$POCl_3$-Mediated Reaction of 1-Acyl-1-Carbamoyl Oximes: A New Entry to Cyanoformamides

Jiming Yang,[a] *Dexuan Xiang,*[a] *Rui Zhang,*[a,b] *Ning Zhang,**[a] *Yongjiu Liang,*[a] *and Dewen Dong**[a,b]

[a] Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun,130022, P.R. China.

[b] Changzhou Institute of Energy Storage Materials & Devices, Changzhou, 213000, P. R. China

E-mail: *ning.zhang@ciac.ac.cn; dwdong@ciac.ac.cn*

Supporting Information

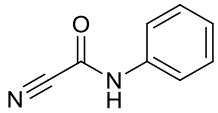
I. General

All reagents were purchased from commercial sources and used without treatment, unless otherwise indicated. ^{1}H NMR and ^{13}C NMR spectra were recorded at 25 ºC at 400 MHz (or 300 MHz) and 100 MHz, respectively. IR spectra (KBr) were recorded on FTIR spectrophotometer in the range of 400~4000 cm^{-1}.

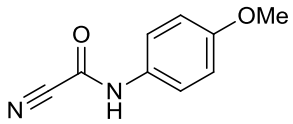
II. Synthesis and analytical data of cyanoformamides

General procedure for the preparation of cyanoformamides (Scheme 1): To a well-stirred solution of 1-acyl-1-carbamoyl oximes **1** (1.0 mmol) in 1,2-dichloroethane (DCE) 5.0 ml was added $POCl_3$ (0.14 mL, 1.5 mmol) dropwise at room temperature within 5 min. The reaction mixture was heated to 80 ºC and stirred for 2.0 h, then cooled to room temperature. The resulting mixture was slowly poured into saturated aqueous NaCl (50 mL), neutralized with saturated aqueous $NaHCO_3$ and extracted with CH_2Cl_2 (3×20 mL). The combined organic phase was washed with water (3×20 mL), dried over $MgSO_4$, filtered and concentrated *in vacuo*. The crude product was purified by silica gel chromatography with ethyl acetate (EtOAc)/petroleum ether (PE) to afford the corresponding cyanoformamides **2.**

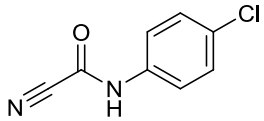
2k and **2n** are known compounds, for their analytical data, see: (1) Katagiri N., Ishikura M.; Morishita Y., Yamaguchi M., *Heterocycles*, **2000**, *52*, 283-289. (2) García-Egido E., Paz J., Iglesias B., Muñoz L., *Org. Biomol. Chem.*, **2009**, *7*, 3991-3999.



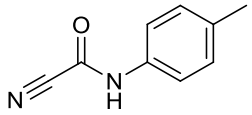
Phenylcarbamoyl cyanide (2a): Prepared according to the general procedure using 2-(hydroxyimino)-3-oxo-*N*-phenylbutanamide **1a** (206 mg, 1.0 mmol). The product was purified by silica gel column chromatography using 20% EtOAc/PE to afford phenylcarbamoyl cyanide **2a** as a colorless solid (121 mg, 83%); mp 104-106 °C ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.27 (m, 1H), 7.40 (t, *J* = 7.2 Hz, 2H), 7.51 (d, *J* = 7.2 Hz, 2H), 8.10 (bs, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ = 112.5, 121.8, 125.7, 129.1, 136.7, 140.7. IR (KBr) 3233, 2234, 1671, 1528, 1442, 1273, 1004, 816 cm^{-1}. Anal. Calcd for $C_8H_6N_2O$: C, 65.75; H, 4.14; N, 19.17. Found: C, 65.47; H, 4.12; N, 19.43.



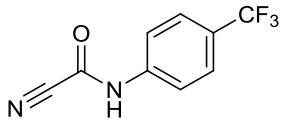
(4-Methoxyphenyl)carbamoyl cyanide (2b): Prepared according to the general procedure using 2-(hydroxyimino)-*N*-(4-methoxyphenyl)-3-oxobutanamide **1b** (236 mg, 1.0 mmol). The product was purified by silica gel column chromatography using 20% EtOAc/PE to afford (4-Methoxyphenyl)carbamoyl cyanide **2b** as a colorless solid (160 mg, 91%); mp 117-119 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 3.81 (s, 3H), 6.90 (d, *J* = 9.0 Hz, 2H), 7.42 (d, *J* = 9.0 Hz, 2H), 7.85 (bs, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ = 55.1, 112.6, 114.1, 121.7, 129.7, 140.1, 156.8. IR (KBr) 3263, 2231, 1668, 1508, 1242, 1173, 1034, 837 cm^{-1}. Anal. Calcd for $C_9H_8N_2O_2$: C, 61.36; H, 4.58; N, 15.90. Found: C, 61.64; H, 4.52; N, 15.73.



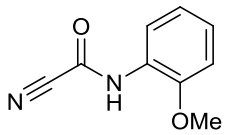
(4-Chlorophenyl)carbamoyl cyanide (2c): Prepared according to the general procedure using *N*-(4-chlorophenyl)-2-(hydroxyimino)-3-oxobutanamide **1c** (240 mg, 1.0 mmol). The product was purified by silica gel column chromatography using 20% EtOAc/PE to afford (4-chlorophenyl)carbamoyl cyanide **2c** as a colorless solid (169 mg, 94%); mp 148-150 °C. ^{1}H NMR (300 MHz, DMSO-d_6) δ = 7.42 (d, *J* = 8.7 Hz, 2H), 7.55 (d, *J* = 8.7 Hz, 2H), 11.92 (bs, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ = 112.3, 121.9, 129.1, 129.5, 135.6, 140.7. IR (KBr) 3259, 2231, 1668, 1555, 1491, 1404, 1256, 1095, 833 cm^{-1}. Anal. Calcd for $C_8H_5ClN_2O$: C, 53.21; H, 2.79; N, 15.51. Found: C, 53.02; H, 2.75; N, 15.59.



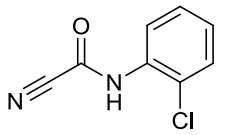
4-Tolylcarbamoyl cyanide (2d): Prepared according to the general procedure using 2-(hydroxyimino)-3-oxo-*N*-(*p*-tolyl)butanamide **1d** (220 mg, 1.0 mmol). The product was purified by silica gel column chromatography using 20% EtOAc/PE to afford p-tolylcarbamoyl cyanide **2d** as a colorless solid (141 mg, 88%); mp 146-148 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 2.35 (s, 3H), 7.19 (d, *J* = 8.1 Hz, 2H), 7.38 (d, *J* = 8.1 Hz, 2H), 7.73 (bs, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 20.8, 111.8, 120.4, 130.0, 132.9, 136.7, 140.3. IR (KBr) 3277, 2231, 1674, 1508, 1406, 1259, 941, 816, 708 cm^{-1}. Anal. Calcd for $C_9H_8N_2O$: C, 67.49; H, 5.03; N, 17.49. Found: C, 67.12; H, 5.06; N, 17.57.



(4-(Trifluoromethyl)phenyl)carbamoyl cyanide (2e): Prepared according to the general procedure using 2-(hydroxyimino)-3-oxo-*N*-(*p*-tolyl)butanamide **1e** (274 mg, 1.0 mmol). The product was purified by silica gel column chromatography using 25% EtOAc/PE to afford (4-(trifluoromethyl)phenyl)carbamoyl cyanide **2e** as a colorless solid (143 mg, 67%); mp 131-133 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.66 (m, 4H), 8.21 (bs, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 111.3, 120.3, 123.5 (q, $^{1}J_{CF}$ = 271), 126.8, 128.7 (q, $^{2}J_{CF}$ = 33), 138.2, 140.4. IR (KBr) 3279, 2237, 1682, 1558, 1329, 1068, 841, 716 cm^{-1}. Anal. Calcd for $C_9H_5F_3N_2O$: C, 50.48; H, 2.35; N, 13.08. Found: C, 50.14; H, 2.31; N, 13.12.

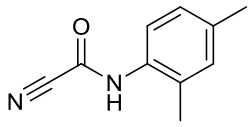


(2-Methoxyphenyl)carbamoyl cyanide (2f): Prepared according to the general procedure using 2-(hydroxyimino)-*N*-(2-methoxyphenyl)-3-oxobutanamide **1f** (236 mg, 1.0 mmol). The product was purified by silica gel column chromatography using 20% EtOAc/PE to afford (2-methoxyphenyl)carbamoyl cyanide **2f** as a colorless solid (167 mg, 95%); mp 113-115 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 3.94 (s, 3H), 6.93-7.02 (m, 2H), 7.17 (t, *J* = 8.1 Hz, 1H), 8.17 (d, *J* = 8.1 Hz, 1H), 8.36 (bs, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 55.9, 110.4, 111.7, 120.8, 121.1, 125.3, 126.5, 139.9, 148.0. IR (KBr) 3271, 2243, 1690, 1545, 1466, 1263, 1117, 932, 737 cm^{-1}. Anal. Calcd for $C_9H_8N_2O_2$: C, 61.36; H, 4.58; N, 15.90. Found: C, 61.18; H, 4.63; N, 15.85.

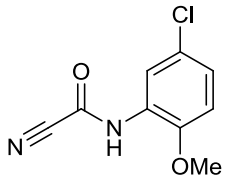


(2-Chlorophenyl)carbamoyl cyanide (2g): Prepared according to the general procedure using *N*-(2-chlorophenyl)-2-(hydroxyimino)-3-oxobutanamide **1g** (240 mg, 1.0 mmol). The product was purified by silica gel column chromatography using 20% EtOAc/PE to afford (2-Chlorophenyl)carbamoyl cyanide **2g** as a colorless solid (151 mg, 84%); mp 76-78 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.20 (t, *J* = 7.8 Hz, 1H), 7.33 (t, *J* = 7.8 Hz, 1H), 7.45 (d, *J* = 7.8 Hz, 1H), 8.18 (bs, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 111.3, 122.7, 123.8, 127.3,

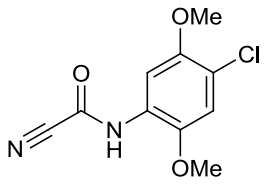
128.0, 129.5, 132.1, 140.3. IR (KBr) 3259, 2233, 1678, 1537, 1445, 1304, 1246, 923, 758 cm^{-1}. Anal. Calcd for $C_8H_5ClN_2O$: C, 53.21; H, 2.79; N, 15.51. Found: C, 53.57; H, 2.86; N, 15.42.



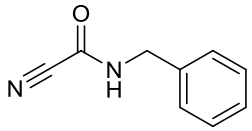
(2,4-Dimethylphenyl)carbamoyl cyanide (2h): Prepared according to the general procedure using *N*-(2,4-dimethylphenyl)-2-(hydroxyimino)-3-oxobutanamide **1h** (234 mg, 1.0 mmol). The product was purified by silica gel column chromatography using 20% EtOAc/PE to afford (2,4-dimethylphenyl)carbamoyl cyanide **2h** as a colorless solid (155 mg, 89%); mp 86-88 °C. ^{1}H NMR (400 MHz, DMSO-d6) δ = 2.16 (s, 3H), 2.24 (s, 3H), 7.00 (d, *J* = 6.0 Hz, 1H), 7.06 (s, 1H), 7.21 (d, *J* = 6.0 Hz, 1H), 11.19 (bs, 1H). ^{13}C NMR (100 MHz, DMSO-d6) δ = 18.0, 20.8, 113.0, 125.6, 127.1, 131.0, 131.5, 132.6, 137.0, 141.9. IR (KBr) 3211, 2237, 1690, 1543, 1234, 816, 698 cm^{-1}. Anal. Calcd for $C_{10}H_{10}N_2O$: C, 68.95; H, 5.79; N, 16.08. Found: C, 68.64; H, 5.75; N, 16.11.



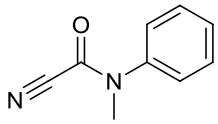
(5-Chloro-2-methoxyphenyl)carbamoyl cyanide (2i): Prepared according to the general procedure using *N*-(5-chloro-2-methoxyphenyl)-2-(hydroxyimino)-3-oxobutanamide **1i** (270 mg, 1.0 mmol). The product was purified by silica gel column chromatography using 20% EtOAc/PE to afford (5-chloro-2-methoxyphenyl)carbamoyl cyanide **2i** as a colorless solid (181 mg, 86%); mp 143-145 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 3.93 (s, 3H), 6.85 (d, *J* = 9.0 Hz, 1H), 7.16 (dd, J_1 = 9.0 Hz, J_2 = 2.7 Hz, 1H), 8.21 (d, *J* = 2.7 Hz, 1H), 8.37 (bs, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 56.2, 112.2, 113.4, 123.4, 123.7, 125.3, 126.9, 141.6, 149.8. IR (KBr) 3281, 2239, 1697, 1535, 1259, 1128, 1028, 814, 685, 646 cm^{-1}. Anal. Calcd for $C_9H_7ClN_2O_2$: C, 51.32; H, 3.35; N, 13.30. Found: C, 51.59; H, 3.37; N, 13.26.



(4-Chloro-2,5-dimethoxyphenyl)carbamoyl cyanide (2j): Prepared according to the general procedure using *N*-(4-chloro-2,5-dimethoxyphenyl)-2-(hydroxyimino)-3-oxobutan amide **1j** (300 mg, 1.0 mmol). The product was purified by silica gel column chromatography using 20% EtOAc/PE to afford (4-chloro-2,5-dimethoxyphenyl)carbamoyl cyanide **2j** as a colorless solid (221 mg, 92%); mp 144-145 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 3.86 (s, 3H), 3.89 (s, 3H), 6.96 (s, 1H), 7.94 (s, 1H), 8.34 (bs, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 56.6, 56.8, 105.7, 111.5, 112.8, 119.2, 124.4, 139.8, 142.0, 149.2. IR (KBr) 3202, 2236, 1686, 1531, 1400, 1215, 1036, 733 cm^{-1}. Anal. Calcd for $C_{10}H_9ClN_2O_3$: C, 49.91; H, 3.77; N, 11.64. Found: C, 50.14; H, 3.62; N, 11.57.

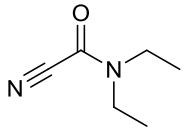


Benzylcarbamoyl cyanide (2k): Prepared according to the general procedure using *N*-benzyl-2-(hydroxyimino)-3-oxobutanamide **1k** (220 mg, 1.0 mmol). The product was purified by silica gel column chromatography using 10% EtOAc/PE to afford benzylcarbamoyl cyanide **2k** as a colorless solid (142 mg, 89%); mp 68-69 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 4.46 (d, *J* = 6.0, 2H), 7.18 (bs, 1H), 7.28-7.38 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 44.4, 111.4, 128.0, 128.4, 129.0, 135.1, 143.2. IR (KBr) 3269, 2237, 1626, 1541, 1460, 1225, 693 cm^{-1}. Anal. Calcd for $C_9H_8N_2O$: C, 67.49; H, 5.03; N, 17.49. Found: C, 67.23; H, 5.09; N, 17.57.

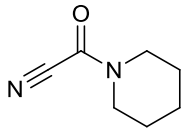


Methyl(phenyl)carbamoyl cyanide (2l): Prepared according to the general procedure using 2-(hydroxyimino)-*N*-methyl-3-oxo-*N*-phenylbutanamide **1l** (220 mg, 1.0 mmol). The product was purified by silica gel column chromatography using 30% EtOAc/PE to afford methyl(phenyl)carbamoyl cyanide **2l** as a colorless solid (133 mg, 83%); mp 57-59 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 3.37 (s, 3H), 7.31 (t, *J* = 8.1 Hz, 2H), 7.48-7.53 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 36.7, 110.6, 126.9, 129.7, 130.1, 139.7, 144.5. IR (KBr) 2229,

1699, 1593, 1495, 1389, 1294, 1136, 908, 775, 694 cm^{-1}. Anal. Calcd for $C_9H_8N_2O$: C, 67.49; H, 5.03; N, 17.49. Found: C, 67.34; H, 5.05; N, 17.58.

