Supporting Information

Selective Thiolative Lactonization of Internal Alkynes Bearing a Hydroxyl Group with Carbon Monoxide and Organic Disulfides Catalyzed by Transition-Metal complexes

Shinya Higashimae, Taichi Tamai, Akihiro Nomoto, and Akiya Ogawa*

Department of Applied Chemistry, Graduate School of Engineering, Osaka Prefecture University, 1-1 Gakuen-cho, Nakaku, Sakai, Osaka 599-8531, Japan

Contents

1. X-ray crystal structure (ORTEP) of 3aa

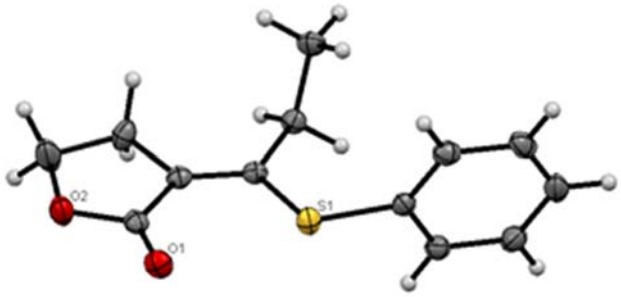
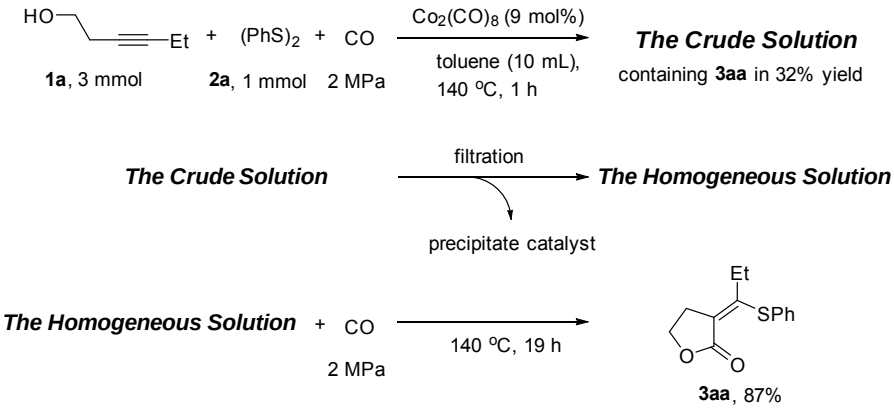


Figure S1. An ORTEP drawing of **3aa** with ellipsoids at 50% probability

2. Catalytic system for cobalt-catalyzed thiolative lactonization

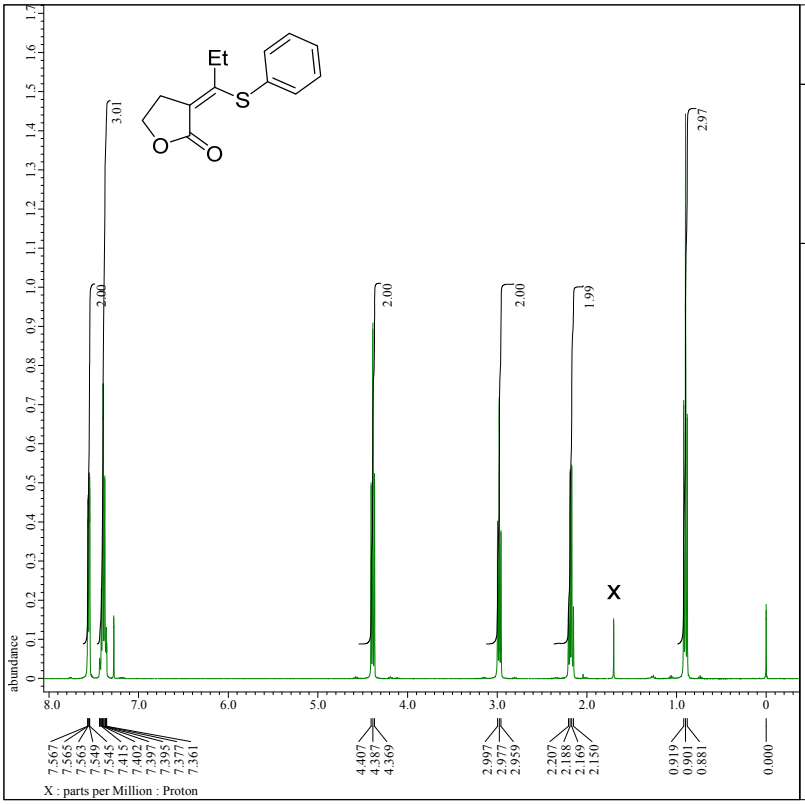
Scheme S1



In a 50 mL stainless steel autoclave with a magnetic stirring bar under a N_2 atmosphere were sequentially placed $Co_2(CO)_8$ (0.09 mmol), distilled toluene (10 mL), 3-hexyn-1-ol (3.0 mmol), and diphenyl disulfide (1.0 mmol). The vessel was purged three times with carbon monoxide and then charged with the same gas to achieve a pressure of 2 MPa. The reaction was conducted with magnetic stirring for 1 h at 140 °C. After removal of the unreacted carbon monoxide, the resulting mixture was filtered through celite with diethyl ether and diethyl ether was removed from the resulting filtrate by evapolation to give the homogeneous solution. The homogeneous solution contained the substrates, the catalyst, and lactone **3aa** (32% yield). Then, the reaction was continued using the resulting homogeneous solution under the pressure of carbon monoxide (2 MPa), affording the desired lactone **3aa** in 87% yield. The results strongly suggest the reaction proceeds by homogeneous catalysis.

3. ^{1}H and ^{13}C NMR spectra

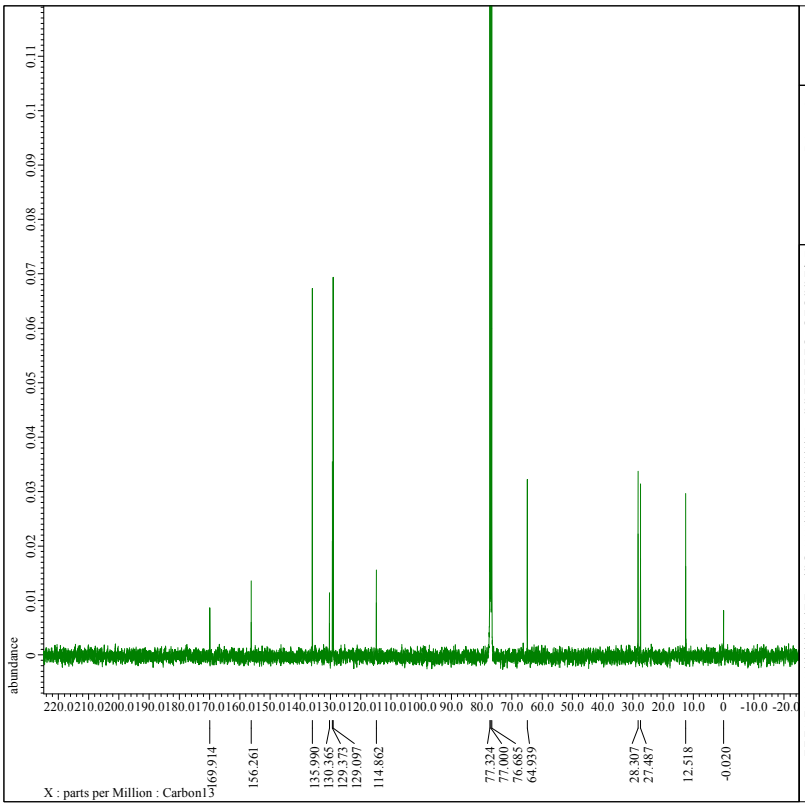
(*Z*)-3-{1-(penylthio)propylidene}dihydrofuran-2-one (3aa)



JEOL RESONANCE

```
---- PROCESSING PARAMETERS ----
dc_balance( 0, FALSE )
sexp( 0.2[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1 )
fft( 1, TRUE, TRUE )
machinephase
ppm
```

```
Filename          = C:\Users\shinya\Desktop\ex
Author            = delta
Experiment        = proton.jxp
Sample_Id         = exp336-crystal3-mae
Solvent           = CHLOROFORM-D
Creation_Time     = 27-MAY-2015 18:38:23
Revision_Time     =  3-JUN-2015 17:16:49
Current_Time      =  3-JUN-2015 17:17:02

Comment           = single_pulse
Data_Format       = 1D COMPLEX
Dim_Size          = 52429
Dim_Title         = Proton
Dim_Units         = [ppm]
Dimensions        = X
Site              = JNM-ECS400
Spectrometer      = DELTA2_NMR

Field_Strength    = 9.2982153[T] (400[MHz])
X_Acq_Duration    = 8.82900992[s]
X_Domain          = 1H
X_Freq            = 395.88430144[MHz]
X_Offset          = 5[ppm]
X_Points          = 65536
X_Prescans        = 1
X_Resolution      = 0.11326298[Hz]
X_Sweep           = 7.42280285[kHz]
X_Sweep_Clipped   = 5.93824228[kHz]
Irr_Domain        = Proton
Irr_Freq          = 395.88430144[MHz]
Irr_Offset        = 5[ppm]
Tri_Domain        = Proton
Tri_Freq          = 395.88430144[MHz]
Tri_Offset        = 5[ppm]
Clipped           = FALSE
Scans             = 16
Total_Scans       = 16

Relaxation_Delay  = 5[s]
Recvr_Gain        = 30
Temp_Get          = 24.2[dC]
X_90_Width        = 11.5[us]
X_Acq_Time        = 8.82900992[s]
X_Angle           = 45[deg]
X_Atn             = 1.3[dB]
X_Pulse           = 5.75[us]
Irr_Mode          = Off
Tri_Mode          = Off
Dante_Presat      = FALSE
Initial_Wait      = 1[s]
Repetition_Time   = 13.82900992[s]
```



