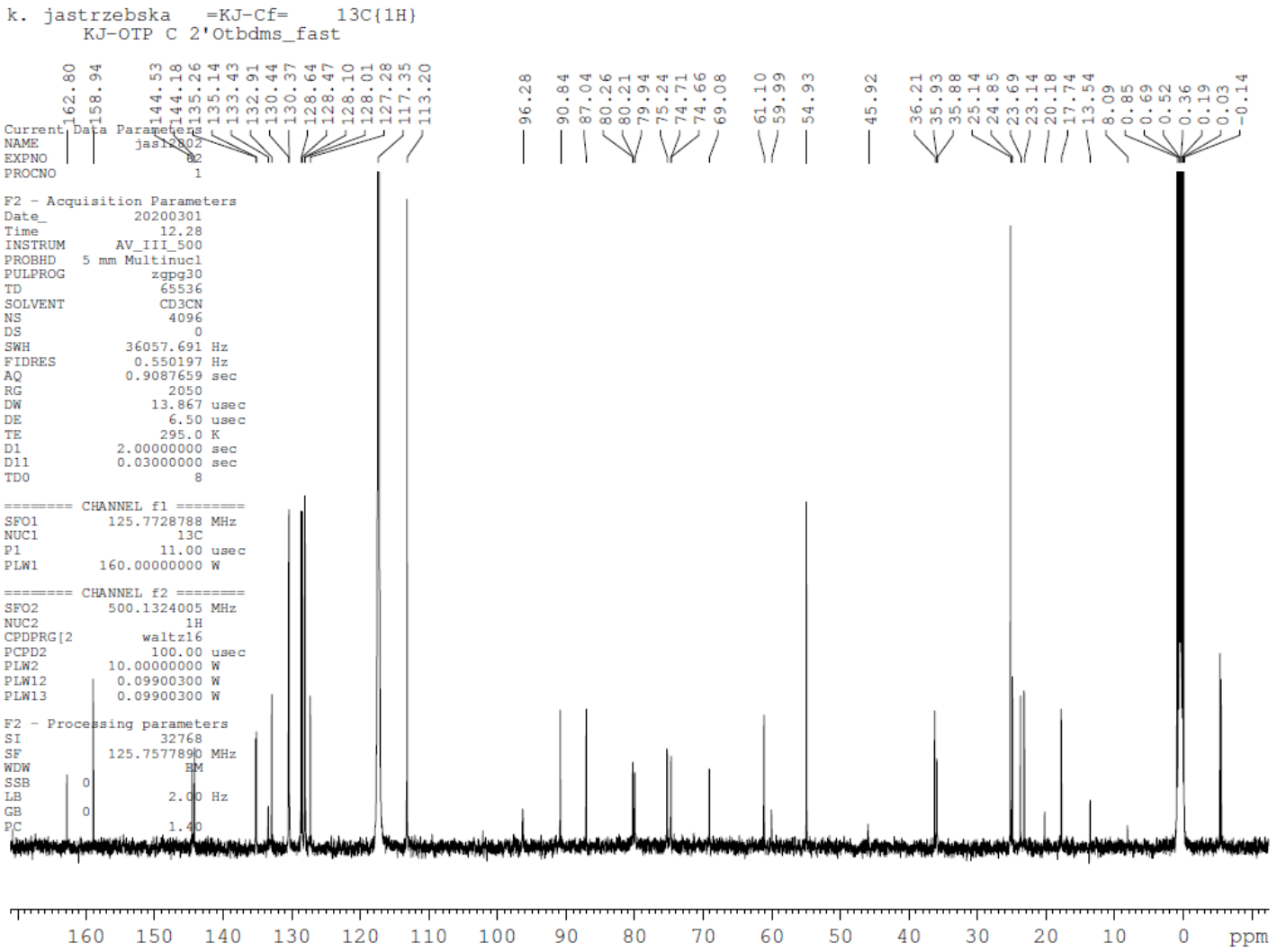
Slow-eluting ^{M}U-OTP; δ (ppm, CD_3CN): 170.20, 165.89, 158.67, 151.93, 149.72, 144.98, 142.98, 135.80, 135.72, 133.84, 132.58, 130.03, 128.66, 127.98, 127.80, 117.36, 113.01, 89.20, 86.14, 83.72, 75.29, 73.67, 71.79, 71.05, 62.90, 54.91, 25.20, 17.78.



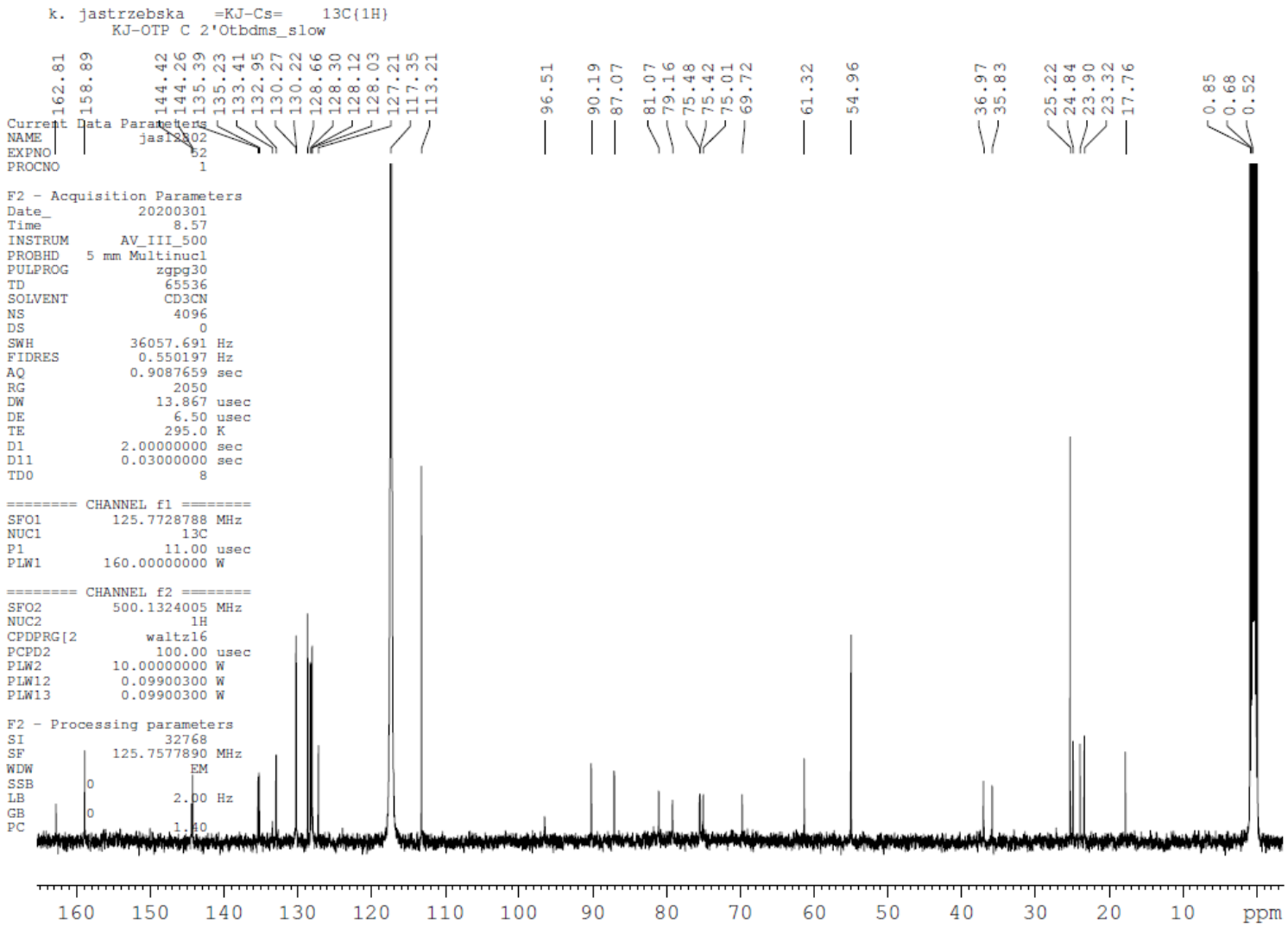
Fast-eluting ^{T}A-OTP; δ (ppm, CD_3CN): 158.71, 158.63, 144.85, 142.80, 135.64, 132.62, 130.10, 128.68, 124.86, 117.36, 113.08, 86.55, 82.76, 82.71, 80.57, 79.73, 78.19, 76.02, 75.97, 69.10, 64.07, 62.68, 58.61, 54.92, 54.90, 45.66, 36.65, 35.96, 35.86, 24.92, 23.79, 21.86, 8.17.



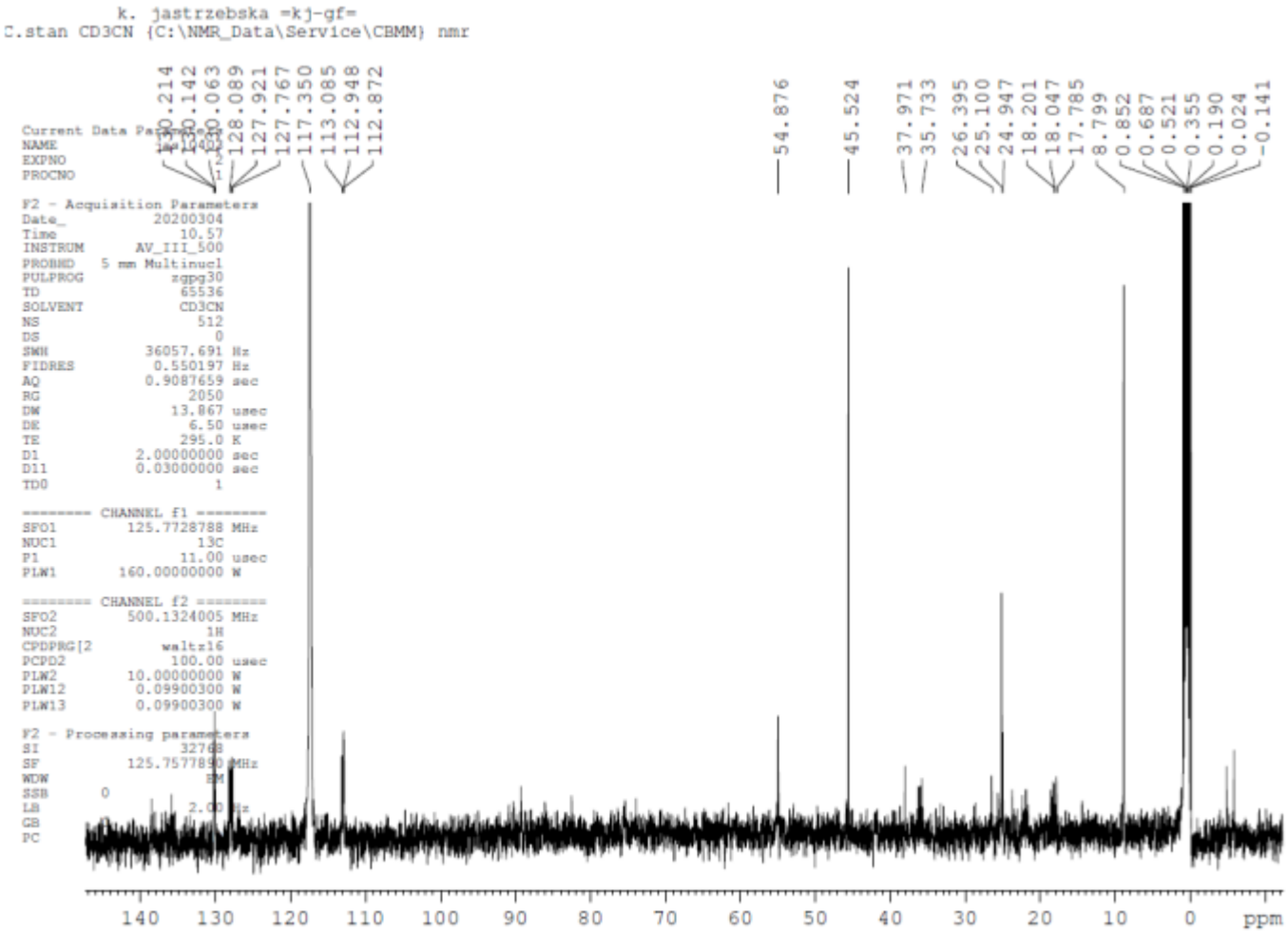
Slow-eluting ^{T}A-OTP; δ (ppm, CD_3CN): 158.72, 158.63, 151.87, 150.13, 144.88, 142.82, 135.81, 135.60, 133.87, 132.62, 130.13, 128.68, 128.19, 127.84, 124.89, 117.35, 113.05, 113.00, 86.87, 86.36, 81.95, 79.78, 78.19, 75.24, 69.51, 64.00, 62.40, 58.29, 54.91, 45.64, 37.97, 36.49, 36.00, 26.40, 25.59, 24.88, 23.59, 23.52, 21.87, 8.23.



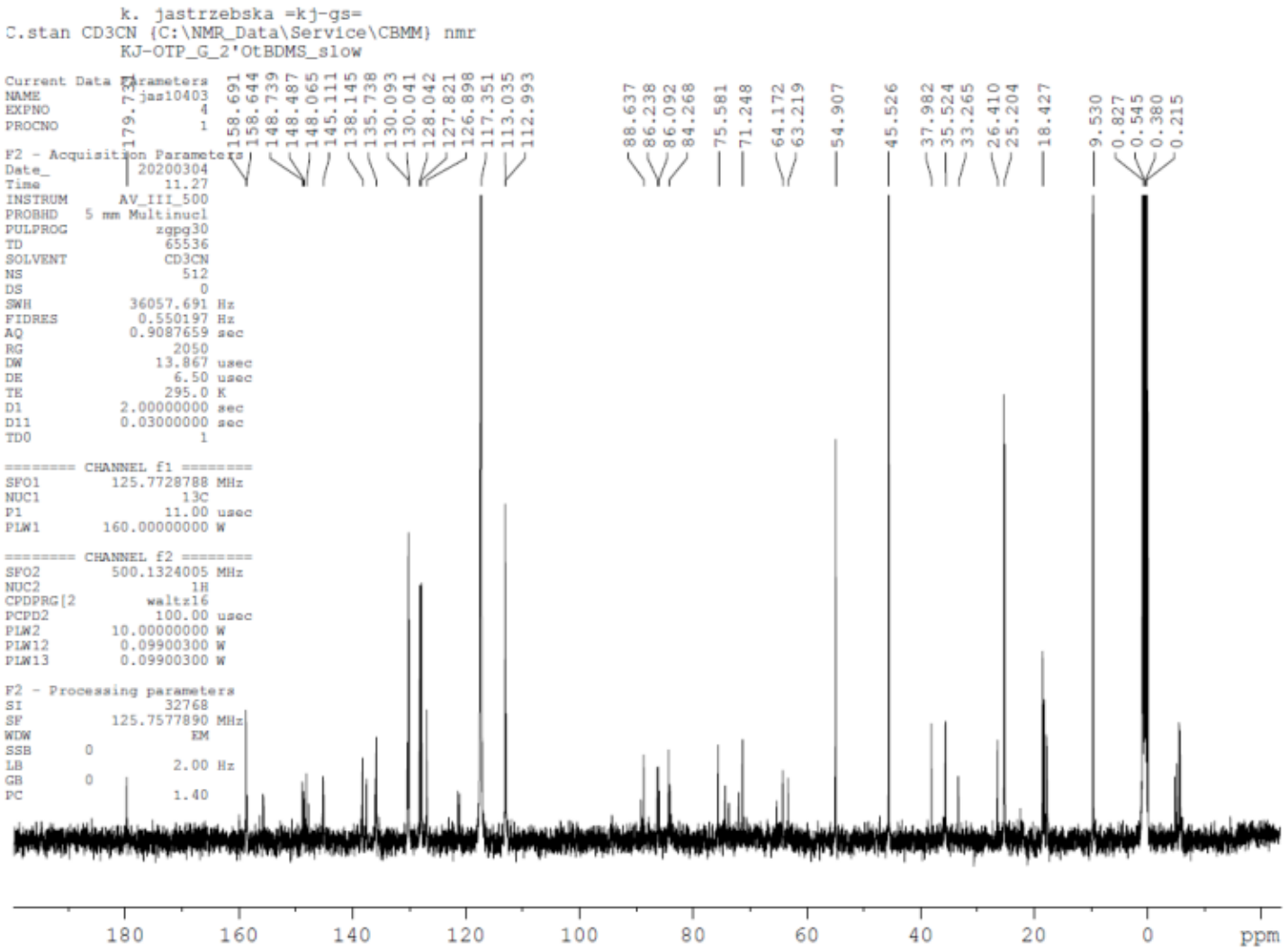
Fast-eluting ^{T}C-OTP; δ (ppm, CD_3CN): 162.80, 158.94, 144.53, 144.18, 135.26, 135.14, 133.43, 132.91, 130.44, 130.37, 128.64, 128.47, 128.10, 128.01, 127.28, 117.35, 113.20, 96.28, 90.84, 87.04, 80.26, 80.21, 79.94, 75.24, 74.71, 74.66, 69.08, 61.10, 59.99, 54.93, 45.92, 36.21, 35.93, 35.88, 25.14, 24.85, 23.69, 23.14, 20.18, 17.74, 13.54, 8.09.



