Supplementary Information

Modular Chiral Dendritic monodentate phosphoramidite ligands for Rh(I)-Catalyzed Asymmetric Hydrogenation: Unprecedented Enhancement of Enantioselectivity

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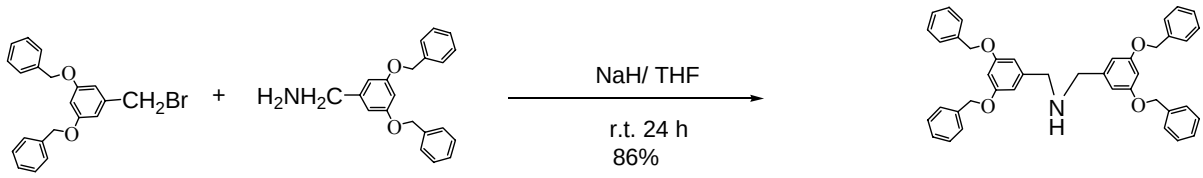
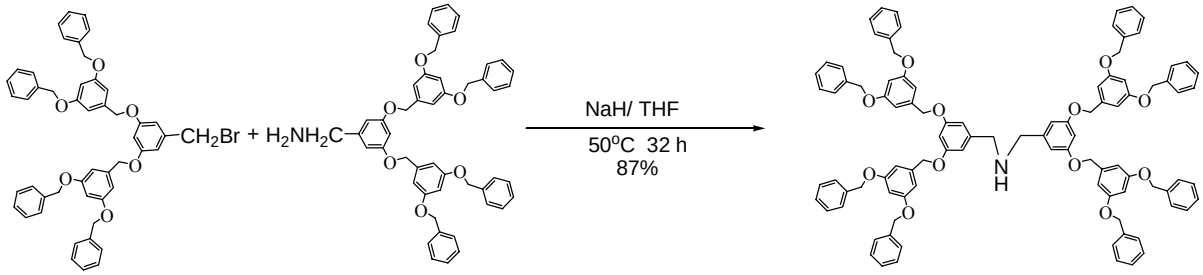
1. General Information

Unless otherwise noted, all experiments were carried out under an inert atmosphere of dry nitrogen by using standard Schlenk-type techniques, 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. Melting points were uncorrected. All enantiomeric excess values were obtained from GC analysis with a Chrompack CHIR-L-VAL chiral 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. Dendrons $G_nCH_2NH_2$[1] and G_nCH_2Br[2], and chiral diol **7b**[3], **7c**[4] were synthesized according to the published methods.

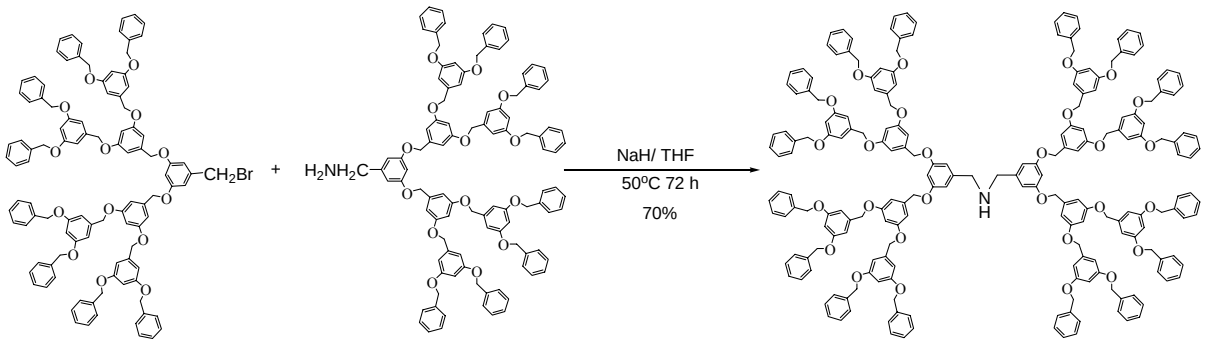
2. The synthesis of dendrons $5G_1$-G_3



G_1CH_2Br $G_1CH_2NH_2$ **$5G_1$**



G_2CH_2Br $G_2CH_2NH_2$ **$5G_2$**



G_3CH_2Br $G_3CH_2NH_2$ **$5G_3$**

Scheme S1. The synthesis of dendrons **$5G_1$-$5G_3$**

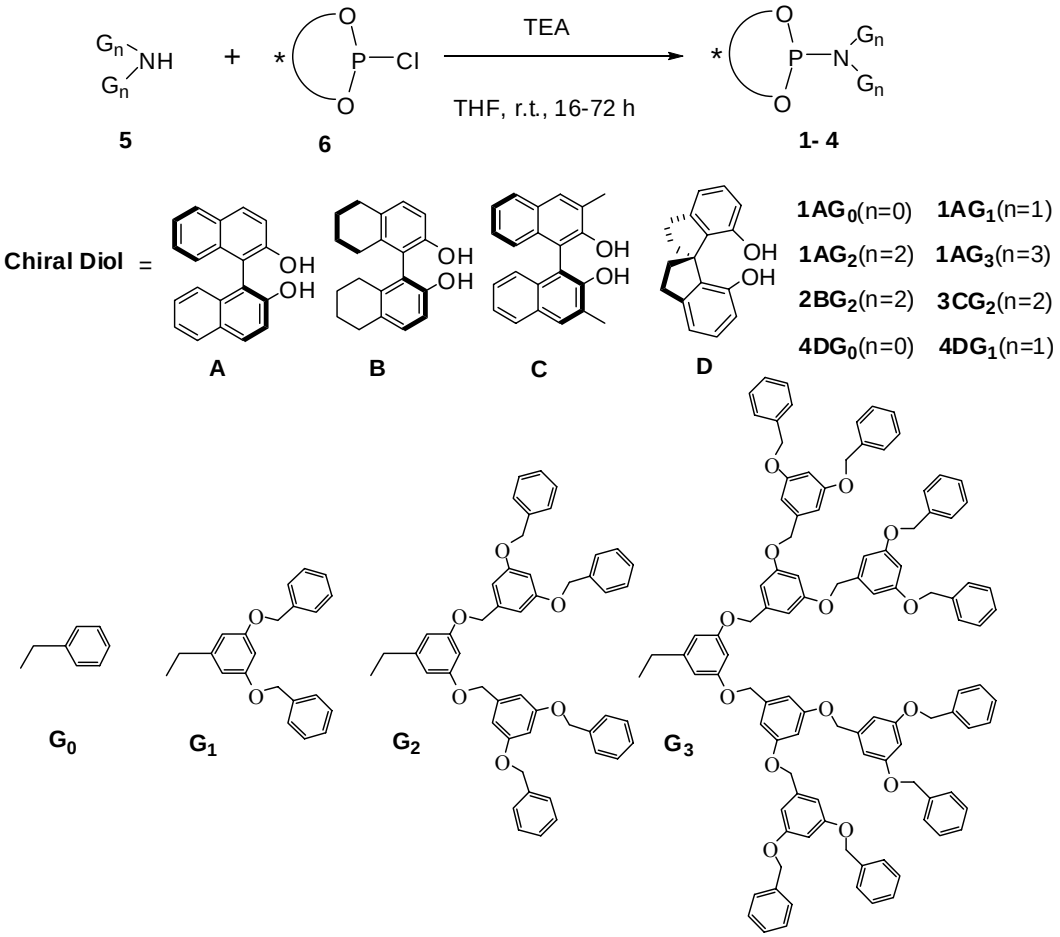
Synthesis of $5G_1$: To a suspension of $G_1CH_2NH_2$ (1.276 g, 4 mmol) and NaH (0.15 g, 6 mmol) in THF (10 mL) was added dropwise a solution of G_1CH_2Br (1.719 g, 4.5 mmol) in THF (20 mL) at 0 ^oC over 10 min and then stirred for 24 h at room temperature under a nitrogen atmosphere. The reaction was followed by TLC. After quenching with saturated aq. ammonium chloride, the solution was extracted with dichloromethane twice. The combined organic layer was washed with brine, and dried over anhydrous Na_2SO_4. The solvent was evaporated and the resulting residue was purified by flash column chromatography to afford the secondary amine **$5G_1$** as a white solid (2.13 g, 86% yield). ^1H NMR (300 MHz, $CDCl_3$) δ = 3.77 (s, 4H), 5.06 (s, 8H), 6.56-6.65 (m, 6H), 7.33-7.46 (m, 20H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 53.2, 70.1, 100.8, 107.2, 107.9, 127.6, 128.0, 128.6, 137.0, 142.9, 160.1. HRMS (Secondary Ion Mass Spectory, SIMS) for $C_{42}H_{39}NO_4$, $[M+H]^+$: Calcd. 622.2958, Found 622.2953.

Synthesis of $5G_2$: To a suspension of $G_2CH_2NH_2$ (2.972 g, 4 mmol) and NaH (0.15 g, 6 mmol) in THF (10 mL) was added dropwise a solution of G_2CH_2Br (3.389 g, 4.2 mmol) in THF (20 mL) at 0 ^oC over 10 min and then stirred for 72 h at 50 ^oC under a nitrogen atmosphere. The reaction was followed by TLC. After quenching with saturated aq. ammonium chloride, the solution was extracted with dichloromethane twice. The combined organic layer was washed with brine, and dried over anhydrous Na_2SO_4. The solvent was evaporated and the resulting residue was purified by flash column chromatography to afford the secondary amine **$5G_2$** as a white foam (5.12 g, 87% yield). ^1H NMR (300 MHz, $CDCl_3$) δ

= 3.74 (s, 4H), 4.96-5.00 (m, 24H), 6.55-6.68 (m, 18H)，7.26-7.40 (m, 40H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 53.2, 70.0, 70.1, 100.7, 101.6, 106.4, 107.1, 127.6, 128.0, 128.6, 136.8, 139.4, 142.9, 160.0, 160.2. HRMS (SIMS) for $C_{98}H_{87}NO_{12}$, $[M+H]^+$: Calcd. 1470.6307, Found 1470.6335.

Synthesis of $5G_3$: To a suspension of $G_3CH_3NH_2$ (3.184 g, 2 mmol) and NaH (0.300 g, 12 mmol) in THF (10 mL) was added dropwise a solution of G_3CH_2Br (4.968 g, 3 mmol) in THF (20 mL) at 0 ^{o}C over 10 min and then stirred for 72 h at 50 ^{o}C under a nitrogen atmosphere. The reaction was followed by TLC. After quenching with saturated aq. ammonium chloride, the solution was extracted with dichloromethane twice. The combined organic layer was washed with brine, and dried over anhydrous Na_2SO_4. The solvent was evaporated and the resulting residue was purified by flash column chromatography to afford the secondary amine **$5G_3$** as a white foam (4.44 g, 70% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ = 3.70 (s, 4H), 4.87-4.98 (m, 56H), 6.50-6.64 (m, 42H)，7.25-7.37 (m，80H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 53.2, 70.0, 70.2, 100.9, 101.8, 106.5, 107.3, 127.6, 127.8, 128.0, 128.2, 128.3, 128.6, 136.9, 139.4, 139.5, 143.1, 160.1, 160.2, 160.2. MS (MALDI-TOF): m/z Calcd for $C_{210}H_{183}NO_{28}$: 3168.69, Found 3206.4 ($[M+K]^+$).

3. General procedure for the synthesis of chiral dendritic monodentate phosphoramidite ligands 1-4



Scheme S2. The synthesis of dendritic monodentate phosphoramidite ligands **1-4**

Synthesis of (*S*)-1AG$_0$[5]: To a solution of dibenzylamine **5G$_0$** (690 mg, 3.5 mmol) and Et_3N (1 mL, 7.0 mmol) in THF (10 mL) at 0 ^oC was added dropwise a solution of (*S*)-[1, 1'-binaphthyl-2,2'-diyl] chlorophosphite (1.225 g, 3.5 mmol) in THF (20 mL). The resulting mixture was stirred at room temperature overnight. The precipitate of Et_3NHCl was filtered over a pad of celite. After the solvent was removed under reduced pressure, the residue was purified by flash column chromatography to give **1AG$_0$** (1.503 g, 84% yield) as a white foam. ^1H NMR (300 MHz, $CDCl_3$): δ = 3.39-3.48 (m, 2H), 4.16-4.24 (m, 2H), 7.11 (d, *J* = 8.8 Hz, 1H), 7.24-7.42 (m, 16H), 7.63 (d, *J* = 8.8 Hz, 1H), 7.74 (d, *J* = 8.8 Hz, 1H), 7.80 (dd, J_1 = 8.8 Hz, J_2 = 1.4 Hz,1H), 7.94 (d, *J* = 8.8 Hz, 1H), 8.00 (d, *J* = 8.8 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 48.1, 48.4, 121.5, 122.2, 122.2, 124.6, 124.9, 126.1, 126.1, 126.9, 127.1, 127.3, 128.2, 128.4, 128.4, 128.9, 130.1, 130.3, 137.9, 137.9, 149.3, 149.8.

Synthesis of (*S*)-1AG$_1$: Followed the similar procedure used in the synthesis of (*S*)-**1AG$_0$.**Yield 67%. $[\alpha]_D^{20}$ = +58.8 (*c* 0.2). ^1H NMR (300 MHz, $CDCl_3$): δ = 3.40-3.49 (m,

2H), 4.07-4.15 (m, 2H)， 5.04 (s, 8H), 6.55-6.58 (m, 6H), 7.18 (d, *J* = 8.8 Hz, 1H), 7.23-7.42 (m, 26H), 7.60 (d, *J* = 8.8 Hz, 1H), 7.76 (d, *J* = 8.7 Hz, 1H), 7.83 (dd, J_1 = 8.1 Hz, J_2 = 1.5 Hz, 1H), 7.93-7.95 (d, *J* = 8.1 Hz, 1H), 8.00-8.02 (d, *J* = 8.8 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 48.5, 48.7, 70.1, 101.2, 107.9, 121.5, 122.1, 124.6, 124.9, 126.1, 126.1, 126.9, 127.1, 127.6, 128.0, 128.2, 128.3, 128.6, 130.2, 130.3, 130.7, 131.5, 136.9, 140.4, 149.2, 149.6, 160.0. ^{31}P NMR (162 MHz, $CDCl_3$): δ = 144.4. HRMS (SIMS) for $C_{62}H_{50}O_6NP$, $[M + H]^+$: Calcd. 936.3454, Found 936.3391.

Synthesis of (*S*)-1AG$_2$: Followed the similar procedure used in the synthesis of (*S*)- **1AG$_0$**. Yield 77%. $[\alpha]_D^{20}$ = +44.5 (*c* 0.2). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.44-3.53 (m, 2H), 4.09-4.16 (m, 2H), 4.90-5.04 (m, 24H), 6.52-6.68 (m, 18H), 7.13 (d, *J* = 8.8 Hz, 1H), 7.17-7.44 (m, 46H), 7.58 (d, *J* = 8.8 Hz, 1H), 7.75 (d, *J* = 8.7 Hz, 2H), 7.91 (t, *J* = 8.6 Hz, 1H) . ^{13}C NMR (75 MHz, CH_2Cl_2): δ = 47.5, 47.8, 69.0, 100.2, 100.6, 105.4, 106.8, 120.4, 123.6, 123.8, 125.0, 125.9, 126.0, 126.5, 126.9, 127.2, 127.3, 127.4, 127.5, 129.2, 129.3, 129.7, 130.4, 131.4, 131.8, 135.8, 138.3, 139.4, 148.2, 148.6, 148.7, 159.0, 159.2. ^{31}P NMR (162 MHz, $CDCl_3$): δ = 146.4. MS (MALDI-TOF): m/z Calcd for $C_{118}H_{98}O_{14}NP$: 1785.0, found 1783.6.

Synthesis of (*S*)-1AG$_3$: Followed the similar procedure used in the synthesis of (*S*)- **1AG$_0$**. Yield 38%. $[\alpha]_D^{20}$ = +24.5 (*c* 0.2). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.36-3.45 (m, 2H), 4.02-4.10 (m, 2H)，4.76-4.85 (m, 56H), 6.41-6.57 (m, 42H), 7.00-7.26 (m, 86H), 7.46 (d, *J* = 8.6 Hz, 2H), 7.63 (d, *J* = 8.6 Hz, 2H), 7.73 (d, *J* = 8.3 Hz, 1H), 7.78 (d, *J* = 8.8 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 47.6, 47.8, 68.9, 69.0, 100.3, 100.7, 105.4, 106.9, 120.4, 121.0, 121.5, 122.9, 123.6, 123.8, 125.1, 125.8, 125.9, 126.1, 126.5, 126.9, 127.2, 127.5, 129.4, 129.6, 130.4, 131.4, 131.7, 135.8, 138.2, 138.3, 139.4, 148.1, 158.9, 159.1, 159.1. ^{31}P NMR (162 MHz, CH_2Cl_2): δ = 146.3. MS (MALDI-TOF): m/z Calcd for $C_{230}H_{194}O_{30}NP$: 3483.0, found 3481.9.

Synthesis of (*S*)-2BG$_2$: Followed the similar procedure used in the synthesis of (*S*)- **1AG$_0$**. Yield 60%. $[\alpha]_D^{20}$ = +4.9 (*c* 0.25). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.70-1.73 (m, 8H), 2.17-2.24 (m, 2H), 2.59-2.78 (m, 6H), 3.35-3.44 (m, 2H), 4.01-4.09 (m, 2H), 4.92-4.97 (m, 24H), 6.50-6.66 (m, 18H), 6.87 (d, *J* = 8.2 Hz, 1H), 7.04-7.10 (m, 3H), 7.28-7.37 (m, 40H). ^{13}C NMR

(75 MHz, $CDCl_3$) δ = 22.3, 22.4., 22.4, 27.8, 29.0, 29.1, 29.7, 49.5, 70.1, 70.1, 101.7, 101.8, 106.4, 107.9, 118.1, 118.9, 125.9, 127.2, 127.5, 127.7, 127.9, 128.2, 128.3, 128.5, 129.7, 130.1, 135.0, 135.6, 136.9, 138.3, 138.4, 139.3, 139.5, 139.5, 145.8, 145.9, 147.6, 147.7, 160.1, 160.1，160.3. ^{31}P NMR (162 MHz, CH_2Cl_2): δ = 139.0. MS (MALDI-TOF): m/z Calcd for $C_{118}H_{106}O_{14}NP$: 1793.1, found 1792.9.

