Supplementary Material
Stereo- and regio-selectivity in acetonitrile oxide cycloaddition to norethisterone acetate

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1. ^{1}H, ^{13}C NMR, NOESY, HSQC, HMBC and HRMS spectra of synthetized compounds

NOTE

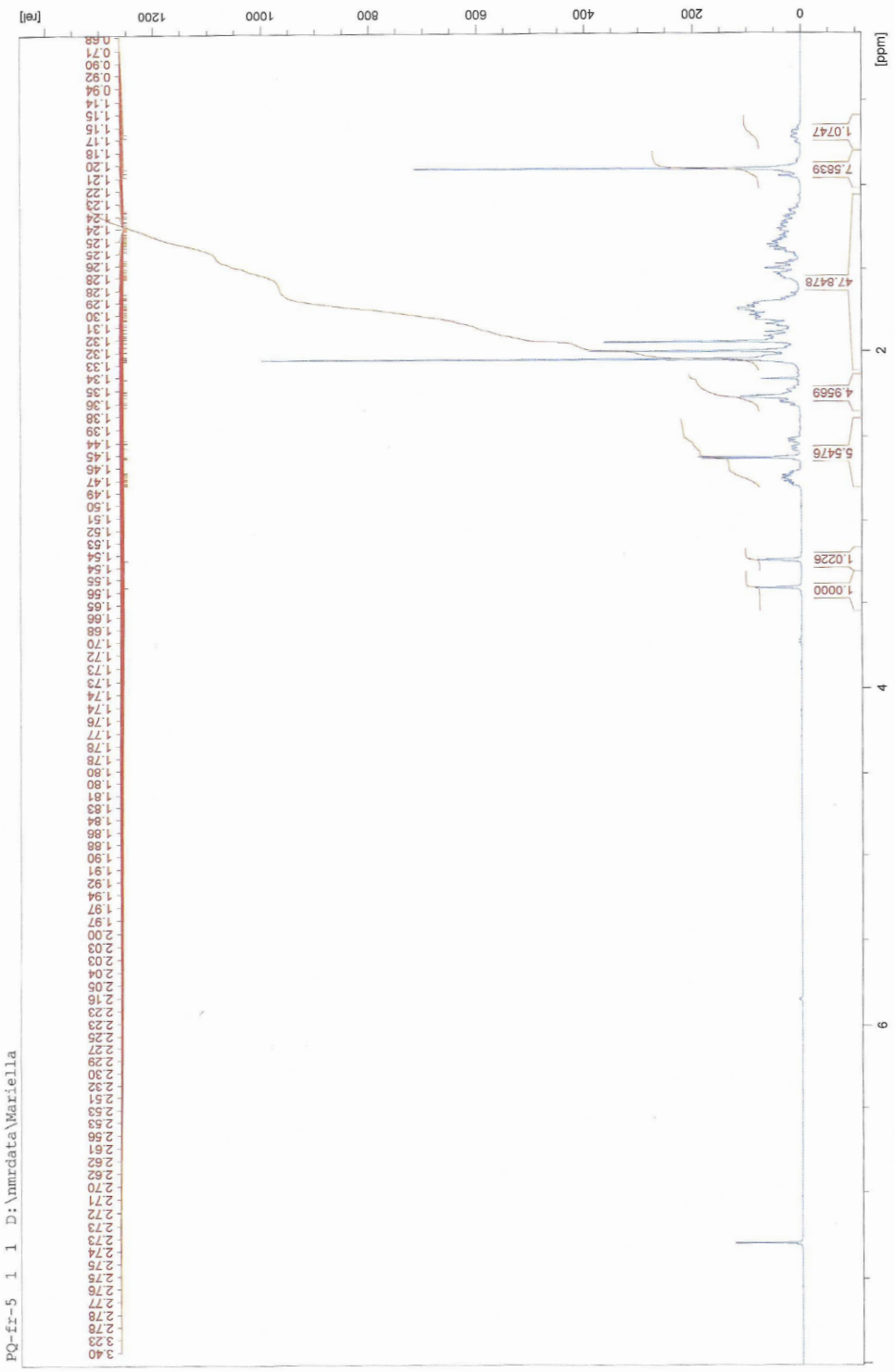
The attached spectra of synthetized compounds refer to samples at the 95% of purity, and sometimes may contain traces of solvents.

However, we checked that the mentioned impurities not affecting the other signals, in order to assign the structure beyond any reasonable doubt.

This was done to save precious pure samples for the subsequent synthetic steps and final analyses.

