An Efficient Protocol for the Cross-Metathesis of Sterically Demanding Olefins

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Supporting Information
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General Experimental Information

Instrumentation

Melting points (m.p.) were determined using a Reichert hot-stage melting point apparatus and are uncorrected.

Infrared spectra (IR) spectra were recorded on a Perkin-Elmer 1600 series Fourier Transform infrared spectrophotometer as thin films of liquid (neat) between sodium chloride plates. IR absorptions (ν_{max}) are reported in wavenumbers (cm^{-1}) with the relative intensities expressed as s (strong), m (medium) or prefixed b (broad).

Proton nuclear magnetic resonance (^1H n.m.r.) spectra were recorded on Bruker DPX300 or DRX400 spectrometers operating at 300 or 400 MHz respectively, as solutions in deuterated solvents as specified. Each resonance was assigned according to the following convention: chemical shift; multiplicity; observed coupling constants (*J* Hz); number of protons. Chemical shifts (δ), measured in parts per million (ppm), are reported relative to the residual proton peak in the solvent used as specified. Multiplicities are denoted as singlet (s), doublet (d), triplet (t), quartet (q), pentet (p), multiplet (m) or prefixed broad (b), or a combination where necessary.

Carbon-13 nuclear magnetic resonance (^{13}C n.m.r.) spectra were recorded on Bruker DPX300 or DRX400 spectrometers operating at 75 or 100 MHz respectively, as solutions in deuterated solvents as specified. Chemical shifts (δ), measured in parts per million (ppm), are reported relative to the residual proton peak in the deuterated solvent (as specified).

Low resolution electrospray ionisation (ESI) mass spectra were recorded on a Micromass Platform Electrospray mass spectrometer (QMS-quadrupole mass electrometry) as solutions in specified solvents. Spectra were recorded in positive and negative modes (ESI^+ and ESI^-) as specified. High resolution electrospray mass spectra (HRMS) were recorded on a Bruker BioApex 47e Fourier Transform mass spectrometer (4.7 Tesla magnet) fitted with an analytical electrospray source. The mass spectrometer was calibrated with an internal standard solution of sodium iodide in MeOH.

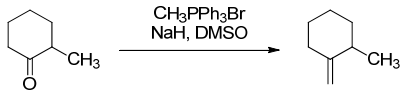
Solvents and Reagents

Dichloromethane (CH_2Cl_2) was supplied by Merck and distilled over CaH prior to use. Diethyl ether (Et_2O), ethyl acetate (EtOAc), hexane and methanol (MeOH) were used as supplied by Merck. (*S*)-(-)-2-Amino-4-pentenoic acid, α-methylstyrene, 2,3-dimethyl-1-butene, (-)-carvone, (-)-β-pinene, camphene, (1*S*)-(-)-camphor, geranyl acetate, (+)-limonene oxide, (1,3-bis-(2,4,6-trimethylphenyl)-2-imidazolidinylidene)dichloro-(*o*-isopropoxyphenylmethylene)ruthenium and benzylidene[1,3-bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene]dichloro-(tricyclohexylphosphine)ruthenium were used as supplied by Aldrich.

Experimental Procedures

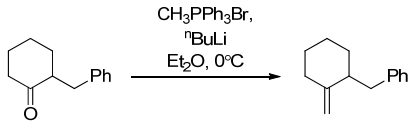
Preparation of Cross Partners

2-Methyl-1-methylenecyclohexane



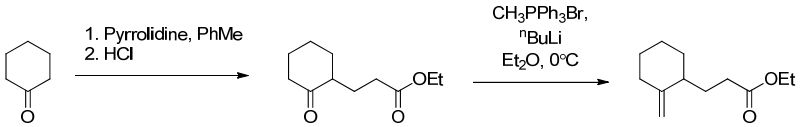
2-Methyl-1-methylenecyclohexane was prepared according to a modified procedure of Corey.[1] Dry DMSO (50 mL) was added to sodium hydride powder (2.54 g, 0.101 mol) under an inert atmosphere. The resultant suspension was stirred for 45 min at 80 ºC or until bubbling of the mixture had ceased and a clear yellow solution remained. After the reaction mixture had returned to r.t., a solution of methyltriphenylphosphonium bromide (35.7 g, 0.100 mol) in dry DMSO (100 mL) was added *via* cannula and allowed to stir for a further 45 min. 2-Methylcyclohexanone (12.3 g, 0.110 mol) was then added to the reaction mixture and left to stir for 16 h. Distillation of the reaction mixture (20 ^{o}C, 0.2 mbar) into a liquid nitrogen trap gave the titled compound as a colourless liquid (9.21 g, 75 %). All spectral data for 2-methyl-1-methylenecyclohexane matched those previously reported.[2]

2-Benzyl-1-methylenecyclohexane



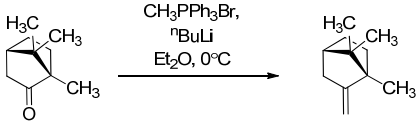
Titled compound was prepared according to a modified procedure of Ghatak.[3] To a stirred suspension of methyltriphenylphosphonium bromide (10.7 g, 30.0 mmol) in diethyl ether (100 mL) at 0 ^{o}C was added ^{n}BuLi (17.3 mL, 26.0 mmol) dropwise. The resultant orange solution was stirred for a further 1 h before 2-benzylcyclohexanone (3.77 g, 20.0 mmol) was added dropwise *via* syringe. The reaction mixture was stirred for 4 h at r.t. before being quenched with saturated NH_4Cl solution and extracted with diethyl ether. The combined organic extracts were washed with brine, dried over $NaSO_4$, filtered and concentrated *in vacuo*. The crude residue was purified *via* flash column chromatography to give the titled compound as a colourless oil (2.98 g, 80%). All spectral data for 2-benzyl-1-methylenecyclohexane matched those previously reported.[4]

Ethyl 3-(2-methylenecyclohexyl)propanoate



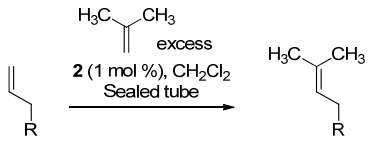
Titled compound was prepared according to the procedure of Renaud.[5] All spectral data for ethyl 3-(2-methylenecyclohexyl)propanoate matched those previously reported.

(1*R*,4*S*)-1,7,7-Trimethyl-2-methylenebicyclo[2.2.1]heptane

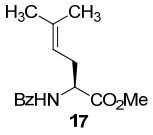


Titled compound was prepared according to the procedure of Yan.[6] All spectral data for 2,7,7-trimethyl-3-methylenebicyclo[2.2.1]heptane matched those previously reported.

General procedure for butenolysis of terminal olefins



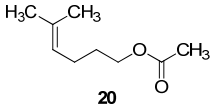
The geminal dimethyl analogues were prepared according to a modified procedure of Grubbs.[7] An oven dried (thick walled) Schlenk vessel with stir bar was flushed with dry nitrogen. The terminal olefinic substrate (1.0 mmol) was added and the vessel was lowered into a liquid nitrogen bath. Catalyst **3** (0.01 mmol) was added to the frozen substrate against a flow of nitrogen. The vessel was evacuated and backfilled with dry nitrogen 3 times before isobutylene (5 mL) was condensed into the vessel. The vessel was sealed and warmed to r.t. before being lowered into an oil bath at 40 °C. The reaction mixture was stirred for 12 h before the vessel was removed from the oil bath and cooled to r.t.. The excess isobutylene was carefully vented and the residue was purified by column chromatography.



17

(*S*)-Methyl 2-benzamido-5-methylhex-4-enoate 17

ν_{max} (neat): 3326bm, 2965m, 2915m, 1747s, 1641s, 1521s, 1493m, 1225m, 1173m cm^{-1}. ^{1}H n.m.r. (400 MHz, $CDCl_3$): δ 7.70 (d, *J* = 7.2 Hz, 2H), 7.39 (t, *J* = 7.2 Hz, 1H), 7.30 (t, *J* = 7.2 Hz, 2H), 6.39 (d, *J* = 7.2 Hz, 1H), 5.03 (t, *J* = 7.2 Hz, 1H), 4.74 (dt, *J* = 5.6 & 7.2 Hz, 1H), 3.66 (s, 3H), 2.66-2.45 (m, 2H), 1.62 (s, 3H), 1.52 (s, 3H). ^{13}C n.m.r. (100 MHz, $CDCl_3$): δ 172.5, 166.9, 136.0, 133.9, 131.4, 128.3, 126.9, 117.6, 52.5, 52.1, 30.5, 25.7, 17.7. LRMS (ESI^+, MeOH): *m/z* 284.0 $[M + Na]^+$, $C_{15}H_{19}NO_3Na$ requires 284.1.

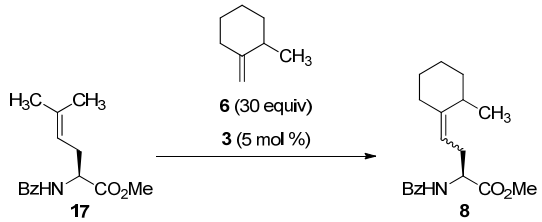


20

5-Methylhex-4-en-1-yl acetate 20

ν_{max} (neat): 2963m, 2931m, 1739s, 1367m, 1235s, 1041m cm^{-1}. ^{1}H n.m.r. (400 MHz, $CDCl_3$): δ 5.12-5.07 (m, 1H), 4.05 (t, *J* = 6.8 Hz, 2H), 2.07-2.02 (m, 2H), 2.04 (s, 3H), 1.71-1.62 (m, 2H), 1.69 (s, 3H), 1.60 (s, 3H). ^{13}C n.m.r. (100 MHz, $CDCl_3$): δ 171.3, 131.9, 124.2, 64.7, 28.3, 27.7, 26.2, 21.1, 17.8. LRMS (ESI^+, MeOH): *m/z* 179.0 $[M + Na]^+$, $C_9H_{16}O_2Na$ requires 179.1.

Representative CM Procedure for Sterically Hindered Olefins

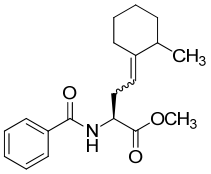


17 **8**

(*S*)-Methyl 2-benzamido-5-methylhex-4-enoate **17** (50.0 mg, 0.191 mmol), 2-methyl-1-methylenecyclohexane (631 mg, 5.74 mmol, 30.0 eq.) and benzene (1 mL) were added to an oven dried Schlenk vessel equipped with a magnetic stir bar. The vessel was sealed and subjected to freeze pump thaw to remove trace oxygen. 2nd Gen. Hoveyda-Grubbs catalyst **3** (6.0 mg, 5.0 mol %) was then added under a flow of N_2 to the reaction mixture. The reaction vessel was then placed under a partial vacuum until the solvent begins to bubble. It was then sealed and heated to 100 °C for 24 h. The reaction mixture was distilled at 0.2 mmHg with a water or liquid N_2 condenser to recover excess cross partner. In all cases, the excess olefin was recovered in >90% yield. The residue was then loaded onto a silica column and eluted with EtOAc : hexane (1 : 5 → 1 : 3) to isolate the cross product(s). In the cases where racemic starting material was used or no *E*/*Z*- selectivity was obtained,

up to 4 diastereo-isomeric cross products may be formed. No attempt was made to separate these isomers and therefore some n.m.r. spectra represent the isomeric mixture of the cross products. An asterisk (*) is used to denote any twinning pairs of peaks where the difference in δ is below 0.1 ppm in the ^{13}C n.m.r. spectrum.

Compound Characterisation

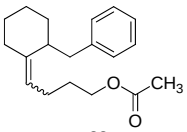


8

(2*S*)-Methyl 2-benzamido-4-(2-methylcyclohexylidene)butanoate 8

Titled compound was prepared according to Representative CM Procedure above. After purification, the titled compound was obtained as a colourless oil (33.1 mg, 55 %).

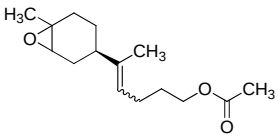
ν_{max} (neat): 3347bm, 2927s, 2851s, 1742s, 1655s, 1537s, 1445m, 1361m, 1246m, 1211s, 1100m, 1073m, 1027m cm^{-1}. ^1H n.m.r. (300 MHz, $CDCl_3$): δ 7.77 (d, *J* = 7.2 Hz, 2H), 7.50 (t, *J* = 7.2 Hz, 1H), 7.43 (t, *J* = 7.2 Hz, 2H), 6.65 (d, *J* = 7.2 Hz, 1H), 5.01 (t, *J* = 7.2 Hz, 1H), 4.83 (dt, *J* = 7.2 & 5.4 Hz, 1H), 3.77 (s, 3H), 2.77-2.55 (m, 2H), 2.44-2.40 (m, 1H), 2.12-2.06 (m, 2H), 1.82-1.37 (m, 6H), 1.00 (d, *J* = 6.6 Hz, 3H). ^{13}C n.m.r. (75 MHz, $CDCl_3$): δ 172.8, 172.7, 167.0, 148.8*, 144.9, 134.3, 131.8, 128.7, 127.2, 127.1, 114.2, 111.9*, 52.8, 52.7, 52.5*, 38.9, 37.4, 36.7, 30.0*, 29.9, 28.9, 28.8, 28.4, 28.3*, 28.2, 28.0, 26.9, 25.2*, 18.8*. (Mixture of 4 isomers) HRMS (ESI^+, MeOH): *m/z* 316.1909 $[M + H]^+$, $C_{19}H_{26}NO_3$ requires 316.1913.



22

4-(2-Benzylcyclohexylidene)butyl acetate 22

Titled compound was prepared according to Representative CM Procedure above, using 5-methylhex-4-en-1-yl acetate **18** (30.0 mg, 0.192 mmol), 2-benzyl-1-methylenecyclohexane (1.07 g, 5.76 mmol, 30 eq.) and **3** (6.0 mg, 5.0 mol %). After purification, the titled compound was obtained as a colourless oil (49.5 mg, 90 %). ^1H n.m.r. (400 MHz, $CDCl_3$): δ 7.18-7.03 (m, 5H), 4.98 (t, *J* = 7.2, 1H), 3.96 (t, *J* = 7.2 Hz, 2H), 2.88 (dd, *J* = 13.6 & 6.4 Hz, 1H), 2.56 (dd, *J* = 13.6 & 8.8 Hz, 1H), 2.32-2.24 (m, 2H), 2.10-2.00 (m, 2H), 2.04 (s, 3H), 1.60-1.20 (m, 8H). All spectral data matched those previously reported.[8]

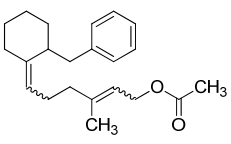


23

5-((3*R*)-6-Methyl-7-oxabicyclo[4.1.0]heptan-3-yl)hex-4-en-1-yl acetate 23

Titled compound was prepared according to Representative CM Procedure above, using 5-methylhex-4-en-1-yl acetate **18** (30 mg, 0.192 mmol), (+)-limonene oxide (877 mg, 5.76 mmol, 30 eq.) and **3** (6.0 mg, 5.0 mol %). After purification, the titled compound was obtained as a colourless oil (42.1 mg, 87 %).

ν_{max} (neat): 2931s, 1738s, 1436m, 1367m, 1241s, 1038m cm^{-1}. ^1H n.m.r. (300 MHz, $CDCl_3$): δ 5.01 (t, *J* = 6.6 Hz, 1H), 4.04 (t, *J* = 6.6 Hz, 2H), 2.97 (d, *J* = 5.1 Hz, 1H), 2.04 (s, 3H), 2.00-1.54 (m, 10H), 1.46-1.33 (m, 2H), 1.30 (s, 3H), 1.27-1.17 (m, 2H). ^{13}C n.m.r. (100 MHz, $CDCl_3$): δ 171.3, 139.2, 123.3, 64.7, 59.6, 57.7, 42.7, 31.0, 30.0, 28.3, 27.4, 26.2, 24.5, 23.3, 21.1, 13.8. HRMS (ESI^+, MeOH): *m/z* 275.1612 $[M + Na]^+$, $C_{15}H_{24}O_2Na$ requires 291.1357.



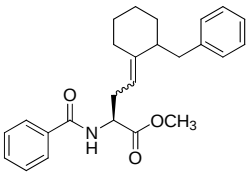
24

6-(2-Benzylcyclohexylidene)-3-methylhex-2-en-1-yl acetate 24

Titled compound was prepared according to Representative CM Procedure above, using geranyl acetate (40.0 mg, 0.204 mmol), 2-benzyl-1-methylenecyclohexane (1.14 g, 6.11 mmol, 30 eq.) and **3** (6.4 mg, 5.0 mol %). After purification, the titled compound was obtained as a colourless oil (35.3

mg, 53 %).

ν_{max} (neat): 2924m, 2855m, 1737s, 1449m, 1367m, 1231s, 1022m cm^{-1}. ^1H n.m.r. (300 MHz, $CDCl_3$): δ 7.30-7.26 (m, 2H), 7.22-7.14 (m, 3H), 5.39-5.26 (m, 1H), 5.05-5.00 (m, 1H), 4.64-4.56 (m, 2H), 2.90 (dd, *J* = 6.0 & 13.8 Hz, 1H), 2.63-2.54 (m, 1H), 2.37-2.28 (m, 2H), 2.15-1.99 (m, 5H), 2.06 (s, 3H), 1.79-1.77 (m, 2H), 1.72 (s, 2H), 1.61 (s, 1H), 1.58-1.27 (m, 5H). ^{13}C n.m.r. (100 MHz, $CDCl_3$): δ 171.2*, 149.1, 142.8, 142.6, 142.3*, 141.7*, 141.1, 129.2, 128.3, 128.1*, 125.9, 125.7*, 120.0, 119.7, 119.3, 118.5, 114.7, 61.5, 61.3, 60.9, 46.2, 46.1, 40.0, 39.0*, 38.8, 32.9, 32.8, 32.7, 32.6, 28.4, 28.3*, 28.1, 27.4*, 25.9, 25.5, 24.3, 24.2*, 23.7, 21.2*, 16.6. (Mixture of 4 isomers) HRMS (ESI^+, MeOH): *m/z* 349.2129 $[M + Na]^+$, $C_{22}H_{30}O_2Na$ requires 349.2138.

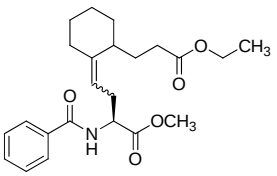


25

(2*S*)-Methyl 2-benzamido-4-(2-benzylcyclohexylidene)butanoate 25

Titled compound was prepared according to Representative CM Procedure above, using (*S*)-Methyl 2-benzamido-5-methylhex-4-enoate **17** (50.0 mg, 0.191 mmol), 2-benzyl-1-methylenecyclohexane (1.07 g, 5.74 mmol, 30 eq.), benzene (1 mL) and HGII **3** (6.0 mg, 5.0 mol%). After purification, the titled compound was obtained as a colourless oil (37.4 mg, 50 %).

ν_{max} (neat): 3326bm, 3060m, 3025m, 2926s, 2853s, 1742s, 1645s, 1528s, 1488s, 1448s, 1355m, 1261m, 1211m, 1178m, 1155m, 1095m, 1028m cm^{-1}. ^1H n.m.r. (400 MHz, $CDCl_3$): δ 7.75 (m, 2H), 7.54-7.50 (m, 1H), 7.46-7.43 (m, 2H), 7.24-7.19 (m, 2H), 7.16-7.09 (m, 3H), 6.56 (d, *J* = 7.2 Hz, 0.5H), 6.51 (d, *J* = 7.2 Hz, 0.5H), 5.00 (t, *J* = 7.6 Hz, 1H), 4.85-4.79 (m, 1H), 3.76 (bs, 3H), 2.89-2.82 (m, 1H), 2.77-2.68 (m, 1H), 2.64-2.55 (m, 1H), 2.40-2.24 (m, 2H), 2.10-2.02 (m, 2H), 1.72-1.54 (m, 2H), 1.52-1.39 (m, 3H), 1.35-1.26 (m, 1H). ^{13}C n.m.r. (100 MHz, $CDCl_3$): δ 172.7, 172.6, 167.0*, 147.0, 146.9, 141.3, 141.2, 134.3, 134.2, 131.8*, 129.1, 129.0, 128.7*, 128.3*,127.2, 125.9, 114.1, 114.0, 52.8, 52.7, 52.5*, 46.4, 46.2, 38.9, 38.8, 33.1*, 29.9, 28.4*, 27.5, 27.3, 24.0, 23.9. (Mixture of isomers). HRMS (ESI^+, MeOH): *m/z* 414.2049 $[M + Na]^+$, $C_{25}H_{29}NO_3Na$ requires 414.2040.

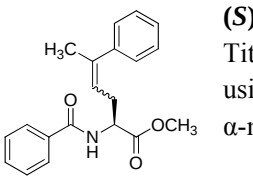


26

(2*S*)-Methyl 2-benzamido-4-(2-(3-ethoxy-3-oxopropyl)cyclohexylidene) butanoate 26

Titled compound was prepared according to Representative CM Procedure above, using (*S*)-Methyl 2-benzamido-5-methylhex-4-enoate **17** (50.0 mg, 0.191 mmol), ethyl 3-(2-methylenecyclohexyl)propanoate (1.12 g, 5.74 mmol, 30 eq.), benzene (1 mL) and HGII **3** (6.0 mg, 5.0 mol %). After purification, the titled compound was obtained as a colourless oil (43.7 mg, 57 %).

