Low Temperature Synthesis of Ordered Mesoporous Stable Anatase Nanocrystals: The Phosphorus Dendrimer Approach

Younes Brahmi[a,b], Nadia Katir[a,c], Mykhailo Ianchuk[c], Vincent Collière[c], El Mokhtar Essassi,[a,b] Armelle Ouali[c], Anne-Marie Caminade[c], Mosto Bousmina[d], Jean Pierre Majoral*[a,c] and Abdelkrim El Kadib*[a]

[*] Y. Brahmi, Dr. N. Katir, Dr. A. El Kadib
(iNANOTECH) Institute of Nanomaterials and Nanotechnology – MAScIR (Moroccan Foundation for Advanced Science, Innovation and Research), ENSET, Avenue de l'Armée Royale, Madinat El Irfane, 10100 Rabat, Morocco.
E-mail: a.elkadib@mascir.com
Y. Brahmi
Université Mohamed V Agdal, Faculté des Sciences. Av. Ibn Battouta, BP 1014, Rabat, Morocco.
M. Ianchuk, V. Collière, Dr. A. Ouali, Dr. A.-M. Caminade, Dr. J. P. Majoral
LCC (Laboratoire de Chimie de Coordination), Université Paul Sabatier. 205 route de Narbonne, 31077 Toulouse cedex, France.
Prof. M. Bousmina
Hassan II Academy of Science and Technology, Rabat, Morocco.

S_1: Experimental section

S_{1a}: Characterization of materials.

General All manipulations were carried out with standard high-vacuum and dry-argon techniques. Chemicals were purchased from Sigma-Aldrich or Strem and used without further purification; solvents were dried and distilled by routine procedures. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded at 25°C with Bruker AV 300, DPX 300 or AMX 400 spectrometers. References for NMR chemical shifts are 85% H_3PO_4 for ^{31}P NMR and $SiMe_4$ for ^{1}H and ^{13}C NMR. The attribution of ^{13}C NMR signals has been done using J_{mod}, two-dimensional HMBC and HMQC. Fourier transformed infrared (FTIR) spectra were obtained with a Perkin-Elmer Spectrum 100FT-IR spectrometer on neat samples (ATR FT-IR). ^{13}C and ^{31}P CP MAS NMR spectra were acquired on a Bruker Avance 400 WB spectrometer operating at 100 MHz and 162 MHz respectively under cross-polarization conditions. The numbering used for NMR is shown on Fig.1. Nitrogen sorption isotherms at 77 K were obtained with a Micromeritics ASAP 2010 apparatus. Prior to measurement, the samples were degassed for 8 h at 120 °C. The surface area (S_{BET}) was determined from BET treatment in the range 0.04–0.3 p/p_0 assuming a surface coverage of the nitrogen molecule estimated to be 13.5 $Å^2$. Thermogravimetric analysis (TGA) was performed on a Pfeiffer Vacuum instrument at a heating rate of 10°C/min under a flow of nitrogen. X-ray powder diffraction (XRD) patterns were recorded on a D8 Advance Bruker AXS system using CuKα radiation with a step size of 0.02° in the 2θ range from 0.3 to 10° for SAXS, and from 0.45 to 87° for WAXS (geometry : Bragg- Brentano, θ/2θ mode). FT-IR spectra of the sample were collected with an ABB Bomem - SPECAC spectrometer in the wavelength range from 4000 to 400 cm^{-1} with a step size of 2 cm^{-1} and collecting 16 scans for each analysis. DRUV spectra were measured in the 200–800 nm range using spectralon as the reference on a Perkin-Elmer Lambda 1050 spectrometer equipped with an integrating sphere (Lapshere, North Sutton, USA). Scanning electronic microscopy (SEM) images were obtained using a JEOL JSM 6700F Transmission electronic microscopy (TEM) images were obtained using JEOL JEM 2010 at an activation voltage of 200 kV.

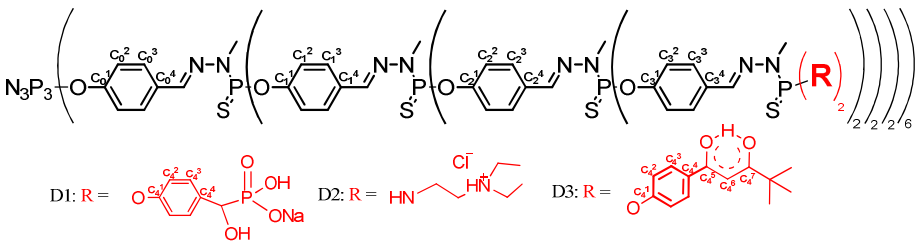
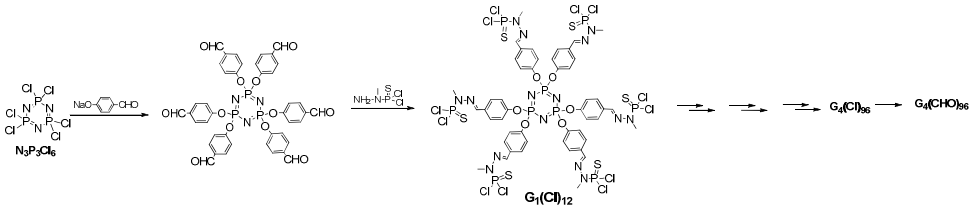


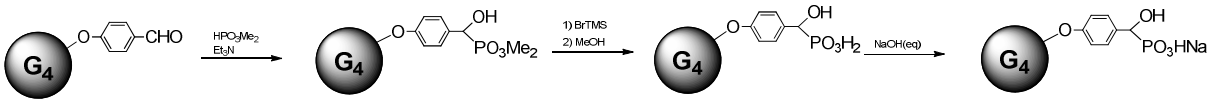
Figure 1. Numbering used for NMR assignments.

S_{1b}: Synthesis and characterization of the starting dendrimers [1]



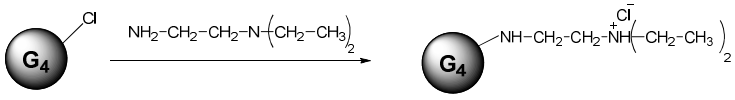
The reaction of hexachlorocyclotriphosphazene core with hydroxybenzaldehyde in basic conditions and then the condensation of the aldehyde groups with a phosphorhydrazide afford the dendrimer of generation one. The repetition of both steps was carried out until the obtaining of the fourth generation **G_4**.

Synthesis of **D_1**:



Dendrimer **$G_4(CHO)_{96}$** was dissolved in THF then triethylamine and dimethylphosphite were added to the reaction mixture and left overnight under good stirring. The residue was washed by a mixture of THF/Et_2O (1/1) to afford the dendrimer (α- hydroxy-dimethylphosphonate) as a white powder in 80% yield. At 0°C (ice bath) the bromotrimethylsilane was added slowly to a suspension dendrimer (α- hydroxy-dimethylphosphonate) in acetonitrile and triethylamine. The reaction mixture was left to react for 6 h at room temperature. Then the anhydrous methanol was added. After 2h, the reaction mixture was evaporated to dryness under reduced pressure. The residue was washed water and ether and the G4(α- hydroxy-phosphonic) was obtained as a white powder with a yield of 51%. At 0°C an aqueous sodium hydroxide was added slowly to a suspension of G4(α-hydroxy-phosphonic) in water. After one hour at room temperature, the clear solution was lyophilized to give the sodium monosalt dendrimer (**D1)** as a white powder with a yield of 82%.

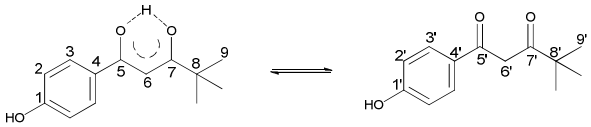
Synthesis of **D_2**:[2]



N,N-Diethylethylenediamine (0.74 mL, 5.27 mmol) was added dropwise by syringe with strong stirring to a solution of dendrimer **$G_4(Cl)_{96}$** (1.22 g, 5.49 10^{-2} mmol) in distilled THF (120 mL) and then the mixture was stirred at room temperature overnight. The solvent was removed by filtration and the white powder was washed with distilled THF (100 mL X 2) and

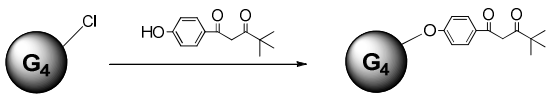
then with distilled pentane (50 mL X 2) to afford the **D2** with a yield of 93%. ^{31}P NMR (121 MHz, CD_3OD) δ 8.4 (P_0), 62.0 ($P_{1,2,3}$), 69.4 (P_4). ^{1}H NMR (300 MHz, DMSO) δ 1.3 (s br, 576H, CH_2-C*H*$_3$), 3.0-3.5 (m, 1038H, N-CH_2 and N-CH_3), 5.6 (s br, 96H, N-H), 7.0-7.5 (m br, 180H, C_0^2H, C_1^2H, C_2^2H, C_3^2H), 7.7-8.2 (m, 270H, CH=N, C_0^3H, C_1^3H, C_2^3H, C_3^3H),10.8 (s br, 96H, $^{+}$N-H), ^{13}C NMR (75 MHz, CD_3OD) δ 9.7 (CH_2-*C*H_3), 33.2 (d, $^2J_{CP}$ = 9.2 Hz, CH_3-N-P_4), 34.3 (d, $^2J_{CP}$ = 10.1 Hz, CH_3-N-$P_{1,2,3}$), 37.7 (CH_2-N-P_4), 49.2 (*C*H_2-CH_3), 53.8 (d, $^3J_{CP}$ = 5.5 Hz, *C*H_2-CH_2-N-P_4), 123.1 (s br, C_0^2, C_1^2, C_2^2, C_3^2), 129.7 (s br, C_0^3, C_1^3, C_2^3, C_3^3), 134.2 (C_0^4, C_1^4, C_2^3), 134.9 (C_3^4), 139.2 (s br, C_3^4-CH=N), 141.5 (s br, CH=N), 152.5 (d, $^3J_{CP}$ = 7.4 Hz, C_3^1), 153.0 (s br, C_0^1, C_1^1, C_2^1,).

Synthesis of 1-(4-hydroxyphenyl)-4,4-dimethylpentane-1,3-dione [3]



N,*N*-dimethylformamide (DMF) (25 mL) and potassium tert-butoxide (KO*t*Bu) (11.2 g, 100 mmol) were heated to 50°C under argon. Methyl pivalate (5.80 g, 50 mmol) was added dropwise, followed by a solution of 4-hydroxy-acetophenone (3.40 g, 25 mmol) in DMF (10 mL). After the completion of the reaction, the reaction mixture was allowed to cool and slowly neutralized with 20% H_2SO_4 solution. Water (300 mL) was added to dissolve the salts and diketone was extracted by dichloromethane (3 x 100 mL). Organic layers were gathered, dried over $MgSO_4$, concentrated in vacuum and purified using column chromatography with pentane and ethyl acetate as eluents to give white powder; yield (82%); ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 1.24 (s, 1.17 H, $H^{9'}$), 1.28 (s, 7.83 H, H^9), 4.21 (s, 0.26H, $H^{6'}$), 6.31 (s, 0.87H, H^6), 6.38 (br s, 1H, C1-OH, $C^{1'}$-OH), 6.93 (d, $^3J_{HH}$ = 9.0 Hz, 2H, H^2, $H^{2'}$), 7.87 (d, $^3J_{HH}$ = 9.0 Hz, 2H, H^3, $H^{3'}$), 16.68 (br s, 0.87H, O-Henol); ^{13}C-{^{1}H} NMR (75.4 MHz, CD_2Cl_2): δ = 25.9 ($C^{9'}$), 27.2 (C^9), 39.2 (C^8), 45.1 ($C^{8'}$), 47.4 ($C^{6'}$), 91.3 (C^6), 115.4 (C^2), 115.5 ($C^{2'}$), 128.0 (C^4), 129.3 (C^3), 129.5 ($C^{4'}$), 131.3 ($C^{3'}$), 159.8 (C^1), 161.0 ($C^{1'}$), 185.8 (C^5), 194.3 ($C^{5'}$), 201.0 (C^7), 211.3 ($C^{7'}$); DCI-MS (NH_3) m/z: 221.1 $[M+ H]^+$.

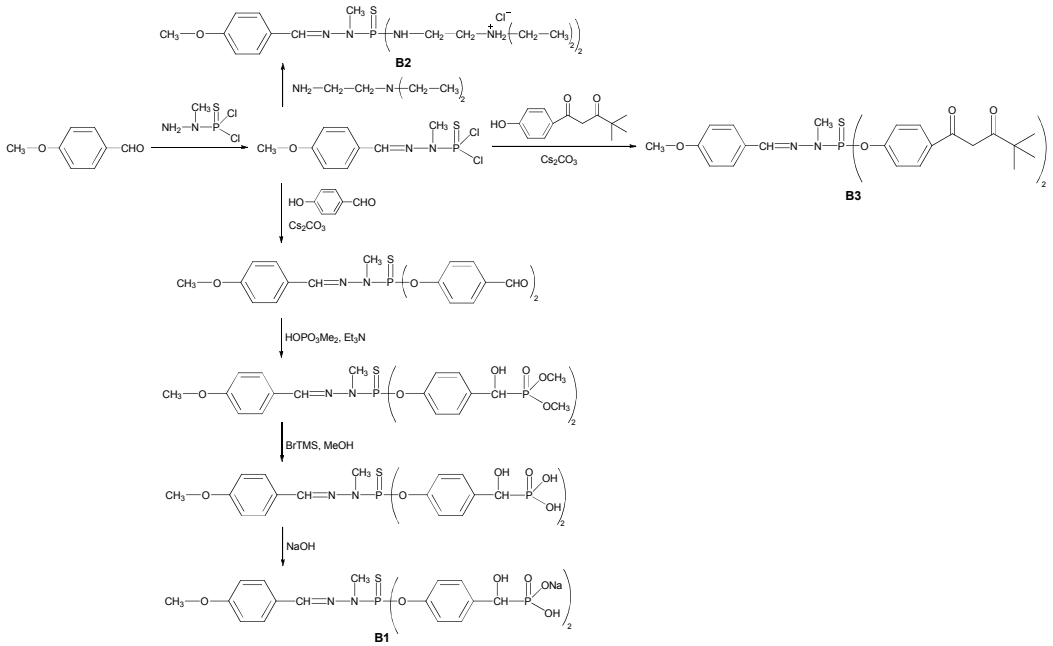
Synthesis of D_3:[3]



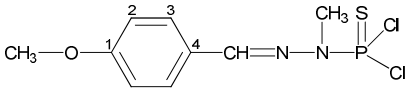
A dendrimer **$G_4(Cl)_{96}$** (0.068 mmol) was dissolved in THF (30 mL), and then appropriate masses of 1-(4-hydroxyphenyl)-4,4-dimethylpentane-1,3-dione (1.05 eq. per chlorine) and of cesium carbonate (1.05 eq. per chlorine) were added. Reaction mixture was stirred overnight at room temperature, and then centrifugated. The solution was precipitated few times in

pentane/Et_2O (9:1) mixture. The resulting powder was filtered and dried under vacuum. **D_3** was obtained as a white powder; yield 94% (2.54 g, 0.0631 mmol). ^{31}P NMR (CD_2Cl_2, 121 MHz): δ = 7.69 (s, P_0), 61.23 (s, P_4), 62.49 (s, P_3), 62.67 (m, P_1, P_2); ^{1}H NMR (CD_2Cl_2,300 MHz): δ = 1.18 (s, 864H, C_4^9-H), 3.32 (m, 270H, C_0^6-H, C_1^6-H, C_2^6-H, C_3^6-H), 6.23 (s, 96H, C_4^6-H), 7.26 (m, 372H,$C_0$2-H, $C_1$2-H, $C_2$2-H, $C_3$2-H, $C_4$2-H), 7.76 (m, 462H, $C_0$3-H, $C_1$3-H, $C_2$3-H, $C_3$3-H, $C_4$3-H, C_0^5-H, C_1^5-H, C_2^5-H, C_3^5-H), 16.41(br s, 96H, O-Henol) ; ^{13}C NMR (CD_2Cl_2, 75 MHz): δ = 27.1 (s, C_4^9), 32.8 (m, C_0^6, C_1^6, C_2^6, C_3^6), 39.6 (s, C_4^8); 91.9 (s,C_4^6), 121.6 (m, C_0^2, C_1^2, C_2^2, C_4^2), 128.4 (m, C_0^3, C_1^3, C_2^3, C_3^3, C_4^3), 132.2 (m, C_0^4, C_1^4, C_2^4, C_3^4), 132.8 (br s, C_4^4), 139.5(m, C_0^5, C_1^5, C_2^5, C_3^5), 151.4 (m, C_0^1, C_1^1, C_2^1, C_3^1), 153.4 (s, C_4^1), 183.5 (s, C_4^5), 202.6 (s, C_4^7).

S_{1C}: Synthesis and characterization of the starting branch-mimicking dendrimers



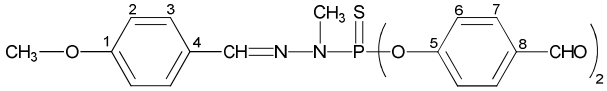
Synthesis of (2-(4-methoxybenzylidene)-1-methylhydrazinyl)phosphonothioic dichloride



A solution of N-methyldichlorothiophosphorhydrazide (18.00 mmol) in chloroform (140 mL) was added to a solution of 4-methoxybenzaldehyde (2.24 g, 16.46 mmol) in chloroform (10 mL) and the reaction mixture was stirred 6 hrs at room temperature. The mixture was concentrated under reduced pressure to about 10 mL and then precipitated with pentane. The powder was filtered off, dissolved in the minimum amount of chloroform (6 mL) and precipitated with pentane. These washings were repeated two times to afford (2-(4-methoxybenzylidene)-1 methylhydrazinyl) phosphonothioic dichloride as a white powder (95%). ^{31}P NMR (121 MHz, $CDCl_3$): δ = 63.44. ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.50 (d, 3H,

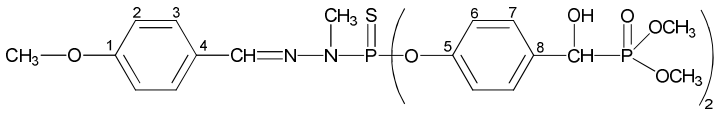
$^{3}J_{PH}$ = 14.3 Hz, N-CH_3), 3.87 (s, 3H, OCH_3), 6.96 (d, 2H, $^{3}J_{HH}$ = 8.8 Hz, H^2), 7.70 (d, 1H, $^{4}J_{PH}$ = 2.8 Hz, CH=N), 7.71 (d, 2H, $^{3}J_{HH}$ = 8.8 Hz, H^3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 31.78 (d, $^{2}J_{CP}$ = 13.2 Hz, CH_3-N), 55.40 (OCH_3), 114.27 (C^2), 126.92 (d, $^{3}J_{CP}$ = 1.6 Hz, C^4), 128.93 (C^3), 141.88 (d, $^{3}J_{CP}$ = 18.7 Hz, CH=N), 160.29 (C^1); DCI-MS (NH_3) m/z = 297.0 $[M+H]^+$.