7a,b

^{1}H-NMR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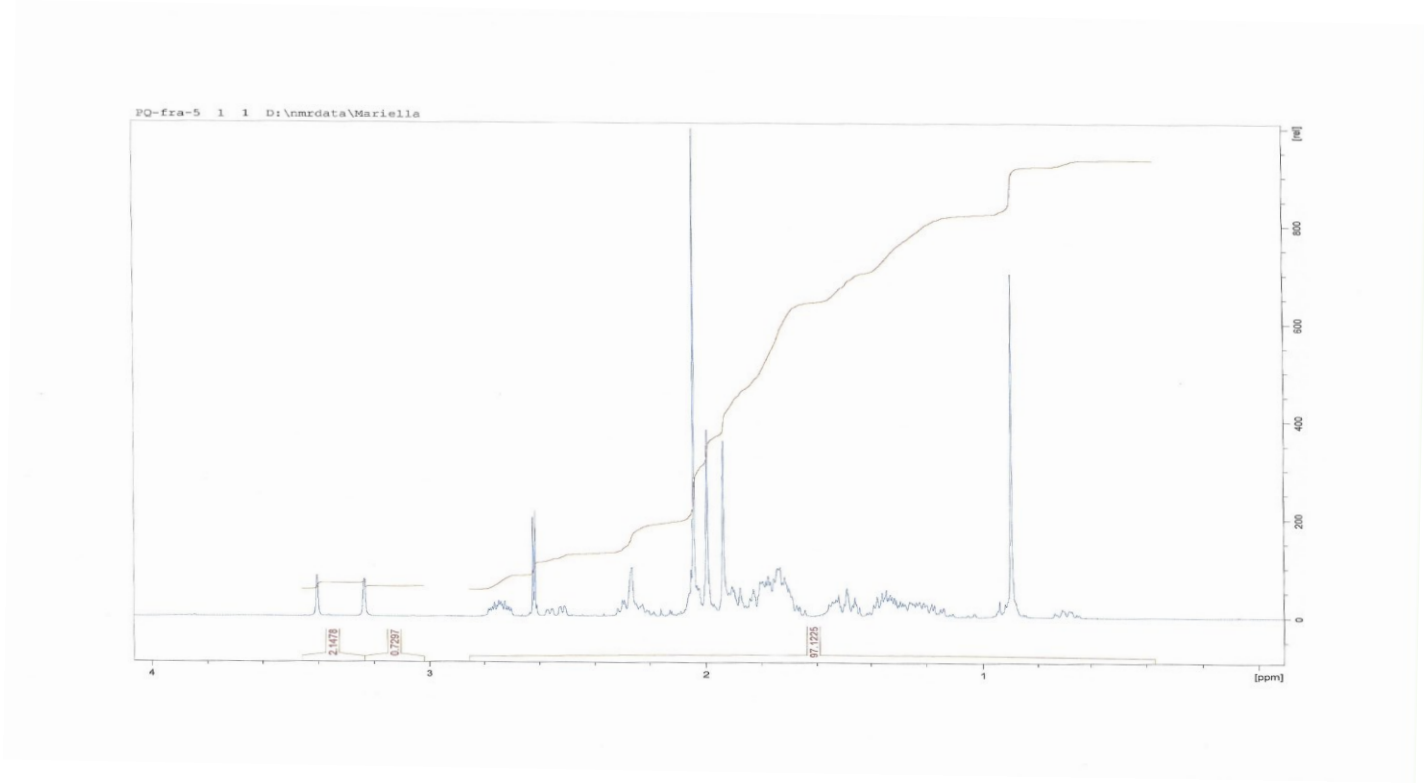
4.9569
5.5476
1.0226
1.0000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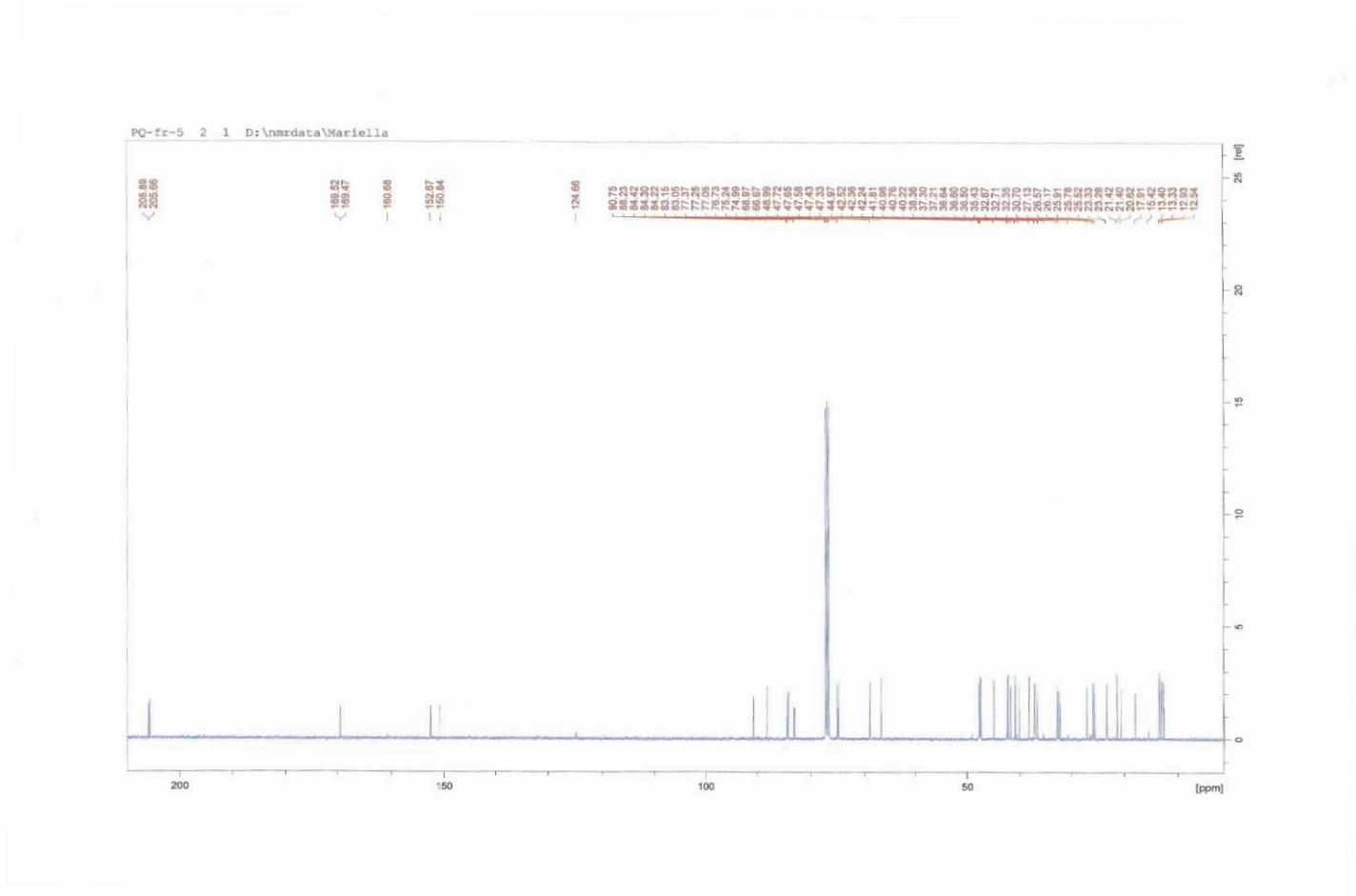
0.7297
97.1225
4
3
2
1
[ppm]
[mg]

^{13}C-NMR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205.66
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169.47
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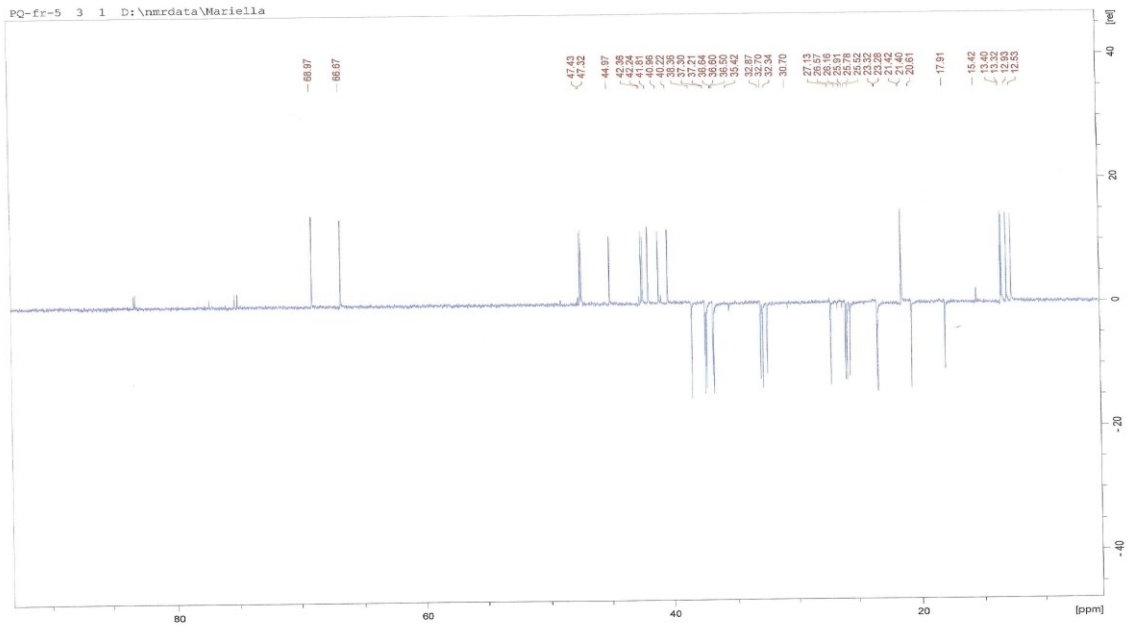
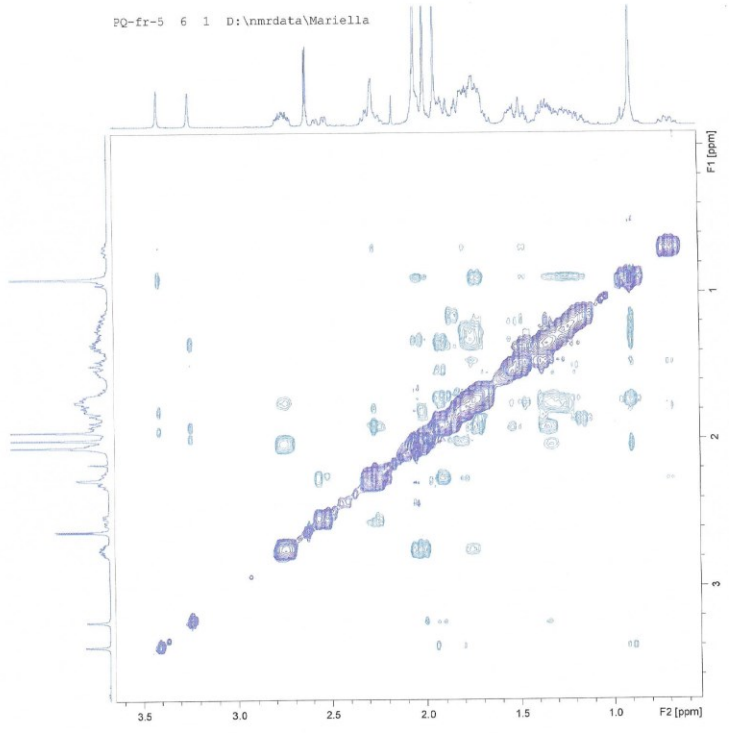
152.67
150.84
124.66
200
150
100
50
[ppm]
[mg]

