

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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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. ^1H and ^{13}C NMR spectra were recorded on a JEOL spectrometer ECS-400, ECS-600 and AL-400. Data for ^1H 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.

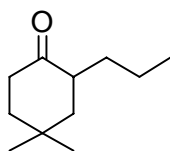
2. Material.

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 Armarego¹. 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-cycloheptanone⁴ (**3h**), 2-allyl-4,4-dimethyl-cyclohexanone⁵ and 2-cycloheptylidene-1,1-dimethylhydrazine⁶ were prepared according to the reported procedures.

3. Preparation and Characterization of enolesters

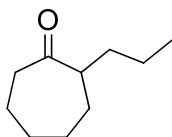
3-1. Synthesis of 2-substituted ketones

4,4-dimethyl-2-propylcyclohexanone⁷ (**3d**)



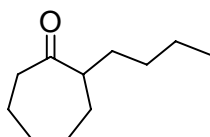
2-allyl-4,4-dimethylcyclohexanone (570 mg, 3.43 mmol, 1 equiv) in t butanol (3.43 mL) was placed in a glass tube with a magnetic stirring bar. $\text{RuCl}_2(\text{PPh}_3)_3$ (16.4 mg, 0.017 mmol, 0.5 mol%) was added and the tube was placed in an autoclave. Hydrogen was introduced into the autoclave at a pressure of 2 MPa after hydrogen replacement, then stirred for 11 h at 30 $^\circ\text{C}$. The resultant solution was purified by silica-gel column chromatography (Hexane : Et_2O = 10:1) to give **3d** (566 mg, 3.36 mmol, 98%) as yellow oil. ^1H 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 $\text{C}_{11}\text{H}_{20}\text{O}$: C, 78.51; H, 11.98. Found: C, 78.24; H, 11.98.

2-propylcycloheptanone⁸ (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 $-5\text{ }^{\circ}\text{C}$ 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 $0\text{ }^{\circ}\text{C}$. 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 $45\text{ }^{\circ}\text{C}$ 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 literature⁸. ^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 $\text{C}_{10}\text{H}_{18}\text{O}$: C, 77.87; H, 11.76. Found: C, 78.01; H, 11.83.

2-butylcycloheptanone^{9,10} (3g)



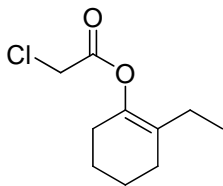
BuLi (1.67 M in hexane, 5.25 mmol, 3.14 mL, 1.05 equiv) was added dropwise to a stirred solution of 2-cycloheptylidene-1,1-dimethylhydrazine (771 mg, 5.0 mmol, 1 equiv) in THF (anhydrous, 20 mL) at $-5\text{ }^{\circ}\text{C}$ under a nitrogen atmosphere and stirred for 1 h. After that, butyl bromide (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 $0\text{ }^{\circ}\text{C}$. 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 $45\text{ }^{\circ}\text{C}$ 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 $\text{C}_{11}\text{H}_{20}\text{O}$: 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 $30\text{ }^{\circ}\text{C}$. 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)

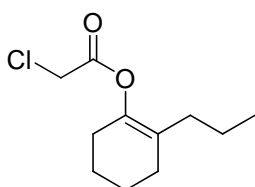
85% yield, yellow oil (4 equiv of 2-chloroacetic anhydride was used.)



$^1\text{H NMR}$ (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). $^{13}\text{C NMR}$ (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 $\text{C}_{10}\text{H}_{15}\text{ClO}_2$: C, 59.26; H, 7.46. Found: C, 59.49; H, 7.47.

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

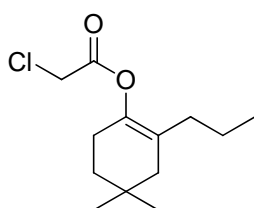
86% yield, yellow oil (2 equiv of chloroacetic anhydride was used.)



$^1\text{H NMR}$ (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, 7.4 Hz, 3 H). $^{13}\text{C NMR}$ (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 $\text{C}_{11}\text{H}_{17}\text{ClO}_2$: 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)

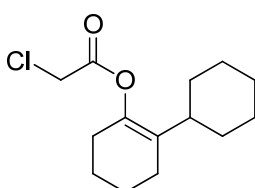
94 %yield, pale yellow oil (3 equiv of 2-chloroacetic anhydride was used.)



$^1\text{H NMR}$ (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). $^{13}\text{C NMR}$ (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 $\text{C}_{13}\text{H}_{21}\text{ClO}_2$: C, 63.79; H, 8.65. Found: C, 64.06; H, 8.79.

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

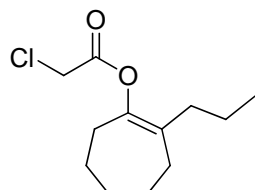
82% yield, yellow oil (2 equiv of chloroacetic anhydride was used.)



$^1\text{H NMR}$ (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). $^{13}\text{C NMR}$ (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 $\text{C}_{14}\text{H}_{21}\text{ClO}_2$: C, 65.49; H, 8.24. Found: C, 65.64; H, 8.29.

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

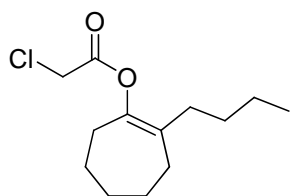
84% yield, pale yellow oil (4 equiv of chloroacetic anhydride was used.)



$^1\text{H NMR}$ (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). $^{13}\text{C NMR}$ (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 $\text{C}_{12}\text{H}_{19}\text{ClO}_2$: C, 62.47; H, 8.30. Found: C, 62.51; H, 8.26.

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

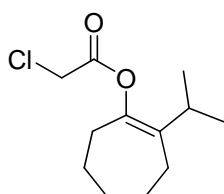
85% yield, pale yellow oil (4 equiv of chloroacetic anhydride was used.)



^1H 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 $\text{C}_{13}\text{H}_{21}\text{ClO}_2$: C, 63.79; H, 8.65. Found: C, 64.04; H, 8.62.

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

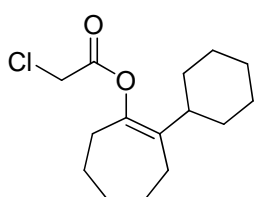
56% yield, yellow oil (2 equiv of chloroacetic anhydride was used.)



^1H 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 $\text{C}_{12}\text{H}_{19}\text{ClO}_2$: C, 62.47; H, 8.30. Found: C, 62.58; H, 8.28.

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

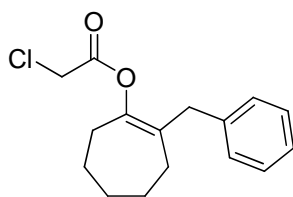
66% yield, yellow oil (2 equiv of chloroacetic anhydride was used.)



^1H 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 $\text{C}_{15}\text{H}_{23}\text{ClO}_2$: C, 66.53; H, 8.56. Found: C, 66.70; H, 8.59.

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

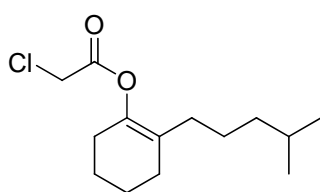
96% yield, pale yellow oil (5 equiv of chloroacetic anhydride was used.)



^1H 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 $\text{C}_{16}\text{H}_{19}\text{ClO}_2$: 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)



^1H 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 $\text{C}_{14}\text{H}_{23}\text{ClO}_2$: C, 64.98; H, 8.96. Found: C, 61.12; H, 7.89.

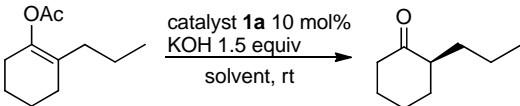
4. General procedure for asymmetric hydrolysis of enolesters catalyzed by PTC

Procedures: A typical experimental procedure for asymmetric hydrolysis of enolesters is described below. A round-bottomed screw cap tube ($\phi 13 \times 100$ 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 $^\circ\text{C}$ 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 $^\circ\text{C}$. 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 chromatography 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 $^\circ\text{C}$, detector 240 $^\circ\text{C}$, oven 40-180 $^\circ\text{C}$, program 3 $^\circ\text{C}/\text{min}$, $t_{\text{major}} = 34.7$ min, $t_{\text{minor}} = 35.6$ min). In case of 1 or 2 mmol-scale and 5 mmol-scale reaction, 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



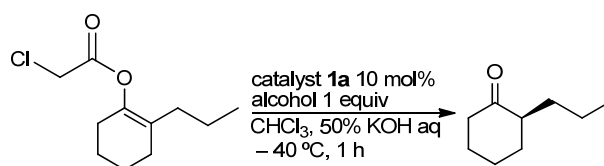
entry	time (h)	solvent	yield (%) ^{a)}	er
1	1	toluene	20	70:30
2	14	toluene	65	64:36
3	1	CHCl_3 ^{b)}	10	79:21

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 CHCl₃ (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 ₃ C-CH ₂ -OH	73	89:11
3	EtOH	66	87:13	8	F-CH ₂ -CH ₂ -OH	42	87:13
4	<i>i</i> PrOH	44	84:16	9	Cl-CH ₂ -CH ₂ -OH	48	90:10
5	<i>t</i> BuOH	2	76:24	10	Br-CH ₂ -CH ₂ -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)}
	0		99
	99	Substrate	0
	88		

a) GC yield.

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

Reaction in homogenous system (CHCl₃): *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 CHCl₃ (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 (CHCl₃/H₂O): *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 °C. The resultant dried residue in 1-neck recovery flask (50 mL) was dissolved with CHCl₃ (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 °C. The resultant dried residue was dissolved with CHCl₃ (0.5 mL) and removed repeatedly. Then the dried residue was further dried in vacuo for 15 min at 0 °C. Then, CHCl₃ (400 μL) and distilled water (100 μL) was added to the residue. The mixture was stirred for 2 min at 25 °C. 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).

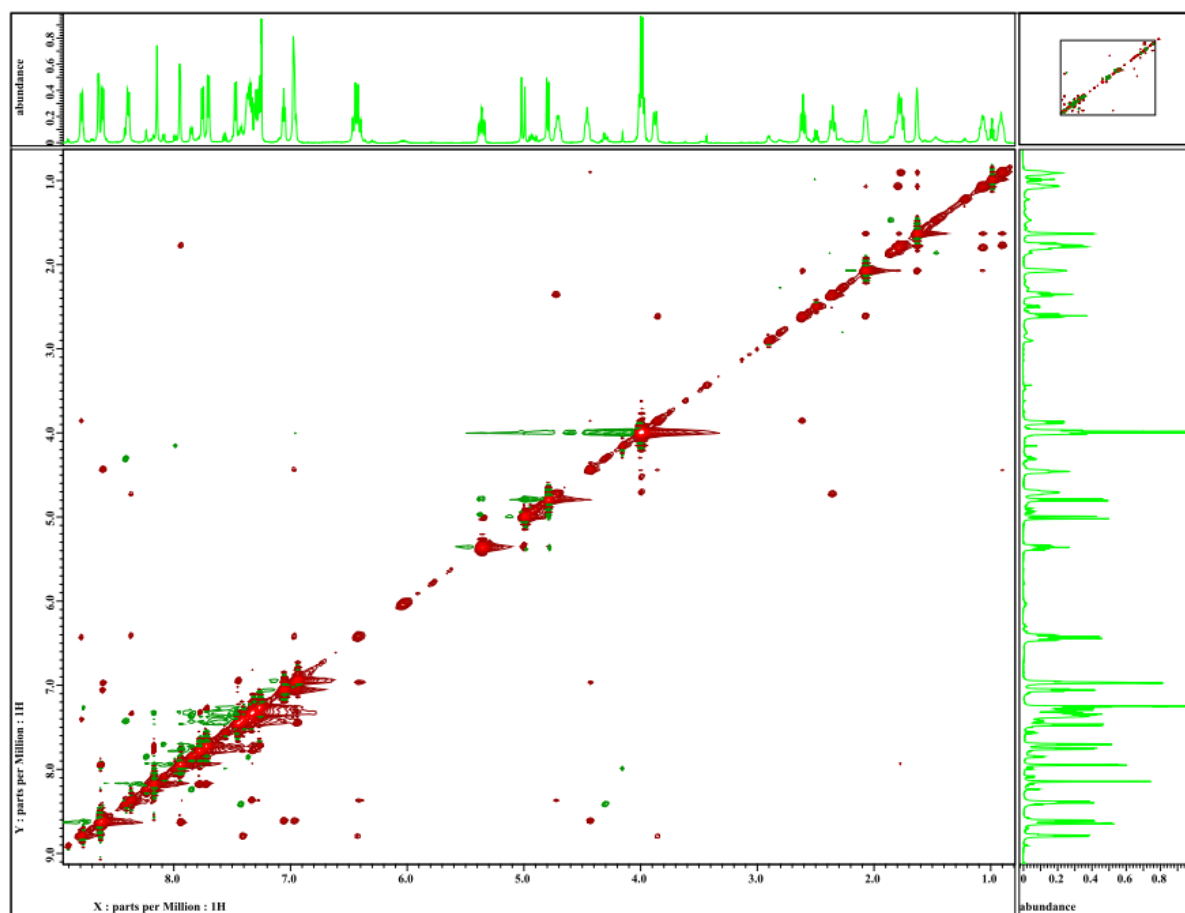
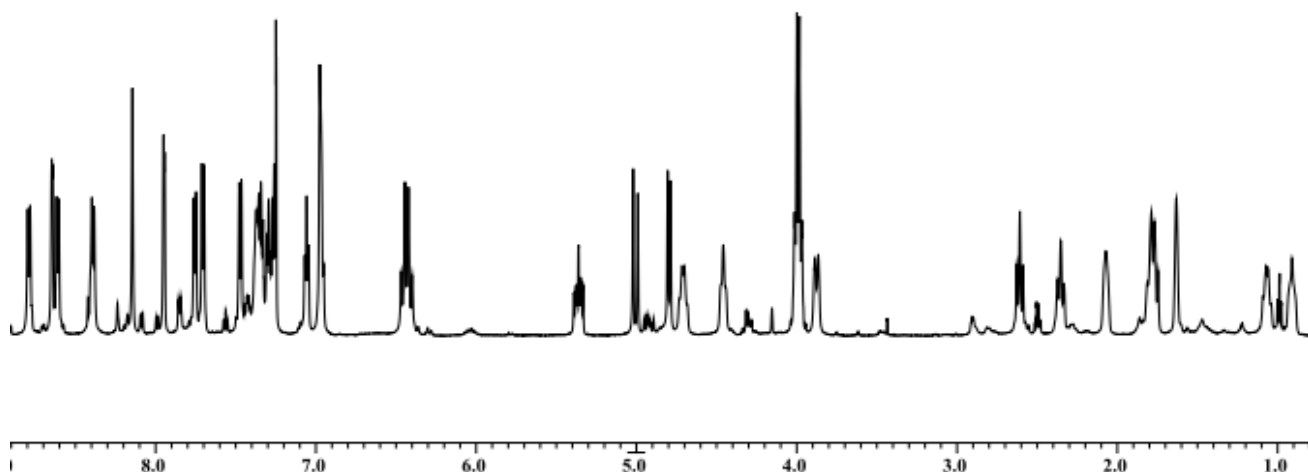
6-4. Asymmetric hydrolysis of enolesters with the in situ generated stoichiometric Q⁺CF₃CH₂O⁻ reagent.

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 CHCl₃ 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 CHCl₃ (400 μL), distilled water (100 μL). Then the mixture was stirred for 2 min at 25 °C. 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).

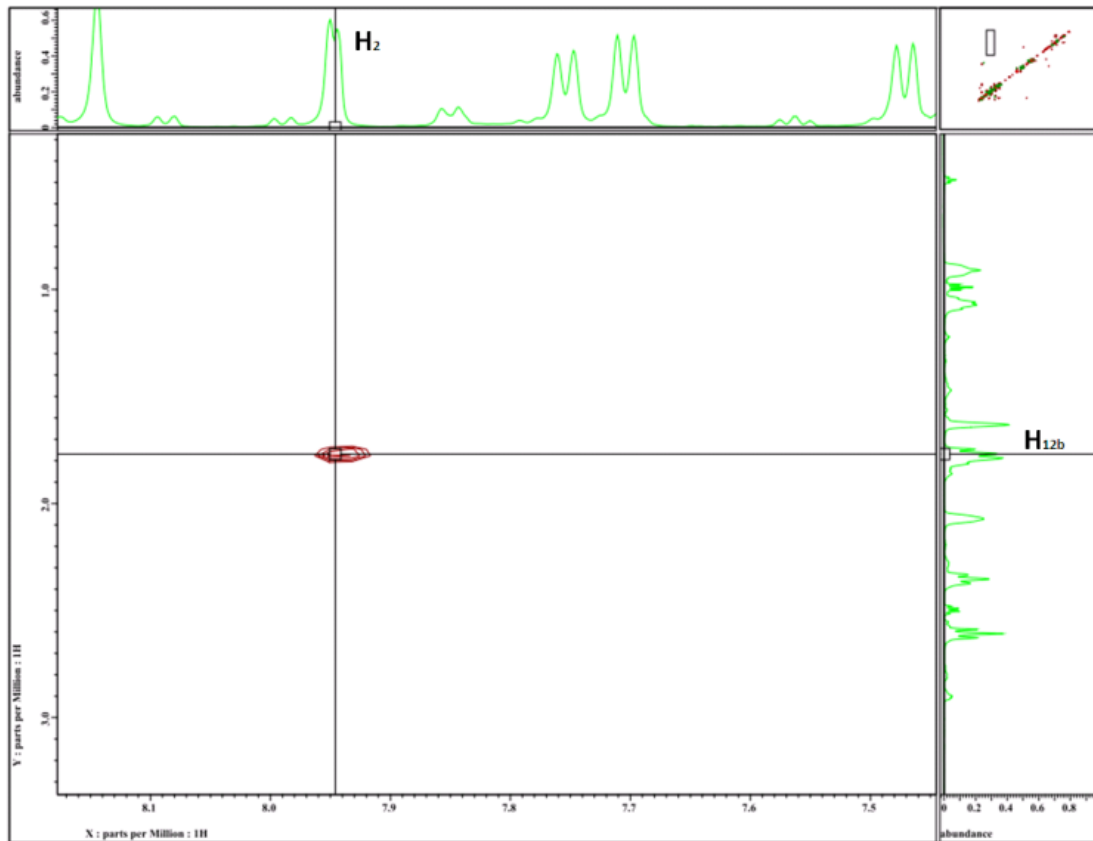
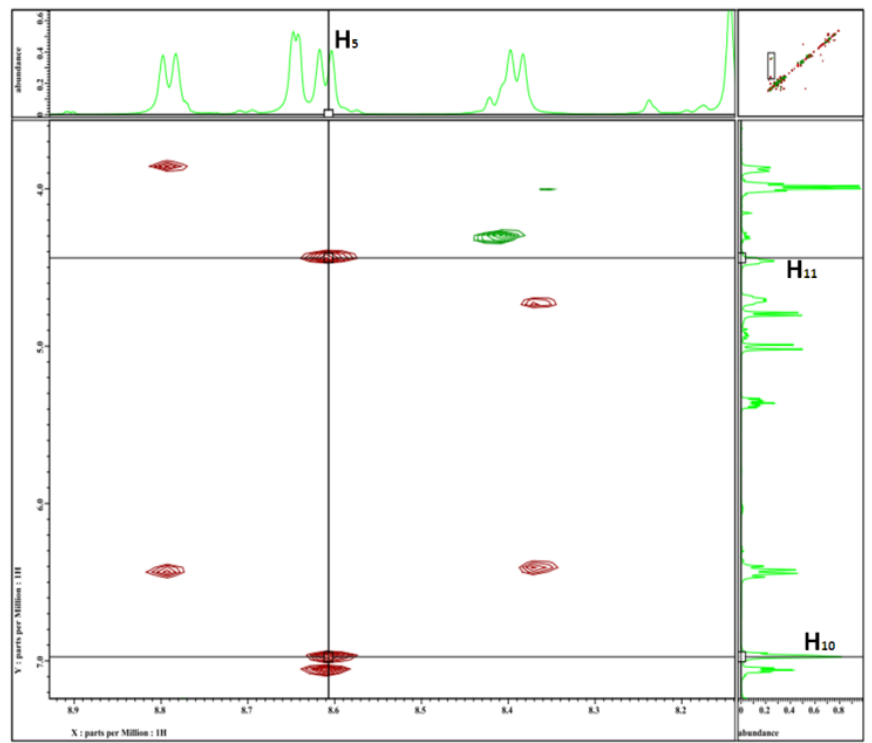
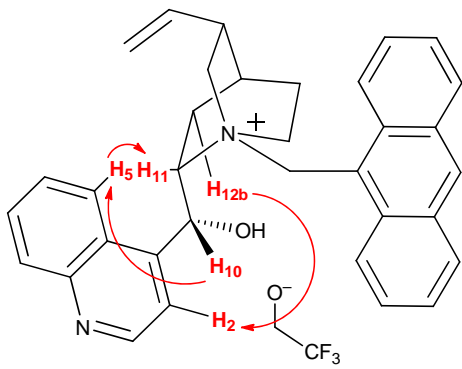
6-5. Preparation method for a sample of NOE experiment of *N*-9-anthracenylmethyl cinchonidinium 2,2,2-trifluoroethanoxide.

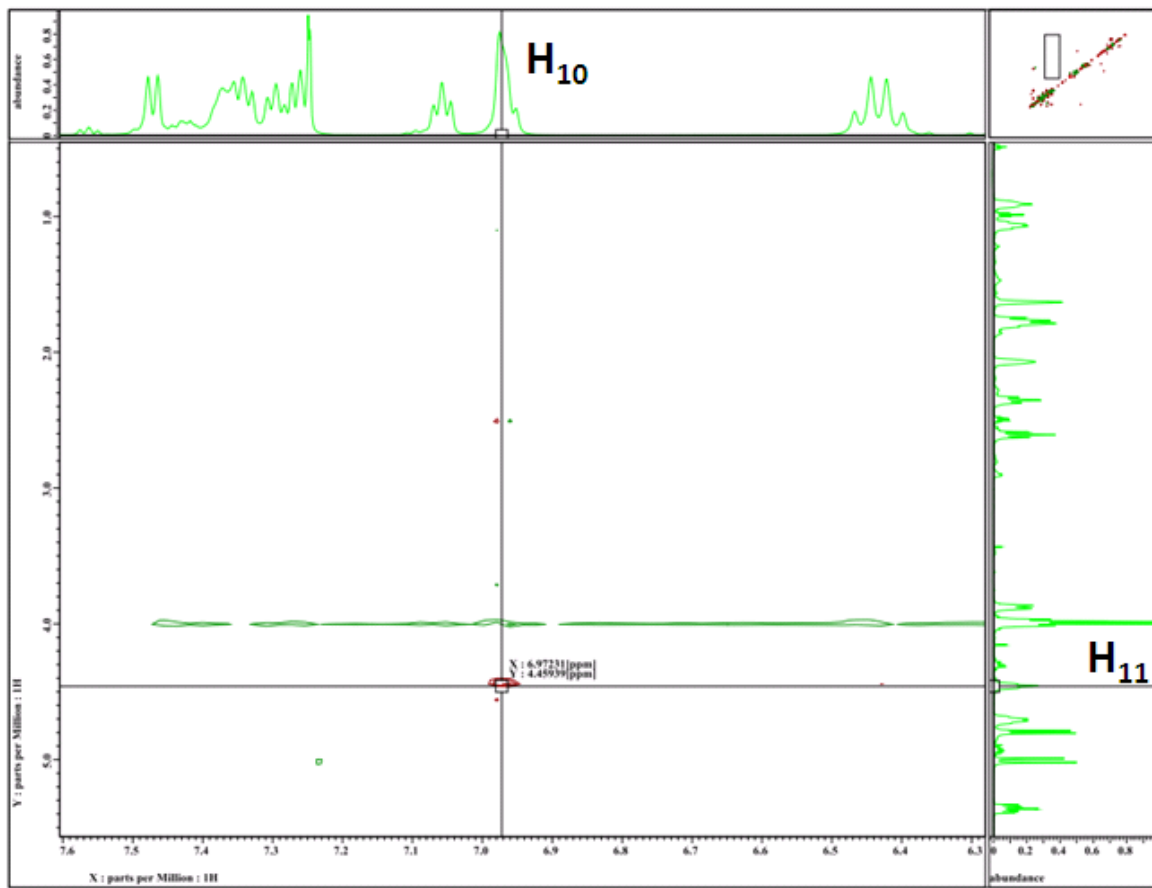
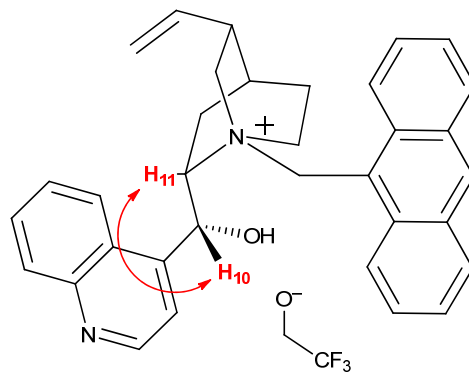
N-9-anthracenylmethyl cinchonidinium chloride (130 mg, 0.25 mmol, 1 equiv) in MeOH solution was passed through a column filled with an anion exchange resin, Amberlyst A-26 OH form (10 meq). 2, 2, 2-Trifluoroethanol (125 mg, 1.25 mmol, 90 μL, 5 equiv) was added to the eluate and stirred for 15 min. The solvent was removed under reduced pressure, then added CDCl₃ (0.5 mL) and removed the solvent again. After that, CDCl₃ (1.0 mL) was added to the residue and 600 μL of the solution was transferred to a NMR tube. D₂O (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. ¹H NMR (600 MHz, CDCl₃): δ = 8.79 (d, *J* = 8.9 Hz, 1 H, H₁₉), 8.64 (d, *J* = 3.4 Hz, 1 H, H₁), 8.61 (d, *J* = 8.3 Hz, 1 H, H₅), 8.39 (d, *J* = 8.9 Hz, 1 H, H₂₉), 8.14 (s, 1 H, H₂₄), 7.95 (d, *J* = 3.4 Hz, 1 H, H₂), 7.75 (d, 8.2 Hz, 1 H, H₂₂), 7.70 (d, *J* = 8.2 Hz, 1 H, H₂₆), 7.47 (d, *J* = 8.3 Hz, 1 H, H₈), 7.40-7.28 (m, 3 H, H₂₀ + H₂₁ + H₂₈), 7.28-7.23 (m, 1 H, H₂₇), 7.06 (t, *J* = 6.8 Hz, 1H, H₆), 6.99-6.94 (m, 1 H, H₇), 6.98 (s, 1H, H₁₀), 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, H₃₃), 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, H₁₁), 4.05-3.93 (m, 3.1H, H₃₅ + 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, H₃₁), 1.90-1.72 (m, 2 H, H_{14b} + H_{12b}), 1.66-1.61 (m, 1H, H₁₃), 1.11-1.02 (m, 1 H, H_{14a}), 0.95-0.87 (m, 1 H, H_{12a}).

^1H and 2D-NOESY chart

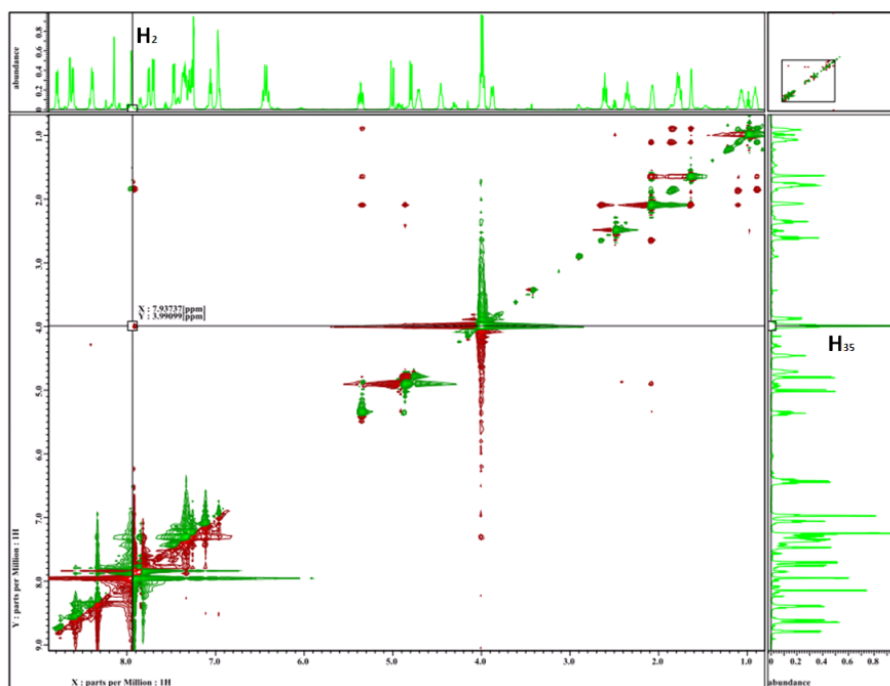


Green: negative, Red: positive





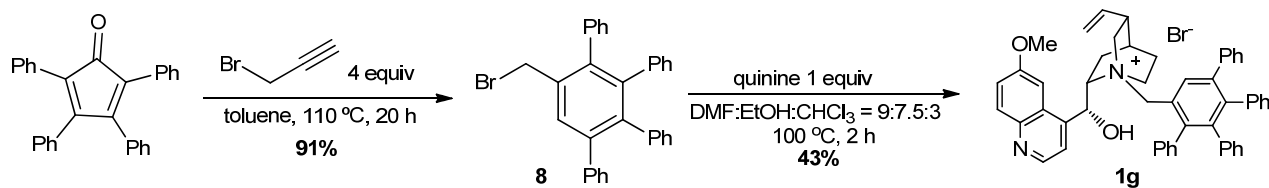
2d-ROESY Chart



Green: negative, Red: positive

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

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



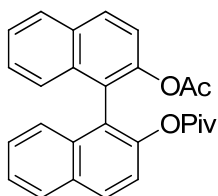
Synthesis of 1-bromomethyl-2,3,4,5-tetraphenyl benzene (**8**)

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. ¹H NMR (600 MHz, CDCl₃): 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). ¹³C NMR (150 MHz, CDCl₃): 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 C₃₁H₂₃Br: 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:CHCl₃ (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. ¹H NMR (400 MHz, CD₃OD) 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). ¹³C NMR (100 MHz, CDCl₃): 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 C₅₁H₄₇N₂O₂ 719.3632 found 719.3641 [M-Br]

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

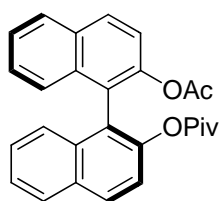


To a mixture of 2'-hydroxy-[1,1'-binaphthalen]-2-yl pivalate (1.14 g, 4.0 mmol) and acetyl chloride (310 μL, 4.4 mmol) in CH₂Cl₂ (10 mL) was added Et₃N (610 μL, 4.4 mmol) at 0 °C and the mixture was stirred at RT for 20 h. The reaction was quenched by adding HCl (1N, 30 mL) and extracted with AcOEt. 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. ¹H 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 C₂₇H₂₄O₄: C 78.62, H 5.86; found: C 78.60, H 5.86.

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

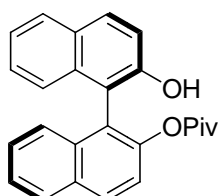
A mixture of the catalyst **1g** (0.01 mmol, 10 mol%) and 1N K₂CO₃ aq (200 μL, 0.2 mmol, 2 equiv) in toluene (200 μL) was stirred at 20 °C. After 20 min, the *rac*-**7** (0.1 mmol, 1 equiv) was added and the mixture was stirred at the same temperature. Silica-gel column chromatography (Hexane: CHCl₃: Et₂O = 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**: [α]_D^{25.5} = + 35.1, (*c* 0.5, CHCl₃), (*R*)-**8**: [α]_D^{24.5} = - 3.63, (*c* 1.0, CHCl₃). *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



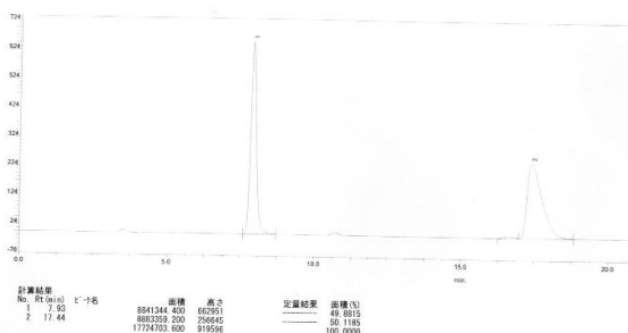
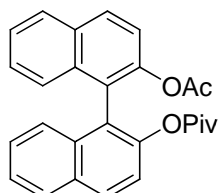
^1H NMR (600 MHz, CDCl_3) δ = 7.99-7.95 (m, 1 H), 7.93-7.89 (m, 1 H), 7.46-7.37 (m, 4 H), 7.31-7.22 (m, 6 H), 1.76 (s, 3 H), 0.76 (s, 9 H). ^{13}C -NMR (100 MHz, CDCl_3) δ = 176.6, 169.2, 147.0, 146.9, 133.5, 133.4, 131.6, 131.5, 129.5, 129.4, 128.1, 128.0, 126.8 (2 carbons), 126.2, 126.1, 125.8, 125.7, 123.7, 123.6, 122.0, 121.9, 38.8, 26.5 (3 carbons), 20.6. elemental analysis calcd (%) for $\text{C}_{27}\text{H}_{24}\text{O}_4$: C 78.62, H 5.86; found: C 78.60, H 5.86.

Product (*R*)-8

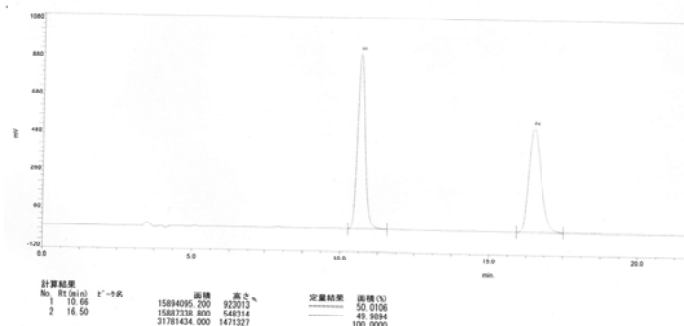
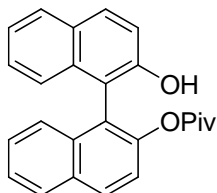


^1H and ^{13}C NMR were in agreement with the literature¹¹. ^1H NMR (400 MHz, CDCl_3) δ = 8.06 (d, J = 6.0 Hz, 1 H), 7.97 (d, J = 5.5 Hz, 1 H), 7.87 (d, J = 6.0 Hz, 1 H), 7.81 (d, J = 5.5 Hz, 1H), 7.50(t, J = 5.5 Hz, 1H), 7.39-7.28 (m, 5H), 7.26-7.21 (m, 1 H), 7.05 (d, J = 5.5 Hz, 1 H), 5.14 (s, 1 H), 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 $\text{C}_{25}\text{H}_{22}\text{O}_3$: C, 81.06; H, 5.99; found: C, 81.11, H, 5.99.

