Supporting information

Pentacyclic coumarin-based blue emitters - the case of bifunctional nucleophilic behavior of amidines

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Instrumentation and Materials

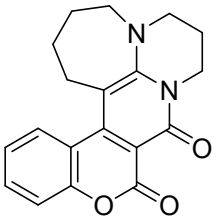
All chemicals were used as received unless otherwise noted. All reported ^{1}H NMR spectra were collected using 500 MHz spectrometers. Chemical shifts (δ ppm) were determined with TMS as the internal reference; *J* values are given in Hz. Chromatography was performed on silicagel (230-400 mesh). Preparative thin layer chromatography (TLC) was carried out using Merck PLC Silica gel 60 F_{254} 1 mm plates. The mass spectra were obtained via electron ionisation (EI-MS) or electrospray ionization (ESI-MS). All photophysical studies have been performed with freshly-prepared air-equilibrated solutions at room temperature (298 K).

A Perkin-Elmer Lambda 25 UV/Vis spectrophotometer and a Hitachi F7000 fluorescence spectrometer were used to acquire the absorption and emission spectra. Spectrophotometric grade solvents were used without further purification. Fluorescence quantum yields were determined in DMSO and in CH_2Cl_2 using 9,10-diphenylanthracene in cyclohexane (**4a**,**b**,**c**,**e**) and quinine sulfate in 0.05 M H_2SO_4 (**3d** and **4d**) as standards.

Experimental part

General procedure for the preparation of compounds 3a-e and 4a-e.

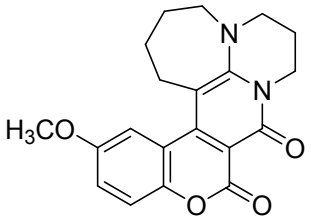
3-Alkoxycarbonyl coumarin **2a-e** (1 mmol) and amidine base **1a,b** (0.5 mmol) were heated at 120-130°C for 2 hr (**1**) or 30 min (**2**). On cooling the reaction was subsequently washed with diethyl ether, *i*-PrOH and filtered.



3a

The crude product was recrystallized from EtOH. Yield 75%. M.p. 307-308°C(dec.)

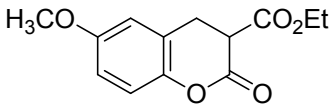
^{1}H NMR ($CDCl_3$): δ 7.89 (dd, J = 8.5, 1.0 Hz, 1H), 7.45 (t, J = 8.0 Hz, 1H), 7.24-7.28 (m, 1H), 7.15 (t, J = 7.5 Hz, 1H), 4.21 (br. s, 2H), 3.68 (br. s. 2H), 3.42 (t, J = 6.5 Hz, 2H), 2.99 (br. s. 2H), 2.10 (quin, J = 6.0 Hz, 2H), 1.97-2.03 (m, 2H), 1.87-1.93 (m, 2H) ppm; ^{13}C NMR ($CDCl_3$): δ 158.4, 158.3, 155.2, 153.8, 150.4, 131.7, 128.8, 122.4, 118.2, 117.7, 98.5, 97.9, 49.4, 38.9, 31.3, 24.8, 24.7, 22.6 ppm; HRMS (EI) calcd for $C_{19}H_{18}N_2O_3$: 322.1317 [$M^{+\cdot}$], found: 322.1317; Anal. Calcd. for $C_{19}H_{18}N_2O_3$ (322.36): C, 70.79; H, 5.63; N, 8.69; Found: C, 70.54; H, 5.74; N, 8.57; λ_{abs} (DCM, $\varepsilon \times 10^{-3}$) 413 (16.2), 278 (21.3) nm.



3b

The crude product was recrystallized from EtOH. Yield 68%. M.p. 320-321°C(dec.)

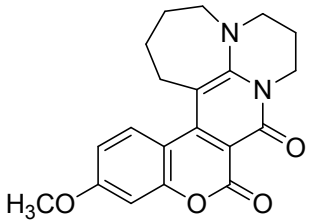
^{1}H NMR ($CDCl_3$): δ 7.36 (d, J = 2.7 Hz, 1H), 7.19 (d, J = 9.2 Hz, 1H), 7.04 (dd, J = 8.9, 2.8 Hz, 1H), 4.21 (br. s, 2H), 3.83 (s, 3H), 3.68 (br. s. 2H), 3.43 (t, J = 6.4 Hz, 2H), 3.00 (br. s. 2H), 2.10 (quin, J = 5.8 Hz, 2H), 2.01 (quin, J = 5.8 Hz, 2H), 1.90 (quin, J = 5.5 Hz, 2H) ppm; ^{13}C NMR ($CDCl_3$): δ 158.7, 158.5, 155.3, 154.4, 150.1, 148.0, 118.4, 118.3, 112.9, 98.4, 98.0, 55.9, 53.1, 49.5, 39.1, 31.2, 24.8, 22.6 ppm; HRMS (EI) calcd for $C_{20}H_{20}N_2O_4$: 352.1423 [$M^{+\cdot}$], found: 352.1426; Anal. Calcd. for $C_{20}H_{20}N_2O_4$ (352.38): C, 68.17; H, 5.72; N, 7.95; Found: C, 67.97; H, 5.84; N, 8.10; λ_{abs} (DCM, $\varepsilon \times 10^{-3}$) 415 (16.3), 277 (20.6) nm.



Ethyl 6-methoxy-2-oxochroman-3-carboxylate, 5b

The diethyl ether solution from the previous step was evaporated and the product was purified by the preparative TLC to yield 0.02 g (8%) of reduced coumarin **5b**. M.p. 93-94°C

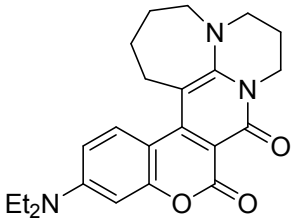
^{1}H NMR ($CDCl_3$): δ 6.99 (d, J = 8.9 Hz, 1H), 6.79 (dd, J = 8.9, 2.9 Hz, 1H), 6.72 (d, J = 2.7 Hz, 1H), 4.15-4.26 (m, 2H), 3.78 (s, 3H), 3.73 (dd, J = 8.4, 6.0 Hz, 1H), 3.37 (dd, J = 16.0, 8.5 Hz, 1H), 3.13 (dd, J = 16.0, 6.0 Hz, 1H), 1.22 (t, J = 7.2 Hz, 2H) ppm; ^{13}C NMR ($CDCl_3$): δ 167.5, 164.9, 156.4, 145.3, 121.7, 117.6, 113.8, 113.3, 62.1, 55.7, 46.3, 31.6, 27.6, 22.6, 13.9 ppm; HRMS (EI) calcd for $C_{13}H_{14}O_5$: 250.0841 [$M^{+\cdot}$], found: 250.0846.



3c

The crude product was recrystallized from EtOH. Yield 51%. M.p. 280-281°C

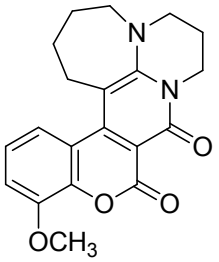
^{1}H NMR ($CDCl_3$): δ 7.79 (d, J = 9.8 Hz, 1H), 6.70-6.74 (m, 2H), 4.19 (br. s, 2H), 3.84 (s, 3H), 3.66 (br. s, 2H), 3.41 (t, J = 6.5 Hz, 2H), 2.95 (br. s, 2H), 2.08 (quin, J = 6.0 Hz, 2H), 2.00 (quin, J = 5.7 Hz, 2H), 1.90 (quin, J = 5.4 Hz, 2H) ppm; ^{13}C NMR ($CDCl_3$): δ 162.2, 158.6, 158.5, 155.6, 155.0, 150.3, 130.0, 111.1, 110.6, 100.9, 97.2, 97.1, 55.6, 52.5, 49.2, 38.8, 31.3, 24.7, 22.6 ppm; HRMS (EI) calcd for $C_{20}H_{20}N_2O_4$: 352.1423 [$M^{+\cdot}$], found: 352.1425; Anal. Calcd. for $C_{20}H_{20}N_2O_4$ (352.38): C, 68.17; H, 5.72; N, 7.95; Found: C, 67.96; H, 5.61; N, 7.81; λ_{abs} (DCM, $\varepsilon \times 10^{-3}$) 404 (19.6), 329 (12.9), 228 (22.5) nm.



3d

The crude product was recrystallized from EtOH. Yield 61%. M.p. 247-248°C

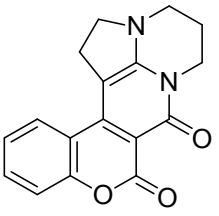
^{1}H NMR ($CDCl_3$): δ 7.70 (d, J = 9.1 Hz, 1H), 6.40-6.55 (m, 2H), 4.16 (br. s, 2H), 3.62 (br. s, 2H), 3.33-3.45 (m, 6H), 2.94 (br. s, 2H), 2.05 (br. s, 2H), 1.97 (br. s, 2H), 1.85 (br. s, 2H), 1.19 (t, J = 6.9 Hz, 6H) ppm; ^{13}C NMR ($CDCl_3$): δ 159.2, 158.8, 156.0, 154.5, 150.9, 150.0, 130.0, 107.0, 106.3, 98.1, 96.6, 96.5, 52.6, 49.1, 44.7, 38.6, 31.4, 24.9, 24.8, 22.8, 12.5 ppm; HRMS (EI) calcd for $C_{23}H_{27}N_3O_3$: 393.2052 [$M^{+\cdot}$], found: 393.2059; Anal. Calcd. for $C_{23}H_{27}N_3O_3$ (393.48): C, 70.21; H, 6.92; N, 10.68; Found: C, 69.96; H, 7.09; N, 10.67; λ_{abs} (DCM, $\varepsilon \times 10^{-3}$) 406 (37.1), 279 (19.7) nm.



3e

The crude product was recrystallized from EtOH. Yield 68%. M.p. 310°C(dec.)

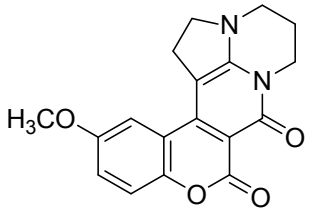
^{1}H NMR ($CDCl_3$): δ 7.44 (d, J = 8.0 Hz, 1H), 7.07 (t, J = 8.2 Hz, 1H), 7.01 (d, J = 7.2 Hz, 1H), 4.21 (br. s, 2H), 3.92 (s, 3H), 3.68 (br. s. 2H), 3.42 (t, J = 6.4 Hz, 2H), 2.96 (br. s, 2H), 2.10 (quin, J = 5.8 Hz, 2H), 2.00 (br. s, 2H), 1.87 (br. s, 2H) ppm; ^{13}C NMR ($CDCl_3$): δ 158.4, 157.8, 155.2, 150.5, 147.9, 143.9, 121.7, 120.1, 118.7, 113.3, 98.4, 98.3, 56.2, 52.7, 49.4, 39.0, 31.3, 24.7, 22.6 ppm; HRMS (EI) calcd for $C_{20}H_{20}N_2O_4$: 352.1423 [$M^{+\cdot}$], found: 352.1424; Anal. Calcd. for $C_{20}H_{20}N_2O_4$ (352.38): C, 68.17; H, 5.72; N, 7.95; Found: C, 67.96; H, 5.68; N, 7.99; λ_{abs} (DCM, $\varepsilon \times 10^{-3}$) 411 (17.3), 282 (27.6) nm.



4a

The crude product was recrystallized from CH_3CN. Yield 71%. M.p. 383°C(dec.)

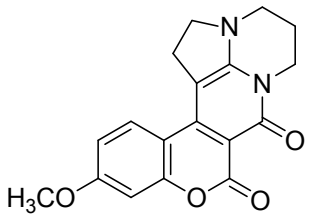
^{1}H NMR (CF_3COOD): δ 7.93 (d, J = 8.2 Hz, 1H), 7.71 (t, J = 8.2 Hz, 1H), 7.50 (t, J = 7.9 Hz, 1H), 7.42 (d, J = 8.5 Hz, 1H), 4.30 (t, J = 6.0 Hz, 2H), 4.21 (t, J = 8.2 Hz, 2H), 3.61-3.67 (m, 4H), 2.39 (br. s, 2H) ppm; ^{13}C NMR (CF_3COOD): δ 167.4, 162.4, 155.4, 151.4, 137.1, 134.5, 126.9, 126.7, 118.2, 110.80, 88.6, 52.6, 41.7, 40.8, 25.5, 17.6 ppm; HRMS (EI) calcd for $C_{17}H_{14}N_2O_3$: 294.1004 [$M^{+\cdot}$], found: 294.1005; Anal. Calcd. for $C_{17}H_{14}N_2O_3$ (294.30): C, 69.38; H, 4.79; N, 9.52; Found: C, 69.10; H, 4.80; N, 9.30; λ_{abs} (DCM, $\varepsilon \times 10^{-3}$) 411 (13.9), 392 (15.1), 294 (13.7), 276 (21.1), 267 (19.1) nm.



4b

The crude product was recrystallized from CH_3CN. Yield 69%. M.p. 371°C(dec.)

^{1}H NMR (CF_3COOD): δ 7.50 (d, J = 2.7 Hz, 1H), 7.42 (d, J = 9.1 Hz, 1H), 7.37 (dd, J = 9.2, 2.5 Hz, 1H), 4.31 (t, J = 5.8 Hz, 2H), 4.23 (t, J = 8.2 Hz, 2H), 3.97 (s, 3H), 3.65-3.70 (m, 4H), 2.41 (quin, J = 5.7 Hz, 2H) ppm; ^{13}C NMR (CF_3COOD): δ 169.7, 164.9, 159.3, 157.7, 148.4, 139.2, 122.4, 121.8, 118.6, 114.5, 113.4, 90.8, 57.8, 54.9, 44.1, 43.1, 27.8, 19.9 ppm; HRMS (EI) calcd for $C_{18}H_{16}N_2O_4$: 324.1110 [$M^{+\cdot}$], found: 324.1113; Anal. Calcd. for $C_{18}H_{16}N_2O_4 \cdot H_2O$ (342.35): C, 63.15; H, 5.30; N, 8.18; Found: C, 62.89; H, 5.27; N, 8.16; λ_{abs} (DCM, $\varepsilon \times 10^{-3}$) 415 (13.6), 395 (14.9), 298 (12.0) nm.

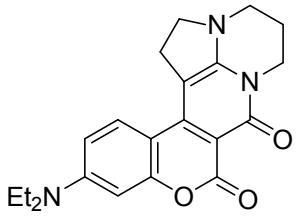


4c

The crude product was recrystallized from CH_3CN.Yield 59%. M.p. 305-306°C(dec.)

^{1}H NMR (CF_3COOD): δ 7.84 (d, J = 9.1 Hz, 1H), 7.08 (dd, J = 9.0 2.6 Hz, 1H), 6.95 (d, J = 2.5 Hz, 1H), 4.27 (t, J = 5.9 Hz, 2H), 4.17 (t, J = 8.2 Hz, 2H), 3.94 (s, 3H), 3.62 (t, J = 5.8 Hz, 2H), 3.57 (t, J =

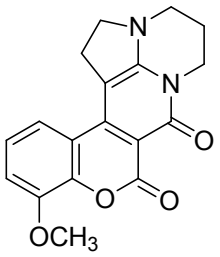
8.5 Hz, 2H), 2.37 (quin, J = 5.8 Hz, 2H) ppm; ^{13}C NMR (CF_3COOD): δ 169.8, 167.0, 164.8, 157.4, 155.6, 139.5, 130.6, 116.6, 111.1, 110.9, 104.8, 90.4, 57.4, 54.8, 44.0, 43.0, 27.7, 20.1 ppm; HRMS (EI) calcd for $C_{18}H_{16}N_2O_4$: 324.1110 [$M^{+\cdot}$], found: 324.1115; Anal. Calcd. for $C_{18}H_{16}N_2O_4 \cdot 0.25H_2O$ (328.83): C, 65.75; H, 5.06; N, 8.52; Found: C, 65.76; H, 5.10; N, 8.39; λ_{abs} (DCM, $\varepsilon \times 10^{-3}$) 400 (18.8), 384 (18.8), 321 (14.5) nm.



