Supporting Information

Metal-Free Oxidative Cross-Coupling of Unfunctionalized Aromatic Compounds

Yasuyuki Kita,* Koji Morimoto, Motoki Ito, Chieko Ogawa, Akihiro Goto, and Toshifumi Dohi

Graduated School of Pharmaceutical Science, Osaka University, 1-6, Yamada-oka, Suita, Osaka, 565-0871, Japan

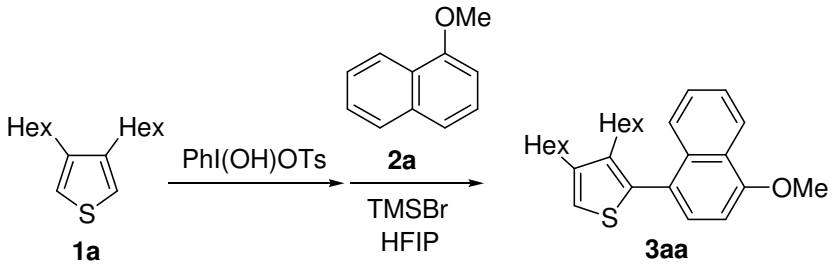
E-mail: kita@ph.ritsumei.ac.jp

General Information Melting point (mp) was measured by Büchi B-545. ^{1}H-NMR and ^{13}C-NMR spectra were recorded on a JEOL JMN-300 spectrometer in $CDCl_3$ with tetramethylsilane as an internal standard. Data are reported as follows: chemical shift in ppm (δ), integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, brs = broad singlet, m = multiplet), coupling constant (Hz). Infrared spectra (IR) were obtained on a Hitachi 270-50 spectrometer; absorptions are reported in reciprocal centimeters with the following relative intensities: s (strong), m (medium), or w (weak). Mass spectra were obtained on a Shimadzu GCMS-QP 5000 instrument with ionization voltages of 70 eV. Elemental analyses and high resolution mass spectra were performed by the Elemental Analysis Section of Osaka University. Column chromatography and TLC were carried out on Merck Silica gel 60 (230-400 mesh) and Merck Silica gel F_{254} plates (0.25 mm), respectively. The spots and bands were detected by UV irradiation (254, 365 nm).

Materials [hydroxyl(tosyloxy)iodo]benzene (PhI(OH)OTs), $PhI(OAc)_2$ (PIDA), TMSBr, 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) are commercially available and used as recieved. Thiophenes (**1a**,[1] **1d**,[2] **1f**,[3]), pyrrole (**2g**)[4] were prepared according to the literatures. 3-(*p*-Tolyl)thiophene **2h**[5] was prepared using the general Suzuki coupling methods. All other starting materials are commercially available. They were used without further purification.

General Experimental Procedure for the Mixed Biaryl Synthesis. **(Scheme 1)**

To a stirred solution of 3,4-dihexylthiophene **1a** (252 mg, 1 mmol) in $(CF_3)_2CHOH$, PhI(OH)OTs (412 mg, 1.05 mmol) was added at room temperature. After stirring for 30 min., 1-methoxynaphthalene **2a** (237 mg, 1.5 mmol) and TMSBr (0.27 mL, 2 mmol) were sequentially added and then stirred for an additional 3 hours under the same conditions, while the reaction progress was checked by TLC or GC. Saturated aqueous sodium hydrogen carbonate was added to the mixture when the reaction completed. The aqueous phase was extracted with CH_2Cl_2. The extract was dried over anhydrous Na_2SO_4 and then evaporated to dryness. The crude residue was purified by column chromatography on silica-gel (eluent: *n*-hexane/AcOEt) to give the pure biaryl **3aa** in 86% yield (351 mg, 0.86 mmol).

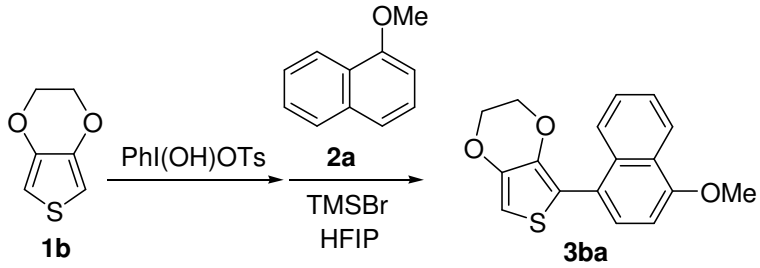


1a **3aa**

(3aa)

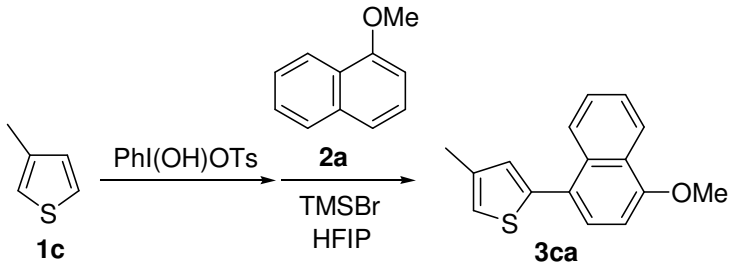
Oil; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 0.72 (3H, t, J = 6.6 Hz), 0.72 (3H, t, J = 6.6 Hz), 0.9-1.10 (6H, m), 1.25-1.46 (8H, m), 1.73 (2H, q, J = 7.8 Hz), 2.30 (2H, m) 2.60 (2H, t, J = 6.6 Hz), 4.03 (3H, s), 6.83 (1H, d, J = 7.8 Hz), 6.99 (1H, s), 7.38 (1H, d, J = 7.8 Hz), 7.42-7.29 (2H, m), 7.64 (1H, dd, J = 7.5, 1.8 Hz), 8.30 (1H, dd, J = 7.5, 1.8 Hz) ppm; ^{13}C-NMR (75 MHz, $CDCl_3$); δ 14,0, 14.1, 22.4, 22.7, 27.4, 29.1, 29.4, 29.8, 30.2, 31.3, 31.8, 55.5, 103.1, 119.0, 122.0, 124.9, 125.1, 125.5, 126.1, 126.7, 129.1, 134.0, 135.8, 140.0, 142.3, 155.5 ppm; IR (KBr): 2928 s, 2855 s, 1585 s, 1508 m, 1462 s, 1383 s, 1319 m, 1159 m, 1024 m, 987 w, 814 m, 763 s, 669 w cm^{-1}; HRFABMS: calcd for $C_{27}H_{36}OS$ $[M + H]^+$ 409.2565, found 409.2553.

(3ba)



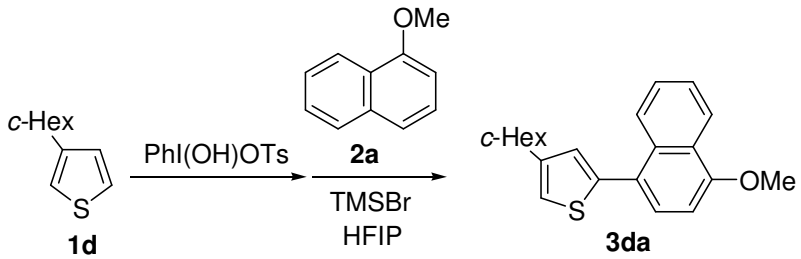
White solid; mp. 178-180 °C; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 3.93 (3H, s), 4.00-4.20 (m, 4H), 6.35 (1H, s), 6.76 (1H, d, J = 7.5 Hz), 7.37-7.43 (3H, m), 7.85 (1H, dd, J = 7.5, 1.8 Hz), 8.22 (1H, dd, J = 7.5, 1.8 Hz) ppm; ^{13}C-NMR (75 MHz, $CDCl_3$): δ 55.8, 64.6, 64.7, 98.4, 103.4, 115.5, 121.9, 122.2, 125.3, 125.7, 126.0, 126.7, 129.2, 132.8, 138.0, 141.4, 155.8 ppm; IR (KBr): 2963 m, 2926 m, 1585 s, 1497 s, 1462 s, 1385 s, 1319 m, 1261 s, 1236 s, 1159 m, 1096 s, 1067 s, 1013 s, 907 m, 812 m, 764 m, 714 w, 686 w cm^{-1}; HRFABMS: calcd for $C_{17}H_{14}O_3S$ $[M]^+$ 298.0664, found 298.0656.

(3ca)



White solid; mp. 100-102 °C; ^{1}H- NMR (300 MHz, $CDCl_3$): δ 2.35 (3H, s), 4.03 (3H, s), 6.82 (1H, d, J = 7.2 Hz), 6.95-6.99 (2H, m), 7.45-7.51 (3H, m), 8.19 (1H, dd, J = 7.5, 1.8 Hz), 8.32 (1H, dd, J = 7.5, 1.8 Hz) ppm; ^{13}C-NMR (75 MHz, $CDCl_3$): δ 15.9, 55.6, 103.2, 120.4, 122.2, 125.0, 125.3, 125.6, 125.7, 126.8, 128.1, 129.4, 132.7, 137.7, 141.9, 155.4 ppm; IR (KBr): 2936 w, 2837 w, 1585 s, 1510 m, 1454 m, 1385 s, 1317 m, 1273 s, 1242 m, 1159 w, 1097 s, 1026 w, 818 m, 745 w, 713 w cm^{-1}; HRFABMS: calcd for $C_{16}H_{14}OS$ $[M]^+$ 254.0765, found 254.0773.

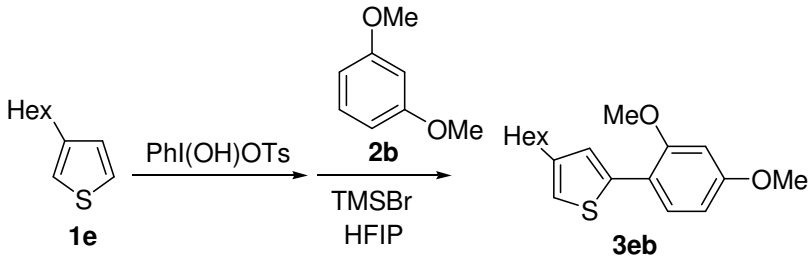
(3da)



1d **3da**

Oil; ^{1}H-NMR: (300 MHz, $CDCl_3$) δ 1.29-1.38 (6H, m), 1.63-1.77 (2H, m), 1.96- 1.99 (2H, m), 2.52-2.60 (1H, m), 3.93 (3H, s), 6.73 (1H, d, J = 8.1 Hz), 6.88 (1H, s), 6.98 (1H, d, J = 1.5 Hz), 7.40-7.43 (3H, m), 8.10-8.13 (1H, m), 8.22-8.25 (1H, m) ppm; ^{13}C-NMR (75 MHz, $CDCl_3$): δ 26.2, 26.6, 34.2, 39.8, 55.5, 103.2, 118.0, 122.1, 125.21, 125.24, 125.55, 125.64, 126.8, 127.2, 128.1, 132.6, 141.5, 149.2, 155.3 ppm; IR (KBr): 2924 s, 2848 s, 1585 s, 1510 m, 1448 s, 1385 s, 1317s, 1242 s, 1159 m, 1097s, 1026 w, 989 w, 815 m, 763 m, 713 m cm^{-1}; HRFABMS: calcd for $C_{21}H_{22}OS$ $[M]^+$ 322.1391, found 322.1399.

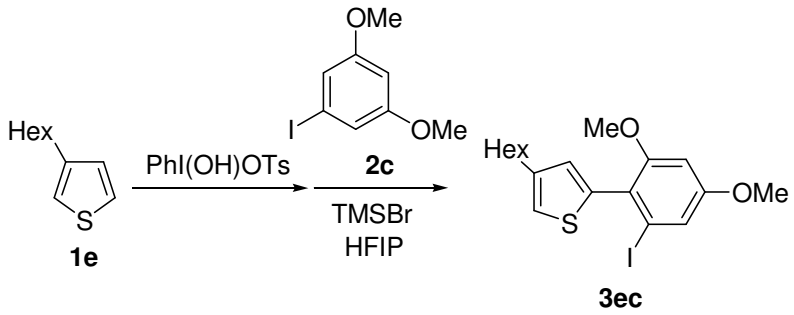
(3eb)



1e **3eb**

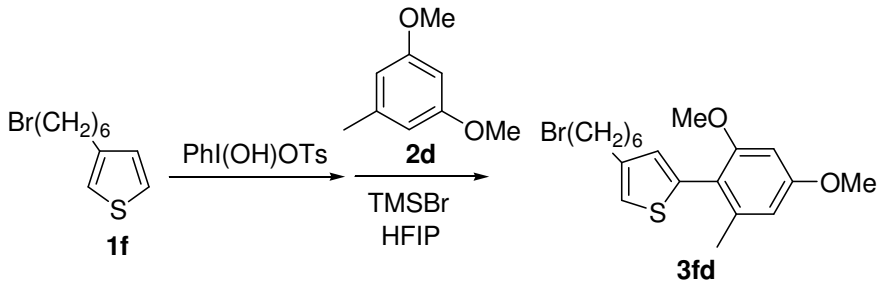
White solid; mp. 38-40 °C; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 0.89 (3H, t, J = 6.4 Hz), 1.29-1.35 (6H, m), 1.68 (2H, m), 2.60 (2H, t, J = 7.5 Hz), 3.82 (3H, s), 3.88 (3H, s), 6.49-6.52 (2H, m), 6.83 (1H, s), 7.21 (1H, s), 7.50 (1H, d, J = 8.8 Hz) ppm; ^{13}C-NMR (75 MHz, $CDCl_3$): δ 14.1, 22.6, 29.1, 30.4, 30.6, 31.7, 55.4, 55.5, 98.9, 104.9, 116.8, 118.9, 125.9, 129.2, 139.1, 142.9, 156.7, 160.0 ppm; IR (KBr): 2928 s, 2855 m, 1611 s, 1578 s, 1504 s, 1462 s, 1435 m, 1304 s, 1273 m, 1159 s, 1130 m, 1032 m, 835 m, 746 w cm^{-1}; HRFABMS: calcd for $C_{18}H_{24}O_2S$ $[M]^+$ 304.1497, found 304.1496.

(3ec)



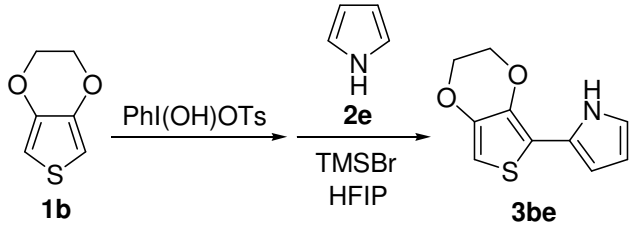
Oil; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 0.86-0.91 (3H, m), 1.25-1.34 (6H, m), 1.65 (2H, t, J = 7.5 Hz), 2.63 (2H, t, J = 7.5 Hz), 3.72 (3H, s), 3.82 (3H, s), 6.49 (1H, d, J = 2.4 Hz), 6.74 (1H, d, J = 1.3 Hz), 6.97 (1H, s, J = 1.3 Hz), 7.07 (1H, d, J = 2.4 Hz) ppm; ^{13}C-NMR (75 MHz, $CDCl_3$): δ 14.1, 21.7, 29.0, 30.3, 30.6, 31.7, 55.7, 56.1, 99.1, 103.6, 115.2, 120.5, 121.7, 129.9, 141.1, 142.7, 158.5, 160.9 ppm; IR (KBr): 3018 w, 2929 w, 1593 w, 1415 w, 1365 m, 1217 m, 1143 w, 1047 w, 908 w, 850 w, 772 s cm^{-1}.

(3fd)



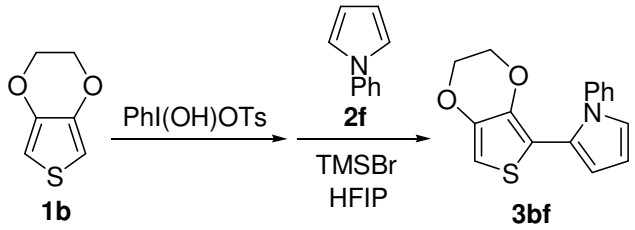
Oil; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 1.38-1.47 (4H, m), 1.66 (2H, q, J = 7.2 Hz), 1.86 (2H, q, J = 7.2 Hz), 2.19 (3H, s), 2.63 (2H, t, J = 7.2 Hz), 3.40 (2H, t, J = 7.2 Hz), 3.73 (3H, s), 3.82 (3H, s), 6.37 (1H, d, J = 1.8 Hz), 6.41 (1H, s), 6.69 (1H, s), 6.94 (1H, s) ppm; ^{13}C-NMR (75 MHz, $CDCl_3$): δ 21.1, 28.0, 28.4, 30.1, 30.4, 32.7, 33.9, 55.3, 55.8, 96.1, 106.4, 116.1, 120.0, 128.9, 137.6, 140.2, 142.3, 158.9, 160.1 ppm; IR (KBr): 2932 s, 2854 m, 1604 s, 1580 s, 1495 w, 1454 s, 1454 s, 1276 w, 1202 s, 1156 s, 1094 s, 1061 m, 931 w, 829 m, 742 m, 642 w cm^{-1}; HRFABMS calcd for $C_{19}H_{25}O_2SBr$ $[M]^+$ 396.0759, found 396.0722.

(3be)



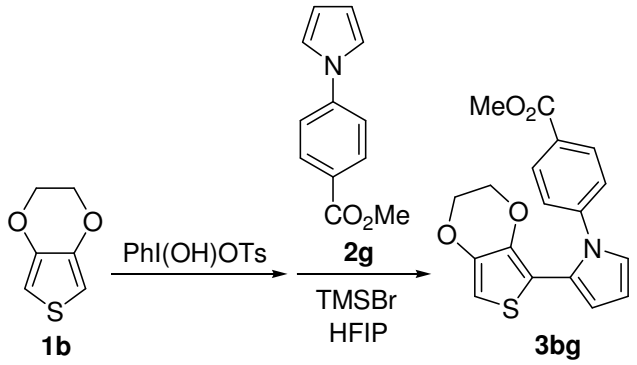
Oil; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 4.21-4.25 (2H, m), 4.29-4.32 (2H, m), 6.11 (1H, s), 6.20-6.23 (1H, m), 6.28-6.33 (1H, m), 6.72-6.73 (1H, m), 9.10 (1H, brs) ppm; ^{13}C-NMR (75 MHz, $CDCl_3$): δ 64.6, 65.0, 94.9, 104.6, 109.0, 111.1, 117.1, 125.5, 135.4, 141.5 ppm; IR (KBr): 3427 w, 3109 w, 2980 w, 2929 w, 2872 w, 1693 w, 1551 m, 1497 s, 1445 s, 1366 s, 1175 m, 1070 s, 910 m, 795 w, 719 s, 654 m cm^{-1}; HRFABMS: calcd for $C_{10}H_9NO_2S$ $[M]^+$ 207.0354, found 207.0357.