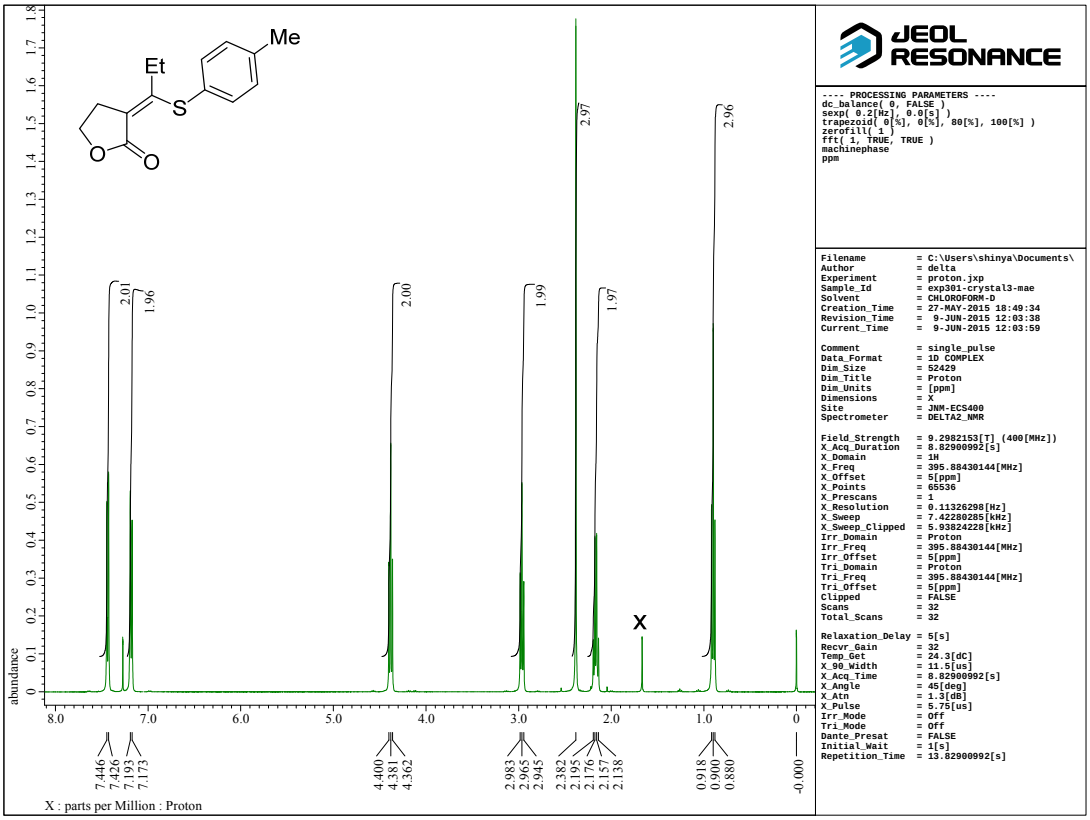
JEOL RESONANCE

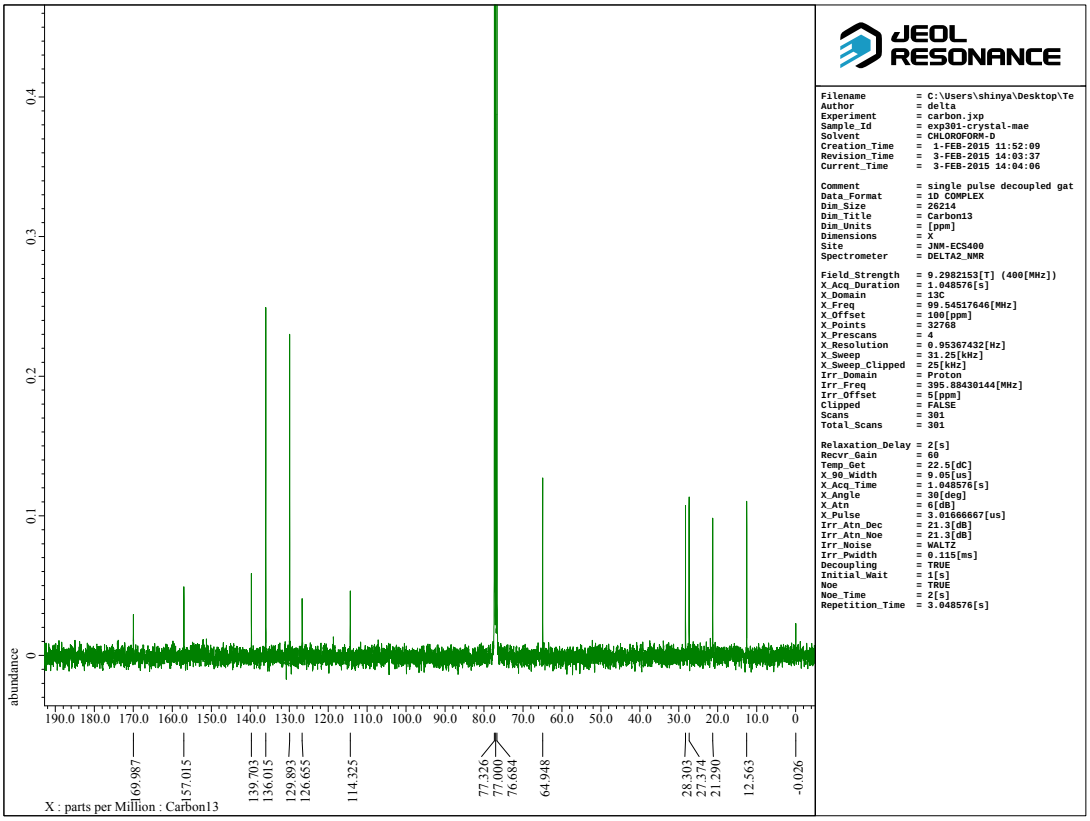
```
---- PROCESSING PARAMETERS ----
dc_balance( 0, FALSE )
sexp( 2.0[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1 )
fft( 1, TRUE, TRUE )
machinephase
ppm
```

以下C:自来:: exp336-crystal-mae_carbon-1-1.jdf

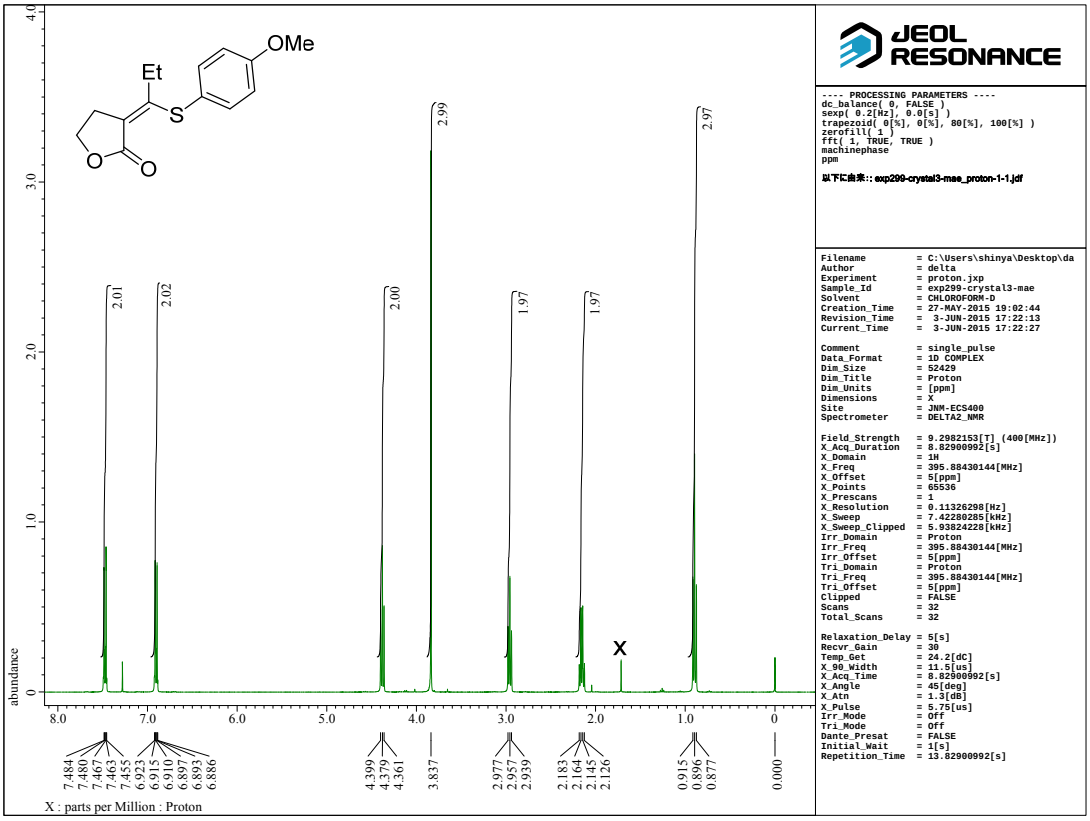
```
Filename          = C:\Users\shinya\Desktop\Te
Author            = delta
Experiment        = carbon.jxp
Sample_Id         = exp336-crystal-mae
Solvent           = CHLOROFORM-D
Creation_Time     =  9-FEB-2015 21:42:19
Revision_Time     = 10-FEB-2015 12:52:01
Current_Time      = 10-FEB-2015 12:52:13

Comment           = single pulse decoupled gat
Data_Format       = 1D COMPLEX
Dim_Size          = 26214
Dim_Title         = Carbon13
Dim_Units         = [ppm]
Dimensions        = X
Site              = JNM-ECX400
Spectrometer      = DELTA2_NMR

Field_Strength    = 9.389766[T] (400[MHz])
X_Acq_Duration    = 1.04333312[s]
X_Domain          = 13C
X_Freq            = 100.52530333[MHz]
X_Offset          = 100[ppm]
X_Points          = 32768
X_Prescans        = 4
X_Resolution      = 0.95846665[Hz]
X_Sweep           = 31.40703518[kHz]
X_Sweep_Clipped   = 25.12562814[kHz]
Irr_Domain        = Proton
Irr_Freq          = 399.78219838[MHz]
Irr_Offset        = 5[ppm]
Clipped           = FALSE
Scans             = 701
Total_Scans       = 701

Relaxation_Delay  = 2[s]
Recvr_Gain        = 46
Temp_Get          = 21.5[dC]
X_90_Width        = 8.7[us]
X_Acq_Time        = 1.04333312[s]
X_Angle           = 30[deg]
X_Atn             = 9[dB]
X_Pulse           = 2.9[us]
Irr_Atn_Dec       = 24.13[dB]
Irr_Atn_Noe       = 24.13[dB]
Irr_Noise         = WALTZ
Irr_Pwidth        = 0.115[ms]
Decoupling        = TRUE
Initial_Wait      = 1[s]
Noe               = TRUE
Noe_Time          = 2[s]
Repetition_Time   = 3.04333312[s]
```

