

Supplementary Material

Revisiting Staudinger and Ruzicka's altered pyrethrolone: the cyclopentadienone dimers derived from pyrethrin I, cinerin I and jasmolin I

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^ACSIRO Manufacturing, Ian Wark Laboratory, Bayview Avenue, Clayton, Vic. 3168, Australia

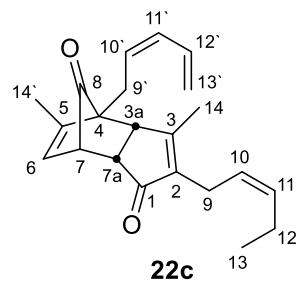
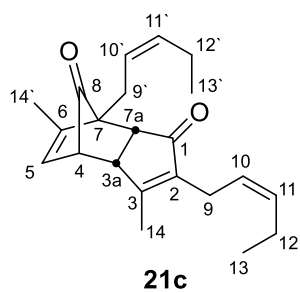
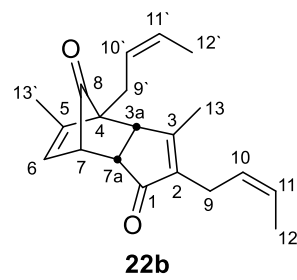
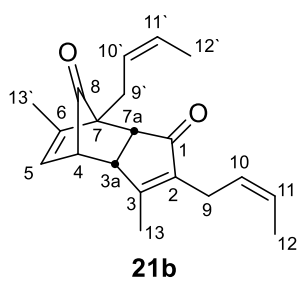
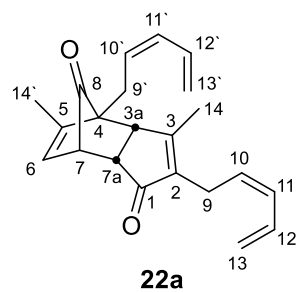
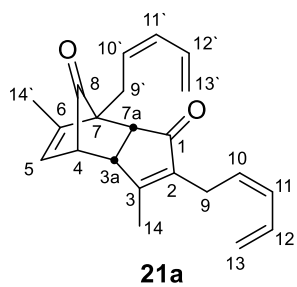
^BSchool of Chemistry and Molecular Biosciences, The University of Queensland, St Lucia, Qld 4072, Australia

^CCollege of Science and Engineering, Flinders University, Adelaide, SA 5042, Australia

^DBotanical Resources Australia Pty Ltd, 44-46 Industrial Drive, Ulverstone, Tas. 7315, Australia

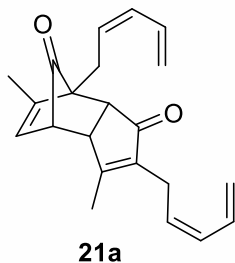
*Correspondence to: Email: jack.ryan@csiro.au

Numbering schemes for cyclopentadienone dimers



1-D and 2-D NMR spectra of compounds 21a-c and 22a-c

Username J. Freemont
JAF-LN2010/1198-50 yellow
Av400_1H CDCl3 C: fre155 11

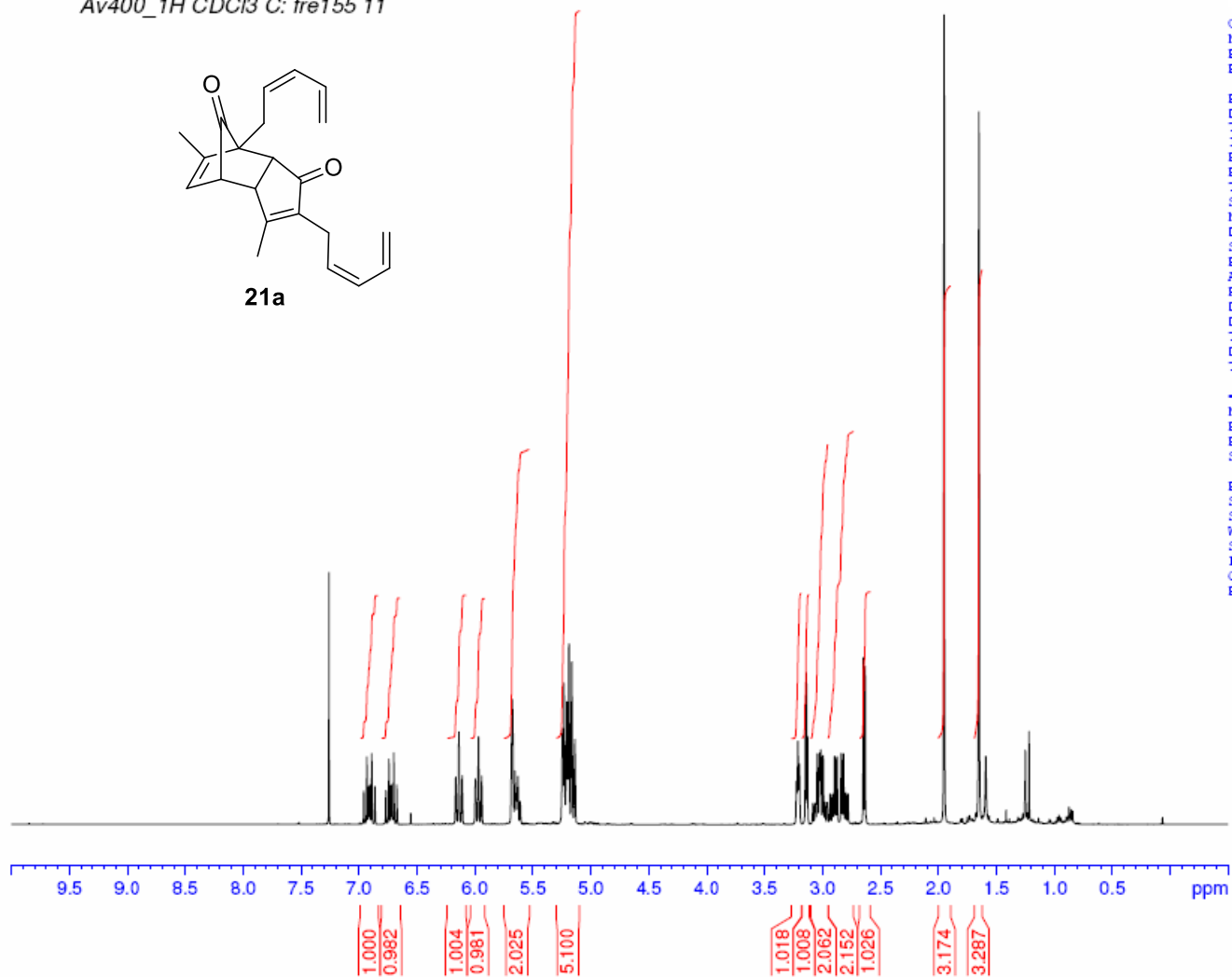


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PROCNO    1

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PULPROG   zg30
TD         32768
SOLVENT   CDCl3
NS         32
DS         2
SWH        5995.204 Hz
FIDRES     0.182959 Hz
AQ         2.7329011 sec
RG         90.5
DW         83.400 usec
DE         12.00 usec
TE         298.0 K
D1         1.00000000 sec
TD0        1

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P1         7.70 usec
PL1        -1.00 dB
SFO1       400.1326104 MHz

F2 - Processing parameters
SI         65536
SF         400.1300095 MHz
WDW        EM
SSB        0
LB         0.10 Hz
GB         0
PC         1.00
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¹H NMR spectrum of dimer **21a**

Username J. Freemont
JAF-LN2010/1198-50 yellow
Av400_13C CDC13 C: fre155 11



Current Data Parameters
NAME freemont40797
EXPNO 11
PROCNO 1

F2 - Acquisition Parameters
Date_ 20101122
Time 5.26
INSTRUM Av400
PROBHD 5 mm PABBI 1H/
PULPROG zgpg30_CSIR0
TD 65536
SOLVENT CDC13
NS 12288
DS 2
SWH 25125.629 Hz
FIDRES 0.383387 Hz
AQ 1.3042164 sec
RG 20642.5
DW 19.900 usec
DE 12.00 usec
TE 298.0 K
D1 1.00000000 sec
D11 0.03000000 sec
L31 1
TD0 1

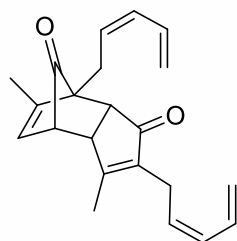
----- CHANNEL f1 -----
NUC1 13C
P1 13.00 usec
PL1 -6.00 dB
SFO1 100.6243395 MHz

----- CHANNEL f2 -----
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NUC2 1H
PCPD2 100.00 usec
PL2 -1.00 dB
PL12 21.27 dB
PL13 27.27 dB
PL30 21.27 dB
PL31 15.27 dB
SFO2 400.1320007 MHz

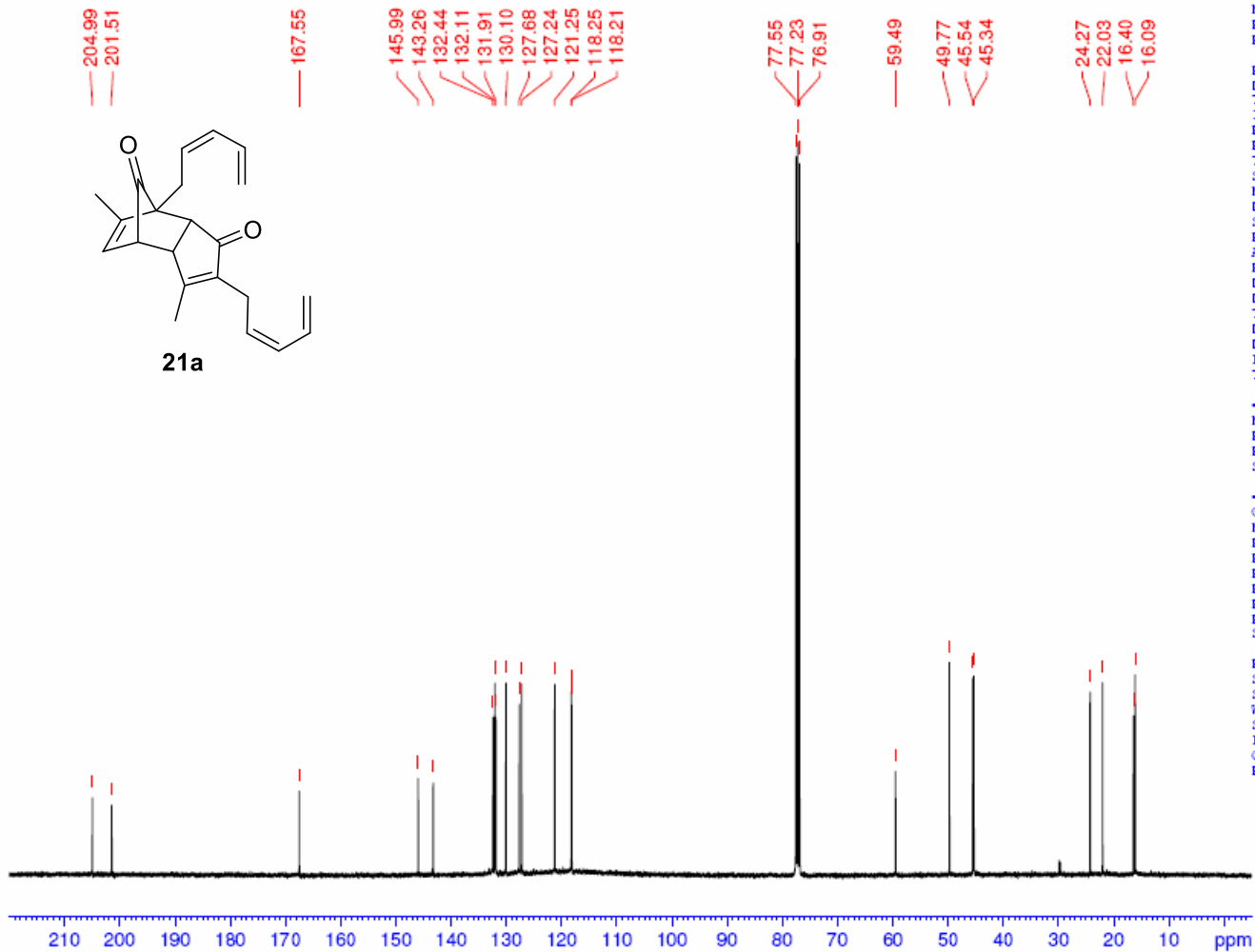
F2 - Processing parameters
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SSB 0
LB 1.00 Hz
GB 0
PC 1.40

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167.55
145.99
143.26
132.44
132.11
131.91
130.10
127.68
127.24
121.25
118.25
118.21

