Supporting Information for

Amphiphilic DNA-Dendron Hybrid: A New Building Block for Functional Assemblies

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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 and ^{13}C NMR spectra were recorded on Bruker AMX 300 Spectrometer (^{1}H: 300 MHz; ^{13}C: 75 MHz) at 298 K. Chemical shifts are reported in parts per million (ppm) relative to the internal standards, partially deuterated solvents or tetramethylsilane (TMS). Coupling constants (J) are denoted in Hz and chemical shifts (δ) in ppm. Multiplicities are denoted as follows: s = singlet, d = doublet, m = multiplet, br = broad. Matrix-assisted laser desorption-ionization (time of flight) mass spectrometry (MALDI-TOF) was performed on a Bruker Biflex III MALDI-TOF spectrometer with α-cyano-4- hydroxylcinnamic acid (CCA) as the matrix. High resolution mass spectrometry (HRMS-FAB) was carried out on a Bruker APEX 47E FTMS spectrometer. Electron spray ionization mass spectrometry was performed on a Thermo Finnigan Surveyor MSQ-Plus Mass spectrometer. Elemental analyses were performed on a Flash EA 1112 Elemental Analyzer.

All chemicals were obtained from Aldrich or Alfa Aesar (Tianjing, China) and used as received unless otherwise mentioned. The organic solvents used for synthesis were dried according to published methods[1]. Water used in all experiments was Milli-Q deionized (15.6 MΩ.cm).

AFM samples were prepared by deposition of 10 μL self-assembled mixture at a concentration of 20 μM onto freshly cleaved mica and dried automatically in air. AFM images were acquired in air in tapping mode on a Veeco MultiMode 8 Scanning Probe Microscope with SNL (Sharp Nitride Lever) probe.

2. Synthesis of Phosphoramidite Functionalized Dendrons

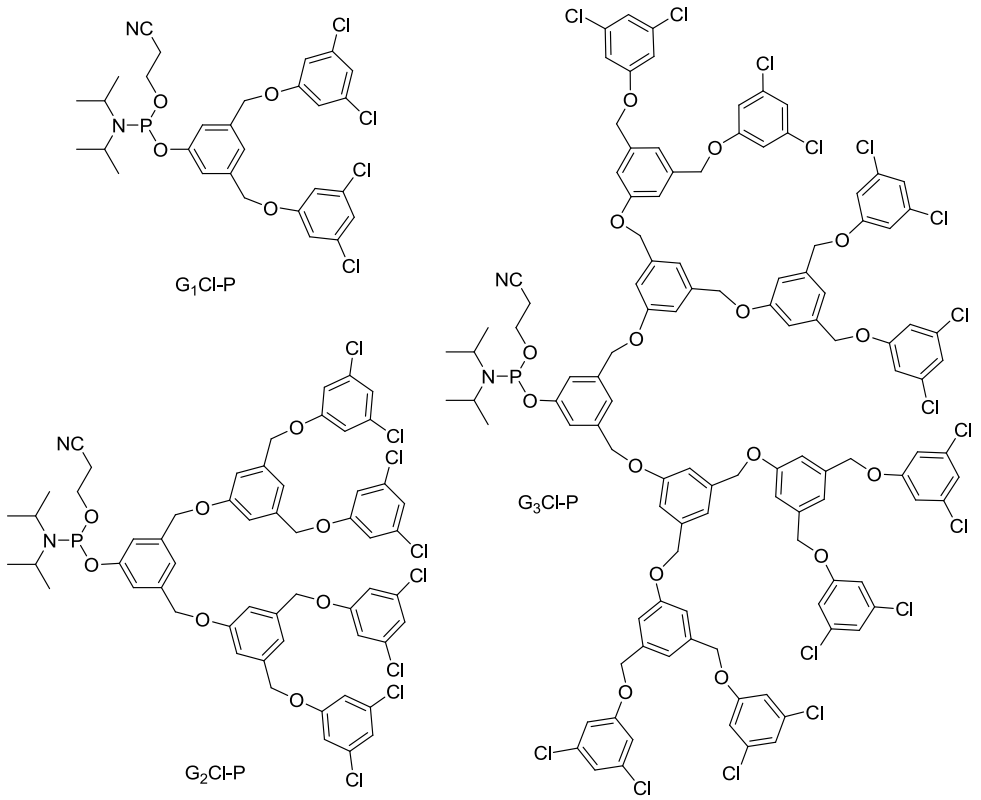
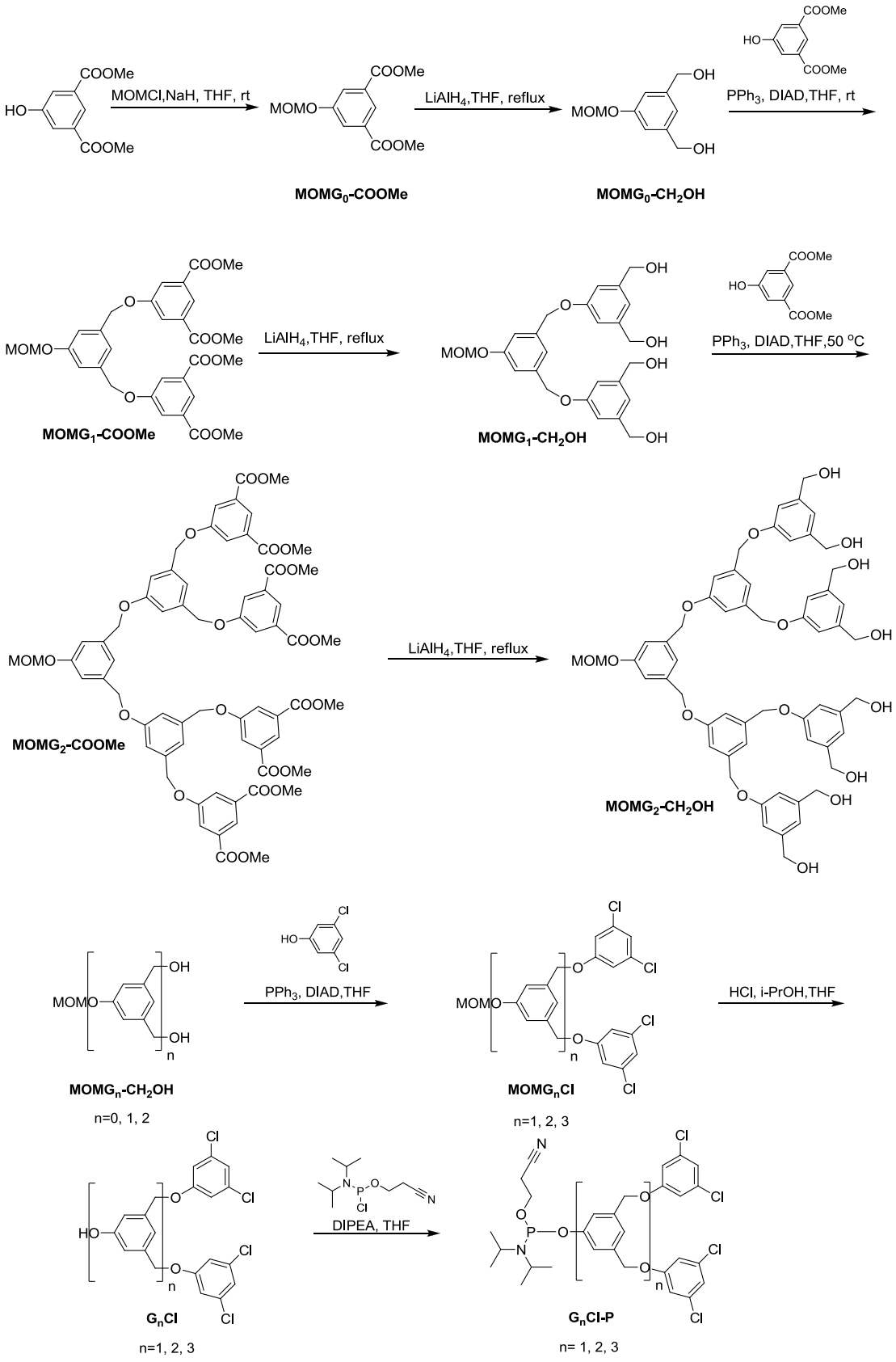


Chart S1. Chemical structures of phosphoramidite functionalized dendrons.



Scheme S1. Synthetic routes to phosphoramidite functionalized dendrons.

2.1 General procedure for the preparation of $MOMG_n$-COOMe

$MOMG_0$-COOMe: Dimethyl 5-hydroxyisophthalate (6.30 g, 30.0 mmol) solution in 70 ml anhydrous THF was added to an ice cooled suspension of NaH (3.60 g, 81.0 mmol, as 60% dispersion in oil) in anhydrous THF (30 mL) dropwise. The mixture was stirred for 2 h and methoxymethyl chloride (MOMCl, 4.35 g, 4.10 mL, 54.0 mmol) was added dropwise. After warming to room temperature, the mixture was stirred overnight. Then the reaction was quenched by dropwise addition of saturated ammonium chloride. The product was extracted with dichloromethane. The extract was dried by anhydrous Na_2SO_4 and concentrated to afford the crude product. Precipitating with petroleum ether afforded pure $MOMG_0$-COOMe (7.08 g, 93% yield) as an off-white solid. ^{1}H NMR (300 MHz, $CDCl_3$, δ): 3.49 (s, CH_3OCH_2, 3H), 3.94 (s, $COOCH_3$, 6H), 5.25 (s, CH_3OCH_2, 2H), 7.88 (d, J = 1.4 Hz, Ar*H*, 2H), 8.34 (d, J = 1.4 Hz, Ar*H*, 1H). ^{13}C NMR (75 MHz, $CDCl_3$, δ): 166.4, 157.6, 132.2, 124.5, 121.9, 94.8, 56.7, 52.8. HRMS-FAB (m/z): $[M+H]^+$ calcd for $C_{12}H_{15}O_6$, 255.0863; found: 255.0863.

$MOMG_1$-COOMe: Diisopropyl azodicarboxylate (DIAD, 5.05 g, 25.0 mmol, 4.95 mL) was added dropwise to an ice-bath cooled solution of $MOMG_0$-CH_2OH (1.98 g, 10.0 mmol), dimethyl 5-hydroxyisophthalate (4.30 g, 20.5 mmol) and triphenylphosphine (PPh_3, 5.77 g, 22.0 mmol) in dry THF (60 mL) via syringe. The reaction mixture was then stirred for 10 min at 0 ^{o}C and then 24 h at room temperature under a nitrogen atmosphere. The reaction was monitored by TLC upon the completion. The crude product was purified as follows: i) The reaction mixture was concentrated to about 20 mL, methanol was added under vigorous stirring, and the precipitate was isolated by filtration; ii) The resulting precipitate was redissolved in THF (20 mL), and precipitated into methanol (200 mL). After filtration, an

off-white solid of $MOMG_1$-COOMe (5.24 g, 90%) was obtained. ^{1}H NMR (300 MHz, $CDCl_3$, δ): 3.50 (s, C*H*$_3$OCH$_2$, 3H), 3.94 (s, COOC*H*$_3$, 12H), 5.13 (s, ArC*H*$_2$O, 4H), 5.22 (s, CH$_3$OC*H*$_2$O, 2H), 7.12 (s, Ar*H*, 2H), 7.18 (s, Ar*H*, 1H), 7.83 (s, Ar*H*, 4H), 8.29 (s, Ar*H*, 2H). ^{13}C NMR (75 MHz, $CDCl_3$, δ): 166.0, 158.6, 157.9, 138.2, 131.9, 123.3, 120.1, 119.7, 115.0, 94.5, 70.1, 56.1, 52.4. HRMS-FAB (*m/z*): $[M+Na]^+$ calcd for $C_{30}H_{30}O_{12}Na$: 605.1629; found: 605.1627.

$MOMG_2$-COOMe: Following the procedure for $MOMG_1$-COOMe, the reaction temperature was 45 ^{o}C**.** $MOMG_1$-CH_2OH (1.60 g, 3.4mmol), dimethyl 5-hydroxyisophthalate (3.22 g, 15.3 mmol), PPh_3 (4.46 g, 17.0 mmol), DIAD (4.13 g, 20.4 mmol, 4.05 mL), and dry THF (60 mL) yielded $MOMG_2$-COOMe (3.80 g, 90%) as an off-white solid after precipitation. ^{1}H NMR (300 MHz, $CDCl_3$, δ): 3.48 (s, C*H*$_3$OCH$_2$, 3H), 3.93 (s, COOC*H*$_3$, 24H), 5.08 (s, ArC*H*$_2$O, 4H), 5.13 (s, ArC*H*$_2$O, 8H), 5.19 (s, CH$_3$OC*H*$_2$O, 2H), 7.05 (s, Ar*H*, 4H), 7.10 (s, Ar*H*, 2H), 7.13 (s, Ar*H*, 2H), 7.17 (s, Ar*H*, 1H), 7.82 (d, *J* = 1.4 Hz, Ar*H*, 8H), 8.29 (t, *J* = 1.4 Hz, Ar*H*, 4H). ^{13}C NMR (75 MHz, $CDCl_3$, δ): 166.0, 159.3, 158.6, 157.8, 138.7, 138.2, 131.9, 123.3, 120.1, 119.7, 118.8, 114.9, 113.6, 94.5, 70.1, 69.9, 56.1, 52.4. (MALDI-TOF): m/z calcd for $C_{66}H_{62}O_{24}$: 1239.2; found: 1261.6 $[M+Na]^+$, 1277.6 $[M+K]^+$. Anal. calcd for $C_{66}H_{62}O_{24}$: C, 63.97; H, 5.04; found: C, 63.78; H, 5.11.

2.2 General procedure for the preparation of MOMGn-CH2OH

$MOMG_0$-CH_2OH: A solution of $MOMG_0$-COOMe (7.65 g, 30.1 mmol) in dry THF (300 mL) was added dropwise to a suspension of lithium aluminum hydride (LAH, 2.50g, 65.9 mmol) in THF at 0 ^{o}C. The reaction mixture was then stirred and refluxed for 1-2 h. The

reaction was quenched successively by dropwise addition of saturated ammonium chloride solution until H_2 evolution ceased. The granular salts were filtered and washed with THF (3 × 50 mL). The combined filtrate was concentrated under reduced pressure. Drying *in vacuo* for 3 h at 50 ℃ afforded MOMG$_0$-CH$_2$OH (5.90 g, 99% yield) as an off-white solid. ^{1}H NMR (300 MHz, d^6-acetone, δ): 3.42 (s, C*H*$_3$OCH$_2$O, 3H), 4.18 (t, *J* = 5.8 Hz, ArCH$_2$O*H*, 2H), 4.59 (d, *J* = 5.8 Hz, ArC*H*$_2$OH, 4H), 5.17 (s, CH$_3$OC*H*$_2$, 2H), 6.92 (s, Ar*H*, 2H), 6.97 (s, Ar*H*, 1H). ^{13}C NMR (75 MHz, d^6-acetone, δ): 158.5, 144.9, 118.9, 113.7, 95.1, 64.6, 64.5, 56.0. HRMS-FAB (*m/z*): $[M+H]^+$ calcd for $C_{10}H_{15}O_4$: 199.0965; found: 199.0967.

MOMG$_1$-CH$_2$OH: Following the procedure for MOMG$_0$-CH$_2$OH. LAH (1.50 g, 39.5 mmol) in THF (50 mL) and MOMG$_1$-COOMe (4.90 g, 8.4 mmol) in THF (100 mL), afforded the MOMG$_1$-CH$_2$OH (3.92 g, 99% yield) as an off-white solid. ^{1}H NMR (300 MHz, d^6-acetone, δ): 3.43 (s, C*H*$_3$OCH$_2$O, 3H), 4.24 (t, *J* = 5.8 Hz, ArCH$_2$O*H*, 4H), 4.58 (d, *J* = 5.8 Hz, ArC*H*$_2$OH, 8H), 5.07 (s, ArC*H*$_2$O, 4H), 5.20 (s, CH$_3$OC*H*$_2$, 2H), 6.92 (s, Ar*H*, 6H), 7.11 (s, Ar*H*, 2H), 7.22 (s, Ar*H*, 1H). ^{13}C NMR (75 MHz, d^6-acetone, δ): 159.9, 158.6, 144.9, 140.3, 120.5, 118.0, 115.4, 112.3, 95.2, 70.1, 64.7, 56.1. HRMS-FAB (*m/z*): $[M+H]^+$ calcd for $C_{26}H_{31}O_8$: 471.2013; found: 471.1998.

MOMG$_2$-CH$_2$OH: Following the procedure for MOMG$_0$-CH$_2$OH. LAH (0.31 g, 8.2 mmol) in THF (50 mL) and MOMG$_2$-COOMe (1.00 g, 0.81 mmol) in THF (50 mL), afforded the MOMG$_2$-CH$_2$OH (0.64 g, 79% yield) as an off-white solid. ^{1}H NMR (300 MHz, d^6-acetone, δ): 3.45 (s, C*H*$_3$OCH$_2$O, 3H), 4.29 (t, *J* = 5.7 Hz, ArCH$_2$O*H*, 8H), 4.61 (d, *J* = 5.4 Hz, ArC*H*$_2$OH, 16H), 5.09 (s, ArC*H*$_2$O, 8H), 5.14 (s, ArC*H*$_2$O, 4H), 5.24 (s, CH$_3$OC*H*$_2$, 2H), 6.95 (s, Ar*H*, 12H), 7.12 (s, Ar*H*, 4H), 7.16 (s, Ar*H*, 2H), 7.20 (s, Ar*H*, 2H), 7.26 (s, Ar*H*, 1H). ^{13}C

NMR (75 MHz, d^6-acetone, δ): 159.7, 159.6, 158.3, 144.5, 144.1, 139.8, 120.4, 119.4, 117.7, 115.3, 113.7,111.9, 94.9, 70.0, 69.8, 64.3, 55.9. (MALDI-TOF): m/z calcd for $C_{58}H_{62}O_{16}$: 1015.1; found: 1037.6 $[M+Na]^+$.