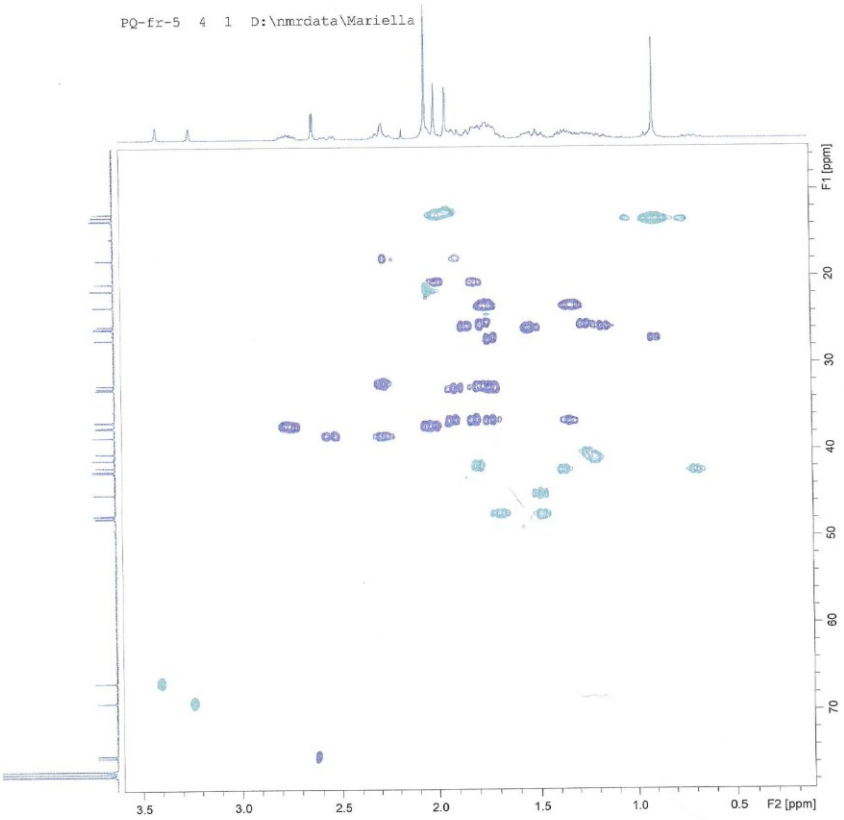
135-DEPT



NOESY



HSQC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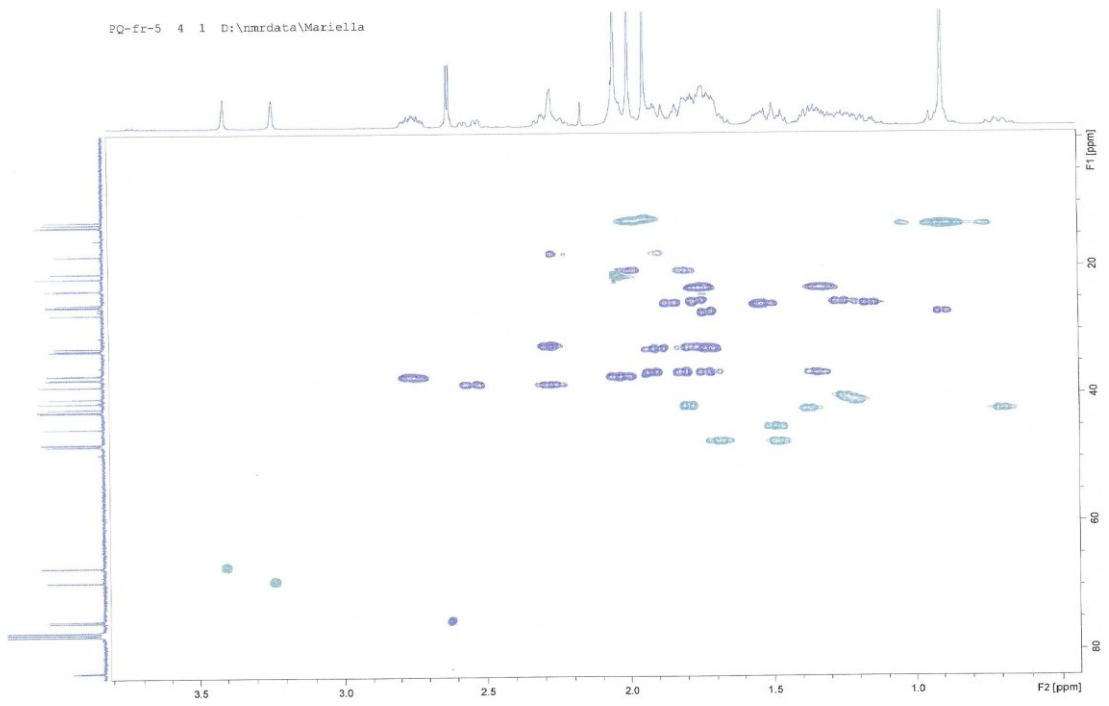
20
30
40
50
60
70
3.5
3.0
2.5
2.0
1.5
1.0
0.5
F2 [ppm]

