Electronic Supplementary Information

Catalytic chemoselective addition of acetonitrile to enolizable aldehydes with cationic Ru complex/DBU combination

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1. General

Infrared (IR) spectra were recorded on a JASCO FT/IR 410 Fourier transform infrared spectrophotometer. NMR spectra were recorded on a JEOL JNM-LA500 spectrometer, operating at 500 MHz for ^{1}H NMR, 125.65 MHz for ^{13}C NMR, and 202.35 MHz for ^{31}P NMR. Chemical shifts in $CDCl_3$ were reported downfield from TMS (= 0) or in the scale relative to $CHCl_3$ (7.24 ppm) for ^{1}H NMR. For ^{13}C NMR, chemical shifts were reported in the scale relative to $CHCl_3$ (77.0 ppm for ^{13}C NMR) as an internal reference. Chemical shifts in C_6D_6 were reported in the scale relative to C_6D_6 (7.15 ppm) for ^{1}H NMR. For ^{13}C NMR, chemical shifts were reported in the scale relative to C_6D_6 (128.0 ppm for ^{13}C NMR) as an internal reference. Chemical shifts for ^{31}P NMR were reported in the scale relative to 85% phosphoric acid as an external standard. FAB mass spectra were measured on JEOL JMS-MS700V. ESI mass spectra were measured on Waters-ZQ4000. Column chromatography was performed with silica gel Merck 60 (230–400 mesh ASTM). Acetonitrile was distilled from CaH_2. Monophosphine and diphosphine CpRu complex were prepared from $CpRu(CH_3CN)_3PF_6$ (section 2). $CpRu(CH_3CN)_3PF_6$ was prepared as reported in the literature (Gill, P. T.; Mann, K. R. *Organometallics* **1982**, *1*, 485. (b) Trost, B. M.; Older, C. M. *Organometallics* **2002**, *21*, 2544.).

2. Preparation of Acetonitrile Solution of Ru-phosphine Complex

$CpRu(PPh_3)(CH_3CN)_2PF_6$ (1a)

A flame-dried flask was charged with $CpRu(CH_3CN)_3PF_6$ (21.7 mg, 0.05 mmol) and triphenylphosphine (13.1mg, 0.05 mmol) under Ar. To the flask was added dry acetonitrile (833 μl) and stirred for 1 h at room temperature. The resulting 0.06 M CH_3CN solution of $CpRu(PPh_3)(CH_3CN)_2PF_6$ (**1a**) was used as catalyst.

$CpRu(PPh_3)_2(CH_3CN)PF_6$ (1b)

A flame-dried flask was charged with $CpRu(CH_3CN)_3PF_6$ (50 mg, 0.115 mmol) and PPh_3 (60.4 mg, 0.23 mmol) under Ar. To the mixture was added $CDCl_3$ (2.0 mL) and the resulting yellow solution was stirred at 50 °C for 2 h. The formation of diphosphine complex **1b** was confirmed by ^{1}H NMR and ^{31}P NMR (δ 42.5 ppm) analysis of small aliquot of the reaction mixture. The solvent was removed under reduced pressure and

CH_3CN (1.92 mL) was refilled to the resulting residue to give 0.06 M CH_3CN solution of **1b**.

3. ESI-MS Analysis of Ru Complex.

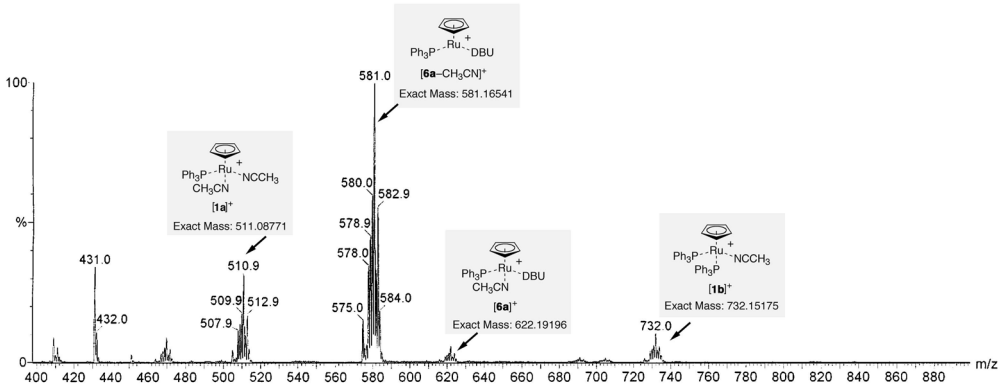
Although the reactions in Table 1 and 2 were performed in CH_3CN/HMPA solvent, ESI-MS analysis of Ru complexes was performed in THF solvent. In the absence of external CH_3CN, it was much easier to compare the stability of Ru monophosphine complex **1a** and diphosphine complex **1b** toward ligand exchange of CH_3CN with DBU.

Preparation of ESI-MS sample

A dried test tube was charged with acetonitrile solution of $CpRu(PPh_3)_2(CH_3CN)PF_6$ (**1b**) (166 μL, 0.01 mmol) under Ar. The solvent was removed under reduced pressure and dried THF (0.5 mL) was refilled. To the THF solution of **1b** was added 0.5 M THF solution of DBU (20 μL, 0.01 mmol) and the resulting mixture was stirred at 50 °C.

