Supporting information

Kinetic Investigation of the Fullerene C_{60} Cyclopropanation Process by Halogenmethylketones under the Conditions of Bingel Reaction

Yulya N. Biglova,*[a,b] Ilshat M. Sakhautdinov,[a] Rustem N. Garifullin,[c] Gulnaz F. Sakhautdinova[a] and Akhat G. Mustafin[a]

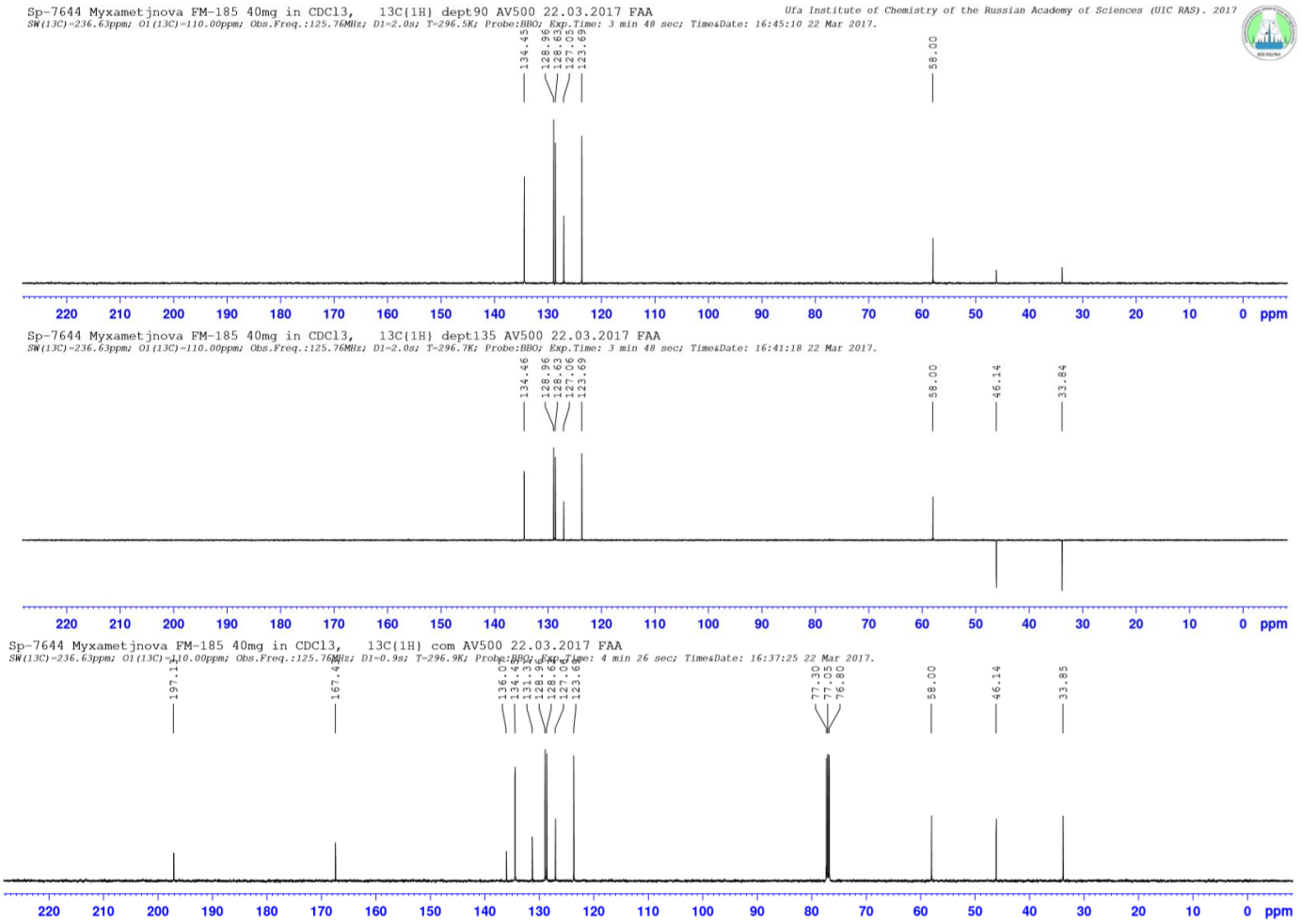
[a.] *Ufa Institute of Chemistry, Ufa Federal Research Centre, Russian Academy of Sciences, 450054, Ufa, Russian Federation. E-mail: bn.yulya@mail.ru*
[b.] *Department of Chemistry, Bashkir State University, 450076, Ufa, Russian Federation*
[c.] *Institute of Mathematics, Ufa Federal Research Centre, Russian Academy of Sciences, 450008, Ufa, Russian Federation*

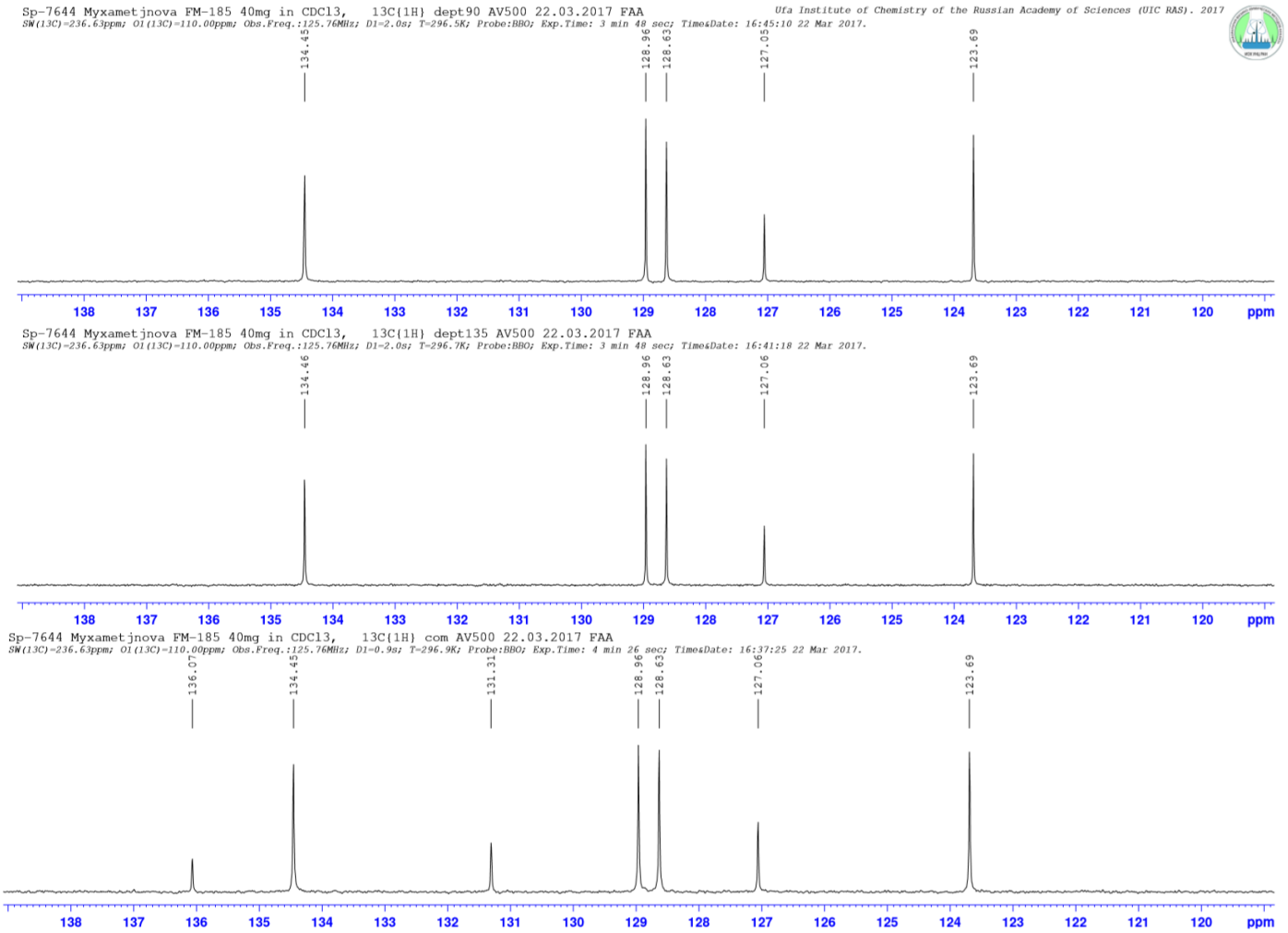
TABLE OF CONTENTS

1. Spectroscopic data of synthesized compounds

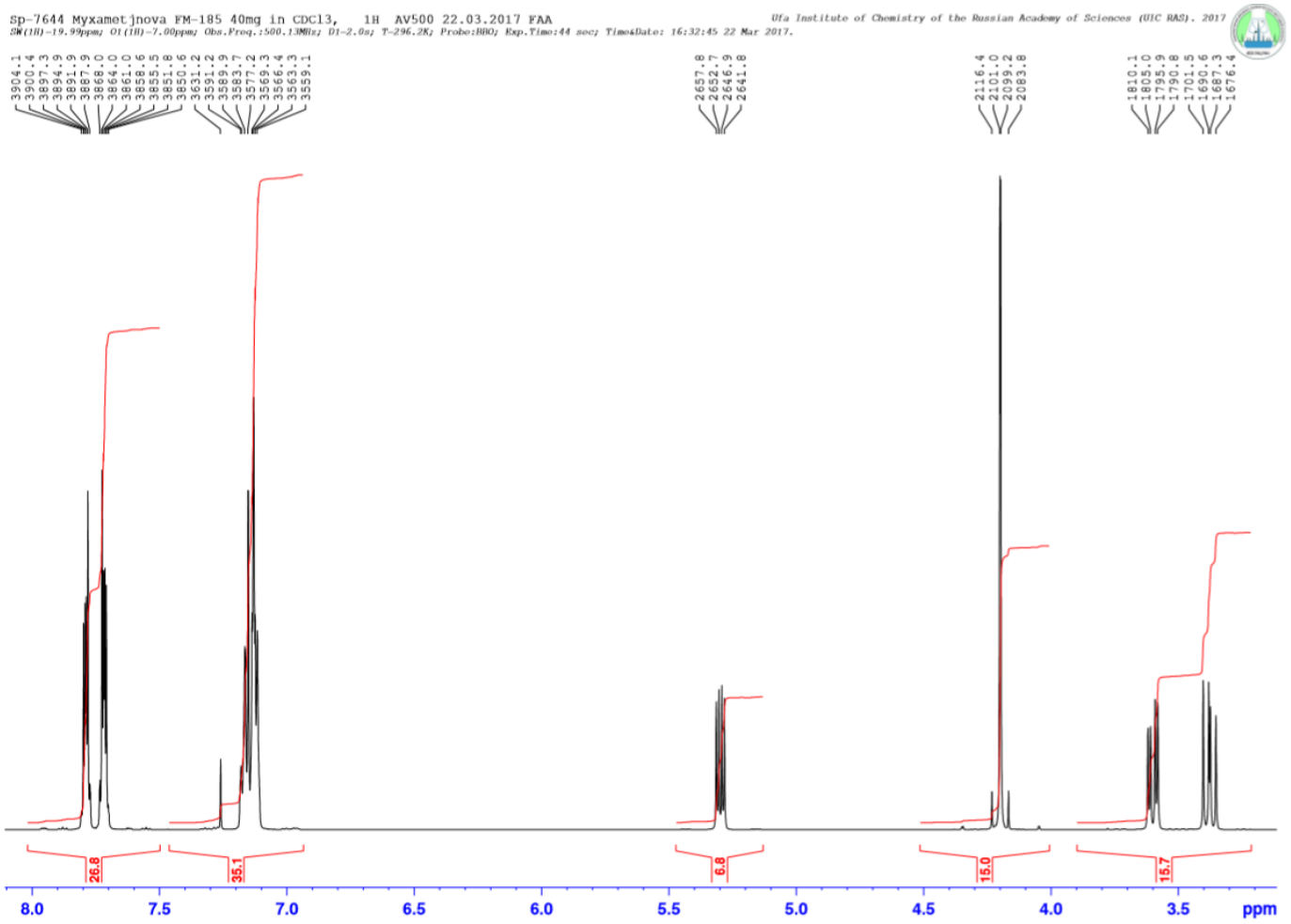
1.1. Spectrum data ^{1}H NMR,^{13}C NMR of halogenmethyl ketones

^{13}C NMR – ‘chloroketone **Cl-K**’

