Electronic Supplementary Material (ESI) for Medicinal Chemistry Communications
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SUPPLEMENTARY INFORMATION

Synthesis and biological activities of ferrocenyl derivatives of paclitaxel

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Contents

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Experimental

Commercially available solvents (HPLC grade – ALDRICH) and reagents (ALDRICH or AKSCI (USA) or HBCChem (USA)) were used as received. Microanalyses (C, H, and N) and MS spectra were performed at The Centre of Molecular and Macromolecular Studies in Łódź (Polish Academy of Sciences), Poland. MS spectra (MALDI-TOF) were recorded on Voyager-Elite, PerSeptive Biosystems Inc. (Framingham, MA, USA), pulse laser at 337 nm was used. ^{1}H and ^{13}C nuclear magnetic resonance spectra were recorded on Bruker Avance III 600 MHz spectrometer operating at 600.26 and 150.95 MHz respectively. Chemical shifts were determined relative to the solvent residual peaks.

Synthesis

General procedure of acylation of taxoids with ferrocene acids.

2'-ferrocenoylpaclitaxel 3

To a solution of 85.4 mg (0.10 mmol) of paclitaxel **1** and 25.4 mg (0.11 mmol) of ferrocenecarboxylic acid and 13 mg (0.11 mmol) of DMAP in 5 ml of anhydrous dichloromethane, diisopropylcarbodiimide (DIC) (25.2 mg, 0.20 mmol, 31 µl) was added and the resulted solution was stirred at 0^{o}C. After 4 h the organic solvent was evaporated and the product was purified by chromatography on silica gel (50 g) using n-hexane – ethyl acetate 1-1 as eluent. Yield: 71 mg, 67%, of an orange crystals.

^{1}H NMR (600.26 MHz, *CDCl$_3$*): δ 1.15 (3 H, s), 1.25 (3 H, s), 1.70 (3 H, s), 1.90 (1 H, t, *J*=12.23 Hz), 2.03 (3 H, s), 2.14 (1 H, dd, *J*=15.25, 8.85 Hz), 2.23 (3 H, s), 2.38 (1 H, dd,

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J=15.25, 9.22 Hz), 2.50 (3 H, s), 2.58 (1 H, ddd, *J*=15.06, 9.03, 6.78 Hz), 3.85 (1 H, d, *J*=6.78 Hz), 4.15 (5 H, s), 4.22 (1 H, d, *J*=8.28 Hz), 4.33 (1 H, d, *J*=8.28 Hz), 4.47 (3 H, br. s.), 4.79 (1 H, br. s.), 4.82 (1 H, br. s.), 4.99 (1 H, d, *J*=9.03 Hz), 5.55 (1 H, d, *J*=3.01 Hz), 5.70 (1 H, d, *J*=7.15 Hz), 6.00 (1 H, d, *J*=6.40 Hz), 6.28 - 6.31 (1 H, m), 6.33 (1 H, s), 7.00 (1 H, d, *J*=8.28 Hz), 7.33 - 7.38 (1 H, m), 7.42 - 7.49 (6 H, m), 7.51 - 7.56 (3 H, m), 7.59 - 7.66 (1 H, m), 7.81 (2 H, d, *J*=7.53 Hz), 8.14 (2 H, d, *J*=7.53 Hz)
^{13}C NMR (150.95 MHz, *CDCl$_3$*): δ 9.61, 14.18, 14.91, 20.80, 22.17, 22.76, 26.82, 35.51, 35.63, 43.18, 45.60, 53.13, 58.54, 60.36, 68.84, 69.99, 70.14, 70.35, 71.69, 71.90, 72.01, 72.11, 74.13, 75.16, 75.62, 76.43, 79.22, 81.08, 84.46, 126.42, 127.02, 128.49, 128.73, 128.80, 129.10, 129.22, 130.21, 132.02, 132.70, 133.64, 133.83, 137.29, 143.00, 167.04, 168.22, 169.75, 170.86, 171.10, 171.22, 203.83

IR (KBr) ν_{max}/cm^{-1}: 3447 (NH), 1720 (C=O)

Elemental analysis calculated for $C_{58}H_{59}FeNO_{15}$ C-65.35, H – 5.58, N – 1.31 found C – 65.40, H – 5.62, N – 1.28

MS (MALDI, HCHA): calculated for $C_{58}H_{59}FeNO_{15}$: 1065.32, found: 1065.28

2'-(3-ferrocenoylpropiolyl)paclitaxel 4

It was prepared in the same method as **3** starting from 3-ferrocenoylpropionic acid (32mg, 0.2 mmol) instead of ferrocenecarboxylic acid. Yield: 77.4 mg, 69% (orange crystals).

1H NMR (600.26 MHz. *CDCl$_3$*): δ 1.14 (3 H, s), 1.23 (3 H, s), 1.68 (3 H, s), 1.82 (1 H, br. s.), 1.86 (1 H, s), 1.87 - 1.90 (1 H, m), 1.93 (3 H, s), 2.14 (1 H, dd, *J*=15.43, 9.03 Hz), 2.22 (3 H, s), 2.34 (1 H, dd, *J*=15.43, 9.41 Hz), 2.44 (3 H, s), 2.49 (1 H, br. s.), 2.51 - 2.58 (1 H, m), 2.79 - 2.86 (2 H, m), 2.99 - 3.06 (1 H, m), 3.06 - 3.14 (1 H, m), 3.81 (1 H, d, *J*=6.78 Hz), 4.22 (5 H, s), 4.31 (1 H, d, *J*=8.28 Hz), 4.39 - 4.46 (1 H, m), 4.52 (2 H, d, *J*=1.13 Hz), 4.77 (2 H, dd, *J*=8.66, 1.13 Hz), 4.96 (1 H, d, *J*=8.66 Hz), 5.52 (1 H, d, *J*=3.76 Hz), 5.68 (1 H, d, *J*=7.15 Hz), 5.95 (1 H, dd, *J*=8.66, 3.39 Hz), 6.25 (1 H, t, *J*=8.85 Hz), 6.28 (1 H, s), 7.08 (1 H, d, *J*=8.66 Hz), 7.33 (1 H, td, *J*=5.46, 2.63 Hz), 7.40 - 7.45 (6 H, m), 7.49 - 7.55 (3 H, m), 7.59 - 7.64 (1 H, m), 7.80 (2 H, d, *J*=7.15 Hz), 8.14 (2 H, d, *J*=7.53 Hz)
13C NMR (150.95 MHz. *CDCl$_3$*): δ 9.94, 14.18, 21.01, 22.60, 23.47, 26.37, 27.47, 28.16, 33.87, 35.58, 36.87, 42.16, 43.10, 46.41, 57.60, 60.33, 69.11, 69.29, 69.94, 71.79, 71.86, 72.29, 72.31, 74.49, 74.58, 75.06, 76.56, 78.24, 78.91, 80.33, 80.99, 84.22, 126.50, 128.17,

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128.68, 128.86, 129.27, 130.18, 133.60, 135.52, 139.18, 156.90, 167.06, 168.14, 169.65, 171.13, 172.20, 201.47, 211.58

IR (KBr) ν_{max}/cm^{-1}: 3432 (NH), 1741 (C=O), 1725 (C=O)

Elemental analysis calculated for $C_{61}H_{63}FeNO_{16}$ C-65.30, H – 5.66, N – 1.25 found C – 65.18, H – 5.72, N – 1.38

MS (MALDI, HCHA): calculated for $C_{61}H_{63}FeNO_{16}$: 1121.35, found: 1121.45

2'-ferrocenoyldocetaxel 5

It was prepared in the same method as **3** starting from docetaxel (80.5 mg, 0.10 mmol) instead of paclitaxel. Yield: 67mg, 66% (orange crystals).

^{1H} NMR (600.26 MHz. *CDCl*$_3$): δ 1.14 (3 H, s), 1.25 (3 H, s), 1.37 (9 H, s), 1.67 (3H, s), 1.77 (3 H, s), 1.87 (1 H, t, *J*=12.42 Hz), 2.03 (3 H, s), 2.11 - 2.19 (1 H, m), 2.34 (1 H, br. s.), 2.48 (3 H, br. s.), 2.56 - 2.65 (1 H, m), 3.97 (1 H, d, *J*=7.15 Hz), 4.11 (5 H, s), 4.19 - 4.25 (2 H, m), 4.29 (1 H, d, *J*=4.52 Hz), 4.34 (1 H, d, *J*=8.66 Hz), 4.44 (2 H, br. s.), 4.76 (1 H, br. s.), 4.81 (1 H, br. s.), 4.99 (1 H, d, *J*=9.04 Hz), 5.25 (1 H, s), 5.43 (1 H, br. s.), 5.55 (1 H, br. s.), 5.71 (1 H, d, *J*=7.15 Hz), 6.25 - 6.35 (1 H, m), 7.30 - 7.35 (1 H, m), 7.38 - 7.42 (2 H, m), 7.43 - 7.47 (2 H, m), 7.52 (2 H, t, *J*=7.72 Hz), 7.60 - 7.64 (1 H, m), 8.13 (2 H, d, *J*=7.53 Hz)
^{13}C NMR (150.95 MHz. *CDCl*$_3$): δ 9.95, 14.15, 20.93, 20.99, 22.68, 26.34, 28.17, 35.58, 36.85, 43.09, 46.42, 57.57, 60.36, 68.92, 69.98, 70.10, 70.44, 71.71, 71.80, 71.85, 74.37, 74.48, 75.09, 76.54, 78.95, 81.00, 84.23, 126.24, 128.18, 128.66, 128.91, 129.30, 130.16, 133.57, 135.43, 167.02, 168.14, 169.69, 170.95, 171.13, 211.53,

IR (KBr) ν_{max}/cm^{-1}: 3447 (NH), 1720 (C=O)

Elemental analysis calculated for $C_{54}H_{61}FeNO_{15}$ C-63.59, H – 6.03, N – 1.37 found C – 63.52, H – 6.11, N – 1.42

MS (MALDI, HCHA): calculated for $C_{54}H_{61}FeNO_{15}$: 1119.34, found: 1119.34

2'-(3-ferrocenoylpropiolyl)docetaxel 6

It was prepared in the same method as **4** starting from docetaxel (80.5 mg, 0.10 mmol) instead of paclitaxel. Yield: 74 mg, 69% (orange crystals).