4d

The crude product was recrystallized from EtOH. Yield 60%. M.p. 305^{o}C(dec.)

^{1}H NMR (DMSO-d_6, T = 323 K): δ 7.62 (d, J = 9.0 Hz, 1H), 6.56 (d, J = 8.3 Hz, 1H), 6.31 (s, 1H), 3.69-3.82 (m, 4H), 3.39 (q, J = 6.8 Hz, 4H), 3.29 (br. s, 2H), 3.22 (t, J = 7.9 Hz, 2H), 2.03 (br. s, 2H), 1.13 (t, J = 6.6 Hz, 6H) ppm; ^{13}C NMR (DMSO-d_6, T = 323 K): δ 158.3, 157.4, 155.1, 155.0, 149.8, 141.2, 127.7, 107.4, 105.0, 96.8, 93.0, 88.2, 51.0, 43.6, 41.3, 36.8, 26.3, 19.1, 12.2 ppm; HRMS (EI) calcd for $C_{21}H_{23}N_3O_3$: 365.1739 [$M^{+\cdot}$], found: 365.1748; Anal. Calcd. for $C_{21}H_{23}N_3O_3 \cdot 0.2H_2O$ (369.03): C, 68.35; H, 6.39; N, 11.39; Found: C, 68.46; H, 6.32; N, 11.40; λ_{abs} (DCM, $\varepsilon \times 10^{-3}$) 399 (38.6), 380 (30.7), 358 (31.9), 270 (15.6) nm.



4e

The crude product was recrystallized from CH_3CN. Yield 76%. M.p. 383-384^{o}C(dec.)

^{1}H NMR (CF_3COOD): δ 7.52 (d, J = 7.9 Hz, 1H), 7.45 (t, J = 8.2 Hz, 1H), 7.36 (d, J = 7.8 Hz, 1H), 4.29 (t, J = 6.0 Hz, 2H), 4.19 (t, J = 8.2 Hz, 2H), 4.02 (s, 3H), 3.59-3.66 (m, 4H), 2.39 (quin, J = 5.8 Hz, 2H) ppm; ^{13}C NMR (CF_3COOD): δ 169.0, 164.8, 157.8, 150.0, 143.5, 139.5, 128.9, 121.0, 119.0, 118.8, 113.7, 91.0, 58.2, 54.9, 44.1, 43.2, 27.9, 19.9 ppm; HRMS (EI) calcd for $C_{18}H_{16}N_2O_4$: 324.1110 [$M^{+\cdot}$], found: 324.1109; Anal. Calcd. for $C_{18}H_{16}N_2O_4 \cdot 0.2H_2O$ (327.93): C, 65.93; H, 5.04; N, 8.54; Found: C, 65.96; H, 5.00; N, 8.36; λ_{abs} (DCM, $\varepsilon \times 10^{-3}$) 410 (15.2), 390 (16.2), 277 (28.4) nm.

Scheme S1. Proposed reaction mechanism for the oxidative cyclisation

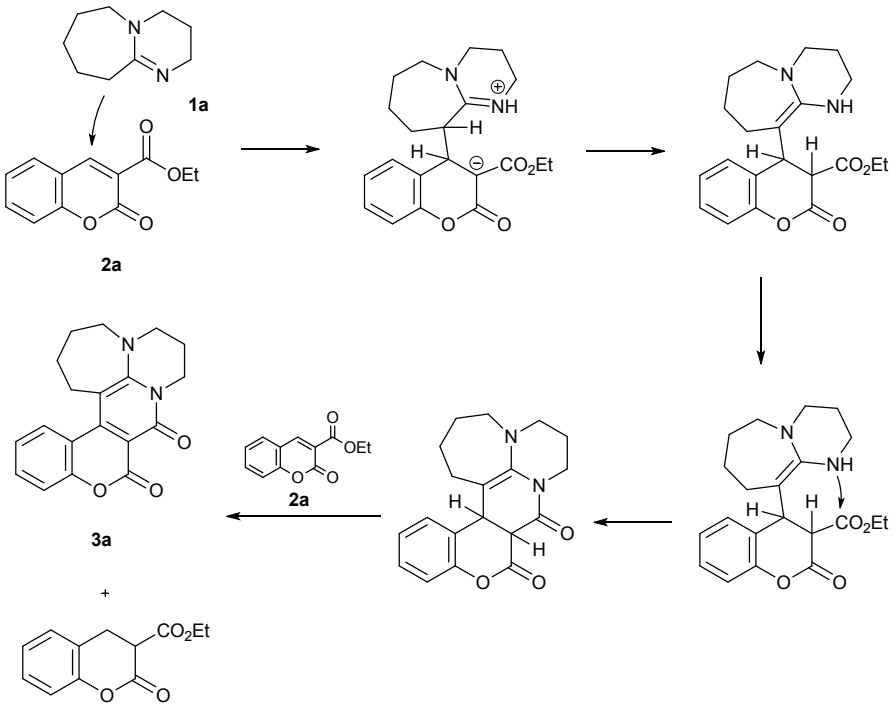
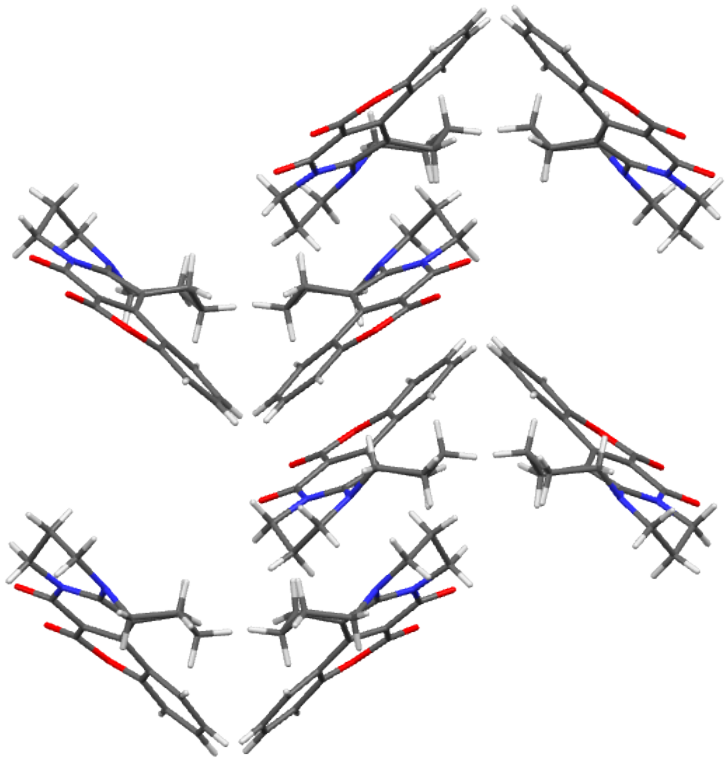
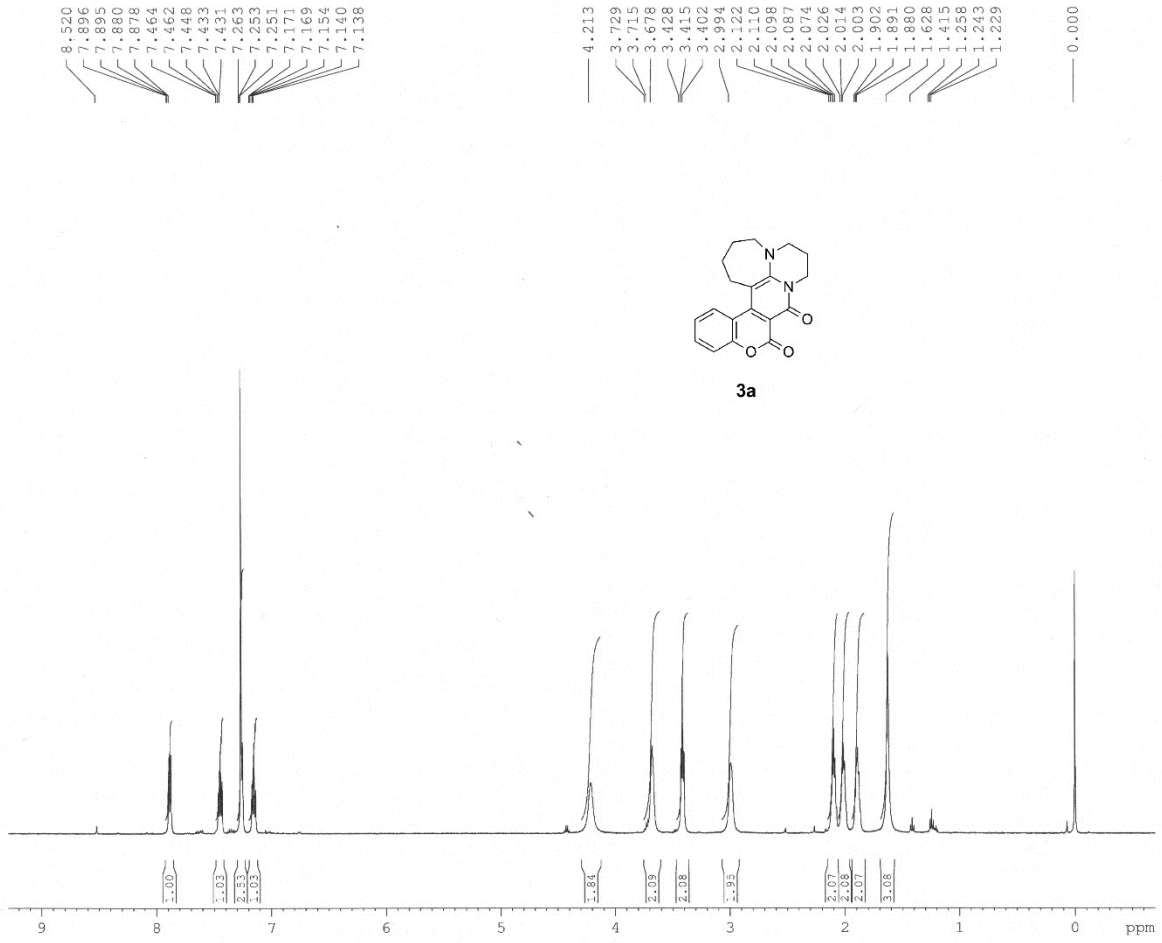


Figure S1. Crystal packing for compound **3a**.





3a

BRUKER

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PROCNO                     1

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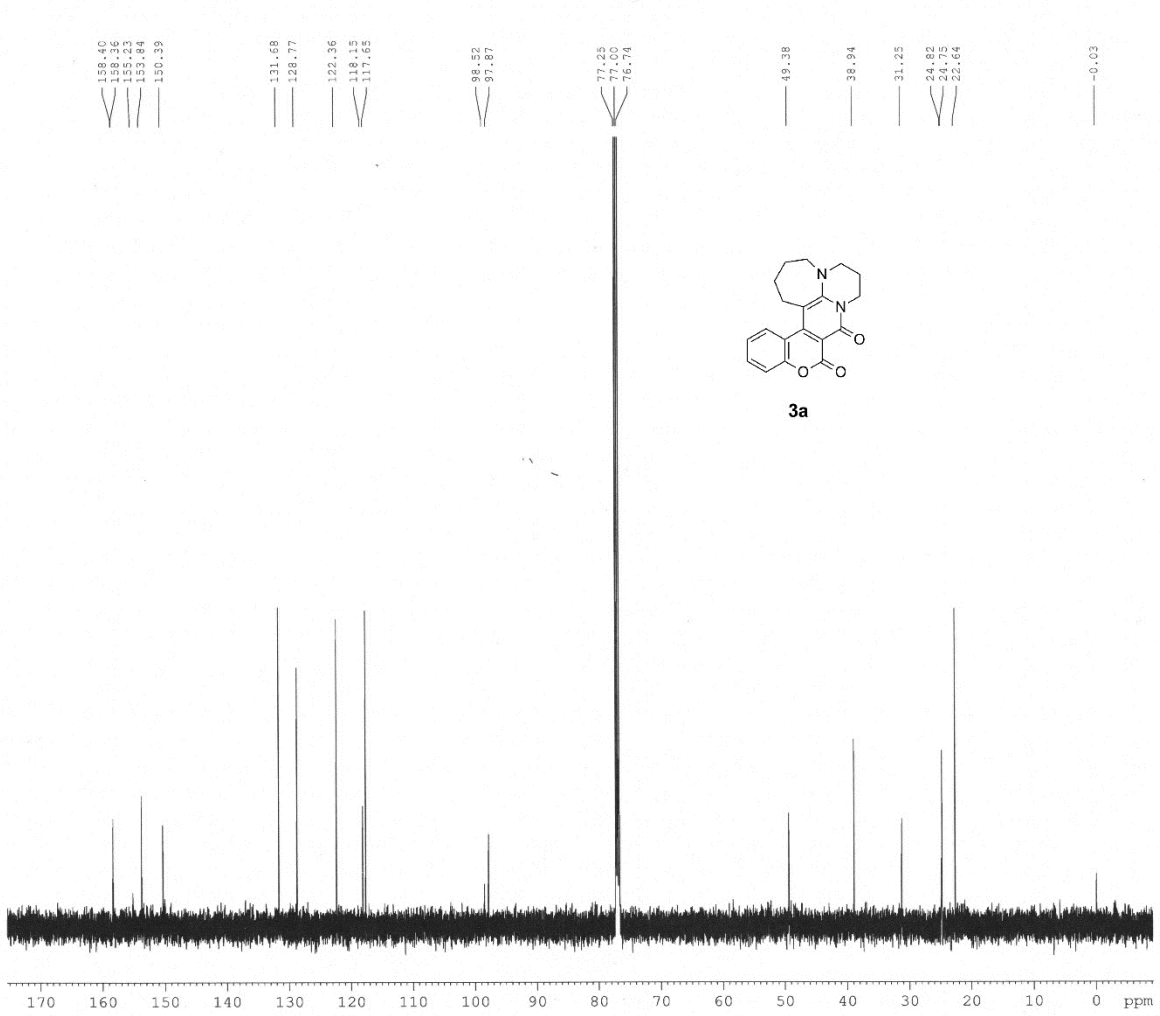