77.55
77.23
76.91
59.49
49.77
45.54
45.34
24.27
22.03
16.40
16.09

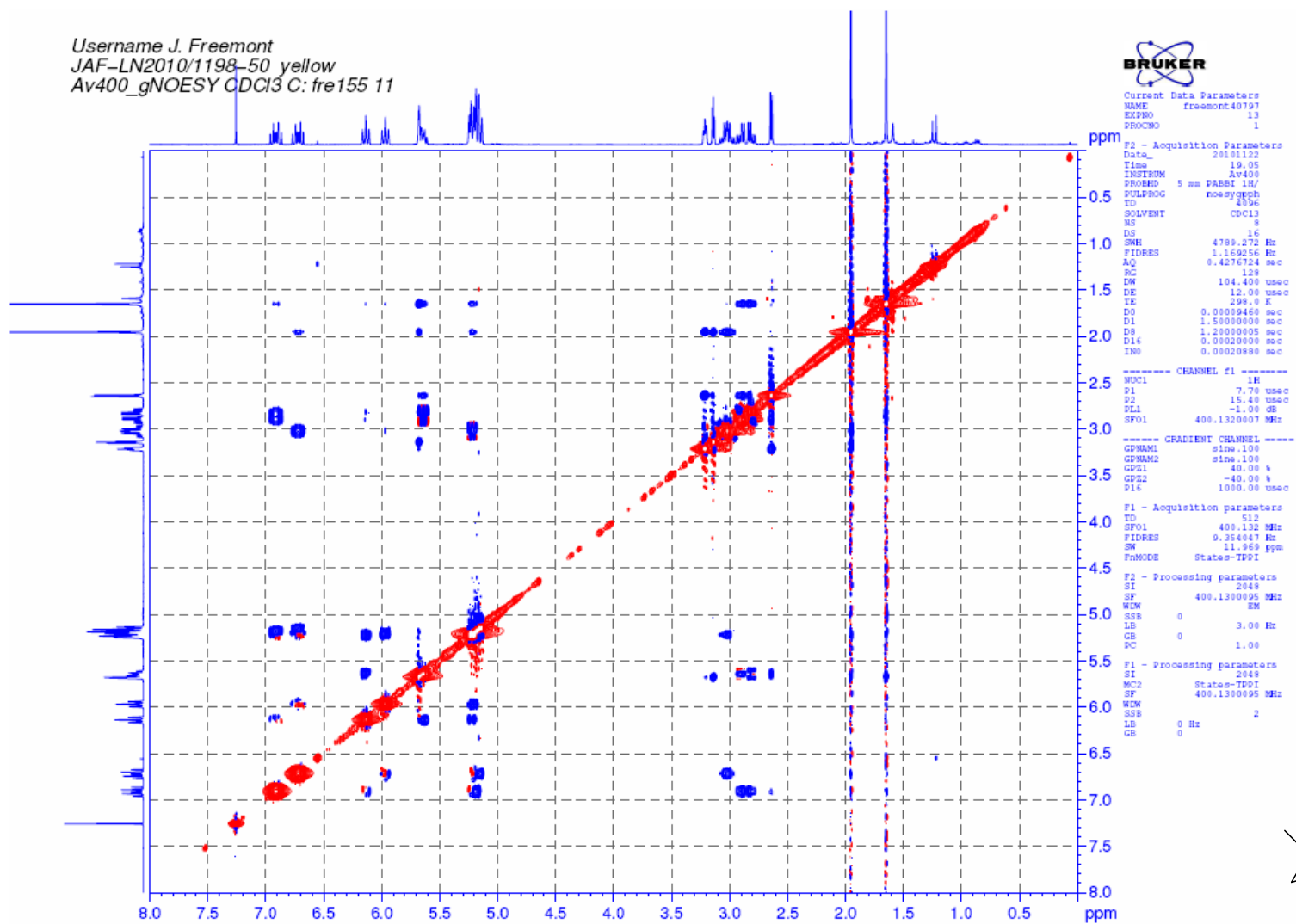


21a

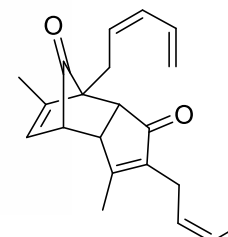


¹³C NMR spectrum of dimer 21a

Username J. Freemont
JAF-LN2010/1198-50 yellow
Av400_gNOESY CDCl3 C: fre155 11



gNOESY NMR spectrum of dimer **21a**



21a

Username J. Freemont
JAF-LN2010/1198-50 yellow
Av400_gHSQC CDC13 C: fre155 11



```
Parameters
NAME      freemont40797
EXPNO     14
PROCNO    1

F2 - Acquisition Parameters
Date_     20101122
Time      9.03
INSTRUM   Av400
PROBHD    5 mm DABBI 1H/
PULPROG   hsqc0d0tggp1p2.2_CSIR
TD         2048
SOLVENT   CDC13
NS         2
DS         16
SWH        4006.410 Hz
FIDRES     1.956255 Hz
AQ         0.2556404 sec
RG         20642.5
RW         124.800 usec
DE         12.00 usec
TE         298.0 K
CST2      145.000000
CST17     -8.500000
D0         0.00000300 sec
D1         1.50000000 sec
D4         0.00172414 sec
D11        0.03000000 sec
D16        0.00020000 sec
D21        0.00344828 sec
D24        0.00086207 sec
IN0        0.0002925 sec

----- CHANNEL f1 -----
NUC1        1H
P1          7.70 usec
P2          15.40 usec
P29         0.10 usec
PL1         -1.00 dB
SFO1        400.1320007 MHz

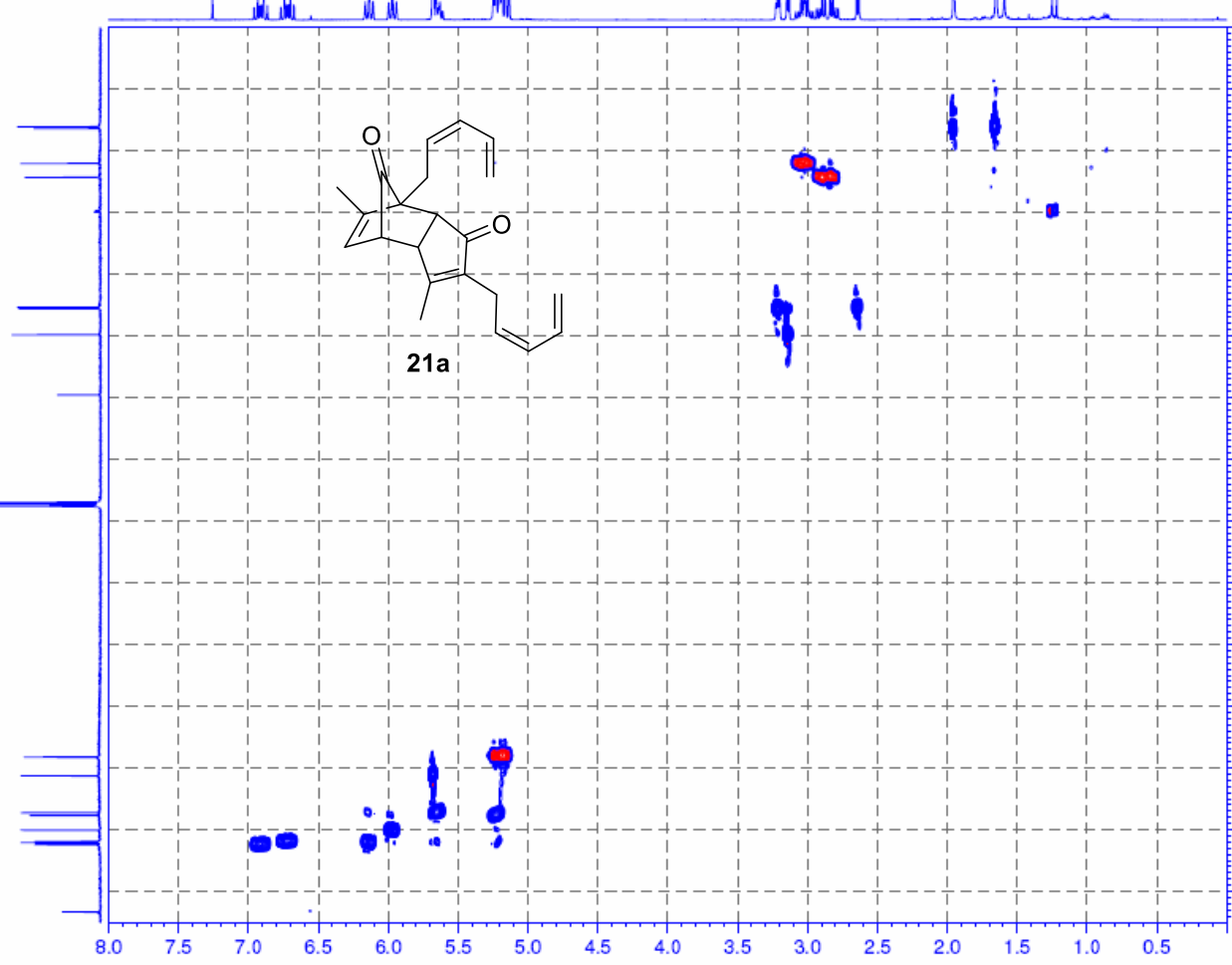
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CPDPRG2    garg4
NUC2        13C
P3          13.00 usec
P14         500.00 usec
P24         2000.00 usec
PCPD2       70.00 usec
PL3         120.00 dB
PL2         -6.00 dB
PL12        9.62 dB
SFO2        100.6208180 MHz
SP3         -0.12 dB
SP7         -0.12 dB
SPNAM3      Crp60, 0.5, 20.1
SPNAM7      Crp60comp, 4
SFOAL3      0.500
SFOAL7      0.500
SPOFFS3     0 Hz
SPOFFS7     0 Hz

----- GRADIENT CHANNEL -----
GPNAM1     sine.100
GPNAM2     sine.100
GPNAM3     sine.100
GPNAM4     sine.100
GPE1       80.00 %
GPE2       20.10 %
GPE3       11.00 %
GPE4       -5.00 %
P16        1000.00 usec
D19        600.00 usec

F1 - Acquisition parameters
TD         256
SFO1        100.6208 MHz
FIDRES     66.818512 Hz
SW         170.000 ppm
F0MODE     Echo-Antiecho

F2 - Processing parameters
SI         2048
SF         400.1300095 MHz
RG         20642.5
RWIN       QSINE
SSB        2
LB         0 Hz
GB         0
PC         1.00

F1 - Processing parameters
--
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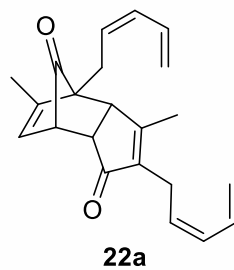
qHSQC NMR spectrum of dimer **21a**

Username J. Freemont
JAF-LN2010/1198-50 Green
Av400_1H CDC13 C: fre155 10



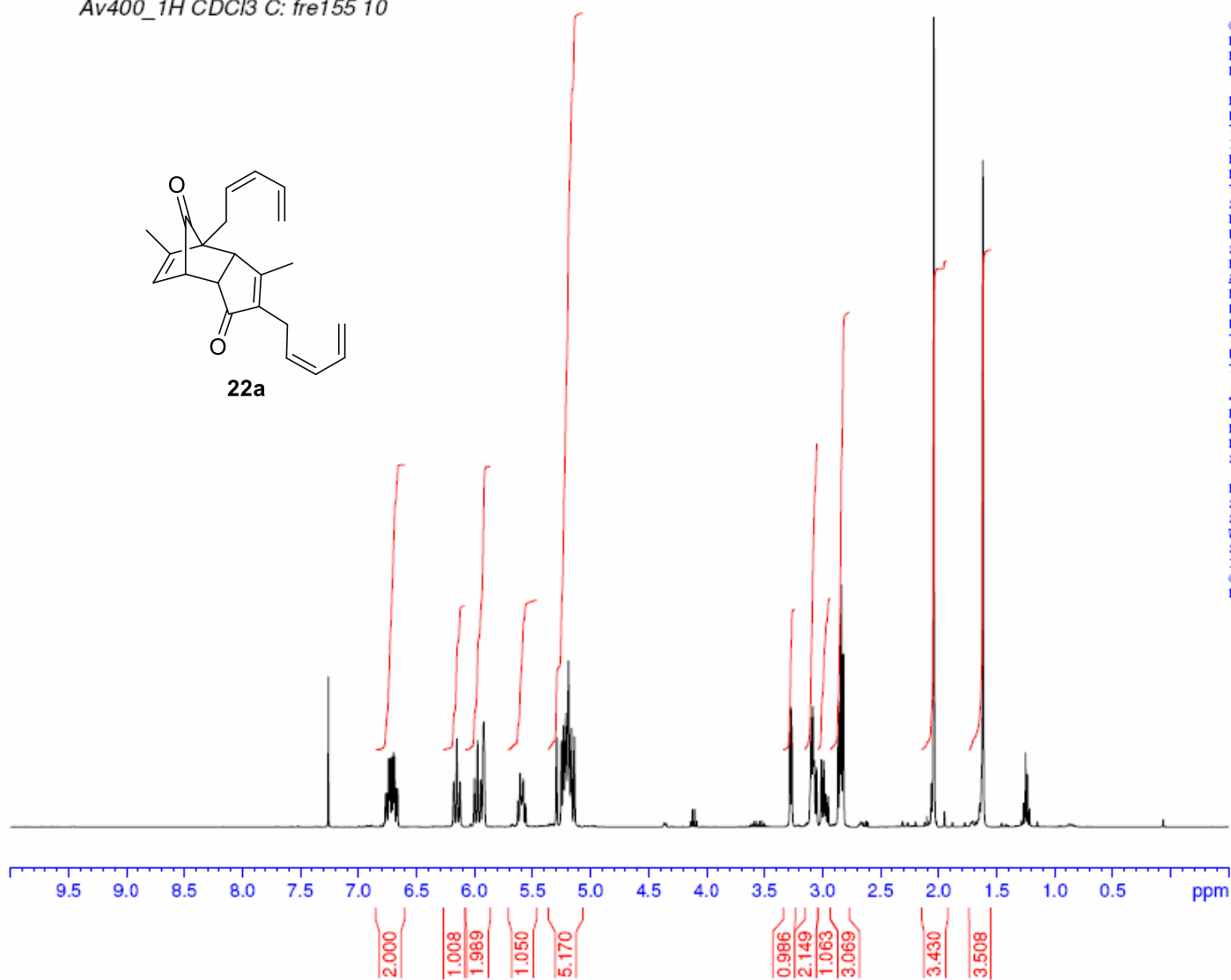
Current Data Parameters
NAME Freemont40796
EXPNO 10
PROCNO 1

F2 - Acquisition Parameters
Date_ 20101121
Time 7.48
INSTRUM Av400
PROBHD 5 mm PABBI 1H/
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 32
DS 2
SWH 5995.204 Hz
FIDRES 0.182959 Hz
AQ 2.7329011 sec
RG 71.8
DW 83.400 usec
DE 12.00 usec
TE 298.0 K
D1 1.00000000 sec
TD0 1



----- CHANNEL f1 -----
NUC1 1H
P1 7.70 usec
PL1 -1.00 dB
SFO1 400.1326104 MHz

F2 - Processing parameters
SI 65536
SF 400.1300094 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 1.00



¹H NMR spectrum of dimer **22a**

Username J. Freemont
JAF-LN2010/1198-50 Green
Av400_13C CDC13 C: fre155 10



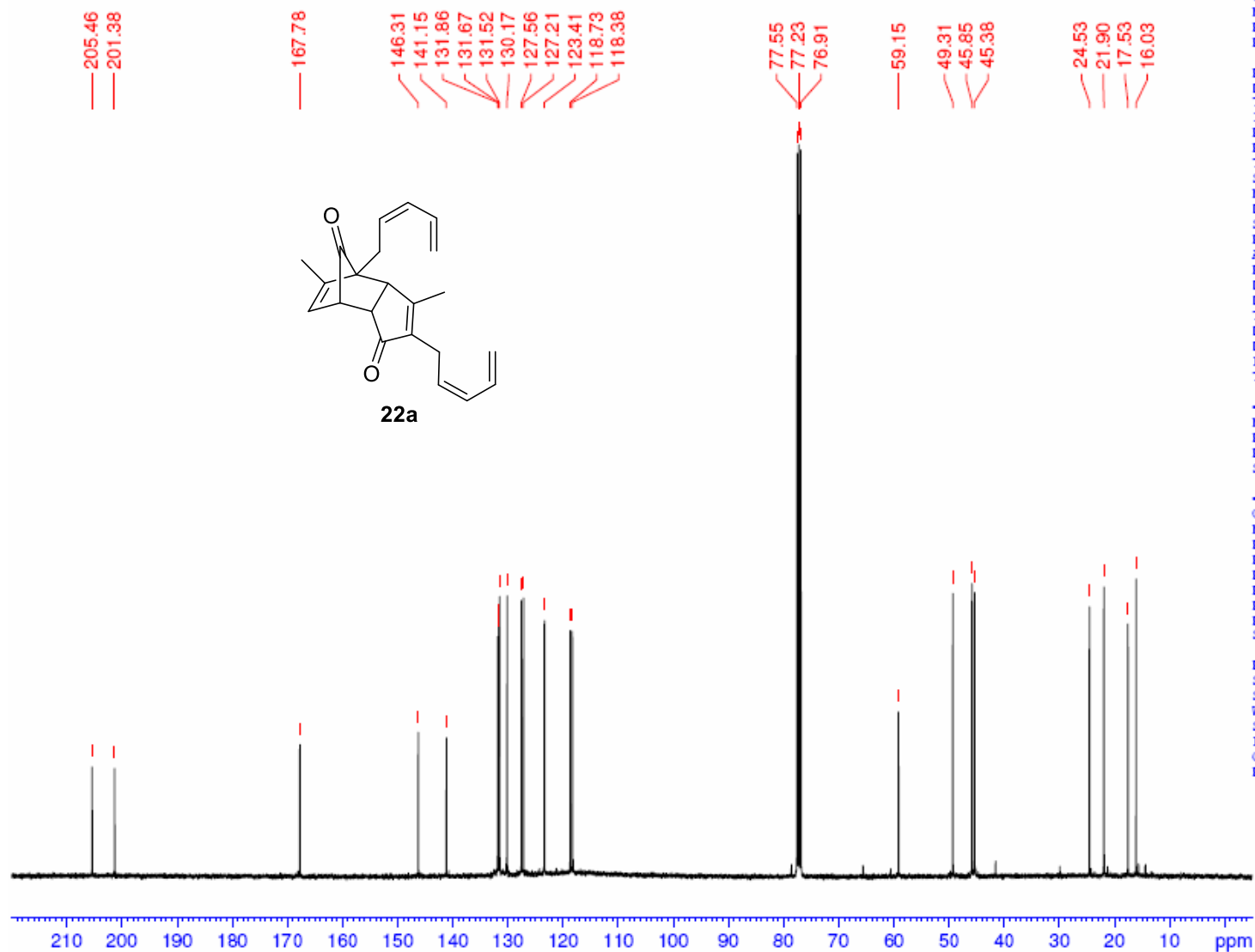
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EXPNO 11
PROCNO 1

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Time 15.55
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PROBHD 5 mm PABBI 1H/
PULPROG zgpg30_CSIRO
TD 65536
SOLVENT CDC13
NS 12288
DS 2
SWH 25125.629 Hz
FIDRES 0.383387 Hz
AQ 1.3042164 sec
RG 20642.5
DW 19.900 usec
DE 12.00 usec
TE 298.0 K
D1 1.00000000 sec
D11 0.03000000 sec
L31 1
TD0 1

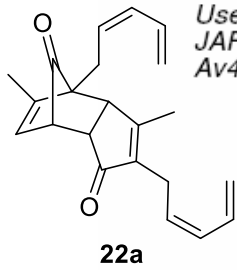
----- CHANNEL f1 -----
NUC1 13C
P1 13.00 usec
PL1 -6.00 dB
SFO1 100.6243395 MHz

----- CHANNEL f2 -----
CPDPRG2 bi_waltz16_32pl
NUC2 1H
PCPD2 100.00 usec
PL2 -1.00 dB
PL12 21.27 dB
PL13 27.27 dB
PL30 21.27 dB
PL31 15.27 dB
SFO2 400.1320007 MHz

F2 - Processing parameters
SI 65536
SF 100.6127491 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40



¹³C NMR spectrum of dimer 22a



Username J. Freemont
 JAF-LN2010/1198-50 Green
 Av400_gNOESY CDCl3 C: fre155 10



Current Data Parameters
 NAME freemont40796
 EXPNO 13
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20101121
 Time 16.07
 INSTRUM Av400
 PROBE 5 mm DABBI 1H/
 PULPROG zgpg30
 ID 4396
 SOLVENT CDCl3
 NS 8
 DS 16
 SWS 4789.272 Hz
 FIDRES 1.169256 Hz
 AQ 0.4276724 sec
 RG 362
 DW 104.400 usec
 DE 12.00 usec
 TE 299.0 K
 D0 0.00009460 sec
 D1 1.50000000 sec
 D8 1.20000005 sec
 D16 0.00020000 sec
 IN0 0.00020880 sec

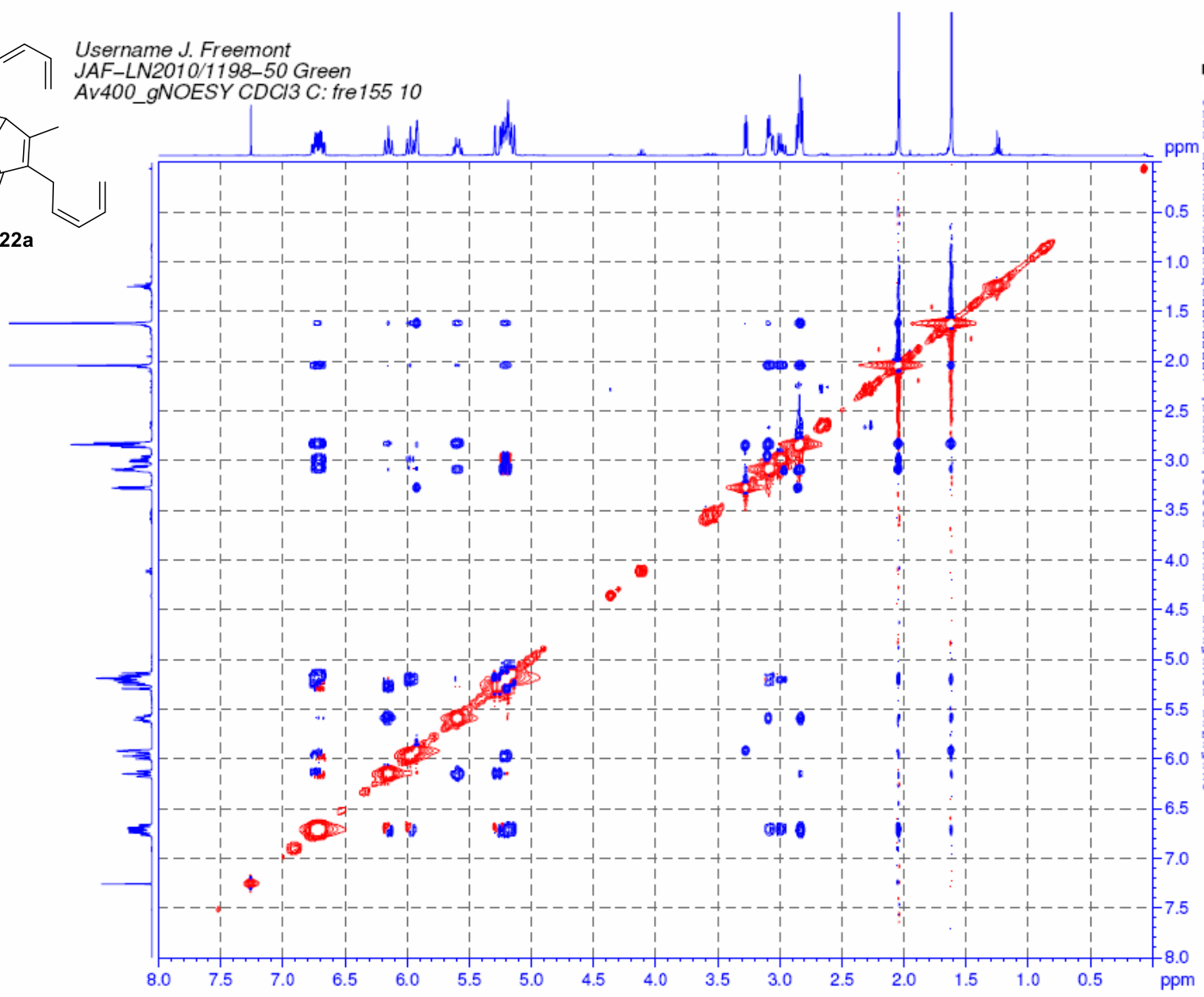
----- CHANNEL f1 -----
 NUCL1 1H
 P1 7.70 usec
 P2 15.40 usec
 PL1 -1.00 dB
 SFO1 400.1320007 MHz

----- GRADIENT CHANNEL -----
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 GPMAM2 sine.100
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 GPC2 -40.00 %
 P16 1000.00 usec

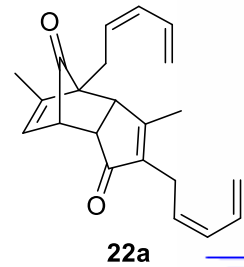
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 FIDRES 9.354047 Hz
 SW 11.969 ppm
 FMODE States-TPPI

F2 - Processing parameters
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 SF 400.1300094 MHz
 WDW EM
 SSS 0
 LB 3.00 Hz
 GB 0
 PC 1.00

F1 - Processing parameters
 SI 2048
 MC2 States-TPPI
 SF 400.1300094 MHz
 WDW EM
 SSS 2
 LB 0 Hz
 GB 0



gNOESY NMR spectrum of dimer 22a



Username J. Freemont
 JAF-LN2010/1198-50 Green
 Av400_gHSQC CDCI3 C: fre155 10