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^{1}H NMR (600.26 MHz, *CDCl$_3$*) δ 1.13 (3 H, s), 1.24 (3 H, s), 1.35 (9 H, s), 1.68 (2 H, s), 1.75 (3 H, s), 1.85 (1 H, t, *J*=12.42 Hz), 1.95 (3 H, s), 2.05 (2 H, s), 2.14 - 2.22 (1 H, m), 2.32 (1 H, br. s.), 2.43 (3 H, br. s.), 2.53 - 2.61 (1 H, m), 2.75 - 2.83 (2 H, m), 2.94 - 3.01 (1 H, m), 3.03 - 3.11 (1 H, m), 3.94 (1 H, d, *J*=6.78 Hz), 4.17 - 4.21 (2 H, m), 4.23 (5 H, s), 4.33 (1 H, d, *J*=8.66 Hz), 4.52 (2 H, s), 4.78 (1 H, br. s.), 4.80 (1 H, br. s.), 4.96 (1 H, d, *J*=9.03 Hz), 5.20 (1 H, s), 5.37 (1 H, br. s.), 5.45 (2 H, br. s.), 5.70 (1 H, d, *J*=6.78 Hz), 6.26 (1 H, br. s.), 7.33 (3 H, d, *J*=7.53 Hz), 7.38 - 7.43 (2 H, m), 7.48 - 7.54 (2 H, m), 7.59 - 7.64 (1 H, m), 8.13 (2 H, d, *J*=7.53 Hz)

^{13}C NMR (150.95 MHz, *CDCl$_3$*) δ 211.58, 201.47, 172.20, 171.13, 169.65, 168.14, 167.06, 156.90, 139.18, 135.52, 133.60, 130.18, 129.27, 128.86, 128.68, 128.17, 126.50, 84.22, 80.99, 80.33, 78.91, 78.24, 76.56, 75.06, 74.58, 74.49, 72.31, 72.29, 71.86, 71.79, 69.94, 69.29, 69.11, 60.37, 57.60, 46.41, 43.10, 42.20, 36.87, 35.58, 33.84, 28.16, 27.47, 26.37, 22.60, 20.89, 14.18, 9.94,

IR (KBr) ν_{max}/cm^{-1}: 3442 (NH), 1741 (C=O), 1717 (C=O)

Elemental analysis calculated for $C_{57}H_{65}FeNO_{16}$ C-63.63, H – 6.09, N – 1.30 found C – 63.57, H – 6.28, N – 1.24

MS (MALDI, HCHA): calculated for $C_{57}H_{65}FeNO_{16}$:1075.67, found: 1075.37

Cytotoxic activity

The sensitivity of the parental and multidrug-resistant cancer cell lines was determined by a modified MTT-reduction assay. Shortly, the cells suspended in 100 µl of medium were seeded on the 96-well plates at the density of 5000 cells/well. The cells were allowed to attach for 24 hours and then the investigated compounds at the desired concentration was administered. The stock solutions of the taxanes were prepared in dimethylsulphoxide (DMSO) and care was taken to keep solvent concentration equal in all wells including controls. The final DMSO concentration did not exceed 0.1% v/v and was proven to be non-toxic to the cells. After 70 hours of incubation, MTT was added to the medium to a final concentration of 1.1 mmole/l. After further 2 hours the medium was removed and the formazane crystals were dissolved in 100 µl of DMSO. The absorbance was measured at 580 nm analytical wavelength and 720 nm reference wavelength. The results were turned into percentage of controls and the IC50 values for each cell line and drug were calculated by GraphPad Prism 4.03 software (GraphPad Inc. La Jolla, California, USA).

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Tubulin affinity

The tubulin affinity was measured with Tubulin Polymerization Assay Biochem Fluorescence Based Kit (Cytoskeleton Inc., Denver, Colorado, USA) according to the manufacturer's instructions. The investigated compounds were added to a reaction medium in a final concentration range from 0.6 up to 3.0 μM. The tubulin polymerization rate was determined from the linear portion of a polymerization curve and plotted against the drug concentration. The affinity constant was calculated by GraphPad Prism 4.03 software (GraphPad Inc. La Jolla, California, USA).

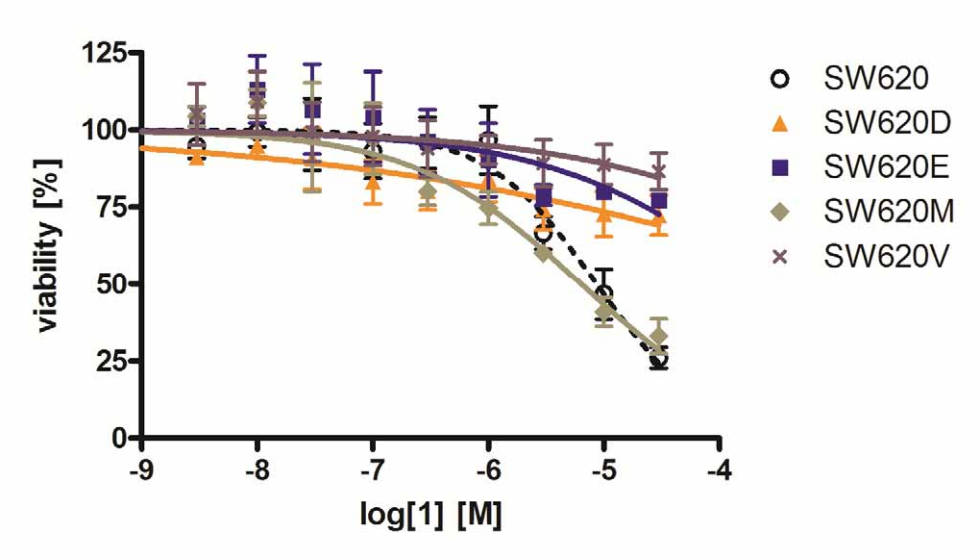

Figure S1. Viability of cancer cell lines in the presence of **1**

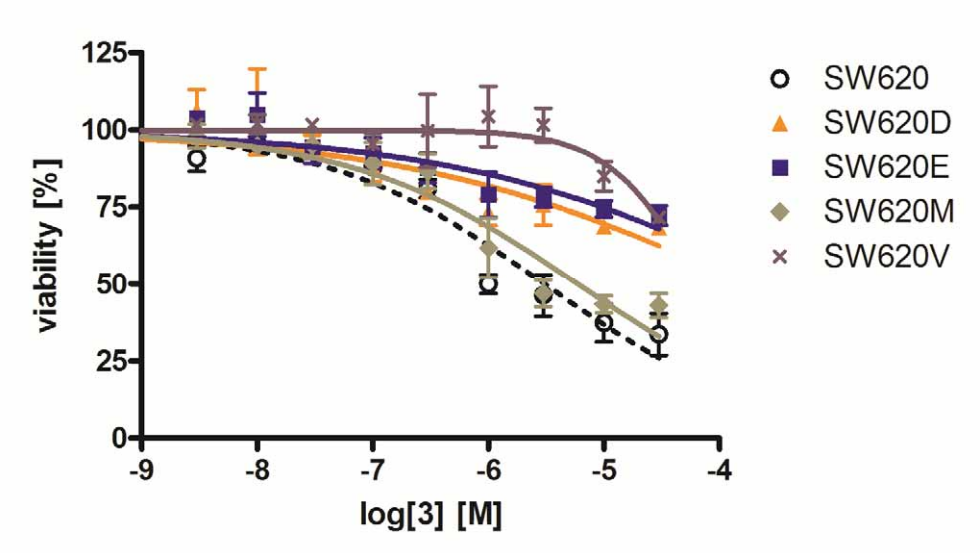

Figure S2. Viability of cancer cell lines in the presence of **3**

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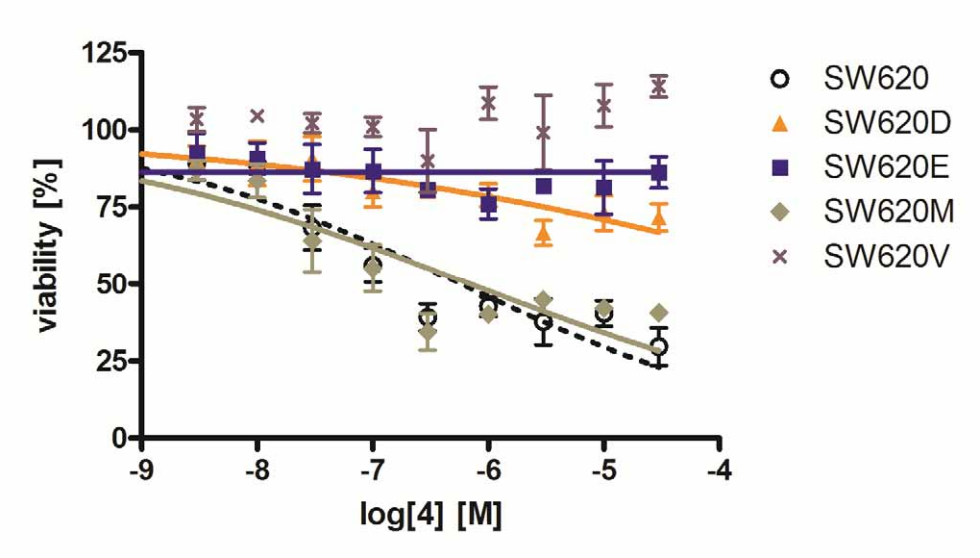