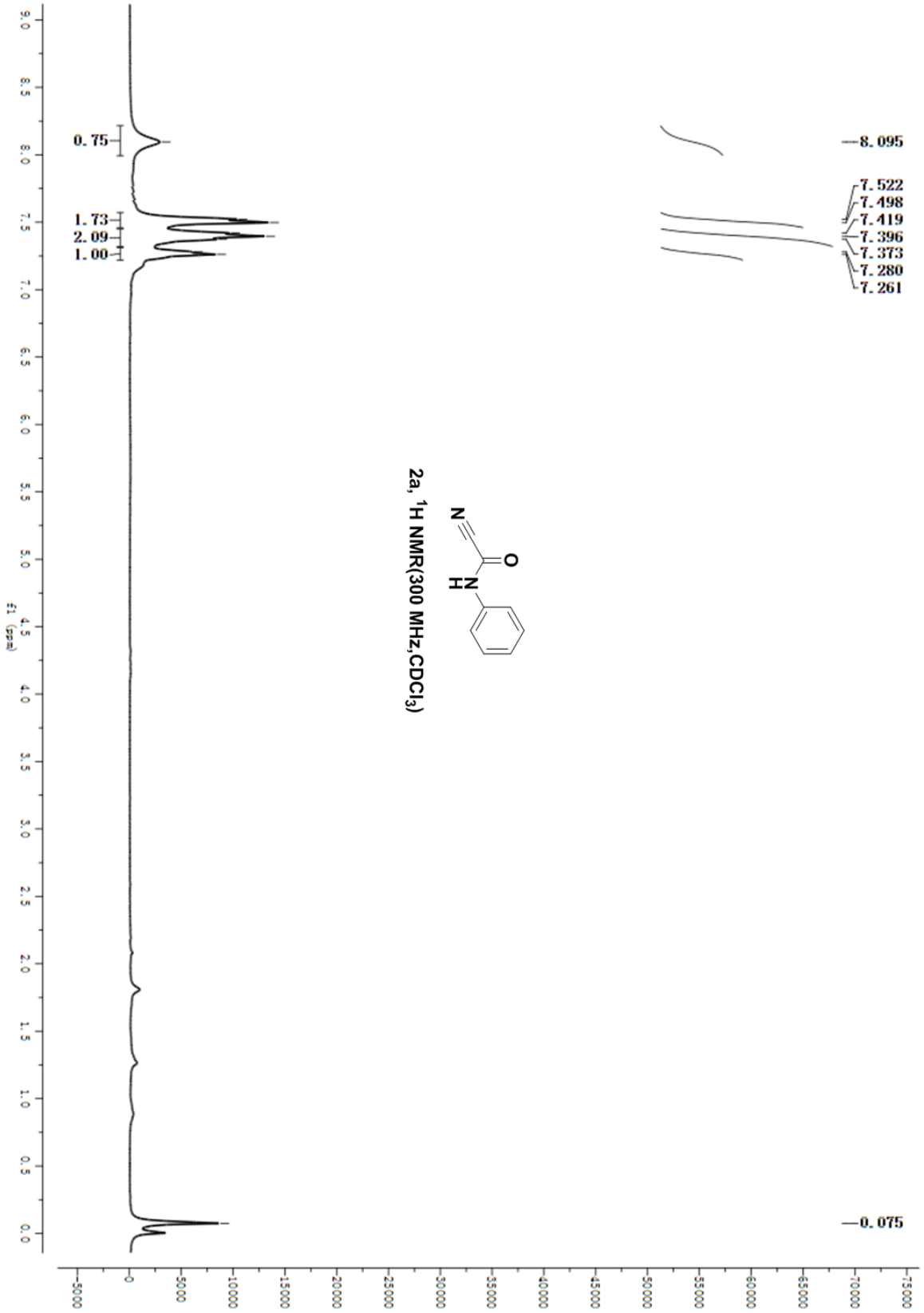


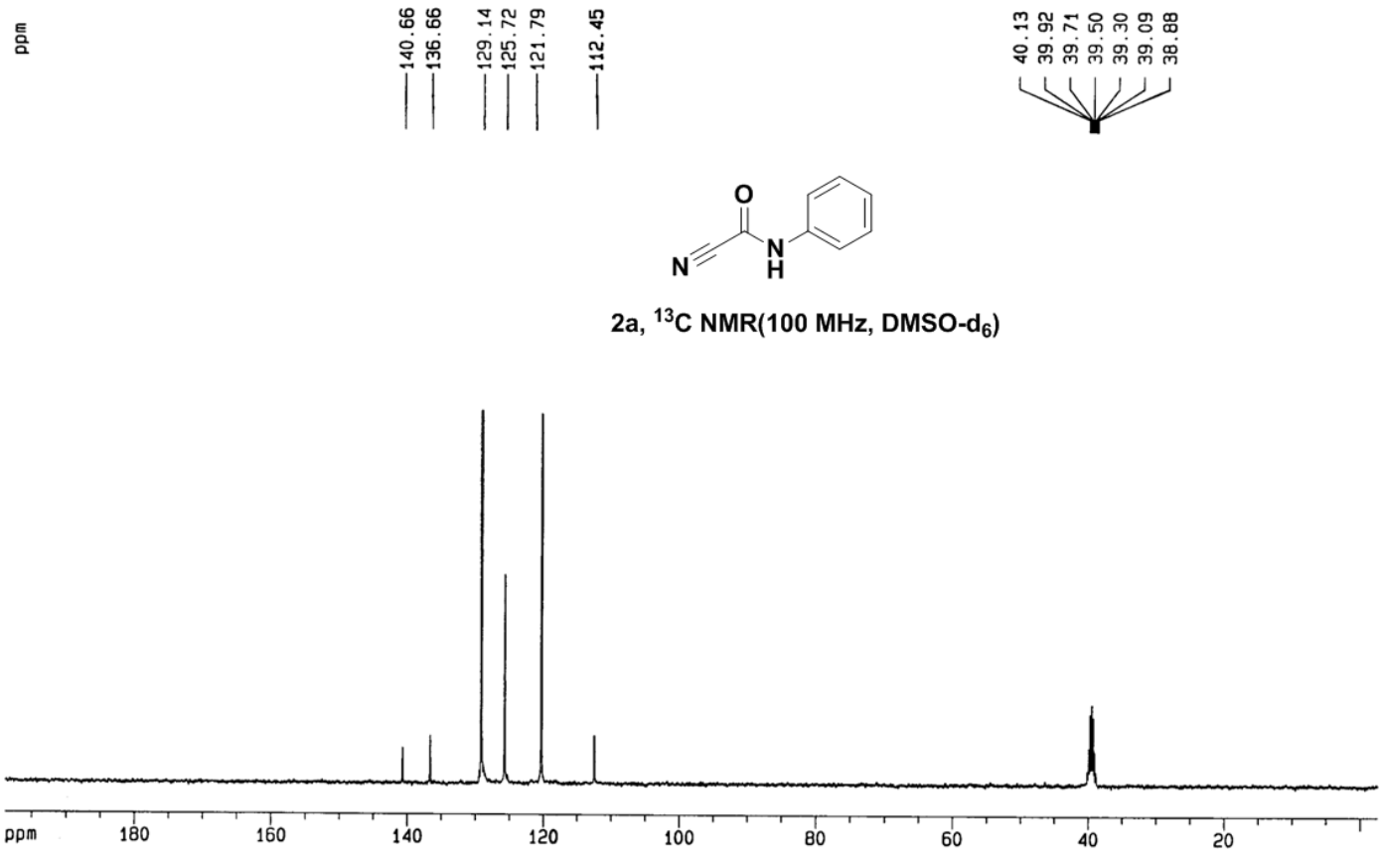
Diethylcarbamoyl cyanide (2m): Prepared according to the general procedure using *N*,*N*-diethyl-2-(hydroxyimino)-3-oxobutanamide **1m** (186 mg, 1.0 mmol). The product was purified by silica gel column chromatography using 10% EtOAc/PE to afford diethylcarbamoyl cyanide **2m** as a colorless oil (107 mg, 85%); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.17 (m, *J* = 7.2 Hz, 3H), δ = 1.30 (m, *J* = 7.2 Hz, 3H), 3.44 (m, *J* = 7.2 Hz, 2H), 3.61 (m, *J* = 7.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 12.3, 14.4, 40.0, 43.6, 110.7, 144.3. IR 2899, 2229, 1631, 1389, 1414, 1136, 919, 763, 698 cm^{-1}. Anal. Calcd for $C_6H_{10}N_2O$: C, 57.12; H, 7.99; N, 22.21. Found: C, 57.34; H, 8.07; N, 22.18.



Piperidine-1-carbonyl cyanide (2n): Prepared according to the general procedure using 2-(hydroxyimino)-1-(piperidin-1-yl)butane-1,3-dione **1n** (198 mg, 1.0 mmol). The product was purified by silica gel column chromatography using 10% EtOAc/PE to afford piperidine-1-carbonyl cyanide **2n** as a colorless oil (99 mg, 72%); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.59 (m, 2H), 1.69 (m, 4H), 3.56 (t, *J* = 6.0 Hz, 2H), 3.68 (m, 2H) ^{13}C NMR (100 MHz, $CDCl_3$) δ = 24.0, 24.9, 26.2, 43.0, 48.1, 110.4, 143.1. IR 2947, 2225,1670, 1448, 1262, 1143, 1011, 900, 838, 721 cm^{-1}. Anal. Calcd for $C_7H_{10}N_2O$: C, 60.85; H, 7.30; N, 20.28. Found: C, 60.69; H, 7.36; N, 20.40.

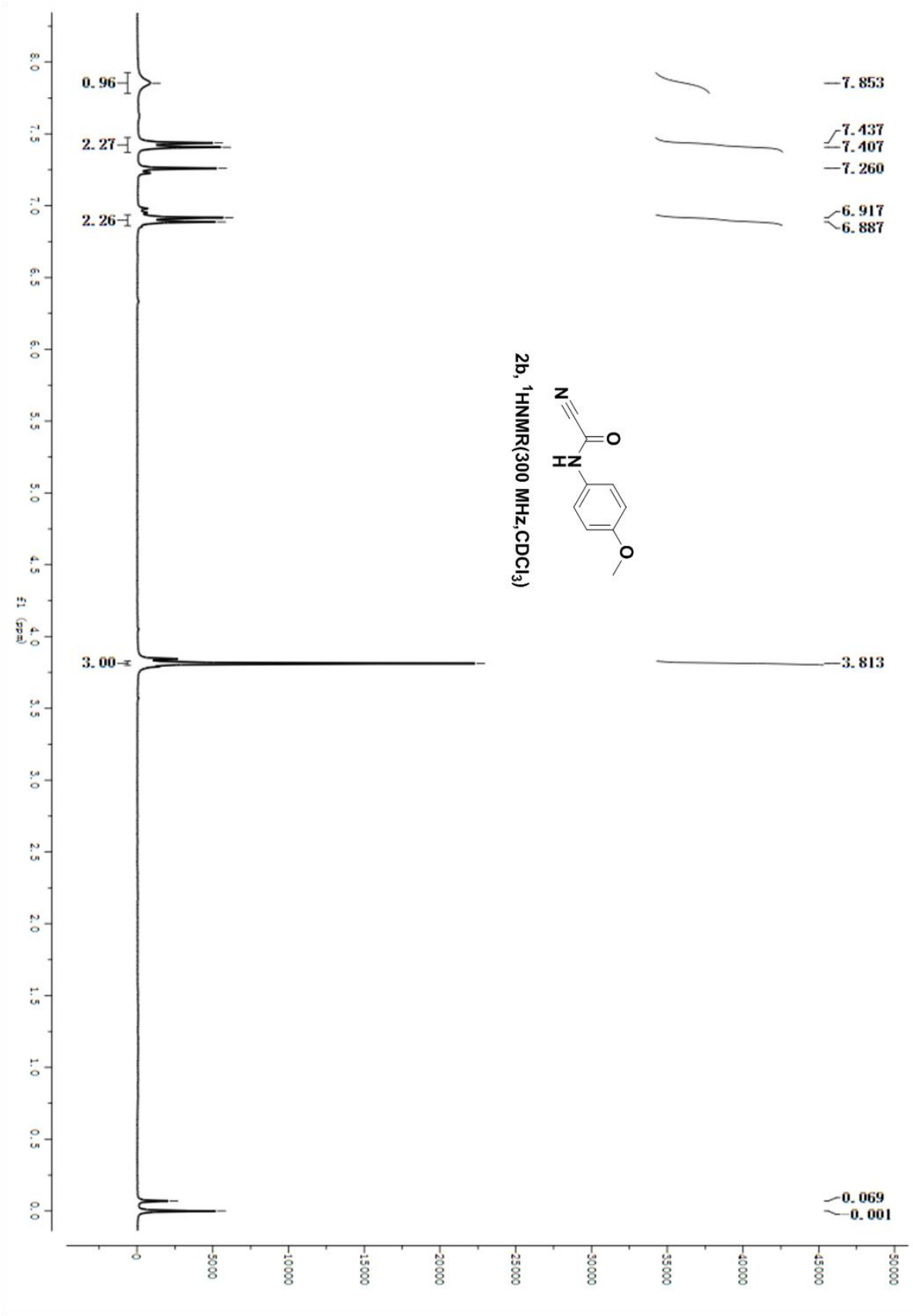
III. Copies of NMR spectra for substrates 2a-n

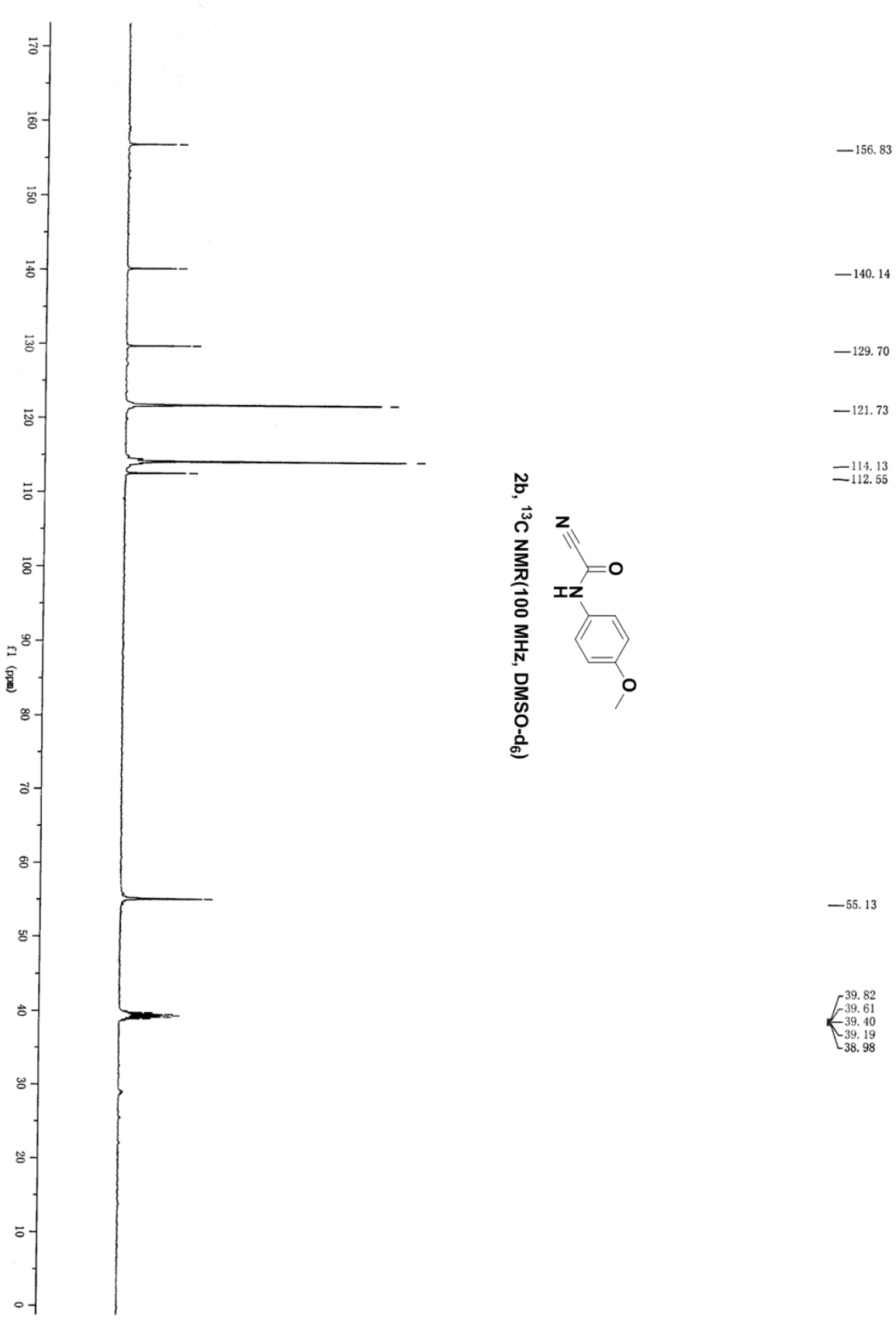


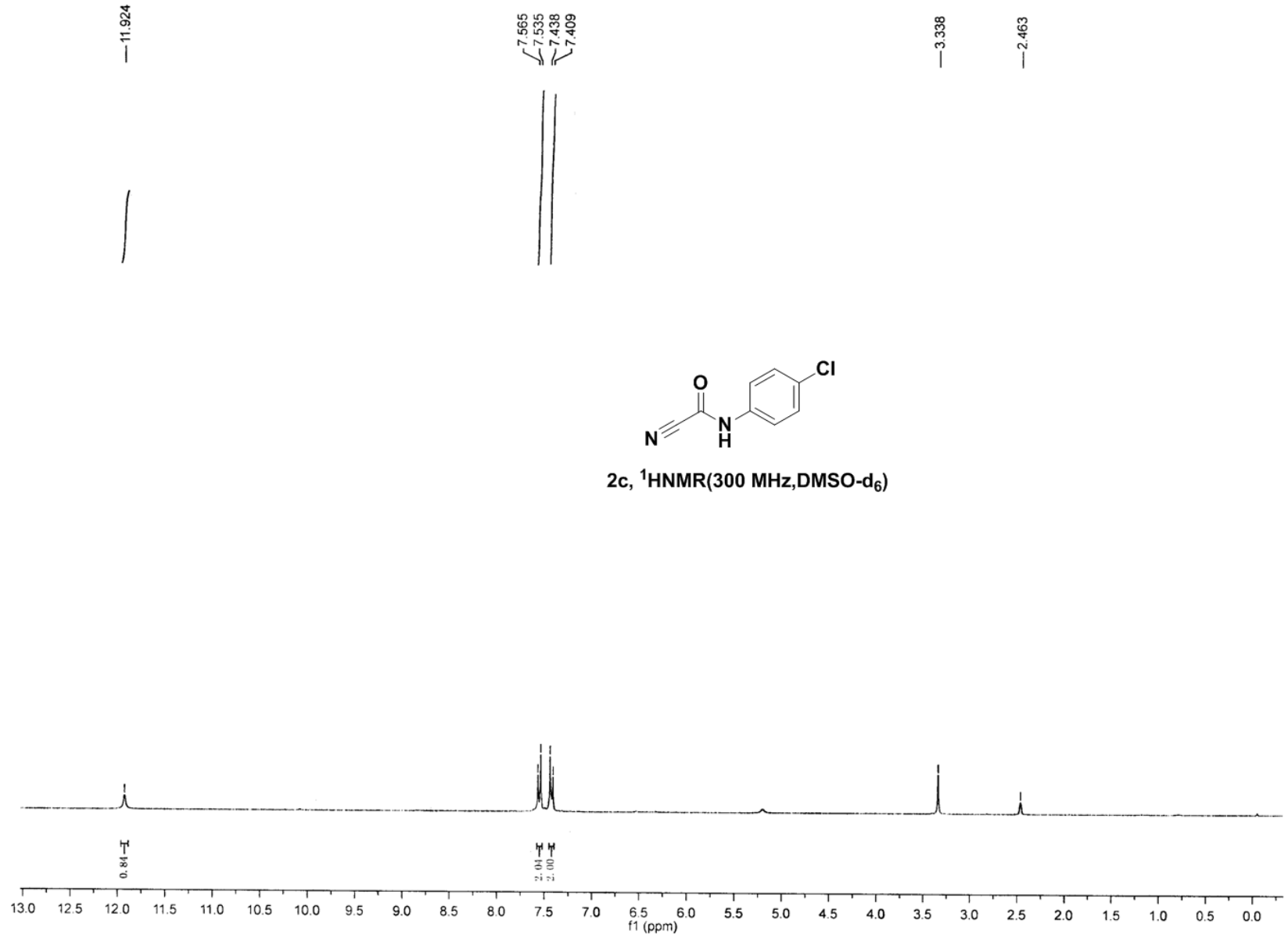


2a, ^{13}C NMR(100 MHz, DMSO-d_6)