Acetonitrile ligands in Ru complex $CpRu(\mathbf{PPh_3})(CH_3CN)_2PF_6$ (**1a**) were readily exchangeable with DBU in THF at 50 °C to give $CpRu(PPh_3)(DBU)(CH_3CN)PF_6$ (**6a**) as shown in Chart S1. Upon addition of DBU (1 equiv to **1a**) to the THF solution of **1a**, the color of the mixture turned to dark brown from yellow and the peak derived from Ru-DBU complex (**6a**) was observed predominantly in ESI-MS spectrum (Chart S1). Although a full characterization of complex **6a** was not accomplished due to its low stability, the formation of **6a** was supported by the intense peak (m/z = 581 for [**6a**-CH_3CN]$^+$, m/z = 622 for [**6a**]$^+$) derived from **6a** in ESI-MS spectra (Chart S1). Although the peak of [**6a**-CH_3CN]$^+$ is much more prominent than the peak of [**6a**]$^+$ under ESI-MS conditions, [**6a**]$^+$ would probably exist in the solution as a dominant species over a coordinatively-unsaturated 16e complex [**6a**-CH_3CN]$^+$.

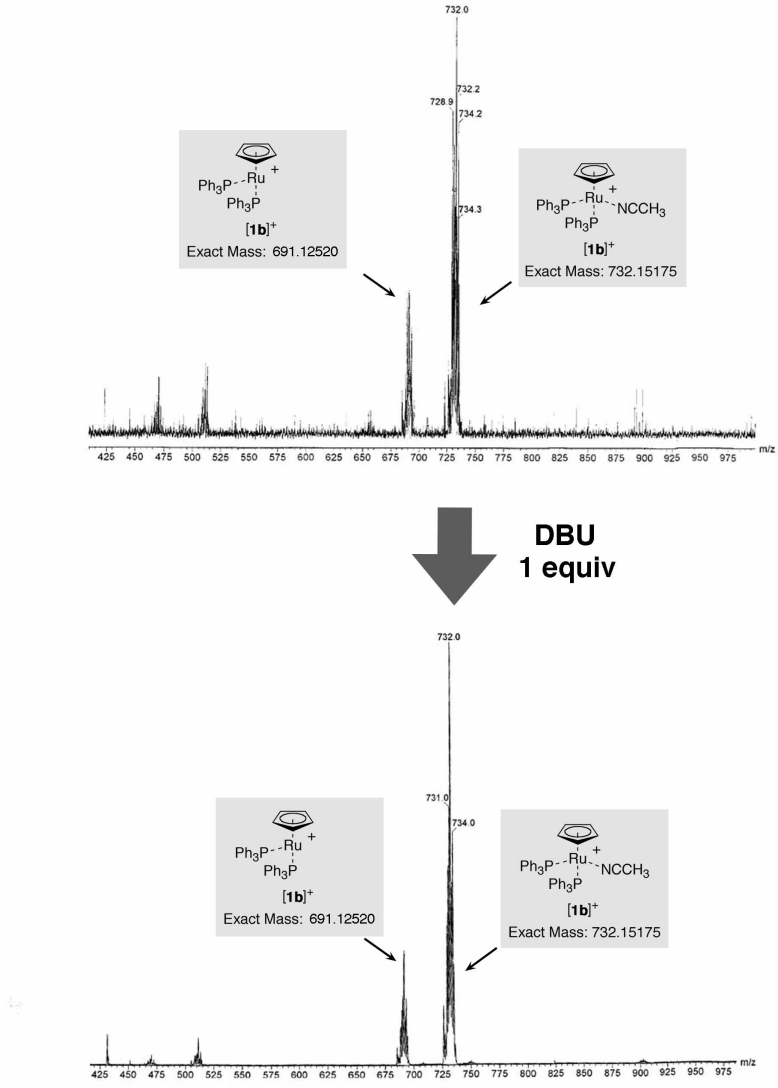
Chart S1. ESI-MS spectrum of **1a** in THF in the presence of DBU (1 equiv to **1a**).



In contrast, when diphosphine complex $CpRu(\mathbf{PPh_3})_2(CH_3CN)PF_6$ (**1b**) was treated with 1 equiv of DBU in THF at 50 °C, Ru-DBU complex $CpRu(PPh_3)_2(DBU)PF_6$ was not

observed in ESI-MS analysis even after 12 h (Chart S2). This observation indicated that coordination of DBU to the Ru center of the diphosphine complex **1b** was disfavored even in the absence of acetonitrile solvent (competitive ligand to the Ru center). Therefore, unstable Ru-DBU complex **6b** generated in catalytic cycle would be readily transformed into acetonitrile complex **1b**, avoiding the accumulation of the unstable Ru-DBU complex **6b**.

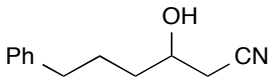
Chart S2. ESI-MS spectrum of 1b in THF in the presence of DBU (1 equiv to **1b**).



4. Spectral Data

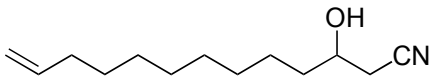
3a, **3b**, **3d**, are known compound. Registry number: **3a**: 155486-16-1, **3b**: 70102-88-4, **3d**: 113576-56-0

3-Hydroxy-6-phenylhexanitrile (3c)



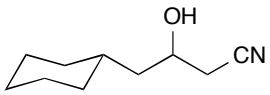
Colorless oil; IR (neat) ν 3452, 2251cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.55-1.70 (m, 3H), 1.72-1.83 (m, 1H), 2.43 (dd, *J* = 6.8, 16.6 Hz, 1H), 2.47 (brs, 1H), 2.50 (dd, *J* = 5.0, 16.6 Hz, 1H), 2.64 (t, *J* = 7.5 Hz 2H), 3.88-3.95 (m, 1H), 7.15-7.20 (m, 3H), 7.26-7.29 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 26.1, 27.1, 35.3, 35.9, 67.5, 117.7, 125.9, 128.3, 128.4, 141.6; ESI-MS *m/z* 212 [M+Na]; HRMS (FAB$^+$) calcd. for $C_{12}H_{14}N$ [M–H_2O+H]$^+$ 172.1121 found 172.1127.

