Supplementary Materials for

Janus Dendritic Phosphines: Synthesis and Application in Suzuki Coupling Reactions

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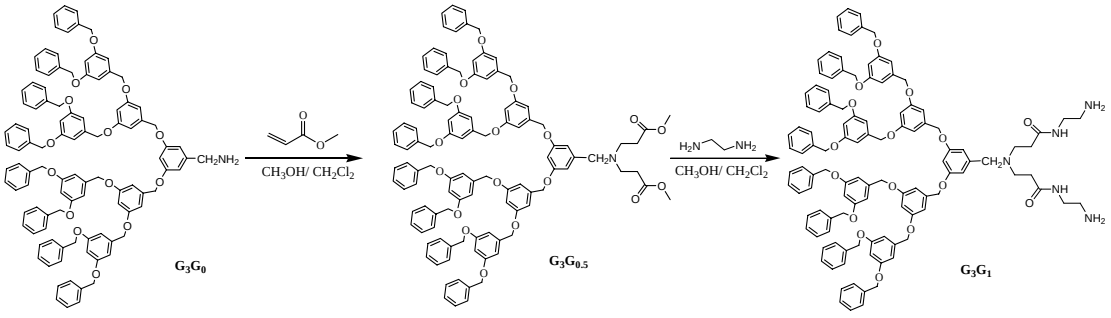
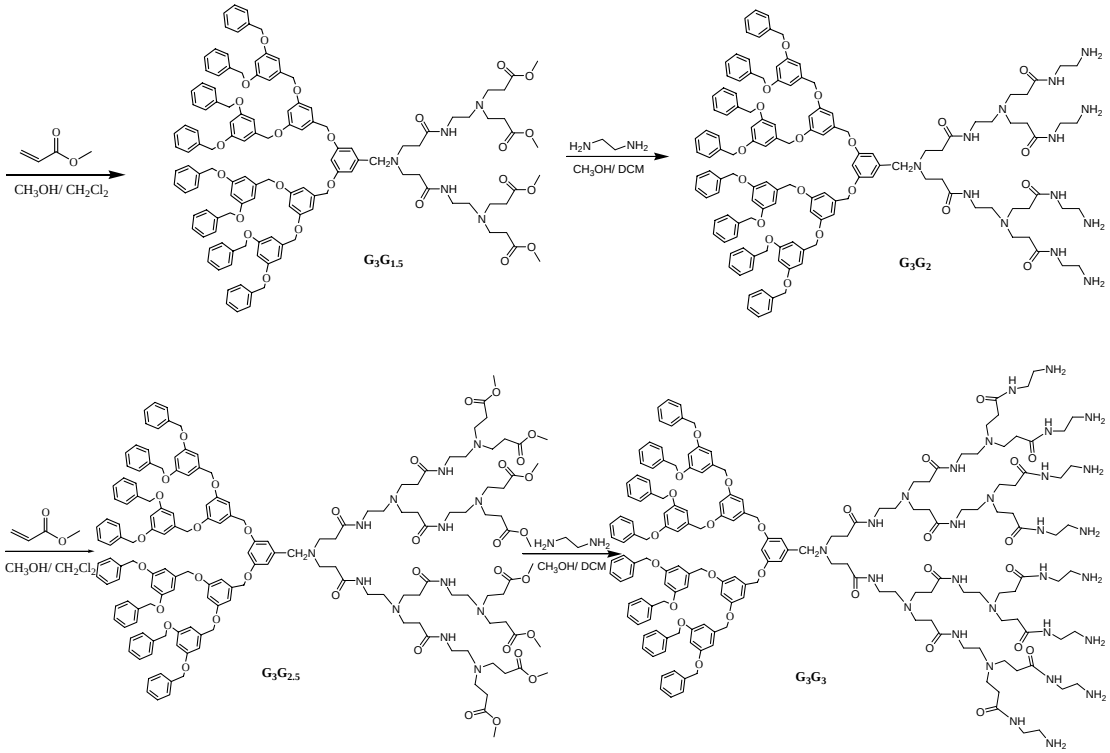
1. General Information

Unless otherwise noted, all experiments were carried out under an inert atmosphere of dry nitrogen by using standard Schlenk-type techniques. ^{1}H NMR, ^{31}P NMR and ^{13}C NMR spectra were recorded on a Bruker Model Avance DMX 300 or 600 Spectrometer (^{1}H 300 MHz, ^{31}P 162 MHz and ^{13}C 75 or 150 MHz respectively). MALDI-TOF mass spectra were obtained on a BIFLEX Ⅲ instrument with α-cyano-4-hydroxycinnamic acid (CCA) as the matrix. Elemental analyses were performed on a Flash EA 1112 Elemental Analyzer. All solvents were dried using standard, published methods and were distilled under a nitrogen atmosphere before use. Bis(diphosphinomethyl)amines ligands was prepared according to the reported procedures.[1] Fréchet-type dendrons were prepared according to the reported procedures.[2] All other chemicals were used as received from Aldrich or Acros without further purification. Transmission electron microscopy (TEM): the chloroform dispersion of catalyst was drop-cast onto a 300 mesh carbon coated copper grid, and TEM pictures were taken on a Hitachi H600 microscopy at an accelerating voltage of 75 kv.

2. Synthetic Route to Janus Dendrimers





Scheme S1. Synthetic route to Janus dendrimers

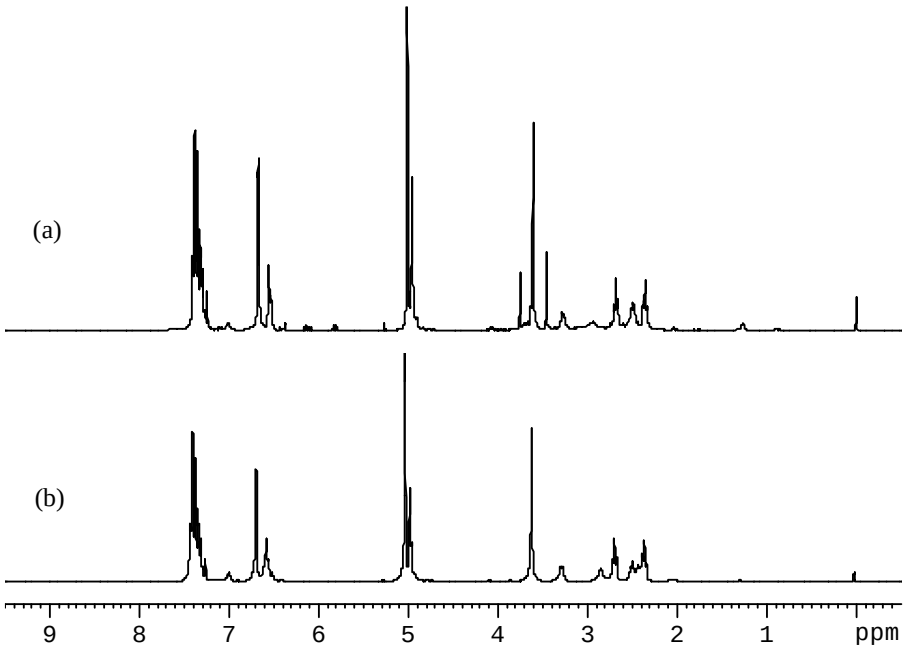
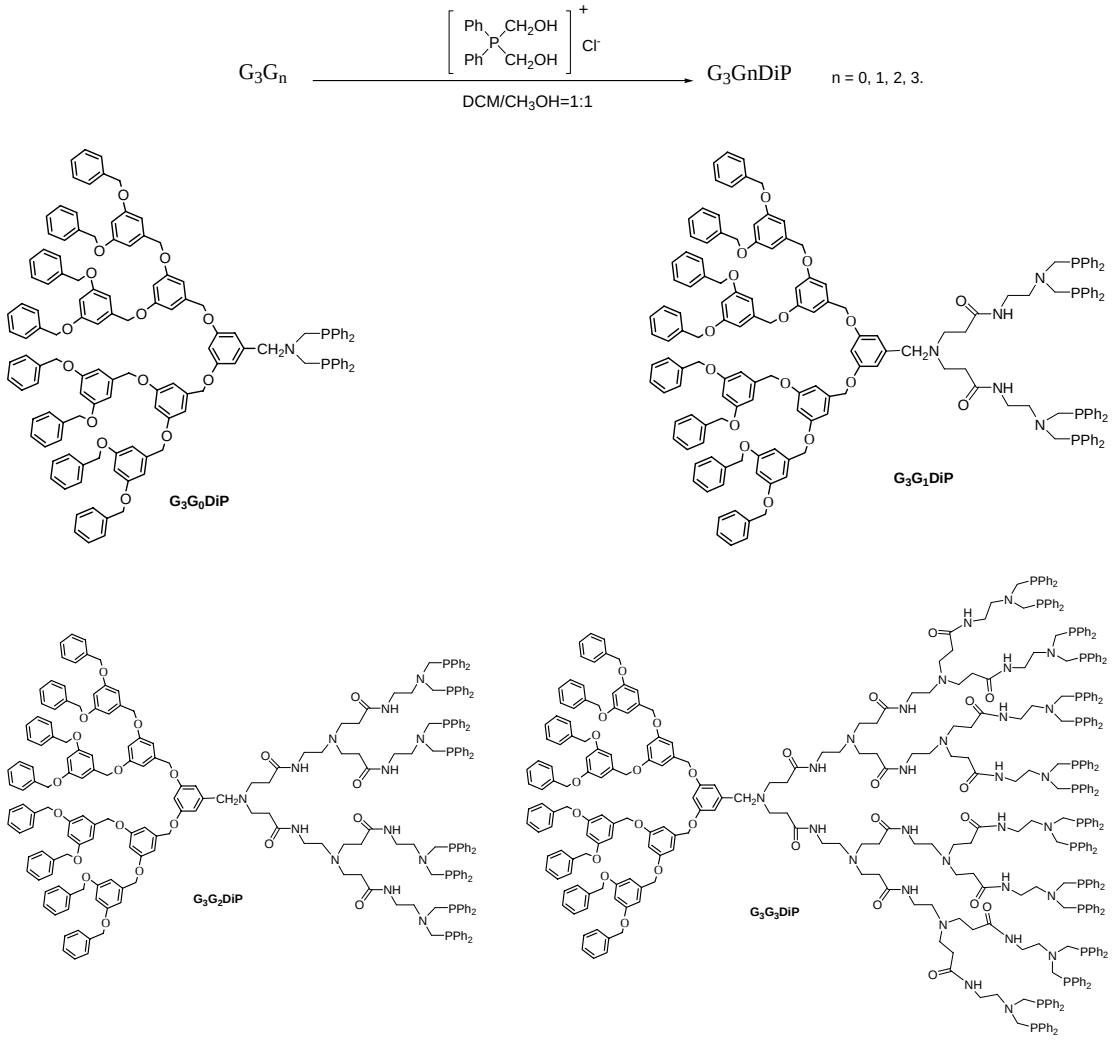


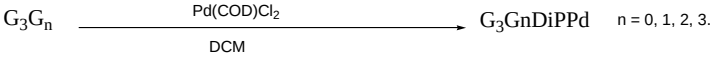
Figure S1. ^{1}H NMR of $\mathbf{G_3G_{1.5}}$: (a) reaction mixture after removal of most of organic solvent and (b) after purification by precipitation in ether and *n*-hexane for three times.

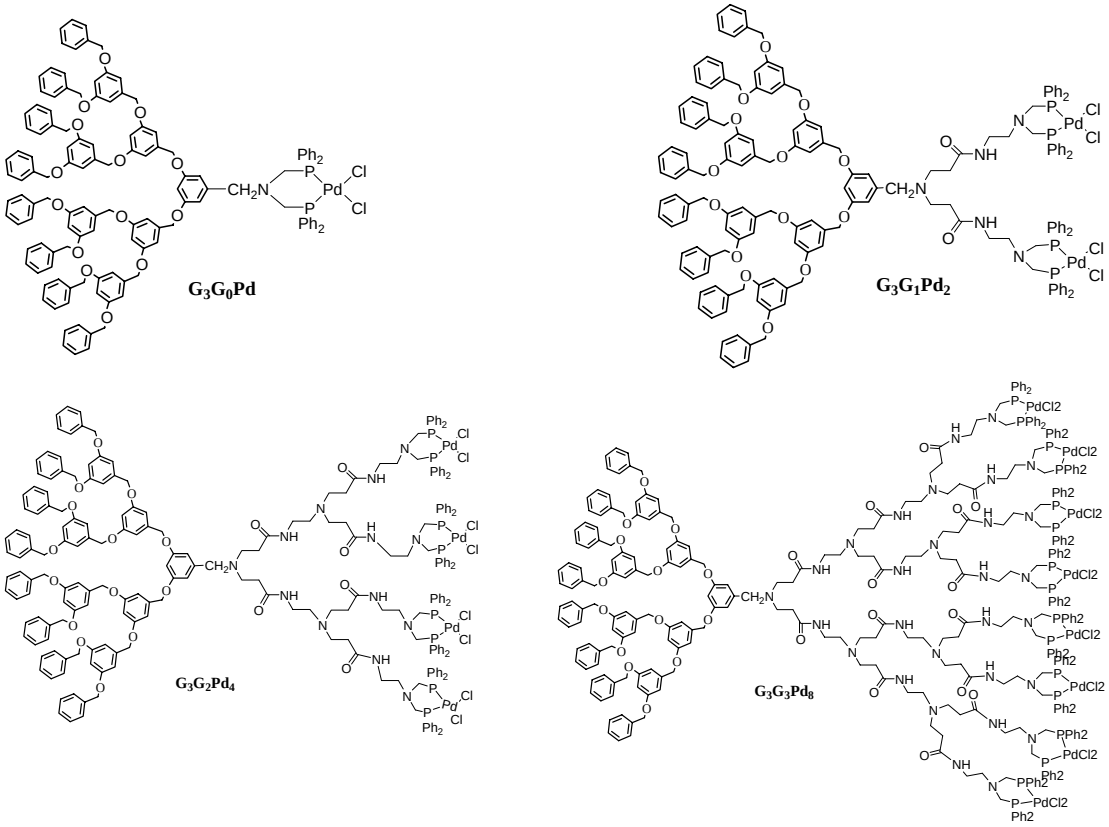
3. Synthesis of Dendritic Bis(diphosphinomethyl)amine Ligands