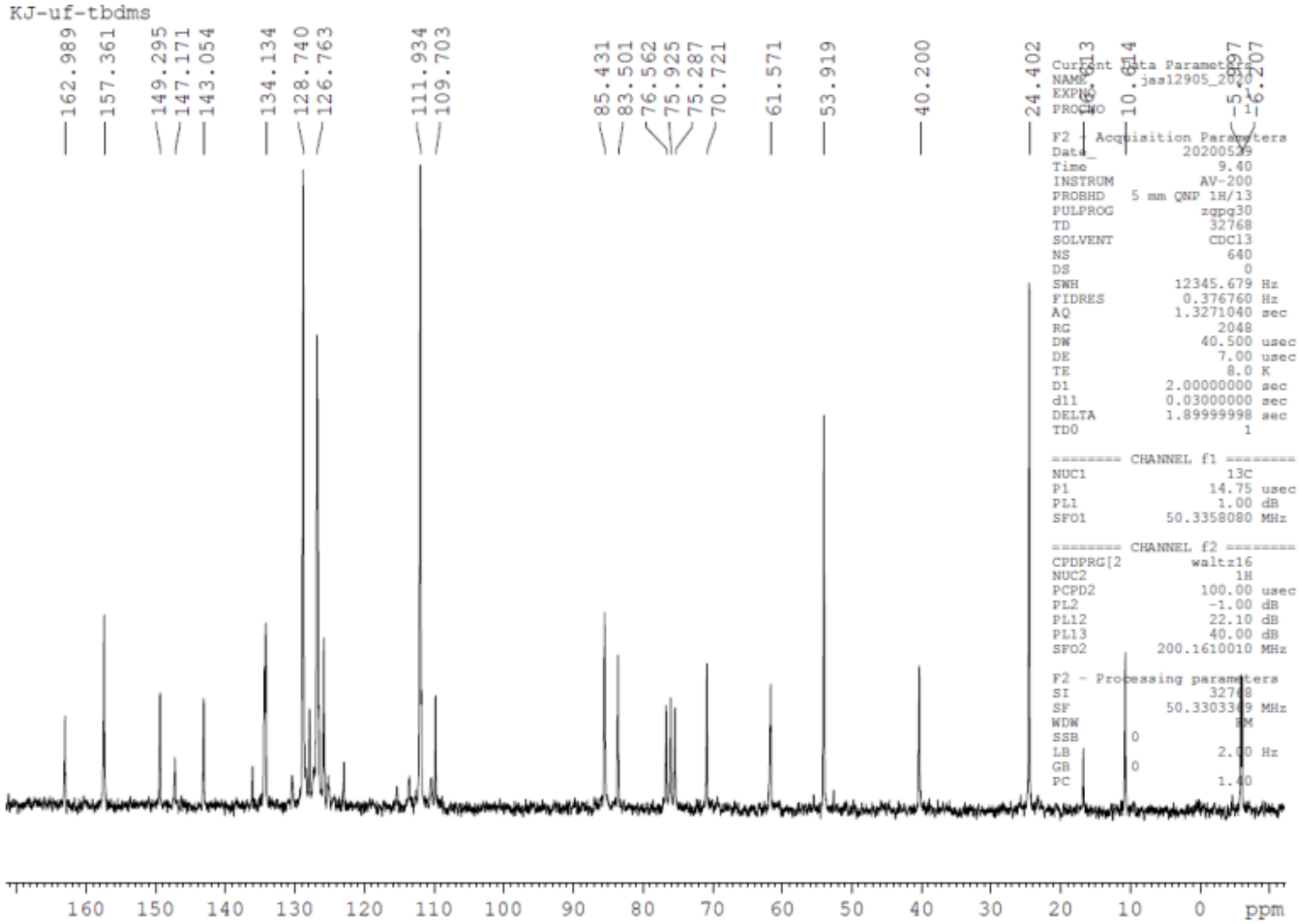
Slow-eluting ^{T}C-OTP; δ (ppm, CD_3CN): 162.81, 158.89, 144.42, 144.26, 135.39, 135.23, 133.41, 132.95, 130.27, 130.22, 128.66, 128.30, 128.12, 128.03, 127.21, 117.35, 113.21, 96.51, 90.19, 87.07, 79.16, 75.48, 75.42, 75.01, 69.72, 61.32, 54.96, 36.97, 35.83, 25.22, 24.84, 23.90, 23.32, 17.76.



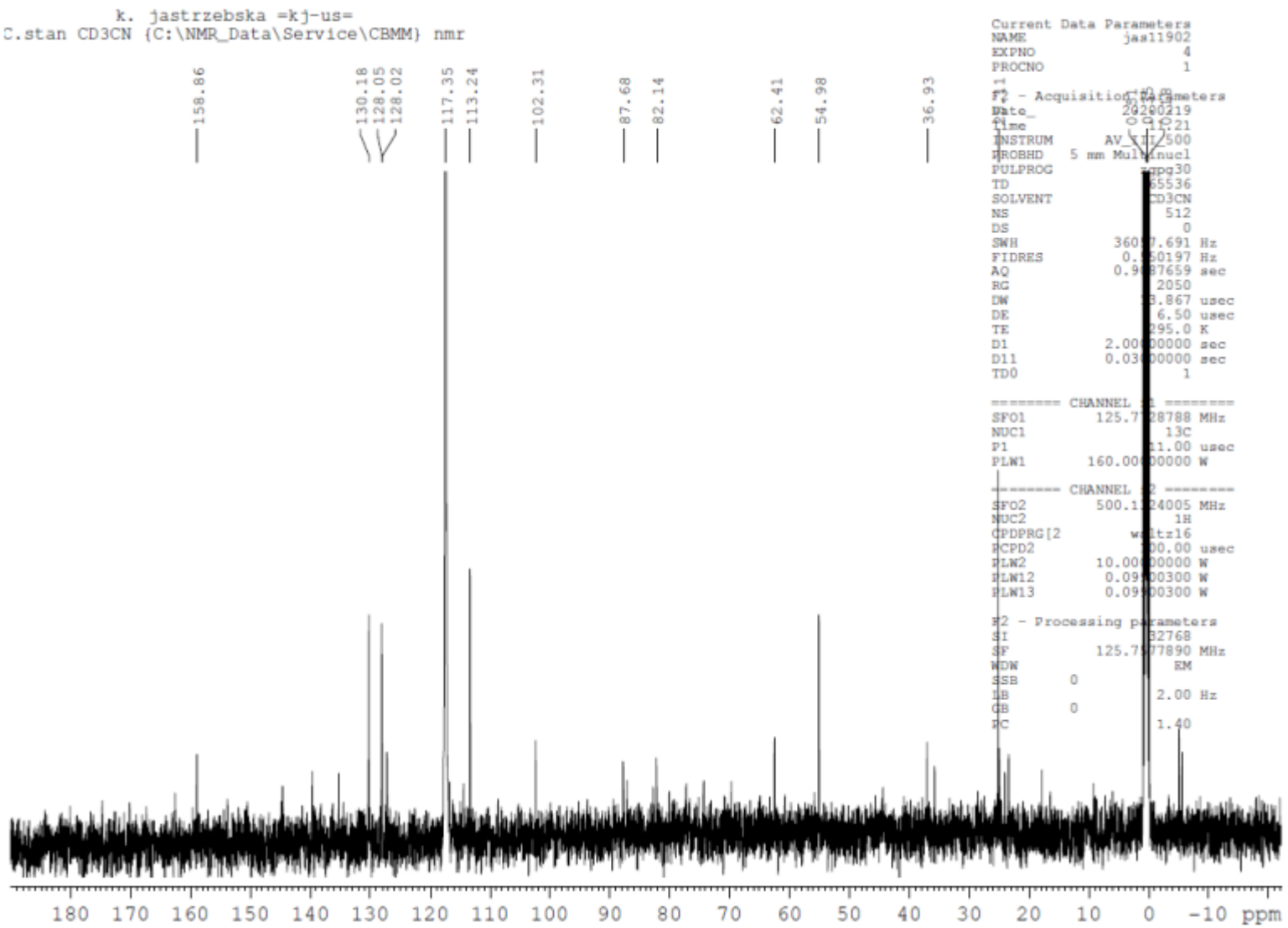
Fast-eluting ^{T}G-OTP; δ (ppm, CD_3CN): 172.18, 158.60, 152.27, 144.41, 143.32, 135.45, 134.00, 132.94, 129.46, 128.70, 113.34, 87.93, 86.84, 83.00, 74.35, 68.81, 62.64, 55.24, 37.00, 36.58, 25.52, 23.74, 17.88, 11.21.



Slow-eluting ^{T}G-OTP; δ (ppm, CD_3CN): 179.73, 158.64, 148.74, 148.49, 148.07, 145.11, 138.15, 135.74, 130.09, 130.04, 128.04, 127.82, 126.90, 117.35, 113.04, 112.99, 88.64, 86.24, 86.09, 84.27, 75.58, 71.25, 64.17, 63.22, 54.91, 45.53, 37.98, 35.52, 33.27, 26.41, 25.20, 18.43, 9.53.



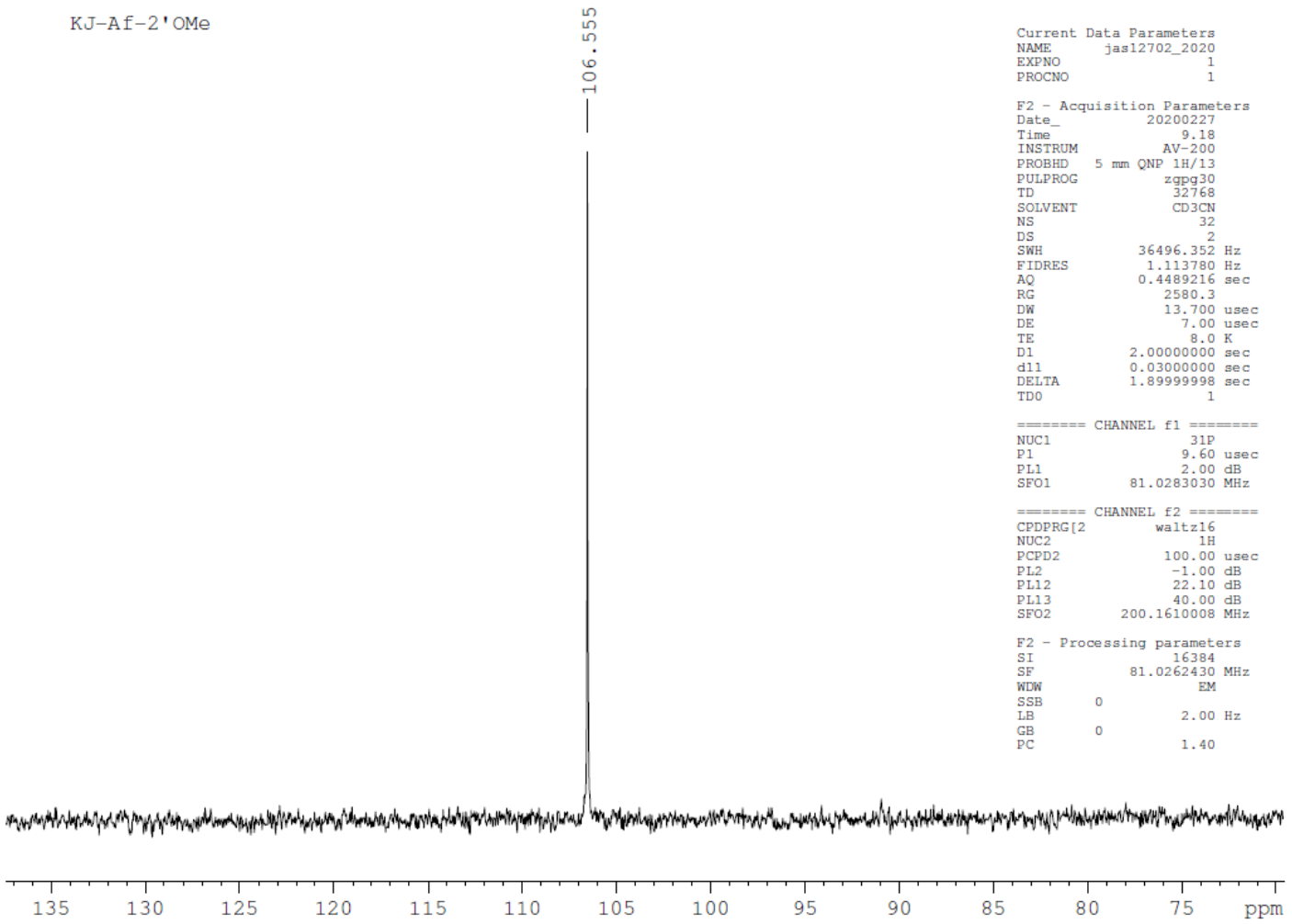
Fast-eluting ^{T}U-OTP; δ (ppm, CD_3CN): 162.99, 157.36, 149.30, 147.17, 143.05, 134.13, 128.74, 126.76, 111.93, 109.70, 85.43, 83.50, 76.56, 75.93, 75.29, 70.72, 61.57, 53.92, 40.20, 24.40, 16.61, 10.61.



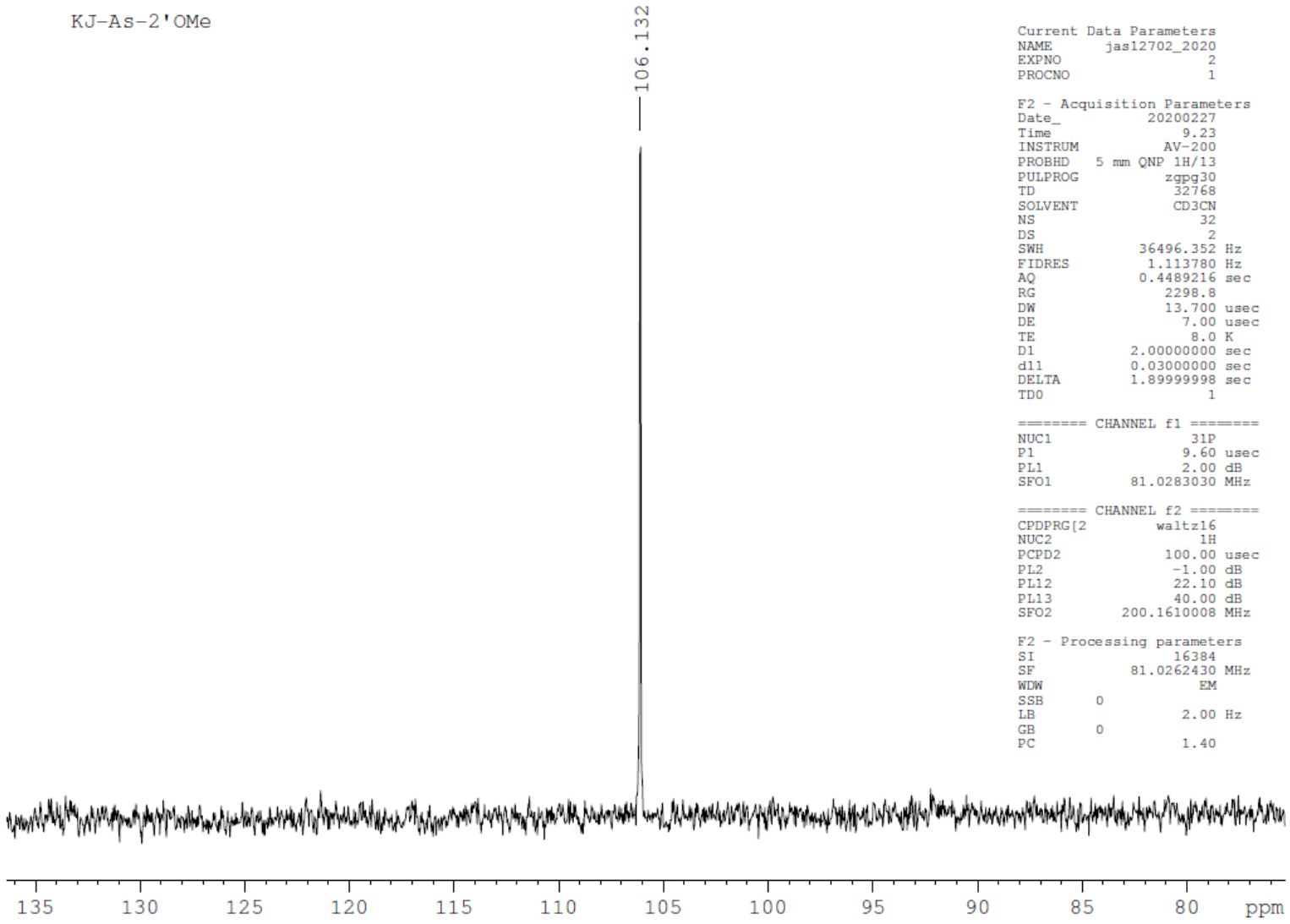
Slow-eluting ^{T}U-OTP; δ (ppm, CD_3CN): 162.13, 158.86, 145.23, 140.33, 135.27, 130.18, 128.05, 128.02, 117.35, 112.24, 102.31, 87.68, 82.14, 62.41, 54.98, 36.93, 25.11, 23.76, 22.80, 18.21, 9.87.

^{31}P NMR spectra for separated P-diastereomers of ^{M}N-OTP and ^{T}N-OTP monomers.

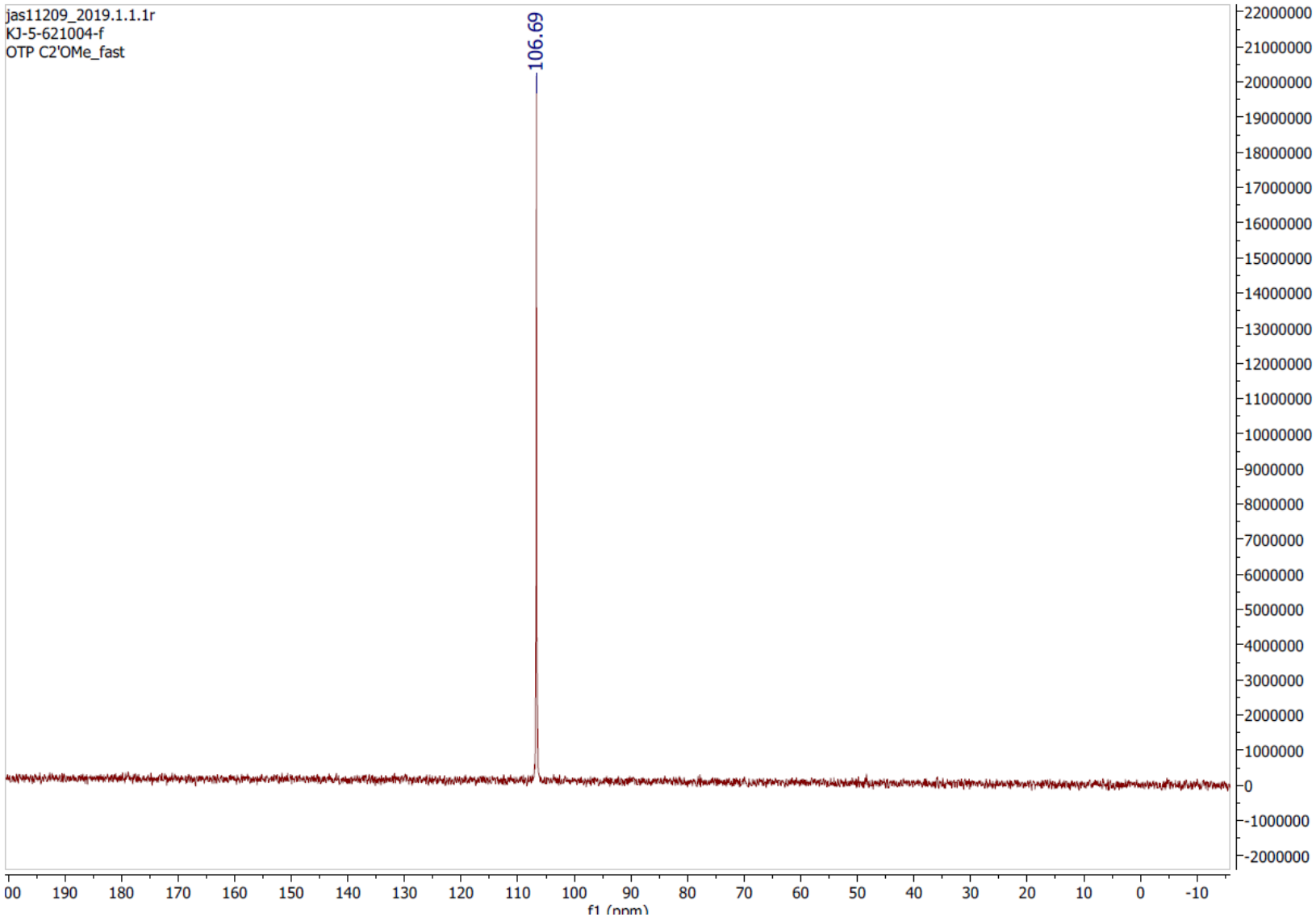
Figure S6. ^{31}P NMR spectra for separated P-diastereomers of ^{M}N-OTP and ^{T}N-OTP monomers.