2.3 General procedure for the preparation of MOMGnCl

$MOMG_1Cl$: Diisopropyl azodicarboxylate (DIAD, 8.03 g, 39.6 mmol, 7.87 mL) was added via syringe to an ice-bath cooled solution of $MOMG_0$-CH_2OH (3.15 g, 15.9 mmol), 3,5-dichlorophenol (5.32 g, 32.6 mmol) and triphenylphosphine (PPh_3, 9.20 g, 35.1 mmol) in dry THF (120 mL) dropwise. The reaction mixture was then stirred for 10 min at 0 ^oC and then 24 h at room temperature under a nitrogen atmosphere. The reaction was monitored by TLC upon the completion. The crude product was purified as follows: i) The reaction mixture was concentrated to about 30 mL, methanol was added under vigorous stirring, and the precipitate was isolated by filtration; ii) The resulting precipitate was redissolved in THF, and precipitated into methanol. After filtration, afforded the $MOMG_1Cl$ (5.60 g, 72% yield) as an off-white solid. ^1H NMR (300 MHz, $CDCl_3$, δ): 3.49 (s, CH_3OCH_2O, 3H), 5.01 (s, $ArCH_2O$, 4H), 5.20 (s, CH_3OCH_2O, 2H), 6.87 (d, J = 1.5 Hz, Ar*H*, 4H), 6.97 (d, J = 1.5 Hz, Ar*H*, 2H), 7.07 (m, Ar*H*, 3H). ^{13}C NMR (75 MHz, $CDCl_3$, δ): 159.7, 158.0, 138.1, 135.6, 121.6, 119.6, 115.1, 114.1, 94.6, 70.2, 56.3. (ESI): m/z calcd for $C_{22}H_{18}Cl_4O_4$: 488.2; found: 488.3 $[M]^-$.

$MOMG_2Cl$: Following the procedure for $MOMG_1Cl$. $MOMG_1$-CH_2OH (3.22 g, 6.9 mmol), 3,5-dichlorophenol (4.80 g, 29.4 mmol), PPh_3 (9.05 g, 34.5 mmol), DIAD (8.30 g, 41.1 mmol, 8.14 mL). After precipitating twice in methanol, afforded $MOMG_2Cl$ (7.45 g, 89% yield) as an off-white solid. ^1H NMR (300 MHz, $CDCl_3$, δ): 3.48 (s, CH_3OCH_2O, 3H),

5.00 (s, ArC*H*$_2$O, 8H), 5.06 (s, ArC*H*$_2$O, 4H), 5.20 (s, CH$_3$O*CH*$_2$O, 2H), 6.85 (d, *J* = 1.4 Hz, Ar*H*, 8H), 6.98 (m, Ar*H*, 8H), 7.01 (s, Ar*H*, 2H), 7.09 (s, Ar*H*, 2H), 7.15 (s, Ar*H*, 1H). ^{13}C NMR (75 MHz, CDCl$_3$, δ): 159.7, 159.5, 158.0, 138.7, 138.2, 135.6, 121.6, 119.8, 118.7, 115.0, 114.1, 113.6, 94.6, 70.2, 70.0, 56.3. (MALDI-TOF): m/z calcd for $C_{50}H_{38}Cl_8O_8$: 1050.5; found: 1073.2 $[M+Na]^+$.

MOMG$_3$Cl: Following the procedure for MOMG$_1$Cl. MOMG$_2$-CH$_2$OH (0.87 g, 0.86 mmol), 3,5-dichlorophenol (1.68 g, 10.3 mmol), PPh$_3$ (3.15 g, 12.0 mmol), DIAD (2.77 g, 13.7 mmol, 2.72 mL). After precipitating twice in methanol, afforded MOMG$_3$Cl (1.43 g, 78% yield) as an off-white solid. ^{1}H NMR (300 MHz, CDCl$_3$, δ): 3.46 (s, C*H*$_3$OCH$_2$O, 3H), 4.97 (s, ArC*H*$_2$O, 16H), 5.05 (s, ArC*H*$_2$O, 12H), 5.18 (s, CH$_3$O*CH*$_2$O, 2H), 6.83 (d, *J* = 1.5 Hz, Ar*H*, 16H), 6.95 (m, Ar*H*, 16H), 7.00 (m, Ar*H*, 8H), 7.07 (m, Ar*H*, 4H), 7.14 (m, Ar*H*, 1H). ^{13}C NMR (75 MHz, CDCl$_3$, δ): 159.7, 159.4, 157.9, 138.8, 138.8, 138.2, 135.6, 121.6, 119.9, 118.8, 118.7, 115.0, 114.1, 113.6, 113.5, 94.6, 70.2, 70.0, 69.9, 56.2. (MALDI-TOF): m/z calcd for $C_{106}H_{78}Cl_{16}O_{16}$: 2175.0; found: 2197.4 $[M+Na]^+$.

2.4 General procedure for the preparation of GnCl –the cleavage of MOM Group

G$_1$Cl: Concentrated HCl (5 mL) was added to an ice cooled solution of MOMG$_1$Cl (5.30 g, 10.9 mmol) in THF/*i*-PrOH (6/1, V/V) mixed solvent (110 mL). The solution was allowed to warm to room temperature. After stirred for 12 h, the solution was concentrated, and extracted with dichloromethane (50 mL × 3). The extract was dried by anhydrous Na$_2$SO$_4$ and concentrated. After purified by flash column chromatography, afforded the G$_1$Cl (4.55 g, 92% yield) as an off-white solid. ^{1}H NMR (300 MHz, CDCl$_3$, δ): 4.86 (s, ArO*H*, 1H), 5.00 (s,

ArC*H*$_2$O, 4H), 6.86 (m, Ar*H*, 6H), 6.98 (m, Ar*H*, 3H). ^{13}C NMR (75 MHz, $CDCl_3$, δ): 159.6, 156.3, 138.4, 135.6, 121.6, 118.4, 114.1, 114.0, 69.9. (ESI): m/z calcd for $C_{20}H_{14}Cl_4O_3$: 444.1; found: 443.3 $[M-H]^-$.

G_2Cl: Following the procedure for G_1Cl. MOMG_2Cl (4.80 g, 4.6 mmol), THF/*i*-PrOH (6/1, V/V) (110 mL), conc. HCl (10 mL). The reaction mixture was precipitated twice by methanol/water (1/1, V/V) mixed solvent, afforded G_2Cl (4.30 g, 94% yield). ^{1}H NMR (300 MHz, $CDCl_3$, δ): 5.00 (s, ArC*H*$_2$O, 8H), 5.04 (s, ArC*H*$_2$O, 4H), 6.85(m, Ar*H*, 10H), 6.97 (s, Ar*H*, 8H), 7.01 (m, Ar*H*, 2H), 7.04 (m, Ar*H*, 1H). ^{13}C NMR (75 MHz, $CDCl_3$, δ): 159.6, 159.4, 156.3, 139.1, 138.2, 135.6, 121.6, 118.7, 118.4, 114.1, 114.0, 113.6, 70.2, 69.8. (MALDI-TOF): m/z calcd for $C_{48}H_{34}Cl_8O_7$: 1006.4; found: 1029.1 $[M+Na]^+$.

G_3Cl: Following the procedure for G_1Cl. MOMG_3Cl (1.20 g, 0.55 mmol), THF/*i*-PrOH (6/1, V/V) (80 mL), conc. HCl (5 mL). The reaction was carried out at 45 ^{o}C for 8 h. The reaction mixture was precipitated twice by methanol/water (1/1, V/V) mixed solvent, afforded G_3Cl (1.10, 94% yield) as an off-whited solid. ^{1}H NMR (300 MHz, $CDCl_3$, δ): 4.97 (s, ArC*H*$_2$O, 8H), 5.02 (m, ArC*H*$_2$O, 12H), 6.83-7.07 (m, Ar*H*, 45H). ^{13}C NMR (75 MHz, $CDCl_3$, δ): 159.7, 159.4, 159.4, 156.2, 139.2, 138.9, 138.2, 135.6, 121.7, 118.8, 118.7, 114.1, 113.9, 113.7, 113.5, 70.2, 70.0, 69.7. (MALDI-TOF): m/z calcd for $C_{104}H_{74}Cl_{16}O_{15}$: 2130.9; found: 2153.3 $[M+Na]^+$.

2.5 General procedure for the preparation of GnCl-P

G_1Cl-P: G_1Cl (1.34 g, 3.0 mmol) was dissolved in anhydrous THF (15 mL). *N*, *N*-Diisopropylethylamine (DIPEA, 1.17 g, 9.0 mmol, 1.50 mL) was added followed by

dropwise addition of 2-cyanothyl *N*, *N*-diisopropylphosphoramidochloridite (0.86 g, 3.6 mmol, 0.85 mL). After 30 h, analytical TLC showed no more starting material existed. The reaction mixture was diluted with ethyl acetate (30 mL). The solution was washed with saturated aqueous solution of $NaHCO_3$ (20 mL × 3) and NaCl (20 mL), dried by anhydrous Na_2SO_4 and concentrated. After purified by flash column chromatography, G_1Cl-P (1.75 g, 90 % yield) was obtained as colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$, δ): 1.15 (d, *J* = 6.6 Hz, CH (CH_3)$_2$, 6H), 1.23 (d, *J* = 6.6 Hz, CH (CH_3)$_2$, 6H), 2.67 (t, *J* = 6.3 Hz, OCH_2CH_2CN, 2H), 3.66-3.79 (m, C*H* (CH_3)$_2$, 2H), 3.85-4.00 (m, OCH_2CH_2CN, 2H), 5.02 (s, $ArCH_2O$, 4H), 6.85 (d, *J* = 1.5 Hz Ar*H*, 4H), 6.97 (m, Ar*H*, 2H), 7.07 (m, Ar*H*, 3H). ^{13}C NMR (75 MHz, $CDCl_3$, δ): 159.6, 155.1, 155.0, 138.1, 135.5, 121.6, 119.9, 118.6, 118.5, 117.6, 114.1, 70.0, 59.2, 58.9, 43.9, 43.8, 24.8, 24.7, 24.5, 24.4, 20.6, 20.5. ^{31}P NMR (162 MHz, $CDCl_3$, δ): 147.0. (MALDI-TOF): m/z calcd for $C_{29}H_{32}Cl_4N_2O_4P$: 644.4; found: 683.1 $[M+K]^+$.

G_2Cl-P: Following the procedure for G_1Cl-P. G_2Cl (1.00 g, 1.0 mmol), DIPEA (0.38 g, 3.0 mmol, 0.49 mL), 2-cyanothyl *N*, *N*-diisopropylphosphoramidochloridite (0.35 g, 1.5 mmol, 0.35 mL). After concentrated, G_2Cl-P (1.10 g, 92% yield) was obtained by precipitated in methanol as an off-white solid. ^{1}H NMR (300 MHz, $CDCl_3$, δ): 1.15 (d, *J* = 6.6 Hz, CH (CH_3)$_2$, 6H), 1.23 (d, *J* = 6.6 Hz, CH(CH_3)$_2$, 6H), 2.64 (t, *J* = 6.3 Hz, OCH_2CH_2CN, 2H), 3.66-3.78 (m, C*H* (CH_3)$_2$, 2H), 3.83-3.93 (m, OCH_2CH_2CN, 2H), 5.00 (s, $ArCH_2O$, 8H), 5.06 (s, $ArCH_2O$, 4H), 6.85-7.16 (m, Ar*H*, 21H). ^{13}C NMR (75 MHz, $CDCl_3$, δ): 159.6, 159.4, 155.0, 154.9, 138.7, 138.1, 135.6, 121.6, 120.1, 118.7, 118.5, 118.4, 117.6, 114.0, 113.6, 70.1, 69.8, 59.1, 58.9, 43.9, 43.8, 24.8, 24.7, 24.5, 24.4, 20.5, 20.4. ^{31}P NMR (162

MHz, $CDCl_3$, δ): 146.5. (MALDI-TOF): m/z calcd for $C_{57}H_{51}Cl_8N_2O_8P$: 1206.6; found: 1245.3 $[M+K]^+$.

G_3Cl-P: Following the procedure for G_1Cl-P. G_3Cl (0.44 g, 0.21 mmol), DIPEA (0.08 g, 0.63 mmol, 0.10 mL), 2-cyanothyl *N*, *N*-diisopropylphosphoramidochloridite (0.059 g, 0.25 mmol, 0.06 mL). After concentrated, G_3Cl-P (0.44 g, 92% yield) was obtained by precipitated in methanol as an off-white solid. ^{1}H NMR (300 MHz, $CDCl_3$, δ): 1.15 (d, *J* = 6.6 Hz, CH $(CH_3)_2$, 6H), 1.21 (d, *J* = 6.9 Hz, CH $(CH_3)_2$, 6H), 2.60 (t, *J* = 6.3 Hz, OCH_2CH_2CN, 2H), 3.66-3.74 (m, $CH(CH_3)_2$, 2H), 3.84-3.90 (m, OCH_2CH_2CN, 2H), 4.97 (s, $ArCH_2O$, 16H), 5.04 (s, $ArCH_2O$, 12H), 6.83-7.15 (m, Ar*H*, 45H). ^{13}C NMR (75 MHz, $CDCl_3$, δ): 159.7, 159.4 159.4, 155.0 ,154.9, 138.9, 138.8, 138.2, 135.6, 121.6, 120.2, 118.9, 118.7, 118.5, 118.4, 117.6, 114.1, 113.6, 113.5, 70.2, 70.0, 69.7, 59.2, 58.9, 44.0, 43.8, 24.8, 24.7, 24.6, 24.5, 20.5, 20.4. ^{31}P NMR (162 MHz, $CDCl_3$, δ): 144.9. (MALDI-TOF): m/z calcd for $C_{113}H_{91}Cl_{16}N_2O_{16}P$: 2331.2; found: 2370.2 $[M+K]^+$.

3. Synthesis DNA-Dendron Conjugates

General Procedure for the preparation DNA-Dendron conjugates: The CPG loaded DNA was synthesized using ABI 394 DNA synthesizer in 1 μmol scale with a standard phosphoramidite DNA synthesis protocol.[2] The DNA-loaded CPG (1 μ mol) was transferred into a vial, then 5-ethylthiotetrazole (100 μmol) and G_nCl-P (50 μmol) were added consequently. After dried *in vacuo*, 0.5 mL anhydrous THF was added under dry nitrogen protection. The reaction mixture was allowed to stay overnight under room temperature. Then CPG was washed twice with anhydrous THF followed by oxidation with iodine and water in

THF. After cleaved by concentrated ammonia solution in 55 ^{o}C for 3 h, the crude product was purified by 10% denaturing polyacrylamide gel electrophoresis (PAGE) with 1×TBE buffer as the running buffer. Identification of the conjugates was achieved by UV shadowing. The respective bands were excised from the gel and incubated in deionized water for 12 h. After centrifugation, the supernatant was desalted with C18 column and dried by lyophilization. The product was analyzed by MALDI-TOF. The purity of G_1-18, G_2Cl-18 and G_2Cl-9 was assessed by 20% PAGE, followed by staining with Stains All, and the purity of G_3Cl-18 was analyzed by 2% agarose gel. The samples were stored at -20 ^{o}C before use.

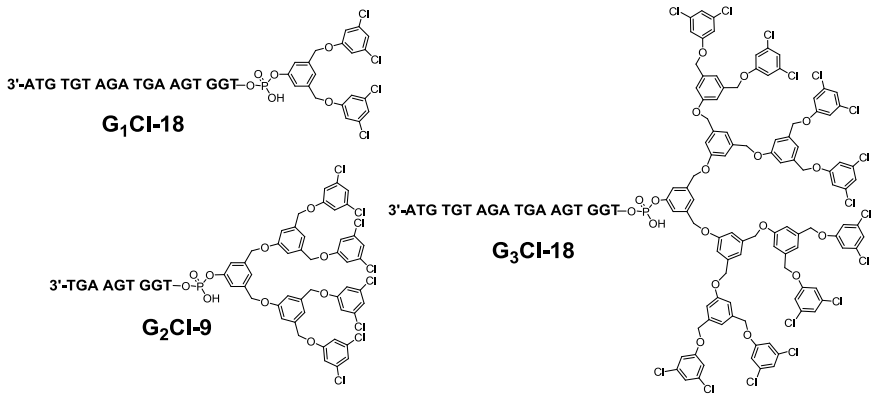


Chart S2. Chemical structures of other DNA-dendron hybrids G1Cl-18, G3Cl-18 and G2Cl-9.

Table S1. MALDI-TOF Results and Isolated Yield of DNA-Dendron Hybrids.

sample	calculated	found	Error (cal.-fou.)	Yield
G_1Cl-18	6140	6144	-4	5.9%
G_2Cl-18	6702	6705	-3	15.6%
G_3Cl-18	7826	7832	-6	1.2%
G_2Cl-9	3862	3862	0	3.8%

4. Formation of Fibers

The G_nCl-DNA was dissolved in water to make a concentrated stock solution. Dilute the stock solution with deionized water to desired concentration and add 5 μL of dichloromethane. After vibration by a vortex mixer and centrifugation at 6000 r/min for 2 min, heated the solution to 90 ^{o}C and kept for 30 min, and then allowed it to cool to room temperature naturally. Keep the assembled solution under 4 ^{o}C for storage before used.

5. CMC Measurement Experiment

By using a stock solution of G_2Cl-18 varying concentrations ranging from 0.05 to 20 μM were prepared. Acetone solution of Nile Red (0.02 mM) 40 μL was added to every tube and sonicated for 10 min. Then the solvent was evaporated under vacuum overnight and the redissolved with 200 μL water. Fluorescence spectra were recorded at room temperature using an excitation wavelength of 550nm.

6. DNA Modified Gold Nanoparticles Preparation and Hybridization with G_2Cl-18 Nanofiber

5 nm gold nanoparticle and thioctic acid modified DNA were prepared and purified according to the published method.[6] 28.6 μL of DNA (87.4 μM) was added to 50 μL solution of Au nanoparticles (3.4 μM). The solution was shaked overnight at room temperature on an orbital shaker at low speed. Then add 12 μL of 1M NaCl and 3 μL 0.4 M phosphate buffer and shake at low speed for another 12 hours at room temperature. Use ultracentrifuge to centrifuge the suspension to form a redcolored solution of nanoparticles.

The concentration of the Au/DNA conjugatets was calculated by measuring the UV absorption of the gold particle at 520 nm wavelength.

G_2Cl-18 was first assembled in 50 mM Tris-HCl buffer at a concentration of 20 μM. Then 5 μL of the assembled solution was mixed with 17 μL of the DNA modified gold nanoparticle (5.8 μM) and kept overnight. The solution was used for TEM sample preparation without further treatment.