(3bf)



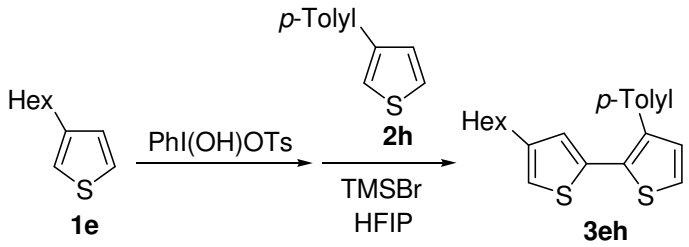
Brown solid; mp. 61-63 °C; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 3.81-3.84 (2H, m), 3.99-4.01 (2H, m), 6.16 (1H, s), 6.33 (1H, dd, J = 3.2, 2.7 Hz), 6.50 (1H, dd, J = 3.2, 1.8 Hz), 6.90 (1H, dd, J = 2.7, 1.8 Hz). 7.20-7.36 (5H, m) ppm; ^{13}C-NMR (75 MHz, $CDCl_3$): δ 64.2, 64.2, 98.2, 108.7, 109.2, 111.7, 123.5, 124.2, 125.7, 126.8, 128.6, 137.8, 140.3, 141.1 ppm; IR (KBr): 3105 w, 2978 w, 2926 w, 2870 w, 1597 m, 1541 m, 1499 s, 1441 s, 1364 s, 1321 m, 1167 s, 1070 s, 1038 m, 910 s, 874 m, 782 w, 694 s cm^{-1}; HRFABMS: calcd for $C_{16}H_{13}NO_2S$ $[M]^+$ 283.0667, found 283.0675.

(3bg)



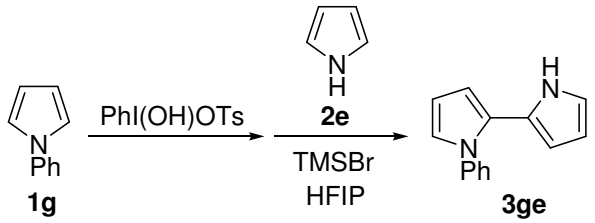
White solid; mp: 128-130 °C; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 3.77-3.79 (2H, m), 3.84 (3H, s), 4.00-4.03 (2H, m), 6.25 (1H, s), 6.38 (1H, dd, J = 3.6, 2.8 Hz), 6.48 (1H, dd, J = 3.6, 1.8 Hz), 6.97 (1H, dd, J = 2.8, 1.8 Hz), 7.30 (2H, d, J = 9.0 Hz), 8.02 (2H, d, J = 9.0 Hz) ppm; ^{13}C-NMR (75 MHz, $CDCl_3$): δ 52.2, 64.2, 64.3, 98.8, 108.2, 110.1, 112.9, 123.2, 123.9, 124.6, 127.9, 130.2, 138.0, 141.2, 144.4, 166.5 ppm; IR (KBr): 3109 w, 2951 w, 2928 w, 2872 w, 1720 s, 1607 s, 1514 s, 1435 s, 1366 s, 1279 s, 1171 m, 1070 s, 910 m, 796 w, 717 m cm^{-1}; HRFABMS: calcd for $C_{18}H_{15}NO_4S$ $[M]^+$ 341.0722, found 341.0739.

(3eh)



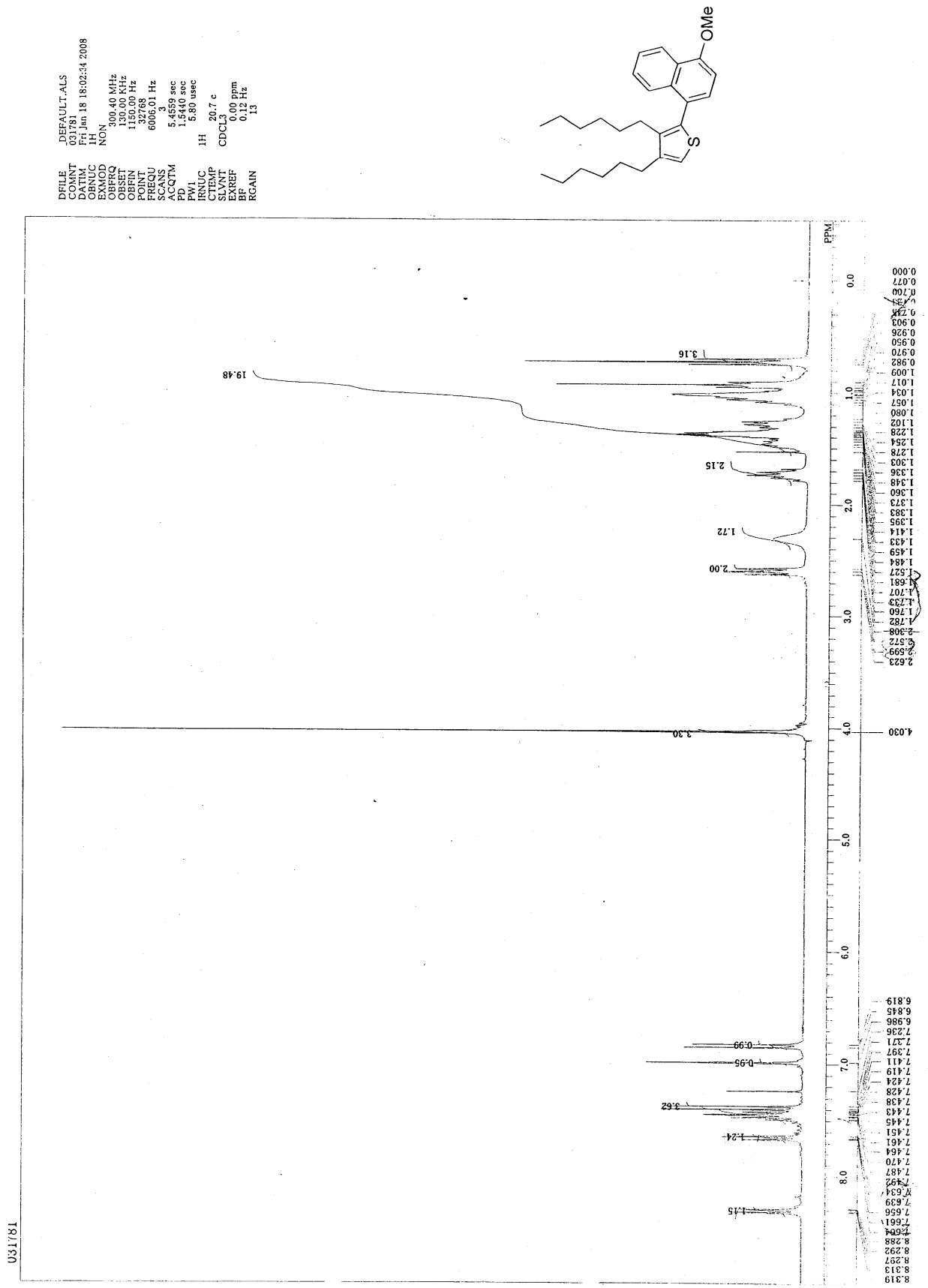
Oil; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 0.86-0.88 (3H, t, J = 6.6 Hz), 1.07-1.32 (6H, m), 1.51-1.53 (2H, m), 2.37 (3H, s), 2.50 (2H, t, J = 7.5 Hz), 6.75 (1H, s), 6.81 (1H, d, J = 1.3Hz), 7.03 (1H, d, J = 5.1Hz), 7.13-7.27 (5H, m) ppm; ^{13}C-NMR (75 MHz, $CDCl_3$): δ 14.1, 21.3, 22.6, 28.9, 30.3, 30.4, 31.7, 120.3, 123.6, 127.9, 129.0, 129.1, 130.5, 131.7, 133.3, 135.6, 137.0, 138.60, 143.4 ppm; IR (KBr): 2953 s, 2926 s, 2855 s, 1730 w, 1504 s, 1454 m, 1275 w, 1182 w, 1109 w, 879 w, 879 w, 818 s, 731 s, 667 m cm^{-1}; HRFABMS: calcd for $C_{21}H_{24}S_2$ $[M]^+$ 340.1319, found 340.1396.

(3ge)

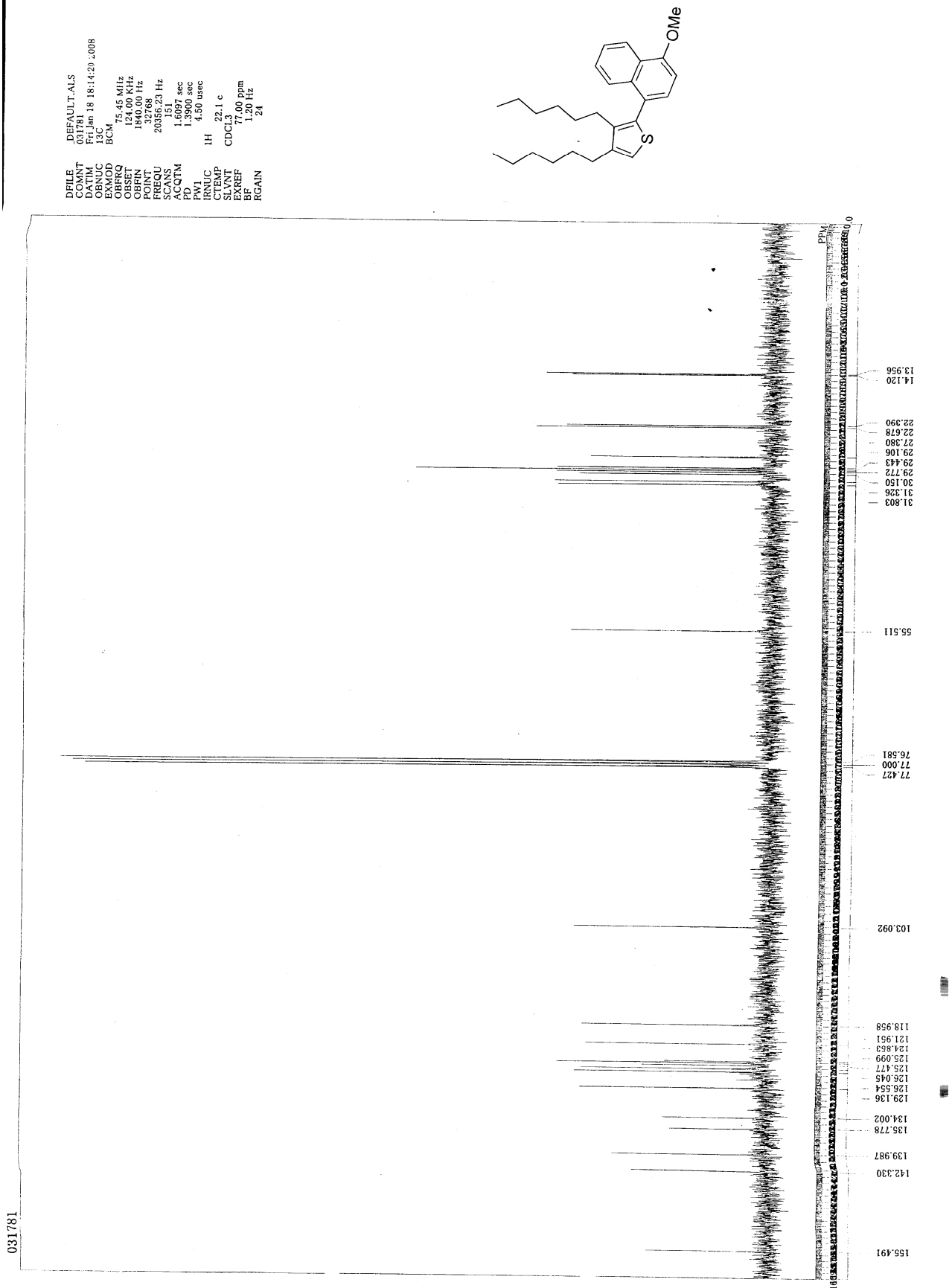


Brown solid; mp: 120-122 ^{o}C; ^{1}H-NMR (300 MHz, $CDCl_3$): δ5.81-5.84 (1H, m), 6.07-6.11 (1H, m), 6.30-6.36 (2H, m), 6.63 (1H, m), 6.85 (1H, dd, J = 2.7, 1.8 Hz), 7.23-7.37 (5H, m), 7.83 (1H, brs) ppm; ^{13}C-NMR (75 MHz, $CDCl_3$): δ 107.5, 108.4, 108.8, 109.0, 117.5, 123.2, 124.2, 125.9, 126.8, 127.2, 129.0, 140.3 ppm; IR (KBr): 3389 m, 3103 w, 3001 w, 2926 w, 2853 w, 1597 m, 1499 s, 1400 m ,1219 m, 1034 m, 907, w, 772 s, 719 s, 667 cm^{-1}; HRFABMS: calcd for $C_{14}H_{12}N_2$ $[M]^+$ 208.1000, found 208.0995.

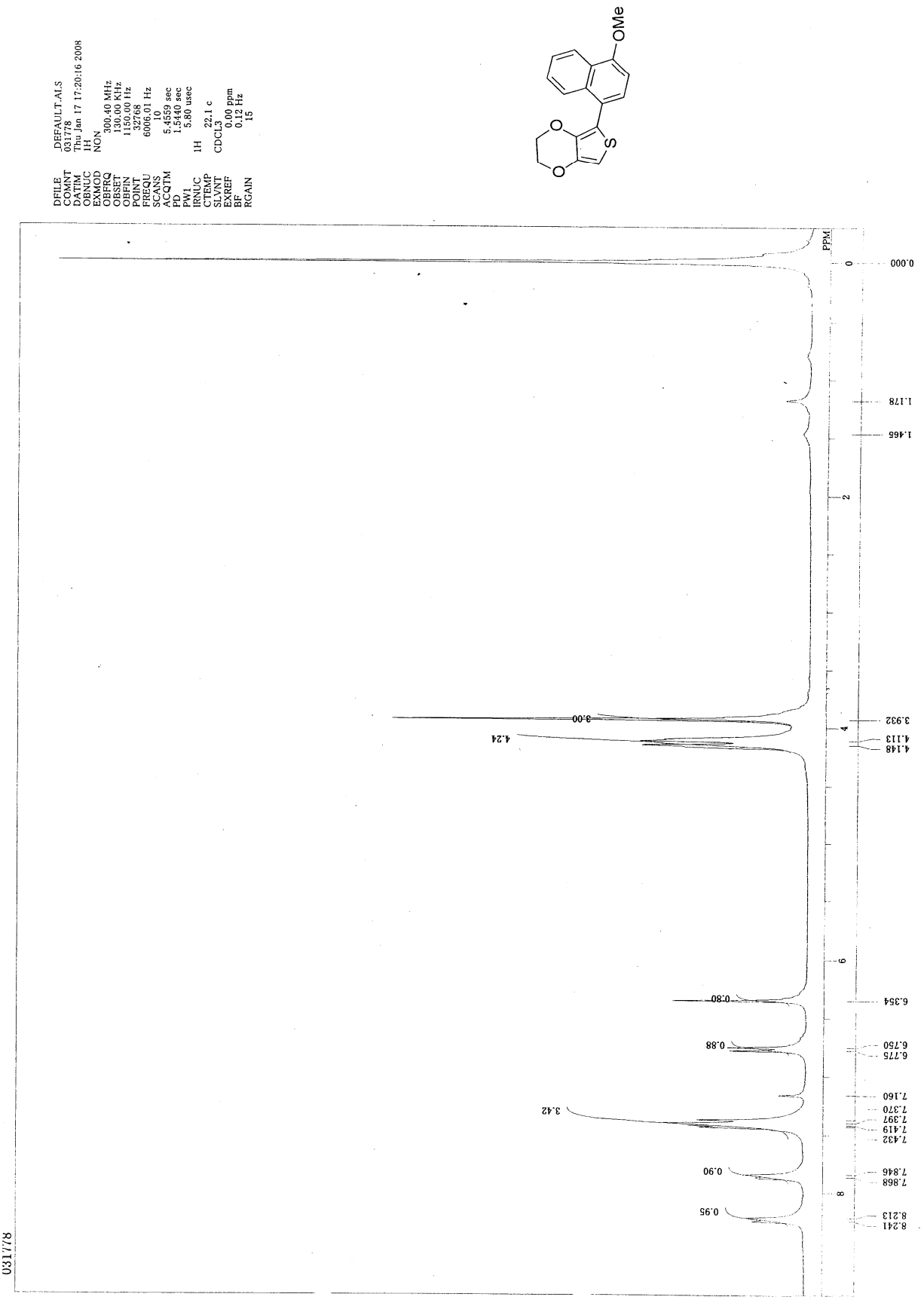
3aa


OMe
S
DFILE _DEFAULT.ALS
COMNT 031781
DATIM Fri Jan 18 18:02:34 2008
OBNUC 1H
EXMOD NON
OBFRQ 300.40 MHz
OBSET 130.00 KHz
OBFIN 11150.00 Hz
POINT 32768
FREQU 6006.01 Hz
SCANS 3
ACQTM 5.4559 sec
PD 1.5440 sec
PW1 5.80 usec
IRNUC 1H
CTEMP 20.7 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 13
PPM
19.48
3.16
2.15
1.72
2.00
3.30
0.99
0.95
3.62
1.24
1.45
4.030
031781

