Catalytic Asymmetric Hydrolysis: Asymmetric Hydrolytic Protonation of Enol Esters Catalyzed by Phase-Transfer Catalysts

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Asymmetric Ester Hydrolysis: Catalytic Asymmetric Protonation of Enolesters Catalyzed by Phase Transfer Catalysts

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Supporting Information

1. General.

Unless otherwise stated, all the reactions were performed in flame-dried glassware under a nitrogen atmosphere using dry solvents. Commercial reagents were used as received. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL spectrometer ECS-400, ECS-600 and AL-400. Data for ^{1}H NMR spectra are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets, ap = apparent, sex =sextet, sep = septet), integration, coupling constant (Hz) and assignment. The enantiomeric excesses were determined by GC or HPLC analysis employing a chiral stationary phase column specified in the individual experiment, by comparing the samples with the appropriate racemic mixtures. GC analysis was carried out using Agilent GC 6850 series II equipped with InertCap CHIRAMIX Column (length 30 m, i.D. 0.25 mm, df. 0.25 μm) from GL Sciences Inc. and CHIRASIL-DEX CB (length 25 m, i.D. 0.25 mm, df. 0.25 μm) from Varian using helium as a carrier gas. GC yields were determined by employing HP-1 (length 30 m, i.D. 0.320 mm, df. 0.25 μm) or HP-INNOWAX (length 30 m, i.D. 0.320 mm, df. 0.25 μm) column from Agilent Technologies using helium as a carrier gas. FAB-MS analysis was performed with an Ultrahigh Performance Mass Spectrometer JMS-HX110A in Institute for Materials Chemistry and Engineering (IMCE). HPLC analysis was performed on a JASCO LC-2000 Plus Series equipped with a variable wavelength detector using chiral stationary columns (Chiracel AD-H, 0.46 cm x 25 cm) from Daicel. Optical rotations were measured on a JASCO DIP-1000 digital polarimeter. Chromatography was performed on silica-gel (Kanto Chemicals, Silica gel 60N, spherical, neutral; particle size 40–100 μm). Abbreviations; Bn = benzyl, conversion = conv, enantiomeric excess = ee, eq = equiv, er = enantiomer ratio, DMAP = *N*,*N*-dimethylaminopyridine, MTPACl = Methoxy-1-(trifluoromethyl)phenylacetyl chloride, piv = pivaloyl, product = pro, RT = room temperature, substrate = sub.

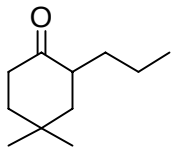
2. Material.

$CDCl_3$, CD_3OD and C_6D_6 were used as solvents for NMR analyses. Chloroform was purified prior to use following the guidelines of Perrin and Armarego[1]. Pyridine (anhydrous), CH_2Cl_2 (anhydrous) and THF (anhydrous, stabilizer free) were used as anhydrous solvents. *N*-9-anthracenylmethyl-cinchonidinium chloride (**1a**, Sigma-Aldrich), *N*-benzylcinchonidinium chloride (**1d**, TOKYO CHEMICAL INDUSTRY CO., LTD.), *N*-benzylcinchoninium chloride (**1e**, TOKYO CHEMICAL INDUSTRY CO., LTD.) and cinchonidine (Wako Pure Chemical Industries, Ltd.) were used as received. All other chemical reagents were used in commercial grade. Catalyst **1b**[2], **1c**[3], 2-isopropyl-cycloheptanone[4] (**3h**), 2-allyl-4,4-dimethyl-cyclohexanone[5] and 2-cycloheptylidene-1,1-dimethylhydrazine[6] were prepared according to the reported procedures.

3. Preparation and Characterization of enolesters

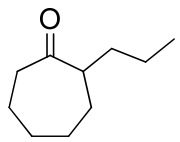
3-1. Synthesis of 2-substituted ketones

4,4-dimethyl-2-propylcyclohexanone[7] (3d)



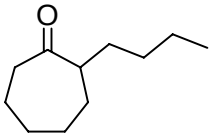
2-allyl-4,4-dimethylcyclohexanone (570 mg, 3.43 mmol, 1 equiv) in ^{t}butanol (3.43 mL) was placed in a glass tube with a magnetic stirring bar. $RuCl_2(PPh_3)_3$ (16.4 mg, 0.017 mmol, 0.5 mol%) was added and the tube was placed in an autoclave. Hydrogen was introduced into the autoclave at a pressure of 2 MPa after hydrogen replacement, then stirred for 11 h at 30 ^{o}C. The resultant solution was purified by silica-gel column chlomatography (Hexane : Et_2O = 10:1) to give **3d** (566 mg, 3.36 mmol, 98%) as yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.44 (td, *J* = 6.4, 14.2 Hz, 1 H), 2.36 (dt, *J* = 6.0, 6.0 Hz, 1 H), 2.22 (dt, *J* = 3.2, 14.2 Hz, 1 H), 1.80-1.55 (m, 4 H), 1.34-1.22 (m, 3 H), 1.19 (s, 3 H), 1.06 (tq, 6.9, 6.9 Hz, 1 H), 0.99 (s, 3 H), 0.87 (t, *J* = 7.4 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 214.1, 46.8, 45.8, 40.2, 38.6, 31.6, 31.2, 30.9, 24.7, 20.3, 14.3. Anal. Calcd (%) for $C_{11}H_{20}O$: C, 78.51; H, 11.98. Found: C, 78.24; H, 11.98.

2-propylcycloheptanone [8] **(3f)**



BuLi (1.67 M in hexane, 5.25 mmol, 3.14 mL, 1.05 equiv) was added dropwise to a stirred solution of 2-cycloheptylidene-1,1-dimethylhydrazine (771 mg, 5.0 mmol, 1 equiv) in THF (anhydrous, 20 mL) at – 5 °C under a nitrogen atmosphere and stirred for 1 h. After that, propyl iodide (893 mg, 512 μL, 5.25 mmol, 1.05 equiv) was added dropwise to the solution, and then the resulting solution was allowed to warm to RT and stirred for 4 h. Distilled water was added to the resultant solution and cooled to 0 °C. Then the solution was acidified with 1N HCl aq to reach pH 1-2 (The mixture was homogenized by adding THF and methanol). After stirring at 45 °C for another 2 h, the solution was extracted with diethylether. The organic extracts were combined, dried over Na_2SO_4 and concentrated. The resultant crude product was purified by silica-gel chromatography (hexane:Et_2O = 20:1) to give **3f** (560 mg, 3.63 mmol, 73%) as pale yellow oil ^{13}C NMR was in agreement with the literature[8]. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.54-2.34 (m, 3 H), 1.89-1.76 (m, 4 H), 1.68-1.48 (m, 2H), 1.40-1.17 (m, 6 H), 0.86 (t, *J* = 7.4 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ =216.8, 52.3, 42.7, 34.6, 31.3, 29.7, 28.5, 24.8, 20.5, 14.2. Anal. Calcd (%) for $C_{10}H_{18}O$: C, 77.87; H, 11.76. Found: C, 78.01; H, 11.83.

2-butylcycloheptanone[9,10] **(3g)**



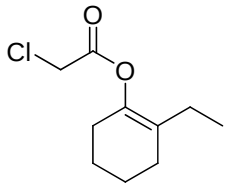
BuLi (1.67 M in hexane, 5.25 mmol, 3.14 mL, 1.05 equiv) was added dropwise to a stirred solution of 2-cycloheptylidene-1,1-dimethylhydrazine (771 mg, 5.0 mmol, 1 equiv) in THF (anhydrous, 20 mL) at – 5 °C under a nitrogen atmosphere and stirred for 1 h. After that, butyl bromide (719 mg, 564 μL, 5.25 mmol, 1.05 equiv) was added dropwise to the solution, and then the resulting solution was allowed to warm to RT and stirred for 4 h. Distilled water was added to the resultant solution and cooled to 0 °C. Then the solution was acidified with 1N HCl aq to reach pH 1-2 (The mixture was homogenized by adding THF and methanol). After stirring at 45 °C for another 2 h, the solution was extracted with diethylether. The organic extracts were combined, dried over Na_2SO_4 and concentrated. The resultant crude product was purified by silica-gel chromatography (hexane:Et_2O = 20:1) to give **3g** (643 mg, 3.82 mmol, 77%) as pale yellow oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.53-2.32 (m, 3 H), 1.90-1.77 (m, 4 H), 1.68-1.50 (m, 2H), 1.38-1.14 (m, 8 H), 0.86 (t, *J* = 6.9 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ =216.9, 52.5, 42.7, 32.2, 31.3, 29.7, 29.5, 28.5, 24.8, 22.9, 14.1. Anal. Calcd (%) for $C_{11}H_{20}O$: C, 78.51; H, 11.98. Found: C, 78.44; H, 11.96.

3-2. Synthesis of enolesters

Procedures: A typical experimental procedure for the preparation of enolesters is described below. Aqueous $HClO_4$ solution (60%, 106.8 μL, 5 mol%) was added to a mixture of 2-propylcyclohexanone **3c** (2.80 g, 20 mmol, 1 equiv) and chloroacetic acid anhydride (6.84 g, 40 mmol, 2 equiv) in CCl_4 (12 mL) and CH_2Cl_2 (12 mL) under air. The reaction mixture was stirred for 14 h at 30 °C. Then, Et_2O (50 mL) and saturated $NaHCO_3$ aq (50 mL) were added to the reaction mixture and stirred for a few minutes. After that, the organic layer was separated and the aqueous layer was extracted with Et_2O (50 mL x 3). Organic layers were combined and dried with Na_2SO_4 followed by evaporation. The resultant crude product was purified by silica-gel column chromatography (Et_2O/Hexane) to give **2c** (3.73 g, 17.2 mmol, 86%) as pale yellow oil.

2-ethylcyclohex-1-en-1-yl 2-chloroacetate (2b)

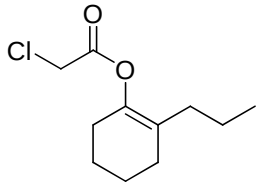
85% yield, yellow oil (4 equiv of 2-chloroacetic anhydride was used.)



^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.12 (s, 2 H), 2.15-2.12 (m, 4 H), 1.93 (q, *J* = 7.9 Hz, 2 H), 1.74-1.66 (m, 2 H), 1.65-1.57 (m, 2 H), 0.92 (t, *J* = 7.8 Hz, 3 H). ^{13}C NMR (400 MHz, $CDCl_3$): δ = 165.7, 141.4, 126.7, 40.9, 27.3, 26.9, 23.2, 23.1, 22.4, 12.0. Anal. Calcd (%) for $C_{10}H_{15}ClO_2$: C, 59.26; H, 7.46. Found: C, 59.49; H, 7.47.

2-propylcyclohex-1-en-1-yl 2-chloroacetate (2c)

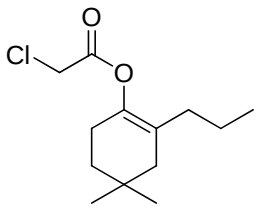
86% yield, yellow oil (2 equiv of chloroacetic anhydride was used.)



^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.11 (s, 2 H), 2.18-2.08 (m, 2 H), 2.08-2.00 (m, 2 H), 1.89 (t, 7.4 Hz, 2 H), 1.74-1.66 (m, 2 H), 1.66-1.56 (m, 2 H), 1.36 (sex, 6.0 Hz, 2 H), 0.85 (t, 7.4Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.7, 142.2, 125.2, 40.9, 32.1, 27.8, 26.9, 23.1, 22.4, 20.5, 14.1. Anal. Calcd (%) for $C_{11}H_{17}ClO_2$: C, 60.97; H, 7.91. Found: C, 61.25; H, 8.00.

4,4-dimethyl-2-propylcyclohex-1-en-1-yl 2-chloroacetate (2d)

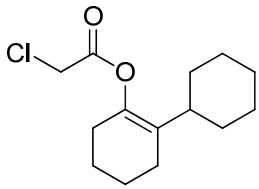
94 %yield, pale yellow oil (3 equiv of 2-chloroacetic anhydride was used.)



^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.12 (s, 2 H), 2.18-2.11(m, 2 H), 1.90-1.80 (m, 4 H), 1.49-1.42 (m, 2 H), 1.39-1.28 (m, 2 H), 0.97-0.92 (m, 6 H), 0.88-0.80 (m, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.8, 141.2, 123.9, 41.8, 40.9, 35.6, 32.1, 29.4, 27.9 (2 carbons), 24.5, 20.4, 14.0. Anal. Calcd (%) for $C_{13}H_{21}ClO_2$: C, 63.79; H, 8.65. Found: C, 64.06; H, 8.79.

[1,1'-bi(cyclohexan)]-1-en-2-yl 2-chloroacetate (**2e**)

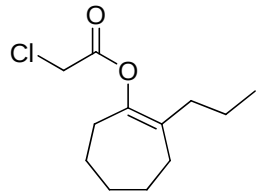
82% yield, yellow oil (2 equiv of chloroacetic anhydride was used.)



^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.11 (s, 2 H), 2.34-2.27 (m, 1 H), 2.13-2.10 (m, 2 H), 2.03-2.00 (m, 2 H), 1.73-1.55 (m, 7 H), 1.46-1.40 (m, 2 H), 1.29-1.03 (m, 5 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.8, 140.8, 129.7, 41.0, 38.1, 30.3 (2 carbons), 27.0, 26.6 (2 carbons), 26.2, 23.8, 22.9, 22.5. Anal. Calcd (%) for $C_{14}H_{21}ClO_2$: C, 65.49; H, 8.24. Found: C, 65.64; H, 8.29.

2-propylcyclohept-1-en-1-yl 2-chloroacetate (**2f**)

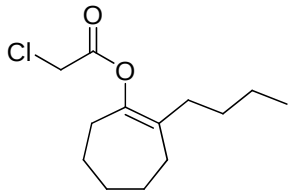
84% yield, pale yellow oil (4 equiv of chloroacetic anhydride was used.)



^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.09 (s, 2 H), 2.30-2.28 (m, 2 H), 2.11-2.08 (m, 2 H), 1.92 (t, J = 7.3 Hz, 2 H), 1.72-1.50 (m, 6 H), 1.34 (tq, 7.4 Hz, 7.4 Hz, 2 H), 0.84 (t, 7.3 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.9, 146.6, 129.9, 40.9, 34.5, 33.0, 31.5, 31.1, 26.4, 25.3, 20.5, 14.0. Anal. Calcd (%) for $C_{12}H_{19}ClO_2$: C, 62.47; H, 8.30. Found: C, 62.51; H, 8.26.

2-butylcyclohept-1-en-1-yl 2-chloroacetate (2g)

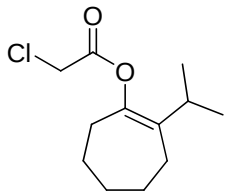
85% yield, pale yellow oil (4 equiv of chloroacetic anhydride was used.)



^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.10 (s, 2 H), 2.33-2.27 (m, 2 H), 2.13-2.07 (m, 2 H), 1.95-1.88 (m, 2 H), 1.73-1.65 (m, 2 H), 1.65-1.57 (m, 2 H), 1.57-1.49 (m, 2 H). 1.34-1.29 (m, 4 H), 0.90-0.83 (t, 6.9 Hz, 3 H) ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.0, 146.3, 130.2, 40.9, 33.0, 32.1, 31.5, 31.1, 29.5, 26.4, 25.3, 22.6, 14.1. Anal. Calcd (%) for $C_{13}H_{21}ClO_2$: C, 63.79; H, 8.65. Found: C, 64.04; H, 8.62.

2-isopropylcyclohept-1-en-1-yl 2-chloroacetate (2h)

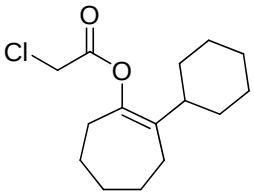
56% yield, yellow oil (2 equiv of chloroacetic anhydride was used.)



^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.12 (s, 2 H), 2.69 (sep, 6.9 Hz, 1 H), 2.32-2.24 (m, 2H), 2.08-2.01 (m, 2 H), 1.75-1.65 (m, 2H), 1.65-1.55 (m, 2 H), 1.55-1.45 (m, 2 H), 0.88 (d, 6.9 Hz, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.9, 144.9, 134.8, 40.9, 33.2, 32.0, 28.2, 26.9, 25.2, 25.1, 20.0(2 carbons). Anal. Calcd (%) for $C_{12}H_{19}ClO_2$: C, 62.47; H, 8.30. Found: C, 62.58; H, 8.28.

2-cyclohexylcyclohept-1-en-1-yl 2-chloroacetate (2i)

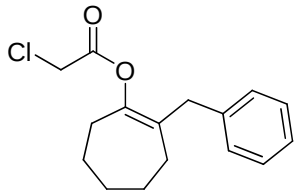
66% yield, yellow oil (2 equiv of chloroacetic anhydride was used.)



^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.11 (s, 2 H), 2.30-2.27 (m, 3 H), 2.09-2.06 (m, 2 H), 1.73-1.58 (m, 7 H), 1.50-1.40 (m, 4 H), 1.29-1.03 (m, 5 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.0, 145.3, 134.5, 40.9, 39.4, 33.2, 32.0, 29.9 (2 carbons), 26.8, 26.37(2 carbons), 26.35, 26.1, 25.3. Anal. Calcd (%) for $C_{15}H_{23}ClO_2$: C, 66.53; H, 8.56. Found: C, 66.70; H, 8.59.

2-benzylcyclohept-1-en-1-yl 2-chloroacetate (2j)

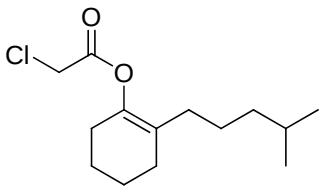
96% yield, pale yellow oil (5 equiv of chloroacetic anhydride was used.)



^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.30-7.23 (m, 2 H), 7.22-7.13 (m, 3 H), 4.11(s, 2 H), 3.30 (s, 2 H), 2.39 (m, 2 H), 2.06-2.01 (m, 2 H), 1.72-1.62 (m, 4 H) 1.45-1.36 (m, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.1, 147.5, 138.9, 129.0 (2 carbons), 128.6, 128.5 (2 carbons), 126.3, 40.9, 38.2, 33.1, 31.3, 30.8, 26.3, 25.2. Anal. Calcd (%) for $C_{16}H_{19}ClO_2$: C, 68.93; H, 6.87. Found: C, 69.06; H, 6.89.

2-(4-methylpentyl)cyclohex-1-en-1-yl 2-chloroacetate (2k)

96% yield, pale yellow oil (4 equiv of chloroacetic anhydride was used)



^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.10 (s, 2 H), 2.16-2.09 (m, 2 H), 2.11-2.07 (m, 2 H), 1.90 (t, J = 7.8 Hz, 2 H), 1.75-1.65 (m, 2 H), 1.65-1.56 (m, 2 H), 1.50 (sep, 6.4 Hz, 1 H), 1.36-1.27 (m, 2 H), 1.15-1.07 (m, 2 H), 0.84 (d, 6.4 Hz, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.7, 142.0, 125.5, 40.9, 38.9, 30.3, 27.88, 27.85, 26.9, 25.1, 23.1, 22.7 (2 carbons), 22.4. Anal. Calcd (%) for $C_{14}H_{23}ClO_2$: C, 64.98; H, 8.96. Found: C, 61.12; H, 7.89.

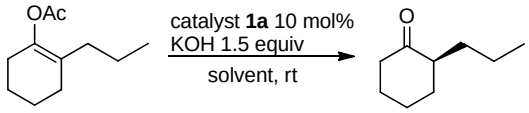
4. General procedure for asymmetric hydrolysis of enolesters catalyzed by PTC

Procedures: A typical experimental procedure for asymmetric hydrolysis of enolesters is described below. A round-bottomed screw cap tube (ϕ13x100 mm) equipped with a magnetic stir bar is charged *N*-9-anthracenylmethyl cinchonidinium chloride (6.1 mg, 0.01 mmol, 10 mol%) and $CHCl_3$ / Mesitylene (267 μL / 133 μL) solution under air, followed by the addition of 2-chloroethanol (6.7 μL, 0.10 mmol, 1 equiv) and 50 % KOH aq (100 μL). Then, the mixture was stirred at – 40 °C for 10 min followed by the addition of enolester **2c** (21.6 mg, 0.10 mmol, 1 equiv). The efficiency of agitation has an effect on the yield and enantioselectivity. The reaction mixture was stirred for 13 h at – 40 °C. Then, the reaction mixture was immediately passed through a thin pad of silica-gel and the resultant crude product was purified by silica-gel column chlomatography to give (*R*)-**3c** (13.9 mg, 99% yield, 92 : 8 er) followed by Chiral GC analysis (Conditions: InertCap CHIRAMIX, length 30 m, i. D. 0.25 mm, df. 0.25 μm; Detector: FID; Temperature; injector 200 °C, detector 240 °C, oven 40-180 °C, program 3 °C/min, t_{major} = 34.7 min, t_{minor} = 35.6 min). In case of 1 or 2 mmol-scale and 5 mmol-scale reraction, a 20-mL Schlenk flask and a 50-mL recovery flask were used for an alternative reaction container respectively.

5. Preliminary results of asymmetric hydrolysis of the acetyl enolate (2a).

Procedures: To the stirred solution of **1a** (6.1 mg, 0.1 mmol, 10 mol%) and solid KOH (85% purity, 9.9 mg, 0.15 mmol, 1.5 equiv) was added **2a** (18.2 mg, 0.1 mmol, 1 equiv) at RT. After the 1-14 h, the reaction mixture was directly passed through a short silica-gel pad. Resultant solution was analyzed by GC (according to general procedure for asymmetric hydrolysis of enolesters catalyzed by PTC.). Obtained preliminary results are shown below.

Table S1 Preliminary results of asymmetric hydrolysis



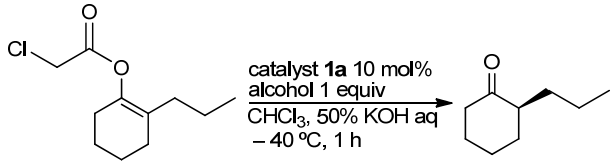
entry	time (h)	solvent	yield (%)[a)]	er
1	1	toluene	20	70:30
2	14	toluene	65	64:36
3	1	$CHCl_3$[b)]	10	79:21

a) GC yield. b) Less than 1% of EtOH was contained in the solvent.

6-1. Effects of alcohols

Procedures: *N*-9-anthracenylmethyl cinchonidinium chloride (6.1 mg, 0.01 mmol, 10 mol%) was added to the $CHCl_3$ (400 μL) under air, followed by the addition of an alcohol (0.05 mmol, 0.5 equiv) and 50% KOH aq (200 μL). Then, the mixture was stirred for 10 min at – 40 °C followed by the addition of enolester **2c** (21.6 mg, 0.10 mmol, 1 equiv). The reaction mixture was stirred for 1 h at – 40 °C. Then, the reaction mixture was immediately passed through a thin pad of silica-gel. Resultant solution was analyzed by GC (according to general procedure for asymmetric hydrolysis of enolesters catalyzed by PTC.). Obtained results are shown below.

Table S1 Preliminary results of asymmetric hydrolysis



entry	alcohol	yield (%)[a]	er	entry	alcohol	yield (%)[a]	er
1	none	30	85:15	6	PhOH	35	83:17
2	MeOH	64	85:15	7	F_3C OH	73	89:11
3	EtOH	66	87:13	8	F OH	42	87:13
4	^{i}PrOH	44	84:16	9	Cl OH	48	90:10
5	^{t}BuOH	2	76:24	10	Br OH	12	75:15

a) GC yield

6-2. Confirmation of mass balance of reaction products

Asymmetric hydrolysis of **3c** was performed according to the general procedures. After 19.5 h, 1 N HCl aq (2 mL) was added to the reaction mixture in order to neutralize KOH aq in the solution. After that, internal standard (diglyme) was added to the solution. The resultant mixture was homogenized by addition of MeOH followed by GC analysis.

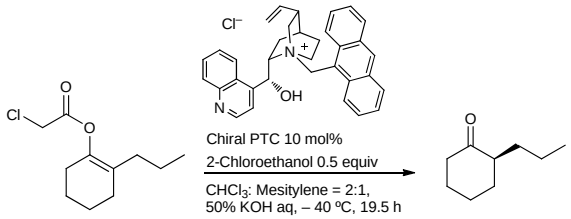


Table S3. Analysis of reaction products

components	yield (%)[a]	components	yield (%)[a]
Cl O O Cl	0	O	99
Cl O OH	99		
HO Cl	88	Substrate	0

a) GC yield.

6-3. Asymmetric hydrolysis of enolesters with the in situ generated stoichiometric Q^+OH^- reagent.

Reaction in homogenious system ($CHCl_3$): *N*-9-anthracenylmethyl cinchonidinium chloride (61 mg, 0.10 mmol, 1 equiv) in MeOH solution in 1-neck recovery flask (50 mL) was passed through a column filled with an anion exchange resin (Amberlyst A-26 OH form, 233 mg, 10 meq). MeOH of the eluate was distilled away under reduced pressure at 0 °C. The resultant dried residue was dissolved with $CHCl_3$ (0.5 mL) and repeatedly dried in vacuo for 15 min at 0 °C. Then, chloroform (1 mL) was added to the dried residue. The mixture was cooled down to – 40 °C and stirred for 5 min. An enolester **2c** (21.7 mg,

0.10 mmol, 1 equiv) was added to the solution and stirred for 4 h at the same temperature. After that, the reaction mixture was immediately passed through thin pad of silica-gel and an internal standard (tridecane) was added to the eluate. Then, the resultant mixture was analyzed by GC ((*R*)-**3c**, 99%, 89:11 er).

Reaction in biphasic system ($CHCl_3/H_2O$): *N*-9-anthracenylmethyl cinchonidinium chloride (61 mg, 0.10 mmol, 1 equiv) in MeOH solution was passed through a column filled with an anion exchange resin (Amberlyst A-26 OH form, 233 mg, 10 meq). MeOH of the eluate was distilled away under reduced pressure at 0 ^oC. The resultant dried residue in 1-neck recovery flask (50 mL) was dissolved with $CHCl_3$ (0.5 mL) and the solution was transferred to a screw vial using MeOH as a solvent. Solvents were removed under reduced pressure at 0 ^oC. The resultant dried residue was dissolved with $CHCl_3$ (0.5 mL) and removed repeatedly. Then the dried residue was further dried in vacuo for 15 min at 0 ^oC. Then, $CHCl_3$ (400 μL) and distilled water (100 μL) was added to the residue. The mixture was stirred for 2 min at 25 ^oC. An enolester **2c** (21.7 mg, 0.10 mmol, 1 equiv) was added to the solution and stirred for 4 h at the same temperature. After that, the reaction mixture was immediately passed through thin pad of silica-gel and an internal standard (tridecane) was added to the eluate. Then, the resultant mixture was analyzed by GC. (*R*)-**3c** (77%, 77:23 er).

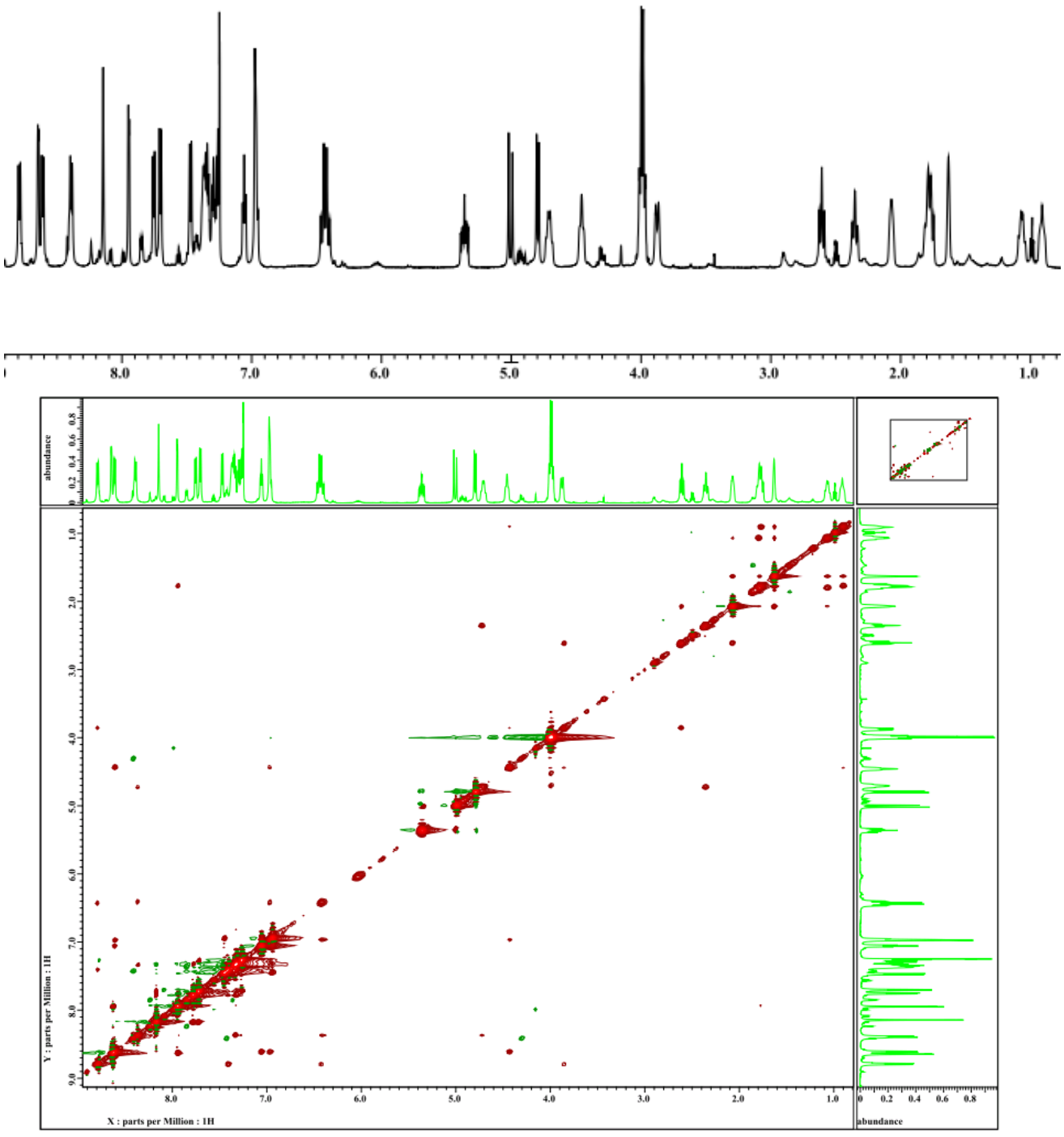
6-4. Asymmetric hydrolysis of enolesters with the in situ generated stoichiometric $Q^+CF_3CH_2O^-$ reagent.

N-9-anthracenylmethyl cinchonidinium chloride (61 mg, 0.10 mmol, 1 equiv) in MeOH solution was passed through a column filled with an anion exchange resin (Amberlyst A-26 OH form, 233 mg, 10 meq). 2,2,2-Trifluoroethanol (125 mg, 1.25 mmol, 90 μL, 5 equiv) was added to the elution and stirred for 15 min at RT. The solvent was removed under reduced pressure, then added $CHCl_3$ and the solution was transferred to a screw vial. Solvents were removed by evaporation and dried in vacuo for 6 h. To the resultant solid was added $CHCl_3$ (400 μL), distilled water (100 μL). Then the mixture was stirred for 2 min at 25 ^oC. An enolester **2c** (21.7 mg, 0.1 mmol, 1 equiv) was added to the solution and stirred for 4 h at the same temperature. After that, the reaction mixture was immediately passed through thin pad of silica-gel and an internal standard (tridecane) was added to the eluate. Then, the resultant mixture was analyzed by GC. (*R*)-**3c** (55%, 69:31 er).

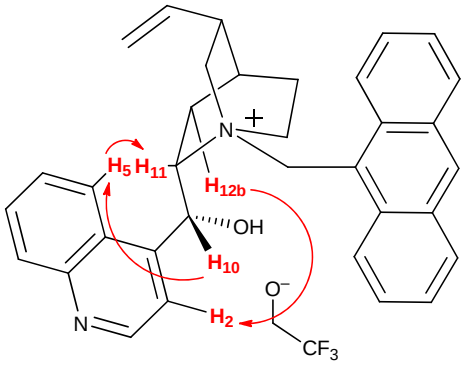
6-5. Preparation method for a sample of NOE experiment of *N*-9-anthracenylmethyl cinchonidinium 2,2,2-trifluoroethanoxide.

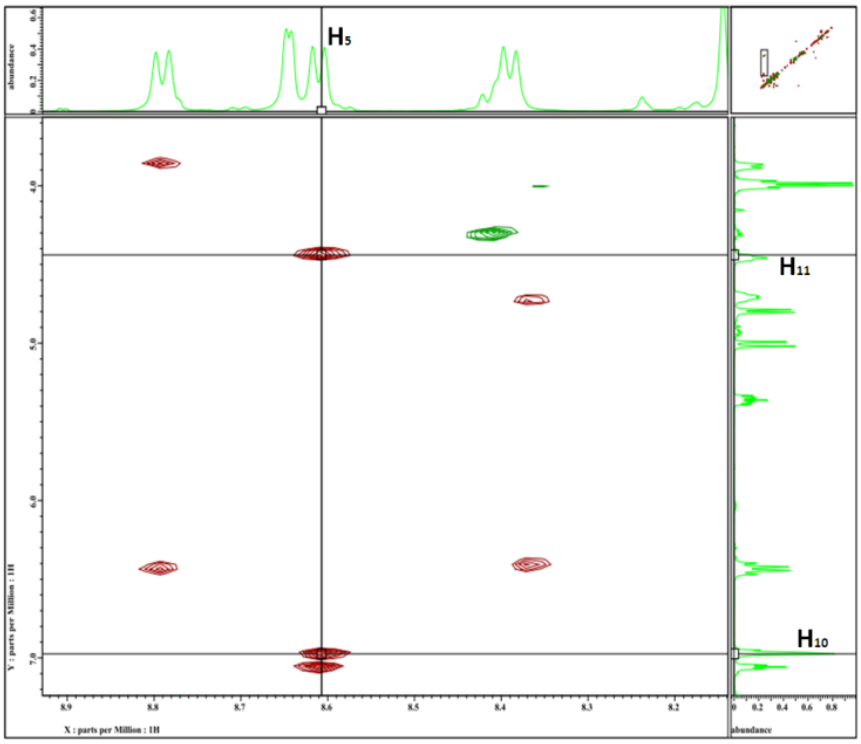
N-9-anthracenylmethyl cinchonidinium chloride (130 mg, 0.25 mmol, 1 equiv) in MeOH solution was passed through a column filled with an anion exchange resin, Amberlyst A-26 OH form (10 meq). 2, 2, 2-Trifluoroethanol (125 mg, 1.25 mmol, 90 μL, 5 equiv) was added to the eluate and stirred for 15 min. The solvent was removed under reduced pressure, then added $CDCl_3$ (0.5 mL) and removed the solvent again. After that, $CDCl_3$ (1.0 mL) was added to the residue and 600μL of the solution was transferred to a NMR tube. D_2O (50 μL) was added to the sample. After that, it was subjected to two freeze-pump-thaw cycles followed by keeping in refrigerator for 12 h. Then, NMR experiments were performed.^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.79 (d, *J* = 8.9 Hz, 1 H, H_{19}), 8.64 (d, *J* = 3.4 Hz, 1 H, H_1), 8.61 (d, J = 8.3 Hz, 1 H, H_5), 8.39 (d, J = 8.9 Hz, 1 H, H_{29}), 8.14 (s, 1 H, H_{24}), 7.95 (d, J = 3.4 Hz, 1 H, H_2), 7.75 (d, 8.2 Hz, 1 H, H_{22}), 7.70 (d, *J* = 8.2 Hz, 1 H, H_{26}), 7.47 (d, *J* = 8.3 Hz, 1 H, H_8), 7.40-7.28 (m, 3 H, H_{20} + H_{21} + H_{28}), 7.28-7.23 (m, 1 H, H_{27}), 7.06 (t, *J* = 6.8 Hz, 1H, H_6), 6.99-6.94 (m, 1 H, H_7), 6.98 (s, 1H, H_{10}), 6.46 (d, *J* = 13.7 Hz, 1 H, H_{16b}), 6.41 (d, *J* = 13.7 Hz, 1 H, H_{16a}), 5.36 (ddd, *J* = 6.6, 11.0, 17.2 Hz, 1 H, H_{33}), 5.01 (d, *J* = 17.2 Hz, 1 H, H_{34a}), (d, *J* = 11.0 Hz, 1 H, H_{34b}), 4.76-4.66 (m, 1 H, H_{15b}), 4.76-4.66 (m, 1 H, H_{15b}), 4.49-4.43 (m, 1 H, H_{11}), 4.05-3.93 (m, 3.1H, H_{35} + excess), 3.92-3.83 (m, 1 H, H_{32b}), 2.61 (t, *J* = 12.4 Hz, H_{32b}), 2.65-2.57 (m, 1 H, H_{32a}), 2.40-2.31 (m, 1 H, H_{15a}), 1.66-1.61 (m, 1 H, H_{31}), 1.90-1.72 (m, 2 H, H_{14b} + H_{12b}), 1.66-1.61 (m, 1H, H_{13}), 1.11-1.02 (m, 1 H, H_{14a}), 0.95-0.87 (m, 1 H, H_{12a}).

