Electronic Supplementary Material (ESI) for RSC Advances.

Synthesis of MacMiillan catalyst modified with ionic liquids as a recoverable catalyst for asymmetric Diels Alder reaction

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1. Synthetic procedure and characterization data of compound 2-4

L-phenylalanine methyl ester hydrochloride (2) [1]

Thionyl chloride (2.2 mL, 30 mmol) was added dropwise in the ice cooled suspension of L-Phenyl alanine (4.125 g, 25 mmol) in methanol (32 mL) over a period of 15 min. The clear solution was stirred at room temperature for 28 h. Solvent was removed in vacuo and Et_2O (20 mL) was added for slurried the solid residue, filtered by vaccum and washed with Et_2O (10 mL) and dried to give L-phenylalanine methyl ester hydrochloride **2** as a white solid (4.0 g, 97%). mp = 159 ºC; $[\alpha]_D^{25}$ = + 16.7 (*c* 1.0, MeOH); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.01–6.94 (m, 5H), 3.92–3.87 (m, 1H), 3.41–3.37 (m, 3H), 3.11–2.96 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) 168.7, 133.7, 128.9 (2C), 128.09 (2C), 126.8, 53.6, 52.0, 35.6 ppm.

(*S*)-2-amino-N-(2-hydroxyethyl)-3-phenylpropanamide (3) [1]

Compound **2** (3.46 g, 15 mmol) was dissolved in ethanolamine (5.5 mL, 92.25 mmol) and allowed to stir at room temperature for 26 h. The reaction mixture was diluted with CH_2Cl_2 (25 mL), washed with K_2CO_3 (20% in 20 mL water). The aqueous phase was extracted with CH_2Cl_2 (3×15 mL), and the combined organic phase was dried over anhydrous Na_2SO_4, filtered and evaporated by rotavapor to give compound **3** (2.62 g, 84%) as a white solid. mp = 76 ºC; $[\alpha]_D^{25}$ = + 11.5 (*c* 1.0, MeOH); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.66 (t, 3H, *J* = 6.22 Hz), 7.25–7.12 (m, 5H), 3.60–3.50 (m, 3H), 3.35–3.30 (m, 2H), 3.15–3.09 (m,1H), 2.73 (brs, 2H), 2.66–2.60 (m, 1H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz) 174.9, 137.4, 129.0 (2C), 128.4 (2C), 126.5, 60.9, 56.2, 41.7, 40.8 ppm.

(S)-5-benzyl-3-(2-hydroxyethyl)-2,2-dimethylimidazolidin-4-one hydrochloride (4) [1]

In a 100 mL round bottom flask fitted with Dean Stark apparatus, L-phenylalanylaminoethanol (2.49 g, 12 mmol), acetone (13 mL) and *i*-PrOH (17 mL) were taken and *p*-TsOH · H_2O (0.07 g, 0.37 mmol) was added in the mixture. The resulting solution was stirred at 85°C for 5 h. The liquid collected in the Dean-Stark trap was discarded. The solvent in the round bottom flask was removed under vacuum to give light brown oil. The oil was diluted with MeOH (1.5 mL) and an ice-cold methanolic HCl solution (prepared from 1.3 mL of acetyl chloride was added to ice-cooled 5 mL Methanol.) was added slowly. Later, Et_2O (25 mL) was slowly added to give white precipitate and further stirred for 30 min, filtered and washed with Et_2O (7 mL). The white solid dried to give (5*R*)-5-benzyl-2,2-dimethyl-3-(2-hydroxyethyl)-imidazolidin-4-one hydrochloride **4** mp = 150.2 ºC; $[\alpha]_D^{25}$ = - 92.2 (*c* 1.2 MeOH); ^{1}H NMR ($CDCl_3$, 400MHz) δ 7.27–7.24 (m, 2H), 7.20–7.17 (m, 3H), 3.78 (t, 1H, *J* = 5.13 Hz), 3.68–3.61 (m, 2H), 3.40–3.34 (m, 1H), 3.14–3.08 (m, 1H), 3.03 (t, 2H), 1.23 (s, 3H), 1.09 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) 175.4, 136.5, 129.3 (2C), 128.4 (2C), 126.7, 76.4, 61.6, 58.5, 43.6, 36.8, 27.5, 26.2 ppm.

5-Bromopentanoyl chloride

5-Bromo valleric acid (5 g, 27.62 mmol) was added to neat $SOCl_2$ (10.67 mL, 147.79 mmol) and stirred at room temperature for 30 min, then at 50 c for 1 h. The excess $SOCl_2$ was evaporated under reduce pressure to give 5-Bromopentanoyl chloride (5.16 g, 94% yield).^{1}H NMR ($CDCl_3$, 400MHz) δ 3.40–3.34 (2H, m), 2.94–2.88 (2H, m), 1.89–1.84 (4H, m) ppm. ^{13}C NMR ($CDCl_3$, 100MHz) 173.2, 45.9, 32.4, 30.9, 23.4 ppm.

Determination of Leaching of catalyst during catalyst recovery

The **IL 8** (10 mg) was dissolved in 5 mL volumetric flask in acetonitrile. Different concentrations (40 µL, 20 µL, 10 µL and 5 µL) were injected to the HPLC. The area of different concentration of catalyst **8** calculated by HPLC using C18 column. After the catalytic reaction, the residue was washed with hexane/diethyl ether (1/1). Solvent was evaporated and the crude compound was make up to 5 mL acetonitrile and checked the quantity of leaching of catalyst **8** by injecting 20 µL quantity of the crude mixture. The area of leached catalyst was determined by using reference area of **IL 8** at (2.5 mg concentration, area 261971)

Table 1. Determination of leaching of the catalyst

Entry	Cycle	Leached catalyst (mg)	Area (mv)
1	0	0.12	13478
2	1	0.1	11708
3	2	0.0	0
4	3	0.01	1480
5	4	0.02	2361
6	5	0.02	2365

2. ^{1}H and ^{13}C NMR data of catalytic products

(1S,2S,3S,4R)-3-phenylbicyclo[2.2.1]hept-5-ene-2-carbaldehyde (14a) and (1R,2S,3S,4S)-3-phenylbicyclo[2.2.1]hept-5-ene-2-carbaldehyde (15a) (*exo/endo* : 1.2/1)
The products were converted to the corresponding alcohols with $NaBH_4$ and enantiomeric excess was determined by HPLC using CHIRALPAK OD-H column, *n*-Hex/IPA = 95/5; flow rate 1.0 ml/min; 210 nm; *exo* isomer (t_{major} = 13.7 min, t_{major} = 17.8 min), *endo* isomer (t_{major} = 14.8 min, t_{minor} = 26.0 min).
^{1}H NMR ($CDCl_3$, 400MHz) δ 9.92 (d, 1.2H, *J* = 2.20 Hz), 9.60 (d, 1H, *J* = 2.20 Hz), 7.33–7.14 (m, 10H), 6.43 (dd, 1H, *J* = 5.86, 3.66 Hz), 6.34 (dd, 1.2H, *J* = 5.86, 3.66 Hz), 6.18 (dd, 1H, *J* = 5.13, 2.20 Hz), 6.08 (dd, 1.2H, *J* = 5.13, 2.93 Hz), 3.73 (t, 1.2H, *J* = 3.66 Hz), 3.33 (s, 1H), 3.22 (d, 2.4H, *J* = 1.46 Hz), 3.13 (s, 1H), 3.09 (d, 1H, *J* = 4.39 Hz) 3.0-2.97 (m, 1H), 2.61-2.59 (m, 1.2H), 1.81 (d, 1.2H, *J* = 8.79), 1.64-1.55 (m, 3H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz) 203.4, 202.7, 143.4, 142.4, 139.1, 136.4, 136.2, 133.6, 128.5 (2C), 128.0 (2C), 127.8 (2C), 127.2 (2C), 126.2, 126.1, 60.7, 59.3, 48.3, 48.2, 47.9, 47.0, 45.5, 45.39, 45.30, 45.0 ppm.

(1S,2S,3S,4R)-3-(4-chlorophenyl)bicyclo[2.2.1]hept-5-ene-2-carbaldehyde (14c) and (1R,2S,3S,4S)-3-(4-chlorophenyl)bicyclo[2.2.1]hept-5-ene-2-carbaldehyde (15c) (*exo/endo* : 1.1/1)
The products were converted to the corresponding alcohols with $NaBH_4$ and enantiomeric excess was determined by HPLC using CHIRALPAK OD-H column, *n*-Hex/IPA = 96/4; flow rate 0.8 ml/min; 230 nm; *exo* isomer (t_{major} = 17.96 min, t_{minor} = 13.36 min), *endo* isomer (t_{major} = 20.01 min, t_{minor} = 17.96 min).
^{1}H NMR ($CDCl_3$, 400MHz) δ 9.80 (d, 1.1H, *J* = 1.83 Hz), 9.50 (d, 1H, *J* = 1.83 Hz), 7.19–7.13 (m, 2.1H), 7.12–7.08 (m, 4.1H), 7.0–6.96 (m, 2H), 6.32 (dd, 1H, *J* = 3.89, 3.21 Hz), 6.26 (dd, 1.1H, *J* = 3.89, 3.21 Hz), 6.08 (dd, 1H, *J* = 4.12, 2.75 Hz), 5.95 (dd, 1.1H, *J* = 4.12, 2.75 Hz), 3.62–3.60 (m, 1.1H), 3.26 (brs, 1H),

3.14 (brs, 1H), 3.09 (brs, 1.1H), 3.0 (brs, 1H), 2.99 (d, 1H, *J* = 5.50 Hz), 2.83–2.81 (m, 1.1H), 2.45–2.44 (m, 1.1H), 1.66 (d, 1.1H, *J* = 8.70 Hz), 1.56–1.45(m, 3H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz) 202.9, 202.2, 142.0, 141.0, 139.0, 136.4, 136.2, 133.7, 131.9, 131.8, 129.1 (2C), 128.6 (2C), 128.5 (2C), 128.1 (2C), 60.9, 59.4, 48.3, 48.1, 47.4, 46.9, 45.3, 45.0, 44.9, 44.6 ppm.

(1S,2S,3S,4R)-3-(4-methoxyphenyl)bicyclo[2.2.1]hept-5-ene-2-carbaldehyde (14d) and (1R,2S,3S,4S)-3-(4-methoxyphenyl)bicyclo[2.2.1]hept-5-ene-2-carbaldehyde (15d) (*exo/endo* : 1.1/1)

The products were converted to the corresponding alcohols with $NaBH_4$ and enantiomeric excess was determined by HPLC using CHIRALPAK OD-H column, *n*-Hex/IPA = 95/5; flow rate 0.8 ml/min; 230 nm; *exo* isomer (t_{major} = 20.72 min, t_{major} = 15.62 min).

^{1}H NMR ($CDCl_3$, 400MHz) δ 9.88 (d, 1.1H, *J* = 2.29 Hz), 9.55 (d, 1H, *J* = 2.29 Hz), 7.16 (d, 2H, *J* = 8.70 Hz), 7.04 (d, 2.2H, *J* = 8.70 Hz), 6.83 (d, 2H, *J* = 8.70 Hz), 6.77 (d, 2.2H, *J* = 8.70 Hz), 6.39 (dd, 1H, *J* = 5.50, 3.21 Hz), 6.31 (dd, 1.1H, *J* = 5.50, 3.21 Hz), 6.14 (dd, 1H, *J* = 5.50, 2.75 Hz), 6.04 (dd, 1.1H, *J* = 5.50, 2.75 Hz), 3.77 (s, 3H), 3.75 (s, 3.1H), 3.63 (t, 1.1H, *J* = 5.04 Hz), 3.29 (s, 1H), 3.16 (d, 2.2H, *J* = 13.74 Hz), 3.04 (s, 1H), 3.0 (d, 1H, *J* = 4.58 Hz), 2.91-2.90 (m, 1.2H), 2.51–2.50 (m, 1.2H), 1.77 (d, 1H, *J* = 8.70 Hz), 1.61–1.56 (m, 3H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz) 203.7, 202.9, 158.0, 157.9, 139.2, 136.5, 136.2, 135.5, 134.5, 133.6, 128.7 (2C), 128.2 (2C), 113.9 (2C), 113.4 (2C), 60.8, 59.6, 55.25, 55.20, 48.6, 48.5, 47.5, 47.0, 45.4, 45.08, 45.0, 44.6 ppm.

(1S,2S,3S,4R)-3-(4-nitrophenyl)bicyclo[2.2.1]hept-5-ene-2-carbaldehyde (14b) and (1R,2S,3S,4S)-3-(4-nitrophenyl)bicyclo[2.2.1]hept-5-ene-2-carbaldehyde (15b) (*exo/endo* : 1.2/1)

The products were converted to the corresponding alcohols with $NaBH_4$ and enantiomeric excess was determined by HPLC using CHIRALPAK AD-H column, *n*-Hex/IPA = 95/5; flow rate 1.0 ml/min; 230 nm; *exo* isomer (t_{major} = 40.40 min, t_{minor} = 42.49 min), *endo* isomer (t_{major} = 44.47 min, t_{minor} = 57.50 min).

^{1}H NMR ($CDCl_3$, 400MHz) δ 9.83 (d, 1.2H, *J* = 1.83 Hz), 9.56 (d, 1H, *J* = 1.83 Hz), 8.06 (d, 2H, *J* = 8.70 Hz), 8.0 (d, 2.2H, *J* = 8.70 Hz), 7.34 (d, 2H, *J* = 8.70 Hz), 7.21 (d, 2.2H, *J* = 8.70 Hz), 6.35 (dd, 1H, *J* = 5.50, 3.21 Hz), 6.32 (dd, 1.2H, *J* = 5.50, 3.21 Hz), 6.12 (dd, 1H, *J* = 5.50, 2.75 Hz), 5.96 (dd, 1.1H, *J* = 5.50, 2.75 Hz), 3.80 (t, 1H, *J* = 3.89 Hz), 3.35 (s, 1H), 3.22 (m, 1.2H), 3.17 (s, 1.2H), 3.13–3.10 (m, 2H), 2.89–2.87 (m, 1H), 2.55 (d, 1.2H, *J* = 4.58 Hz), 1.70–1.67 (m, 1H), 1.63–1.60 (m, 1H), 1.53 (brs, 2.2H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz) 202.1, 201.5, 151.5, 150.5, 146.3, 146.2, 138.9, 136.8, 135.8, 133.8, 128.5 (2C), 128.1 (2C), 123.6 (2C), 123.2 (2C), 61.03, 59.4, 48.3, 47.8, 47.5, 47.03, 45.4, 45.3, 45.02, 44.8 ppm.

(1S,2R,3S,4R)-3-methylbicyclo[2.2.1]hept-5-ene-2-carbaldehyde (11) and (1R,2R,3S,4S)-3-methylbicyclo[2.2.1]hept-5-ene-2-carbaldehyde (12) (*exo/endo* : 1/1.2)

Prepared according to the general procedure with (*E*)-crotonaldehyde.The enantiomeric excess was determined by GC using β-DEX chiral column. ^{1}H NMR (C_6H_6, 400MHz) δ 9.43 (brs, 1H), 9.17 (d, 1.2H, *J* = 1.91 Hz), 5.97–5.94 (m, 1.2H), 5.88–5.85 (m, 2H), 5.77–5.76 (m, 1.2H), 2.68 (brs, 1H), 2.62 (brs, 1H), 2.38 (s, 1H), 2.16–2.12 (m, 2.2H), 1.90–1.88 (m, 1H), 1.60–1.55 (m, 1.2H), 1.33 (brs, 1H), 1.26–1.18 (m, 3H), 1.13 (d, 1.2H, *J* = 8.39 Hz), 0.84 (d, 3.2H, *J* = 6.10 Hz), 0.65 (d, 3H, *J* = 6.87 Hz) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz) 202.5, 201.7, 138.6, 136.4, 135.6, 132.7, 61.2, 59.9, 49.0, 47.6, 47.5, 45.9, 45.2, 45.1, 36.0, 35.4, 20.7, 18.7.

References

[1] T. O. Kristense, K. Vestli, M. G. Jakobsen, F. K. Hansen, T. Hansen, *J. Org. Chem.* 75 (2010) 162.

Mass Spectra of Compounds

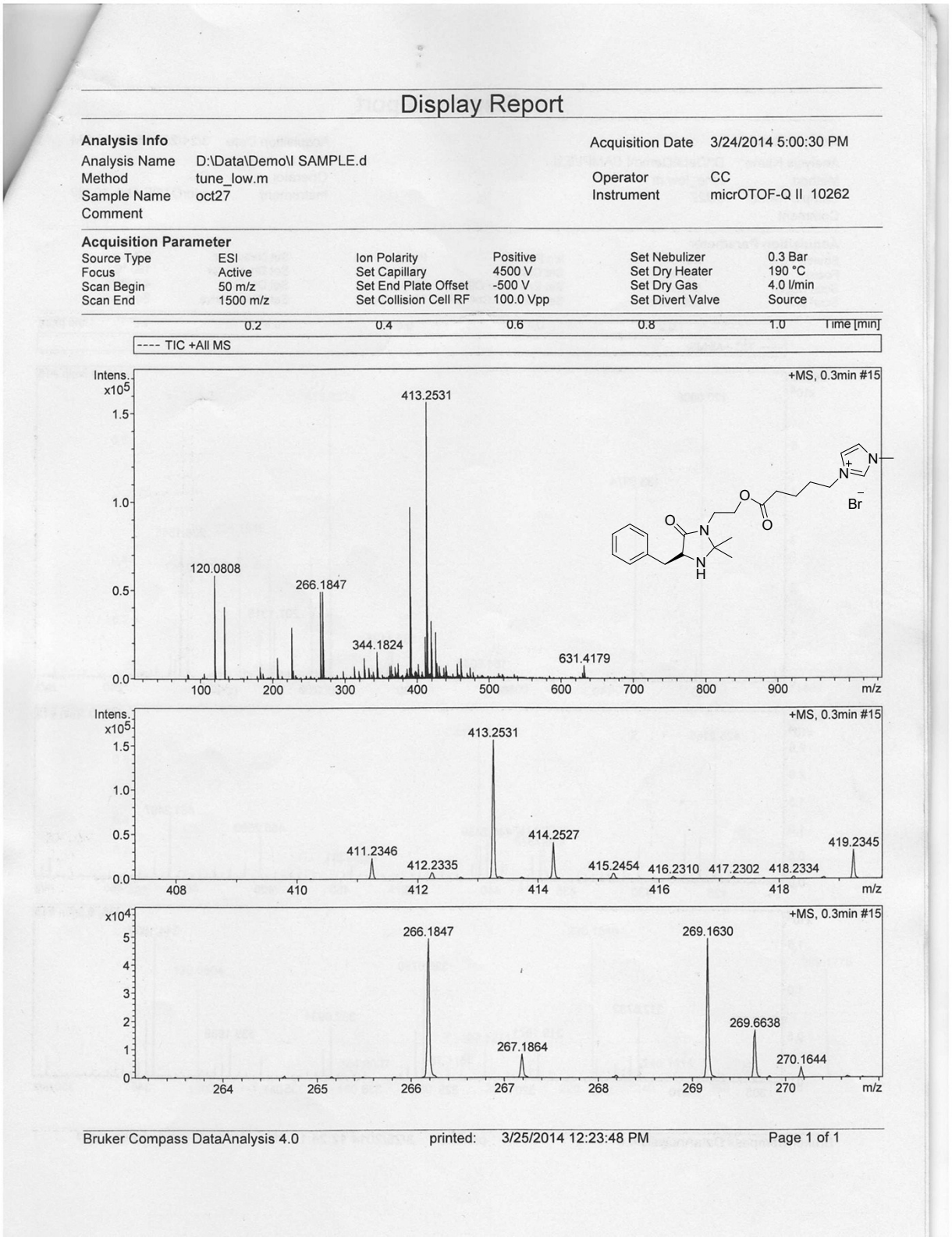


Figure 1 : HRMS data of IL 6.

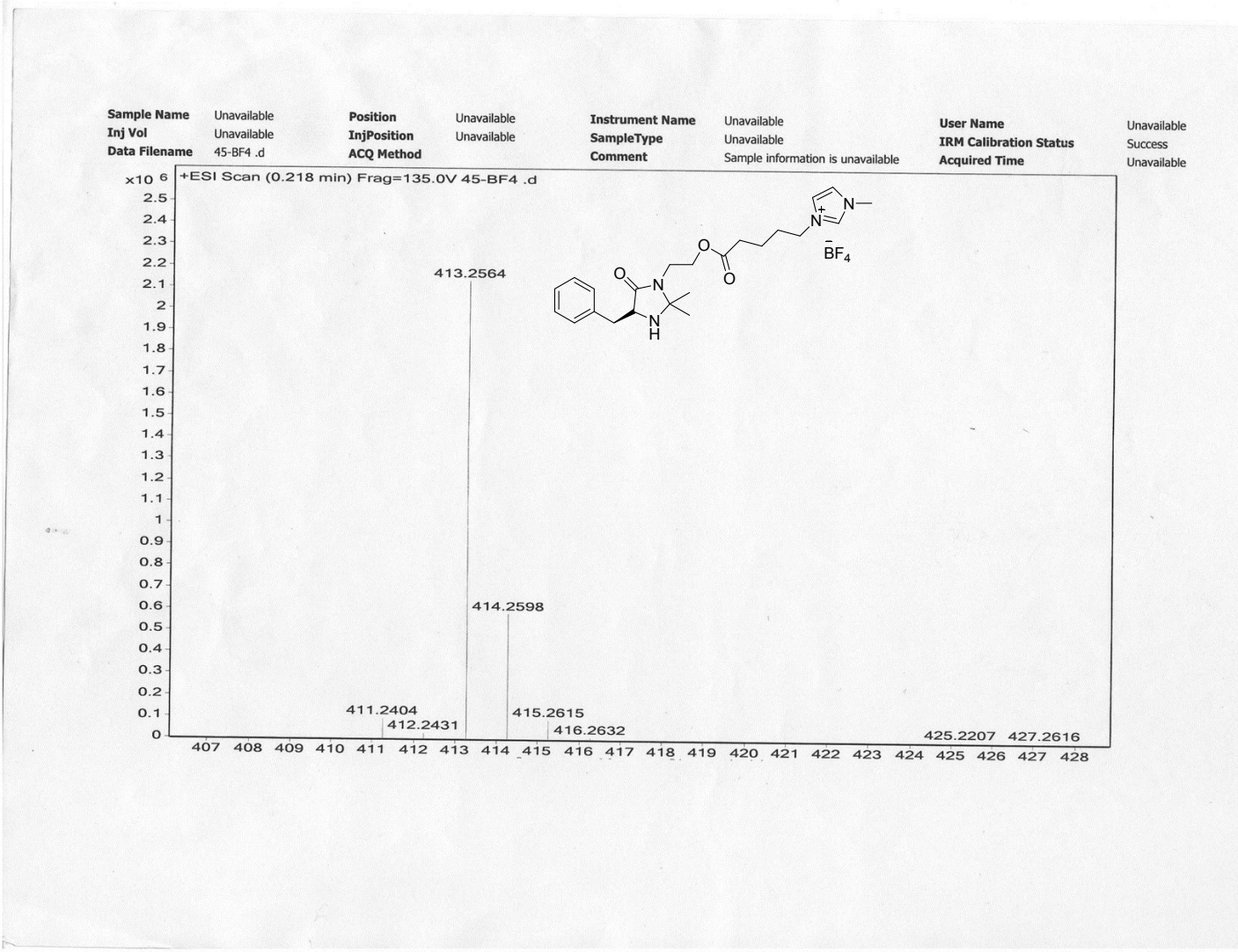


Figure 2 : HRMS data of IL 7.