Synthesis of O,O-bis(4-formylphenyl) (2-(4-methoxybenzylidene)-1 methylhydrazinyl) phosphonothioate



To a solution of (2-(4-methoxybenzylidene)-1 methylhydrazinyl) phosphonothioic dichloride (1.00 g, 3.37 mmol) in THF (10 mL) were added 4-hydroxybenzaldehyde (0.90 g, 7.37 mmol) and cesium carbonate (3.29 g, 10.10 mmol). The mixture was stirred at room temperature for 10h. The mixture was filtered and evaporated. The residue was then dissolved in the minimum amount of $CHCl_3$ and precipitated with pentane. The resulting powder was filtered off and dried to afford O,O-bis(4-formylphenyl) (2-(4-methoxybenzylidene)-1 methylhydrazinyl) phosphonothioate as a white powder in 96 % yield. ^{31}P NMR (121 MHz, $CDCl_3$): δ = 60.60. ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.40 (d, 3H, $^{3}J_{PH}$ = 11.1 Hz, N-CH_3), 3.86 (s, 3H, OCH_3), 6.94 (d, 2H, $^{3}J_{HH}$ = 8.7 Hz, H^2), 7.42 (dd, 4H, $^{3}J_{HH}$ = 8.5 Hz, $^{4}J_{PH}$ = 1.3 Hz, H^6), 7.63 (d, 2H, $^{3}J_{HH}$ = 8.9 Hz, H^3), 7.65 (s, 1H, CH=N), 7.89 (d, 4H, $^{3}J_{HH}$ = 8.6 Hz, H^7), 9.98 (s, 2H, CHO); ^{13}C NMR (101 MHz, $CDCl_3$) δ 32.85 (d, $^{2}J_{CP}$ = 13.6 Hz, CH_3-N), 55.40 (OCH_3), 114.28 (C^2), 122.08 (d, $^{3}J_{CP}$= 5.0 Hz, C^6), 127.18 (C^4), 128.53 (C^3), 131.43 (d, $^{4}J_{CP}$= 1.0 Hz, C^7), 133.64 (d, $^{5}J_{CP}$= 1.6 Hz, C^8), 140.63 (d, $^{3}J_{CP}$ = 13.8 Hz, CH=N), 155.28 (d, $^{2}J_{CP}$= 7.2 Hz, C^5), 161.01 (C^1), 190.79 (CHO); DCI-MS (NH_3) m/z = 469.2 $[M+H]^+$.

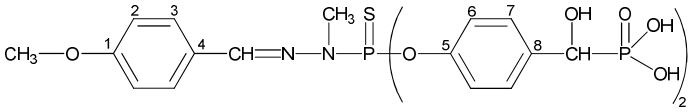
Synthesis of tetramethyl (((((2-(4-methoxybenzylidene)-1-methylhydrazinyl) phosphorothioyl) bis(oxy))bis(4,1-phenylene))bis(hydroxymethylene))bis(phosphonate)



To a solution of O,O-bis(4-formylphenyl) (2-(4-methoxybenzylidene)-1 methylhydrazinyl) phosphonothioate (0.80 g, 1.71 mmol) in THF (1 mL) were added triethylamine (0.01 mL, 8.5 10^{-2} mmol) and dimethylphophite (0.35 mL, 3.76 mmol). The mixture left overnight under good stirring and then evaporated. The residue was dissolved in minimum of $CHCl_3$ and precipitated with pentane. The resulting powder was filtered off and the procedure was repeated twice to afford the desired compound as a white powder in 93% yield. ^{31}P NMR (121 MHz, $CDCl_3$): δ = 23.26 (P=O), 62.42 (P=S). ^{1}H NMR (400 MHz,

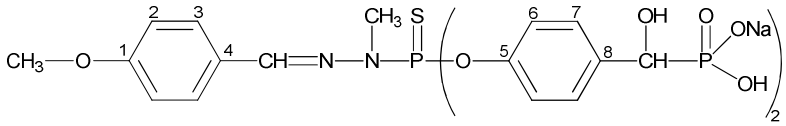
$CDCl_3$) δ 3.33 (d, 3H, $^3J_{PH}$ = 10.7 Hz, N-CH_3), 3.62 (d, $^3J_{PH}$ = 10.4 Hz, 6H, P-OCH_3), 3.66 (d, $^3J_{PH}$ = 10.4 Hz, 6H, P-OCH_3OCH_3), 3.84 (s, 3H, OCH_3), 4.69 (s br, 2H, OH), 5.01(d, 2H, $^2J_{PH}$ = 11.2 Hz, CH-OH), 6.93 (d, 2H, $^3J_{HH}$ = 8.7 Hz, H^2), 7.23 (d, 4H, $^3J_{HH}$ = 8.1 Hz, H^6), 7.44 (d, 4H, $^3J_{HH}$ = 7.0 Hz, H^7), 7.61 (s, CH=N), 7.65 (d, 2H, $^3J_{HH}$ = 8.7 Hz, H^3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 32.90 (d, $^2J_{CP}$ = 13.1 Hz, CH_3-N), 53.73 (d, $^2J_{CP}$ = 7.3 Hz, P-OCH_3), 53.89 (d, $^2J_{CP}$ = 6.2 Hz, P-OCH_3), 55.37 (OCH_3), 69.91 (d, $^1J_{CP}$ = 161.2 Hz, CH-OH), 114.19 (C^2), 121.41 (s br, C^6), 127.61 (C^4), 128.30 (d, $^3J_{CP}$= 5.5 Hz, C^7), 128.45 (C^3), 133.66 (C^8), 139.74 (d, $^3J_{CP}$ = 13.8 Hz, CH=N), 150.52 and 150.55 (2d, $^2J_{CP}$= 7.2 Hz, C^5), 160.74 (C^1).

Synthesis of (((((2-(4-methoxybenzylidene)-1-methylhydrazinyl)phosphorothioyl)bis(oxy)) bis (4,1-phenylene))bis(hydroxymethylene))diphosphonic acid



To a suspension of tetramethyl (((((2-(4-methoxybenzylidene)-1-methylhydrazinyl) phosphorothioyl) bis(oxy))bis(4,1-phenylene))bis(hydroxymethylene))bis(phosphonate) (0.60 g 0.87 mmol) in acetonitrile (1.5 mL) and triethylamine (0.24 mL, 1.73 mmol) bromotrimethylsilane (0.48 mL, 3.64 mmol) was added slowly at 0°C. The reaction mixture was lstirred for 12 h at room temperature and then the anhydrous methanol (2 mL) was added. After 2h, the reaction mixture was evaporated to dryness under reduced pressure. The residue was washed water and ether and final compound was obtained as a yellow powder with a yield of 75%. ^{31}P NMR (121 MHz, DMSO): δ = 17.41, 17.44 (P=O), 62.64 (P=S). ^{1}H NMR (300 MHz, DMSO) δ 3.32 (d, 3H, $^3J_{PH}$ = 11.0 Hz, N-CH_3), 3.78 (s, 3H, OCH_3), 4.54 (s br, 6H, OH), 4.65(d, 2H, $^2J_{PH}$ = 13.8 Hz, CH-OH), 7.01 (d, 2H, $^3J_{HH}$ = 8.8 Hz, H^2), 7.10 (d, 4H, $^3J_{HH}$ = 8.1 Hz, H^6), 7.40 (d, 4H, $^3J_{HH}$ = 7.3 Hz, H^7), 7.68 (d, 2H, $^3J_{HH}$ = 8.7 Hz, H^3), 7.91 (s br, CH=N); ^{13}C NMR (75 MHz, DMSO) δ 33.36 (d, $^2J_{CP}$ = 12.1 Hz, CH_3-N), 55.70 (OCH_3), 70.61 (d, $^1J_{CP}$ = 157.4 Hz, CH-OH), 114.76 (C^2), 120.31 (s, C^6), 127.94 (C^4), 128.76 (C^3), 129.06 (d, $^3J_{CP}$= 4.7 Hz, C^7), 138.39 (C^8), 141.64 (d, $^3J_{CP}$ = 14.1 Hz, CH=N), 149.21 and 149.25 (2d, $^2J_{CP}$= 6.7 Hz, C^5), 160.77 (C^1); FAB-MS m/z = 655 $[M+Na]^+$, 633 $[M+H]^+$.

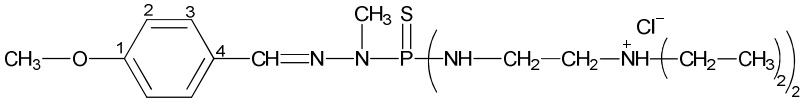
Synthesis of B1



The sodium monosalt form was obtained by adding aqueous sodium hydroxide (0.1N, 7.00 mL, 0.70 mmol) to a suspension of (((((2-(4-methoxybenzylidene)-1-methylhydrazinyl)phosphorothioyl)bis(oxy)) bis (4,1-phenylene)) bis(hydroxymethylene))

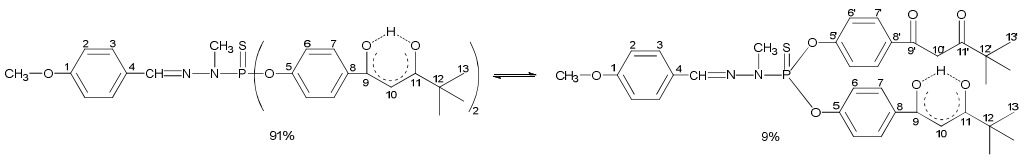
diphosphonic acid (0.44 g, 0.70 mmol) in water (16 mL) at 0°C. After 1h the solution was lyophilized to give the desired compound as a white powder in 93% yield. ^{31}P NMR (121 MHz, D_2O): δ = 16.10, 16.12 (P=O), 64.58 (P=S). ^{1}H NMR (300 MHz, D_2O) δ 3.12 (d, 3H, $^{3}J_{PH}$ = 10.7 Hz, N-CH_3), 3.60 (s, 3H, OCH_3), 4.68 (d, 2H, $^{2}J_{PH}$ = 10.3 Hz, CH-OH), 6.77 (d, 2H, $^{3}J_{HH}$ = 8.5 Hz, H^2), 7.08 (d, 4H, $^{3}J_{HH}$ = 8.2 Hz, H^6), 7.35 (d, 4H, $^{3}J_{HH}$ = 7.7 Hz, H^7), 7.46 (d, 2H, $^{3}J_{HH}$ = 8.5 Hz, H^3), 7.60 (s br, CH=N). ^{13}C NMR (75 MHz, D_2O) δ 32.46 (d, $^{2}J_{CP}$ = 11.4 Hz, CH_3-N), 55.33 (OCH_3), 71.57 (d, $^{1}J_{CP}$ = 151.9 Hz, CH-OH), 114.22 (C^2), 120.80 (d, $^{3}J_{CP}$= 2.4 Hz, C^6), 127.29 (C^4), 128.57 (d, $^{3}J_{CP}$= 4.7 Hz, C^7), 128.69 (C^3), 137.50 (C^8), 142.46 (d, $^{3}J_{CP}$ = 14.3 Hz, CH=N), 149.16 and 149.20 (2d, $^{2}J_{CP}$= 7.2 Hz, C^5), 160.14 (C^1).

Synthesis of B2



To a solution of (2-(4-methoxybenzylidene)-1 methylhydrazinyl) phosphonothioic dichloride (0.50 g, 1.69 mmol) in distilled THF (1 mL) was added N,N-Diethylethylenediamine (0.39 g, 3.36 mmol). After stirring overnight at room temperature, the solvent was removed by filtration. The white powder was washed with distilled THF (2 X 3 mL) and distilled pentane (2 X 3 mL) and final compound was obtained as a white powder with a yield of 90%. ^{31}P NMR (162 MHz, CD_3OD) δ 70.28. ^{1}H NMR (400 MHz, CD_3OD) δ 1.33 (t, 12H, $^{3}J_{HH}$ = 7.3 Hz, CH_2-CH_3), 3.13-3.50 (m, 19H, N-CH_2 and N-CH_3), 3.84 (s, 3H, OCH_3), 6.97 (d, 2H, $^{3}J_{HH}$ = 8.8 Hz, H^2), 7.72 (s, 1H, CH=N), 7.73 (d, 2H, $^{3}J_{HH}$ = 8.5 Hz, H^3); ^{13}C NMR (75 MHz, CD_3OD) δ 7.68 (CH_2-$C$$H_3$), 30.93 (d, $^{2}J_{CP}$ = 11.0 Hz, CH_3-N), 36.01 (CH_2-N-P), 47.53 ($C$$H_2$-$CH_3$), 52.17 (d, $^{3}J_{CP}$ = 6.9 Hz, $C$$H_2$-$CH_2$-N-P), 54.40 ($OCH_3$), 113.73 ($C^2$), 127.97 ($C^3$), 128.25 ($C^4$), 138.94 (d, $^{3}J_{CP}$ = 12.8 Hz, CH=N), 160.65 (C^1); ESI-MS m/z = 493.4 $[M- Cl]^+$, 229.4 $[M- 2Cl]^{2+}$.

Synthesis of B3



The dendron with chlorine atoms at the surface $MeOC_6H_4CH$=N-N(Me)-P(S)Cl_2 (0.99 g, 3.33 mmol) was dissolved in THF, and then 1-(4-hydroxyphenyl)-4,4-dimethylpentane-1,3-dione (1.54 g, 7 mmol) and the cesium carbonate (2.28 g, 7 mmol) were added. Reaction mixture was stirred overnight at room temperature, and then centrifugated. The solution was concentrated under the vacuum and purified using flash column chromatography with pentane

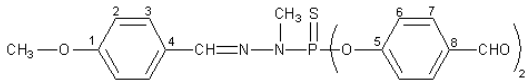
and ethyl acetate as eluents to give white powder; yield (91%); ^{31}P NMR (121 MHz, CD_2Cl_2): δ = 61.15 (s, P'), 61.41 (s, P); ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 1.22 (s, 0.81H, $H^{13'}$), 1.26 (s, 17.19H, H^{13}), 3.41 (d, $^{3}J_{HP}$ = 10.4 Hz, 3 H, NCH_3), 3.86 (s, 3H, OCH_3), 4.18 (s, 0.18H, H^{10}), 6.31 (s, 1.91H, H^{10}), 6.96 (d, $^{3}J_{HH}$ = 9.0 Hz, 2H, H^{2}), 7.36 (d, $^{3}J_{HH}$ = 8.7 Hz, 4H, H^{6}, $H^{6'}$), 7.66 (d, $^{3}J_{HH}$ = 9.0 Hz, 2H, H^{3}), 7.70 (d, $^{4}J_{HP}$ = 1.8 Hz, 1H, C=H), 7.93 (d, $^{3}J_{HH}$ = 8.7 Hz, 4H, H^{7}, $H^{7'}$), 16.56 (br s, 1.91H, O-Henol); ^{13}C NMR (75.4 MHz, CD_2Cl_2): δ = 25.9 ($C^{13'}$), 27.0 (C^{13}), 32.7 (d, $^{3}J_{CP}$ = 12.8 Hz, NCH_3), 39.6 (C^{12}), 47.5 ($C^{10'}$), 55.3 (OCH_3), 92.0 (C^{10}), 114.1 (C^{2}), 121.5 (d, $^{3}J_{CP}$ = 4.5 Hz, C^{6}, $C^{6'}$), 127.3 (brs, C^{4}), 128.4 (C^{3}), 128.6 (d, $^{4}J_{CP}$ = 0.7 Hz, C^{7}), 130.3 ($C^{7'}$), 132.7 (C^{8}), 140.5 (d, $^{4}J_{CP}$ = 14.3 Hz, CH=N), 153.6 (d, $^{3}J_{CP}$ = 6.7 Hz, C^{5}), 160.9 (C^{1}), 183.7 (C^{9}), 202.7 (C^{11}).

[1] a) N. Launay, A.-M. Caminade, R. Lahana, J.-P. Majoral, *Angew. Chem. Int. Ed.* **1994**, *33*, 1589; b) N. Launay, A.-M. Caminade, J.-P. Majoral, *J. Am. Chem. Soc.* **1995**, *117*, 3282.

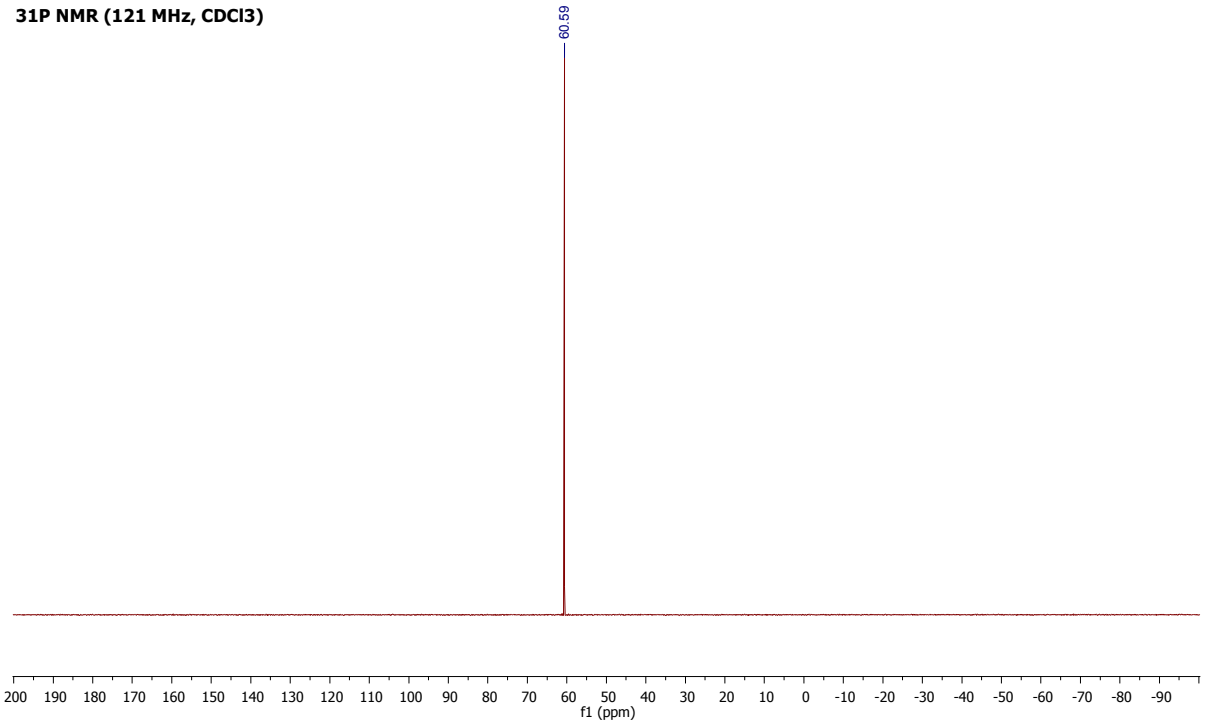
[2] C. Loup, M.-A. Zanta, A.-M. Caminade, J.-P. Majoral, B. Meunier, *Chem. Eur. J.* **1999**, *5*, 3644.

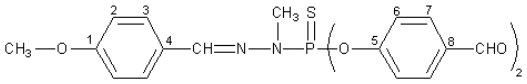
[3] M. Keller, M. Ianchuk, S. Ladeira, M. Taillefer, A.-M. Caminade, J.-P. Majoral, A. Ouali, *Eur. J. Org. Chem.* **2012**, *2012*, 1056.

