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Electronic Supplementary Information

CF_2-containing acetylenephosphonates in heterocyclization reactions: the first synthesis of 2-difluoromethyl azaxanth-3-ylphosphonates

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General remarks

All reagents from commercial suppliers were used without further purification. All solvents were freshly distilled before use from appropriate drying agents. All other reagents were recrystallized. Reactions were performed under atmosphere of dry argon. Analytical TLCs were performed with silica gel 60 F_{254} plates. Visualization was accomplished by UV light or spraying by $Ce(SO_4)_2$ solution in 5% H_2SO_4. Column chromatography was carried out using silica gel 60 (230–400 mesh ASTM). Melting points were determined without correction. NMR spectra were obtained on a spectrometer operating at 400 MHz for ^{1}H (TMS), 376 MHz for ^{19}F ($CFC1_3$), 161 MHz for ^{31}P (H_3PO_4) and 100 MHz for ^{13}C (TMS). All measurements were accomplished in the solution in $CDCl_3$. Mass spectrometry was established on a MicroTOF-Q fitted with an ESI source.

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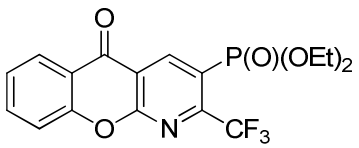
Method A General procedure for the preparation of azaxanthones (**3a–l**)

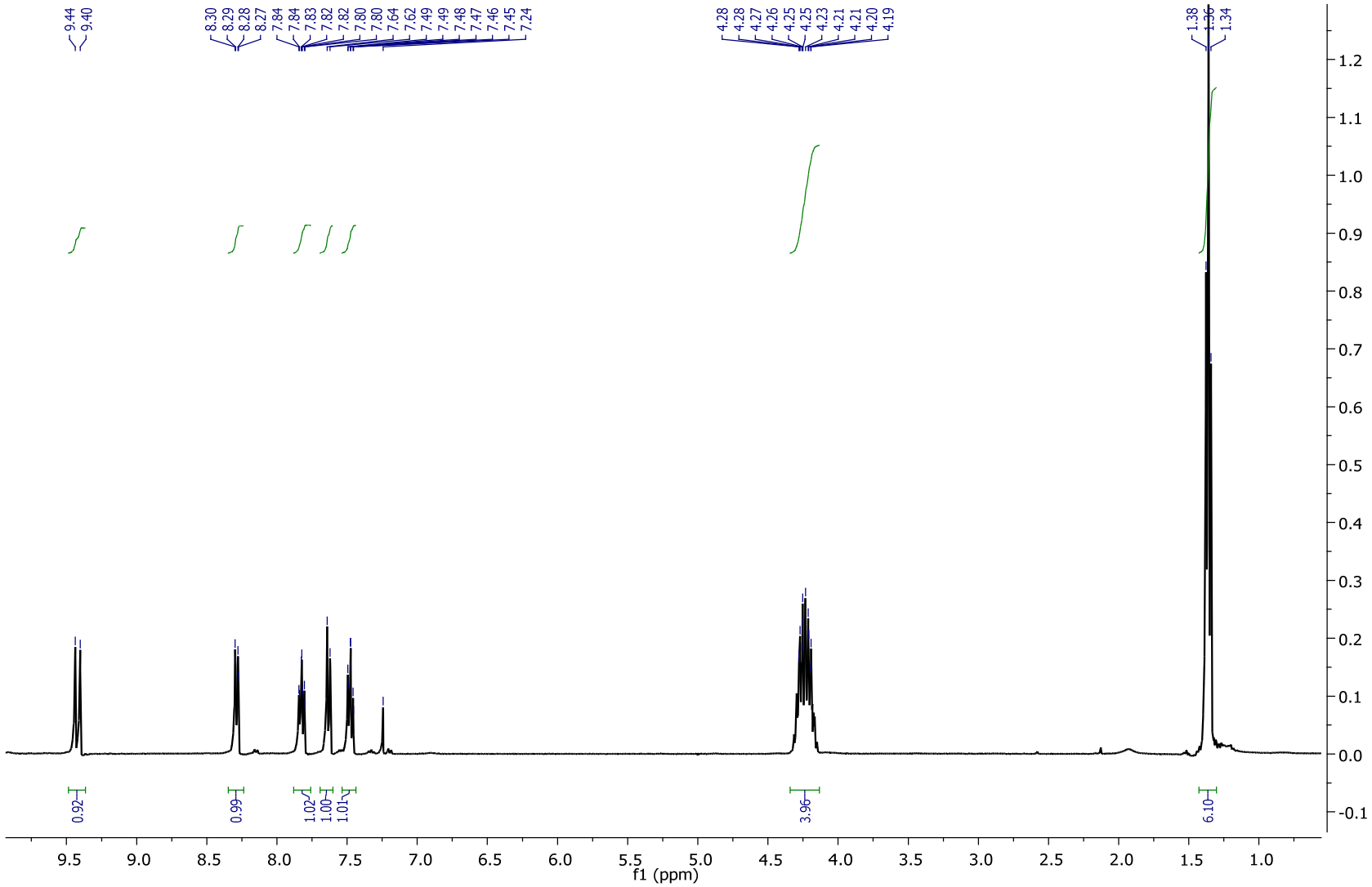
The 2-amino-3-formylchromone derivative (5 mmol) was dissolved in dry DMSO (20 ml) at ambient temperature. Afterwards an amine (5 mmol) was rapidly added and stirring for 10–15 min at RT. To the reaction mixture the acetylene (5 mmol) was then added. The solution was stirred for additional 4-12 hours at room temperature and after that diluted with Et_2O (250 ml) and washed with H_2O (3×150 ml). The ethereal phases were combined and dried over $MgSO_4$, filtered off and washed with diethyl ether (2×50 ml). The solvent was evaporated and the residue was purified by flash column chromatography on silica gel using DCM:EtOAc (5:1 ratio) as eluent.

1. *Diethyl (5-oxo-2-(trifluoromethyl)-5,10a-dihydro-4aH-chromeno-[2,3-b]pyridin-3-yl)phosphonate (**3a**)*



Yellowish crystals (94%); mp 122-125 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.36 (t, *J* = 7.1 Hz, 6H), 4.24 (m, 4H), 7.47 (td, *J* = 7.3 Hz, *J* = 0.6 Hz, 1H), 7.63 (d, *J* = 8.4 Hz, 1H), 7.82 (td, *J* = 7.2 Hz, *J* = 1.2 Hz, 1H), 8.29 (dd, *J* = 8.0 Hz, *J* = 1.7 Hz, 1H), 9.42 (d, $^{3}J_{H–P}$ = 13.9 Hz, 1H); ^{13}C NMR (100 MHz): δ 16.3 (d, *J* = 7.7 Hz), 63.6 (d, *J* = 6.5 Hz), 117.4 (d, $^{2}J_{C–P}$ = 11.6 Hz) 118.8, 121.5 (d, $^{1}J_{C–P}$ = 189.8 Hz), 122.5 (q, $^{1}J_{C–F}$ = 278.8 Hz), 125.9, 127.1, 136.7, 147.2 (d, $^{3}J_{C–P}$ = 7.8 Hz), 152.4 (qd, $^{2}J_{C–F}$ = 36.1 Hz, $^{2}J_{C–P}$ = 11.7 Hz), 155.6, 175.8; ^{19}F NMR (376 MHz): δ –64.2; ^{31}P NMR (161 MHz): δ 10.9; MS (ESI) *m/z*: $[M]^+$ 401 (25%), $[M+Na]^+$ 424 (32%), $[2M+Na]^+$ 825 (100%); HRMS calcd for $[M+Na]^+$ $(C_{17}H_{15}F_3NNaO_5P)^+$ 424.0532; found 424.0512.

^{1}H NMR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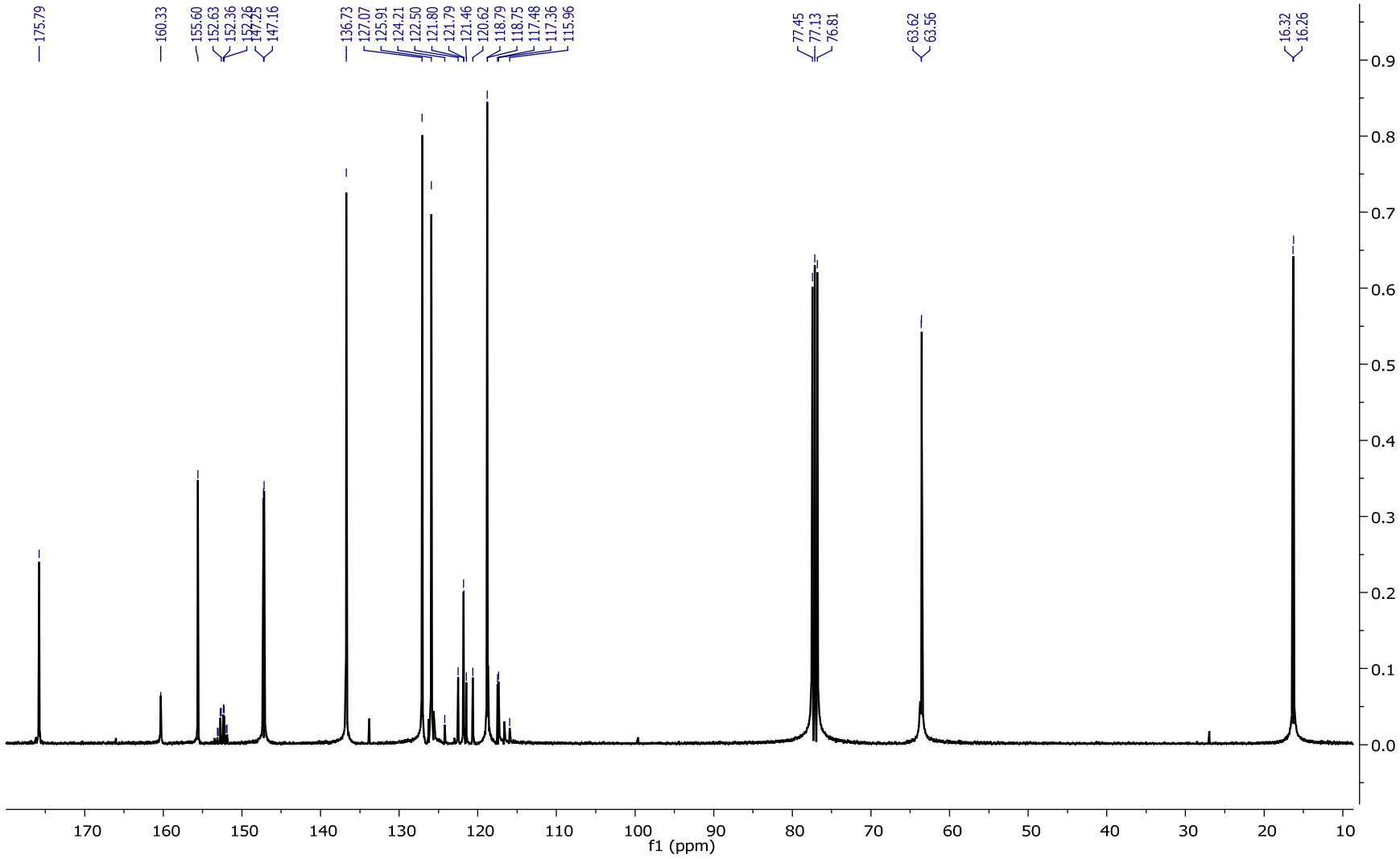
f1 (ppm)

^{13}C NMR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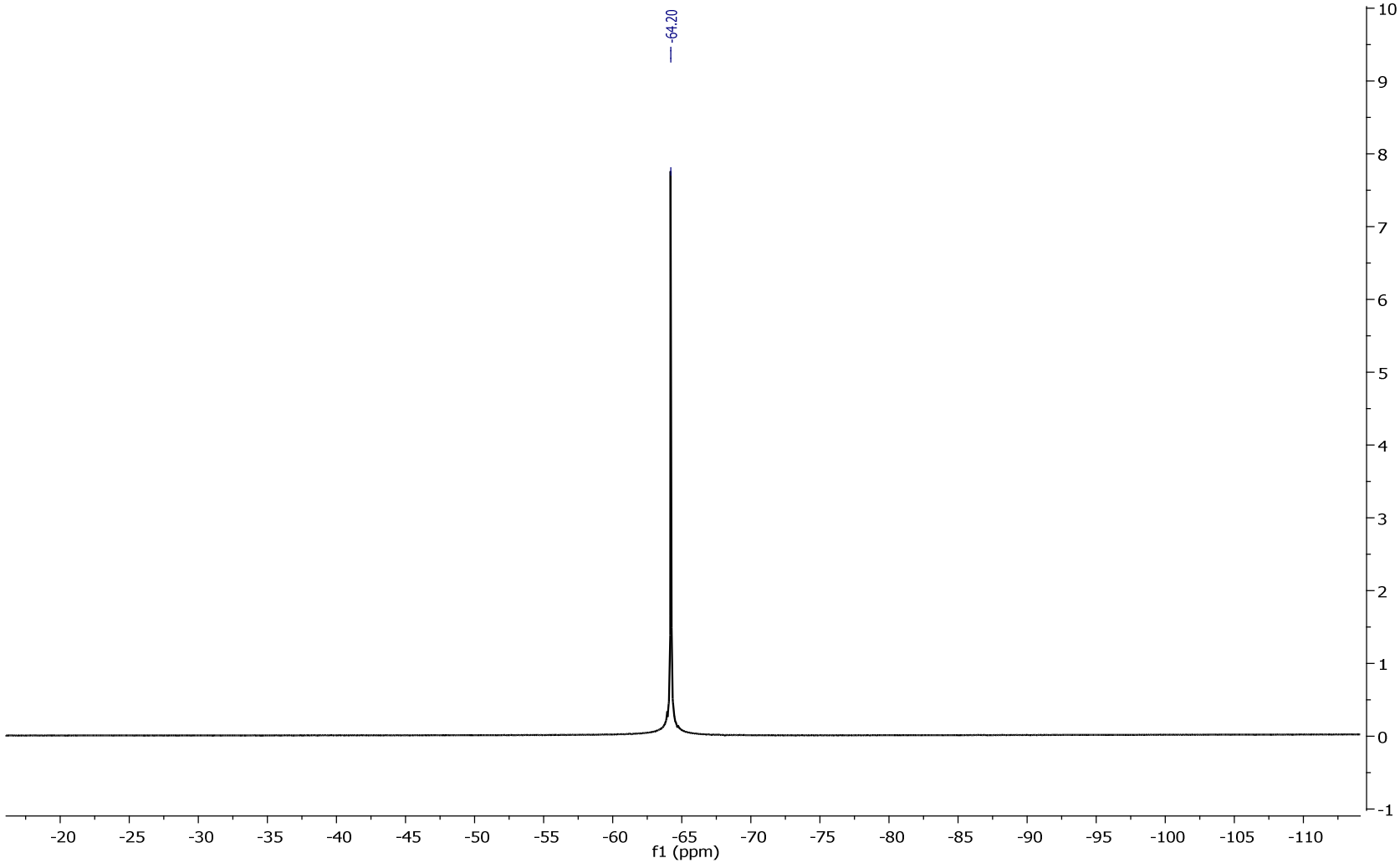
f1 (ppm)

^{19}F NMR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f1 (ppm)

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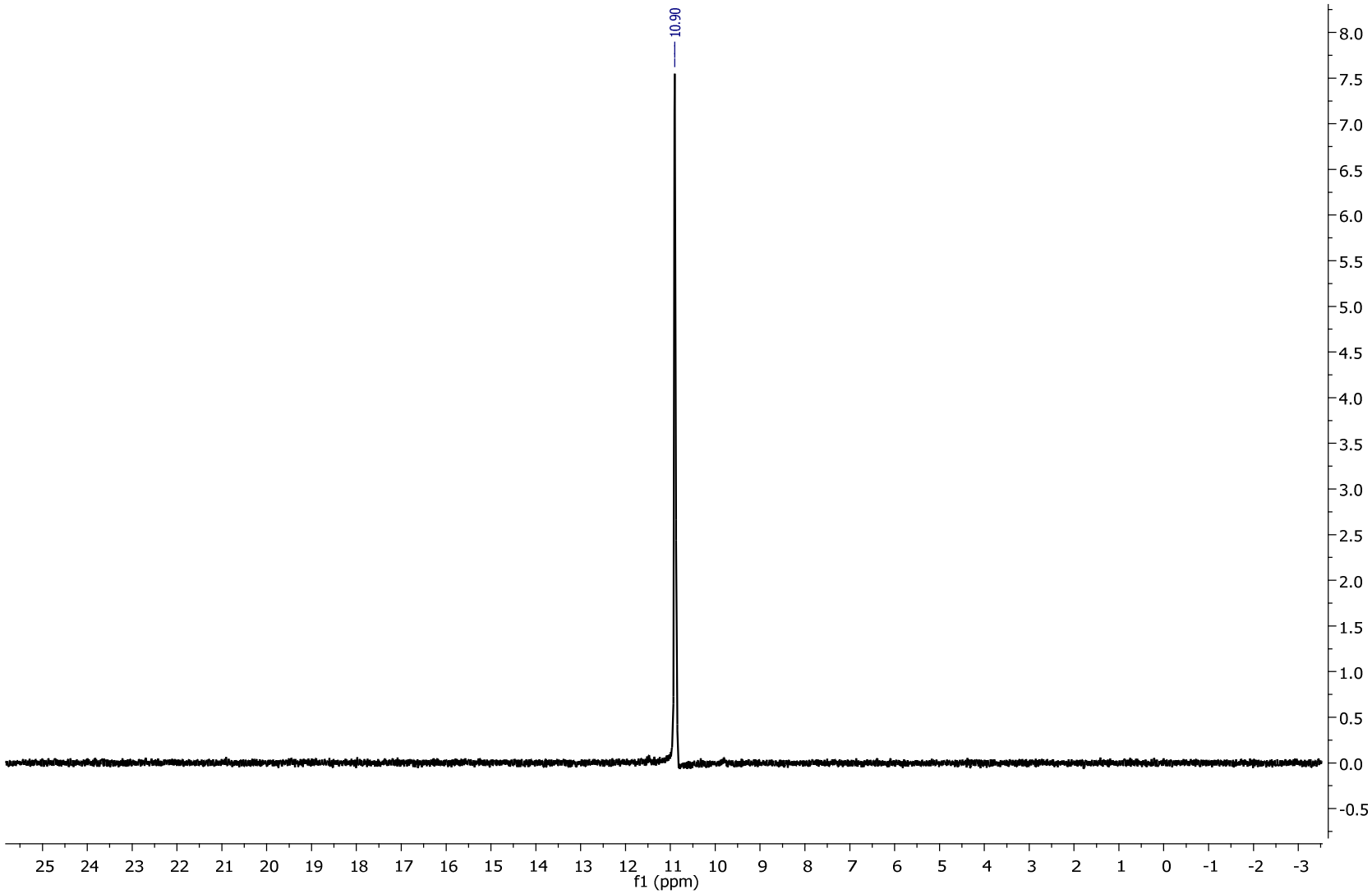
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2.0
1.5
1.0
0.5
0.0
-0.5
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f1 (ppm)

Display Report

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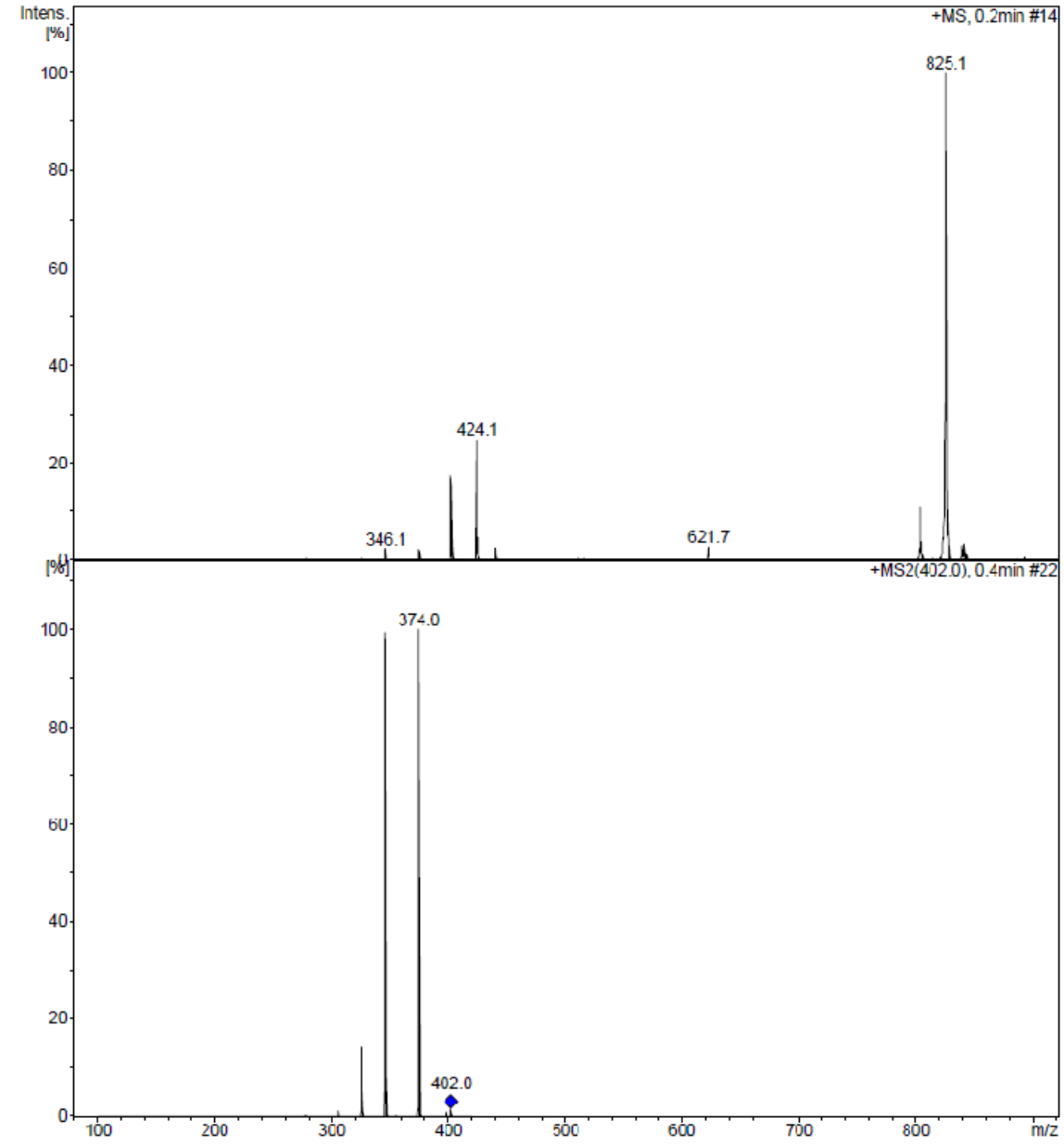

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HRMS

Mass Spectrum SmartFormula Report

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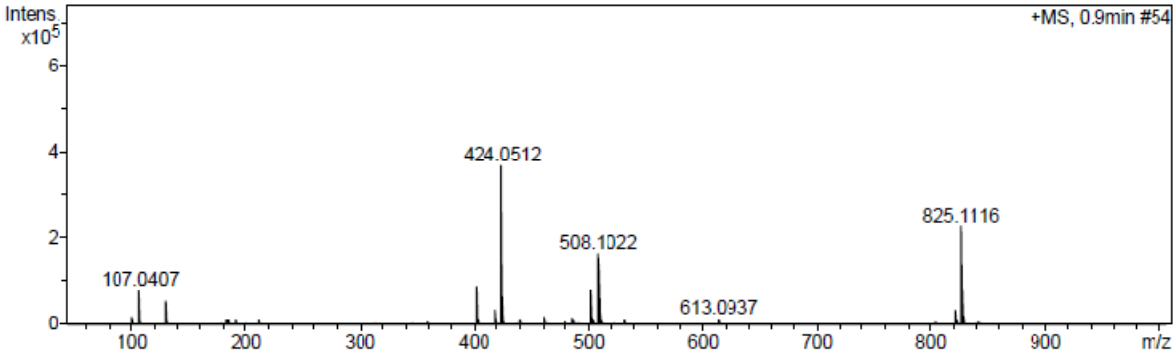

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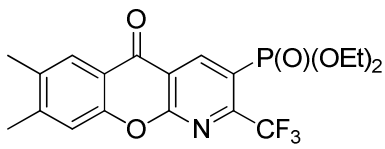
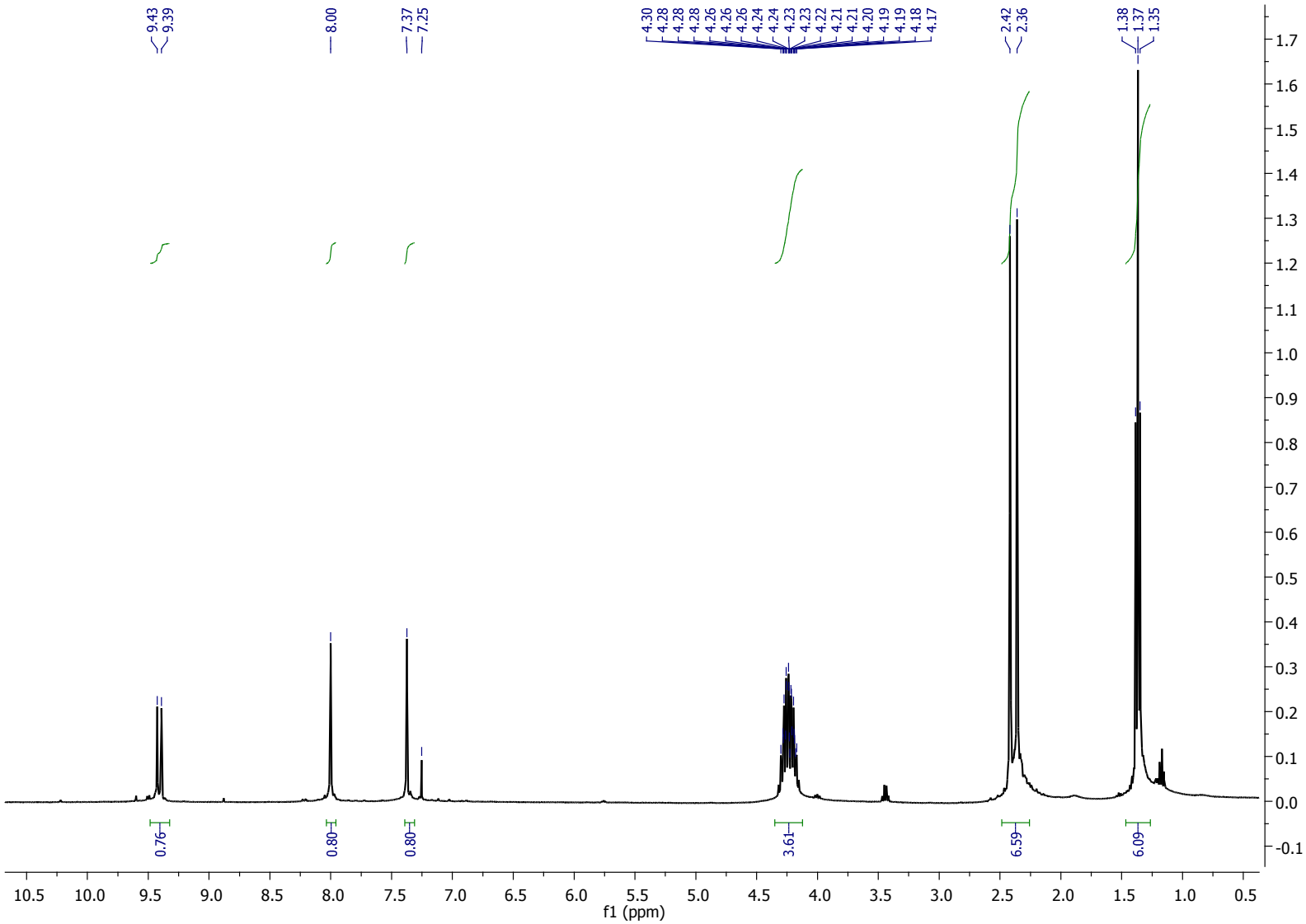
2. *Diethyl (7,8-dimethyl-5-oxo-2-(trifluoromethyl)-5,10a-dihydro-4aH-chromeno[2,3-b]pyridin-3-yl)-phosphonate (**3b**)*



Orange crystals (93%); mp 120–123 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.37 (t, J = 7.2 Hz, 6H), 2.36 (s, 3H), 2.42 (s, 3H), 4.25 (m, 4H), 7.37 (s, 1H), 8.00 (s, 1H), 9.41 (d, $^{3}J_{H–P}$ = 14.0 Hz, 1H); ^{13}C NMR (100 MHz): δ 16.3 (d, J = 6.6 Hz), 19.3, 20.9, 63.5 (d, J = 6.2 Hz), 117.5 (d, $^{2}J_{C–P}$ = 11.7 Hz), 118.8, 119.6, 120.5 (q, $^{1}J_{C–F}$ = 277.9 Hz), 121.2 (d, $^{1}J_{C–P}$ = 191.0 Hz), 126.6, 135.7, 147.1 (d, $^{3}J_{C–P}$ = 7.2 Hz), 147.9, 152.0 (qd, $^{2}J_{C–F}$ = 37.2 Hz, $^{2}J_{C–P}$ = 10.4 Hz), 154.1, 175.5; ^{19}F NMR (376 MHz): δ –64.1; ^{31}P NMR (161 MHz): δ 11.1; MS (ESI) *m/z*: $[M+Na]^+$ 452 (20%), $[2M+Na]^+$ 881 (100%); HRMS (ESI) calcd for $[M+Na]^+$ $(C_{19}H_{19}F_3NNaO_5P)^+$ 452.0845; found 452.0834.

^{1}H NMR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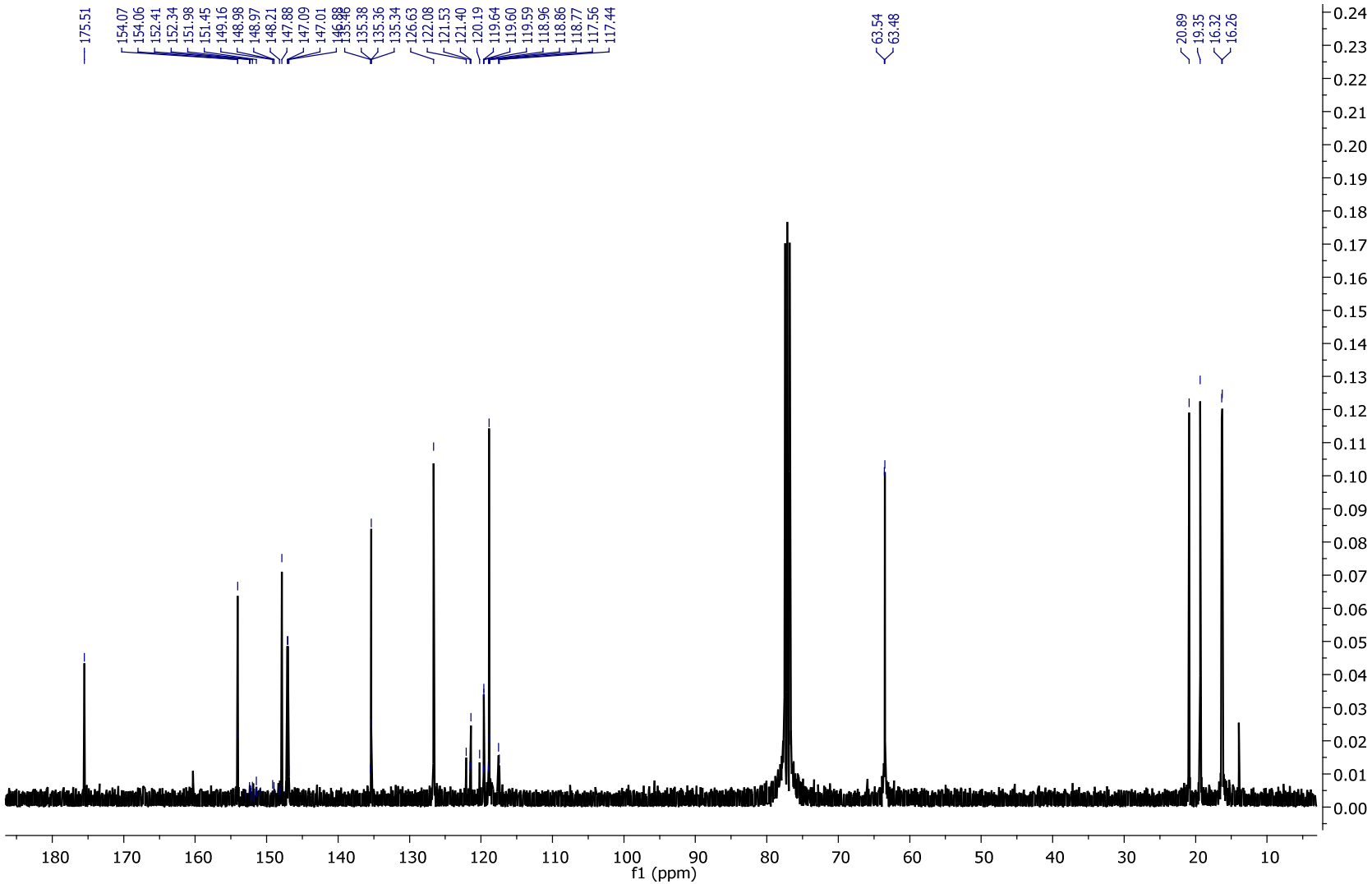
^{13}C NMR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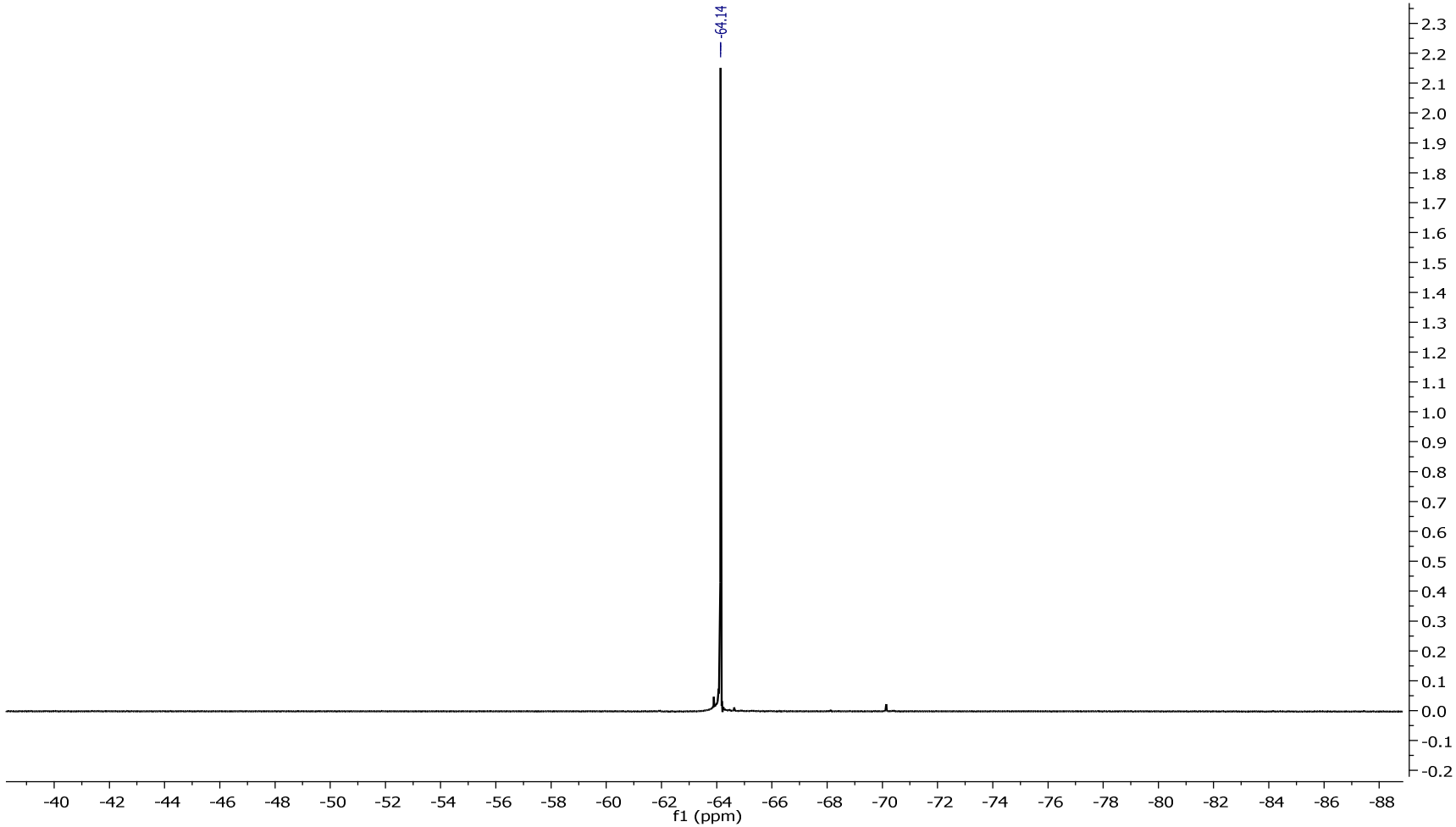
^{19}F NMR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0.0
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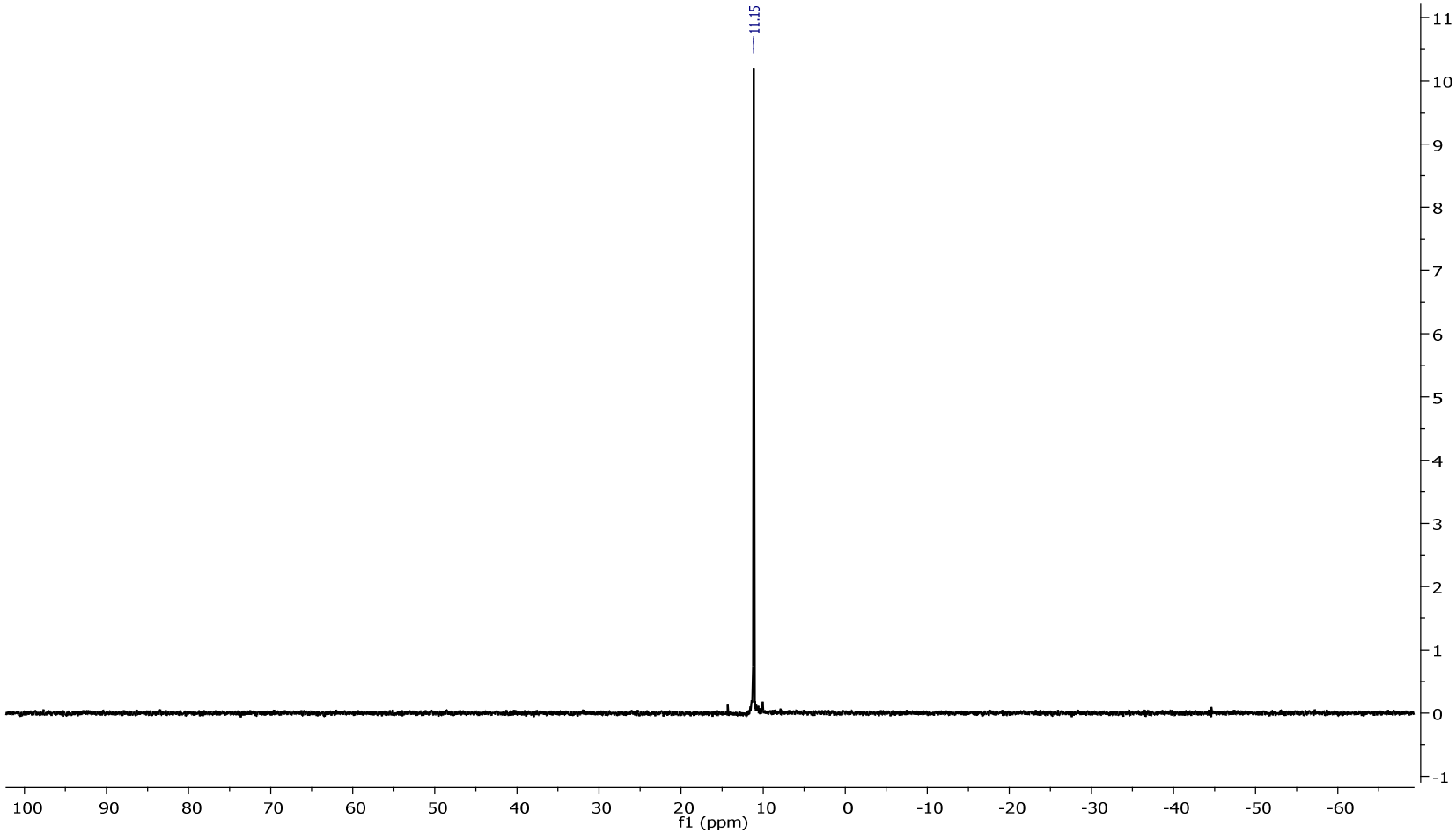
-40 -42 -44 -46 -48 -50 -52 -54 -56 -58 -60 -62 -64 -66 -68 -70 -72 -74 -76 -78 -80 -82 -84 -86 -88
f1 (ppm)

^{31}P NMR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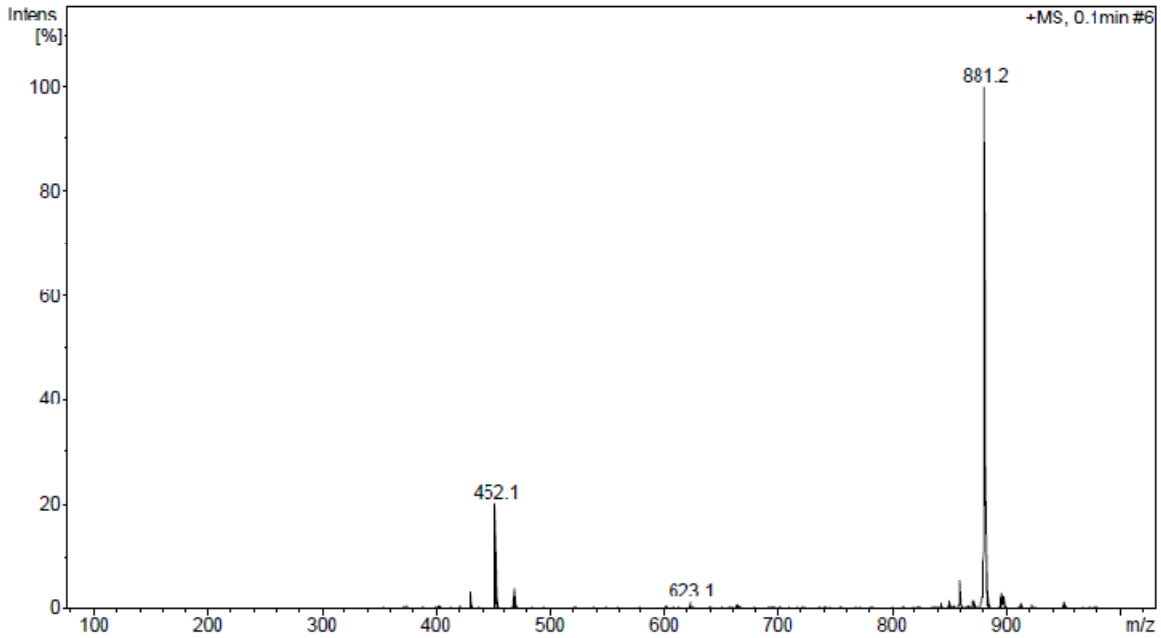

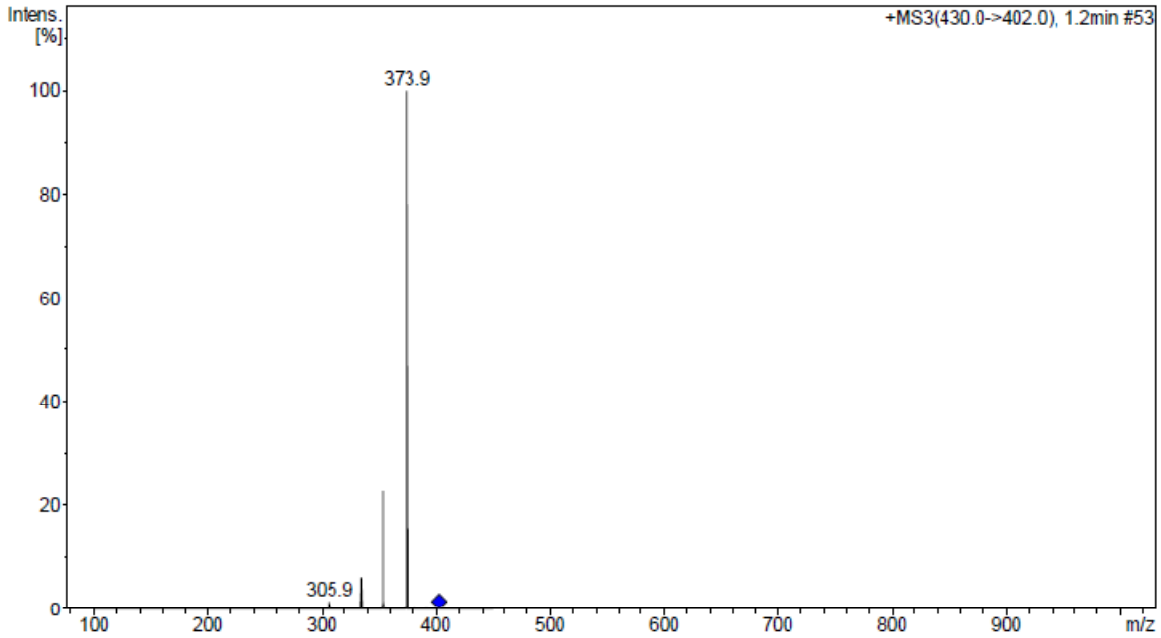

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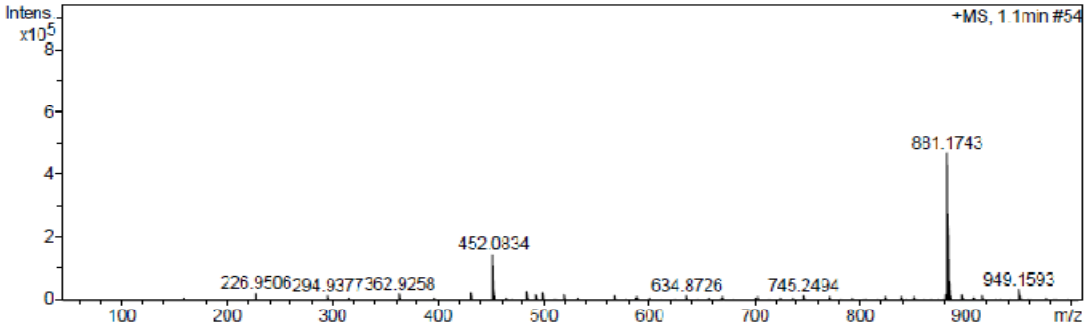

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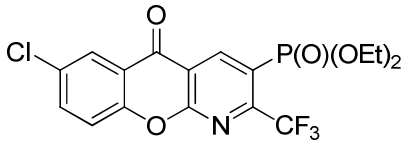
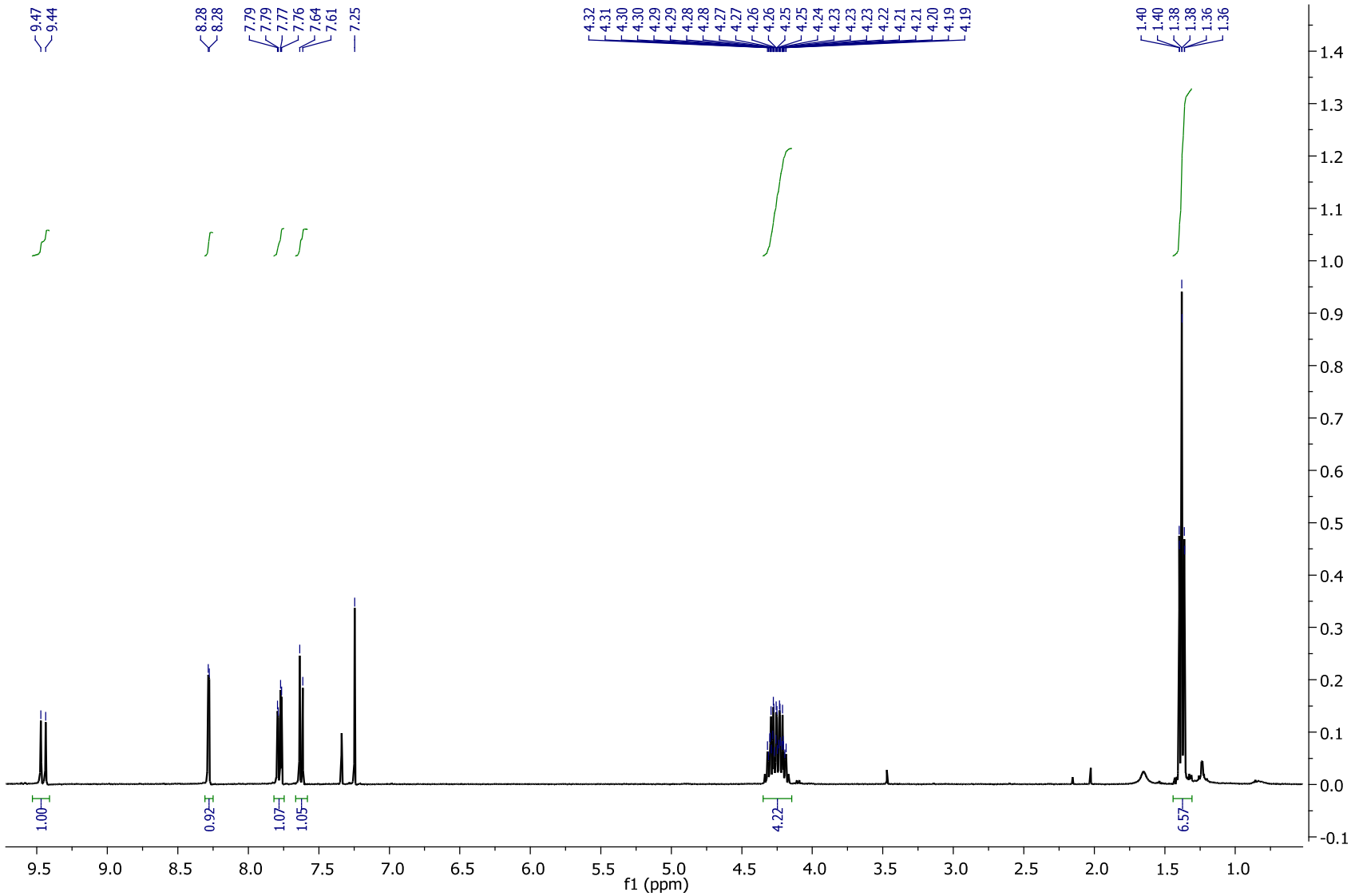
3. *Diethyl (7-chloro-5-oxo-2-(trifluoromethyl)-5,10a-dihydro-4aH-chromeno[2,3-b]pyridin-3-yl)-phosphonate (**3c**)*



Yellowish crystals (94%); mp 152–156 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.38 (t, *J* = 7.1 Hz, 6H), 4.25 (m, 4H), 7.62 (d, *J* = 8.9 Hz, 1H), 7.78 (dd, *J* = 8.9 Hz, *J* = 2.6 Hz, 1H), 8.28 (d, *J* = 2.6 Hz, 1H), 9.46 (d, $^{3}J_{H–P}$ = 13.9 Hz, 1H); ^{13}C NMR (100 MHz): δ 16.3 (d, *J* = 6.4 Hz), 63.7 (d, *J* = 6.1 Hz), 117.1 (d, $^{2}J_{C–P}$ = 10.9 Hz), 120.0 (q, $^{1}J_{C–F}$ = 277.4 Hz), 122.0 (d, $^{1}J_{C–P}$ = 189.7 Hz) 123.0 (d, *J* = 0.9 Hz), 126.4, 128.4, 131.9, 136.8, 147.4 (d, $^{3}J_{C–P}$ = 8.5 Hz), 152.7 (qd, $^{2}J_{C–F}$ = 37.0 Hz, $^{2}J_{C–P}$ = 10.6 Hz), 153.9, 174.8; ^{19}F NMR (376 MHz): δ –64.2; ^{31}P NMR (161 MHz): δ 10.6; MS (ESI) *m/z*: $[M+Na]^+$ 458; HRMS (ESI) calcd for $[M+Na]^+$ $(C_{17}H_{14}ClF_3NNaO_5P)^+$ 458.0142; found 458.0130.