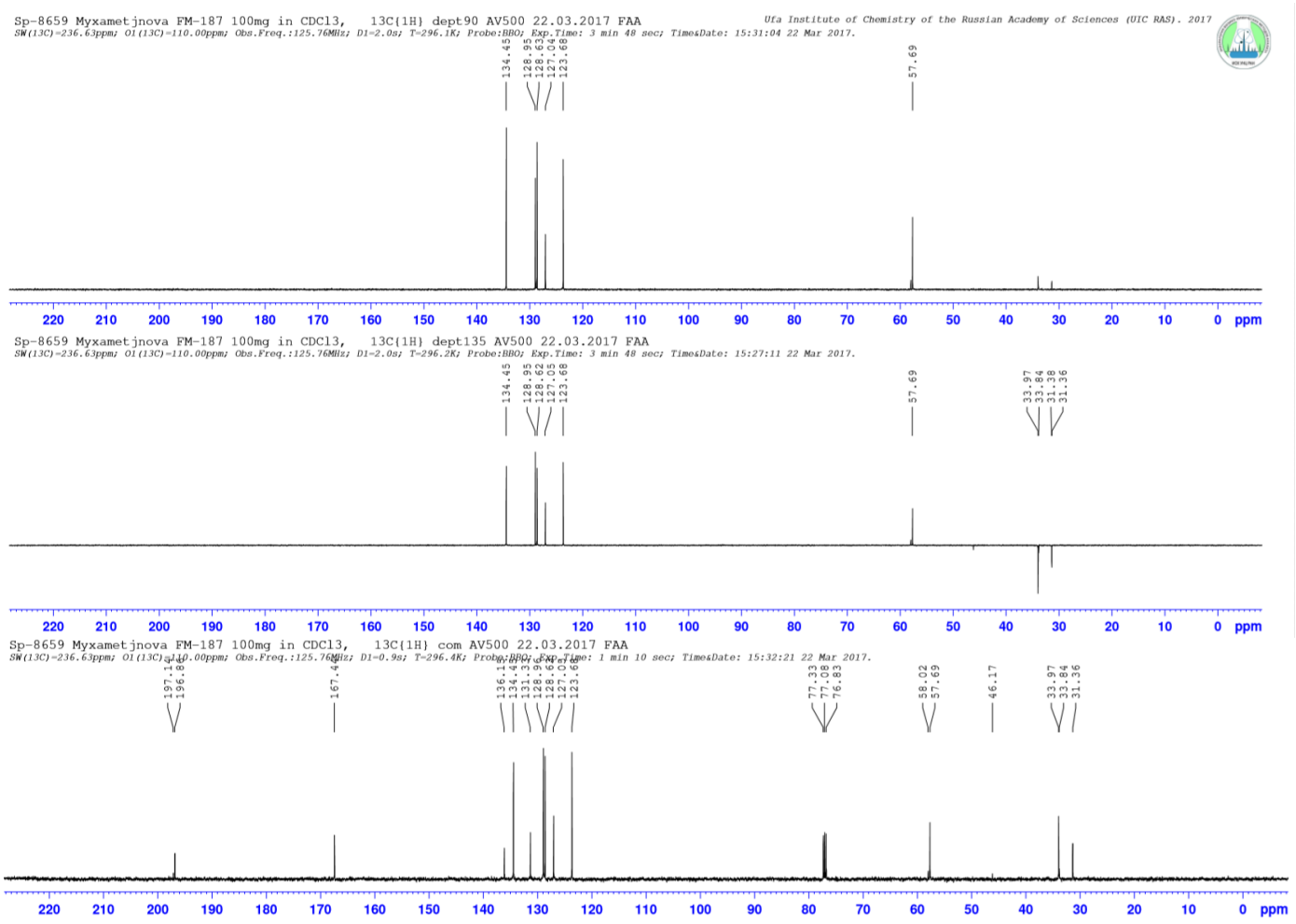


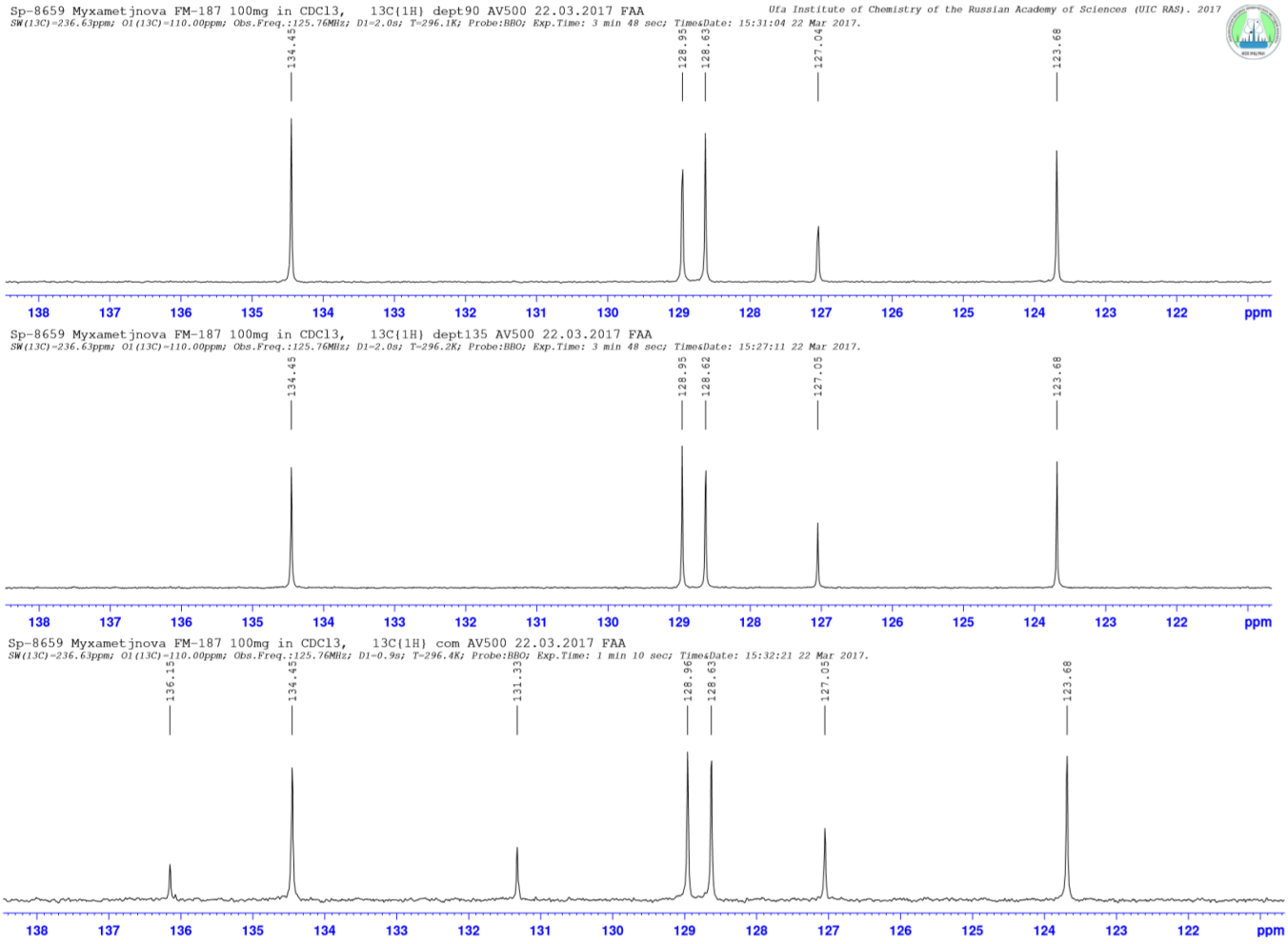

Sp-7644 Myxametjnova FM-185 40mg in CDCl3, 13C{1H} dept90 AV500 22.03.2017 FAA
Ufa Institute of Chemistry of the Russian Academy of Sciences (UIC RAS). 2017
SW(13C)=236.63ppm; O1(13C)=110.00ppm; Obs.Freq.:125.76MHz; D1=2.0s; T=296.5K; Probe:BBO; Exp.Time: 3 min 48 sec; Time&Date: 16:45:10 22 Mar 2017.
134.45
128.96
128.63
127.05
123.69
Sp-7644 Myxametjnova FM-185 40mg in CDCl3, 13C{1H} dept135 AV500 22.03.2017 FAA
SW(13C)=236.63ppm; O1(13C)=110.00ppm; Obs.Freq.:125.76MHz; D1=2.0s; T=296.7K; Probe:BBO; Exp.Time: 3 min 48 sec; Time&Date: 16:41:18 22 Mar 2017.
134.46
128.96
128.63
127.06
123.69
Sp-7644 Myxametjnova FM-185 40mg in CDCl3, 13C{1H} com AV500 22.03.2017 FAA
SW(13C)=236.63ppm; O1(13C)=110.00ppm; Obs.Freq.:125.76MHz; D1=0.9s; T=296.9K; Probe:BBO; Exp.Time: 4 min 26 sec; Time&Date: 16:37:25 22 Mar 2017.
136.07
134.45
131.31
128.96
128.63
127.06
123.69
138 137 136 135 134 133 132 131 130 129 128 127 126 125 124 123 122 121 120 ppm

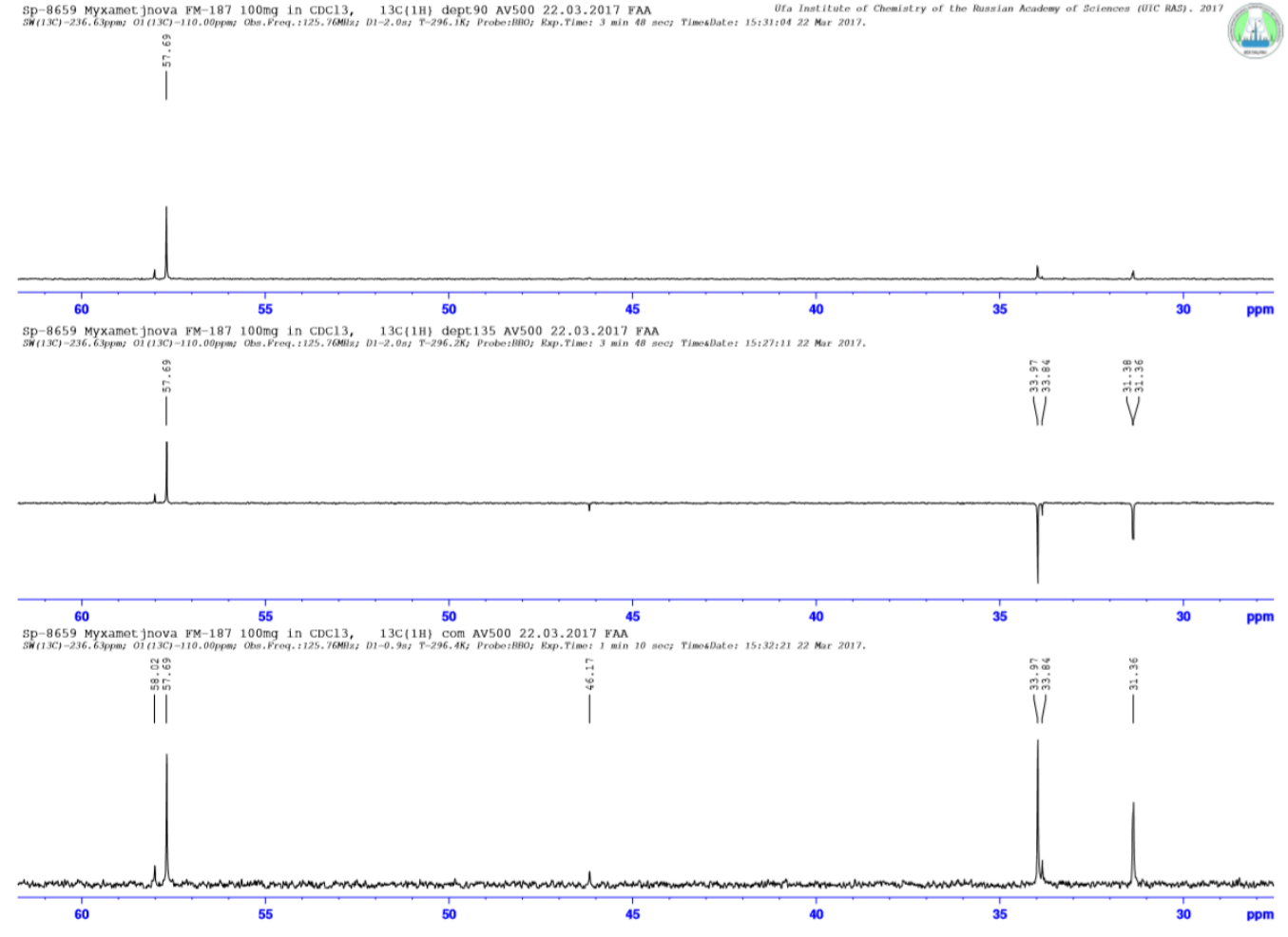
^{1}H NMR – ‘chloroketone **Cl-K**’



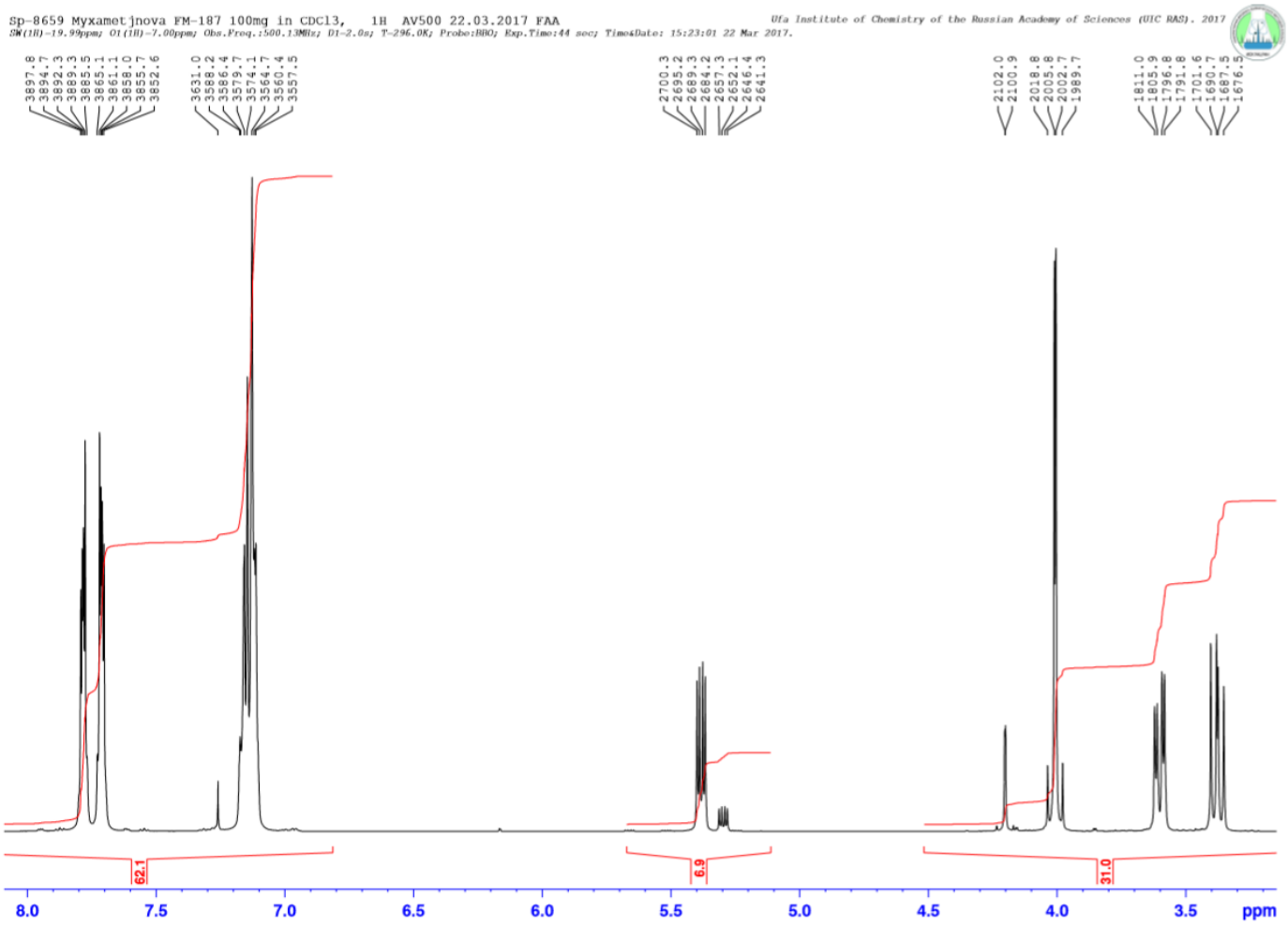
^{13}C NMR – ‘bromoketone **Br-K**’