S2: NMR spectroscopy of novel compounds

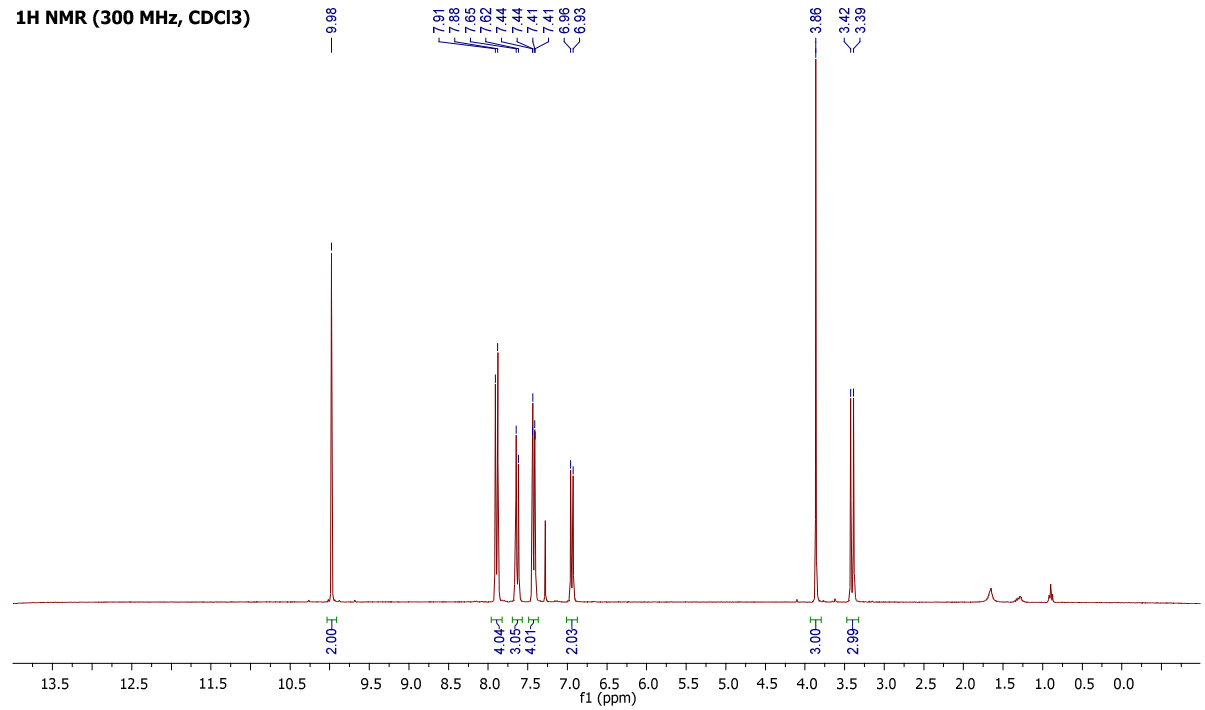


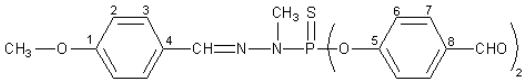
31P NMR (121 MHz, CDCl3)



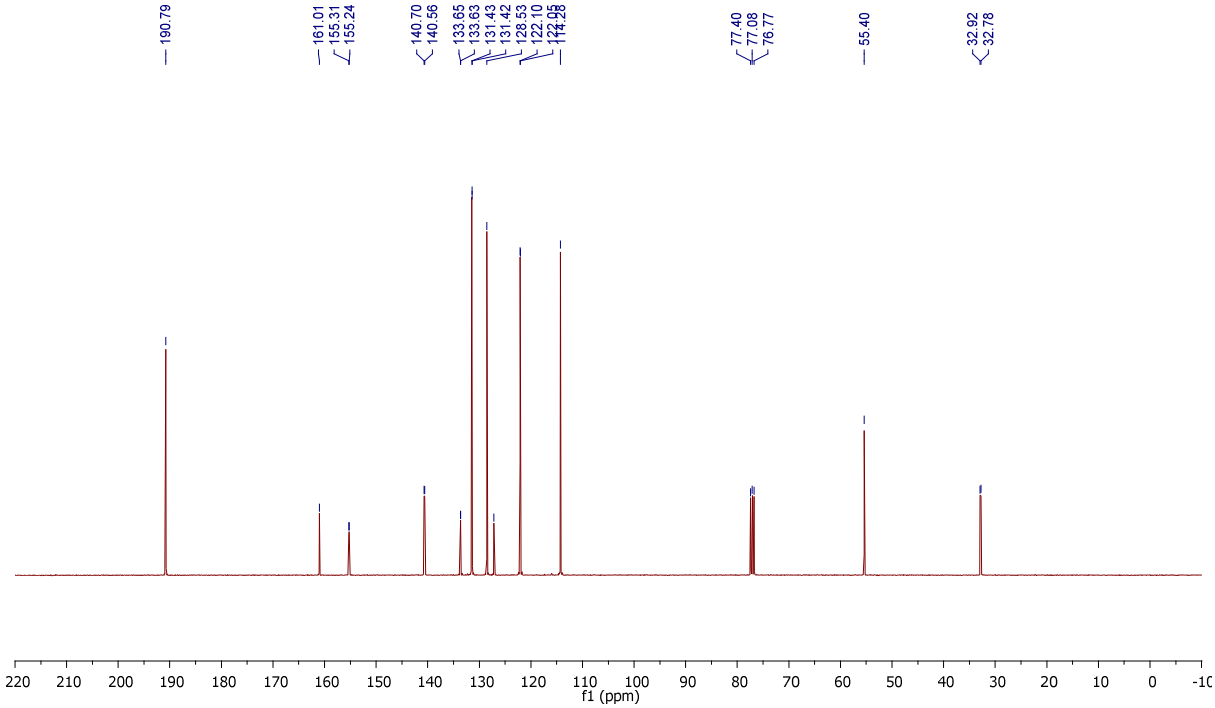


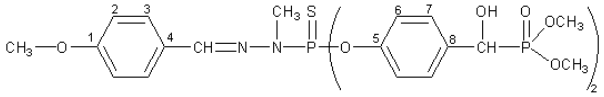
1H NMR (300 MHz, CDCl3)



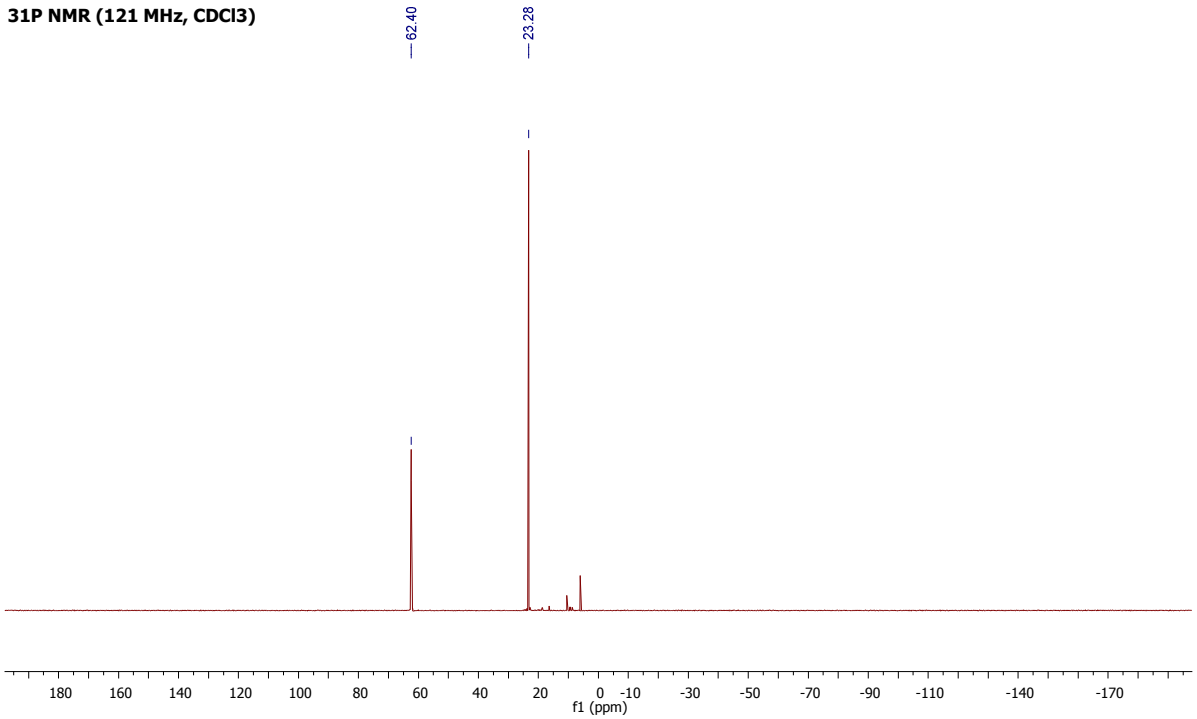


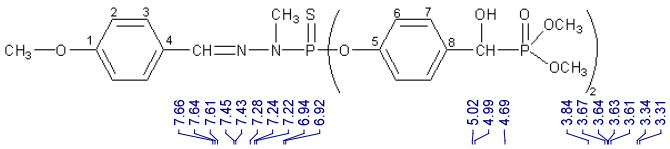
13C NMR (101 MHz, CDCl3)



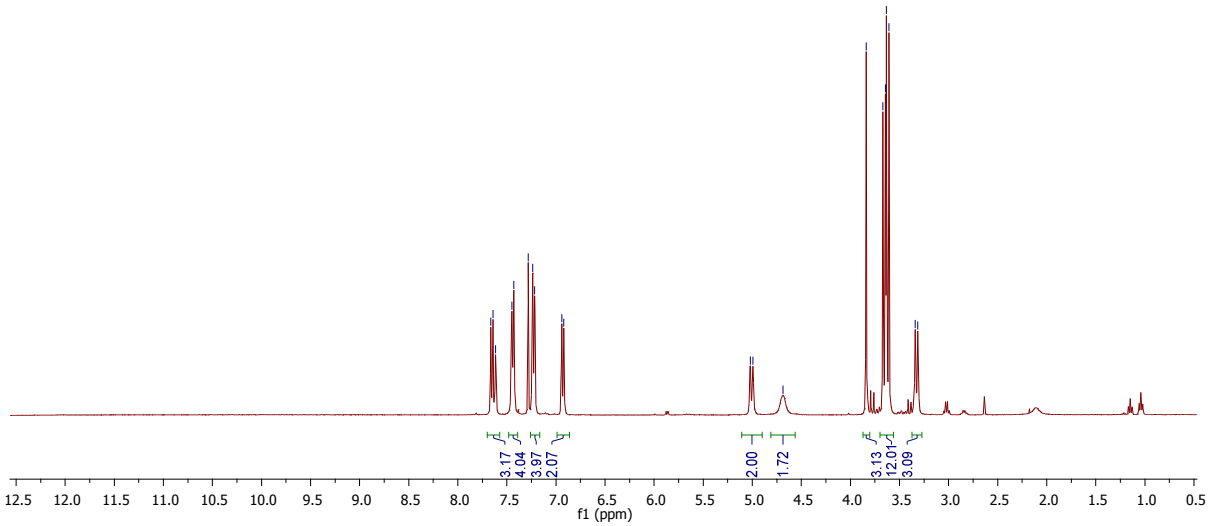


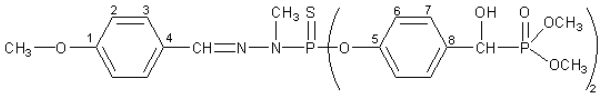
31P NMR (121 MHz, CDCl3)



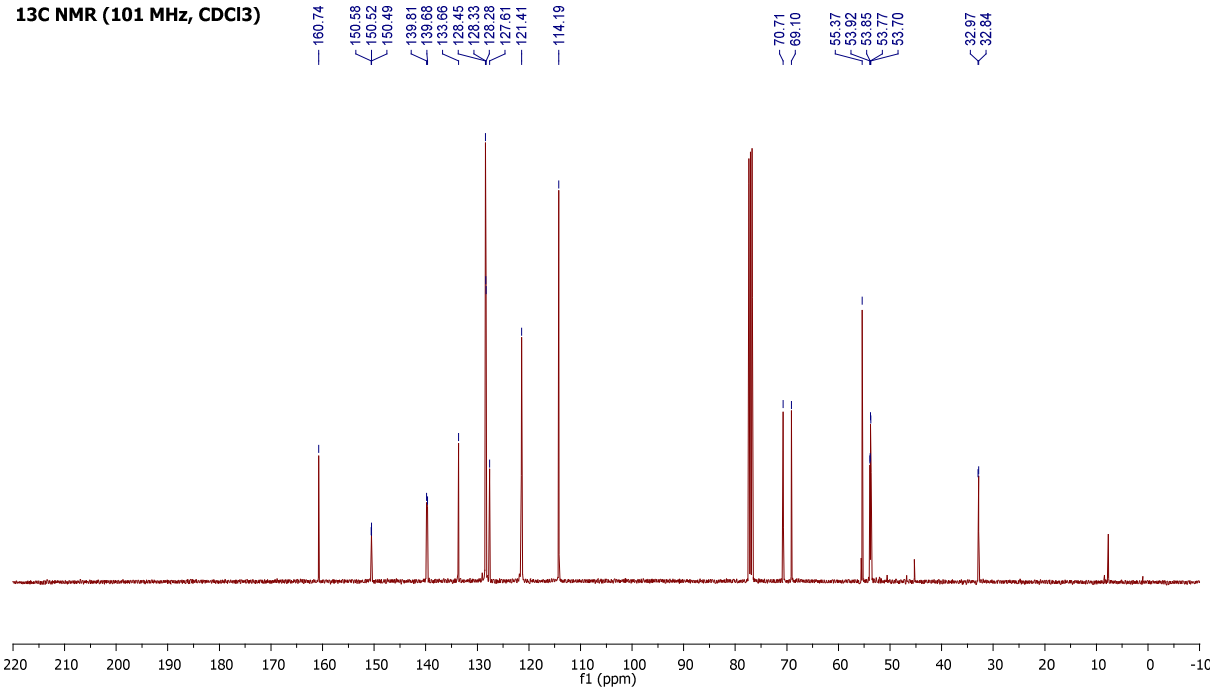


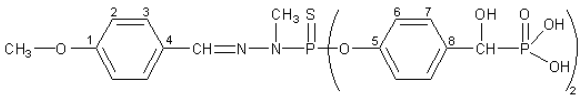
1H NMR (400 MHz, CDCl3)



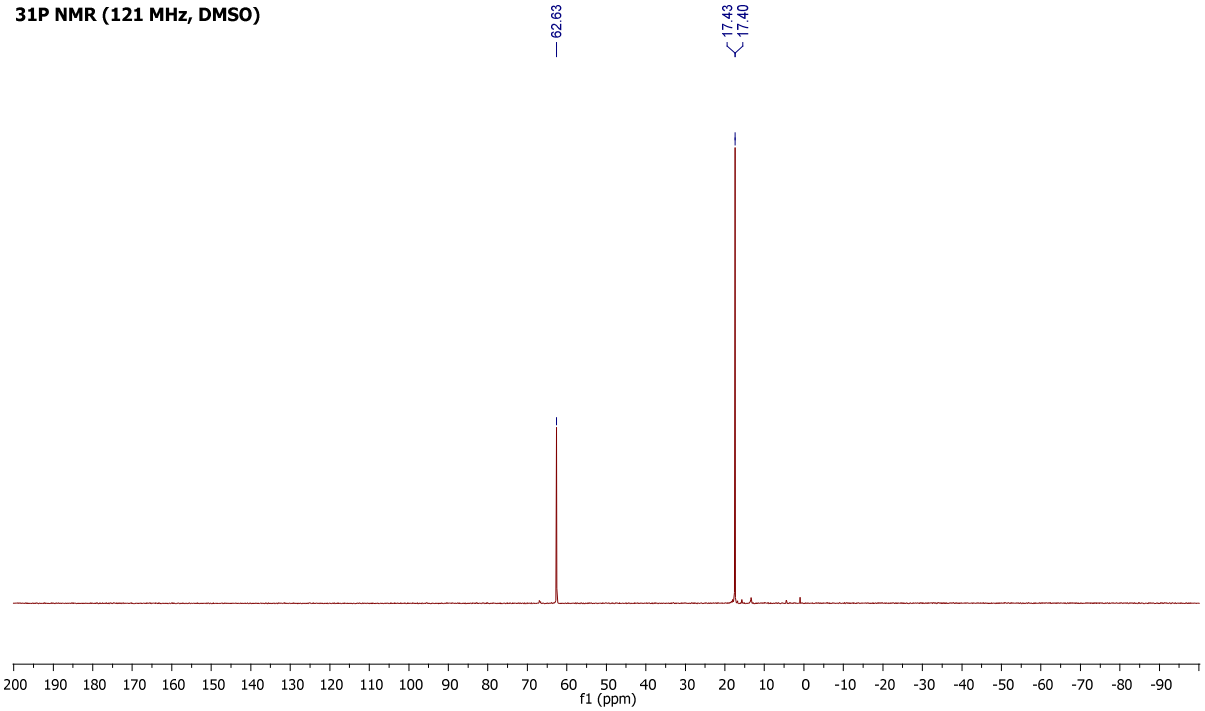


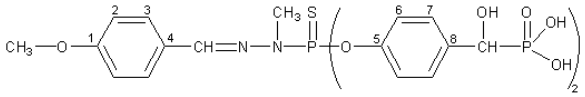
13C NMR (101 MHz, CDCl3)



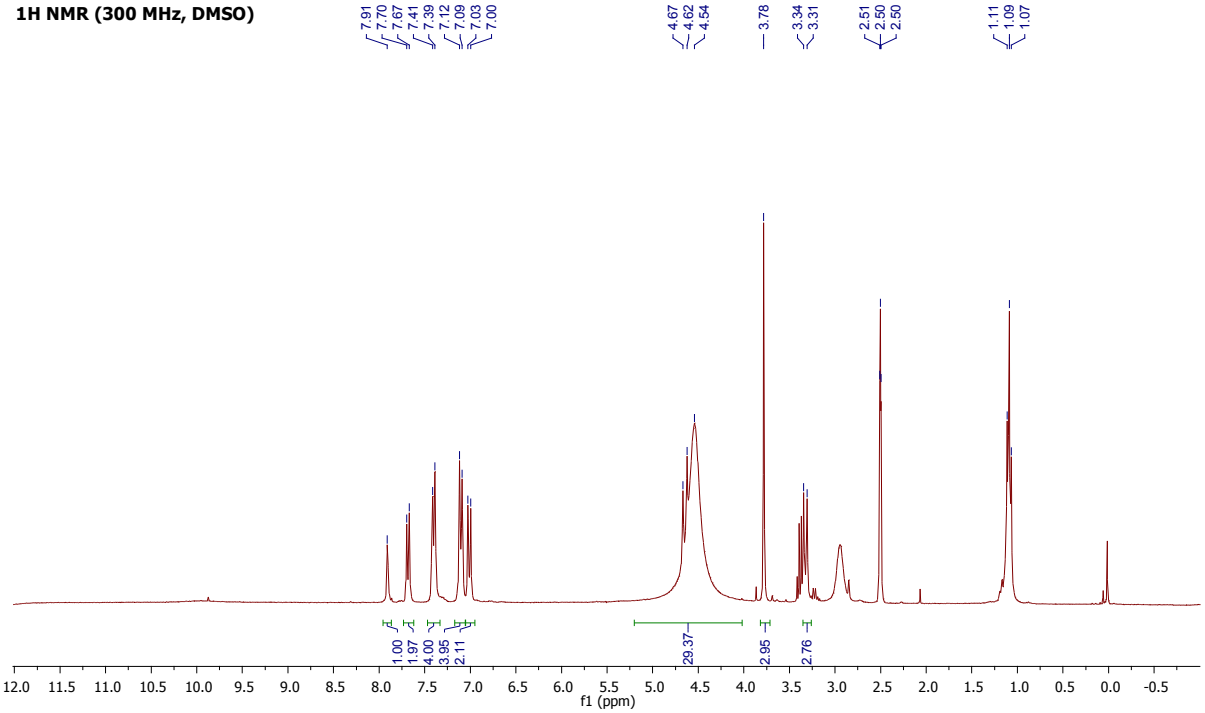


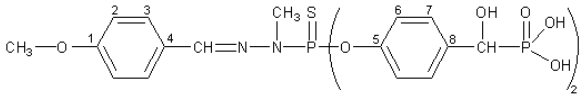
31P NMR (121 MHz, DMSO)



