

Scalable Synthesis of Highly Reactive 1,3-Diaminodienes from Vinamidinium Salts and Their Use in Diels-Alder Reactions

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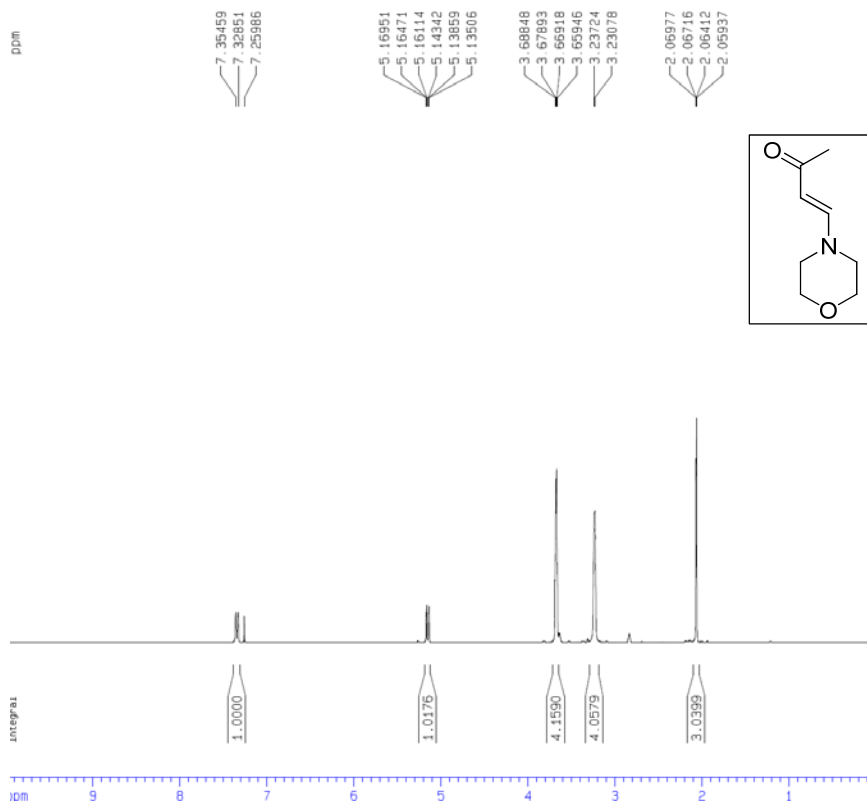
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Copies of NMR Spectra

(3E)-4-morpholinyl-3-buten-2-one (11a)



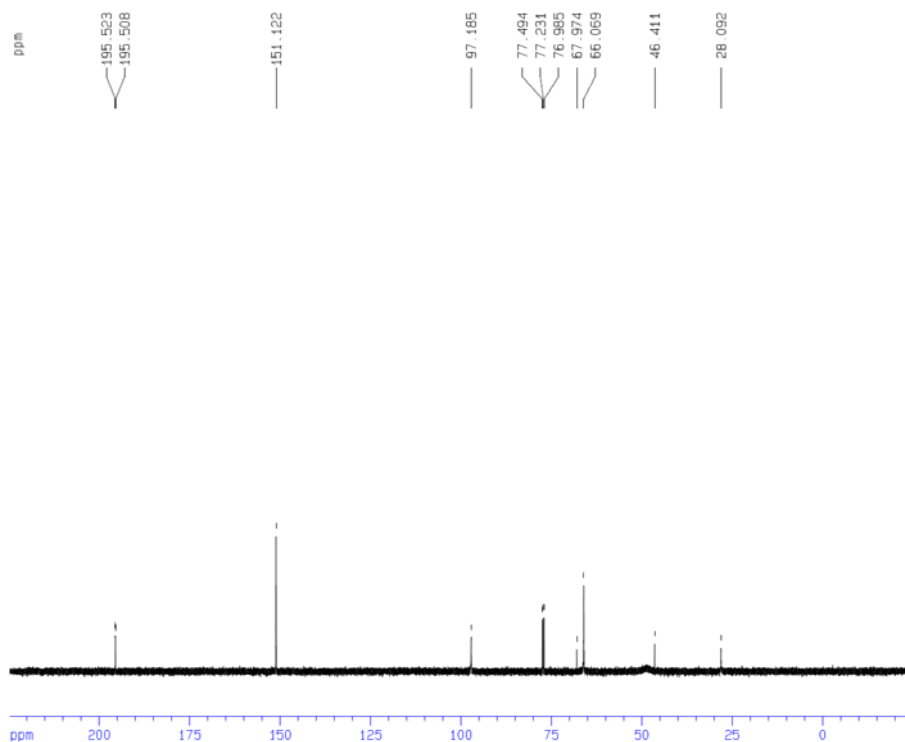
Current Data Parameters
NAME SZ-3-167-3 Nov 17th
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20111117
Time 15.27
INSTRUM spect
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PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 8
DS 2
SWH 6006.006 Hz
FIDRES 0.183289 Hz
AQ 2.7279861 sec
RG 64
DN 83.250 usec
DE 6.00 usec
TE 298.0 K
D1 1.00000000 sec
MDRES 0.00000000 sec
MCNRK 0.01500000 sec

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NUC1 1H
P1 10.00 usec
PL1 0.50 dB
SFO1 500.3325017 MHz

F2 - Processing parameters
SI 32768
SF 500.3300121 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 20.00 cm
CY 5.00 cm
F1P 10.000 ppm
F1 5003.30 Hz
F2P 0.000 ppm
F2 0.00 Hz
PPMCH 0.50000 ppm/cm
HZCM 250.16501 Hz/cm



Current Data Parameters
NAME SZ-3-167-2 Nov 18
EXPNO 3
PROCNO 1

F2 - Acquisition Parameters
Date_ 20111118
Time 20.27
INSTRUM spect
PROBHD 5 mm TXI 13C-2
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 483
DS 4
SWH 31446.541 Hz
FIDRES 0.479036 Hz
AQ 1.6405724 sec
RG 16384
DN 15.000 usec
DE 6.00 usec
TE 298.0 K
D1 0.00000000 sec
d13 0.03000000 sec
MDRES 0.00000000 sec
MCNRK 0.01000000 sec

===== CHANNEL f1 =====
NUC1 13C
P1 15.00 usec
PL1 -2.50 dB
SFO1 125.7703194 MHz

===== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 0.00 dB
PLA12 21.16 dB
SFO2 500.1300000 MHz

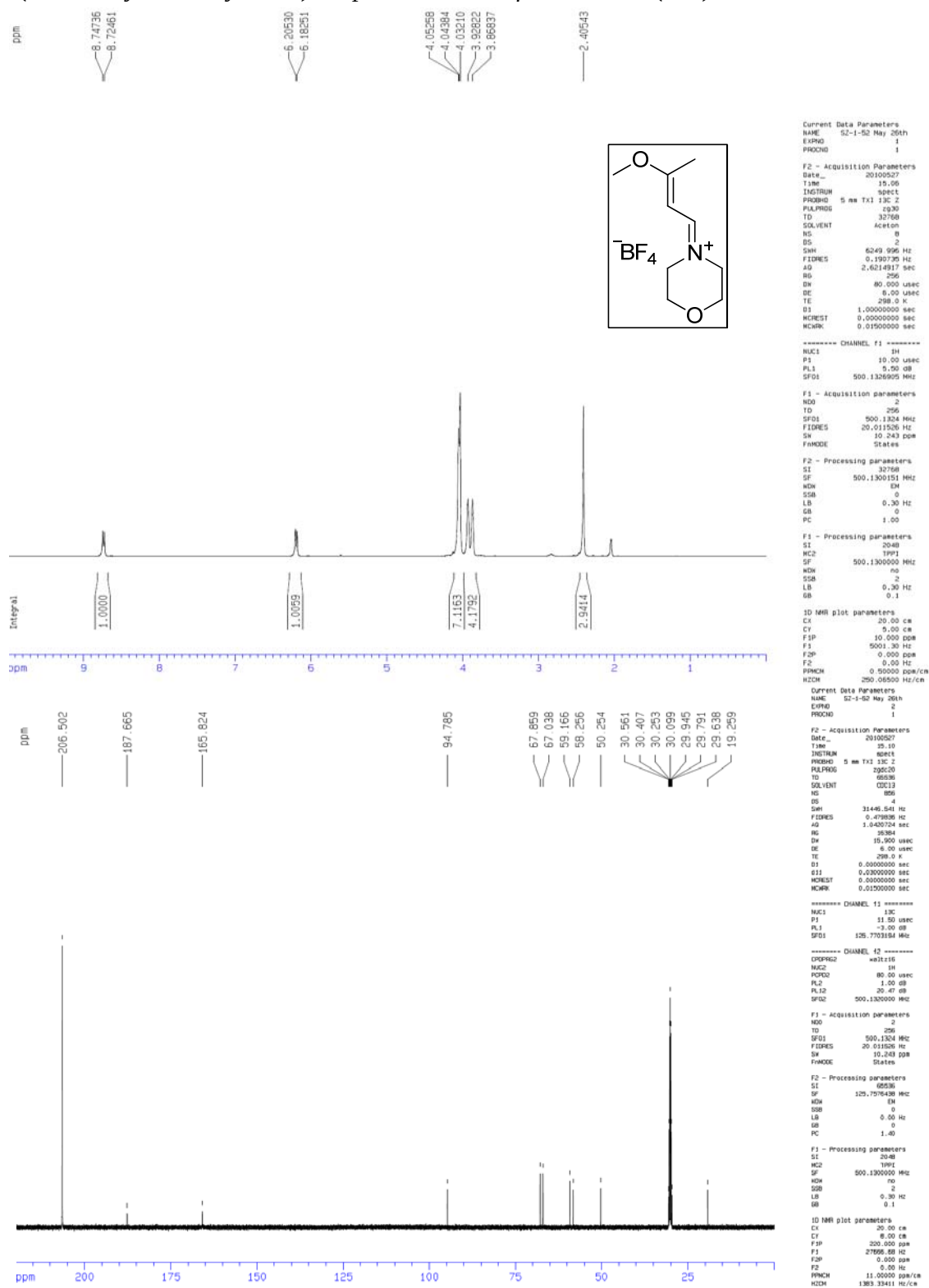
F1 - Acquisition parameters
MD 2
TD 256
SFO1 500.1300000 MHz
FIDRES 20.011026 Hz
SR 10.243 ppm
FROCK 32.4164