3a

BRUKER

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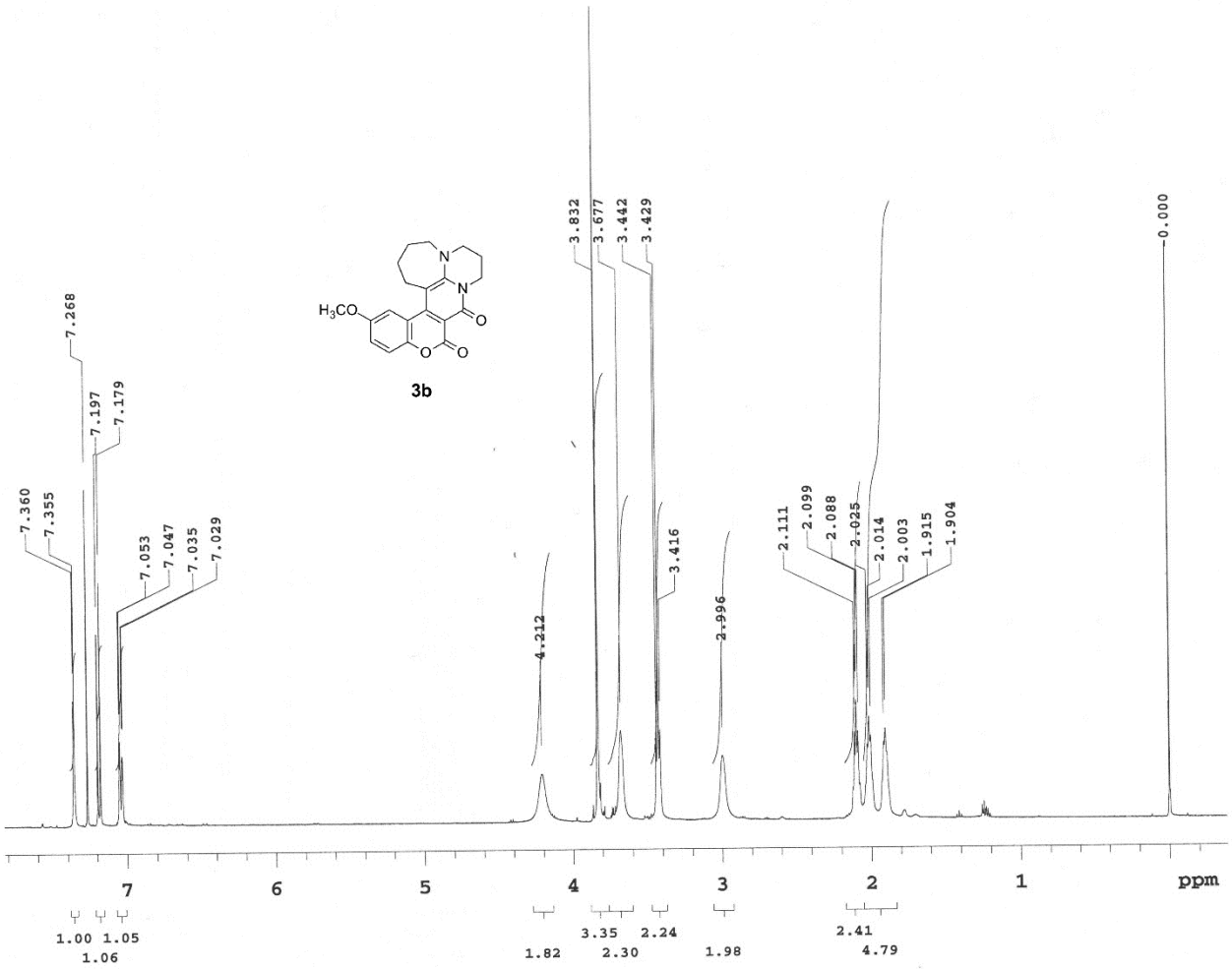
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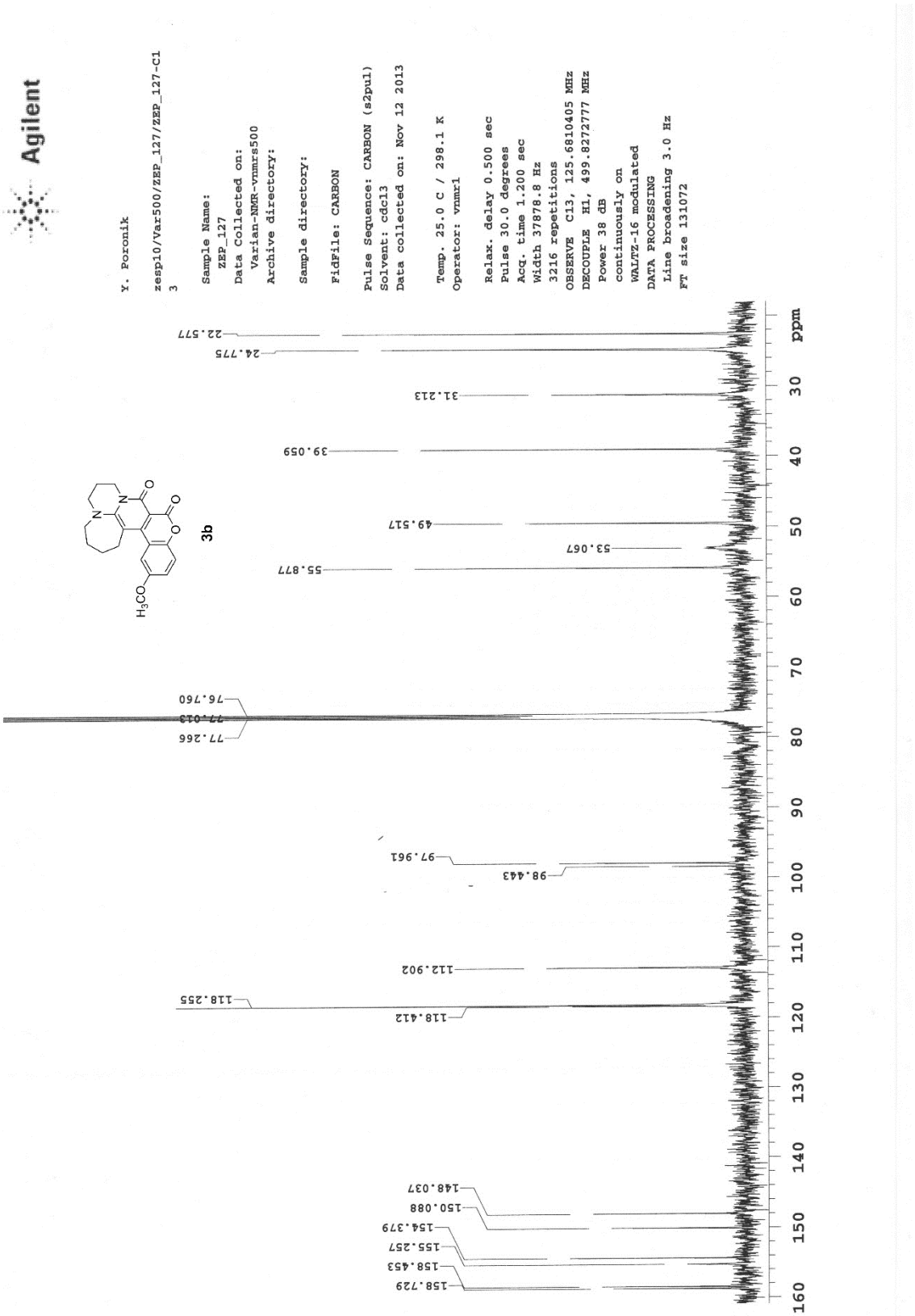
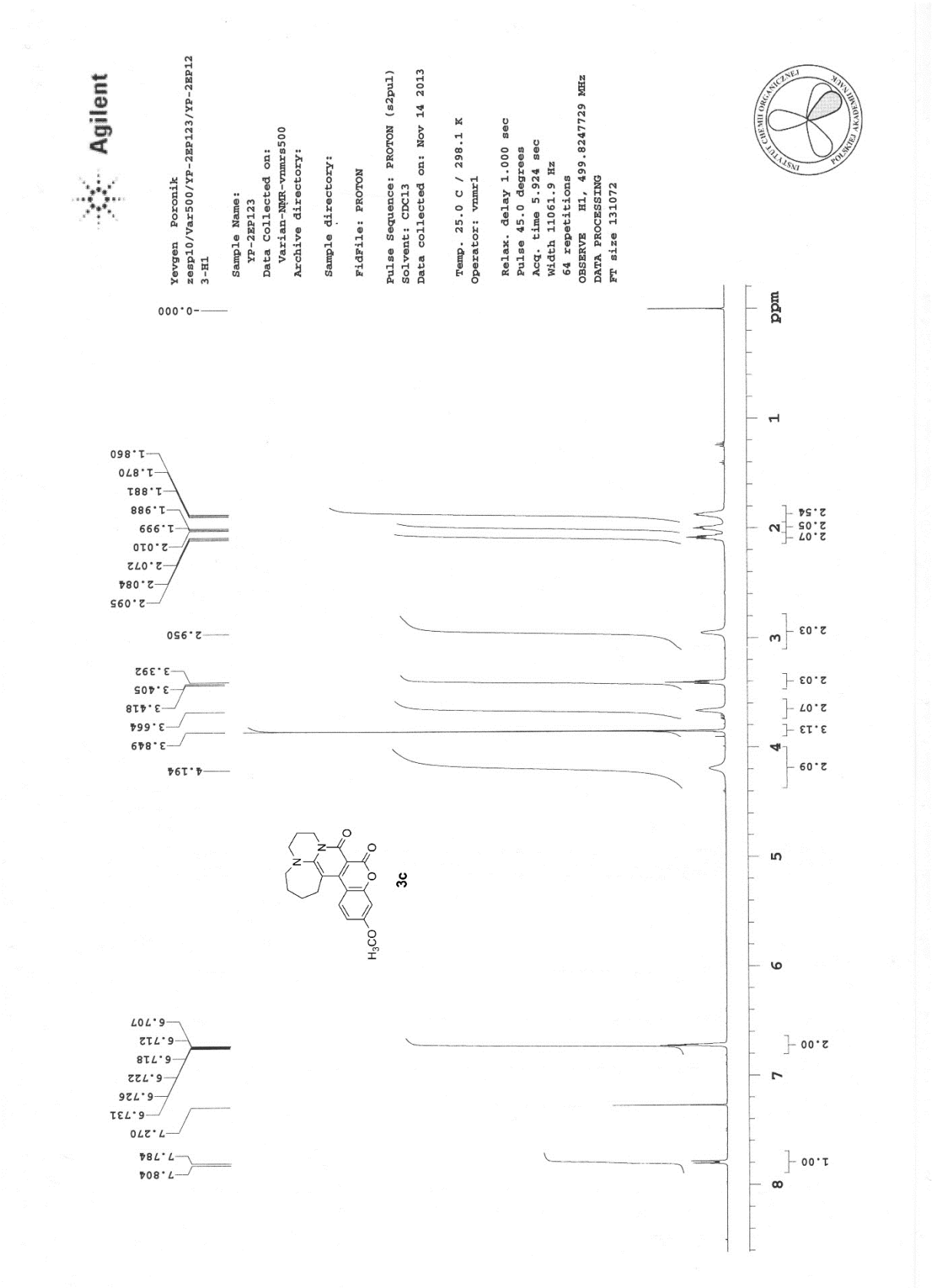
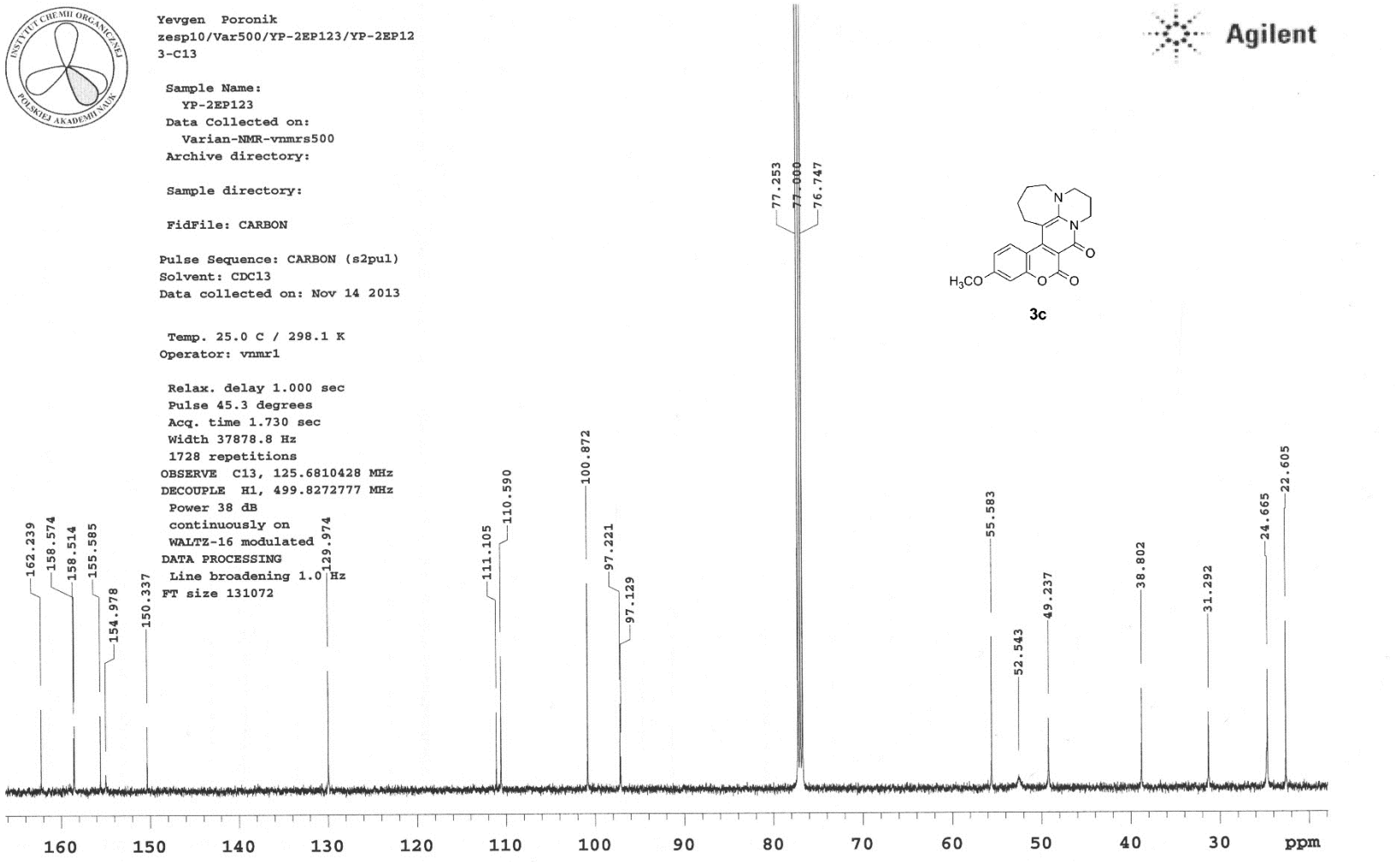
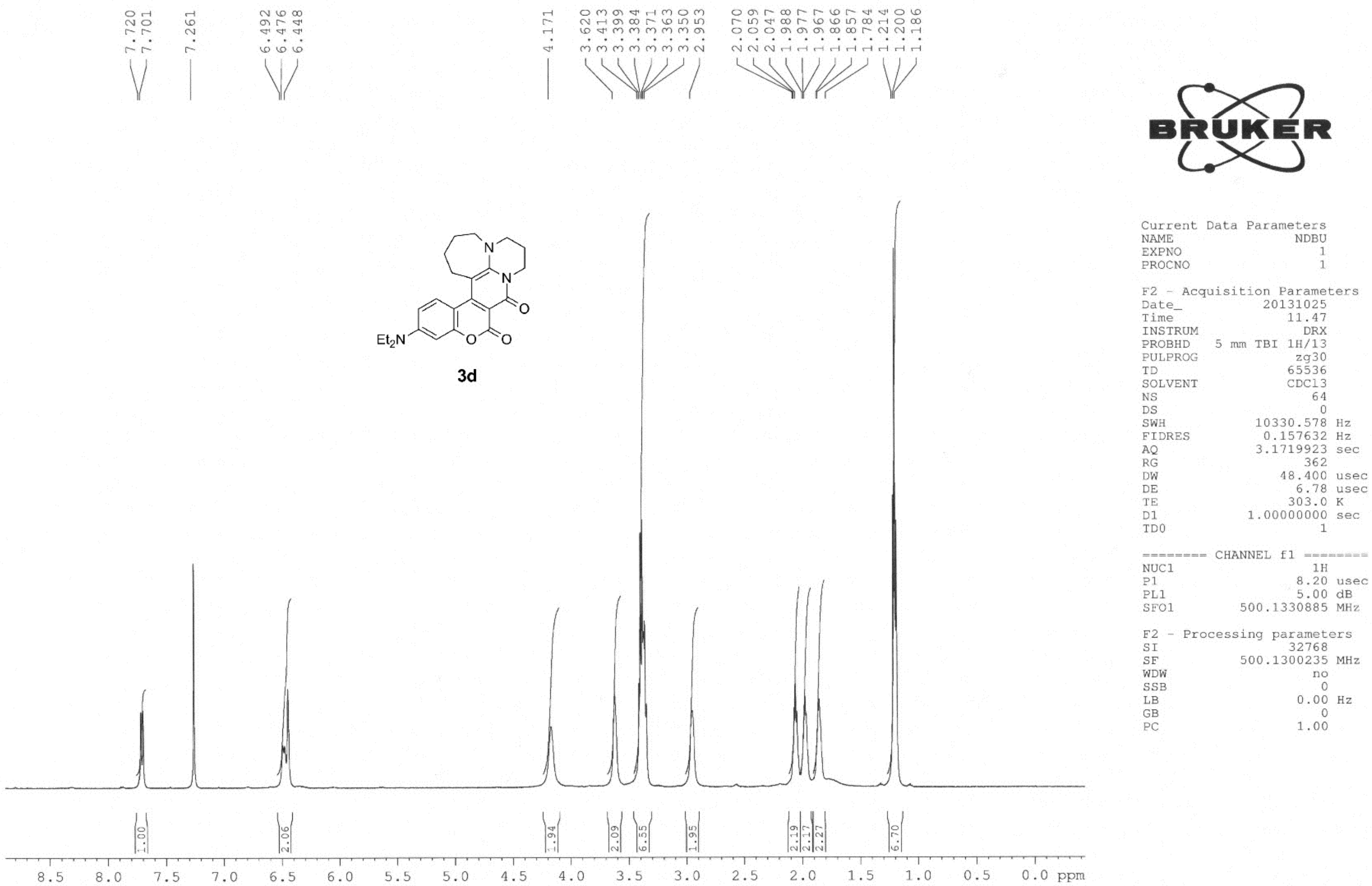
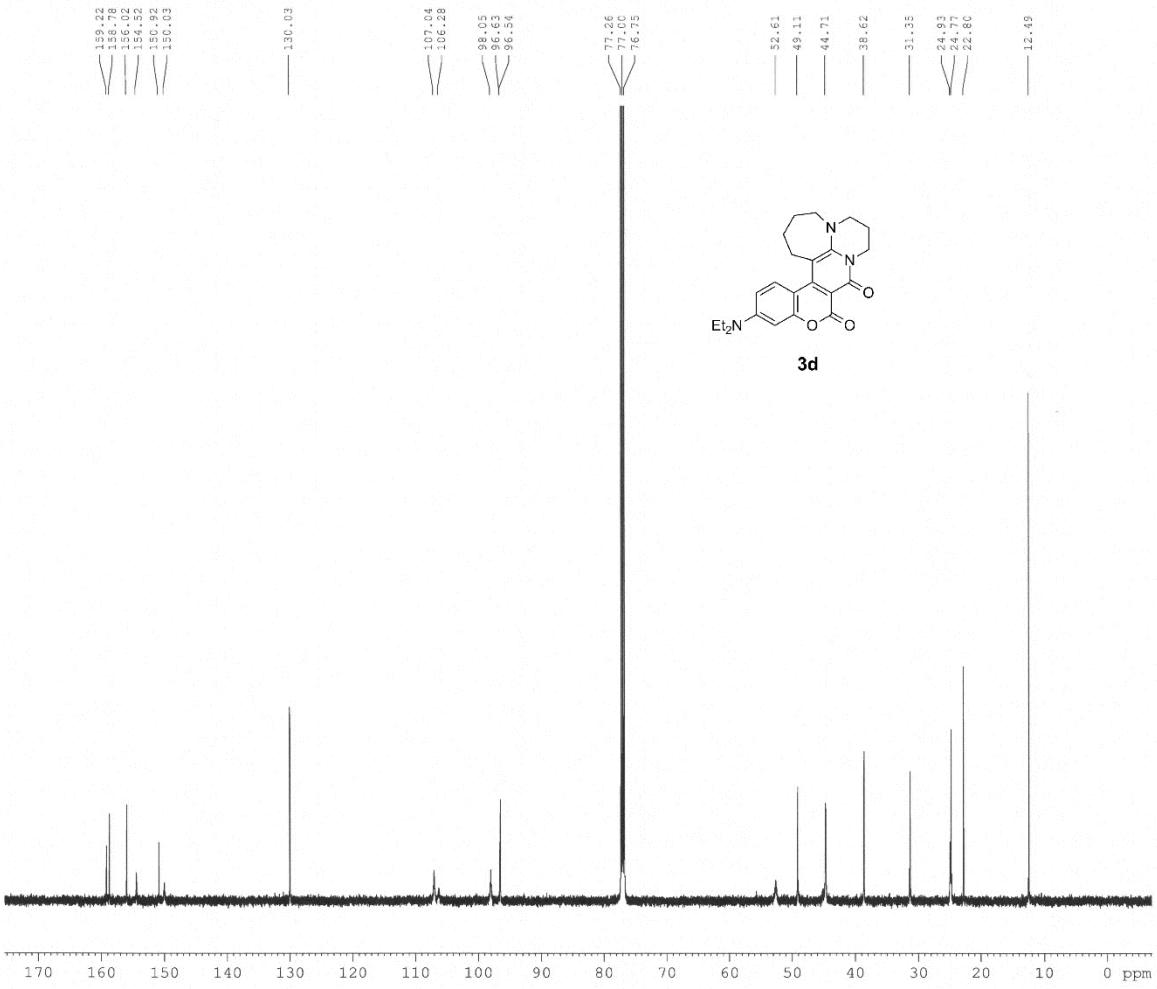
4.212
3.832
3.677
3.442
3.429
3.416
2.996
2.111
2.099
2.088
2.025
2.014
2.003
1.915
1.904
0.000
ppm
1.00 1.05
1.06
1.82
3.35 2.24
2.30
1.98
2.41
4.79