Scheme S2. Synthesis of dendritic bis(diphosphinomethyl)amine ligands

4. (1) Synthesis of Dendritic Pd catalysts





Scheme S3. Synthesis of dendritic bis(diphosphinomethyl)amines Pd catalysts

(2) TEM images of the recycled dendritic Pd-catalysts

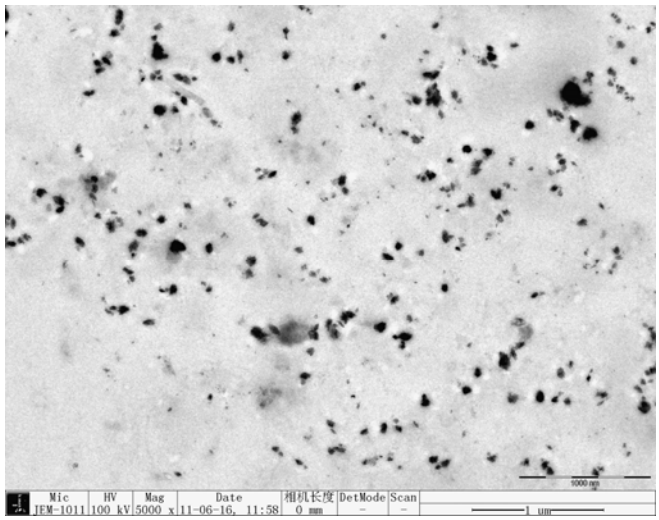


Figure S0. TEM images of **$G_3G_2Pd_4$** catalyst at the third cycle.

5. References

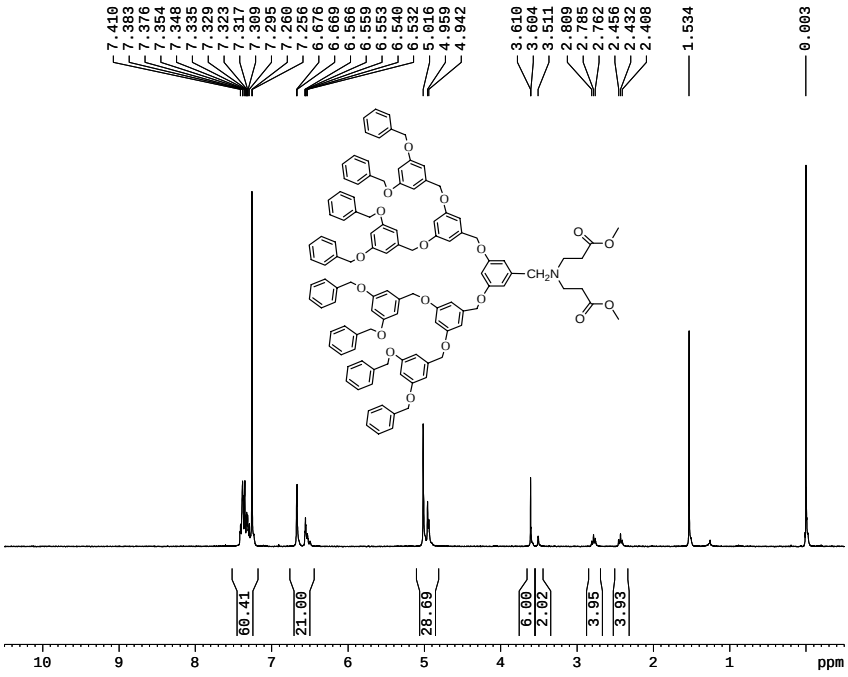
[1] J. Fawcett, P. A. T. Hoye, R. D. W.Kemmitt, D. J. Law, D. R. Russel. *J. Chem. Soc. Dalton Trans.* **1993**, 2563-2569.

[2] C. J. Hawker, J. M. J. Fréchet *J. Am. Chem. Soc.* **1990**, *112*, 7638-7647.

6.

^{1}H, ^{13}C, ^{31}P NMR and MS Spectra of Janus Dendrimers

Figure S1. ^{1}H, ^{13}C NMR and MS spectra of Janus dendrimer $\mathbf{G_3G_{0.5}}$

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PULPROG            zg30
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SOLVENT           CDCl3
NS                   16
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SWH            8992.806 Hz
FIDRES         0.137219 Hz
AQ             3.6438515 sec
RG                  362
DW               55.600 usec
DE                6.00 usec
TE                300.6 K
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MCREST       0.00000000 sec
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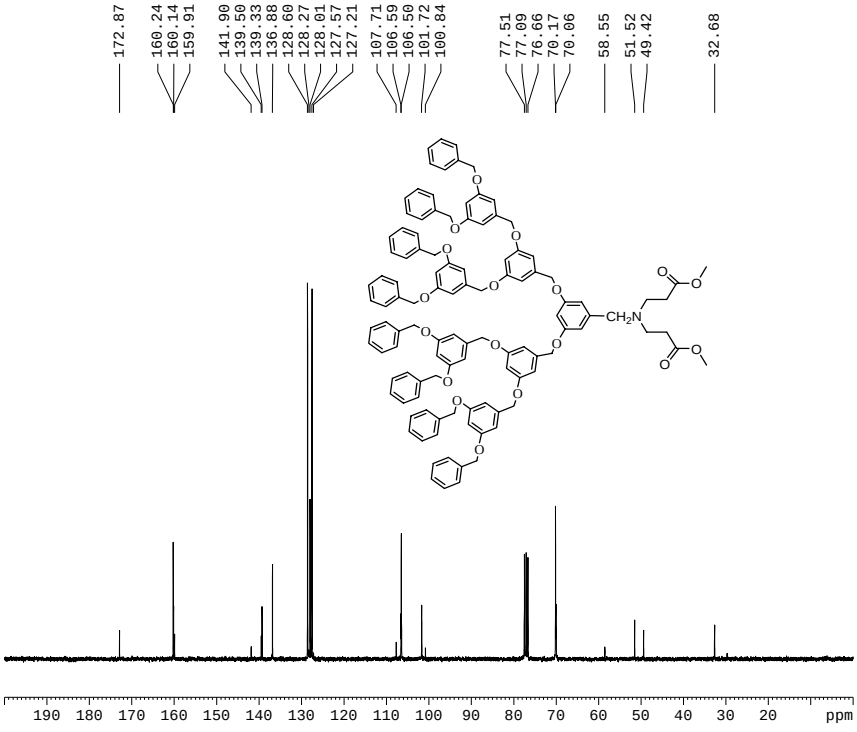


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PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                  299
DS                    4
SWH           17985.611 Hz
FIDRES         0.274439 Hz
AQ             1.8219508 sec
RG                  512
DW               27.800 usec
DE                6.00 usec
TE                302.2 K
D1           2.00000000 sec
d11          0.03000000 sec
DELTA        1.89999998 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

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P1               12.50 usec
PL1               2.00 dB
SFO1         75.4752953 MHz

======== CHANNEL f2 ========
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NUC2                1H
PCPD2            80.00 usec
PL2              -1.00 dB
PL12             20.16 dB
PL13             16.98 dB
SFO2        300.1312005 MHz

F2 - Processing parameters
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SF          75.4677490 MHz
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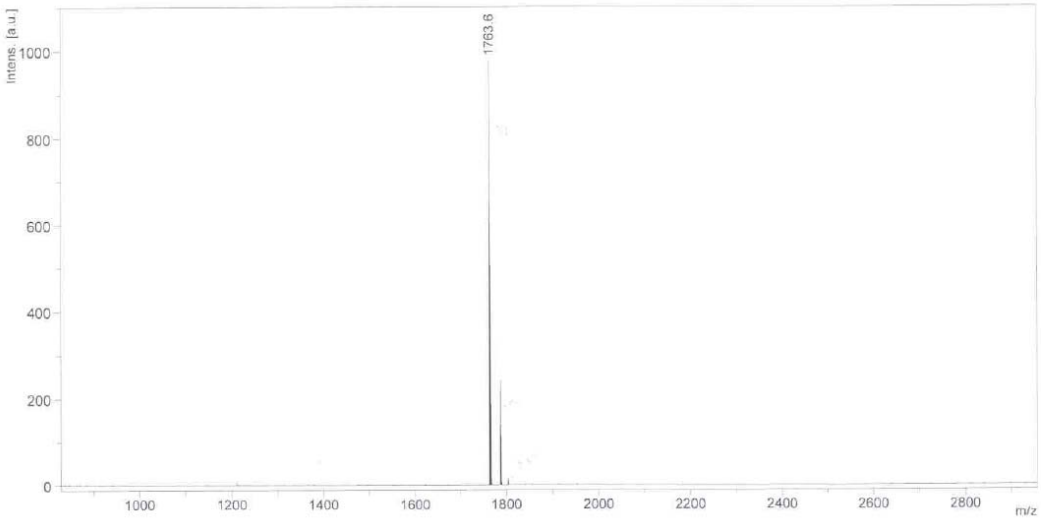
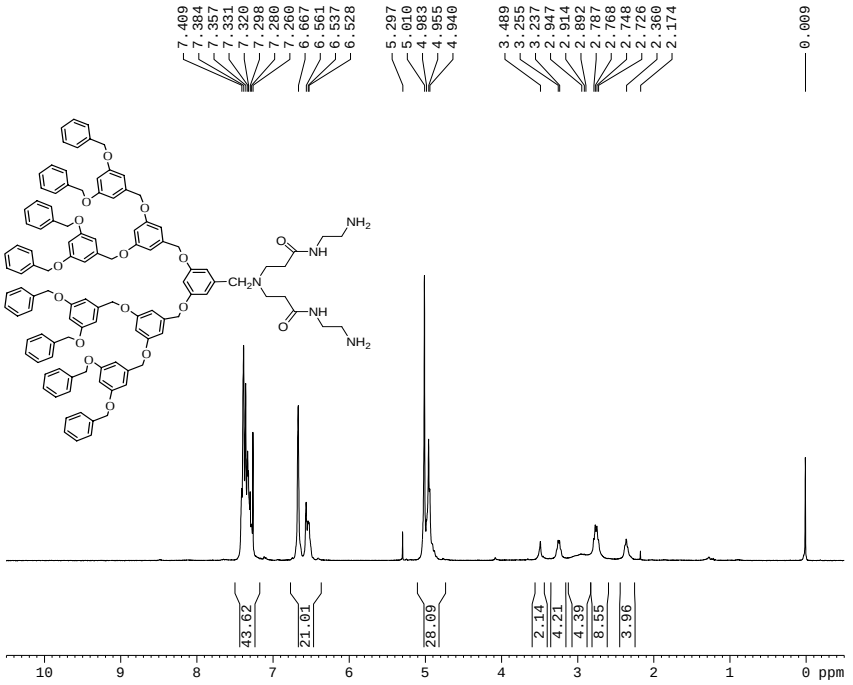


Figure S2. ^{1}H ^{13}C NMR and MS spectra of Janus dendrimer $\mathbf{G_3G_1}$

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PULPROG            zg30
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SOLVENT           CDCl3
NS                   16
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SWH            8992.806 Hz
FIDRES         0.137219 Hz
AQ             3.6438515 sec
RG                287.4
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PL1                -1.00 dB
SFO1         300.1324010 MHz

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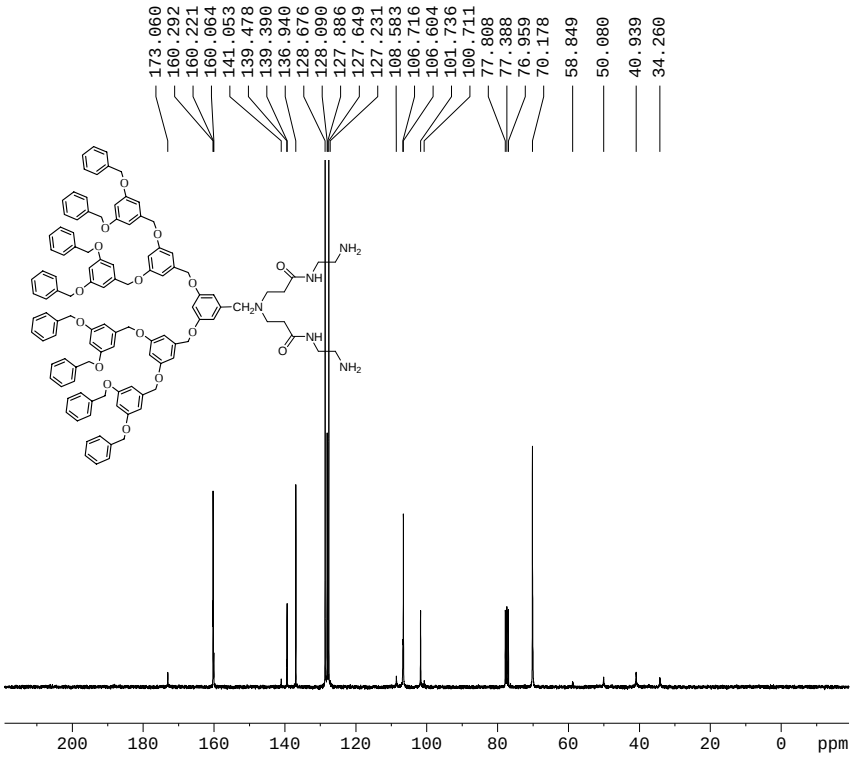