HMBC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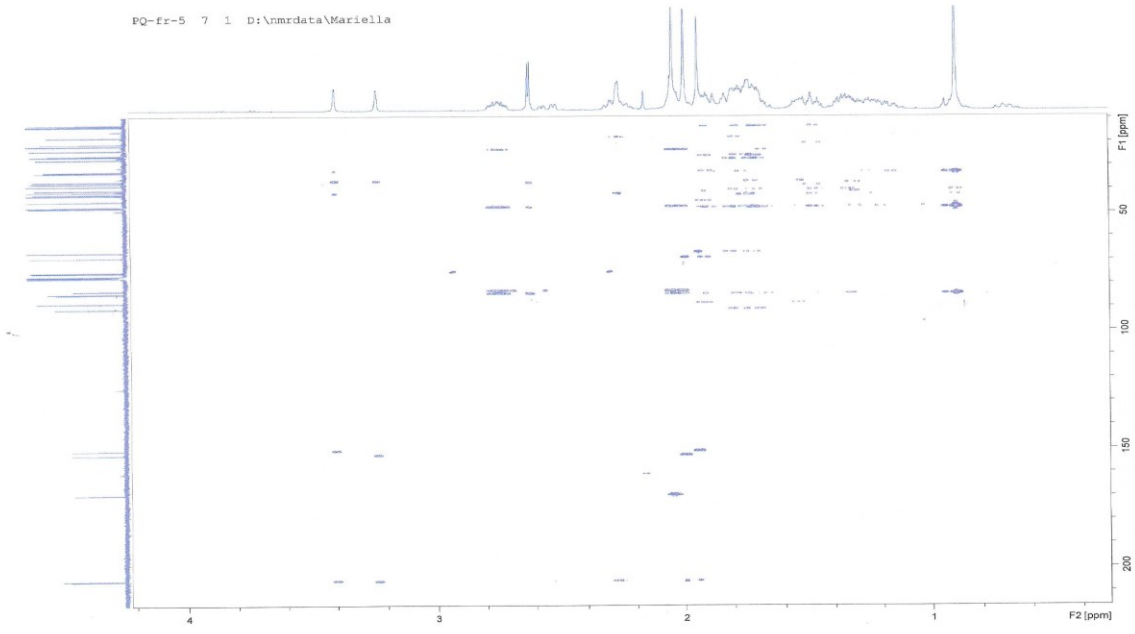
F1 [ppm]
F2 [ppm]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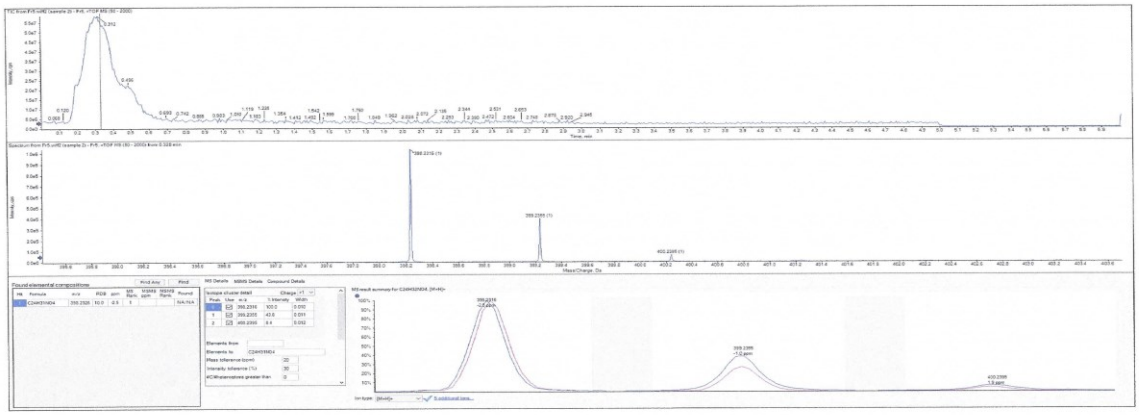
F1 [ppm]
F2 [ppm]

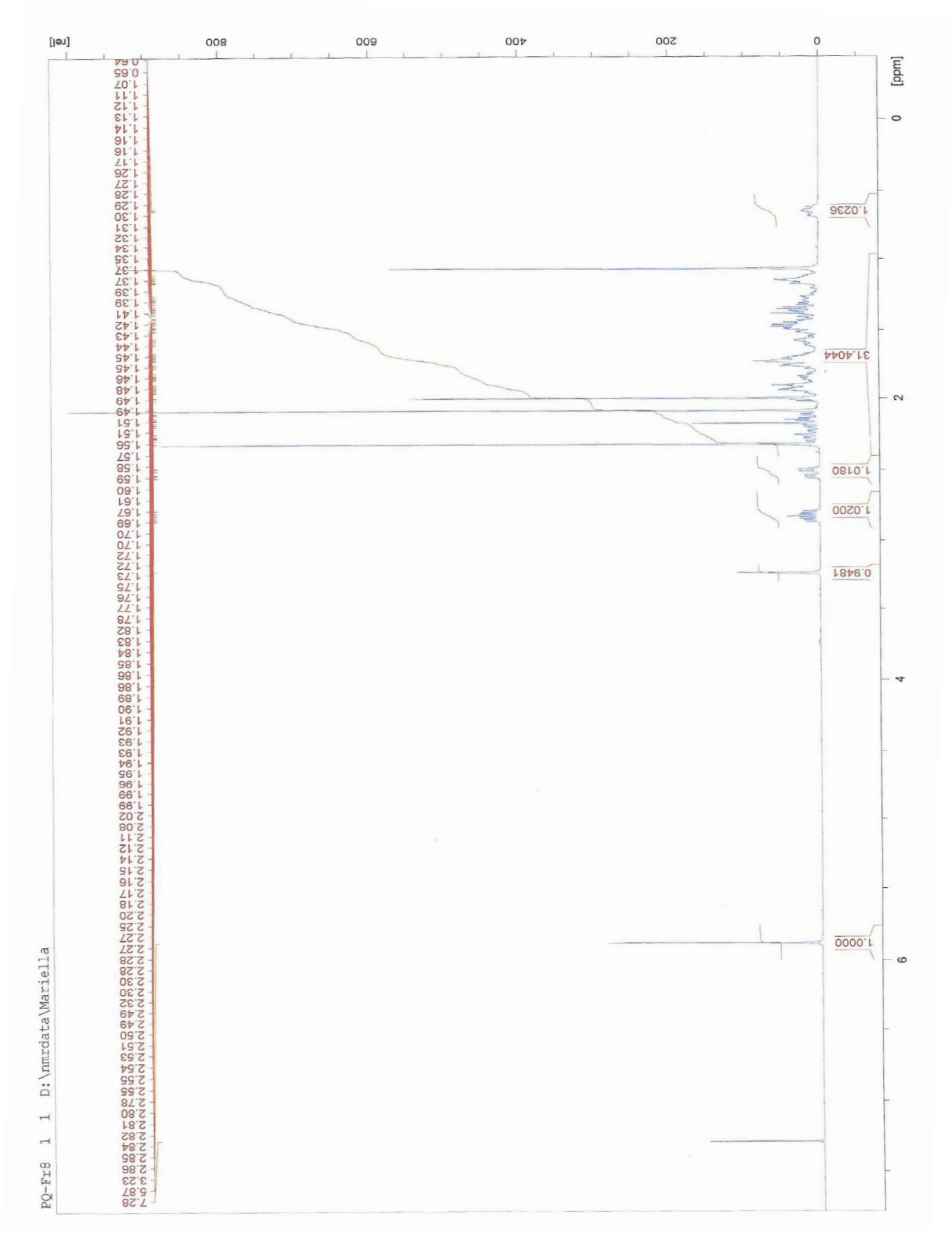
HRMS

Sample Name	Formula	Adduct/Charge	Precursor Mass	Found At Mass	Mass Error
Fr 5	C24H31NO4	[M+H]+	398.2326	398.2316	-2.5 ppm



