^{15}N-Labeled Ionic Probe Attachment MS for Carbon Clusters

Fumihiro Ito and Kentaro Yamaguchi*

Faculty of Pharmaceutical Sciences at Kagawa Campus, Tokushima Bunri University,
1314-1 Shido, Sanuki, Kagawa 769-2193, Japan.

Electronic Supplementary Information

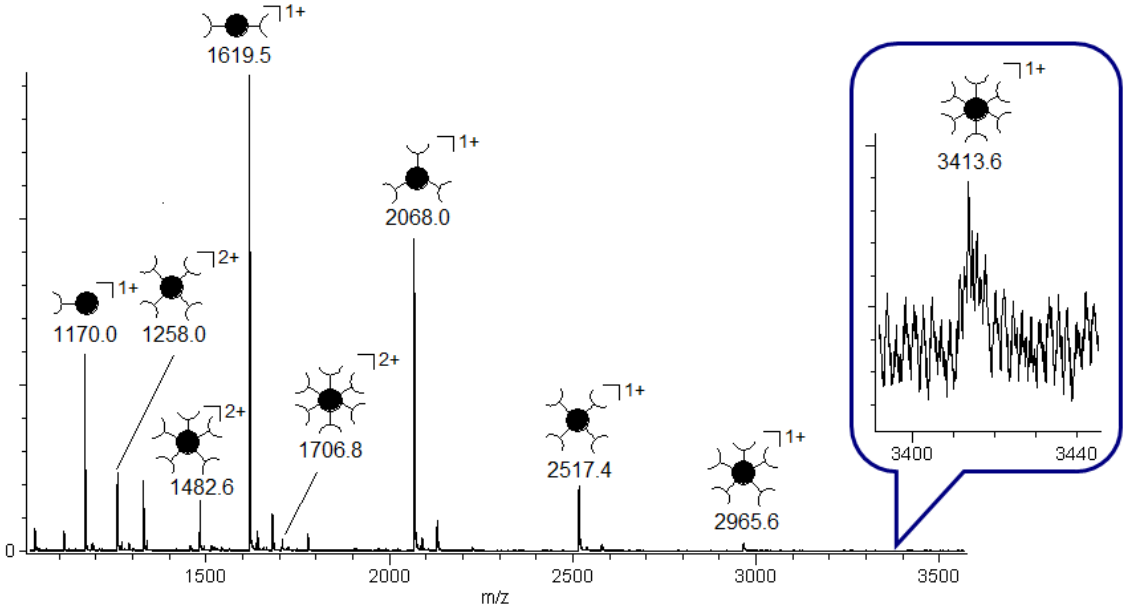
Table Contents

1. Multiply charged ionization of fullerene C_{60}, C_{70} and its derivative using Sar-TMpybox **2**

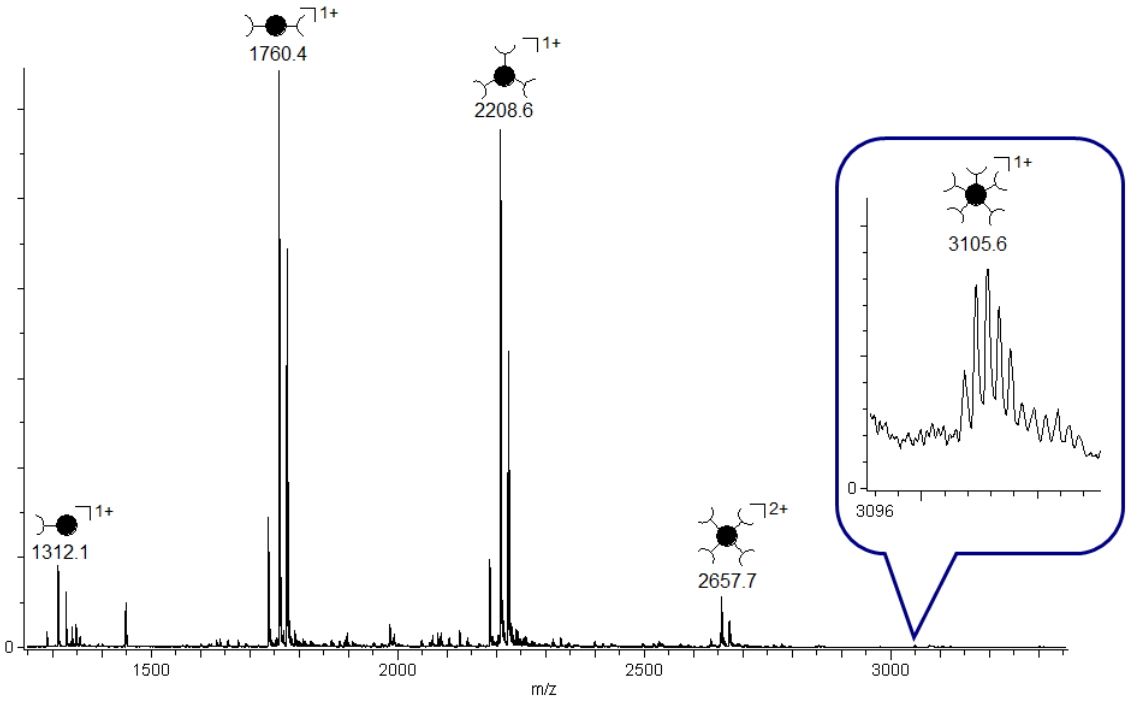
Under N_2, suspension of **2**, C_{60} and benzaldedhyde in toluene was stirred at reflux for 24 h. After this reaction mixture was filtered, the filtrate was evaporated *in vacuo*. The residue was washed with Et_2O. This modified C_{60} was added to solution of ^{14}N or ^{15}N-**3** in MeCN. After the whole was stirred at room temperature for 2 h, a part of this solution was diluted by MeCN and detected it by CSI-MS.

2. CSI mass spectra of fullerene derivatives

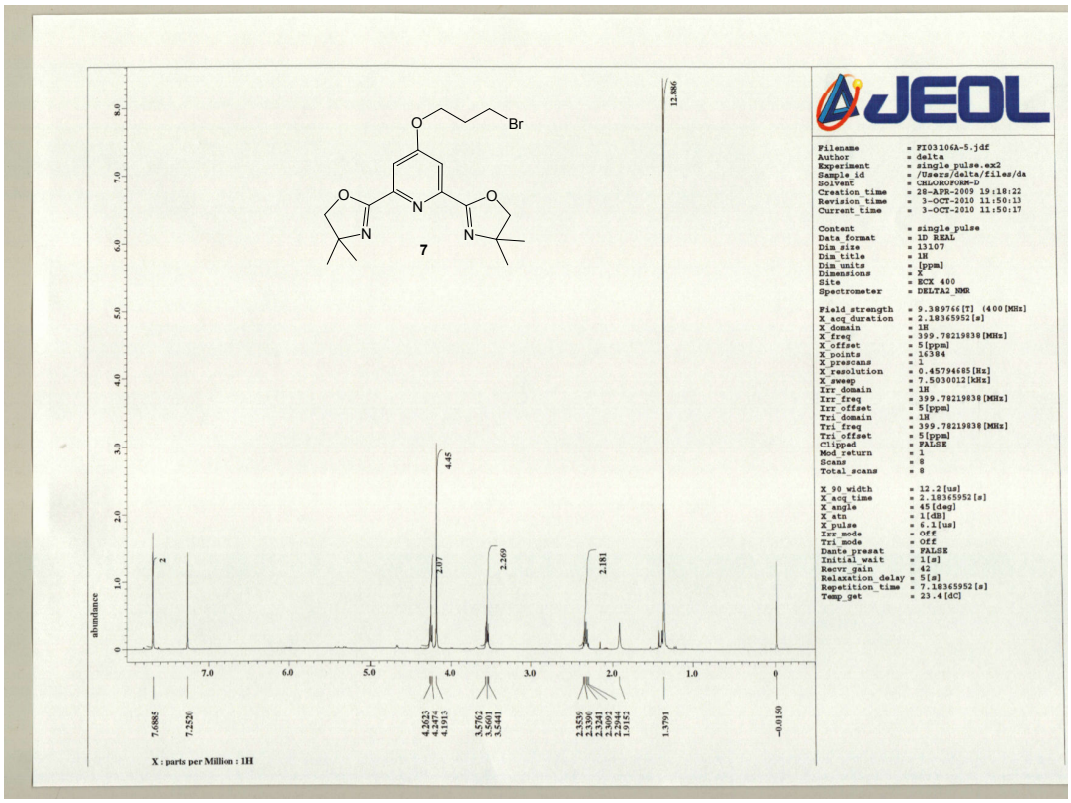
2-1. C_{60} derivatives.