HPLC chart of *rac*-7



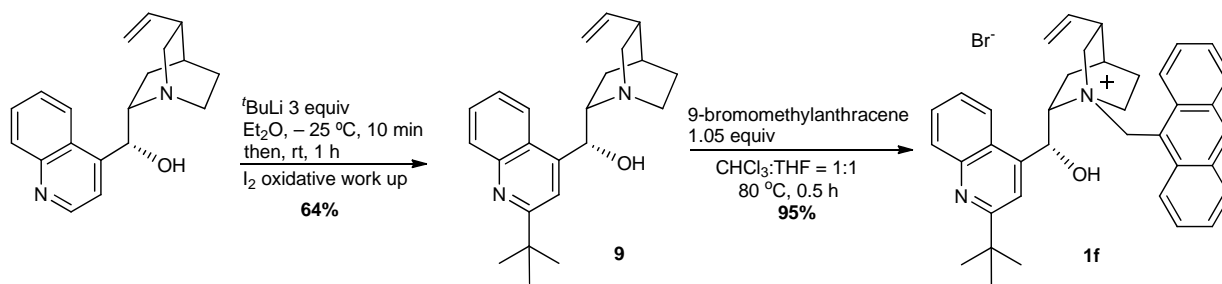
HPLC chart of *rac*-8



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

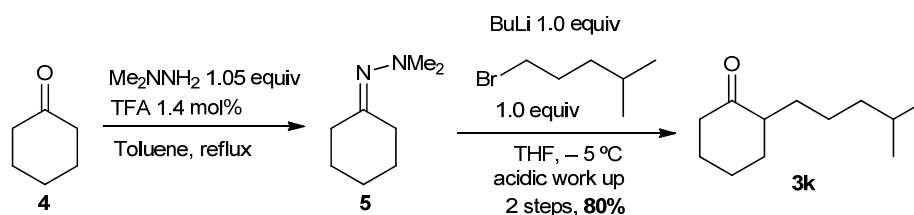
To the stirred solution of (–)-cinchonidine (883 mg, 3 mmol, 1 equiv) in dry Et_2O (15 mL) at $-25\text{ }^\circ\text{C}$ was added $t\text{-BuLi}$ (1.57M in pentane, 5.73 mL, 9 mmol, 3 equiv) in one portion and stirred for 10 min. Then, the reaction mixture was allowed to warm up to RT and stirred for another 1 h. Reaction was monitored by TLC analysis (toluene:MeOH:Et₃N = 10:1:1, $t\text{-Bu}$ 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, $\text{Na}_2\text{S}_2\text{O}_3$ 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:Et₃N = 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 ($\text{CH}_2\text{Cl}_2:\text{MeOH} = 4:1$)

^1H NMR (400 MHz, CDCl_3): $\delta = 8.07$ (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): $\delta = 169.0, 148.3, 147.7, 142.0, 130.4, 128.7, 125.9, 123.9, 122.6, 115.2, 114.4, 72.4, 60.3, 57.2, 43.4, 40.1, 38.3, 30.2$ (3 carbons), 28.1, 27.7, 21.4. FABMS m/z calculated for $\text{C}_{23}\text{H}_{30}\text{N}_2\text{O}$ 351.24 found 351.29 [M+H] Anal. Calcd (%) for $\text{C}_{23}\text{H}_{30}\text{N}_2\text{O}$: C, 78.82; H, 8.63; N, 7.99 Found: C, 78.38; H, 8.63; N; 7.89.

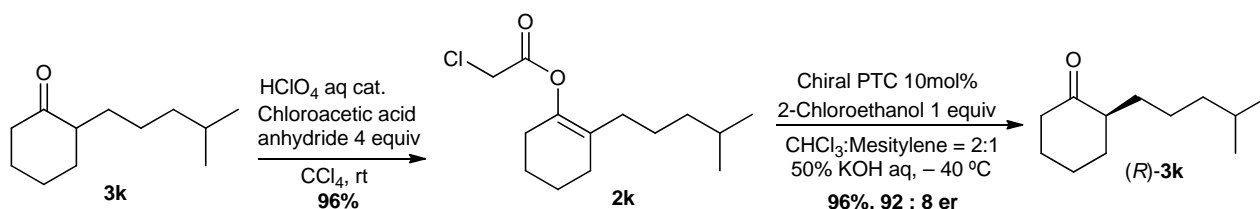
Synthesis of 1f

To the stirred solution of amine **9** (73 mg, 0.2 mmol, 1 equiv) in $\text{CHCl}_3\text{-THF}$ (1:1) was added 9-bromomethylantracene (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 $80\text{ }^\circ\text{C}$ 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). ^1H NMR (600 MHz, CDCl_3): $\delta = 8.81$ (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): $\delta = 169.0, 147.5, 145.1, 137.5, 133.4, 133.3, 132.3, 131.60, 131.55, 129.8, 129.7, 129.6, 129.2, 127.93, 127.88, 126.9, 125.2, 124.5, 123.9, 123.1, 122.7, 118.0, 117.0, 116.3, 78.2, 68.6, 66.2, 62.3, 55.4, 51.9, 38.3, 38.0, 29.2$ (3 carbons), 26.0, 24.9, 21.8. FABMS m/z calculated for $\text{C}_{38}\text{H}_{41}\text{N}_2\text{O}^+$ 541.32 found 541.38 [M].

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

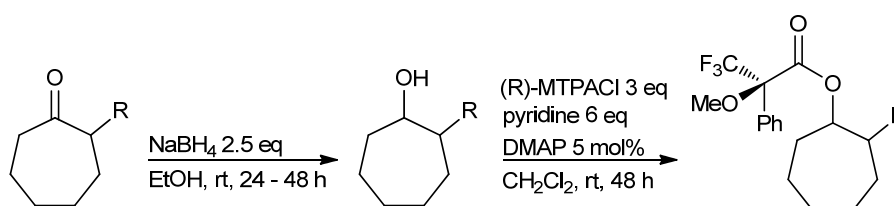


To a stirred solution of cyclohexanone (4.91 g, 50 mmol, 1 equiv) and *N,N*-dimethyl hydrazine (3.16 g, 52.5 mmol, 1.05 equiv) in toluene (40 mL) was added trifluoroacetic acid (80 mg, 0.7 mmol, 1.4 mol%). The mixture was refluxed for 5 h. After that, the resulting solution was cooled to RT. Then, distilled 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 $-5\text{ }^\circ\text{C}$ 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 $0\text{ }^\circ\text{C}$. Then the solution was acidified with concentrated HCl aq to reach pH = 1-2. After stirring at $45\text{ }^\circ\text{C}$ 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 ^1H NMR was in agreement with the literature¹². ^1H 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 $\text{C}_{12}\text{H}_{22}\text{O}$: 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.

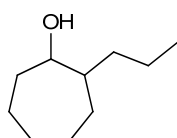
8. Derivatization of ketones to the corresponding alcohol and Mosher's esters



General procedure: reduction of ketones

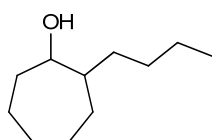
A typical experimental procedure for the reduction of ketones is described below. To the stirred solution of a ketone (0.01 mmol, 1 equiv) in absolute EtOH (0.5 mL) was added NaBH₄ (9.5 mg, 0.25 mmol, 2.5 equiv) followed by stirring at RT for 24-48 h. The reaction mixture was monitored by TLC. After the substrate was completely converted, the reaction mixture was quenched with water and 1N HCl aq. The resultant solution was extracted with Et₂O (x 3). After that, the organic layer was combined and dried over Na₂SO₄. The crude product was concentrated and purified by silica-gel chromatography to give the corresponding alcohol.

2-propyl-cycloheptanol (10f)¹³



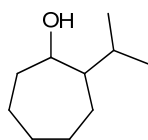
0.0758 mmol (11.7 mg) of 2-propylcyclohepanone **3f** (Table 2, entry 5) was used. The product (diastereomeric mixture) was obtained as colorless oil (11.5 mg, 0.0736 mmol, 97%). ¹H NMR (600 MHz, CDCl₃): δ = 3.94-3.89 (m, 0.66 H), 3.49-3.44 (m, 0.34 H), 1.80-1.15 (m, 16 H), 0.93-0.86 (m, 3H). ¹³C NMR (150 MHz, CDCl₃): 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%). ¹H NMR (600 MHz, CDCl₃): 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). ¹³C NMR (150 MHz, CDCl₃): 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.

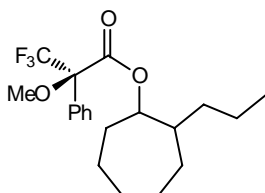
2-isopropyl-cycloheptanol(10h)¹⁵



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%). ¹H NMR of major isomer (600 MHz, CDCl₃): 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). ¹³C NMR of major isomer (100 MHz, CDCl₃): δ = 71.5, 50.2, 36.9, 31.4, 28.2, 27.9, 24.1, 22.2, 21.1. Anal. Calcd (%) for C₁₀H₂₀O: C, 76.86; H, 12.90. Found: C, 76.44; H, 12.64.

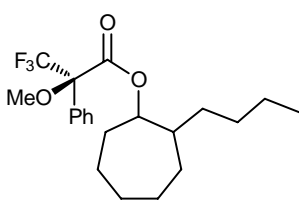
Mosher's esterification

(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 CH₂Cl₂ (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 Et₂O. The crude was washed with saturated CuSO₄ aq and extracted with Et₂O (x3). The resultant solution was concentrated and purified by silica-gel chromatography (Hexane/Et₂O = 50:1-40:1) to give the corresponding ester (93%) as colorless oil. ¹H NMR (600 MHz, CDCl₃): 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).

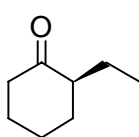
(2R)-2-butylcycloheptyl 3,3,3-trifluoro-2-methoxy-2-phenylpropanoate(11g)



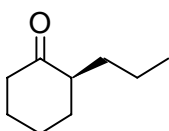
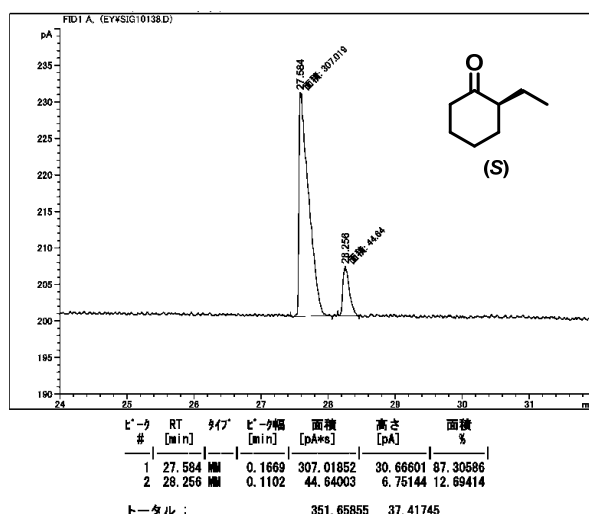
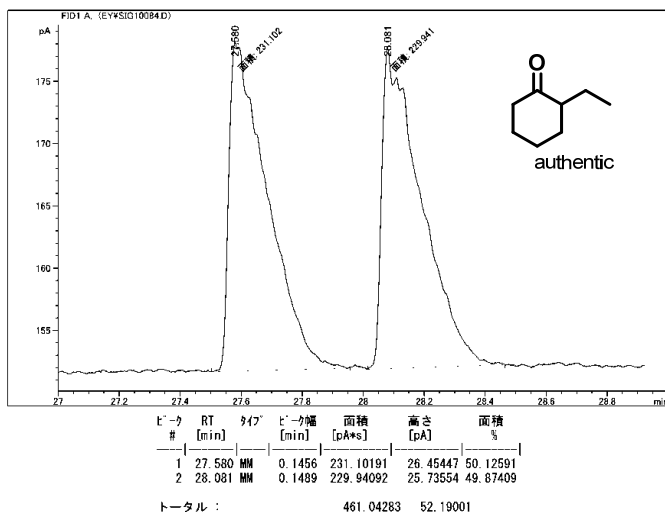
To the stirred solution of an alcohol (0.059 mmol, 1 equiv) in dry CH₂Cl₂ (0.5 mL) was added (*R*)-MTPACl (29.8 mg, 0.118 mmol, 2.0 equiv), dry pyridine (18.7 mg, 0.16 mmol, 4 equiv) and *N,N*-dimethyl aminopyridine (1mg, 4 μmol, 7 mol%) followed by stirring at RT for 48 h. The reaction mixture was monitored by TLC. After the substrate was completely converted, the reaction mixture was diluted with Et₂O. The crude was washed with saturated CuSO₄

aq and extracted with Et₂O (x3). The resultant solution was concentrated and purified by silica-gel chromatography (Hexane/Et₂O = 50:1-40:1) to give the corresponding ester (99%) as inhomogeneous colorless oil. ¹H NMR (600 MHz, C₆D₆): 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

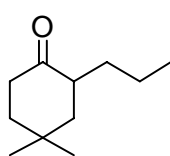
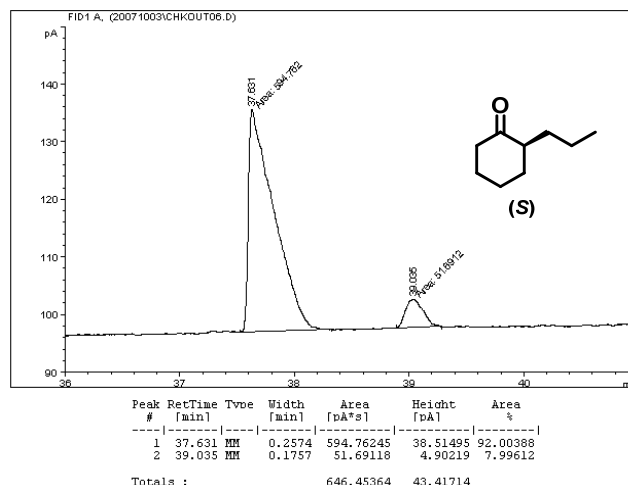
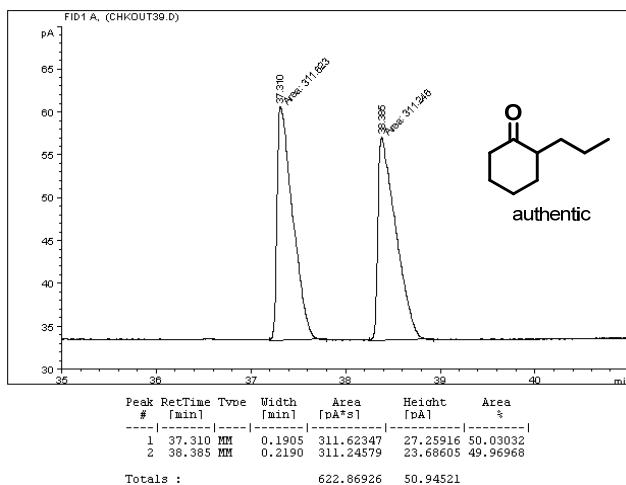


The product ((*S*)-(+)-2-ethylcyclohexanone) was obtained as a colorless oil and 87: 13 er. ¹H and ¹³C NMR were in agreement with the literature¹⁶. ¹H NMR (400 MHz, CDCl₃): δ = 2.40-1.90 (m, 5 H), 1.90-1.54 (m, 4 H), 1.44-1.29 (m, 1 H), 1.29-1.15 (m, 1 H), 0.86 (t, *J* = 7.3 Hz, 3 H). ¹³C NMR (100 MHz, CDCl₃): δ = 213.6, 52.4, 42.1, 33.5, 28.1, 24.9, 22.5, 11.8. Anal. Calcd (%) for C₈H₁₄O: 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. [α]_D^{25.6} = + 36.1, (*c* 0.5, CHCl₃) The absolute configuration was established by comparison of the optical rotation to the literature value for (*R*)-(-)-2-ethylcyclohexanone: [α]_D²⁵ = - 23.6 (*c* 4.31, MeOH)^{17,18}.

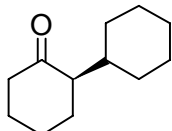
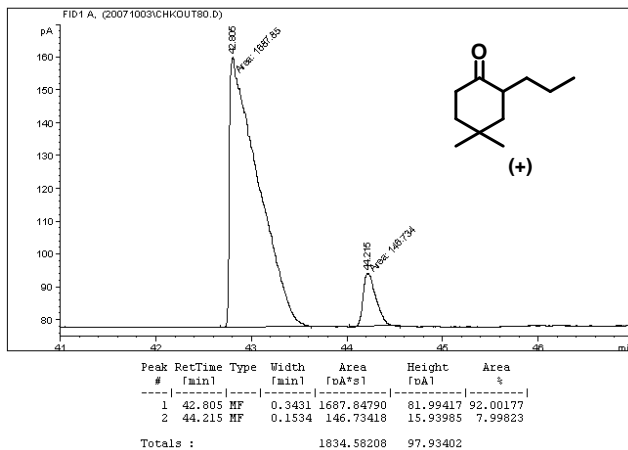
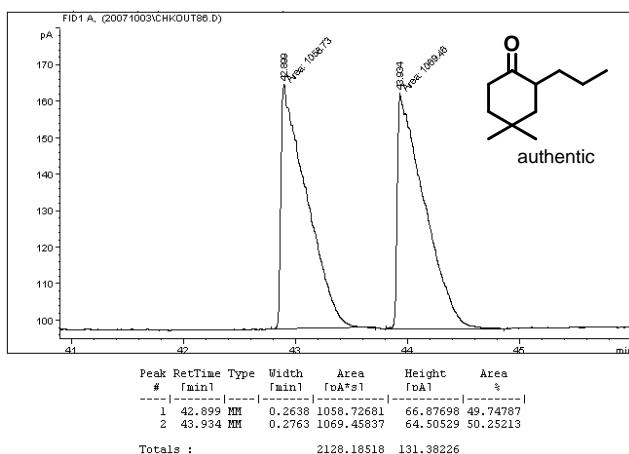


The product ((*S*)-(+)-2-propylcyclohexanone) was obtained as a pale yellow oil and 92: 8 er. ¹H and ¹³C NMR were in agreement with the literature¹⁹. ¹H NMR (400 MHz, CDCl₃): δ = 2.39-2.231 (m, 1 H), 2.31-2.20 (m, 2H), 2.12-1.92 (m, 2 H), 1.86-1.56 (m, 4 H), 1.42-1.08 (m, 4 H), 0.87 (t, *J* = 6.9 Hz, 3 H). ¹³C NMR (100 MHz, CDCl₃): δ = 213.7, 50.6, 42.0, 33.9, 31.7, 28.1, 24.9, 20.4, 14.3. Anal. Calcd (%) for C₉H₁₆O: 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. [α]_D^{22.5} = + 33.5, (*c* 1.0, CHCl₃) 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.

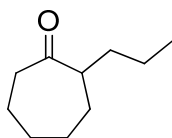
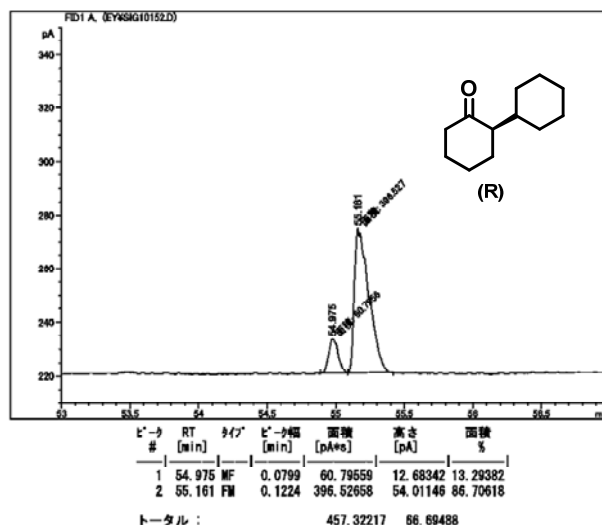
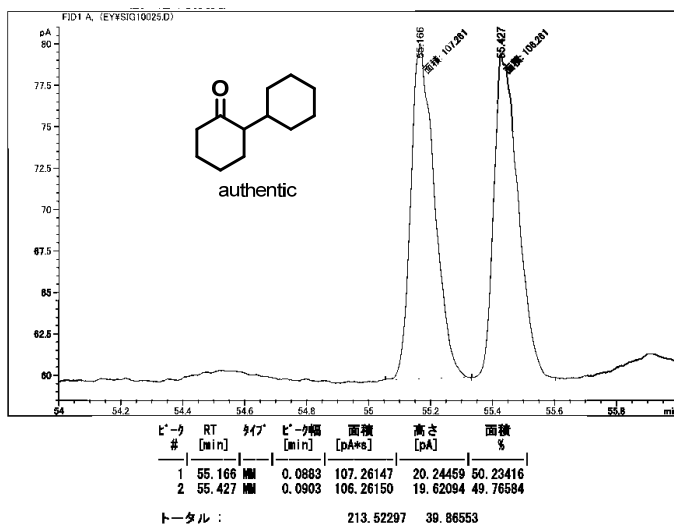


The product⁷ ((+)-4,4-dimethyl-2-propylcyclohexanone) was obtained as a pale yellow oil and 92: 8 er. ¹H NMR (400 MHz, CDCl₃): δ = 2.44 (td, J = 6.4, 14.2 Hz, 1 H), 2.36 (dt, J = 6.0, 6.0 Hz, 1 H), 2.22 (dt, J = 3.2, 14.2 Hz, 1 H), 1.80-1.55 (m, 4 H), 1.34-1.22 (m, 3 H), 1.19 (s, 3 H), 1.06 (tq, 6.9, 6.9 Hz, 1 H), 0.99 (s, 3 H), 0.87 (t, J = 7.4 Hz, 3 H). ¹³C NMR (100 MHz, CDCl₃): 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 C₁₁H₂₀O: 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, CHCl₃)

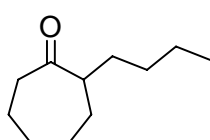
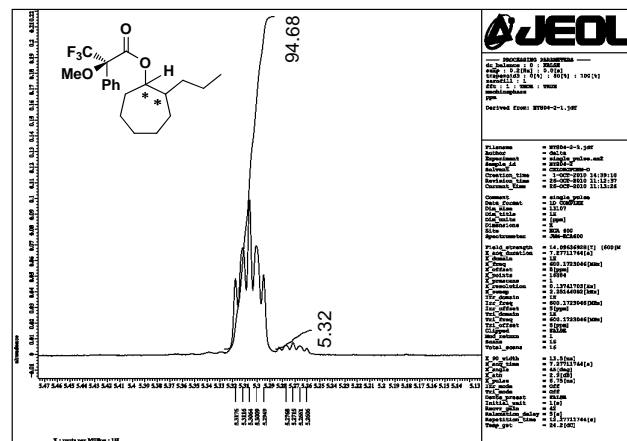
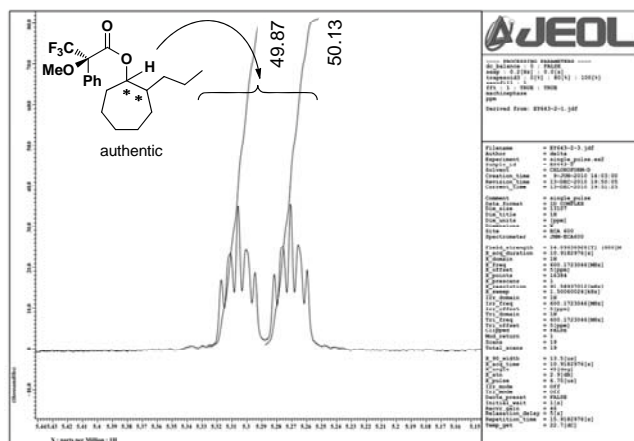


The product ((*R*)-(+)-2-cyclohexylcyclohexanone) was obtained as a colorless oil and 87: 13 er and ¹H and ¹³C NMR were in agreement with the literature¹². ¹H NMR (400 MHz, CDCl₃): δ = 2.39-2.29 (m, 1 H), 2.28-2.18 (m, 1 H), 2.11-2.01 (m, 1 H), 1.98-1.45 (m, 12 H), 1.33-1.18 (m, 2 H), 1.16-0.80 (m, 3 H). ¹³C NMR (100 MHz, CDCl₃): 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 C₁₂H₂₀O: 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, CHCl₃) The absolute configuration was established by comparison of the

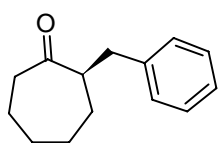
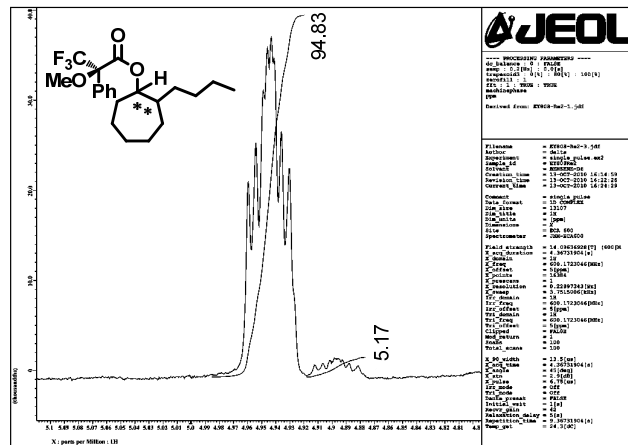
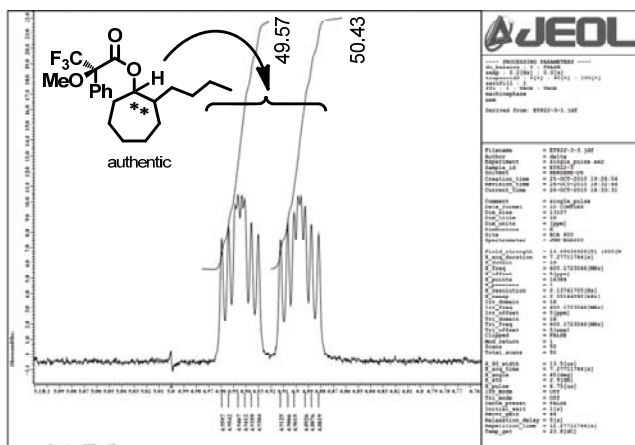
optical rotation to the literature value for (*S*)-(-)-2-cyclohexylcyclohexanone: $[\alpha]_D^{24.3} = -38.1$ (c 1.58, MeOH)²¹.



The product (2-(+)-propylcycloheptanone) was obtained as a pale yellow oil and 94.5: 5.5 er and ¹³C NMR was in agreement with the literature⁸. ¹H NMR (400 MHz, CDCl₃): 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). ¹³C NMR (100 MHz, CDCl₃): δ = 216.8, 52.3, 42.7, 34.6, 31.3, 29.7, 28.5, 24.8, 20.5, 14.2. Anal. Calcd (%) for C₁₀H₁₈O: C, 77.87; H, 11.76. Found: C, 78.01; H, 11.83. $[\alpha]_D^{25.3} = +49.7$ (c 1.0, CHCl₃). Enantiomeric ratio (er) was determined by ¹H NMR after the product was reduced and esterified to the corresponding Mosher's ester (600 MHz, C₆D₆, major isomer : δ = 5.33-5.29 ppm, minor isomer : δ = 5.29-5.25 ppm).

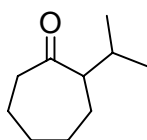
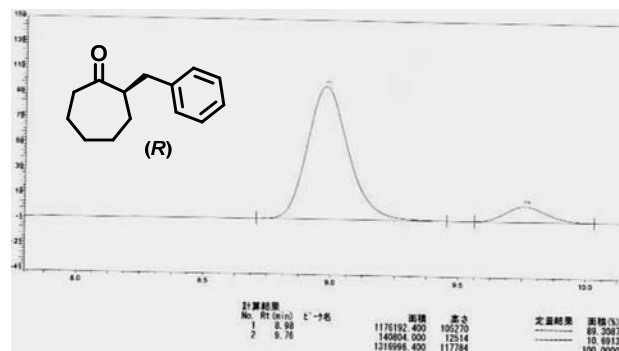
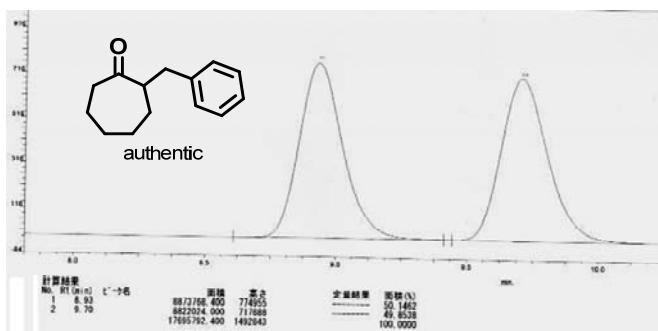


The product⁹ (2-(+)-butylcycloheptanone) was obtained as a pale yellow oil and 95: 5 er. ¹H NMR (400 MHz, CDCl₃): δ = 2.53-2.32 (m, 3 H), 1.90-1.77 (m, 4 H), 1.68-1.50 (m, 2H), 1.38-1.14 (m, 8 H), 0.86 (t, J = 6.9 Hz, 3 H). ¹³C NMR (100 MHz, CDCl₃): δ = 216.9, 52.5, 42.7, 32.2, 31.3, 29.7, 29.5, 28.5, 24.8, 22.9, 14.1. Anal. Calcd (%) for C₁₁H₂₀O: C, 78.51; H, 11.98. Found: C, 78.44; H, 11.96. $[\alpha]_D^{25.3} = +49.7$ (c 1.0, CHCl₃) Enantiomeric ratio (er) was determined by ¹H NMR after the product was reduced and esterified to the corresponding Mosher's ester (600 MHz, C₆D₆, major isomer : δ = 4.97-4.92 ppm, minor isomer : δ = 4.92-4.87 ppm).



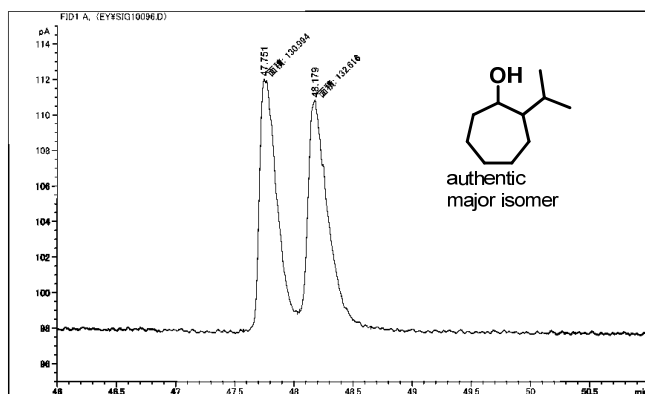
The product ((*R*)-(+)-2-benzylcycloheptanone) was obtained as a colorless oil and 89.5: 10.5 er and ^{13}C NMR was in agreement with the literature²². ^1H NMR (400 MHz, CDCl_3): δ = 7.29-7.22 (m, 2 H), 7.21-7.11 (m, 3 H), 3.06 (dd, J = 6.0, 13.8 Hz, 1 H), 2.86-2.75 (m, 1 H), 2.54 (dd, J = 8.7, 13.8 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 $\text{C}_{14}\text{H}_{18}\text{O}$: C, 83.12; H, 8.97. Found: C, 82.87; H, 8.88. Enantiomeric ratio (er) was determined by HPLC with a Chiralcel AD-H column (conditions, Hexane : EtOH = 100 : 1, flow rate = 1 mL / min, 25 °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}.

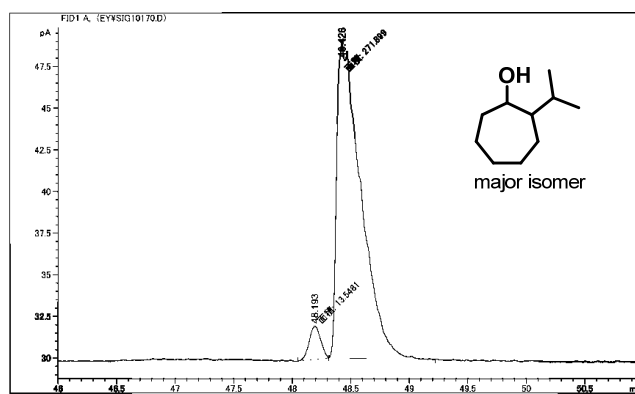


The product ((+)-isopropylcycloheptanone) was obtained as a pale yellow oil and 95: 5 er, and ^1H and ^{13}C NMR was in agreement with the literature⁴. ^1H NMR (400 MHz, CDCl_3): δ = 2.49 (td, J = 3.2, 12.8 Hz, 1 H), 2.40-2.30 (m, 1 H), 2.19-2.10 (m, 1 H), 2.00-1.80 (m, 5 H), 1.60-1.42 (m, 1 H), 1.42-1.12 (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 $\text{C}_{10}\text{H}_{18}\text{O}$: 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 °C [hold 10 min.], rate of temperature increase: 2 °C/min up to 120 °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).

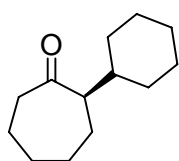


ピーク #	RT [min]	ワイド	ピーク幅 [min]	面積 [pA*s]	高さ [pA]	面積 %
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2	48.179	MM	0.1819	132.61604	12.15015	50.30770

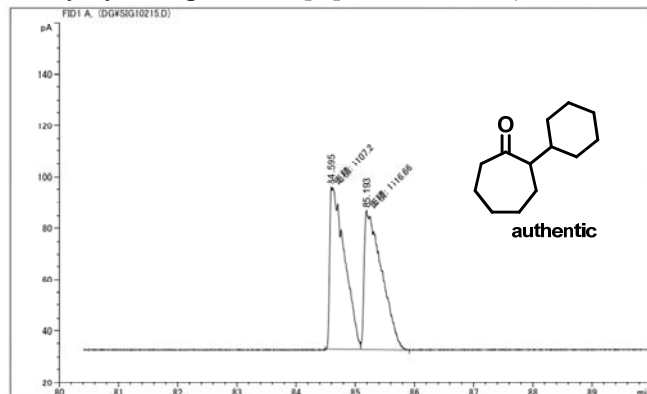


ピーク #	RT [min]	ワイド	ピーク幅 [min]	面積 [pA*s]	高さ [pA]	面積 %
1	48.193	MM	0.1124	13.54809	2.00891	4.74626
2	48.426	MM	0.2397	271.89936	18.90436	95.25374

トータル : 285.44744 20.91327

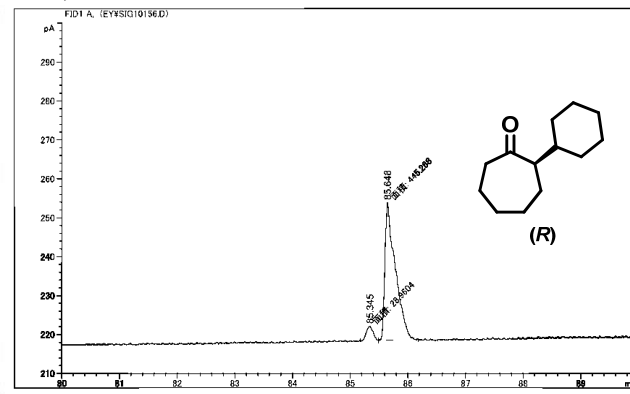


The product ((*R*)-(+)-2-cyclohexylcycloheptanone) was obtained as a colorless oil and 94: 6 er, and ^{13}C NMR was in agreement with the literature¹². ^1H NMR (400 MHz, CDCl_3): δ = 2.52 (dt, J = 3.2, 12.4 Hz, 1 H), 2.35-2.28 (m, 1 H), 2.21-2.14 (m, 1 H), 1.98-1.79 (m, 4 H), 1.75-1.40 (m, 7 H), 1.40-1.07 (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 $\text{C}_{13}\text{H}_{22}\text{O}$: 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.



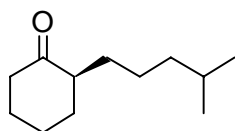
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1	84.595	MF	0.2923	1107.19861	63.13494	49.78731
2	85.193	FM	0.3438	1116.65857	54.13449	50.21269

トータル : 2223.85718 117.26943



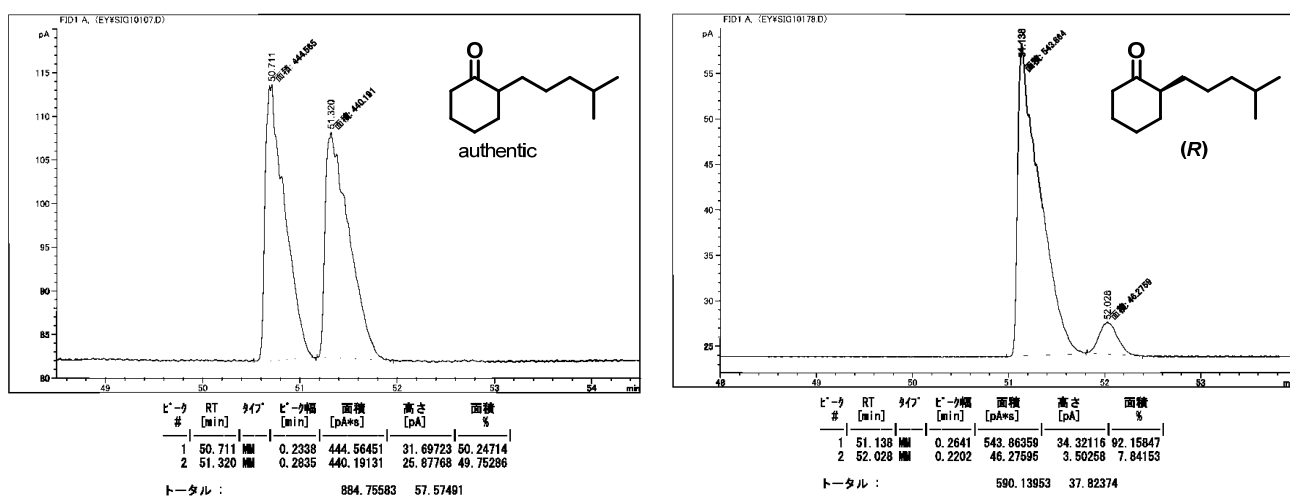
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2	85.648	FM	0.2097	445.26846	35.38125	93.89315

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 ^1H NMR was in agreement with the literature¹². ^1H 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 $\text{C}_{12}\text{H}_{22}\text{O}$: 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.



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 chloroacetyl group seem to be less reactive compared to PNP esters derived from *N*-benzoyl aminoacids.

