

Cu(I) Catalyst in DMF: An Efficient Catalytic System for the Synthesis of Furans from 2-(1-Alkynyl)-2-alken-1-ones

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General Procedure for the cyclization of 2-(1-alkynyl)-2-alken-1-ones. The preparation of **3a** is representative. To a mixture of 2-(1-alkynyl)-2-alken-1-one **1a** (0.040 g, 0.2 mmol), MeOH (0.010 g, 0.3 mmol), Cu(I)Br (0.003 g, 0.02 mmol) was added DMF (0.2 mL) and the mixture was stirred until the disappearance of starting material on TLC at 80 °C. Water (10 ml) was added and the product was extracted with ethyl acetate. The extracts were washed with water and dried over anhydrous sodium sulfate. The solvent was removed, and the residue was then filtered through a short silica gel column using hexane/AcOEt, 99:1 as an eluent to give pure product **3a** (0.037 g, 81%).

Structure of **3a**, **3f**, **3i**, **3j**, **3l**, **3n** are known in the literature.¹ The characterization data for the newly synthesized compounds **3b**, **3c**, **3e**, **3g**, **3h**, **3k**, **3m**, **3o** as well as the copies of the ¹H NMR spectra of all products are given below.

(3b). ¹H NMR (CDCl₃, 400 MHz) δ 7.61 (d, *J* = 7.6 Hz, 2H), 7.34 (t, *J* = 7.6 Hz, 2H), 7.20 (t, *J* = 7.6 Hz, 1H), 6.61 (s, 1H), 4.37 (t, *J* = 4.4 Hz, 1H), 3.62-3.51 (m, 2H), 2.75-2.68 (m, 1H), 2.63-2.56 (m, 1H), 2.10-2.01 (m, 1H), 1.96-1.91 (m, 1H), 1.85-1.78 (m, 2H), 1.64-1.54 (m, 2H), 1.46-1.37 (m, 2H), 0.94 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (CDCl₃, 100 MHz) δ 152.6, 152.1, 131.1, 128.5, 126.7, 123.5, 120.4, 105.2, 71.0, 68.4, 32.3, 28.9, 23.3, 19.5, 19.1, 14.0; HRMS calcd for C₁₈H₂₂O₂ (M⁺) 270.1620, found 270.1614.

(3c). ¹H NMR (CDCl₃, 400 MHz) δ 7.62-7.59 (d, *J* = 7.6 Hz, 2H), 7.33 (t, *J* = 7.6 Hz, 2H), 7.21 (t, *J* = 7.6 Hz, 1H), 6.58 (s, 1H), 4.46-4.44 (t, *J* = 4.0 Hz, 1H), 3.86-3.79 (m, 1H), 2.74-2.69 (m, 1H), 2.62-2.57 (m, 1H), 2.09-2.02 (m, 1H), 1.87-1.80 (m, 3H), 1.23 (t, *J* = 7.2 Hz, 6H); ¹³C NMR (CDCl₃, 100 MHz) δ 152.5, 152.2, 131.2, 128.4, 126.7, 123.4, 120.9, 104.9, 69.4, 68.5, 29.8, 23.3, 23.2, 22.8, 19.2; HRMS calcd for C₁₇H₂₀O₂ (M⁺) 256.1463, found 256.1458.

(3e). ¹H NMR (CDCl₃, 400 MHz) δ 7.54 (d, *J* = 8.0 Hz, 2H), 7.27 (t, *J* = 8.0 Hz, 2H), 7.14 (t, *J* = 8.0 Hz, 1H); 6.54 (s, 1H), 5.83-5.75 (m, 1H), 5.07-4.96 (m, 2H), 4.33 (t, *J* = 4.4 Hz, 1H), 3.58-3.52 (m, 2H), 2.67-2.62 (m, 1H), 2.57-2.50 (m, 1H), 2.34-2.29 (m, 2H), 2.00-1.96 (m, 1H), 1.88-1.84 (m, 1H), 1.79-1.63 (m, 3H); ¹³C NMR (CDCl₃, 100 MHz) δ 152.7, 152.1, 135.3, 131.1, 128.5, 126.8, 123.4, 120.2, 116.2, 105.2, 71.1, 67.9, 34.7, 28.9, 23.3, 19.1; HRMS calcd for C₁₈H₂₀O₂ (M⁺) 268.1463, found 268.1461.

(3g). ^1H NMR (CDCl_3 , 400 MHz) δ 7.69 (d, $J = 8.4$ Hz, 2H), 7.58 (d, $J = 8.4$ Hz, 2H), 6.76 (s, 1H), 4.29 (t, $J = 4.0$ Hz, 1H), 3.45 (s, 3H), 2.77-2.70 (m, 1H), 2.66-2.58 (m, 1H), 2.17-1.92 (m, 2H), 1.88-1.79 (m, 2H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 153.9, 150.7, 134.14, 128.2, 125.6, 123.2, 120.4, 107.3, 72.3, 56.2, 28.3, 23.3, 18.9; HRMS calcd for $\text{C}_{16}\text{H}_{15}\text{F}_3\text{O}_2$ (M^+) 296.1024, found 296.1019.

(3h). ^1H NMR (CDCl_3 , 400 MHz) δ 7.50 (d, $J = 8.4$ Hz, 2H), 7.15 (d, $J = 8.4$ Hz, 2H), 6.58 (s, 1H), 4.29 (t, $J = 4.0$ Hz, 1H), 3.44 (s, 3H), 2.75-2.65 (m, 1H), 2.64-2.55 (m, 1H), 2.32 (s, 3H), 2.1-1.77 (m, 4H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 152.3, 136.6, 129.4, 128.7, 123.3, 119.7, 104.5, 72.3, 56.1, 28.5, 23.3, 21.3, 19.0; HRMS calcd for $\text{C}_{16}\text{H}_{18}\text{O}_2$ (M^+) 242.1307, found 242.1301.

(3k). ^1H NMR (CDCl_3 , 400 MHz) δ 7.74-7.07 (m 10H), 6.70 (s, 1H), 6.46 (s, 1H), 4.27 (m, 1H), 1.27 (d, $J = 6.0$ Hz, 3H), 1.24 (d, $J = 6.0$ Hz, 3H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 154.4, 150.6, 146.6, 131.3, 128.8, 128.7, 128.5, 128.3, 128.2, 124.8, 123.8, 121.6, 116.2, 103.4, 96.0, 70.6, 23.7, 22.5; HRMS calcd for $\text{C}_{20}\text{H}_{18}\text{O}_3$ (M^+) 306.1256, found 306.1257.