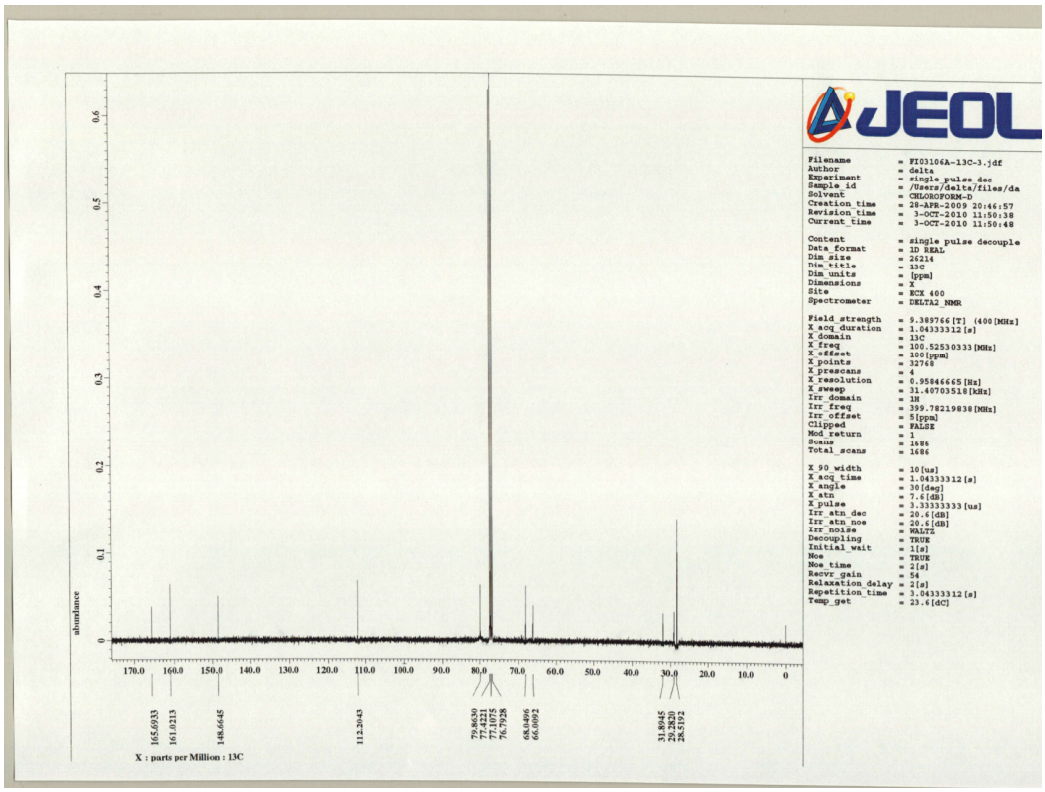


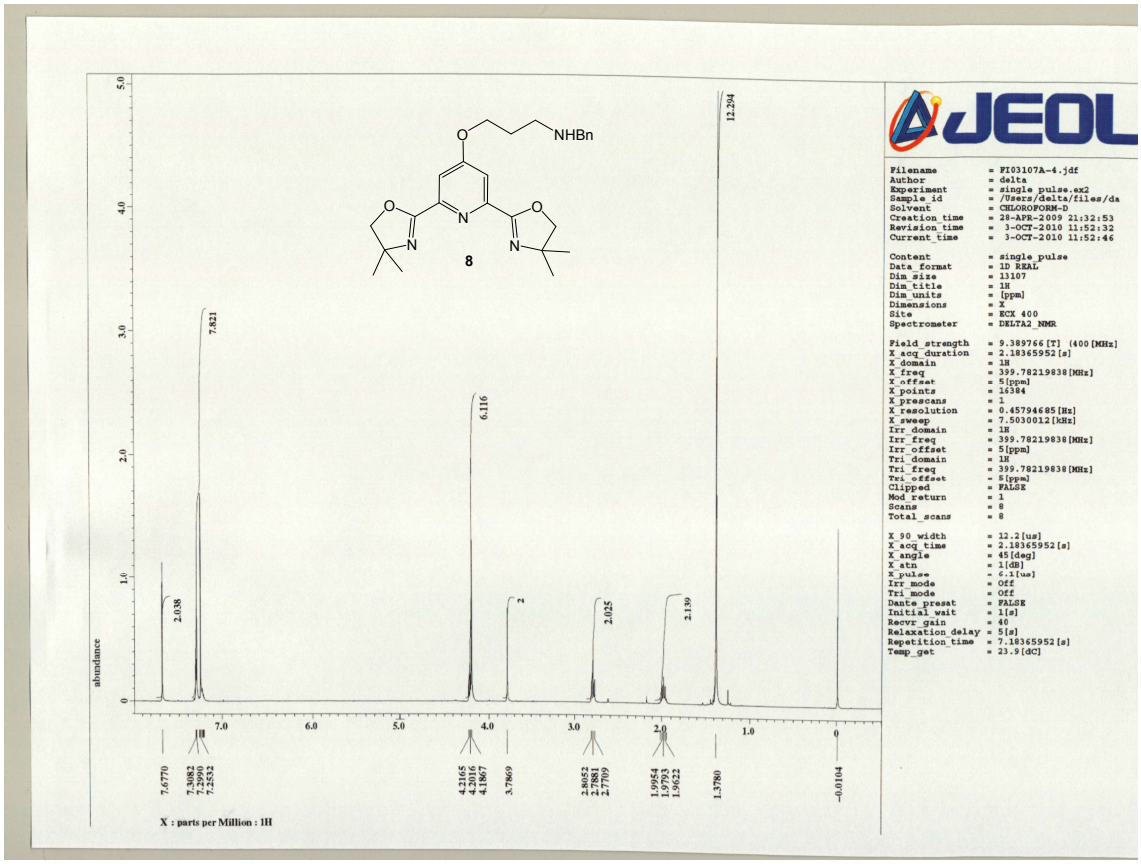
2-2. C_{70} derivatives.

