

SUPPORTING INFORMATION for the article entitled

A mild method for the efficient, [3,3]-sigmatropic rearrangement of *N,O*-diacyl hydroxylamines

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General Methods

Melting points were determined using a hot stage melting point apparatus. Optical Rotations were obtained using an automatic polarimeter, using 1dm cell with chloroform as the solvent, at a wavelength of 589 nm (sodium D line), and are quoted as $[\alpha]_D$, concentration c (g/100 mL) and recorded at room temperature. Proton nuclear magnetic resonance (^1H NMR) spectra were recorded on a 300 MHz or 400 MHz spectrometer. The ^1H spectra were run in deuteriochloroform (CDCl_3) with δ 7.26 (residual CHCl_3) used as an internal reference. Carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded at 75 MHz or at 100 MHz with a 300 MHz or 400 MHz spectrometer and were run in deuteriochloroform (CDCl_3) solutions with δ 77.16 (CDCl_3 solvent resonance) used as an internal reference. Accurate mass determinations were made at high resolution on an accurate mass LC-TOF system; ESI Conditions: 6L/min N_2 , 325 °C drying gas temp., capillary voltage: 3500v, Fragmentor voltage: 150v. Infrared (IR) spectra were recorded neat on a FTIR equipped with a diamond ATR (cm^{-1} scale) and MCT detector. Analytical thin layer chromatography (TLC) was performed on silica gel 60 F_{254} . Detection was by UV light or stained using potassium permanganate dip. Flash Chromatography was performed using silica gel 60 (230-400 mesh).

Dichloromethane was distilled over P_2O_5 . Triethylamine (NEt_3) was distilled over sodium wire. Trimethylsilyl trifluoromethanesulfonate (TMSOTf) and other commercially available reagents were purchased and used as received. All reactions were carried out under an argon atmosphere.

N,O-diacyl hydroxylamine starting materials were prepared according to the literature.¹

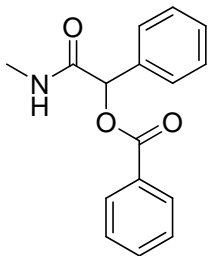
General [3,3] sigmatropic rearrangement procedure using a 1:1 ratio of TMSOTf to NEt₃: Preparation of 2-(methyldamino)-2-oxo-1-phenylethyl benzoate (**6a**)

N-(benzoyloxy)-*N*-methyl-2-phenylacetamide (**5a**) (200 mg, 0.743 mmol) was dissolved in 3 mL dry DCM and the temperature lowered to -78 °C. To this, TMSOTf (135 µL, 0.743 mmol) was added, followed 5 min later by NEt₃ (104 µL, 0.743mmol). After stirring at this temperature for 30 min, the reaction was removed from the cooling bath, allowed to warm to room temperature, sealed and left to stir overnight. The reaction was quenched by pouring directly onto a silica gel plug and eluted with EtOAc. Solvent removal *in vacuo* left a white solid which upon spectroscopic analysis, proved to be pure **6a** (150 mg, 75%).

In all other examples where a mixture of products **6** and **7** were present, a crude ¹H NMR after the plug was used to determine product ratios. Then further column chromatography to separate the two products was undertaken.

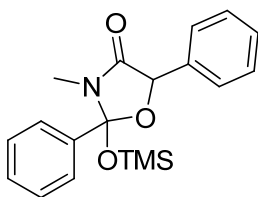
General [3,3] sigmatropic rearrangement procedure using a 2:2 ratio of TMSOTf to NEt₃: Preparation of 3-methyl-2,5-diphenyl-2-(trimethylsilyloxy)oxazolidin-4-one (**7a**)

N-(benzoyloxy)-*N*-methyl-2-phenylacetamide (**5a**) (100 mg, 0.371 mmol) was dissolved in 1.5 mL dry DCM and the temperature lowered to -78 °C. To this, TMSOTf (135 µL, 0.743 mmol) was added, followed 5 min later by NEt₃ (104 µL, 0.743 mmol). After stirring at this temperature for 30 min, the reaction was removed from the cooling bath, allowed to warm to room temperature, sealed and left to stir overnight. The reaction was quenched by pouring directly onto a silica gel plug and eluted with EtOAc. Solvent removal *in vacuo* left a white solid which upon spectroscopic analysis, showed a 10:1 mixture of **7a:6a** in a combined 90% yield. Column chromatography (20% EtOAc/Hexane) afforded **7a** as a white solid (102 mg, 80%).



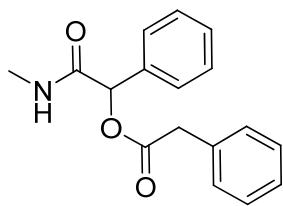
2-(methylamino)-2-oxo-1-phenylethyl benzoate (6a)

mp 142-143 °C; ^1H NMR (300 MHz, CDCl_3) δ 8.10-8.14 (2H, m), 7.28-7.65 (8H, m), 6.37 (1H, s), 6.20 (1H, brs), 2.90 (3H, d, $J=4.8$); ^{13}C NMR (75 MHz, CDCl_3) 169.1, 165.1, 135.8, 133.8, 130.0, 129.5, 128.9, 128.8, 128.8, 127.5, 76.1, 26.4; FT-IR $\nu_{\text{max}}/\text{cm}^{-1}$ 3311s, 3092w, 3065w, 3036w, 2949w, 1725vs, 1661vs, 1561s, 1496m, 1449m, 1315s, 1245vs, 1113s, 1025m, 985m, 708m, 683m; ESI-HRMS m/z 270.1124, 292.0947 ($\text{C}_{16}\text{H}_{15}\text{NO}_3 + \text{H}^+$ requires 270.1130, $\text{C}_{16}\text{H}_{15}\text{NO}_3 + \text{Na}^+$ requires 292.0950).



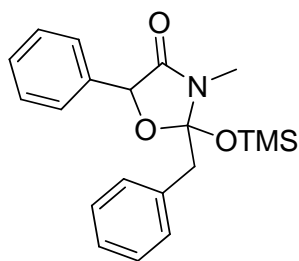
3-methyl-2,5-diphenyl-2-(trimethylsilyloxy)oxazolidin-4-one (7a)

mp 62-63 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.20-7.62 (10H, m), 5.52 (1H, s), 2.70 (3H, s), 0.22 (9H, s); ^{13}C NMR (100 MHz, CDCl_3) 169.5, 139.5, 135.5, 129.5, 128.9, 128.7, 128.7, 128.4, 127.0, 126.9, 126.8, 110.7, 78.6, 25.7, 1.2; FT-IR $\nu_{\text{max}}/\text{cm}^{-1}$ 3035w, 2957w, 1716s, 1424m, 1231m, 1090m, 1062m, 1035m, 869m, 839m, 760m, 698m; ESI-HRMS m/z 342.1519 ($\text{C}_{19}\text{H}_{23}\text{NO}_3\text{Si} + \text{H}^+$ requires 342.1525).



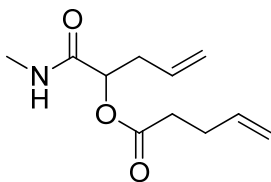
2-(methylamino)-2-oxo-1-phenylethyl 2-phenylacetate (6b)

mp 91-93 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.26-7.40 (10H, m), 6.10 (1H, s), 5.73 (1H, brs), 3.76 (2H, s), 2.7 (3H, d, $J=4.8$); ^{13}C NMR (100 MHz, CDCl_3) 169.5, 168.9, 135.5, 133.6, 129.4, 129.0, 129.0, 128.8, 127.6, 127.4, 75.7, 41.6, 26.1; FT-IR $\nu_{\text{max}}/\text{cm}^{-1}$ 3302s, 3092w, 3064w, 3032w, 2947w, 2917w, 1732s, 1663vs, 1566m, 1498m, 1453m, 1410m, 1355m, 1191m, 1155s, 866m; ESI-HRMS m/z 284.1281 ($\text{C}_{17}\text{H}_{17}\text{NO}_3 + \text{H}^+$ requires 284.1287).



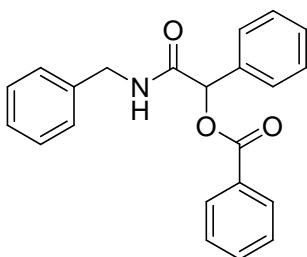
2-benzyl-3-methyl-5-phenyl-2-(trimethylsilyloxy)oxazolidin-4-one (7b)

^1H NMR (400 MHz, CDCl_3) δ 7.16-7.26 (8H, m), 6.98-7.00 (2H, m), 5.25 (1H, s), 3.21 (2H, s), 2.97 (3H, s), 0.15 (9H, s); ^{13}C NMR (100 MHz, CDCl_3) 170.3, 135.4, 134.6, 131.0, 130.5, 128.7, 128.6, 128.5, 128.4, 127.5, 127.2, 127.1, 111.6, 79.2, 45.7, 26.2, 1.1; FT-IR $\nu_{\text{max}}/\text{cm}^{-1}$ 3089w, 3064m, 3032m, 2957m, 2930m, 2899m, 1719vs, 1453m, 1432s, 1395s, 1252s, 1162m, 1087s, 1070s, 1017m, 840s, 697m, 638m; ESI-HRMS m/z 356.1674 ($\text{C}_{20}\text{H}_{25}\text{NO}_3\text{Si} + \text{H}^+$ requires 356.1682).



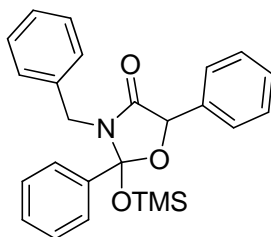
1-(methylamino)-1-oxopent-4-en-2-yl hex-5-enoate (6c)

^1H NMR (400 MHz, CDCl_3) δ 6.08 (1H, br), 5.84 (1H, dddd, $J=6.4, 10.2, 12.5, 16.7$), 5.71 (1H, dddd, $J=7.1, 10.2, 14.2, 17.1$), 5.27 (1H, dd, $J=4.7, 7$), 5.06-5.13 (4H, m), 2.82 (3H, d, $J=3.8$), 2.65-2.71 (1H, m), 2.53-2.60 (1H, m), 2.48-2.52 (2H, m), 2.40-2.44 (2H, m); ^{13}C NMR (100 MHz, CDCl_3) 171.6, 169.8, 136.7, 132.4, 118.9, 116.0, 73.2, 36.4, 33.6, 28.9, 26.0; FT-IR $\nu_{\text{max}}/\text{cm}^{-1}$ 3306br, 3080m, 2980m, 2942m, 1742vs, 1660vs, 1543s, 1370m, 1243m, 1160m, 918m, 843m; ESI-HRMS m/z 212.1282 ($\text{C}_{11}\text{H}_{17}\text{NO}_3 + \text{H}^+$ requires 212.1287).



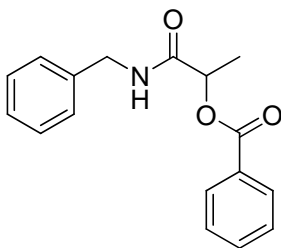
2-(benzylamino)-2-oxo-1-phenylethyl benzoate (6d)²

^1H NMR (400 MHz, CDCl_3) δ 7.21–8.19 (15H, m), 6.46 (1H, br), 6.39 (1H, s), 4.56 (1H, dd, $J=5.8, 15.2$), 4.48 (1H, dd, $J=5.9, 15.2$).



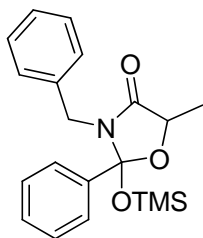
3-benzyl-2,5-diphenyl-2-(trimethylsilyloxy)oxazolidin-4-one (7d)²

^1H NMR (400 MHz, CDCl_3) δ 7.00–7.61 (15H, m), 5.60 (1H, s), 4.43 (1H, d, $J=15.2$ Hz), 4.21 (1H, d, $J=15.2$ Hz), 0.88 (s, 9H).



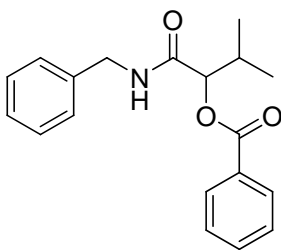
1-(benzylamino)-1-oxopropan-2-yl benzoate (6e)²

¹H NMR (400 MHz, CDCl₃) δ 7.24–8.05 (10H, m), 6.46 (1H, br), 5.54 (1H, q, *J*=6.9), 4.51 (2H, dd, *J*=2.0, 5.9), 1.65 (3H, d, *J*=6.6).



3-benzyl-5-methyl-2-phenyl-2-(trimethylsilyloxy)oxazolidin-4-one (7e)²

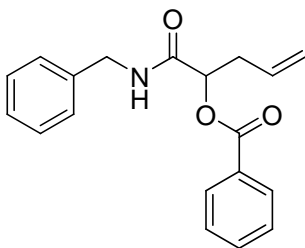
¹H NMR (400 MHz, CDCl₃) δ 6.99–7.48 (10H, m), 4.71 (1H, q, *J*=6.7), 4.39 (1H, d, *J*=15.2), 4.10 (1H, d, *J*=15.2), 1.63 (3H, d, *J*=6.8), 0.83 (9H, s).



1-(benzylamino)-3-methyl-1-oxobutan-2-yl benzoate (6f)

mp 112–113 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.10–8.13 (1H, m), 8.06–8.08 (2H, m), 7.58–7.63 (1H, m), 7.45–7.49 (3H, m), 7.24–7.33 (3H, m), 5.38 (1H, d, *J*=4), 4.56 (1H, dd, *J*=6, 14.8), 4.44 (1H, dd, *J*=6, 14.8), 2.49–2.53 (1H, m), 1.07 (6H, dd, *J*=7.2, 10.4); ¹³C NMR (100 MHz, CDCl₃) 169.5, 165.7, 138.0, 133.8, 130.3, 129.9, 129.5, 128.9, 128.8, 128.6, 127.7, 127.7, 78.8, 43.4, 31.0, 19.1, 17.2; FT-IR ν_{max}/cm⁻¹ 3257m, 3090m,

2974m, 2936m, 1719s, 1655s, 1562m, 1430m, 1293m, 1248s, 1116m, 992m, 741m, 708m, 677m; ESI-HRMS m/z 312.1597 ($C_{19}H_{21}NO_3 + H^+$ requires 312.1600).