12-Cyano-11-hydroxydodec-1-ene (3e)



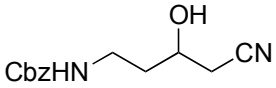
Colorless oil; IR (neat) ν 3435, 2252, 1640 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.19-1.32 (m, 12H), 1.53-1.55 (m, 2H), 1.92 (brs, 1H), 1.94 -1.99 (m, 2H), 2.41 (dd, *J* = 6.4, 16.5 Hz, 1H), 2.45 (dd, *J* = 5.0, 16.5 Hz, 1H), 3.85-3.96 (m, 1H), 4.86 (brd, *J* = 10.4 Hz, 1H), 4.92 (brd, *J* = 17.1 Hz, 1H), 5.73 (dddd, *J* = 6.7, 6.7, 10.4, 17.1 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 25.3, 26.1, 28.8, 29.0, 29.2, 29.3, 29.4, 33.7, 36.5, 67.8, 114.1, 117.7, 139.1; ESI-MS *m/z* 232 [M+Na]$^+$; HRMS (FAB$^+$) calcd. for $C_{13}H_{24}NO$ [M+H]$^+$ 210.1852, found 210.1856.

4-Cyclohexyl-3-hydroxybutanitrile (3f)



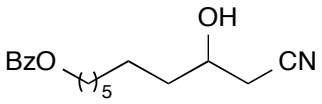
Colorless solid; IR (KBr) ν 3436, 2251cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.84-0.99 (m, 2H), 1.10-1.23 (m, 3H), 1.33-1.45 (m, 2H), 1.48-1.52 (m, 1H), 1.61-1.73 (m, 5H), 2.28 (brd, *J* = 3.7 Hz, 1H), 2.44 (dd, *J* = 6.4, 16.7 Hz, 1H), 2.53 (dd, *J* = 4.6, 16.7 Hz, 1H), 4.03 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 26.0, 26.1, 26.3, 26.6, 32.5, 33.8, 33.8, 44.2, 65.3, 117.8; ESI-MS *m/z* 190 [M+Na]$^+$; HRMS (FAB$^+$) calcd. for $C_{10}H_{18}NO$ [M+H]$^+$ 168.1382, found 168.1383.

5-Benzyloxycarbamoyl-3-hydroxypentanitrile (3g)



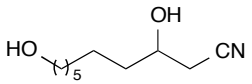
Colorless solid; IR (KBr) ν 3352, 2251, 1698, 1533 cm^{-1}; ^{1}H NMR (C_6D_6) δ 0.98-1.07 (m, 2H), 1.66 (dd, *J* = 5.8, 16.8 Hz, 1H), 1.72 (dd, *J* = 6.1, 16.8 Hz, 1H), 2.46-2.52 (m, 1H), 3.07-3.12 (m, 1H), 3.28-3.35 (m, 1H), 3.60 (brd, *J* = 4.5 Hz, 1H), 4.19 (brs, 1H), 4.98 (s, 2H), 7.04-7.28 (m, 5H); ^{13}C NMR (C_6D_6) δ 25.3, 36.8, 37.1, 64.6, 67.1, 117.6, 128.4, 128.5, 128.7, 137.0, 157.6; ESI-MS *m/z* 271 [M+Na]$^+$; HRMS (FAB$^+$) calcd. for $C_{13}H_{17}N_2O_3$ [M+H]$^+$ 249.1239, found 249.1238.

10-Benzoyloxy-3-hydroxydecanitrile (3h)



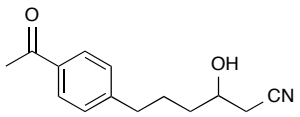
Colorless oil; IR (neat) ν 3479, 2251, 1698, 1716 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.33-1.44 (m, 8H), 1.54-1.59 (m, 2H), 1.70-1.77 (m, 2H), 2.46 (dd, *J* = 6.4, 16.5 Hz, 1H), 2.52 (dd, *J* = 4.5, 16.5 Hz, 1H), 2.53 (brs, 1H), 3.85-3.95 (m, 1H), 4.28 (t, *J* = 6.7 Hz, 2H), 7.41 (dd, *J* = 7.6, 7.9 Hz, 2H), 7.53 (t, *J* = 7.6 Hz, 1H), 8.01 (d, *J* = 7.9 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 25.2, 25.8, 26.0, 28.5, 29.0, 29.1, 36.4, 65.0, 67.6, 117.7, 128.3, 129.4, 130.3, 132.8, 166.7; ESI-MS *m*/*z* 312 $[M+Na]^+$; HRMS (FAB^+) calcd. for $C_{17}H_{24}NO_3$ $[M+H]^+$ 290.1751, found 290.1750.