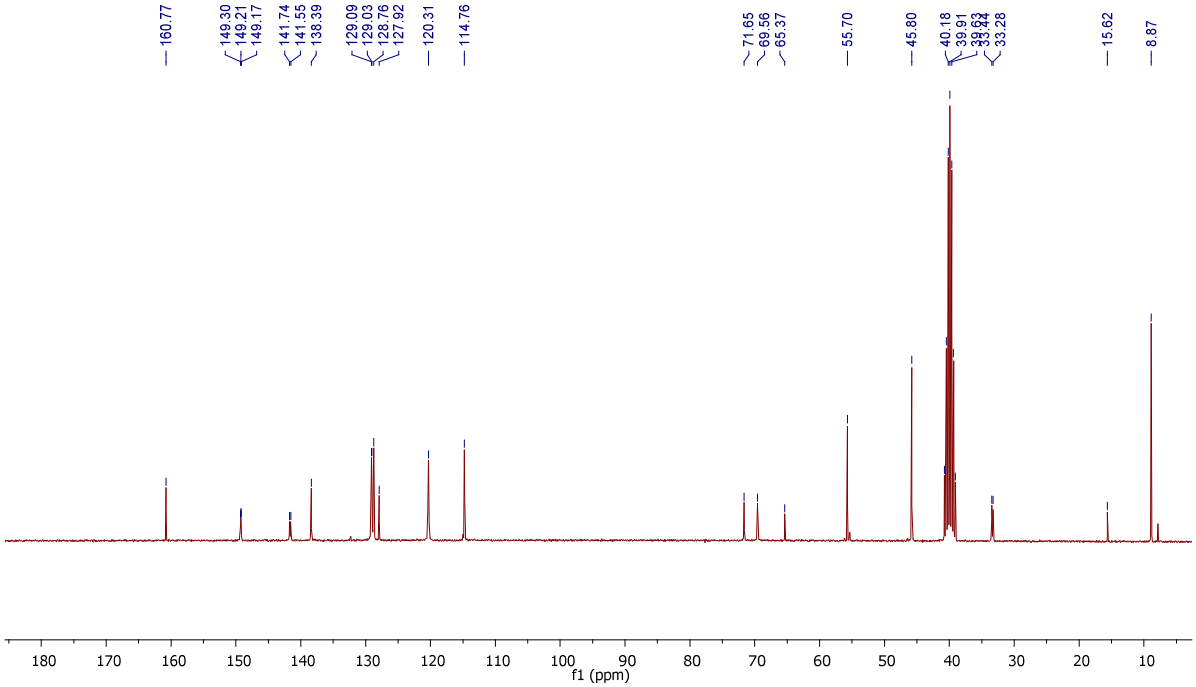


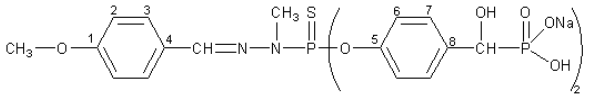
1H NMR (300 MHz, DMSO)





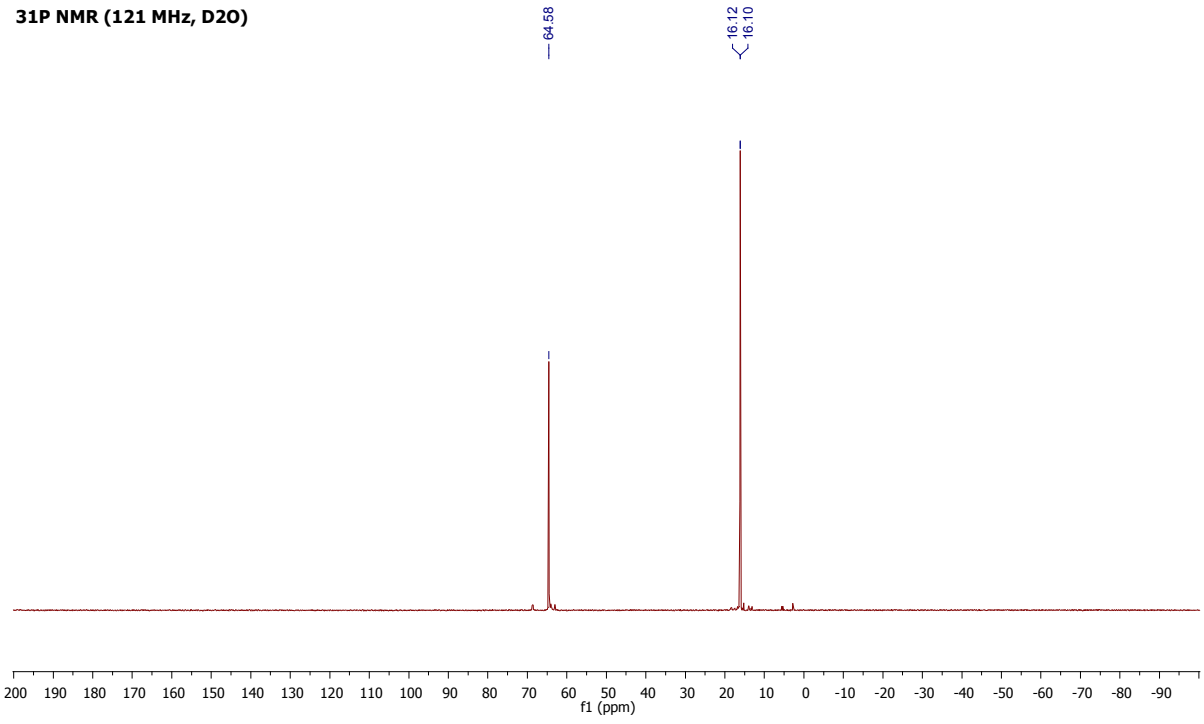
13C NMR (75 MHz, DMSO)

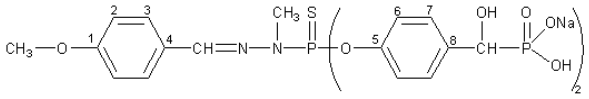




B1

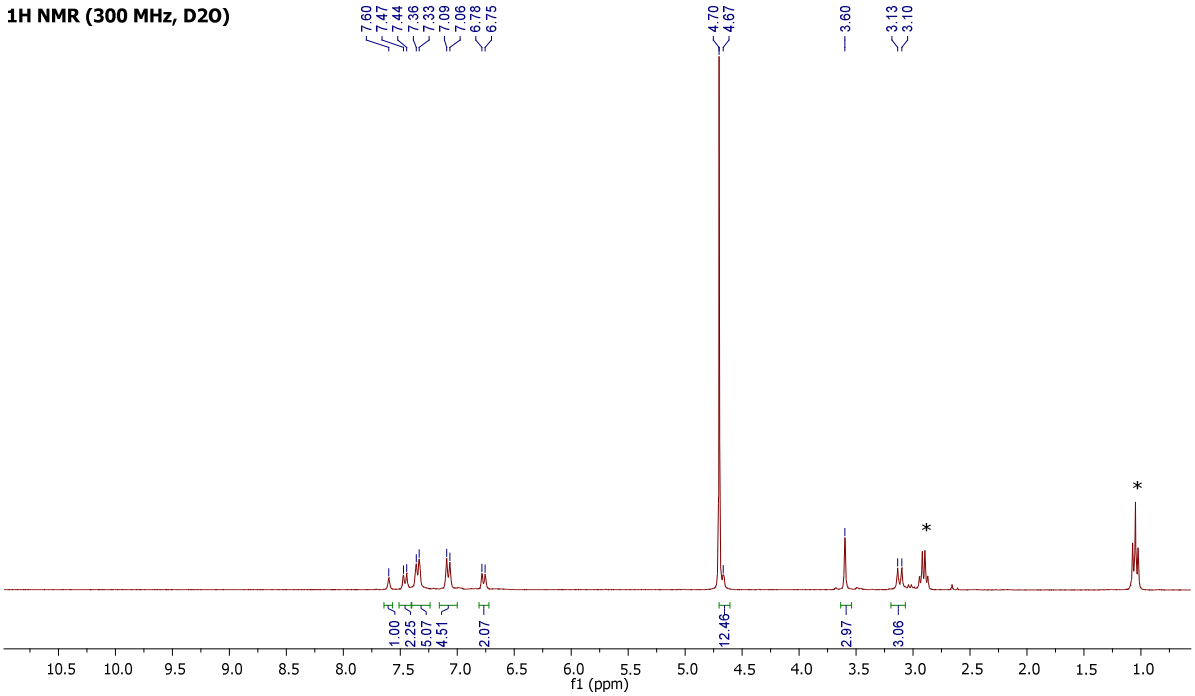
31P NMR (121 MHz, D2O)

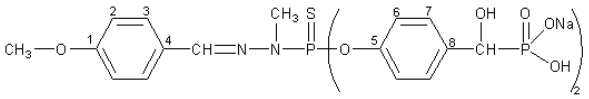




B1

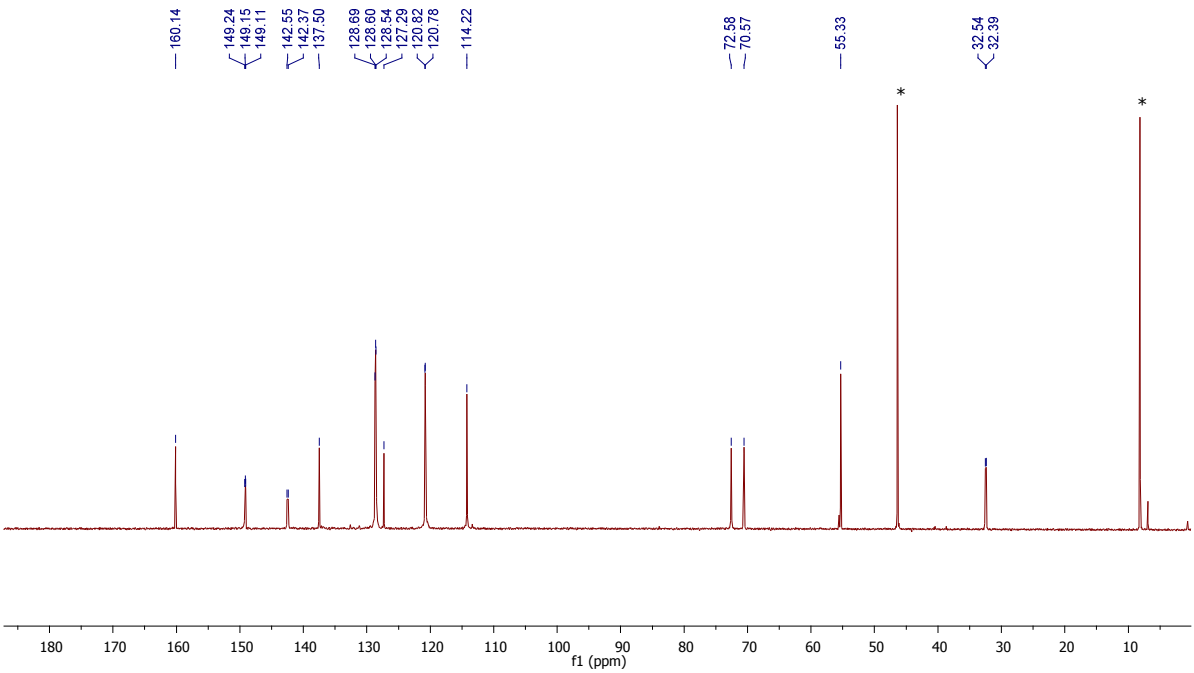
1H NMR (300 MHz, D2O)

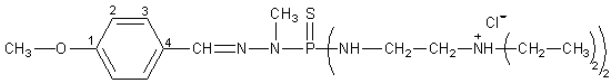




B1

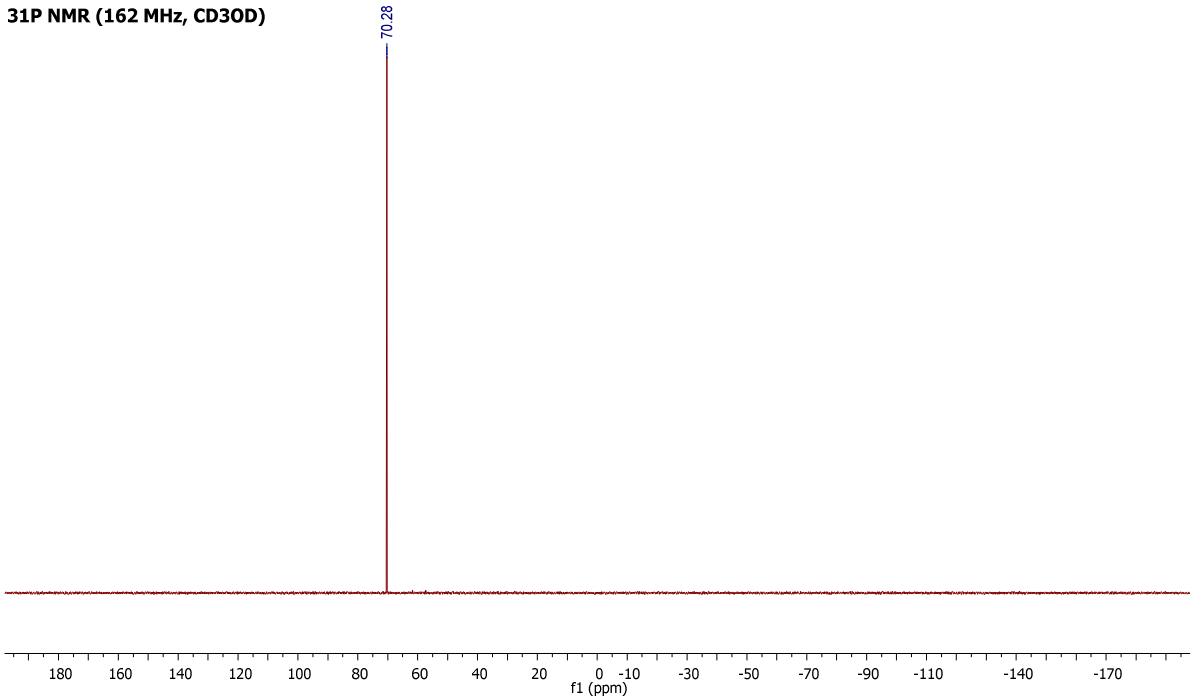
13C NMR (75 MHz, D2O)

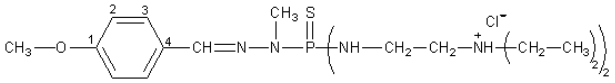




B2

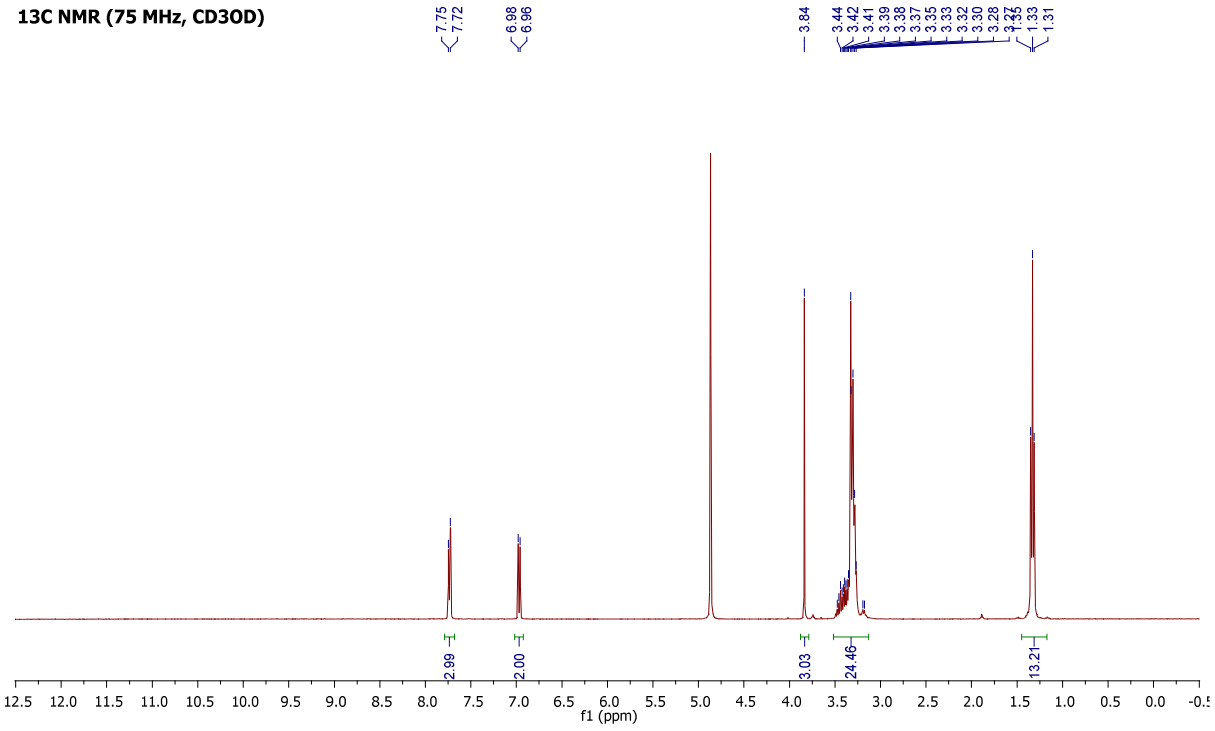
31P NMR (162 MHz, CD3OD)

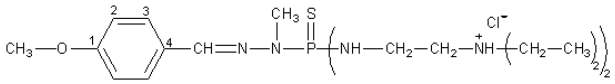




B2

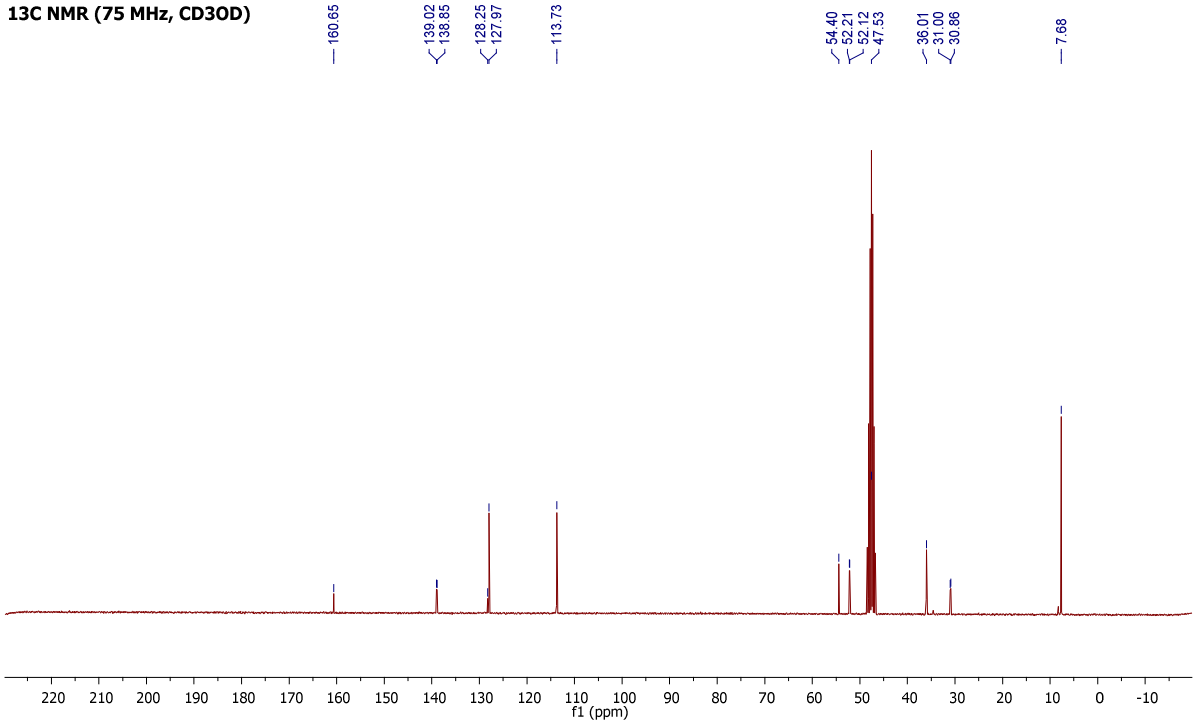
13C NMR (75 MHz, CD3OD)