ν_{max} (neat): 3346bm, 2925s, 2853m, 1731s, 1660s, 1651s, 1531s, 1488m, 1446m, 1371m, 1261m, 1210m, 1177m cm^{-1}. ^1H n.m.r. (300 MHz, $CDCl_3$): δ 7.82-7.79 (m, 2H), 7.53-7.40 (m, 3H), 6.5 (d, *J* = 7.5 Hz, 1H), 5.04 (t, *J* = 7.5 Hz, 1H), 4.86 (dt, *J* = 7.5 & 5.4 Hz, 1H), 4.09 (q, *J* = 7.2 Hz, 2H), 3.78 (s, 3H), 2.84-2.56 (m, 2H), 2.21 (t, *J* = 7.6 Hz, 2H), 2.14-2.01 (m, 3H), 1.97-1.82 (m, 1H), 1.71-1.55 (m, 5H), 1.32-1.26 (m, 2H), 1.22 (t, *J* = 7.2H, 3H). ^{13}C n.m.r. (75 MHz, $CDCl_3$): δ 174.0, 172.7*, 167.0*, 146.0, 134.2*, 131.8, 128.7*, 127.2*, 115.0*, 60.4, 60.3, 52.8*, 52.6, 52.5, 44.5, 44.4, 33.7*, 32.7*, 30.0*, 28.2*, 27.1*, 26.2, 23.0*, 14.4. (Mixture of isomers). HRMS (ESI^+, MeOH): *m/z* 424.2087 $[M + Na]^+$, $C_{23}H_{31}NO_5Na$ requires 424.2094.



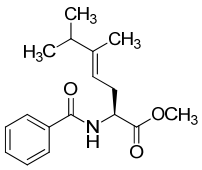
27

(*S*)-Methyl 2-benzamido-5-phenylhex-4-enoate 27

Titled compound was prepared according to Representative CM Procedure above, using (*S*)-Methyl 2-benzamido-5-methylhex-4-enoate **17** (50.0 mg, 0.191 mmol), α-methylstyrene (677 mg, 5.74 mmol, 30 eq.), benzene (1 mL) and HGII **3** (6.0

mg, 5.0 mol %). After purification, the titled compound was obtained as a colourless oil (59.9 mg, 97 %).

ν_{max} (neat): 3345bm, 1739s, 1646s, 1602w, 1533s, 1489s, 1436m, 1266m, 1217m, 1179m cm^{-1}. ^1H n.m.r. (400 MHz, $CDCl_3$): δ 7.80-7.78 (m, 2H), 7.51 (tt, *J* = 7.2 & 1.6 Hz, 1H), 7.46-7.41 (m, 2H), 7.36-7.22 (m, 5H), 6.80 (d, *J* = 7.6 Hz, 1H), 5.70 (tq, *J* = 7.6 & 1.2 Hz, 1H), 4.99 (dt, *J* = 7.6 & 5.8 Hz, 3.80 (s, 3H), 2.99-2.77 (m, 2H), 2.04 (s, 3H). ^{13}C n.m.r. (100 MHz, $CDCl_3$): δ 172.6, 167.1, 143.4, 139.4, 134.1, 131.9, 128.7, 128.4, 127.2, 127.1, 125.9, 121.2, 60.5, 52.7, 52.6, 31.7, 16.3. (Mixture of isomers). HRMS (ESI^+, MeOH): *m/z* 346.1417 $[M + Na]^+$, $C_{20}H_{21}NO_3Na$ requires 346.1414.



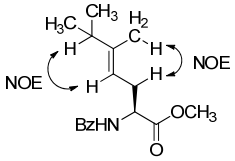
28

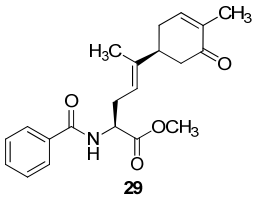
(*S*,*E*)-Methyl 2-benzamido-5,6-dimethylhept-4-enoate 28

Titled compound was prepared according to Representative CM Procedure above, using (*S*)-Methyl 2-benzamido-5-methylhex-4-enoate **17** (50.0 mg, 0.191 mmol), 2,3-dimethyl-1-butene (482 mg, 5.74 mmol, 30 eq.), benzene (1 mL) and HGII **3** (6.0 mg, 5.0 mol %). After purification, the titled compound was obtained as a colourless oil (39.2 mg, 71 %).

ν_{max} (neat): 3347bm, 2961m, 1741s, 1651s, 1532s, 1488m, 1435m, 1361m, 1270m, 1215m cm^{-1}. ^1H n.m.r. (600 MHz, $CDCl_3$): δ 7.77 (dd, *J* = 7.8 & 1.2 Hz, 2H), 7.50 (tt, *J* = 7.8 & 1.2 Hz, 1H), 7.43 (td, *J* = 7.8 & 1.2 Hz, 2H), 6.66 (d, *J* = 7.2 Hz, 1H), 5.12 (t, *J* = 7.2 Hz, 1H), 4.85 (dt, *J* = 7.8 & 5.4 Hz, 1H), 3.76 (s, 3H), 2.72-2.55 (m, 2H), 2.25 (septet, *J* = 6.6 Hz, 1H), 1.57 (s, 3H), 0.97 (d, *J* = 6.6 Hz, 3H), 0.96 (d, *J* = 6.6 Hz, 3H). ^{13}C n.m.r. (100 MHz, $CDCl_3$): δ 172.8, 167.0, 146.3, 134.2, 131.8, 128.7, 127.1, 115.2, 52.5, 52.4, 37.1, 30.7, 21.5, 13.5. (Three signals overlapping). HRMS (ESI^+, MeOH): *m/z* 312.1573 $[M + Na]^+$, $C_{17}H_{23}NO_3Na$ requires 312.1570.

NOESY experiment:





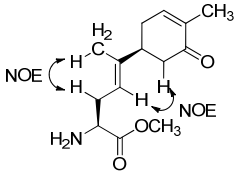
29

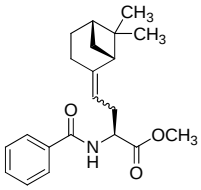
(*S*,*E*)-Methyl 2-benzamido-5-((S)-4-methyl-5-oxocyclohex-3-en-1-yl)hex-4-enoate 29

Titled compound was prepared according to Representative CM Procedure above, using (*S*)-Methyl 2-benzamido-5-methylhex-4-enoate **17** (50.0 mg, 0.191 mmol), (-)-carvone (861 mg, 5.74 mmol, 30 eq.), benzene (1 mL) and HGII **3** (6.0 mg, 5.0 mol %). After purification, the titled compound was obtained as a colourless oil (29.2 mg, 43 %).

ν_{max} (neat): 3391bm, 2960s, 2922s, 2852m, 1739s, 1653s, 1533m, 1447m, 1436m, 1362, 1262s, 1104s, 1026s cm^{-1}. ^1H n.m.r. (600 MHz, $CDCl_3$): δ 7.77 (dd, *J* = 7.8 & 1.2 Hz, 2H), 7.52 (tt, *J* = 7.8 & 1.2 Hz, 1H), 7.45 (tt, *J* = 7.8 & 1.2 Hz, 2H), 6.72-6.70 (m, 1H), 6.68 (d, *J* = 7.2 Hz, 1H), 5.21 (tt, *J* = 6.6 & 1.2 H, 1H), 4.88 (dt, *J* = 7.2 & 5.4 Hz, 1H), 3.78 (s, 3H), 2.78-2.73 (m, 1H), 2.70-2.65 (m, 1H), 2.62-2.58 (m, 1H), 2.47 (ddd, *J* = 16.2, 3.6 & 1.5 Hz, 1H), 2.35 (dd, *J* = 16.2 & 13.2 Hz, 1H), 2.32-2.24 (m, 2H), 1.77 (dt, *J* = 2.4 & 1.2 Hz, 3H), 1.63 (d, *J* = 0.6 Hz, 3H). ^{13}C n.m.r. (75 MHz, $CDCl_3$): δ 199.7, 172.6, 167.0, 144.6, 141.2, 135.6, 134.1, 132.0, 128.8, 127.1, 118.5, 52.7, 52.5, 44.5, 43.3, 31.4, 31.0, 15.8, 14.4. HRMS (ESI^+, MeOH): *m/z* 378.1670 $[M + Na]^+$, $C_{21}H_{25}NO_4Na$ requires 378.1676.

NOESY experiment:



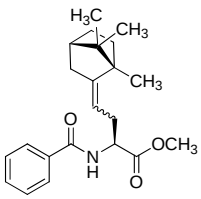


30

(S)-Methyl 2-benzamido-4-((1R,5S)-6,6-dimethylbicyclo[3.1.1]heptan-2-ylidene)butanoate 30

Titled compound was prepared according to Representative CM Procedure above, using (*S*)-Methyl 2-benzamido-5-methylhex-4-enoate **17** (50.0 mg, 0.191 mmol), (-)-β-pinene (781 mg, 5.74 mmol, 30 eq.), benzene (1 mL) and HGII **3** (6.0 mg, 5.0 mol %). After purification, the titled compound was obtained as a colourless oil (23.5 mg, 36 %).

ν_{max} (neat): 3335bm, 2951m, 2921m, 2869m, 1741s, 1652s, 1525s, 1488m, 1439m, 1361m, 1212m, 1179m cm^{-1}. ^1H n.m.r. (300 MHz, $CDCl_3$): δ 7.79-7.76 (m, 2H), 7.50-7.48 (m, 1H), 7.45-7.40 (m, 2H), 6.68 (d, *J* = 7.2 Hz, 1H), 4.92-4.89 (m, 1H), 4.88-4.82 (m, 1H), 3.77 (s, 3H), 2.61-2.51 (m, 2H), 2.39-2.27 (m, 3H), 1.97-1.94 (m, 1H), 1.85-1.80 (m, 2H), 1.63-1.59 (m, 2H), 1.19 (s, 3H), 0.65 (s, 3H). ^{13}C n.m.r. (100 MHz, $CDCl_3$): δ 172.9, 167.0, 147.4, 134.3, 131.8, 128.7, 127.2, 114.4, 52.9, 52.6, 45.3, 40.9, 40.6, 30.2, 27.9, 26.1, 23.8, 22.1, 20.0. (Mixture of isomers). HRMS (ESI^+, MeOH): *m/z* 364.1886 $[M + Na]^+$, $C_{21}H_{27}NO_3Na$ requires 364.1883.

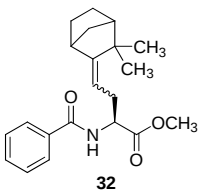


31

(*S*)-Methyl 2-benzamido-4-((1*S*,4*S*)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-ylidene)butanoate 31

Titled compound was prepared according to Representative CM Procedure above, using (*S*)-Methyl 2-benzamido-5-methylhex-4-enoate **17** (50.0 mg, 0.191 mmol), (1*R*,4*S*)-1,7,7-trimethyl-2-methylenebicyclo[2.2.1]heptane (861 mg, 5.74 mmol, 30 eq.), benzene (1 mL) and HGII **3** (6.0 mg, 5.0 mol %). After purification, the titled compound was obtained as a colourless oil (16.3 mg, 24 %).

ν_{max} (neat): 3331bm, 2952s, 2869m, 1742s, 1651s, 1520s, 1486m, 1446m, 1366m, 1265m, 1215m cm^{-1}. ^1H n.m.r. (300 MHz, $CDCl_3$): δ 7.82-7.76 (m, 2H), 7.53-7.40 (m, 3H), 6.63 (d, *J* = 6.9 Hz, 1H), 4.97 (tt, *J* = 7.5 & 2.4 Hz, 1H), 4.85 (dt, *J* = 7.5 & 5.7 Hz, 1H), 3.78 (s, 3H), 2.71-2.51 (m, 2H), 2.47-2.40 (m, 1H), 2.30-2.26 (m, 1H), 1.83-1.70 (m, 3H), 1.65-1.58 (m, 2H), 1.28-1.04 (m, 3H), 0.87 (s, 3H), 0.86 (s, 3H), 0.66 (s, 3H). ^{13}C n.m.r. (100 MHz, $CDCl_3$): δ 172.9, 166.9, 155.0, 134.2, 131.8, 128.7, 127.2, 109.3, 52.6, 52.5, 51.5, 47.4, 44.6, 35.3, 34.9, 31.6, 28.1, 19.8, 18.9, 12.9. (Mixture of isomers). HRMS (ESI^+, MeOH): *m/z* 378.2041 $[M + Na]^+$, $C_{22}H_{29}NO_3Na$ requires 378.2040.



32

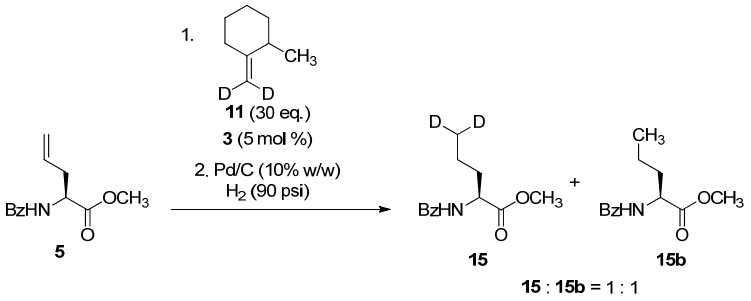
(2*S*)-Methyl 2-benzamido-4-(3,3-dimethylbicyclo[2.2.1]heptan-2-ylidene)butanoate 32

Titled compound was prepared according to Representative CM Procedure above, using (*S*)-Methyl 2-benzamido-5-methylhex-4-enoate **17** (50.0 mg, 0.191 mmol), camphene (781 mg, 5.74 mmol, 30 eq.), benzene (1 mL) and HGII **3** (6.0 mg, 5.0 mol %). After purification, the titled compound was obtained as a colourless oil (22.1 mg, 34 %).

ν_{max} (neat): 3340bm, 2952s, 2873m, 1742s, 1644s, 1538s, 1488m, 1435m, 1362m, 1209m cm^{-1}. ^1H n.m.r. (300 MHz, $CDCl_3$): δ 7.80-7.76 (m, 2H), 7.52-7.47 (m, 1H), 7.45-7.40 m, 2H), 6.65 (bm, 1H), 5.18-5.11 (m, 0.8H), 5.00-4.93 (m, 0.2H), 4.87-4.79 (m, 1H), 3.77 (s, 3H), 2.77-2.45 (m, 2H), 2.37-

2.23 (m, 1H), 2.03-1.99 (m, 1H), 1.91-1.65 (m, 4H), 1.27-1.00 (m, 2H), 0.97-0.95 (m, 3H), 0.88-0.83 (m, 3H). ^{13}C n.m.r. (100 MHz, $CDCl_3$): δ 172.9, 166.9, 152.4, 134.2, 131.8, 128.7, 127.2, 111.2, 53.8, 52.5, 47.7, 44.5, 39.0, 35.3, 31.7, 31.6, 28.9, 21.9, 20.8. (Major diasteromer). HRMS (ESI$^+$, MeOH): *m/z* 364.1886 $[M + Na]^+$, $C_{21}H_{27}NO_3Na$ requires 364.1883.

Deuterium labeling experiment



The CM reaction was performed according to Representative CM Procedure above, using (*S*)-methyl 2-benzamidopent-4-enoate **5** (50.0 mg, 0.214 mmol), **11** (720 mg, 6.43 mmol, 30 eq.), benzene (1 mL) and HGII **3** (6.7 mg, 5 mol %). After distillation of volatiles (0.2 mmHg, 40 ^{o}C), the residue was diluted with methanol (5 mL) and transferred to a Fisher-Porter tube equipped with a stir bar. Pd/C (10% w/w, 11 mg) was added and the reaction vessel was charged with H_2 (90 psi). The heterogeneous reaction mixture was left to stir for 16 h at room temperature. The excess H_2 was carefully vented, the reaction mixture filtered, concentrated *in vacuo* and purified *via* column chromatography to yield a 1:1 mixture of the compound **15** and **15b** (46% combined yield).

Analysis of the 1:1 mixture of compound **15** and **15b**.

^{1}H n.m.r. (300 MHz, $CDCl_3$): δ 7.83-7.80 (m, 2H), 7.55-7.42 (m, 3H), 6.66 (bd, *J* = 6.3 Hz, 1H), 4.85 (dt, *J* = 7.5 & 5.4 Hz, 1H), 3.80 (s, 3H), 2.00-1.72 (m, 2H), 1.46-1.35 (m, 2H), 1.00-0.94 (m, 2H).

^{2}D n.m.r. (61 MHz, $CHCl_3$): δ 0.72 (bs, 2D).

LRMS (ESI$^+$, MeOH): *m/z* 238.2 $[M + H]^+$, $C_{13}H_{16}D_2NO_3$ requires 238.1.