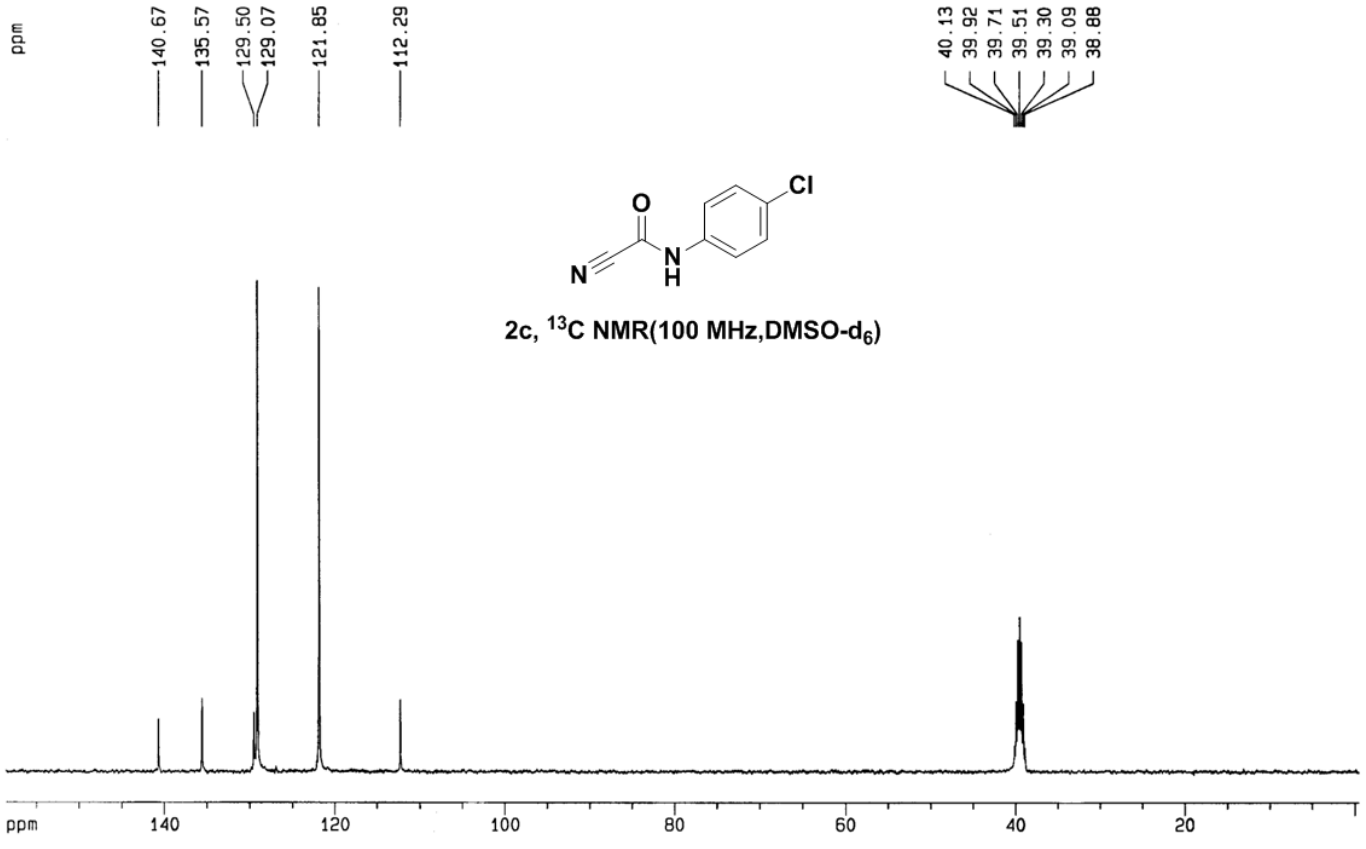
```
Current Data Parameters
NAME                  XDX
EXPNO                   4
PROCNO                  1

F2 - Acquisition Parameters
Date_            20110418
Time                20.56
INSTRUM             av400
PROBHD   5 mm QNP 1H/13
PULPROG              zgdc
TD                  16384
SOLVENT              DMSO
NS                    626
DS                      0
SWH             25062.656 Hz
FIDRES          1.529703 Hz
AQ              0.3269108 sec
RG                   8192
DW                19.950 usec
DE                 6.00 usec
TE                300.0 K
D1           0.69999999 sec
d11          0.03000000 sec

======== CHANNEL f1 ========
NUC1                 13C
P1                2.70 usec
PL1               -3.00 dB
SFO1         100.5785294 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2             80.00 usec
PL2               -2.00 dB
PL12              17.37 dB
SFO2         399.9515998 MHz

F2 - Processing parameters
SI                   65536
SF          100.5675536 MHz
WDW                  EM
SSB                   0
LB                 4.00 Hz
GB                    0
PC                 2.00

1D NMR plot parameters
CX                22.00 cm
CY                 6.00 cm
F1P              198.881 ppm
F1             20000.94 Hz
F2P              -2.555 ppm
F2              -256.96 Hz
PPMCM          9.15617 ppm/cm
HZCM          920.81360 Hz/cm
```


2b, ^{1}HNMR(300 MHz,CDCl$_3$)
0.96
2.27
2.26
3.00
7.853
7.437
7.407
7.260
6.917
6.887
3.813
0.069
0.001
f1 (ppm)


156.83
140.14
129.70
121.73
114.13
112.55
55.13
39.82
39.61
39.40
39.19
38.98
f1 (ppm)
2b, ^{13}C NMR(100 MHz, DMSO-d_6)



2c, ^{1}HNMR(300 MHz,DMSO-d_6)



2c, ^{13}C NMR(100 MHz,DMSO-d_6)

xdx12.9 (4)

Current Data Parameters

NAME	XDX
EXPNO	11
PROCNO	1

F2 - Acquisition Parameters

Date_	20111209
Time	21.03
INSTRUM	av400
PROBHD	5 mm QNP 1H/13
PULPROG	zgdc
TD	16384
SOLVENT	DMSO
NS	332
DS	0
SWH	25062.656 Hz
FIDRES	1.529703 Hz
AQ	0.3269108 sec
RG	8192
DW	19.950 usec
DE	6.00 usec
TE	300.0 K
D1	0.69999999 sec
d11	0.03000000 sec

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

NUC1	13C
P1	2.90 usec
PL1	-3.00 dB
SFO1	100.5785294 MHz

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

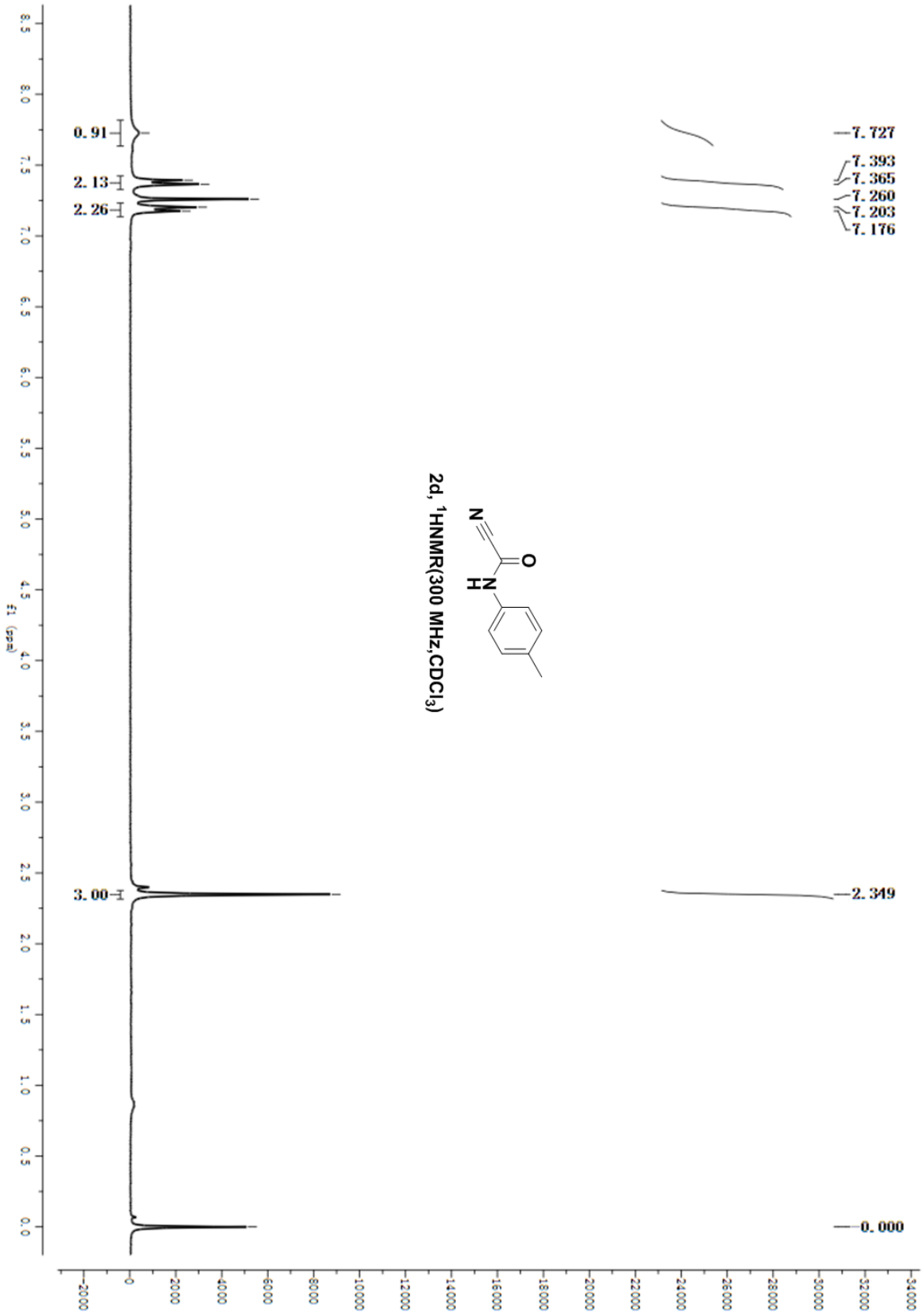
CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL2	-3.00 dB
PL12	18.20 dB
SFO2	399.9515998 MHz

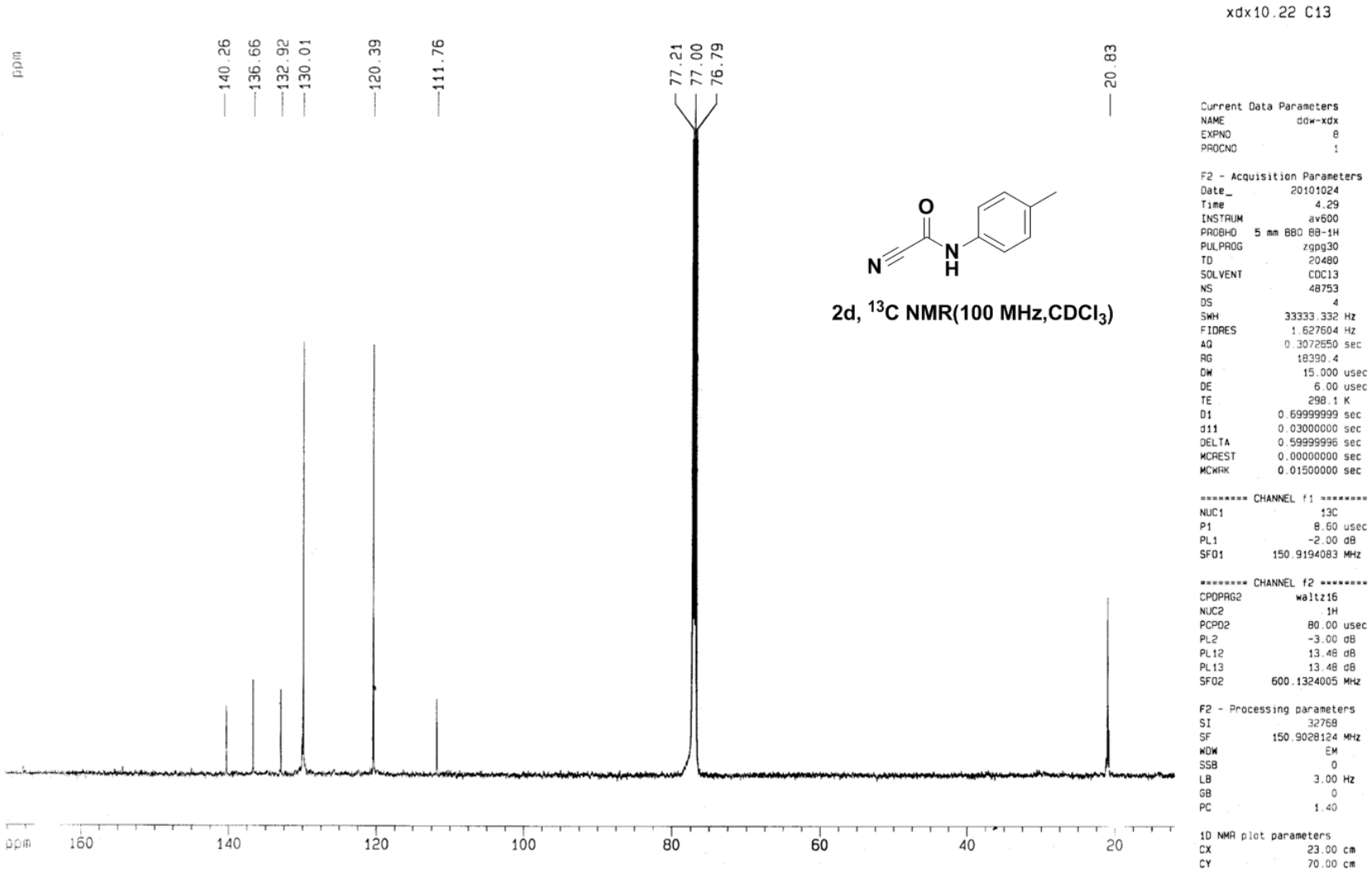
F2 - Processing parameters

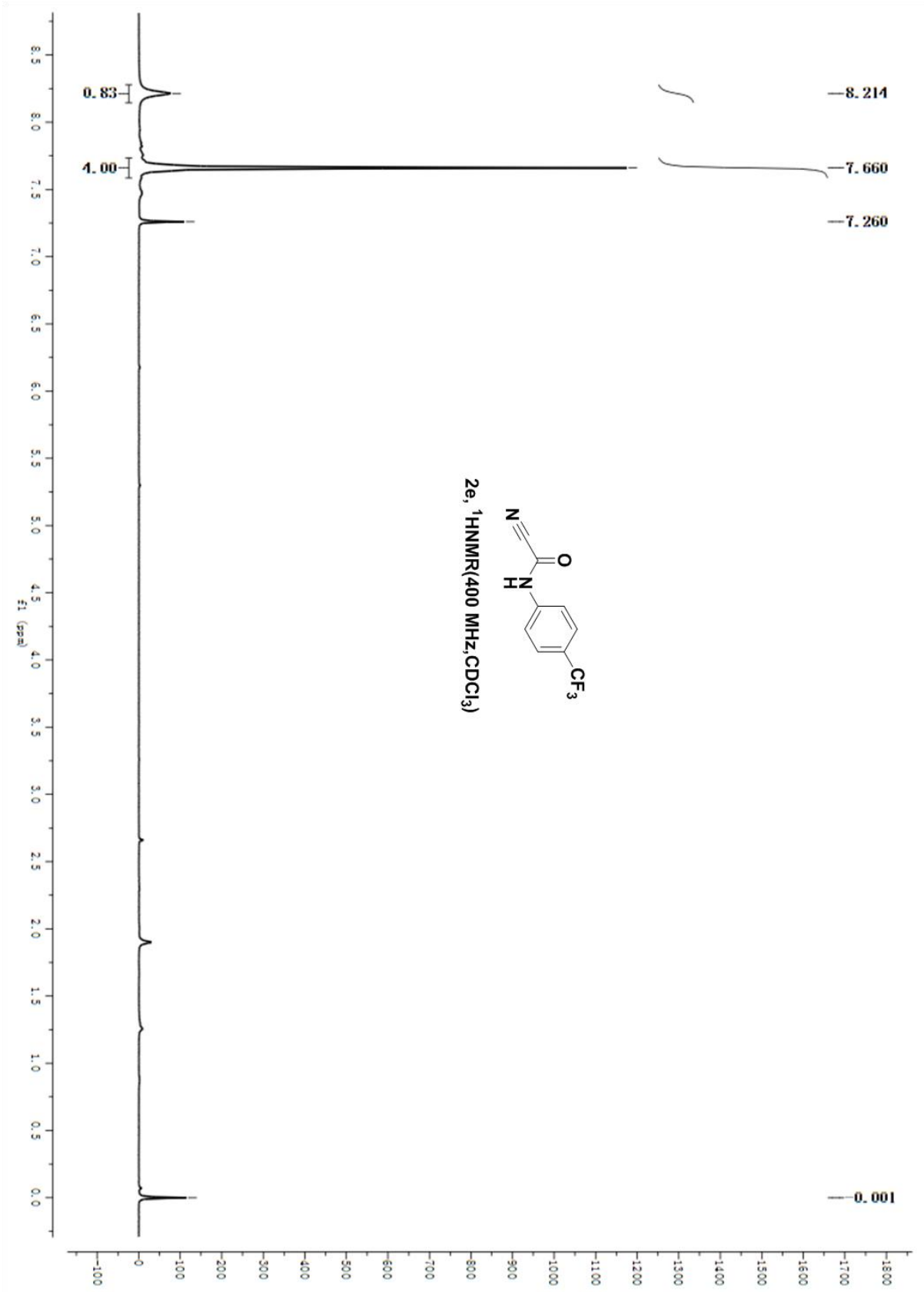
SI	65536
SF	100.5675556 MHz
WDW	EM
SSB	0
LB	4.00 Hz
GB	0
PC	1.00