Figure S3. Viability of cancer cell lines in the presence of **4**

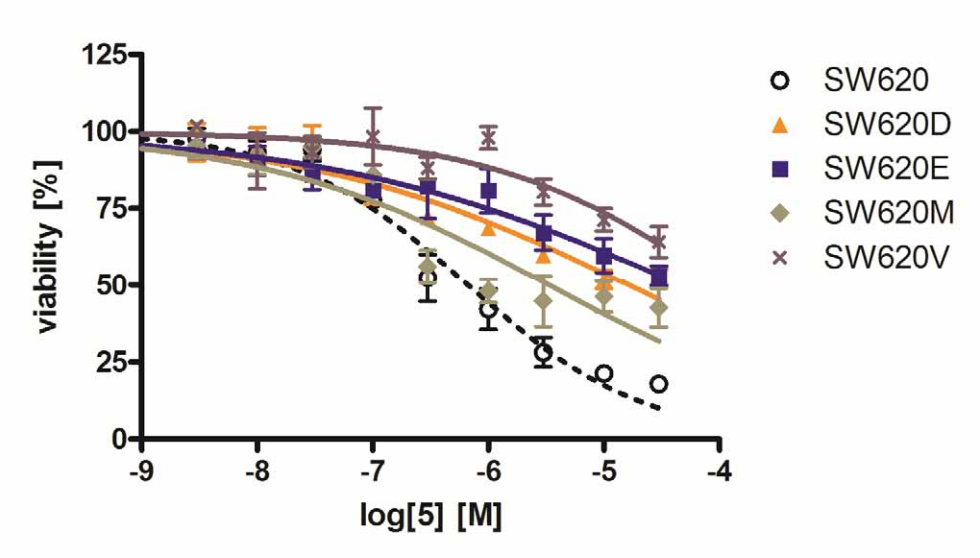

Figure S4. Viability of cancer cell lines in the presence of **5**

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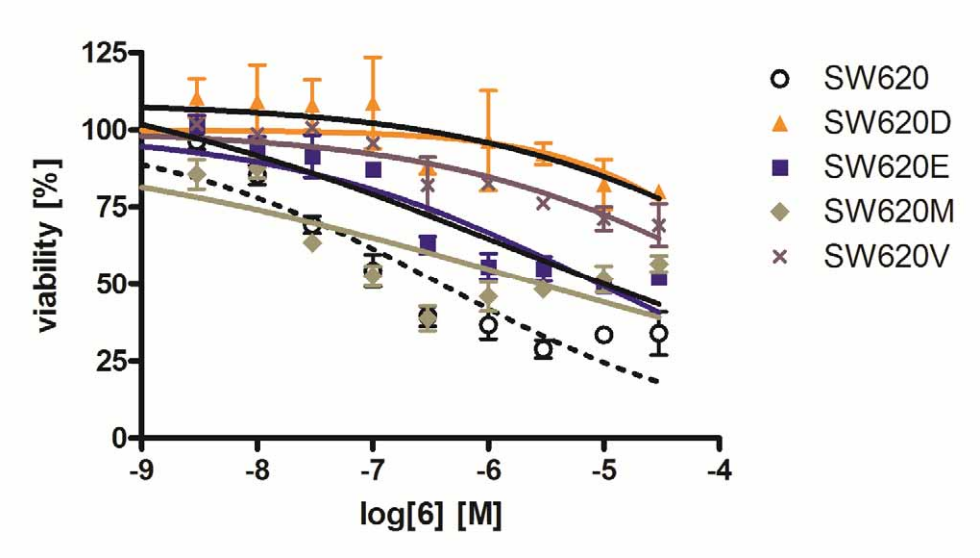

Figure S5. Viability of cancer cell lines in the presence of **6**

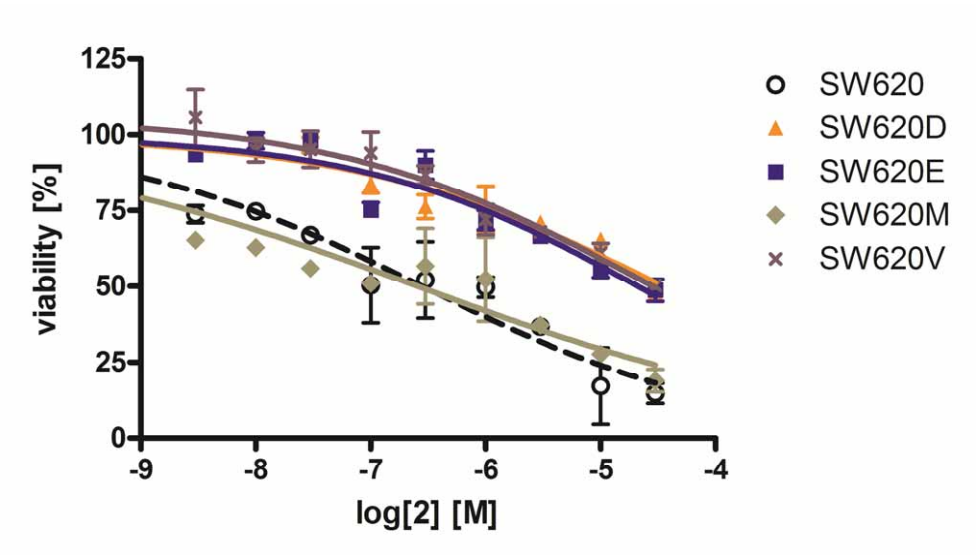

Figure S6. Figure S1. Viability of cancer cell lines in the presence of **2**

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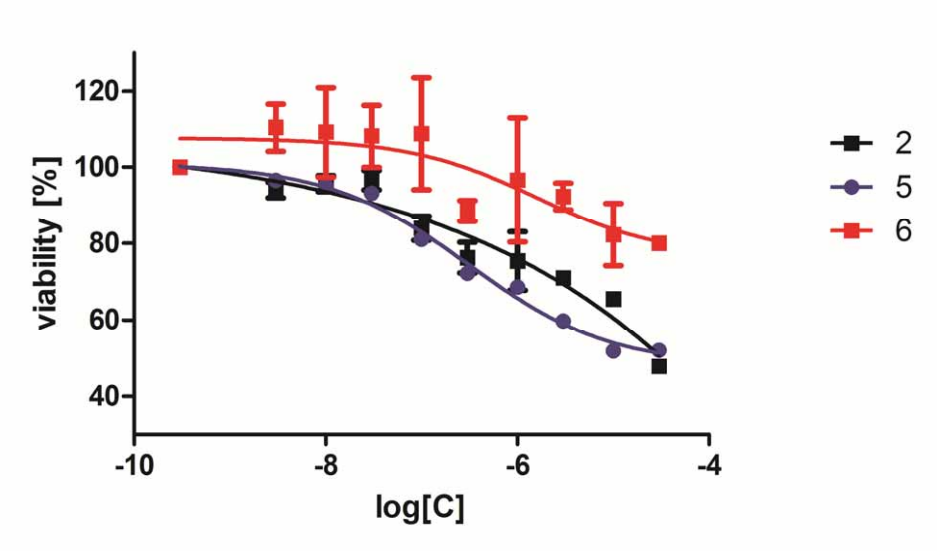


