Supplementary Information

Supramolecular Chiral Dendritic Monophosphites Assembled by Hydrogen Bonding and Their Use in the Rh-Catalyzed Asymmetric Hydrogenation

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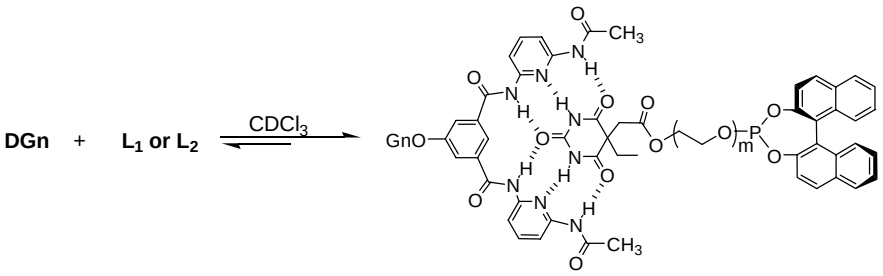
1. General Method

Unless otherwise noted, all experiments were carried out under an inert atmosphere of dry nitrogen by using standard Schlenk-type techniques, or performed in a nitrogen-filled glovebox. ^{1}H NMR, ^{13}C NMR and ^{31}P NMR spectra were recorded on a Bruker Model Avance DMX 300 or 400 Spectrometer (^{1}H 300 MHz, ^{13}C 75 MHz and ^{31}P 162 MHz, respectively). Chemical shifts (δ) are given in ppm and are referenced to residual solvent peaks (^{1}H and ^{13}C NMR) or to an external standard (85% H_3PO_4, ^{31}P NMR). MALDI-TOF mass spectra were obtained on a BIFLEX Ⅲ instrument with α-cyano-4-hydroxycinnamic acid (CCA) as the matrix. All enantiomeric excess values were obtained from GC analysis with a Chrompack CHIR-L-VAL column. All solvents were dried using standard, published methods and were distilled under a nitrogen atmosphere before use. All other chemicals were used as received from Aldrich or Acros without further purification.

2. Synthesis and Characterization of the Supramolecular Dendritic Chiral Monophosphite Ligands



DG_1L_1 ($Gn = G_1$; $m = 3$)
DG_2L_1 ($Gn = G_2$; $m = 3$)
DG_3L_1 ($Gn = G_3$; $m = 3$)
DG_1L_2 ($Gn = G_1$; $m = 1$)
DG_2L_2 ($Gn = G_2$; $m = 1$)
DG_3L_2 ($Gn = G_3$; $m = 1$)

Figure S1: Supramolecular dendritic chiral monophosphite ligands

DGnL: The complexation between **DGn** and $\mathbf{L_1}$ or $\mathbf{L_2}$ was observed when an equal amount of **DGn** and $\mathbf{L_1}$ or $\mathbf{L_2}$ was mixed in $CDCl_3$. The formation of **DGnL** was confirmed by ^{1}H, ^{31}P NMR. As shown in **Figure S2-7**, it was noted that the signals of

NH protons of **DGn** and **L** shifted significantly downfield. In the ^{31}P NMR spectrum, only one new peak at ca. 139 ppm was observed without appearing the signals of the free ligands. These results revealed the formation of supramolecular chiral dendritic monophosphite ligands.

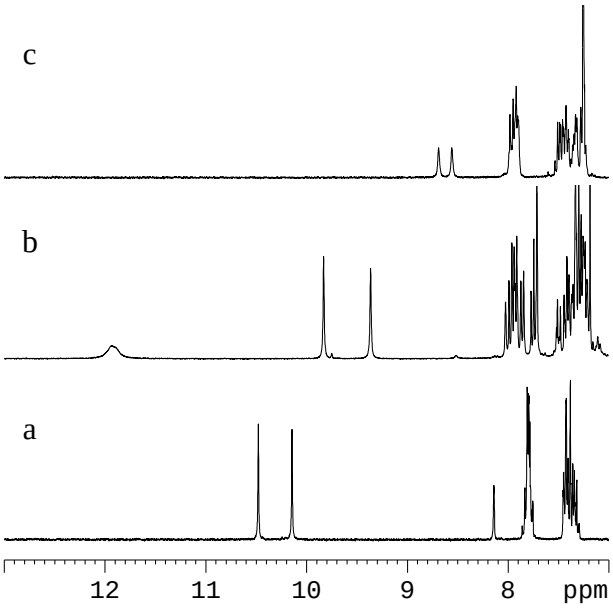


Figure S2. Partial ^{1}H NMR Spectra ($CDCl_3$, 300 MHz, 295k, 8.0 mM) of (a) free receptor **DG_1**(in DMSO-d_6), (b) **DG_1** and **L_1**, (c) free ligand **L_1**.

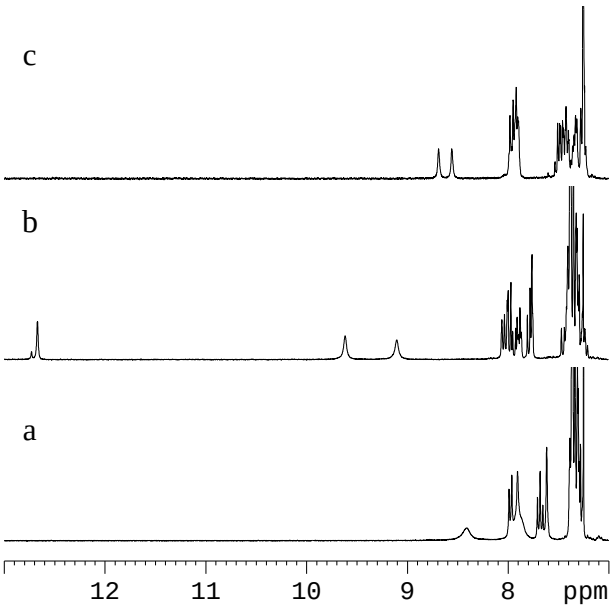


Figure S3. Partial ^{1}H NMR Spectra ($CDCl_3$, 300 MHz, 295k, 8.0 mM) of (a) free receptor **DG_2**, (b) **DG_2** and **L_1**, (c) free ligand **L_1**.

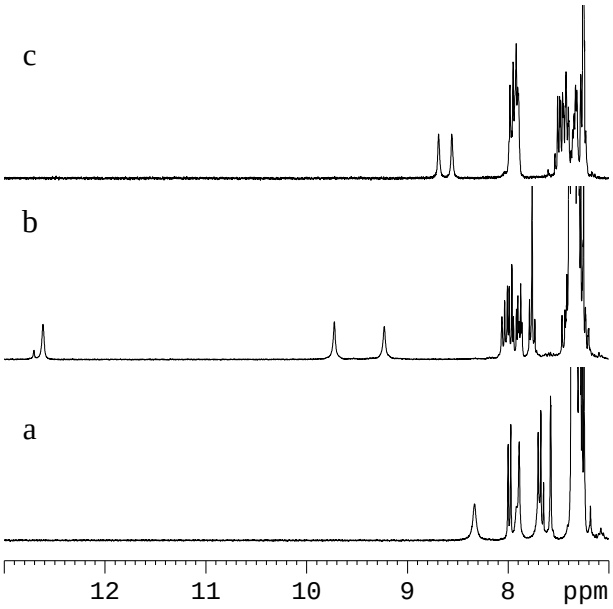


Figure S4. Partial ^{1}H NMR Spectra ($CDCl_3$, 300 MHz, 295k, 8.0 mM) of (a) free receptor **DG_3**, (b) **DG_3** and **L_1**, (c) free ligand **L_1**.

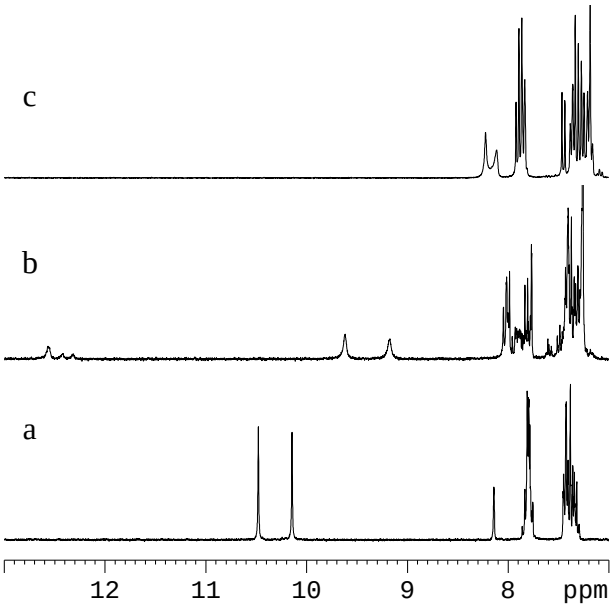


Figure S5. Partial ^{1}H NMR Spectra ($CDCl_3$, 300 MHz, 295k, 8.0 mM) of (a) free receptor **DG_1** (in DMSO-d_6), (b) **DG_1** and **L_2**, (c) free ligand **L_2**.

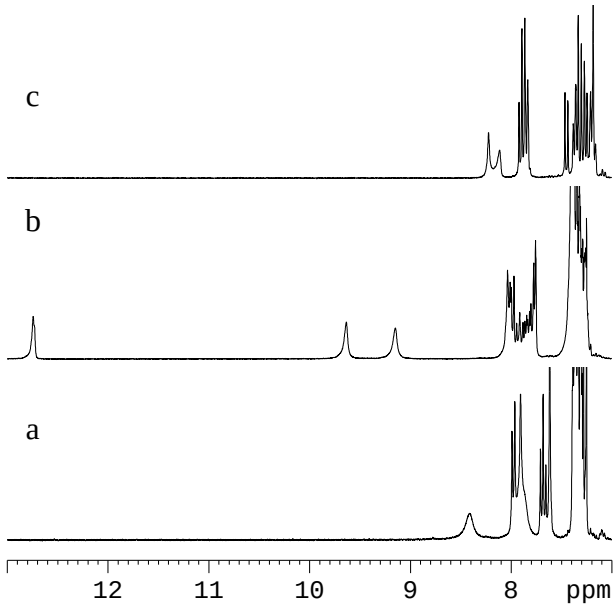


Figure S6. Partial ^{1}H NMR Spectra ($CDCl_3$, 300 MHz, 295k, 8.0 mM) of (a) free receptor **DG_2**, (b) **DG_2** and **L_2**, (c) free ligand **L_2**.