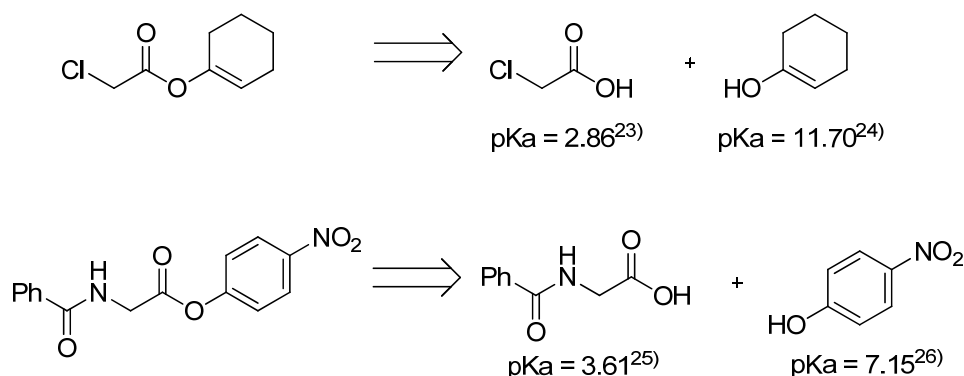
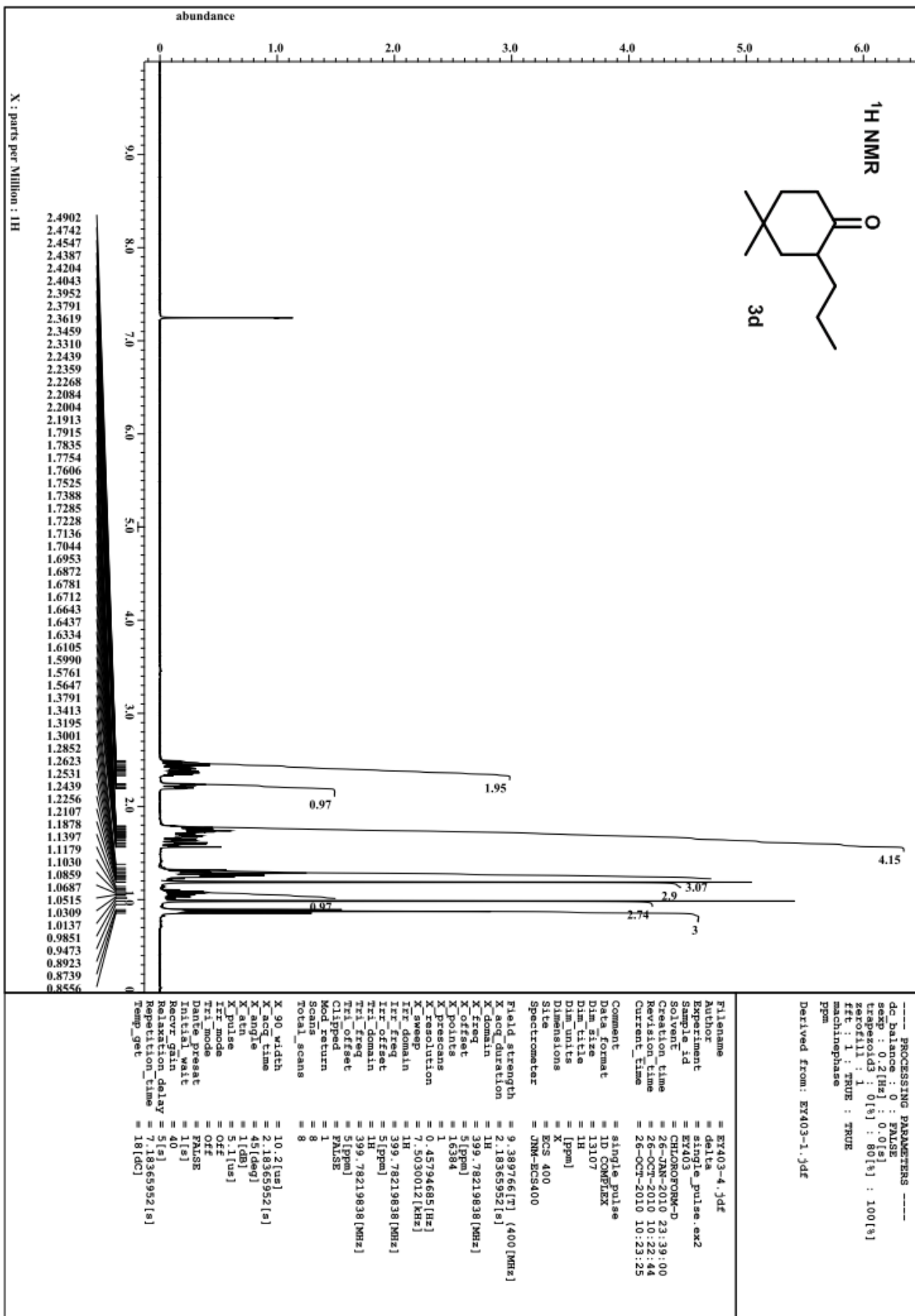


Fig. S1 Comparison of pKa values between product acids and alcohols (in water)

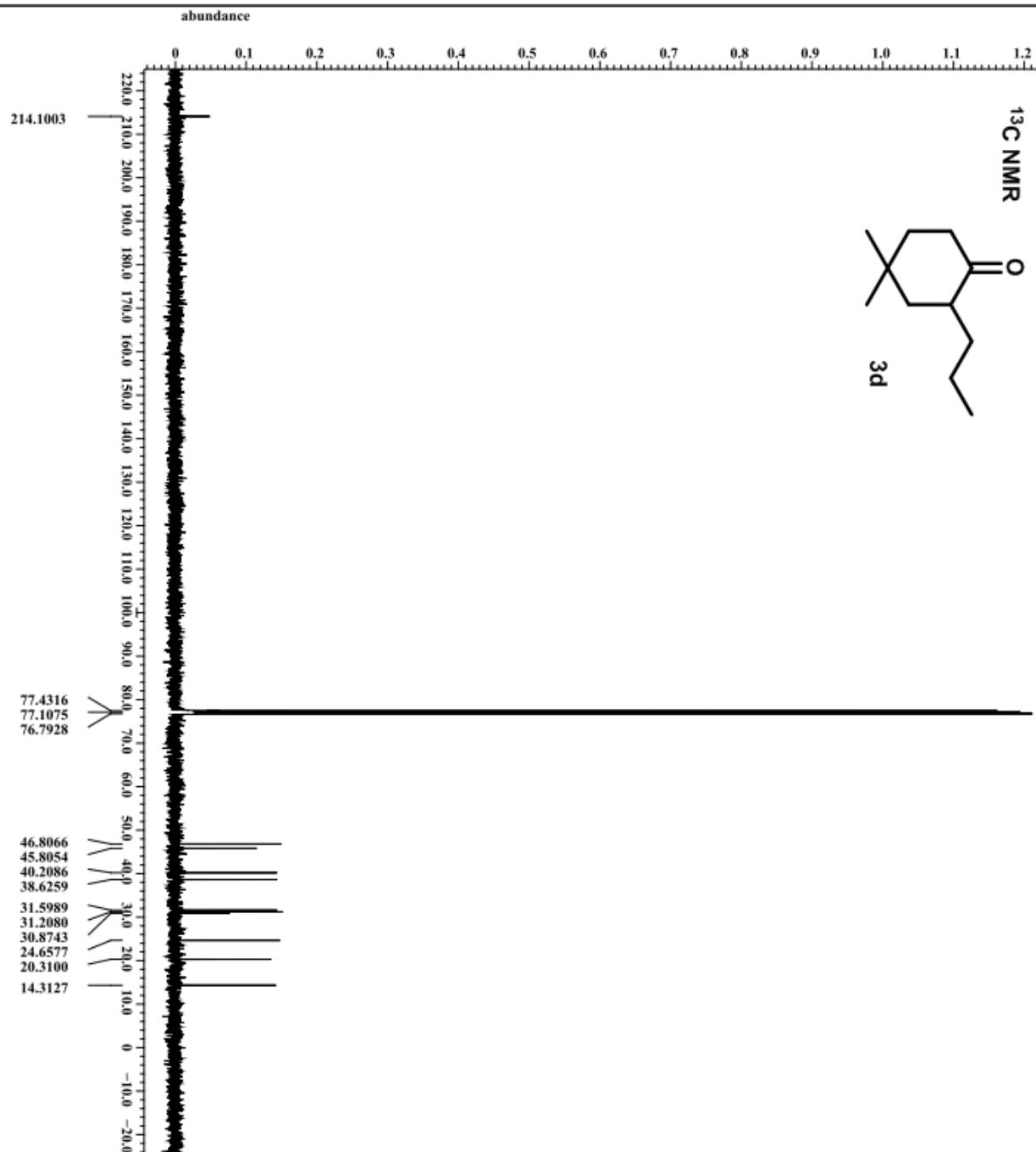
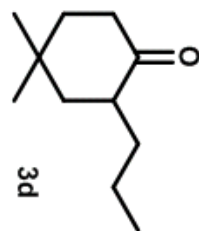
11. References

- Perrin, D. D.; Armarego, W. L. F.; *Purification of Laboratory Chemicals*; 3rd ed., Pergamon Press, Oxford, 1988
- Lygo, B.; Crosby, J.; Lowdon, T. R.; Peterson, J. A.; Wainwright, P. G. *Tetrahedron* **2001**, *57*, 2403.
- Poulsen, T. B.; Bernardi, L.; Bell, M.; Jørgensen, K. A. *Angew. Chem. Int. Ed.* **2006**, *45*, 6551.
- Malosh, C. F.; Ready, J. M. *J. Am. Chem. Soc.* **2004**, *126*, 10240.
- Chou, H.-H.; Wu, H.-M.; Wu, J.-D.; Ly, T. W.; Jan, N.-W.; Shia, K.-S.; Liu, H.-J. *Org. Lett.*, **2008**, *10*, 121.
- Lin, H.-H.; Chang, W.-S.; Luo, S.-Y.; Sha, C.-K. *Org. Lett.* **2004**, *19*, 3289.
- Guiard, B. et al. *Bull. Soc. Chim. Fr.* **1974**, 3021.
- Li, L.; Guo, Q.; Xue, S. *J. Org. Chem.* **2008**, *73*, 3516.
- Miyamoto, N.; Isiyama, S.; Utimoto, K.; Nozaki, H. *Tetrahedron*, **1973**, *29*, 2365.

- 10) Borowitz, I. J.; Casper, E. W. R.; Crouch, R. K.; Yee, K. C. *J. Org. Chem.* **1972**, *37*, 3873.
- 11) Takasaki, M.; Motoyama, Y.; Yoon, S.-H.; Mochida, I.; Nagashima, H. *J. Org. Chem.* **2007**, *72*, 10291.
- 12) Soorukram, D.; Knochel, P. *Angew. Chem. Int. Ed.* **2006**, *45*, 3686.
- 13) Braude et al. *J. Chem. Soc.* **1953**, 2202.
- 14) Sehgal, R. K.; Koenigsberger, R. U.; Howard, T. J. *J. Org. Chem.* **1975**, *40*, 3073.
- 15) Lhuguenot et al. *Bull. Soc. Chim. Fr.* **1967**, 4129.
- 16) Pecunioso, A.; Menicagli, R. *J. Org. Chem.* **1988**, *53*, 45.
- 17) Meyers, A. I.; Williams, D. R.; Druelinger, M. *J. Am. Chem. Soc.* **1976**, *98*, 3032–3033.
- 18) Meyers, A. I.; Williams, D. R.; Erickson, G. W.; White, S.; Druelinger, M. *J. Am. Chem. Soc.* **1981**, *103*, 3081–3087.
- 19) Takahashi, T.; Nakao, N.; Koizumi, T. *Tetrahedron: Asymmetry*, **1997**, *8*, 3293.
- 20) Hiroi, K.; Achiwa, K.; Yamada, S. *Chem. Pharm. Bull.* 1972, *20*, 246.
- 21) Cheon, C. H.; Yamamoto, H. *J. Am. Chem. Soc.* **2008**, *130*, 9246.
- 22) Ranu, B. C.; Dutta, J.; Guchhait, S. K. *Org. Lett.* **2001**, *3*, 2603.
- 23) Dippy, J.F.J.; Hughes, S.R.C.; Rozanski, A. *J. Chem. Soc.* **1959**, 2492.
- 24) Keeffe, J. E.; Kresge, A. J. *The Chemistry of Enols*. (Wiley, Chichester, 1990)
- 25) Drugarin, C.; Balint, M.-A. *Acta Chimica Hungarica*, **1986**, *123*, 31.
- 26) Mock, W. L.; Morsch, L. A. *Tetrahedron*, **2001**, *57*, 2957.



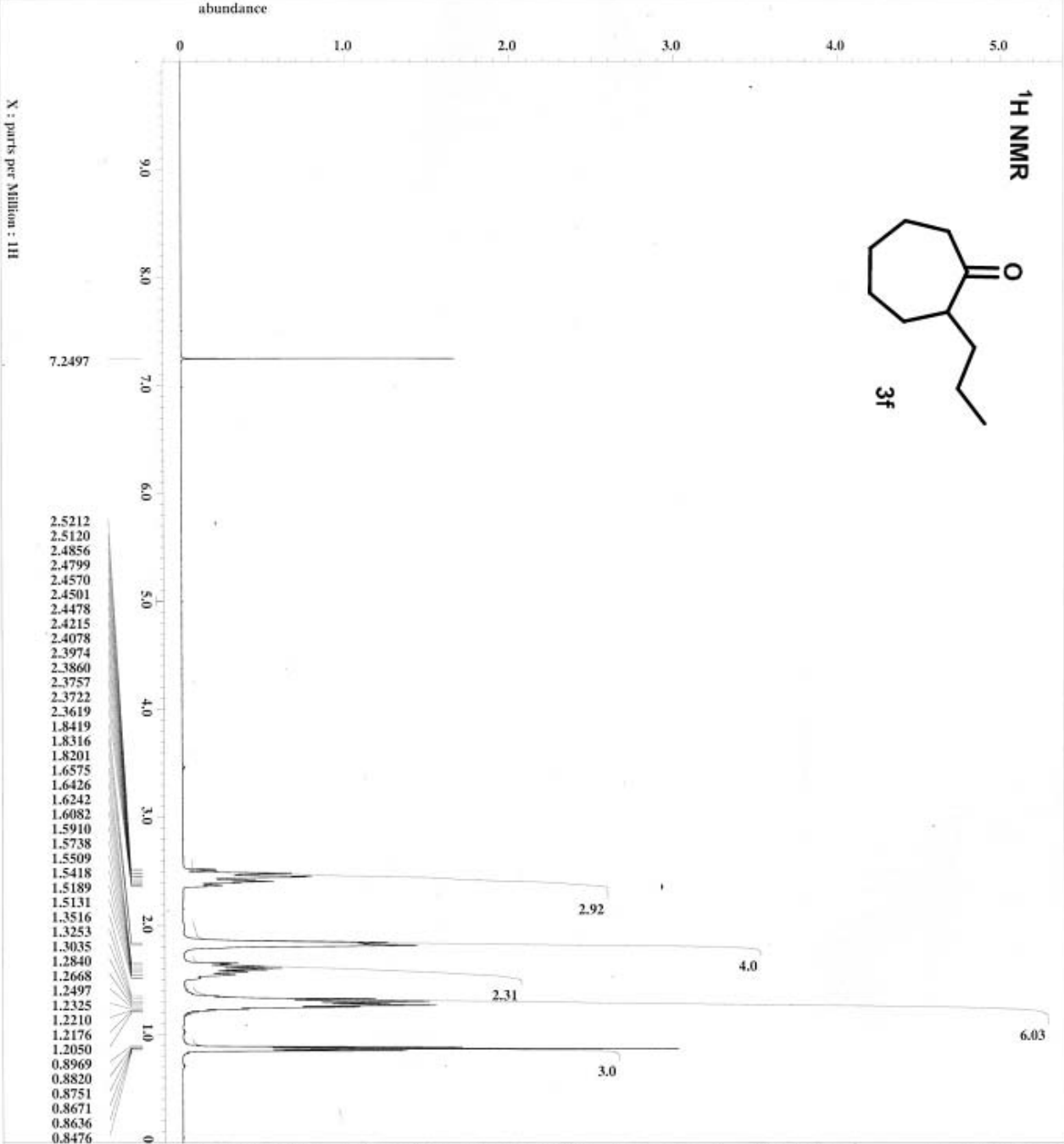
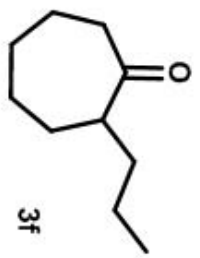
¹³C NMR



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¹H NMR



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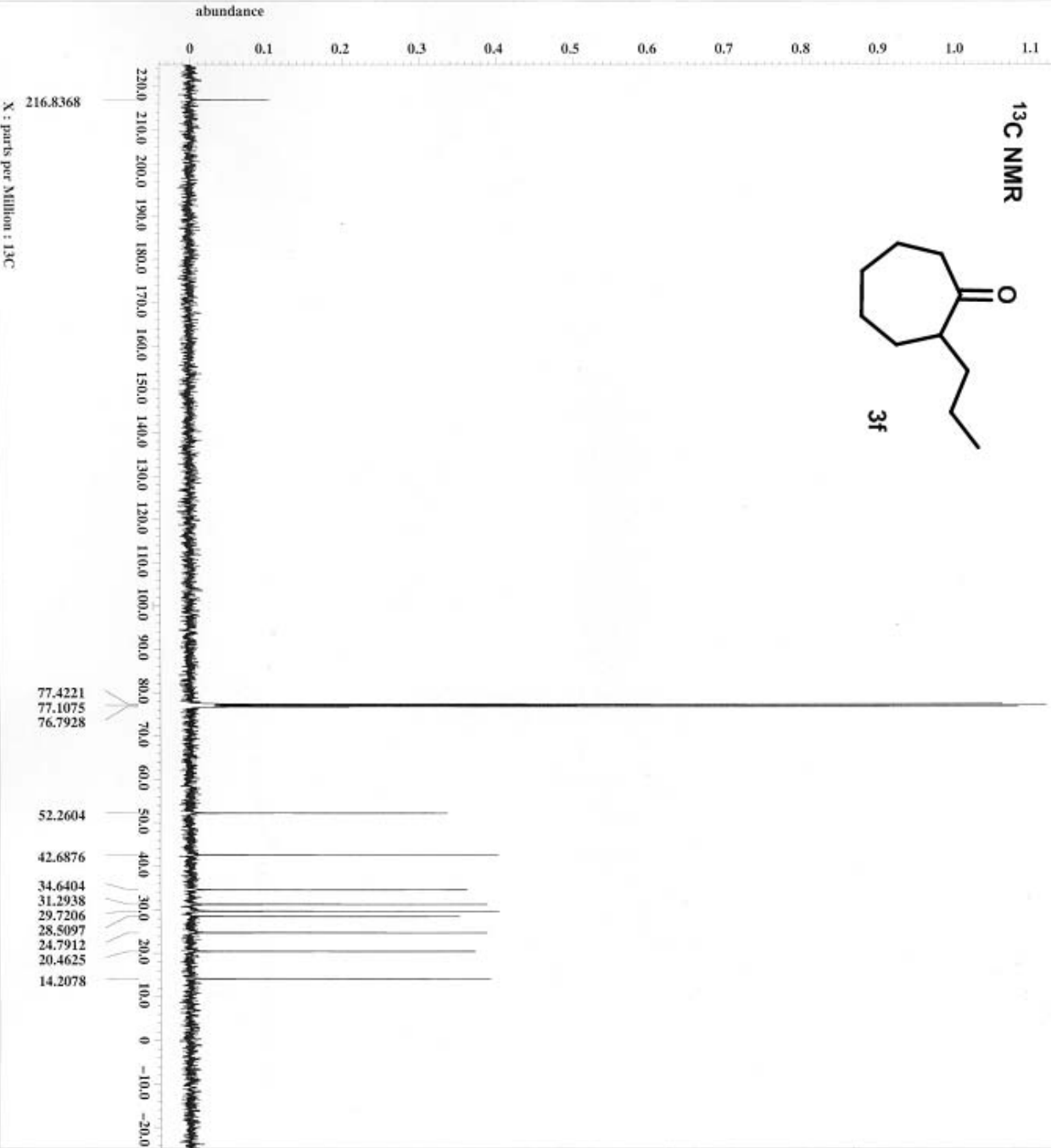
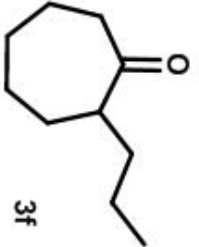
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13C NMR

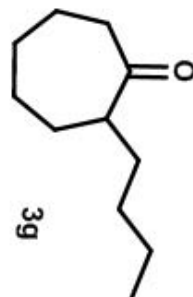


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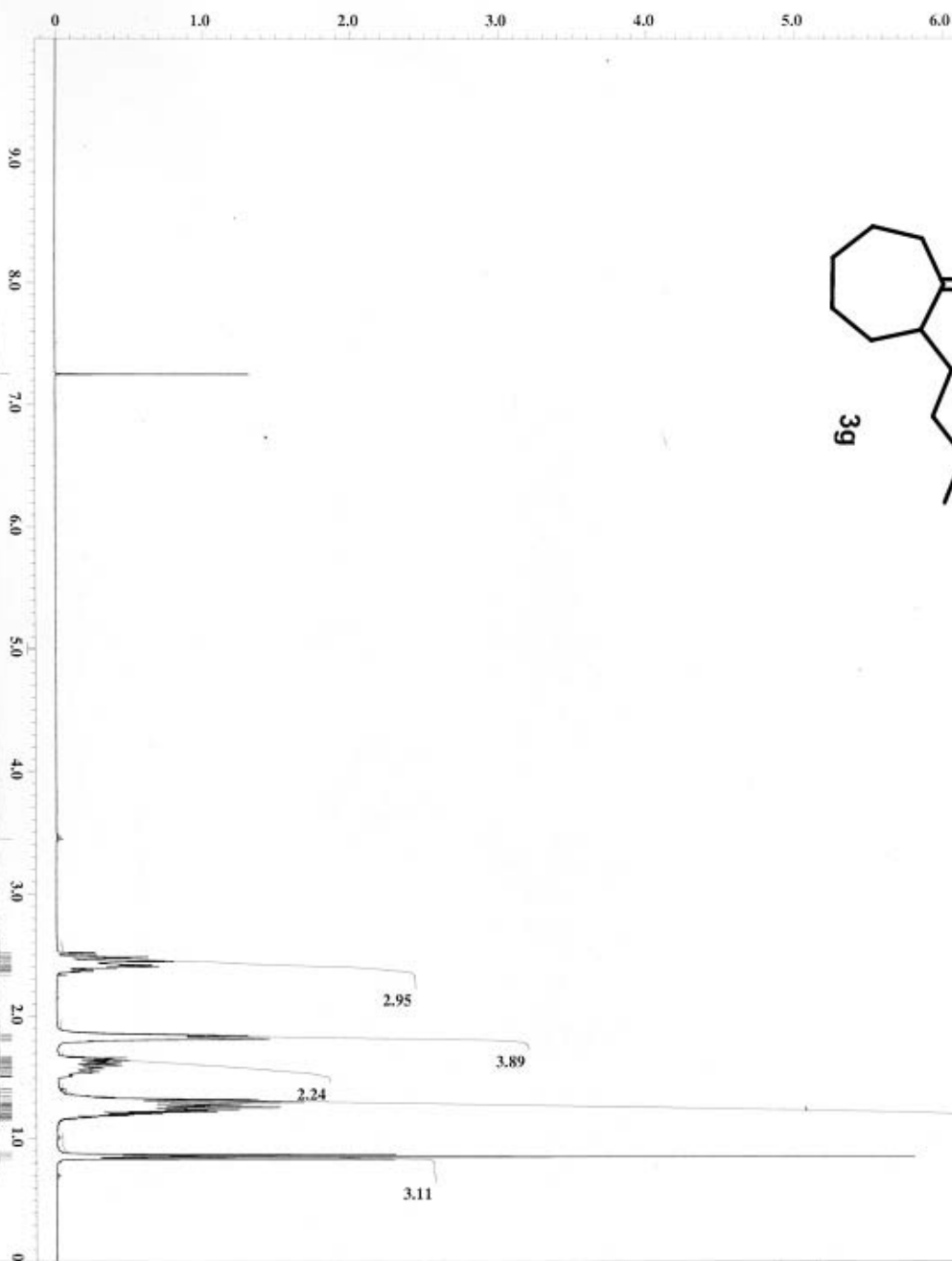
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¹H NMR



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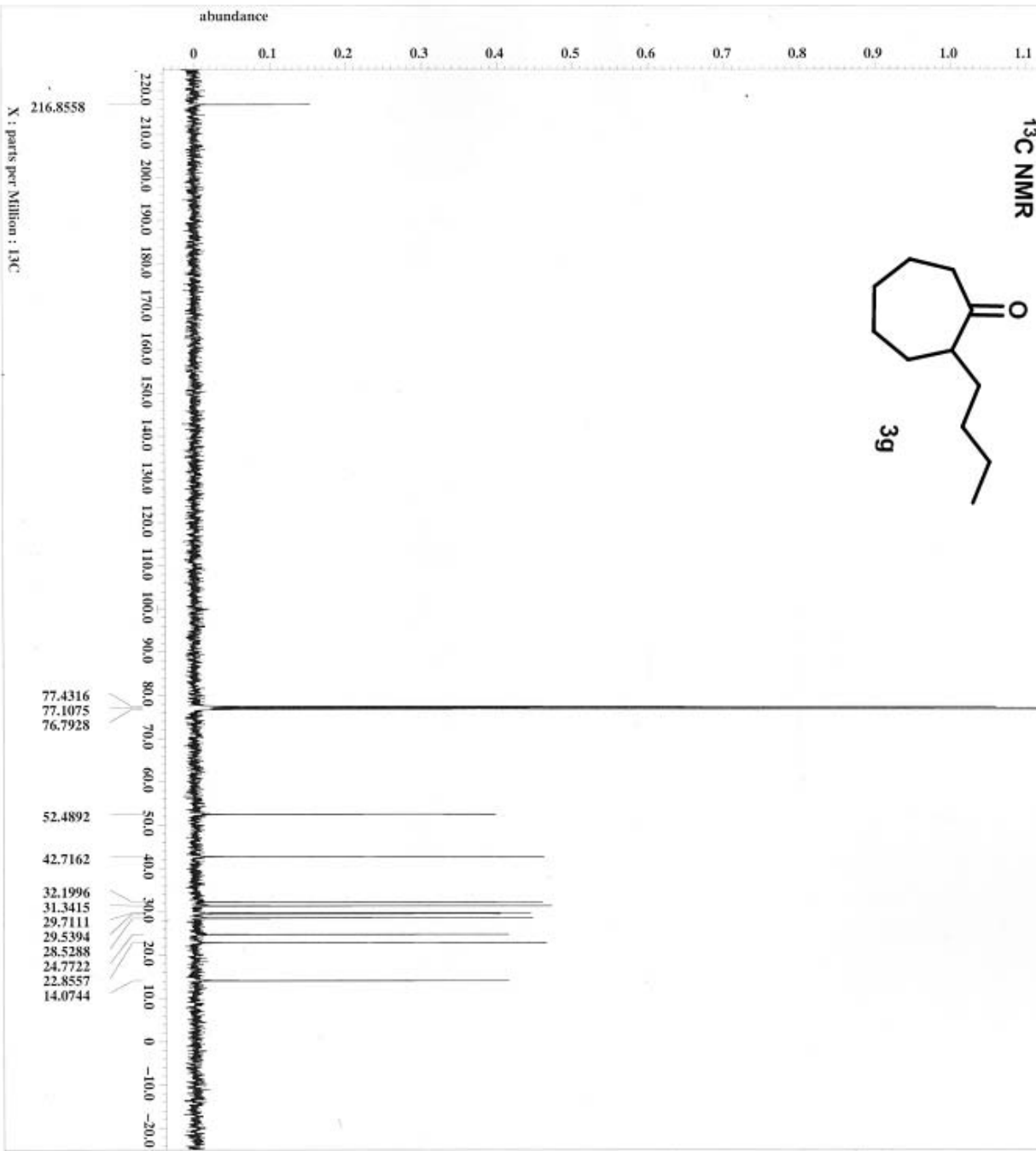
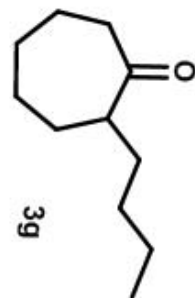
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Field_strength = 9.389766[T] (400[Mhz])
X_acq_duration = 2.18365952[s]
X_domain       = 1H
X_freq         = 399.78219838[Mhz]
X_offset       = 51[ppm]
X_p0lns       = 16384
X_prescans    = 1
X_resolution  = 0.457946851[Mhz]
X_sweep       = 7.5030012[Mhz]
Irr_domain    = 1H
Irr_freq      = 399.78219838[Mhz]
Irr_offset    = 51[ppm]
Irr_domain    = 1H
Irr_freq      = 399.78219838[Mhz]
Irr_offset    = 51[ppm]
Clipped       = FALSE
Mod_return    = 1
Scans         = 8
Total_scans   = 8

X_g0_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      = OF2
Irr_mode      = OF2
Dante_presat  = FALSE
Initial_wait  = 1[s]
Recvr_gain    = 33
Relaxation_delay = 7.18365952[s]
Repetition_time = 21.2[sec]
Temp_get      =
    
```

¹³C NMR



X : parts per Million : 13C

----- PROCESSING PARAMETERS -----
 dc_balance : 0 : FALSE
 temp : 210 [K] : 0.0 [0]
 tempcor : 1 : 0 [0] : 100 [0]
 zprocfl : TRUE : TRUE
 machinename :
 ppm
 Derived from: EY639C-1.fid

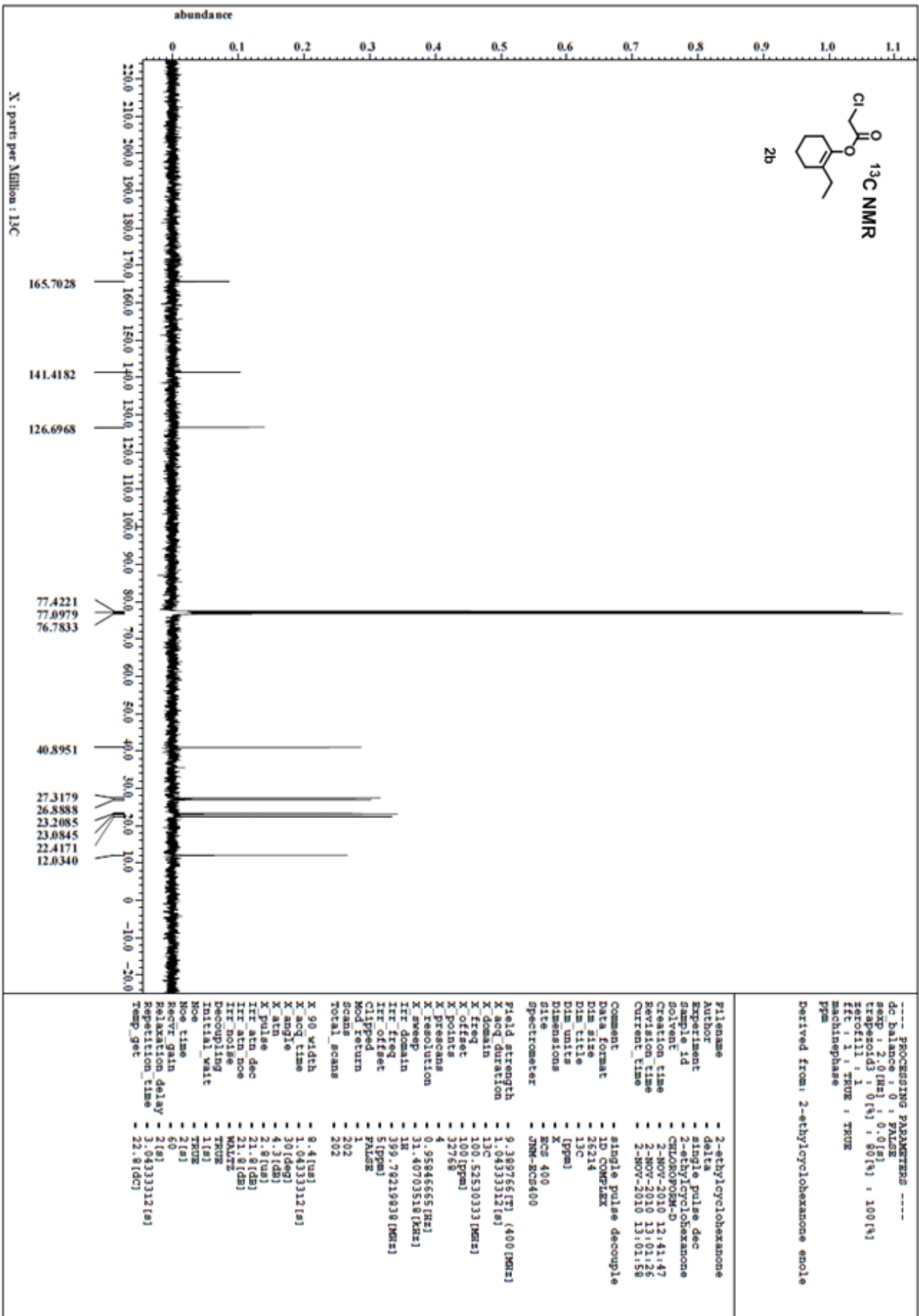
```

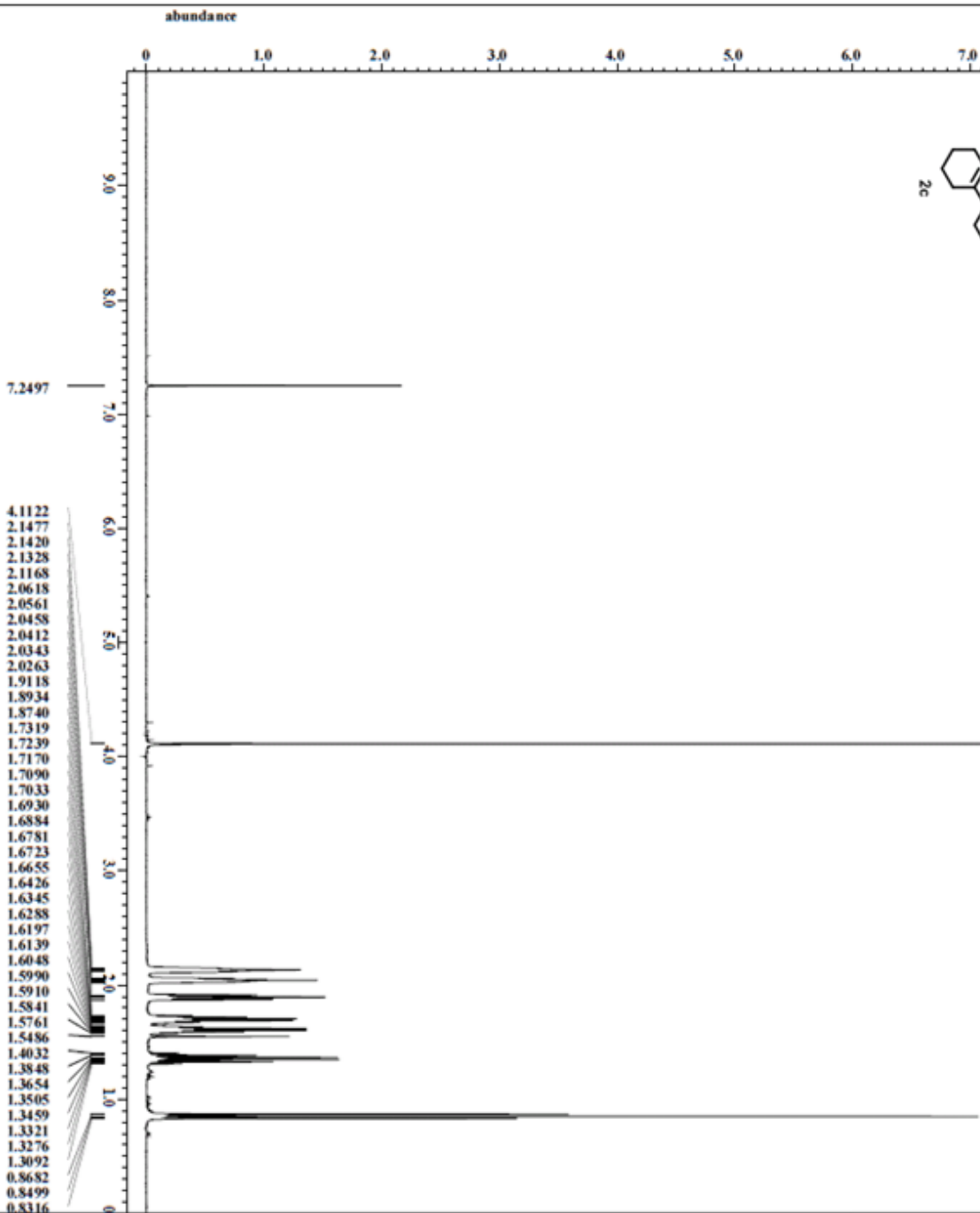
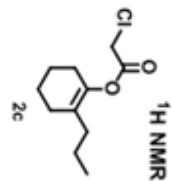
File Name      = EY639C-2.fid
Author         = delta
Experiment    = single_pulse_dec
Sample ID     = EY639C
Solvent       = CHLOROFORM-D
Creation Time = 3-JUN-2010 20:12:49
Revision Time = 3-JUN-2010 20:29:38
Current Time  = 3-JUN-2010 20:30:13