Sp-8659 Myxametjnova FM-187 100mg in CDCl3, 13C{1H} dept90 AV500 22.03.2017 FAA
Ufa Institute of Chemistry of the Russian Academy of Sciences (UIC RAS). 2017
SW(13C)=236.63ppm; O1(13C)=110.00ppm; Obs.Freq.:125.76MHz; D1=2.0s; T=296.1K; Probe:BBO; Exp.Time: 3 min 48 sec; Time&Date: 15:31:04 22 Mar 2017.
134.45
128.95
128.63
127.04
123.68
Sp-8659 Myxametjnova FM-187 100mg in CDCl3, 13C{1H} dept135 AV500 22.03.2017 FAA
SW(13C)=236.63ppm; O1(13C)=110.00ppm; Obs.Freq.:125.76MHz; D1=2.0s; T=296.2K; Probe:BBO; Exp.Time: 3 min 48 sec; Time&Date: 15:27:11 22 Mar 2017.
134.45
128.95
128.62
127.05
123.68
Sp-8659 Myxametjnova FM-187 100mg in CDCl3, 13C{1H} com AV500 22.03.2017 FAA
SW(13C)=236.63ppm; O1(13C)=110.00ppm; Obs.Freq.:125.76MHz; D1=0.9s; T=296.4K; Probe:BBO; Exp.Time: 1 min 10 sec; Time&Date: 15:32:21 22 Mar 2017.
136.15
134.45
131.33
128.96
128.63
127.05
123.68
138 137 136 135 134 133 132 131 130 129 128 127 126 125 124 123 122 ppm

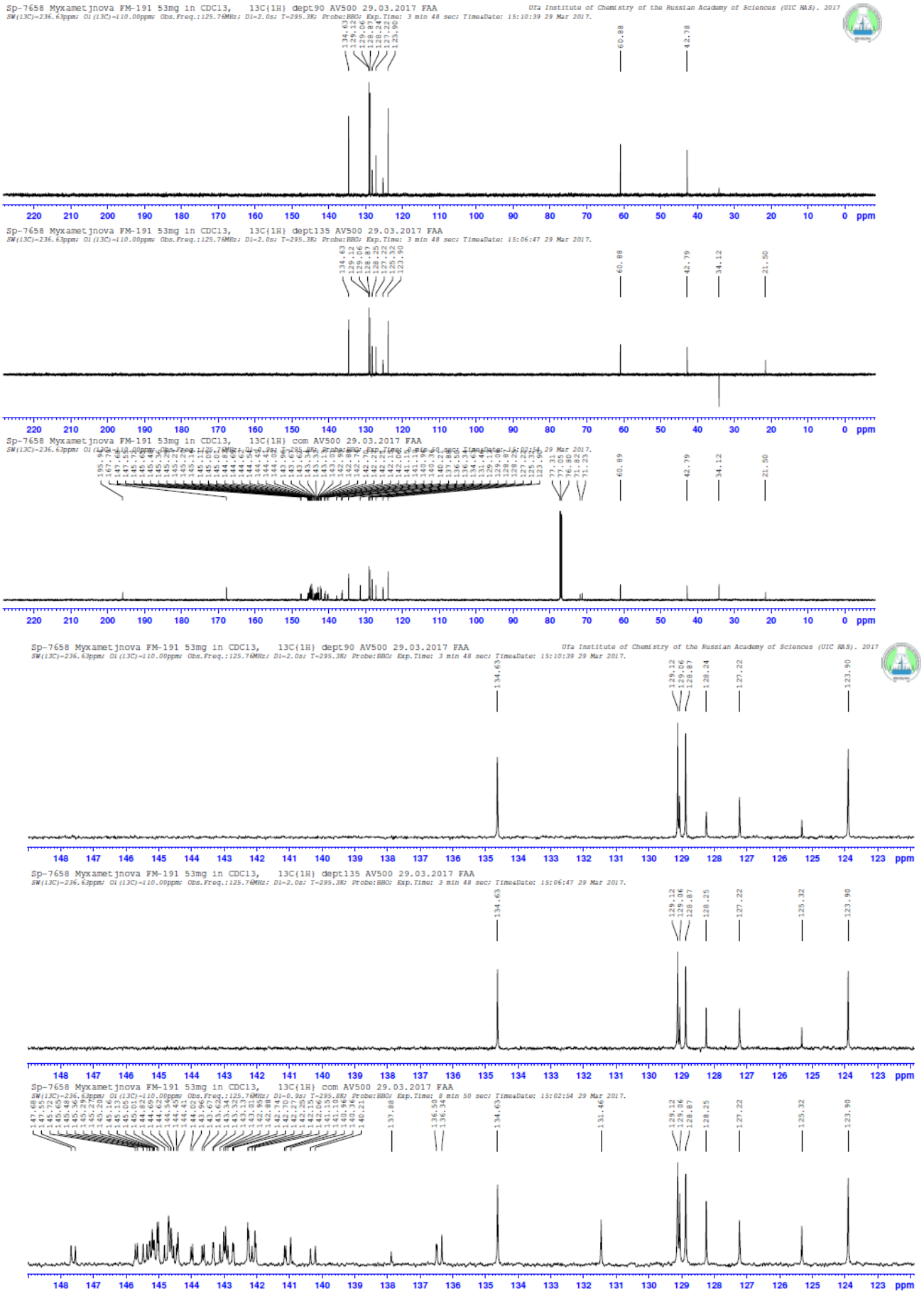

Sp-8659 Myxametjnova FM-187 100mg in CDCl3, 13C{1H} dept90 AV500 22.03.2017 FAA
Ufa Institute of Chemistry of the Russian Academy of Sciences (UIC RAS). 2017
SW(13C)=236.63ppm; O1(13C)=110.00ppm; Obs.Freq.:125.76MHz; D1=2.0s; T=296.1K; Probe:BBO; Exp.Time: 3 min 48 sec; Time&Date: 15:31:04 22 Mar 2017.
57.69
Sp-8659 Myxametjnova FM-187 100mg in CDCl3, 13C{1H} dept135 AV500 22.03.2017 FAA
SW(13C)=236.63ppm; O1(13C)=110.00ppm; Obs.Freq.:125.76MHz; D1=2.0s; T=296.2K; Probe:BBO; Exp.Time: 3 min 48 sec; Time&Date: 15:27:11 22 Mar 2017.
57.69
33.97
33.84
31.38
31.36
Sp-8659 Myxametjnova FM-187 100mg in CDCl3, 13C{1H} com AV500 22.03.2017 FAA
SW(13C)=236.63ppm; O1(13C)=110.00ppm; Obs.Freq.:125.76MHz; D1=0.9s; T=296.4K; Probe:BBO; Exp.Time: 1 min 10 sec; Time&Date: 15:32:21 22 Mar 2017.
58.02
57.69
46.17
33.97
33.84
31.36
60 55 50 45 40 35 30 ppm

^{1}H NMR – ‘bromoketone **Br-K**’

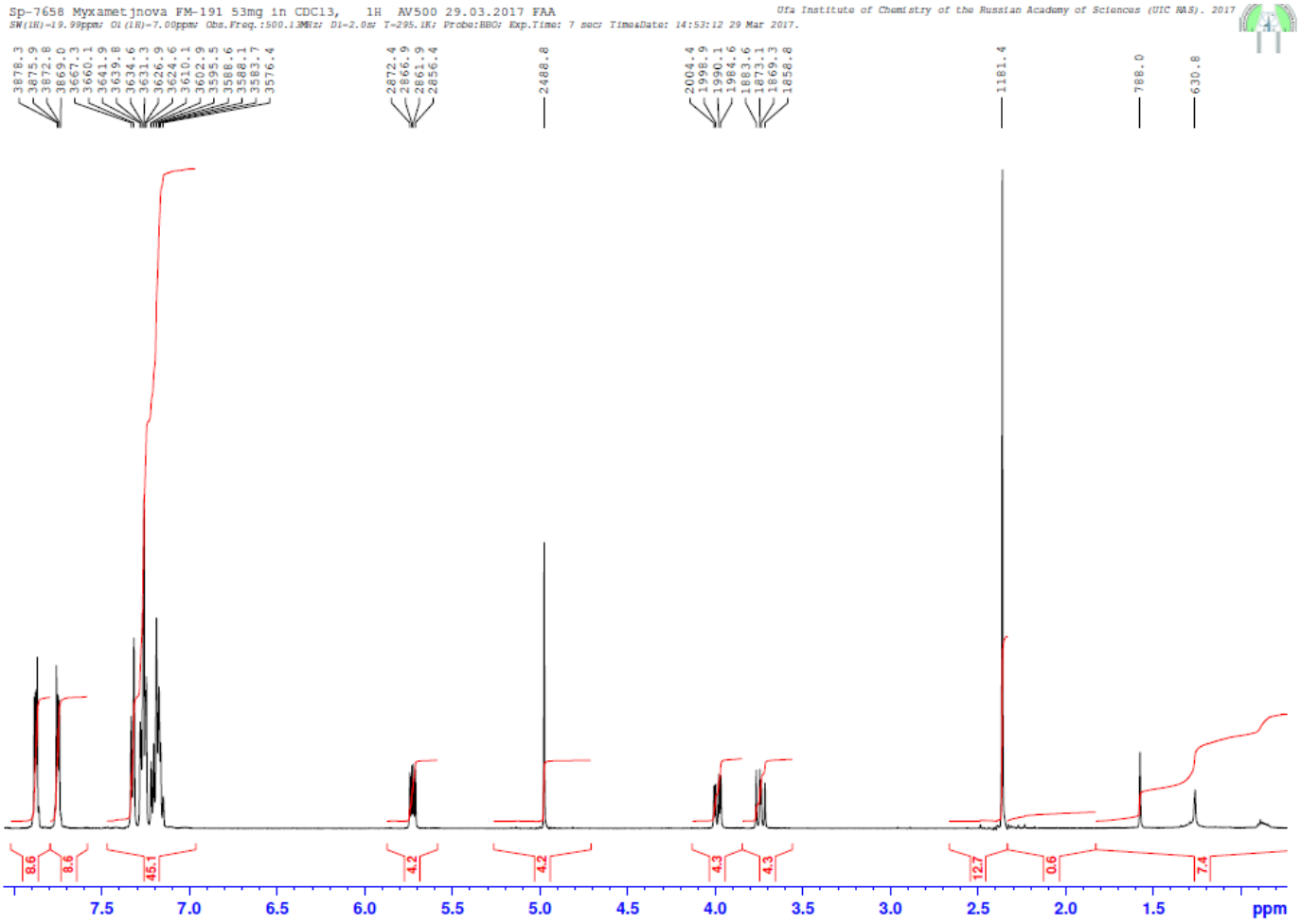


1.2. Spectrum data ^{1}H NMR,^{13}C NMR and MS-MALDI of mono-adduct MMF and bis-adduct DMF methanofullerenes

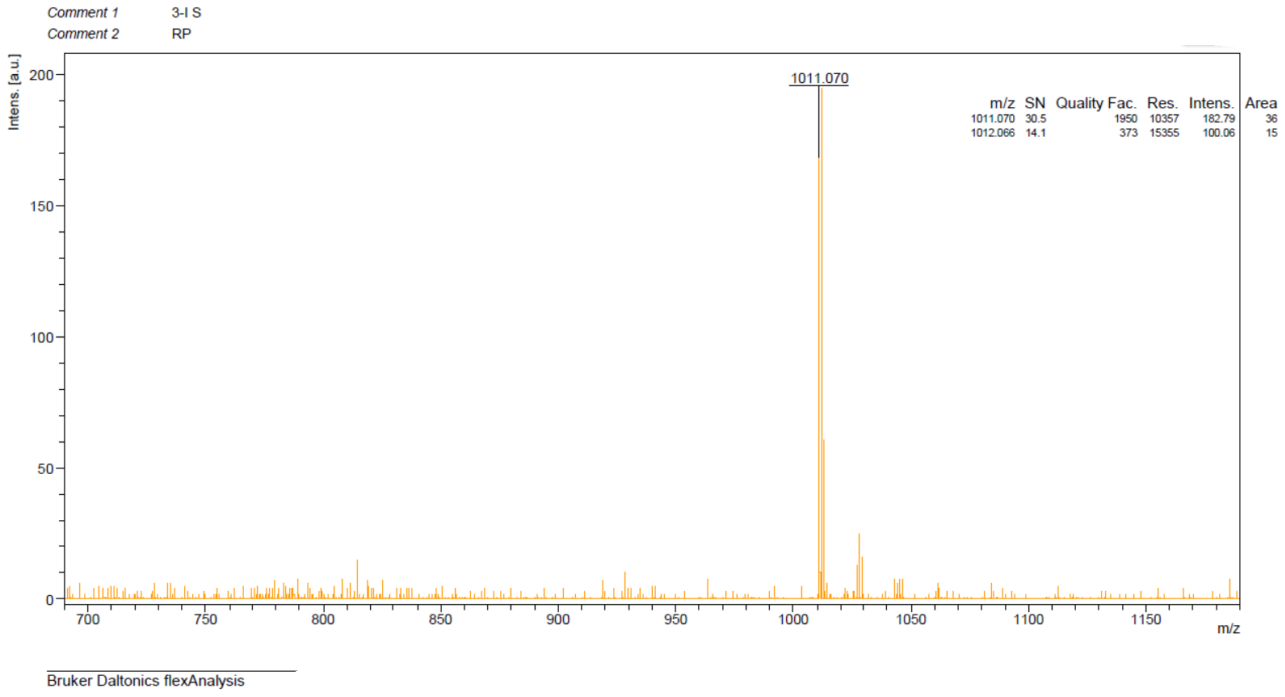
^{13}C NMR – ‘mono-adduct **MMF**’