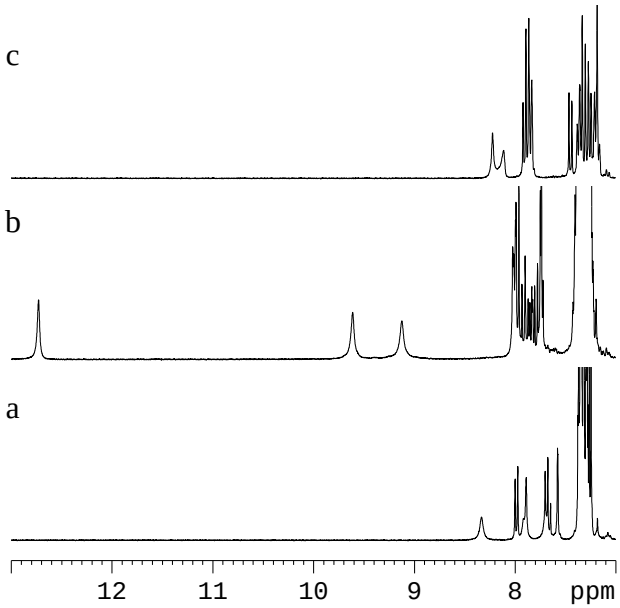
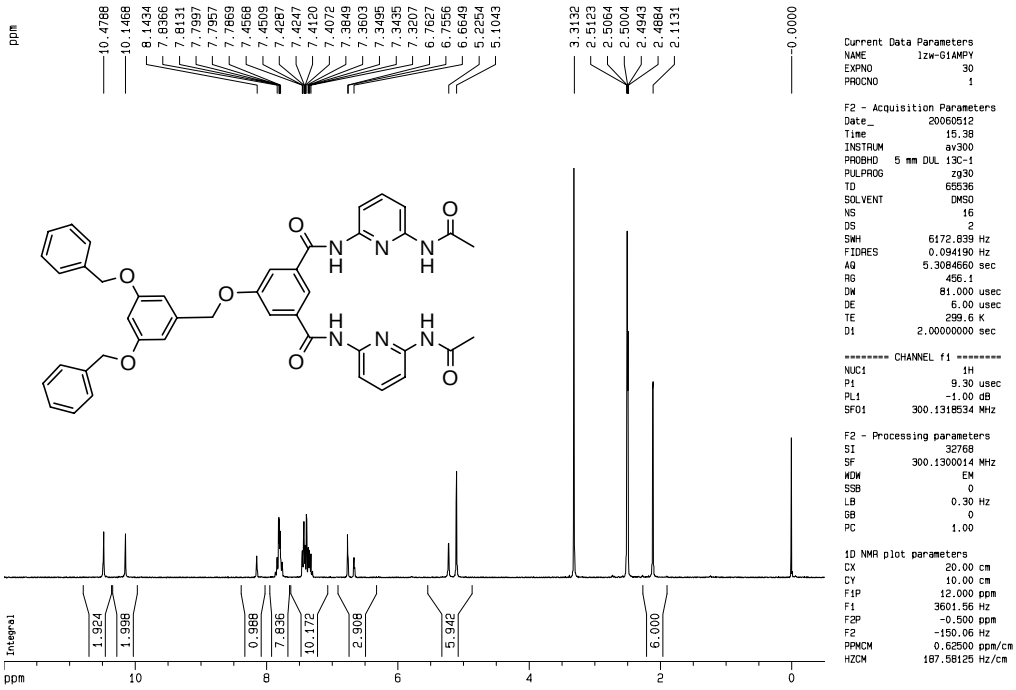
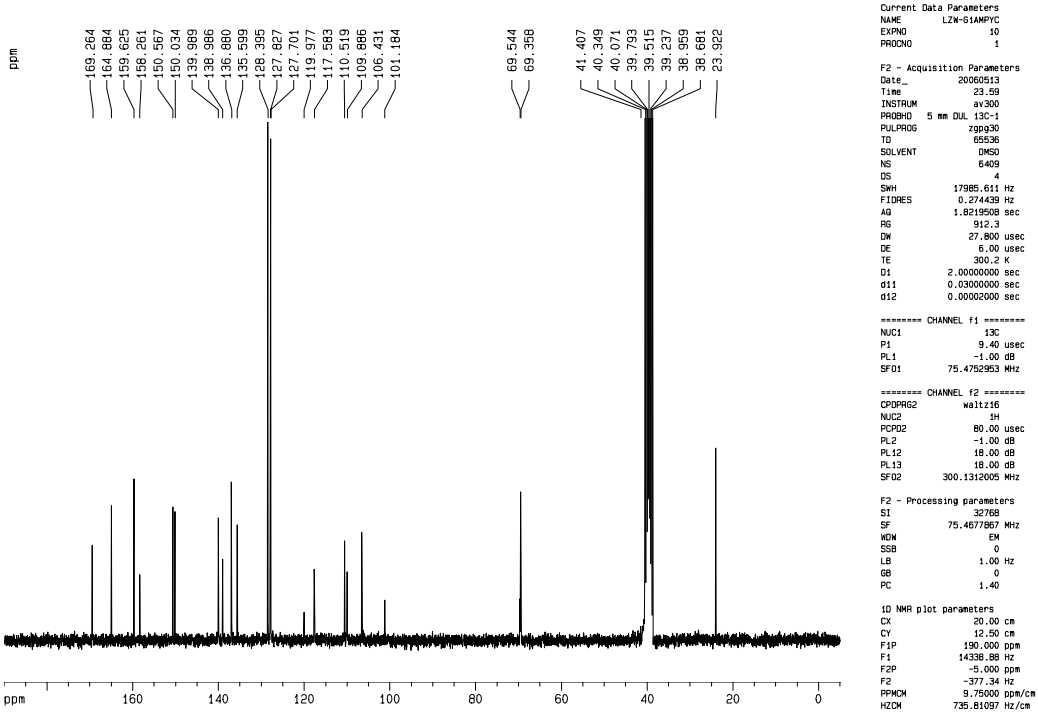


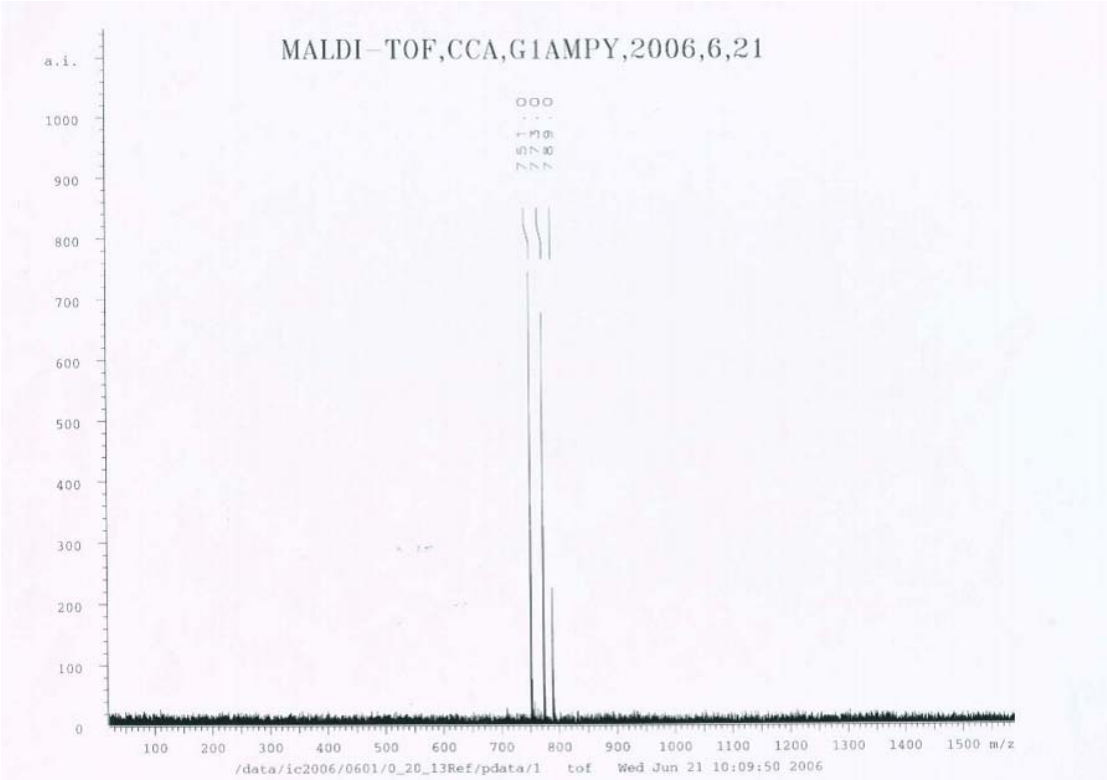
Figure S7. Partial ^{1}H NMR Spectra ($CDCl_3$, 300 MHz, 295k, 8.0 mM) of (a) free receptor **DG_3**, (b) **DG_3** and **L_2**, (c) free ligand **L_2**.

3. Representative NMR Spectra

^{1}H and ^{13}C NMR of **DG_1**







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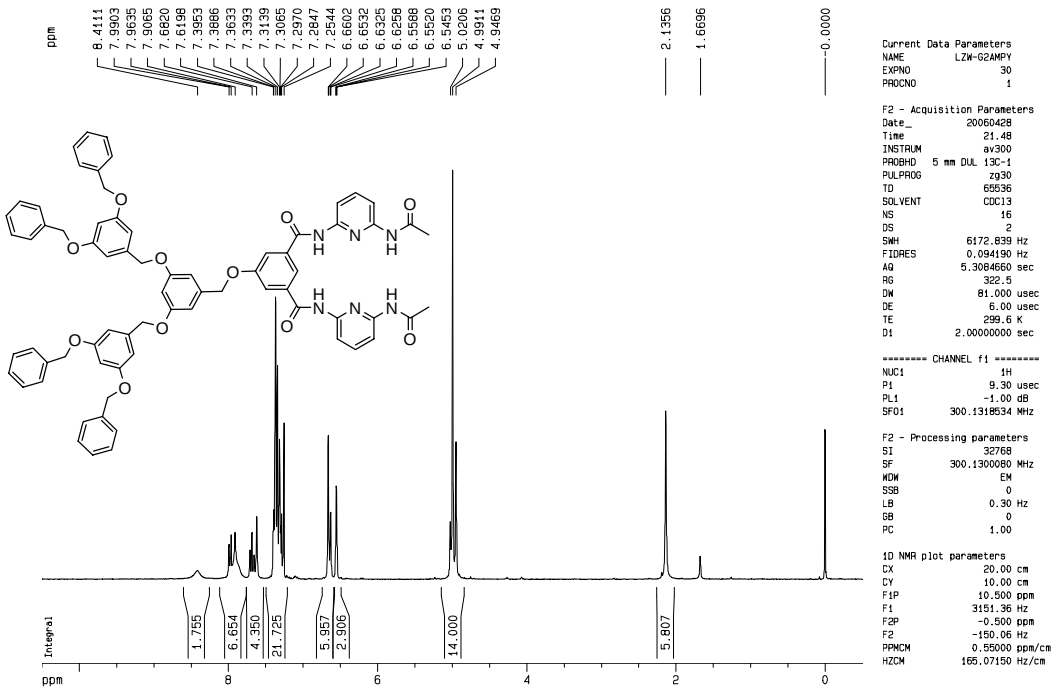