7. Nile Red Encapsulation Experiments

To the assembled solution of G_2Cl-18 (20 μM) 50 μL in 0.5 mL vial, the acetone solution of Nile Red (0.038 mM) 10 μL was added. The acetone was evaporated by opening the microcentrifuge tube cap overnight and the final volume of the solution became about 30-40 μL. The resultant solution was diluted to about 500 μL directly for the fluorescence spectroscopy experiment. The fluorescence spectra were acquired on a HITACHI Fluorescence Spectrophotometer F-4500 and the excitation wavelength is 550 nm.

Fluorescence microscopy experiment: The coverslips were cleaned by sonication in detergent, ultrapure water, acetone, ethanol, NaOH/ethanol, ultrapure water for 30 min each, and boiled in 1/3 H_2O_2/H_2SO_4 for 2 h. The clean coverslips were stored in ultrapure water until use. Immediately prior to use, two coverslips were dried by nitrogen flow. 7 μL of a solution were deposited onto one slide and covered by a second one. The DNA solution was drawn under the capillary forces created by the two slides and sealed with vacuum grease.

Samples were imaged on an Olympus Reflected Fluorescence System (the microscope was Olympus B × 51). Blue light (420-480 nm) was filtered from a mercury arc lamp (Olympus

U-RFL-T) for excitation. The emitted fluorescence passed through a dichroic mirror (DM 500). Images were recorded to a computer via a cooled CCD camera (Q-IMAGING RETIGA 2000R) using the corresponding software (Image-Pro Express Version 6.0).

8. Cryo-TEM and TEM Experiment

Cryo-TEM samples were prepared in a controlled environment vitrification system (CEVS) at 28 ^{o}C.[3] A micropipet was used to load 5 μL of the assembled solution of G_nCl-DNA onto a lacey support TEM grid that was held with tweezers. The excess solution was blotted with a piece of filter paper, resulting in the formation of thin films suspending the mesh holes. After waiting for about 10 s to release any stress induced during blotting, the samples were quickly plunged into a reservoir of liquid ethane (cooled by liquid nitrogen) at its melting temperature. The vitrified samples were then stored in liquid nitrogen until they were transferred to a cryogenic sample holder (Gatan 626) and examined with a JEM 2200FS TEM (200 keV) at about -174 ^{o}C. The images were recorded on a Gatan multiscan CCD and processed into a digital micrograph.

TEM samples were prepared by drop casting 7 μL of solution on carbon coated copper grids. After 5 min, the excess solution was blotted with a piece of filter paper. Then a drop of 1 wt % uranyl acetate aqueous solution was deposited onto the surface of the sample-loaded grid. After 5 min, the excess uranyl acetate aqueous solution was blotted with a piece of filter paper. The sample-loaded grid was dried overnight. TEM images were recorded on a JEOL JEM-1011 microscope operated at 100 KeV.

9. Figures

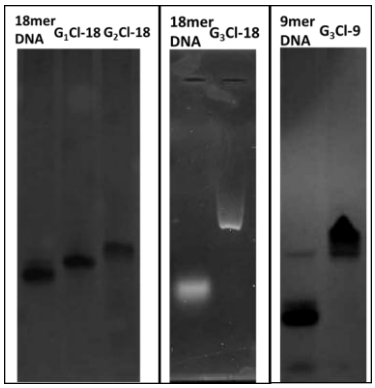


Figure S1. The gel electrophoresis results of the G_nCl-DNA hybrids.

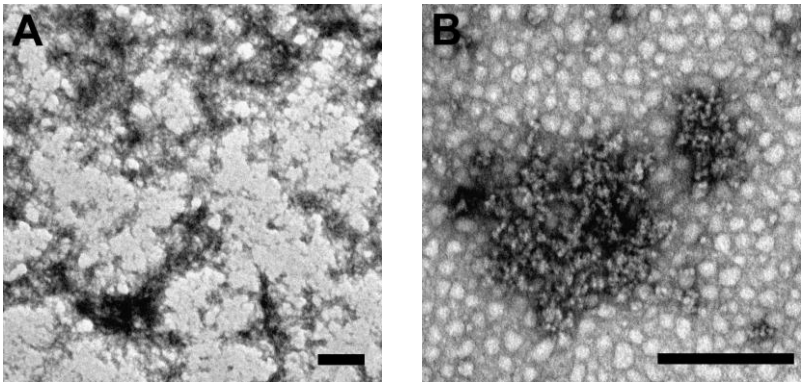


Figure S2. The TEM images of the G_2Cl-18 nanofibers without annealing. The scale bar is 200 nm.

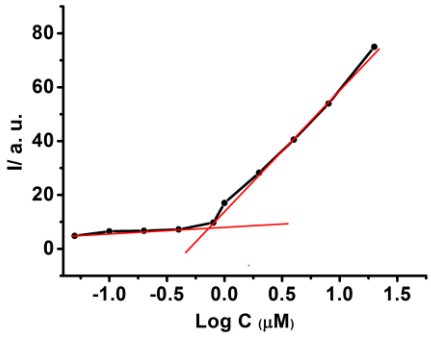


Figure S3. CMC determination curve of G_2Cl-18.

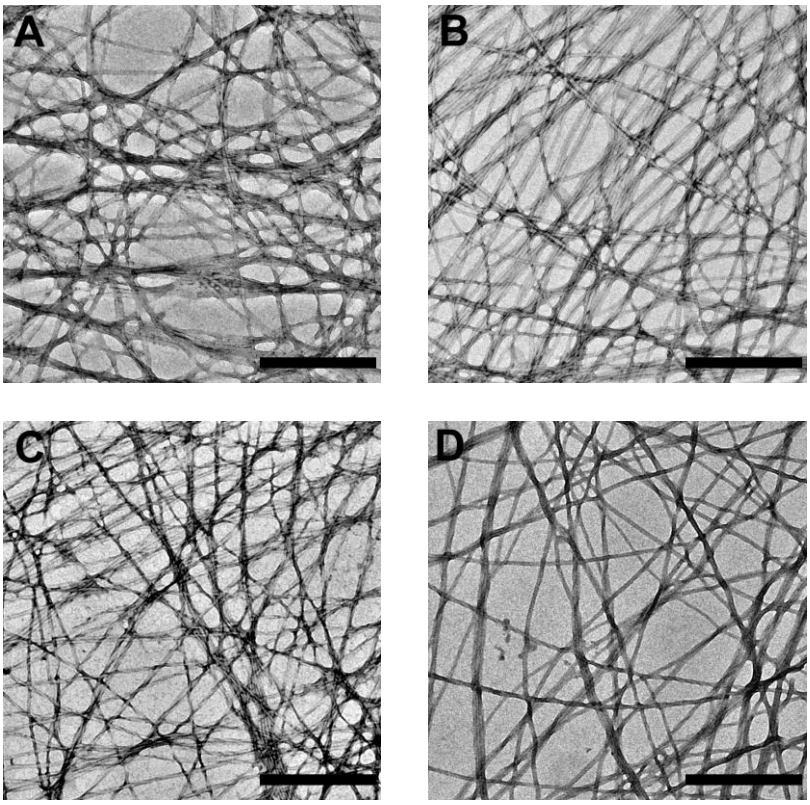


Figure S4. The TEM images of the G_2Cl-18 nanofibers at different concentrations: (A) 1 μM, (B) 10 μM, (C) 20 μM and (D) 50 μM. The scale bar is 500 nm.

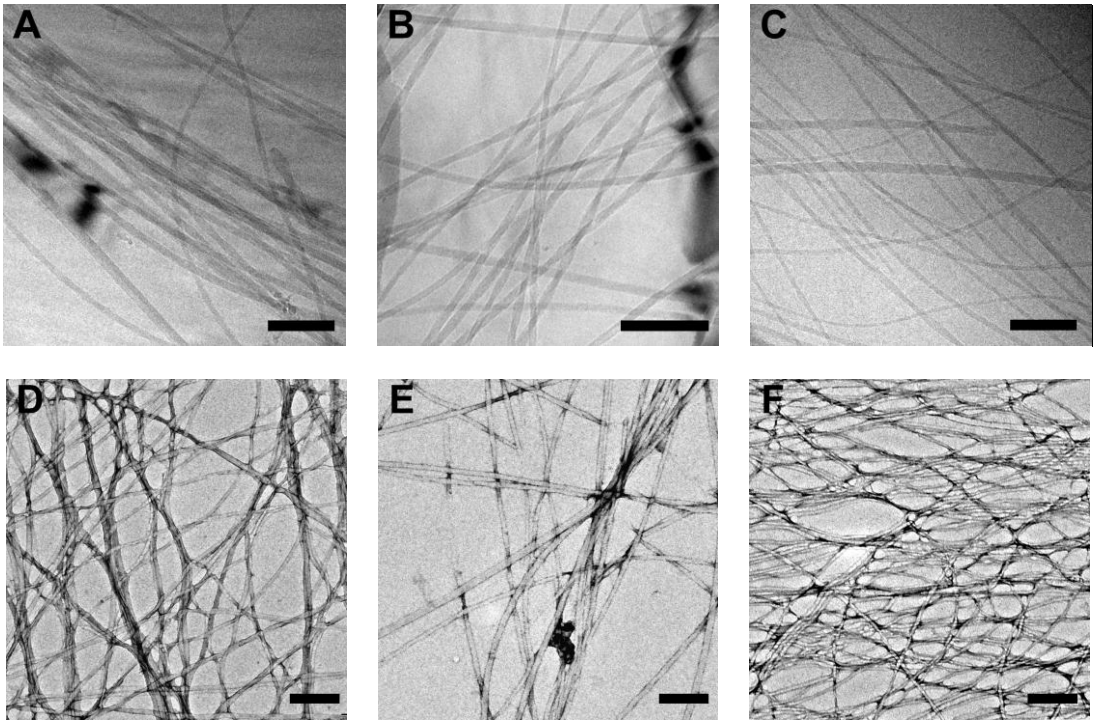


Figure S5. Cryo-TEM and TEM image of (A and D) G_1Cl-18, (B and E) G_3C-18 and (C and F) G_2Cl-9. The scale bar is 200 nm.

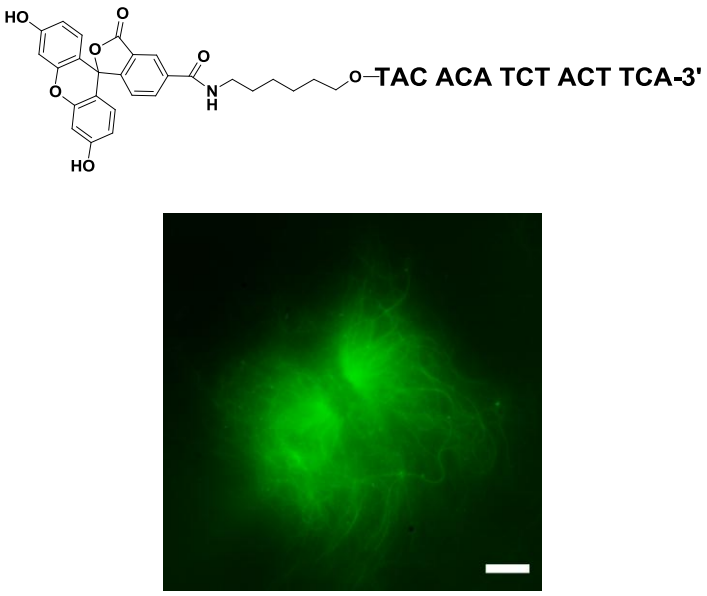


Figure S6. The chemical structure of FAM-15 and fluorescent images of the G_2Cl-18 nanofibers hybridized with FAM-15. The scale bar is 20 μm.

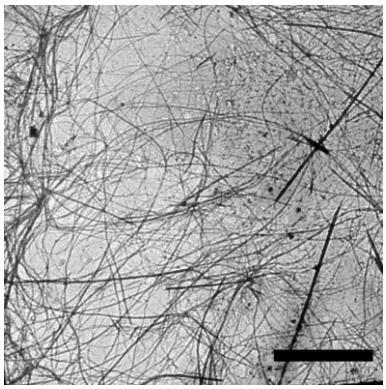


Figure S7. The TEM images of the G_2Cl-18 nanofibers after Nile Red encapsulated. The scale bar is 10 μm.

10. ^{1}H NMR, ^{13}C NMR, ^{31}P NMR and MALDI-TOF Spectra

10.1 MALDI-TOF Spectra of G_nCl-DNA

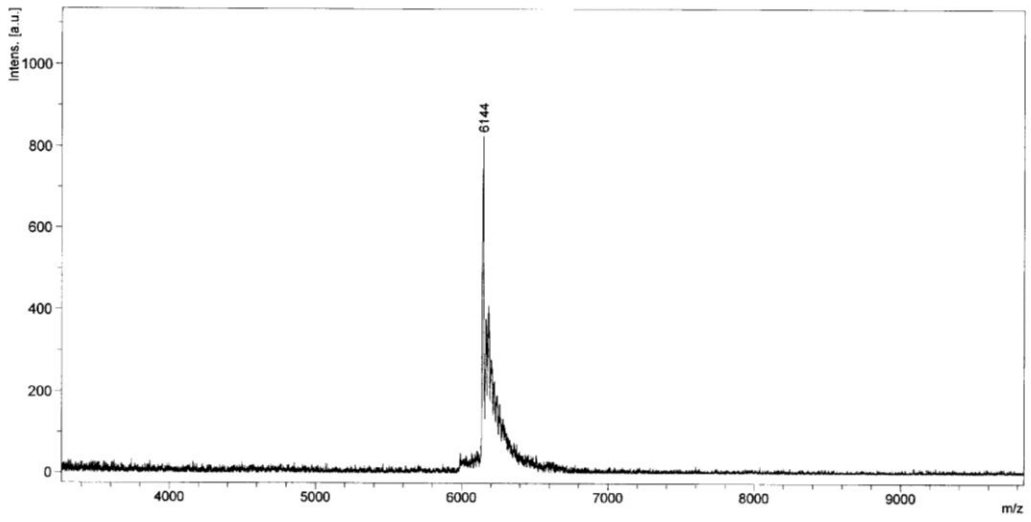


Figure S8. MALDI-TOF spectra of **G_1Cl-18**

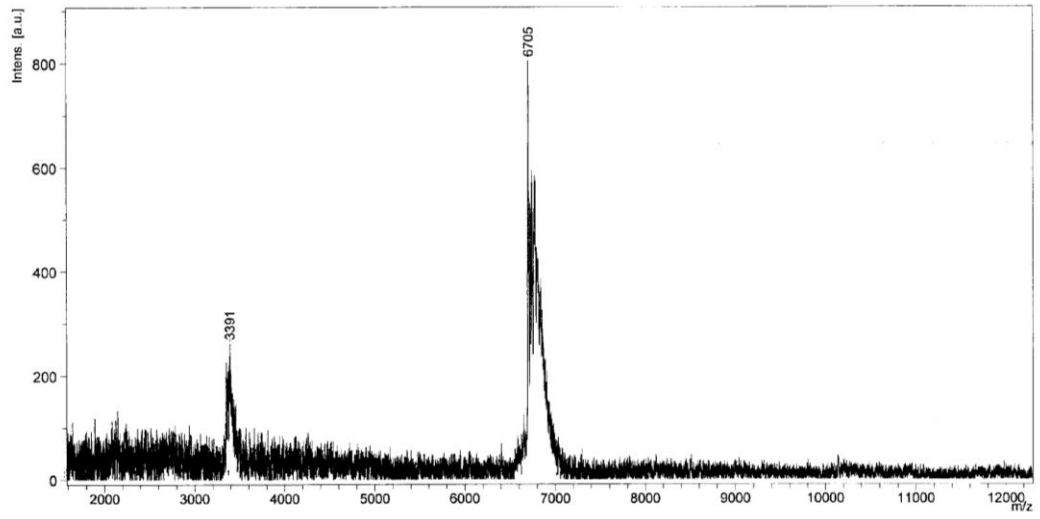


Figure S9. MALDI-TOF spectra of **G_2Cl-18.**

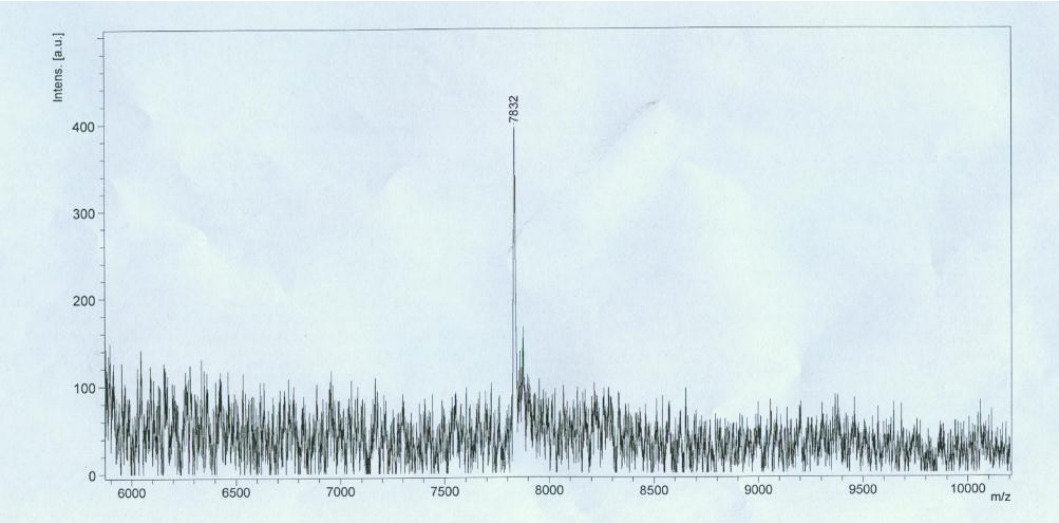


Figure S10. MALDI-TOF spectra of **G_3Cl-18.**

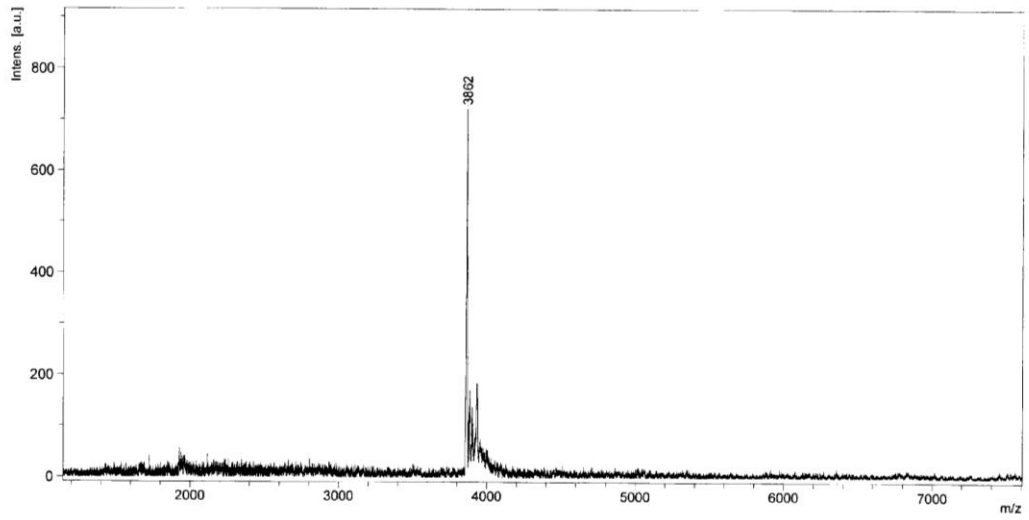


Figure S11. MALDI-TOF spectra of **G_2Cl-9**.