8

^{1}H-NMR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600
400
200
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[ppm]
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2
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6
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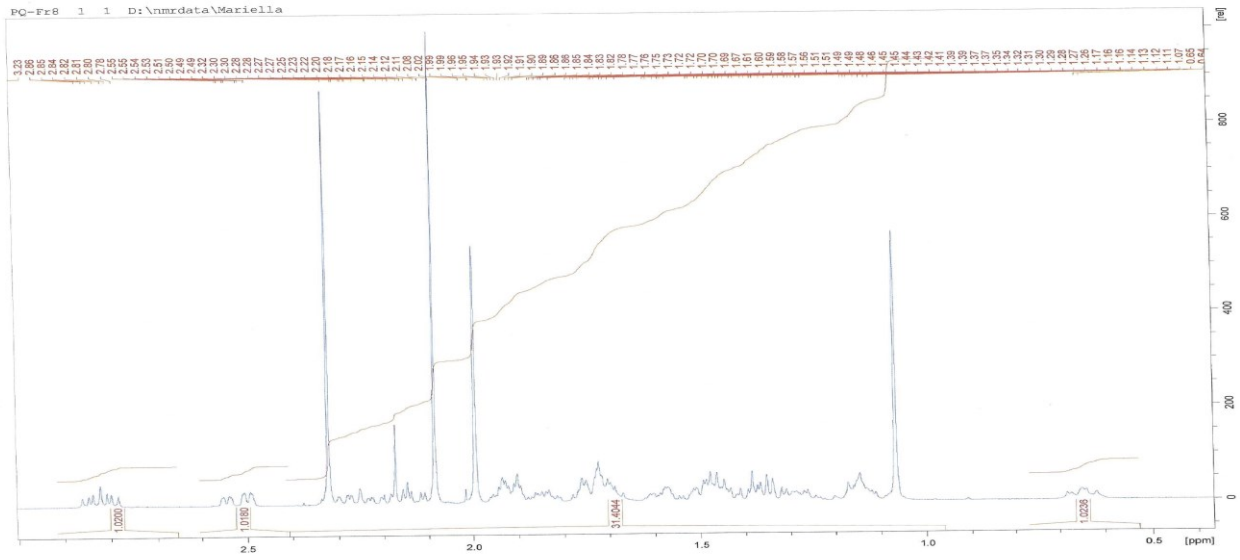
1.0180
1.0200
0.9481
1.0000
PQ-Fr8 1 1 D:\nmrdata\Mariella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1.5
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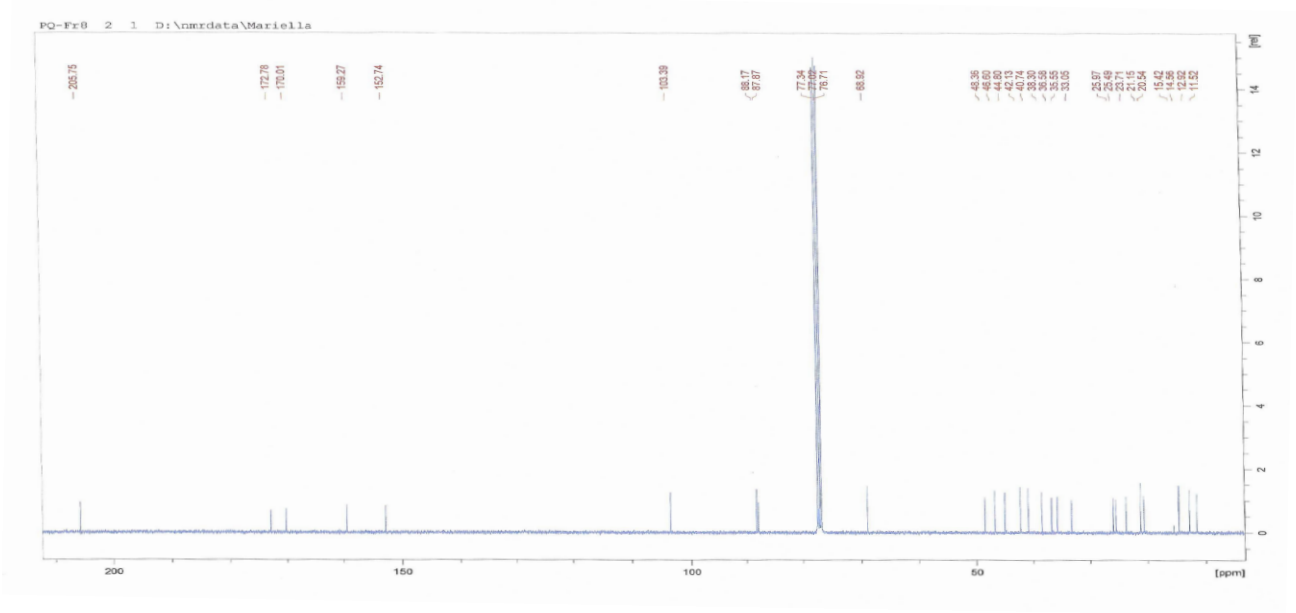
0.5
[ppm]