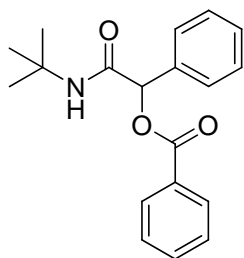


1-(benzylamino)-1-oxopent-4-en-2-yl benzoate (6g)

mp 103-104 °C; 1H NMR (400 MHz, $CDCl_3$) δ 8.12 (1H, d, $J=7.12$), 8.03 (1H, d, $J=7.8$), 7.25-7.63 (8H, m), 6.40 (1H, br), 5.83 (1H, dddd, $J=7.0, 10.2, 14.2, 17.1$), 5.56 (1H, dd, $J=4.9, 6.8$), 5.18 (1H, dm, $J=17.1$), 5.12 (1H, dm, $J=10.2$), 4.56 (1H, dd, $J=6, 15$), 4.46 (1H, dd, $J=6, 15$), 2.74-2.88 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.2, 165.3, 137.8, 133.7, 132.1, 130.2, 129.8, 129.3, 128.8, 128.5, 127.6, 119.2, 73.67, 43.3, 36.4; FT-IR ν_{max}/cm^{-1} 3306b, 3066m, 3033m, 2930m, 1722vs, 1662s, 1602w, 1539m, 1452m, 1316w, 1267s, 1176w, 1110m, 1070m, 1027w, 922w, 711m; ESI-HRMS m/z 310.1440 ($C_{19}H_{19}NO_3 + H^+$ requires 310.1443).

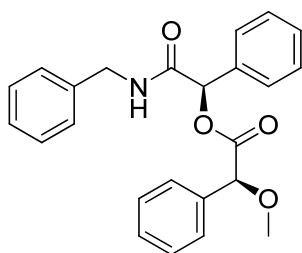
Preparation of 2-(*tert*-butylamino)-2-oxo-1-phenylethyl benzoate (6h):

N-(benzoyloxy)-*N-tert*-butyl-2-phenylacetamide (40 mg, 0.128 mmol) was dissolved in 1 mL dry DCM and the temperature lowered to -78 °C. To this, TMSOTf (47 μ L, 0.257 mmol) was added, followed 5 min later by NEt_3 (36 μ L, 0.257 mmol). After stirring at this temperature for 30 min, the reaction was warmed to room temperature, then heated to reflux and left overnight. The reaction was quenched by pouring directly onto a silica gel plug and eluted with EtOAc. Solvent removal *in vacuo* left an oil which upon spectroscopic analysis, showed approximately 25% conversion to **7h**. A pure sample of **7h** could not be obtained, even after extensive chromatography. Thus spectroscopic data reported here are for an impure sample with only selected resonances included (see scanned spectra for full details).



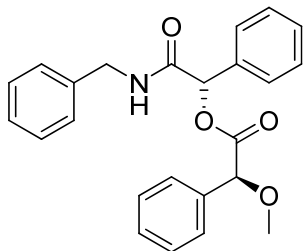
2-(*tert*-butylamino)-2-oxo-1-phenylethyl benzoate (6h)

^1H NMR (CDCl_3 , 400 MHz) δ 7.27-8.10 (10H, m), 6.22 (1H, s), 5.97 (1H, brs), 1.37 (9H, s); ^{13}C NMR (CDCl_3 , 100 MHz) 167.3, 164.9, 76.1, 51.6, 28.7; ESI-HRMS m/z 312.1594 ($\text{C}_{19}\text{H}_{22}\text{NO}_3 + \text{H}^+$ requires 312.1600).



(S)-((R)-2-(benzylamino)-2-oxo-1-phenylethyl) 2-methoxy-2-phenylacetate (9)

mp 77-79 °C; $[\alpha]_{\text{D}}^{25} = -40.0^\circ$ (c 1.0, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 7.26-7.32 (13H, m), 7.14-7.16 (2H, m), 6.20 (1H, br), 6.13 (1H, s), 4.89 (1H, s), 4.37 (2H, d, $J=5.8$), 3.40 (3H, s); ^{13}C NMR (100 MHz, CDCl_3) 169.0, 168.0, 137.7, 135.7, 135.1, 129.1, 129.1, 128.9, 128.9, 128.8, 127.8, 127.2, 127.0, 82.83, 76.0, 57.8, 43.5; FT-IR $\nu_{\text{max}}/\text{cm}^{-1}$ 3297br, 3063m, 3031m, 2928s, 2829w, 1751vs, 1661vs, 1530m, 1495m, 1453m, 1358w, 1259m, 1166s, 1103s, 1028m, 731m, 695s; ESI-HRMS m/z 390.1699 ($\text{C}_{24}\text{H}_{23}\text{NO}_4 + \text{H}^+$ requires 390.1705).



(S)-((S)-2-(benzylamino)-2-oxo-1-phenylethyl) 2-methoxy-2-phenylacetate (10**)**

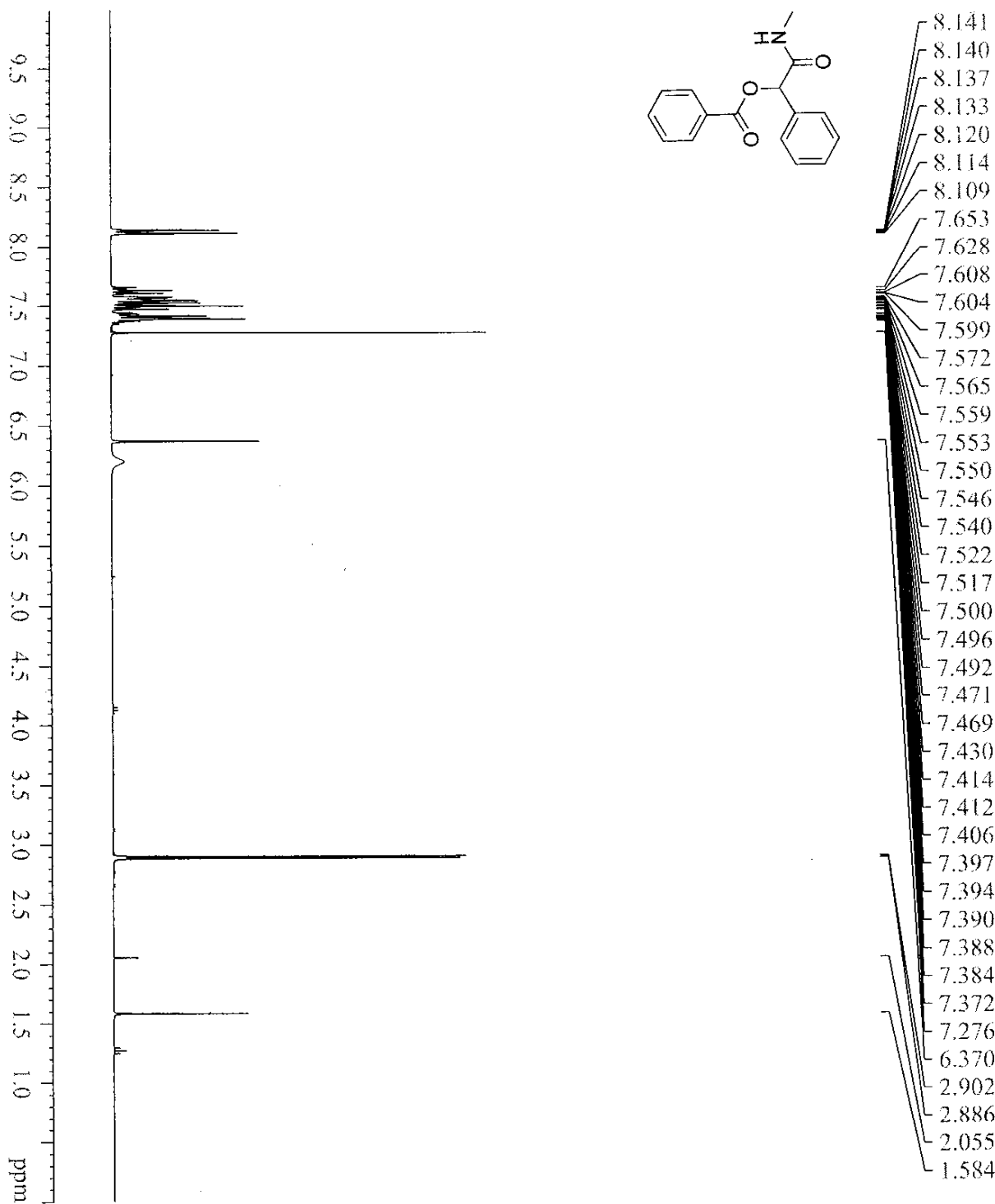
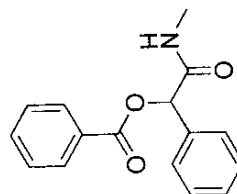
$[\alpha]_D^{25} = 58.9^\circ$ (c 1.0, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 7.28-7.41 (12H, m), 7.20-7.23 (3H, m), 6.23 (1H, s), 5.80 (1H, br), 4.83 (1H, s), 4.24 (1H, dd, $J=6, 14.8$), 4.15 (1H, dd, $J=6, 14.8$), 3.38 (3H, s); ^{13}C NMR (100 MHz, CDCl_3) 168.6, 168.0, 137.6, 135.9, 135.2, 129.2, 128.9, 128.8, 127.8, 127.7, 127.5, 127.2, 82.4, 75.6, 57.6, 43.3; FT-IR $\nu_{\text{max}}/\text{cm}^{-1}$ 3414s, 3308br, 3064m, 3032m, 2930w, 2830s, 1754vs, 1668vs, 1603s, 1527s, 1496s, 1454s, 1359s, 1243s, 1167s, 1109s, 1029w, 1002w, 734m, 697m; ESI-HRMS m/z 390.1702 ($\text{C}_{24}\text{H}_{23}\text{NO}_4 + \text{H}^+$ requires 390.1705).

Procedure for diastereomeric product determination

N-benzyl-(*S*)-mandelamide (100 mg, 0.414 mmol), (*S*)-(*O*-methyl)mandelic acid (69 mg, 0.414 mmol), EDCI.HCl (240 mg, 1.243 mmol) and DMAP (152 mg, 1.243 mmol) were all combined and dissolved in 3 mL DCM. The reaction was left stirring overnight at room temperature, then quenched with water. The layers were separated, and the organics washed with 1M HCl, then brine. The solvent was removed *in vacuo* and the crude material was purified using column chromatography (40% EtOAc/Hexane) to give **10** in 85% yield. Spectral data was identical with that of the rearranged material.

References

1. Clark, A. J.; Al-Faiyaz, Y. S. S.; Broadhurst, M. J. Patel, D.; Peacock, J. L. *J. Chem. Soc., Perkin Trans. 1.* **2000**, 1117-1127.
2. Kamimura, A.; Omata, Y.; Kakehi, A.; Shirai, M. *Tetrahedron.* **2002**, 58, 8763-8770.



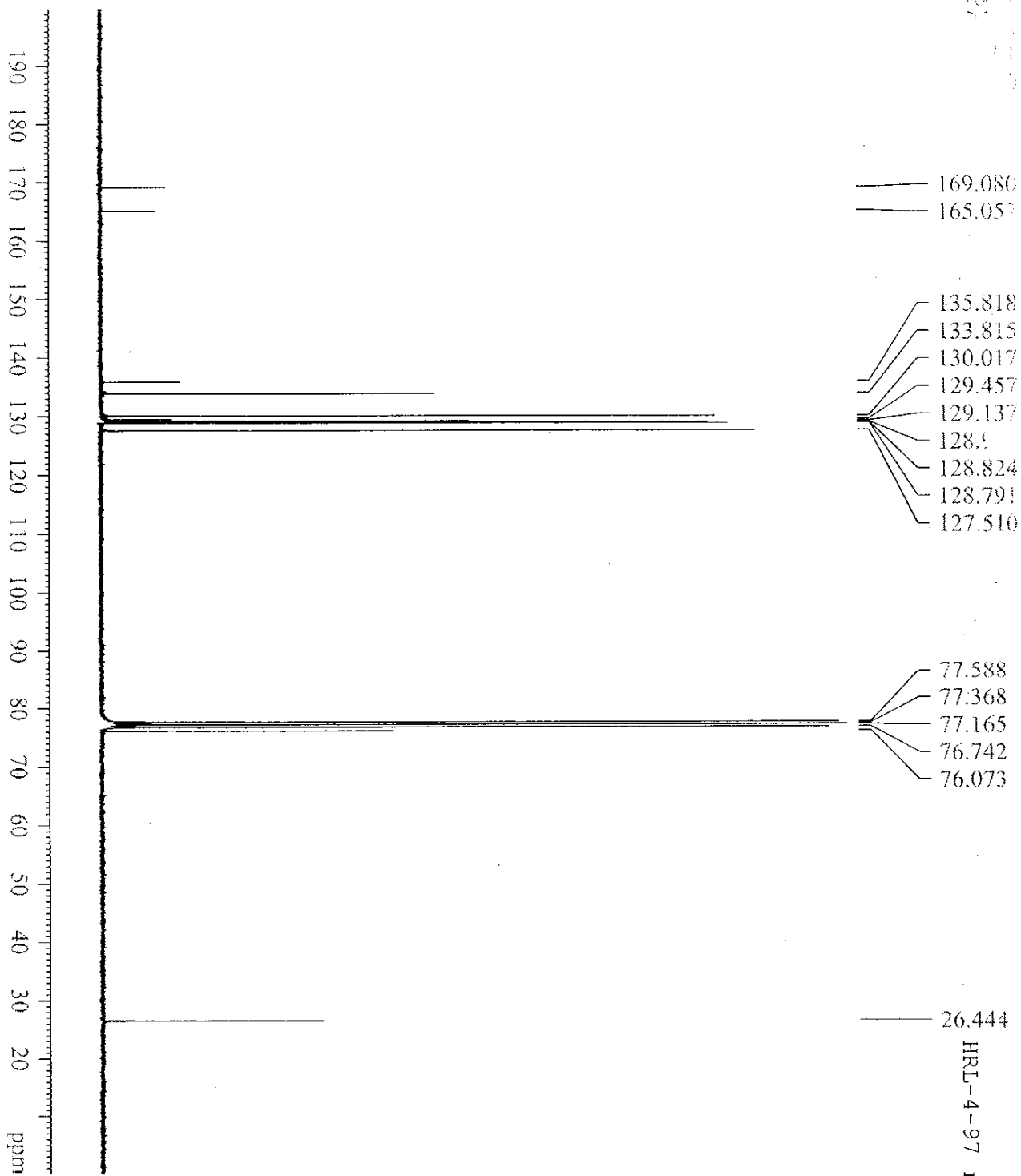
HRL-4-97 recryst from EtOAc

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PROCNO 1

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SOLVENT CDCl3
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DS 2
SWH 8997.806 Hz
FIDRES 0.274439 Hz
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RG 724.1
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DE 15.00 usec
TE 303.2 K
D1 2.00000000 sec
TD0 1