References

(1) Greenwald, R.; Chaykovsky, M.; Corey, E. J. *J. Org. Chem.* **1963**, *28*, 1128-1129.
(2) Meyers A. I.; Ford M. E. *J. Org. Chem.* **1976**, *41*, 1735-1742.
(3) Pal S.; Mukhopadhyaya J. K.; Ghatak U. R. *J. Org. Chem.* **1994**. 59, 2687-2694.
(4) Bailey W. F.; Daskapan T.; Rampalli S. *J. Org. Chem.* **2003**, *68*, 1334-1338.
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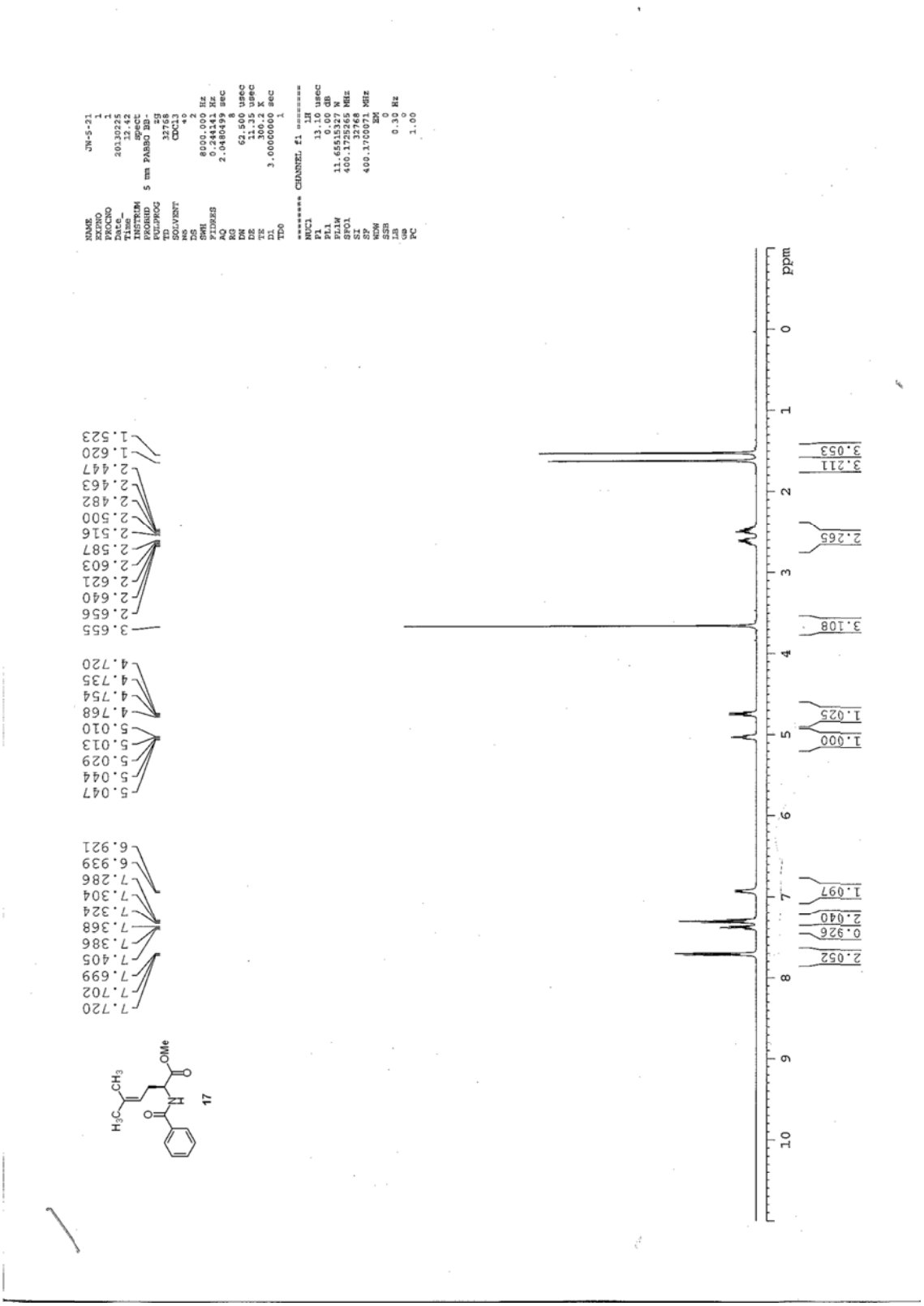
(6) Yan T. H.; Tsai C. C.; Chien C. T.; Cho C. C.; Huang P. C. *Org. Lett.* **2004**, *6*, 4961-4963.
(7) Chatterjee, A. K.; Sanders D. P.; Grubbs R. H. *Org. Lett.* **2002**, *4*, 1939-1942.
(8) Stewart I. C.; Douglas C. J.; Grubbs R. H. *Org. Lett.* **2008**, *10*, 441-444.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DE 11.35 usec
TE 300.2 K
D1 3.00000000 sec
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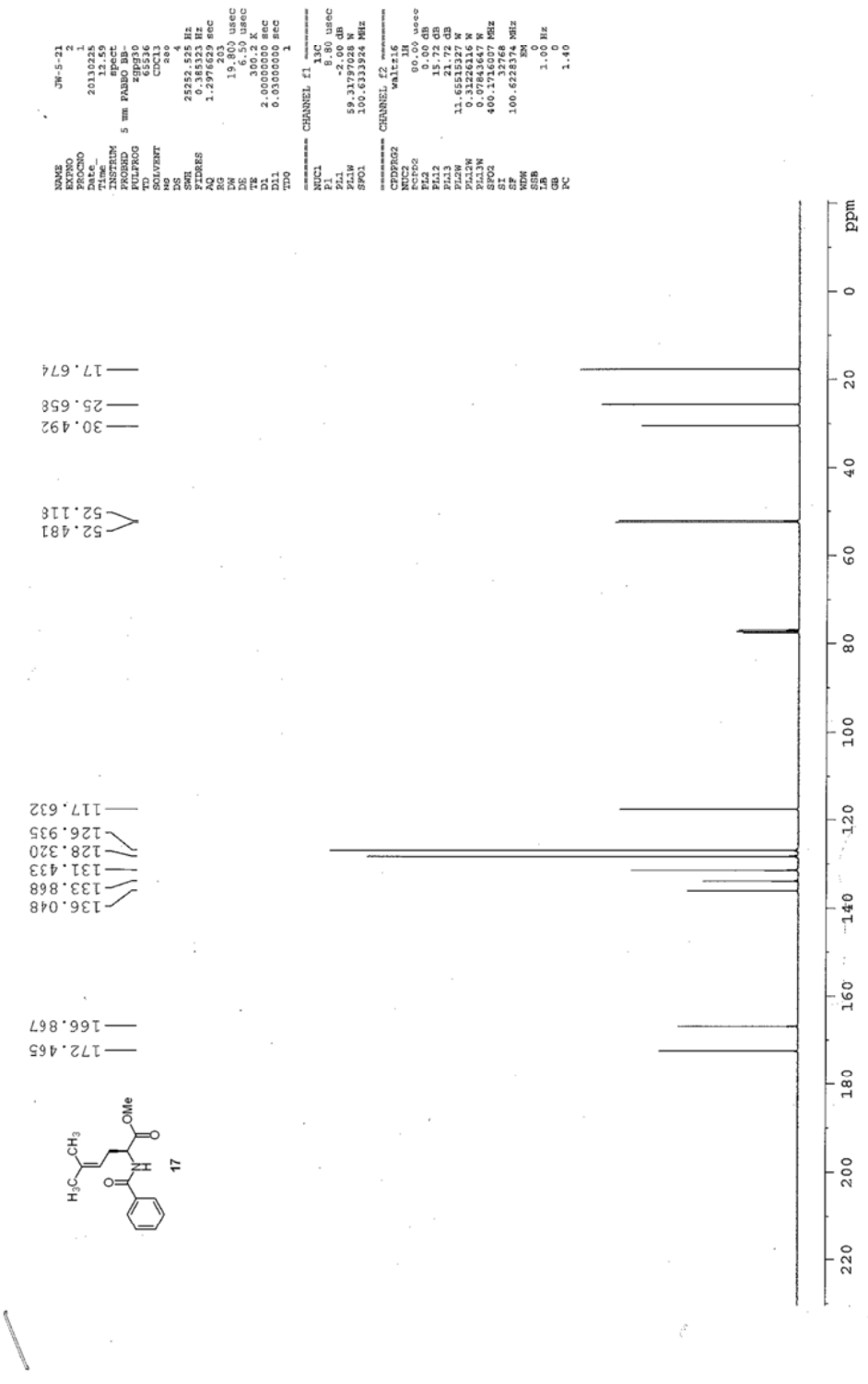
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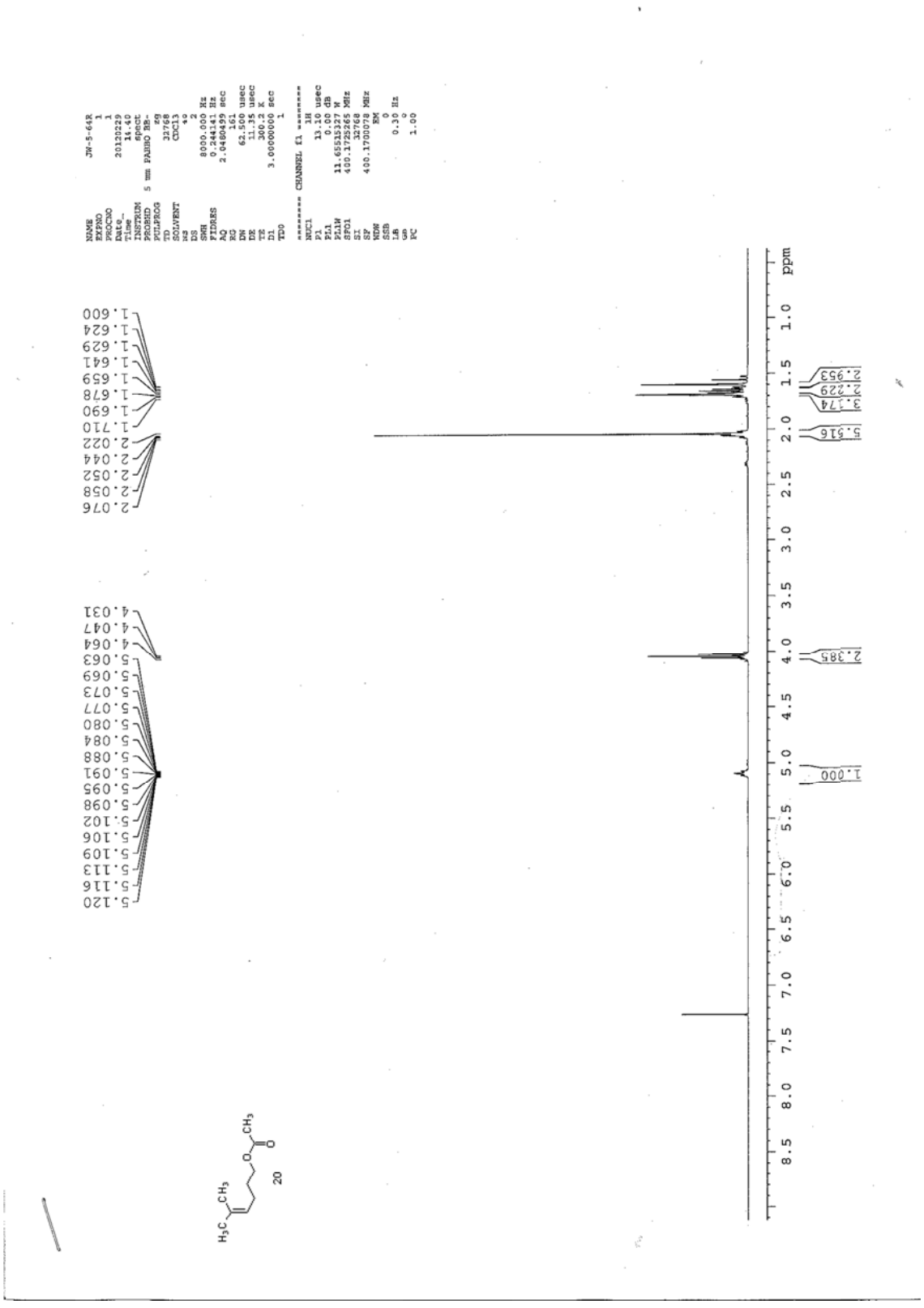
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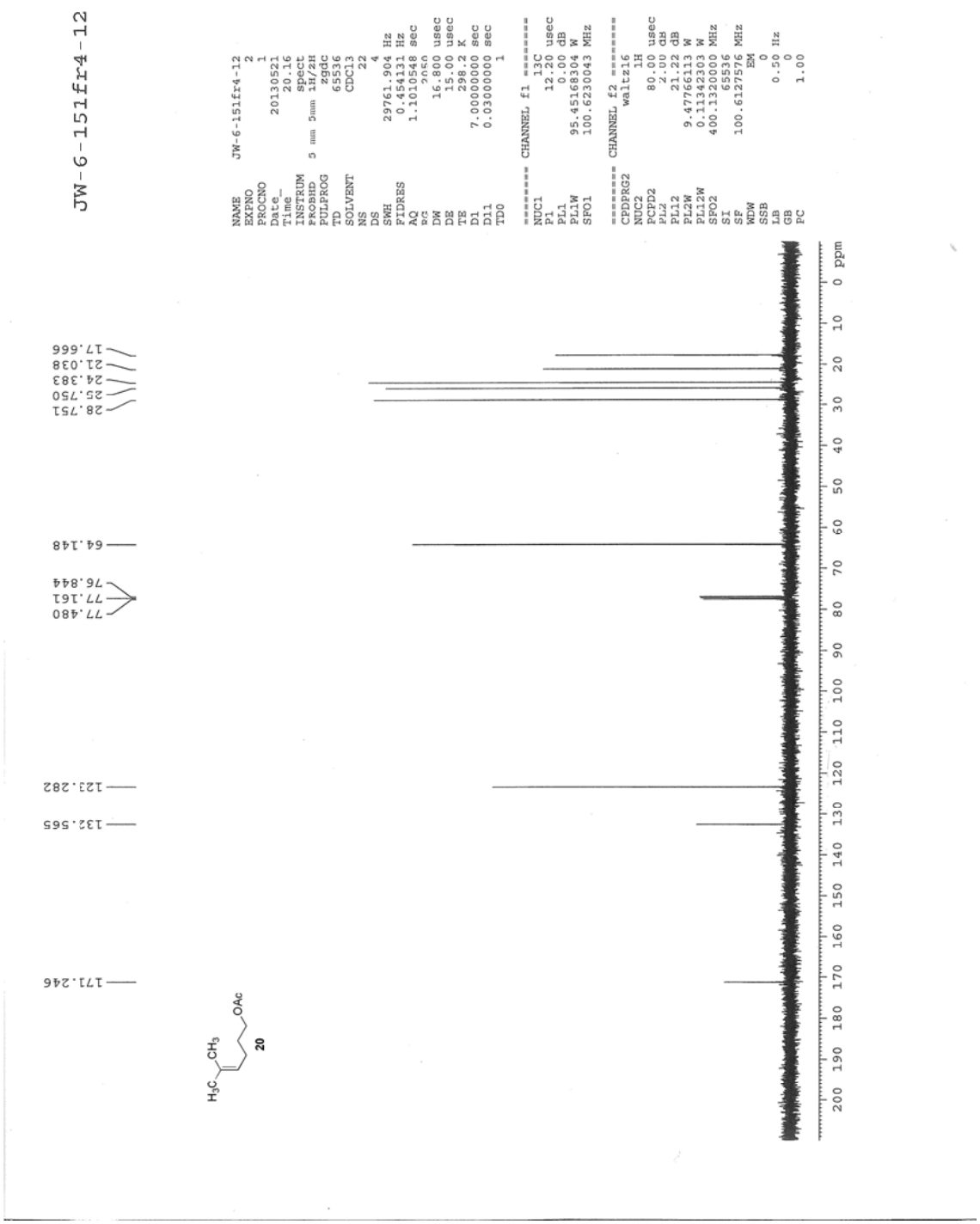
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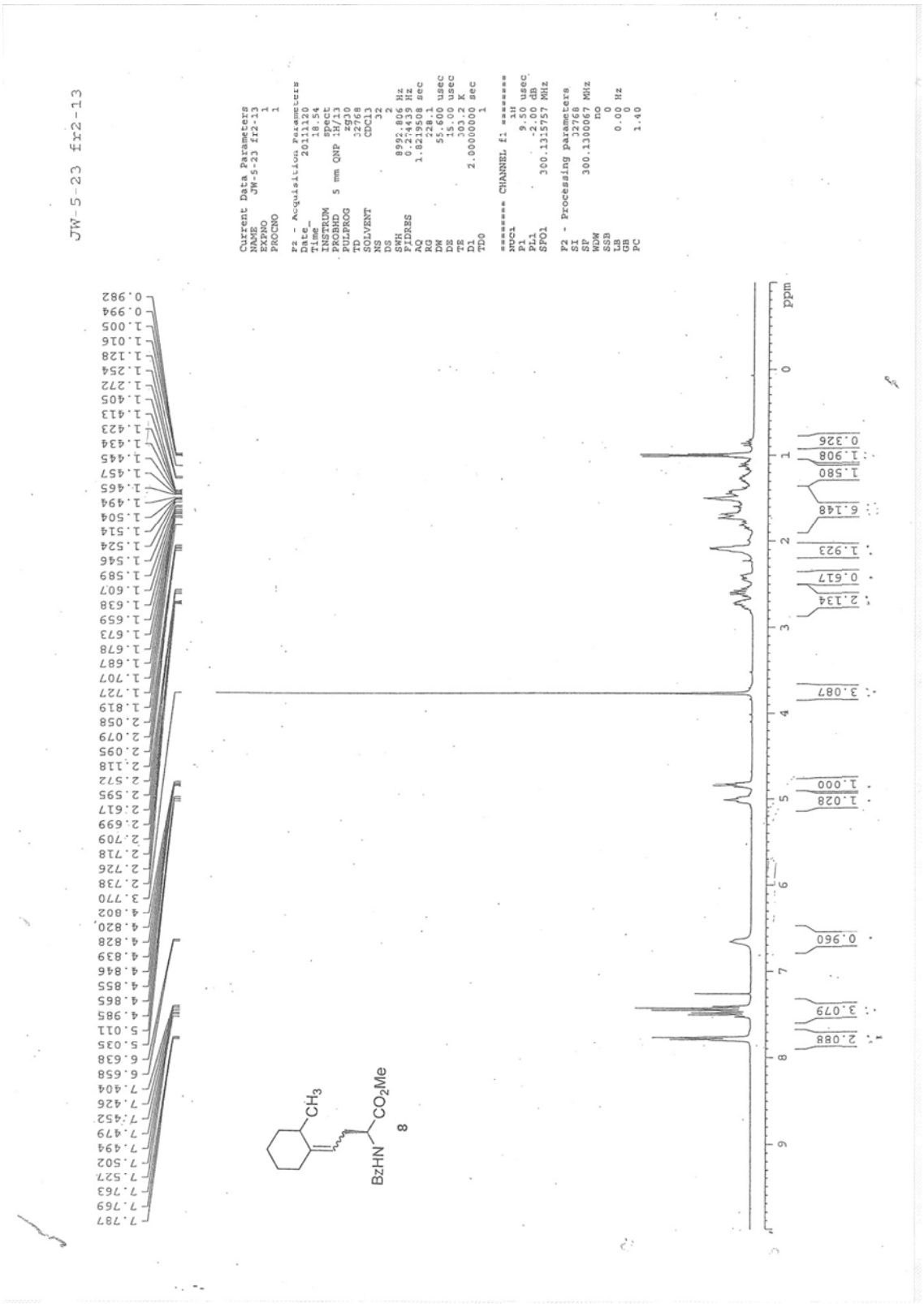
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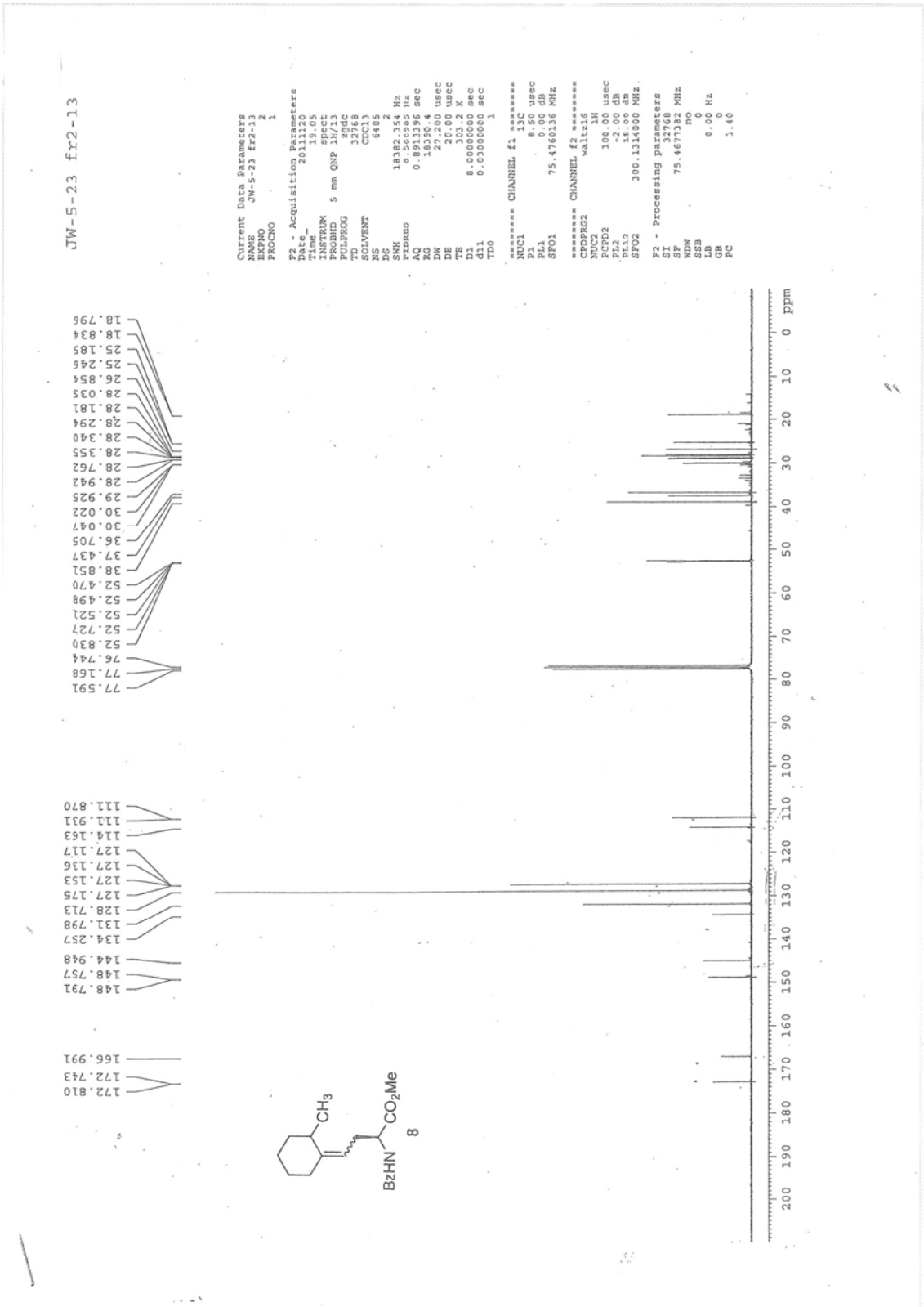
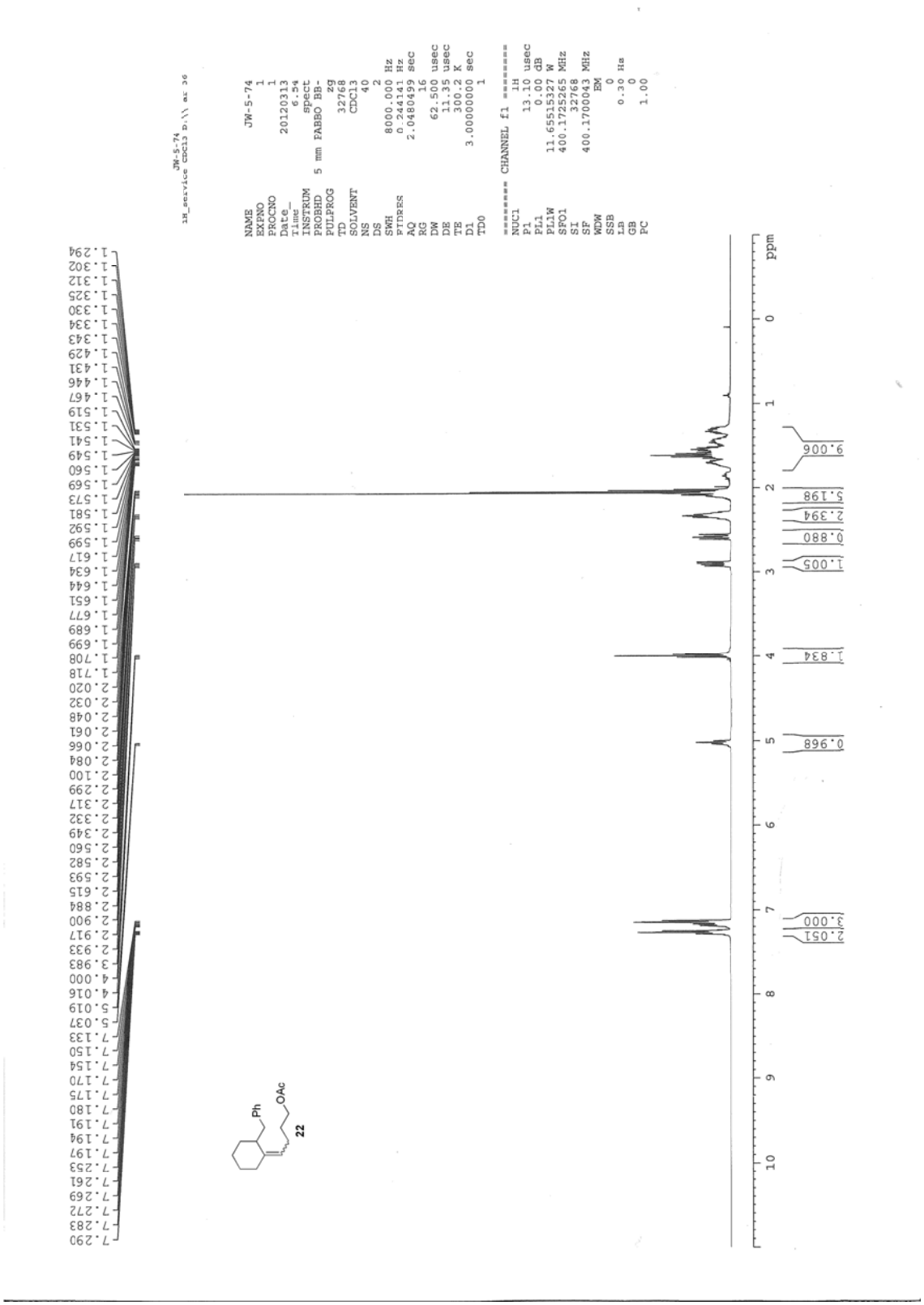
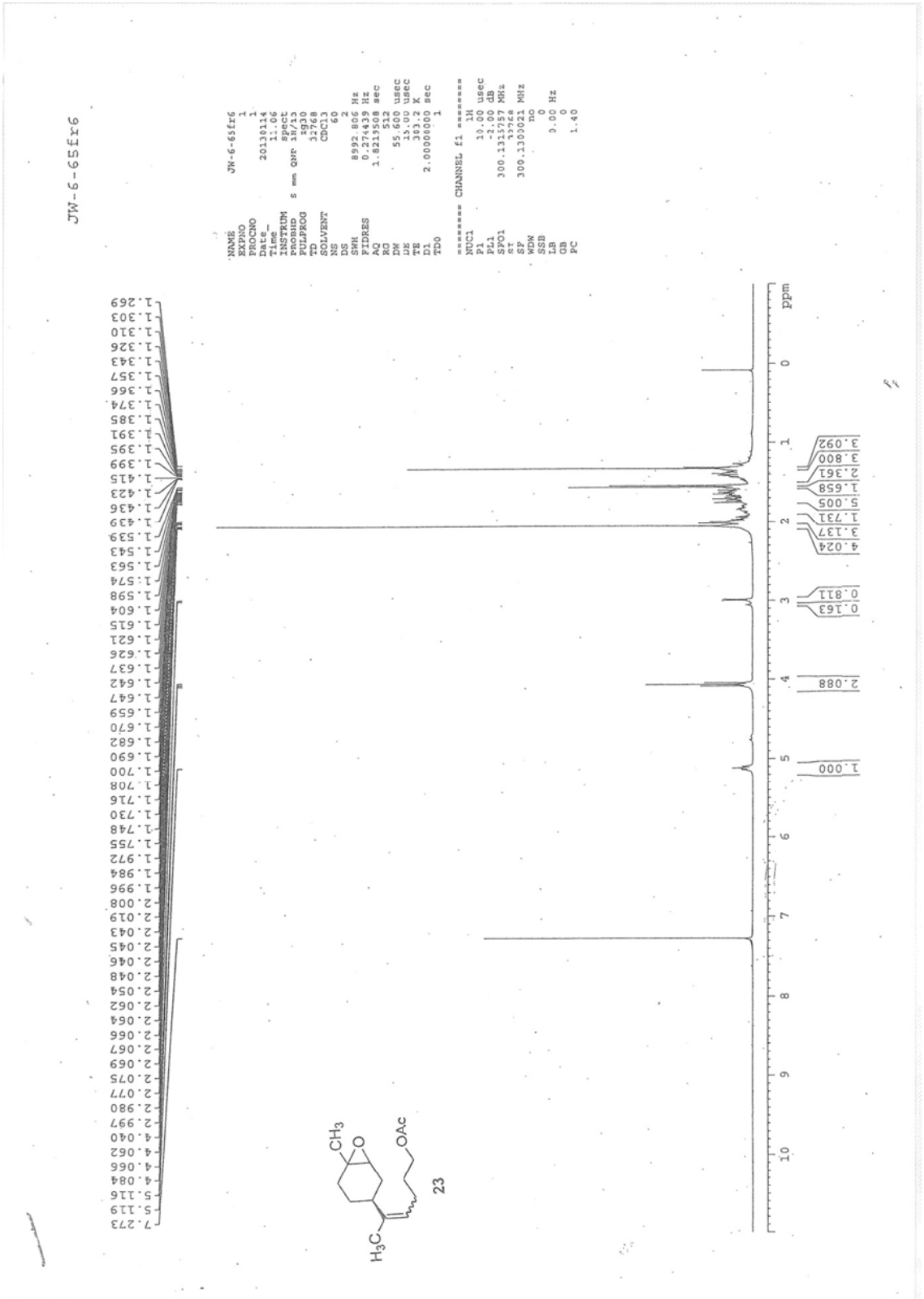
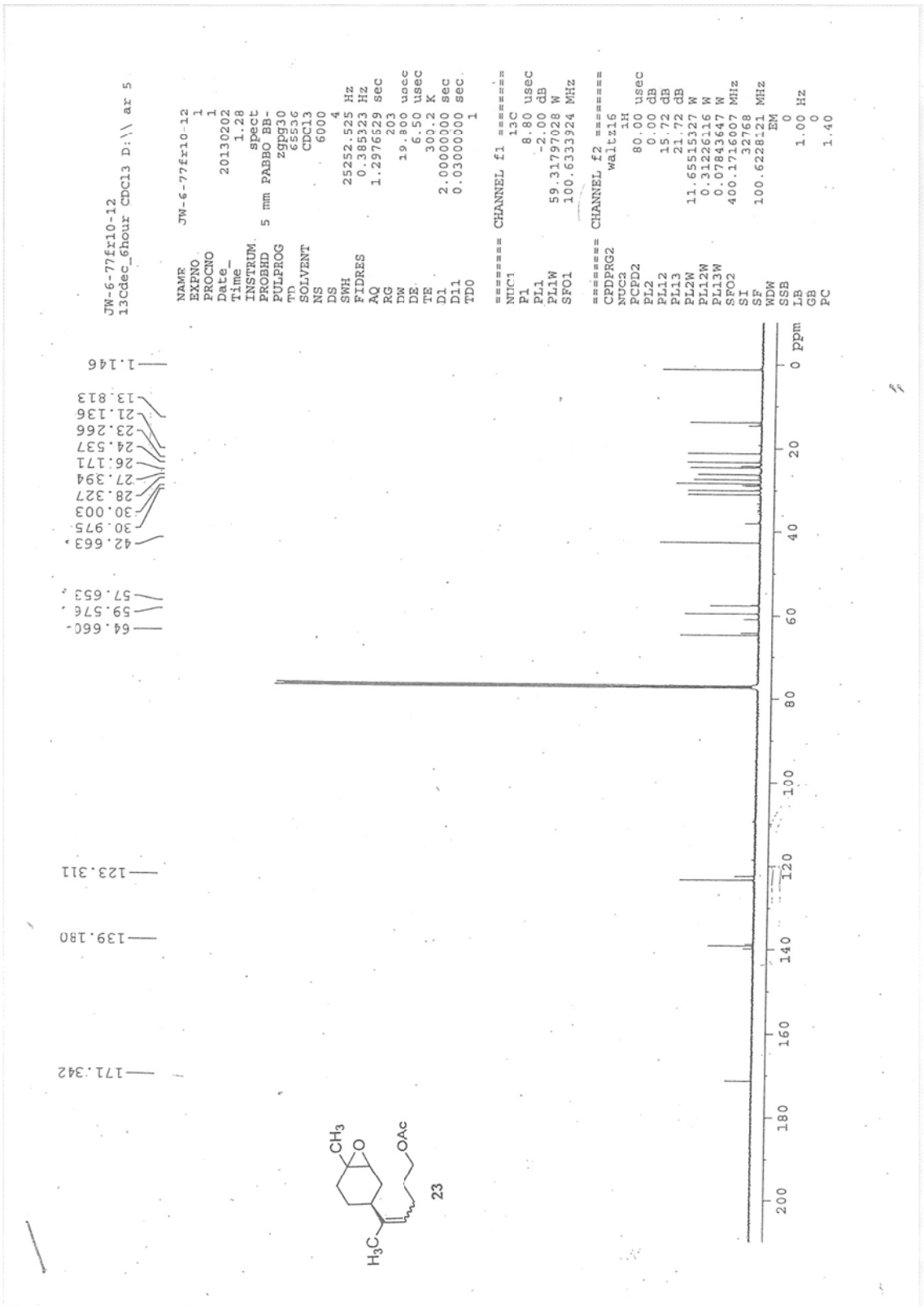
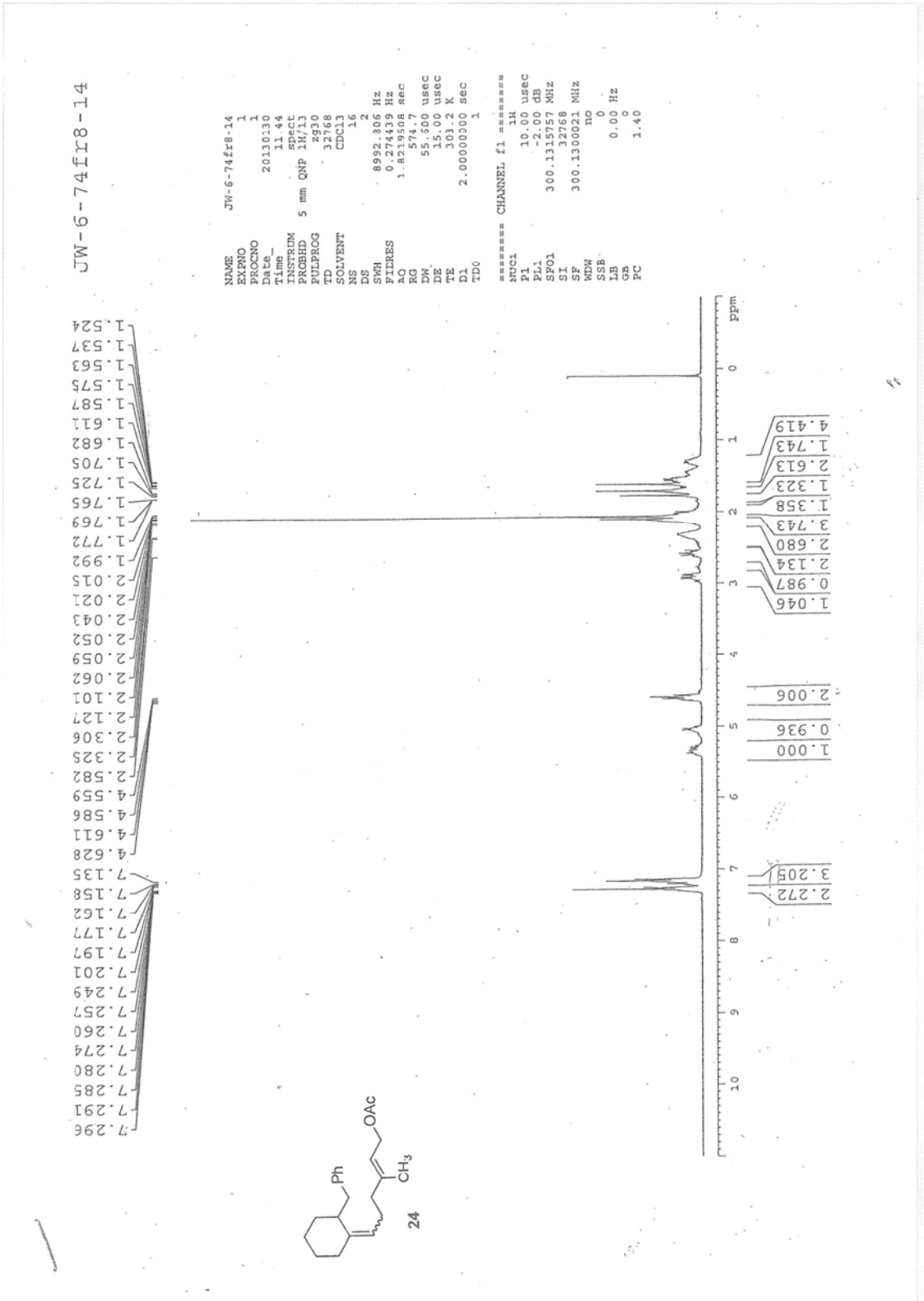
1.494
1.504
1.514
1.524
1.546
1.589
1.607
1.638
1.659
1.673
1.678
1.687
1.707
1.727
1.819
2.058
2.079
2.095
2.118
2.572
2.595
2.617
2.699
2.709
2.718
2.726
2.738
2.770
3.802
4.820
4.828
4.839
4.846
4.855
4.865
4.985
5.011
5.035
6.638
6.658
7.404
7.426
7.452
7.479
7.494
7.502
7.527
7.763
7.769
7.787
CH3
CO2Me
BzHN
8
2.088
3.079
0.960
1.000
1.028
3.087
2.134
0.617
1.923
6.148
1.580
1.908
0.326