Synthesis of (*S*)-3CG$_2$: Followed the similar procedure used in the synthesis of (*S*)- **1AG$_0$**. Yield 93%. $[\alpha]_D^{20}$ = +92.8 (*c* 0.2). ^1H NMR (300 MHz, $CDCl_3$): δ = 2.16 (s, 3H), 2.71 (s, 3H), 3.51-3.59 (m, 2H), 4.15-4.23 (m, 2H), 4.89-4.94 (m, 24H), 6.47-6.64 (m, 18H), 7.10-7.40 (m, 46H), 7.60 (s, 1H), 7.69 (d, *J* = 8.2 Hz, 1H), 7.78 (s, 1H), 7.81 (d, *J* = 8.2 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 17.4, 29.4, 48.6, 48.9, 69.7, 69.8, 101.2, 101.4, 106.2, 107.7, 108.0, 121.9, 124.2, 124.6, 124.8, 124.9, 126.7, 126.8, 127.1, 127.2, 127.5, 127.6, 128.0, 128.1, 128.3, 129.3, 129.6, 129.8, 129.9, 130.3, 131.1, 131.2, 131.5, 136.6, 139.1, 140.0, 148.1, 148.8, 159.7, 160.0. ^{31}P NMR (162 MHz, $CDCl_3$): δ = 140.3. MS (MALDI-TOF): m/z Calcd for $C_{120}H_{102}O_{14}NP$: 1813.1, found 1811.9 ($[M-H]^-$).

Synthesis of (*S*)-4DG$_0$: Followed the similar procedure used in the synthesis of (*S*)- **1AG$_0$**. Yield 43%. $[\alpha]_D^{20}$ = -134.2 (*c* 0.21). ^1H NMR (300 MHz, $CDCl_3$): δ = 1.91-1.98 (m, 2H), 2.15-2.22 (m, 2H), 2.66-2.85 (m, 2H), 2.97-3.06 (m, 2H), 3.23-3.32 (m, 2H), 3.85-3.92 (m, 2H), 6.03 (d, *J* = 7.8 Hz, 1H), 6.77-6.87 (m, 2H), 7.07 (t, *J* = 7.6 Hz, 2H), 7.21-7.36 (m, 11H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 30.5, 31.0, 38.2, 38.4, 48.5, 48.8, 58.9, 120.5, 121.3, 121.3, 121.4, 121.5, 121.6, 127.3, 128.3, 128.5, 128.5, 129.3, 138.4, 140.6, 142.3, 145.0, 145.8, 145.9, 146.2, 146.3, 148.4, 148.5. ^{31}P NMR (121MHz, $CDCl_3$): δ = 122.2. MS (MALDI-TOF): m/z Calcd for $C_{31}H_{28}O_2NP$: 477.5, found 478.2. HRMS (SIMS) for $C_{31}H_{28}O_2NP$, $[M+H]^+$: Calcd. 478.1936, Found 478.1930.

Synthesis of (*R*)-4DG$_1$: Followed the similar procedure used in the synthesis of (*S*)- **1AG$_0$**. Yield 40%. $[\alpha]_D^{20}$ = +71.7 (*c* 0.1). ^1H NMR (300 MHz, $CDCl_3$): δ = 1.92-2.02 (m, 2H), 2.18-2.24 (m, 2H), 2.70-2.88 (m, 2H), 2.98-3.09 (m, 2H), 3.20-3.29 (m, 2H), 3.76-3.81 (m, 2H), 5.03 (s, 8H), 6.23 (d, *J* = 7.2 Hz, 1H), 6.55 (br, 6H), 6.85-6.93 (m, 2H), 7.07 (d, *J* = 8.6 Hz, 2H), 7.22-7.41 (m, 21H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 29.5, 29.9, 31.7, 37.3, 48.0, 48.3, 57.8, 69.0, 100.3, 107.3, 119.5, 120.4, 126.4, 126.8, 127.5, 135.9, 139.5, 139.8, 141.2, 141.2, 144.0,

144.8, 145.2, 145.3, 147.4, 158.9. ^{31}P NMR (162 MHz, $CDCl_3$): δ = 123.1. MS (MALDI-TOF): m/z Calcd for $C_{59}H_{52}O_6NP$: 902.0, found 902.5. HRMS (SIMS) for $C_{59}H_{52}O_6NP$, $[M + H]^+$: Calcd. 902.3610, Found 902.3631.

4. Preparation of Rh/1 catalysts and their ^{31}P NMR spectra

A mixture of $[Rh(COD)_2]^+BF_4^-$ (1.2 mg, 0.003 mmol) and **1** (0.006 mmol) in CH_2Cl_2 (0.5 mL) was stirred at room temperature for 2 h in glovebox. The organic solvent was removed, providing the *in situ* catalysts.

[Rh(1AG$_0$)(COD)]$^+$BF$_4^-$: ^{31}P NMR (162 MHz, $CDCl_3$): δ = 134.6 (dd, $J_{Rh\text{-}P}$ = 235.5 Hz, $J_{P\text{-}P}$ = 37.3 Hz), 139.7 (dd, $J_{Rh\text{-}P}$ = 236.8 Hz, $J_{P\text{-}P}$ = 37.6 Hz), 140.2 (d, $J_{Rh\text{-}P}$ = 238.6 Hz).

[Rh(1AG$_1$)(COD)]$^+$BF$_4^-$: ^{31}P NMR (162 MHz, $CDCl_3$): δ = 134.9 (dd, $J_{Rh\text{-}P}$ = 236.6 Hz, $J_{P\text{-}P}$ = 35.3 Hz), 139.1 (dd, $J_{Rh\text{-}P}$ = 238.0 Hz, $J_{P\text{-}P}$ = 35.6 Hz), 140.0 (d, $J_{Rh\text{-}P}$ = 240.5 Hz).

[Rh(1AG$_2$)(COD)]$^+$BF$_4^-$: ^{31}P NMR (162 MHz, $CDCl_3$): δ = 135.1 (dd, $J_{Rh\text{-}P}$ = 236.6 Hz, $J_{P\text{-}P}$ = 35.5 Hz), 138.8 (dd, $J_{Rh\text{-}P}$ = 237.9 Hz, $J_{P\text{-}P}$ = 35.3 Hz), 140.2 (d, $J_{Rh\text{-}P}$ = 239.9 Hz).

[Rh(1AG$_2$)(COD)]$^+$BF$_4^-$: ^{31}P NMR (162 MHz, $CDCl_3$): δ = 134.9 (dd, $J_{Rh\text{-}P}$ = 236.6 Hz, $J_{P\text{-}P}$ = 33.7 Hz), 138.5 (dd, $J_{Rh\text{-}P}$ = 239.1 Hz, $J_{P\text{-}P}$ = 34.2 Hz), 140.1 (d, $J_{Rh\text{-}P}$ = 240.9 Hz).

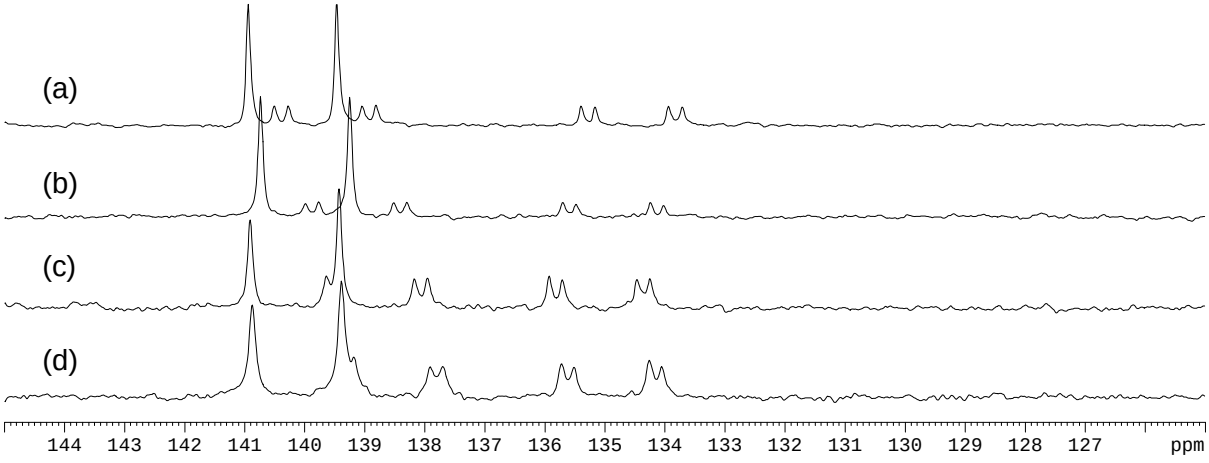


Figure S1. ^{31}P NMR spectra of dendritic Rh catalyst: (a) [Rh(**1AG$_0$**)(COD)]$^+$BF$_4^-$; (b) [Rh(**1AG$_1$**)(COD)]$^+$BF$_4^-$; (c) [Rh(**1AG$_2$**)(COD)]$^+$BF$_4^-$; (d) [Rh(**1AG$_3$**)(COD)]$^+$BF$_4^-$.

The results of ^{31}P NMR spectra show that all dendritic catalysts $[Rh(\mathbf{1})_2(COD)]BF_4$ are present in solution as two isomers. Similar to the corresponding small molecular Rh-catalysts,[6] both isomers might differ in the relative position of the two dendritic phosphoramidite ligands, i.e. group of $N(Gn)_2$ on the same or different hemisphere of the square planar complex.

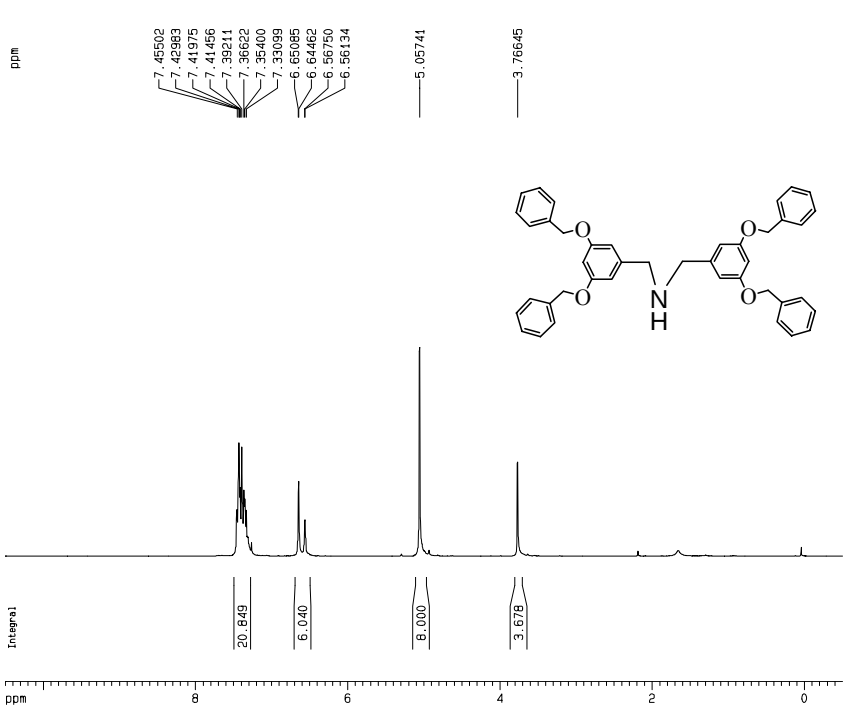
5. General procedure for the Rh-catalyzed asymmetric hydrogenation and catalyst recycling using Rh/1AG$_2$ as catalyst

A mixture of $[Rh(COD)_2]^+BF^-_4$ (0.40 mg, 0.001 mmol) and **1AG$_2$** (3.90 mg, 0.002 mmol) in CH_2Cl_2 (1.0 mL) was stirred at room temperature for 2 h in glovebox. The mixture was transferred by a syringe to a stainless steel autoclave, in which the corresponding substrate (0.1 mmol) was charged in CH_2Cl_2 (0.5 mL) before hand. The hydrogenation was performed at room temperature under 20 atm H_2 pressure for a given time.

After carefully venting of hydrogen, most of the reaction solvent was removed under reduced pressure. n-Hexane was then added and the catalyst was precipitated and recovered via filtration. The recovered catalyst was reused in the next catalytic cycle. The n-hexane layer was used to determine the conversion and enantioselectivity of the reduced product by GC with a 25 m Chiralsi L-Val capillary column.

6. ^{1}H NMR, ^{13}C NMR and MS spectra of dendrons $5G_1$-$5G_3$

Figure S1. ^{1}H NMR, ^{13}C NMR and MS spectra of dendrimer $\mathbf{5G_1}$

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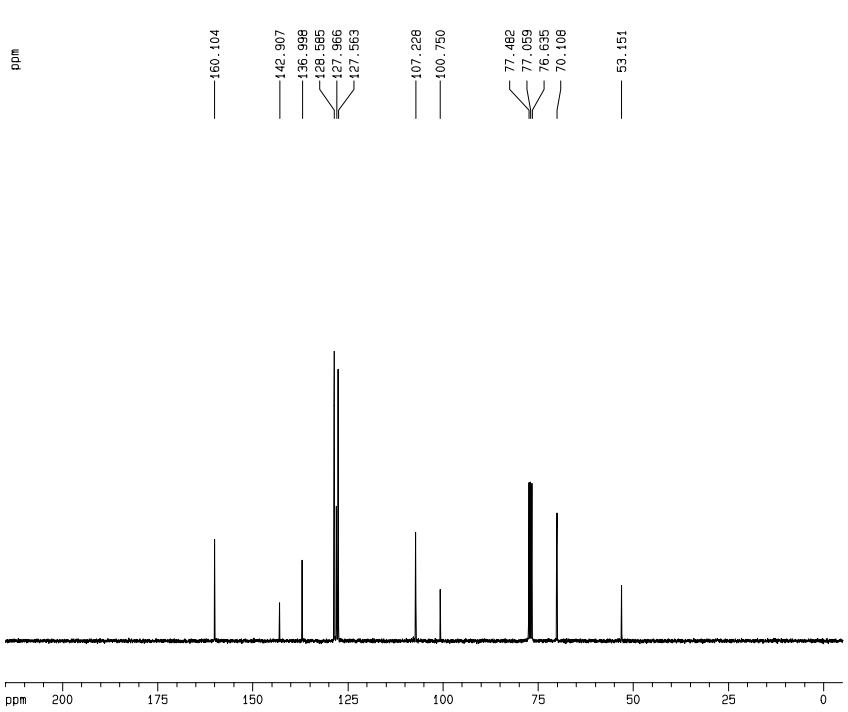
DE                  6.00 usec
TE                 298.4 K
D1             2.00000000 sec

======== CHANNEL f1 ========
NUC1                   1H
P1                   9.30 usec
PL1                 -1.00 dB
SFO1          300.1318534 MHz

F2 - Processing parameters
SI                     32768
SF            300.1300055 MHz
WDW                       EM
SSB                        0
LB                      0.35 Hz
GB                         0
PC                      1.00