Agilent
Y. Poronik
zesp10/Var500/ZEP_127/ZEP_127-C1
3
Sample Name:
ZEP_127
Data Collected on:
Varian-NMR-vnmrs500
Archive directory:
Sample directory:
FidFile: CARBON
Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Nov 12 2013
Temp. 25.0 C / 298.1 K
Operator: vnmr1
Relax. delay 0.500 sec
Pulse 30.0 degrees
Acq. time 1.200 sec
Width 37878.8 Hz
3216 repetitions
OBSERVE C13, 125.6810405 MHz
DECOUPLE H1, 499.8272777 MHz
Power 38 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 3.0 Hz
FT size 131072
3b
22.577
24.775
31.213
39.059
49.517
53.067
55.877
76.760
77.013
77.266
97.961
98.443
112.902
118.255
118.412
148.037
150.088
154.379
155.257
158.453
158.729
ppm


Agilent
Yevgen Poronik
zesp10/Var500/YP-2EP123/YP-2EP12
3-H1
Sample Name:
YP-2EP123
Data Collected on:
Varian-NMR-vnmrs500
Archive directory:
Sample directory:
FidFile: PROTON
Pulse Sequence: PROTON (s2pul)
Solvent: CDCl3
Data collected on: Nov 14 2013
Temp. 25.0 C / 298.1 K
Operator: vnmr1
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 5.924 sec
Width 11061.9 Hz
64 repetitions
OBSERVE H1, 499.8247729 MHz
DATA PROCESSING
FT size 131072
INSTYTUT CHEMII ORGANICZNEJ
POLSKIEJ AKADEMII NAUK
ppm
3c
H3CO

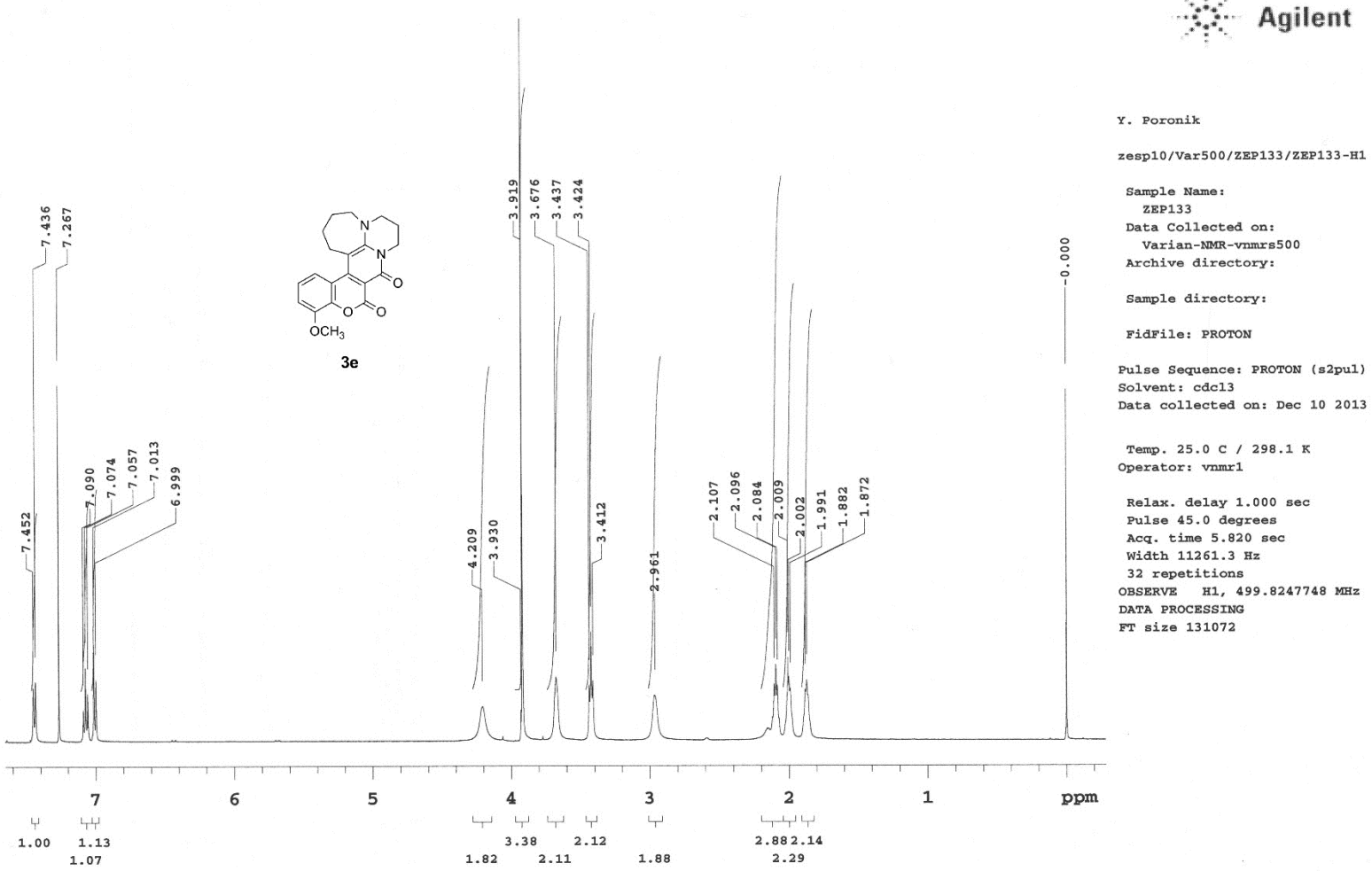

Yevgen Poronik
zesp10/Var500/YP-2EP123/YP-2EP12
3-C13
Sample Name:
YP-2EP123
Data Collected on:
Varian-NMR-vnmrs500
Archive directory:
Sample directory:
FidFile: CARBON
Pulse Sequence: CARBON (s2pul)
Solvent: CDCl3
Data collected on: Nov 14 2013
Temp. 25.0 C / 298.1 K
Operator: vnmr1
Relax. delay 1.000 sec
Pulse 45.3 degrees
Acq. time 1.730 sec
Width 37878.8 Hz
1728 repetitions
OBSERVE C13, 125.6810428 MHz
DECOUPLE H1, 499.8272777 MHz
Power 38 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Agilent
3c
162.239
158.574
158.514
155.585
154.978
150.337
129.974
111.105
110.590
100.872
97.221
97.129
77.253
77.000
76.747
55.583
52.543
49.237
38.802
31.292
24.665
22.605
160
150
140
130
120
110
100
90
80
70
60
50
40
30
ppm

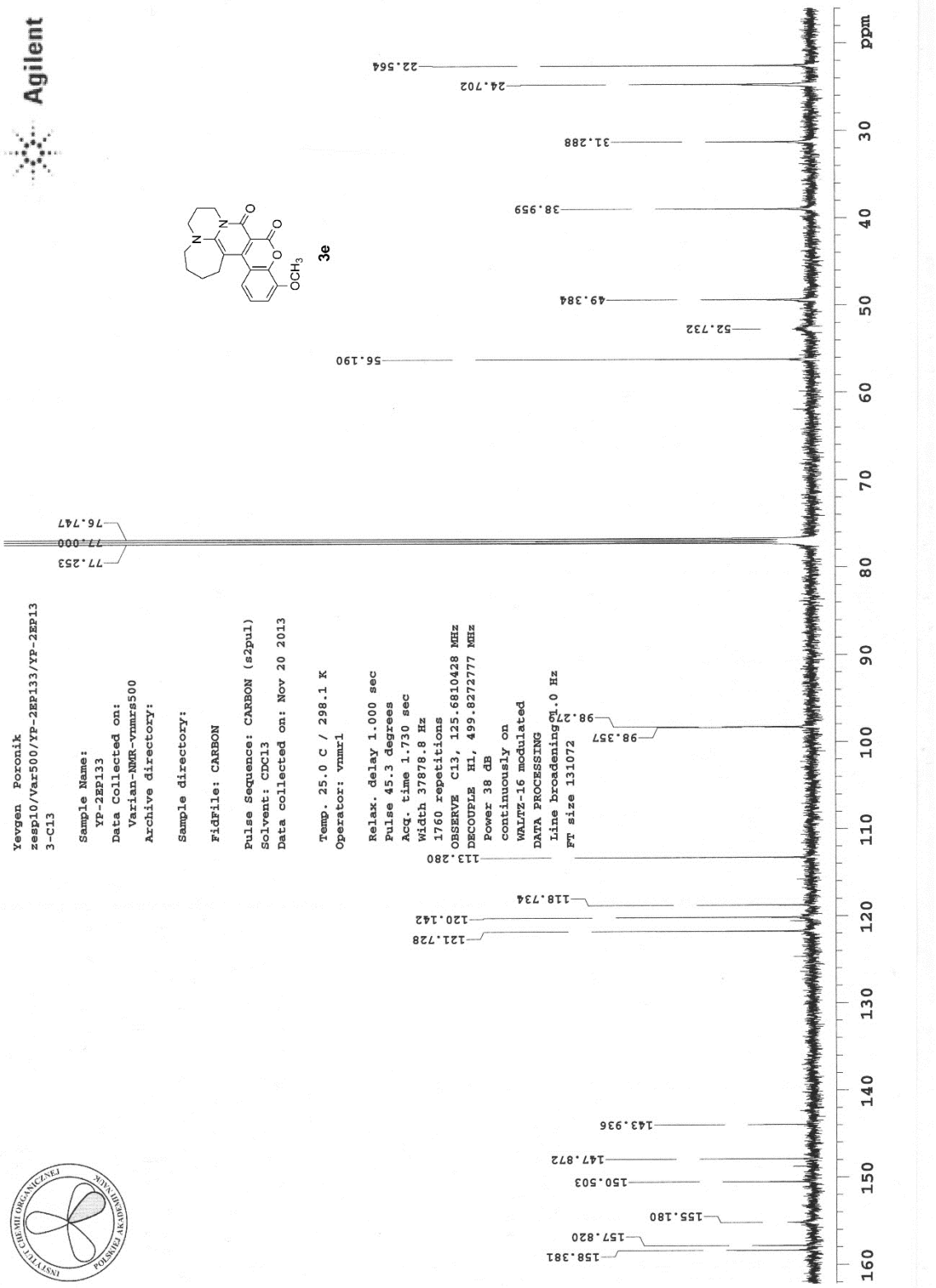

7.720
7.701
7.261
6.492
6.476
6.448
4.171
3.620
3.413
3.399
3.384
3.371
3.363
3.350
2.953
2.070
2.059
2.047
1.988
1.977
1.967
1.866
1.857
1.784
1.214
1.200
1.186
Et2N
N
N
O
O
O
3d
1.00
2.06
1.94
2.09
6.55
1.95
2.19
2.17
2.27
6.70
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
BRUKER
Current Data Parameters
NAME NDBU
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20131025
Time 11.47
INSTRUM DRX
PROBHD 5 mm TBI 1H/13
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 64
DS 0
SWH 10330.578 Hz
FIDRES 0.157632 Hz
AQ 3.1719923 sec
RG 362
DW 48.400 usec
DE 6.78 usec
TE 303.0 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 8.20 usec
PL1 5.00 dB
SFO1 500.1330885 MHz
F2 - Processing parameters
SI 32768
SF 500.1300235 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00