Comment
Data Format   = ID COMPLEX
Dir Size     = 26214
Dir Title    = 13c
Dir Units    = [ppm]
Dimensions   = X
Site         = XCS 400
Spectrometer = JNM-EC6400

Field Strength = 9.389766 [T] (400 [MHz])
X.acq_duration = 1.043333121 [s]
X.dum          = 13c
X.freq        = 100.52530333 [MHz]
X.offset      = 100 [ppm]
X.polarity    = 32768
X.prescans    = 4
X.sweep       = 0.95846665 [Hz]
X.acquisition = 31.40703528 [MHz]
X.domain      = 1H
X.f2         = 399.78219838 [MHz]
X.f1         = 5 [ppm]
X.offfreq    = FALSE
X.ref         = 1
X.ref_name    = TMS-d
X.ref_pos    = 207.0
X.ref_scans   = 207.0
X.ref_wait    = 207.0

X.gp_width    = 8.4 [us]
X.acq_time    = 1.043333121 [s]
X.angle       = 30 [deg]
X.angle2     = 4.3 [dB]
X.evs         = 2.8 [us]
X.pulse       = 21.8 [dB]
X.pulse_dec  = 21.8 [dB]
X.ref_name    = TMS-d
X.ref_pos    = 1 [ppm]
X.ref_wait    = 21 [s]
X.ref_scans   = 60
X.ref_time    = 3.043333121 [s]
X.ref_delay   = 21 [s]
X.ref_time    = 3.043333121 [s]
X.ref_time    = 21.4 [dc]
    
```

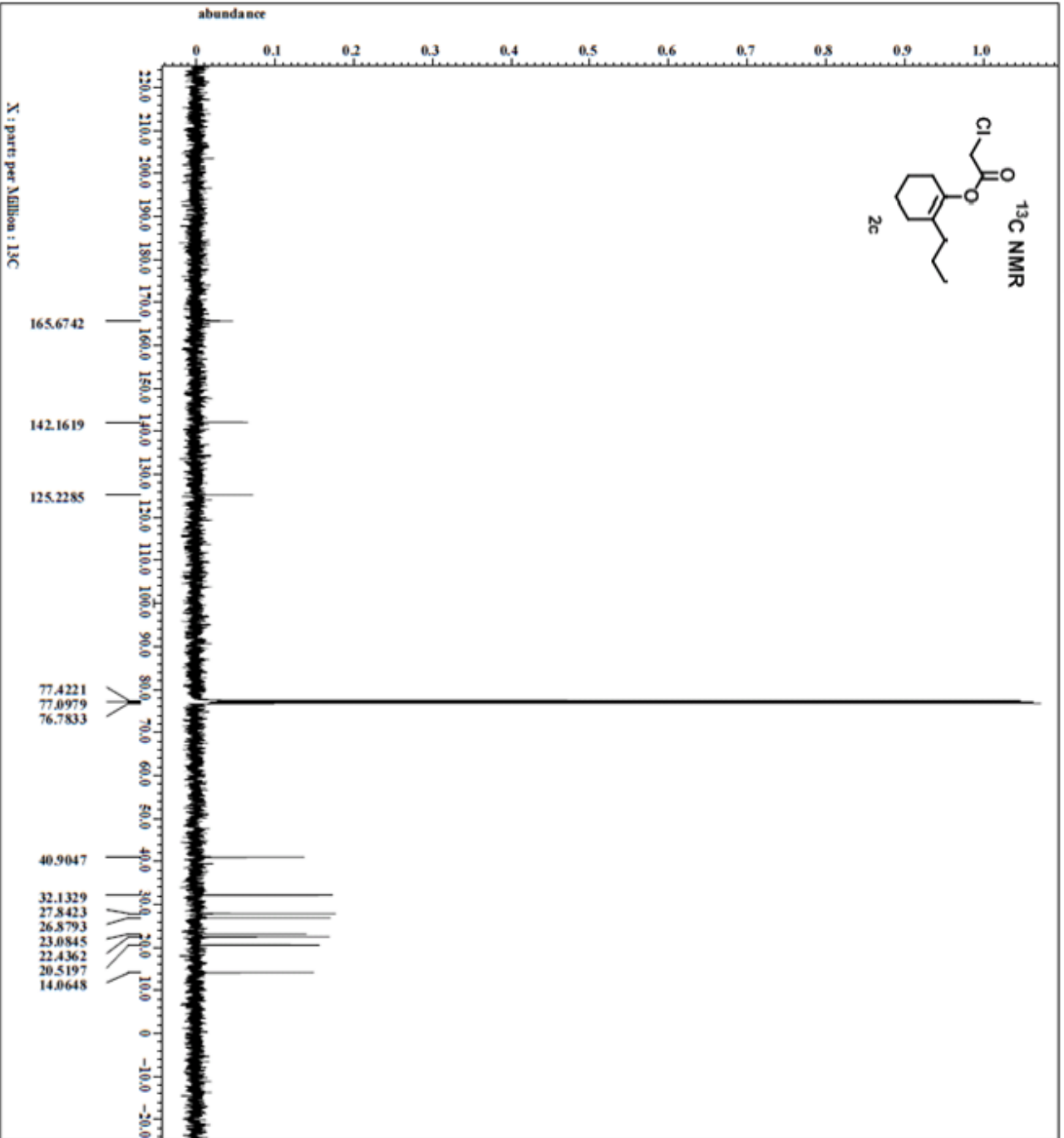
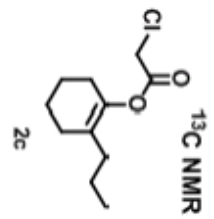


----- PROCESSING PARAMETERS -----
 dc balance : 0 : PALSE
 freq : 0.2 (kHz) : 0.0 (s)
 trapoids : 0 (ts) : 80 (ts) : 100 (ts)
 zerofill : 1
 itc : 1 : TROR : TROR
 machinephase
 ppm

Derived from: ERI40-1.jdf

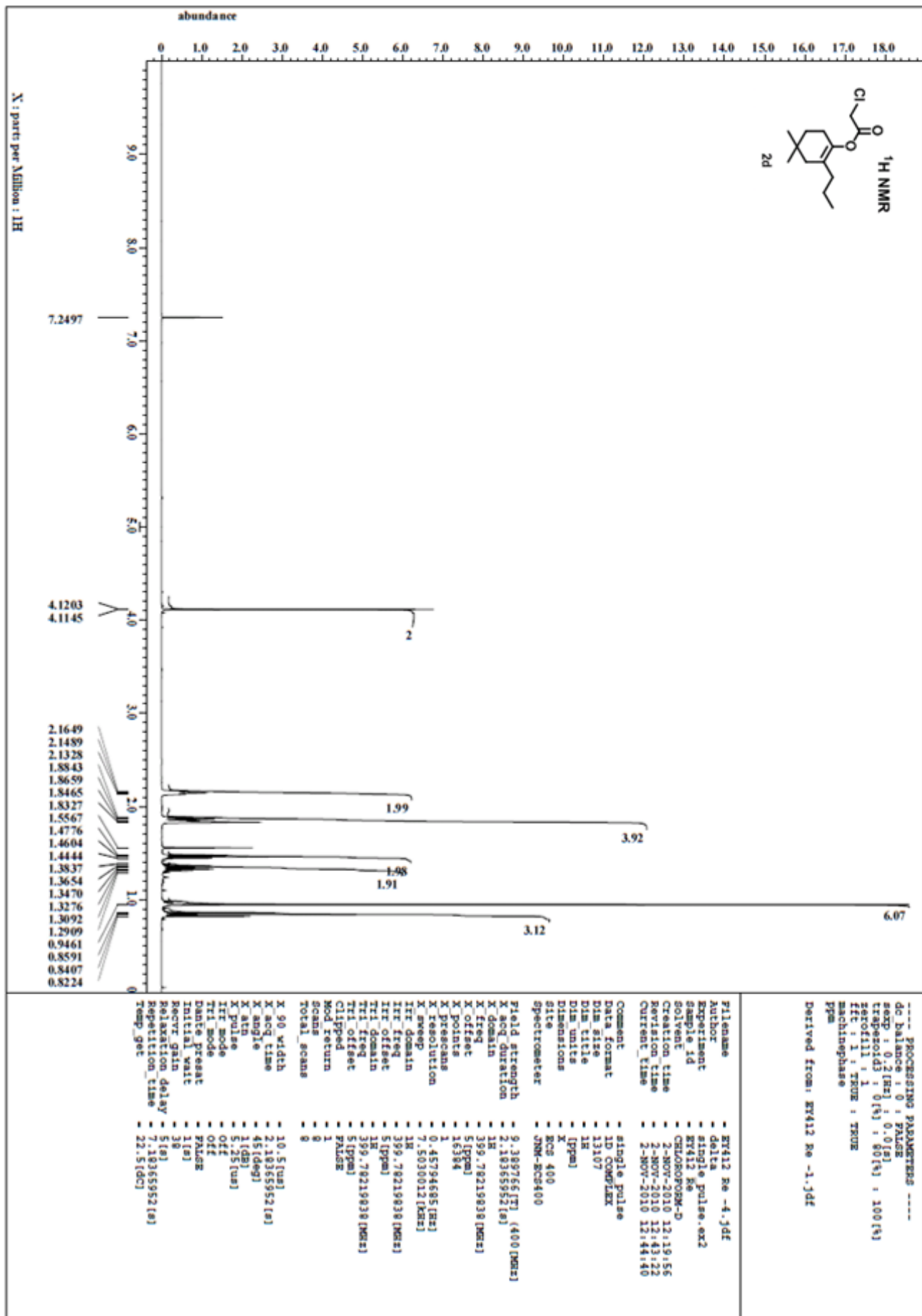
 filename : ERI40-1.jdf
 Author :
 Experiment : single_pulse.ex2
 Sample Id : ERI40
 Solvent : CHLOROFORM-D
 Creation time : 15-JUN-2009 10:30:28
 Revision time : 2-NOV-2010 12:23:59
 Current time : 2-NOV-2010 12:24:54
 Comment :
 Data format : single pulse
 ID COMPLEX
 Dim size : 13107
 Dim title : 1H
 Dim units : (ppm)
 Dimensions : X
 Site : RCG 400
 Spectrometer : JNM-ECX400
 Field strength : 9.3897617 (400 (MHz))
 X acq duration : 2.1835952 (s)
 1H :
 X domain :
 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)
 1H :
 X domain :
 X freq : 399.78219838 (MHz)
 X offset : 5 (ppm)
 1H :
 X domain :
 X freq : 399.78219838 (MHz)
 X offset : 5 (ppm)
 Clipped :
 Mod return : PALSE
 Scans : 1
 Total_scans : 8
 X 90 width : 10.2 (us)
 X acq time : 2.1835952 (s)
 X angle : 45 (deg)
 X atq : 1 (ds)
 X pulse : 6 (us)
 X pulse mode : off (us)
 X r mode : off
 Dark presat : PALSE
 Invert presat : 4 (s)
 Recv1 gain : 5 (s)
 Relaxation delay : 7.1835952 (s)
 Repetition time : 20.6 (ds)
 temp_get :

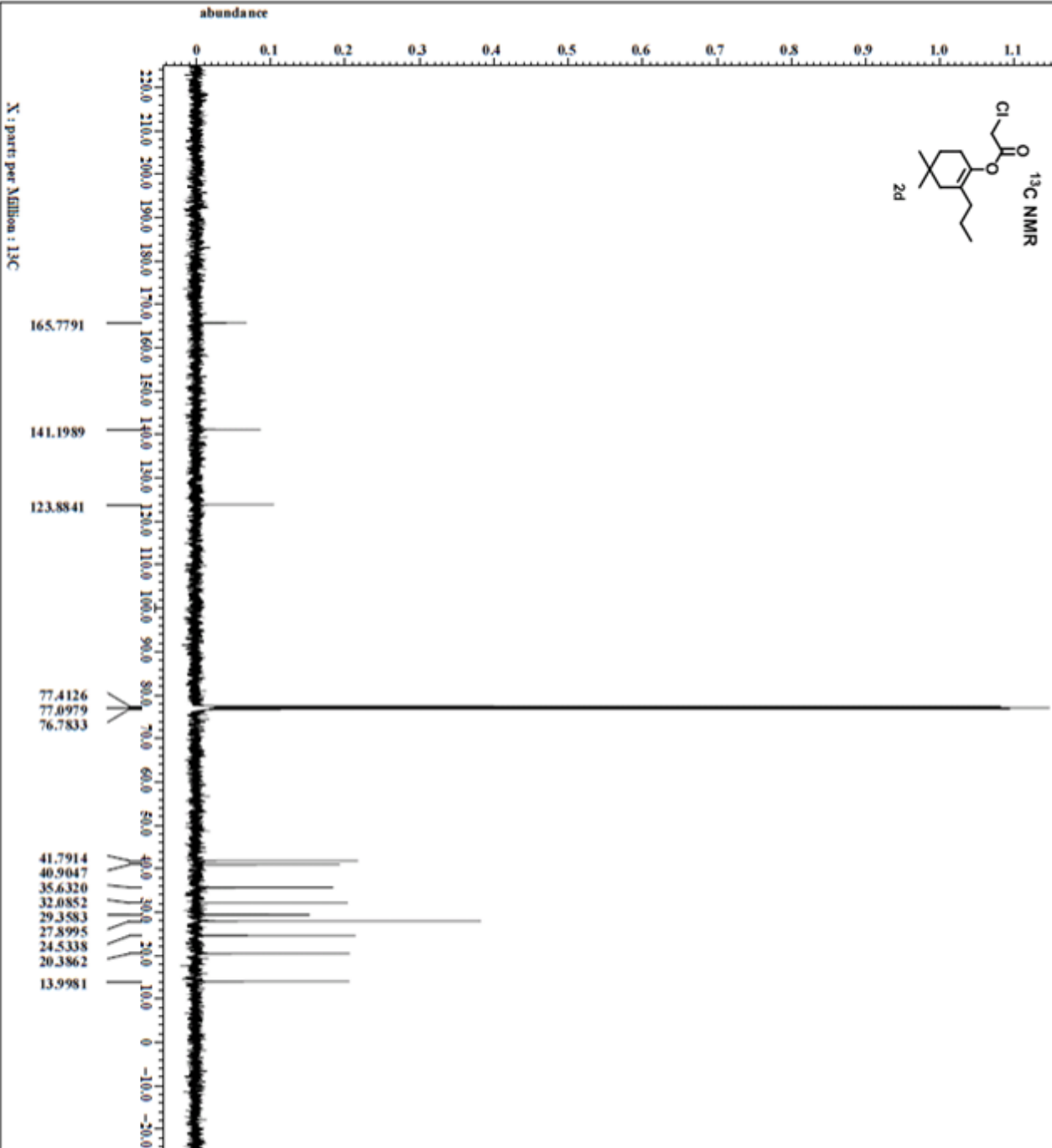
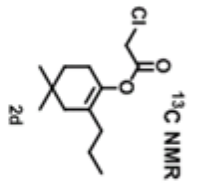
X : parts per Million : 1H



----- PROCESSING PARAMETERS -----
 dc balance : 0 : PULS
 smp : 2.01 (Hz) : 0.01 (s)
 tprepdq3 : 0 (%) : 60 (%) : 100 (%)
 zerofill : 1
 zft : 1 : TRUE : TRUE
 machinphase
 ppm
 Derived from: EY140re C-1.jdf

File name: EY140re C-3.jdf
 Author:
 Experiment:
 Sample ID:
 Sample C:
 Solvent: CDCl3
 Reaction time:
 Revision time:
 Current time:
 Comment:
 Data format:
 ID: COMPLEX
 DIM size:
 DIM title:
 DIM units:
 Dimensions:
 X:
 Site:
 Spectrometer:
 JMR-EC6400
 Field strength: 9.39766 (T) (400 (MHz))
 X_acq_duration: 1.04333 (s)
 X_domain:
 X_freq: 100.5250333 (MHz)
 X_offset: 100 (ppm)
 X_points: 32768
 X_prescans: 4
 X_resolution: 0.9584665 (Hz)
 X_sweep: 31.4070318 (KHz)
 Irr_domain:
 Irr_freq: 399.78219838 (MHz)
 Irr_offset: 5 (ppm)
 Clipped:
 Mod_return:
 Scans: 1
 Total_scans: 135
 X_90_width: 8.4 (us)
 X_acq_time: 1.04333 (s)
 X_angle:
 X_atn:
 X_pulse:
 Irr_atn_dec:
 Irr_atn_poe:
 Irr_noise:
 Decoupling:
 Initial_wait:
 Mode_time:
 Recv_gain:
 Relaxation_delay: 2 (s)
 Repetition_time: 2.94333 (s)
 Temp_get: 22.5 (dC)

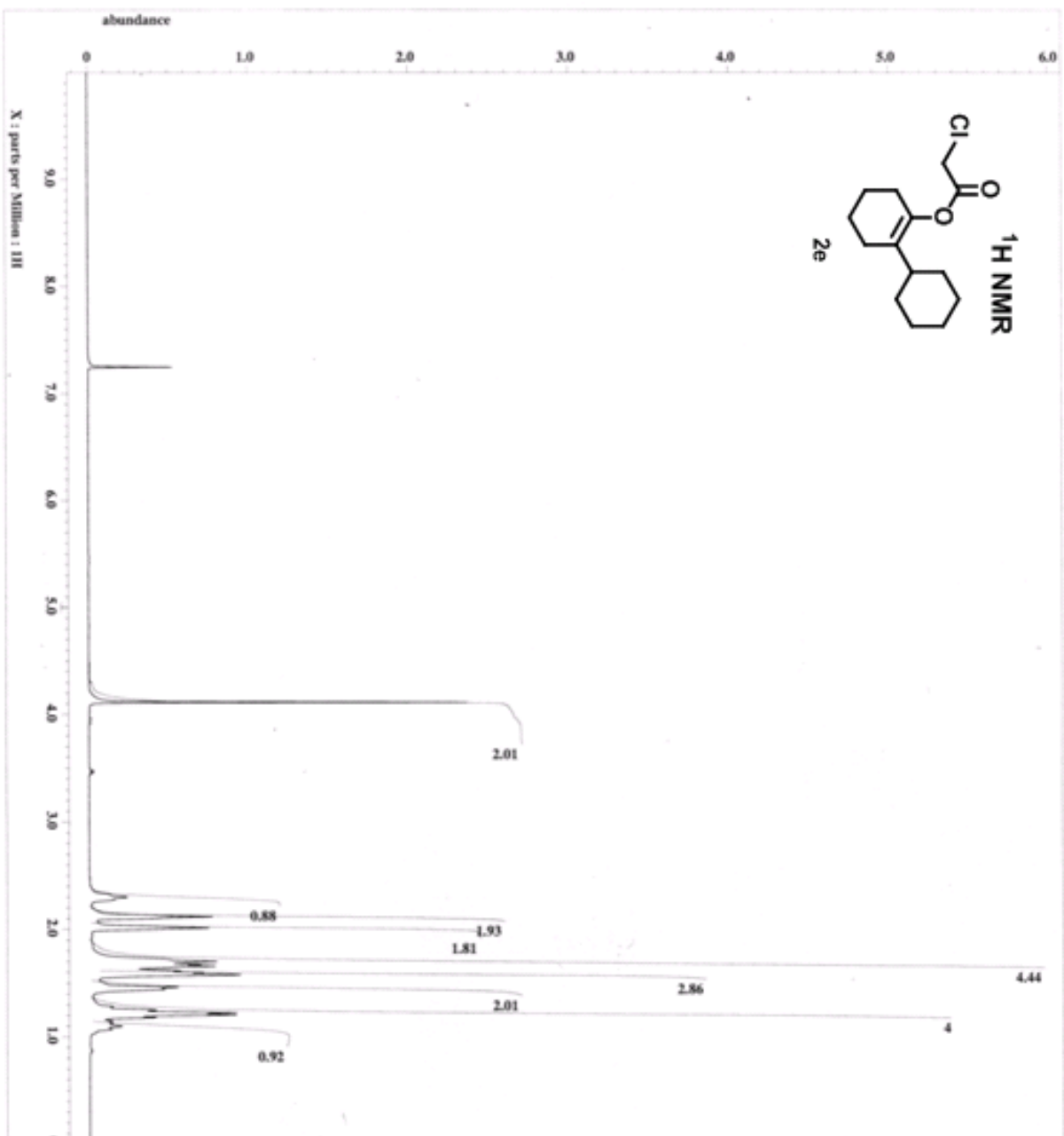




X: parts per Million : 13C

----- PROCESSING PARAMETERS -----
 dc balance : 0 : FALSE
 temp : 2.0 (Hz) : 0.0 (s)
 trapzoid3 : 0 (%) : 90 (%) : 100 (%)
 zerofill : 1
 zft : 1 : TRUE : TRUE
 machinephase
 ppm
 Derived from: EX413C-1.jdf

filename -- EX413C-2.jdf
 author --
 experiment --
 sample_id --
 solvent -- CDCl3
 creation_time -- 2-NOV-2010 12:16:23
 revision_time -- 2-NOV-2010 12:49:52
 current_time -- 2-NOV-2010 12:48:41
 Comment -- single pulse decouple
 Data format -- 1D COMPLEX
 Data size -- 26214
 Data title -- 13C
 Dimensions --
 X (ppm) --
 Y (ppm) --
 Z (ppm) --
 Site -- ECH 400
 Spectrometer -- JNM-ECX400
 field_strength -- 9.38976617 (400 MHz)
 X_acq_duration -- 1.0433312 (s)
 X_domain -- 13C
 X_freq -- 100.5253033 (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 -- 399.79219838 (MHz)
 irr_offset -- 5 (ppm)
 Clipped --
 Mod_return --
 Scans -- 1
 Total_scans -- 202
 X_90_width -- 8.4 (us)
 X_acq_time -- 1.0433312 (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 --
 MALT --
 Decoupling -- TRUE
 Initial_wait -- 1 (s)
 Noe_time --
 Recv_gain -- 2 (s)
 Recv_gain_delay -- 2 (s)
 Repetition_delay -- 2.0433312 (s)
 Repetition_time -- 2.0433312 (s)
 temp_get --



```

----- PROCESSING PARAMETERS -----
DE: Delay: 0.100 PALSE
RG: 0.100000000 0.0100
TR: 0.010000000 0.0100
SFO: 400.1464018
AQ: 1.000000000
RG2: 1.000000000
SI: 32768
WDW: EM
SSB: 0
LB: 0.300000000
GB: 0
PC: 1.000000000
MC: 1.000000000
DC: 0.000000000
SC: 0.000000000
TC: 0.000000000
EC: 0.000000000
BC: 0.000000000
AC: 0.000000000
Derived from: EY142-a-1.j62
  
```

```

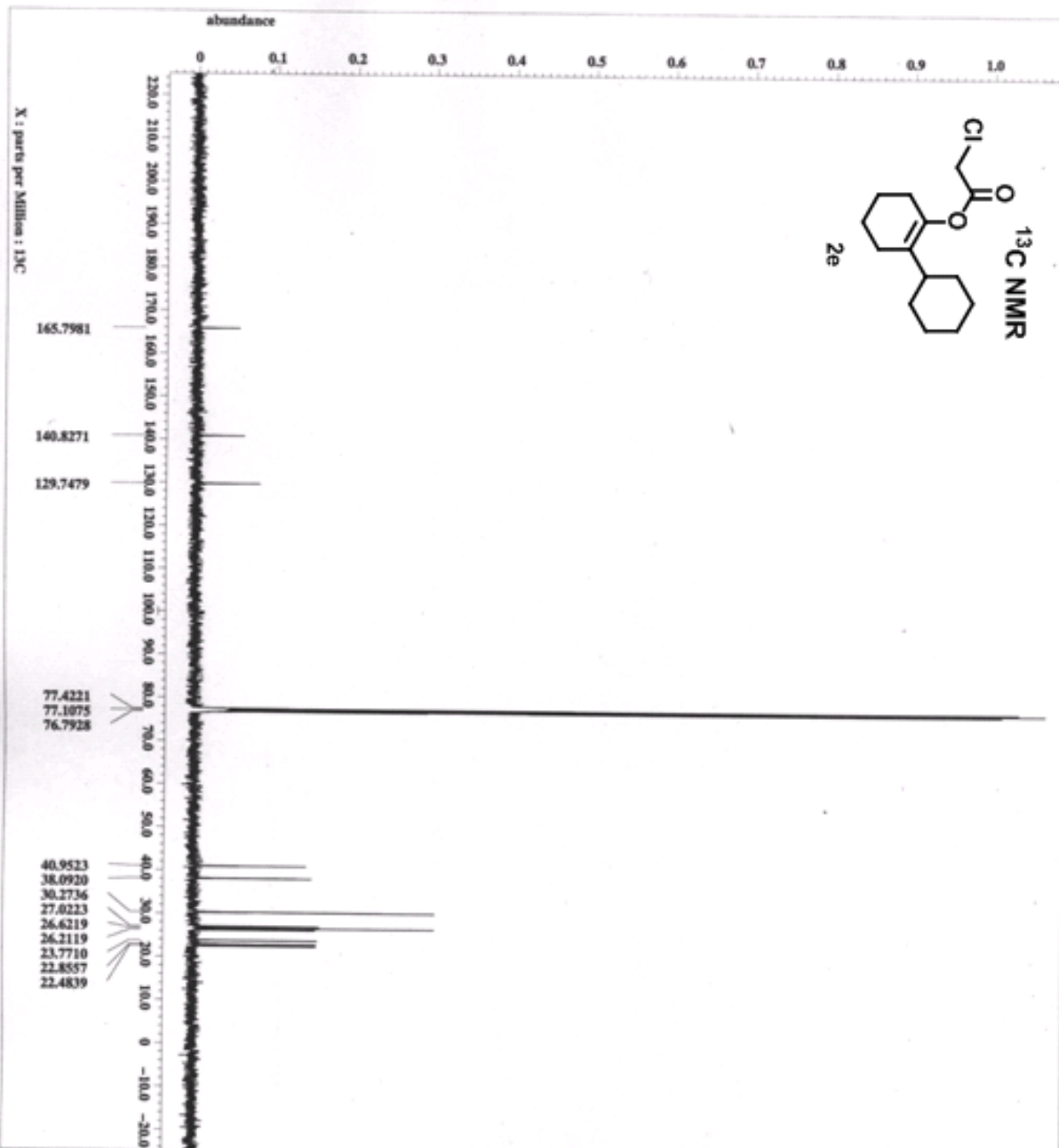
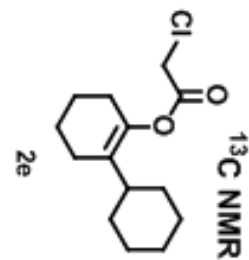
=====
NAME          EY142-a-1.j62
EXPNO         2
PROCNO        1
PROCNAME      EY142-a
DATE_         20101016
TIME          16:13:21
INSTRUM       spect
PROBHD        zgpg30
PULPROG       zgpg30
PCPROG        zgpg30
RECPROG       zgpg30
TD            65536
SFO           400.1464018
AQ            1.00000000
RG            32768
WDW           EM
SSB           0
LB            0.30000000
GB            0
PC            1.00000000
MC            1.00000000
DC            0.00000000
SC            0.00000000
TC            0.00000000
EC            0.00000000
BC            0.00000000
AC            0.00000000
=====
  
```

```

=====
NAME          EY142-a-1.j62
EXPNO         2
PROCNO        1
PROCNAME      EY142-a
DATE_         20101016
TIME          16:13:21
INSTRUM       spect
PROBHD        zgpg30
PULPROG       zgpg30
PCPROG        zgpg30
RECPROG       zgpg30
TD            65536
SFO           400.1464018
AQ            1.00000000
RG            32768
WDW           EM
SSB           0
LB            0.30000000
GB            0
PC            1.00000000
MC            1.00000000
DC            0.00000000
SC            0.00000000
TC            0.00000000
EC            0.00000000
BC            0.00000000
AC            0.00000000
=====
  
```

```

=====
NAME          EY142-a-1.j62
EXPNO         2
PROCNO        1
PROCNAME      EY142-a
DATE_         20101016
TIME          16:13:21
INSTRUM       spect
PROBHD        zgpg30
PULPROG       zgpg30
PCPROG        zgpg30
RECPROG       zgpg30
TD            65536
SFO           400.1464018
AQ            1.00000000
RG            32768
WDW           EM
SSB           0
LB            0.30000000
GB            0
PC            1.00000000
MC            1.00000000
DC            0.00000000
SC            0.00000000
TC            0.00000000
EC            0.00000000
BC            0.00000000
AC            0.00000000
=====
  
```



----- PROCESSING PARAMETERS -----
 de_balance : 0 : FALSE
 sump : 2.0 [Hz] : 0.0 [s]
 trapezoid1 : 0 [N] : 80 [N] : 100 [N]
 sscrfill : 1
 f1c : 1 : TMS : TMS
 machimpbase
 ppm
 Derived from: K143-ac-1.16f

```

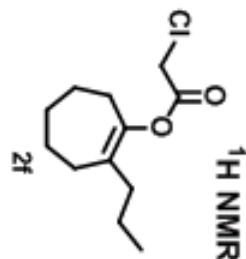
=====
Filename          = K143-ac-2.16f
Author            = dshs
Experiment        = single_pulse_dec
Sample_1d         = K143-ac
Solvent           = CHLOROFORM-D
Creation_time     = 16-07M-2010 17:18:20
Rev1sion_time    = 16-07M-2010 17:33:47
Current_time      = 16-07M-2010 17:33:53

Comment
=====
Data_format      = single pulse decouple
ID_complex       = 1D COMPLEX
Dia_file         = 28214
Dia_title        = 13C
Dia_units        = [ppm]
Dimensions       = X
Size             = 800 400
Sfile            = 08M-K08460

P1aid_strength   = 9.389766 [V] (400 [kHz])
K_eq_dvoretion   = 1.04333312 [s]
K_gain           = 100.5293033 [Hz]
K_freq          = 100.6 [ppm]
K_offset        = 32748
K_police        = 4
K_pulses        = 0.93846665 [Hz]
K_resolution     = 31.40703318 [Hz]
K_sweep         = 399.78218038 [Hz]
Irr_domain      = 5 [ppm]
Irr_freq        = PALSR
Irr_offset      = 1
Mod_return       = 303
Socms           = 303

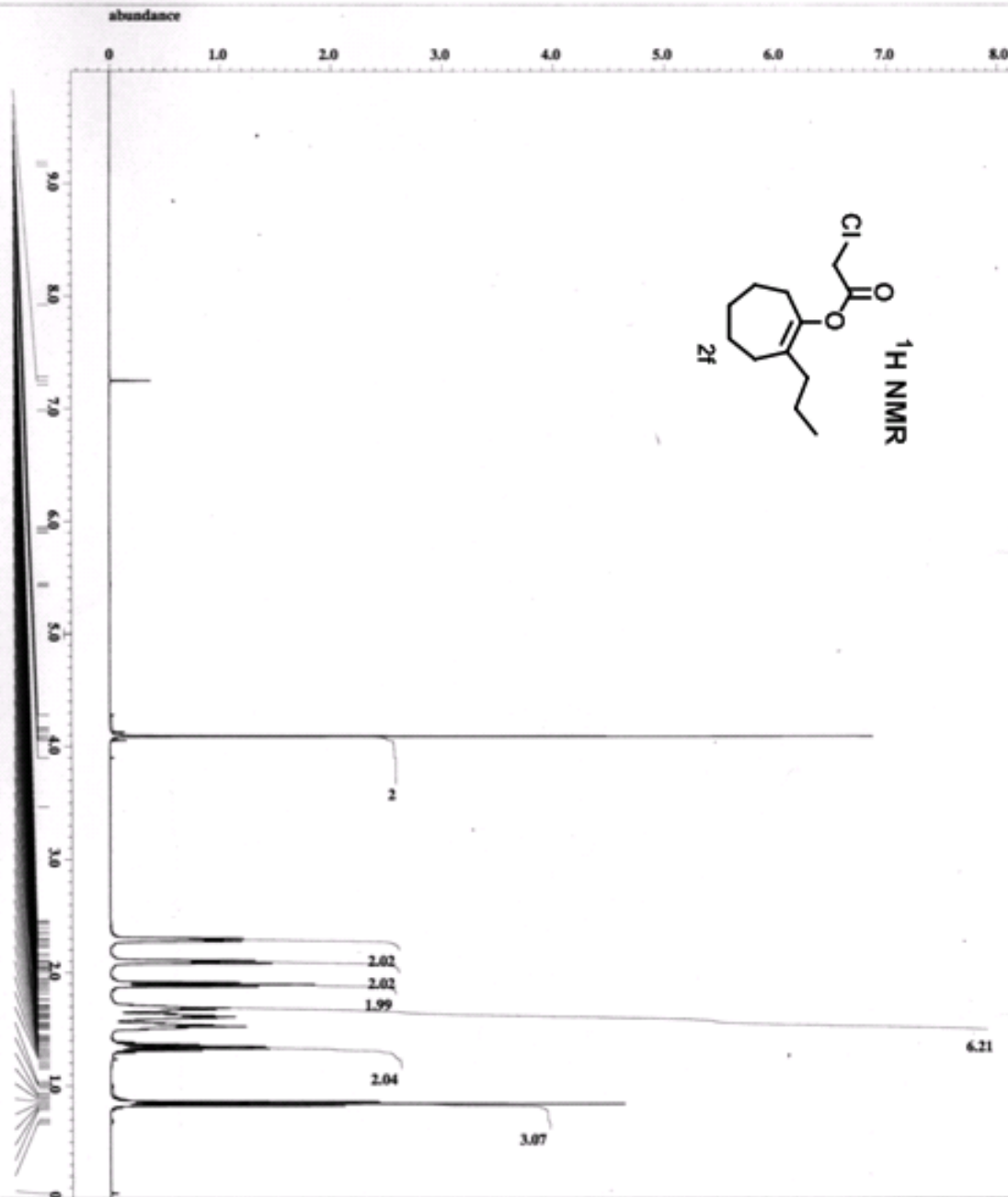
K_j9_widch       = 8.4 [us]
K_aeq_class      = 1.04333312 [s]
K_angle         = 20 [deg]
K_atn           = 4.3 [db]
K_pulse         = 2.8 [us]
Irr_atn_dec     = 21.8 [db]
Irr_atn_poc     = 21.8 [db]
NSC              = NSC78
PDECPOLING      = TMS
PDELTA1_walt    = 1 [s]
PDELTA2         = 2 [s]
PDELTA3         = 2 [s]
PDELTA4         = 40
PDELTA5         = 3.64333312 [s]
PDELTA6         = 21.8 [db]
Temp_spt        = 21.8 [deg]
=====

```



7.2486
4.2806
4.1306
4.0928
4.0744
4.0550
3.9015
2.3413
2.3047
2.2909
2.2772
2.2531
2.2394
2.1477
2.1099
2.0973
2.0836
2.0607
2.0458
2.0343
2.0252
1.9530
1.9347
1.9163
1.8980
1.8785
1.8602
1.8407
1.7709
1.7560
1.7170
1.7056
1.7021
1.6895
1.6758
1.6609
1.6368
1.6311
1.6242
1.6105
1.6002
1.5819
1.5532
1.5475
1.5395
1.5257
1.5131
1.4982
1.4501
1.4226
1.4100
1.4043
1.3860
1.3676
1.3482
1.3298
1.3115
1.2932
1.2737
1.2554
1.2336
1.0148
0.9965
0.9175
0.8980
0.8797
0.8602
0.8419
0.8235
0.8052
0.7869
0.6838
0.0492

X : parts per Million : III



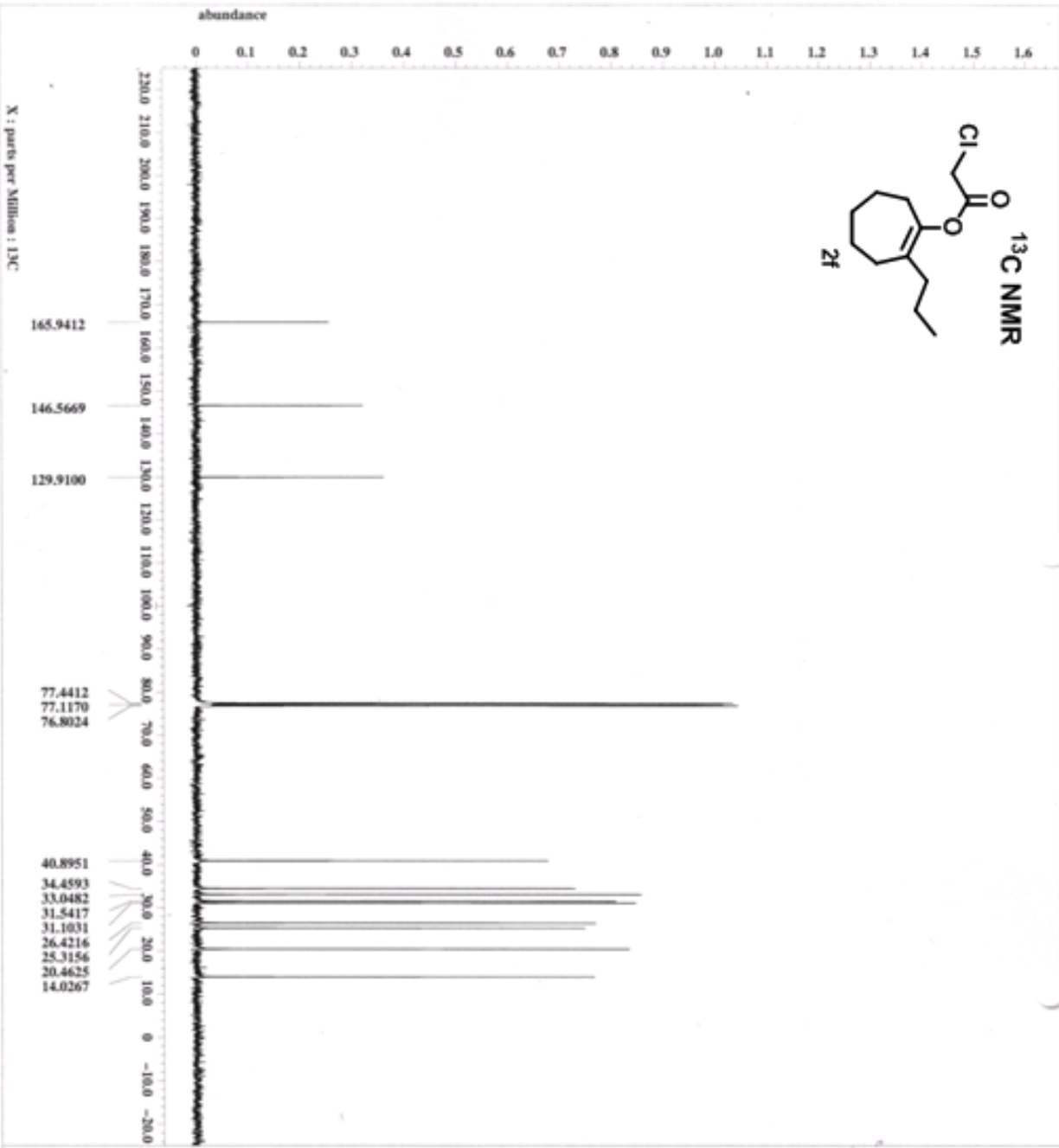
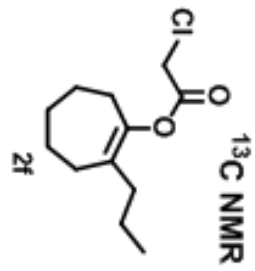
```