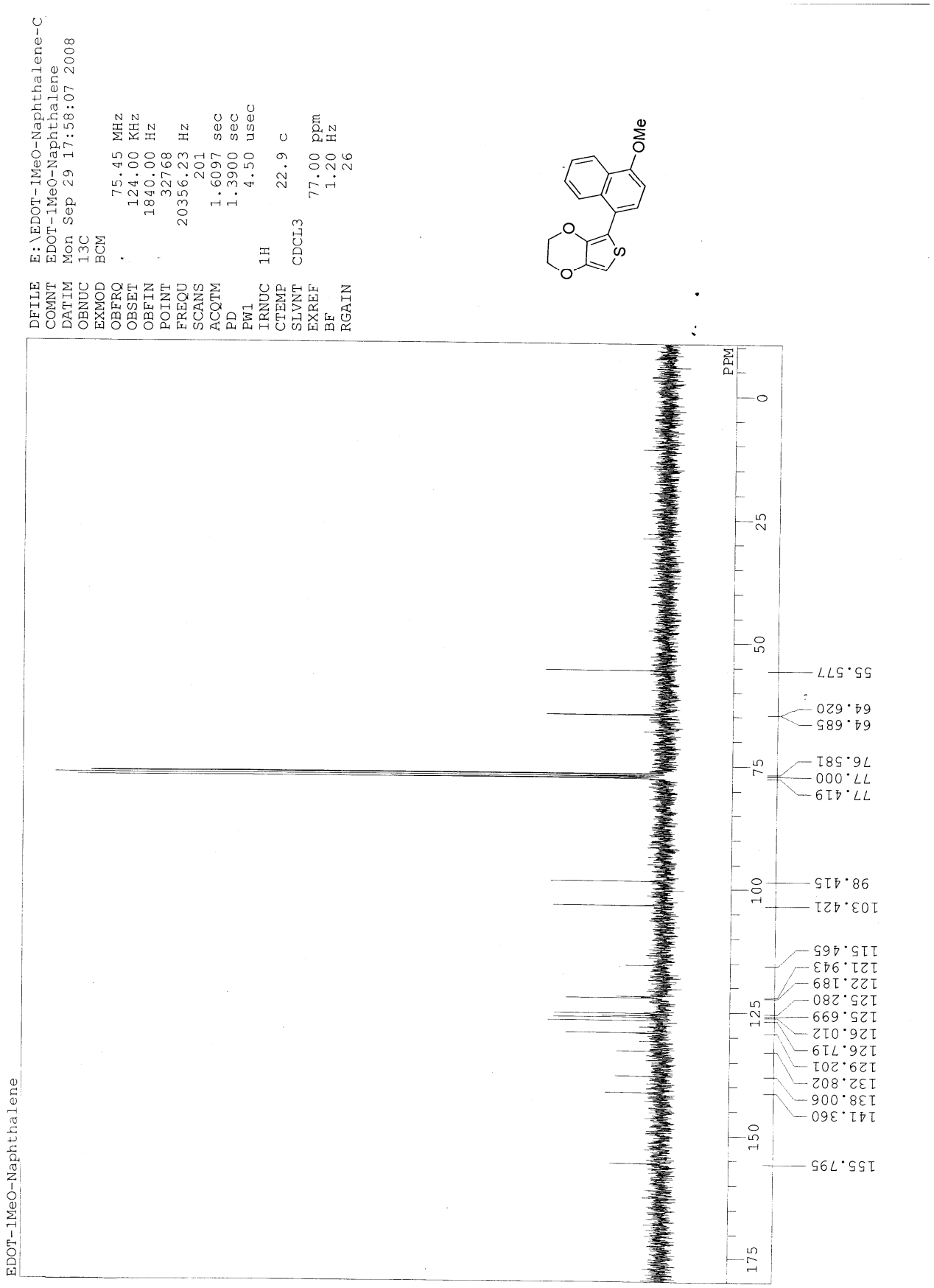
3aa


DFILE DEFAULT.ALS
COMNT 031781
DATIM Fri Jan 18 18:14:20 2008
OBNUC 13C
EXMOD BCM
OBFRQ 75.45 MHz
OBSET 124.00 KHz
OBFIN 1840.00 Hz
POINT 32768
FREQU 20356.23 Hz
SCANS 151
ACQTM 1.6097 sec
PD 1.3900 sec
PW1 4.50 usec
IRNUC 1H
CTEMP 22.1 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 1.20 Hz
RGAIN 24
OMe
S
031781
PPM
13.956
14.120
22.390
22.678
27.380
29.106
29.443
29.772
30.150
31.326
31.803
55.511
76.581
77.000
77.427
103.092
118.958
121.961
124.863
125.099
125.477
126.045
126.654
129.136
134.002
135.778
139.987
142.330
155.491

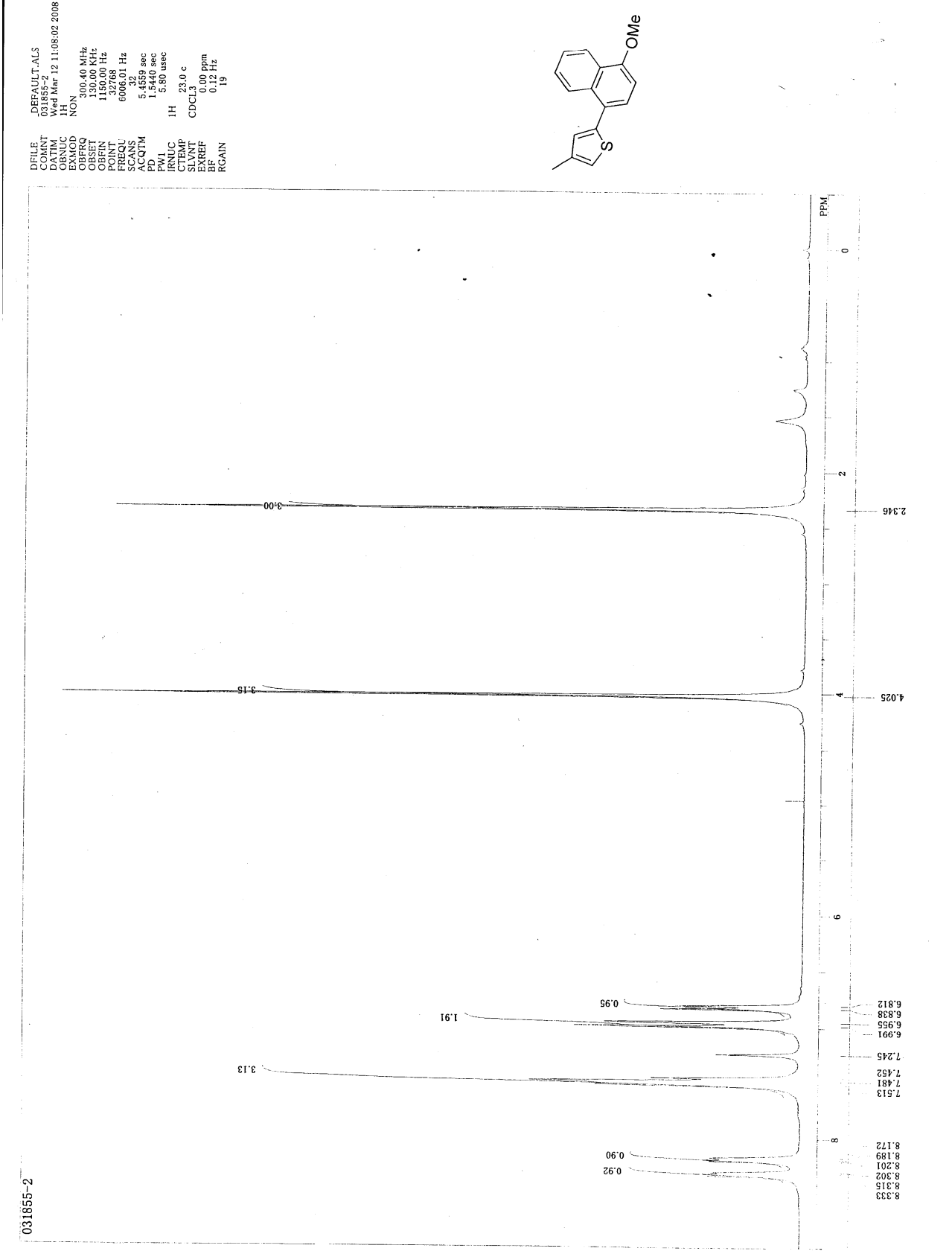
3ba


DFILE DEFAULT.AI.S
COMNT 031778
DATIM Thu Jan 17 17:20:16 2008
OBNUC 1H
EXMOD NON
OBFRQ 300.40 MHz
OBSET 130.00 KHz
OBFIN 1150.00 Hz
POINT 32768
FREQU 6006.01 Hz
SCANS 16
ACQTM 5.4559 sec
PD 1.5440 sec
PW1 5.80 usec
IRNUC 1H
CTEMP 22.1 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 15
OMe
S
O
O
PPM
0.000
1.178
1.465
3.932
4.113
4.148
6.354
6.750
6.775
7.160
7.370
7.397
7.419
7.432
7.846
7.868
8.213
8.241
3.00
4.24
0.80
0.88
3.42
0.90
0.95
031778

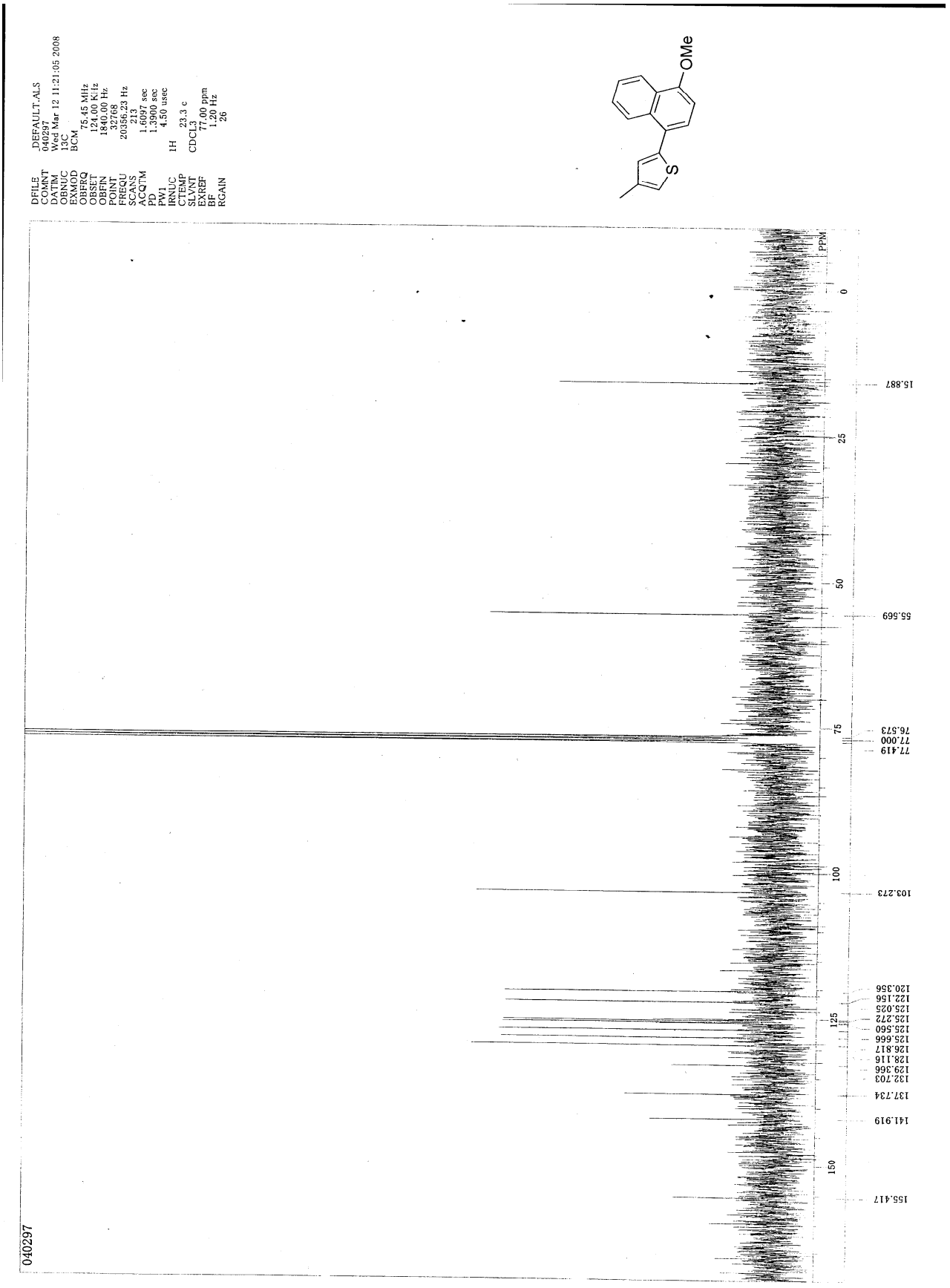
3ba


DFILE E:\EDOT-1MeO-Naphthalene-C
COMNT EDOT-1MeO-Naphthalene
DATIM Mon Sep 29 17:58:07 2008
OBNUC 13C
EXMOD BCM
OBFRQ 75.45 MHz
OBSET 124.00 KHz
OBFIN 1840.00 Hz
POINT 32768
FREQU 20356.23 Hz
SCANS 201
ACQTM 1.6097 sec
PD 1.3900 sec
PW1 4.50 usec
IRNUC 1H
CTEMP 22.9 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 1.20 Hz
RGAIN 26
OMe
O
O
S
EDOT-1MeO-Naphthalene
PPM
0
25
50
75
100
125
150
175
55.577
64.685
64.620
76.581
77.000
77.419
98.415
103.421
115.465
121.943
122.189
125.280
125.699
126.012
126.719
129.201
132.802
138.006
141.360
155.795

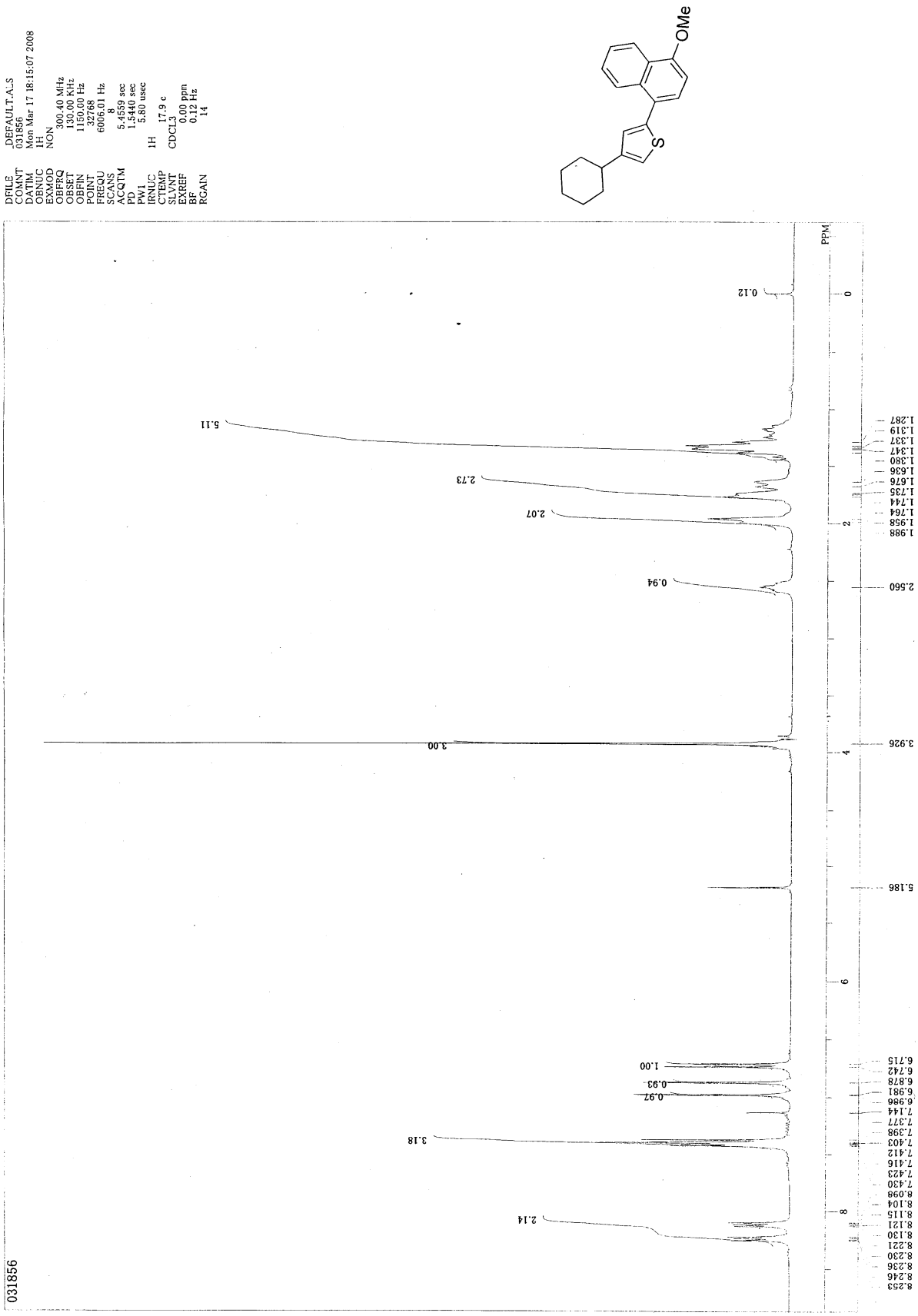
3ca


DFILE DEFAULT.ALS
COMNT 031855-2
DATIM Wed Mar 12 11:08:02 2008
OBNUC 1H
EXMOD NON
OBFRQ 300.40 MHz
OBSET 130.00 KHz
OBFIN 1150.00 Hz
POINT 32768
FREQU 6006.01 Hz
SCANS 32
ACQTM 5.4559 sec
PD 1.5440 sec
PW1 5.80 usec
IRNUC 1H
CTEMP 23.0 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 19
OMe
S
PPM
031855-2
3.00
3.15
3.13
1.91
0.95
0.92
0.90
2.346
4.025
8.333
8.315
8.302
8.201
8.189
8.172
7.513
7.481
7.452
7.245
6.991
6.955
6.838
6.812