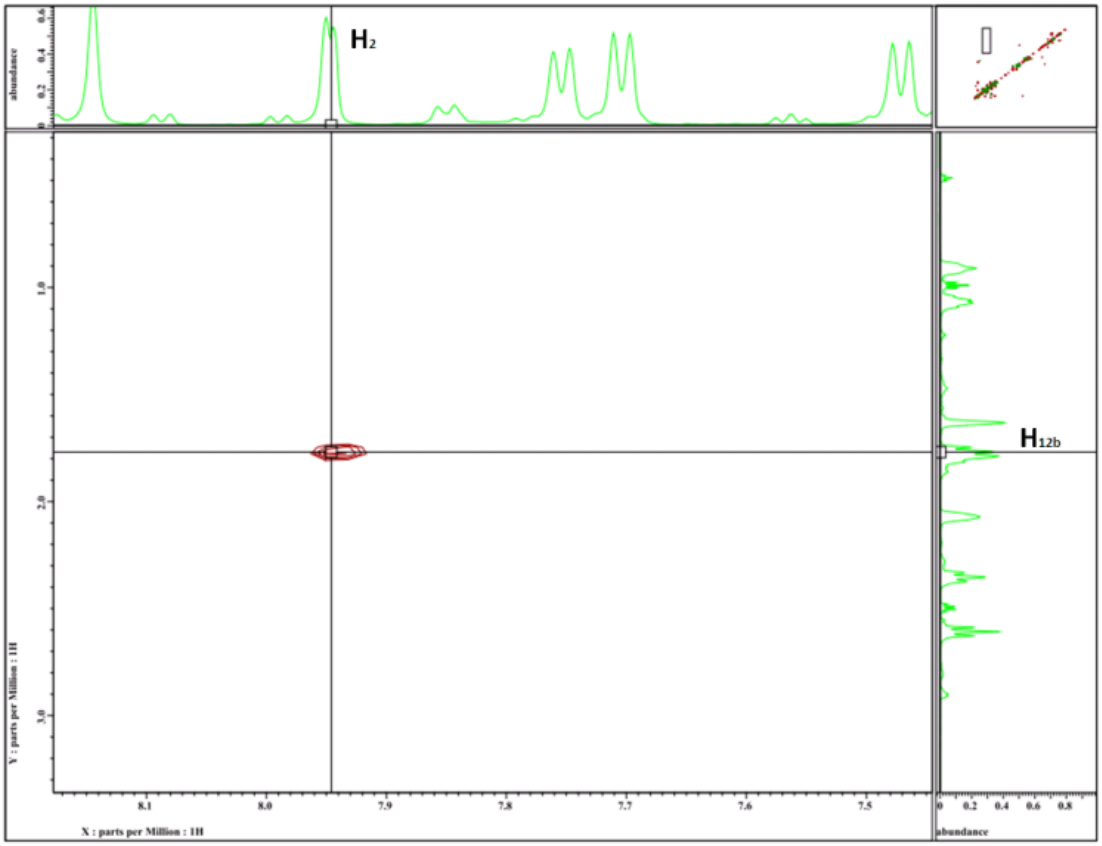
^{1}H and 2D-NOESY chart

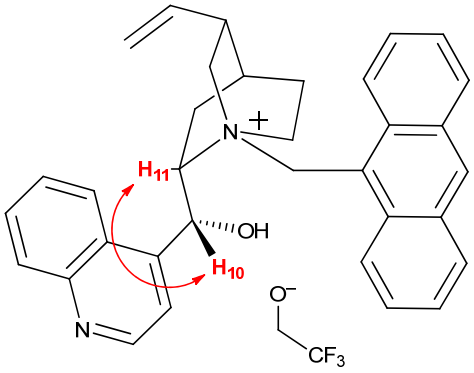


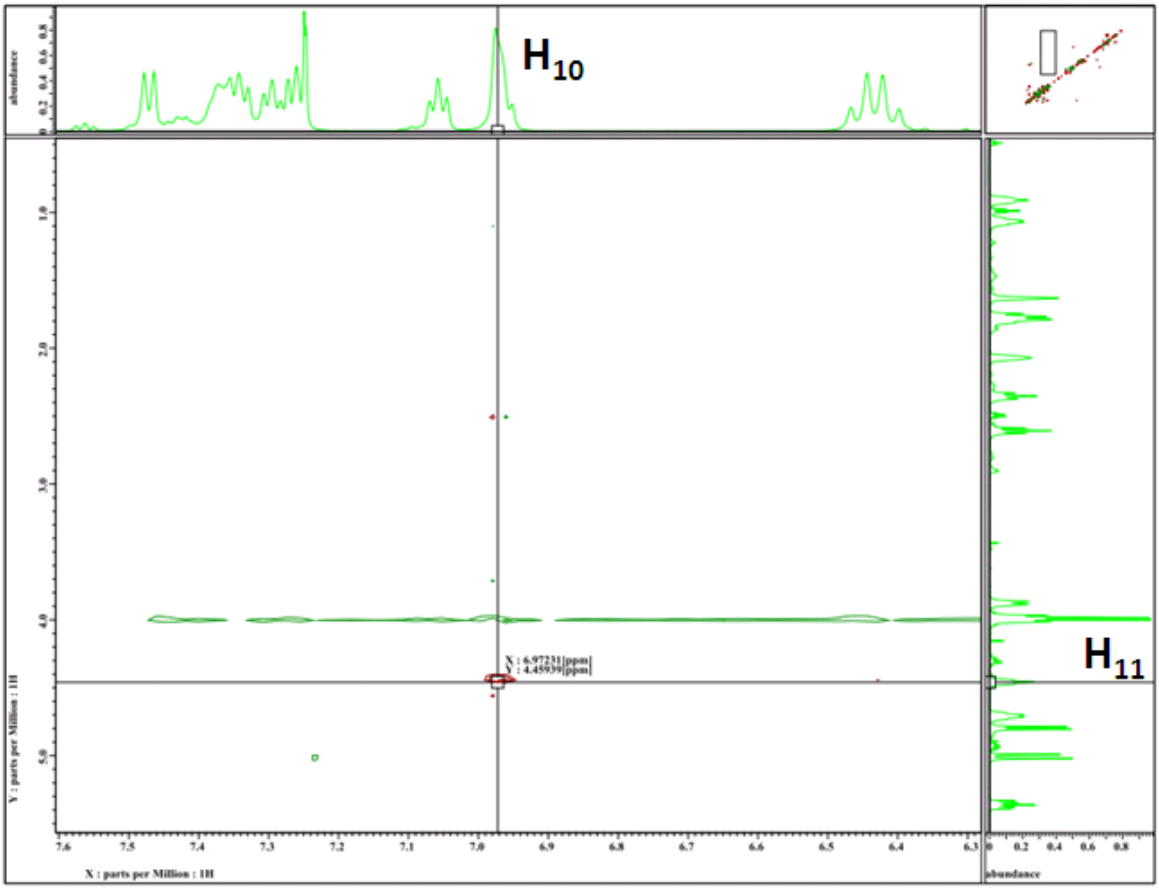
Green: negative, Red: positive


H5 H11
H12b
OH
H10
H2
O⁻
CF3
N
N

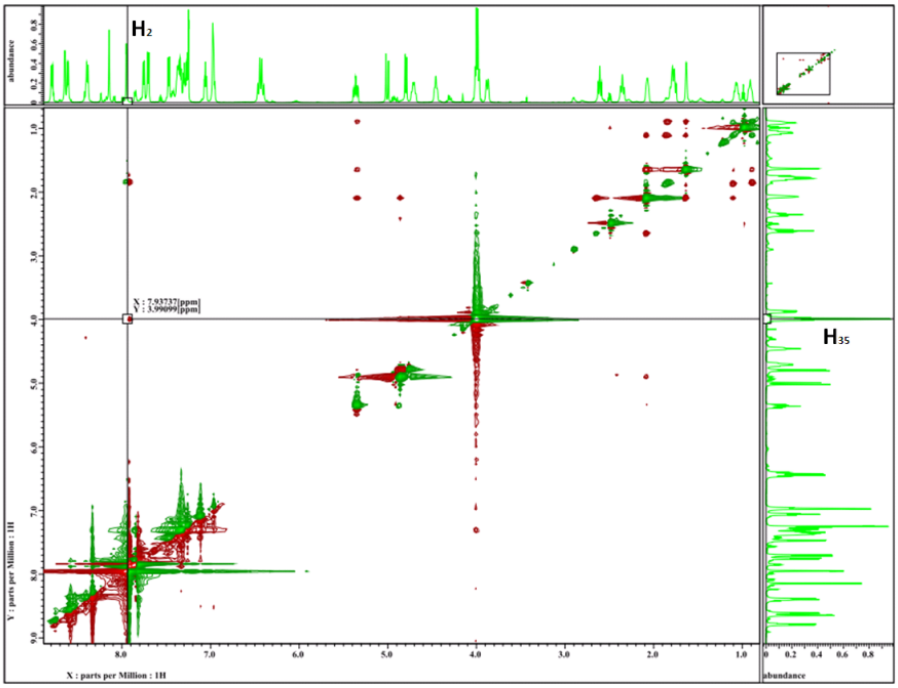

H5
H11
H10
X : parts per Million : 1H
Y : parts per Million : 1H
abundance


H2
H12b
X : parts per Million : 1H
Y : parts per Million : 1H
abundance


H11
N
OH
H10
O⁻
CF3
N


H10
H11
X : parts per Million : 1H
Y : parts per Million : 1H
abundance

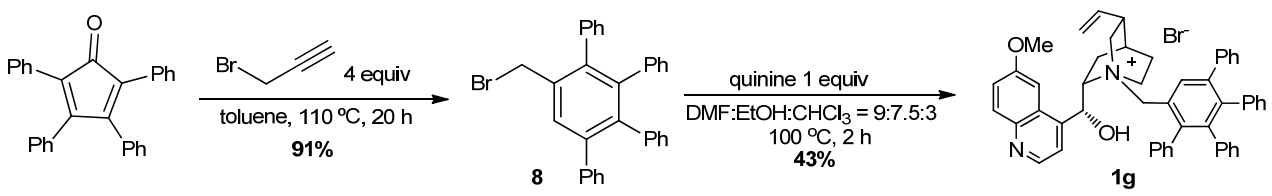
2d-ROESY Chart



Green: negative, Red: positive

6-6. Kinetic resolution of an aryl ester bearing binaphthyl backbone

6-6-1. Synthesis of the catalyst and substrate



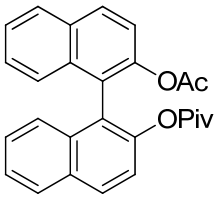
Synthesis of 1-bromomethyl-2,3,4,5-tetraphenyl benzene (8)

To a stirred solution of tetraphenyl cyclopentadienone (3.85 g, 10 mmol, 1 equiv) in toluene (10 mL) was added propargyl bromide (3.01 mL, 40 mmol, 4 equiv). After stirring for 8 h at 110 °C the reaction mixture was allowed to cool down to RT. Resultant white precipitate was filtrated and washed with hexane to give **8** (4.36 g, 9.1 mmol, 91%) as white solid. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.64 (s, 1 H), 7.20-7.11 (m, 10 H), 6.92-6.88 (m, 3 H), 6.86-6.81 (m, 3 H), 6.81-6.77 (m, 2 H), 6.76-6.72(m, 2 H), 4.40 (s, 2 H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 142.2, 141.5, 141.4, 140.9, 140.6, 139.8, 139.6, 138.7, 135.1, 131.5, 131.4(2 carbons), 131.2 (2 carbons), 130.3 (2 carbons), 129.9 (2 carbons), 127.7 (2 carbons), 127.6 (2 carbons), 127.0 (2 carbons), 126.8, 126.7 (2 carbons), 126.5, 125.8, 125.6, 32.8. Anal. Calcd (%) for $C_{31}H_{23}Br$: C, 78.32; H, 4.88. Found: C, 78.29; H, 4.86.

Synthesis of catalyst 1g

A stirred solution of quinine (1 mmol, 324 mg, 1 equiv) in DMF:EtOH:$CHCl_3$ (9:7.5:1, 200 μL) solution was added 1-bromomethyl-2,3,4,5-tetraphenyl benzene **8** (1 mmol, 475 mg, 1 equiv). The mixture was allowed to warm up to 100 °C. After 2 h, the reaction mixture was cooled to RT. The resultant solution was evaporated and purified by Silica-gel column chromatography to give **1g** (344 mg, 0.43 mmol, 43%) as pale pink powder. ^{1}H NMR (400 MHz, CD_3OD) δ =8.73-8.67 (m, 1 H), 7.97 (d, J = 9.2 Hz, 1 H), 8.00-7.95 (m, 2 H), 7.77 (d, J = 4.6 Hz, 1H) 7.48 (dd, J = 2.3, 9.6 Hz, 1 H), 7.31-7.10 (m, 8 H), 6.91-6.71 (m, 12 H), 6.49 (s, 1 H), 5.63-5.52 (m, 1H), 5.59 (d, J = 12.4 Hz, 1 H), 4.96-4.84 (m, 3 H), 4.05 (s, 3 H), 3.95-3.85 (m, 1 H), 3.78 (t, J = 11.4 Hz, 1 H), 3.64-3.55 (m, 1 H), 3.55-3.44 (m, 1 H), 3.28 (s, 1 H), 3.04-2.94 (m, 1 H), 2.76 (s, 1 H), 2.16-2.24 (m, 2 H), 1.98 (s, 1 H), 1.95-1.84 (m, 1 H), 1.31-1.20 (m, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.7, 146.9, 144.5, 144.0, 143.6, 143.3, 143.1, 141.7, 140.8, 139.6, 139.2, 138.6, 137.5, 135.6, 131.6, 131.4, 131.04, 131.00, 130.94, 130.6, 129.7, 128.1, 128.0, 127.6, 127.1, 126.8, 126.6, 125.9, 125.6, 124.4, 121.4, 120.2, 115.8, 101.4, 68.4, 64.9, 61.8, 61.1, 55.4, 53.5, 51.6, 37.6, 26.3, 24.5, 21.2. HRMS (FAB+) m/z calculated for $C_{51}H_{47}N_2O_2$ 719.3632 found 719.3641 [M-Br]

Synthesis of 2'-acetoxy-[1,1'-binaphthalen]-2-yl pivalate (7)

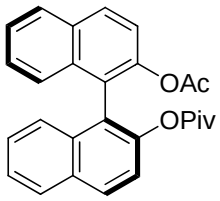


To a mixture of 2'-hydroxy-[1,1'-binaphthalen]-2-yl pivalate (1.14 g, 4.0 mmol) and acetyl chloride (310 μL, 4.4 mmol) in CH_2Cl_2 (10 mL) was added Et_3N (610 μL, 4.4 mmol) at 0 °C and the mixture was stirred at RT for 20 h. The reaction was quenched by adding HCl (1N, 30 mL) and extracted with AcOEt. The resulting extracts were washed with brine, and dried, and concentrated under reduced pressure. The crude product was purified by silica-gel column chromatography to give **6** (1.63 g, 3.96 mmol, 99%) as white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.99-7.95 (m, 1 H), 7.93-7.89 (m, 1 H), 7.46-7.37 (m, 4 H), 7.31-7.22 (m, 6 H), 1.76 (s, 3 H), 0.76 (s, 9 H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ = 176.6, 169.2, 147.0, 146.9, 133.5, 133.4, 131.6, 131.5, 129.5, 129.4, 128.1, 128.0, 126.8 (2 carbons), 126.2, 126.1, 125.8, 125.7, 123.7, 123.6, 122.0, 121.9, 38.8, 26.5 (3 carbons), 20.6. elemental analysis calcd (%) for $C_{27}H_{24}O_4$: C 78.62, H 5.86; found: C 78.60, H 5.86.

6-6-2. Asymmetric hydrolysis of the acetate ester

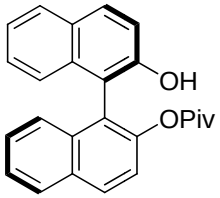
A mixture of the catalyst **1g** (0.01 mmol, 10 mol%) and 1N K_2CO_3 aq (200 μL, 0.2 mmol, 2 equiv) in toluene (200 μL) was stirred at 20 °C. After 20 min, the *rac*-**7** (0.1 mmol, 1 equiv) was added and the mixture was stirred at the same temperature. Silica-gel column chromatography (Hexane: $CHCl_3$: Et_2O = 20:6.5:1) was carried out to give (*S*)-**8** (15% yield, 78:22 er) and (*R*)-**7** (80% yield, 43.5:56.5 er); HPLC analysis: CHIRALPAK AD-H (+), hexane/2-propanol = 20/1, flow rate = 1.0 mL/min, 25 °C, **7**: t_{major} = 7.9 min, t_{minor} = 17.4 min, **8**: t_{major} = 10.6 min, t_{minor} = 16.5 min)(*S*)-**7**: $[\alpha]_D^{25.5}$ = + 35.1, (*c* 0.5, $CHCl_3$), (*R*)-**8**: $[\alpha]_D^{24.5}$ = – 3.63, (*c* 1.0, $CHCl_3$). k_{rel} = 4.1 (The k_{rel} value was calculated from ee_{sub} and ee_{pro} with equations as follows.: conv = $ee_{sub}/(ee_{sub}+ee_{pro})$, k_{rel} = ln[(1 – conv (1 + ee_{pro})] /ln[(1 – conv (1 – ee_{pro})])

Recovered substrate (*S*)-7



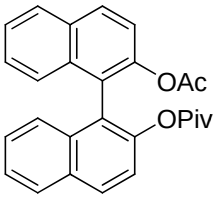
^{1}H NMR (600 MHz, CDCl3) δ = 7.99-7.95 (m, 1 H), 7.93-7.89 (m, 1 H), 7.46-7.37 (m, 4 H), 7.31-7.22 (m, 6 H), 1.76 (s, 3 H), 0.76 (s, 9 H). 13C-NMR (100 MHz, CDCl3) δ = 176.6, 169.2, 147.0, 146.9, 133.5, 133.4, 131.6, 131.5, 129.5, 129.4, 128.1, 128.0, 126.8 (2 carbons), 126.2, 126.1, 125.8, 125.7, 123.7, 123.6, 122.0, 121.9, 38.8, 26.5 (3 carbons), 20.6. elemental analysis calcd (%) for $C_{27}H_{24}O_4$: C 78.62, H 5.86; found: C 78.60, H 5.86.

Product (*R*)-8

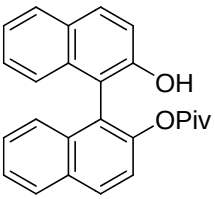


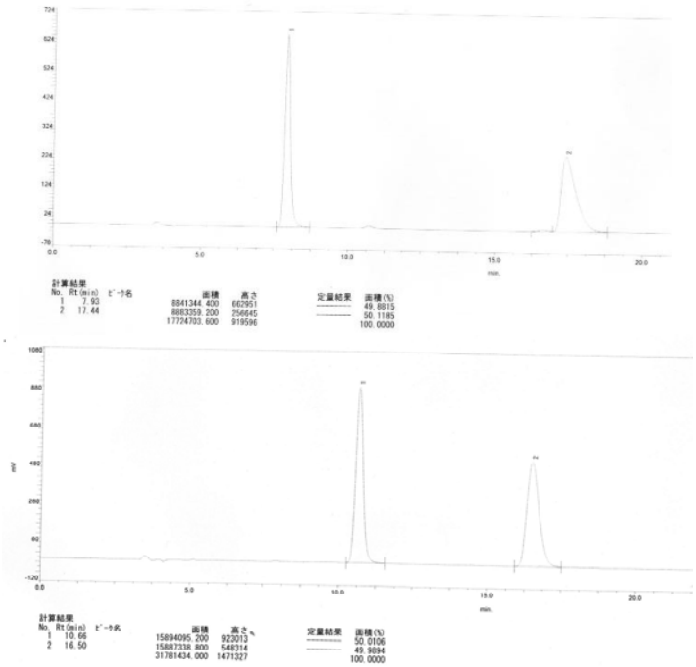
^{1}H and ^{13}C NMR were in agreement with the literature[11]. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.06 (d, *J* = 6.0 Hz, 1 H), 7.97 (d, *J* = 5.5 Hz, 1 H), 7.87 (d, *J* = 6.0 Hz, 1 H), 7.81 (d, *J* = 5.5 Hz, 1H), 7.50(t, *J* = 5.5 Hz, 1H), 7.39-7.28 (m, 5H), 7.26-7.21 (m, 1 H), 7.05 (d, *J* = 5.5 Hz, 1 H), 5.14 (s, 1 H), 0.78 (s, 9 H). ^{13}C NMR (150 MHz, $CDCl_3$) δ = 177.9, 151.8, 148.4, 133.7, 133.6, 132.3, 130.8, 130.4, 129.1, 128.4, 128.0, 127.5, 126.7, 126.3, 125.7, 124.6, 123.6, 123.1, 121.9, 118.3, 114.3, 38.8, 26.5(3 carbons). elemental analysis calcd (%) for $C_{25}H_{22}O_3$: C, 81.06; H, 5.99; found: C, 81.11, H, 5.99.

HPLC chart of ***rac*-7**



HPLC chart of ***rac*-8**

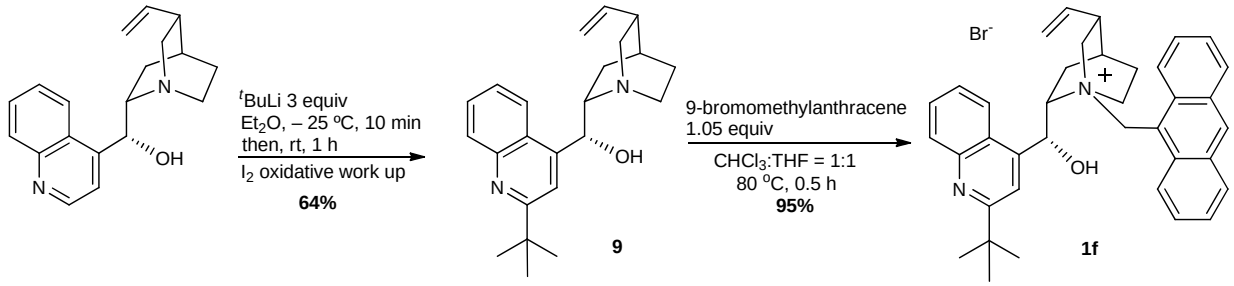




HPLC chart of recovered substrate (*S*)-7 and product (*R*)-8

7. Formal synthesis of the biologically-active natural product

7-1. Synthesis of catalyst 1f



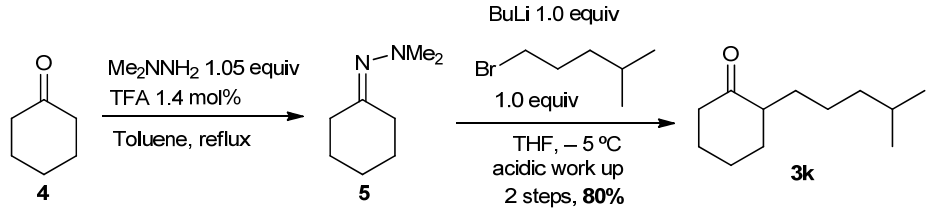
Synthesis of amine 9

To the stirred solution of (–)-cinchonidine (883 mg, 3 mmol, 1 equiv) in dry Et_2O (15 mL) at –25 °C was added ^{t}BuLi (1.57M in pentane, 5.73 mL, 9 mmol, 3 equiv) in one portion and stirred for 10 min. Then, the reaction mixture was allowed to warm up to RT and stirred for another 1 h. Reaction was monitored by TLC analysis (toluene:MeOH:Et_3N = 10:1:1, ^{t}Bu adducts turn blue under the UV irradiation). AcOH was added to quench the residual basic reagents in cool bath, then EtOAc (30 mL) and H_2O (30 mL) was added followed by the addition of I_2 until strong brown color persists. After that, $Na_2S_2O_3$ aq was added to quench residual I_2. The reaction mixture was extracted with EtOAc. The organic layer was dried with Na_2SO_4 and evaporated. The crude mixture was purified by silica-gel column chromatography (toluene:MeOH:Et_3N = 20:1:1) to give the product **9** (704 mg, 1.92 mmol, 64%) as white solid. Analytical sample was prepared by the PTLC purification (CH_2Cl_2:MeOH = 4:1)
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.07 (d, *J* = 8.2 Hz, 1 H), 7.90 (d, *J* = 8.7 Hz , 1 H), 7.72, (s, 1 H), 7.63 (t, *J* = 7.8 Hz, 1H), 7.39 (t, J =7.4 Hz, 1H), 5.71 (ddd, *J* =7.8, 10.1, 17.4 Hz, 1 H), 5.66 (s, 1 H), 4.93 (d, *J* = 17.4 Hz, 1 H), 4.88 (d, *J* = 10.1 Hz, 1 H), 3.53-3.43 (m, 1 H), 3.12-3.00 (m, 2 H), 2.70-2.59 (m, 2 H), 2.29-2.20 (m, 1 H), 1.80-1.65 (m, 4 H), 1.50-1.40 (m, 11 H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 169.0, 148.3, 147.7, 142.0, 130.4, 128.7, 125.9, 123.9, 122.6, 115.2, 114.4, 72.4, 60.3, 57.2, 43.4, 40.1, 38.3, 30.2 (3 carbons), 28.1, 27.7, 21.4. FABMS m/z calculated for $C_{23}H_{30}N_2O$ 351.24 found 351.29 [M+H] Anal. Calcd (%) for $C_{23}H_{30}N_2O$: C, 78.82; H, 8.63; N, 7.99 Found: C, 78.38; H, 8.63, N; 7.89.

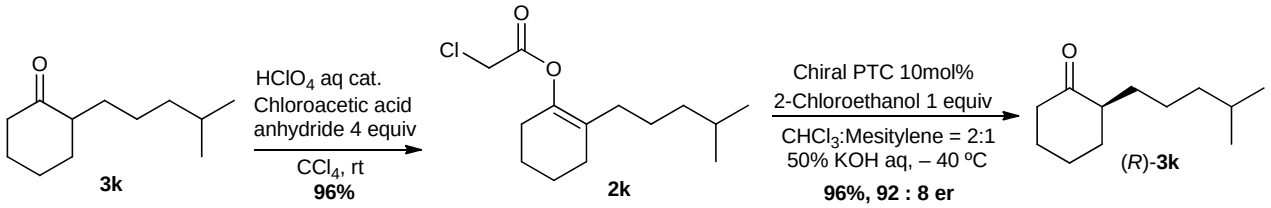
Synthesis of 1f

To the stirred solution of amine **9** (73 mg, 0.2 mmol, 1 equiv) in $CHCl_3$-THF (1:1) was added 9-bromomethylanthracene (57 mg, 0.21 mmol, 1.05 equiv) followed by concentration with nitrogen gas stream down to a volume 0.2 mL. The mixture was stirred at 80 °C for 10 min. Then, the solution was allowed to cool down to RT. After that, resultant precipitate was dissolved with $CHCl_3$. To the solution was added Et_2O dropwise to solidify the product. The resulting solid was filtrated and washed with Et_2O to give the product (118 mg, 0.19 mmol, 95%) as pale yellow powder. Analytical sample was prepared by the PTLC purification (EtOAc:MeOH = 4:1). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.81 (d, J = 8.9 Hz, 1 H), 8.68 (s, 1 H), 8.60-8.54 (m, 1 H), 8.54-8.48 (m, 1 H), 8.16-8.09 (m, 4 H), 7.82-7.70 (m, 4 H), 7.60-7.52 (m, 2 H), 7.01 (s, 1 H), 6.36 (d, J = 13.7 Hz, 1 H), 5.86 (d, J = 13.7 Hz, 1 H), 5.66 (ddd, *J* = 7.6, 9.6, 17.2 Hz, 1 H), 5.00 (d, *J* = 17.2 Hz, 1 H), 4.92 (d, *J* = 9.6 Hz, 1 H), 4.66-4.59 (m, 1 H), 4.48-4.40 (m, 1 H), 3.90-3.84 (m, 1 H), 3.13 (t, *J* = 11.7 Hz, 1 H), 2.76-2.66 (m, 1 H), 2.36 (br s, 1 H), 2.24-2.14 (m, 1 H), 2.12-2.00 (m, 1 H), 1.87 (s, 1 H), 1.66-1.20 (s, 9 H), 1.45-1.37 (m, 1 H), 1.35-1.20 (m, 1 H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 169.0, 147.5, 145.1, 137.5, 133.4, 133.3, 132.3, 131.60, 131.55, 129.8, 129.7, 129.6, 129.2, 127.93, 127.88, 126.9, 125.2, 124.5, 123.9, 123.1, 122.7, 118.0, 117.0, 116.3, 78.2, 68.6, 66.2, 62.3, 55.4, 51.9, 38.3, 38.0, 29.2 (3 carbons), 26.0, 24.9, 21.8. FABMS m/z calculated for $C_{38}H_{41}N_2O^+$ 541.32 found 541.38 [M].

Synthesis of (*R*)-3k from cyclohexanone (4)

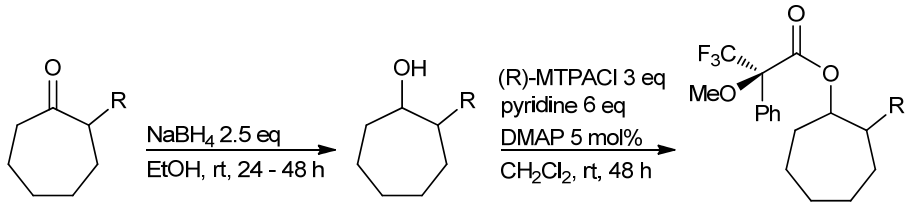


To a stirred solution of cyclohexanone (4.91 g, 50 mmol, 1 equiv) and *N, N*-dimethyl hydrazine (3.16 g, 52.5 mmol, 1.05 equiv) in toluene (40 mL) was added trifluoroacetic acid (80 mg, 0.7 mmol, 1.4 mol%). The mixture was refluxed for 5 h. After that, the resulting solution was cooled to RT. Then, distilled water was added to the solution and extracted with Et_2O. The organic layer was dried over Na_2SO_4. The solution was evaporated and purified by distillation under reduced pressure to give colorless oil (yield of **7**: 6.13 g, 43.7 mmol, 87%) laced with toluene (molar ratio = 10 : 1). This was used without further purification. BuLi (1.67 M in hexane, 10.5 mmol, 6.30 mL, 1.0 equiv) was added dropwise to a stirred solution of **7** (1.47 g, 10.5 mmol, 1 equiv) in THF (anhydrous, 20 mL) at –5 ^{o}C under a nitrogen atmosphere and stirred for 1 h. After that, 1-bromo-4-methylpentane (1.733 g, 10.5 mmol, 1 equiv) was added dropwise to the solution, and then the resulting solution was allowed to warm to RT and stirred for 5 h. The resultant solution was added water and cooled to 0 ^{o}C. Then the solution was acidified with concentrated HCl aq to reach pH = 1-2. After stirring at 45 ^{o}C for another 3 h, the solution was extracted with Et_2O. The organic extracts were combined, dried over Na_2SO_4, and concentrated to give yellow oil. Silica-gel column chromatography of the crude residue by eluting with diethylether/hexane (1:30-1:20) afforded **3k** (1.76 g, 9.66 mmol, 92%) as a colorless oil and ^{1}H NMR was in agreement with the literature[12]. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.40-2.32 (m, 1 H), 2.32-2.18 (m, 2H), 2.13-2.04 (m, 1 H), 2.04-1.92 (m, 1 H), 1.88-1.79 (m, 1 H), 1.79-1.57 (m, 3 H), 1.51 (sep, *J* = 6.4 Hz, 1 H), 1.42-1.31 (m, 1H), 1.31-1.08 (m, 5 H), 0.84 (d, *J* = 6.9 Hz, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 213.8, 50.9, 42.1, 39.1, 33.9, 29.7, 28.1, 27.9, 25.0, 24.9, 22.71, 22.66. Anal. Calcd (%) for $C_{12}H_{22}O$: C, 79.06; H, 12.16. Found: C, 79.03; H, 12.12.



2k was synthesized according to the general method (pale yellow oil, 96% yield). Asymmetric hydrolysis of **2k** was performed according to the general method of Asymmetric hydrolysis of enolesters (cat. **1f** was used in place of cat. **1a**). (*R*)-(+)-2-(4-Methylpentyl)cycloheptanone was obtained in 96% yield and 92: 8 er as a colorless oil.

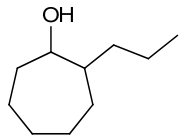
8. Derivatization of ketones to the corresponding alcohol and Mosher's esters



General procedure: reduction of ketones

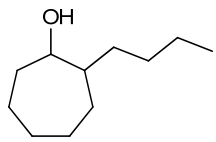
A typical experimental procedure for the reduction of ketones is described below. To the stirred solution of a ketone (0.01 mmol, 1 equiv) in absolute EtOH (0.5 mL) was added $NaBH_4$ (9.5 mg, 0.25 mmol, 2.5 equiv) followed by stirring at RT for 24-48 h. The reaction mixture was monitored by TLC. After the substrate was completely converted, the reaction mixture was quenched with water and 1N HCl aq. The resultant solution was extracted with Et_2O (x 3). After that, the organic layer was combined and dried over Na_2SO_4. The crude product was concentrated and purified by silica-gel chromatography to give the corresponding alcohol.

2-propyl-cycloheptanol (10f)[13]



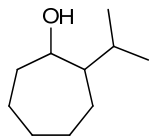
0.0758 mmol (11.7 mg) of 2-propylcyclohepanone **3f** (Table 2, entry 5) was used. The product (diastereomeric mixture) was obtained as colorless oil (11.5 mg, 0.0736 mmol, 97%). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 3.94-3.89 (m, 0.66 H), 3.49-3.44 (m, 0.34 H), 1.80-1.15 (m, 16 H), 0.93-0.86 (m, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): major isomer, δ = 73.4, 44.2, 35.6, 35.2, 28.3, 27.2, 26.8, 22.0, 21.0, 14.5. minor isomer, δ = 73.4, 47.2, 36.8, 36.5, 29.1, 28.7,26.9, 22.3, 20.2, 14.6.

2-butyl-cycloheptanol (10g)[9,14]



0.097 mmol (16.3 mg) of 2-butylcycloheptanone **3g** (Table 2, entry 6) was used. The product (diastereomixture) was obtained as colorless oil (0.0916 mmol, 15.6 mg, 94%). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 3.94-3.89 (m, 0.7 H), 3.71-3.20 (m, 0.3 H), 1.80-1.10 (m, 18 H), 0.95-0.80 (m, 3 H). ^{13}C NMR (150 MHz, $CDCl_3$): major isomer, δ = 73.4, 44.5, 35.6, 32.6, 30.2, 28.3, 27.2, 26.85, 23.1, 22.0, 14.2. minor isomer, δ = 73.4, 47.4, 36.5, 34.2, 29.4, 29.1, 28.8, 26.91, 23.2, 22.3, 14.2.

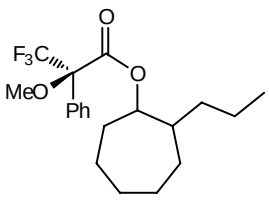
2-isopropyl-cycloheptanol(10h)[15]



0.097 mmol (15 mg) of 2-isopropylcycloheptanone **3h** (Table 2, entry 7) was used. The product was obtained as colorless oil in 93% yield (major isomer: 10.8 mg, 0.0691 mmol, 71%, minor isomer: 3.3 mg, 0.0211 mmol, 22%). ^{1}H NMR of major isomer (600 MHz, $CDCl_3$): δ = 4.13-4.09 (m, 1 H), 1.76-1.67 (m, 3 H), 1.67-1.49 (m, 5 H), 1.48-1.35 (m, 3 H), 1.19-1.13 (m, 2 H), 0.95 (t, *J* = 5.5 Hz, 6 H). ^{13}C NMR of major isomer (100 MHz, $CDCl_3$): δ = 71.5, 50.2, 36.9, 31.4, 28.2, 27.9, 24.1, 22.2, 21.1. Anal. Calcd (%) for $C_{10}H_{20}O$: C, 76.86; H, 12.90. Found: C, 76.44; H, 12.64.

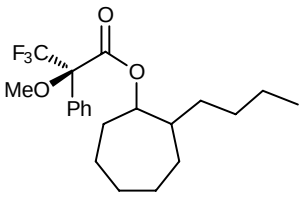
Mosher's esterification

(2*R*)-2-propylcycloheptyl 3,3,3-trifluoro-2-methoxy-2-phenylpropanoate (11f)



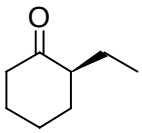
To the stirred solution of an alcohol (0.0644 mmol, 1 equiv) in dry CH_2Cl_2 (0.5 mL) was added (*R*)-MTPACl (32.5 mg, 0.129 mmol, 2.0 equiv), dry pyridine (20.4 mg, 0.258 mmol, 4 equiv) and *N*,*N*-dimethyl aminopyridine (1 mg, 4 μmol, 6 mol%) followed by stirring at RT for 48 h. The reaction mixture was monitored by TLC. After the substrate was completely converted, the reaction mixture was diluted with Et_2O. The crude was washed with saturated $CuSO_4$ aq and extracted with Et_2O (x3). The resultant solution was was concentrated and purified by silica-gel chromatography (Hexane/Et_2O = 50:1-40:1) to give the corresponding ester (93%) as colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.56-7.49 (m, 2 H), 7.41-7.35 (m, 3 H), 5.32-5.29 (m,0.335 H), 5.29-5.24 (m, 0.335 H), 4.96-4.88 (m, 0.33 H), 3.57-3.50 (m, 3 H), 1.95-1.00 (m, 15 H), 0.90-0.71 (m, 3 H).

(2*R*)-2-butylcycloheptyl 3,3,3-trifluoro-2-methoxy-2-phenylpropanoate(11g)

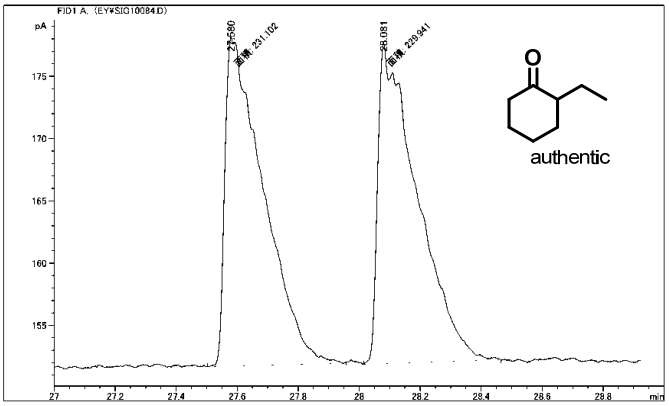


To the stirred solution of an alcohol (0.059 mmol, 1 equiv) in dry CH_2Cl_2 (0.5 mL) was added (*R*)-MTPACl (29.8 mg, 0.118 mmol, 2.0 equiv), dry pyridine (18.7 mg, 0.16 mmol, 4 equiv) and *N*,*N*-dimethyl aminopyridine (1mg, 4 μmol,.7 mol%) followed by stirring at RT for 48 h. The reaction mixture was monitored by TLC. After the substrate was completely converted, the reaction mixture was diluted with Et_2O. The crude was washed with saturated $CuSO_4$ aq and extracted with Et_2O (x3). The resultant solution was was concentrated and purified by silica-gel chromatography (Hexane/Et_2O = 50:1-40:1) to give the corresponding ester (99%) as inhomogeneous colorless oil. ^{1}H NMR (600 MHz, C_6D_6): δ = 7.71-7.63 (m, 2 H), 7.08-7.01 (m, 2 H), 7.01-6.95 (m, 1 H), 5.28-5.22 (m, 0.72 H), 4.96-4.93 (m, 0.14 H), 4.92-4.88 (m, 0.14 H), 3.43-3.39 (m, 3 H), 1.83-0.74 (m, 20 H).

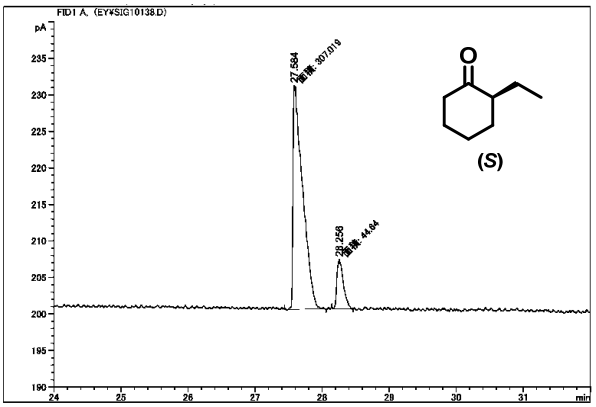
9. Analysis of hydrolyzed products



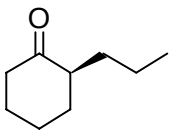
The product ((*S*)-(+)-2-ethyl-cyclohexanone) was obtained as a colorless oil and 87: 13 er . ^{1}H and ^{13}C NMR were in agreement with the literature[16]. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.40-1.90 (m, 5 H), 1.90-1.54 (m, 4 H), 1.44-1.29 (m, 1 H), 1.29-1.15 (m, 1 H), 0.86 (t, J = 7.3 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 213.6, 52.4, 42.1, 33.5, 28.1, 24.9, 22.5, 11.8. Anal. Calcd (%) for $C_8H_{14}O$: C, 76.14; H, 11.18. Found: C, 76.30; H, 11.21. Enantiomeric ratio (er) was determined by GC with a CHIRASIL-DEX CB column (conditions, starting temperature: 60 °C [hold 10 min.], rate of temperature increase: 2 °C/min up to 120 °C), t_r (major) = 27.6 min., t_r (minor) = 28.3 min.$[\alpha]_D^{25.6}$ = + 36.1, (*c* 0.5, $CHCl_3$) The absolute configuration was established by comparison of the optical rotation to the literature value for (*R*)-(–)-2-ethylcyclohexanone: $[\alpha]_D^{25}$ = – 23.6 (*c* 4.31, MeOH) [17,18].



ピーク #	RT [min]	タイプ	ピーク幅 [min]	面積 [pA*s]	高さ [pA]	面積 %
1	27.580	MM	0.1456	231.10191	26.45447	50.12591
2	28.081	MM	0.1489	229.94092	25.73554	49.87409
トータル：				461.04283	52.19001	

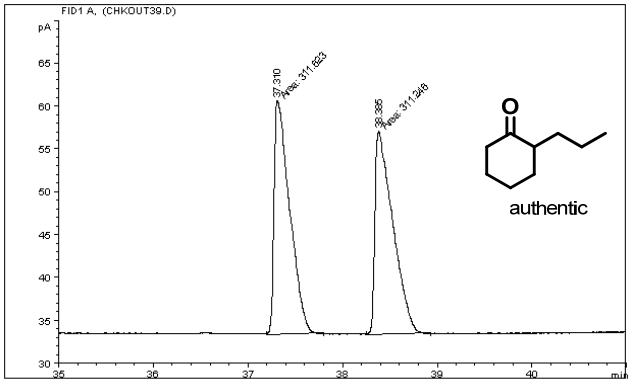


ピーク #	RT [min]	タイプ	ピーク幅 [min]	面積 [pA*s]	高さ [pA]	面積 %
1	27.584	MM	0.1669	307.01852	30.66601	87.30586
2	28.256	MM	0.1102	44.64003	6.75144	12.69414
トータル：				351.65855	37.41745	

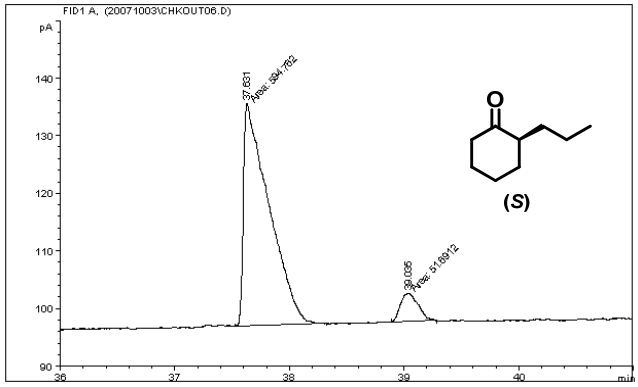


The product ((*S*)-(+)-2-propylcyclohexanone) was obtained as a pale yellow oil and 92: 8 er. ^{1}H and ^{13}C NMR were in agreement with the literature[19]. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.39-2.2.31 (m, 1 H), 2.31-2.20 (m, 2H), 2.12-1.92 (m, 2 H), 1.86-1.56 (m, 4 H), 1.42-1.08 (m, 4 H), 0.87 (t, *J* = 6.9 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 213.7, 50.6, 42.0, 33.9, 31.7, 28.1, 24.9, 20.4, 14.3. Anal. Calcd (%) for $C_9H_{16}O$: C, 77.09; H, 11.50. Found: C, 77.01; H, 11.50. Enantiomeric ratio (er) was determined by GC with a InertCap CHIRAMIX Column (conditions, starting temperature: 40 °C [hold 0 min.], rate of temperature increase: 3 °C/min up to 120 °C [hold 15 min.]), t_r (major) = 37.5 min., t_r (minor) = 38.7 min.$[\alpha]_D^{22.5}$ = + 33.5, (*c* 1.0, $CHCl_3$) The absolute configuration was established by comparison of the

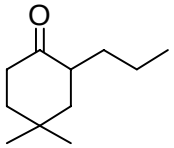
optical rotation to the literature value for (*R*)-(–)-2-propylcyclohexanone: $[\alpha]_D^{25}$ = –25.7 (*c* 0.82, MeOH)[20].