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PROCNO                 1

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PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                  407
DS                    4
SWH           17985.611 Hz
FIDRES         0.274439 Hz
AQ             1.8219508 sec
RG                4096
DW               27.800 usec
DE                6.00 usec
TE                673.2 K
D1            2.00000000 sec
d11           0.03000000 sec
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MCREST        0.00000000 sec
MCWRK         0.01500000 sec

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PL1                 2.00 dB
SFO1         75.4752953 MHz

======== CHANNEL f2 ========
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PCPD2              80.00 usec
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PL13               16.98 dB
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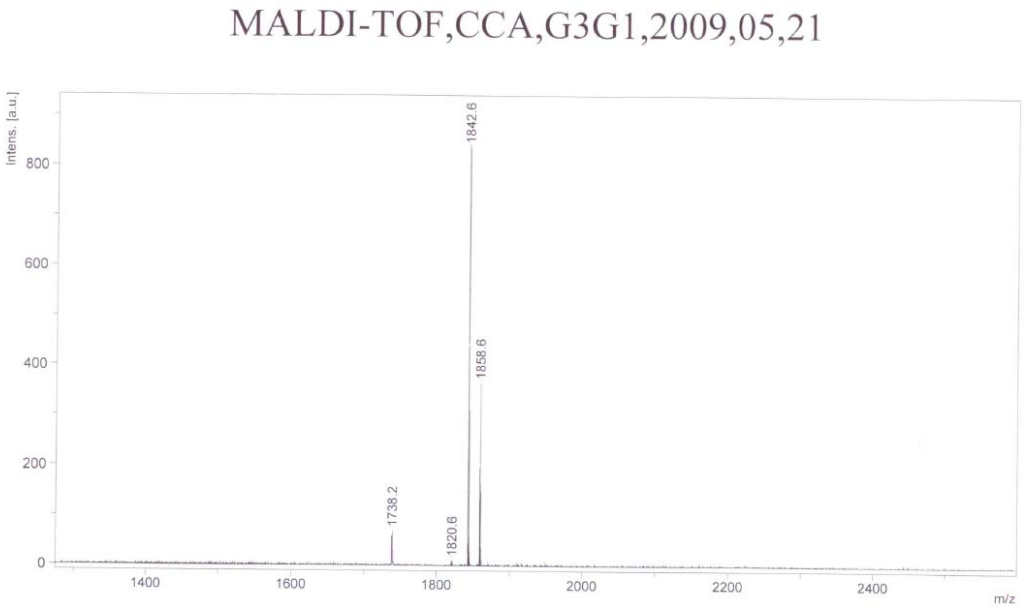
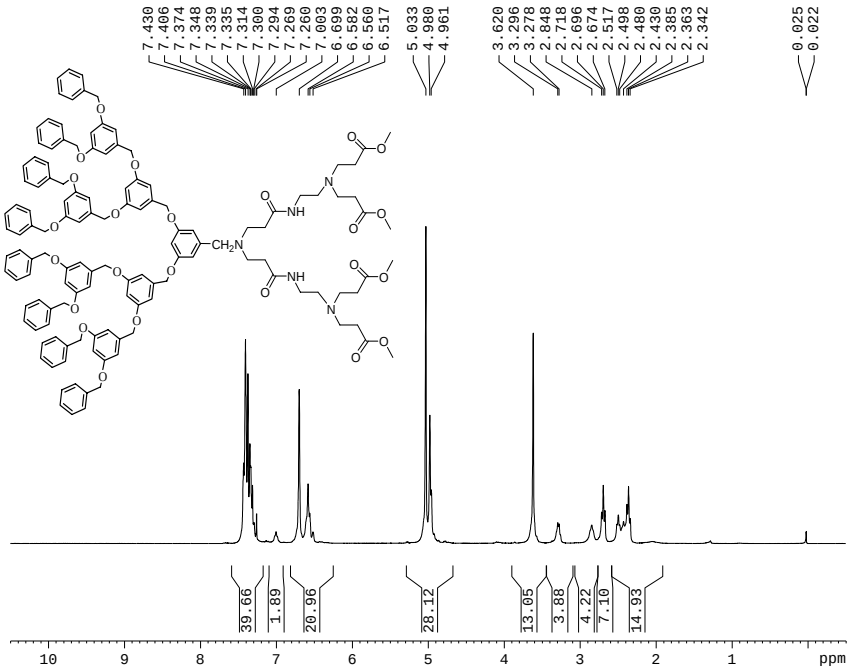


Figure S3. ^{1}H, ^{13}C NMR and MS spectra of Janus dendrimer $\mathbf{G_3G_{1.5}}$

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SOLVENT           CDCl3
NS                   16
DS                    0
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FIDRES         0.137219 Hz
AQ             3.6438515 sec
RG                 90.5
DW               55.600 usec
DE                6.00 usec
TE                299.1 K
D1            1.00000000 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

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P1                7.00 usec
PL1              -1.00 dB
SFO1        300.1324010 MHz

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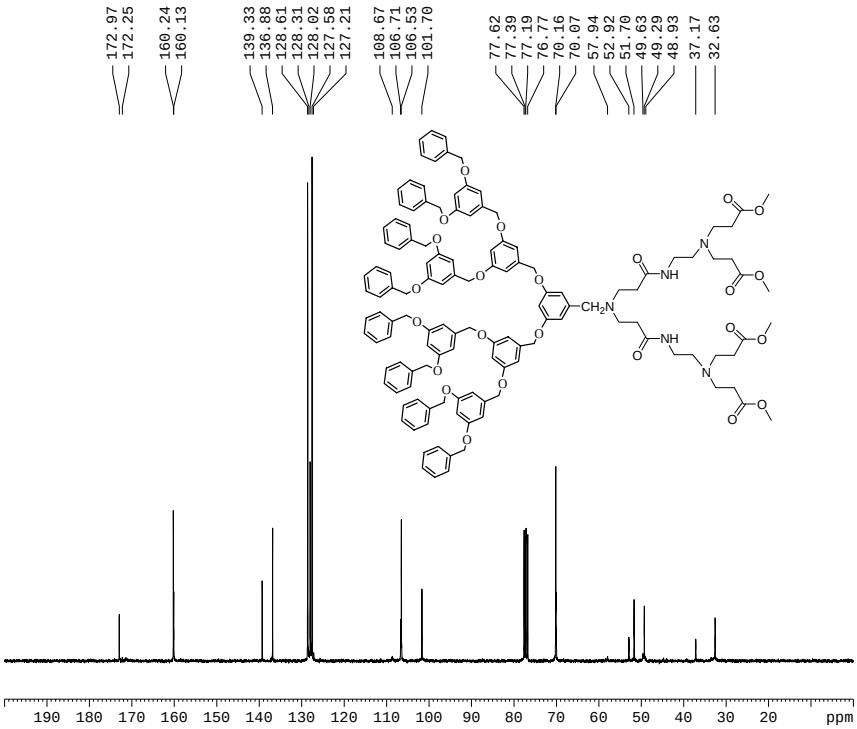


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PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                  652
DS                    4
SWH           17985.611 Hz
FIDRES         0.274439 Hz
AQ             1.8219508 sec
RG                1625.5
DW               27.800 usec
DE                6.00 usec
TE                302.6 K
D1            2.00000000 sec
d11           0.03000000 sec
DELTA         1.89999998 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                13C
P1               12.50 usec
PL1               2.00 dB
SFO1         75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                1H
PCPD2            80.00 usec
PL2              -1.00 dB
PL12             20.16 dB
PL13             16.98 dB
SFO2        300.1312005 MHz

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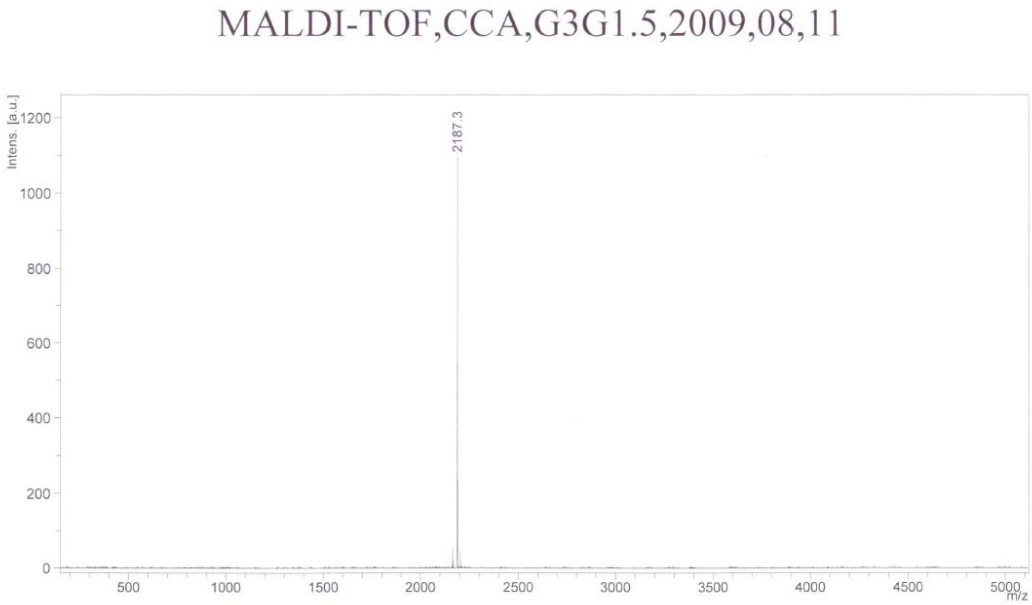
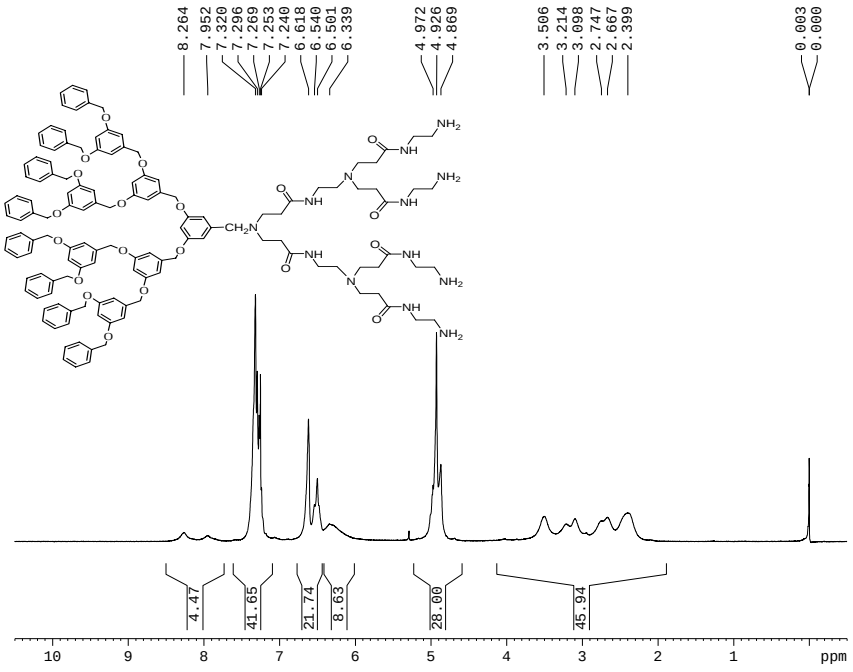


Figure S4. ^{1}H, ^{13}C NMR and MS spectra of Janus dendrimer $\mathbf{G_3G_2}$

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AQ             3.6438515 sec
RG                322.5
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DE                6.00 usec
TE                300.0 K
D1           1.00000000 sec
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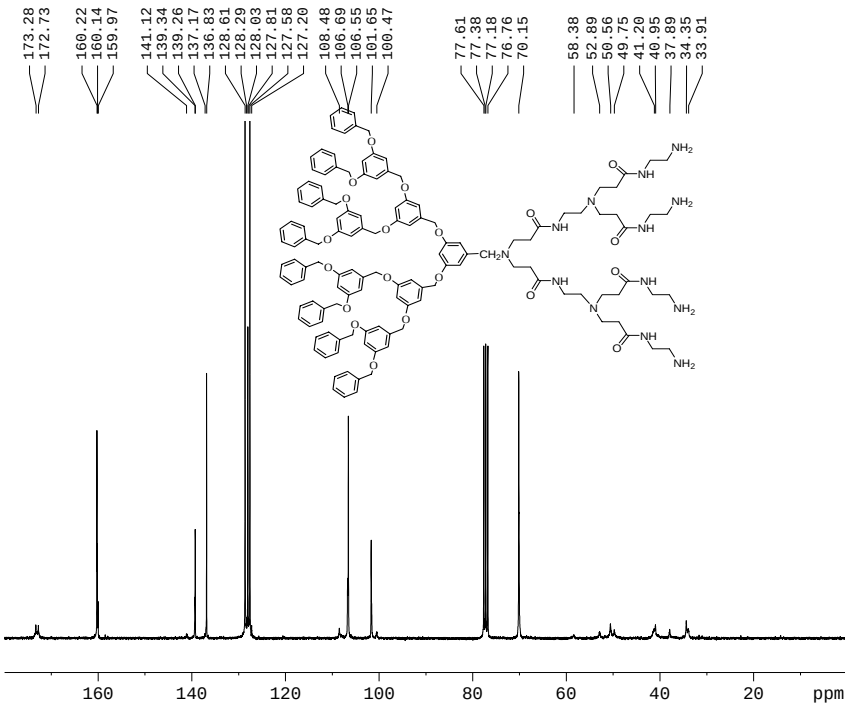