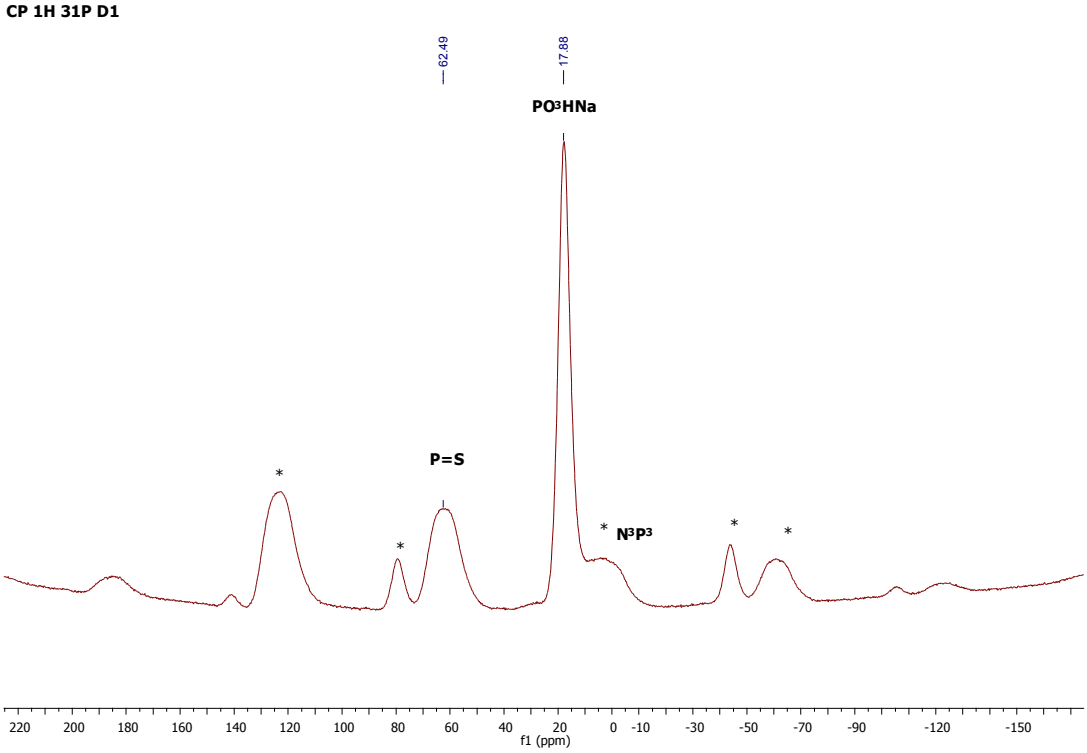
B2

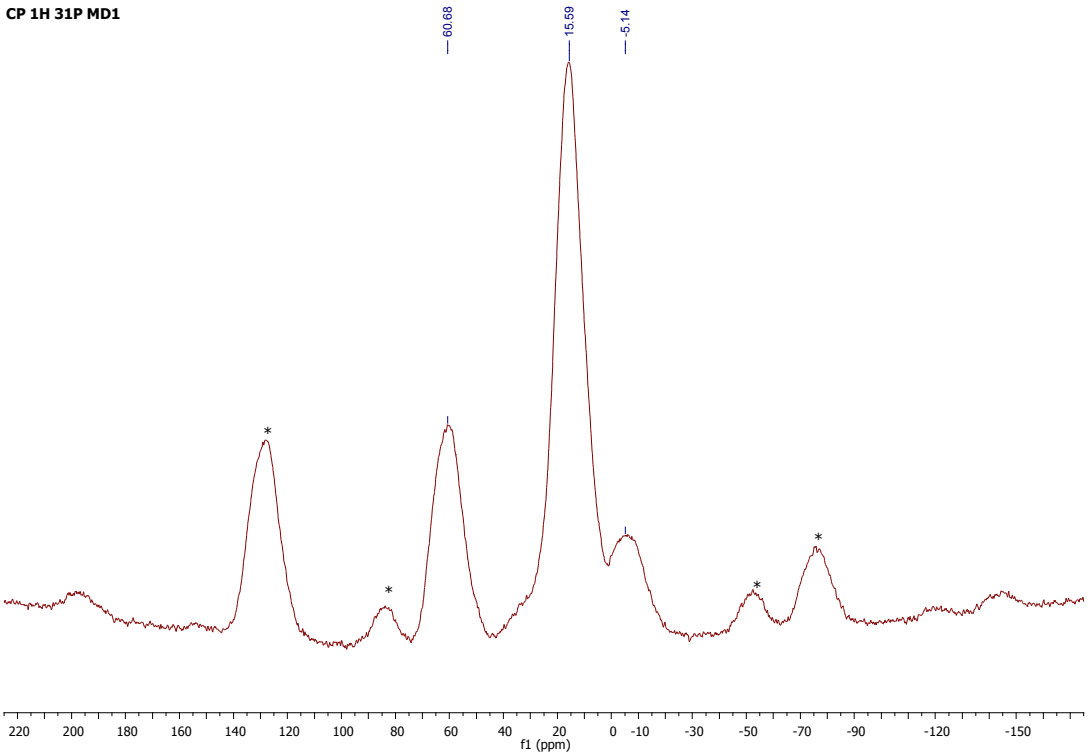
13C NMR (75 MHz, CD3OD)



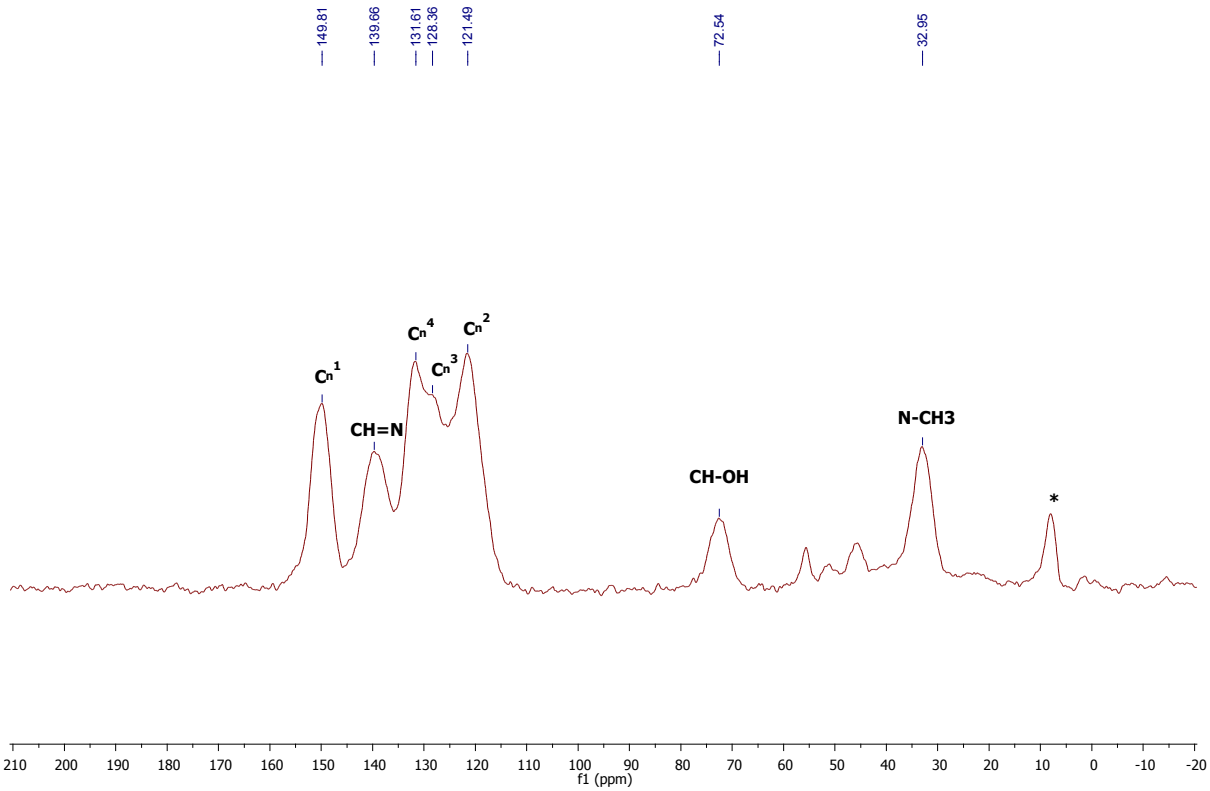
S3: ^{31}P CP MAS NMR and ^{13}C CP MAS NMR spectrum of the starting dendrimers and the resulting hybrid materials