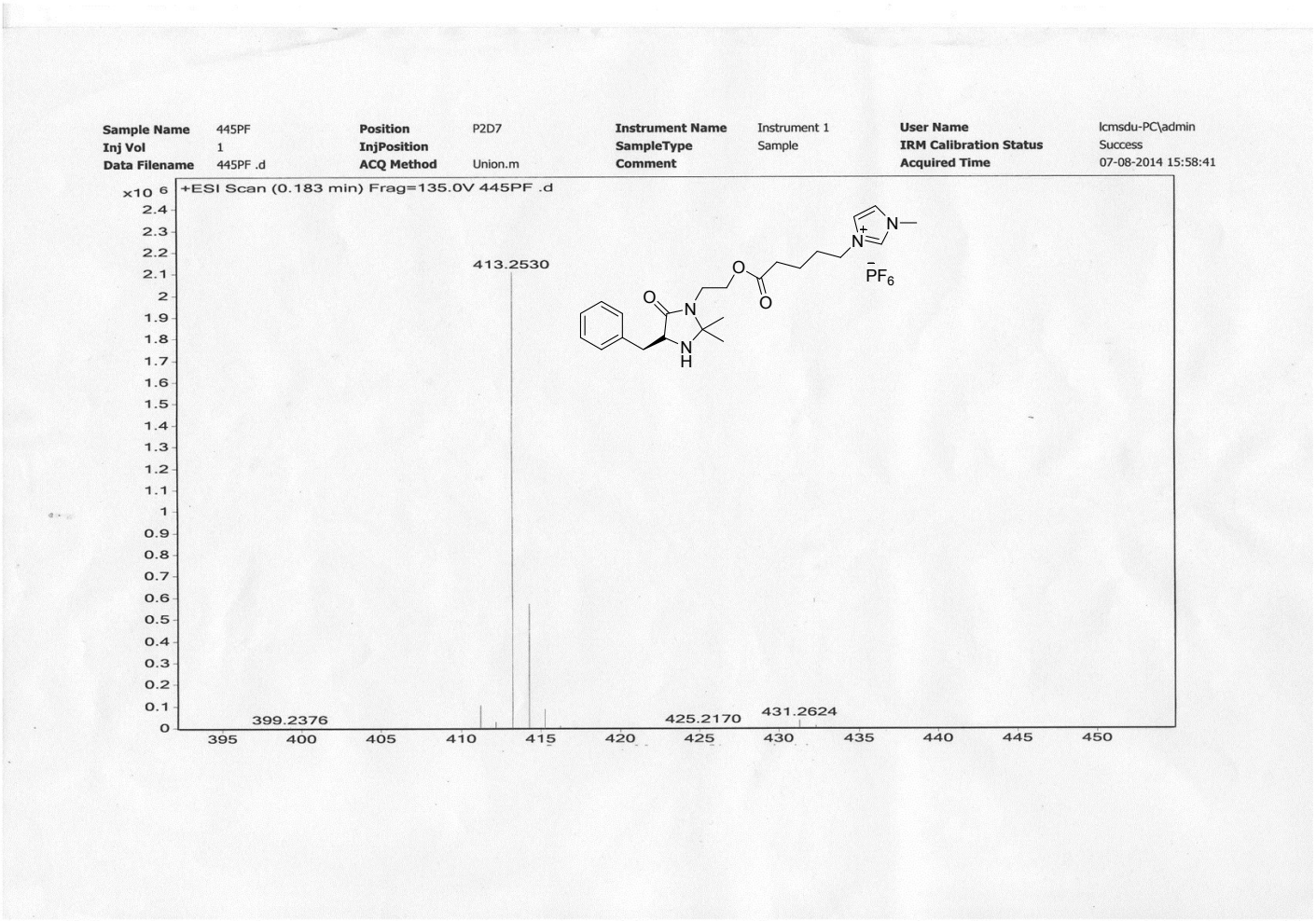


Figure 3 : HRMS data of IL 8.

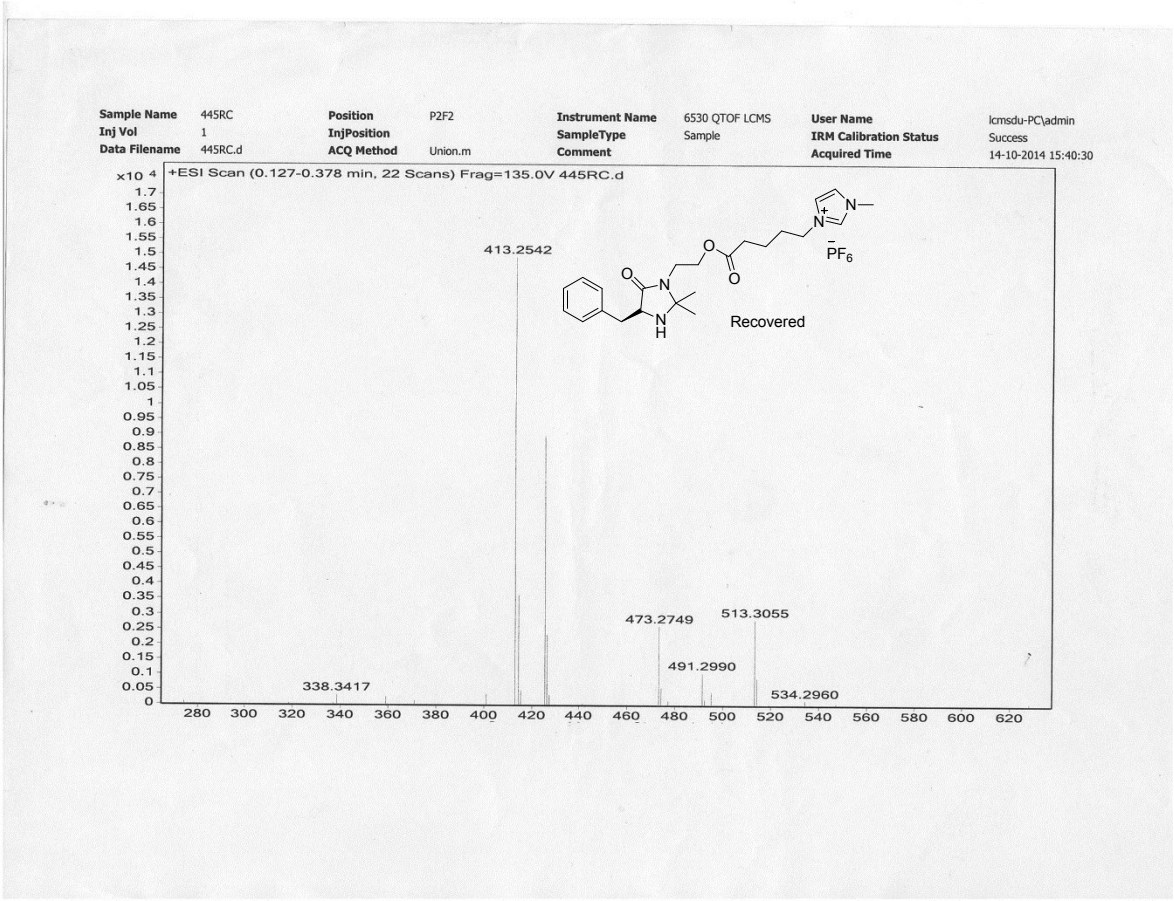


Figure 4 : HRMS data of recovered IL 8 after catalytic reaction.

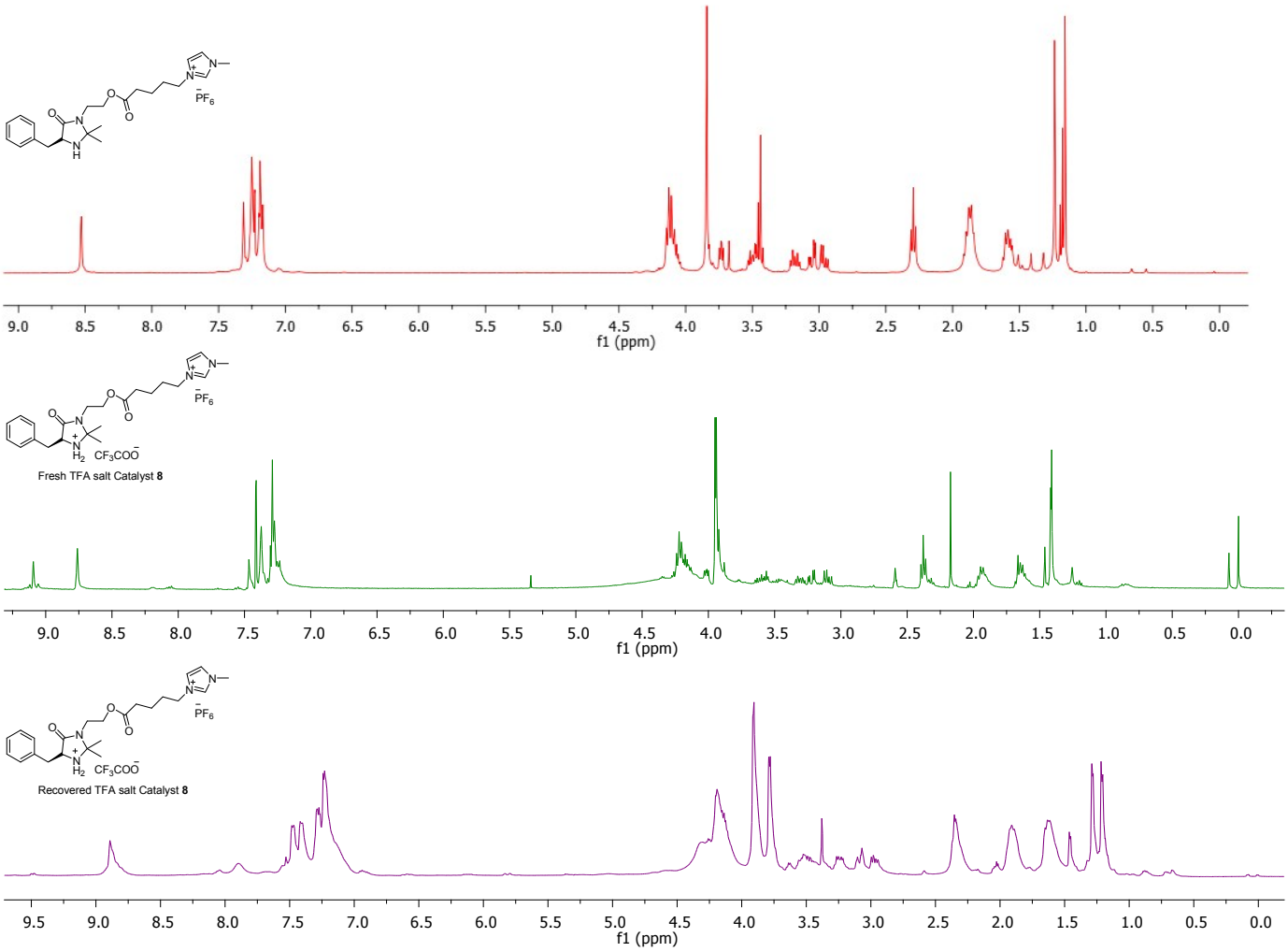


Figure 5. ^{1}H and fresh ionic liquids, its TFA salt and recovered TFA salt

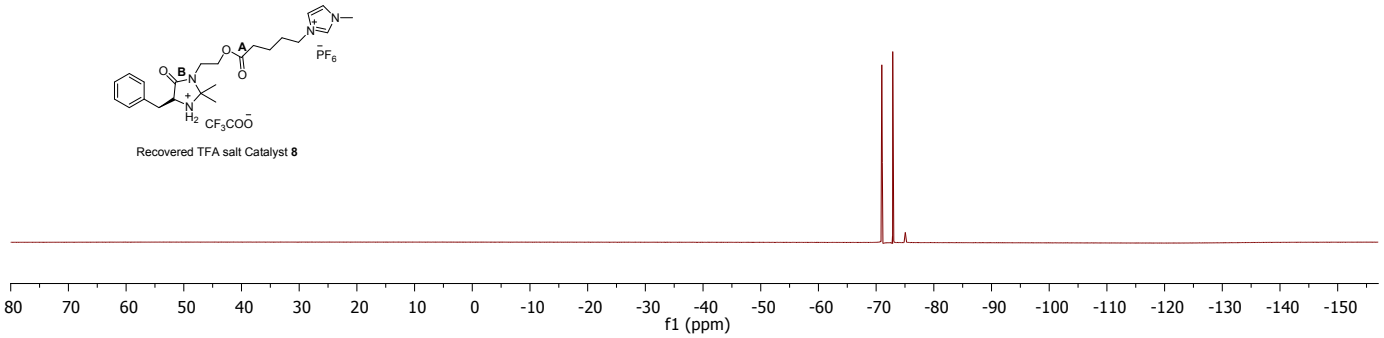
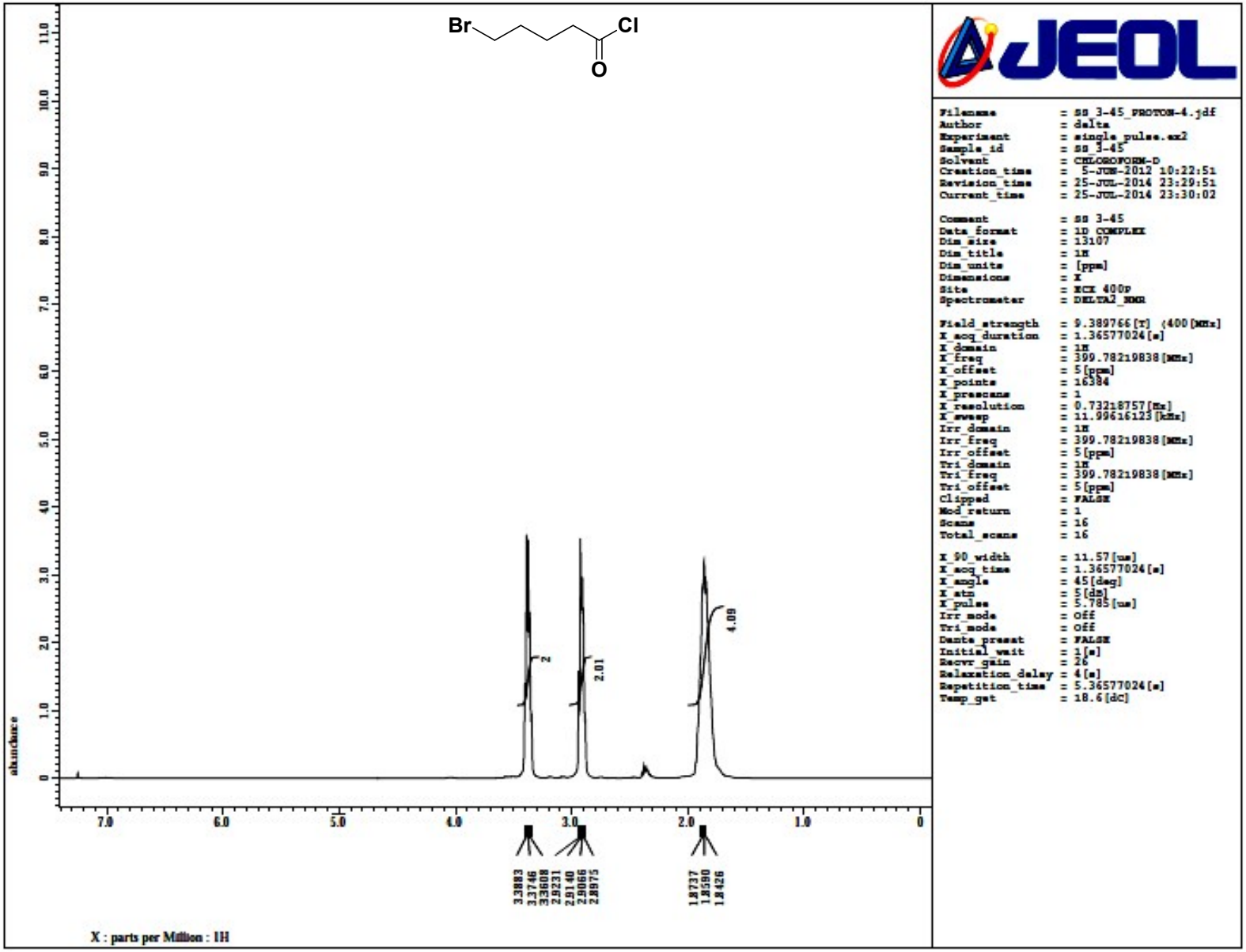


Figure 6 : ^{19}F NMR of recovered IL 8.TFA salt.



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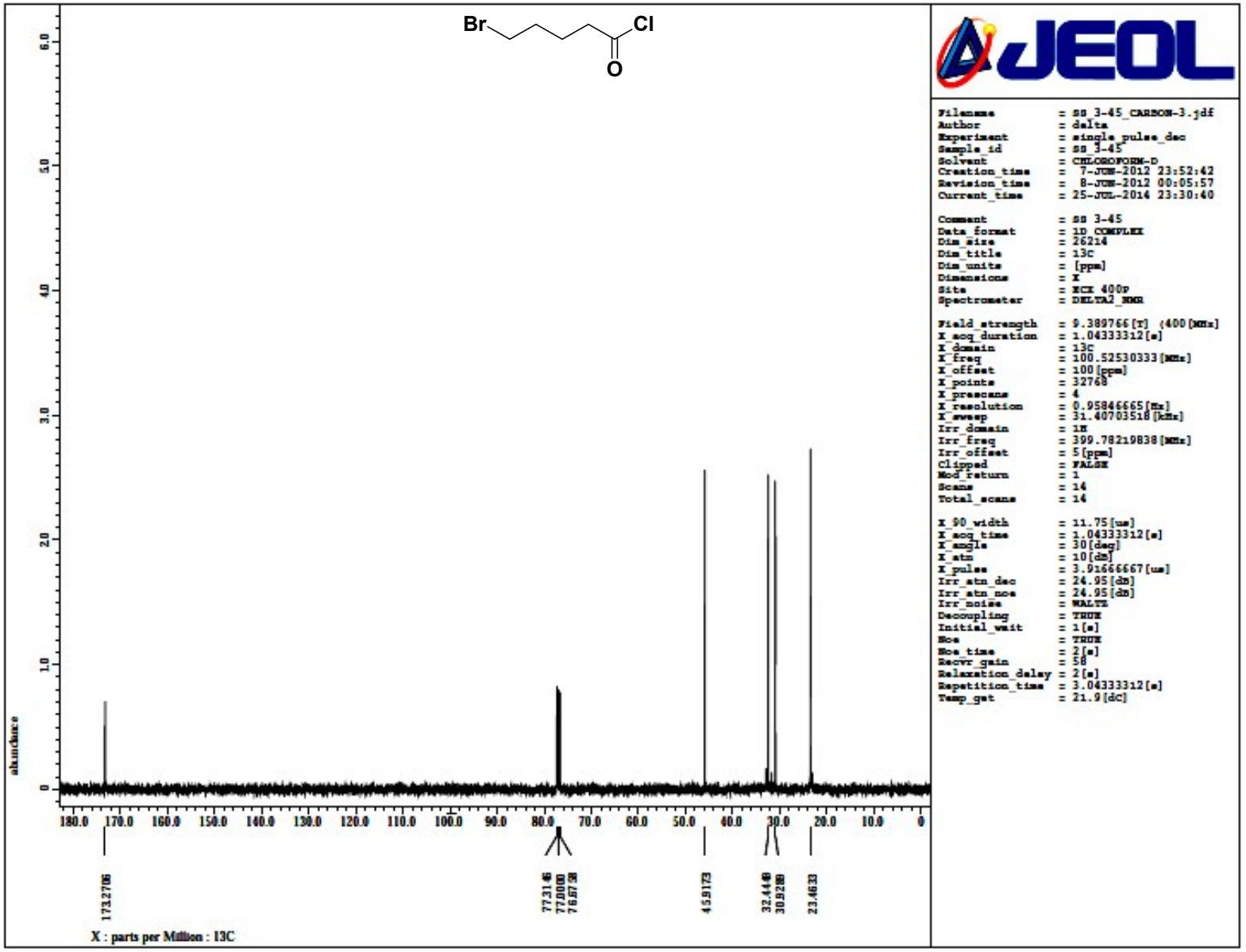

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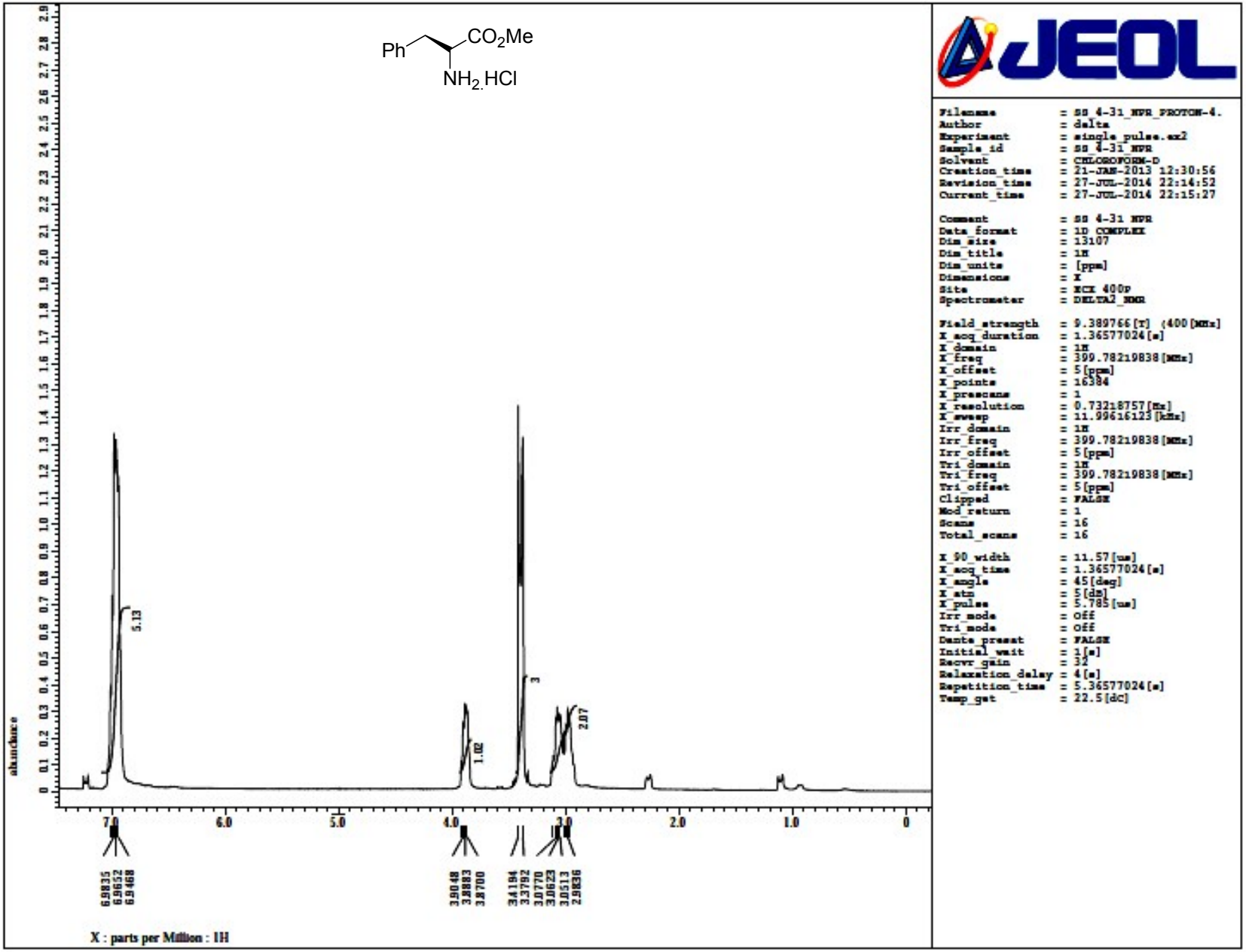

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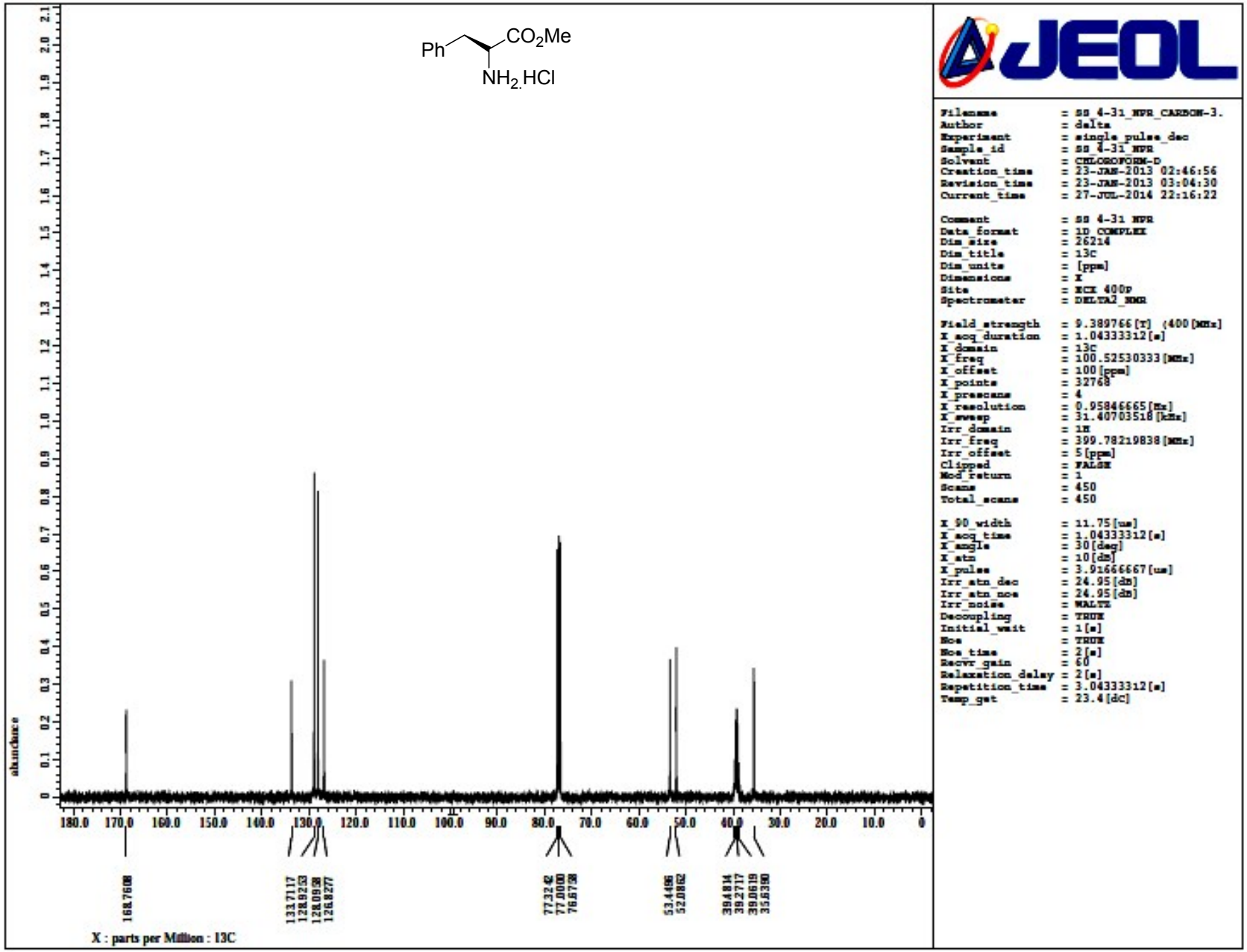