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HRL-4-97 recryst from EtOAc

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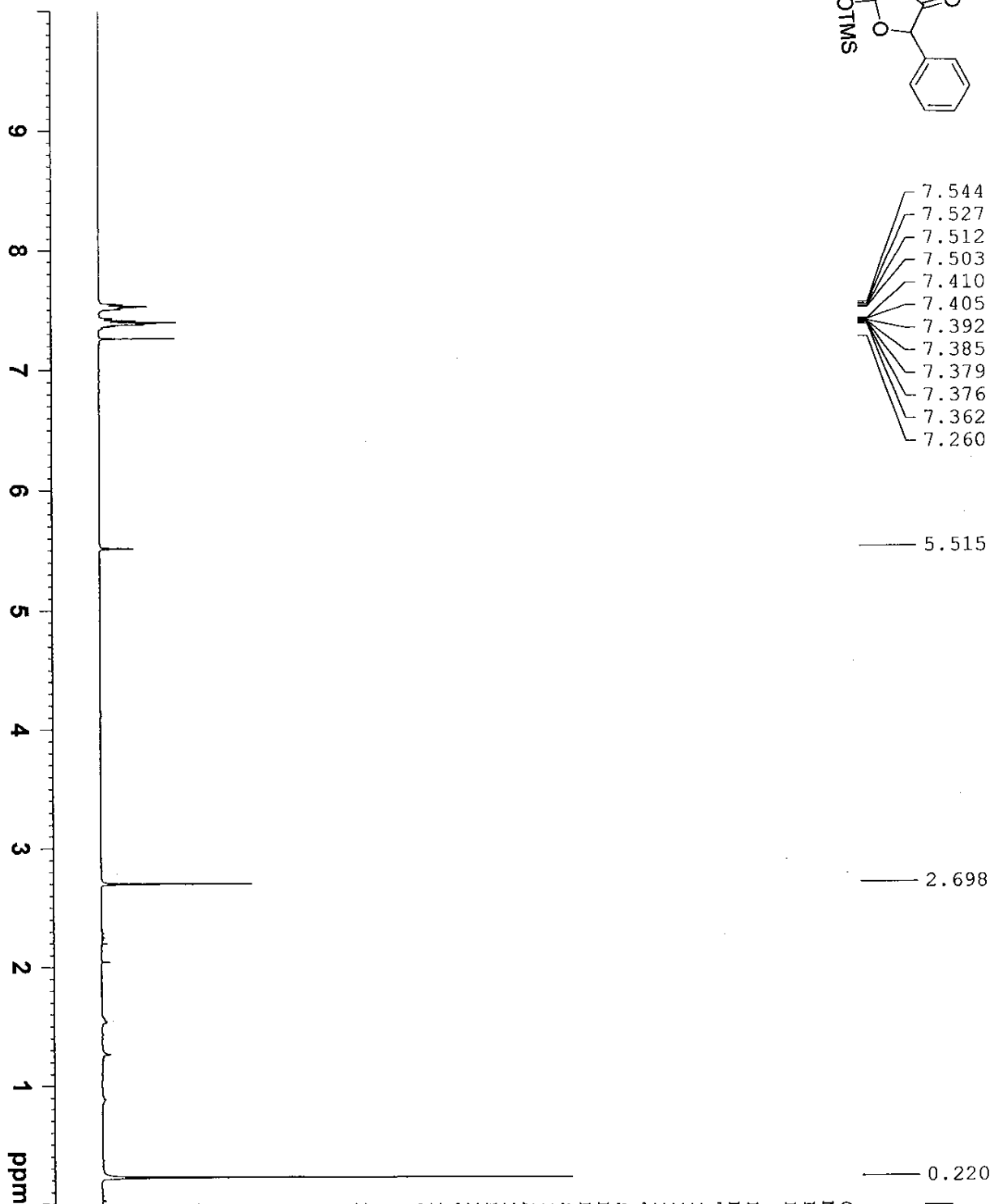
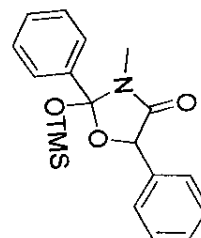
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D1 4.00000000 sec
d11 0.03000000 sec
TD0 1

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PL1 0.00 dB
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===== CHANNEL f2 =====
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¹H NMR (400 MHz, CDCl₃) **7a**



Current Data Parameters
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PROCNO 1

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D1 5.00000000 sec
TD0 1

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P1 8.00 usec
PL1 1.95 dB
PL1W 9.58740711 W
SFO1 400.1322007 MHz
F2 - Processing parameters
SI 32768
SF 400.1300099 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

HRL-4-98 2eq.

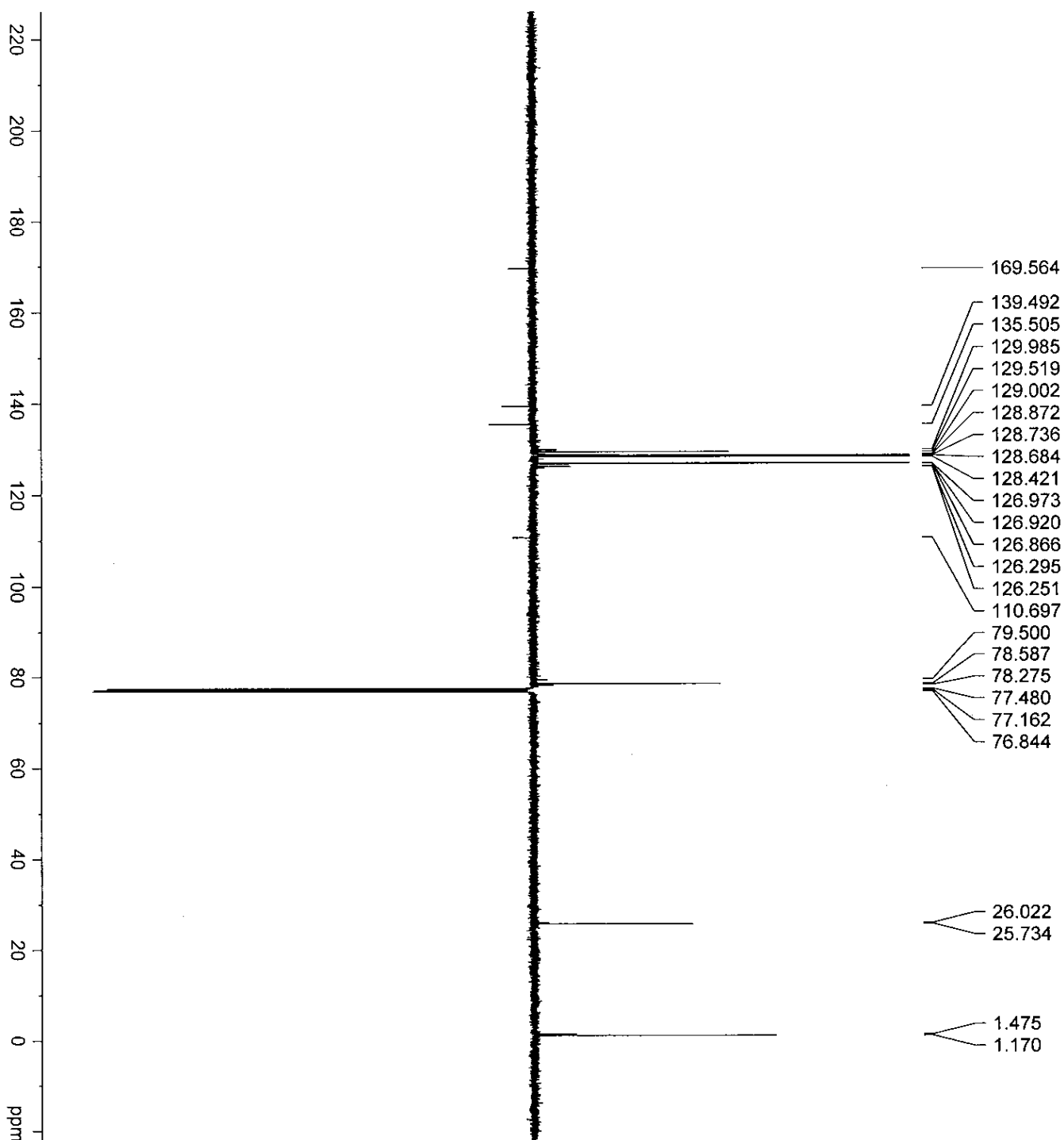
Current Data Parameters
NAME hrl-4-98
EXPNO 2
PROCNO 1

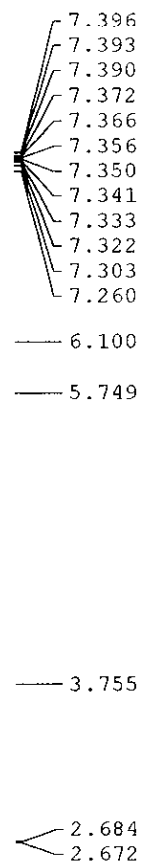
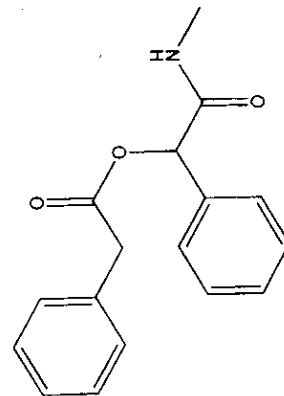
F2 - Acquisition Parameters
Date_ 20090330
Time 17.05
INSTRUM spect
PROBHD 5 mm 5mm 1H/2H
PULPROG jmod
TD 65536
SOLVENT CDCl₃
NS 7268
DS 4
SWH 25000.000 Hz
FIDRES 0.381470 Hz
AQ 1.3107700 sec
RG 2050
DW 20.000 usec
DE 15.00 usec
TE 303.2 K
CNST2 145.0000000
CNST11 1.0000000
D1 6.0000000 sec
D20 0.00689655 sec
TD0 1

===== CHANNEL f1 =====
NUC1 ¹³C
P1 12.20 usec
P2 24.40 usec
PL1 0.00 dB
PL1W 95.45168304 W
SFO1 100.6230043 MHz

===== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 ¹H
PCPD2 100.00 usec
PL2 2.00 dB
PL12 23.16 dB
PL2W 9.47766113 W
PL12W 0.07256065 W
SFO2 400.1320000 MHz

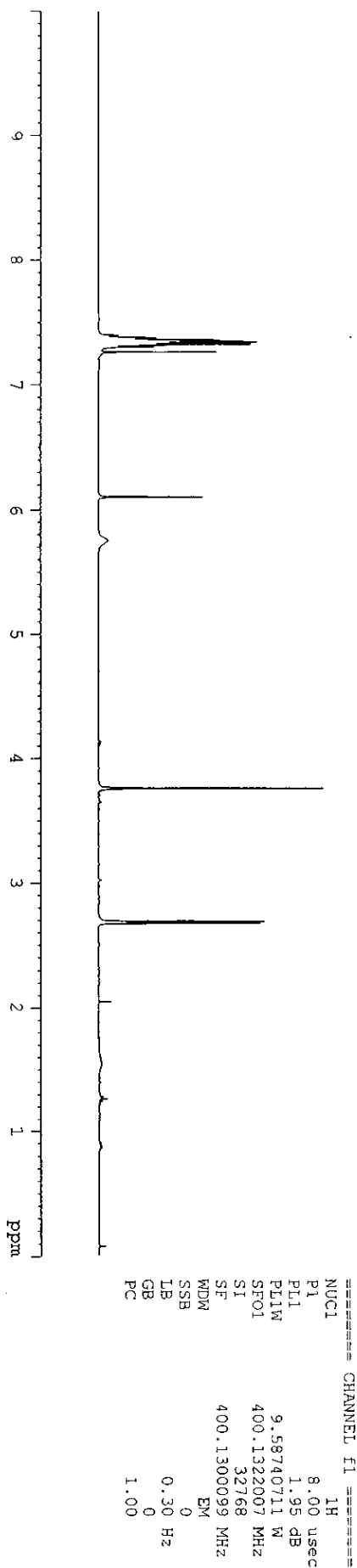
F2 - Processing parameters
SI 65536
SF 100.6127525 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.00