1D NMR plot parameters
CX                     20.00 cm
CY                      5.00 cm
F1P                   10.500 ppm
F1                  3151.36 Hz
F2P                   -0.500 ppm
F2                  -150.06 Hz
PPMCM                0.55000 ppm/cm
HZCM               165.07150 Hz/cm
```

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Current Data Parameters
NAME      ZF-G1G1-NEW-C
EXPNO                 10
PROCNO                 1

F2 - Acquisition Parameters
Date_           20061226
Time               21.39
INSTRUM             av300
PROBHD   5 mm DUL 13C-1
PULPROG           zgpg30
TD                  65536
SOLVENT             CDCl3
NS                    582
DS                      4
SWH            17985.611 Hz
FIDRES          0.274439 Hz
AQ              1.8219508 sec
RG                  406.4
DW                 27.800 usec
DE                  6.00 usec
TE                 297.6 K
D1             2.00000000 sec
d11            0.03000000 sec
d12            0.00002000 sec

======== CHANNEL f1 ========
NUC1                  13C
P1                   9.40 usec
PL1                 -1.00 dB
SFO1          75.4752953 MHz

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

F2 - Processing parameters
SI                     32768
SF            75.4677490 MHz
WDW                       EM
SSB                        0
LB                      1.00 Hz
GB                         0
PC                      1.40

1D NMR plot parameters
CX                     20.00 cm
CY                      7.00 cm
F1P                  215.000 ppm
F1                  16225.57 Hz
F2P                   -5.000 ppm
F2                  -377.34 Hz
PPMCM               11.00000 ppm/cm
HZCM               830.14520 Hz/cm
```
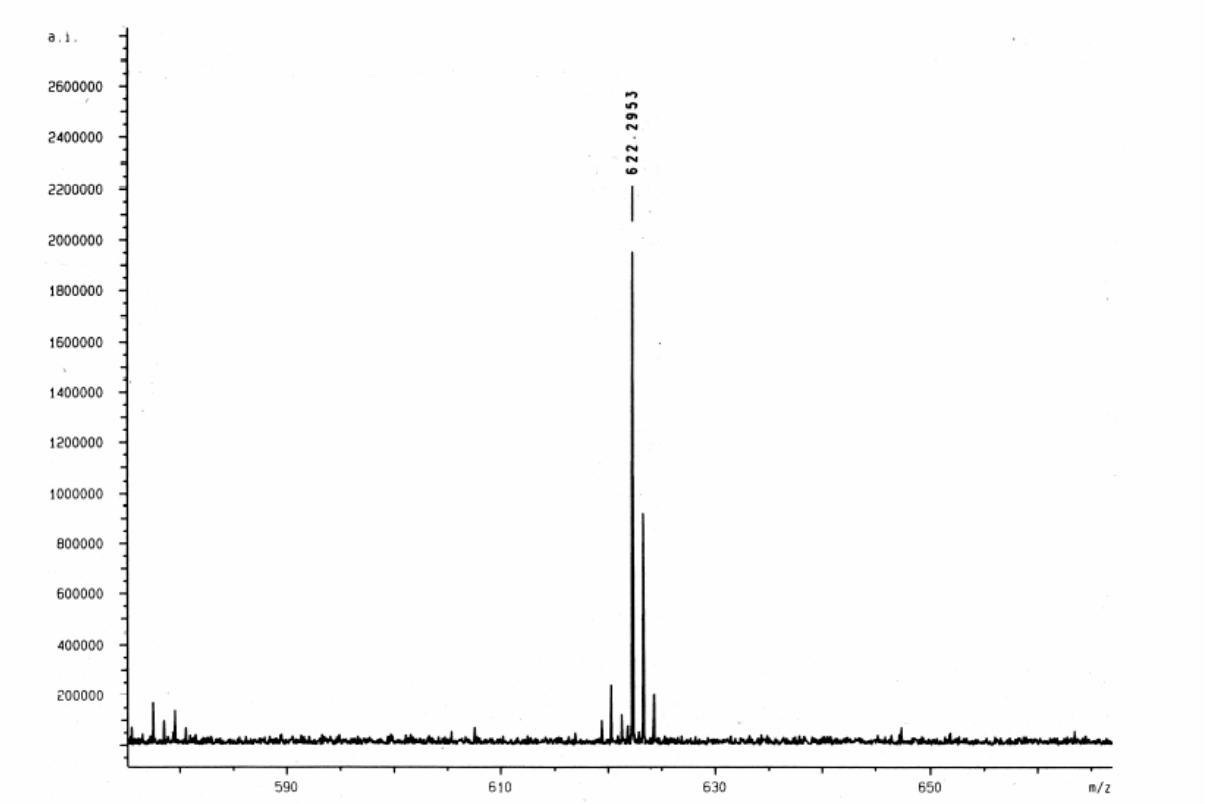
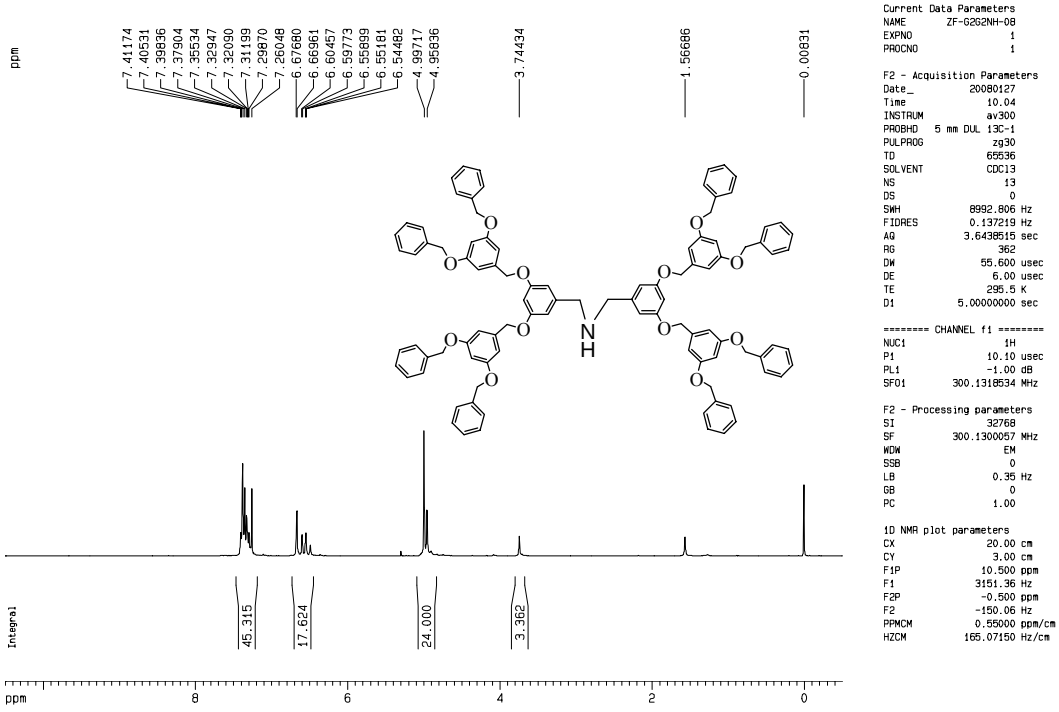
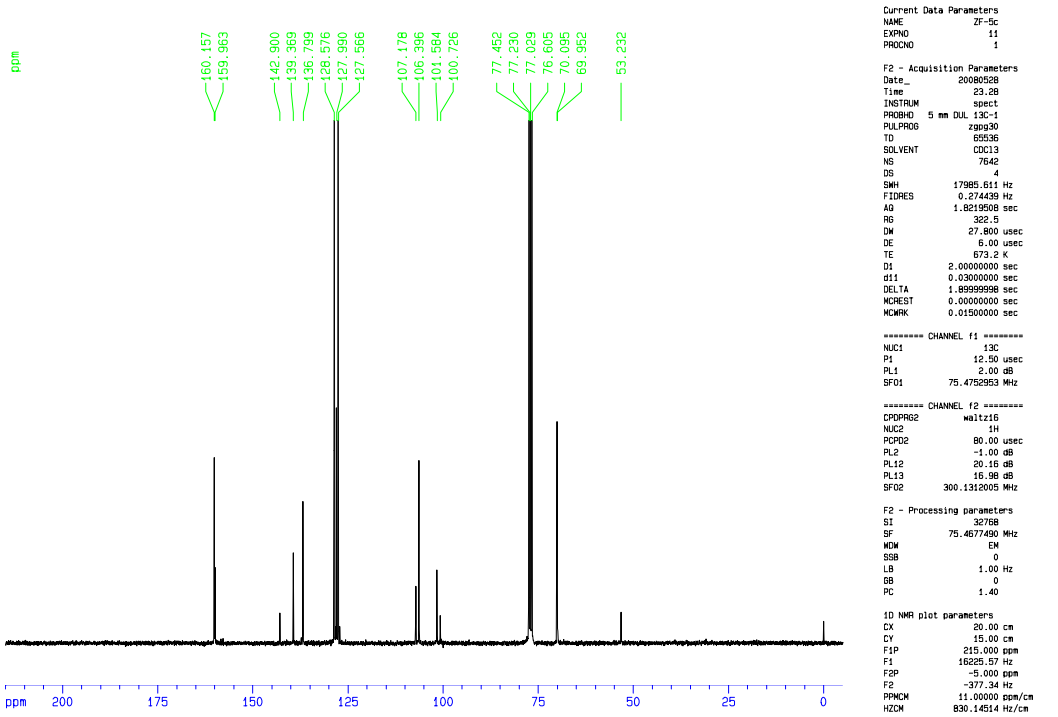


a.i.
2600000
2400000
2200000
2000000
1800000
1600000
1400000
1200000
1000000
800000
600000
400000
200000
622.2953
590
610
630
650
m/z

Figure S2. ^{1}H NMR, ^{13}C NMR and MS spectra of dendrimer **5G$_2$**




```
Current Data Parameters
NAME        ZF-G2G2NH-08
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20080127
Time               10.04
INSTRUM            av300
PROBHD   5 mm DUL 13C-1
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    13
DS                     0
SWH             8992.806 Hz
FIDRES          0.137219 Hz
AQ              3.6438515 sec
RG                   362
DW                55.600 usec
DE                 6.00 usec
TE                295.5 K
D1             5.00000000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                 10.10 usec
PL1                -1.00 dB
SFO1         300.1318534 MHz

F2 - Processing parameters
SI                 32768
SF          300.1300057 MHz
WDW                   EM
SSB                    0
LB                  0.35 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 20.00 cm
CY                  3.00 cm
F1P               10.500 ppm
F1              3151.36 Hz
F2P                -0.500 ppm
F2               -150.06 Hz
PPMCM           0.55000 ppm/cm
HZCM          165.07150 Hz/cm
```




```
Current Data Parameters
NAME                 ZF-5c
EXPNO                   11
PROCNO                   1

F2 - Acquisition Parameters
Date_           20080528
Time               23.28
INSTRUM            spect
PROBHD   5 mm DUL 13C-1
PULPROG          zgpg30
TD                 65536
SOLVENT            CDCl3
NS                  7642
DS                     4
SWH            17985.611 Hz
FIDRES          0.274439 Hz
AQ              1.8219508 sec
RG                 322.5
DW                27.800 usec
DE                 6.00 usec
TE                673.2 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

F2 - Processing parameters
SI                 32768
SF          75.4677490 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40

1D NMR plot parameters
CX                 20.00 cm
CY                 15.00 cm
F1P               215.000 ppm
F1              16225.57 Hz
F2P                -5.000 ppm
F2               -377.34 Hz
PPMCM          11.00000 ppm/cm
HZCM          830.14514 Hz/cm
```

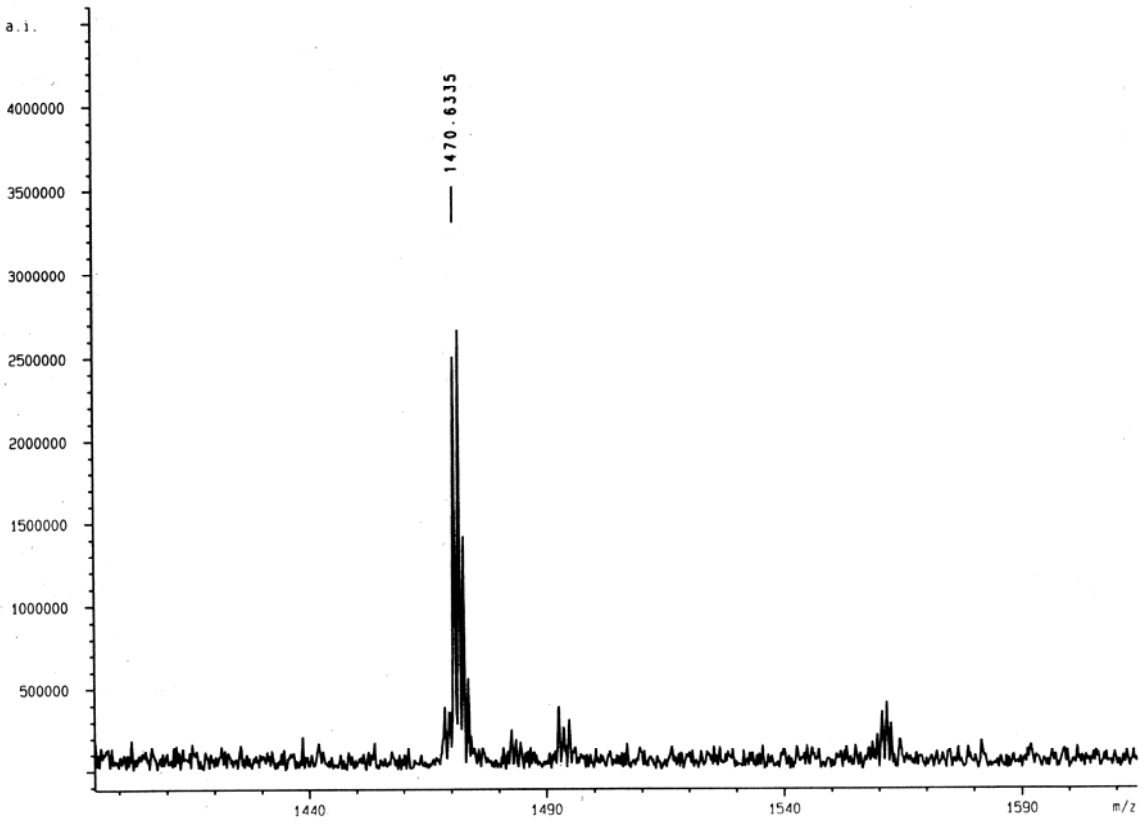
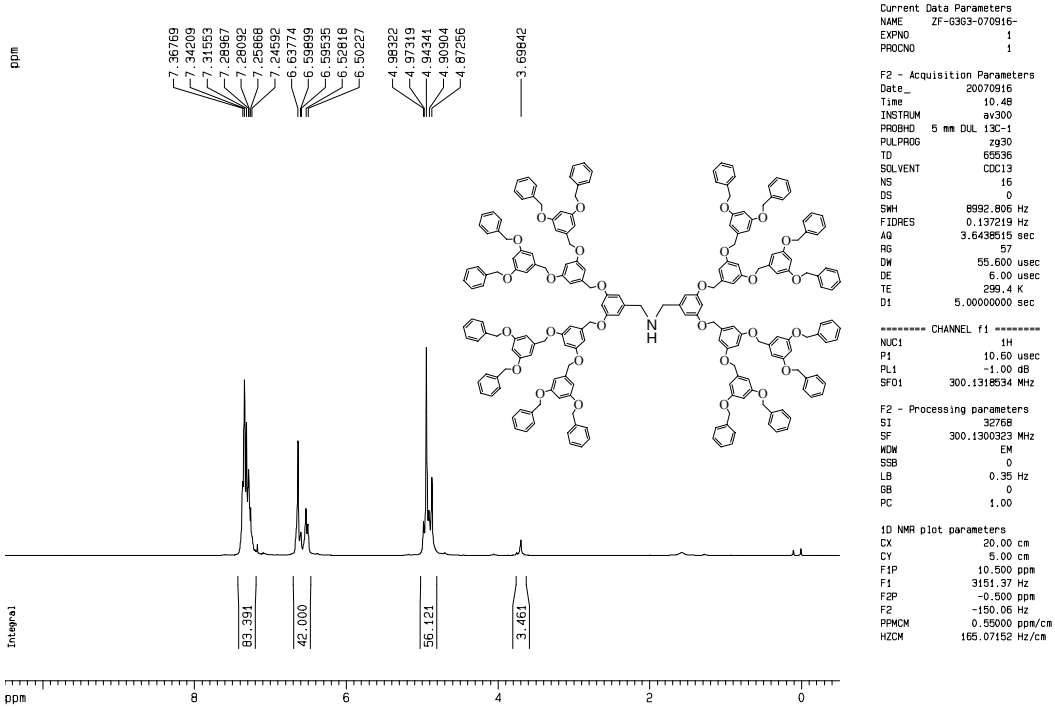
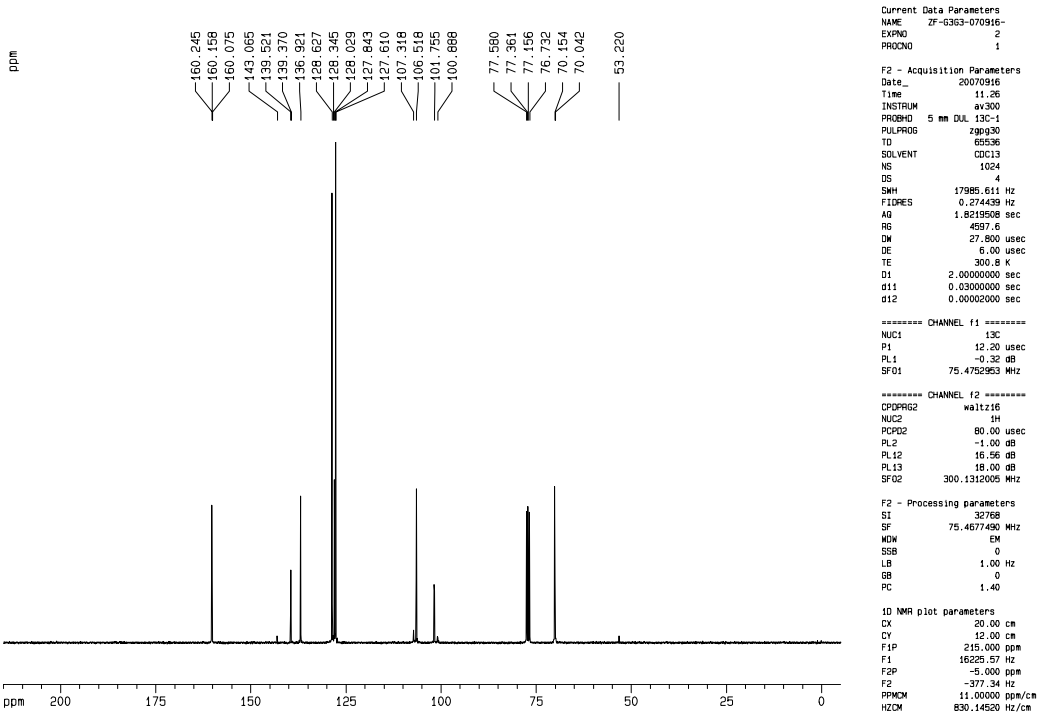

a.i.
4000000
3500000
3000000
2500000
2000000
1500000
1000000
500000
1470.6335
1440
1490
1540
1590
m/z

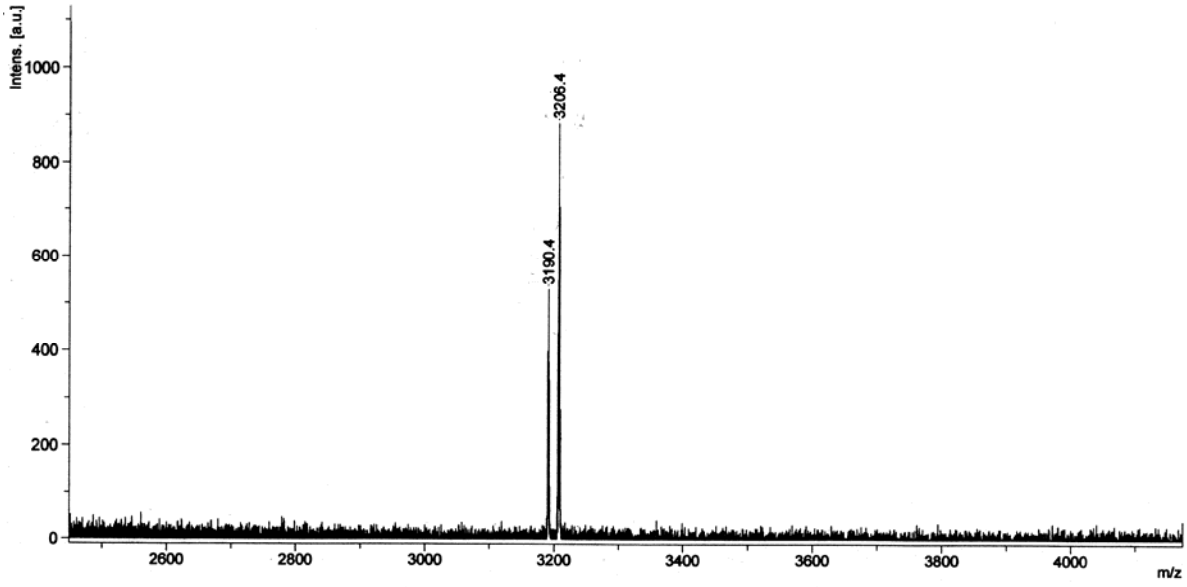
Figure S3. ^{1}H NMR, ^{13}C NMR and MS spectra of dendrimer **5G$_3$**




```
Current Data Parameters
NAME      ZF-G3G3-070916-
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20070916
Time               10.48
INSTRUM            av300
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                    57
DW                55.600 usec
DE                 6.00 usec
TE                299.4 K
D1             5.00000000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                 10.60 usec
PL1                -1.00 dB
SFO1         300.1318534 MHz

F2 - Processing parameters
SI                 32768
SF           300.1300323 MHz
WDW                   EM
SSB                    0
LB                  0.35 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 20.00 cm
CY                  5.00 cm
F1P               10.500 ppm
F1              3151.37 Hz
F2P                -0.500 ppm
F2               -150.06 Hz
PPMCM           0.55000 ppm/cm
HZCM          165.07152 Hz/cm
```