----- PROCESSING PARAMETERS -----
do_balance : 0 : FALSE
esep : 0.2[Hz] : 0.01[Hz]
tempref : 0[Hz] : 80[Hz] : 100[Hz]
srfreq : 1 : TRUE : TRUE
machines :
  ppm
Derived from: RT640-1.J02

P1: name
  RT640-1.J02
Author
  gdlc
Experiment
  single_pulse_ew2
Sample_ID
  RT640
Solvent
  CHLOROFORM-D
Creation_time
  7-2008-2010 23:42:35
Revision_time
  7-2008-2010 23:59:41
Current_time
  7-2008-2010 23:00:22

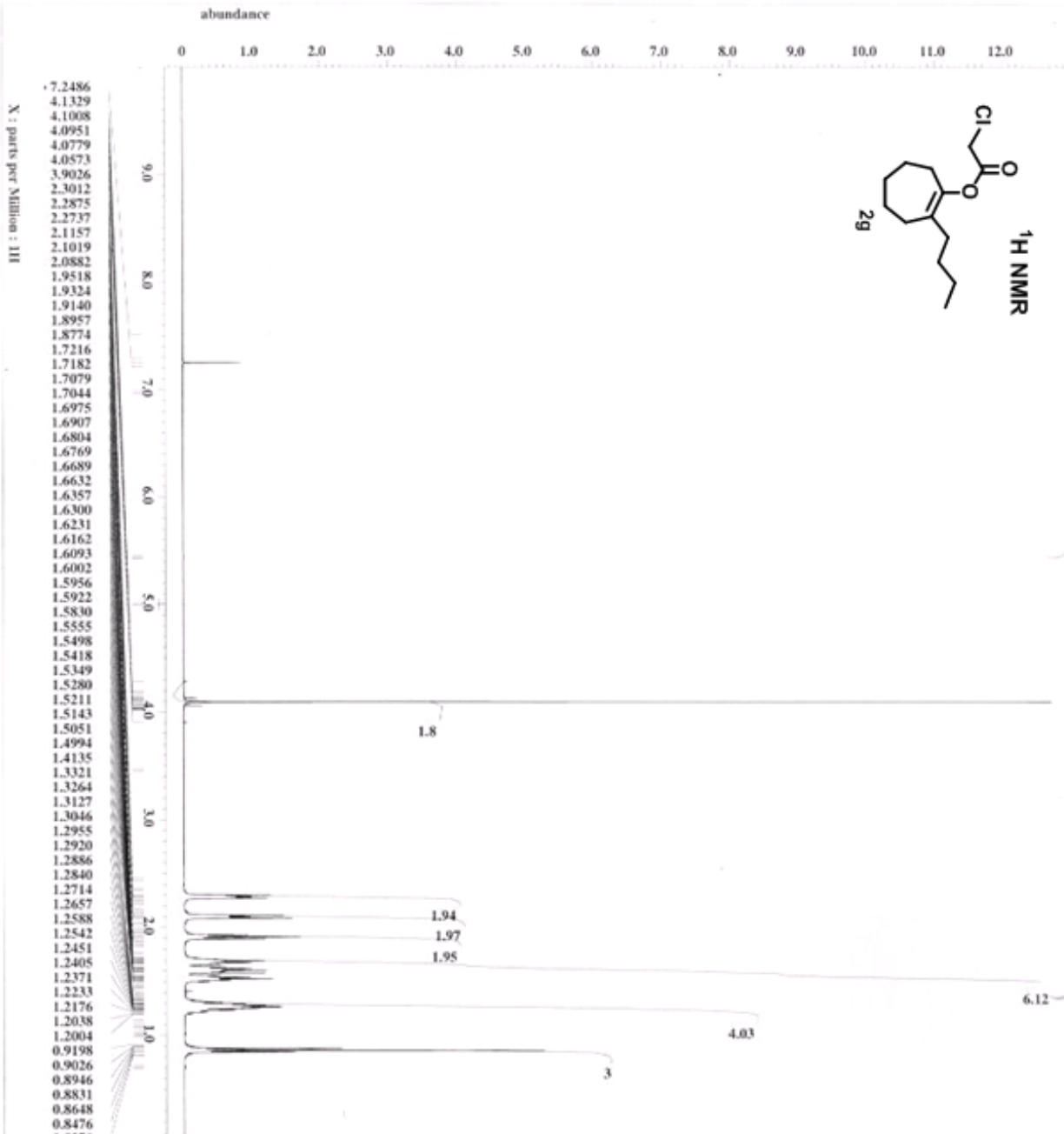
Comment
  Data format
  1D COMPLEX
  13107
  1H
  1H
  D1m, title
  D1m, units
  [ppm]
  X
  Dimensions
  400
  400
  400
  SFC
  JMR-DC6400

Spectrum
  field_strength
  9.38976617 [400 MHz]
  K.domain
  2.18359521[e]
  K.freq
  399.78219838 [MHz]
  K.offest
  91 [ppm]
  K.pulprg
  zgpg30
  K.pulseq
  1
  K.gprescan
  0.45794685 [Hz]
  K.resolutilon
  7.50305012 [Hz]
  K.sweep
  1H
  Irf_domain
  399.78219838 [MHz]
  Irf_freq
  51 [ppm]
  Irf_offest
  1H
  Irf_domain
  399.78219838 [MHz]
  Irf_freq
  51 [ppm]
  Irf_offest
  1H
  CLipped
  FALSE
  Mode_return
  1
  Name
  8
  Total_scans
  8
  K_90_width
  10.5 [us]
  K_acq_time
  2.18359521[e]
  K_ahn
  45 [deg]
  K_atn
  1 [dB]
  K_pulse
  5.25 [us]
  Irf_mode
  OF2
  Irf_mode
  OF2
  Data_preset
  PALSR
  Initial_valt
  1 [us]
  Acqr_gain
  28
  Relaxation_delay
  7.18359521[e]
  Repetition_time
  21.8 [sec]
  Temp_set
  
```

----- PROCESSING PARAMETERS -----
 dq_balance : 0 : FALSE
 sweep : 2.0 [Hz] : 0.0 [s]
 reresolve : 0 [Hz] : 80 [Hz] : 100 [Hz]
 zerofill : 1
 nuc1 : 13 : TRUE : TRUE
 nuc2 : 13 : TRUE : TRUE
 nuc3 : 13 : TRUE : TRUE
 ppm
 Derived from: EY640C-1.Jdf

Filename : EY640C-1.Jdf
 Author :
 Experiment :
 Sample_Id : EY640C
 Solvent : CHLOROFORM-D
 Creation_Time : 7-20M-2010 23:12:16
 Revision_Time : 7-20M-2010 23:12:16
 Current_Time : 7-20M-2010 23:12:16
 Comment :
 Data_Format : * single pulse decouple
 ID_COMPLEX :
 Dia_Size : 26214
 Dia_Unit : 13C
 Dia_Title :
 Dia_Units : [ppm]
 Dimensions : X
 Size :
 Site : ECG 400
 Spectrometer : JNM-ECX400
 Field_Strength : * 9.389766 [Hz] (400 [MHz])
 K_acq_duration : 1.043333 [s]
 K_domain : 13C
 K_freq : 100.5250333 [MHz]
 K_offset : 100 [ppm]
 K_pulses : 32768
 K_prescans : 4
 K_resolution : * 0.9584645 [Hz]
 K_sweep : 31.4070318 [MHz]
 Irr_domain : 1W
 Irr_freq : 399.78219838 [MHz]
 Irr_offset : 5 [ppm]
 C11Speed : PALMR
 Mod_return : 1
 Secans : 208
 Total_Scans : 208
 K_90_width : * 8.4 [us]
 K_acq_time : * 1.043333 [s]
 K_angle : * 30 [deg]
 K_atn : * 4.3 [dB]
 K_pulse : * 2.8 [us]
 Irr_atn_dac : * 21.8 [dB]
 Irr_atn_doe : * 21.8 [dB]
 Irr_noise : * WALTZ
 Decoupling : * TWOR
 Initial_Wait : * 1 [s]
 Hsu_Time : * 2 [s]
 Recv_Gain : * 40
 Relaxation_Delay : * 2 [s]
 Repetition_Time : * 1.043333 [s]
 Temp_Sett : * 21.5 [C]



----- PROCESSING PARAMETERS -----
 ac_balance : 0 : FALSE
 temp : 0.2[Hz] : 0.0[s]
 threshold : 0 [%] : 80 [%] : 100 [%]
 ref : 1 : TMS : TMS
 machinename :
 ppm
 Derived from: KW641-1.fid

FileNames : KW641-3.fid
 Author :
 Experiment : single_pulse-ew2
 Sample_ID : KW641
 Solvent : CDCl3/POPCN-D
 Creation_Time : 7-JUN-2010 21:03:40
 Revision_Time : 7-JUN-2010 21:20:24
 Current_Time : 7-JUN-2010 21:20:49

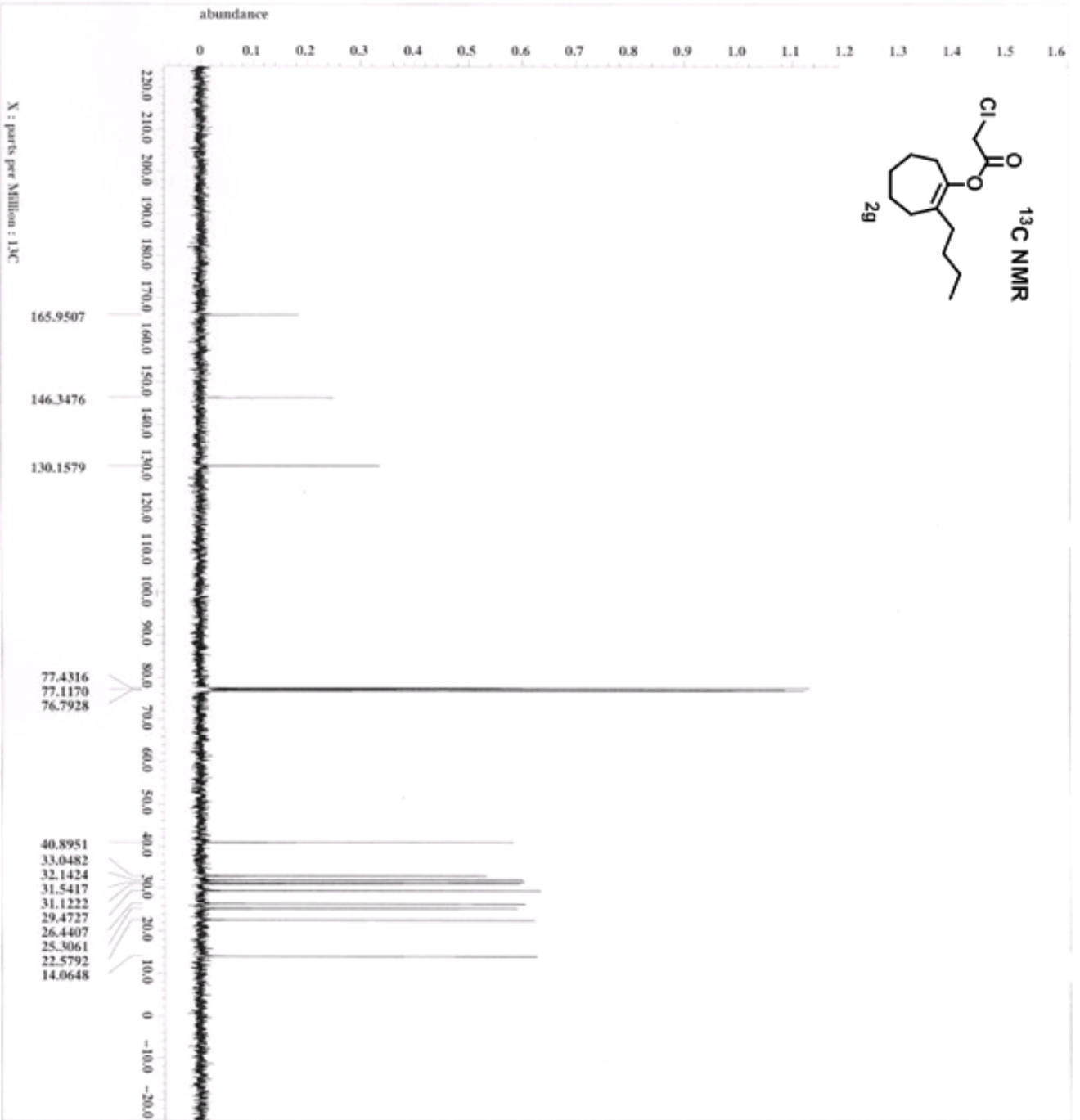
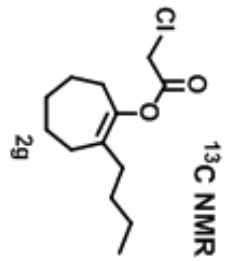
Comment :
 Data_Format : single pulse
 Data_Steps : 13107
 Dir_List :
 Dir_Unit : [ppm]
 Dimensions : X
 File :
 Site : KCS 400
 Spectrometer : JNM-ECX400

Field_strength : 9.38976171 [400 [MHz]]
 X_acq_duration : 2.18365921[s]
 X_domain : 1H
 X_freq : 399.782198380 [MHz]
 X_offset : 5 [ppm]
 X_points : 16384
 X_prescans : 1
 X_resolution : 0.45794685 [Hz]
 X_sweep : 7.5020012 [kHz]
 Irr_domain : 1H
 Irr_freq : 399.782198380 [MHz]
 Irr_offset : 5 [ppm]
 Tri_domain : 1H
 Tri_freq : 399.782198380 [MHz]
 Tri_offset : 5 [ppm]
 Clipped : FALSE
 Mod_return : 1
 Scans : 8
 Total_scans : 8

X_90_width : 10.9 [us]
 X_acq_time : 2.18365921[s]
 X_angle : 45 [deg]
 X_atn : 1 [dB]
 X_pulse : 5.25 [us]
 Irr_mode : OFE
 Tri_mode : OFE
 Dante_presat : FALSE
 Initial_wait : 1[s]
 Recvr_gain : 30
 Relaxation_delay : 7.18365921[s]
 Repetition_time : 20.9 [s]
 Temp_99c :

7.2486
 4.1329
 4.1008
 4.0951
 4.0779
 4.0573
 3.9026
 2.3012
 2.2875
 2.2737
 2.1157
 2.1019
 2.0882
 1.9518
 1.9324
 1.9140
 1.8957
 1.8774
 1.7216
 1.7182
 1.7079
 1.7044
 1.6975
 1.6907
 1.6804
 1.6769
 1.6689
 1.6632
 1.6357
 1.6300
 1.6231
 1.6162
 1.6093
 1.6002
 1.5956
 1.5922
 1.5830
 1.5555
 1.5498
 1.5418
 1.5349
 1.5280
 1.5211
 1.5143
 1.5051
 1.4994
 1.4135
 1.3321
 1.3264
 1.3127
 1.3046
 1.2955
 1.2920
 1.2886
 1.2840
 1.2714
 1.2657
 1.2588
 1.2542
 1.2451
 1.2405
 1.2371
 1.2233
 1.2176
 1.2038
 1.2004
 0.9198
 0.9026
 0.8946
 0.8831
 0.8648
 0.8476
 0.8270

X : parts per Million : 1H



----- PROCESSING PARAMETERS -----
 dc_balance : 0 : FALSE
 freq : 2.0161 : 0.0161
 temperature : 0 : 80 : 80 : 1
 ref : 1 : TRUE : TRUE
 machinephase
 ppm

Derived from: KY641C-2_copy-4

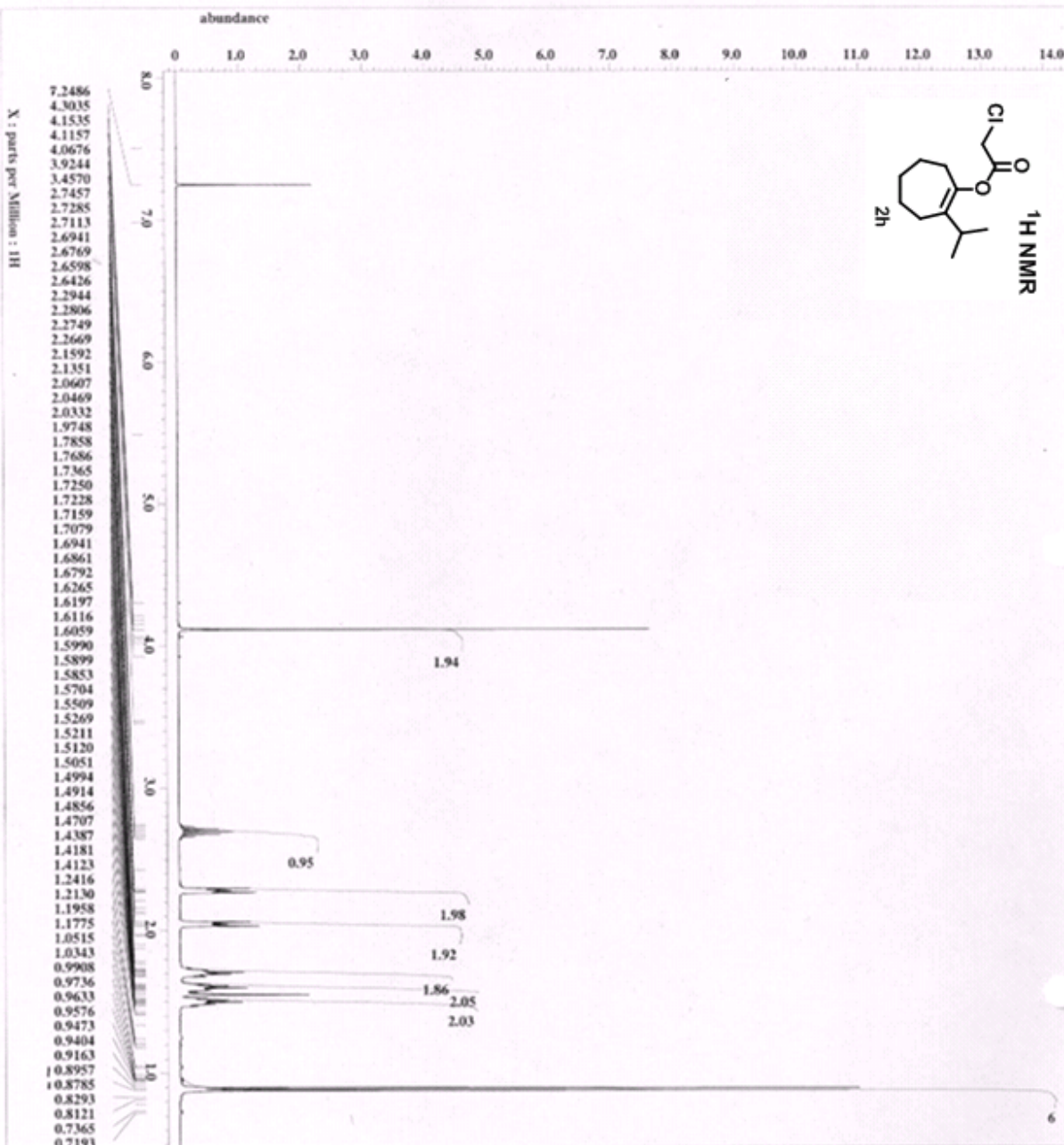
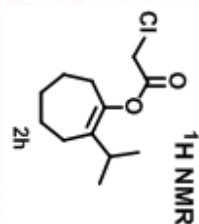
Filename : KY641C-2_0
 Author :
 Experiment :
 Sample_ID : KY641C-2
 Solvent :
 Creation_time : 7-JUN-2011
 Revision_time : 7-JUN-2011
 Current_time : 7-JUN-2011

Comment :
 Data_Format : single pul
 Dia_size : 10 COMPLEX
 Dia_title : 26214
 Dia_units : 13C
 Dimensions :
 Site : X
 Spectrometer : ECR 400
 JMR-KCS400

Field_strength : 9.38976617
 X_acq_duration : 1.0433312
 X_domain : 13C
 X_freq : 100.525309
 X_offset : 100.000000
 X_pulses : 32768
 X_prescans : 4
 X_resolution : 0.95846665
 X_sweep : 31.40703511
 X_domain : 13C
 X_freq : 399.782198
 X_offset : 510000
 X_resolution : 100.000000
 X_sweep : 31.40703511

IR_domain :
 IR_freq : 399.782198
 IR_offset : 510000
 CLIPPED : FALSE
 Incomplete_copy : TRUE
 Mod_return : 1
 Scans : 102
 Total_scans : 102

X_90_width : 8.4[us]
 X_acq_time : 1.0433312
 X_angle : 30[deg]
 X_atn : 4.3[dB]
 X_pulse : 2.8[us]
 IR_atn_dec : 21.8[dB]
 IR_atn_pos : 21.8[dB]
 HALFT :
 IR_noise : TRUE
 Decoupling : TRUE
 Initial_wait : 1[us]
 Recv_time : TRUE
 Recv_gain : 60
 Relaxation_delay : 2[us]
 Repetition_time : 3.0433312
 Temp_ges : 21.1[deg]



```

----- PROCESSING PARAMETERS -----
qc_balance : 0 : PALSE
temp : 0.21[Hz] : 0.01[s]
trap(sold) : 0 [%] : 80 [%] : 100 [%]
refill : 1
etc : 1 : TRUC : TRUC
machinphase
ppm
Derived from: EY208-1.5df

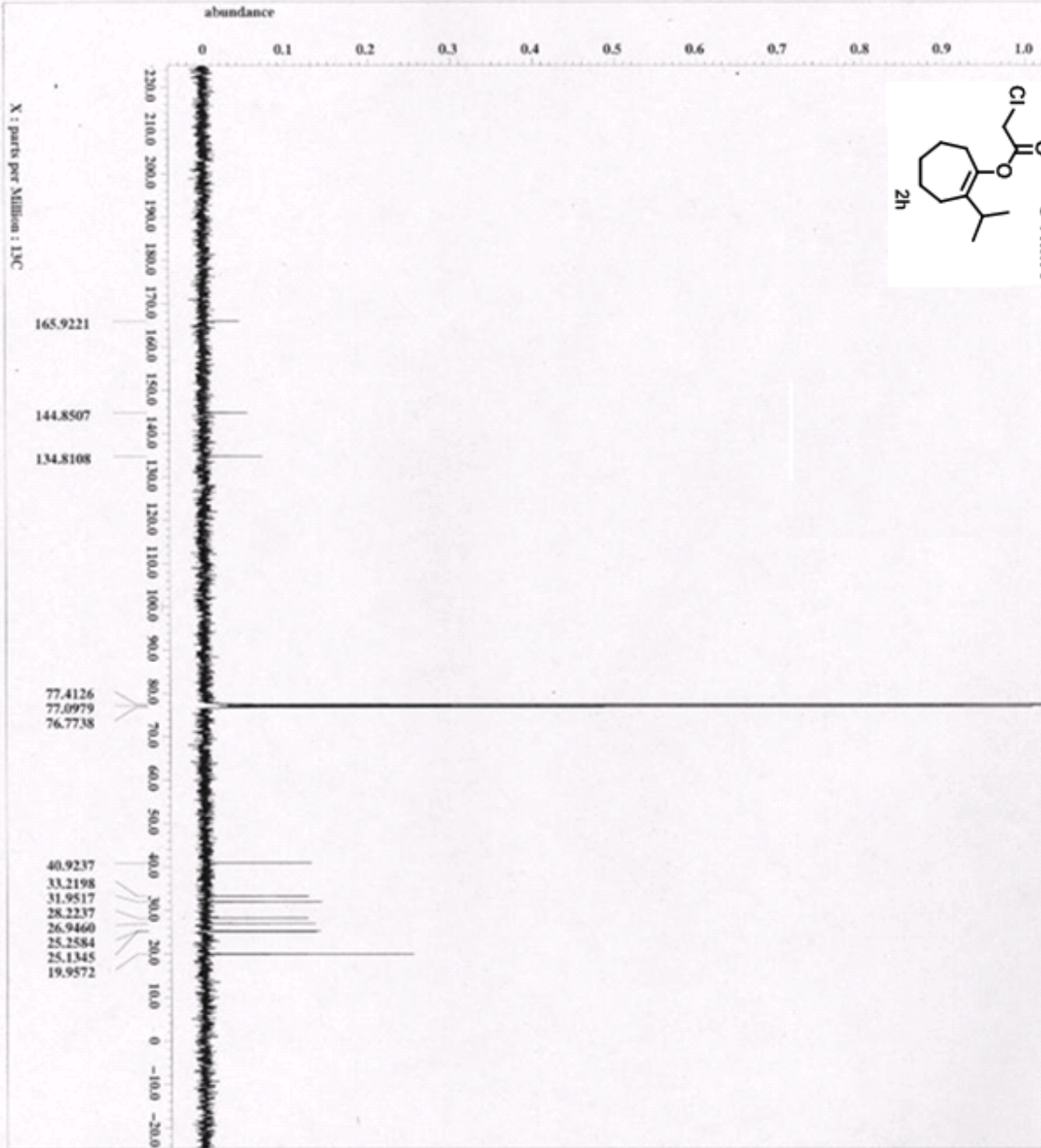
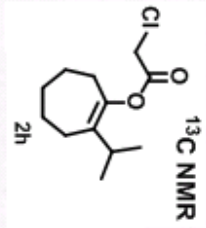
File Name          = EY208-1.5df
Date               = date
Author            =
Experiment        = single_pulse.exe
Sample_Jd         = EY208
Solvent           = CH2CL2/FORM-D
Creation_time     = 5-AUG-2009 11:23:43
Revision_time    = 5-AUG-2009 11:26:15
Current_time      = 5-AUG-2009 11:26:47

Comment
Data format      = single_pulse
ID COMPLEX       =
Dil. size        = 13107
Dil. title       =
Dil. units       = [ppm]
Dimensions       = X
Site             = ECU 400
Spectrometer     = JNM-ECX400

Field strength   = 9.1897661[Hz] (400[MHz])
Acq duration     = 2.181859521[s]
X_domain         =
X_freq           = 399.78219838[MHz]
X_offset         = 51[ppm]
X_police         = 16384
X_prescan        = 0.457946851[Hz]
X_resolution     = 7.50300212[MHz]
X_sweep          = 18
F1_domain        =
F1_freq          = 399.78219838[MHz]
F1_offset        = 51[ppm]
F1_domain        =
F1_freq          = 399.78219838[MHz]
Mod return       = PALSE
Scans            = 1
Total_scans      = 8

X_90_width      = 10.21[us]
X_acq_time       = 2.181859521[s]
X_angle          = 45[deg]
X_atn            = 1[GM]
X_pulse         = 5.11[us]
X_mode           = OFE
X_offset         = OFE
Dmote_preat     = PALSE
Tril_mode        = 1[s]
Initial_wait     = 40
Recvr_gain       = 51[s]
Relaxation_delay = 7.181859521[s]
Repetition_time = 231[sec]
Temp_cel         =

```



```

----- PROCESSING PARAMETERS -----
dc_balance : 0 : FALSE
resol : 2.0 [Hz] : 0.016
residuals : 0 [Hz] : 80 [Hz] : 100 [Hz]
f2 : 125.761 [MHz] : TRUE
machine : TRUC
machinephase
ppm

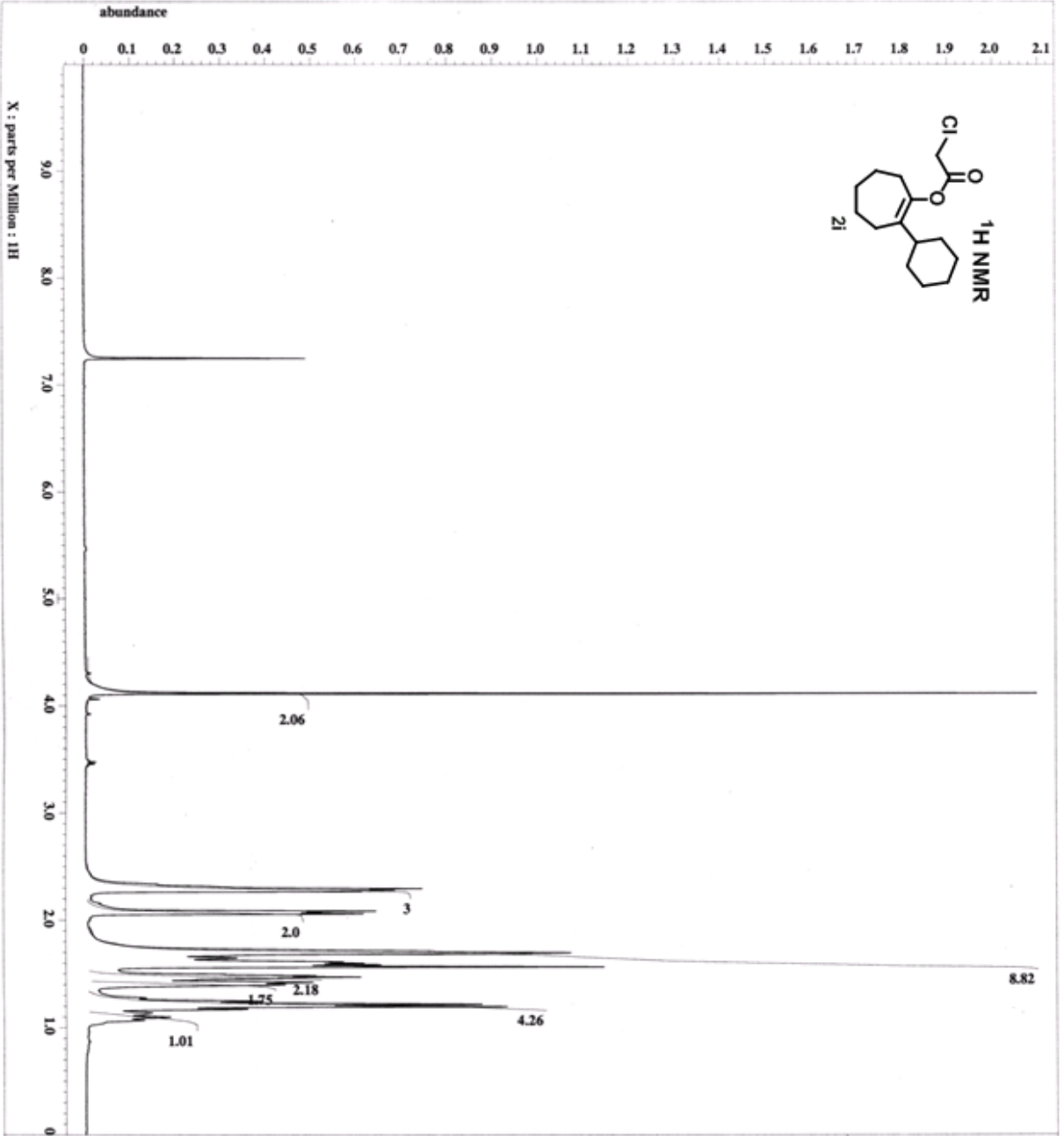
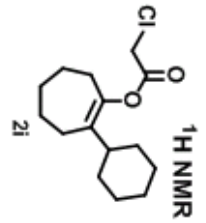
Derived from: EY208 13C_copy-3.fdd

Filename = EY208 13C_copy-3.fdd
Author =
Experiment =
Sample_id = EY208 13C
Solvent = CHLOROFORM-D
Creation_time = 5-AUG-2009 11:28:09
Revision_time = 5-AUG-2009 11:37:00
Current_time = 5-AUG-2009 11:37:10

Comment =
  * single pulse decouple
  * 1D_CPMAS
Data_format = 2d214
Dir_name = 13C
Dilution = [ppm]
Dimensions = X
Site = X
Spectrometer = JNM-EC6400