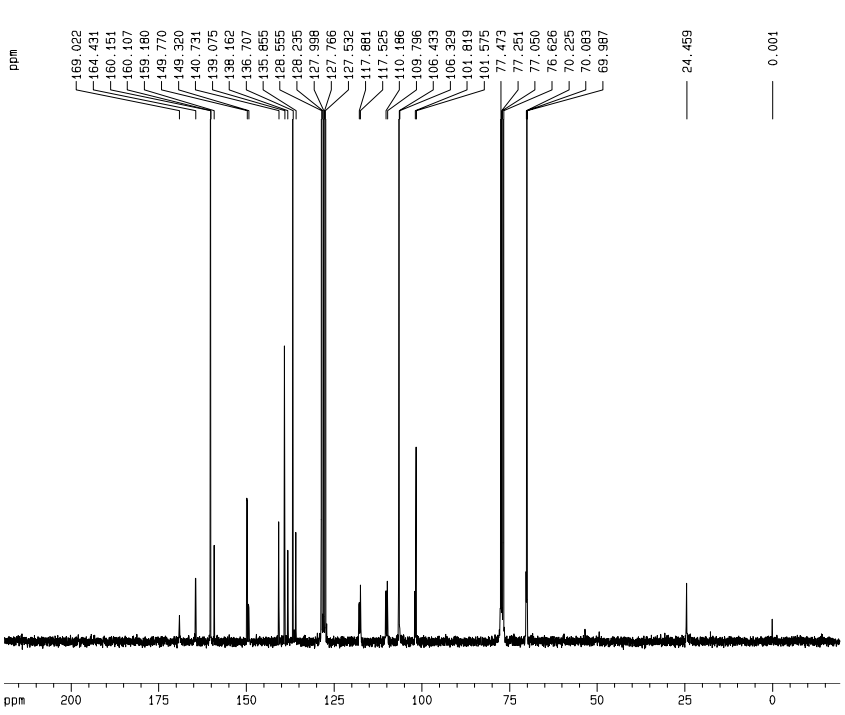


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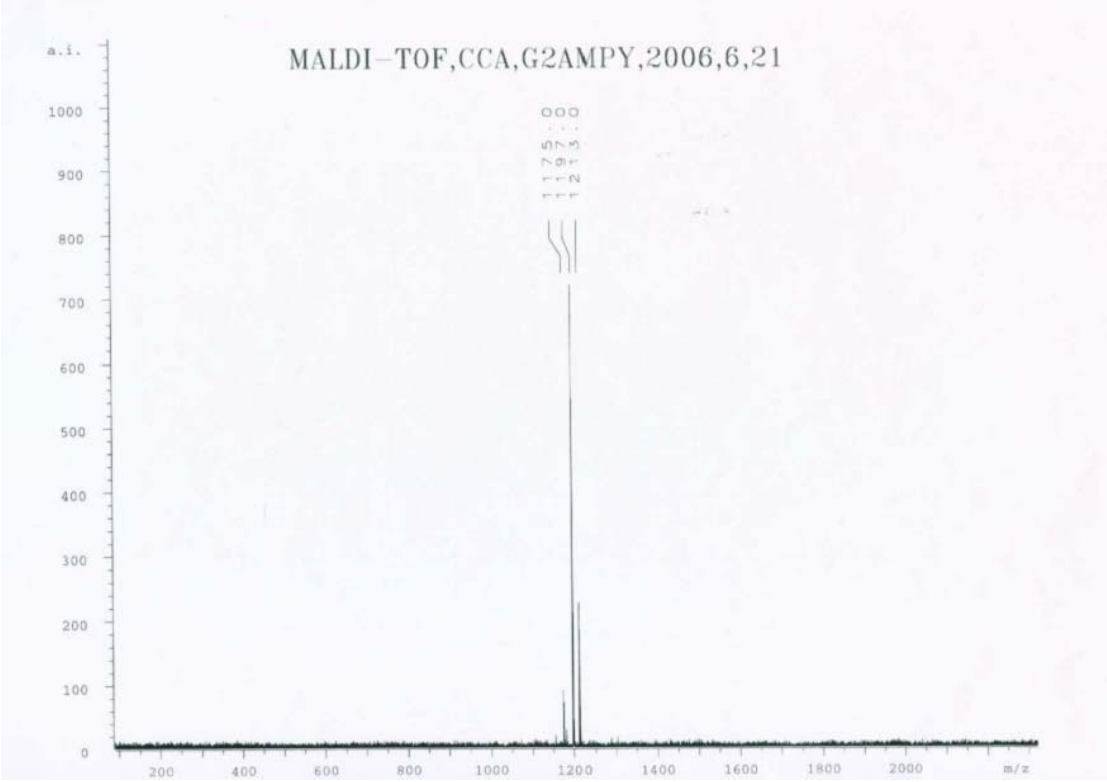
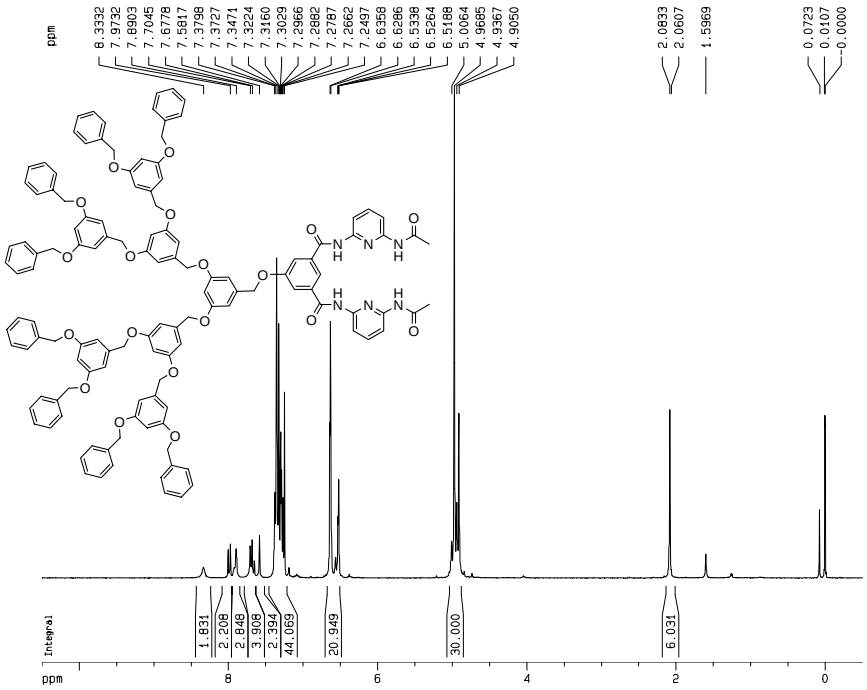


^{1}H and ^{13}C NMR of **DG_3**

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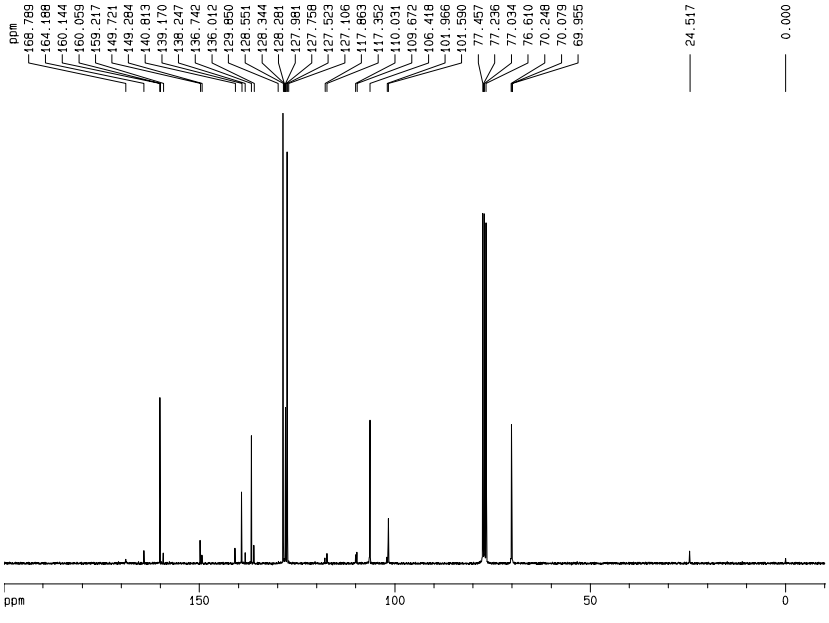