^{13}C-NMR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170.01
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152.74
103.39
88.17
87.87
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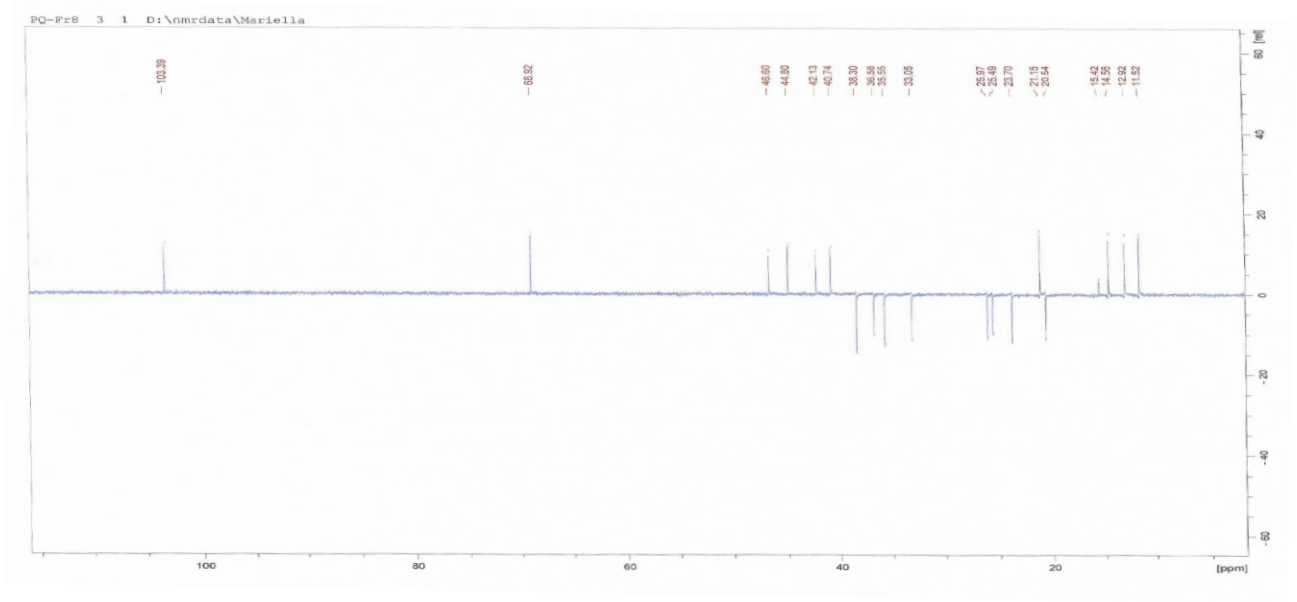
76.71
68.92
49.36
49.60
49.83
42.13
40.74
38.30
36.58
34.55
33.05
25.97
25.49
23.71
21.15
20.54
15.42
14.56
14.52
11.52
200
150
100
50
[ppm]

135-DEPT



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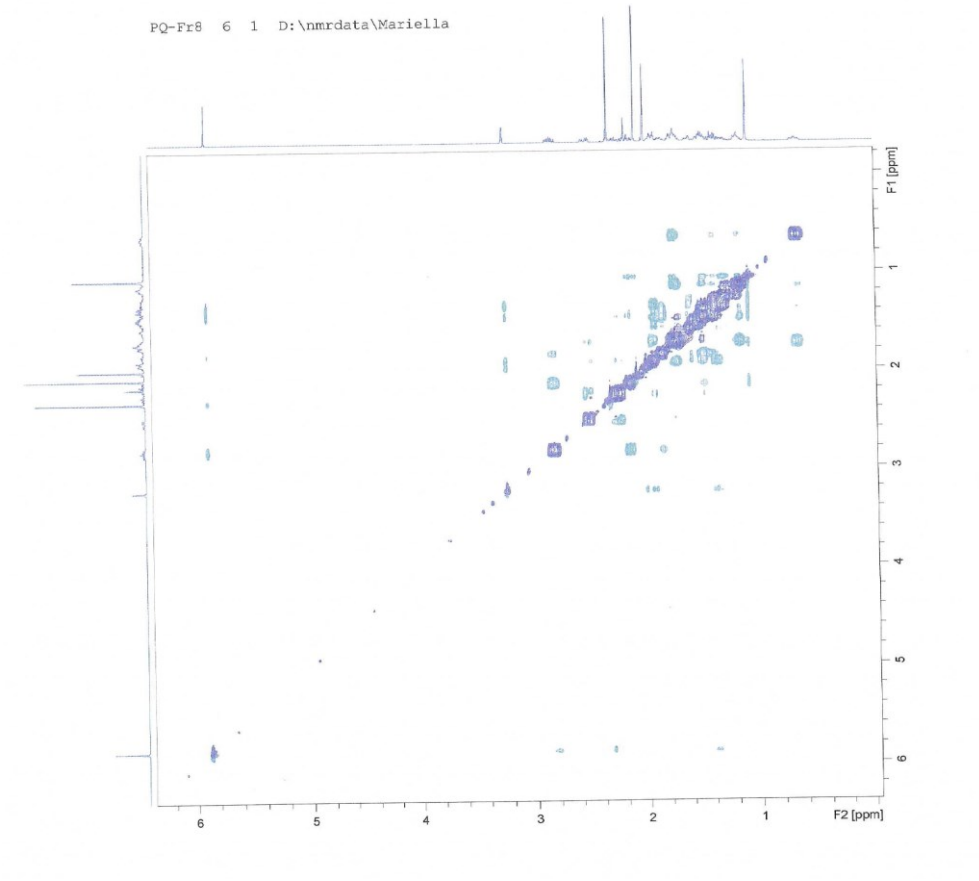
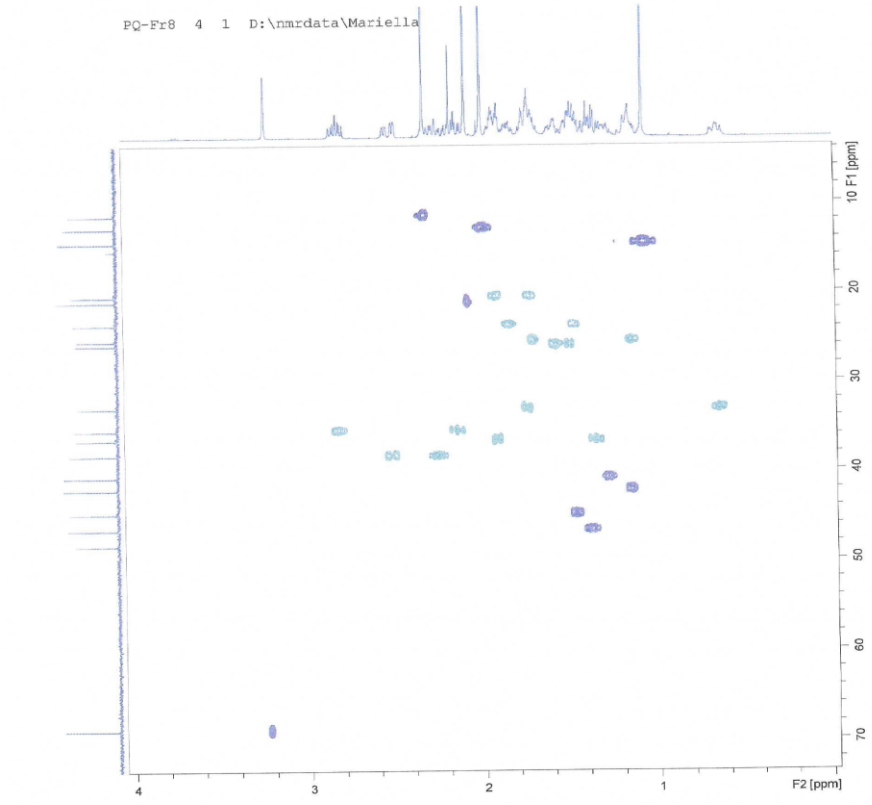