^{1}H NMR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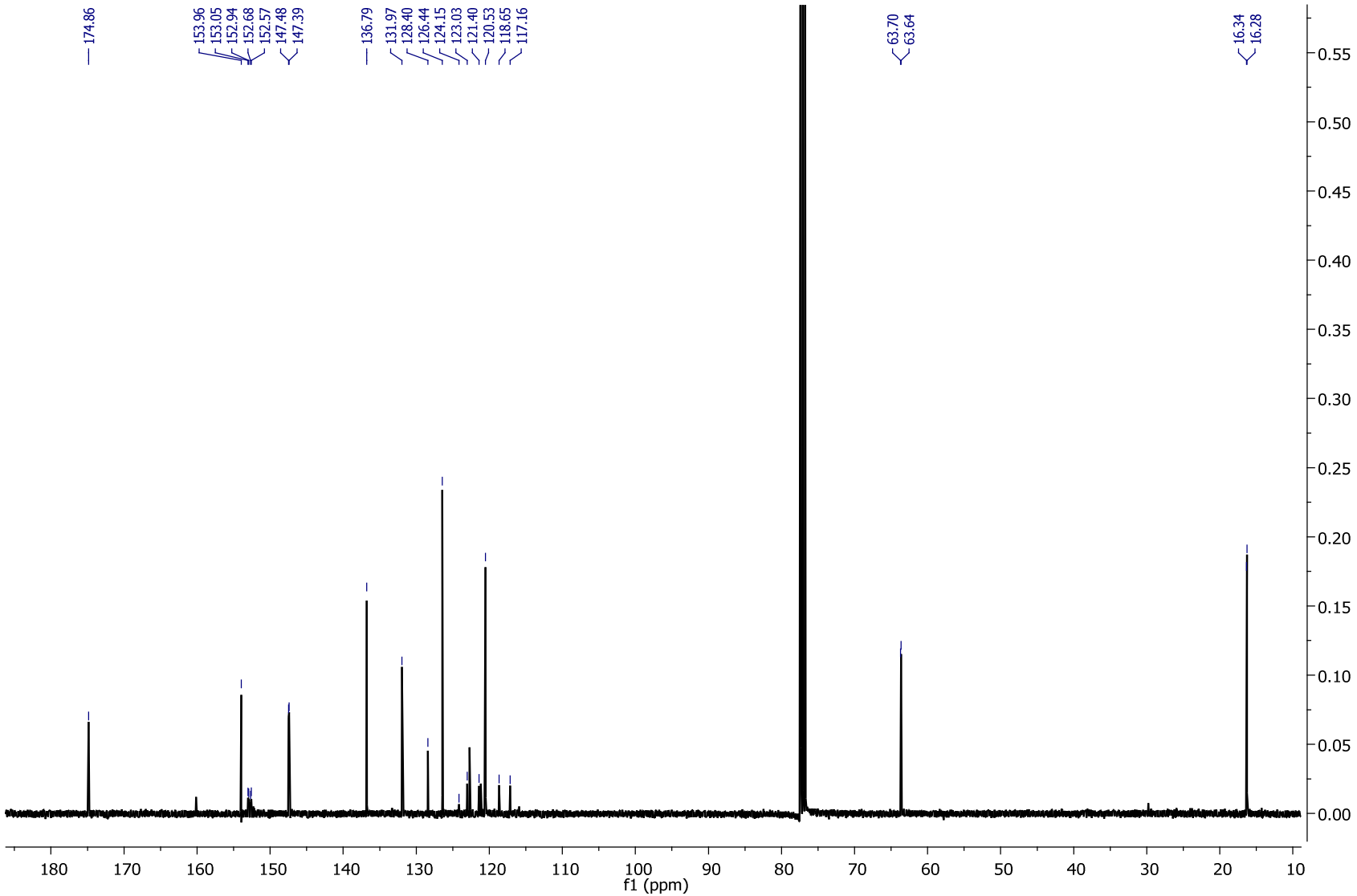
4.22
6.57
f1 (ppm)

^{13}C NMR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117.16
63.70
63.64
16.34
16.28
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0.50
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0.05
0.00
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170
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30
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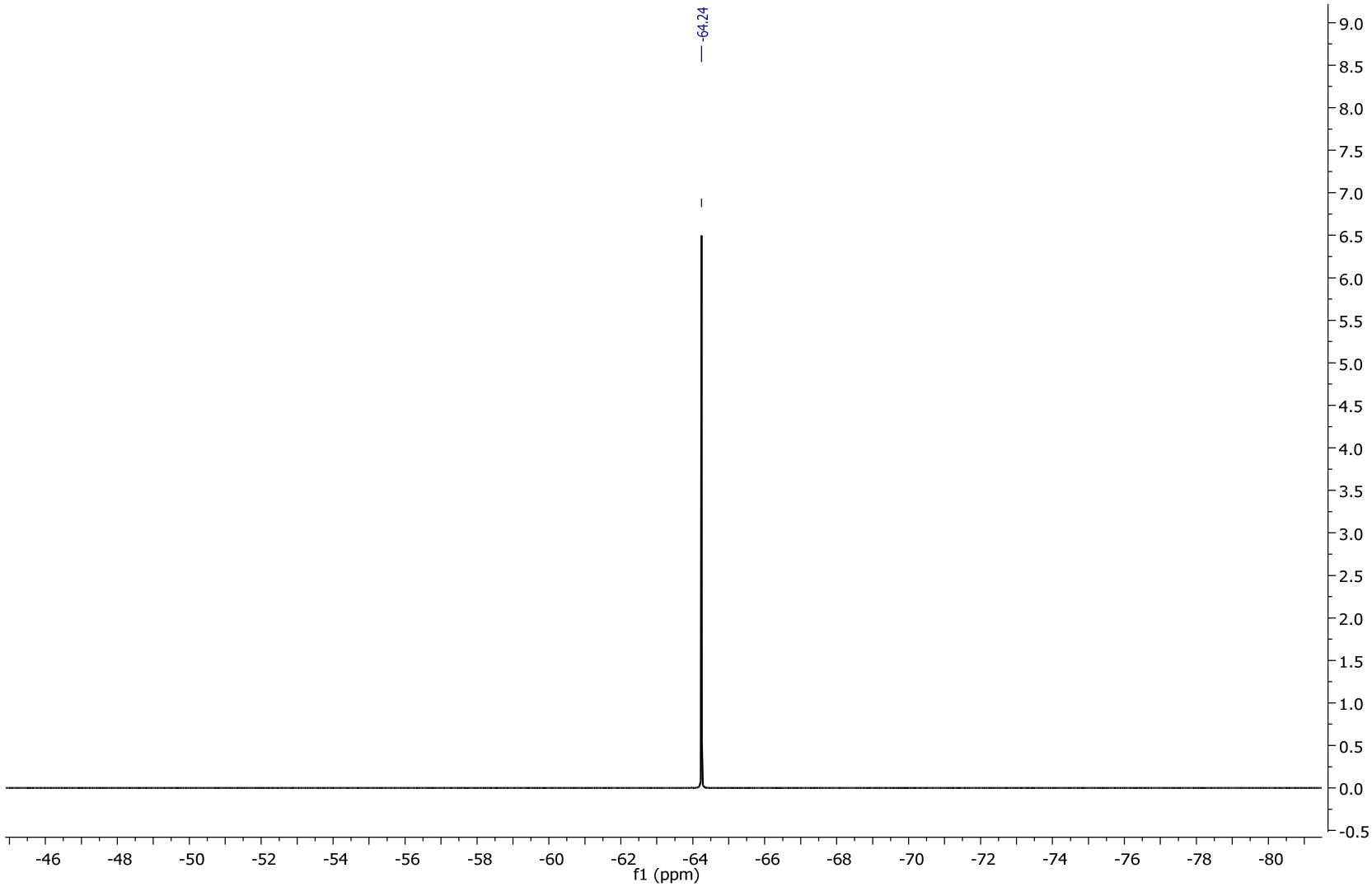
10
f1 (ppm)

^{19}F NMR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-54
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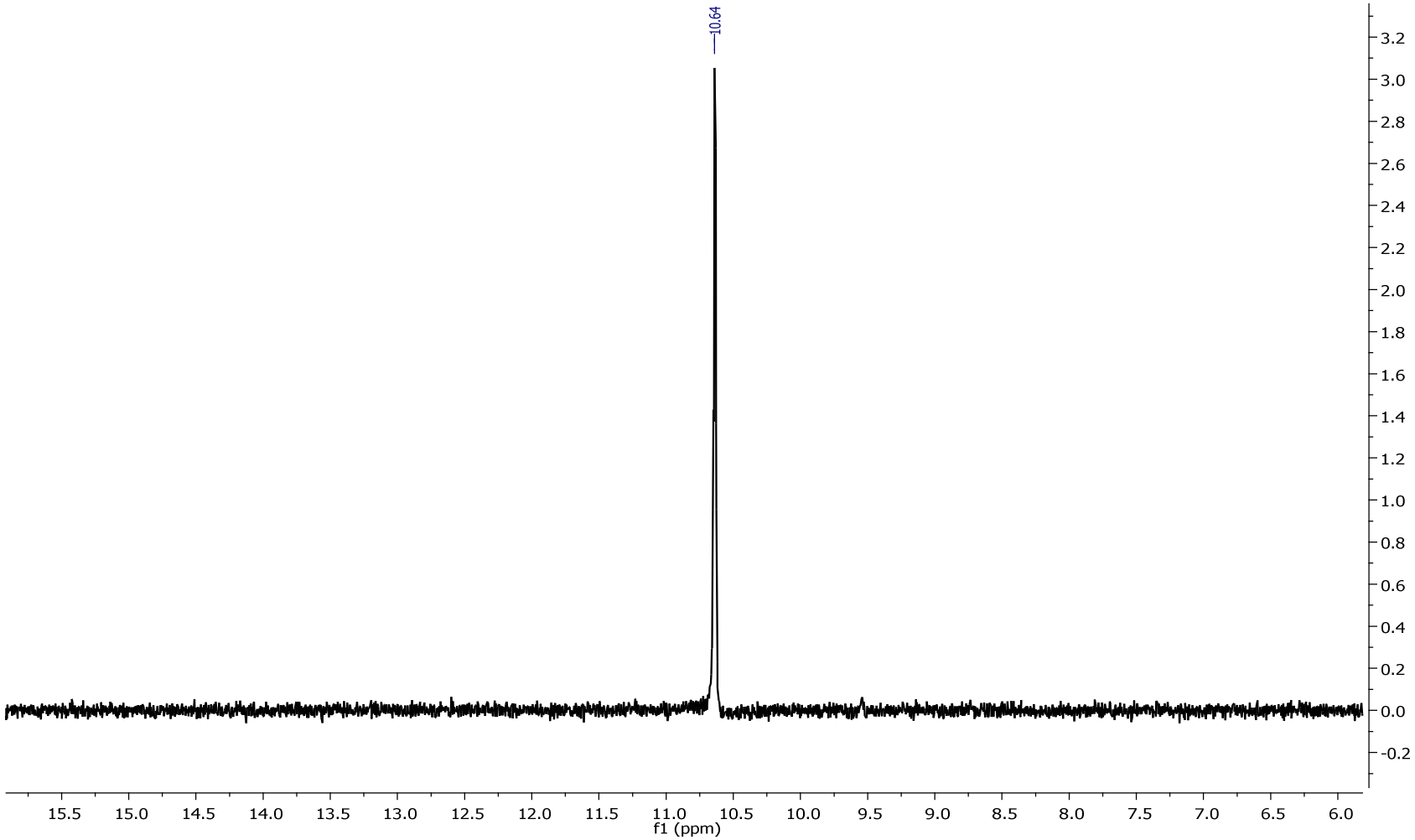
f1 (ppm)

^{31}P NMR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0.2
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15.0
14.5
14.0
13.5
13.0
12.5
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
f1 (ppm)

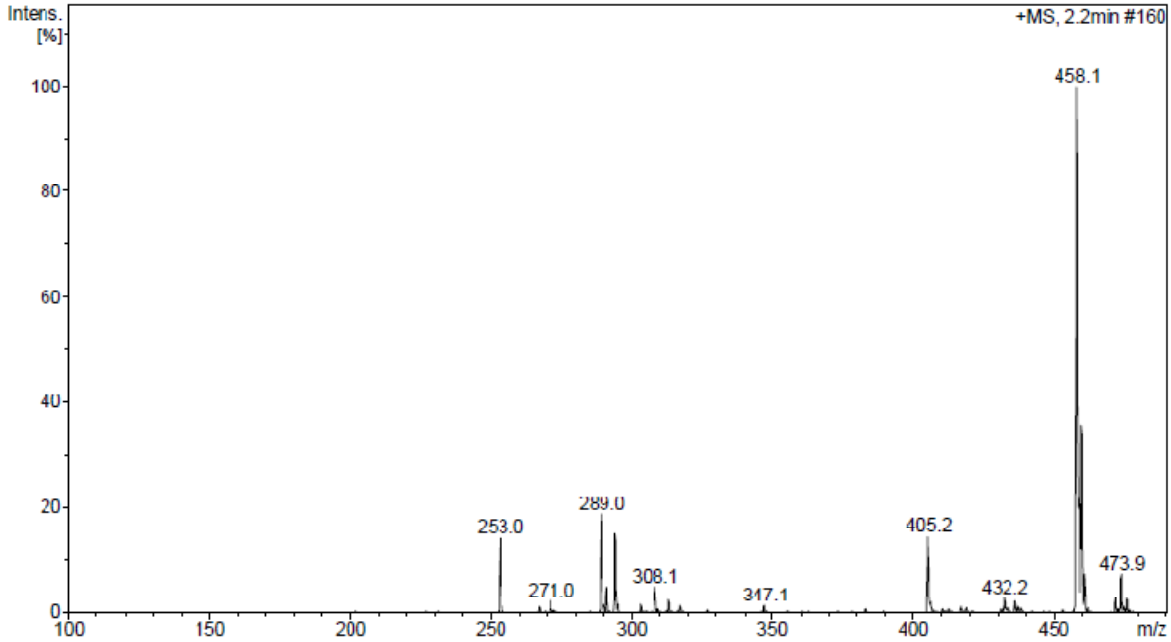
Display Report

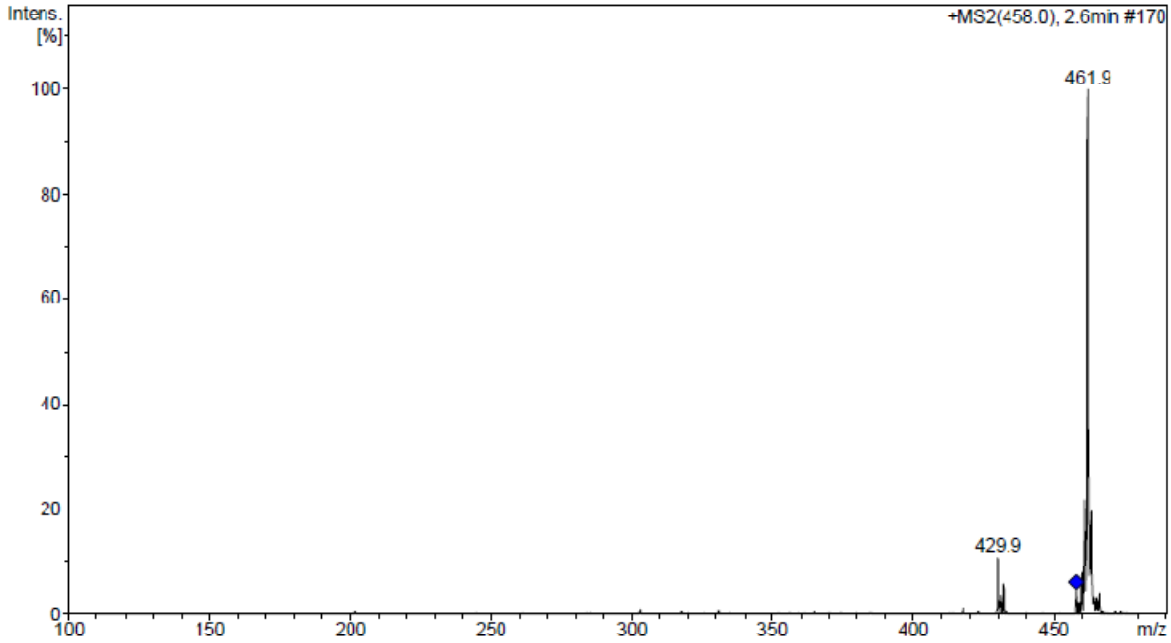
Analysis Info

Analysis Name	G:\Data B\Blazej ION TRAP\BD61_02052010.d	Acquisition Date	2010-05-02 16:23:04
Method	DEF_MS.M	Operator	farnoosh
Sample Name	Tina-shikimates	Instrument	HCTultra
Comment	in Methanol		

Acquisition Parameter

Ion Source Type	ESI	Ion Polarity	Positive	Alternating Ion Polarity	off
Mass Range Mode	Ultra Scan	Scan Begin	100 m/z	Scan End	1000 m/z
Capillary Exit	109.9 Volt	Skimmer	40.0 Volt	Trap Drive	52.7
Accumulation Time	1755 ßs	Averages	10 Spectra	Auto MS/MS	off





HRMS

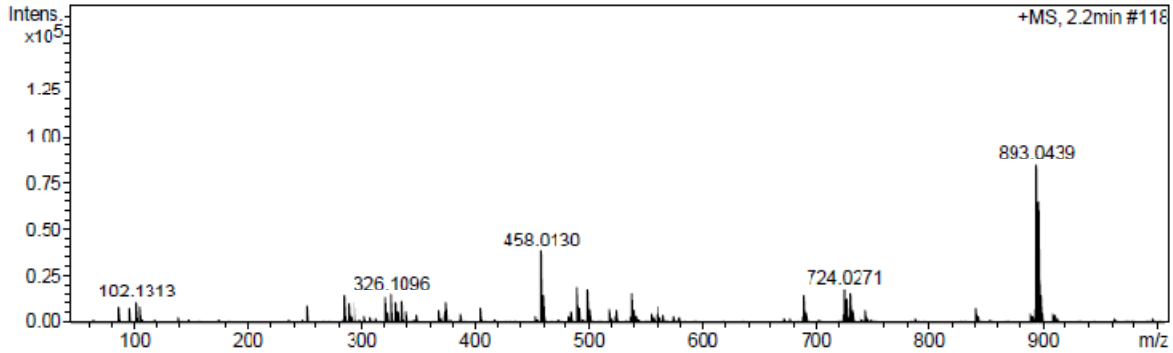
Mass Spectrum SmartFormula Report

Analysis Info

Analysis Name	G:\Data B\Blazej TOF\BD61_02052010.d	Acquisition Date	2010 05 02 16:30:34
Method	tune_low_sodiumformat_pos_anja.m	Operator	Bruker Customer
Sample Name		Instrument / Ser#	micrOTOF 129
Comment	in methanol		

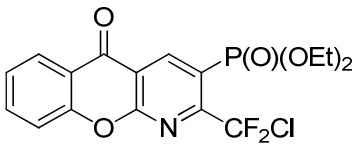
Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	1000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Source



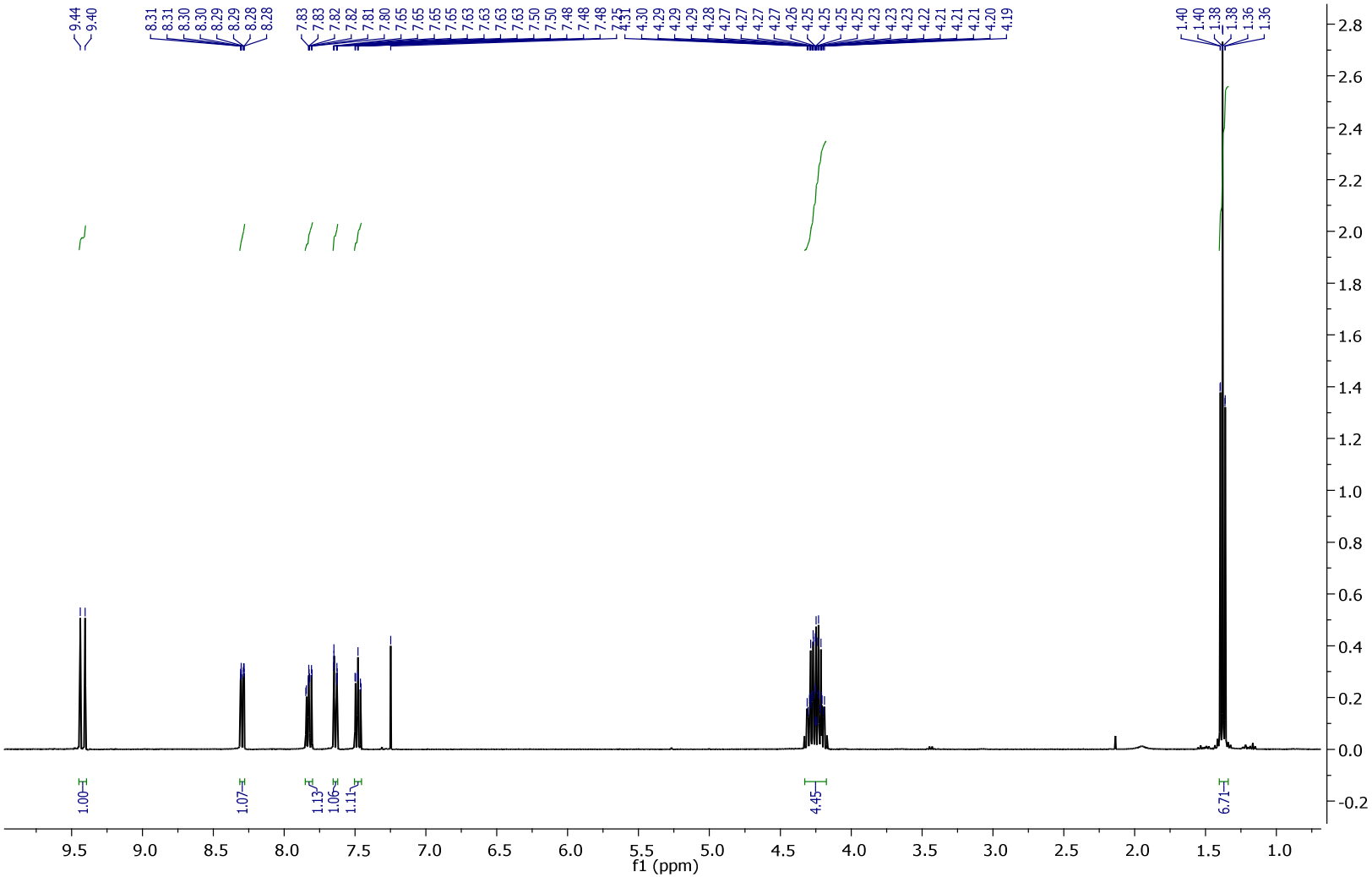
Meas. m/z	Formula	m/z	err [ppm]	Mean err [ppm]	N-Rule	mSigma	err [mDa]
458.0130							
	C 17 H 14 Cl F 3 N Na O 5 P	458.0142	2.7	3.1	ok	14.88	1.2

4. *Diethyl (2-(chlorodifluoromethyl)-5-oxo-5,10a-dihydro-4aH-chromeno[2,3-b]pyridin-3-yl)-phosphonate (**3d**)*

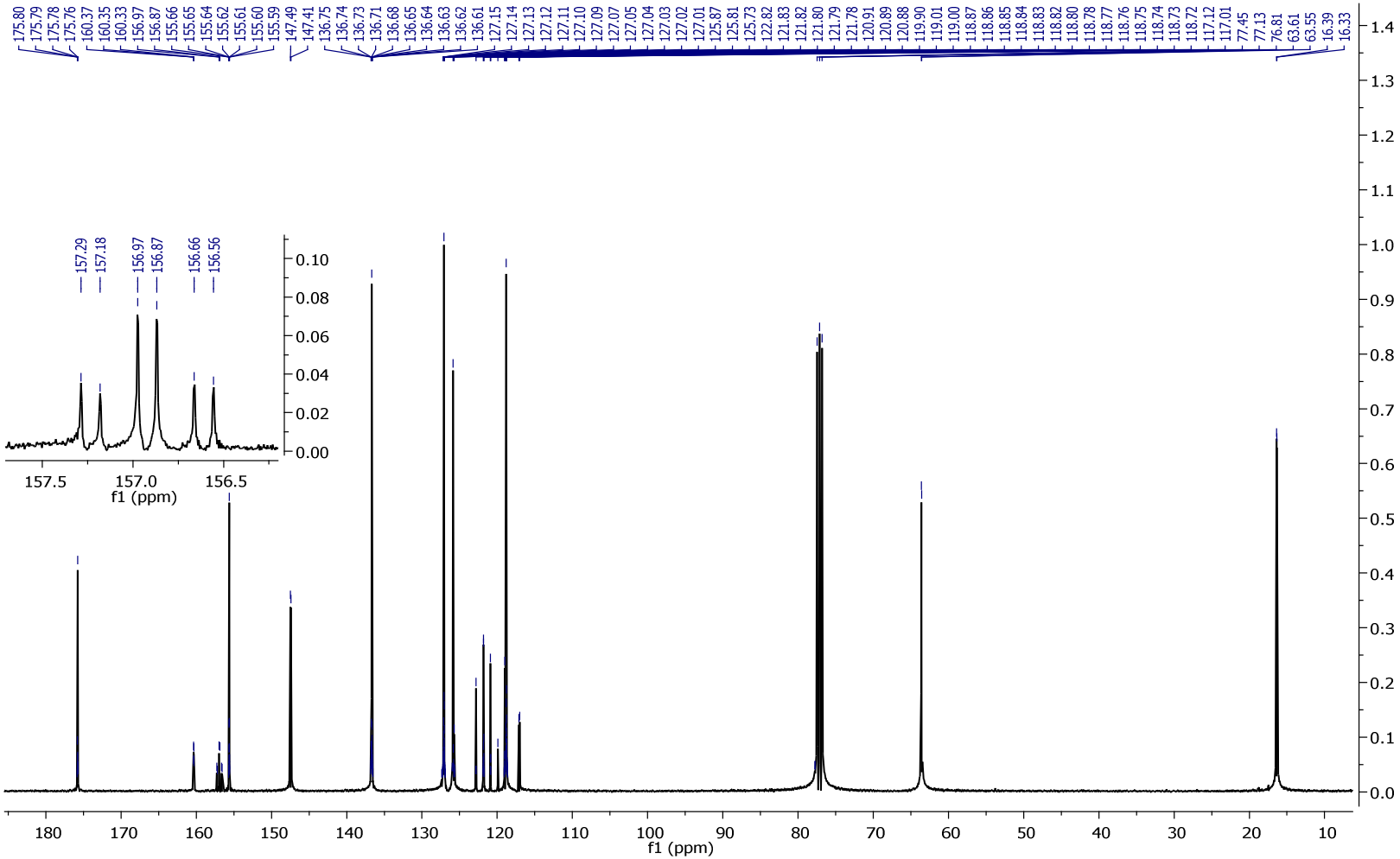


Yellowish crystals (84%); mp 123–125 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.38 (t, *J* = 7.1 Hz, 6H), 4.25 (m, 4H), 7.48 (td, *J* = 7.4 Hz, *J* = 1.0 Hz, 1H), 7.64 (dd, *J* = 8.4 Hz, *J* = 1.1 Hz, 1H), 7.83 (td, *J* = 8.5 Hz, *J* = 1.7 Hz, 1H), 8.29 (dd, *J* = 7.9 Hz, *J* = 1.7 Hz, 1H), 9.42 (d, $^{3}J_{H–P}$ = 14.0 Hz, 1H); ^{13}C NMR (100 MHz): δ 16.3 (d, *J* = 6.6 Hz), 63.5 (d, *J* = 6.4 Hz), 117.1 (d, $^{2}J_{C–P}$ = 10.9 Hz), 118.8, 120.5 (d, $^{1}J_{C–P}$ = 189.2 Hz), 121.8, 122.8 (t, $^{1}J_{C–F}$ = 292.6 Hz), 125.8, 127.1, 136.7, 147.4 (d, $^{3}J_{C–P}$ = 8.6 Hz), 155.6, 156.9 (td, $^{2}J_{C–F}$ = 31.5 Hz, $^{2}J_{C–P}$ = 10.6 Hz), 175.8; ^{19}F NMR (376 MHz): δ –53.5; ^{31}P NMR (161 MHz): δ 11.2; MS (ESI) *m/z*: $[M+H]^+$ 418 (45%), $[M+Na]^+$ 440 (35%), $[2M+Na]^+$ 857 (100%); HRMS (ESI) calcd for $[M+Na]^+$ $(C_{17}H_{15}ClF_2NNaO_5P)^+$ 440.0237; found 440.0233.

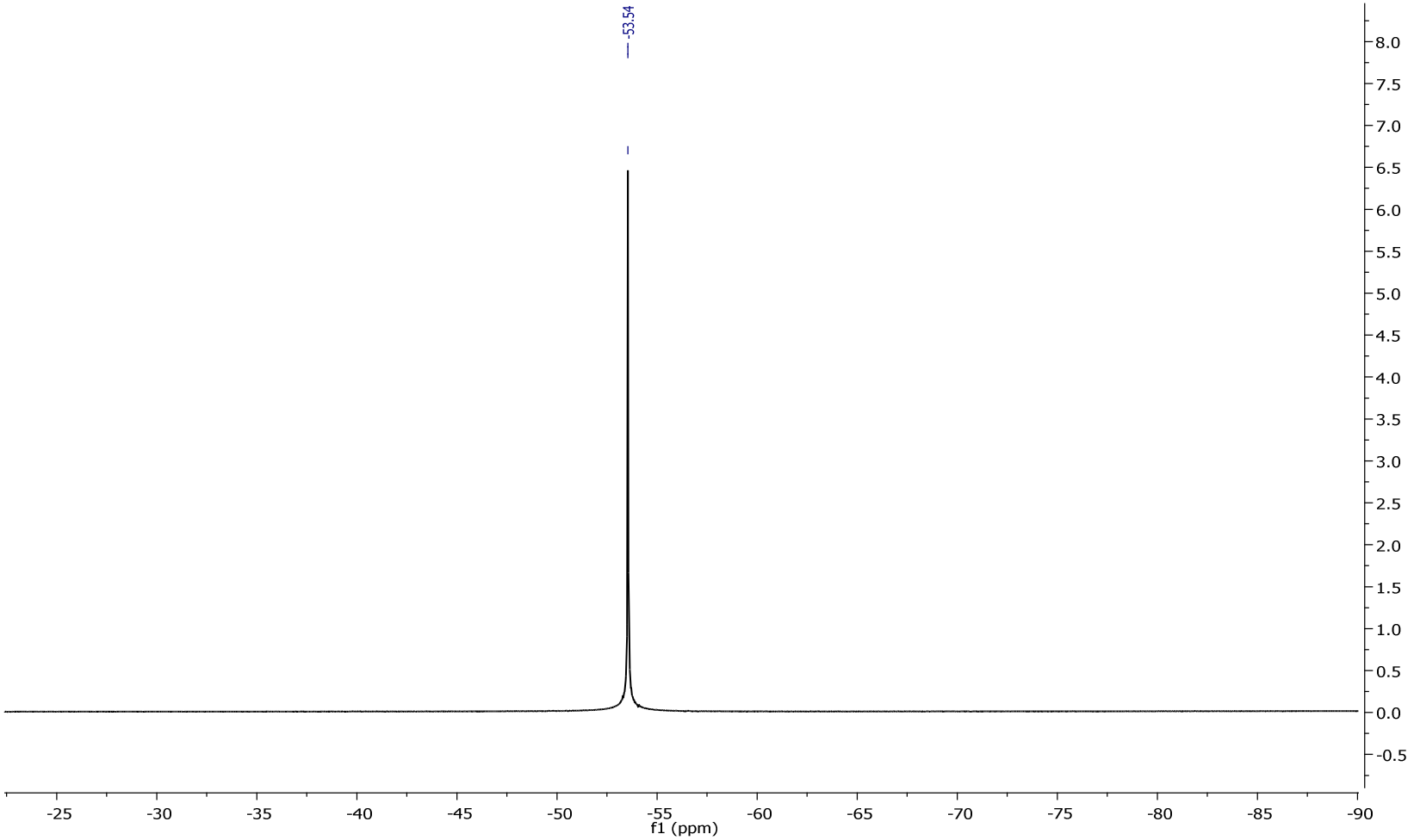
^{1}H NMR


9.44
9.40
8.31
8.31
8.30
8.30
8.29
8.29
8.28
8.28
7.83
7.83
7.82
7.82
7.81
7.80
7.65
7.65
7.65
7.63
7.63
7.63
7.63
7.50
7.50
7.48
7.48
7.48
4.31
4.30
4.29
4.29
4.29
4.28
4.27
4.27
4.27
4.27
4.26
4.25
4.25
4.25
4.25
4.23
4.23
4.23
4.22
4.21
4.21
4.21
4.20
4.19
1.40
1.40
1.38
1.38
1.36
1.36
1.00
1.07
1.13
1.06
1.11
4.45
6.71
f1 (ppm)

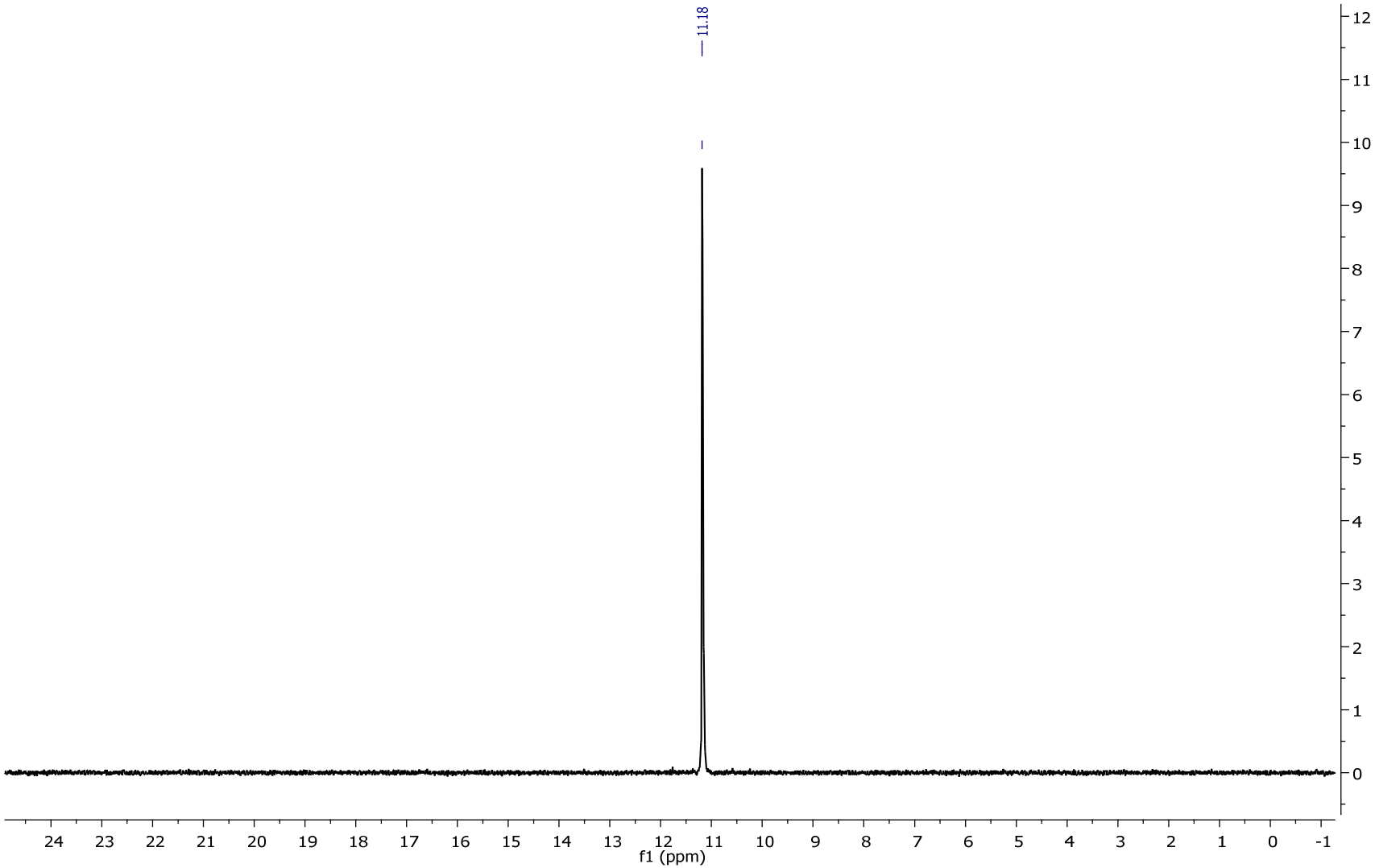
^{13}C NMR


175.80 175.79 175.78 175.76 160.37 160.35 160.33 156.97 156.87 155.66 155.65 155.64 155.62 155.61 155.60 155.59 147.49 147.41 136.75 136.74 136.73 136.71 136.68 136.65 136.64 136.63 136.62 136.61 127.15 127.14 127.13 127.12 127.11 127.10 127.09 127.07 127.05 127.04 127.03 127.02 127.01 125.87 125.81 125.73 122.82 121.83 121.82 121.80 121.79 121.78 120.91 120.89 120.88 119.90 119.01 119.00 118.87 118.86 118.85 118.84 118.83 118.82 118.80 118.78 118.77 118.76 118.75 118.74 118.73 118.72 117.12 117.01 77.45 77.13 76.81 63.61 63.55 16.39 16.33
157.29 157.18 156.97 156.87 156.66 156.56
157.5 157.0 156.5
f1 (ppm)
0.10 0.08 0.06 0.04 0.02 0.00
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)
1.4 1.3 1.2 1.1 1.0 0.9 0.8 0.7 0.6 0.5 0.4 0.3 0.2 0.1 0.0

^{19}F NMR


-53.54
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-25
-30
-35
-40
-45
-50
-55
-60
-65
-70
-75
-80
-85
-90
f1 (ppm)

^{31}P NMR



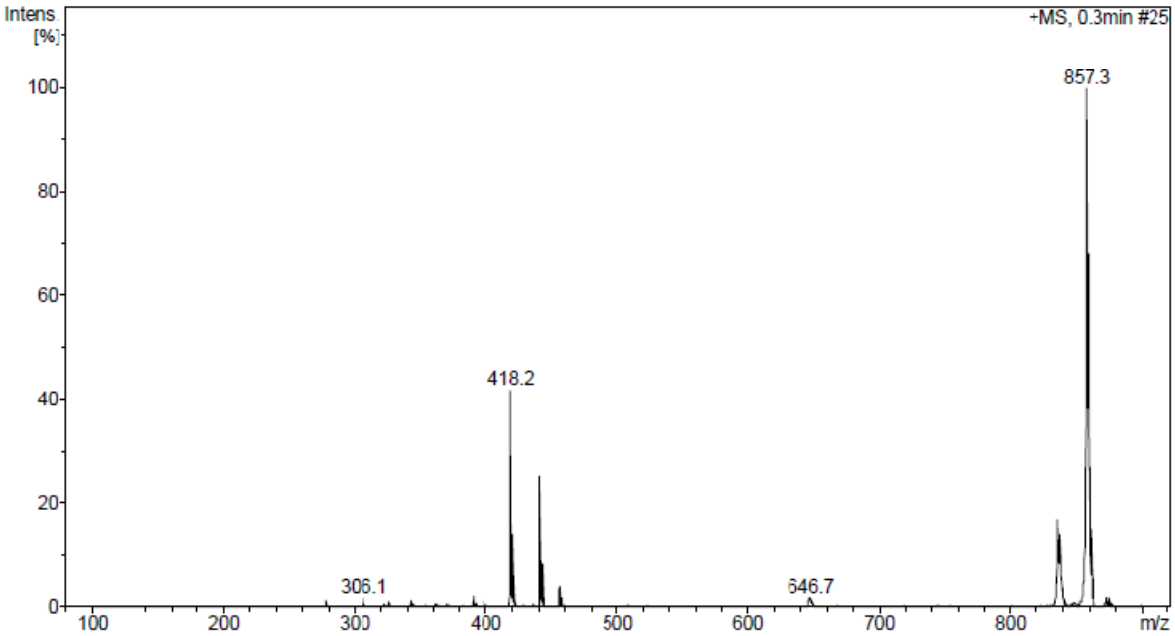
Display Report

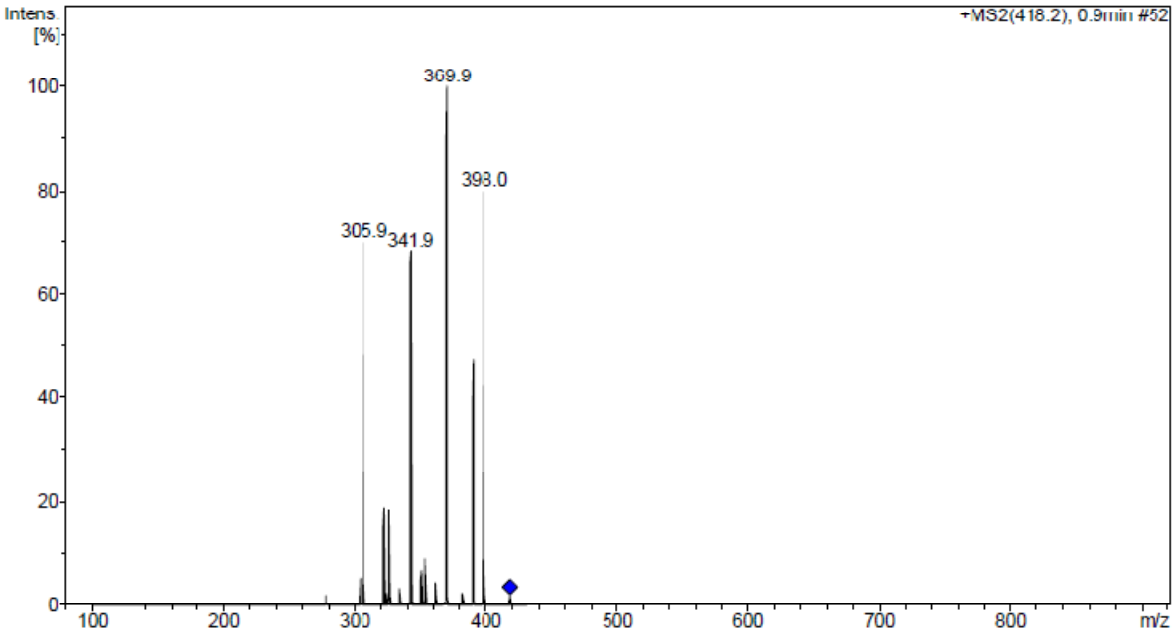
Analysis Info

Analysis Name	G:\Data B\Blazej ION TRAP\BD133_01112010.d	Acquisition Date	2010-11-01 10:49:46
Method	DEF_MS.M	Operator	farnoosh
Sample Name	Default	Instrument	HCTultra
Comment	in methanol		