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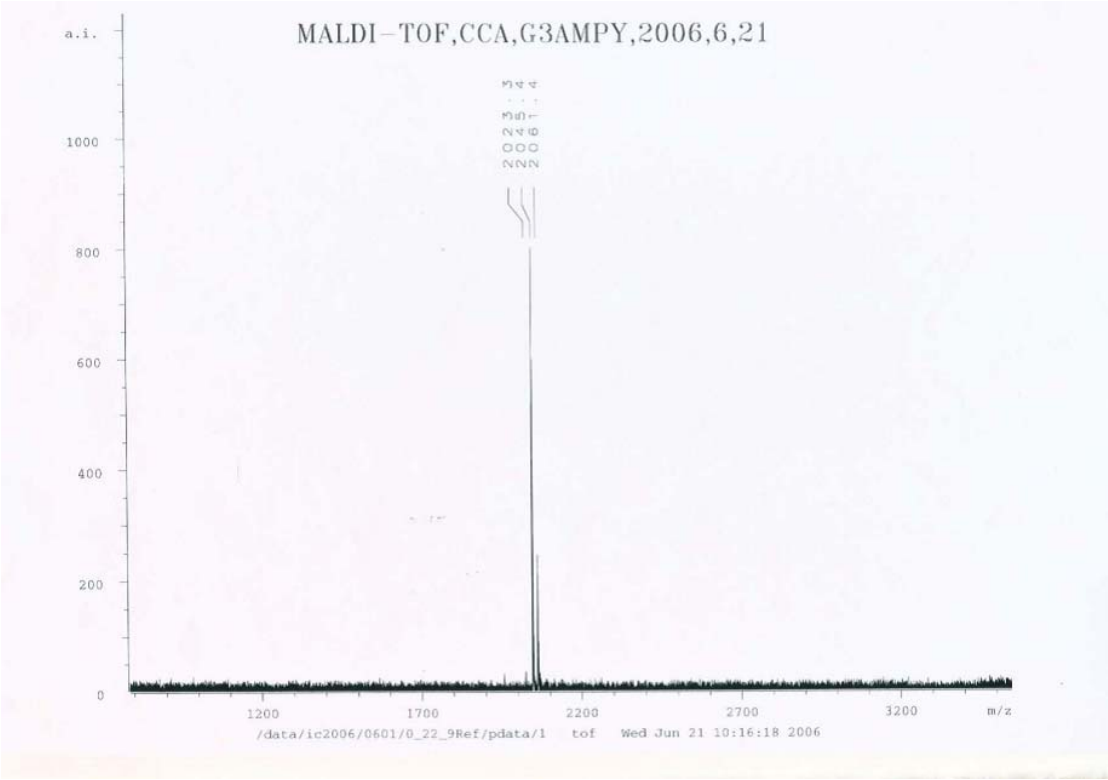
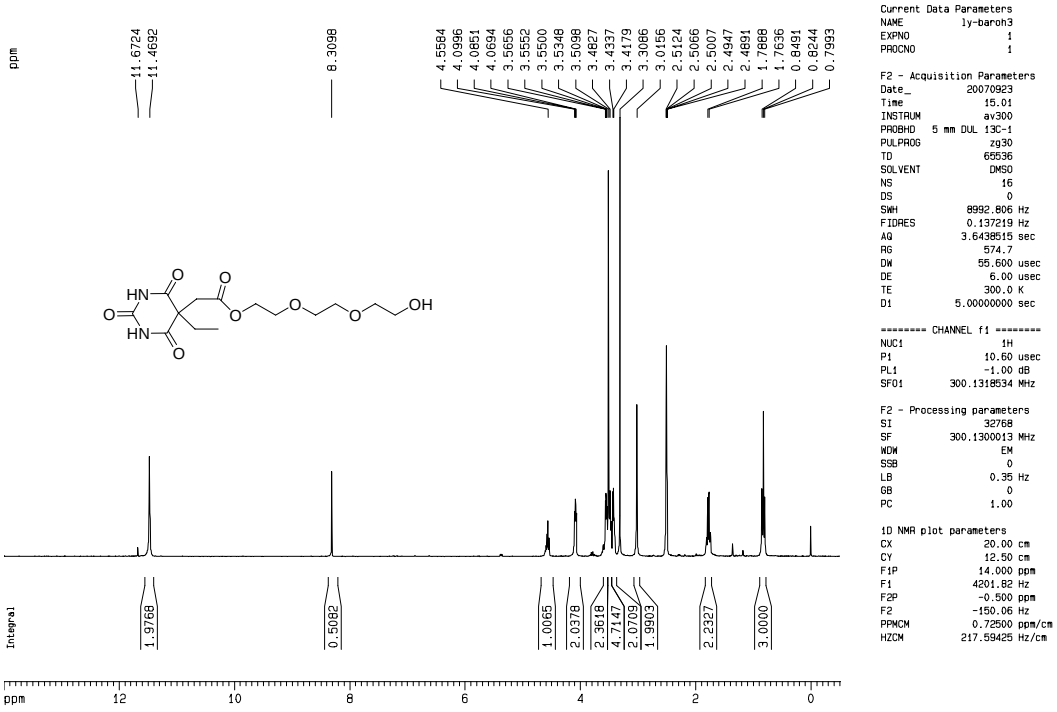
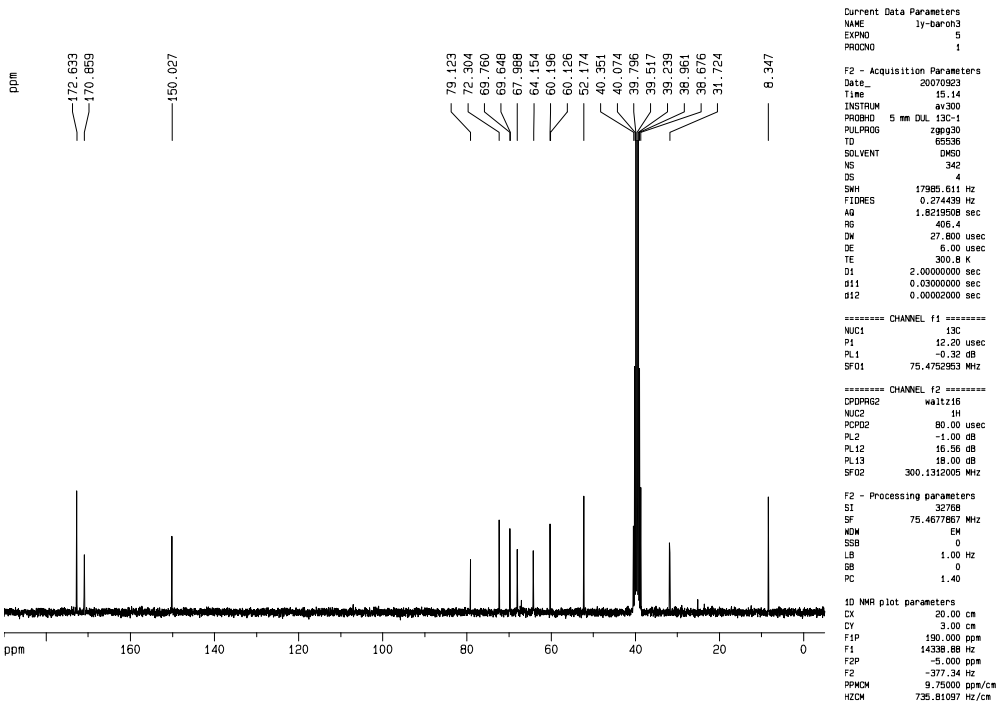