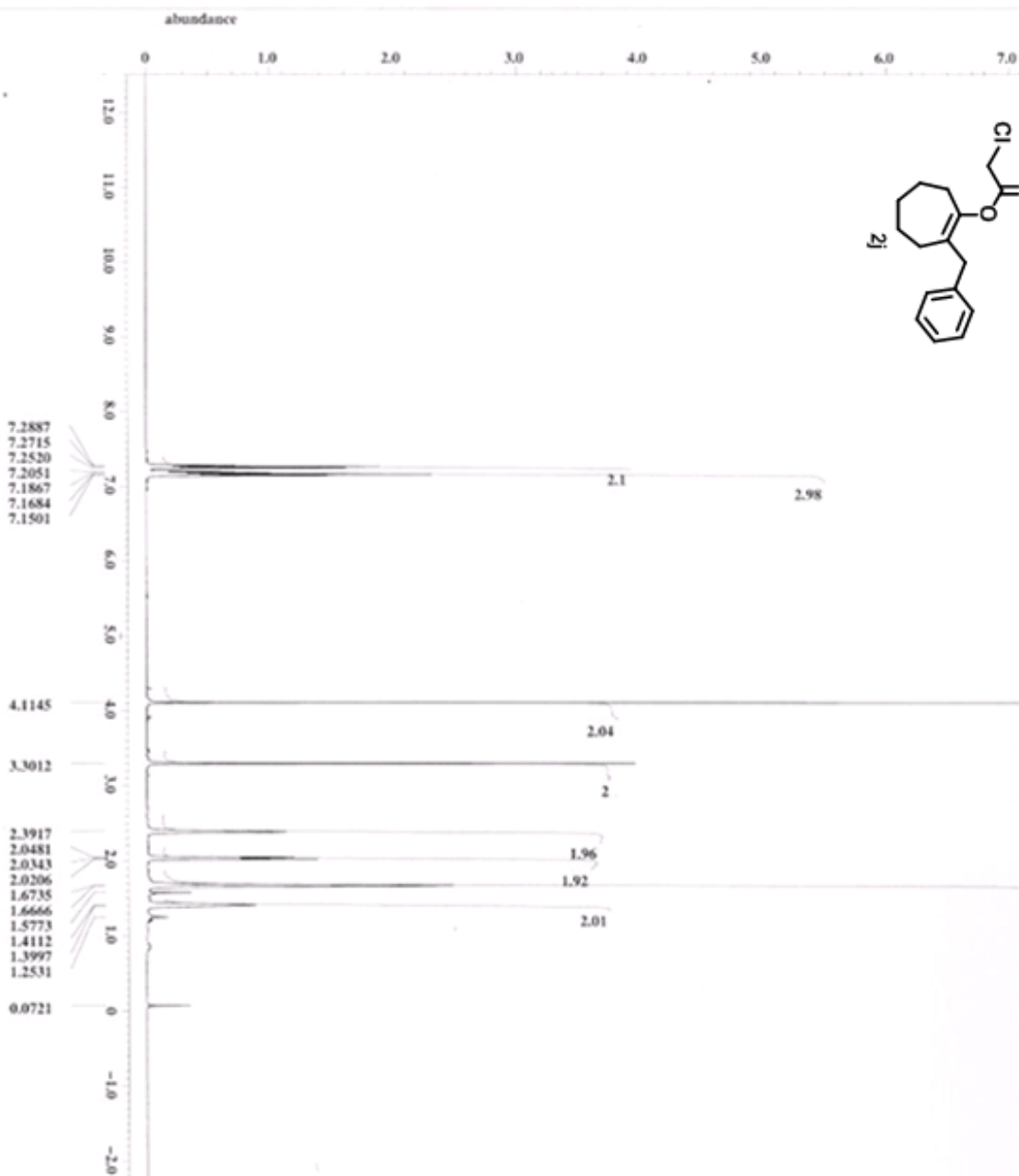
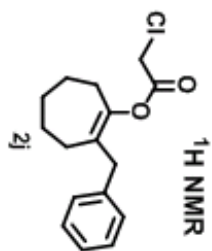
Field_strength = 9.389766 [T] (400 [MHz])
Acq_duration = 1.0633312 [s]
Domain = 13C
Freq = 100.5350333 [MHz]
Offset = 100 [ppm]
Points = 32768
Preprocs = 4
Resolution = 0.9584665 [Hz]
Sweep = 31.40703518 [kHz]
Irr_domain = 1W
Irr_freq = 399.78219838 [MHz]
Irr_offset = 5 [ppm]
C11ppd = FALSE
Incomplete_copy = TRUE
Mod_return = 1
Scans = 201.0
Total_scans = 201.0

X_90_width = 8.4 [us]
X_acq_time = 1.0633312 [s]
X_angle = 10 [deg]
X_atn = 2.8 [dB]
X_cp = 3.8 [dB]
X_pulse = 22 [dB]
X_rf_atn_dec = 22 [dB]
X_rf_atn_inc = 22 [dB]
X_rf_atn = 22 [dB]
X_rf_atn = 22 [dB]
Decoupling = TRUE
Initial_wait = 1 [s]
Xpwr = TRUE
Xpwr = 2 [g]
Xpwr = 40
Relaxation_delay = 2 [s]
Relaxation_delay = 3.0433312 [s]
Temp_set = 23.3 [degC]
  
```



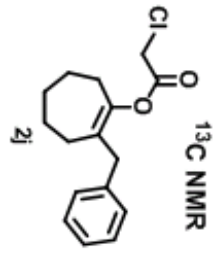
----- PROCESSING PARAMETERS -----
 dc_balance : 0 : FALSE
 hscq : 0.2 [Hz] : 0.0 [s]
 trapsoild3 : 0 [%] : 80 [%] : 100 [%]
 zerofill : 1
 etc : 1 : TRUE : TRUE
 machinename
 ppm
 Derived from: EY264-2.jdt

Filename = EY264-4.jdt
 Author = delta
 Experiment = single_pulse.exe
 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 = ID COMPLEX
 Dia_size = 13107
 Dia_ticlie = 1H
 Dia_units = [ppm]
 Dimensions = X
 Site = XCS 400
 Spectrometer = JNM-ECZ400
 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_pulprg = 16384
 X_procscm = 1
 X_resolution = 0.45849727 [Hz]
 X_sweep = 7.51201823 [kHz]
 Irr_domain = 1H
 Irr_freq = 399.78219838 [MHz]
 Irr_offset = 5 [ppm]
 Tri_domain = 1H
 Tri_freq = 399.78219838 [MHz]
 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 = OFE
 Tri_mode = OFE
 Dance_preatc = FALSE
 Initial_wait = 1 [s]
 Recv_gain = 38
 Relaxation_delay = 2.18103808 [s]
 Repetition_time = 2.18103808 [s]
 Temp_set = 21.31 [C]

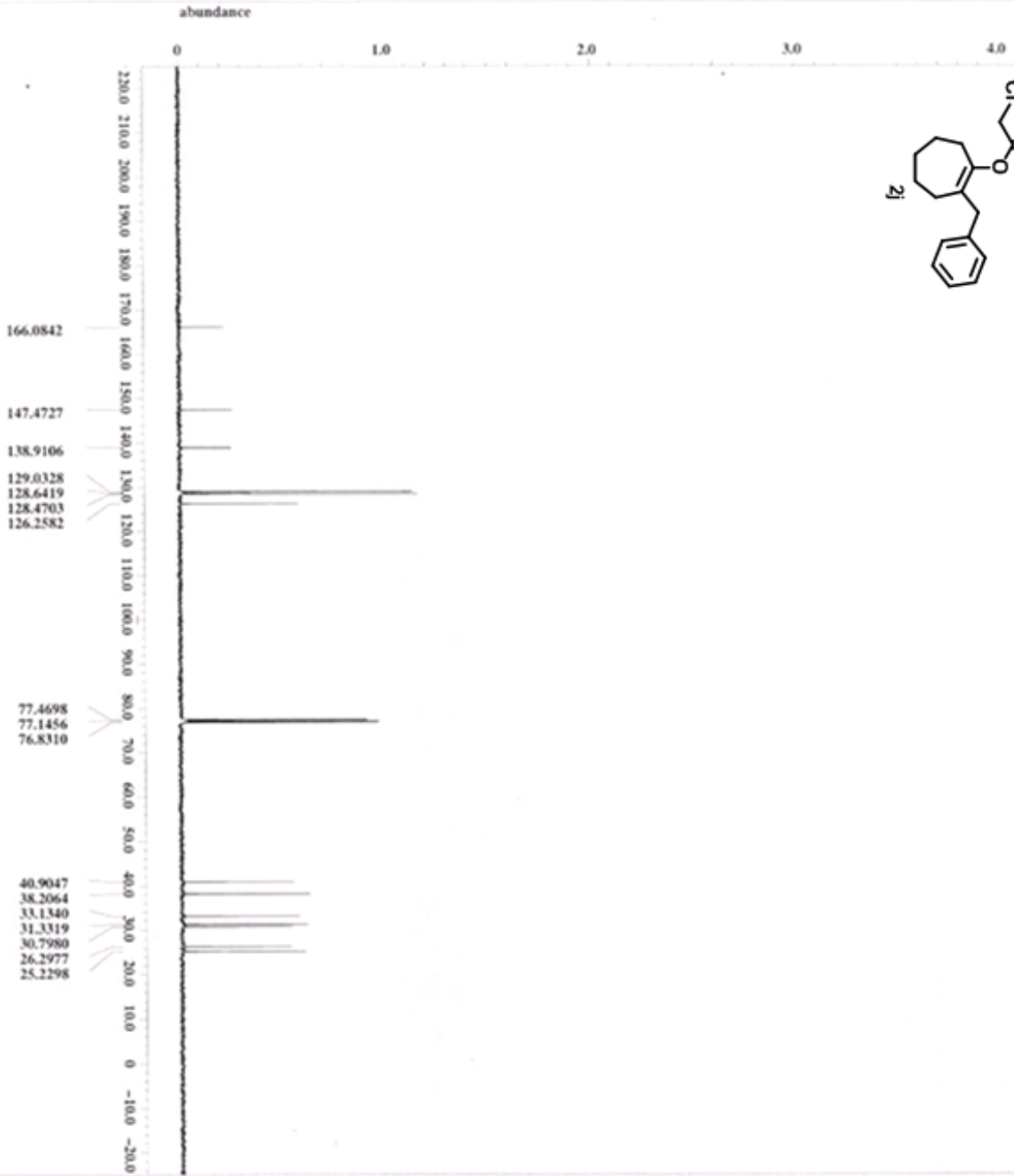


----- PROCESSING PARAMETERS -----
 dc_balance : 0 : FALSE
 smp : 0.3 [Hz] : 0.0 [s]
 tps (ppm) : 0 [N] : 80 [N] : 100 [N]
 zerofill : 1
 f2c : 1 : TRUE : TRUE
 machbase
 ppm
 Derived from: EX475 tms-1.5dd

Filename : EX475 tms-1.5dd
 Author :
 Experiment :
 Sample_Idx :
 SOLVENT : CDCl3
 Acquisition_Time : 19-FEB-2010 23:49:17
 Resolution_Time : 19-FEB-2010 23:09:07
 Current_Time : 19-FEB-2010 23:09:20
 Comment :
 Data_Format : * single_pulse
 ID_Complex :
 Dia_Axis : 131.07
 Dia_Unit : [ppm]
 Dimensions : X
 Site : X
 ECR : 400
 Spectrometer : JNM-ECX400
 Field_Strength : 9.38766 [T] (400 [MHz])
 X_Acq_Duration : 2.1836592 [s]
 X_Domain : 1K
 X_Freq : 399.78219838 [MHz]
 X_Offset : 5 [ppm]
 X_Points : 16384
 X_Pressure : 1
 X_Resolution : 0.45794685 [Hz]
 X_Sweep : 7.5030012 [kHz]
 ZF_Domain : 1K
 ZF_Freq : 399.78219838 [MHz]
 ZF_Offset : 5 [ppm]
 ZF_Domain : 1K
 ZF_Freq : 399.78219838 [MHz]
 ZF_Offset : 5 [ppm]
 Mod_Return : FALSE
 Num_Scans : 1
 Secans : 8
 Total_Scans : 8
 X_90_Width : 10.2 [us]
 X_Acq_Time : 2.1836592 [s]
 X_Angle : 45 [deg]
 X_Atn : 1 [dB]
 X_Pulse : 5.1 [us]
 ZF_Mode : ORT
 ZF_Offset : 0 [ppm]
 Dance_Preset : FALSE
 Initial_Volt : 1 [V]
 Recv_Txain_Delay : 7 [ns]
 Repetition_Time : 2.1836592 [s]
 Temp_Spec : 18.6 [C]



X : parts per Million : 13C



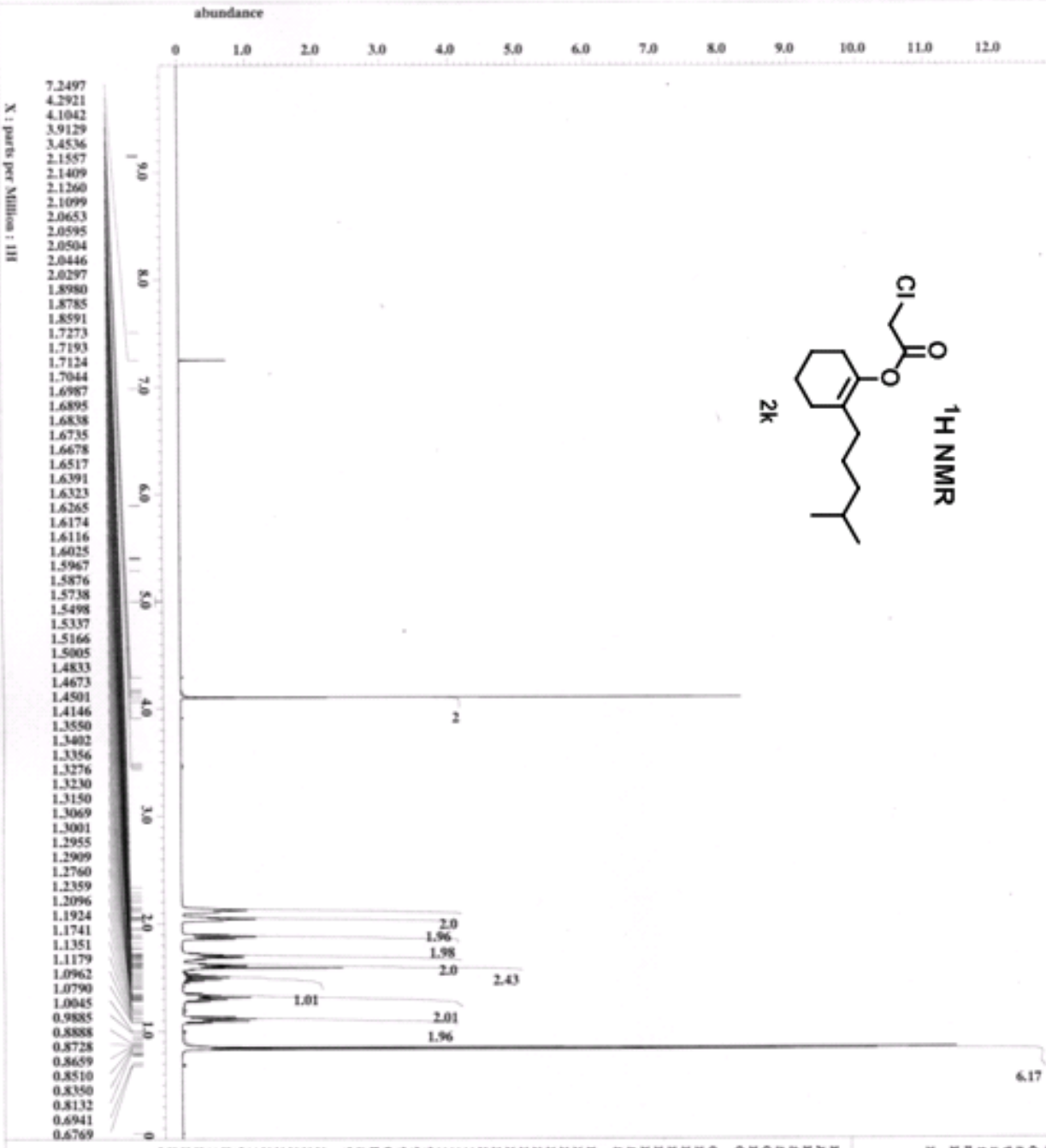
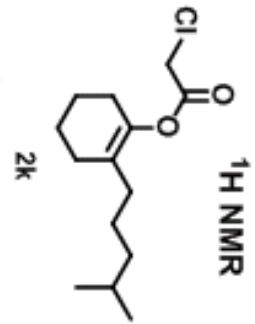
----- PROCESSING PARAMETERS -----
 dc balance : 0 : FALSE
 freq : 125.761 (MHz) : 0.016
 trapratio : 0 (dB) : 80 (dB) : 100 (dB)
 resolution : 1
 ref : 1 : TMS : TMS
 machtype : phase
 ppm
 Derived from: EY475 true C-1.fid

Filename = EY475 true C-2.fid
 Author = delta
 Experiment = single_pulse_dec
 Sample_id = EY475 true C
 Solvent = CDCl3
 Creation_time = 19-FEB-2010 23:09:18
 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 = ECH 400
 Spectrometer = JNM-ECX400

Field_strength = 9.389766 (T) (400 (MHz))
 Acq_duration = 1.0413312 (s)
 Domain = 13C
 Freq = 100.5253033 (MHz)
 Offset = 100 (ppm)
 Points = 32768
 Prescans = 4
 Resolution = 0.9584665 (Hz)
 Sweep = 31.40703518 (kHz)
 Irf_domain = 1H
 Irf_freq = 399.78219838 (MHz)
 Irf_offset = 5 (ppm)
 Clipped = FALSE
 Mod_return = 1
 Scans = 162
 Total_scans = 162

X 90_width = 8.4 (us)
 X acq_time = 1.0413312 (s)
 X angle = 30 (deg)
 X alt = 4.3 (dB)
 X pulse = 2.8 (us)
 Irf_acq_dec = 22 (dB)
 Irf_acq_noise = 22 (dB)
 Irf_noise = 20 (dB)
 Decoupling = TMS
 Initial_wait = 1 (s)
 Noise_time = 2 (s)
 Recvr_gain = 60
 Relaxation_delay = 2 (s)
 Repetition_time = 3.0413312 (s)
 Temp_get = 18.8 (C)

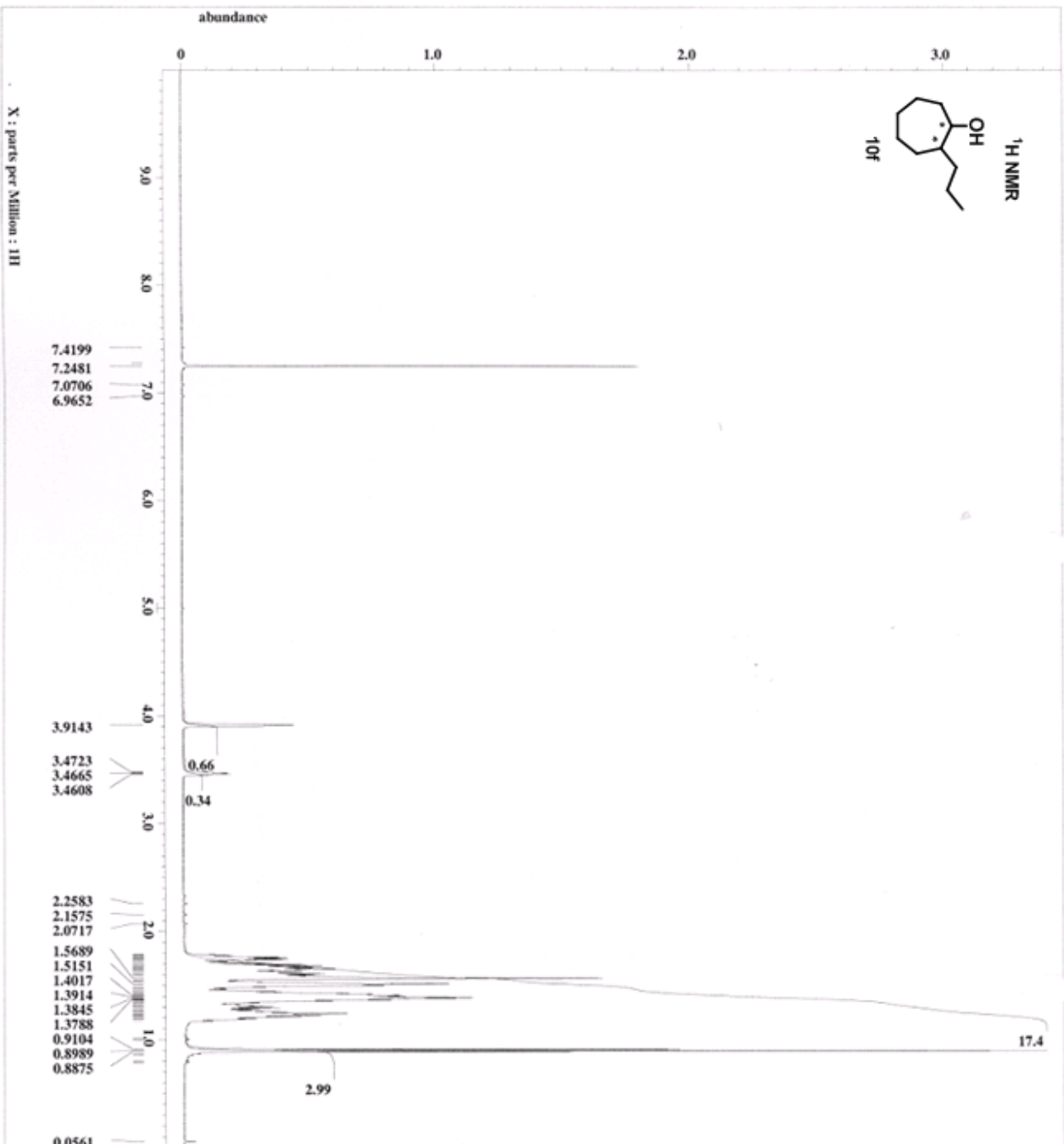
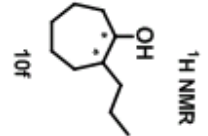


X : parts per Million : 1H

----- PROCESSING PARAMETERS -----
 ac_balance : 0 : FALSE
 acq : 0.21[Hz] : 0.01[s]
 c16pct : 0.01[Hz] : 801[N] : 100[N]
 c16pct : 1
 c16pct : 1 : TRUE : TRUE
 machimpbase :
 ppm
 Derived from: EY655-1.fid

```

PILNAME      EY655-1.fid
AUTHOR
EXPERIMENT   EY655
SAMPLE_ID    CHEMORFORM-D
SOLVENT      CDCl3
CREATION_TIME 14-09-2010 23:04:02
REVISION_TIME 14-09-2010 23:21:46
CURRENT_TIME  14-09-2010 23:22:11
-----
COMMENT
DATA_FORMAT  1D CompF1X
DIR_PATH     131.07
DIR_TITLE    [ppm]
DIR_UNITS
DIMENSIONS
SILE          0
SOLVENT      CDCl3
SPECTROMETER JNM-PC8400
-----
FIELD_STRENGTH 9.209766171 [400[MHz]]
DIR_DIRECTION  -2.18565921[s]
DIR_ANGLE     359.782198987[MHz]
DIR_ANGLE     359.782198987[MHz]
DIR_ANGLE     16384
DIR_ANGLE     1
DIR_ANGLE     0.457944851[Hz]
DIR_ANGLE     7.30300121[MHz]
DIR_ANGLE     359.782198987[MHz]
DIR_ANGLE     359.782198987[MHz]
DIR_ANGLE     359.782198987[MHz]
DIR_ANGLE     PALSER
DIR_ANGLE     1
DIR_ANGLE     8
DIR_ANGLE     8
-----
X_90_width    = 10.5[us]
X_acq_time     = 2.18565921[s]
X_ang1         = 451[deg]
X_ang2         = 1[deg]
X_ang3         = 5.25[us]
X_pulse        = OFF
X_pulse2       = OFF
X_pulse3       = OFF
X_pulse4       = PALSER
X_pulse5       = 1[s]
X_pulse6       = 30
X_pulse7       = 7.18565921[s]
X_pulse8       = 21.31[deg]
  
```



```

----- PROCESSING PARAMETERS -----
dc_balance : 0 : FALSE
smp : 0.2[Hz] : 0.0[s]
trepoid(s) : 0(s) : 80(s) : 100(s)
zerofill : 1
f1 : 1 : TMR : TMR
machnepname
ppm

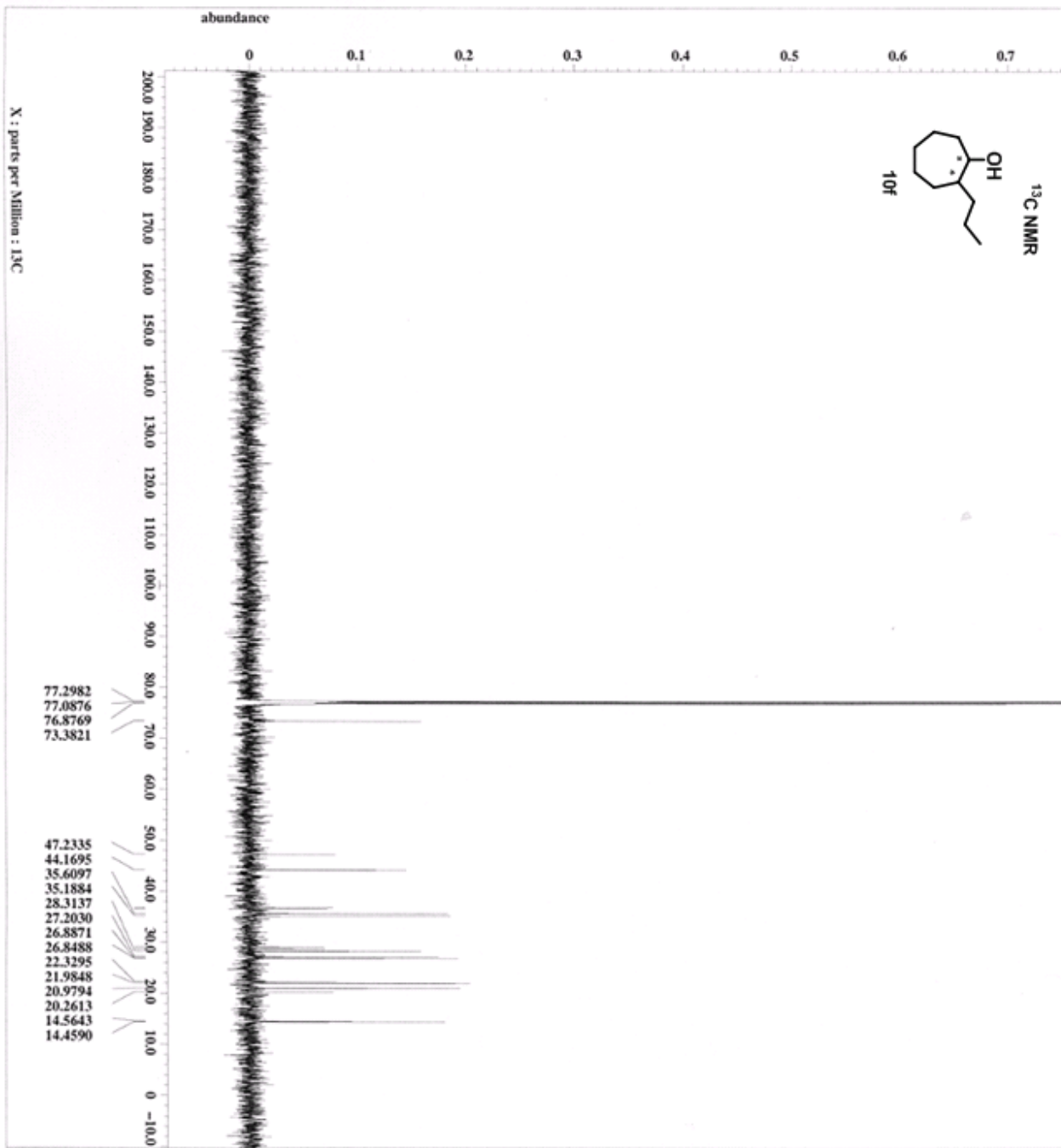
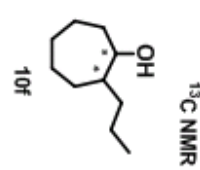
Derived from: EY818-4-1.jdt

Filename = EY818-4-3.jdt
Author = delta
Experiment = single_pulse.exe2
Sample_id = EY818-4
Solvent = CHLOROFORM-D
Creation_time = 21-OCT-2010 18:16:14
Revision_time = 21-OCT-2010 18:15:17
Current_time = 21-OCT-2010 18:16:11

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 = 14.09616281[s] (600)M
X.acq_duration = 1.4548921[s]
X.domain = 1H
X.freq = 600.1721046[MHz]
X.offset = 5[ppm]
X.points = 16384
X.prescans = 1
X.resolution = 0.68732384[Hz]
X.sweep = 11.26126126[MHz]
IRF_domain = 1H
IRF_freq = 600.1721046[MHz]
IRF_offset = 5[ppm]
TRF_domain = 1H
TRF_freq = 600.1721046[MHz]
TRF_offset = 5[ppm]
Clipped = FALSE
Mod_return = 1
Scans = 8
Total_scans = 8
X.g0_width = 13.5[us]
X.acq_time = 1.4548921[s]
X.angle = 45[deg]
X.atn = 2.3[db]
X.pulse = 6.75[us]
IRF_mode = OFF
TRF_mode = OFF
Dante_preset = FALSE
Initial_wait = 1[s]
Recvr_gain = 44
Relaxation_delay = 5[s]
Repetition_time = 6.4548921[s]
Temp_cwt = 23.6[degC]

```



X : parts per Million : 13C

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

----- PROCESSING PARAMETERS -----
 dc_balance : 0 : FALSE
 temp : 2.0 (Hz) : 0.0 (s)
 trapzoid3 : 0 (%) : 80 (%) : 100 (%)
 zero_fill : 1
 zft : 1 : TRUE : TRUE
 machinephase
 ppm
 Derived from: EY1818C_copy-5.jdt

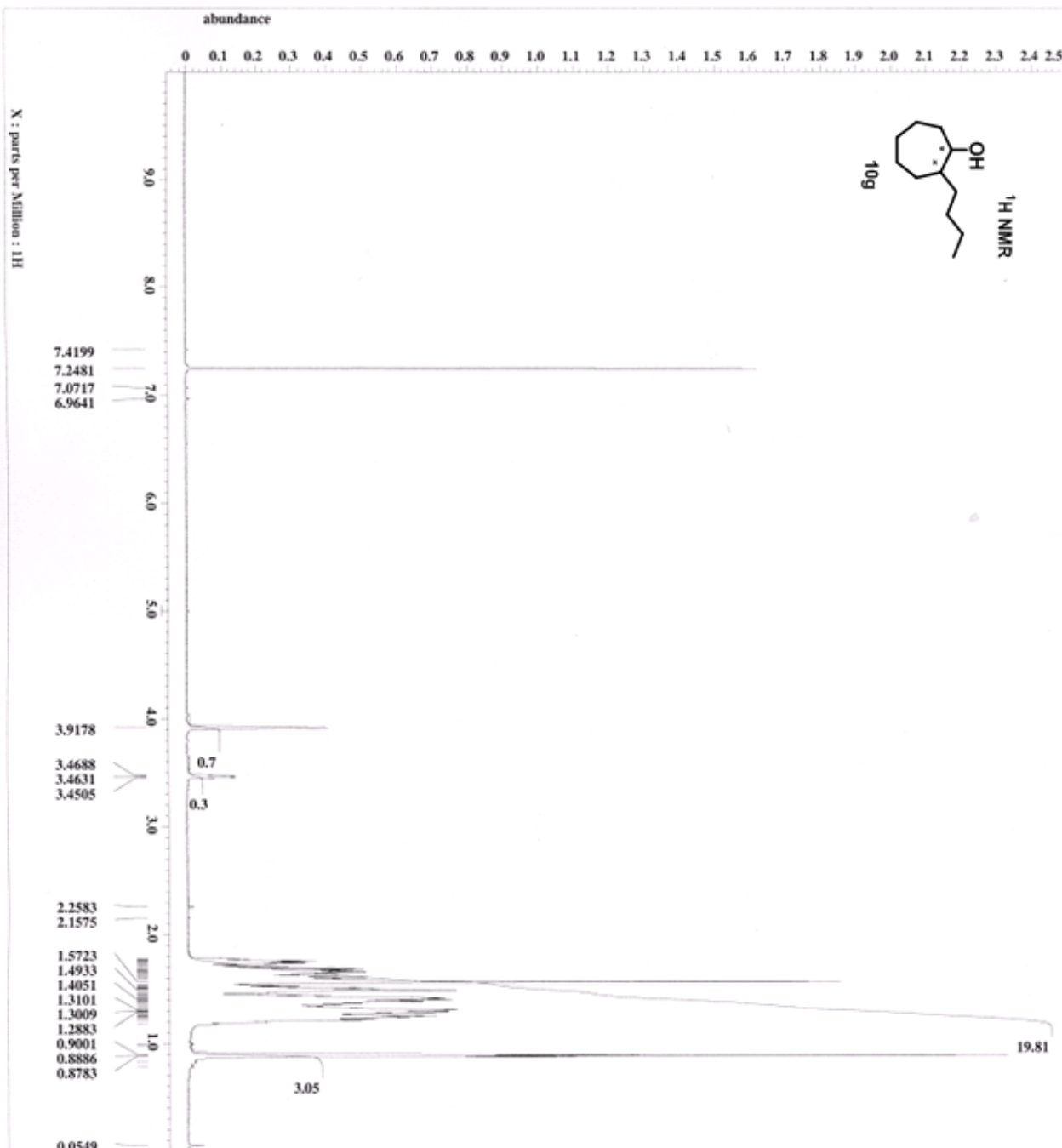
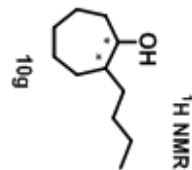
```

Filename = EY1818C_copy-7.jdt
Author = delta
Experiment = single_pulse_dec
Sample_id = EY1818C
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) (600.1M)
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)
KALTZ = TRUE
Decoupling = 1 (s)
Initial_wait = TRUE
Noe_time = 2 (s)
Noe_gain = 56
Relaxation_delay = 2 (s)
Repetition_time = 2.69206016 (s)
Temp_get = 24.5 (dC)
  
```



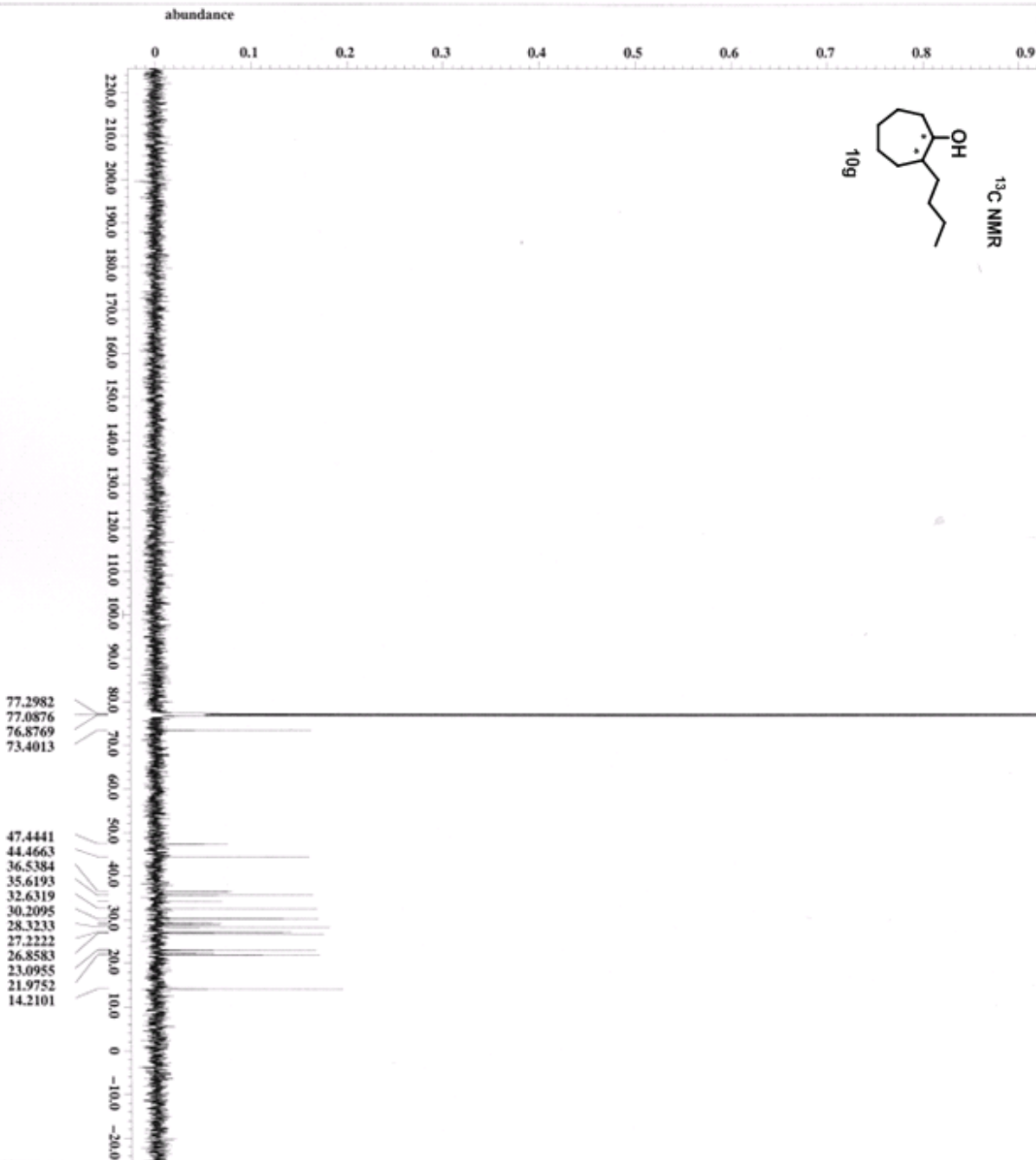
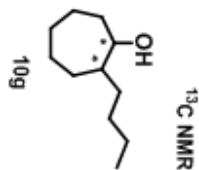
```