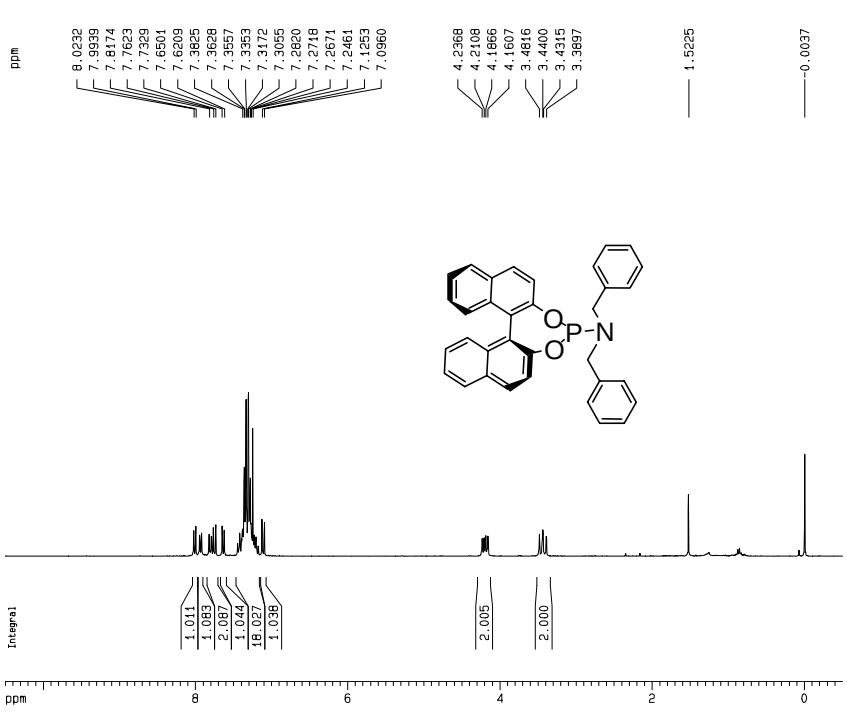



```
Current Data Parameters
NAME      ZF-G3G3-070916-
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20070916
Time               11.26
INSTRUM            av300
PROBHD   5 mm DUL 13C-1
PULPROG          zgpg30
TD                 65536
SOLVENT            CDCl3
NS                  1024
DS                     4
SWH            17985.611 Hz
FIDRES          0.274439 Hz
AQ              1.8219508 sec
RG                 4597.6
DW                27.800 usec
DE                 6.00 usec
TE                300.8 K
D1             2.00000000 sec
d11            0.03000000 sec
d12            0.00002000 sec

======== CHANNEL f1 ========
NUC1                 13C
P1                 12.20 usec
PL1                -0.32 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           75.4677490 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40

1D NMR plot parameters
CX                 20.00 cm
CY                 12.00 cm
F1P               215.000 ppm
F1              16225.57 Hz
F2P                -5.000 ppm
F2               -377.34 Hz
PPMCM          11.00000 ppm/cm
HZCM          830.14520 Hz/cm
```

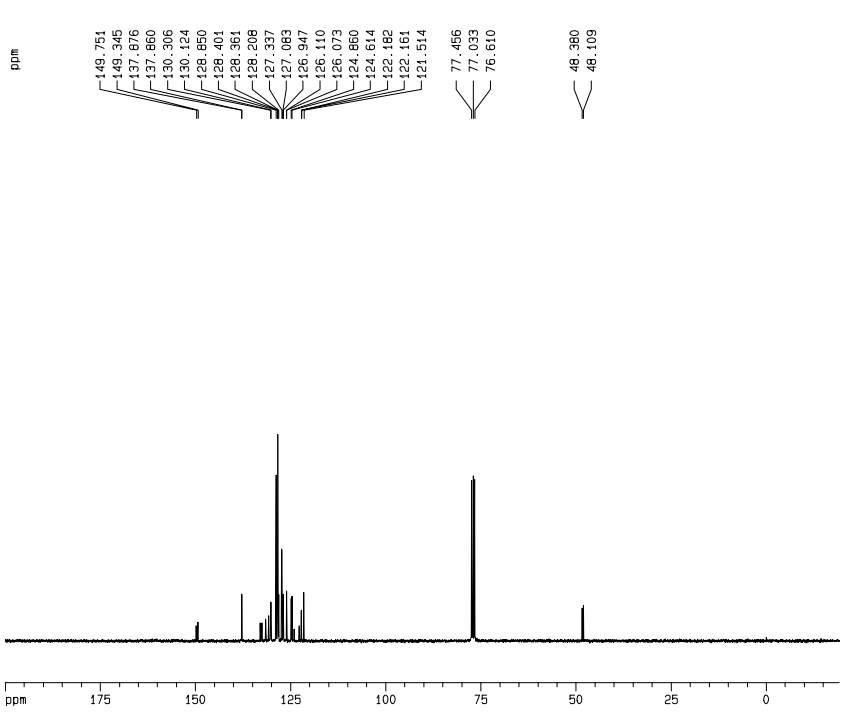

Intens. [a.u.]
1000
800
600
400
200
0
3206.4
3190.4
2600
2800
3000
3200
3400
3600
3800
4000
m/z

7. ^{1}H NMR, ^{13}C NMR, ^{31}P NMR and MS spectra of the chiral dendritic monodentate phosphoramidite ligands

Figure S4. ^{1}H NMR, ^{13}C NMR spectra of **1AG$_0$**

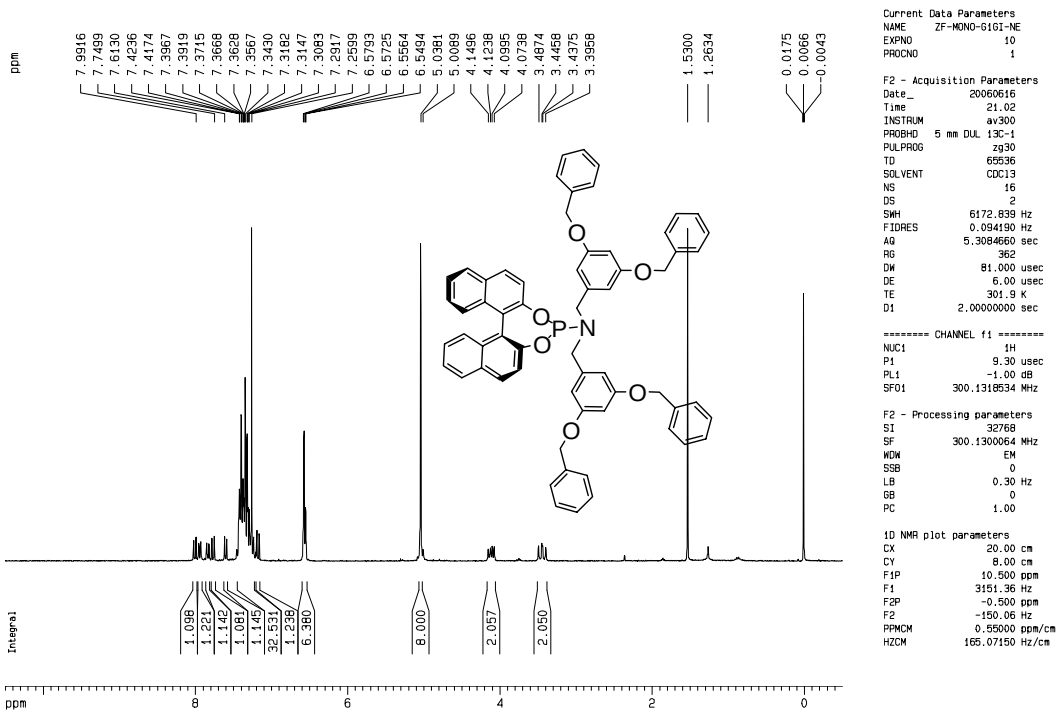



```
Current Data Parameters
NAME         ZF-MONOGOGO
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_          20070905
Time              19.53
INSTRUM           av300
PROBHD   5 mm DUL 13C-1
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                    7
DS                    0
SWH            8992.806 Hz
FIDRES         0.137219 Hz
AQ             3.6438515 sec
RG                322.5
DW               55.600 usec
DE                6.00 usec
TE                299.0 K
D1          5.00000000 sec

======== CHANNEL f1 ========
NUC1                1H
P1                10.60 usec
PL1               -1.00 dB
SFO1        300.1318534 MHz

F2 - Processing parameters
SI                32768
SF          300.1300104 MHz
WDW                  EM
SSB                   0
LB                 0.35 Hz
GB                    0
PC                 1.00

1D NMR plot parameters
CX                20.00 cm
CY                 1.50 cm
F1P              10.500 ppm
F1              3151.36 Hz
F2P              -0.500 ppm
F2              -150.06 Hz
PPMCM            0.55000 ppm/cm
HZCM           165.07150 Hz/cm
```

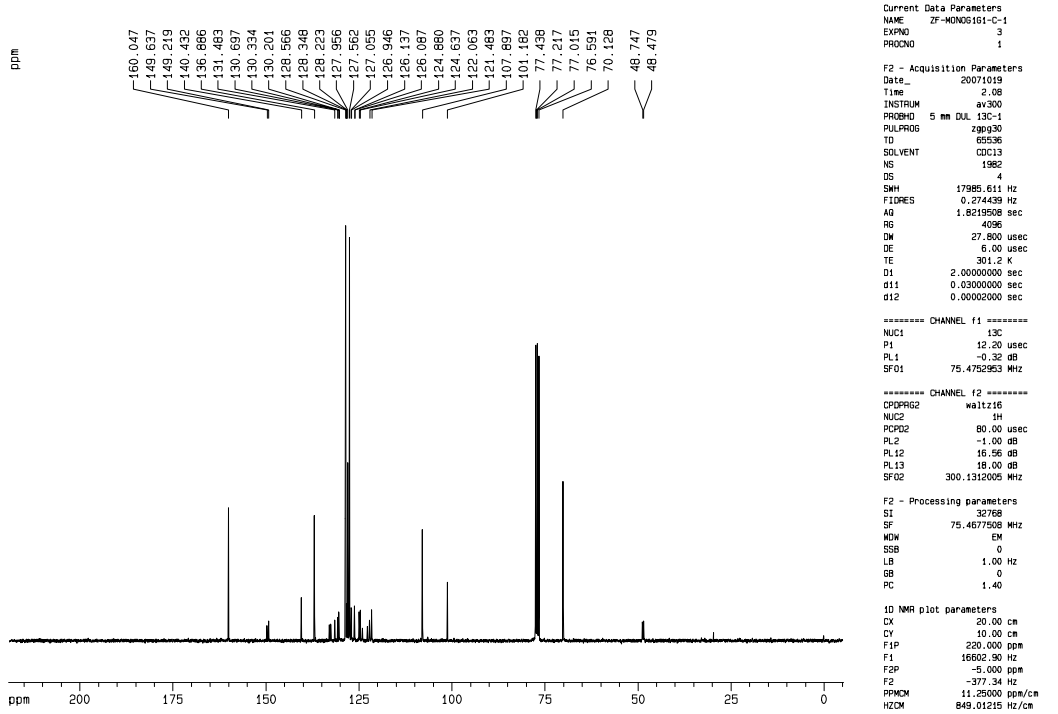



```
Current Data Parameters
NAME      ZF-070923-GOMON
EXPNO                   2
PROCNO                  1

F2 - Acquisition Parameters
Date_          20070923
Time              13.14
INSTRUM           av300
PROBHD   5 mm DUL 13C-1
PULPROG         zgpg30
TD                65536
SOLVENT           CDCl3
NS                 1024
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                300.7 K
D1          2.00000000 sec
d11         0.03000000 sec
d12         0.00002000 sec

======== CHANNEL f1 ========
NUC1                13C
P1                12.20 usec
PL1               -0.32 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          75.4677490 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40

1D NMR plot parameters
CX                20.00 cm
CY                 5.00 cm
F1P             200.000 ppm
F1             15093.55 Hz
F2P             -20.000 ppm
F2             -1509.36 Hz
PPMCM          11.00000 ppm/cm
HZCM          830.14526 Hz/cm
```

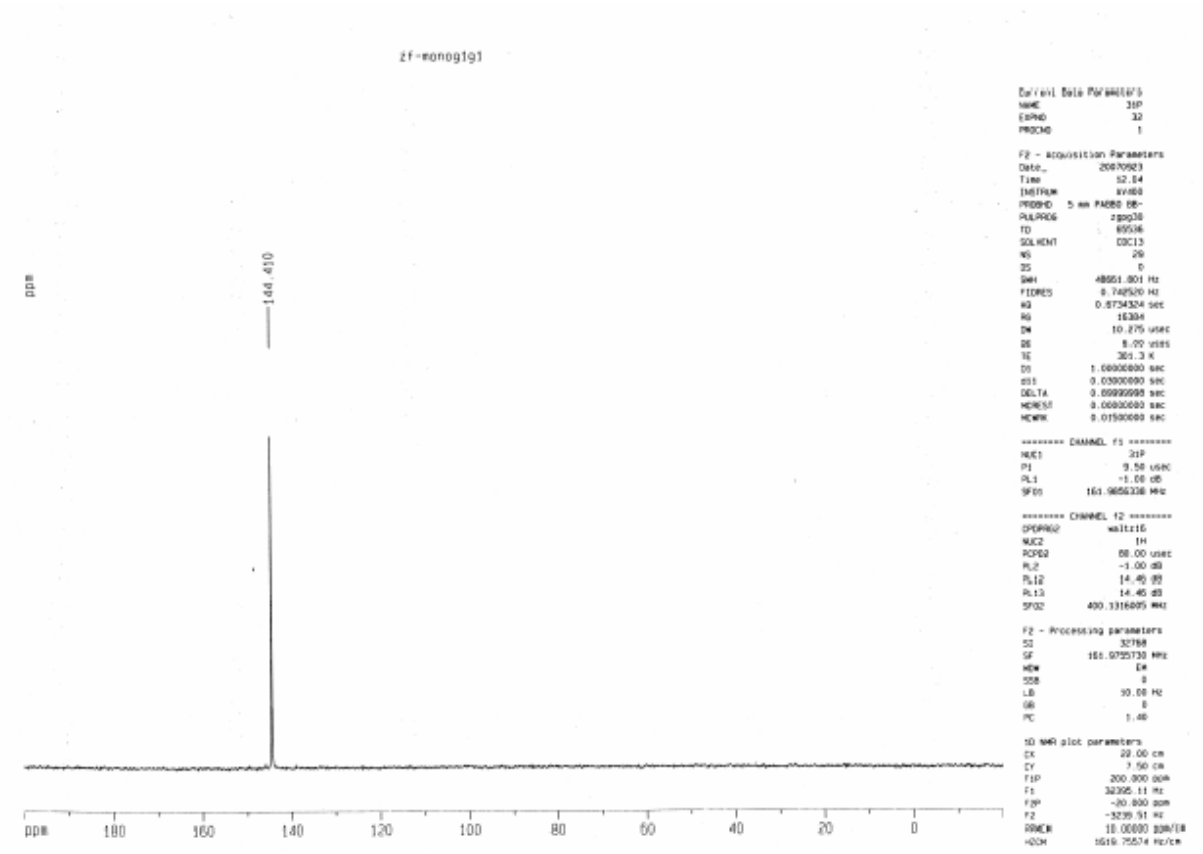
Figure S5. ^{1}H NMR, ^{13}C NMR, ^{31}P NMR and MS spectra of **1AG$_1$**




```
Current Data Parameters
NAME      ZF-MONO-G1G1-NE
EXPNO                 10
PROCNO                 1

F2 - Acquisition Parameters
Date_           20060616
Time               21.02
INSTRUM            av300
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                 6.00 usec
TE                301.9 K
D1             2.00000000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                  9.30 usec
PL1                -1.00 dB
SFO1         300.1318534 MHz

F2 - Processing parameters
SI                 32768
SF           300.1300064 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 20.00 cm
CY                  8.00 cm
F1P               10.500 ppm
F1              3151.36 Hz
F2P                -0.500 ppm
F2              -150.06 Hz
PPMCM           0.55000 ppm/cm
HZCM          165.07150 Hz/cm
```




```
Current Data Parameters
NAME      ZF-MONOG1G1-C-1
EXPNO                  3
PROCNO                 1

F2 - Acquisition Parameters
Date_           20071019
Time               2.08
INSTRUM            av300
PROBHD   5 mm DUL 13C-1
PULPROG          zgpg30
TD                 65536
SOLVENT            CDCl3
NS                  1982
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                301.2 K
D1             2.00000000 sec
d11            0.03000000 sec
d12            0.00002000 sec

======== CHANNEL f1 ========
NUC1                 13C
P1                 12.20 usec
PL1                -0.32 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           75.4677508 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40

1D NMR plot parameters
CX                 20.00 cm
CY                 10.00 cm
F1P               220.000 ppm
F1              16602.90 Hz
F2P                -5.000 ppm
F2              -377.34 Hz
PPMCM          11.25000 ppm/cm
HZCM          849.01215 Hz/cm
```