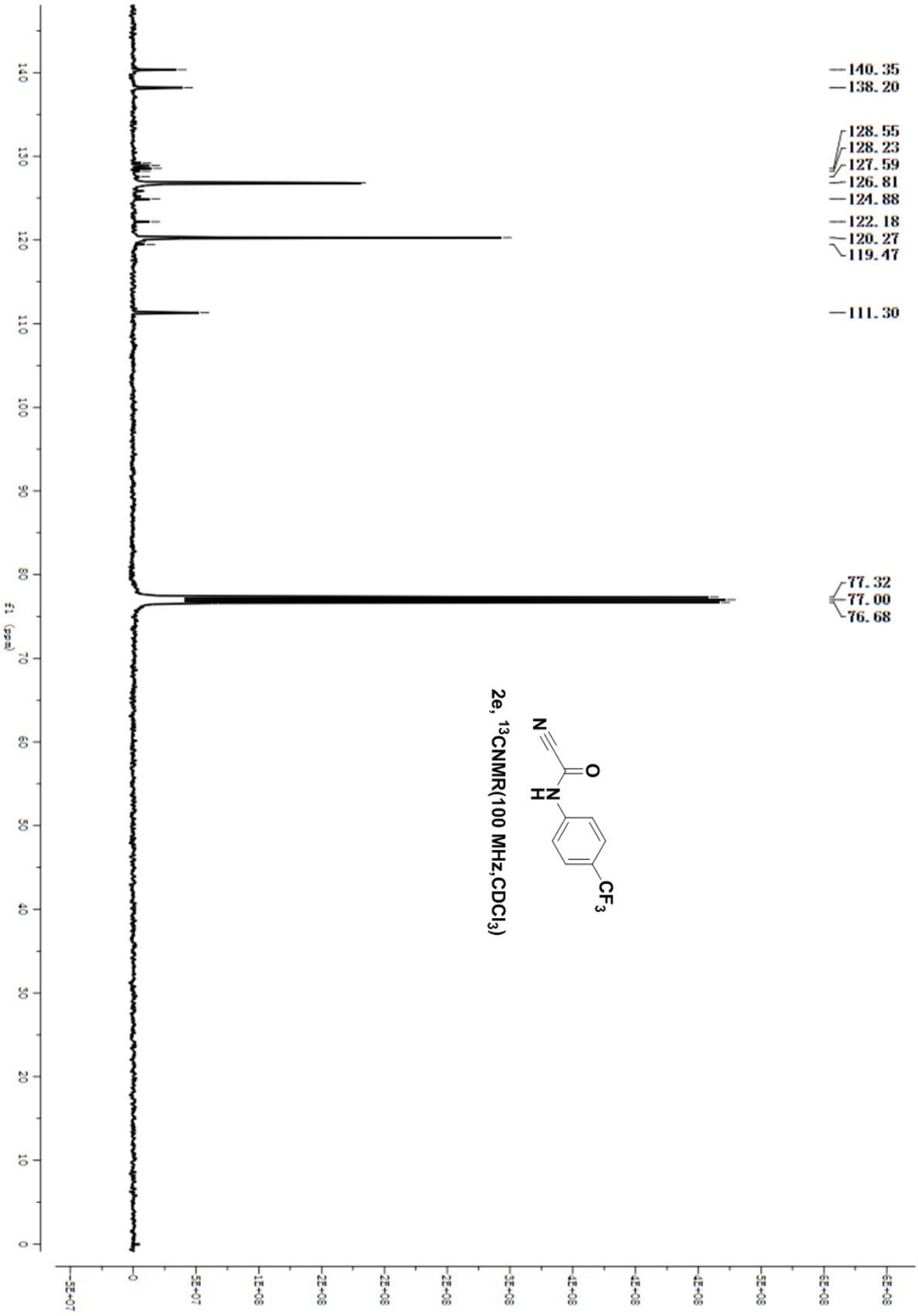
1D NMR plot parameters

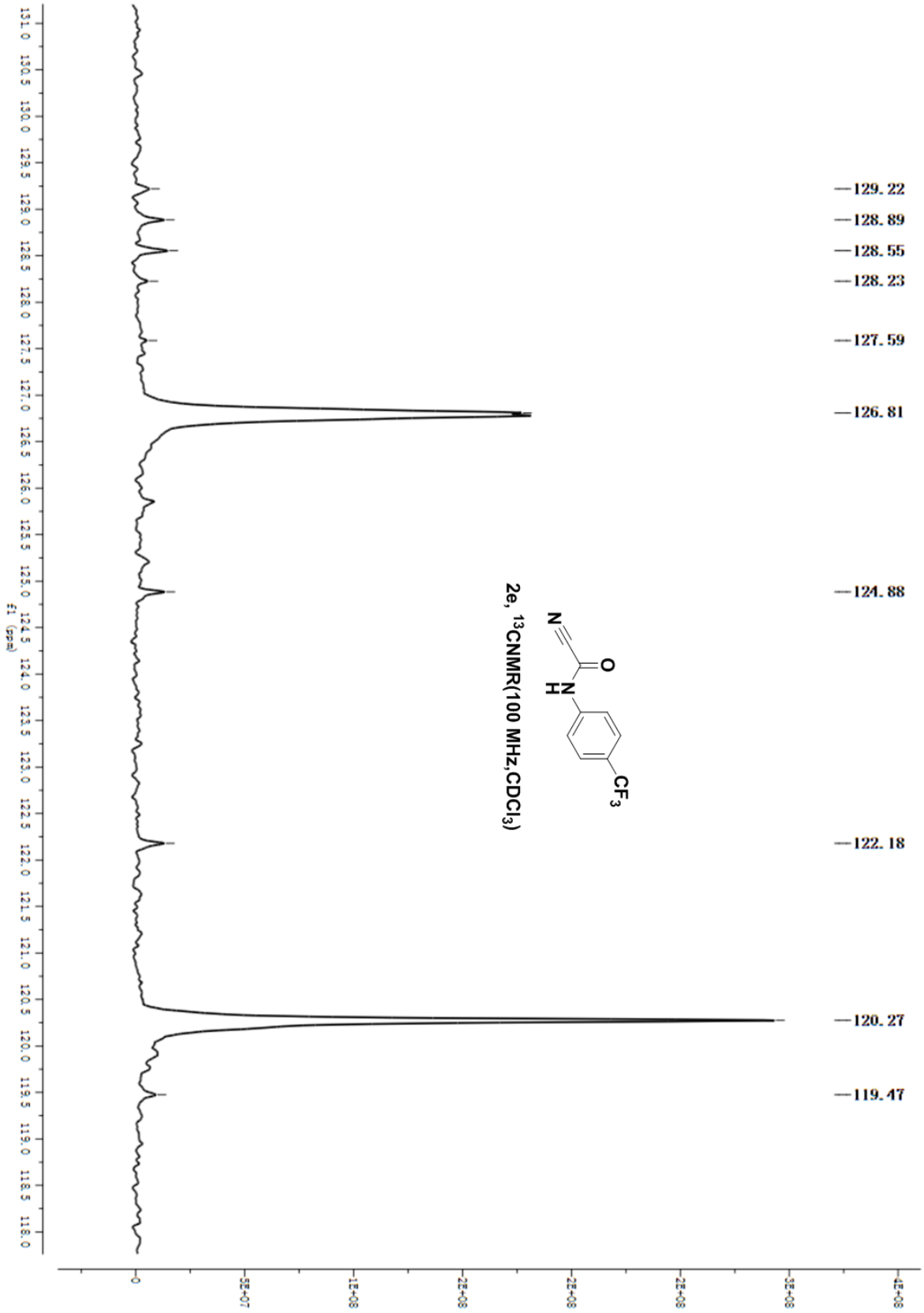
CX	22.00 cm
CY	8.00 cm
F1P	158.546 ppm
F1	15944.57 Hz
F2P	-0.451 ppm
F2	-45.34 Hz
PPMCM	7.22712 ppm/cm
HZCM	726.81409 Hz/cm

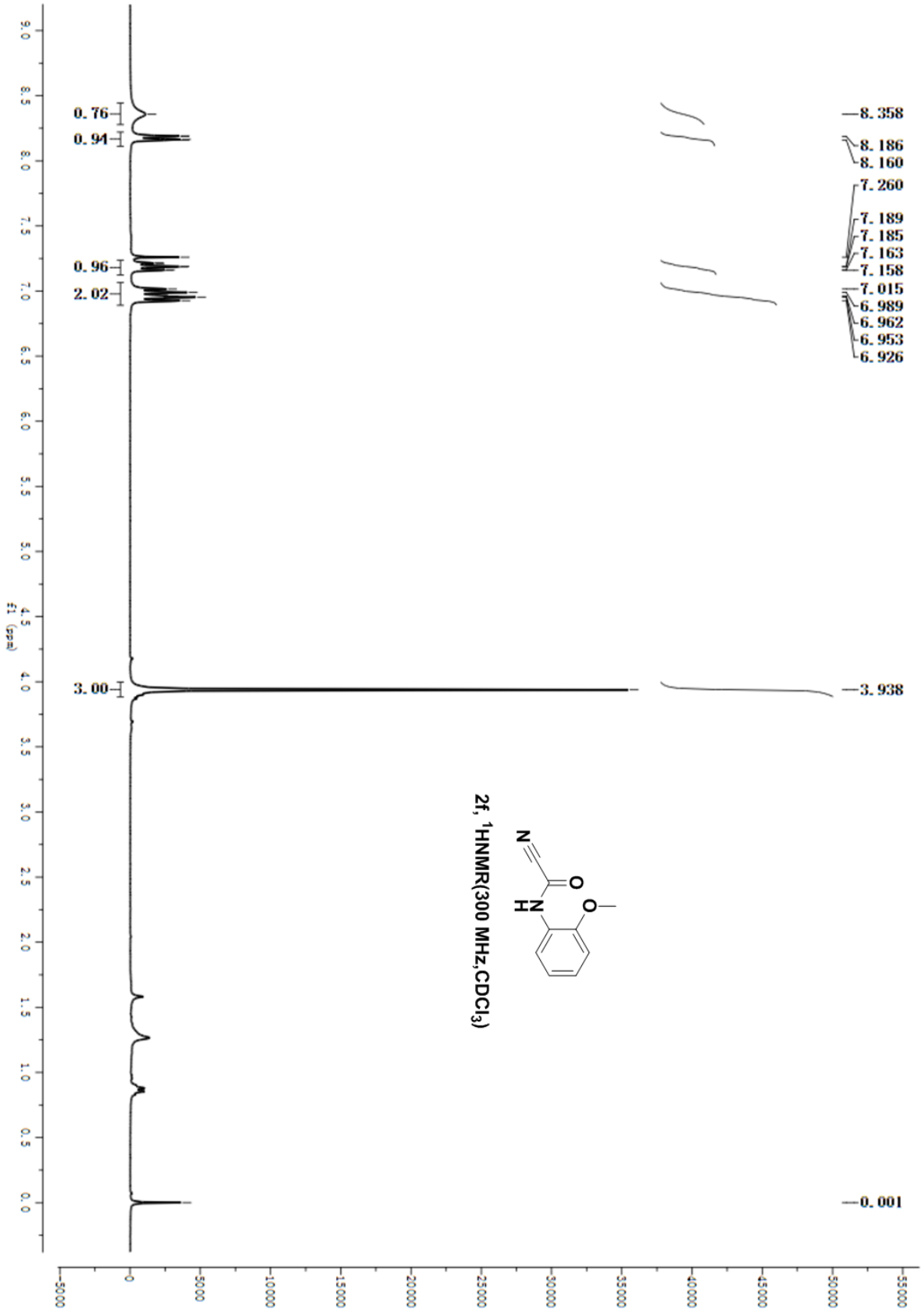

2d, ^{1}HNMR(300 MHz,CDCl$_3$)
0.91
2.13
2.26
3.00
2.349
0.000
7.727
7.393
7.365
7.260
7.203
7.176
f1 (ppm)

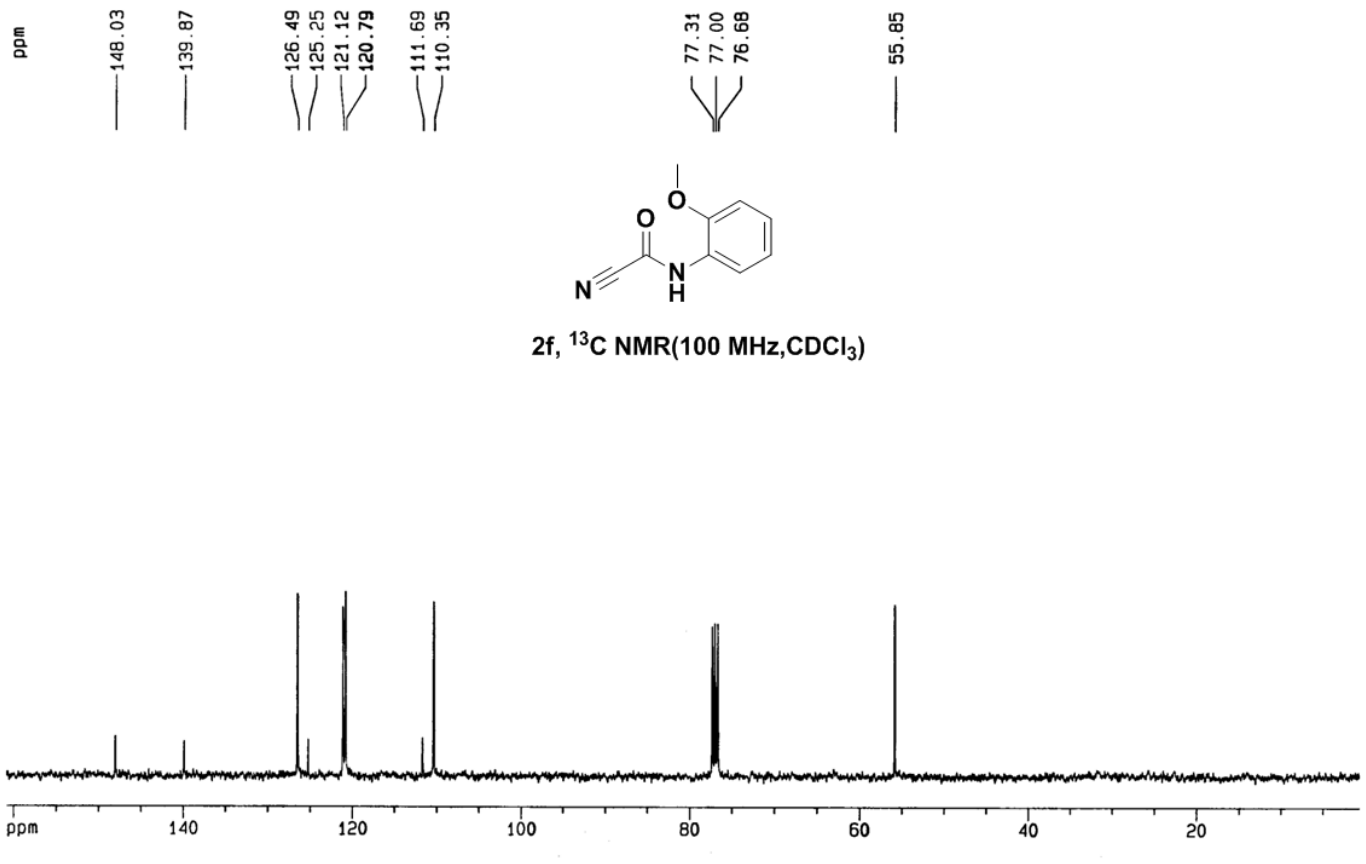

xdx10.22 C13
ppm
140.26
136.66
132.92
130.01
120.39
111.76
77.21
77.00
76.79
20.83
O
N
H
N
2d, ^{13}C NMR(100 MHz,CDCl$_3$)
ppm
160
140
120
100
80
60
40
20
Current Data Parameters
NAME ddw-xdx
EXPNO 8
PROCNO 1
F2 - Acquisition Parameters
Date_ 20101024
Time 4.29
INSTRUM av600
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 20480
SOLVENT CDCl3
NS 48753
DS 4
SWH 33333.332 Hz
FIDRES 1.627604 Hz
AQ 0.3072650 sec
RG 18390.4
DW 15.000 usec
DE 6.00 usec
TE 298.1 K
D1 0.69999999 sec
d11 0.03000000 sec
DELTA 0.59999996 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 13C
P1 8.60 usec
PL1 -2.00 dB
SFO1 150.9194083 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -3.00 dB
PL12 13.48 dB
PL13 13.48 dB
SFO2 600.1324005 MHz
F2 - Processing parameters
SI 32768
SF 150.9028124 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40
1D NMR plot parameters
CX 23.00 cm
CY 70.00 cm
F1P 170.267 ppm