Acquisition Parameter

Ion Source Type	ESI	Ion Polarity	Positive	Alternating Ion Polarity	off
Mass Range Mode	Ultra Scan	Scan Begin	100 m/z	Scan End	900 m/z
Capillary Exit	220.0 Volt	Skimmer	40.0 Volt	Trap Drive	78.0
Accumulation Time	300 µs	Averages	10 Spectra	Auto MS/MS	off





HRMS

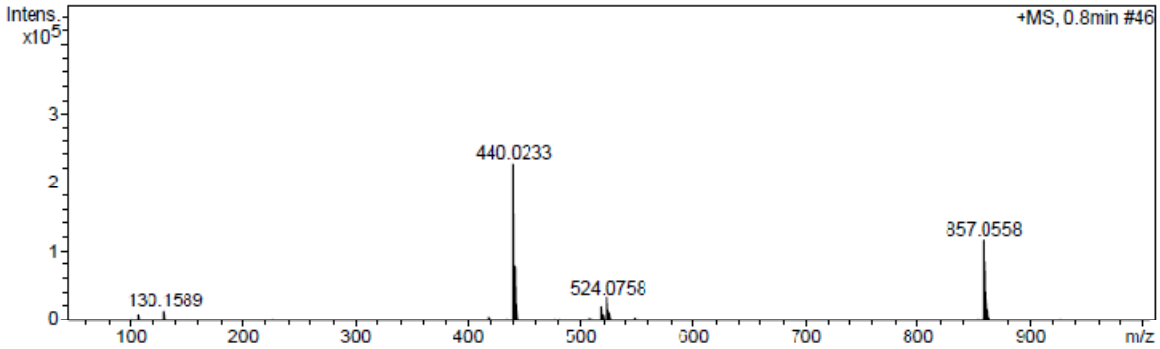
Mass Spectrum SmartFormula Report

Analysis Info

Analysis Name	G:\Data B\Blazej TOF\BD133_01112010.d	Acquisition Date	2010-11-01 10:28:13
Method	tune low.m	Operator	Bruker Customer
Sample Name		Instrument / Ser#	micrOTOF 129
Comment	in methanol		

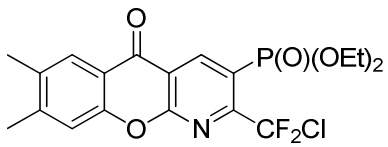
Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	1000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Source



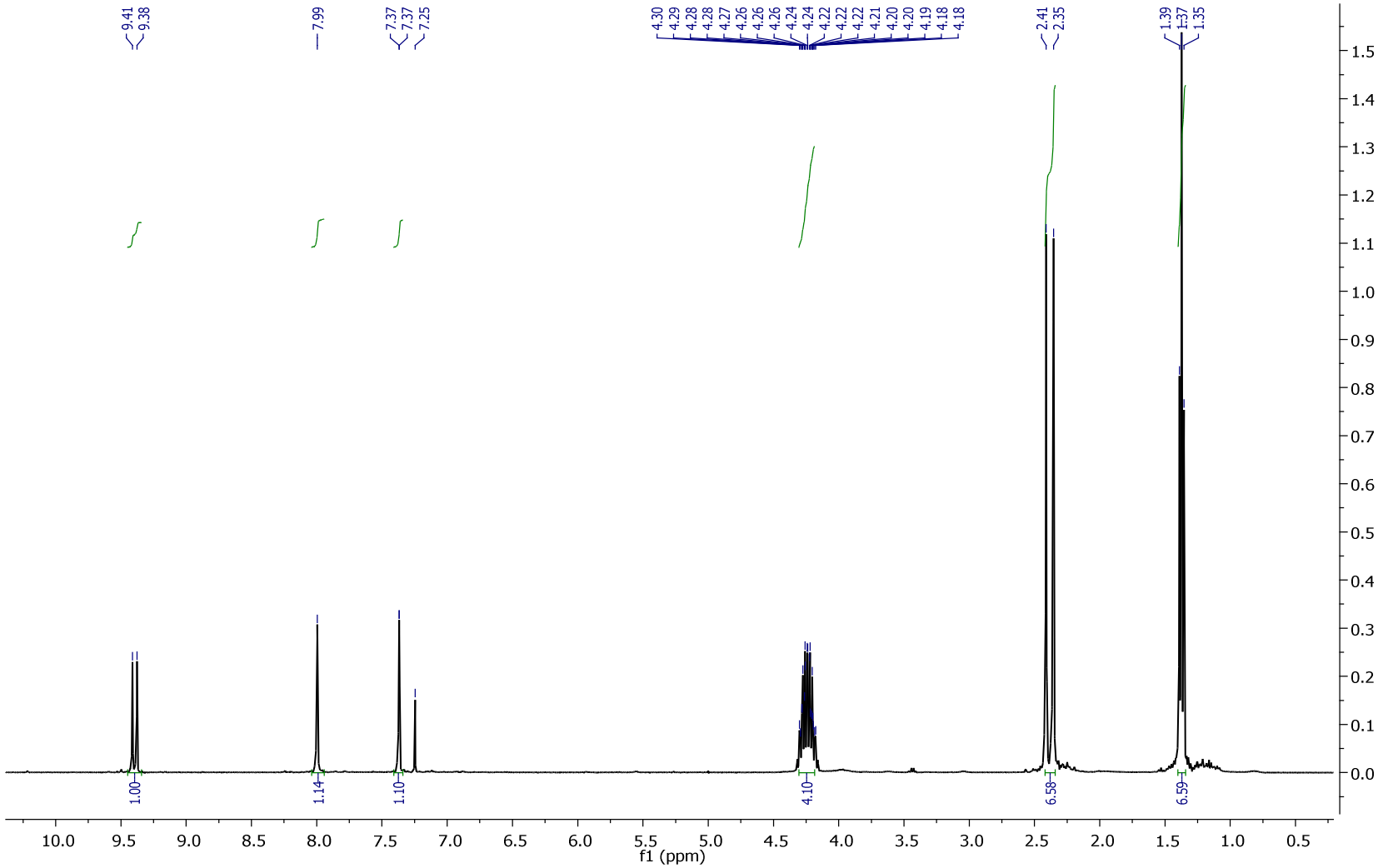
Meas. m/z	Formula	m/z	err [ppm]	Mean err [ppm]	rdb	N-Rule	e—Conf	mSigma
440.0233								
	C 17 H 15 Cl F 2 N Na O 5 P	440.0237	0.8	0.5	9.5	ok	even	3.93

5. *Diethyl (2-(chlorodifluoromethyl)-7,8-dimethyl-5-oxo-5,10a-dihydro-4aH-chromeno[2,3-b]pyridin-3-yl)phosphonate (**3e**)*

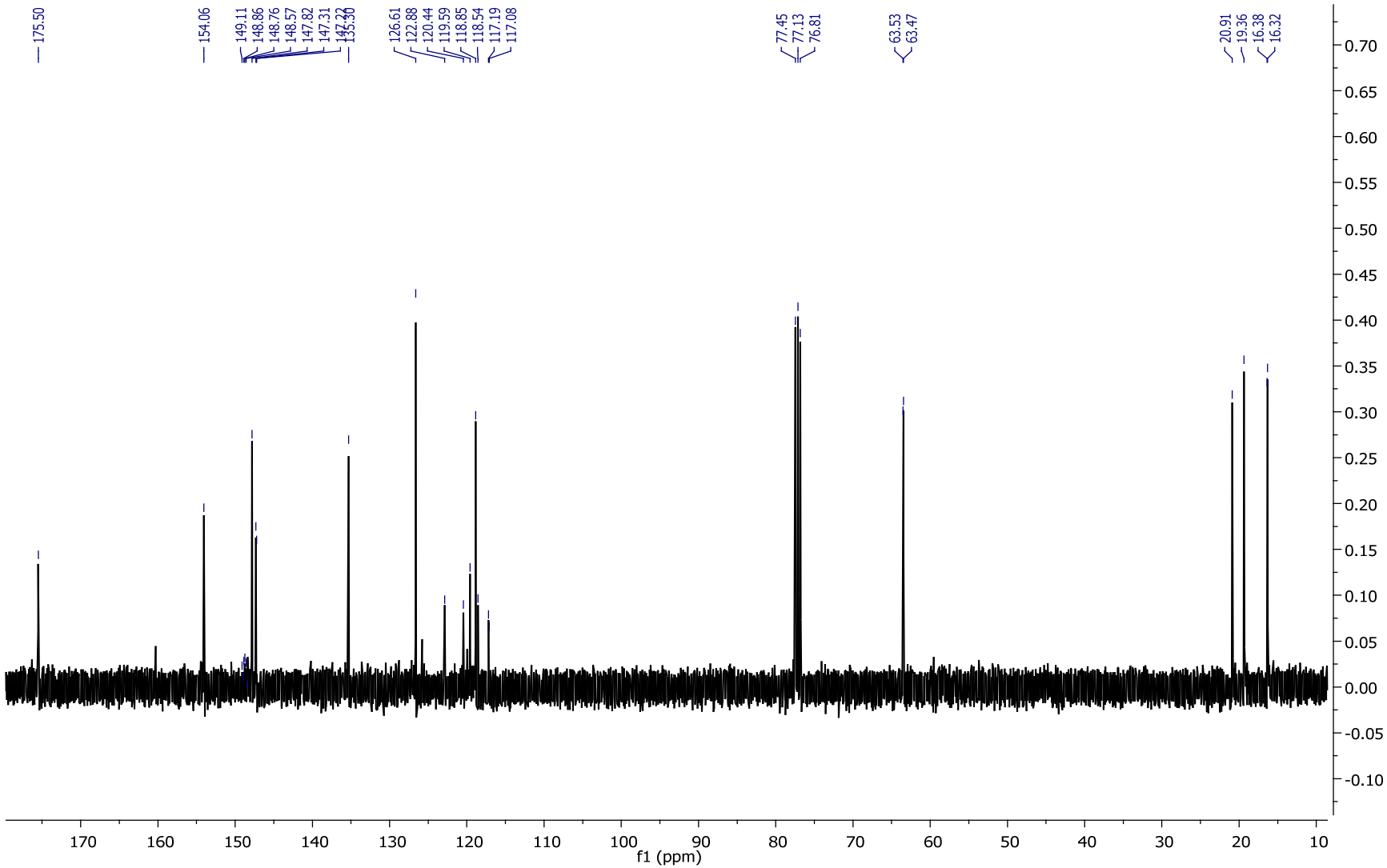


Orange crystals (84%); mp 130–133 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.37 (t, J = 7.1 Hz, 6H), 2.35 (s, 3H), 2.41 (s, 3H), 4.24 (m, 4H), 7.37 (s, 1H), 7.99 (s, 1H), 9.39 (d, $^{3}J_{H–P}$ = 14.0 Hz, 1H); ^{13}C NMR (100 MHz): δ 16.3 (d, J = 6.4 Hz), 19.3, 20.9, 63.5 (d, J = 6.1 Hz), 117.1 (d, $^{2}J_{C–P}$ = 10.1 Hz), 118.8, 119.4 (d, $^{1}J_{C–P}$ = 191.4 Hz), 119.5, 122.8 (t, $^{1}J_{C–F}$ = 293.2 Hz), 126.6, 135.3, 147.3 (d, $^{3}J_{C–P}$ = 9.5 Hz), 147.8, 154.1,157.8 (td, $^{2}J_{C–F}$ = 27.5 Hz, $^{2}J_{C–P}$ = 11.8 Hz), 175.5; ^{19}F NMR (376 MHz): δ –53.3; ^{31}P NMR (161 MHz): δ 11.4 (t, $^{4}J_{P–F}$ = 1.0 Hz); MS (ESI) *m/z*: $[M+H]^+$ 446 (20%), $[M+Na]^+$ 468 (100%); HRMS (ESI) calcd for $[M+Na]^+$ $(C_{19}H_{19}ClF_2NNaO_5P)^+$ 468.0550; found 468.0552.

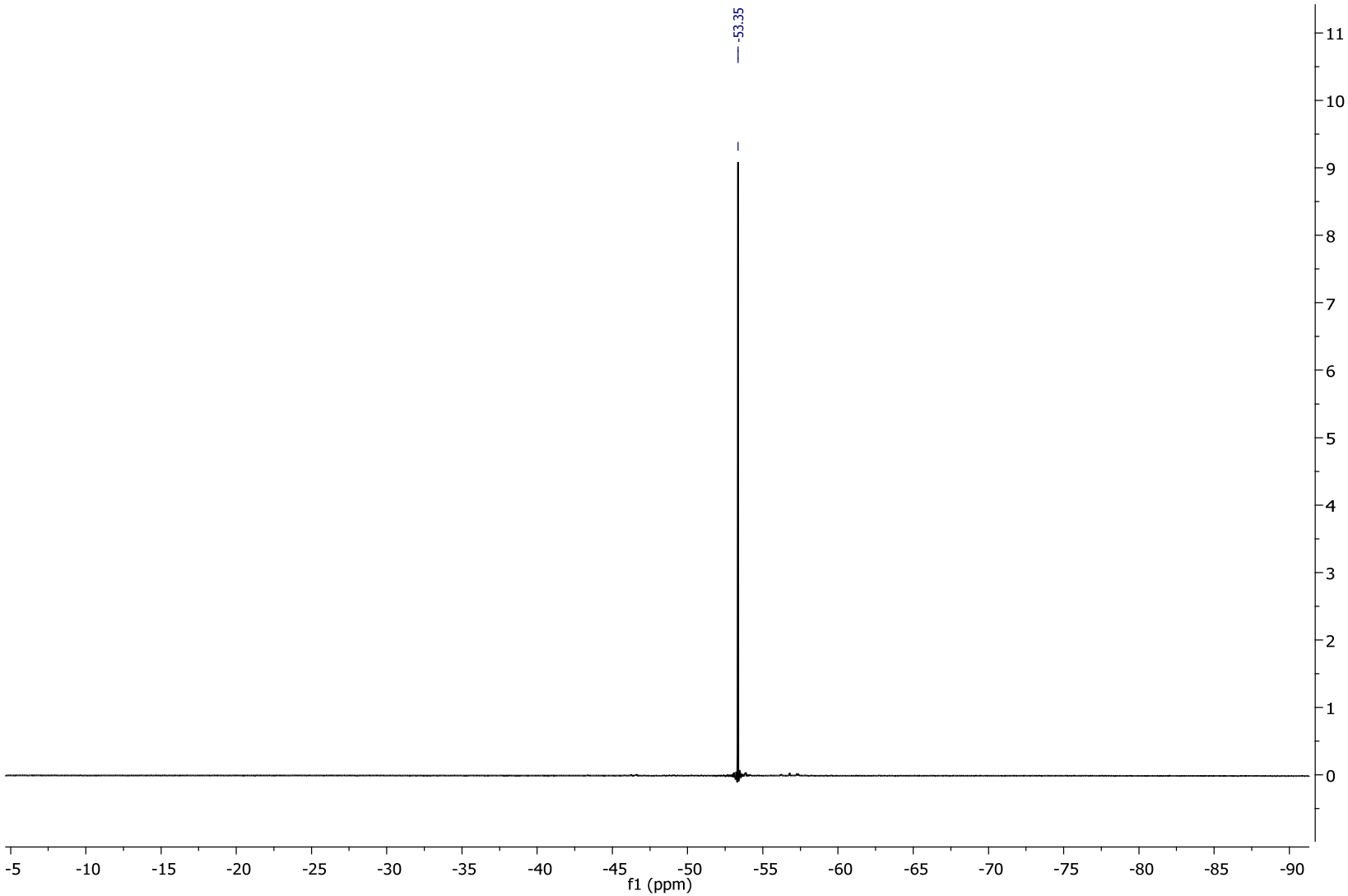
^{1}H NMR


9.41
9.38
7.99
7.37
7.37
7.25
4.30
4.29
4.28
4.28
4.27
4.26
4.26
4.26
4.24
4.24
4.22
4.22
4.22
4.21
4.20
4.20
4.19
4.18
4.18
2.41
2.35
1.39
1.37
1.35
1.00
1.14
1.10
4.10
6.58
6.59
f1 (ppm)

^{13}C NMR


175.50
154.06
149.11
148.86
148.76
148.57
147.82
147.31
126.61
122.88
120.44
119.59
118.85
118.54
117.19
117.08
77.45
77.13
76.81
63.53
63.47
20.91
19.36
16.38
16.32
f1 (ppm)

^{19}F NMR


-53.35
11
10
9
8
7
6
5
4
3
2
1
0
-5
-10
-15
-20
-25
-30
-35
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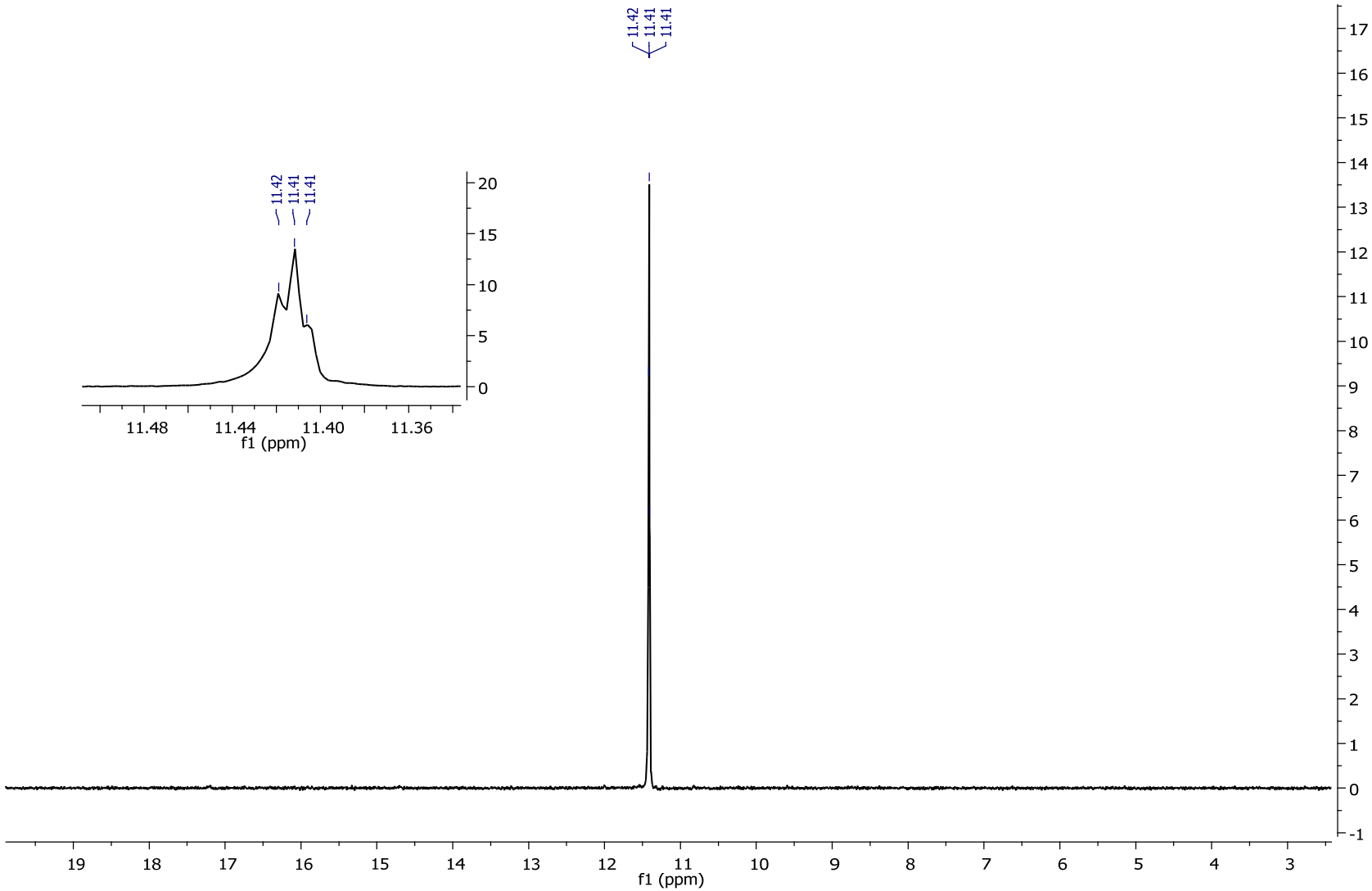
-75
-80
-85
-90
f1 (ppm)

^{31}P NMR



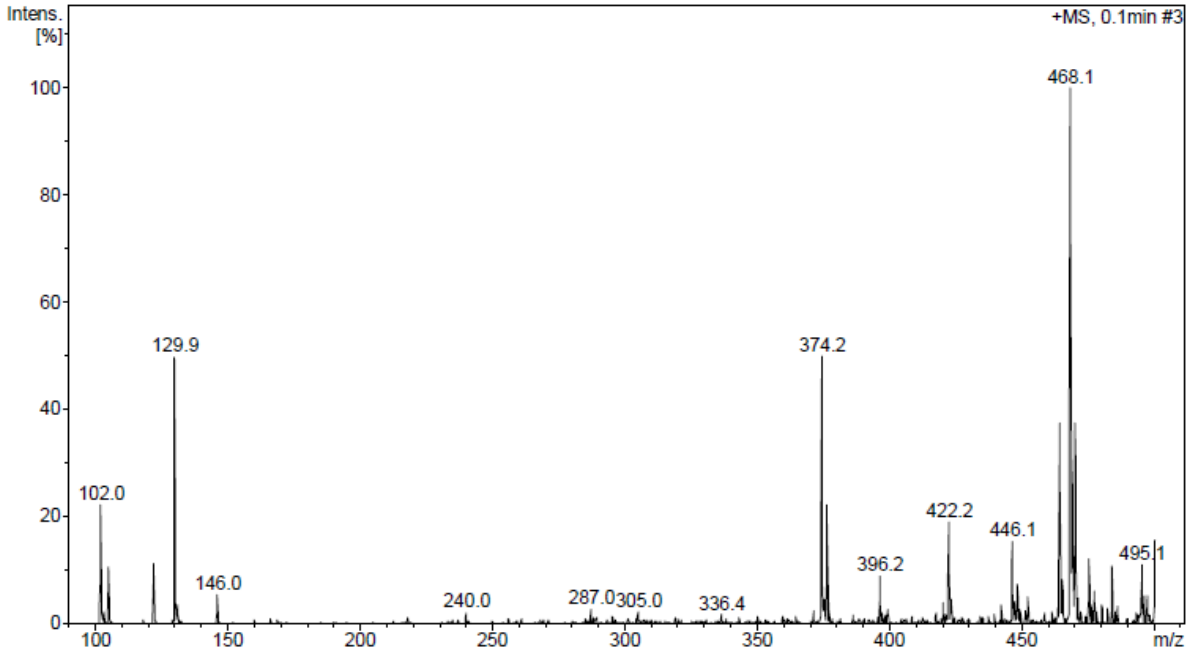
Display Report

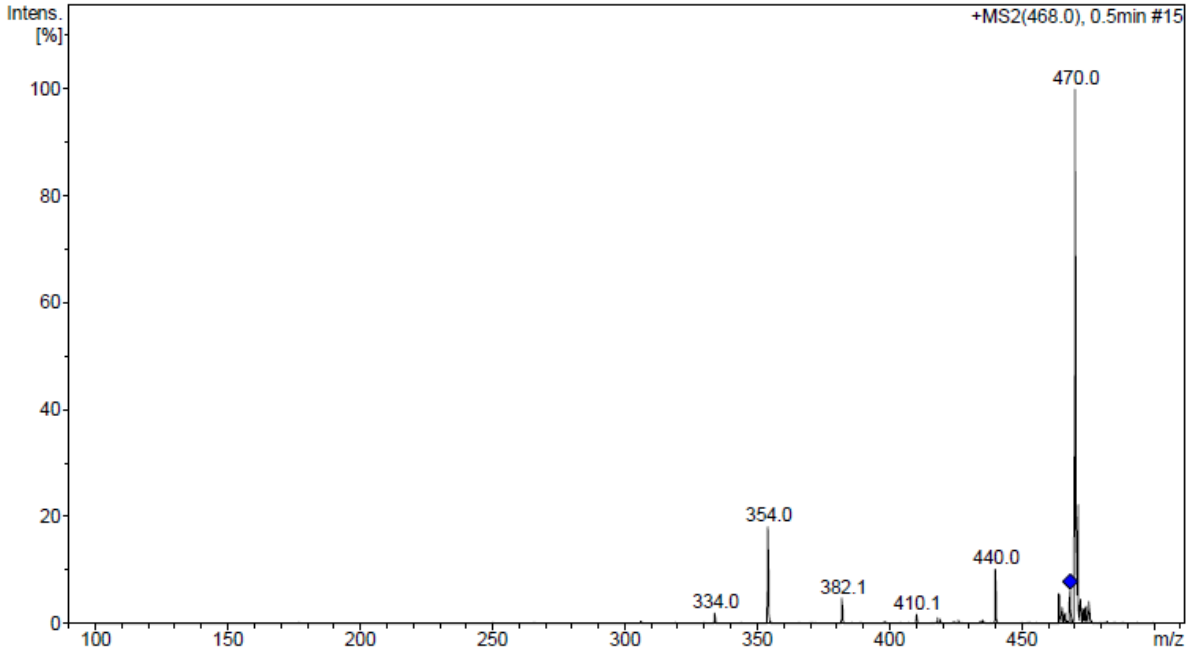
Analysis Info

Analysis Name	G:\Data B\Blazej ION TRAP\BD121102010-.d	Acquisition Date	2010-10-14 17:50:31
Method	DEF_MS.M	Operator	famoosh
Sample Name	0	Instrument	HCTultra
Comment	in methanol		

Acquisition Parameter

Ion Source Type	ESI	Ion Polarity	Positive	Alternating Ion Polarity	off
Mass Range Mode	Ultra Scan	Scan Begin	100 m/z	Scan End	500 m/z
Capillary Exit	115.8 Volt	Skimmer	40.0 Volt	Trap Drive	62.3
Accumulation Time	8255 Šs	Averages	10 Spectra	Auto MS/MS	off





HRMS

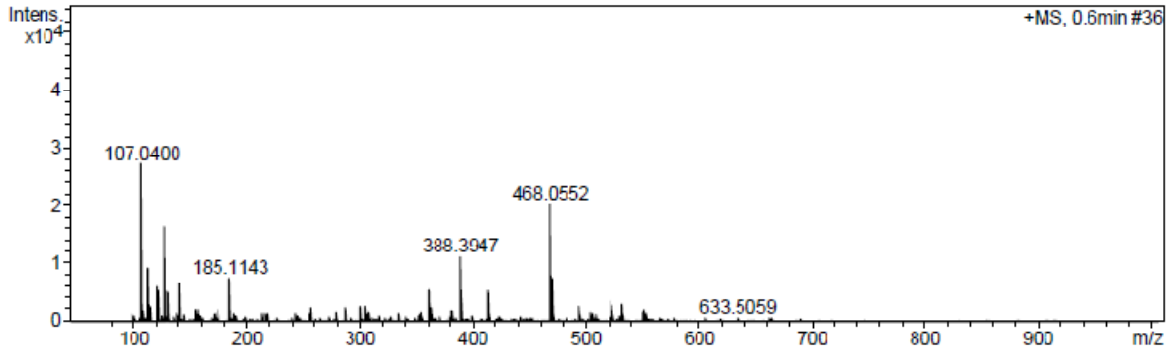
Mass Spectrum SmartFormula Report

Analysis Info

Analysis Name	G:\Data B\Blazej TOF\BD121_14102010-.3.d	Acquisition Date	2010-10-14 11:15:08
Method	tune_low.m	Operator	Bruker Customer
Sample Name	cistus tea	Instrument / Ser#	micrOTOF 129
Comment	in Methanol		

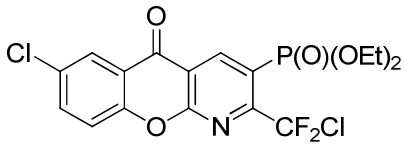
Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	1000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Source



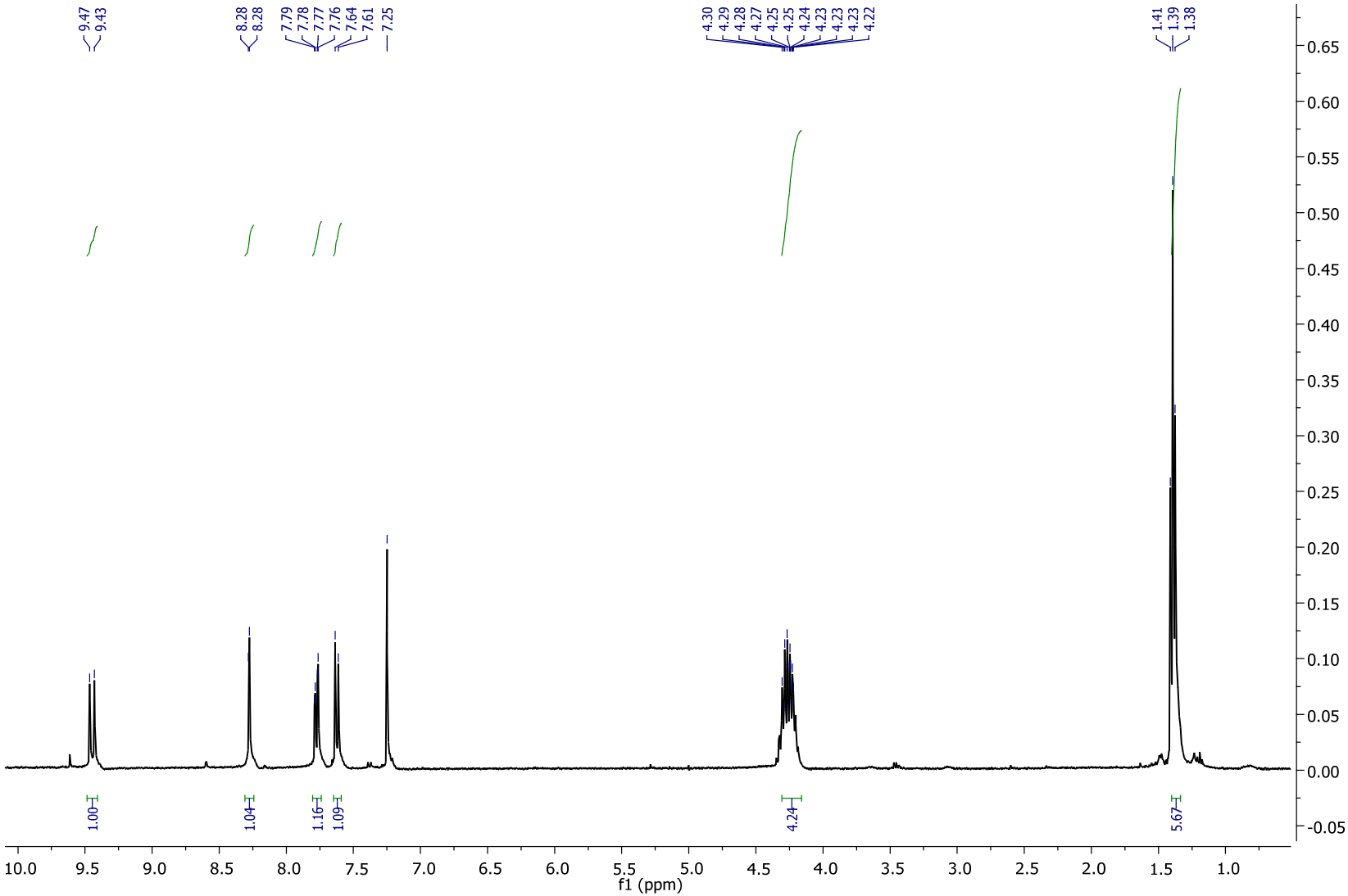
Meas. m/z	Formula	m/z	err [ppm]	Mean err [ppm]	rdb	N-Rule	e—Conf	mSigma
468.0552	C 19 H 19 Cl F 2 N Na O 5 P	468.0550	-0.5	-0.7	9.5	ok	even	6.58

6. *Diethyl (7-chloro-2-(chlorodifluoromethyl)-5-oxo-5,10a-dihydro-4aH-chromeno[2,3-b]pyridin-3-yl)phosphonate (**3f**)*

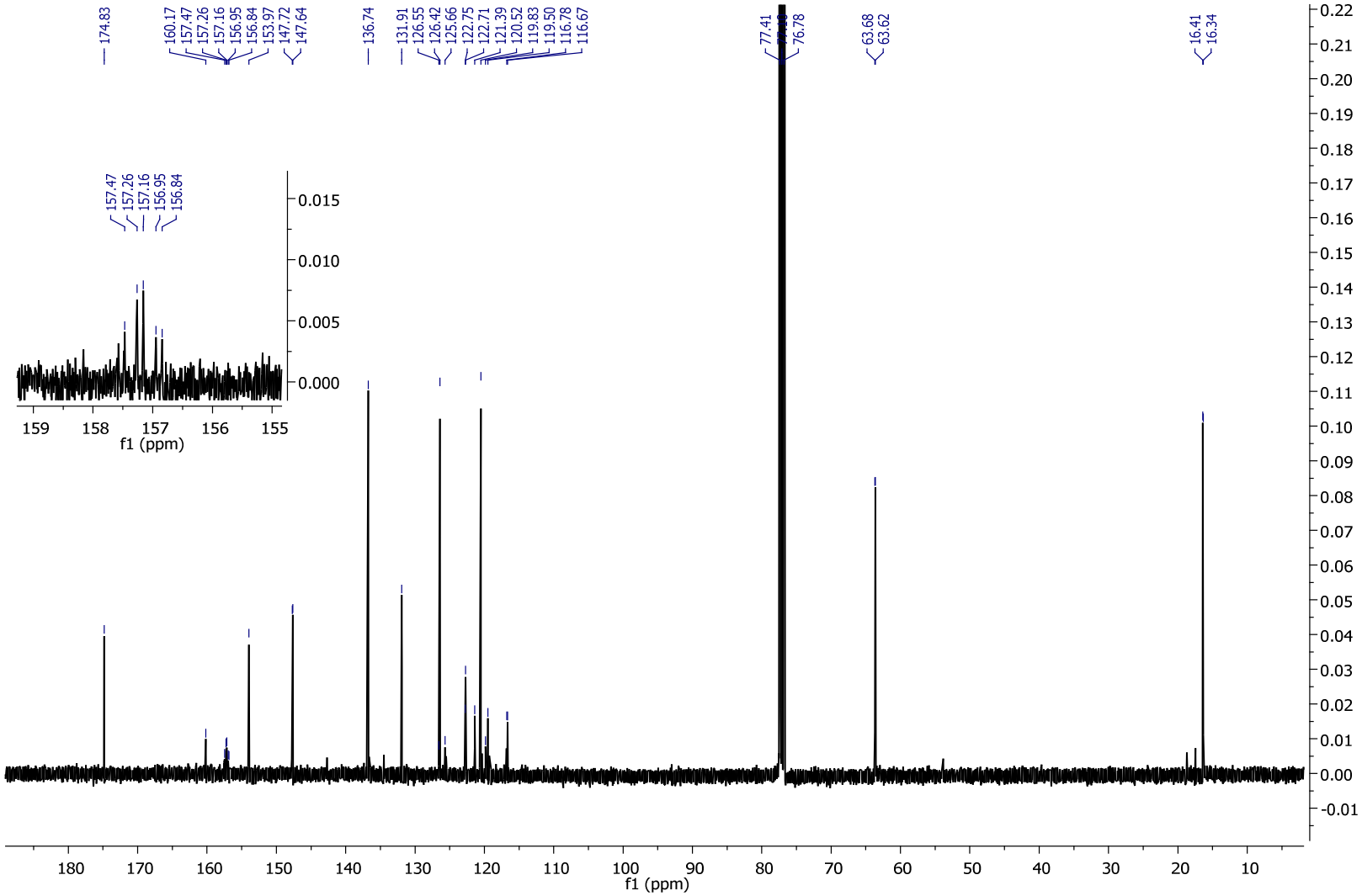


Orange crystals (85%); mp 135–138 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.39 (t, *J* = 7.1 Hz, 6H), 4.25 (m, 4H), 7.63 (d, *J* =8.3 Hz, 1H), 7.77 (d, *J* = 6.3 Hz, 1H), 8.28 (s, 1H), 9.46 (d, $^{3}J_{H–P}$ = 13.9 Hz, 1H); ^{13}C NMR (100 MHz): δ 16.3 (d, *J* = 6.4 Hz), 63.6 (d, *J* = 6.2 Hz), 116.7 (d, $^{2}J_{C–P}$ = 10.7 Hz), 119.7 (d, $^{1}J_{C–P}$ = 190.2 Hz), 120.5, 122.7 (t, $^{1}J_{C–F}$ = 294.7 Hz), 126.4, 131.9, 136.7, 147.6 (d, $^{3}J_{C–P}$ = 8.5 Hz), 153.9, 157.1 (td, $^{2}J_{C–F}$ = 32.2 Hz, $^{2}J_{C–P}$ = 10.3 Hz), 174.8; ^{19}F NMR (376 MHz): δ –53.6; ^{31}P NMR (161 MHz): δ 10.9; MS (ESI) m/z: $[M+Na]^+$ 474; HRMS (ESI) calcd for $[M+Na]^+$ $(C_{17}H_{14}Cl_2F_2NNaO_5P)^+$ 473.9847; found 473.9862.

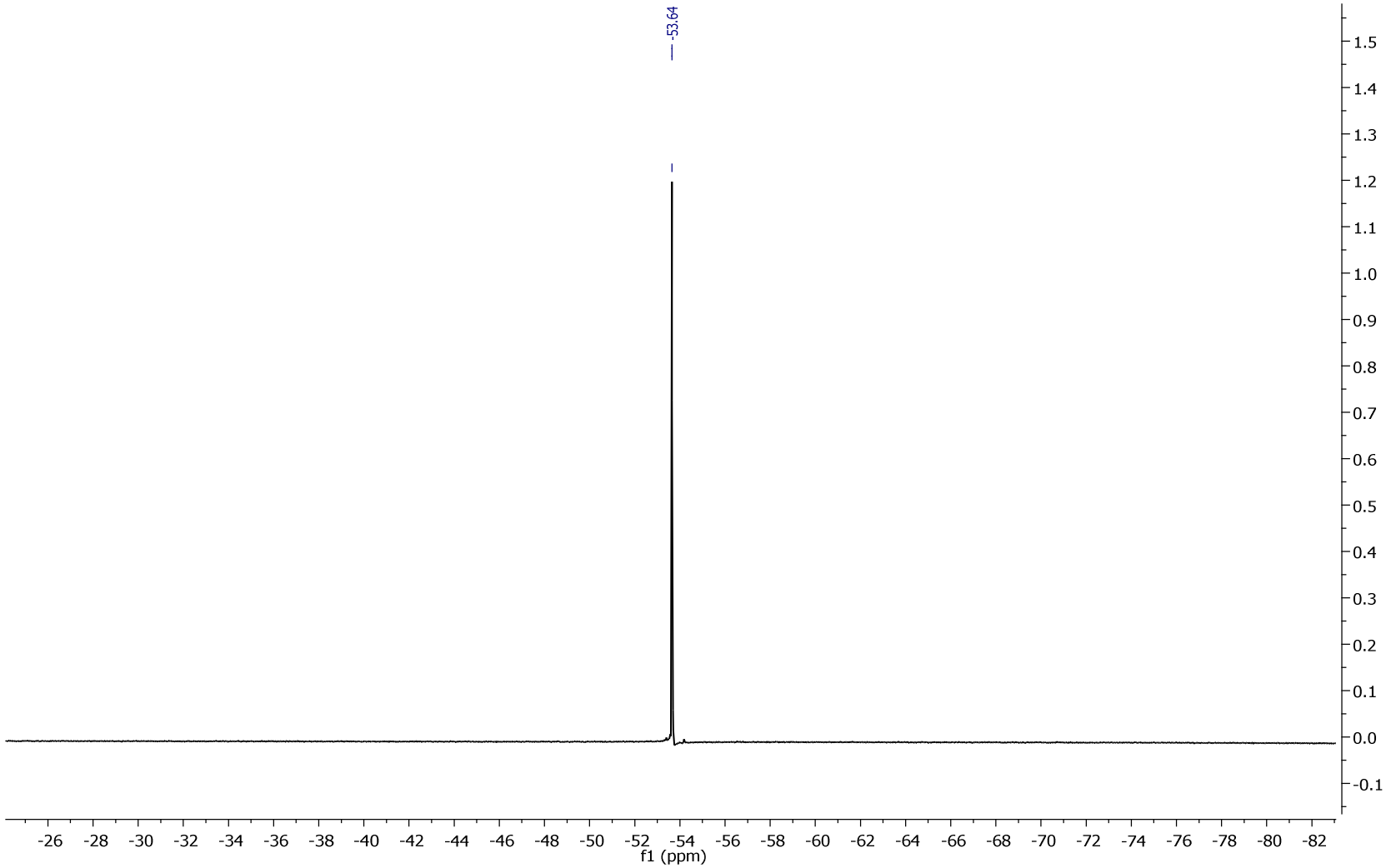
^{1}H NMR


9.47
9.43
8.28
8.28
7.79
7.78
7.77
7.76
7.64
7.61
7.25
4.30
4.29
4.28
4.27
4.25
4.25
4.24
4.23
4.23
4.23
4.22
1.41
1.39
1.38
1.00
1.04
1.16
1.09
4.24
5.67
f1 (ppm)

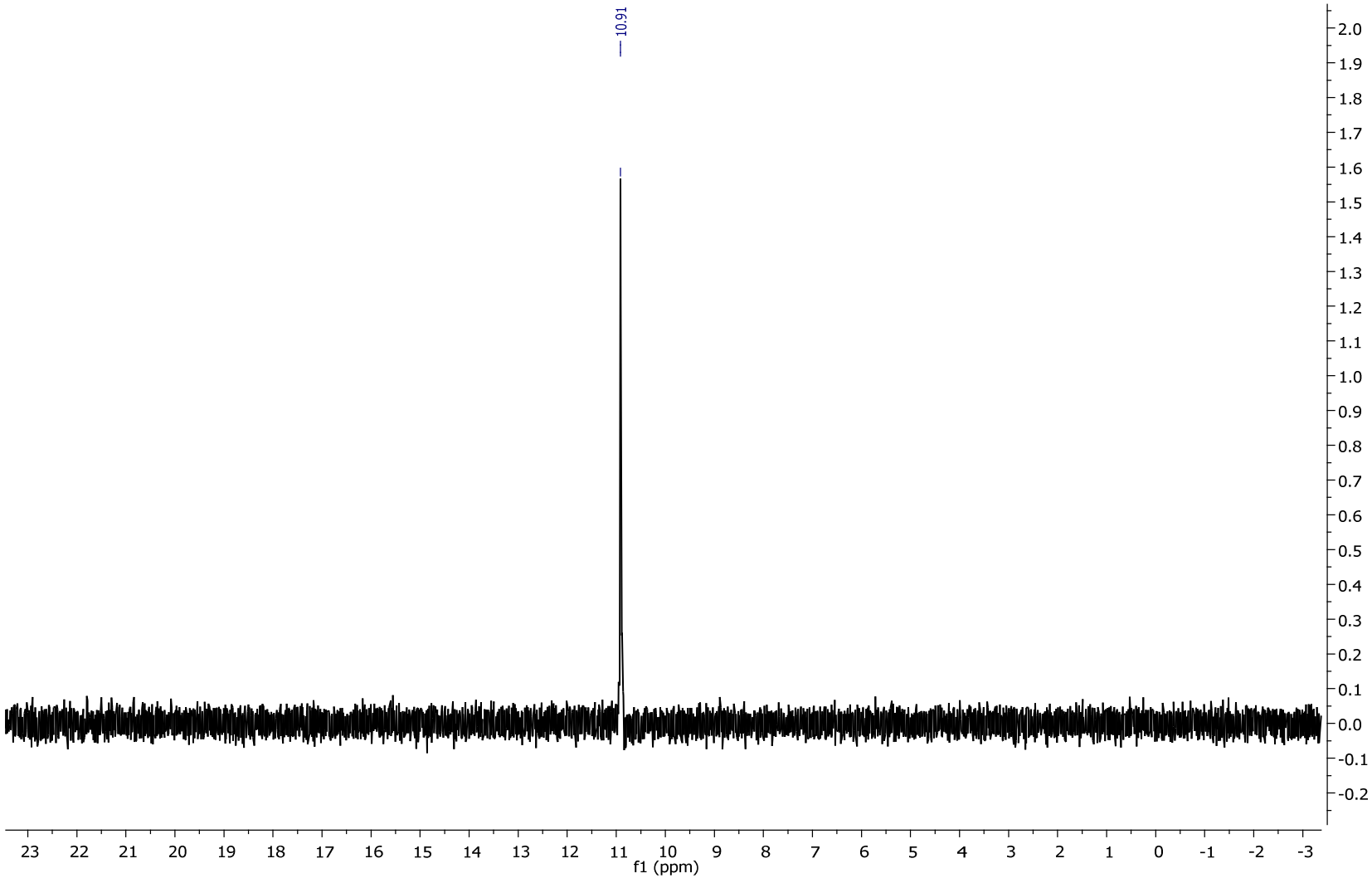
^{13}C NMR


174.83
160.17
157.47
157.26
157.16
156.95
156.84
153.97
147.72
147.64
136.74
131.91
126.55
126.42
125.66
122.75
122.71
121.39
120.52
119.83
119.50
116.78
116.67
77.41
76.78
63.68
63.62
16.41
16.34
f1 (ppm)

^{19}F NMR


-53.64
1.5
1.4
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
-0.1
-26 -28 -30 -32 -34 -36 -38 -40 -42 -44 -46 -48 -50 -52 -54 -56 -58 -60 -62 -64 -66 -68 -70 -72 -74 -76 -78 -80 -82
f1 (ppm)