Figure S7. Viability of SW620D cell line in the presence of **2, 5** and **6**

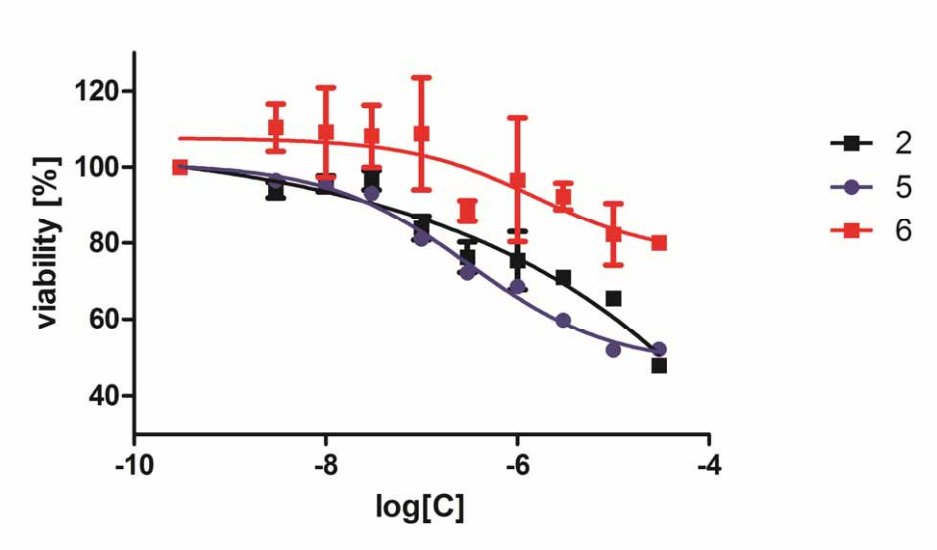
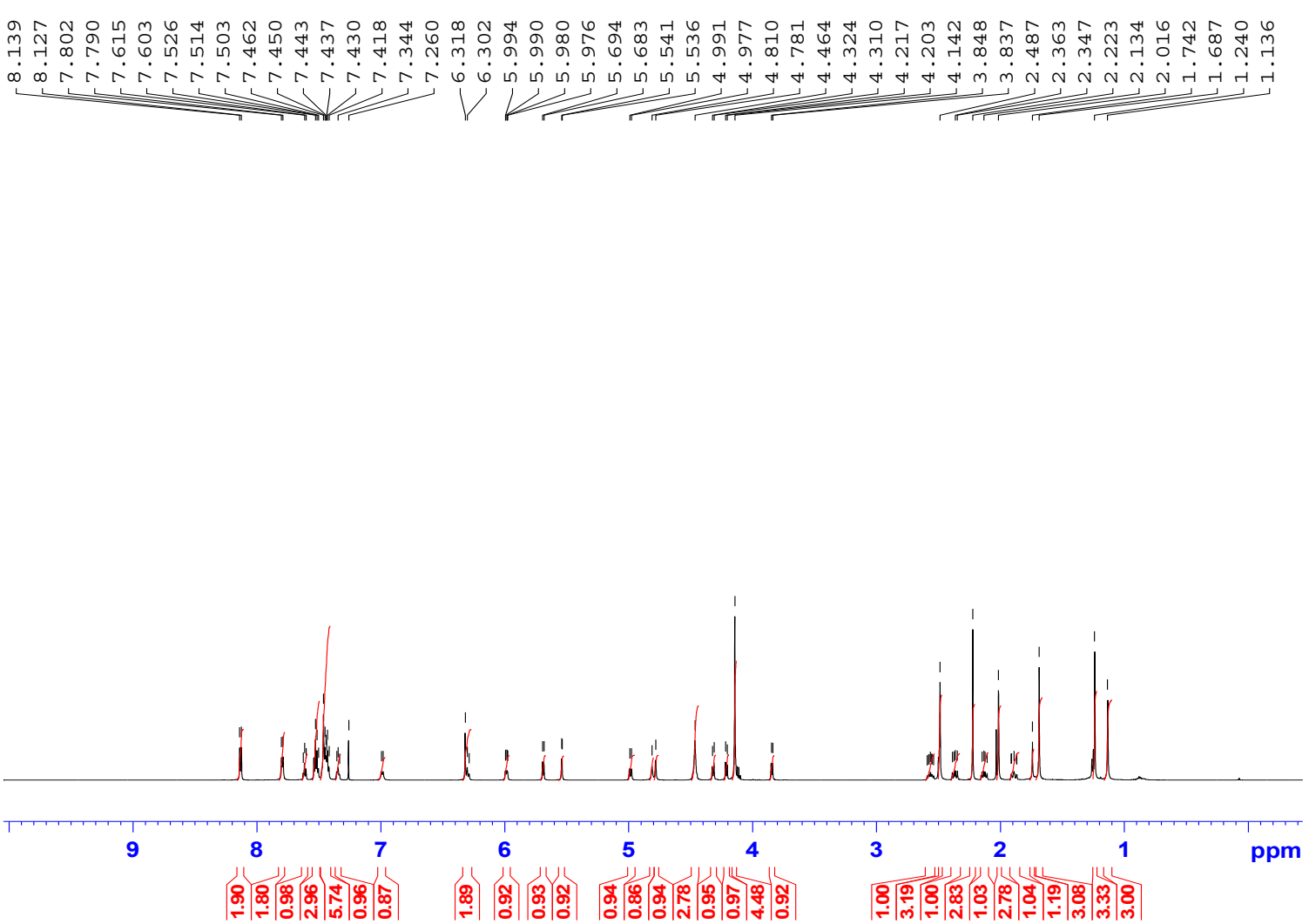


Figure S8. Viability of SW620E cell line in the presence of **2, 5** and **6**

^{1}H NMR of **3**

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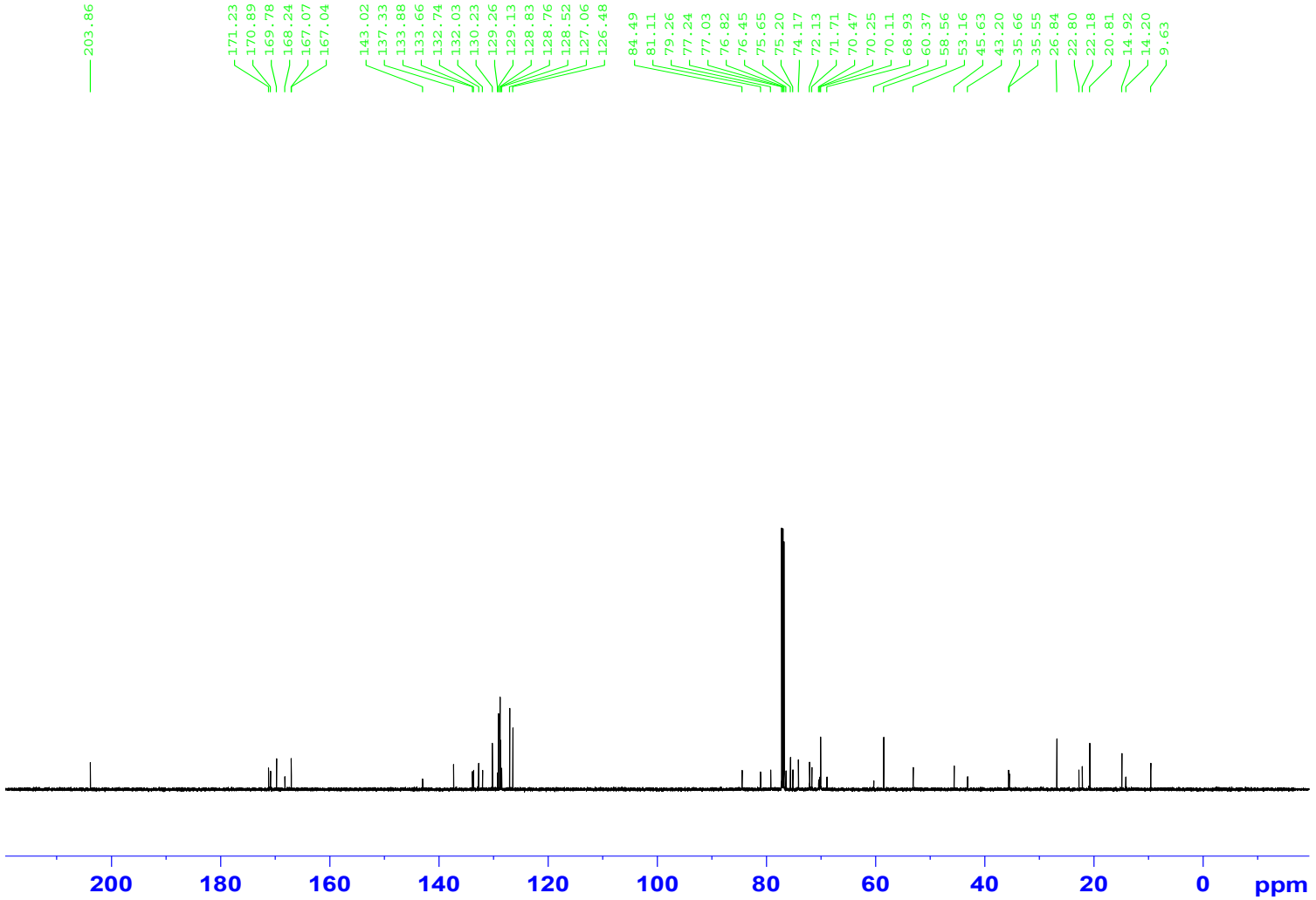
^{13}C NMR of **3**

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F2 - Processing parameters
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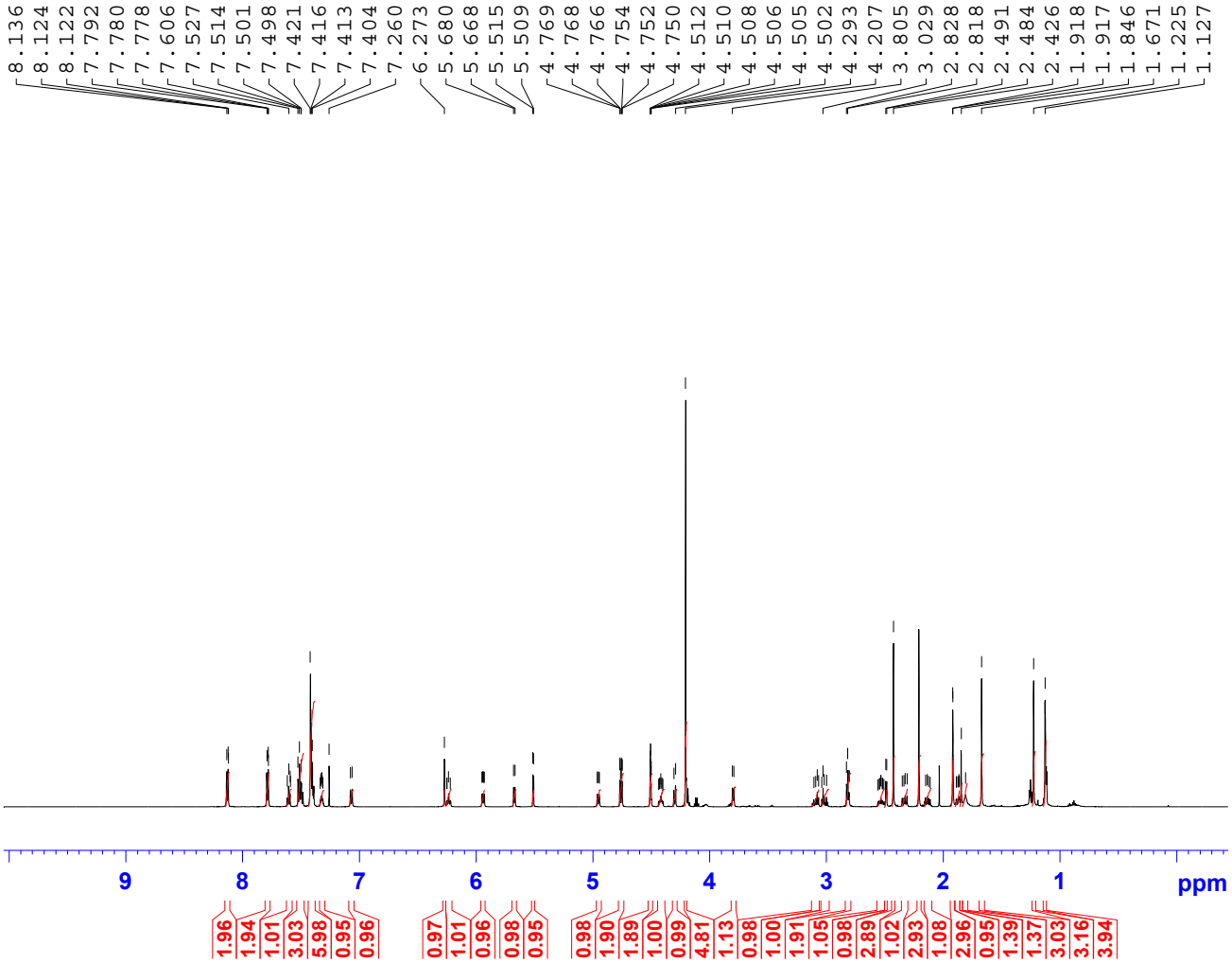
^{1}H NMR of **4**