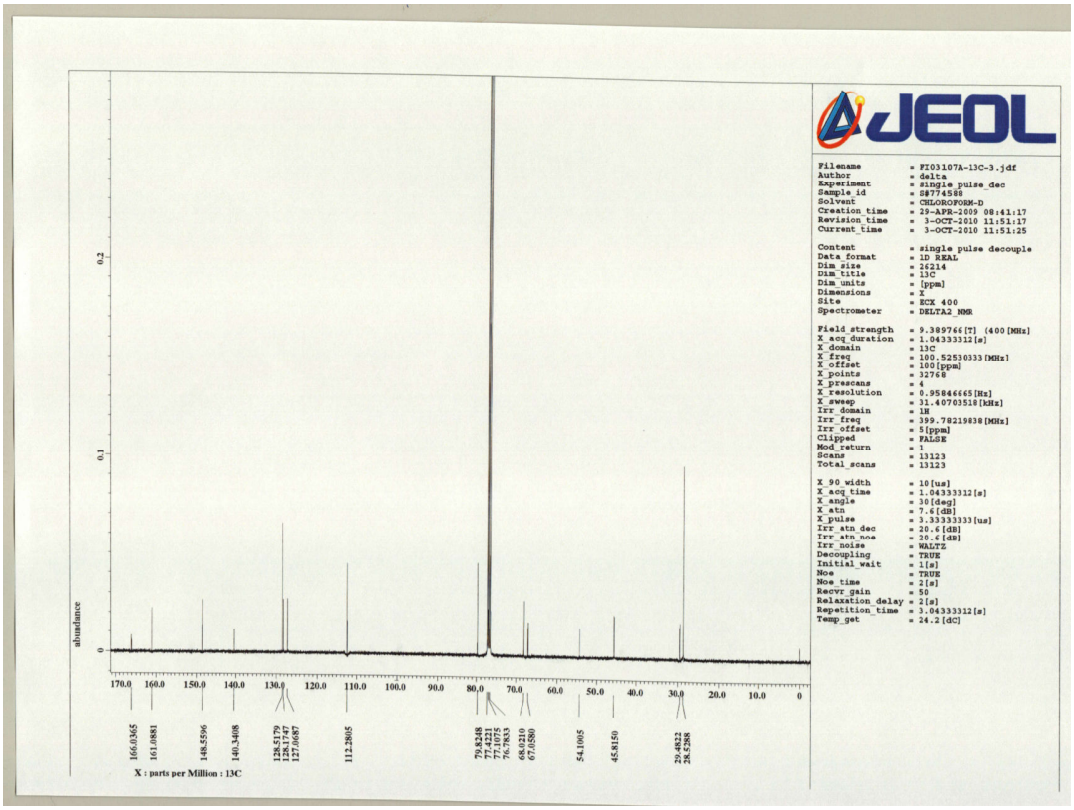


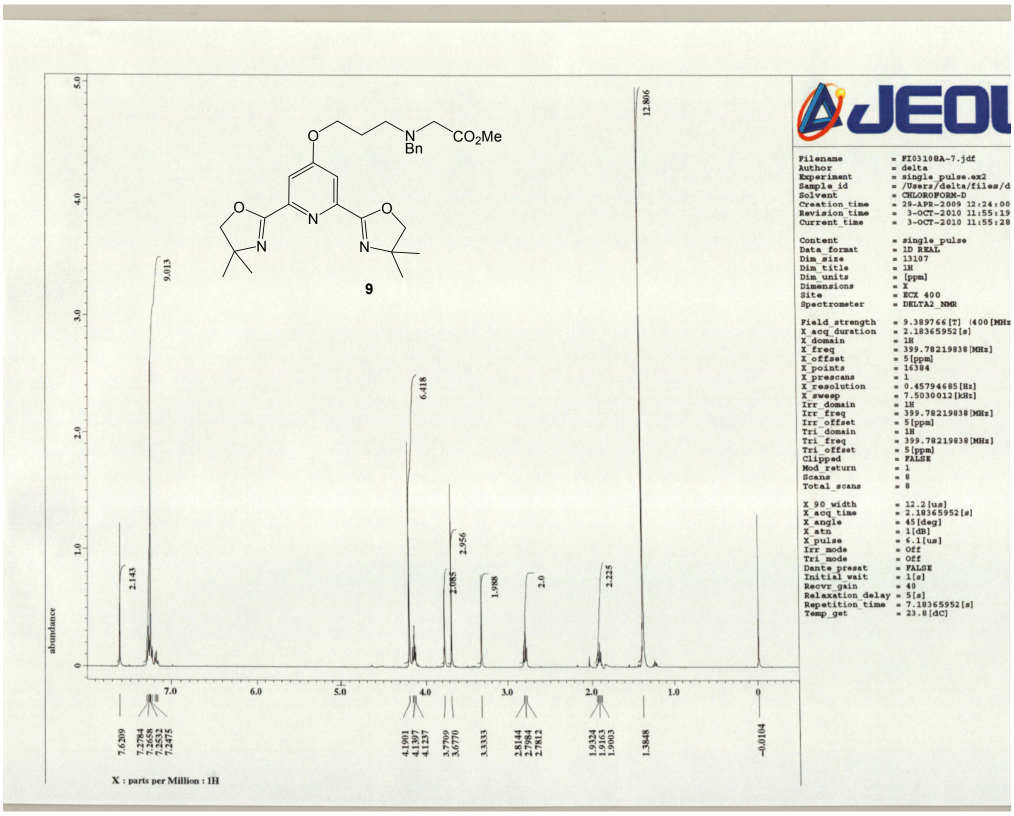
3. ^{1}H NMR and ^{13}C NMR spectra of **1**, **2**, **6** ~ **10** and **12**