```

arameters
NAME      fremont40796
EXPNO    14
PROCNO   1

F2 - Acquisition Parameters
Date_    20101121
Time     19.45
INSTRUM  Av400
PROBHD   5 mm PABBI 1H/
PULPROG  zgpg30
TD        2048
SOLVENT  CDCl3
NS        2
DS        16
SWH       4006.410 Hz
FIDRES    1.956255 Hz
AQ        0.2556404 sec
RG         13004
DW        124.800 usec
DE        12.00 usec
TE        298.0 K
CSTI2     145.0000000
CSTI7     -0.5000000
D0        0.00000300 sec
D1        1.50000000 sec
D4        0.00172414 sec
D11       0.03000000 sec
D16       0.00020000 sec
D21       0.00344828 sec
D24       0.00086207 sec
IN0       0.00002925 sec

----- CHANNEL f1 -----
NUC1      1H
P1        7.70 usec
P2        15.40 usec
P28       0.10 usec
PL1       -1.00 dB
SFO1      400.1320007 MHz

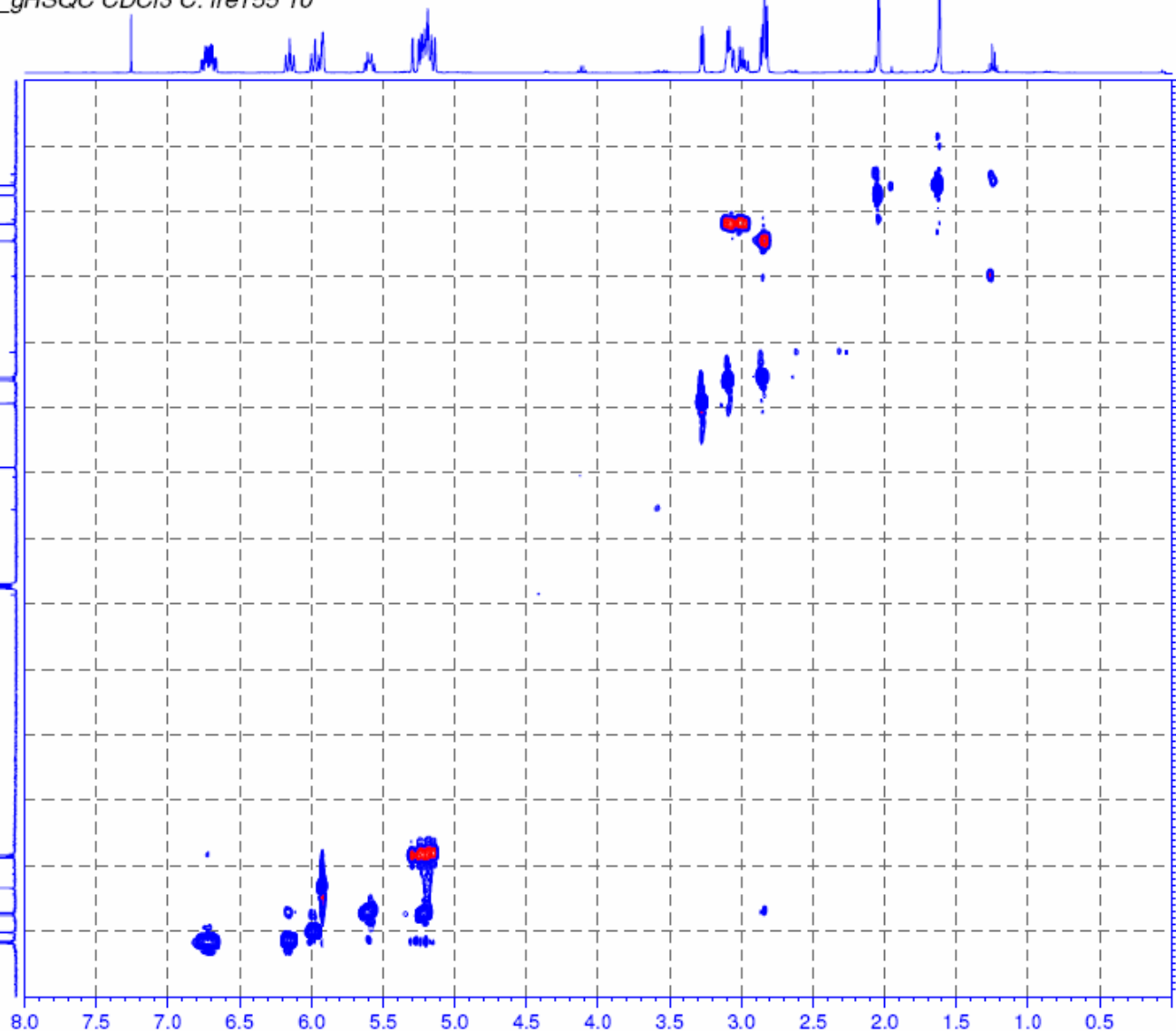
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CPDPRG2   gprg4
NUC2      13C
P3        13.00 usec
P14       500.00 usec
P24       2000.00 usec
PCPD2     70.00 usec
PL8       120.00 dB
PL2       -6.00 dB
PL12      8.62 dB
SFO2      100.6208180 MHz
SP3       -0.12 dB
SP7       -0.12 dB
SFO3      Crp60,0.5,20.1
SFO4      Crp60comp,4
SFOAL3    0.500
SFOAL7    0.500
SPOFFS3   0 Hz
SPOFFS7   0 Hz

----- GRADIENT CHANNEL -----
GPMAM1    sine.100
GPMAM2    sine.100
GPMAM3    sine.100
GPMAM4    sine.100
GPE1      90.00 %
GPE2      20.10 %
GPE3      11.00 %
GPE4      -5.00 %
P16       1000.00 usec
P19       600.00 usec

F1 - Acquisition parameters
TD        256
SFO1      100.6208 MHz
FIDRES    66.818512 Hz
SW         170.000 ppm
PRMODE    Echo-Antiecho

F2 - Processing parameters
SI         2048
SF         400.1300094 MHz
WIDW      QSIINE
SSE        2
LB         0 Hz
GB         0
PC         1.00

F1 - Processing parameters
  
```



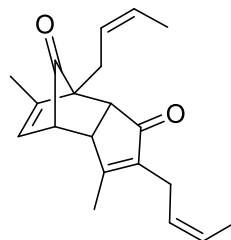
qHSQC NMR spectrum of dimer **22a**



Username Oliver Hutt
HUTT-IV-13 TS C1 Dimer
Av400_1H CDCl3 C: hut12a 20

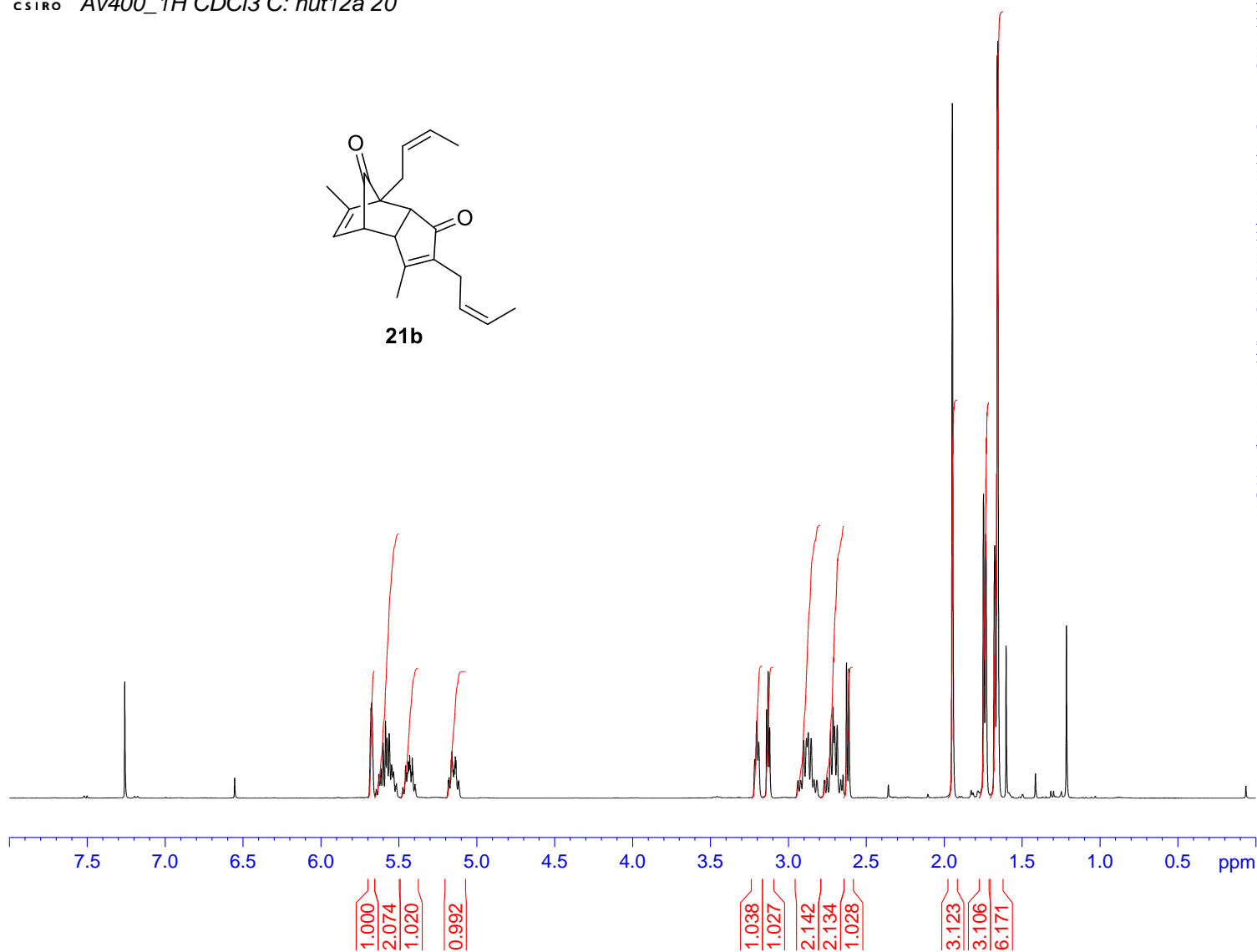


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EXPNO 10
PROCNO 1
Date_ 20101012
Time_ 13.32
INSTRUM Av400
PROBHD 5 mm PABBI 1H/
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 32
DS 2
SWH 5995.204 Hz
FIDRES 0.182959 Hz
AQ 2.7329011 sec
RG 90.5
DW 83.400 usec
DE 12.00 usec
TE 298.0 K
D1 1.0000000 sec
TDO 1



21b

===== CHANNEL f1 =====
NUC1 1H
P1 7.70 usec
PL1 -1.00 dB
SFO1 400.1326104 MHz
SI 65536
SF 400.1300095 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 1.00



¹H NMR spectrum of dimer 21b



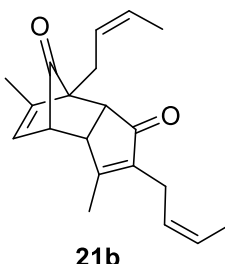
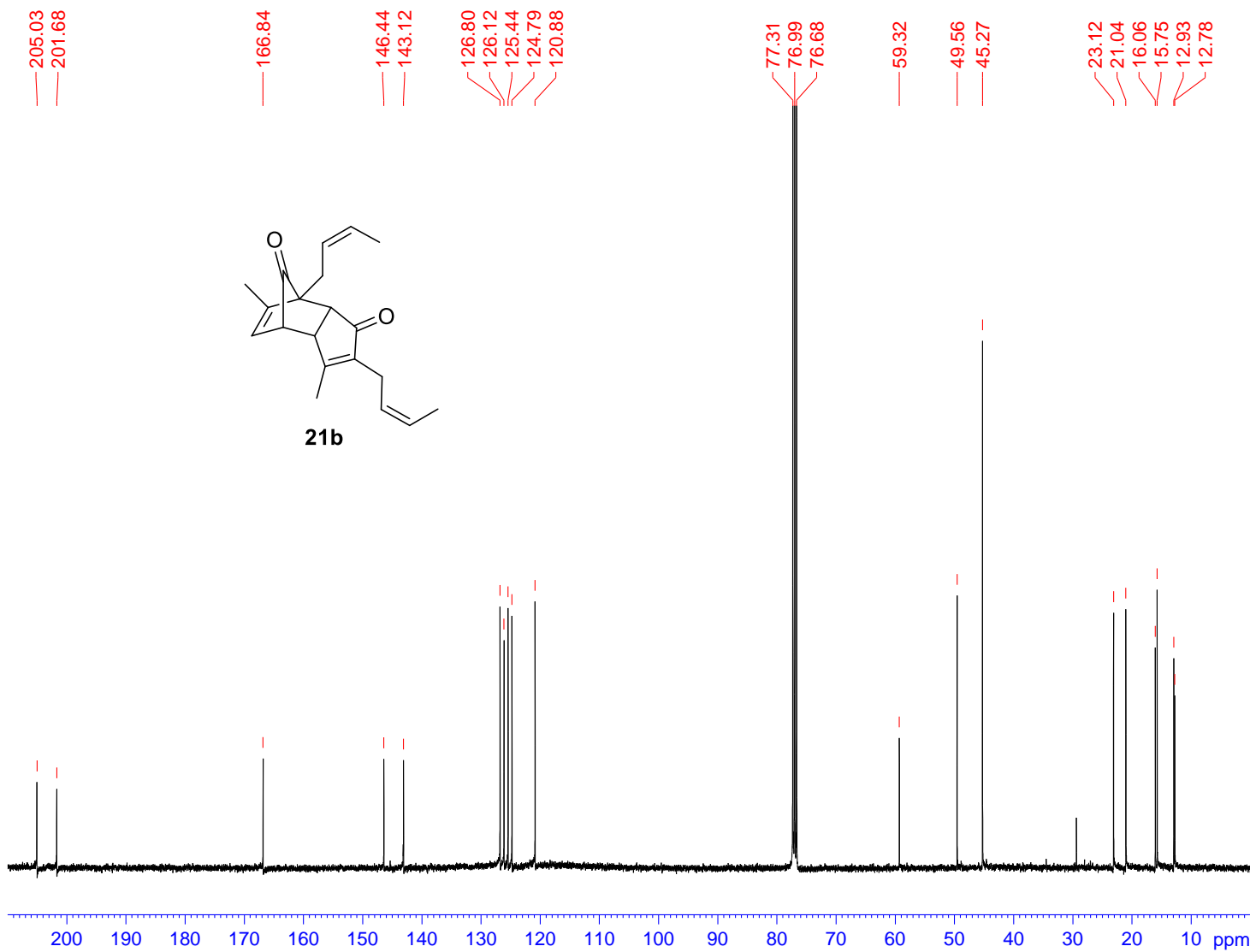
Username Oliver Hutt
HUTT-IV-13 TS C1 Dimer
Av400_13C CDCl3 C: hut12a 20



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EXPNO     15
PROCNO    1
Date_     20101013
Time      7.59
INSTRUM   Av400
PROBHD    5 mm PABBI 1H/
PULPROG   zgpg30_CSIRO
TD         65536
SOLVENT   CDCl3
NS         7000
DS         2
SWH        25125.629 Hz
FIDRES     0.383387 Hz
AQ         1.3042164 sec
RG         20642.5
DW         19.900 usec
DE         12.00 usec
TE         298.0 K
D1         1.00000000 sec
D11        0.03000000 sec
L31        1
TD0        1
```

```
===== CHANNEL f1 =====
NUC1       13C
P1         13.00 usec
PL1        -6.00 dB
SFO1       100.6243395 MHz
```

```
===== CHANNEL f2 =====
CPDPRG2    bi_waltz16_32pl
NUC2       1H
PCPD2      100.00 usec
PL2        -1.00 dB
PL12       21.27 dB
PL13       27.27 dB
PL30       21.27 dB
PL31       15.27 dB
SFO2       400.1320007 MHz
SI         65536
SF         100.6127719 MHz
WDW        EM
SSB        0
LB         1.00 Hz
GB         0
PC         1.40
```



¹³C NMR spectrum of dimer **21b**



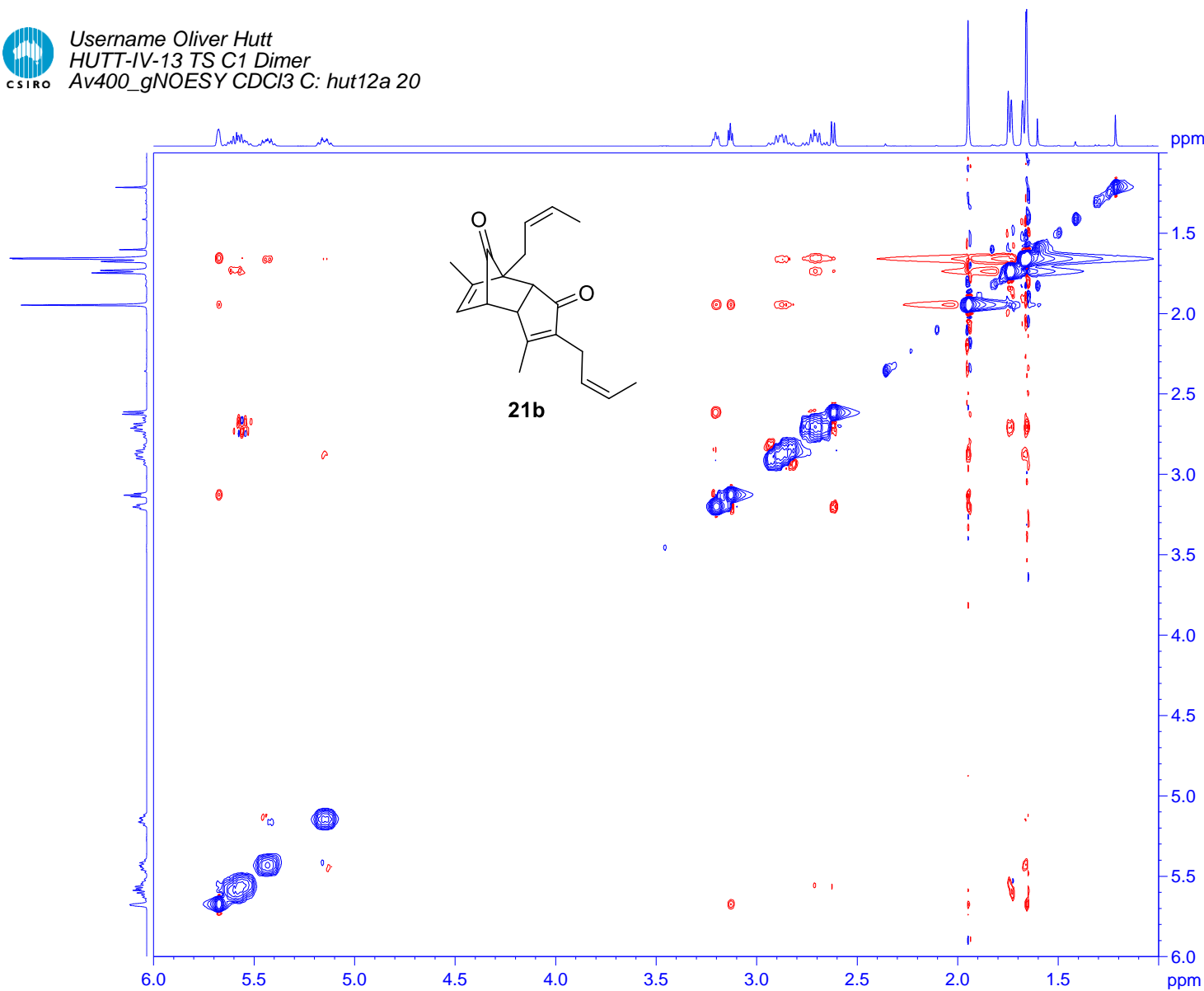
Username Oliver Hutt
HUTT-IV-13 TS C1 Dimer
Av400_gNOESY CDCl3 C: hut12a 20