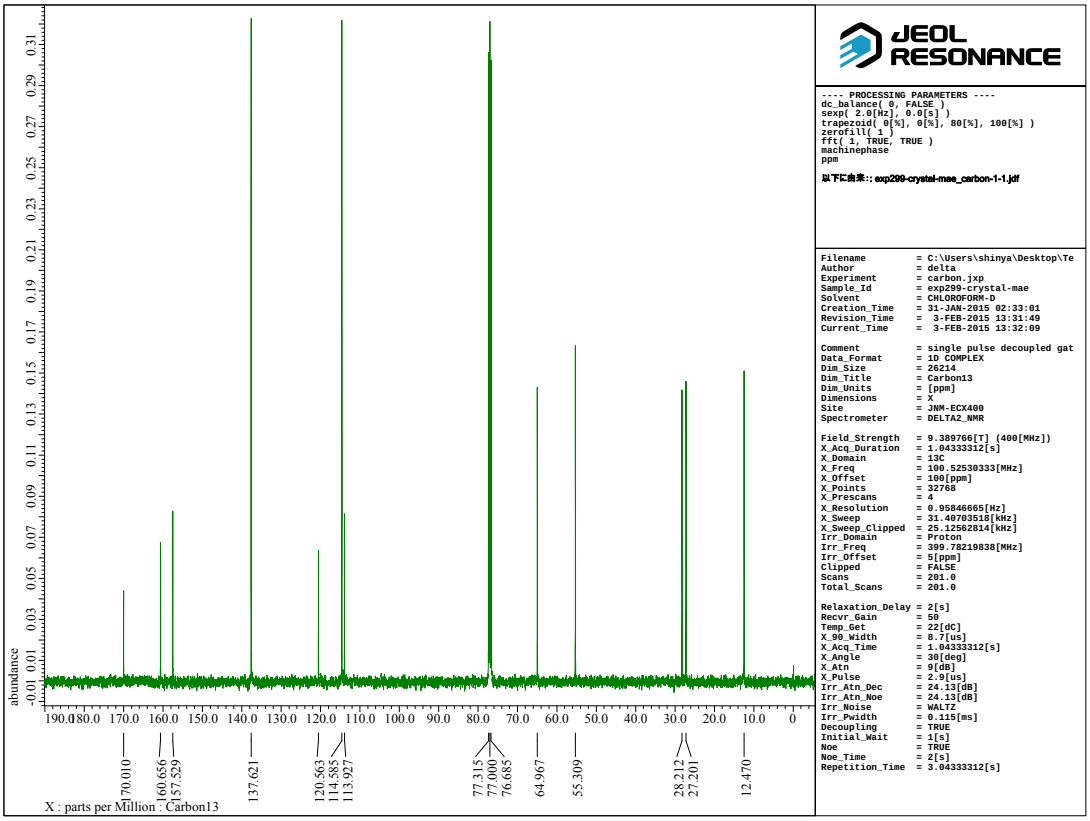
(Z)-3-{1-(p-tolylthio)propylidene}dihydrofuran-2-one (3ab)



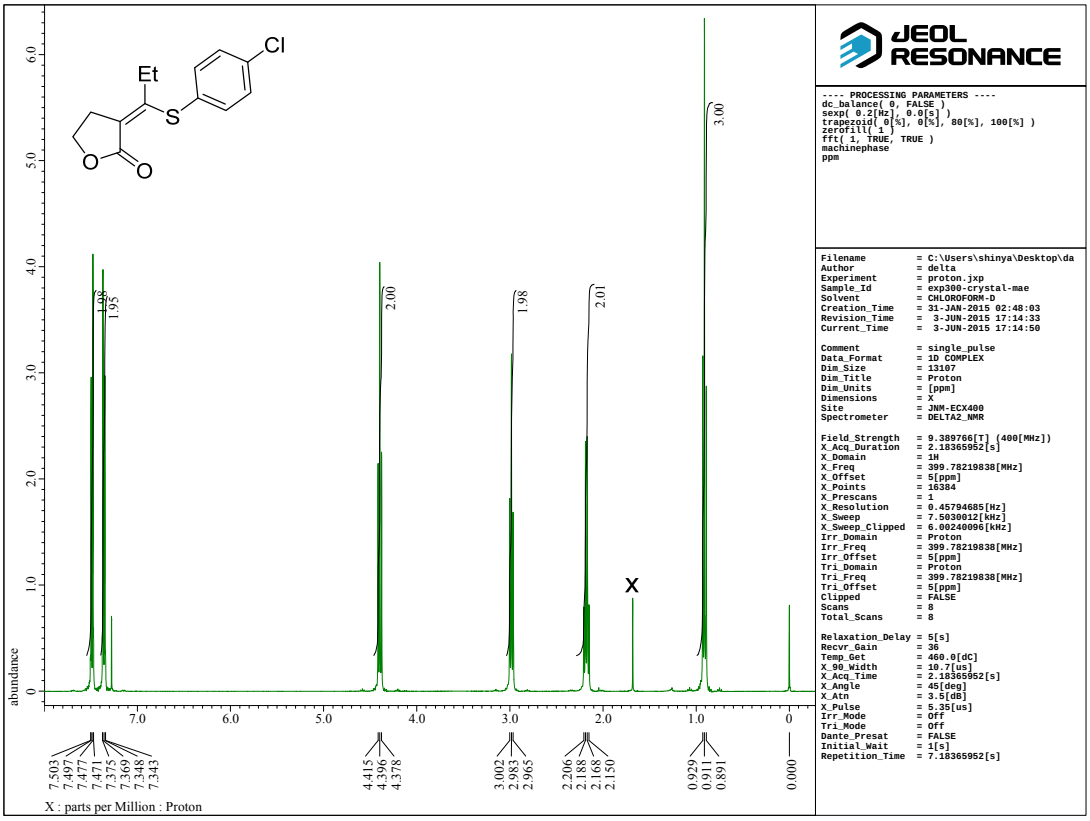


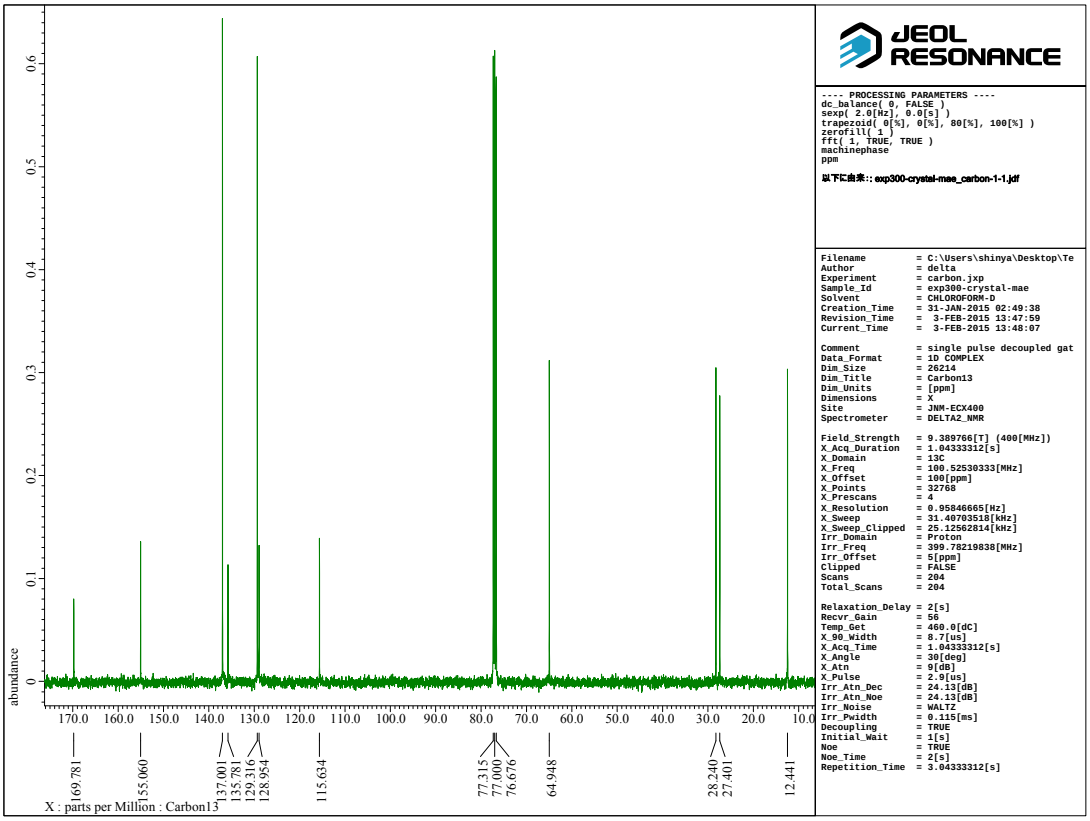
(Z)-3-{1- (4-methoxyphenylthio)propylidene}dihydrofuran-2-one (3ac)