zf-monog1g1
ppm
144.410
ppm
180
160
140
120
100
80
60
40
20
0

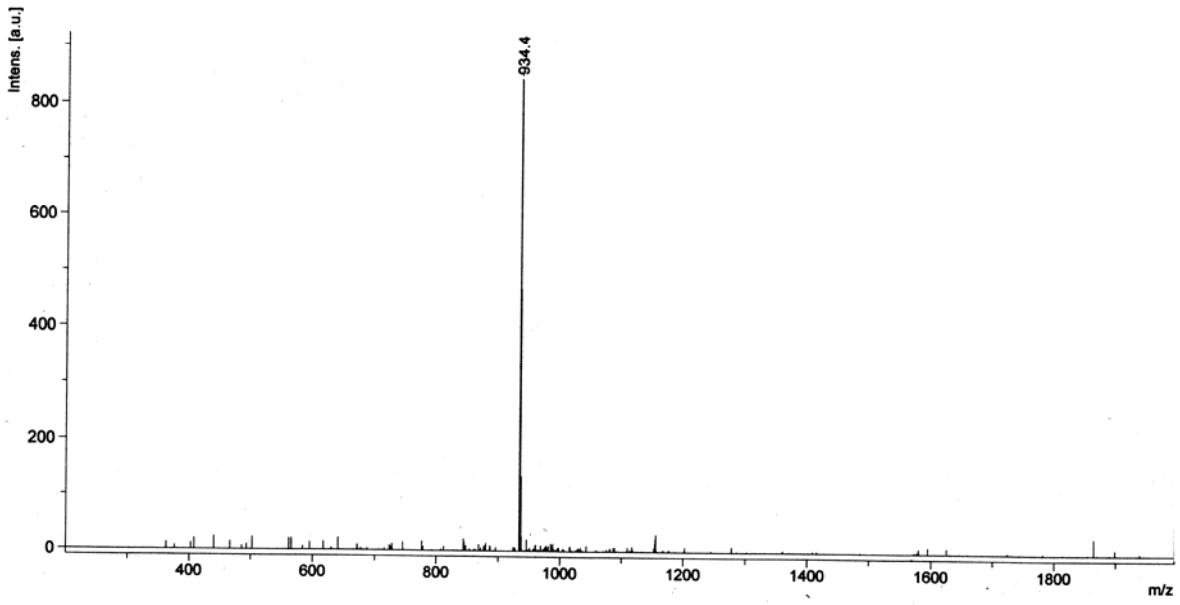
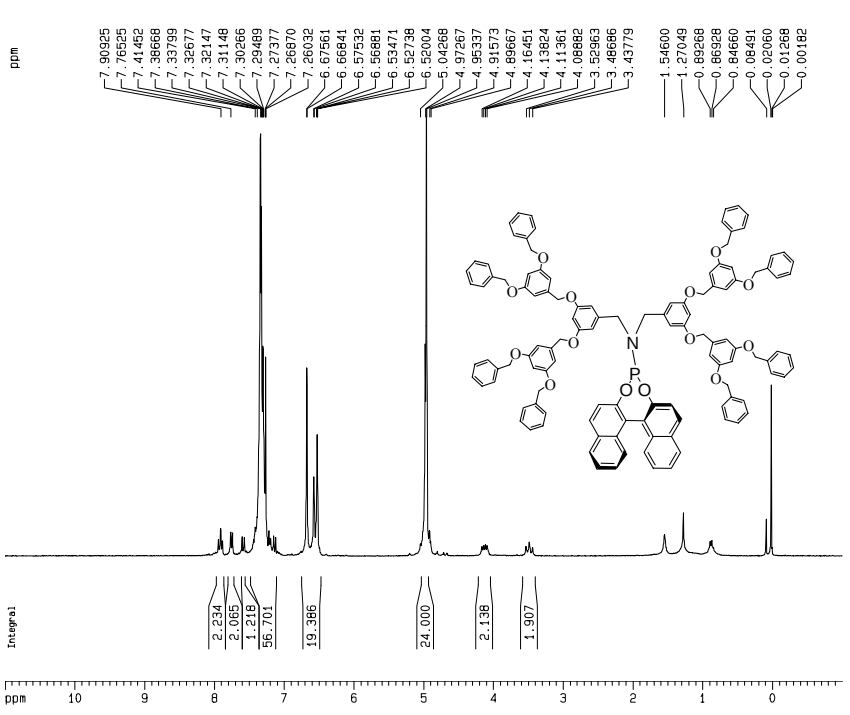
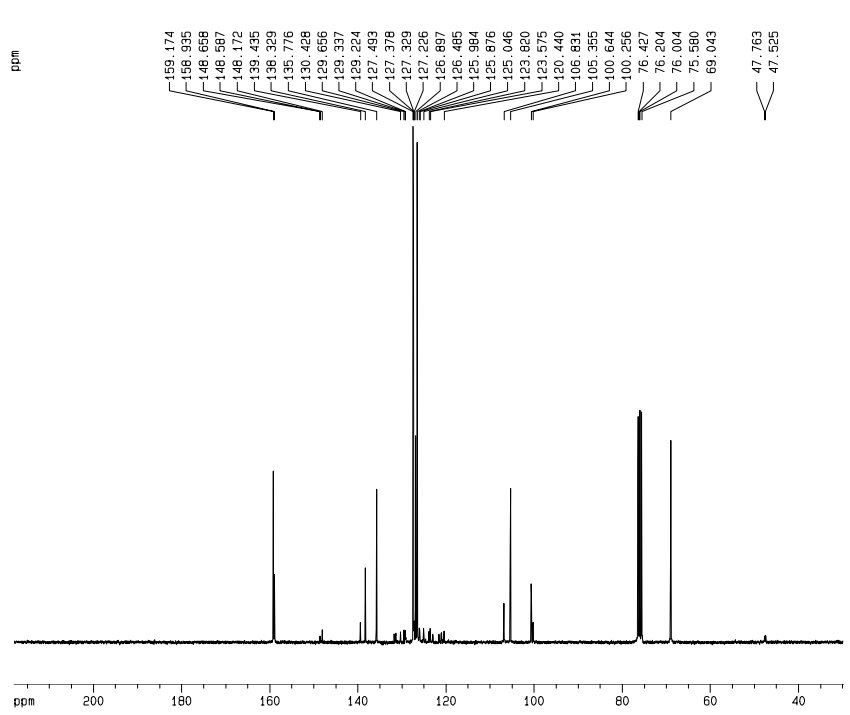

Intens. [a.u.]
934.4
800
600
400
200
0
400
600
800
1000
1200
1400
1600
1800
m/z

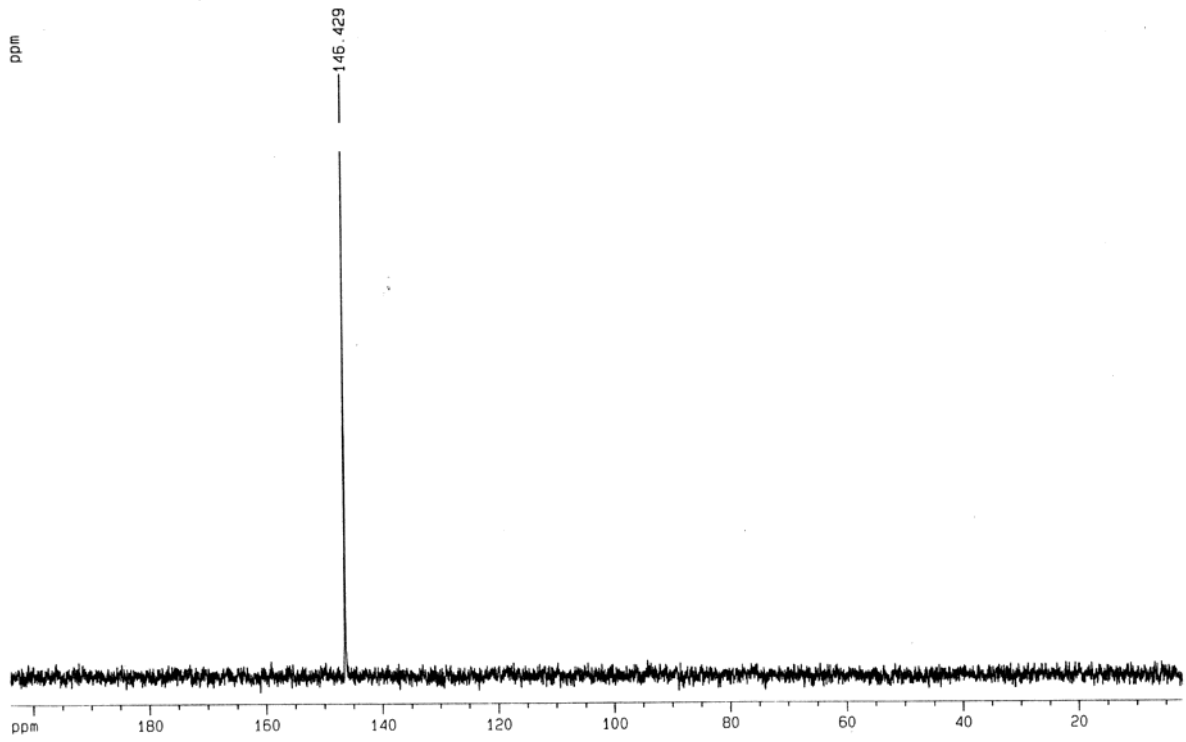
Figure S6. ^{1}H NMR, ^{13}C NMR, ^{31}P NMR and MS spectra of **1AG$_2$**




```
Current Data Parameters
NAME      ZF-070923-G2MON
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_           20070923
Time               12.24
INSTRUM            av300
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                 287.4
DW                55.600 usec
DE                 6.00 usec
TE                300.3 K
D1             5.00000000 sec

======== CHANNEL f1 ========
NUC1                   1H
P1                 10.60 usec
PL1                -1.00 dB
SFO1         300.1318534 MHz

F2 - Processing parameters
SI                 32768
SF          300.1300060 MHz
WDW                   EM
SSB                    0
LB                  0.35 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 20.00 cm
CY                 12.50 cm
F1P               11.000 ppm
F1              3301.43 Hz
F2P               -1.000 ppm
F2              -300.13 Hz
PPMCM           0.60000 ppm/cm
HZCM          180.07800 Hz/cm
```




```
Current Data Parameters
NAME      ZF-G2G2MONO-10
EXPNO                   2
PROCNO                  1

F2 - Acquisition Parameters
Date_           20071014
Time               9.05
INSTRUM            av300
PROBHD   5 mm DUL 13C-1
PULPROG          zgpg30
TD                 65536
SOLVENT            CDCl3
NS                  1358
DS                     4
SWH            17985.611 Hz
FIDRES          0.274439 Hz
AQ              1.8219508 sec
RG                 9195.2
DW                27.800 usec
DE                 6.00 usec
TE                299.3 K
D1             2.00000000 sec
d11            0.03000000 sec
d12            0.00002000 sec

======== CHANNEL f1 ========
NUC1                  13C
P1                 12.20 usec
PL1                -0.32 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          75.4678307 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40

1D NMR plot parameters
CX                 20.00 cm
CY                 12.50 cm
F1P              220.000 ppm
F1             16602.92 Hz
F2P               30.000 ppm
F2              2264.04 Hz
PPMCM           9.50000 ppm/cm
HZCM          716.94440 Hz/cm
```


ppm
146.429
ppm
180
160
140
120
100
80
60
40
20

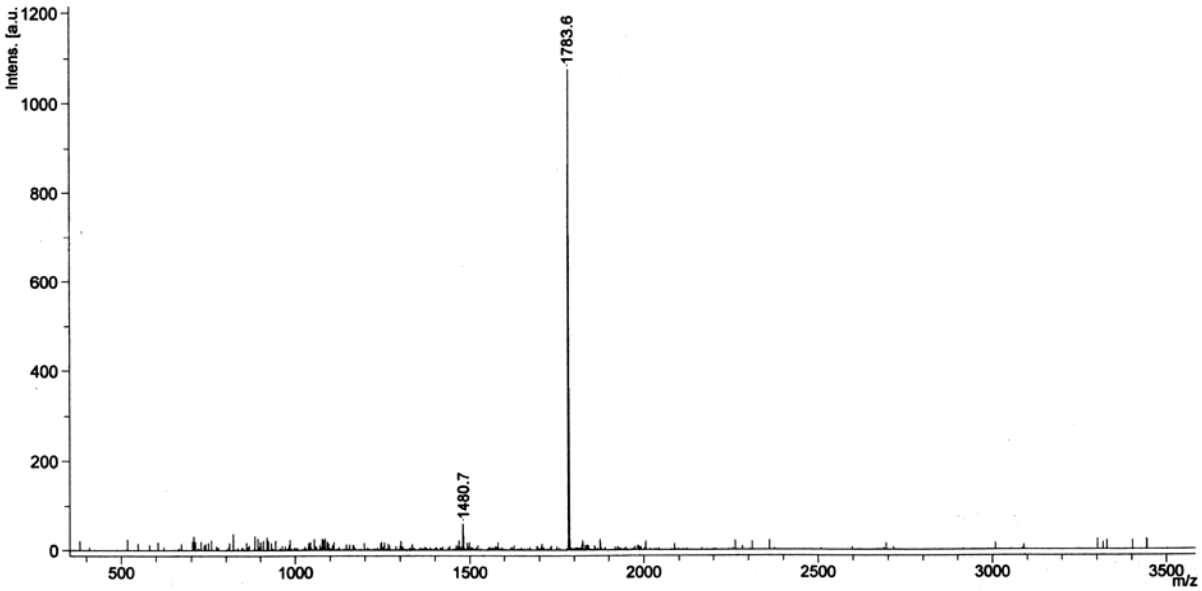
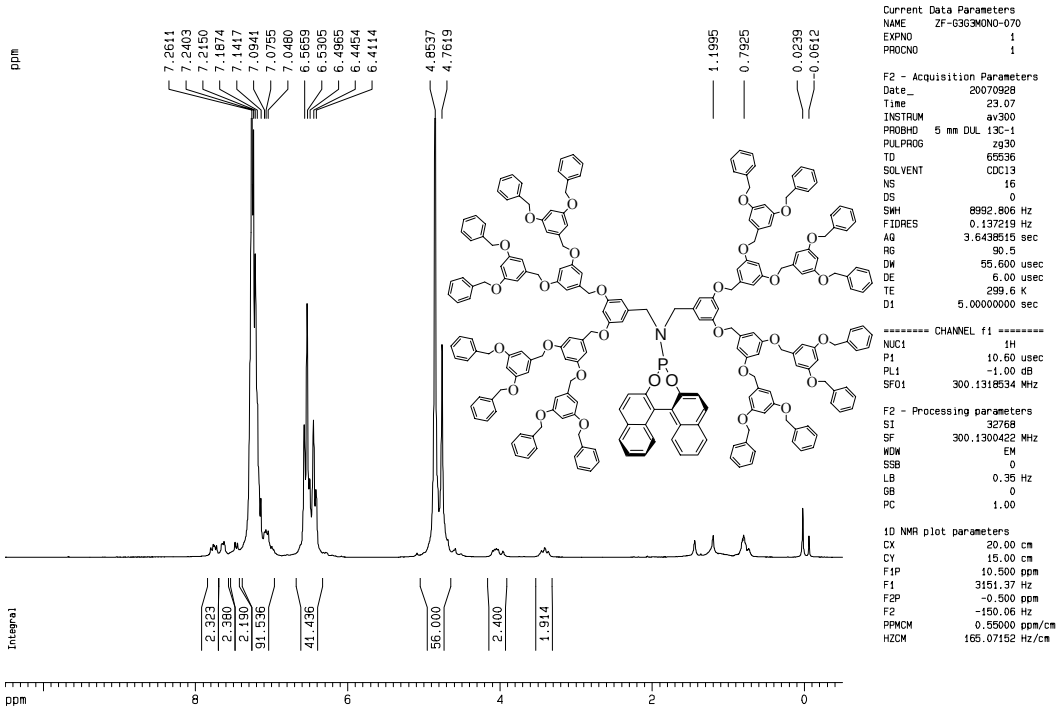
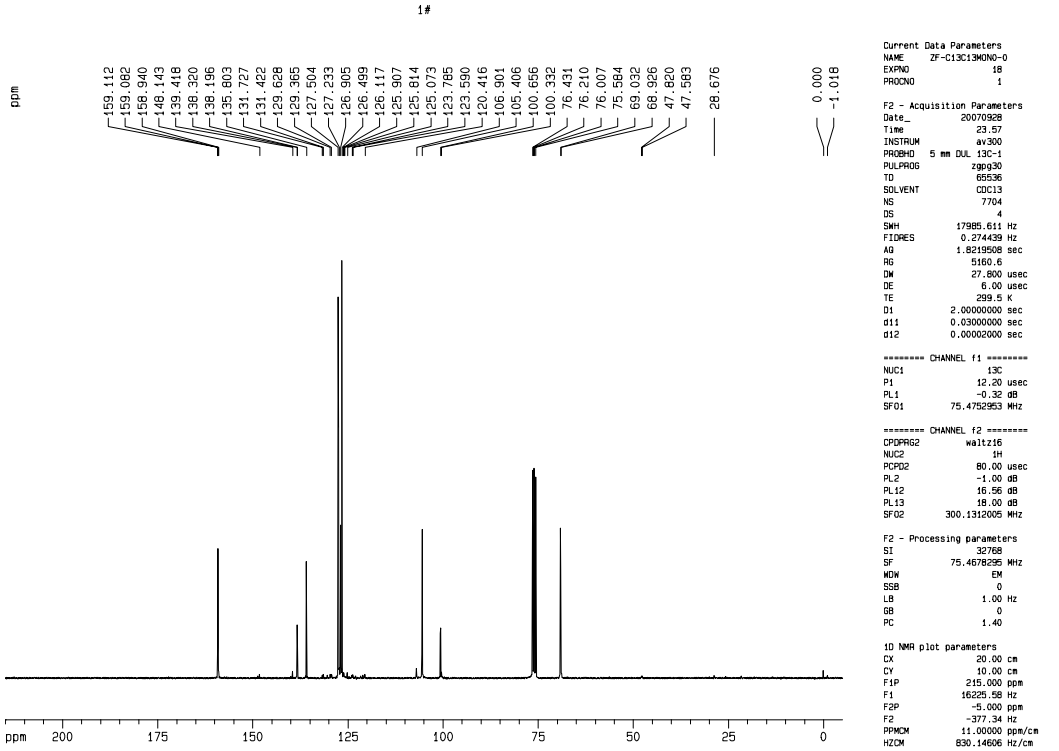
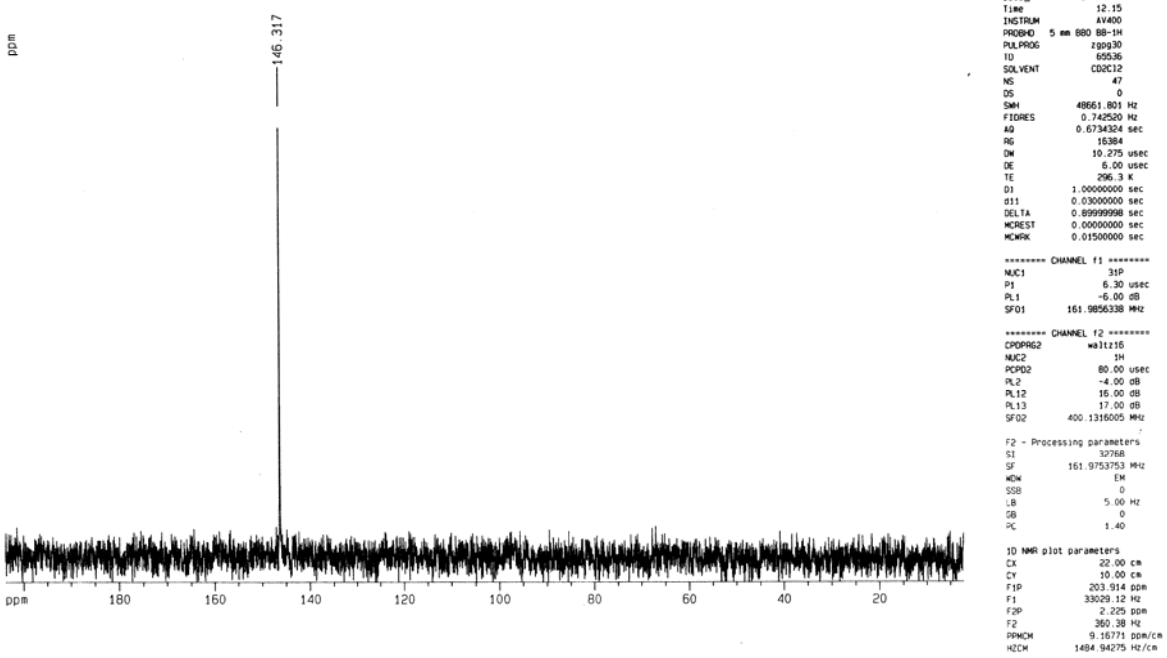