F2 - Processing parameters
SI 65536
SF 125.7677019 MHz
WDW EM
SSB 0
LB 0.00 Hz
GB 0
PC 1.40

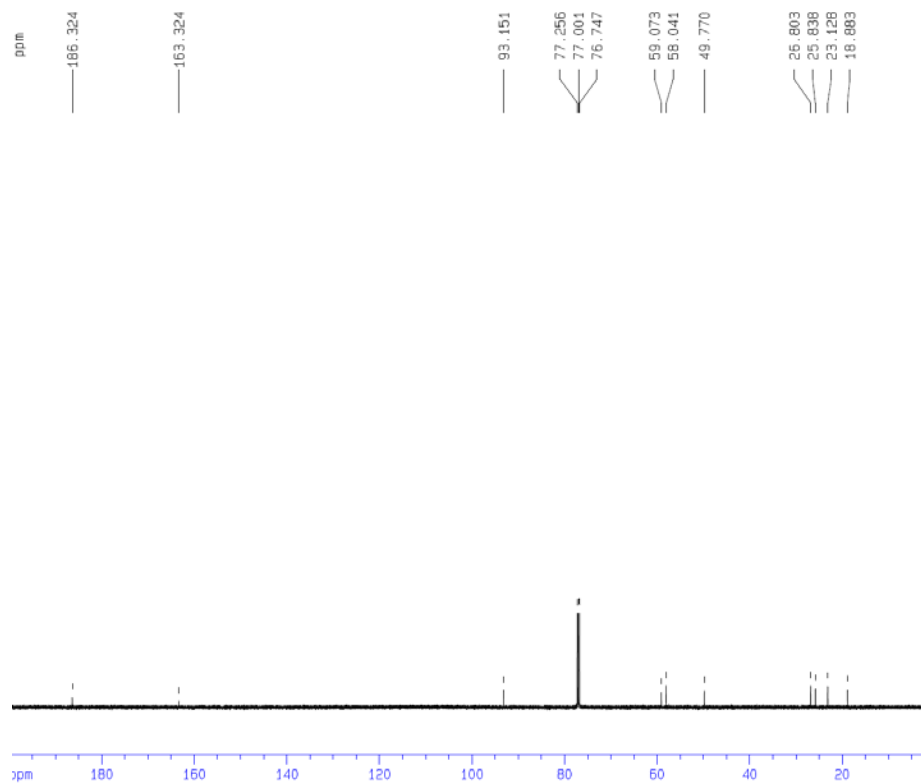
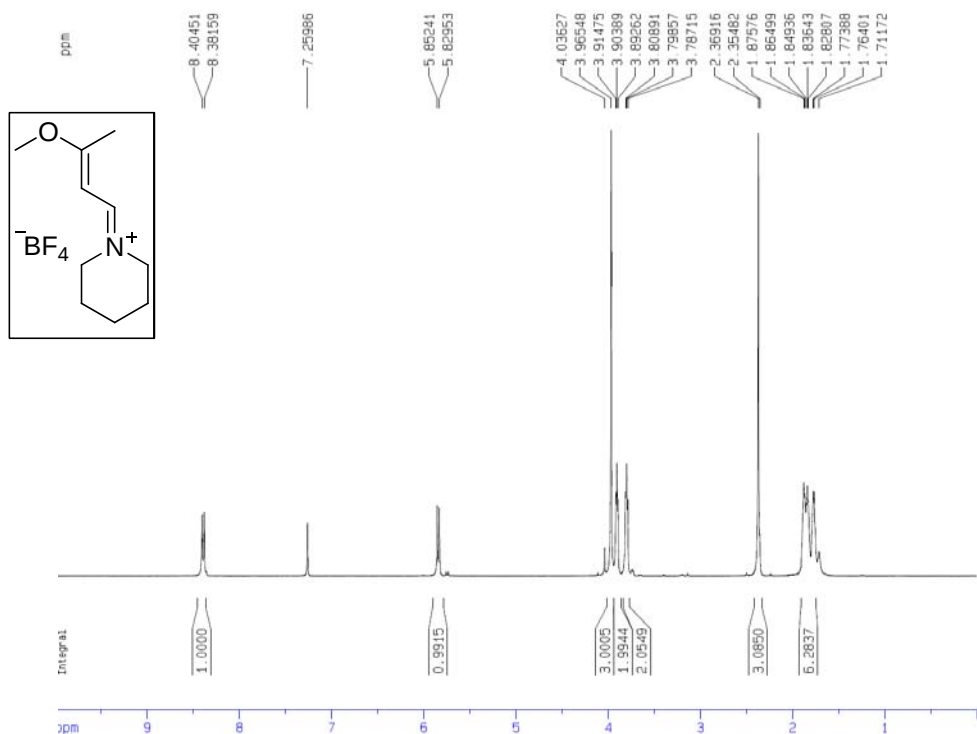
F1 - Processing parameters
SI 256
NUC2 13C
SF 500.1300000 MHz
WDW NO
SSB 2
LB 0.30 Hz
GB 0.1

1D NMR plot parameters
CX 20.00 cm
CY 3.00 cm
F1P 505.157 ppm
F1 25015.38 Hz
F2P -24.799 ppm
F2 -3118.89 Hz
PPMCH 121.45782 ppm/cm
HZCM 1571.89885 Hz/cm

(Z)-1-(3-methoxybut-2-enylidene)morpholinium tetrafluoroborate (**12a**)



(Z)-1-(3-methoxybut-2-enylidene)piperidinium tetrafluoroborate (**12b**)



Current Data Parameters
NAME S2-2-28 Aug 14th
EXPNO 3
PROCNO 1

F2 - Acquisition Parameters
Date_ 20110830
Time 10.23
INSTRUM spect
PROBHD 5 mm Txi 13C Z
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 8
DS 2
SWH 6009.615 Hz
FIDRES 0.182399 Hz
AQ 2.7263477 sec
RG 256
DA 83.290 usec
DE 6.00 usec
TE 298.0 K
D1 1.00000000 sec
HOREST 0.00000000 sec
HOREK 0.01500000 sec

===== CHANNEL f1 =====
NUC1 13C
P1 11.50 usec
PL1 5.50 dB
SFO1 500.132606 MHz

F1 - Acquisition parameters
ND0 2
TD 256
SFO1 500.1324 MHz
FIDRES 20.011526 Hz
SN 10.243 dB
FwMODE States

F2 - Processing parameters
SI 32768
SF 500.130136 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 1.00

F1 - Processing parameters
SI 2048
HC2 TPP1
SF 500.130000 MHz
WDW GC34
SSB 2
LB 0.30 Hz
GB 0.1

1D NMR plot parameters
CX 20.00 cm
CY 10.00 cm
FJP 10.000 ppm
F1 5001.30 Hz
F2P 0.000 ppm
F2 0.00 Hz
PPHCH 0.50000 ppm/cm
H2CH 200.00000 Hz/cm

Current Data Parameters
NAME S2-2-28 Aug 14th
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20130814
Time 09.05
INSTRUM spect
PROBHD 5 mm Txi 13C Z
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1884
DS 4
SWH 31446.541 Hz
FIDRES 0.478936 Hz
AQ 1.0403734 sec
RG 30384
DA 15.900 usec
DE 6.00 usec
TE 298.0 K
D1 0.00000000 sec
HOREST 0.00000000 sec
HOREK 0.01500000 sec

===== CHANNEL f1 =====
NUC1 13C
P1 11.50 usec
PL1 -3.00 dB
SFO1 125.7703184 MHz

===== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 1.00 dB
PL12 20.47 dB
SFO2 500.132000 MHz