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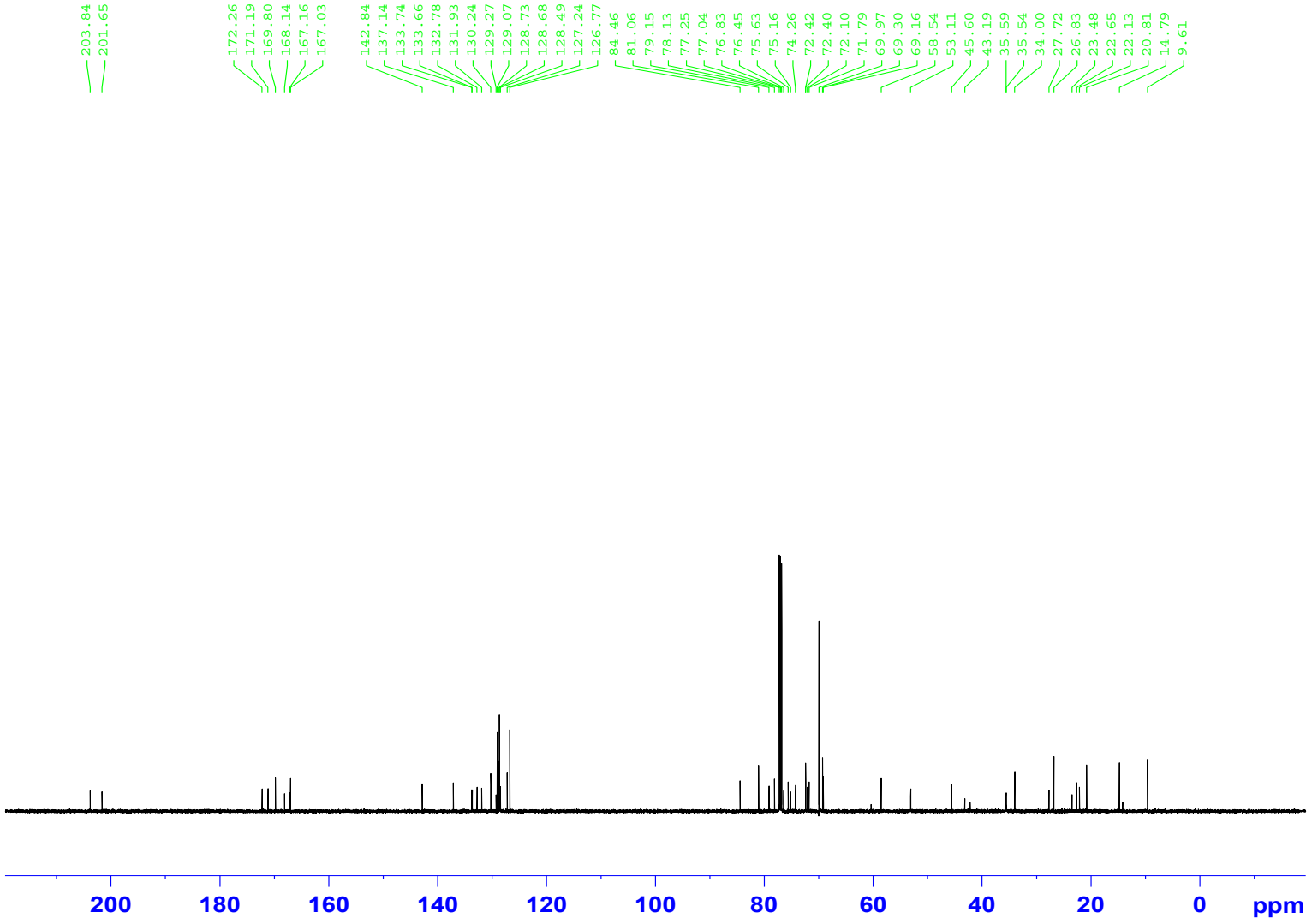
^{13}C NMR of **4**



BRUKER

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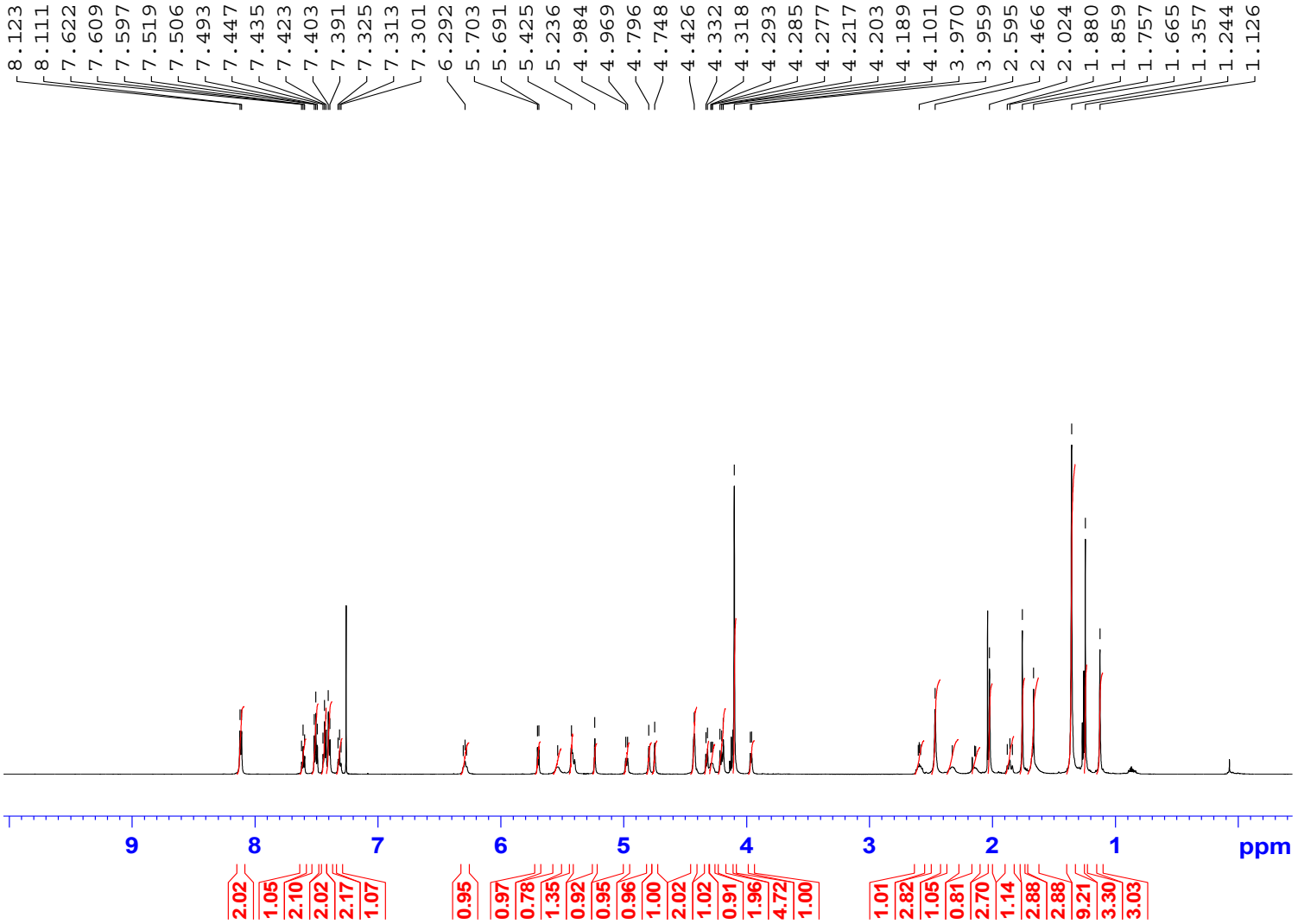
^{1}H NMR of **5**

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DS                            2
SWH                   12335.526 Hz
FIDRES                 0.188225 Hz
AQ                    2.6564426 sec
RG                          203
DW                       40.533 usec
DE                        8.50 usec
TE                       302.0 K
D1                    1.00000000 sec
TD0                           1

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SFO1                600.2637069 MHz