Intens. [a.u.]
1200
1000
800
600
400
200
0
1783.6
1480.7
500
1000
1500
2000
2500
3000
3500
m/z

Figure S7. ^{1}H NMR, ^{13}C NMR, ^{31}P NMR and MS spectra of **1AG$_3$**








```
Current Data Parameters
NAME                  hou-31p
EXPNO                     145
PROCNO                      1

F2 - Acquisition Parameters
Date_              20070423
Time                   12.15
INSTRUM                AV400
PROBHD   5 mm BBO BB-1H
PULPROG             zgpg30
TD                      65536
SOLVENT                CD2Cl2
NS                         47
DS                          0
SWH                48661.801 Hz
FIDRES                0.742520 Hz
AQ                    0.6734324 sec
RG                        16384
DW                    10.275 usec
DE                     6.00 usec
TE                     296.3 K
D1                 1.00000000 sec
d11                0.03000000 sec
DELTA              0.89999998 sec
MCREST             0.00000000 sec
MCWRK              0.01500000 sec

======== CHANNEL f1 ========
NUC1                      31P
P1                     6.30 usec
PL1                   -6.00 dB
SF01              161.9856338 MHz

======== CHANNEL f2 ========
CPDPRG2                waltz16
NUC2                       1H
PCPD2                 80.00 usec
PL2                   -4.00 dB
PL12                  16.00 dB
PL13                  17.00 dB
SF02              400.1316005 MHz

F2 - Processing parameters
SI                        32768
SF                161.9753753 MHz
WDW                        EM
SSB                         0
LB                     5.00 Hz
GB                          0
PC                       1.40

1D NMR plot parameters
CX                    22.00 cm
CY                    10.00 cm
F1P                  203.914 ppm
F1                  33029.12 Hz
F2P                   2.225 ppm
F2                   360.38 Hz
PPMCM                9.16771 ppm/cm
HZCM                1484.94275 Hz/cm
```

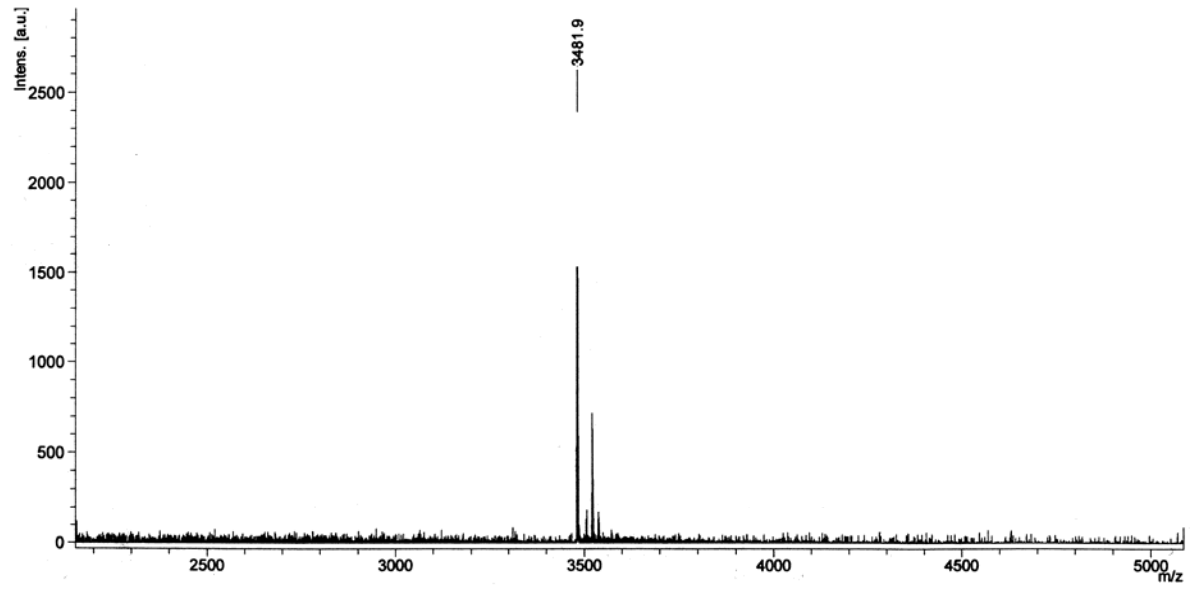
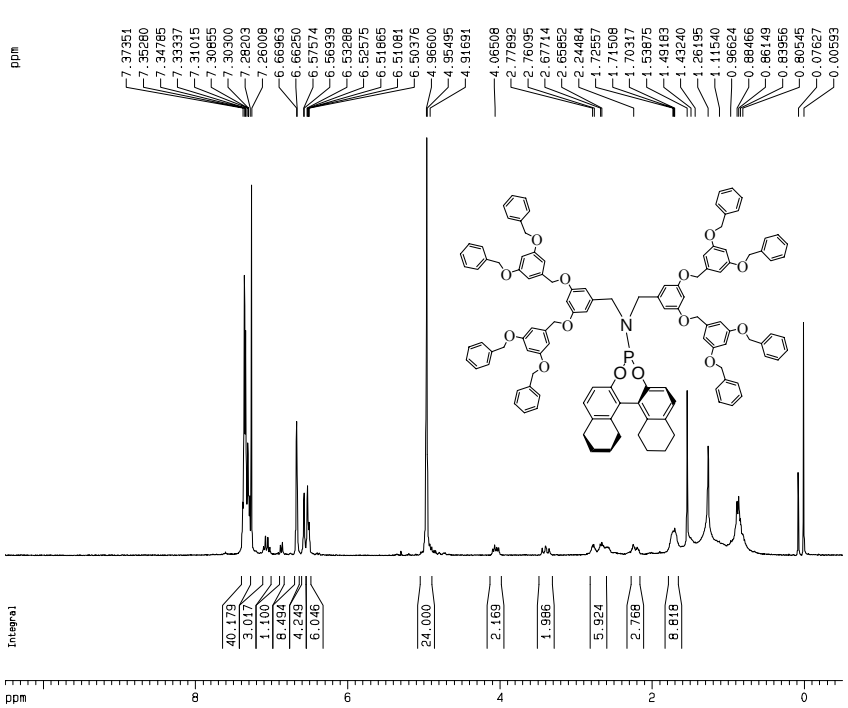
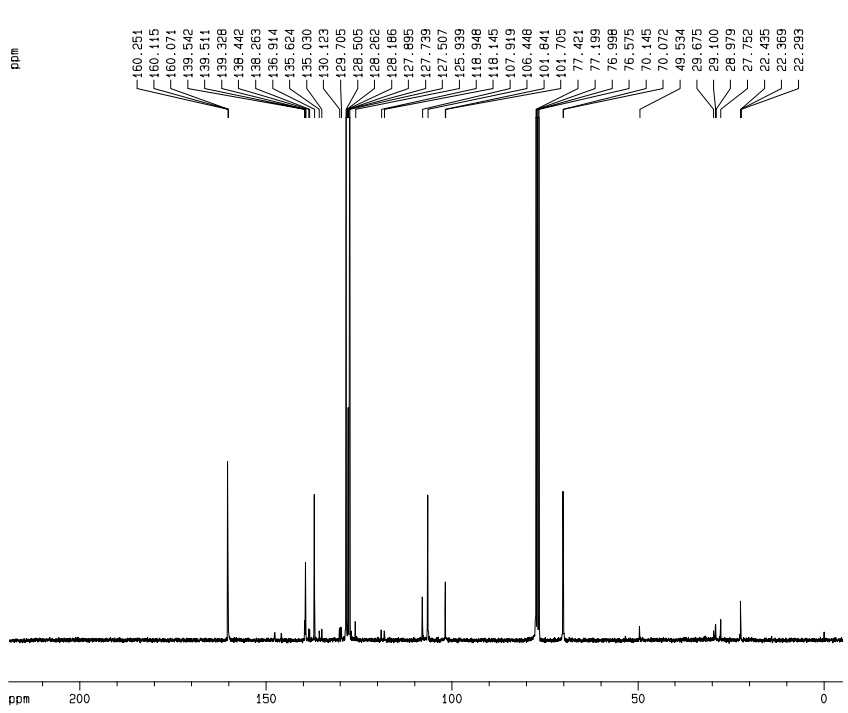


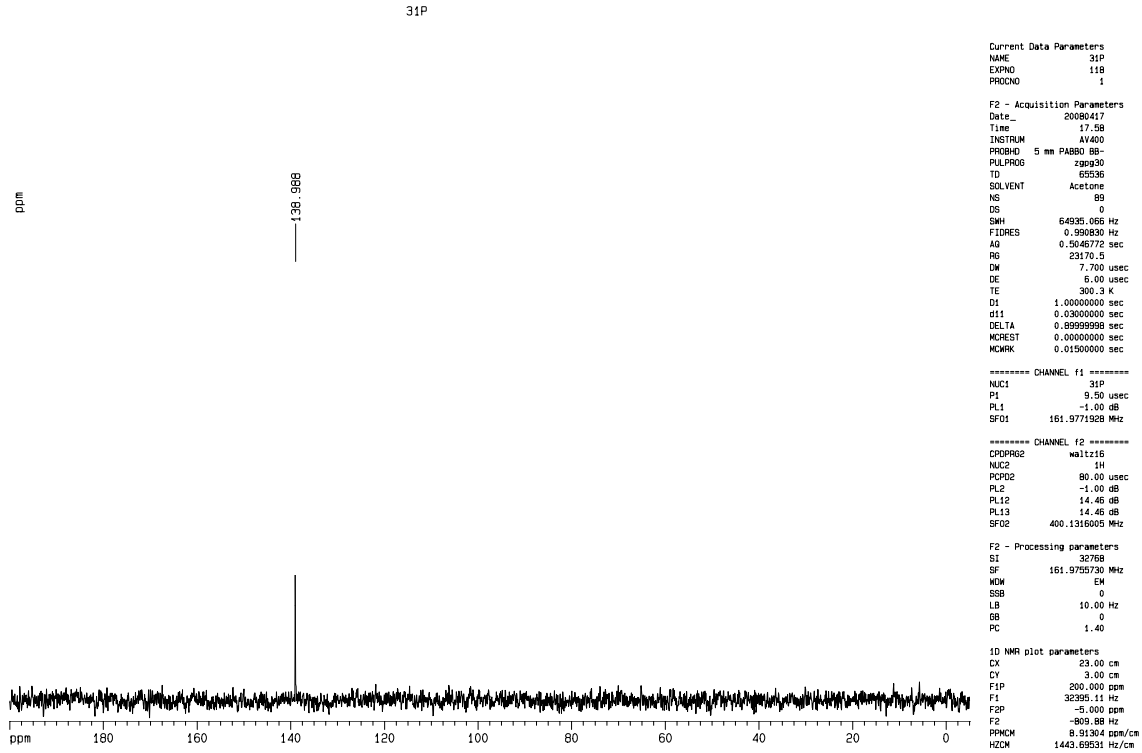
Figure S8. ^{1}H NMR, ^{13}C NMR, ^{31}P NMR and MS spectra of **2BG$_2$**




```
Current Data Parameters
NAME          ZF-0511-H8
EXPNO                 10
PROCNO                 1

F2 - Acquisition Parameters
Date_          20080511
Time              10.38
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                  362
DW               55.600 usec
DE                6.00 usec
TE                299.3 K
D1             1.00000000 sec
MCREST         0.00000000 sec
MCWRK          0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                  7.00 usec
PL1                -1.00 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

1D NMR plot parameters
CX                 20.00 cm
CY                 10.00 cm
F1P               10.500 ppm
F1              3151.36 Hz
F2P               -0.500 ppm
F2              -150.06 Hz
PPMCM           0.55000 ppm/cm
HZCM          165.07150 Hz/cm
```




```
Current Data Parameters
NAME      ZF-HB-BINOL-G2
EXPNO                 20
PROCNO                 1

F2 - Acquisition Parameters
Date_          20080309
Time              14.29
INSTRUM             av300
PROBHD   5 mm DUL 13C-1
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                 3929
DS                    4
SWH           17985.611 Hz
FIDRES         0.274439 Hz
AQ             1.8219508 sec
RG                812.7
DW               27.800 usec
DE                6.00 usec
TE                303.1 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              16.98 dB
PL13              16.98 dB
SFO2         300.1312005 MHz

F2 - Processing parameters
SI                 32768
SF           75.4677490 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40

1D NMR plot parameters
CX                 20.00 cm
CY                 15.00 cm
F1P              220.000 ppm
F1             16602.90 Hz
F2P               -5.000 ppm
F2              -377.34 Hz
PPMCM          11.25000 ppm/cm
HZCM          849.01215 Hz/cm
```


31P
ppm
139.988
ppm
180
160
140
120
100
80
60
40
20
0
Current Data Parameters
NAME 31P
EXPNO 118
PROCNO 1
F2 - Acquisition Parameters
Date_ 20080417
Time 17.58
INSTRUM AV400
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT Acetone
NS 89
DS 0
SWH 64935.066 Hz
FIDRES 0.990830 Hz
AQ 0.5046772 sec
RG 23170.5
DW 7.700 usec
DE 6.00 usec
TE 300.3 K
D1 1.00000000 sec
d11 0.03000000 sec
DELTA 0.89999998 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 31P
P1 9.50 usec
PL1 -1.00 dB
SFO1 161.9771928 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -1.00 dB
PL12 14.46 dB
PL13 14.46 dB
SFO2 400.1316005 MHz
F2 - Processing parameters
SI 32768
SF 161.9755730 MHz
WDW EM
SSB 0
LB 10.00 Hz
GB 0
PC 1.40
1D NMR plot parameters
CX 23.00 cm
CY 3.00 cm
F1P 200.000 ppm
F1 32395.11 Hz
F2P -5.000 ppm
F2 -809.88 Hz
PPMCM 8.91304 ppm/cm
HZCM 1443.69531 Hz/cm

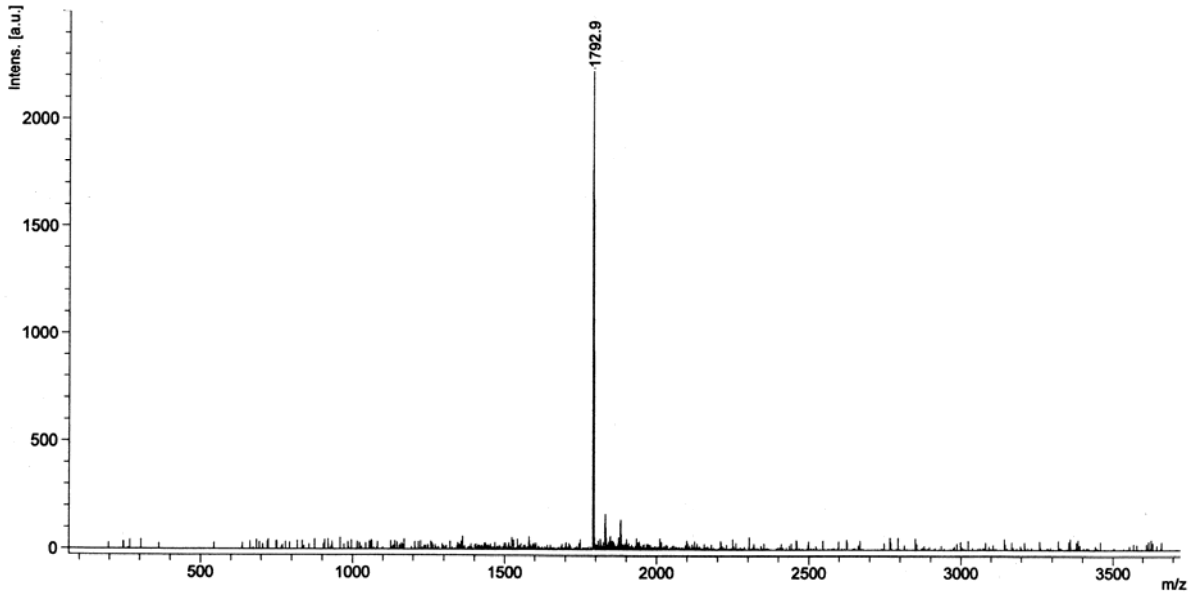
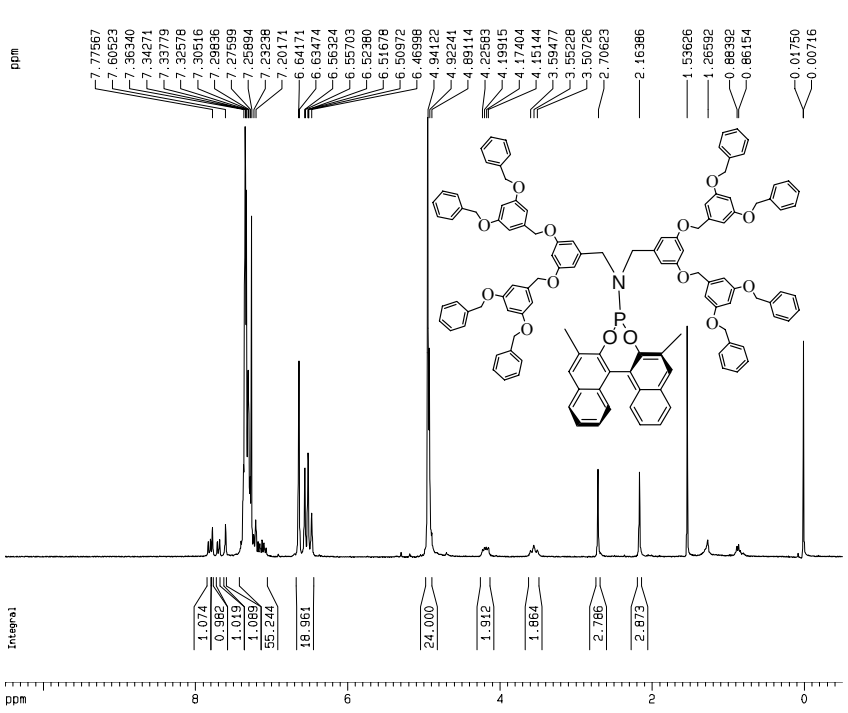
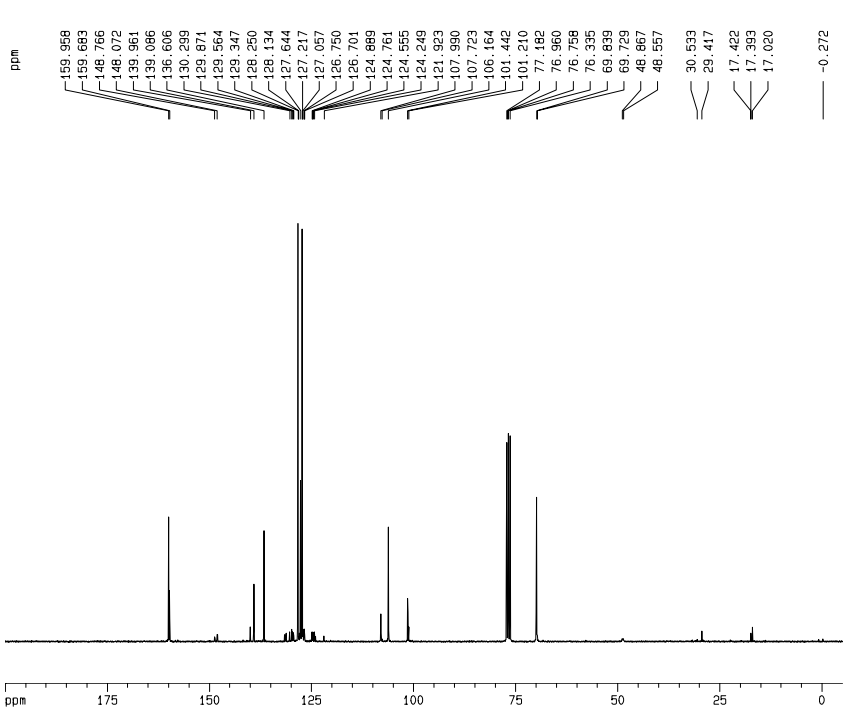