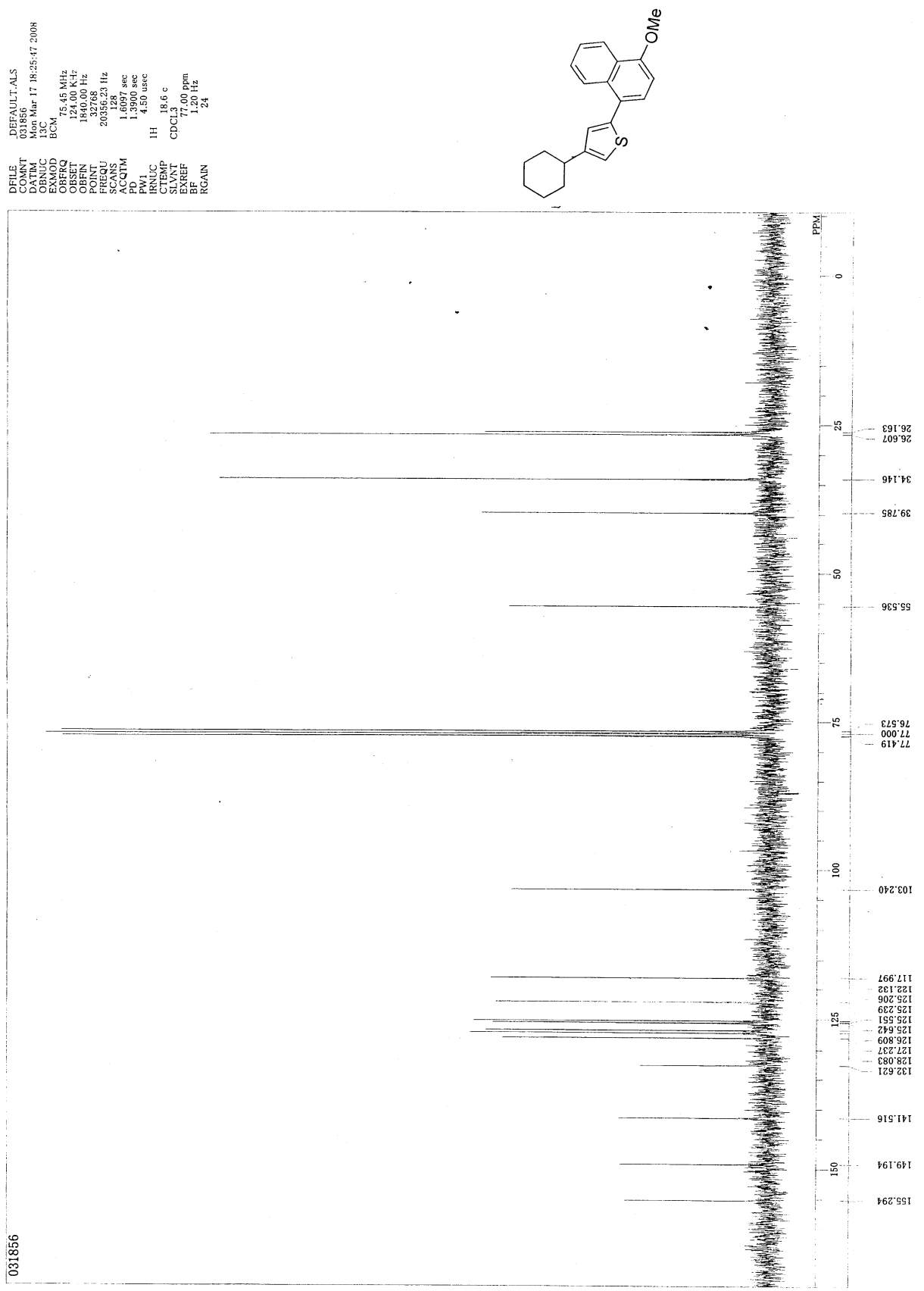
3ca


DFILE DEFAULT.ALS
COMNT 040297
DATIM Wed Mar 12 11:21:05 2008
OBNUC 13C
EXMOD BCM
OBFRQ 75.45 MHz
OBSET 124.00 KHz
OBFIN 1840.00 Hz
POINT 32768
FREQU 20356.23 Hz
SCANS 213
ACQTM 1.6097 sec
PD 1.3900 sec
PW1 4.50 usec
IRNUC 1H 23.3 c
CTEMP
SLVNT CDCL3
EXREF 77.00 ppm
BF 1.20 Hz
RGAIN 26
OMe
S
PPM
0
25
50
75
100
125
150
15.887
55.569
76.573
77.000
77.419
103.273
120.356
122.156
125.025
125.272
125.560
125.666
126.817
128.116
129.366
132.703
137.734
141.919
155.417
040297

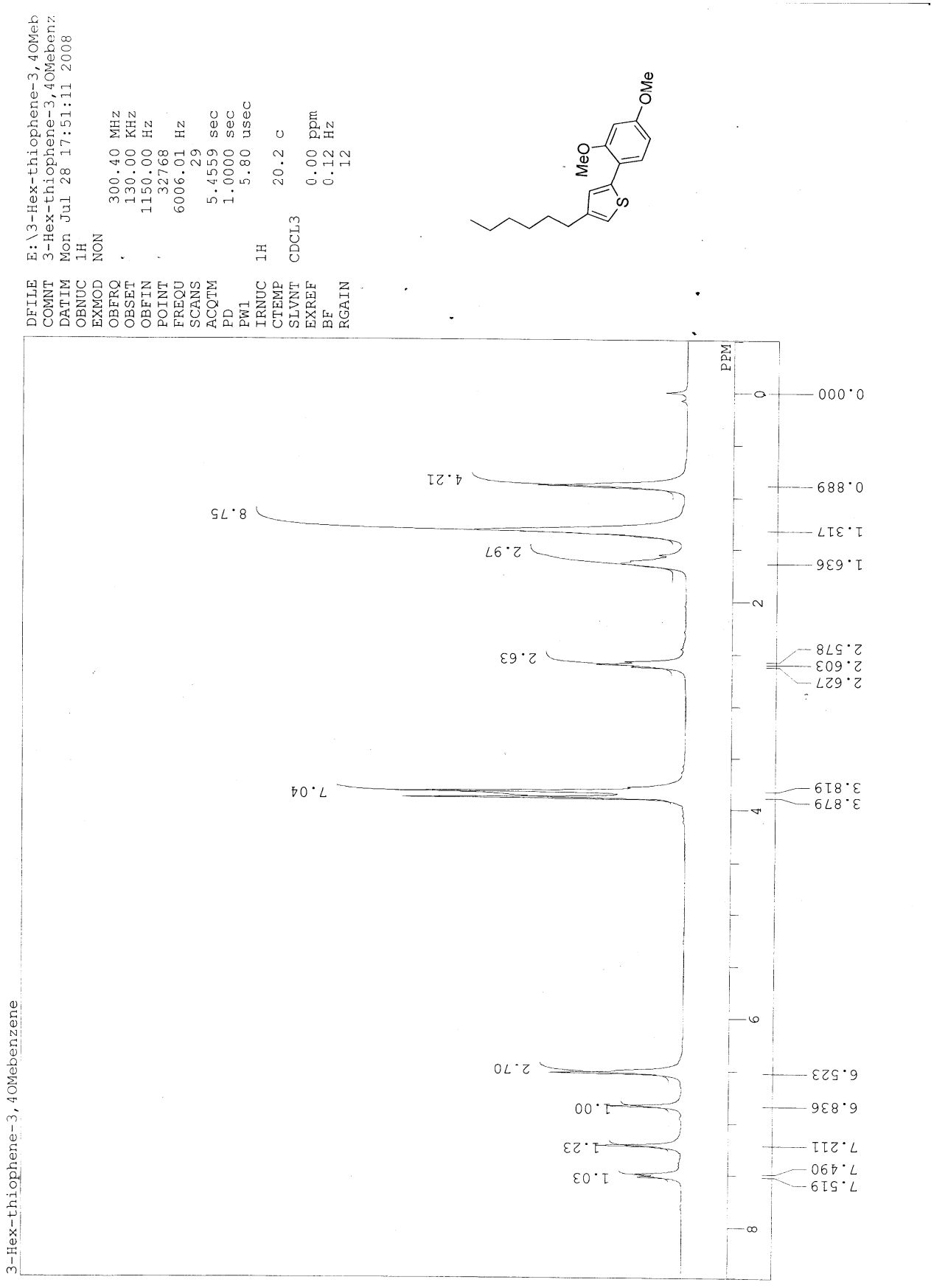
3da


DFILE DEFAULT.A.S
COMNT 031856
DATIM Mon Mar 17 18:15:07 2008
OBNUC 1H
EXMOD NON
OBFRQ 300.40 MHz
OBSET 150.00 KHz
OBFIN 1150.00 Hz
POINT 32768
FREQU 6006.01 Hz
SCANS 8
ACQTM 5.4559 sec
PD 1.5440 sec
PW1 5.80 usec
IRNUC 1H
CTEMP 17.9 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 14
OMe
S
PPM
031856

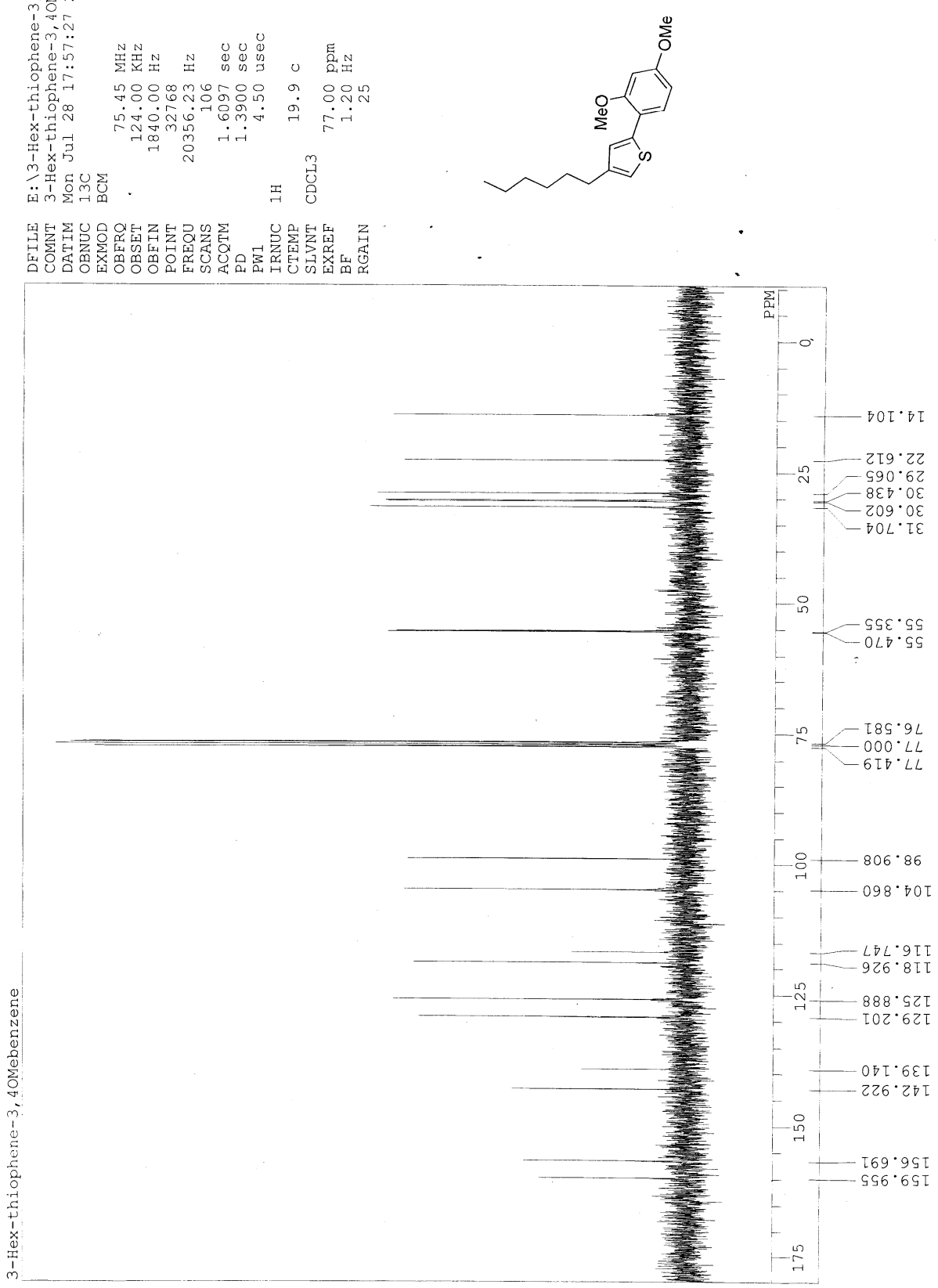
3da


DFILE DEFAULT.ALS
COMNT 031856
DATIM Mon Mar 17 18:25:47 2008
OBNUC 13C
EXMOD BCM
OBFRQ 75.45 MHz
OBSET 124.00 KHz
OBFIN 1840.00 Hz
POINT 32768
FREQU 20356.23 Hz
SCANS 128
ACQTM 1.6097 sec
PD 1.3900 sec
PW1 4.50 usec
IRNUC 1H
CTEMP 18.6 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 1.20 Hz
RGAIN 24
OMe
S
PPM
0
25
50
75
100
125
150
26.163
26.607
34.146
39.785
55.536
76.573
77.000
77.419
103.240
117.997
122.132
125.206
125.239
125.551
125.642
126.809
127.237
128.083
132.621
141.516
149.194
155.294
031856

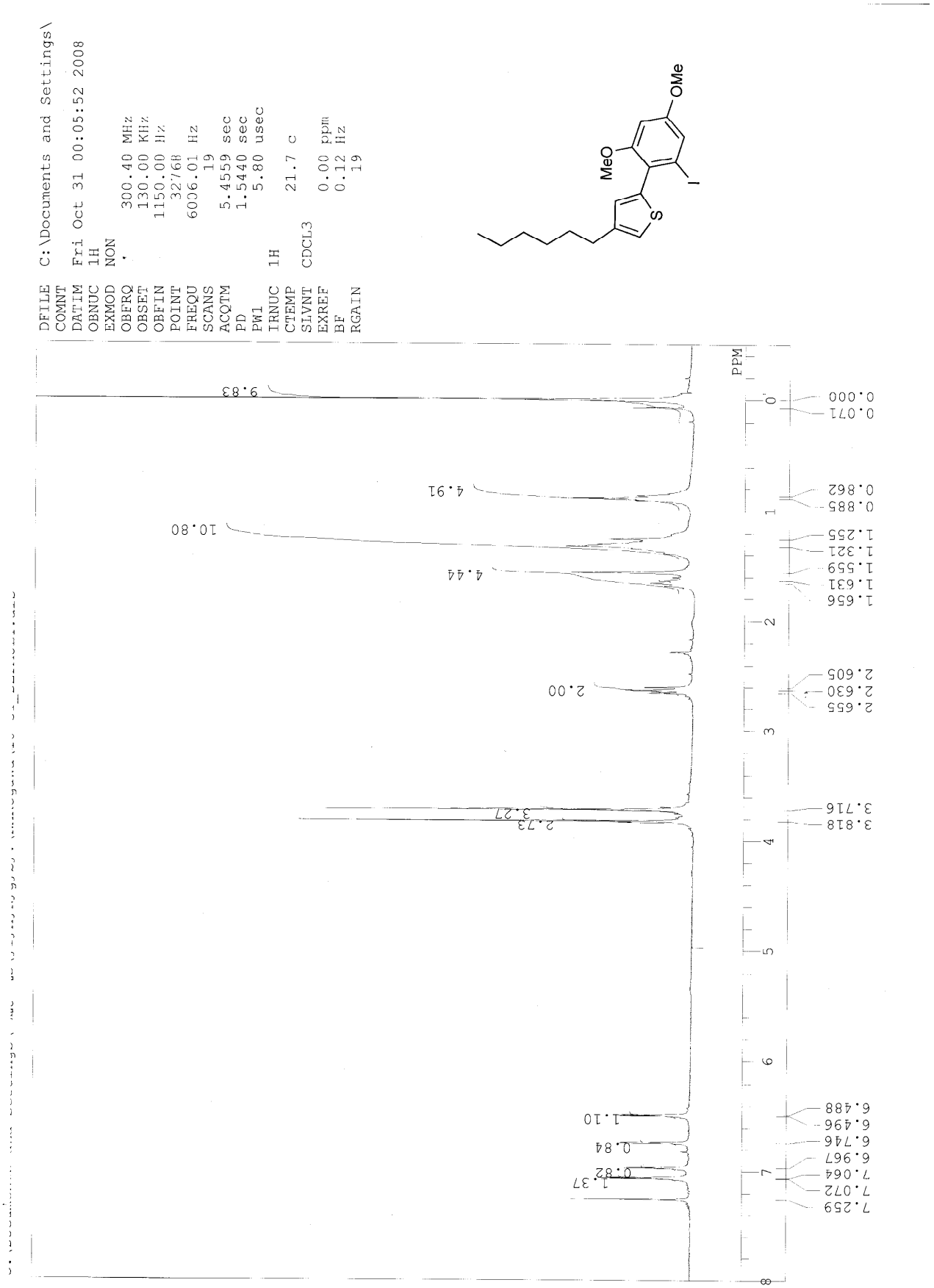
3eb


3-Hex-thiophene-3,4OMebenzene
DFILE E:\3-Hex-thiophene-3,4OMeb
COMNT 3-Hex-thiophene-3,4OMebenz
DATIM Mon Jul 28 17:51:11 2008
OBNUC 1H
EXMOD NON
OBFRQ 300.40 MHz
OBSET 130.00 KHz
OBFIN 1150.00 Hz
POINT 32768
FREQU 6006.01 Hz
SCANS 29
ACQTM 5.4559 sec
PD 1.0000 sec
PW1 5.80 usec
IRNUC 1H
CTEMP 20.2 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 12
MeO
OMe
S
PPM
0.000
0.889
1.317
1.636
2.578
2.603
2.627
3.819
3.879
7.211
7.490
7.519
6.523
6.836
2.70
1.00
1.23
1.03
7.04
2.63
8.75
4.21
2.97