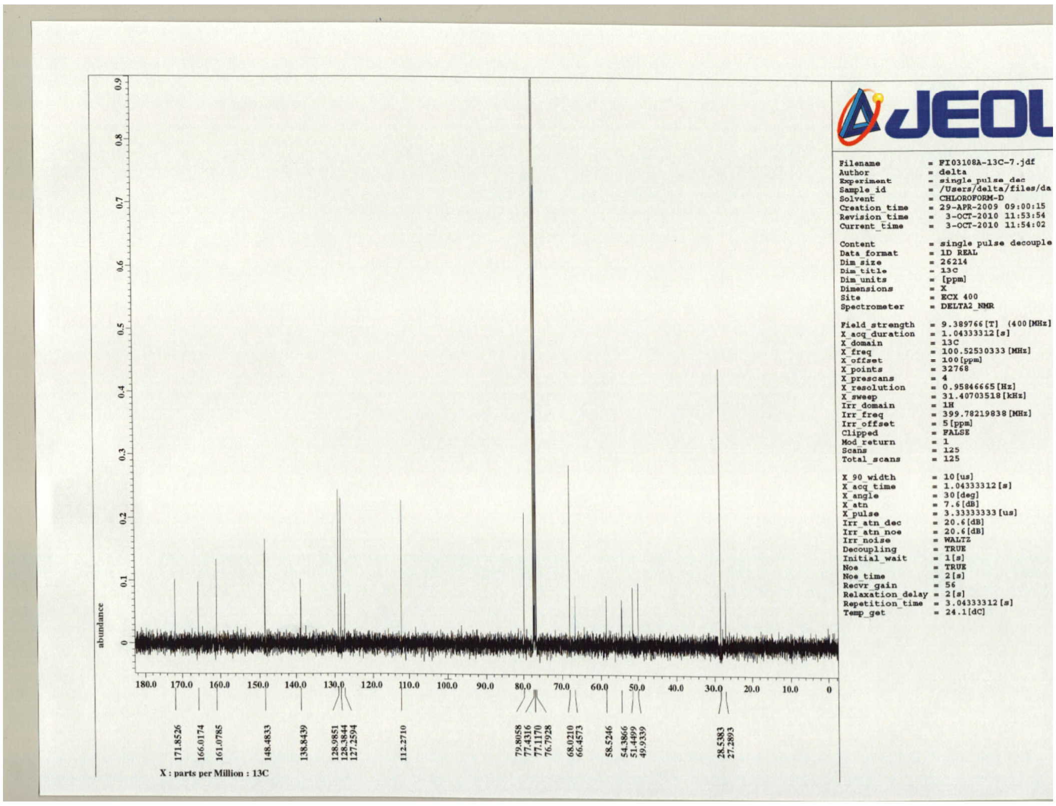


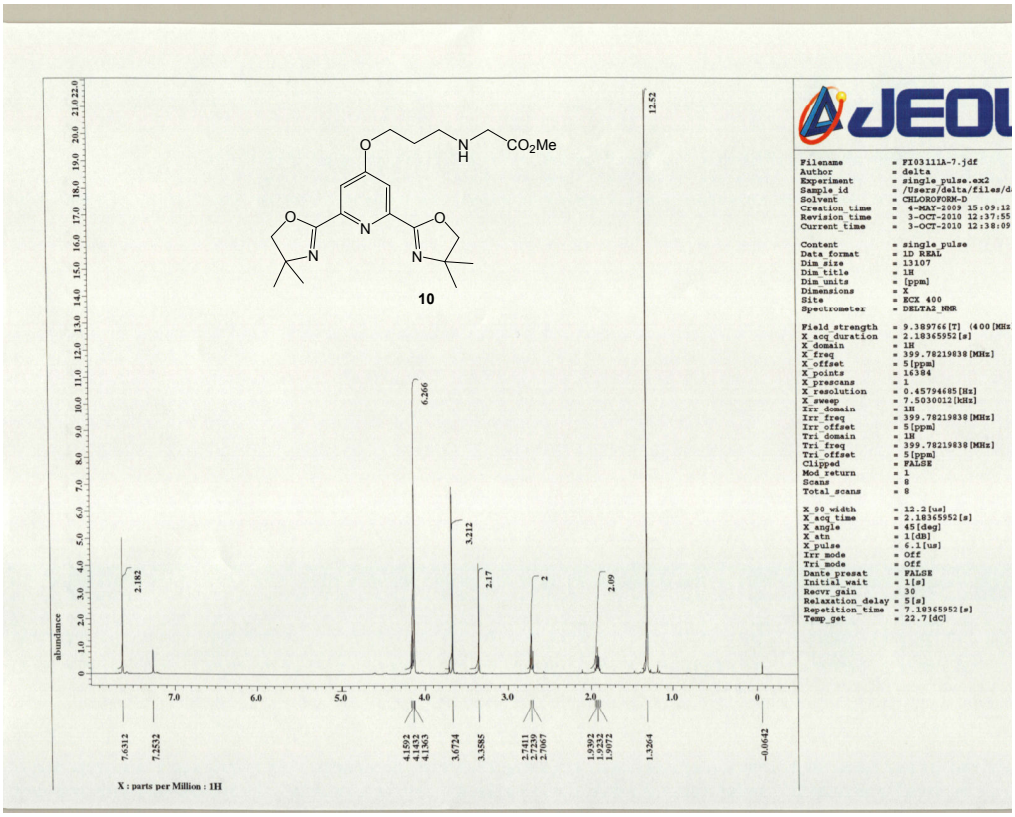


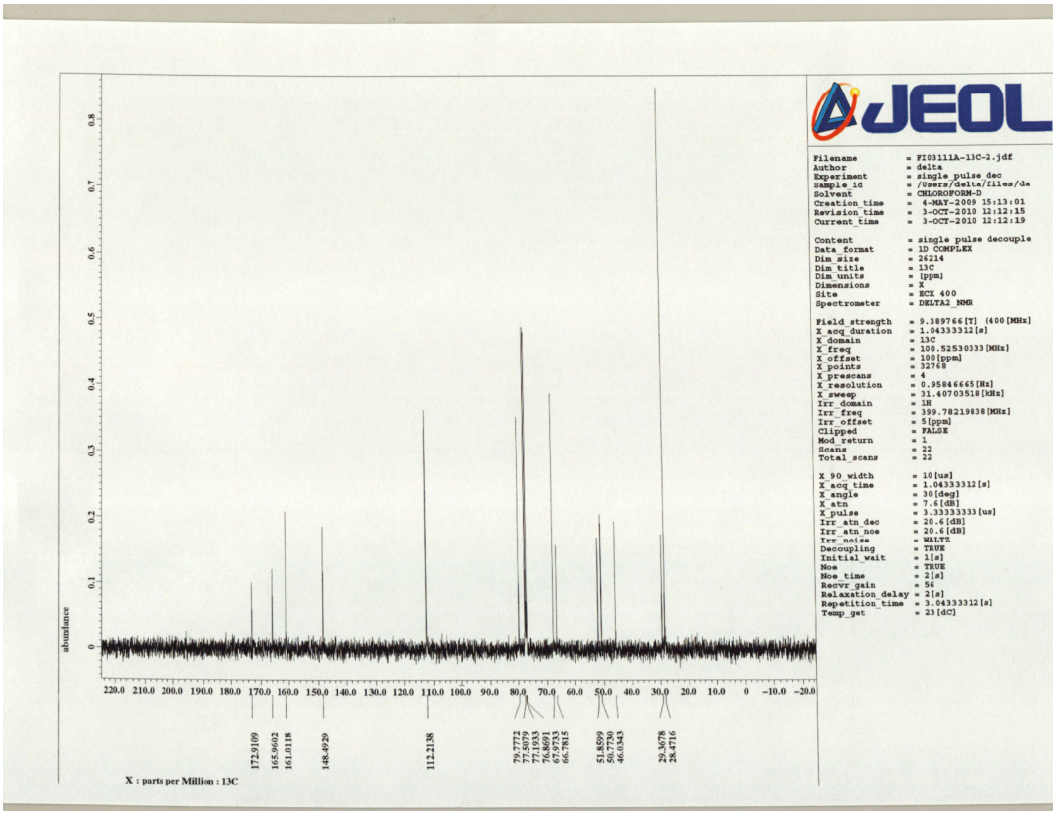

NHBn
8
JEOL
Filename = FI03107A-4.jdf
Author = delta
Experiment = single_pulse.ex2
Sample_id = /Users/delta/files/da
Solvent = CHLOROFORM-D
Creation_time = 28-APR-2009 21:32:53
Revision_time = 3-OCT-2010 11:52:32
Current_time = 3-OCT-2010 11:52:46
Content = single pulse
Data_format = 1D REAL
Dim_size = 13107
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = ECX 400
Spectrometer = DELTA2_NMR
Field_strength = 9.389766[T] (400[MHz]
X_acq_duration = 2.18365952[s]
X_domain = 1H
X_freq = 399.78219838[MHz]
X_offset = 5[ppm]
X_points = 16384
X_prescans = 1
X_resolution = 0.45794685[Hz]
X_sweep = 7.5030012[kHz]
Irr_domain = 1H
Irr_freq = 399.78219838[MHz]
Irr_offset = 5[ppm]
Tri_domain = 1H
Tri_freq = 399.78219838[MHz]
Tri_offset = 5[ppm]
Clipped = FALSE
Mod_return = 1
Scans = 8
Total_scans = 8
X_90_width = 12.2[us]
X_acq_time = 2.18365952[s]
X_angle = 45[deg]
X_atn = 1[dB]
X_pulse = 6.1[us]
Irr_mode = Off
Tri_mode = Off
Dante_presat = FALSE
Initial_wait = 1[s]
Recvr_gain = 40
Relaxation_delay = 5[s]
Repetition_time = 7.18365952[s]
Temp_get = 23.9[dC]
abundance
X : parts per Million : 1H