----- PROCESSING PARAMETERS -----
dc balance : 0 : PULSE
sweep : 0.2 [Hz] : 0.0 [s]
expandold3 : 0 (%) : 80 (%) : 100 (%)
zerofill : 1
fft : 1 : TRUX : TRUX
machinephase
ppm
Derived from: EY819-1.fid

Filename      = EY819-3.fid
Author
Experiment    = single_pulse.exe2
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
Data_format  = single_pulse
ID_COMPLEX   = 13107
Dim_size     = 1H
Dim_title    = [ppm]
Dimensions   = X
Site         = KCA 500
Spectrometer = JNM-ECA600

Field_strength = 14.09636928 [T] (600 [M
X_acq_duration = 1.45489921[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]
IR_domain     = 600.1723046 [MHz]
IR_freq       = 5 [ppm]
IR_offset     = 1H
IR1_domain    = 600.1723046 [MHz]
IR1_freq     = 5 [ppm]
IR1_offset    = PULSE
Clipped
Mod_return    = 1
Scans         = 8
Total_scans   = 8
X_90_width    = 13.5 [us]
X_acq_time    = 1.45489921[s]
X_angle       = 45 [deg]
X_atn         = 2.9 [dB]
X_pulse       = 6.75 [us]
IR_mode       = Off
IR1_mode      = Off
Dance_preset = PULSE
Initial_walt = 1 [s]
Recvr_gain    = 42
Relaxation_delay = 5 [s]
Relaxation_time = 6.45489921[s]
Temp_get      = 23.7 [degC]
  
```



```

----- PROCESSING PARAMETERS -----
dc_dataorg 0 : PULPRO
exp 0 [Hz] : 0 [Hz]
expresol0 [Hz] : 80 [Hz] : 80 [Hz]
expresol1 [Hz] : 100 [Hz]
fft : 1 : TRUE : TRUE
machinephase
ppm
Derived from: EY819C_copy-2.fid
  
```

```

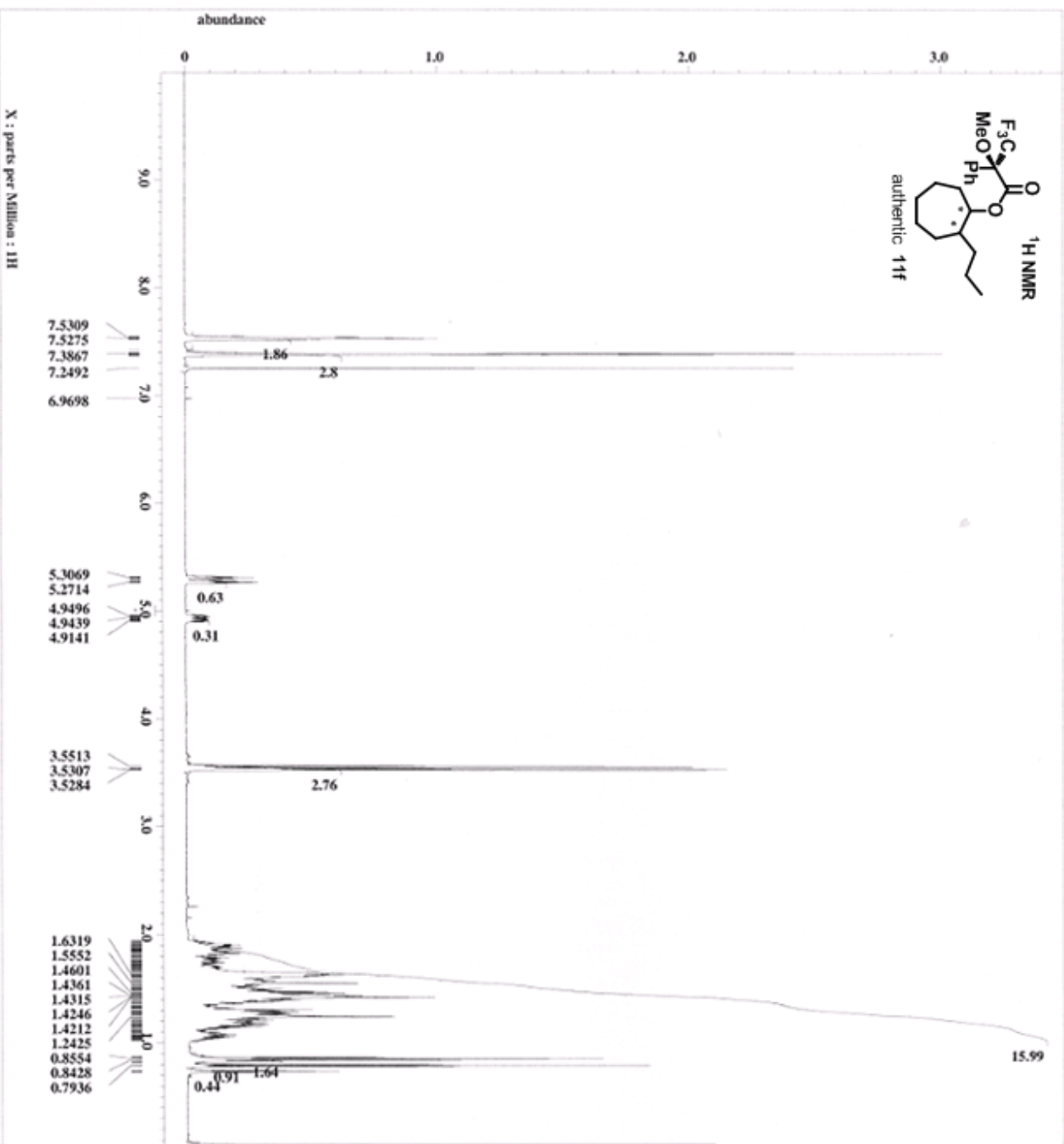
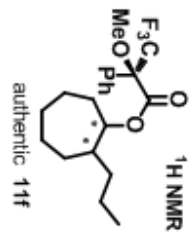
Filename = EY819C_copy-4.fid
Author =
Experiment =
Sample_id = EY819C
Solvent = CHLOROFORM-D
Creation_time = 21-OCT-2010 18:58:16
Revision_time = 21-OCT-2010 19:04:12
Current_time = 21-OCT-2010 19:04:25

Comment =
Data_format = single pulse decouple
Data_size = 26214
Dim_title = 13C
Dim_units = [ppm]
Dimensions = X
Site = KCA 600
Spectrometer = JNM-ECA600

Field_strength = 14.09636928 [Hz] (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 = 47.34888485 [kHz]
Irr_domain = 1H
Irr_freq = 600.17230446 [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_nos = 17.91 [dB]
Irr_noise = NMR
Decoupling = TRUE
Inlet1_wait = 1 [s]
Noe = TRUE
Noe_time = 21 [s]
Recvr_gain = 54
Relaxation_delay = 2 [s]
Repetition_time = 2.69206016 [s]
Temp_get = 24.5 [deg]
  
```

X : parts per Million : 13C



----- PROCESSING PARAMETERS -----
de_data.ms 0 FALSER
Sweep 0.3 [Hz] 5.0 [s]
F2 (Hz) 100 [MHz]
F1 (MHz) 80 [MHz]
ZOR (mm) 5
F2 (Hz) 100 [MHz]
F1 (MHz) 80 [MHz]
MachinPhase
ppm
Derived from: EY921 R-2-1.fid

=====

File Name = EY921 R-2-1.fid
Author = delta
Experiment = single_pulse.ex2
Sample Id = EY921
Solvent = CHLOROFORM-D
Creation Time = 13-DEC-2010 17:00:48
Revision Time = 13-DEC-2010 17:14:31
Current Time = 13-DEC-2010 17:14:54

=====

Comment = single_pulse
Data Format = 1D COMPLEX
Dir_Acqs = 131107
Dir_Exp = [RM]
Dir_Units = [RM]
Dimensions = [RM]
XCA 600
Site = UNK-CCN600
Spectrometer = UNK-CCN600

=====

Field Strength = 14.06635928 [T] (600 [M])
Acq Duration = 1.49489921 [s]
Domain = RM
Freq = 600.122046 [MHz]
Offset = 5 [ppm]
Points = 16384
Resolution = 0.68723284 [Hz]
Sweep = 11.26125126 [MHz]
Domain = RM
Freq = 600.122046 [MHz]
Offset = 5 [ppm]
Clipped = FALSER
Mod_Return = 1
Scans = 8
Total_Scans = 8

=====

X_90_Width = 13.5 [us]
X_Acq_Time = 1.45489921 [s]
X_Angle = 45 [deg]
X_Attn = 2.9 [dB]
X_Pulse = 6.75 [us]
X_Mode = ORF
X_Offset = ORF
X_Phase = FALSER
Initial_Volt = 1 [V]
Dante_Preset = 18
Recv_Gain = 5 [dB]
Relaxation_Delay = 6.45489921 [s]
Repetition_Time = 20.6 [s]
Temp_Gac = 20.6 [C]



----- PROCESSING PARAMETERS -----
 dc_balanc2 [Hz] : 0 [Hz] PALSE
 tempoc2 [Hz] : 0 [Hz]
 tempoc3 [Hz] : 0 [Hz] : 80 [Hz] : 100 [Hz]
 rrfill : 1 : TRUE : TRUE
 ffc : 1 : TRUE : TRUE
 machinephase
 ppm

Derived from: EY822-1.jdf

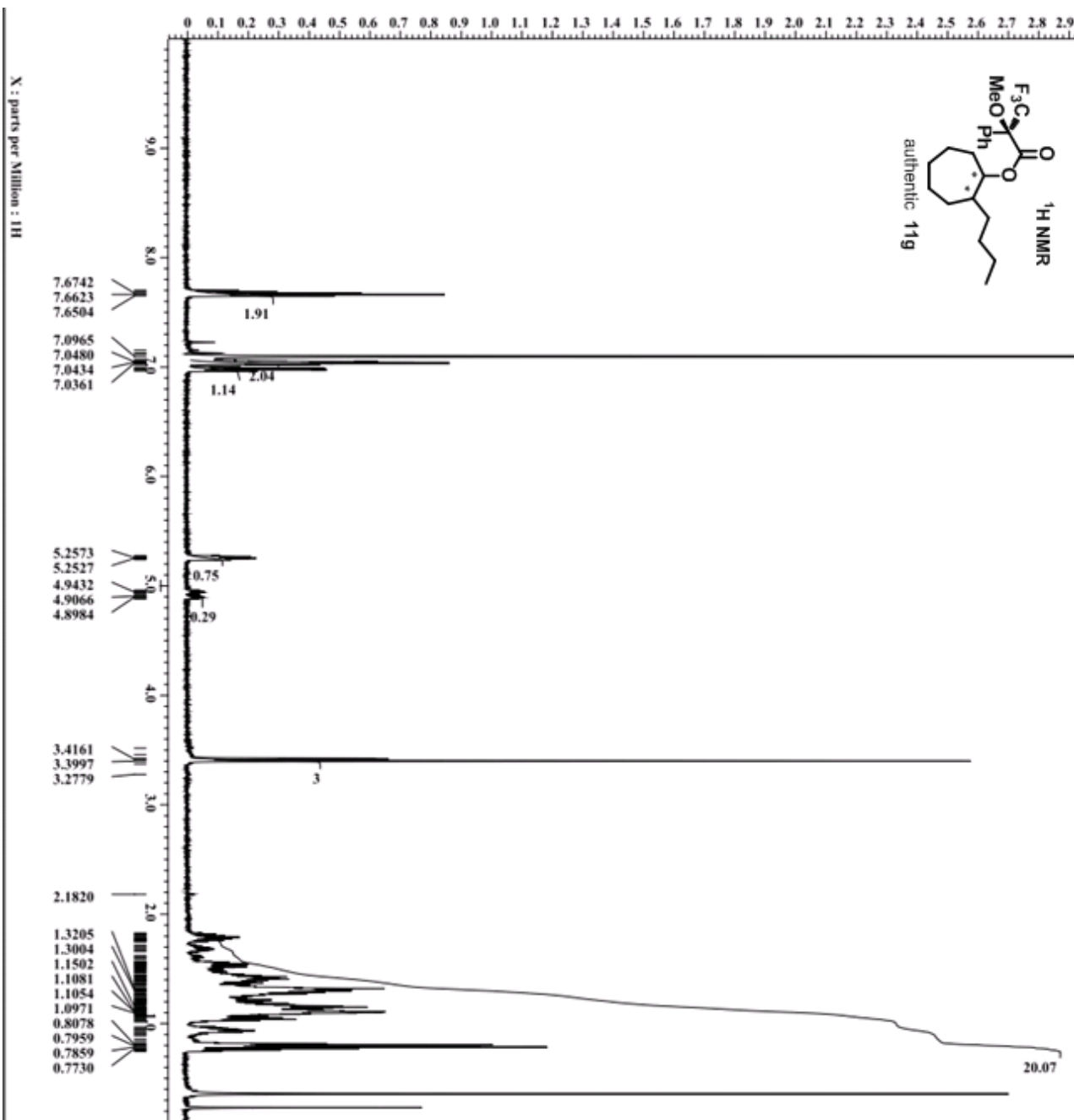
```

Filename      = EY822-4.jdf
Author        = delta
Experiment    = single_pulse.en2
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
Data_format  = single_pulse
Dim_size     = 1D COMPLEX
Dim_title    = 16384
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]
irf_domain    = 1H
irf_freq      = 600.1723046 [MHz]
irf_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]
X_pulse       = 6.75 [us]
Tri_pulse     = OFF
Tri_node     = PALSE
Tri_offset   = 4 [s]
Dantec_preat = 4 [s]
Initial_wait = 4 [s]
Reover_gain   = 2 [s]
Relaxation_delay = 6.81993472 [s]
Repetition_time = 23.8 [dc]
Temp_get      =
  
```



X: parts per Million : 1H



```

----- PROCESSING PARAMETERS -----
dc balance : 0 : PALSE
aesp : 0.2 [Hz] : 0.0 [s]
tspold3 : 0 [%] : 80 [%] : 100 [%]
srf : 1 : TRUR : TRUR
mach : machinebase
ppm
DerivEd From: EY736 RE2 600-1.9dF

```

```

=====
File name      = EY736 RE2 600-3.9dF
Author
Experiment     =
Sample ID      =
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
=====

```

```

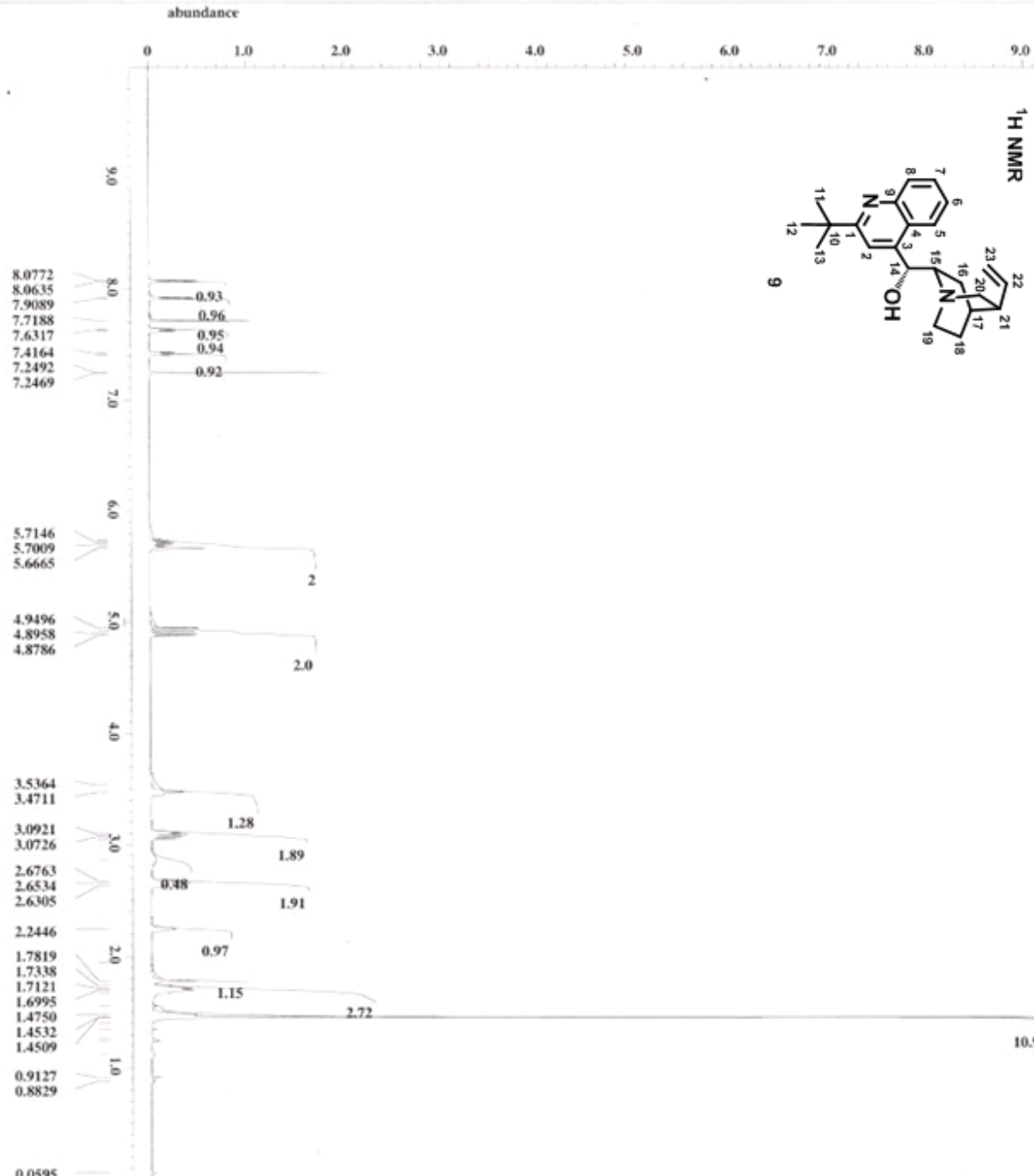
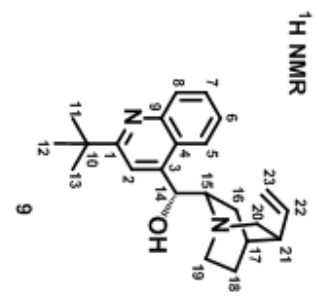
Comment
Data format    = 1D COREFEX
Dir. file      = 13107
Dir. title     = 1H
Dir. units     = [ppm]
Dimensions     = X
Site           = NCA 600
Spectrometer   = JNM-ECA600
=====

```

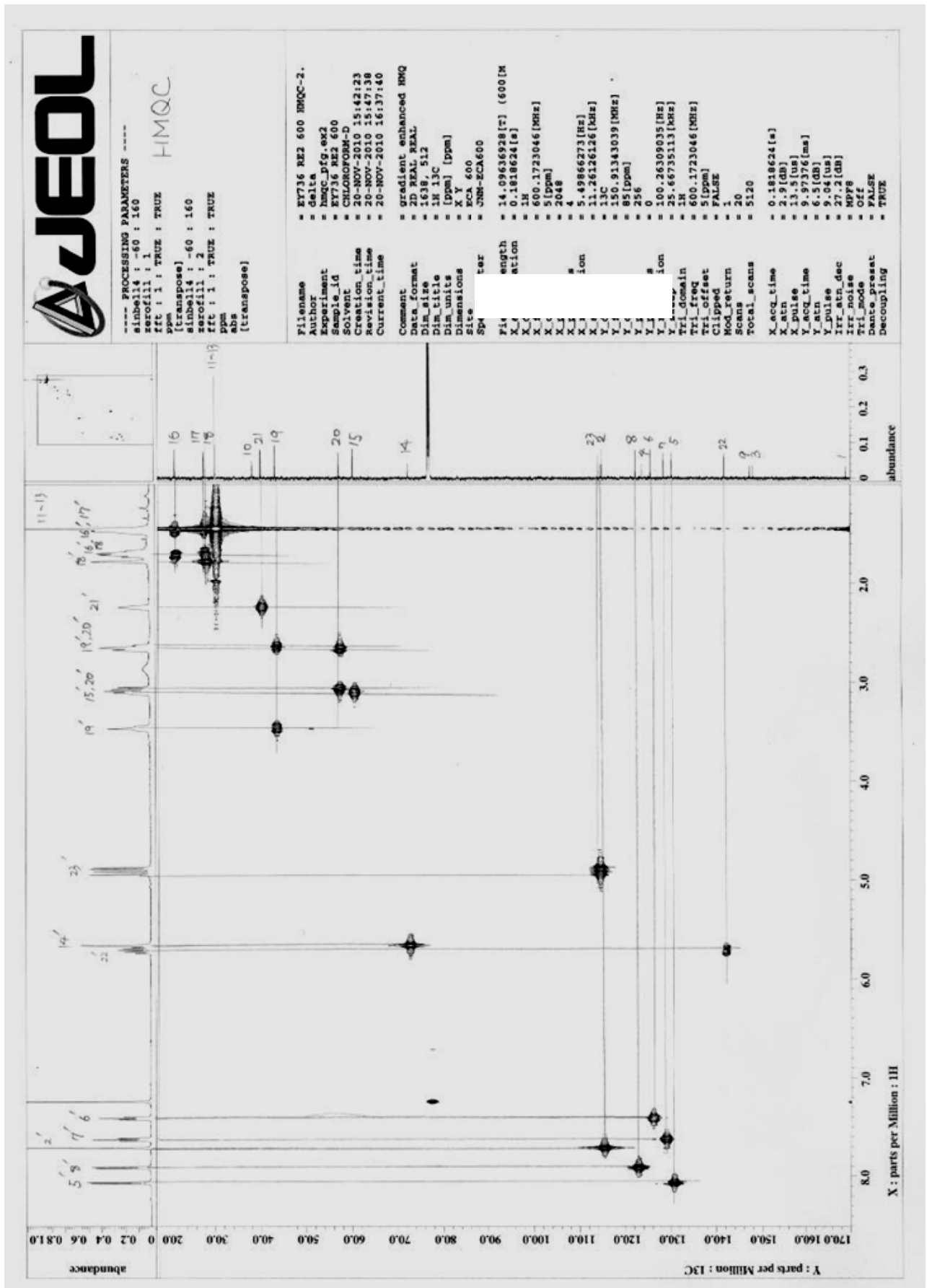
```

Field strength = 14.08636928 [T] (600.1M
K1acq_duration = 1.45489921 [s]
K1domain       = 1H
K1freq         = 600.1723046 [MHz]
K1offset       = 5 [ppm]
K1points       = 16384
K1prescan      = 0.6873284 [Hz]
K1sweep        = 11.7612616 [MHz]
K1resolution   = 0.600.1723046 [MHz]
K1ir_domain    = 1H
K1ir_freq      = 5 [ppm]
K1ir_offset    = 600.1723046 [MHz]
K1tr1_domain   = 1H
K1tr1_freq     = 5 [ppm]
K1tr1_offset   = PALSR
K1clipped      = 1
K1Mod_return   = 8
K1Scans        = 8
K190_width     = 13.5 [us]
K1acq_time     = 1.45489921 [s]
K1Angle        = 49 [deg]
K1Atn          = 2.9 [dB]
K1pulses       = 6.75 [us]
K1ir_mode      = ORF
K1tr1_mode     = PALSR
K1Dante preset = 1 [a]
K1Initial wait = 46
K1recvr_gain   = 5 [a]
K1Relaxation delay = 6.45489921 [s]
K1Repetition time = 21.91 [s]
K1Temp_get     = 21.91 [C]