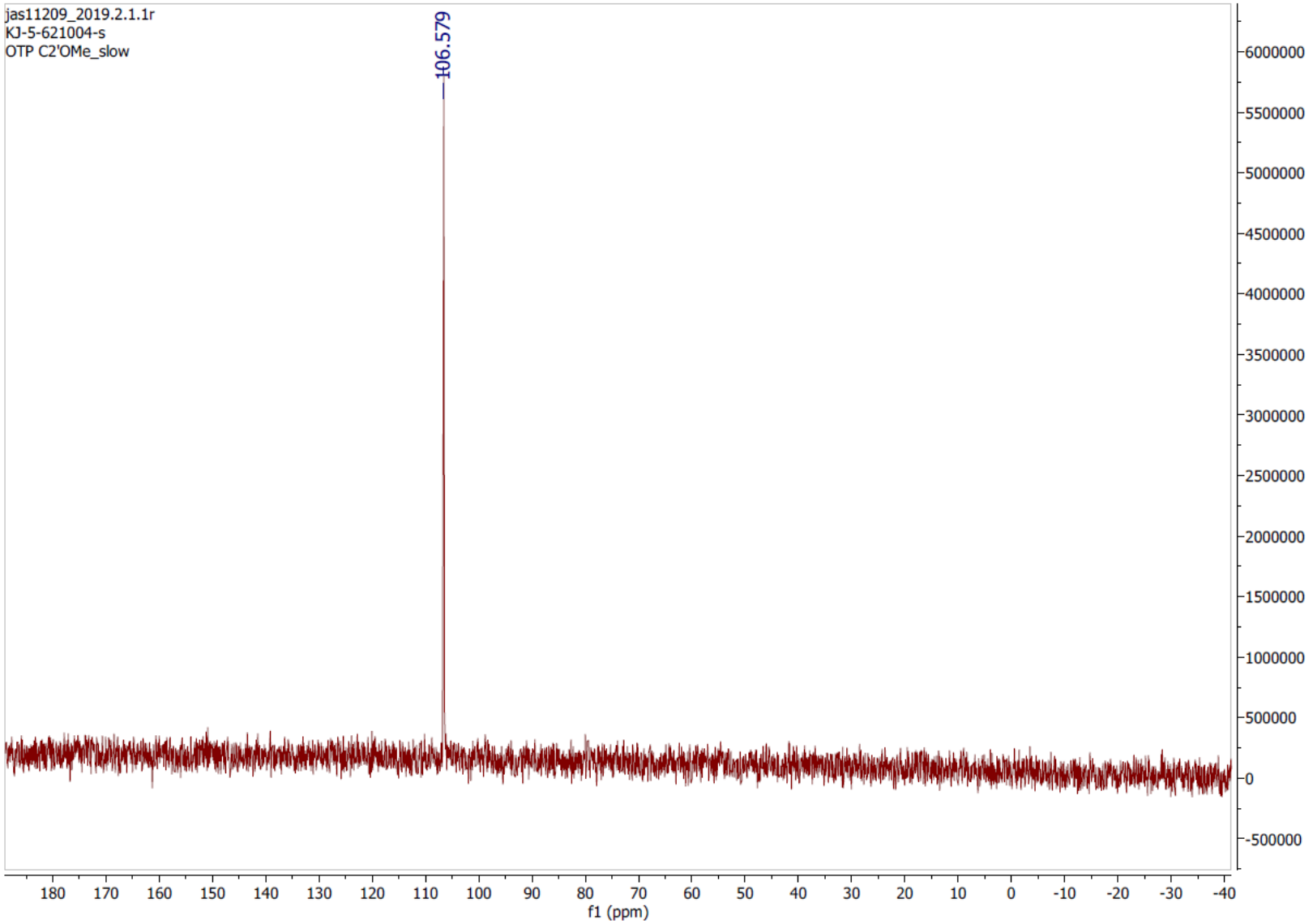
Fast-eluting ^{M}A-OTP in CD_3CN; δ (ppm)



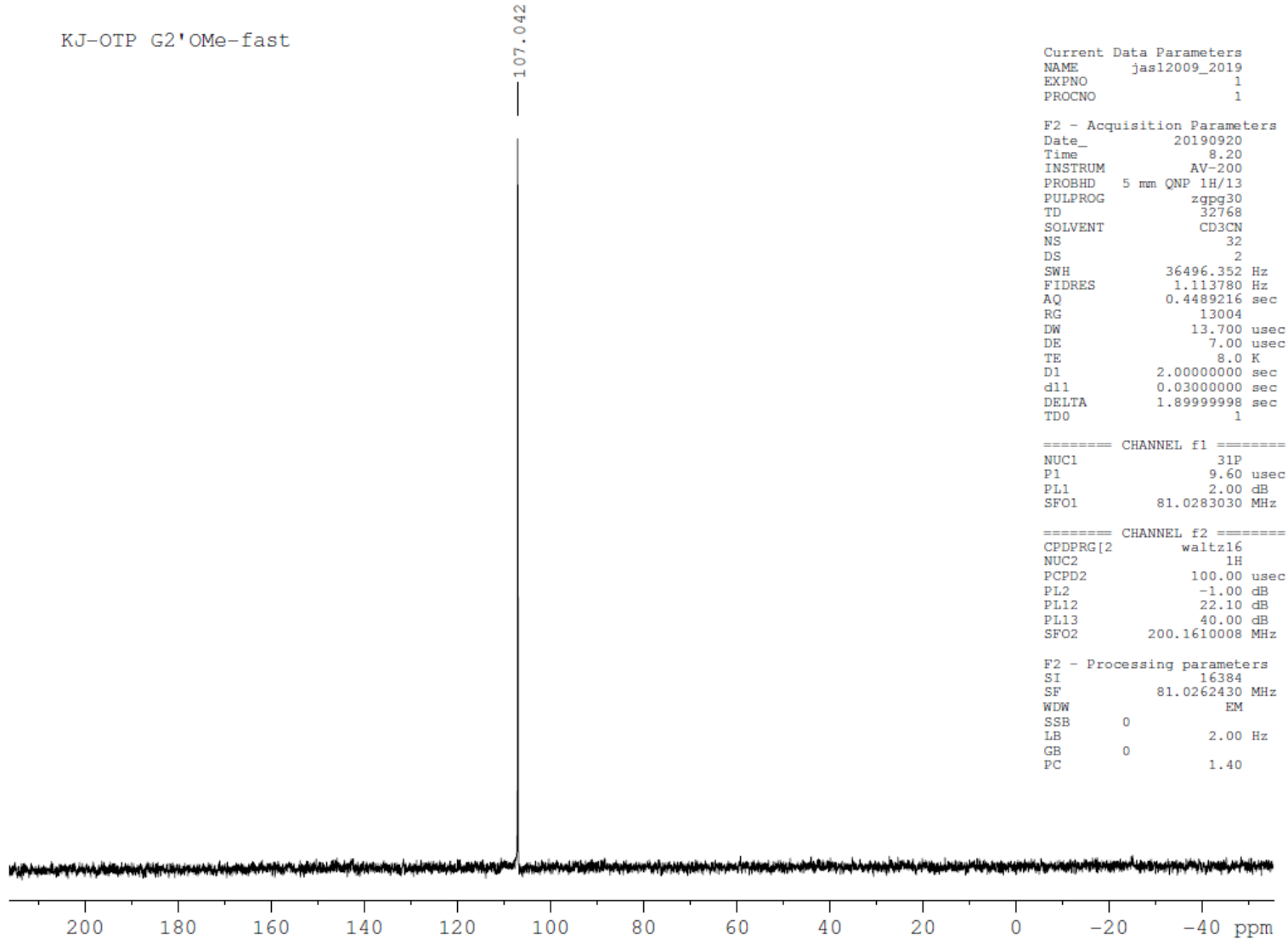
Slow-eluting ^{M}A-OTP in CD_3CN; δ (ppm)



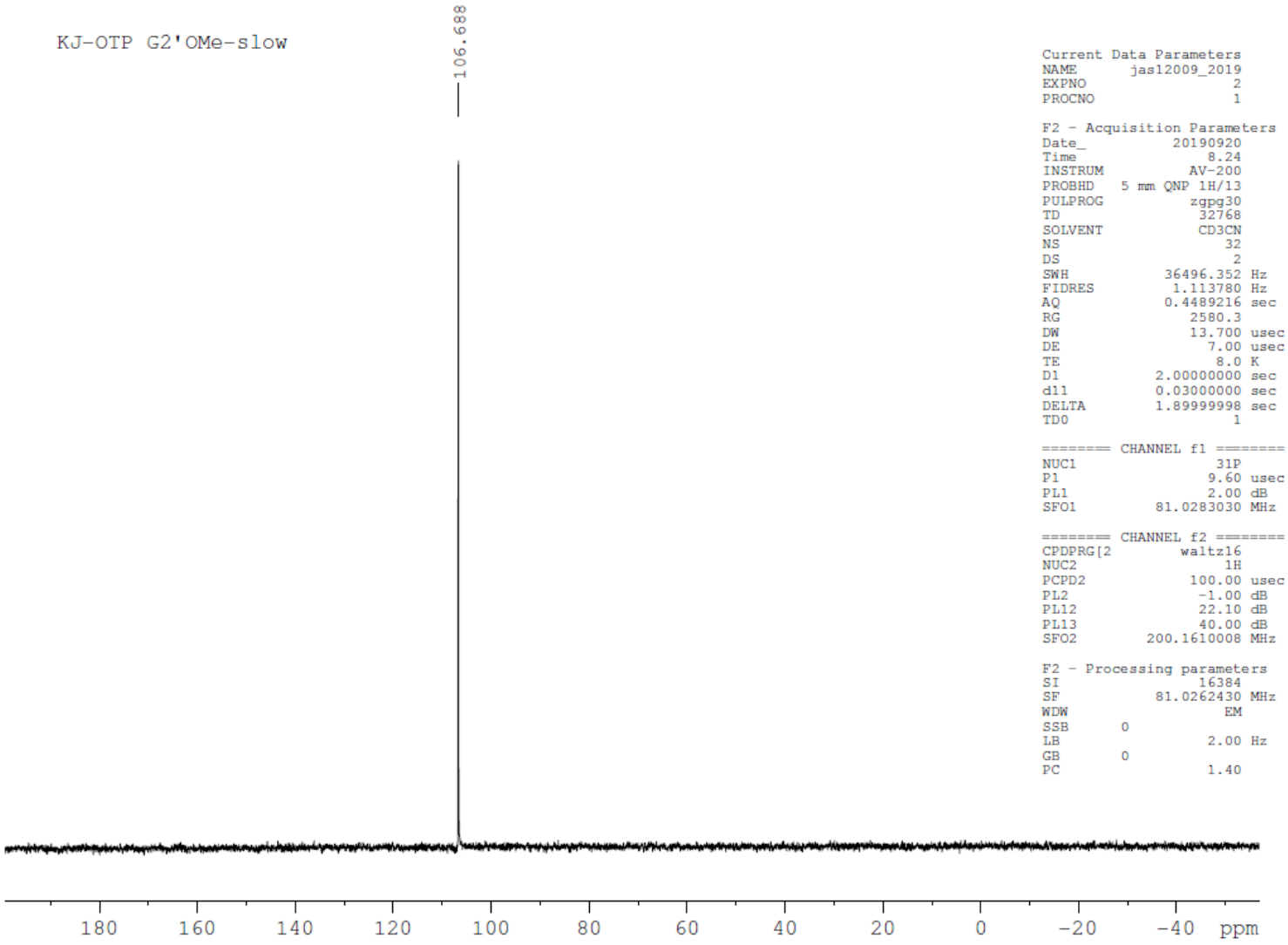
Fast-eluting ^{M}C-OTP in CD_3CN; δ (ppm)



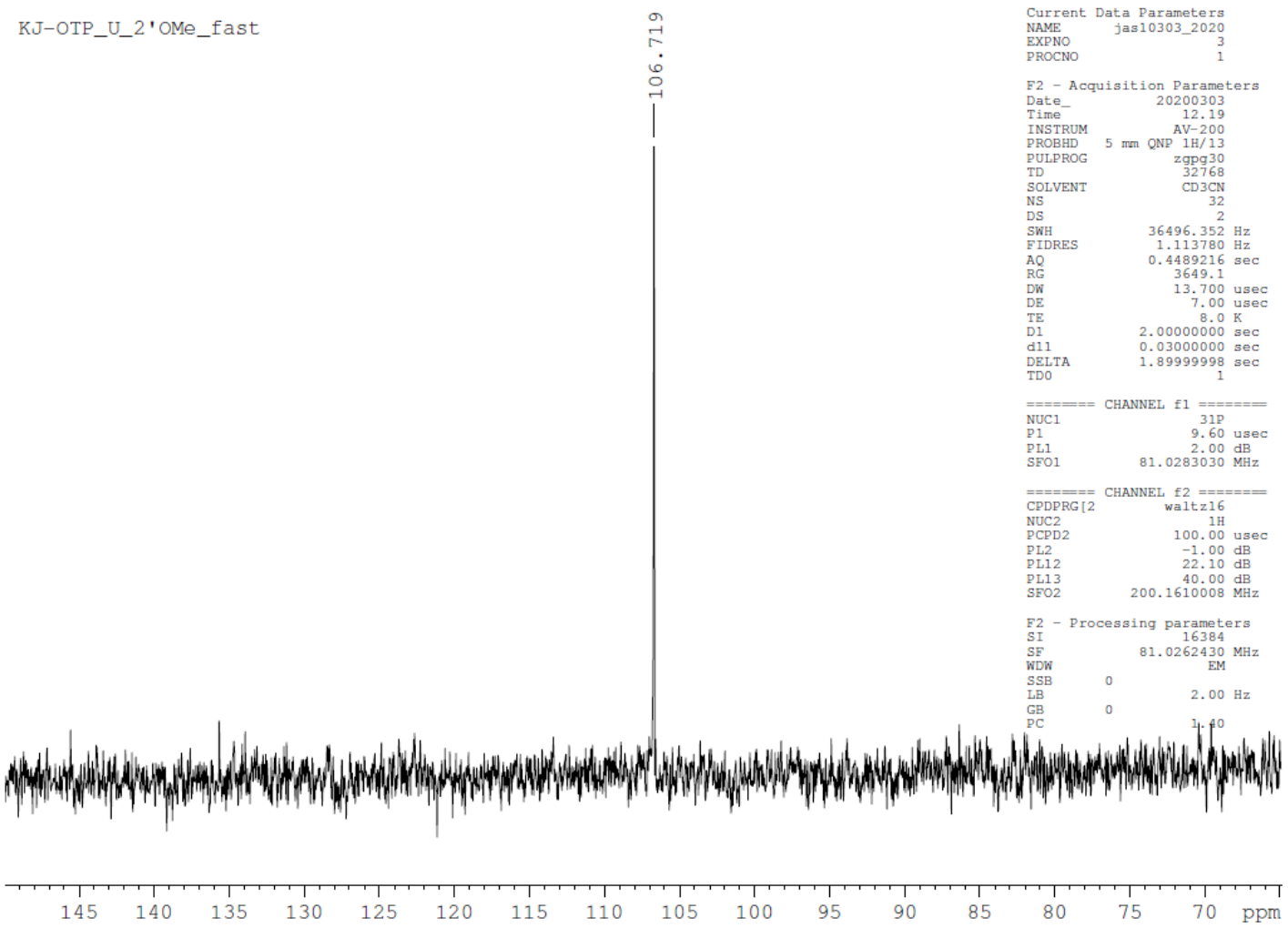
Slow-eluting ^{M}C-OTP in CD_3CN; δ (ppm)



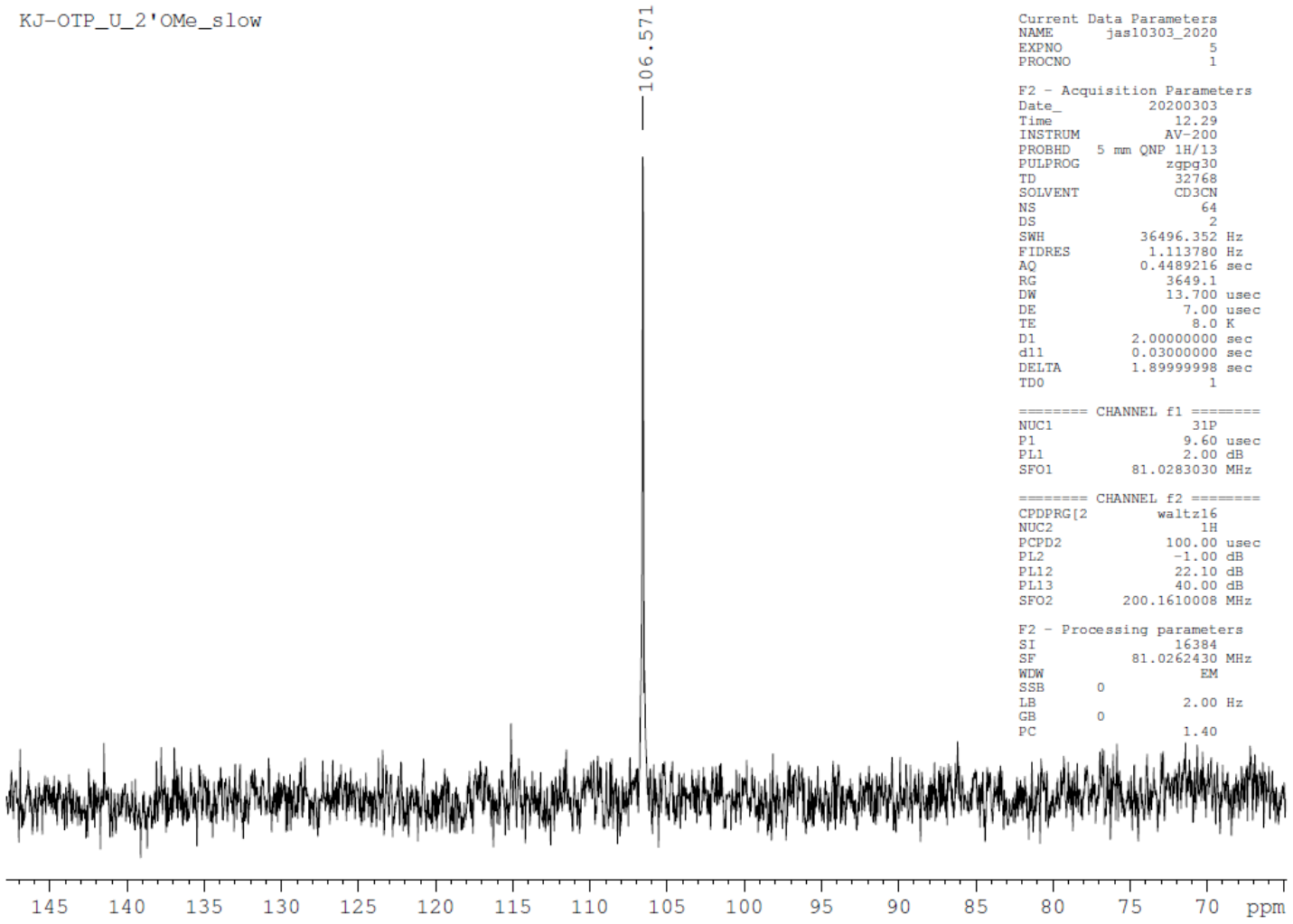
Fast-eluting ^{M}G-OTP in CD_3CN; δ (ppm)