(3m). ^1H NMR (CDCl_3 , 400 MHz) δ 7.67-7.25 (m, 15H), 6.63 (s, 1H), 5.69 (s, 1H), 3.79-3.76 (m, 1H), 1.27 (2d, $J = 6.0$ Hz, 6H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 154.6, 141.8, 134.4, 133.8, 131.3, 129.9, 128.6, 128.5, 128.4, 128.3, 127.9, 127.4, 126.4, 124.1, 122.3, 105.5, 72.6, 69.1, 22.5, 22.1; HRMS calcd for $\text{C}_{28}\text{H}_{24}\text{O}_2$ (M^+) 392.1776, found 392.1774.

(3o). ^1H NMR (CDCl_3 , 400 MHz) δ 7.56 (d, $J = 7.6$ Hz, 2H), 7.40-7.16 (m, 7H), 6.47 (s, 1H), 5.43 (s, 1H), 3.70-3.63 (m, 1H), 2.37 (s, 3H), 1.22 (d, $J = 6.0$ Hz, 6H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 151.5, 148.2, 142.4, 130.9, 128.4, 128.3, 127.2, 126.7, 126.6, 123.3, 123.1, 105.6, 72.9, 68.6, 22.3, 12.3; HRMS calcd for $\text{C}_{21}\text{H}_{22}\text{O}_2$ (M^+) 306.1620, found 306.1618.