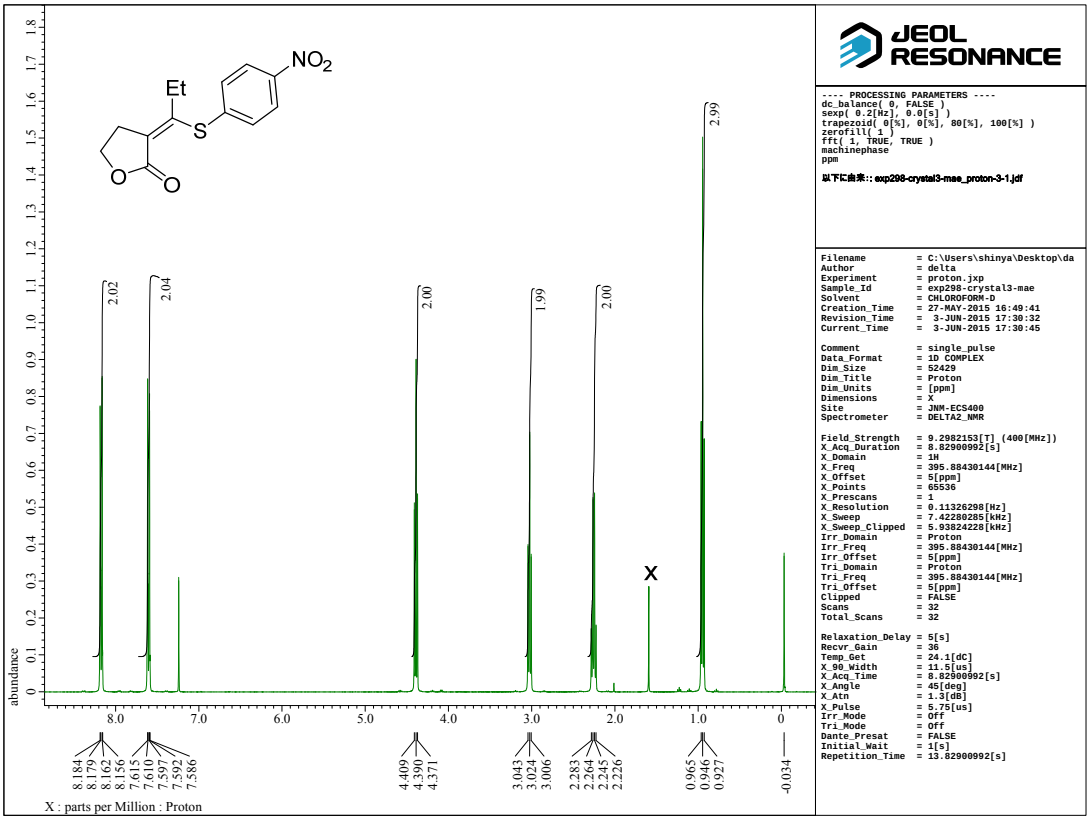


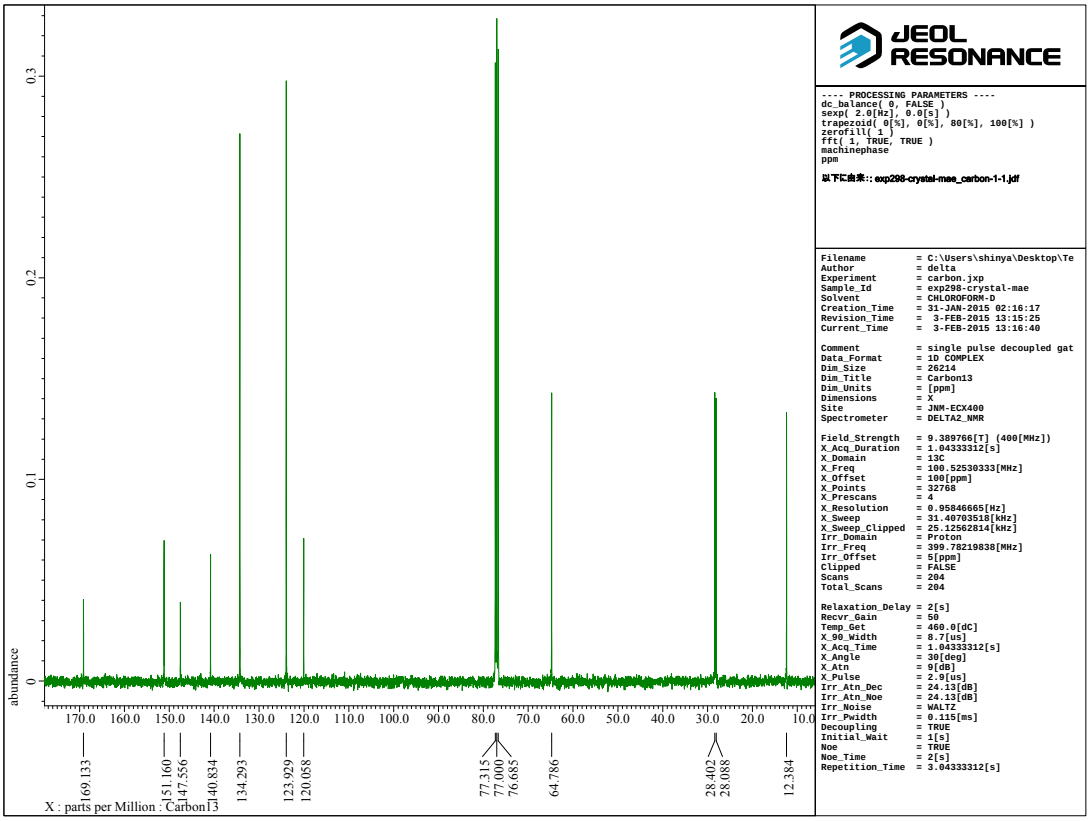
(Z)-3-{1-(4-chlorophenylthio)propylidene}dihydrofuran-2-one (3ad)



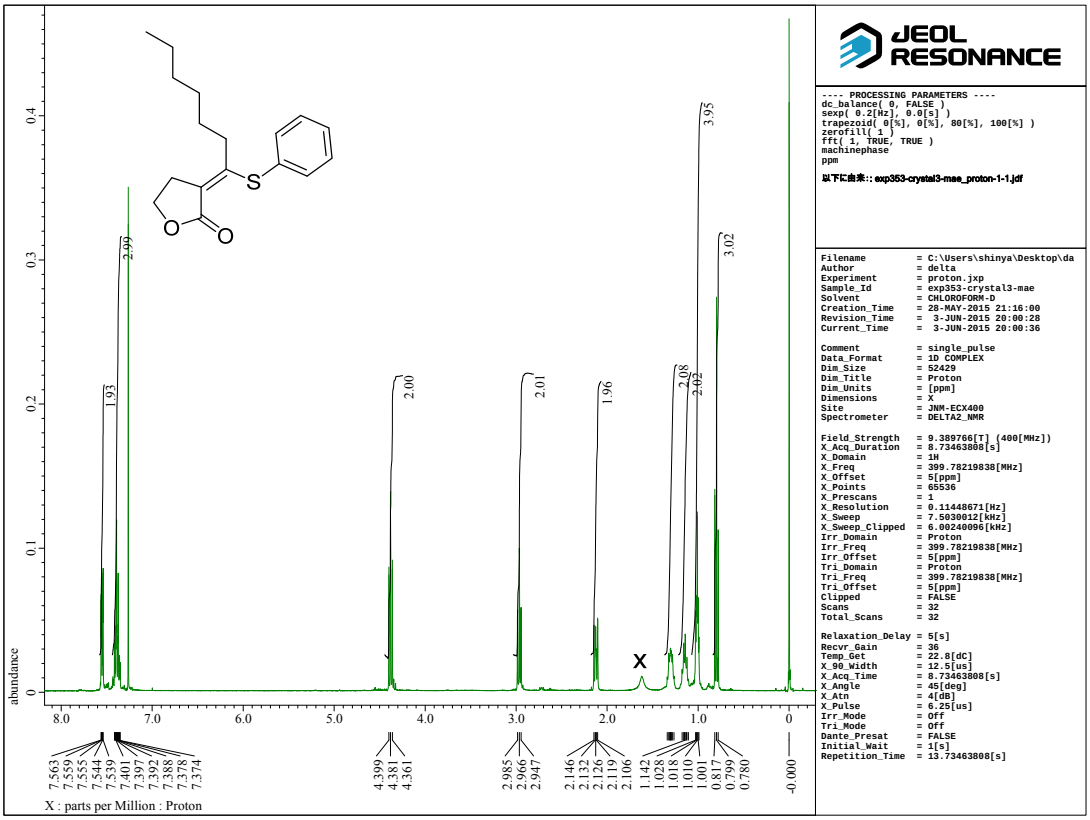


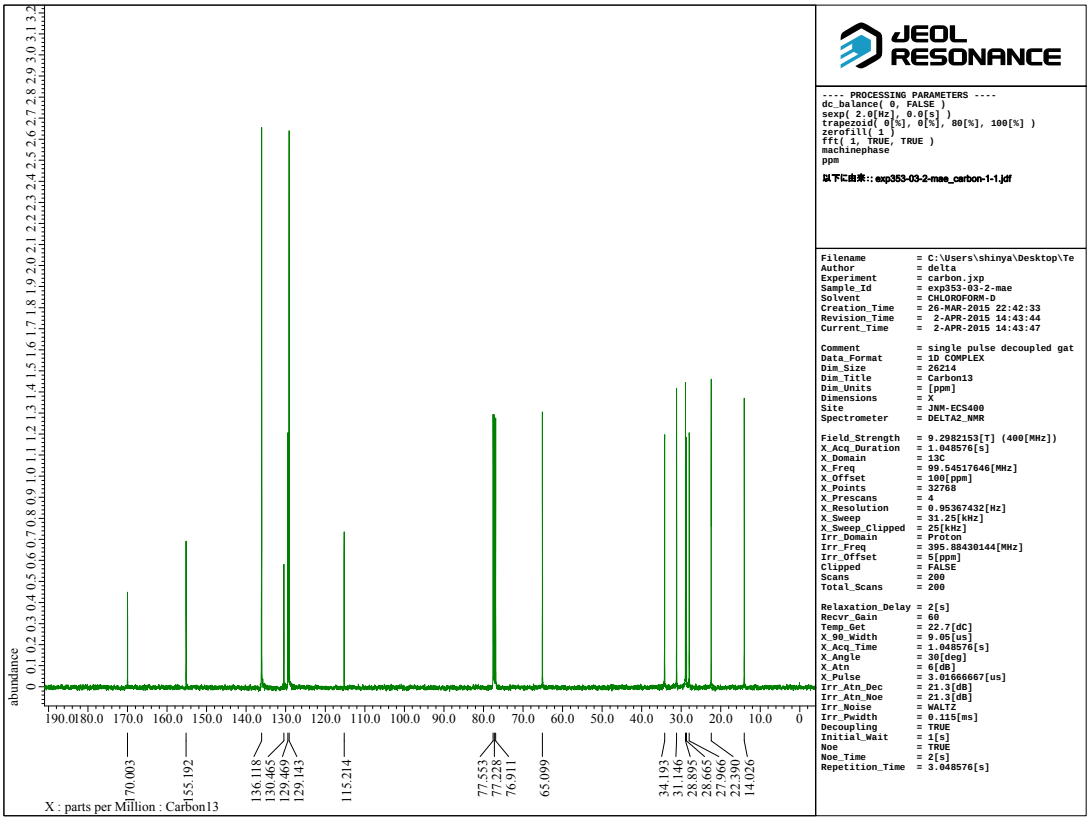
(Z)-3-{1-(4-nitrophenylthio)propylidene}dihydrofuran-2-one (3ae)