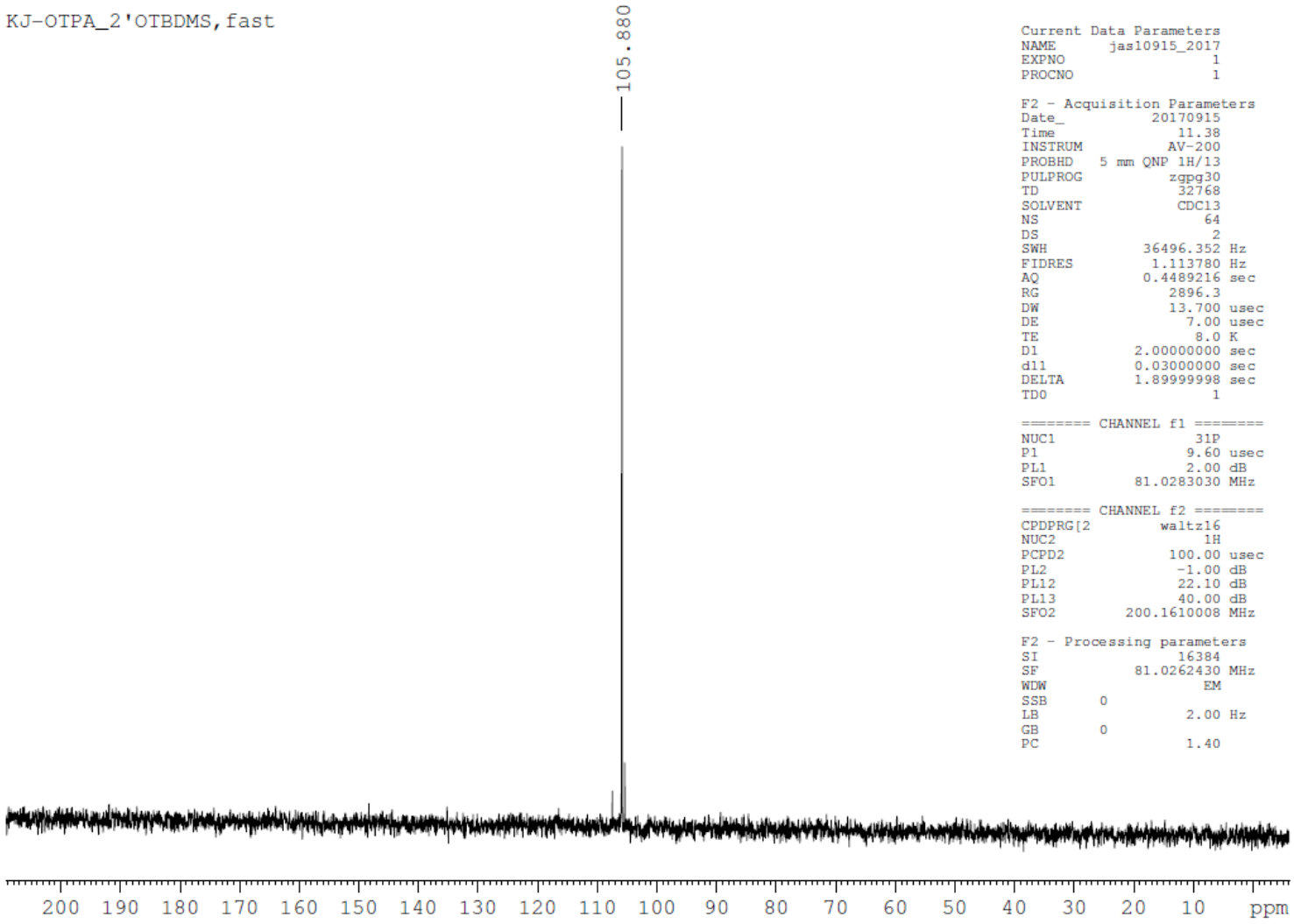
Slow-eluting ^{M}G-OTP in CD_3CN; δ (ppm)



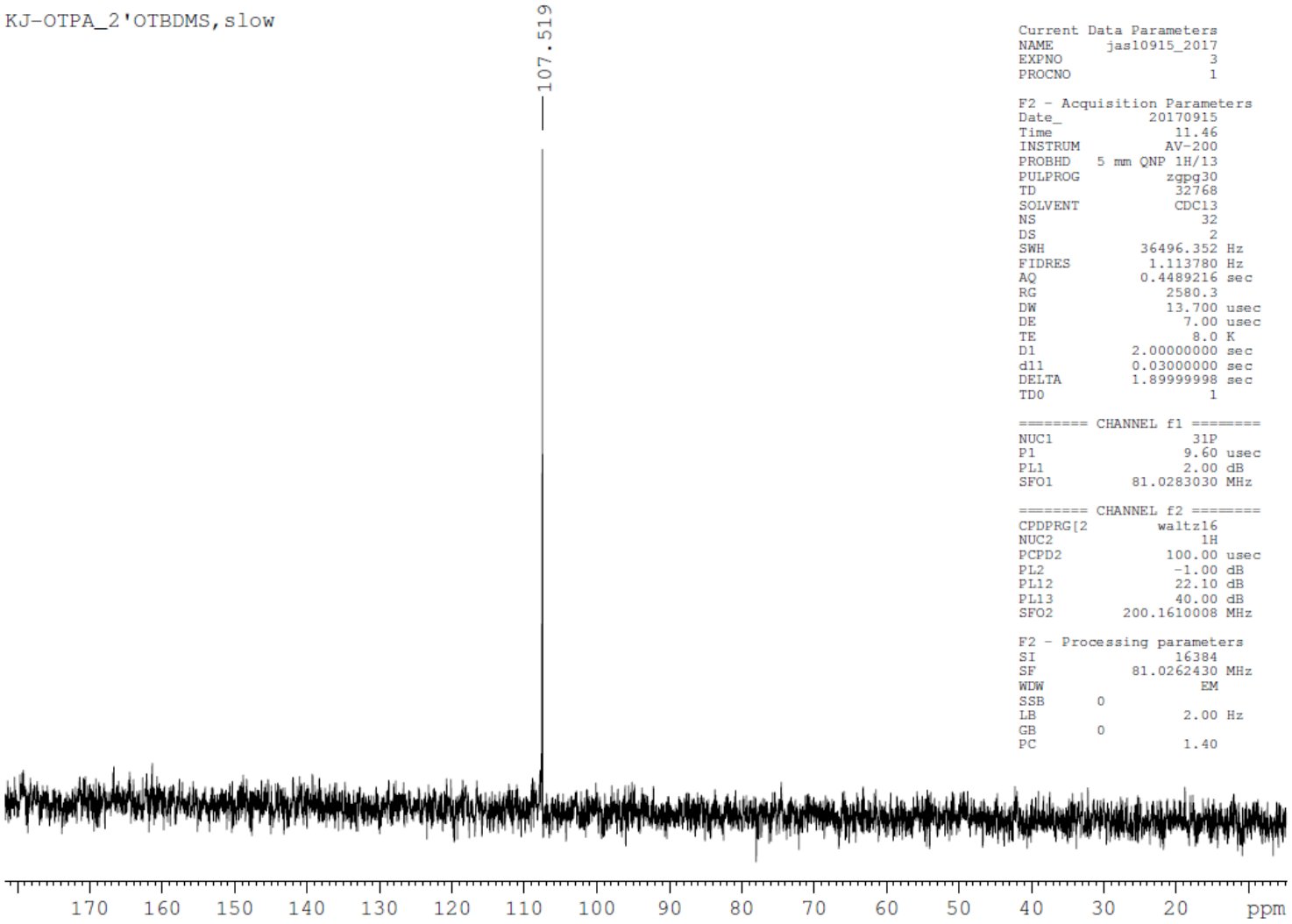
Fast-eluting ^{M}U-OTP in CD_3CN; δ (ppm)



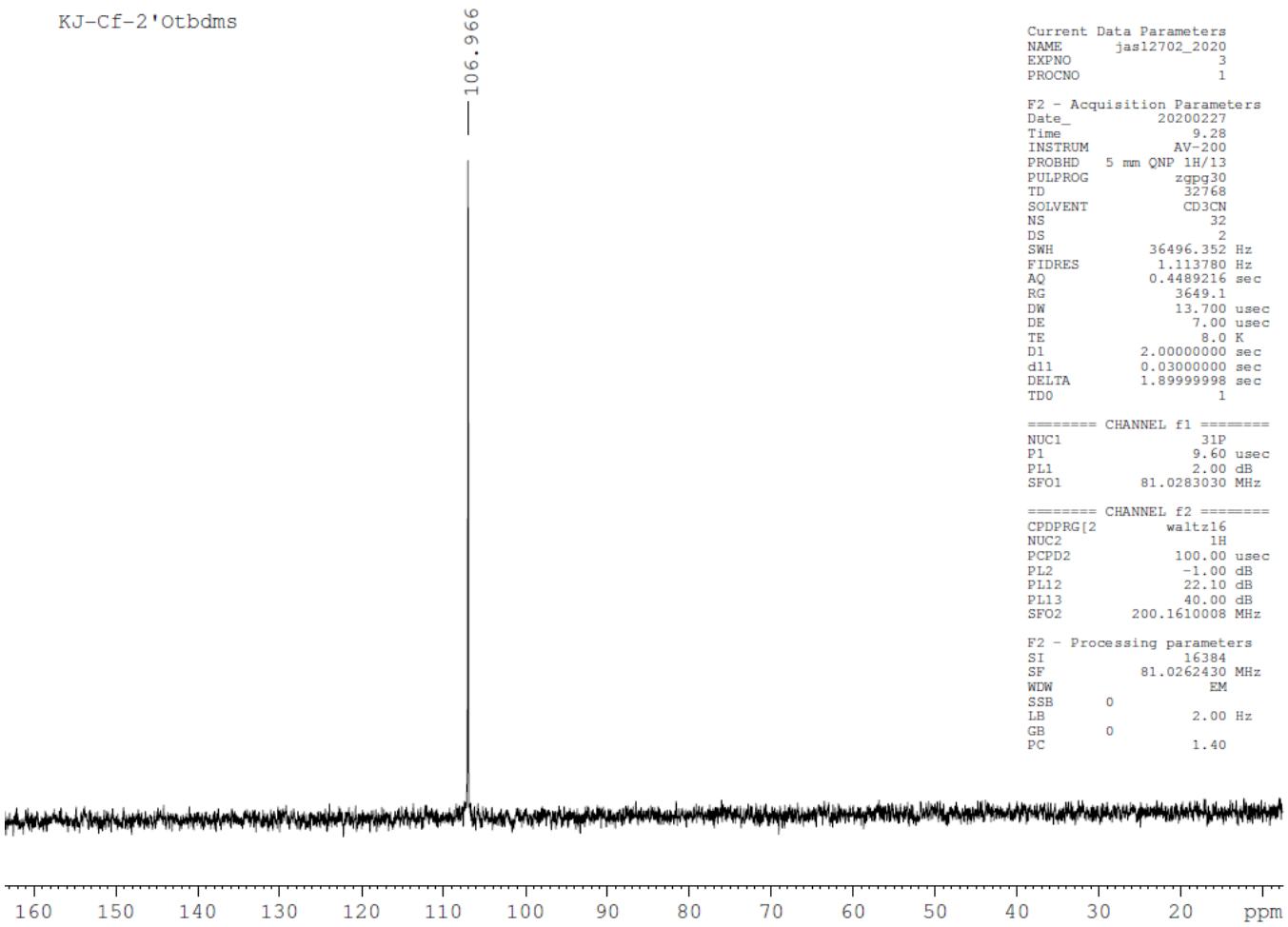
Slow-eluting ^{M}U-OTP in CD_3CN; δ (ppm)



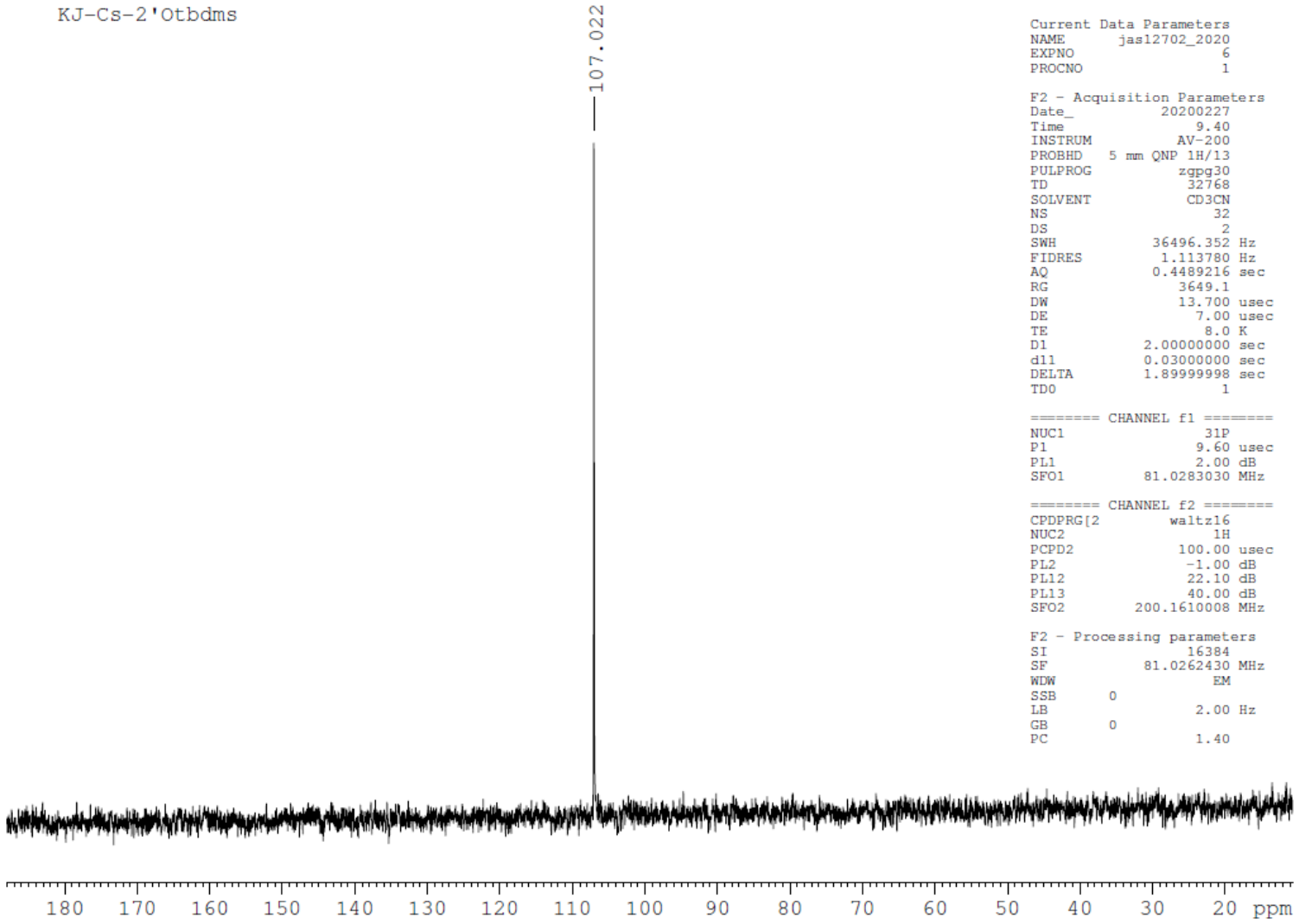
Fast-eluting ^{T}A-OTP in CD_3CN; δ (ppm)



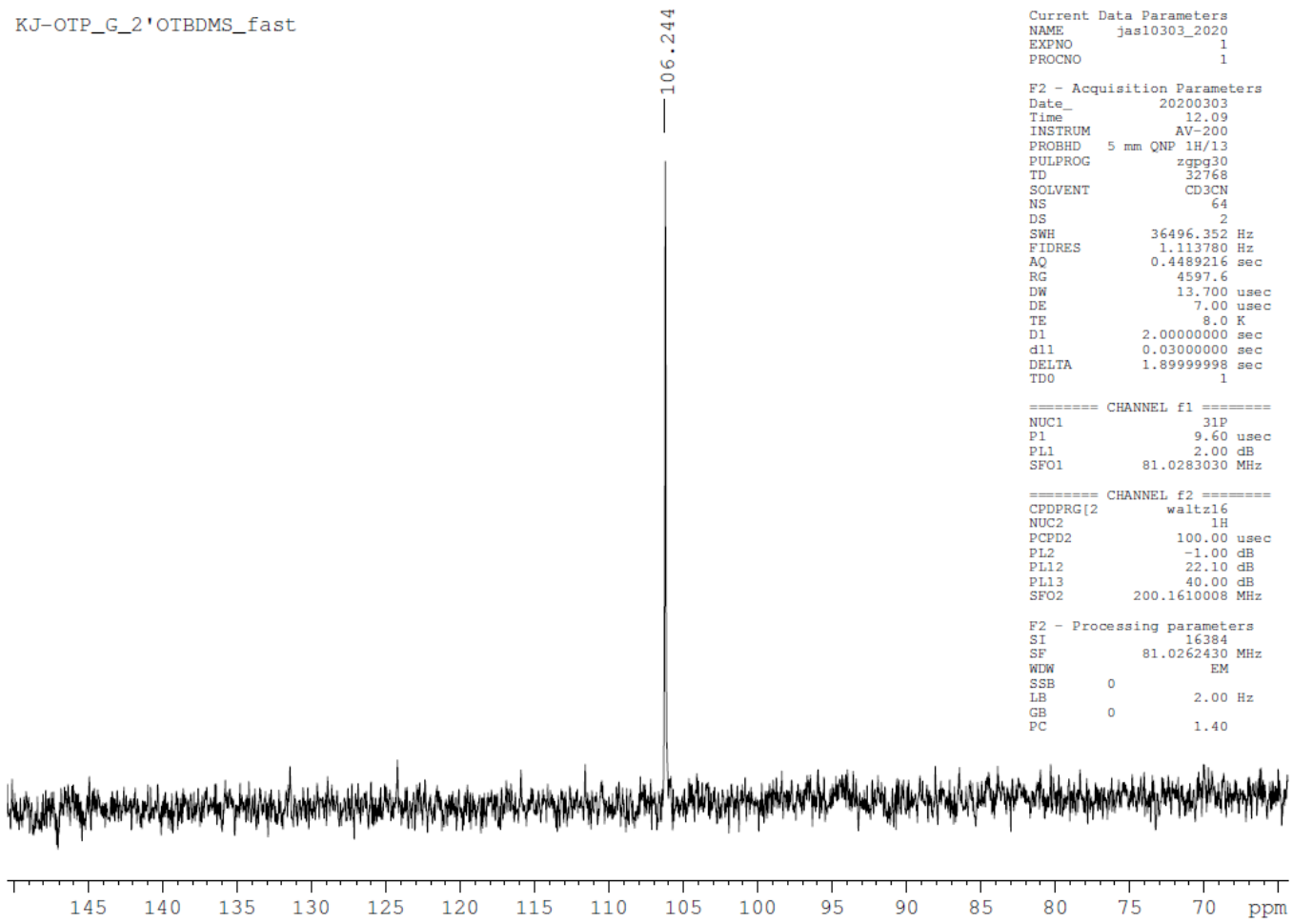
Slow-eluting ^{T}A-OTP in CD_3CN; δ (ppm)