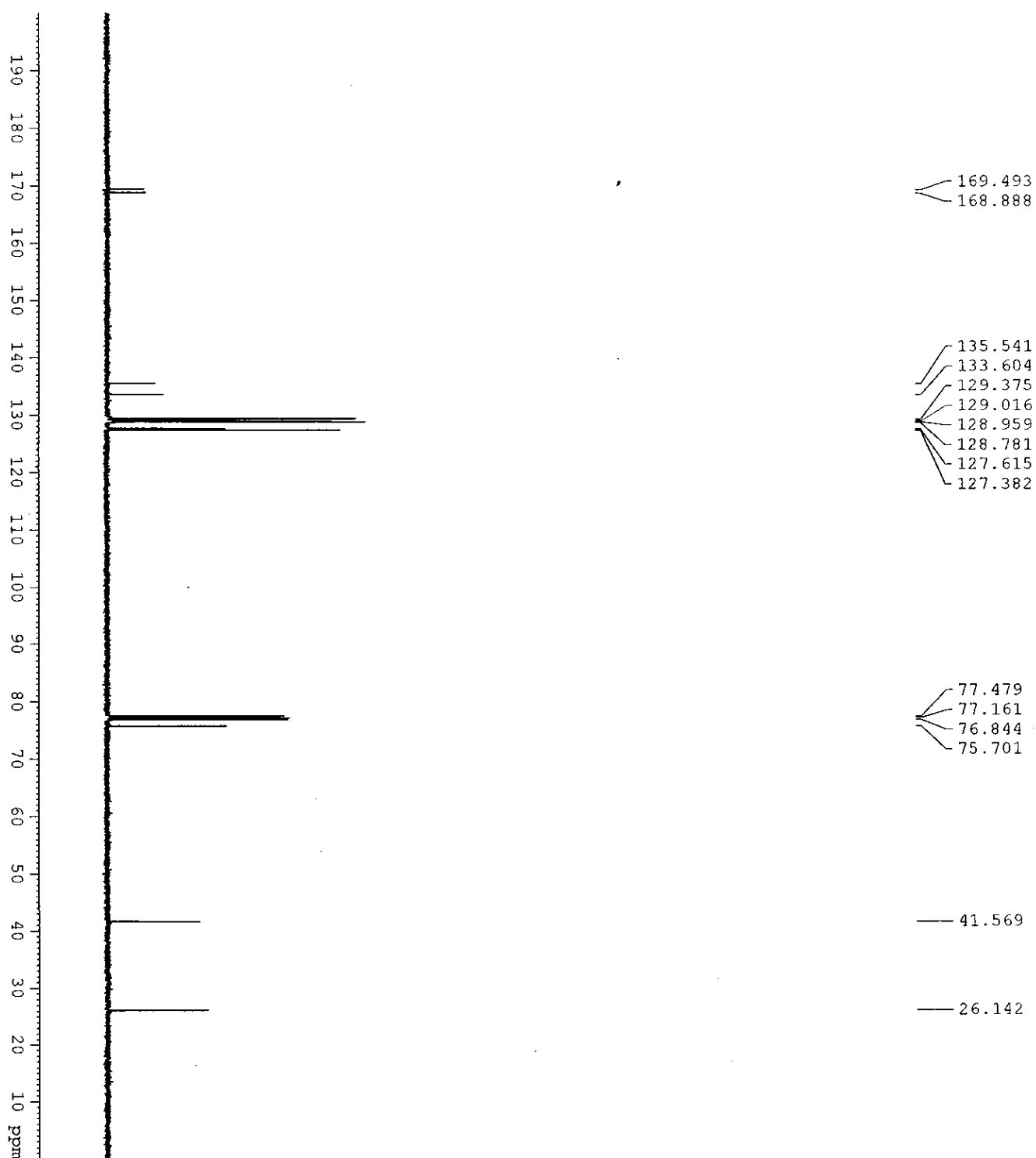


Avance III -1H Spectrum

¹H NMR (400 MHz, CDCl₃) **6b**



¹³C NMR (100 MHz, CDCl₃) **6b**



NAME hrl-5-35

EXENO 3

PROCNO 1

Date 20090723

Time 14.01

INSTRUM spect

PROBHD 5 mm 1H/2H

PULPROG zgpg30

TD 65536

SOLVENT CDCl3

NS 565

DS 4

SWH 22059.824 Hz

FIDRES 0.336591 Hz

AQ 1.4855326 sec

RG 2050

DM 22.667 usec

DE 12.00 usec

TE 303.2 K

D1 2.00000000 sec

D11 0.03000000 sec

TD0 1

===== CHANNEL f1 =====

NUC1 13C

P1 14.00 usec

PL1 0.00 dB

PL1W 95.45168304 W

SFO1 100.6223263 MHz

===== CHANNEL f2 =====

CPDPRG2 waltz16

NUC2 1H

PCPD2 80.00 usec

PL2 1.95 dB

PL12 22.20 dB

PL13 28.00 dB

PL2W 9.58740711 W

PL12W 0.09051095 W

PL13W 0.02380681 W

SFO2 400.1316005 MHz

SI 32768

SF 100.6127585 MHz

WDW EM

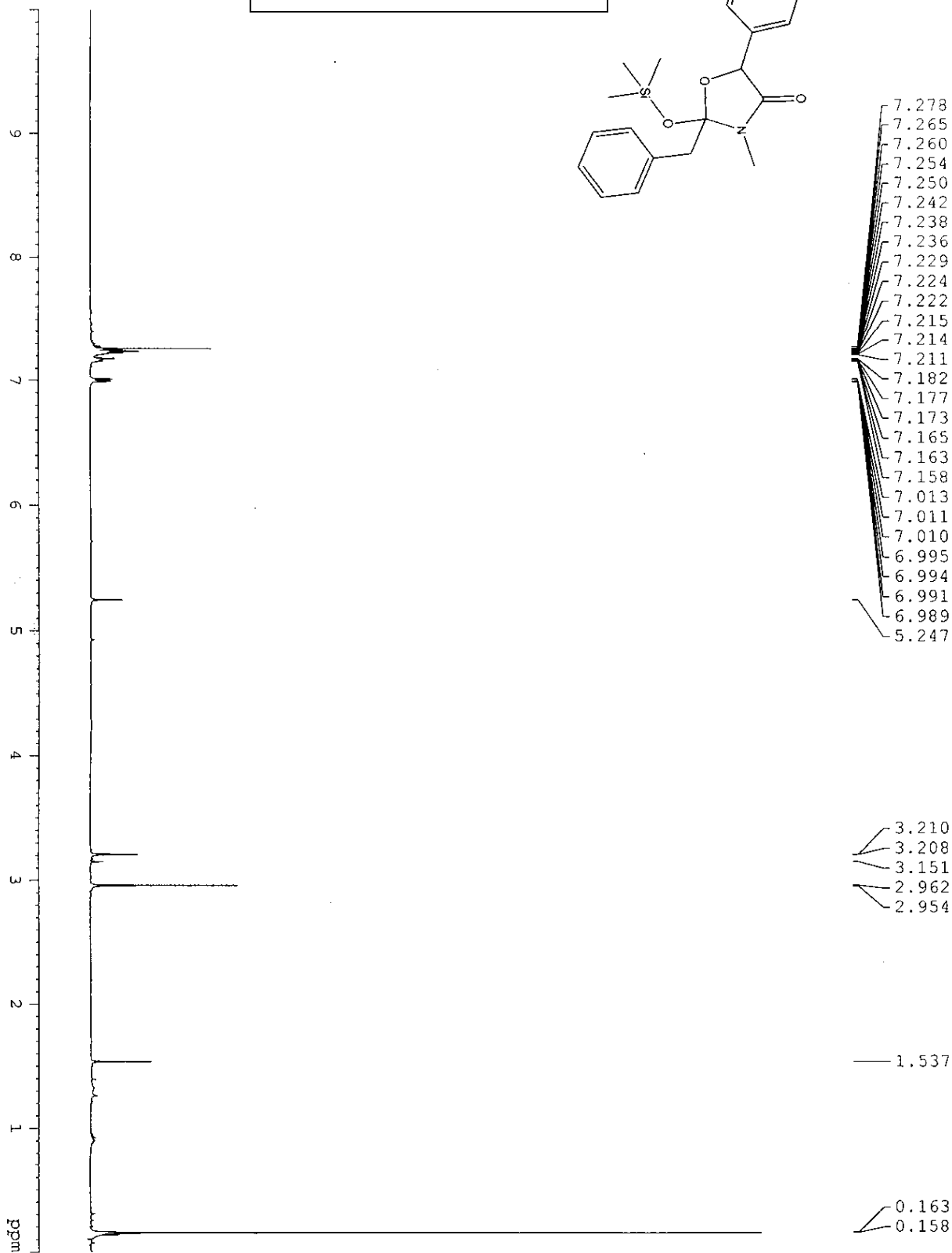
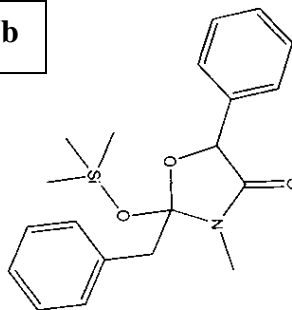
SSB 0

LB 1.00 Hz

GB 0

PC 1.40

¹H NMR (400 MHz, CDCl₃) **7b**

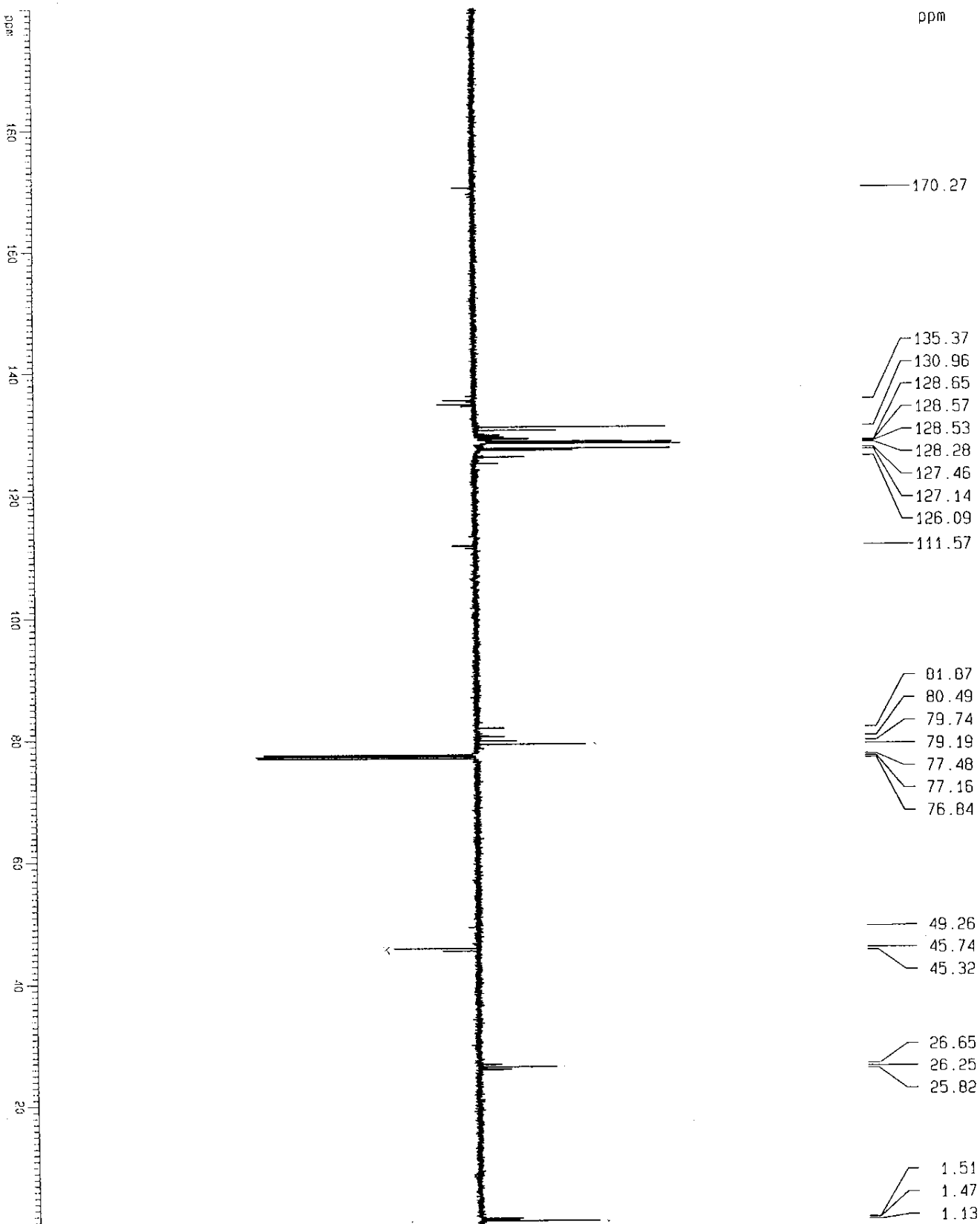


Avance III -1H Spectrum

```
NAME          hrl-5-39c
EXPNO         4
PROCNO        1
Date_         20090728
Time          20.36
INSTRUM       spect
PROBHD        5 mm 5mm 1H/2H
PULPROG       zg
TD            48976
SOLVENT       CDCl3
NS            8
DS            2
SWH           4807.692 Hz
FIDRES        0.100002 Hz
AQ            4.9999542 sec
RG            161
DE            104.000 usec
TE            303.2 K
D1            5.00000000 sec
TD0           1

===== CHANNEL f1 =====
NUC1          1H
P1            8.00 usec
PL1          1.95 dB
PL1W          9.58740711 W
SFO1          400.132007 MHz
SI            32768
SF            400.1300098 MHz
WDW           EM
SSB           0
LB            0.30 Hz
GB            0
PC            1.00
```

¹³C NMR (100 MHz, CDCl₃) 7b



ppm

170.27

135.37
130.96
128.65
128.57
128.53
128.28
127.46
127.14
126.09
111.57

81.87
80.49
79.74
79.19
77.48
77.16
76.84

49.26
45.74
45.32

26.65
26.25
25.82

1.51
1.47
1.13

DNX 400

Current Data Parameters
NAME hrl-3-99-4thQ-D-lug
EXPNO 5
PROCNO 1

F2 - Acquisition Parameters
Date_ 20080522
Time 7.59
INSTRUM spect
PROBHD 5 mm Multinucl
PULPROG 1mod
TD 65536
SOLVENT
NS 3230
DS 4
SWH 25125.629 Hz
FIDRES 0.363367 Hz
AQ 1.3042164 sec
RG 9195.2
DM 19.900 usec
DE 15.00 usec
TE 303.2 K
CNS12 145.000000
CNS111 1.000000
D1 6.00000000 sec
d20 0.00669655 sec
DELTA 0.0001477 sec
MCREST 0.00000000 sec
MCMRK 0.01500000 sec