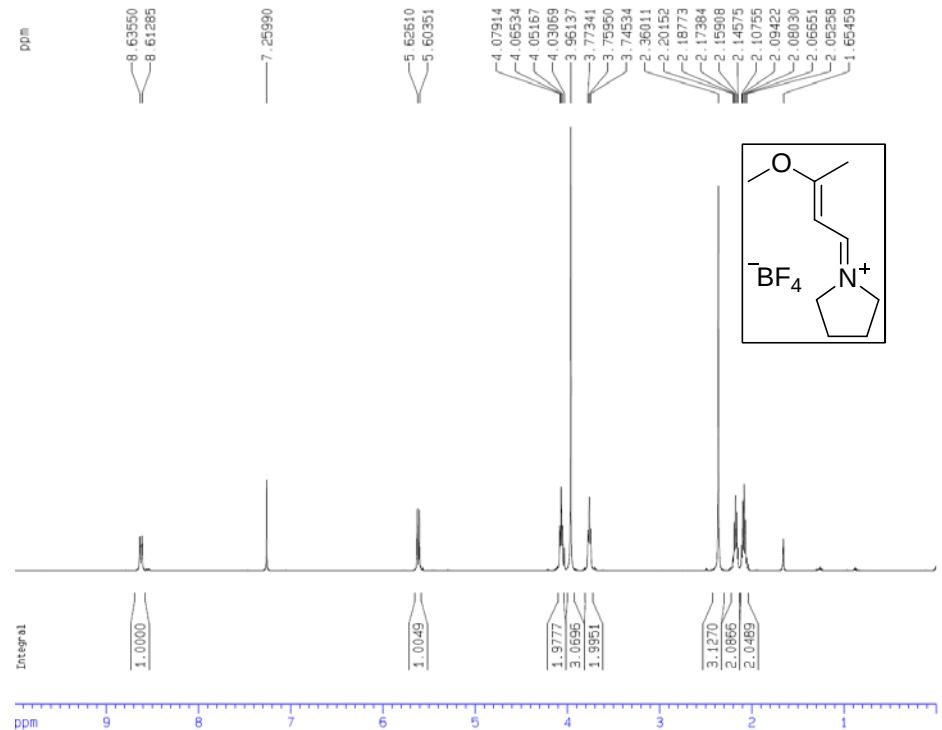
F1 - Acquisition parameters
ND0 2
TD 256
SFO1 500.1324 MHz
FIDRES 20.011526 Hz
SN 10.243 dB
FwMODE States

F2 - Processing parameters
SI 65536
SF 125.7577911 MHz
WDW EM
SSB 0
LB 0.00 Hz
GB 0
PC 1.40

F1 - Processing parameters
SI 2048
HC2 TPP1
SF 500.130000 MHz
WDW EM
SSB 2
LB 0.30 Hz
GB 0.1

1D NMR plot parameters
CX 20.00 cm
CY 2.00 cm
FJP 200.000 ppm
F1 2501.30 Hz
F2P 0.000 Hz
F2 62.88 Hz
PPHCH 9.37500 ppm/cm
H2CH 125.43408 Hz/cm

(Z)-1-(3-methoxybut-2-enylidene)pyrrolidinium tetrafluoroborate (**12c**)



Current Data Parameters
NAME S2-2-144 Aug 14th
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20110814
Time 14.21
INSTRUM spect
PROBHD 5 mm T1 13C Z
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 8
DS 2
SWH 6009.615 Hz
FIDRES 0.183399 Hz
AQ 2.7263477 sec
RG 256
OW 83.200 usec
DE 6.00 usec
TE 298.0 K
D1 1.00000000 sec
MCREST 0.00000000 sec
MCWK 0.01500000 sec

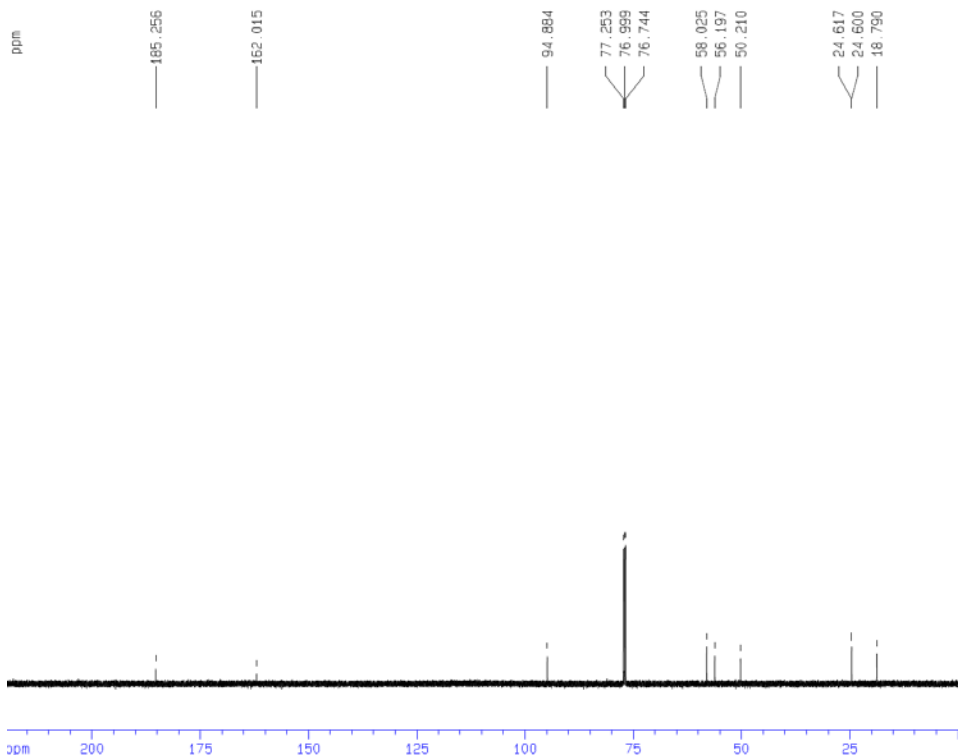
===== CHANNEL f1 =====
NUC1 1H
P1 11.00 usec
PL1 5.50 dB
SFO1 500.132000 MHz

F1 - Acquisition Parameters
NUC2 13C
TD 256
SFO1 500.1324 MHz
FIDRES 20.011526 Hz
SQ 10.243 dB
FNAME States

F2 - Processing parameters
SI 32768
SF 500.1300136 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 1.00

F1 - Processing parameters
SI 2048
MC2 TPPI
SF 500.1300000 MHz
WDW GSI
SSB 0
LB 0.30 Hz
GB 0.1

1D NMR plot parameters
CX 20.00 cm
CY 10.00 cm
F1P 10.000 ppm
F1 5001.30 Hz
F2P 0.000 ppm
F2 0.00 Hz
PRCHN 0.00000 ppm/cm
HZCH 250.06500 Hz/cm



Current Data Parameters
NAME S2-2-144 Aug 14th
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20110814
Time 14.24
INSTRUM spect
PROBHD 5 mm T1 13C Z
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 4
SWH 31446.541 Hz
FIDRES 0.470886 Hz
AQ 1.0400724 sec
RG 16384
OW 15.900 usec
DE 6.00 usec
TE 298.0 K
D1 0.00000000 sec
D11 0.00000000 sec
MCREST 0.00000000 sec
MCWK 0.01500000 sec

===== CHANNEL f1 =====
NUC1 13C
P1 11.00 usec
PL1 -3.00 dB
SFO1 125.7703194 MHz

===== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 0.00 dB
PL32 21.16 dB
SFO2 500.1320000 MHz

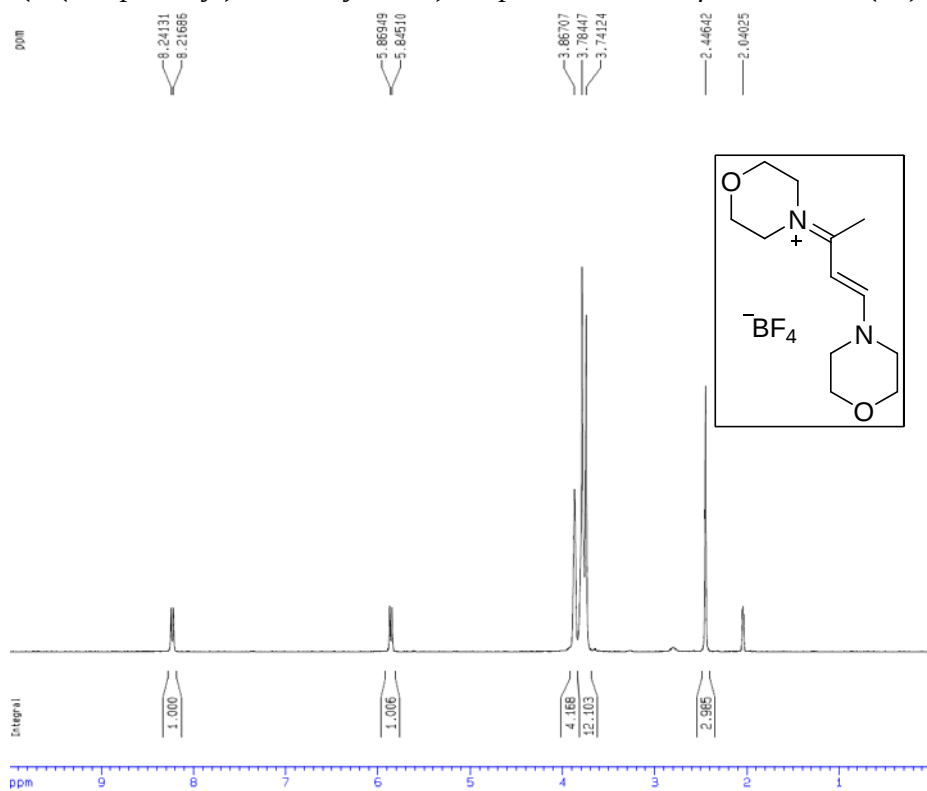
F1 - Acquisition Parameters
NUC2 13C
TD 256
SFO1 500.1324 MHz
FIDRES 20.011526 Hz
SQ 10.243 dB
FNAME States