^{1}H and ^{13}C NMR of **5a**

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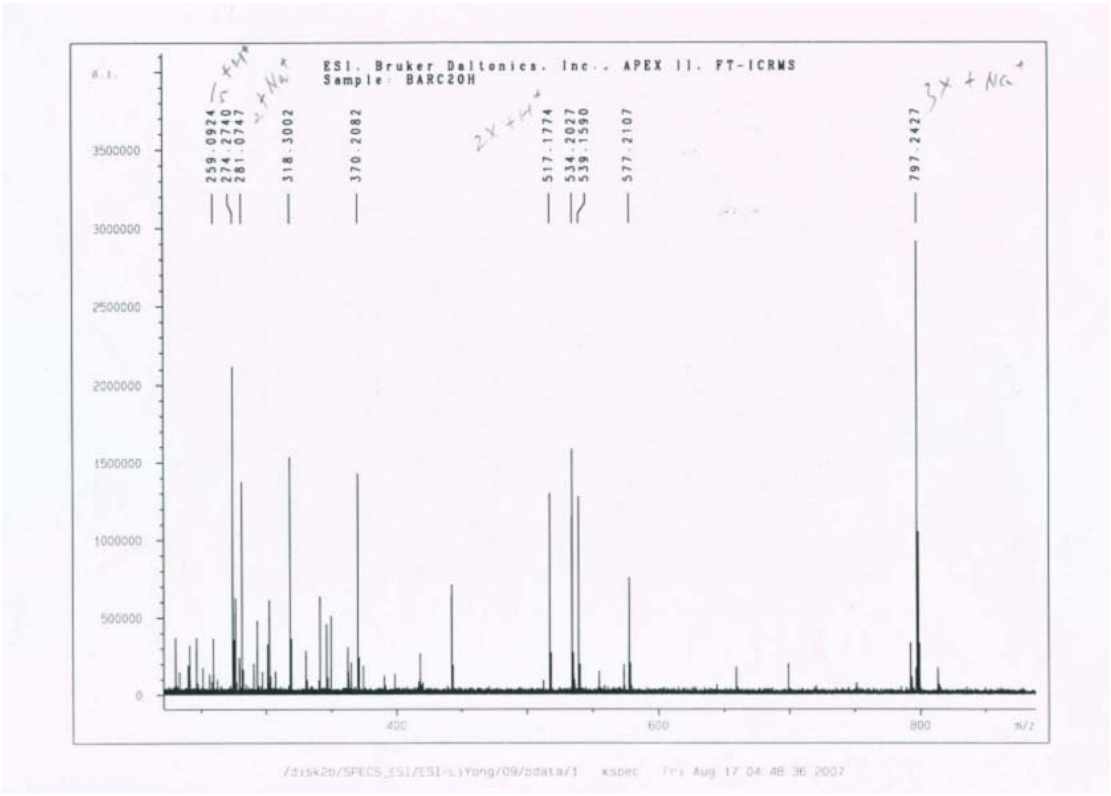
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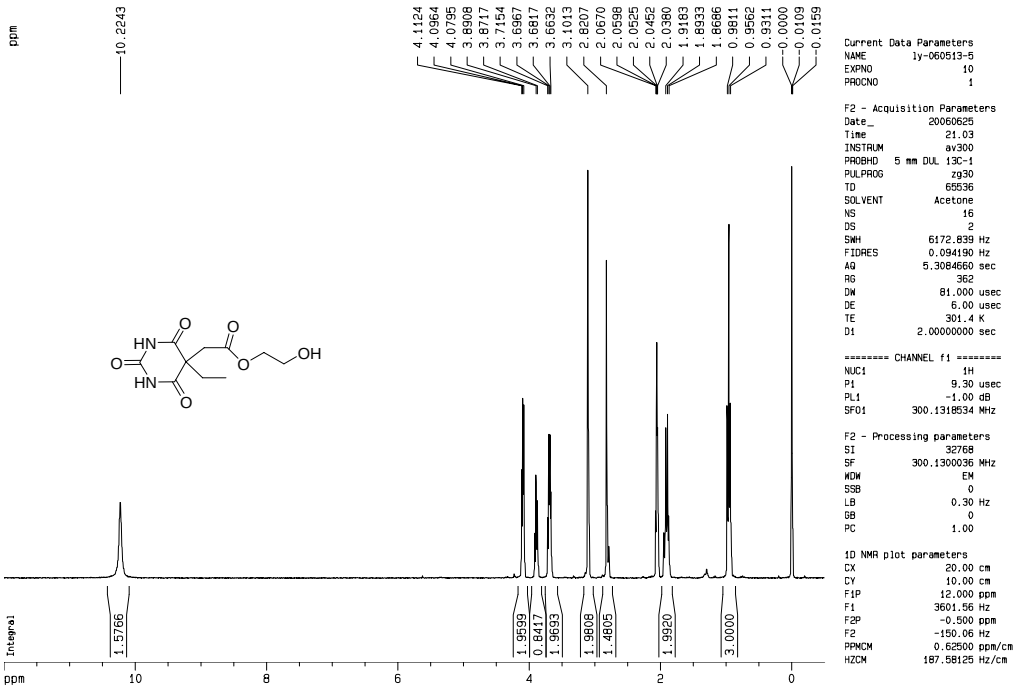
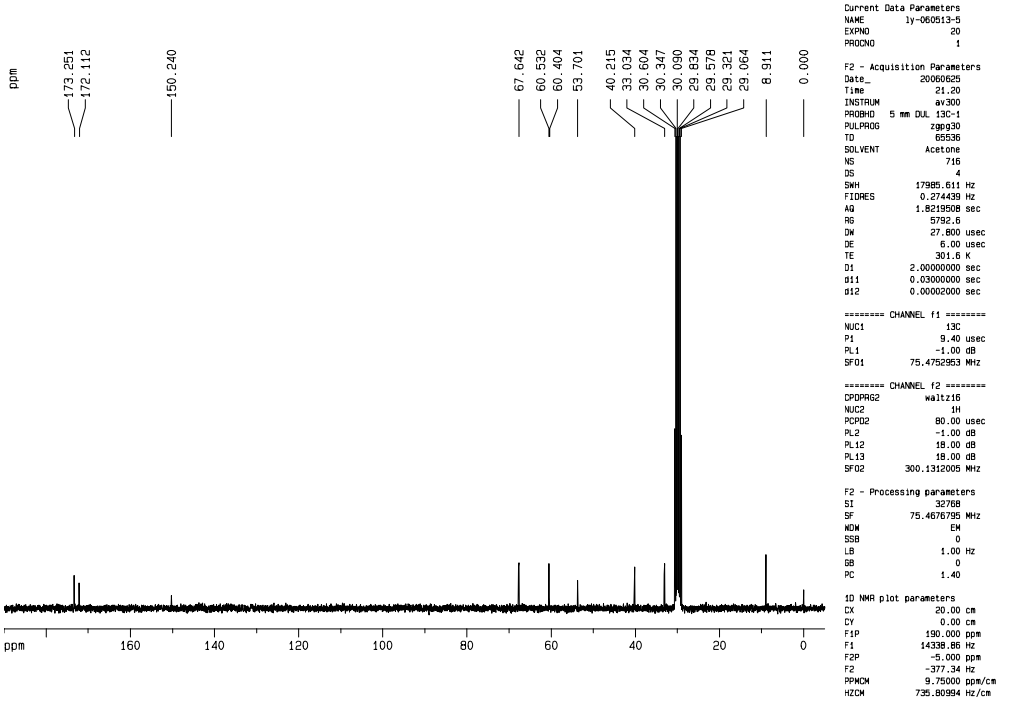
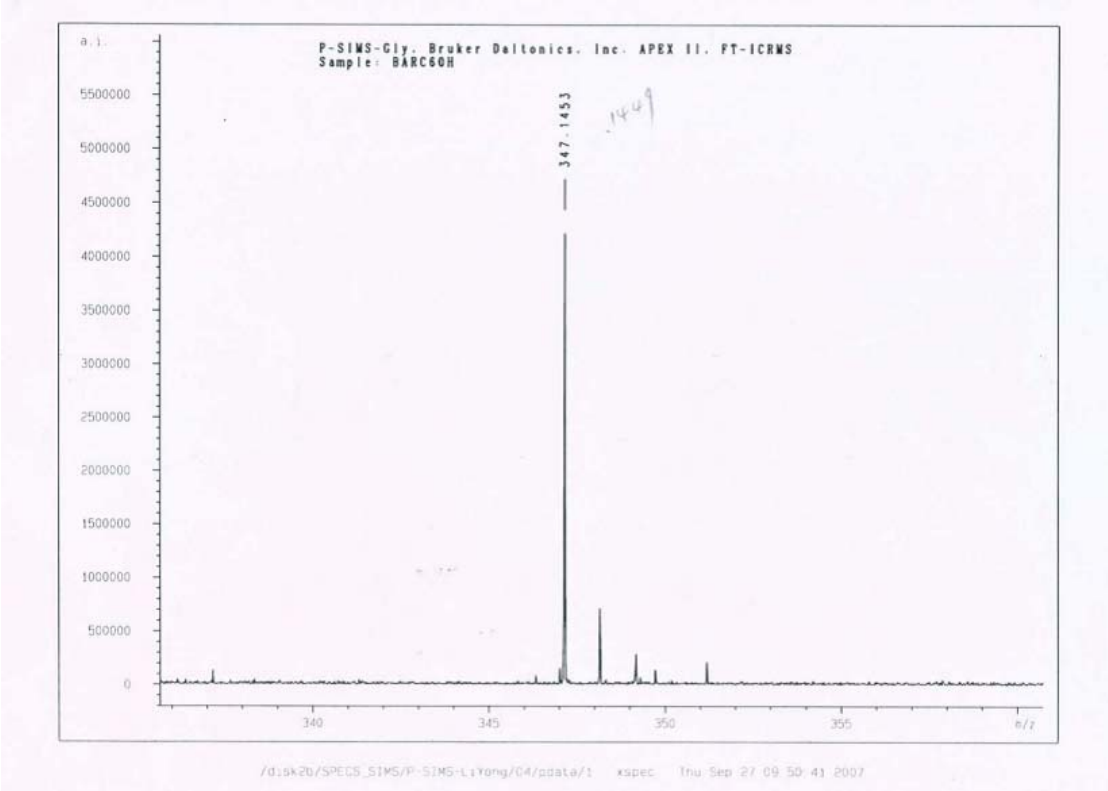
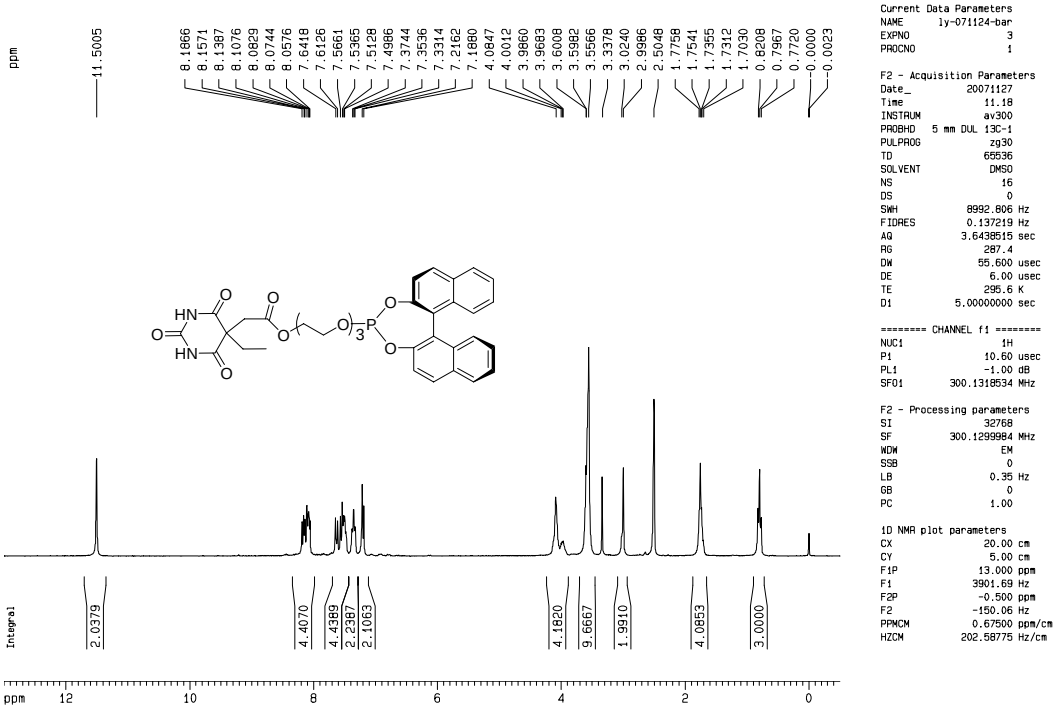
^{1}H and ^{13}C NMR of **5b**

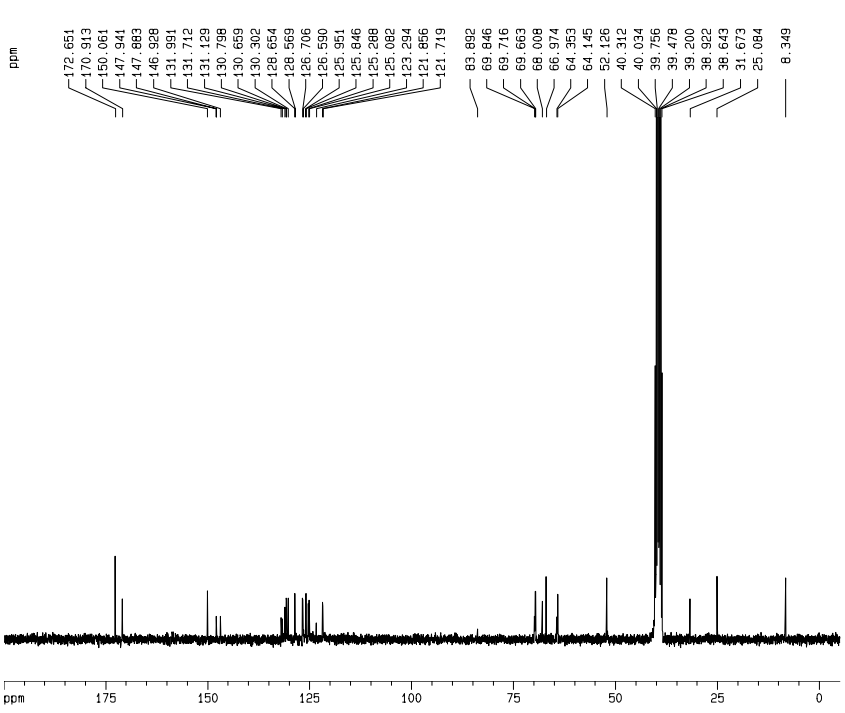






^{1}H, ^{13}C and ^{31}P NMR of **L_1**



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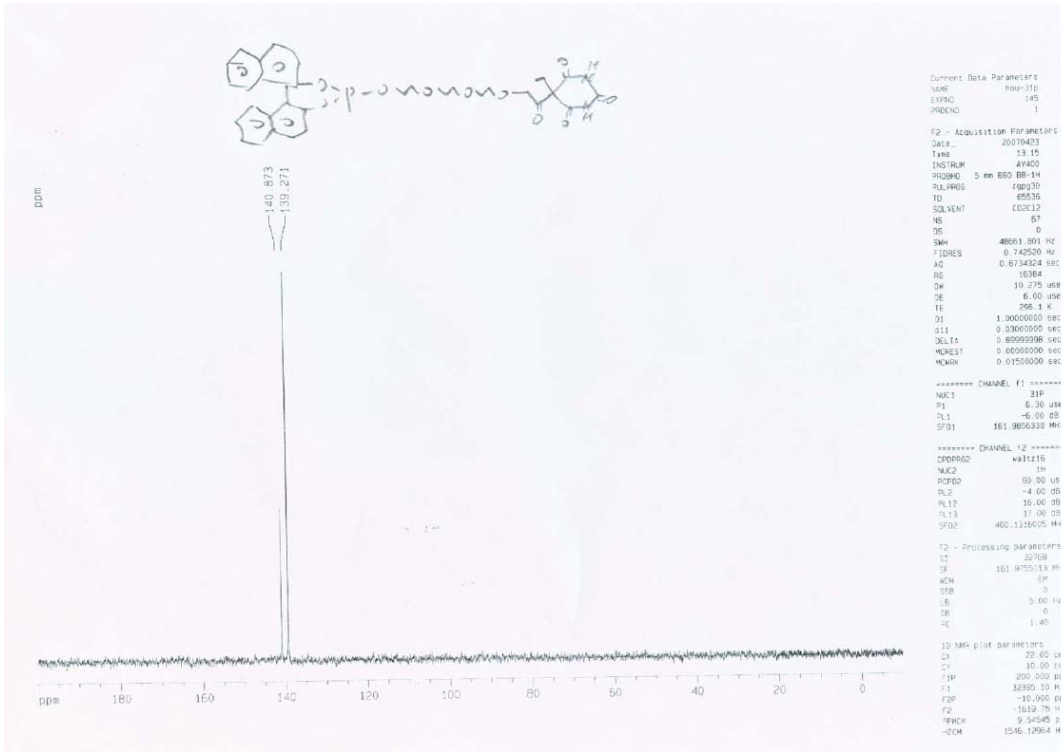