3,10-Dihydroxydecanitrile (3i)

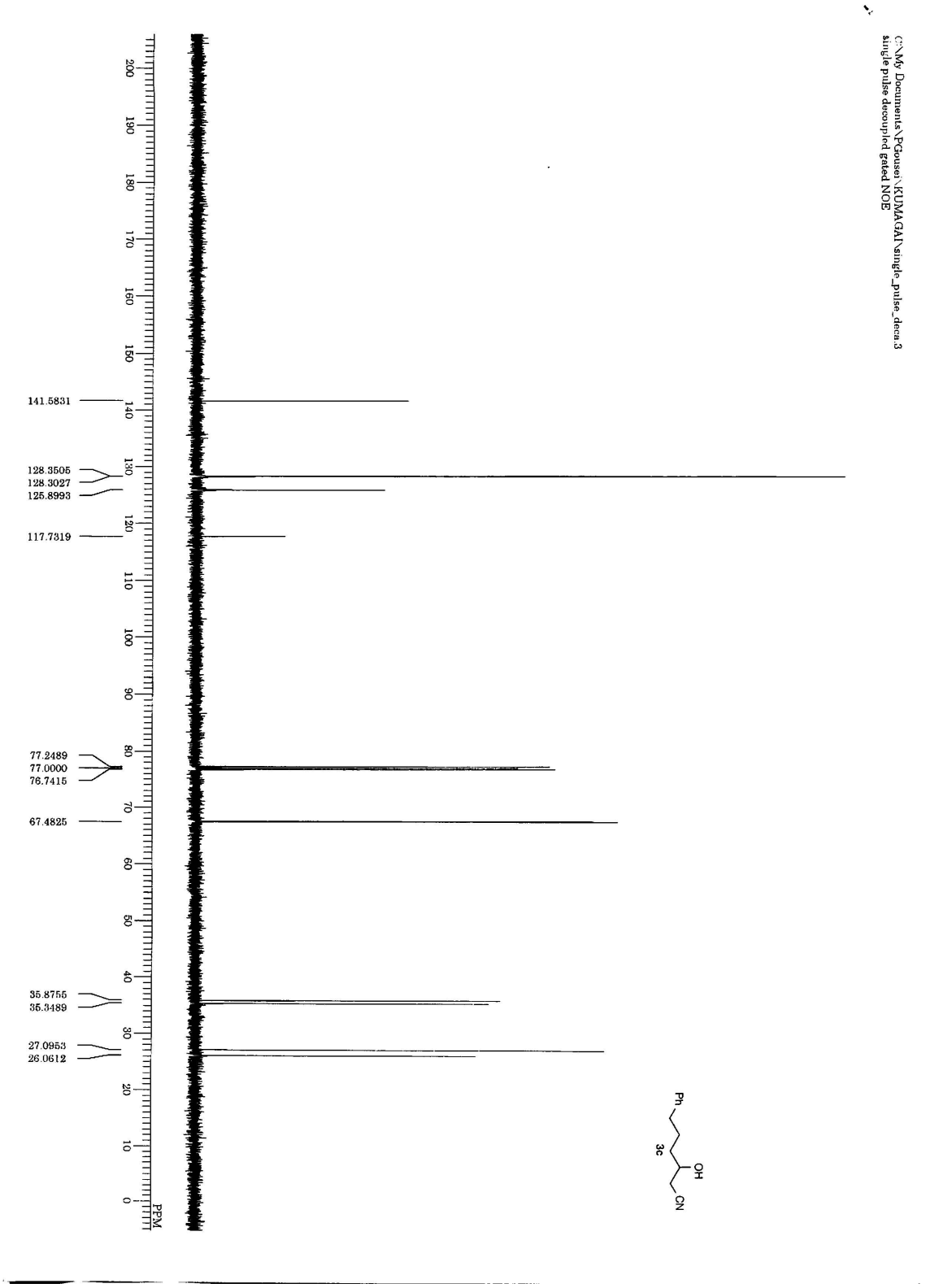


Colorless oil; IR (neat) ν 3391, 2252 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.32-1.45 (m, 9H), 1.51-1.60 (m, 4H), 2.08 (d, *J* = 5.2 Hz, 1H), 2.46 (dd, *J* = 6.5, 16.5 Hz, 1H), 2.54 (dd, *J* = 4.8, 16.5 Hz, 1H), 3.62 (t, *J* = 6.8 Hz, 2H), 3.89-3.94 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 25.1, 25.4, 26.0, 29.1, 29.1, 32.4, 36.3, 62.6, 67.4, 117.9; ESI-MS *m*/*z* 208 $[M+Na]^+$; HRMS (FAB^+) calcd. for $C_{10}H_{20}NO_2$ $[M+H]^+$ 186.1489, found 186.1494.

3-Hydroxy-6-(4-acetyl)phenylhexanitrile (3j)