F2 - Processing parameters
SI 65536
SF 125.7577920 MHz
WDW EM
SSB 0
LB 0.00 Hz
GB 0
PC 1.40

F1 - Processing parameters
SI 2048
MC2 TPPI
SF 500.1300000 MHz
WDW NO
SSB 0
LB 0.30 Hz
GB 0.1

1D NMR plot parameters
CX 20.00 cm
CY 10.00 cm
F1P 200.000 ppm
F1 27886.71 Hz
F2P 0.000 ppm
F2 0.00 Hz
PRCHN 11.00000 ppm/cm
HZCH 1369.39569 Hz/cm

(Z)-1-(3-(morpholinyl)but-2-enylidene)morpholinium tetrafluoroborate (**4a**)



Current Data Parameters
NAME: 52-1-54 Jan 15h
EXPNO: 2
PROCNO: 1

F2 - Acquisition Parameters
Date_: 20100801
Time: 15.15
INSTRUM: spect
PROBHD: 5 mm TXI 13C Z
PULPROG: zg30
TD: 32768
SOLVENT: acetone
NS: 8
DS: 2
SWH: 5249.996 Hz
FIDRES: 0.190795 Hz
AQ: 2.6214917 sec
RG: 256
DA: 60.000 usec
DE: 6.00 usec
TE: 298.0 K
D1: 0.0000000 sec
MCHST: 0.0000000 sec
MCHW: 0.0000000 sec

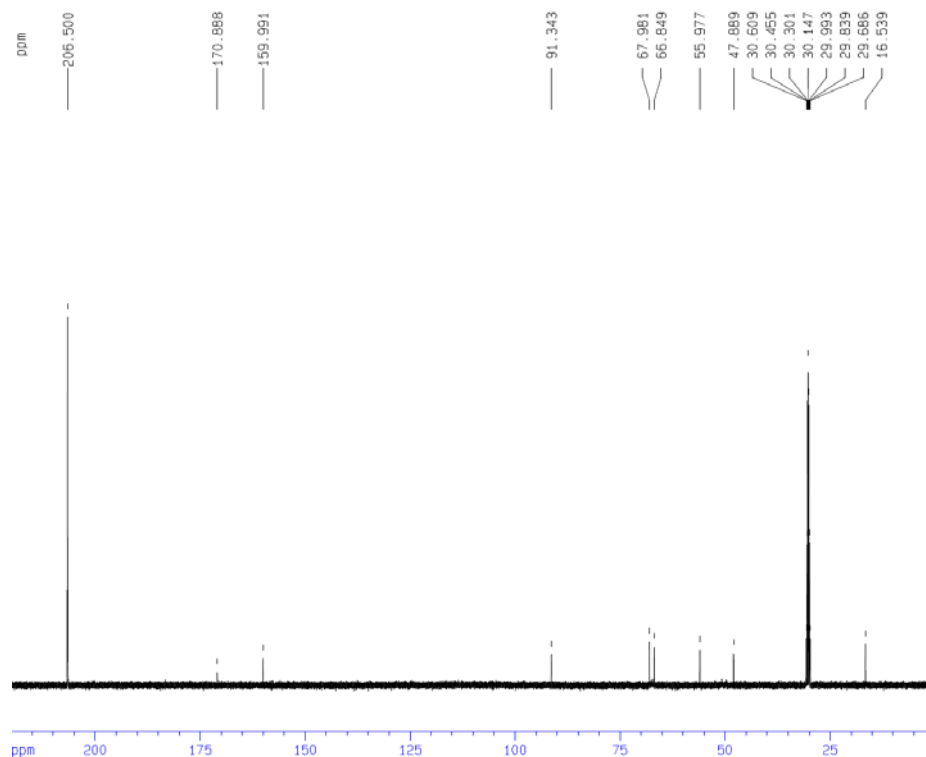
===== CHANNEL f1 =====
NUC1: 13C
P1: 10.00 usec
PL1: 0.00 dB
SFO1: 500.130000 MHz

F1 - Acquisition parameters
ND0: 2
TD: 256
SFO1: 500.1304 MHz
FIDRES: 20.011526 Hz
SW: 10.243 ppm
FWDDE: Status

F2 - Processing parameters
SI: 32768
SF: 500.1300147 MHz
WDW: EM
SSB: 0
LB: 0.30 Hz
GB: 0
PC: 1.00

F1 - Processing parameters
SI: 256
HC2: 1991
SF: 500.1300000 MHz
WDW: EM
SSB: 2
LB: 0.30 Hz
GB: 0.1

1D 1H NMR plot parameters
CX: 20.00 cm
CY: 19.00 cm
F1P: 10.000 ppm
F1: 50001.30 Hz
F2P: 0.000 ppm
F2: 0.00 Hz
PRNCH: 0.00000 ppm/cm
H2CH: 298.00000 Hz/cm



Current Data Parameters
NAME: 52-1-54 Jan 15h
EXPNO: 3
PROCNO: 1

F2 - Acquisition Parameters
Date_: 20100801
Time: 21.18
INSTRUM: spect
PROBHD: 5 mm TXI 13C Z
PULPROG: zgpg30
TD: 65536
SOLVENT: CDCl3
NS: 708
DS: 4
SWH: 31446.581 Hz
FIDRES: 0.478856 Hz
AQ: 1.0420724 sec
RG: 2884
DA: 15.990 usec
DE: 6.00 usec
TE: 298.0 K
D1: 0.0000000 sec
D11: 0.0000000 sec
MCHST: 0.0000000 sec
MCHW: 0.0000000 sec

===== CHANNEL f1 =====
NUC1: 13C
P1: 11.50 usec
PL1: -3.00 dB
SFO1: 125.7702194 MHz

===== CHANNEL f2 =====
CPDPRG2: waltz16
NUC2: 1H
P2P2: 80.00 usec
PL2: 1.00 dB
PL12: 20.47 dB
SFO2: 500.130000 MHz

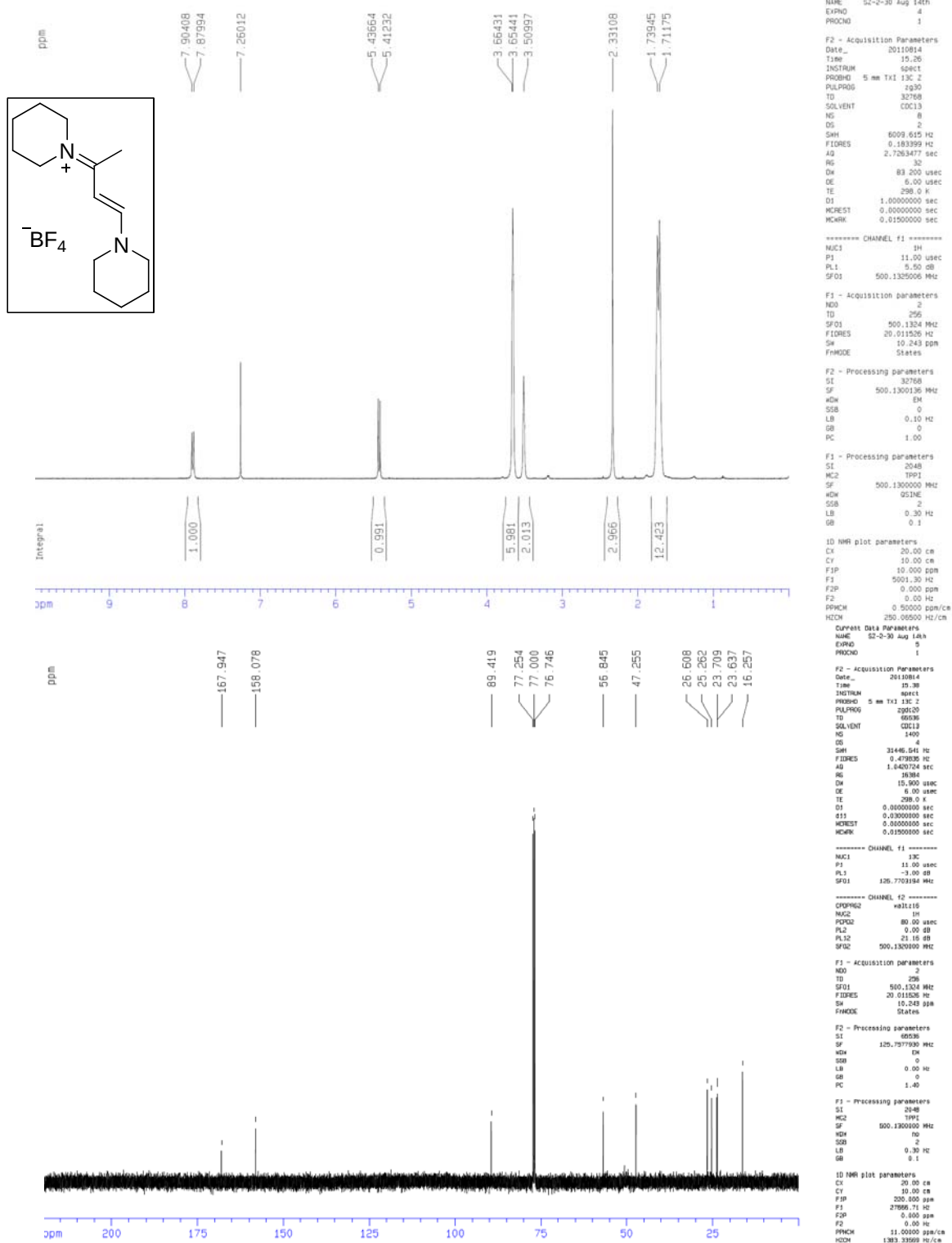
F1 - Acquisition parameters
ND0: 2
TD: 256
SFO1: 500.1304 MHz
FIDRES: 20.011526 Hz
SW: 10.243 ppm
FWDDE: Status