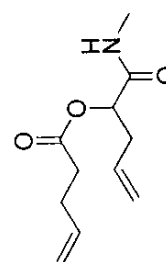
===== CHANNEL f1 =====
NUC1 13C
P1 11.60 usec
P2 23.20 usec
PL1 0.00 dB
SF01 100.629643 MHz

===== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 4.00 dB
PL12 26.00 dB
SF02 400.132000 MHz

F2 - Processing parameters
SI 65536
SF 100.6127535 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 22.00 cm
CY 4.04 cm
FIP 200.000 ppm
F1 20122.55 Hz
F2P -0.000 ppm
F2 -0.00 Hz
PPMCM 9.09091 ppm/c
HZCM 914.66144 Hz/cm

¹H NMR (400 MHz, CDCl₃) **6c**



ppm

ppm

- 7.2600
- 6.0818
5.8499
5.8329
5.7216
5.7037
5.1113
5.1073
5.1008
5.0727
5.0683
5.0641
5.0603
- 4.1272
4.1094
- 2.8309
2.8186
2.5060
2.5023
2.4866
2.4845
2.4227
2.4194
2.4016
2.0381
1.3926
1.2726
1.2548
0.8807
0.8690
0.8527

Avance DRX400 NMR Spectrometer

Current Data Parameters
NAME HRL-3-91m1x-9-12
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters

Date_ 20080514
Time 20:58
INSTRUM spect
PROBHD 5 mm Multinucl
PULPROG zg30
TO 32768
SOLVENT CDCl₃
NS 64
DS 2
SWH 4789.272 Hz
FIDRES 0.146157 Hz
AQ 3.4210291 sec
RG 322.5
OW 104.400 usec
DE 15.00 usec
TE 303.2 K
D1 3.00000000 sec
MCRES1 0.00000000 sec
MCRESK 0.01500000 sec

===== CHANNEL f1 =====

NUC1 ¹H
P1 8.50 usec
PL1 4.00 dB
SFO1 400.1320006 MHz

F2 - Processing parameters

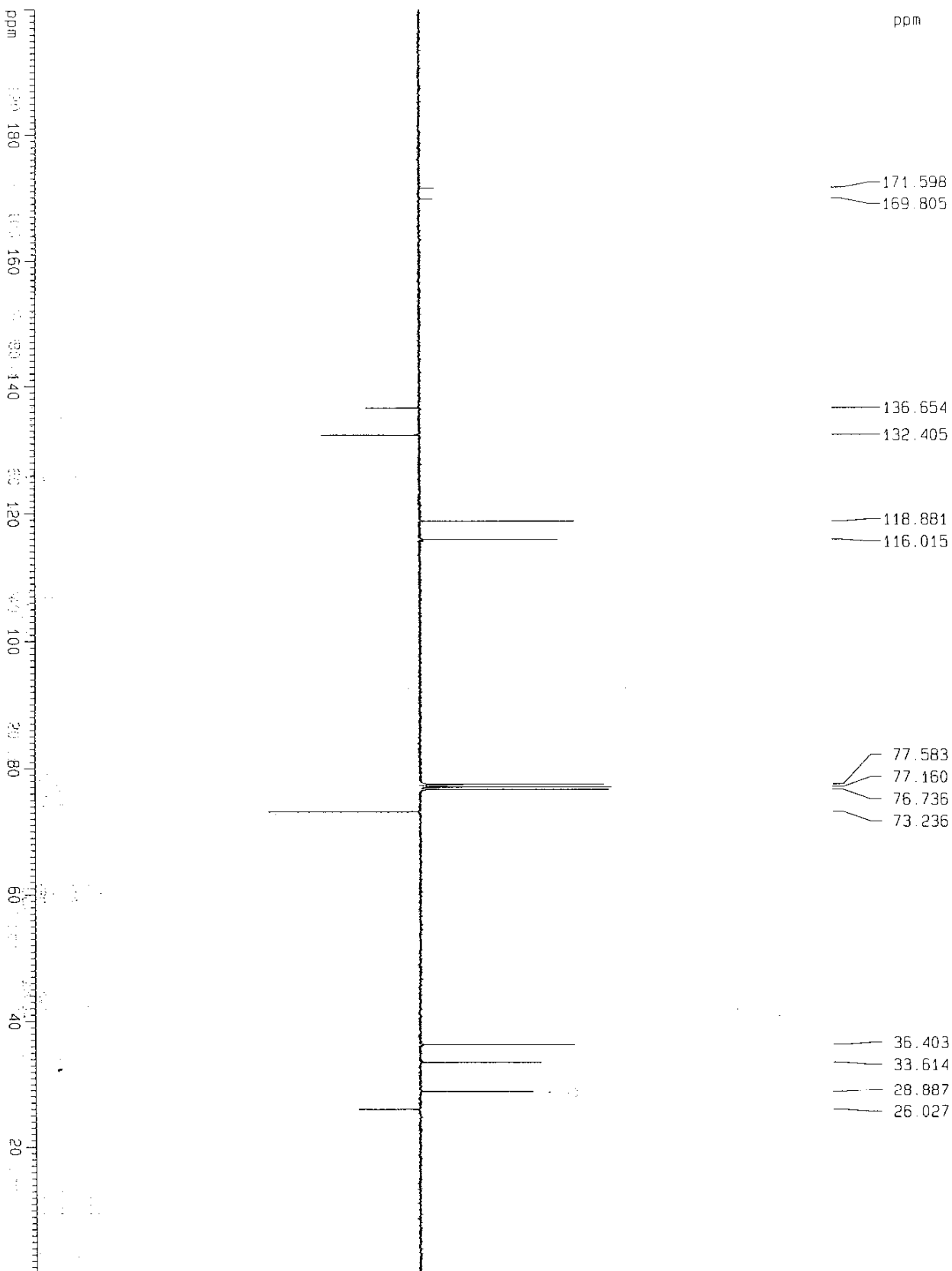
SF 32768
SF 400.1300090 MHz
WDW EM
SSB 0
LB 0.20 Hz
GB 0
PC 1.00

1D NMR plot parameters

CX 22.00 cm
CY 10.50 cm
F1P 10.000 ppm
F1 4001.30 Hz
F2P 0.000 ppm
F2 0.00 Hz
PPMCM 0.45455 ppm/cm
HZCM 181.87727 Hz/cm

¹³C NMR (100 MHz, CDCl₃) 6c

Avance 300 Monash University
EC3-125B in D2O



Current Data Parameters
NAME hrl-3-9tmix-9-12
EXPNO 3
PROCNO 1

F2 - Acquisition Parameters
Date_ 20080514
Time 21.23
INSTRUM spect
PROBHD 5 mm QNP 1H/1
PULPROG jmod
TD 32768
SOLVENT DMSO
NS 10836
DS 4
SWH 18382.354 Hz
FIDRES 0.560985 Hz
AQ 0.8913396 sec
RG 13004
DM 27.200 us
DE 20.00 us
TE 304.2 K
CNS12 145.000000
CNS111 1.000000
O1 3.00000000 se
O2 0.00696655 se
DELTA 0.00001082 se
MCREST 0.00000000 se
MCMRK 0.01500000 se

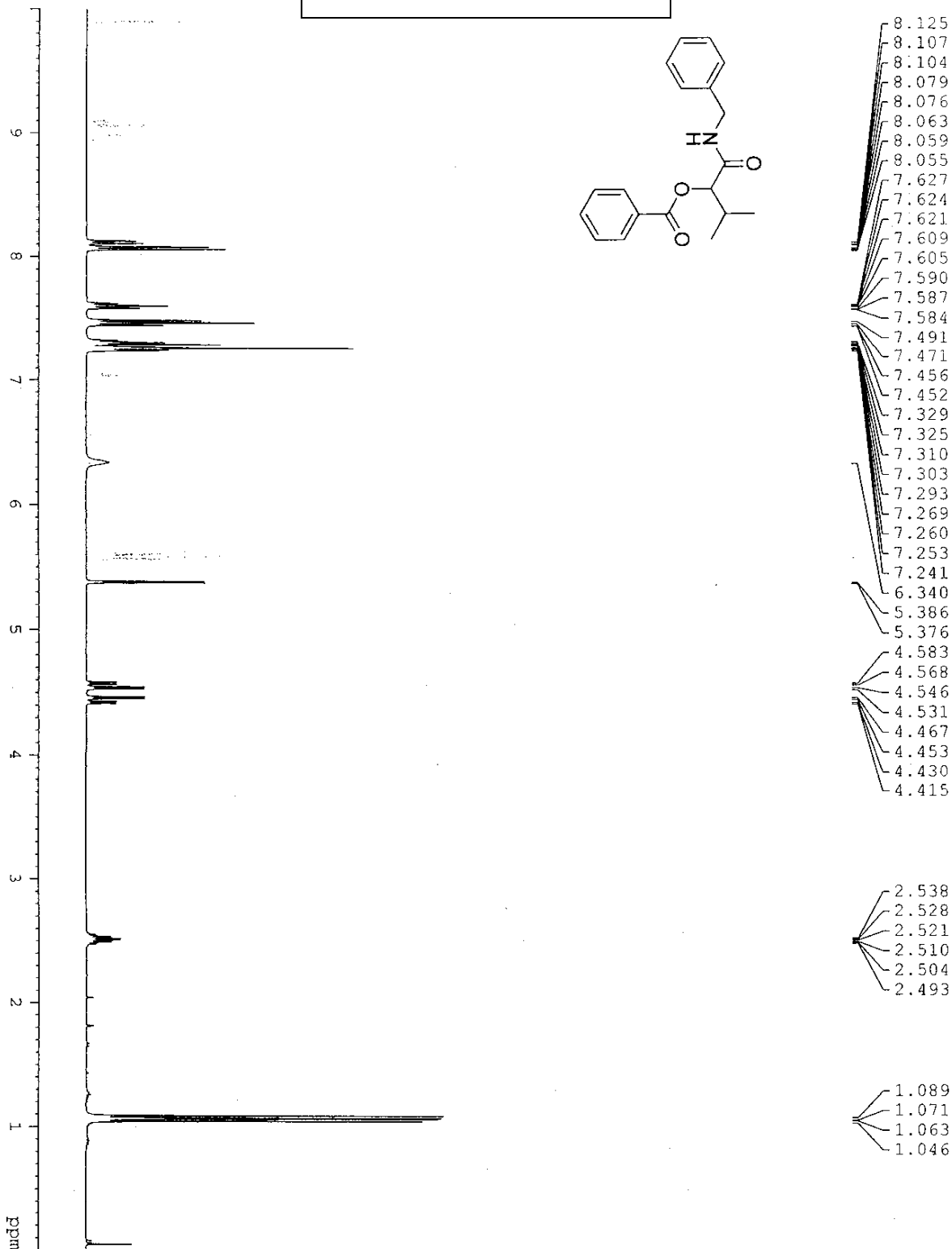
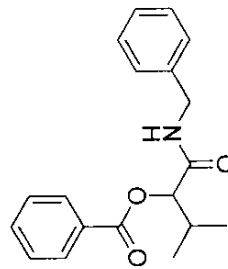
===== CHANNEL f1 =====
NUC1 13C
P1 8.50 us
O2 17.00 us
PL1 0.00 dB
SF01 75.4760145 MHz

===== CHANNEL f2 =====
CPOPRG2 waltz16
NUC2 1H
PCPO2 100.00 us
PL2 -2.00 dB
PL12 15.00 dB
SF02 300.1314256 MHz

F2 - Processing parameters
SI 32768
SF 75.4677366 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

1D NMR plot parameters
CX 23.00 cm
CY 3.50 cm
F1P 200.000 dB
F1 15093.55 Hz
F2P 0.000 dB
F2 0.00 Hz
PPMCH 8.69655 dB
H2CH 656.24115 Hz

¹H NMR (400 MHz, CDCl₃) **6f**



hr1-4-116 f12-16

NAME hr1-4-116-12-16
EXPNO 1
PROCNO 1
Date_ 20090429
Time 18.49
INSTRUM spect
PROBHD 5 mm 5mm 1H/2H
PULPROG zg
TD 48076
FIDRES 0.100002 Hz
AQ 4.999542 sec
RG 45.2
DE 104.000 usec
TE 303.2 K
D1 5.0000000 sec
TDO 1
===== CHANNEL f1 =====
NUC1 1H
P1 8.00 usec
PL1 1.95 dB
PL1W 9.58740711 W
SFO1 400.1322007 MHz
SI 32768
SF 400.130097 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