0.83
4.00
8.214
7.660
7.260
0.001
2e, ^{1}HNMR(400 MHz,CDCl$_3$)
f1 (ppm)


140.35
138.20
128.55
128.23
127.59
126.81
124.88
122.18
120.27
119.47
111.30
77.32
77.00
76.68
f1 (ppm)
2e, 13CNMR(100 MHz,CDCl3)
N
O
H
N
CF3


129.22
128.89
128.55
128.23
127.59
126.81
124.88
122.18
120.27
119.47
2e, ^{13}CNMR(100 MHz,$CDCl_3$)
f1 (ppm)


8.358
8.186
8.160
7.260
7.189
7.185
7.163
7.158
7.015
6.989
6.962
6.953
6.926
3.938
0.001
0.76
0.94
0.96
2.02
3.00
f1 (ppm)
2f, 1HNMR(300 MHz,CDCl3)



2f, ^{13}C NMR(100 MHz,$CDCl_3$)

xdx4.8 (3)

Current Data Parameters
NAME XDX
EXPNO 21
PROCNO 1

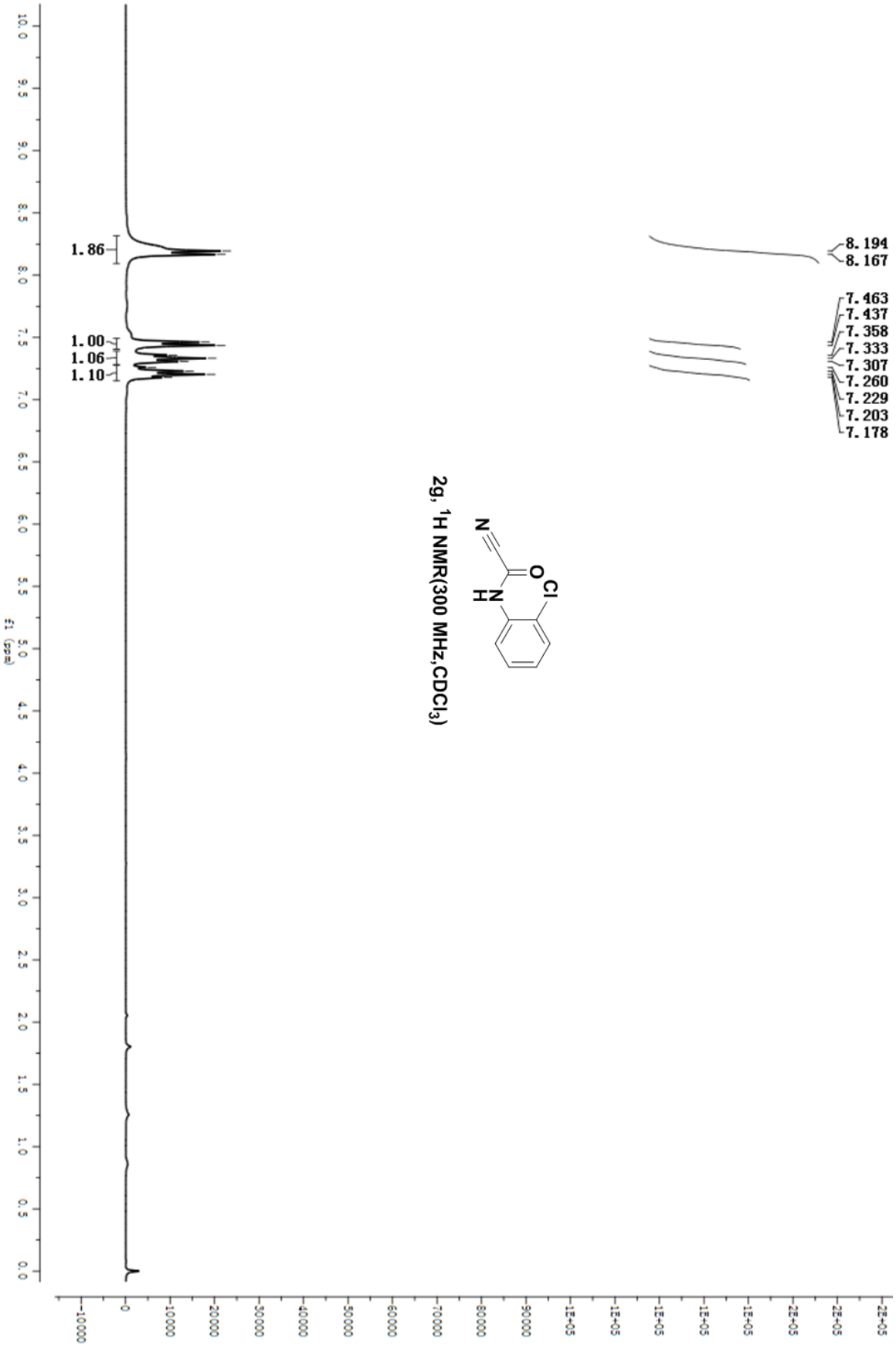
F2 - Acquisition Parameters
Date_ 20110411
Time 17.25
INSTRUM av400
PROBHD 5 mm QNP 1H/13
PULPROG zgdc
TD 16384
SOLVENT CDCl3
NS 302
DS 0
SWH 25062.656 Hz
FIDRES 1.529703 Hz
AQ 0.3269108 sec
RG 8192
DW 19.950 usec
DE 6.00 usec
TE 300.0 K
D1 0.69999999 sec
d11 0.03000000 sec

======== CHANNEL f1 ========
NUC1 13C
P1 2.70 usec
PL1 -3.00 dB
SFO1 100.5785294 MHz

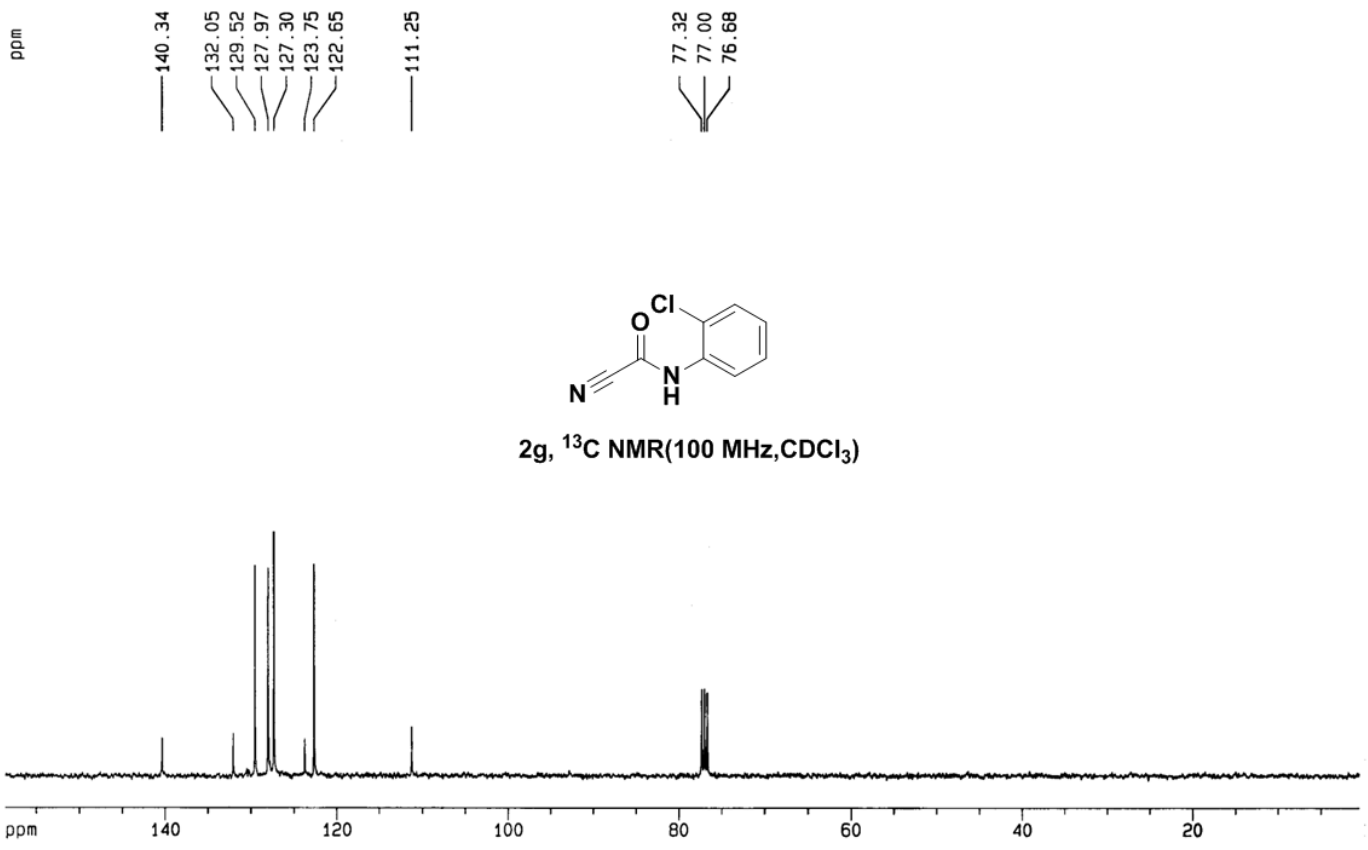
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -3.00 dB
PL12 17.37 dB
SFO2 399.9515998 MHz

F2 - Processing parameters
SI 65536
SF 100.5675164 MHz
WDW EM
SSB 0
LB 4.00 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 22.00 cm
CY 3.00 cm
F1P 160.836 ppm
F1 16174.92 Hz
F2P 0.721 ppm
F2 72.49 Hz
PPMCM 7.27798 ppm/c
HZCM 731.92877 Hz/c#



2g, ^{1}H NMR(300 MHz,$CDCl_3$)



2g, ^{13}C NMR(100 MHz,$CDCl_3$)

xdx12.9 (3)

Current Data Parameters
NAME XDX
EXPNO 12
PROCNO 1

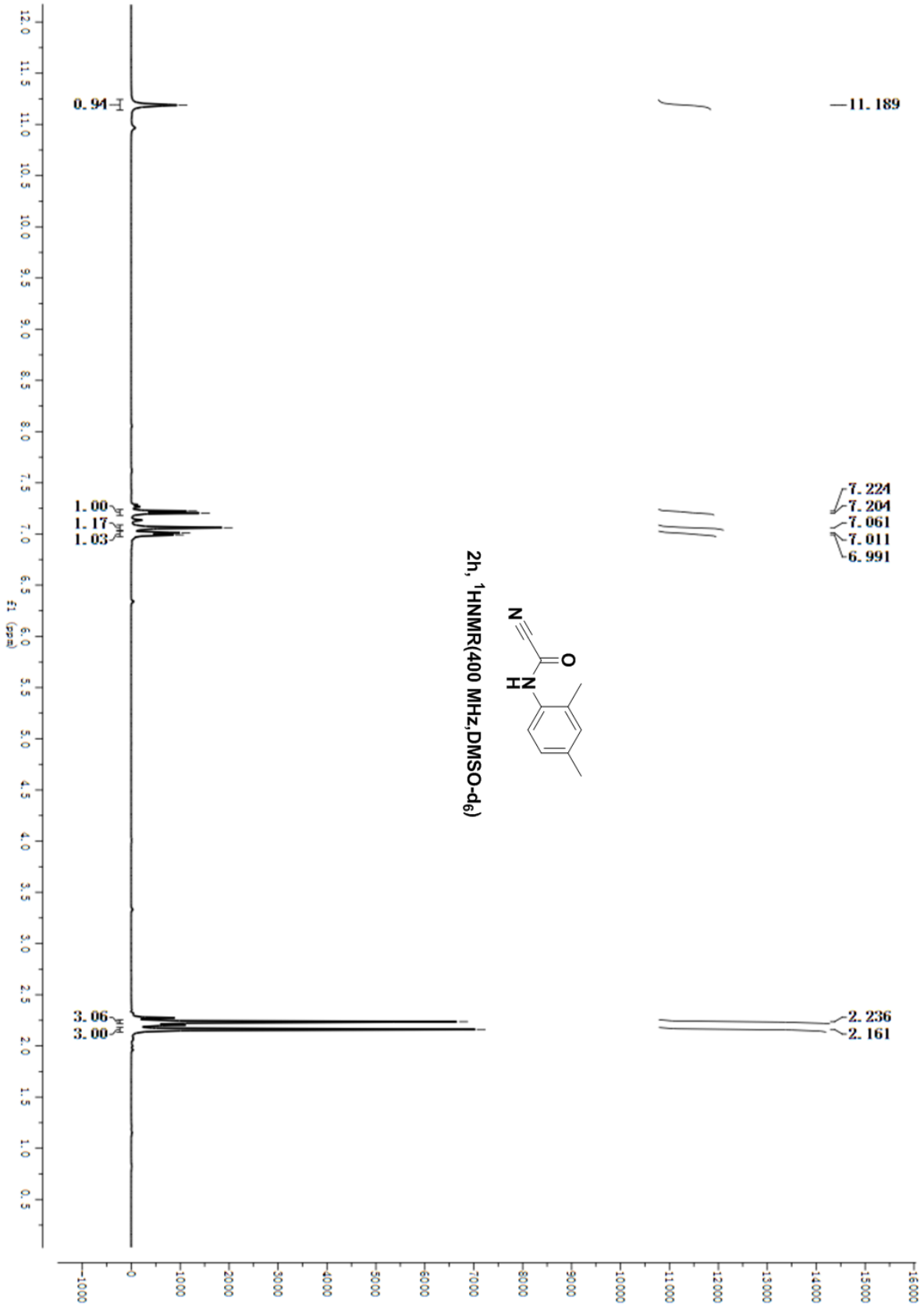
F2 - Acquisition Parameters
Date_ 20111209
Time 18.14
INSTRUM av400
PROBHD 5 mm QNP 1H/13
PULPROG zgdc
TD 16384
SOLVENT CDCl3
NS 132
DS 0
SWH 25062.656 Hz
FIDRES 1.529703 Hz
AQ 0.3269108 sec
RG 8192
DW 19.950 usec
DE 6.00 usec
TE 300.0 K
D1 0.69999999 sec
d11 0.03000000 sec

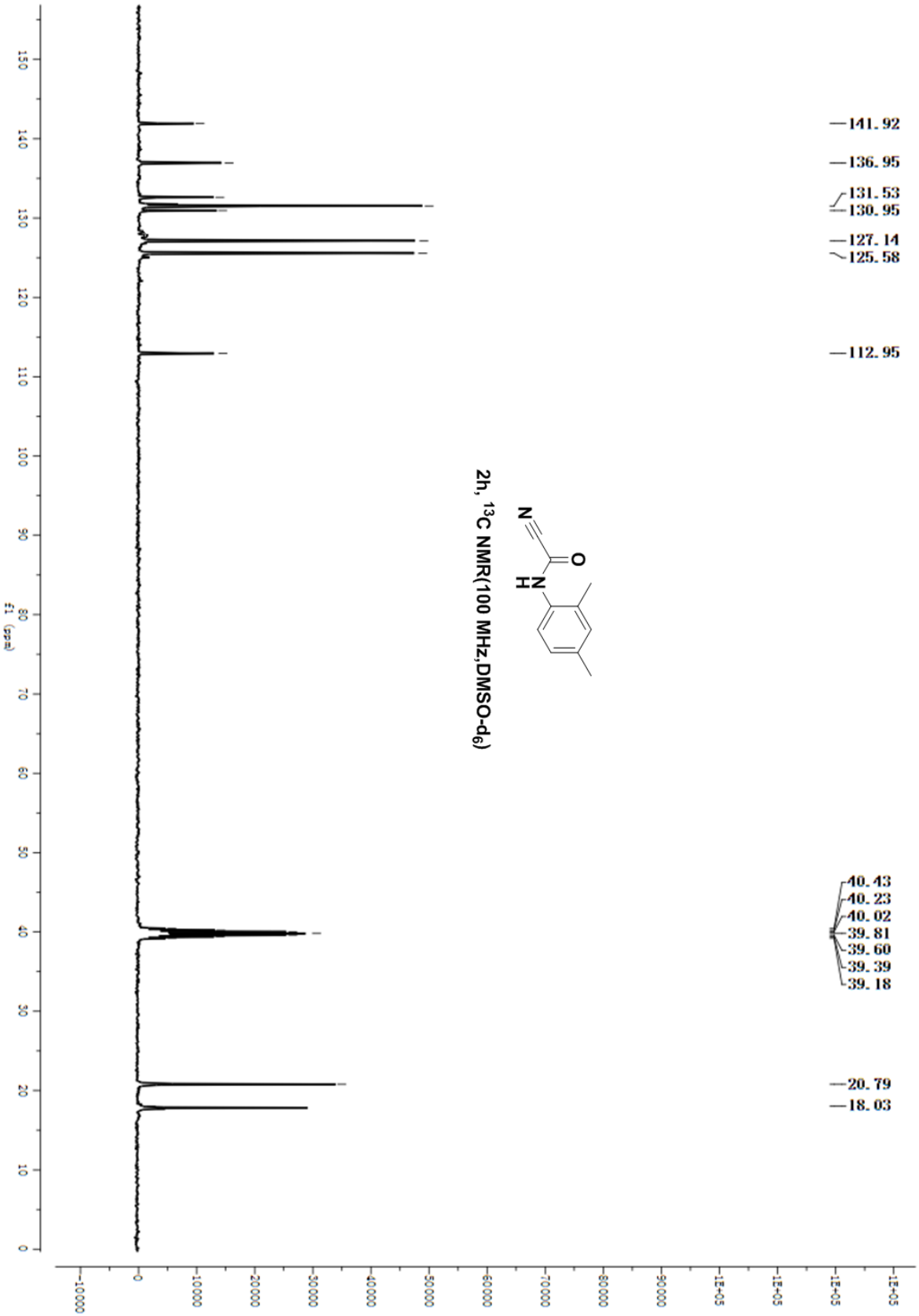
======== CHANNEL f1 ========
NUC1 13C
P1 2.90 usec
PL1 -3.00 dB
SFO1 100.5785294 MHz