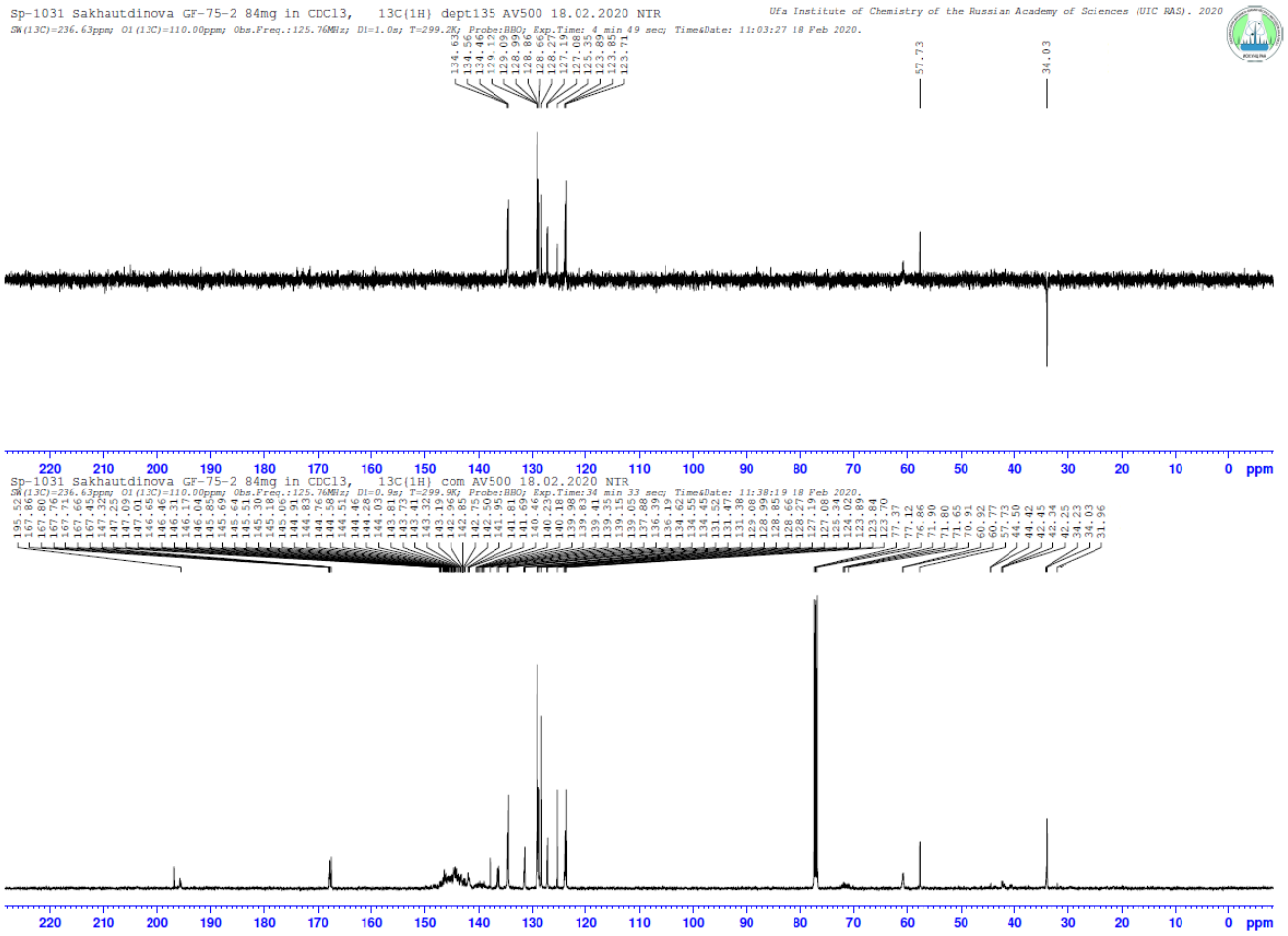
^{1}H NMR – ‘mono-adduct **MMF**’



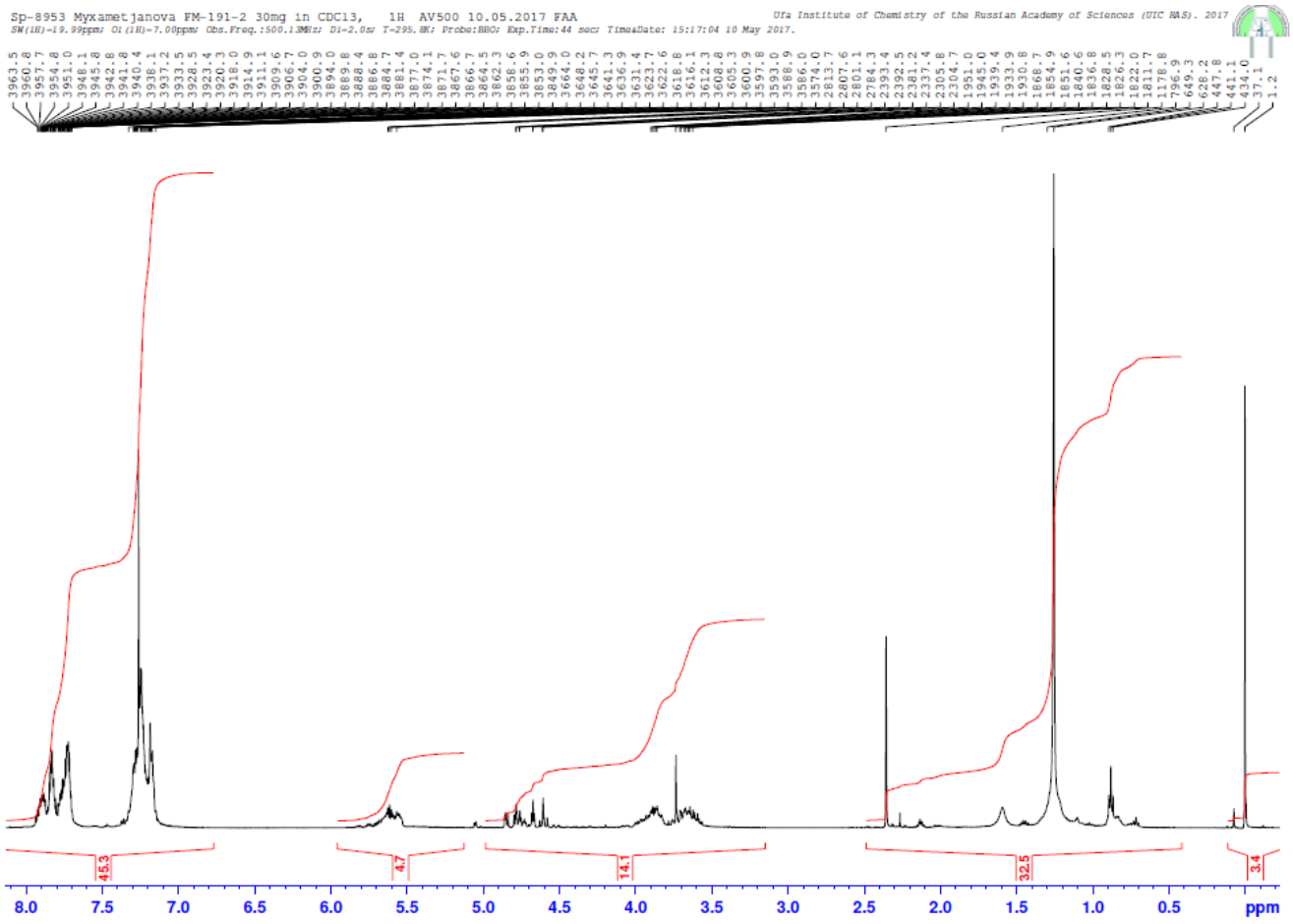
MS-MALDI – ‘mono-adduct **MMF**’



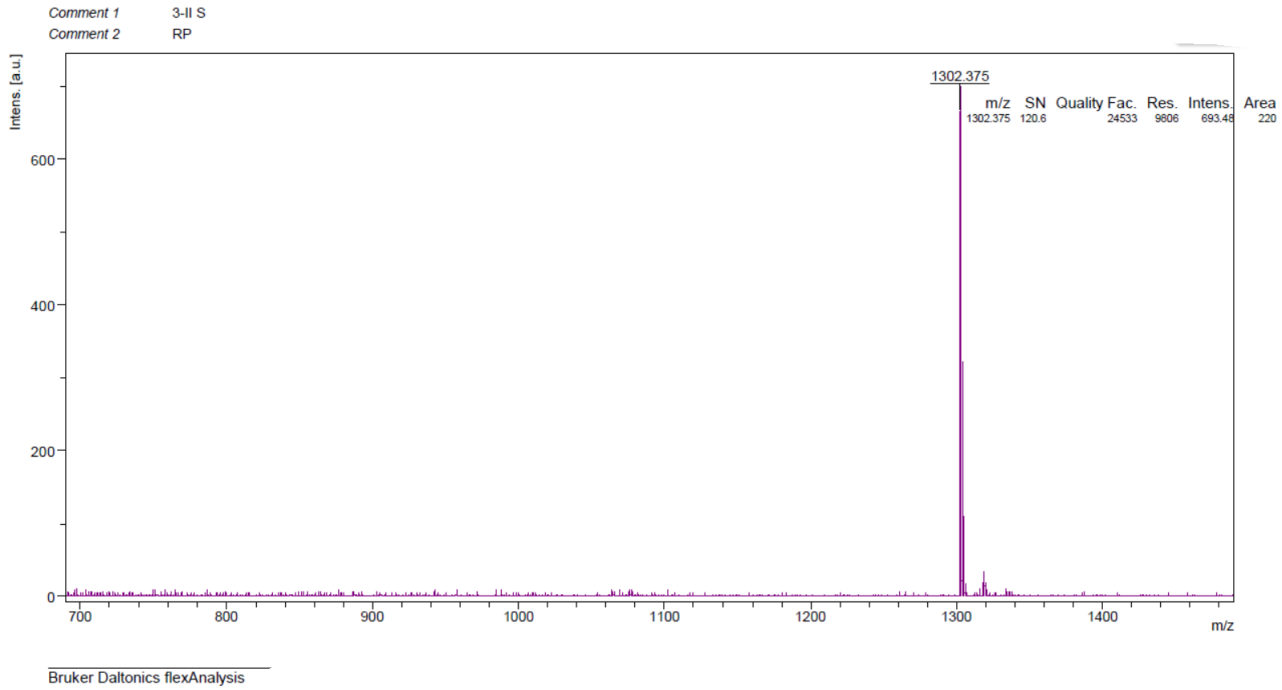
^{13}C NMR – ‘bis-adduct **DMF**’



^{1}H NMR – ‘bis-adduct **DMF**’



MS-MALDI – ‘bis-adduct **DMF**’



2. HPLC quantification method

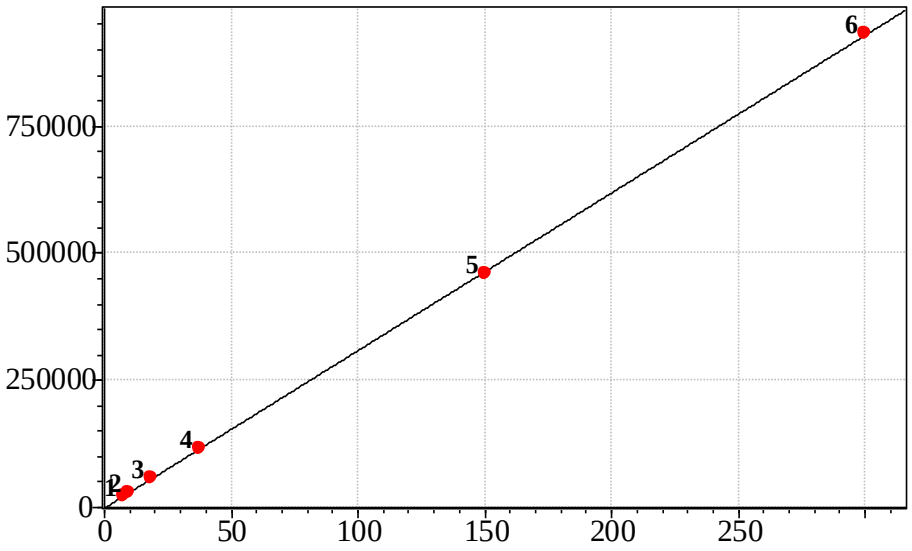
2.1. Optimization of HPLC conditions

When selecting chromatographic conditions, the acetonitrile and toluene mixtures in reverse phase HPLC in isocratic mode were initially used. The eluents of the toluene/acetonitrile composition were tested in the following volume ratios: 1: 9; 1: 4; 3: 7; 1: 1; 7: 3. It was found that the eluent of the composition toluene/acetonitrile = 1: 1, *v/v* is optimal, in which the substances obtain good separation and symmetrical peak shapes, but a short retention time. In other systems, poor separation of the test substances was observed, either due to short retention times, where the outgoing detected individual compounds overlap, or the chromatographic peaks had an asymmetric shape.