¹³C NMR (100 MHz, CDCl₃) **6f**

ppm

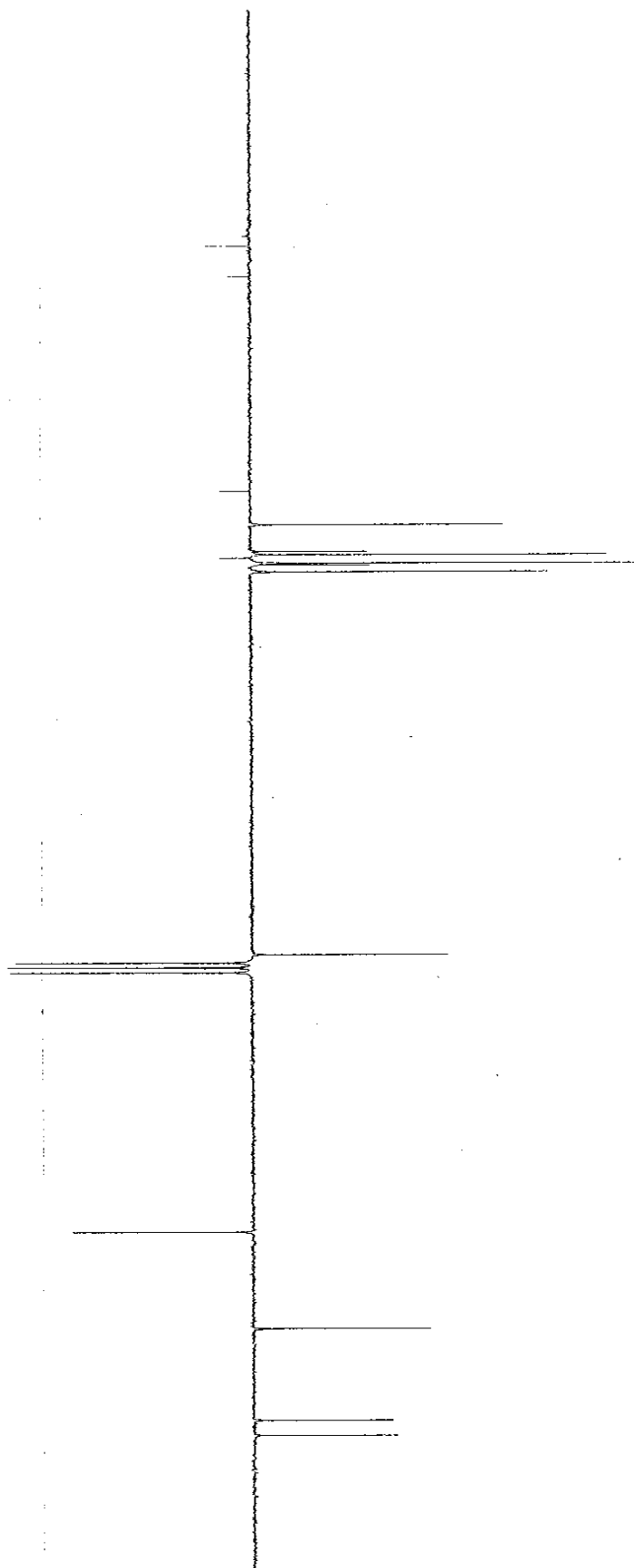
169.534
165.675

138.059
133.768
130.331
129.917
129.493
128.884
128.827
128.606
127.739
127.703

78.843
77.800
77.165
76.530

43.352
31.007

19.145
17.230



Current Data Parameters
NAME h-1-4-15-12-16
EXPNO 3
PROCNO 1

F2 - Acquisition Parameters
Date_ 20090430
Time 9.22

INSTRUM spect
PROBHD 5 mm DUL 13C-1
PULPROG 1mod
TD 32768
SOLVENT CDCl3
NS 9511
DS B
SWH 11574.074 Hz
FIDRES 0.35313 Hz
AQ 1.4150276 sec
RG 13390.4
JM 43.200 usec
DE 20.00 usec
TE 303.2 K
CNS12 145.0000000
CNS111 1.0000000
D1 4.00000000 sec
D20 0.00689555 sec
DELTA 0.00601528 sec
MCREST 0.00000000 sec
KCMRK 0.01500000 sec

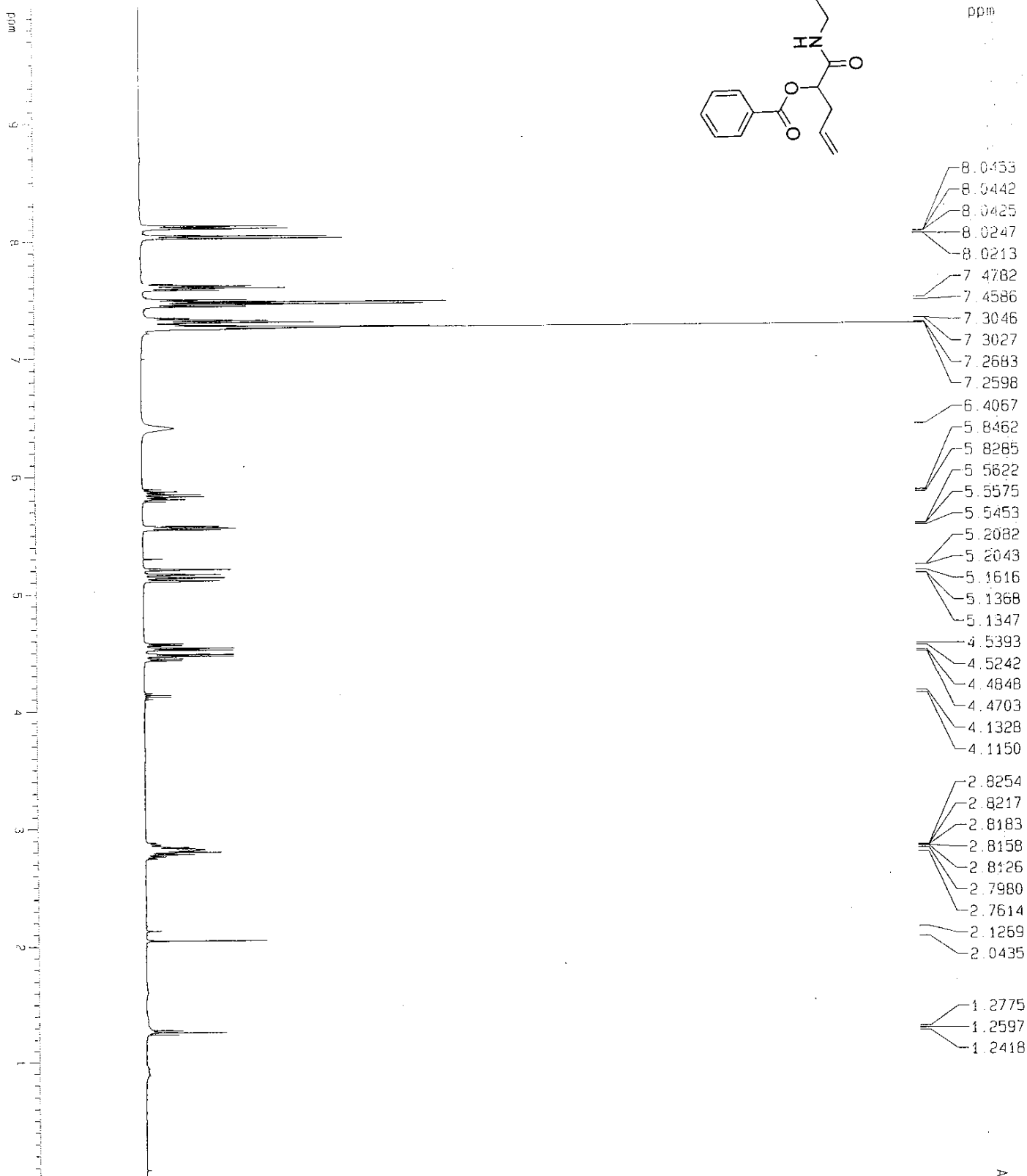
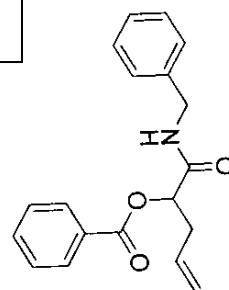
===== CHANNEL f1 =====
NUC1 13C
P1 12.00 usec
P2 24.00 usec
PL1 2.00 dB
SF01 50.3280129 MHz

===== CHANNEL f2 =====
COPPRG2 waltz16
NUC2 1H
PCPD2 160.00 usec
PL2 0.00 dB
PL12 20.45 dB
SF02 200.1309054 MHz

F2 - Processing Parameters
SI 32768
SF 50.3282203 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.00

13 NMR plot parameters
CX 22.00 um
CY 3.49 cm
FID 319.000 ppm
F1 127.703 Hz
F2 127.739 Hz
F3 127.703 Hz
F4 127.703 Hz
F5 127.703 Hz
F6 127.703 Hz
F7 127.703 Hz
F8 127.703 Hz
F9 127.703 Hz
F10 127.703 Hz
F11 127.703 Hz
F12 127.703 Hz
F13 127.703 Hz
F14 127.703 Hz
F15 127.703 Hz
F16 127.703 Hz
F17 127.703 Hz
F18 127.703 Hz
F19 127.703 Hz
F20 127.703 Hz
F21 127.703 Hz
F22 127.703 Hz
F23 127.703 Hz
F24 127.703 Hz
F25 127.703 Hz
F26 127.703 Hz
F27 127.703 Hz
F28 127.703 Hz
F29 127.703 Hz
F30 127.703 Hz
F31 127.703 Hz
F32 127.703 Hz
F33 127.703 Hz
F34 127.703 Hz
F35 127.703 Hz
F36 127.703 Hz
F37 127.703 Hz
F38 127.703 Hz
F39 127.703 Hz
F40 127.703 Hz
F41 127.703 Hz
F42 127.703 Hz
F43 127.703 Hz
F44 127.703 Hz
F45 127.703 Hz
F46 127.703 Hz
F47 127.703 Hz
F48 127.703 Hz
F49 127.703 Hz
F50 127.703 Hz
F51 127.703 Hz
F52 127.703 Hz
F53 127.703 Hz
F54 127.703 Hz
F55 127.703 Hz
F56 127.703 Hz
F57 127.703 Hz
F58 127.703 Hz
F59 127.703 Hz
F60 127.703 Hz
F61 127.703 Hz
F62 127.703 Hz
F63 127.703 Hz
F64 127.703 Hz
F65 127.703 Hz
F66 127.703 Hz
F67 127.703 Hz
F68 127.703 Hz
F69 127.703 Hz
F70 127.703 Hz
F71 127.703 Hz
F72 127.703 Hz
F73 127.703 Hz
F74 127.703 Hz
F75 127.703 Hz
F76 127.703 Hz
F77 127.703 Hz
F78 127.703 Hz
F79 127.703 Hz
F80 127.703 Hz
F81 127.703 Hz
F82 127.703 Hz
F83 127.703 Hz
F84 127.703 Hz
F85 127.703 Hz
F86 127.703 Hz
F87 127.703 Hz
F88 127.703 Hz
F89 127.703 Hz
F90 127.703 Hz
F91 127.703 Hz
F92 127.703 Hz
F93 127.703 Hz
F94 127.703 Hz
F95 127.703 Hz
F96 127.703 Hz
F97 127.703 Hz
F98 127.703 Hz
F99 127.703 Hz
F100 127.703 Hz

¹H NMR (400 MHz, CDCl₃) **6g**



Avance DRX400 NMR Spectrometer

Current Data Parameters
NAME n1-4-44-2
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20081211
Time 18.25
INSTRUM spect
PROBHD 5 mm Multinuc1
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 64
DS 2
SMH 4789.272 Hz
FIDRES 0.146157 Hz
AQ 3.4210291 sec
RG 456.1
OW 104.400 usec
DE 15.50 usec
TE 303.2 K
D1 3.00000000 sec
MCREST 0.00000000 sec
MCNMRK 0.01500000 sec

===== CHANNEL f1 =====
NUC1 ¹H
P1 8.50 usec
PL1 4.00 dB
SF01 400.1320006 MHz

F2 - Processing parameters
SI 32768
SF 400.1320009 MHz
WDW EM
SSB 0
LB 0.20 Hz
GB 0
PC 1.00

1D NMR Plot Parameters
CX 22.00 cm
CY 15.13 cm
F1P 10.000 ppm
F1 4001.30 Hz
F2P 0.000 ppm
F2 0.00 Hz
PPMCK 0.45455 ppm/cm
HZCM 181.87727 Hz/cm

¹³C NMR (100 MHz, CDCl₃) **6g**



DRX 400

ppm

169.16
165.30

137.79
133.66
132.10
130.21
129.77
129.27
128.76
128.49
127.60
119.16

77.34
77.02
76.70
73.67

43.27
36.35

Current Data Parameters
NAME hr1-4-44-2
EXPNO 4
PROCNO 1

F2 - Acquisition Parameters
Date_ 20081212
Time 17.38

INSTRUM spect
PROBHD 5 mm MUltiNuc1
PULPROG 1m0d
TD 65536
SOLVENT NS
DS 4
SMH 25125.629 Hz
FIDRES 0.38387 Hz
AQ 1.3042164 sec
RG 9195.2
OW 19.900 usec
DE 15.50 usec
TE 303.2 K
CNS12 145.000000
CNS111 1.000000
SI 6
a20 0.00689655 sec
DELTA 0.00001477 sec
MCREST 0.00000000 sec
MCMRK 0.01500000 sec

***** CHANNEL f1 *****

NUC1 ¹³C
P1 11.60 usec
a2 23.20 usec
PL1 0.00 dB
SF01 100.6229643 MHz

***** CHANNEL f2 *****

CPDPRG2 waltz16
NUC2 ¹H
PCPD2 100.00 usec
PL2 4.00 dB
PL12 28.00 dB
SF02 400.1320000 MHz