Intens. [a.u.]
1792.9
2000
1500
1000
500
0
500
1000
1500
2000
2500
3000
3500
m/z

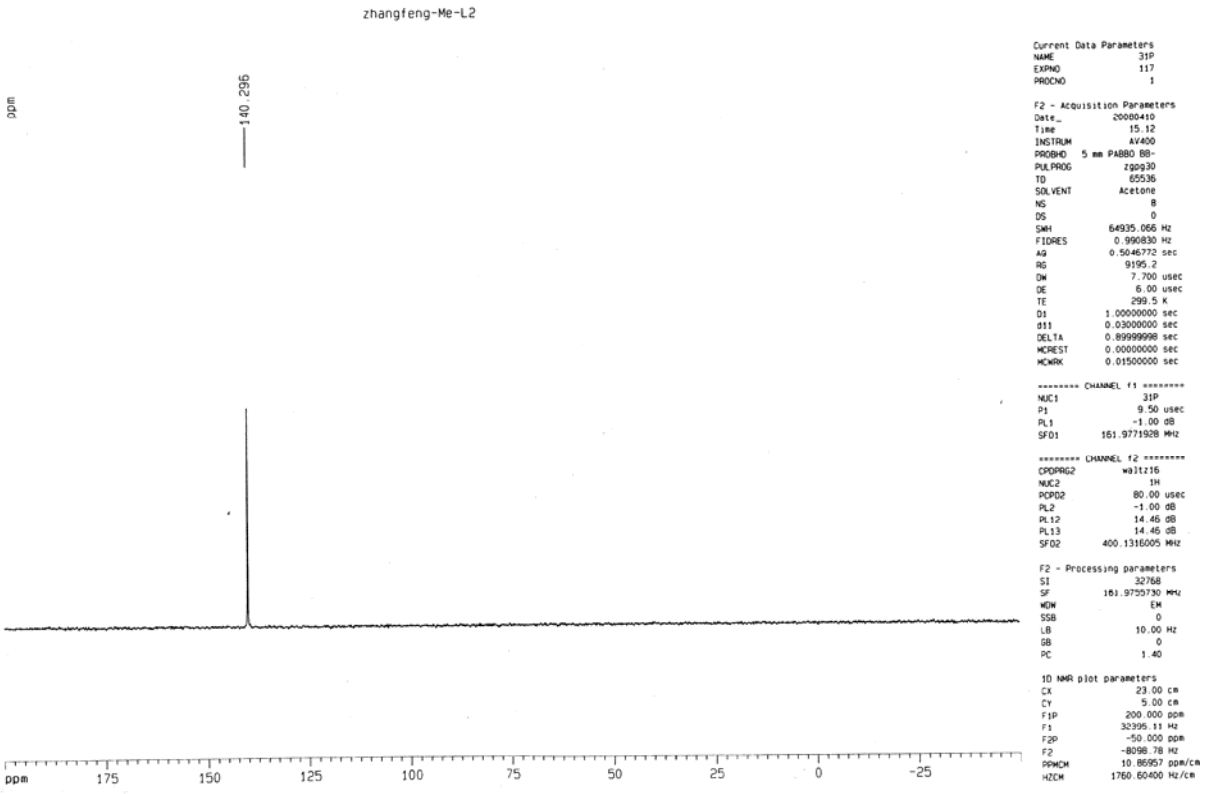
Figure S9. ^{1}H NMR, ^{13}C NMR, ^{31}P NMR and MS spectra of **3CG$_2$**




```
Current Data Parameters
NAME          ZF-0511-Me
EXPNO                 10
PROCNO                 1

F2 - Acquisition Parameters
Date_           20080511
Time               10.32
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                   362
DW                55.600 usec
DE                 6.00 usec
TE                299.3 K
D1             1.00000000 sec
MCREST         0.00000000 sec
MCWRK          0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                 7.00 usec
PL1               -1.00 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

1D NMR plot parameters
CX                 20.00 cm
CY                 15.00 cm
F1P               10.500 ppm
F1              3151.36 Hz
F2P               -0.500 ppm
F2              -150.06 Hz
PPMCM           0.55000 ppm/cm
HZCM          165.07150 Hz/cm
```




```
Current Data Parameters
NAME      zhangf-80413-Me
EXPNO                 10
PROCNO                 1

F2 - Acquisition Parameters
Date_           20080413
Time               12.36
INSTRUM            av300
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                  8192
DW                27.800 usec
DE                 6.00 usec
TE                301.5 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

F2 - Processing parameters
SI                 32768
SF           75.4677726 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40

1D NMR plot parameters
CX                 20.00 cm
CY                 10.00 cm
F1P               200.000 ppm
F1              15093.56 Hz
F2P               -5.000 ppm
F2              -377.34 Hz
PPMCM          10.25000 ppm/cm
HZCM          773.54468 Hz/cm
```


zhangfeng-Me-L2
ppm
140.296
ppm
175
150
125
100
75
50
25
0
-25
Current Data Parameters
NAME 31P
EXPNO 117
PROCNO 1
F2 - Acquisition Parameters
Date_ 20080410
Time 15.12
INSTRUM AV400
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT Acetone
NS 8
DS 0
SWH 64935.066 Hz
FIDRES 0.990830 Hz
AQ 0.5046772 sec
RG 9195.2
DW 7.700 usec
DE 6.00 usec
TE 299.5 K
D1 1.00000000 sec
d11 0.03000000 sec
DELTA 0.89999998 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 31P
P1 9.50 usec
PL1 -1.00 dB
SFO1 161.9771928 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -1.00 dB
PL12 14.46 dB
PL13 14.46 dB
SFO2 400.1316005 MHz
F2 - Processing parameters
SI 32768
SF 161.9755730 MHz
WDW EM
SSB 0
LB 10.00 Hz
GB 0
PC 1.40
1D NMR plot parameters
CX 23.00 cm
CY 5.00 cm
F1P 200.000 ppm
F1 32395.11 Hz
F2P -50.000 ppm
F2 -8098.78 Hz
PPMCM 10.86957 ppm/cm
HZCM 1760.60400 Hz/cm

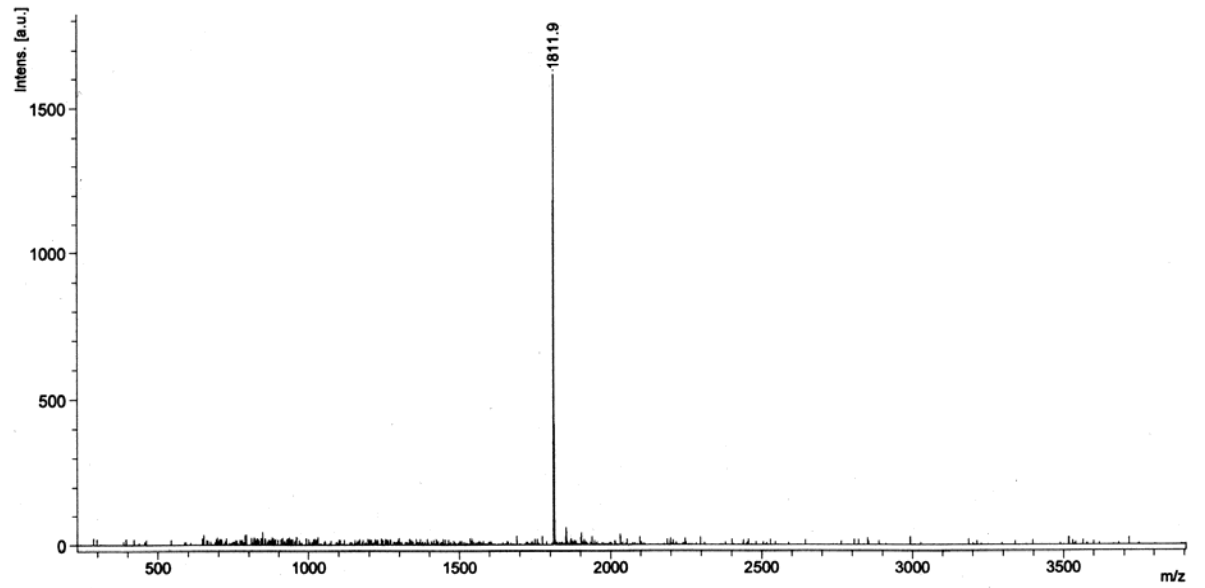
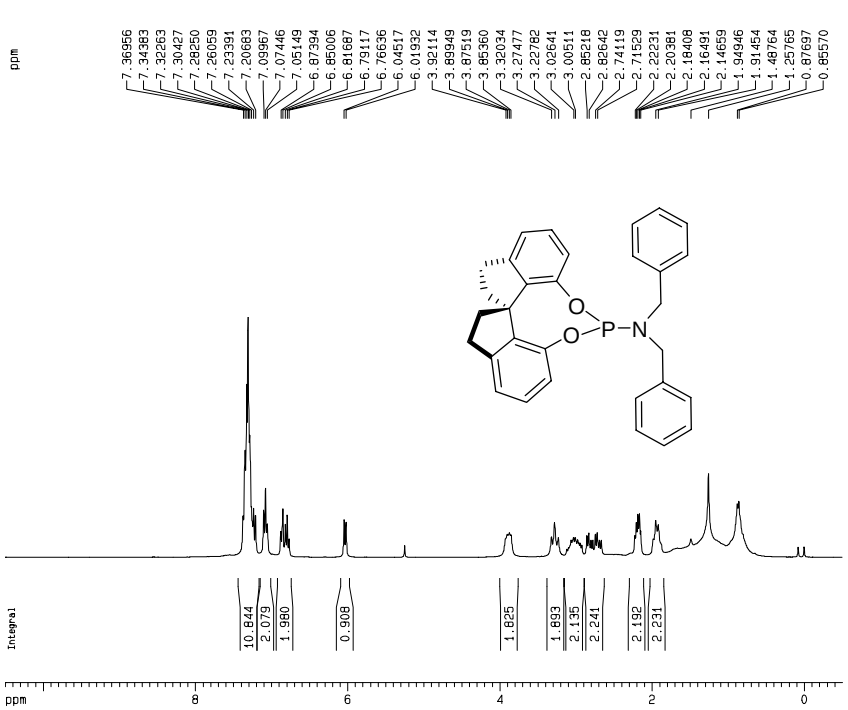
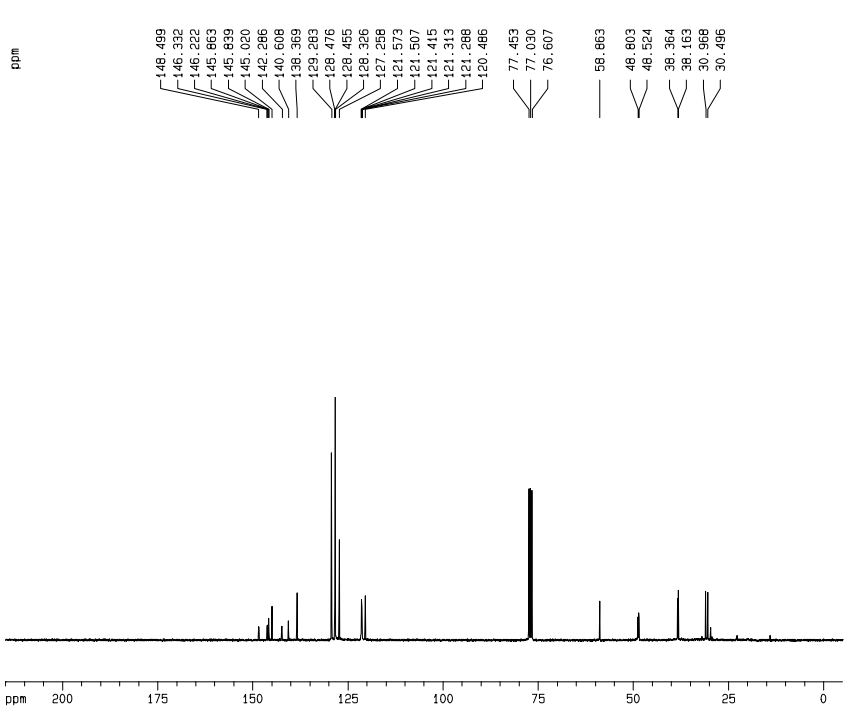

Intens. [a.u.]
1811.9
1500
1000
500
0
500
1000
1500
2000
2500
3000
3500
m/z

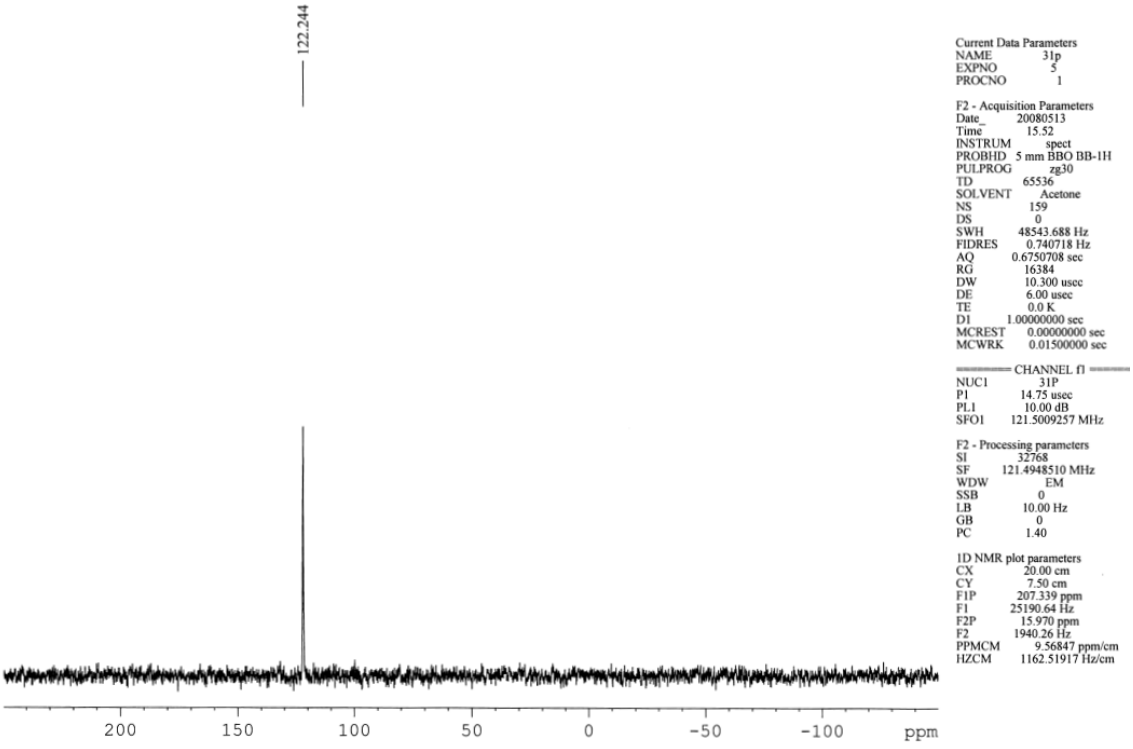
Figure S10. ^{1}H NMR, ^{13}C NMR, ^{31}P NMR and MS spectra of **4DG$_0$**




```
Current Data Parameters
NAME         ZF-080510-3
EXPNO                 10
PROCNO                 1

F2 - Acquisition Parameters
Date_          20080510
Time              11.27
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                  80.6
DW                55.600 usec
DE                 6.00 usec
TE                299.3 K
D1             1.00000000 sec
MCREST         0.00000000 sec
MCWRK          0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                  7.00 usec
PL1                -1.00 dB
SFO1         300.1324010 MHz

F2 - Processing parameters
SI                 32768
SF           300.1300229 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 20.00 cm
CY                  2.00 cm
F1P               10.500 ppm
F1              3151.37 Hz
F2P               -0.500 ppm
F2              -150.06 Hz
PPMCM            0.55000 ppm/cm
HZCM           165.07152 Hz/cm
```




```
Current Data Parameters
NAME         ZF-080510-3
EXPNO                 11
PROCNO                 1

F2 - Acquisition Parameters
Date_          20080510
Time              11.32
INSTRUM           spect
PROBHD   5 mm DUL 13C-1
PULPROG          zgpg30
TD                 65536
SOLVENT            CDCl3
NS                  1024
DS                     4
SWH            17985.611 Hz
FIDRES          0.274439 Hz
AQ              1.8219508 sec
RG                14596.5
DW                27.800 usec
DE                 6.00 usec
TE                300.0 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

F2 - Processing parameters
SI                 32768
SF           75.4677490 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40

1D NMR plot parameters
CX                 20.00 cm
CY                  6.00 cm
F1P              215.000 ppm
F1             16225.57 Hz
F2P               -5.000 ppm
F2              -377.34 Hz
PPMCM           11.00000 ppm/cm
HZCM           830.14520 Hz/cm
```