Colorless oil; IR (neat) ν 3455, 2250, 1678 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.56-1.70 (m, 3H), 1.77-1.86 (m, 1H), 2.46 (dd, *J* = 6.3, 16.6 Hz, 1H), 2.52 (dd, *J* = 5.1, 16.6 Hz, 1H), 2.55 (s, 3H), 2.66-2.70 (m, 2H), 2.78 (brd, *J* = 5.1Hz, 1H), 3.85-3.92 (m, 1H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.84 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 26.2, 26.5, 26.8, 35.4, 35.8, 67.4, 117.6, 128.5, 128.6, 135.0, 147.6, 198.1; ESI-MS *m*/*z* 254 $[M+Na]^+$; HRMS (FAB^+) calcd. for $C_{14}H_{18}NO_2$ $[M+H]^+$ 232.1332, found 232.1340.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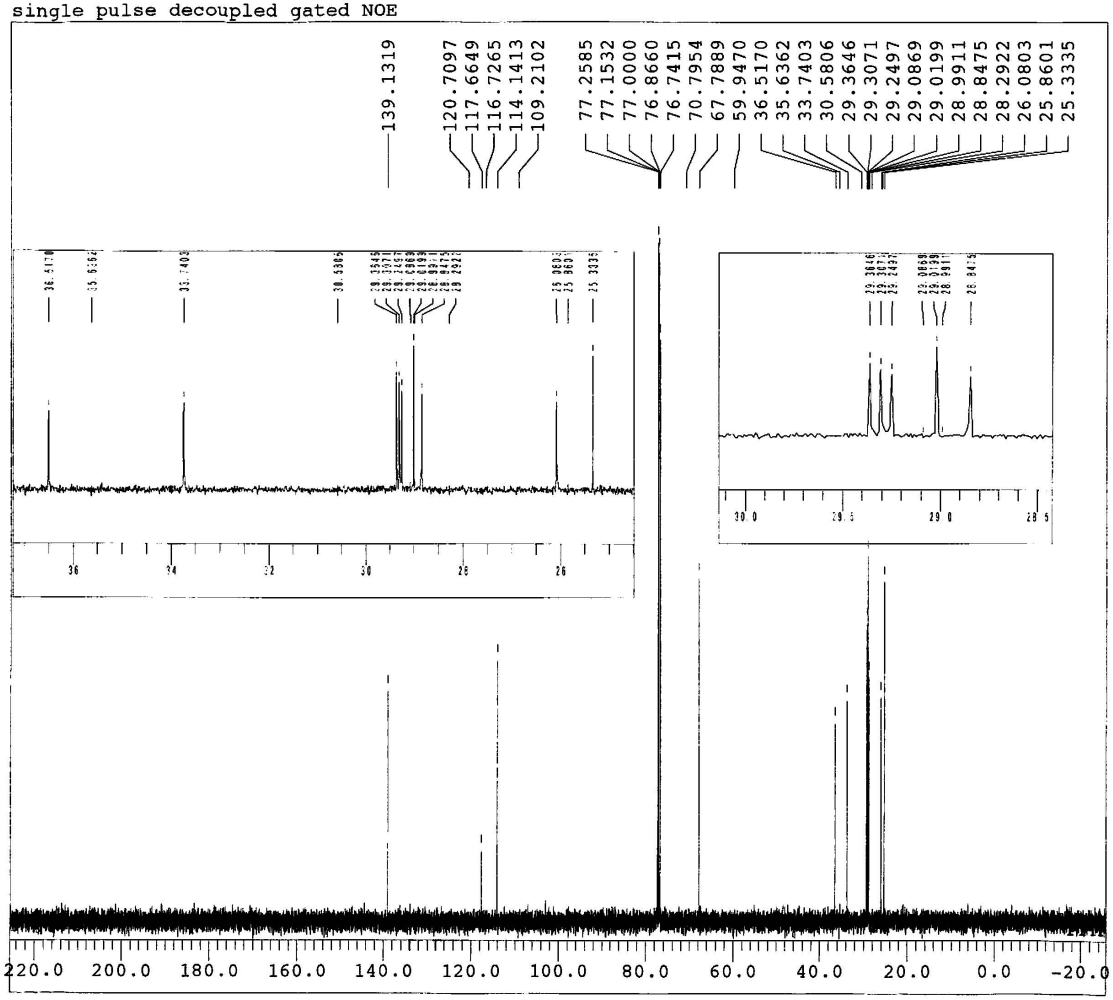

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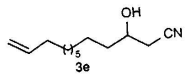