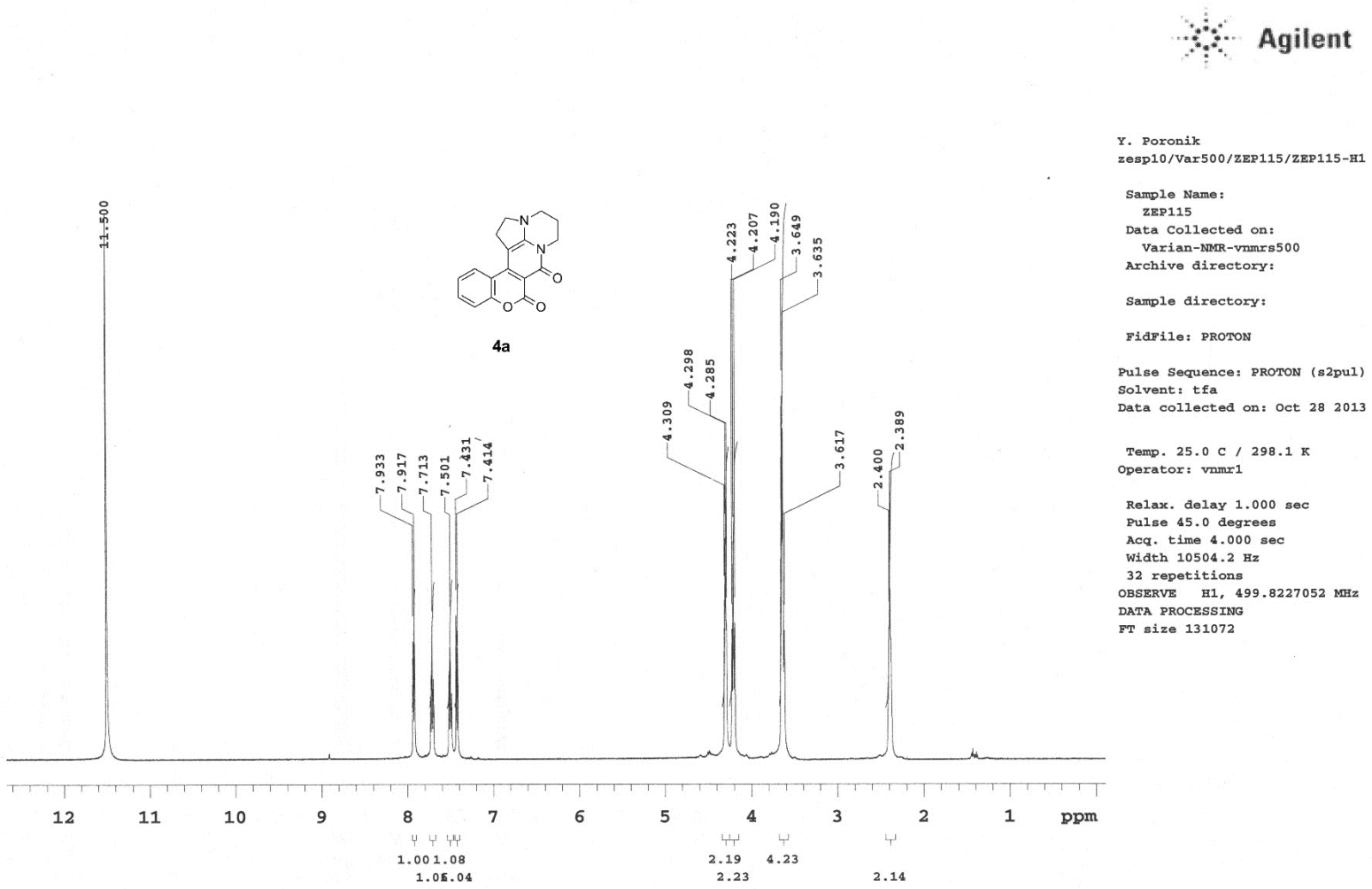


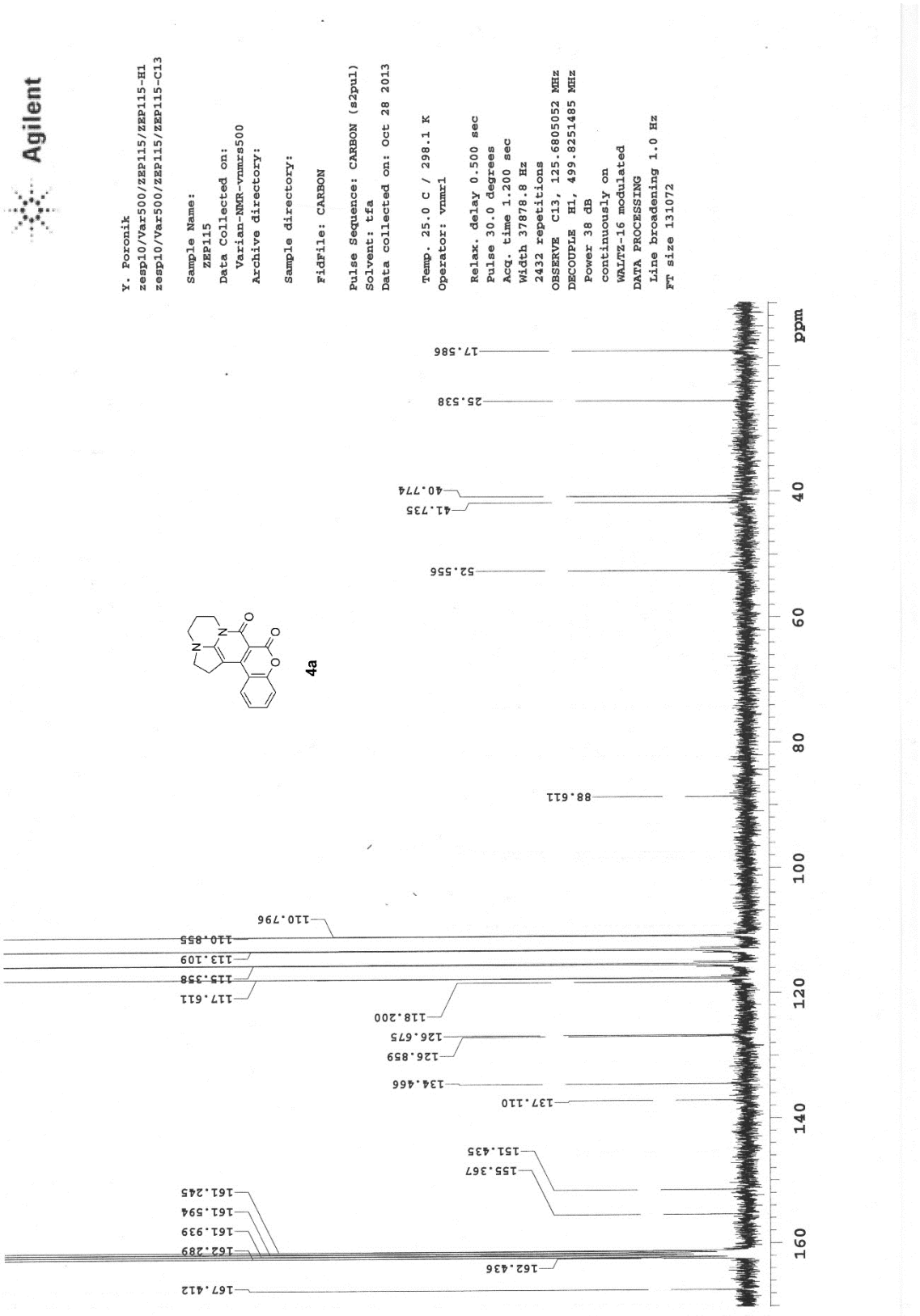
BRUKER

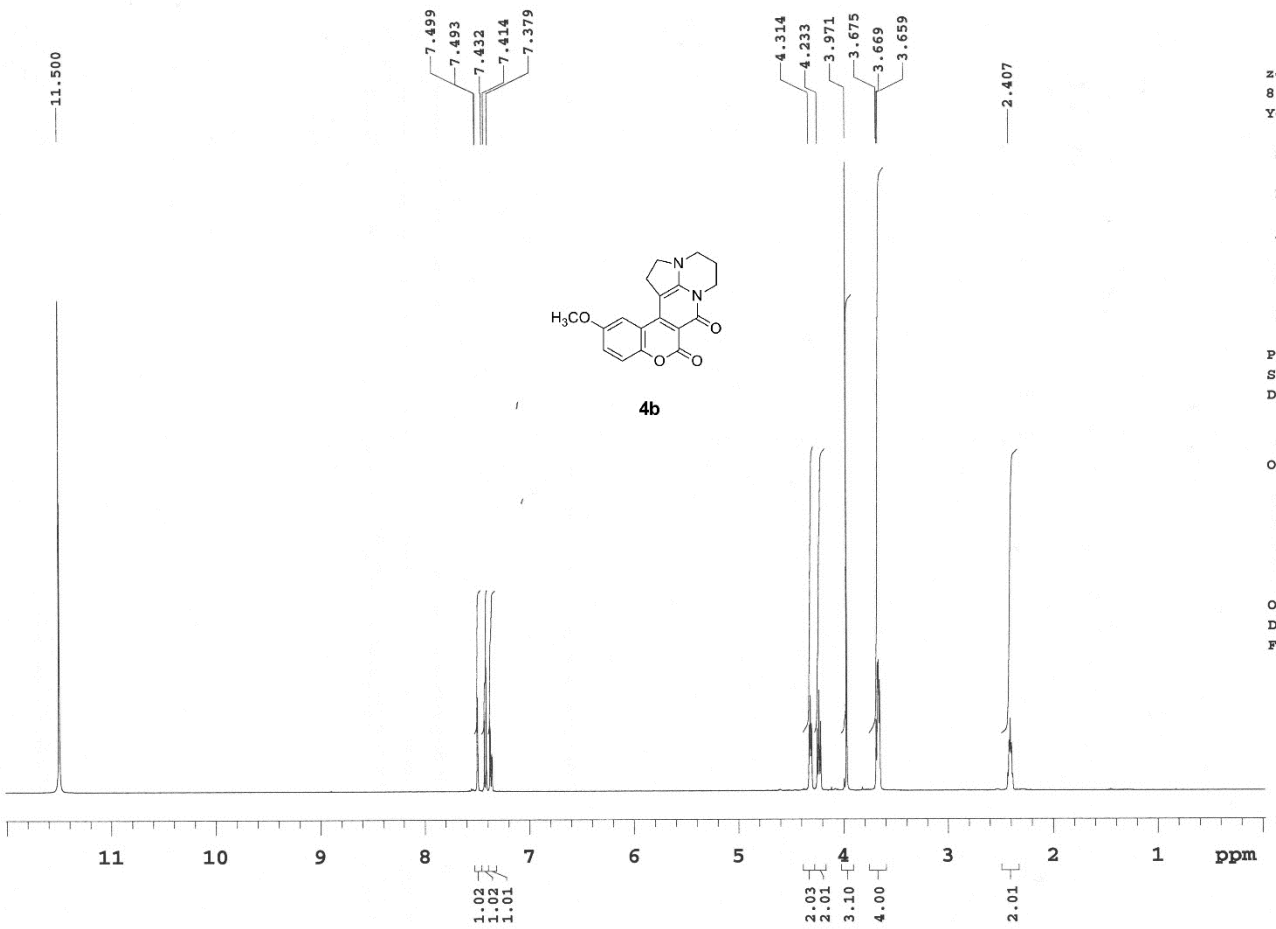
```
Current Data Parameters
NAME                  ZEP117
EXPNO                      2
PROCNO                     1

F2 - Acquisition Parameters
Date_              20131211
Time                  15.24
INSTRUM                 DRX
PROBHD   5 mm TBI 1H/13
PULPROG                zgpg
TD                    65536
SOLVENT               CDCl3
NS                    30000
DS                        4
SWH               32679.738 Hz
FIDRES            0.498653 Hz
AQ                1.0027508 sec
RG                    32768
DW                   15.300 usec
DE                    7.10 usec
TE                   303.0 K
D1                1.00000000 sec
d11               0.03000000 sec
DELTA             0.89999998 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                    13C
P1                     5.00 usec
PL1                   -3.00 dB
SFO1           125.7703643 MHz

======== CHANNEL f2 ========
CPDPRG2              waltz16
NUC2                    1H
PCPD2                 98.00 usec
PL2                    3.00 dB
PL12                  23.00 dB
PL13                  32.00 dB
SFO2           500.1320005 MHz

F1 - Acquisition parameters
ND0                        1
TD                       128
SFO1              500.132 MHz
FIDRES           7.812500 Hz
SW                    1.999 ppm
FnMODE                   QF

F2 - Processing parameters
SI                     262144
SF             125.7577955 MHz
WDW                      EM
SSB                       0
LB                     0.50 Hz
GB                        0
PC                     1.40

F1 - Processing parameters
SI                      1024
MC2                       QF
SF             500.1300000 MHz
WDW                    SINE
SSB                       0
LB                     0.30 Hz
GB                      0.1
```


Agilent
Y. Poronik
zesp10/Var500/ZEP133/ZEP133-H1
Sample Name:
ZEP133
Data Collected on:
Varian-NMR-vnmrs500
Archive directory:
Sample directory:
FidFile: PROTON
Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Dec 10 2013
Temp. 25.0 C / 298.1 K
Operator: vnmr1
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 5.820 sec
Width 11261.3 Hz
32 repetitions
OBSERVE H1, 499.8247748 MHz
DATA PROCESSING
FT size 131072
7.452
7.436
7.267
7.090
7.074
7.057
7.013
6.999
4.209
3.930
3.919
3.676
3.437
3.424
3.412
2.961
2.107
2.096
2.084
2.009
2.002
1.991
1.882
1.872
0.000
OCH3
3e
7
6
5
4
3
2
1
ppm
1.00
1.13
1.07
1.82
3.38
2.11
2.12
1.88
2.88
2.14
2.29