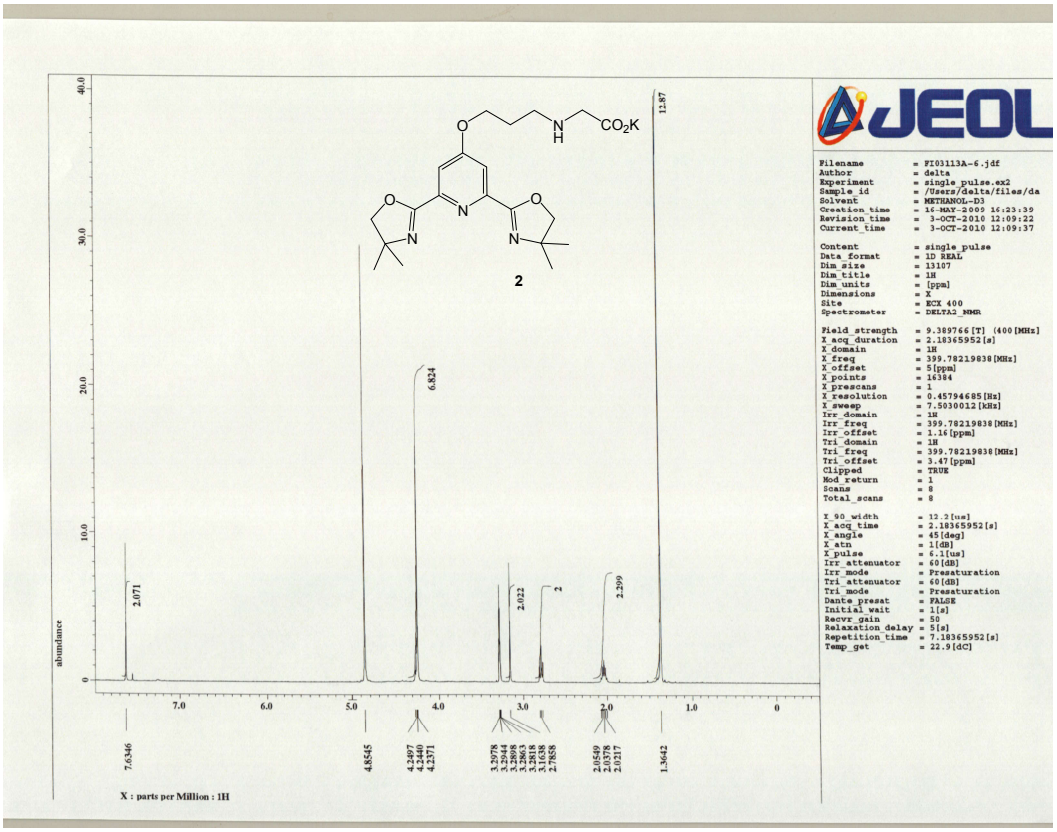

JEOL
Filename = FI03107A-13C-3.jdf
Author = delta
Experiment = single_pulse_dec
Sample_id = S#774580
Solvent = CHLOROFORM-D
Creation_time = 29-APR-2009 08:41:17
Revision_time = 3-OCT-2010 11:51:17
Current_time = 3-OCT-2010 11:51:25
Content = single pulse decouple
Data_format = 1D REAL
Dim_size = 26214
Dim_title = 13C
Dim_units = [ppm]
Dimensions = X
Site = ECX 400
Spectrometer = DELTA2_NMR
Field_strength = 9.389766[T] (400[MHz]
X_acq_duration = 1.04333312[s]
X_domain = 13C
X_freq = 100.52530333[MHz]
X_offset = 100[ppm]
X_points = 32768
X_prescans = 4
X_resolution = 0.95844665[Hz]
X_sweep = 31.40703518[kHz]
Irr_domain = 1H
Irr_freq = 399.78219838[MHz]
Irr_offset = 5[ppm]
Clipped = FALSE
Mod_return = 1
Scans = 13123
Total_scans = 13123
X_90_width = 10[us]
X_acq_time = 1.04333312[s]
X_angle = 30[deg]
X_atn = 7.6[dB]
X_pulse = 3.33333333[us]
Irr_atn_dec = 20.6[dB]
Irr_atn_noe = 20.6[dB]
Irr_noise = WALTZ
Decoupling = TRUE
Initial_wait = 1[s]
Noe = TRUE
Noe_time = 2[s]
Recvr_gain = 50
Relaxation_delay = 2[s]
Repetition_time = 3.04333312[s]
Temp_get = 24.2[dC]
abundance
X : parts per Million : 13C

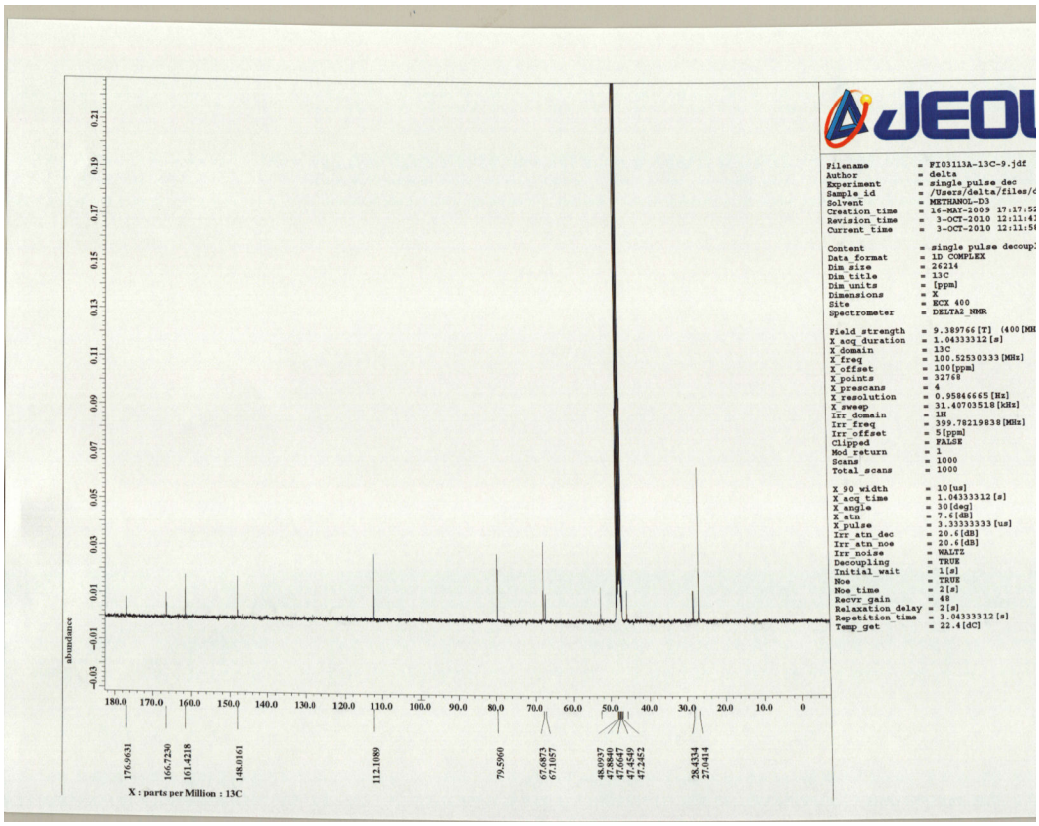

CO2Me
Bn
9
12.806
9.013
6.418
2.956
2.085
1.988
2.0
2.225
2.143
abundance
X : parts per Million : 1H
7.6209
7.2784
7.2658
7.2532
7.2475
4.1901
4.1397
4.1237
3.7709
3.6770
3.3333
2.8144
2.7984
2.7812
1.9324
1.9163
1.9003
1.3848
-0.0104

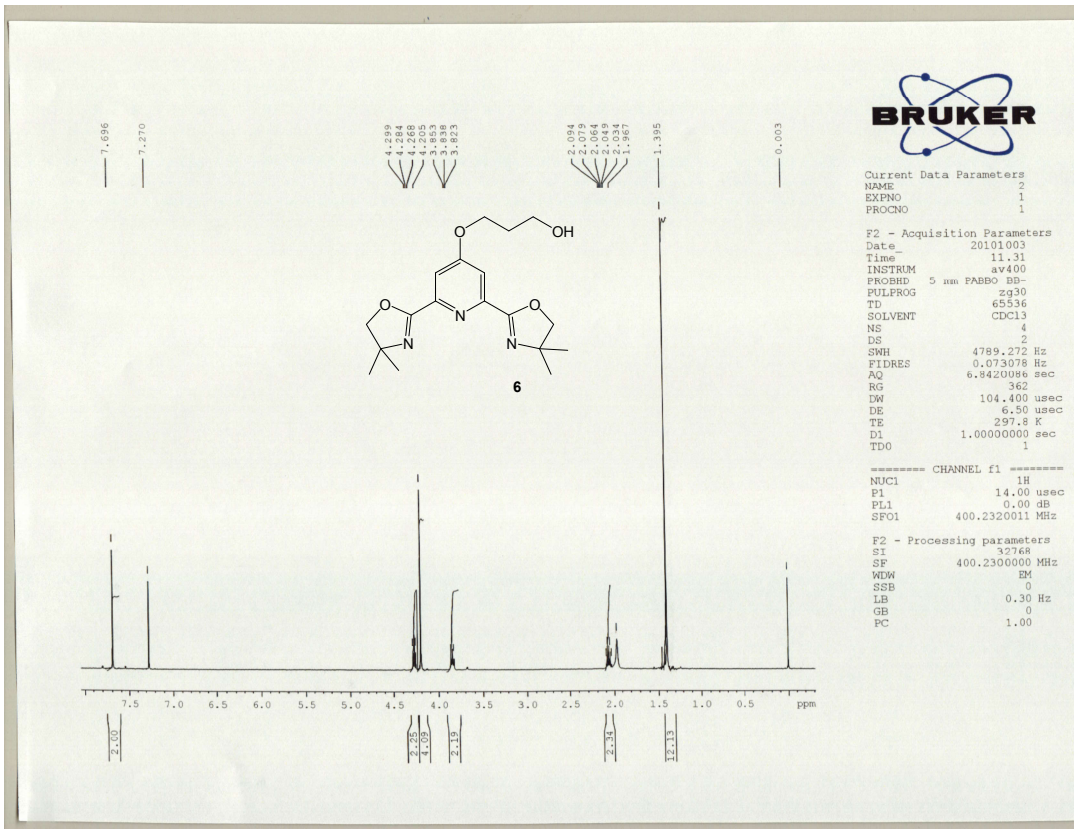

abundance
X : parts per Million : 13C
171.8526
166.0174
161.0785
148.4833
138.8439
128.9851
128.3844
127.2594
112.2710
79.8058
77.4316
77.1170
76.7928
68.0210
66.4573
58.5246
54.3866
51.4499
49.9339
28.5383
27.2893