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NS                 5111
DS                    4
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FIDRES         0.274439 Hz
AQ             1.8219508 sec
RG                724.1
DW               27.800 usec
DE                6.00 usec
TE                300.9 K
D1           2.00000000 sec
d11          0.03000000 sec
DELTA        1.89999998 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
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P1               12.50 usec
PL1               2.00 dB
SFO1         75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                1H
PCPD2            80.00 usec
PL2              -1.00 dB
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PL13             16.98 dB
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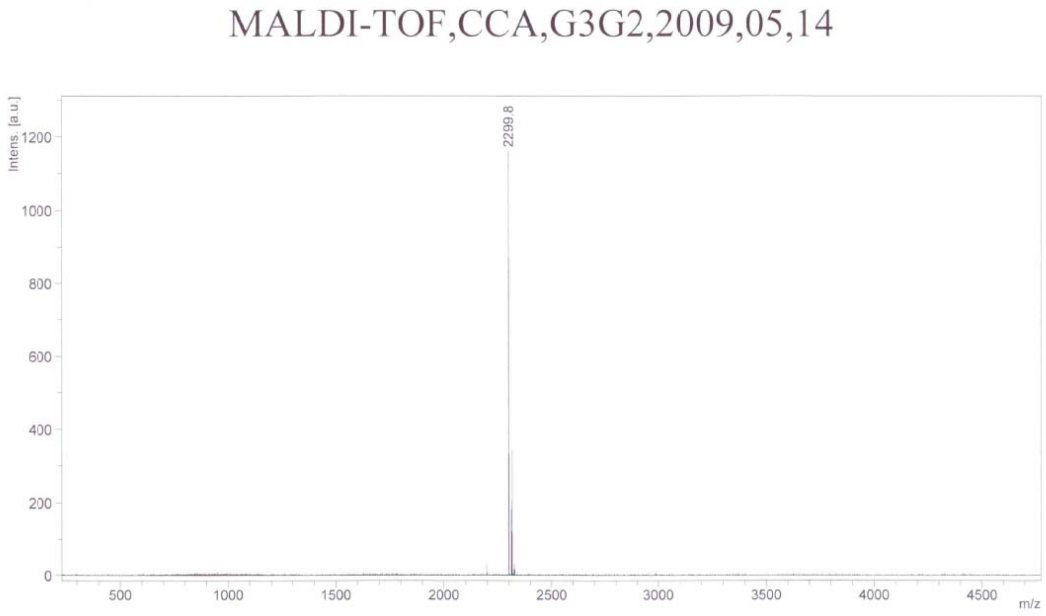
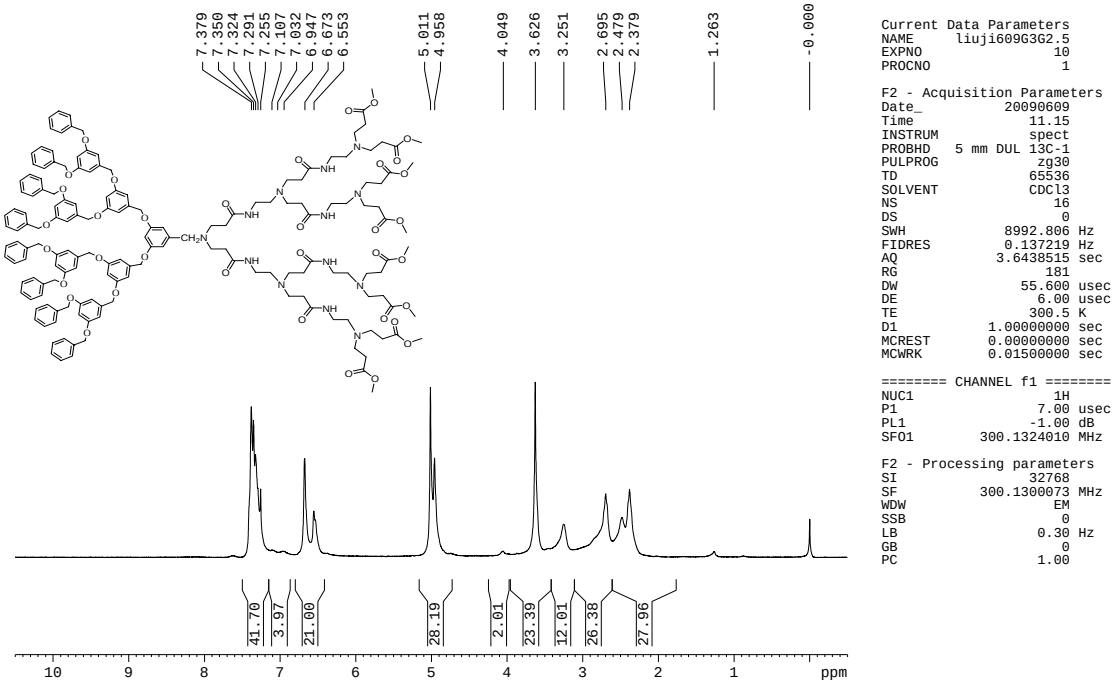
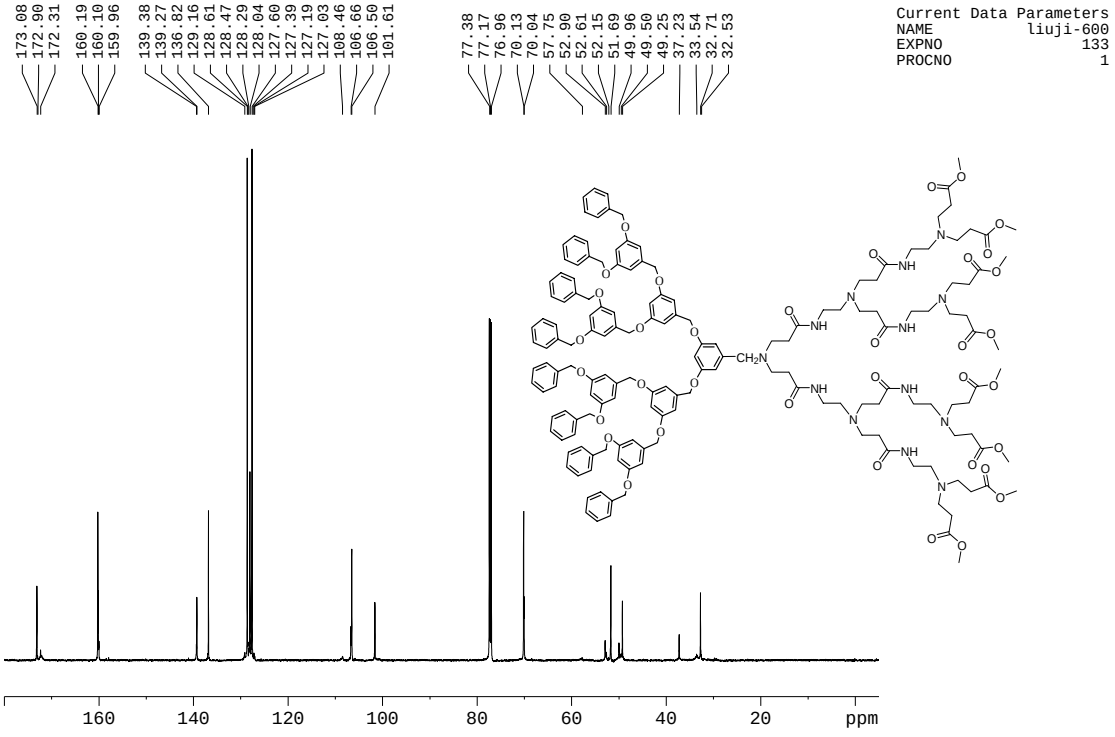


Figure S5. ^{1}H, ^{13}C NMR and MS spectra of Janus dendrimer $\mathbf{G_3G_{2.5}}$





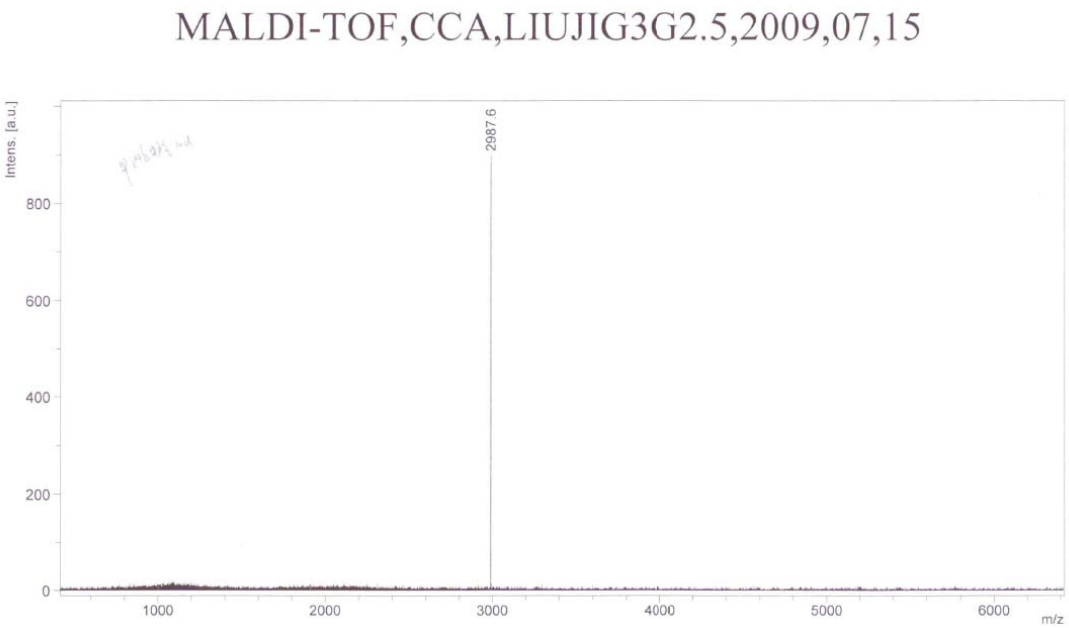
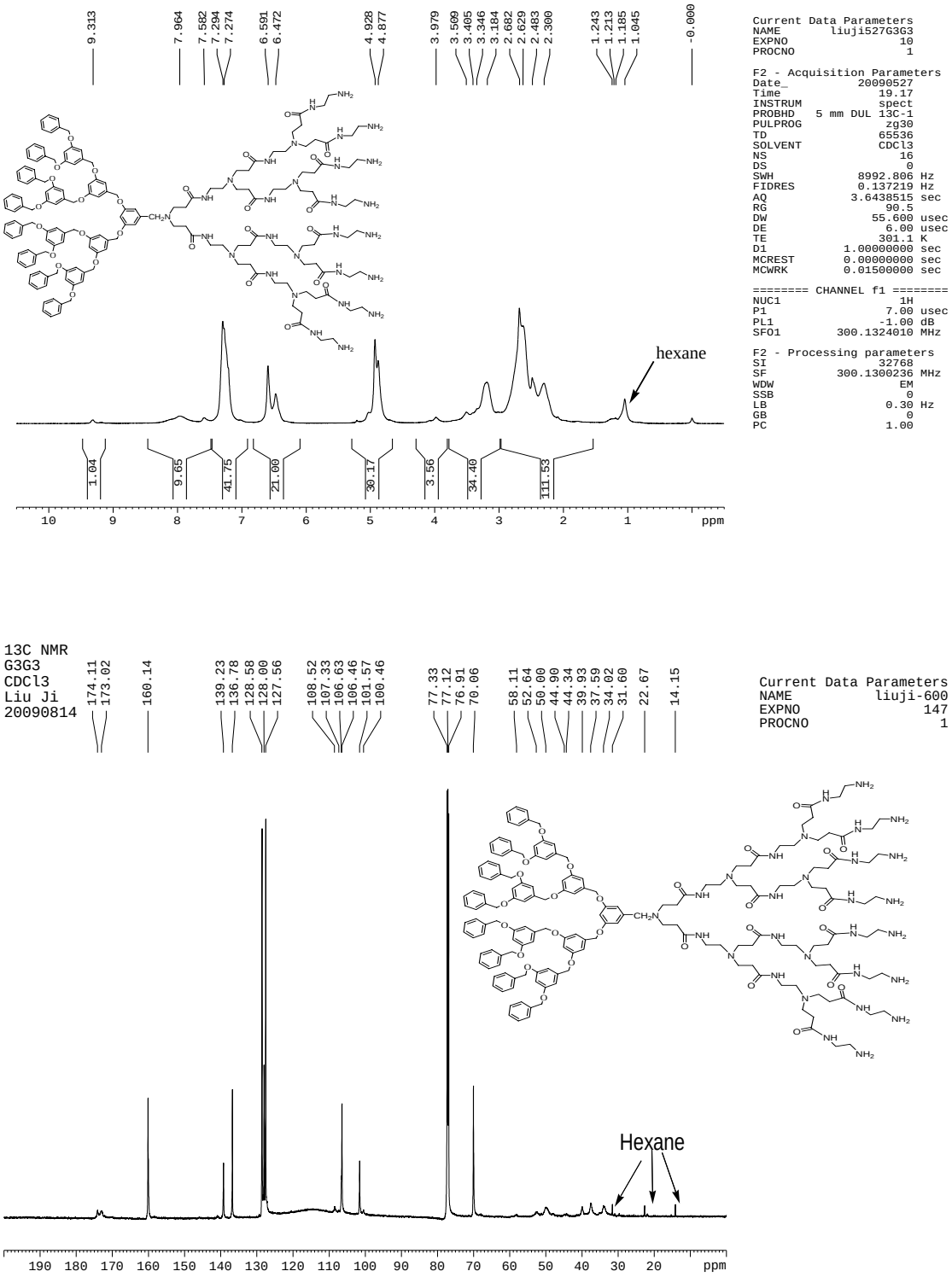