2.2. Linear calibration models for single component

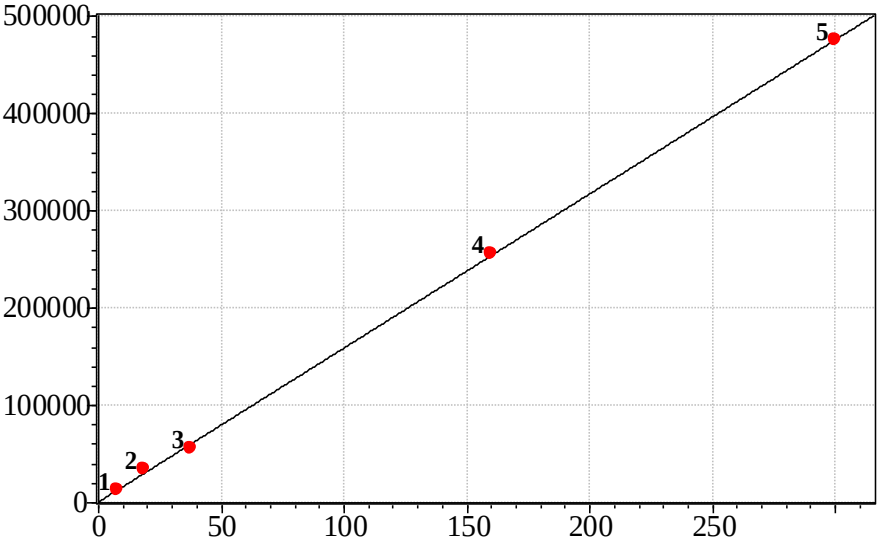
Absolute grading method for HPLC: peak area *vs.* concentration plots

Resulting solutions were injected into the column and the peak areas obtained at the retention times 4.98, 2.16 and 1.81 min at a flow rate of 1.0 ml min^{-1} in toluene/acetonitrile (1:1, *v/v*) were measured at a wavelength of 330 nm for C_{60}, **MMF** and **DMF**, respectively. Calibration plots by plotting peak area *vs.* concentration were constructed to allow determination of HPLC yields for reactions with different concentrations. Each measurement represented the average of three replicates. Predictable, linear trends were observed in all cases (Fig. S1- S3).



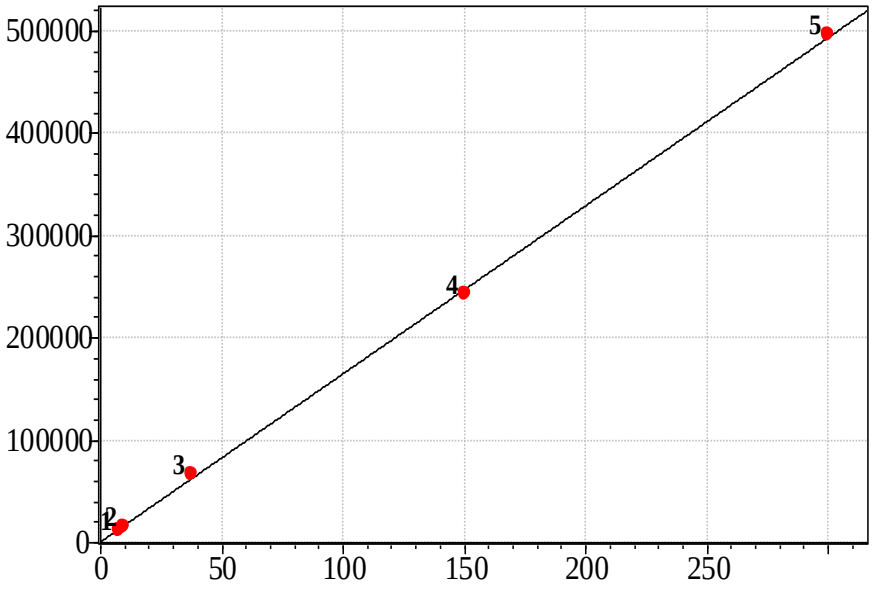
Y = aX + b
a = 3100,78
b = -1267,48
R^2 = 0,9999482
R = 0,9999741
RSS = 3,424787e+007
External standard
Average RF: 3,072718e+003
RFCO: 1,810465e+001
RF %CKO: 0,589206
25.04.2018 15:52:36

Fig. S1 Peak area *vs.* concentration plot of C_{60}



Y = aX + b
a = 1584.68
b = 971.604
R^2 = 0.9998067
R = 0.9999033
RSS = 3.036853e+007
External standard
Average RF: 1.635018e+003
RF CO: 1.121889e+002
RF %CKO: 6.861631
25.04.2018 17:22:15

Fig. S2 Peak area *vs.* concentration plot of **MMF**

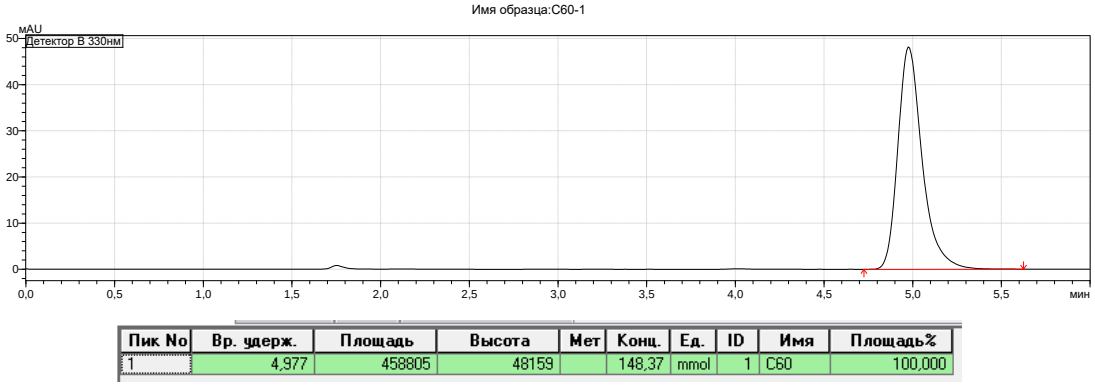


Y = aX + b
a = 1642.74
b = 979.536
R^2 = 0.9996769
R = 0.9998384
RSS = 5.510637e+007
External standard
Average RF: 1.677762e+003
RF CO: 6.925881e+001
RF %CKO: 4.128047
25.04.2018 18:46:11

Fig. S3 Peak area *vs.* concentration plot of **DMF**

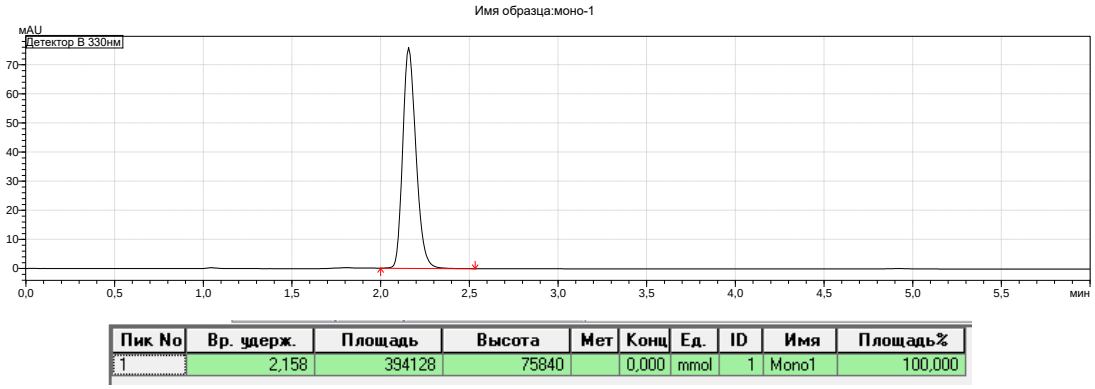
2.3. Direct comparison *vs.* authentic sample

For purposes of quantification it was decided to compare all HPLC chromatograms with the authentic standards at a wavelength of 330 nm (Fig. S4-S6).



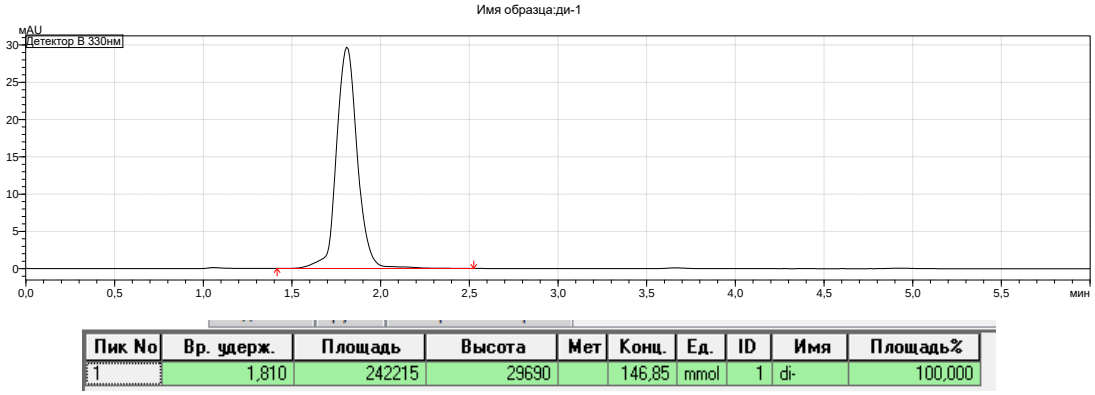
Пик No	Вр. удерж.	Площадь	Высота	Мет	Конц.	Ед.	ID	Имя	Площадь%
1	4,977	458805	48159		148,37	mmol	1	C60	100,000

Fig. S4 HPLC data for C_{60} in in toluene/acetonitrile (1:1).



Пик No	Вр. удерж.	Площадь	Высота	Мет	Конц	Ед.	ID	Имя	Площадь%
1	2,158	394128	75840		0,000	mmol	1	Mono1	100,000

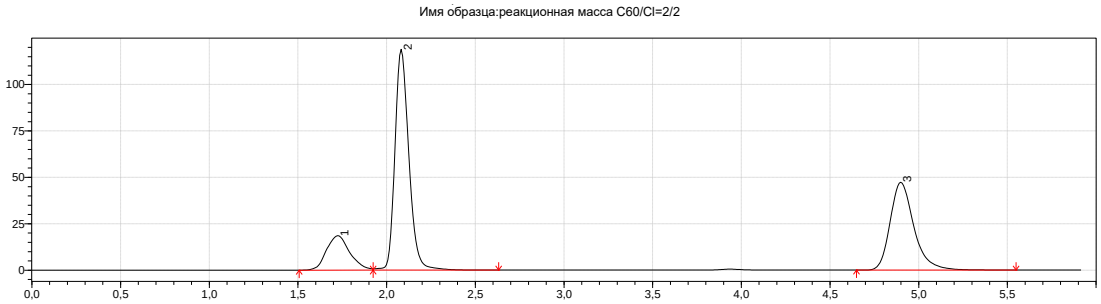
Fig. S5 HPLC data for **MMF** in toluene/acetonitrile (1:1).



Пик No	Вр. удерж.	Площадь	Высота	Мет	Конц.	Ед.	ID	Имя	Площадь%
1	1,810	242215	29690		146,85	mmol	1	di-	100,000

Fig. S6 HPLC data for **DMF** in toluene/acetonitrile (1:1).

For an example reaction quantification comparing the peak areas of the chromatograms reveals a yield of returned C_{60} (peak at 4.98 min), yield of **MMF** (peak at 2.16 min) and **DMF** (peak at 1.81 min) by HPLC in toluene/acetonitrile (1:1) at a wavelength of 330 nm (Fig. S7).



Пик No	Вр. удерж.	Площадь	Высота	Мет	Конц.	Ед.	ID	Имя	Площадь%
1	1,810	169038	18551		102,3	mmol	1	di-	13,448
2	2,166	649289	118861	V	0,000				51,654
3	4,983	438660	47277		0,000				34,898

Fig. S7 HPLC data for the reaction of C_{60} with 2-(4-chloro-3-oxo-1-phenylbutan-2-yl)isoindoline-1,3-dione (**Cl-K**) in toluene/acetonitrile (1:1).

3. The effect of halogenmethylketones consumption on the kinetic of the process

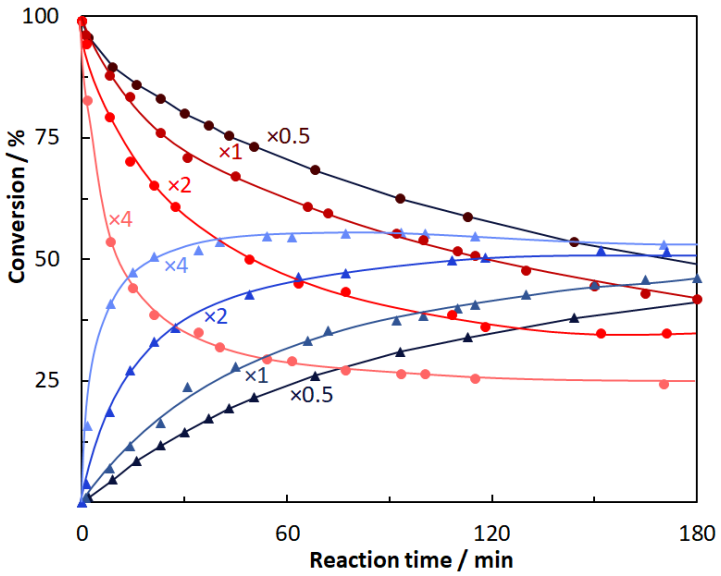


Fig. S8 Kinetic curves for consumption of fullerene C_{60} (●) and accumulation of monoaddition **MMF** (▲) from the reaction time with (a) 0.5, (b) 1.0, (c) 2.0 and (d) 4.0 equiv. of C_{60}: **Cl-K** in the initial mixture at room temperature (294 K).