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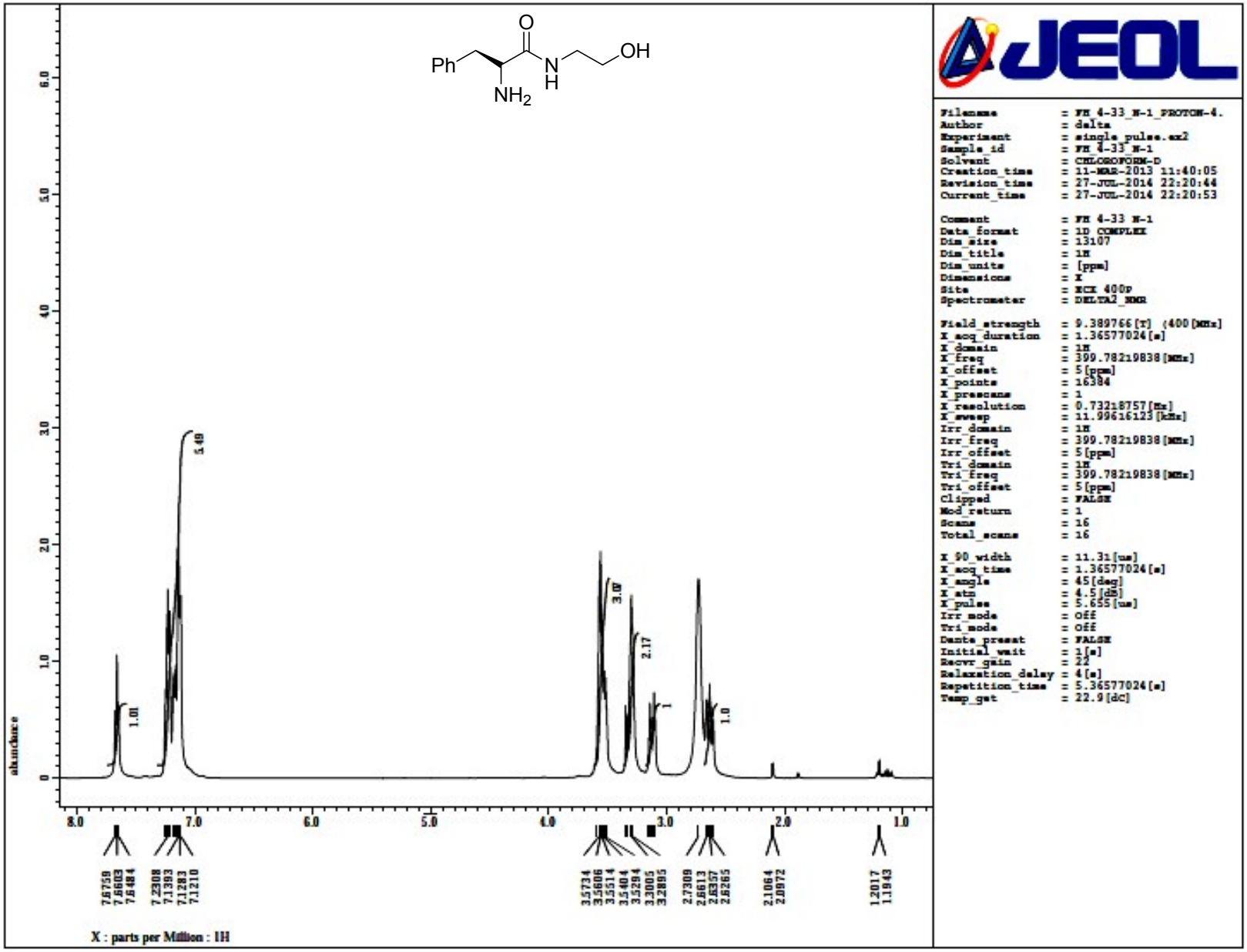
Solvent           : CHLOROFORM-D
Creation_time     : 23-JAN-2013 02:46:56
Revision_time     : 23-JAN-2013 03:04:30
Current_time      : 27-JUL-2014 22:16:22

Comment           : SS 4-31 NPR
Data_format       : 1D COMPLEX
Dim_size          : 26214
Dim_title         : 13C
Dim_units         : [ppm]
Dimensions        : X
Site              : NCX 400P
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             : 450
Total_scans       : 450

X_90_width        : 11.75[us]
X_acq_time        : 1.04333312[s]
X_angle           : 30[deg]
X_atn             : 10[dB]
X_pulse           : 3.91666667[us]
Irr_atn_dec       : 24.95[dB]
Irr_atn_noe       : 24.95[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          : 23.4[dC]
```



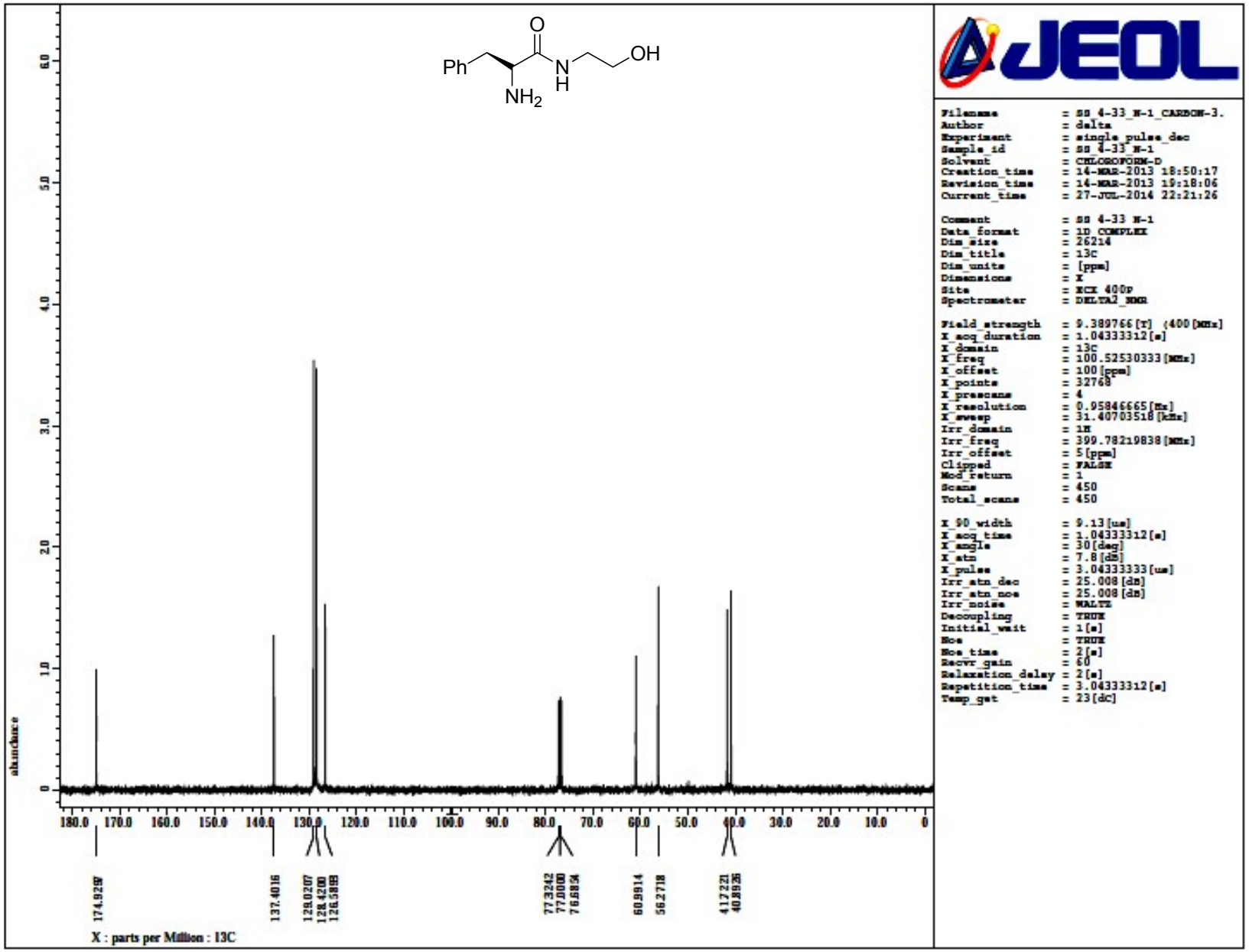
JEOL

```
Filename          = FH_4-33_N-1_PROTON-4.
Author            = delta
Experiment        = single_pulse.ex2
Sample_id         = FH_4-33_N-1
Solvent           = CHLOROFORM-D
Creation_time     = 11-MAR-2013 11:40:05
Revision_time     = 27-JUL-2014 22:20:44
Current_time      = 27-JUL-2014 22:20:53

Comment           = FH 4-33 N-1
Data_format       = 1D COMPLEX
Dim_size          = 13107
Dim_title         = 1H
Dim_units         = [ppm]
Dimensions        = X
Site              = NCX 400p
Spectrometer      = DELTA2_NMR

Field_strength    = 9.389766[T] (400[MHz])
X_acq_duration    = 1.36577024[s]
X_domain          = 1H
X_freq            = 399.78219838[MHz]
X_offset          = 5[ppm]
X_points          = 16384
X_prescans        = 1
X_resolution      = 0.73218757[Hz]
X_sweep           = 11.99616123[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             = 16
Total_scans       = 16

X_90_width        = 11.31[us]
X_acq_time        = 1.36577024[s]
X_angle           = 45[deg]
X_atn             = 4.5[dB]
X_pulse           = 5.655[us]
Irr_mode          = Off
Tri_mode          = Off
Dante_presat      = FALSE
Initial_wait      = 1[s]
Recvr_gain        = 22
Relaxation_delay  = 4[s]
Repetition_time   = 5.36577024[s]
Temp_get          = 22.9[dC]
```



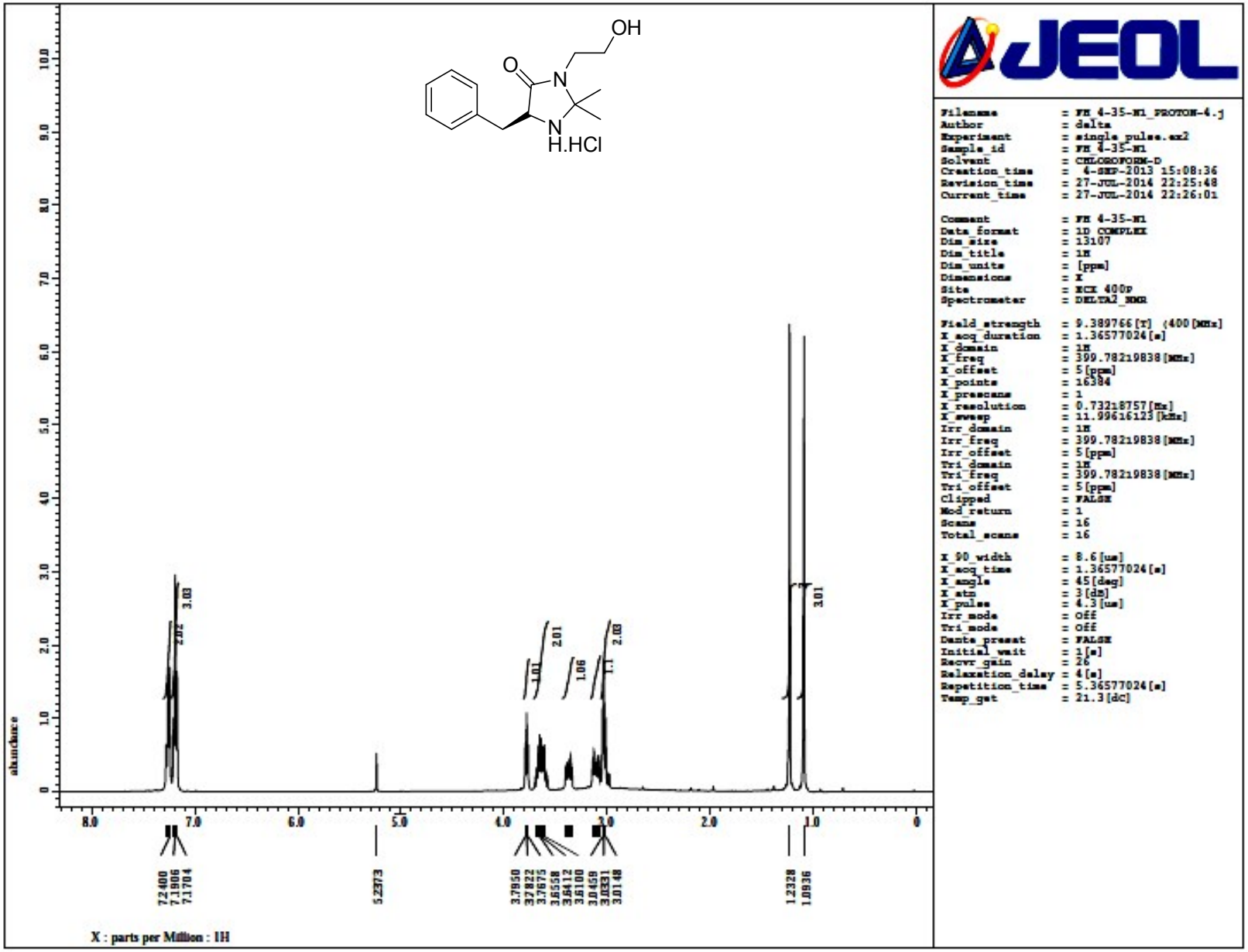
JEOL

```
Filename          : SS 4-33_N-1_CARBON-3.
Author            : delta
Experiment        : single_pulse_dec
Sample_id         : SS 4-33_N-1
Solvent           : CHLOROFORM-D
Creation_time     : 14-MAR-2013 18:50:17
Revision_time     : 14-MAR-2013 19:18:06
Current_time      : 27-JUL-2014 22:21:26

Comment           : SS 4-33 N-1
Data_format       : 1D COMPLEX
Dim_size          : 26214
Dim_title         : 13C
Dim_units         : [ppm]
Dimensions        : X
Site              : NCX 400P
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             : 450
Total_scans       : 450

X_90_width        : 9.13[us]
X_acq_time        : 1.04333312[s]
X_angle           : 30[deg]
X_atn             : 7.8[dB]
X_pulse           : 3.04333333[us]
Irr_atn_dec       : 25.00[dB]
Irr_atn_noe       : 25.00[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[dC]
```



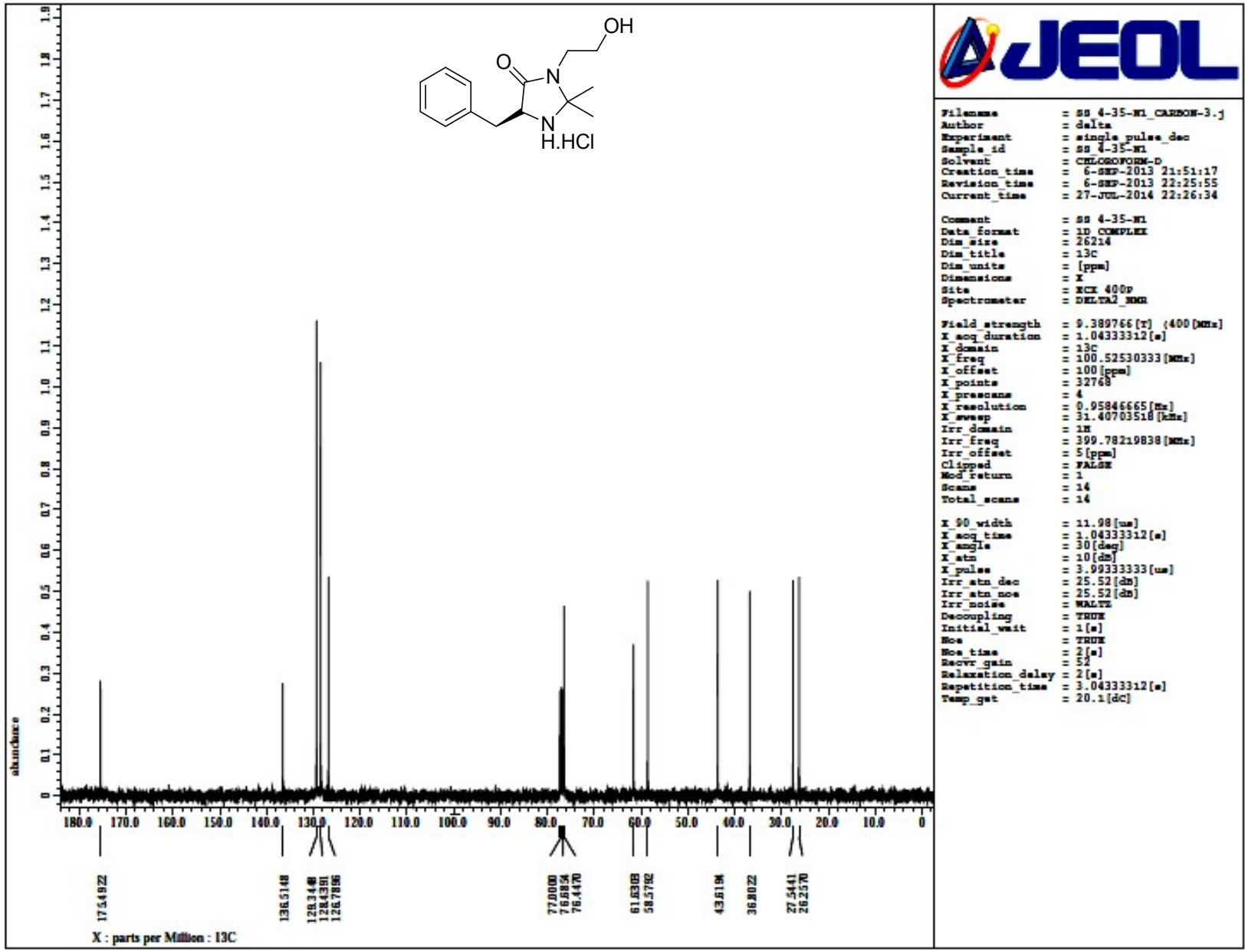
JEOL

```
Filename          = FH 4-35-N1_PROTON-4.j
Author            = delta
Experiment        = single_pulse.ex2
Sample_id         = FH 4-35-N1
Solvent           = CHLOROFORM-D
Creation_time     =  4-SEP-2013 15:08:36
Revision_time     = 27-JUL-2014 22:25:48
Current_time      = 27-JUL-2014 22:26:01

Comment           = FH 4-35-N1
Data_format       = 1D COMPLEX
Dim_size          = 13107
Dim_title         = 1H
Dim_units         = [ppm]
Dimensions        = X
Site              = NCX 400p
Spectrometer      = DELTA2_NMR

Field_strength    = 9.389766[T] (400[MHz]
X_acq_duration    = 1.36577024[s]
X_domain          = 1H
X_freq            = 399.78219838[MHz]
X_offset          = 5[ppm]
X_points          = 16384
X_prescans        = 1
X_resolution      = 0.73218757[Hz]
X_sweep           = 11.99616123[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             = 16
Total_scans       = 16

X_90_width        = 8.6[us]
X_acq_time        = 1.36577024[s]
X_angle           = 45[deg]
X_atn             = 3[dB]
X_pulse           = 4.3[us]
Irr_mode          = Off
Tri_mode          = Off
Dante_presat      = FALSE
Initial_wait      = 1[s]
Recvr_gain        = 26
Relaxation_delay  = 4[s]
Repetition_time   = 5.36577024[s]
Temp_get          = 21.3[dC]
```

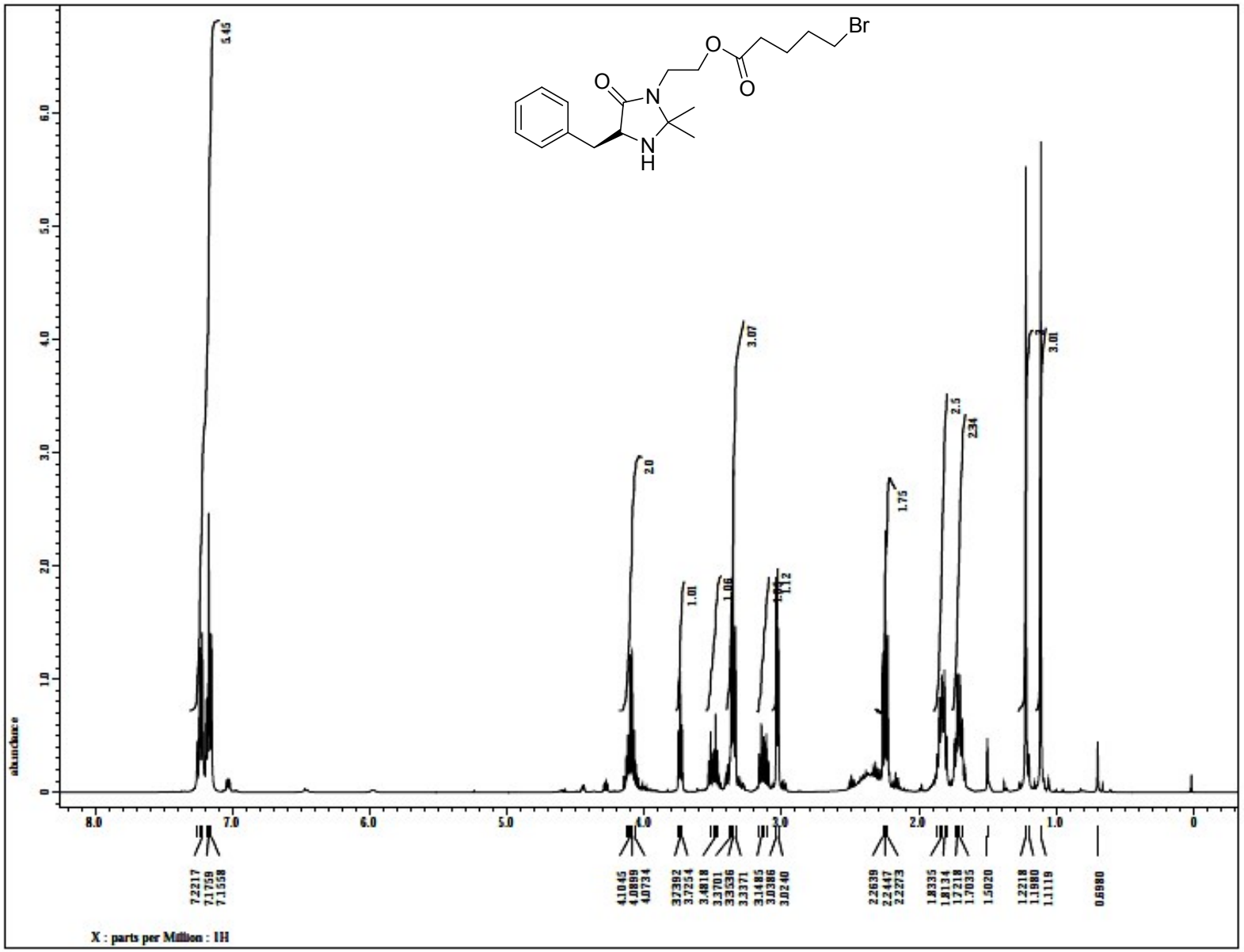


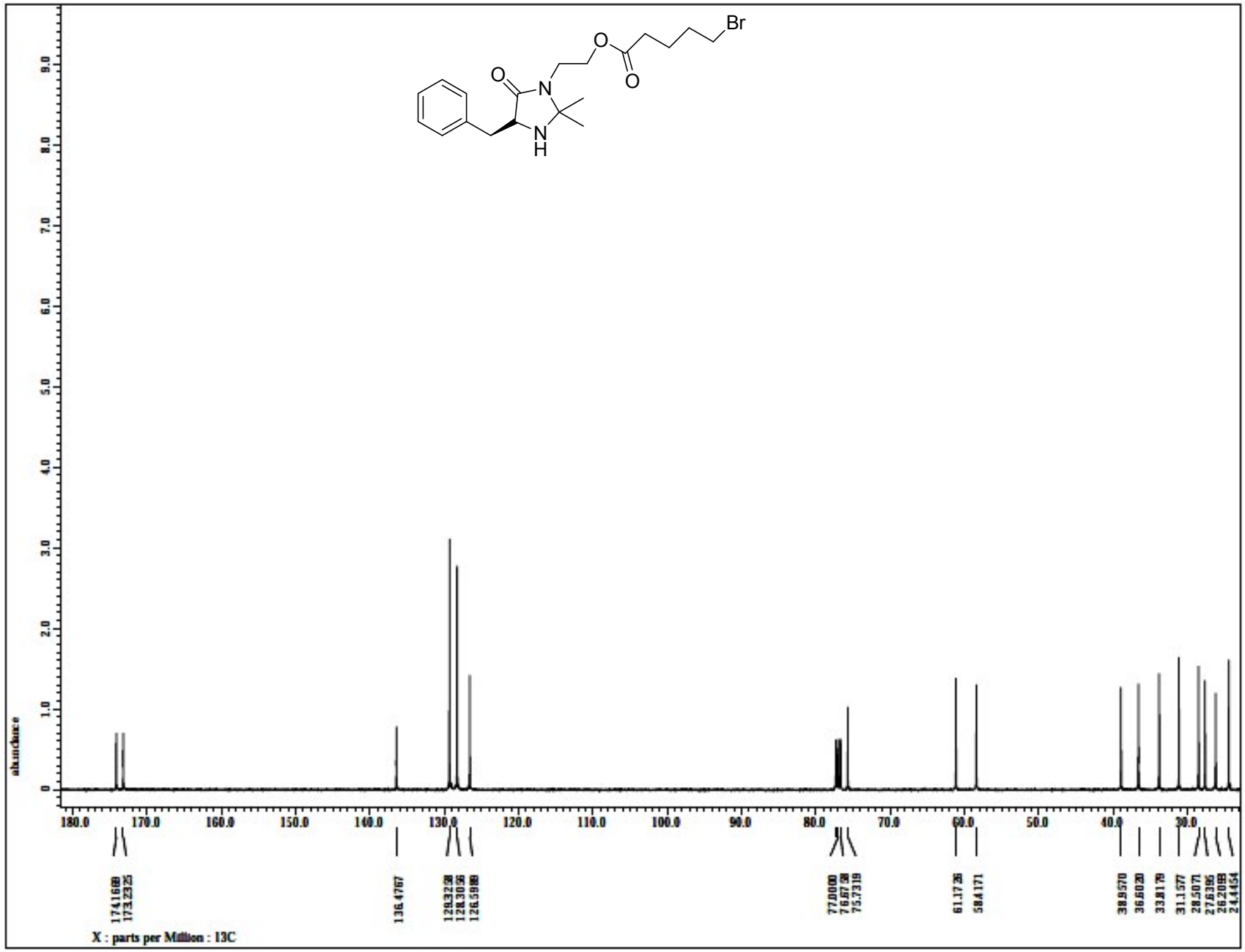