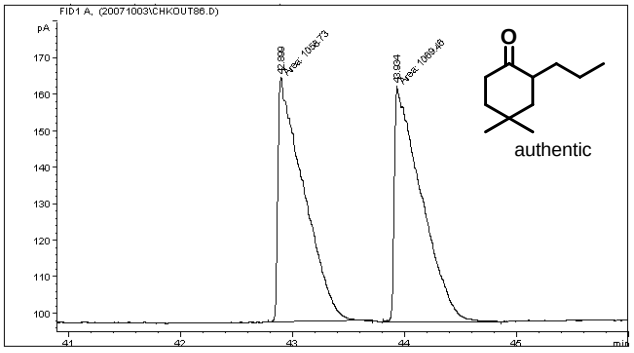
Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	37.310	MM	0.1905	311.62347	27.25916	50.03032
2	38.385	MM	0.2190	311.24579	23.68605	49.96968
Totals :				622.86926	50.94521	



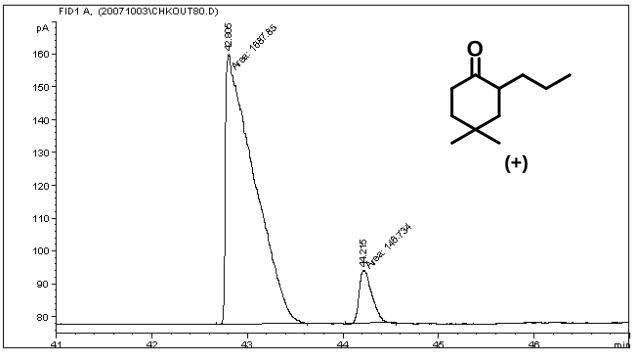
Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	37.631	MM	0.2574	594.76245	38.51495	92.00388
2	39.035	MM	0.1757	51.69118	4.90219	7.99612
Totals :				646.45364	43.41714	



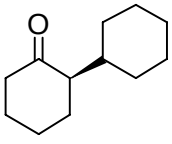
The product[7] ((+)-4,4-dimethyl-2-propylcyclohexanone) was obtained as a pale yellow oil and 92: 8 er. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.44 (td, *J* = 6.4, 14.2 Hz, 1 H), 2.36 (dt, *J* = 6.0, 6.0 Hz, 1 H), 2.22 (dt, *J* = 3.2, 14.2 Hz, 1 H), 1.80-1.55 (m, 4 H), 1.34-1.22 (m, 3 H), 1.19 (s, 3 H), 1.06 (tq, 6.9, 6.9 Hz, 1 H), 0.99 (s, 3 H), 0.87 (t, *J* = 7.4 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 214.1, 46.8, 45.8, 40.2, 38.6, 31.6, 31.2, 30.9, 24.7, 20.3, 14.3. Anal. Calcd (%) for $C_{11}H_{20}O$: C, 78.51; H, 11.98. Found: C, 78.24; H, 11.98. Enantiomeric ratio (er) was determined by GC with a InertCap CHIRAMIX Column (conditions, starting temperature: 40 °C [hold 0 min.], rate of temperature increase: 3 °C/min up to 120 °C [hold 15 min.]), t_r (major) = 42.9 min., t_r (minor) = 44.1 min. $[\alpha]_D^{25.9}$ = + 26.6, (*c* 1.0, $CHCl_3$)



Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	42.899	MM	0.2638	1058.72681	66.87698	49.74787
2	43.934	MM	0.2763	1069.45837	64.50529	50.25213
Totals :				2128.18518	131.38226	

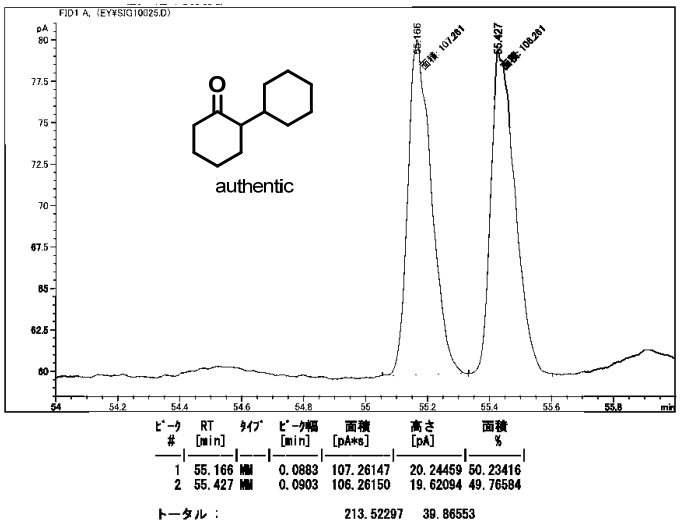


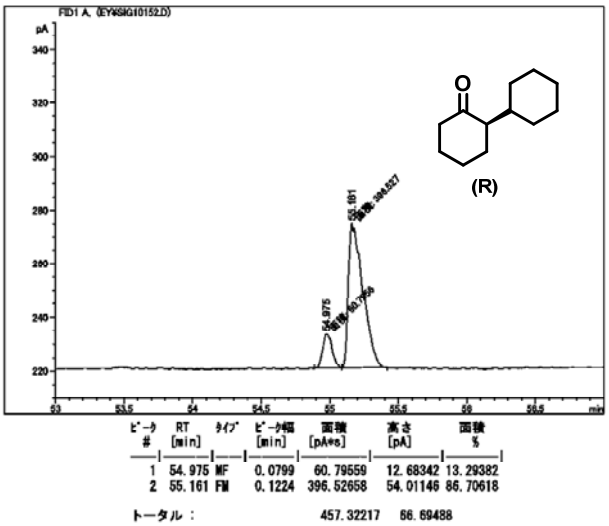
Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	42.805	MF	0.3431	1687.84790	81.99417	92.00177
2	44.215	MF	0.1534	146.73418	15.93985	7.99823
Totals :				1834.58208	97.93402	

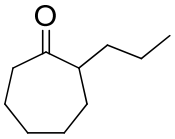


The product ((*R*)-(+)-2-cyclohexylcyclohexanone) was obtained as a colorless oil and 87: 13 er and ^{1}H and ^{13}C NMR were in agreement with the literature[12]. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.39-2.29 (m, 1 H), 2.28-2.18 (m, 1 H), 2.11-2.01 (m, 1 H), 1.98-1.45 (m, 12 H), 1.33-1.18 (m, 2 H), 1.16-0.80 (m, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 213.8, 56.6, 41.9, 36.1, 31.6, 29.42, 29.37, 28.0, 26.6, 26.5, 24.0. Anal. Calcd (%) for $C_{12}H_{20}O$: C, 79.94; H, 11.18. Found: C, 79.78; H, 11.27. Enantiomeric ratio (er) was determined by GC with a CHIRASIL-DEX CB column (conditions, starting temperature: 40 °C [hold 1 min.], rate of temperature increase: 2 °C/min up to 160 °C), t_r (minor) = 55.1 min., t_r (major) = 55.3 min. $[\alpha]_D^{24.8}$ = + 46.1, (*c* 1.0, $CHCl_3$) The absolute configuration was established by comparison of the

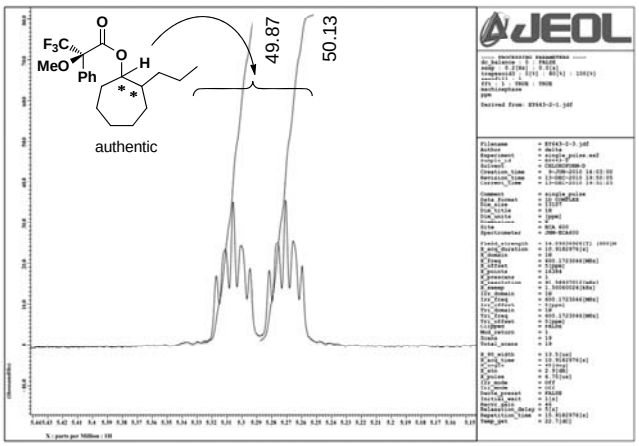
optical rotation to the literature value for (*S*)-(–)-2-cyclohexylcyclohexanone: $[\alpha]_D^{24.3}$ = – 38.1 (*c* 1.58, MeOH)[21].

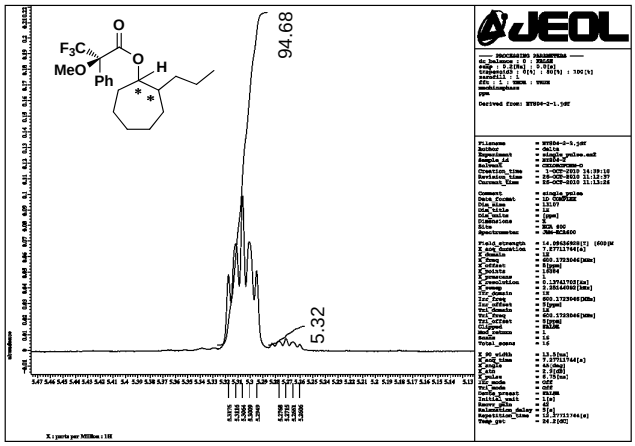


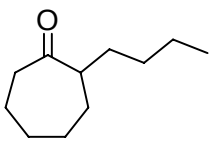




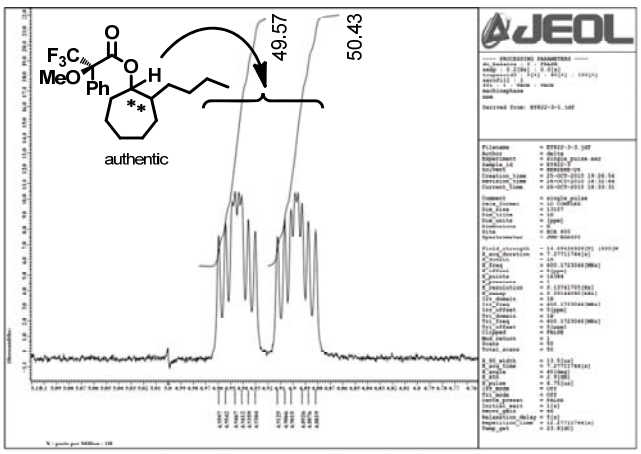
The product (2-(+)-propylcycloheptanone) was obtained as a pale yellow oil and 94.5: 5.5 er and ^{13}C NMR was in agreement with the literature[8]. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.54-2.34 (m, 3 H), 1.89-1.76 (m, 4 H), 1.68-1.48 (m, 2H), 1.40-1.17 (m, 6 H), 0.86 (t, *J* = 7.4 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ =216.8, 52.3, 42.7, 34.6, 31.3, 29.7, 28.5, 24.8, 20.5, 14.2. Anal. Calcd (%) for $C_{10}H_{18}O$: C, 77.87; H, 11.76. Found: C, 78.01; H, 11.83. $[\alpha]_D^{25.3}$ = + 49.7 (*c* 1.0, $CHCl_3$). Enantiomeric ratio (er) was determined by ^{1}H NMR after the product was reduced and esterified to the corresponding mosher's ester (600 MHz, C_6D_6, major isomer : δ = 5.33-5.29 ppm, minor isomer : δ = 5.29-5.25 ppm).

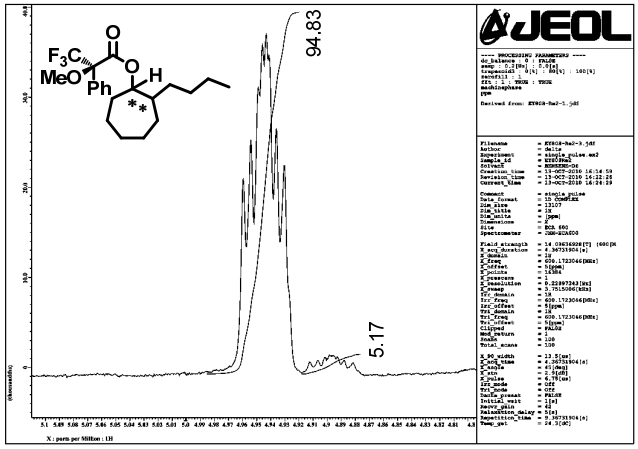


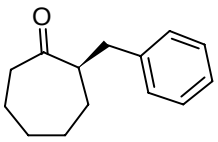




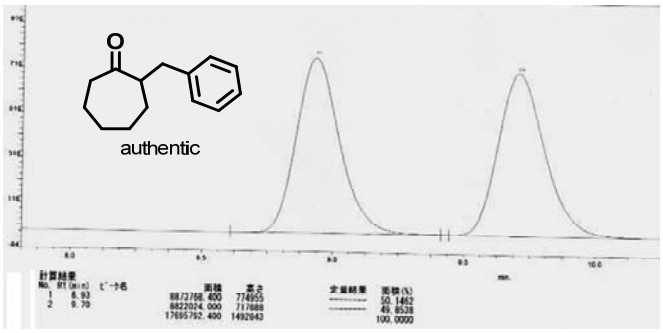
The product[9] (2-(+)-butylcycloheptanone) was obtained as a pale yellow oil and 95: 5 er. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.53-2.32 (m, 3 H), 1.90-1.77 (m, 4 H), 1.68-1.50 (m, 2H), 1.38-1.14 (m, 8 H), 0.86 (t, *J* = 6.9 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ =216.9, 52.5, 42.7, 32.2, 31.3, 29.7, 29.5, 28.5, 24.8, 22.9, 14.1. Anal. Calcd (%) (%) for $C_{11}H_{20}O$: C, 78.51; H, 11.98. Found: C, 78.44; H, 11.96. $[\alpha]_D^{25.3}$ = + 49.7 (*c* 1.0, $CHCl_3$) Enantiomeric ratio (er) was determined by ^{1}H NMR after the product was reduced and esterified to the corresponding mosher's ester (600 MHz, C_6D_6, major isomer : δ = 4.97-4.92 ppm, minor isomer : δ = 4.92-4.87 ppm).

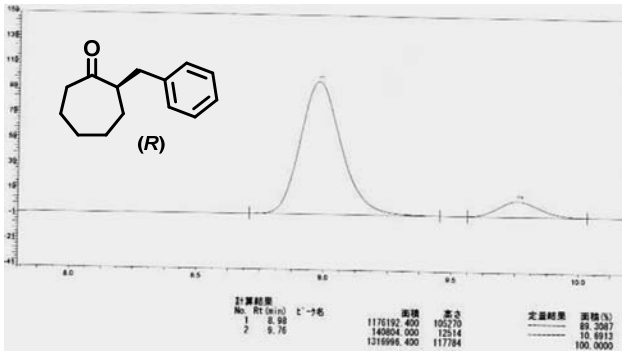


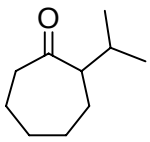




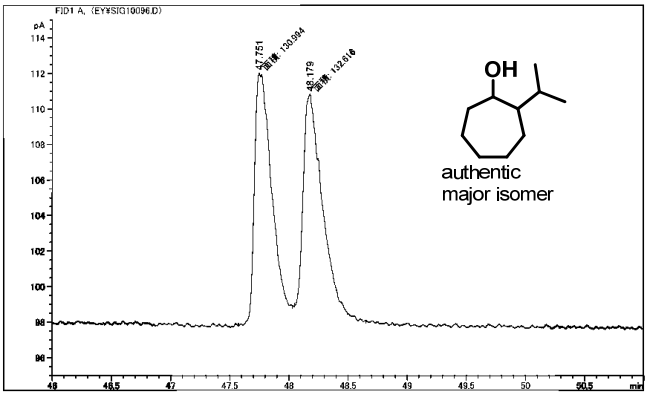
The product ((*R*)-(+)-2-benzylcycloheptanone) was obtained as a colorless oil and 89.5: 10.5 er and ^{13}C NMR was in agreement with the literature[22]. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.29-7.22 (m, 2 H), 7.21-7.11 (m, 3 H), 3.06 (dd, *J* = 6.0, 13.8 Hz, 1 H), 2.86-2.75 (m, 1 H), 2.54 (dd, *J* = 8.7, 13.8 Hz, 1 H), 2.48-2.40 (m, 2H), 1.90-1.70 (m, 4 H), 1.68-1.54 (m, 1 H), 1.38-1.22 (m, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 215. 7, 140.1, 129.2, 128.4, 126.1, 53.7, 43.3, 38.0, 30.4, 29.4, 28.7, 24.3. Anal. Calcd (%) for $C_{14}H_{18}O$: C, 83.12; H, 8.97. Found: C, 82.87; H, 8.88. Enantiomeric ratio (er) was determined by HPLC with a Chiracel AD-H column (conditions, Hexane : EtOH = 100 : 1, flow rate = 1 mL / min, 25 ^{o}C), t_r (minor) = 8.9 min., t_r (major) = 9.7 min. $[\alpha]_D^{26.7}$ = + 54.1, (*c* 1.0, $CHCl_3$) The absolute configuration was established by comparison of the optical rotation to the literature value for (*R*)-(+)-2-benzylcyclohexanone: $[\alpha]_D$ = + 41.4 (*c* = 5, MeOH, 88% ee)[17,18].



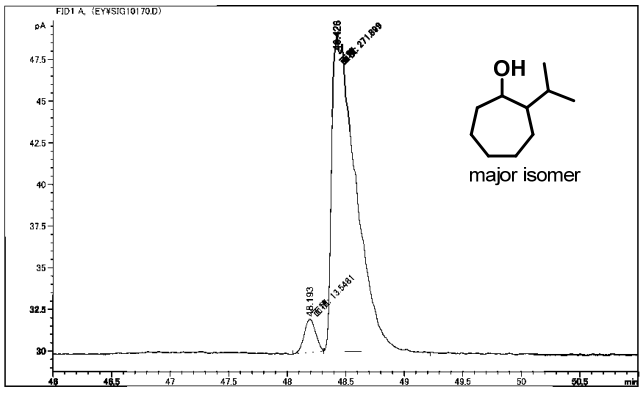




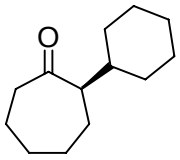
The product ((+)-isopropylcycloheptanone) was obtained as a pale yellow oil and 95: 5 er, and ^{1}H and ^{13}C NMR was in agreement with the literature[4]. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.49 (td, *J* = 3.2, 12.8 Hz, 1 H), 2.40-2.30 (m, 1 H), 2.19-2.10 (m, 1 H), 2.00-1.80 (m, 5 H),1.60-1.42 (m, 1 H), 1.42-1.12 (m, 3 H), 0.87 (dd, J = 6.4, 12.8 Hz, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ =217.2, 59.8, 42.9, 30.6, 30.1, 28.2, 27.8,25.5, 21.1, 19.6. Anal. Calcd (%) for $C_{10}H_{18}O$: C, 77.87; H, 11.76. Found: C, 77.81; H, 11.89. Enantiomeric ratio (er) was determined by GC with a CHIRASIL-DEX CB column (conditions, starting temperature: 60 ^{o}C [hold 10 min.], rate of temperature increase: 2 ^{o}C/min up to 120 ^{o}C) after the product was reduced to the corresponding alcohol (major isomer). t_r (major) = 48.2 min., t_r (minor) = 48.4 min. $[\alpha]_D^{30.0}$ = + 95.5, (*c* 1.0, $CHCl_3$).



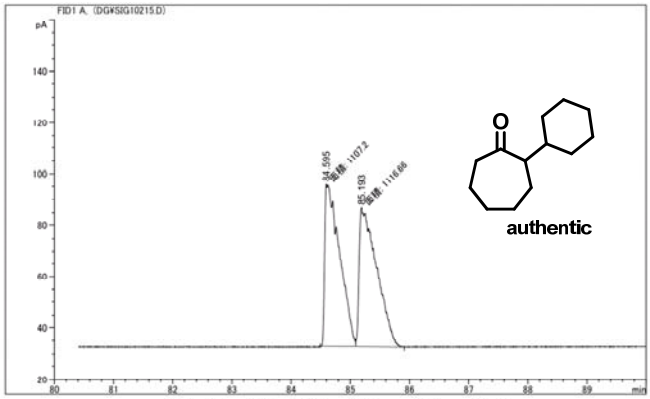
ピーク #	RT [min]	タイプ	ピーク幅 [min]	面積 [pA*s]	高さ [pA]	面積 %
1	47.751	MM	0.1587	130.99377	13.75960	49.69230
2	48.179	MM	0.1819	132.61604	12.15015	50.30770



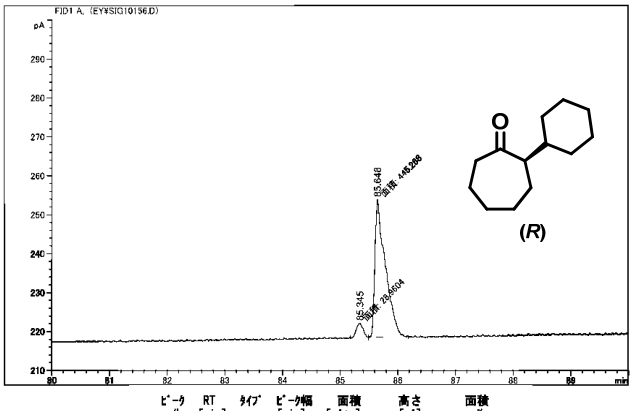
ピーク #	RT [min]	タイプ	ピーク幅 [min]	面積 [pA*s]	高さ [pA]	面積 %
1	48.193	MM	0.1124	13.54809	2.00891	4.74626
2	48.426	MM	0.2397	271.89935	18.90436	95.25374
トータル：				285.44744	20.91327	



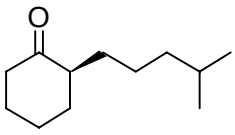
The product ((*R*)-(+)-2-cyclohexylcycloheptanone) was obtained as a colorless oil and 94: 6 er, and ^{13}C NMR was in agreement with the literature[12]. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.52 (dt, J = 3.2, 12.4 Hz, 1 H), 2.35-2.28 (m, 1 H), 2.21-2.14 (m, 1 H), 1.98-1.79 (m, 4 H), 1.75-1.40 (m, 7 H), 1.40-1.07 (m, 6 H), 1.17-0.84 (m, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 217.4, 59.3, 42.8, 40.7, 31.4, 30.2, 30.0, 27.9, 27.8, 26.47, 26.44, 25.8. Anal. Calcd (%) for $C_{13}H_{22}O$: C, 79.94; H, 11.18. Found: C, 79.98; H, 11.25. Enantiomeric ratio (er) was determined by GC with a CHIRASIL-DEX CB column (conditions, starting temperature: 60 °C [hold 1 min.], rate of temperature increase: 1 °C/min up to 160 °C). t_r (major) = 85.3 min., t_r (minor) = 85.6 min. $[\alpha]_D^{25.8}$ = + 78.3, (*c* 1.0, $CHCl_3$) The absolute configuration was established by comparison of the optical rotation to the literature value for (*R*)-(+)-2-cyclohexylcycloheptanone: $[\alpha]_D^{20}$ = + 87.3 (*c* 0.284, CH_2Cl_2) [11].



ピーク #	RT [min]	タイプ	ピーク幅 [min]	面積 [pA*s]	高さ [pA]	面積 %
1	84.595	MF	0.2923	1107.19861	63.13494	49.78731
2	85.193	FM	0.3438	1116.65857	54.13449	50.21269
トータル：				2223.85718	117.26943	

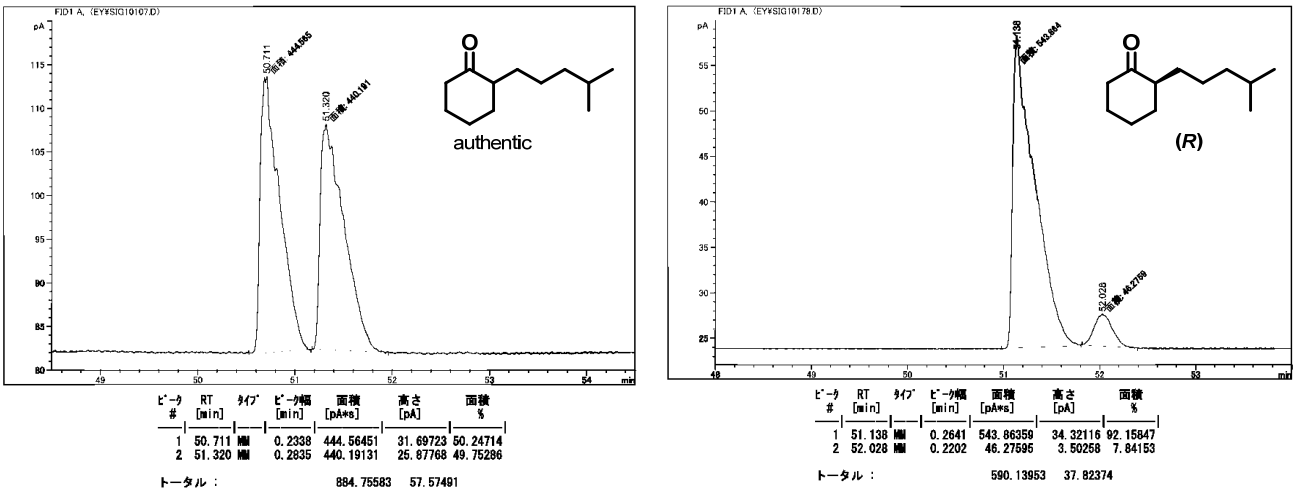


ピーク #	RT [min]	タイプ	ピーク幅 [min]	面積 [pA*s]	高さ [pA]	面積 %
1	85.345	MF	0.1328	28.96045	3.63491	6.10685
2	85.648	FM	0.2097	445.26846	35.38125	93.89315
トータル：				474.22891	39.01616	



The product ((*R*)-(+)-2-(4-methylpentyl)cycloheptanone) was obtained as a colorless oil and 92: 8 er, and ^{1}H NMR was in agreement with the literature[12]. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.40-2.32 (m, 1 H), 2.32-2.18 (m, 2H), 2.13-2.04 (m, 1 H), 2.04-1.92 (m, 1 H), 1.88-1.79 (m, 1 H), 1.79-1.57 (m, 3 H), 1.51 (sep, *J* = 6.4, Hz, 1 H) 1.42-1.31 (m, 1 H), 1.31-1.08 (m, 5 H), 0.84 (d, *J* = 6.9 Hz, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 213.8, 50.9, 42.1, 39.1, 33.9, 29.7, 28.1, 27.9, 25.0, 24.9, 22.71, 22.66. Anal. Calcd (%) for $C_{12}H_{22}O$: C, 79.06; H, 12.16. Found: C, 79.03; H, 12.12. Enantiomeric ratio (er) was determined by GC with a CHIRASIL-DEX CB column (conditions, starting temperature: 60 °C [hold 10 min.], rate of temperature increase: 2 °C/min up to 120 °C). t_r (major) = 51.1 min., t_r (minor) =

52.0 min. $[\alpha]_D^{24.4}$ = + 20.1, (*c* 1.0, $CHCl_3$). The absolute configuration was established by comparison of the optical rotation to the literature value for (*R*)-(+)-2-(4-Methylpentyl)cycloheptanone: $[\alpha]_D^{20}$ = + 18.4 (*c* 3.75, Et_2O) [12].



ピーク #	RT [min]	タイプ	ピーク幅 [min]	面積 [pA*s]	高さ [pA]	面積 %
1	50.711	MM	0.2338	444.56451	31.69723	50.24714
2	51.320	MM	0.2835	440.19131	25.87768	49.75286
トータル：				884.75583	57.57491	

ピーク #	RT [min]	タイプ	ピーク幅 [min]	面積 [pA*s]	高さ [pA]	面積 %
1	51.138	MM	0.2641	543.86359	34.32116	92.15847
2	52.028	MM	0.2202	46.27595	3.50258	7.84153
トータル：				590.13953	37.82374	

10. Reactivity of enolesters bearing chloroacetyl group and PNP amino acid esters

The pKa values of products (alcohols and acids) are described below (Fig. S1). The pKa value of cyclohexenol is 4.55 point larger than *p*-nitrophenol, although chloroacetic acid is more acidic than *N*-benzoylglycine by 0.75 point. Therefore, enolesters bearing chloroacethyl group seem to be less reactive compared to PNP esters derived from *N*-benzoyl aminoacids.

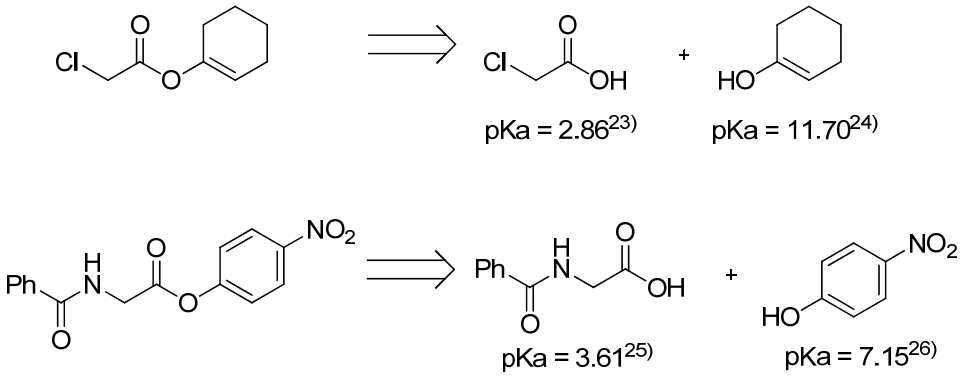


Fig. S1 Comparison of pKa values between product acids and alcohols (in water)

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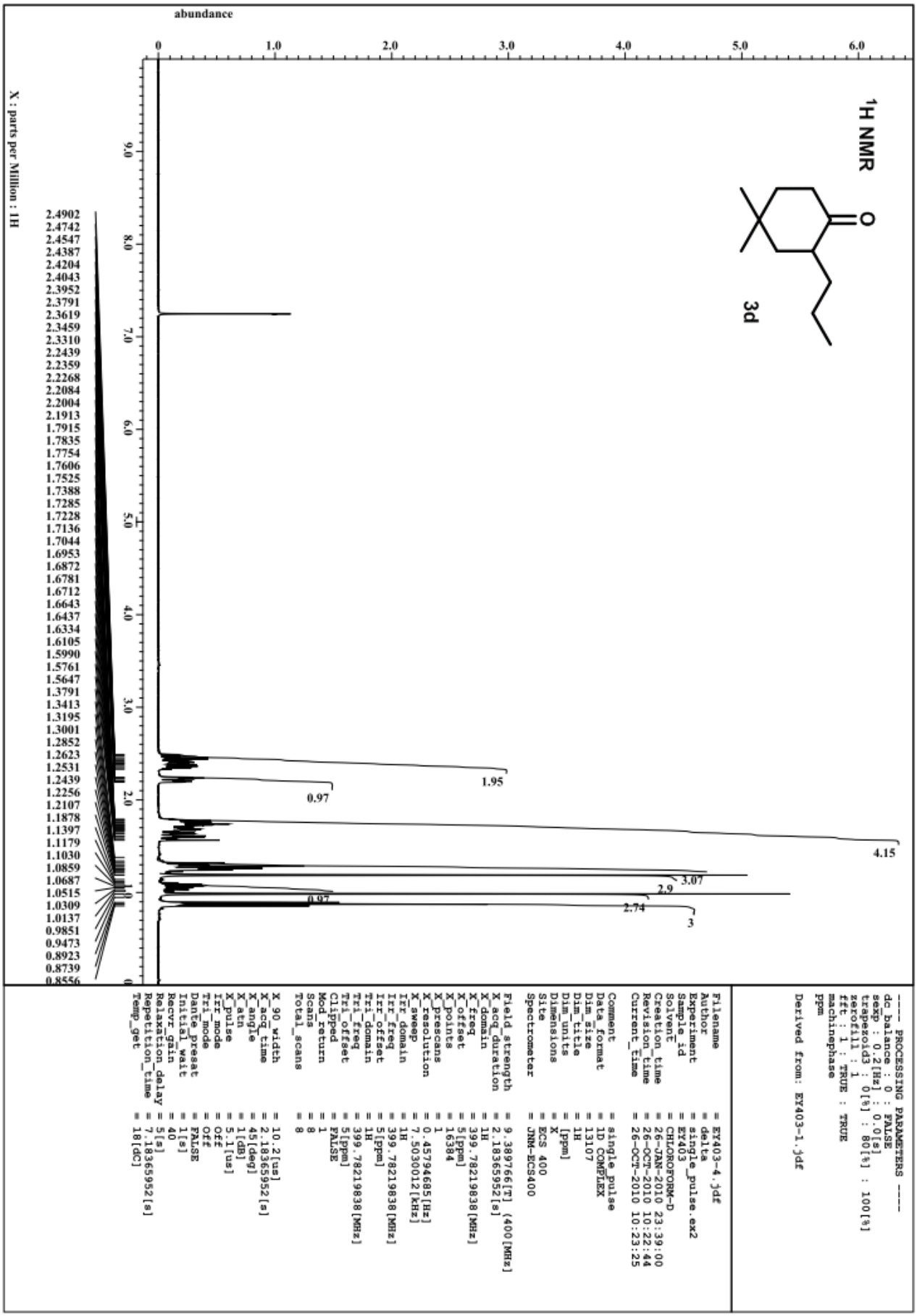
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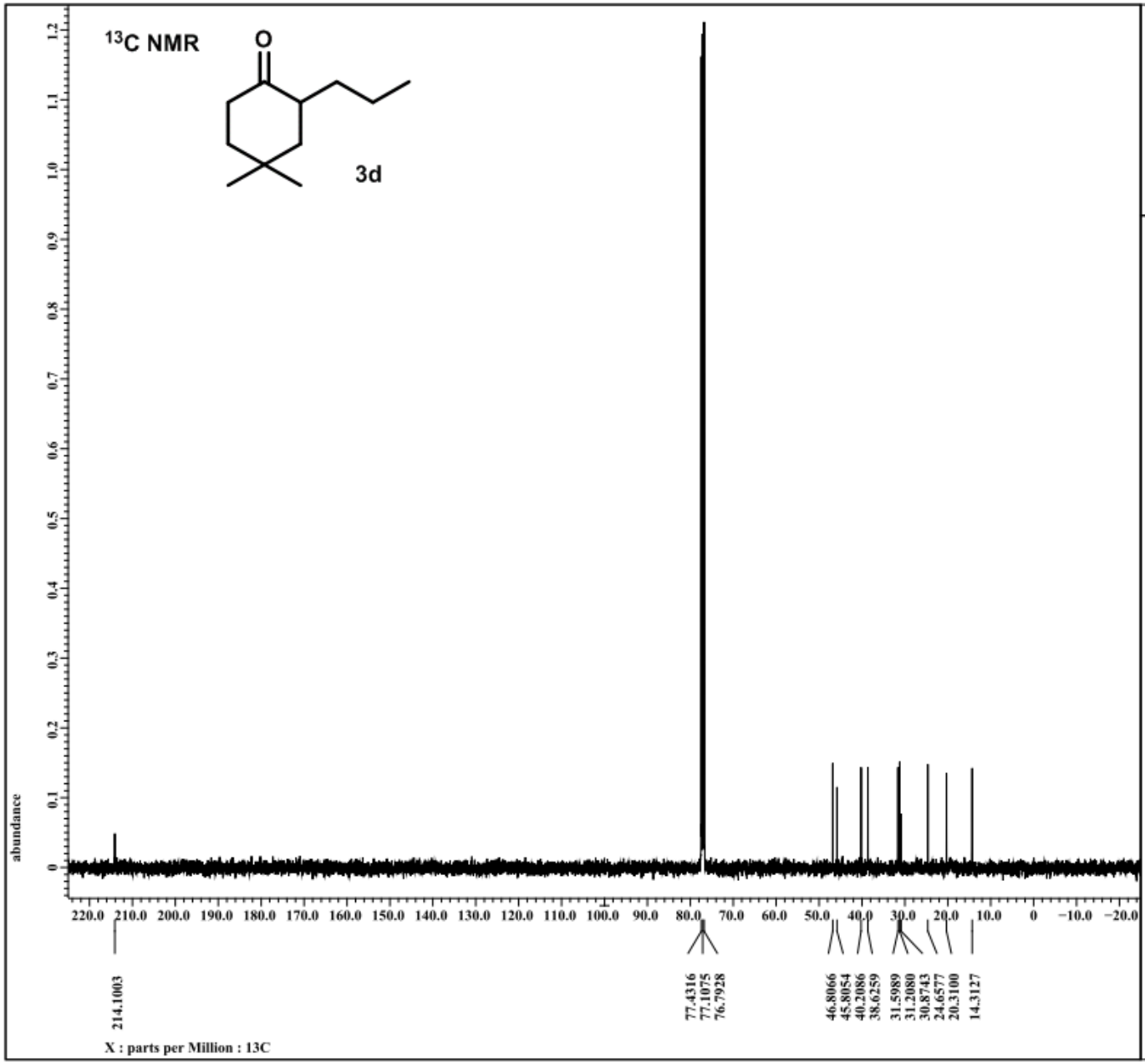
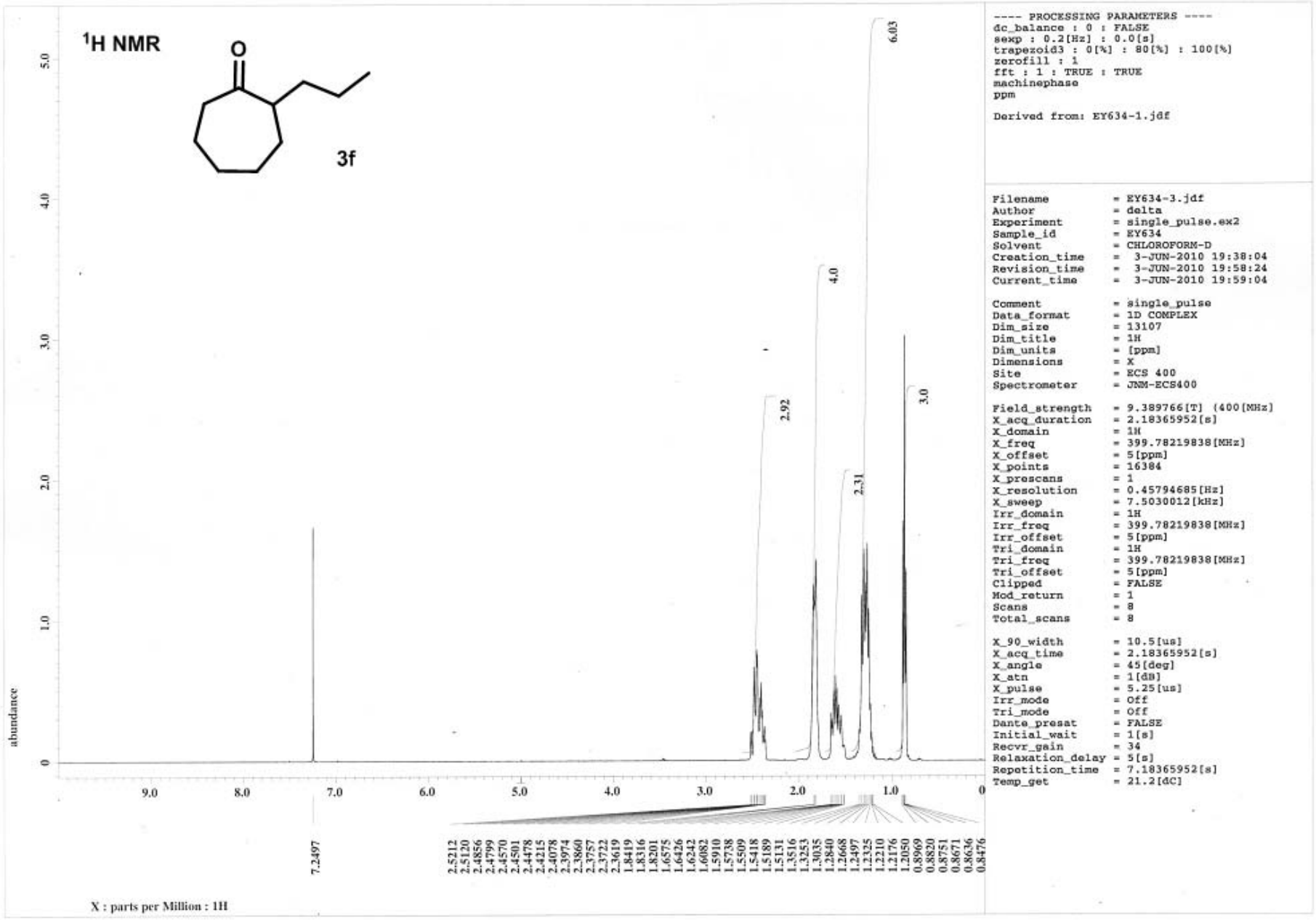
0
1.0
2.0
3.0
4.0
5.0
6.0
¹H NMR
O
3d
1.95
0.97
4.15
3.07
2.9
0.97
2.74
3
X : parts per Million : 1H
2.4902
2.4742
2.4547
2.4387
2.4204
2.4043
2.3952
2.3791
2.3619
2.3459
2.3310
2.2439
2.2359
2.2268
2.2084
2.2004
2.1913
1.7915
1.7835
1.7754
1.7606
1.7525
1.7388
1.7285
1.7228
1.7136
1.7044
1.6953
1.6872
1.6781
1.6712
1.6643
1.6437
1.6334
1.6105
1.5990
1.5761
1.5647
1.3791
1.3413
1.3195
1.3001
1.2852
1.2623
1.2531
1.2439
1.2256
1.2107
1.1878
1.1397
1.1179
1.1030
1.0859
1.0687
1.0515
1.0309
1.0137
0.9851
0.9473
0.8923
0.8739
0.8556
---- PROCESSING PARAMETERS ----
dc_balance : 0 : FALSE
sexp : 0.2[Hz] : 0.0[s]
trapezoid3 : 0[%] : 80[%] : 100[%]
zerofill : 1
fft : 1 : TRUE : TRUE
machinephase
ppm
Derived from: EY403-1.jdf
Filename = EY403-4.jdf
Author = delta
Experiment = single_pulse.ex2
Sample_id = EY403
Solvent = CHLOROFORM-D
Creation_time = 26-JAN-2010 23:39:00
Revision_time = 26-OCT-2010 10:22:44
Current_time = 26-OCT-2010 10:23:25
Comment = single_pulse
Data_format = 1D COMPLEX
Dim_size = 13107
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = ECS 400
Spectrometer = JNM-ECS400
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 = 10.2[us]
X_acq_time = 2.18365952[s]
X_angle = 45[deg]
X_atn = 1[dB]
X_pulse = 5.1[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 = 18[dC]