7.2 ^{1}H NMR, ^{13}C NMR, ^{31}P NMR and MALDI-TOF Spectra of Organic Compounds

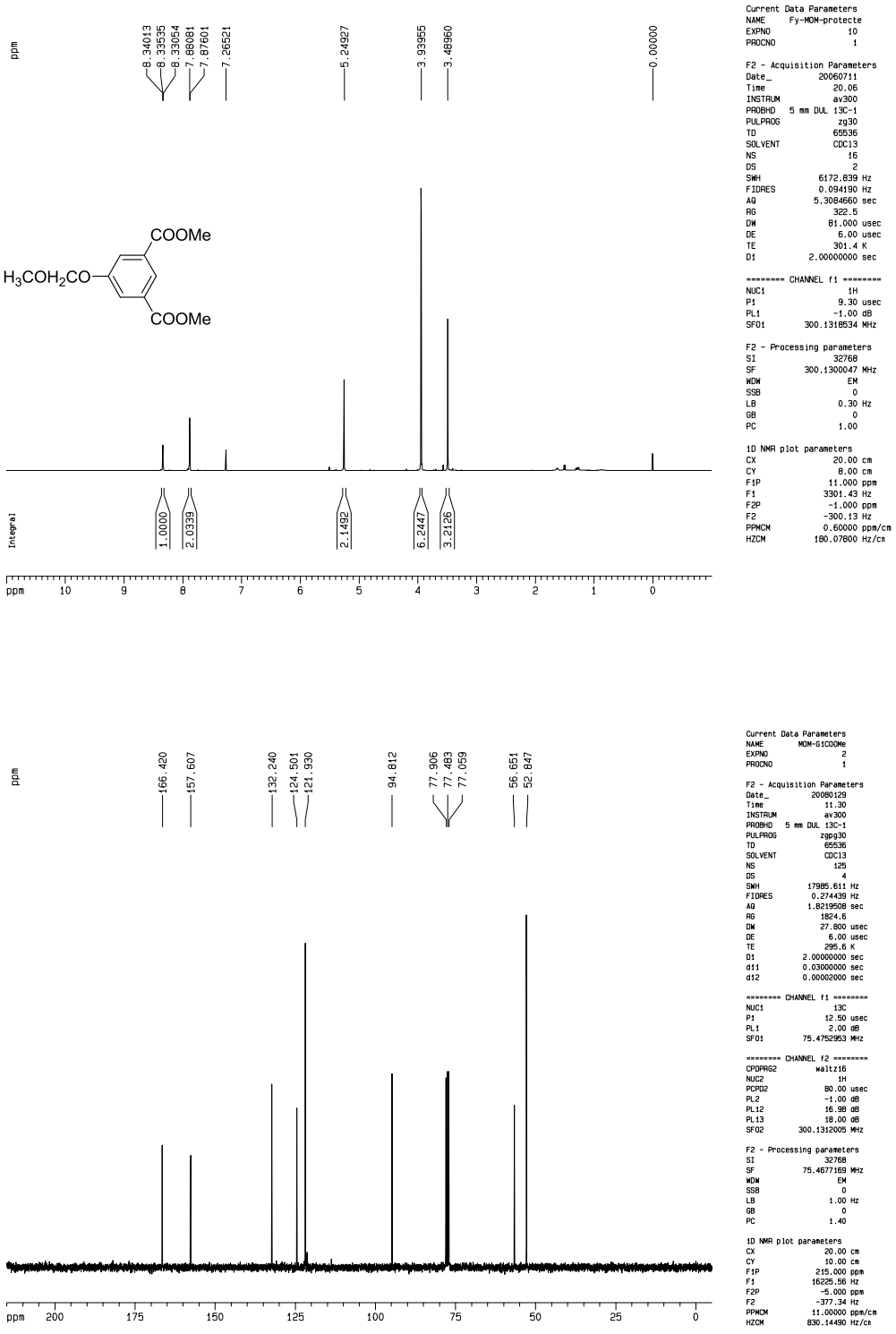


Figure S12. ^{1}H NMR and ^{13}C NMR spectra of **MOMG$_0$-COOMe**

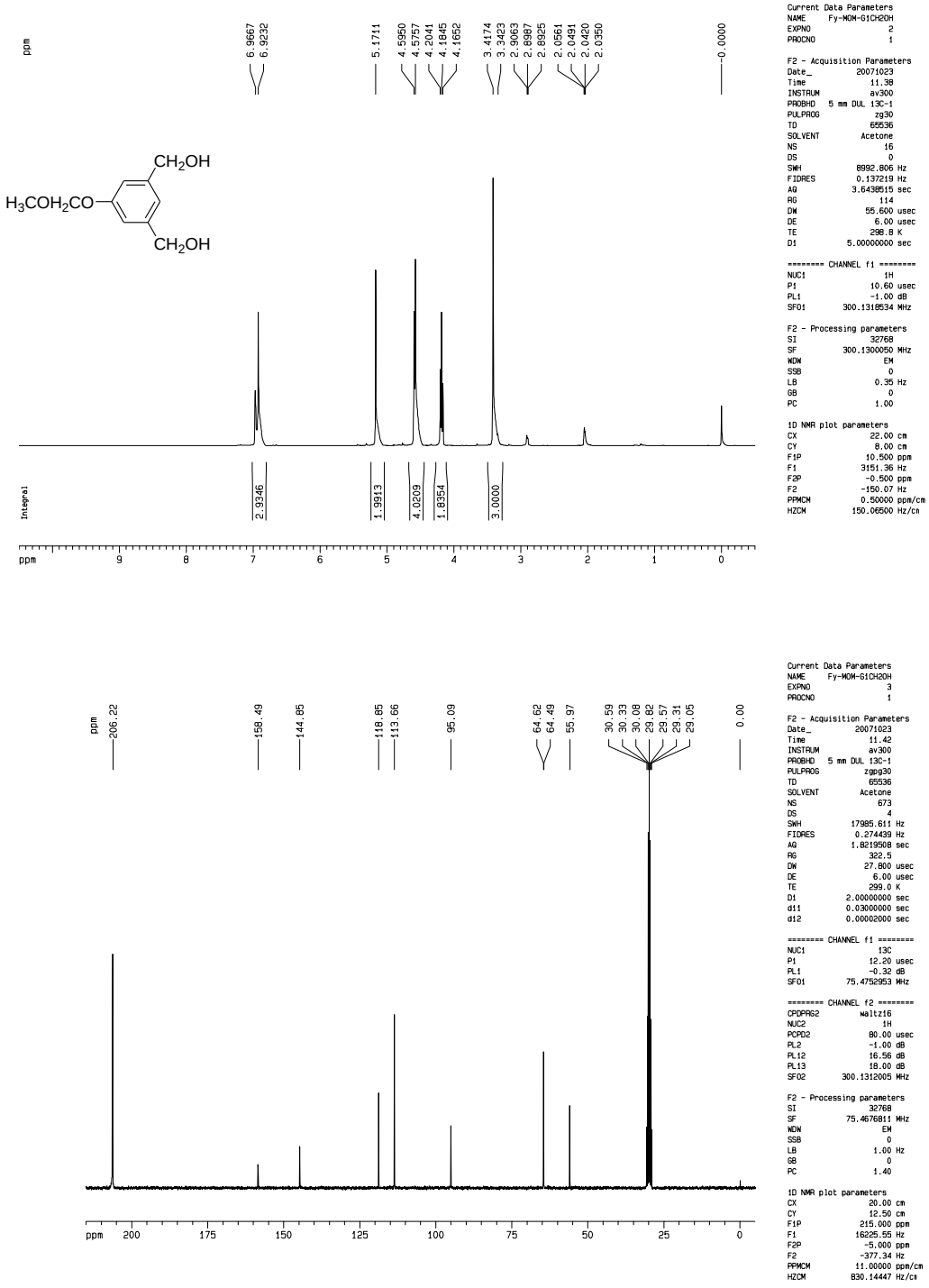
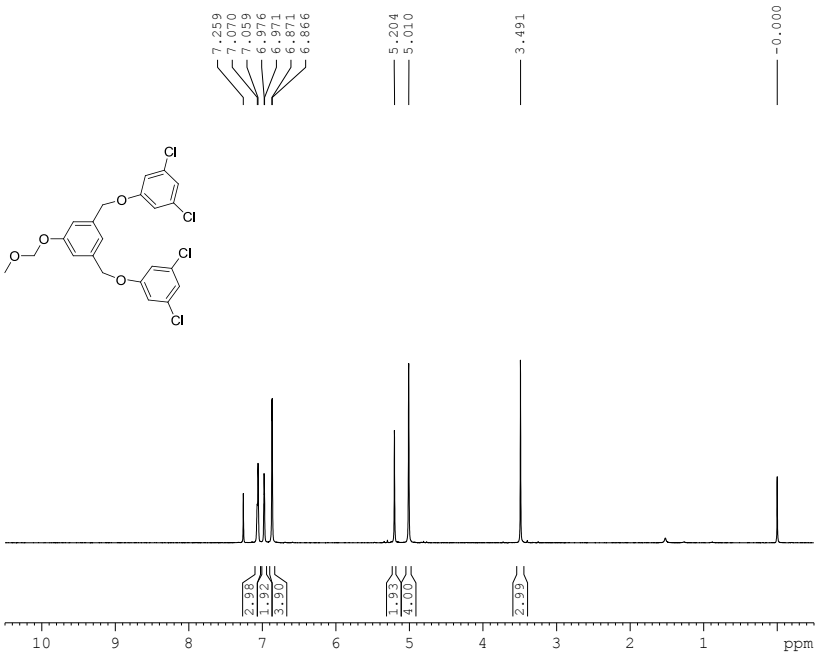


Figure S13. ^{1}H NMR and ^{13}C NMR spectra of **MOMG$_0$-CH$_2$OH**

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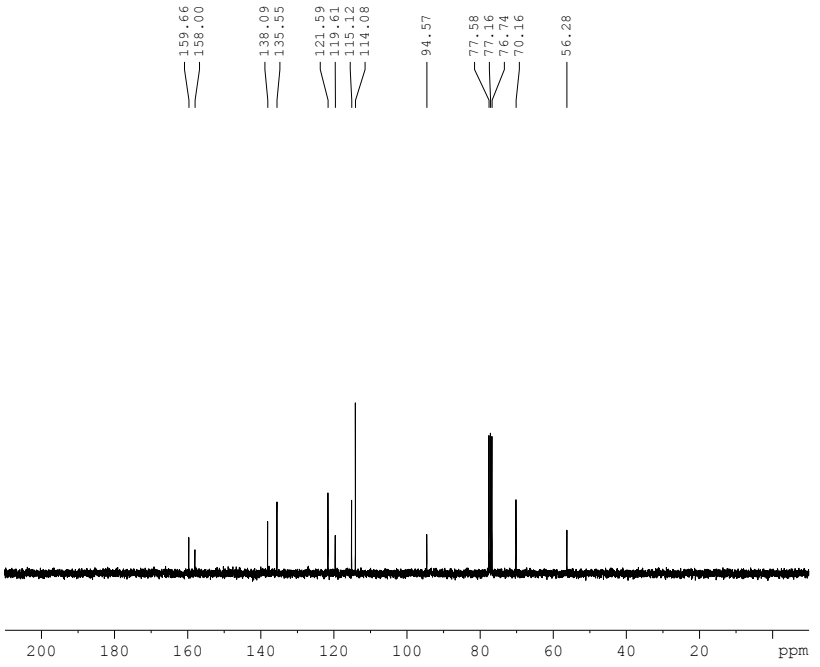


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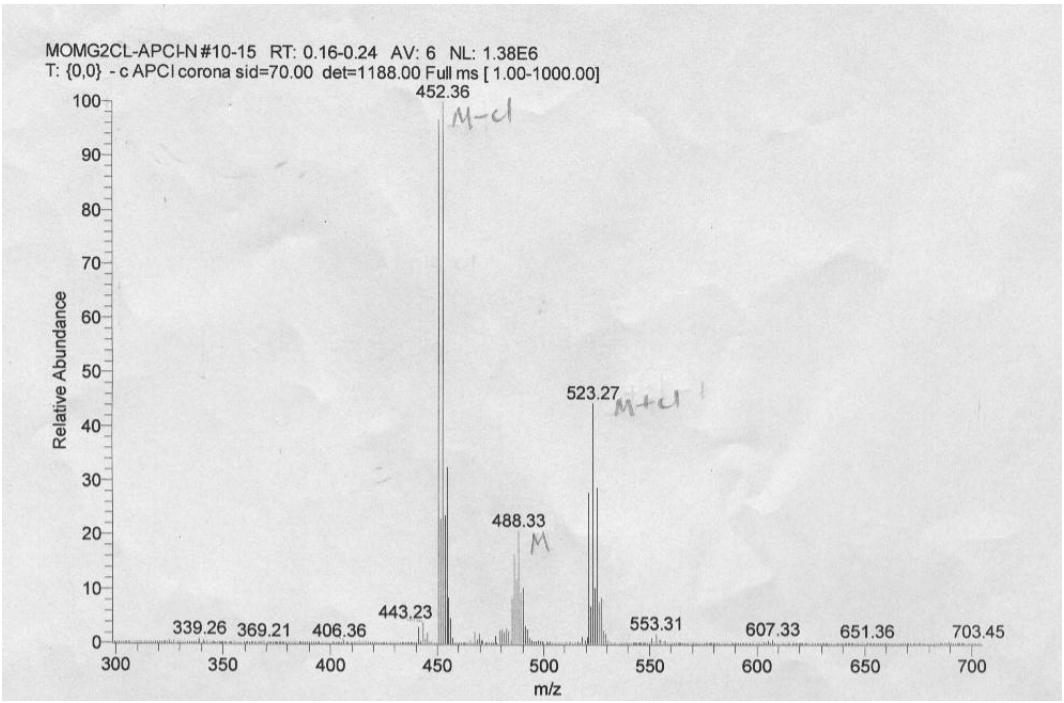
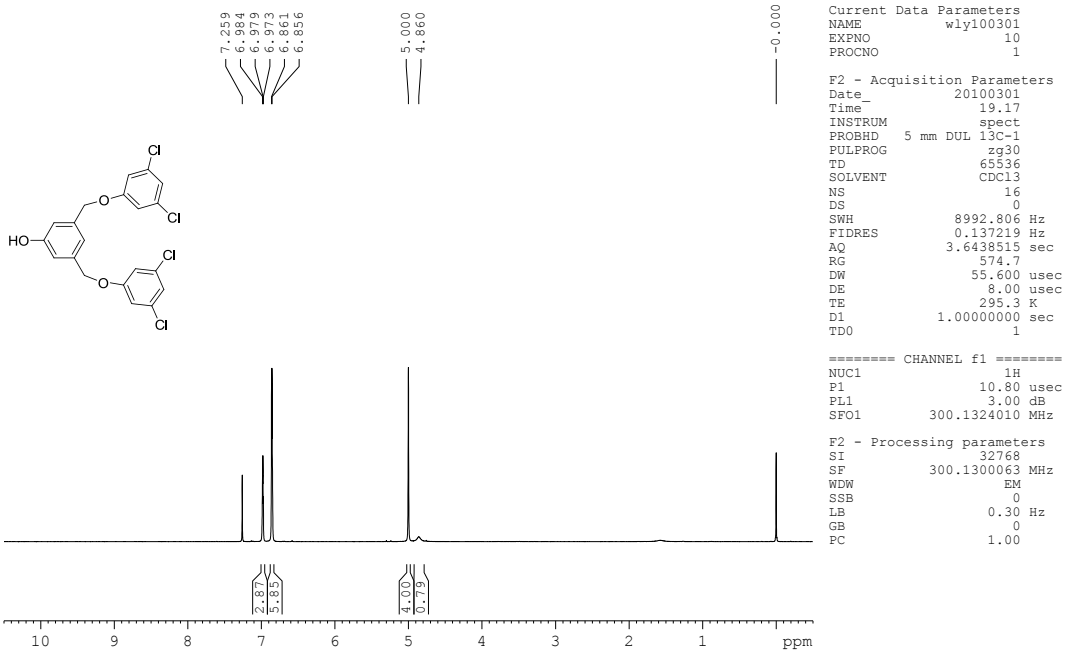
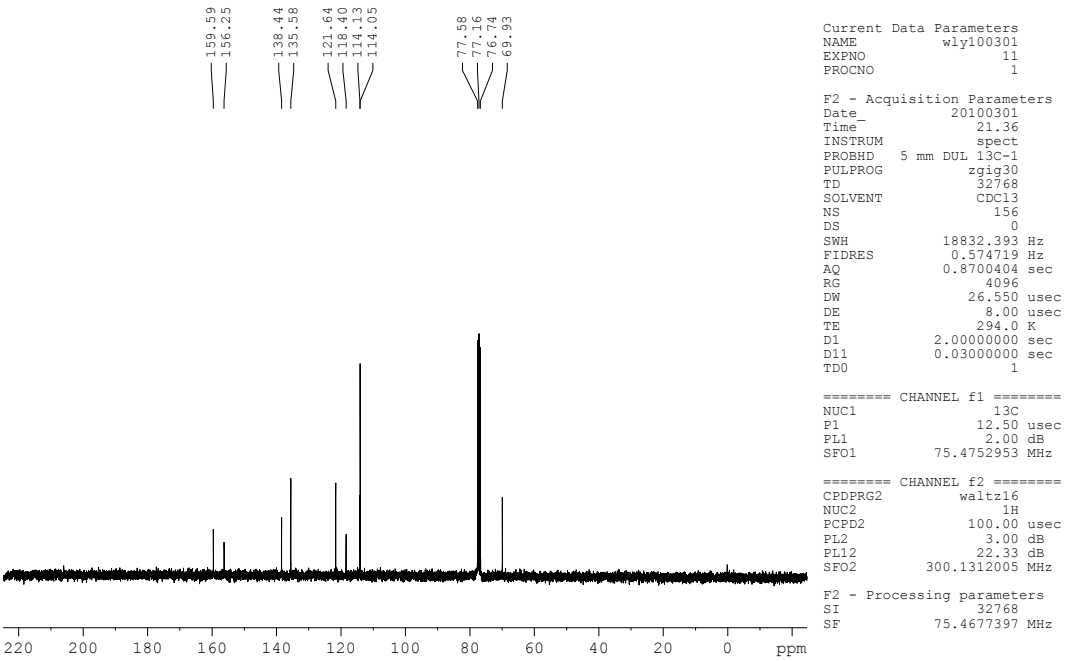