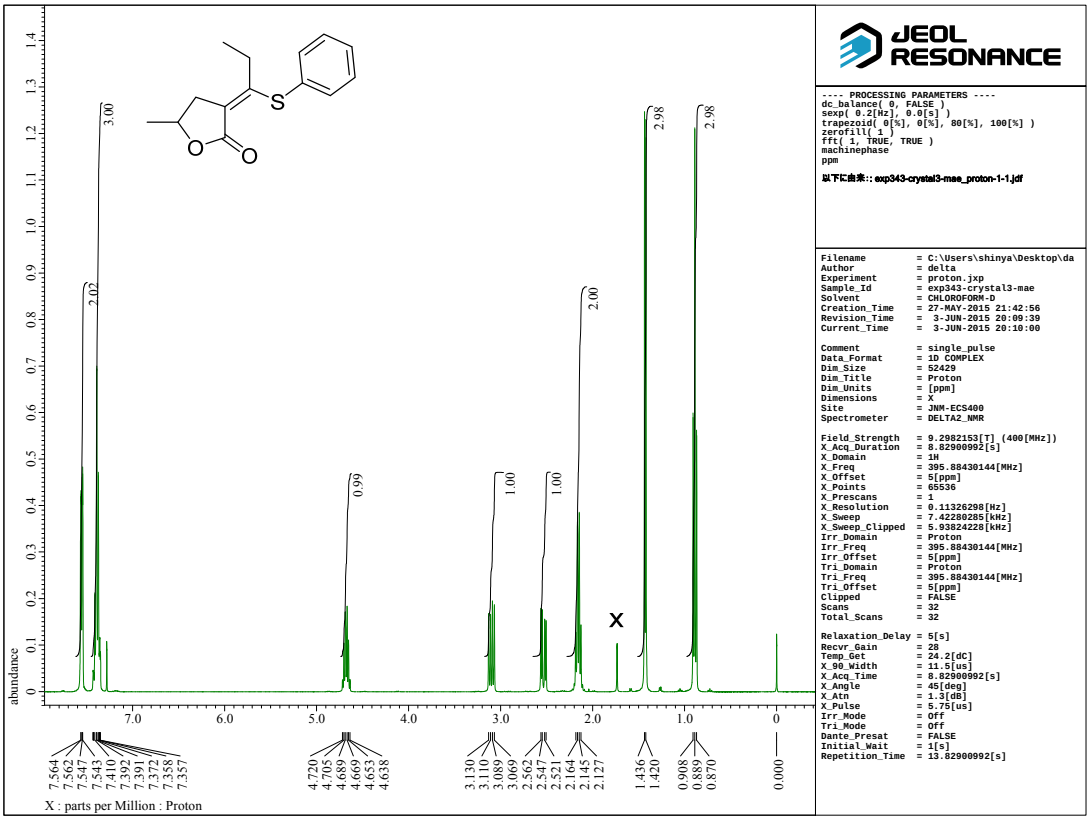


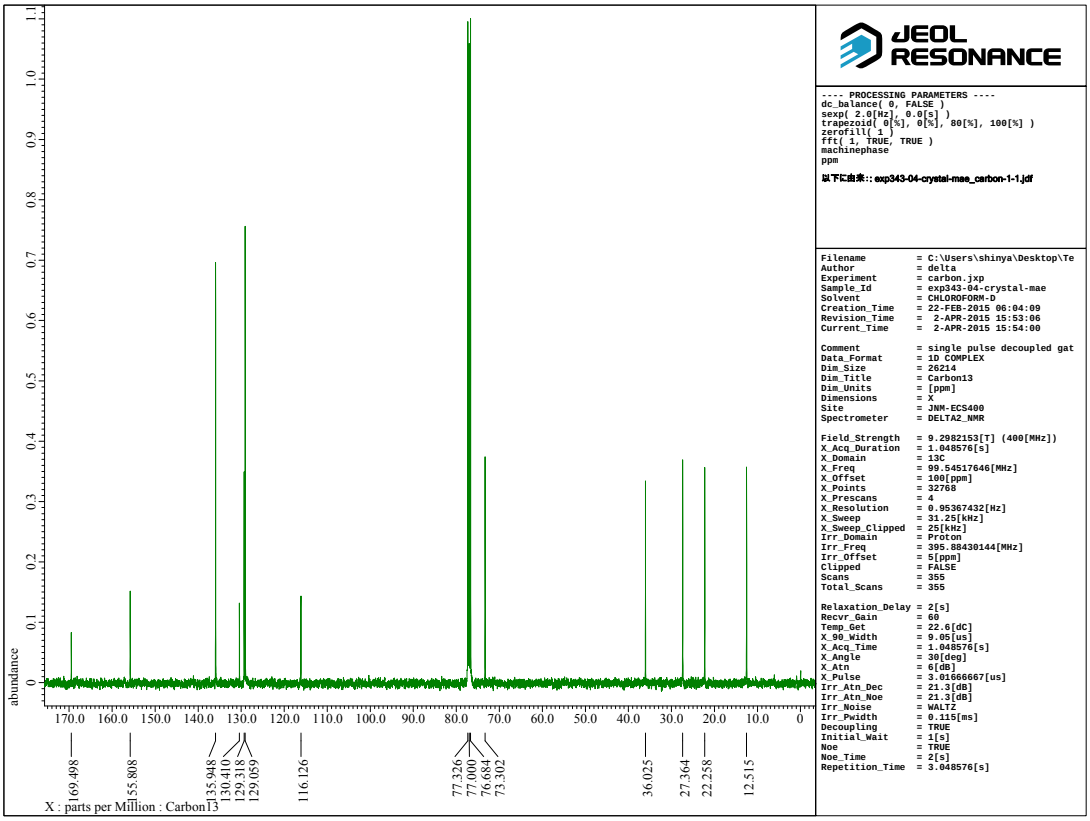
(Z)-3-{1-(phenylthio)heptylidene}dihydrofuran-2-one (3ba)



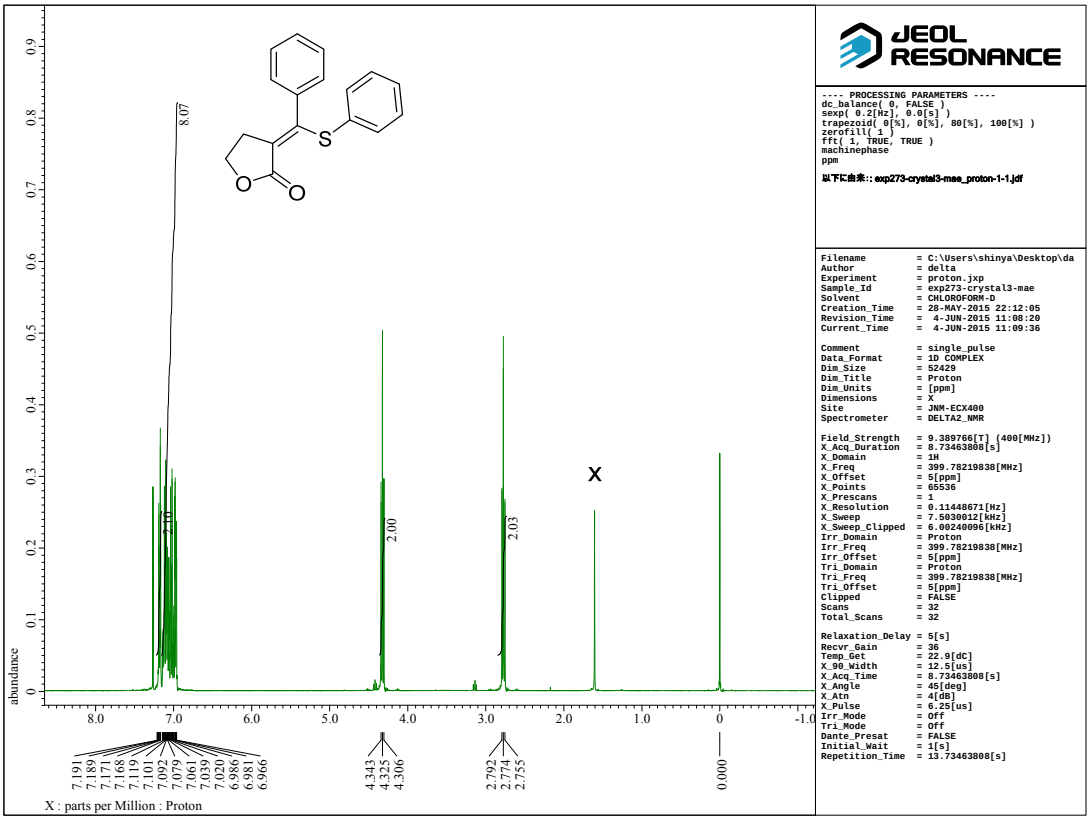


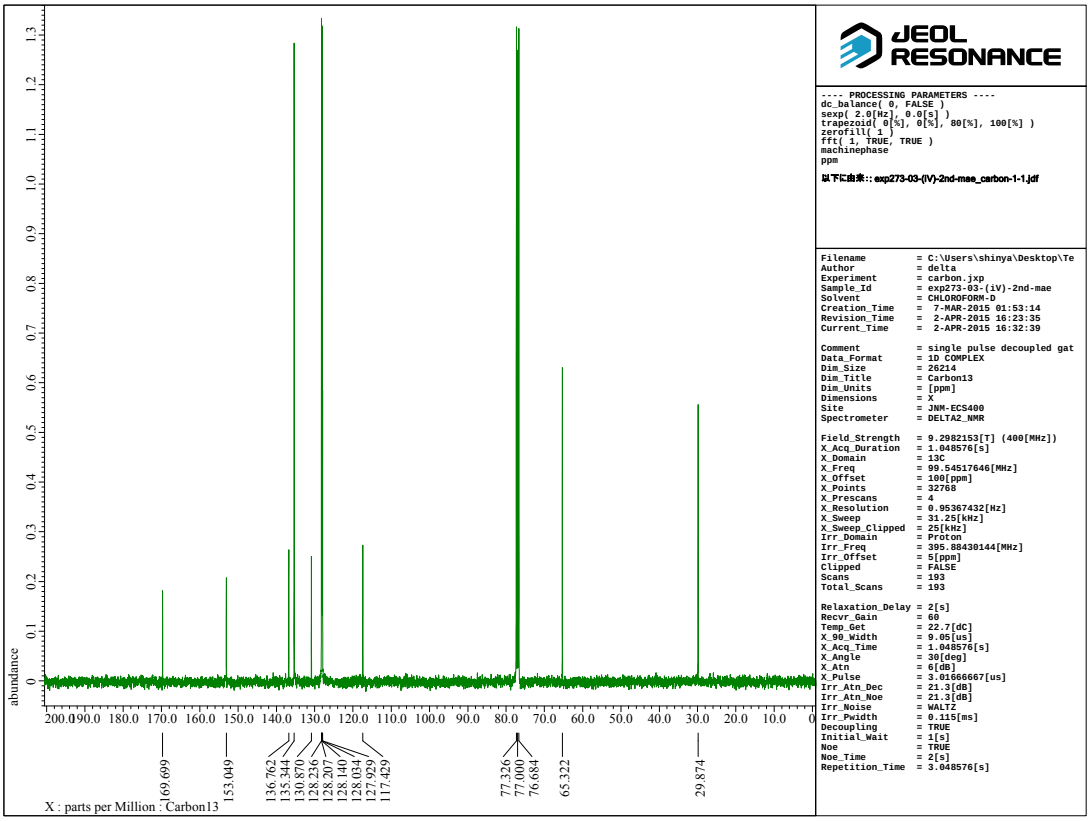
(Z)-5-methyl-3-{1-(phenylthio)propylidene}dihydrofuran-2-one (3ca).