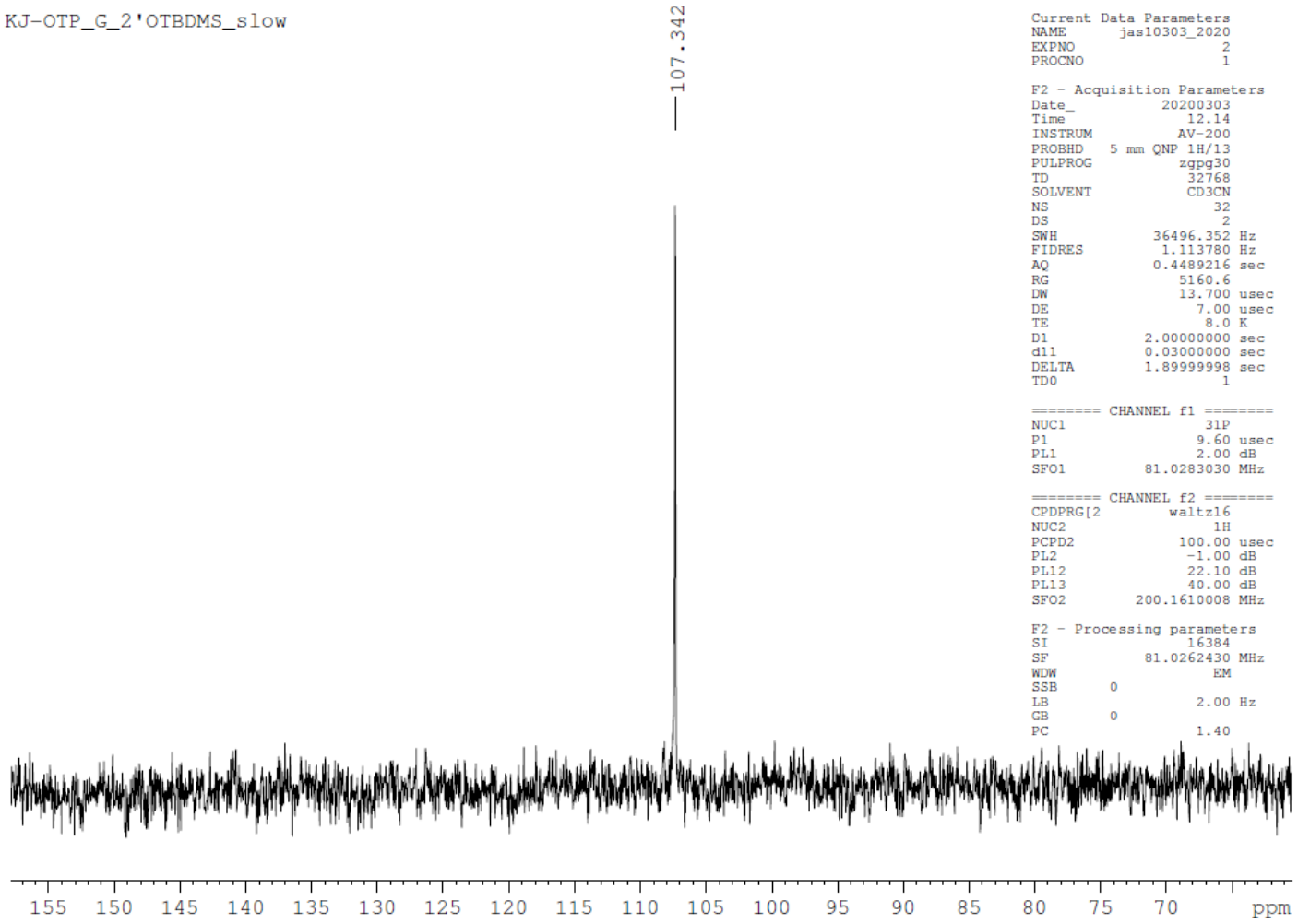
Fast-eluting ^{T}C-OTP in CD_3CN; δ (ppm)



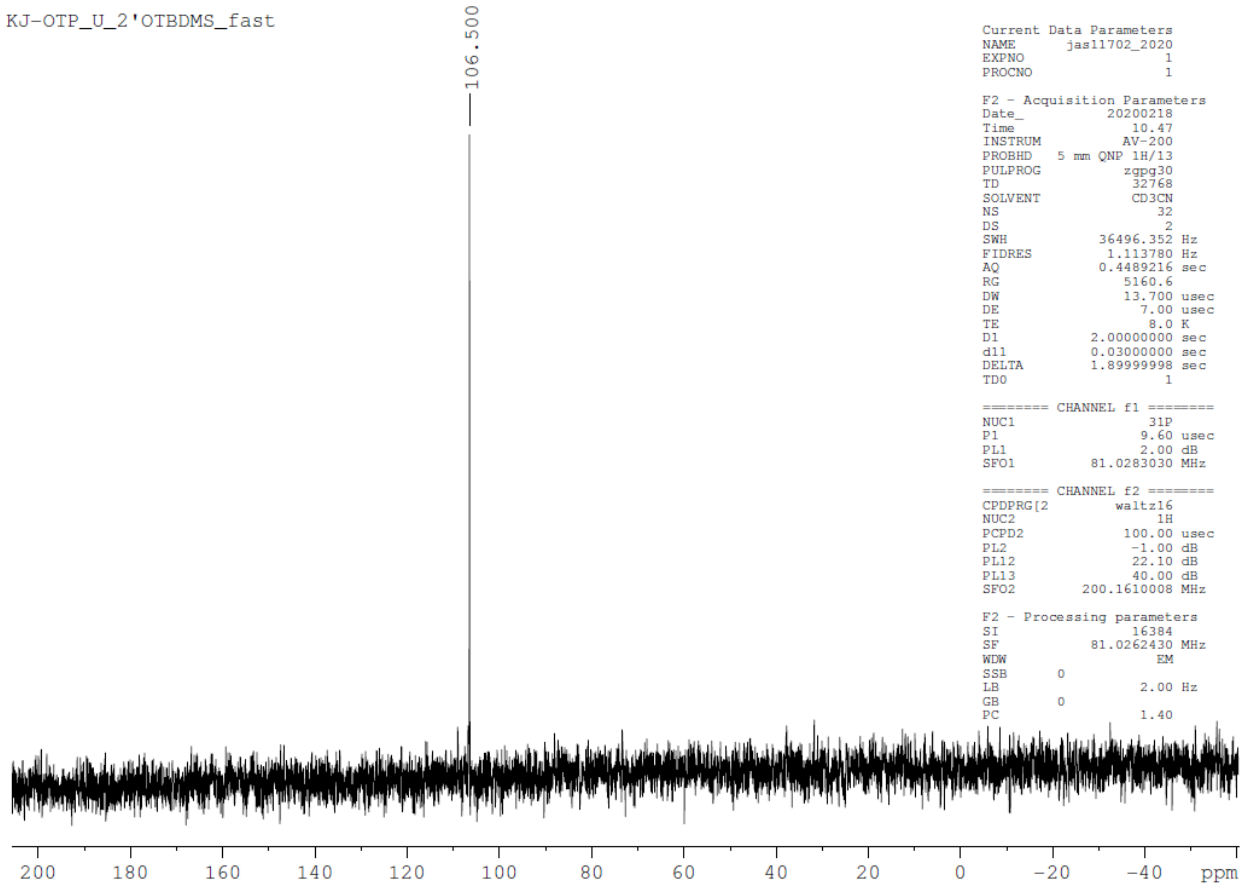
Slow-eluting ^{T}C-OTP in CD_3CN; δ (ppm)



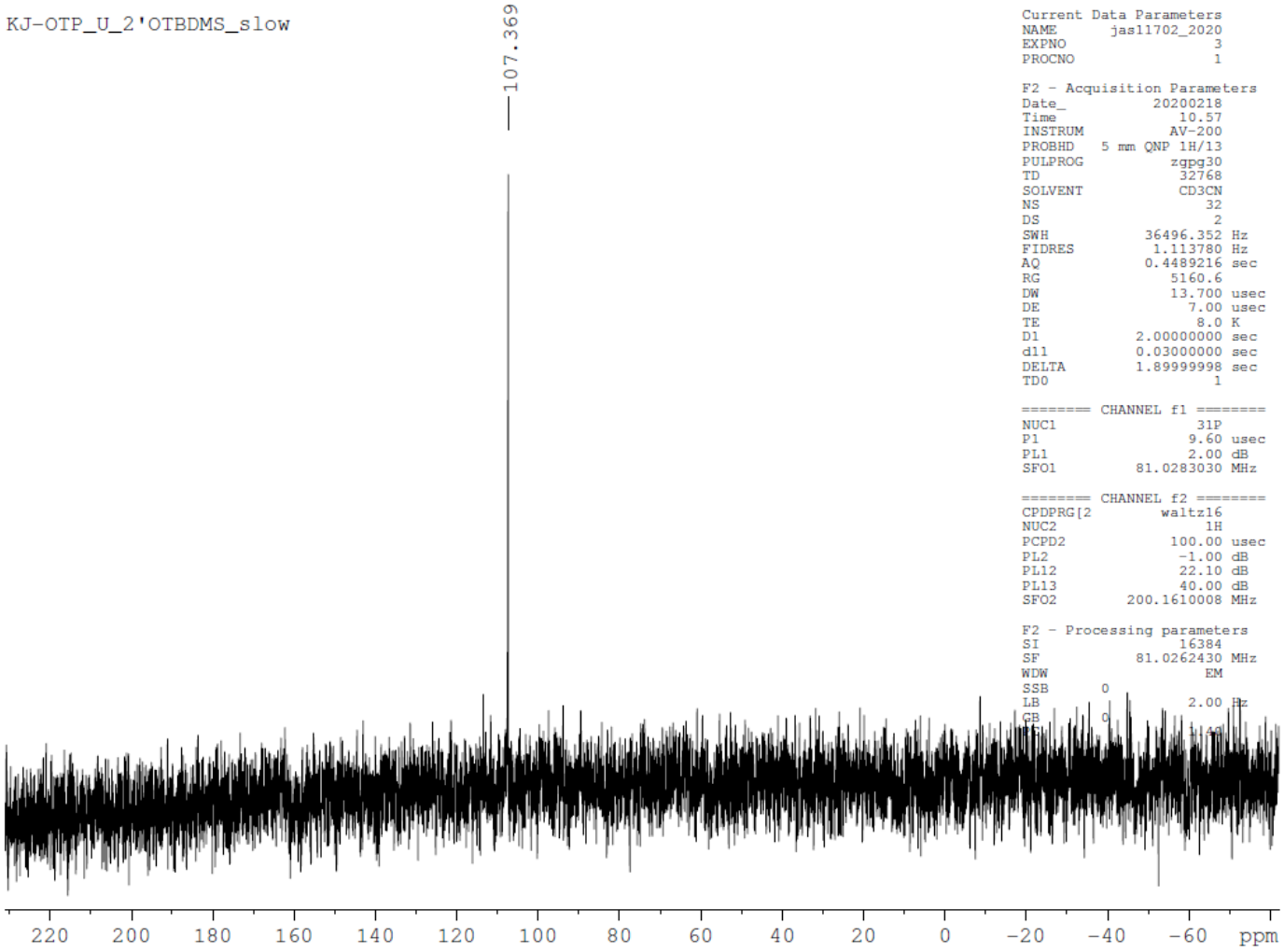
Fast-eluting ^{T}G-OTP in CD_3CN; δ (ppm)



Slow-eluting ^{T}G-OTP in CD_3CN; δ (ppm)



Fast-eluting ^{T}U-OTP in CD_3CN; δ (ppm)



Slow-eluting ^{T}U-OTP in CD_3CN; δ (ppm)

Crystallography of the detritylated *fast*-eluting 3a monomer.

Details of X-ray Data Collection and Reduction.

X-ray quality crystals of detritylated fast-eluting **3a** (colorless transparent plates) were grown by recrystallization from a mixture of ethyl acetate and methanol (4:1 v/v). A suitable crystal with a size of 0.11 × 0.08 × 0.02 mm was selected and mounted on a suitable support. Data were collected using an XtaLAB Synergy, Dualflex, HyPix diffractometer at T = 100.00(10) K. Data were measured with ω scans of 0.5° per frame for 1.0/0.5 s using CuK_α radiation. The maximum resolution that achieved was Θ = 78.431° (0.79 Å). The total number of runs and images was based on the strategy calculation of the program *CrysAlisPro* (Rigaku, v1.171.41.86a, 2020), and the unit cell was refined using *CrysAlisPro* based on 3835 reflections, 2% of the observed reflections.

Data reduction, scaling and absorption corrections were performed with *CrysAlisPro*. The final completeness is 99.80 % out to 78.431° in Θ. Numerical absorption correction based on Gaussian integration over a multifaceted crystal model was performed witk *CrysAlisPro*. The empirical absorption correction was calculated using spherical harmonics as implemented in SCALE3 ABSPACK. The absorption coefficient μ of this material is 2.567 mm^{-1} at this wavelength (λ = 1.542 Å) and the minimum and maximum transmissions are 0.761 and 1.000, respectively.

The structure was solved and the space group $P2_1$ (# 4) was determined with the structure solution program *XT* (Sheldrick, 2015) using intrinsic phasing with *Olex2* (Bourhis et al., 2015) as a graphical interface and refined by least squares with version 2018/3 of *ShelXL* (Sheldrick, 2015). All non-hydrogen atoms were refined anisotropically. The positions of the hydrogen atoms were calculated geometrically and refined using the riding model. The final structure was validated using CheckCif (http://checkcif.iucr.org) and deposited in the Cambridge Crystallographic Data Centre (CCDC) under accession number 2063388. Data acquisition, processing, and refinement statistics are shown in Table S1.

References

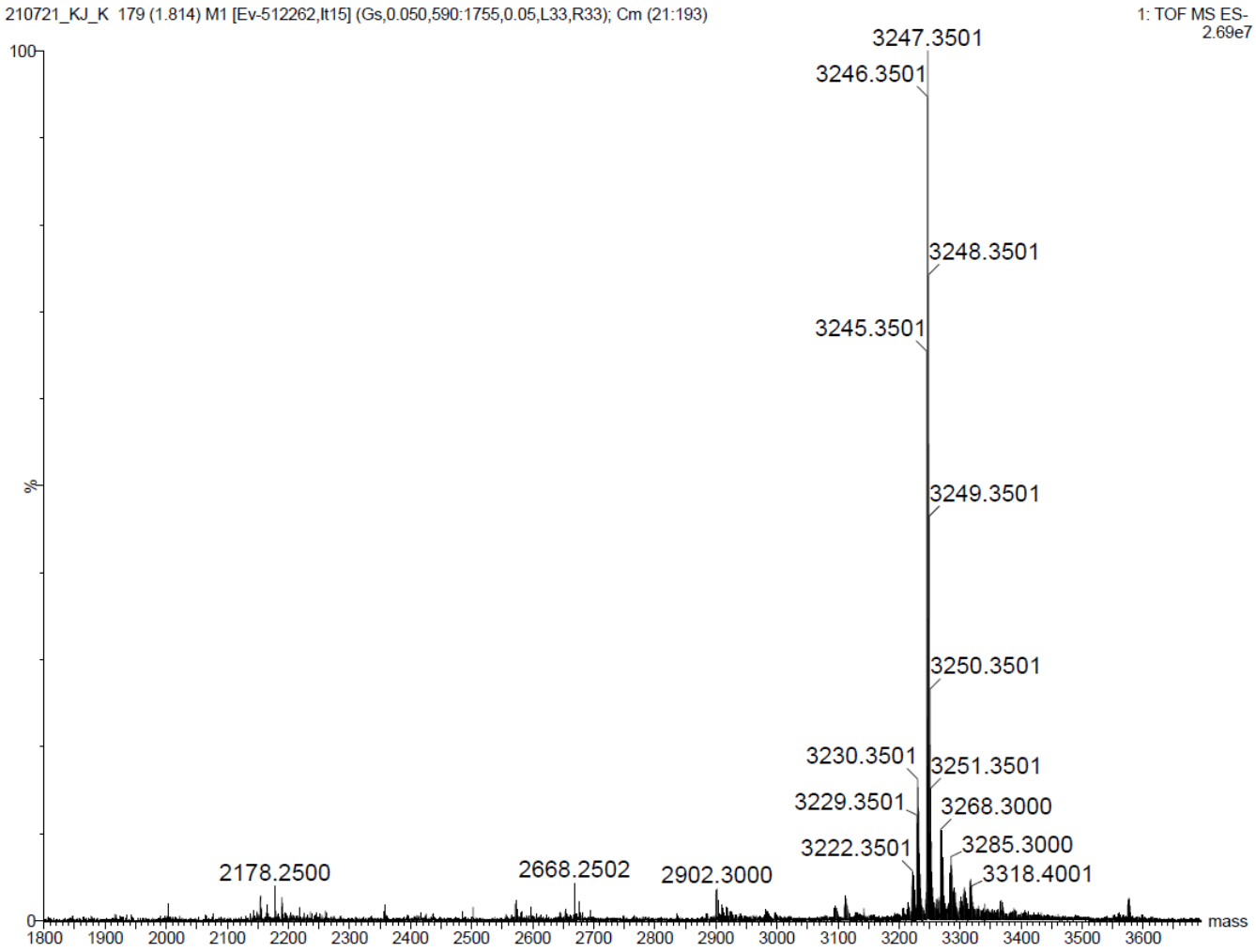
1. Sheldrick GM (2015) SHELXT - Integrated space-group and crystal-structure determination. *Acta Crystallogr A Found Adv.* **71**, 3–8.
2. Bourhis LJ, Dolomanov OV, Gildea RJ, Howard JAK, Puschmann H (2015) The anatomy of a comprehensive constrained, restrained refinement program for the modern computing enviroment -Olex2 dissected. *Acta Crystallogr A Found Adv.* **71**, 59–75.
3. Sheldrick GM (2015) Crystal structure refinement with SHELXL. *Acta Crystallogr C Struct Chem*. **71**, 3–8.

Table S1. The data-collection, processing and refinement statistics.