References

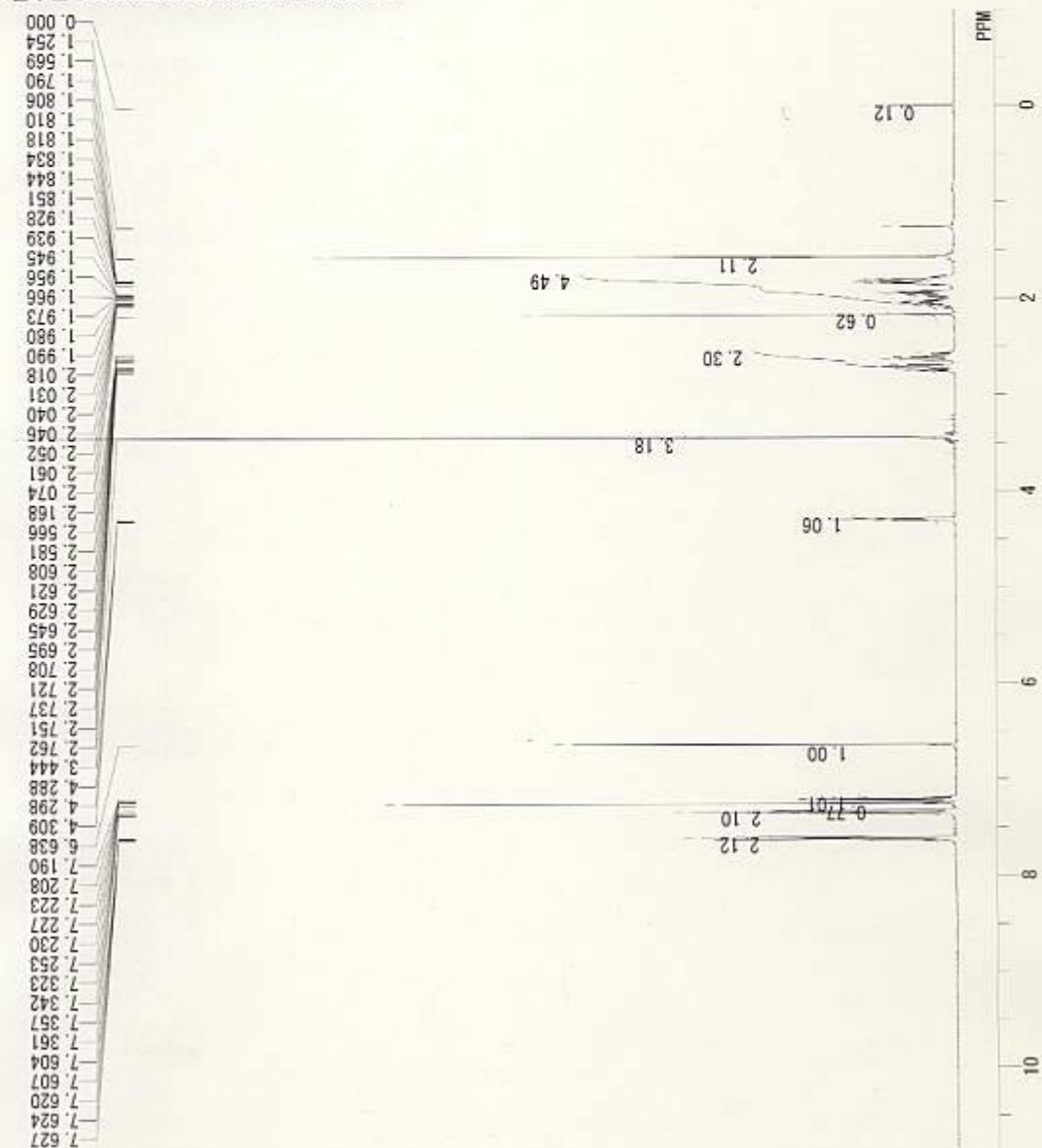
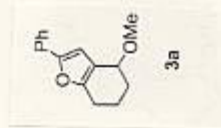
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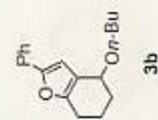
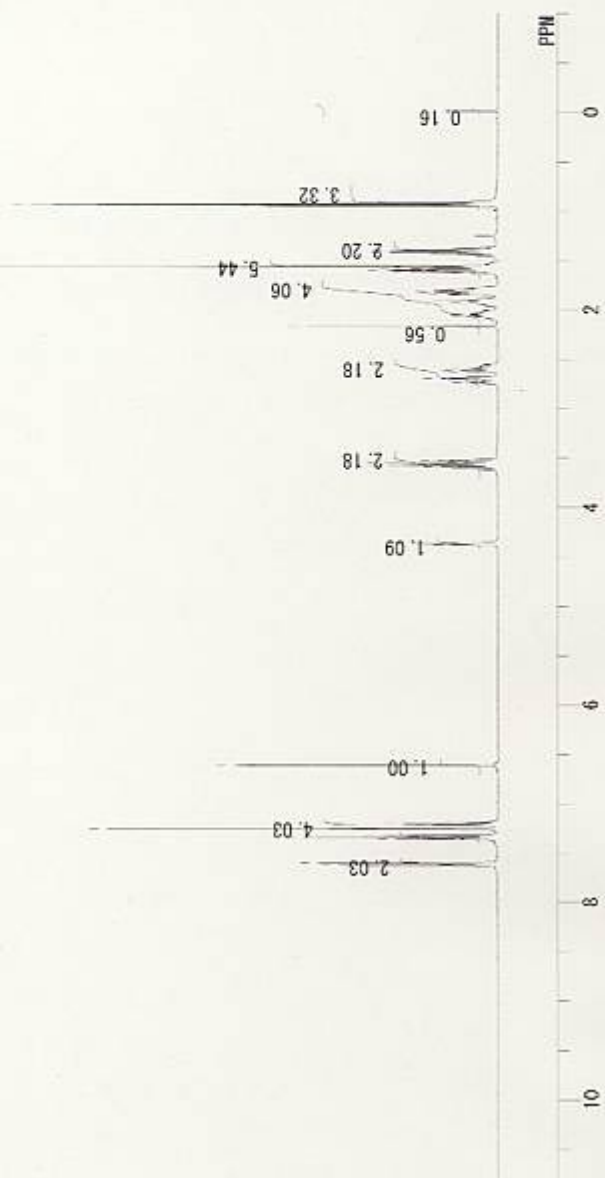
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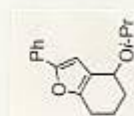
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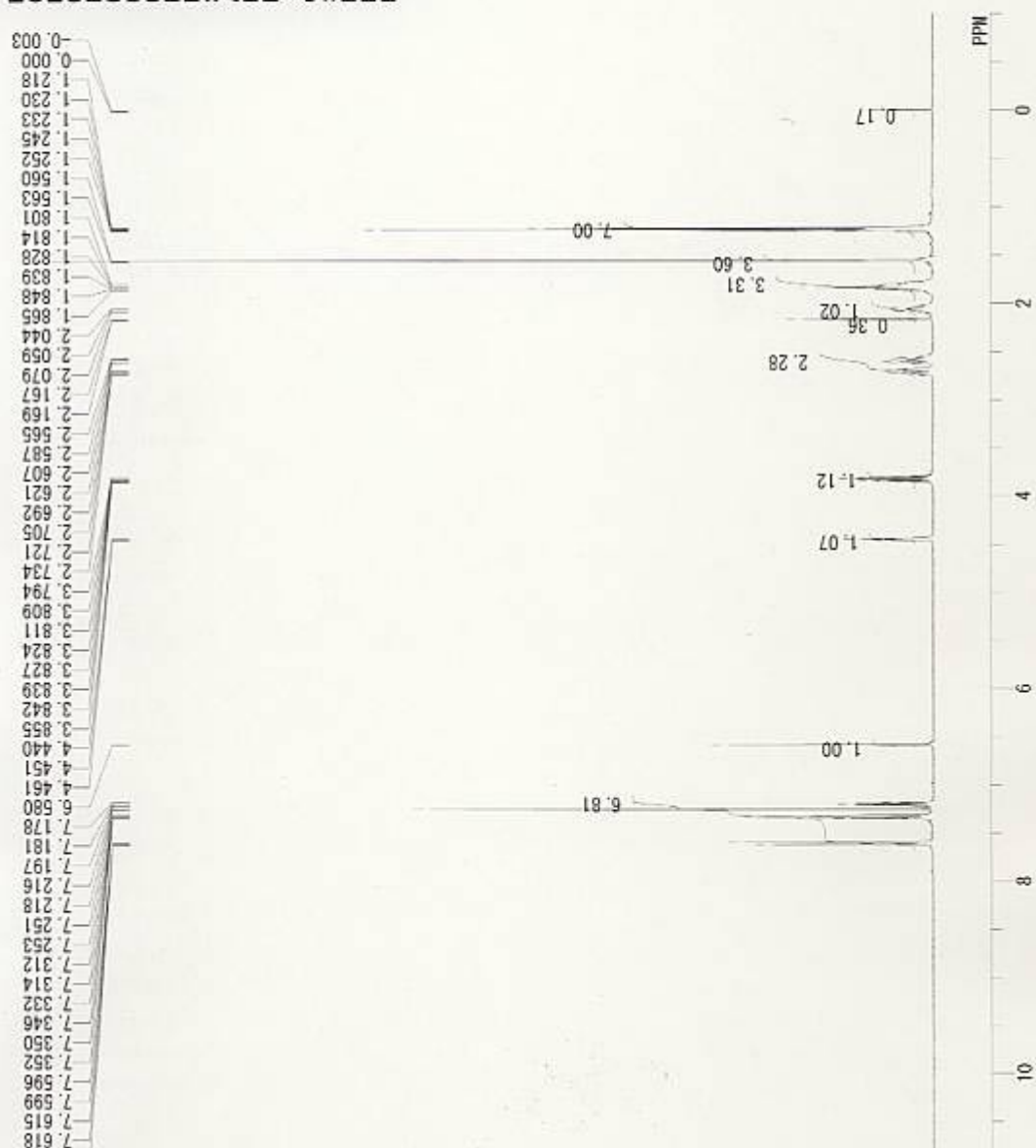