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NAME      hut40250
EXPNO    12
PROCNO    1
Date_     20101012
Time      23.19
INSTRUM   Av400
PROBHD    5 mm PABBI 1H/
PULPROG   noesyppph
TD         4096
SOLVENT   CDCl3
NS         8
DS         16
SWH        4789.272 Hz
FIDRES     1.169256 Hz
AQ         0.4276724 sec
RG         128
DW         104.400 usec
DE         12.00 usec
TE         298.0 K
DO         0.00009460 sec
D1         1.50000000 sec
D8         1.20000005 sec
D16        0.00020000 sec
IN0        0.00020880 sec

===== CHANNEL f1 =====
NUC1       1H
P1         7.70 usec
P2         15.40 usec
PL1        -1.00 dB
SFO1       400.1320007 MHz

===== GRADIENT CHANNEL =====
GPNAM1     sine.100
GPNAM2     sine.100
GPZ1        40.00 %
GPZ2       -40.00 %
F16         1000.00 usec
TD          1
TD          512
SFO1        400.132 MHz
FIDRES      9.354047 Hz
SW          11.969 ppm
F16MODE     States-TPPI
SI          2048
SF          400.1300095 MHz
WDW         EM
SSB         0
LB          3.00 Hz
GB          0
PC          1.00
SI          2048
MC2         States-TPPI
SF          400.1300095 MHz
WDW         QSINE
SSB         2
LB          0.00 Hz
GB          0
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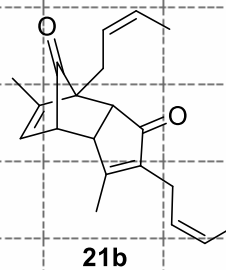
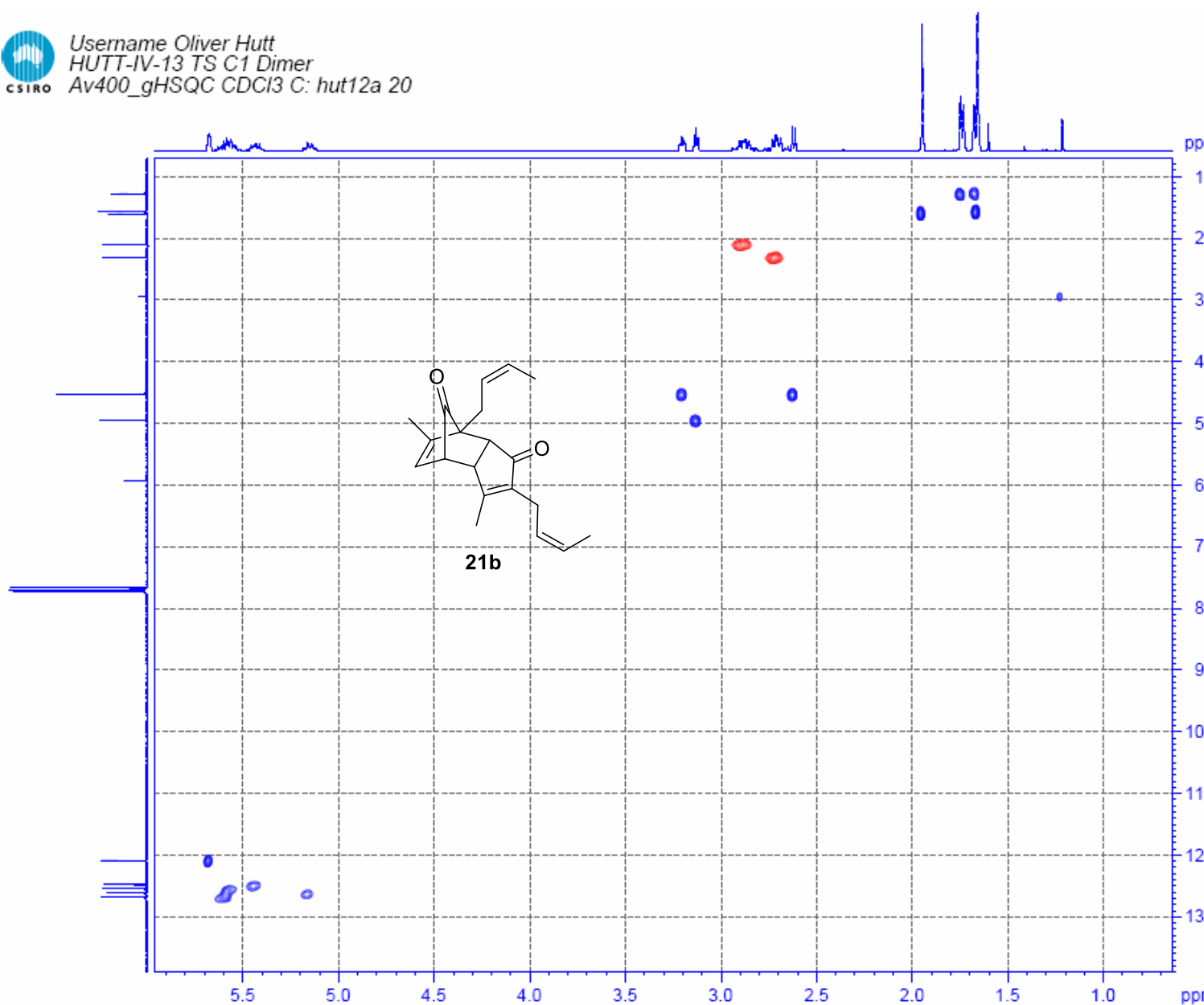
gNOESY NMR spectrum of dimer **21b**



Username Oliver Hutt
HUTT-IV-13 TS C1 Dimer
Av400_gHSQC CDC13 C: hut12a 20



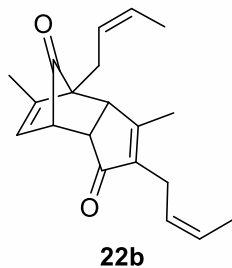
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EXPNO     13
PROCNO    1
Date_     20101013
Time      2.57
INSTRUM   Av400
PROBHD    5 mm F4BBI 1H/
PULPROG   hsqcadatgpgp1ap2_2_CSIRO
TD         2048
SOLVENT   CDC13
RG         2
DE         16
AQH        4006.410 Hz
FIDRES    1.956255 Hz
AQ         0.2556404 sec
RG         9195.2
DW         124.900 usec
DE         12.00 usec
TE         298.0 K
CNET2     145.0000000
CNET17    -0.5000000
D0         0.00000300 sec
D1         1.50000000 sec
D4         0.00172414 sec
D11        0.03000000 sec
D16        0.00020000 sec
D21        0.00344828 sec
D24        0.00086207 sec
IN0        0.00002925 sec
----- CHANNEL f1 -----
NUC1       1H
P1         7.70 usec
P2         15.40 usec
P28        0.10 usec
PL1        -1.00 dB
SFO1       400.1320007 MHz
----- CHANNEL f2 -----
CPDPRG2   garp4
NUC2       13C
P3         13.00 usec
P14        500.00 usec
P24        2000.00 usec
PCPD2     70.00 usec
PL0        120.00 dB
PL2        -6.00 dB
PL12       8.62 dB
SFO2       100.6208180 MHz
SFO3       -0.12 dB
SFO7       -0.12 dB
SFO6       Crp60, 0.5, 20.1
SFOAM7     Crp60comp, 4
SFOAL3     0.500
SFOAL7     0.500
SFOFFL3    0.00 Hz
SFOFFL7    0.00 Hz
----- GRADIENT CHANNEL -----
GRNAM1    sine, 100
GRNAM2    sine, 100
GRNAM3    sine, 100
GRNAM4    sine, 100
CP21      80.00 %
CP22      20.10 %
CP23      11.00 %
CP24      -5.00 %
P16       1000.00 usec
P19       600.00 usec
MD0        2
TD         256
SFO1       100.6208 MHz
FIDRES    66.818512 Hz
AQ         170.000 ppm
FPMODE    Echo-AntiEcho
SI         2048
SF         400.1300072 MHz
MDW        QSIGN
SFB         2
LB         0.00 Hz
PC         0
PC2        1.00
PC4        1024
MC2        echo-antiEcho
SF         100.6127436 MHz
MDW        QSIGN
SFB         2
LB         0.00 Hz
GB         0
```



qHSQC NMR spectrum of dimer 21b

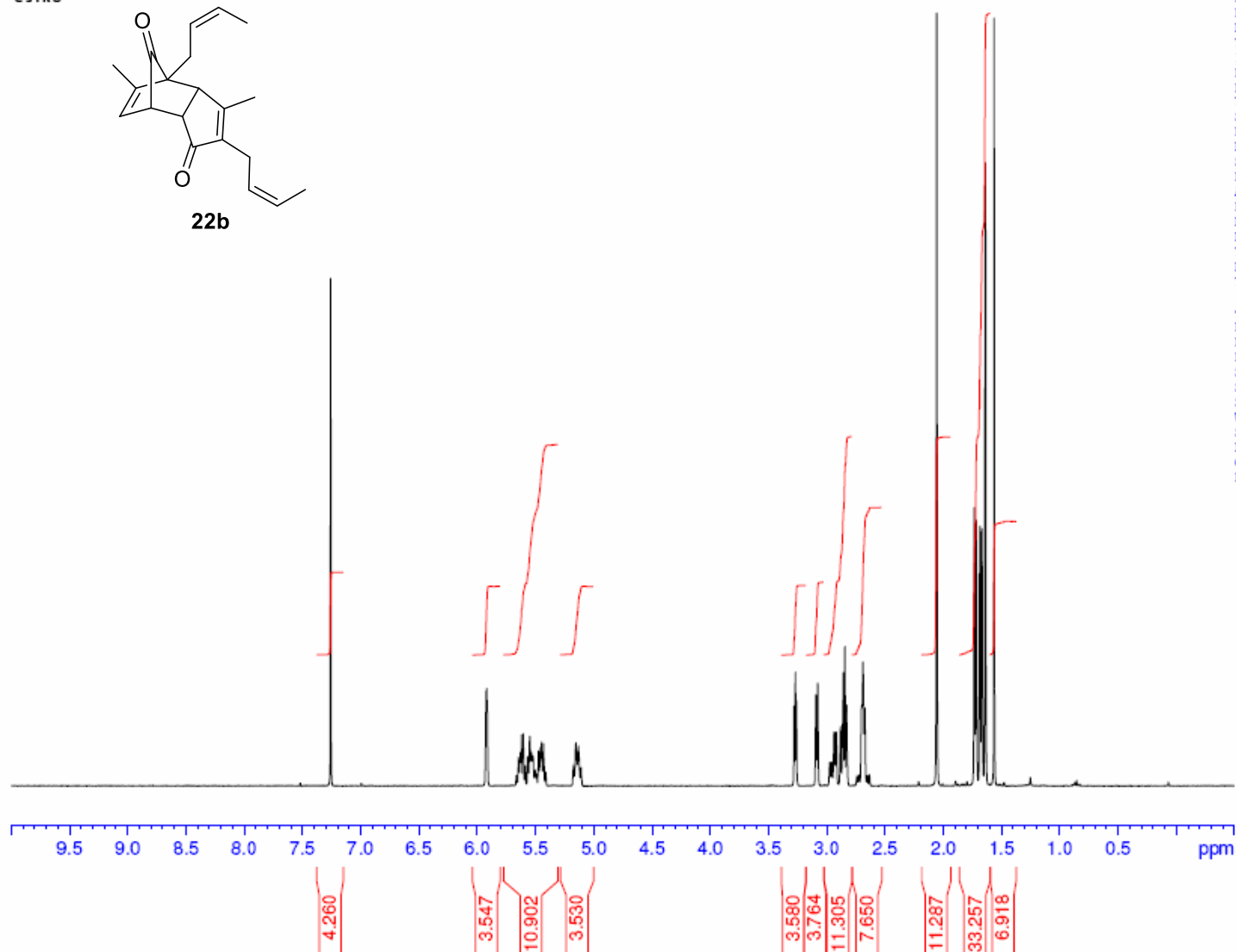


Username J. Freemont
Cinerin I AIBN Adduct
Av400_1H_A4 CDCl3 C: fre155 47



```
NAME      freemont40808
EXPNO     1
PROCNO    1
Date_     20101215
Time      16.10
INSTRUM   Av400
PROBHD    5 mm PABBI 1H/
PULPROG   zg30
TD         32768
SOLVENT   CDCl3
NS         32
DS         2
SWH        5995.204 Hz
FIDRES     0.182959 Hz
AQ         2.7329011 sec
RG         322.5
DW         83.400 usec
DE         12.00 usec
TE         298.0 K
D1         1.00000000 sec
TD0        1
```

```
----- CHANNEL f1 -----
NUC1      1H
P1         7.70 usec
PL1        -1.00 db
SFO1      400.1326104 MHz
SI         65536
SF         400.1300095 MHz
WDW        EM
SSB         0
LB         0.10 Hz
GB         0
PC         1.00
```



¹H NMR spectrum of dimer **22b**



Username Oliver Hutt
HUTT-IV-13 BS
Av400_13C CDCl3 C: hut12a 55



```
NAME      hutt40258
EXPNO     10
PROCNO    1
Date_     20101017
Time_     9.17
INSTRUM   Av400
PROBHD    5 mm PABBI 1H/
PULPROG   zgpg30_CSIRO
TD        65536
SOLVENT   CDCl3
NS        7500
DS        2
SWH       25125.629 Hz
FIDRES    0.393397 Hz
AQ        1.3042164 sec
RG        20642.5
DW        19.900 usec
DE        12.00 usec
TE        298.0 K
D1        1.00000000 sec
D11       0.03000000 sec
L31       1
TDO       1
```

205.59
201.50

167.20

146.71

141.08

126.19

126.05

125.46

124.88

123.02

77.32

77.00

76.68

59.07

49.13

45.60

45.20

23.43

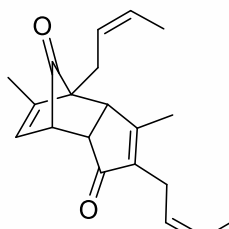
20.95

17.11

15.73

13.06

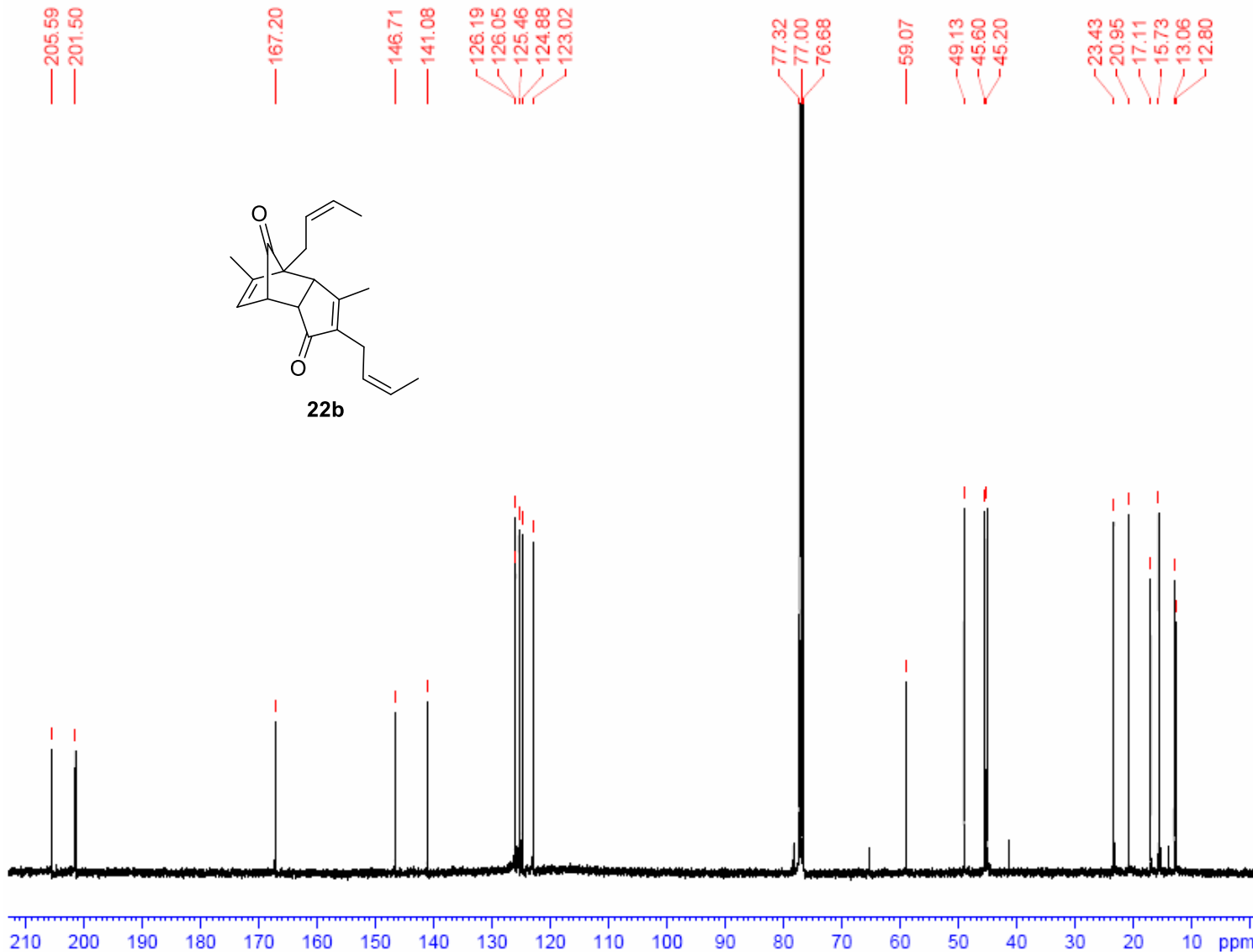
12.80



22b

```
----- CHANNEL f1 -----
NUC1      13C
P1        13.00 usec
PL1       -6.00 dB
SFO1     100.6243395 MHz
```