Figure S6. ^{1}H, ^{13}C NMR and MS spectra of Janus dendrimer **G_3G_3**



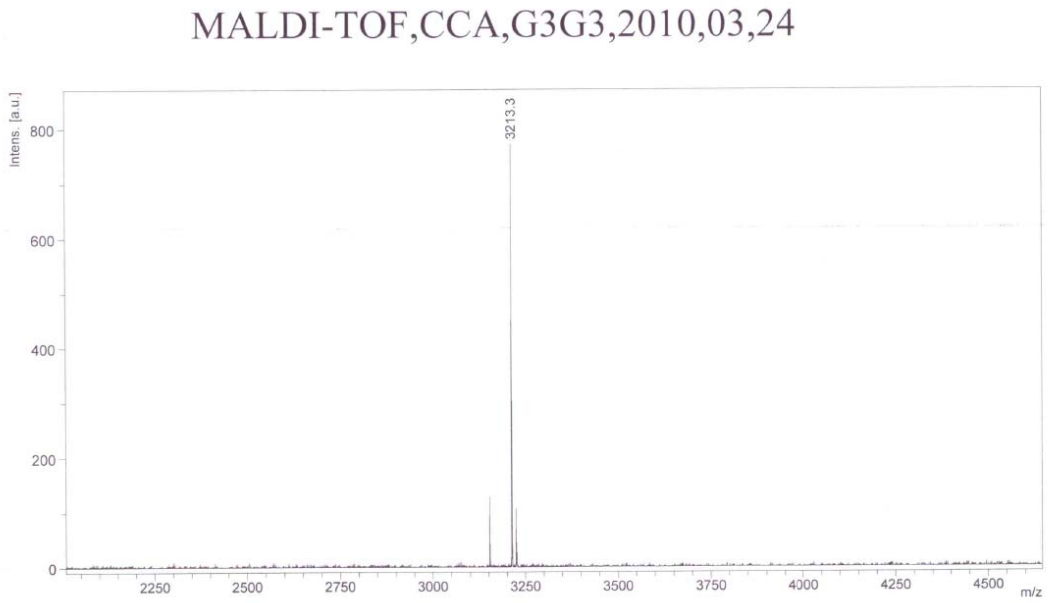
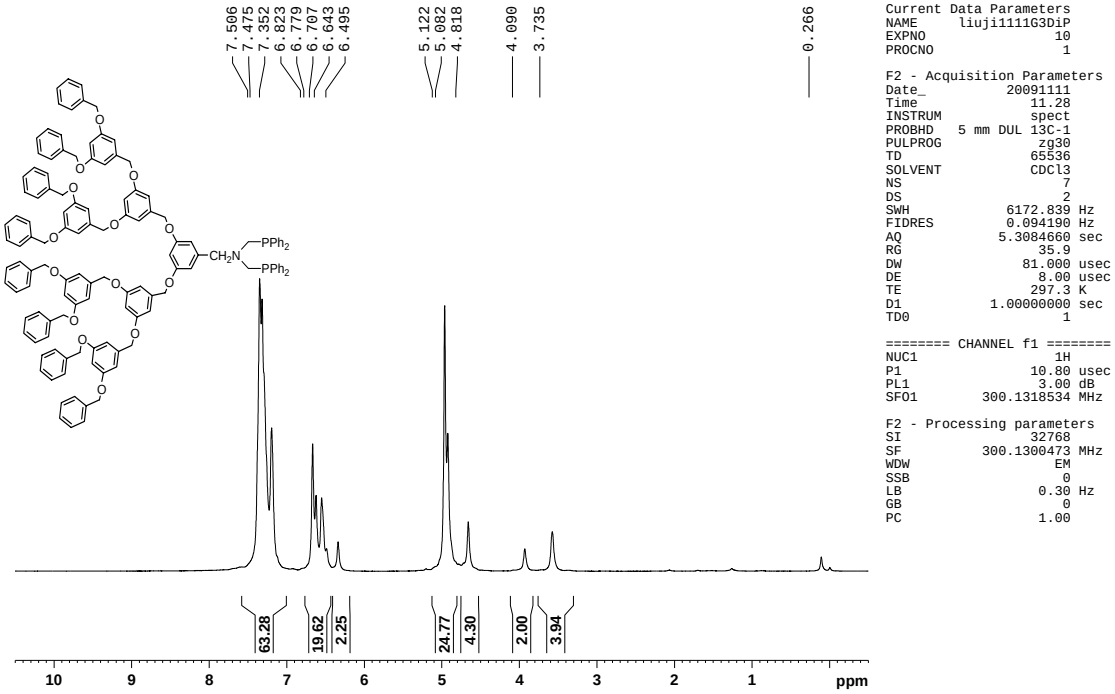
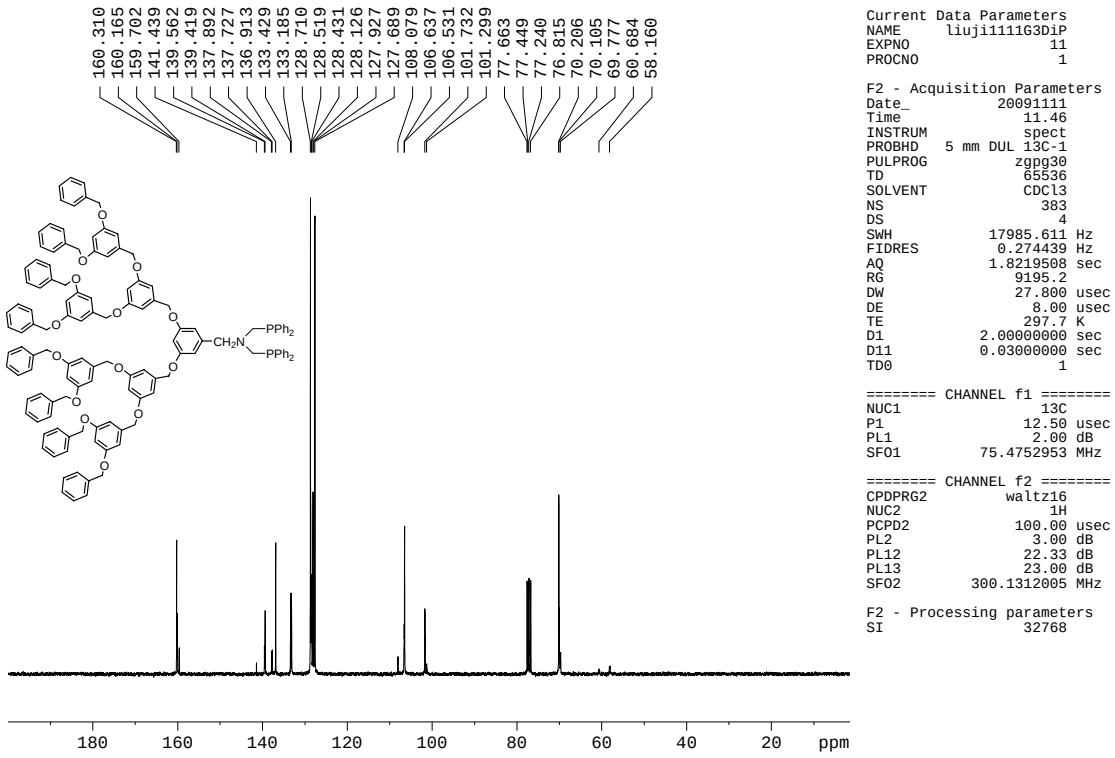
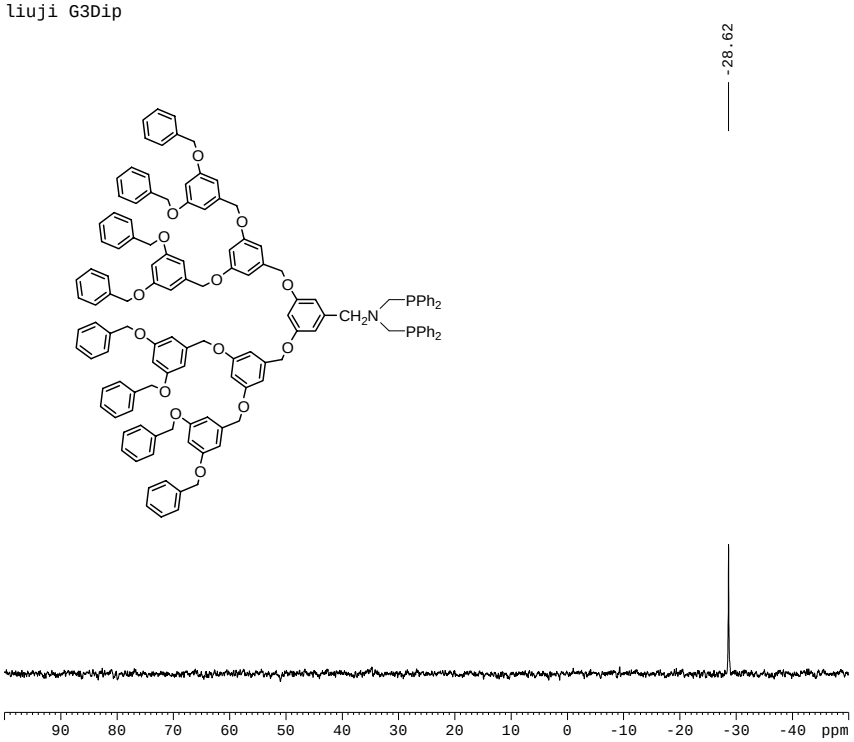


Figure S7. ^{1}H, ^{13}C, ^{31}P NMR and MS spectra of Janus dendrimer **G_3DiP**





liuji G3Dip

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======== CHANNEL f2 ========
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PL12             19.08 dB
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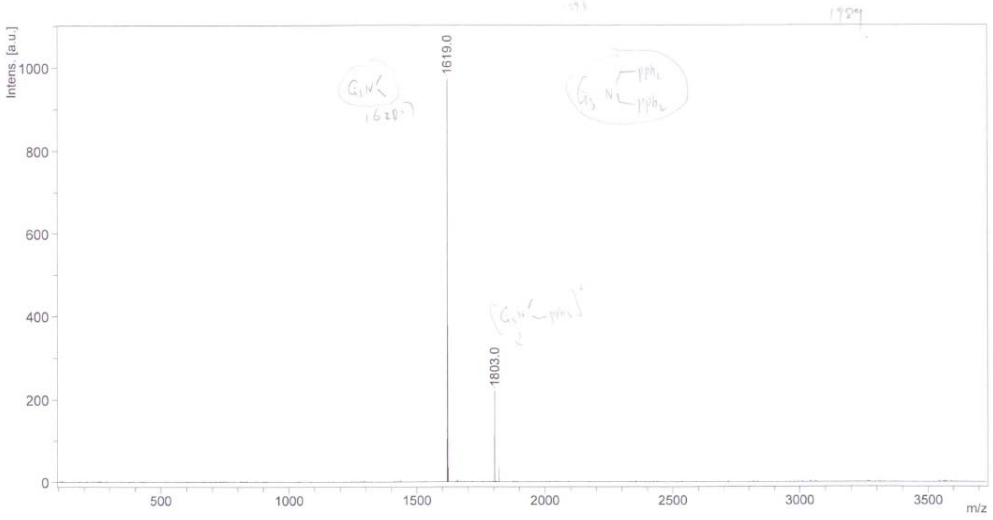
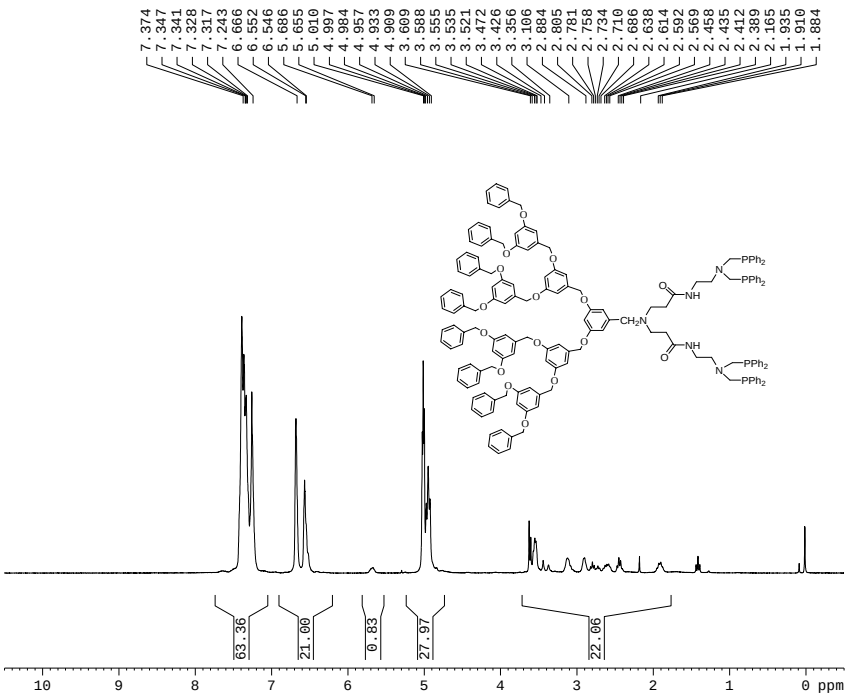


Figure S8. ^{1}H, ^{13}C, ^{31}P NMR and MS spectra of Janus dendrimer **G_3G_1DiP**