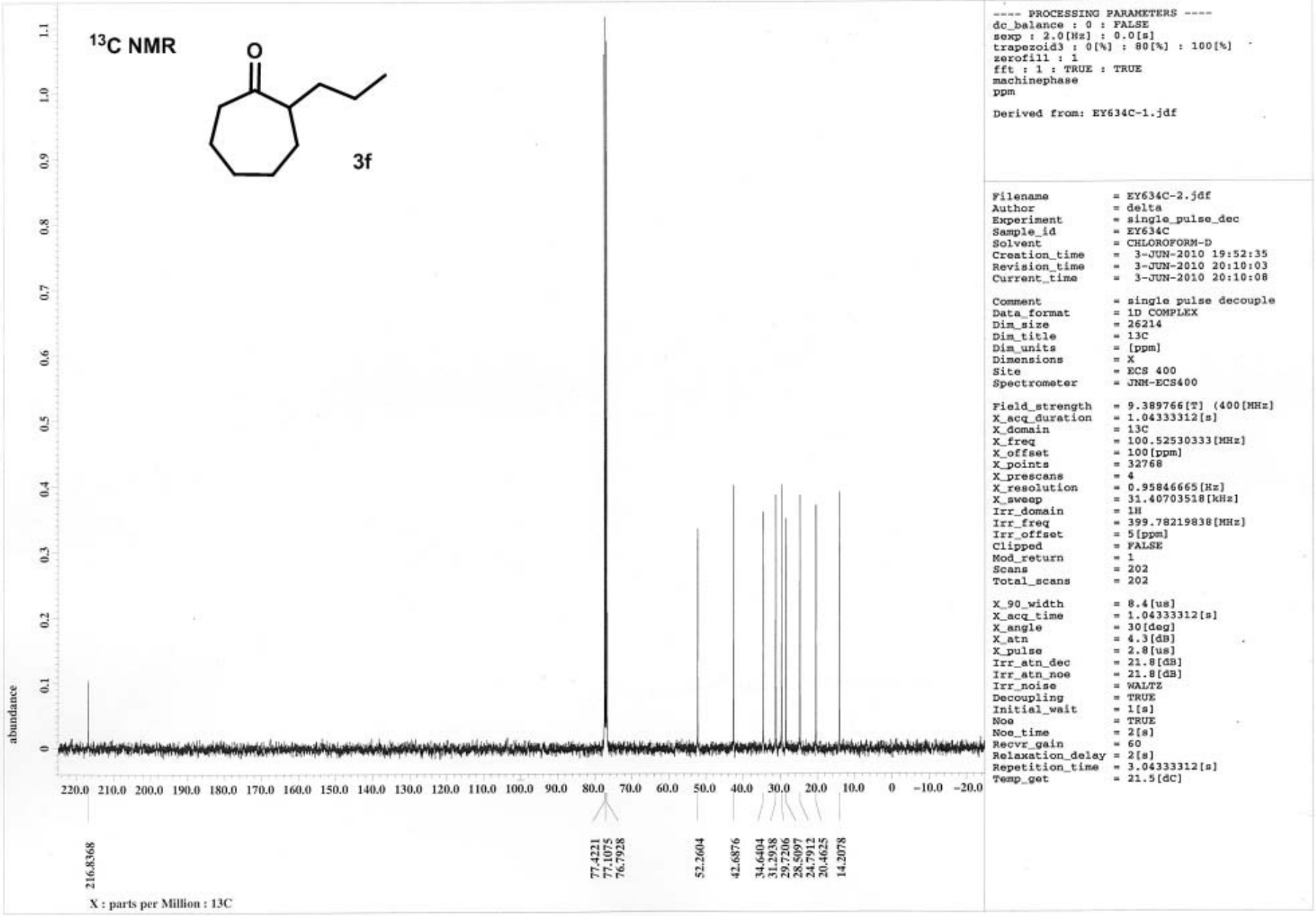

```
---- PROCESSING PARAMETERS ----
dc_balance : 0 : FALSE
sexp : 2.0[Hz] : 0.0[s]
trapezoid3 : 0[%] : 80[%] : 100[%]
zerofill : 1
fft : 1 : TRUE : TRUE
machinephase
ppm

Derived from: EY403 C-1.jdf
```

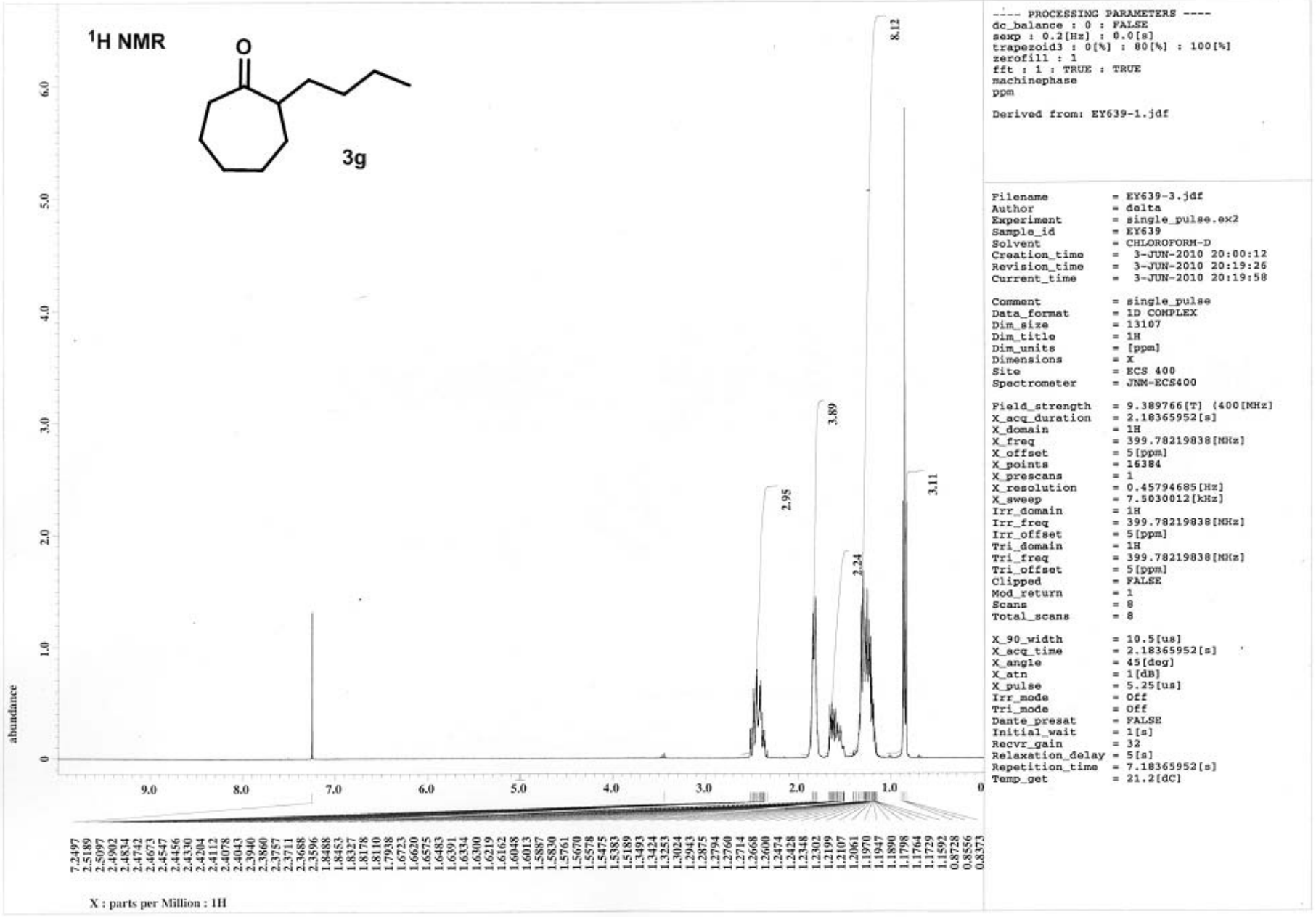
```
Filename          = EY403 C-3.jdf
Author            = delta
Experiment        = single_pulse_dec
Sample_id         = EY403 C
Solvent           = CHLOROFORM-D
Creation_time     = 27-JAN-2010 00:05:36
Revision_time     = 26-OCT-2010 10:24:13
Current_time      = 26-OCT-2010 10:24:57

Comment           = single pulse decouple
Data_format       = 1D COMPLEX
Dim_size          = 26214
Dim_title         = 13C
Dim_units         = [ppm]
Dimensions        = X
Site              = ECS 400
Spectrometer      = JNM-ECS400

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             = 203.0
Total_scans       = 203.0

X_90_width        = 8.4[us]
X_acq_time        = 1.04333312[s]
X_angle           = 30[deg]
X_atn             = 4.3[dB]
X_pulse           = 2.8[us]
Irr_atn_dec       = 22[dB]
Irr_atn_noe       = 22[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          = 18.3[dC]
```

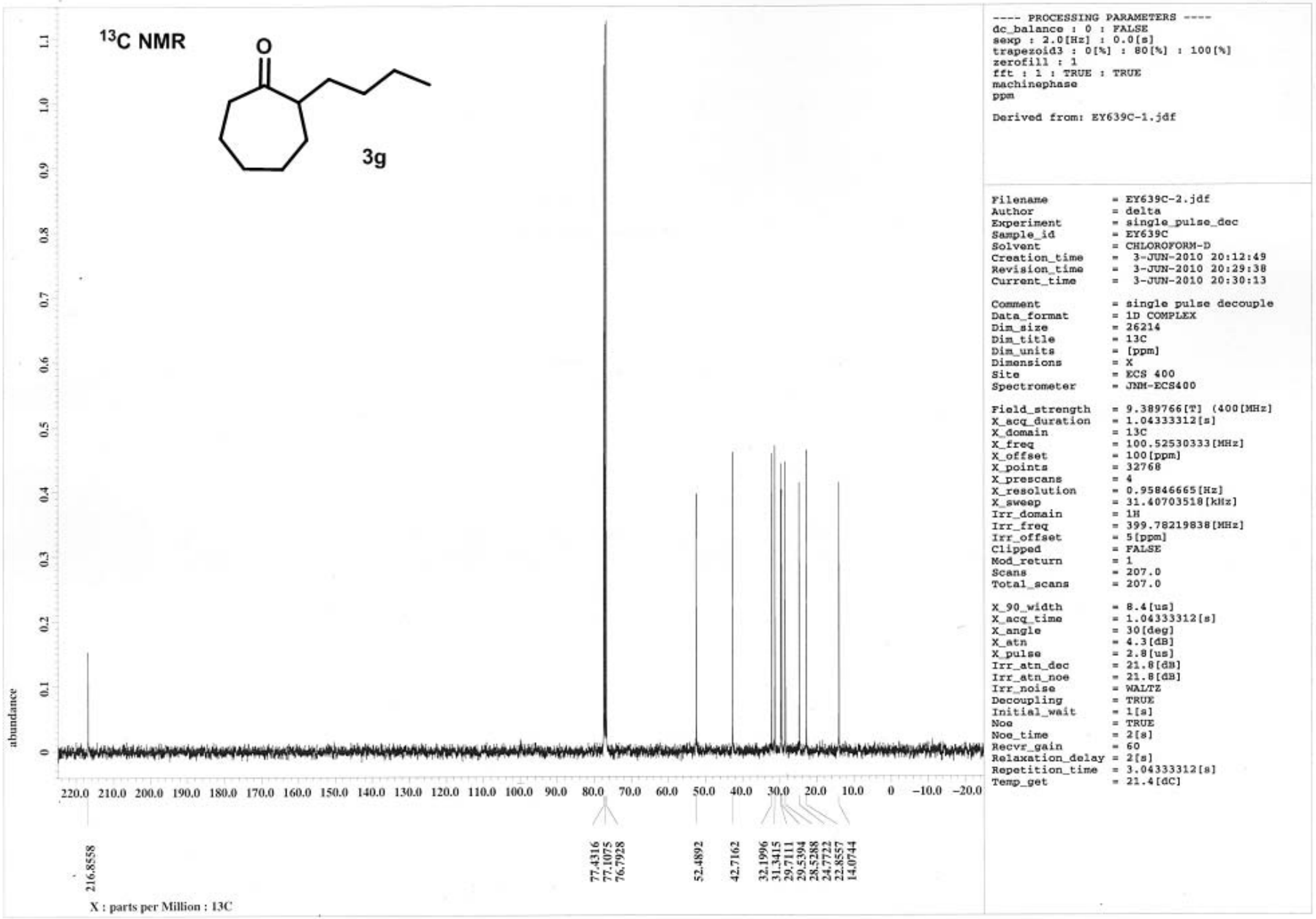


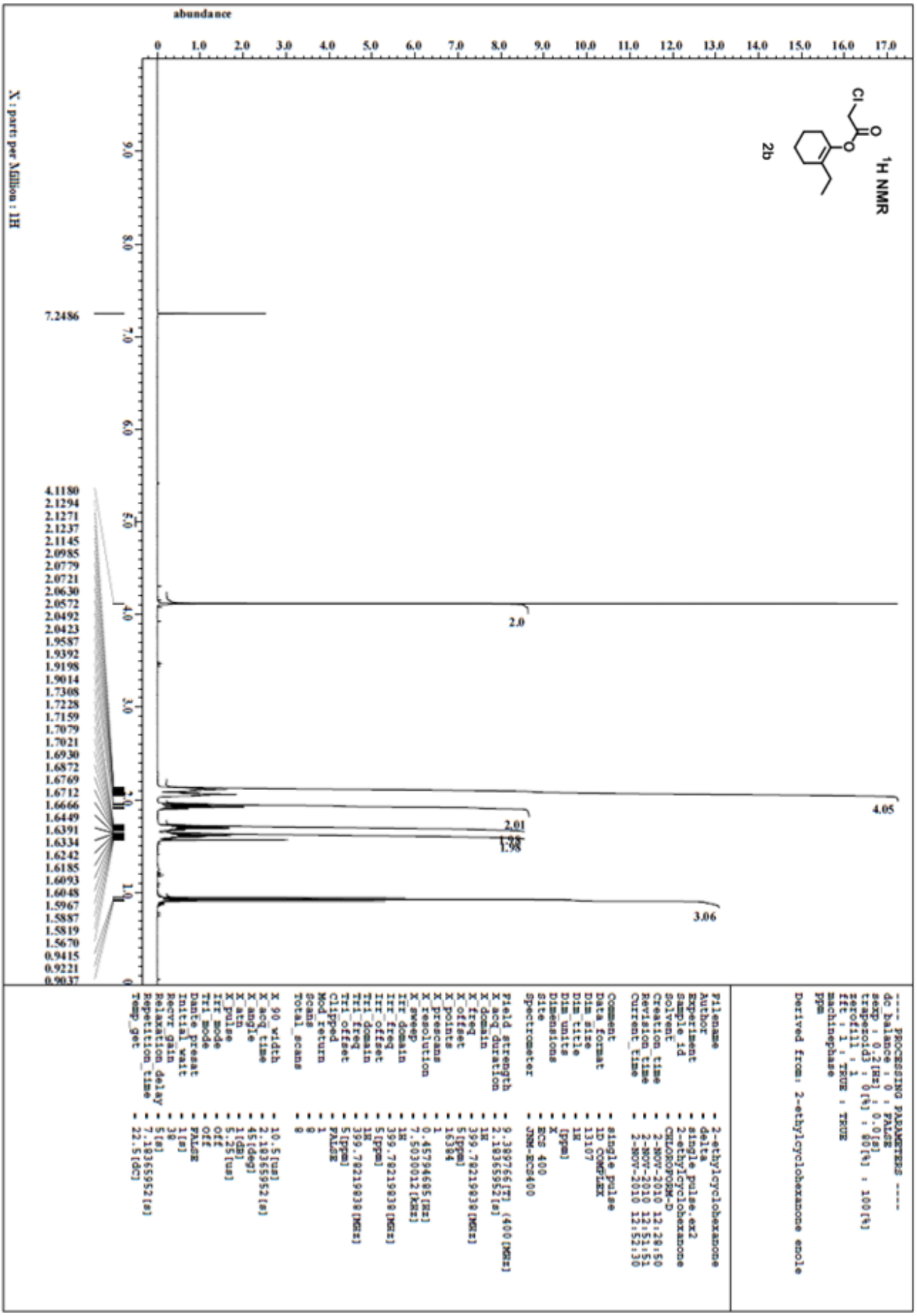

```
---- PROCESSING PARAMETERS ----
dc_balance : 0 : FALSE
sexp : 0.2[Hz] : 0.0[s]
trapezoid3 : 0[%] : 80[%] : 100[%]
zerofill : 1
fft : 1 : TRUE : TRUE
machinephase
ppm

Derived from: EY634-1.jdf
```

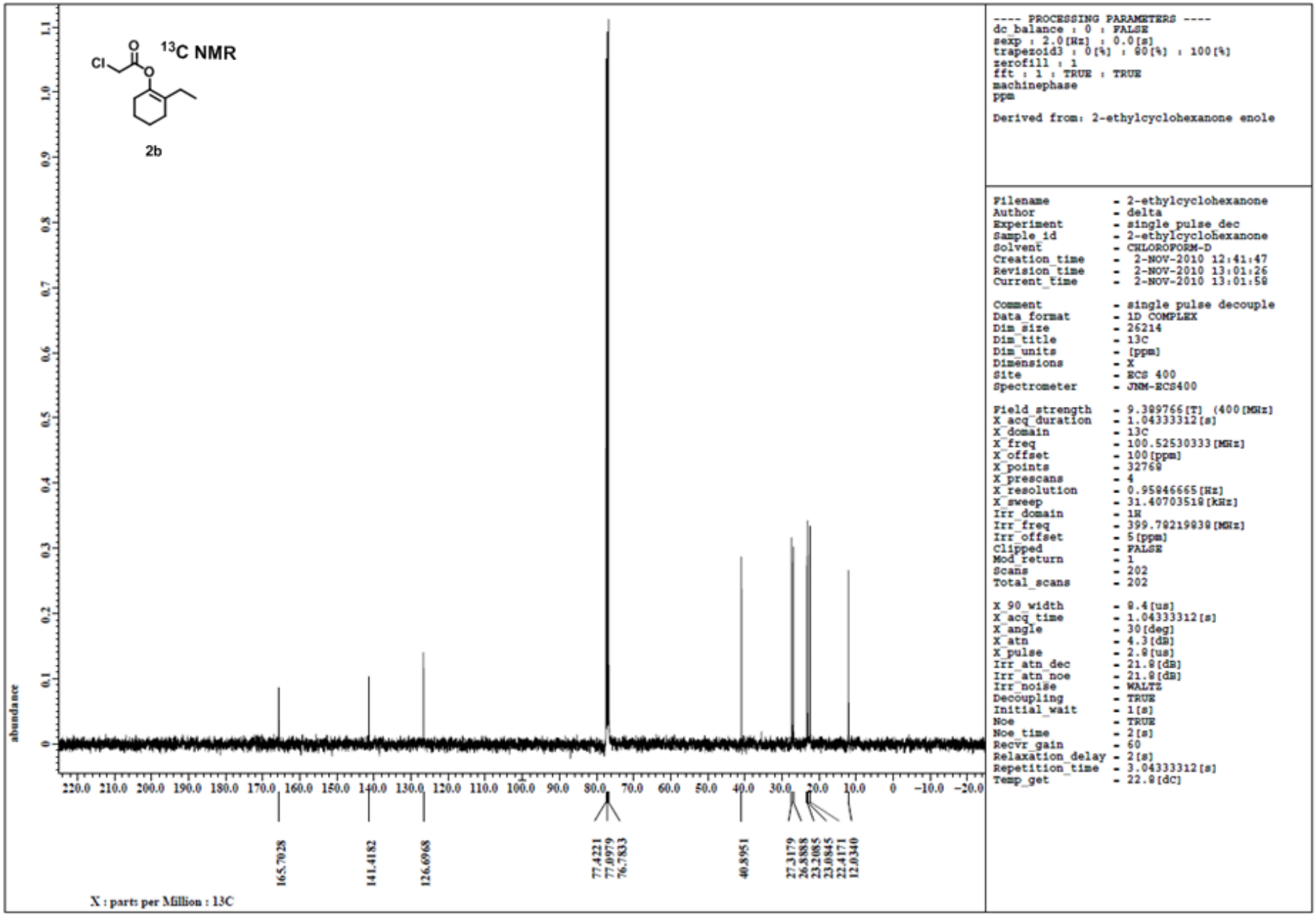
```
Filename          = EY634-3.jdf
Author            = delta
Experiment        = single_pulse.ex2
Sample_id         = EY634
Solvent           = CHLOROFORM-D
Creation_time     =  3-JUN-2010 19:38:04
Revision_time     =  3-JUN-2010 19:58:24
Current_time      =  3-JUN-2010 19:59:04

Comment           = single_pulse
Data_format       = 1D COMPLEX
Dim_size          = 13107
Dim_title         = 1H
Dim_units         = [ppm]
Dimensions        = X
Site              = ECS 400
Spectrometer      = JNM-ECS400

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        = 10.5[us]
X_acq_time        = 2.18365952[s]
X_angle           = 45[deg]
X_atn             = 1[dB]
X_pulse           = 5.25[us]
Irr_mode          = Off
Tri_mode          = Off
Dante_presat      = FALSE
Initial_wait      = 1[s]
Recvr_gain        = 34
Relaxation_delay  = 5[s]
Repetition_time   = 7.18365952[s]
Temp_get          = 21.2[dC]
```

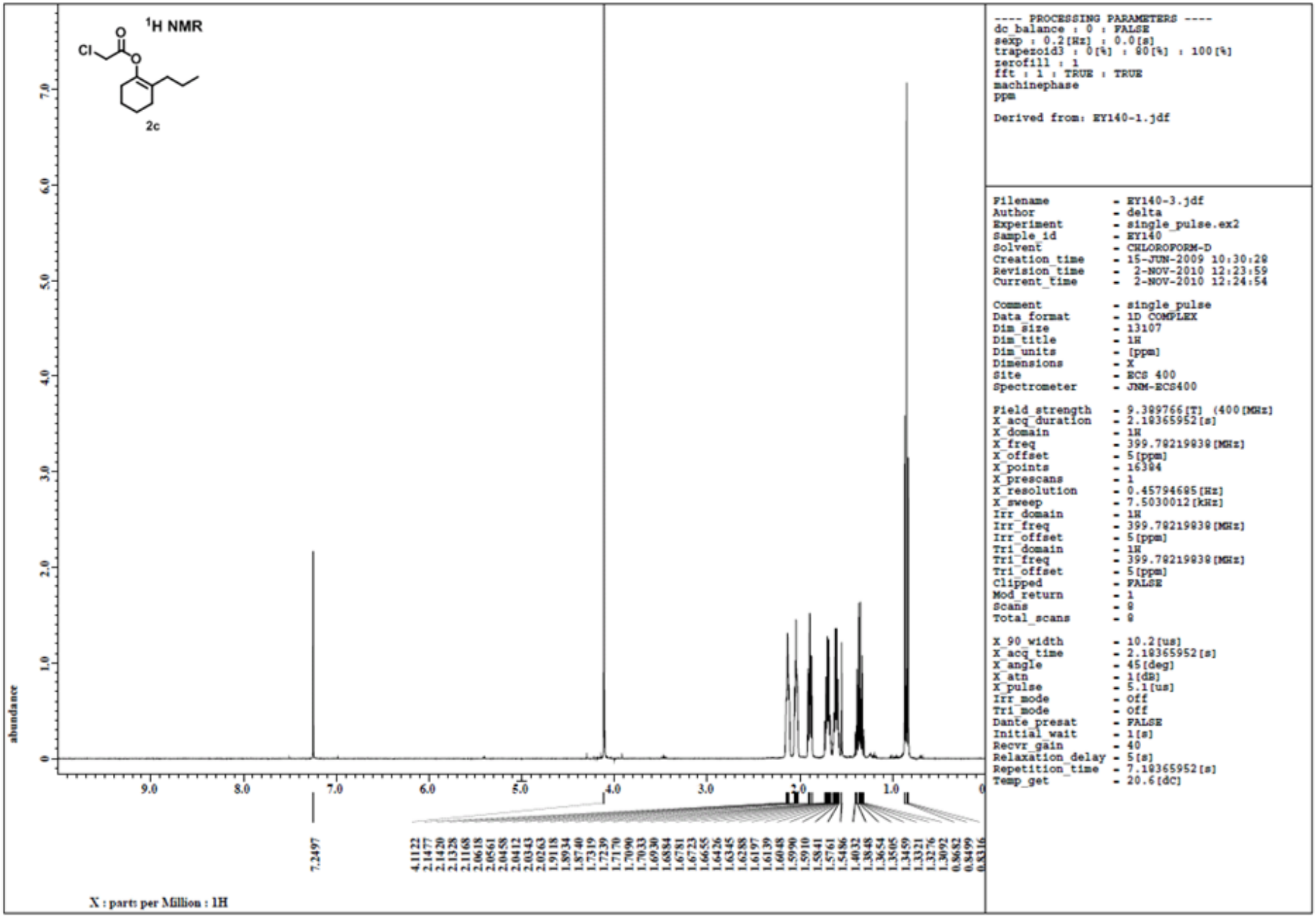

^{13}C NMR
O
3f
abundance
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
216.8368
77.4221
77.1075
76.7928
52.2604
42.6876
34.6404
31.2938
29.7206
28.5097
24.7912
20.4625
14.2078
X : parts per Million : 13C
---- PROCESSING PARAMETERS ----
dc_balance : 0 : FALSE
sexp : 2.0[Hz] : 0.0[s]
trapezoid3 : 0[%] : 80[%] : 100[%]
zerofill : 1
fft : 1 : TRUE : TRUE
machinephase
ppm
Derived from: EY634C-1.jdf
Filename = EY634C-2.jdf
Author = delta
Experiment = single_pulse_dec
Sample_id = EY634C
Solvent = CHLOROFORM-D
Creation_time = 3-JUN-2010 19:52:35
Revision_time = 3-JUN-2010 20:10:03
Current_time = 3-JUN-2010 20:10:08
Comment = single pulse decouple
Data_format = 1D COMPLEX
Dim_size = 26214
Dim_title = 13C
Dim_units = [ppm]
Dimensions = X
Site = ECS 400
Spectrometer = JNM-ECS400
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 = 202
Total_scans = 202
X_90_width = 8.4[us]
X_acq_time = 1.04333312[s]
X_angle = 30[deg]
X_atn = 4.3[dB]
X_pulse = 2.8[us]
Irr_atn_dec = 21.8[dB]
Irr_atn_noe = 21.8[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 = 21.5[dC]

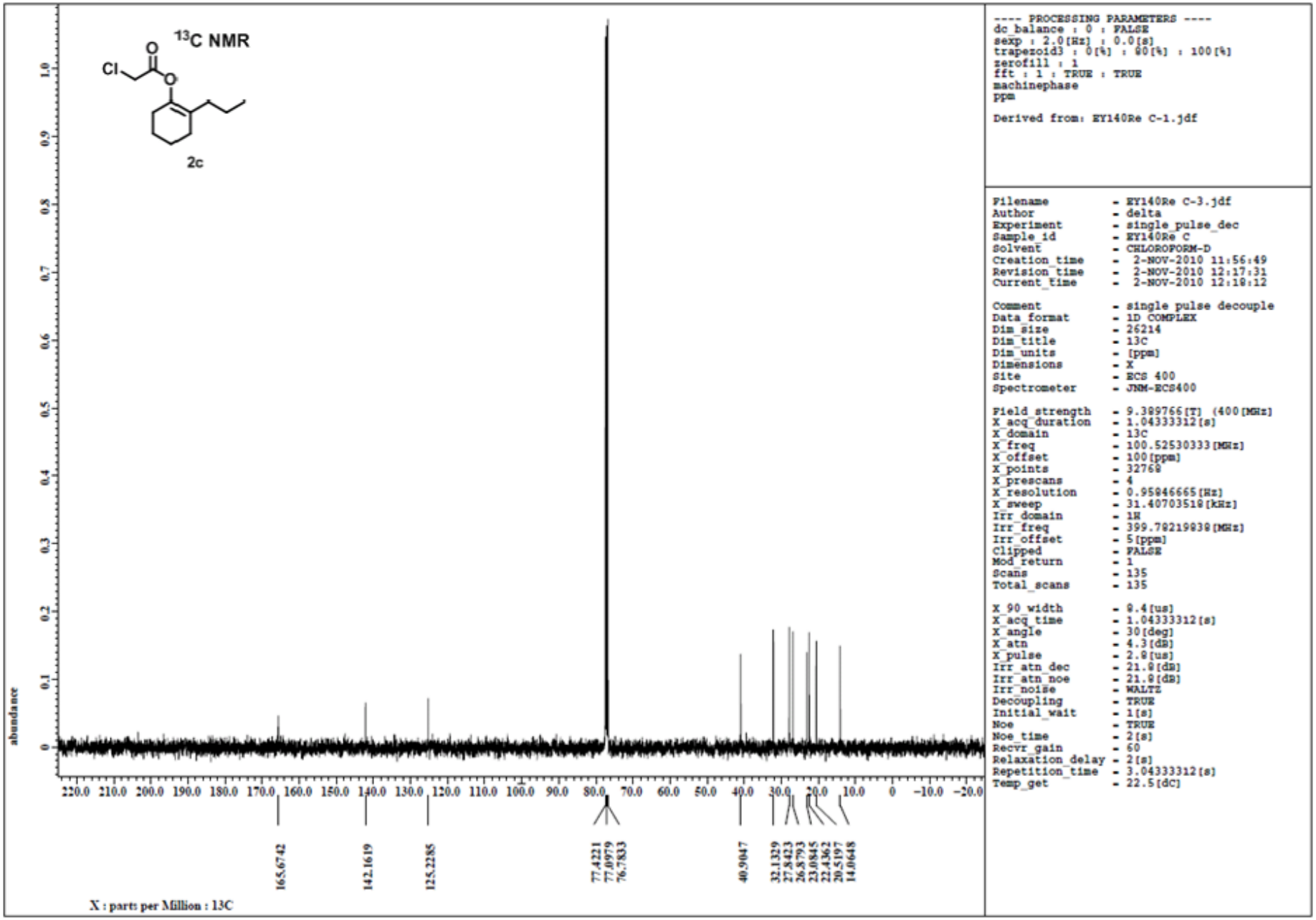

^{1}H NMR
O
3g
8.12
3.89
3.11
2.95
2.24
abundance
X : parts per Million : 1H
---- PROCESSING PARAMETERS ----
dc_balance : 0 : FALSE
sexp : 0.2[Hz] : 0.0[s]
trapezoid3 : 0[%] : 80[%] : 100[%]
zerofill : 1
fft : 1 : TRUE : TRUE
machinephase
ppm
Derived from: EY639-1.jdf
Filename = EY639-3.jdf
Author = delta
Experiment = single_pulse.ex2
Sample_id = EY639
Solvent = CHLOROFORM-D
Creation_time = 3-JUN-2010 20:00:12
Revision_time = 3-JUN-2010 20:19:26
Current_time = 3-JUN-2010 20:19:58
Comment = single_pulse
Data_format = 1D COMPLEX
Dim_size = 13107
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = ECS 400
Spectrometer = JNM-ECS400
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 = 10.5[us]
X_acq_time = 2.18365952[s]
X_angle = 45[deg]
X_atn = 1[dB]
X_pulse = 5.25[us]
Irr_mode = Off
Tri_mode = Off
Dante_presat = FALSE
Initial_wait = 1[s]
Recvr_gain = 32
Relaxation_delay = 5[s]
Repetition_time = 7.18365952[s]
Temp_get = 21.2[dC]

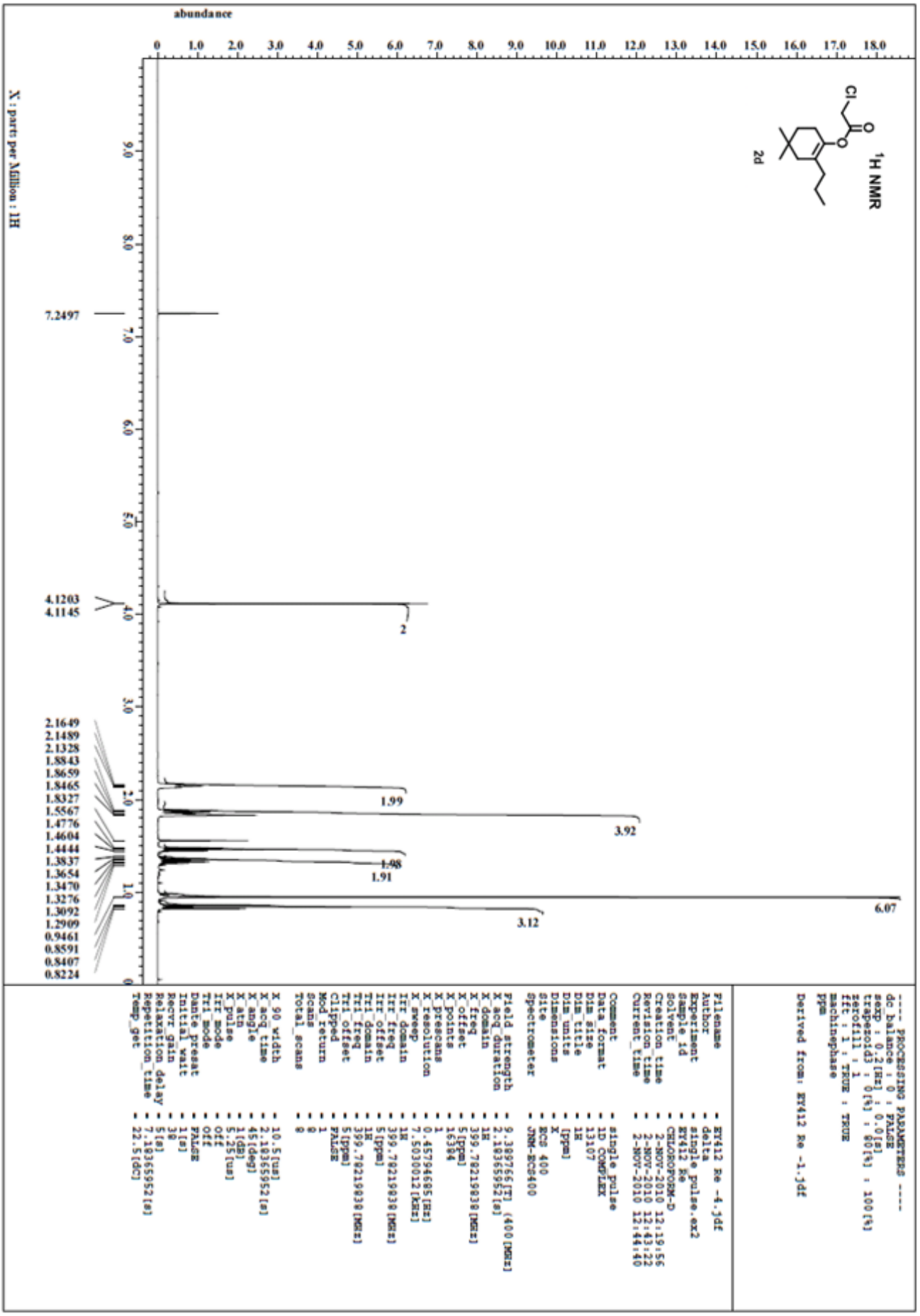

^{13}C NMR
O
3g
abundance
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 −10.0 −20.0
216.8558
77.4316
77.1075
76.7928
52.4892
42.7162
32.1996
31.3415
29.7111
29.5394
28.5288
24.7722
22.8557
14.0744
X : parts per Million : 13C
---- PROCESSING PARAMETERS ----
dc_balance : 0 : FALSE
sexp : 2.0[Hz] : 0.0[s]
trapezoid3 : 0[%] : 80[%] : 100[%]
zerofill : 1
fft : 1 : TRUE : TRUE
machinephase
ppm
Derived from: EY639C-1.jdf
Filename = EY639C-2.jdf
Author = delta
Experiment = single_pulse_dec
Sample_id = EY639C
Solvent = CHLOROFORM-D
Creation_time = 3-JUN-2010 20:12:49
Revision_time = 3-JUN-2010 20:29:38
Current_time = 3-JUN-2010 20:30:13
Comment = single pulse decouple
Data_format = 1D COMPLEX
Dim_size = 26214
Dim_title = 13C
Dim_units = [ppm]
Dimensions = X
Site = ECS 400
Spectrometer = JNM-ECS400
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 = 207.0
Total_scans = 207.0
X_90_width = 8.4[us]
X_acq_time = 1.04333312[s]
X_angle = 30[deg]
X_atn = 4.3[dB]
X_pulse = 2.8[us]
Irr_atn_dec = 21.8[dB]
Irr_atn_noe = 21.8[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 = 21.4[dC]

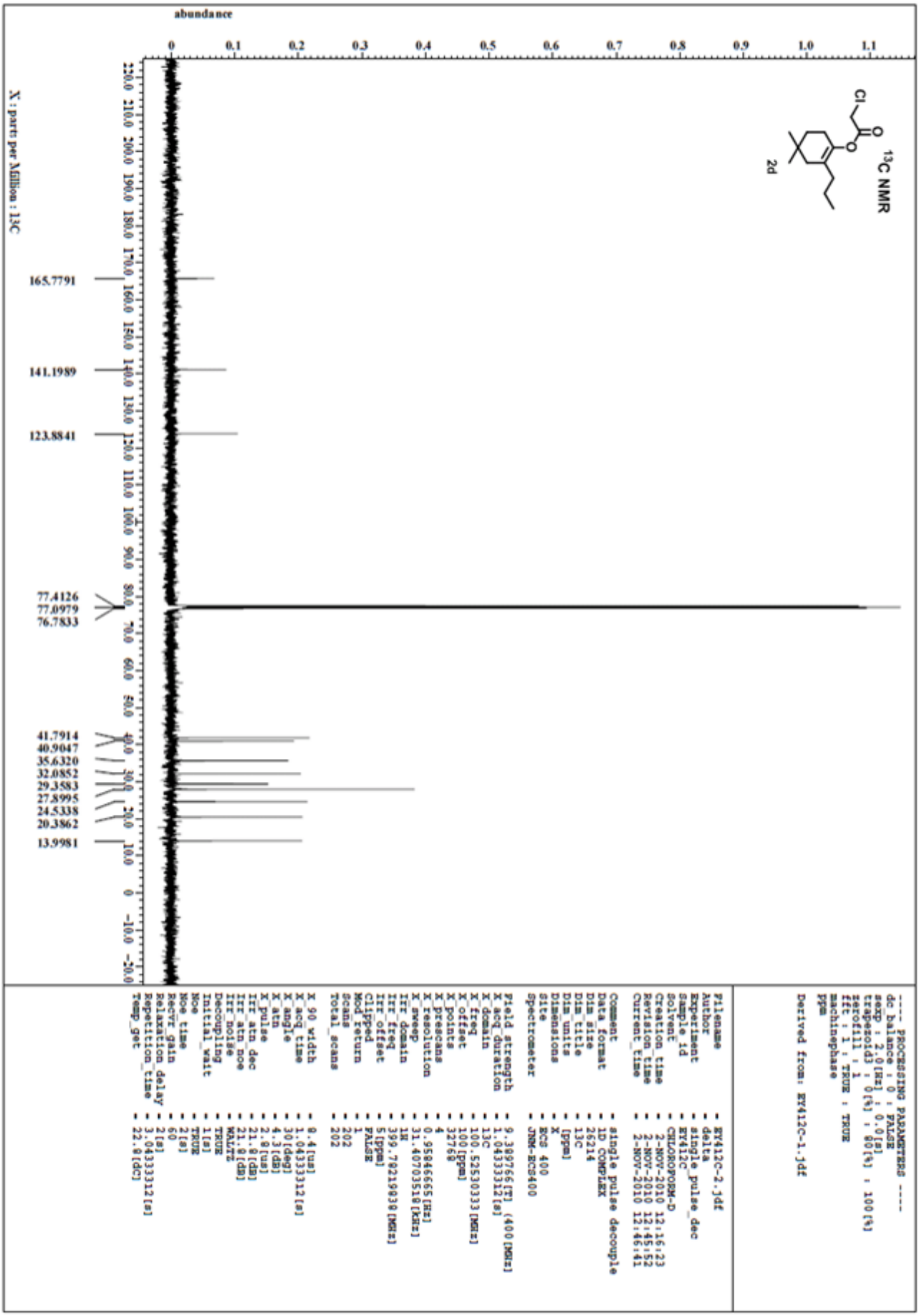

abundance
0 1.0 2.0 3.0 4.0 5.0 6.0 7.0 8.0 9.0 10.0 11.0 12.0 13.0 14.0 15.0 16.0 17.0
X : parts per Million : 1H
7.2486
4.1180
2.1294
2.1271
2.1237
2.1145
2.0985
2.0779
2.0721
2.0630
2.0572
2.0492
2.0423
1.9587
1.9392
1.9198
1.9014
1.7308
1.7228
1.7159
1.7079
1.7021
1.6930
1.6872
1.6769
1.6712
1.6666
1.6449
1.6391
1.6334
1.6242
1.6185
1.6093
1.6048
1.5967
1.5887
1.5819
1.5670
0.9415
0.9221
0.9037
2.0
4.05
2.01
1.98
3.06
Cl
O
O
2b
1H NMR
---- PROCESSING PARAMETERS ----
dc_balance : 0 : FALSE
sexp : 0.2[Hz] : 0.0[s]
trapezoid3 : 0[%] : 60[%] : 100[%]
zerofill : 1
fft : 1 : TRUE : TRUE
machinephase
ppm
Derived from: 2-ethylcyclohexanone enole
Filename - 2-ethylcyclohexanone
Author - delta
Experiment - single_pulse.ex2
sample_id - 2-ethylcyclohexanone
solvent - CHLOROFORM-D
Creation_time - 2-NOV-2010 12:20:50
Revision_time - 2-NOV-2010 12:51:51
Current_time - 2-NOV-2010 12:52:30
Comment - single_pulse
Data_format - 1D COMPLEX
Dim_size - 13107
Dim_title - 1H
Dim_units - [ppm]
Dimensions - X
site - ECS 400
Spectrometer - JNM-ECS400
Field_strength - 9.389766[T] (400[MHz])
X_acq_duration - 2.183655952[s]
X_domain - 1H
X_freq - 399.78219038[MHz]
X_offset - 5[ppm]
X_points - 16384
X_prescans - 1
X_resolution - 0.45794605[Hz]
X_sweep - 7.5030012[kHz]
irr_domain - 1H
irr_freq - 399.78219038[MHz]
irr_offset - 5[ppm]
tri_domain - 1H
tri_freq - 399.78219038[MHz]
tri_offset - 5[ppm]
Clipped - FALSE
Mod_return - 1
scans - 8
Total_scans - 8
X_90_width - 10.5[us]
X_acq_time - 2.183655952[s]
X_angle - 45[deg]
X_atn - 1[dB]
X_pulse - 5.25[us]
irr_mode - off
tri_mode - off
Dante_presat - FALSE
Initial_wait - 1[s]
Recyc_grain - 30
Relaxation_delay - 5[s]
Repetition_time - 7.183655952[s]
Temp_get - 22.5[dC]