F2 - Processing parameters
SI: 65536
SF: 125.7576371 MHz
WDW: EM
SSB: 0
LB: 0.00 Hz
GB: 0
PC: 1.40

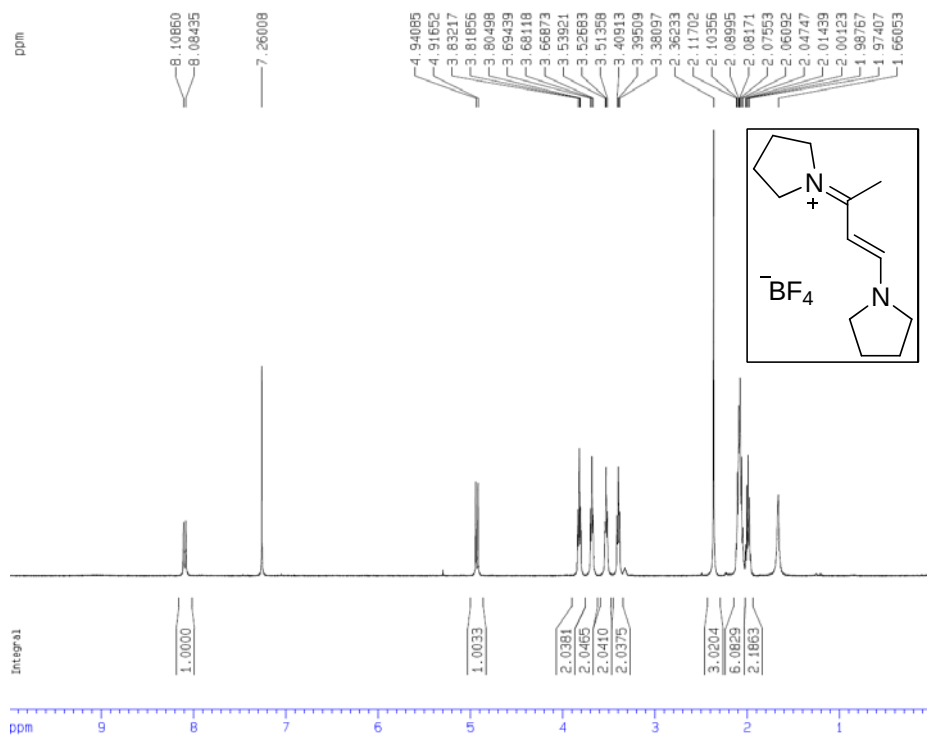
F1 - Processing parameters
SI: 256
HC2: 1991
SF: 500.1300000 MHz
WDW: EM
SSB: 2
LB: 0.30 Hz
GB: 0.1

1D 1H NMR plot parameters
CX: 20.00 cm
CY: 8.00 cm
F1P: 200.000 ppm
F1: 27896.88 Hz
F2P: 0.000 ppm
F2: 0.00 Hz
PRNCH: 11.00000 ppm/cm
H2CH: 1989.33988 Hz/cm

(Z)-1-(3-(piperidinyl)but-2-enylidene)piperidinium tetrafluoroborate (**4b**)



(Z)-1-(3-(pyrrolidiny)but-2-enylidene)pyrrolidinium tetrafluoroborate (**4c**)



Current Data Parameters
NAME 52-2-148 Aug 14th
EXPNO 3
PROCNO 1

F2 - Acquisition Parameters
Date_ 20110814
Time 15:29
INSTRUM spect
PROBHD 5 mm TXI 13C Z
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 8
DS 2
SH 6009.415 Hz
FIDRES 0.183399 Hz
AQ 2.7263477 sec
RG 256
DM 83.200 usec
DE 6.00 usec
TE 298.0 K
D1 1.00000000 sec
MCREST 0.00000000 sec
MCNFR 0.01500000 sec

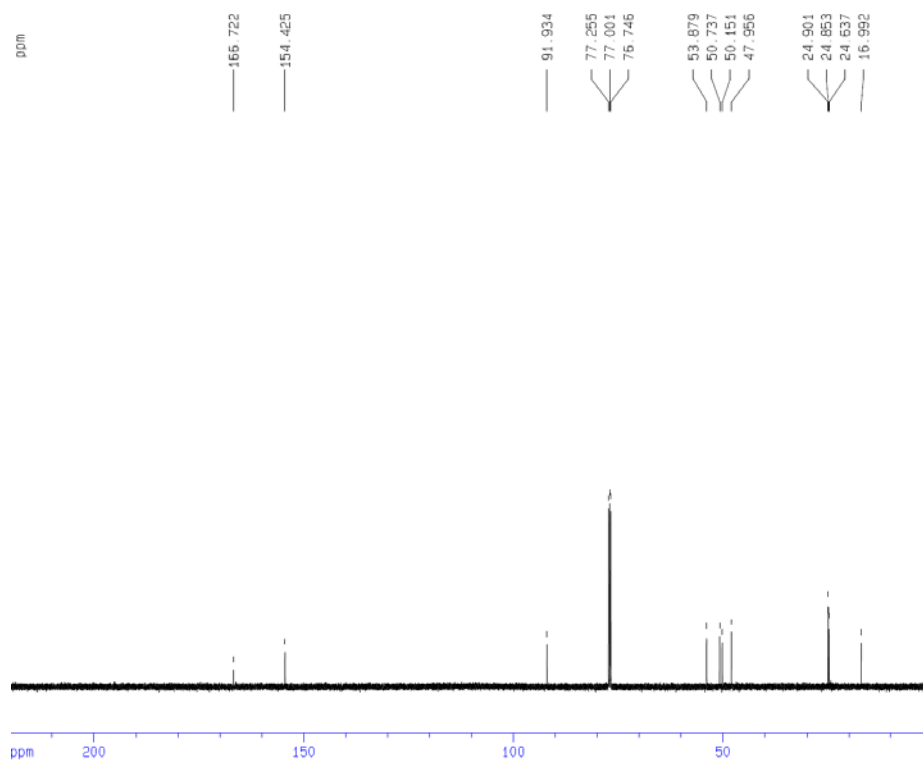
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NUC1 1H
P1 11.00 usec
PL1 0.00 dB
SFO1 500.1325006 MHz

F1 - Acquisition parameters
ND0 2
TD 256
SFO1 500.13024 MHz
FIDRES 20.011526 Hz
SN 10.243 ppm
FMODE States

F2 - Processing parameters
SI 32768
SF 500.1300135 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 1.00

F1 - Processing parameters
SI 2048
HC2 TPP1
SF 500.1300000 MHz
WDW none
SSB 2
LB 0.30 Hz
GB 0.1

1D NMR plot parameters
CX 20.00 cm
CY 10.00 cm
F1P 10.000 ppm
F1 5001.30 Hz
F2P 0.000 ppm
F2 0.00 Hz
PRNCH 0.50000 ppm/cm
HZCM 250.06500 Hz/cm



Current Data Parameters
NAME 52-2-148 Aug 14th
EXPNO 4
PROCNO 1

F2 - Acquisition Parameters
Date_ 20110814
Time 16:35
INSTRUM spect
PROBHD 5 mm TXI 13C Z
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1987
DS 4
SH 31446.541 Hz
FIDRES 0.478836 Hz
AQ 1.8480714 sec
RG 18384
DM 15.900 usec
DE 6.00 usec
TE 298.0 K
D1 0.00000000 sec
D11 0.00000000 sec
MCREST 0.00000000 sec
MCNFR 0.01500000 sec