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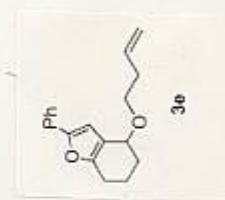
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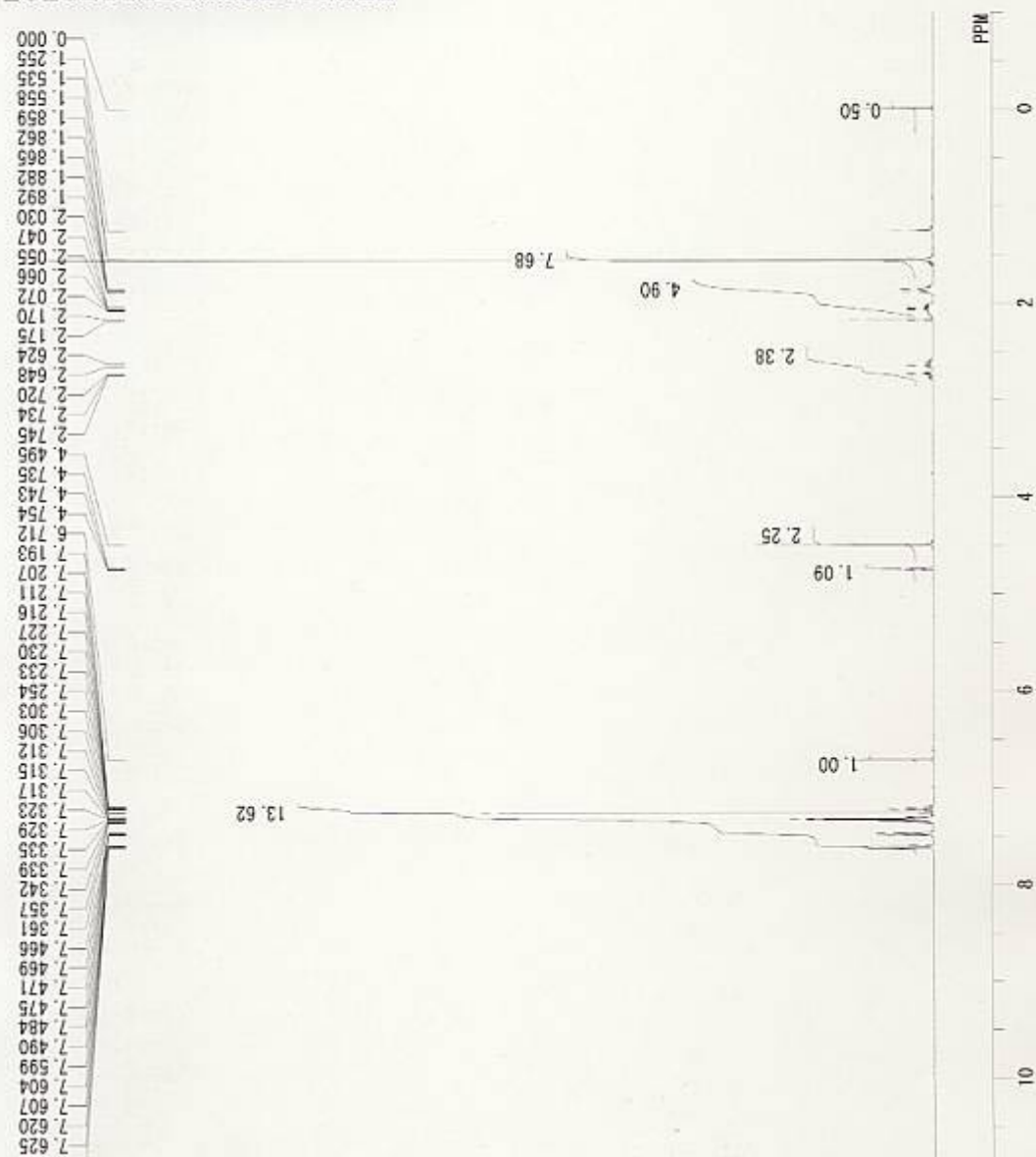
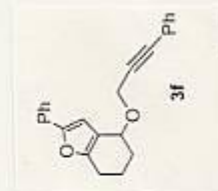
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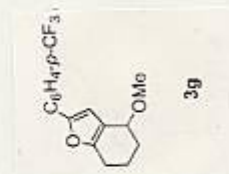