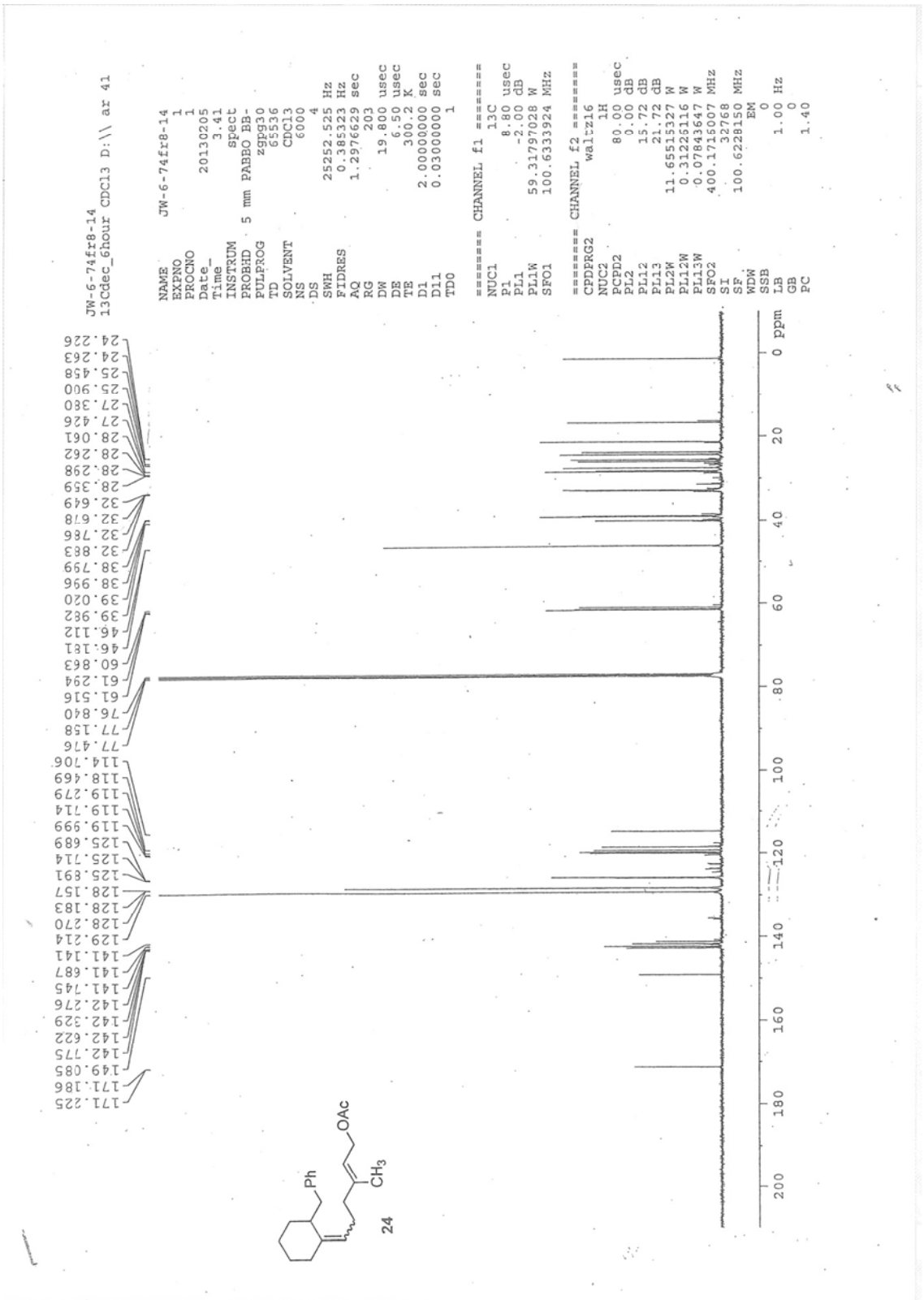

JW-5-23 fr2-13
Current Data Parameters
NAME JW-5-23 fr2-13
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20111120
Time_ 13.55
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zgdc
TD 32768
SOLVENT CDCl3
NS 6405
DS 2
SWH 18382.354 Hz
FIDRES 0.560890 Hz
AQ 0.8899396 sec
RG 181.4
DW 27.200 usec
DE 20.00 usec
TE 303.2 K
D1 8.00000000 sec
d11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.50 usec
PL1 0.00 dBm
SFO1 75.4760136 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 -2.00 dB
PL12 16.00 dB
SFO2 300.1314000 MHz
F2 - Processing parameters
SI 32768
SF 75.4677382 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.40
77.591
77.168
76.744
52.830
52.727
52.521
52.498
52.470
38.851
37.437
36.705
30.047
30.022
29.925
28.942
28.762
28.355
28.340
28.294
28.181
28.035
26.854
25.246
25.185
18.834
18.796
172.810
172.743
166.991
148.791
148.757
144.948
134.257
131.798
128.713
127.175
127.153
127.136
127.117
114.163
111.931
111.870
CH3
CO2Me
BzHN
8
ppm