===== CHANNEL f1 =====
NUC1 13C
P1 11.00 usec
PL1 -3.00 dB
SFO1 125.7703154 MHz

===== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 0.00 dB
PL12 21.16 dB
SFO2 500.1320000 MHz

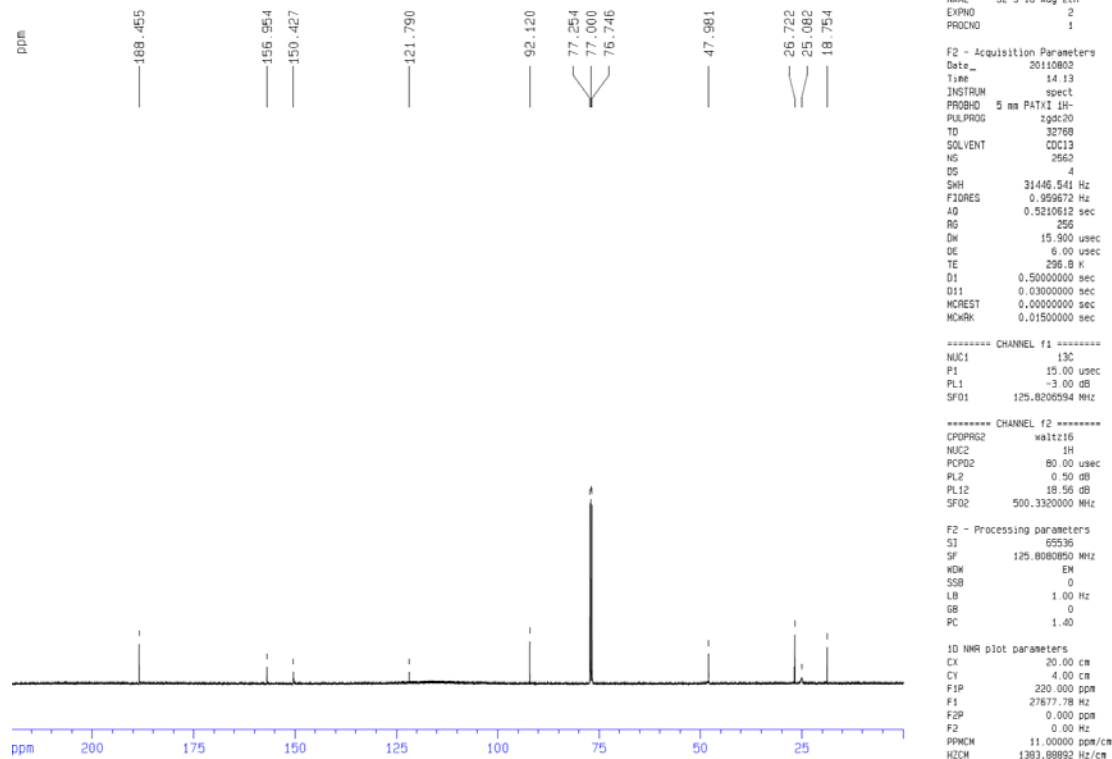
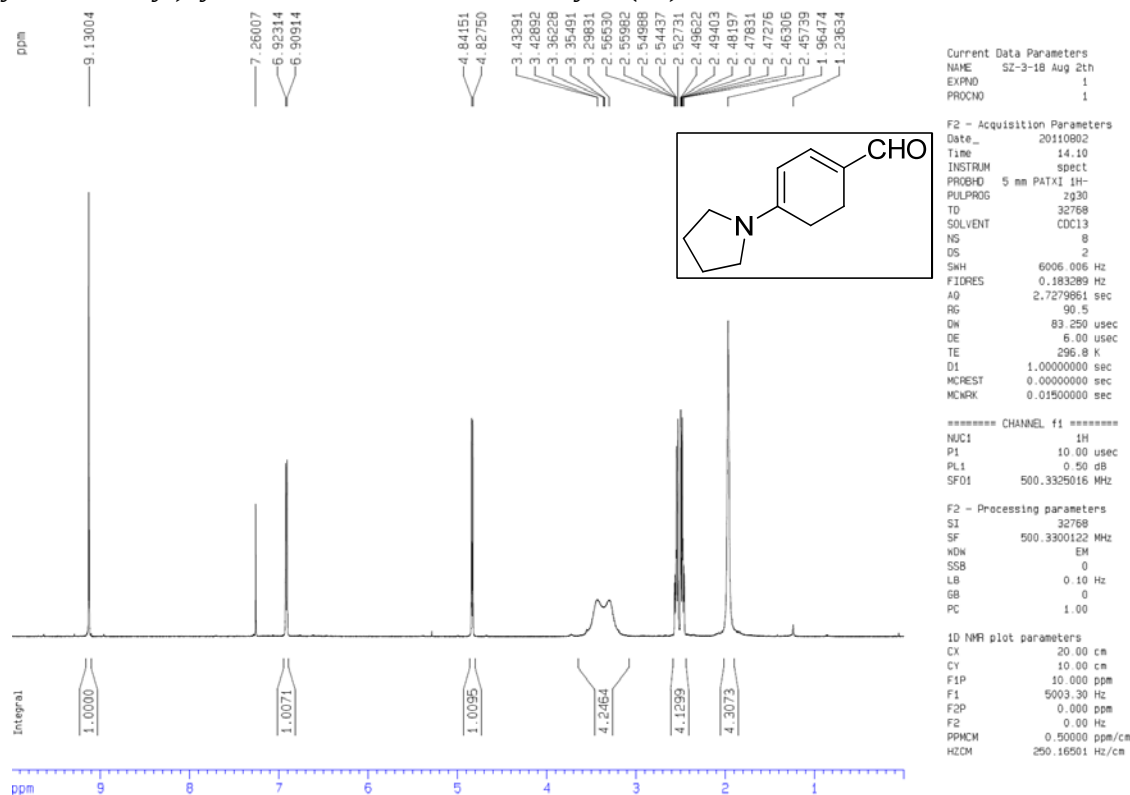
F1 - Acquisition parameters
ND0 2
TD 256
SFO1 500.13024 MHz
FIDRES 20.011526 Hz
SN 10.243 ppm
FMODE States

F2 - Processing parameters
SI 65536
SF 125.7577954 MHz
WDW EM
SSB 0
LB 0.00 Hz
GB 0
PC 1.40

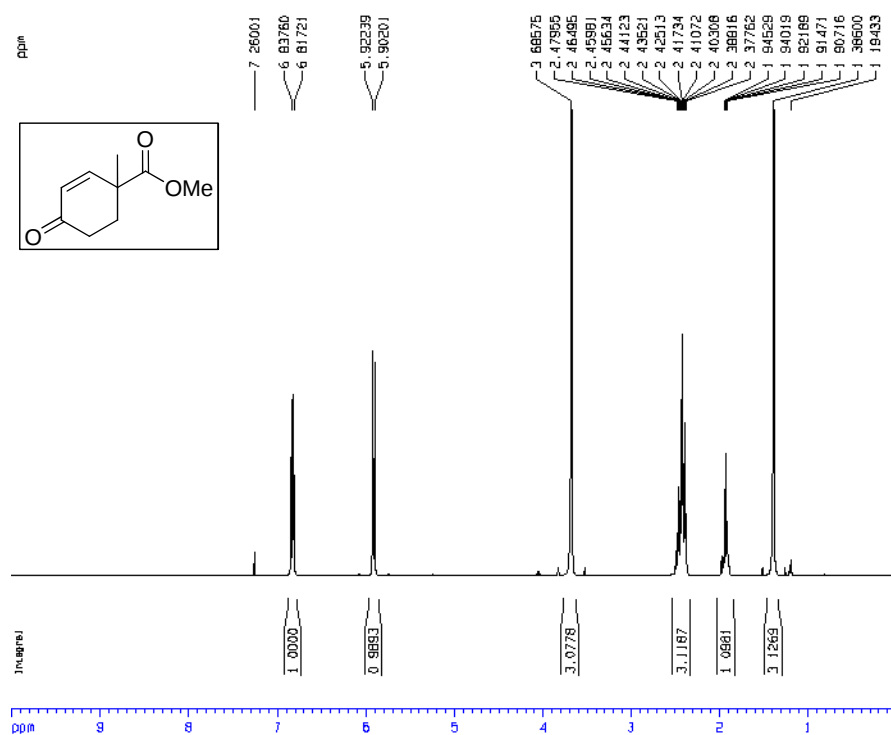
F1 - Processing parameters
SI 2048
HC2 TPP1
SF 500.1300000 MHz
WDW none
SSB 2
LB 0.30 Hz
GB 0.1

1D NMR plot parameters
CX 20.00 cm
CY 4.00 cm
F1P 220.000 ppm
F1 27088.11 Hz
F2P 0.000 ppm
F2 0.00 Hz
PRNCH 11.00000 ppm/cm
HZCM 1363.33989 Hz/cm