4. Arrhenius plots of the rate constants

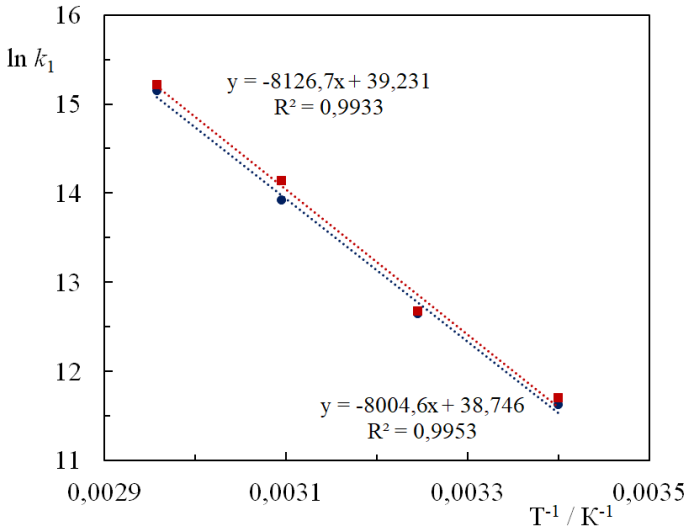


Fig. S9 Arrhenius plots of the rate constants of the first stage of the Bingel reaction for the equiv. molar ratio C_{60} : **Cl-K** (●) or C_{60} : **Br-K** (■) in the initial mixture.

5. The calculation of the reaction rate constant by using the computer algebra system MAPLE 16

Theoretical Modeling of the Kinetic Process

$$\mathrm{A} + \mathrm{B} + \mathrm{C} \overset{k_1}{\rightarrow} \mathrm{D}$$

$$\mathrm{D} + \mathrm{B} + \mathrm{C} \overset{k_2}{\rightarrow} \mathrm{E}$$

It is known that the concentrations of A(t), B(t), C(t), D(t), E(t) substances satisfy the system of differential equations:

$$\begin{aligned}
\frac{dA(t)}{dt} &= -k_1 A(t)B(t)C(t),\\
\frac{dB(t)}{dt} &= -B(t)C(t)\big(k_1 A(t) + k_2 D(t)\big),\\
\frac{dC(t)}{dt} &= -B(t)C(t)\big(k_1 A(t) + k_2 D(t)\big),\\
\frac{dD(t)}{dt} &= B(t)C(t)\big(k_1 A(t) - k_2 D(t)\big),\\
\frac{dE(t)}{dt} &= -k_2 B(t)C(t)D(t),
\end{aligned}$$

where k_1, k_2 are the reaction rate coefficients. This system has three simple first integrals (conservation laws)

$$B(t) - C(t) = B_0 - C_0, \qquad A(t) - B(t) - E(t) = A_0 - B_0 - E_0,$$
$$A(t) + D(t) + E(t) = A_0 + D_0 + E_0.$$

Here $A_0, B_0, C_0,\ D_0 = 0, E_0 = 0$ concentration of substances at the initial time. These conservation laws have a simple interpretation - the concentrations of substances B and C vary proportionally. The first integrals allow us to exclude B(t), C(t), D(t) from the system of equations and obtain a system of equations for two unknowns A(t), E(t):

$$\begin{aligned}
\frac{dA(t)}{dt} &= -k_1 A(t)\big(A_0 - C_0 - A(t) + E(t)\big)\big(A_0 - B_0 - A(t) + E(t)\big),\\
\frac{dE(t)}{dt} &= -k_2\big(A_0 - C_0 - A(t) + E(t)\big)\big(A_0 - B_0 - A(t) + E(t)\big)\big(A_0 - A(t) - E(t)\big).
\end{aligned}$$

This system has a nontrivial first integral

$$W(t) = \frac{1}{A_0}\Big(kA(t) - (k-1)\big(A_0 - E(t)\big)\Big)\left(\frac{A(t)}{A_0}\right)^{-k} - 1,$$

where k is the ratio k_2/k_1. The value of this integral is 0. Knowing the experimental dependences of A(t), E(t) curves, we a minimizing functional for finding k can be composed

$$f(k) = \sum_{i=1}^{N} W^2(t_i, k) \to min$$

k values are found from the derivative to be equal to zero

$$f'(k) = 0$$

From $W(t) = 0$, E(t) can be expressed

$$E(t) = \frac{A_0}{k-1}\left(\left(\frac{A(t)}{A_0}\right)^{-k} - k\frac{A(t)}{A_0} + k - 1\right)$$

and a differential equation for $A(t)$ function is obtained:

$$\frac{dA(t)}{dt} = -\frac{k_1}{(k-1)^2}A(t)A_0^2\left(\left(\frac{A(t)}{A_0}\right)^{-k} + (k-1)\left(2 - \frac{C_0}{A_0}\right) + (1-2k)\frac{A(t)}{A_0}\right)\left(\left(\frac{A(t)}{A_0}\right)^{-k} + (k-1)\left(2 - \frac{B_0}{A_0}\right) + (1-2k)\frac{A(t)}{A_0}\right).$$

For a given k_1 value, this equation can be solved by the Runge-Kutta method and the results of numerical calculations are to be compared with the experimental data. Using the golden section method, such a k_1 value is determined when the solution deviation will be minimal.

So, Fig. S10-S11 reveals the kinetic curves obtained during the experiment (squares) and after a mathematical modeling (solid line) implemented in MAPLE. Good convergence between the two representations of the kinetic data is observed.

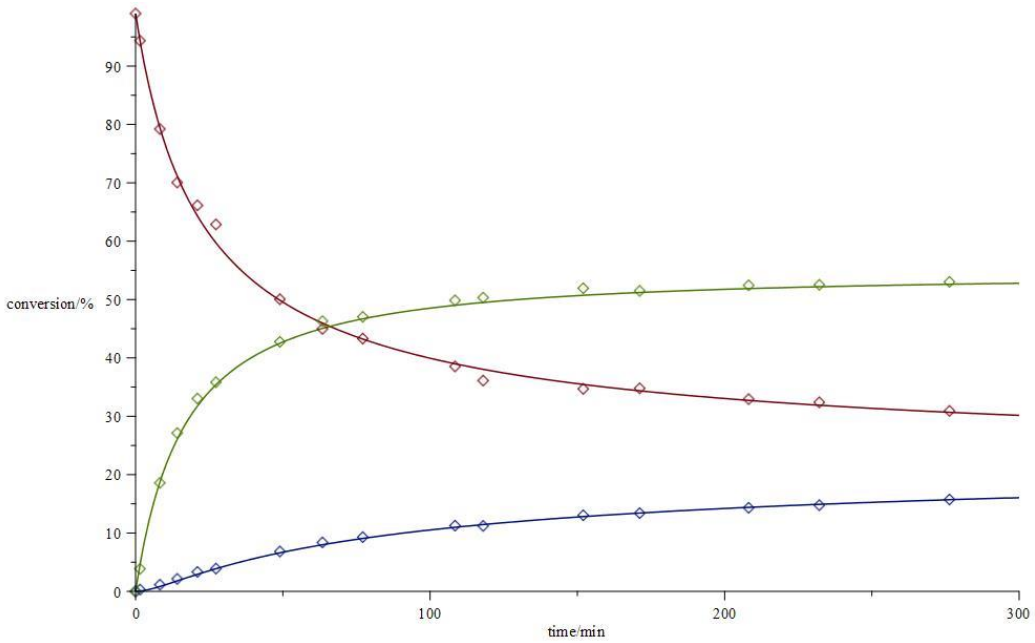


Fig. S10 Kinetic curves decrease of fullerene C_{60} and increase of **MMF** and **DMF** from reaction time at molar ratio of reagents in the initial mixture C_{60}: **Cl-K** = 1:2. Squares represent the observed experimental concentrations during the reaction time. Solid line is the result of theoretical mathematical modeling.

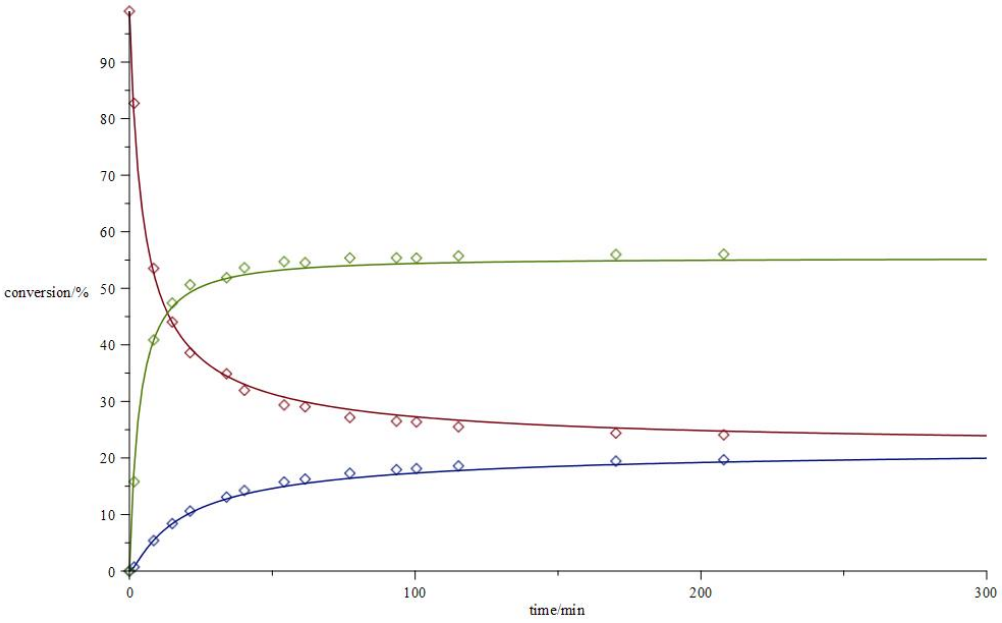


Fig. S11 Kinetic curves decrease of fullerene C_{60} and increase of **MMF** and **DMF** from reaction time at molar ratio of reagents in the initial mixture C_{60}: **Cl-K** = 1:4. Squares represent the observed experimental concentrations during the reaction time. Solid line is the result of theoretical mathematical modeling.

6. List of Cartesian coordinates for the optimized structures

1 – H; 6 – C; 7 - N; 8 - O; 17 - Cl; 35 – Br.

B3LYP/6-31G(d), toluene

	C_{60}= -2285.89729 Хартри						
6	0.729729000	-1.004386000	3.338076000	6	2.609312000	2.349921000	-0.594483000
6	1.180727000	0.383641000	3.338076000	6	1.428585000	3.207769000	-0.594483000
6	0.000000000	1.241490000	3.338076000	6	0.729729000	3.434841000	0.594483000
6	-1.180727000	0.383641000	3.338076000	6	-0.729729000	3.434841000	0.594483000
6	-0.729729000	-1.004386000	3.338076000	6	-1.428585000	3.207769000	-0.594483000
6	-1.428585000	-1.966279000	2.603255000	6	-2.609312000	2.349921000	-0.594483000
6	-0.698856000	-2.970665000	1.835972000	6	-3.041229000	1.755438000	0.594483000
6	0.698856000	-2.970665000	1.835972000	6	-3.492227000	0.367410000	0.594483000
6	1.428585000	-1.966279000	2.603255000	6	-3.492227000	-0.367410000	-0.594483000
6	2.609312000	-1.582638000	1.835972000	6	-3.041229000	-1.755438000	-0.594483000
6	3.041229000	-0.253334000	1.835972000	6	-2.311500000	-1.992541000	-1.835972000
6	2.311500000	0.751052000	2.603255000	6	-1.180727000	-2.814096000	-1.835972000
6	2.311500000	1.992541000	1.835972000	6	0.000000000	-2.430455000	-2.603255000
6	1.180727000	2.814096000	1.835972000	6	1.180727000	-2.814096000	-1.835972000
6	0.000000000	2.430455000	2.603255000	6	2.311500000	-1.992541000	-1.835972000
6	-1.180727000	2.814096000	1.835972000	6	2.311500000	-0.751052000	-2.603255000
6	-2.311500000	1.992541000	1.835972000	6	3.041229000	0.253334000	-1.835972000
6	-2.311500000	0.751052000	2.603255000	6	2.609312000	1.582638000	-1.835972000
6	-3.041229000	-0.253334000	1.835972000	6	1.428585000	1.966279000	-2.603255000
6	-2.609312000	-1.582638000	1.835972000	6	0.698856000	2.970665000	-1.835972000
6	-2.609312000	-2.349921000	0.594483000	6	-0.698856000	2.970665000	-1.835972000
6	-1.428585000	-3.207769000	0.594483000	6	-1.428585000	1.966279000	-2.603255000
6	-0.729729000	-3.434841000	-0.594483000	6	-2.609312000	1.582638000	-1.835972000
6	0.729729000	-3.434841000	-0.594483000	6	-3.041229000	0.253334000	-1.835972000
6	1.428585000	-3.207769000	0.594483000	6	-2.311500000	-0.751052000	-2.603255000
6	2.609312000	-2.349921000	0.594483000	6	-1.180727000	-0.383641000	-3.338076000
6	3.041229000	-1.755438000	-0.594483000	6	0.000000000	-1.241490000	-3.338076000
6	3.492227000	-0.367410000	-0.594483000	6	1.180727000	-0.383641000	-3.338076000
6	3.492227000	0.367410000	0.594483000	6	0.729729000	1.004386000	-3.338076000
6	3.041229000	1.755438000	0.594483000	6	-0.729729000	1.004386000	-3.338076000
Cl-K$^-$ = -1434.24674							
6	3.104227000	0.292827000	0.330221000	6	-0.840903000	1.498545000	-1.018937000
6	2.597514000	-0.869061000	-0.243798000	6	-1.792290000	2.480498000	-1.227142000
6	4.469838000	0.520710000	0.430665000	1	-1.193932000	0.060821000	2.229232000
6	3.436834000	-1.858782000	-0.734740000	17	-2.520354000	3.488060000	0.084999000
6	5.327119000	-0.466604000	-0.071672000	8	-0.203912000	0.920620000	-1.945997000
6	4.817553000	-1.639148000	-0.645554000	6	-2.317885000	-0.905309000	0.688173000
1	4.854144000	1.431987000	0.879658000	6	-2.247348000	-2.128761000	1.367863000
1	3.032046000	-2.764797000	-1.175977000	6	-3.129033000	-0.832886000	-0.454664000
1	6.403132000	-0.323280000	-0.016741000	6	-2.946977000	-3.250561000	0.920534000
1	5.506270000	-2.388164000	-1.027748000	6	-3.826050000	-1.952961000	-0.908419000
6	1.946422000	1.131962000	0.756367000	6	-3.740462000	-3.168042000	-0.224535000
6	1.101654000	-0.820385000	-0.169161000	1	-1.629069000	-2.205272000	2.260438000
7	0.788121000	0.401122000	0.464697000	1	-2.869357000	-4.188392000	1.466795000
8	1.986393000	2.237365000	1.270641000	1	-4.443209000	-1.872857000	-1.800721000
8	0.339646000	-1.710660000	-0.480601000	1	-4.288238000	-4.038656000	-0.578543000
6	-0.518406000	1.070875000	0.456711000	1	-2.001900000	2.890677000	-2.206131000
6	-1.622747000	0.320693000	1.252084000	1	-3.205772000	0.110785000	-0.987707000
				1	-2.388050000	1.080663000	1.448847000
				1	-0.338263000	1.981342000	1.034409000
Br-K$^-$ = -3545.76082							
6	3.406163000	-0.600467000	-0.268331000	6	-1.750159000	-1.697834000	1.305792000