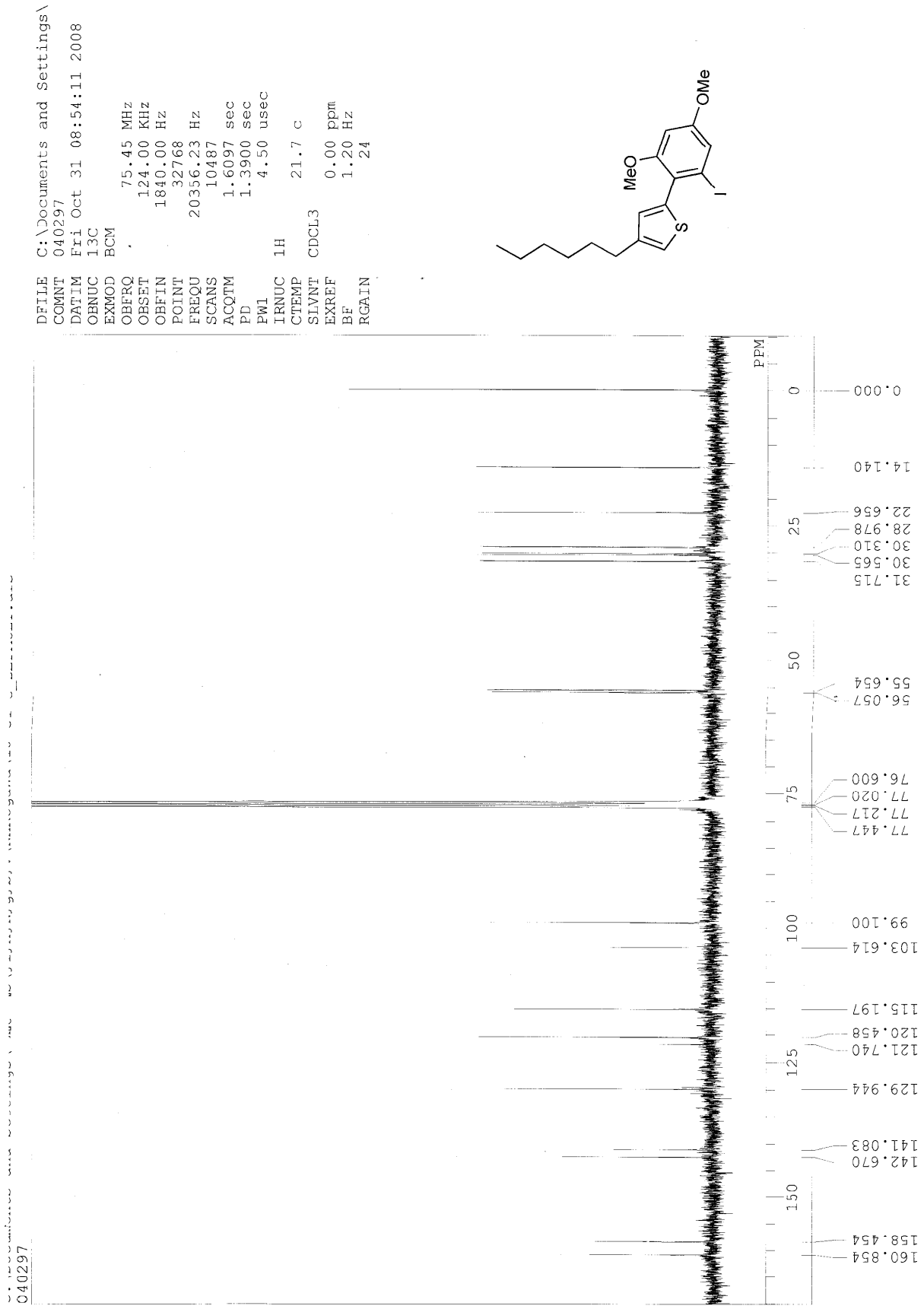
3eb


DFILE E:\3-Hex-thiophene-3,4OMeb
COMNT 3-Hex-thiophene-3,4OMebenz
DATIM Mon Jul 28 17:57:27 2008
OBNUC 13C
EXMOD BCM
OBFRQ 75.45 MHz
OBSET 124.00 KHz
OBFIN 1840.00 Hz
POINT 32768
FREQU 20356.23 Hz
SCANS 106
ACQTM 1.6097 sec
PD 1.3900 sec
PW1 4.50 usec
IRNUC 1H
CTEMP 19.9 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 1.20 Hz
RGAIN 25
MeO
OMe
S
3-Hex-thiophene-3,4OMebenzene
PPM
0
25
50
75
100
125
150
175
14.104
22.612
29.065
30.438
30.602
31.704
55.355
55.470
76.581
77.000
77.419
98.908
104.860
116.747
118.926
125.888
129.201
139.140
142.922
156.691
159.955

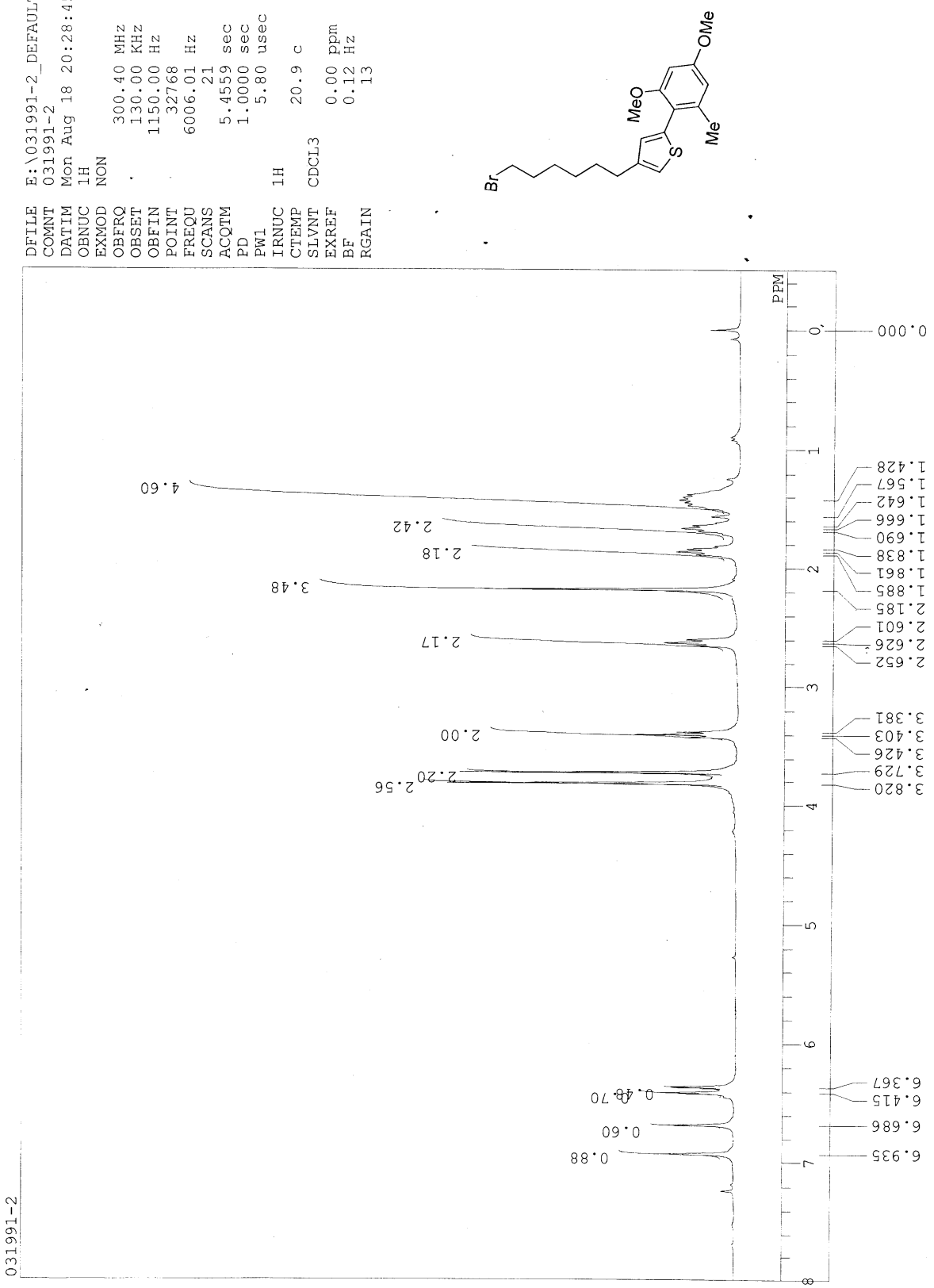
3ec


DFILE C:\Documents and Settings\
COMNT
DATIM Fri Oct 31 00:05:52 2008
OBNUC 1H
EXMOD NON
OBFRQ 300.40 MHz
OBSET 130.00 KHz
OBFIN 1150.00 Hz
POINT 32768
FREQU 6006.01 Hz
SCANS 19
ACQTM 5.4559 sec
PD 1.5440 sec
PW1 5.80 usec
IRNUC 1H
CTEMP 21.7 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 19
MeO
OMe
I
S
PPM
9.83
4.91
10.80
4.44
2.00
2.73
3.27
1.10
0.84
0.82
1.37
7.259
7.072
7.064
6.967
6.746
6.496
6.488
3.818
3.716
2.655
2.630
2.605
1.656
1.631
1.559
1.321
1.255
0.862
0.885
0.071
0.000

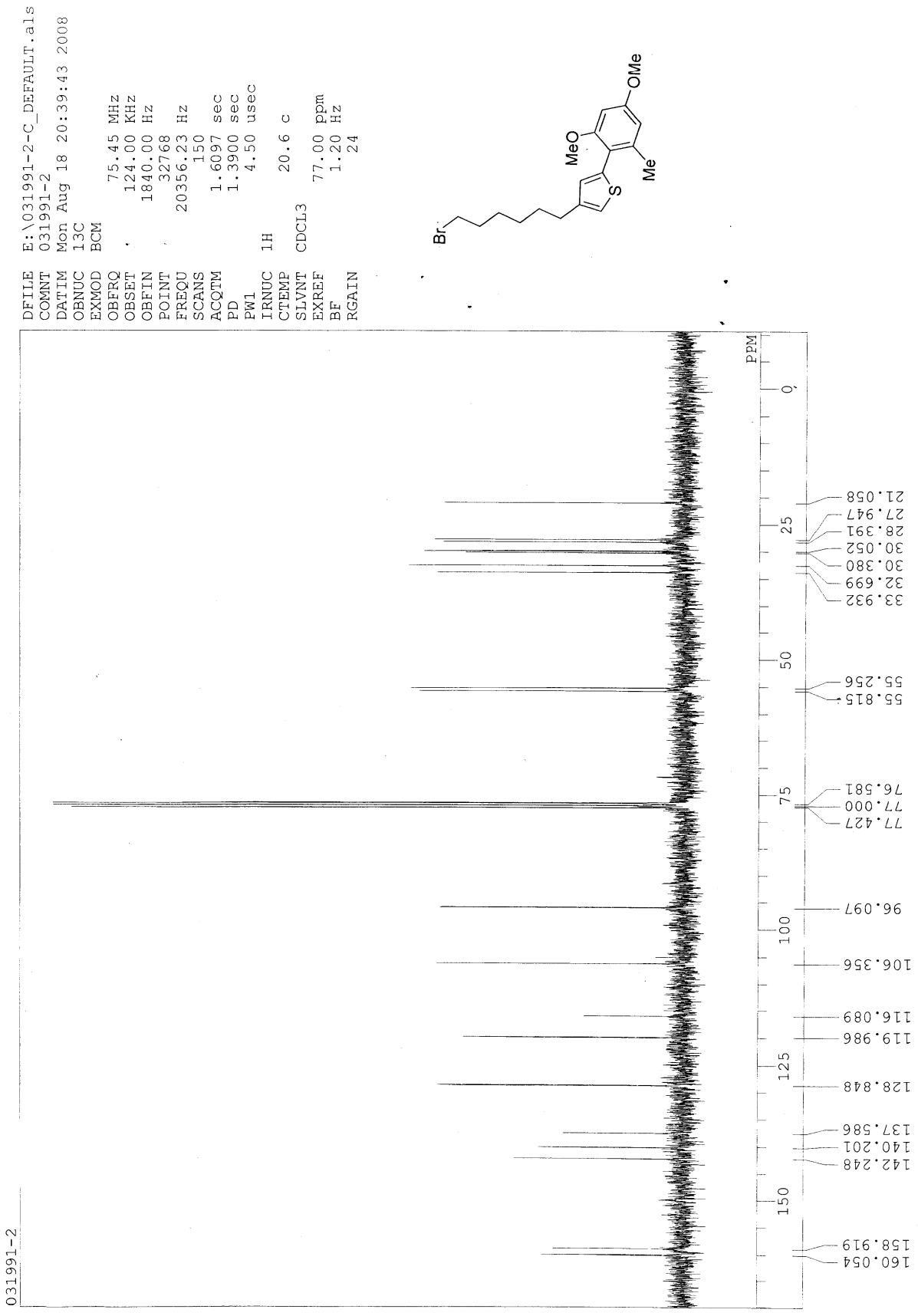
3ec


DFILE C:\Documents and Settings\
COMNT 040297
DATIM Fri Oct 31 08:54:11 2008
OBNUC 13C
EXMOD BCM
OBFRQ 75.45 MHz
OBSET 124.00 KHz
OBFIN 1840.00 Hz
POINT 32768
FREQU 20356.23 Hz
SCANS 10487
ACQTM 1.6097 sec
PD 1.3900 sec
PW1 4.50 usec
IRNUC 1H
CTEMP 21.7 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 1.20 Hz
RGAIN 24
MeO
OMe
I
S
040297
PPM
0.000
14.140
22.656
28.978
30.310
30.565
31.715
55.654
56.057
76.600
77.020
77.217
77.447
99.100
103.614
115.197
120.458
121.740
129.944
141.083
142.670
158.454
160.854

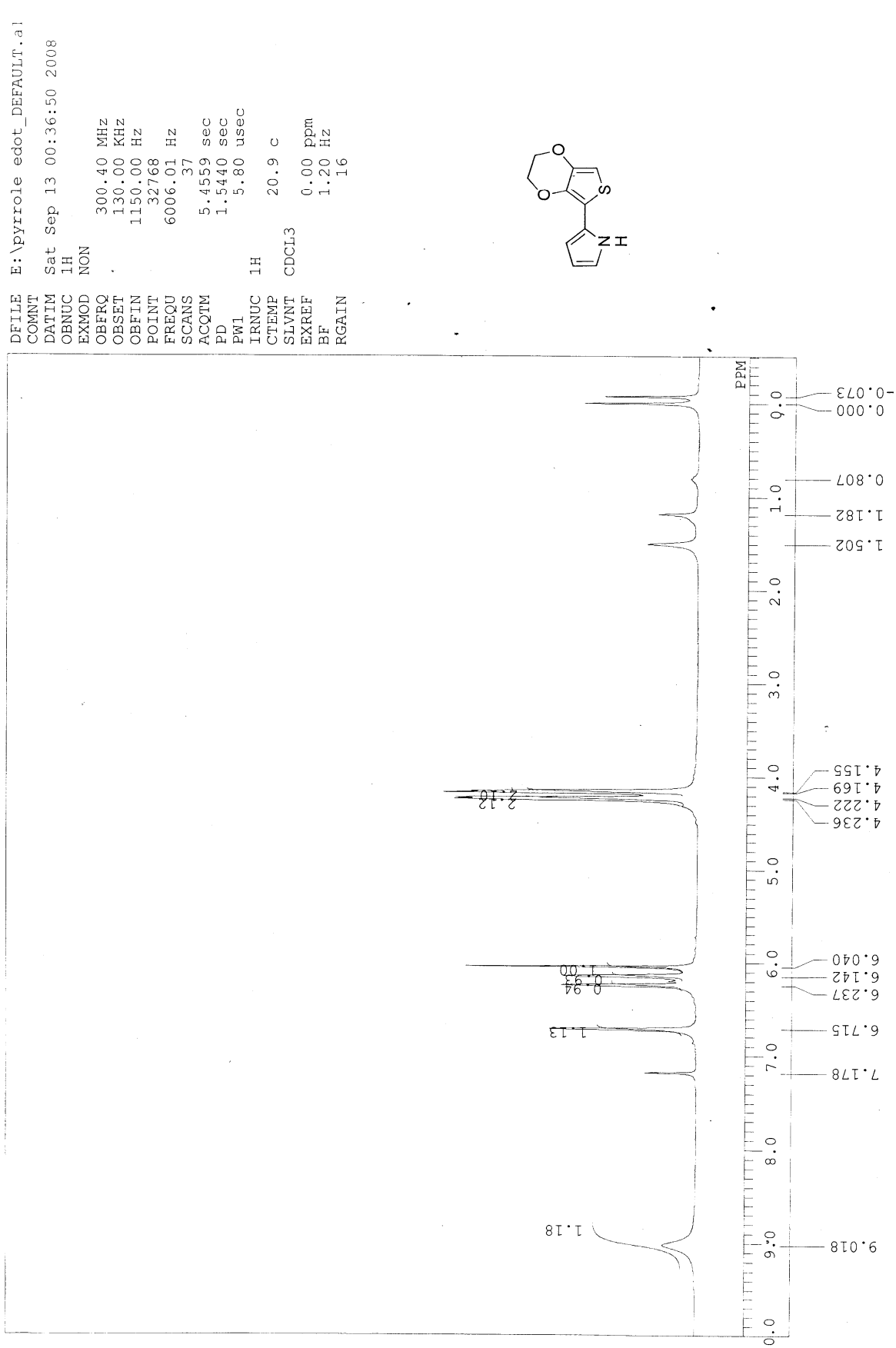
3fd


DFILE E:\031991-2_DEFAULT.als
COMNT 031991-2
DATIM Mon Aug 18 20:28:45 2008
OBNUC 1H
EXMOD NON
OBFRQ 300.40 MHz
OBSET 130.00 KHz
OBFIN 1150.00 Hz
POINT 32768
FREQU 6006.01 Hz
SCANS 21
ACQTM 5.4559 sec
PD 1.0000 sec
PW1 5.80 usec
IRNUC 1H
CTEMP 20.9 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 13
MeO
OMe
Me
S
Br
031991-2
PPM
0.000
1.428
1.567
1.642
1.666
1.690
1.838
1.861
1.885
2.185
2.601
2.626
2.652
3.381
3.403
3.426
3.729
3.820
6.367
6.415
6.686
6.935
0.88
0.60
0.48 0.70
2.20 2.56
2.00
2.17
3.48
2.18
2.42
4.60