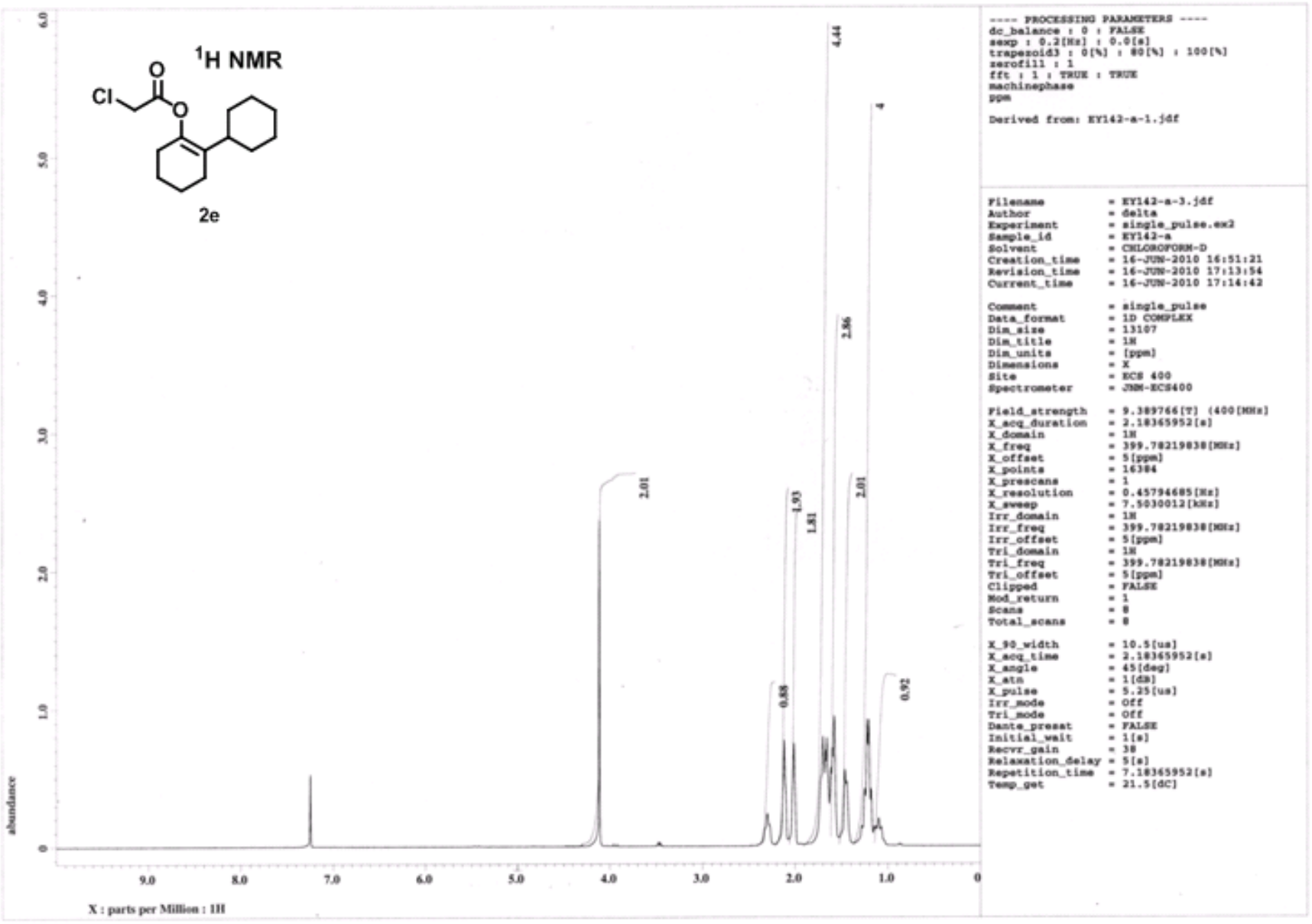

^{13}C NMR
2b
abundance
X : parts per Million : 13C
165.7028
141.4182
126.6968
77.4221
77.0979
76.7833
40.8951
27.3179
26.5888
23.2085
23.0845
22.4171
12.0340
---- PROCESSING PARAMETERS ----
dc_balance : 0 : FALSE
sexp : 2.0[Hz] : 0.0[s]
trapezoid3 : 0[%] : 80[%] : 100[%]
zerofill : 1
fft : 1 : TRUE : TRUE
machinephase
ppm
Derived from: 2-ethylcyclohexanone enole
Filename - 2-ethylcyclohexanone
Author - delta
Experiment - single_pulse_dec
Sample_id - 2-ethylcyclohexanone
Solvent - CHLOROFORM-D
Creation_time - 2-NOV-2010 12:41:47
Revision_time - 2-NOV-2010 13:01:26
Current_time - 2-NOV-2010 13:01:59
Comment - single pulse decouple
Data_format - 1D COMPLEX
Dim_size - 26214
Dim_title - 13C
Dim_units - [ppm]
Dimensions - X
Site - ECS 400
Spectrometer - JNM-ECS400
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 - 31.40703519[kHz]
Irr_domain - 1H
Irr_freq - 399.79219939[MHz]
Irr_offset - 5[ppm]
Clipped - FALSE
Mod_return - 1
Scans - 202
Total_scans - 202
X_90_width - 9.4[us]
X_acq_time - 1.04333312[s]
X_angle - 30[deg]
X_atn - 4.3[dB]
X_pulse - 2.9[us]
Irr_atn_dec - 21.9[dB]
Irr_atn_noe - 21.9[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 - 22.9[dC]


^{1}H NMR
Cl
O
O
2c
abundance
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
7.2497
4.1122
2.1477
2.1420
2.1325
2.1168
2.0618
2.0561
2.0458
2.0412
2.0343
2.0263
1.9118
1.8934
1.8740
1.7319
1.7239
1.7170
1.7090
1.7033
1.6930
1.6884
1.6781
1.6723
1.6655
1.6426
1.6345
1.6288
1.6197
1.6139
1.6048
1.5990
1.5910
1.5841
1.5761
1.5486
1.4032
1.3848
1.3654
1.3505
1.3459
1.3321
1.3276
1.3092
0.8682
0.8499
0.8316
X : parts per Million : 1H
---- PROCESSING PARAMETERS ----
dc_balance : 0 : FALSE
sexp : 0.2[Hz] : 0.0[s]
trapezoid3 : 0[%] : 90[%] : 100[%]
zerofill : 1
fft : 1 : TRUE : TRUE
machinephase
ppm
Derived from: EY140-1.jdf
Filename - EY140-3.jdf
Author - delta
Experiment - single_pulse.ex2
Sample_id - EY140
Solvent - CHLOROFORM-D
Creation_time - 15-JUN-2009 10:30:20
Revision_time - 2-NOV-2010 12:23:59
Current_time - 2-NOV-2010 12:24:54
Comment - single_pulse
Data_format - 1D COMPLEX
Dim_size - 13107
Dim_title - 1H
Dim_units - [ppm]
Dimensions - X
Site - ECS 400
Spectrometer - JNM-ECS400
Field_strength - 9.389766[T] (400[MHz])
X_acq_duration - 2.10365952[s]
X_domain - 1H
X_freq - 399.78219838[MHz]
X_offset - 5[ppm]
X_points - 16384
X_prescans - 1
X_resolution - 0.45794695[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 - 10.2[us]
X_acq_time - 2.10365952[s]
X_angle - 45[deg]
X_atn - 1[dB]
X_pulse - 5.1[us]
Irr_mode - Off
Tri_mode - Off
Dante_presat - FALSE
Initial_wait - 1[s]
Recvr_gain - 40
Relaxation_delay - 5[s]
Repetition_time - 7.10365952[s]
Temp_get - 20.6[dC]


^{13}C NMR
Cl
O
O
2c
abundance
X : parts per Million : 13C
165.6742
142.1619
125.2285
77.4221
77.0979
76.7833
40.9047
32.1329
27.8423
26.8793
23.0845
22.4362
20.5197
14.0648
---- PROCESSING PARAMETERS ----
dc_balance : 0 : FALSE
sexp : 2.0[Hz] : 0.0[s]
trapezoid3 : 0[%] : 90[%] : 100[%]
zerofill : 1
fft : 1 : TRUE : TRUE
machinephase
ppm
Derived from: EY140Re C-1.jdf
Filename - EY140Re C-3.jdf
Author - delta
Experiment - single_pulse_dec
Sample_id - EY140Re C
Solvent - CHLOROFORM-D
Creation_time - 2-NOV-2010 11:56:49
Revision_time - 2-NOV-2010 12:17:31
Current_time - 2-NOV-2010 12:18:12
Comment - single pulse decouple
Data_format - 1D COMPLEX
Dim_size - 26214
Dim_title - 13C
Dim_units - [ppm]
Dimensions - X
Site - ECS 400
Spectrometer - JNM-ECS400
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 - 0.95946665[Hz]
X_sweep - 31.40703510[kHz]
Irr_domain - 1H
Irr_freq - 399.78219039[MHz]
Irr_offset - 5[ppm]
Clipped - FALSE
Mod_return - 1
Scans - 135
Total_scans - 135
X_90_width - 9.4[us]
X_acq_time - 1.04333312[s]
X_angle - 30[deg]
X_atn - 4.3[dB]
X_pulse - 2.9[us]
Irr_atn_dec - 21.0[dB]
Irr_atn_noe - 21.0[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 - 22.5[dC]

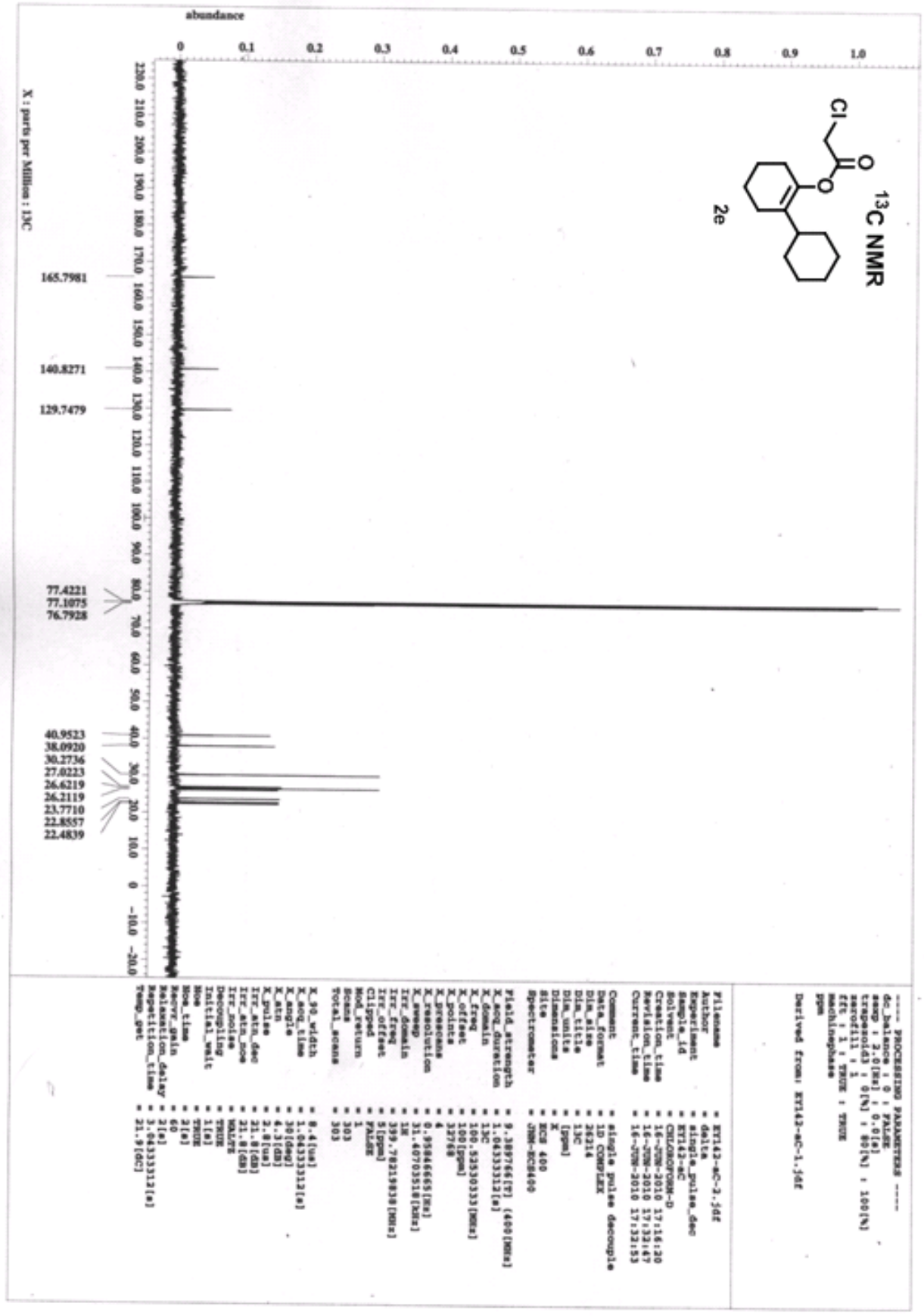

abundance
X : parts per Million : 1H
2d
1H NMR
7.2497
4.1203
4.1145
2.1649
2.1489
2.1328
1.8843
1.8659
1.8465
1.8327
1.5567
1.4776
1.4604
1.4444
1.3837
1.3654
1.3470
1.3276
1.3092
1.2909
0.9461
0.8591
0.8407
0.8224
2
1.99
3.92
1.98
1.91
6.07
3.12
---- PROCESSING PARAMETERS ----
dc_balance : 0 : FALSE
sexp : 0.2[Hz] : 0.0[s]
trapezoid3 : 0[%] : 90[%] : 100[%]
zerofill : 1
fft : 1 : TRUE : TRUE
machinephase
ppm
Derived from: ET412 Re -1.jdf
Filename - ET412 Re -4.jdf
Author - delta
Experiment - single_pulse.ex2
sample_id - ET412 Re
solvent - CHLOROFORM-D
Creation_time - 2-NOV-2010 12:19:56
Revision_time - 2-NOV-2010 12:43:22
Current_time - 2-NOV-2010 12:44:40
Comment - single_pulse
Data_format - 1D COMPLEX
Dim_size - 13107
Dim_title - 1H
Dim_units - [ppm]
Dimensions - X
Site - Acs 400
Spectrometer - JNM-ECS400
Field_strength - 9.389766[T] (400[MHz])
X_acq_duration - 2.183655952[s]
X_domain - 1H
X_freq - 399.78219038[MHz]
X_offset - 5[ppm]
X_points - 16384
X_prescans - 1
X_resolution - 0.45794685[Hz]
X_sweep - 7.5030012[kHz]
XR_domain - 1H
irr_freq - 399.78219038[MHz]
irr_offset - 5[ppm]
tri_domain - 1H
tri_freq - 399.78219038[MHz]
tri_offset - 5[ppm]
Clipped - FALSE
Mod_return - 1
scans - 8
Total_scans - 8
X_90_width - 10.5[us]
X_acq_time - 2.183655952[s]
X_angle - 45[deg]
X_atn - 1[dB]
X_pulse - 5.25[us]
irr_mode - off
tri_mode - off
Dante_preset - FALSE
Initial_wait - 1[s]
Recyc_gain - 30
Relaxation_delay - 5[s]
Repetition_time - 7.183655952[s]
Temp_get - 22.5[dC]

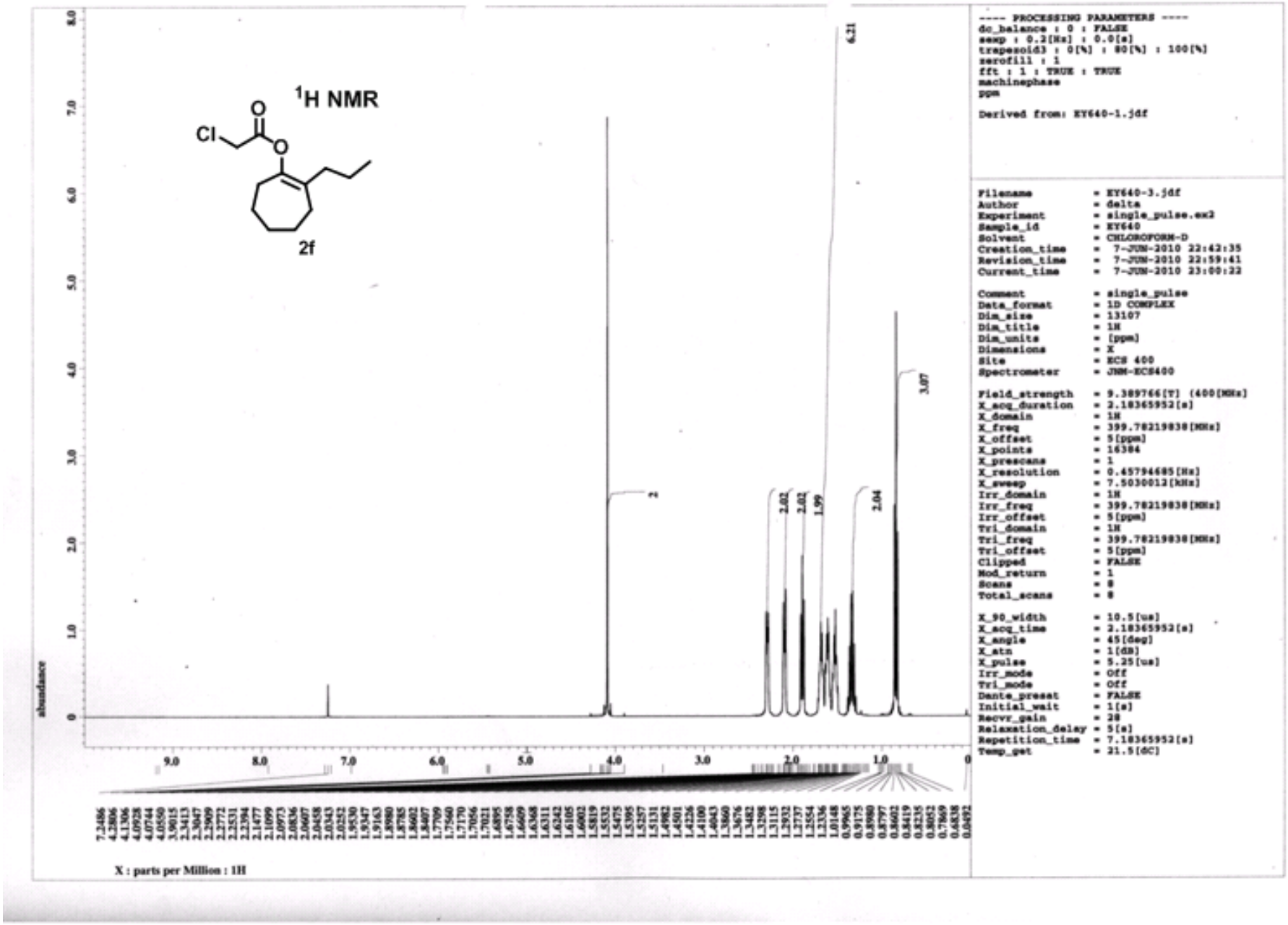

abundance
X : parts per Million : 13C
13C NMR
2d
Cl
O
O
165.7791
141.1989
123.8841
77.4126
77.0979
76.7833
41.7914
40.9047
35.6320
32.0852
29.3583
27.8995
24.5338
20.3862
13.9981
---- PROCESSING PARAMETERS ----
dc_balance : 0 : FALSE
exp : 2.0[Hz] : 0.0[s]
trapezoid3 : 0[%] : 80[%] : 100[%]
zerofill : 1
fft : 1 : TRUE : TRUE
machinephase
ppm
Derived from: EY412C-1.jdf
Filename - EY412C-2.jdf
Author - delta
Experiment - single_pulse_dec
sample_id - EY412C
solvent - CHLOROFORM-D
Creation_time - 2-NOV-2010 12:16:23
Revision_time - 2-NOV-2010 12:45:52
current_time - 2-NOV-2010 12:46:41
Comment - single pulse decouple
Data format - 1D COMPLEX
Dim_size - 26214
Dim_title - 13C
Dim_units - [ppm]
Dimensions - X
site - ECS 400
Spectrometer - JNM-ECS400
Field_strength - 9.389766[T] (400[MHz]
X_acq_duration - 1.043333[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 - 31.40703516[KHz]
irr_domain - 1H
irr_freq - 399.79219939[MHz]
irr_offset - 5[ppm]
CliPped - FALSE
Mod_return - 1
scans - 202
total_scans - 202
X_90_width - 9.4[us]
X_acq_time - 1.043333[s]
X_angle - 30[deg]
X_atn - 4.3[dB]
X_pulse - 2.8[us]
irr_atn_dec - 21.0[dB]
irr_atn_noe - 21.0[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 - 3.043333[s]
temp_get - 22.8[dC]

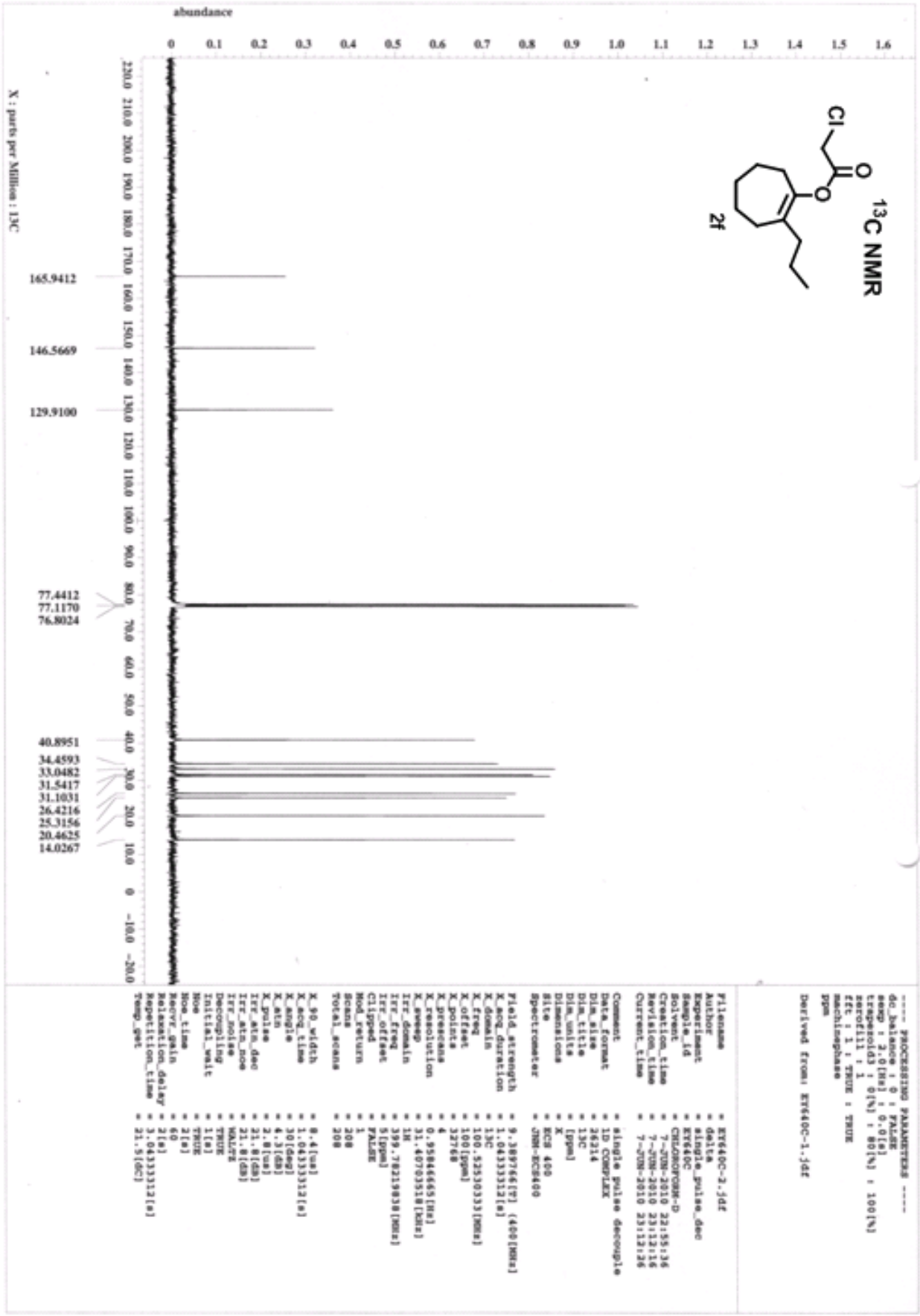


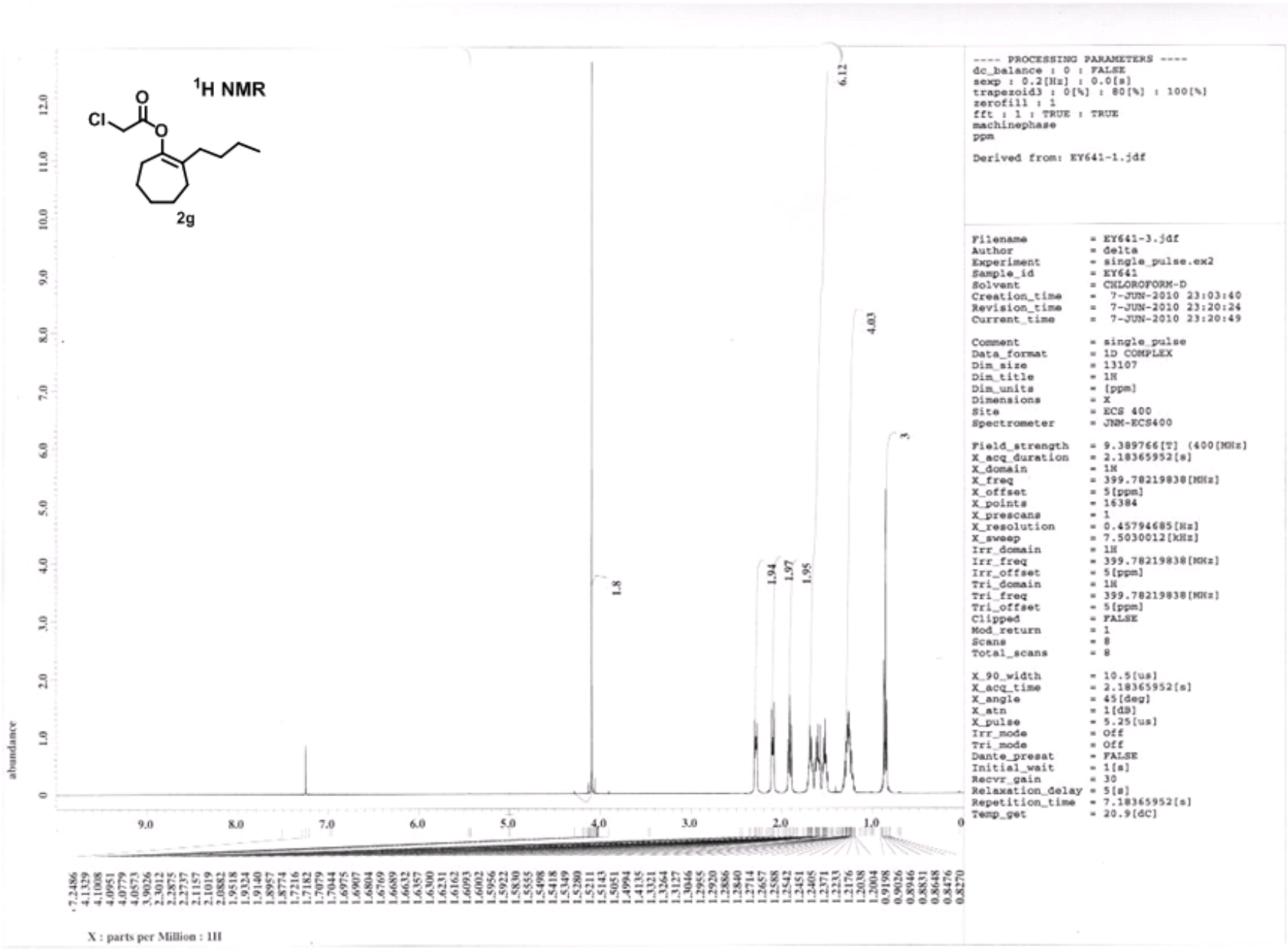

```
---- PROCESSING PARAMETERS ----
dc_balance : 0 : FALSE
sexp : 0.2[Hz] : 0.0[s]
trapezoid3 : 0[%] : 80[%] : 100[%]
zerofill : 1
fft : 1 : TRUE : TRUE
machinephase
ppm

Derived from: EY142-a-1.jdf
```

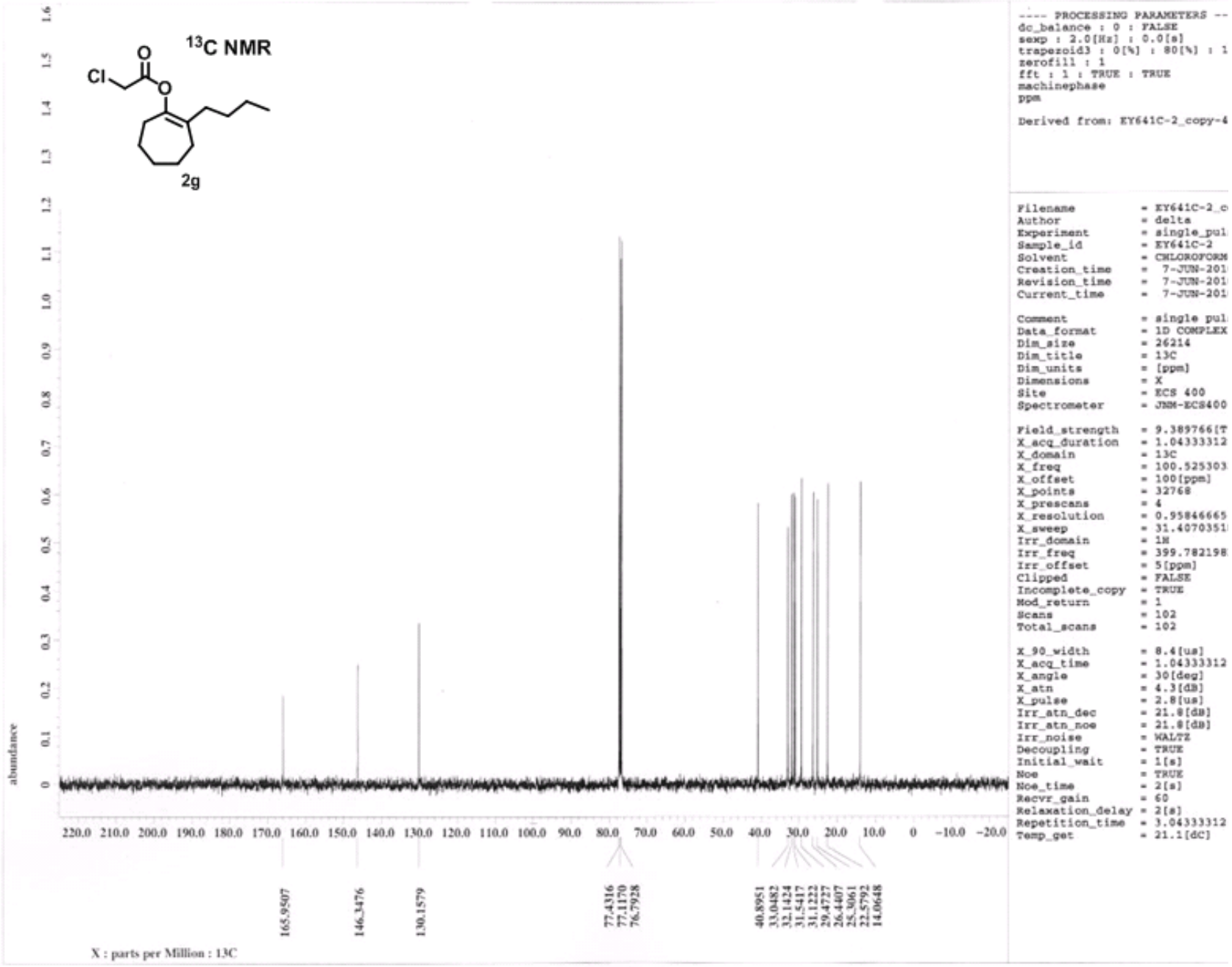
```
Filename            = EY142-a-3.jdf
Author              = delta
Experiment          = single_pulse.ex2
Sample_id           = EY142-a
Solvent             = CHLOROFORM-D
Creation_time       = 16-JUN-2010 16:51:21
Revision_time       = 16-JUN-2010 17:13:54
Current_time        = 16-JUN-2010 17:14:42

Comment             = single_pulse
Data_format         = 1D COMPLEX
Dim_size            = 13107
Dim_title           = 1H
Dim_units           = [ppm]
Dimensions          = X
Site                = ECS 400
Spectrometer        = JNM-ECS400

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          = 10.5[us]
X_acq_time          = 2.18365952[s]
X_angle             = 45[deg]
X_atn               = 1[dB]
X_pulse             = 5.25[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            = 21.5[dC]
```

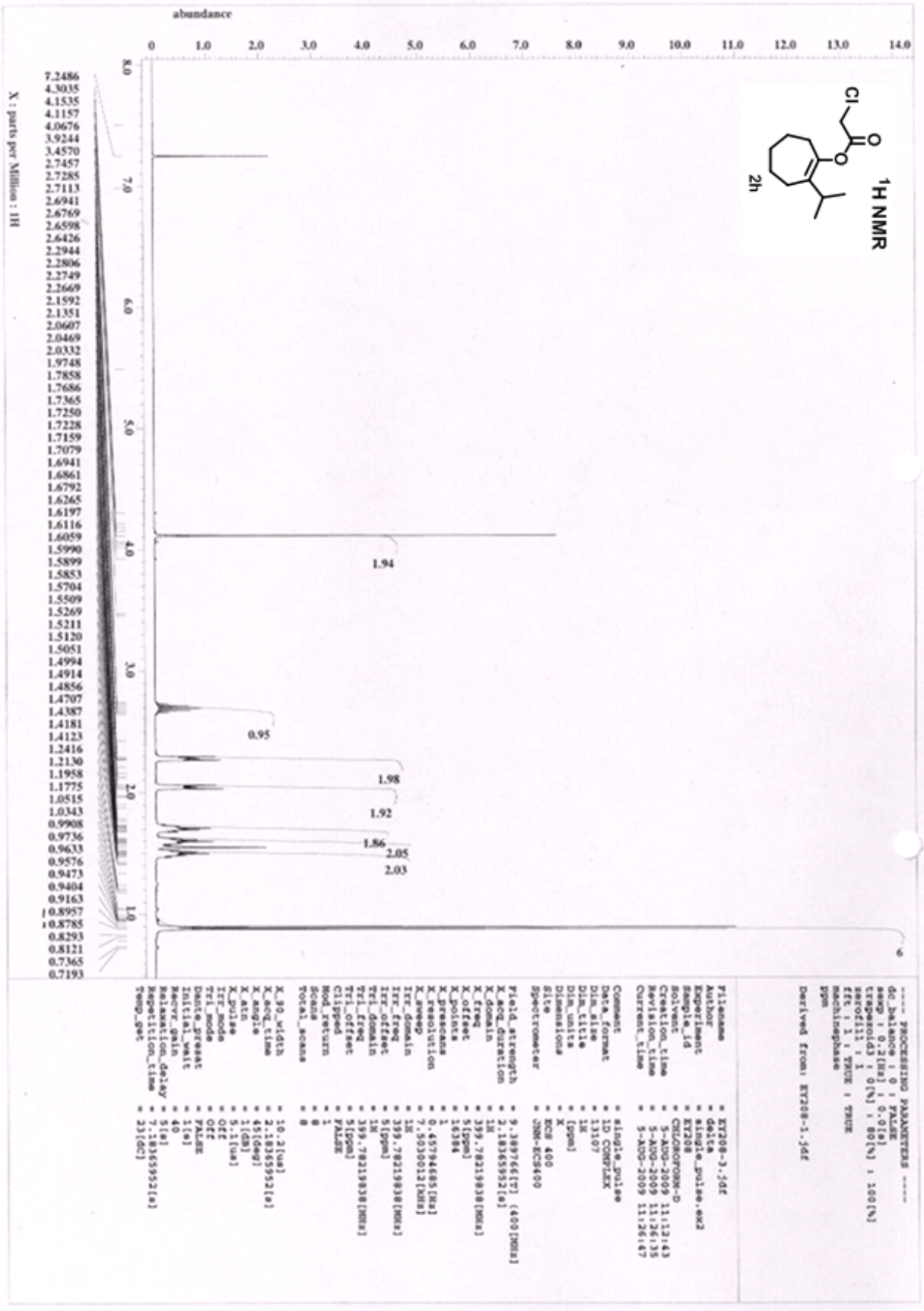

abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
^{13}C NMR
Cl
O
O
2e
X : parts per Million : 13C
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
165.7981
140.8271
129.7479
77.4221
77.1075
76.7928
40.9523
38.0920
30.2736
27.0223
26.6219
26.2119
23.7710
22.8557
22.4839
----- PROCESSING PARAMETERS -----
dc_balance : 0 : FALSE
expp : 2.0[Hz] : 0.0[s]
trapezoid3 : 0[%] : 80[%] : 100[%]
exponfill : 1
fft : 1 : TRUE : TRUE
machinephase
ppm
Derived from: RY143-aC-1.fdf
Filename = RY142-aC-2.fdf
Author = delta
Experiment = single_pulse_dec
Sample_id = RY142-aC
Solvent = CHLOROFORM-D
Creation_time = 16-JUN-2010 17:16:20
Revision_time = 16-JUN-2010 17:32:47
Current_time = 16-JUN-2010 17:32:53
Comment = single pulse decouple
Data_format = 1D COMPLEX
Dim_size = 26214
Dim_title = 13C
Dim_units = [ppm]
Dimensions = X
Site = RCS 400
Spectrometer = JNM-ECS400
Field_strength = 9.389766[T] (400[MHz])
X_acq_duration = 1.043333312[s]
X_domain = 13C
X_freq = 100.525030333[MHz]
X_offset = 100[ppm]
X_points = 32768
X_prescans = 4
X_resolution = 0.958466665[Hz]
X_sweep = 31.407035518[kHz]
Irr_domain = 1H
Irr_freq = 399.782159838[MHz]
Irr_offset = 5[ppm]
Clipped = FALSE
Mod_return = 1
Scans = 303
Total_scans = 303
X_90_width = 8.4[us]
X_acq_time = 1.043333312[s]
X_angle = 30[deg]
X_atn = 4.3[dB]
X_pulse = 2.8[us]
Irr_atn_dec = 21.8[dB]
Irr_atn_pse = 21.8[dB]
Irr_noise = WALTZ
Decoupling = TRUE
Initial_wait = 1[s]
Noe = TRUE
Noe_time = 2[s]
Recyc_gain = 60
Relaxation_delay = 2[s]
Repetition_time = 3.643333312[s]
Temp_get = 21.9[6C]

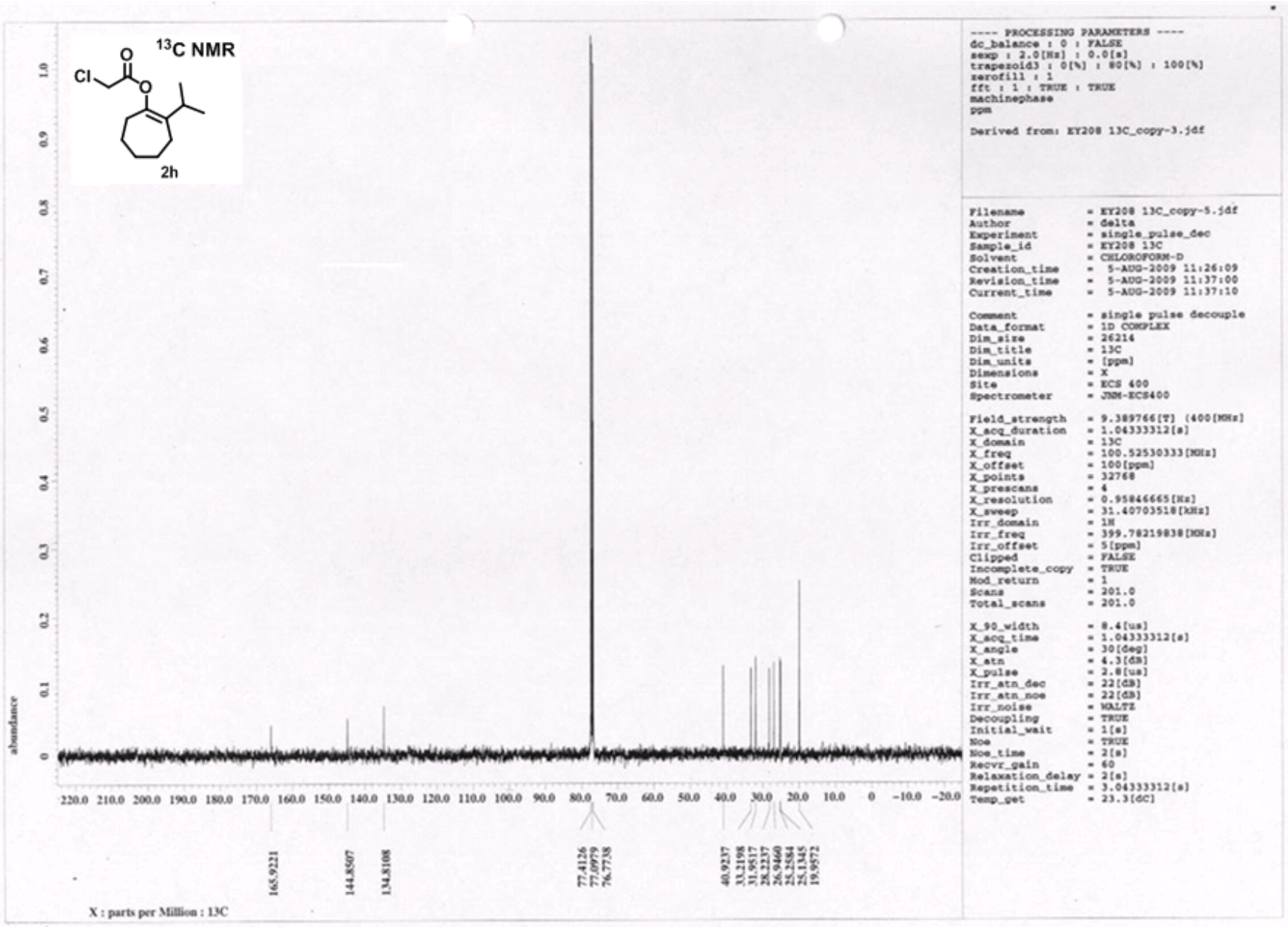

^{1}H NMR
Cl
O
O
2f
abundance
X : parts per Million : 1H
---- PROCESSING PARAMETERS ----
dc_balance : 0 : FALSE
sexp : 0.2[Hz] : 0.0[s]
trapezoid3 : 0[%] : 80[%] : 100[%]
zerofill : 1
fft : 1 : TRUE : TRUE
machinephase
ppm
Derived from: EY640-1.jdf
Filename = EY640-3.jdf
Author = delta
Experiment = single_pulse.ex2
Sample_id = EY640
Solvent = CHLOROFORM-D
Creation_time = 7-JUN-2010 22:42:35
Revision_time = 7-JUN-2010 22:59:41
Current_time = 7-JUN-2010 23:00:22
Comment = single_pulse
Data_format = 1D COMPLEX
Dim_size = 13107
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = ECS 400
Spectrometer = JNM-ECS400
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 = 10.5[us]
X_acq_time = 2.18365952[s]
X_angle = 45[deg]
X_atn = 1[dB]
X_pulse = 5.25[us]
Irr_mode = Off
Tri_mode = Off
Dante_presat = FALSE
Initial_wait = 1[s]
Recvr_gain = 28
Relaxation_delay = 5[s]
Repetition_time = 7.18365952[s]
Temp_get = 21.5[dC]