S_{3a}: ^{31}P CP MAS NMR and ^{13}C CP MAS NMR spectrum of and MD1

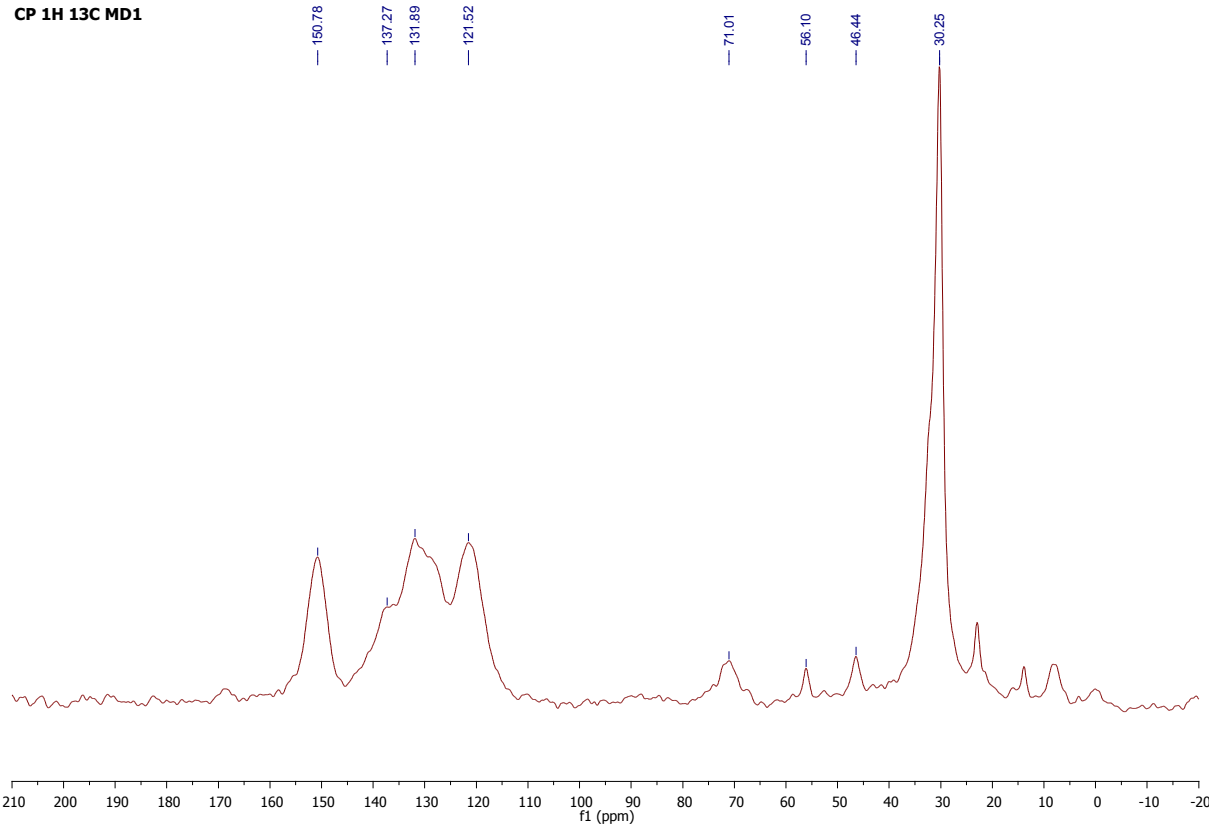




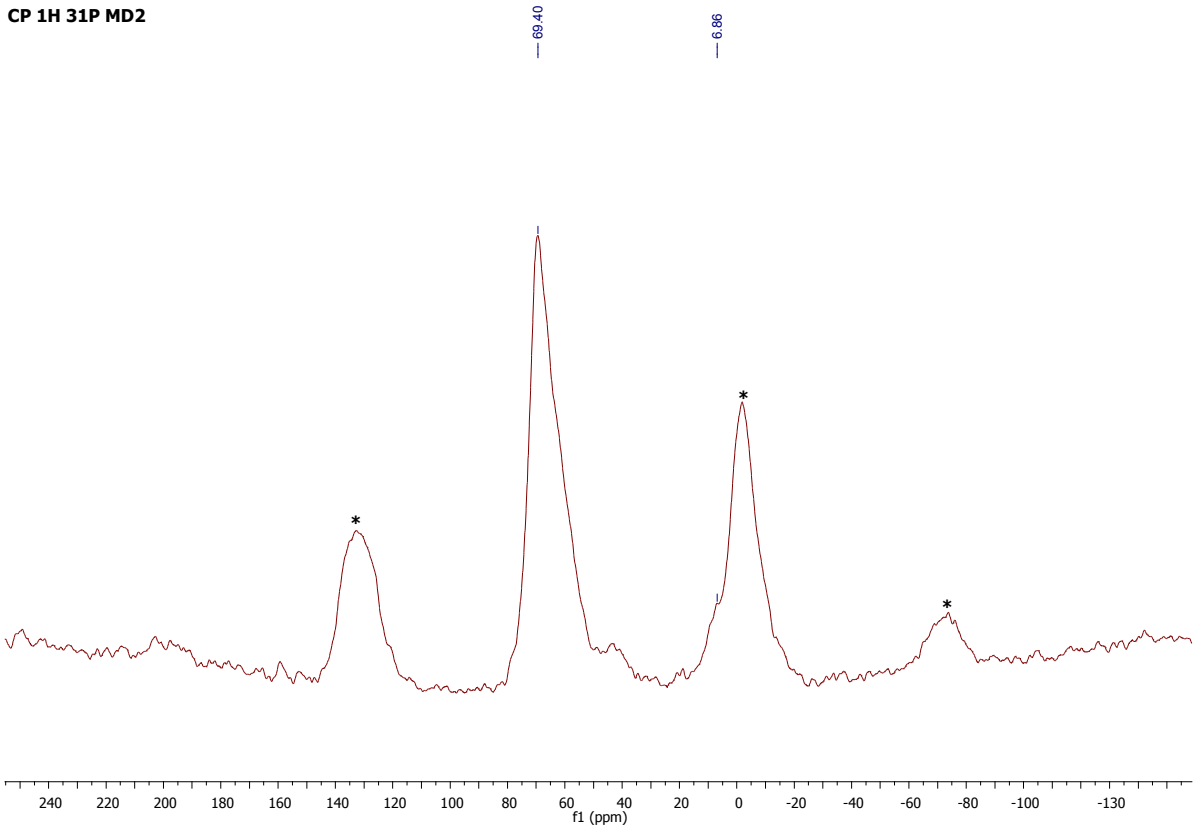
CP 1H-13C D1

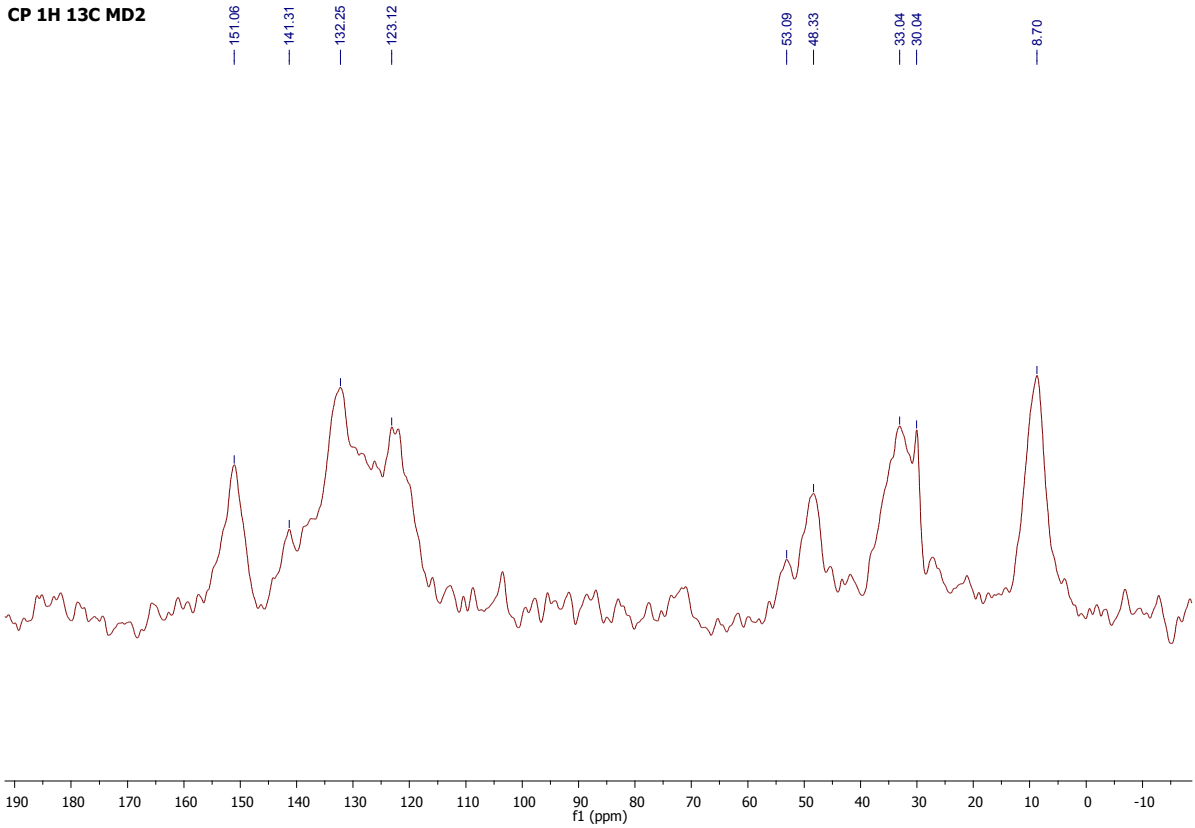


CP 1H 13C MD1

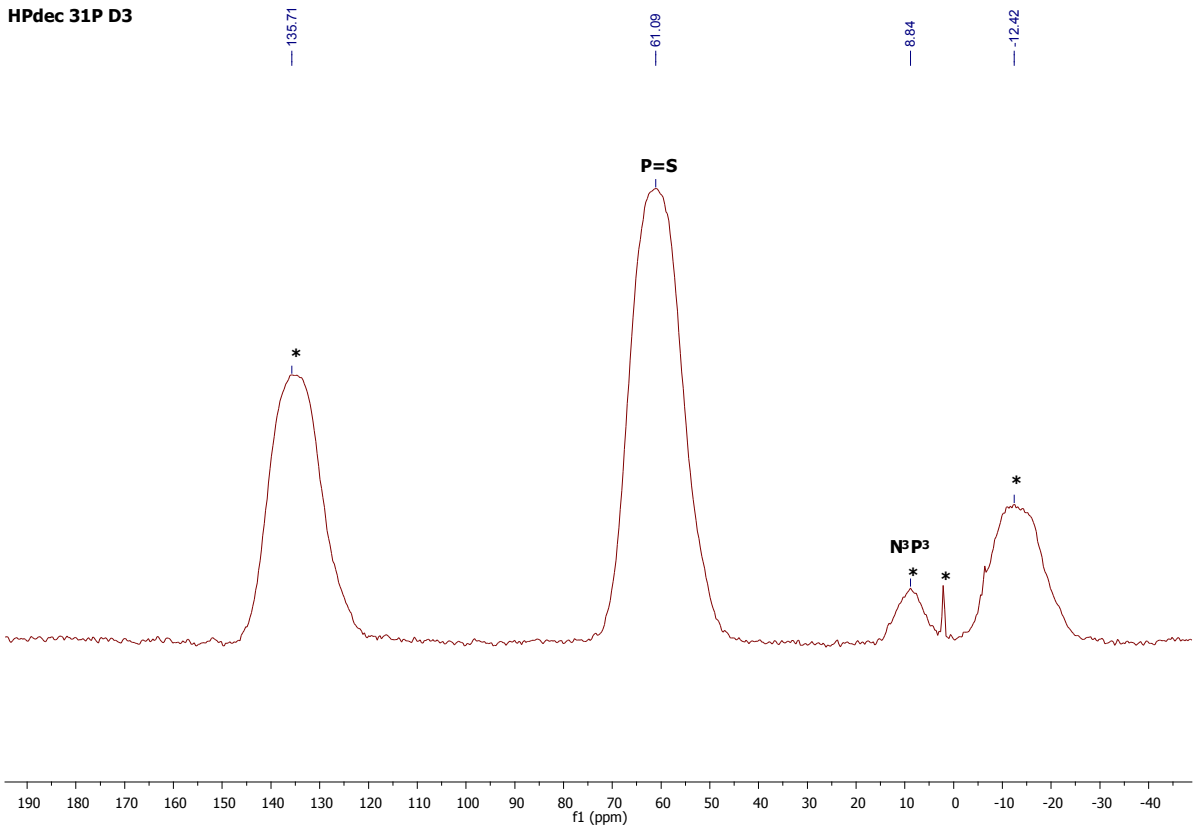


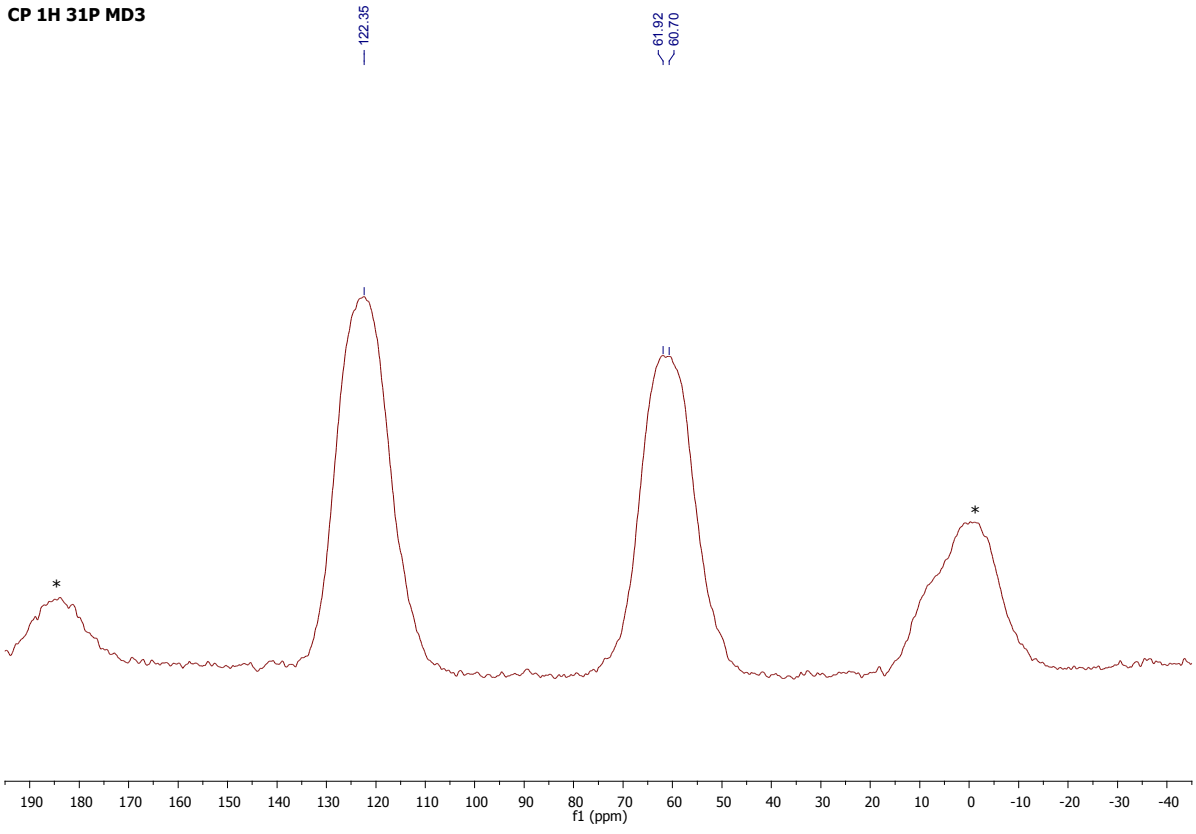
S_{3b}: ^{31}P CP MAS NMR and ^{13}C CP MAS NMR spectrum of MD2