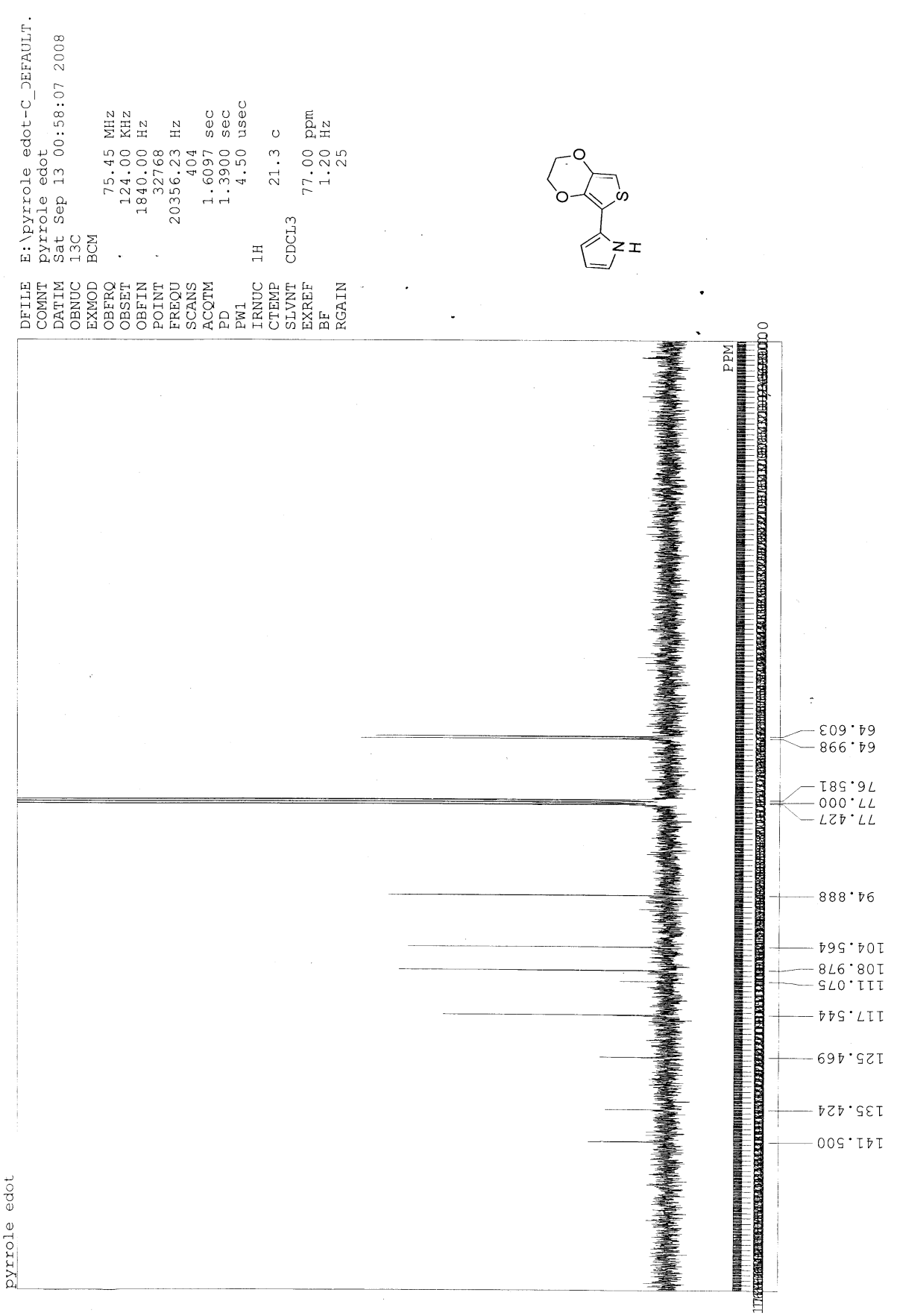
3fd


DFILE E:\031991-2-C_DEFAULT.als
COMNT 031991-2
DATIM Mon Aug 18 20:39:43 2008
OBNUC 13C
EXMOD BCM
OBFRQ 75.45 MHz
OBSET 124.00 KHz
OBFIN 1840.00 Hz
POINT 32768
FREQU 20356.23 Hz
SCANS 150
ACQTM 1.6097 sec
PD 1.3900 sec
PW1 4.50 usec
IRNUC 1H
CTEMP 20.6 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 1.20 Hz
RGAIN 24
Br
MeO
OMe
Me
S
031991-2
PPM
0
25
50
75
100
125
150
21.058
27.947
28.391
30.052
30.380
32.699
33.932
55.815
55.256
76.581
77.000
77.427
96.097
106.356
116.089
119.986
128.848
137.586
140.201
142.248
158.919
160.054

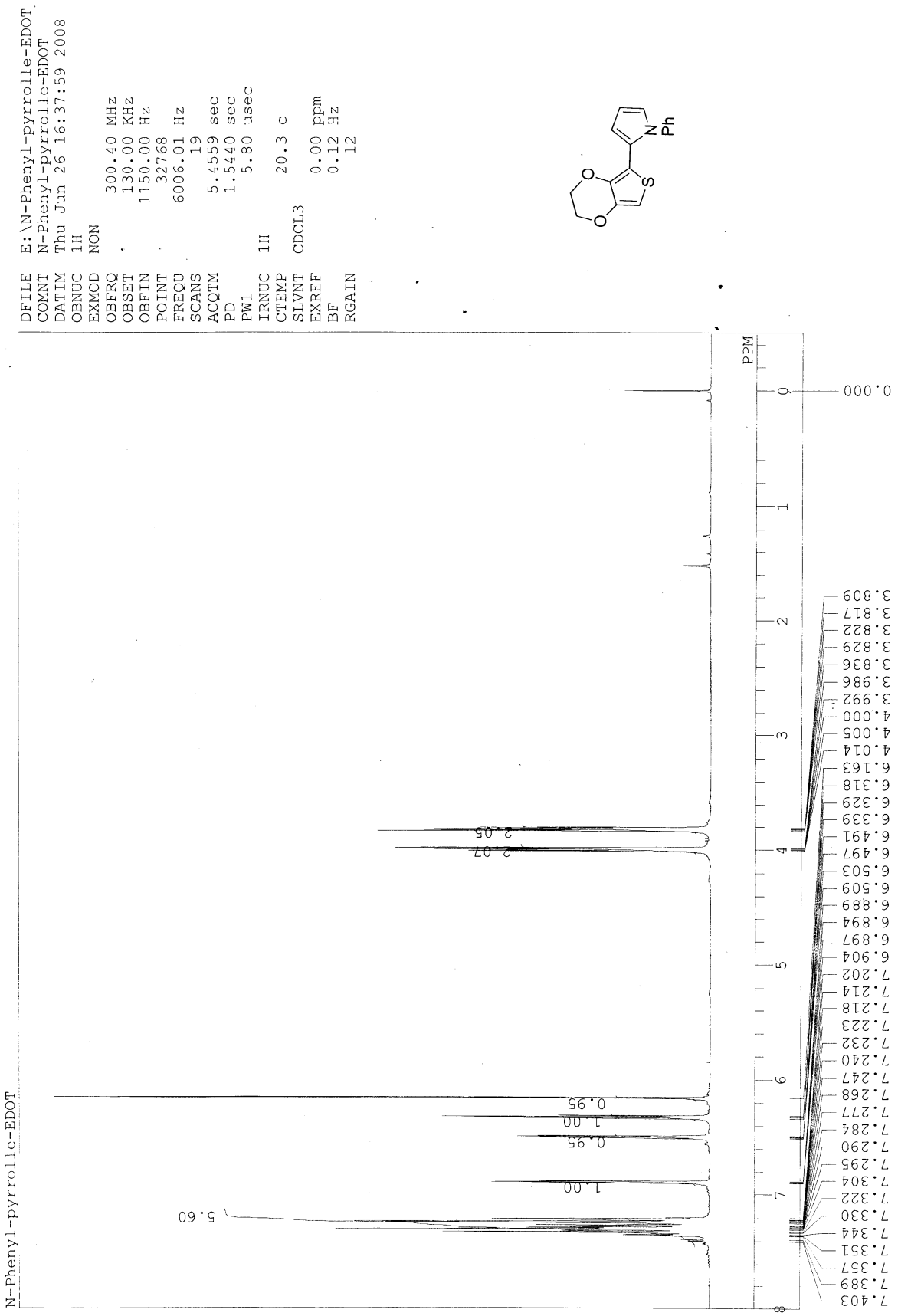
3be


DFILE E:\pyrrole edot_DEFAULT.a1
COMNT
DATIM Sat Sep 13 00:36:50 2008
OBNUC 1H
EXMOD NON
OBFRQ 300.40 MHz
OBSET 130.00 KHz
OBFIN 1150.00 Hz
POINT 32768
FREQU 6006.01 Hz
SCANS 37
ACQTM 5.4559 sec
PD 1.5440 sec
PW1 5.80 usec
IRNUC 1H
CTEMP 20.9 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 1.20 Hz
RGAIN 16
PPM
-0.073
0.000
0.807
1.182
1.502
4.155
4.169
4.222
4.236
6.040
6.142
6.237
6.715
7.178
9.018
2.12
1.00
0.94
1.13
1.18

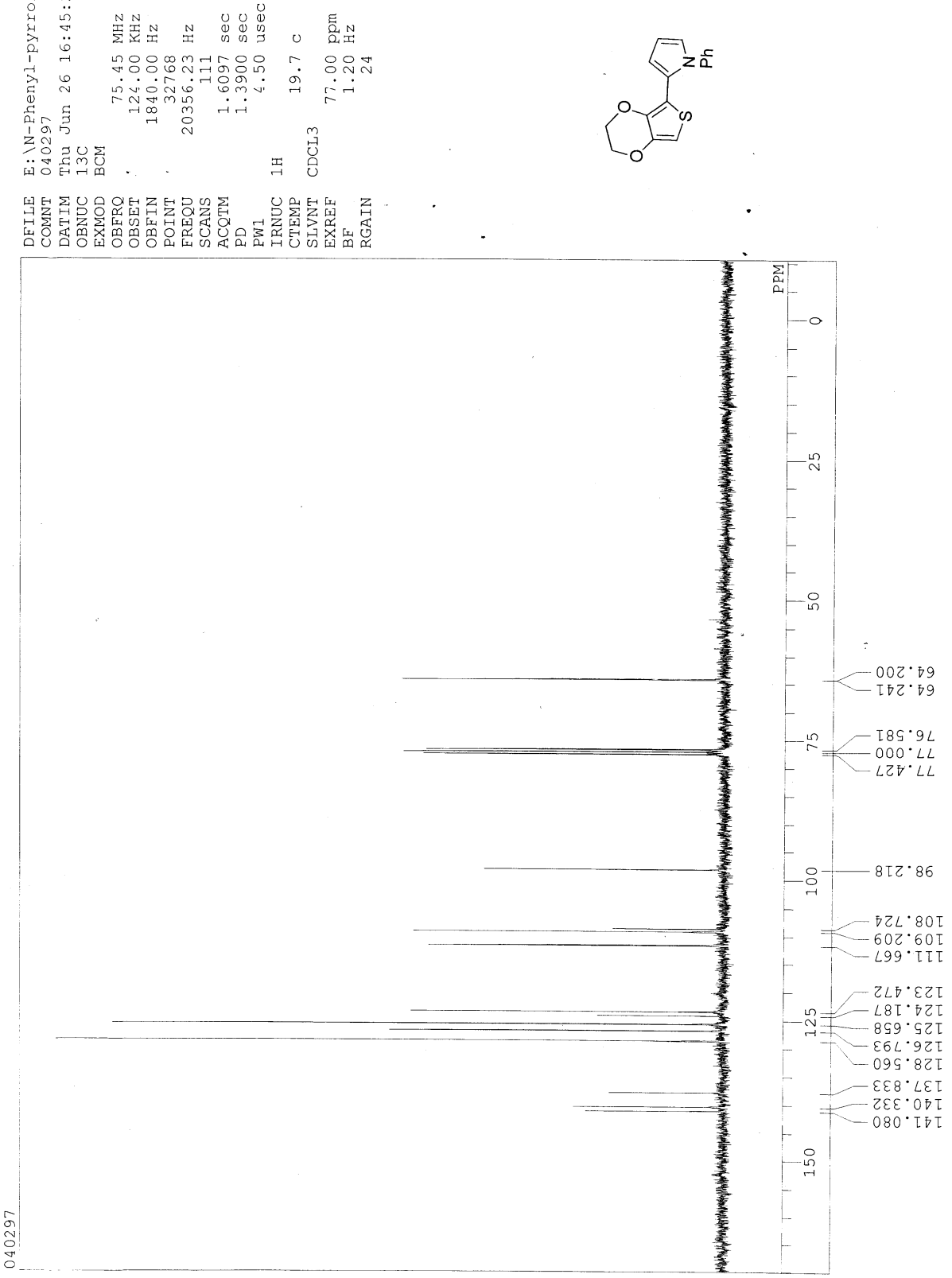
3be


DFILE E:\pyrrole edot-C_DEFAULT.
COMNT pyrrole edot
DATIM Sat Sep 13 00:58:07 2008
OBNUC 13C
EXMOD BCM
OBFRQ 75.45 MHz
OBSET 124.00 KHz
OBFIN 1840.00 Hz
POINT 32768
FREQU 20356.23 Hz
SCANS 404
ACQTM 1.6097 sec
PD 1.3900 sec
PW1 4.50 usec
IRNUC 1H
CTEMP 21.3 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 1.20 Hz
RGAIN 25
O
O
S
N
H
pyrrole edot
PPM
64.603
64.998
76.581
77.000
77.427
94.888
104.564
108.978
111.075
117.544
125.469
135.424
141.500

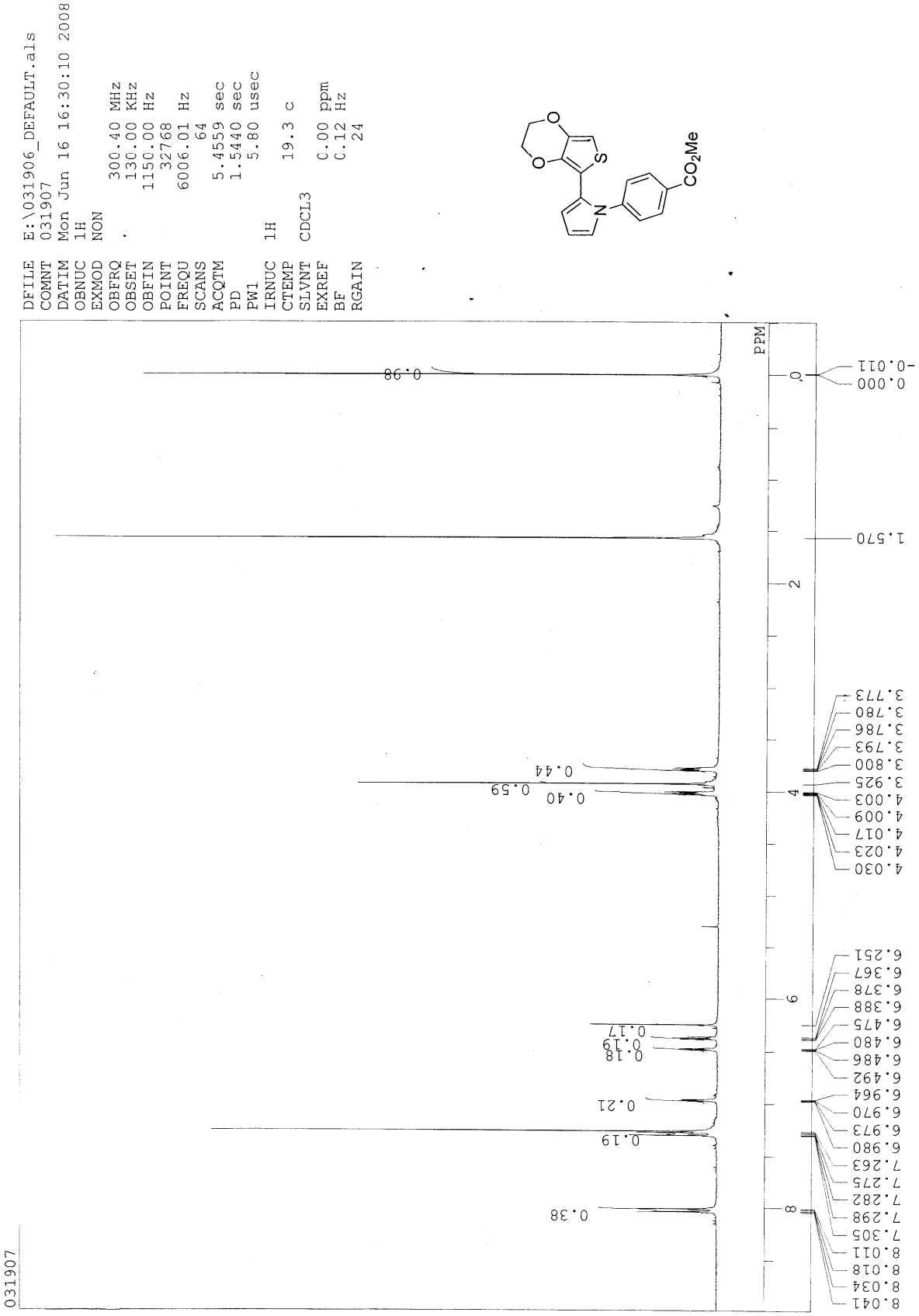
3bf


DFILE E:\N-Phenyl-pyrrolle-EDOT
COMNT N-Phenyl-pyrrolle-EDOT
DATIM Thu Jun 26 16:37:59 2008
OBNUC 1H
EXMOD NON
OBFRQ 300.40 MHz
OBSET 130.00 KHz
OBFIN 1150.00 Hz
POINT 32768
FREQU 6006.01 Hz
SCANS 19
ACQTM 5.4559 sec
PD 1.5440 sec
PW1 5.80 usec
IRNUC 1H
CTEMP 20.3 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 12
N
Ph
O
O
S
N-Phenyl-pyrrolle-EDOT
PPM
0.000
3.809
3.817
3.822
3.829
3.836
3.986
3.992
4.000
4.005
4.014
6.163
6.318
6.329
6.339
6.491
6.497
6.503
6.509
6.889
6.894
6.897
6.904
7.202
7.214
7.218
7.223
7.232
7.240
7.247
7.268
7.277
7.284
7.290
7.295
7.304
7.322
7.330
7.344
7.351
7.357
7.389
7.403
5.60
2.05
2.07
0.95
1.00
0.95
1.00