```
----- CHANNEL f2 -----
CPDPRG2   bi_waltz16_32pl
NUC2      1H
PCPD2     100.00 usec
PL2       -1.00 dB
PL12      21.27 dB
PL13      27.27 dB
PL30      21.27 dB
PL31      15.27 dB
SFO2     400.1320007 MHz
SI        65536
SF        100.6127719 MHz
WDW       EM
SSB       0
LB        1.00 Hz
GB        0
PC        1.40
```



¹³C NMR spectrum of dimer 22b



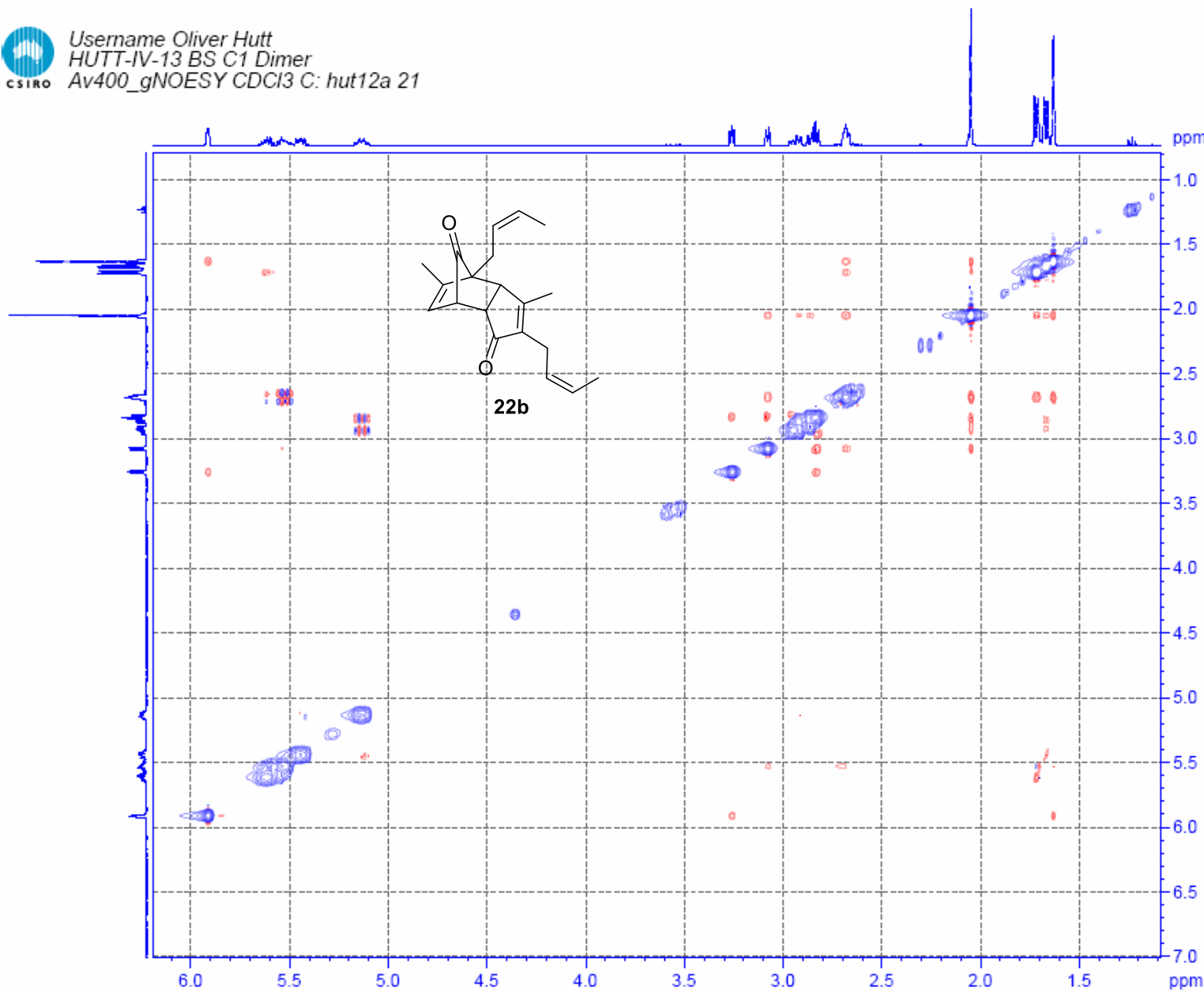
Username Oliver Hutt
HUTT-IV-13 BS C1 Dimer
Av400_gNOESY CDCl3 C: hut12a 21



```
NAME      hut140251
EXPNO     11
PROCNO    1
Date_     20101012
Time      19.11
INSTRUM   Av400
PROBHD    5 mm DABBI 1H/
PULPROG   noesyzgpg30
TD         1336
SOLVENT   CDCl3
NS         8
DS         16
SWH        4789.272 Hz
FIDRES     1.169256 Hz
AQ         0.4276724 sec
RG         352
DK         104.400 usec
DE         12.00 usec
TE         298.0 K
DQ         0.00009460 sec
D1         1.50000000 sec
d8         1.20000005 sec
D16        0.00020000 sec
IN0        0.00020880 sec

----- CHANNEL f1 -----
NUC1       1H
P1         7.70 usec
P2         15.40 usec
PL1        -1.00 dB
SFO1       400.1320007 MHz

----- GRADIENT CHANNEL -----
GPNAM1     gms.100
GPNAM2     gms.100
GPE1       40.00 %
GPE2       -40.00 %
P16        1000.00 usec
MD0        1
TD          512
SFO1       400.132 MHz
FIDRES     9.354047 Hz
SW         11.969 PPM
PRMODE     States-TPPI
SI         2048
SF         400.1300095 MHz
AQ         0
LB         3.00 Hz
GB         0
PC         1.00
SI         2048
MD0        States-TPPI
SF         400.1300095 MHz
AQ         0
LB         3.00 Hz
GB         0
```



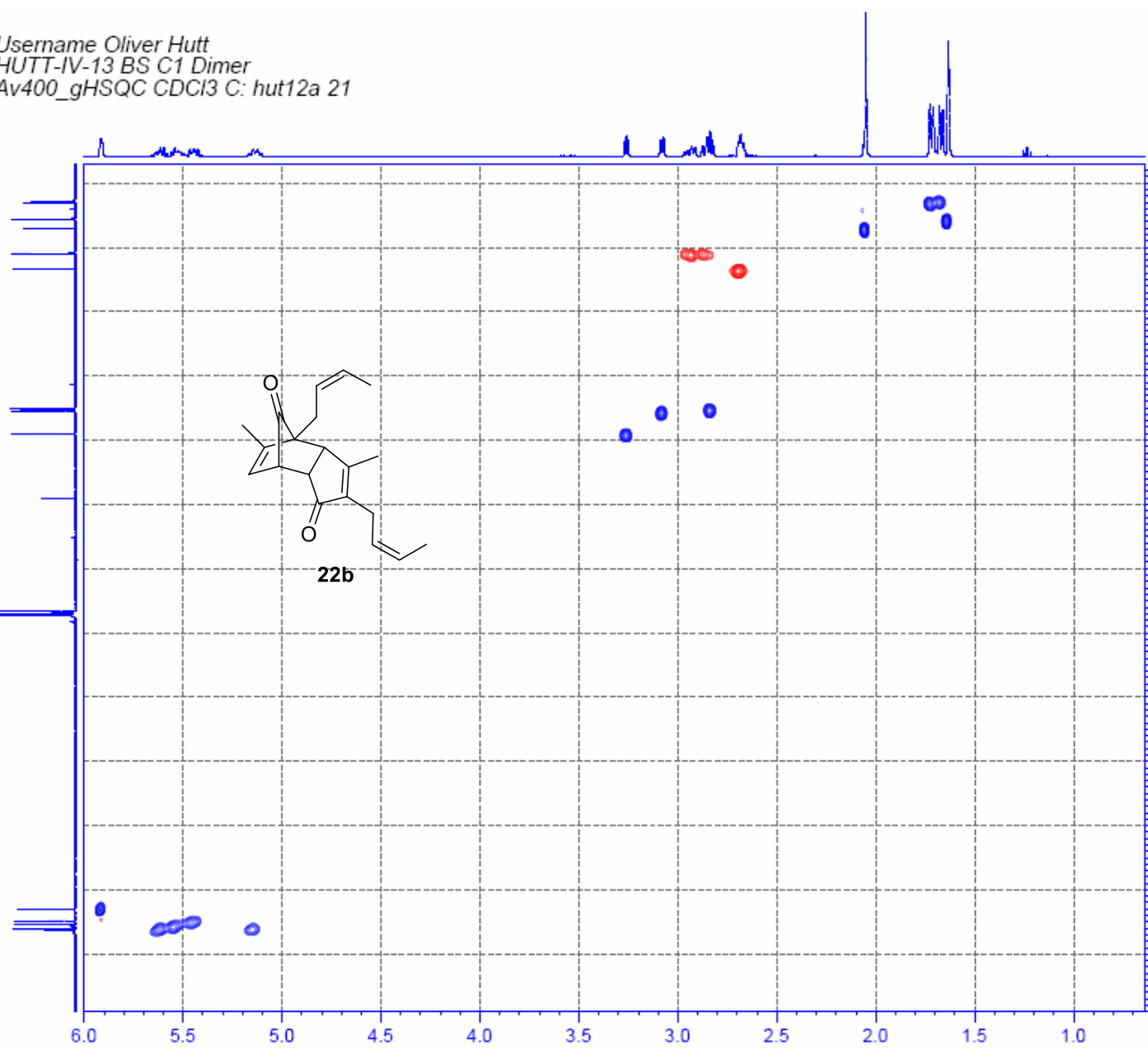
gNOESY NMR spectrum of dimer 22b



Username Oliver Hutt
HUTT-IV-13 BS C1 Dimer
Av400_gHSQC CDCI3 C: hut12a 21



```
NAME      hut140251
EXPNO     12
PROCNO    1
Date_     20101012
Time      23.40
INSTRUM   Av400
PROBHD    5 mm DABBI 1H/
PULPROG   huqadsetgpgatop2_2_CSIRO
TD         2048
SOLVENT   CDCl3
NS         2
DS         16
SWH        4006.410 Hz
FIDRES     1.956255 Hz
AQ         0.2556404 sec
RG         6502
DW         124.800 usec
DE         12.00 usec
TE         298.0 K
CNC12     145.8000000
CNC17     -0.5000000
D0         0.00000300 sec
D1         1.50000000 sec
D4         0.00172414 sec
D11       0.03000000 sec
D16       0.00920000 sec
D21       0.00344828 sec
D24       0.00986207 sec
IN0       0.00002925 sec
----- CHANNEL f1 -----
NUC1       1H
P1         7.70 usec
P2         15.40 usec
P28        0.10 usec
PL1        -1.00 dB
SFO1       400.1320007 MHz
----- CHANNEL f2 -----
CPDPRG2    gprg4
NUC2       13C
P3         13.00 usec
P14        500.00 usec
P24        2000.00 usec
PCPD2     70.00 usec
PL3        120.00 dB
PL12       -6.00 dB
PL122      -8.62 dB
SFO2       100.6208180 MHz
SD3        -0.12 dB
SD7        -0.12 dB
SFO3       Crp60, 0.5, 20.1
SFO3MY     Crp60comp, 4
SFO3L3     0.500
SFO3L7     0.500
SFO3FL3    0.00 Hz
SFO3FL7    0.00 Hz
----- GRADIENT CHANNEL -----
G2NAM1     sins, 100
G2NAM2     sins, 100
G2NAM3     sins, 100
G2NAM4     sins, 100
G2E1       80.00 %
G2E2       20.10 %
G2E3       11.00 %
G2E4       -5.00 %
P16        1900.00 usec
D19        600.00 usec
MD0        2
TD         256
SFO1       100.6208 MHz
FIDRES     66.818512 Hz
SW         170.000 ppm
PRMODE     Echo-Antiecho
SI         2048
SF         400.1300072 MHz
WDW        QWINE
SSB        2
LB         0.00 Hz
GB         0
PC         1.00
SI         1024
MC1        echo-antiecho
SF         100.6127436 MHz
WDW        QWINE
SSB        2
LB         0.00 Hz
GB         0
```



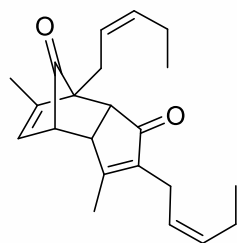
qHSQC NMR spectrum of dimer 22b



Username Oliver Hutt
HUTT-IV-14 J1 TS
Av400_1H CDCl3 C: hut12a 35

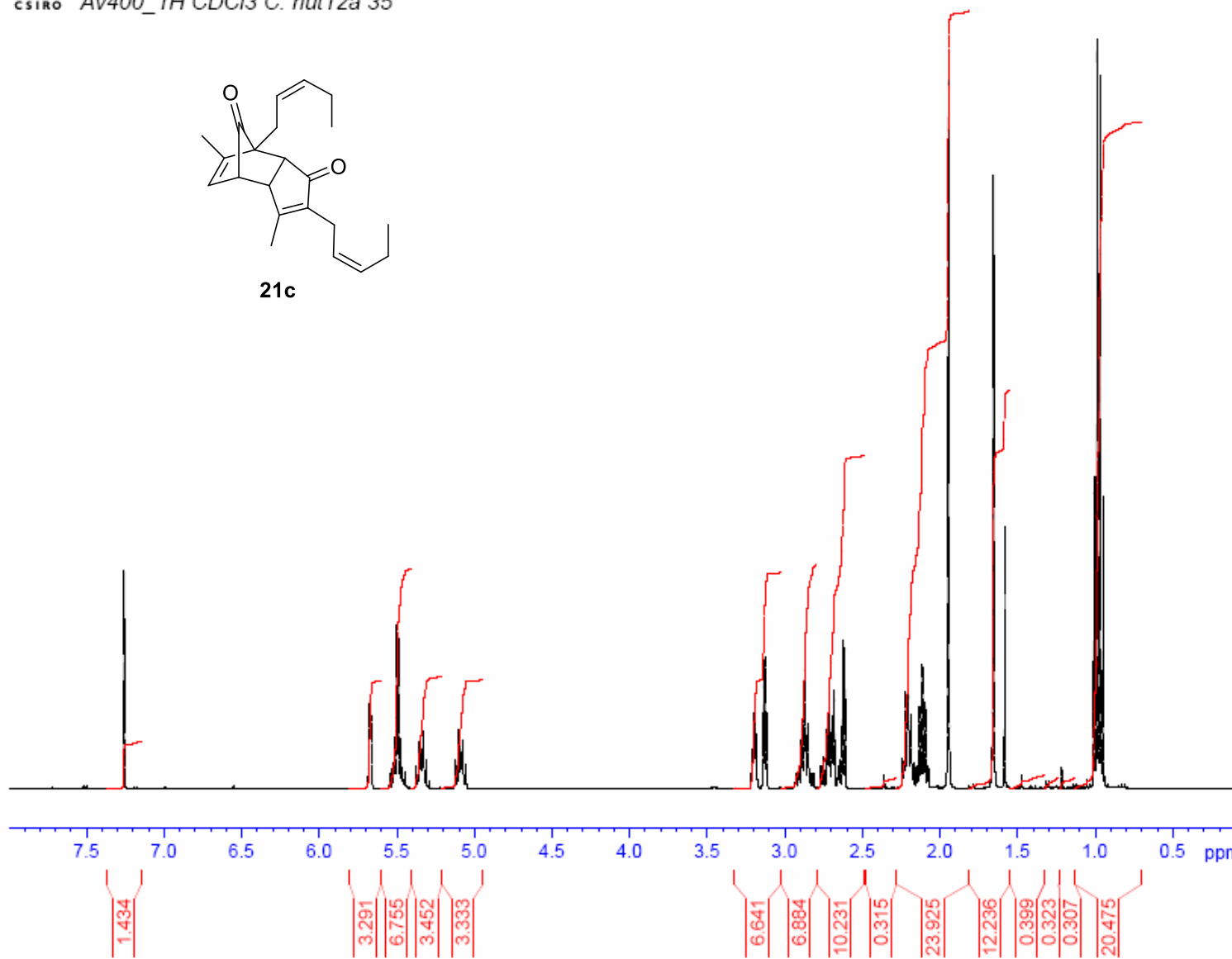


```
NAME      hutt40253
EXPNO     10
PROCNO    1
Date_     20101013
Time      15.53
INSTRUM   Av400
PROBHD    5 mm PABBI 1H/
PULPROG   zg30
TD        32768
SOLVENT   CDCl3
NS        32
DS        2
SWH       5995.204 Hz
FIDRES    0.182959 Hz
AQ        2.7329011 sec
RG        90.5
DW        93.400 usec
DE        12.00 usec
TE        299.0 K
D1        1.00000000 sec
TDO       1
```



21c

```
----- CHANNEL f1 -----
NUC1     1H
P1       7.70 usec
PL1      -1.00 dB
SFO1     400.1326104 MHz
SI       65536
SF       400.1300095 MHz
WDW      EM
SSB      0
LB       0.10 Hz
GB       0
PC       1.00
```



¹H NMR spectrum of dimer **21c**



Username Oliver Hutt
HUTT-IV-14 TS
Av400_13C CDCl3 C: hut12a 56



```
NAME      hut140259
EXPNO     10
PROCNO    1
Date_     20101017
Time      14.18
INSTRUM   Av400
PROBHD    5 mm FABS1 1H/
PULPROG   zgpg30_CSIRO
TD         65536
SOLVENT   CDCl3
NS         7500
DS         2
SWH        25125.629 Hz
FIDRES     0.393397 Hz
AQ         1.3042164 sec
RG         20642.5
DW         19.900 usec
DE         12.00 usec
TE         299.0 K
D1         1.00000000 sec
D11        0.03000000 sec
L31        1
TDO        1
```

```
----- CHANNEL f1 -----
NUC1       13C
P1         13.00 usec
PL1        -6.00 dB
SFO1       100.6243395 MHz
```