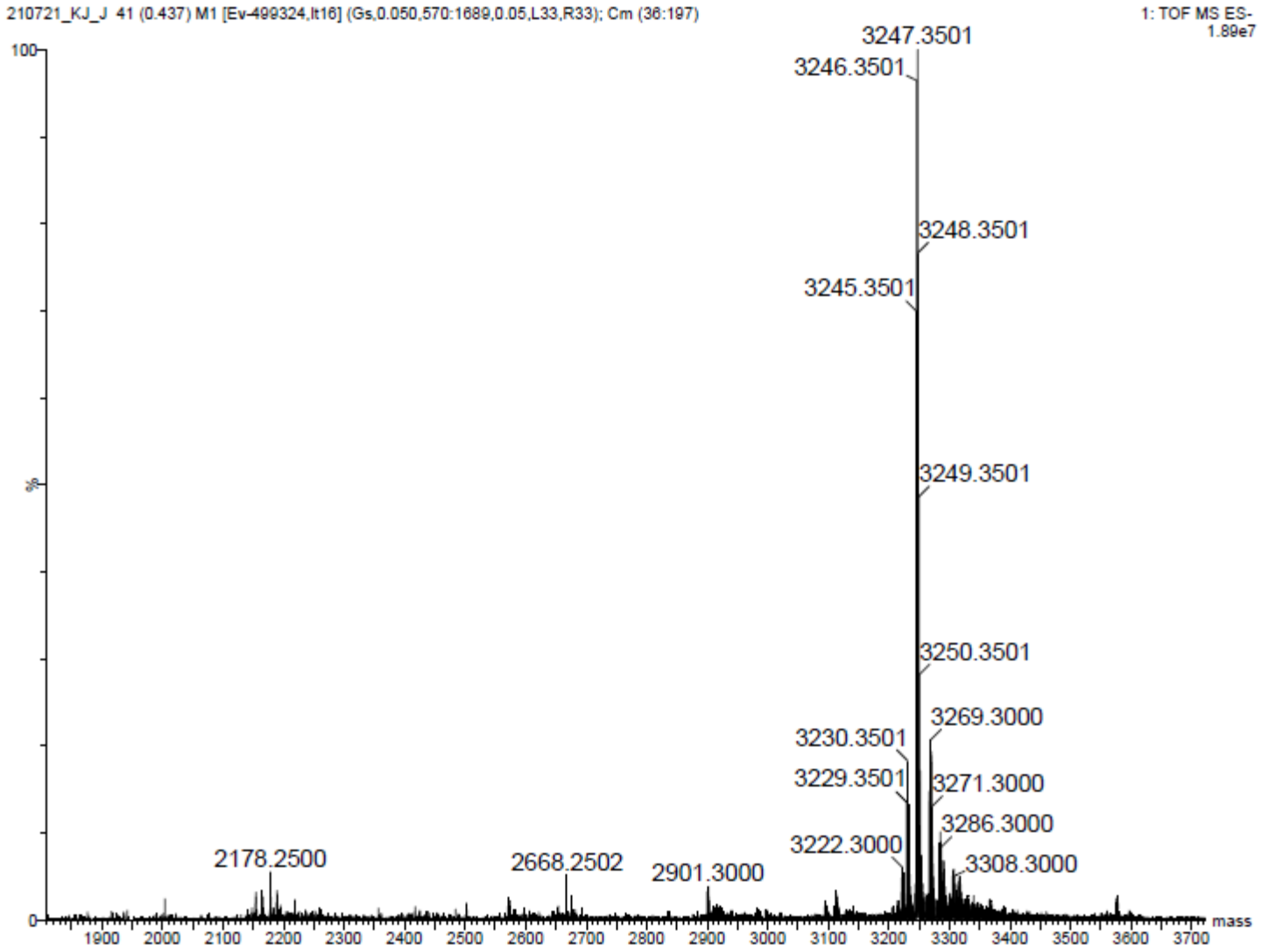
Compound	**detritylated *fast*-eluting 3a**
Crystal data	
CCDC	2063388
Chemical formula	$C_{30}H_{44}N_5O_7PS_2Si$
Formula weight	709.88
Crystal system	monoclinic
Space group	$P2_1$
Temperature (K)	100.00(10)
a [Å]	7.02449(6)
b [Å]	39.0527(2)
c [Å]	25.57042(18)
β (°)	89.9888(7)
V [Å^3]	7014.61(8)
Z	8
d_{calc} [g/cm^3]	1.344
Crystal dimensions [mm]	0.11 × 0.08 × 0.02
Radiation type	CuK_α
Wavelength (Å)	1.54184
μ [mm^{-1}]	2.567
Data collection	
Reflections measured	226823
Range/indices (*h*, *k*, *l*)	-8, 7; -49, 49; -32, 32
θ (max, min) [°]	78.431, 2.263
Total no. of unique data	29194
No. of observed data, I > 2σ(I)	27039
R_{int}	0.0802

Refinement	
R [$F^2 > 2\sigma$ (F^2)]	0.0563
$wR(F^2)$	0.1439
S	1.06
No. of reflections	29194
No. of parameters	1811
No. of restraints	358
H-atom treatment	H-atom parameters constrained
$\Delta\rho$ (min, max), e/Å^3	-0.365, 0.956
Absolute structure parameter	-0.006(5)

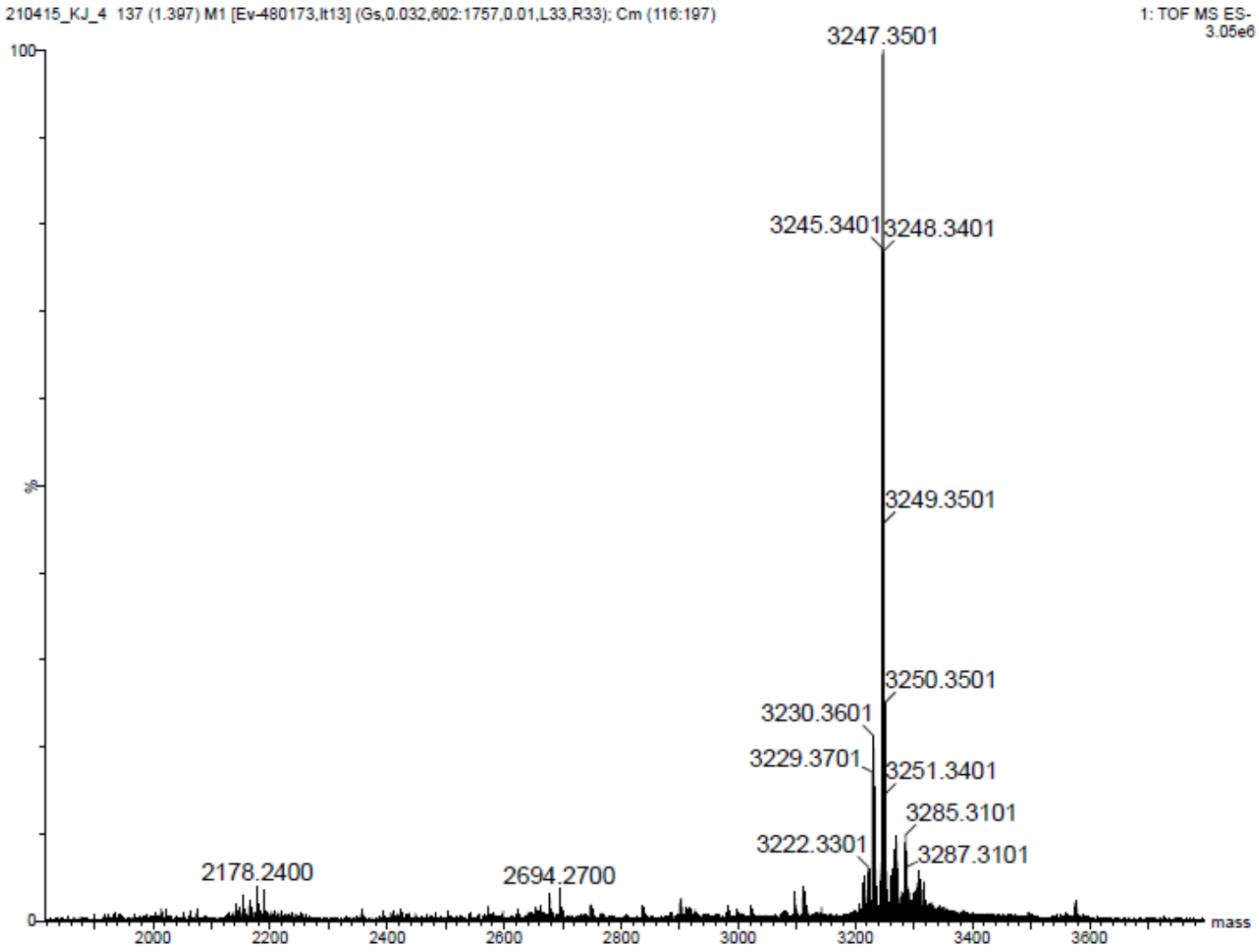
MALDI-TOF mass spectra recorded for chimeric PS-oligonucleotides.