Figure S14. ^{1}H NMR, ^{13}C NMR and ESI spectra of **MOMG$_1$Cl.**





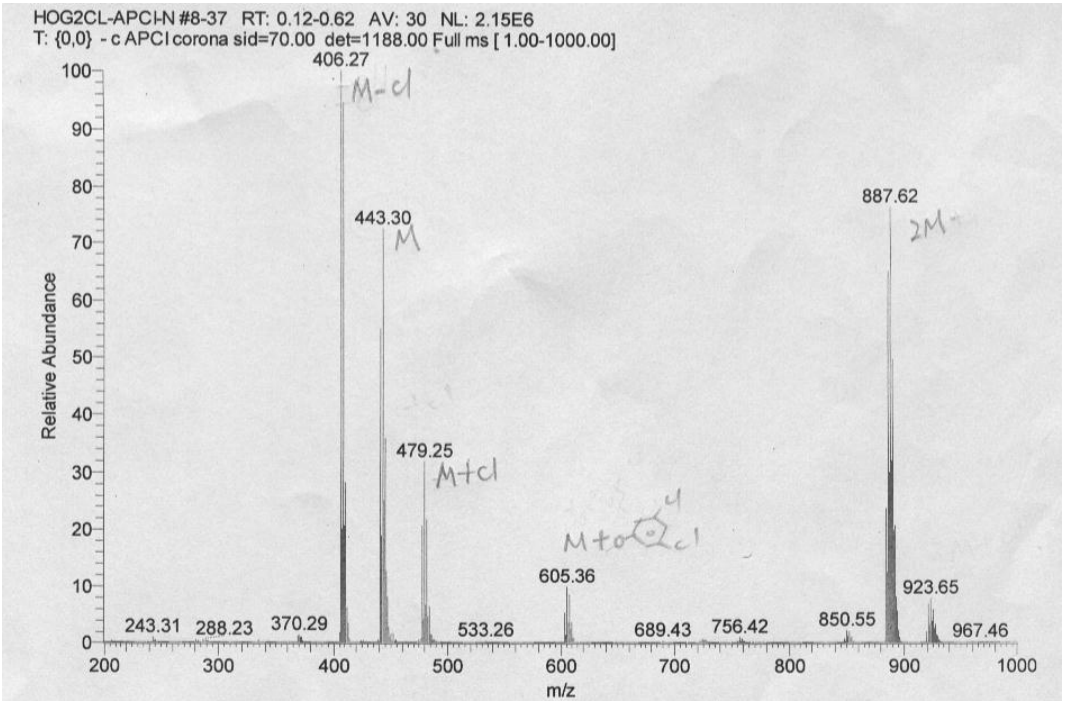
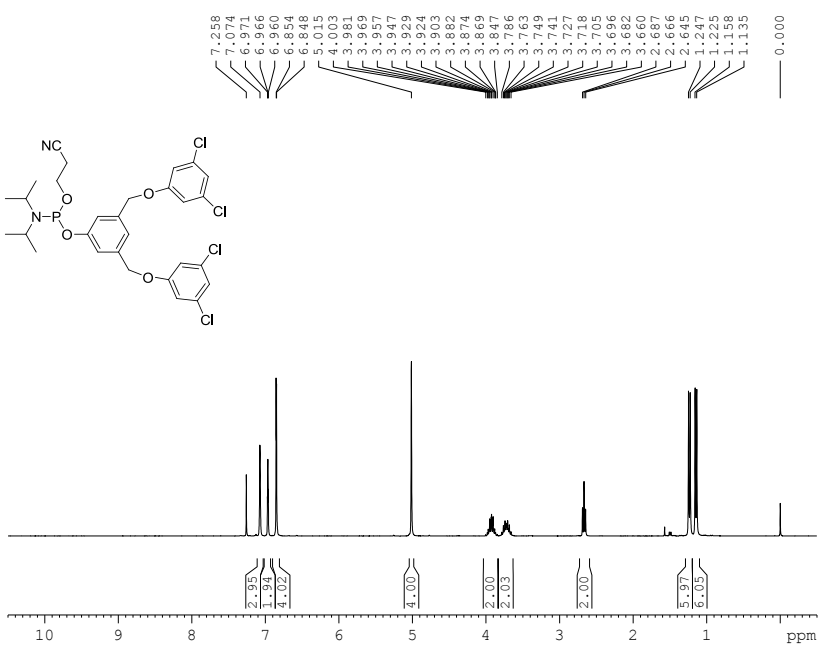


Figure S15. ^{1}H NMR, ^{13}C NMR and ESI spectra of **G_1Cl.**

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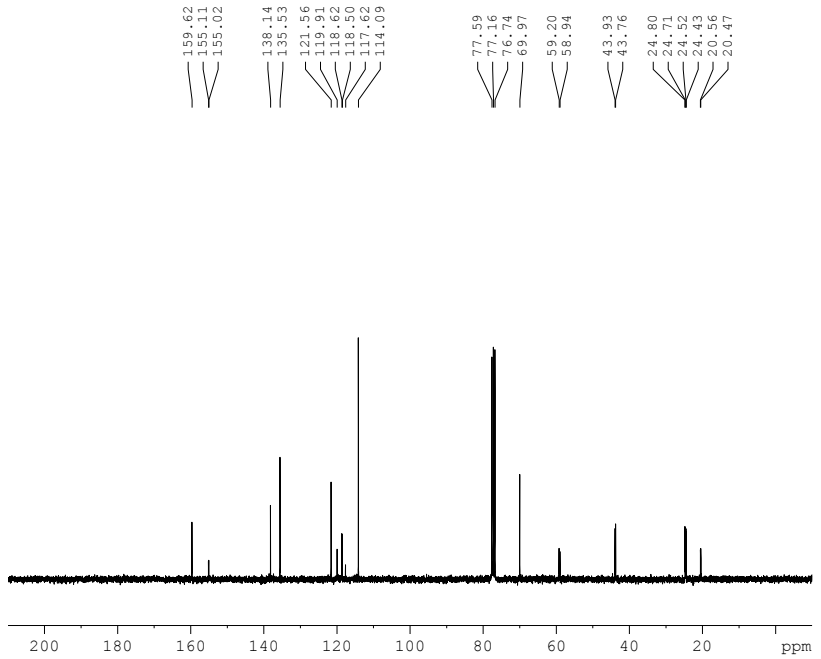


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TE                294.6 K
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PL1                2.00 dB
SFO1         75.4752953 MHz

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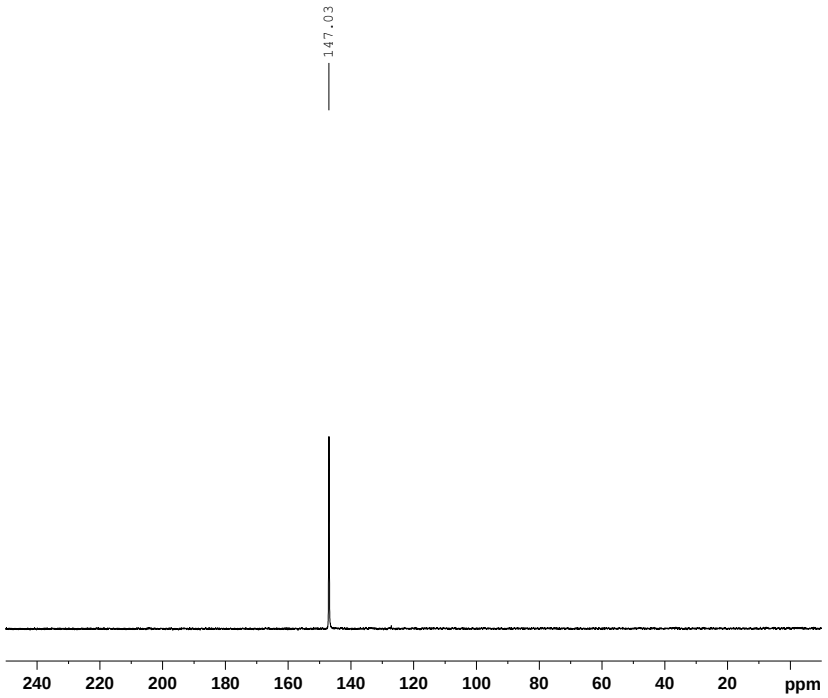


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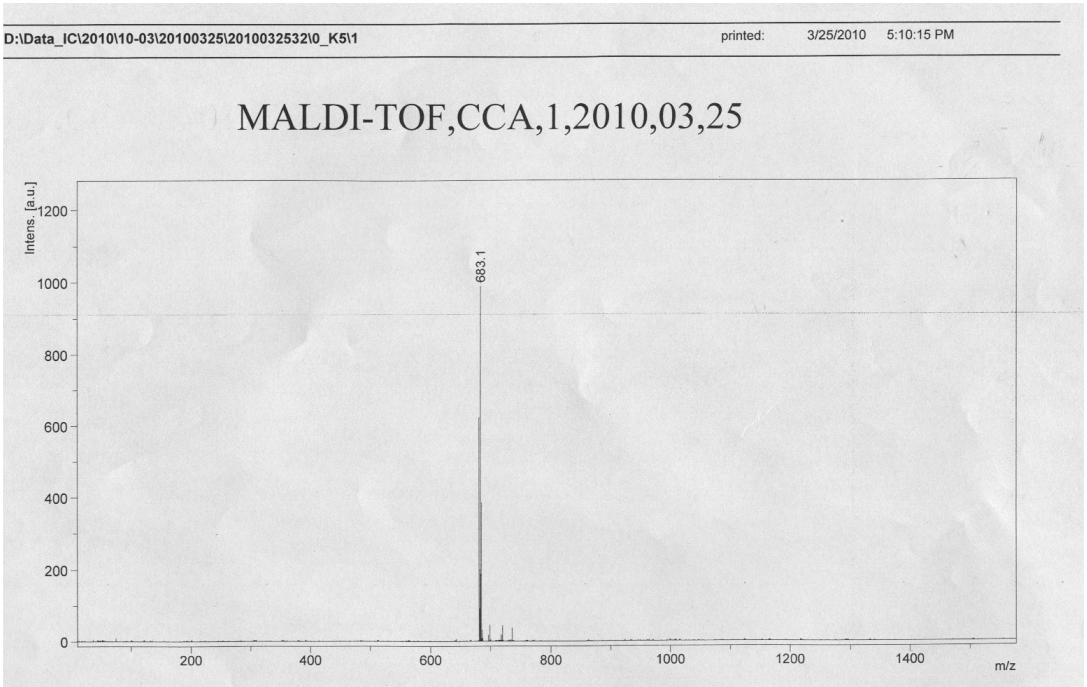


Figure S16. ^{1}H NMR ,^{13}C NMR, ^{31}P NMR and MALDI-TOF spectra of **G_1Cl-P**.