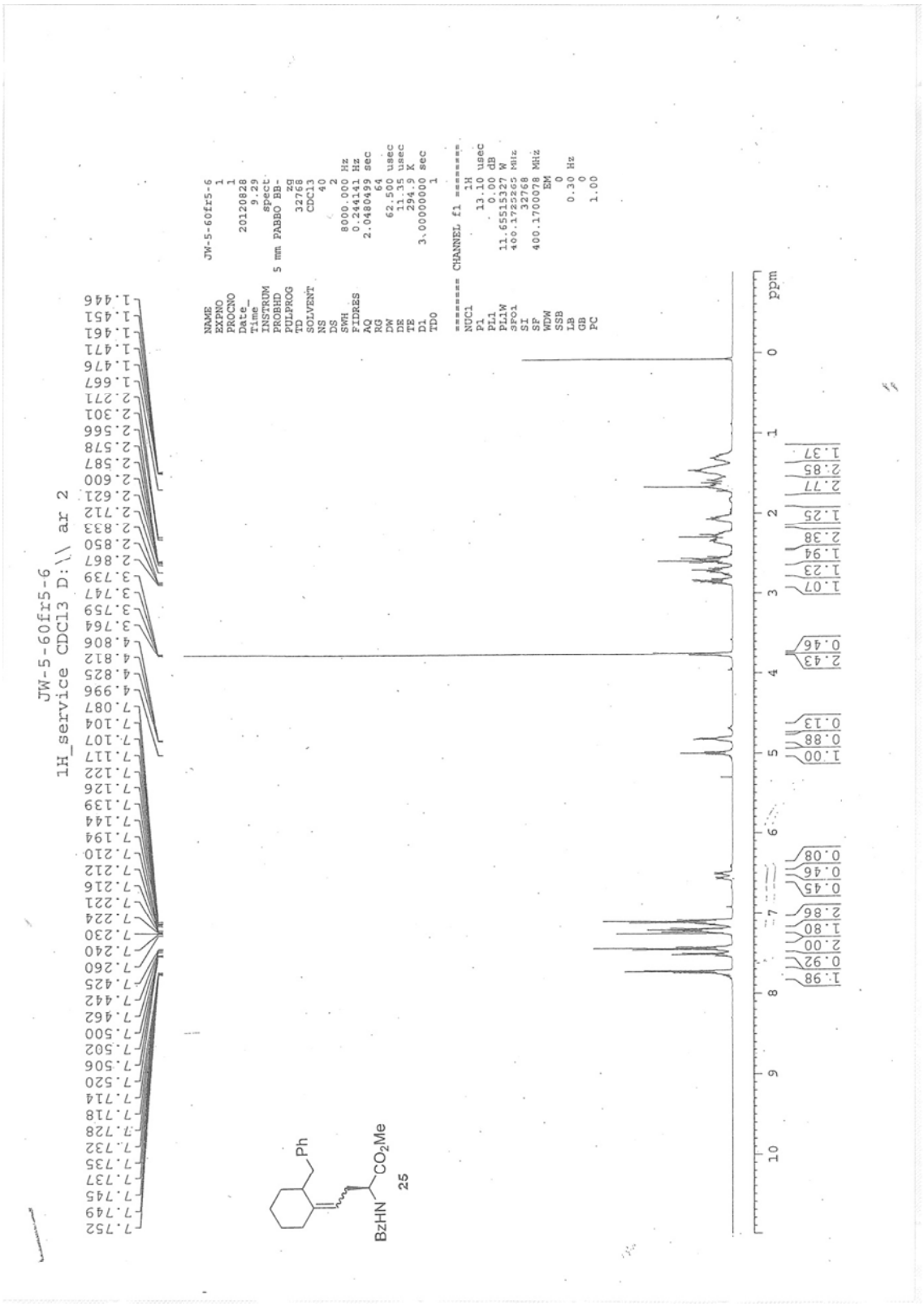

JW-5-74
1H_service CDCl3 D:\\ as 36
NAME JW-5-74
EXPNO 1
PROCNO 1
Date_ 20120313
Time_ 6.54
INSTRUM spect
PROBHD 5 mm FABBO BB-
PULPROG zg
TD 32768
SOLVENT CDCl3
NS 40
DS 2
SWH 8000.000 Hz
FIDRES 0.244141 Hz
AQ 2.0480499 sec
RG 16
DW 62.500 usec
DE 11.35 usec
TE 300.2 K
D1 3.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 13.10 usec
PL1 0.00 dB
PL1W 11.65515327 W
SFO1 400.1725265 MHz
SI 32768
SF 400.1700043 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
Ph
OAc
22
ppm
9.006
5.198
2.394
0.880
1.005
1.834
0.968
3.000
2.051

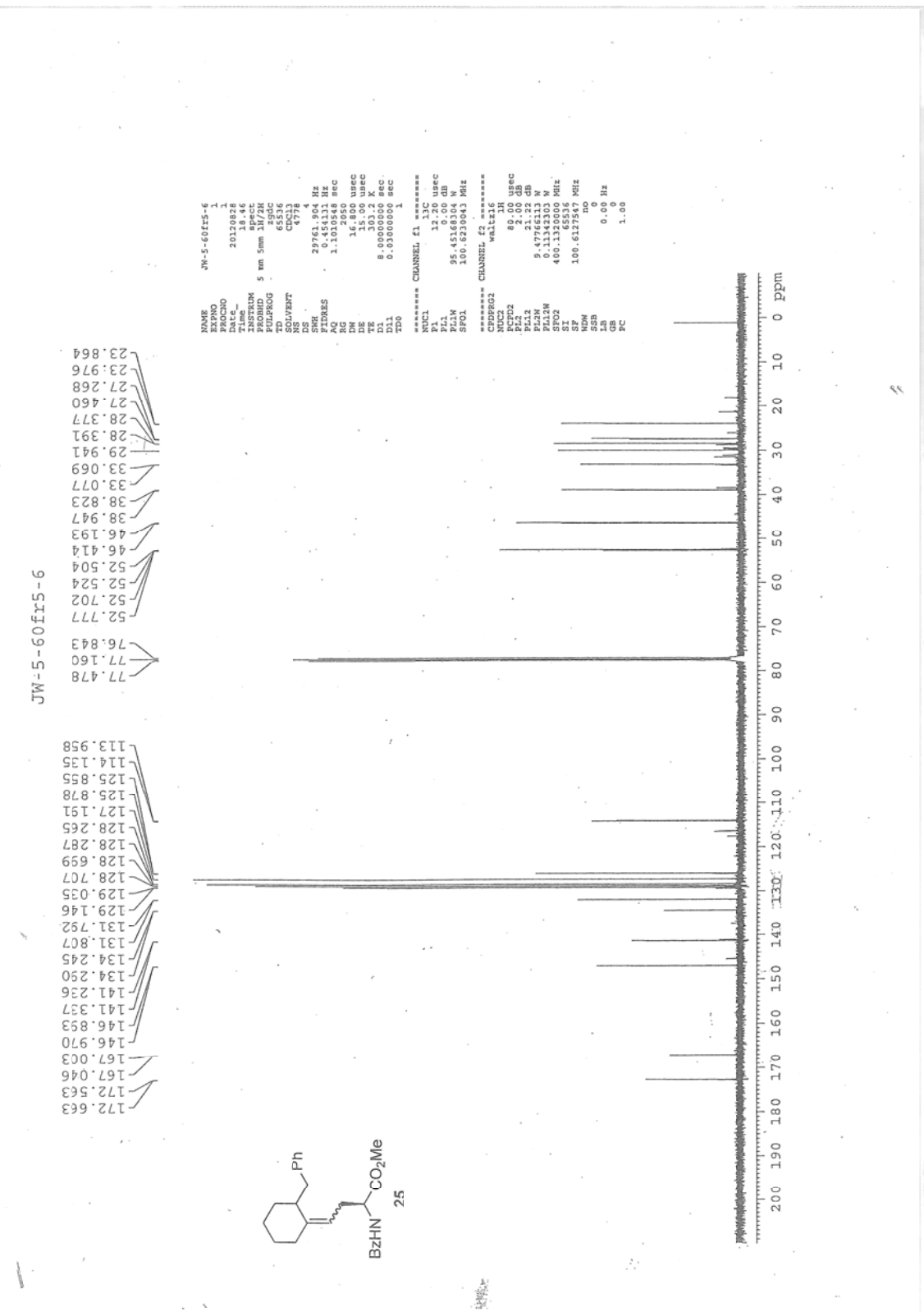

JW-6-65fr6
NAME JW-6-65fr6
EXPNO 1
PROCNO 1
Date_ 20130114
Time_ 11.06
INSTRM spect
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 60
DS 2
SWH 8992.806 Hz
FIDRES 0.274439 Hz
AQ 1.8219508 sec
RG 512
DW 55.600 usec
DE 15.00 usec
TE 303.2 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 10.00 usec
PL1 -2.00 dB
SFO1 300.1315757 MHz
SI 32768
SF 300.1300021 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.40
1.000
2.088
0.163
0.811
4.024
3.137
1.731
5.005
1.658
2.361
3.800
3.092
ppm
CH3
O
OAc
H3C
23

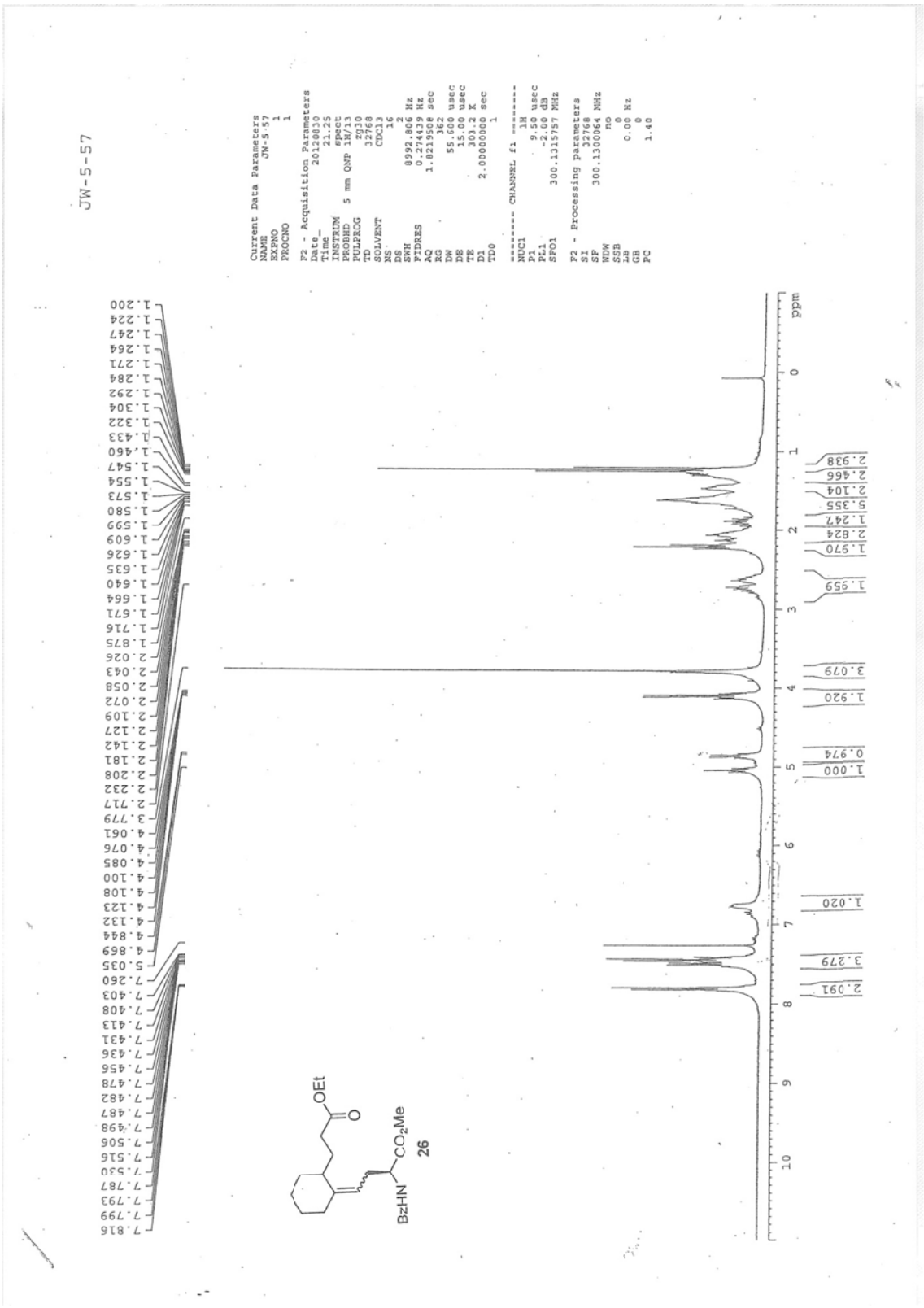

JW-6-77fr10-12
13Cdec_6hour CDCl3 D:\\ ar 5
NAME JW-6-77fr10-12
EXPNO 1
PROCNO 1
Date_ 20130202
Time 1.28
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 6000
DS 4
SWH 25252.525 Hz
FIDRES 0.385323 Hz
AQ 1.2976529 sec
RG 203
DW 19.800 usec
DE 6.50 usec
TE 300.2 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.80 usec
PL1 -2.00 dB
PL1W 59.31797028 W
SFO1 100.6333924 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 0.00 dB
PL12 15.72 dB
PL13 21.72 dB
PL2W 11.65515327 W
PL12W 0.31226116 W
PL13W 0.07843647 W
SFO2 400.1716007 MHz
SI 32768
SF 100.6228121 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
1.146
13.813
21.136
23.266
24.537
26.171
27.394
28.327
30.003
30.975
42.663
57.653
59.576
64.660
123.311
139.180
171.342
0 ppm
20
40
60
80
100
120
140
160
180
200
CH3
O
OAc
H3C
23

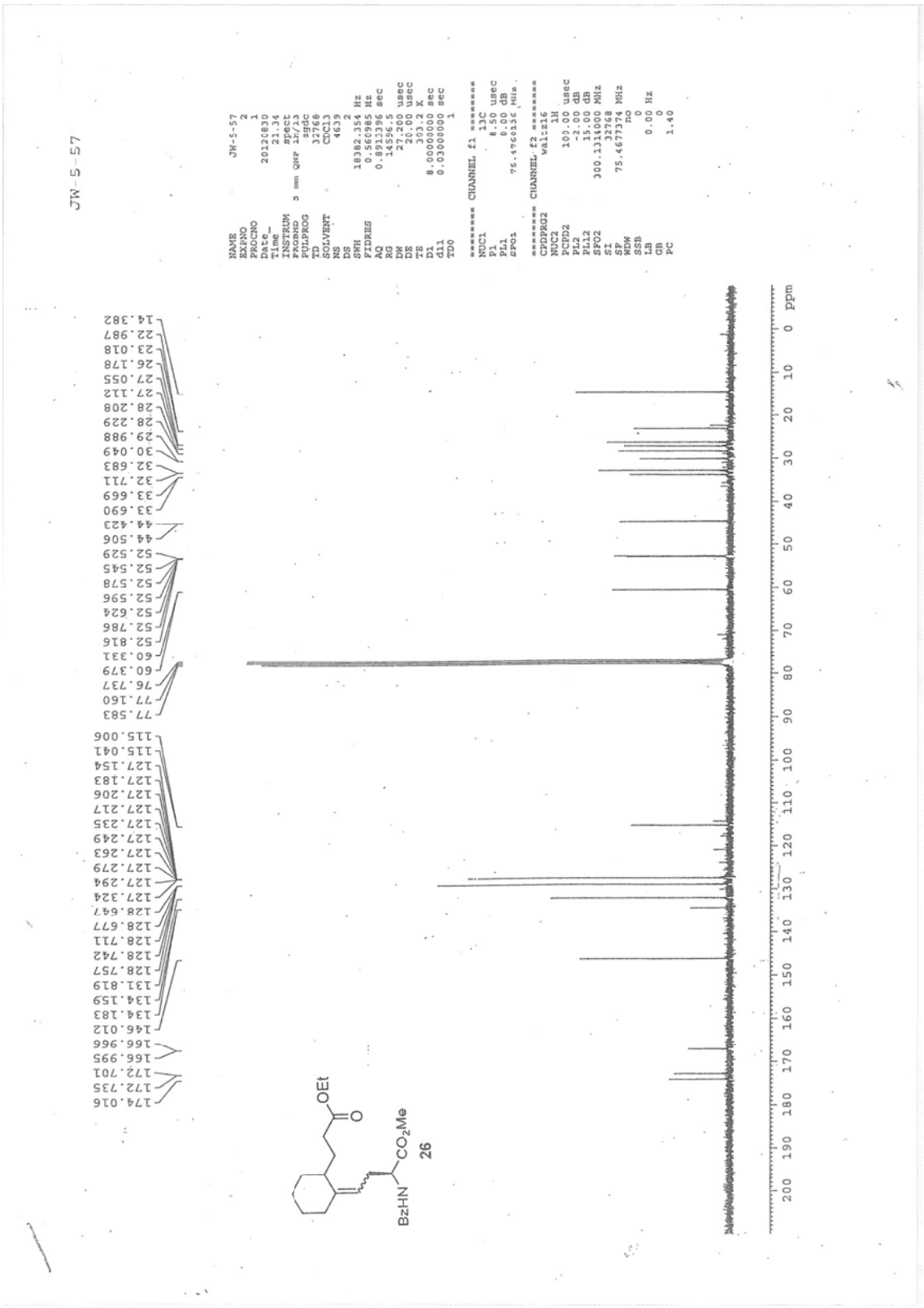

JW-6-74fr8-14
NAME JW-6-74fr8-14
EXPNO 1
PROCNO 1
Date_ 20130130
Time 11.44
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 2
SWH 8992.806 Hz
FIDRES 0.274439 Hz
AQ 1.8219508 sec
RG 574.7
DW 55.600 usec
DE 15.00 usec
TE 303.2 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 10.00 usec
PL1 -2.00 dB
SFO1 300.1315757 MHz
SI 32768
SF 300.1300021 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.40
ppm
7.296
7.291
7.285
7.280
7.274
7.260
7.257
7.249
7.201
7.197
7.177
7.162
7.158
7.135
4.628
4.611
4.586
4.559
2.582
2.325
2.306
2.127
2.101
2.062
2.059
2.052
2.043
2.021
2.015
1.992
1.772
1.769
1.765
1.725
1.705
1.682
1.611
1.587
1.575
1.563
1.537
1.524
2.272
3.205
1.000
0.936
2.006
1.046
0.987
2.134
2.680
3.743
1.358
1.323
2.613
1.743
4.419
Ph
OAc
CH3
24

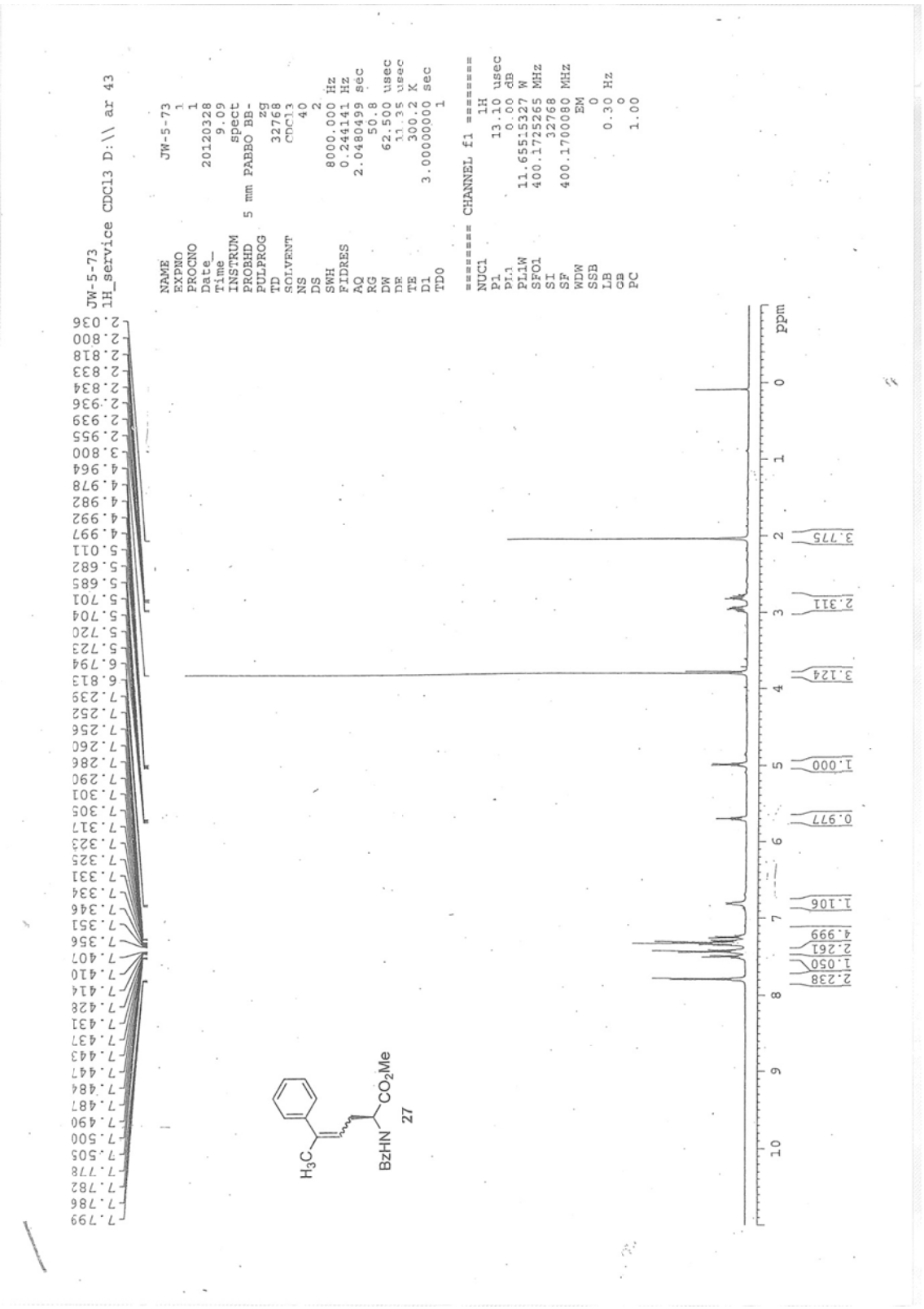

JW-6-74fr8-14
13Cdec_6hour CDCl3 D:\\ ar 41
NAME JW-6-74fr8-14
EXPNO 1
PROCNO 1
Date_ 20130205
Time_ 3.41
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 6000
DS 4
SWH 25252.525 Hz
FIDRES 0.385323 Hz
AQ 1.2976629 sec
RG 203
DW 19.800 usec
DE 6.50 usec
TE 300.2 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.80 usec
PL1 -2.00 dB
PL1W 59.31797028 W
SFO1 100.6333924 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 0.00 dB
PL12 15.72 dB
PL13 21.72 dB
PL2W 11.65515327 W
PL12W 0.31225116 W
PL13W 0.07843647 W
SFO2 400.1715007 MHz
SI 32768
SF 100.6228150 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
171.225
171.186
149.085
142.775
142.622
142.329
142.276
141.745
141.687
141.141
129.214
128.270
128.183
128.157
125.891
125.714
125.689
119.999
119.714
119.279
118.469
114.706
77.476
77.158
76.840
61.516
61.294
60.863
46.181
46.112
39.982
39.020
38.996
38.799
32.883
32.786
32.678
32.649
28.359
28.298
28.262
28.061
27.426
27.380
25.900
25.458
24.263
24.226
0 ppm
Ph
OAc
CH3
24