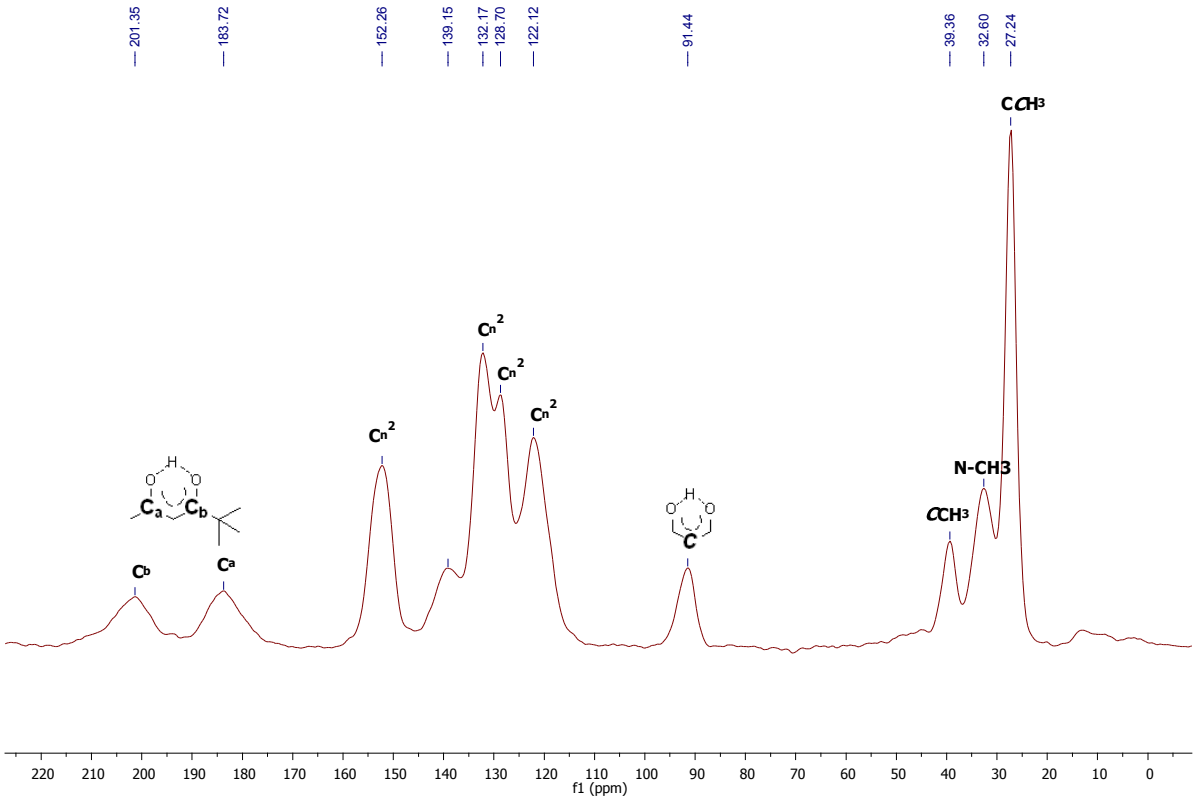


S_{3c}: ^{31}P CP MAS NMR and ^{13}C CP MAS NMR spectrum of D3 and MD3

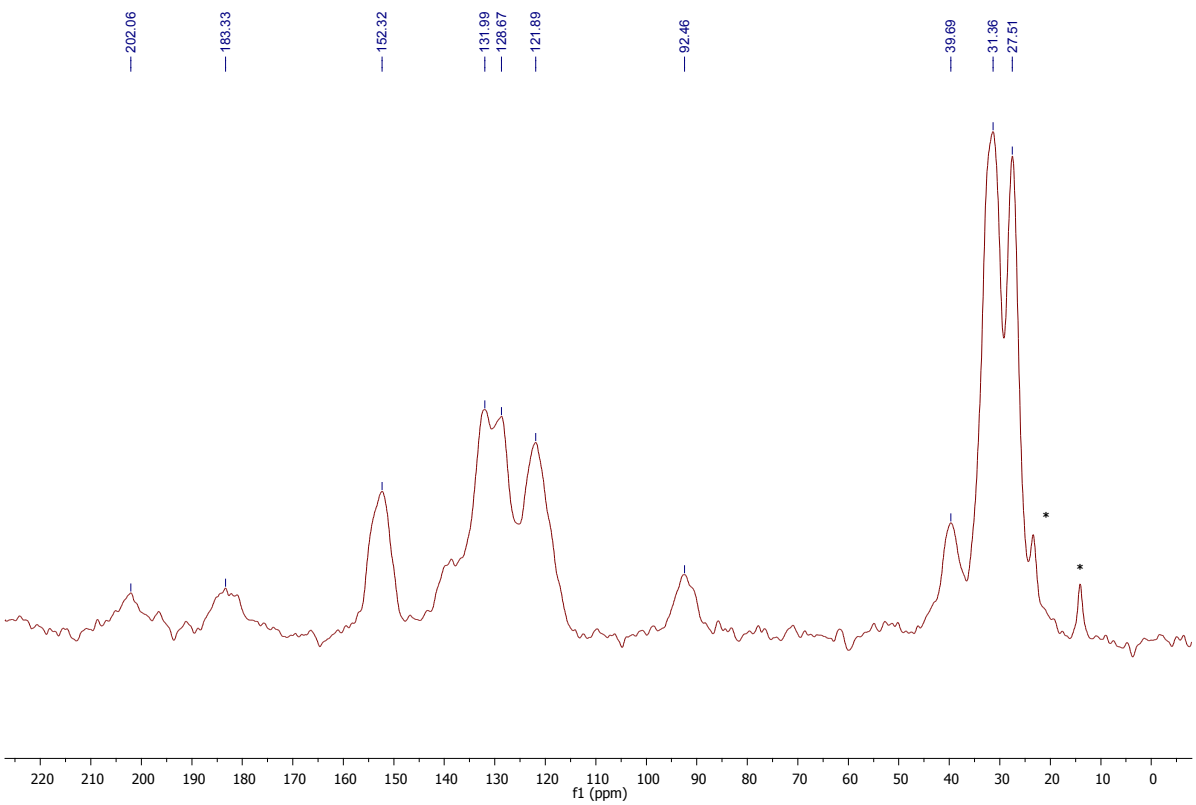




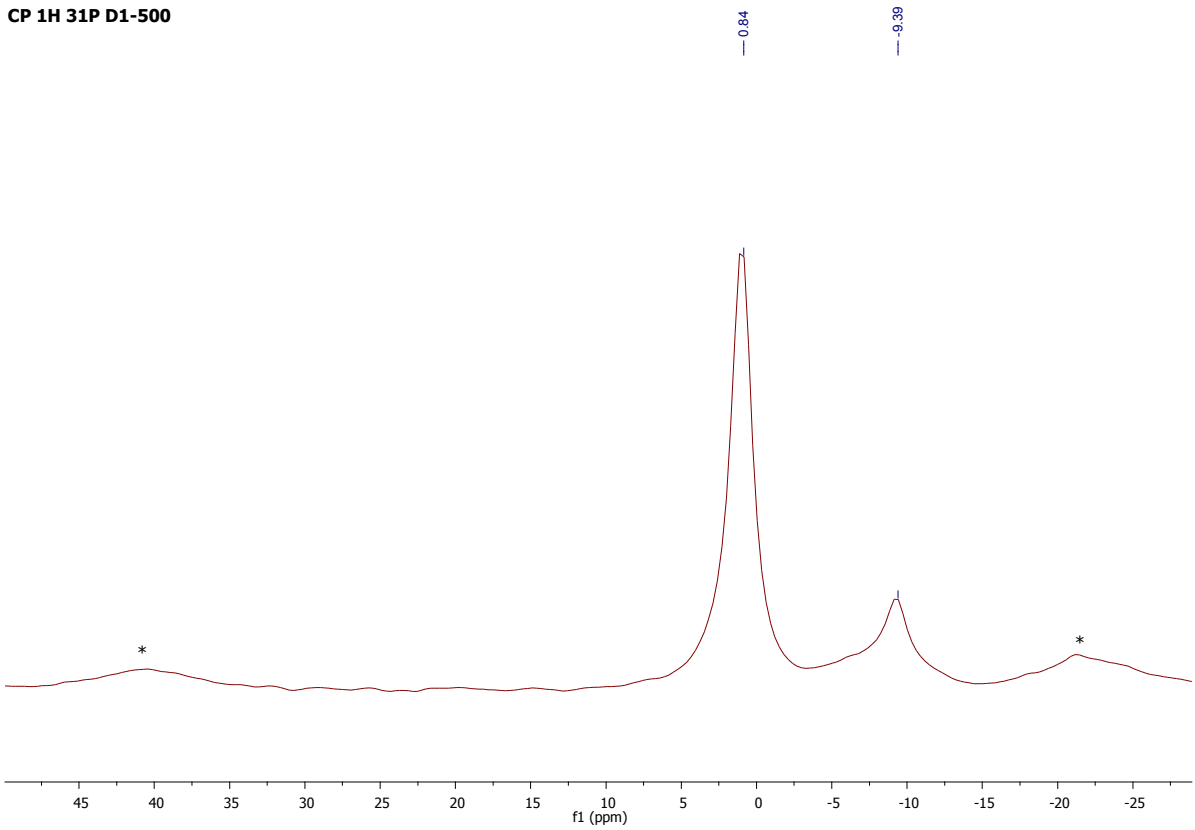
CP 1H-13C D3

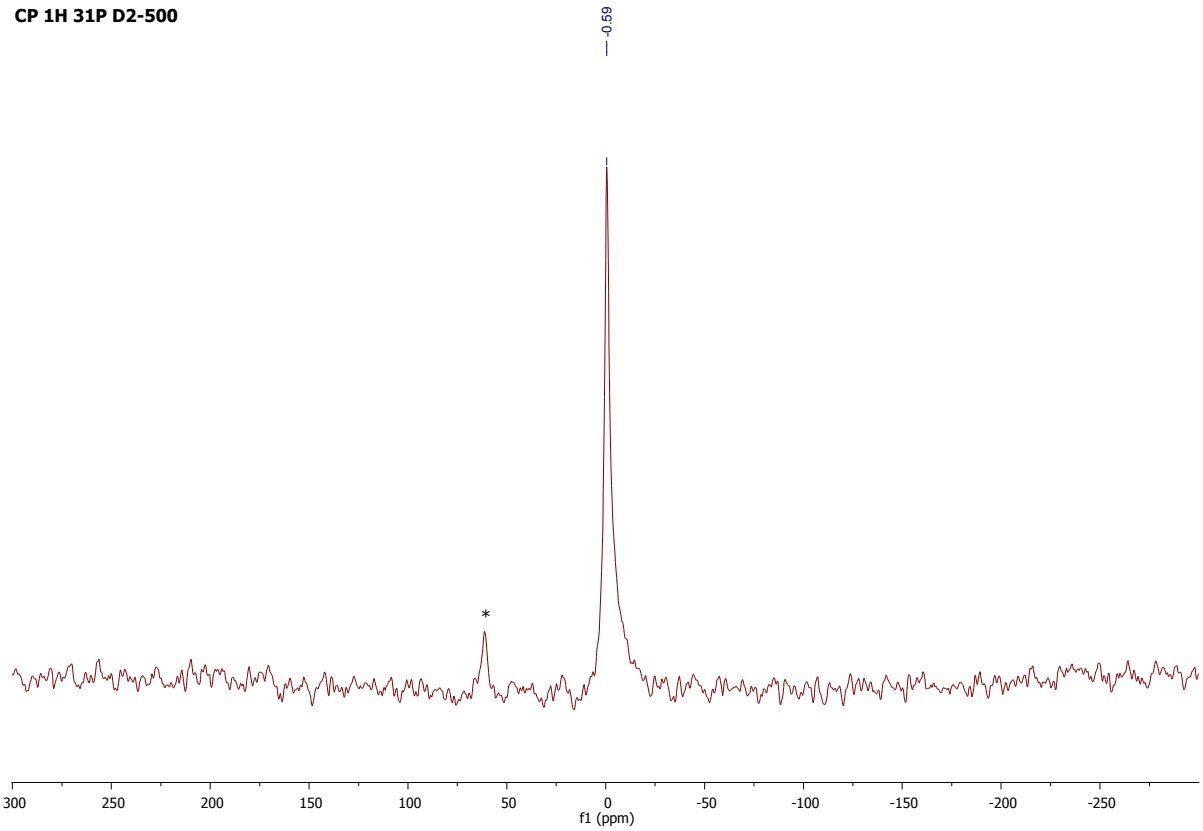


CP 1H 13C MD3

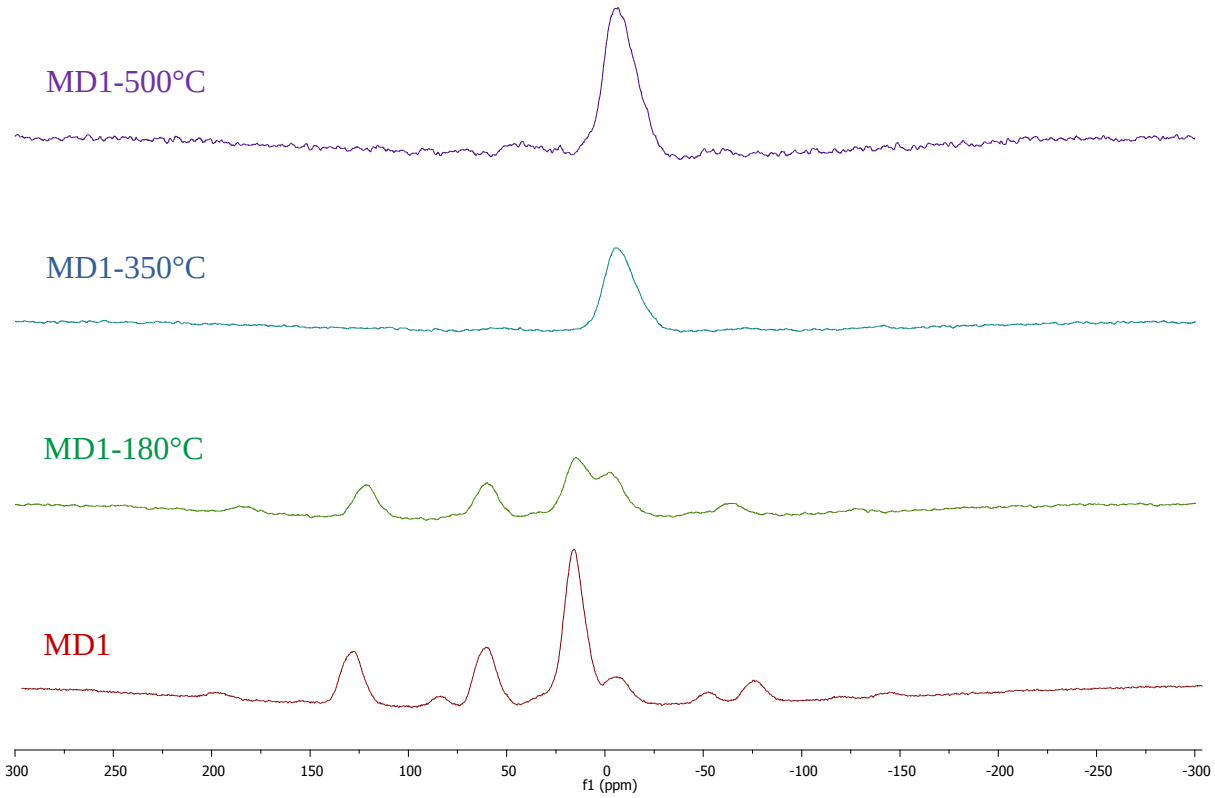


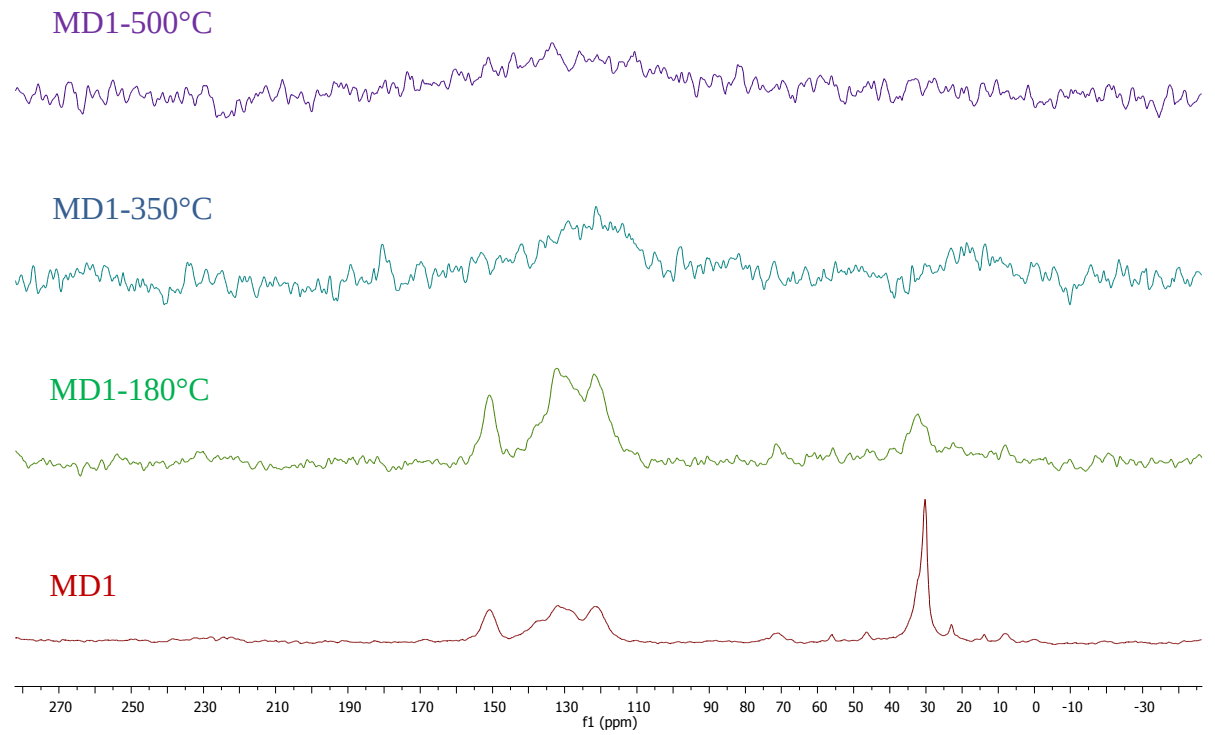
S_{3d}: ^{31}P CP MAS NMR spectrum of and D1-500 and D2-500