```
----- CHANNEL f2 -----
CPDPRG2   bi_waltz16_32pl
NUC2       1H
PCPD2     100.00 usec
PL2        -1.00 dB
PL12       21.27 dB
PL13       27.27 dB
PL30       21.27 dB
PL31       15.27 dB
SFO2       400.1320007 MHz
SI         65536
SF         100.6127719 MHz
WDW        EM
SSB        0
LB         1.00 Hz
GB         0
PC         1.40
```

204.96
201.65

166.77

146.43
143.10

134.54

132.52

124.47

123.75

120.89

77.31

76.99

76.67

59.29

49.58

45.26

45.20

23.35

21.26

20.56

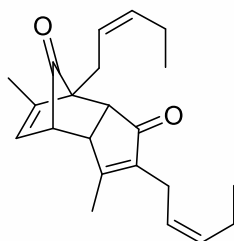
20.53

16.05

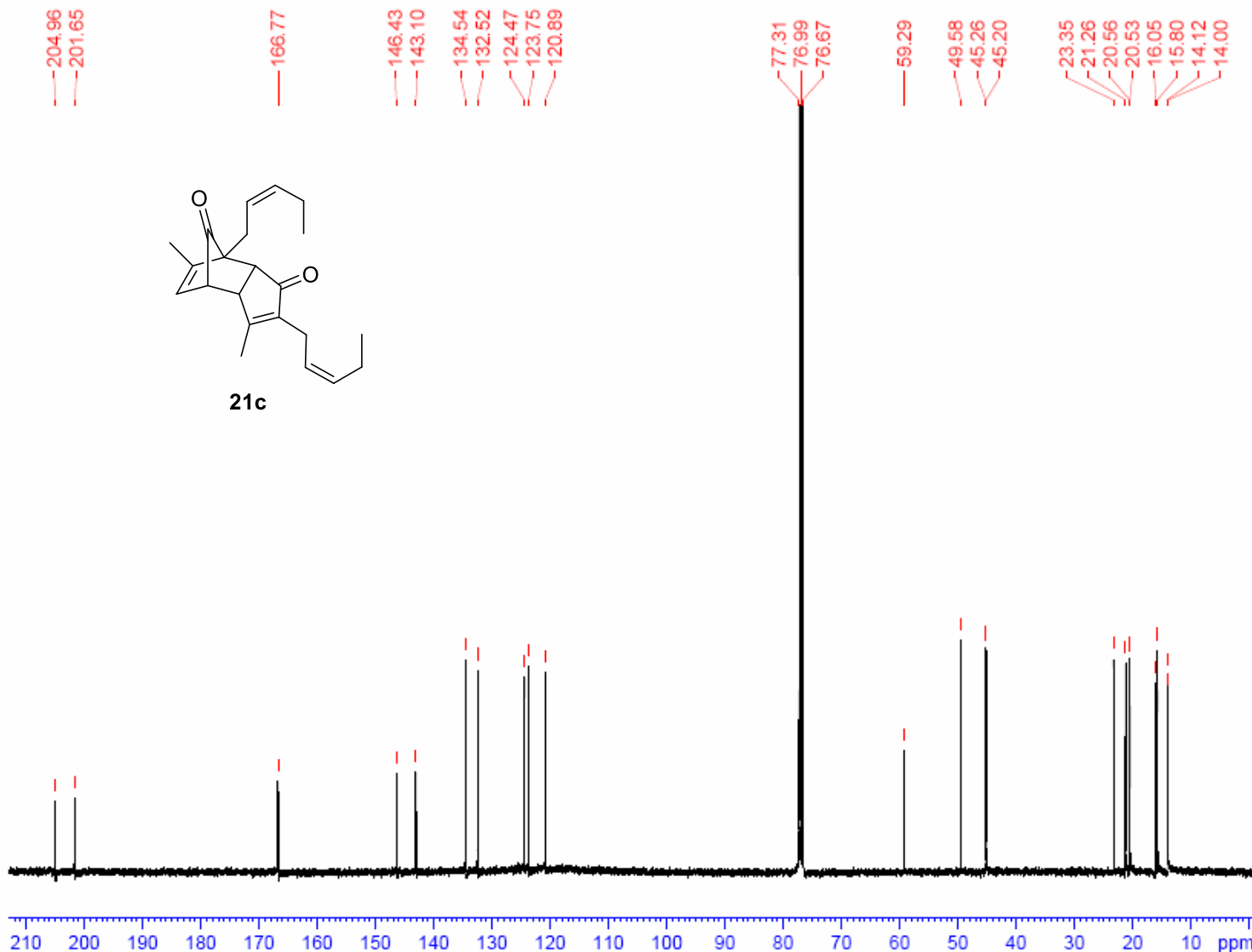
15.80

14.12

14.00



21c



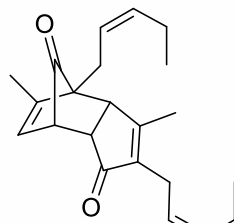
¹³C NMR spectrum of dimer 21c



Username J. Freemont
Jasmolin I AIBN Adduct
Av400_1H_A4 CDCl3 C: fre155 6

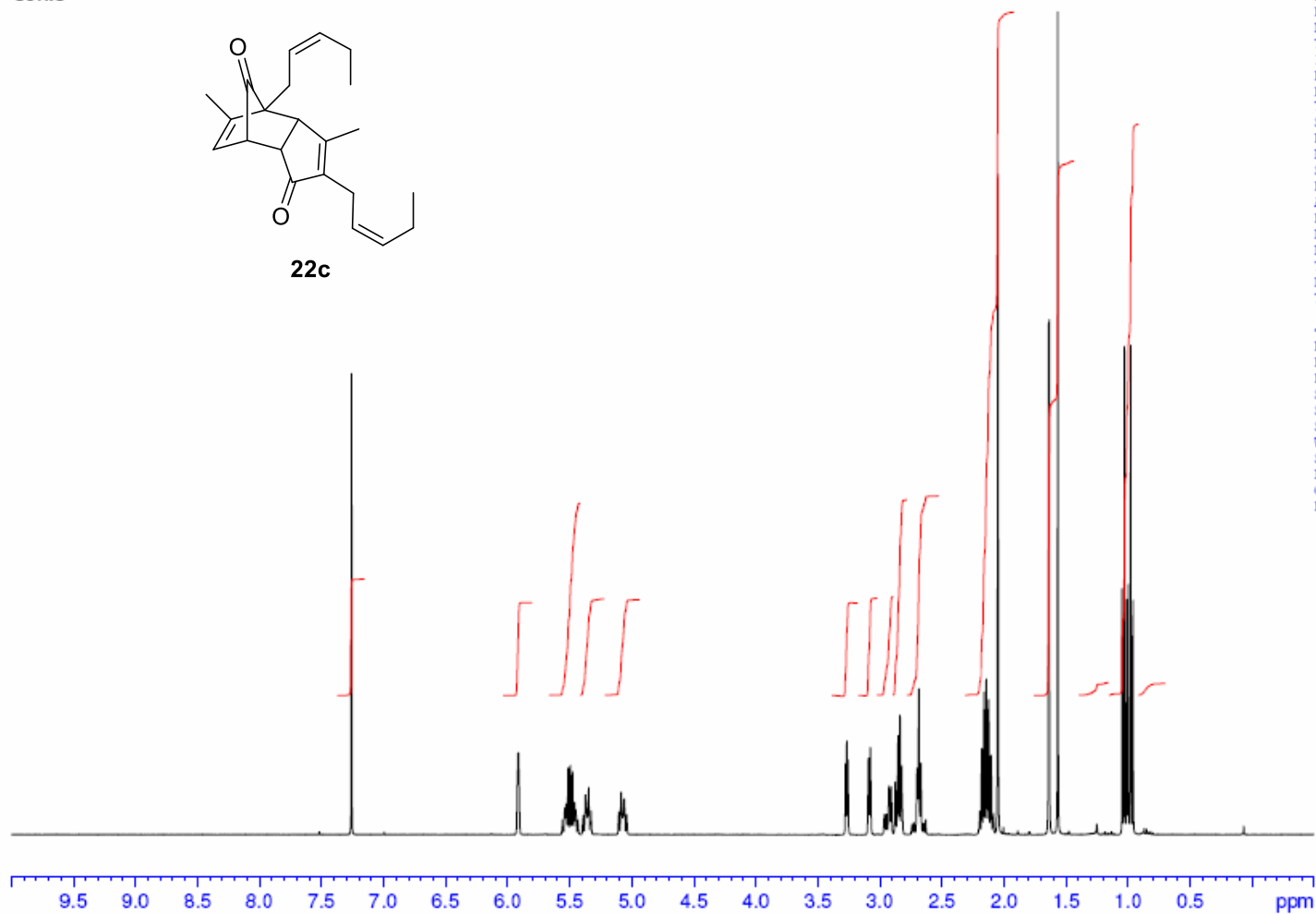


```
NAME      J. Freemont40809
EXPNO     10
PROCNO    1
Date_     20101216
Time      17.46
INSTRUM   Av400
PROBHD    5 mm PABBI 1H/
PULPROG   zg30
TD         32768
SOLVENT   CDCl3
NS         32
DS         2
SWH       5995.204 Hz
FIDRES    0.182959 Hz
AQ         2.7329011 sec
RG         256
DW         83.400 usec
DE         12.00 usec
TE         298.0 K
D1         1.0000000 sec
TD0        1
```



22c

```
----- CHANNEL f1 -----
NUC1      1H
P1         7.70 usec
PL1        -1.00 dB
SFO1      400.1326104 MHz
SI         65536
SF         400.1300095 MHz
WDW        EM
SSB         0
LB         0.10 Hz
GB         0
PC         1.00
```



3.754
2.999
6.212
3.115
3.084
2.978
3.139
3.198
6.329
6.463
22.128
17.300
0.412
18.508
0.381

¹H NMR spectrum of dimer 22c



Username Oliver Hutt
HUTT-IV-14 BS
Av400_13C CDCl3 C: hut12a 4



```
NAME      hut140260
EXPNO     10
PROCNO    1
Date_     20101017
Time      19.20
INSTRUM   Av400
PROBHD    5 mm PABBI 1H/
PULPROG   zgpg30_CSIRO
TD         65536
SOLVENT   CDCl3
NS         7500
DS         2
SWH       25125.629 Hz
FIDRES    0.393397 Hz
AQ         1.3042164 sec
RG         20642.5
DW         19.900 usec
DE         12.00 usec
TE         298.0 K
D1         1.00000000 sec
D11        0.03000000 sec
L31        1
TDO        1
```

205.57
201.46

167.17

146.71
141.06

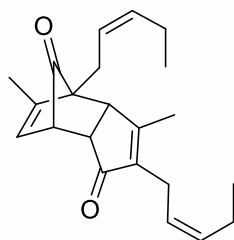
133.97
132.60
124.36
123.77
123.04

77.31
76.99
76.67

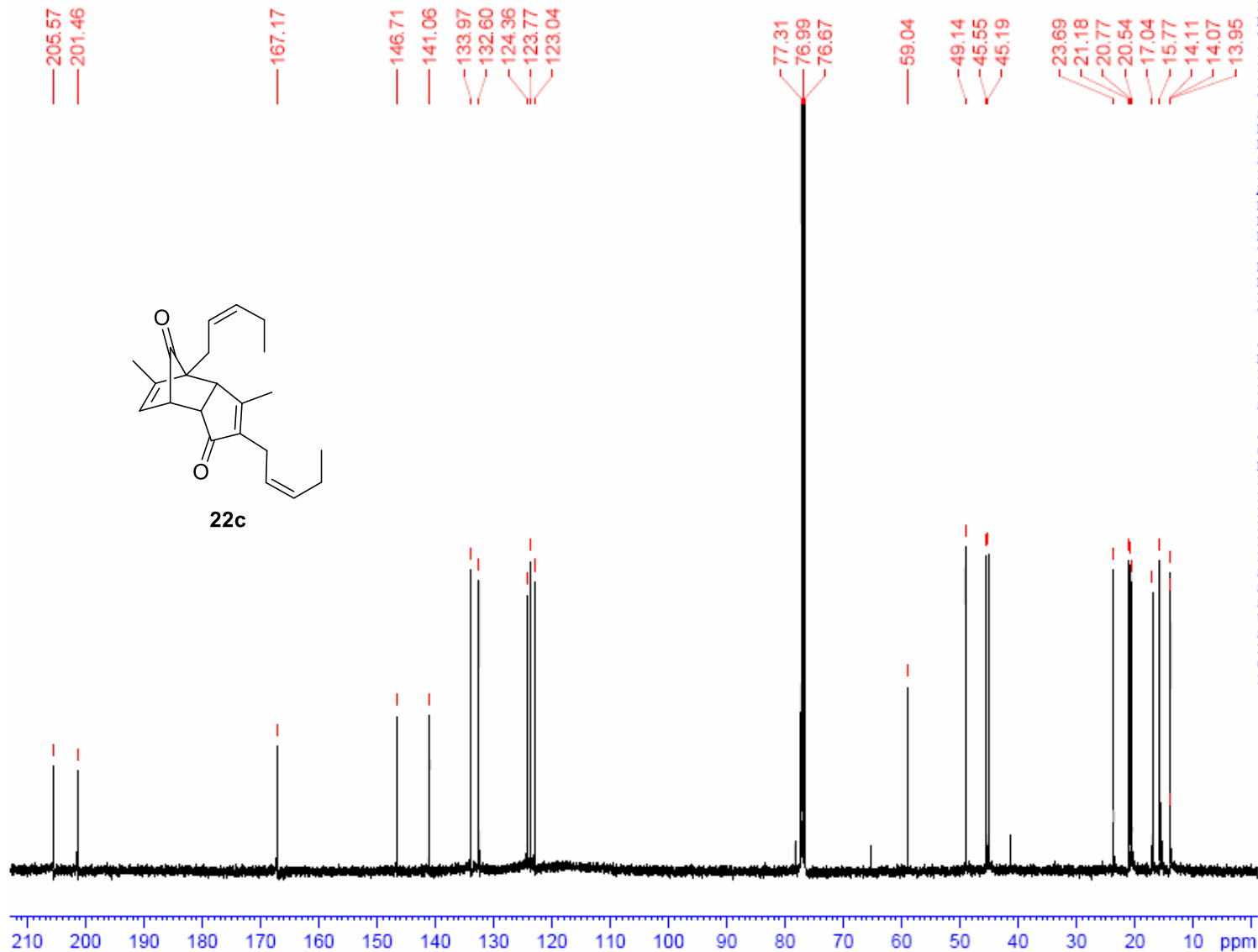
59.04

49.14
45.55
45.19

23.69
21.18
20.77
20.54
17.04
15.77
14.11
14.07
13.95



22c

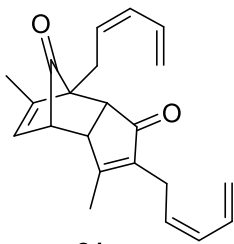


```
----- CHANNEL f1 -----
NUC1      13C
P1         13.00 usec
PL1        -6.00 dB
SFO1      100.6243395 MHz
```