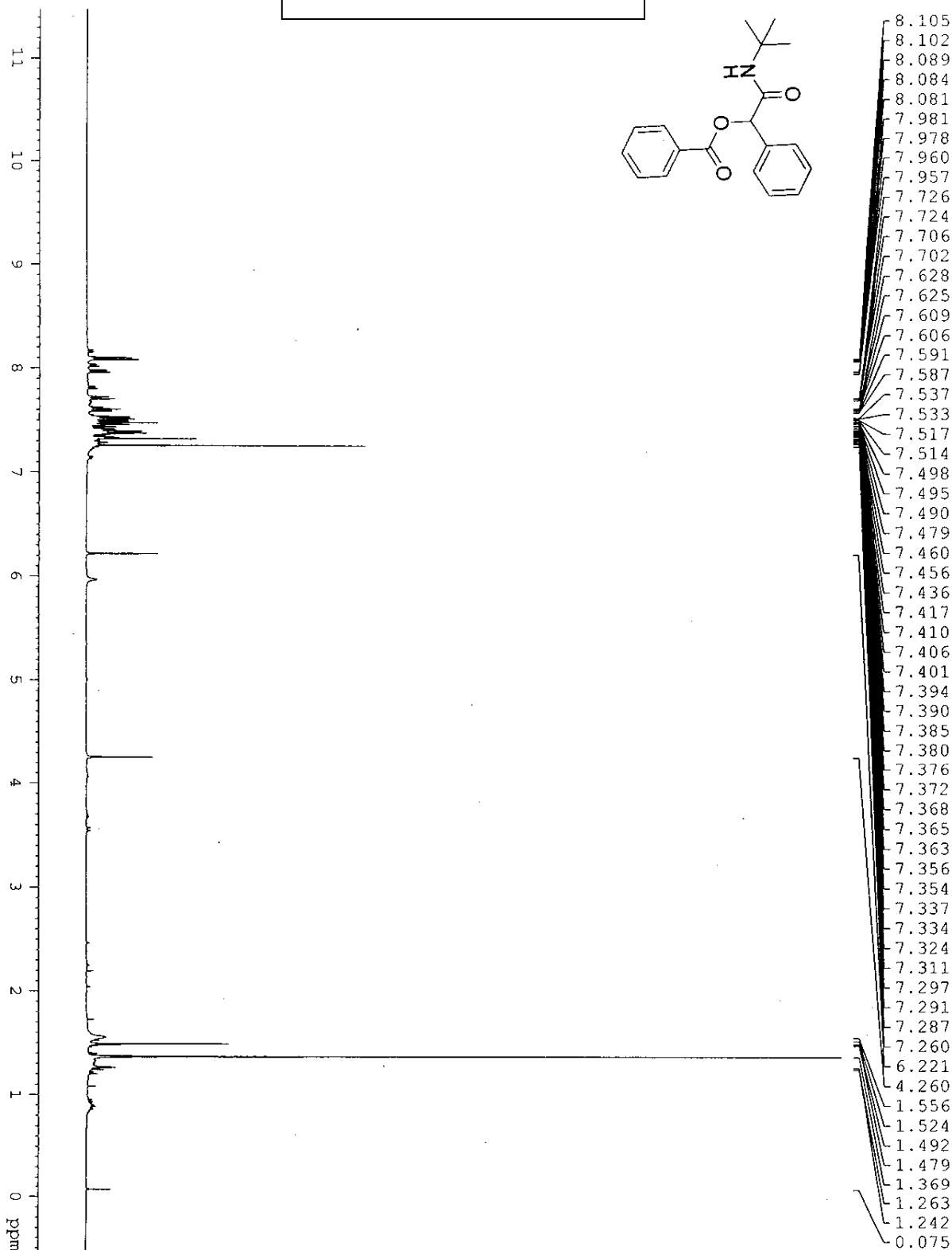
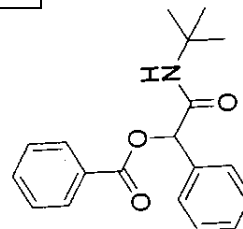
F2 - Processing parameters

SI 65536
SF 100.6127670 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.00

10 NMR plot parameters

CX 22.00 cm
CY 12.34 cm
F1P 200.000 ppm
F1 201.2255 Hz
F2P -0.000 ppm
F2 -0.00 Hz
PPMCM 9.0981 ppm/cm
HZCM 914.66156 Hz/cm

¹H NMR (400 MHz, CDCl₃) 6h

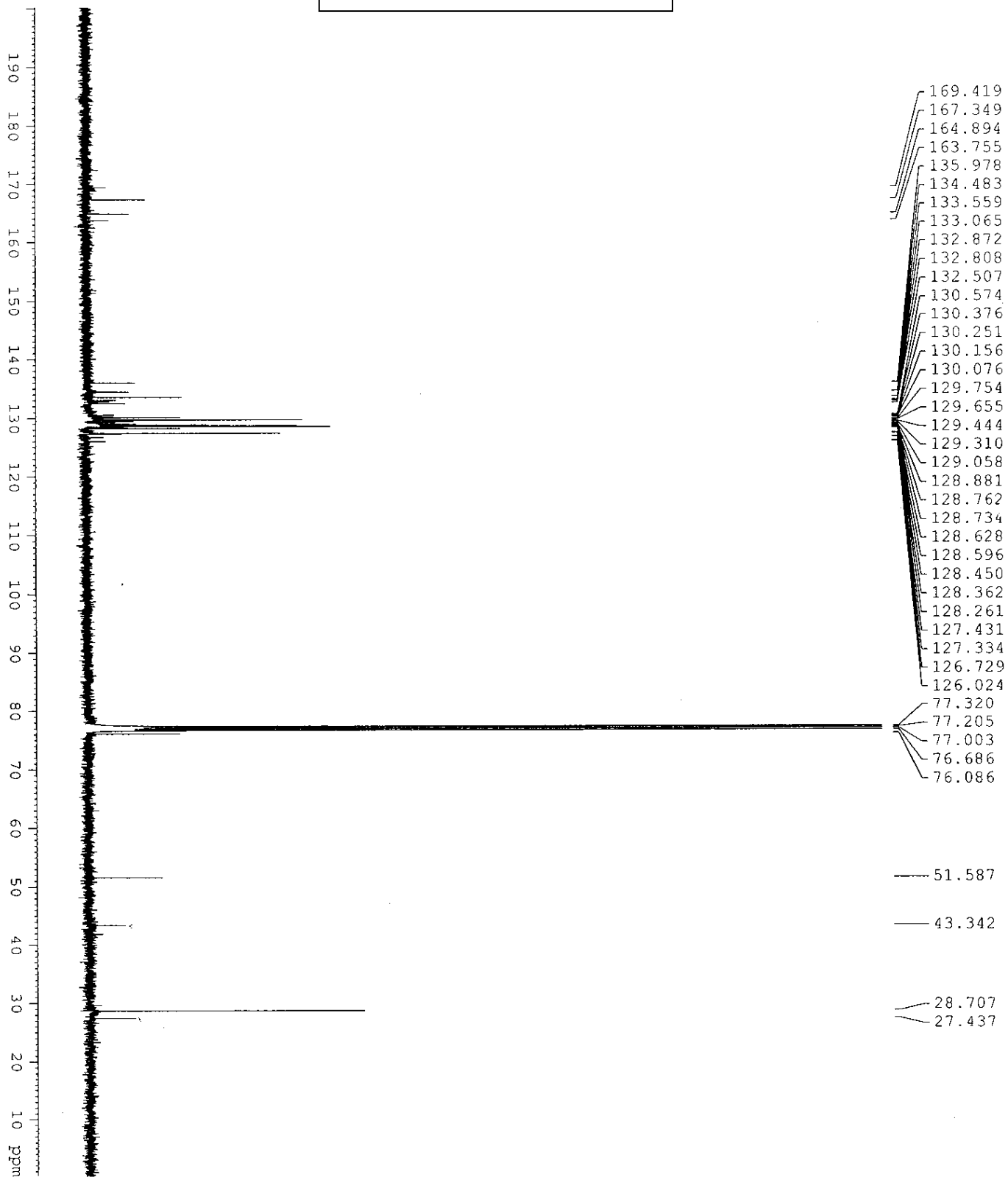


hrl-4-100-7-8 t-bu 2eq

```
NAME hrl-4-100-7-8
EXPNO 1
PROCNO 1
Date_ 20090403
Time_ 18.07
INSTRUM spect
PROBHD 5 mm 5mm 1H/2H
PULPROG zg
TD 48076
SOLVENT CDCl3
NS 32
DS 2
SWH 4807.692 Hz
FIDRES 0.100002 Hz
AQ 4.999542 sec
RG 181
DM 104.000 usec
DE 14.56 usec
TE 303.2 K
D1 5.00000000 sec
TDO 1

===== CHANNEL f1 =====
NUC1 1H
P1 8.00 usec
PL1 1.95 dB
PL1W 9.58740711 W
SFO1 400.1322007 MHz
SI 32768
SF 400.1300097 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
```

¹³C NMR (100 MHz, CDCl₃) 6h



Acquire III - 13C with 1H Presaturated Decoupling

NAME	hrl-4-100-7-8
EXPNO	4
PROCNO	1
Date_	20090403
Time	22.17
INSTRUM	spect
PROBHD	5 mm 5mm 1H/2H
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	5640
DS	4
SWH	22058.824 Hz
FIDRES	0.336591 Hz
AQ	1.4855326 sec
RG	2050
DW	22.667 usec
DE	12.00 usec
TE	303.2 K
D1	10.0000000 sec
D11	0.0300000 sec
TD0	1

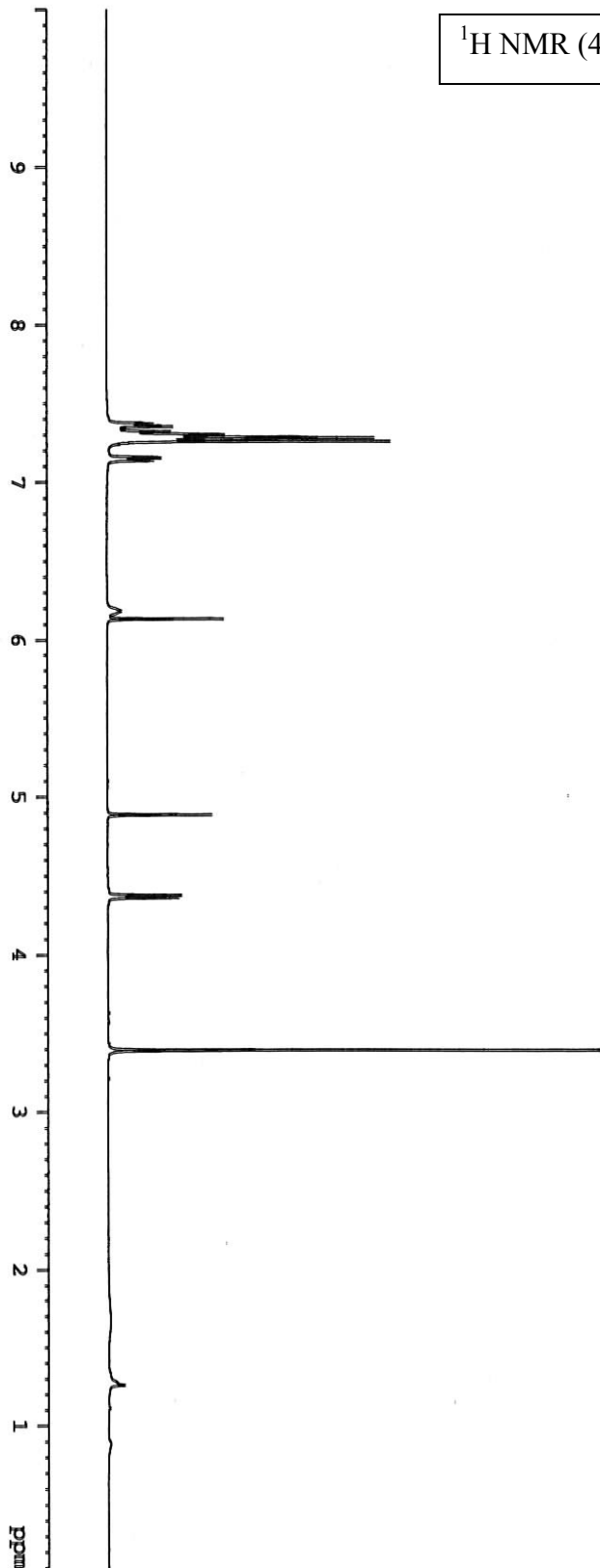
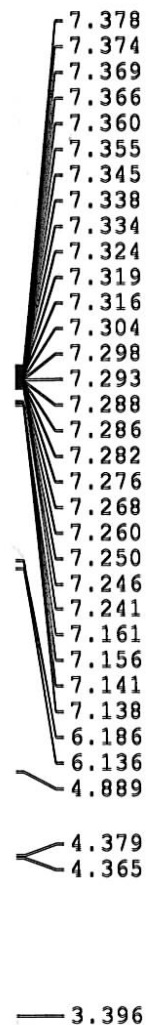
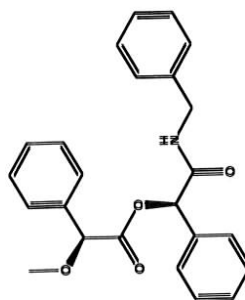
===== CHANNEL f1 =====

NUC1	13C
P1	14.00 usec
PL1	0.00 dB
PL1W	95.45168304 W
SFO1	100.6223263 MHz

===== CHANNEL f2 =====

CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL2	1.95 dB
PL12	22.20 dB
PL13	28.00 dB
PL2W	9.58740711 W
PL12W	0.09051095 W
PL13W	0.02380681 W
SFO2	400.1316005 MHz
SI	32768
SF	100.6127690 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

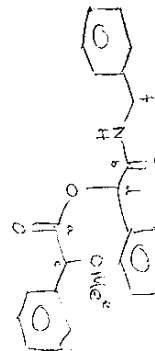
¹H NMR (400 MHz, CDCl₃) **9**



```

NAME          hr1-3-114-3c
EXPNO         1
PROCNO        1
Date_         20090825
Time_         12.42
INSTRUM       spect
PROBHD        5 mm 5mm 1H/2H
PULPROG       zgpg
TD            48076
SOLVENT       CDCl3
NS            32
DS            2
SWH           4807.692 Hz
FIDRES        0.100002 Hz
AQ            4.999542 sec
RG            161
IDW           104.000 usec
DE            14.56 usec
TE            303.2 K
D1            5.0000000 sec
TD0           1

===== CHANNEL f1 =====
NUC1          1H
P1            8.00 usec
PL1           1.95 dB
PL1W          9.58740711 W
SFO1          400.1322007 MHz
SI            32768
SF            400.1300098 MHz
WDW           EM
SSB           0
LB            0.30 Hz
GB            0
PC            1.00
  
```



Avance 300 Monash University
EC3-125B in D2O

ppm

169.007
167.964

137.705
135.735
135.075
129.115
129.089
128.926
128.894
128.805
127.783
127.182
127.039