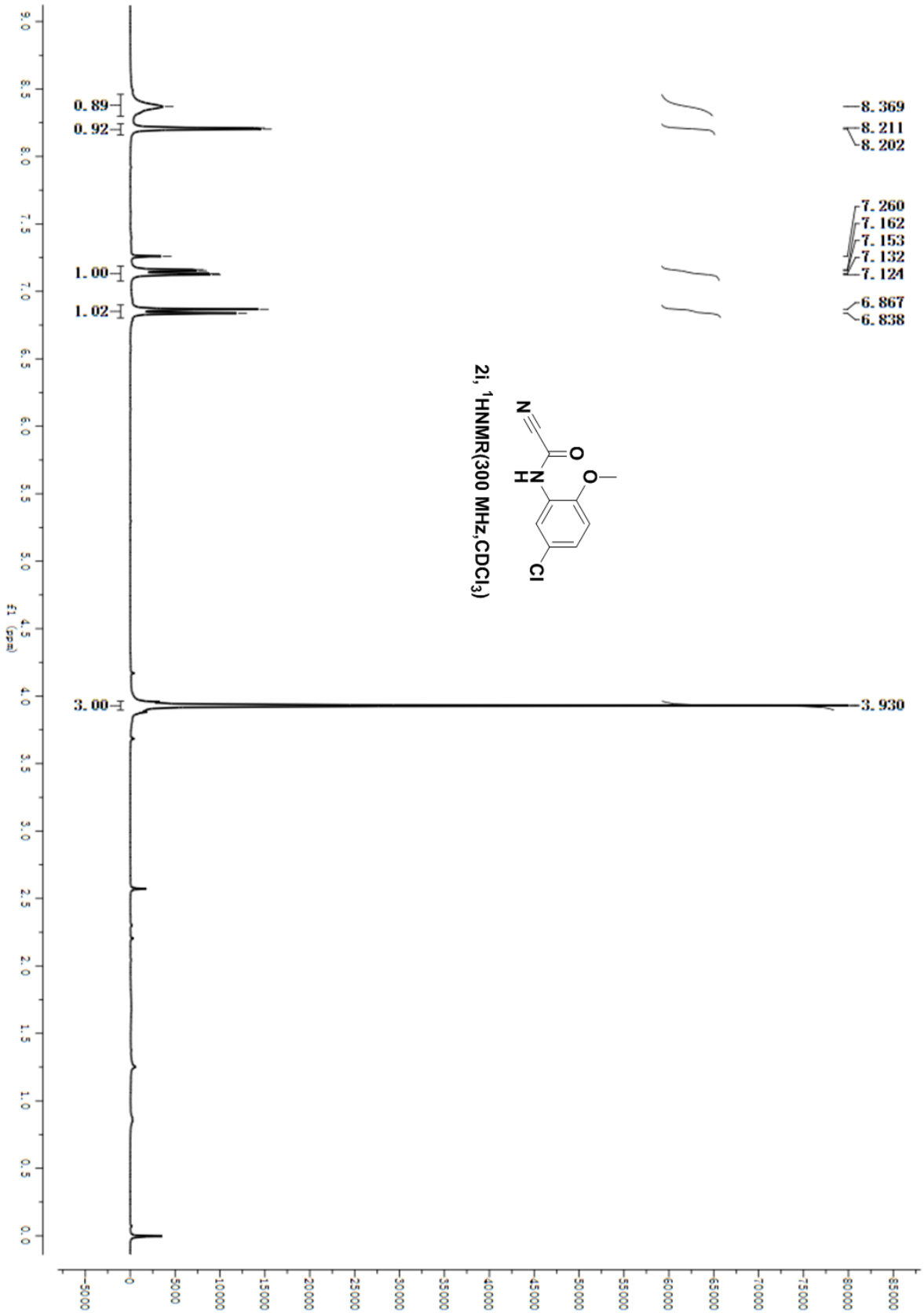
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -3.00 dB
PL12 18.20 dB
SFO2 399.9515998 MHz

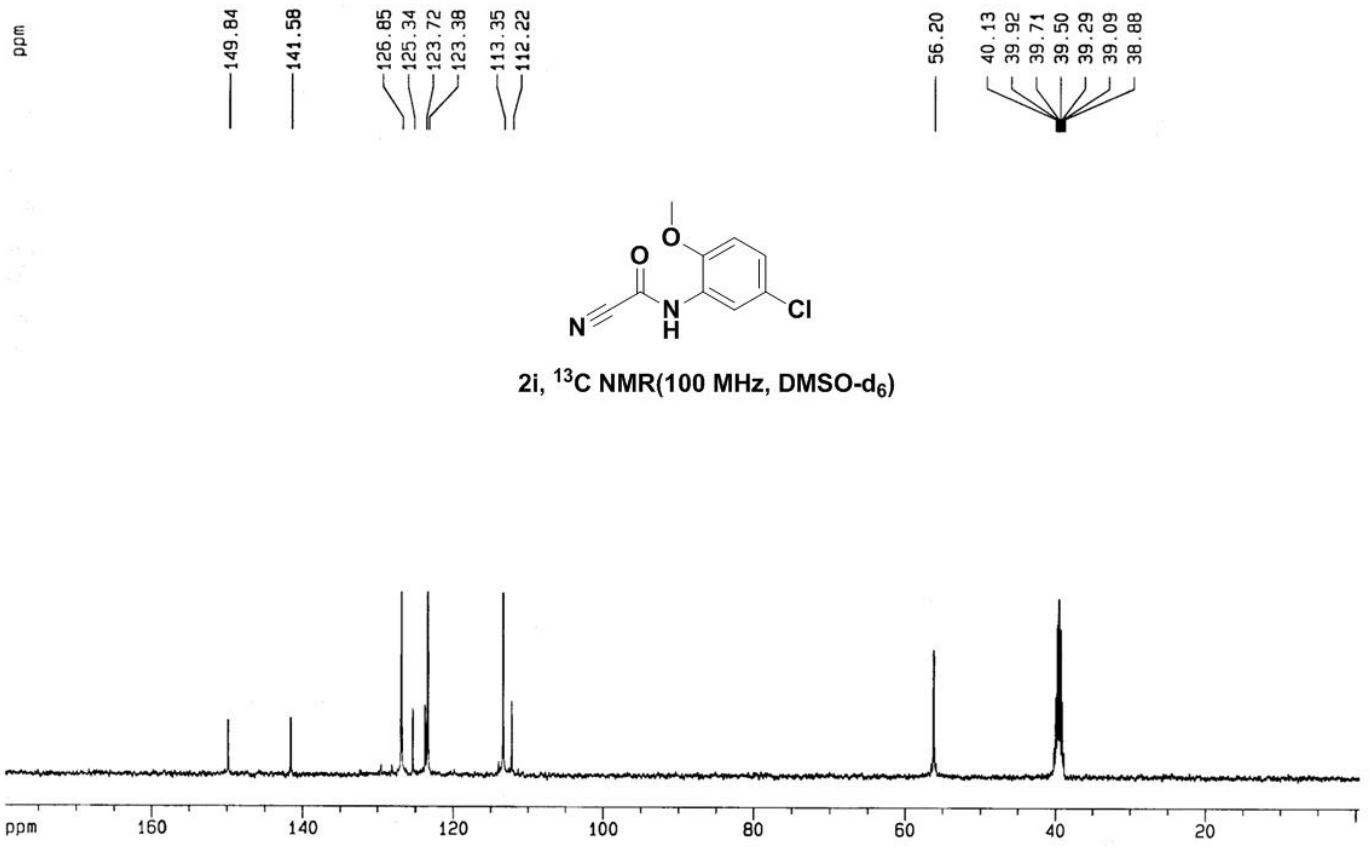
F2 - Processing parameters
SI 65536
SF 100.5675190 MHz
WDW EM
SSB 0
LB 4.00 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 22.00 cm
CY 4.00 cm
F1P 158.589 ppm
F1 15948.91 Hz
F2P 0.552 ppm
F2 55.52 Hz
PPMCM 7.18350 ppm/cm
HZCM 722.42688 Hz/cm


2h, ^{1}HNMR(400 MHz,DMSO-d_6)
11.189
7.224
7.204
7.061
7.011
6.991
2.236
2.161
0.94
1.00
1.17
1.03
3.06
3.00
f1 (ppm)


141.92
136.95
131.53
130.95
127.14
125.58
112.95
40.43
40.23
40.02
39.81
39.60
39.39
39.18
20.79
18.03
2h, 13C NMR(100 MHz,DMSO-d6)
f1 (ppm)


2i, ^{1}HNMR(300 MHz,CDCl$_3$)
8.369
8.211
8.202
7.260
7.162
7.153
7.132
7.124
6.867
6.838
3.930
0.89
0.92
1.00
1.02
3.00
f1 (ppm)



2i, ^{13}C NMR(100 MHz, DMSO-d_6)

xdx12.5 (2)

Current Data Parameters

NAME	XDX
EXPNO	2
PROCNO	1

F2 - Acquisition Parameters

Date_	20111205
Time	22.31
INSTRUM	av400
PROBHD	5 mm PHDUL 13C
PULPROG	zgdc
TD	16384
SOLVENT	DMSO
NS	212
DS	0
SWH	25062.656 Hz
FIDRES	1.529703 Hz
AQ	0.3269108 sec
RG	8192
DW	19.950 usec
DE	6.00 usec
TE	300.0 K
D1	0.69999999 sec
d11	0.03000000 sec

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

NUC1	13C
P1	2.90 usec
PL1	-3.00 dB
SFO1	100.5785294 MHz

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

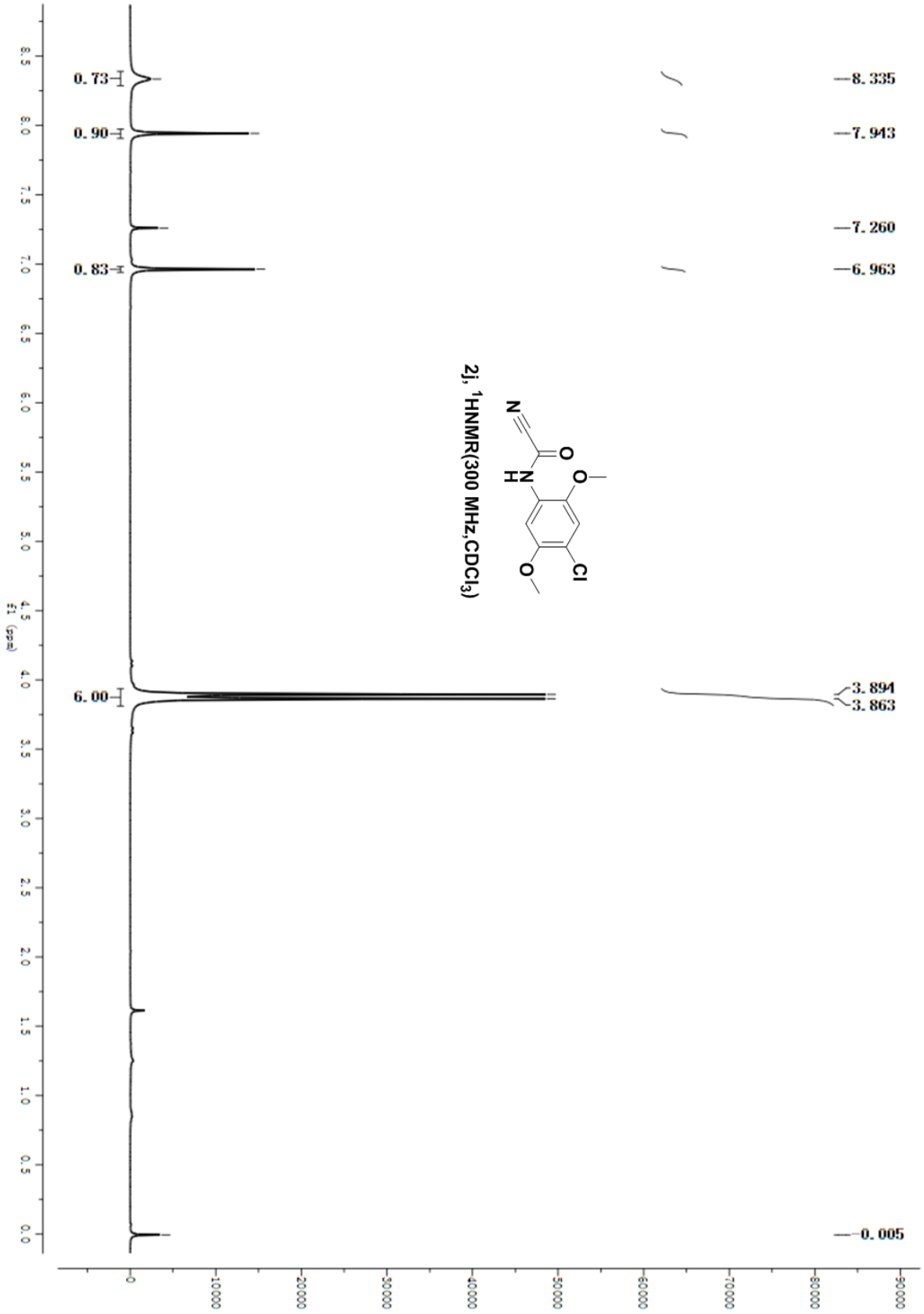
CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL2	-3.00 dB
PL12	18.20 dB
SFO2	399.9515998 MHz

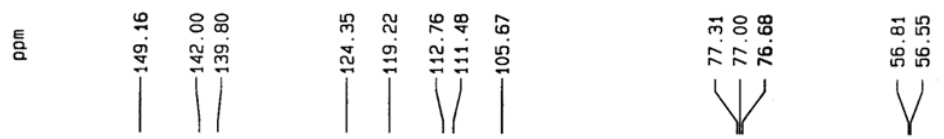
F2 - Processing parameters

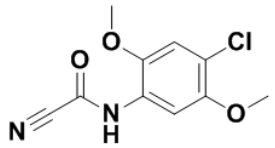
SI	65536
SF	100.5675552 MHz
WDW	EM
SSB	0
LB	4.00 Hz
GB	0
PC	1.00

1D NMR plot parameters

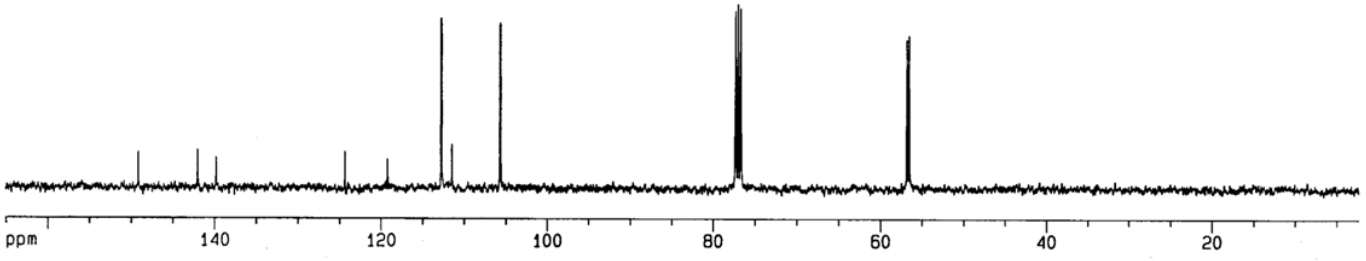
CX	22.00 cm
CY	3.00 cm
F1P	179.344 ppm
F1	18036.20 Hz
F2P	-0.447 ppm
F2	-44.95 Hz
PPMCM	8.17232 ppm/cm
HZCM	821.87030 Hz/cm


2j, ^{1}HNMR(300 MHz,CDCl$_3$)
0.73
0.90
0.83
6.00
8.335
7.943
7.260
6.963
3.894
3.863
0.005
f1 (ppm)





2j, ^{13}C NMR(100 MHz,$CDCl_3$)



xdx4.8 (2)