Agilent
Yevgen Poznik
zesp10/Var500/YP-2EP133/YP-2EP13
3-C13
Sample Name:
YP-2EP133
Data Collected on:
Varian-NMR-vnmrs500
Archive directory:
Sample directory:
FidFile: CARBON
Pulse Sequence: CARBON (s2pul)
Solvent: CDCl3
Data collected on: Nov 20 2013
Temp. 25.0 C / 298.1 K
Operator: vnmrl
Relax. delay 1.000 sec
Pulse 45.3 degrees
Acq. time 1.730 sec
Width 37878.8 Hz
1760 repetitions
OBSERVE C13, 125.6810428 MHz
DECOUPLE H1, 499.8272777 MHz
Power 38 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
3e
77.253
77.000
76.747
56.190
52.732
49.384
38.959
31.288
24.702
22.564
98.357
98.274
113.280
118.734
120.142
121.728
143.936
147.872
150.503
155.180
157.820
158.381
ppm


Agilent
Y. Poronik
zesp10/Var500/ZEP115/ZEP115-H1
Sample Name:
ZEP115
Data Collected on:
Varian-NMR-vnmrs500
Archive directory:
Sample directory:
FidFile: PROTON
Pulse Sequence: PROTON (s2pul)
Solvent: tfa
Data collected on: Oct 28 2013
Temp. 25.0 C / 298.1 K
Operator: vnmr1
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 4.000 sec
Width 10504.2 Hz
32 repetitions
OBSERVE H1, 499.8227052 MHz
DATA PROCESSING
FT size 131072
11.500
7.933
7.917
7.713
7.501
7.431
7.414
4.309
4.298
4.285
4.223
4.207
4.190
3.649
3.635
3.617
2.400
2.389
4a
12
11
10
9
8
7
6
5
4
3
2
1
ppm
1.00
1.08
1.05
5.04
2.19
2.23
4.23
2.14


Agilent
Y. Poronik
zesp10/Var500/ZEP115/ZEP115-H1
zesp10/Var500/ZEP115/ZEP115-C13
Sample Name:
ZEP115
Data Collected on:
Varian-NMR-vnmrs500
Archive directory:
Sample directory:
FidFile: CARBON
Pulse Sequence: CARBON (s2pul)
Solvent: tfa
Data collected on: Oct 28 2013
Temp. 25.0 C / 298.1 K
Operator: vnmr1
Relax. delay 0.500 sec
Pulse 30.0 degrees
Acq. time 1.200 sec
Width 37878.8 Hz
2432 repetitions
OBSERVE C13, 125.6805052 MHz
DECOUPLE H1, 499.8251485 MHz
Power 38 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
4a
17.586
25.538
40.774
41.735
52.556
88.611
110.796
110.855
113.109
115.358
117.611
118.200
126.675
126.859
134.466
137.110
151.435
155.367
161.245
161.594
161.939
162.289
162.436
167.412
ppm
160
140
120
100
80
60
40



Agilent

zesp10/Var500/YP-2EP128/YP-2EP128-H1
Yevgen Poronik

Sample Name:
YP-2EP128
Data Collected on:
Varian-NMR-vnmrs500
Archive directory:

Sample directory:

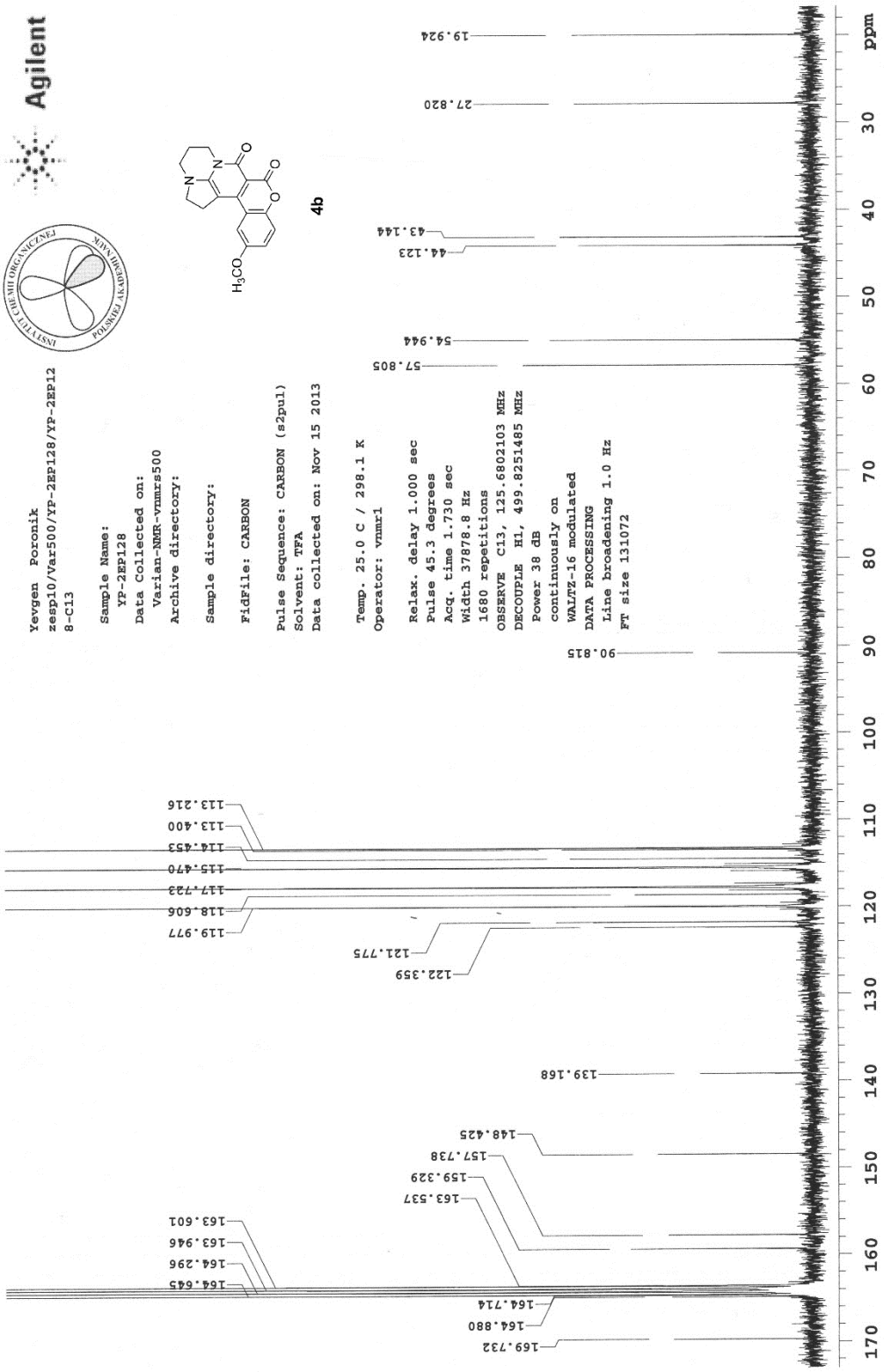
FidFile: PROTON

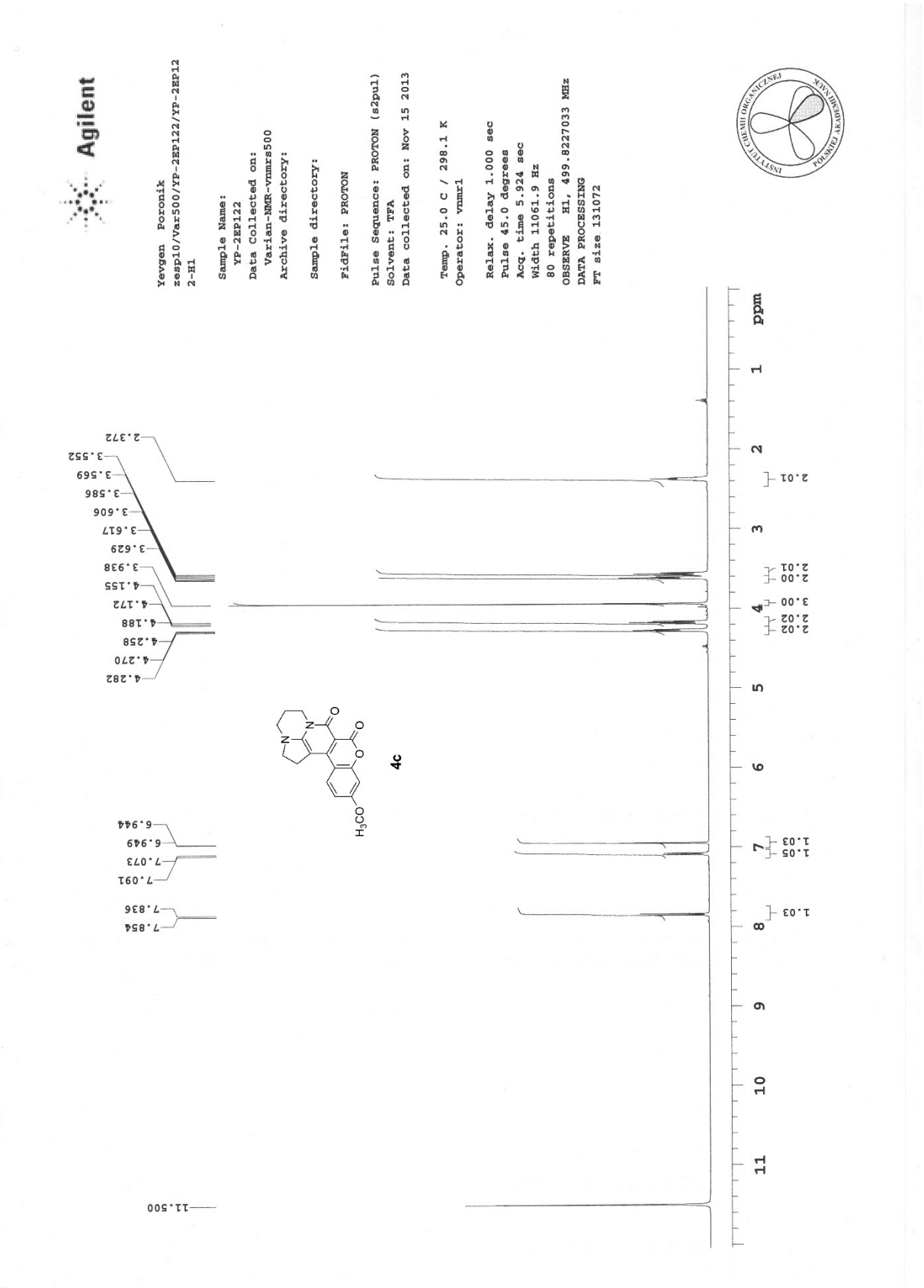
Pulse Sequence: PROTON (s2pul)
Solvent: TFA
Data collected on: Nov 15 2013