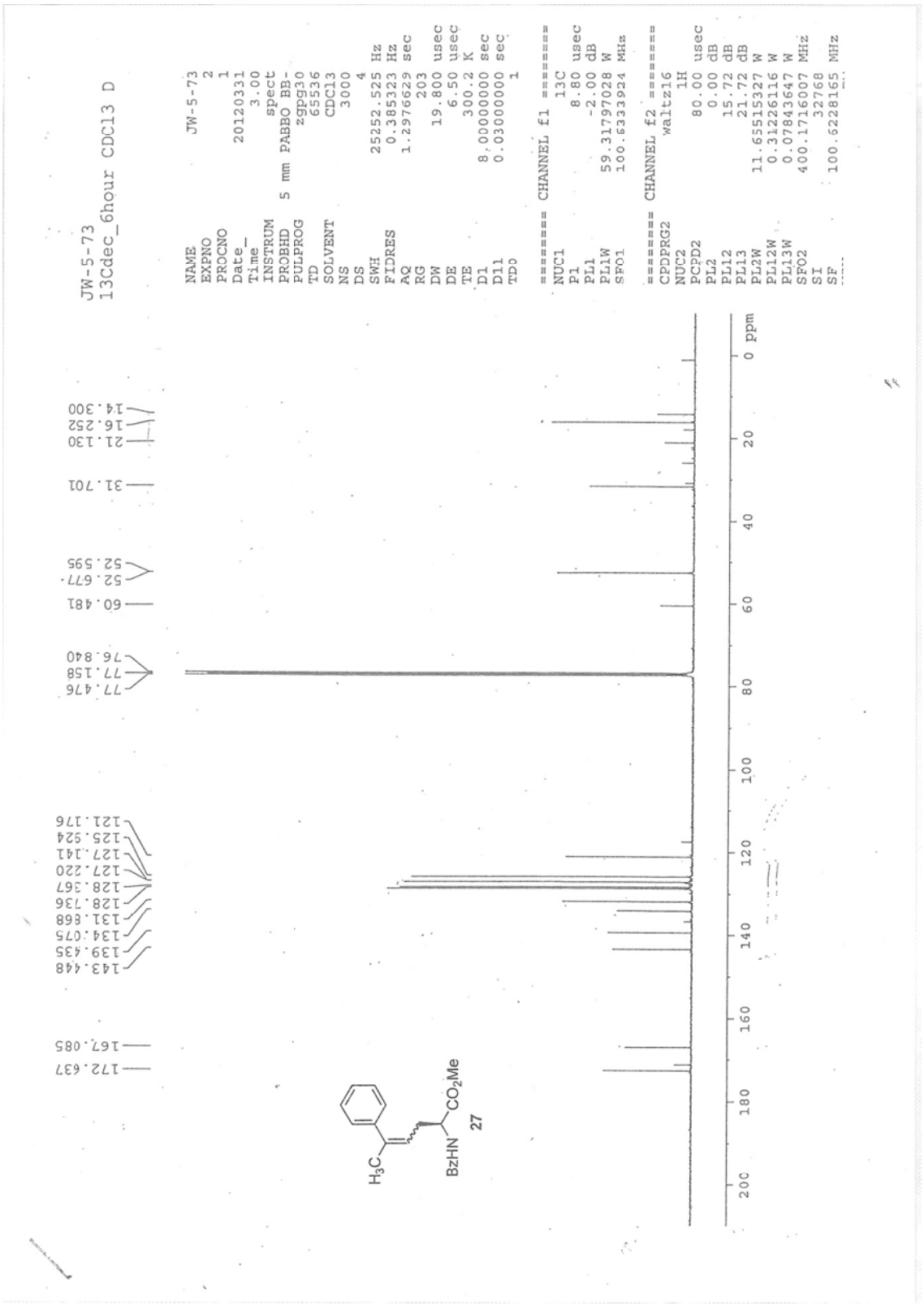

JW-5-60fr5-6
1H_service CDCl3 D:\\ ar 2
NAME JW-5-60fr5-6
EXPNO 1
PROCNO 1
Date_ 20120828
Time_ 9.29
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg
TD 32768
SOLVENT CDCl3
NS 40
DS 2
SWH 8000.000 Hz
FIDRES 0.244141 Hz
AQ 2.0480499 sec
RG 64
DW 62.500 usec
DE 11.35 usec
TE 294.9 K
D1 3.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 13.10 usec
PL1 0.00 dB
PL1W 11.65515327 W
SFO1 400.1725265 MHz
SI 32768
SF 400.1700078 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
Ph
CO2Me
BzHN
25
ppm

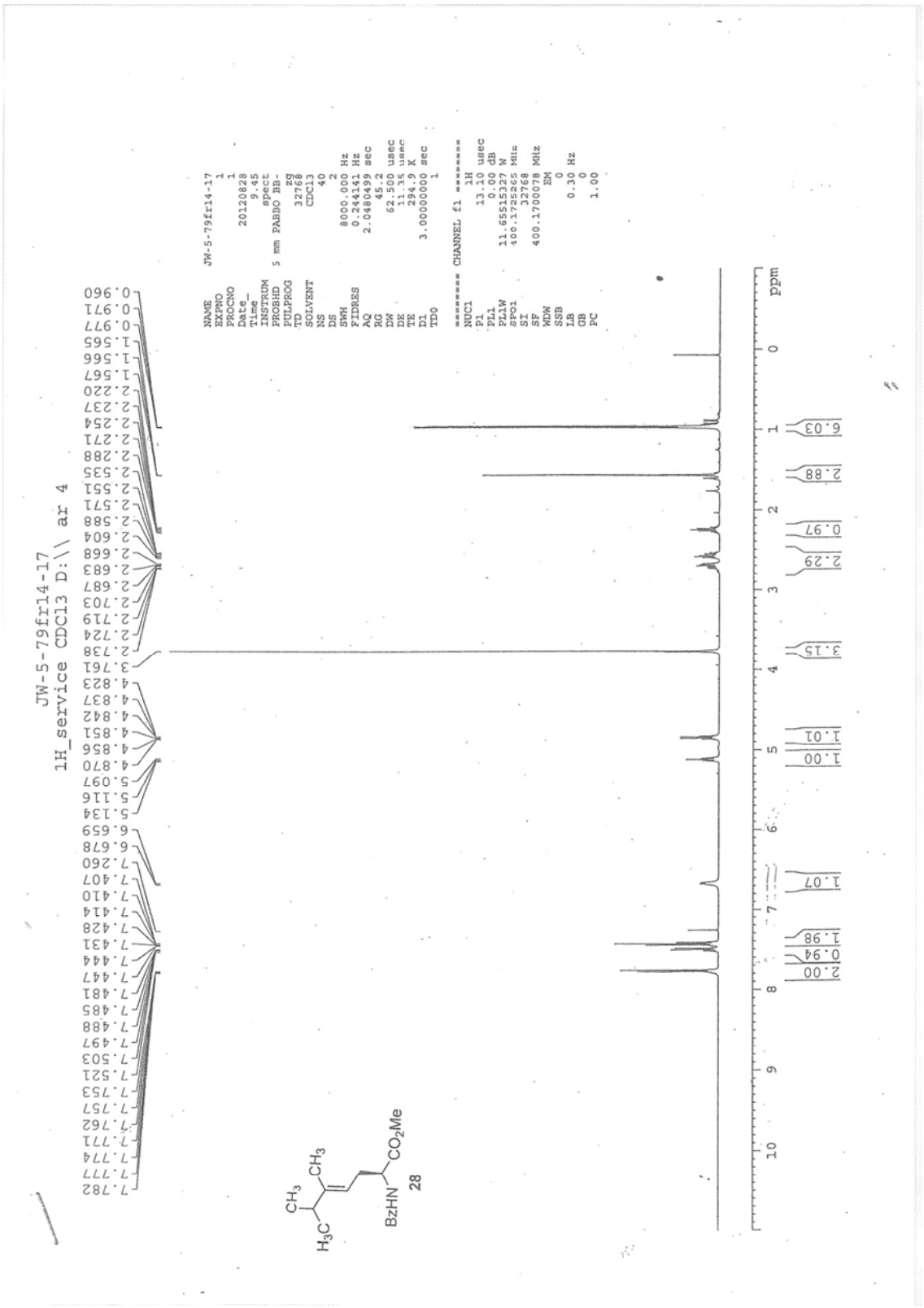

JW-5-60fr5-6
23.864
23.976
27.268
27.460
28.377
28.391
29.941
33.069
33.077
38.823
38.947
46.193
46.414
52.504
52.524
52.702
52.777
76.843
77.160
77.478
113.958
114.135
125.855
125.878
127.191
128.265
128.287
128.659
128.707
129.035
129.146
131.792
131.807
134.245
134.290
141.236
141.337
146.853
146.970
167.003
167.046
172.563
172.663
Ph
CO2Me
BzHN
25
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

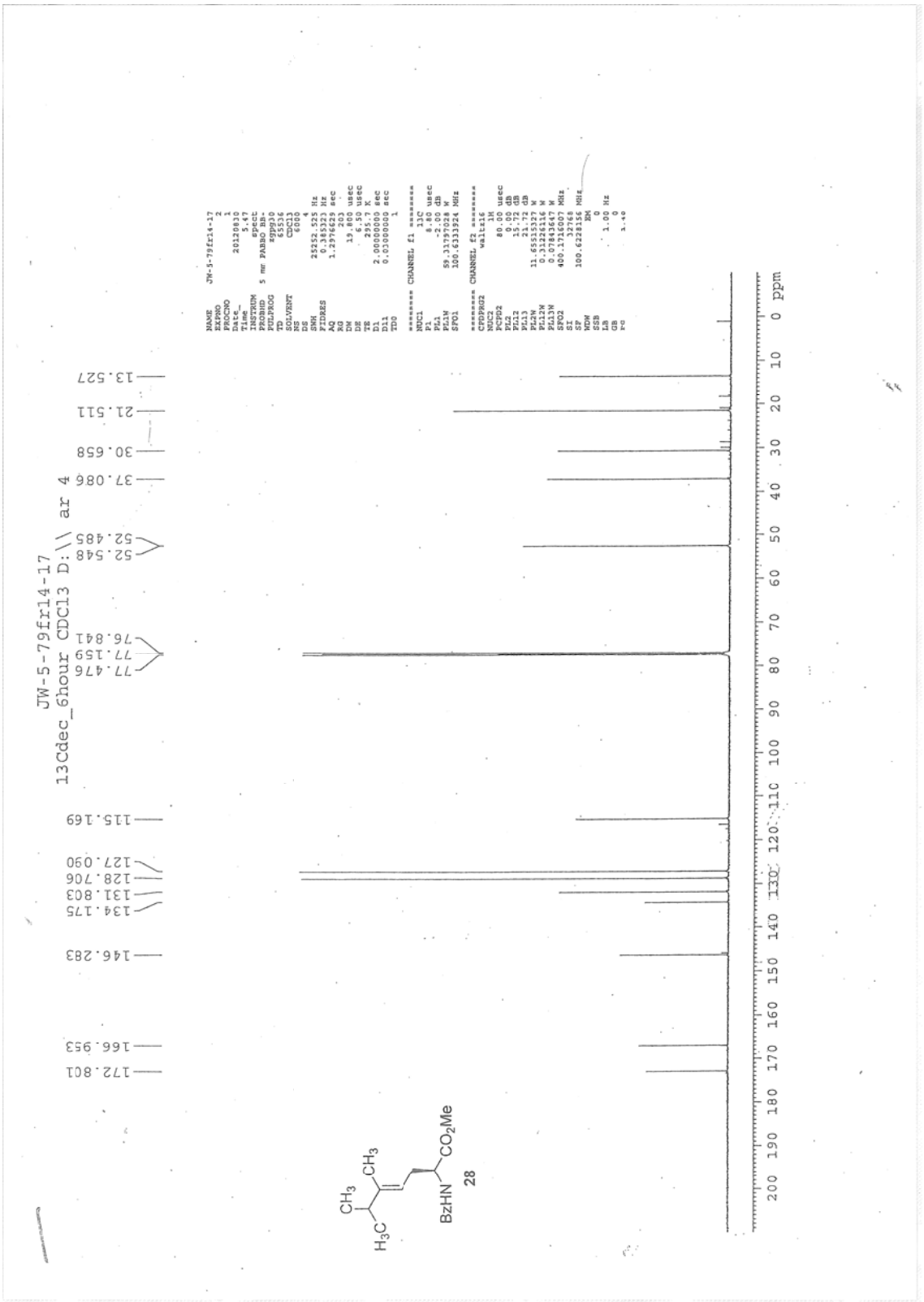

JW-5-57
Current Data Parameters
NAME JW-5-57
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20120830
Time 21.25
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 2
SWH 8992.806 Hz
FIDRES 0.274439 Hz
AQ 1.8219508 sec
RG 362
DW 55.600 usec
DE 15.00 usec
TE 303.2 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 9.50 usec
PL1 -2.00 dB
SFO1 300.1315757 MHz
F2 - Processing parameters
SI 32768
SF 300.1300066 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.40
ppm
2.091
3.279
1.020
0.974
1.000
1.920
3.079
1.959
1.970
2.824
1.247
5.355
2.104
2.466
2.938
OEt
O
CO2Me
BzHN
26

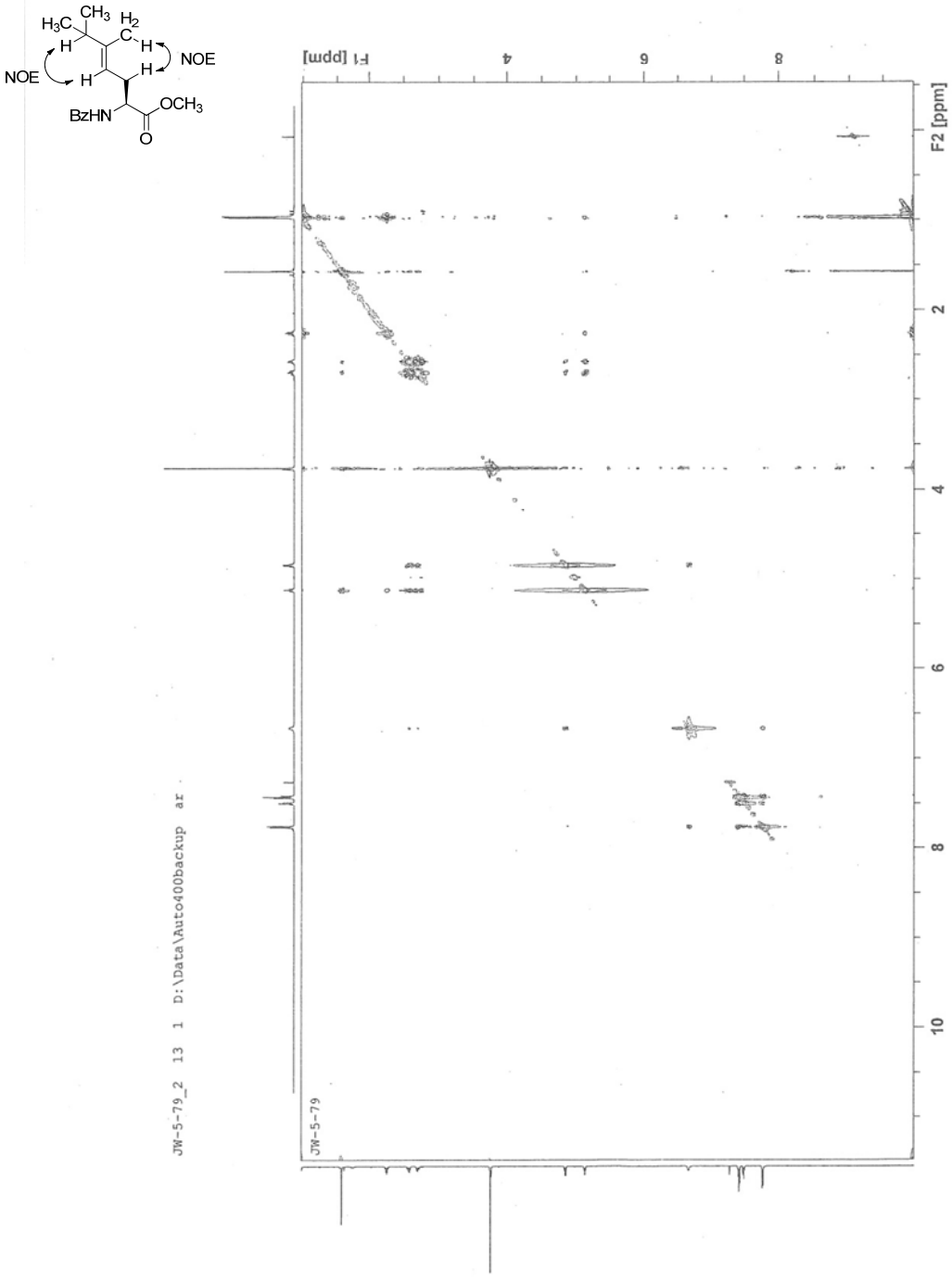

JW-5-57
NAME JW-5-57
EXPNO 2
PROCNO 1
Date_ 20120830
Time_ 21.34
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zgdc
TD 32768
SOLVENT CDCl3
NS 4639
DS 2
SWH 18382.352 Hz
FIDRES 0.560985 Hz
AQ 0.891396 sec
RG 145965
DW 27.200 usec
DE 20.00 usec
TE 303.2 K
D1 8.00000000 sec
d11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.50 usec
PL1 0.00 dB
SFO1 75.4760136 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 103.00 usec
PL2 -2.00 dB
PL12 15.00 dB
SFO2 300.1316000 MHz
SI 32768
SF 75.4677394 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.40
OEt
O
CO2Me
BzHN
26
ppm

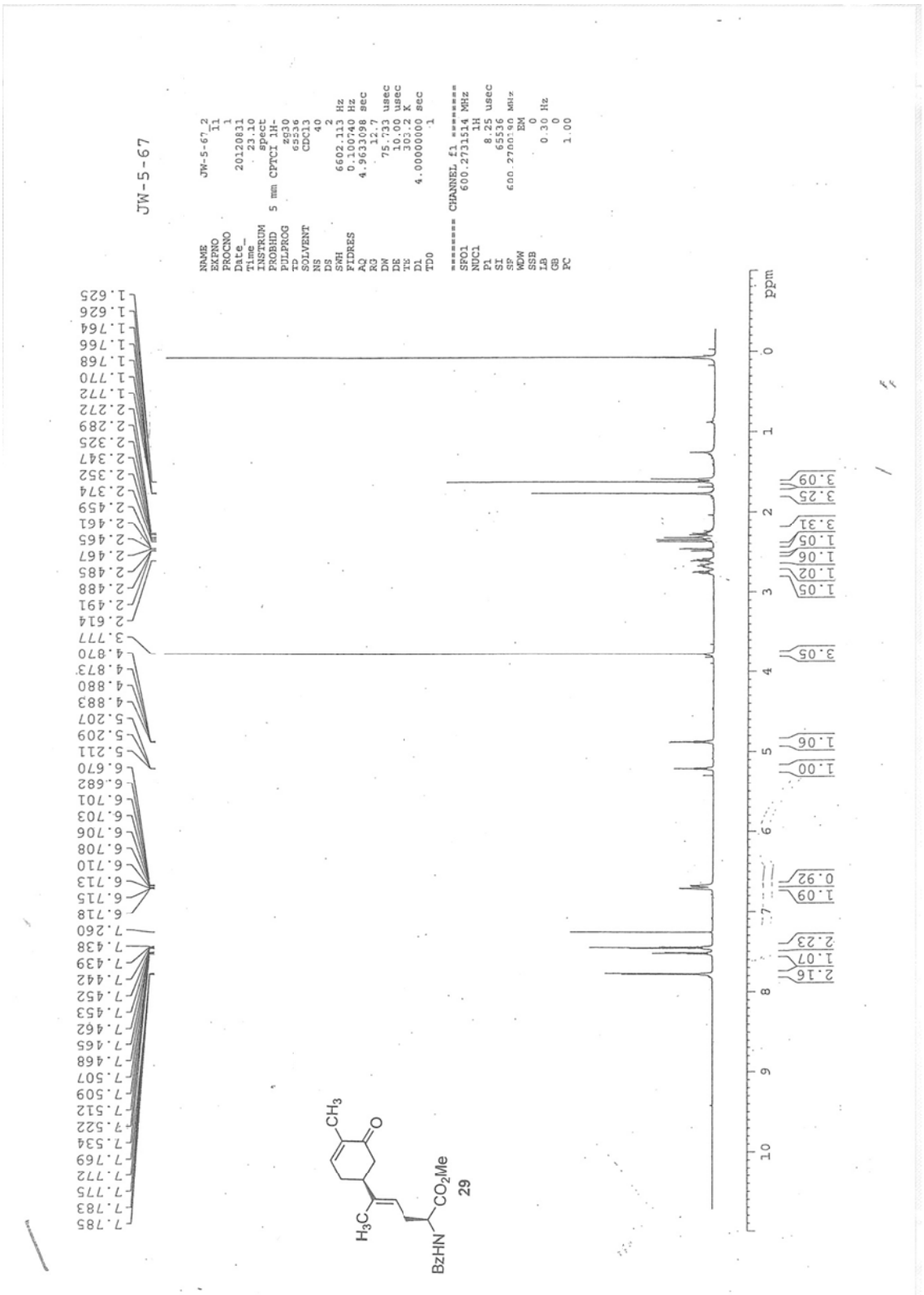

JW-5-73
1H_service CDCl3 D:\\ ar 43
NAME JW-5-73
EXPNO 1
PROCNO 1
Date_ 20120328
Time 9.09
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg
TD 32768
SOLVENT CDCl3
NS 40
DS 2
SWH 8000.000 Hz
FIDRES 0.244141 Hz
AQ 2.0480499 sec
RG 50.8
DW 62.500 usec
DE 11.35 usec
TE 300.2 K
D1 3.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 13.10 usec
PL1 0.00 dB
PL1W 11.65515327 W
SFO1 400.1725265 MHz
SI 32768
SF 400.1700080 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
2.036 2.800 2.818 2.833 2.834 2.936 2.939 2.955 3.800 4.964 4.978 4.982 4.992 4.997 5.011 5.682 5.685 5.701 5.704 5.720 5.723 6.794 6.813 7.239 7.252 7.256 7.260 7.286 7.290 7.301 7.305 7.317 7.323 7.325 7.331 7.334 7.346 7.351 7.356 7.407 7.410 7.414 7.428 7.431 7.437 7.443 7.447 7.484 7.487 7.490 7.500 7.505 7.778 7.782 7.786 7.799
3.775
2.311
3.124
1.000
0.977
1.106
4.999
2.261
1.050
2.238
ppm
H3C
BzHN
CO2Me
27