F2 - Processing parameters
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SF                  600.2600174 MHz
WDW                          EM
SSB               0
LB                        0.30 Hz
GB                0
PC                        1.00
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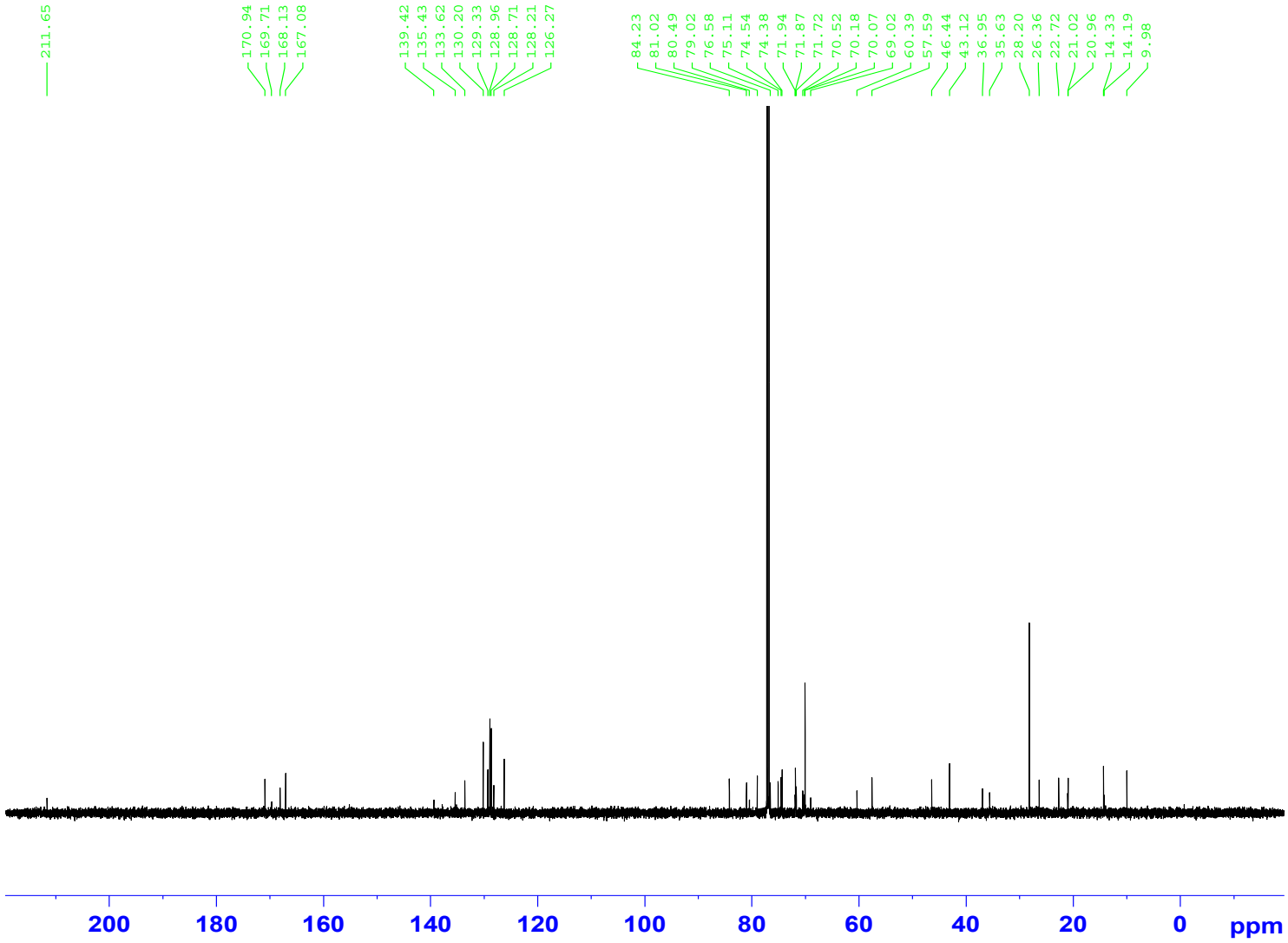
^{13}C NMR of **5**

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EXPNO                  10
PROCNO                  1

F2 - Acquisition Parameters
Date_            20111212
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INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                  1024
DS                     4
SWH            36057.691 Hz
FIDRES          0.550197 Hz
AQ             0.9088159 sec
RG                  2050
DW                13.867 usec
DE                  8.50 usec
TE                 302.0 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                 10.50 usec
PL1       0 dB
PL1W         91.93504333 W
SFO1        150.9505906 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2              90.00 usec
PL2                -3.00 dB
PL12               16.26 dB
PL13               18.00 dB
PL2W         30.57242203 W
PL12W         0.36251819 W
PL13W         0.24284537 W
SFO2        600.2624010 MHz

F2 - Processing parameters
SI                 32768
SF          150.9354970 MHz
WDW                   no
SSB       0
LB        0 Hz
GB        0
PC                  1.40
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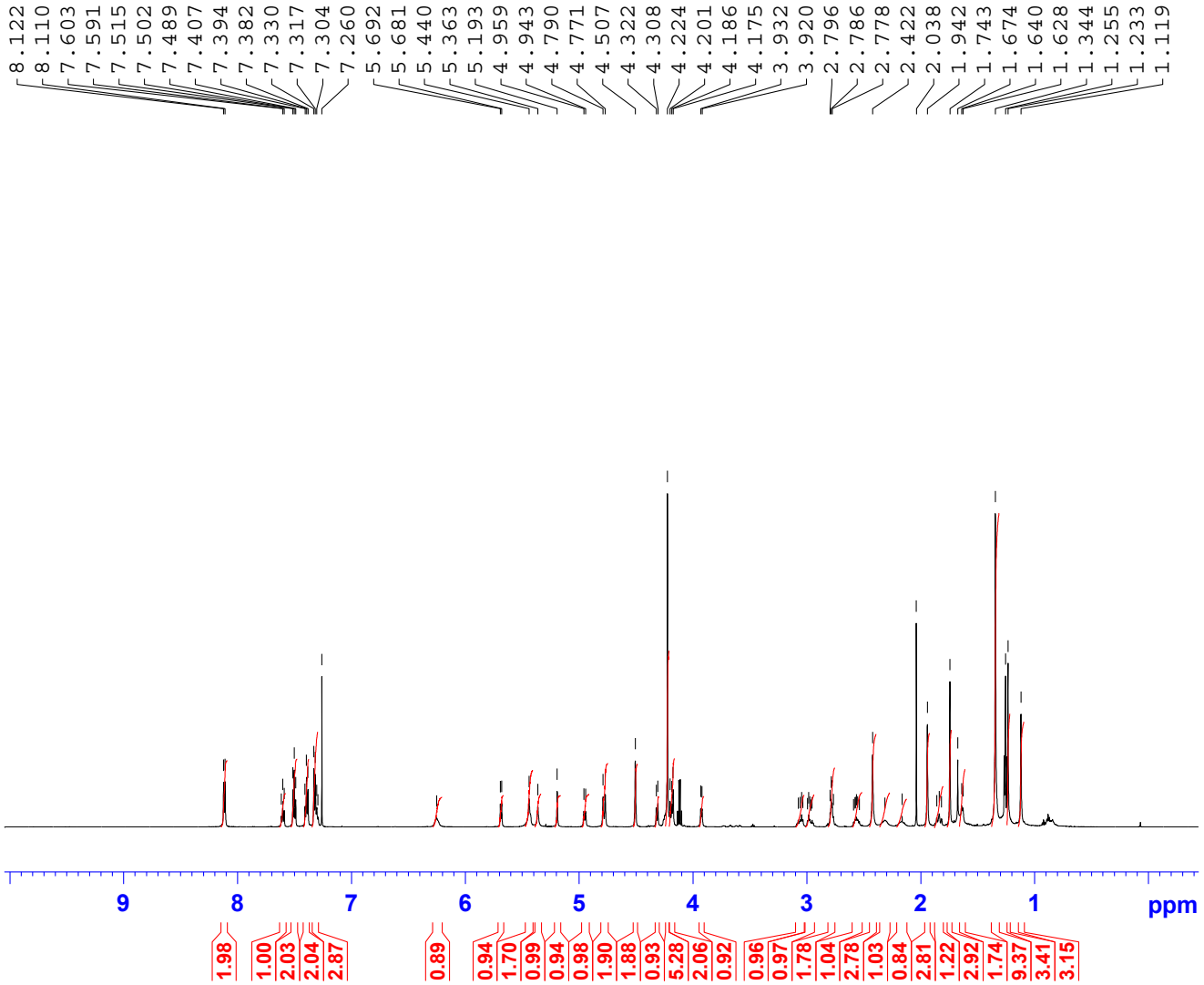
^{1}H NMR of **6**

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EXPNO                12
PROCNO                1

F2 - Acquisition Parameters
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Time              16.00
INSTRUM           spect
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PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                   16
DS                    2
SWH           12335.526 Hz
FIDRES         0.188225 Hz
AQ            2.6564426 sec
RG                  181
DW               40.533 usec
DE                8.50 usec
TE                301.9 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                  1H
P1                 9.40 usec
PL1               -3.00 dB
PL1W        30.57242203 W
SFO1        600.2637069 MHz