HSQC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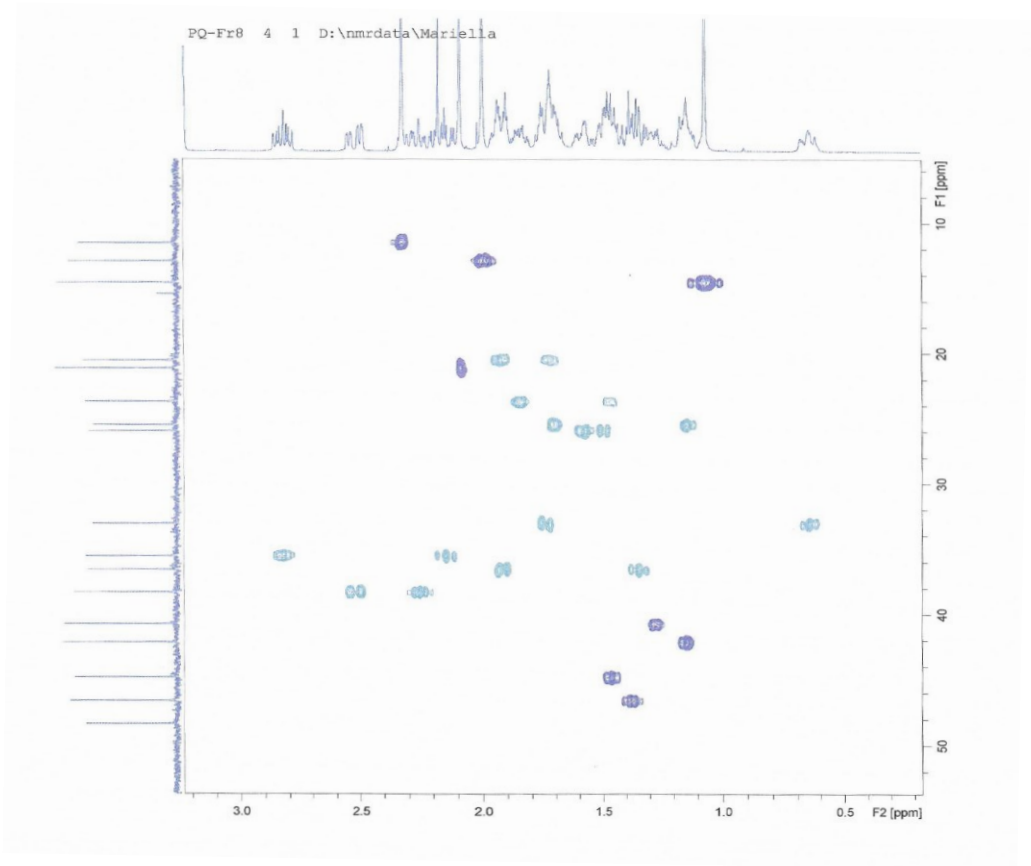
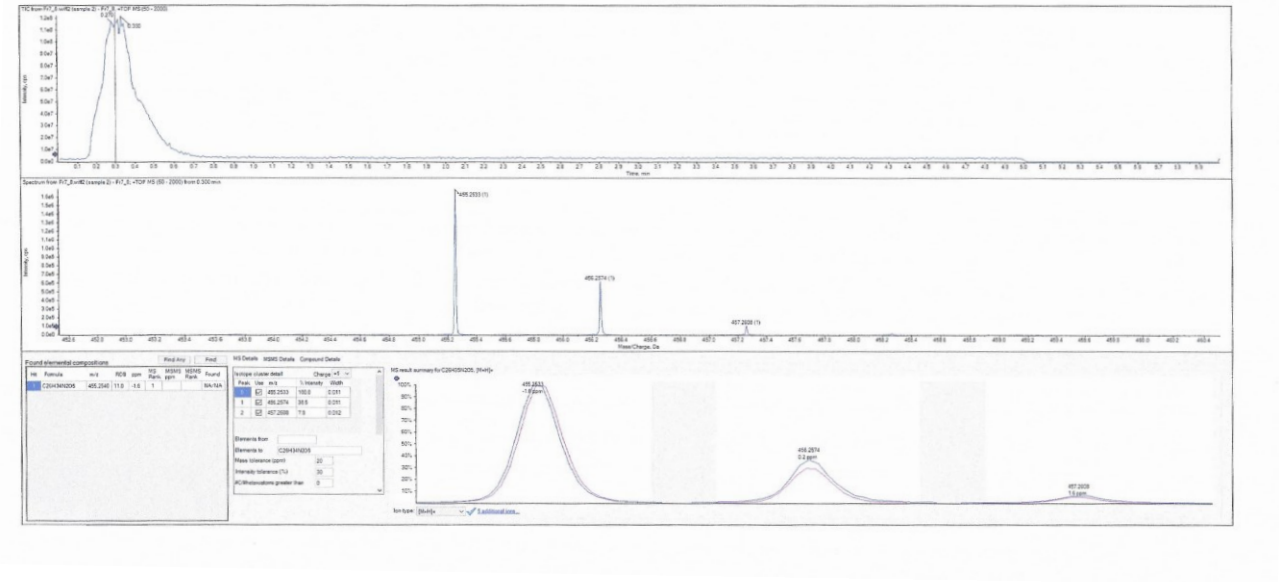
F1 [ppm]
F2 [ppm]

HMBC


PQ-Fr8 4 1 D:\nmrdata\Mariella
F1 [ppm]
F2 [ppm]

HRMS

Sample Name	Formula	Adduct/Charge	Precursor Mass	Found At Mass	Mass Error
Fr 7_8	C26H34N2O5	[M+H]+	455.2540	455.2533	-1.6 ppm



2. CIF file for compound **8**

checkCIF/PLATON report

Structure factors have been supplied for datablock(s) ME-F7-NOR

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: ME-F7-NOR

```
Bond precision:   C-C = 0.0038 A          Wavelength=0.71070

Cell:              a=8.2484(6)     b=12.1929(8)     c=24.2730(14)
                   alpha=90        beta=90          gamma=90
Temperature:       298 K

                  Calculated                Reported
Volume            2441.2(3)                 2441.2(3)
Space group       P 21 21 21                P 21 21 21
Hall group        P 2ac 2ab                 P 2ac 2ab
Moiety formula    C26 H34 N2 O5             C26 H34 N2 O5
Sum formula       C26 H34 N2 O5             C26 H34 N2 O5
Mr                454.55                    454.55
Dx,g cm-3         1.237                     1.237
Z                 4                         4
Mu (mm-1)         0.086                     0.086
F000              976.0                     976.0
F000'             976.46
h,k,lmax          11,17,34                  11,17,34
Nref              7165[ 4033]               7065
Tmin,Tmax         0.980,0.994               0.861,0.994
Tmin'             0.965

Correction method= # Reported T Limits: Tmin=0.861 Tmax=0.994
AbsCorr = MULTI-SCAN
```

```
Data completeness= 1.75/0.99        Theta(max)= 30.063

R(reflections)= 0.0497( 4076)                wR2(reflections)=
                                             0.1329( 7065)
S = 0.991                   Npar= 298
```