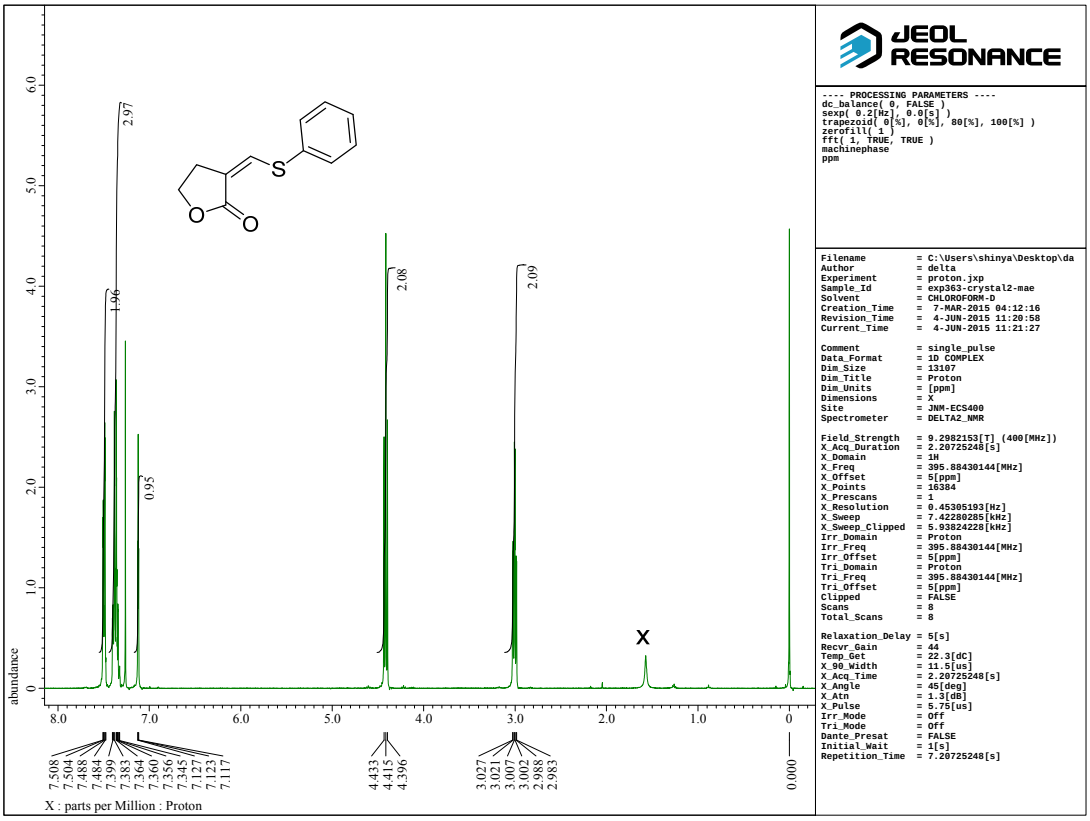


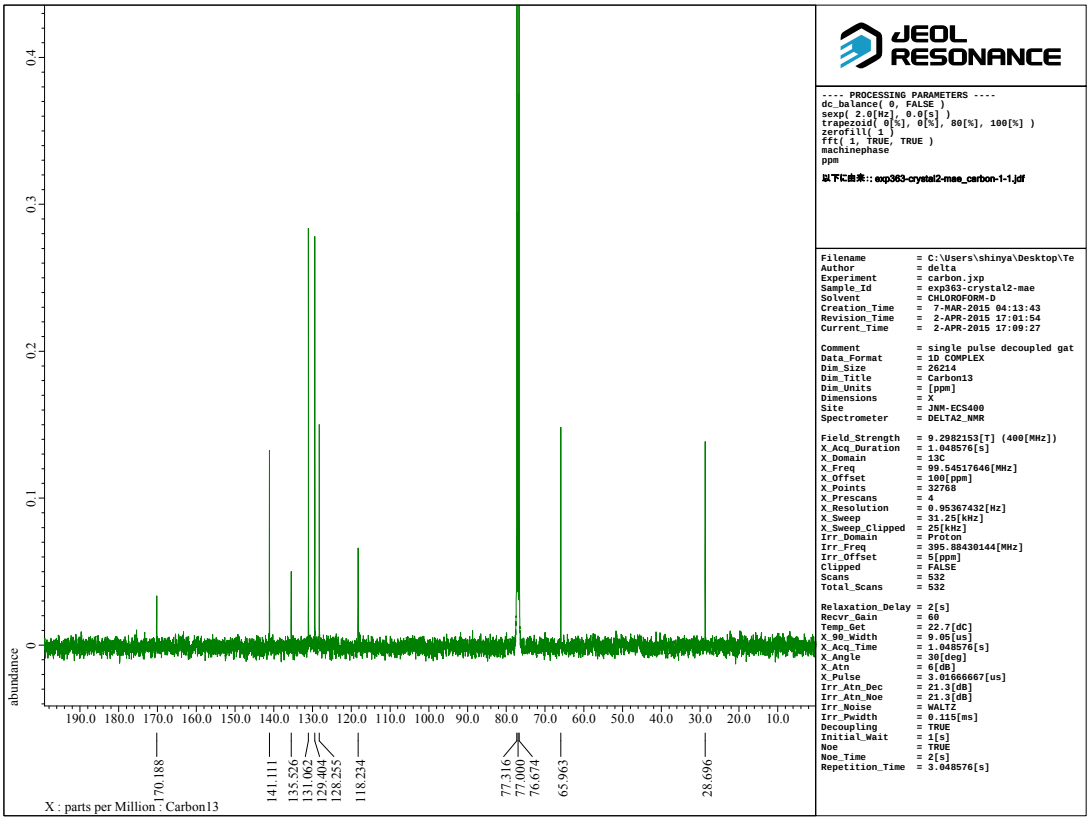
(Z)-3-{1-phenyl-1-(phenylthio)methylene}dihydrofuran-2-one (3da)



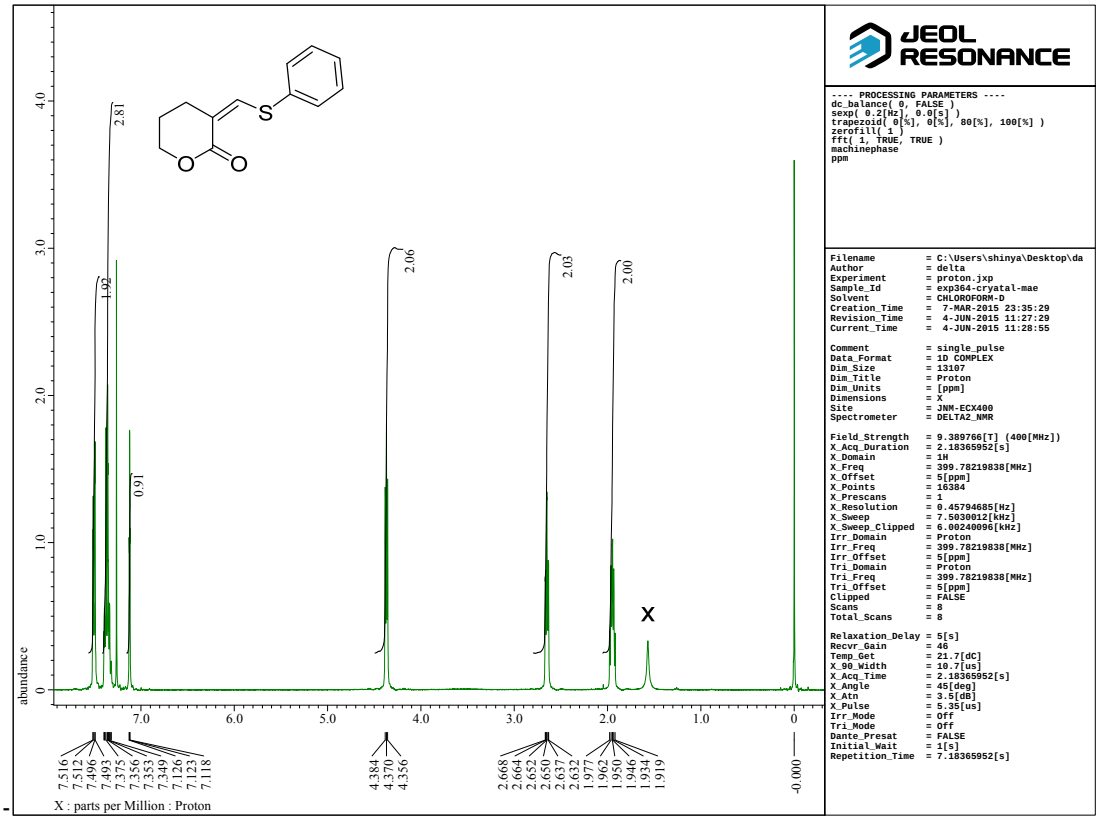


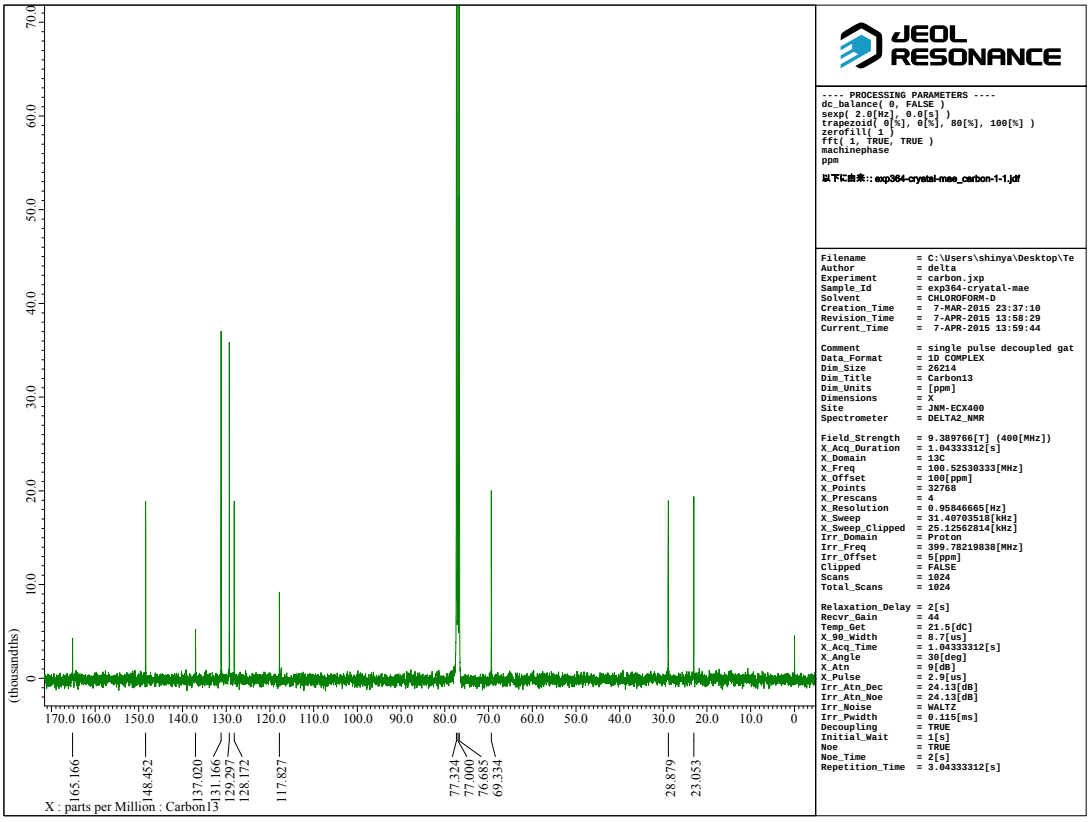
(Z)-3-{(phenylthio)methylene}dihydrofuran-2-one (3ea).