Current Data Parameters
NAME XDX
EXPNO 20
PROCNO 1

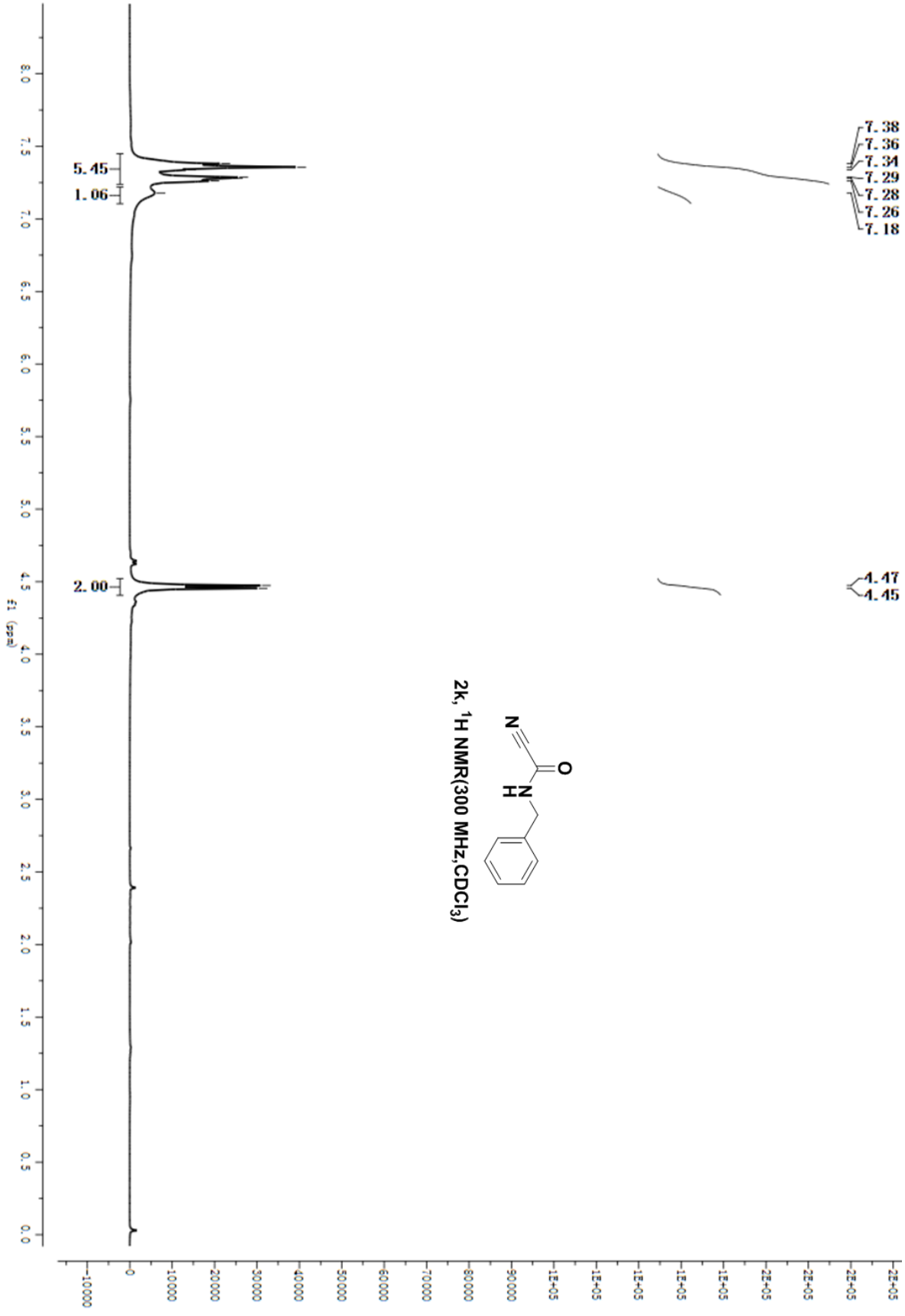
F2 - Acquisition Parameters
Date_ 20110411
Time 17.00
INSTRUM av400
PROBHD 5 mm QNP 1H/13
PULPROG zgdc
TD 16384
SOLVENT CDCl3
NS 596
DS 0
SWH 25062.656 Hz
FIDRES 1.529703 Hz
AQ 0.3269108 sec
RG 8192
DW 19.950 usec
DE 6.00 usec
TE 300.0 K
D1 0.69999999 sec
d11 0.03000000 sec

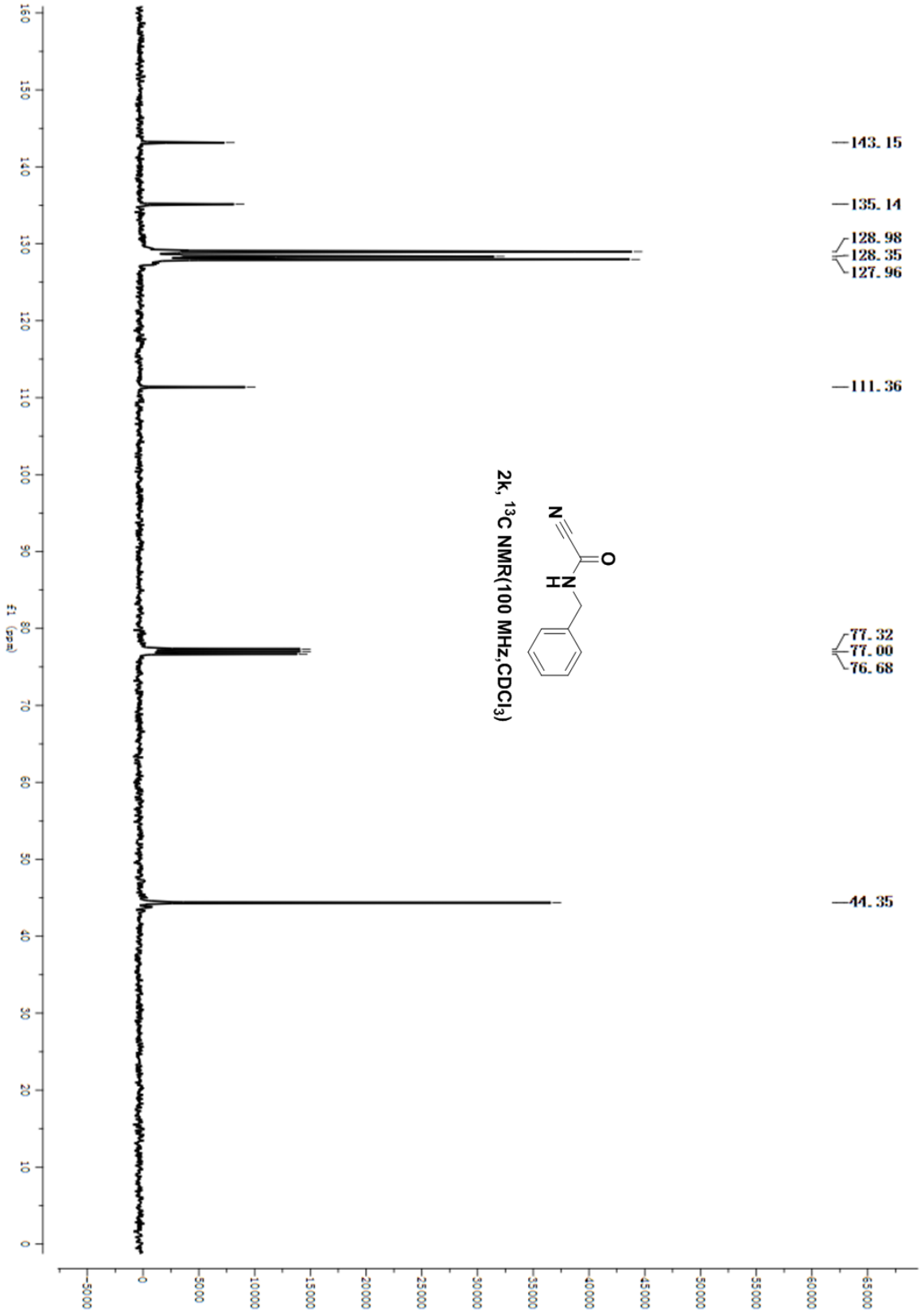
======== CHANNEL f1 ========
NUC1 13C
P1 2.70 usec
PL1 -3.00 dB
SFO1 100.5785294 MHz

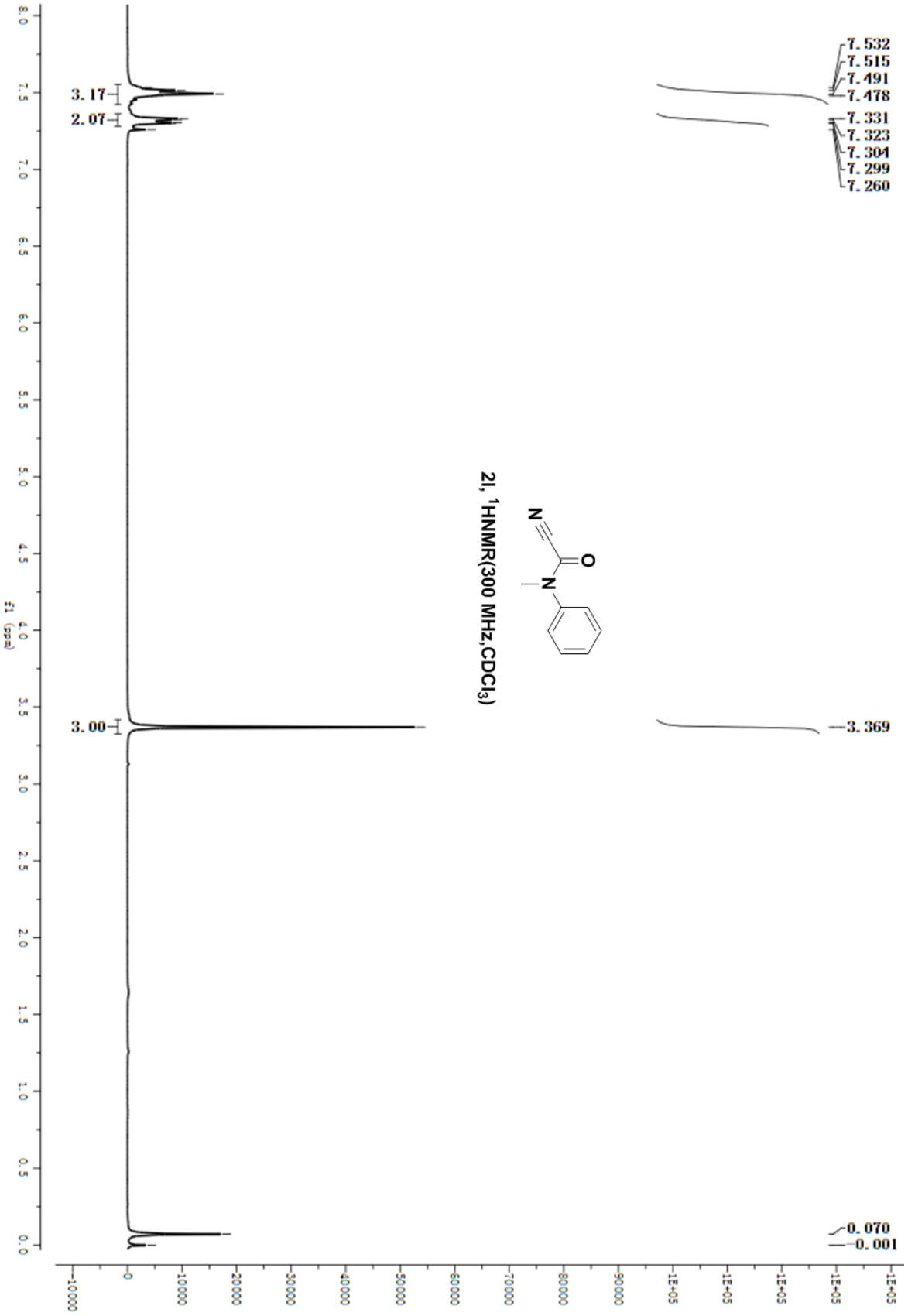
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -3.00 dB
PL12 17.37 dB
SFO2 399.9515998 MHz

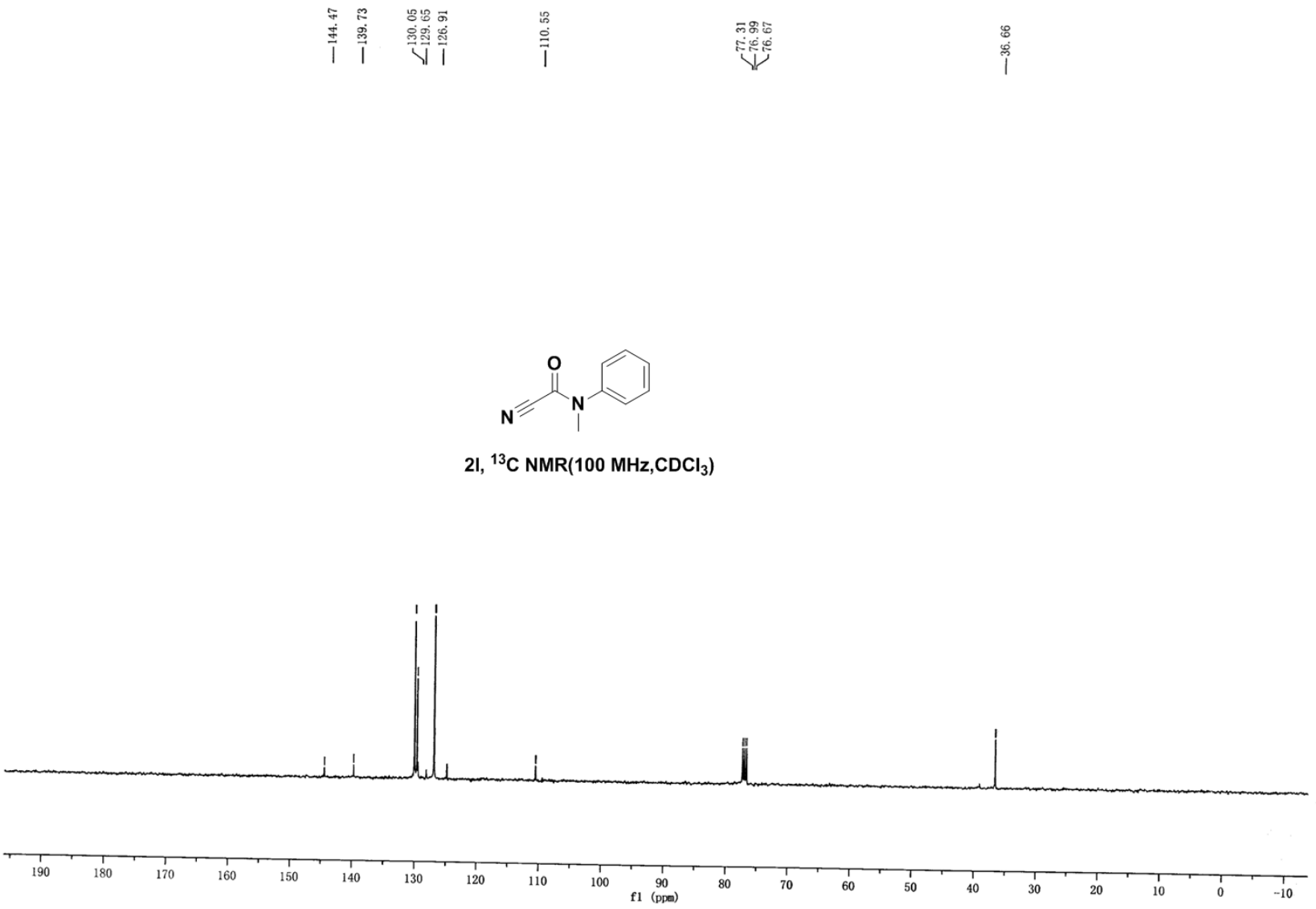
F2 - Processing parameters
SI 65536
SF 100.5675125 MHz
WDW EM
SSB 0
LB 4.00 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 22.00 cm
CY 3.00 cm
F1P 165.071 ppm
F1 16600.79 Hz
F2P 2.373 ppm
F2 238.64 Hz
PPMCM 7.39537 ppm/cm
HZCM 743.73407 Hz/cm

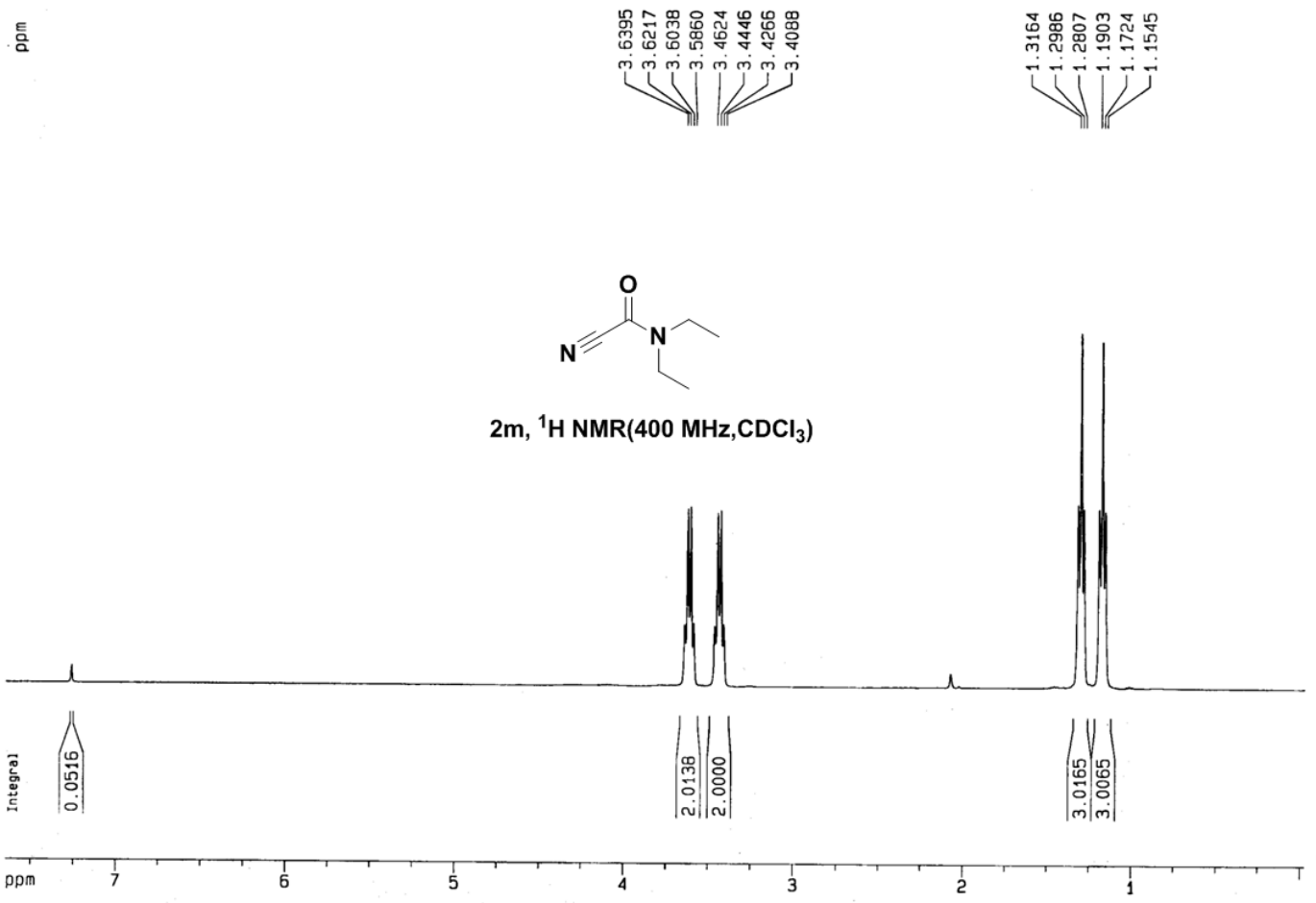

7.38
7.36
7.34
7.29
7.28
7.26
7.18
5.45
1.06
2.00
4.47
4.45
f1 (ppm)
2k, ^{1}H NMR(300 MHz,CDCl$_3$)