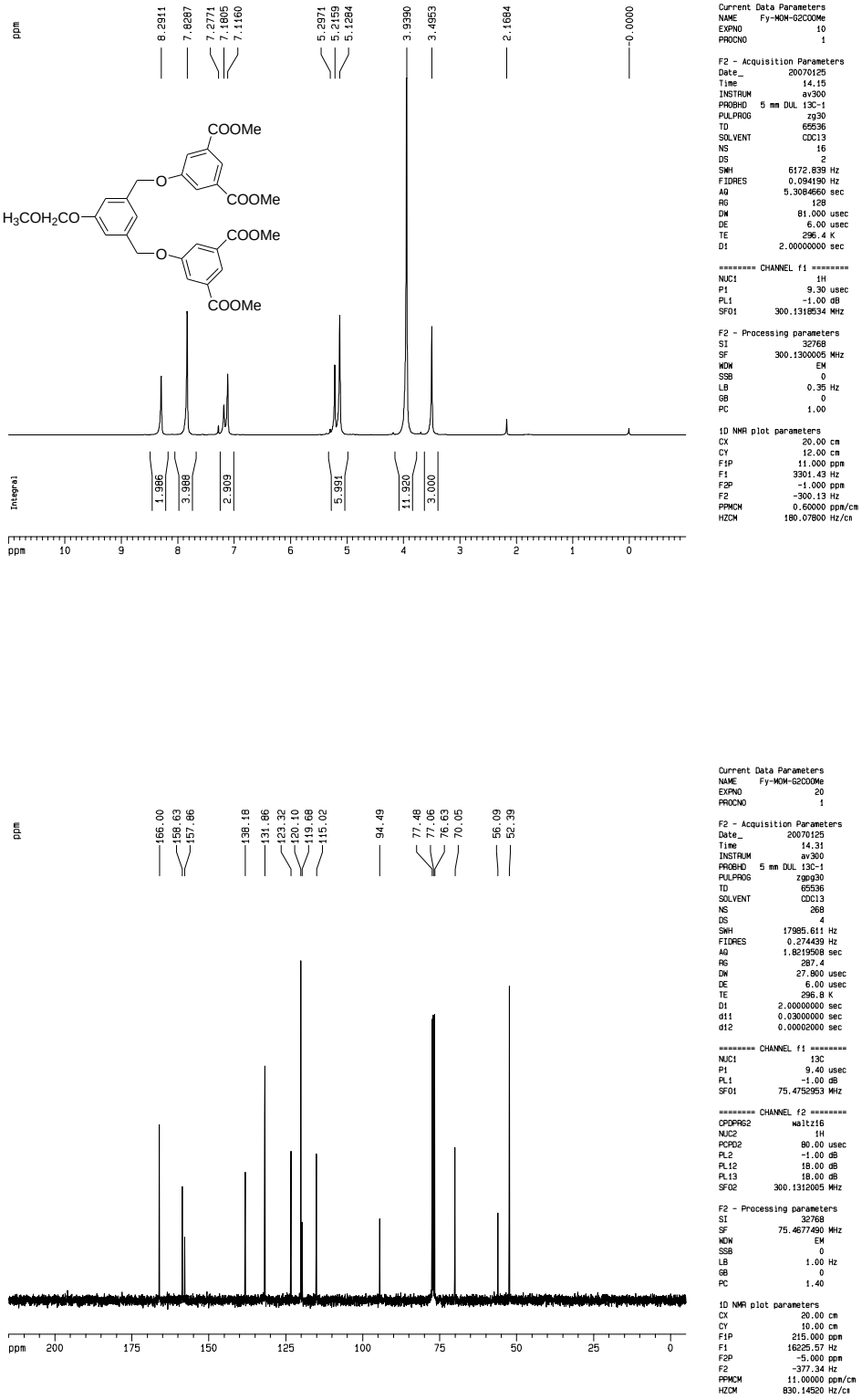


Figure S17. ^{1}H NMR and ^{13}C NMR spectra of **MOMG$_1$-COOMe**

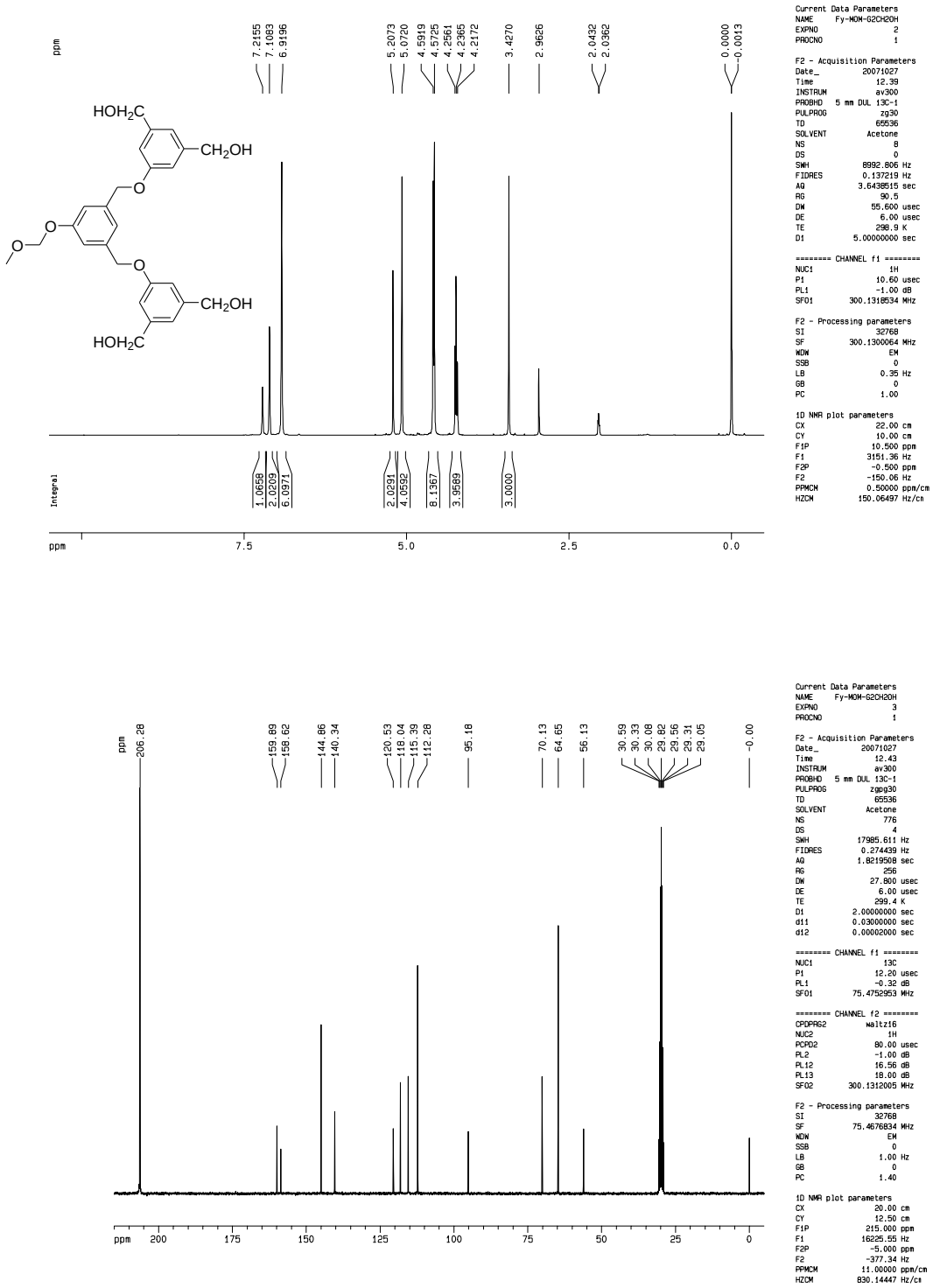
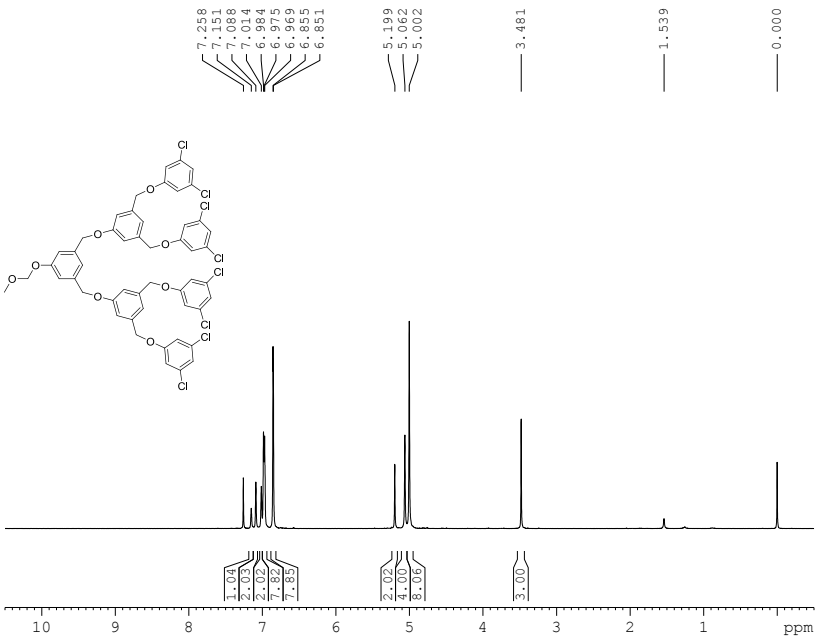


Figure S18. ^{1}H NMR and ^{13}C NMR spectra of **MOM-G$_1$CH$_2$OH**

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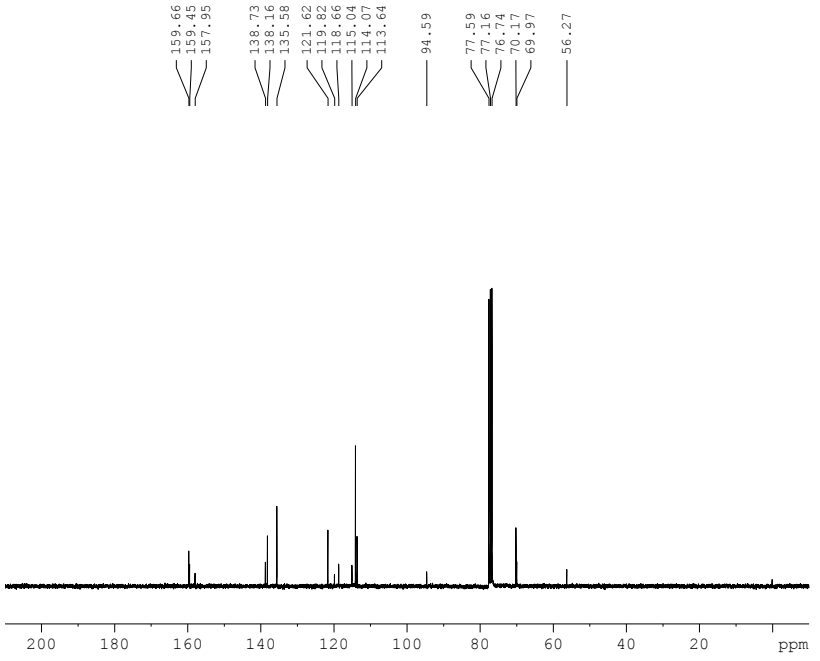


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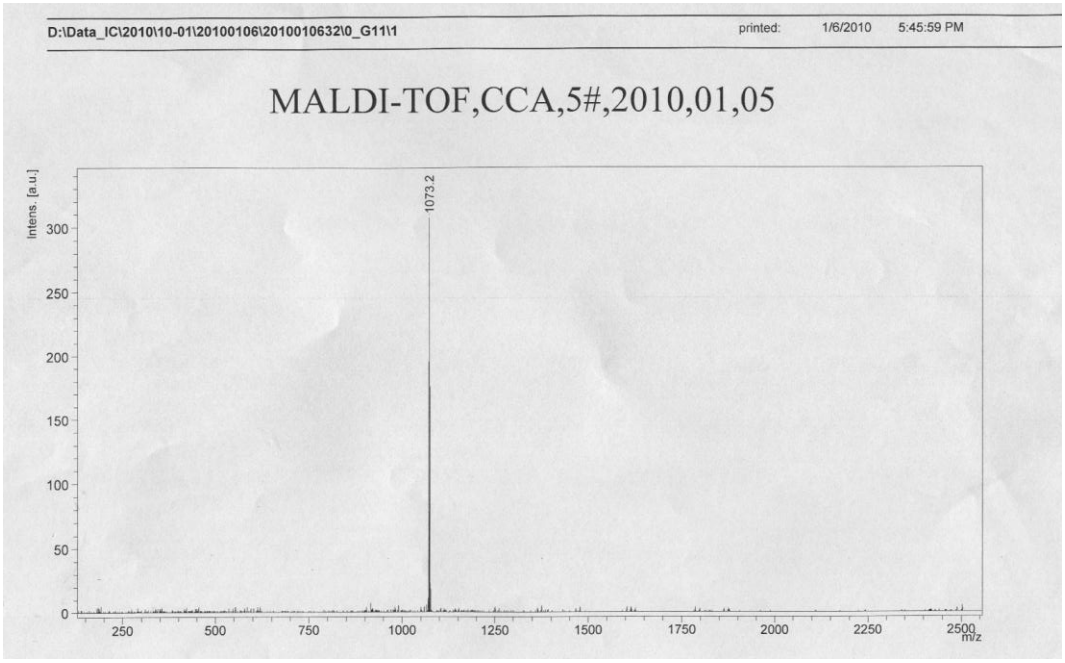
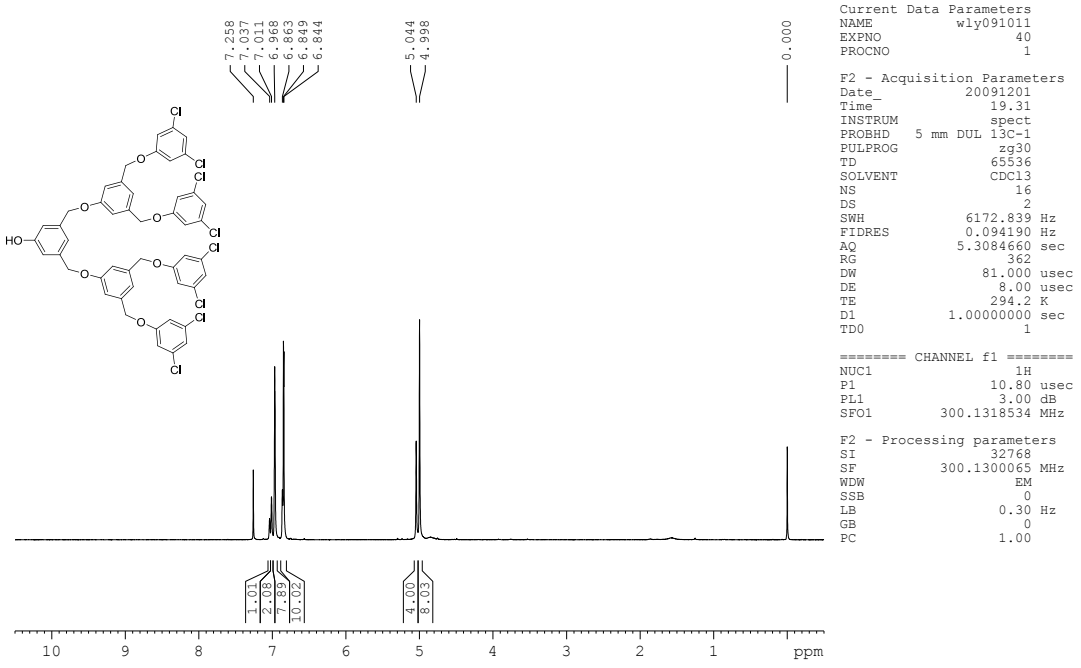
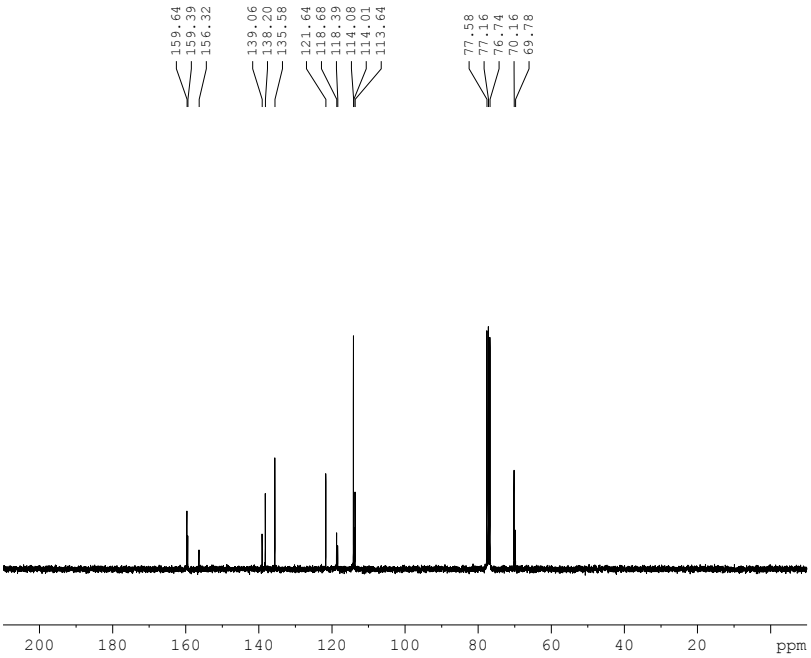


Figure S19. ^{1}H NMR, ^{13}C NMR and MALDI-TOF spectra of **MOMG$_2$Cl**



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Current Data Parameters
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EXPNO                       20
PROCNO                       1

F2 - Acquisition Parameters
Date_               20091013
Time                   11.36
INSTRUM                spect
PROBHD    5 mm DUL 13C-1
PULPROG             zgpg30
TD                     65536
SOLVENT                CDCl3
NS                       376
DS                         4
SWH                17985.611 Hz
FIDRES             0.274439 Hz
AQ                 1.8219508 sec
RG                    4597.6
DW                    27.800 usec
DE                     8.00 usec
TE                    297.7 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
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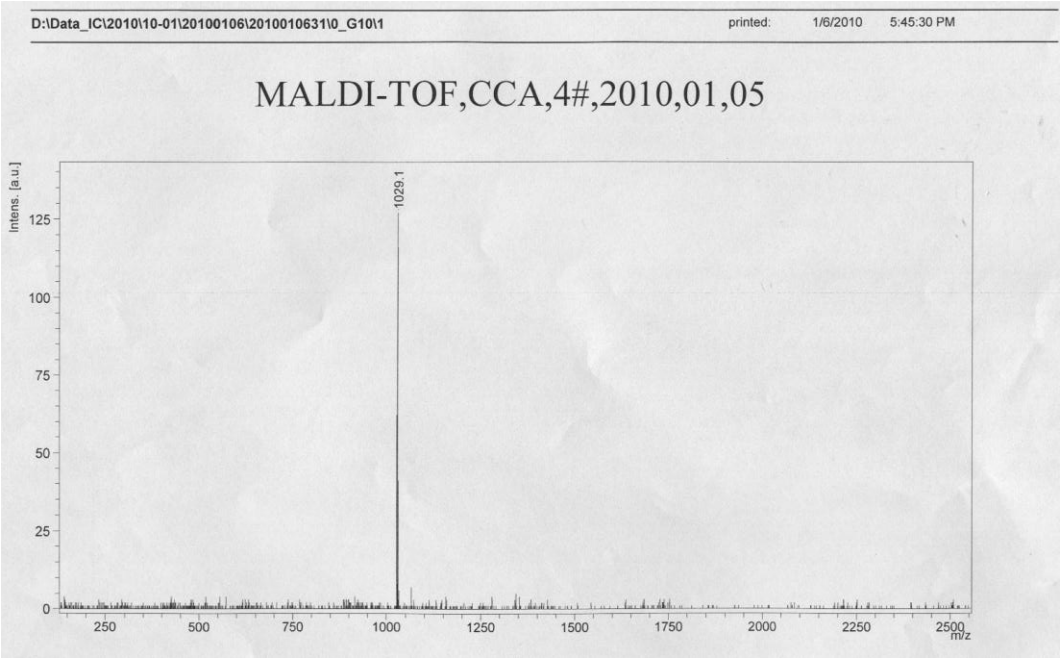
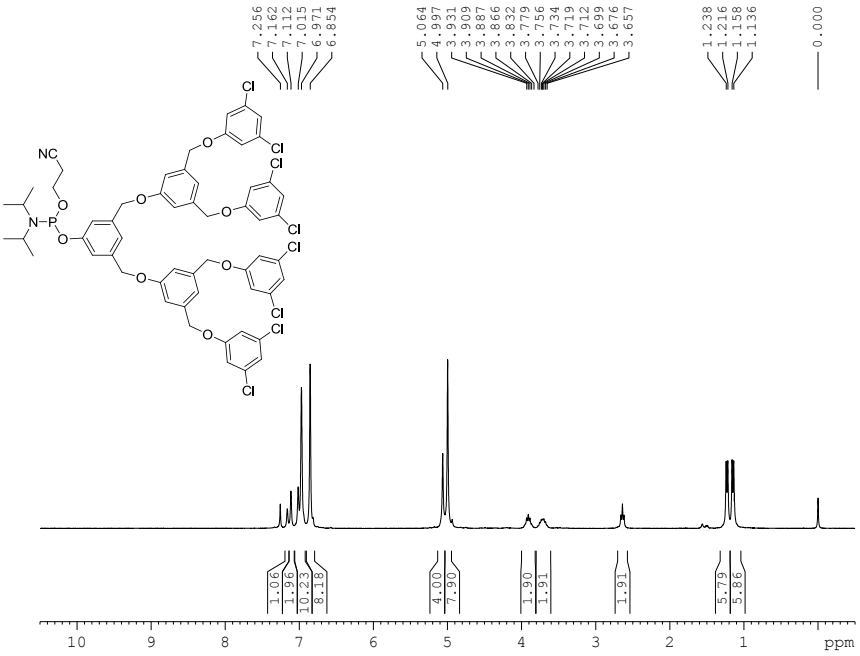
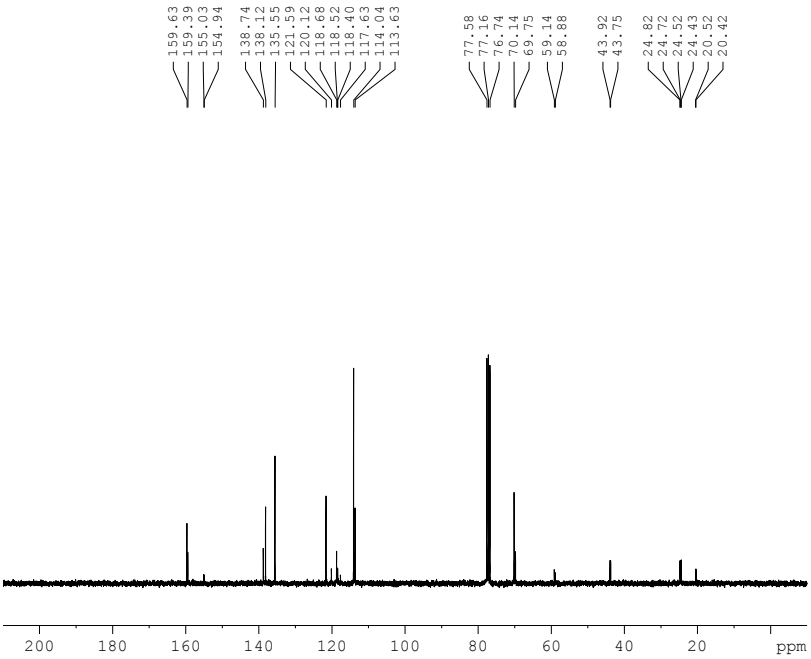