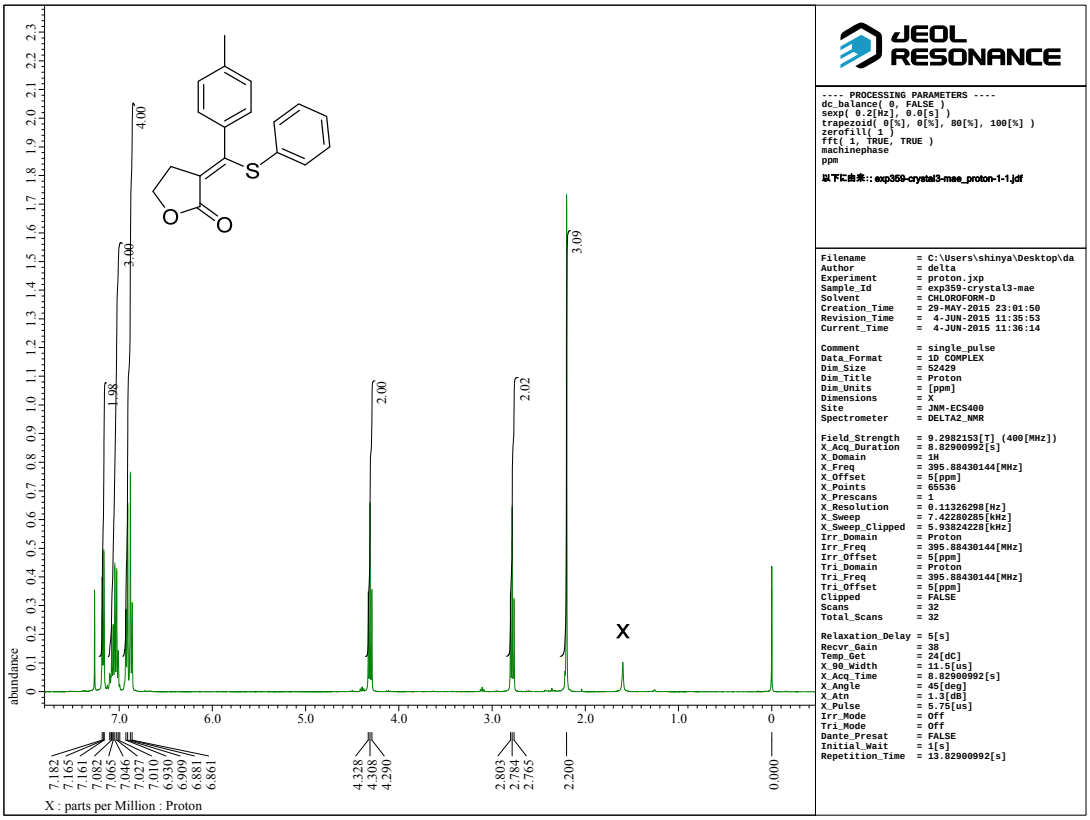


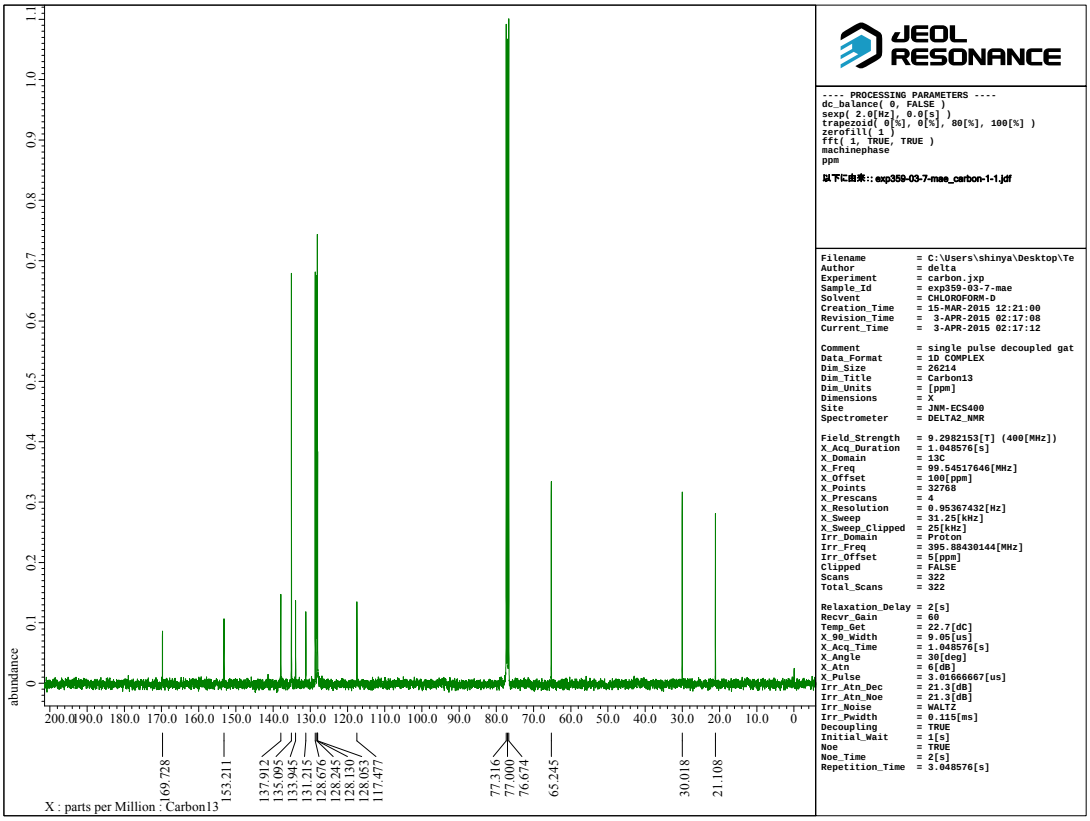
(Z)-3-{(phenylthio)methylene}tetrahydropyran-2-one (3fa).



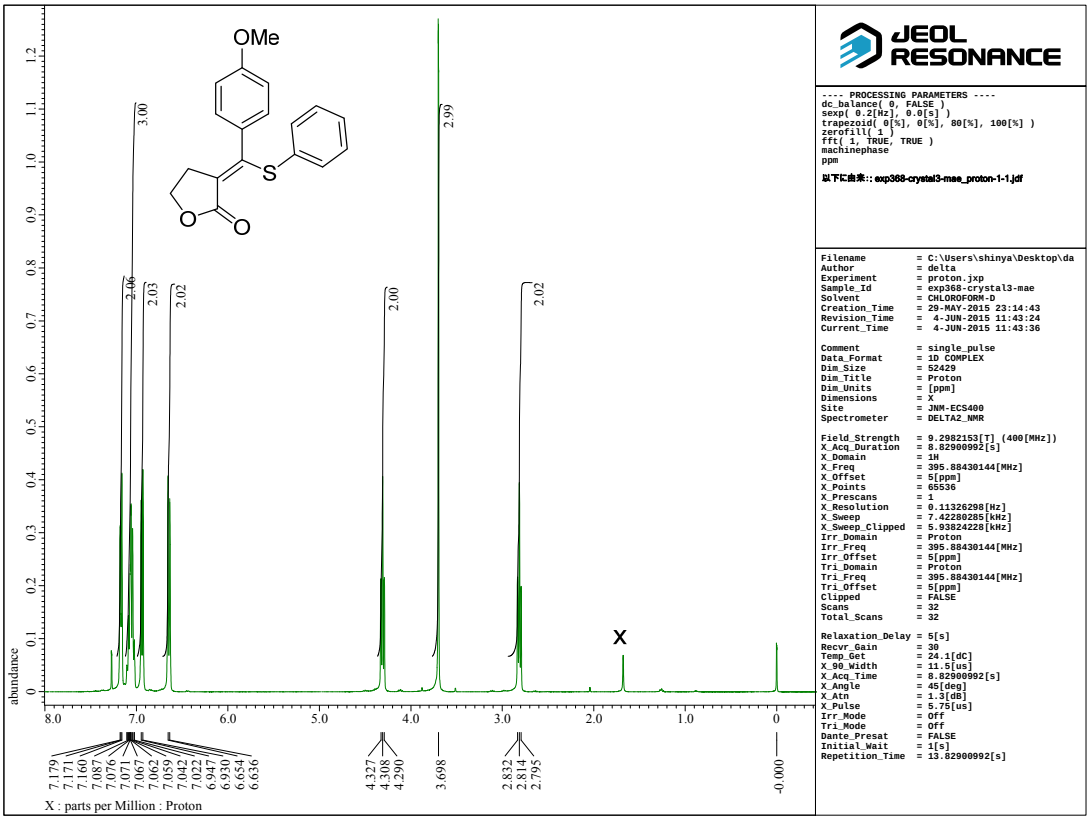


(Z)-3-{1-(phenylthio)-1-(p-tolyl)methylene}dihydrofuran-2-one (3ga).

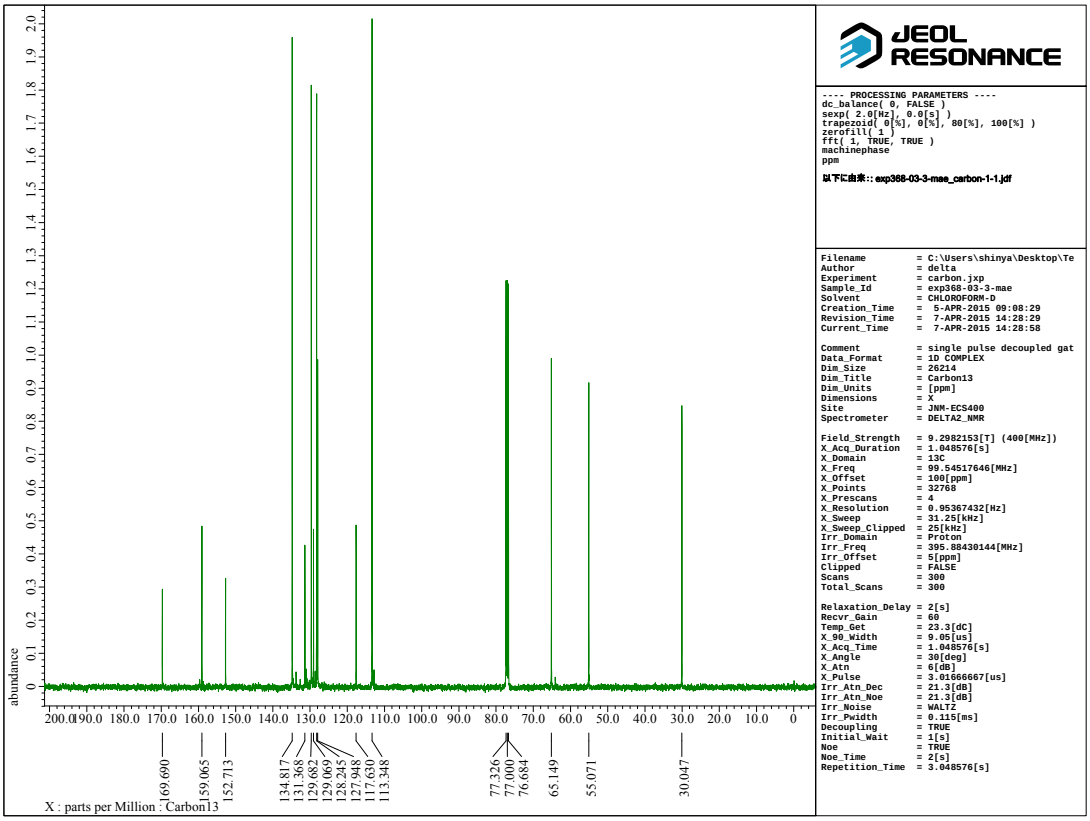




(Z)-3-{1-(4-methoxyphenyl)-1-(phenylthio)methylene}dihydrofuran-2-one (3ha).