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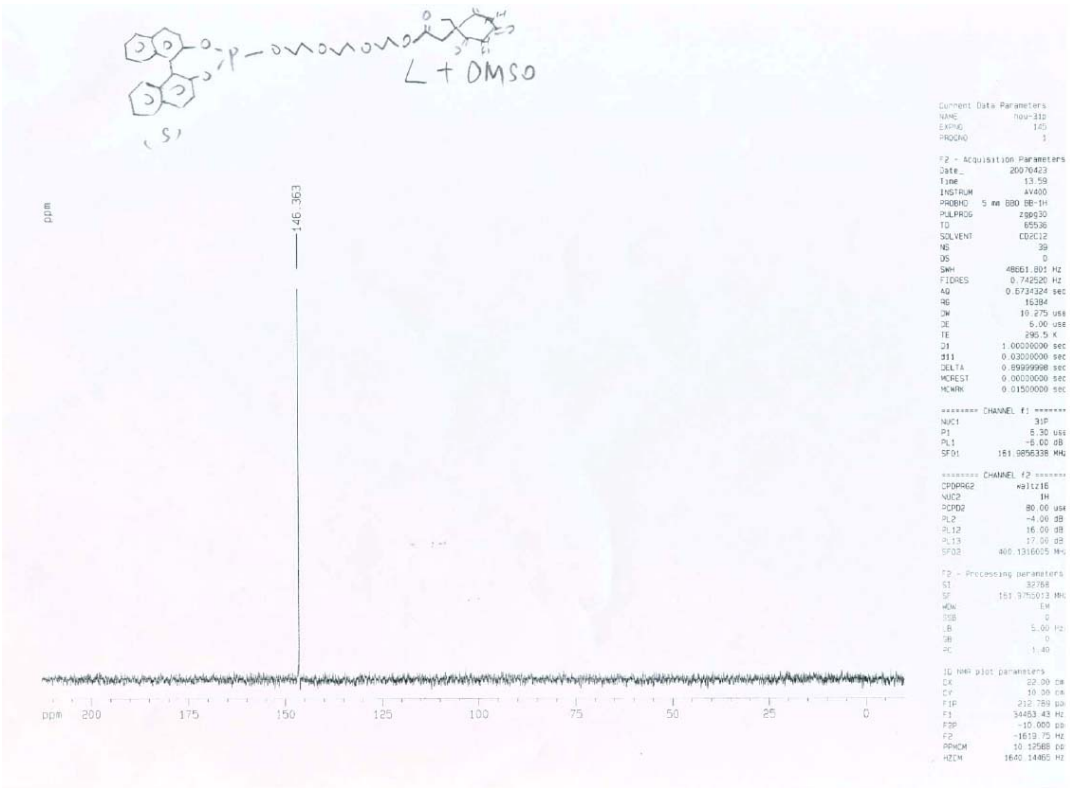
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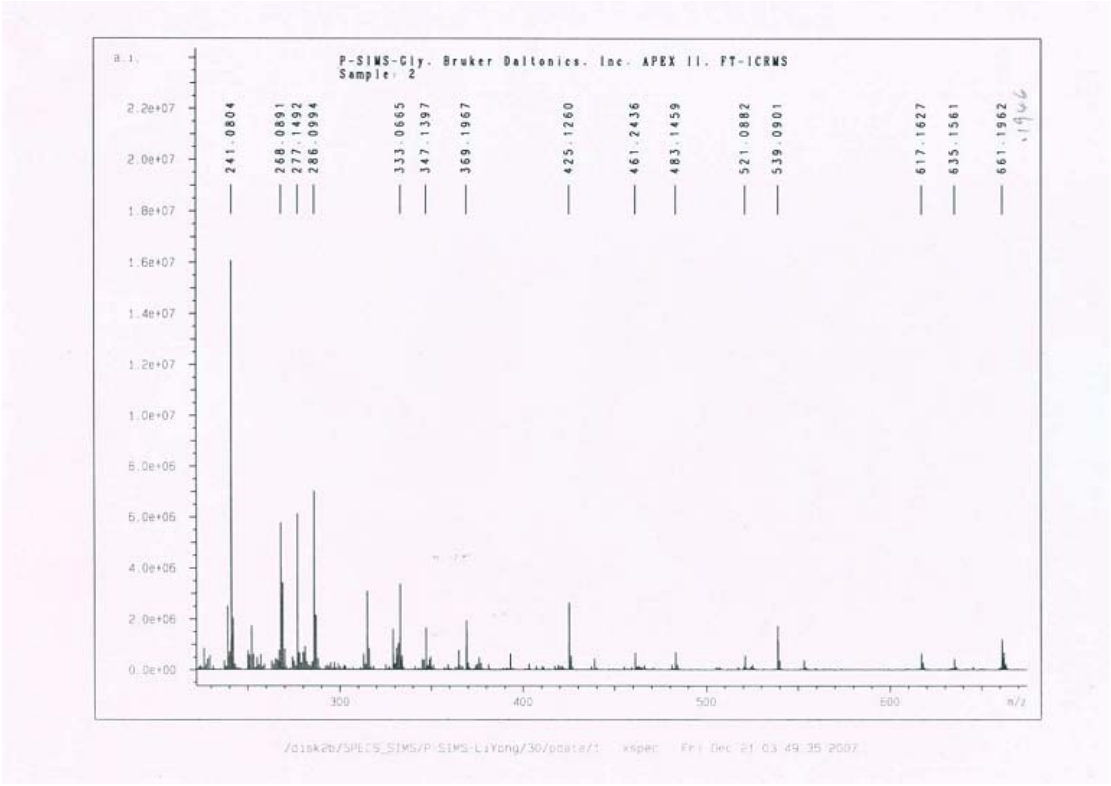
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400
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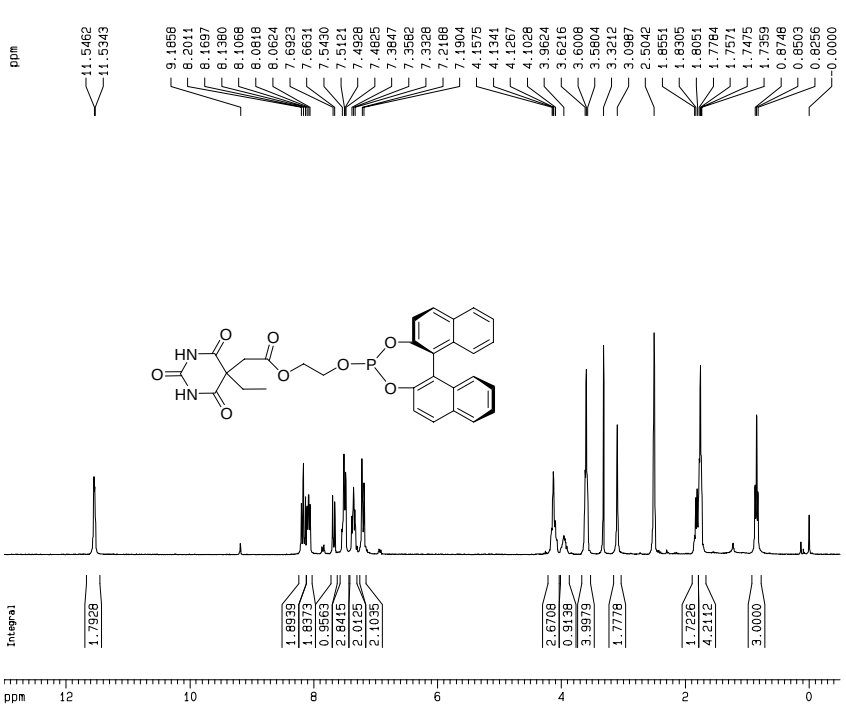
m/z

^{1}H, ^{13}C and ^{31}P NMR of $\mathbf{L_2}$

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HZCM         202.58775 Hz/cm
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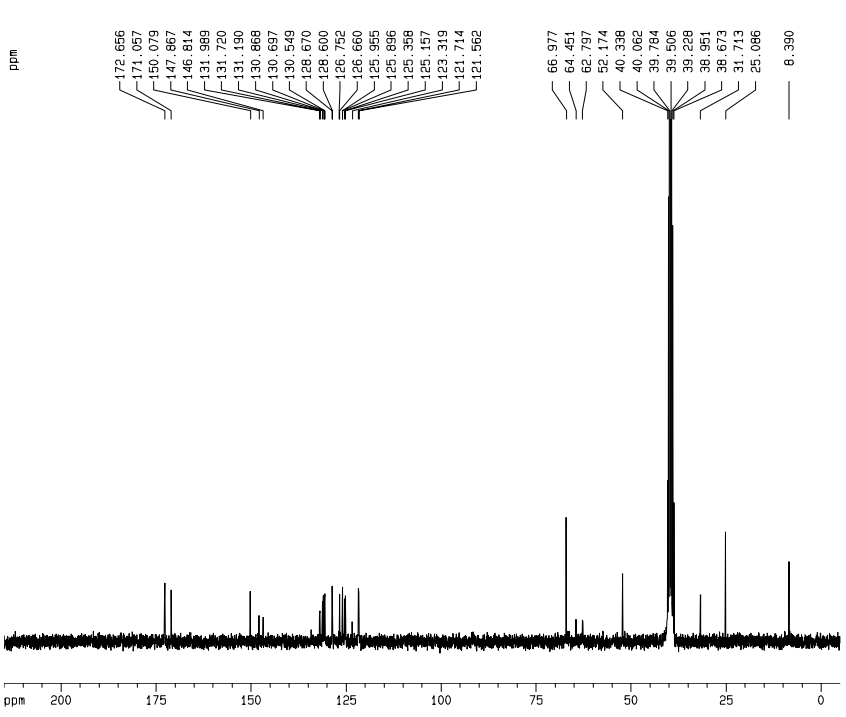


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Current Data Parameters
NAME         ly-070827-1
EXPNO                 11
PROCNO                 1

F2 - Acquisition Parameters
Date_          20070827
Time              19.41
INSTRUM           av300
PROBHD   5 mm DUL 13C-1
PULPROG         zgpg30
TD               65536
SOLVENT           DMSO
NS                  673
DS                    4
SWH           17985.611 Hz
FIDRES        0.274439 Hz
AQ            1.8219508 sec
RG                362
DW               27.800 usec
DE                6.00 usec
TE               299.5 K
D1          2.00000000 sec
d11         0.03000000 sec
d12         0.00002000 sec

======== CHANNEL f1 ========
NUC1                13C
P1                14.20 usec
PL1               -5.00 dB
SFO1        75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                 1H
PCPD2             80.00 usec
PL2               -1.00 dB
PL12              16.56 dB
PL13              18.00 dB
SFO2        300.1312005 MHz

F2 - Processing parameters
SI                32768
SF           75.4677867 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40