143.15
135.14
128.98
128.35
127.96
111.36
77.32
77.00
76.68
44.35
2k, ^{13}C NMR(100 MHz,CDCl$_3$)
f1 (ppm)


2l, ^{1}HNMR(300 MHz,CDCl$_3$)
7.532
7.515
7.491
7.478
7.331
7.323
7.304
7.299
7.260
3.369
3.17
2.07
3.00
0.070
0.001
f1 (ppm)



2l, ^{13}C NMR(100 MHz,$CDCl_3$)



2m, ^{1}H NMR(400 MHz,$CDCl_3$)

xdx-0110-1

Current Data Parameters

NAME	XDX
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

Date_	20120110
Time	19.36
INSTRUM	av400
PROBHD	5 mm PHDUL 13C
PULPROG	zg
TD	16384
SOLVENT	CDCl3
NS	4
DS	0
SWH	4194.631 Hz
FIDRES	0.256020 Hz
AQ	1.9530228 sec
RG	32
DW	119.200 usec
DE	6.00 usec
TE	313.0 K
D1	10.00000000 sec

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

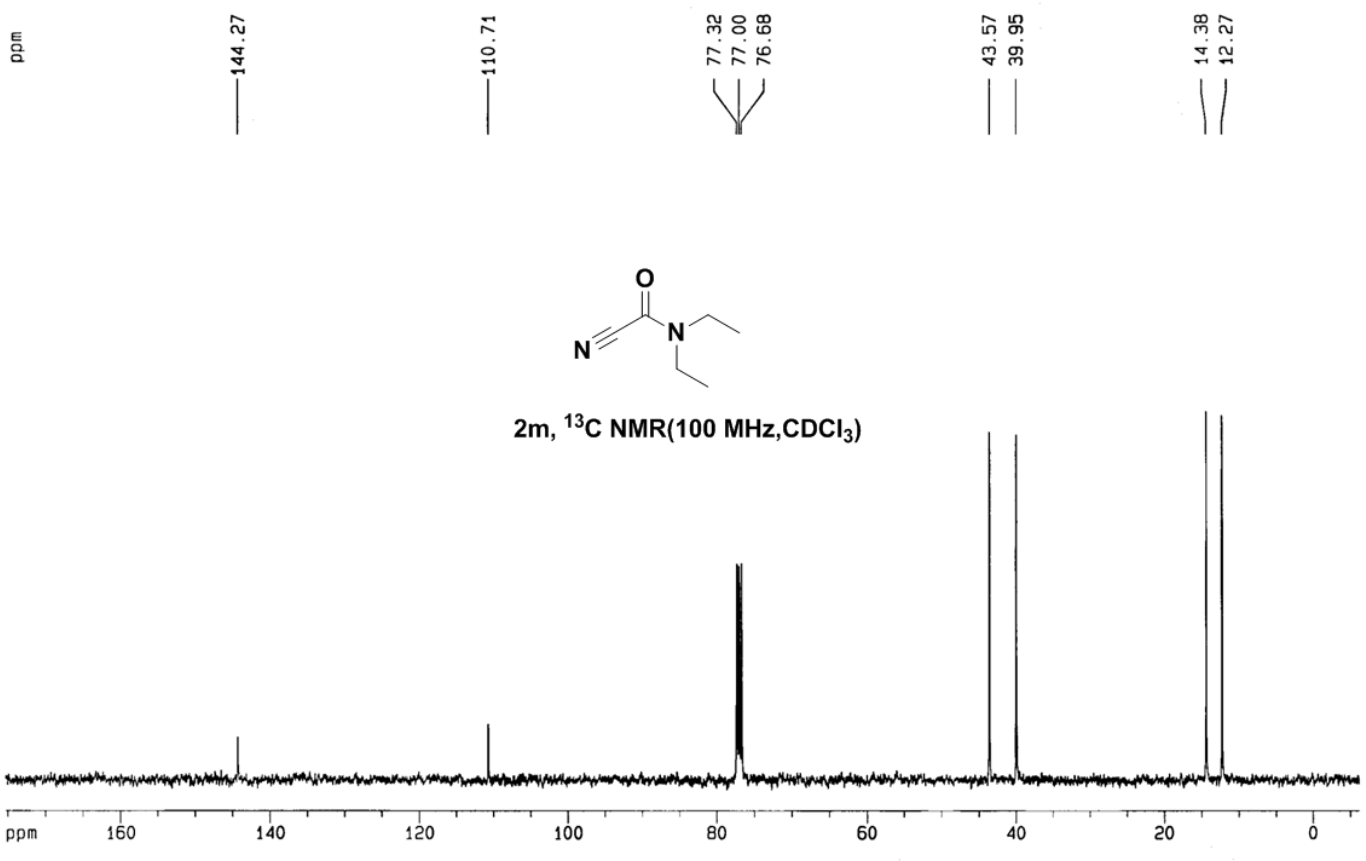
NUC1	1H
P1	8.00 usec
PL1	-3.00 dB
SFO1	399.9519607 MHz

F2 - Processing parameters

SI	65536
SF	399.9500101 MHz
WDW	EM
SSB	0
LB	0.50 Hz
GB	0
PC	1.00

1D NMR plot parameters

CX	22.00 cm
CY	6.00 cm
F1P	7.647 ppm
F1	3058.22 Hz
F2P	-0.028 ppm
F2	-11.14 Hz
PPMCM	0.34884 ppm/c
HZCM	139.51659 Hz/cm



2m, ^{13}C NMR(100 MHz,$CDCl_3$)

xdx-0110-1

Current Data Parameters

NAME	XDX
EXPNO	2
PROCNO	1

F2 - Acquisition Parameters

Date_	20120110
Time	19.37
INSTRUM	av400
PROBHD	5 mm PHDUL 13C
PULPROG	zgdc
TD	16384
SOLVENT	CDCl3
NS	439
DS	0
SWH	25062.656 Hz
FIDRES	1.529703 Hz
AQ	0.3269108 sec
RG	8192
DW	19.950 usec
DE	6.00 usec
TE	300.0 K
D1	0.50000000 sec
d11	0.03000000 sec

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

NUC1	13C
P1	2.90 usec
PL1	-3.00 dB
SFO1	100.5785294 MHz

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

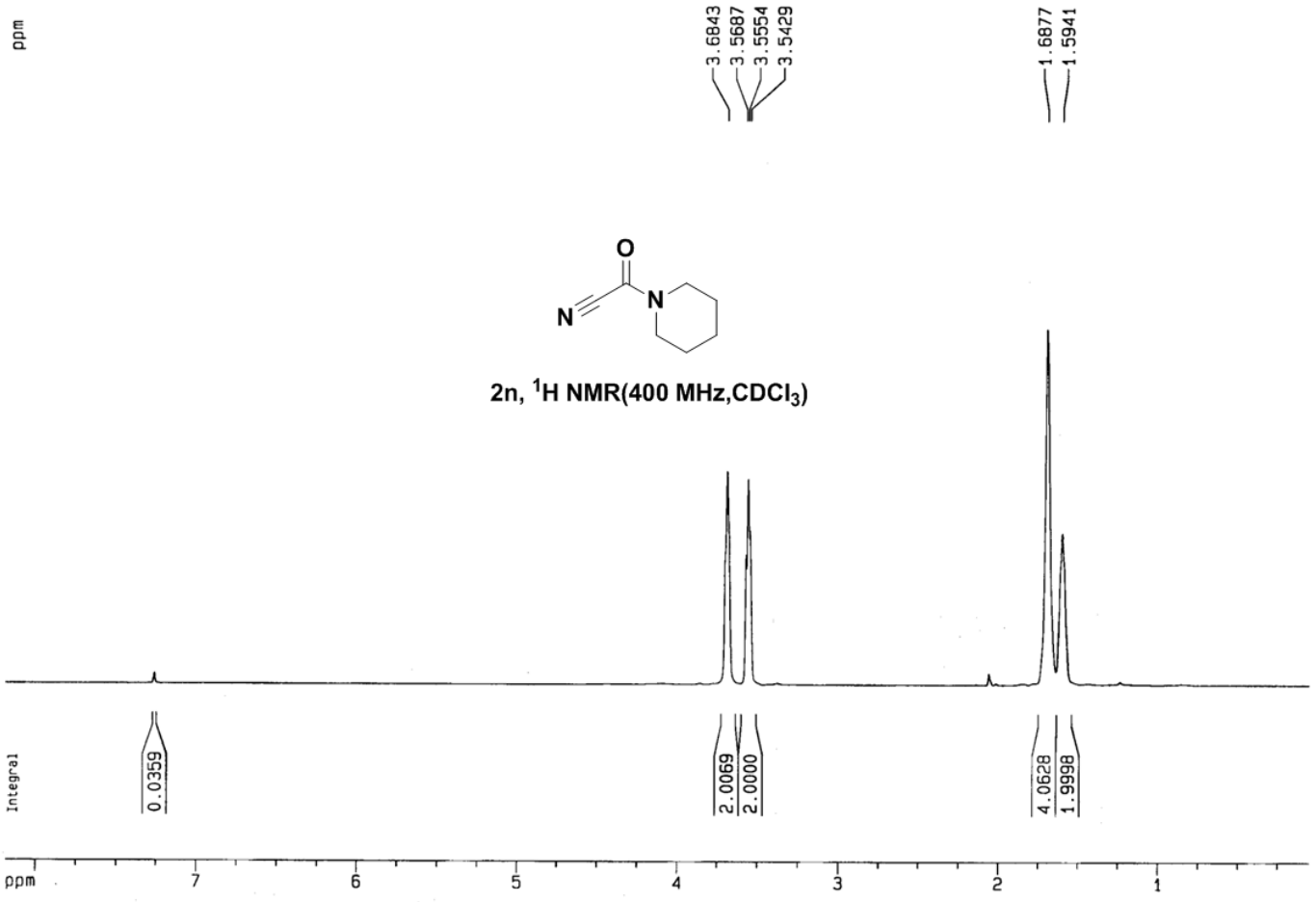
CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL2	-3.00 dB
PL12	18.20 dB
SFO2	399.9515998 MHz

F2 - Processing parameters

SI	65536
SF	100.5675137 MHz
WDW	EM
SSB	0
LB	4.00 Hz
GB	0
PC	1.00

1D NMR plot parameters

CX	22.00 cm
CY	6.00 cm
F1P	175.338 ppm
F1	17633.31 Hz
F2P	-6.124 ppm
F2	-615.91 Hz
PPMCM	8.24829 ppm/cm
HZCM	829.50983 Hz/cm



xdx-0110-2

Current Data Parameters

NAME	XDX
EXPNO	3
PROCNO	1

F2 - Acquisition Parameters

Date_	20120110
Time	19.51
INSTRUM	av400
PROBHD	5 mm PHOUL 13C
PULPROG	zg
TD	16384
SOLVENT	CDCl3
NS	4
DS	0
SWH	4222.973 Hz
FIDRES	0.257750 Hz
AQ	1.9399157 sec
RG	32
DW	118.400 usec
DE	6.00 usec
TE	313.0 K
D1	10.00000000 sec

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

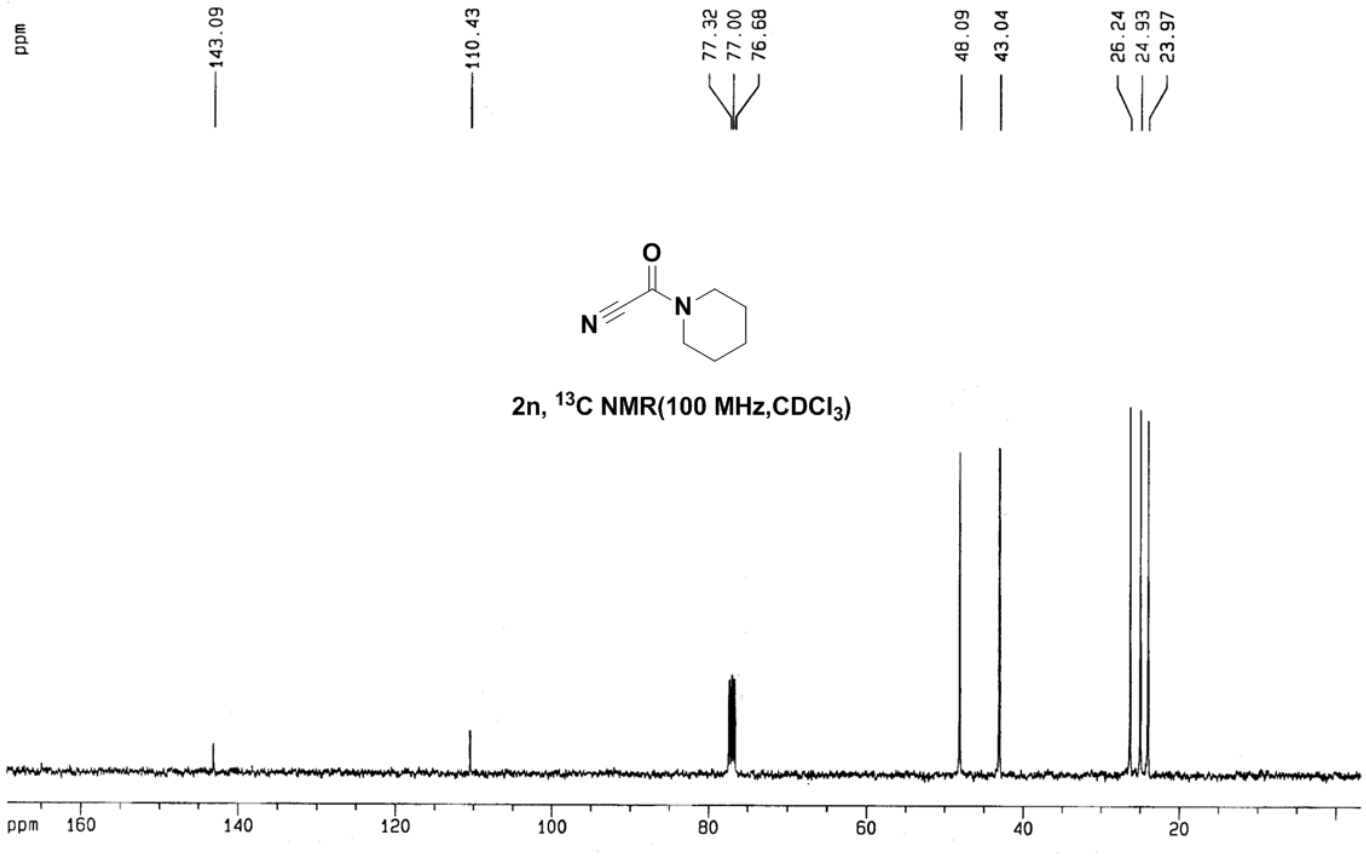
NUC1	1H
P1	8.00 usec
PL1	-3.00 dB
SFO1	399.9520025 MHz

F2 - Processing parameters

SI	65536
SF	399.9500105 MHz
WDW	EM
SSB	0
LB	0.50 Hz
GB	0
PC	1.00

1D NMR plot parameters

CX	22.00 cm
CY	6.00 cm
F1P	8.186 ppm
F1	3274.04 Hz
F2P	0.055 ppm
F2	22.10 Hz
PPMCM	0.36959 ppm/c
HZCM	147.81555 Hz/cm



2n, ^{13}C NMR(100 MHz,$CDCl_3$)

xdx-0110-2

```
Current Data Parameters
NAME                  XDX
EXPNO                   4
PROCNO                  1

F2 - Acquisition Parameters
Date_            20120110
Time                19.44
INSTRUM             av400
PROBHD   5 mm PHDUL 13C
PULPROG              zgdc
TD                  16384
SOLVENT             CDCl3
NS                    469
DS                      0
SWH            25062.656 Hz
FIDRES          1.529703 Hz
AQ             0.3269108 sec
RG                   8192
DW                19.950 usec
DE                 6.00 usec
TE                300.0 K
D1             0.50000000 sec
d11            0.03000000 sec

======== CHANNEL f1 ========
NUC1                 13C
P1                2.90 usec
PL1               -3.00 dB
SFO1         100.5785294 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2             80.00 usec
PL2               -3.00 dB
PL12              18.20 dB
SFO2         399.9515998 MHz

F2 - Processing parameters
SI                  65536
SF           100.5675164 MHz
WDW                  EM
SSB                   0
LB                 4.00 Hz
GB                    0
PC                 1.00

1D NMR plot parameters
CX                22.00 cm
CY                 6.00 cm
F1P              169.357 ppm
F1             17031.86 Hz
F2P              -3.151 ppm
F2              -316.90 Hz
PPMCM            7.84130 ppm/cm
HZCM           788.58014 Hz/cm
```