```
----- CHANNEL f2 -----
CPDPRG2   bi_waltz16_32pl
NUC2      1H
PCPD2     100.00 usec
PL2        -1.00 dB
PL12       21.27 dB
PL13       27.27 dB
PL30       21.27 dB
PL31       15.27 dB
SFO2      400.1320007 MHz
SI         65536
SF         100.6127719 MHz
WDW        EM
SSB        0
LB         1.00 Hz
GB         0
PC         1.40
```

¹³C NMR spectrum of dimer 22c

HPLC traces of compound 21a-c and 22a-c.



21a

Current Date 19/11/2010

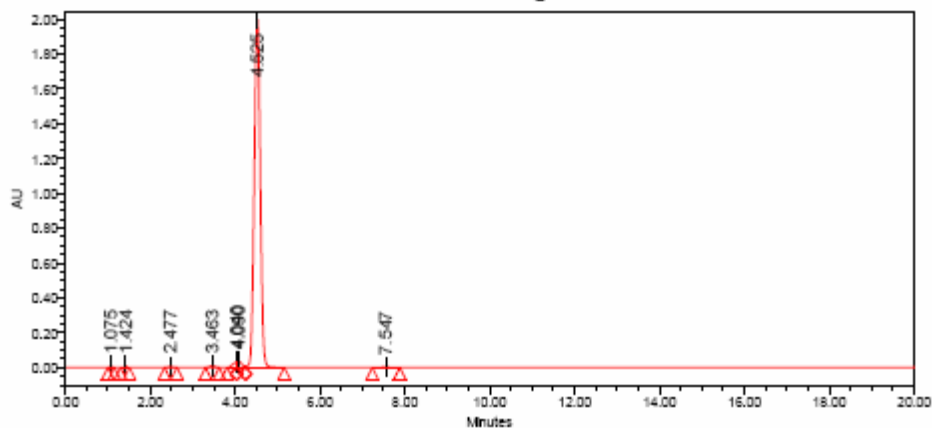
1 of 1

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Run Information

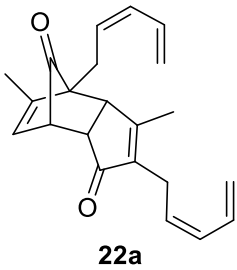
Sample Name: JAF-50 spot 1 55%ACN/H2O Date Acquired: 18/11/2010 5:40:29 PM EST
Detector: PDA 223.0 nm Acq Method Set : Isocratic 100% A1
HplcColumn: 150x4.6mm BEH C18 Date Processed: 19/11/2010 9:08:35 AM EST
FlowRate: 0.4 mL / min Processing Method: nkh
MobilePhase: 55% ACN / H2O

HPLC Chromatogram



The Results

Name	R.Time	Area	% Area	Height	% Height
1	1.075	27530	0.14	9382	0.45
2	1.424	27598	0.14	7761	0.37
3	2.477	26844	0.13	4773	0.23
4	3.463	65589	0.32	8144	0.39
5	4.040	183043	0.90	28772	1.38
6	4.090	248560	1.22	31637	1.51
7	4.525	19732672	96.94	1997522	95.54
8	7.547	44182	0.22	2803	0.13



Current Date 19/11/2010

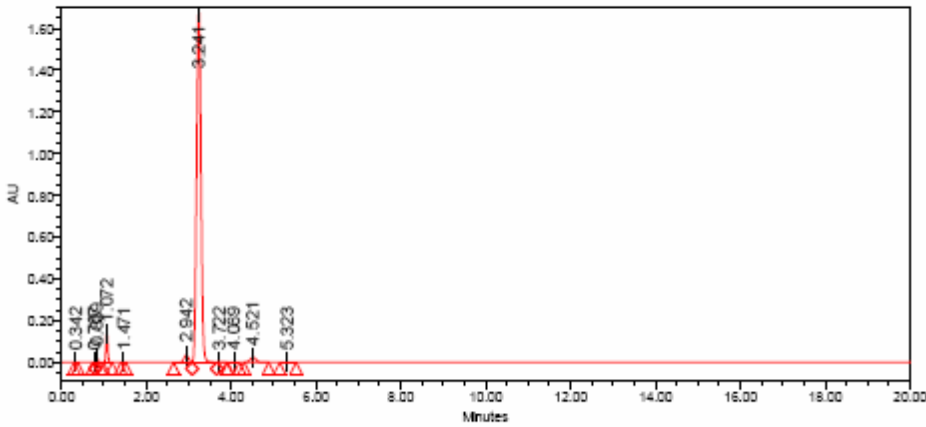
1 of 1

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Run Information

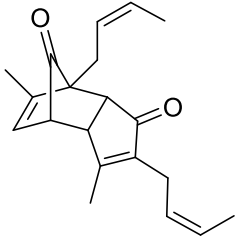
Sample Name: JAF-50 spot 2 55%ACN/H2O Date Acquired: 18/11/2010 8:08:37 PM EST
 Detector: PDA 223.0 nm Acq Method Set : Isocratic 100% A1
 HplcColumn: 150x4.6mm BEH C18 Date Processed: 19/11/2010 9:09:30 AM EST
 FlowRate: 0.4 mL / min Processing Method: nkh
 MobilePhase: 55% ACN / H2O

HPLC Chromatogram



The Results

Name	R.Time	Area	% Area	Height	% Height
1	0.342	1665	0.01	899	0.05
2	0.787	4845	0.04	2718	0.14
3	0.839	56118	0.43	20441	1.07
4	1.072	389671	2.99	135801	7.14
5	1.471	3537	0.03	1042	0.05
6	2.942	261657	2.01	33430	1.76
7	3.241	12067323	92.63	1682499	88.46
8	3.722	6800	0.05	873	0.05
9	4.069	6407	0.05	830	0.04
10	4.521	224015	1.72	23097	1.21
11	5.323	5155	0.04	465	0.02



21b

Current Date 14/10/2010

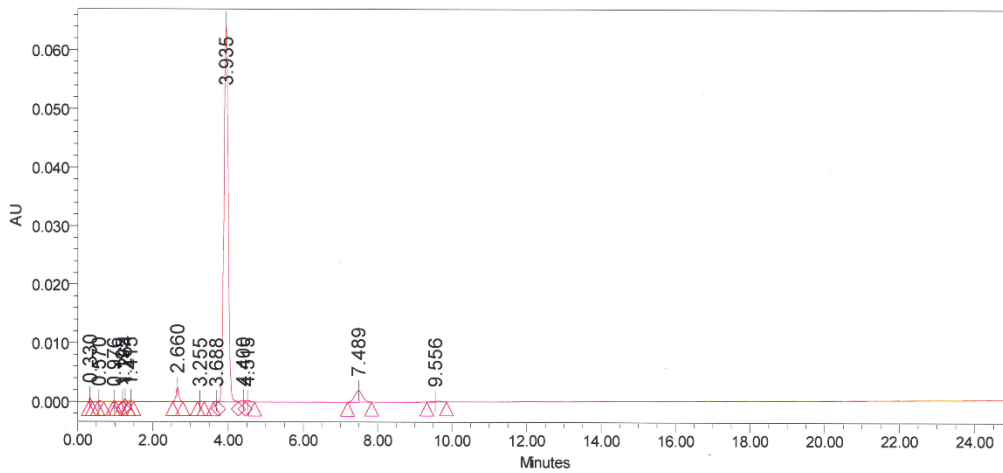
1 of 2

CSIRO Molecular & Health Technologies

Run Information

Sample Name: Hutt-IV-13 C1-TS 55%ACN/H2O Date Acquired: 13/10/2010 10:47:20 PM EST
 Detector: PDA 223.0 nm Acq Method Set: Isocratic 100% A1
 HplcColumn: 50x2.1mm BEH C18 Date Processed: 14/10/2010 8:37:53 AM EST
 FlowRate: 0.4 mL / min Processing Method: nkh
 MobilePhase: 55% ACN / H2O

HPLC Chromatogram

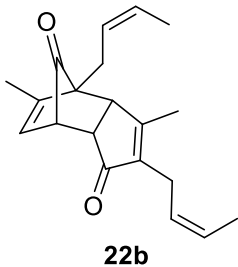


The Results

Name	RTime	Area	% Area	Height	% Height
1	0.330	2037	0.36	735	1.02
2	0.570	828	0.15	211	0.29
3	0.976	340	0.06	131	0.18
4	1.195	183	0.03	82	0.11
5	1.264	1686	0.30	455	0.63
6	1.415	881	0.16	241	0.33
7	2.660	12713	2.27	2426	3.37
8	3.255	472	0.08	87	0.12
9	3.688	553	0.10	105	0.15
10	3.935	504322	90.21	64845	90.18
11	4.400	2186	0.39	273	0.38
12	4.515	2072	0.37	235	0.33
13	7.489	28558	5.11	1950	2.71

The Results

Name	RTime	Area	% Area	Height	% Height
14	9.556	2213	0.40	128	0.18



Current Date 16/12/2010

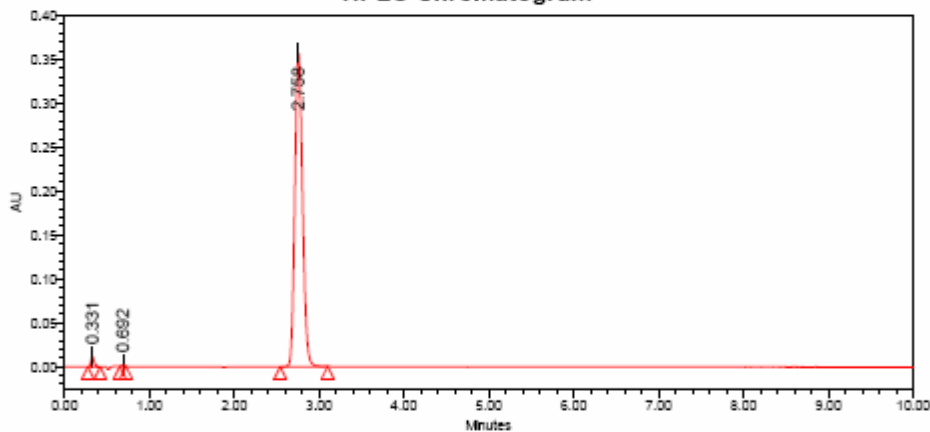
1 of 1

CSIRO Molecular & Health Technologies

Run Information

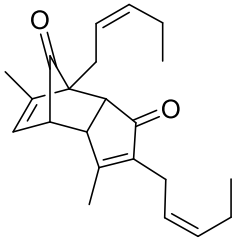
Sample Name: Hutt-IV-13 C1-BS pure 55%ACN/H2O Date Acquired: 15/12/2010 4:44:28 PM EST
 Detector: PDA Spectrum (190-400)nm Acq Method Set : Isocratic 100% A1
 HplcColumn: 50x2.1mm BEH C18 Date Processed: 16/12/2010 9:53:13 AM EST
 FlowRate: 0.4 mL / min Processing Method: nkh
 MobilePhase: 55% ACN / H2O

HPLC Chromatogram



The Results

Name	R.Time	Area	% Area	Height	% Height
1	0.331	31625	1.38	11362	3.07
2	0.692	2677	0.12	1268	0.34
3	2.758	2257156	98.50	357629	96.59



21c

Current Date 14/10/2010

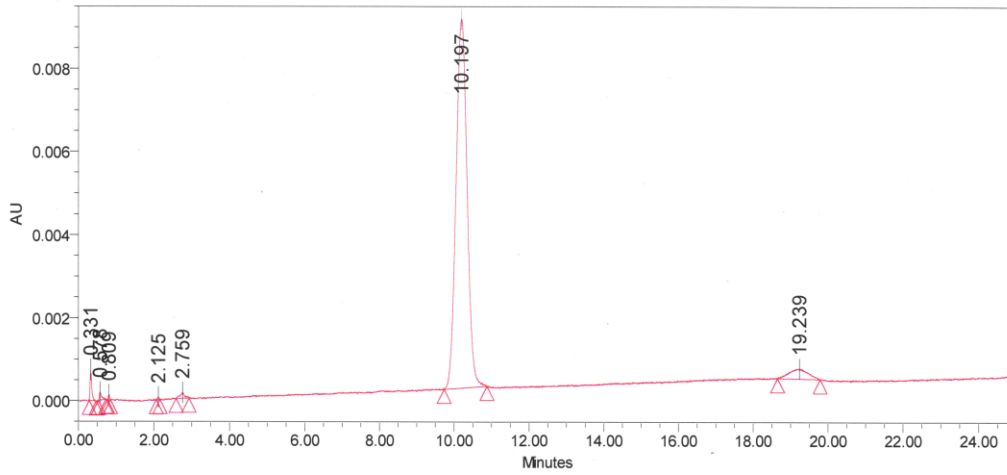
1 of 1

CSIRO Molecular & Health Technologies

Run Information

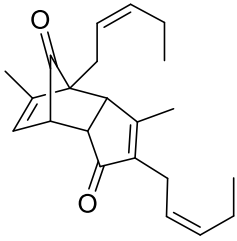
Sample Name: Hutt-IV-14 J1-TS 55%ACN/H2O Date Acquired: 13/10/2010 11:38:51 PM EST
 Detector: PDA 223.0 nm Acq Method Set: Isocratic 100% A1
 HplcColumn: 50x2.1mm BEH C18 Date Processed: 14/10/2010 8:39:37 AM EST
 FlowRate: 0.4 mL / min Processing Method: nkh
 MobilePhase: 55% ACN / H2O

HPLC Chromatogram



The Results

Name	R.Time	Area	% Area	Height	% Height
1	0.331	2290	1.18	757	7.26
2	0.578	862	0.44	204	1.96
3	0.809	293	0.15	123	1.18
4	2.125	203	0.10	65	0.63
5	2.759	1153	0.59	142	1.36
6	10.197	180844	93.06	8889	85.29
7	19.239	8677	4.47	242	2.33



22c

Current Date 16/12/2010

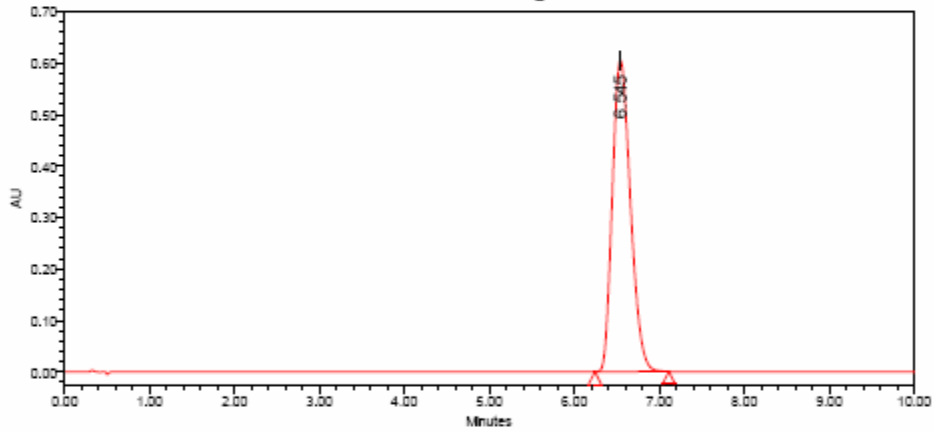
1 of 1

CSIRO Molecular & Health Technologies

Run Information

Sample Name: Hutt-IV-14 J1-BS Pure 55%ACN/H2O Date Acquired: 16/12/2010 6:04:52 PM EST
Detector: PDA Spectrum (180-400)nm Acq Method Set : Isocratic 100% A1
HplcColumn: 50x2.1mm BEH C18 Date Processed: 16/12/2010 6:15:23 PM EST
FlowRate: 0.4 mL / min Processing Method: nkh
MobilePhase: 55% ACN / H2O

HPLC Chromatogram



The Results

Name	R.Time	Area	% Area	Height	% Height
1	6.545	8974269	100.00	604827	100.00

Representative HPLC traces of refined pyrethrum extracts, and samples produced by heating the extracts at 230°C for 8 and 15 min

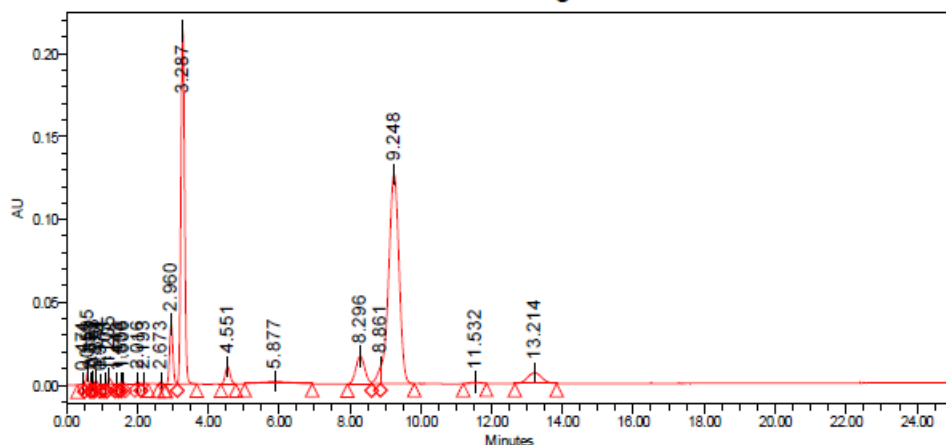
Refined Concentrate, 1mg/mL

CSIRO Materials Science & Engineering

Run Information

Sample Name: Ref conc 1mg/mL 55%ACN/H2O Date Acquired: 18/10/2010 6:57:50 PM EST
 Detector: PDA 223.0 nm Acq Method Set: Isocratic 100% A1
 HplcColumn: 50x2.1mm BEH C18 50x2.1mm BEH Date Processed: 19/10/2010 10:17:39 AM EST
 FlowRate: 0.4mL/min 0.4 mL / min Processing Method: nkh
 MobilePhase: 55% ACN / H2O

HPLC Chromatogram



The Results

	Name	R.Time	Area	% Area	Height	% Height
1		0.474	5659	0.11	1043	0.23
2		0.596	27991	0.54	8025	1.79
3		0.696	2808	0.05	1081	0.24
4		0.758	6784	0.13	2279	0.51
5		0.851	10410	0.20	2392	0.53
6		0.974	1781	0.03	482	0.11
7		1.103	2396	0.05	729	0.16
8		1.205	23903	0.46	4145	0.93
9		1.443	1702	0.03	450	0.10
10		1.536	2823	0.05	836	0.19
11		1.606	5472	0.11	1294	0.29
12		2.016	5292	0.10	1074	0.24
13		2.193	3297	0.06	586	0.13
14		2.673	6344	0.12	1203	0.27

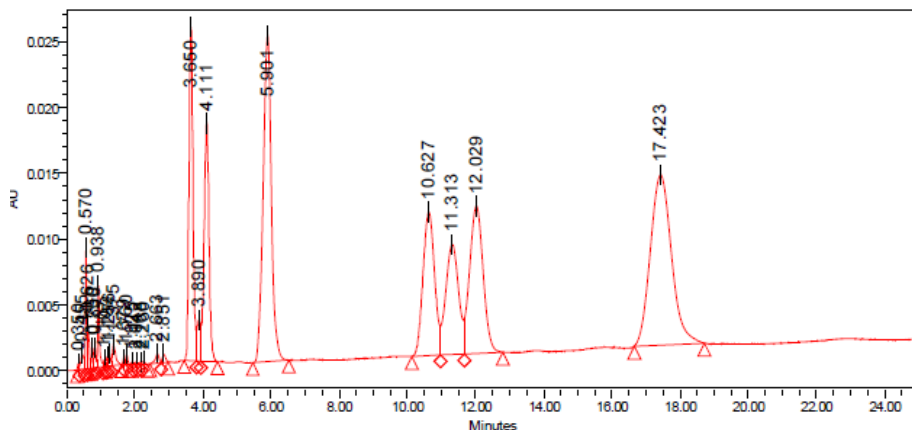
15		2.960	237418	4.57	36258	8.11	Cinerin II
16		3.287	1532948	29.50	213319	47.70	Pyrethrin II
17		4.551	99540	1.92	10372	2.32	Jasmolin II
18		5.877	75665	1.46	1274	0.28	
19		8.296	287786	5.54	16595	3.71	Cinerin I
20		8.861	64953	1.25	10149	2.27	
21		9.248	2594643	49.93	126343	28.25	Pyrethrin I
22		11.532	17571	0.34	847	0.19	
23		13.214	178982	3.44	6434	1.44	Jasmolin I

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Run Information

Sample Name: JAF-1198-18a 55%ACN/H2O Date Acquired: 27/07/2010 6:56:06 PM EST
 Detector: PDA 223.0 nm Acq Method Set: Isocratic 100% A1
 HplcColumn: 50x2.1mm BEH C18 50x2.1mm BEH Date Processed: 18/10/2010 4:50:52 PM EST
 FlowRate: 0.4mL/min 0.4 mL / min Processing Method: nkh
 MobilePhase: 55% ACN / H2O

HPLC Chromatogram



The Results

Name	R.Time	Area	% Area	Height	% Height
1	0.350	1400	0.06	441	0.30
2	0.466	7032	0.31	1150	0.79
3	0.570	22755	1.00	9228	6.36
4	0.626	11664	0.51	3341	2.30
5	0.780	5209	0.23	1547	1.07
6	0.836	4649	0.20	1502	1.04
7	0.938	20864	0.92	6207	4.28
8	1.107	1966	0.09	497	0.34
9	1.192	2608	0.11	738	0.51
10	1.256	3659	0.16	979	0.68
11	1.375	10509	0.46	1561	1.08
12	1.679	1496	0.07	396	0.27
13	1.780	2988	0.13	743	0.51
14	1.925	782	0.03	199	0.14

15	2.042	992	0.04	189	0.12
16	2.168	823	0.04	170	0.12
17	2.280	1061	0.05	218	0.15
18	2.663	5404	0.24	712	0.49
19	2.851	3970	0.17	613	0.42
20	3.650	20899	9.18	25334	17.47
21	3.890	22177	0.97	3131	2.16
22	4.111	181366	7.97	18077	12.46
23	5.901	413169	18.15	24748	17.06
24	10.627	257887	11.33	10906	7.52
25	11.313	220821	9.70	8357	5.78
26	12.029	309688	13.47	11165	7.70
27	17.423	555384	24.40	12903	8.90

Cinerin II

Pyrethrin II

Jasmolin II

Cinerin I

Pyrethrin I

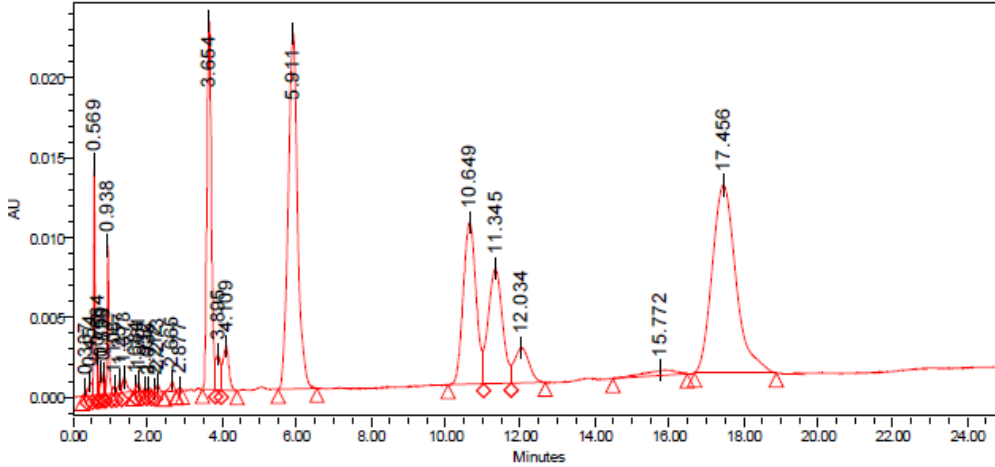
Jasmolin I

CSIRO Materials Science & Engineering

Run Information

Sample Name: JAF-1198-18b 55%ACN/H2O Date Acquired: 27/07/2010 7:21:50 PM EST
 Detector: PDA 223.0 nm Acq Method Set: Isocratic 100% A1
 HplcColumn: 50x2.1mm BEH C18 50x2.1mm BEH Date Processed: 18/10/2010 4:53:04 PM EST
 FlowRate: 0.4mL/min 0.4 mL / min Processing Method: nkh
 MobilePhase: 55% ACN / H2O

HPLC Chromatogram



The Results

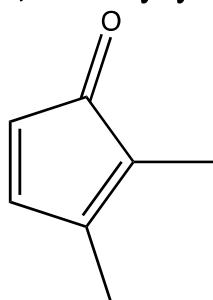
	Name	R.Time	Area	% Area	Height	% Height
1		0.337	1400	0.08	461	0.39
2		0.454	5493	0.31	894	0.76
3		0.569	36641	2.06	14456	12.35
4		0.664	5824	0.33	2163	1.85
5		0.759	5236	0.29	1397	1.19
6		0.836	3685	0.21	1282	1.10
7		0.938	28901	1.63	9322	7.97
8		1.108	2064	0.12	425	0.36
9		1.257	4526	0.25	851	0.73
10		1.373	7518	0.42	942	0.81
11		1.684	819	0.05	291	0.25
12		1.781	2949	0.16	621	0.53
13		1.932	1210	0.07	271	0.23
14		2.035	1298	0.07	221	0.19
15		2.212	625	0.04	151	0.13
16		2.273	2695	0.15	494	0.42
17		2.665	4538	0.26	596	0.51
18		2.877	849	0.05	158	0.14
19		3.654	191531	10.78	23114	19.75
20		3.865	18119	1.02	2218	1.89
21		4.109	30711	1.73	2784	2.38
22		5.911	387715	21.82	22314	19.07
23		10.649	245184	13.80	10159	8.68
24		11.345	188568	10.61	7188	6.14
25		12.034	56292	3.34	2192	1.87
26		15.772	18882	1.06	305	0.26
27		17.456	520383	29.29	11796	10.05

Cinerin II
 Pyrethrin II
 Jasmolin II
 Cinerin I
 Pyrethrin I
 Jasmolin I

Computed geometries and energies

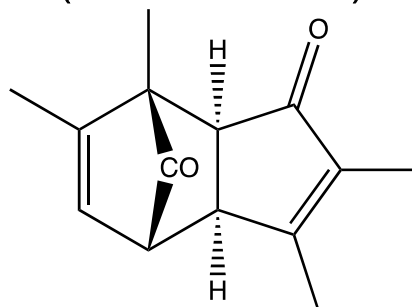
Cartesian coordinates and energies of computed structures are listed below.

2,3-dimethylcyclopenta-2,4-dien-1-one (6d)



C	0.842177	-1.623840	0.000018
C	-0.493782	-1.631052	-0.000018
C	-1.028673	-0.214736	-0.000008
C	0.006141	0.647348	-0.000008
H	1.532317	-2.455005	0.000016
H	-1.143738	-2.497371	-0.000048
C	1.260571	-0.180700	0.000068
O	2.404318	0.244348	0.000023
C	0.042057	2.136827	-0.000027
H	0.573000	2.516784	0.879664
H	0.573512	2.516745	-0.879421
H	-0.962557	2.562419	-0.000324
C	-2.490133	0.050459	-0.000026
H	-2.958798	-0.410147	0.877963
H	-2.719599	1.116388	-0.000184
H	-2.958836	-0.410428	-0.877845
0 imaginary frequencies			
ZPE			0.128696
E			-346.881580
H 298.15 K			-346.743830
G 298.15 K, 1 mol L ⁻¹			-346.782280

19d ($\Delta G = -20.3$ kcal mol⁻¹)

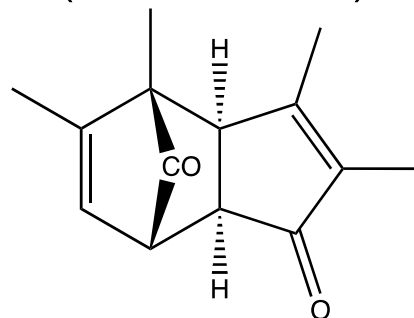


C	-1.985819	-1.613643	-0.359653
C	-0.575138	-1.676124	0.194786
C	-1.273340	0.536594	0.214248
C	-2.400136	-0.333134	-0.363810
H	-2.537734	-2.475444	-0.713712
C	0.370483	-0.979057	-0.842955
H	0.298450	-1.482551	-1.808910
C	-0.126773	0.493476	-0.870087
H	-0.519419	0.821635	-1.832832
H	-0.230470	-2.629912	0.583014
C	2.209827	0.390531	-0.191442
C	1.808521	-0.888825	-0.388165
C	3.535998	0.911160	0.255890
H	3.950303	1.598069	-0.489085
H	3.431506	1.478006	1.186837
H	4.256232	0.109877	0.422594
C	-0.733028	-0.526402	1.193604
O	-0.542751	-0.463772	2.383450
C	-3.686233	0.232456	-0.855939
H	-3.511705	0.959181	-1.657381
H	-4.335640	-0.557497	-1.240308
H	-4.218735	0.760940	-0.058602
C	-1.652929	1.881717	0.789723
H	-1.990802	2.563807	0.006083
H	-2.460969	1.768733	1.516992