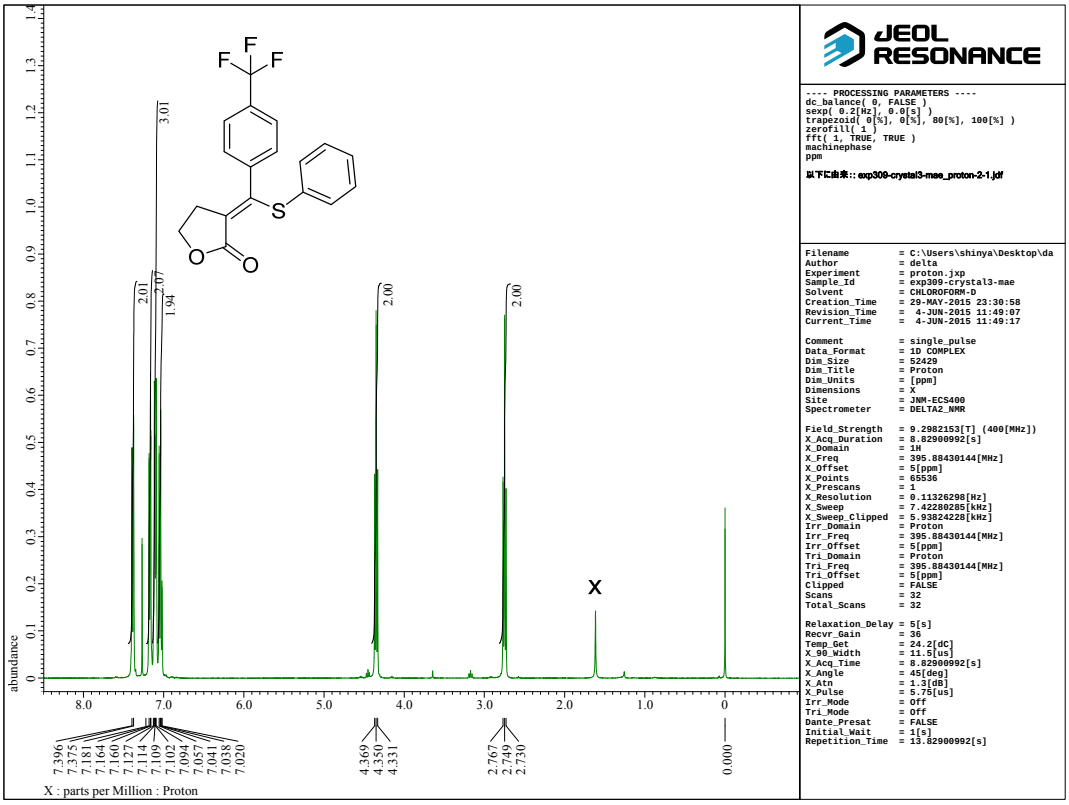


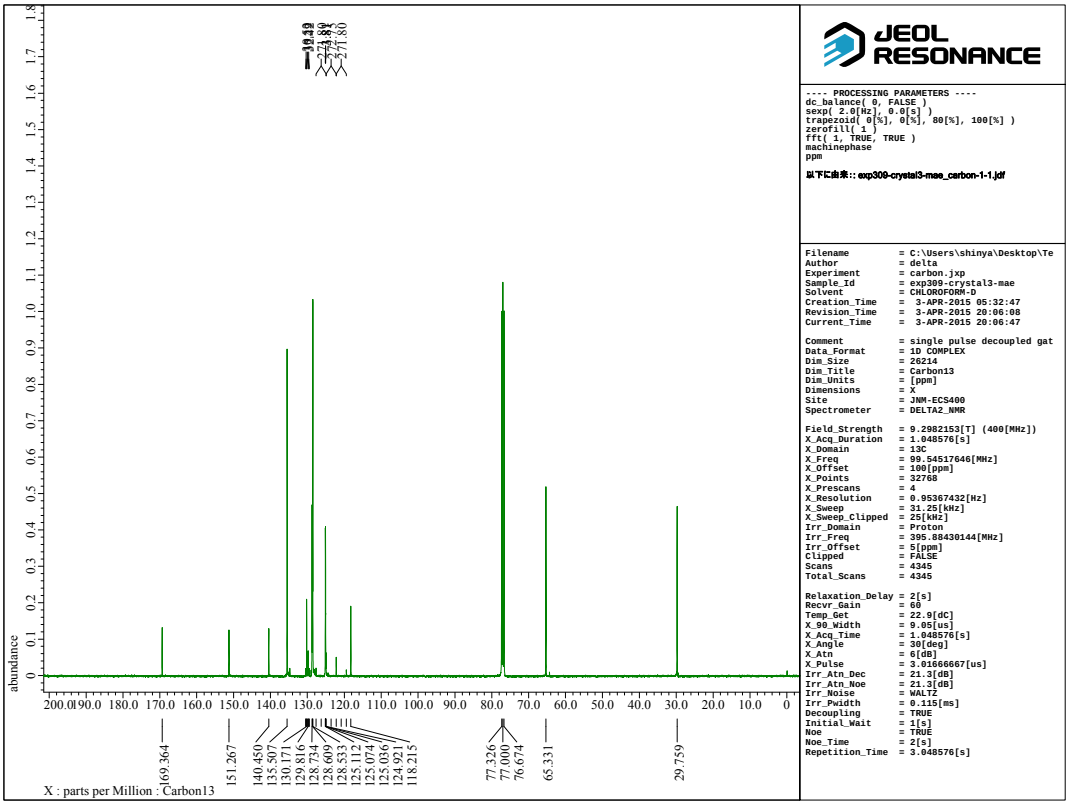

```
---- PROCESSING PARAMETERS ----
dc_balance( 0, FALSE )
sexp( 0.2[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1 )
fft( 1, TRUE, TRUE )
machinephase
ppm

以下に由来:: exp368-crystal3-mae_proton-1-1.jdf

Filename          = C:\Users\shinya\Desktop\da
Author            = delta
Experiment        = proton.jxp
Sample_Id         = exp368-crystal3-mae
Solvent           = CHLOROFORM-D
Creation_Time     = 29-MAY-2015 23:14:43
Revision_Time     =  4-JUN-2015 11:43:24
Current_Time      =  4-JUN-2015 11:43:36

Comment           = single_pulse
Data_Format       = 1D COMPLEX
Dim_Size          = 52429
Dim_Title         = Proton
Dim_Units         = [ppm]
Dimensions        = X
Site              = JNM-ECS400
Spectrometer      = DELTA2_NMR

Field_Strength    = 9.2982153[T] (400[MHz])
X_Acq_Duration    = 8.82900992[s]
X_Domain          = 1H
X_Freq            = 395.88430144[MHz]
X_Offset          = 5[ppm]
X_Points          = 65536
X_Prescans        = 1
X_Resolution      = 0.11326298[Hz]
X_Sweep           = 7.42280285[kHz]
X_Sweep_Clipped   = 5.93824228[kHz]
Irr_Domain        = Proton
Irr_Freq          = 395.88430144[MHz]
Irr_Offset        = 5[ppm]
Tri_Domain        = Proton
Tri_Freq          = 395.88430144[MHz]
Tri_Offset        = 5[ppm]
Clipped           = FALSE
Scans             = 32
Total_Scans       = 32

Relaxation_Delay  = 5[s]
Recvr_Gain        = 30
Temp_Get          = 24.1[dC]
X_90_Width        = 11.5[us]
X_Acq_Time        = 8.82900992[s]
X_Angle           = 45[deg]
X_Atn             = 1.3[dB]
X_Pulse           = 5.75[us]
Irr_Mode          = Off
Tri_Mode          = Off
Dante_Presat      = FALSE
Initial_Wait      = 1[s]
Repetition_Time   = 13.82900992[s]
```




```
---- PROCESSING PARAMETERS ----
dc_balance( 0, FALSE )
sexp( 2.0[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1 )
fft( 1, TRUE, TRUE )
machinephase
ppm

以下に由来:: exp368-03-3-mae_carbon-1-1.jdf

Filename          = C:\Users\shinya\Desktop\Te
Author            = delta
Experiment        = carbon.jxp
Sample_Id         = exp368-03-3-mae
Solvent           = CHLOROFORM-D
Creation_Time     =  5-APR-2015 09:08:29
Revision_Time     =  7-APR-2015 14:28:29
Current_Time      =  7-APR-2015 14:28:58

Comment           = single pulse decoupled gat
Data_Format       = 1D COMPLEX
Dim_Size          = 26214
Dim_Title         = Carbon13
Dim_Units         = [ppm]
Dimensions        = X
Site              = JNM-ECS400
Spectrometer      = DELTA2_NMR

Field_Strength    = 9.2982153[T] (400[MHz])
X_Acq_Duration    = 1.048576[s]
X_Domain          = 13C
X_Freq            = 99.54517646[MHz]
X_Offset          = 100[ppm]
X_Points          = 32768
X_Prescans        = 4
X_Resolution      = 0.95367432[Hz]
X_Sweep           = 31.25[kHz]
X_Sweep_Clipped   = 25[kHz]
Irr_Domain        = Proton
Irr_Freq          = 395.88430144[MHz]
Irr_Offset        = 5[ppm]
Clipped           = FALSE
Scans             = 300
Total_Scans       = 300

Relaxation_Delay  = 2[s]
Recvr_Gain        = 60
Temp_Get          = 23.3[dC]
X_90_Width        = 9.05[us]
X_Acq_Time        = 1.048576[s]
X_Angle           = 30[deg]
X_Atn             = 6[dB]
X_Pulse           = 3.01666667[us]
Irr_Atn_Dec       = 21.3[dB]
Irr_Atn_Noe       = 21.3[dB]
Irr_Noise         = WALTZ
Irr_Pwidth        = 0.115[ms]
Decoupling        = TRUE
Initial_Wait      = 1[s]
Noe               = TRUE
Noe_Time          = 2[s]
Repetition_Time   = 3.048576[s]
```

(Z)-3-[1-(phenylthio)-1-{4-(trifluoromethyl)phenyl}methylene]dihydrofuran-2-one (3ia).





(Z)-3-{1-(4-methoxyphenyl)-1-(phenylthio)methylene}tetrahydropyran-2-one (3ja).