4-(pyrrolidin-1-yl)cyclohexa-1,3-dienecarbaldehyde (21)



Methyl 1-methyl-4-oxocyclohex-2-enecarboxylate (22)



Current Data Parameters
NAME: 52-3-166-1 Rev JB
EXPNO: 1
PROCNO: 1

F2 - Acquisition Parameters
Date_: 20111116
Time: 20.08
INSTRUM: spect
PROBHD: 5 mm TCI 13C Z
PULPROG: zgpg30
TD: 32768
SOLVENT: CDCl3
NS: 8
DS: 2
SWH: 6006.816 MHz
FIDRES: 0.183360 Hz
AQ: 2.7263477 sec
RG: 32
DN: 83.2800 usec
DE: 6.00 usec
TE: 298.0 K
D1: 1.00000000 sec
MRES1: 0.00000000 sec
MRES2: 0.01500000 sec

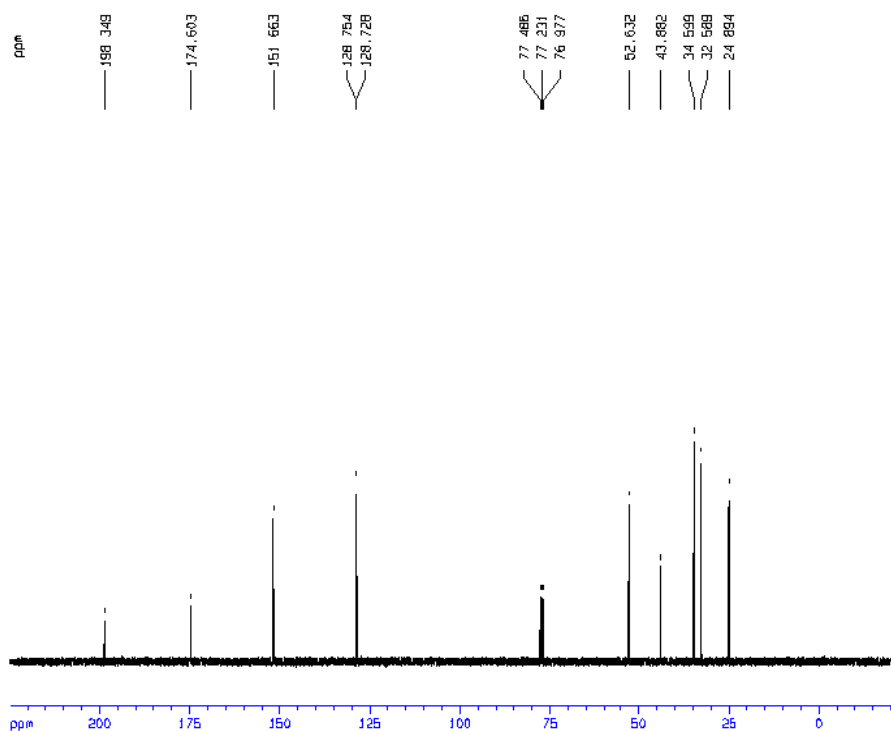
===== CHANNEL f1 =====
NUC1: 13C
P1: 11.00 usec
PL1: 0.00 dB
SFO1: 500.132000 MHz

F2 - Acquisition Parameters
Date_: 20111116
Time: 20.08
INSTRUM: spect
PROBHD: 5 mm TCI 13C Z
PULPROG: zgpg30
TD: 32768
SOLVENT: CDCl3
NS: 8
DS: 2
SWH: 6006.816 MHz
FIDRES: 0.183360 Hz
AQ: 2.7263477 sec
RG: 32
DN: 83.2800 usec
DE: 6.00 usec
TE: 298.0 K
D1: 1.00000000 sec
MRES1: 0.00000000 sec
MRES2: 0.01500000 sec

F2 - Processing parameters
SI: 32768
SF: 500.130000 MHz
WDW: EM
SSB: 0
LB: 0.10 Hz
GB: 0
PC: 1.00

F1 - Processing parameters
SI: 2048
SF: 500.130000 MHz
WDW: EM
SSB: 0
LB: 0.10 Hz
GB: 0
PC: 1.00

JD NMR plot parameters
CX: 20.00 cm
CY: 20.00 cm
F1P: 20.000000 cm
F2: 500.130000 MHz
F3P: 0.000000 cm
F4: 0.00 MHz
PPM0: 0.000000 ppm/ppm
HLEN: 280.000000 Hz/cm



Current Data Parameters
NAME: 52-3-166-1 Rev JB
EXPNO: 2
PROCNO: 1

F2 - Acquisition Parameters
Date_: 20111116
Time: 20.15
INSTRUM: spect
PROBHD: 5 mm TCI 13C Z
PULPROG: zgpg30
TD: 32768
SOLVENT: CDCl3
NS: 8
DS: 2
SWH: 21446.841 MHz
FIDRES: 0.402026 MHz
AQ: 1.0400724 sec
RG: 16384
DN: 10.5000 usec
DE: 6.00 usec
TE: 298.0 K
D1: 0.01000000 sec
D11: 0.01000000 sec
MRES1: 0.00000000 sec
MRES2: 0.01000000 sec

===== CHANNEL f1 =====
NUC1: 13C
P1: 11.00 usec
PL1: -3.00 dB
SFO1: 125.761154 MHz

===== CHANNEL f2 =====
NAME: 1H
NUC2: 1H
P2: 80.00 usec
PL2: 0.00 dB
PL12: 21.15 dB
SFO2: 500.130000 MHz

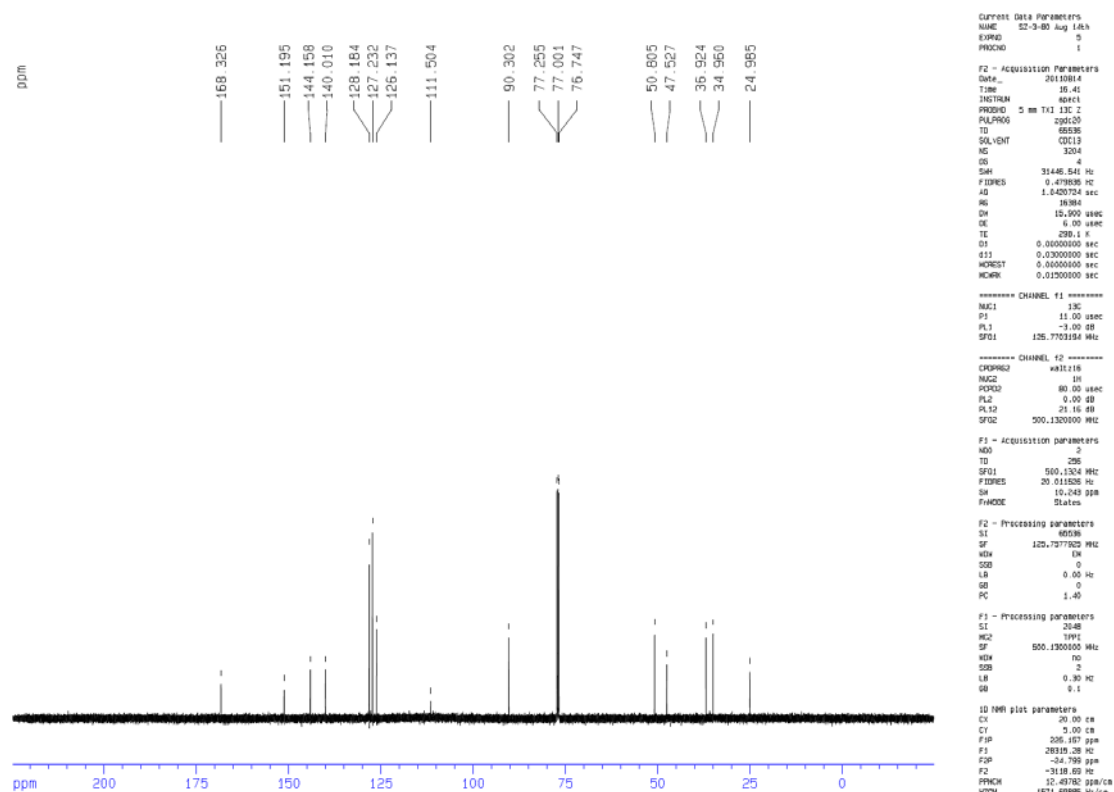
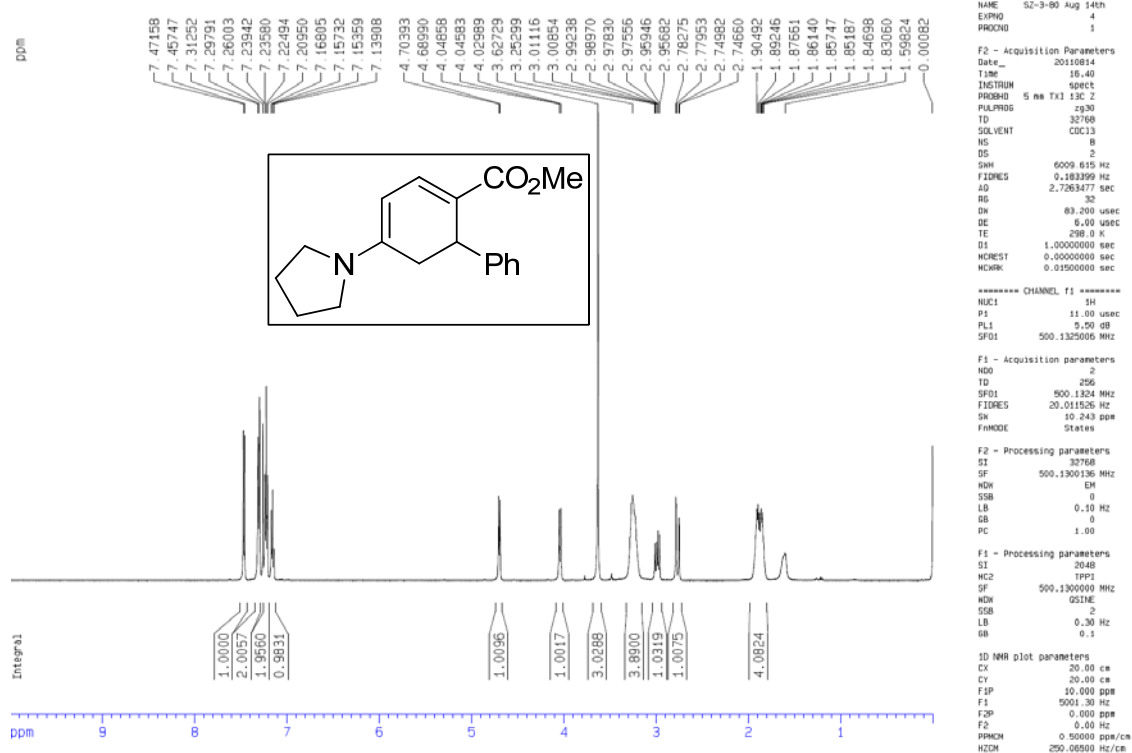
F1 - Acquisition Parameters
SI: 32768
SF: 500.130000 MHz
WDW: EM
SSB: 0
LB: 0.10 Hz
GB: 0
PC: 1.00