```
Filename          = SS 4-35-N1_CARBON-3.j
Author            = delta
Experiment        = single_pulse_dec
Sample_id         = SS 4-35-N1
Solvent           = CHLOROFORM-D
Creation_time     =  6-SEP-2013 21:51:17
Revision_time     =  6-SEP-2013 22:25:55
Current_time      = 27-JUL-2014 22:26:34

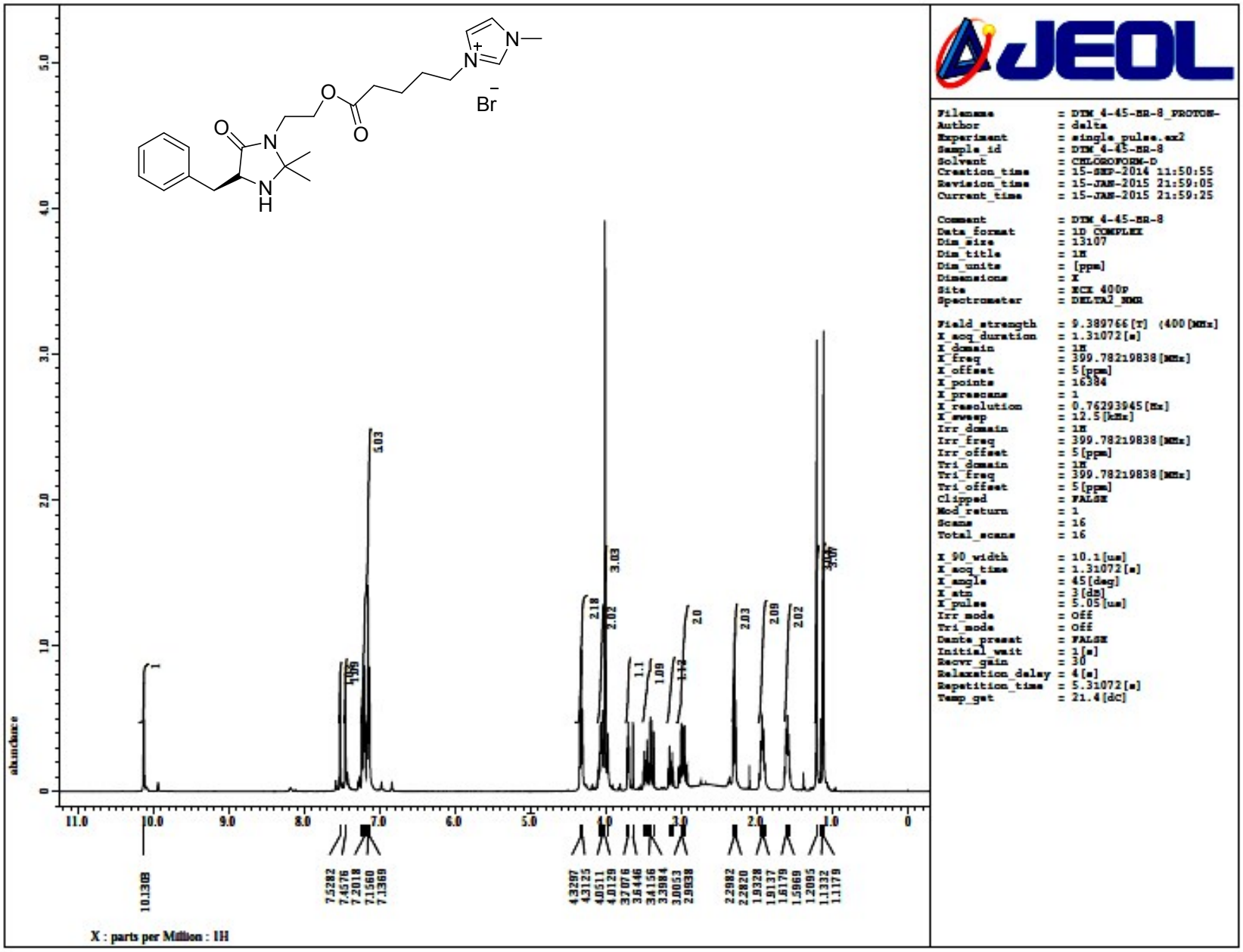
Comment           = SS 4-35-N1
Data_format       = 1D COMPLEX
Dim_size          = 26214
Dim_title         = 13C
Dim_units         = [ppm]
Dimensions        = X
Site              = NCX 400P
Spectrometer      = DELTA2_NMR

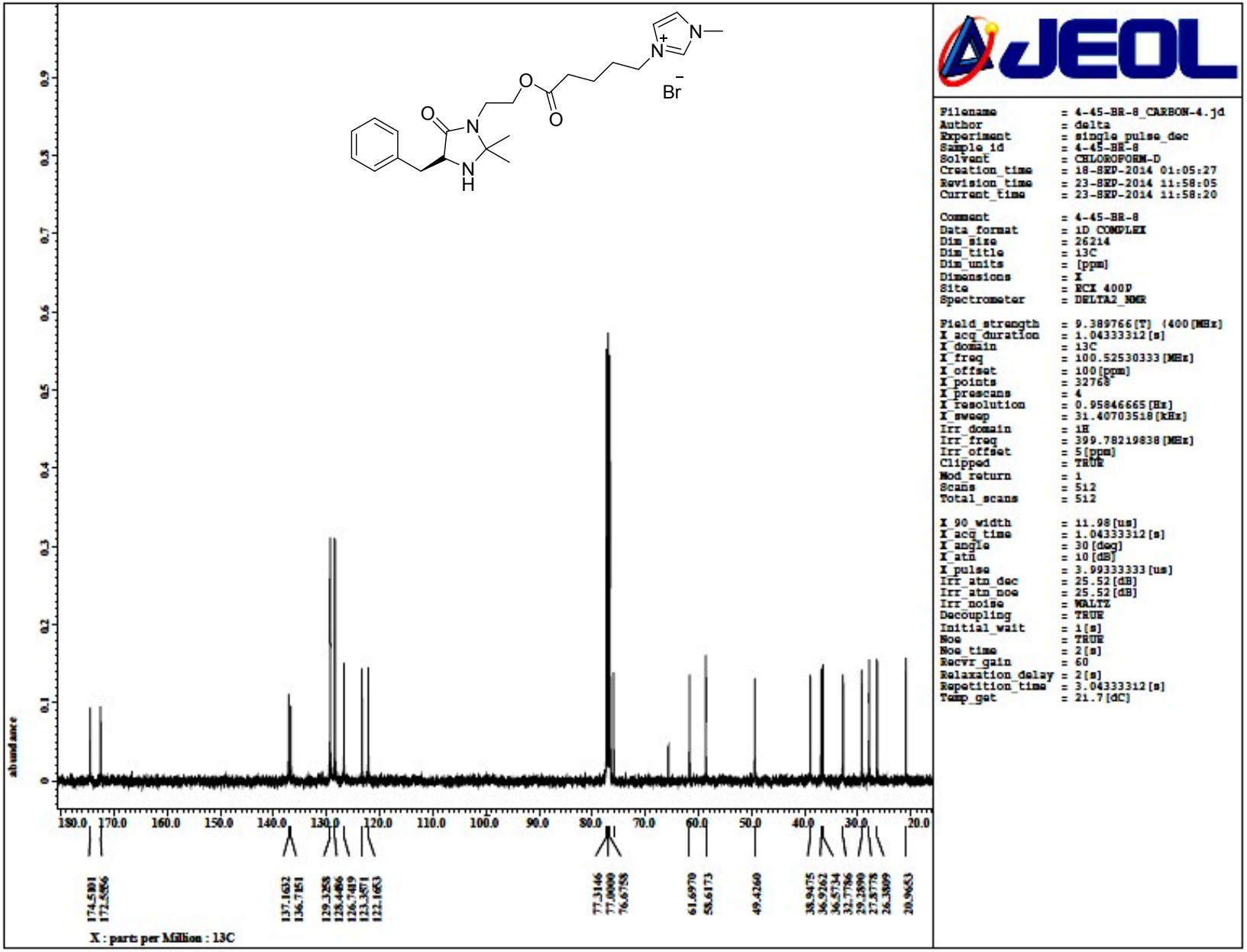
Field_strength    = 9.389766[T]  (400[MHz]
X_acq_duration    = 1.04333312[s]
X_domain          = 13C
X_freq            = 100.52530333[MHz]
X_offset          = 100[ppm]
X_points          = 32768
X_prescans        = 4
X_resolution      = 0.95846665[Hz]
X_sweep           = 31.40703518[kHz]
Irr_domain        = 1H
Irr_freq          = 399.78219838[MHz]
Irr_offset        = 5[ppm]
Clipped           = FALSE
Mod_return        = 1
Scans             = 14
Total_scans       = 14