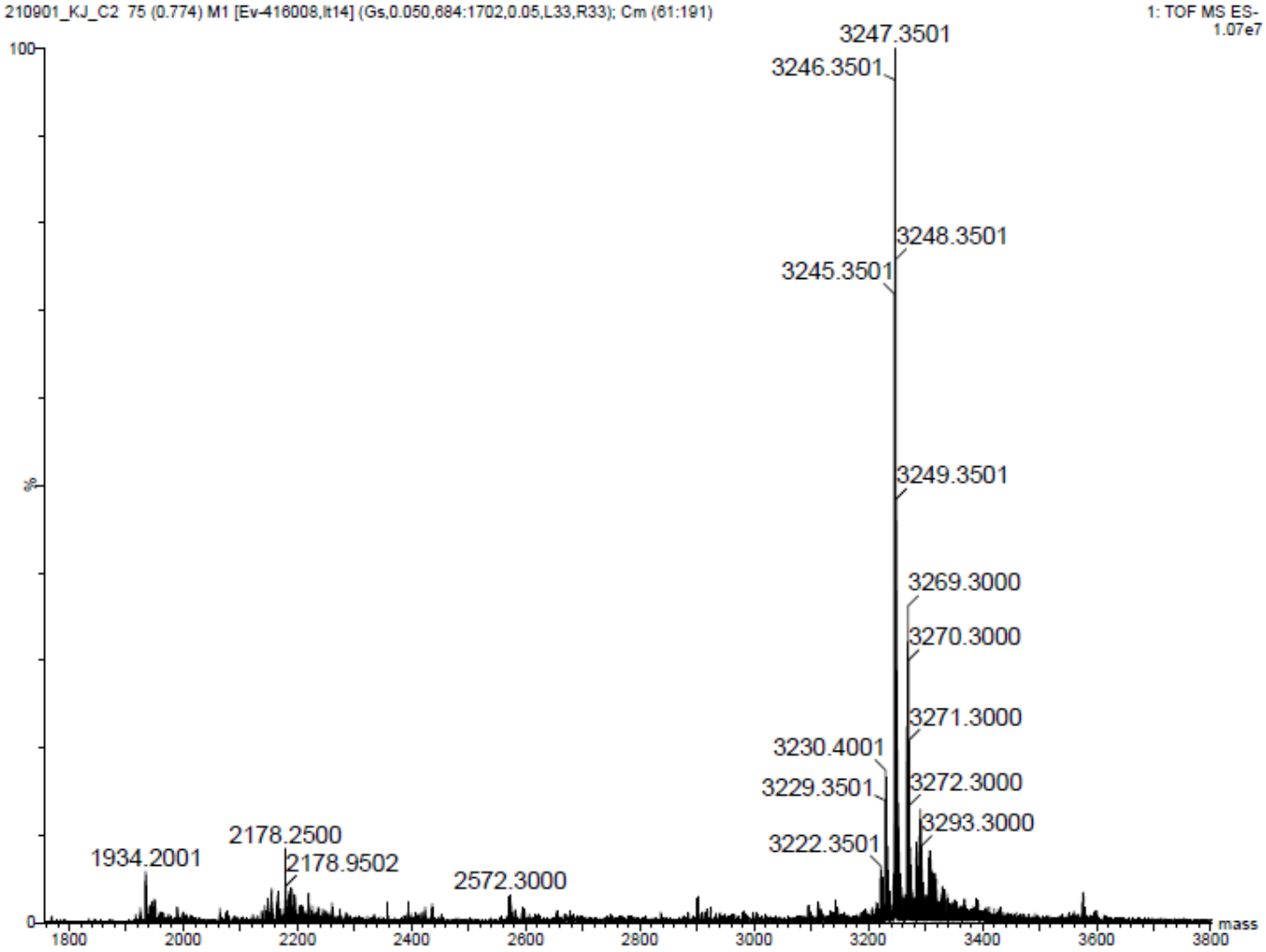
^{M}AR oligomer



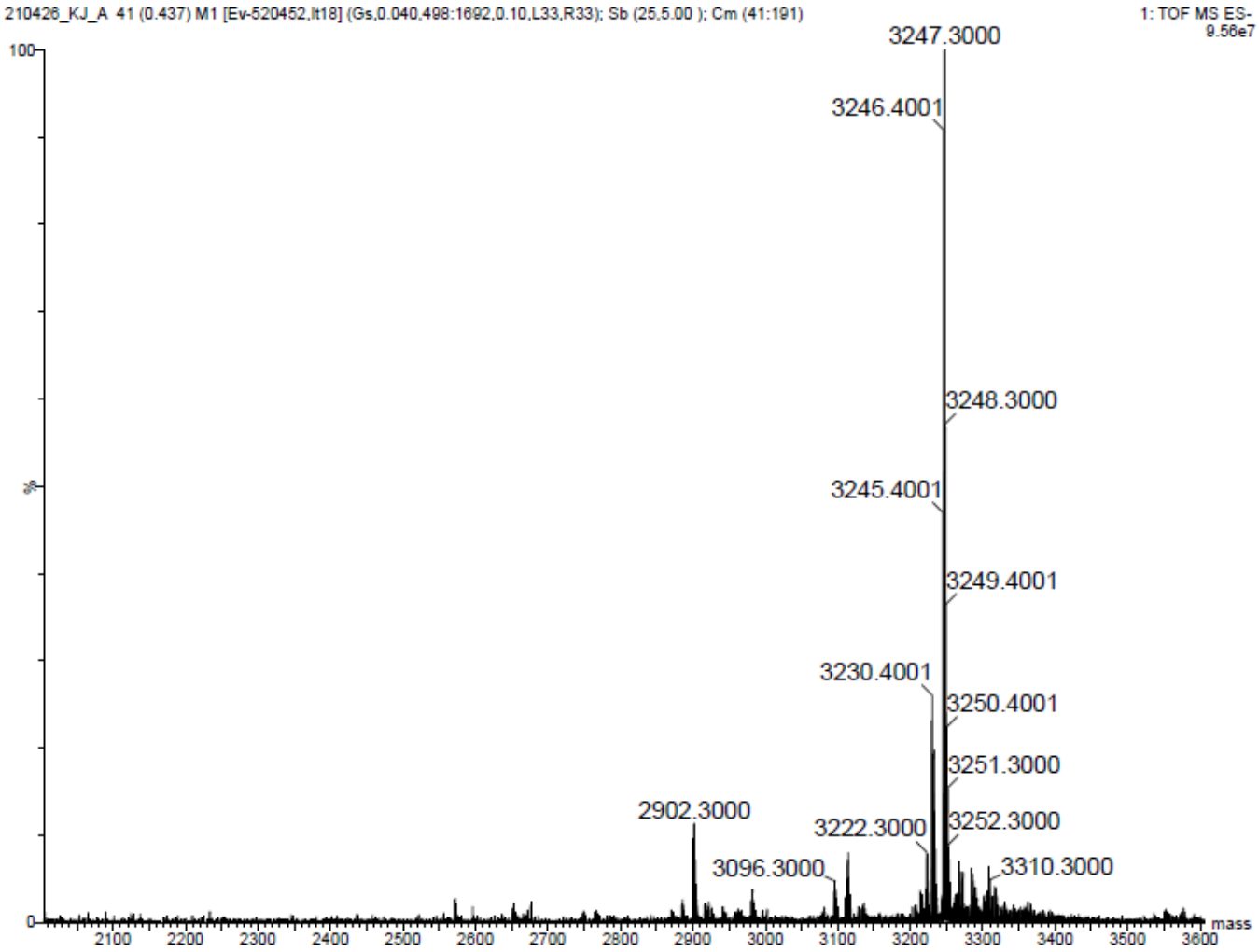
^{M}AS oligomer



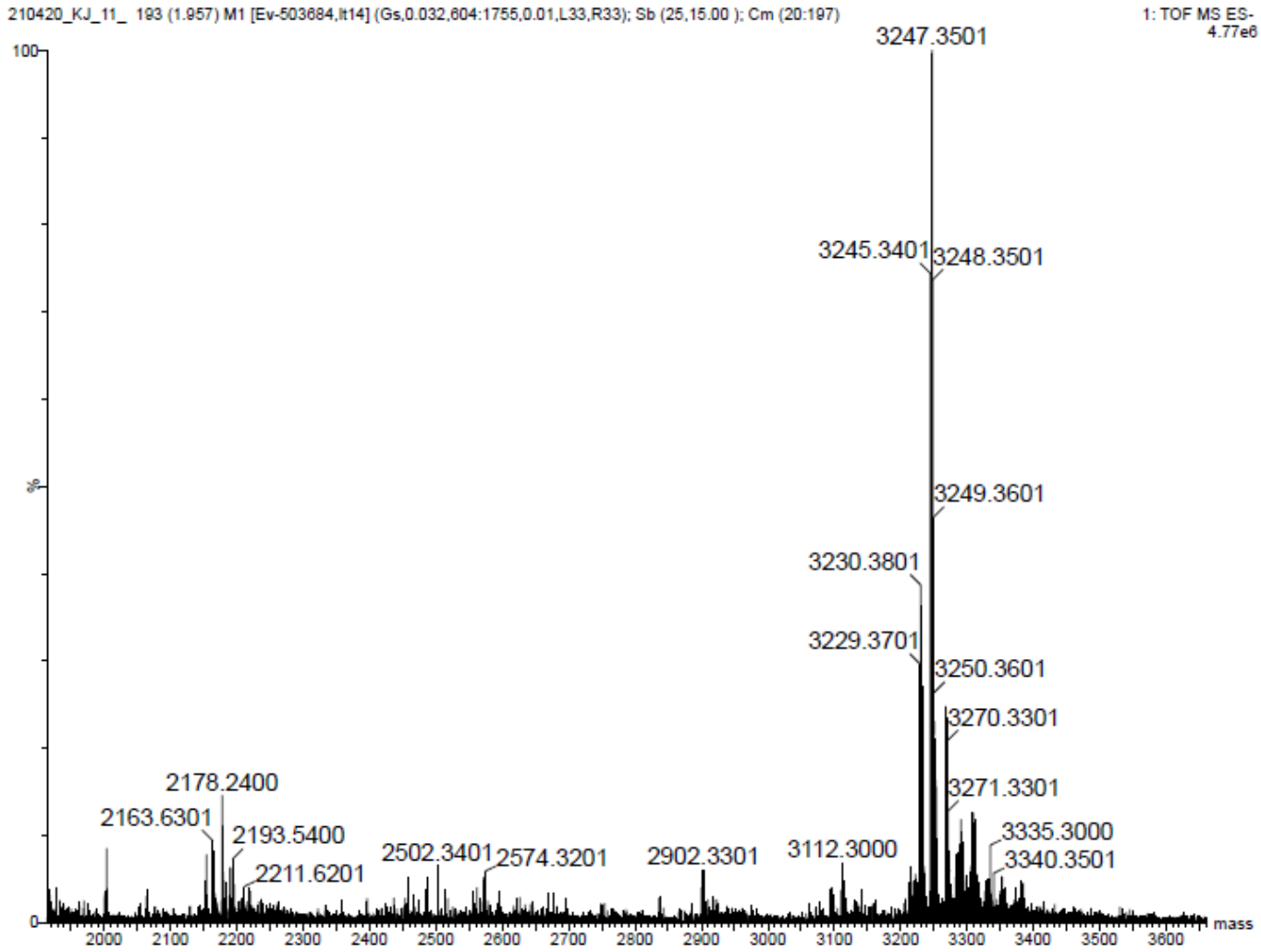
^{M}CR oligomer



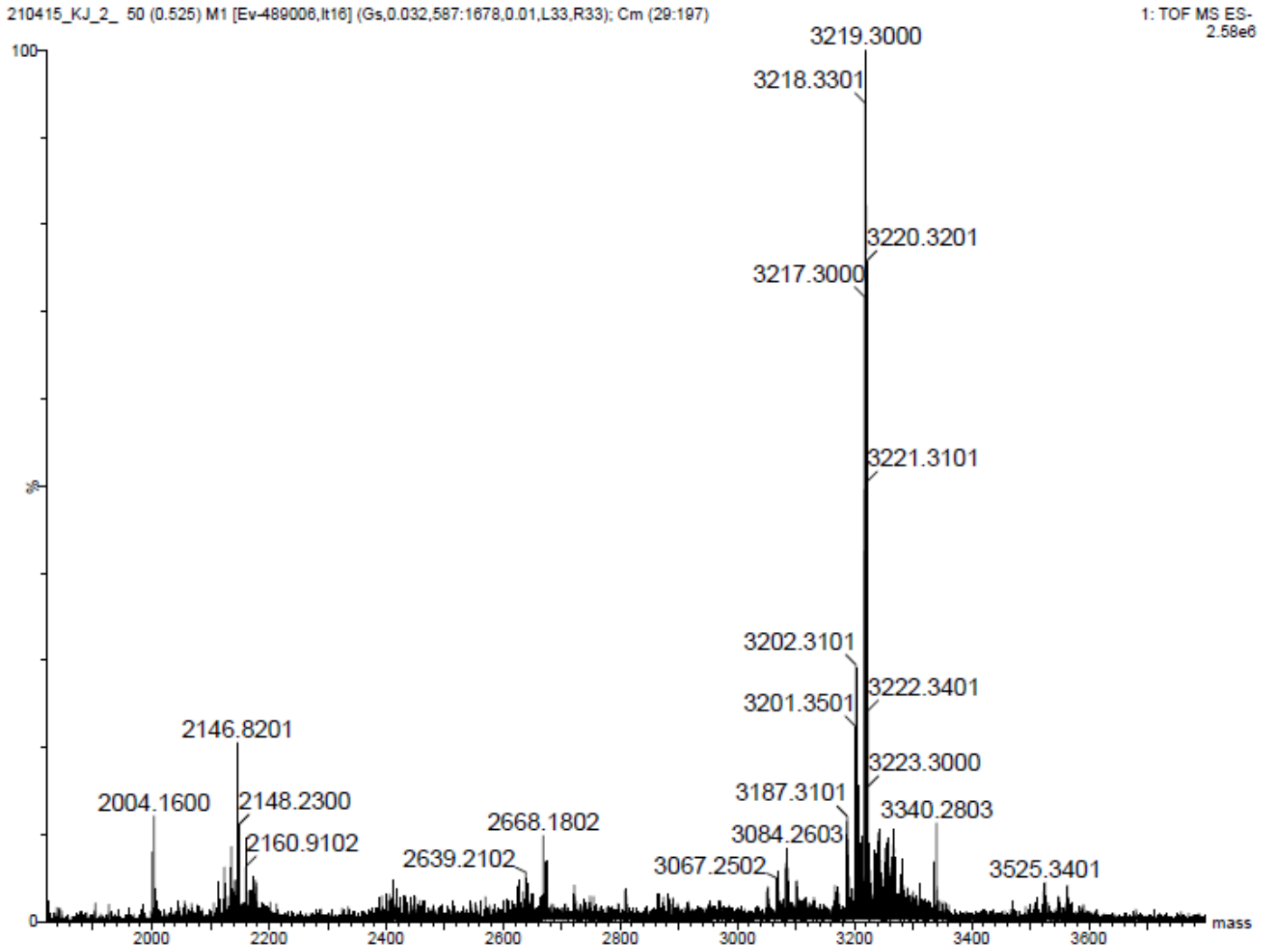
^{M}CS oligomer



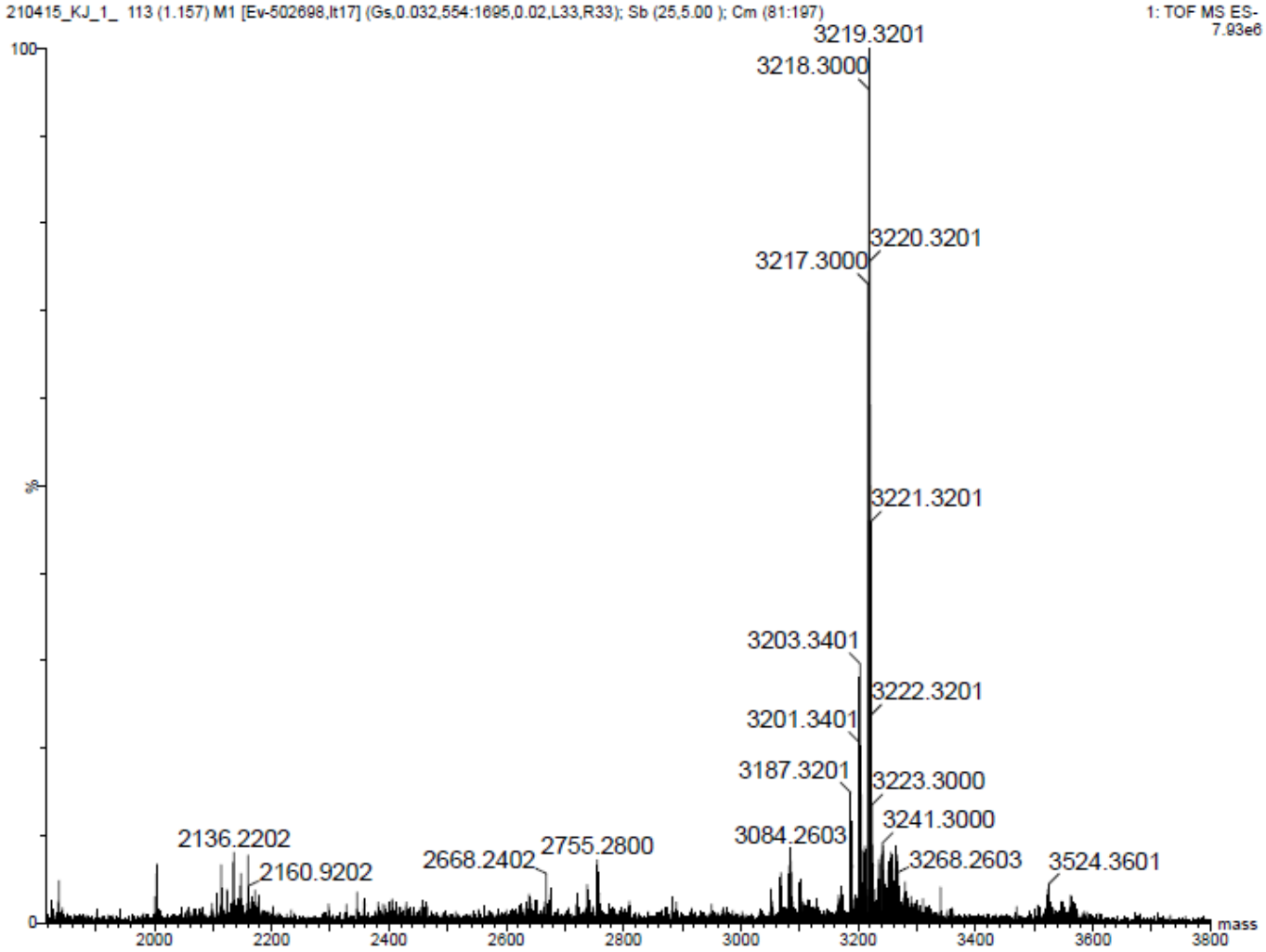
^{M}GR oligomer



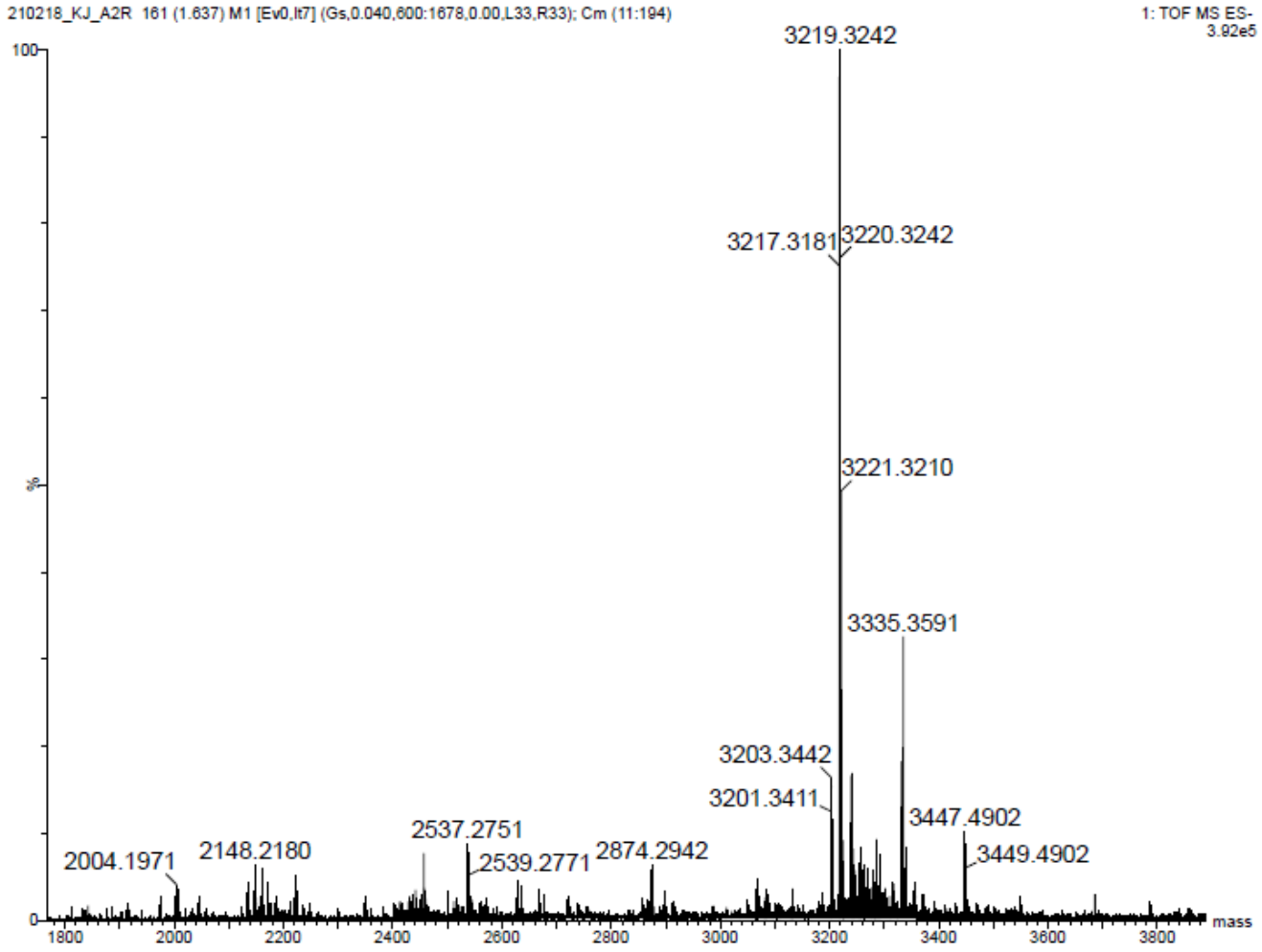
^{M}GS oligomer



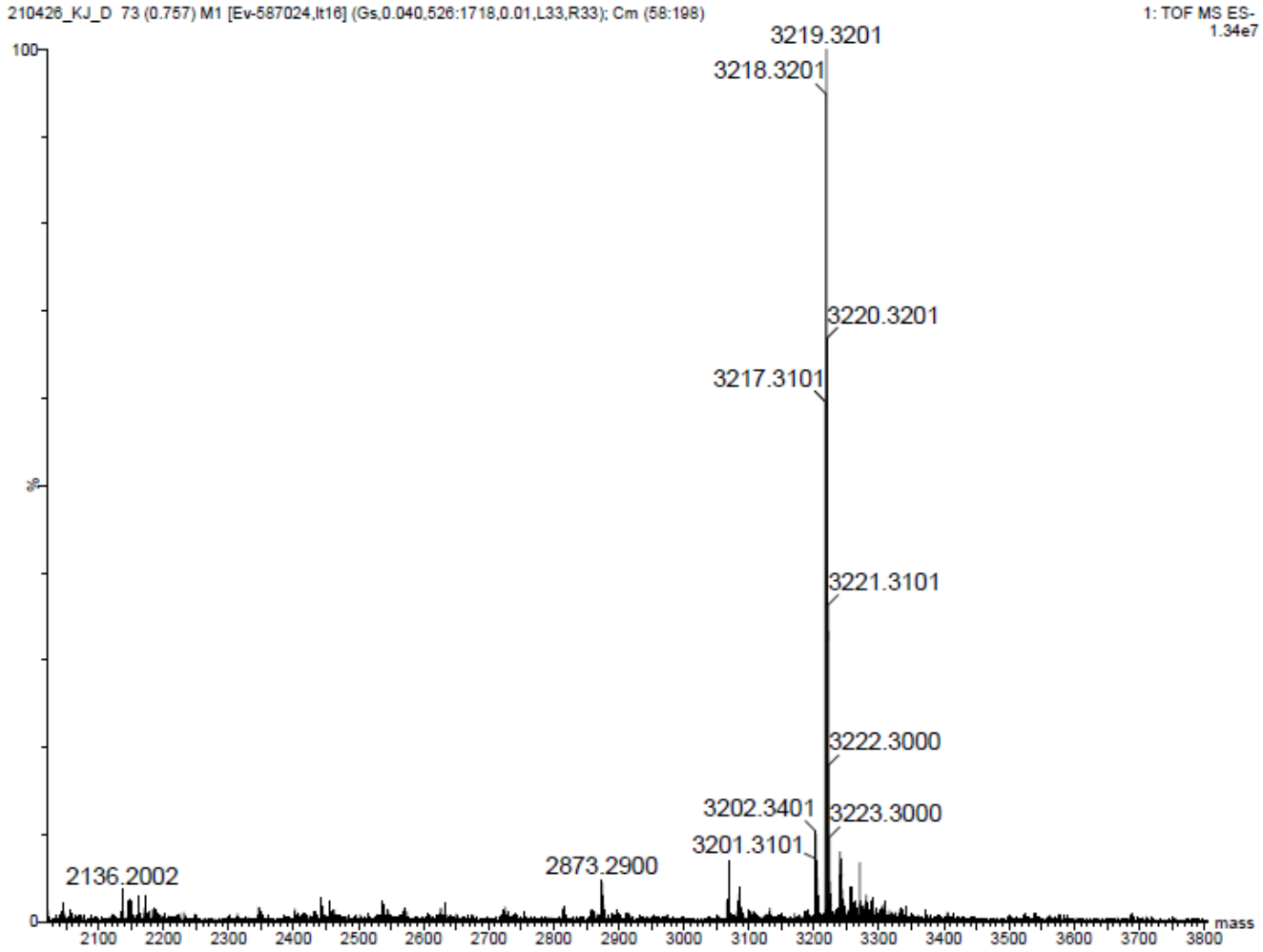
^{M}UR oligomer



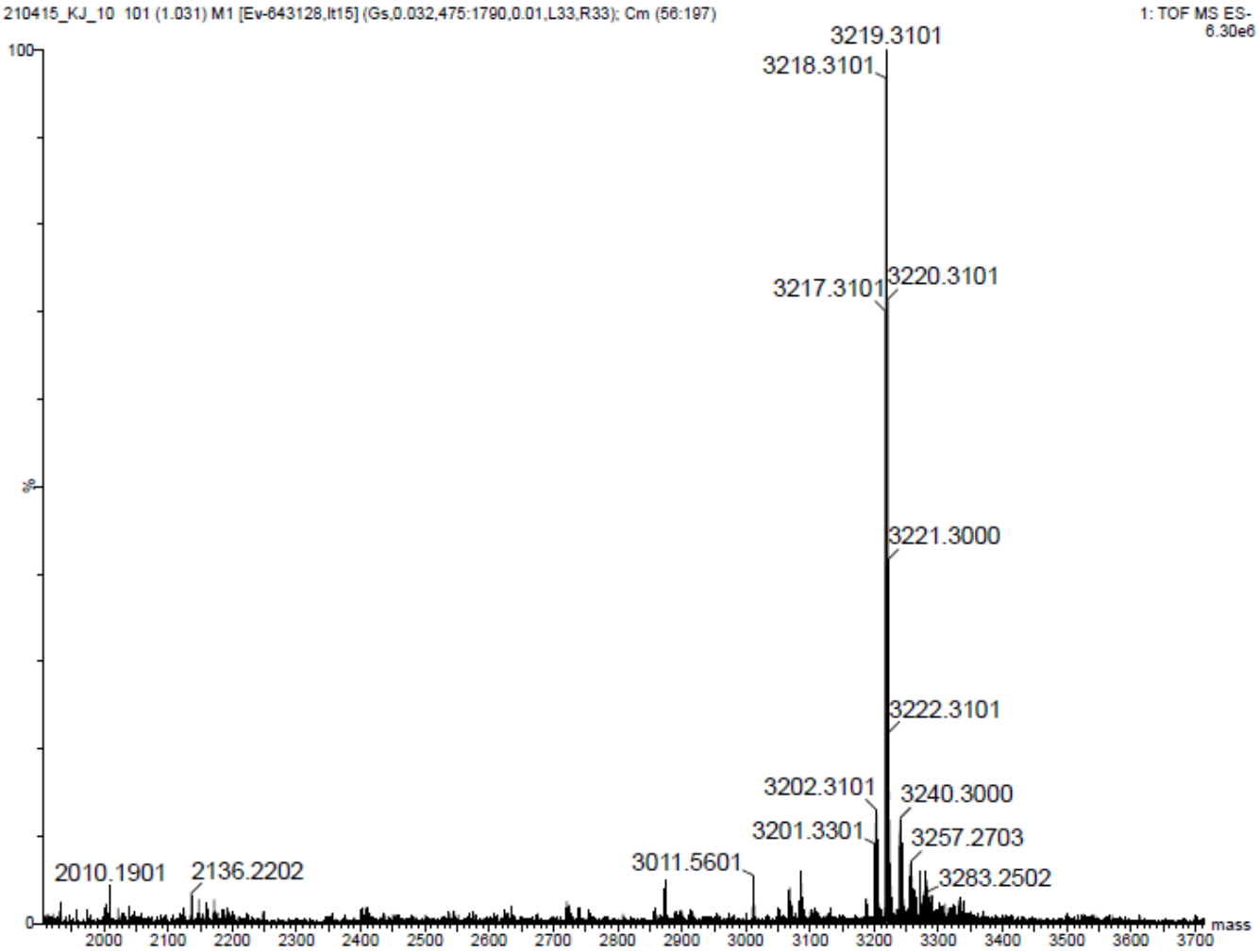
[M]US oligomer


210218_KJ_A2R 161 (1.637) M1 [Ev0,It7] (Gs,0.040,600:1678,0.00,L33,R33); Cm (11:194)
1: TOF MS ES-
3.92e5
100
%
0
3219.3242
3217.3181
3220.3242
3221.3210
3335.3591
3203.3442
3201.3411
3447.4902
3449.4902
2004.1971
2148.2180
2537.2751
2539.2771
2874.2942
1800
2000
2200
2400
2600
2800
3000
3200
3400
3600
3800
mass