H	-0.804976	2.344522	1.297213
C	1.109241	1.303876	-0.515236
O	1.173229	2.531063	-0.520628
C	2.605884	-2.130693	-0.202104
H	2.567079	-2.741606	-1.110656
H	3.648571	-1.928376	0.042156
H	2.175131	-2.739304	0.600860
0 imaginary frequencies			
ZPE			0.264767
E			-693.823150
H 298.15 K			-693.542146
G 298.15 K, 1 mol L ⁻¹			-693.596930

19d-TS ($\Delta G^\ddagger = 14.0 \text{ kcal mol}^{-1}$)

C	-2.115213	-1.688251	-0.013164
C	-0.858629	-1.751910	0.570056
C	-1.611154	0.501784	0.468870
C	-2.569825	-0.340840	-0.093796
H	-2.658131	-2.530111	-0.424600
C	0.518486	-0.939940	-1.113319
H	0.197735	-1.770909	-1.722436
C	0.041206	0.368871	-1.216003
H	-0.703816	0.730807	-1.906902
H	-0.322208	-2.637737	0.875841
C	2.220933	0.369803	-0.205632
C	1.868270	-0.911382	-0.480664
C	3.426479	0.914339	0.478735
H	3.958118	1.621004	-0.167703
H	3.143754	1.463401	1.383348
H	4.120381	0.123089	0.765479
C	-0.611314	-0.399662	1.142846
O	0.209833	-0.081970	1.986103
C	-3.827240	0.108022	-0.760751
H	-3.602309	0.637731	-1.694653
H	-4.472096	-0.739465	-1.001484
H	-4.388185	0.803501	-0.128728
C	-1.752808	1.953010	0.769351
H	-0.827362	2.365418	1.172766
H	-2.025723	2.521161	-0.123737
H	-2.543669	2.111992	1.512338
C	1.131185	1.252319	-0.707680
O	1.146671	2.479041	-0.734996
C	2.618446	-2.163715	-0.199158
H	2.684255	-2.779287	-1.102886
H	3.627085	-1.970026	0.166482
H	2.087200	-2.761819	0.549870
1 imaginary frequency			
ZPE			0.258913
E			-693.760313
H 298.15 K			-693.483839
G 298.15 K, 1 mol L ⁻¹			-693.542179

20d ($\Delta G = -19.4 \text{ kcal mol}^{-1}$)



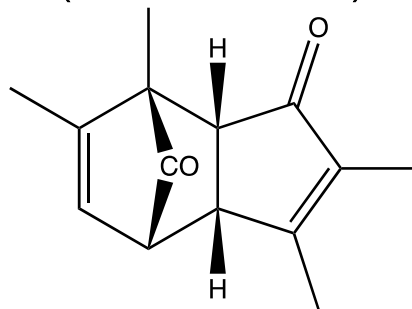
C	-2.091061	-1.533837	-0.404032
C	-0.697293	-1.720554	0.166918
C	-1.218025	0.540856	0.228518
C	-2.398947	-0.224025	-0.389270
H	-2.703447	-2.341883	-0.784494
C	0.299770	-1.083016	-0.850051
H	0.198819	-1.546184	-1.832171
C	-0.045498	0.433418	-0.832408
H	-0.402554	0.815706	-1.791066
H	-0.426640	-2.705977	0.535355
C	1.253571	1.105950	-0.451981
C	2.243067	0.215490	-0.190698
C	1.749795	-1.145015	-0.399045
O	2.392411	-2.182358	-0.247000
C	1.390727	2.592401	-0.420031
H	1.345453	2.965976	0.608377
H	2.353166	2.904989	-0.832759
H	0.592198	3.076560	-0.983957
C	3.648399	0.483252	0.236429
H	3.859147	1.551570	0.295278
H	3.839387	0.043551	1.221082
H	4.359397	0.025574	-0.458909
C	-0.777879	-0.581294	1.188956
O	-0.593551	-0.559383	2.381128
C	-3.627833	0.450377	-0.891533
H	-3.382693	1.175124	-1.676154
H	-4.330361	-0.278699	-1.301900
H	-4.131859	1.004706	-0.093275
C	-1.520681	1.889596	0.842342
H	-1.760781	2.630095	0.076213
H	-2.375384	1.812420	1.519138
H	-0.673402	2.258814	1.421546
0 imaginary frequencies			
ZPE			0.264695
E			-693.821470
H 298.15 K			-693.540491
G 298.15 K, 1 mol L ⁻¹			-693.595479

20d-TS ($\Delta G^\ddagger = 14.9 \text{ kcal mol}^{-1}$)

C	-2.164432	-1.654631	-0.043074
C	-0.908135	-1.721399	0.534176
C	-1.655008	0.536861	0.491718
C	-2.602474	-0.296537	-0.100054
H	-2.708972	-2.483529	-0.476059
C	0.464162	-1.080880	-1.085504
H	0.097796	-1.871653	-1.720387
C	0.220790	0.282108	-1.246482
H	-0.509848	0.720925	-1.908908
H	-0.381828	-2.607244	0.859852
C	1.352556	1.052499	-0.689629
C	2.280923	0.203968	-0.165416
C	1.819213	-1.180420	-0.431170
O	2.432639	-2.213993	-0.196496
C	1.398893	2.539102	-0.734117
H	0.745976	2.967349	0.033004
H	2.407190	2.920965	-0.570015
H	1.035249	2.903668	-1.699464
C	3.547066	0.494429	0.561910
H	3.747143	1.565714	0.610310
H	3.501832	0.112299	1.587632
H	4.398917	0.004270	0.078228
C	-0.650889	-0.348749	1.116683
O	0.203847	-0.059175	1.941600
C	-3.862854	0.167477	-0.748419
H	-4.407756	0.863076	-0.102610
H	-3.639059	0.706772	-1.676814
H	-4.517784	-0.670667	-0.993339
C	-1.796415	1.993250	0.779071
H	-1.855476	2.586709	-0.137889
H	-2.712596	2.188955	1.348454
H	-0.953041	2.355261	1.369012

1 imaginary frequency

ZPE		0.259022	
E		-693.759146	
H 298.15 K		-693.482655	
G 298.15 K, 1 mol L ⁻¹		-693.540803	

21d ($\Delta G = -21.9 \text{ kcal mol}^{-1}$)

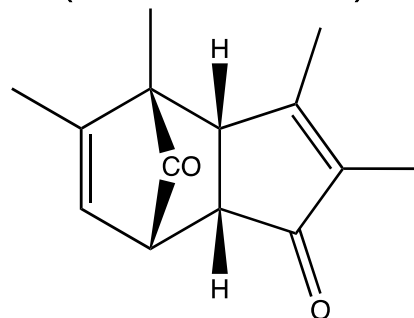
C	-0.606152	0.799439	1.546315
C	-0.684744	1.711688	0.341586
C	-1.475478	-0.387067	-0.265519
C	-1.050973	-0.425274	1.206378
H	-0.210310	1.095544	2.509590
C	0.356051	1.216328	-0.736521
C	-0.173517	-0.185965	-1.132426
H	-0.697595	2.782912	0.519149
C	2.078494	-0.342256	-0.240432
C	1.745310	0.971205	-0.213812
C	3.340756	-1.006118	0.202487
H	3.134736	-1.722658	1.004560
H	3.789502	-1.571489	-0.620537
H	4.075232	-0.287397	0.566726
C	-1.940113	1.086367	-0.276693
O	-2.975938	1.573212	-0.656270
C	-1.110302	-1.656231	2.043022
H	-0.495164	-2.452265	1.610339
H	-0.753607	-1.453592	3.055564
H	-2.132561	-2.043230	2.107164
C	-2.448309	-1.432792	-0.757833
H	-2.008140	-2.430956	-0.707431
H	-3.360602	-1.430448	-0.155486
H	-2.724668	-1.237152	-1.797133
C	0.966287	-1.125907	-0.788292
O	0.951632	-2.345143	-0.944349
C	2.562937	2.110359	0.279857
H	2.074479	2.572762	1.145590
H	3.570412	1.812884	0.570601
H	2.630624	2.886990	-0.489860
H	-0.426083	-0.270668	-2.191452
H	0.366713	1.921557	-1.571136

0 imaginary frequencies

ZPE		0.264618	
E		-693.825764	
H 298.15 K		-693.544905	
G 298.15 K, 1 mol L ⁻¹		-693.599510	

21d-TS ($\Delta G^\ddagger = 4.3 \text{ kcal mol}^{-1}$)

C	-0.257031	0.657741	1.696686
C	-0.863356	1.683620	0.999995
C	-1.544261	-0.399474	0.102066
C	-0.656091	-0.610943	1.187283
H	0.458444	0.779537	2.499570
C	0.384024	1.308608	-1.174883
C	-0.227073	0.091347	-1.522349
H	-0.775860	2.744279	1.183815
C	1.748155	-0.323756	-0.280208
C	1.584579	1.040095	-0.426502
C	2.838331	-1.050379	0.425199
H	2.503105	-2.038424	0.748466
H	3.701120	-1.203031	-0.235268
H	3.188032	-0.494957	1.298468
C	-1.877517	1.078231	0.120916
O	-2.816495	1.616839	-0.454446
C	-0.311619	-1.935578	1.776314
H	-0.011852	-2.653011	1.006922
H	0.493614	-1.844451	2.507034
H	-1.184956	-2.362831	2.283710
C	-2.461186	-1.429039	-0.467611
H	-1.908548	-2.313610	-0.792531
H	-3.181435	-1.750527	0.293372
H	-3.019511	-1.031446	-1.316847
C	0.731416	-0.988580	-1.113965
O	0.687544	-2.176563	-1.430702
C	2.485677	2.094959	0.120297
H	2.012732	3.077573	0.086229
H	2.772072	1.875694	1.152112
H	3.411078	2.142579	-0.464893
H	-0.958065	-0.038743	-2.307892
H	0.087338	2.288057	-1.520512
1 imaginary frequency			
ZPE			0.259600
E			-693.777962
H 298.15 K			-693.501239
G 298.15 K, 1 mol L ⁻¹			-693.557781

22d ($\Delta G = -21.5 \text{ kcal mol}^{-1}$)

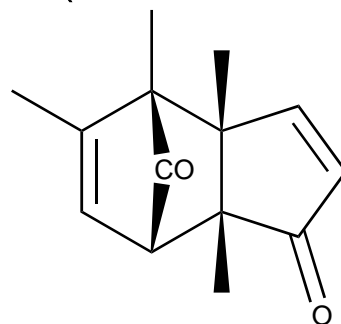
C	0.714671	-0.940238	1.497244
C	0.874262	-1.741089	0.219601
C	1.388610	0.482427	-0.223875
C	1.003816	0.351650	1.250830
H	0.386693	-1.359791	2.439865
C	-0.238970	-1.297320	-0.788357
C	0.092825	0.187943	-1.091630
H	1.022367	-2.812701	0.312488
C	-2.107504	0.131988	-0.195221
C	-3.464548	0.480539	0.321651
H	-3.678545	1.545377	0.227039
H	-4.238422	-0.077369	-0.215243
H	-3.551988	0.207105	1.378454
C	2.028517	-0.916648	-0.362975
O	3.107496	-1.239867	-0.793243
C	0.946801	1.504706	2.192142
H	0.219622	2.251012	1.856604
H	0.662729	1.172324	3.193319
H	1.915465	2.010980	2.257528
C	2.231013	1.663895	-0.647247
H	1.711201	2.607829	-0.474118
H	3.171144	1.688310	-0.089615
H	2.469515	1.599739	-1.712032
C	-1.150537	0.944919	-0.707748
H	0.346421	0.362942	-2.140638
H	-0.226929	-1.929172	-1.678592
C	-1.634803	-1.254848	-0.195217
O	-2.259757	-2.231696	0.212874
C	-1.232531	2.417060	-0.907362
H	-2.242889	2.801295	-0.766112
H	-0.570012	2.933268	-0.204803
H	-0.888013	2.681442	-1.912216
0 imaginary frequencies			
ZPE			0.264809
E			-693.825337
H 298.15 K			-693.544347
G 298.15 K, 1 mol L ⁻¹			-693.598756

22d-TS ($\Delta G^\ddagger = 3.2 \text{ kcal mol}^{-1}$)

C	-0.114525	-0.404316	-1.577421
C	-0.546817	-1.559198	-0.917916
C	-1.804278	0.309851	-0.177062
C	-0.880848	0.722933	-1.123285
H	0.638476	-0.356849	-2.350740
C	0.546717	-1.559222	0.917922
C	0.114525	-0.404321	1.577459
H	-0.340011	-2.576282	-1.219919
C	1.804263	0.309748	0.177038
C	2.824805	1.124663	-0.538356
H	3.753114	1.187615	0.043431
H	3.078114	0.676754	-1.502002
H	2.474819	2.144477	-0.708789
C	-1.782858	-1.166393	-0.155144
O	-2.611424	-1.919401	0.349168
C	-0.684531	2.114618	-1.620331
H	0.343015	2.273100	-1.952223
H	-1.341629	2.299695	-2.478291
H	-0.931869	2.854774	-0.857714
C	-2.824811	1.124771	0.538344
H	-2.474854	2.144594	0.708766
H	-3.753138	1.187688	-0.043418
H	-3.078089	0.676861	1.501998
C	0.880895	0.722877	1.123310
H	-0.638476	-0.356809	2.350776
H	0.339859	-2.576296	1.219920
C	1.782776	-1.166488	0.155126
O	2.611301	-1.919547	-0.349176
C	0.684740	2.114593	1.620338
H	0.931011	2.854665	0.857288
H	-0.342469	2.272859	1.953360
H	1.342792	2.300037	2.477486

1 imaginary frequency

ZPE		0.259427
E		-693.778481
H 298.15 K		-693.501685
G 298.15 K, 1 mol L ⁻¹		-693.559522

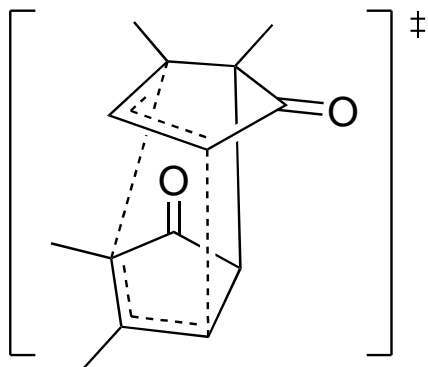
18d ($\Delta G = -12.2 \text{ kcal mol}^{-1}$)

C	0.551554	-0.919813	-1.655140
C	1.646982	-1.456943	-1.097093
C	1.120675	0.535115	0.196569
C	0.073275	0.328258	-0.972852
H	0.035776	-1.318934	-2.521736
C	-0.306490	-0.992731	1.603297
C	0.244191	0.414095	1.498347
H	2.169132	-2.349671	-1.417497
C	-1.312578	0.103803	-0.193775
C	-1.198640	-1.188632	0.616048
C	-2.587766	0.307739	-0.981212
H	-2.657501	1.324873	-1.368928
H	-3.457066	0.134959	-0.341777
H	-2.646306	-0.384503	-1.824711
C	2.069219	-0.659351	0.055243
O	3.021173	-0.884781	0.793392
C	-0.035336	1.484411	-1.970693
H	-0.398010	2.395918	-1.490460
H	-0.724727	1.225739	-2.776912
H	0.936873	1.696421	-2.419118
C	1.906001	1.845283	0.187414
H	1.239670	2.703890	0.295774
H	2.476125	1.966288	-0.735844
H	2.608374	1.851415	1.024200
C	-1.035432	1.072034	0.972198
O	-1.648789	2.041278	1.344117
C	-1.944600	-2.431966	0.276695
H	-1.700908	-3.233263	0.978009
H	-1.696829	-2.770499	-0.735442
H	-3.026640	-2.267372	0.300716
H	0.698991	0.844519	2.386210
H	0.017649	-1.719572	2.337167

0 imaginary frequencies

ZPE		0.264956
E		-693.812424
H 298.15 K		-693.531840
G 298.15 K, 1 mol L ⁻¹		-693.583987

18d-to-21d-TS (Cope rearrangement, $\Delta G^\ddagger = 0.5 \text{ kcal mol}^{-1}$)



C	0.340028	-0.590792	-1.769531
C	1.099265	-1.575759	-1.171063
C	1.319726	0.417299	0.126424
C	0.420326	0.631470	-1.069818
H	-0.265433	-0.727366	-2.657366
C	-0.247679	-1.236327	1.266825
C	0.346444	0.121377	1.397787
H	1.196257	-2.603037	-1.495670
C	-1.672987	0.187960	0.185640
C	-1.416086	-1.166790	0.541229
C	-2.840664	0.695092	-0.581862
H	-3.750144	0.644655	0.030543
H	-3.019037	0.098204	-1.479286
H	-2.699120	1.737961	-0.869992
C	1.923128	-0.972850	-0.136693
O	2.889517	-1.449475	0.454484
C	0.115068	1.960580	-1.668443
H	-0.255679	2.678003	-0.932168
H	-0.614615	1.863973	-2.474677
H	1.031152	2.389262	-2.094130
C	2.311823	1.521424	0.443776
H	1.797264	2.441283	0.728271
H	2.942224	1.733253	-0.423578
H	2.955876	1.217887	1.271812
C	-0.833854	1.022444	1.045234
O	-0.983907	2.201640	1.345104
C	-2.240456	-2.321788	0.080767
H	-1.884241	-3.257078	0.515989
H	-2.193927	-2.410218	-1.010141
H	-3.293480	-2.188141	0.346688
H	0.883055	0.339469	2.318066
H	0.180470	-2.135474	1.687307
1 imaginary frequency			
ZPE			0.261989
E			-693.788724
H 298.15 K			-693.510799
G 298.15 K, 1 mol L ⁻¹			-693.563743