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

```
STRVA01_ALERT_4_C           Flack test results are ambiguous.
          From the CIF: _refine_ls_abs_structure_Flack    0.400
          From the CIF: _refine_ls_abs_structure_Flack_su    0.700
PLAT241_ALERT_2_C High  MainResAtom  Ueq as Compared to Neighbours        C11 Check
PLAT242_ALERT_2_C Low   MainResAtom  Ueq as Compared to Neighbours        C10 Check
PLAT242_ALERT_2_C Low   MainResAtom  Ueq as Compared to Neighbours        C12 Check
```

Alert level G

```
PLAT032_ALERT_4_G Std. Uncertainty on Flack Parameter Value High .      0.700 Report
PLAT395_ALERT_2_G Deviating  X-O-Y   Angle From 120 for O1       .      108.3 Degree
PLAT395_ALERT_2_G Deviating  X-O-Y   Angle From 120 for O4       .      109.4 Degree
PLAT791_ALERT_4_G Model has Chirality at C1         (Sohncke SpGr)          S Verify
PLAT791_ALERT_4_G Model has Chirality at C4         (Sohncke SpGr)          S Verify
PLAT791_ALERT_4_G Model has Chirality at C5         (Sohncke SpGr)          R Verify
PLAT791_ALERT_4_G Model has Chirality at C8         (Sohncke SpGr)          S Verify
PLAT791_ALERT_4_G Model has Chirality at C9         (Sohncke SpGr)          S Verify
PLAT791_ALERT_4_G Model has Chirality at C13        (Sohncke SpGr)          R Verify
PLAT791_ALERT_4_G Model has Chirality at C14        (Sohncke SpGr)          S Verify
PLAT791_ALERT_4_G Model has Chirality at C17        (Sohncke SpGr)          S Verify
PLAT916_ALERT_2_G Hooft y and Flack x Parameter Values Differ by .       0.20 Check
PLAT941_ALERT_3_G Average HKL Measurement Multiplicity ...........        4.2 Low
PLAT969_ALERT_5_G The 'Henn et al.' R-Factor-gap value ...........      2.050 Note
              Predicted wR2: Based on SigI**2  6.48 or SHELX Weight 13.40
PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density.          0 Info
PLAT992_ALERT_5_G Repd & Actual _reflns_number_gt Values Differ by          2 Check
```

```
  0 ALERT level A = Most likely a serious problem - resolve or explain
  0 ALERT level B = A potentially serious problem, consider carefully
  4 ALERT level C = Check. Ensure it is not caused by an omission or oversight
 16 ALERT level G = General information/check it is not something unexpected

  0 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
  7 ALERT type 2 Indicator that the structure model may be wrong or deficient
  1 ALERT type 3 Indicator that the structure quality may be low
 10 ALERT type 4 Improvement, methodology, query or suggestion
  2 ALERT type 5 Informative message, check
```

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

PLATON version of 15/01/2026; check.def file version of 02/01/2026

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duplicate check

A reduced cell check using CCDC's cellCheckCSD service has found that one or more structures in this CIF are similar to those previously published in the CSD or the ICSD.

Datablock ME-F7-NOR - ellipsoid plot

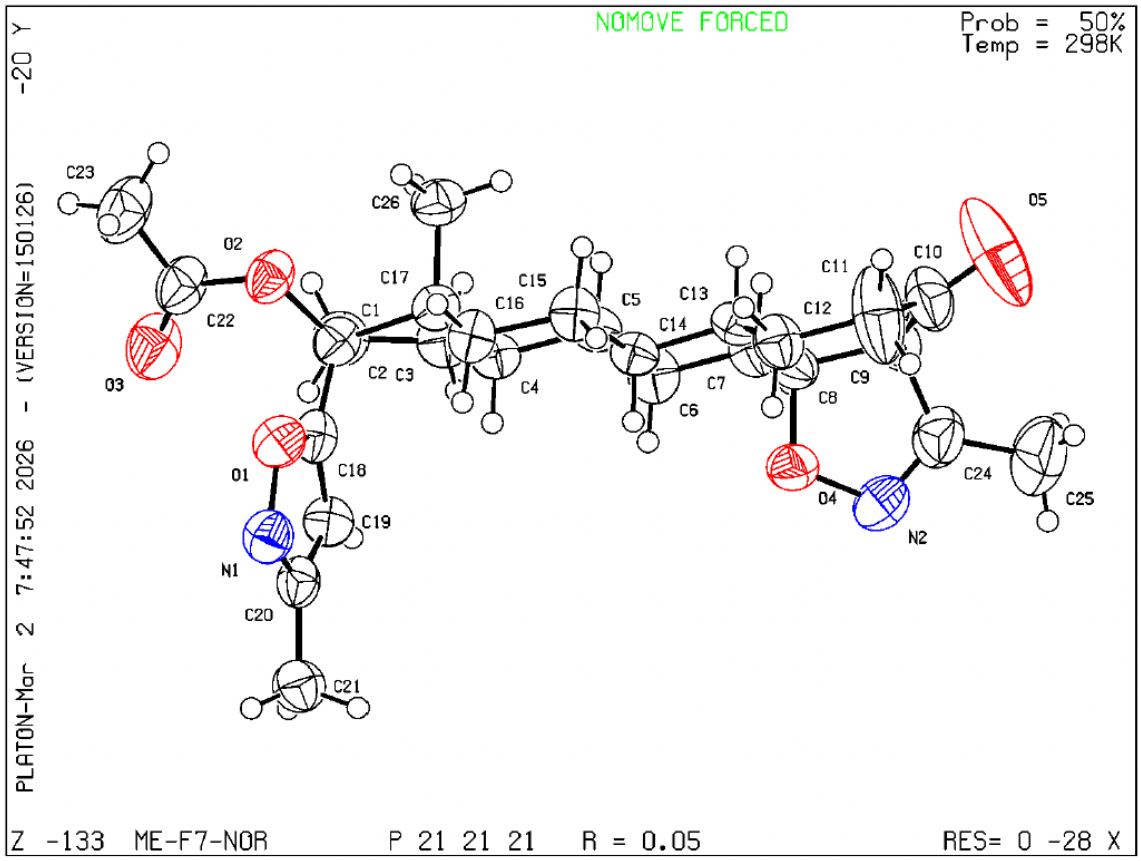

Table S1. Crystallographic data of compound **8**

	ME-F7
formula	$C_{26}H_{34}N_2O_5$
M [g/mol]	454.55
dimension[mm]	0.07x0.20x0.42
colour	pale yellow
crystal system	orthorhombic
space group	*P* $2_12_12_1$ (n. 19)
a [Å]	8.2484(6)
b [Å]	12.1929(8)
c [Å]	24.2730(14)
V [Å^3]	2441.2(3)
Z	4
ρ_{calcd} [g/cm^3]	1.237
μ Mo K_α [mm^{-1}]	0.086
θ range [°]	1.7-30.1
measured reflections	16951
independent reflections	7065
R_{int}	0.036
strong reflections ($I_0>2\sigma(I_0)$)	4076
refined parameters	298
*R*1, *wR*2 (strong reflections)	0.0497, 0.1159
*R*1, *wR*2 (all reflections)	0.0930, 0.1329
GooF	0.991
Max/min residuals [eÅ^{-3}]	0.19/-0.19