X_90_width        = 11.98[us]
X_acq_time        = 1.04333312[s]
X_angle           = 30[deg]
X_atn             = 10[dB]
X_pulse           = 3.99333333[us]
Irr_atn_dec       = 25.52[dB]
Irr_atn_noe       = 25.52[dB]
Irr_noise         = WALTZ
Decoupling        = TRUE
Initial_wait      = 1[s]
Noe               = TRUE
Noe_time          = 2[s]
Recvr_gain        = 52
Relaxation_delay  = 2[s]
Repetition_time   = 3.04333312[s]
Temp_get          = 20.1[dC]
```


Br
O
O
O
N
N
H
abundance
X : parts per Million : 1H


Br
O
O
O
N
N
H
abundance
X : parts per Million : 13C


Br
abundance
X : parts per Million : 1H
Filename = DTM_4-45-BR-8_PROTON-
Author = delta
Experiment = single_pulse.ex2
Sample_id = DTM_4-45-BR-8
Solvent = CHLOROFORM-D
Creation_time = 15-SEP-2014 11:50:55
Revision_time = 15-JAN-2015 21:59:05
Current_time = 15-JAN-2015 21:59:25
Comment = DTM_4-45-BR-8
Data_format = 1D COMPLEX
Dim_size = 13107
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = NCH 400P
Spectrometer = DELTA2_NMR
Field_strength = 9.389766[T] (400[MHz]
X_acq_duration = 1.31072[s]
X_domain = 1H
X_freq = 399.78219838[MHz]
X_offset = 5[ppm]
X_points = 16384
X_prescans = 1
X_resolution = 0.76293945[Hz]
X_sweep = 12.5[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 = 16
Total_scans = 16
X_90_width = 10.1[us]
X_acq_time = 1.31072[s]
X_angle = 45[deg]
X_atn = 3[dB]
X_pulse = 5.05[us]
Irr_mode = Off
Tri_mode = Off
Dante_presat = FALSE
Initial_wait = 1[s]
Recvr_gain = 30
Relaxation_delay = 4[s]
Repetition_time = 5.31072[s]
Temp_get = 21.4[dC]

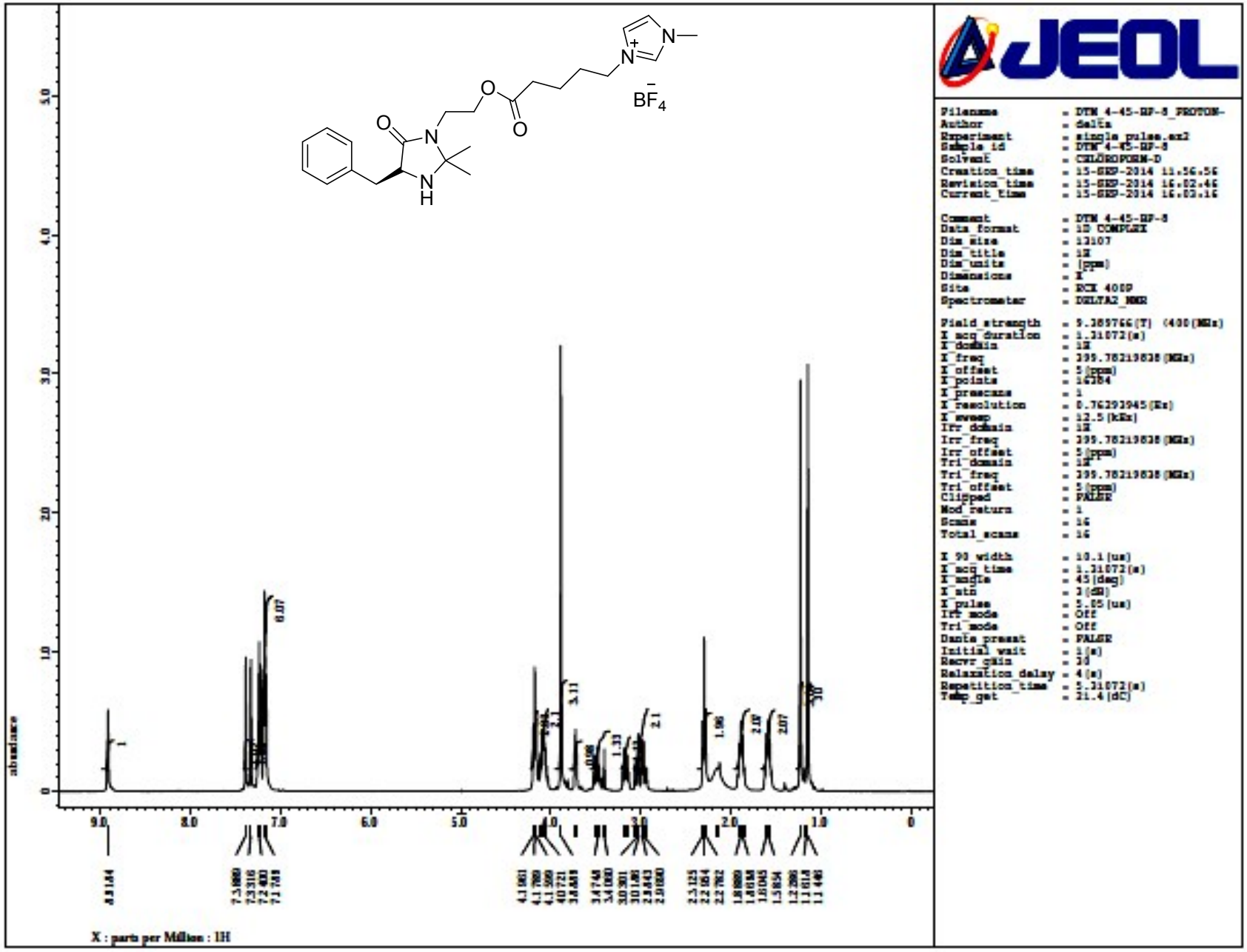


Filename = 4-45-BR-8_CARBON-4.jd
Author = delta
Experiment = single_pulse_dec
Sample_id = 4-45-BR-8
Solvent = CHLOROFORM-D
Creation_time = 18-SEP-2014 01:05:27
Revision_time = 23-SEP-2014 11:58:05
Current_time = 23-SEP-2014 11:58:20

Comment = 4-45-BR-8
Data_format = 1D COMPLEX
Dim_size = 26214
Dim_title = 13C
Dim_units = [ppm]
Dimensions = X
Site = RCI 400P
Spectrometer = DELTA2_NMR

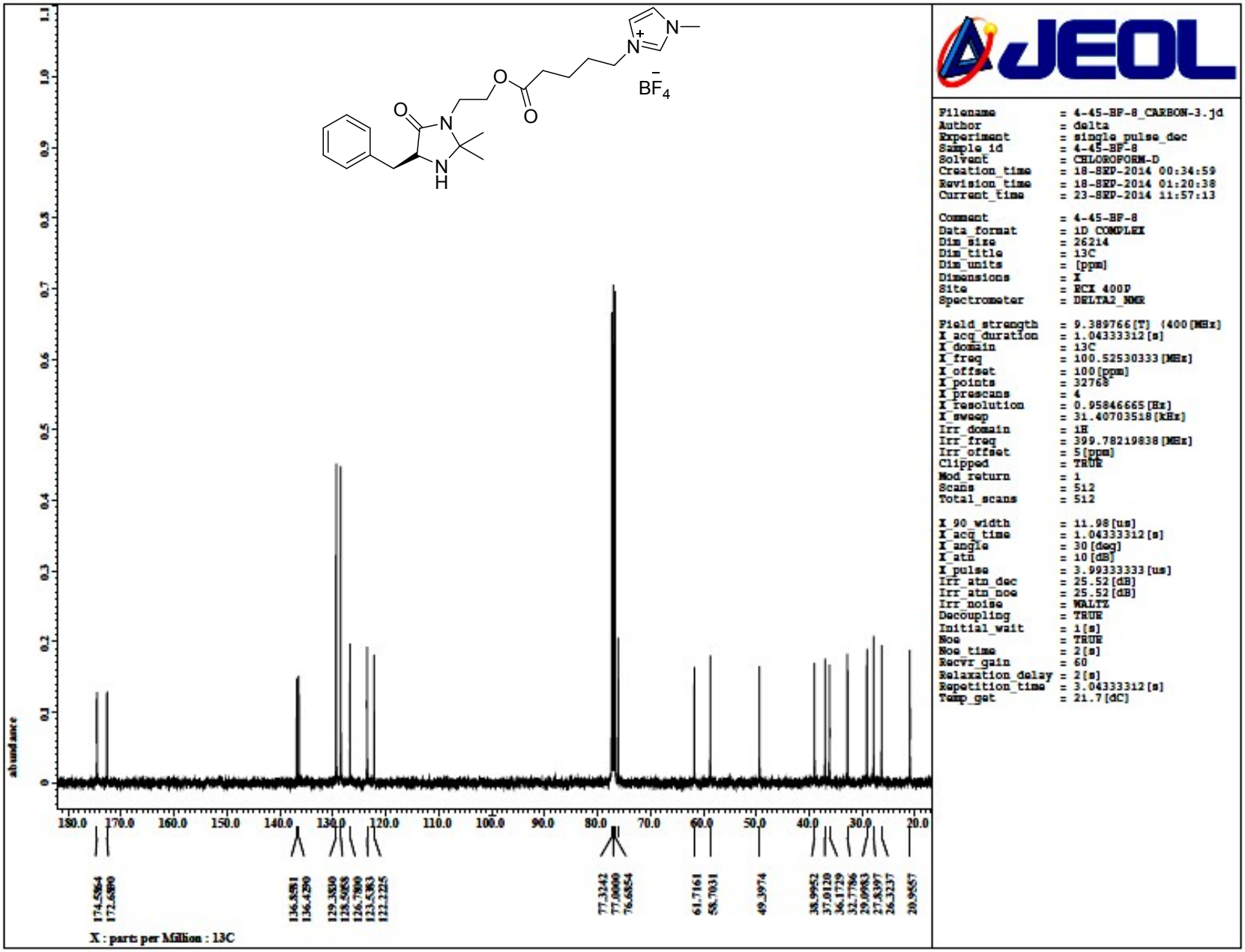
Field_strength = 9.389766[T] (400[MHz]
X_acq_duration = 1.04333312[s]
X_domain = 13C
X_freq = 100.52530333[MHz]
X_offset = 100[ppm]
X_points = 32768
X_prescans = 4
X_resolution = 0.95846665[Hz]
X_sweep = 31.40703518[kHz]
Irr_domain = 1H
Irr_freq = 399.78219838[MHz]
Irr_offset = 5[ppm]
Clipped = TRUE
Mod_return = 1
Scans = 512
Total_scans = 512

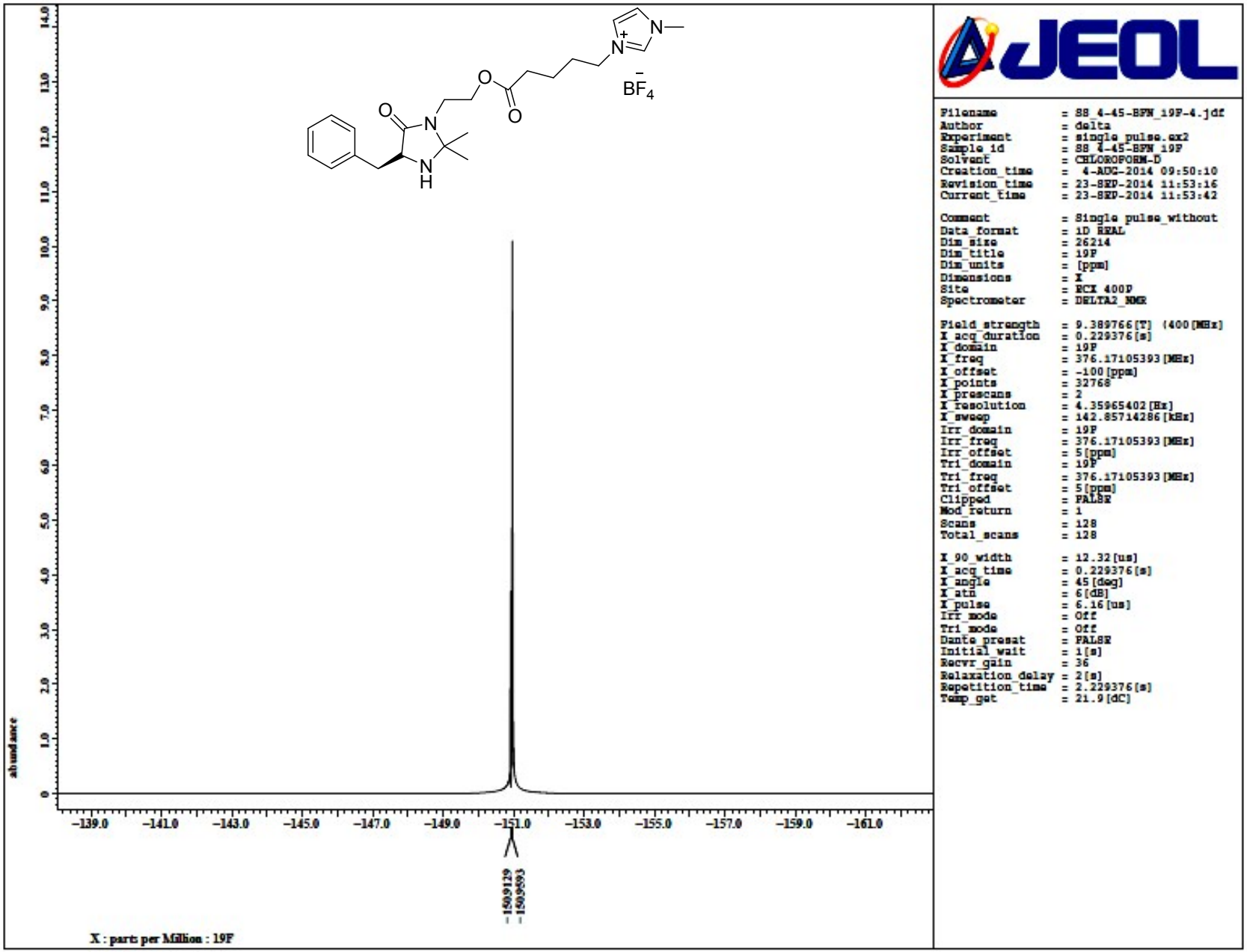
X_90_width = 11.98[us]
X_acq_time = 1.04333312[s]
X_angle = 30[deg]
X_atn = 10[dB]
X_pulse = 3.99333333[us]
Irr_atn_dec = 25.52[dB]
Irr_atn_noe = 25.52[dB]
Irr_noise = WALTZ
Decoupling = TRUE
Initial_wait = 1[s]
Noe = TRUE
Noe_time = 2[s]
Recvr_gain = 60
Relaxation_delay = 2[s]
Repetition_time = 3.04333312[s]
Temp_get = 21.7[dC]

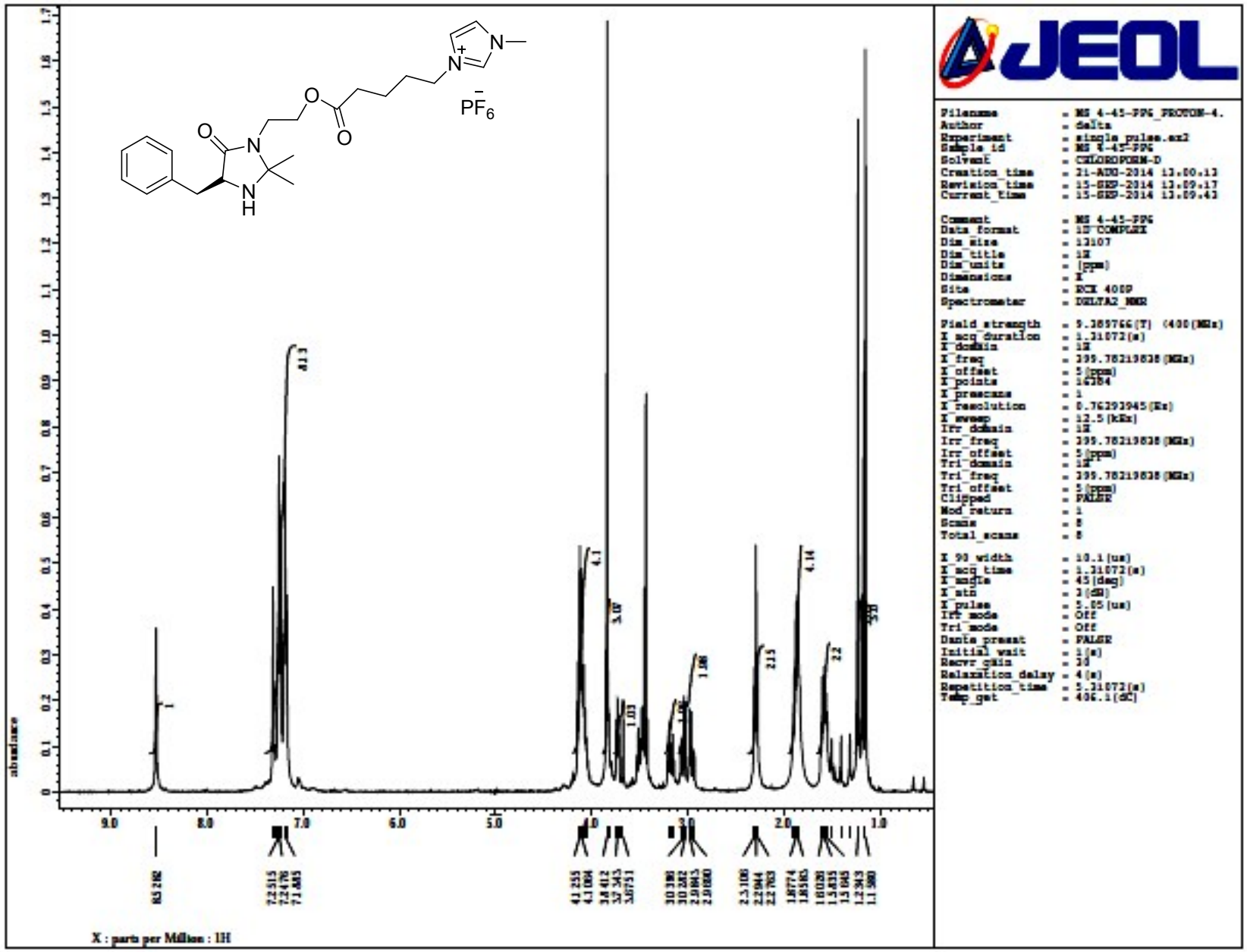


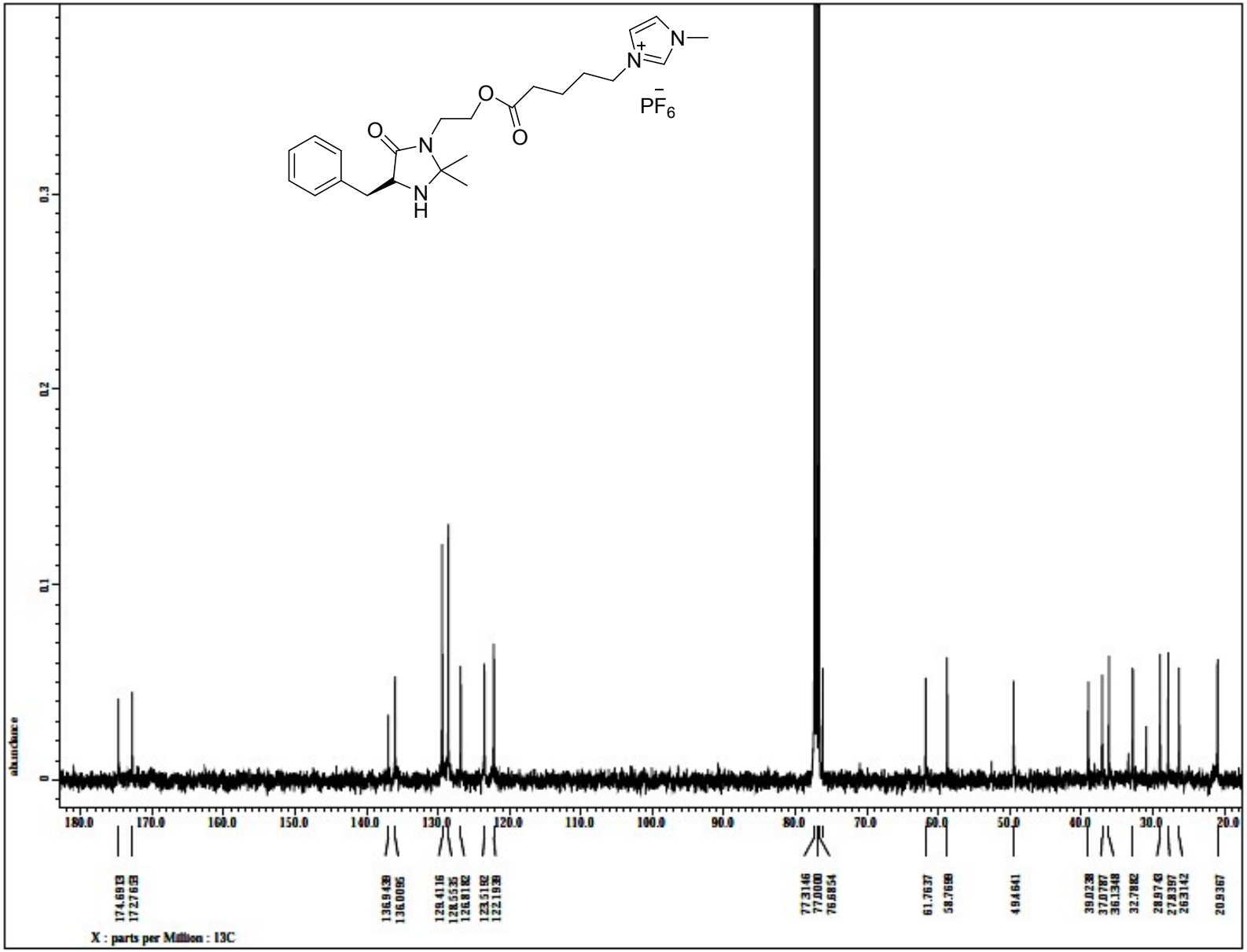
JEOL

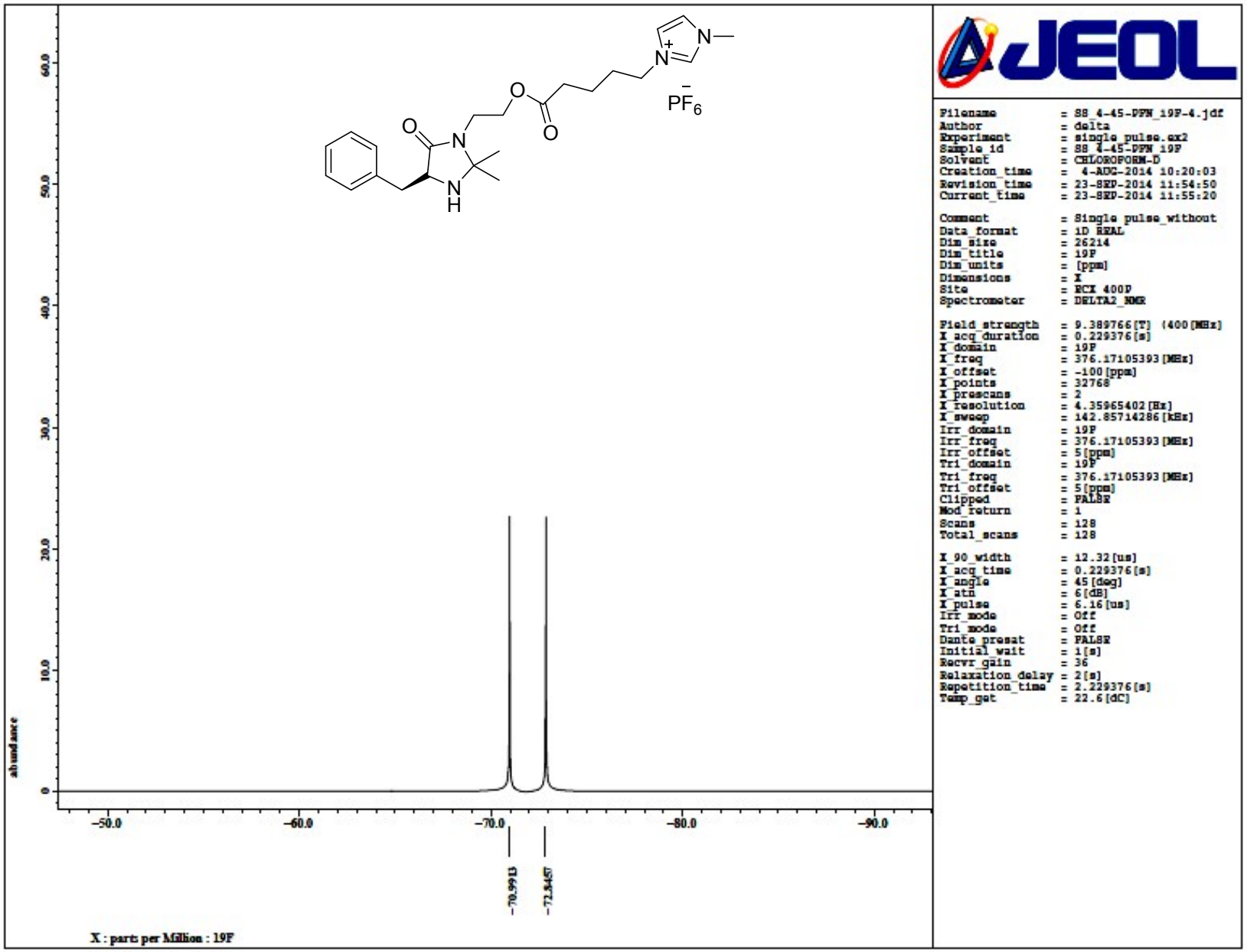
Filename	DTN 4-45-BF-8_PROTON-
Author	delta
Experiment	single_pulse.ex2
Sample_id	DTN 4-45-BF-8
Solvent	CHLOROFORM-D
Creation_time	15-SEP-2014 11.56.56
Revision_time	15-SEP-2014 16.02.46
Current_time	15-SEP-2014 16.03.16
Comment	DTN 4-45-BF-8
Data_format	1D COMPLEX
Dim_size	13107
Dim_title	1H
Dim_units	[ppm]
Dimensions	X
Site	RCX 400P
Spectrometer	DELTA2_NMR
Field_strength	9.389766(T) (400(MHz)
X_acq_duration	1.31072(s)
X_domain	1H
X_freq	399.78219638(MHz)
X_offset	5(ppm)
X_points	16384
X_prescans	1
X_resolution	0.76293945(Hz)
X_sweep	12.5(kHz)
Irr_domain	1H
Irr_freq	399.78219638(MHz)
Irr_offset	5(ppm)
Tri_domain	1H
Tri_freq	399.78219638(MHz)
Tri_offset	5(ppm)
Clipped	FALSE
Mod_return	1
Scans	16
Total_scans	16
X_90_width	10.1(us)
X_acq_time	1.31072(s)
X_angle	45(deg)
X_atn	1(dB)
X_pulse	5.05(us)
Irr_mode	Off
Tri_mode	Off
Davis_preset	FALSE
Initial_wait	1(s)
Recvr_gain	30
Relaxation_delay	4(s)
Repetition_time	5.31072(s)
Temp_get	21.4(dC)


JEOL
Filename = 4-45-BF-8_CARBON-3.jd
Author = delta
Experiment = single_pulse_dec
Sample_id = 4-45-BF-8
Solvent = CHLOROFORM-D
Creation_time = 18-SEP-2014 00:34:59
Revision_time = 18-SEP-2014 01:20:38
Current_time = 23-SEP-2014 11:57:13
Comment = 4-45-BF-8
Data_format = 1D COMPLEX
Dim_size = 26214
Dim_title = 13C
Dim_units = [ppm]
Dimensions = X
Site = RCX 400P
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 = TRUE
Mod_return = 1
Scans = 512
Total_scans = 512
X_90_width = 11.98[us]
X_acq_time = 1.04333312[s]
X_angle = 30[deg]
X_atn = 10[dB]
X_pulse = 3.99333333[us]
Irr_atn_dec = 25.52[dB]
Irr_atn_noe = 25.52[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 = 21.7[dC]
BF4
abundance
X : parts per Million : 13C


abundance
X : parts per Million : 19F
-150.9129
-150.9593
Filename = SS 4-45-BFN 19F-4.jdf
Author = delta
Experiment = single_pulse.ex2
Sample_id = SS 4-45-BFN 19F
Solvent = CHLOROFORM-D
Creation_time = 4-AUG-2014 09:50:10
Revision_time = 23-SEP-2014 11:53:16
Current_time = 23-SEP-2014 11:53:42
Comment = Single pulse without
Data_format = 1D REAL
Dim_size = 26214
Dim_title = 19F
Dim_units = [ppm]
Dimensions = X
Site = RCX 400P
Spectrometer = DELTA2_NMR
Field_strength = 9.389766[T] (400[MHz]
X_acq_duration = 0.229376[s]
X_domain = 19F
X_freq = 376.17105393[MHz]
X_offset = -100[ppm]
X_points = 32768
X_prescans = 2
X_resolution = 4.35965402[Hz]
X_sweep = 142.85714286[kHz]
Irr_domain = 19F
Irr_freq = 376.17105393[MHz]
Irr_offset = 5[ppm]
Tri_domain = 19F
Tri_freq = 376.17105393[MHz]
Tri_offset = 5[ppm]
Clipped = FALSE
Mod_return = 1
Scans = 128
Total_scans = 128
X_90_width = 12.32[us]
X_acq_time = 0.229376[s]
X_angle = 45[deg]
X_atn = 6[dB]
X_pulse = 6.16[us]
Irr_mode = Off
Tri_mode = Off
Dante_presat = FALSE
Initial_wait = 1[s]
Recvr_gain = 36
Relaxation_delay = 2[s]
Repetition_time = 2.229376[s]
Temp_get = 21.9[dC]


PF6
X : parts per Million : 1H
Filename - MS 4-45-PP6_PROTON-4.
Author - delta
Experiment - single_pulse.exp
Sample_id - MS 4-45-PP6
Solvent - CHLOROFORM-D
Creation_time - 21-AUG-2014 13.00.13
Revision_time - 15-SEP-2014 13.09.17
Current_time - 15-SEP-2014 13.09.43
Comment - MS 4-45-PP6
Data_format - 1D COMPLEX
Dim_size - 13107
Dim_title - 1H
Dim_units - [ppm]
Dimensions - X
Site - RCH 400P
Spectrometer - DELTA2_NMR
Field_strength - 9.389766[T] (400[MHz])
X_acq_duration - 1.31072[s]
X_domain - 1H
X_freq - 399.78219838[MHz]
X_offset - 5[ppm]
X_points - 16384
X_prescans - 1
X_resolution - 0.76291945[Hz]
X_sweep - 12.5[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 - 10.1[us]
X_acq_time - 1.31072[s]
X_angle - 45[deg]
X_atn - 3[dB]
X_pulse - 5.05[us]
Irr_mode - Off
Tri_mode - Off
Decpl_present - FALSE
Initial_wait - 1[s]
Recvr_gain - 30
Relaxation_delay - 4[s]
Repetition_time - 5.31072[s]
Temp_get - 406.1[dC]


abundance
X : parts per Million : 13C



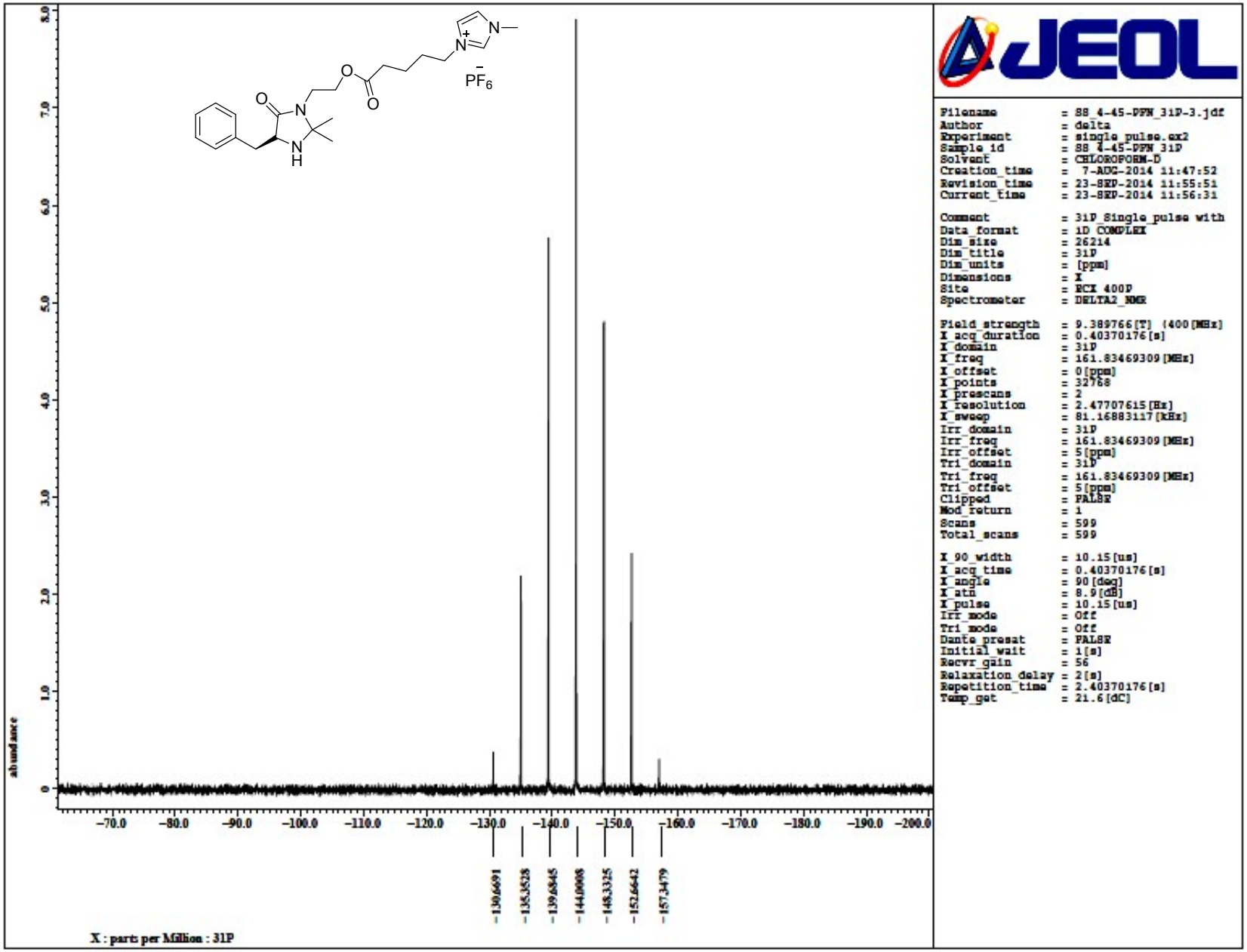
JEOL

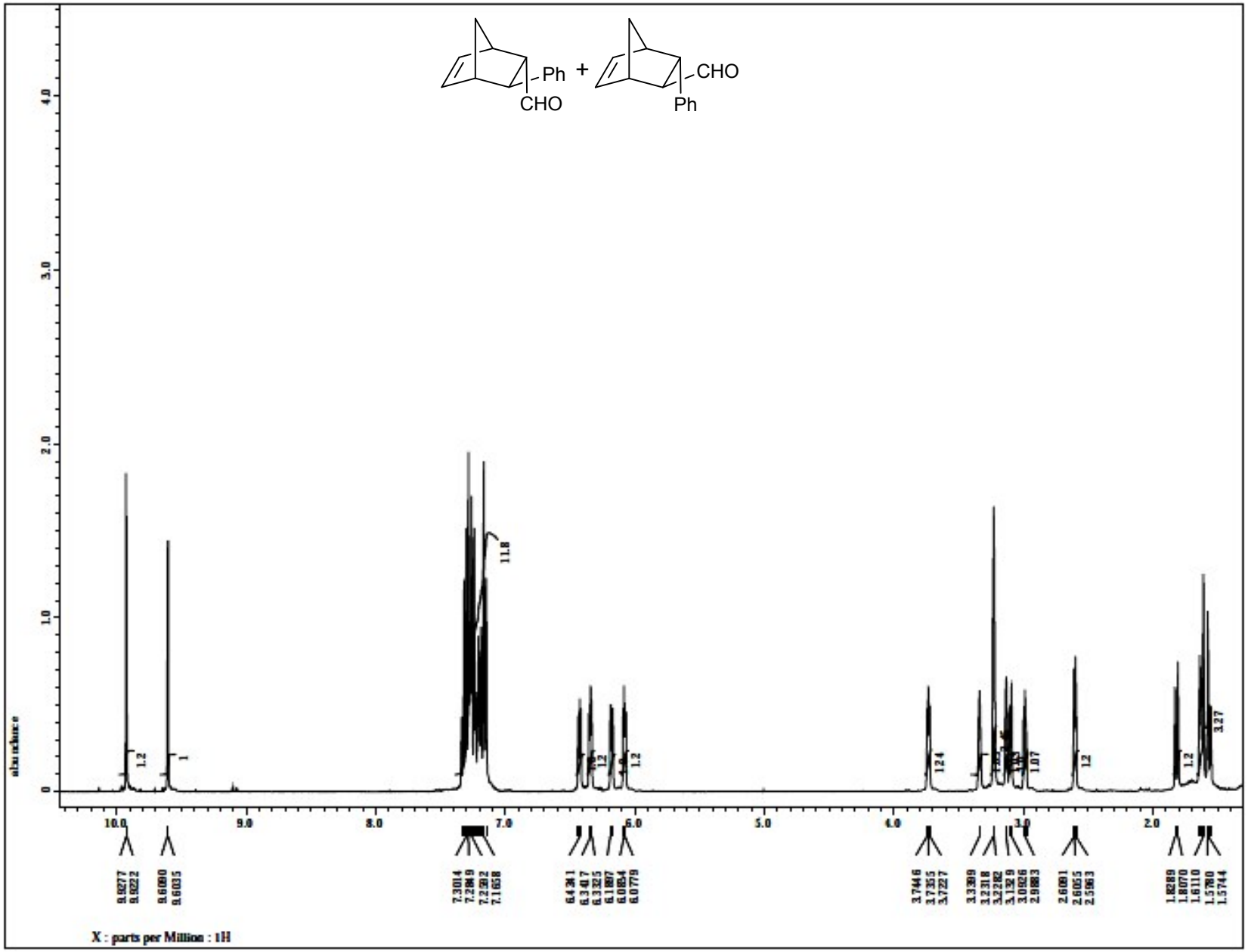
```
Filename          = SS_4-45-PFN_19F-4.jdf
Author            = delta
Experiment        = single_pulse.ex2
Sample_id         = SS_4-45-PFN_19F
Solvent           = CHLOROFORM-D
Creation_time     =  4-AUG-2014 10:20:03
Revision_time     = 23-SEP-2014 11:54:50
Current_time      = 23-SEP-2014 11:55:20