10
X : parts per Million : 1H


X : parts per Million : 13C


2
JEOL
Filename = FI03113A-6.jdf
Author = delta
Experiment = single_pulse.ex2
Sample_id = /Users/delta/files/da
Solvent = METHANOL-D3
Creation_time = 16-MAY-2009 16:23:39
Revision_time = 3-OCT-2010 12:09:22
Current_time = 3-OCT-2010 12:09:37
Content = single pulse
Data_format = 1D REAL
Dim_size = 13107
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = ECX 400
Spectrometer = DELTA2_NMR
Field_strength = 9.389766[T] (400[MHz]
X_acq_duration = 2.18365952[s]
X_domain = 1H
X_freq = 399.78219838[MHz]
X_offset = 5[ppm]
X_points = 16384
X_prescans = 1
X_resolution = 0.45794685[Hz]
X_sweep = 7.5030012[kHz]
Irr_domain = 1H
Irr_freq = 399.78219838[MHz]
Irr_offset = 1.16[ppm]
Tri_domain = 1H
Tri_freq = 399.78219838[MHz]
Tri_offset = 3.47[ppm]
Clipped = TRUE
Mod_return = 1
Scans = 8
Total_scans = 8
X_90_width = 12.2[us]
X_acq_time = 2.18365952[s]
X_angle = 45[deg]
X_atn = 1[dB]
X_pulse = 6.1[us]
Irr_attenuator = 60[dB]
Irr_mode = Presaturation
Tri_attenuator = 60[dB]
Tri_mode = Presaturation
Dante_presat = FALSE
Initial_wait = 1[s]
Recvr_gain = 50
Relaxation_delay = 5[s]
Repetition_time = 7.18365952[s]
Temp_get = 22.9[dC]
abundance
X : parts per Million : 1H


JEOL
Filename = FI03113A-13C-9.jdf
Author = delta
Experiment = single_pulse_dec
Solvent = METHANOL-D3
Content = single pulse decoupl
Data_format = 1D COMPLEX
Dim_size = 26214
Dim_title = 13C
Dim_units = [ppm]
Dimensions = X
Site = ECX 400
Spectrometer = DELTA2_NMR
X_acq_duration = 1.04333312[s]
X_domain = 13C
X_freq = 100.52530333[MHz]
X_offset = 100[ppm]
X_points = 32768
X_prescans = 4
X_resolution = 0.95846665[Hz]
X_sweep = 31.40703518[kHz]
Irr_domain = 1H
Irr_freq = 399.78219838[MHz]
Irr_offset = 5[ppm]
Clipped = FALSE
Mod_return = 1
Scans = 1000
Total_scans = 1000
X_90_width = 10[us]
X_acq_time = 1.04333312[s]
X_angle = 30[deg]
X_atn = 7.6[dB]
X_pulse = 3.33333333[us]
Irr_atn_dec = 20.6[dB]
Irr_atn_noe = 20.6[dB]
Irr_noise = WALTZ
Decoupling = TRUE
Initial_wait = 1[s]
Noe = TRUE
Noe_time = 2[s]
Recvr_gain = 48
Relaxation_delay = 2[s]
Repetition_time = 3.04333312[s]
Temp_get = 22.4[dC]
abundance
X : parts per Million : 13C



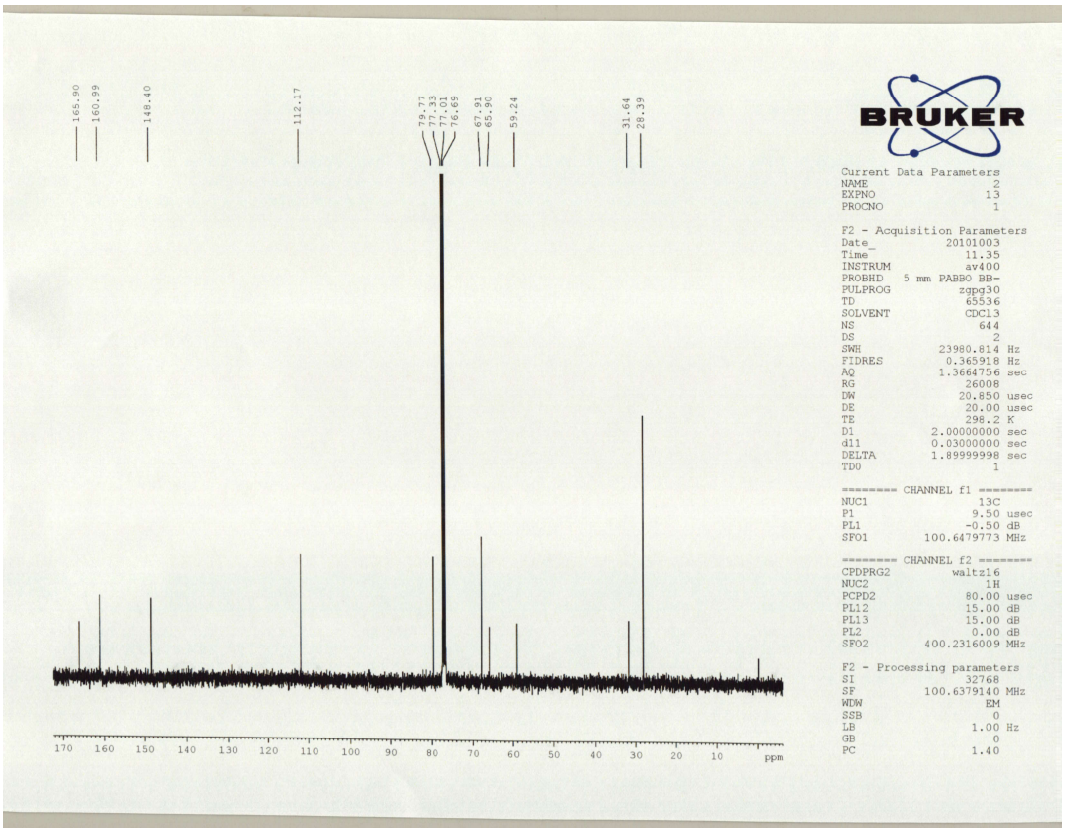
BRUKER

Current Data Parameters
NAME 2
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20101003
Time 11.31
INSTRUM av400
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 4
DS 2
SWH 4789.272 Hz
FIDRES 0.073078 Hz
AQ 6.8420086 sec
RG 362
DW 104.400 usec
DE 6.50 usec
TE 297.8 K
D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 1H
P1 14.00 usec
PL1 0.00 dB
SFO1 400.2320011 MHz

F2 - Processing parameters
SI 32768
SF 400.2300000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



BRUKER

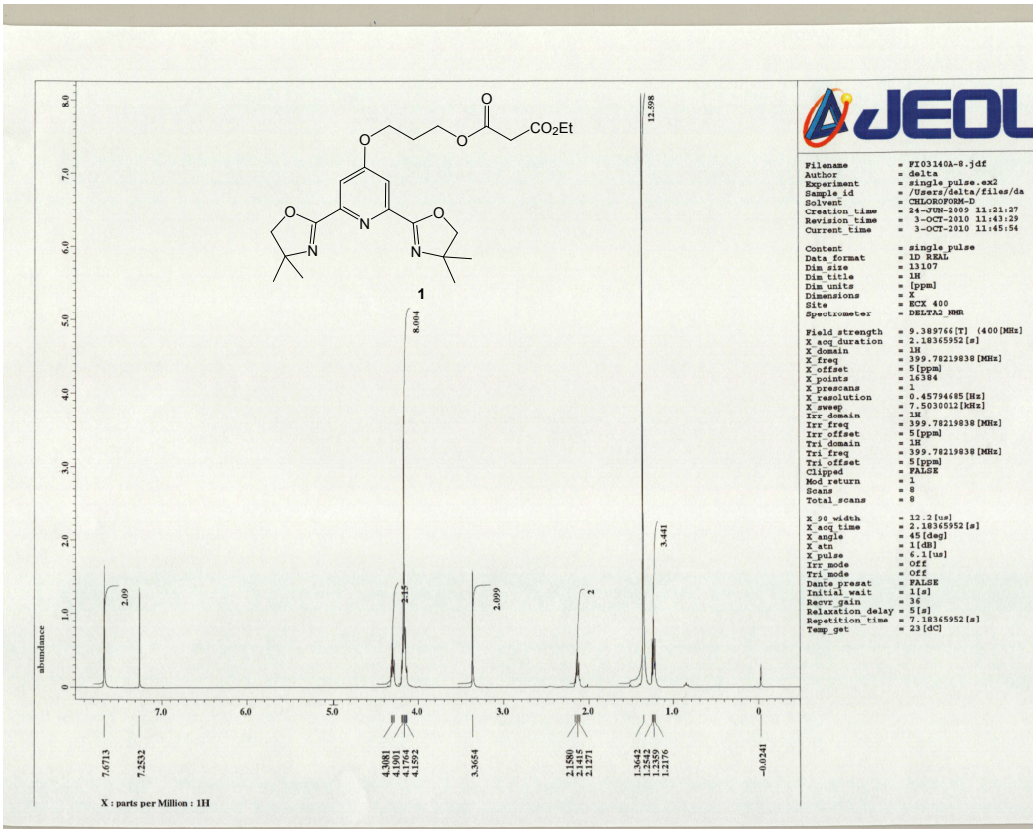
Current Data Parameters
NAME 2
EXPNO 13
PROCNO 1