6	3.144680000	0.704066000	0.139277000	1	-0.661875000	0.639768000	-2.182044000
6	4.693416000	-1.119613000	-0.266188000	8	0.060180000	-0.351225000	1.919048000
6	4.161419000	1.548348000	0.561784000	6	-1.908212000	1.517128000	-0.672792000
6	5.727212000	-0.279994000	0.168354000	6	-1.594737000	2.818870000	-1.086044000
6	5.464513000	1.034025000	0.577925000	6	-2.955239000	1.351209000	0.247776000
1	4.886638000	-2.139422000	-0.585915000	6	-2.291519000	3.923392000	-0.594622000
1	3.947589000	2.566074000	0.874686000	6	-3.648061000	2.454343000	0.749570000
1	6.748238000	-0.651847000	0.190720000	6	-3.322299000	3.745681000	0.330316000
1	6.285776000	1.662040000	0.913489000	1	-0.786122000	2.967447000	-1.796929000
6	2.106314000	-1.225875000	-0.652354000	1	-2.025637000	4.923116000	-0.931865000
6	1.677075000	0.960554000	-0.016286000	1	-4.452068000	2.300606000	1.466173000
7	1.124370000	-0.236870000	-0.509662000	1	-3.867358000	4.603809000	0.717830000
8	1.921804000	-2.370057000	-1.031404000	1	-2.085364000	-1.940394000	2.304539000
8	1.116611000	2.027604000	0.130471000	1	-3.218103000	0.348407000	0.568249000
6	-0.293311000	-0.618520000	-0.466175000	1	-2.020848000	-0.346274000	-1.664997000
6	-1.226083000	0.313724000	-1.299441000	1	-0.311683000	-1.580079000	-0.984382000
6	-0.672282000	-0.880595000	1.033082000	35	-2.840339000	-2.566754000	-0.063334000
MMF-Int(Cl) = -3720.164852							
6	-0.635463000	-0.027043000	1.863575000	6	4.088253000	2.847061000	-0.711216000
6	-1.139354000	1.066041000	0.888156000	6	4.667667000	1.953210000	-1.698329000
6	-1.116055000	0.268396000	-0.447913000	6	3.664797000	1.713609000	-2.727762000
6	-0.981505000	-1.137712000	-0.179795000	6	3.573535000	0.449668000	-3.328659000
6	-0.683320000	-1.317316000	1.231218000	6	4.451438000	-0.620942000	-2.892371000
6	0.141493000	-2.373391000	1.640127000	6	3.694500000	-1.865108000	-2.892908000
6	1.126640000	-2.135657000	2.664195000	6	3.920958000	-2.822766000	-1.899173000
6	1.229105000	-0.861739000	3.236578000	6	4.917606000	-2.586627000	-0.869296000
6	0.341161000	0.207947000	2.819342000	6	5.635490000	-1.385379000	-0.866457000
6	1.098990000	1.466775000	2.856695000	6	5.893905000	-0.687401000	0.380146000
6	0.876199000	2.383646000	1.811801000	6	5.817243000	0.741717000	0.118641000
6	-0.130243000	2.208116000	0.820108000	6	5.516677000	0.923311000	-1.292304000
6	0.400179000	2.669576000	-0.414774000	6	5.409970000	-0.392917000	-1.901828000
6	0.138923000	2.052107000	-1.657582000	6	-2.591763000	1.601253000	1.163790000
6	-0.594716000	0.781910000	-1.626284000	6	-3.681895000	0.524522000	1.077513000
6	-0.006601000	-0.108026000	-2.610898000	6	-4.697688000	0.647532000	-0.084278000
6	0.061374000	-1.485608000	-2.370046000	8	-3.722657000	-0.404997000	1.853152000
6	-0.444592000	-2.017256000	-1.129707000	7	-5.489917000	-0.571067000	-0.163100000
6	0.439523000	-3.093587000	-0.703409000	6	-5.605010000	1.917014000	-0.011915000
6	0.725649000	-3.267159000	0.648055000	6	-5.009096000	3.184093000	-0.595342000
6	2.079604000	-3.576408000	1.071147000	6	-4.887567000	4.341724000	0.184662000
6	2.326618000	-2.876671000	2.322679000	6	-4.609270000	3.239812000	-1.940054000
6	3.582799000	-2.313920000	2.564278000	6	-4.370918000	5.520697000	-0.357905000
6	3.690045000	-0.995644000	3.173804000	6	-4.090656000	4.414462000	-2.483607000
6	2.529653000	-0.285777000	3.494242000	6	-3.968936000	5.559998000	-1.692975000
6	2.444961000	1.150243000	3.241572000	1	-5.193532000	4.317586000	1.227524000
6	3.553677000	1.812718000	2.675644000	1	-4.703840000	2.356696000	-2.568523000
6	3.320648000	2.795592000	1.635740000	1	-4.277007000	6.404627000	0.267571000
6	2.020059000	3.079299000	1.217911000	1	-3.780245000	4.434776000	-3.524968000
6	1.722297000	3.260101000	-0.179238000	1	-3.559131000	6.473895000	-2.114862000
6	2.730875000	3.149851000	-1.135672000	6	-5.263260000	-1.551803000	-1.146089000
6	2.479476000	2.467090000	-2.391070000	6	-6.452122000	-0.982367000	0.777669000
6	1.204762000	1.904660000	-2.608357000	6	-6.164846000	-2.687942000	-0.804605000
6	1.108889000	0.580201000	-3.218653000	6	-6.874851000	-2.348876000	0.348203000
6	2.263506000	-0.126164000	-3.566956000	6	-6.355539000	-3.903908000	-1.444968000
6	2.339922000	-1.557471000	-3.307483000	6	-7.804926000	-3.213973000	0.906255000
6	1.258315000	-2.224647000	-2.726154000	6	-7.289862000	-4.786039000	-0.886959000
6	1.493806000	-3.221913000	-1.693274000	6	-8.003068000	-4.446425000	0.269782000
6	2.798889000	-3.514901000	-1.288698000	1	-5.797682000	-4.159495000	-2.340615000
6	3.098267000	-3.697844000	0.122129000	1	-8.353220000	-2.944549000	1.803791000

6	4.404264000	-3.117025000	0.381104000	1	-7.463765000	-5.749547000	-1.357744000
6	4.642471000	-2.443002000	1.583376000	1	-8.720030000	-5.152029000	0.680142000
6	5.397837000	-1.198324000	1.581883000	8	-4.490663000	-1.442521000	-2.078238000
6	4.823344000	-0.312589000	2.578286000	8	-6.865263000	-0.322775000	1.710657000
6	4.735696000	1.062178000	2.319362000	1	-4.120937000	0.675001000	-1.015556000
6	5.254304000	1.596070000	1.066940000	1	-6.511447000	1.662926000	-0.574587000
6	4.375745000	2.671943000	0.643670000	1	-5.922457000	2.083981000	1.020068000
				1	-2.784884000	2.405233000	0.454798000
				17	-2.712179000	2.393027000	2.807543000
MMF-Int(Br) = -5831.682248							
6	0.516728000	-0.284615000	-1.643150000	6	5.504974000	1.819680000	-0.069642000
6	1.027459000	0.799438000	-0.660411000	6	5.058366000	2.998079000	0.776249000
6	0.879600000	0.034078000	0.687854000	6	4.428770000	4.108760000	0.198624000
6	0.675203000	-1.366758000	0.439779000	6	-4.853774000	2.090032000	1.567677000
6	0.447971000	-1.560330000	-0.982414000	6	-3.926848000	1.814875000	2.657853000
6	-0.415148000	-2.573995000	-1.417445000	6	-3.945928000	0.561276000	3.286352000
6	-1.324846000	-2.301796000	-2.501407000	6	-4.861328000	-0.464629000	2.821268000
6	-1.317235000	-1.037145000	-3.102553000	6	-4.183276000	-1.751859000	2.891684000
6	-0.390607000	-0.013263000	-2.655163000	6	-4.409511000	-2.715759000	1.904186000
6	-1.067359000	1.288326000	-2.763676000	6	-5.329542000	-2.444020000	0.814199000
6	-0.851836000	2.211451000	-1.723470000	6	-5.973953000	-1.203545000	0.747407000
6	0.086594000	2.003169000	-0.673399000	6	-6.116915000	-0.520424000	-0.525821000
6	-0.485041000	2.521313000	0.519054000	6	-5.968908000	0.907275000	-0.288699000
6	-0.331558000	1.917839000	1.786793000	6	-5.739733000	1.103550000	1.133573000
6	0.324392000	0.606245000	1.822813000	6	-5.748646000	-0.202436000	1.774676000
6	-0.371860000	-0.224505000	2.788611000	6	2.509203000	1.248996000	-0.833259000
6	-0.508991000	-1.601052000	2.572317000	6	3.584438000	0.165903000	-0.719827000
6	0.033803000	-2.191139000	1.374098000	6	4.767219000	0.471932000	0.231259000
6	-0.887815000	-3.223380000	0.918742000	8	3.505575000	-0.890539000	-1.307338000
6	-1.106728000	-3.409840000	-0.444022000	7	5.676533000	-0.662108000	0.250681000
6	-2.451060000	-3.646678000	-0.938132000	6	5.299193000	3.010769000	2.159269000
6	-2.584659000	-2.962816000	-2.215832000	6	4.048803000	5.202651000	0.980689000
6	-3.788925000	-2.331465000	-2.539807000	6	4.921369000	4.101122000	2.941655000
6	-3.781411000	-1.023615000	-3.178731000	6	4.296113000	5.203752000	2.353170000
6	-2.563935000	-0.391368000	-3.444555000	1	4.208742000	4.103803000	-0.865841000
6	-2.407095000	1.041686000	-3.215536000	1	5.787485000	2.158135000	2.627225000
6	-3.504253000	1.783103000	-2.730891000	1	3.554508000	6.050495000	0.513645000
6	-3.271367000	2.771969000	-1.697353000	1	5.115893000	4.090826000	4.011123000
6	-1.981504000	2.990317000	-1.212493000	1	3.999031000	6.053293000	2.962498000
6	-1.753859000	3.183628000	0.196211000	6	5.730951000	-1.576759000	1.316441000
6	-2.819967000	3.156362000	1.094238000	6	6.474584000	-1.069083000	-0.833493000
6	-2.680859000	2.489160000	2.375830000	6	6.664809000	-2.654002000	0.881076000
6	-1.456894000	1.856203000	2.676343000	6	7.106861000	-2.352985000	-0.408386000
6	-1.476050000	0.543030000	3.316385000	6	7.094408000	-3.791197000	1.549619000
6	-2.689171000	-0.085319000	3.610180000	6	7.996311000	-3.178327000	-1.080756000
6	-2.837400000	-1.514563000	3.375478000	6	7.990228000	-4.633271000	0.877746000
6	-1.767321000	-2.258701000	2.872235000	6	8.433434000	-4.331940000	-0.416371000
6	-2.004147000	-3.262370000	1.846278000	1	6.745078000	-4.017954000	2.552267000
6	-3.299585000	-3.489383000	1.374460000	1	8.334315000	-2.937752000	-2.084014000
6	-3.527828000	-3.684794000	-0.047977000	1	8.346591000	-5.535663000	1.366441000
6	-4.778790000	-3.032192000	-0.393263000	1	9.126389000	-5.005752000	-0.912459000
6	-4.908995000	-2.374994000	-1.620856000	8	5.133417000	-1.462883000	2.369383000
6	-5.585674000	-1.087444000	-1.686445000	8	6.624129000	-0.454994000	-1.870997000
6	-4.903132000	-0.260270000	-2.664213000	1	4.345164000	0.515746000	1.242605000
6	-4.748459000	1.112841000	-2.429119000	1	6.567793000	1.636187000	0.119082000
6	-5.305013000	1.706205000	-1.220168000	1	5.419847000	2.058049000	-1.131992000
6	-4.388428000	2.738371000	-0.767922000	1	2.698647000	2.061354000	-0.132871000
6	-4.167412000	2.925824000	0.598407000	35	2.794360000	2.098292000	-2.621017000

MMF-TS(Cl)