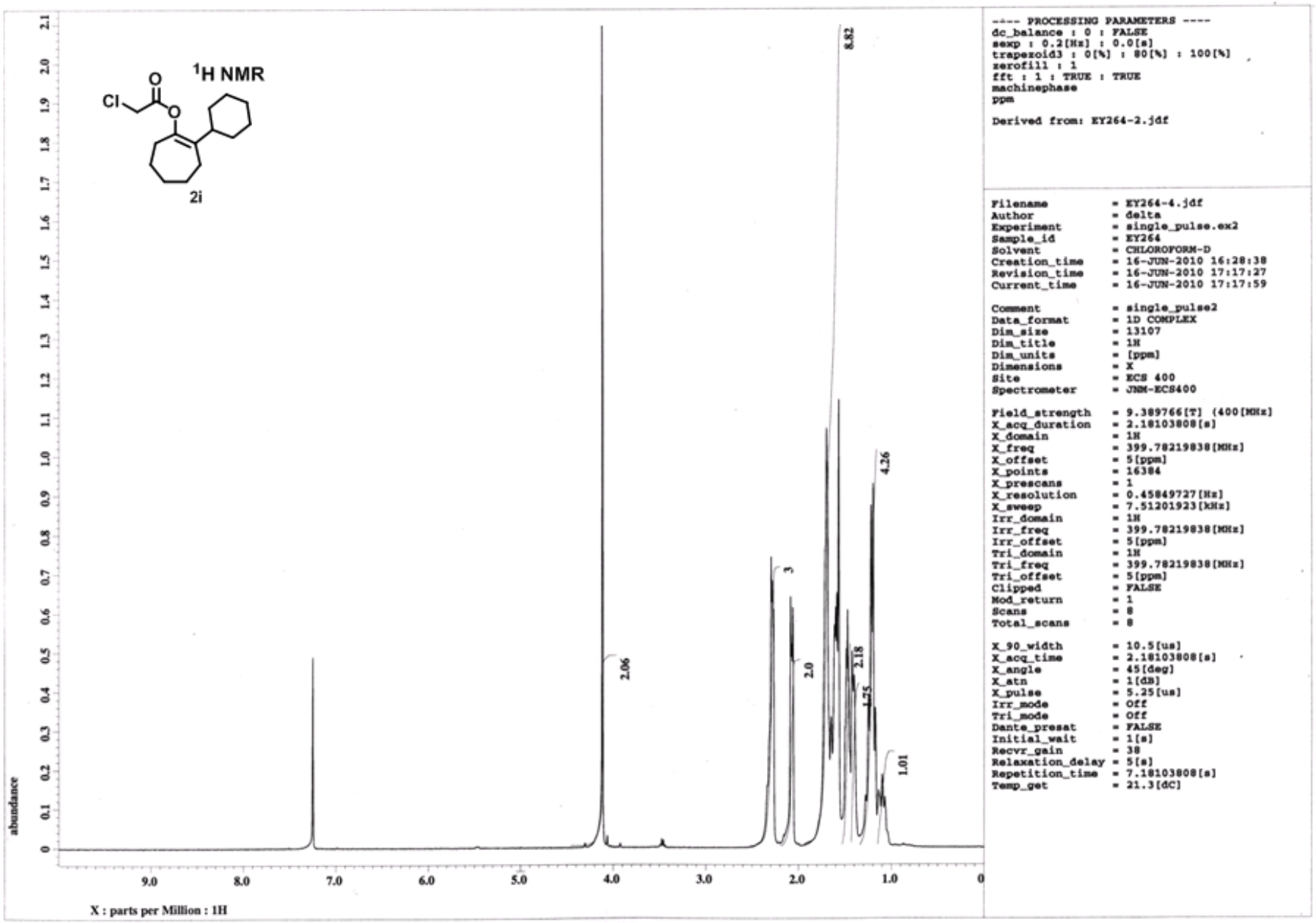

abundance
X : parts per Million : 13C
^{13}C NMR
2f
Cl
O
O
165.9412
146.5669
129.9100
77.4412
77.1170
76.8024
40.8951
34.4593
33.0482
31.5417
31.1031
26.4216
25.3156
20.4625
14.0267


^{1}H NMR
Cl
O
O
2g
abundance
X : parts per Million : 1H
6.12
4.03
3
1.8
1.94
1.97
1.95
---- PROCESSING PARAMETERS ----
dc_balance : 0 : FALSE
sexp : 0.2[Hz] : 0.0[s]
trapezoid3 : 0[%] : 80[%] : 100[%]
zerofill : 1
fft : 1 : TRUE : TRUE
machinephase
ppm
Derived from: EY641-1.jdf
Filename = EY641-3.jdf
Author = delta
Experiment = single_pulse.ex2
Sample_id = EY641
Solvent = CHLOROFORM-D
Creation_time = 7-JUN-2010 23:03:40
Revision_time = 7-JUN-2010 23:20:24
Current_time = 7-JUN-2010 23:20:49
Comment = single_pulse
Data_format = 1D COMPLEX
Dim_size = 13107
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = ECS 400
Spectrometer = JNM-ECS400
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 = 10.5[us]
X_acq_time = 2.18365952[s]
X_angle = 45[deg]
X_atn = 1[dB]
X_pulse = 5.25[us]
Irr_mode = Off
Tri_mode = Off
Dante_presat = FALSE
Initial_wait = 1[s]
Recvr_gain = 30
Relaxation_delay = 5[s]
Repetition_time = 7.18365952[s]
Temp_get = 20.9[dC]


13C NMR
2g
abundance
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
165.9507
146.3476
130.1579
77.4316
77.1170
76.7928
40.8951
33.0482
32.1424
31.5417
31.1222
29.4727
26.4407
25.3061
22.5792
14.0648
X : parts per Million : 13C
---- PROCESSING PARAMETERS --
dc_balance : 0 : FALSE
sexp : 2.0[Hz] : 0.0[s]
trapezoid3 : 0[%] : 80[%] : 1
zerofill : 1
fft : 1 : TRUE : TRUE
machinephase
ppm
Derived from: EY641C-2_copy-4
Filename = EY641C-2_c
Author = delta
Experiment = single_pul
Sample_id = EY641C-2
Solvent = CHLOROFORM
Creation_time = 7-JUN-201
Revision_time = 7-JUN-201
Current_time = 7-JUN-201
Comment = single pul
Data_format = 1D COMPLEX
Dim_size = 26214
Dim_title = 13C
Dim_units = [ppm]
Dimensions = X
Site = ECS 400
Spectrometer = JNM-ECS400
Field_strength = 9.389766[T
X_acq_duration = 1.04333312
X_domain = 13C
X_freq = 100.525303
X_offset = 100[ppm]
X_points = 32768
X_prescans = 4
X_resolution = 0.95846665
X_sweep = 31.4070351
Irr_domain = 1H
Irr_freq = 399.782198
Irr_offset = 5[ppm]
Clipped = FALSE
Incomplete_copy = TRUE
Mod_return = 1
Scans = 102
Total_scans = 102
X_90_width = 8.4[us]
X_acq_time = 1.04333312
X_angle = 30[deg]
X_atn = 4.3[dB]
X_pulse = 2.8[us]
Irr_atn_dec = 21.8[dB]
Irr_atn_noe = 21.8[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
Temp_get = 21.1[dC]

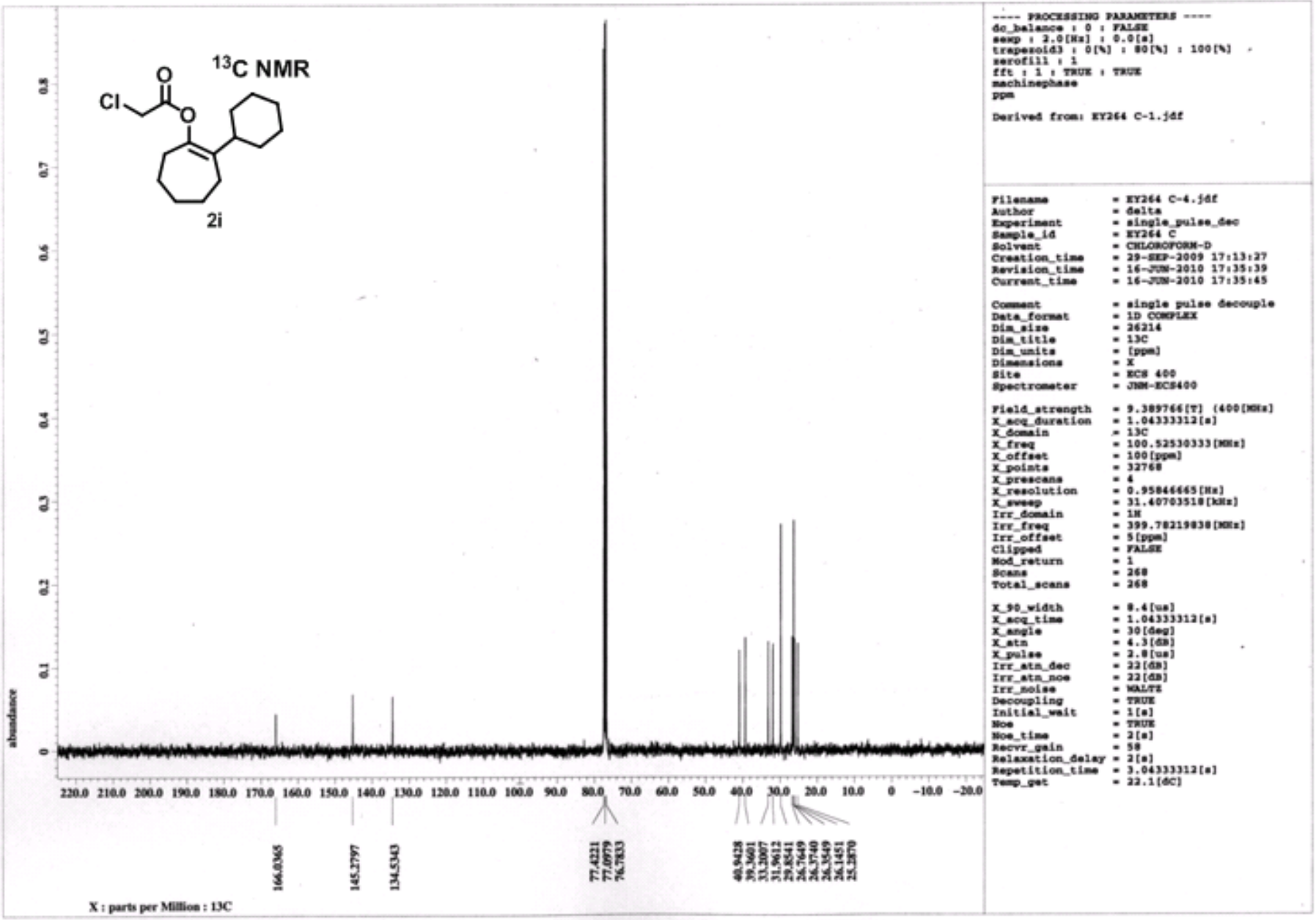

abundance
X : parts per Million : 1H
1H NMR
Cl
O
O
2h
1.94
0.95
1.98
1.92
1.86
2.05
2.03
6

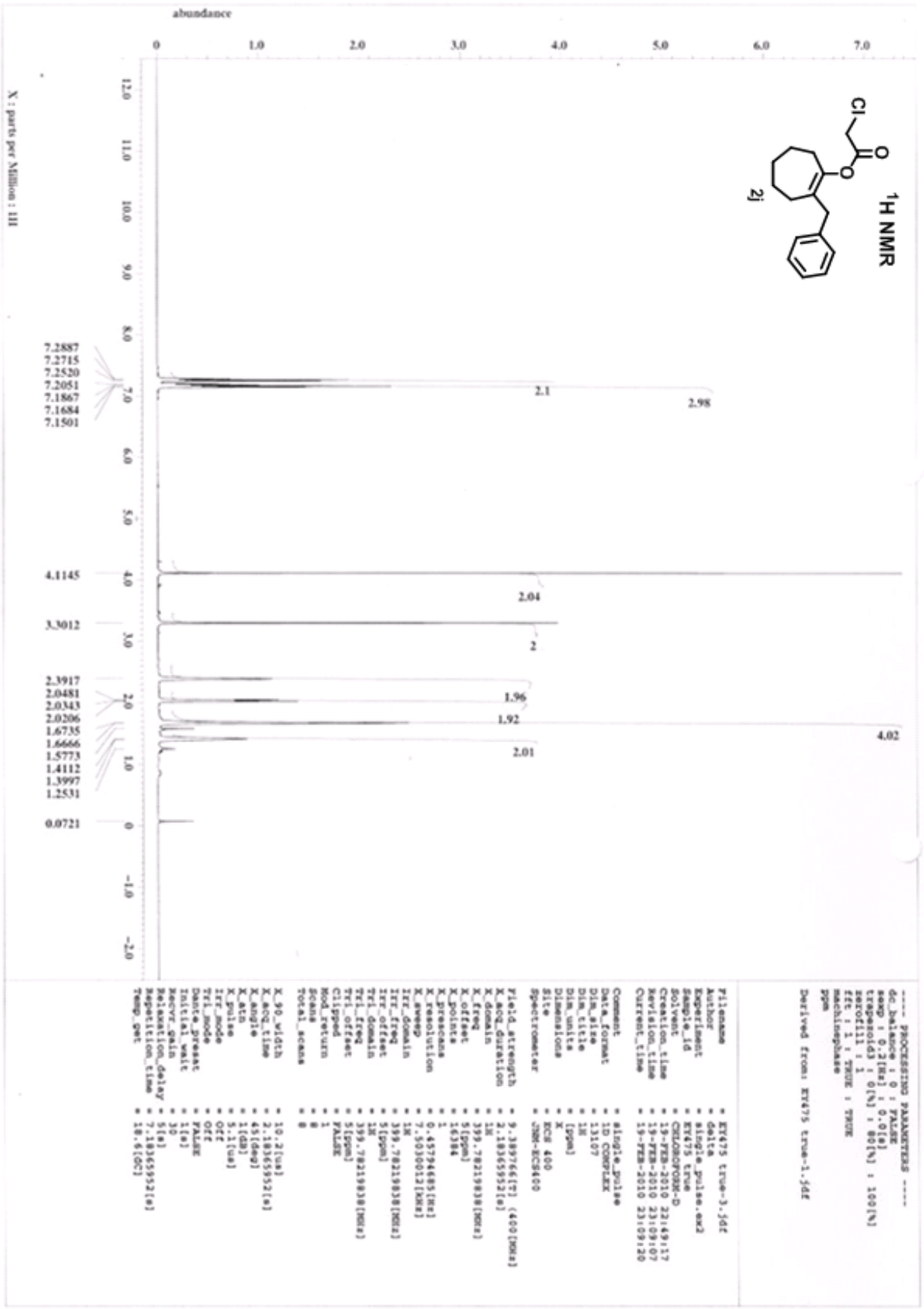

^{13}C NMR
Cl
O
O
2h
abundance
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
165.9221
144.8507
134.8108
77.4126
77.0979
76.7738
40.9237
33.2198
31.9517
28.2237
26.9460
25.2584
25.1345
19.9572
X : parts per Million : 13C
---- PROCESSING PARAMETERS ----
dc_balance : 0 : FALSE
sexp : 2.0[Hz] : 0.0[s]
trapezoid3 : 0[%] : 80[%] : 100[%]
zerofill : 1
fft : 1 : TRUE : TRUE
machinephase
ppm
Derived from: EY208 13C_copy-3.jdf
Filename = EY208 13C_copy-5.jdf
Author = delta
Experiment = single_pulse_dec
Sample_id = EY208 13C
Solvent = CHLOROFORM-D
Creation_time = 5-AUG-2009 11:26:09
Revision_time = 5-AUG-2009 11:37:00
Current_time = 5-AUG-2009 11:37:10
Comment = single pulse decouple
Data_format = 1D COMPLEX
Dim_size = 26214
Dim_title = 13C
Dim_units = [ppm]
Dimensions = X
Site = ECS 400
Spectrometer = JNM-ECS400
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
Incomplete_copy = TRUE
Mod_return = 1
Scans = 201.0
Total_scans = 201.0
X_90_width = 8.4[us]
X_acq_time = 1.04333312[s]
X_angle = 30[deg]
X_atn = 4.3[dB]
X_pulse = 2.8[us]
Irr_atn_dec = 22[dB]
Irr_atn_noe = 22[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 = 23.3[dC]

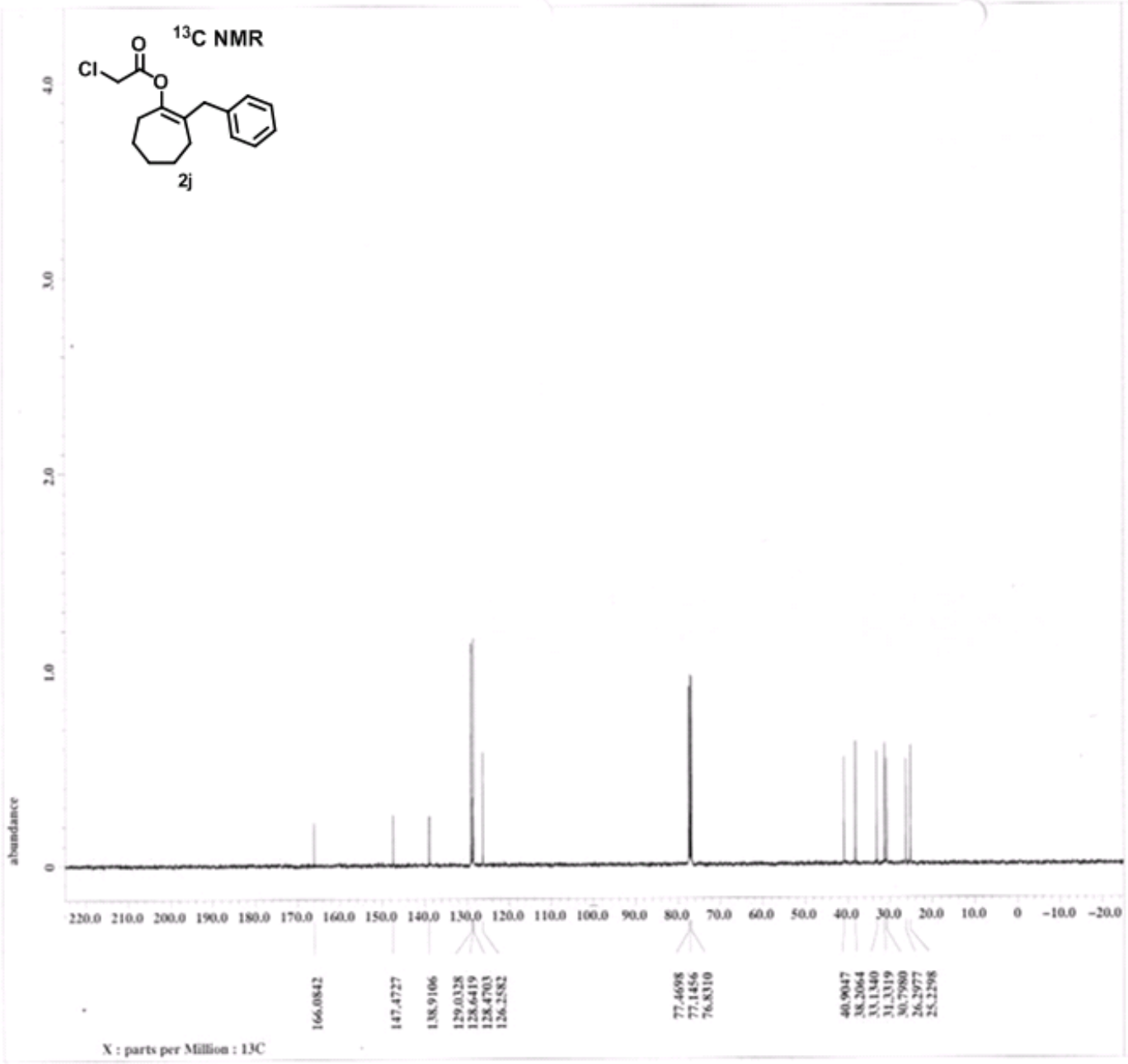



```
---- PROCESSING PARAMETERS ----
dc_balance : 0 : FALSE
sexp : 0.2[Hz] : 0.0[s]
trapezoid3 : 0[%] : 80[%] : 100[%]
zerofill : 1
fft : 1 : TRUE : TRUE
machinephase
ppm

Derived from: EY264-2.jdf
```

Filename	= EY264-4.jdf
Author	= delta
Experiment	= single_pulse.ex2
Sample_id	= EY264
Solvent	= CHLOROFORM-D
Creation_time	= 16-JUN-2010 16:28:38
Revision_time	= 16-JUN-2010 17:17:27
Current_time	= 16-JUN-2010 17:17:59
Comment	= single_pulse2
Data_format	= 1D COMPLEX
Dim_size	= 13107
Dim_title	= 1H
Dim_units	= [ppm]
Dimensions	= X
Site	= ECS 400
Spectrometer	= JNM-ECS400
Field_strength	= 9.389766[T] (400[MHz]
X_acq_duration	= 2.18103808[s]
X_domain	= 1H
X_freq	= 399.78219838[MHz]
X_offset	= 5[ppm]
X_points	= 16384
X_prescans	= 1
X_resolution	= 0.45849727[Hz]
X_sweep	= 7.51201923[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	= 10.5[us]
X_acq_time	= 2.18103808[s]
X_angle	= 45[deg]
X_atn	= 1[dB]
X_pulse	= 5.25[us]
Irr_mode	= Off
Tri_mode	= Off
Dante_presat	= FALSE
Initial_wait	= 1[s]
Recvr_gain	= 38
Relaxation_delay	= 5[s]
Repetition_time	= 7.18103808[s]
Temp_get	= 21.3[dC]

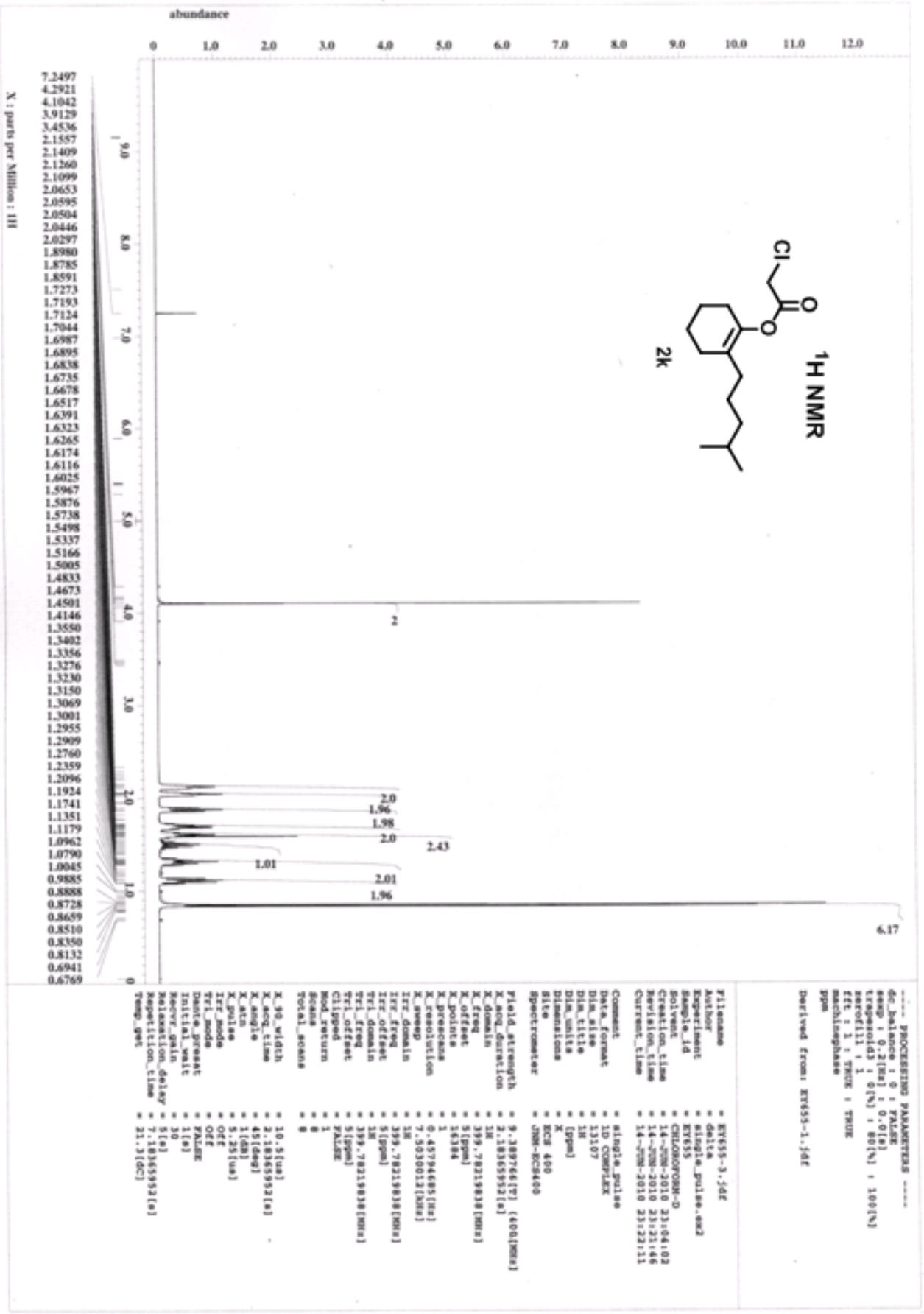

^{13}C NMR
Cl
O
O
2i
abundance
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
166.0365
145.2797
134.5343
77.4221
77.0979
76.7833
40.9428
39.3601
33.2007
31.9612
29.8541
26.7649
26.3740
26.3549
26.1451
25.3870
X : parts per Million : 13C
---- PROCESSING PARAMETERS ----
dc_balance : 0 : FALSE
sexp : 2.0[Hz] : 0.0[s]
trapezoid3 : 0[%] : 80[%] : 100[%]
zerofill : 1
fft : 1 : TRUE : TRUE
machinephase
ppm
Derived from: EY264 C-1.jdf
Filename = EY264 C-4.jdf
Author = delta
Experiment = single_pulse_dec
Sample_id = EY264 C
Solvent = CHLOROFORM-D
Creation_time = 29-SEP-2009 17:13:27
Revision_time = 16-JUN-2010 17:35:39
Current_time = 16-JUN-2010 17:35:45
Comment = single pulse decouple
Data_format = 1D COMPLEX
Dim_size = 26214
Dim_title = 13C
Dim_units = [ppm]
Dimensions = X
Site = ECS 400
Spectrometer = JNM-ECS400
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 = 268
Total_scans = 268
X_90_width = 8.4[us]
X_acq_time = 1.04333312[s]
X_angle = 30[deg]
X_atn = 4.3[dB]
X_pulse = 2.8[us]
Irr_atn_dec = 22[dB]
Irr_atn_noe = 22[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 = 22.1[dC]

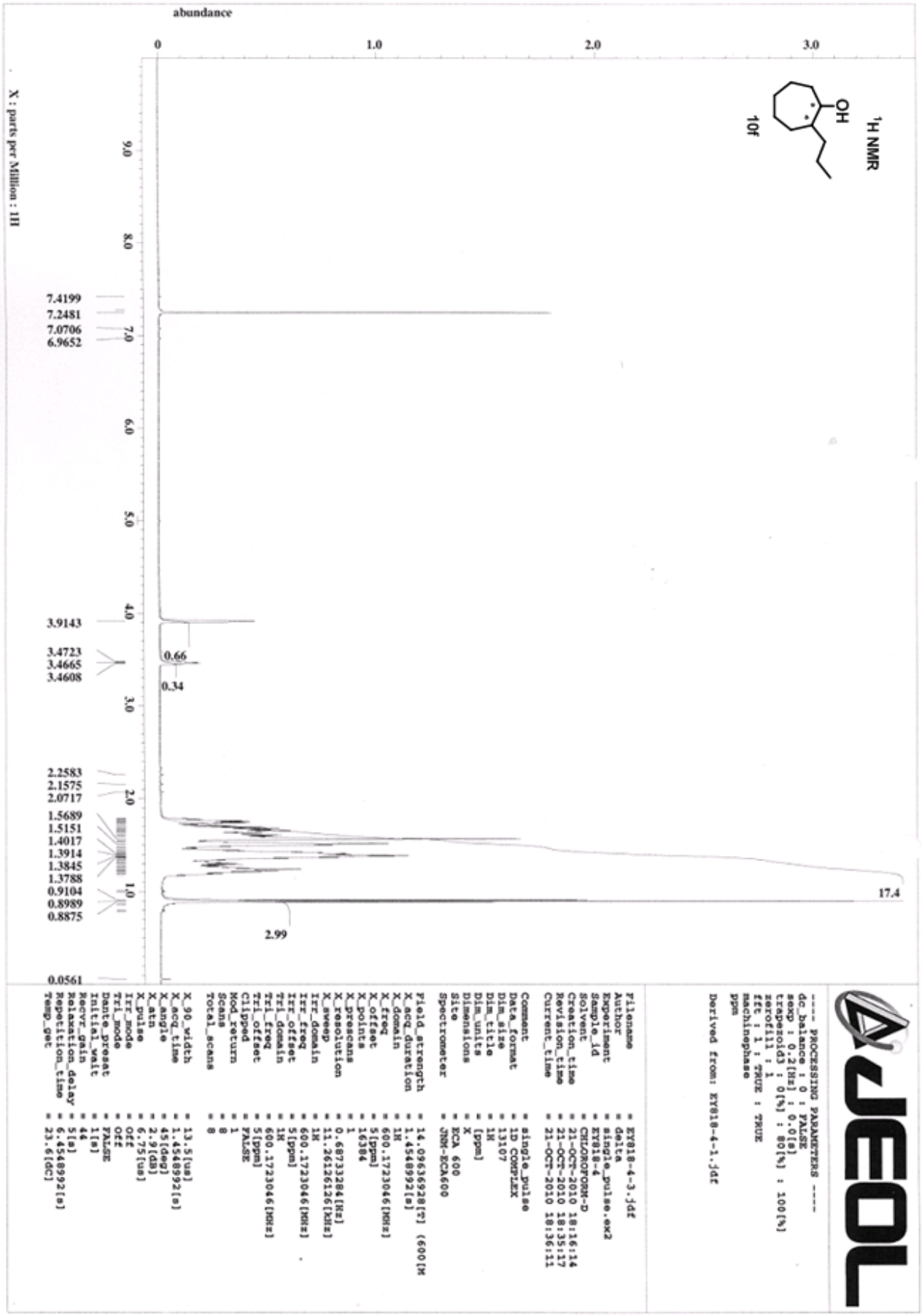

abundance
X : parts per Million : 111
7.2887
7.2715
7.2520
7.2051
7.1867
7.1684
7.1501
4.1145
3.3012
2.3917
2.0481
2.0343
2.0206
1.6735
1.6666
1.5773
1.4112
1.3997
1.2531
0.0721
2.1
2.98
2.04
2
1.96
1.92
4.02
2.01
2j
^{1}H NMR

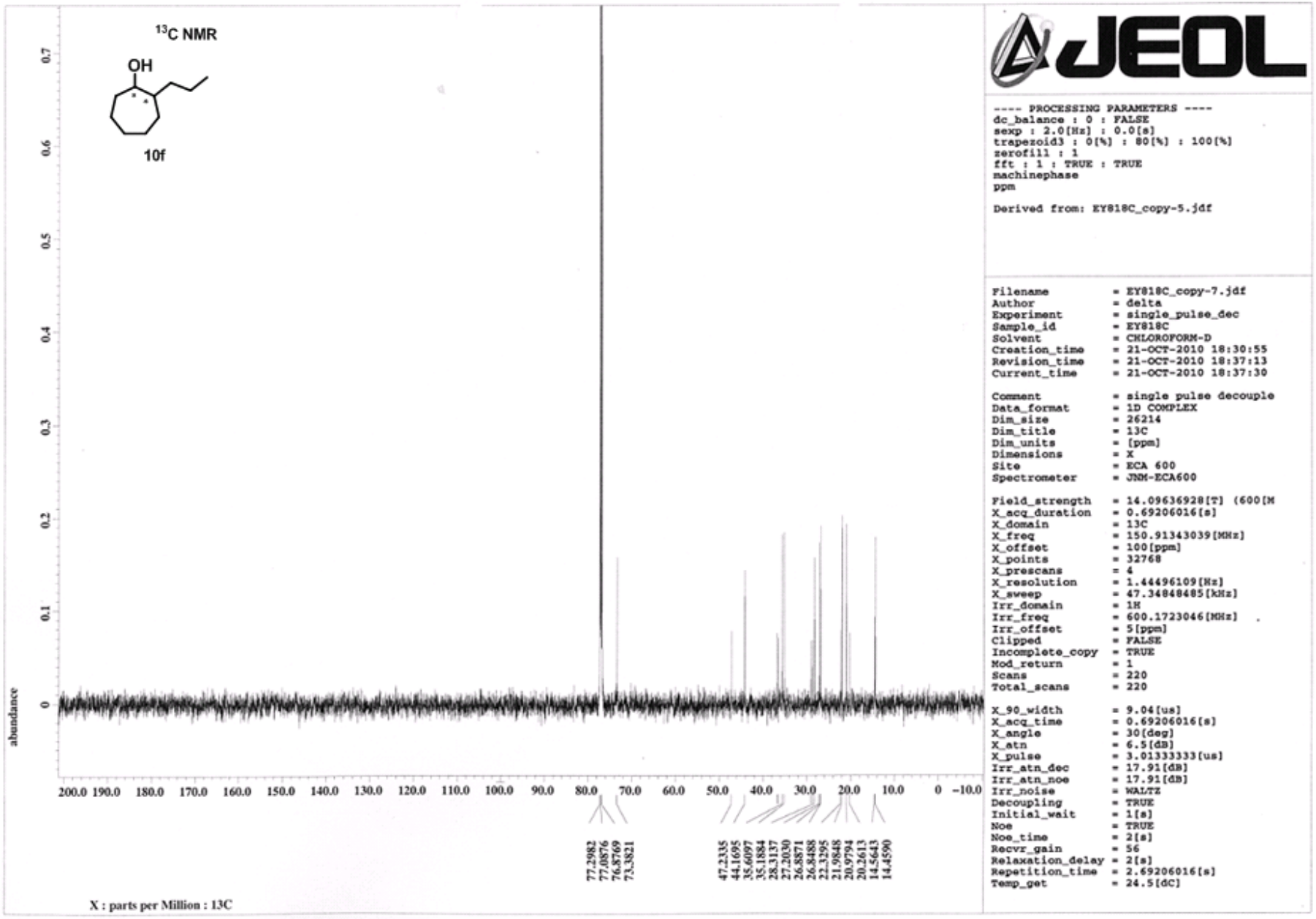


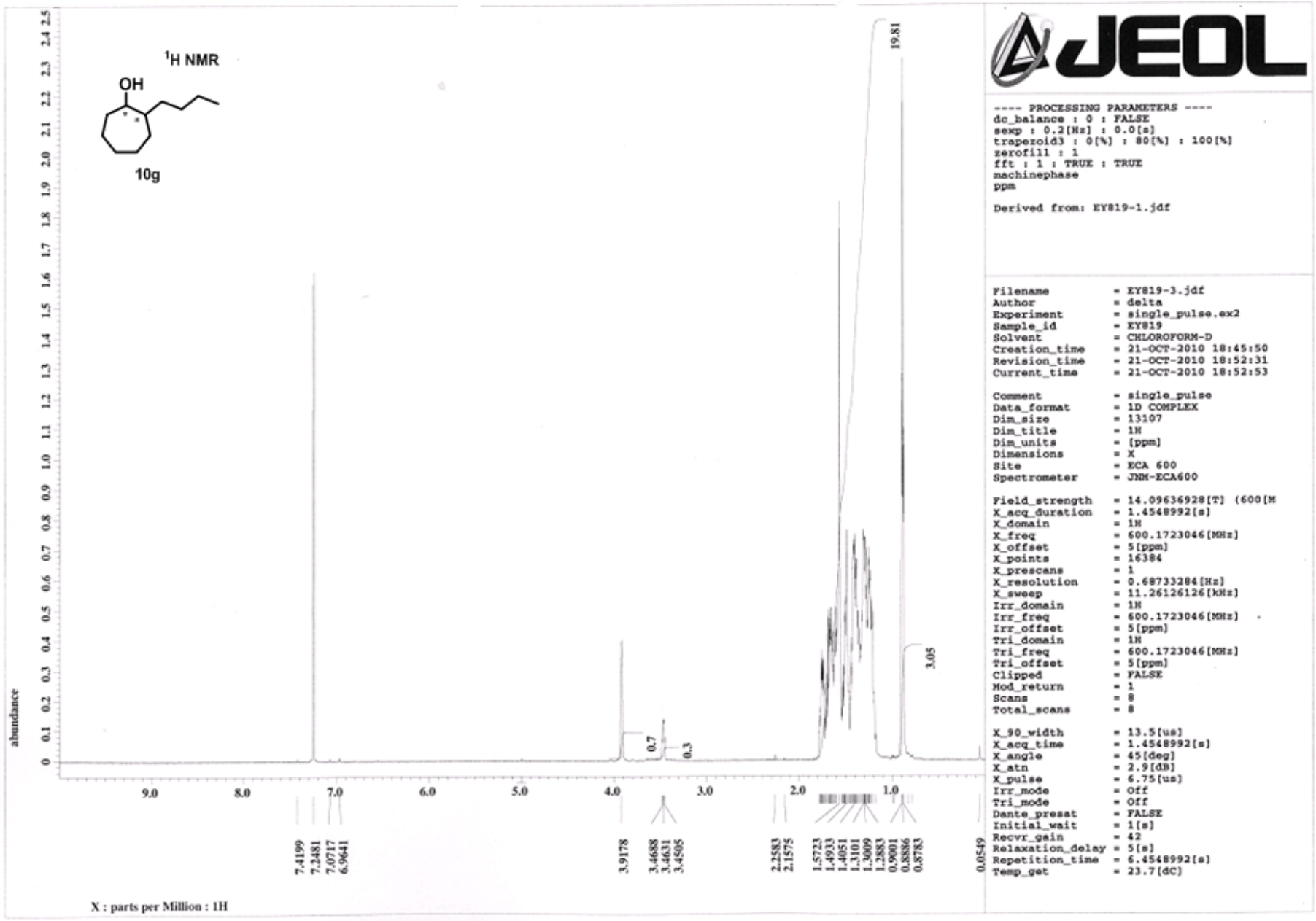

```
---- PROCESSING PARAMETERS ----
dc_balance : 0 : FALSE
sexp : 2.0[Hz] : 0.0[s]
trapezoid3 : 0[%] : 80[%] : 100[%]
zerofill : 1
fft : 1 : TRUE : TRUE
machinephase
ppm

Derived from: EY475 true C-1.jdf
```