^{31}P NMR


10.91
2.0
1.9
1.8
1.7
1.6
1.5
1.4
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
-0.1
-0.2
23 22 21 20 19 18 17 16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

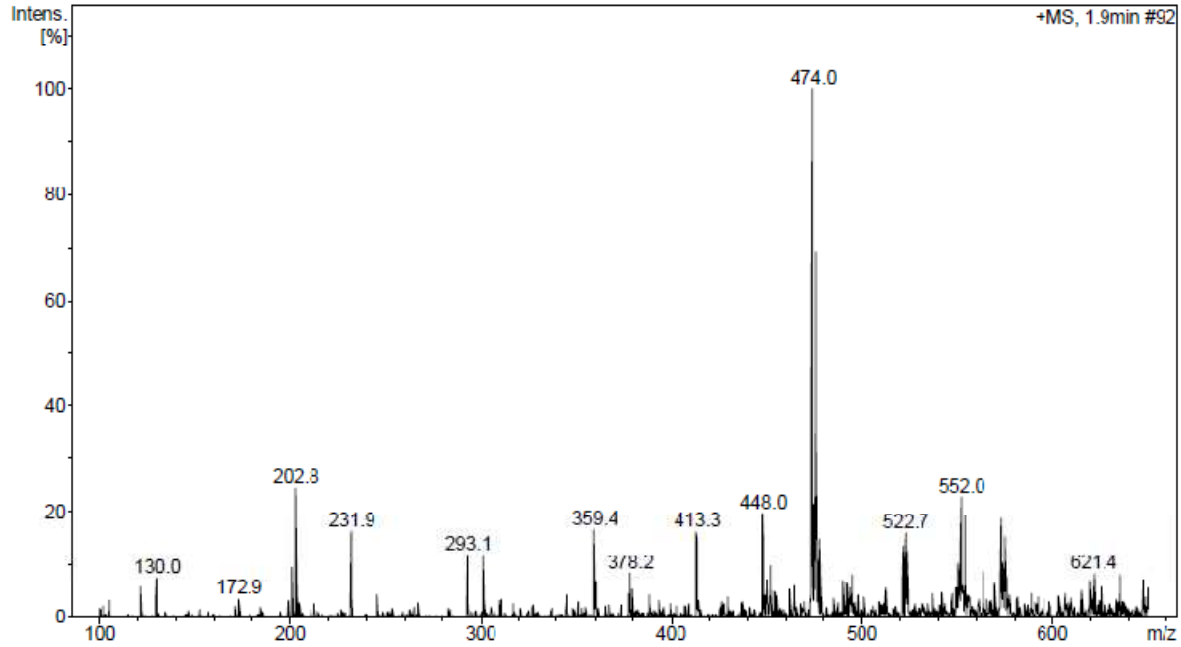
Display Report

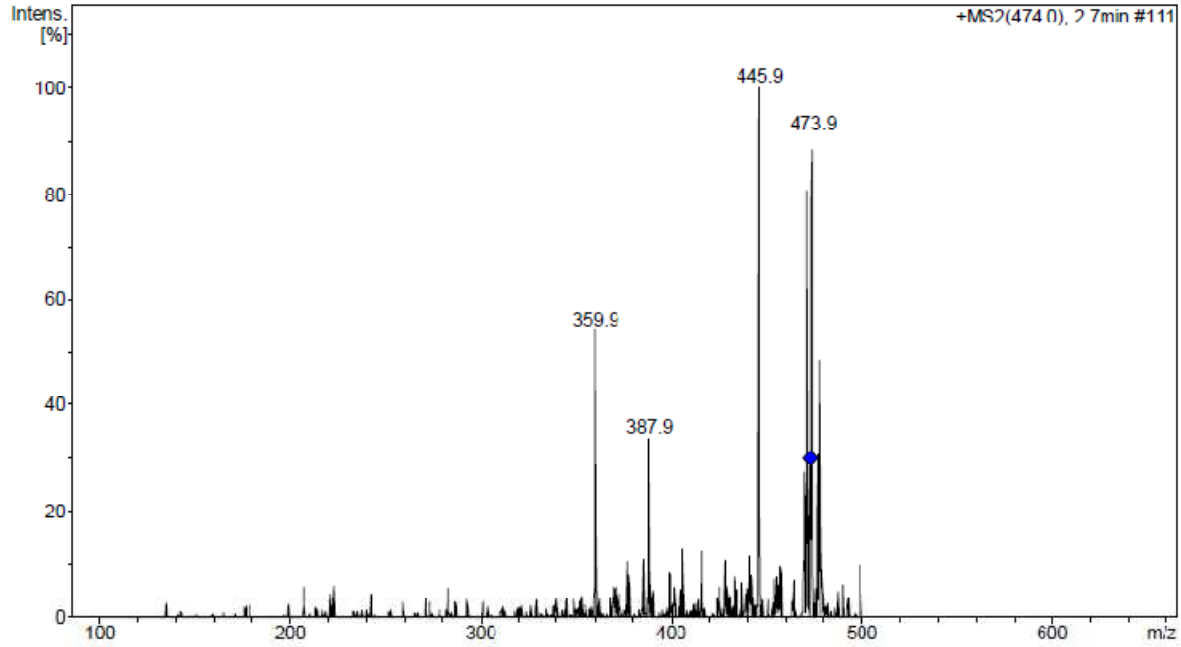
Analysis Info

Analysis Name	G:\Data B\Blazej ION TRAP\BD122_151020.d	Acquisition Date	2010-10-15 10:40:58
Method	DEF_MS.M	Operator	farnocsh
Sample Name	Sativa	Instrument	HCTultra
Comment	in Methanol		

Acquisition Parameter

Ion Source Type	ESI	Ion Polarity	Positive	Alternating Ion Polarity	off
Mass Range Mode	Ultra Scan	Scan Begin	100 m/z	Scan End	650 m/z
Capillary Exit	220.0 Volt	Skimmer	40.0 Volt	Trap Drive	78.0
Accumulation Time	10387 ŠS	Averages	10 Spectra	Auto MS/MS	off





HRMS

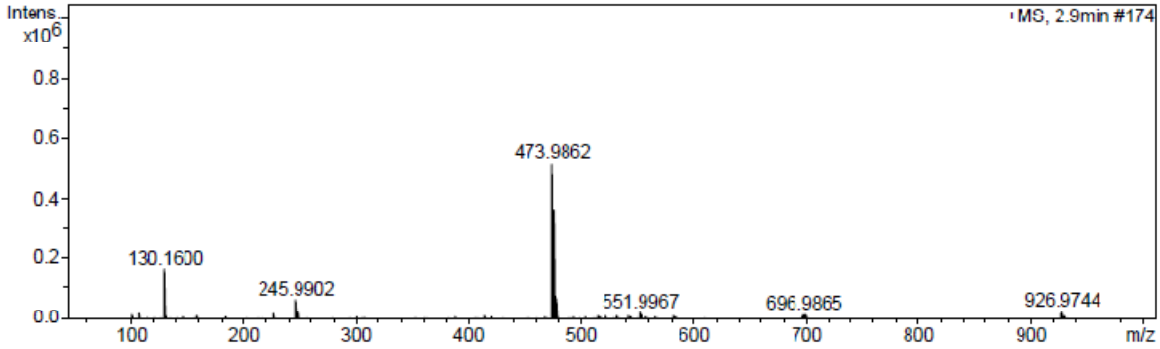
Mass Spectrum SmartFormula Report

Analysis Info

Analysis Name	G:\Data B\Blazej TOF\BD122_14102010-2.d	Acquisition Date	2010-10-14 11:38:08
Method	tune_low.m	Operator	Bruker Customer
Sample Name	cistus tea	Instrument / Ser#	micrOTOF 129
Comment	in Methanol		

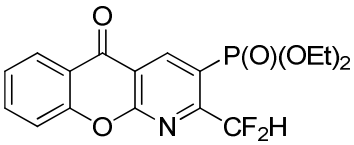
Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	1000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Source



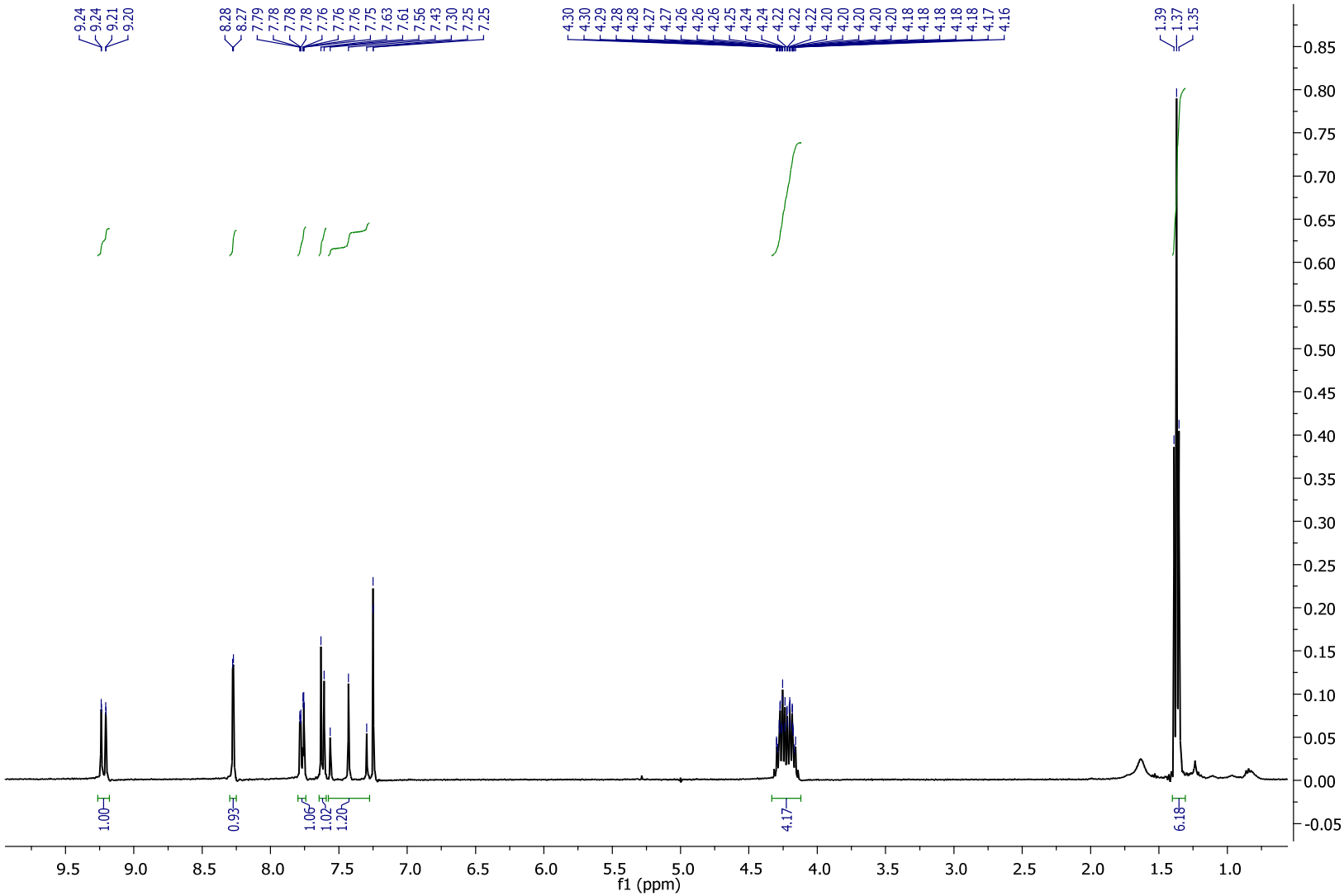
Meas. m/z	Formula	m/z	err [ppm]	Mean err [ppm]	rdb	N-Rule	e—Conf	mSigma
473.9862	C 17 H 14 Cl 2 F 2 N Na C 5 P	473.9847	-3.2	-1.3	9.5	ok	even	16.81

7. *Diethyl (2-(difluoromethyl)-5-oxo-5,10a-dihydro-4aH-chromeno-[2,3-b]pyridin-3-yl)phosphonate* ***(3g)***

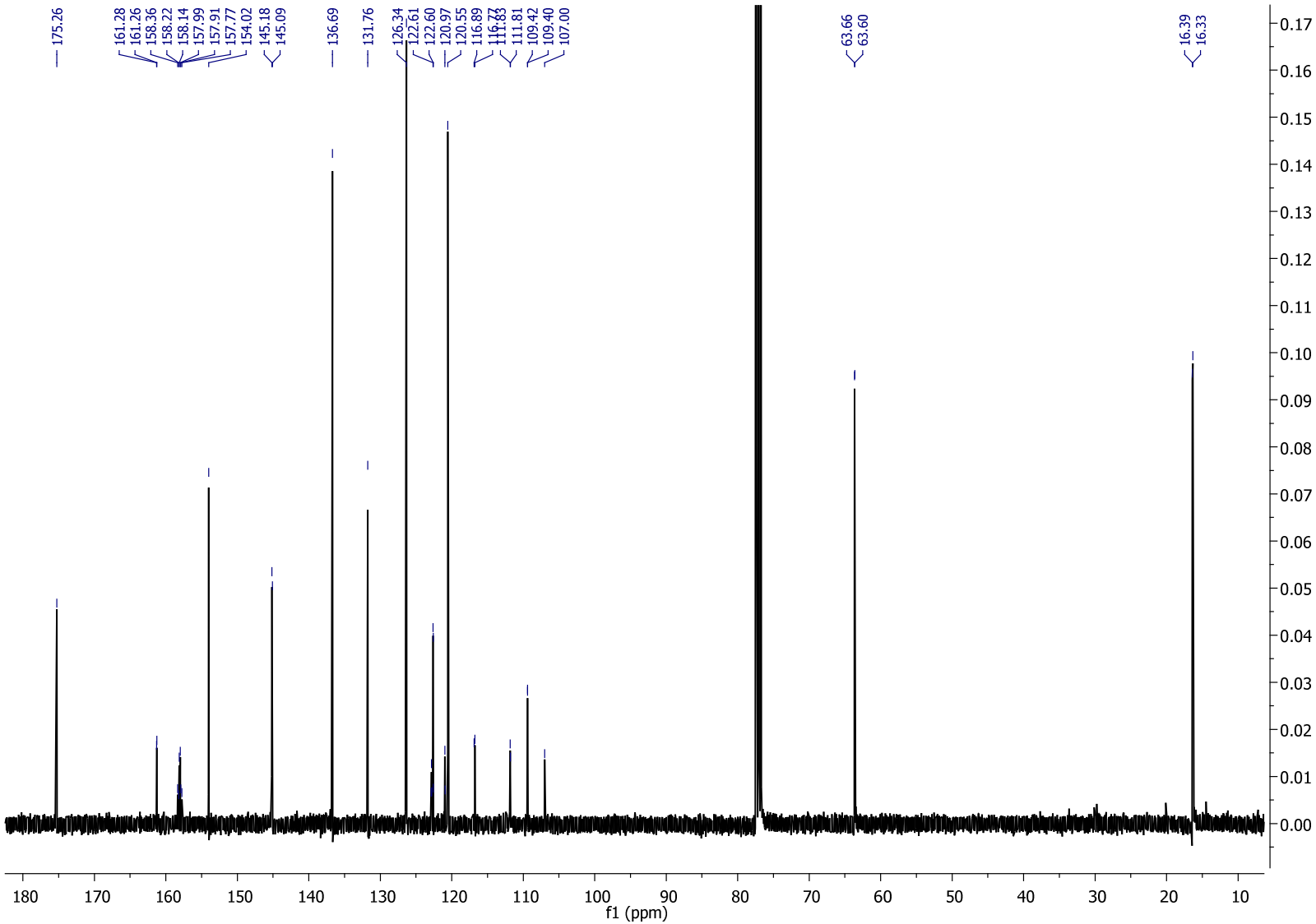


Yellowish crystals (51%); mp 120–122 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.37 (t, *J* = 7.1 Hz, 6H), 4.24 (m, 4H), 7.43 (t, $^{2}J_{H–F}$ = 53.6 Hz, 1H), 7.63 (d, *J* = 8.9 Hz, 2H), 7.77 (dd, *J* = 8.9 Hz, *J* = 2.6 Hz, 1H), 8.28 (d, *J* = 2.6 Hz, 1H), 9.22 (d, $^{3}J_{H–P}$ = 13.3 Hz, 1H); ^{13}C NMR (100 MHz): δ 16.3 (d, *J* = 6.7 Hz), 63.6 (d, *J* = 6.1 Hz), 109.4 (t, $^{1}J_{C–F}$ = 244.2 Hz), 116.9 (d, $^{2}J_{C–P}$ = 11.0 Hz), 120.5, 121.5 (d, $^{1}J_{C–P}$ = 190.0 Hz), 122.6, 126.3, 131.7, 136.6, 146.1 (d, $^{3}J_{C–P}$ = 8.9 Hz), 154.5, 158.9 (td, $^{2}J_{C–F}$ = 21.5 Hz, $^{2}J_{C–P}$ = 13.5 Hz), 160.3, 175.2; ^{19}F NMR (376 MHz) δ –117.2 (d, $^{2}J_{F–H}$ = 53.7 Hz); ^{31}P NMR (161 MHz) δ 12.0 (t, $^{4}J_{P–F}$ = 1.4 Hz); MS (ESI) *m/z*: $[M+Na]^+$ 406 (50%), $[2M+Na]^+$ 789 (100%); HRMS (ESI) calcd for $[M+Na]^+$ $(C_{17}H_{16}F_2NNaO_5P)^+$ 406.0626; found 406.0636.

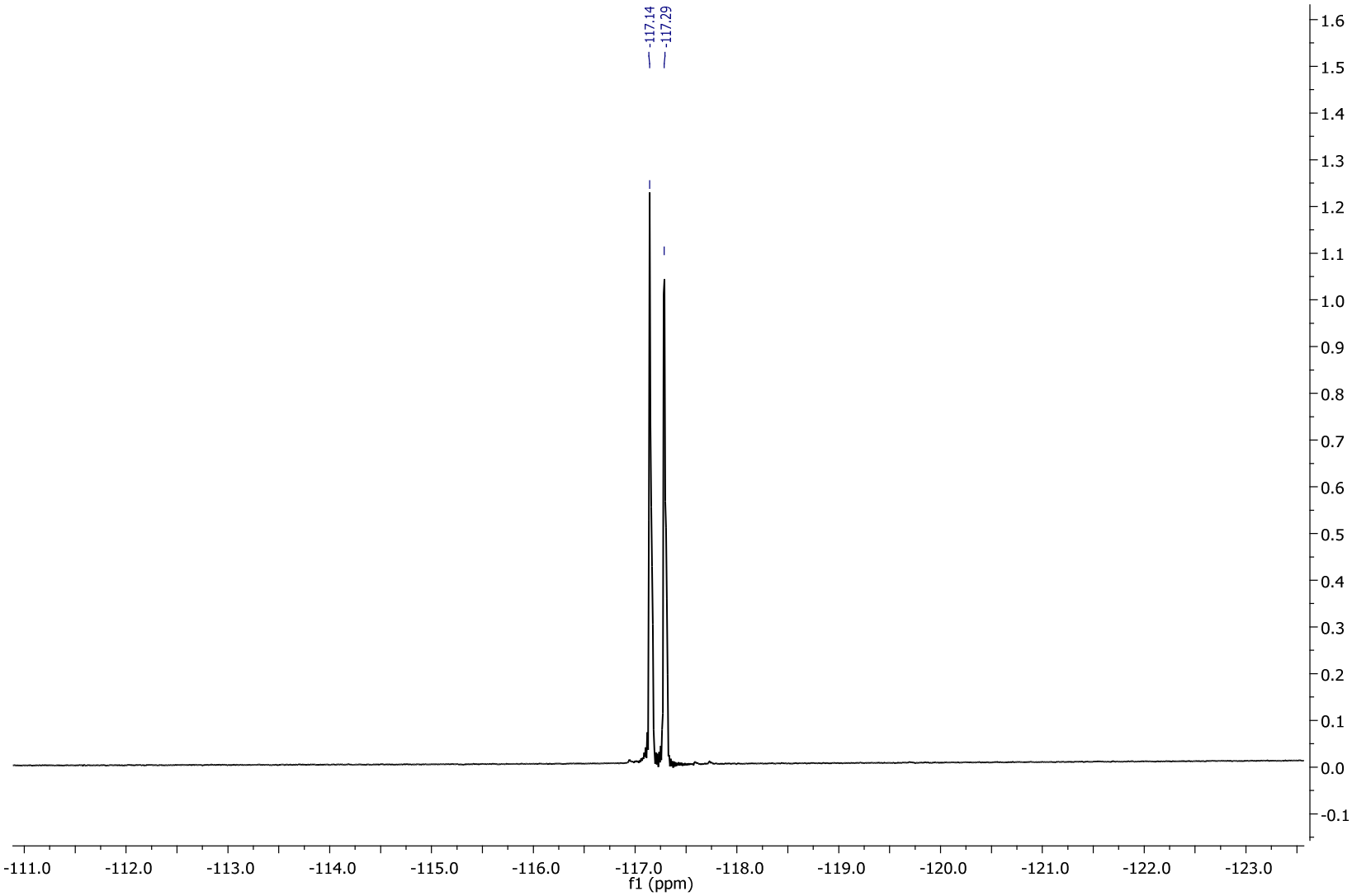
^{1}H NMR


9.24
9.24
9.21
9.20
8.28
8.27
7.79
7.78
7.78
7.78
7.76
7.76
7.76
7.75
7.63
7.61
7.56
7.43
7.30
7.25
7.25
4.30
4.30
4.29
4.28
4.28
4.27
4.27
4.26
4.26
4.26
4.25
4.24
4.24
4.22
4.22
4.22
4.20
4.20
4.20
4.20
4.20
4.18
4.18
4.18
4.18
4.17
4.16
1.39
1.37
1.35
1.00
0.93
1.06
1.02
1.20
4.17
6.18
f1 (ppm)

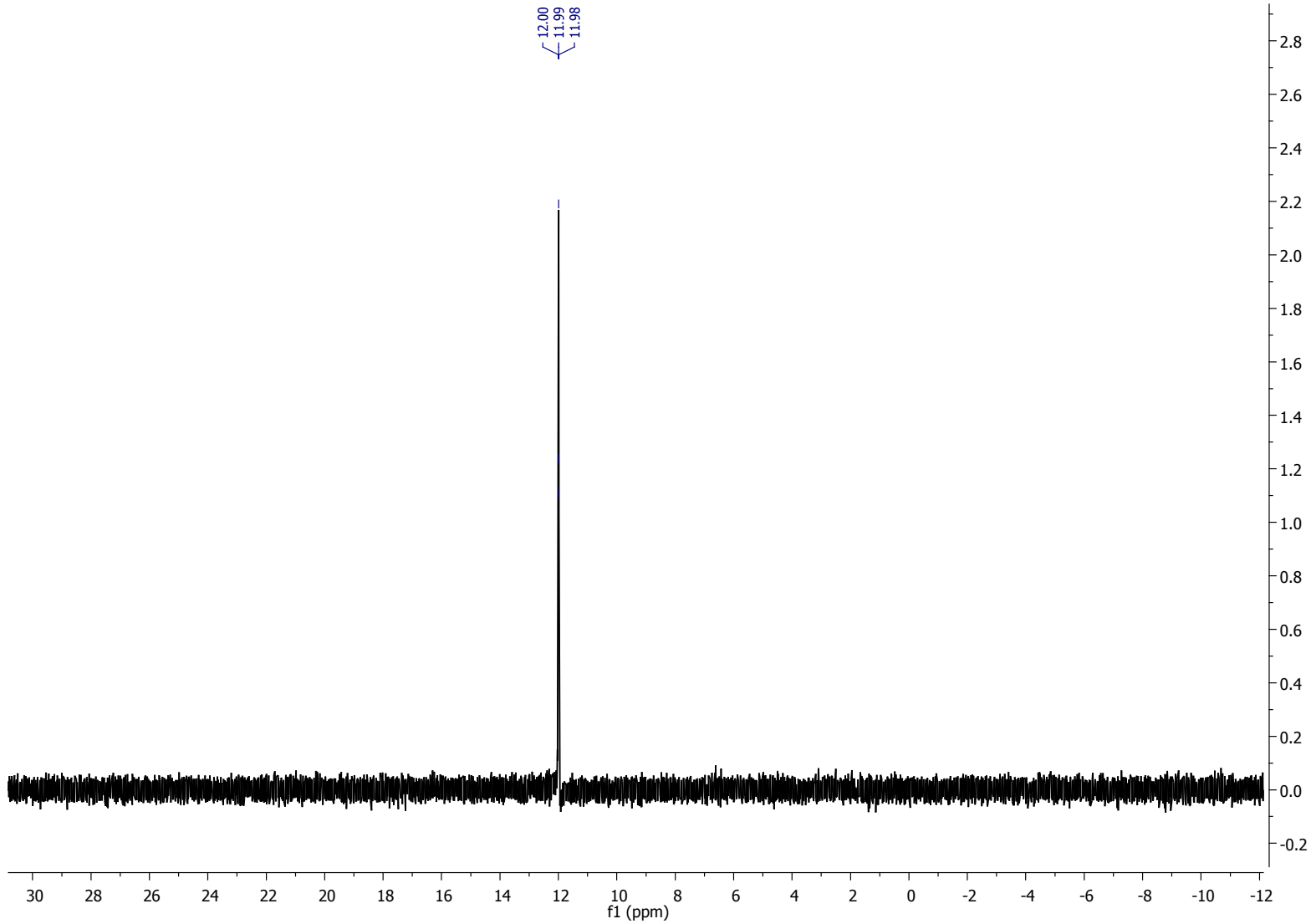
^{13}C NMR


175.26
161.28
161.26
158.36
158.22
158.14
157.99
157.91
157.77
154.02
145.18
145.09
136.69
131.76
126.34
122.61
122.60
120.97
120.55
116.89
116.77
111.83
111.81
109.42
109.40
107.00
63.66
63.60
16.39
16.33
f1 (ppm)

^{19}F NMR


-117.14
-117.29
1.6
1.5
1.4
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
-0.1
-111.0
-112.0
-113.0
-114.0
-115.0
-116.0
-117.0
-118.0
-119.0
-120.0
-121.0
-122.0
-123.0
f1 (ppm)

^{31}P NMR


12.00
11.99
11.98
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
-0.2
30 28 26 24 22 20 18 16 14 12 10 8 6 4 2 0 -2 -4 -6 -8 -10 -12
f1 (ppm)

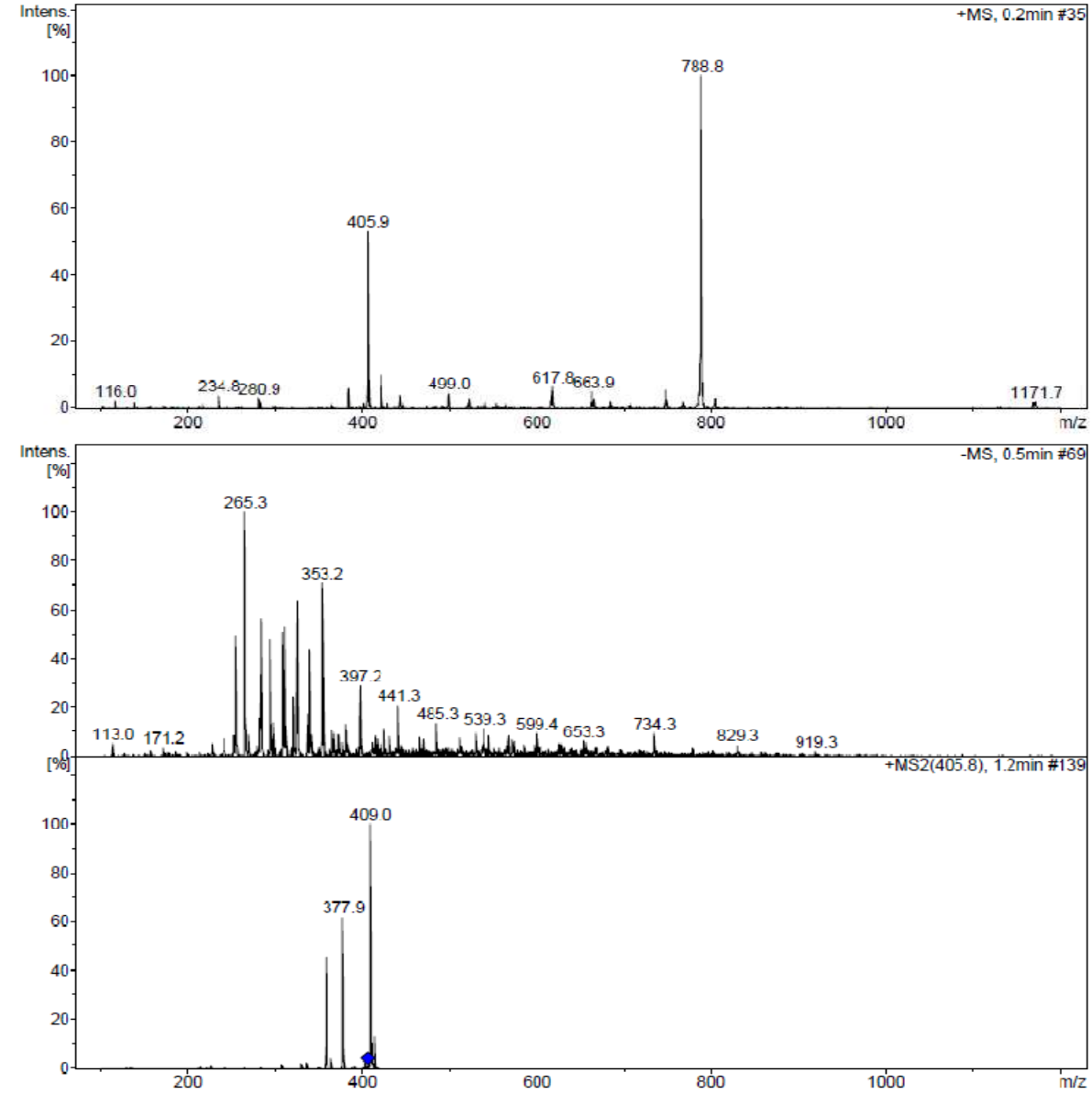
Display Report

Analysis Info

Analysis Name	G:\Data B\Blazej ION TRAP\BD132B_30112010.d	Acquisition Date	2010-11-30 10:54:39
Method	DEF_MS.M	Operator	farnoosh
Sample Name	Default	Instrument	HCTultra
Comment	in Methanol		

Acquisition Parameter

Ion Source Type	ESI	Ion Polarity	Positive	Alternating Ion Polarity	off
Mass Range Mode	Ultra Scan	Scan Begin	100 m/z	Scan End	1200 m/z
Capillary Exit	109.0 Volt	Skimmer	40.0 Volt	Trap Drive	51.2
Accumulation Time	118 µs	Averages	5 Spectra	Auto MS/MS	off



Bruker Compass DataAnalysis 4.0 printed: 2009-08-14 21:16:14 Page 1 of 1

HRMS

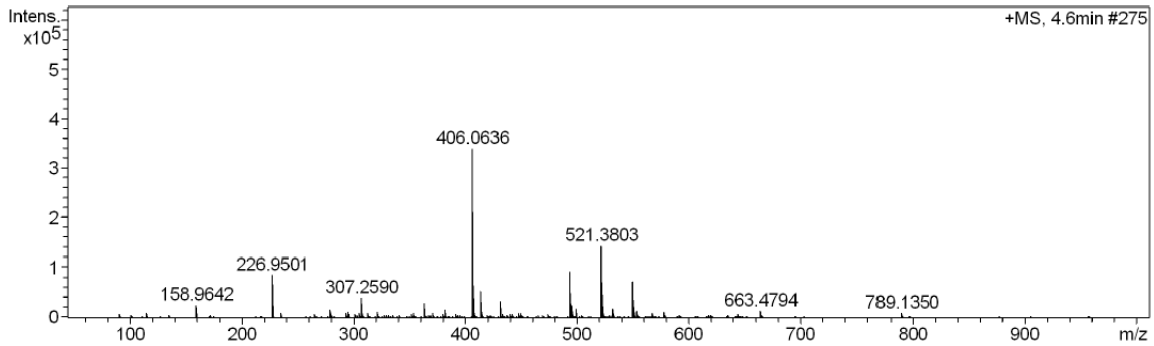
Mass Spectrum SmartFormula Report

Analysis Info

Analysis Name	E:\Data B\Blazej TOF\BD132B_30112010.d	Acquisition Date	11/30/2010 11:26:06 AM
Method	tune_low.m	Operator	Bruker Customer
Sample Name		Instrument / Ser#	micrOTOF 129
Comment	in methanol		

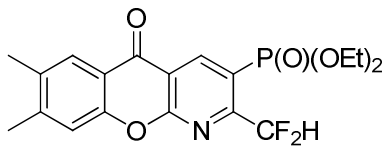
Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	1000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Source



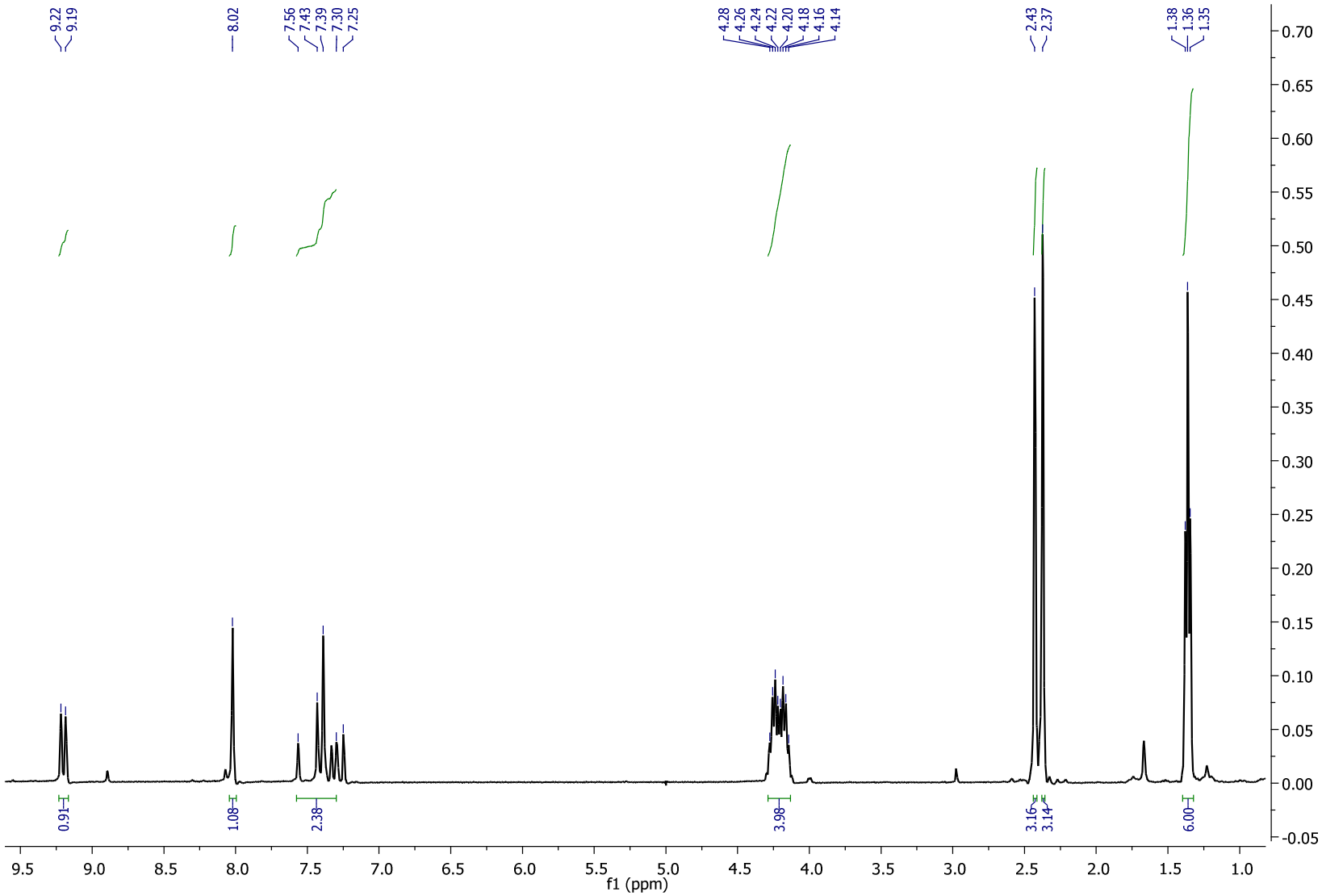
Meas. m/z	Formula	m/z	err [ppm]	Mean err [ppm]	rdb	N-Rule	mSigma	err [mDa]
406.0636	C 17 H 16 F 2 N Na O 5 P	406.0626	-2.3	-1.6	9.5	ok	1.3	-0.9

8. *Diethyl (2-(difluoromethyl)-7,8-dimethyl-5-oxo-5,10a-dihydro-4aH-chromeno[2,3-b]pyridin-3-yl)-phosphonate (**3h**)*

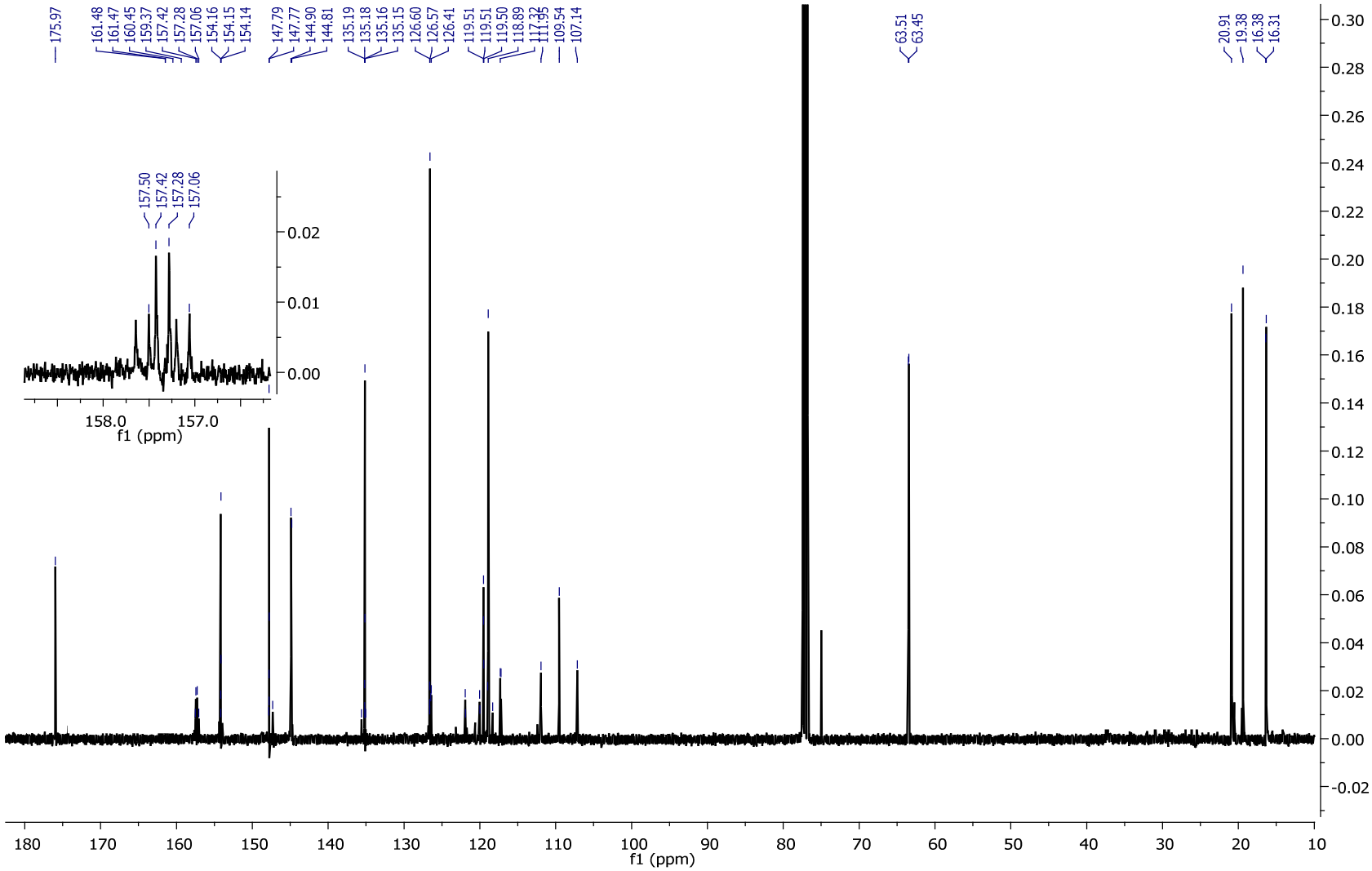


Orange crystals (49%); mp 125–128 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.36 (t, J = 6.9 Hz, 6H), 2.37 (s, 3H), 2.43 (s, 3H), 4.20 (m, 4H), 7.39 (s, 1H), 7.43 (t, $^{2}J_{H–F}$ = 53.3 Hz, 1H), 8.02 (s, 1H), 9.21 (d, $^{3}J_{H–P}$ = 13.2 Hz, 1H); ^{13}C NMR (100 MHz): δ 16.3 (d, J = 7.5 Hz), 19.4, 20.9, 63.5 (d, J = 6.8 Hz), 109.5 (t, $^{1}J_{C–F}$ = 242.2 Hz), 117.3 (d, $^{2}J_{C–P}$ = 9.7 Hz), 118.9, 119.5, 121.5 (dt, $^{1}J_{C–P}$ = 189.5 Hz, $^{3}J_{C–F}$ = 3.8 Hz), 126.5, 135.1, 144.9 (d, $^{3}J_{C–P}$ = 10.6 Hz), 147.7, 154.1, 157.4 (td, $^{2}J_{C–F}$ = 23.4 Hz, $^{2}J_{C–P}$ = 14.5 Hz), 175.9; ^{19}F NMR (376 MHz) δ –117.2 (d, $^{2}J_{F–H}$ = 53.4 Hz); ^{31}P NMR (161 MHz): δ 12.5; MS (ESI) *m/z*: $[M+H]^+$ 412 (50%), $[M+Na]^+$ 434 (100%); HRMS (ESI) calcd for $[M+H]^+$ ($C_{19}H_{21}F_2NO_5P$) 412.1120; found 412.1119.