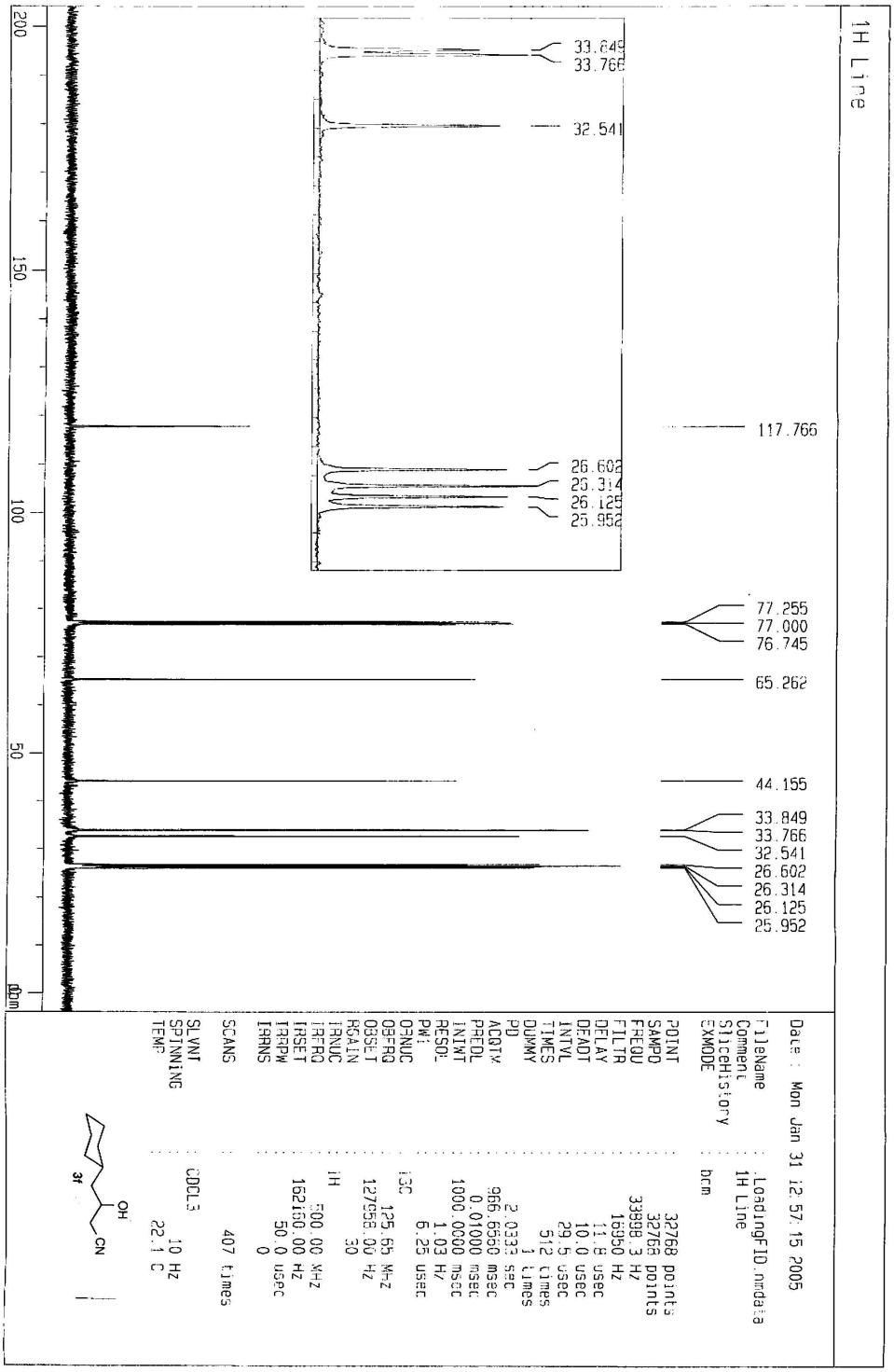
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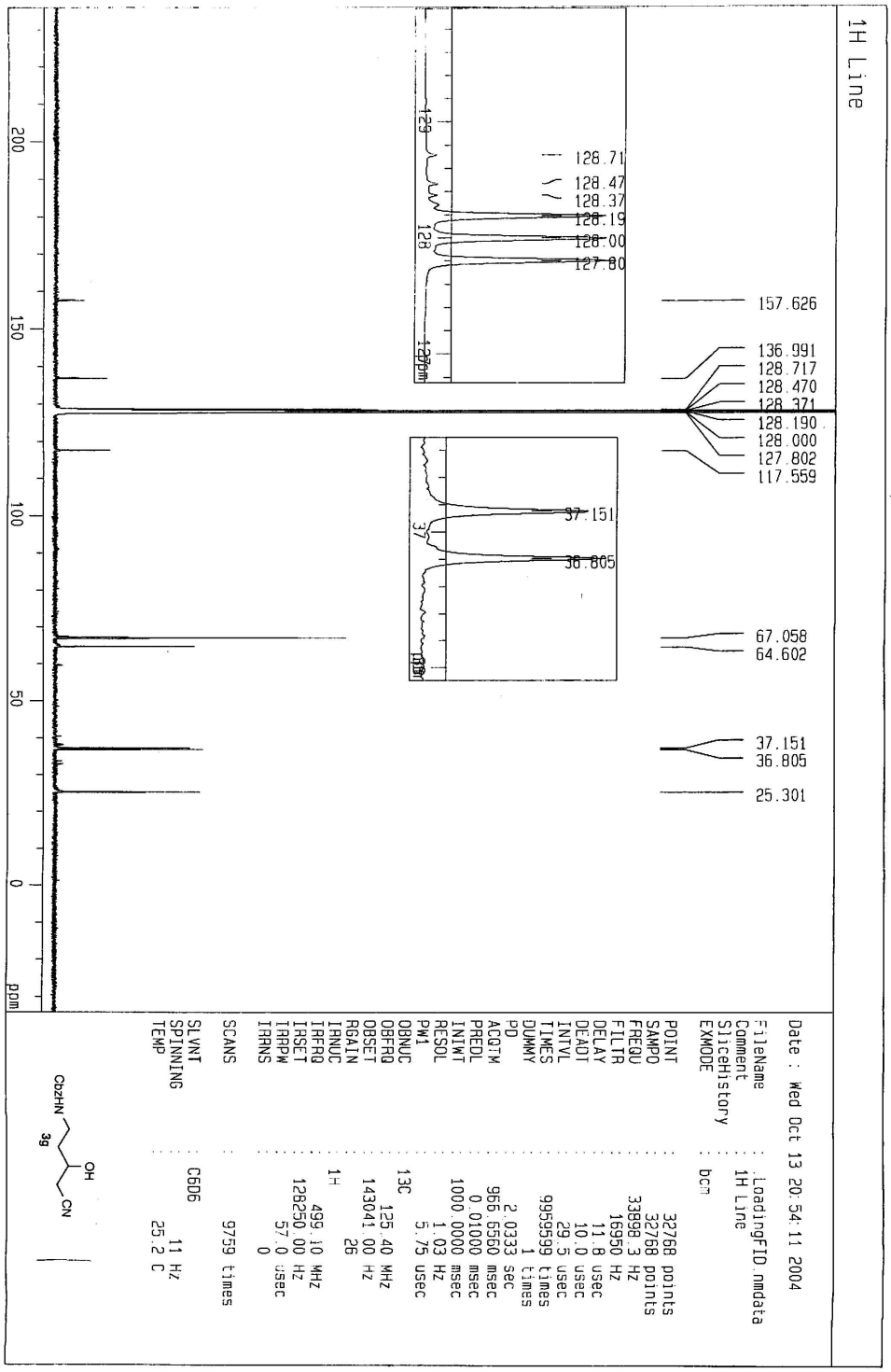
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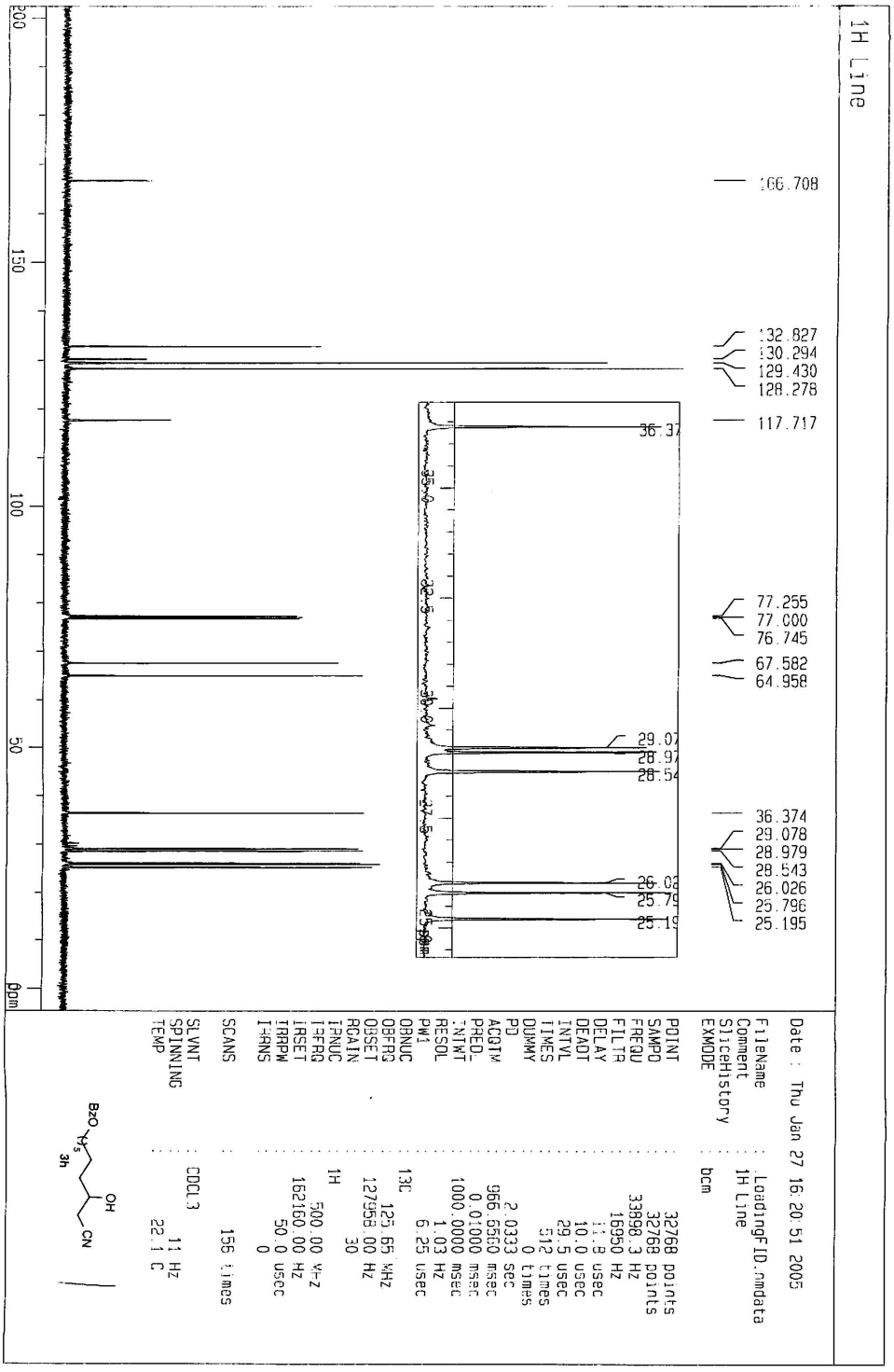
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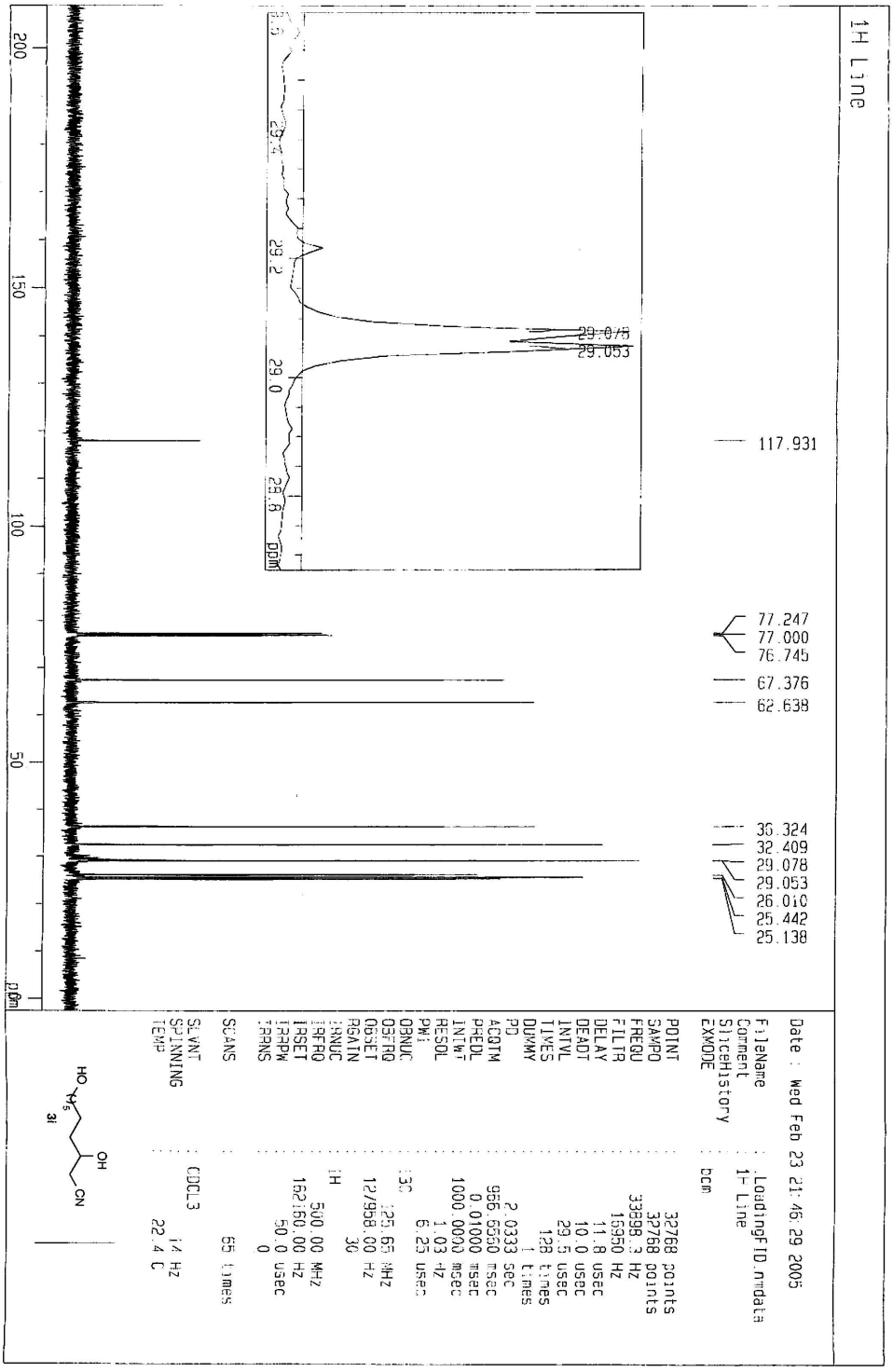