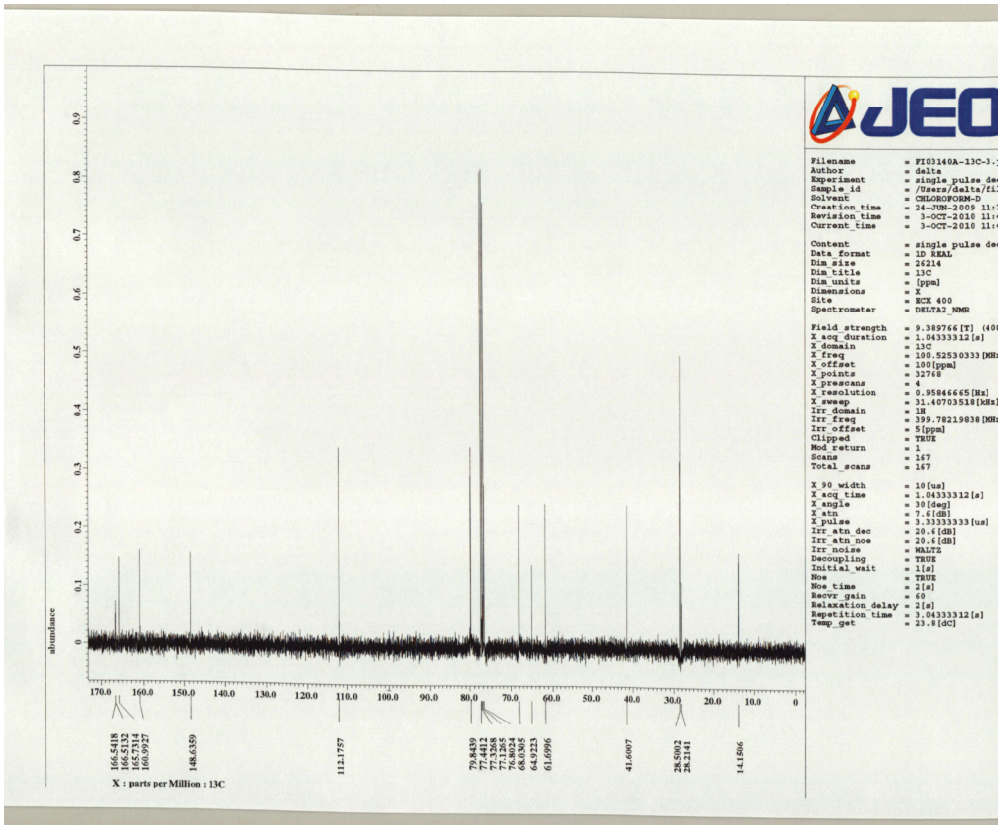
F2 - Acquisition Parameters
Date_ 20101003
Time 11.35
INSTRUM av400
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 644
DS 2
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664756 sec
RG 26008
DW 20.850 usec
DE 20.00 usec
TE 298.2 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1

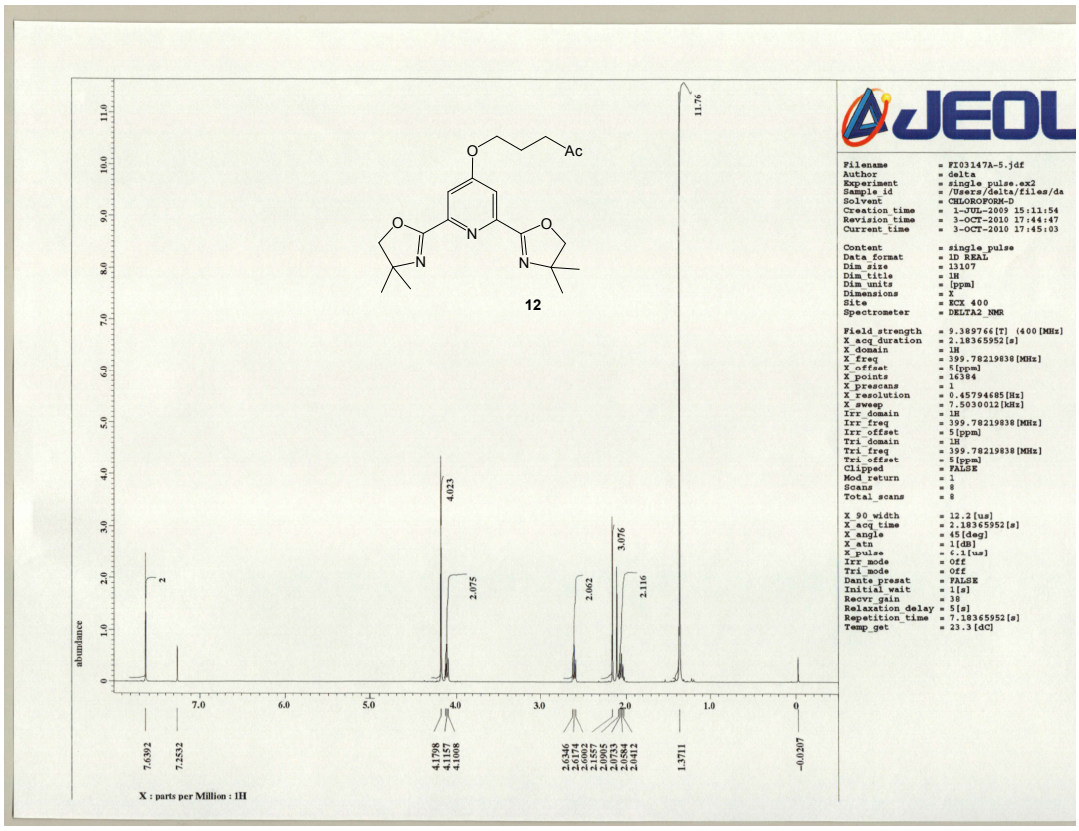
======== CHANNEL f1 ========
NUC1 13C
P1 9.50 usec
PL1 -0.50 dB
SFO1 100.6479773 MHz

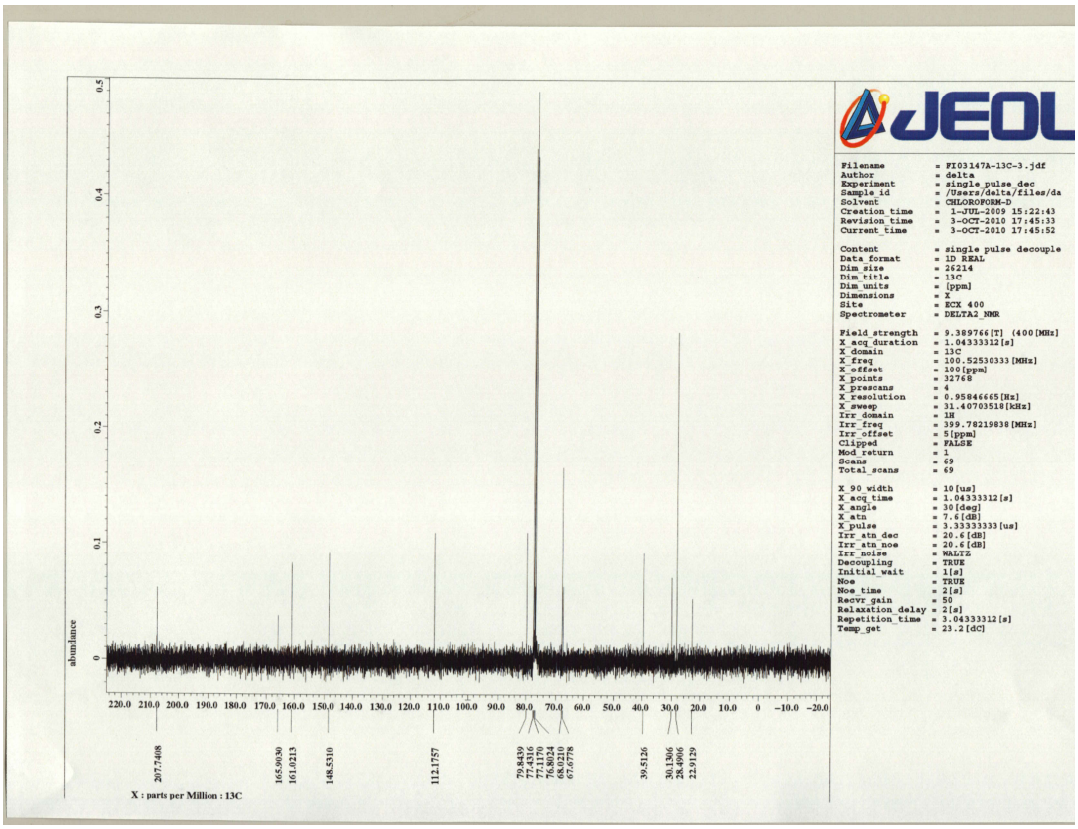
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL12 15.00 dB
PL13 15.00 dB
PL2 0.00 dB
SFO2 400.2316009 MHz