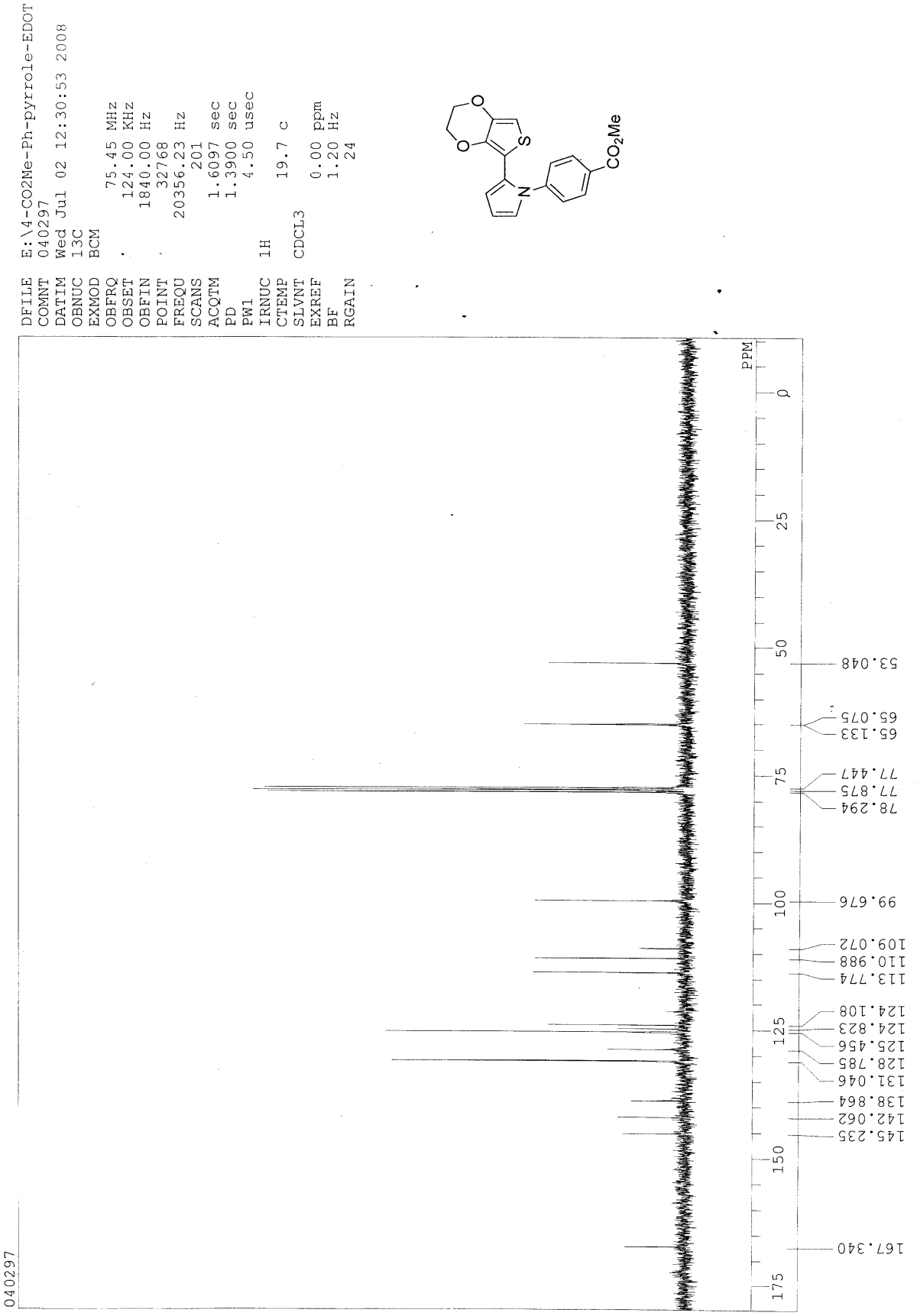
3bf


DFILE E:\N-Phenyl-pyrrolle-EDOT-
COMNT 040297
DATIM Thu Jun 26 16:45:23 2008
OBNUC 13C
EXMOD BCM
OBFRQ 75.45 MHz
OBSET 124.00 KHz
OBFIN 1840.00 Hz
POINT 32768
FREQU 20356.23 Hz
SCANS 111
ACQTM 1.6097 sec
PD 1.3900 sec
PW1 4.50 usec
IRNUC 1H
CTEMP 19.7 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 1.20 Hz
RGAIN 24
040297
PPM
0
25
50
75
100
125
150
64.200
64.241
76.581
77.000
77.427
98.218
108.724
109.209
111.667
123.472
124.187
125.658
126.793
128.560
137.833
140.332
141.080
N
Ph
O
O
S

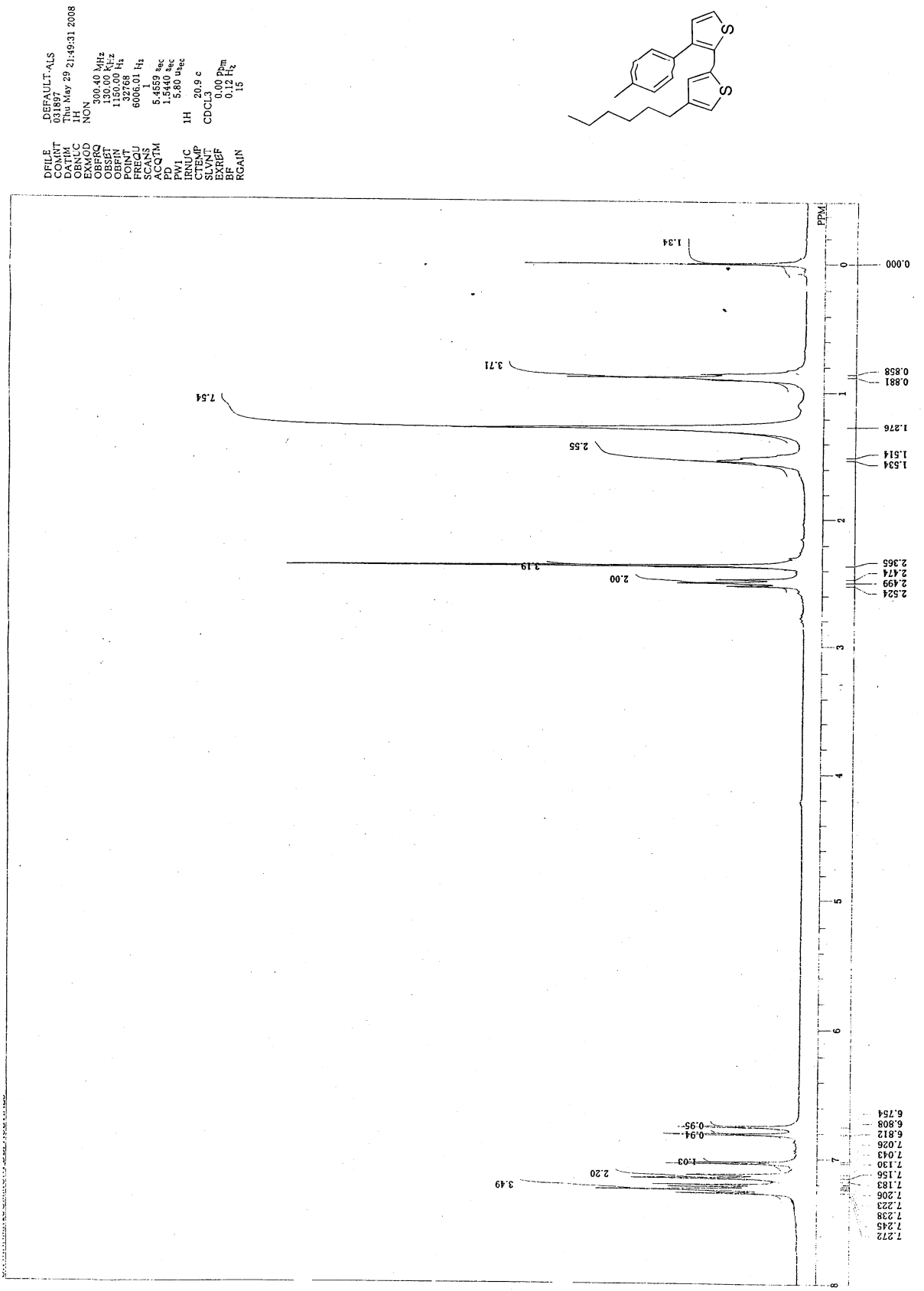
3bg


DFILE E:\031906_DEFAULT.als
COMNT 031907
DATIM Mon Jun 16 16:30:10 2008
OBNUC 1H
EXMOD NON
OBFRQ 300.40 MHz
OBSET 130.00 KHz
OBFIN 11500.00 Hz
POINT 32768
FREQU 6006.01 Hz
SCANS 64
ACQTM 5.4559 sec
PD 1.5440 sec
PW1 5.80 usec
IRNUC 1H
CTEMP 19.3 c
SLVNT CDCL3
EXREF C.00 ppm
BF C.12 Hz
RGAIN 24
CO2Me
031907
PPM
0.98
0.44
0.40
0.59
0.38
0.19
0.21
0.18
0.19
0.17
-0.011
0.000
1.570
3.773
3.780
3.786
3.793
3.800
3.925
4.003
4.009
4.017
4.023
4.030
6.251
6.367
6.378
6.388
6.475
6.480
6.486
6.492
6.964
6.970
6.973
6.980
7.263
7.275
7.282
7.298
7.305
8.011
8.018
8.034
8.041

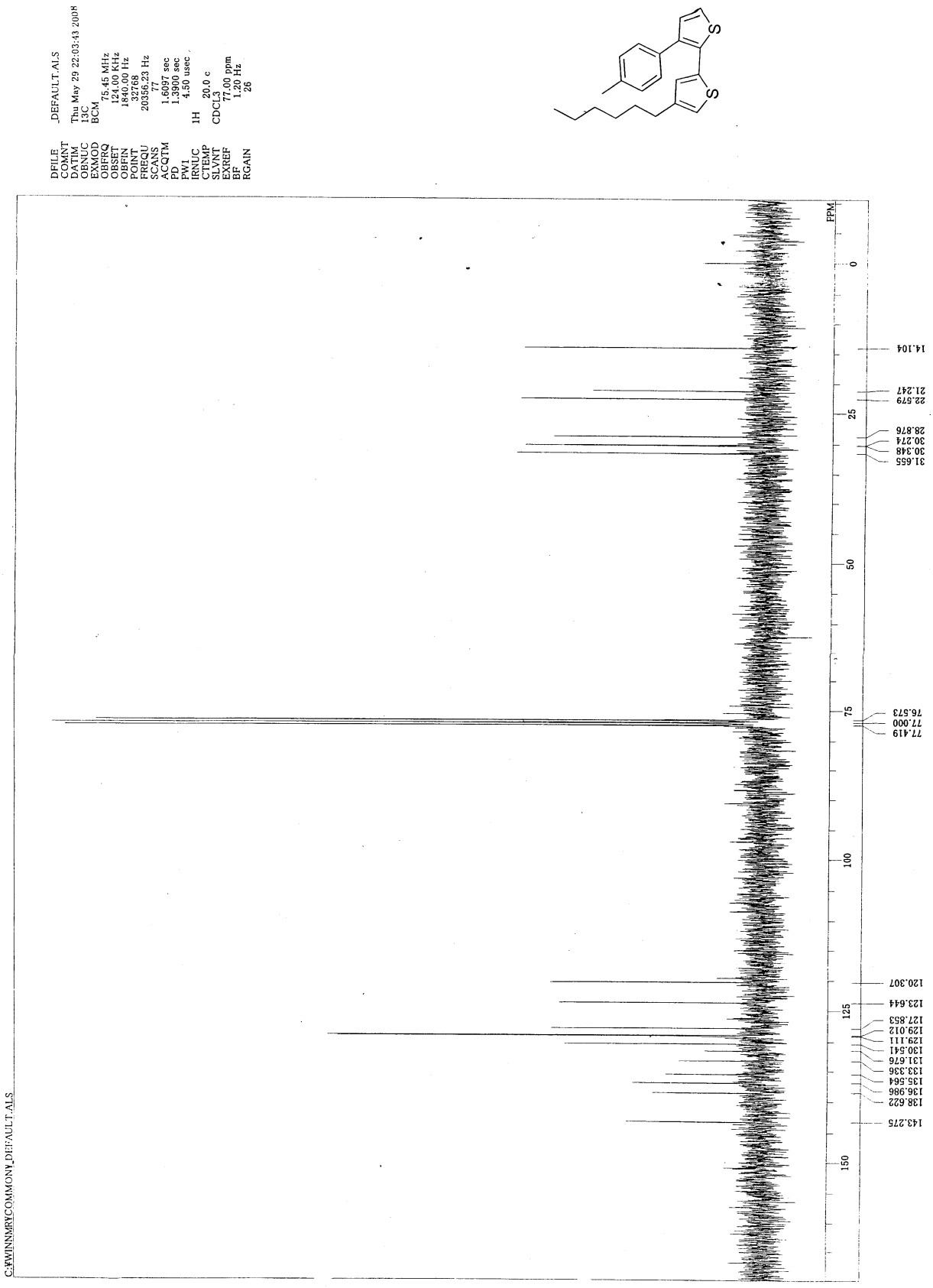
3bg


DFILE E:\4-CO2Me-Ph-pyrrole-EDOT
COMNT 040297
DATIM Wed Jul 02 12:30:53 2008
OBNUC 13C
EXMOD BCM
OBFRQ 75.45 MHz
OBSET 124.00 KHz
OBFIN 1840.00 Hz
POINT 32768
FREQU 20356.23 Hz
SCANS 201
ACQTM 1.6097 sec
PD 1.3900 sec
PW1 4.50 usec
IRNUC 1H
CTEMP 19.7 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 1.20 Hz
RGAIN 24
CO2Me
040297
PPM
53.048
65.075
65.133
77.447
77.875
78.294
99.676
109.072
110.988
113.774
124.108
124.823
125.456
128.785
131.046
138.864
142.062
145.235
167.340

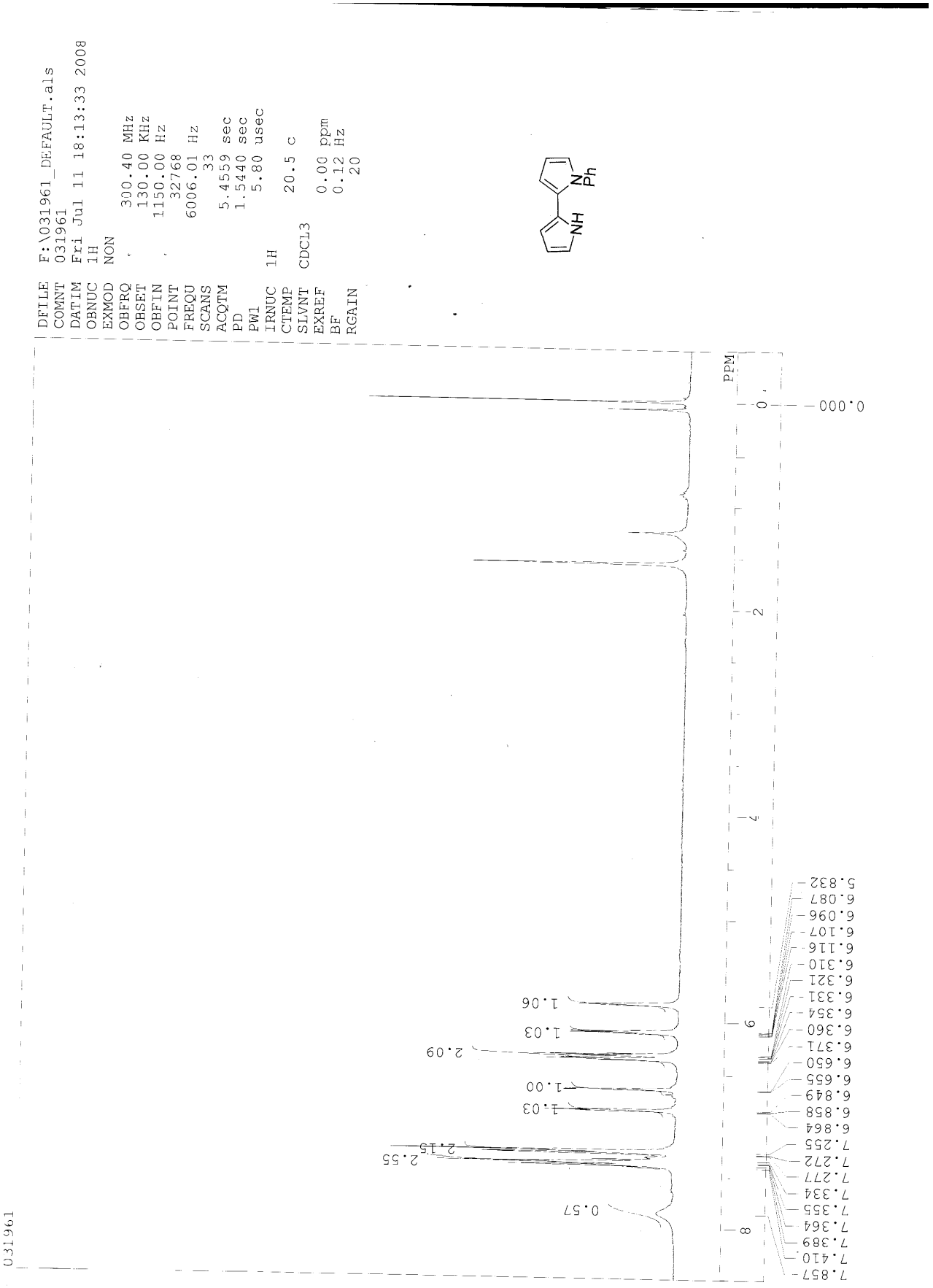
3eh


DFILE DEFAULT.ALS
COMNT 031897
DATIM Thu May 29 21:49:31 2008
OBNUC 1H
EXMOD NON
OBFRQ 300.40 MHz
OBSET 150.00 KHz
OBFIN 1150.00 Hz
POINT 32768
FREQU 6006.01 Hz
SCANS 1
ACQTM 5.4559 sec
PD 1.5440 sec
PW1 5.80 usec
IRNUC 1H
CTEMP 20.9 c
SLVNT CDCL3
EXREF 0.00 Ppm
BF 0.12 Hz
RGAIN 15
PPM
0.000
0.858
0.881
1.276
1.514
1.534
2.365
2.474
2.499
2.524
6.754
6.808
6.812
7.026
7.043
7.130
7.156
7.183
7.206
7.223
7.238
7.245
7.272
1.34
3.71
7.54
2.55
3.19
2.00
0.95
0.94
1.03
2.20
3.49