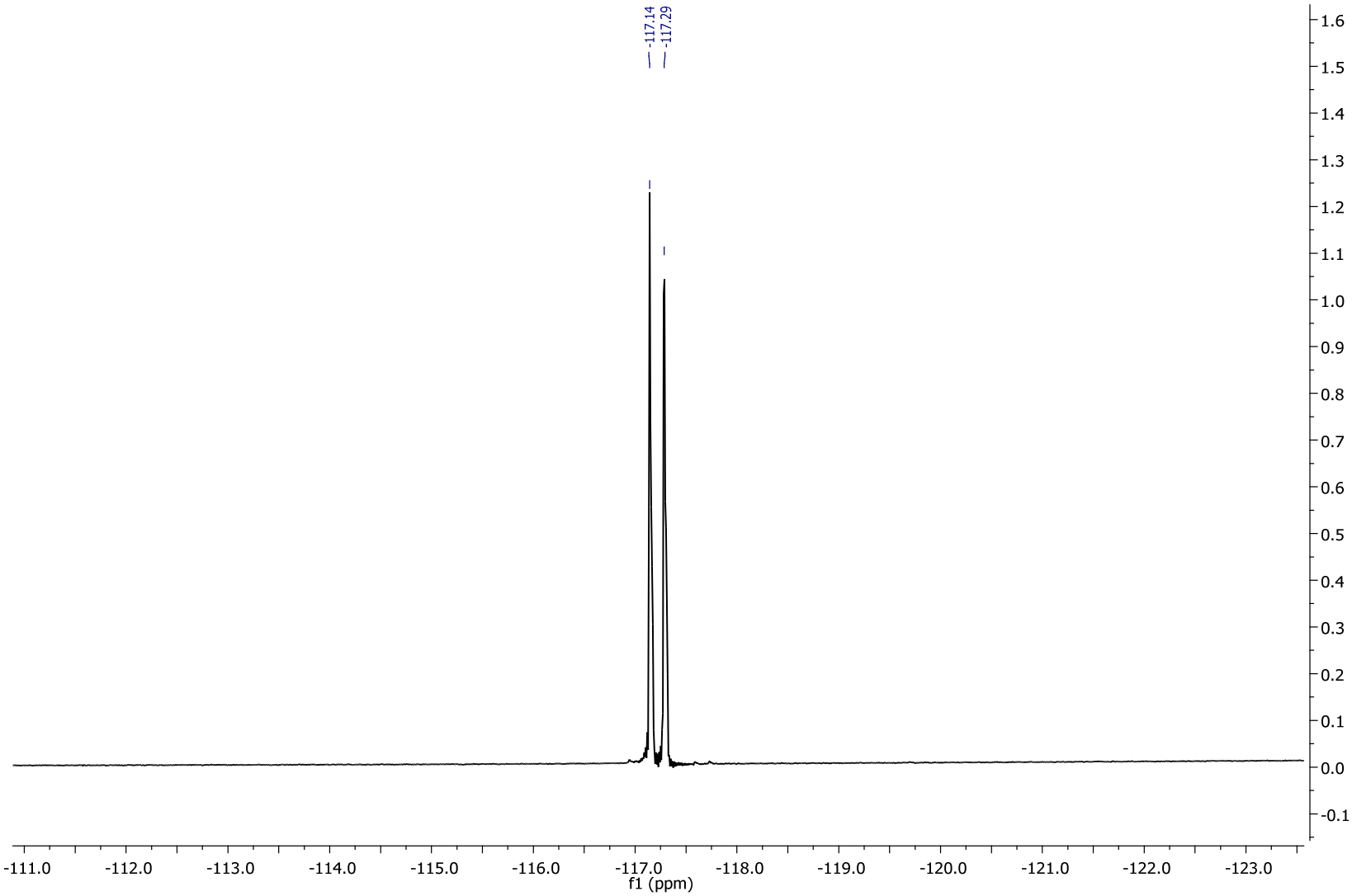
^{1}H NMR


9.22
9.19
8.02
7.56
7.43
7.39
7.30
7.25
4.28
4.26
4.24
4.22
4.20
4.18
4.16
4.14
2.43
2.37
1.38
1.36
1.35
0.91
1.08
2.38
3.98
3.16
3.14
6.00
f1 (ppm)

^{13}C NMR


175.97
161.48
161.47
160.45
159.37
157.42
157.28
157.06
154.16
154.15
154.14
147.79
147.77
144.90
144.81
135.19
135.18
135.16
135.15
126.60
126.57
126.41
119.51
119.51
119.50
118.89
117.32
111.95
109.54
107.14
63.51
63.45
20.91
19.38
16.38
16.31
157.50
157.42
157.28
157.06
158.0
157.0
f1 (ppm)
f1 (ppm)

^{19}F NMR


-117.14
-117.29
1.6
1.5
1.4
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
-0.1
-111.0
-112.0
-113.0
-114.0
-115.0
-116.0
-117.0
-118.0
-119.0
-120.0
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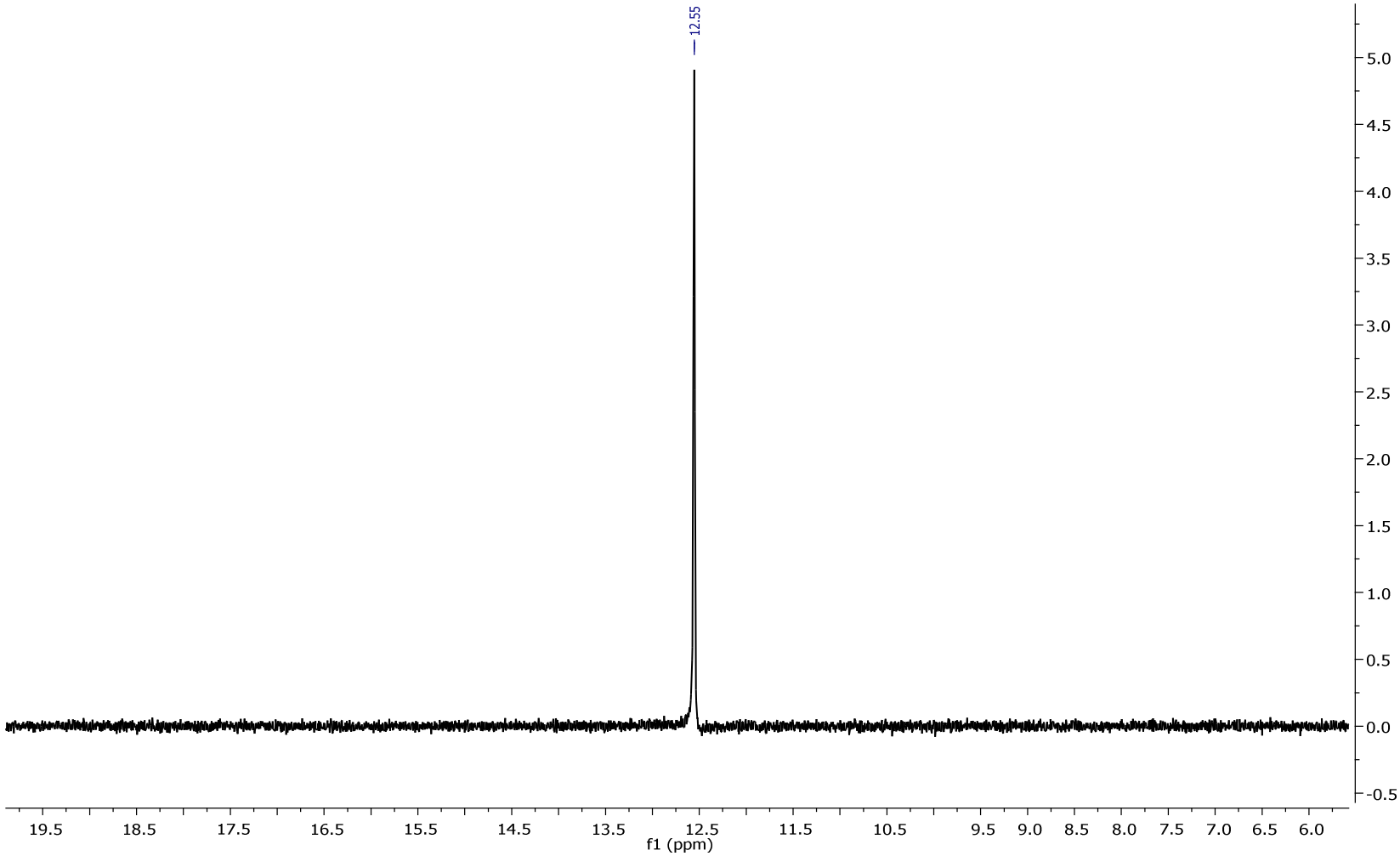
-122.0
-123.0
f1 (ppm)

^{31}P NMR


12.55
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
19.5
18.5
17.5
16.5
15.5
14.5
13.5
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
f1 (ppm)

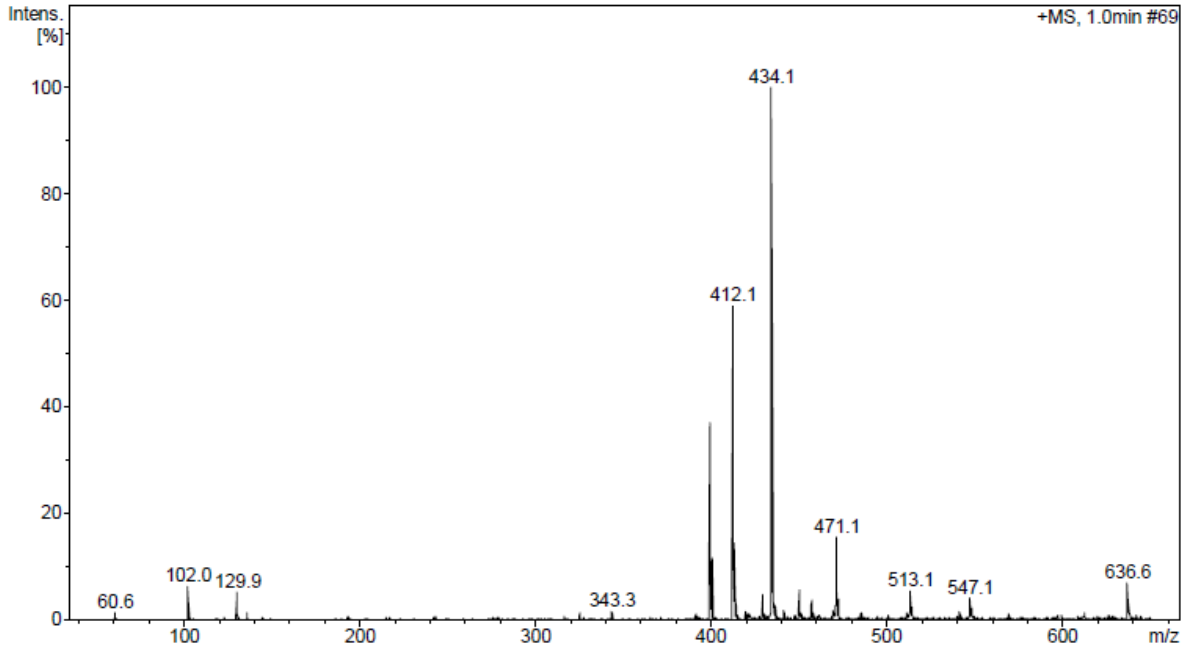
Display Report

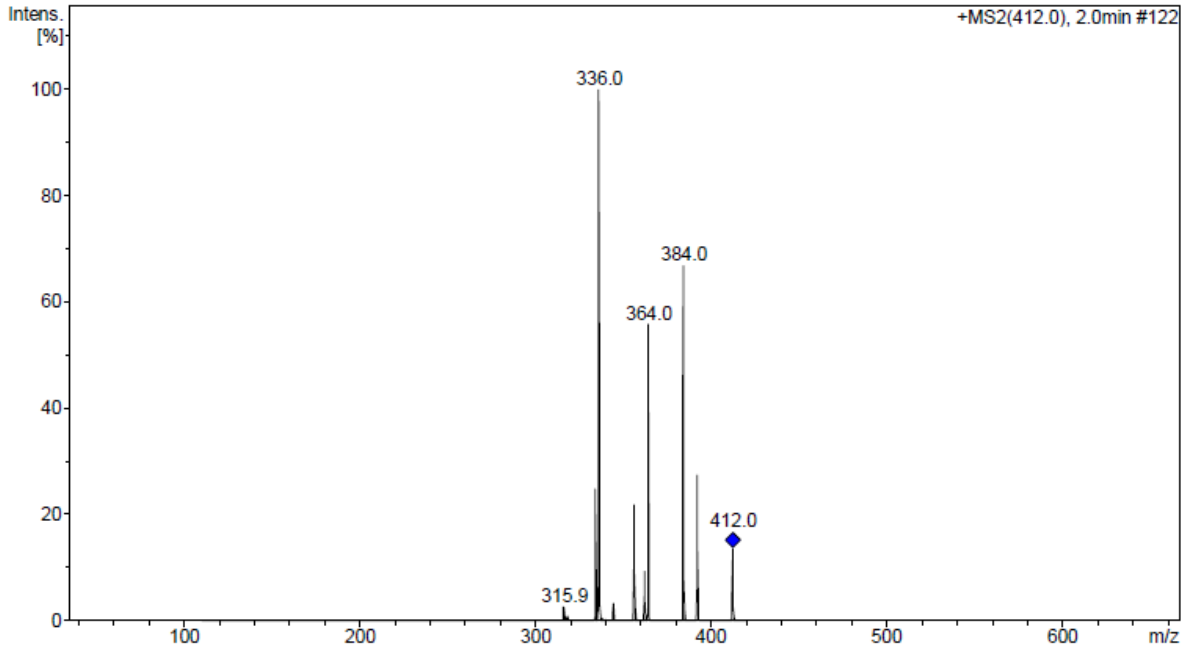
Analysis Info

Analysis Name	G:\Data B\Blazej ION TRAP\BD_97_20092010.d	Acquisition Date	2010-09-20 14:36:07
Method	Aga.DEF.MS.Sugar.m	Operator	farnoosh
Sample Name	Lac20.09.10.	Instrument	HCTultra
Comment	in methanol		

Acquisition Parameter

Ion Source Type	ESI	Ion Polarity	Negative	Alternating Ion Polarity	off
Mass Range Mode	Ultra Scan	Scan Begin	50 m/z	Scan End	650 m/z
Capillary Exit	-109.9 Volt	Skimmer	-40.0 Volt	Trap Drive	57.9
Accumulation Time	2272 Šs	Averages	10 Spectra	Auto MS/MS	off





HRMS

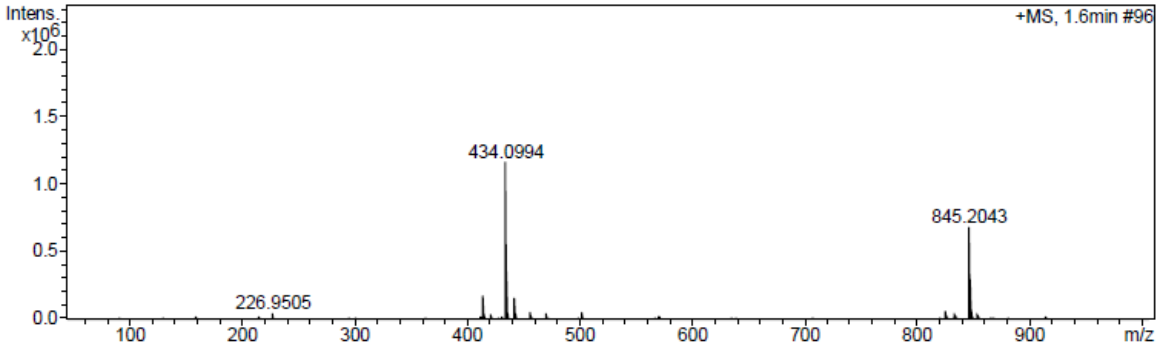
Mass Spectrum SmartFormula Report

Analysis Info

Analysis Name	G:\Data B\Blazej TOF\BD_97_20092010.d	Acquisition Date	2010-09-20 14:37:43
Method	tune_low.m	Operator	Bruker Customer
Sample Name		Instrument / Ser#	micrOTOF 129
Comment	in methanol		

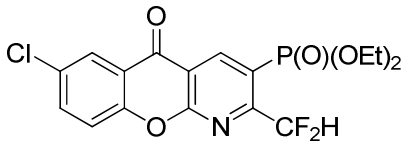
Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	1000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Source



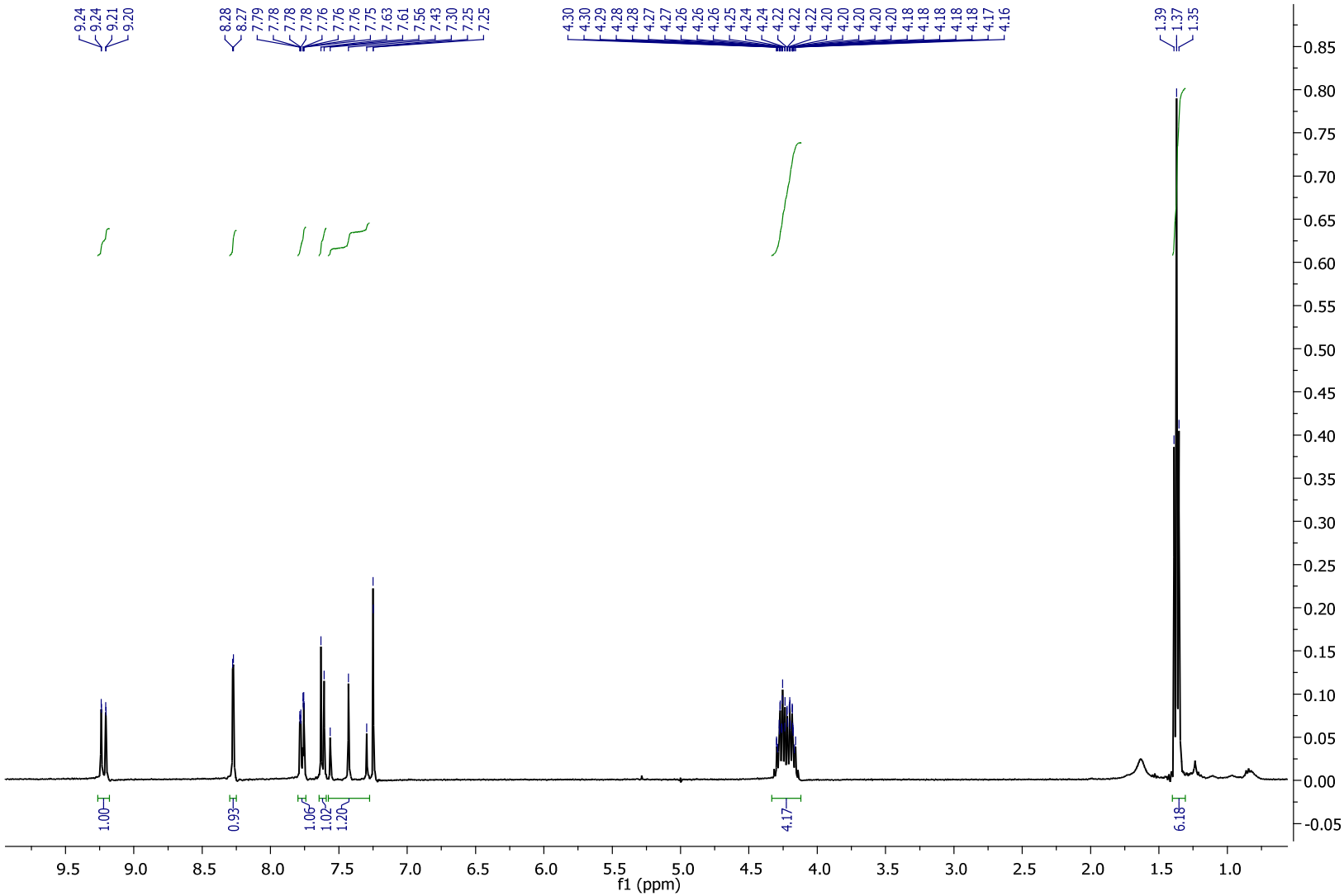
Meas. m/z	Formula	m/z	err [ppm]	Mean err [ppm]	rdb	N-Rule	e— Conf	mSigma
412.1119								
	C 19 H 21 F 2 N O 5 P	412.1120	0.3	-3.0	9.5	ok	even	44.53

9. *Diethyl (7-chloro-2-(difluoromethyl)-5-oxo-5,10a-dihydro-4aH-chromeno[2,3-b]pyridin-3-yl)phosphonate (**3i**)*



Yellowish crystals (51%); mp 126–129 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.37 (t, J = 7.1 Hz, 6H), 4.22 (m, 4H), 7.43 (t, $^{2}J_{H–F}$ = 54.0 Hz, 1H), 7.62 (d, J = 8.9 Hz, 1H), 7.76 (dd, J = 8.9 Hz, J = 2.6 Hz, 1H), 8.27 (d, J = 2.6 Hz, 1H), 9.22 (d, $^{3}J_{H–P}$ = 13.3 Hz, 1H); ^{13}C NMR (100 MHz): δ 16.3 (d, J = 6.3 Hz), 63.6 (d, J = 5.8 Hz), 109.4 (td, $^{1}J_{C–F}$ = 243.8 Hz, $^{3}J_{C–P}$ = 1.5 Hz), 116.7 (d, $^{2}J_{C–P}$ = 11.1 Hz), 120.5, 121.8 (dt, $^{1}J_{C–P}$ = 189.6 Hz, $^{3}J_{C–F}$ = 3.8 Hz), 122.6, 126.3, 131.7, 136.6, 145.1 (d, $^{3}J_{C–P}$ = 8.8 Hz), 154.0, 157.9 (td, $^{2}J_{C–F}$ = 22.3 Hz, $^{2}J_{C–P}$ = 14.1 Hz), 175.2; ^{19}F NMR (376 MHz) δ –117.3 (d, $^{2}J_{F–H}$ = 53.9 Hz); ^{31}P NMR (161 MHz) δ 11.9 (t, $^{4}J_{P–F}$ = 1.4 Hz); MS (ESI) *m/z*: $[M+H]^+$ 418 (20%), $[M+Na]^+$ 440 (100%); HRMS (ESI) calcd for $[M+Na]^+$ ($C_{17}H_{15}ClF_2NNaO_5P$) 440.0237; found 440.0244.

^{1}H NMR


9.24
9.24
9.21
9.20
8.28
8.27
7.79
7.78
7.78
7.78
7.76
7.76
7.76
7.75
7.63
7.61
7.56
7.43
7.30
7.25
7.25
4.30
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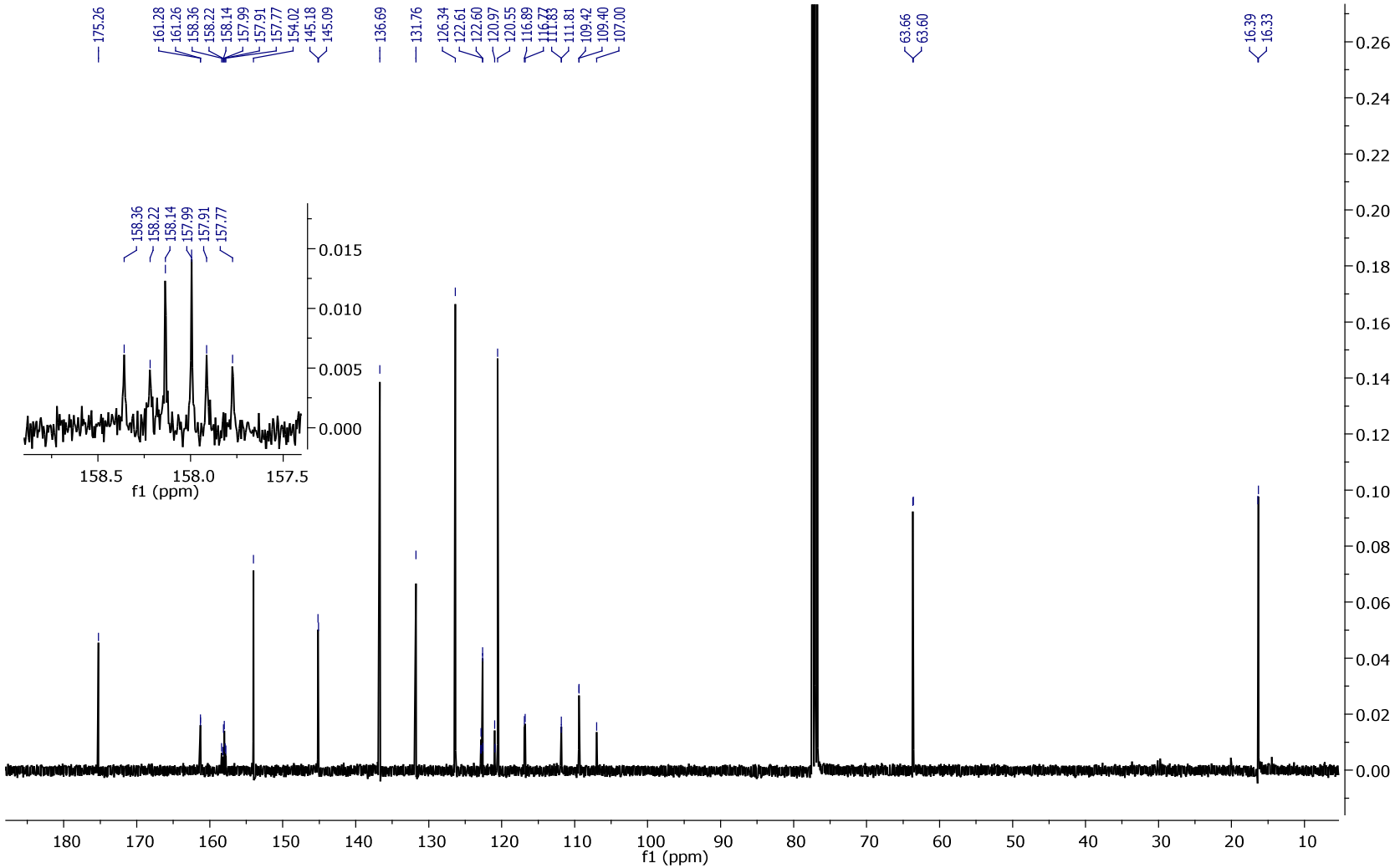
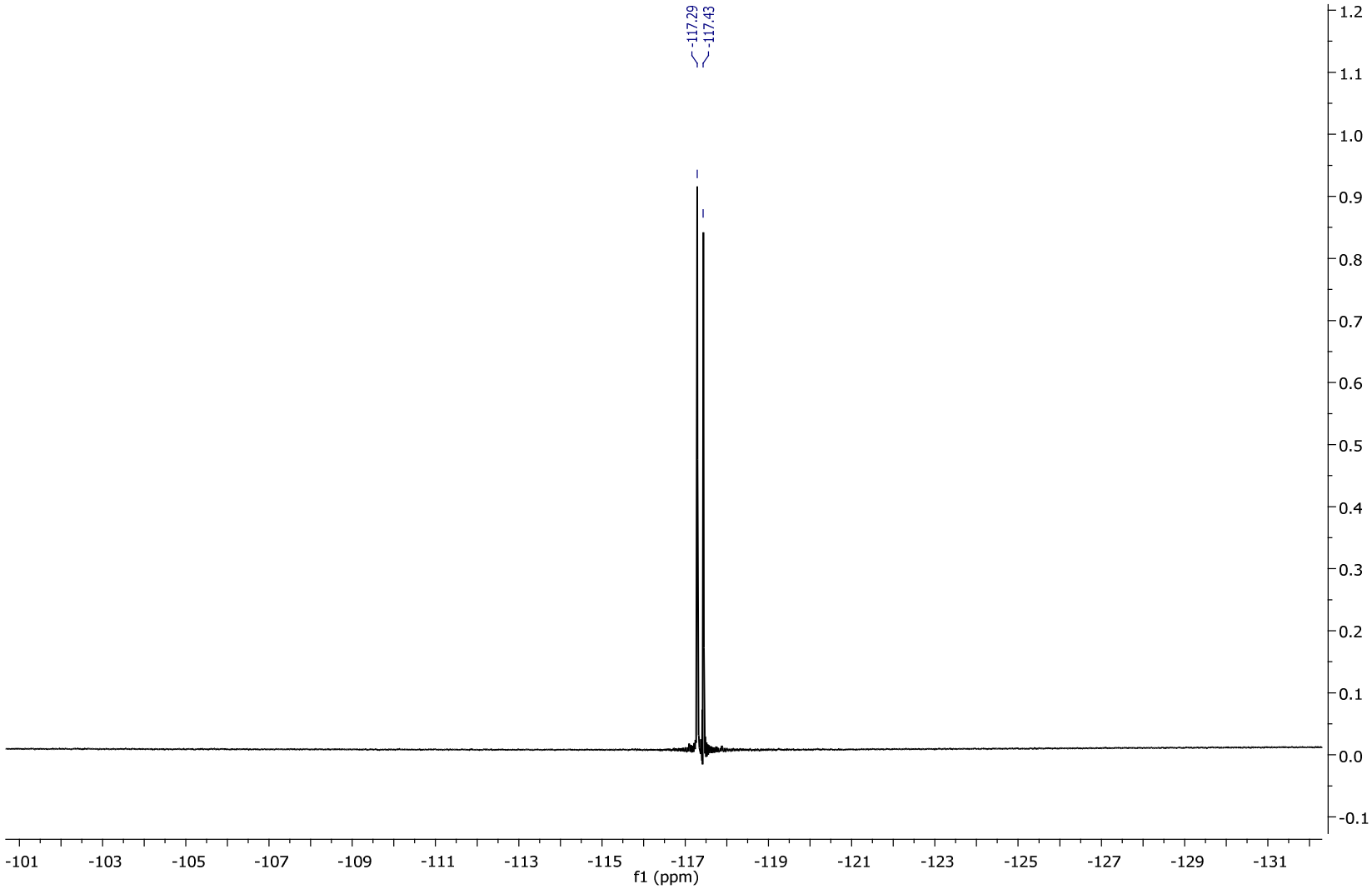
4.29
4.28
4.28
4.27
4.27
4.26
4.26
4.26
4.25
4.24
4.24
4.22
4.22
4.22
4.20
4.20
4.20
4.20
4.20
4.18
4.18
4.18
4.18
4.17
4.16
1.39
1.37
1.35
1.00
0.93
1.06
1.02
1.20
4.17
6.18
f1 (ppm)

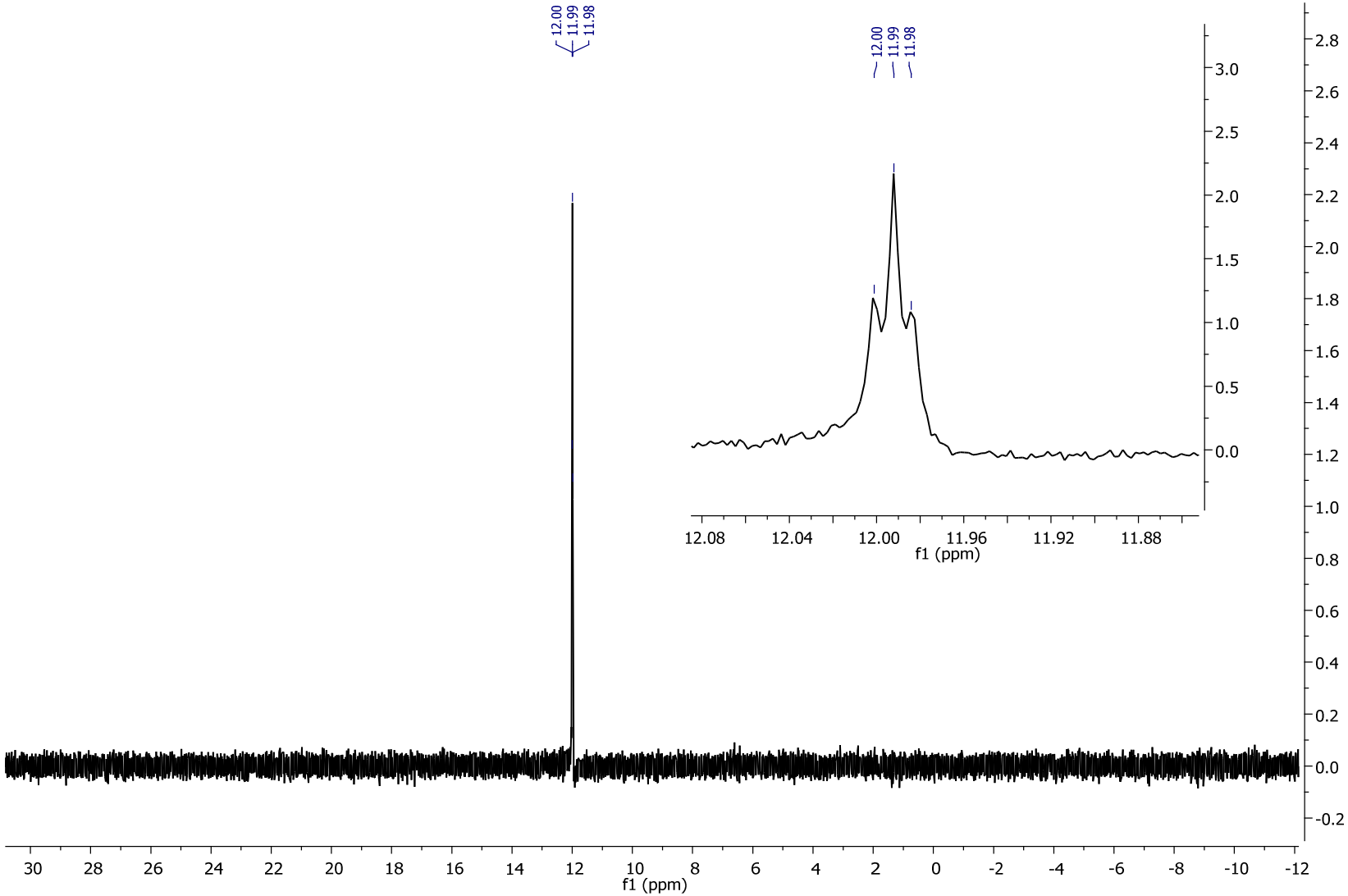
^{13}C NMR


175.26
161.28
161.26
158.36
158.22
158.14
157.99
157.91
157.77
154.02
145.18
145.09
136.69
131.76
126.34
122.61
122.60
120.97
120.55
116.89
116.77
111.83
111.81
109.42
109.40
107.00
63.66
63.60
16.39
16.33
158.36
158.22
158.14
157.99
157.91
157.77
0.015
0.010
0.005
0.000
158.5
158.0
157.5
f1 (ppm)
0.26
0.24
0.22
0.20
0.18
0.16
0.14
0.12
0.10
0.08
0.06
0.04
0.02
0.00
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

^{19}F NMR


-117.29
-117.43
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
-0.1
-101
-103
-105
-107
-109
-111
-113
-115
-117
-119
-121
-123
-125
-127
-129
-131
f1 (ppm)

^{31}P NMR



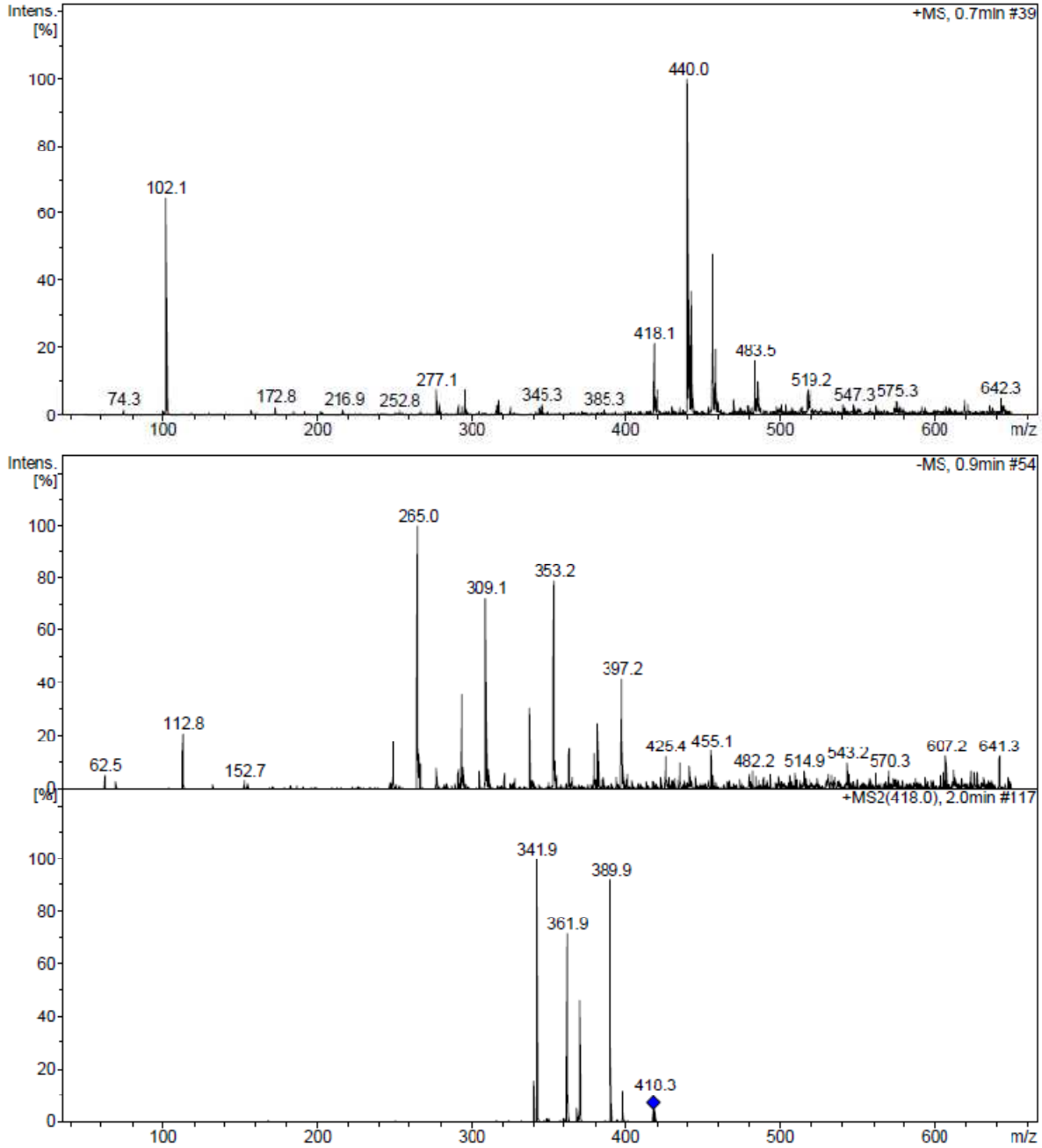
Display Report

Analysis Info

Analysis Name	G:\Data B\Blazej ION TRAP\BD98_1409201.d	Acquisition Date	2010-09-14 16:24:25
Method	DEF_MS.M	Operator	farnoosh
Sample Name	0	Instrument	HCTultra
Comment	in methanol		

Acquisition Parameter

Ion Source Type	ESI	Ion Polarity	Positive	Alternating Ion Polarity	off
Mass Range Mode	Ultra Scan	Scan Begin	50 m/z	Scan End	650 m/z
Capillary Exit	109.9 Volt	Skimmer	40.0 Volt	Trap Drive	52.7
Accumulation Time	3131 ßs	Averages	10 Spectra	Auto MS/MS	off



HRMS

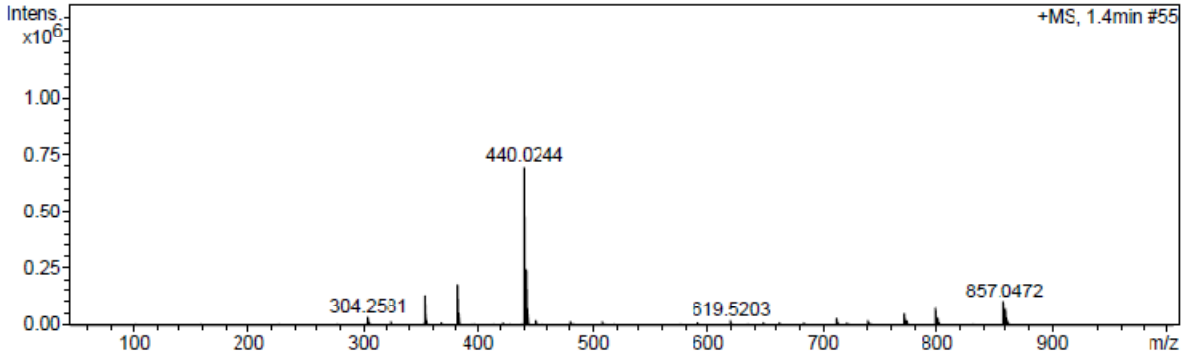
Mass Spectrum SmartFormula Report

Analysis Info

Analysis Name	G:\Data B\Blazej TOF\BD-98-14092010-3.d	Acquisition Date	2010-09-14 16:59:06
Method	tune_low.m	Operator	Bruker Customer
Sample Name		Instrument / Ser#	micrOTOF 129
Comment	in Methanol		

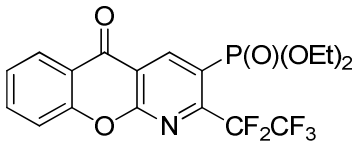
Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	1000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Source



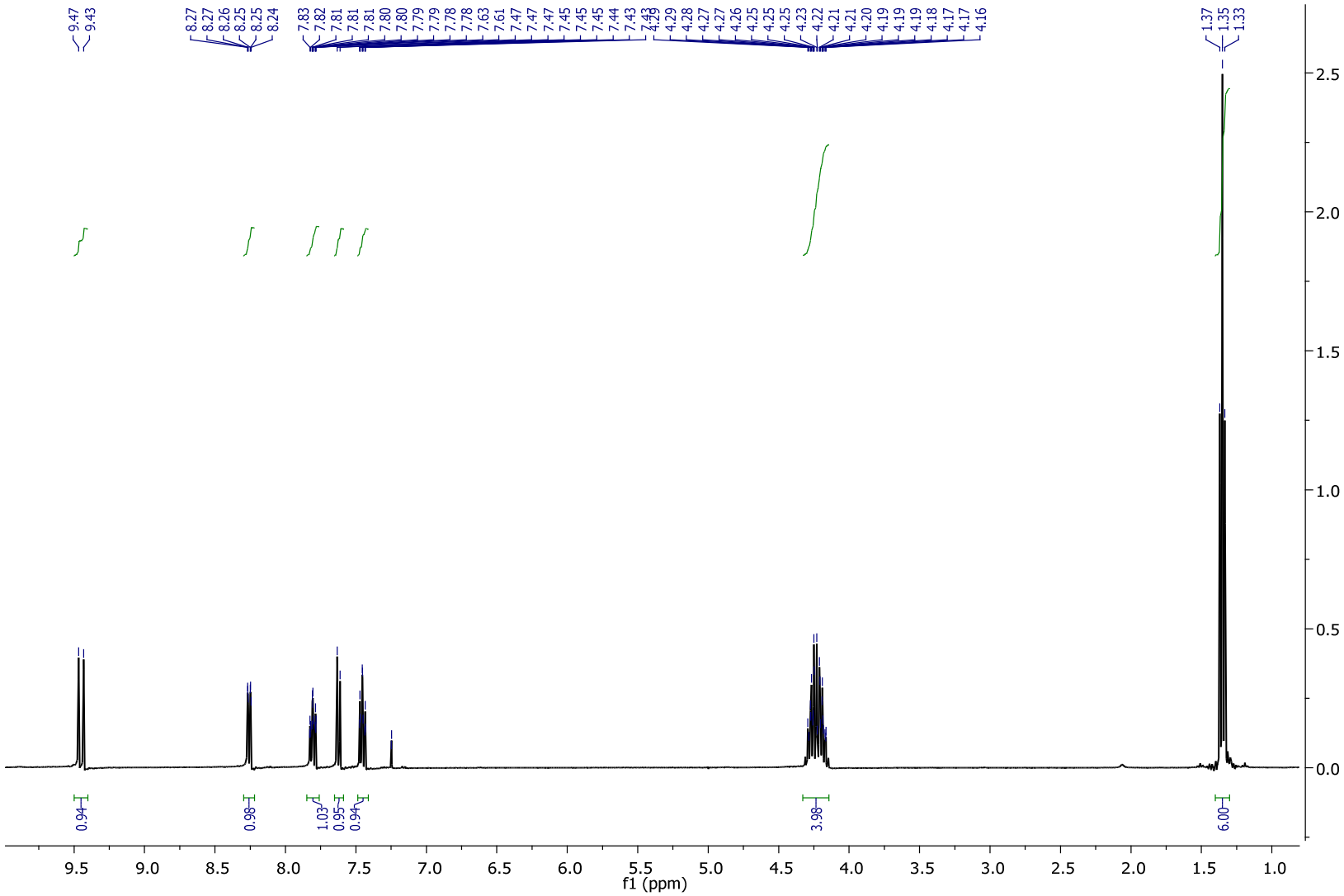
Meas. m/z	#	Formula	m/z	err [ppm]	Mean err [ppm]	rdb	N-Rule	e—Conf	mSigma	Std I	Std Mean m/z	Std I VarNorm	Std m/z Diff	Std Comb Dev
440.0244	1	C 17 H 15 Cl F 2 N Na O 5 P	440.0237	-1.6	1.1	9.5	ok	even	18.93	0.0303	0.0016	0.0096	0.0025	0.8427

10. *Diethyl (5-oxo-2-(perfluoroethyl)-5,10a-dihydro-4aH-chromeno-[2,3-b]pyridin-3-yl)phosphonate (**3j**)*

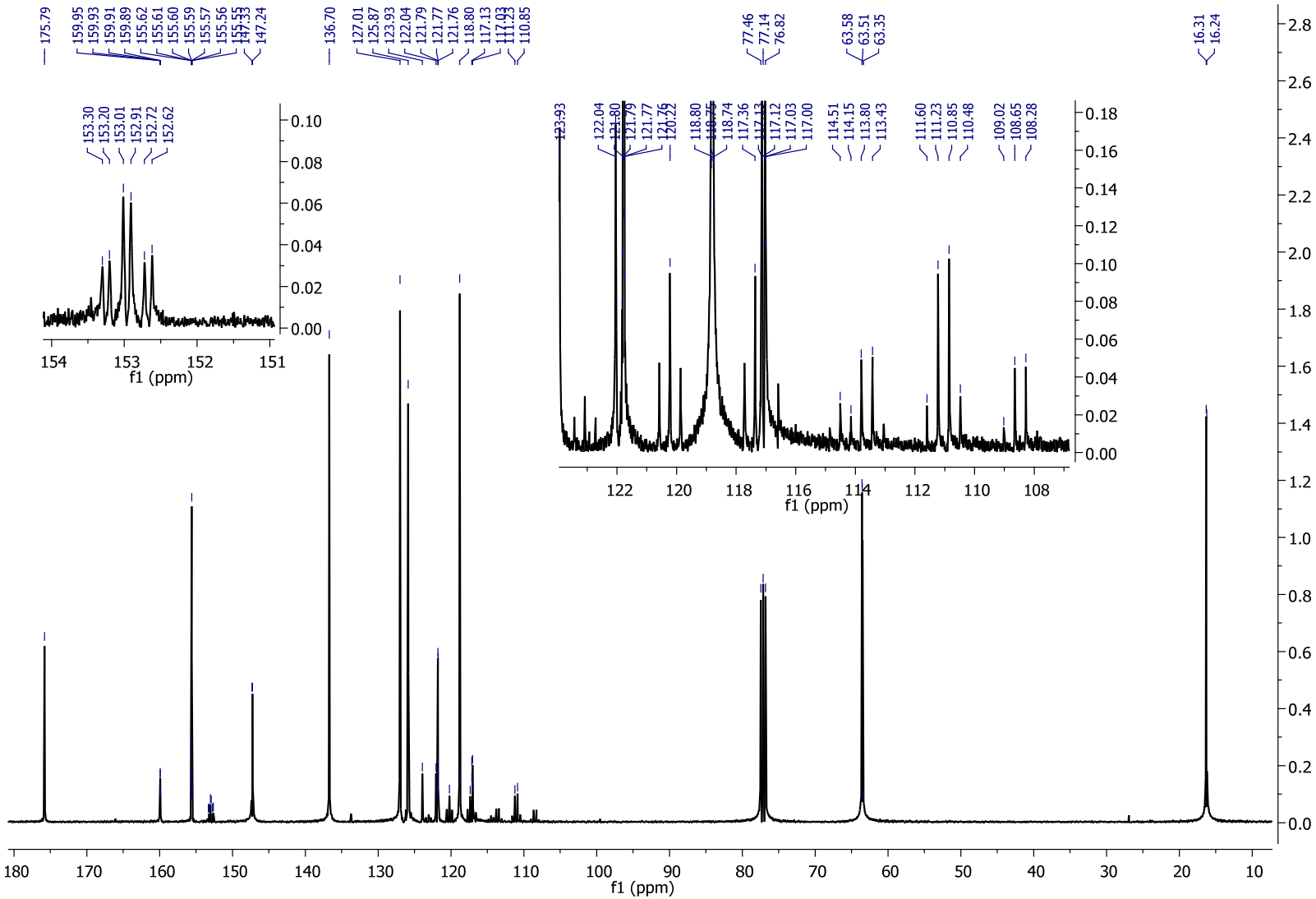


Yellowish crystals (77%); mp 100–104 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.35 (t, *J* = 7.1 Hz, 6H), 4.22 (m, 4H), 7.45 (td, *J* = 7.1 Hz, *J* = 1.1 Hz, 1H), 7.61 (d, *J* = 8.5 Hz, 1H), 7.81 (td, *J* = 7.4 Hz, *J* = 1.7 Hz, 1H), 8.26 (dd, *J* = 7.7 Hz, *J* = 1.4 Hz, 1H), 9.45 (d, $^{3}J_{H–P}$ = 14.1 Hz, 1H); ^{13}C NMR (100 MHz): δ 16.2 (d, *J* = 7.2 Hz), 63.5 (d, *J* = 6.3 Hz), 111.1 (tq, $^{1}J_{C–F}$ = 264.6 Hz, $^{2}J_{C–F}$ = 37.5 Hz), 117.1 (d, $^{2}J_{C–P}$ = 13.1 Hz), 118.1, 118.8 (qt, $^{1}J_{C–F}$ = 287.1 Hz, $^{2}J_{C–F}$ = 37.5 Hz), 121.7, 123.1 (d, $^{1}J_{C–P}$ = 189.5 Hz), 125.8, 127.0, 136.7, 147.2 (d, $^{3}J_{C–P}$ = 8.5 Hz), 153.0 (td, $^{2}J_{C–F}$ = 25.6 Hz, $^{2}J_{C–P}$ = 9.3 Hz), 155.6, 175.8; ^{19}F NMR (376 MHz): δ –80.2 (s, 3F), –109.6 (s, 2F); ^{31}P NMR (161 MHz): δ 11.2 (t, $^{4}J_{P–F}$ = 1.7 Hz); MS (ESI) *m/z*: $[M+H]^+$ 452 (50%), $[M+Na]^+$ 474 (100%); HRMS (ESI) calcd for $[M+Na]^+$ $(C_{18}H_{15}F_5NNaO_5P)^+$ 474.0500; found 474.0480.