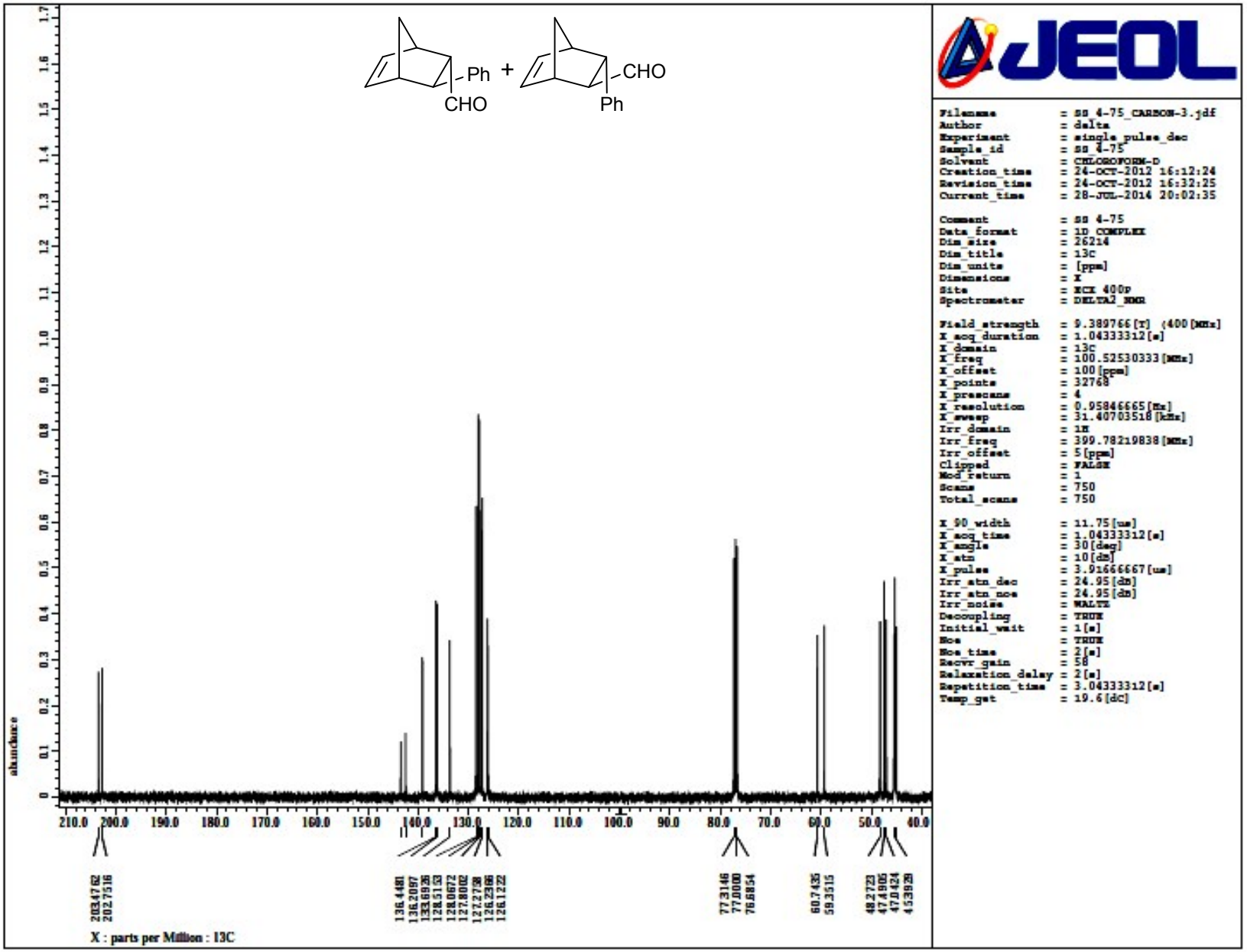
Comment           = Single pulse without
Data_format       = 1D REAL
Dim_size          = 26214
Dim_title         = 19F
Dim_units         = [ppm]
Dimensions        = X
Site              = RCX 400P
Spectrometer      = DELTA2_NMR

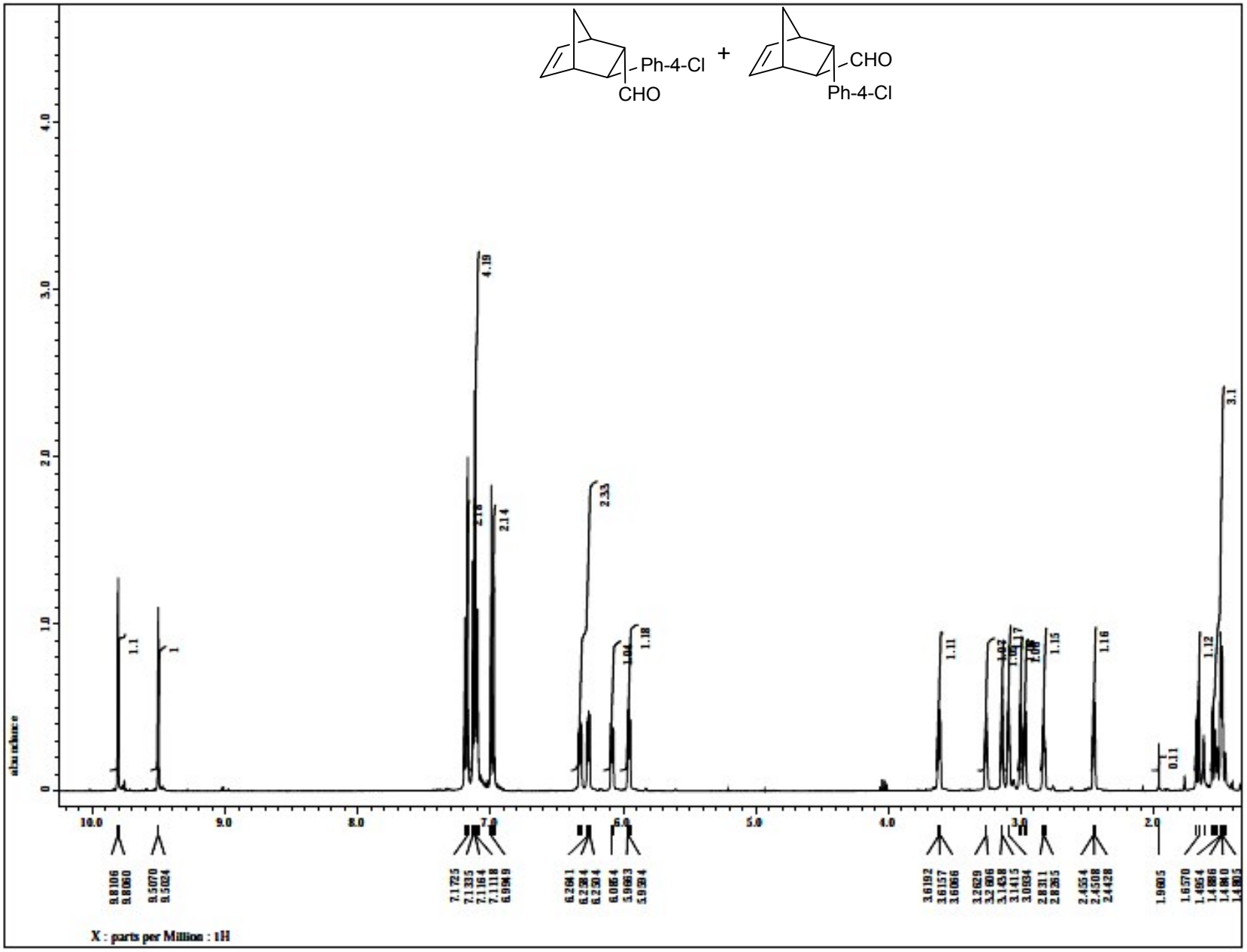
Field_strength    = 9.389766[T] (400[MHz]
X_acq_duration    = 0.229376[s]
X_domain          = 19F
X_freq            = 376.17105393[MHz]
X_offset          = -100[ppm]
X_points          = 32768
X_prescans        = 2
X_resolution      = 4.35965402[Hz]
X_sweep           = 142.85714286[kHz]
Irr_domain        = 19F
Irr_freq          = 376.17105393[MHz]
Irr_offset        = 5[ppm]
Tri_domain        = 19F
Tri_freq          = 376.17105393[MHz]
Tri_offset        = 5[ppm]
Clipped           = FALSE
Mod_return        = 1
Scans             = 128
Total_scans       = 128