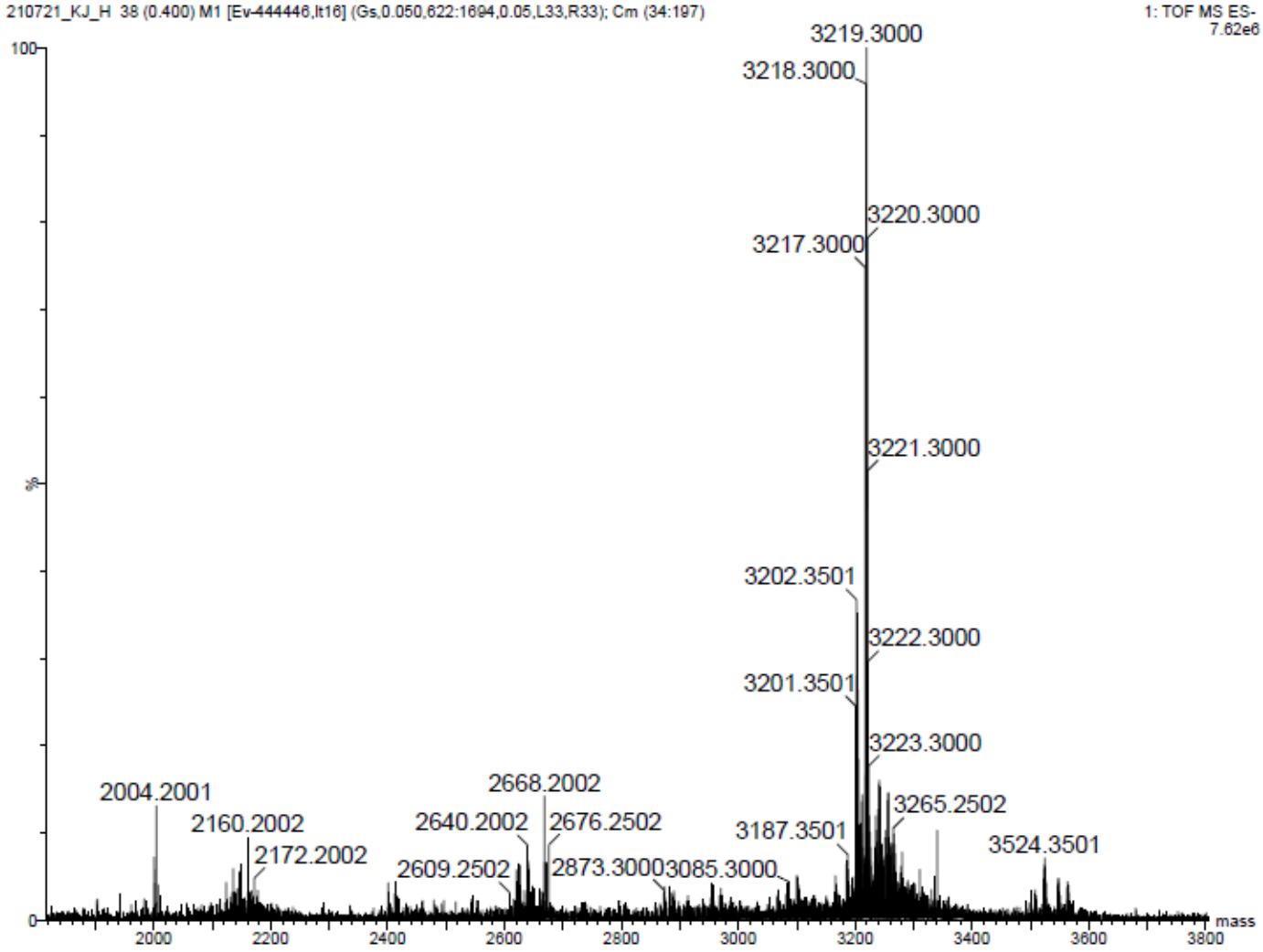
AR oligomer


210426_KJ_D 73 (0.757) M1 [Ev-587024,It16] (Gs,0.040,526:1718,0.01,L33,R33); Cm (58:198)
1: TOF MS ES-
1.34e7
100
%
0
3219.3201
3218.3201
3220.3201
3217.3101
3221.3101
3222.3000
3202.3401
3223.3000
3201.3101
2873.2900
2136.2002
mass
2100
2200
2300
2400
2500
2600
2700
2800
2900
3000
3100
3200
3300
3400
3500
3600
3700
3800

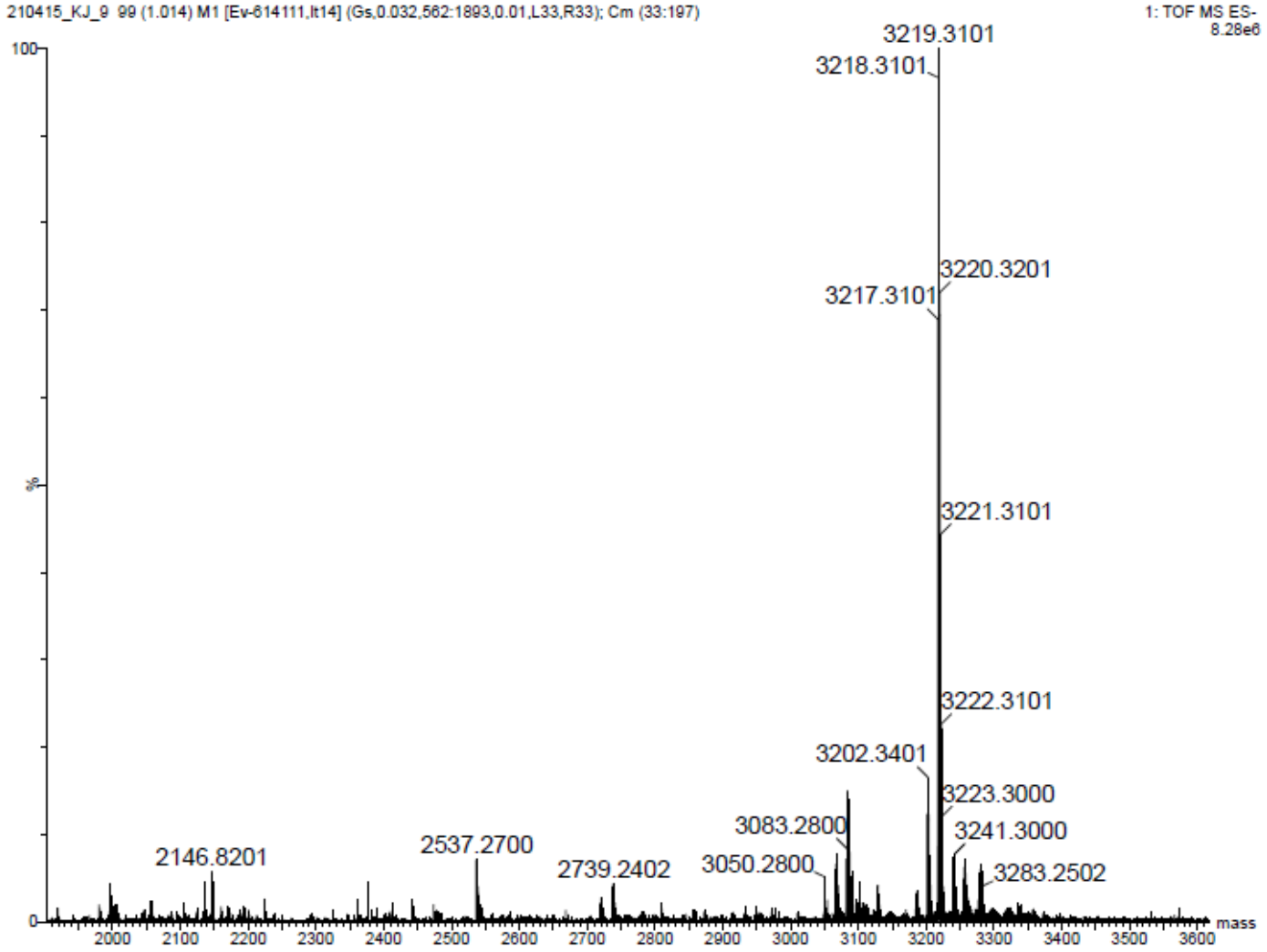
AS oligomer


210415_KJ_10 101 (1.031) M1 [Ev-643128,It15] (Gs,0.032,475:1790,0.01,L33,R33); Cm (56:197)
1: TOF MS ES-
6.30e6
100
%
0
3219.3101
3218.3101
3217.3101
3220.3101
3221.3000
3222.3101
3202.3101
3240.3000
3201.3301
3257.2703
3283.2502
3011.5601
2010.1901
2136.2202
2000 2100 2200 2300 2400 2500 2600 2700 2800 2900 3000 3100 3200 3300 3400 3500 3600 3700
mass

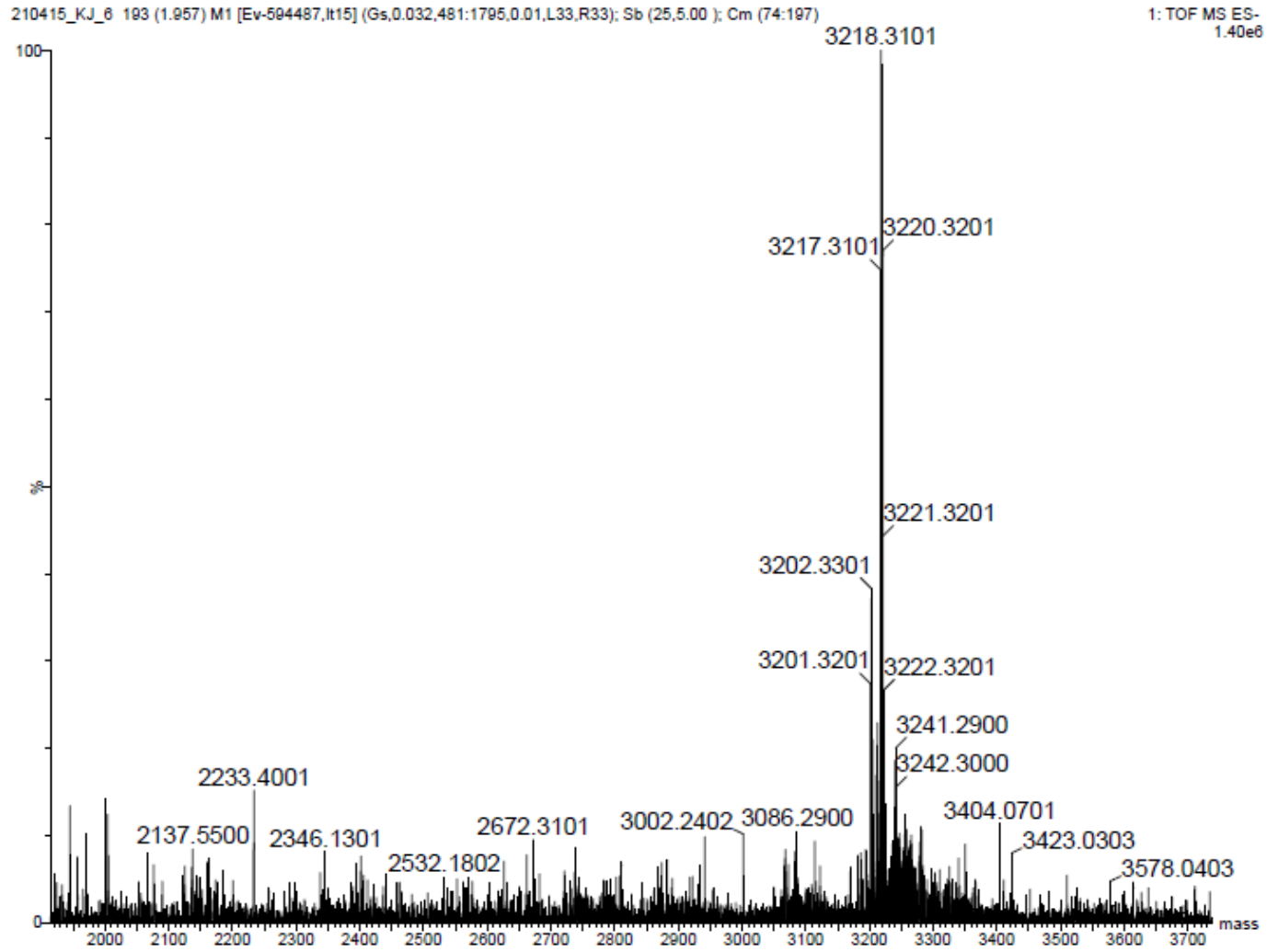
CR oligomer

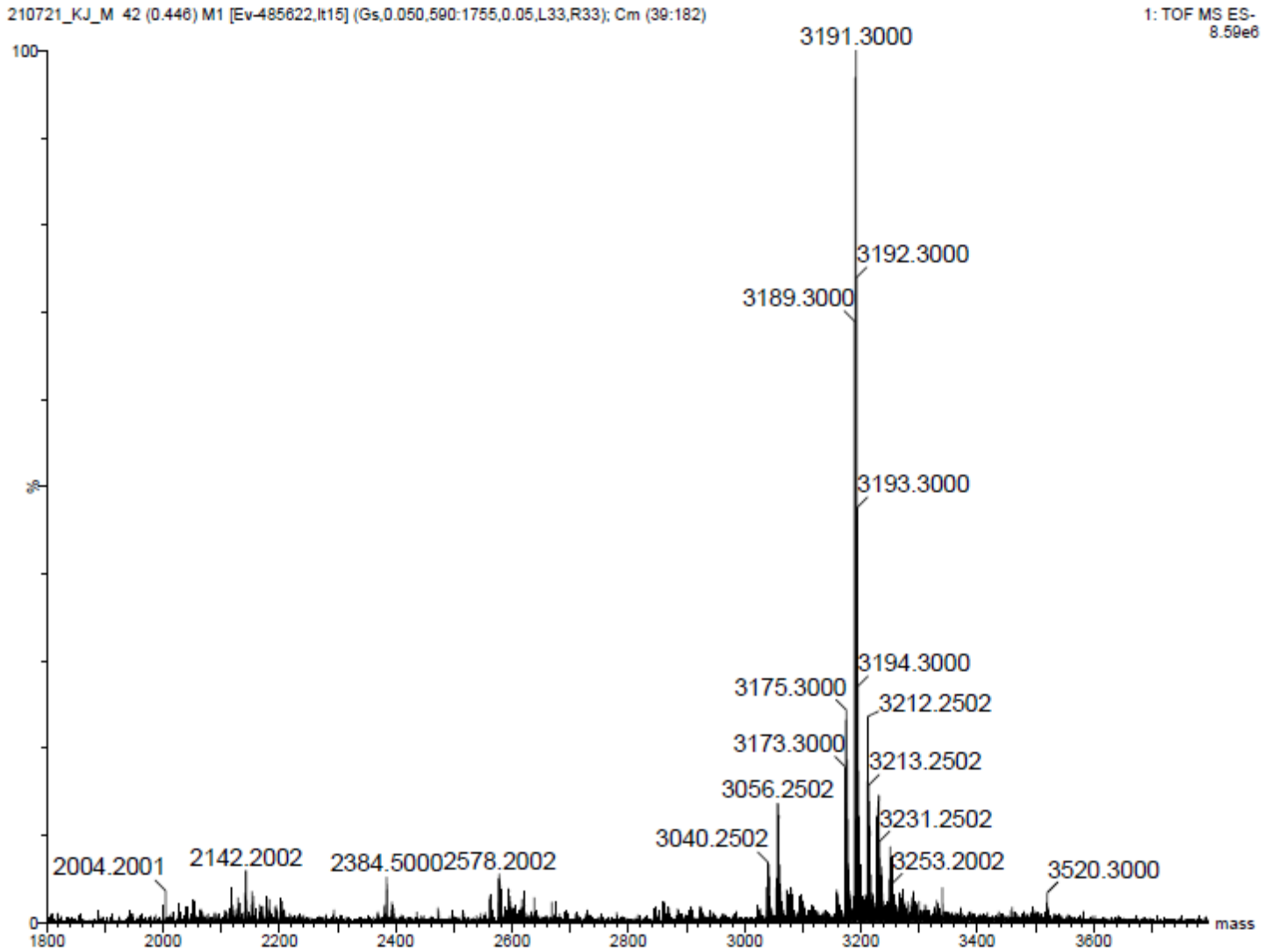

210721_KJ_H 38 (0.400) M1 [Ev-444446,It16] (Gs,0.050,622:1694,0.05,L33,R33); Cm (34:197)
1: TOF MS ES-
7.62e6
100
%
0
3219.3000
3218.3000
3220.3000
3217.3000
3221.3000
3202.3501
3222.3000
3201.3501
3223.3000
2004.2001
2668.2002
3265.2502
2160.2002
2640.2002
2676.2502
3187.3501
3524.3501
2172.2002
2609.2502
2873.3000
3085.3000
2000
2200
2400
2600
2800
3000
3200
3400
3600
3800
mass

CS oligomer


210415_KJ_9 99 (1.014) M1 [Ev-614111,lt14] (Gs,0.032,562:1893,0.01,L33,R33); Cm (33:197)
1: TOF MS ES-
8.28e6
100
%
0
3219.3101
3218.3101
3220.3201
3217.3101
3221.3101
3222.3101
3202.3401
3223.3000
3083.2800
3241.3000
2146.8201
2537.2700
2739.2402
3050.2800
3283.2502
2000
2100
2200
2300
2400
2500
2600
2700
2800
2900
3000
3100
3200
3300
3400
3500
3600
mass

GR oligomer


210415_KJ_6 193 (1.957) M1 [Ev-594487,It15] (Gs,0.032,481:1795,0.01,L33,R33); Sb (25,5.00); Cm (74:197)
1: TOF MS ES-
1.40e6
100
%
0
3218.3101
3220.3201
3217.3101
3221.3201
3202.3301
3201.3201
3222.3201
3241.2900
3242.3000
2233.4001
3404.0701
2137.5500
2346.1301
2672.3101
3002.2402
3086.2900
3423.0303
2532.1802
3578.0403
2000 2100 2200 2300 2400 2500 2600 2700 2800 2900 3000 3100 3200 3300 3400 3500 3600 3700
mass
GS oligomer


210721_KJ_M 42 (0.446) M1 [Ev-485622,lt15] (Gs,0.050,590:1755,0.05,L33,R33); Cm (39:182)
1: TOF MS ES-
8.59e6
100
%
0
3191.3000
3192.3000
3189.3000
3193.3000
3194.3000
3175.3000
3212.2502
3173.3000
3213.2502
3056.2502
3231.2502
3040.2502
3253.2002
2004.2001
2142.2002
2384.5000
2578.2002
3520.3000
1800
2000
2200
2400
2600
2800
3000
3200
3400
3600
mass

US oligomer

Table S2. Efficiency of coupling (cpl) with 2 and 3 in synthesis of [PS]-{DNA:^{M}RNA} and [PS]-{DNA:RNA}, respectively, calculated from the DMT^{+} decay assay. PSCh = [PS]-Chimeric oligomer.

sequence	PSCh	1st cpl. with **2**	2nd cpl. with **2**	PSCh	1st cpl. with **3**	2nd cpl. with **3**
t gtcAgctAg	^{M}**AR**	-	-	**AR**	0.75	0.81
	^{M}**AS**	0.76	0.72	**AS**	0.86	0.85
tgtCagCtag	^{M}**CR**	0.82	0.74	**CR**	0.84	0.83
	^{M}**CS**	0.84	0.83	**CS**	0.77	0.86
tGtcaGtag	^{M}**GR**	0.77	0.69	**GR**	0.90	0.55
	^{M}**GS**	0.83	0.70	**GS**	0.63	0.85
tgUcagUag	^{M}**UR**	0.78	0.81	**UR**	0.64	0.84
	^{M}**US**	0.85	0.82	**US**	0.89	0.75
		AVG: 0.78			AVG: 0.79	