F2 - Processing parameters
SI                32768
SF          600.2600174 MHz
WDW                  EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
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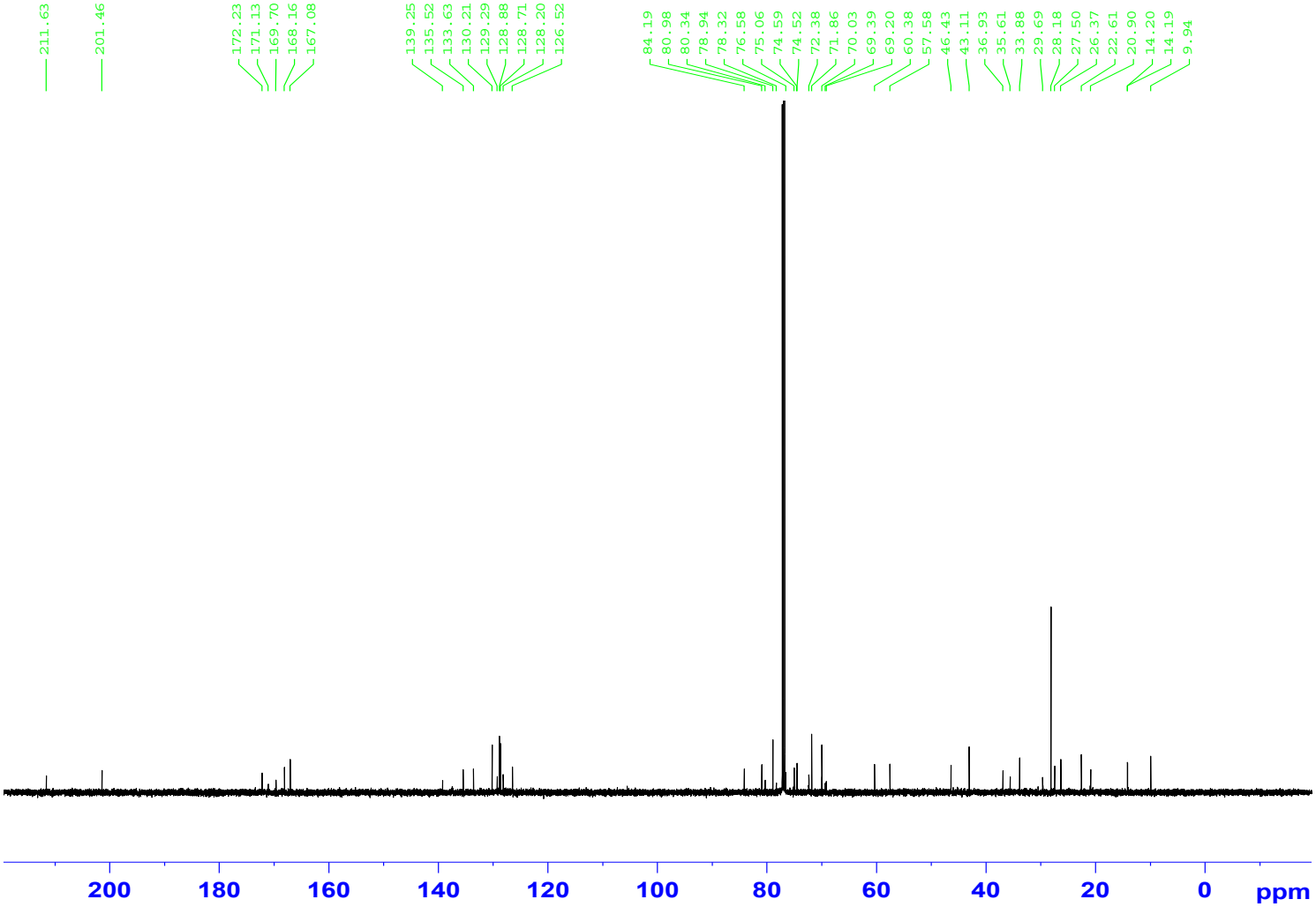
^{13}C NMR of **6**

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Current Data Parameters
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EXPNO                  10
PROCNO                  1

F2 - Acquisition Parameters
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PROBHD   5 mm PABBO BB-
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                  1024
DS                     4
SWH            36057.691 Hz
FIDRES          0.550197 Hz
AQ              0.9088159 sec
RG                  2050
DW                13.867 usec
DE                 8.50 usec
TE                302.0 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  13C
P1                 10.50 usec
PL1       0 dB
PL1W         91.93504333 W
SFO1        150.9505906 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                  1H
PCPD2              90.00 usec
PL2                -3.00 dB
PL12               16.26 dB
PL13               18.00 dB
PL2W         30.57242203 W
PL12W         0.36251819 W
PL13W         0.24284537 W
SFO2        600.2624010 MHz

F2 - Processing parameters
SI                 32768
SF          150.9354970 MHz
WDW                   no
SSB       0
LB        0 Hz
GB        0
PC                 1.40
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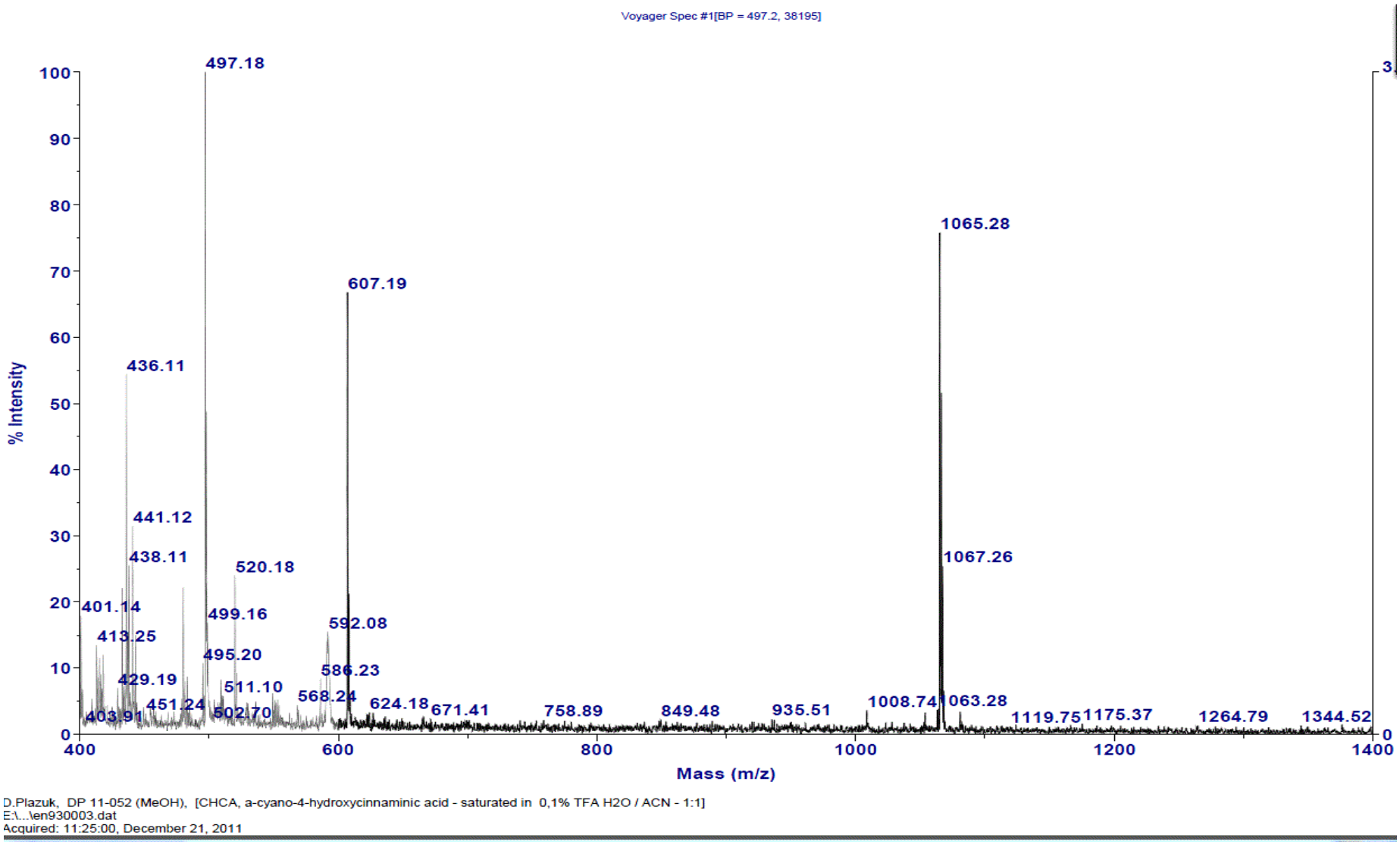
MALDI-MS for 3



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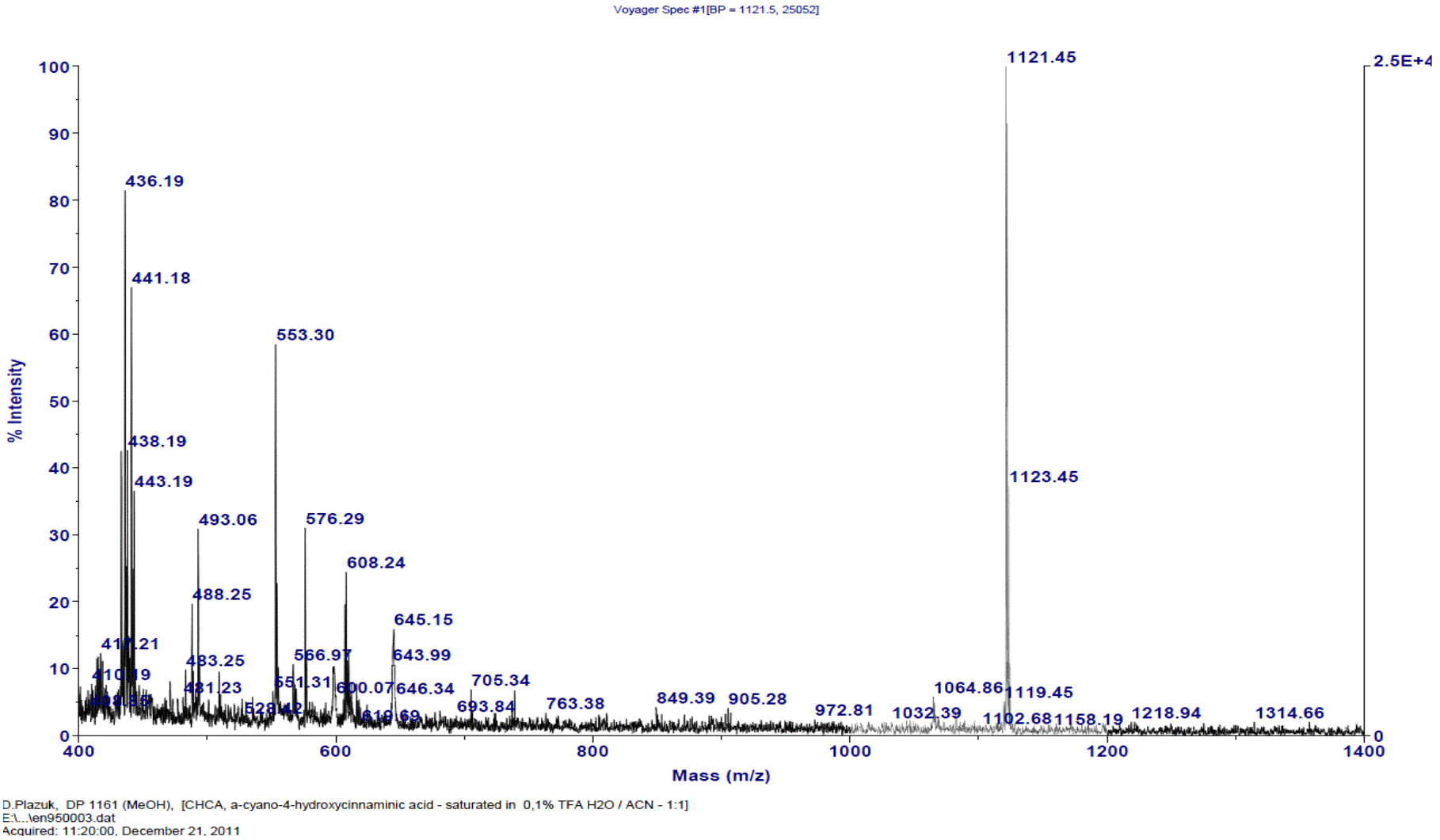
MALDI-MS for 4