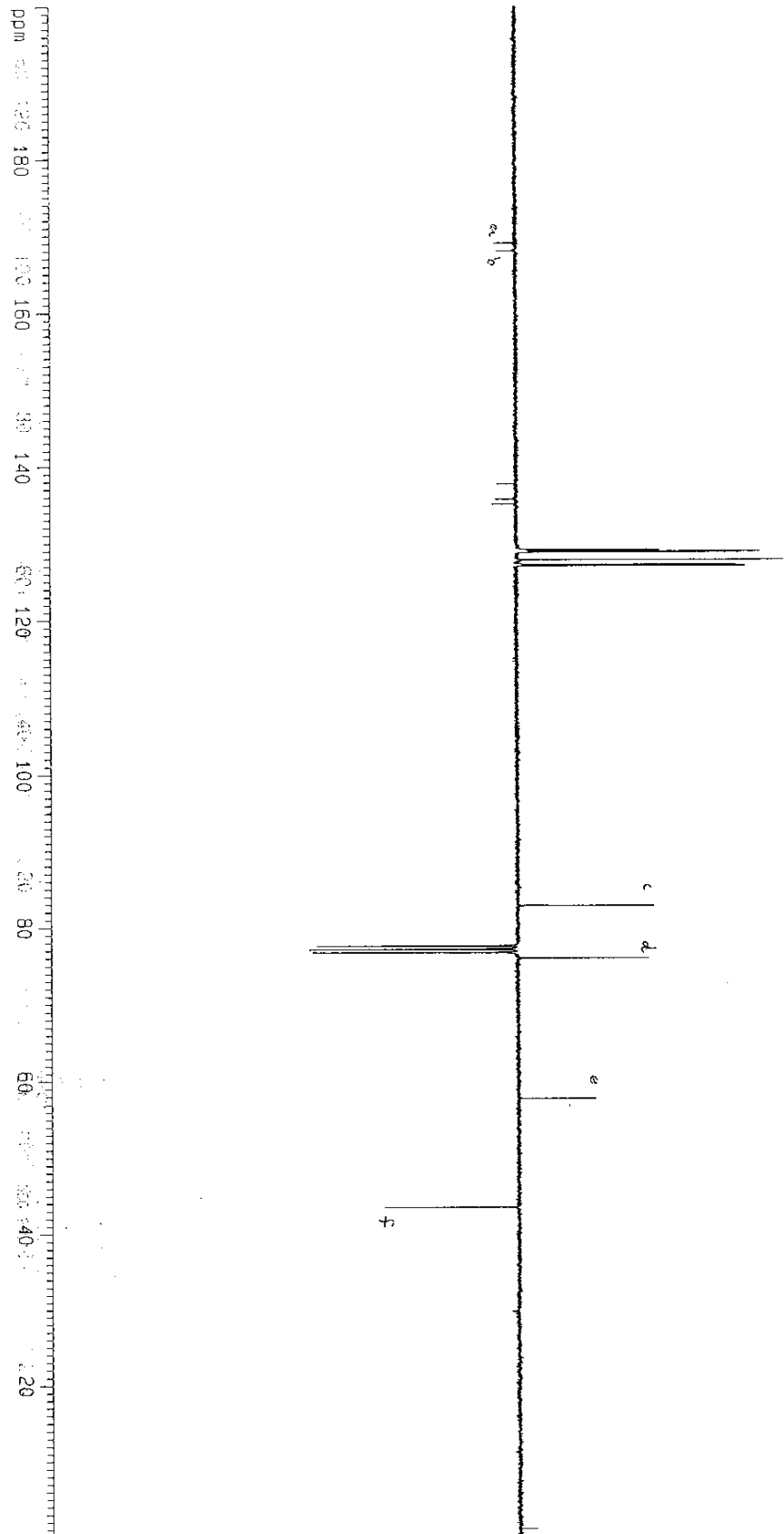
82.832
77.584
77.161
76.738
75.989

57.772

43.516

1.161

^{13}C NMR (100 MHz, CDCl_3) **9**



Current Data Parameters
NAME hr1-3-114-3
EXPNO 3
PROCNO 1

F2 - Acquisition Parameters
Date_ 20080618
Time 23.16

INSTRUM spect
PROBHD 5 mm GNP 1H/1
PULPROG jmod
TD 32768
SOLVENT DMSO
NS 7339
DS 2

SMH 18382.354 Hz
FIDRES 0.560985 Hz
AQ 0.8913396 s
RG 13004

DM 27.200 us
DE 20.00 us
TE 303.2 K

CNST2 145.000000
CNST11 1.000000
D1 3.00000000 s
d20 0.00689655 s

DELTA 0.00901082 s
MCREST 0.00900000 s
MCMBK 0.01500000 s

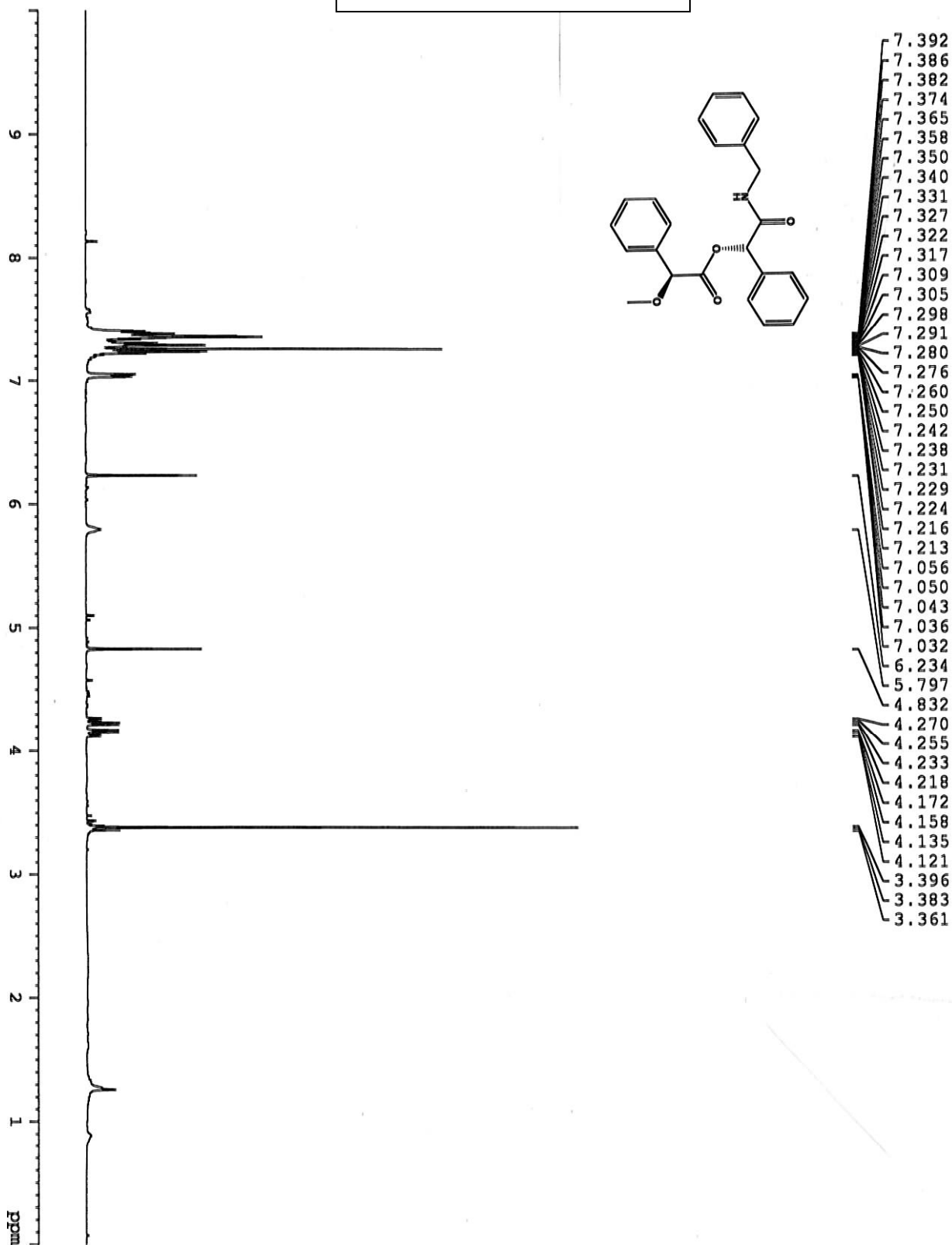
===== CHANNEL f1 =====
NUC1 ^{13}C
P1 8.50 us
P2 17.00 us
PL1 0.00 dB
SF01 75.4760145 MHz

===== CHANNEL f2 =====
CPDPRG2 mslr216
NUC2 ^1H
PCPD2 100.00 us
PL2 -2.00 dB
PL12 15.00 dB
SF02 300.1314256 MHz

F2 - Processing parameters
SI 32768
SF 75.4677366 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

1D NMR plot parameters
CX 23.00 cm
CY 4.10 cm
F1P 200.000 MHz
F1 15093.55 MHz
F2P 0.000 MHz
F2 0.00 MHz
PPMCM 8.66565 MHz
HZCM 556.24115 MHz

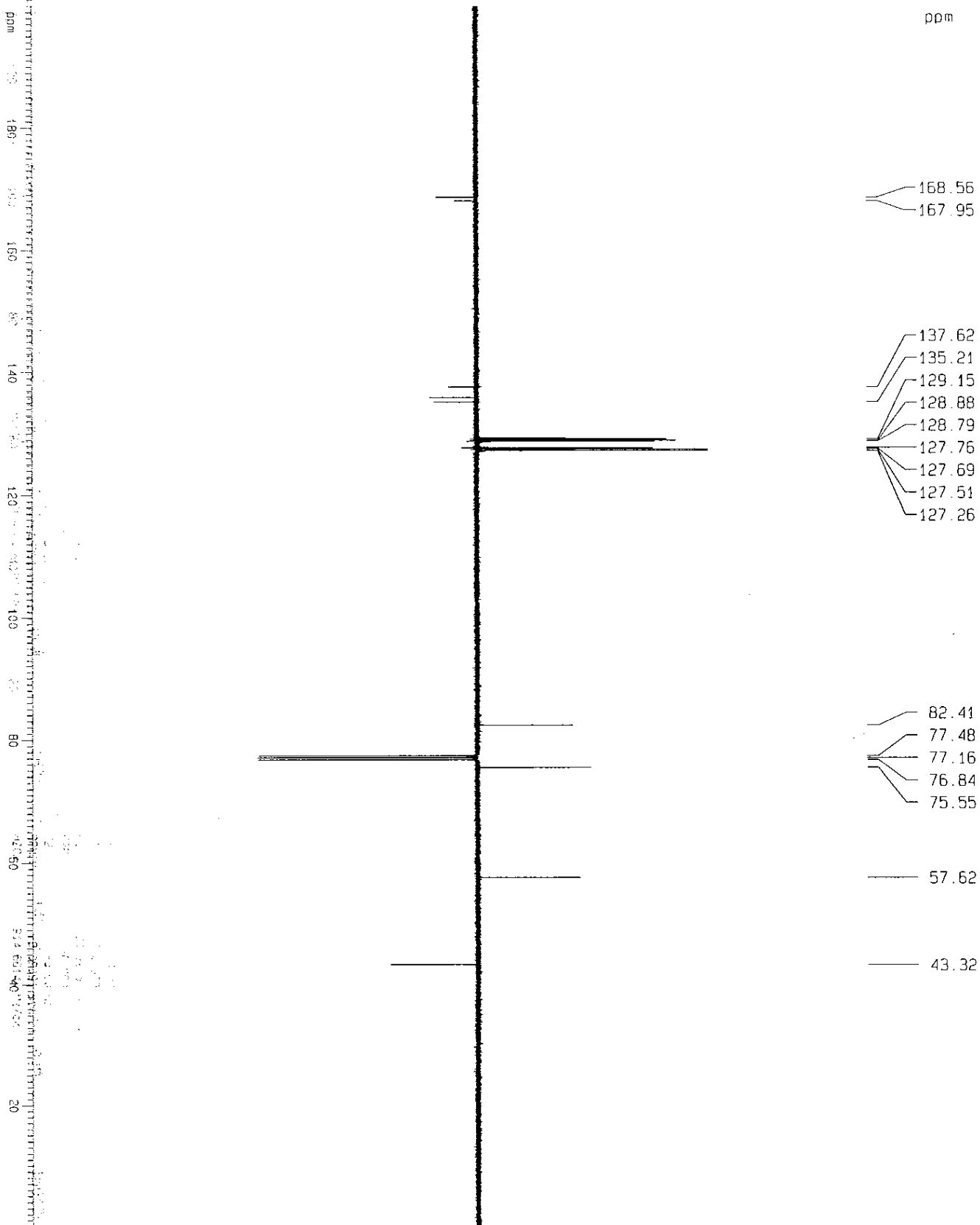
¹H NMR (400 MHz, CDCl₃) **10**



NAME hr1-3-114-2c
EXPNO 1
PROCNO 1
Date_ 20090825
Time_ 12.55
INSTRUM spect
PROBHD 5 mm 5mm 1H/2H
PULPROG zg
TD 48076
SOLVENT CDCl3
NS 32
DS 2
SWH 4807.692 Hz
FIDRES 0.100002 Hz
AQ 4.999542 sec
RG 161
DM 104.000 usec
DE 14.56 usec
TE 303.2 K
D1 5.0000000 sec
TD0 1

===== CHANNEL f1 =====
NUC1 1H
P1 8.00 usec
PL1 1.95 dB
PL1W 9.58740711 W
SFO1 400.1322007 MHz
SI 32768
SF 400.1300098 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

¹³C NMR (100 MHz, CDCl₃) **10**



Current Data Parameters
NAME hr-1-3-114-2
EXPNO 3
PROCNO 1

F2 - Acquisition Parameters
Date_ 20080620
Time 19.15

INSTRUM spect
PROBHD 5 mm Multinucl
PULPROG jmod
TD 65536
SOLVENT
NS 9027

DS 4
SWH 25125.629 Hz
FIDRES 0.383387 Hz
AQ 1.3042164 sec
RG 9195.2
DM 19.900 usec
DE 15.00 usec
TE 303.2 K

CNST2 145.000000
CNST11 1.000000
D1 6.0000000 sec
d20 0.00689655 sec
DELTA 0.0001477 sec
MCHES1 0.0000000 sec
MCHRS 0.0150000 sec

===== CHANNEL f1 =====
NUC1 ¹³C
P1 11.60 usec
PL2 23.20 usec
PL1 0.00 dB
SFO1 100.6229643 MHz

===== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 ¹H
PCPD2 100.00 usec
PL2 4.00 dB
PL12 28.00 dB
SFO2 400.1320000 MHz

F2 - Processing parameters
SI 65536
SF 100.6127531 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 22.00 cm
CY 4.22 cm
FIP 200.000 ppm
F1 20122.55 Hz
F2P -0.000 ppm
F2 -0.00 Hz
PPMCM 9.09091 ppm/c
HZCM 914.66144 Hz/cm