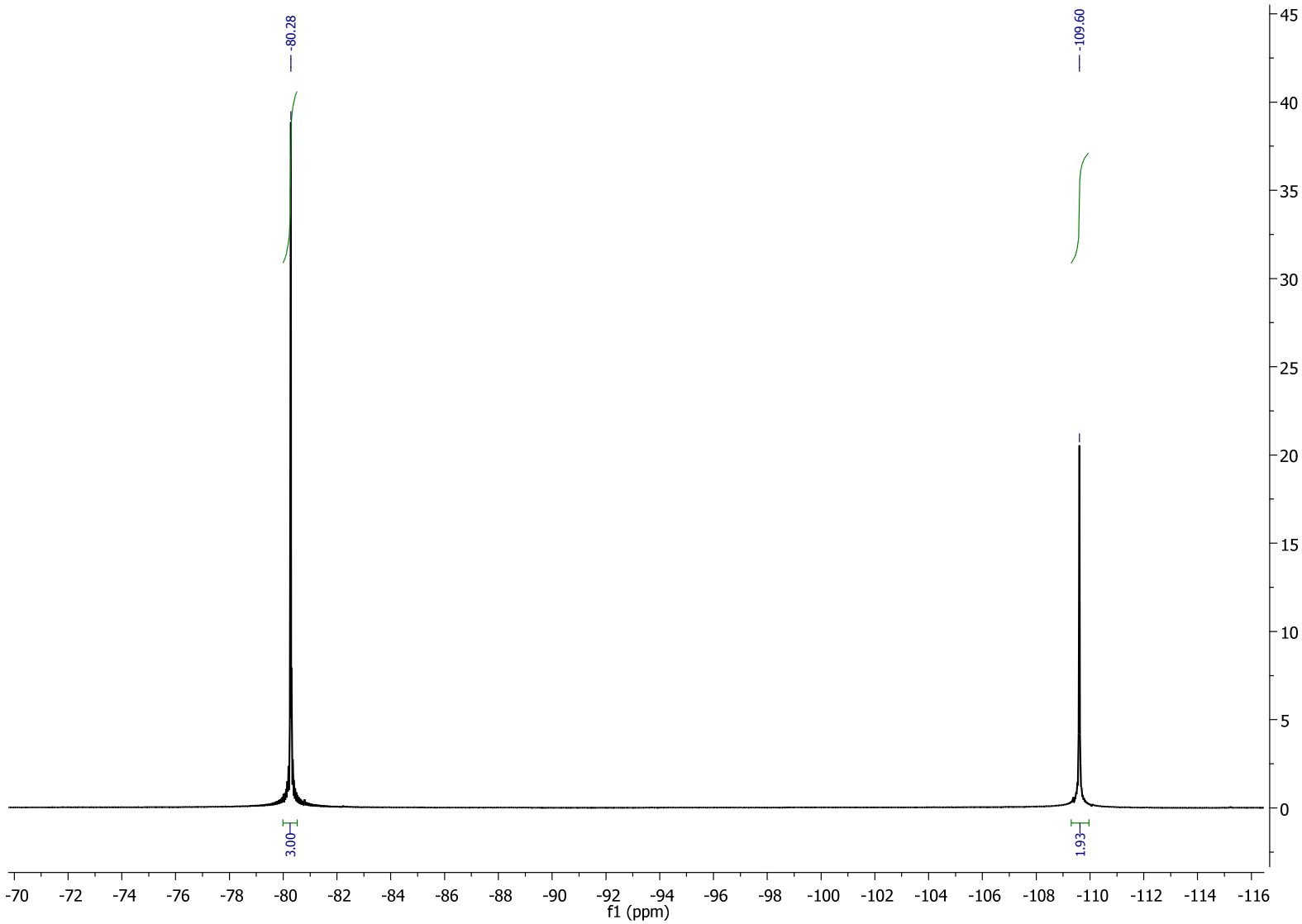
^{1}H NMR


9.47
9.43
8.27
8.27
8.26
8.25
8.25
8.24
7.83
7.82
7.81
7.81
7.81
7.80
7.80
7.79
7.79
7.78
7.78
7.63
7.61
7.47
7.47
7.47
7.45
7.45
7.45
7.44
7.43
7.43
4.29
4.29
4.28
4.27
4.27
4.26
4.25
4.25
4.25
4.23
4.22
4.21
4.21
4.20
4.19
4.19
4.19
4.18
4.17
4.17
4.16
1.37
1.35
1.33
0.94
0.98
1.03
0.95
0.94
3.98
6.00
2.5
2.0
1.5
1.0
0.5
0.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)

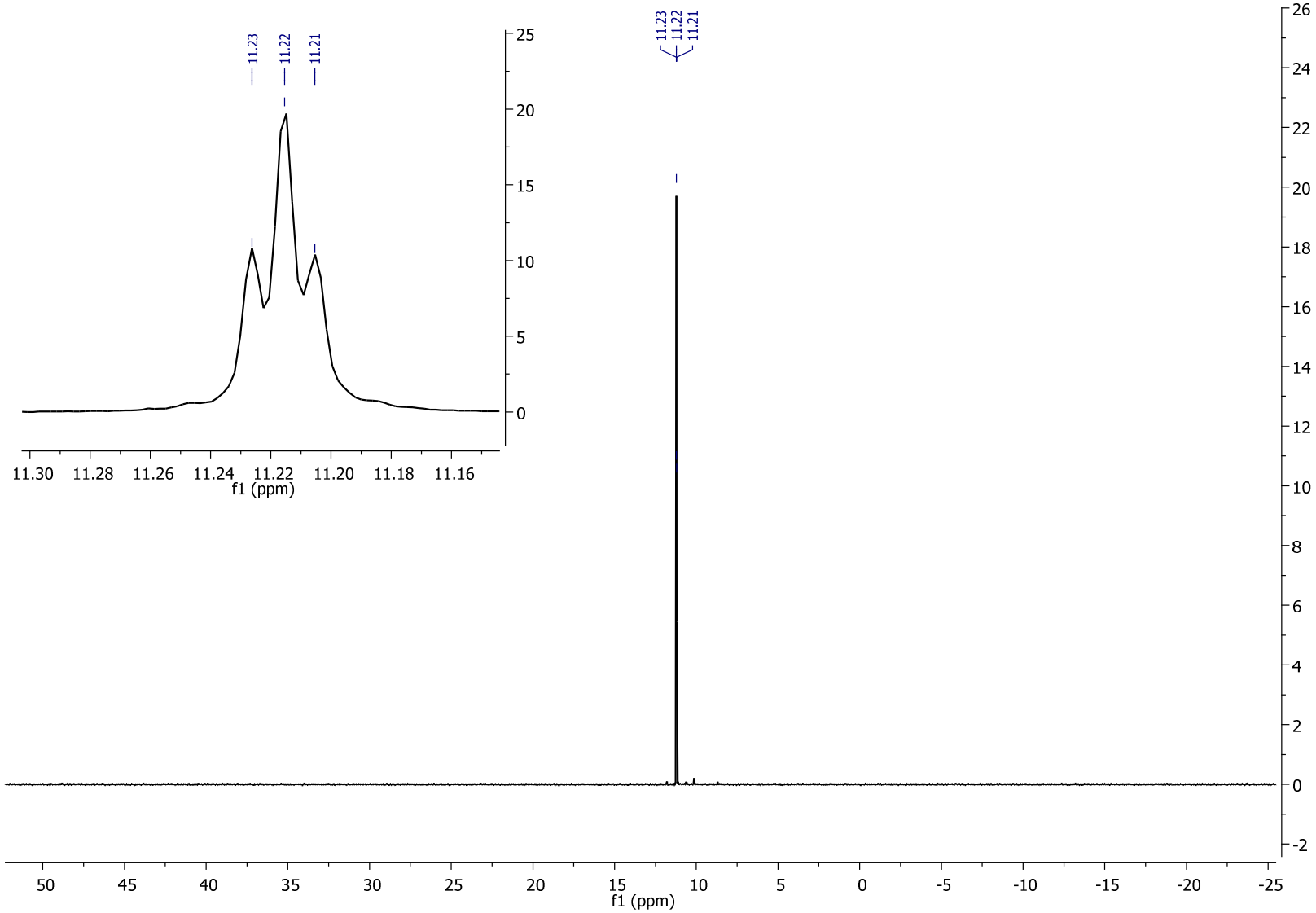
^{13}C NMR


175.79
159.95
159.93
159.91
159.89
155.62
155.61
155.60
155.59
155.57
155.56
147.24
136.70
127.01
125.87
123.93
122.04
121.79
121.77
121.76
118.80
117.13
110.85
77.46
77.14
76.82
63.58
63.51
63.35
16.31
16.24
153.30
153.20
153.01
152.91
152.72
152.62
f1 (ppm)
123.93
122.04
121.80
121.79
121.77
120.22
118.80
118.74
117.36
117.12
117.03
117.00
114.51
114.15
113.80
113.43
111.60
111.23
110.85
110.48
109.02
108.65
108.28
f1 (ppm)
f1 (ppm)

^{19}F NMR



^{31}P NMR


11.23
11.22
11.21
11.30 11.28 11.26 11.24 11.22 11.20 11.18 11.16
f1 (ppm)
50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25
f1 (ppm)

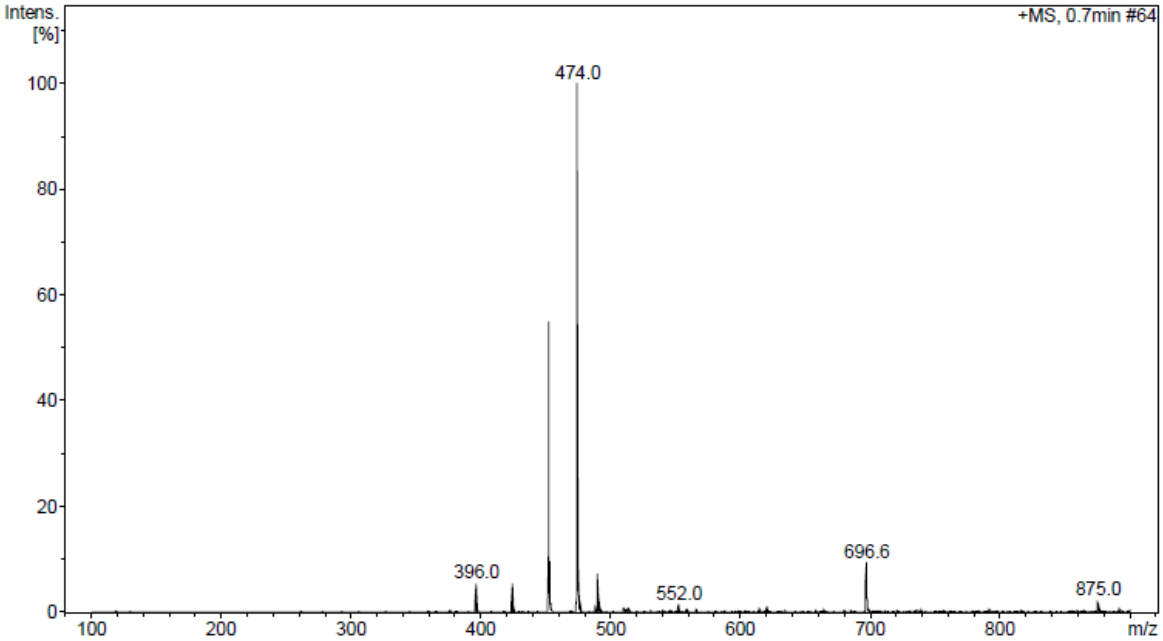
Display Report

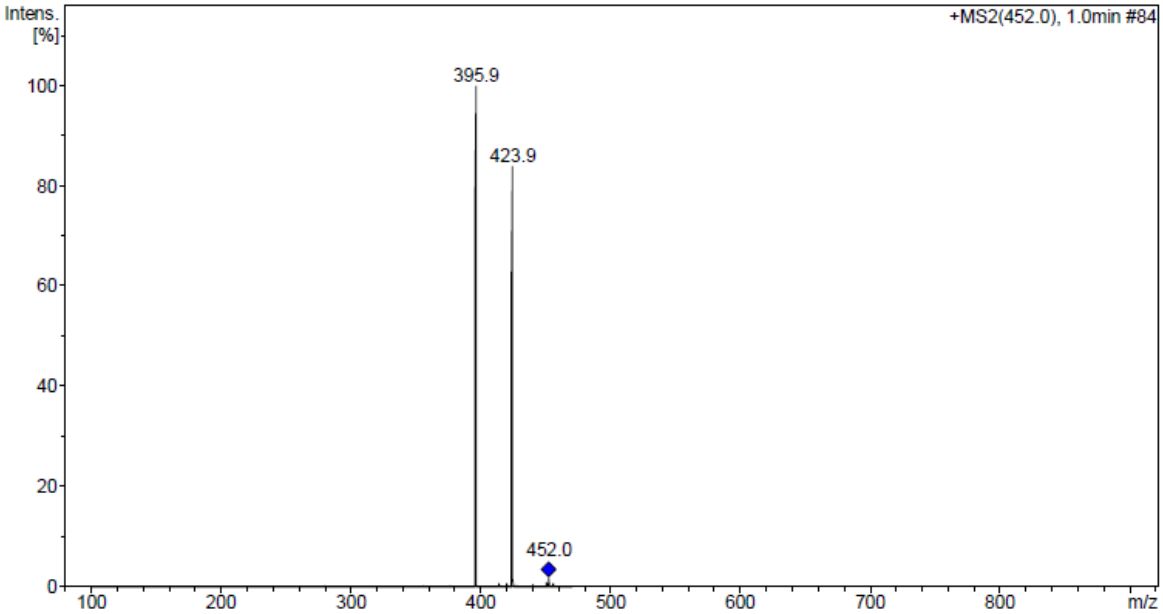
Analysis Info

Analysis Name	G:\Data B\Blazej ION TRAP\BD134_01112010.d	Acquisition Date	2010-11-01 11:07:33
Method	DEF_MS.M	Operator	famoosh
Sample Name	0	Instrument	HCTultra
Comment	in methanol		

Acquisition Parameter

Ion Source Type	ESI	Ion Polarity	Positive	Alternating Ion Polarity	off
Mass Range Mode	Ultra Scan	Scan Begin	100 m/z	Scan End	900 m/z
Capillary Exit	220.0 Volt	Skimmer	40.0 Volt	Trap Drive	78.0
Accumulation Time	300 Ss	Averages	10 Spectra	Auto MS/MS	off





HRMS

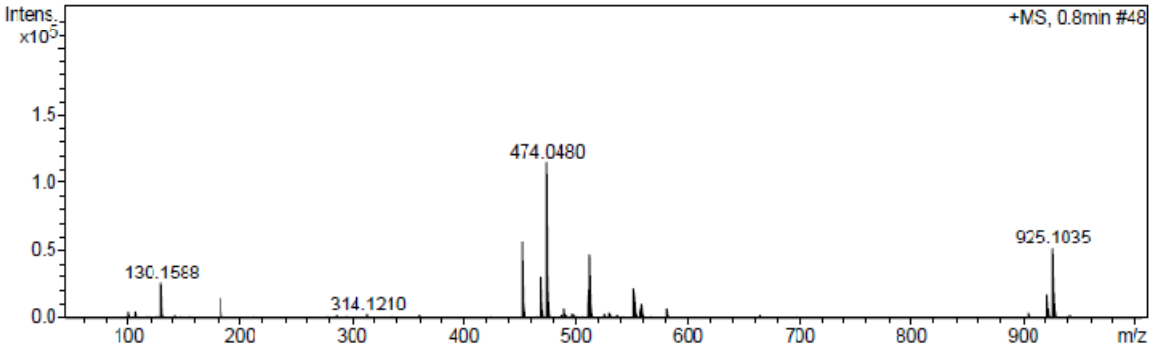
Mass Spectrum SmartFormula Report

Analysis Info

Analysis Name	G:\Data B\Blazej TOF\BD134_01112010.d	Acquisition Date	2010-11-01 11:02:25
Method	tune_low.m	Operator	Bruker Customer
Sample Name		Instrument / Ser#	micrOTOF 129
Comment	in methanol		

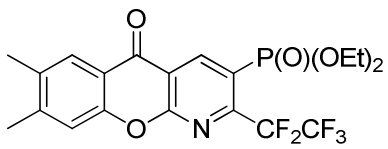
Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	1000 m/z	Set End Plate Offset	500 V	Set Divert Valve	Source



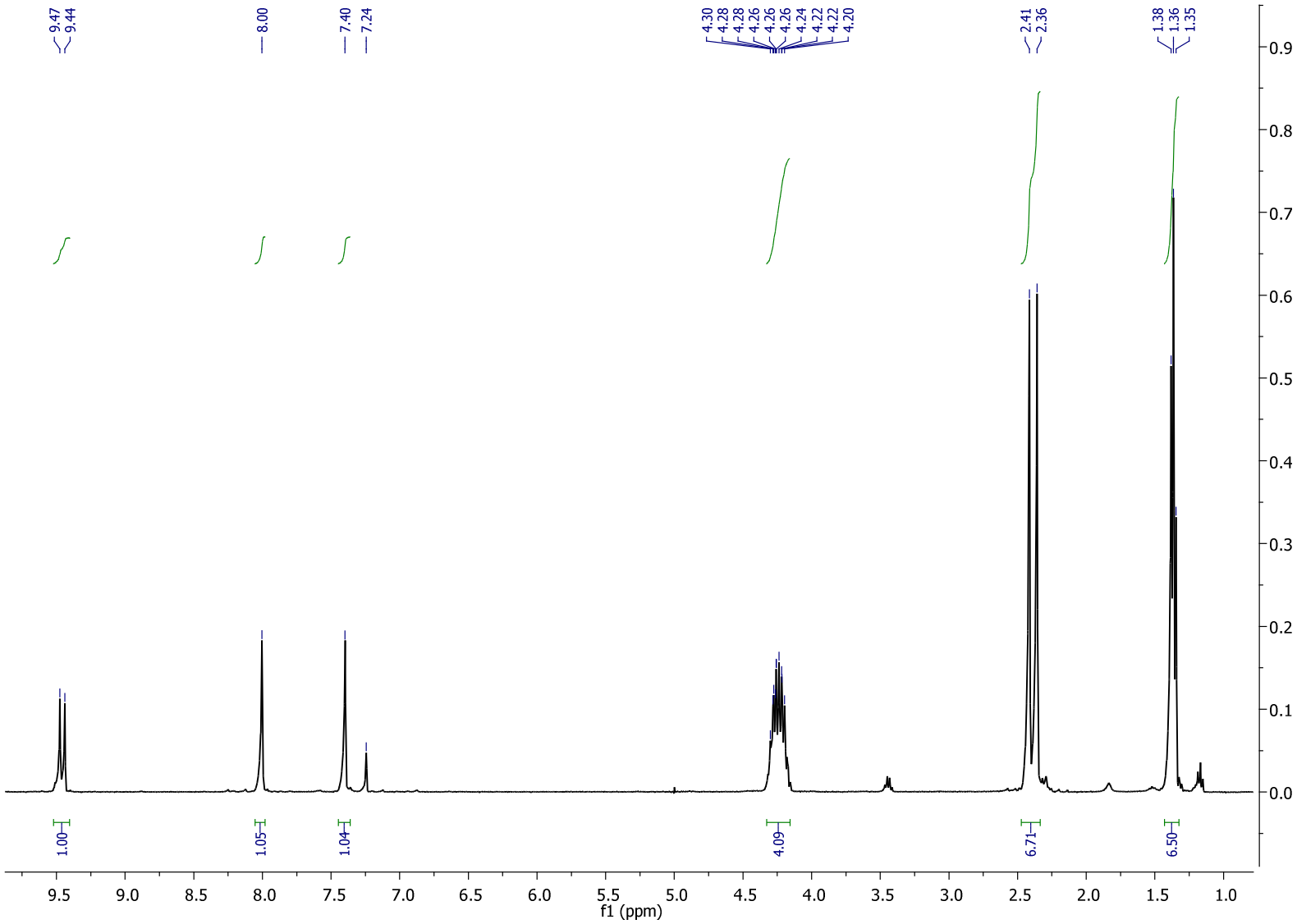
Meas. m/z	Formula	m/z	err [ppm]	Mean err [ppm]	rdb	N-Rule	e— Conf	mSigma
474.0480								
	C 18 H 15 F 5 N Na O 5 P	474.0500	4.2	4.2	9.5	ok	even	6.27

11. *Diethyl (7,8-dimethyl-5-oxo-2-(perfluoroethyl)-5H-chromeno-[2,3-b]pyridin-3-yl)phosphonate (**3k**)*

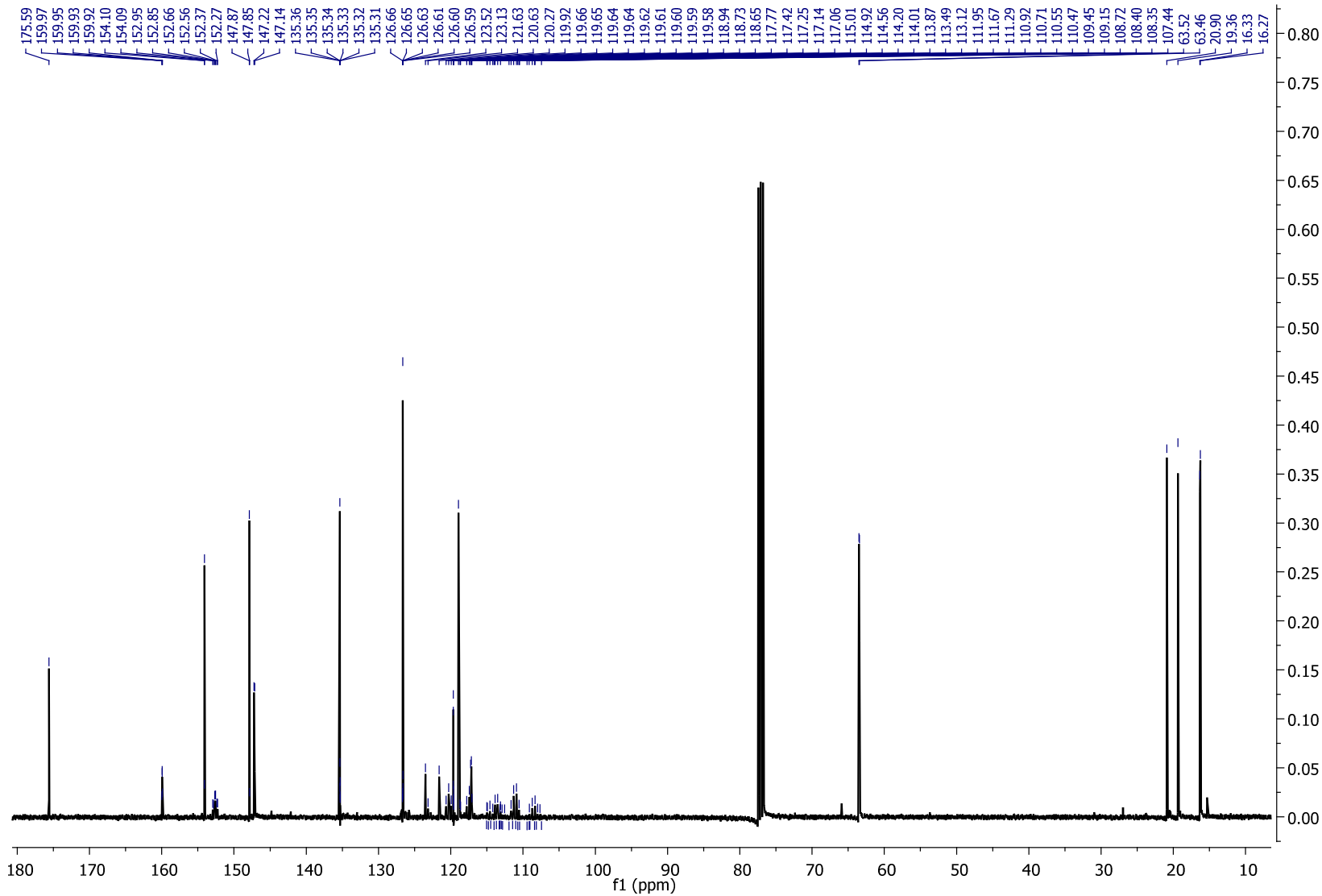


Yellowish crystals (76%); mp 115–118 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.36 (t, J = 7.1 Hz, 6H), 2.36 (s, 3H), 2.41 (s, 3H), 4.25 (m, 4H), 7.40 (s, 1H), 8.00 (s, 1H), 9.45 (d, $^{3}J_{H–P}$ = 14.0 Hz); ^{13}C NMR (100 MHz): δ 16.3 (d, J = 6.9 Hz), 19.4, 20.9, 63.5 (d, J = 5.8 Hz), 111.1 (tq, $^{1}J_{C–F}$ = 261.6 Hz, $^{2}J_{C–F}$ = 36.2 Hz), 117.2 (d, $^{2}J_{C–P}$ = 12.7 Hz), 118.7 (qt, $^{1}J_{C–F}$ = 287.2 Hz, $^{2}J_{C–F}$ = 37.1 Hz), 118.9, 122.3 (d, $^{1}J_{C–P}$ = 190.4 Hz), 126.6, 135.4, 147.2 (d, $^{3}J_{C–P}$ = 7.9 Hz), 152.6 (td, $^{2}J_{C–F}$ = 29.4 Hz, $^{2}J_{C–P}$ = 9.4 Hz), 154.1, 159.9, 176.6; ^{19}F NMR (376 MHz): δ –80.2 (s, 3F), –109.5 (s, 2F); ^{31}P NMR (161 MHz): 11.4 (t, $^{4}J_{P–F}$ = 1.2 Hz); MS (ESI) *m/z*: $[M+H]^+$ 480; HRMS (ESI) calcd for $[M+Na]^+$ $(C_{20}H_{19}F_5NNaO_5P)^+$ 502.0813; found 502.0823.

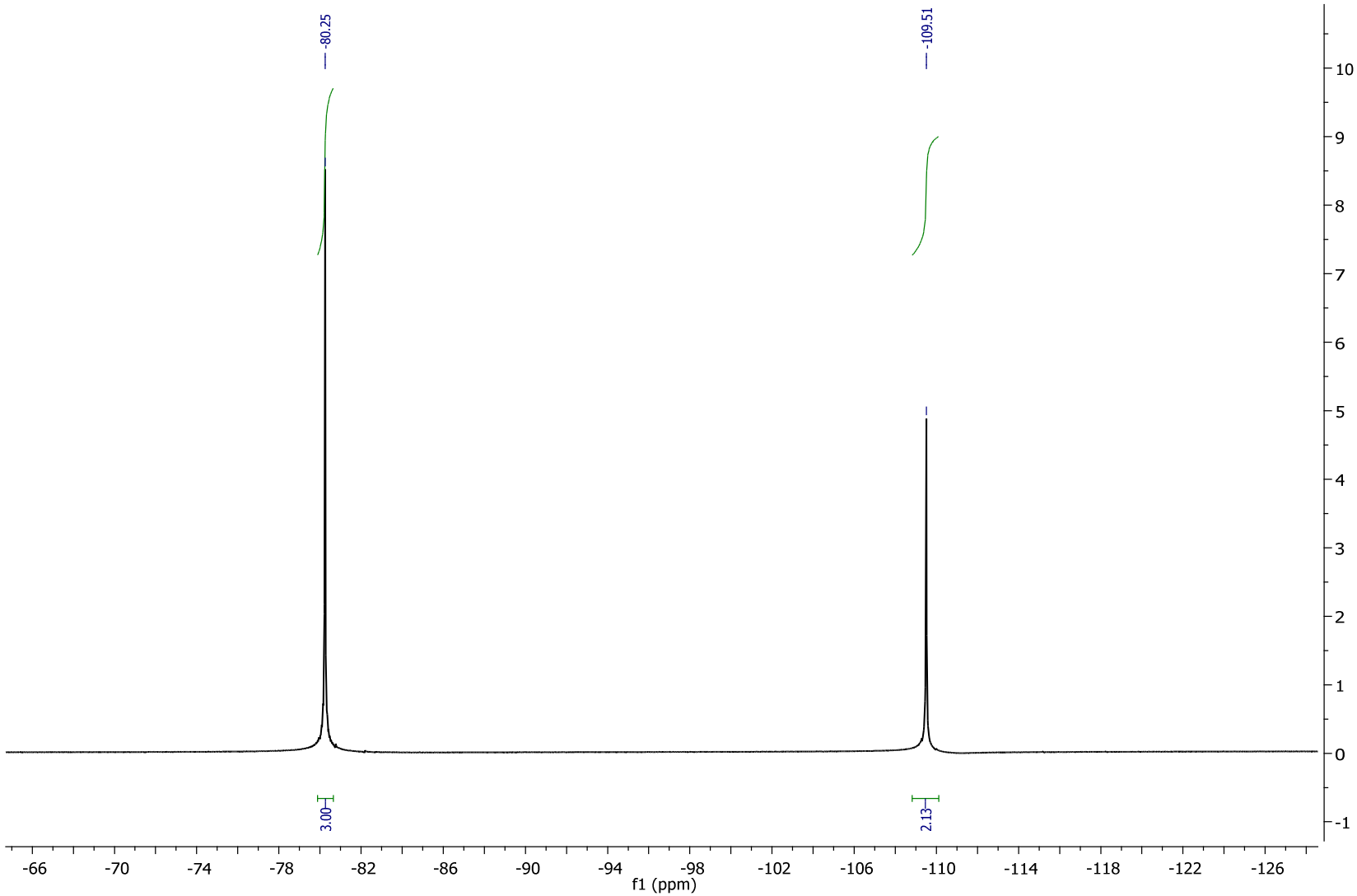
^{1}H NMR


9.47
9.44
8.00
7.40
7.24
4.30
4.28
4.28
4.26
4.26
4.26
4.24
4.22
4.22
4.20
2.41
2.36
1.38
1.36
1.35
1.00
1.05
1.04
4.09
6.71
6.50
f1 (ppm)

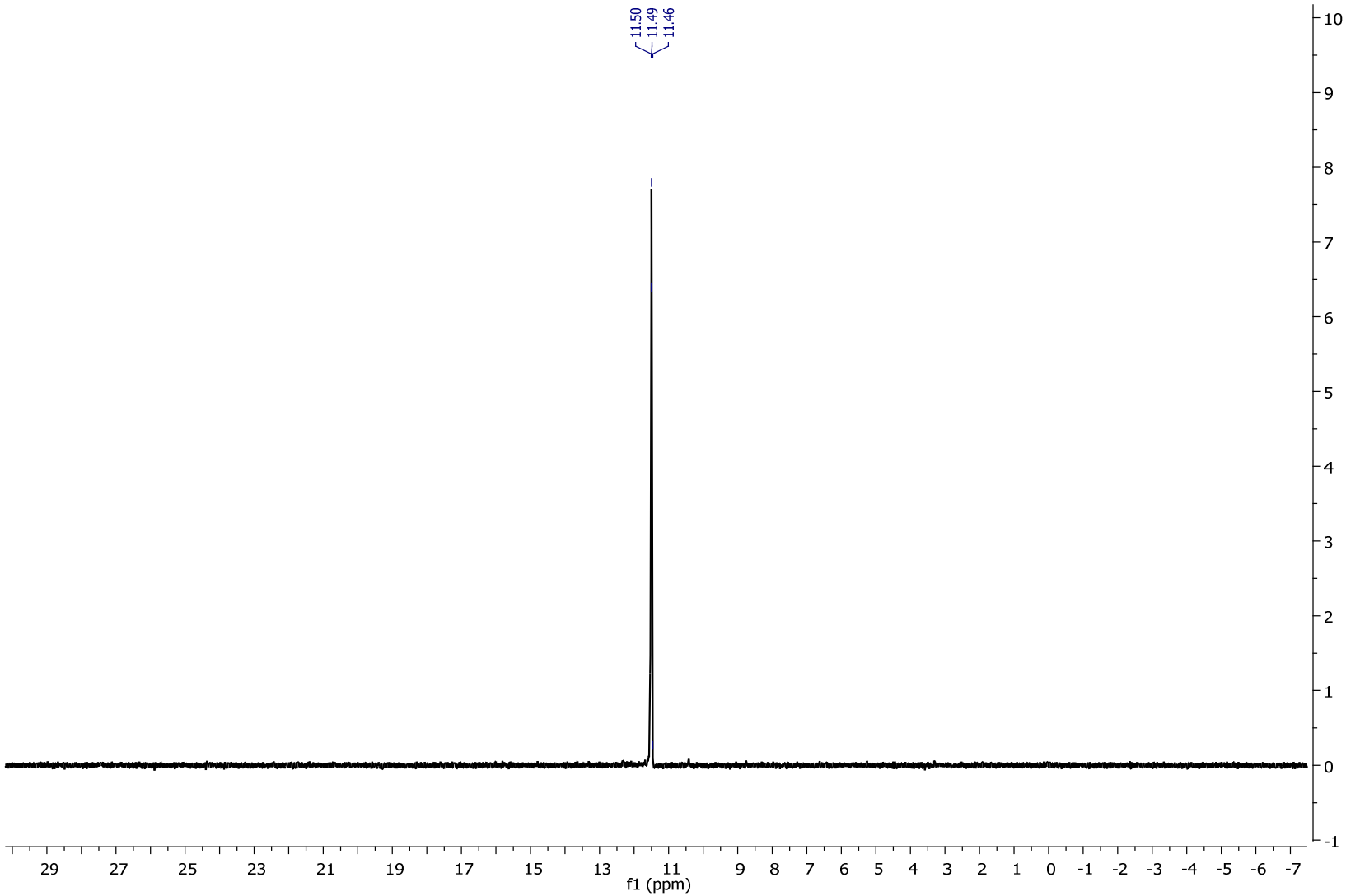
^{13}C NMR


175.59 159.97 159.95 159.93 159.92 154.10 154.09 152.95 152.85 152.66 152.56 152.37 152.27 147.87 147.85 147.22 147.14 135.36 135.35 135.34 135.33 135.32 135.31 126.66 126.65 126.63 126.61 126.60 126.59 123.52 123.13 121.63 120.63 120.27 119.92 119.66 119.65 119.64 119.64 119.62 119.61 119.60 119.59 119.58 118.94 118.73 118.65 117.77 117.42 117.25 117.14 117.06 115.01 114.92 114.56 114.20 114.01 113.87 113.49 113.12 111.95 111.67 111.29 110.92 110.71 110.55 110.47 109.45 109.15 108.72 108.40 108.35 107.44 63.52 63.46 20.90 19.36 16.33 16.27
0.80
0.75
0.70
0.65
0.60
0.55
0.50
0.45
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0.00
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

^{19}F NMR


-80.25
-109.51
3.00
2.13
10
9
8
7
6
5
4
3
2
1
0
-1
-66
-70
-74
-78
-82
-86
-90
-94
-98
-102
-106
-110
-114
-118
-122
-126
f1 (ppm)

^{31}P NMR


11.50
11.49
11.46
10
9
8
7
6
5
4
3
2
1
0
-1
29 27 25 23 21 19 17 15 13 11 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4 -5 -6 -7
f1 (ppm)

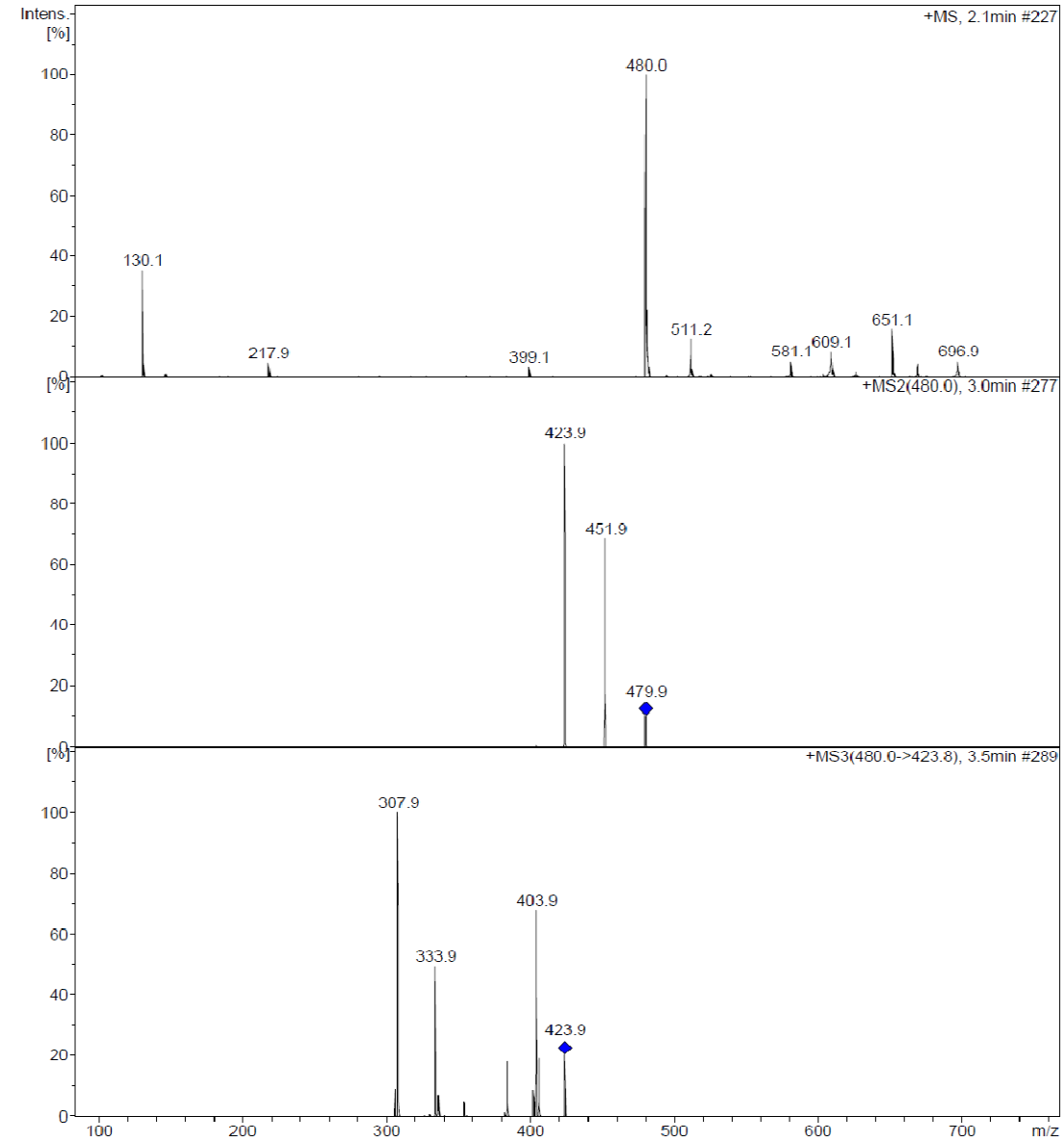
Display Report

Analysis Info

Analysis Name	G:\Data B\Blazej ION TRAP\BD138B_14122010.d	Acquisition Date	2010-12-14 12:02:01
Method	DEF_MS.M	Operator	farnoosh
Sample Name	0	Instrument	HCTultra
Comment	in 1 mM HCl		

Acquisition Parameter

Ion Source Type	ESI	Ion Polarity	Positive	Alternating Ion Polarity	off
Mass Range Mode	Ultra Scan	Scan Begin	100 m/z	Scan End	750 m/z
Capillary Exit	128.5 Volt	Skimmer	40.0 Volt	Trap Drive	58.6
Accumulation Time	13420 ŠS	Averages	10 Spectra	Auto MS/MS	off



Bruker Compass DataAnalysis 4.0 printed: 2009-10-26 19:44:01 Page 1 of 1

HRMS

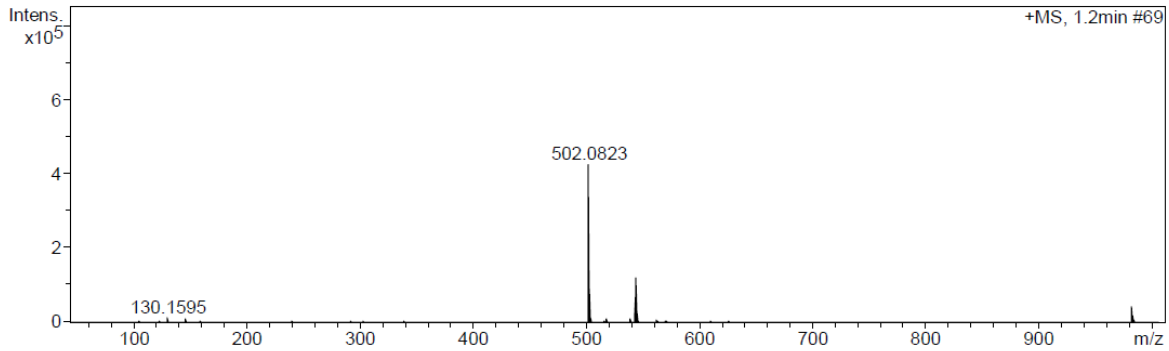
Mass Spectrum SmartFormula Report

Analysis Info

Analysis Name	G:\Data B\Blazej TOF\BD138B_14122010.d	Acquisition Date	2010-12-14 11:21:59
Method	tune_low.m	Operator	Bruker Customer
Sample Name		Instrument / Ser#	micrOTOF 129
Comment	in ACN		

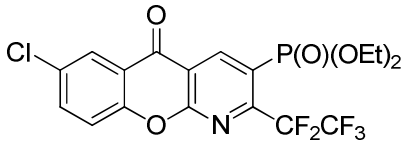
Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	1000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Source



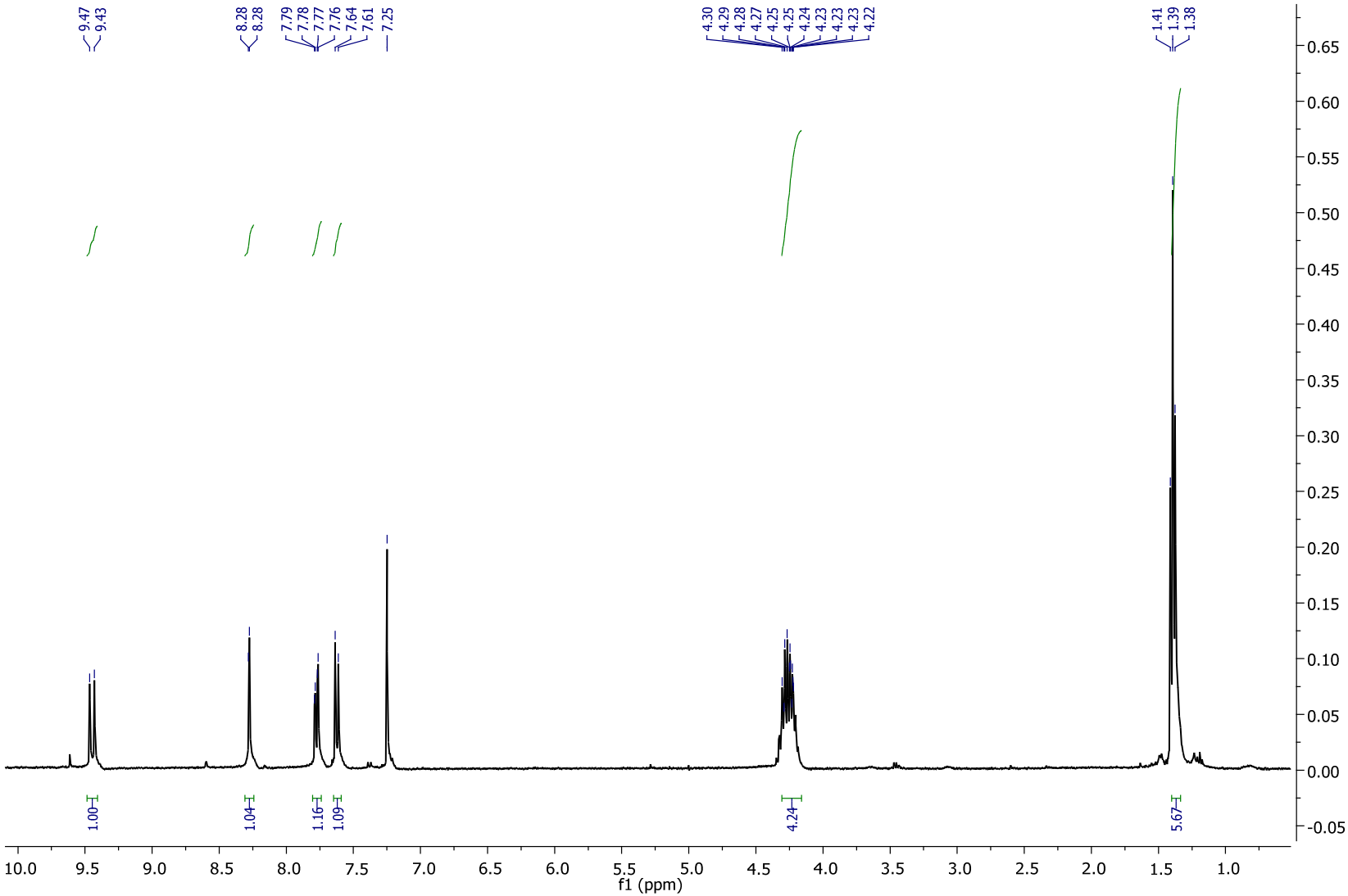
Meas. m/z	Formula	m/z	err [ppm]	Mean err [ppm]	rdb	N-Rule	e— Conf	mSigma
502.0823								
	C 20 H 19 F 5 N Na O 5 P	502.0813	-2.0	-0.9	9.5	ok	even	3.73

12. *Diethyl (7-chloro-5-oxo-2-(perfluoroethyl)-5H-chromeno[2,3-b]pyridin-3-yl)phosphonate (**3l**)*

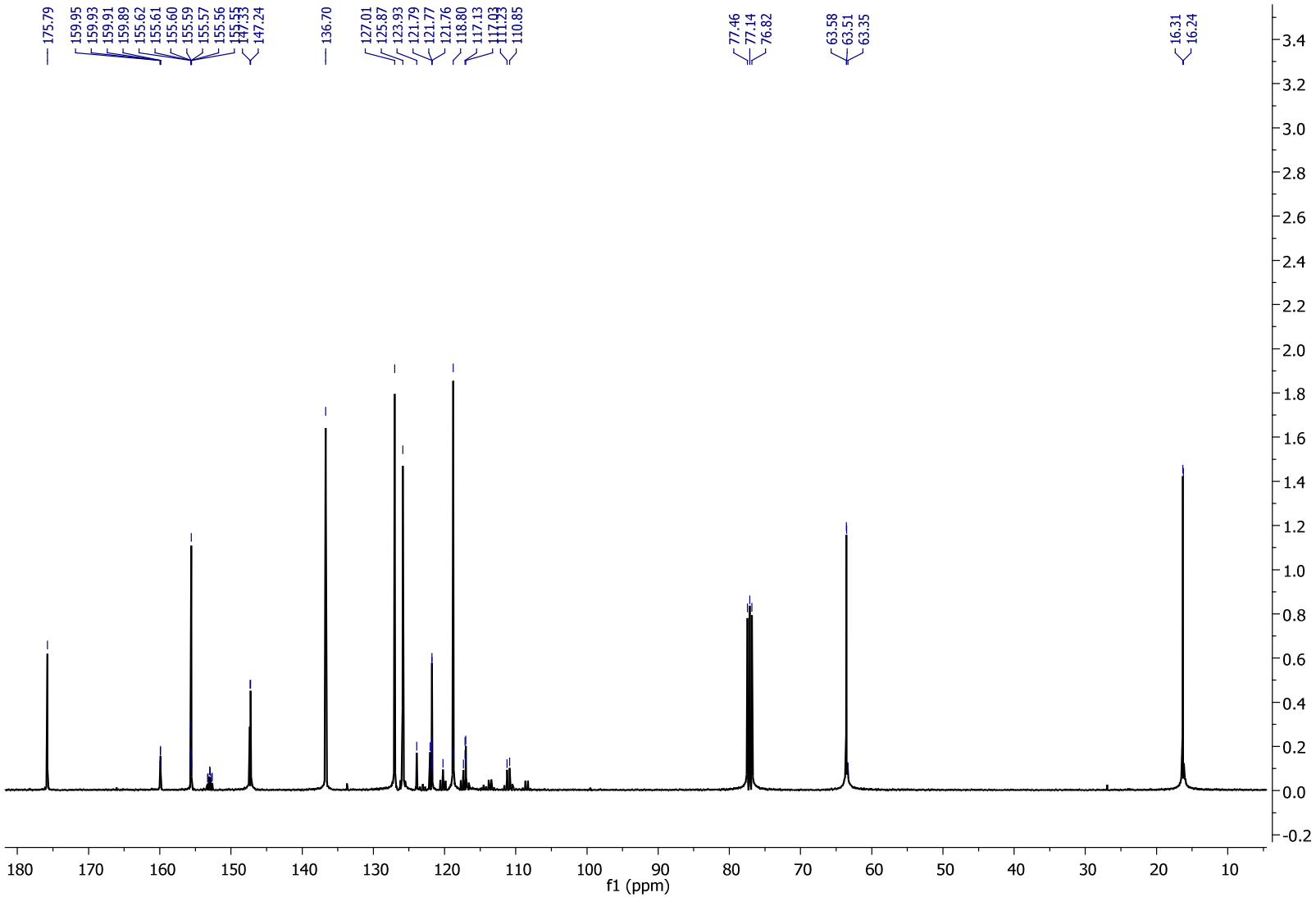


Green crystals (78%); mp 150–153 °C ; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.39 (t, *J* = 6.9 Hz, 6H), 4.25 (m, 4H), 7.63 (d, *J* = 7.7 Hz, 1H), 7.77 (dd, *J* = 7.9 Hz, *J* = 1.2 Hz, 1H), 8.28 (d, *J* = 1.1 Hz, 1H), 9.45 (d, $^{3}J_{H–P}$ = 15.1 Hz); ^{13}C NMR (100 MHz): δ 16.2 (d, *J* = 6.9 Hz), 63.5 (d, *J* = 5.8 Hz), 110.9 (tq, $^{1}J_{C–F}$ = 261.6 Hz, $^{2}J_{C–F}$ = 36.2 Hz), 117.0 (d, $^{2}J_{C–P}$ = 12.5 Hz), 118.9 (qt, $^{1}J_{C–F}$ = 287.2 Hz, $^{2}J_{C–F}$ = 37.1 Hz), 118.8, 121.4 (d, $^{1}J_{C–P}$ = 190.4 Hz), 123.6, 127.0, 136.7, 147.3 (d, $^{3}J_{C–P}$ = 7.9 Hz), 155.4 (td, $^{2}J_{C–F}$ = 29.4 Hz, $^{2}J_{C–P}$ = 9.4 Hz), 156.1, 159.9, 176.6; ^{19}F NMR (376 MHz): δ –80.2 (s, 3F), –109.5 (s, 2F); ^{31}P NMR (161 MHz): 11.2 (t, $^{4}J_{P–F}$ = 1.4 Hz); MS (ESI) *m/z*: $[M+Na]^+$ 508; HRMS (ESI) calcd for $[M+Na]^+$ $(C_{18}H_{14}ClF_5NNaO_5P)^+$ 508.0110; found 508.0112.