6	-0.488439106	-0.723970738	0.966230332	6	4.321879668	2.749171487	-0.472090128
6	-0.935740823	0.670906555	0.478913299	6	4.851456044	2.271850807	-1.738364278
6	-0.986566241	0.431088518	-1.068504848	6	3.829408065	2.468571261	-2.759159463
6	-0.903090863	-0.980316539	-1.338792928	6	3.680736696	1.524260383	-3.786820111
6	-0.596687269	-1.681322405	-0.104667295	6	4.523915472	0.341369013	-3.807314437
6	0.196802735	-2.835451798	-0.144087135	6	3.716940600	-0.786467860	-4.253949530
6	1.202476381	-3.035741238	0.871230086	6	3.913672399	-2.052521419	-3.695597475
6	1.362932226	-2.067828637	1.870855226	6	4.930307297	-2.251362429	-2.673964957
6	0.509605903	-0.895065829	1.909366633	6	5.701199038	-1.164944224	-2.244004201
6	1.326479597	0.235357131	2.383747183	6	5.999890416	-0.993688088	-0.832926601
6	1.133968228	1.482598559	1.782421801	6	5.979126917	0.431931091	-0.538347015
6	0.103024410	1.726533514	0.814239555	6	5.667321488	1.139305350	-1.770917992
6	0.625760430	2.598378780	-0.162597304	6	5.500896616	0.151622371	-2.826634859
6	0.326564342	2.488206826	-1.548685126	6	-2.336777232	0.995782483	0.062671027
6	-0.452717441	1.346895549	-1.978713500	6	-3.364531888	-0.034071285	-0.252424777
6	0.088960654	0.863722175	-3.243257377	6	-4.468396987	0.344634657	-1.280433780
6	0.105643660	-0.503645581	-3.528012914	8	-3.328338678	-1.159597210	0.217591030
6	-0.412059178	-1.451742980	-2.562115111	7	-5.424743394	-0.754552135	-1.357256194
6	0.435151926	-2.632785972	-2.593233309	6	-5.170981321	1.723255867	-1.099860057
6	0.730219420	-3.314265344	-1.412313297	6	-4.489422503	2.884590039	-1.803298736
6	2.076678114	-3.802074953	-1.172501474	6	-3.984658803	3.971890711	-1.075222100
6	2.368543163	-3.630459681	0.244130431	6	-4.389197586	2.912898668	-3.204346938
6	3.651187063	-3.245482492	0.646793993	6	-3.399610794	5.059774023	-1.731553646
6	3.818880100	-2.255469615	1.701566806	6	-3.800206309	3.995035477	-3.861004785
6	2.691923285	-1.676134540	2.292975341	6	-3.303985378	5.075932346	-3.124650811
6	2.666690247	-0.251025129	2.597386423	1	-4.044056040	3.959515108	0.009915145
6	3.789908488	0.538429873	2.290611586	1	-4.777359812	2.080231209	-3.789247966
6	3.587644920	1.850023690	1.706769756	1	-3.007849754	5.889322190	-1.147775602
6	2.291983759	2.310522360	1.462425470	1	-3.728314600	3.994131028	-4.946267362
6	1.980795790	3.008105393	0.239496381	1	-2.840553966	5.917935155	-3.633251150
6	2.970242714	3.228493291	-0.713139899	6	-5.352784357	-1.740308441	-2.354111043
6	2.673712354	3.067873181	-2.131785943	6	-6.325543233	-1.111055532	-0.334689785
6	1.379547530	2.681198782	-2.518324779	6	-6.329162561	-2.798881786	-1.960869323
6	1.224803093	1.691620832	-3.580200299	6	-6.909170438	-2.423979338	-0.748789967
6	2.347590417	1.128503478	-4.197159229	6	-6.681389872	-3.979380441	-2.601665277
6	2.368910148	-0.298044032	-4.488802500	6	-7.865093678	-3.214617835	-0.125775805
6	1.268476334	-1.097122216	-4.167647242	6	-7.643003943	-4.788607151	-1.979723378
6	1.474216553	-2.414495639	-3.586260752	6	-8.225956481	-4.411776373	-0.760842644
6	2.770313500	-2.885128146	-3.358077661	1	-6.221161384	-4.262308630	-3.543905723
6	3.078777007	-3.593049362	-2.125150790	1	-8.306969677	-2.913905604	0.819718032
6	4.411866666	-3.196865687	-1.702323692	1	-7.940232321	-5.724167099	-2.446598846
6	4.692763913	-3.030475900	-0.340208593	1	-8.966197947	-5.061291991	-0.300591716
6	5.500338727	-1.904419582	0.102604035	8	-4.639499133	-1.696642203	-3.340279818
6	4.971270665	-1.434074315	1.372812577	8	-6.584829994	-0.448974722	0.649007887
6	4.943450866	-0.062511721	1.652117846	1	-3.964450560	0.334731691	-2.255664138
6	5.466035405	0.887146117	0.677632752	1	-6.176980380	1.608458275	-1.521413240
6	4.624442585	2.072210921	0.713598457	1	-5.296189993	1.938104752	-0.037194526
				1	-2.422613755	1.939862092	-0.462395963
				17	-3.238331966	1.199741720	2.331613443

MMF-TS(Br)

6	-0.613552824	-0.695666191	1.281103973	6	4.196765950	2.777476034	-0.157216486
6	-1.060854541	0.699211102	0.793786941	6	4.726342326	2.300155354	-1.423490636
6	-1.111679959	0.459393065	-0.753631207	6	3.704294347	2.496875808	-2.444285821
6	-1.028204581	-0.952011992	-1.023919286	6	3.555622978	1.552564930	-3.471946469
6	-0.721800987	-1.653017858	0.210206347	6	4.398801754	0.369673560	-3.492440796
6	0.071689017	-2.807147251	0.170786507	6	3.591826881	-0.758163313	-3.939075888
6	1.077362663	-3.007436691	1.186103727	6	3.788558681	-2.024216872	-3.380723834

6	1.237818508	-2.039524090	2.185728867	6	4.805193579	-2.223057882	-2.359091316
6	0.384492185	-0.866761281	2.224240275	6	5.576085320	-1.136639677	-1.929130560
6	1.201365879	0.263661678	2.698620824	6	5.874776698	-0.965383541	-0.518052960
6	1.008854510	1.510903106	2.097295443	6	5.854013198	0.460235638	-0.223473373
6	-0.022089308	1.754838062	1.129113197	6	5.542207770	1.167609897	-1.456044350
6	0.500646712	2.626683327	0.152276337	6	5.375782897	0.179926918	-2.511761218
6	0.201450624	2.516511373	-1.233811484	6	-2.461890950	1.024087031	0.377544668
6	-0.577831160	1.375200096	-1.663839859	6	-3.489645606	-0.005766737	0.062448865
6	-0.036153064	0.892026722	-2.928383735	6	-4.593510706	0.372939204	-0.965560139
6	-0.019470058	-0.475341033	-3.213139272	8	-3.453452397	-1.131292663	0.532464672
6	-0.537172896	-1.423438433	-2.247241469	7	-5.549857113	-0.726247588	-1.042382552
6	0.310038208	-2.604481425	-2.278359667	6	-5.296095039	1.751560414	-0.784986415
6	0.605105702	-3.285960797	-1.097439656	6	-4.614536222	2.912894587	-1.488425095
6	1.951564395	-3.773770406	-0.857627833	6	-4.109772521	4.000195258	-0.760348458
6	2.243429445	-3.602155134	0.559004072	6	-4.514311304	2.941203215	-2.889473296
6	3.526073345	-3.217177945	0.961667635	6	-3.524724512	5.088078571	-1.416680005
6	3.693766382	-2.227165068	2.016440448	6	-3.925320027	4.023340024	-3.546131144
6	2.566809567	-1.647829993	2.607848983	6	-3.429099096	5.104236893	-2.809777170
6	2.541576529	-0.222720582	2.912260065	1	-4.169169758	3.987819655	0.324788786
6	3.664794770	0.566734420	2.605485227	1	-4.902473530	2.108535756	-3.474374324
6	3.462531202	1.878328237	2.021643397	1	-3.132963472	5.917626737	-0.832901960
6	2.166870040	2.338826907	1.777299111	1	-3.853428319	4.022435575	-4.631393721
6	1.855682072	3.036409940	0.554370023	1	-2.965667684	5.946239702	-3.318377508
6	2.845128996	3.256797838	-0.398266258	6	-5.477898075	-1.712003894	-2.039237401
6	2.548598635	3.096177728	-1.816912302	6	-6.450656952	-1.082750985	-0.019816144
6	1.254433812	2.709503329	-2.203451138	6	-6.454276279	-2.770577239	-1.645995682
6	1.099689374	1.719925379	-3.265326658	6	-7.034284156	-2.395674791	-0.433916326
6	2.222476699	1.156808025	-3.882285587	6	-6.806503590	-3.951075894	-2.286791636
6	2.243796430	-0.269739485	-4.173928859	6	-7.990207396	-3.186313288	0.189097837
6	1.143362616	-1.068817669	-3.852773600	6	-7.768117661	-4.760302604	-1.664849737
6	1.349102835	-2.386191092	-3.271387111	6	-8.351070199	-4.383471826	-0.445969002
6	2.645199782	-2.856823598	-3.043204020	1	-6.346275102	-4.234004083	-3.229032081
6	2.953663289	-3.564744814	-1.810277149	1	-8.432083395	-2.885601057	1.134591674
6	4.286752948	-3.168561140	-1.387450050	1	-8.065346039	-5.695862552	-2.131725205
6	4.567650195	-3.002171353	-0.025334952	1	-9.091311665	-5.032987444	0.014281926
6	5.375225008	-1.876115035	0.417477676	8	-4.764612851	-1.668337656	-3.025406176
6	4.846156947	-1.405769768	1.687686218	8	-6.709943712	-0.420670175	0.963881529
6	4.818337147	-0.034207174	1.966991487	1	-4.089564278	0.363036238	-1.940790497
6	5.340921687	0.915450664	0.992506393	1	-6.302094098	1.636762822	-1.206539598
6	4.499328866	2.100515468	1.028472098	1	-5.421303712	1.966409299	0.277679115
				1	-2.547727474	1.968166639	-0.147522322
				35	-3.077619459	1.941069898	2.687673059
	MMF = -3259.85529						
6	0.926675000	-1.207219000	1.030020000	6	-2.693051000	1.847005000	-2.860798000
6	1.220074000	0.261742000	0.984700000	6	-3.994169000	2.021525000	-2.225572000
6	0.346694000	0.873274000	2.035092000	6	-3.805249000	2.846157000	-1.035350000
6	-0.235532000	-0.192876000	2.821358000	6	-4.540287000	2.577105000	0.122301000
6	0.115608000	-1.465535000	2.204468000	6	-5.496149000	1.477146000	0.141501000
6	-0.798089000	-2.525820000	2.233064000	6	-5.441571000	0.854344000	1.461714000
6	-0.975925000	-3.346786000	1.051751000	6	-5.569240000	-0.532448000	1.586186000
6	-0.234230000	-3.061509000	-0.100974000	6	-5.751806000	-1.357746000	0.396229000
6	0.727324000	-1.970697000	-0.112780000	6	-5.804002000	-0.762022000	-0.866923000
6	0.673166000	-1.340526000	-1.449038000	6	-5.112538000	-1.379169000	-1.994521000
6	0.818656000	0.032491000	-1.598384000	6	-4.559615000	-0.313513000	-2.822987000
6	1.158888000	0.942803000	-0.457512000	6	-4.908040000	0.963556000	-2.206256000
6	0.237569000	2.113081000	-0.594456000	6	-5.675718000	0.685872000	-0.997590000
6	-0.422202000	2.678594000	0.488304000	6	2.436586000	0.972595000	0.384187000
6	-0.367226000	2.046104000	1.827550000	6	3.653234000	0.212322000	-0.018047000

6	-1.672570000	2.216748000	2.448073000	6	5.012957000	0.896759000	0.229032000
6	-2.216811000	1.204084000	3.248578000	8	3.593252000	-0.930345000	-0.497047000
6	-1.480741000	-0.030621000	3.439618000	7	6.079423000	-0.090808000	0.112811000
6	-2.434075000	-1.135007000	3.462888000	6	5.281324000	2.135345000	-0.688754000
6	-2.099871000	-2.354833000	2.871365000	6	4.490578000	3.381258000	-0.335471000
6	-3.086608000	-3.075223000	2.074380000	6	3.568710000	3.925463000	-1.245382000
6	-2.390565000	-3.689571000	0.947567000	6	4.685851000	4.035248000	0.895933000
6	-3.004749000	-3.742794000	-0.306485000	6	2.852051000	5.086794000	-0.932557000
6	-2.229654000	-3.457992000	-1.511118000	6	3.969048000	5.193811000	1.211901000
6	-0.877702000	-3.122270000	-1.408139000	6	3.048206000	5.722512000	0.298011000
6	-0.320845000	-2.056567000	-2.233414000	1	3.414824000	3.437372000	-2.203548000
6	-1.146477000	-1.373181000	-3.134340000	1	5.408801000	3.642455000	1.606681000
6	-1.022348000	0.065710000	-3.263417000	1	2.143629000	5.491643000	-1.648114000
6	-0.076125000	0.747521000	-2.488844000	1	4.132938000	5.686248000	2.165225000
6	-0.428298000	2.021769000	-1.875303000	1	2.492728000	6.622028000	0.542637000
6	-1.705905000	2.562677000	-2.059335000	6	6.628004000	-0.729674000	1.249514000
6	-2.388101000	3.179512000	-0.937729000	6	6.551631000	-0.670040000	-1.089816000
6	-1.760126000	3.224112000	0.314109000	6	7.552526000	-1.767797000	0.729177000
6	-2.530894000	2.944489000	1.520203000	6	7.502753000	-1.736400000	-0.672649000
6	-3.889952000	2.632374000	1.428550000	6	8.366590000	-2.666250000	1.406591000
6	-4.452884000	1.570359000	2.257719000	6	8.266822000	-2.602417000	-1.443355000
6	-3.634125000	0.872768000	3.149956000	6	9.142043000	-3.548710000	0.635030000
6	-3.769053000	-0.575626000	3.282586000	6	9.092471000	-3.517487000	-0.767437000
6	-4.715057000	-1.263040000	2.515719000	1	8.397970000	-2.684188000	2.490179000
6	-4.366524000	-2.539986000	1.898852000	1	8.221422000	-2.572503000	-2.526138000
6	-5.006308000	-2.597451000	0.589434000	1	9.787951000	-4.266271000	1.129761000
6	-4.340041000	-3.187708000	-0.489122000	1	9.700492000	-4.211893000	-1.337560000
6	-4.393926000	-2.564489000	-1.809418000	8	6.355132000	-0.433530000	2.421733000
6	-3.092126000	-2.734798000	-2.441981000	8	6.244559000	-0.314976000	-2.234650000
6	-2.561167000	-1.715539000	-3.236592000	1	5.033524000	1.221965000	1.277658000
6	-3.311332000	-0.478729000	-3.431747000	1	6.353970000	2.347067000	-0.594376000
6	-2.358327000	0.625315000	-3.448372000	1	5.111512000	1.849681000	-1.729381000
				1	2.632072000	1.941211000	0.829554000