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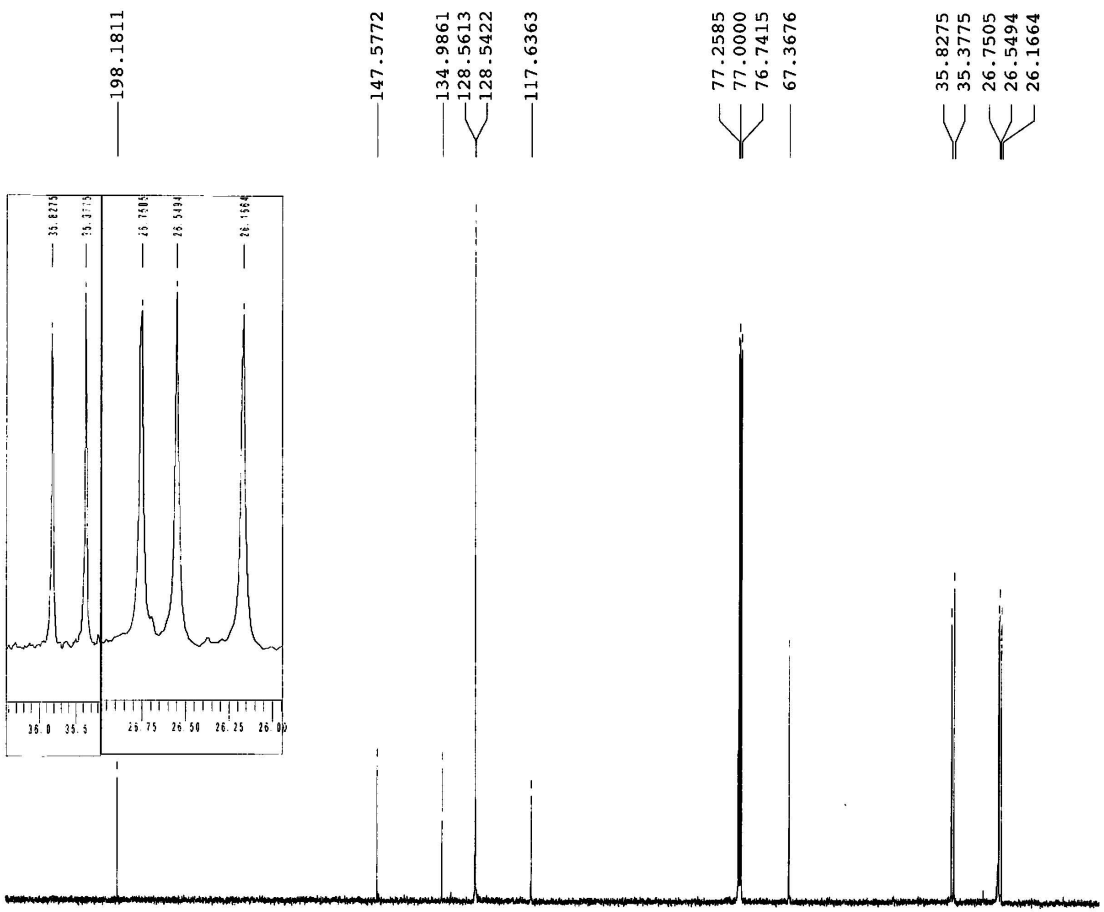
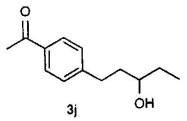
single pulse decoupled gated NOE



DFILE	C:\My Documents\PGousei\KUM
COMNT	single pulse decoupled gate
DATIM	04-02-2005 11:10:50
OBNUC	13C
EXMOD	single_pulse_dec
OBFRQ	124.51 MHz
OBSET	3.45 KHz
OBFIN	6.0 Hz
POINT	40961
FREQU	48828.9 Hz
SCANS	548
ACQTM	0.839 sec
PD	2.000 sec
PW1	3.6 us
IRNUC	1H
CTEMP	17.4 c
SLVNT	D2O
EXREF	77.00 ppm
BF	0.12 Hz
RGAIN	60



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