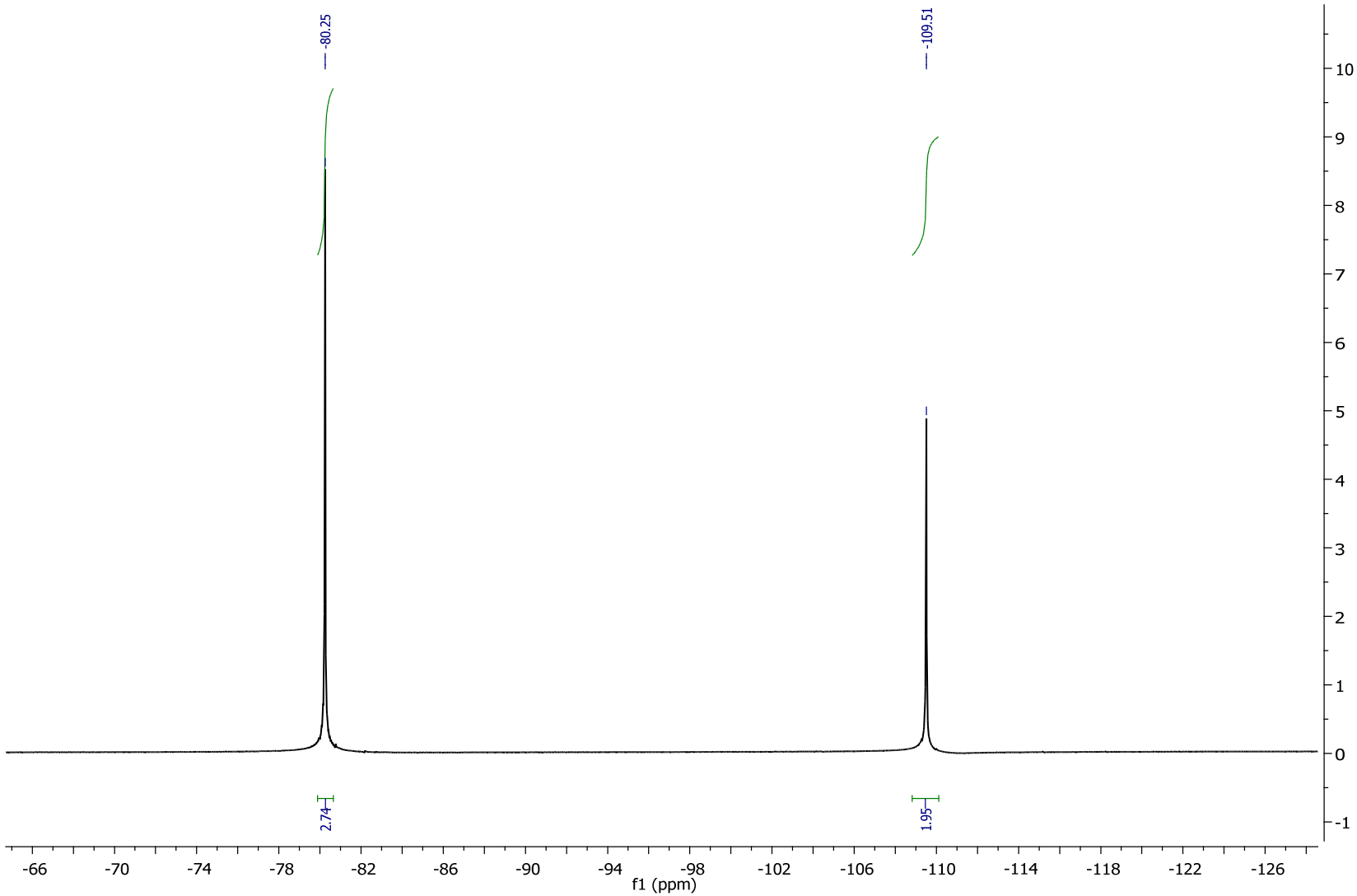
^{1}H NMR


9.47
9.43
8.28
8.28
7.79
7.78
7.77
7.76
7.64
7.61
7.25
4.30
4.29
4.28
4.27
4.25
4.25
4.24
4.23
4.23
4.23
4.22
1.41
1.39
1.38
1.00
1.04
1.16
1.09
4.24
5.67
f1 (ppm)

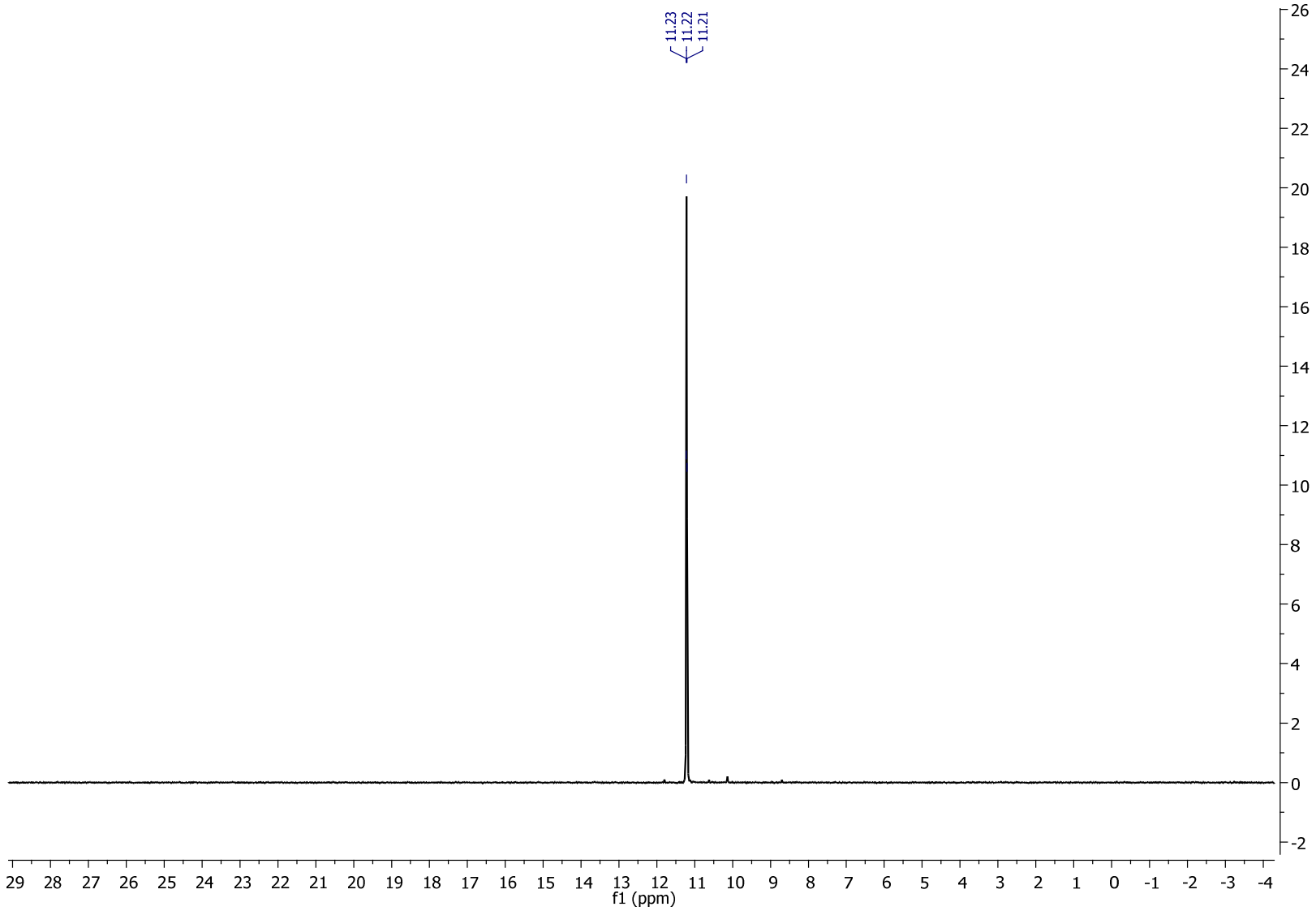
^{13}C NMR


175.79
159.95
159.93
159.91
159.89
155.62
155.61
155.60
155.59
155.57
155.56
147.24
136.70
127.01
125.87
123.93
121.79
121.77
121.76
118.80
117.13
110.85
77.46
77.14
76.82
63.58
63.51
63.35
16.31
16.24
f1 (ppm)

^{19}F NMR


-80.25
-109.51
2.74
1.95
10
9
8
7
6
5
4
3
2
1
0
-1
-66
-70
-74
-78
-82
-86
-90
-94
-98
-102
-106
-110
-114
-118
-122
-126
f1 (ppm)

^{31}P NMR



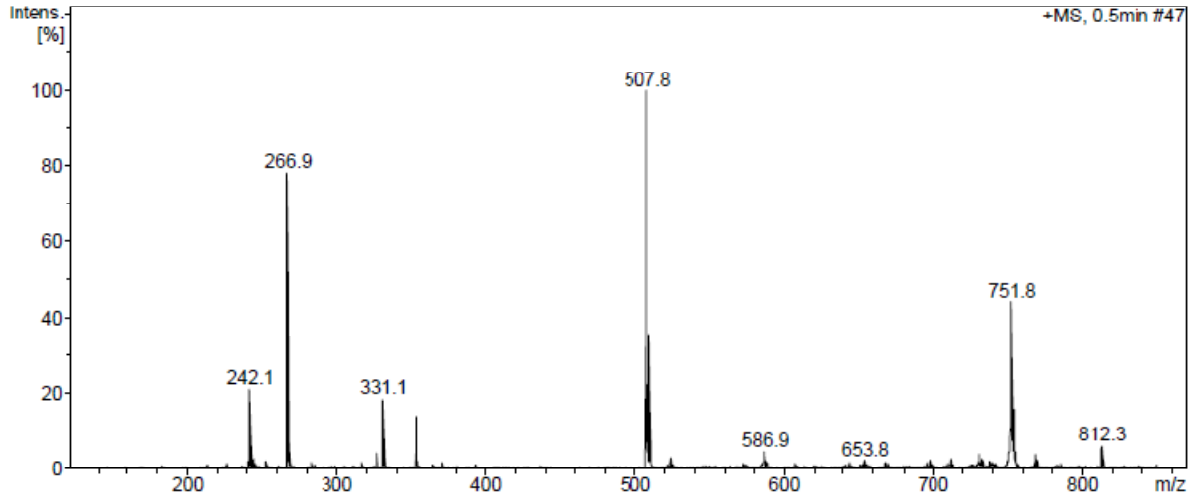
Display Report

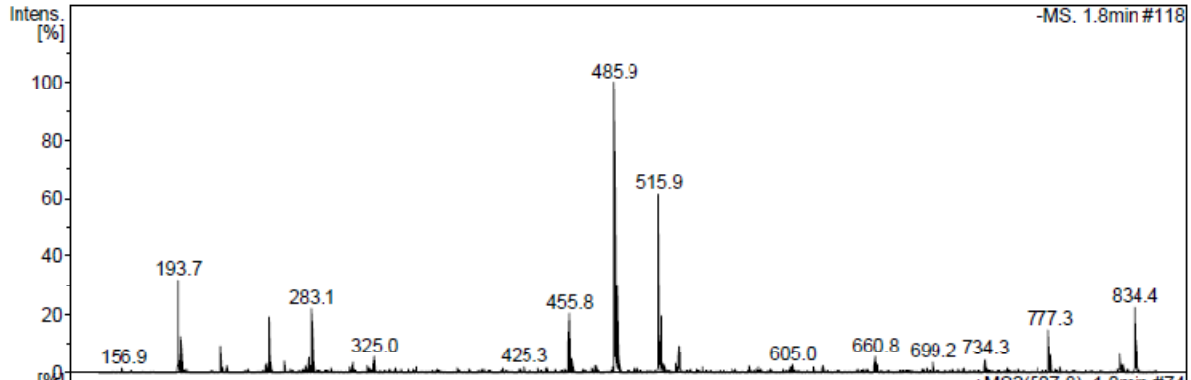
Analysis Info

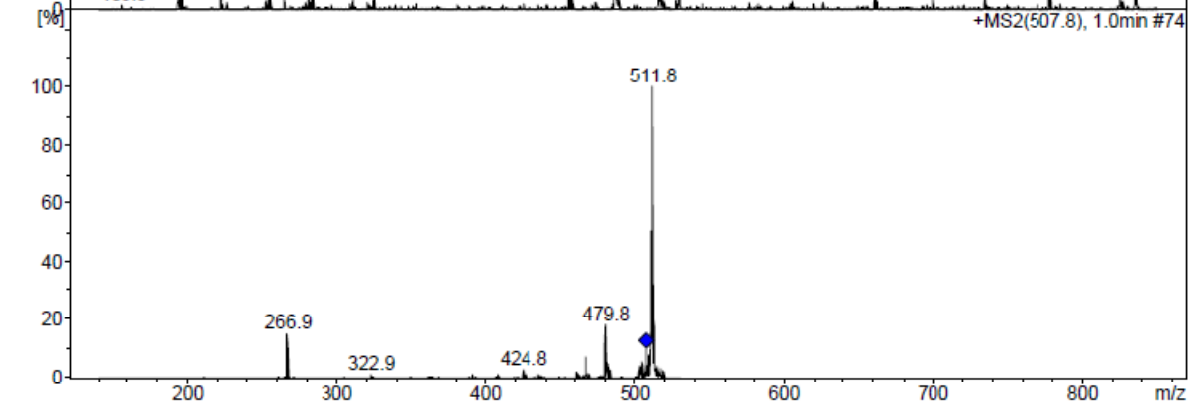
Analysis Name	G:\Data B\Blazej ION TRAP\BD137B_22112010.d	Acquisition Date	2010-11-22 11:05:44
Method	DEF_MS.M	Operator	farnoosh
Sample Name	VG21	Instrument	HCTultra
Comment	in methanol		

Acquisition Parameter

Ion Source Type	ESI	Ion Polarity	Positive	Alternating Ion Polarity	off
Mass Range Mode	Ultra Scan	Scan Begin	50 m/z	Scan End	850 m/z
Capillary Exit	113.5 Volt	Skimmer	40.0 Volt	Trap Drive	58.6
Accumulation Time	80 µs	Averages	10 Spectra	Auto MS/MS	off







HRMS

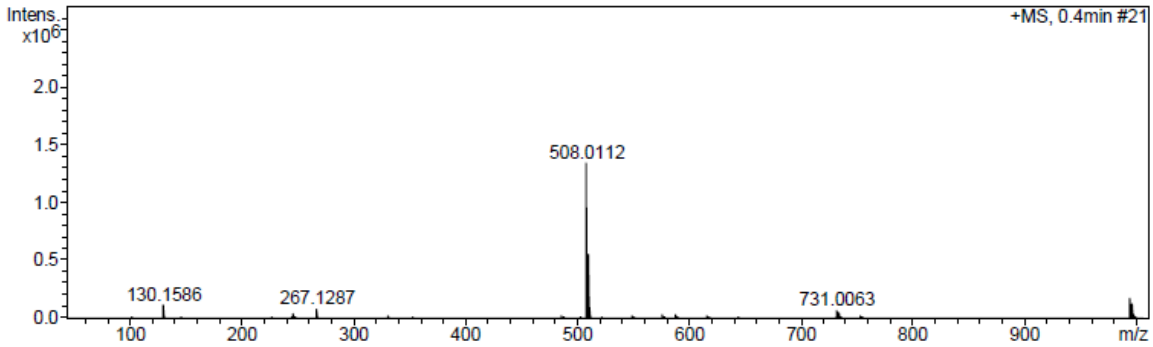
Mass Spectrum SmartFormula Report

Analysis Info

Analysis Name	G:\Data B\Blazej TOF\BD137B_22112010.d	Acquisition Date	2010-11-22 11:11:37
Method	tune_low.m	Operator	Bruker Customer
Sample Name		Instrument / Ser#	micrOTOF 129
Comment	in Methanol		

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	5.8 psi
Focus	Active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	1000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Source



Meas. m/z	Formula	m/z	err [ppm]	Mean err [ppm]	rdb	N-Rule	e—Conf	mSigma
508.0112	C 18 H 14 Cl F 5 N Na O 5 P	508.0110	-0.4	3.1	9.5	ok	even	31.83

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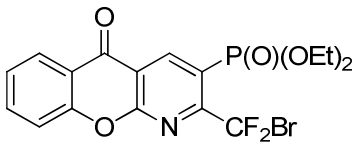
Method B: General procedure for the preparation of azaxanthones (**3m–o**)

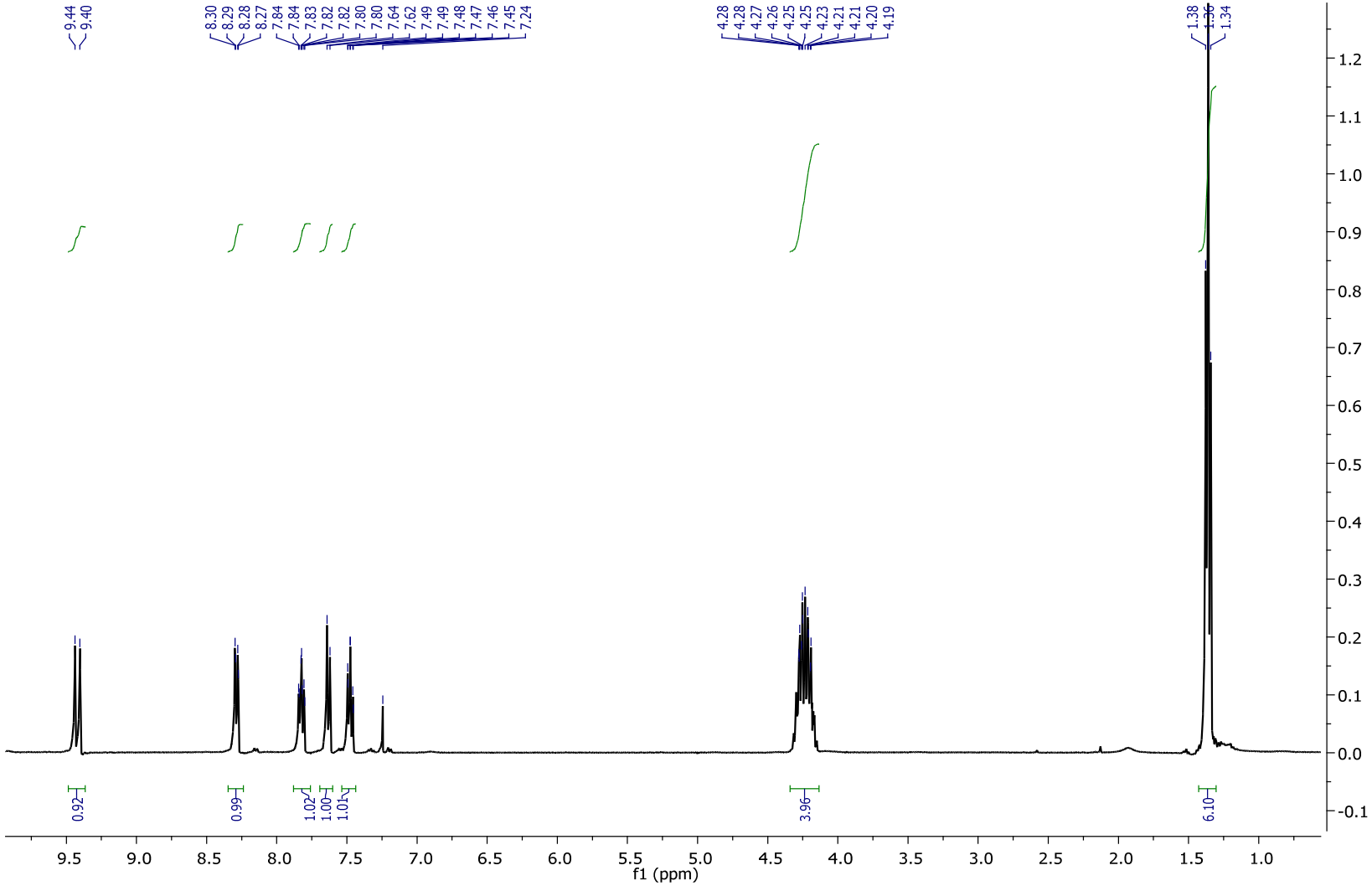
To a mixture of K_2CO_3 (5mol%) and the 2-amino-3-formylchromone derivative (5 mmol) dry DMF (20 ml) was added at ambient temperature. To the reaction mixture the acetylene (5 mmol) was charged slowly. The solution was stirred for 8–9 hours at room temperature and subsequently concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel using DCM:EtOAc (5:1 ratio) as eluent.

13. *Diethyl (2-(bromodifluoromethyl)-5-oxo-5H-chromeno[2,3-b]-pyridin-3-yl)phosphonate (**3m**)*



Orange crystals (62%); mp 88–90 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.36 (t, J = 7.3 Hz, 6H), 4.25 (m, 4H), 7.51 (t, J = 8.5 Hz, 1H), 7.67 (d, J = 8.5 Hz, 1H), 7.85 (td, J = 7.0 Hz, J = 1.9 Hz, 1H), 8.29 (dd, J = 8.2 Hz, J = 1.8 Hz, 1H), 9.42 (d, $^{3}J_{H–P}$ = 13.0 Hz, 1H); ^{13}C NMR (100 MHz): δ 16.4 (d, J = 7.3 Hz), 63.6 (d, J = 6.0 Hz), 114.7 (t, $^{1}J_{C–F}$ = 307.1 Hz), 117.8 (d, $^{2}J_{C–P}$ = 12.7 Hz), 118.8, 119.2 (d, $^{1}J_{C–P}$ = 191.1 Hz), 121.8, 125.8, 136.7, 147.5 (d, $^{3}J_{C–P}$ = 5.0 Hz), 155.6, 158.1 (td, $^{2}J_{C–F}$ = 28.7 Hz, $^{2}J_{C–P}$ = 11.6 Hz), 175.8; ^{19}F NMR (376 MHz): δ –49.8; ^{31}P NMR (161 MHz): δ 11.4; MS (ESI) *m/z*: $[M+Na]^+$ 484; HRMS (ESI) calcd for $[M+Na]^+$ $(C_{17}H_{15}BrF_2NNaO_5P)^+$ 483.9731; found 483.9729.

^{1}H NMR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9.40
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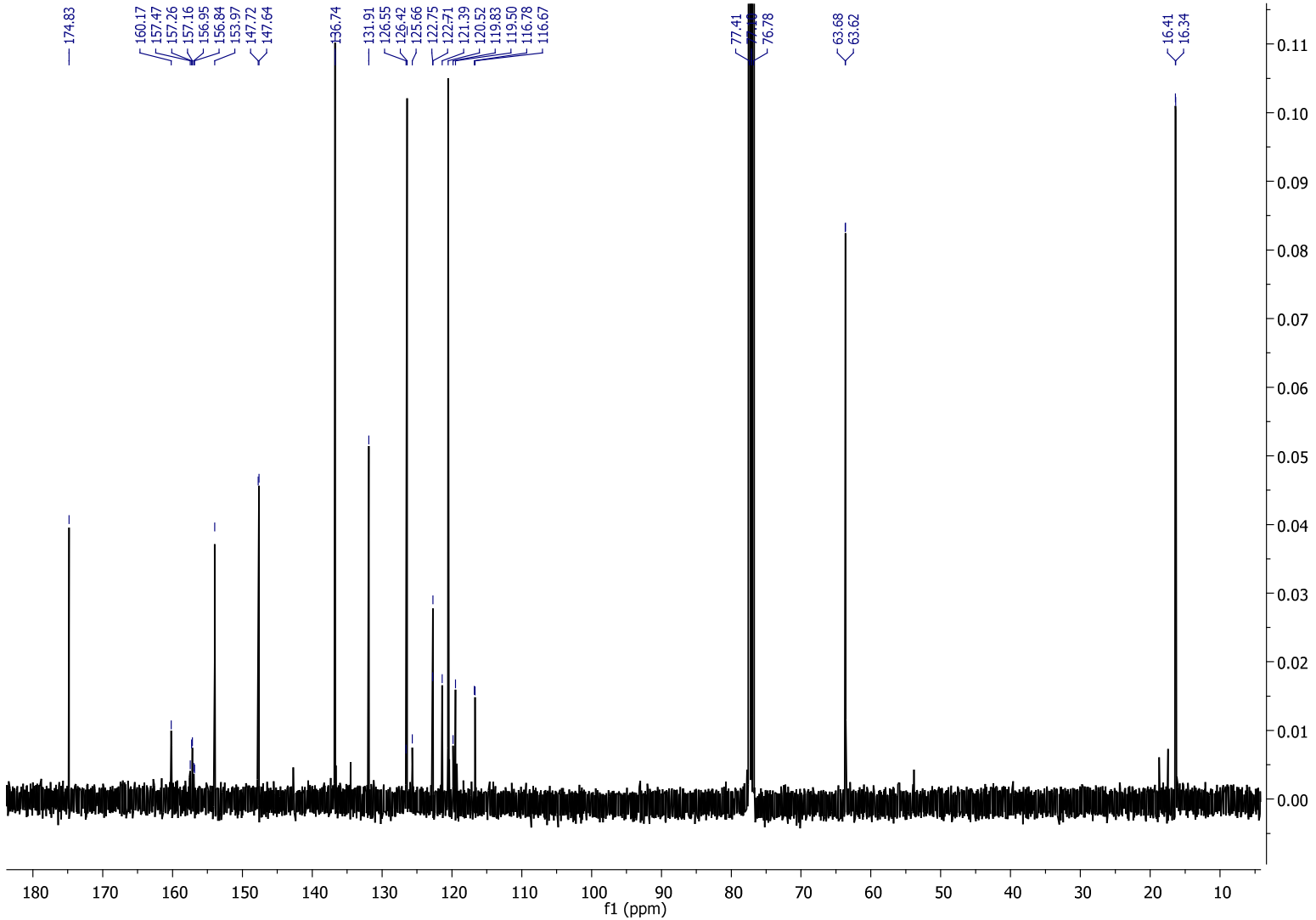
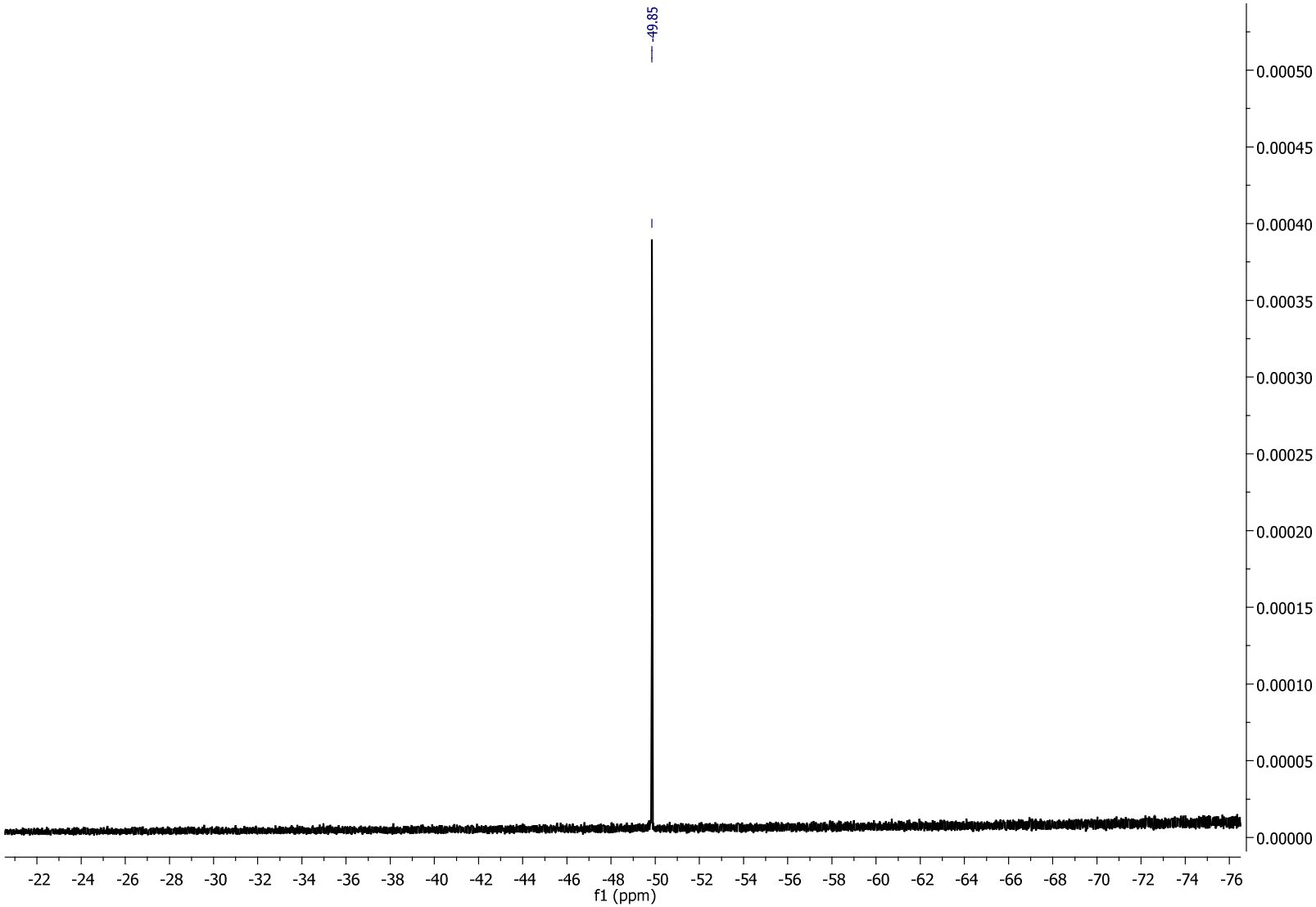
8.29
8.28
8.27
7.84
7.84
7.83
7.82
7.82
7.80
7.80
7.64
7.62
7.49
7.49
7.48
7.47
7.46
7.45
7.24
4.28
4.28
4.27
4.26
4.25
4.25
4.23
4.21
4.21
4.20
4.19
1.38
1.36
1.34
0.92
0.99
1.02
1.00
1.01
3.96
6.10
f1 (ppm)

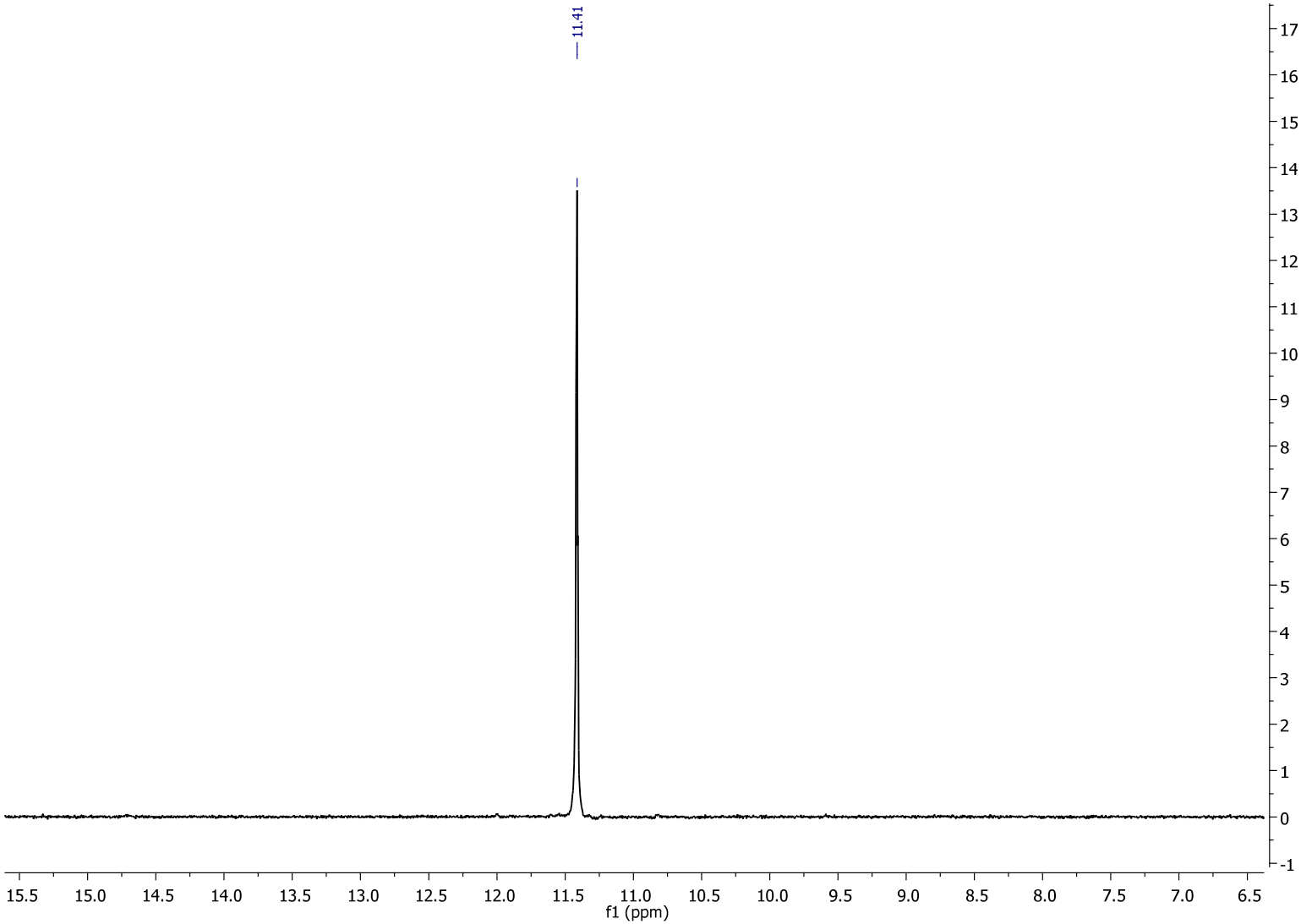
^{13}C NMR


174.83
160.17
157.47
157.26
157.16
156.95
156.84
153.97
147.72
147.64
136.74
131.91
126.55
126.42
125.66
122.75
122.71
121.39
120.52
119.83
119.50
116.78
116.67
77.41
76.78
63.68
63.62
16.41
16.34
0.11
0.10
0.09
0.08
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0.00
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

^{19}F NMR


-49.85
0.00050
0.00045
0.00040
0.00035
0.00030
0.00025
0.00020
0.00015
0.00010
0.00005
0.00000
-22 -24 -26 -28 -30 -32 -34 -36 -38 -40 -42 -44 -46 -48 -50 -52 -54 -56 -58 -60 -62 -64 -66 -68 -70 -72 -74 -76
f1 (ppm)

^{31}P NMR


11.41
17
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
15.5
15.0
14.5
14.0
13.5
13.0
12.5
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
f1 (ppm)

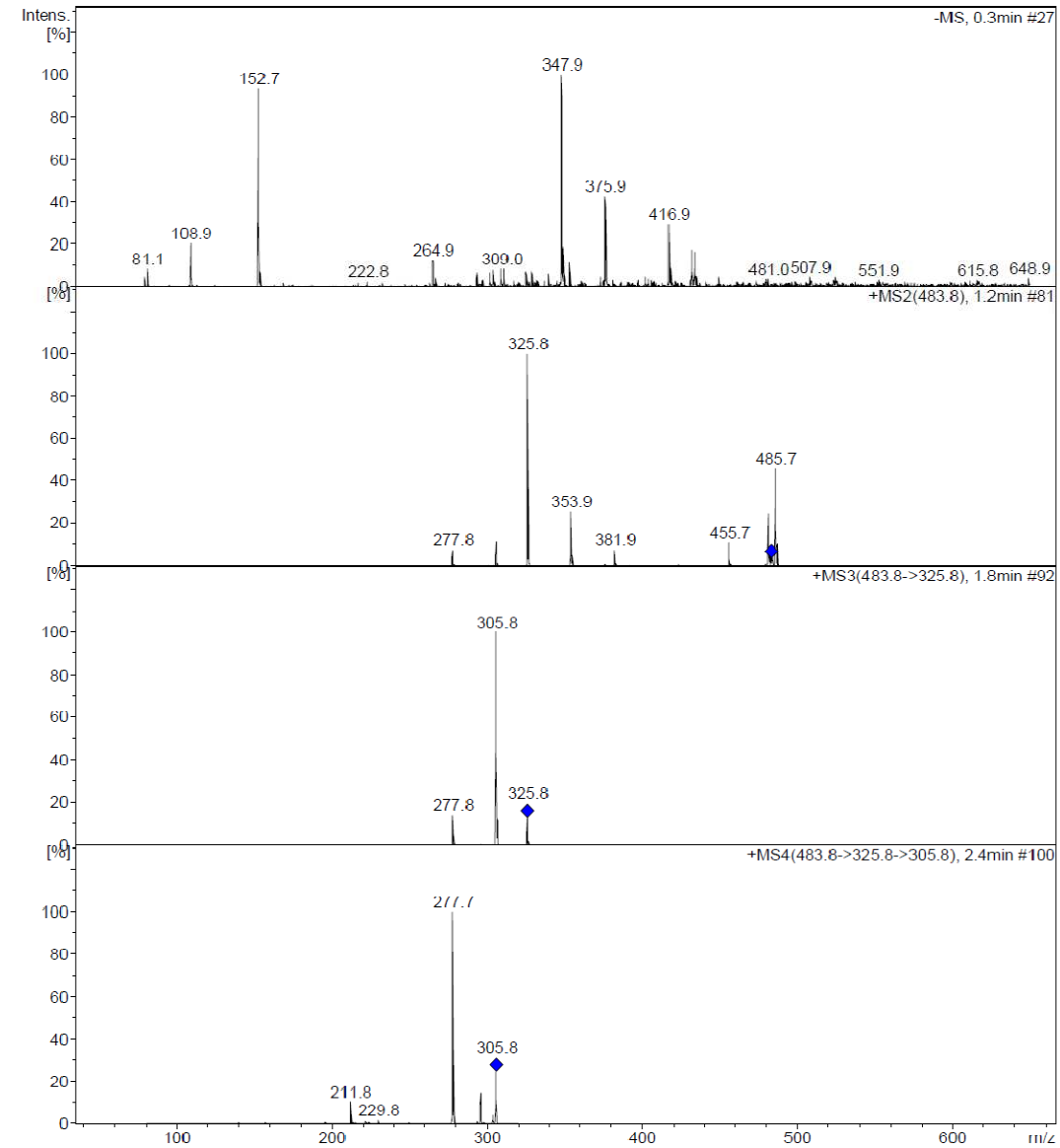
Display Report

Analysis Info

Analysis Name	G:\Data B\Blazej ION TRAP\BD141D_06122010_.d	Acquisition Date	2010-12-06 14:52:38
Method	DEF_MS.M	Operator	farnoosh
Sample Name	160/180-PC	Instrument	HCTultra
Comment	in acn		

Acquisition Parameter

Ion Source Type	ESI	Ion Polarity	Positive	Alternating Ion Polarity	off
Mass Range Mode	Ultra Scan	Scan Begin	50 m/z	Scan End	650 m/z
Capillary Exit	109.8 Volt	Skimmer	40.0 Volt	Trap Drive	58.6
Accumulation Time	382 µs	Averages	10 Spectra	Auto MS/MS	off



Bruker Compass DataAnalysis 4.0 printed: 2009-10-26 19:47:48 Page 1 of 1

HRMS

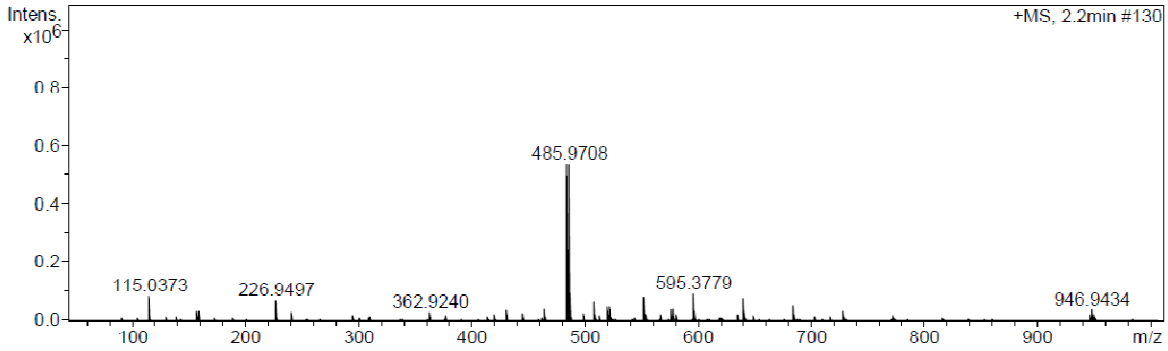
Mass Spectrum SmartFormula Report

Analysis Info

Analysis Name	G:\Data B\Blazej TOF\BD141D_06122010.d	Acquisition Date	2010-12-06 14:52:59
Method	tune_low.m	Operator	Bruker Customer
Sample Name		Instrument / Ser#	micrOTOF 129
Comment	in ACN		

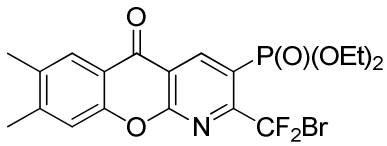
Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	1000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Source



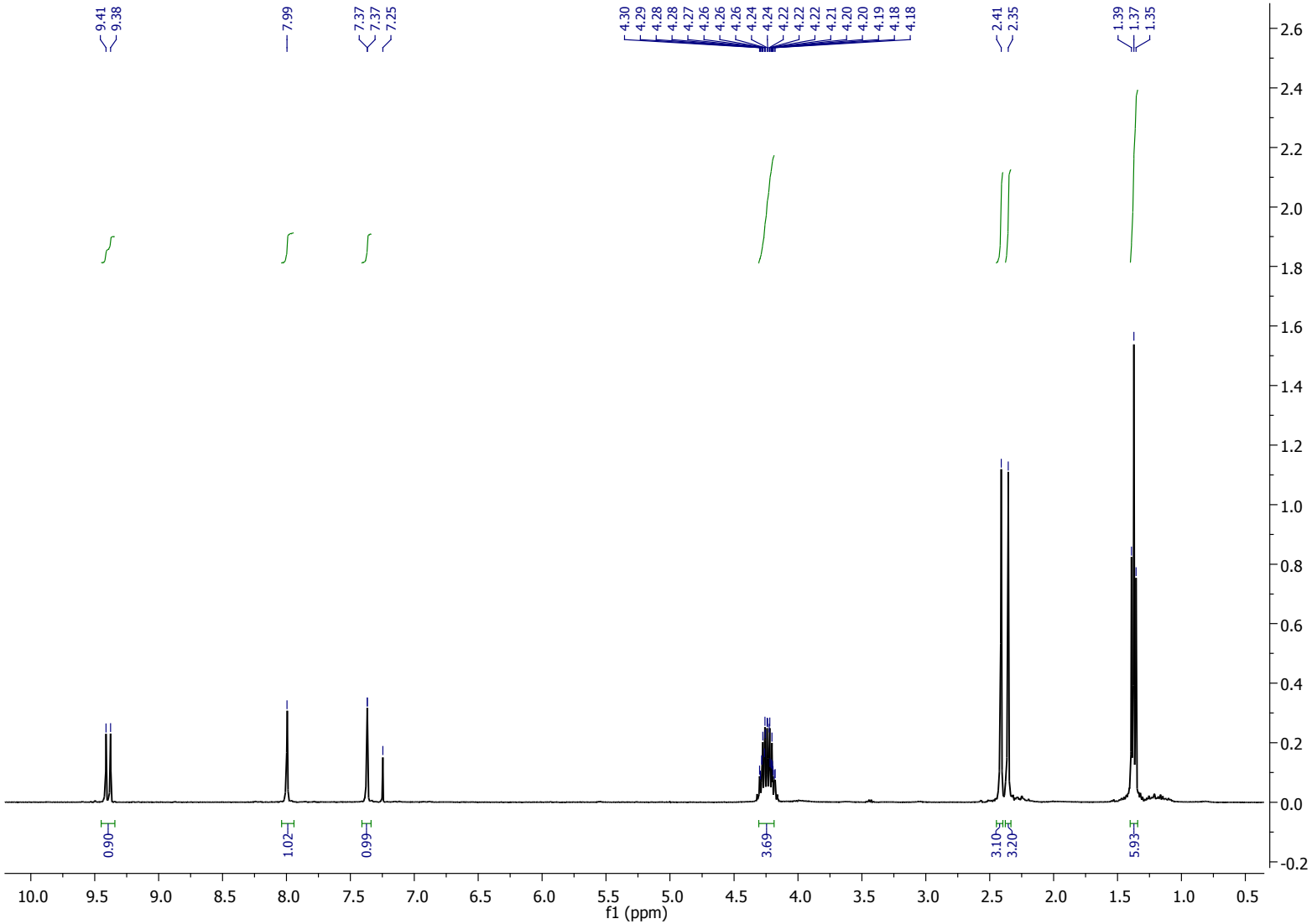
Meas. m/z	Formula	m/z	err [ppm]	Mean err [ppm]	rdb	N-Rule	e—Conf	mSigma
483.9729	C 17 H 15 Br F 2 N Na O 5 P	483.9731	0.5	1.5	9.5	ok	even	4.02

14. *Diethyl (2-(bromodifluoromethyl)-7,8-dimethyl-5-oxo-5H-chrom-eno[2,3-b]pyridin-3-yl)phosphonate* ***(3n)***



Orange crystals (62%); mp 100–103 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.37 (t, *J* = 8.1 Hz, 6H), 2.35 (s, 3H), 2.41 (s, 3H), 4.25 (m, 4H), 7.37 (s, 1H), 7.99 (s, 1H), 9.40 (d, $^{3}J_{H–P}$ = 13.4 Hz, 1H); ^{13}C NMR (100 MHz): δ 16.4 (d, *J* = 5.8 Hz), 19.4, 20.9, 63.5 (d, *J* = 7.5 Hz), 114.9 (t, $^{1}J_{C–F}$ = 306.8 Hz), 117.1 (d, $^{2}J_{C–P}$ = 13.6 Hz), 119.4 (d, $^{1}J_{C–P}$ = 189.5 Hz), 118.9, 119.6, 126.7, 135.3, 136.7, 147.8 (d, $^{3}J_{C–P}$ = 7.8 Hz), 154.1, 158.0 (td, $^{2}J_{C–F}$ = 28.2 Hz, $^{2}J_{C–P}$ = 10.7 Hz), 175.6; ^{19}F NMR (376 MHz): δ –49.8; ^{31}P NMR (161 MHz): δ 11.5; MS (ESI) *m/z*: 490 $[M+H]^+$; HRMS (ESI) calcd for $[M+H]^+$ $(C_{19}H_{20}BrF_2NO_5P)^+$ 490.0225; found 490.0222.