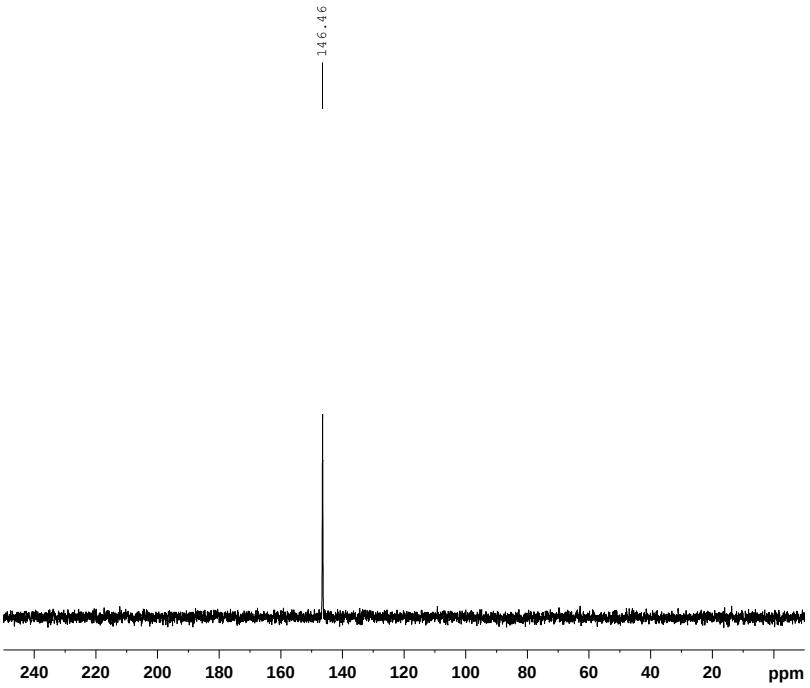
Figure S20. ^{1}H NMR, ^{13}C NMR and MALDI-TOF spectra of **G_2Cl.**




```
Current Data Parameters
NAME          wly100118
EXPNO                10
PROCNO                1

F2 - Acquisition Parameters
Date_          20100118
Time              22.14
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                  181
DW               81.000 usec
DE                8.00 usec
TE               294.4 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          300.1300068 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00
```




```
Current Data Parameters
NAME          wly100118
EXPNO                20
PROCNO                1

F2 - Acquisition Parameters
Date_          20100120
Time              15.24
INSTRUM           spect
PROBHD   5 mm DUL 13C-1
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                  248
DS                    4
SWH           17985.611 Hz
FIDRES        0.274439 Hz
AQ            1.8219508 sec
RG                11585.2
DW               27.800 usec
DE                8.00 usec
TE               294.3 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
```



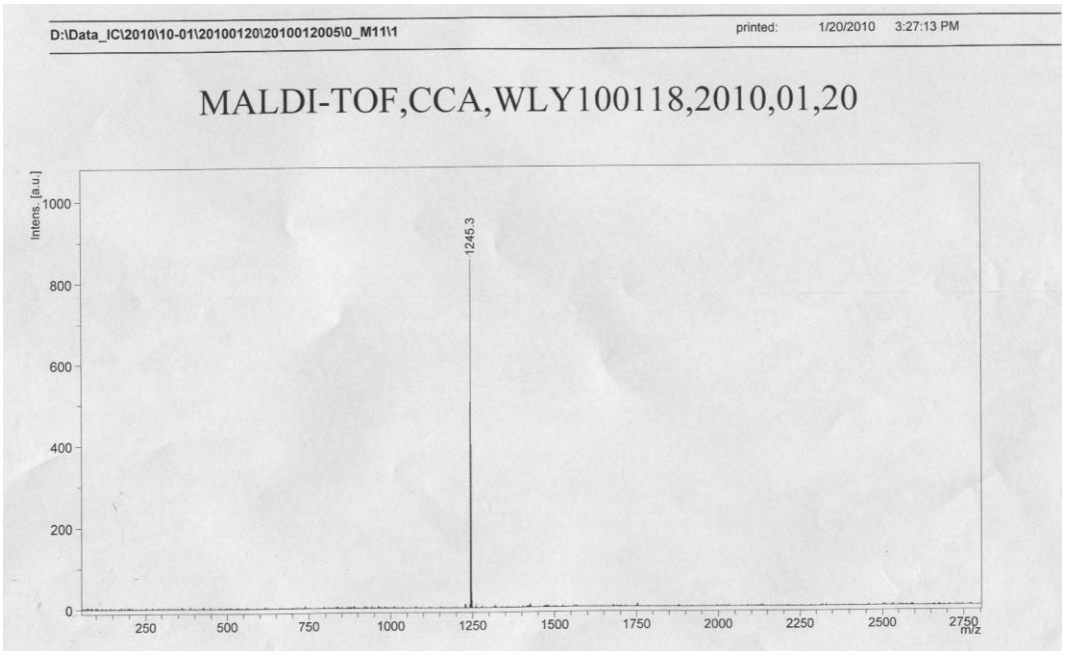


Figure S21. ^{1}H NMR, ^{13}C NMR, ^{32}P NMR and MALDI-TOF spectra of **G_2Cl-P.**

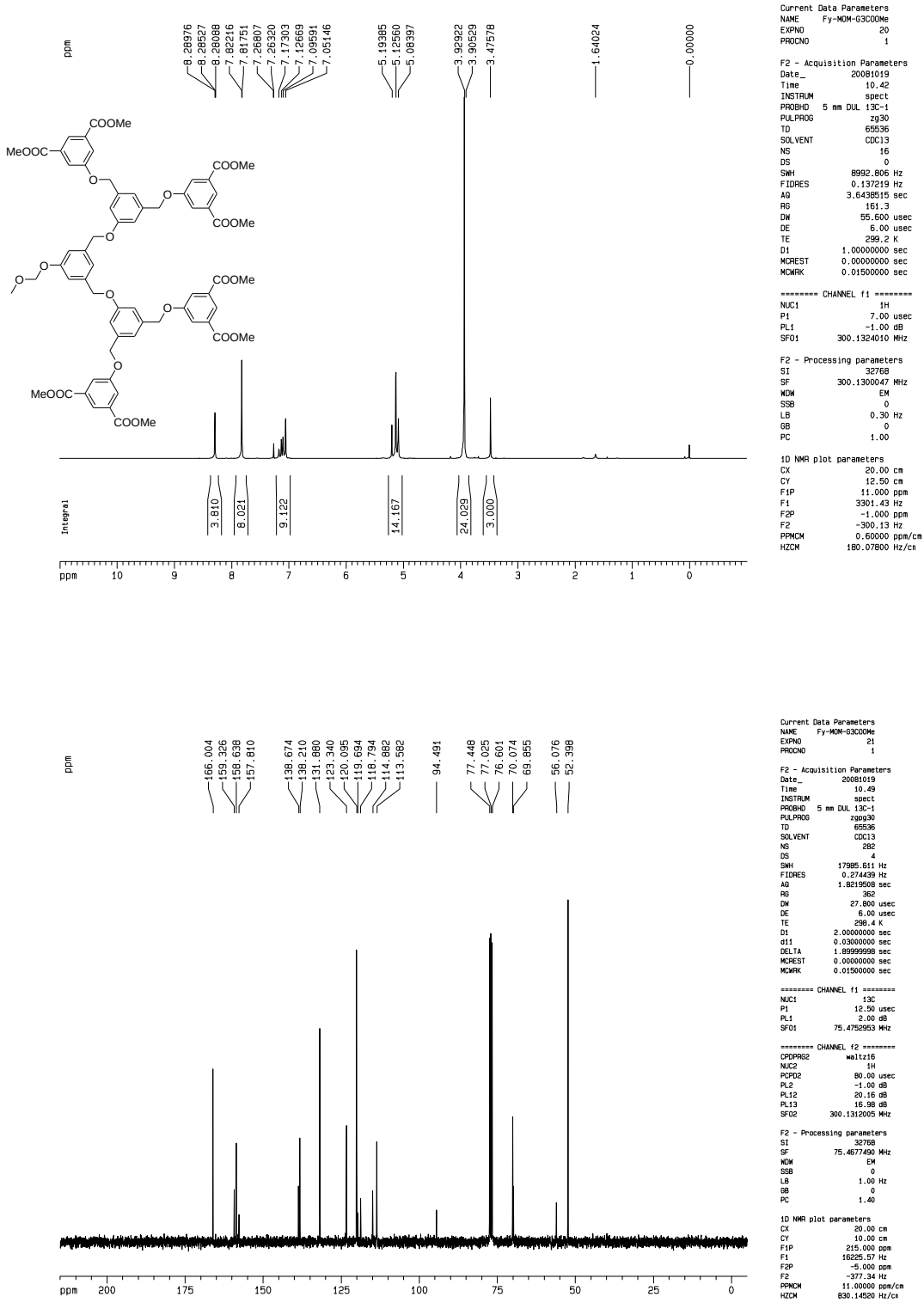
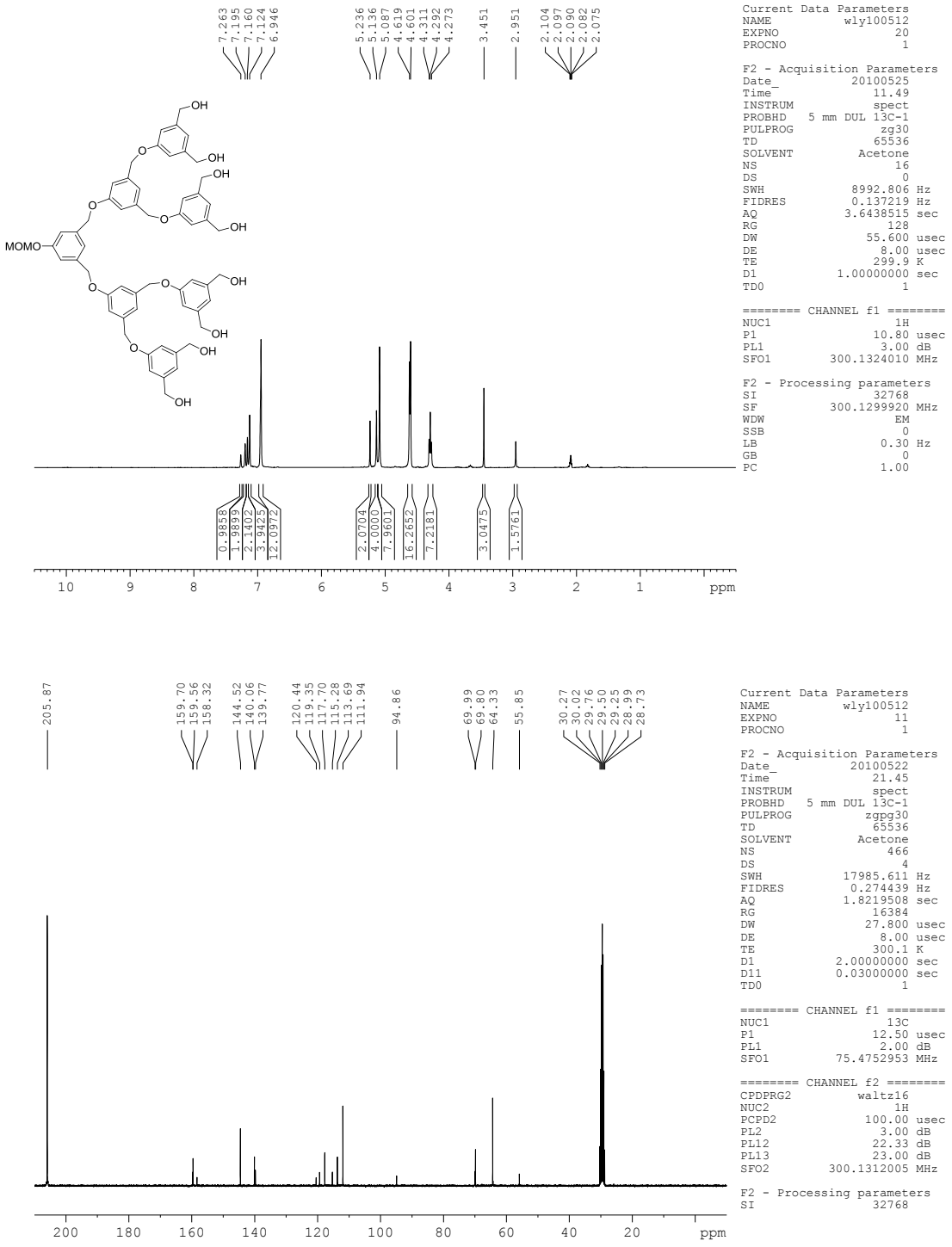


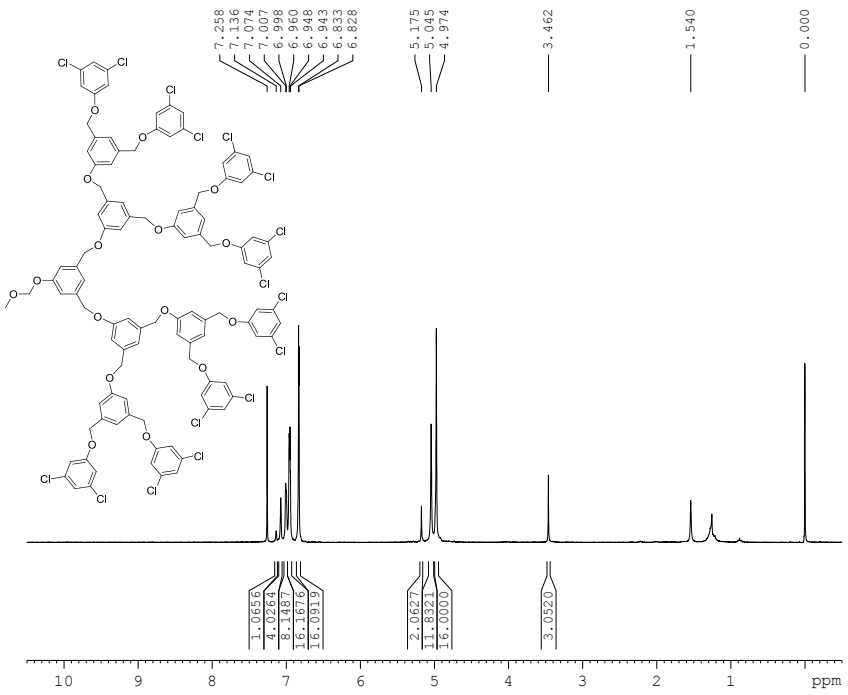
Figure S22. ^{1}H NMR and ^{13}C NMR spectra of **MOMG$_2$-COOMe.**



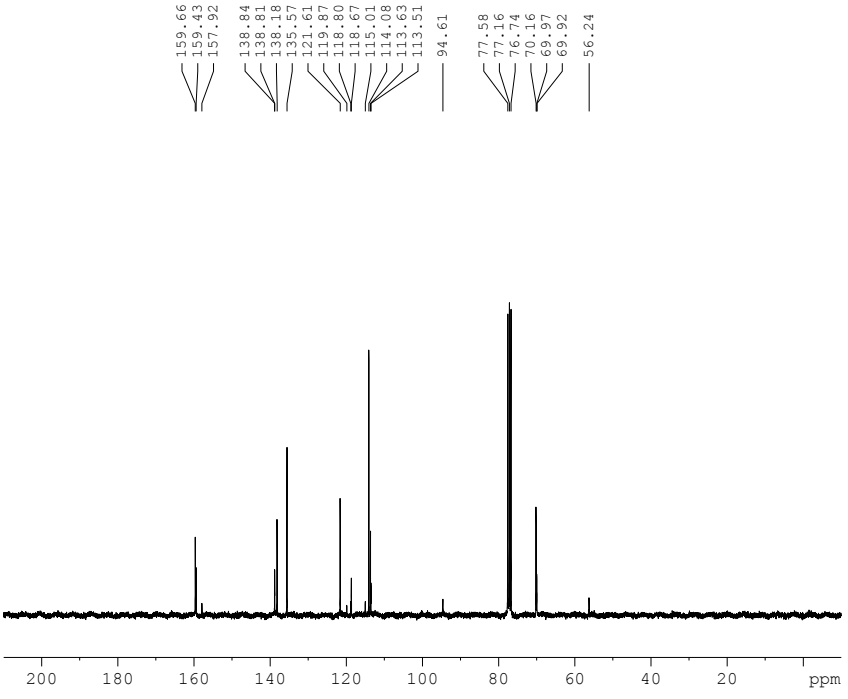

```
Current Data Parameters
NAME          wly100512
EXPNO                20
PROCNO                1

F2 - Acquisition Parameters
Date_          20100525
Time              11.49
INSTRUM           spect
PROBHD   5 mm DUL 13C-1
PULPROG           zg30
TD               65536
SOLVENT        Acetone
NS                   16
DS                    0
SWH            8992.806 Hz
FIDRES        0.137219 Hz
AQ            3.6438515 sec
RG                  128
DW               55.600 usec
DE                8.00 usec
TE                299.9 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          300.1299920 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00
```

```
Current Data Parameters
NAME          wly100512
EXPNO                11
PROCNO                1

F2 - Acquisition Parameters
Date_          20100522
Time              21.45
INSTRUM           spect
PROBHD   5 mm DUL 13C-1
PULPROG         zgpg30
TD               65536
SOLVENT        Acetone
NS                  466
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                300.1 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
```

Figure S23. ^{1}H NMR and ^{13}C NMR spectra of **MOMG$_2$-CH$_2$OH.**




```
Current Data Parameters
NAME                 wly100511
EXPNO                       70
PROCNO                       1

F2 - Acquisition Parameters
Date_               20100605
Time                   14.29
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                     574.7
DW                    55.600 usec
DE                     8.00 usec
TE                    298.6 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                300.1300067 MHz
WDW                         EM
SSB                          0
LB                        0.30 Hz
GB                           0
PC                        1.00
```




```
Current Data Parameters
NAME                 wly100511
EXPNO                      110
PROCNO                       1

F2 - Acquisition Parameters
Date_               20100607
Time                   11.10
INSTRUM                spect
PROBHD     5 mm DUL 13C-1
PULPROG             zgpg30
TD                    65536
SOLVENT               CDCl3
NS                      606
DS                        4
SWH               17985.611 Hz
FIDRES             0.274439 Hz
AQ                 1.8219508 sec
RG                   18390.4
DW                    27.800 usec
DE                     8.00 usec
TE                    299.6 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
```