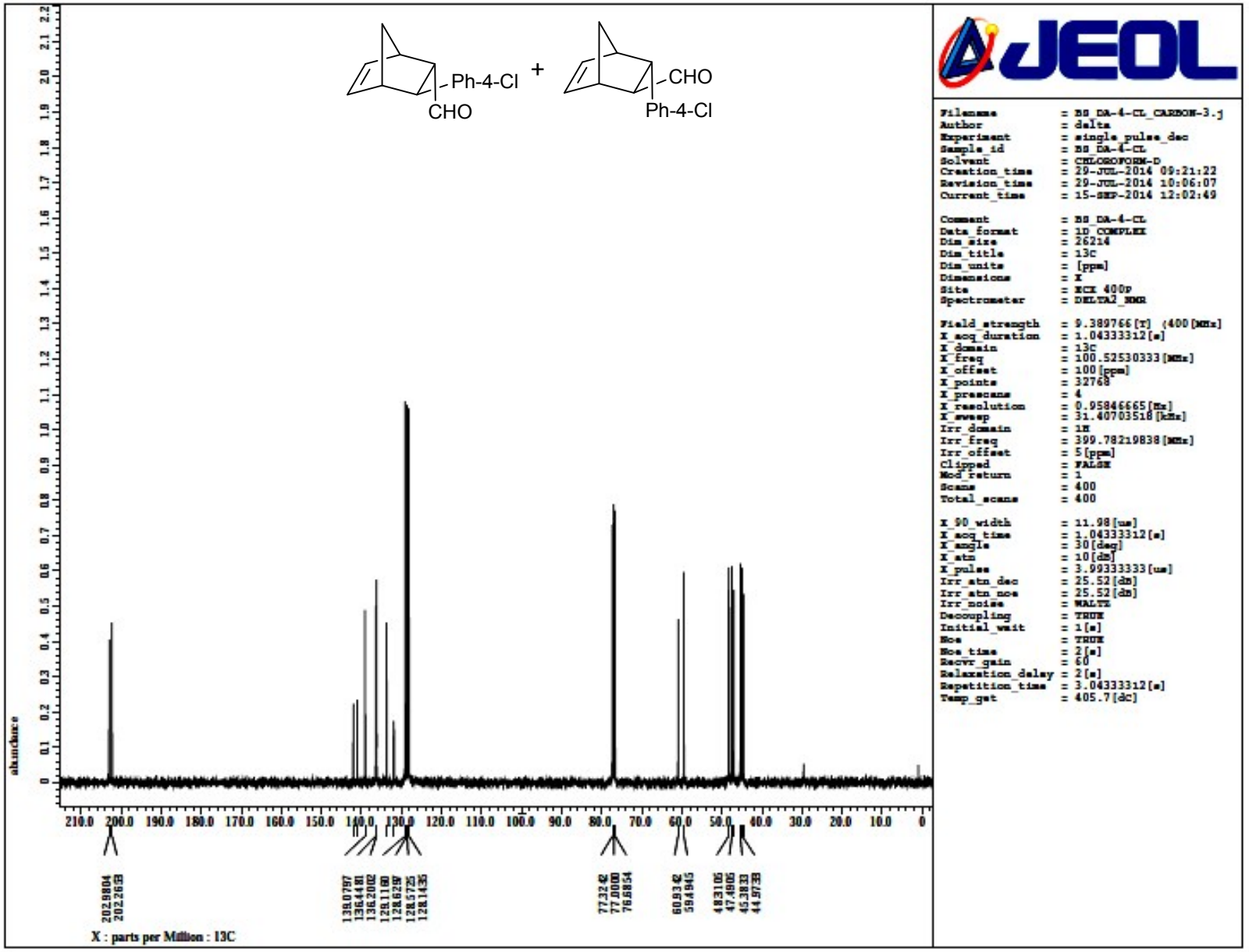
X_90_width        = 12.32[us]
X_acq_time        = 0.229376[s]
X_angle           = 45[deg]
X_atn             = 6[dB]
X_pulse           = 6.16[us]
Irr_mode          = Off
Tri_mode          = Off
Dante_presat      = FALSE
Initial_wait      = 1[s]
Recvr_gain        = 36
Relaxation_delay  = 2[s]
Repetition_time   = 2.229376[s]
Temp_get          = 22.6[dC]
```

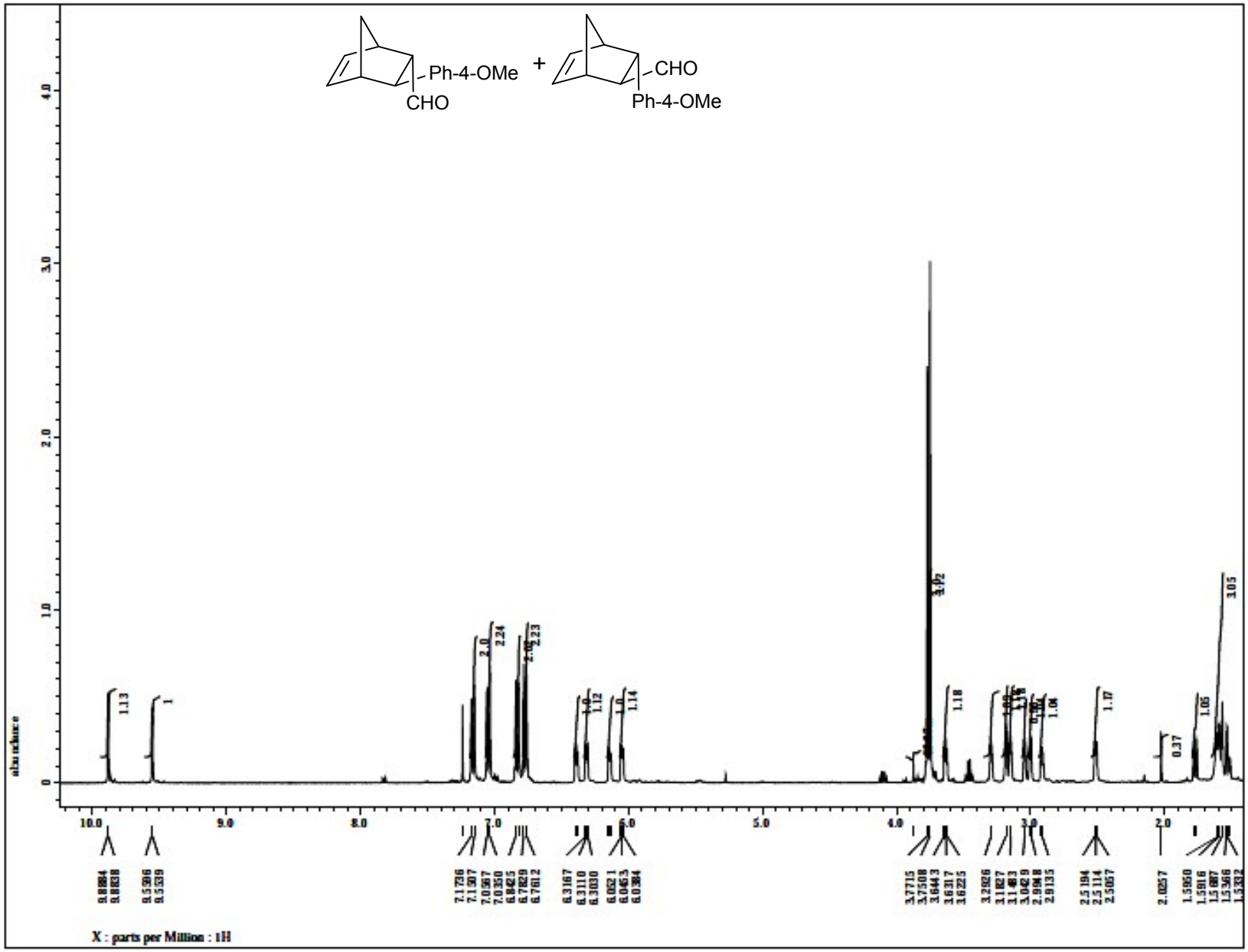

JEOL
Filename = 88_4-45-PFN_31P-3.jdf
Author = delta
Experiment = single_pulse.ex2
Sample_id = 88_4-45-PFN_31P
Solvent = CHLOROFORM-D
Creation_time = 7-AUG-2014 11:47:52
Revision_time = 23-SEP-2014 11:55:51
Current_time = 23-SEP-2014 11:56:31
Comment = 31P Single pulse with
Data_format = 1D COMPLEX
Dim_size = 26214
Dim_title = 31P
Dim_units = [ppm]
Dimensions = X
Site = RCX 400P
Spectrometer = DELTA2_NMR
Field_strength = 9.389766[T] (400[MHz]
X_acq_duration = 0.40370176[s]
X_domain = 31P
X_freq = 161.83469309[MHz]
X_offset = 0[ppm]
X_points = 32768
X_prescans = 2
X_resolution = 2.47707615[Hz]
X_sweep = 81.16883117[kHz]
Irr_domain = 31P
Irr_freq = 161.83469309[MHz]
Irr_offset = 5[ppm]
Tri_domain = 31P
Tri_freq = 161.83469309[MHz]
Tri_offset = 5[ppm]
Clipped = FALSE
Mod_return = 1
Scans = 599
Total_scans = 599
X_90_width = 10.15[us]
X_acq_time = 0.40370176[s]
X_angle = 90[deg]
X_atn = 8.9[dB]
X_pulse = 10.15[us]
Irr_mode = Off
Tri_mode = Off
Dante_presat = FALSE
Initial_wait = 1[s]
Recvr_gain = 56
Relaxation_delay = 2[s]
Repetition_time = 2.40370176[s]
Temp_get = 21.6[dC]
abundance
X : parts per Million : 31P
-130.6691
-135.3528
-139.6845
-144.0008
-148.3325
-152.6642
-157.3479

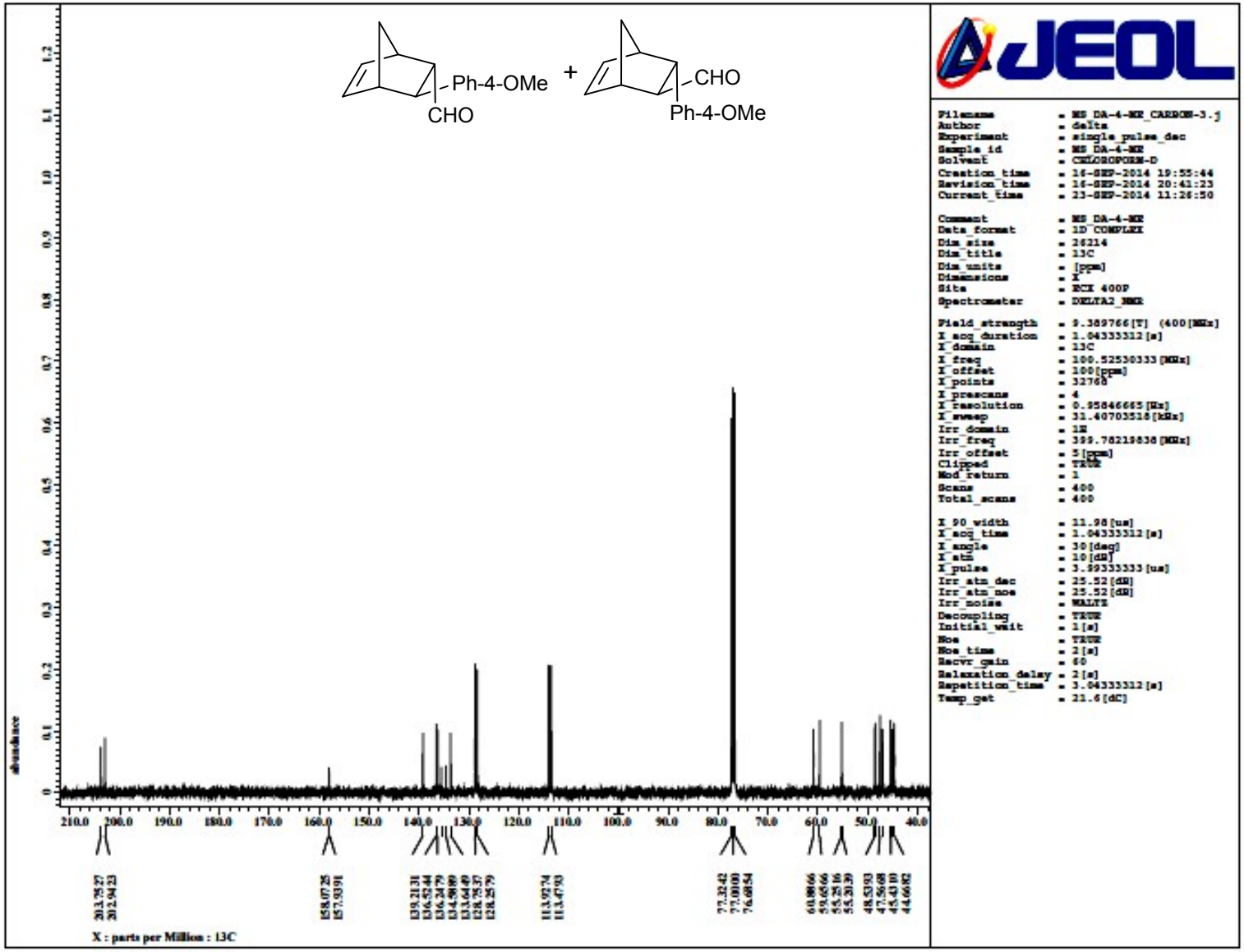

Ph
CHO
+
CHO
Ph
abundance
X : parts per Million : 1H

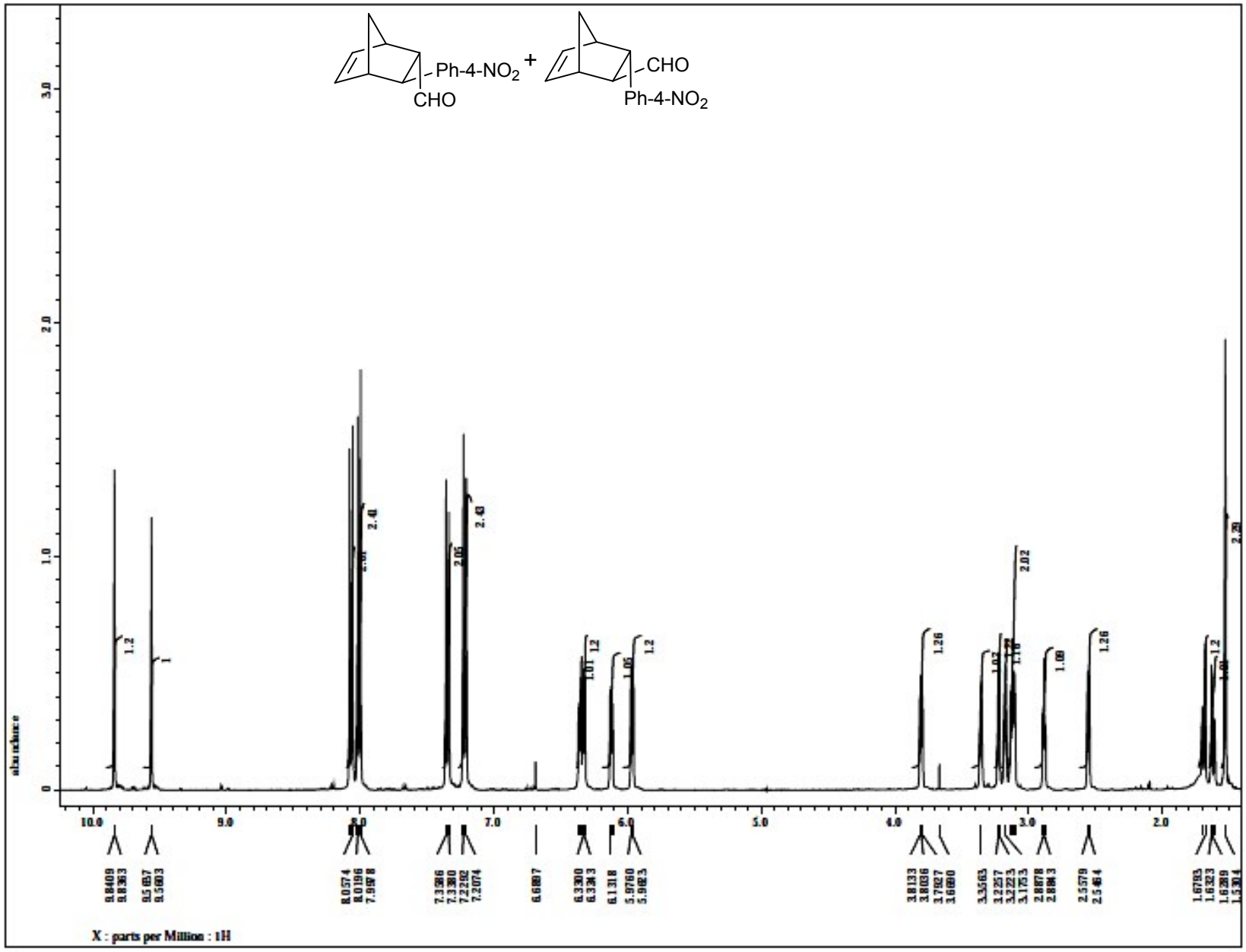

Ph
CHO
+
CHO
Ph
abundance
X : parts per Million : 13C
Filename : SS 4-75_CARBON-3.jdf
Author : delta
Experiment : single_pulse_dec
Sample_id : SS 4-75
Solvent : CHLOROFORM-D
Creation_time : 24-OCT-2012 16:12:24
Revision_time : 24-OCT-2012 16:32:25
Current_time : 28-JUL-2014 20:02:35
Comment : SS 4-75
Data_format : 1D COMPLEX
Dim_size : 26214
Dim_title : 13C
Dim_units : [ppm]
Dimensions : X
Site : NCX 400P
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 : 750
Total_scans : 750
X_90_width : 11.75[us]
X_acq_time : 1.04333312[s]
X_angle : 30[deg]
X_atn : 10[dB]
X_pulse : 3.91666667[us]
Irr_atn_dec : 24.95[dB]
Irr_atn_noe : 24.95[dB]
Irr_noise : WALTZ
Decoupling : TRUE
Initial_wait : 1[s]
Noe : TRUE
Noe_time : 2[s]
Recvr_gain : 58
Relaxation_delay : 2[s]
Repetition_time : 3.04333312[s]
Temp_get : 19.6[dC]

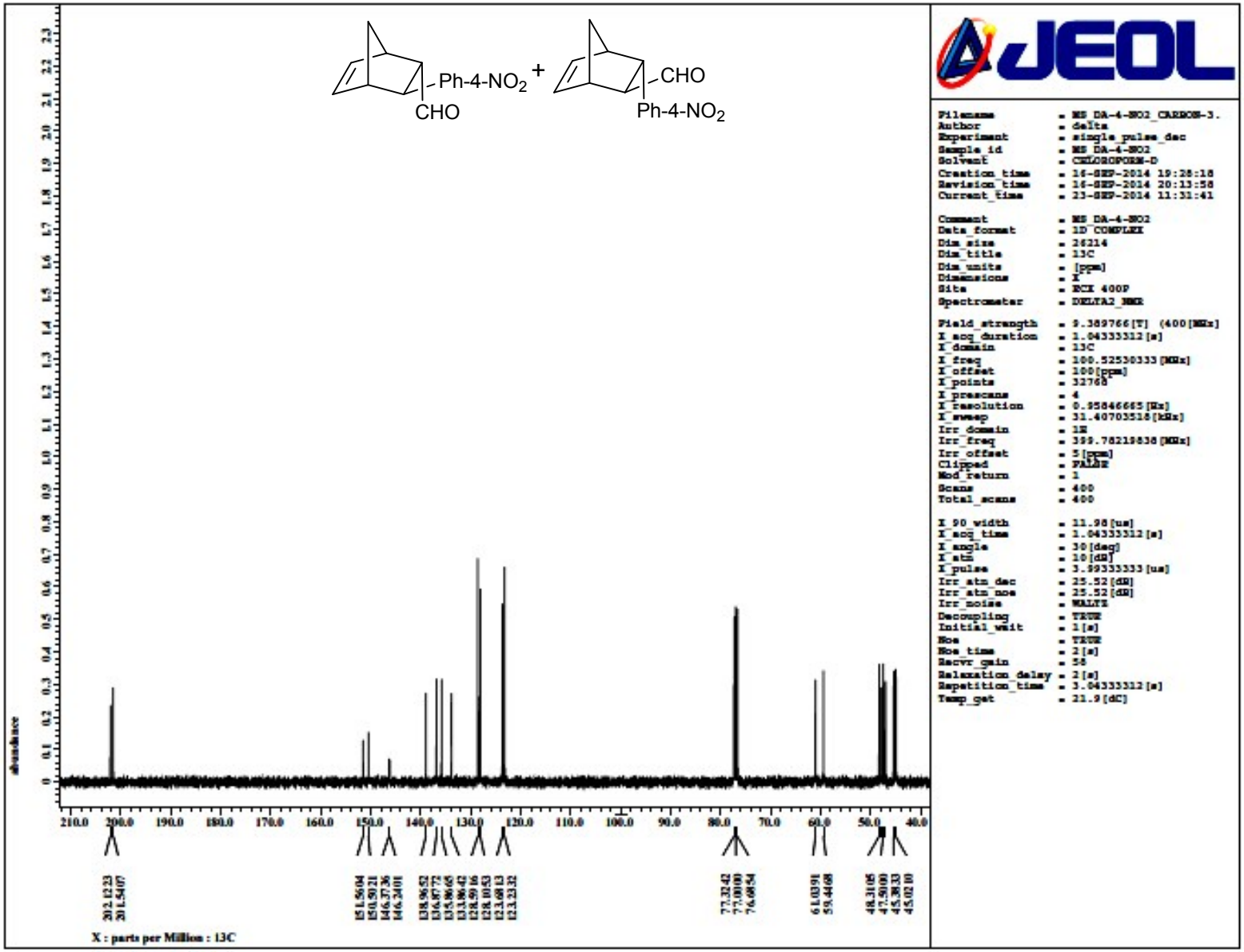

Ph-4-Cl
CHO
+
CHO
Ph-4-Cl
X : parts per Million : 1H

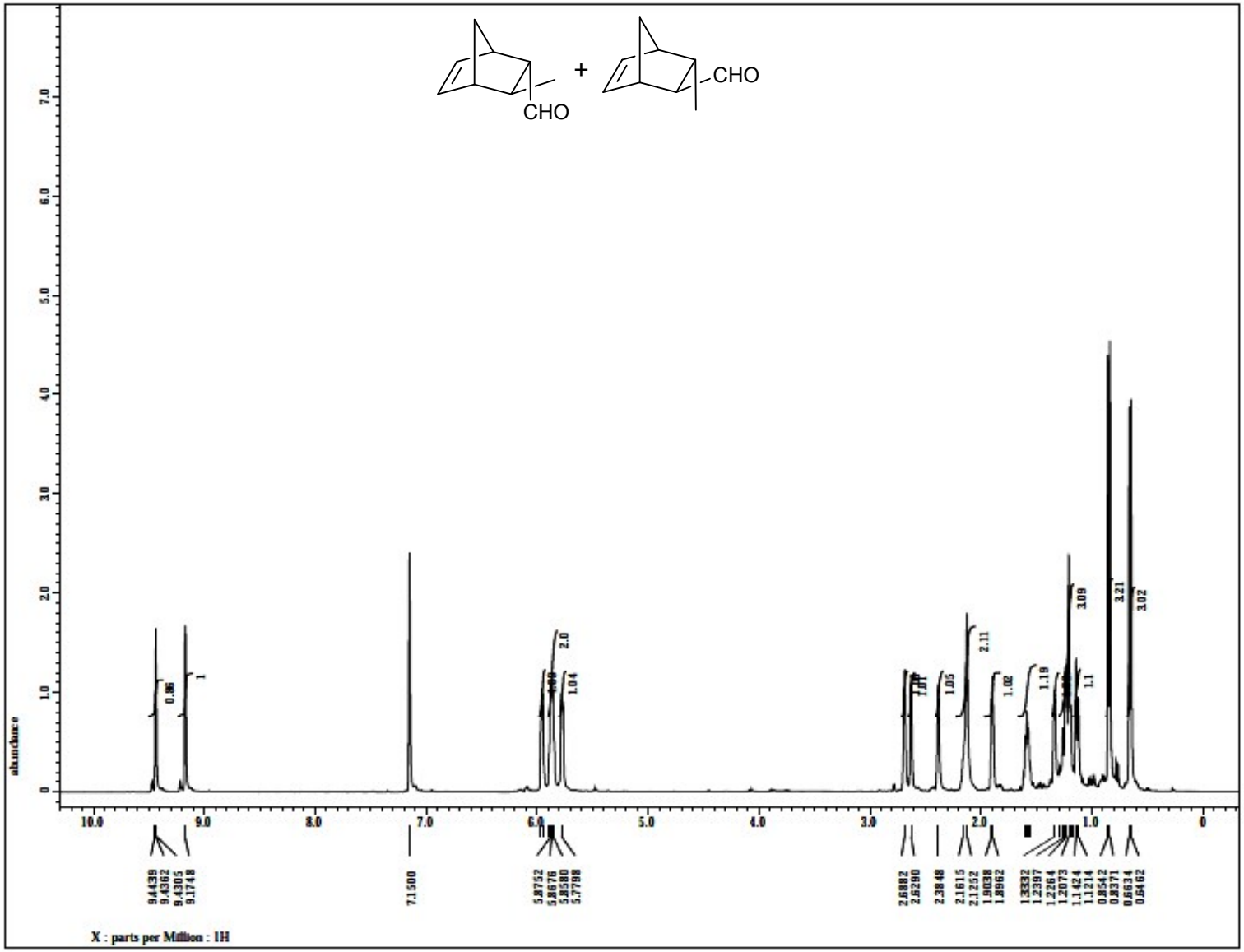

Ph-4-Cl
CHO
+
CHO
Ph-4-Cl
abundance
X : parts per Million : 13C
Filename = BS_DA-4-CL_CARBON-3.j
Author = delta
Experiment = single_pulse_dec
Sample_id = BS_DA-4-CL
Solvent = CHLOROFORM-D
Creation_time = 29-JUL-2014 09:21:22
Revision_time = 29-JUL-2014 10:06:07
Current_time = 15-SEP-2014 12:02:49
Comment = BS_DA-4-CL
Data_format = 1D COMPLEX
Dim_size = 26214
Dim_title = 13C
Dim_units = [ppm]
Dimensions = X
Site = NCE 400P
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 = 400
Total_scans = 400
X_90_width = 11.98[us]
X_acq_time = 1.04333312[s]
X_angle = 30[deg]
X_atn = 10[dB]
X_pulse = 3.99333333[us]
Irr_atn_dec = 25.52[dB]
Irr_atn_noe = 25.52[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 = 405.7[dC]

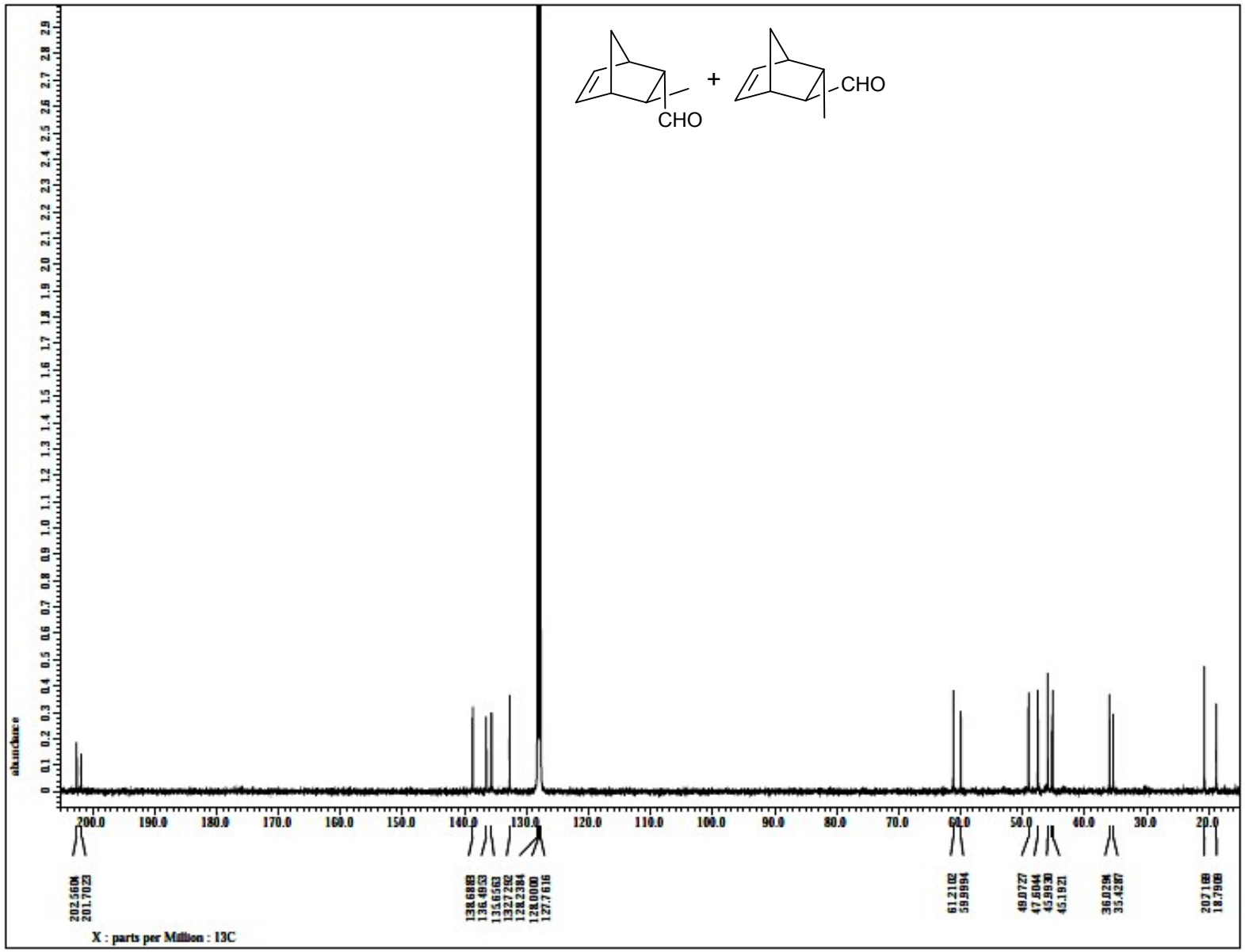

Ph-4-OMe
CHO
+
CHO
Ph-4-OMe
X : parts per Million : 1H


Ph-4-OMe
CHO
+
CHO
Ph-4-OMe
JEOL
Filename = MS_DA-4-MX_CARBON-3.j
Author = delta
Experiment = single_pulse_dec
Sample_id = MS_DA-4-MX
Solvent = CHLOROFORM-D
Creation_time = 16-SEP-2014 19:55:44
Revision_time = 16-SEP-2014 20:41:23
Current_time = 23-SEP-2014 11:26:50
Comment = MS_DA-4-MX
Data_format = 1D COMPLEX
Dim_size = 26214
Dim_title = 13C
Dim_units = [ppm]
Dimensions = X
Site = RCX 400P
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 = 399.78219836[MHz]
Irr_offset = 5[ppm]
Clipped = TRUE
Mod_return = 1
Scans = 400
Total_scans = 400
X_90_width = 11.98[us]
X_acq_time = 1.04333312[s]
X_angle = 30[deg]
X_atn = 10[dB]
X_pulse = 3.99333333[us]
Irr_atn_dec = 25.52[dB]
Irr_atn_noe = 25.52[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 = 21.6[dC]
abundance
X : parts per Million : 13C

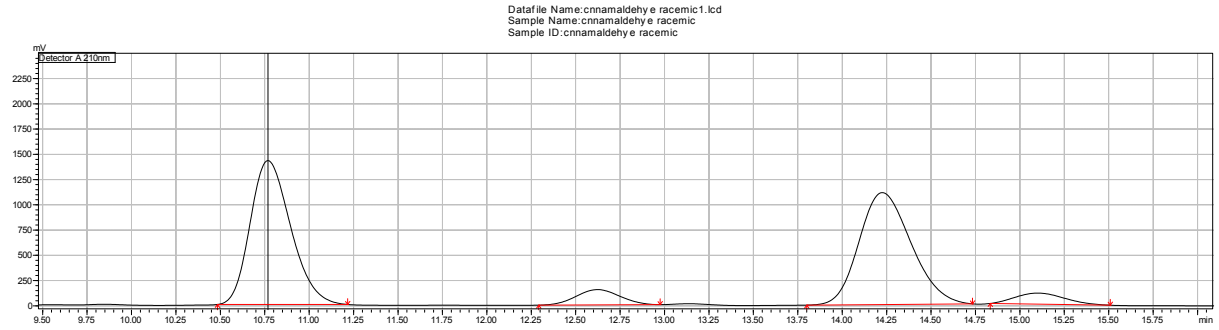

Ph-4-NO2
CHO
+
CHO
Ph-4-NO2
X : parts per Million : 1H


Ph-4-NO2
CHO
+
CHO
Ph-4-NO2
abundance
X : parts per Million : 13C
JEOL
Filename = MS DA-4-NO2_CARBON-3.
Author = delta
Experiment = single_pulse_dec
Sample_id = MS DA-4-NO2
Solvent = CHLOROFORM-D
Creation_time = 16-SEP-2014 19:28:18
Revision_time = 16-SEP-2014 20:13:58
Current_time = 23-SEP-2014 11:31:41
Comment = MS DA-4-NO2
Data_format = 1D COMPLEX
Dim_size = 26214
Dim_title = 13C
Dim_units = [ppm]
Dimensions = X
Site = NCX 400P
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 = 399.78219836[MHz]
Irr_offset = 5[ppm]
Clipped = FALSE
Mod_return = 1
Scans = 400
Total_scans = 400
X_90_width = 11.98[us]
X_acq_time = 1.04333312[s]
X_angle = 30[deg]
X_atn = 10[dB]
X_pulse = 3.99333333[us]
Irr_atn_dec = 25.52[dB]
Irr_atn_noe = 25.52[dB]
Irr_noise = WALTZ
Decoupling = TRUE
Initial_wait = 1[s]
Noe = TRUE
Noe_time = 2[s]
Recvr_gain = 58
Relaxation_delay = 2[s]
Repetition_time = 3.04333312[s]
Temp_get = 21.9[dC]

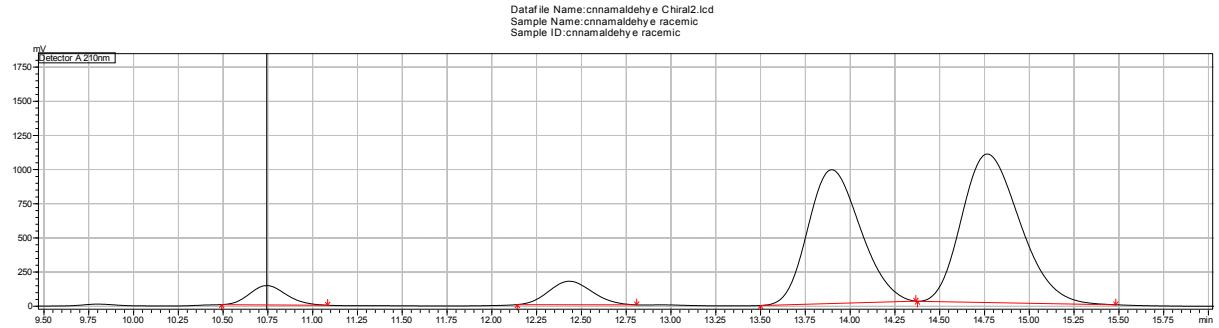

CHO
+
CHO
abundance
X : parts per Million : 1H


CHO