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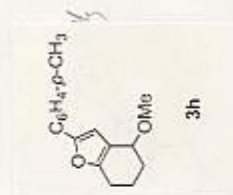
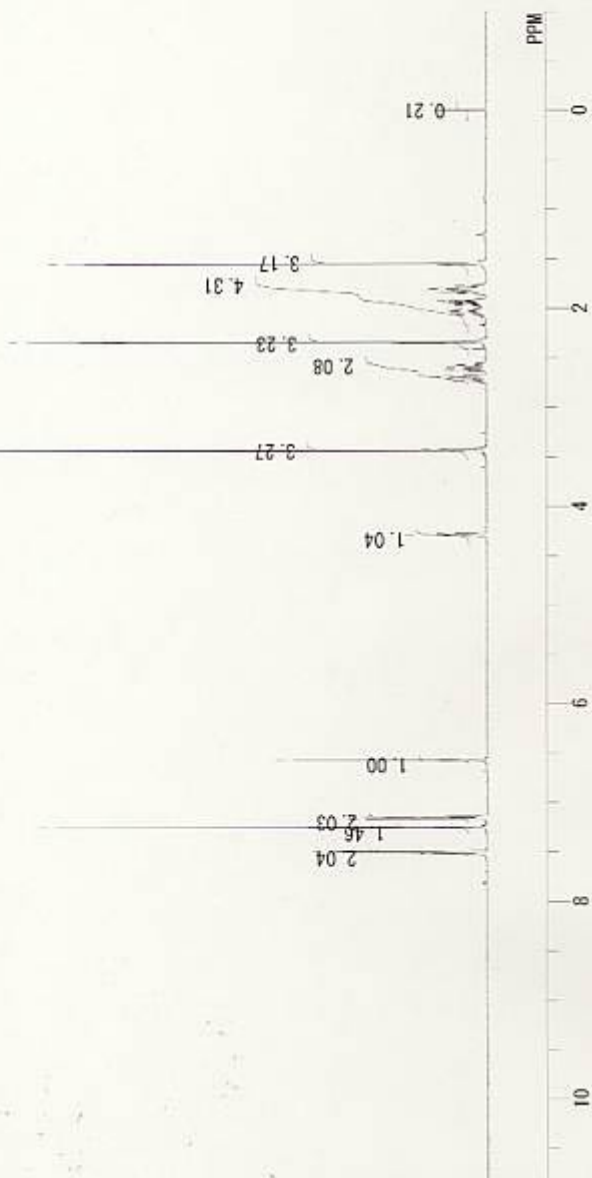
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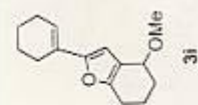
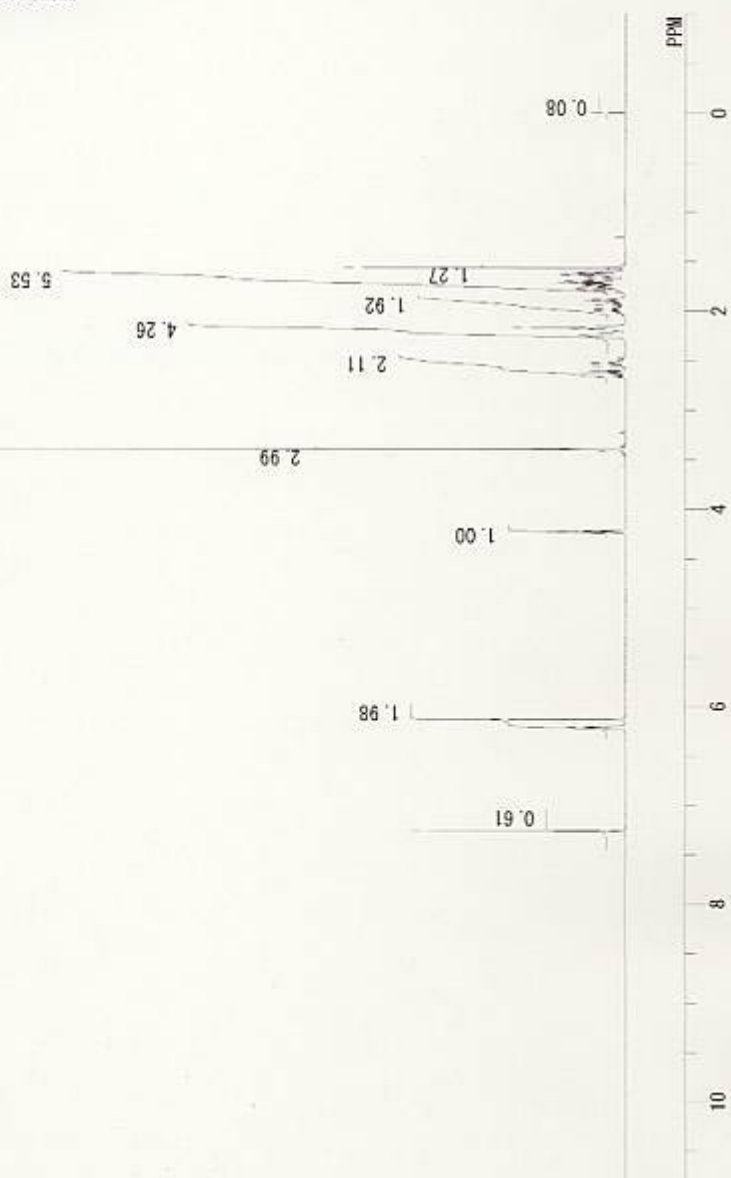
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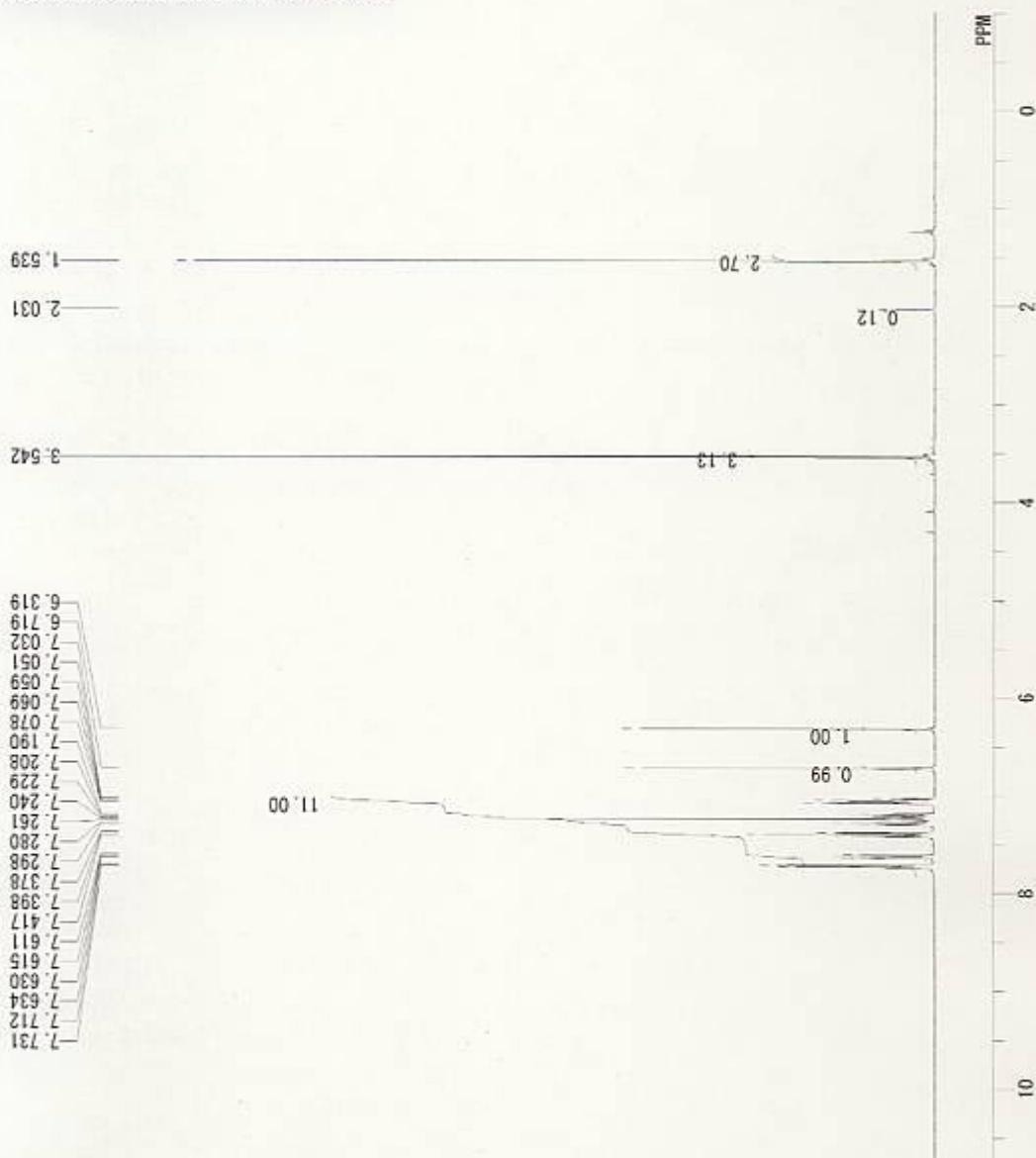
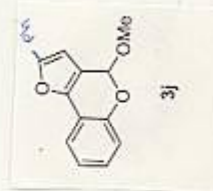