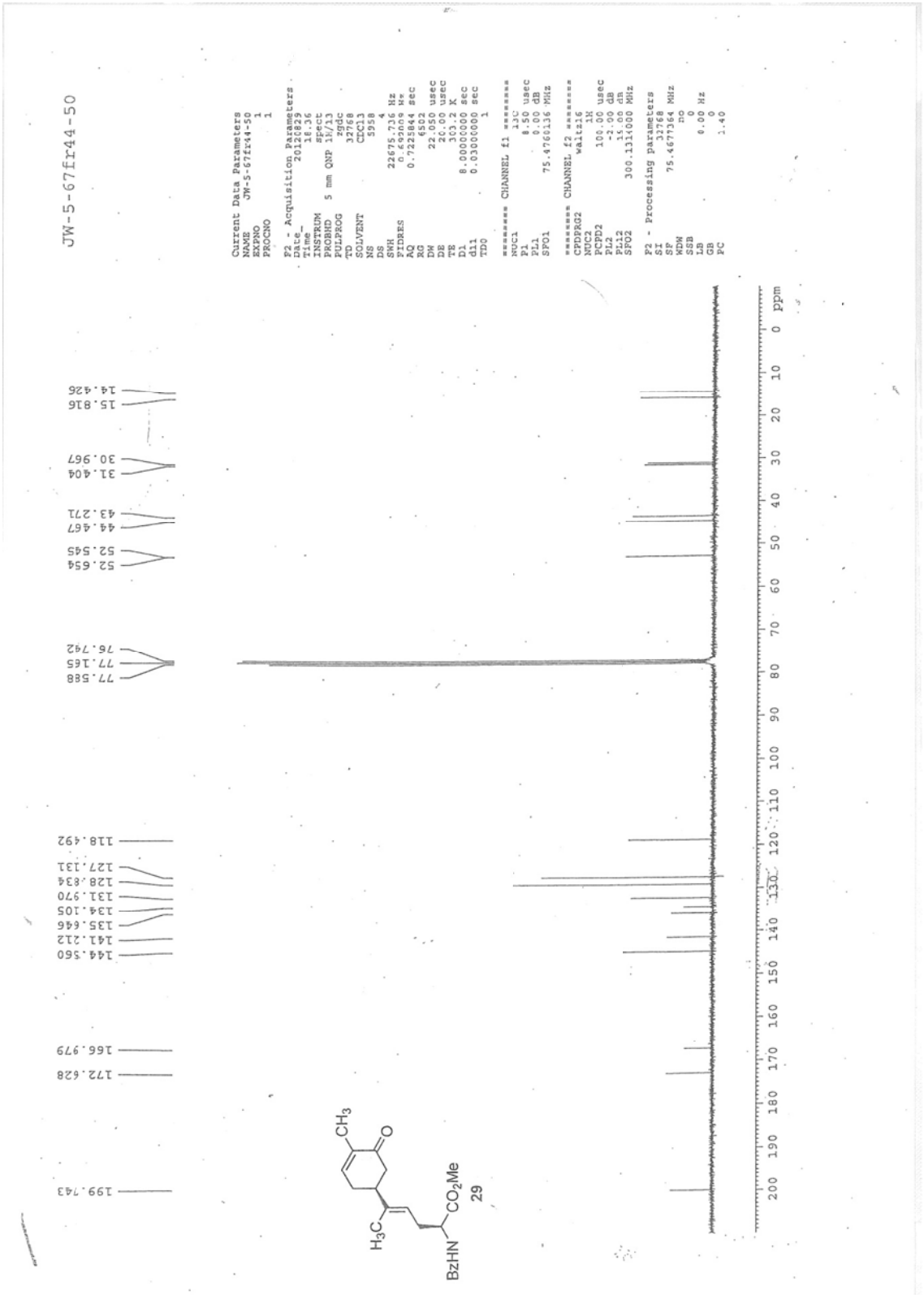

JW-5-73
13Cdec_6hour CDCl3 D
NAME JW-5-73
EXPNO 2
PROCNO 1
Date_ 20120331
Time_ 3.00
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 3000
DS 4
SWH 25252.525 Hz
FIDRES 0.385323 Hz
AQ 1.2976629 sec
RG 203
DW 19.800 usec
DE 6.50 usec
TE 300.2 K
D1 8.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.80 usec
PL1 -2.00 dB
PL1W 59.31797028 W
SFO1 100.6339924 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 0.00 dB
PL12 15.72 dB
PL13 21.72 dB
PL2W 11.65515327 W
PL12W 0.31226116 W
PL13W 0.07843647 W
SFO2 400.1716007 MHz
SI 32768
SF 100.6228165 MHz
14.300
16.252
21.130
31.701
52.595
52.677
60.481
76.840
77.158
77.476
121.176
125.924
127.141
127.220
128.367
128.736
131.868
134.075
139.435
143.448
167.085
172.637
0 ppm
H3C
BzHN
CO2Me
27

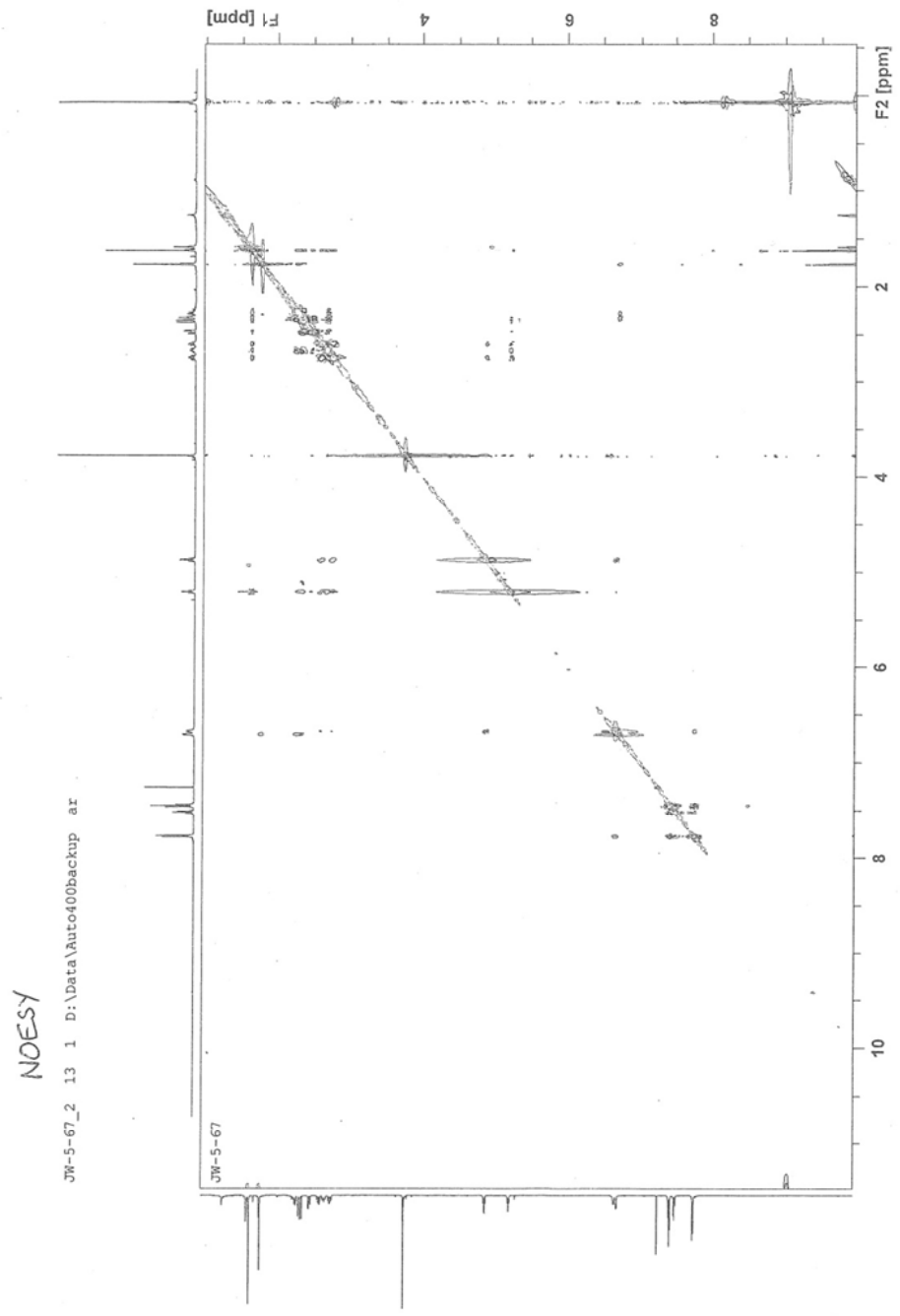

JW-5-79fr14-17
1H_service CDCl3 D:\\ ar 4
NAME JW-5-79fr14-17
EXPNO 1
PROCNO 1
Date_ 20120828
Time_ 9.45
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg
TD 32768
SOLVENT CDCl3
NS 40
DS 2
SWH 8000.000 Hz
FIDRES 0.244141 Hz
AQ 2.0480499 sec
RG 45.2
DW 62.500 usec
DE 11.35 usec
TE 294.9 K
D1 3.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 13.10 usec
PL1 0.00 dB
PL1W 11.65515327 W
SFO1 400.1725265 MHz
SI 32768
SF 400.1700078 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
ppm
6.03
2.88
0.97
2.29
3.15
1.00
1.01
1.07
1.98
0.94
2.00
BzHN
CO2Me
CH3
H3C
28

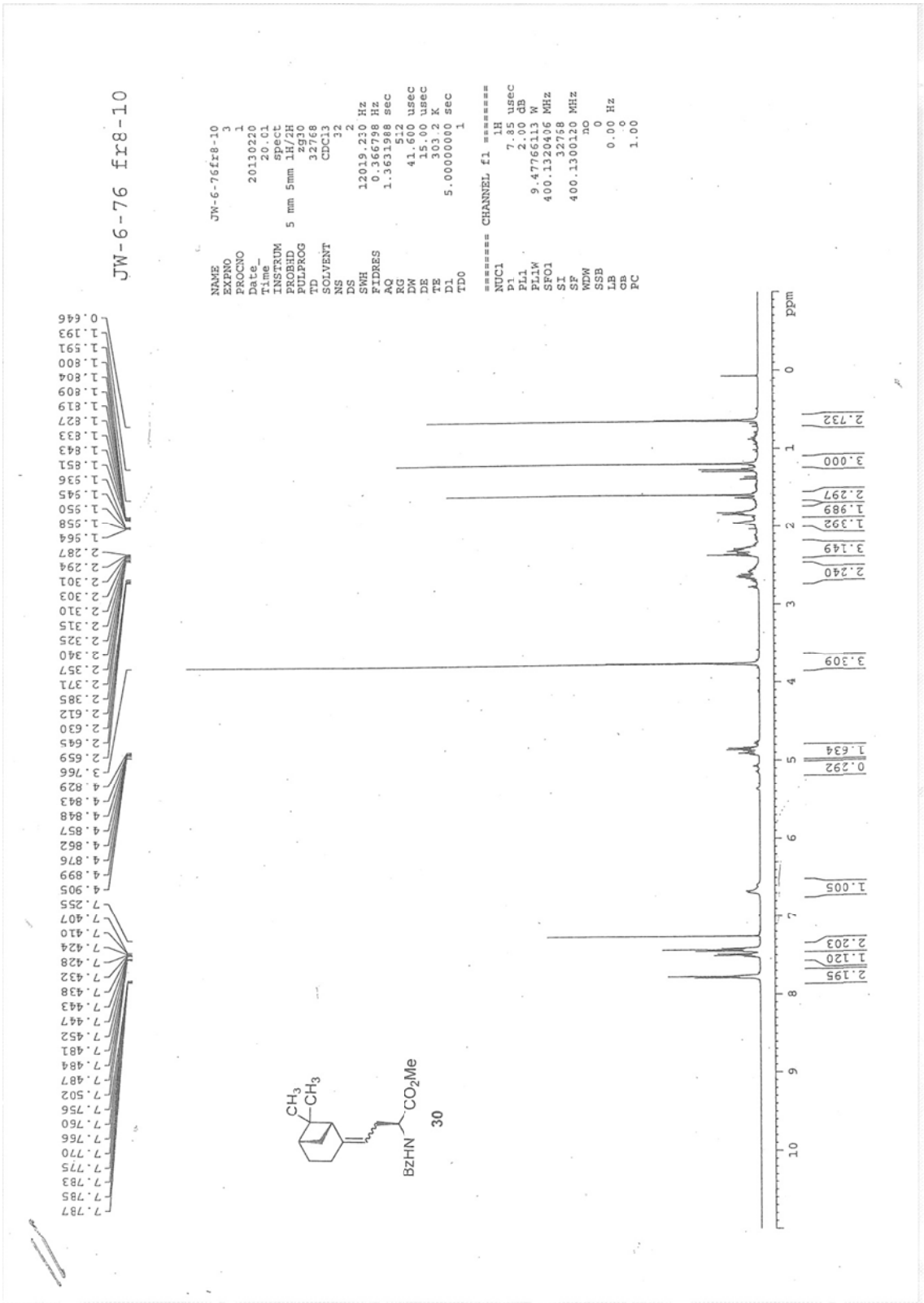

JW-5-79fr14-17
13Cdec_6hour CDCl3 D:\\ ar 4
13.527
21.511
30.658
37.086
52.485
52.548
76.841
77.159
77.476
115.169
127.090
128.706
131.803
134.175
146.283
166.953
172.801
0 ppm
28

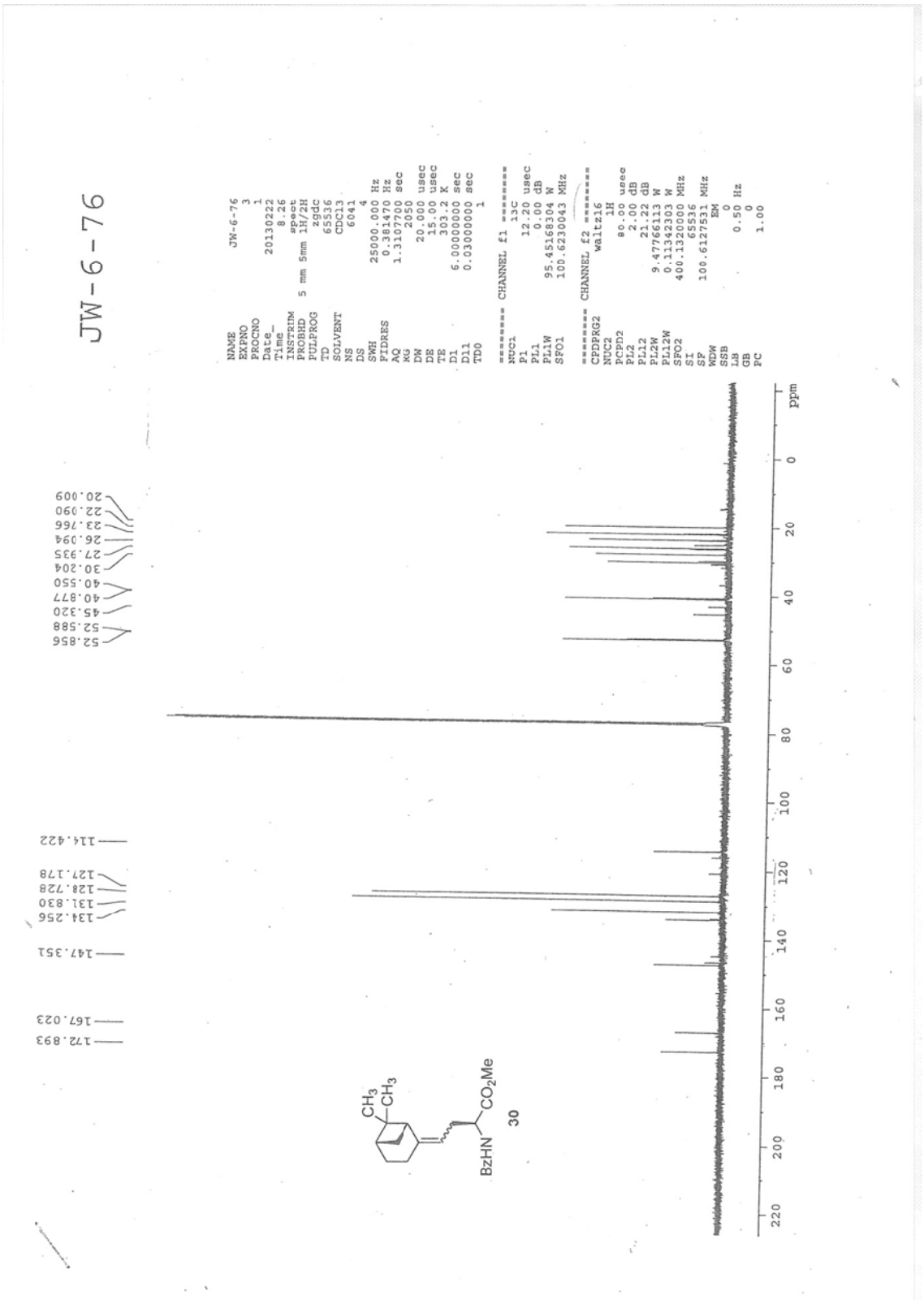

H3C
CH3
H2
C
H
H
NOE
NOE
H
H
BzHN
OCH3
O
F1 [ppm]
8
6
4
F2 [ppm]
2
4
6
8
10
JW-5-79
JW-5-79_2 13 1 D:\Data\Auto400backup ar