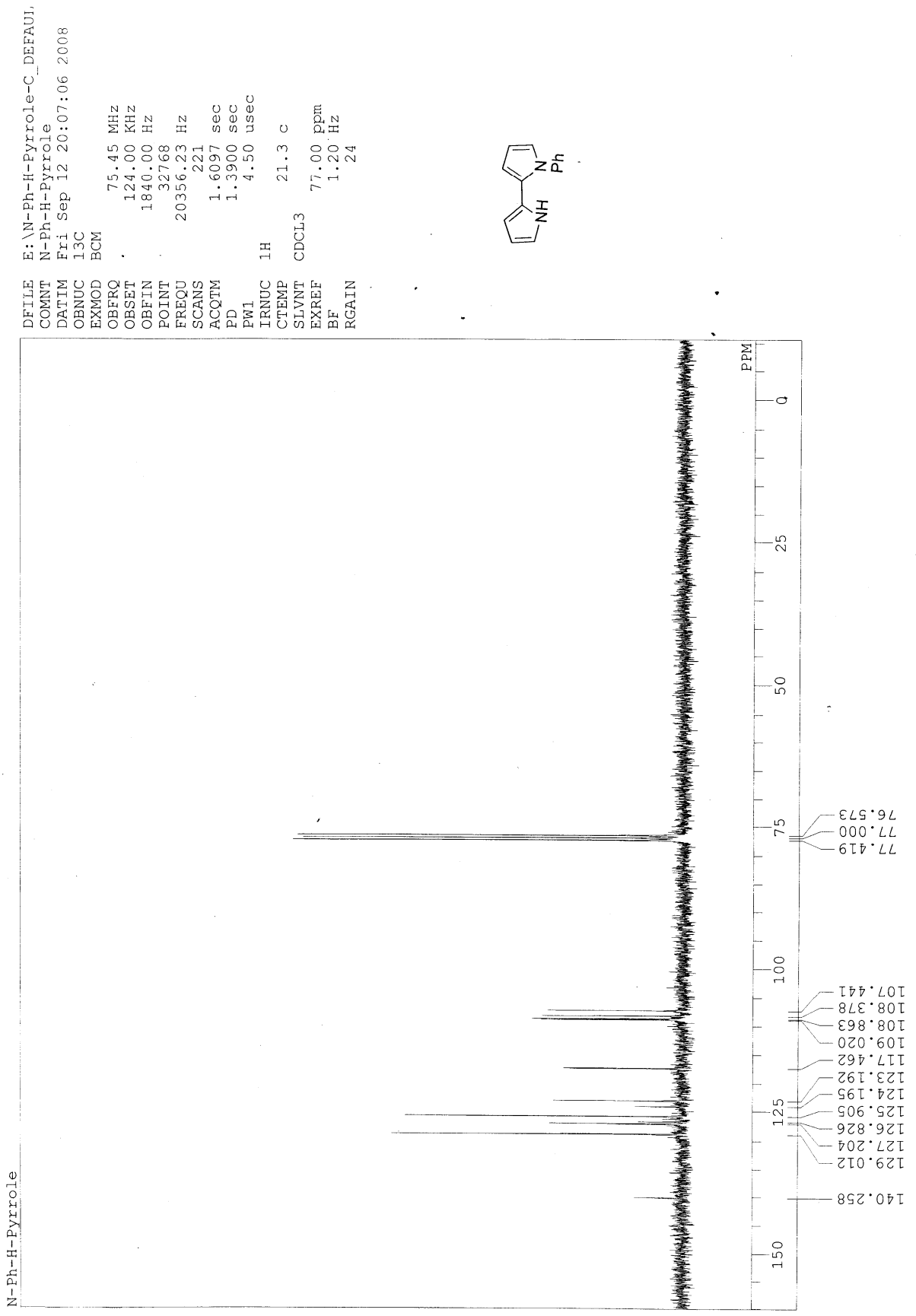
3eh


DFILE DEFAULT.ALS
COMNT
DATIM Thu May 29 22:03:43 2008
OBNUC 13C
EXMOD BCM
OBFRQ 75.45 MHz
OBSET 124.00 KHz
OBFIN 1840.00 Hz
POINT 32768
FREQU 2035.623 Hz
SCANS 77
ACQTM 1.6097 sec
PD 1.3900 sec
PW1 4.50 usec
IRNUC 1H
CTEMP 20.0 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 1.20 Hz
RGAIN 26
S
S
PPM
0
25
50
75
100
125
150
14.104
21.247
22.679
28.876
30.274
30.348
31.655
76.573
77.000
77.419
120.307
123.644
127.853
129.012
129.111
130.541
131.676
133.336
135.564
136.986
138.622
143.275
C:\WINNMR\COMMON_DEFAULT.ALS

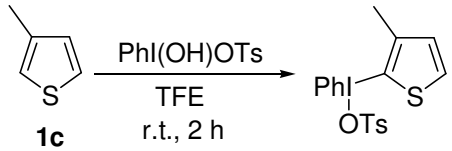
3ge


DFILE F:\031961_DEFAULT.als
COMNT 031961
DATIM Fri Jul 11 18:13:33 2008
OBNUC 1H
EXMOD NON
OBFRQ 300.40 MHz
OBSET 130.00 KHz
OBFIN 1150.00 Hz
POINT 32768
FREQU 6006.01 Hz
SCANS 33
ACQTM 5.4559 sec
PD 1.5440 sec
PW1 5.80 usec
IRNUC 1H
CTEMP 20.5 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 20
Ph
NH
PPM
0.000
0.57
2.55
2.15
1.03
1.00
2.09
1.03
1.06
7.857
7.410
7.389
7.364
7.355
7.334
7.277
7.272
7.255
6.864
6.858
6.849
6.655
6.650
6.371
6.360
6.354
6.331
6.321
6.310
6.116
6.107
6.096
6.087
5.832
031961

3ge


DFILE E:\N-Ph-H-Pyrrole-C_DEFAUL
COMNT N-Ph-H-Pyrrole
DATIM Fri Sep 12 20:07:06 2008
OBNUC 13C
EXMOD BCM
OBFRQ 75.45 MHz
OBSET 124.00 KHz
OBFIN 1840.00 Hz
POINT 32768
FREQU 20356.23 Hz
SCANS 221
ACQTM 1.6097 sec
PD 1.3900 sec
PW1 4.50 usec
IRNUC 1H
CTEMP 21.3 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 1.20 Hz
RGAIN 24
N
Ph
NH
N-Ph-H-Pyrrole
PPM
0
25
50
75
100
125
150
140.258
129.012
127.204
126.826
125.905
124.195
123.192
117.462
109.020
108.863
108.378
107.441
77.419
77.000
76.573

Praparation of Diaryliodonium(III) Salts 4c-OTs. **(Scheme 3)**



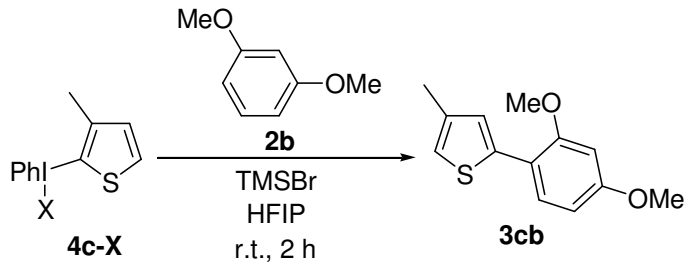
To a stirred solution of 3-methylthiophene **1c** (98 mg, 1 mmol) in 2,2,2-trifluoroethanol (TFE, 5 mL), [hydroxyl(tosyloxy)iodo]benzene (392 mg, 1 mmol) was added in one portion at room temperature under air, and it was stirred for 2 h. MeOH was then added to the reaction mixture when the solvents were removed under vacuum. The resulting oily crude **4c-OTs** was precipitated by the addition of Et_2O with stirring. The precipitate was filtered and dried *in vacuo* to give pure **4c-OTs** (480 mg, 98%) as a white powder.

(4c-OTs)[6)]

White powder; mp: 165 °C; ^{1}H-NMR (300 MHz, CD_3OD): δ 2.33 (3H, s), 2.49 (3H, s), 7.03 (1H, d, J = 5.1 Hz), 7.19 (2H, d, J = 7.2 Hz), 7.46-7.49 (2H, m), 7.59-7.67 (3H, m), 7.83 (1H, d, J = 5.1 Hz), 8.05 (2H, d, J = 7.8 Hz) ppm; ^{13}C-NMR (75.5 MHz, CD_3OD): δ 17.5, 21.3, 98.4, 118.4, 126.9, 129.8, 131.0, 133.0, 133.1, 133.4, 135.4, 137.7, 141.6, 150.0 ppm.

The corresponding **4c-Br** was prepared from **4c-OTs** by treatment of KBr in MeOH/water. The resulting insoluble **4c-Br** could be collected by simple filtration.

Reaction of Diaryliodonium(III) Salts 4c-X with Nucleophile 2b. **(Scheme 3)**

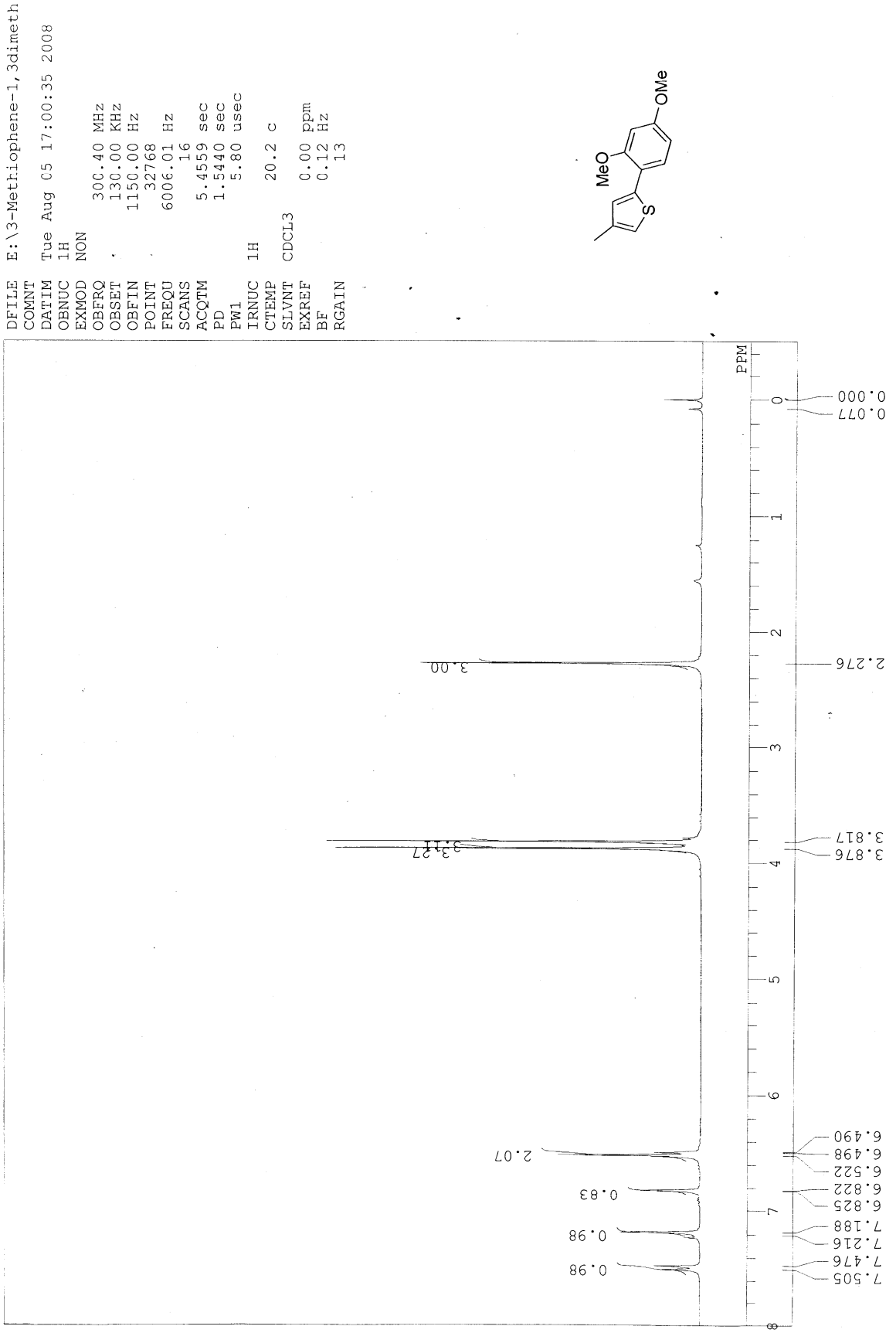


To a stirred solutions of **4c-X** (0.5 mmol) in HFIP, 1,3-dimethoxybenzene **2b** (104 mg, 0.75 mmol) and TMSBr (0.13 mL, 1 mmol) were sequentially added. The reaction mixtures are then stirred for an additional 2 hours under the same conditions. Saturated aqueous sodium hydrogen carbonate was added to the mixtures, and the aqueous phases were extracted with CH_2Cl_2. The extracts were dried over anhydrous Na_2SO_4 and then evaporated to dryness. The crude residues were purified by column chromatography on silica-gel (eluent: *n*-hexane/AcOEt) to give the pure biaryl **3cb** (102 mg, 87%).

(3cb)

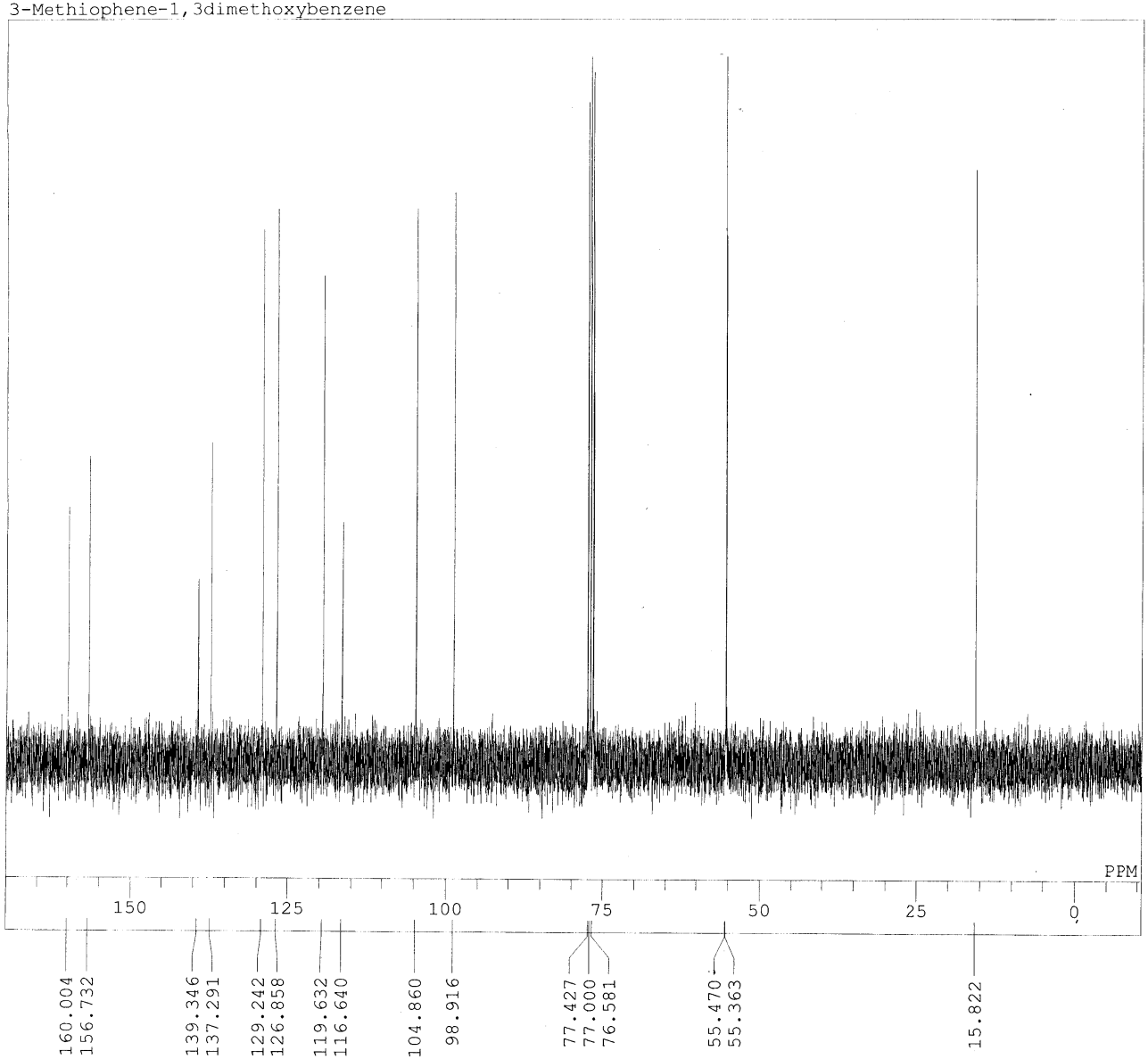
White solid; mp. 38-40 °C; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 2.27 (3H, s), 3.82 (3H, s), 3.88 (3H, s), 6.49-6.52 (2H, m), 6.82 (1H, d, J = 1.8 Hz), 7.19 (1H, s), 7.50 (1H, d, J = 8.7 Hz) ppm; ^{13}C-NMR (75 MHz, $CDCl_3$): δ 15.8, 55.3, 55.5, 98.9, 104.9, 116.6, 119.6, 126.9, 129.2, 137.3, 139.3, 156.7, 160.0 ppm; IR (KBr): 2935 w, 2833 w, 1609 s, 1574 s, 1504 s, 1454 s, 1301 s, 1273 s, 1209 s, 1159 s, 1130 m, 1030 s, 935 w, 833 m, 799 w, 748 m cm^{-1}; HRFABMS: calcd for $C_{13}H_{14}O_2S$ $[M]^+$ 234.0715, found 234.0715.

3cb

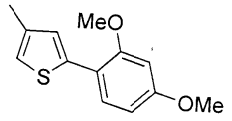

DFILE E:\3-Methiophene-1,3dimeth
COMNT
DATIM Tue Aug 05 17:00:35 2008
OBNUC 1H
EXMOD NON
OBFRQ 300.40 MHz
OBSET 130.00 KHz
OBFIN 1150.00 Hz
POINT 32768
FREQU 6006.01 Hz
SCANS 16
ACQTM 5.4559 sec
PD 1.5440 sec
PW1 5.80 usec
IRNUC 1H
CTEMP 20.2 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 13
MeO
OMe
S
PPM
0.000
0.077
2.276
3.817
3.876
6.490
6.498
6.522
6.822
6.825
7.188
7.216
7.476
7.505
3.00
3.27
2.07
0.83
0.98
0.98

3cb

3-Methiophene-1,3dimethoxybenzene



DFILE	E:\3-Methiophene-1,3dimeth
COMNT	3-Methiophene-1,3dimethoxy
DATIM	Tue Aug 05 16:57:35 2008
OBNUC	13C
EXMOD	BCM
OBFRQ	75.45 MHz
OBSET	124.00 KHz
OBFIN	1840.00 Hz
POINT	32768
FREQU	20356.23 Hz
SCANS	206
ACQTM	1.6097 sec
PD	1.3900 sec
PW1	4.50 usec
IRNUC	1H
CTEMP	20.5 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.12 Hz
RGAIN	24



References

1) Oswald, F.; Islam, D.-M. S.; Araki, Y.; Troiani, V.; de la Cruz, P.; Moreno, A.; Ito, O.; Langa, F. *Chem. Eur. J.* **2007**, *13*, 3924.
2) Bongini, A.; Barbarella, G.; Favaretto, L.; Sotgiu, G.; Zambianchi, M.; Casarini, D. *Tetrahedron* **2002**, *58*, 10151.
3) Baeuerle, P.; Wuerthner, F.; Heid, S. *Angew. Chem.* **1990**, *102*, 414.
4) Nakazaki, J.; Chung, I.-G.; Matsuhita, M. M.; Sugawara, T.; Watanabe, R.; Izuoka, A.; Kawada, Y. *J. Mater. Chem.* **2003**, *13*, 1011.
5) Rieke, R. D.; Kim, S.-H.; Wu, X. *J. Org. Chem.* **1997**, *62*, 6921.
6) Dohi, T.; Ito, M.; Morimoto, K.; Minamitsuji, Y.; Takenaga, N.; Kita, Y. *Chem. Commun.* **2007**, 4152.