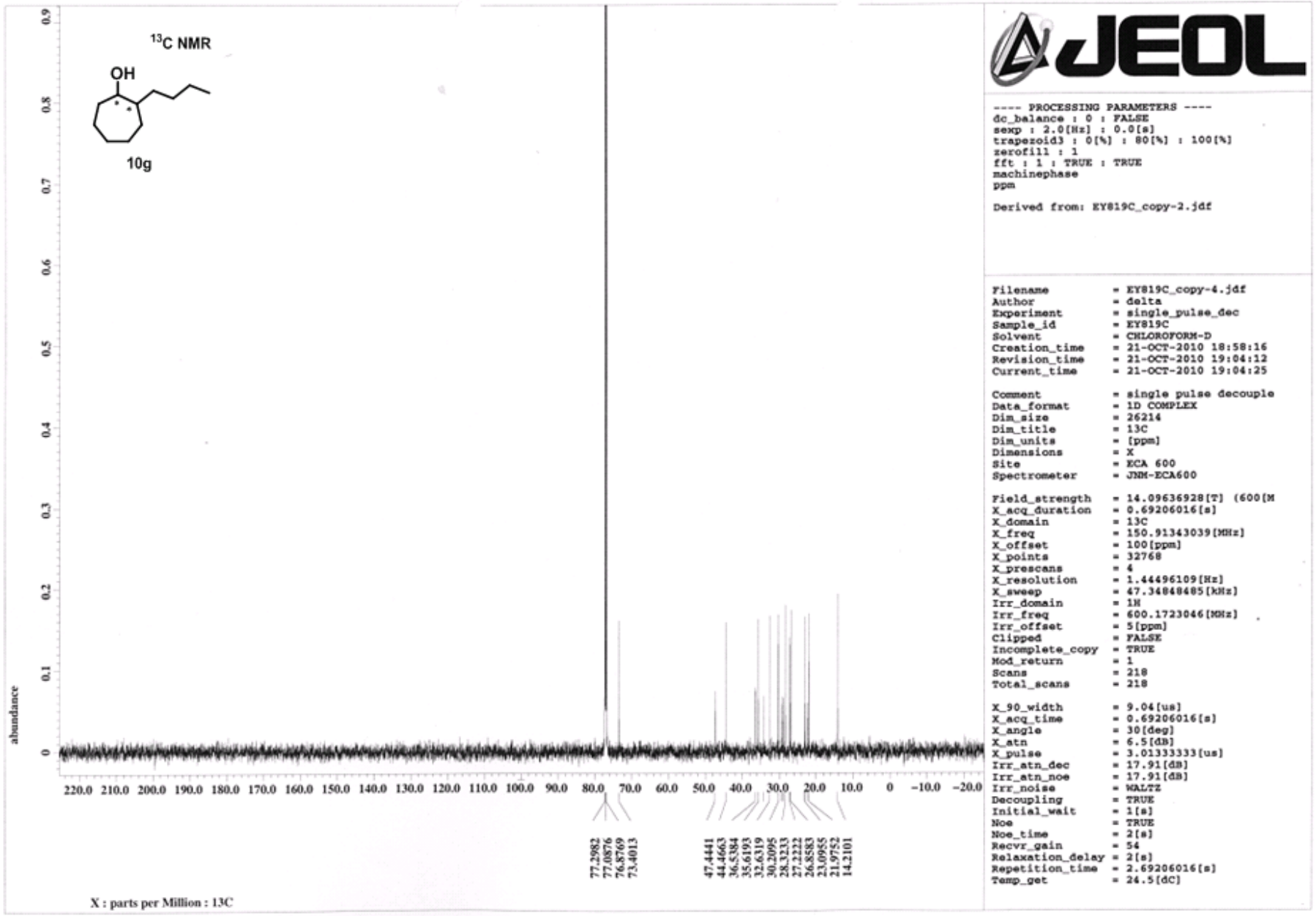
```
Filename          = EY475 true C-2.jdf
Author            = delta
Experiment        = single_pulse_dec
Sample_id         = EY475 true C
Solvent           = CHLOROFORM-D
Creation_time     = 19-FEB-2010 23:00:18
Revision_time     = 19-FEB-2010 23:15:59
Current_time      = 19-FEB-2010 23:16:06

Comment           = single pulse decouple
Data_format       = 1D COMPLEX
Dim_size          = 26214
Dim_title         = 13C
Dim_units         = [ppm]
Dimensions        = X
Site              = ECS 400
Spectrometer      = JNM-ECS400

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             = 162
Total_scans       = 162

X_90_width        = 8.4[us]
X_acq_time        = 1.04333312[s]
X_angle           = 30[deg]
X_atn             = 4.3[dB]
X_pulse           = 2.8[us]
Irr_atn_dec       = 22[dB]
Irr_atn_noe       = 22[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          = 18.8[dC]
```


abundance
0 1.0 2.0 3.0 4.0 5.0 6.0 7.0 8.0 9.0 10.0 11.0 12.0
Cl
O
O
O
2k
1H NMR
X : parts per Million : 1H
7.2497
4.2921
4.1042
3.9129
3.4536
2.1557
2.1409
2.1260
2.1099
2.0653
2.0595
2.0504
2.0446
2.0297
1.8980
1.8785
1.8591
1.7273
1.7193
1.7124
1.7044
1.6987
1.6895
1.6838
1.6735
1.6678
1.6517
1.6391
1.6323
1.6265
1.6174
1.6116
1.6025
1.5967
1.5876
1.5738
1.5498
1.5337
1.5166
1.5005
1.4833
1.4673
1.4501
1.4146
1.3550
1.3402
1.3356
1.3276
1.3230
1.3150
1.3069
1.3001
1.2955
1.2909
1.2760
1.2359
1.2096
1.1924
1.1741
1.1351
1.1179
1.0962
1.0790
1.0045
0.9885
0.8888
0.8728
0.8659
0.8510
0.8350
0.8132
0.6941
0.6769
2.0
1.96
1.98
2.0
2.43
1.01
2.01
1.96
6.17
---- PROCESSING PARAMETERS ----
dc_balance : 0 : FALSE
exsep : 0.2[Hz] : 0.0[%]
trapezoid3 : 0[%] : 80[%] : 100[%]
zerofill : 1
fft : 1 : TRUE : TRUE
manichemphase
ppm
Derived from: EY655-1.jdf
Filename = EY655-1.jdf
Author = delta
Experiment = single_pulse.exp
Sample_id = EY655
Solvent = CHLOROFORM-D
Creation_time = 14-JUN-2010 23:04:02
Revision_time = 14-JUN-2010 23:21:46
Current_time = 14-JUN-2010 23:22:11
Comment = single_pulse
Data_format = 1D COMPLEX
Dim_size = 13107
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = ECS 400
Spectrometer = JNM-ECS400
Field_strength = 9.389766[T] (400[MHz])
X_acq_duration = 2.183659552[s]
X_domain = 1H
X_freq = 399.7821983[MHz]
X_offset = 5[ppm]
X_points = 16384
X_prescans = 1
X_resolution = 0.4579468[Hz]
X_sweep = 7.503001[kHz]
Irr_domain = 1H
Irr_freq = 399.7821983[MHz]
Irr_offset = 5[ppm]
Tri_domain = 1H
Tri_freq = 399.7821983[MHz]
Tri_offset = 5[ppm]
Clipped = FALSE
Mod_return = 1
Scans = 8
Total_scans = 8
X_90_width = 10.5[us]
X_acq_time = 2.183659552[s]
X_angle = 45[deg]
X_atn = 1[dB]
X_pulse = 5.25[us]
Irr_mode = off
Tri_mode = off
Decpl_preset = FALSE
Initial_wait = 1[s]
Recyc_gain = 30
Relaxation_delay = 5[s]
Repetition_time = 7.183659552[s]
Temp_get = 21.3[dC]


abundance
0
1.0
2.0
3.0
^{1}H NMR
OH
10f
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
7.4199
7.2481
7.0706
6.9652
3.9143
3.4723
3.4665
3.4608
0.66
0.34
2.2583
2.1575
2.0717
1.5689
1.5151
1.4017
1.3914
1.3845
1.3788
0.9104
0.8989
0.8875
0.0561
17.4
2.99
X : parts per Million : 1H
---- PROCESSING PARAMETERS ----
dc_balance : 0 : FALSE
sexp : 0.2[Hz] : 0.0[s]
trapezoid3 : 0[%] : 80[%] : 100[%]
zerofill : 1
fft : 1 : TRUE : TRUE
machinephase
ppm
Derived from: EY818-4-1.jdf
Filename = EY818-4-3.jdf
Author = delta
Experiment = single_pulse.ex2
Sample_id = EY818-4
Solvent = CHLOROFORM-D
Creation_time = 21-OCT-2010 18:16:14
Revision_time = 21-OCT-2010 18:35:17
Current_time = 21-OCT-2010 18:36:11
Comment = single_pulse
Data_format = 1D COMPLEX
Dim_size = 131072
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = ECA 600
Spectrometer = JNM-ECA600
Field_strength = 14.09636928[T] (600[M
X_acq_duration = 1.454899[s]
X_domain = 1H
X_freq = 600.1723046[MHz]
X_offset = 5[ppm]
X_points = 16384
X_prescans = 1
X_resolution = 0.687332[Hz]
X_sweep = 11.262126[kHz]
1H
Irr_freq = 600.1723046[MHz]
Irr_offset = 5[ppm]
tri_domain = 1H
tri_freq = 600.1723046[MHz]
tri_offset = 5[ppm]
Clipped = FALSE
Mod_return = 1
Scans = 8
Total_scans = 8
X_90_width = 13.5[us]
X_acq_time = 1.454899[s]
X_angle = 45[deg]
X_atn = 2.9[dB]
X_pulse = 6.75[us]
Irr_mode = Off
tri_mode = Off
Dante_preset = FALSE
Initial_wait = 1[s]
Recvr_gain = 44
Relaxation_delay = 5[s]
Repetition_time = 6.454899[s]
Temp_get = 23.6[dC]


13C NMR
OH
10f
abundance
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0
77.2982
77.0876
76.8769
73.3821
47.2335
44.1695
35.6097
35.1884
28.3137
27.2030
26.8871
26.8488
22.3295
21.9848
20.9794
20.2613
14.5643
14.4590
X : parts per Million : 13C
JEOL
---- PROCESSING PARAMETERS ----
dc_balance : 0 : FALSE
sexp : 2.0[Hz] : 0.0[s]
trapezoid3 : 0[%] : 80[%] : 100[%]
zerofill : 1
fft : 1 : TRUE : TRUE
machinephase
ppm
Derived from: EY818C_copy-5.jdf
Filename = EY818C_copy-7.jdf
Author = delta
Experiment = single_pulse_dec
Sample_id = EY818C
Solvent = CHLOROFORM-D
Creation_time = 21-OCT-2010 18:30:55
Revision_time = 21-OCT-2010 18:37:13
Current_time = 21-OCT-2010 18:37:30
Comment = single pulse decouple
Data_format = 1D COMPLEX
Dim_size = 26214
Dim_title = 13C
Dim_units = [ppm]
Dimensions = X
Site = ECA 600
Spectrometer = JNM-ECA600
Field_strength = 14.09636928[T] (600[M
X_acq_duration = 0.69206016[s]
X_domain = 13C
X_freq = 150.91343039[MHz]
X_offset = 100[ppm]
X_points = 32768
X_prescans = 4
X_resolution = 1.44496109[Hz]
X_sweep = 47.34848485[kHz]
Irr_domain = 1H
Irr_freq = 600.1723046[MHz]
Irr_offset = 5[ppm]
Clipped = FALSE
Incomplete_copy = TRUE
Mod_return = 1
Scans = 220
Total_scans = 220
X_90_width = 9.04[us]
X_acq_time = 0.69206016[s]
X_angle = 30[deg]
X_atn = 6.5[dB]
X_pulse = 3.01333333[us]
Irr_atn_dec = 17.91[dB]
Irr_atn_noe = 17.91[dB]
Irr_noise = WALTZ
Decoupling = TRUE
Initial_wait = 1[s]
Noe = TRUE
Noe_time = 2[s]
Recvr_gain = 56
Relaxation_delay = 2[s]
Repetition_time = 2.69206016[s]
Temp_get = 24.5[dC]

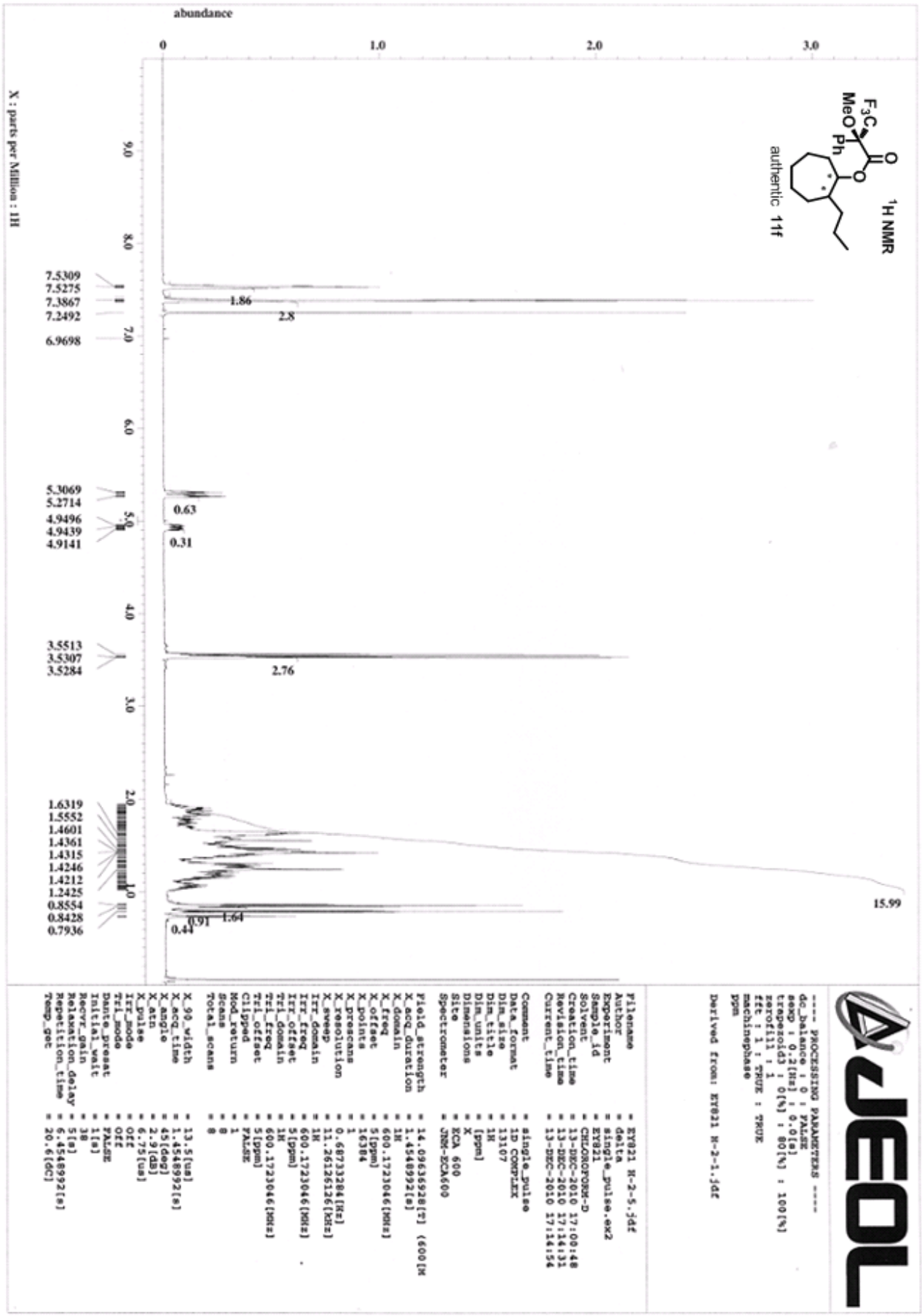

^{1}H NMR
OH
10g
abundance
X : parts per Million : 1H
19.81
3.05
0.7
0.3
7.4199
7.2481
7.0717
6.9641
3.9178
3.4688
3.4631
3.4505
2.2583
2.1575
1.5723
1.4933
1.4051
1.3101
1.3009
1.2883
0.9001
0.8886
0.8783
0.0549
---- PROCESSING PARAMETERS ----
dc_balance : 0 : FALSE
sexp : 0.2[Hz] : 0.0[s]
trapezoid3 : 0[%] : 80[%] : 100[%]
zerofill : 1
fft : 1 : TRUE : TRUE
machinephase
ppm
Derived from: EY819-1.jdf
Filename = EY819-3.jdf
Author = delta
Experiment = single_pulse.ex2
Sample_id = EY819
Solvent = CHLOROFORM-D
Creation_time = 21-OCT-2010 18:45:50
Revision_time = 21-OCT-2010 18:52:31
Current_time = 21-OCT-2010 18:52:53
Comment = single_pulse
Data_format = 1D COMPLEX
Dim_size = 13107
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = ECA 600
Spectrometer = JNM-ECA600
Field_strength = 14.09636928[T] (600[M
X_acq_duration = 1.4548992[s]
X_domain = 1H
X_freq = 600.1723046[MHz]
X_offset = 5[ppm]
X_points = 16384
X_prescans = 1
X_resolution = 0.68733284[Hz]
X_sweep = 11.26126126[kHz]
Irr_domain = 1H
Irr_freq = 600.1723046[MHz]
Irr_offset = 5[ppm]
Tri_domain = 1H
Tri_freq = 600.1723046[MHz]
Tri_offset = 5[ppm]
Clipped = FALSE
Mod_return = 1
Scans = 8
Total_scans = 8
X_90_width = 13.5[us]
X_acq_time = 1.4548992[s]
X_angle = 45[deg]
X_atn = 2.9[dB]
X_pulse = 6.75[us]
Irr_mode = Off
Tri_mode = Off
Dante_presat = FALSE
Initial_wait = 1[s]
Recvr_gain = 42
Relaxation_delay = 5[s]
Repetition_time = 6.4548992[s]
Temp_get = 23.7[dC]

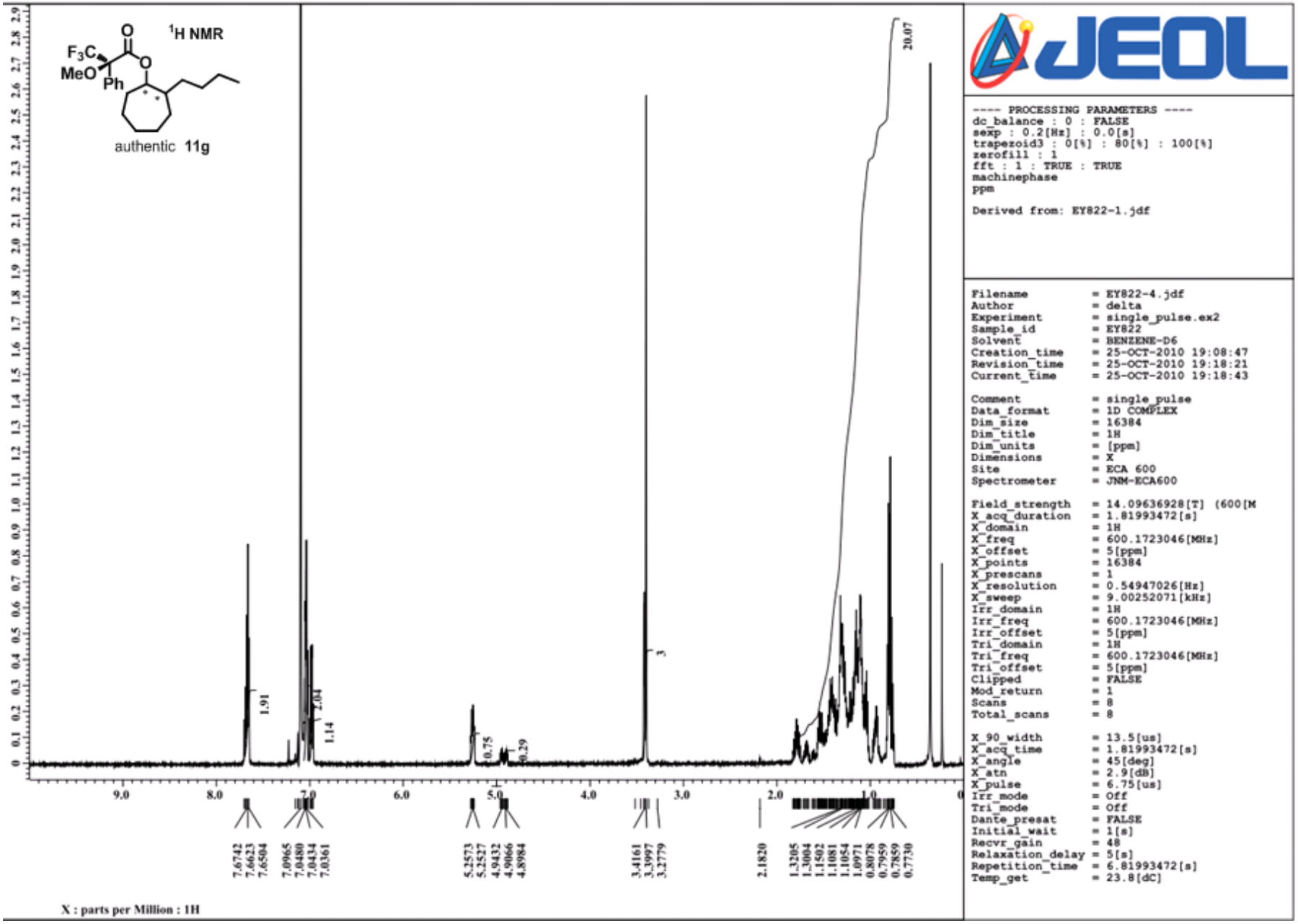


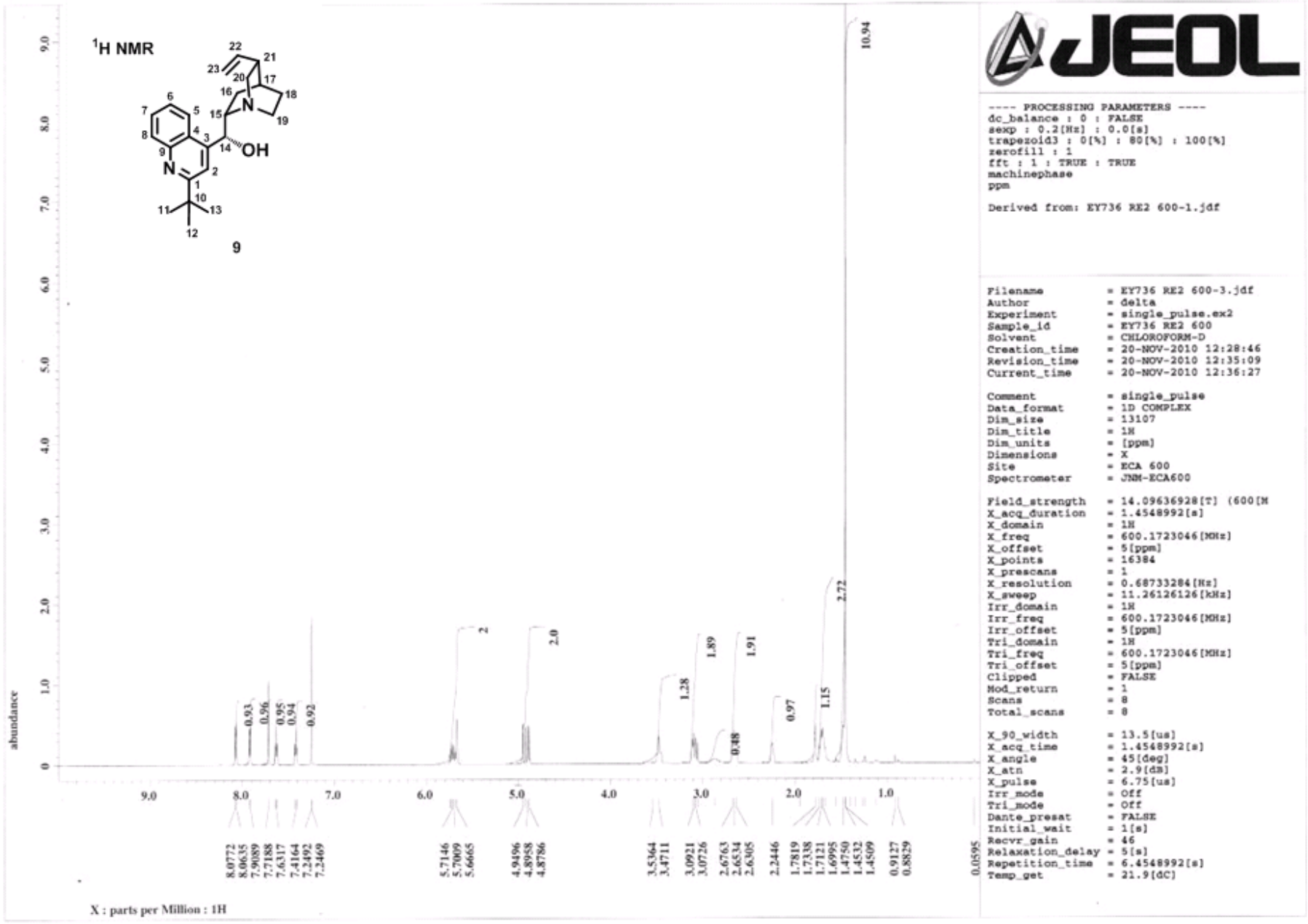
JEOL

```
---- PROCESSING PARAMETERS ----
dc_balance : 0 : FALSE
sexp : 2.0[Hz] : 0.0[s]
trapezoid3 : 0[%] : 80[%] : 100[%]
zerofill : 1
fft : 1 : TRUE : TRUE
machinephase
ppm

Derived from: EY819C_copy-2.jdf
```

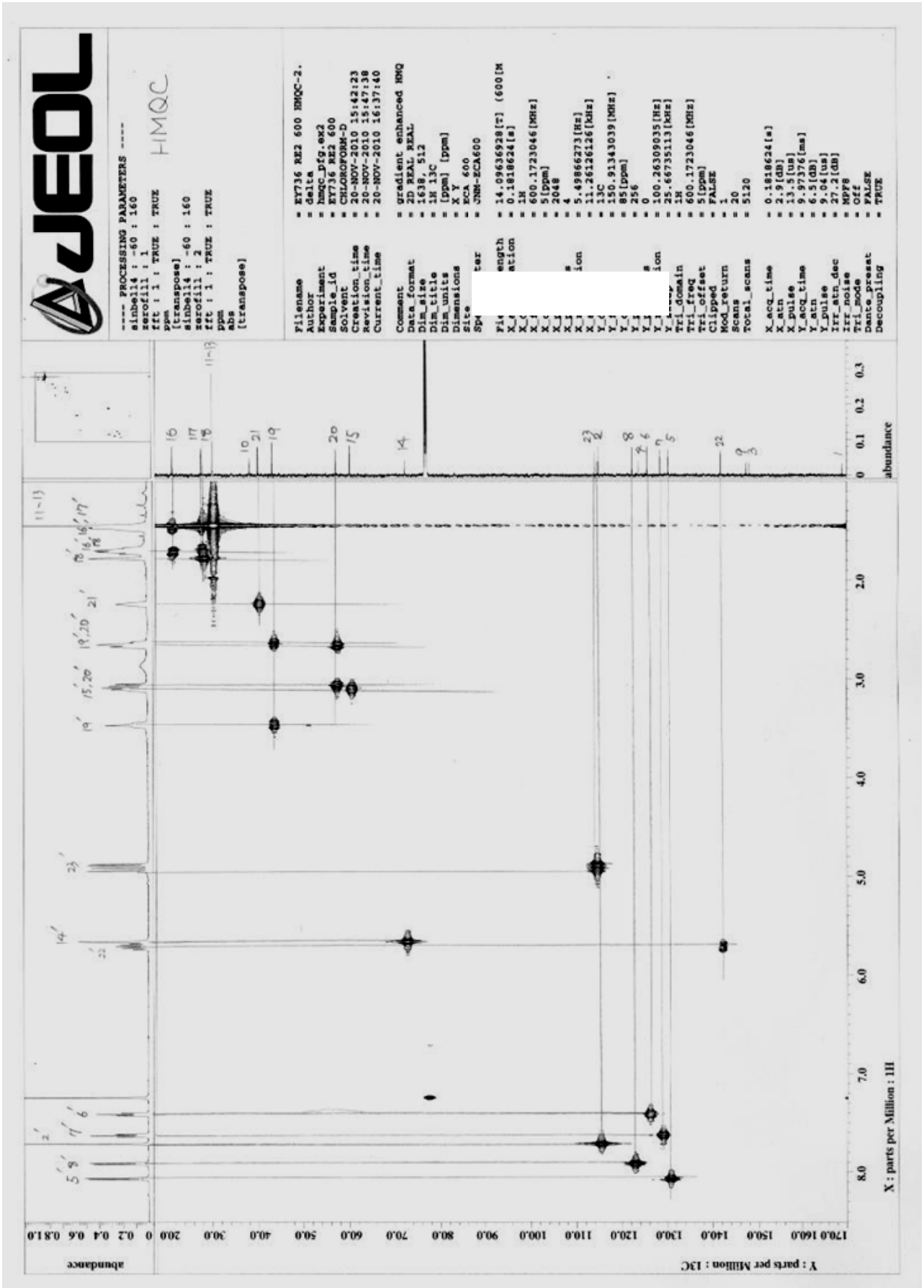
```
Filename          = EY819C_copy-4.jdf
Author            = delta
Experiment        = single_pulse_dec
Sample_id         = EY819C
Solvent           = CHLOROFORM-D
Creation_time     = 21-OCT-2010 18:58:16
Revision_time     = 21-OCT-2010 19:04:12
Current_time      = 21-OCT-2010 19:04:25

Comment           = single pulse decouple
Data_format       = 1D COMPLEX
Dim_size          = 26214
Dim_title         = 13C
Dim_units         = [ppm]
Dimensions        = X
Site              = ECA 600
Spectrometer      = JNM-ECA600

Field_strength    = 14.09636928[T] (600[M
X_acq_duration    = 0.69206016[s]
X_domain          = 13C
X_freq            = 150.91343039[MHz]
X_offset          = 100[ppm]
X_points          = 32768
X_prescans        = 4
X_resolution      = 1.44496109[Hz]
X_sweep           = 47.34848485[kHz]
Irr_domain        = 1H
Irr_freq          = 600.1723046[MHz]
Irr_offset        = 5[ppm]
Clipped           = FALSE
Incomplete_copy   = TRUE
Mod_return        = 1
Scans             = 218
Total_scans       = 218

X_90_width        = 9.04[us]
X_acq_time        = 0.69206016[s]
X_angle           = 30[deg]
X_atn             = 6.5[dB]
X_pulse           = 3.01333333[us]
Irr_atn_dec       = 17.91[dB]
Irr_atn_noe       = 17.91[dB]
Irr_noise         = WALTZ
Decoupling        = TRUE
Initial_wait      = 1[s]
Noe               = TRUE
Noe_time          = 2[s]
Recvr_gain        = 54
Relaxation_delay  = 2[s]
Repetition_time   = 2.69206016[s]
Temp_get          = 26.5[dC]
```


abundance
0
1.0
2.0
3.0
X : parts per Million : 1H
authentic 11f
1H NMR
7.5309
7.5275
7.3867
7.2492
6.9698
1.86
2.8
5.3069
5.2714
4.9496
4.9439
4.9141
0.63
0.31
3.5513
3.5307
3.5284
2.76
1.6319
1.5552
1.4601
1.4361
1.4315
1.4246
1.4212
1.2425
0.8554
0.8428
0.7936
0.44
0.91
1.64
15.99
---- PROCESSING PARAMETERS ----
dc_balance : 0 : FALSE
expp : 0.2[Hz] : 0.0[s]
trapezoid3 : 0[%] : 80[%] : 100[%]
zerofill : 1
fft : 1 : TRUE : TRUE
machinephase
ppm
Derived from: EY021 H-2-1.jdf
Filename = EY021 H-2-5.jdf
Author = delta
Experiment = single_pulse.ex2
Sample_id = EY021
Solvent = CHLOROFORM-D
Creation_time = 13-DEC-2010 17:08:48
Revision_time = 13-DEC-2010 17:14:31
Current_time = 13-DEC-2010 17:14:54
Comment = single_pulse
Data_format = 1D COMPLEX
Dim_size = 13107
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = ECA 600
Spectrometer = JNM-ECA600
Field_strength = 14.0963692[T] (600[M
X_acq_duration = 1.4548992[s]
X_domain = 1H
X_freq = 600.1723046[MHz]
X_offset = 5[ppm]
X_points = 16384
X_prescans = 1
X_resolution = 0.68733284[Hz]
X_sweep = 11.26126126[kHz]
Irr_domain = 1H
Irr_freq = 600.1723046[MHz]
Irr_offset = 5[ppm]
Tri_domain = 1H
Tri_freq = 600.1723046[MHz]
Tri_offset = 5[ppm]
Clipped = FALSE
Mod_return = 1
Scans = 8
Total_scans = 8
X_90_width = 13.5[us]
X_acq_time = 1.4548992[s]
X_angle = 45[deg]
X_atn = 2.9[dB]
X_pulse = 6.75[us]
Irr_mode = Off
Tri_mode = Off
Decpr_mode = Off
Decpr_pulse = FALSE
Initial_wait = 1[s]
Recyr_delay = 30
Relaxation_delay = 5[s]
Repetition_time = 6.4548992[s]
Temp_get = 20.6[dC]

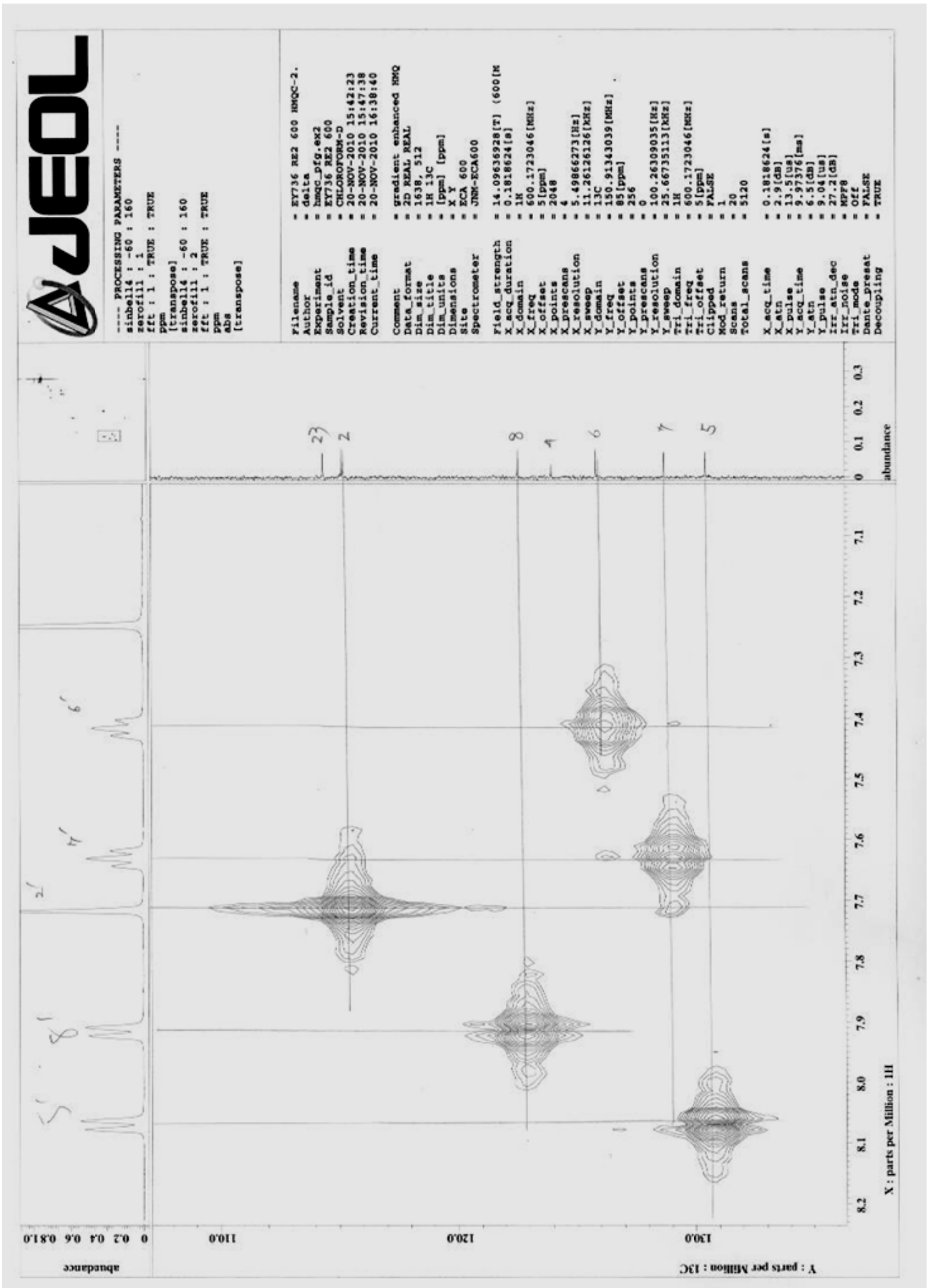

^{1}H NMR
authentic 11g
X : parts per Million : 1H
---- PROCESSING PARAMETERS ----
dc_balance : 0 : FALSE
sexp : 0.2[Hz] : 0.0[s]
trapezoid3 : 0[%] : 80[%] : 100[%]
zerofill : 1
fft : 1 : TRUE : TRUE
machinephase
ppm
Derived from: EY822-1.jdf
Filename = EY822-4.jdf
Author = delta
Experiment = single_pulse.ex2
Sample_id = EY822
Solvent = BENZENE-D6
Creation_time = 25-OCT-2010 19:08:47
Revision_time = 25-OCT-2010 19:18:21
Current_time = 25-OCT-2010 19:18:43
Comment = single_pulse
Data_format = 1D COMPLEX
Dim_size = 16384
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = ECA 600
Spectrometer = JNM-ECA600
Field_strength = 14.09636928[T] (600[M
X_acq_duration = 1.81993472[s]
X_domain = 1H
X_freq = 600.1723046[MHz]
X_offset = 5[ppm]
X_points = 16384
X_prescans = 1
X_resolution = 0.54947026[Hz]
X_sweep = 9.00252071[kHz]
Irr_domain = 1H
Irr_freq = 600.1723046[MHz]
Irr_offset = 5[ppm]
Tri_domain = 1H
Tri_freq = 600.1723046[MHz]
Tri_offset = 5[ppm]
Clipped = FALSE
Mod_return = 1
Scans = 8
Total_scans = 8
X_90_width = 13.5[us]
X_acq_time = 1.81993472[s]
X_angle = 45[deg]
X_atn = 2.9[dB]
X_pulse = 6.75[us]
Irr_mode = Off
Tri_mode = Off
Dante_presat = FALSE
Initial_wait = 1[s]
Recvr_gain = 48
Relaxation_delay = 5[s]
Repetition_time = 6.81993472[s]
Temp_get = 23.8[dC]


^{1}H NMR
9
abundance
X : parts per Million : 1H
---- PROCESSING PARAMETERS ----
dc_balance : 0 : FALSE
sexp : 0.2[Hz] : 0.0[s]
trapezoid3 : 0[%] : 80[%] : 100[%]
zerofill : 1
fft : 1 : TRUE : TRUE
machinephase
ppm
Derived from: EY736 RE2 600-1.jdf
Filename = EY736 RE2 600-3.jdf
Author = delta
Experiment = single_pulse.ex2
Sample_id = EY736 RE2 600
Solvent = CHLOROFORM-D
Creation_time = 20-NOV-2010 12:28:46
Revision_time = 20-NOV-2010 12:35:09
Current_time = 20-NOV-2010 12:36:27
Comment = single_pulse
Data_format = 1D COMPLEX
Dim_size = 13107
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = ECA 600
Spectrometer = JNM-ECA600
Field_strength = 14.09636928[T] (600[M
X_acq_duration = 1.4548992[s]
X_domain = 1H
X_freq = 600.1723046[MHz]
X_offset = 5[ppm]
X_points = 16384
X_prescans = 1
X_resolution = 0.68733284[Hz]
X_sweep = 11.26126126[kHz]
Irr_domain = 1H
Irr_freq = 600.1723046[MHz]
Irr_offset = 5[ppm]
Tri_domain = 1H
Tri_freq = 600.1723046[MHz]
Tri_offset = 5[ppm]
Clipped = FALSE
Mod_return = 1
Scans = 8
Total_scans = 8
X_90_width = 13.5[us]
X_acq_time = 1.4548992[s]
X_angle = 45[deg]
X_atn = 2.9[dB]
X_pulse = 6.75[us]
Irr_mode = Off
Tri_mode = Off
Dante_presat = FALSE
Initial_wait = 1[s]
Recvr_gain = 46
Relaxation_delay = 5[s]
Repetition_time = 6.4548992[s]
Temp_get = 21.9[dC]

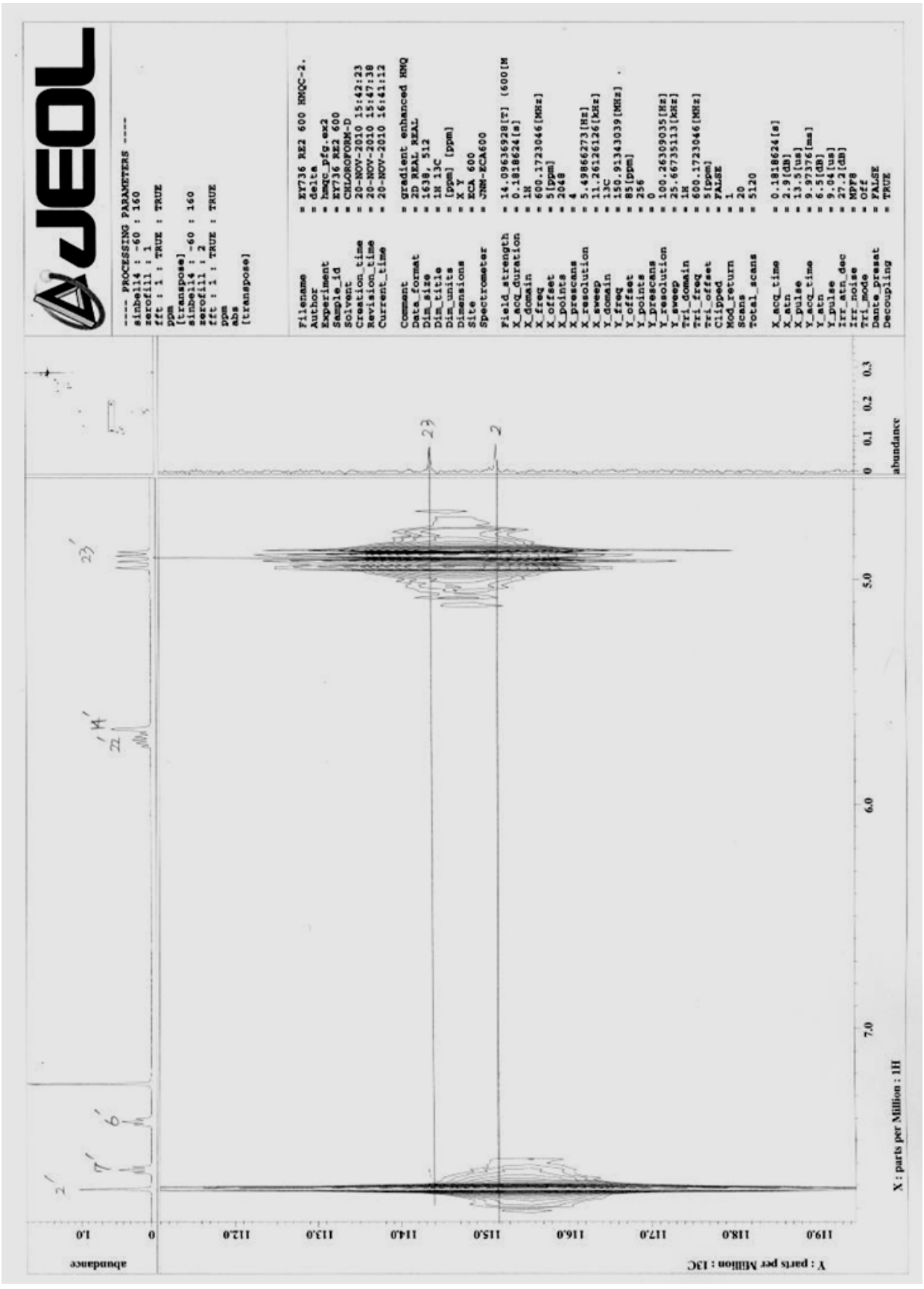
Overall picture of HMQC (compound 9)