+
CHO
abundance
X : parts per Million : 13C

(1R,3R,4S)-3-phenylbicyclo[2.2.1]hept-5-ene-2-carbaldehyde and (1R,2S,3R,4S)-3-phenylbicyclo [2.2.1] hept-5-ene-2-carbaldehyde : HPLC conditions: Daicel Chiralcel OD-H column, Hexane/IPA (96 : 4), 1 ml/min., 210 nm.

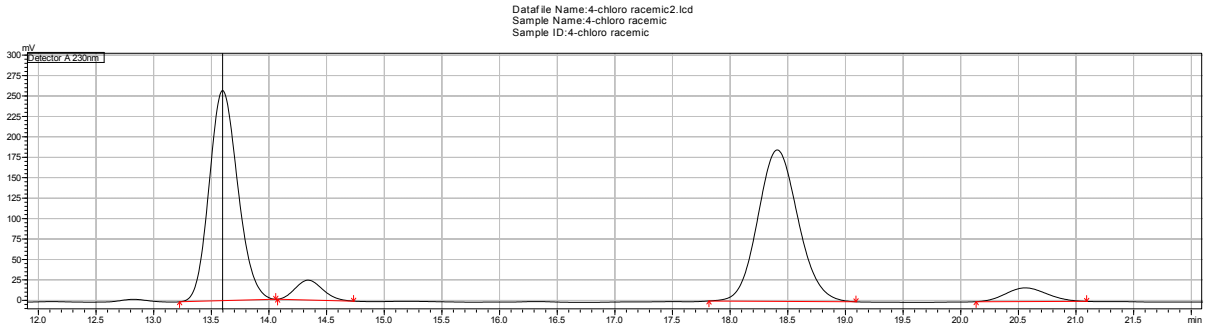


Peak	Ret. Time	Area	Height	Conc.	Area%
1	10.768	22546349	1425099	45.304	45.304 (exo)
2	12.622	2584002	151539	5.192	5.192 (endo)
3	14.226	22524433	1108584	45.260	45.260 (exo)
4	15.101	2111923	109650	4.244	4.244 (endo)
Total		49766707	2794872	100.000	100.000

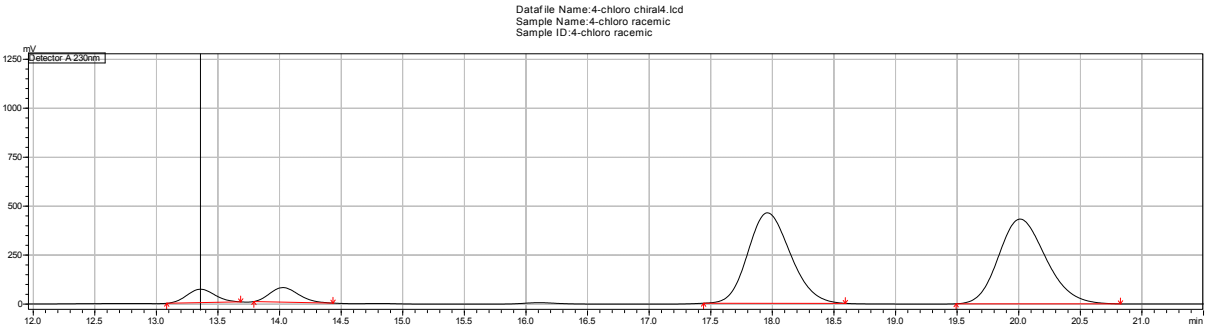


Peak	Ret. Time	Area	Height	Conc.	Area%
1	10.743	2008299	141376	4.069	4.069 (exo)
2	12.432	2895021	172031	5.866	5.866 (endo)
3	13.897	19958948	979508	40.440	40.440 (exo)
4	14.766	24492334	1087196	49.625	49.625 (endo)
Total		49354602	2380112	100.000	100.000

(1R,3R,4S)-3-(4-chlorophenyl)bicyclo[2.2.1]hept-5-ene-2-carbaldehyde and (1R,2S,3R,4S)-3-(4-chlorophenyl)bicyclo[2.2.1]hept-5-ene-2-carbaldehyde : HPLC conditions: Daicel Chiralcel OD-H column, Hexane/IPA (96 : 4), 0.8 ml/min., 230 nm.

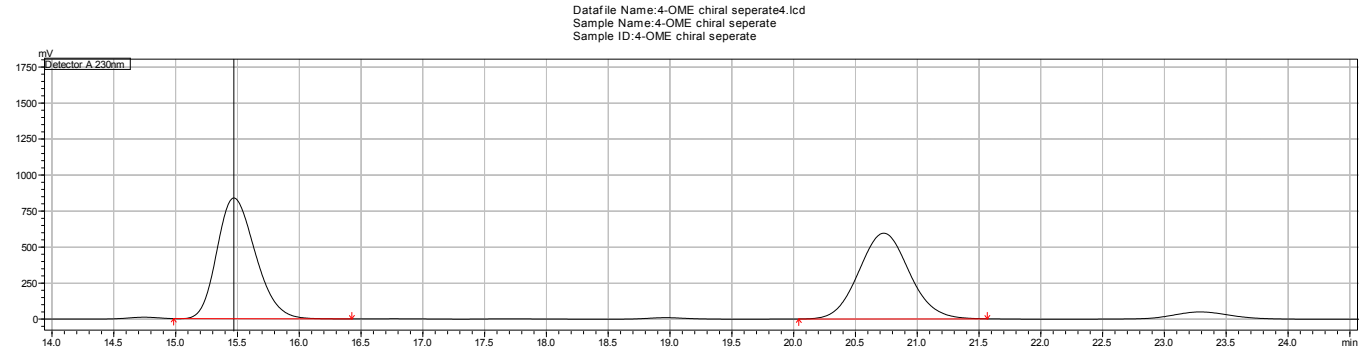


Peak	Ret. Time	Area	Height	Conc.	Area%
1	13.598	4431173	257148	45.474	45.474 (exo)
2	14.339	399294	24257	4.098	4.098 (endo)
3	18.409	4496334	185303	46.142	46.142 (exo)
4	20.560	417694	16749	4.286	4.286 (endo)
Total		9744494	483458	100.000	100.000

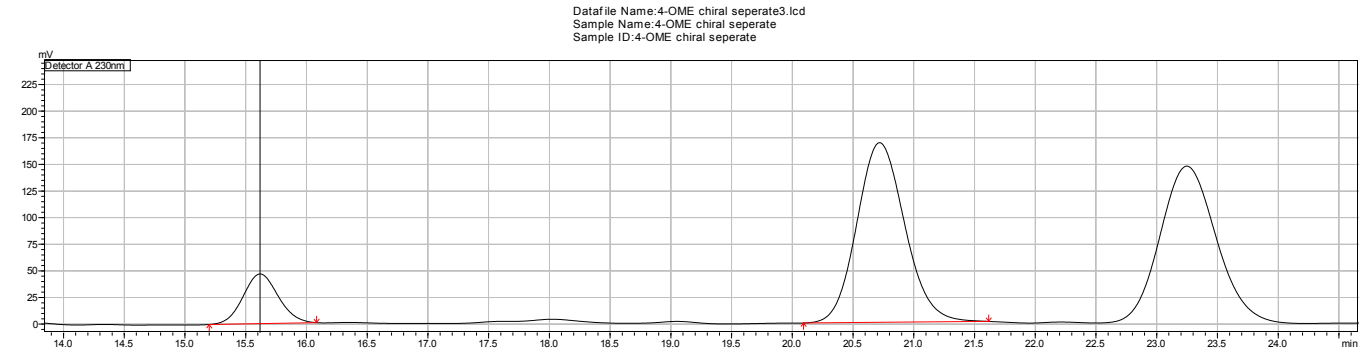


Peak	Ret. Time	Area	Height	Conc.	Area%
1	13.358	1078512	68644	4.328	4.328 (exo)
2	14.027	1193151	74026	4.788	4.788 (endo)
3	17.960	11091711	461775	44.507	44.507 (exo)
4	20.011	11558055	432663	46.378	46.378 (endo)
Total		24921429	1037109	100.000	100.000

(1S,3R,4R)-3-(4-methoxyphenyl)bicyclo[2.2.1]heptane-2-carbaldehyde and (1S,2S,3R,4R)-3-(4-methoxyphenyl)bicyclo[2.2.1]heptane-2-carbaldehyde : HPLC conditions: Daicel Chiralcel OD-H column, Hexane/IPA (95 : 5), 0.8 ml/min., 230 nm.

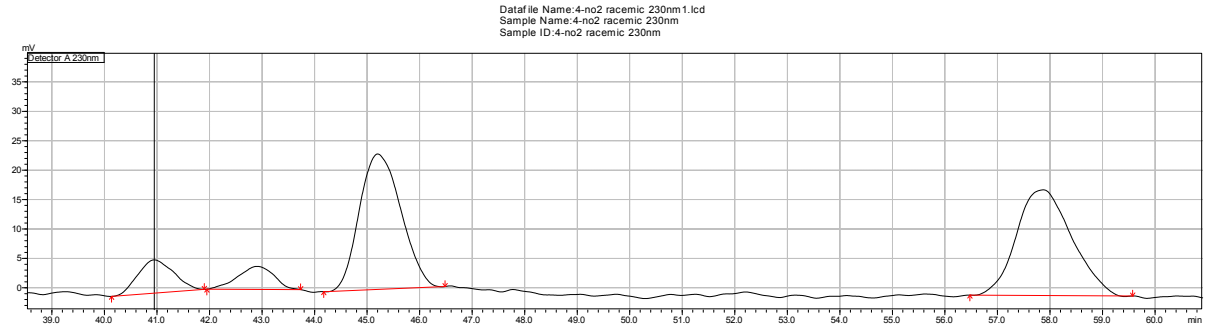


Peak	Ret. Time	Area	Height	Conc.	Area%
1	15.471	18095790	838075	51.653	51.653 (exo)
2	20.730	16937713	595246	48.347	48.347 (exo)
Total		35033502	1433321	100.000	100.000

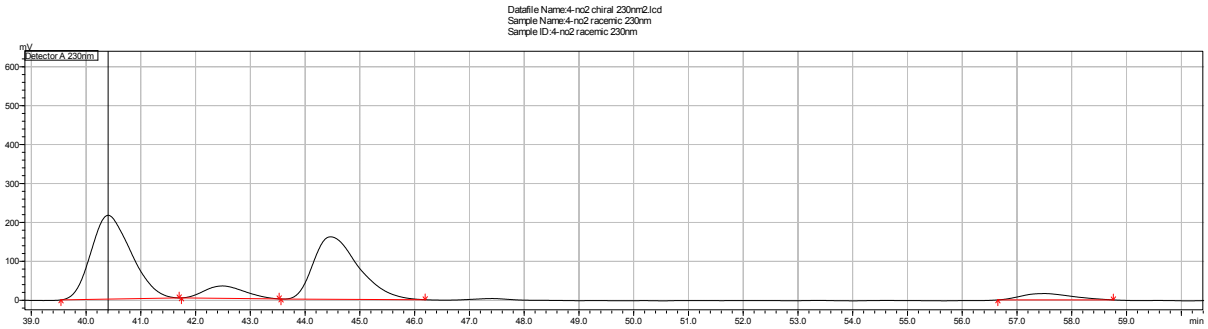


Peak	Ret. Time	Area	Height	Conc.	Area%
1	15.618	937248	46649	16.848	16.848 (exo)
2	20.719	4625840	168750	83.152	83.152 (exo)
Total		5563087	215400	100.000	100.000

(1S,4R,6S)-5-methyl-6-(4-nitrophenyl)bicyclo[2.2.1]hept-2-ene and (1S,4R,5S,6S)-5-methyl-6-(4-nitrophenyl)bicyclo[2.2.1]hept-2-ene : HPLC conditions: Daicel Chiralcel AD-H column, Hexane/IPA (96 : 5), 1.0 ml/min., 230 nm.



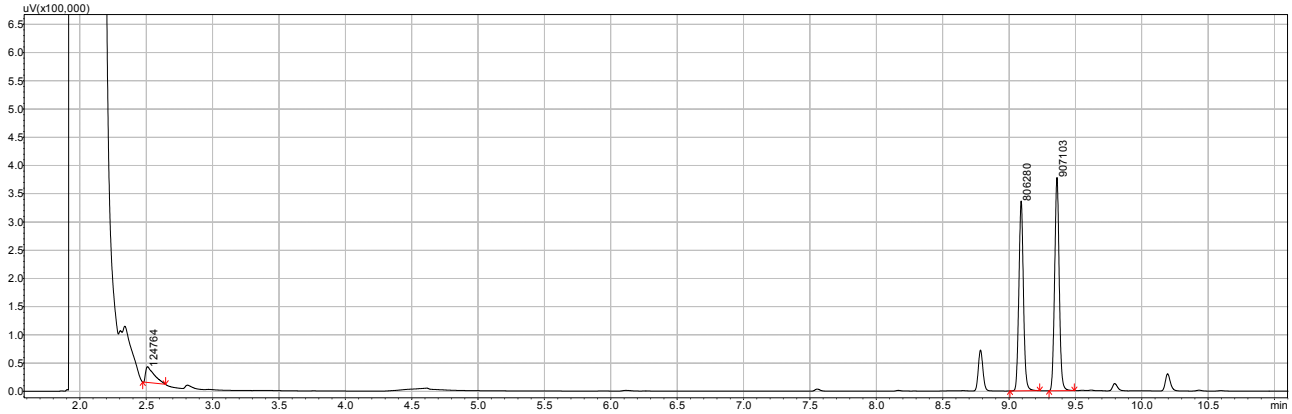
Peak	Ret. Time	Area	Height	Conc.	Area%
1	40.948	268078	5649	8.813	8.813 (exo)
2	42.900	187994	3914	6.180	6.180 (exo)
3	45.199	1269970	23027	41.748	41.748 (endo)
4	57.873	1315949	17964	43.259	43.259 (endo)
Total		3041992	50554	100.000	100.000



Peak	Ret. Time	Area	Height	Conc.	Area%
1	40.404	10932871	215431	47.978	47.978 (exo)
2	42.490	1616889	31720	7.096	7.096 (exo)
3	44.466	9186078	160450	40.312	40.312 (endo)
4	57.504	1051591	16296	4.615	4.615 (endo)
Total		22787428	423896	100.000	100.000

GC Chromatogram:

3-methylbicyclo[2.2.1]hept-5-ene-2-carbaldehyde : Conversion of the product was determined using capillary RTX column (30 m × 0.25 mm): injector temperature 220°C, Pressure 88.6 kPa, column flow rate 1.10 ml/min, column temp 65 °C for 5 min. then 120 °C, temperature program 15°C/min, detector temp. = 250°C.

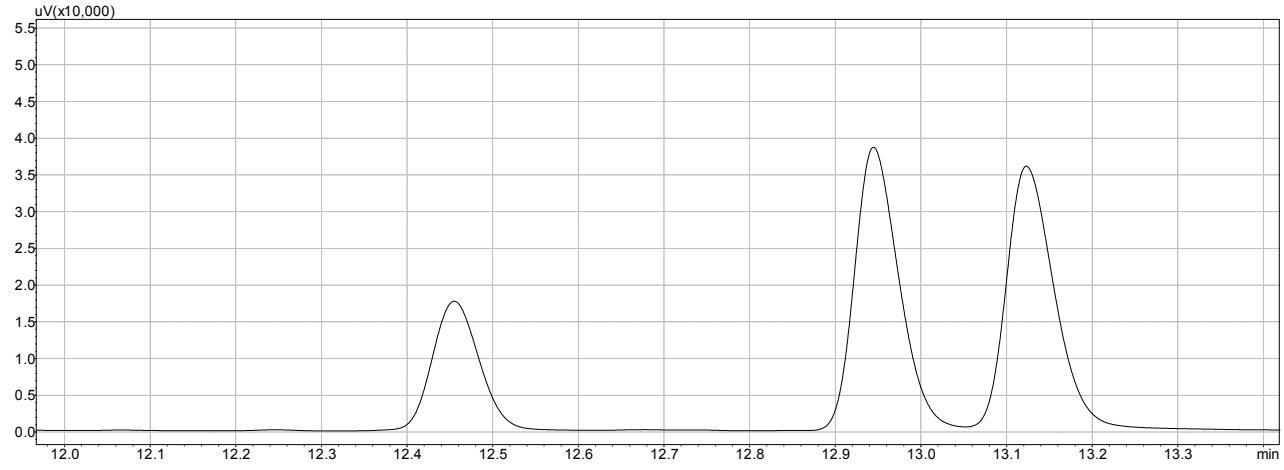


Peak	Ret.Time	Area	Height	Area%
1	2.510	124764.2	27386.6	6.7875
2	9.091	806280.5	330709.6	43.8637
3	9.361	907103.4	367640.0	49.3488

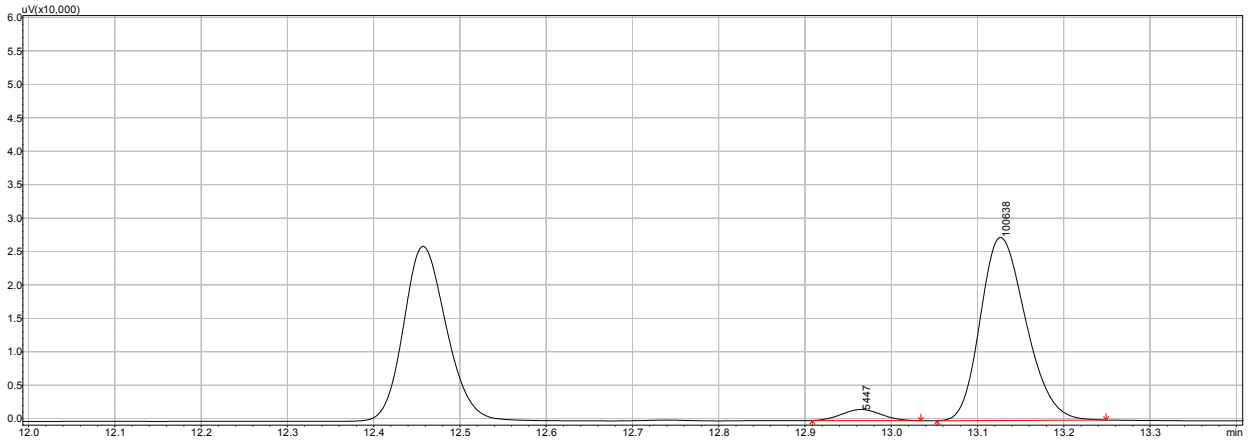
Enantiomeric excess of the product 12

(Table 5, entry 1, fresh cycle)

GC condition : column information β-Dex L = 30m, 0.25mm ID, injector temperature 220°C, Pressure 88.6 kPa, column flow rate 1.10 ml/min, column temp 65 °C for 5 min. then 120 °C, temperature program 15°C/min, detector temp. = 250°C.

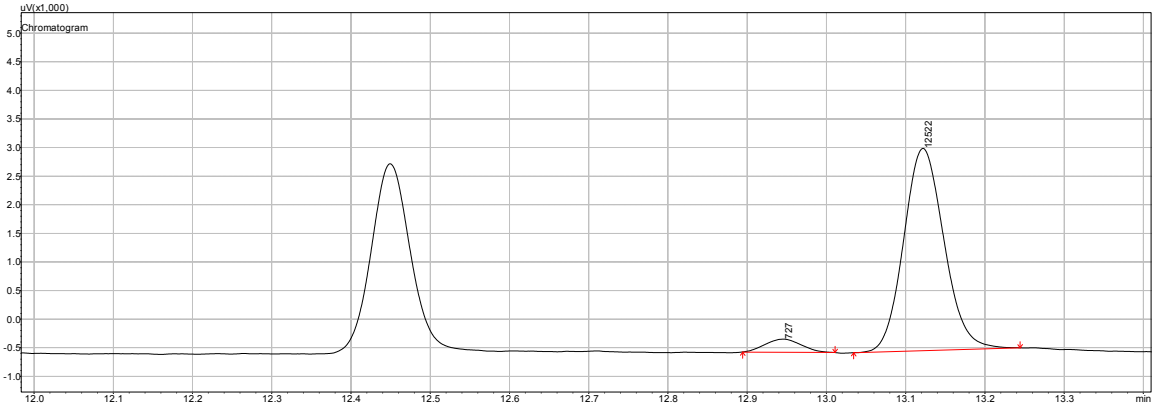


Peak	Ret.Time	Area	Height	Conc.	Area%
1	12.945	136015.8	37765.1	50.19428	50.1943 (endo)
2	13.123	134962.9	35241.2	49.80572	49.8057 (endo)



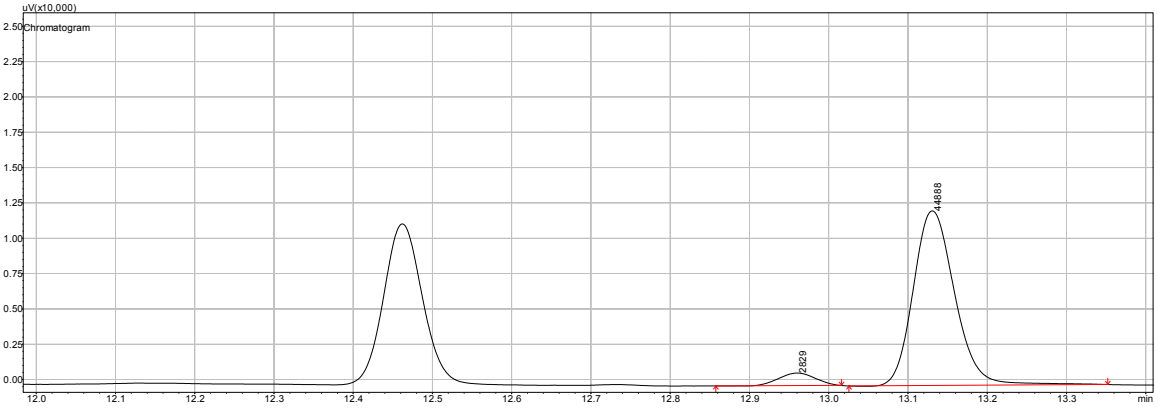
Peak	Ret.Time	Area	Height	Conc.	Area%
1	12.965	5446.8	1676.9	5.13439	5.1344
2	13.127	100637.7	27083.6	94.86561	94.8656

(Table 5, entry 2, 1st recycle)



Peak	Ret.Time	Area	Height	Conc.	Area%
1	12.945	726.8	227.3	5.48603	5.4860
2	13.122	12521.6	3482.7	94.51397	94.5140

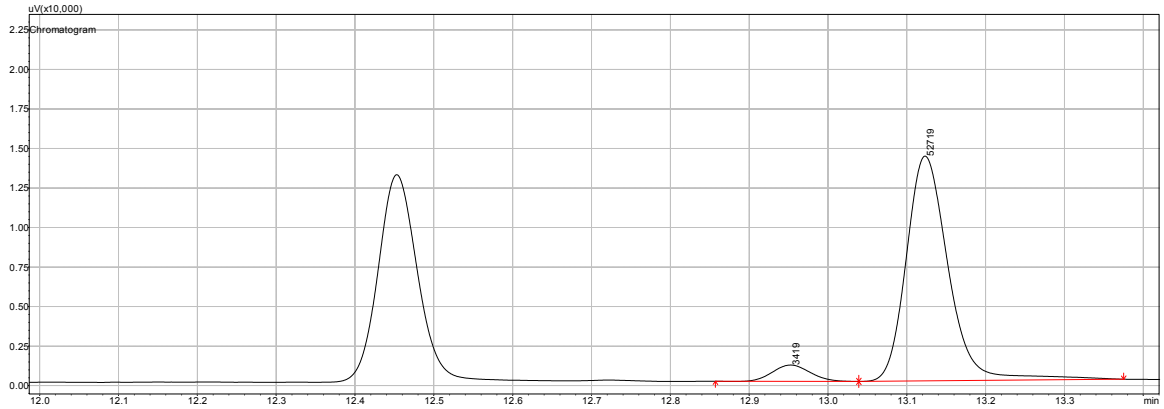
(Table 5, entry 3, 2nd recycle)



Peak	Ret.Time	Area	Height	Conc.	Area%

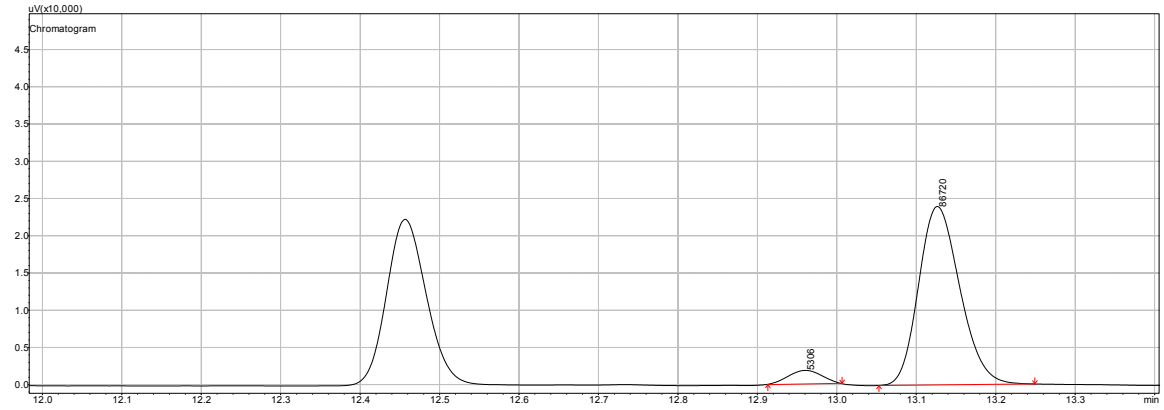
1	12.960	2829.3	886.1	5.92936	5.9294
2	13.131	44887.5	12344.4	94.07064	94.0706

(Table 5, entry 4, 3rd recycle)



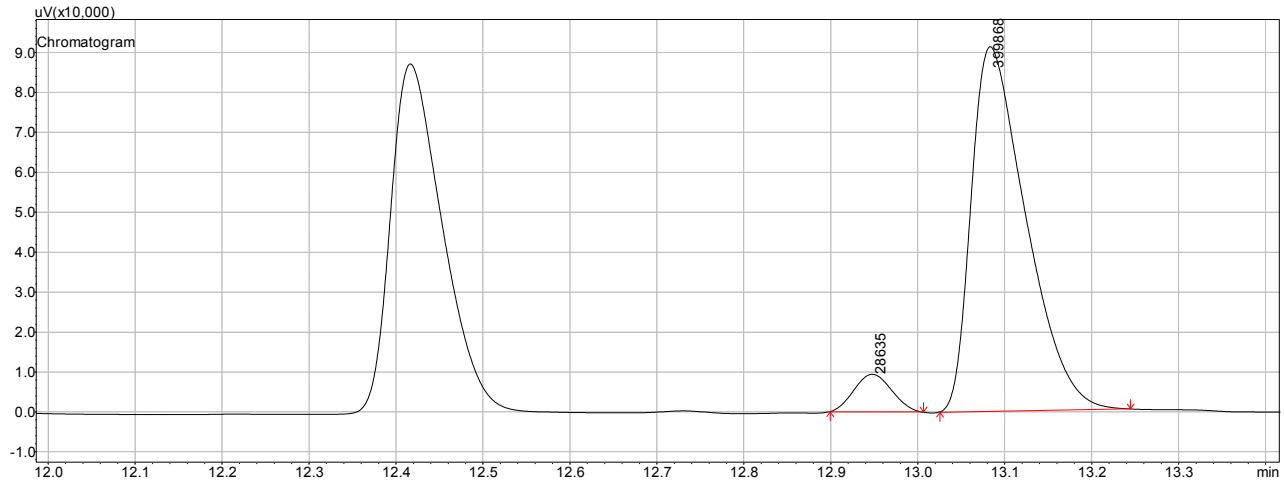
Peak	Ret.Time	Area	Height	Conc.	Area%
1	12.953	3418.5	1030.1	6.08953	6.0895
2	13.123	52719.3	14101.4	93.91047	93.9105

(Table 5, entry 5, 4th recycle)



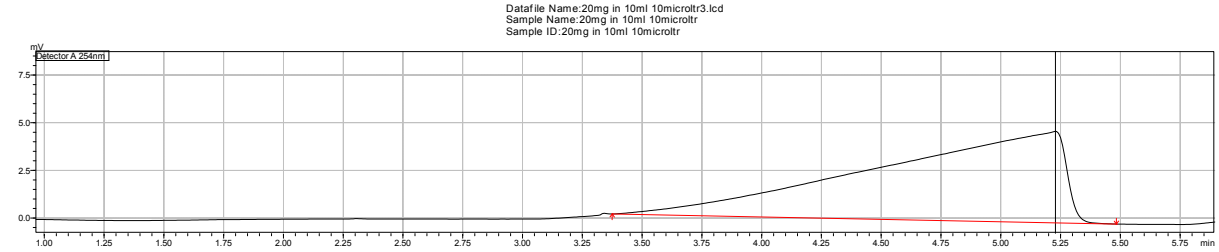
Peak	Ret.Time	Area	Height	Conc.	Area%
1	12.961	5305.9	1801.6	5.76568	5.7657
2	13.127	86719.6	23616.0	94.23432	94.2343

(Table 5, entry 6, 5th recycle)



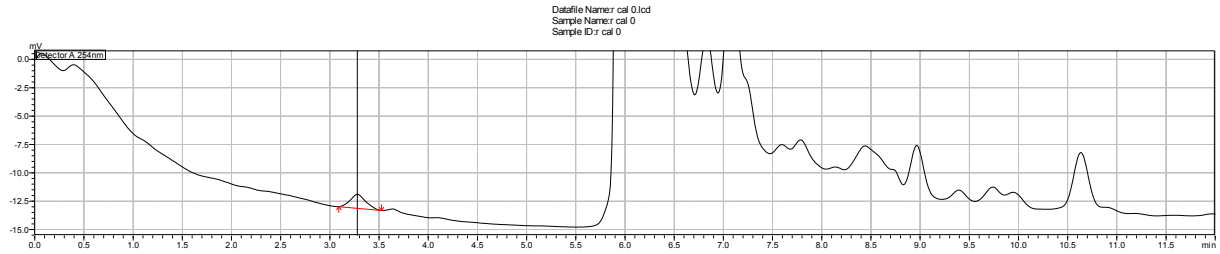
Peak	Ret.Time	Area	Height	Conc.	Area%
1	12.948	28635.1	9430.4	6.68258	6.6826
2	13.084	399868.0	91166.3	93.31742	93.3174

HPLC chromatogram for fresh and leached catalyst:



Fresh catalyst

Peak	Ret. Time	Area
1	5.228	261971
Total		261971



Recovered catalyst and product

Peak	Ret. Time	Area
1	3.279	13438
Total		13438