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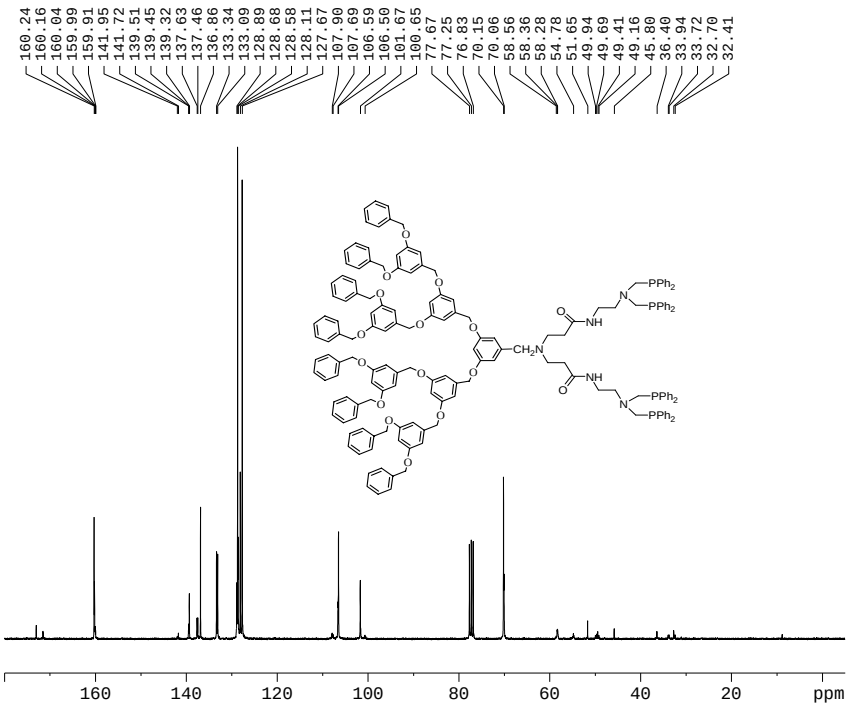
TD                65536
SOLVENT           CDCl3
NS                   16
DS                    0
SWH            8992.806 Hz
FIDRES         0.137219 Hz
AQ             3.6438515 sec
RG                228.1
DW                55.600 usec
DE                 8.00 usec
TE                293.8 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 1H
P1                10.80 usec
PL1                3.00 dB
SFO1         300.1324010 MHz

F2 - Processing parameters
SI                32768
SF           300.1300061 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00
```



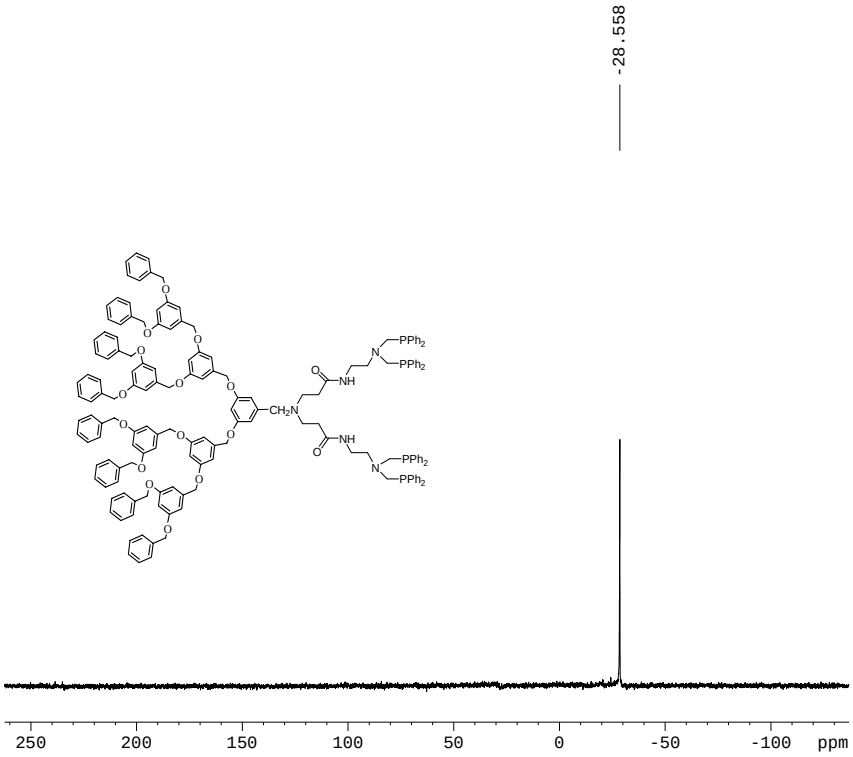

```
Current Data Parameters
NAME      liuji100124G3G1DiP
EXPNO                   21
PROCNO                   1

F2 - Acquisition Parameters
Date_           20100124
Time               9.52
INSTRUM           spect
PROBHD   5 mm DUL 13C-1
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                 1411
DS                    4
SWH           17985.611 Hz
FIDRES         0.274439 Hz
AQ             1.8219508 sec
RG                16384
DW                27.800 usec
DE                 8.00 usec
TE                294.2 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                13C
P1                12.50 usec
PL1                2.00 dB
SFO1         75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2            100.00 usec
PL2                3.00 dB
PL12              22.33 dB
PL13              23.00 dB
SFO2         300.1312005 MHz

F2 - Processing parameters
SI                32768
```




```
Current Data Parameters
NAME            31P NMR
EXPNO               155
PROCNO                1

F2 - Acquisition Parameters
Date_           20090918
Time               16.17
INSTRUM            spect
PROBHD   5 mm BBO BB-1H
PULPROG          zgig30
TD                32768
SOLVENT           CDCl3
NS                   64
DS                    0
SWH           48543.688 Hz
FIDRES         1.481436 Hz
AQ            0.3375604 sec
RG                16384
DW               10.300 usec
DE                6.00 usec
TE                 0.0 K
D1           1.00000000 sec
d11          0.03000000 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                31P
P1                14.75 usec
PL1               10.00 dB
SFO1        121.5023828 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                1H
PCPD2             88.00 usec
PL2                4.00 dB
PL12              19.08 dB
SFO2        300.1321998 MHz

F2 - Processing parameters
SI                 32768
```

MALDI-TOF,CCA,G3G1DiP,2009,09,14

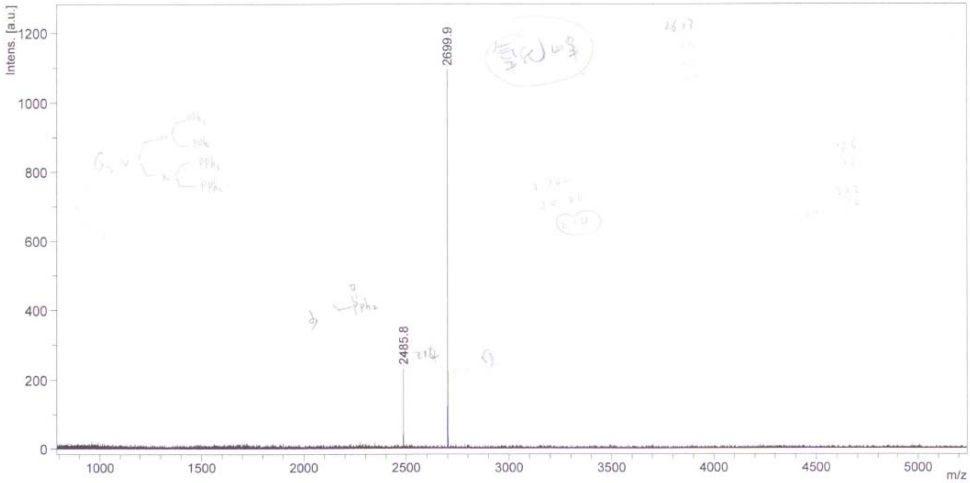
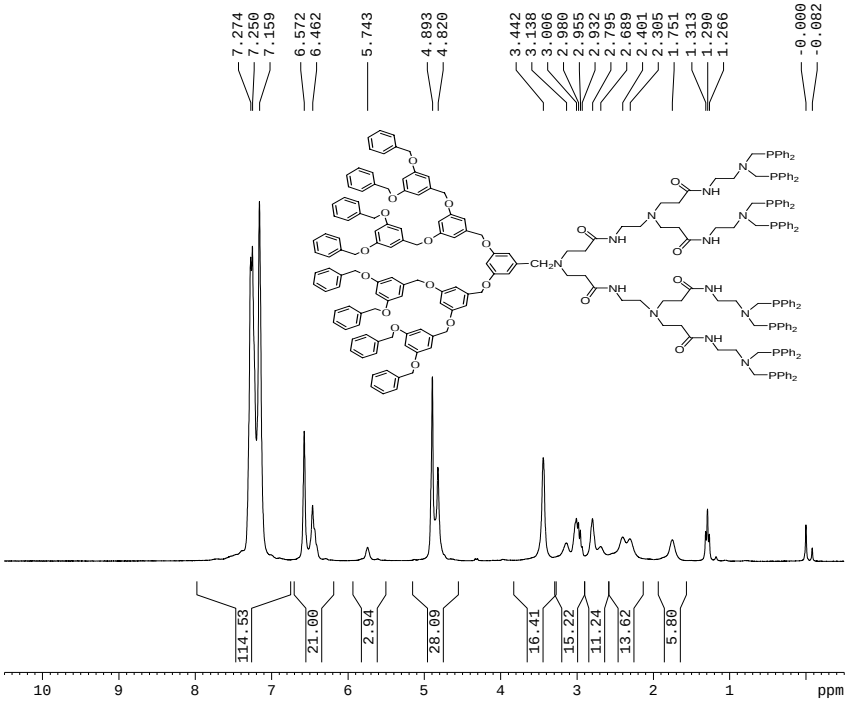


Figure S9. ^{1}H, ^{13}C, ^{31}P NMR and MS spectra of Janus dendrimer **G_3G_2DiP**

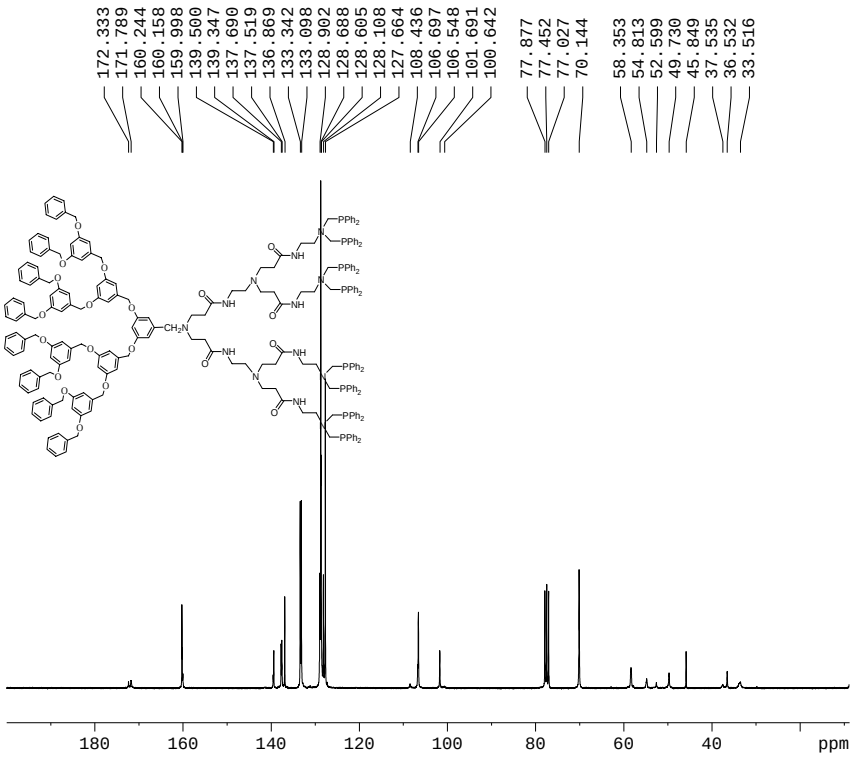



```
Current Data Parameters
NAME      liuji100131G3G2DiP
EXPNO                 10
PROCNO                 1

F2 - Acquisition Parameters
Date_           20100131
Time                9.16
INSTRUM           spect
PROBHD   5 mm DUL 13C-1
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                   16
DS                    0
SWH            8992.806 Hz
FIDRES         0.137219 Hz
AQ             3.6438515 sec
RG                   64
DW                55.600 usec
DE                 8.00 usec
TE                294.6 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 1H
P1                10.80 usec
PL1                3.00 dB
SFO1        300.1324010 MHz

F2 - Processing parameters
SI                32768
SF          300.1300387 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00
```




```
Current Data Parameters
NAME      liuji100131G3G2DiP
EXPNO                 20
PROCNO                 1