1D NMR plot parameters
CX                20.00 cm
CY                 3.00 cm
F1P              215.000 ppm
F1            16225.58 Hz
F2P              -5.000 ppm
F2             -377.34 Hz
PPMCM         11.00000 ppm/cm
HZCM         830.14563 Hz/cm
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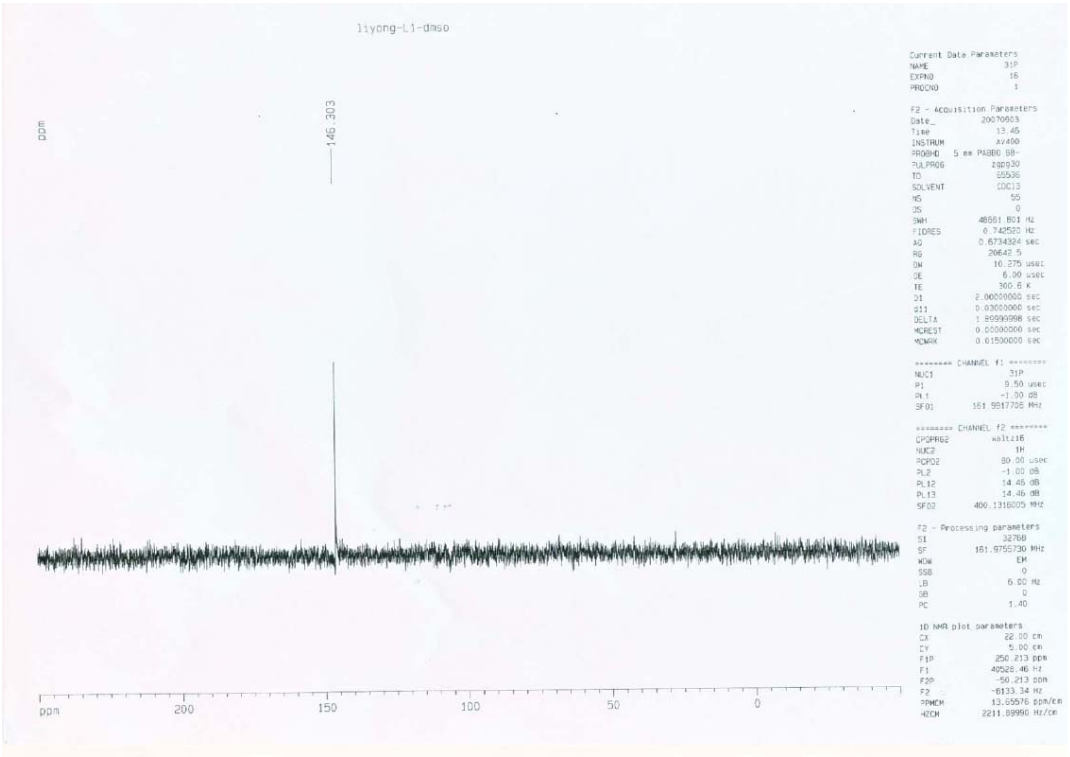
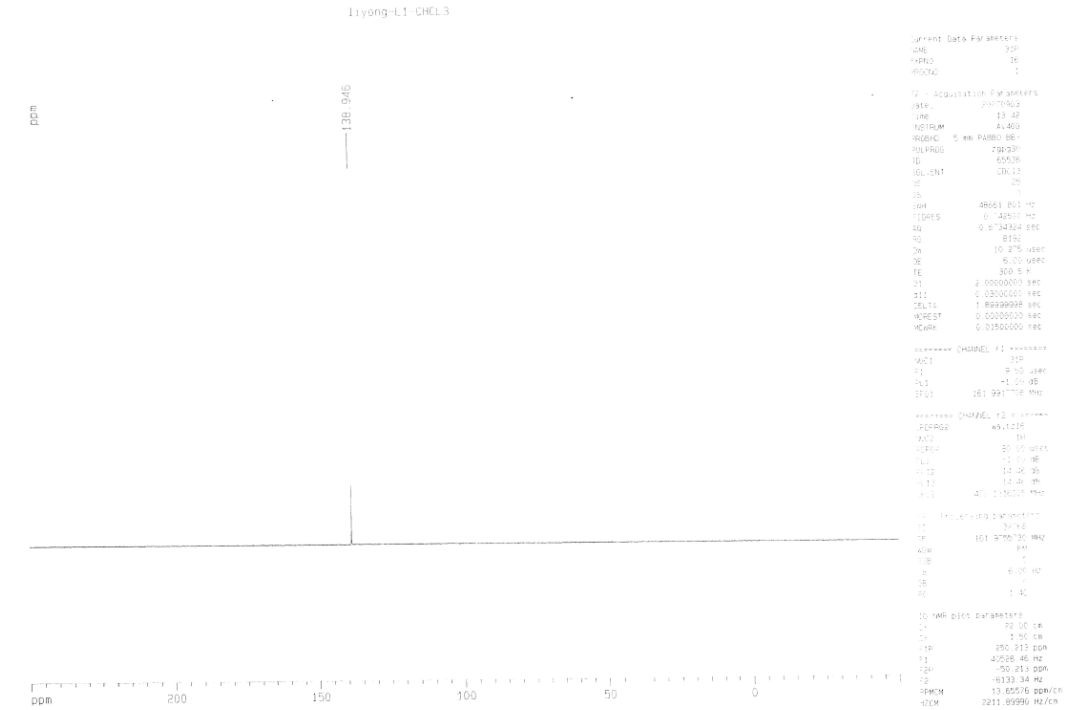
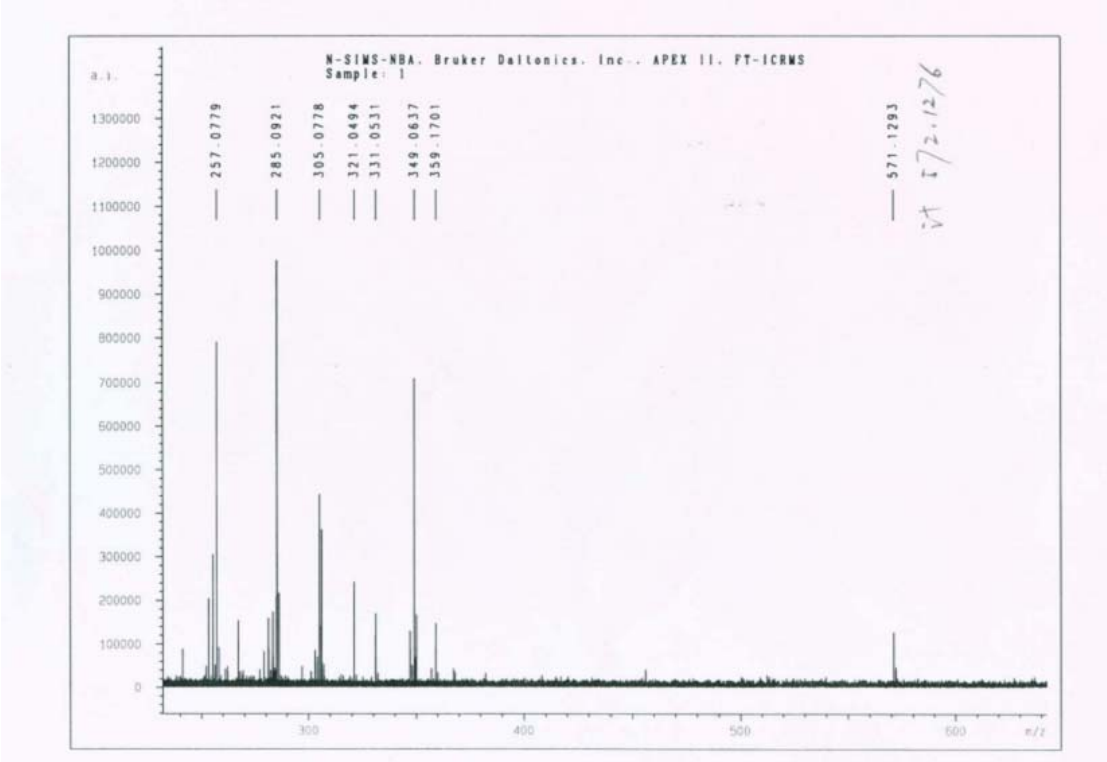
L_2 in DMSO-d_6



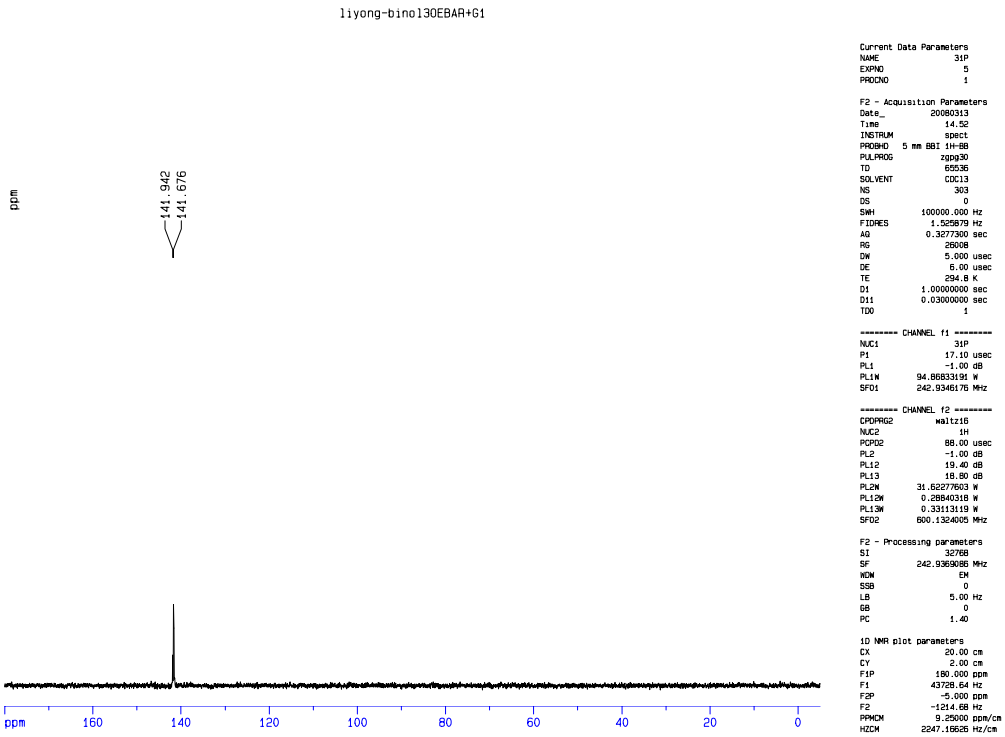
L_2 in CDCl3





^{31}P NMR of supramolecular chiral dendritic monophosphite ligands DGnL:

^{31}P NMR of **DG_1L_1** in $CDCl_3$

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Current Data Parameters
NAME                   31P
EXPNO                    5
PROCNO                   1