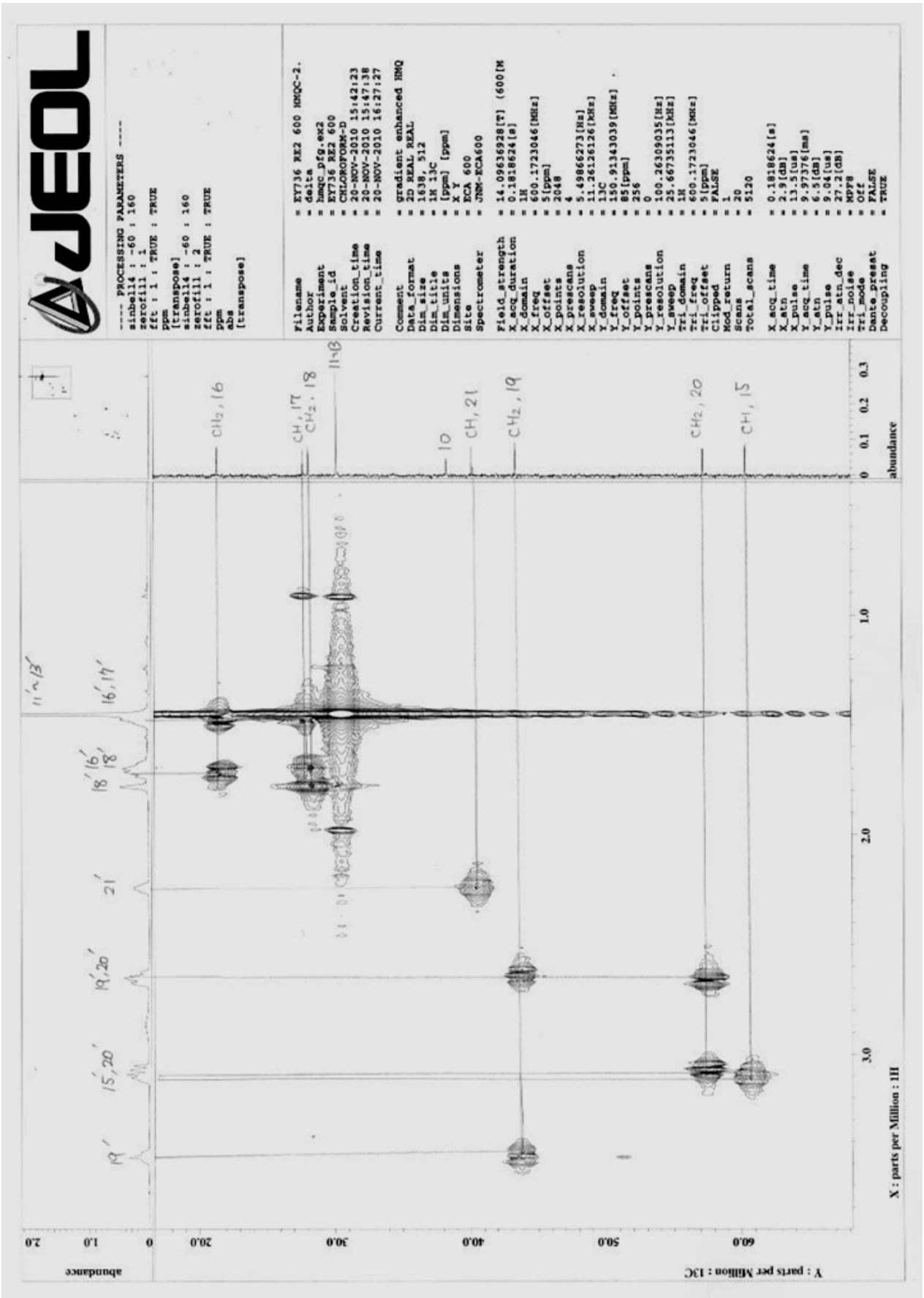
Expanded figure 1 of HMQC (compound 9)



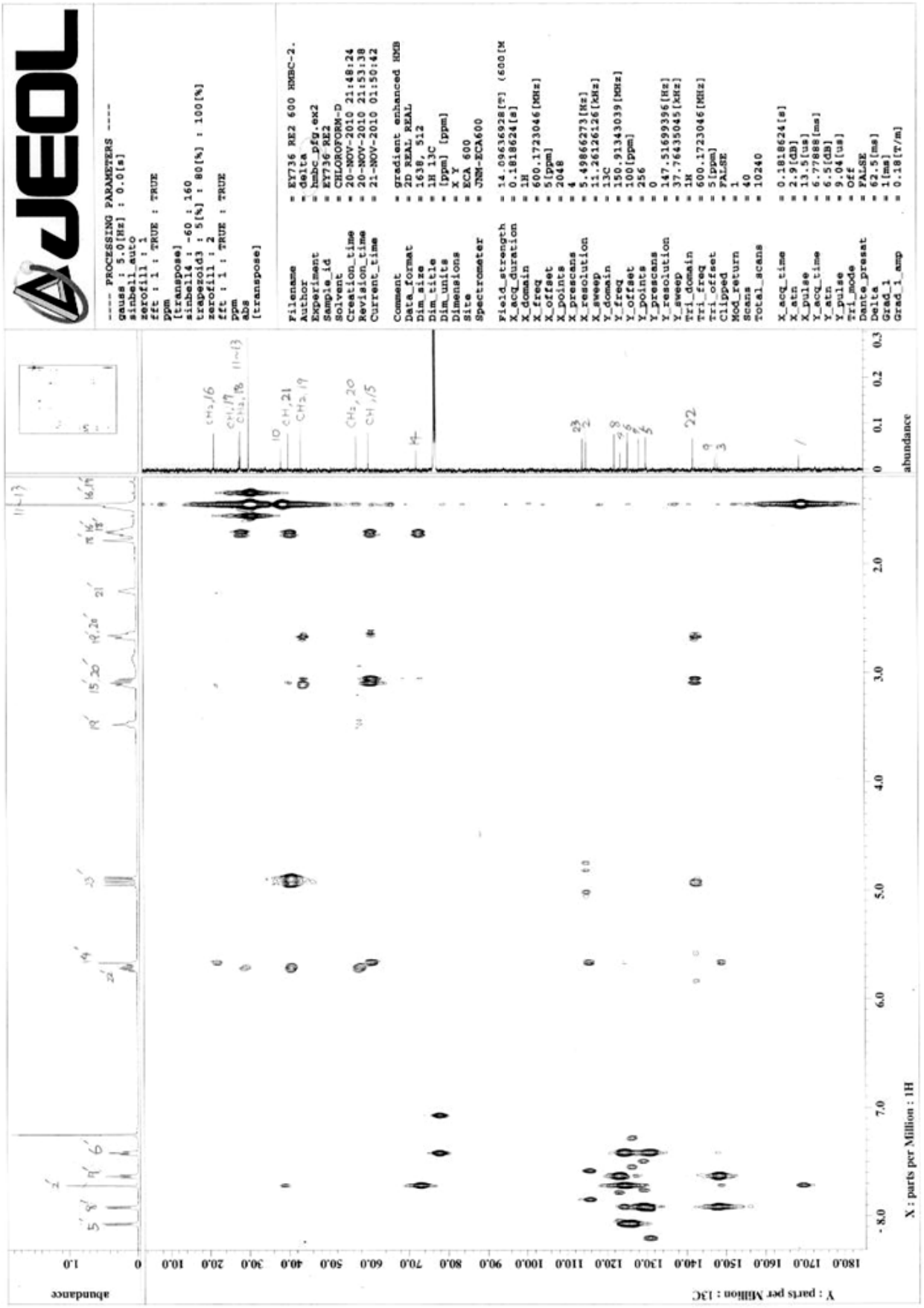
Expanded figure 2 of HMQC (compound 9)



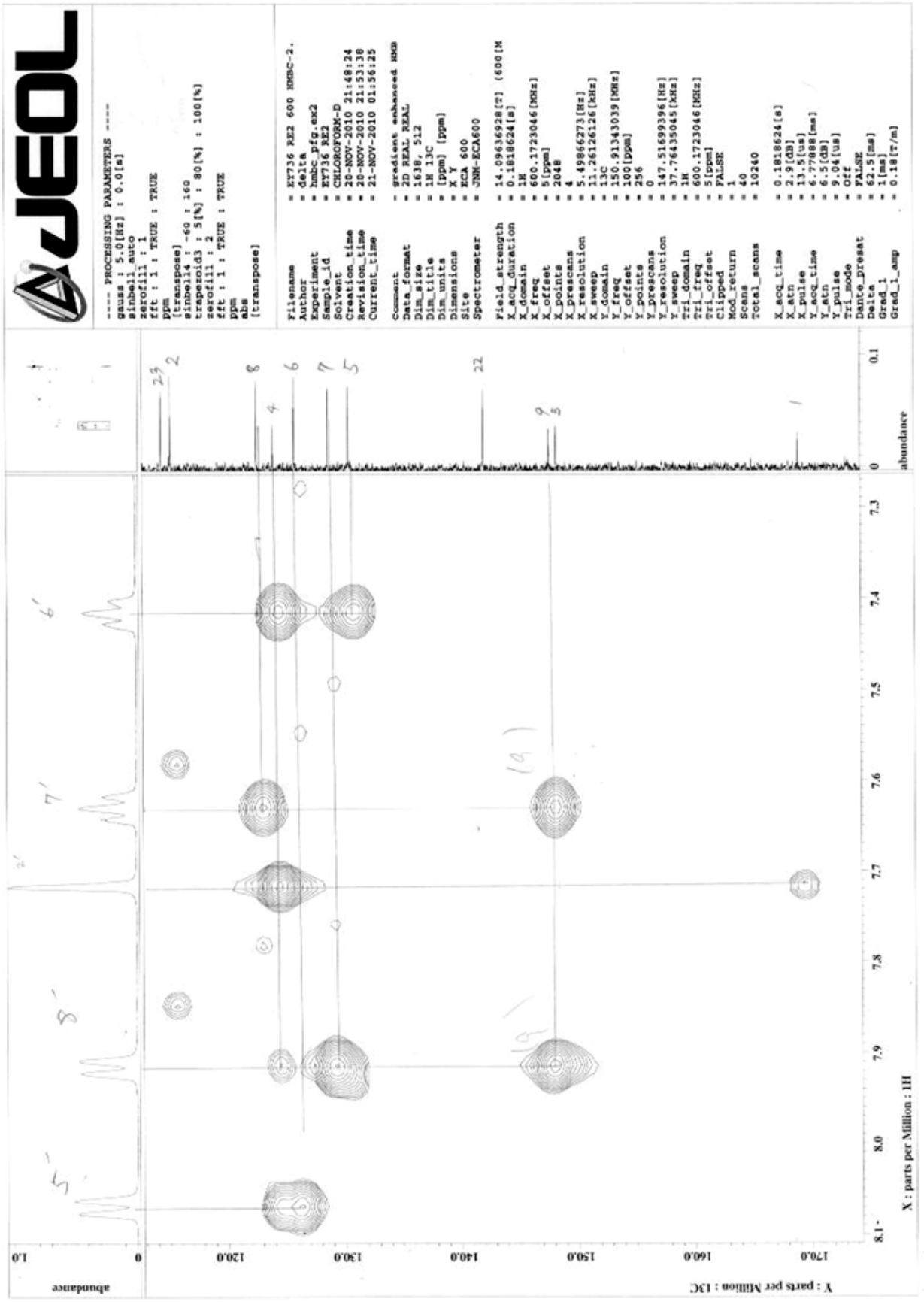
Expanded figure 3 of HMQC (compound 9)



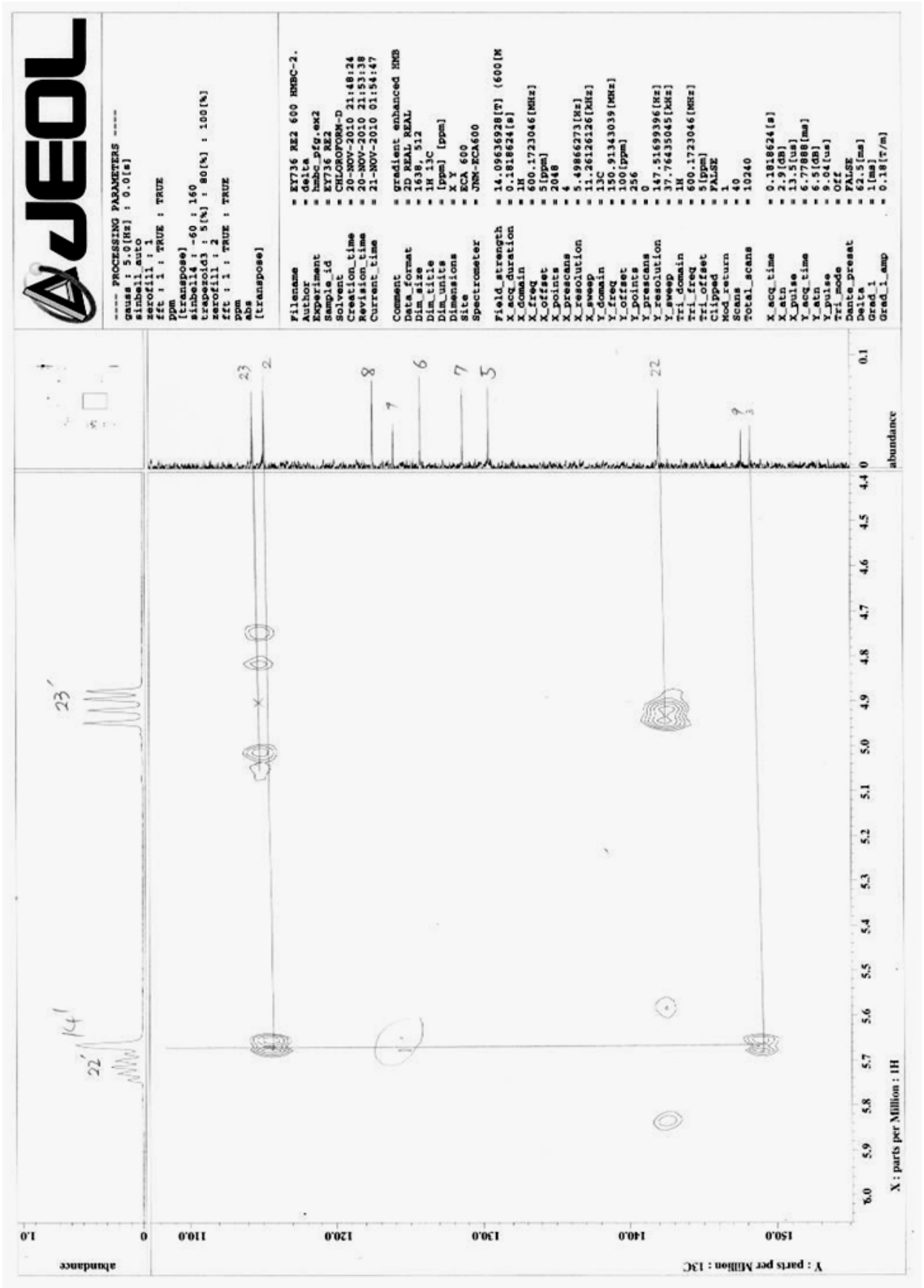
Overall picture of HMBC (compound 9)



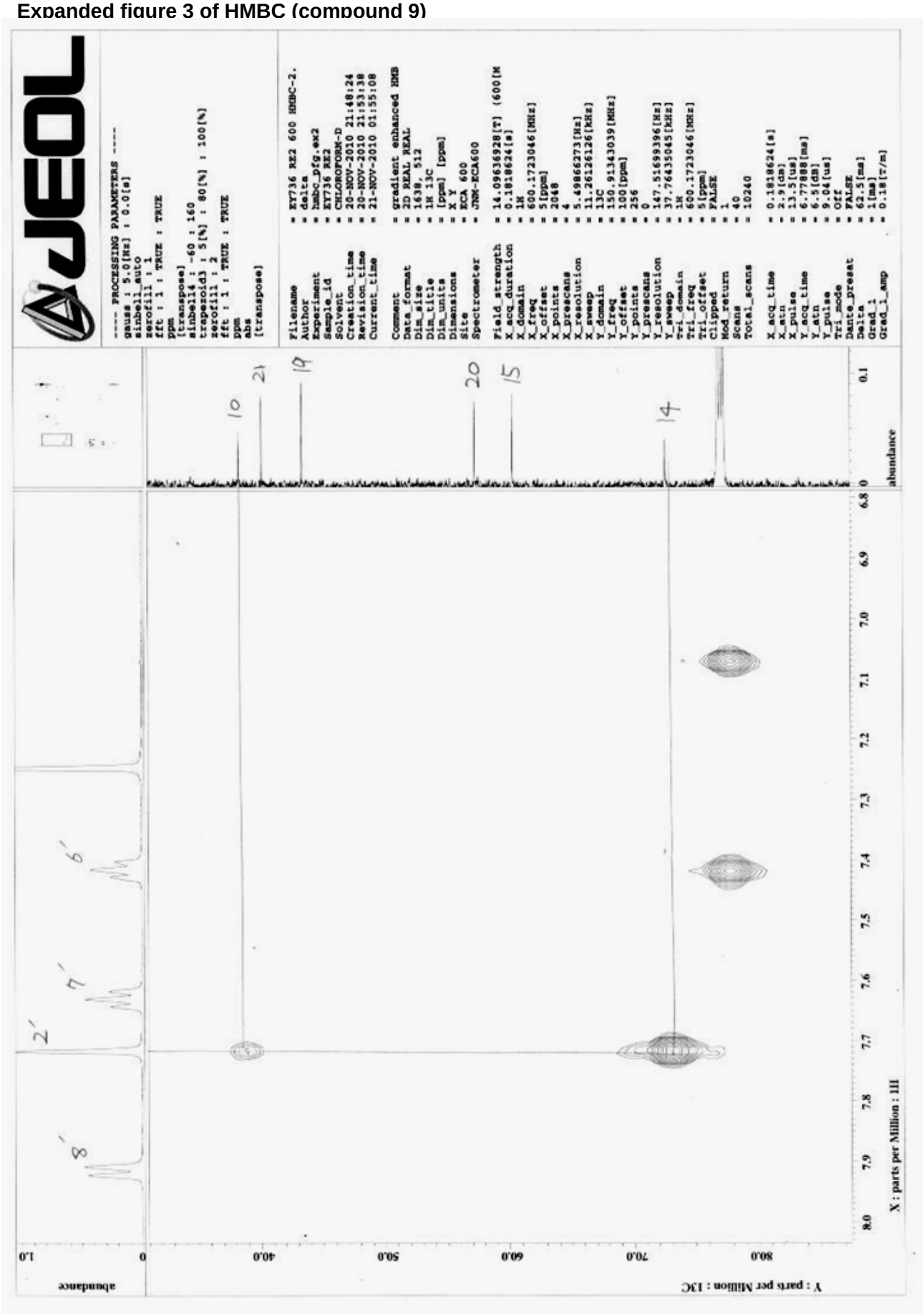
Expanded figure 1 of HMBC (compound 9)



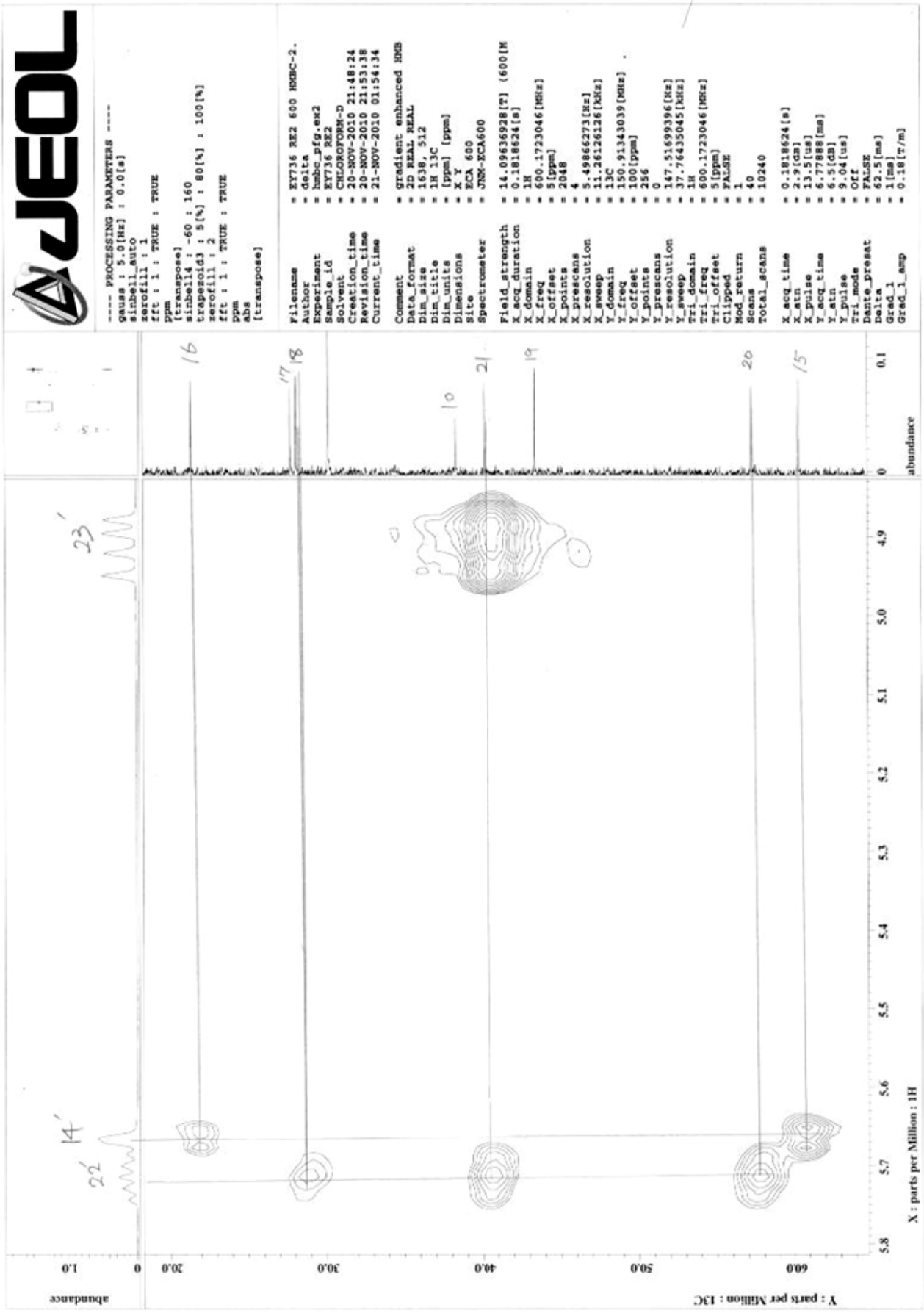
Expanded figure 2 of HMBC (compound 9)



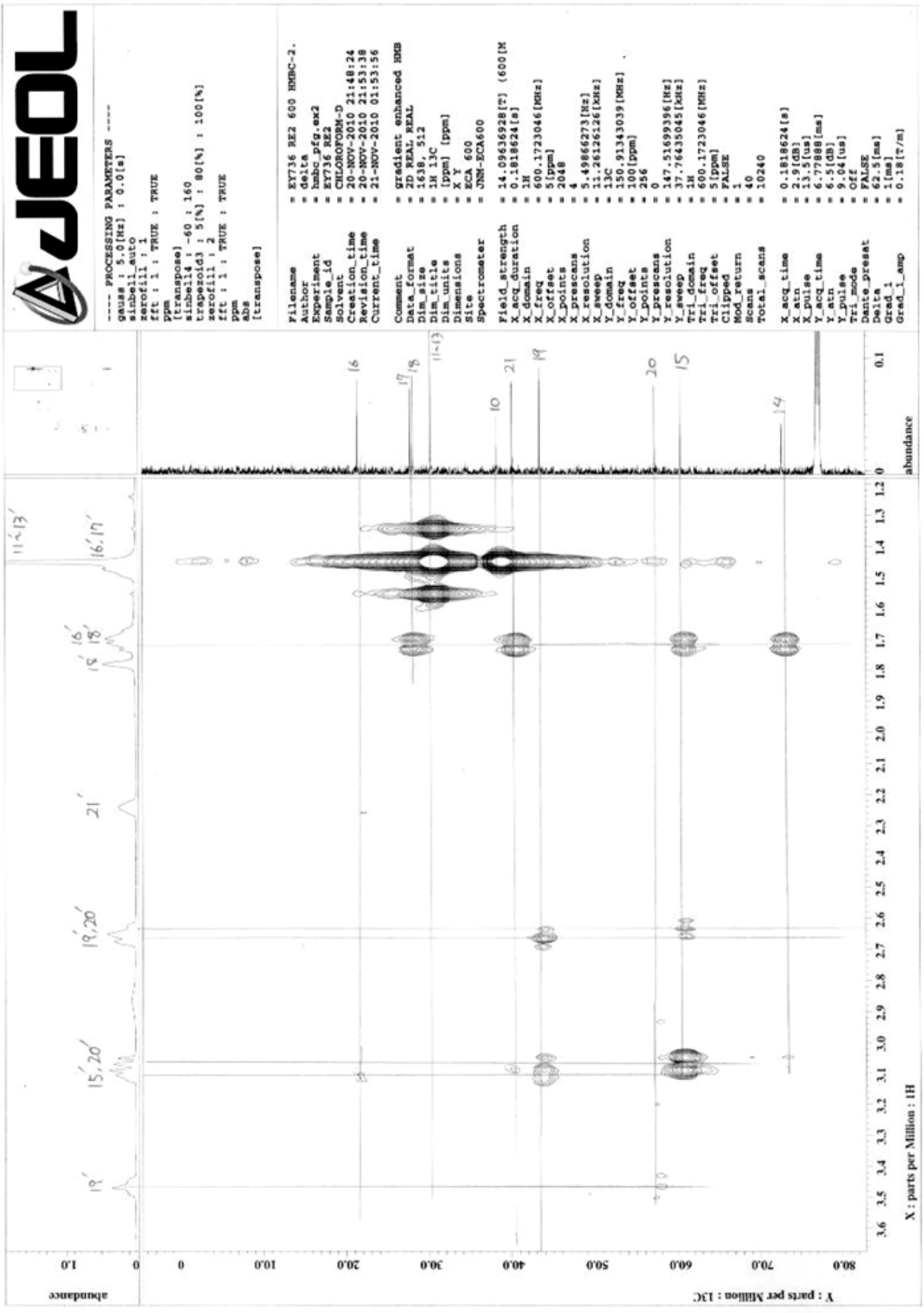
Expanded figure 3 of HMBC (compound 9)



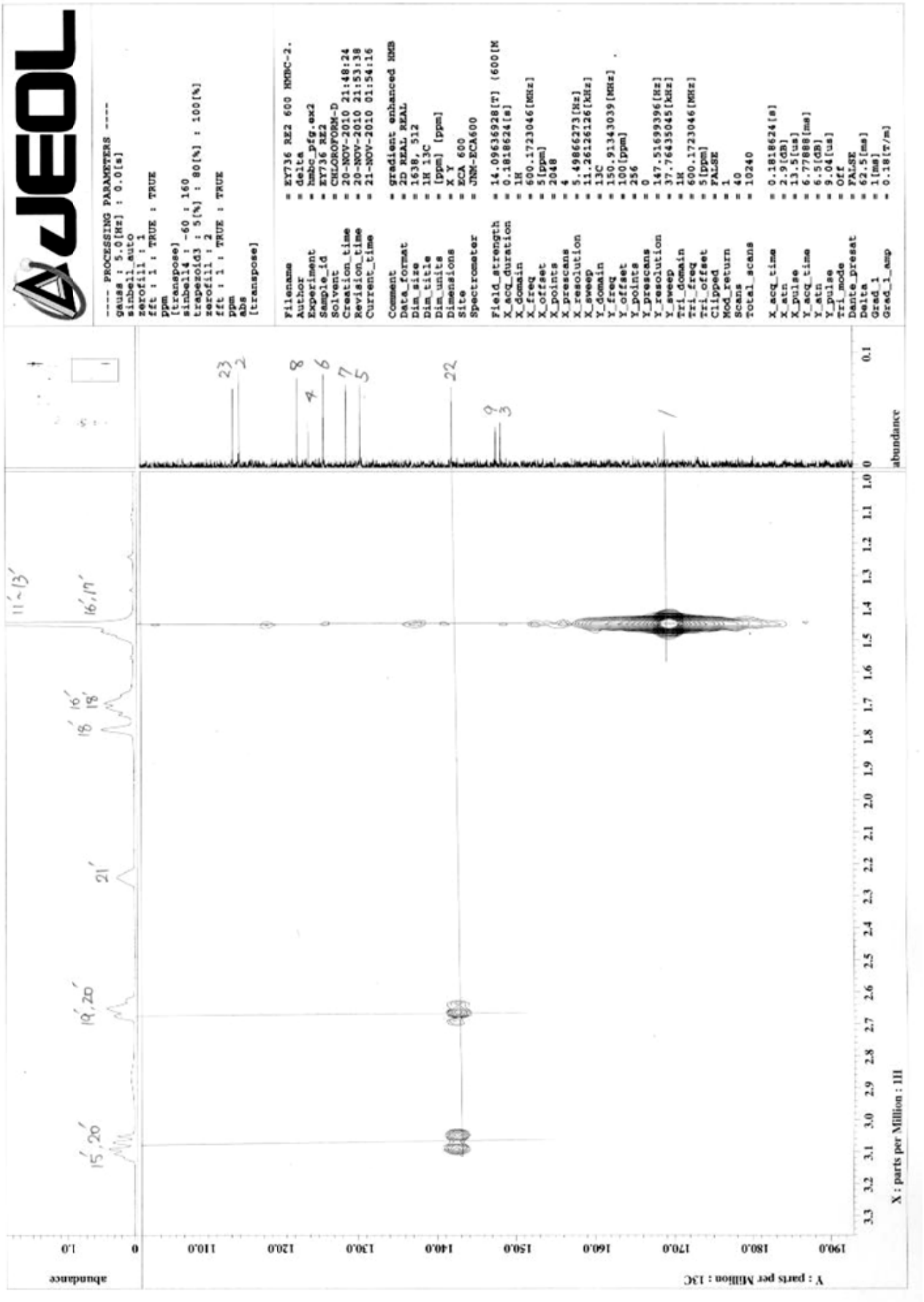
Expanded figure 4 of HMBC (compound 9)

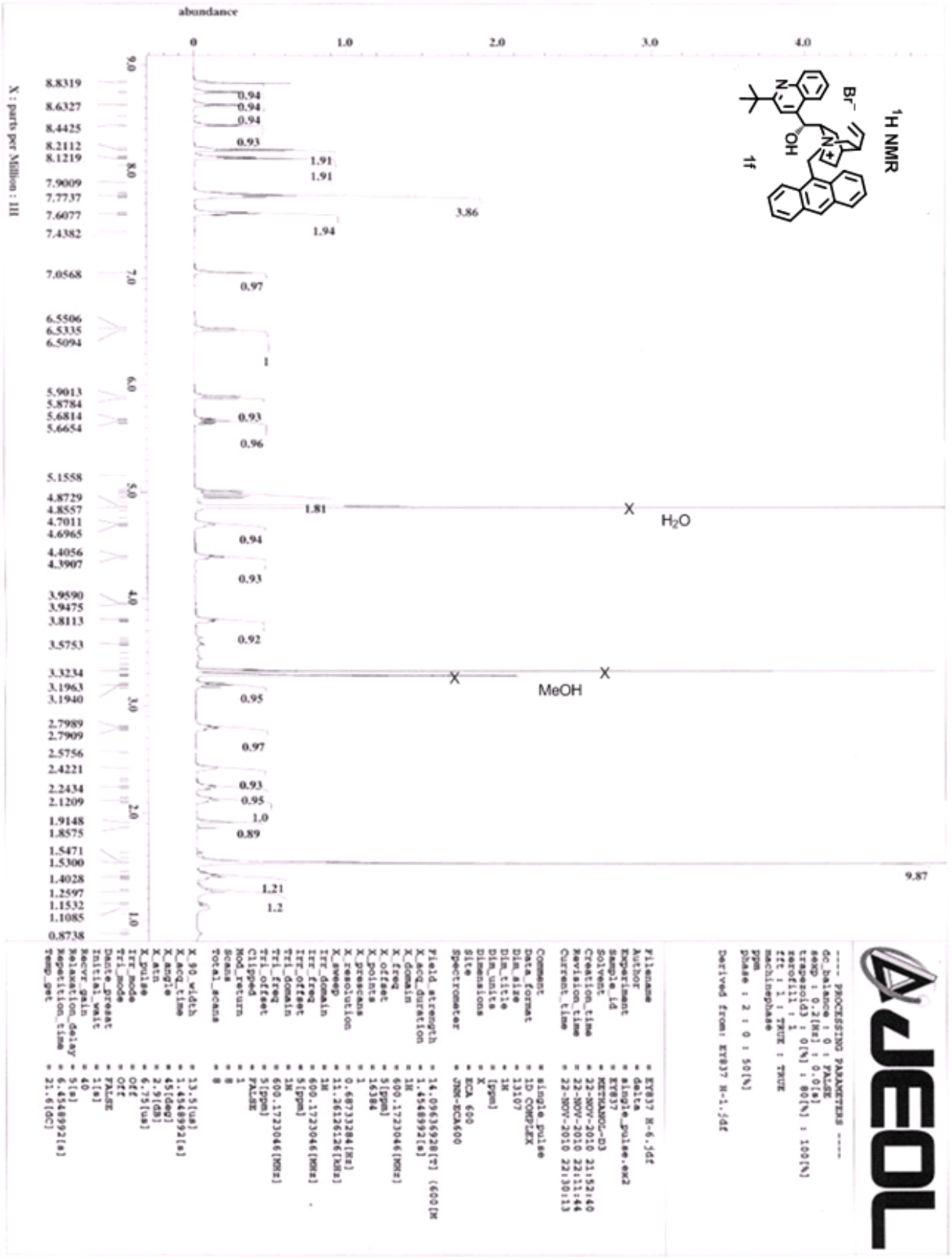


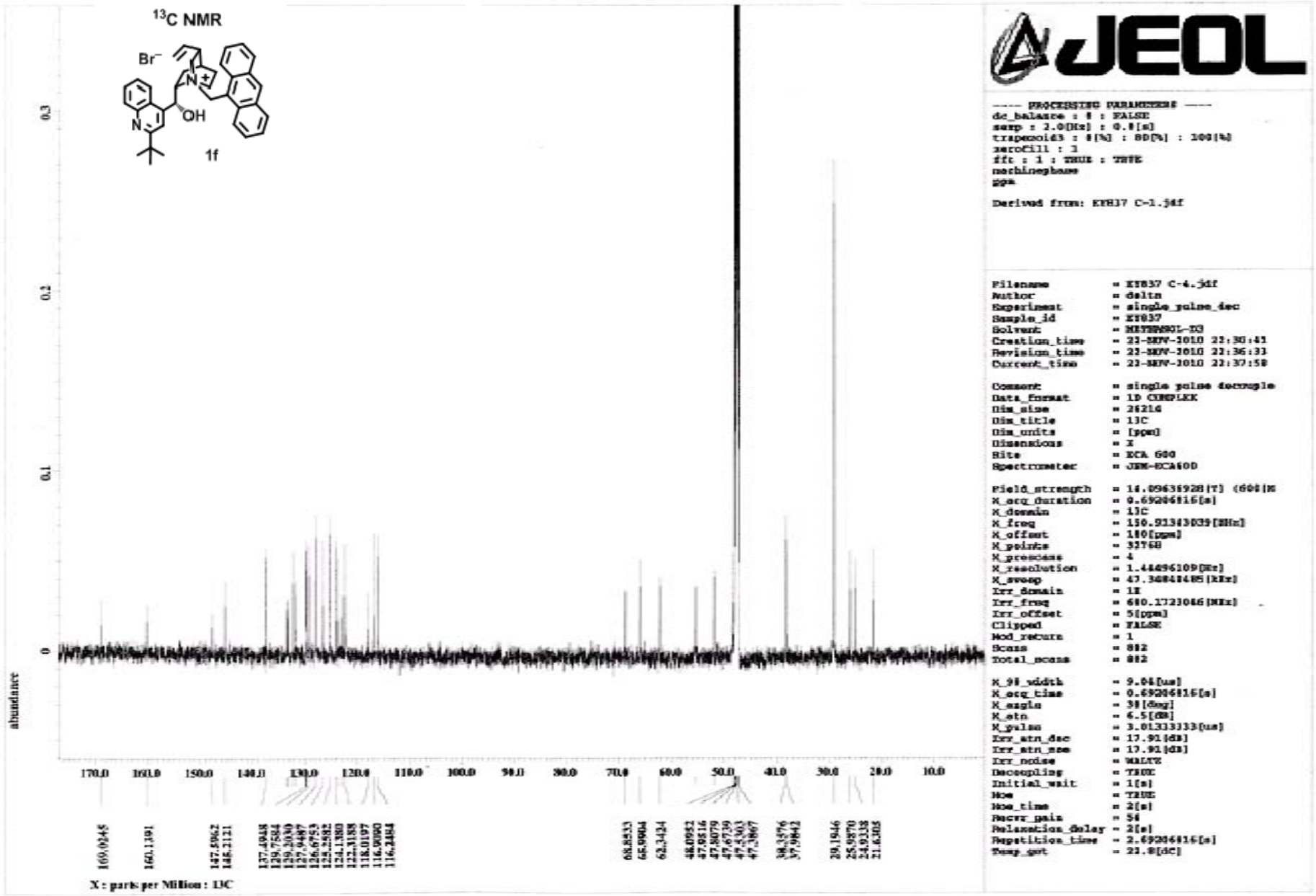
Expanded figure 5 of HMBC (compound 9)



Expanded figure 6 of HMBC (compound 9)




abundance
X : parts per Million : 111
^{1}H NMR
1f
Br⁻
OH
H_2O
MeOH
9.87


^{13}C NMR
Br⁻
OH
1f
abundance
0.3
0.2
0.1
0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
169.0245
160.1391
147.5962
146.2121
137.4948
129.7584
129.2049
127.9487
126.6753
125.2582
124.1380
122.3188
118.0197
116.0090
116.2484
68.8533
65.9904
62.3424
48.0952
47.8816
47.8079
47.6739
47.5403
47.3867
38.3576
37.9842
29.1946
25.9870
24.9338
21.6305
X : parts per Million : 13C
----- PROCESSING PARAMETERS -----
dc_balance : 0 : FALSE
sexp : 2.0[Hz] : 0.8[s]
trapezoid3 : 0[%] : 80[%] : 100[%]
zeroFill : 3
fft : 1 : TRUE : TRUE
machinephase
ppm
Derived from: KY837 C-1.jdf
Filename = KY837 C-4.jdf
Author = delta
Experiment = single_pulse_dec
Sample_id = KY837
Solvent = METHANOL-D3
Creation_time = 23-NOV-2010 22:30:41
Revision_time = 23-NOV-2010 22:36:33
Current_time = 23-NOV-2010 22:37:58
Comment = single pulse decouple
Data_format = 1D COMPLEX
Dim_size = 262144
Dim_title = 13C
Dim_units = [ppm]
Dimensions = X
Site = ECA 600
Spectrometer = JNM-ECA600
Field_strength = 14.09635928[T] (600[M
X_acq_duration = 0.69206816[s]
X_domain = 13C
X_freq = 150.91343039[MHz]
X_offset = 180[ppm]
X_points = 32768
X_prescans = 4
X_resolution = 1.44496109[Hz]
X_sweep = 47.36848485[kHz]
Irr_domain = 1H
Irr_freq = 600.1723046[MHz]
Irr_offset = 5[ppm]
Clipped = FALSE
Mod_return = 1
Scans = 832
Total_scans = 832
X_90_width = 9.04[us]
X_acq_time = 0.69206816[s]
X_angle = 30[deg]
X_atn = 6.5[dB]
X_pulse = 3.01333333[us]
Irr_atn_dec = 17.91[dB]
Irr_atn_one = 17.91[dB]
Irr_noise = WALTZ
Decoupling = TRUE
Initial_wait = 1[s]
Noe = TRUE
Noe_time = 2[s]
Recvr_gain = 56
Relaxation_delay = 2[s]
Repetition_time = 2.69206816[s]
Temp_get = 23.8[dC]