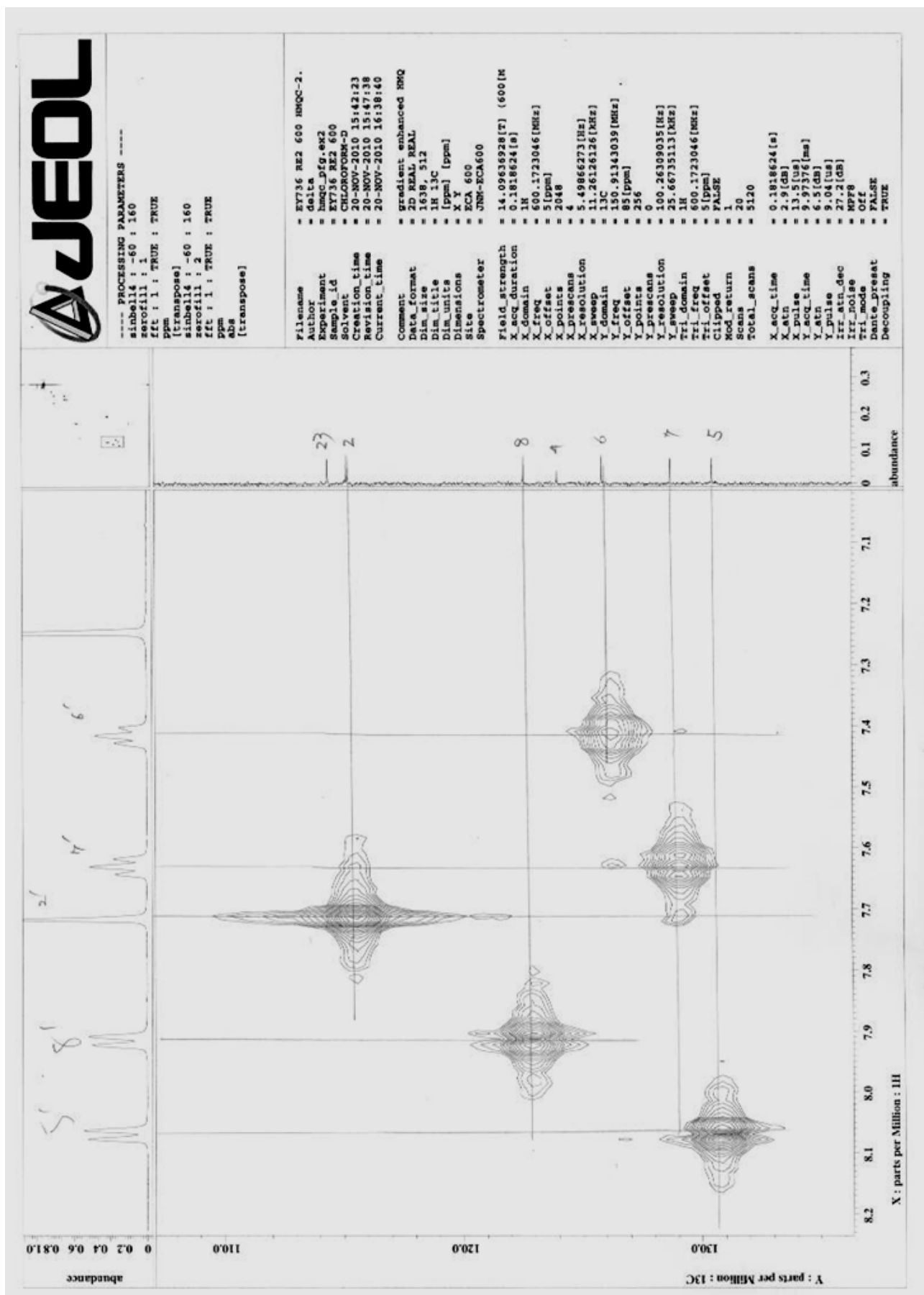
```



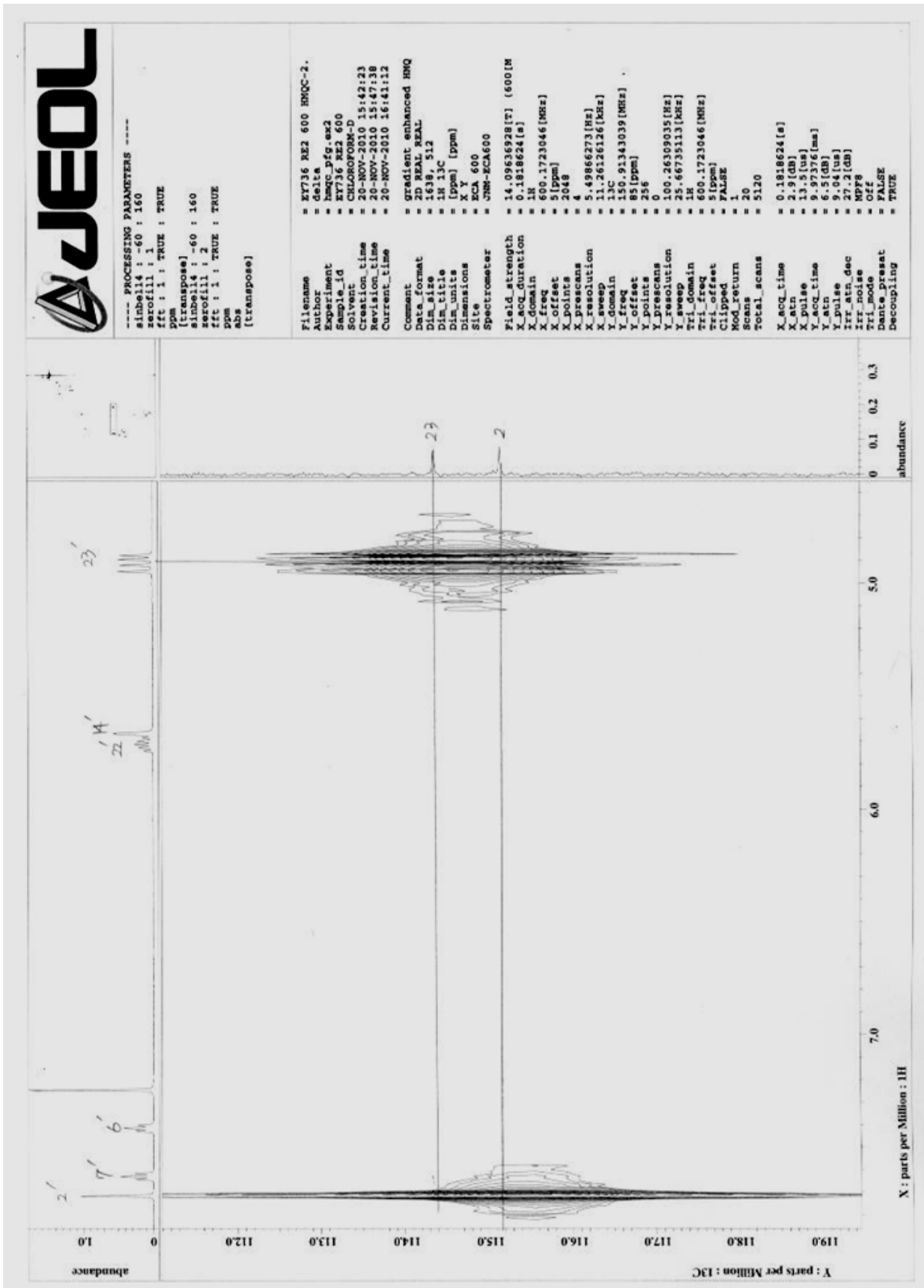
Overall picture of HMQC (compound 9)



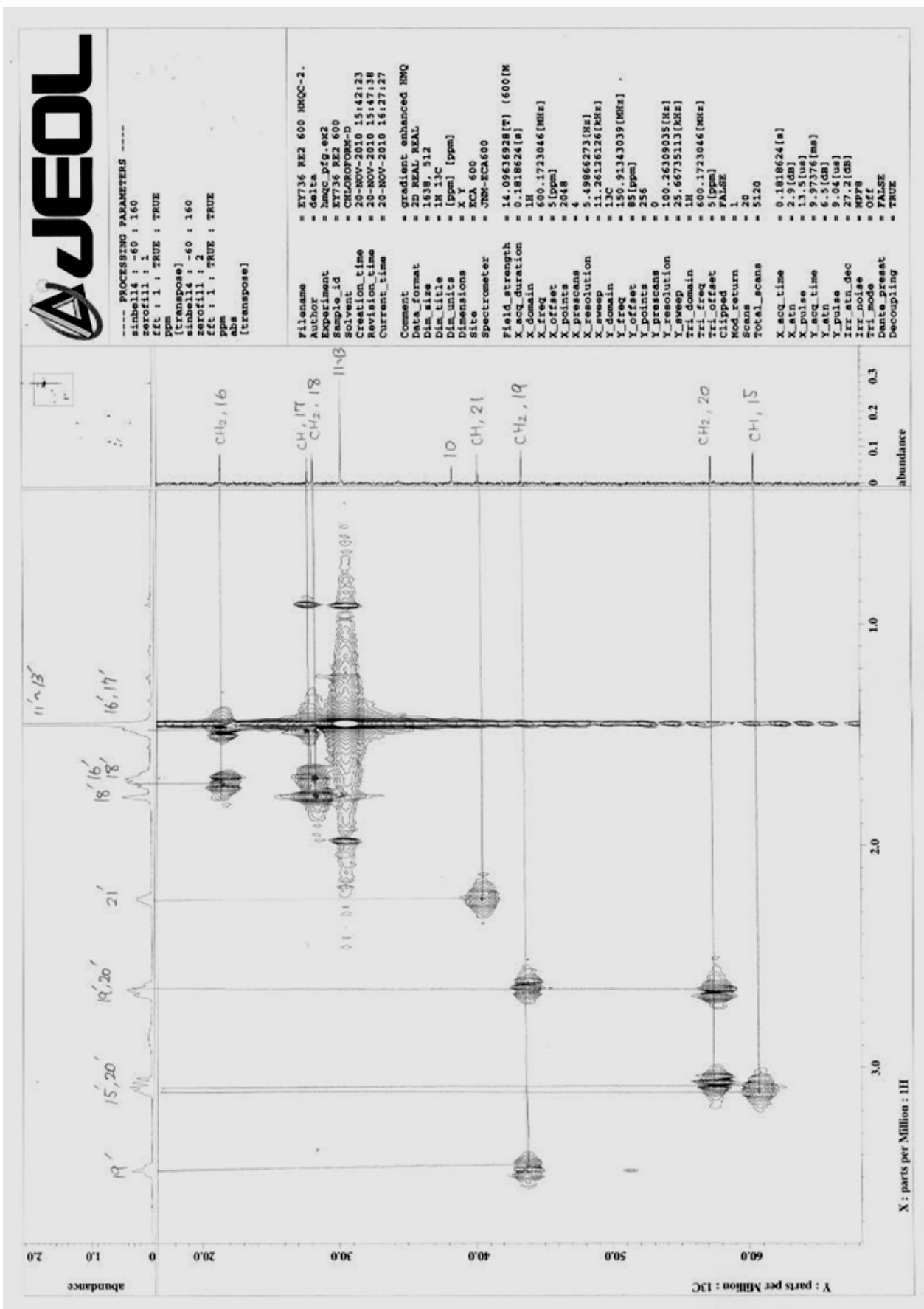
Expanded figure 1 of HMQC (compound 9)



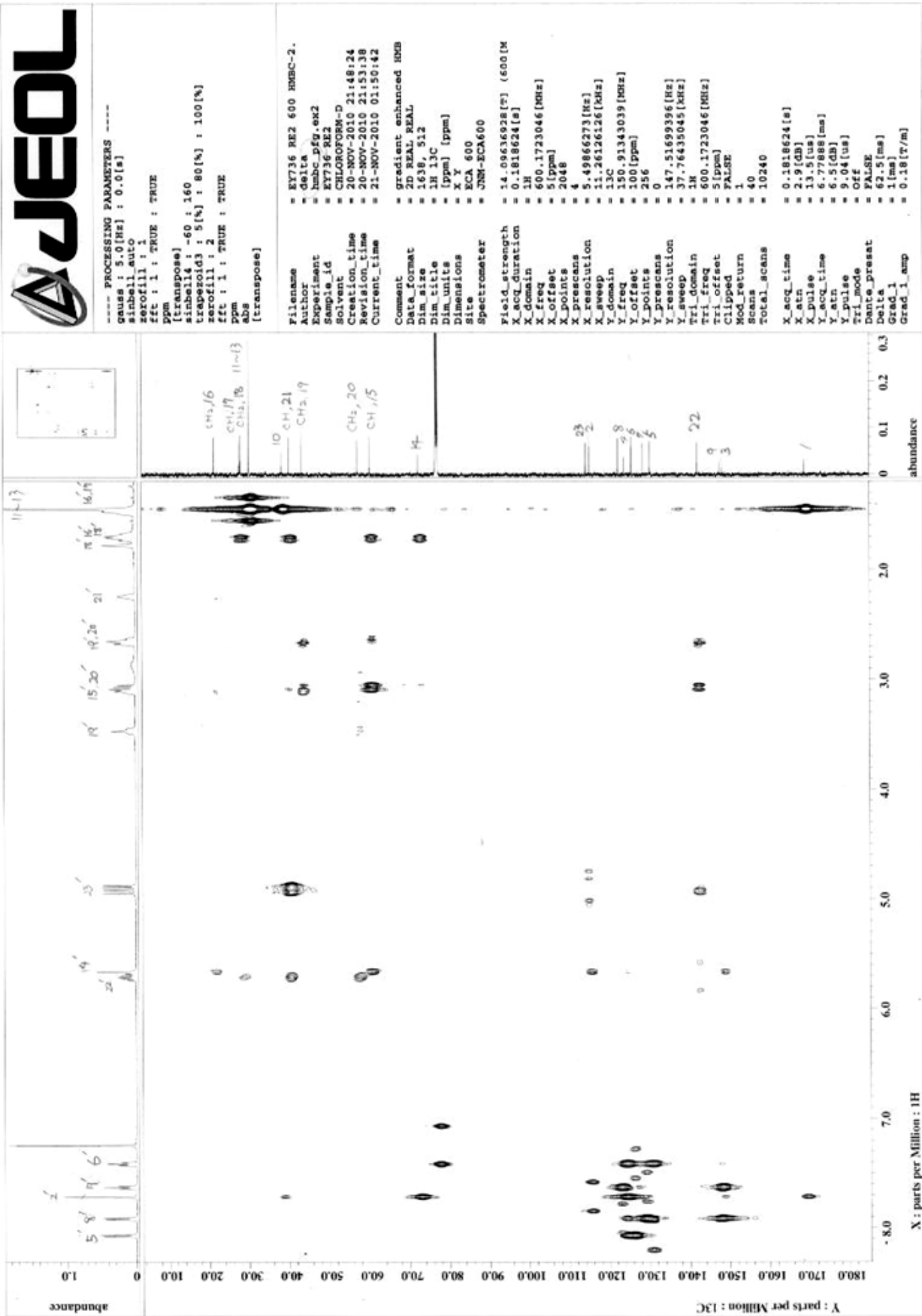
Expanded figure 2 of HMQC (compound 9)



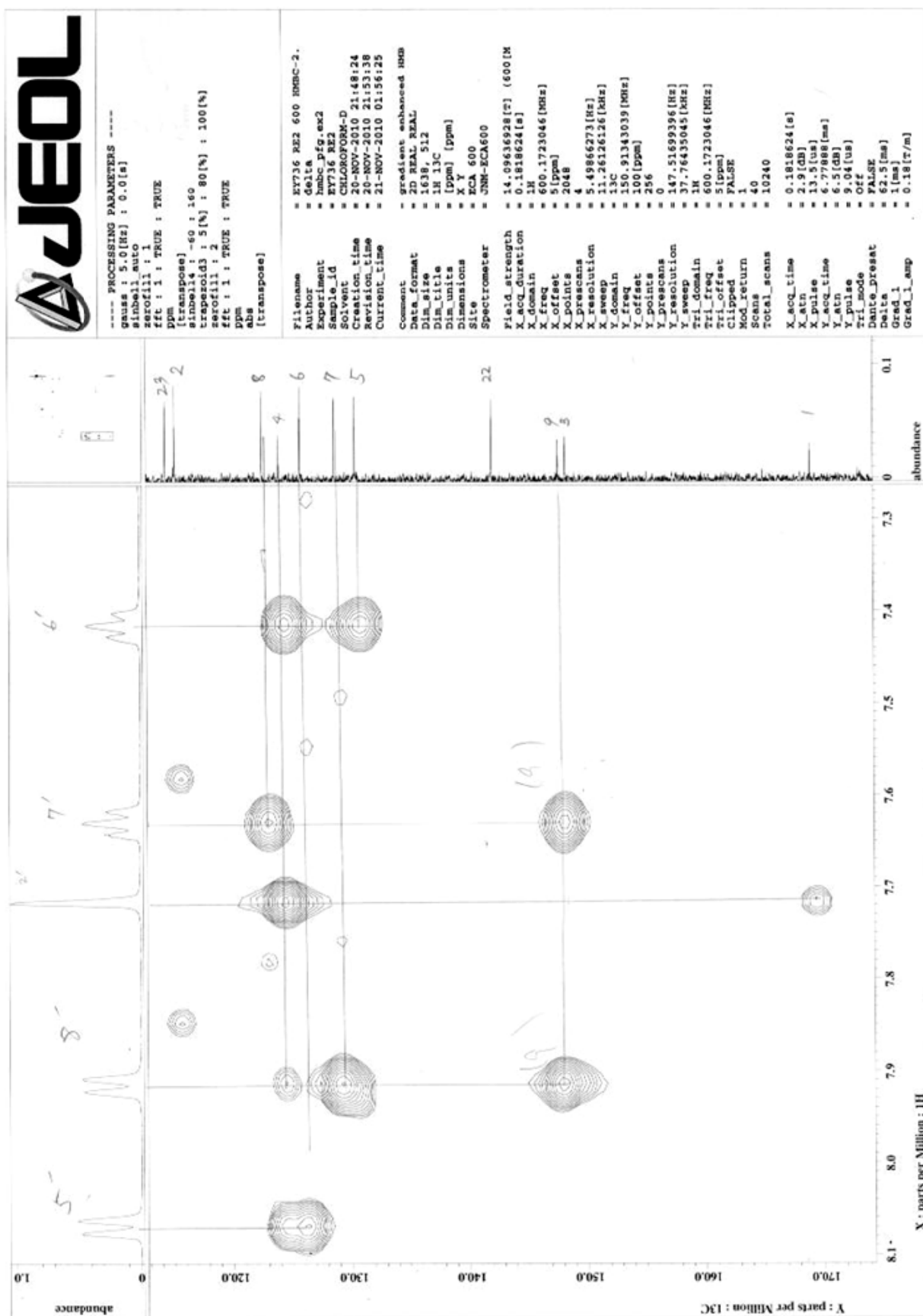
Expanded figure 3 of HMQC (compound 9)



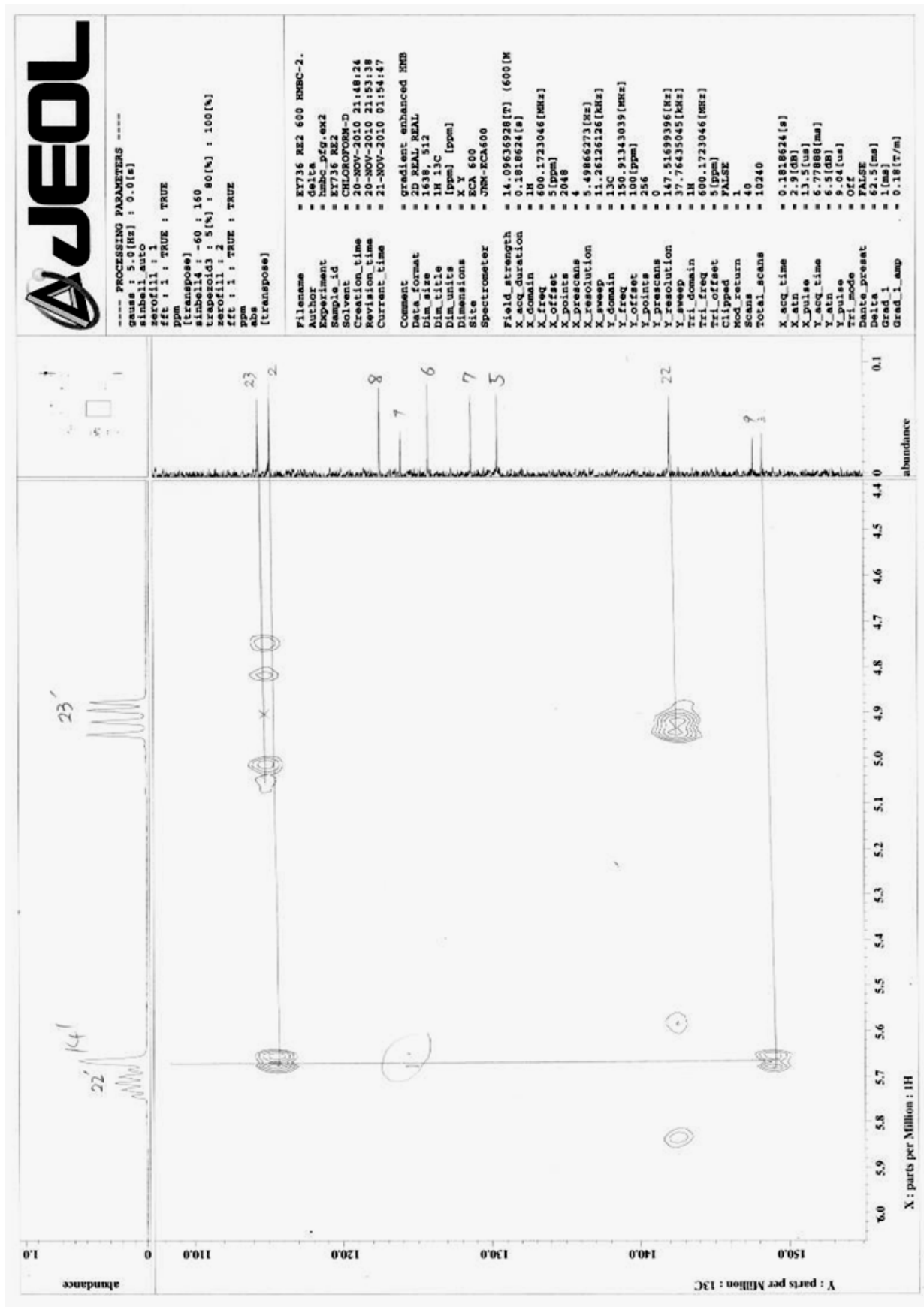
Overall picture of HMBC (compound 9)



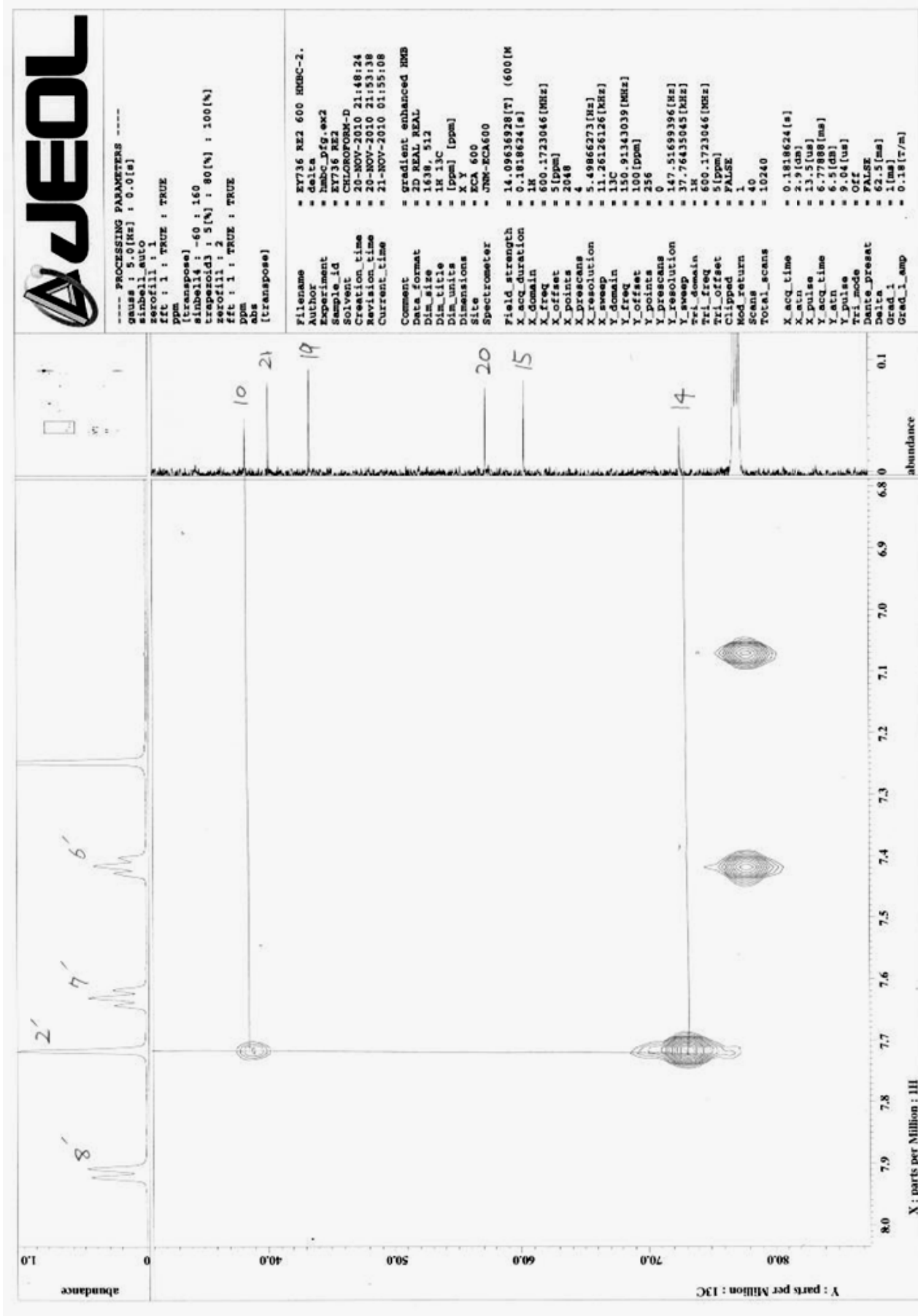
Expanded figure 1 of HMBC (compound 9)



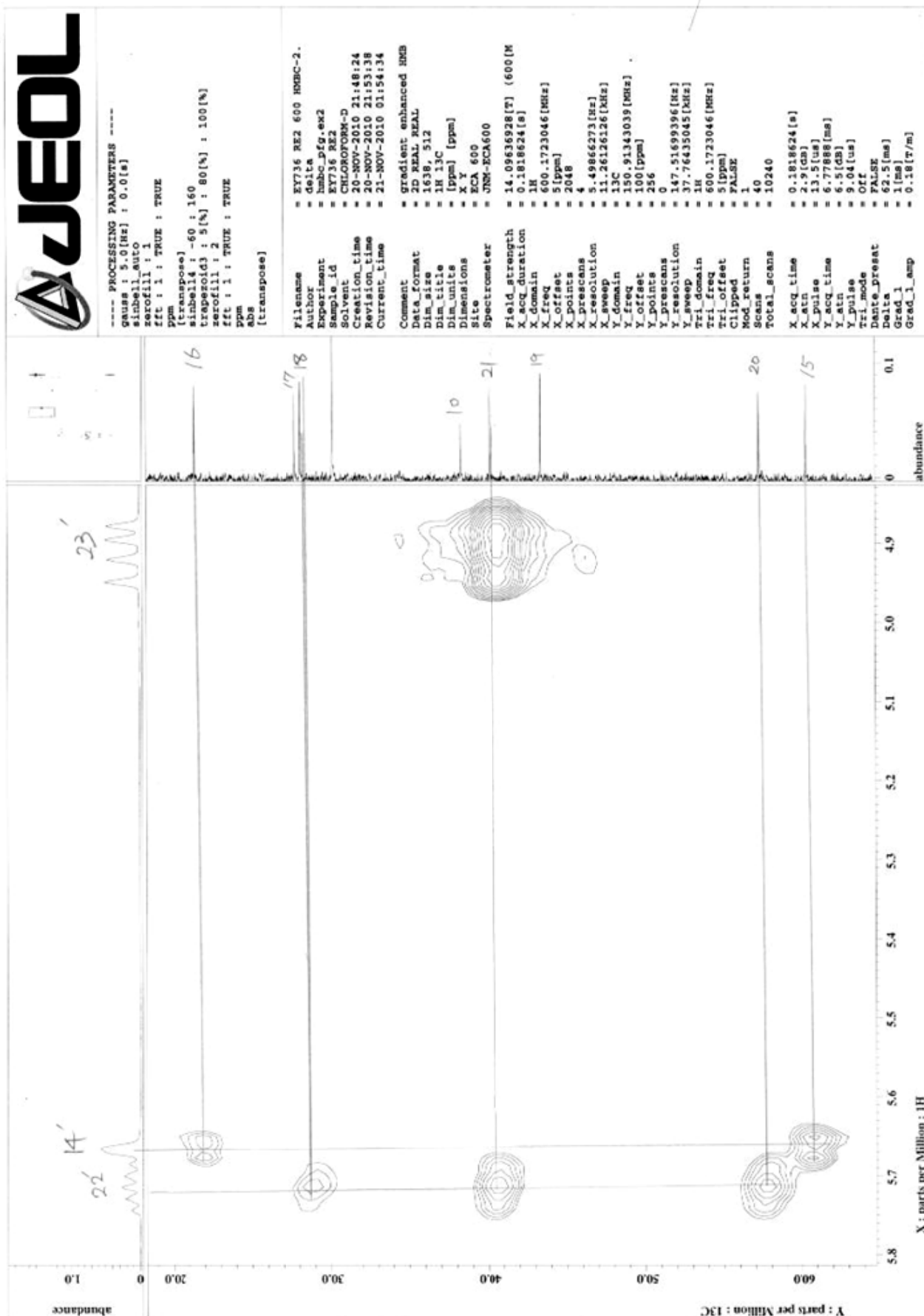
Expanded figure 2 of HMBC (compound 9)



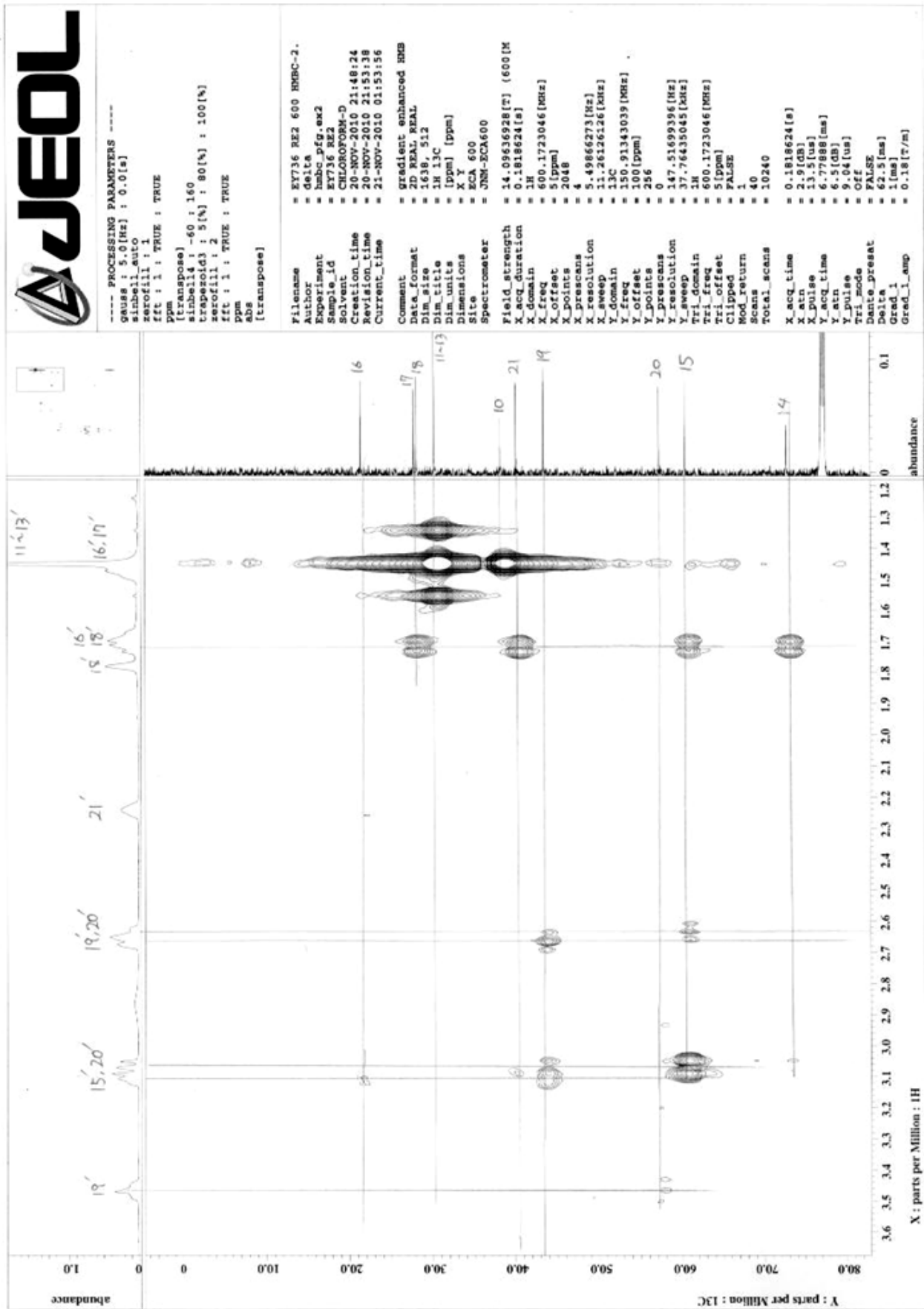
Expanded figure 3 of HMBC (compound 9)



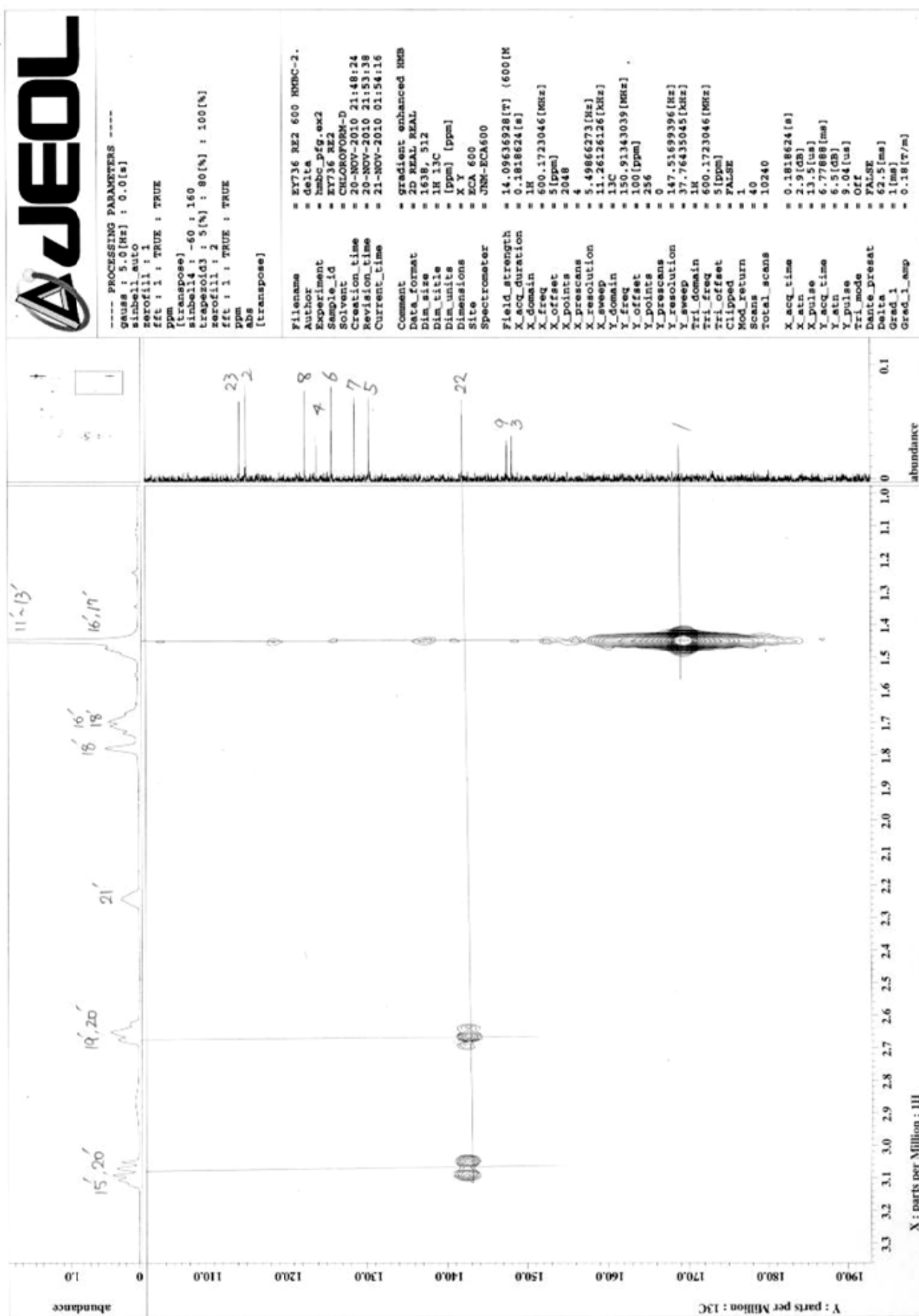
Expanded figure 4 of HMBC (compound 9)

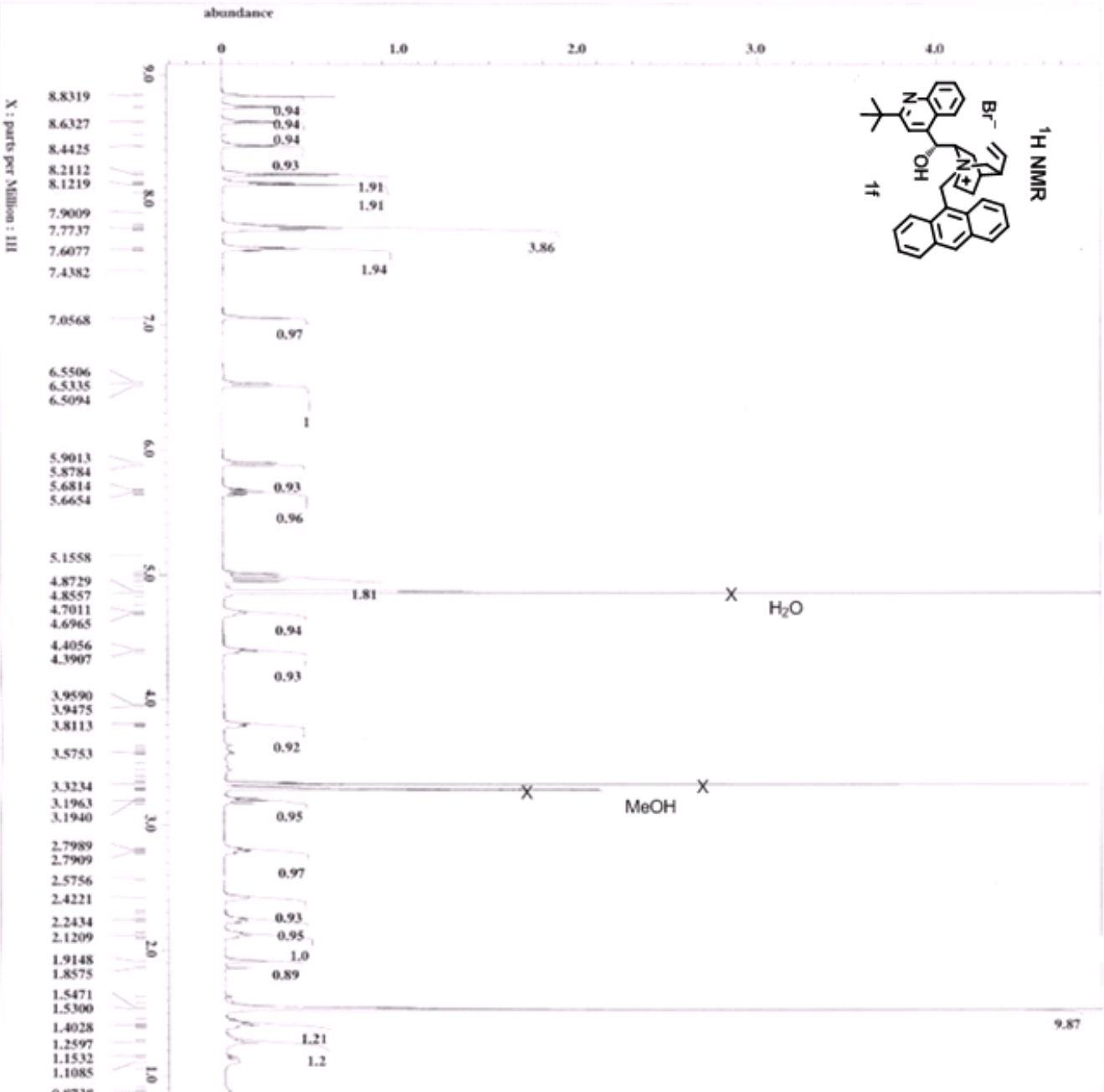
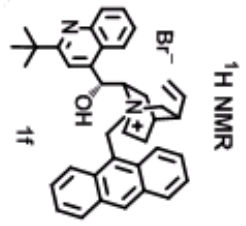


Expanded figure 5 of HMBC (compound 9)



Expanded figure 6 of HMBC (compound 9)





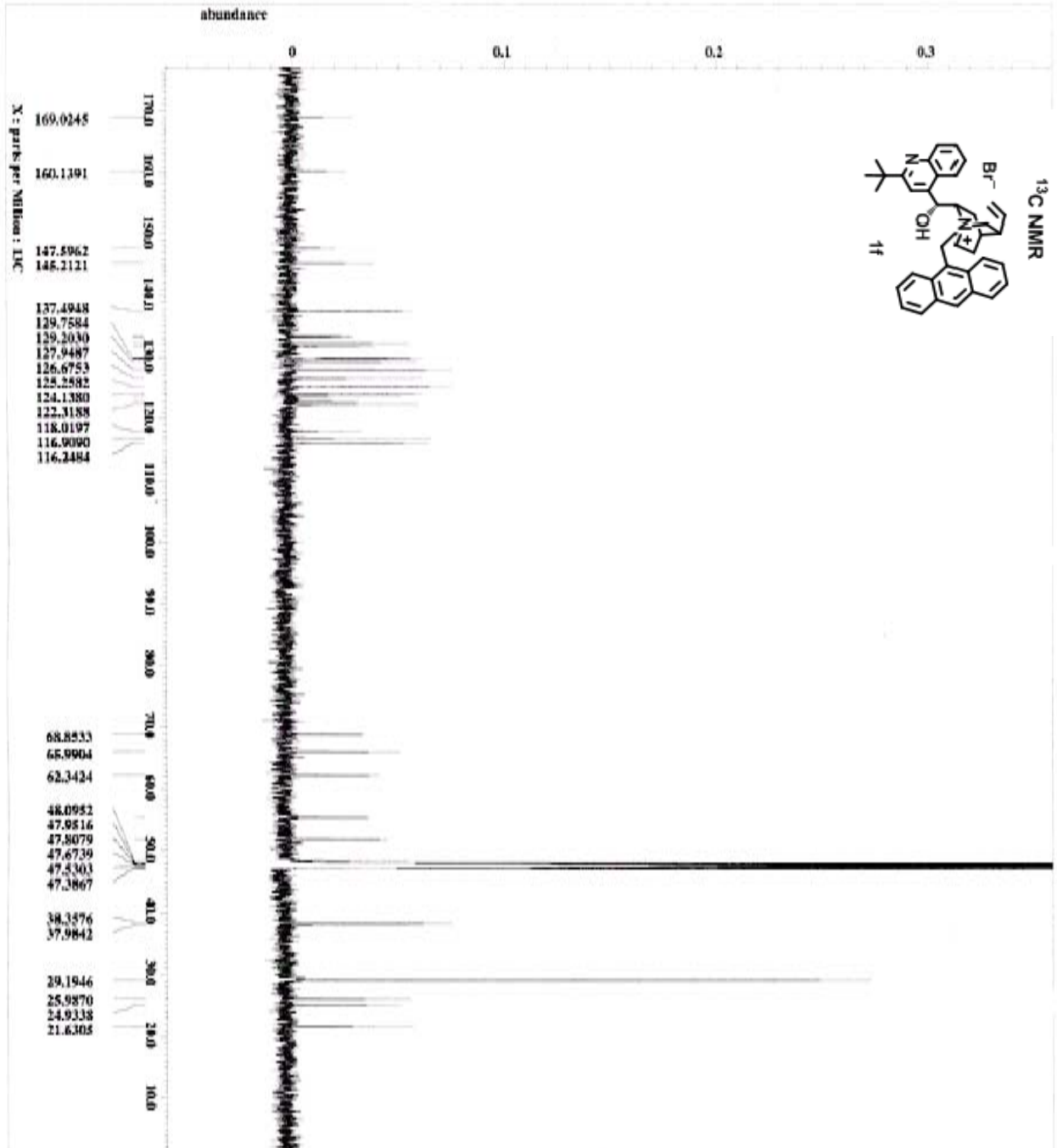
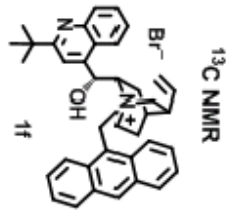
----- PROCESSING PARAMETERS -----
DC Balance : 0 : FALSE
Temp : 0.2183 : 0.01s
Temperature : 0 [N] : 80 [N] : 100 [N]
AcroFill : 1
F1 : 1 : TRUE : TRUE
MachInPhase
Phase : 2 : 0 : 50 [N]
Derived from: XY837 H-1.fid

Filename : XY837 H-6.fid
Author :
Experiment :
Sample Id : XY837
SOLVENT :
KIRKLAND-D3
Creation Time : 22-NOV-2010 21:52:40
Revision Time : 22-NOV-2010 22:11:44
Current Line : 22-NOV-2010 22:10:13

Comment :
Data Format : single pulse
ID COMPLEX :
Dil. Size : 13107
Dil. Title :
Dil. Units : [ppm]
Dimensions : X
EQA 600
Site :
Spectrometer : JNM-ECX600

Field Strength : 14.09636320817 [600 MHz]
Acq. Duration : 1.48489921s
X Domain :
X Freq : 600.17230461002 [MHz]
X Offset : 16384
X Polarity :
X Prescans : 1
X Resolution : 0.68733284182 [Hz]
X Sweep : 11.26181261002 [Hz]
Trf. Domain :
Trf. Freq : 600.17230461002 [MHz]
Trf. Offset : 5 [ppm]
Trf. Domain :
Trf. Freq : 600.17230461002 [MHz]
Trf. Offset : 5 [ppm]
Mod. Return :
Scans : 1
Total Scans : 8

X 90 Width : 13.5 [us]
K Acq. Time : 1.48489921s
K Angle : 49 [deg]
K Gain : 2.75 [dB]
K Kin :
K Pulse : 6.75 [us]
Trf. Mode : ORT
Dante Presat : PALSE
Initial Wait : 1[s]
Recvr. Gain : 40
Relaxation Delay : 5[s]
Rep. Time : 6.48489921s
Temp. Set : 21.6 [deg]



----- PROCESSING PARAMETERS -----
 dc_balance : 1 : FALSE
 samp : 2.000000 : 0.8161
 crpcoales : 8150 : 80000 : 100000
 xrcf : 1
 xrcf : 1 : TRUE : TRUE
 matchingbase :
 gpa

Decoded from: EMB17 C-1.341

Parameter	Value
Filename	" EMB17 C-1.341
Factor	" 0.010
Decomment	" single pulse dec
Sample_id	" EMB17
Acquire	" 2000000000
Resolution	" 2000000000
Revolution	" 2000000000
Current	" 2000000000
Comment	" single pulse dec
Data format	" ID_CHEMICAL
DM_size	" 2000000000
DM_elec	" 13C
DM_unit	" LPMU
Dimensions	" 1
File	" ECA_040
Spectrometer	" JNM-CX400
Field_strength	" 125.7619281 (MHz)
Nuc1	" 13C
Nuc2	" 13C
Nuc3	" 13C
Nuc4	" 13C
Nuc5	" 13C
Nuc6	" 13C
Nuc7	" 13C
Nuc8	" 13C
Nuc9	" 13C
Nuc10	" 13C
Nuc11	" 13C
Nuc12	" 13C
Nuc13	" 13C
Nuc14	" 13C
Nuc15	" 13C
Nuc16	" 13C
Nuc17	" 13C
Nuc18	" 13C
Nuc19	" 13C
Nuc20	" 13C
Nuc21	" 13C
Nuc22	" 13C
Nuc23	" 13C
Nuc24	" 13C
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Nuc26	" 13C
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Nuc28	" 13C
Nuc29	" 13C
Nuc30	" 13C
Nuc31	" 13C
Nuc32	" 13C
Nuc33	" 13C
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Nuc36	" 13C
Nuc37	" 13C
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Nuc43	" 13C
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Nuc45	" 13C
Nuc46	" 13C
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Nuc67	" 13C
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Nuc69	" 13C
Nuc70	" 13C
Nuc71	" 13C
Nuc72	" 13C
Nuc73	" 13C
Nuc74	" 13C
Nuc75	" 13C
Nuc76	" 13C
Nuc77	" 13C
Nuc78	" 13C
Nuc79	" 13C
Nuc80	" 13C
Nuc81	" 13C
Nuc82	" 13C
Nuc83	" 13C
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Nuc90	" 13C
Nuc91	" 13C
Nuc92	" 13C
Nuc93	" 13C
Nuc94	" 13C
Nuc95	" 13C
Nuc96	" 13C
Nuc97	" 13C
Nuc98	" 13C
Nuc99	" 13C
Nuc100	" 13C