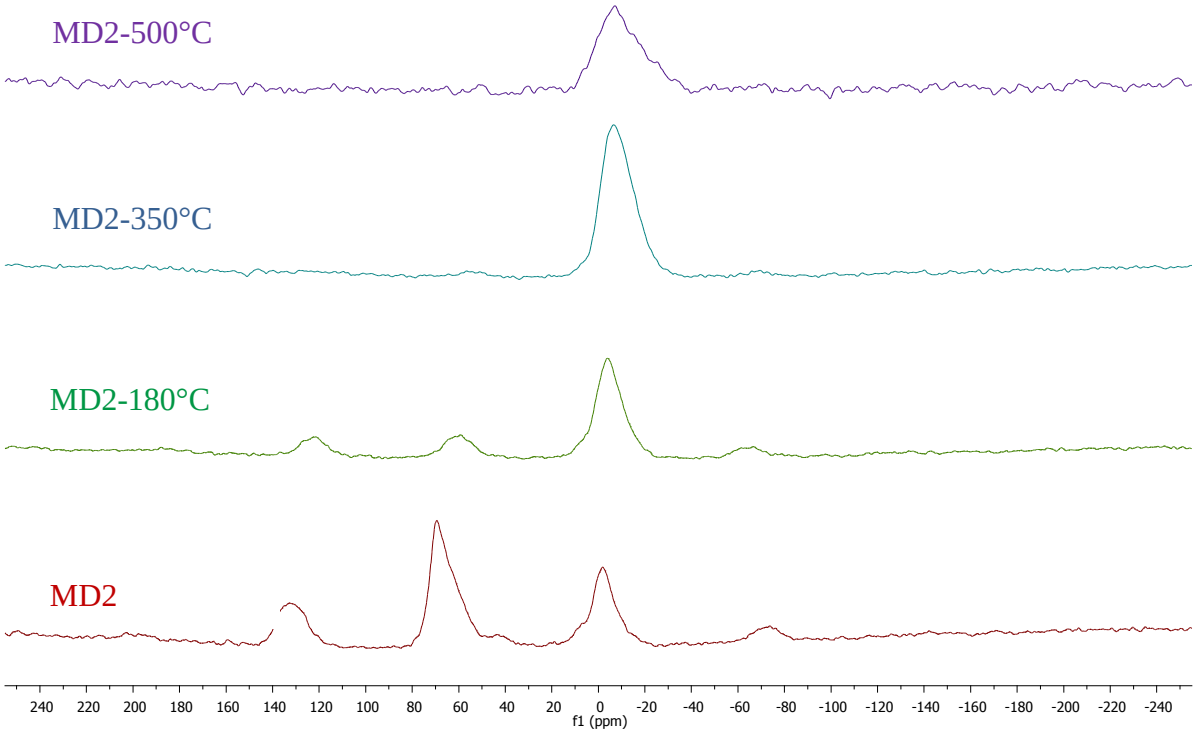


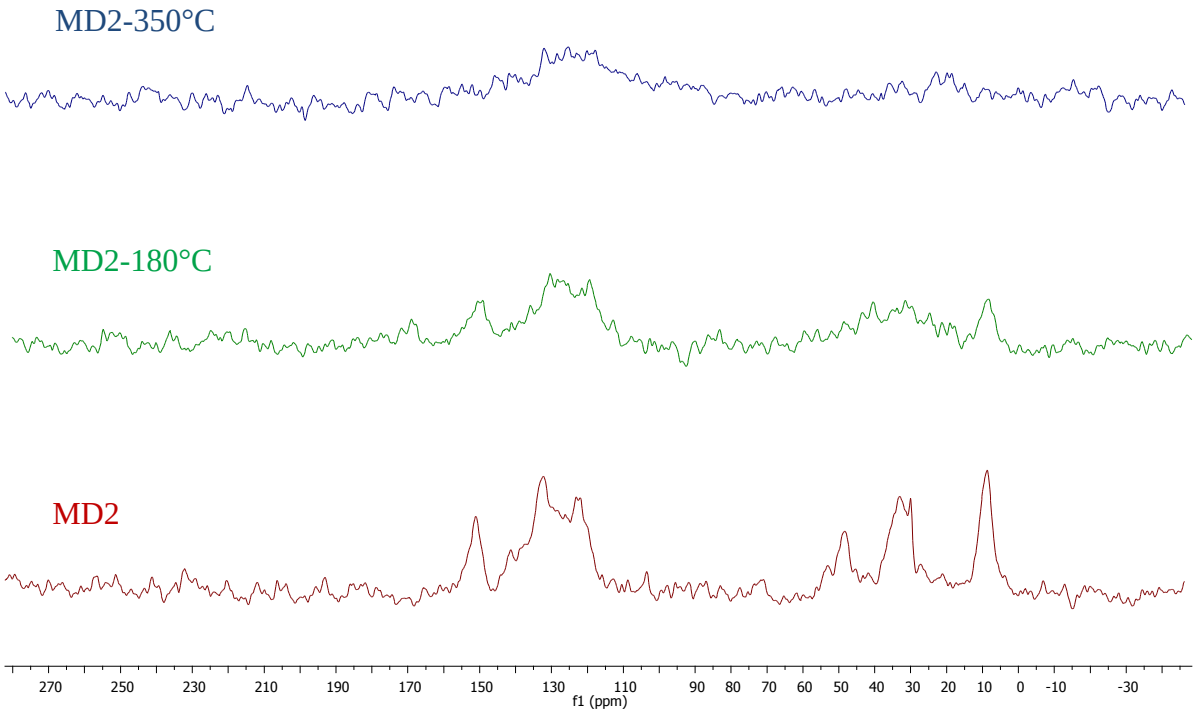


S_{3e}: NMR spectroscopy of annealed materials

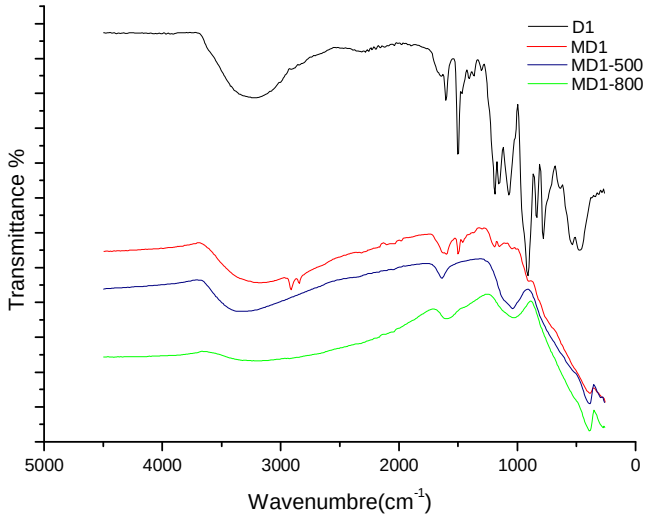


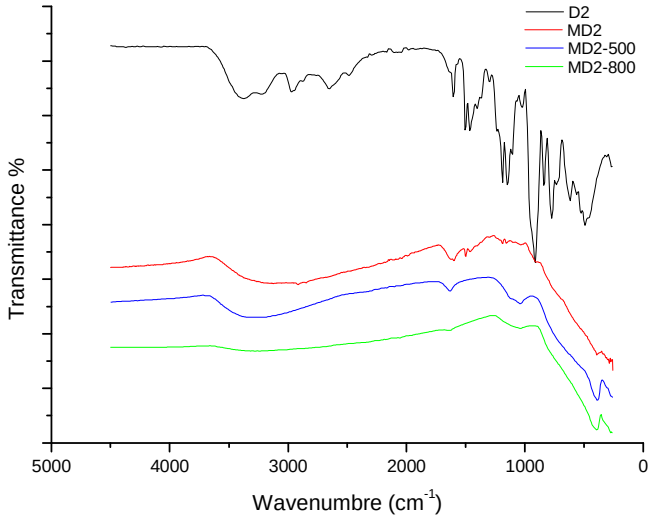


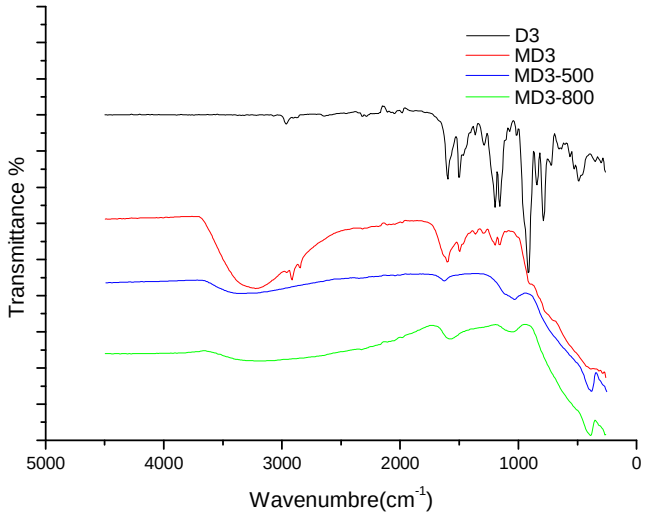




S4: FTIR of dendrimers and hybrid materials

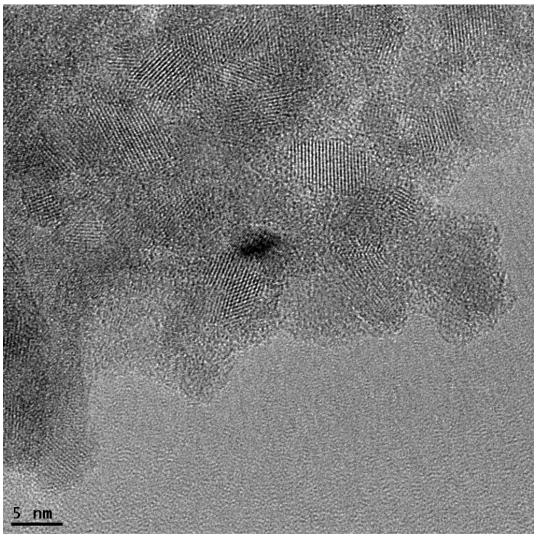


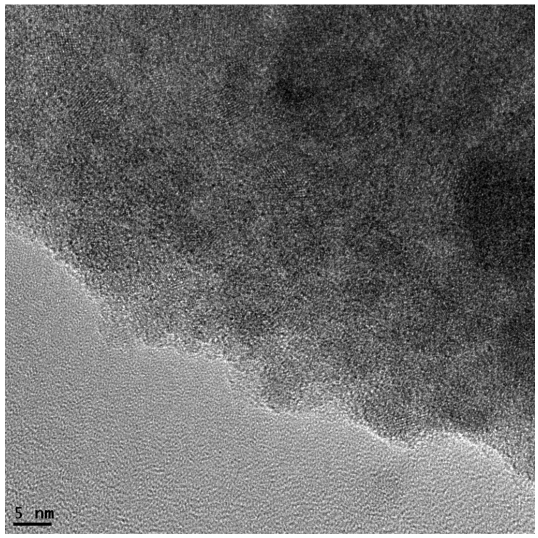




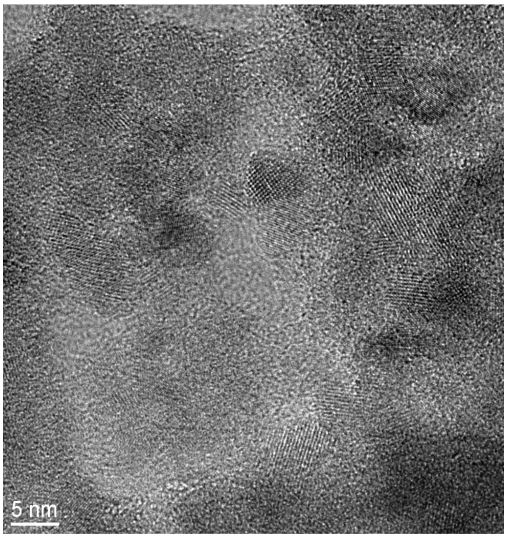
S5: TEM analysis of hybrid materials

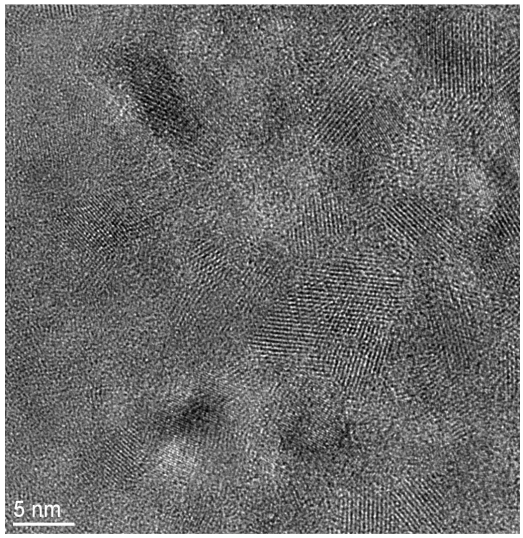
S_{5a}:TEM analysis of MD1



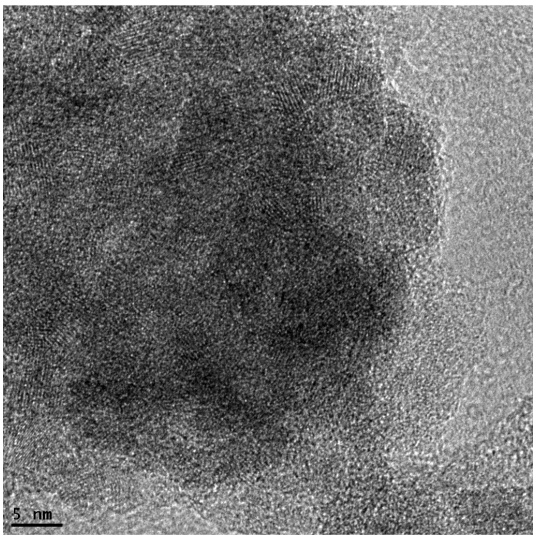


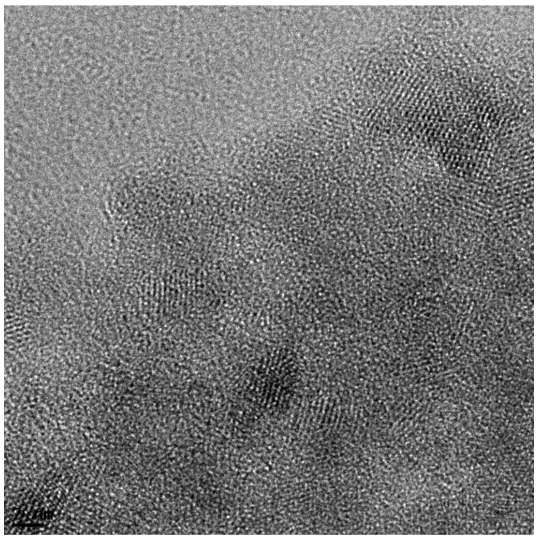
S_{5b}:TEM analysis of MD2



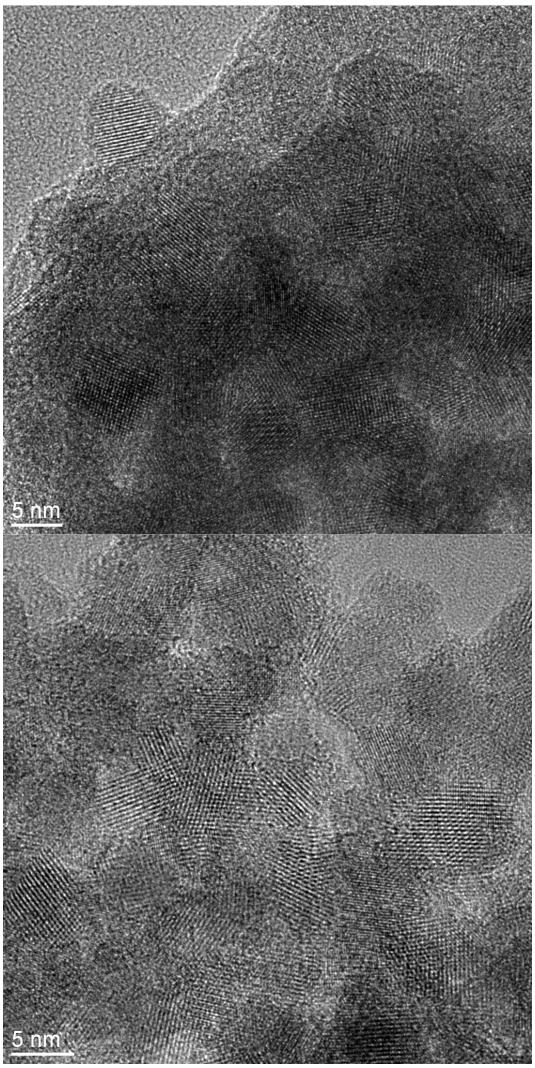


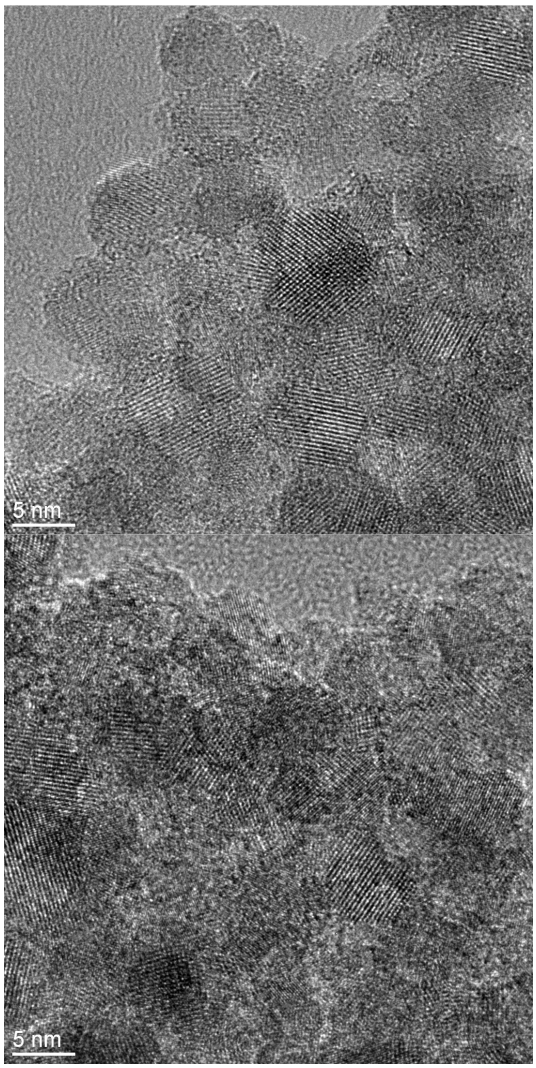
S_{5c}:TEM analysis of MD3



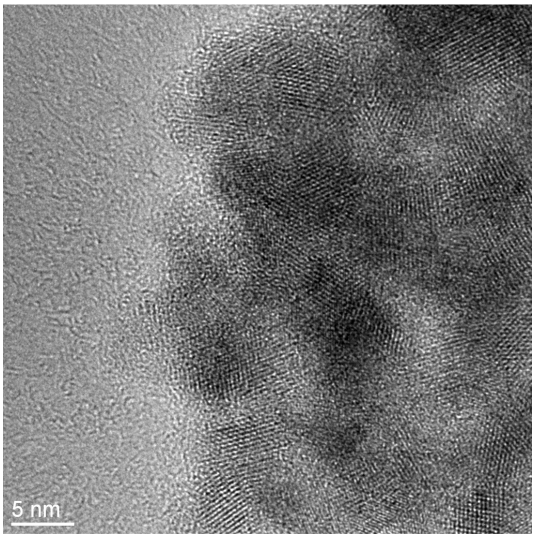


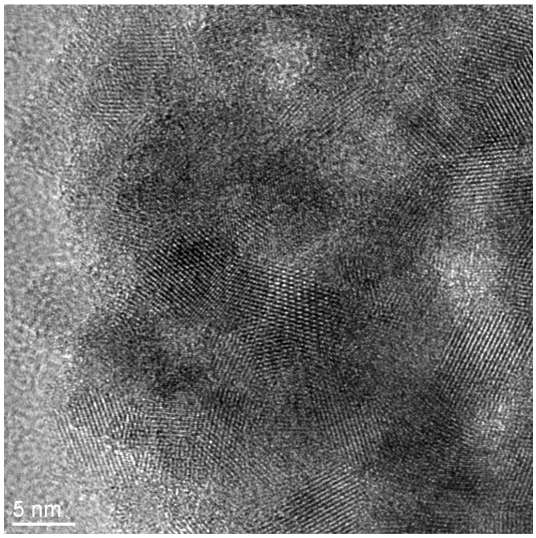
S_{5d}:TEM analysis of MD1-500



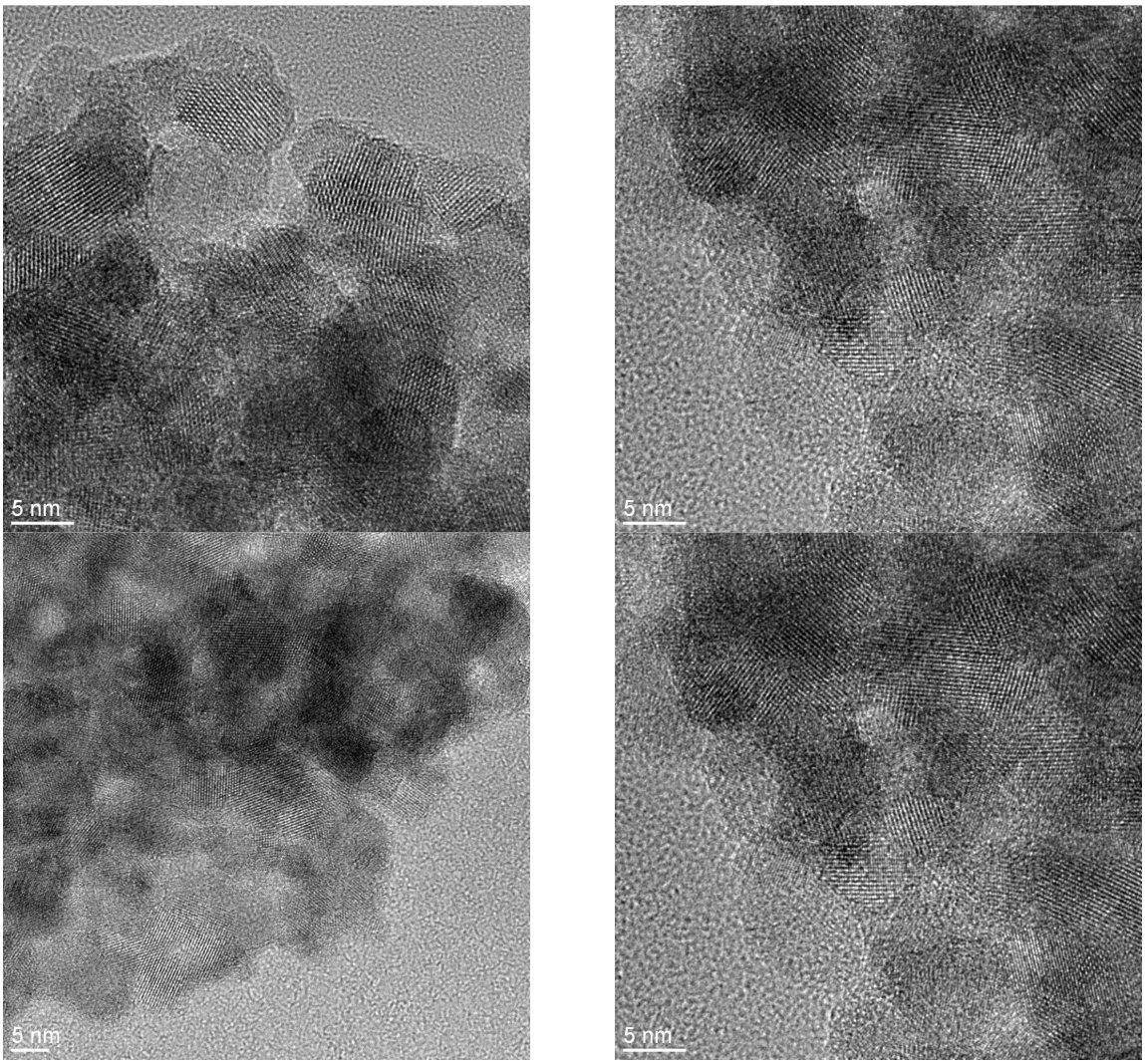


S_{5e}:TEM analysis of MD2-500



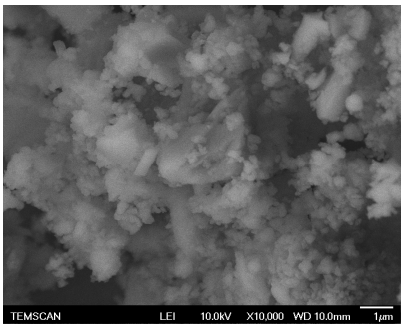


S_{5f}:TEM analysis of MD3-500

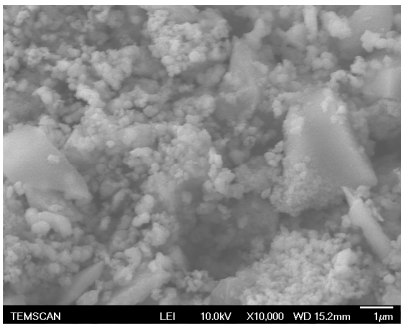


S6: SEM analysis of hybrid materials

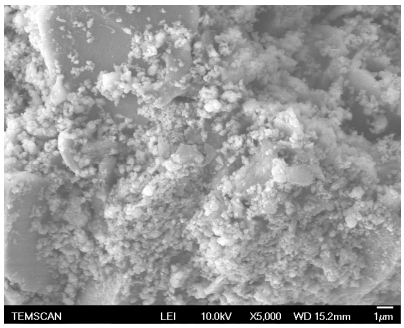
S_{6a}: SEM analysis of MD1



MD1

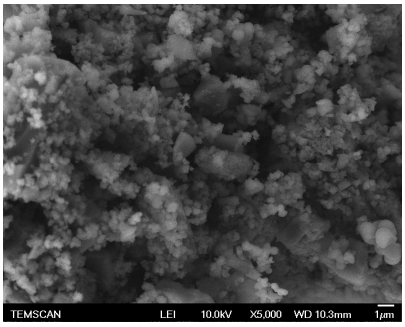


MD1(T = 180°C)

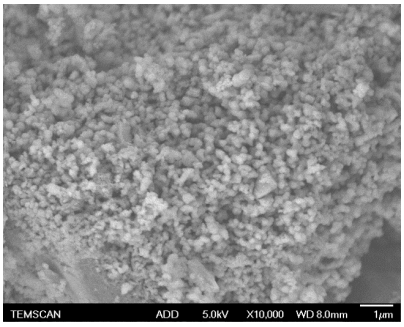


MD1(T = 350°C)

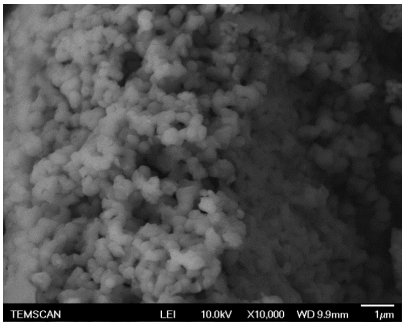
S_{6b}: SEM analysis of MD2



MD2

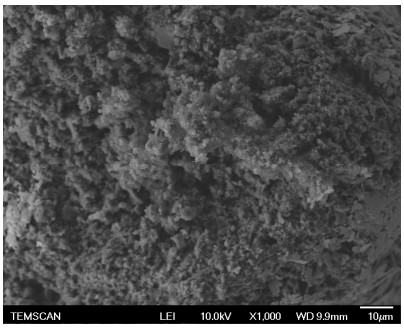


MD2(T = 350°C)

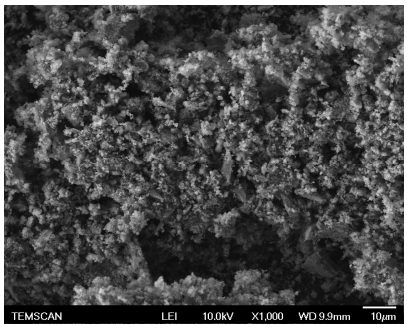


MD2-500

S_{6c}: SEM analysis of MD3

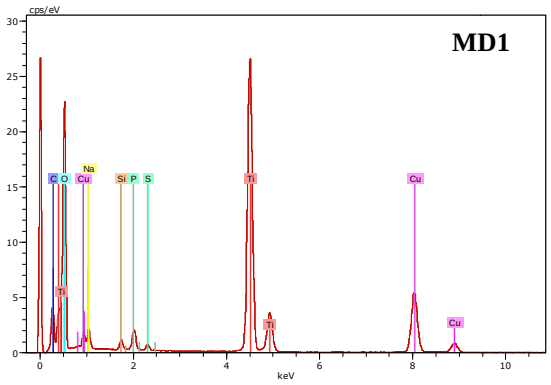


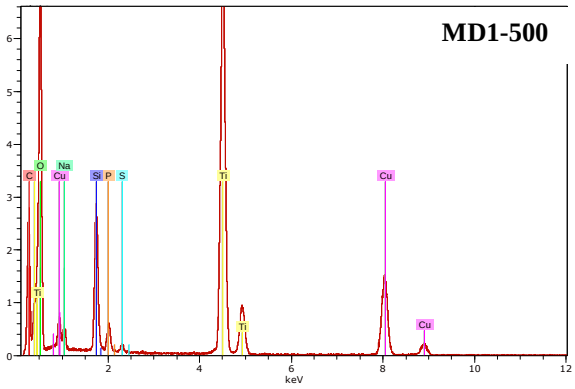
MD3

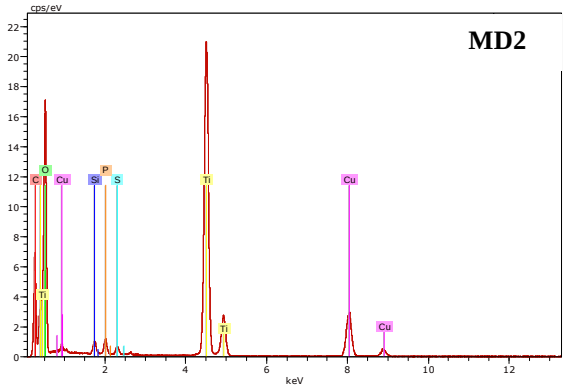


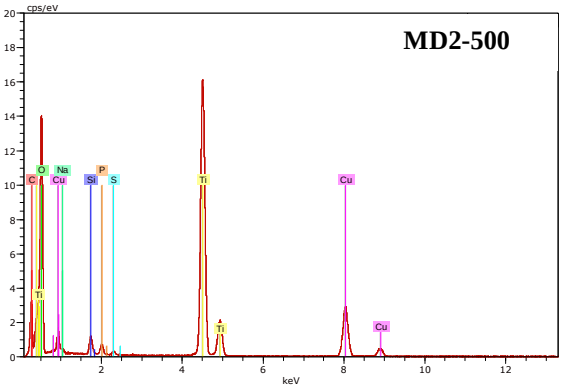
MD3-500

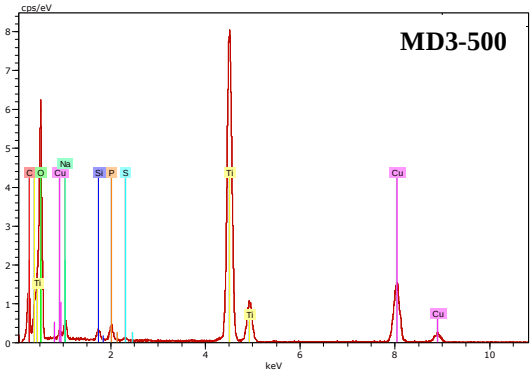
S7: EDX analysis of hybrid materials



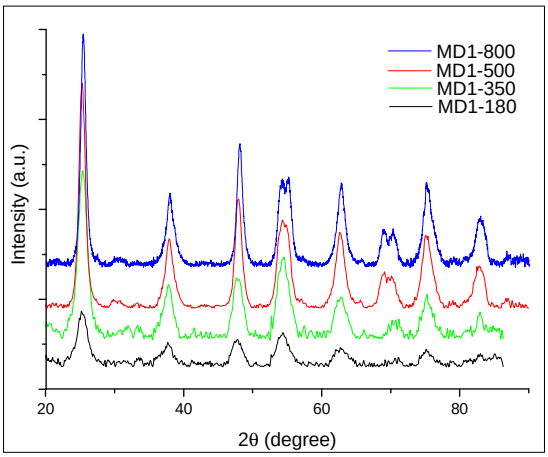


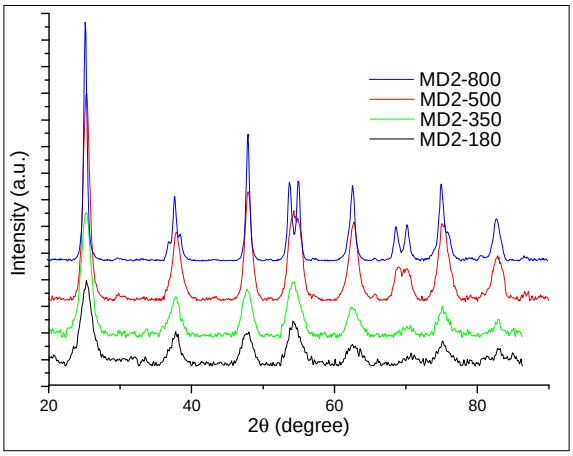


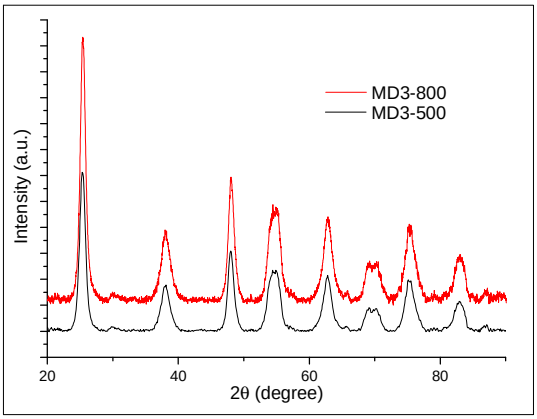




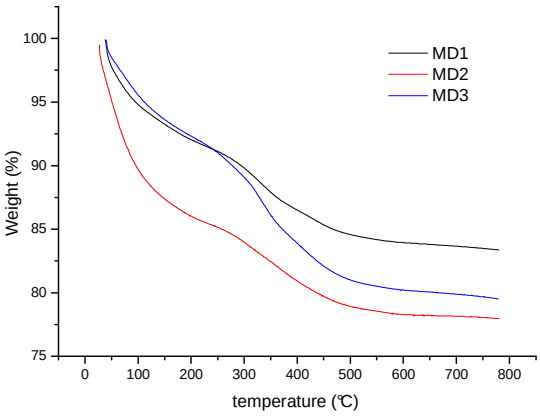
S8: X-ray diffraction analysis of hybrid materials

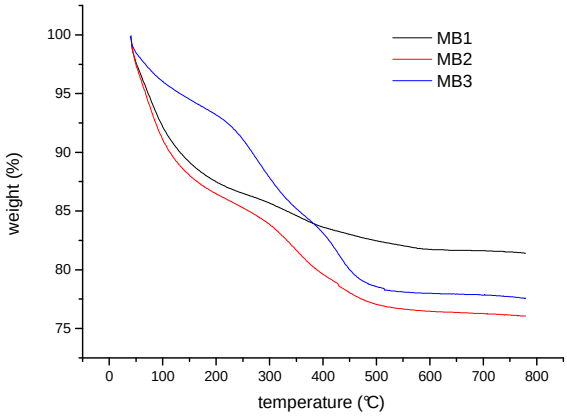






S9: TG analysis of hybrid materials





S10: C, H, N elemental analysis of hybrid materials

	C (%)	H (%)	N (%)
MD1	9.35	2.88	1.16
MD2	7.90	3.26	2.15
MD3	10.95	3.74	1.46
MD2-500	0.13	0.36	1.13
MD3-500	0.11	0.13	0.82