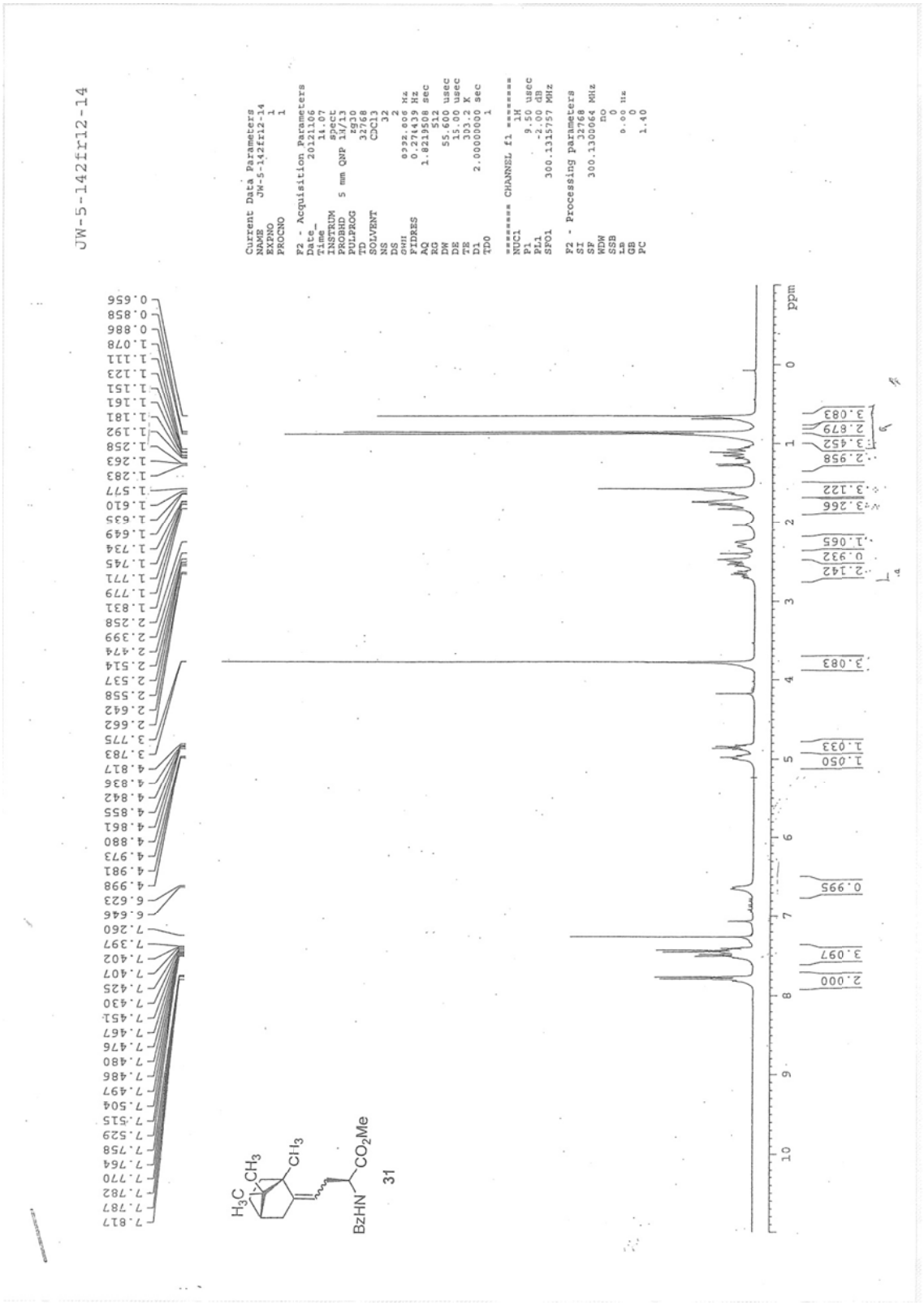

JW-5-67
NAME JW-5-67_2
EXPNO 11
PROCNO 1
Date_ 20120831
Time_ 23.10
INSTRUM spect
PROBHD 5 mm CPTCI 1H-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 40
DS 2
SWH 6602.113 Hz
FIDRES 0.100740 Hz
AQ 4.9633098 sec
RG 12.7
DW 75.733 usec
DE 10.00 usec
TE 303.2 K
D1 4.00000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 600.2731514 MHz
NUC1 1H
P1 8.25 usec
SI 65536
SF 600.2700190 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
ppm
1.625 1.626 1.764 1.766 1.768 1.770 1.772 2.272 2.289 2.325 2.347 2.352 2.374 2.459 2.461 2.465 2.467 2.485 2.488 2.491 2.614 3.777 4.870 4.873 4.880 4.883 5.207 5.209 5.211 6.670 6.682 6.701 6.703 6.706 6.708 6.710 6.713 6.715 6.718 7.260 7.438 7.439 7.442 7.452 7.453 7.462 7.465 7.468 7.507 7.509 7.512 7.522 7.534 7.769 7.772 7.775 7.783 7.785
3.09 3.25 3.31 1.05 1.06 1.02 1.05 3.05 1.06 1.00 1.09 0.92 2.23 1.07 2.16
CH3 O H3C CO2Me BzHN
29

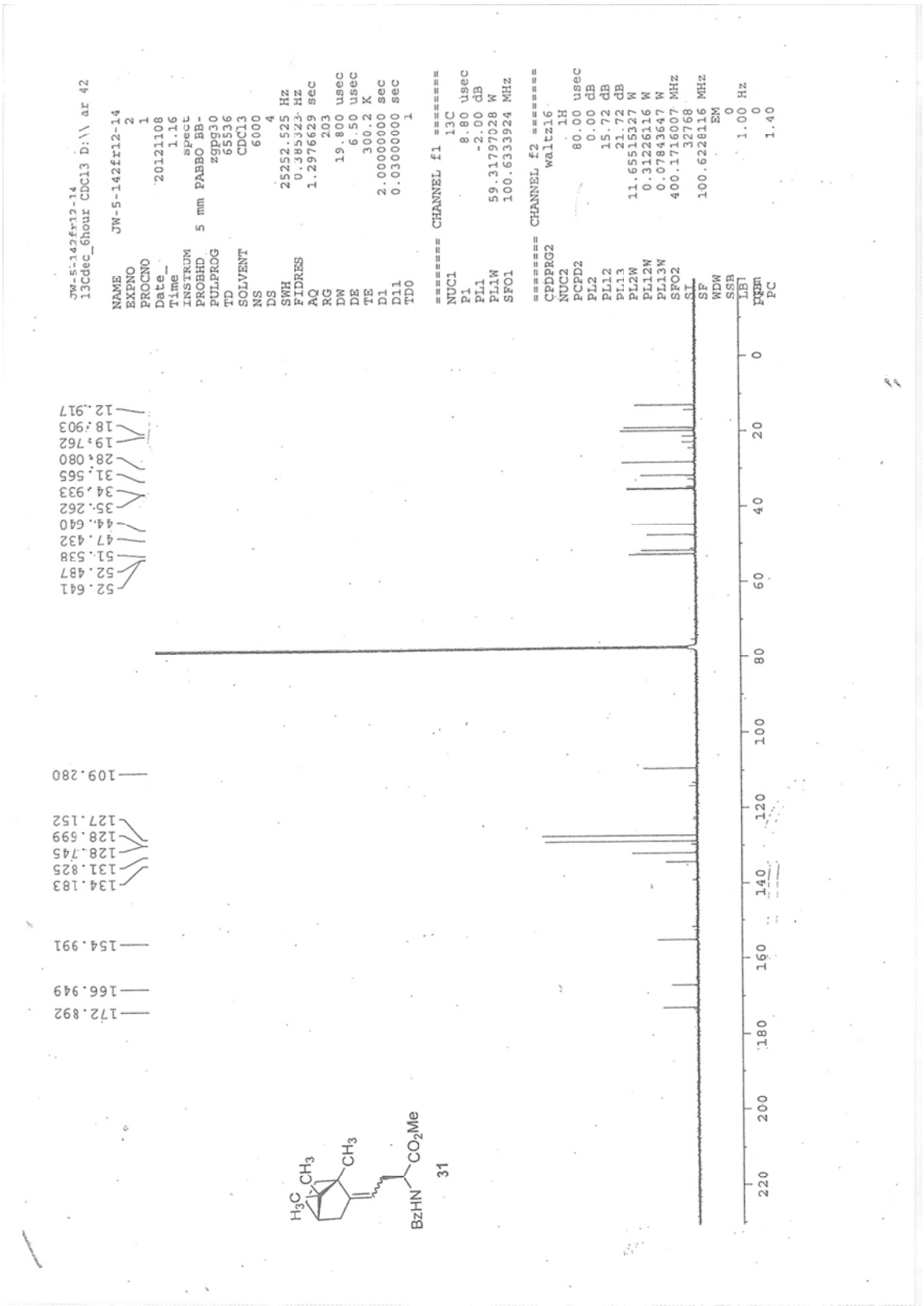

JW-5-67fr44-50
Current Data Parameters
NAME JW-5-67fr44-50
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20120823
Time_ 18.36
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zgdc
TD 32768
SOLVENT CDCl3
NS 5958
DS 4
SWH 22675.736 Hz
FIDRES 0.692000 Hz
AQ 0.7225864 sec
RG 6502
DW 22.050 usec
DE 20.00 usec
TE 303.2 K
D1 8.00000000 sec
d11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.50 usec
PL1 0.00 dB
SFO1 75.4760136 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 -2.00 dB
PL12 16.00 dB
SFO2 300.1311000 MHz
F2 - Processing parameters
SI 32768
SF 75.4677364 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.40
199.743
172.628
166.979
144.560
141.212
135.646
134.105
131.970
128.834
127.131
118.492
77.588
77.165
76.742
52.654
52.545
44.467
43.271
31.404
30.967
15.816
14.426
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm
CH3
O
H3C
CO2Me
BzHN
29

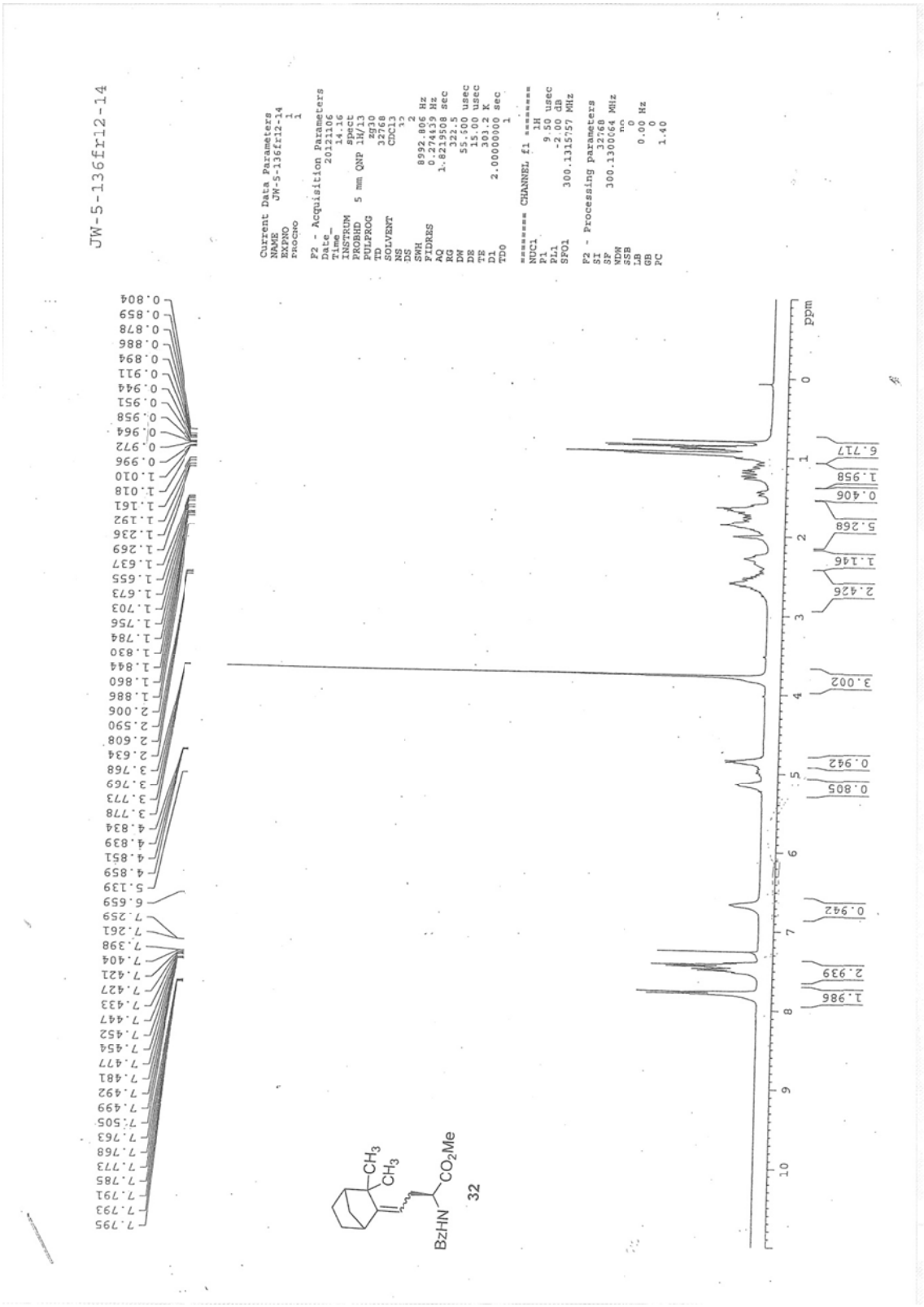

NOESY
JW-5-67_2 13 1 D:\Data\Auto400backup ar
JW-5-67
F1 [ppm]
F2 [ppm]

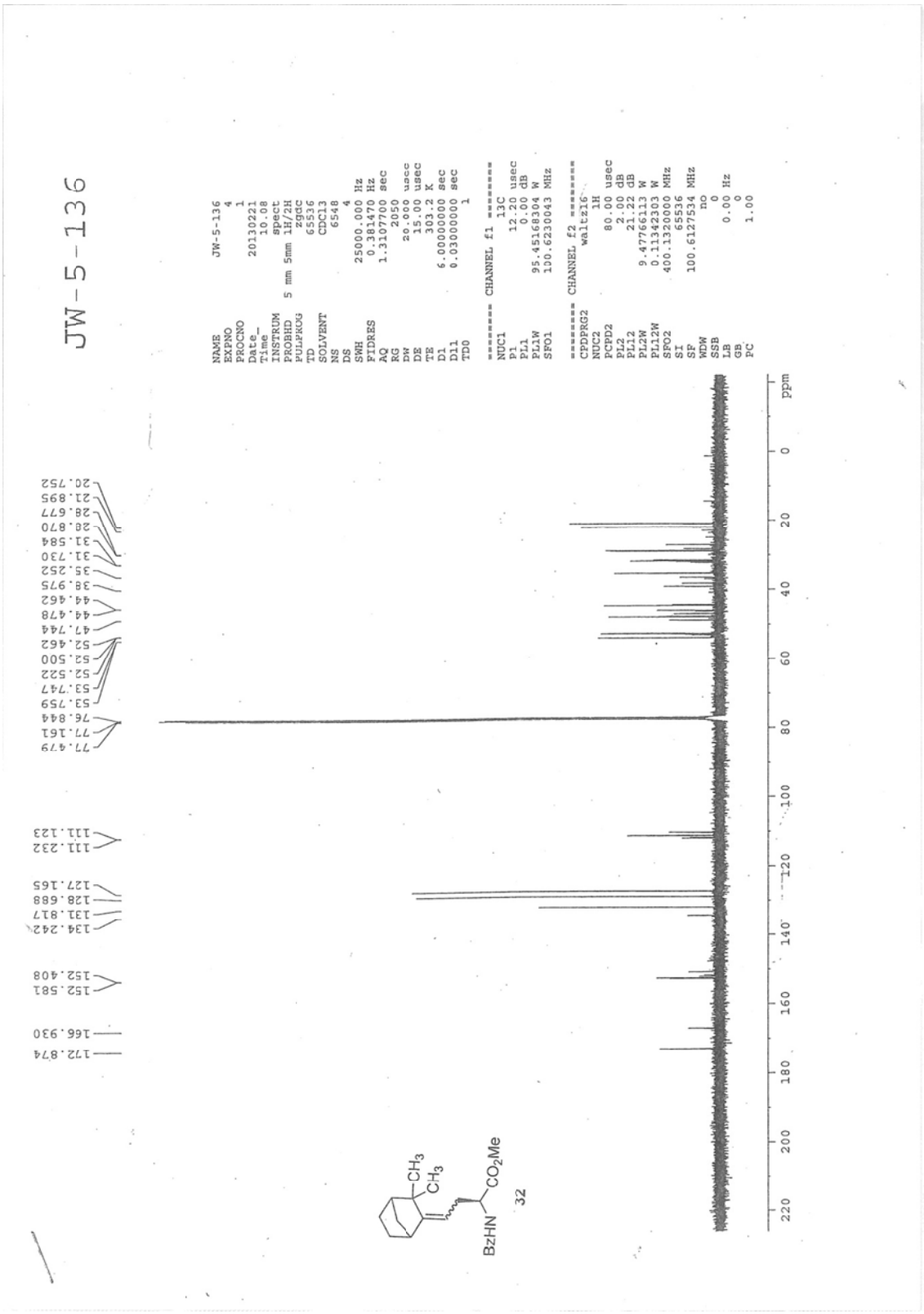

JW-6-76 fr8-10
NAME JW-6-76fr8-10
EXPNO 3
PROCNO 1
Date_ 20130220
Time_ 20.01
INSTRUM spect
PROBHD 5 mm 1H/2H
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 32
DS 2
SWH 12019.230 Hz
FIDRES 0.366798 Hz
AQ 1.3631908 sec
RG 512
DW 41.600 usec
DE 15.00 usec
TE 303.2 K
D1 5.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 7.85 usec
PL1 2.00 dB
PL1W 9.47766113 W
SFO1 400.1320406 MHz
SI 32768
SF 400.1300120 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00
ppm
2.195
1.120
2.203
1.005
0.292
1.634
3.309
2.240
3.149
1.392
1.989
2.297
3.000
2.732
CH3
CH3
CO2Me
BzHN
30


JW-6-76
NAME JW-6-76
EXPNO 3
PROCNO 1
Date_ 20130222
Time 8.26
INSTRUM spect
PROBHD 5 mm 1H/2H
PULPROG zgdc
TD 65536
SOLVENT CDCl3
NS 6041
DS 4
SWH 25000.000 Hz
FIDRES 0.381470 Hz
AQ 1.31077700 sec
RG 2050
DW 20.000 usec
DE 15.00 usec
TE 303.2 K
D1 6.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 12.20 usec
PL1 0.00 dB
PL1W 95.45168304 W
SFO1 100.6230043 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 2.00 dB
PL12 21.22 dB
PL2W 9.47766113 W
PL12W 0.11342303 W
SFO2 400.1320000 MHz
SI 65536
SF 100.6127531 MHz
WDW EM
SSB 0
LB 0.50 Hz
GB 0
PC 1.00
172.893
167.023
147.351
134.256
131.830
128.728
127.178
114.422
52.856
52.588
45.320
40.877
40.550
30.204
27.935
26.094
23.766
22.090
20.009
CH3
CH3
CO2Me
BzHN
30
ppm


JW-5-142fr12-14
Current Data Parameters
NAME JW-5-142fr12-14
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20121106
Time_ 14.07
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 32
DS 2
SWH 8922.606 Hz
FIDRES 0.272439 Hz
AQ 1.8219568 sec
RG 512
DW 55.600 usec
DE 15.00 usec
TE 303.2 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 9.50 usec
PL1 -2.00 dB
SFO1 300.1315757 MHz
F2 - Processing parameters
SI 32768
SF 300.1300064 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.40
ppm
2.000
3.097
0.995
1.050
1.033
3.083
2.142
0.932
1.065
3.266
3.122
2.958
3.452
2.879
3.083
H3C
CH3
CH3
BzHN
CO2Me
31


JW-5-142fr12-14
13Cdec_6hour CDCl3 D:\\ ar 42
NAME JW-5-142fr12-14
EXPNO 2
PROCNO 1
Date_ 20121108
Time_ 1.16
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 6000
DS 4
SWH 25252.525 Hz
FIDRES 0.385323 Hz
AQ 1.2976629 sec
RG 203
DW 19.800 usec
DE 6.50 usec
TE 300.2 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.80 usec
PL1 -2.00 dB
PL1W 59.31797028 W
SFO1 100.6333924 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 0.00 dB
PL12 15.72 dB
PL13 21.72 dB
PL2W 11.65515327 W
PL12W 0.31226116 W
PL13W 0.07843647 W
SFO2 400.1716007 MHz
SI 32768
SF 100.6228116 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
52.641
52.487
51.538
47.432
44.640
35.262
34.933
31.565
28.080
19.762
18.903
12.917
109.280
134.183
131.825
128.745
128.599
127.152
154.991
166.949
172.892
31


JW-5-136fr12-14
Current Data Parameters
NAME JW-5-136fr12-14
EXPNO 1
PROCNO 1
P2 - Acquisition Parameters
Date_ 20121106
Time 14.16
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 2
DS 2
SWH 8992.806 Hz
FIDRES 0.274439 Hz
AQ 1.8219508 sec
RG 322.5
DW 55.500 usec
DE 15.00 usec
TE 301.2 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 9.50 usec
PL1 -2.00 dB
SFO1 300.1315757 MHz
P2 - Processing parameters
SI 32768
SF 300.1300064 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.40
ppm
6.717
1.958
0.406
5.268
1.146
2.426
3.002
0.805
0.942
0.942
2.939
1.986
CH3
CH3
BzHN
CO2Me
32


JW-5-136
NAME JW-5-136
EXPNO 4
PROCNO 1
Date_ 20130221
Time 10.08
INSTRUM spect
PROBHD 5 mm 1H/2H
PULPROG zgdc
TD 65536
SOLVENT CDCl3
NS 6548
DS 4
SWH 25000.000 Hz
FIDRES 0.381470 Hz
AQ 1.3107700 sec
RG 2050
DW 20.000 usec
DE 15.00 usec
TE 303.2 K
D1 6.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 12.20 usec
PL1 0.00 dB
PL1W 95.45168304 W
SFO1 100.6230043 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 2.00 dB
PL12 21.22 dB
PL2W 9.47766113 W
PL12W 0.11342303 W
SFO2 400.1320000 MHz
SI 65536
SF 100.6127534 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00
77.479
77.161
76.844
53.759
53.747
52.522
52.500
52.462
47.744
44.478
44.462
38.975
35.252
31.730
31.584
28.870
28.677
21.895
20.752
172.874
166.930
152.581
152.408
134.242
131.817
128.688
127.165
111.232
111.123
ppm
CH3
CH3
CO2Me
BzHN
32