F2 - Processing parameters
SI: 32768
SF: 125.761154 MHz
WDW: EM
SSB: 0
LB: 0.10 Hz
GB: 0
PC: 1.00

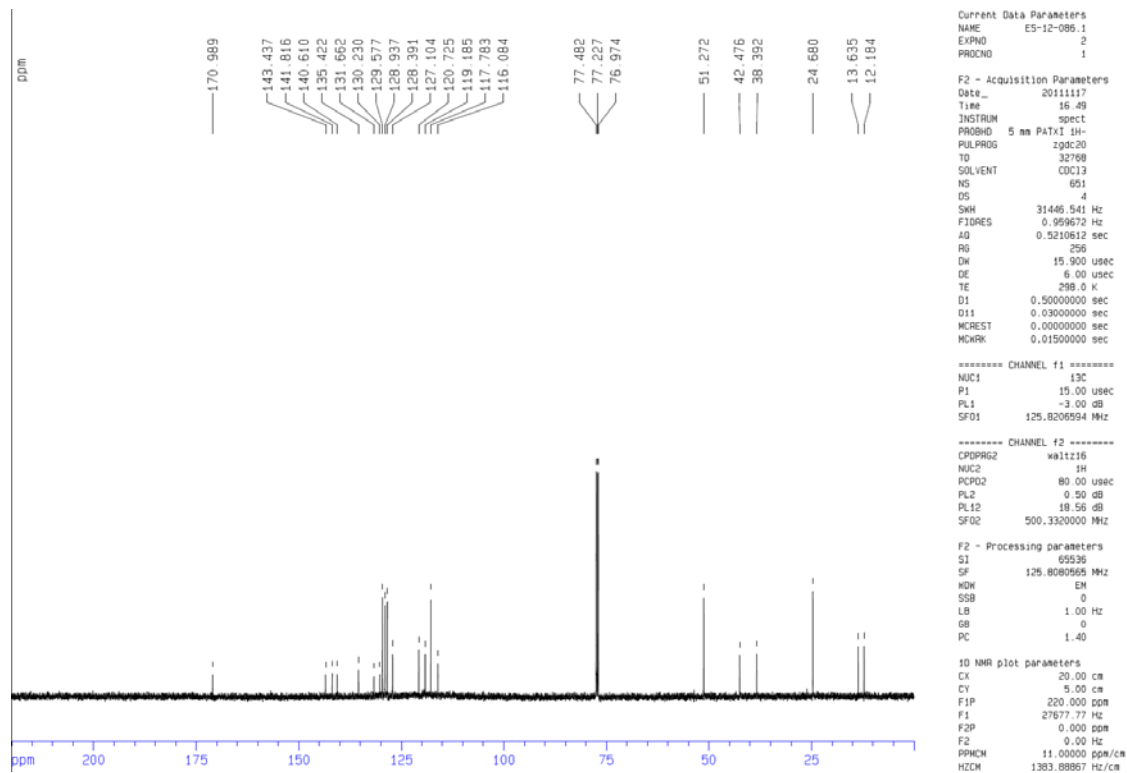
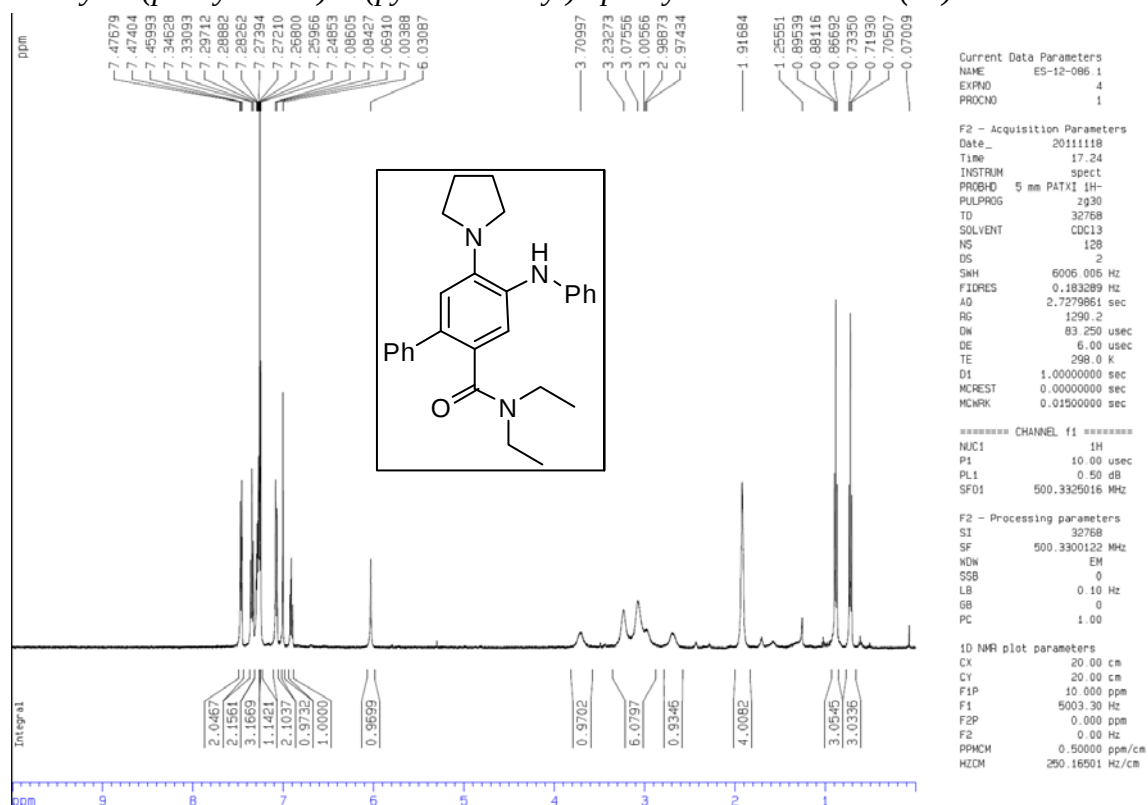
F1 - Processing parameters
SI: 2048
SF: 500.130000 MHz
WDW: EM
SSB: 0
LB: 0.10 Hz
GB: 0
PC: 1.00

JD NMR plot parameters
CX: 20.00 cm
CY: 20.00 cm
F1P: 20.000000 cm
F2: 500.130000 MHz
F3P: 0.000000 cm
F4: 0.00 MHz
PPM0: 0.000000 ppm/ppm
HLEN: 280.000000 Hz/cm

Methyl 6-phenyl-4-(pyrrolidin-1-yl)cyclohexa-1,3-dienecarboxylate (23)



N,N-diethyl-4-(phenylamino)-5-(pyrrolidin-1-yl)biphenyl-2-carboxamide (27)



Competition Experiment Between Rawal's Diene (**28**) and Diaminodiene **5c**