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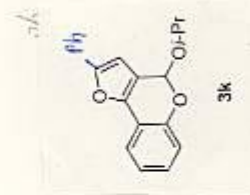
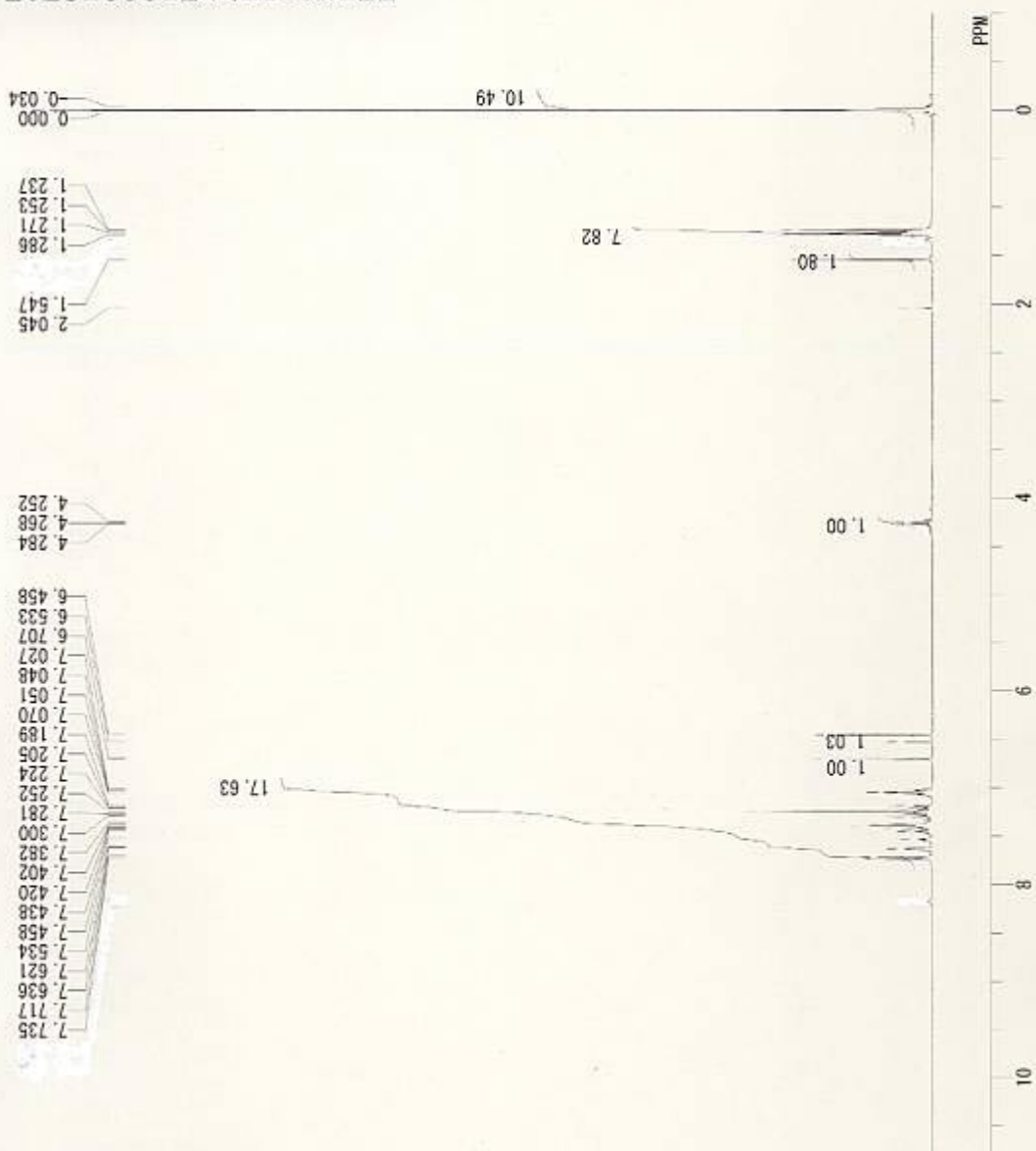
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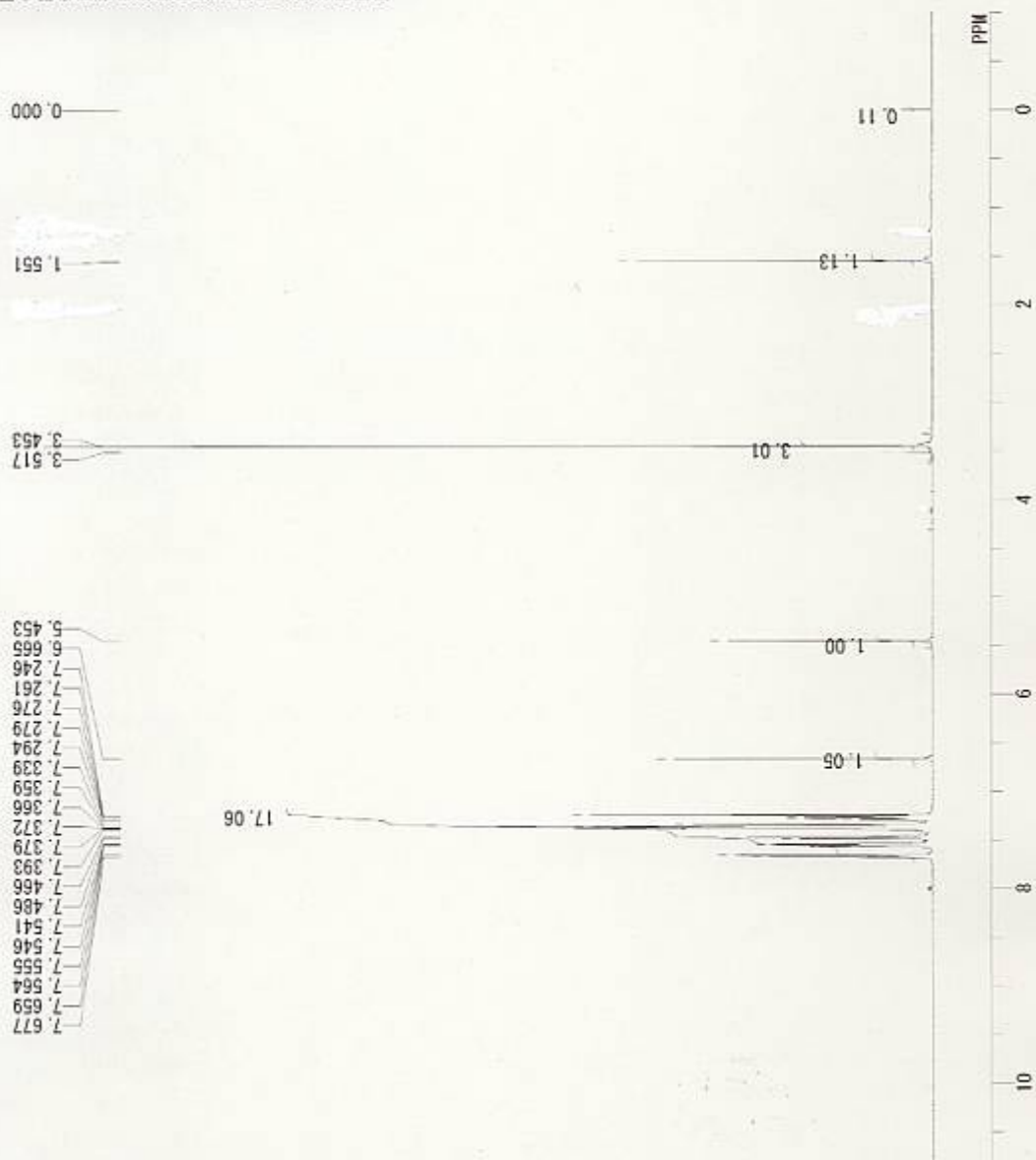