F2 - Acquisition Parameters
Date_               20080313
Time                   14.52
INSTRUM                spect
PROBHD   5 mm BBI 1H-BB
PULPROG             zppg30
TD                   65536
SOLVENT              CDCl3
NS                     303
DS                       0
SWH             100000.000 Hz
FIDRES            1.525879 Hz
AQ                0.3277300 sec
RG                    2808
DW                   5.000 usec
DE                   6.00 usec
TE                   294.8 K
D1                1.00000000 sec
D11               0.03000000 sec
TD0                      1

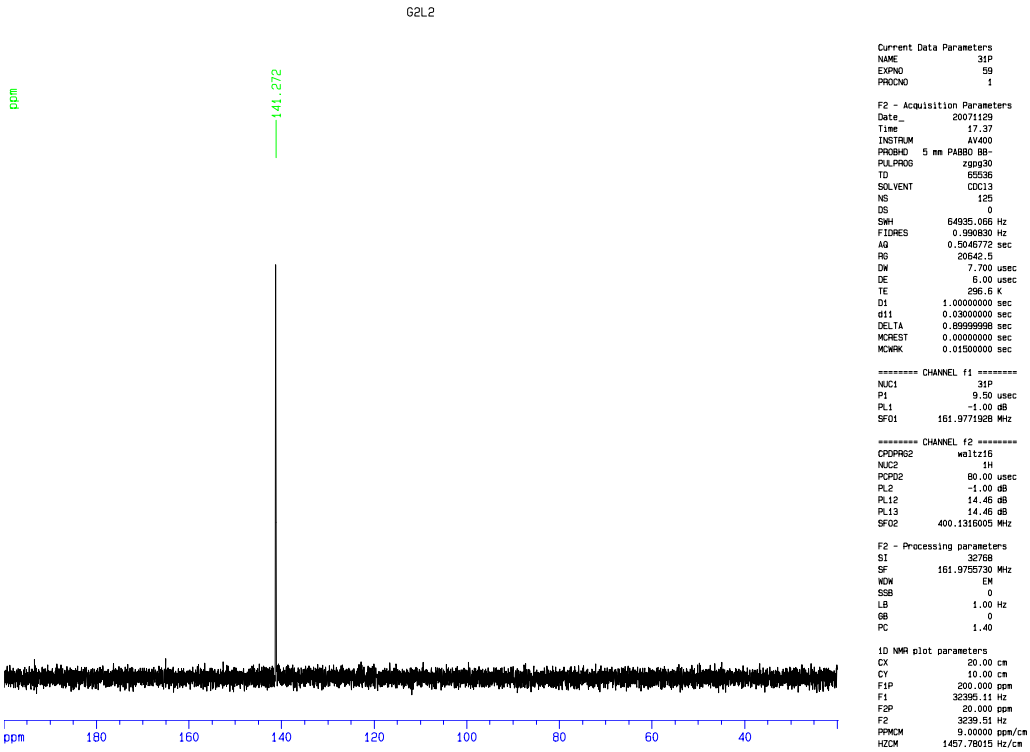
======== CHANNEL f1 ========
NUC1                   31P
P1                   17.10 usec
PL1                  -1.00 dB
PL1W           94.86833191 W
SFO1           242.9346176 MHz

======== CHANNEL f2 ========
CPDPRG2              waltz16
NUC2                    1H
PCPD2                88.00 usec
PL2                  -1.00 dB
PL12                 19.40 dB
PL13                 18.80 dB
PL2W           31.62277603 W
PL12W           0.28840318 W
PL13W           0.33113119 W
SFO2           600.1324005 MHz

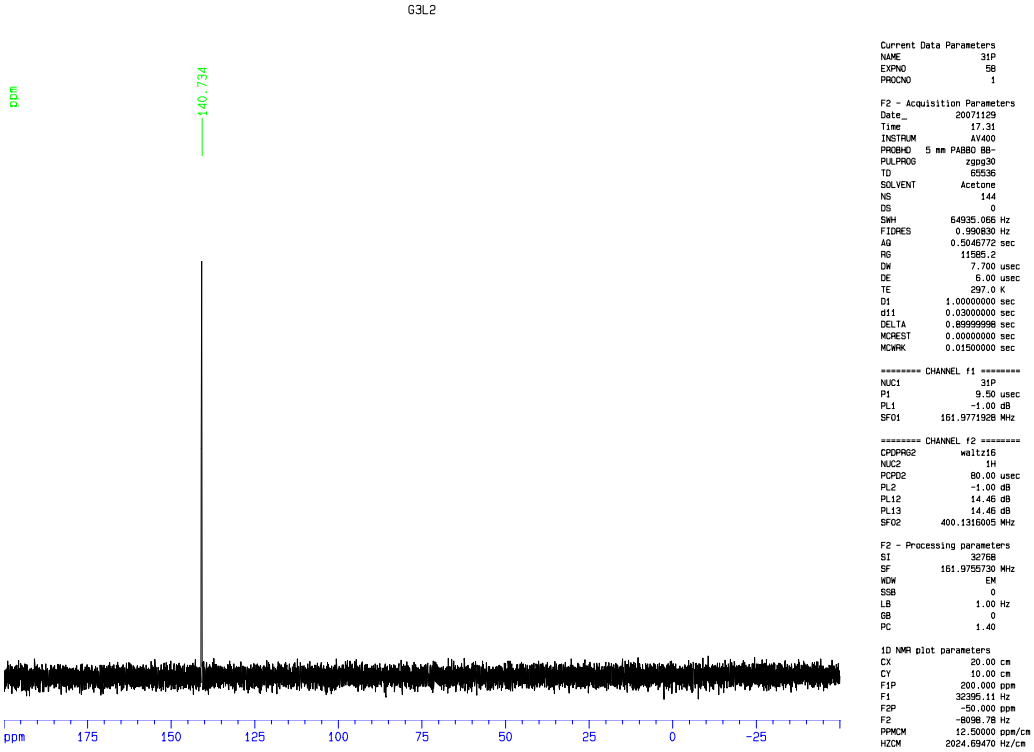
F2 - Processing parameters
SI                     32768
SF               242.9369086 MHz
WDW                       EM
SSB                       0
LB                     5.00 Hz
GB                        0
PC                     1.40

1D NMR plot parameters
CX                    20.00 cm
CY                     2.00 cm
F1P                  180.000 ppm
F1                 43728.64 Hz
F2P                  -5.000 ppm
F2                 -1214.68 Hz
PPMCM             9.25000 ppm/cm
HZCM           2247.16626 Hz/cm
```

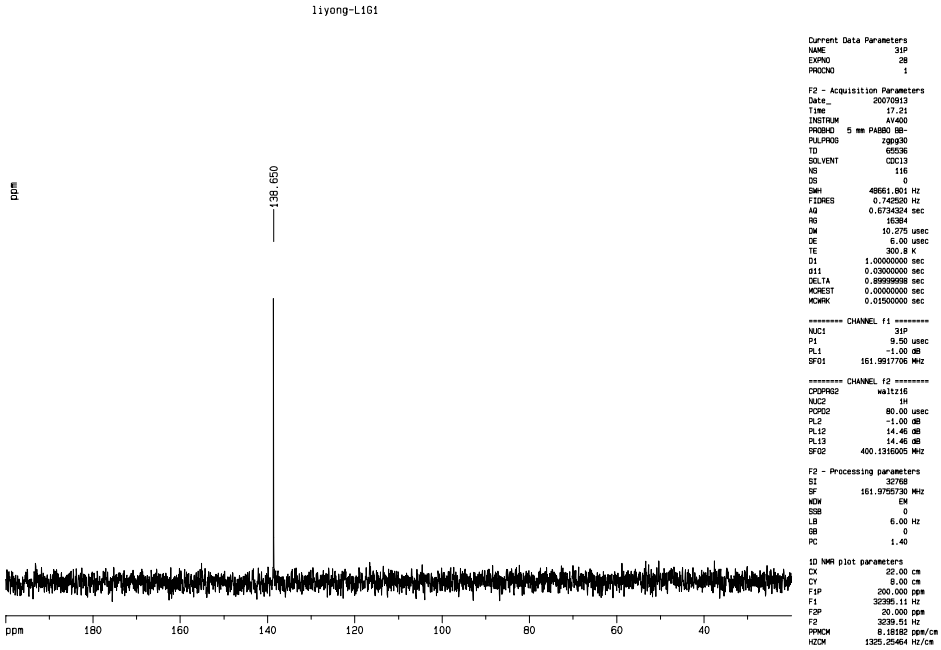
^{31}P NMR of **DG_2L_1** in $CDCl_3$



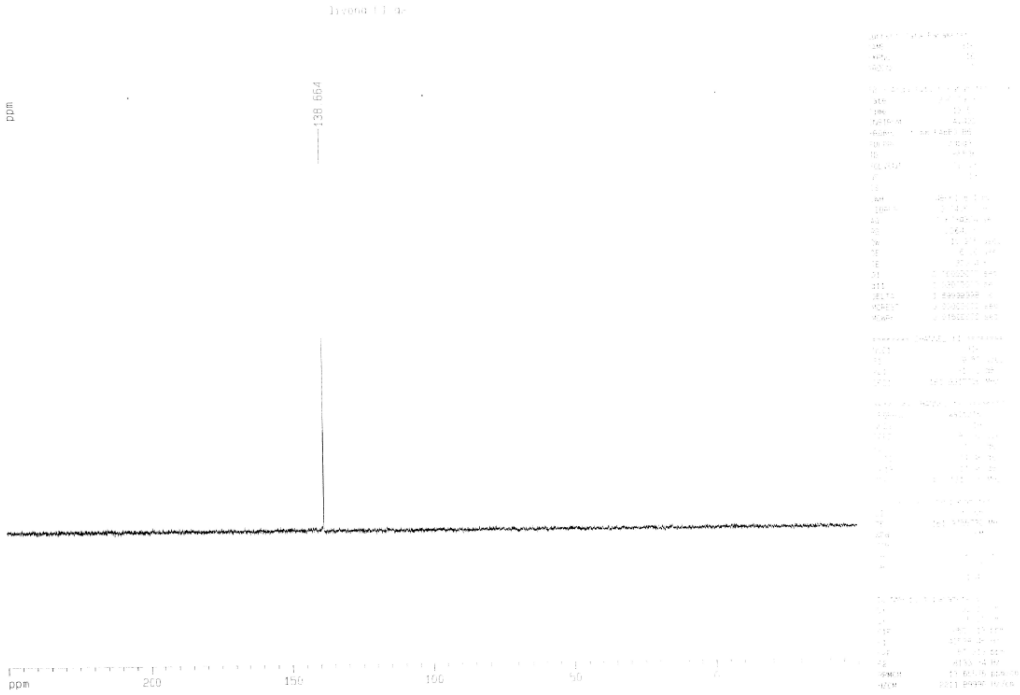
^{31}P NMR of **DG_3L_1** in $CDCl_3$



^{31}P NMR of **DG_1L_2** in $CDCl_3$



^{31}P NMR of **DG_2L_2** in $CDCl_3$



^{31}P NMR of **DG_3L_2** in $CDCl_3$