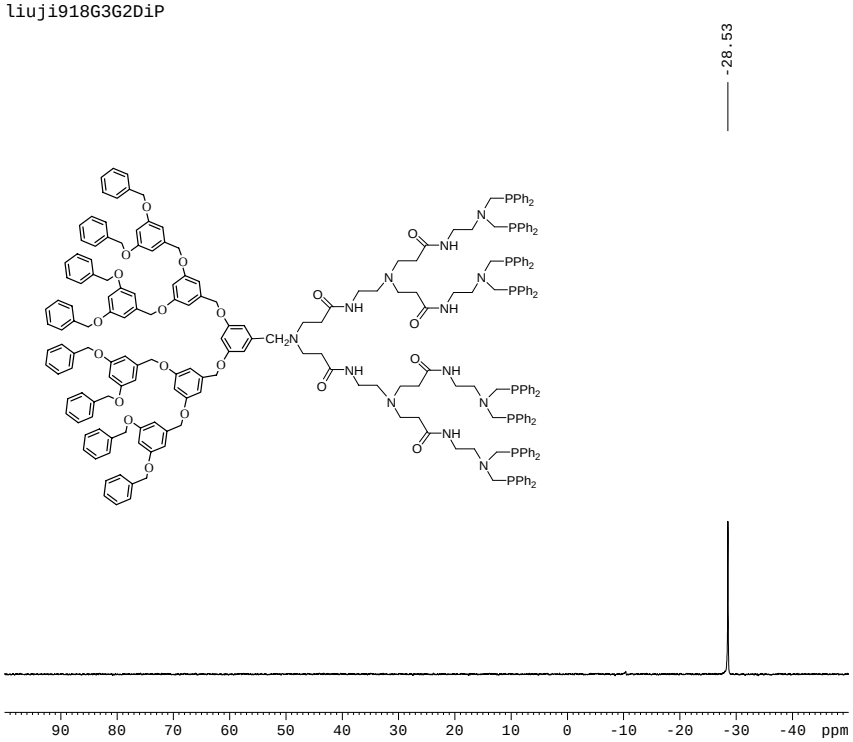
F2 - Acquisition Parameters
Date_           20100131
Time                9.27
INSTRUM           spect
PROBHD   5 mm DUL 13C-1
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                 2812
DS                    4
SWH           17985.611 Hz
FIDRES         0.274439 Hz
AQ             1.8219508 sec
RG                13004
DW                27.800 usec
DE                 8.00 usec
TE                295.1 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                13C
P1                12.50 usec
PL1                2.00 dB
SFO1         75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2            100.00 usec
PL2                3.00 dB
PL12               22.33 dB
PL13               23.00 dB
SFO2        300.1312005 MHz

F2 - Processing parameters
SI                32768
```

liuji918G3G2DiP




```
Current Data Parameters
NAME             31P NMR
EXPNO                156
PROCNO                 1

F2 - Acquisition Parameters
Date_           20090918
Time               16.20
INSTRUM             spect
PROBHD   5 mm BBO BB-1H
PULPROG          zgig30
TD                32768
SOLVENT           CDCl3
NS                   50
DS                    0
SWH           48543.688 Hz
FIDRES         1.481436 Hz
AQ             0.3375604 sec
RG                16384
DW                10.300 usec
DE                 6.00 usec
TE                  0.0 K
D1           1.00000000 sec
d11          0.03000000 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                31P
P1                14.75 usec
PL1               10.00 dB
SFO1        121.5023828 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                1H
PCPD2            88.00 usec
PL2               4.00 dB
PL12             19.08 dB
SFO2        300.1321998 MHz

F2 - Processing parameters
SI                 32768
SF          121.4947578 MHz
WDW                   EM
SSB                    0
LB                  5.00 Hz
GB                     0
PC                  1.40
```

MALDI-TOF,CCA,G3G2DIP,2009,09,16

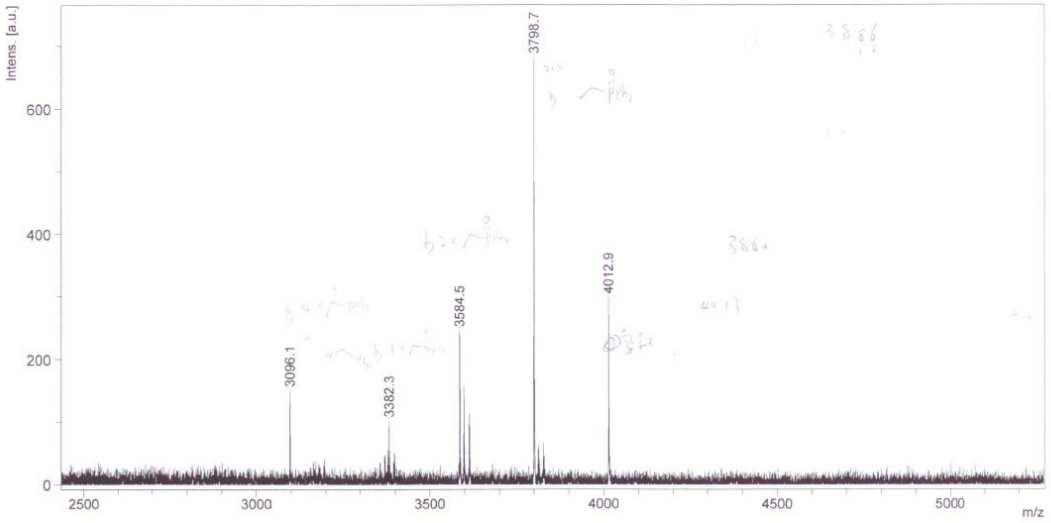
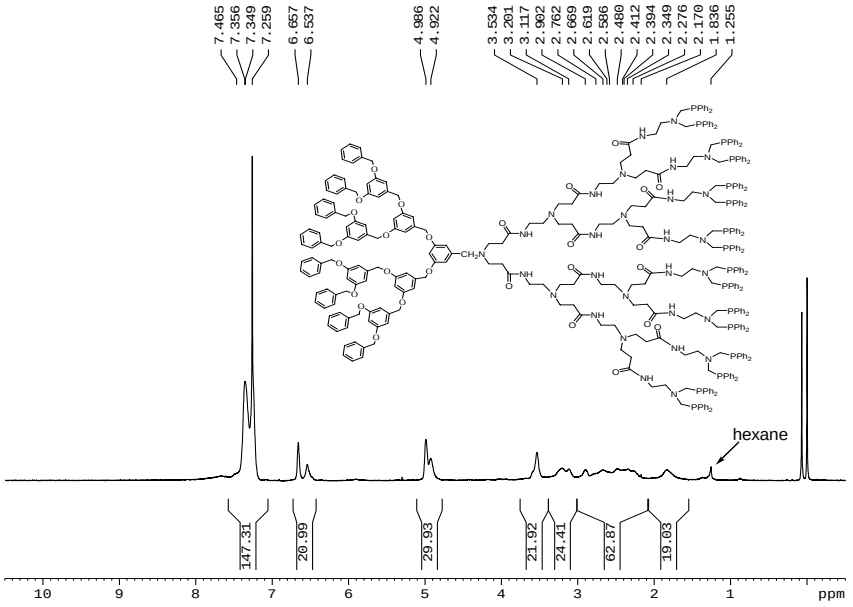


Figure S10. ^{1}H, ^{13}C and ^{31}P NMR of Janus dendrimer **G_3G_3DiP**

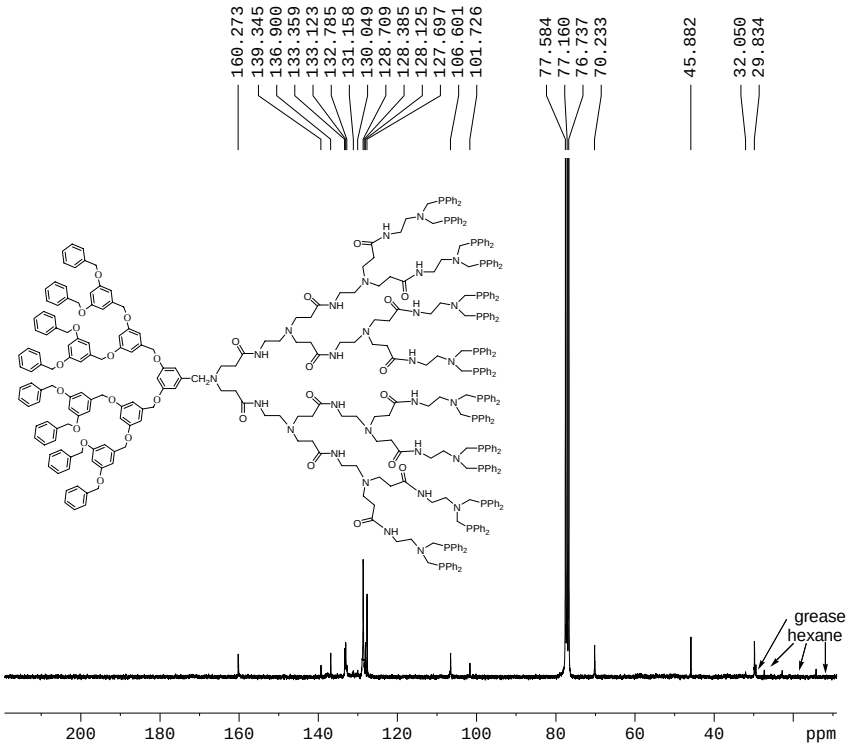



```
Current Data Parameters
NAME      liuji1022G3G3DiP
EXPNO                  10
PROCNO                  1

F2 - Acquisition Parameters
Date_           20091022
Time              20.21
INSTRUM           spect
PROBHD   5 mm DUL 13C-1
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                   16
DS                    2
SWH            6172.839 Hz
FIDRES         0.094190 Hz
AQ             5.3084660 sec
RG                  362
DW               81.000 usec
DE                8.00 usec
TE               297.5 K
D1             1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 1H
P1                10.80 usec
PL1                3.00 dB
SFO1         300.1318534 MHz

F2 - Processing parameters
SI                32768
SF           300.1300061 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00
```




```
Current Data Parameters
NAME      liuji20101219G3G3Di
EXPNO                  11
PROCNO                  1

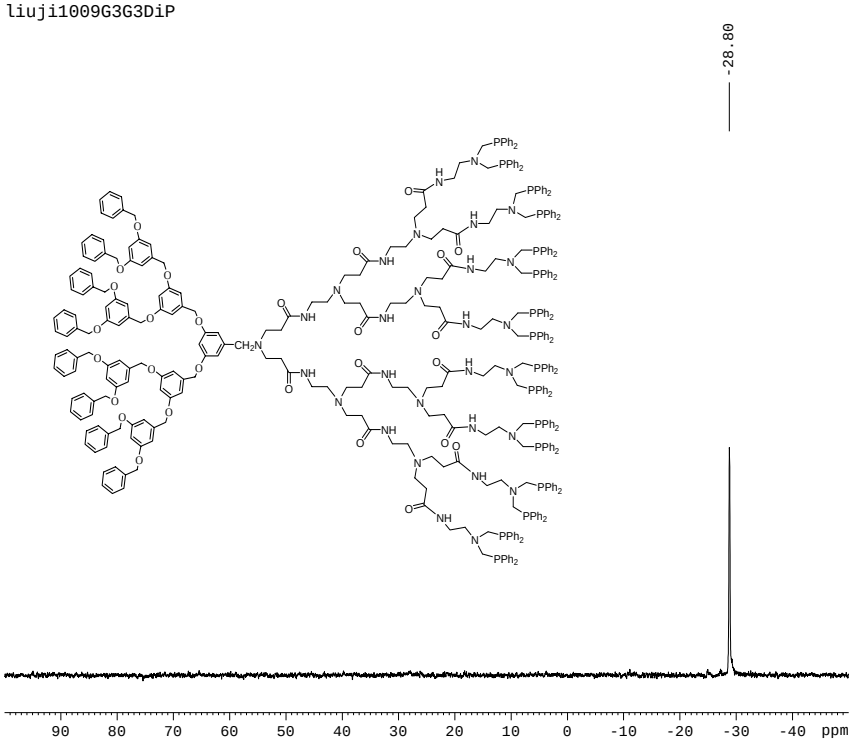
F2 - Acquisition Parameters
Date_           20101218
Time              23.15
INSTRUM           spect
PROBHD   5 mm DUL 13C-1
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                13684
DS                    4
SWH           17985.611 Hz
FIDRES         0.274439 Hz
AQ             1.8219508 sec
RG               14596.5
DW               27.800 usec
DE                8.00 usec
TE               298.6 K
D1          2.00000000 sec
D11         0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                13C
P1                12.50 usec
PL1                2.00 dB
SFO1          75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2            100.00 usec
PL2                3.00 dB
PL12               22.33 dB
PL13               23.00 dB
SFO2         300.1312005 MHz

F2 - Processing parameters
SI                32768
```

liuji1009G3G3DiP




```
Current Data Parameters
NAME             31P NMR
EXPNO                162
PROCNO                 1

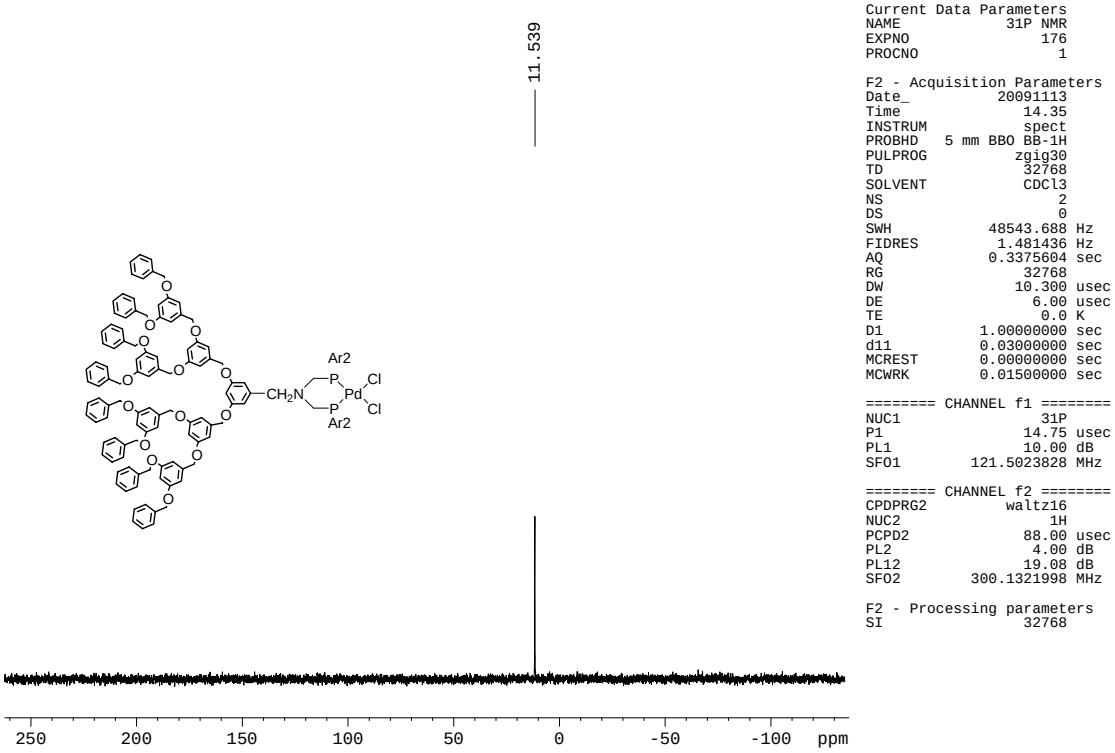
F2 - Acquisition Parameters
Date_           20091016
Time               15.47
INSTRUM            spect
PROBHD   5 mm BBO BB-1H
PULPROG          zgig30
TD                32768
SOLVENT           CDCl3
NS                  134
DS                    0
SWH           48543.688 Hz
FIDRES         1.481436 Hz
AQ            0.3375604 sec
RG                32768
DW               10.300 usec
DE                6.00 usec
TE                 0.0 K
D1           1.00000000 sec
d11          0.03000000 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1               31P
P1               14.75 usec
PL1              10.00 dB
SFO1       121.5023828 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                1H
PCPD2            88.00 usec
PL2               4.00 dB
PL12             19.08 dB
SFO2       300.1321998 MHz