C:\Documents and Settings\VAI\Users\VO

Thu Nov 04 11:55:35 2004

DFILE
COMMIT
DATIN
DIRUC
EXMOD
OBFRO
OBFIN
POINT
FREQ
SCANS
ACQIN
PD
PWI
IRNUC
CTEMP
SLVIT
EXREF
BF
RGAIN

1H
NON
399.65 MHz
124.00 KHz
10500.00 Hz
32768
7953.60 Hz
8
4.0993 sec
2.9010 sec
5.50 usec
1H
CDCL3
23.7 c
0.00 ppm
0.10 Hz
15

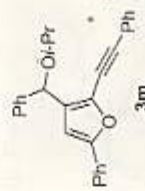
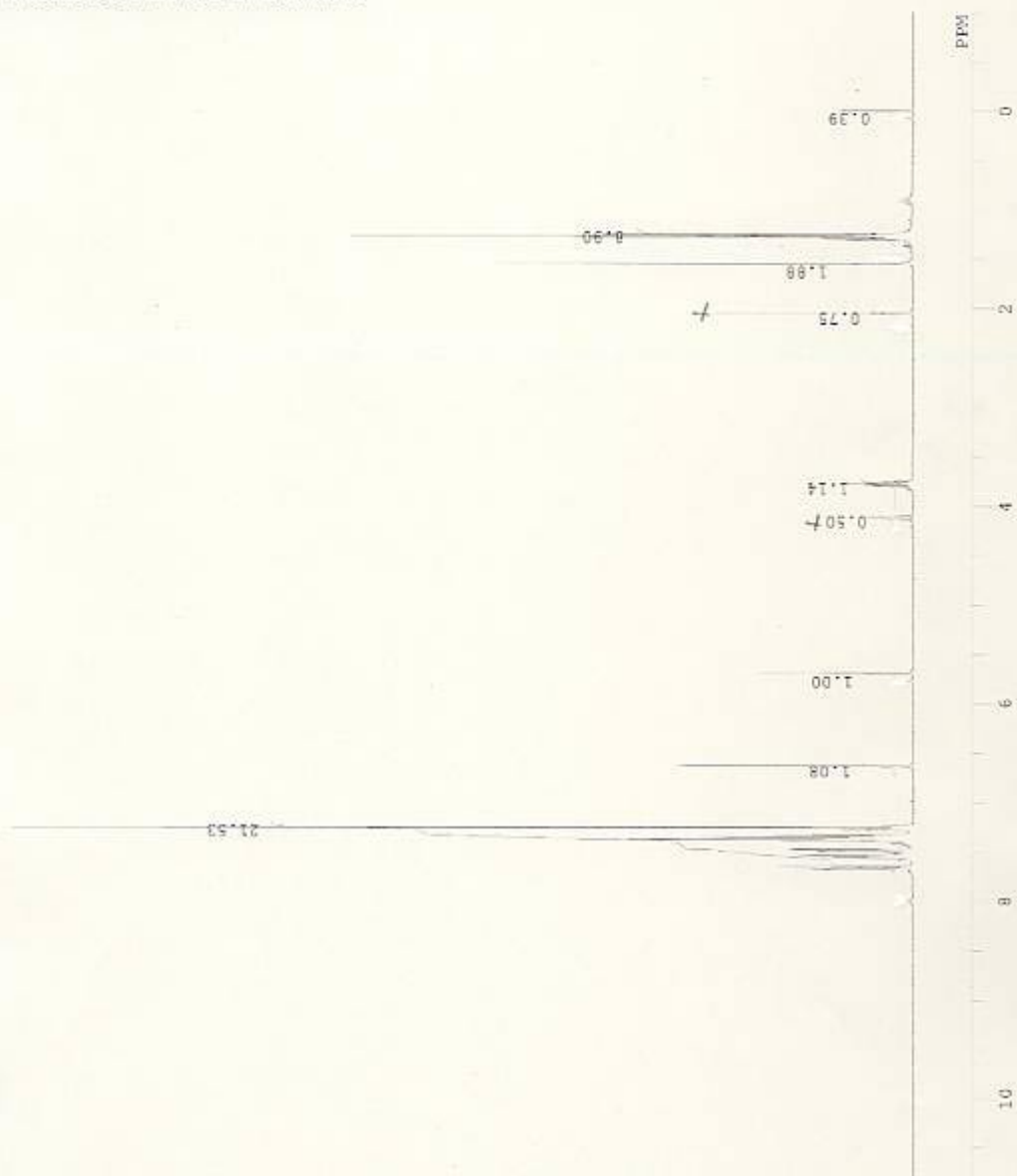