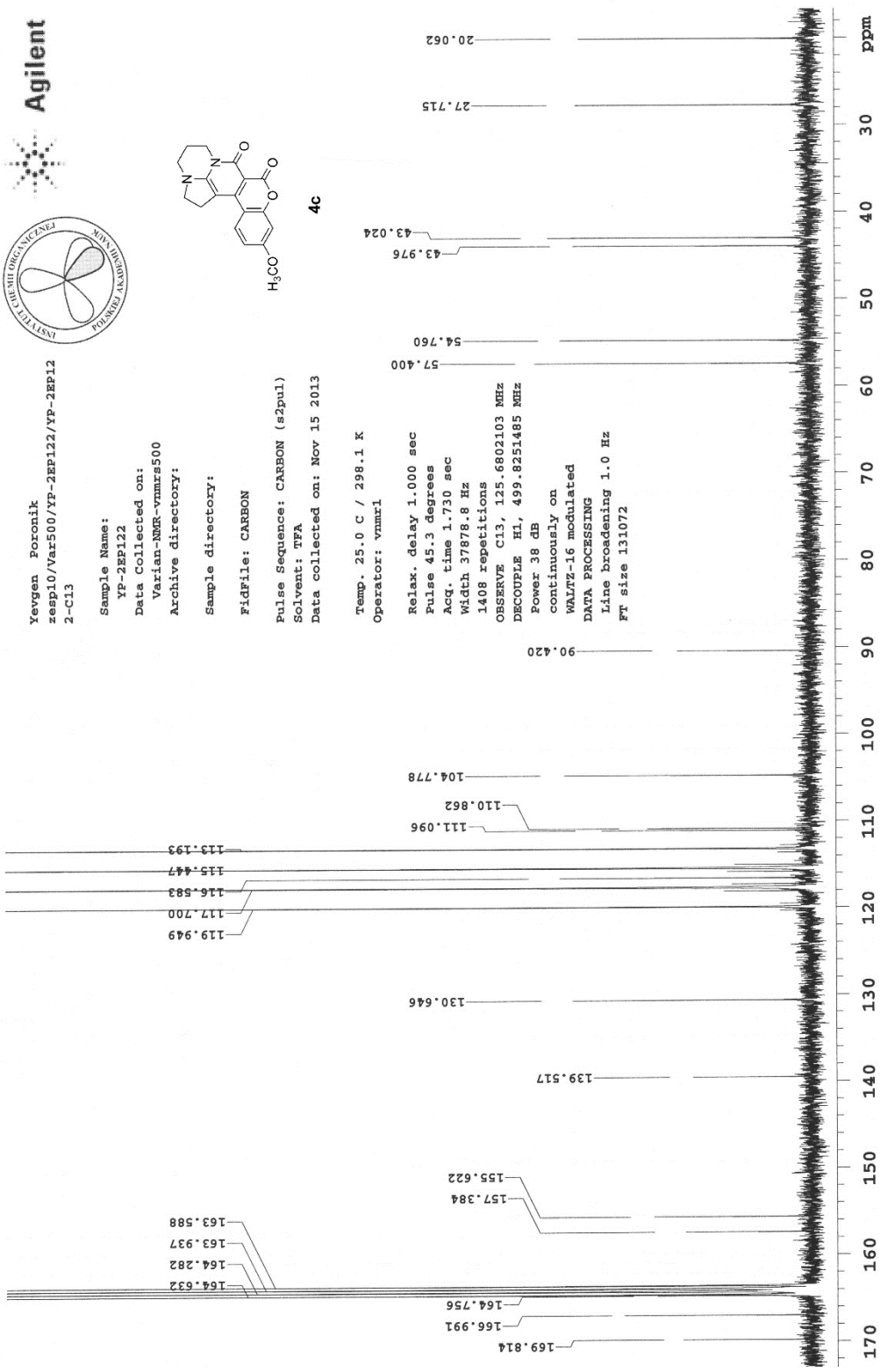
Temp. 25.0 C / 298.1 K
Operator: vnmr1

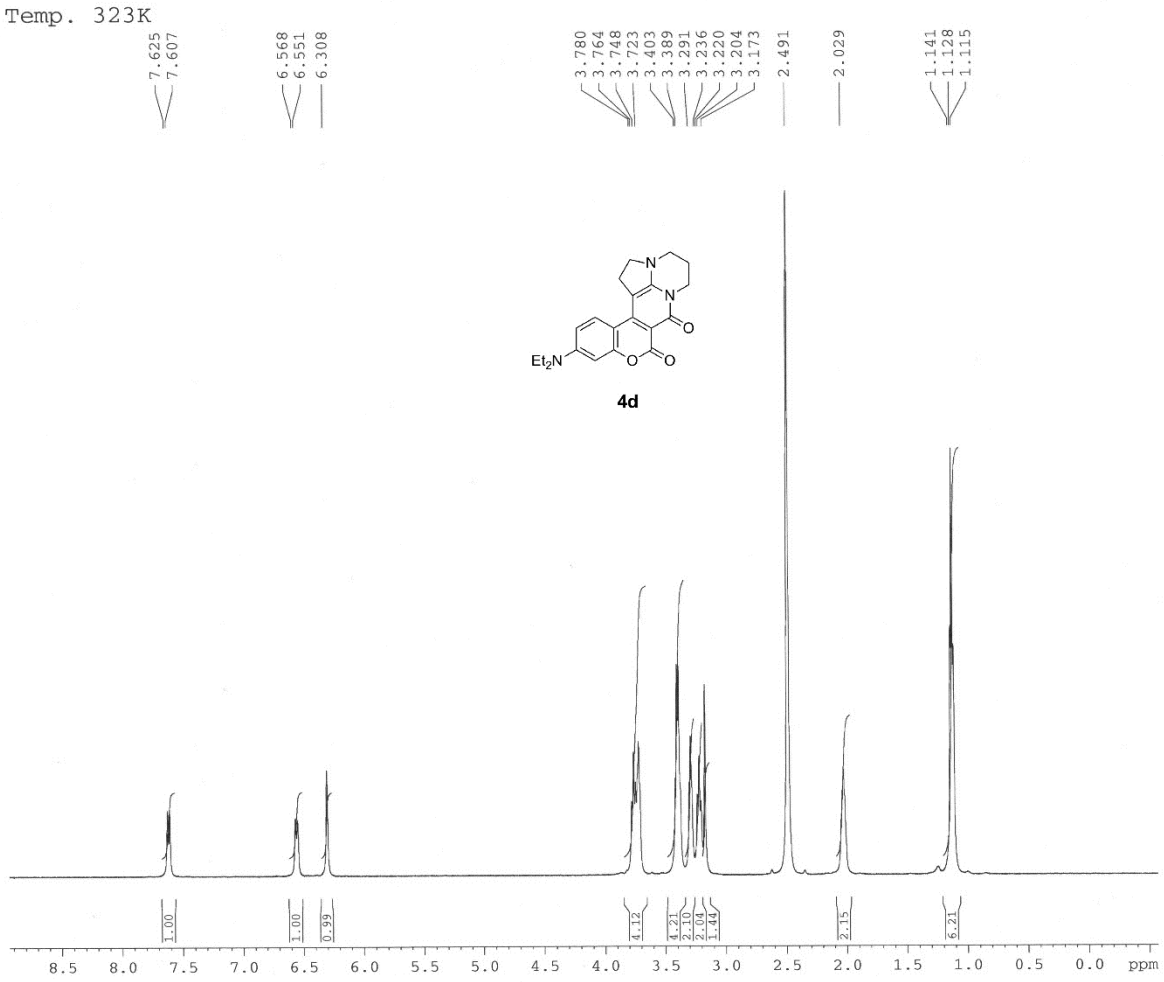
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 5.924 sec
Width 11061.9 Hz
64 repetitions
OBSERVE H1, 499.8227043 MHz
DATA PROCESSING
FT size 131072

INSTYTUT CHEMII ORGANICZNEJ POLSKIEJ AKADEMII NAUK


Agilent
Yevgen Poznik
zesp10/Var500/YP-2EP128/YP-2EP12
8-C13
Sample Name:
YP-2EP128
Data Collected on:
Varian-NMR-vnmrs500
Archive directory:
Sample directory:
FidFile: CARBON
Pulse Sequence: CARBON (s2pul)
Solvent: TFA
Data collected on: Nov 15 2013
Temp. 25.0 C / 298.1 K
Operator: vnmr1
Relax. delay 1.000 sec
Pulse 45.3 degrees
Acq. time 1.730 sec
Width 37878.8 Hz
1680 repetitions
OBSERVE C13, 125.6802103 MHz
DECOUPLE H1, 499.8251485 MHz
Power 38 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
4b
H3CO
19.924
27.820
43.144
44.123
54.944
57.805
90.815
113.216
113.400
114.453
115.470
117.723
118.606
119.977
121.775
122.359
139.168
148.425
157.738
159.329
163.537
163.601
163.946
164.296
164.645
164.714
164.880
169.732
ppm


Agilent
Yevgen Poronik
zesp10/Var500/YP-2EP122/YP-2EP12
2--H1
Sample Name:
YP-2EP122
Data Collected on:
Varian-NMR-vnmrs500
Archive directory:
Sample directory:
FidFile: PROTON
Pulse Sequence: PROTON (s2pul)
Solvent: TFA
Data collected on: Nov 15 2013
Temp. 25.0 C / 298.1 K
Operator: vnmr1
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 5.924 sec
Width 11061.9 Hz
80 repetitions
OBSERVE H1, 499.8227033 MHz
DATA PROCESSING
FT size 131072
4c
H3CO
ppm


Agilent
Yevgen Poznik
zesp10/Var500/YP-2EP122/YP-2EP12
2-C13
Sample Name:
YP-2EP122
Data Collected on:
Varian-NMR-vnmrs500
Archive directory:
Sample directory:
FidFile: CARBON
Pulse Sequence: CARBON (s2pul)
Solvent: TFA
Data collected on: Nov 15 2013
Temp. 25.0 C / 298.1 K
Operator: vnmr1
Relax. delay 1.000 sec
Pulse 45.3 degrees
Acq. time 1.730 sec
Width 37878.8 Hz
1408 repetitions
OBSERVE C13, 125.6802103 MHz
DECOUPLE H1, 499.8251485 MHz
Power 38 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
4c
20.062
27.715
43.024
43.976
54.760
57.400
90.420
104.778
110.862
111.096
113.193
115.447
116.583
117.700
119.949
130.646
139.517
155.622
157.384
163.588
163.937
164.282
164.632
164.756
166.991
169.814
ppm



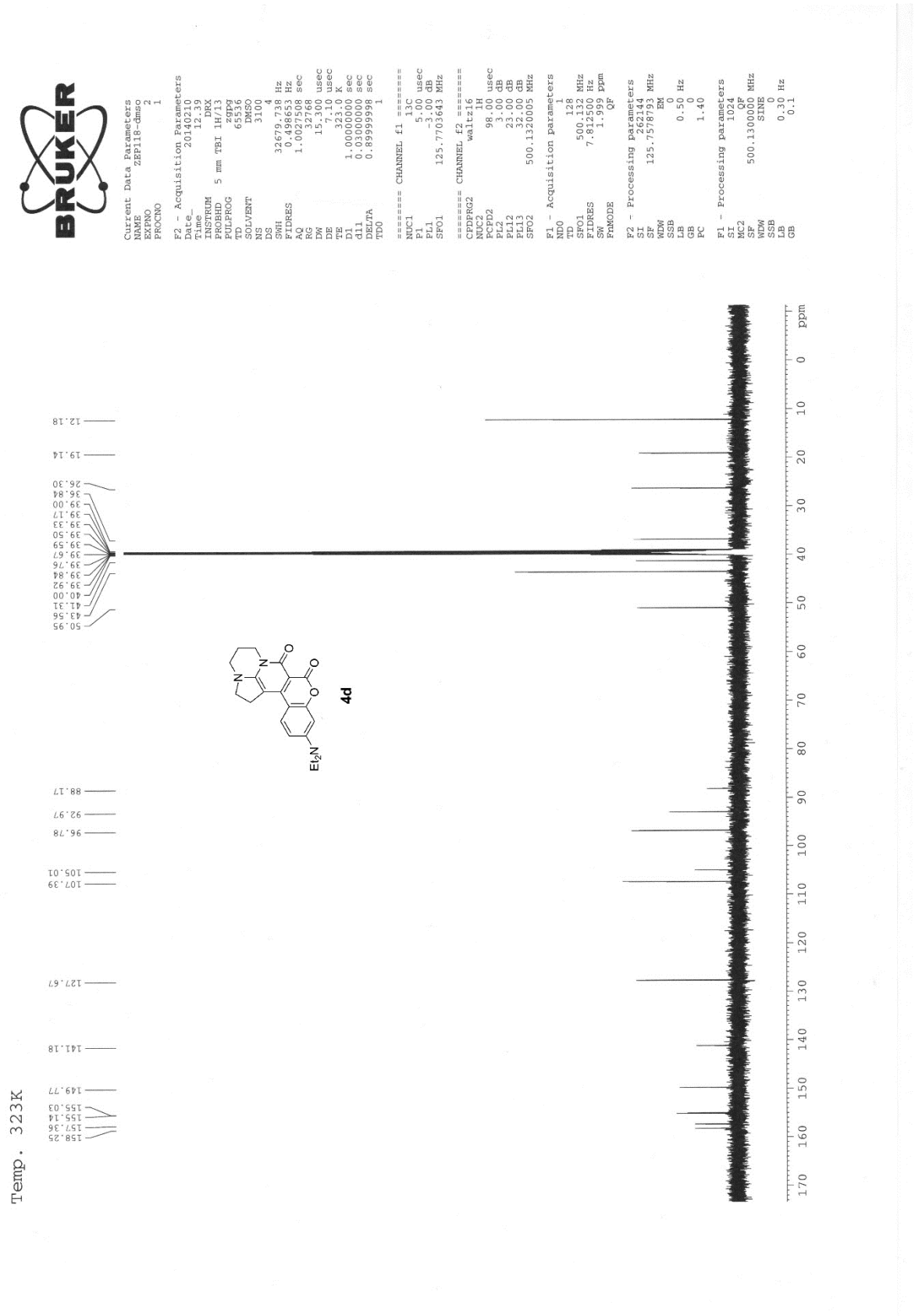
BRUKER

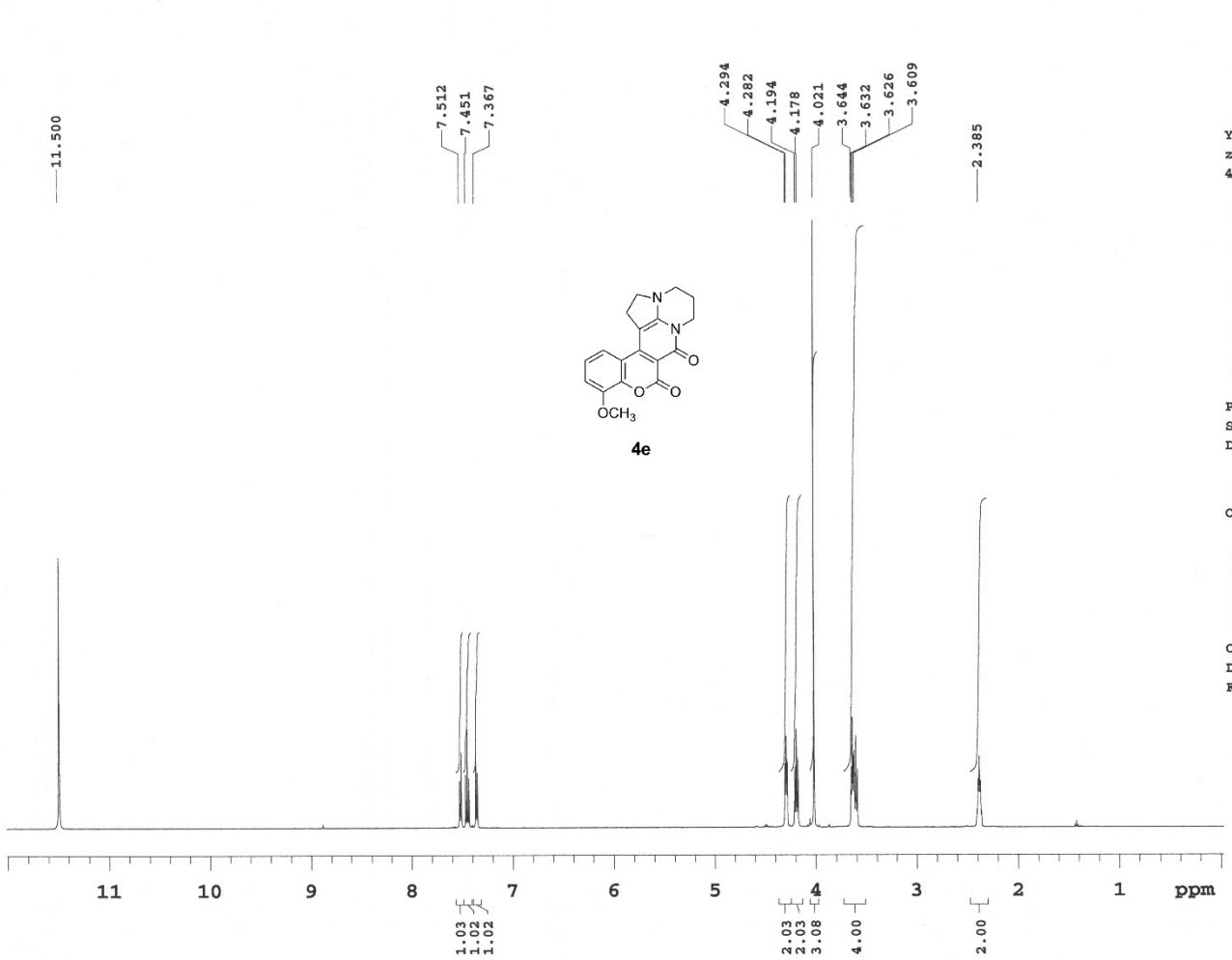
Current Data Parameters
NAME ZEP118-dmso
EXPNO 11
PROCNO 1

F2 - Acquisition Parameters
Date_ 20140210
Time 12.31
INSTRUM DRX
PROBHD 5 mm TBI 1H/13
PULPROG zg30
TD 65536
SOLVENT DMSO
NS 16
DS 0
SWH 10330.578 Hz
FIDRES 0.157632 Hz
AQ 3.1719923 sec
RG 181
DW 48.400 usec
DE 6.78 usec
TE 323.1 K
D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 1H
P1 8.20 usec
PL1 5.00 dB
SFO1 500.1330885 MHz

F2 - Processing parameters
SI 32768
SF 500.1300094 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00


Temp. 323K
4d
Et2N
ppm



Agilent

Yevgen Poronik
zesp10/Var500/YP-2EP134/YP-2EP134-H1

Sample Name:
YP-2EP134
Data Collected on:
Varian-NMR-vnmrs500
Archive directory:

Sample directory:

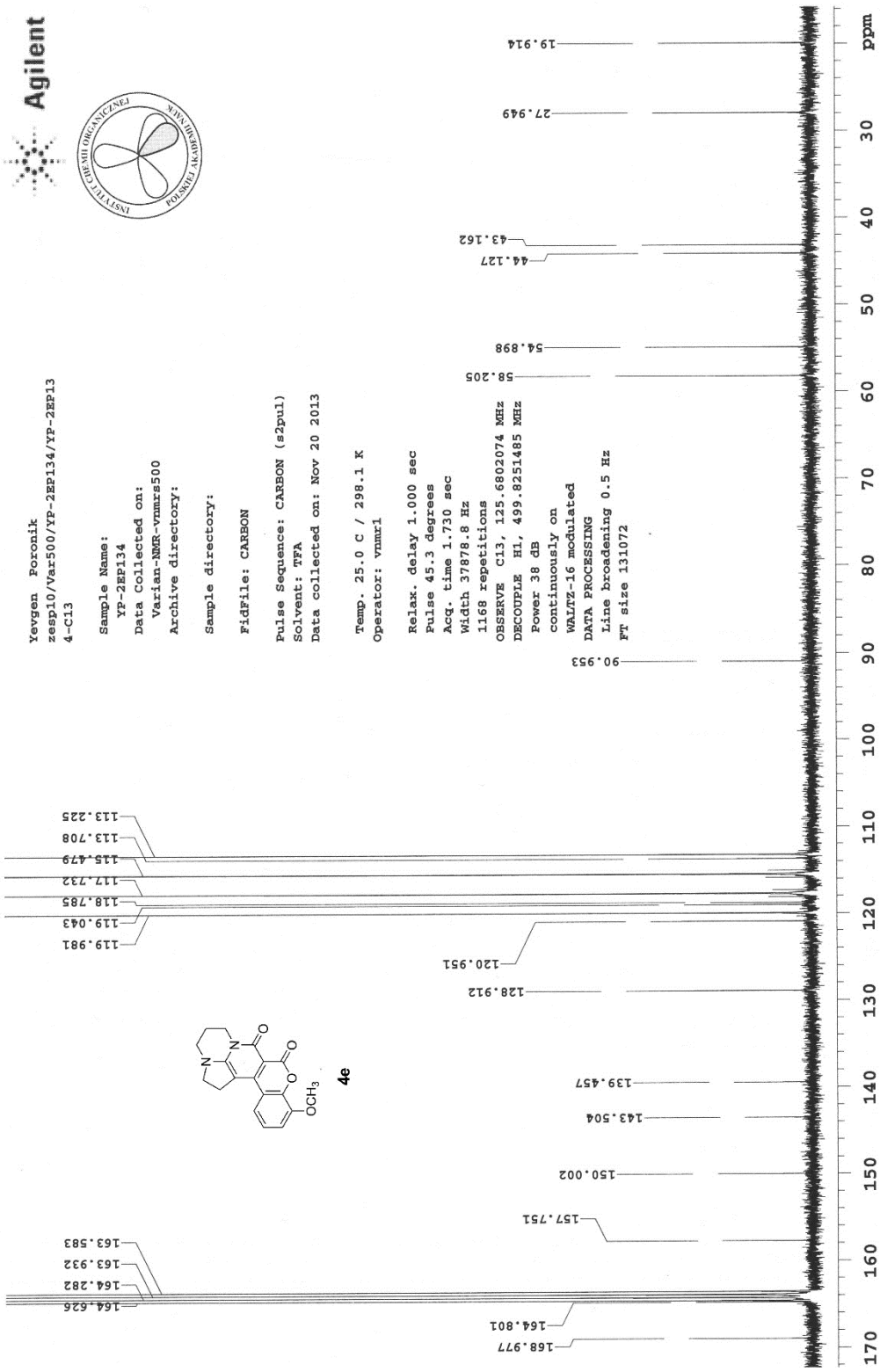
FidFile: PROTON

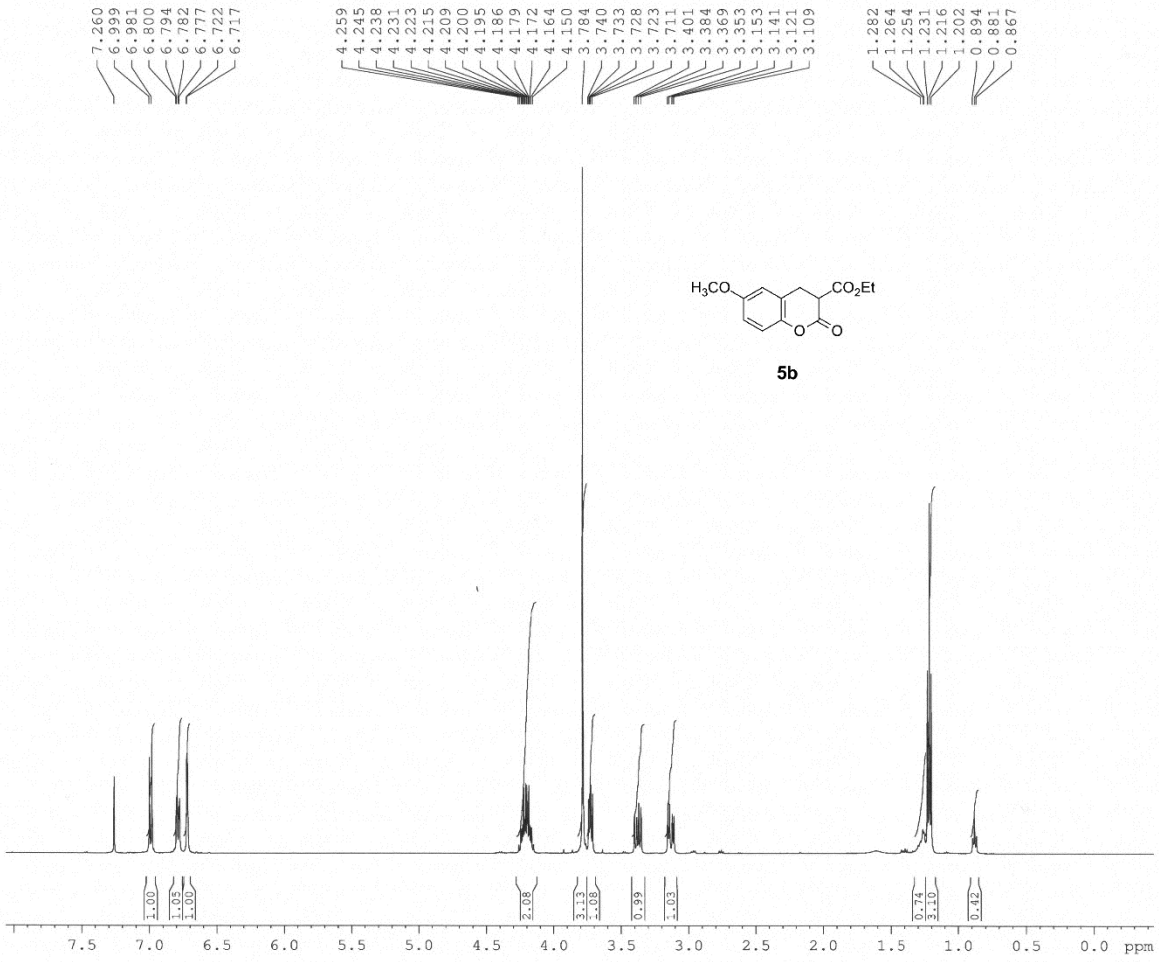
Pulse Sequence: PROTON (s2pul)
Solvent: TFA
Data collected on: Nov 20 2013

Temp. 25.0 C / 298.1 K
Operator: vnmr1

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 5.924 sec
Width 11061.9 Hz
88 repetitions
OBSERVE H1, 499.8227054 MHz
DATA PROCESSING
FT size 131072

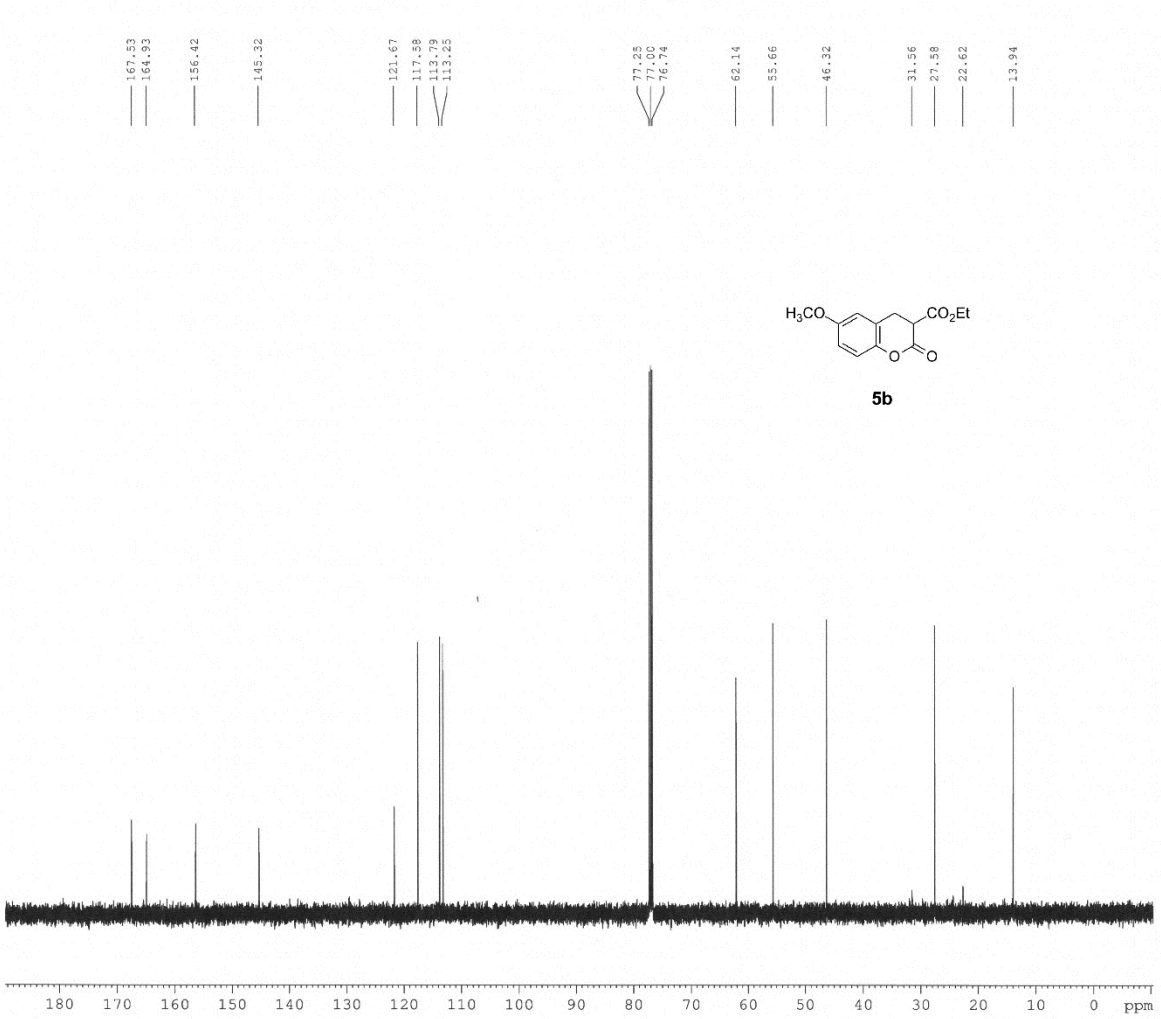
INSTYTUT CHEMII ORGANICZNEJ POLSKIEJ AKADEMII NAUK


Agilent
Yevgen Poronik
zesp10/Var500/YP-2EP134/YP-2EP13
4-C13
Sample Name:
YP-2EP134
Data Collected on:
Varian-NMR-vnmrs500
Archive directory:
Sample directory:
FidFile: CARBON
Pulse Sequence: CARBON (s2pul)
Solvent: TFA
Data collected on: Nov 20 2013
Temp. 25.0 C / 298.1 K
Operator: vnmr1
Relax. delay 1.000 sec
Pulse 45.3 degrees
Acq. time 1.730 sec
Width 37878.8 Hz
1168 repetitions
OBSERVE C13, 125.6802074 MHz
DECOUPLE H1, 499.8251485 MHz
Power 38 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 131072
19.914
27.949
43.162
44.127
54.898
58.205
90.953
113.225
113.708
115.479
117.732
118.785
119.043
119.981
120.951
128.912
139.457
143.504
150.002
157.751
164.801
168.977
163.583
163.932
164.282
164.626
OCH3
4e
ppm



BRUKER

```
Current Data Parameters
NAME                  ZEP137
EXPNO                      1
PROCNO                     1

F2 - Acquisition Parameters
Date_              20140130
Time                  13.41
INSTRUM                 DRX
PROBHD   5 mm TBI 1H/13
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       32
DS                        0
SWH               10330.578 Hz
FIDRES             0.157632 Hz
AQ                 3.1719923 sec
RG                     161.3
DW                    48.400 usec
DE                     6.78 usec
TE                    303.0 K
D1                1.00000000 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                      1H
P1                     8.20 usec
PL1                    5.00 dB
SFO1           500.1330885 MHz

F2 - Processing parameters
SI                     32768
SF             500.1300234 MHz
WDW                       no
SSB                        0
LB                     0.00 Hz
GB                         0
PC                      1.00
```



BRUKER

```
Current Data Parameters
NAME                  ZEP137
EXPNO                      3
PROCNO                     1

F2 - Acquisition Parameters
Date_                20140130
Time                    14.13
INSTRUM                   DRX
PROBHD    5 mm TBI 1H/13
PULPROG                 zgpg
TD                     65536
SOLVENT                CDCl3
NS                       750
DS                         4
SWH                32679.738 Hz
FIDRES             0.498653 Hz
AQ                 1.0027508 sec
RG                     32768
DW                    15.300 usec
DE                     7.10 usec
TE                     303.0 K
D1                 1.00000000 sec
d11                0.03000000 sec
DELTA              0.89999998 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                     13C
P1                      5.00 usec
PL1                    -3.00 dB
SFO1              125.7703643 MHz

======== CHANNEL f2 ========
CPDPRG2                waltz16
NUC2                       1H
PCPD2                  98.00 usec
PL2                     3.00 dB
PL12                   23.00 dB
PL13                   32.00 dB
SFO2              500.1320005 MHz

F1 - Acquisition parameters
ND0                        1
TD                       128
SFO1                500.132 MHz
FIDRES             7.812500 Hz
SW                     1.999 ppm
FnMODE                    QF

F2 - Processing parameters
SI                    262144
SF                125.7577939 MHz
WDW                       EM
SSB                        0
LB                      0.50 Hz
GB                         0
PC                      1.40

F1 - Processing parameters
SI                      1024
MC2                       QF
SF                500.1300000 MHz
WDW                     SINE
SSB                        0
LB                      0.30 Hz
GB                       0.1
```

BRUKER
Current Data Parameters
NAME ZEP137
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20140130
Time 13.48
INSTRUM DRX
PROBHD 5 mm TBI 1H/13
PULPROG dept135
TD 65536
SOLVENT MeOD
NS 211
DS 4
SWH 30030.029 Hz
FTDRES 0.458222 Hz
AQ 1.0912244 sec
RG 1290.2
DW 16.650 usec
DE 6.78 usec
TE 303.0 K
CNST2 145.0000000
D1 2.00000000 sec
d2 0.00344828 sec
d12 0.00002000 sec
DELTA 0.00001783 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 14.00 usec
p2 28.00 usec
PL1 -3.00 dB
SFO1 125.7703643 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
P3 9.00 usec
p4 18.00 usec
PCPD2 80.00 usec
PL2 3.00 dB
PL12 26.00 dB
SFO2 500.1320005 MHz
F2 - Processing parameters
SI 32768
SF 125.7577939 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
13.94
27.58
46.32
55.66
62.14
113.25
113.79
117.58
CO2Et
H3CO
O
O
5b
0 ppm

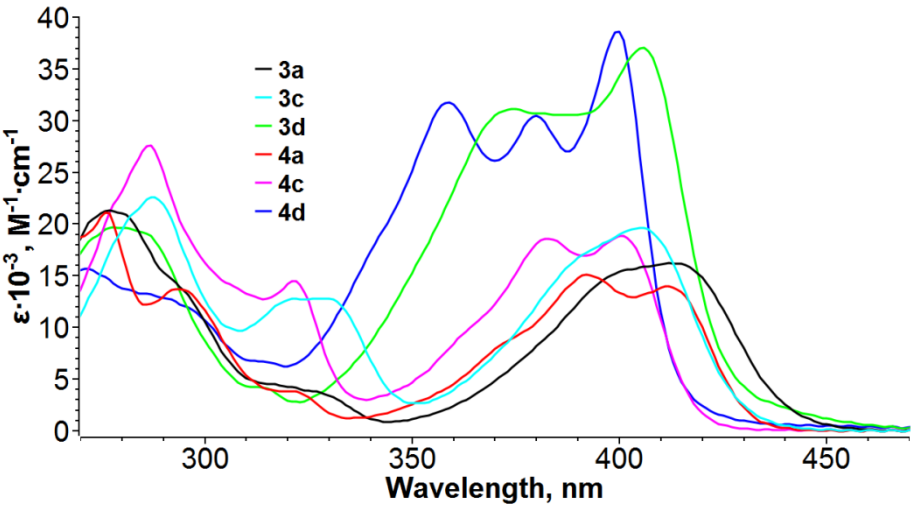


Figure S2. Absorption spectra of compounds **3a**, **3c**, **3d**, **4a**, **4c**, **4d** in DCM.