F2 - Processing parameters
SI                32768
SF         121.4947578 MHz
WDW                EM
SSB                 0
LB               5.00 Hz
GB                  0
PC               1.40
```

Figure S11. ^{31}P NMR of Janus dendrimer catalyst **G_3DiPPd**




```
Current Data Parameters
NAME            31P NMR
EXPNO               176
PROCNO                1

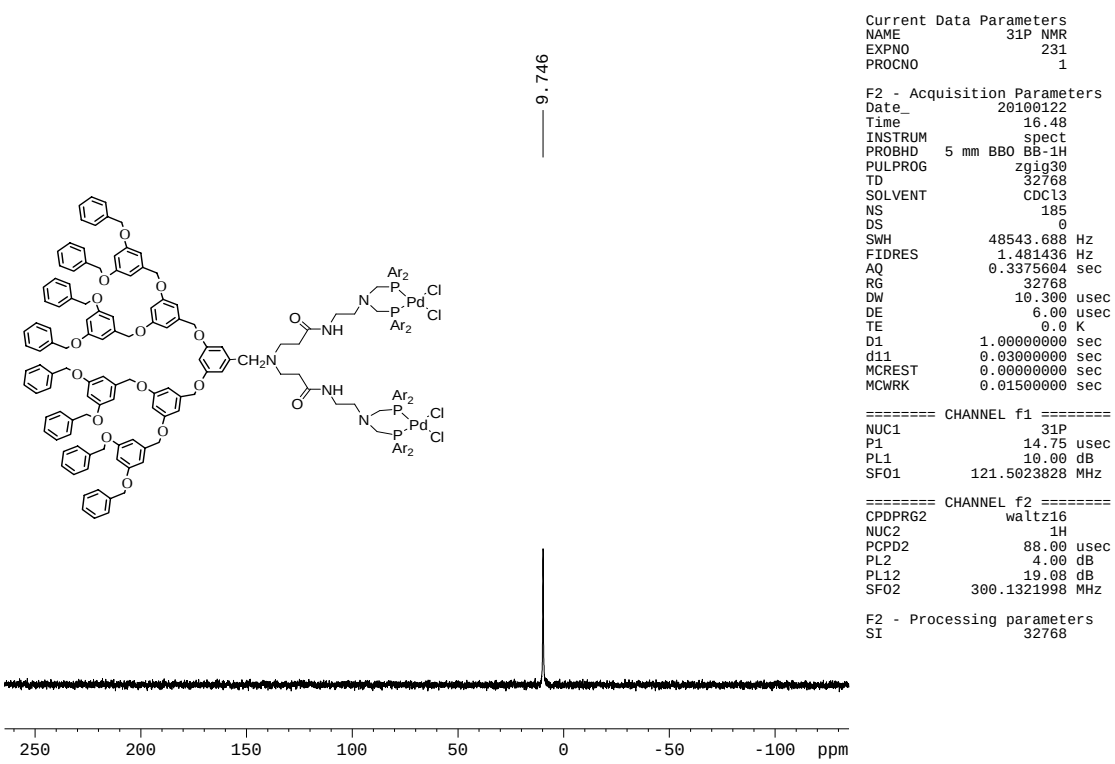
F2 - Acquisition Parameters
Date_          20091113
Time              14.35
INSTRUM           spect
PROBHD   5 mm BBO BB-1H
PULPROG          zgig30
TD                32768
SOLVENT           CDCl3
NS                    2
DS                    0
SWH           48543.688 Hz
FIDRES         1.481436 Hz
AQ            0.3375604 sec
RG                32768
DW               10.300 usec
DE                6.00 usec
TE                 0.0 K
D1           1.00000000 sec
d11          0.03000000 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                31P
P1               14.75 usec
PL1              10.00 dB
SFO1        121.5023828 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                1H
PCPD2            88.00 usec
PL2               4.00 dB
PL12             19.08 dB
SFO2        300.1321998 MHz

F2 - Processing parameters
SI                32768
```

Figure S12. ^{31}P NMR of Janus dendrimer catalyst **G_3G_2DiPPd$_2$**




```
Current Data Parameters
NAME            31P NMR
EXPNO               231
PROCNO                1

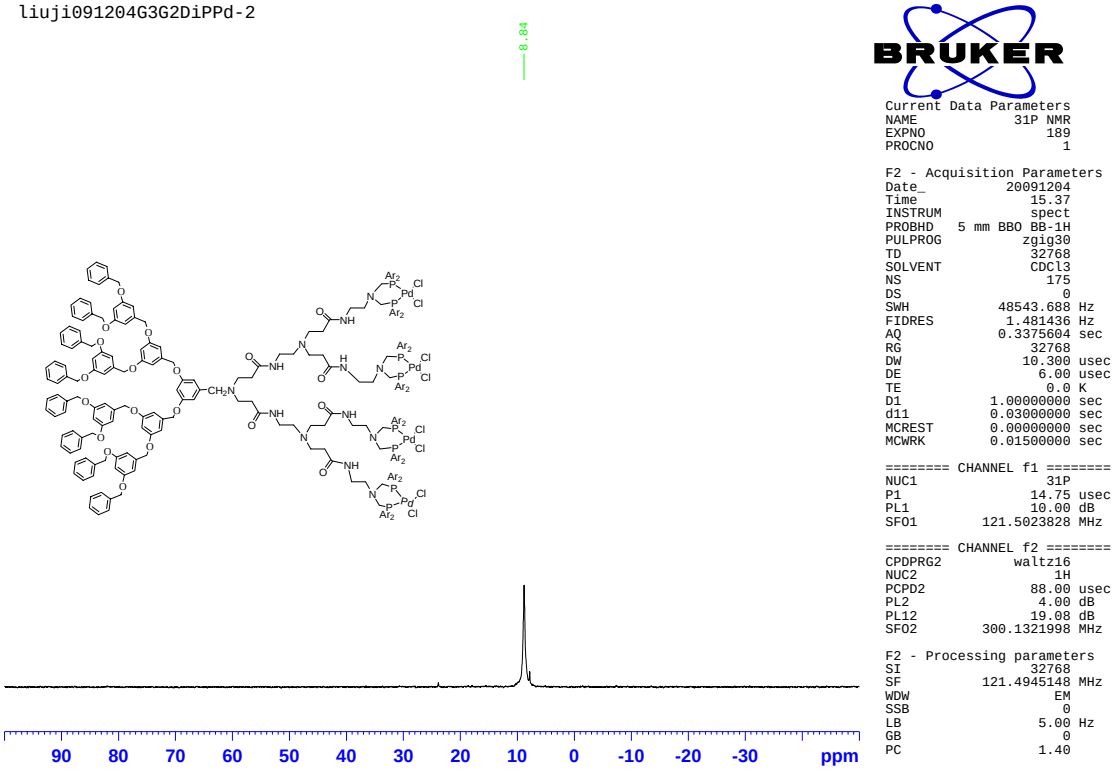
F2 - Acquisition Parameters
Date_          20100122
Time              16.48
INSTRUM           spect
PROBHD   5 mm BBO BB-1H
PULPROG          zgig30
TD                32768
SOLVENT           CDCl3
NS                  185
DS                    0
SWH           48543.688 Hz
FIDRES         1.481436 Hz
AQ            0.3375604 sec
RG                32768
DW               10.300 usec
DE                 6.00 usec
TE                  0.0 K
D1           1.00000000 sec
d11          0.03000000 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                31P
P1                14.75 usec
PL1               10.00 dB
SFO1        121.5023828 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                1H
PCPD2             88.00 usec
PL2                4.00 dB
PL12              19.08 dB
SFO2        300.1321998 MHz

F2 - Processing parameters
SI                32768
```

Figure S13. ^{31}P NMR of Janus dendrimer catalyst $\mathbf{G_3G_2DiPPd_4}$




```
Current Data Parameters
NAME                  31P NMR
EXPNO                     189
PROCNO                      1

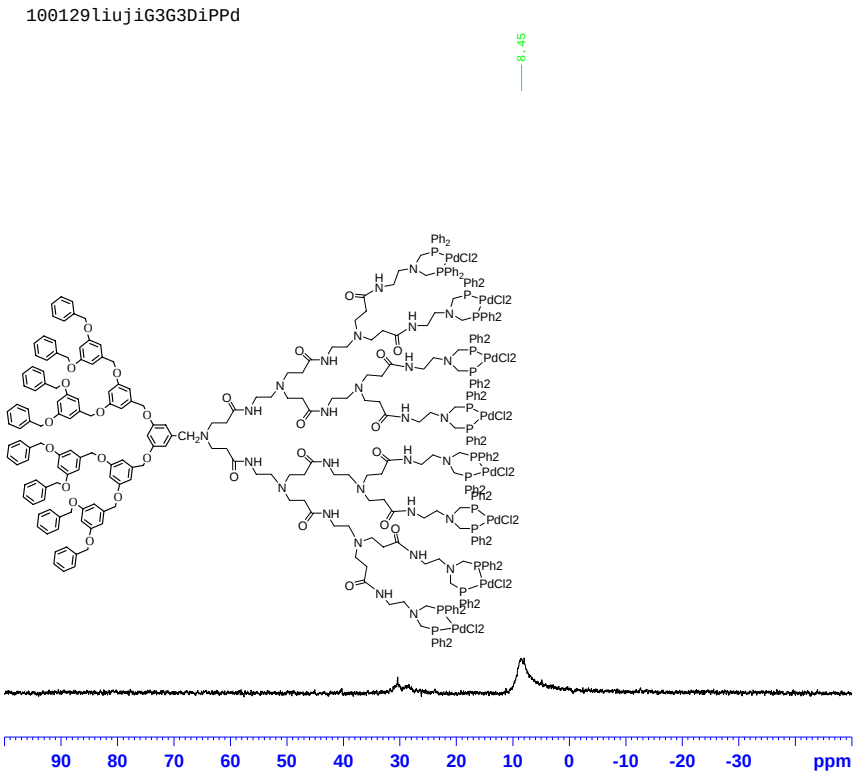
F2 - Acquisition Parameters
Date_              20091204
Time                  15.37
INSTRUM               spect
PROBHD   5 mm BBO BB-1H
PULPROG             zgig30
TD                    32768
SOLVENT               CDCl3
NS                      175
DS                        0
SWH               48543.688 Hz
FIDRES             1.481436 Hz
AQ                0.3375604 sec
RG                    32768
DW                   10.300 usec
DE                    6.00 usec
TE                     0.0 K
D1                1.00000000 sec
d11               0.03000000 sec
MCREST            0.00000000 sec
MCWRK             0.01500000 sec

======== CHANNEL f1 ========
NUC1                    31P
P1                    14.75 usec
PL1                   10.00 dB
SFO1          121.5023828 MHz

======== CHANNEL f2 ========
CPDPRG2             waltz16
NUC2                    1H
PCPD2                 88.00 usec
PL2                    4.00 dB
PL12                  19.08 dB
SFO2          300.1321998 MHz

F2 - Processing parameters
SI                    32768
SF            121.4945148 MHz
WDW                      EM
SSB                       0
LB                     5.00 Hz
GB                        0
PC                     1.40
```

Figure S14. ^{31}P NMR of Janus dendrimer catalyst **G_3G_3DiPPd$_8$**




```
Current Data Parameters
NAME                  31P NMR
EXPNO                     236
PROCNO                      1

F2 - Acquisition Parameters
Date_              20100129
Time                  16.44
INSTRUM               spect
PROBHD   5 mm BBO BB-1H
PULPROG              zgig30
TD                    32768
SOLVENT               CDCl3
NS                      361
DS                        0
SWH               48543.688 Hz
FIDRES             1.481436 Hz
AQ                0.3375604 sec
RG                     8192
DW                   10.300 usec
DE                    6.00 usec
TE                     0.0 K
D1              1.00000000 sec
d11             0.03000000 sec
MCREST          0.00000000 sec
MCWRK           0.01500000 sec

======== CHANNEL f1 ========
NUC1                   31P
P1                   14.75 usec
PL1                  10.00 dB
SFO1          121.5023828 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                   1H
PCPD2                88.00 usec
PL2                   4.00 dB
PL12                 19.08 dB
SFO2          300.1321998 MHz

F2 - Processing parameters
SI                    32768
SF            121.4945149 MHz
WDW                      EM
SSB                       0
LB                     5.00 Hz
GB                        0
PC                     1.40
```