122.244
200
150
100
50
0
-50
-100
ppm
Current Data Parameters
NAME 31p
EXPNO 5
PROCNO 1
F2 - Acquisition Parameters
Date_ 20080513
Time 15.52
INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 65536
SOLVENT Acetone
NS 159
DS 0
SWH 48543.688 Hz
FIDRES 0.740718 Hz
AQ 0.6750708 sec
RG 16384
DW 10.300 usec
DE 6.00 usec
TE 0.0 K
D1 1.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
CHANNEL f1
NUC1 31P
P1 14.75 usec
PL1 10.00 dB
SFO1 121.5009257 MHz
F2 - Processing parameters
SI 32768
SF 121.4948510 MHz
WDW EM
SSB 0
LB 10.00 Hz
GB 0
PC 1.40
1D NMR plot parameters
CX 20.00 cm
CY 7.50 cm
F1P 207.339 ppm
F1 25190.64 Hz
F2P 15.970 ppm
F2 1940.26 Hz
PPMCM 9.56847 ppm/cm
HZCM 1162.51917 Hz/cm

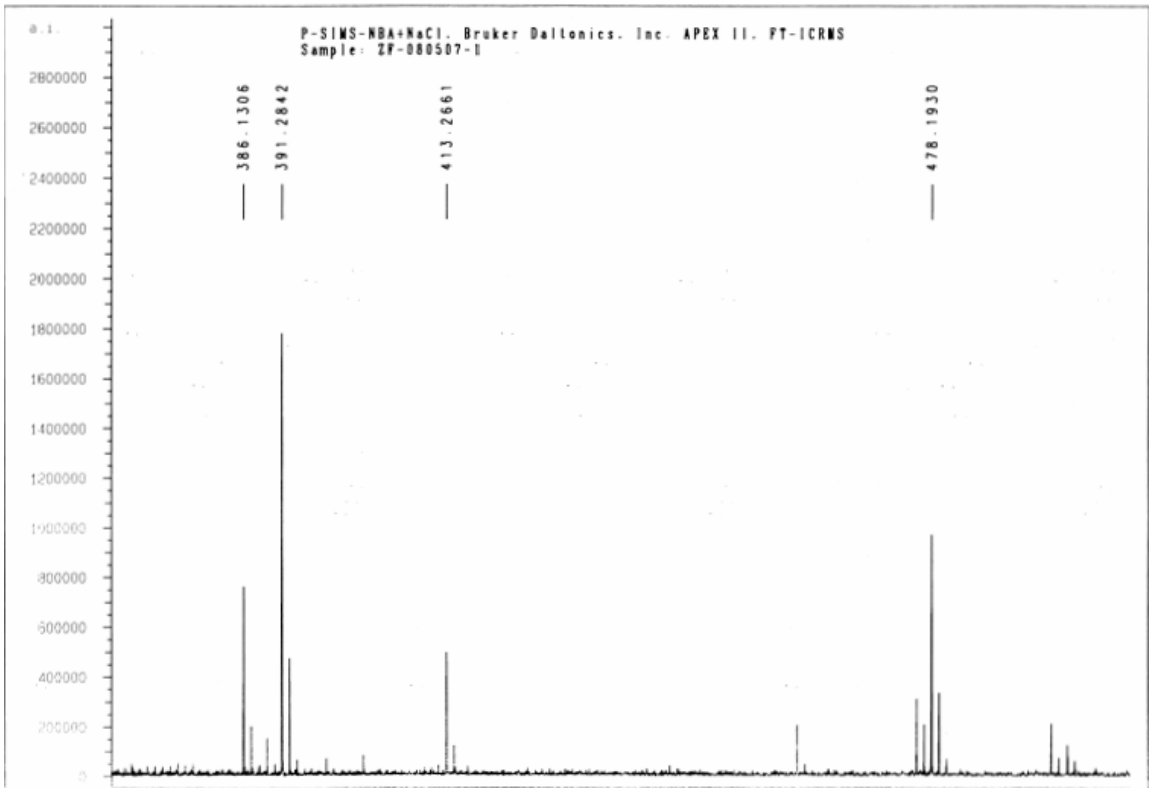
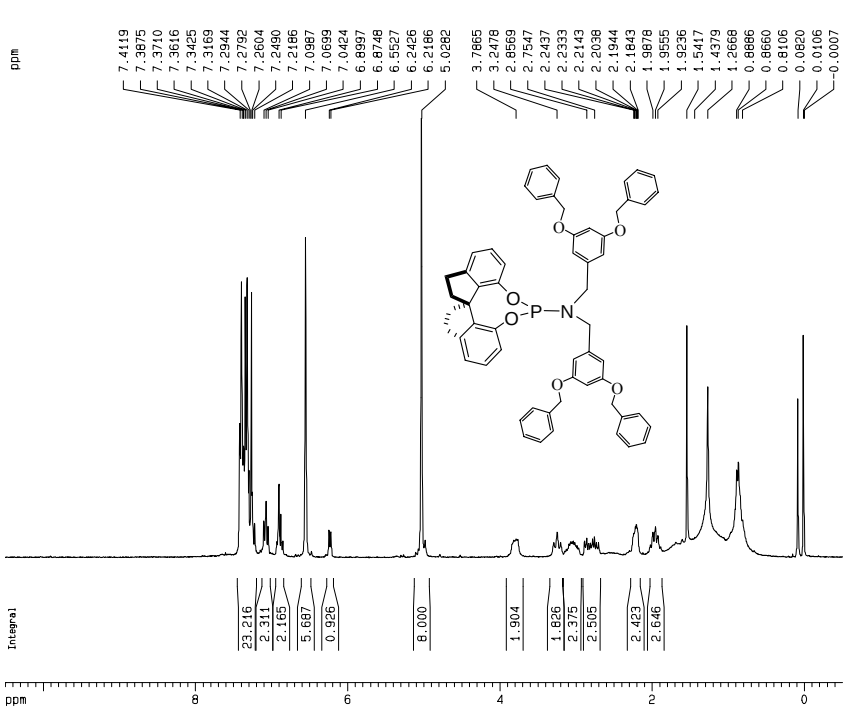
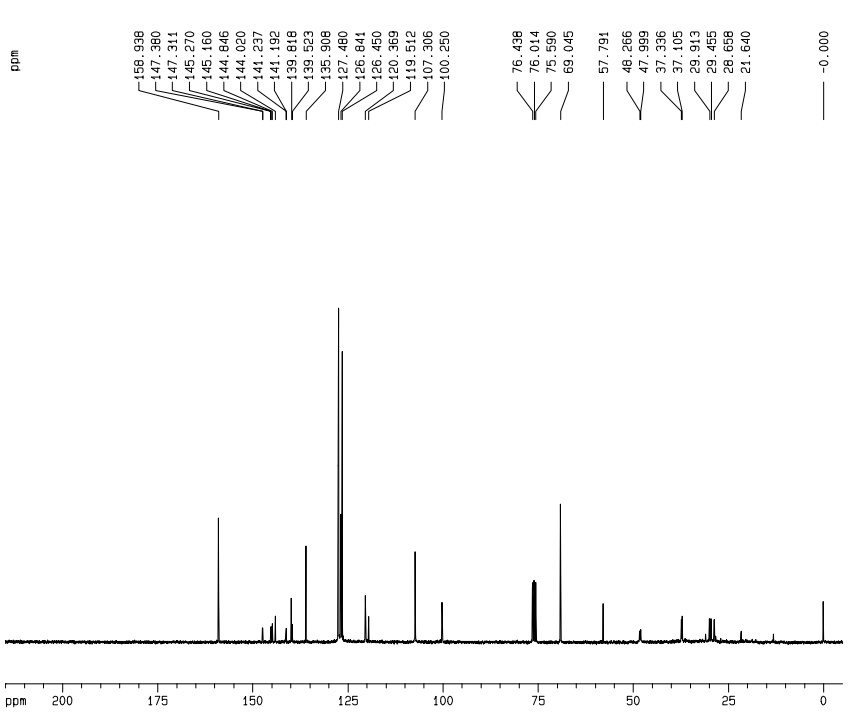

P-SIMS-NBA+NaCl. Bruker Daltonics. Inc. APEX II. FT-ICRMS
Sample: ZF-080507-1
386.1306
391.2842
413.2661
478.1930
2800000
2600000
2400000
2200000
2000000
1800000
1600000
1400000
1200000
1000000
800000
600000
400000
200000
0

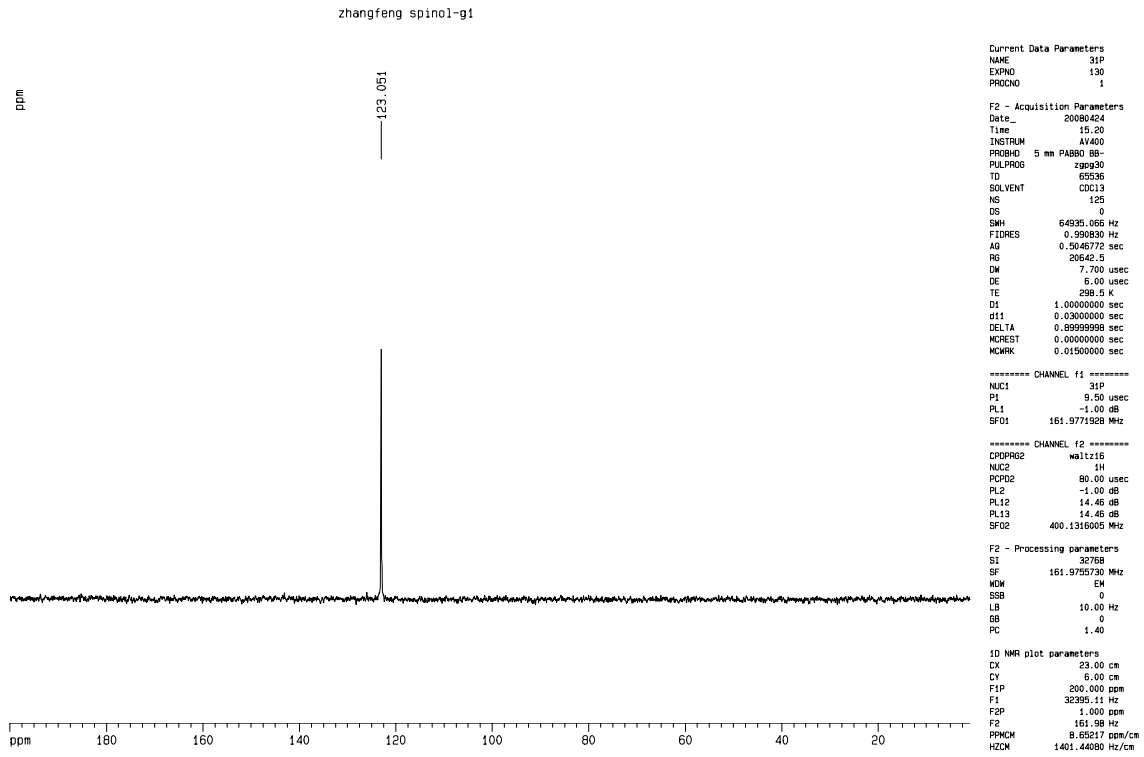
Figure S11. ^{1}H NMR, ^{13}C NMR, ^{31}P NMR and MS spectra of **4DG$_1$**

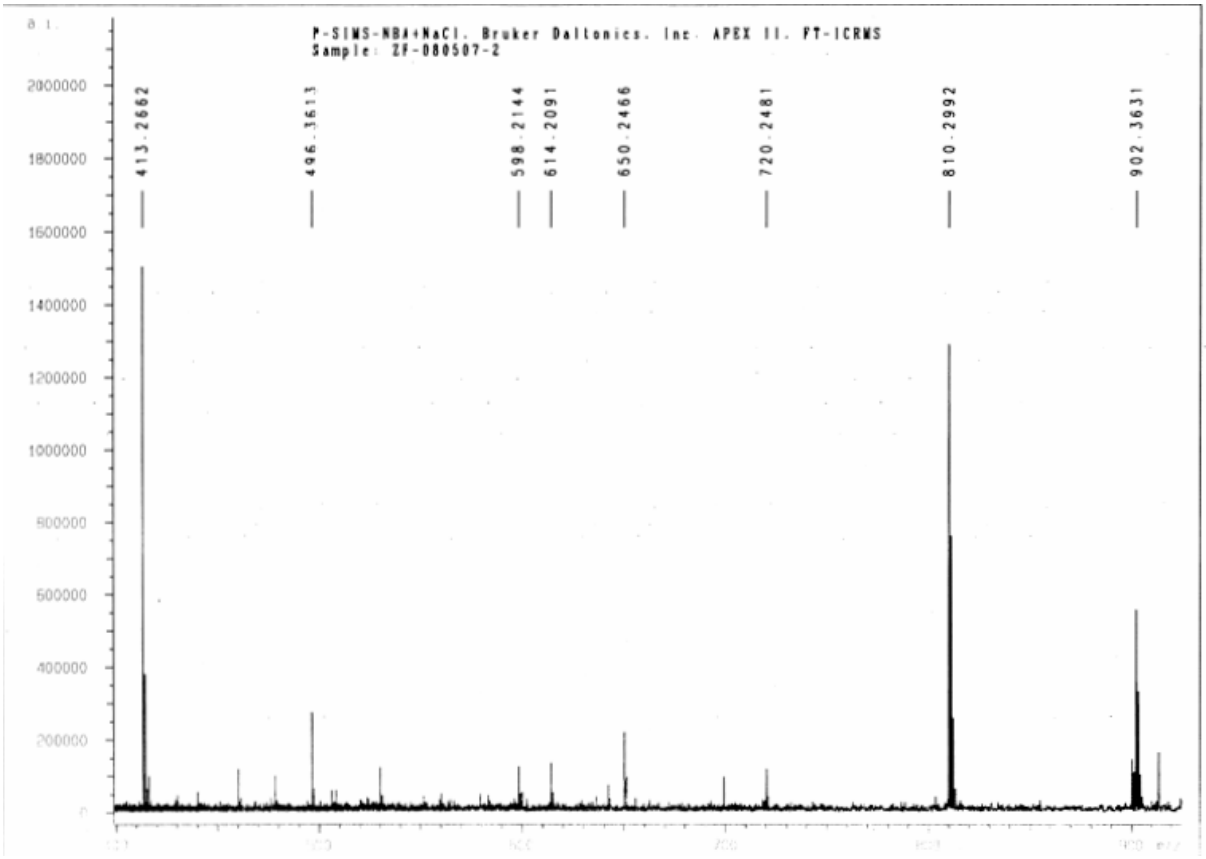



```
Current Data Parameters
NAME         ZF-080510-2
EXPNO                 21
PROCNO                 1

F2 - Acquisition Parameters
Date_          20080510
Time              11.22
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                  362
DW               55.600 usec
DE                6.00 usec
TE               299.2 K
D1             1.00000000 sec
MCREST         0.00000000 sec
MCWRK          0.01500000 sec

======== CHANNEL f1 ========
NUC1                 1H
P1                 7.00 usec
PL1                -1.00 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

1D NMR plot parameters
CX                20.00 cm
CY                12.50 cm
F1P               10.500 ppm
F1              3151.36 Hz
F2P               -0.500 ppm
F2              -150.06 Hz
PPMCM             0.55000 ppm/cm
HZCM            165.07150 Hz/cm
```




```
Current Data Parameters
NAME     ZF-0511-SPINOL-
EXPNO                 11
PROCNO                 1

F2 - Acquisition Parameters
Date_          20080511
Time              10.53
INSTRUM           spect
PROBHD   5 mm DUL 13C-1
PULPROG         zgpg30
TD                65536
SOLVENT           CDCl3
NS                  236
DS                    4
SWH           17985.611 Hz
FIDRES         0.274439 Hz
AQ             1.8219508 sec
RG                456.1
DW               27.800 usec
DE                6.00 usec
TE               301.7 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

F2 - Processing parameters
SI                32768
SF           75.4678377 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40

1D NMR plot parameters
CX                20.00 cm
CY                 8.00 cm
F1P              215.000 ppm
F1             16225.59 Hz
F2P               -5.000 ppm
F2              -377.34 Hz
PPMCM            11.00000 ppm/cm
HZCM           830.14618 Hz/cm
```


zhangfeng spinol-g1
ppm
123.051
ppm 180 160 140 120 100 80 60 40 20
Current Data Parameters
NAME 31P
EXPNO 130
PROCNO 1
F2 - Acquisition Parameters
Date_ 20080424
Time 15.20
INSTRUM AV400
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 125
DS 0
SWH 64935.065 Hz
FIDRES 0.990830 Hz
AQ 0.5046772 sec
RG 2064.5
DW 7.700 usec
DE 6.00 usec
TE 298.5 K
D1 1.00000000 sec
d11 0.03000000 sec
DELTA 0.89999998 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 31P
P1 9.50 usec
PL1 -1.00 dB
SFO1 161.9771928 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -1.00 dB
PL12 14.46 dB
PL13 14.46 dB
SFO2 400.1316005 MHz
F2 - Processing parameters
SI 32768
SF 161.9755730 MHz
WDW EM
SSB 0
LB 10.00 Hz
GB 0
PC 1.40
1D NMR plot parameters
CX 23.00 cm
CY 6.00 cm
F1P 200.000 ppm
F1 32395.11 Hz
F2P 1.000 ppm
F2 161.98 Hz
PPMCM 8.65217 ppm/cm
HZCM 1401.44080 Hz/cm


P-SIMS-NBA+NaCl, Bruker Daltonics, Inc. APEX II, FT-ICRMS
Sample: ZF-080507-2
413.2662
496.3613
598.2144
614.2091
650.2466
720.2481
810.2992
902.3631
2000000
1800000
1600000
1400000
1200000
1000000
800000
600000
400000
200000

References

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