F2 - Processing parameters
SI 32768
SF 100.6379140 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40


O
O
O
CO2Et
O
N
O
N
N
1
12.598
8.004
3.441
2.09
2.15
2.099
2
abundance
X : parts per Million : 1H
JEOL
Filename = FI03140A-8.jdf
Author = delta
Experiment = single_pulse.ex2
Sample_id = /Users/delta/files/da
Solvent = CHLOROFORM-D
Creation_time = 24-JUN-2009 11:21:27
Revision_time = 3-OCT-2010 11:43:29
Current_time = 3-OCT-2010 11:45:54
Content = single_pulse
Data_format = 1D REAL
Dim_size = 13107
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = RCX 400
Spectrometer = DELTA2_NMR
Field_strength = 9.389766[T] (400[MHz]
X_acq_duration = 2.18365952[s]
X_domain = 1H
X_freq = 399.78219838[MHz]
X_offset = 5[ppm]
X_points = 16384
X_prescans = 1
X_resolution = 0.45794685[Hz]
X_sweep = 7.5030012[kHz]
Irr_domain = 1H
Irr_freq = 399.78219838[MHz]
Irr_offset = 5[ppm]
Tri_domain = 1H
Tri_freq = 399.78219838[MHz]
Tri_offset = 5[ppm]
Clipped = FALSE
Mod_return = 1
Scans = 8
Total_scans = 8
X_90_width = 12.2[us]
X_acq_time = 2.18365952[s]
X_angle = 45[deg]
X_atn = 1[dB]
X_pulse = 6.1[us]
Irr_mode = Off
Tri_mode = Off
Dante_presat = FALSE
Initial_wait = 1[s]
Recvr_gain = 36
Relaxation_delay = 5[s]
Repetition_time = 7.18365952[s]
Temp_get = 23[dC]
7.6713
7.2532
4.1081
4.1001
4.1764
4.1592
3.3654
2.1580
2.1415
2.1271
1.3642
1.2543
1.2359
1.2176
-0.0241


abundance
X : parts per Million : 13C
JEOL
Filename = FI03140A-13C-3.
Author = delta
Experiment = single_pulse de
Sample_id = /Users/delta/fi
Solvent = CHLOROFORM-D
Creation_time = 24-JUN-2009 11:
Revision_time = 3-OCT-2010 11:
Current_time = 3-OCT-2010 11:
Content = single_pulse de
Data_format = 1D REAL
Dim_size = 26214
Dim_title = 13C
Dim_units = [ppm]
Dimensions = X
Site = RCX 400
Spectrometer = DELTA2_NMR
Field_strength = 9.389766[T] (40
X_acq_duration = 1.04333312[s]
X_domain = 13C
X_freq = 100.52530333[MH
X_offset = 100[ppm]
X_points = 32768
X_prescans = 4
X_resolution = 0.95846665[Hz]
X_sweep = 31.40703518[kHz]
Irr_domain = 1H
Irr_freq = 399.78219838[MH
Irr_offset = 5[ppm]
Clipped = TRUE
Mod_return = 1
Scans = 167
Total_scans = 167
X_90_width = 10[us]
X_acq_time = 1.04333312[s]
X_angle = 30[deg]
X_atn = 7.6[dB]
X_pulse = 3.33333333[us]
Irr_atn_dec = 20.6[dB]
Irr_atn_noe = 20.6[dB]
Irr_noise = WALTZ
Decoupling = TRUE
Initial_wait = 1[s]
Noe = TRUE
Noe_time = 2[s]
Recvr_gain = 60
Relaxation_delay = 2[s]
Repetition_time = 3.04333312[s]
Temp_get = 23.8[dC]
165.5418
165.5132
165.7314
160.9927
148.6359
112.1757
79.8439
77.4412
77.3368
77.1295
76.8034
68.0305
64.9223
61.6996
41.6007
28.5002
28.2141
14.1506


O
Ac
O
N
O
N
N
12
11.76
4.023
3.076
2.075
2.062
2.116
2
abundance
X : parts per Million : 1H
JEOL
Filename = FI03147A-5.jdf
Author = delta
Experiment = single_pulse.ex2
Sample_id = /Users/delta/files/da
Solvent = CHLOROFORM-D
Creation_time = 1-JUL-2009 15:11:54
Revision_time = 3-OCT-2010 17:44:47
Current_time = 3-OCT-2010 17:45:03
Content = single_pulse
Data_format = 1D REAL
Dim_size = 13107
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = ECX 400
Spectrometer = DELTA2_NMR
Field_strength = 9.389766[T] (400[MHz]
X_acq_duration = 2.18365952[s]
X_domain = 1H
X_freq = 399.78219838[MHz]
X_offset = 5[ppm]
X_points = 16384
X_prescans = 1
X_resolution = 0.45794685[Hz]
X_sweep = 7.5030012[kHz]
Irr_domain = 1H
Irr_freq = 399.78219838[MHz]
Irr_offset = 5[ppm]
Tri_domain = 1H
Tri_freq = 399.78219838[MHz]
Tri_offset = 5[ppm]
Clipped = FALSE
Mod_return = 1
Scans = 8
Total_scans = 8
X_90_width = 12.2[us]
X_acq_time = 2.18365952[s]
X_angle = 45[deg]
X_atn = 1[dB]
X_pulse = 6.1[us]
Irr_mode = Off
Tri_mode = Off
Dante_presat = FALSE
Initial_wait = 1[s]
Recvr_gain = 38
Relaxation_delay = 5[s]
Repetition_time = 7.18365952[s]
Temp_get = 23.3[dC]


abundance
X : parts per Million : 13C
JEOL
Filename = FI03147A-13C-3.jdf
Author = delta
Experiment = single_pulse_dec
Sample_id = /Users/delta/files/da
Solvent = CHLOROFORM-D
Creation_time = 1-JUL-2009 15:22:43
Revision_time = 3-OCT-2010 17:45:33
Current_time = 3-OCT-2010 17:45:52
Content = single pulse decouple
Data_format = 1D REAL
Dim_size = 26214
Dim_title = 13C
Dim_units = [ppm]
Dimensions = X
Site = ECX 400
Spectrometer = DELTA2_NMR
Field_strength = 9.389766[T] (400[MHz]
X_acq_duration = 1.04333312[s]
X_domain = 13C
X_freq = 100.52530333[MHz]
X_offset = 100[ppm]
X_points = 32768
X_prescans = 4
X_resolution = 0.95846665[Hz]
X_sweep = 31.40703518[kHz]
Irr_domain = 1H
Irr_freq = 399.78219838[MHz]
Irr_offset = 5[ppm]
Clipped = FALSE
Mod_return = 1
Scans = 69
Total_scans = 69
X_90_width = 10[us]
X_acq_time = 1.04333312[s]
X_angle = 30[deg]
X_atn = 7.6[dB]
X_pulse = 3.33333333[us]
Irr_atn_dec = 20.6[dB]
Irr_atn_noe = 20.6[dB]
Irr_noise = WALTZ
Decoupling = TRUE
Initial_wait = 1[s]
Noe = TRUE
Noe_time = 2[s]
Recvr_gain = 50
Relaxation_delay = 2[s]
Repetition_time = 3.04333312[s]
Temp_get = 23.2[dC]