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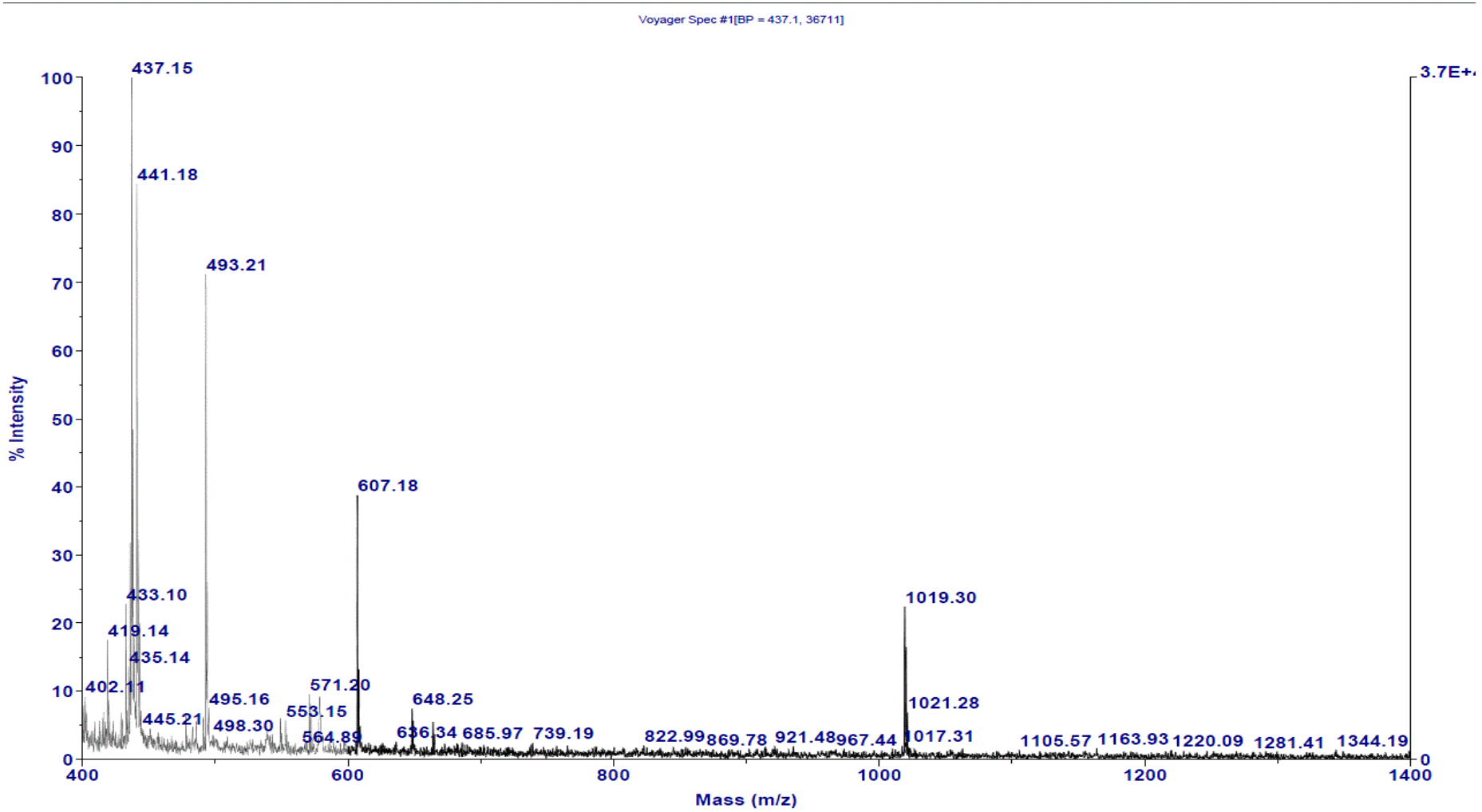
MALDI-MS for 5



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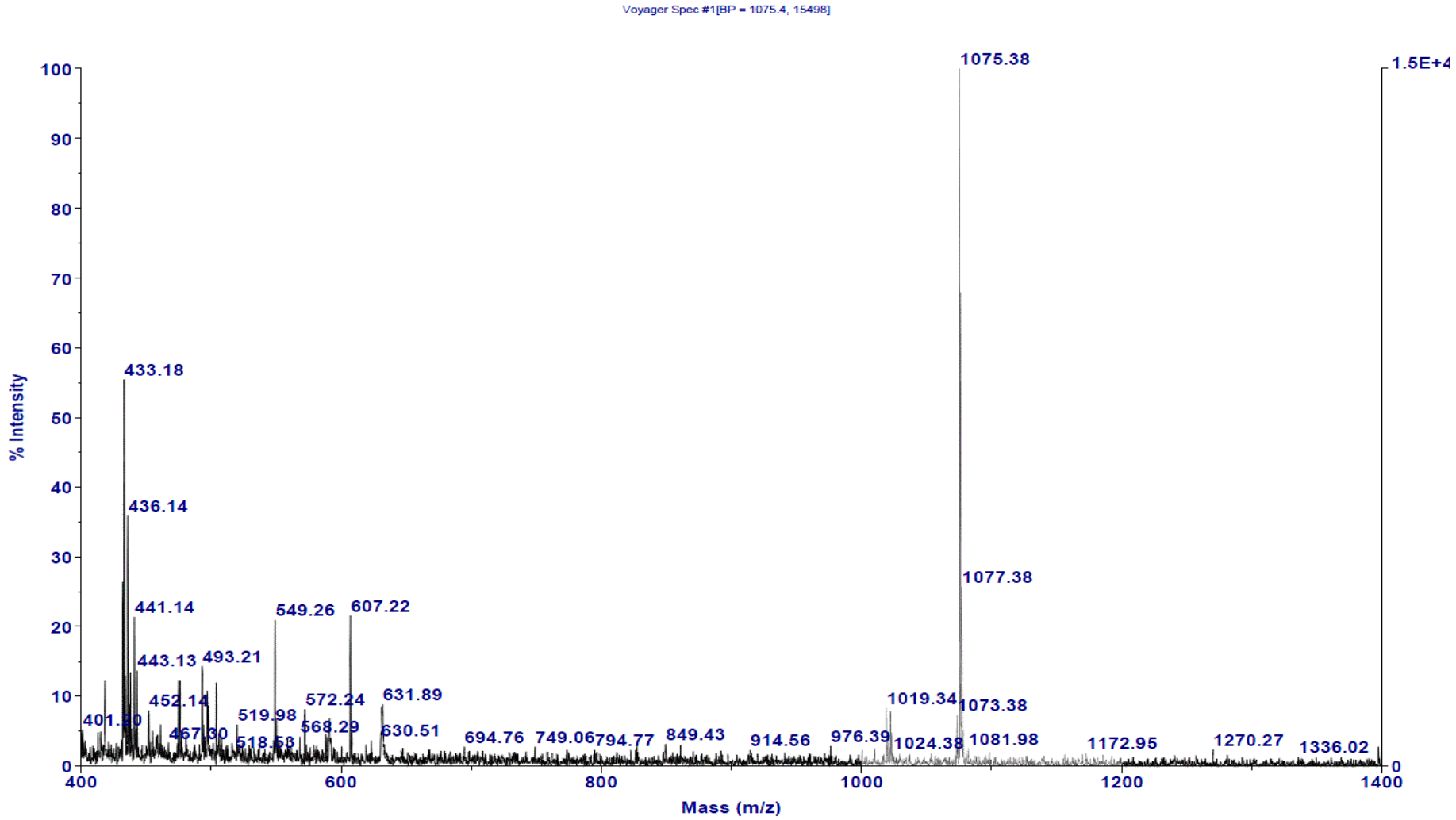
MALDI-MS for 6



D.Plazuk, DP 11-053 (MeOH), [CHCA, a-cyano-4-hydroxycinnaminic acid - saturated in 0,1% TFA H2O / ACN - 1:1]
E:\...\en940001.dat
Acquired: 11:21:00, December 21, 2011