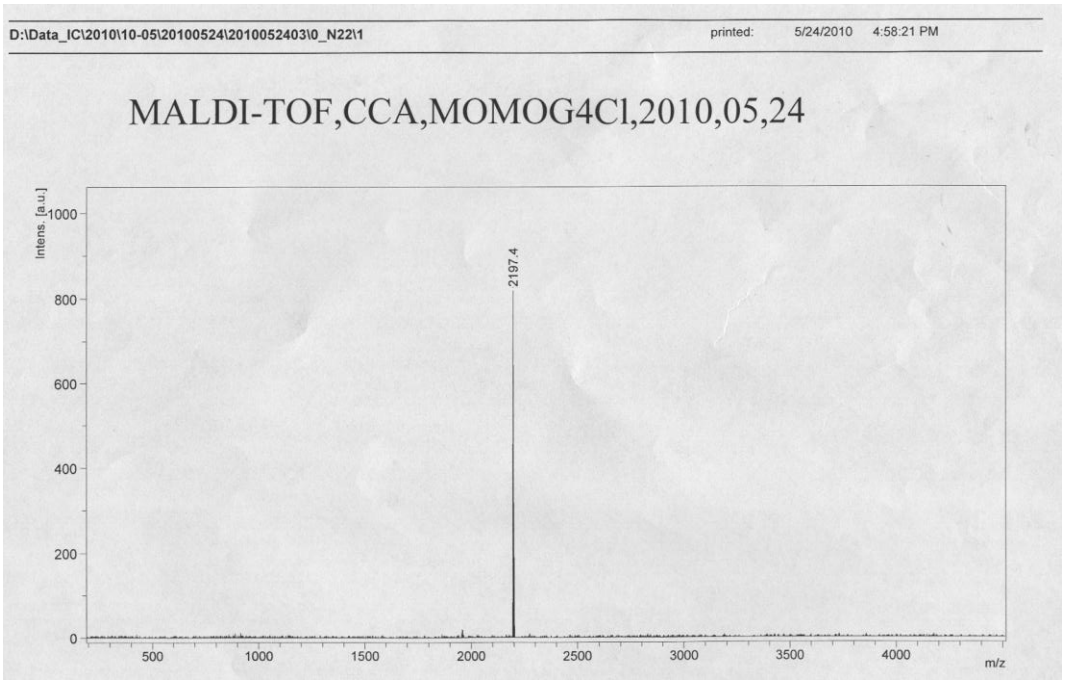
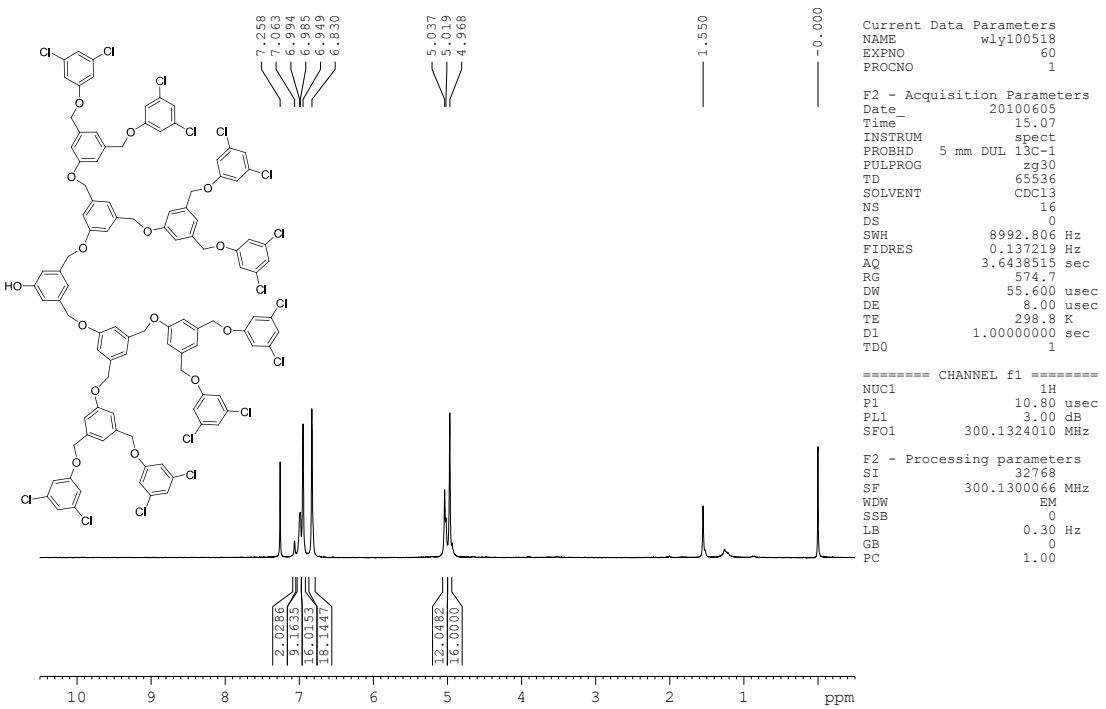
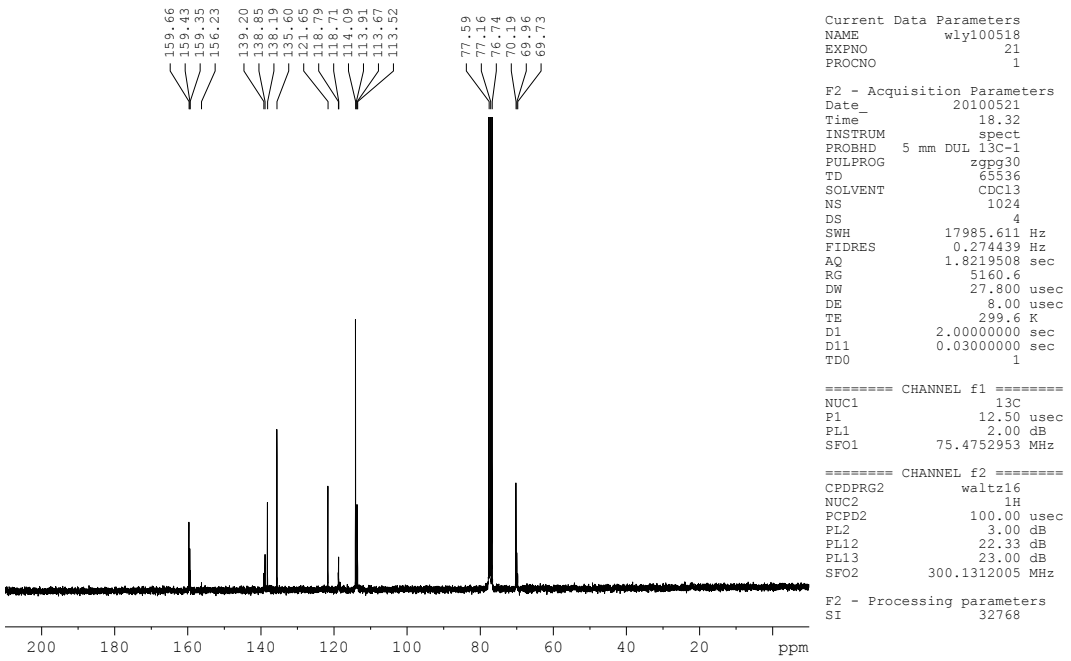


Figure S24. ^{1}H NMR,^{13}C NMR and MALDI-TOF spectra of **MOMG$_3$Cl.**





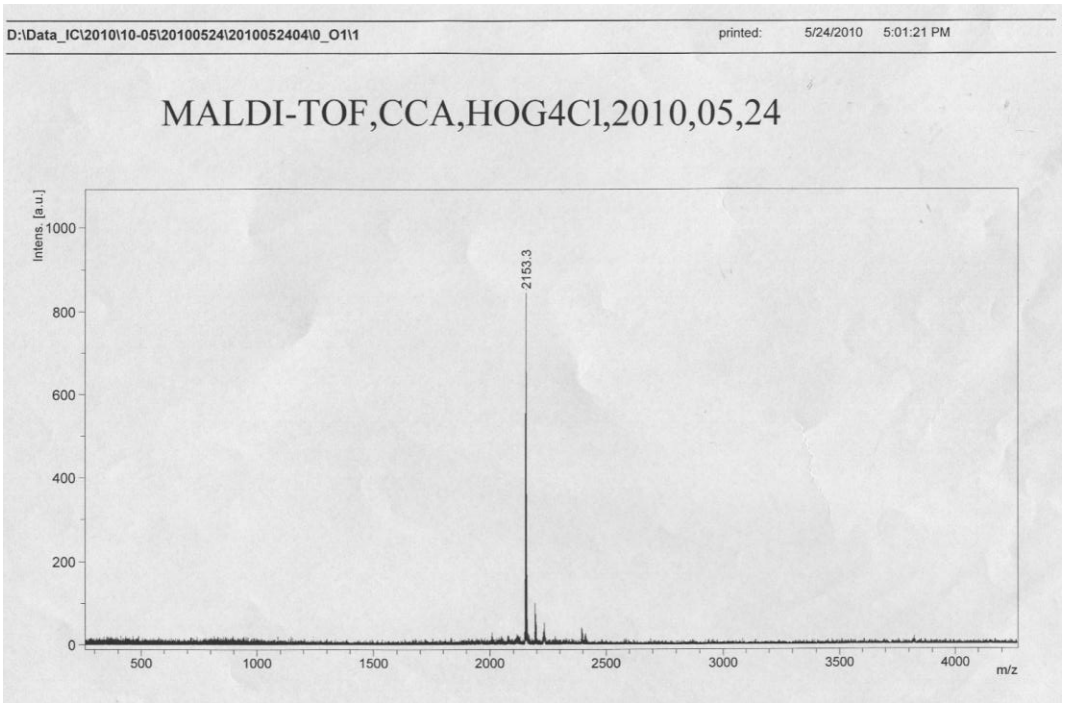
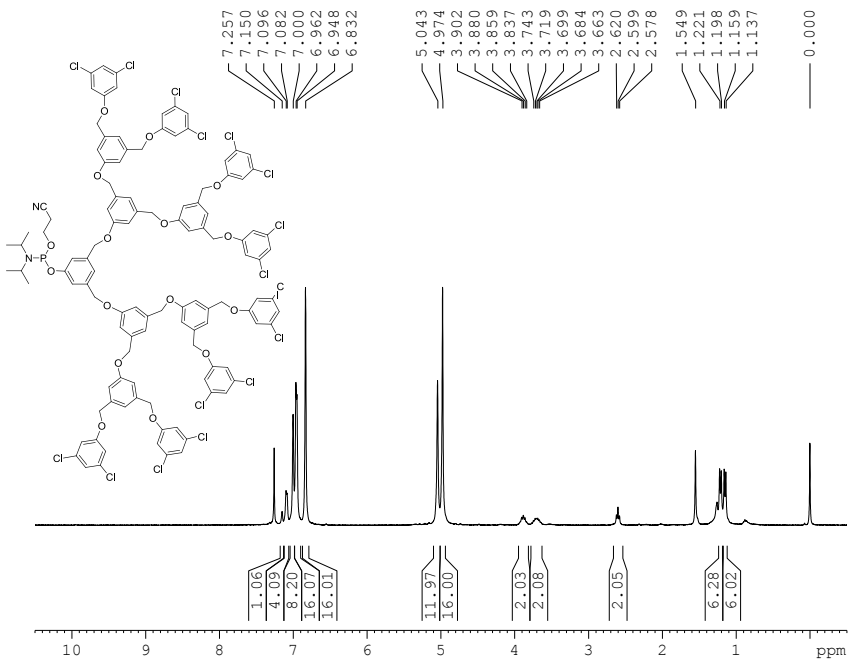
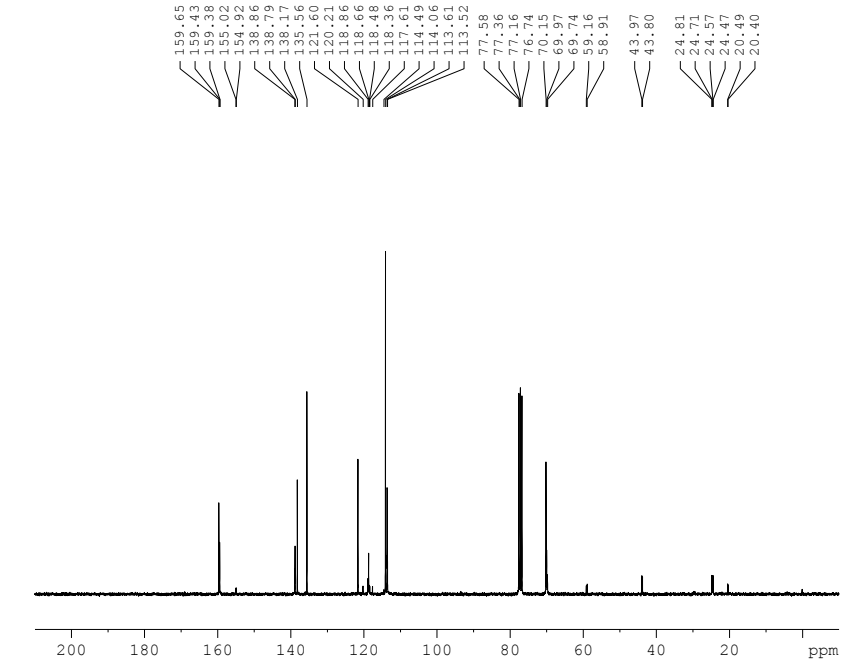


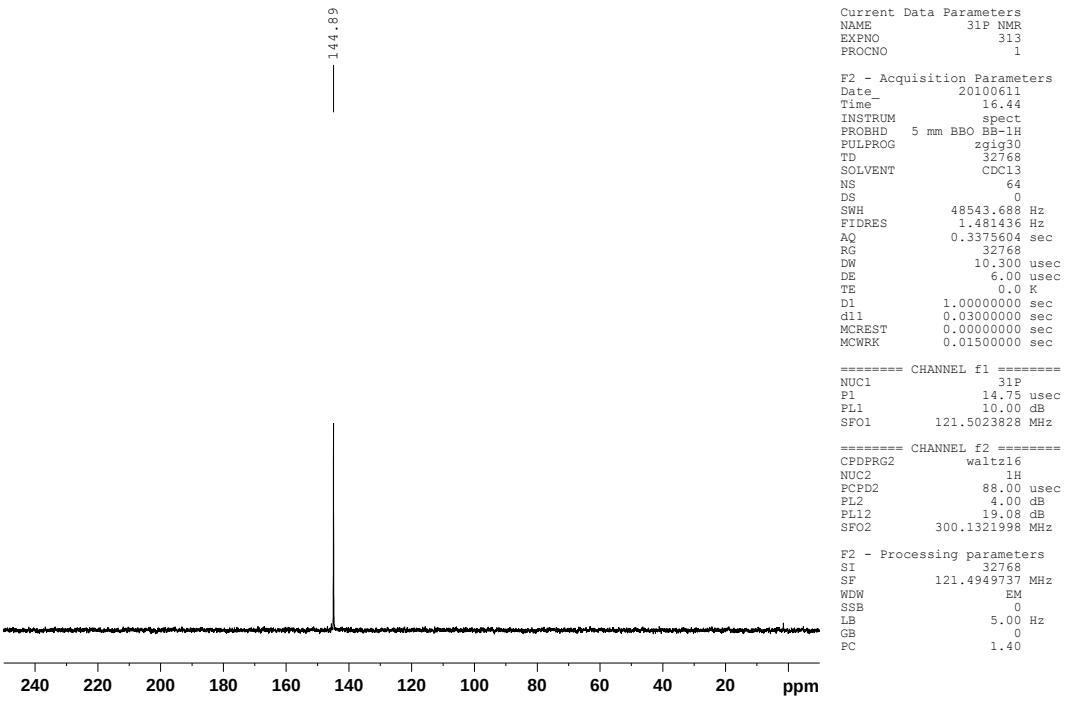
Figure S25. ^{1}H NMR,^{13}C NMR and MALDI-TOF spectra of **G_3Cl.**




```
Current Data Parameters
NAME         wly100609-2
EXPNO                 90
PROCNO                 1

F2 - Acquisition Parameters
Date_           20100621
Time               13.32
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                456.1
DW               55.600 usec
DE                8.00 usec
TE               299.4 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           300.1300070 MHz
WDW                   EM
SSB                    0
LB                 0.30 Hz
GB                     0
PC                 1.00
```




```
Current Data Parameters
NAME         wly100609-2
EXPNO                 81
PROCNO                 1

F2 - Acquisition Parameters
Date_           20100621
Time               11.09
INSTRUM            spect
PROBHD   5 mm DUL 13C-1
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                 1603
DS                    4
SWH           17985.611 Hz
FIDRES         0.274439 Hz
AQ             1.8219508 sec
RG                4597.6
DW               27.800 usec
DE                8.00 usec
TE               299.5 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
```



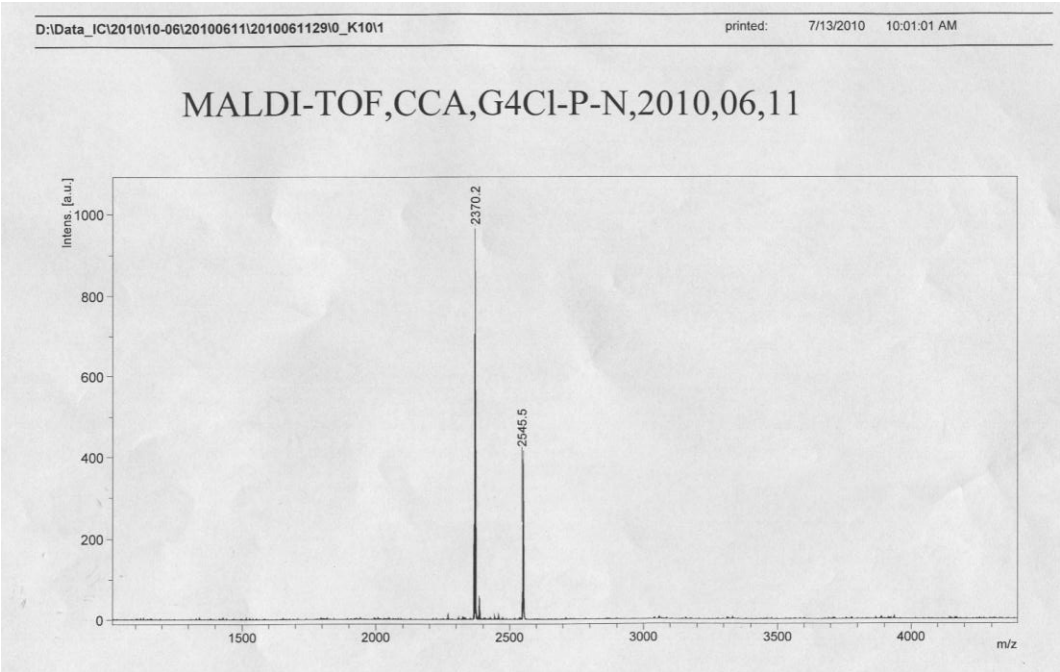


Figure S26. ^{1}H NMR, ^{13}C NMR,^{31}P NMR and MALDI-TOF spectra of **G_3Cl-P**.

11.References

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