5-45-2
 5-45-2
 5-45-2

DEFILE C:\WINNMR98\COMMON\DEFAULT.ALS

COMPT 5-45-2
 DATIM Mon Nov 29 22:20:06 2004

CHNUC 1H
 EXXOD NON
 OBSFQ 399.65 MHz
 OBSFQ 124.00 KHz
 OBSFQ 10500.0 Hz
 POINT 32768
 FREQU 7993.6 Hz
 SCANS 8
 ACQTM 4.099 sec
 PD 2.901 sec
 PW1 5.5 us
 TRUNC 1H
 TRUNC 23.0 c
 CTEMP
 SLVNT CDCL3
 EXREF 0.00 ppm
 RF 0.10 Hz
 RGAIN 20



C:\Documents and Settings\All Users\WD

DFILE
COMMIT
DATIM
OBNUC
EXMOD
OBFRQ
OBSET
OBFIN
POINT
FREQ
SCANS
ACQTM
PD
PW1
IRNUC
CTEMP
SLVNT
EXREF
BF
RGAIN

0.000

1.545

2.377

3.352
3.373

5.197

6.482
7.166
7.184
7.203
7.249
7.263
7.280
7.294
7.314
7.324
7.333
7.344
7.362
7.380
7.397
7.562
7.580

Thu Mar 17 13:31:33 2005

1H
NON

399.65 MHz
124.00 KHz
10500.00 Hz

32768
7993.60 Hz

4.0993 sec
2.9010 sec

5.50 usec

8

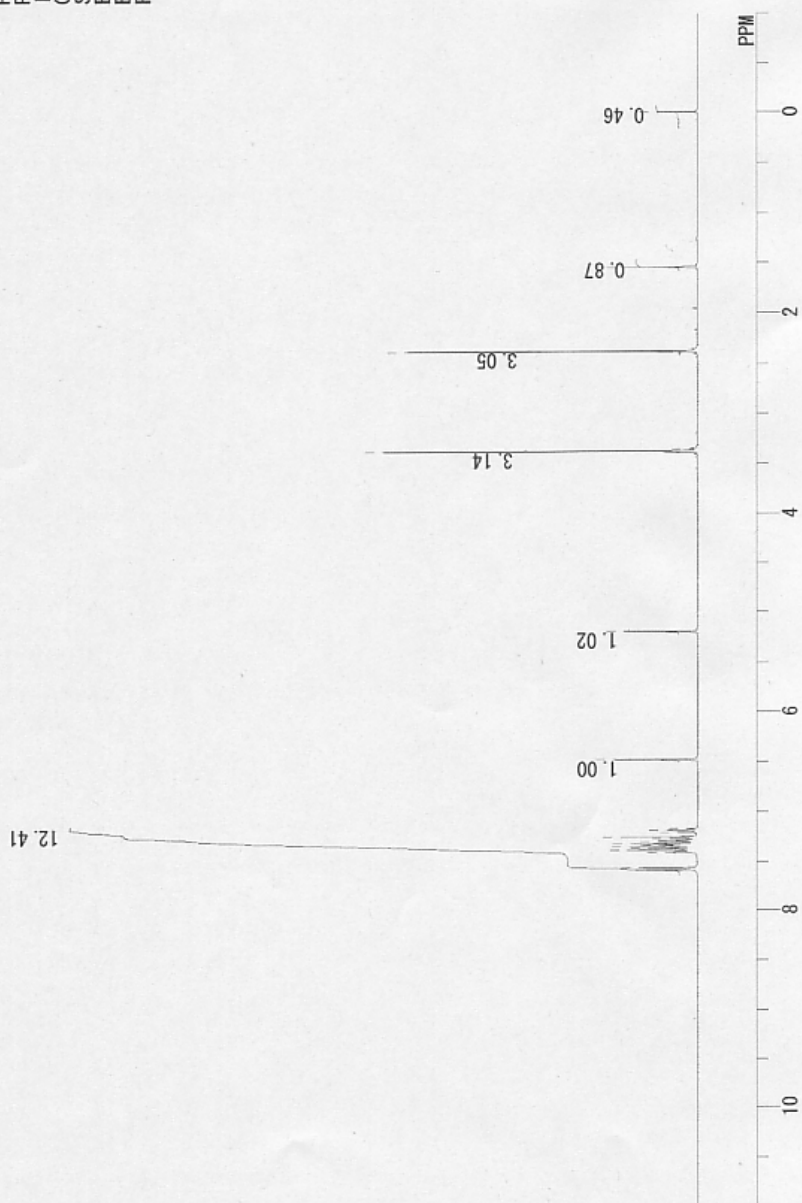
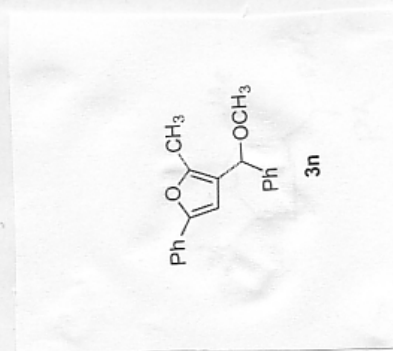
1H

21.8 c

CDCL3

0.00 ppm
0.10 Hz

17



C:\Documents and Settings\All Users\0

DFILE COMINT
 DATIM Thu Mar 17 12:12:00 2005
 OBNUC 1H
 EXMOD NON
 OBFREQ 399.65 MHz
 OBFSET 124.00 KHz
 OBFIN 10500.00 Hz
 POINT 32768
 FREQU 7993.60 Hz
 SCANS 8
 ACQTM 4.0993 sec
 PD 2.9010 sec
 PW1 5.50 usec
 IRNUC 1H
 CTEMP 22.1 C
 SLVNT CDCL3
 EXREF 0.00 ppm
 BF 0.10 Hz
 RGAIN 14