^{1}H NMR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9.38
7.99
7.37
7.37
7.25
4.30
4.29
4.28
4.28
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4.26
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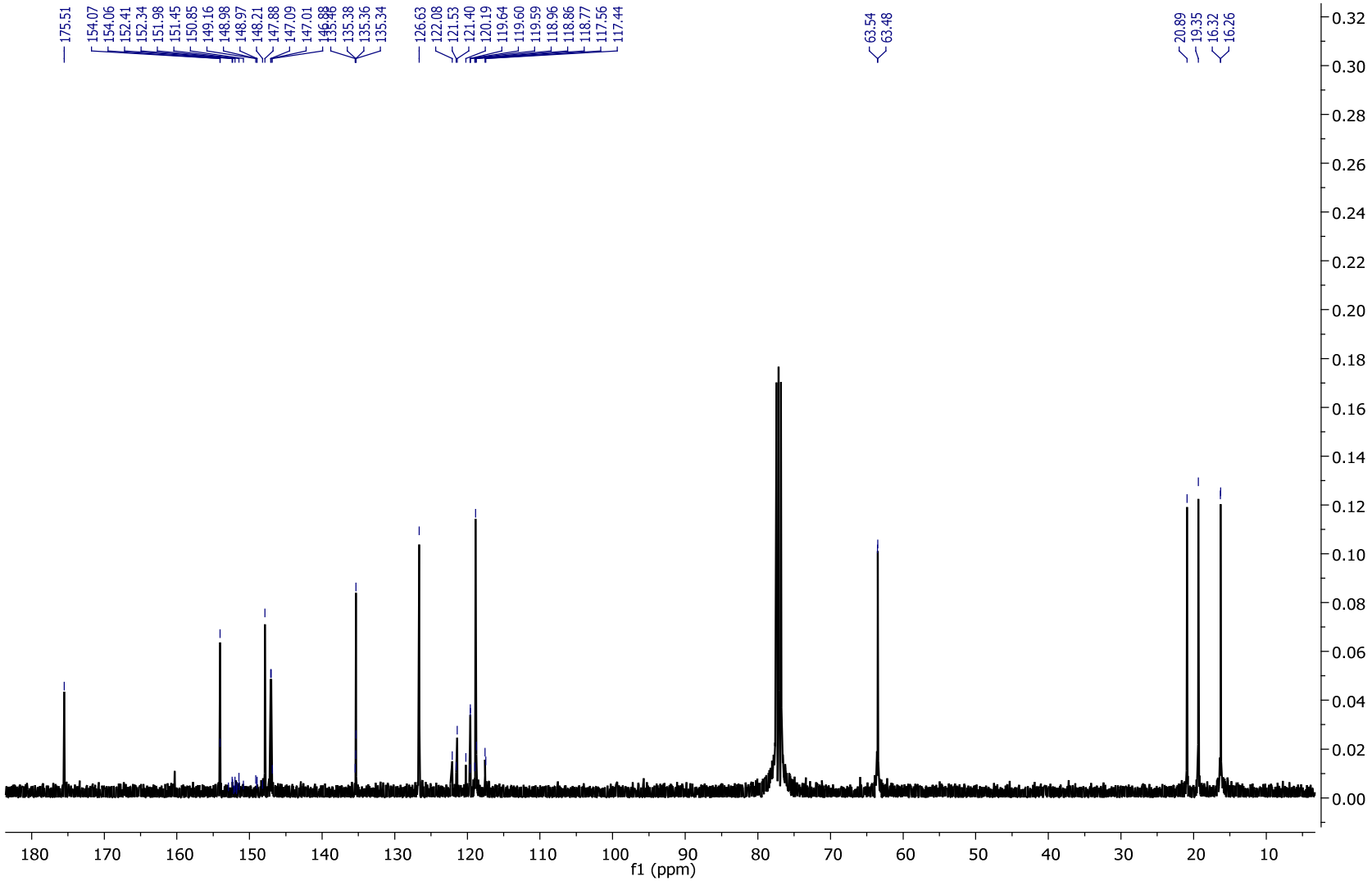
4.24
4.24
4.22
4.22
4.22
4.21
4.20
4.20
4.19
4.18
4.18
2.41
2.35
1.39
1.37
1.35
0.90
1.02
0.99
3.69
3.10
3.20
5.93
f1 (ppm)

^{13}C NMR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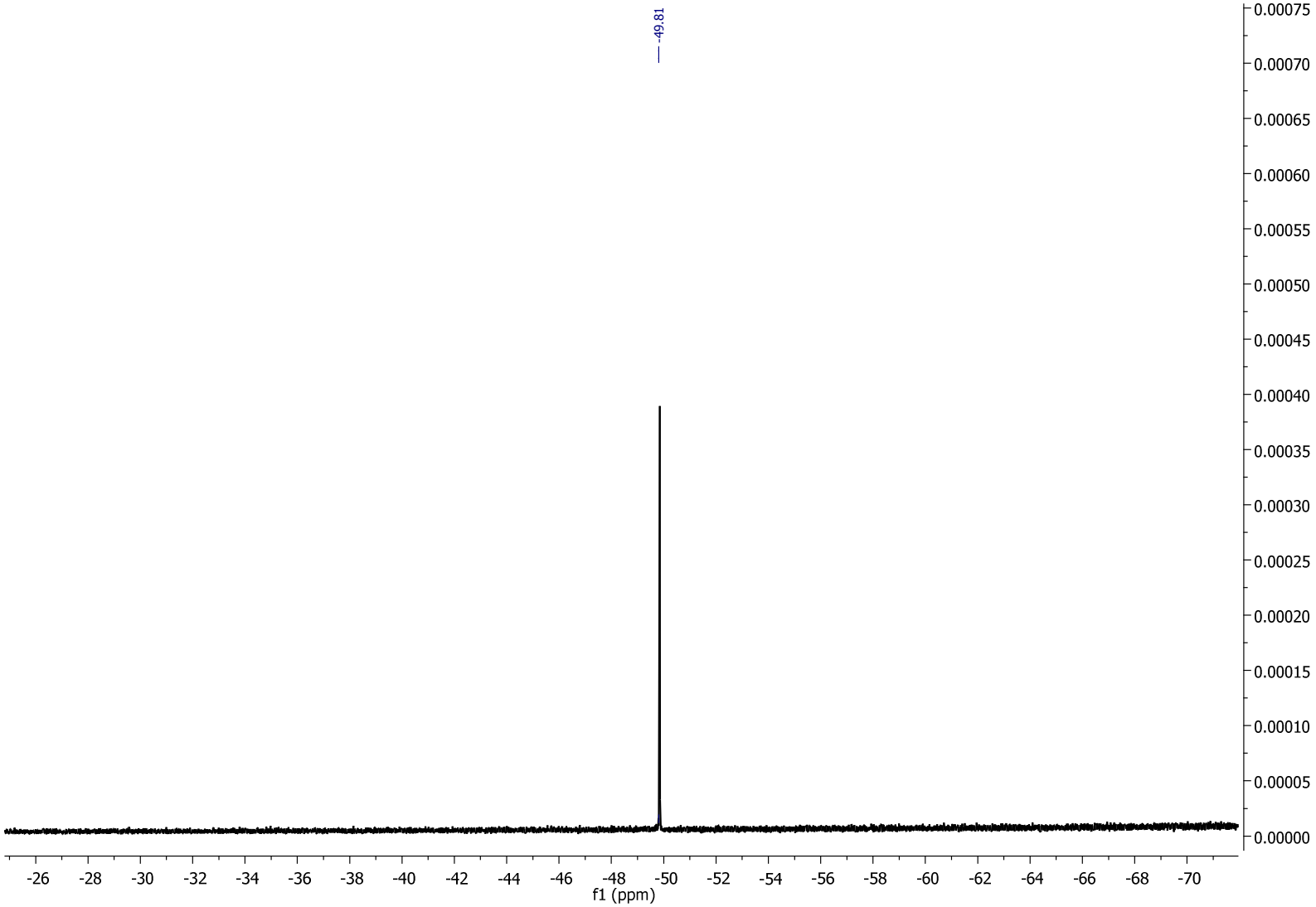
154.07
154.06
152.41
152.34
151.98
151.45
150.85
149.16
148.98
148.97
148.21
147.88
147.09
147.01
135.38
135.36
135.34
126.63
122.08
121.53
121.40
120.19
119.64
119.60
119.59
118.96
118.86
118.77
117.56
117.44
63.54
63.48
20.89
19.35
16.32
16.26
f1 (ppm)

^{19}F NMR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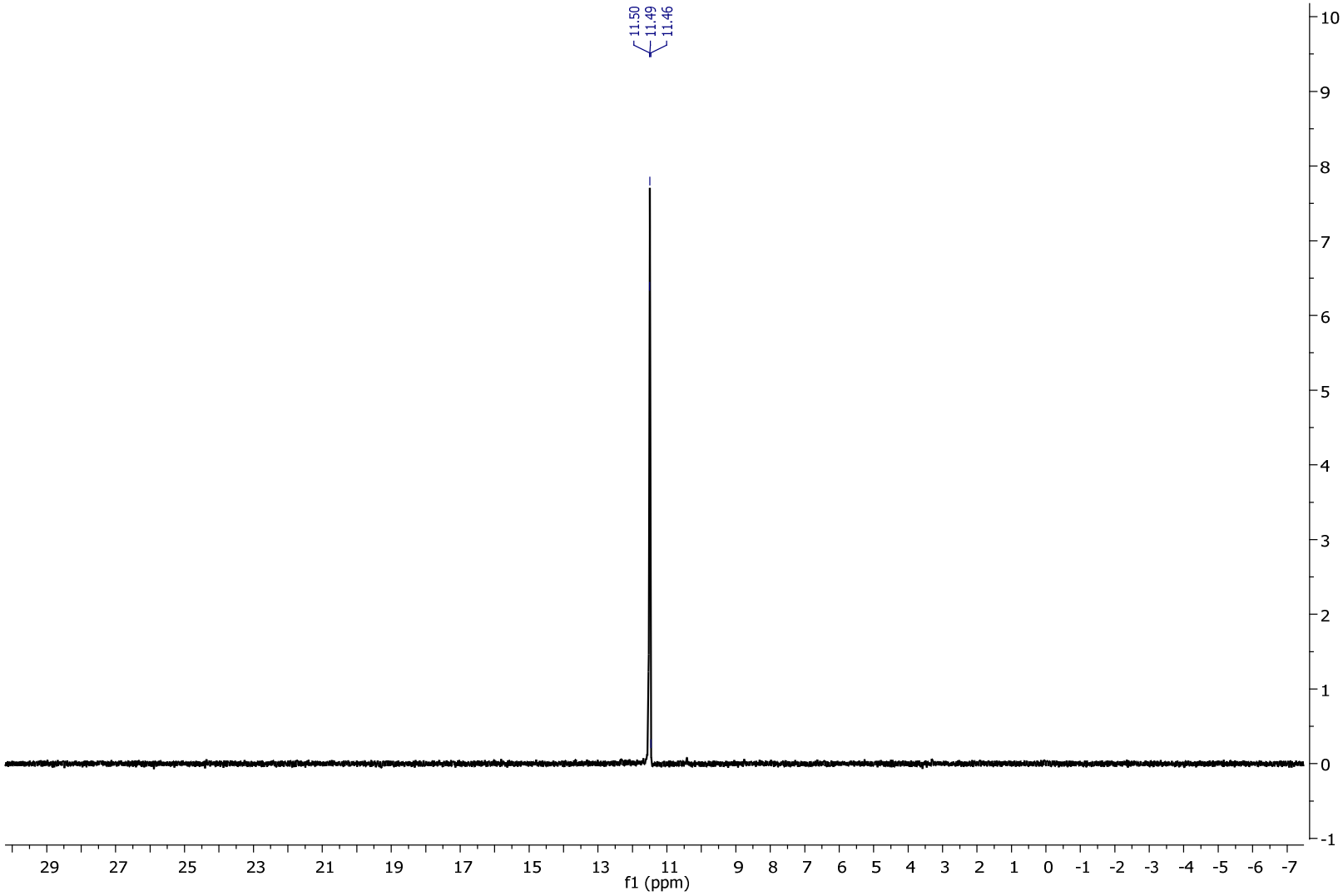
0.00070
0.00065
0.00060
0.00055
0.00050
0.00045
0.00040
0.00035
0.00030
0.00025
0.00020
0.00015
0.00010
0.00005
0.00000
-26 -28 -30 -32 -34 -36 -38 -40 -42 -44 -46 -48 -50 -52 -54 -56 -58 -60 -62 -64 -66 -68 -70
f1 (ppm)

^{31}P NMR


11.50
11.49
11.46
10
9
8
7
6
5
4
3
2
1
0
-1
29 27 25 23 21 19 17 15 13 11 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4 -5 -6 -7
f1 (ppm)

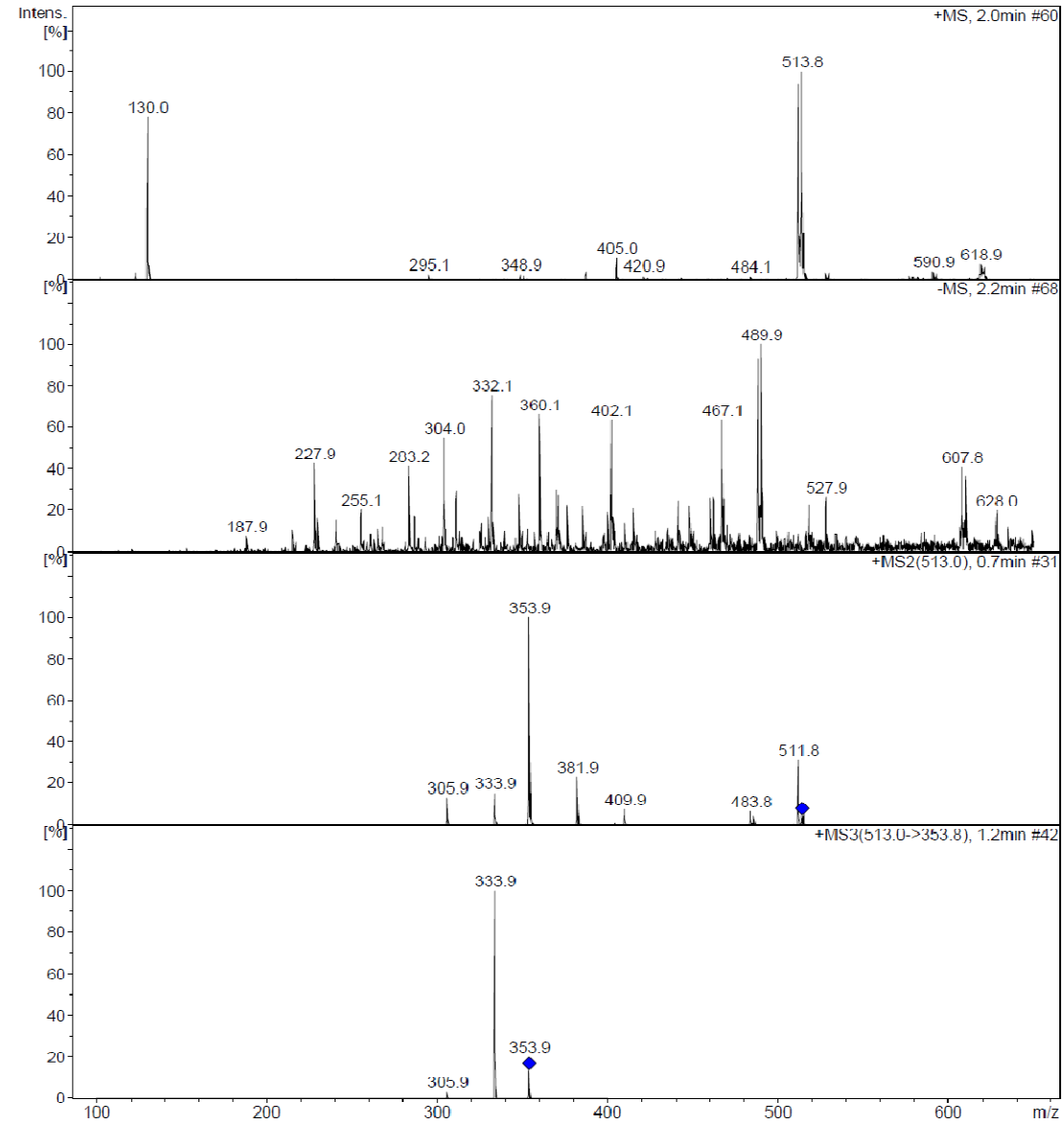
Display Report

Analysis Info

Analysis Name	G:\Data B\Blazej ION TRAP\BD153_14122010.d	Acquisition Date	2010-12-14 12:17:50
Method	DEF_MS.M	Operator	farnoosh
Sample Name	0	Instrument	HCTultra
Comment	acn		

Acquisition Parameter

Ion Source Type	ESI	Ion Polarity	Positive	Alternating Ion Polarity	off
Mass Range Mode	Ultra Scan	Scan Begin	200 m/z	Scan End	650 m/z
Capillary Exit	128.5 Volt	Skimmer	40.0 Volt	Trap Drive	58.6
Accumulation Time	337 µs	Averages	10 Spectra	Auto MS/MS	off



Bruker Compass DataAnalysis 4.0 printed: 2009-10-26 19:56:00 Page 1 of 1

HRMS

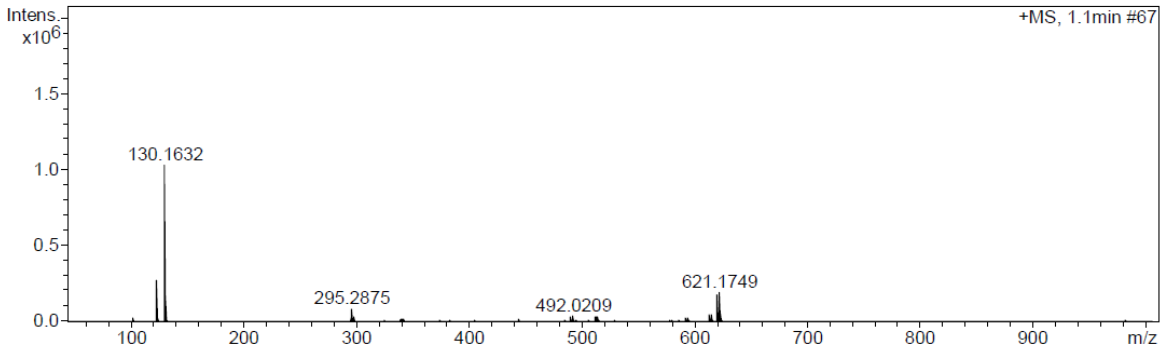
Mass Spectrum SmartFormula Report

Analysis Info

Analysis Name	G:\Data B\Blazej TOF\BD153_14122010.d	Acquisition Date	2010-12-14 10:37:13
Method	tune_low.m	Operator	Bruker Customer
Sample Name		Instrument / Ser#	micrOTOF 129
Comment	in ACN		

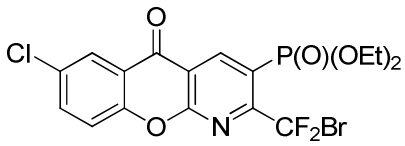
Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	1000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Source



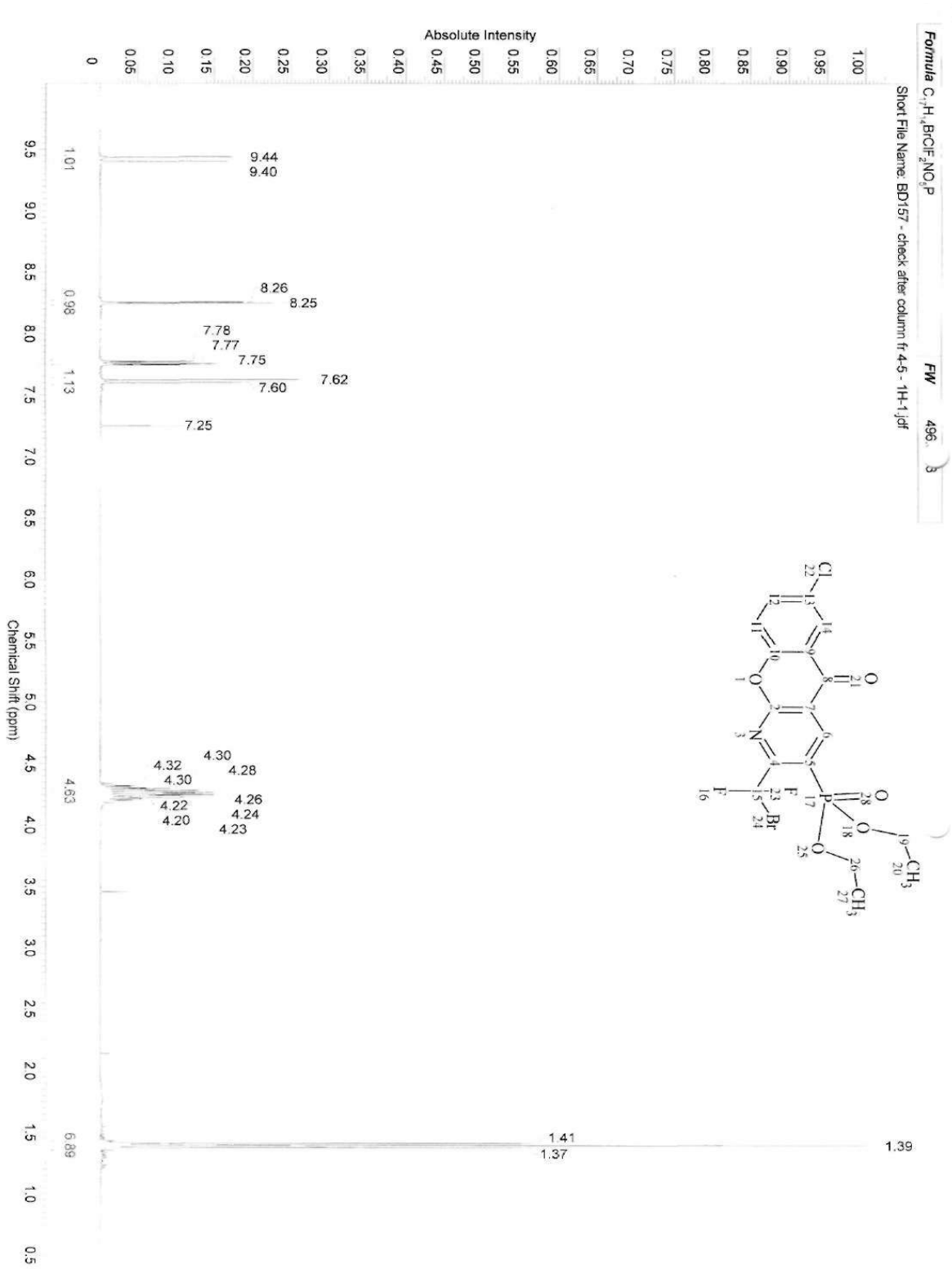
Meas. m/z	Formula	m/z	err [ppm]	Mean err [ppm]	rdb	N-Rule	e— Conf	mSigma
490.0225								
	C 19 H 20 Br F 2 N O 5 P	490.0225	0.1	-0.3	9.5	ok	even	41.70

15. *Diethyl (2-(bromodifluoromethyl)-7-chloro-5-oxo-5H-chromeno-[2,3-b]pyridin-3-yl)phosphonate* ***(3o)***

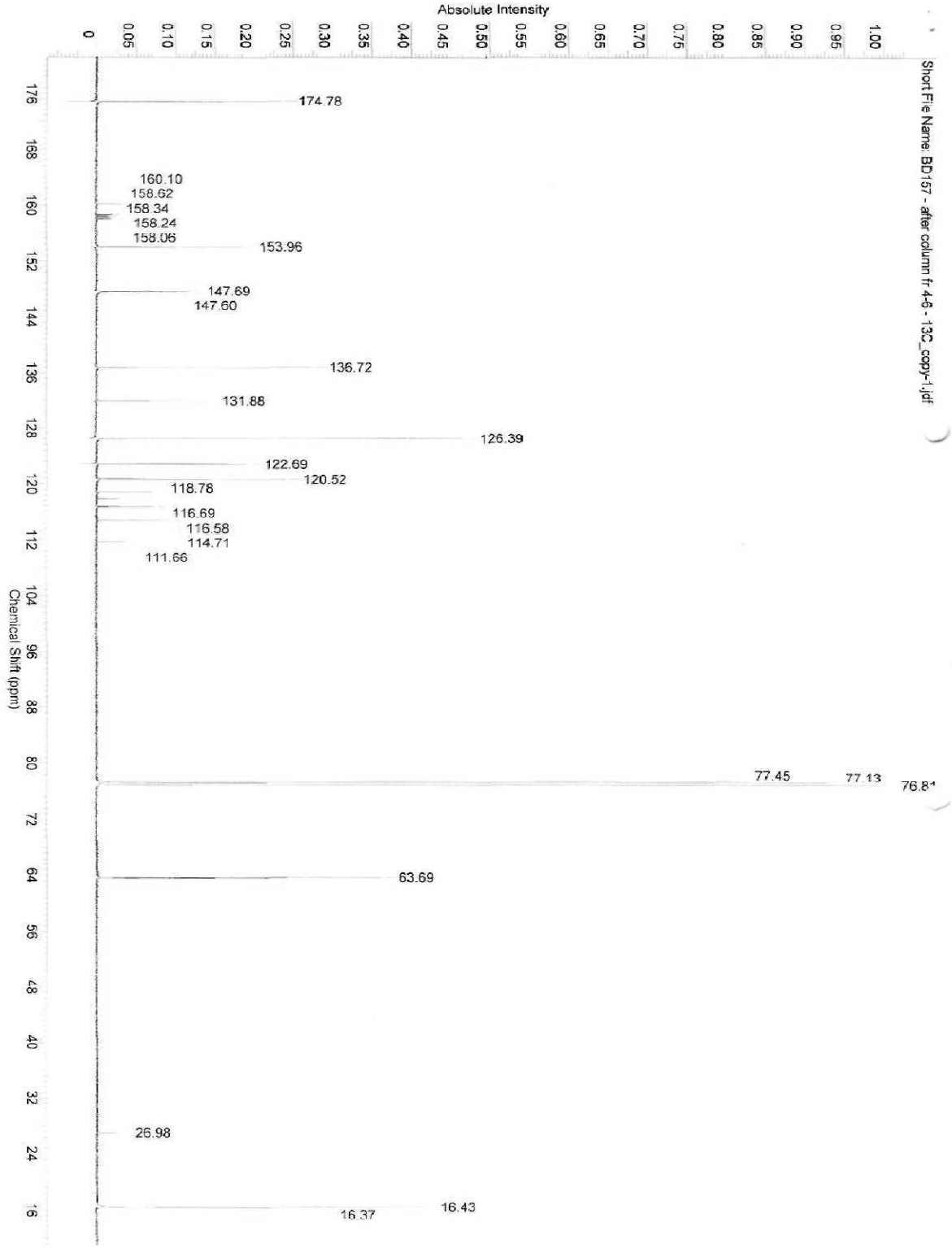


Orange crystals (63%); mp 115–119 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.39 (t, *J* = 7.9 Hz, 6H), 4.26 (m, 4H), 7.61 (d, *J* = 8.6 Hz, 1H), 7.76 (dd, *J* = 8.6 Hz, *J* = 2.1 Hz, 1H), 8.25 (d, *J* = 2.7 Hz, 1H), 9.42 (d, $^{3}J_{H–P}$ = 13.7 Hz, 1H); ^{13}C NMR (100 MHz): δ 16.4 (d, *J* = 5.6 Hz), 63.6 (d, *J* = 7.9 Hz), 114.7 (t, $^{1}J_{C–F}$ = 306.4 Hz), 116.6 (d, $^{2}J_{C–P}$ = 10.7 Hz), 119.4 (d, $^{1}J_{C–P}$ = 191.1 Hz), 120.5, 122.7, 126.4, 131.9, 136.7, 147.8 (d, $^{3}J_{C–P}$ = 8.5 Hz), 153.9, 158.4 (td, $^{2}J_{C–F}$ = 27.9 Hz, $^{2}J_{C–P}$ = 10.6 Hz), 174.8; ^{19}F NMR (376 MHz): δ –50.0; ^{31}P NMR (161 MHz): δ 10.9; MS (ESI) *m/z*: $[M+H]^+$ 495 (100%), $[M+Na]^+$ 518 (75%); HRMS (ESI) calcd for $[M+Na]^+$ $(C_{17}H_{14}BrClF_2NNaO_5P)^+$ 517.9342; found 517.9365.

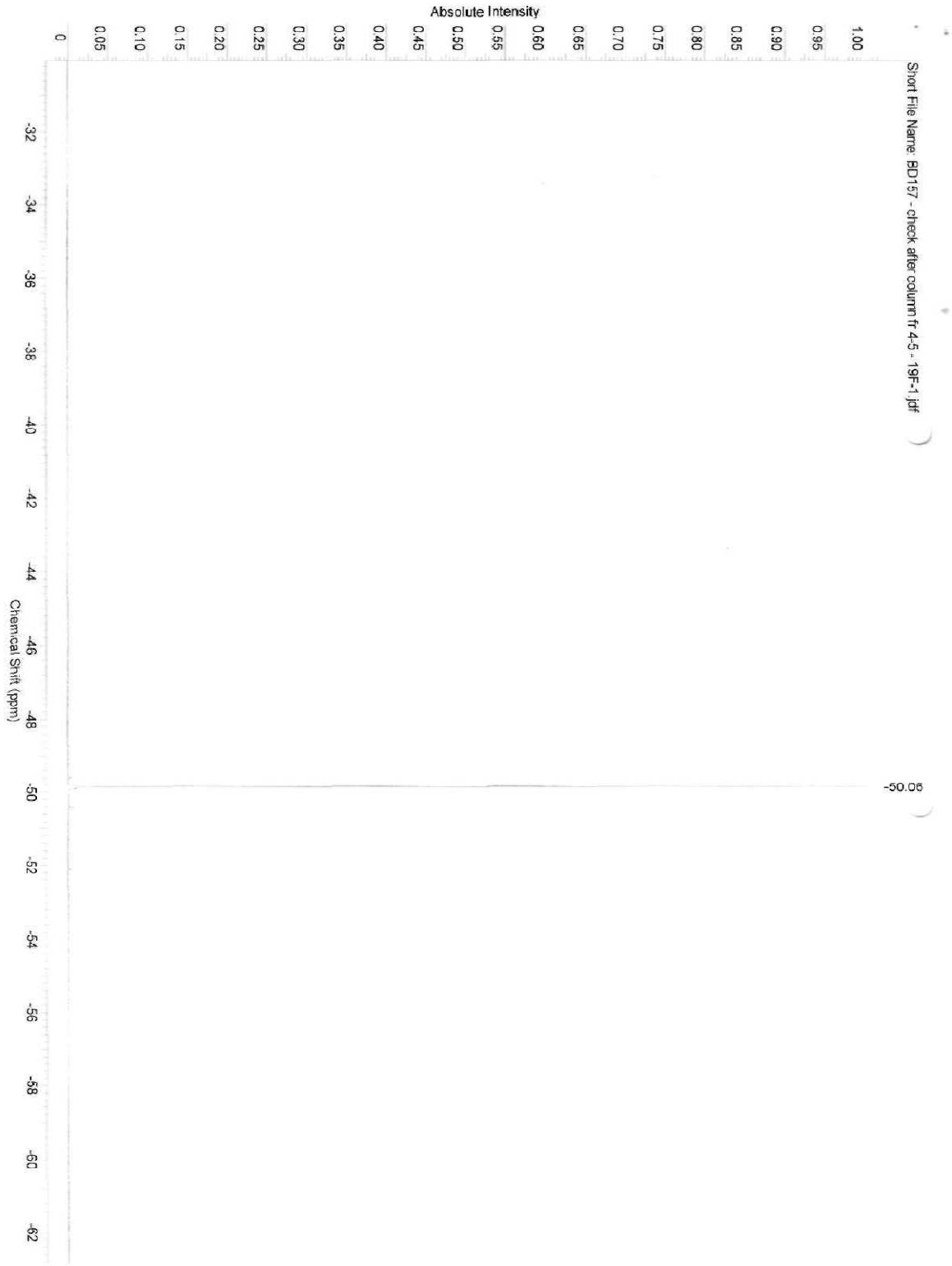
^{1}H NMR


Formula C17H18BrClF2NO5P
FW 496.
Short File Name: BD157 - check after column fr 4-5 - 1H-1.jdf
Absolute Intensity
Chemical Shift (ppm)
9.44
9.40
8.26
8.25
7.78
7.77
7.75
7.62
7.60
7.25
4.32
4.30
4.30
4.28
4.22
4.20
4.26
4.24
4.23
1.41
1.37
1.39
1.01
0.98
1.13
4.63
6.89

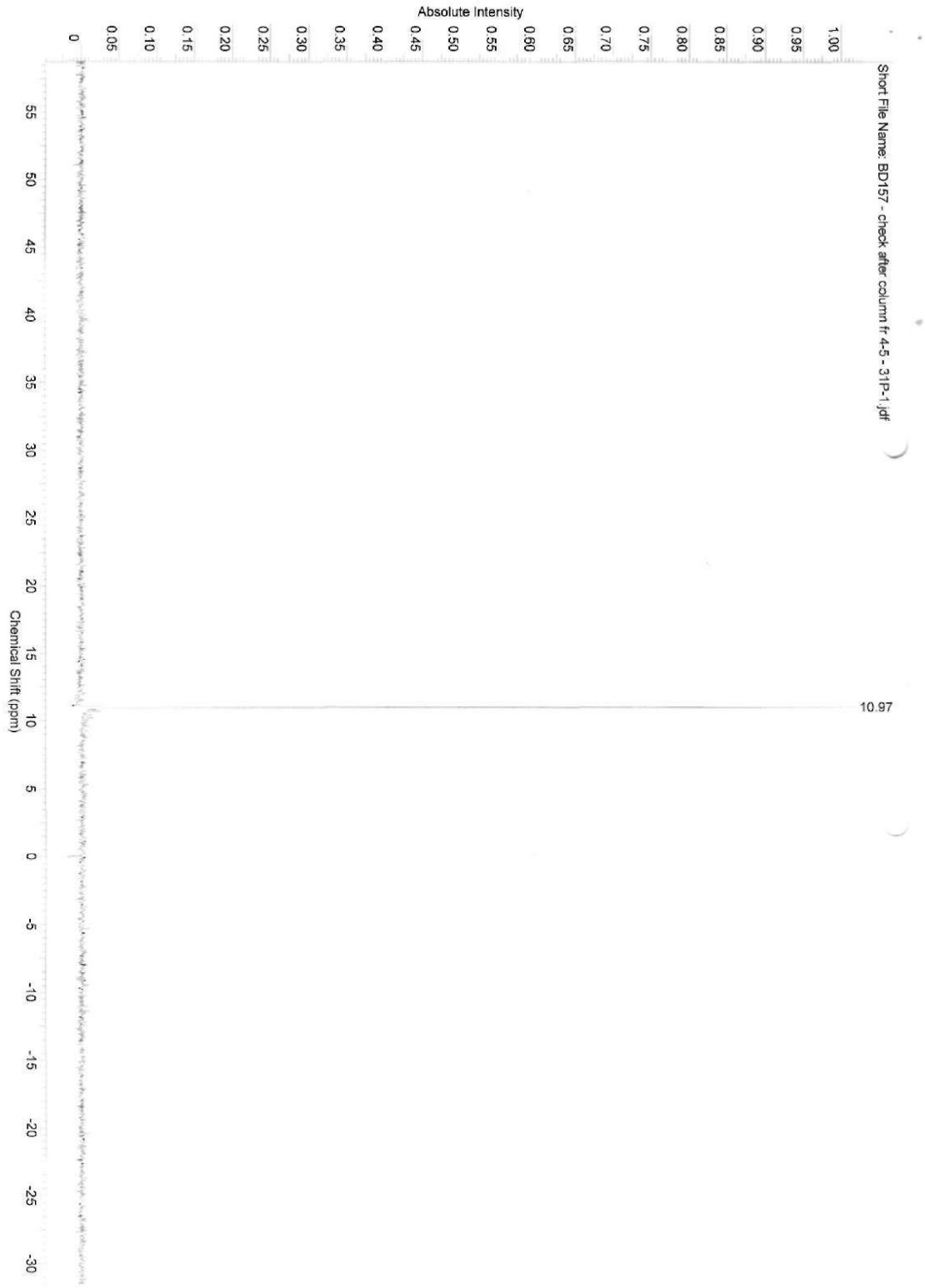
^{13}C NMR


Absolute Intensity
Short File Name: BD157 - after column fr 4-6 - 13C_copy-1.jdf
Chemical Shift (ppm)
174.78
160.10
158.62
158.34
158.24
158.06
153.96
147.69
147.60
136.72
131.88
126.39
122.69
120.52
118.78
116.69
116.58
114.71
111.66
77.45
77.13
76.81
63.69
26.98
16.37
16.43

^{19}F NMR


Short File Name: BD157 - check after column fr 4-5 - 19F-1.jdf
-50.06
Absolute Intensity
1.00
0.95
0.90
0.85
0.80
0.75
0.70
0.65
0.60
0.55
0.50
0.45
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0
Chemical Shift (ppm)
-32
-34
-38
-36
-40
-42
-44
-46
-48
-50
-52
-54
-56
-58
-60
-62

^{31}P NMR


Short File Name: BD157 - check after column fr 4-5 - 31P-1.jdf
10.97
Absolute Intensity
1.00
0.95
0.90
0.85
0.80
0.75
0.70
0.65
0.60
0.55
0.50
0.45
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0
Chemical Shift (ppm)
55
50
45
40
35
30
25
20
15
10
5
0
-5
-10
-15
-20
-25
-30

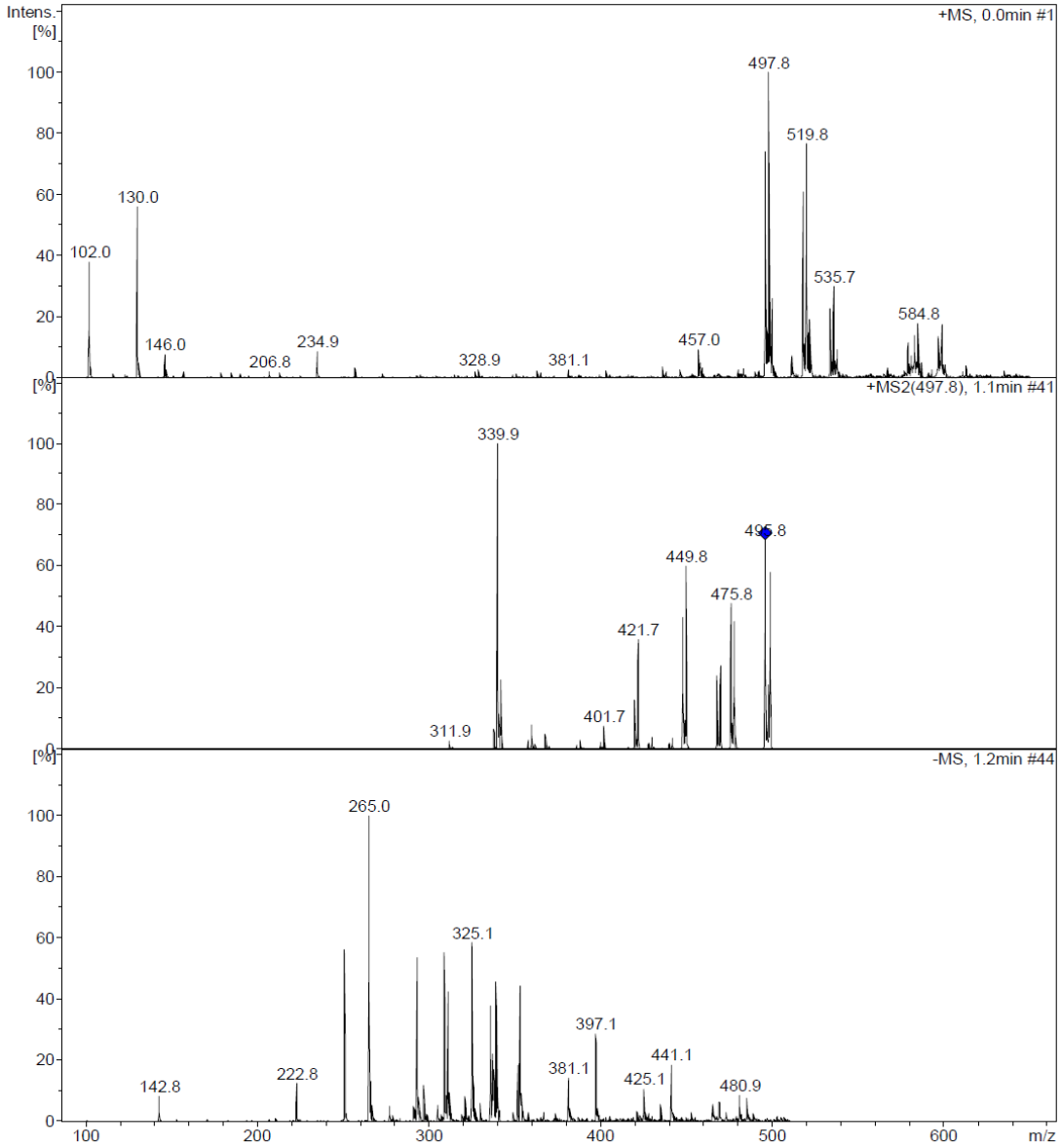
Display Report

Analysis Info

Analysis Name	G:\Data B\Blazej ION TRAP\BD157_14122010.d	Acquisition Date	2010-12-14 12:08:28
Method	DEF_MS.M	Operator	farnoosh
Sample Name	0	Instrument	HCTultra
Comment	acn		

Acquisition Parameter

Ion Source Type	ESI	Ion Polarity	Positive	Alternating Ion Polarity	off
Mass Range Mode	Ultra Scan	Scan Begin	100 m/z	Scan End	650 m/z
Capillary Exit	128.5 Volt	Skimmer	40.0 Volt	Trap Drive	58.6
Accumulation Time	2771 µs	Averages	10 Spectra	Auto MS/MS	off



Bruker Compass DataAnalysis 4.0 printed: 2009-10-26 19:52:20 Page 1 of 1

HRMS

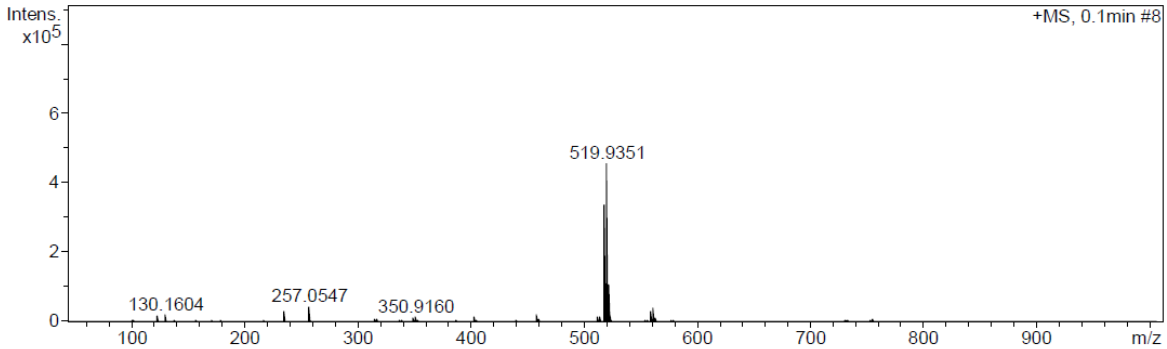
Mass Spectrum SmartFormula Report

Analysis Info

Analysis Name	G:\Data B\Blazej TOF\BD157_14122010.d	Acquisition Date	2010-12-14 10:53:06
Method	tune_low.m	Operator	Bruker Customer
Sample Name		Instrument / Ser#	micrOTOF 129
Comment	in ACN		

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	1000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Source



Meas. m/z	Formula	m/z	err [ppm]	Mean err [ppm]	rdb	N-Rule	e—Conf	mSigma
517.9365	C 17 H 14 Br Cl F 2 N Na O 5 P	517.9342	-4.4	-4.4	9.5	ok	even	13.27