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Viologen-based dendritic macromolecular asterisks: synthesis and interplay with gold nanoparticles

Nadia Katir,[a] **Abdelkrim El Kadib,***[a] **Vincent Collière,**[b] **Jean Pierre Majoral,***[b] **Mosto Bousmina.**[a,c]

[a] *Euro-Mediterranean University of Fez, Fès-Shore, Route de Sidi harazem, Fès, Morocco E-mail: a.elkadib@ueuromed.org*

[b] *Laboratoire de Chimie de Coordination, Centre National de la Recherche Scientifique, 205 route de Narbonne, 31077 Toulouse Cedex 4, France*

[c] *Hassan II Academy of Science and Technology, Avenue Mohammed VI, 10222 Rabat, Morocco*

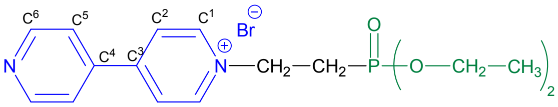
S1: Experimental section

S1a: Characterization of materials.

General The manipulations were carried out with standard high-vacuum and dry-argon techniques. Solvents were dried and distilled according to standard procedures. All reagents were purchased from Sigma-Aldrich or Strem and were used without further purification. Dendrimer $N_3P_3(NMe\text{-}NH_2)_6$ was synthesized using published procedures.[1] ^{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). UV 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). Fluorescence anisotropy measurements were performed on a K2 fluorimeter (ISS, Champaign, IL). Transmission electronic microscopy (TEM) images were obtained using JEOL JEM 2010 at an activation voltage of 200 kV.

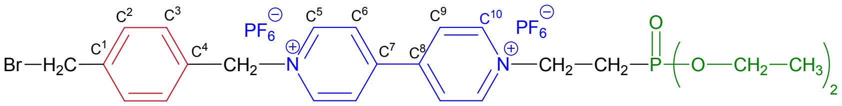
S1b: Synthesis and characterization of the viologen-monomers asterisks

Synthesis of 1-(2-(diethoxyphosphoryl)ethyl)-4,4'-bipyridinium bromide (P1) [2]



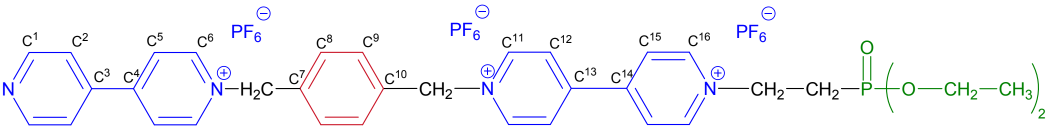
4,4'-Bipyridine (0.50 g, 3.20 mmol) was reacted in (0.78g, 3.20 mmol) 2-bromoethane-diethylphosphonate for 21h at 50°C. The resulting solid was filtered, washed with diethyl ether (15 mL X 6) and dried in vacuo to give 1.15 g (89%) of compound **P1** as pale yellow powder. ^{1}H NMR (400 MHz, CD_3CN) δ 1.25 (t, $^3J_{HH}$ = 7.0 Hz, 6H, $OCH_2\text{-}\underline{CH_3}$), 2.70 (dt, $^2J_{PH}$ = 18.1 Hz, $^3J_{HH}$ = 7.3 Hz, 2H, $CH_2\text{-}\underline{CH_2}\text{-}P$), 4.07 (dq, $^3J_{PH}$ = 14.1 Hz , $^3J_{HH}$ = 7.1 Hz, 4H, $O\underline{CH_2}\text{-}CH_3$), 4.98 (dt, $^3J_{PH}$ = 13.9 Hz, $^3J_{HH}$ = 7.6 Hz, 2H, $\underline{CH_2}\text{-}CH_2\text{-}P$), 7.89 (d, $^3J_{HH}$ = 6.2 Hz, 2H, H^5), 8.46 (d, $^3J_{HH}$ = 6.9 Hz, 2H, H^2), 8.85 (d, $^3J_{HH}$ = 6.2 Hz, 2H, H^6), 9.29 (d, $^3J_{HH}$ = 7.0 Hz, 2H, H^1); ^{13}C NMR (101 MHz, CD_3CN) δ 15.71 (d, $^3J_{PC}$ = 6.0 Hz, $OCH_2\text{-}\underline{CH_3}$), 26.78 (d, $^1J_{PC}$ = 140.0 Hz, $CH_2\text{-}\underline{CH_2}\text{-}P$), 55.79 (d, $^2J_{PC}$ = 3.3 Hz, $\underline{CH_2}\text{-}CH_2P$), 62.22 (d, $^2J_{PC}$ = 6.4 Hz, $O\underline{CH_2}\text{-}CH_3$), 121.98 ($C^2$), 125.64 ($C^6$), 141.29 ($C^4$), 145.87 ($C^1$), 150.96 ($C^5$), 154.14 ($C^3$); $^{31}P\{^1H\}$ NMR (122 MHz, CD_3CN) δ 24.19; ESI m/z 321.3 $[M\text{-} Br]^+$; IR (neat): ν 2987 (OCH_3), 1641 (C=N) cm^{-1}.

Synthesis of (P2)



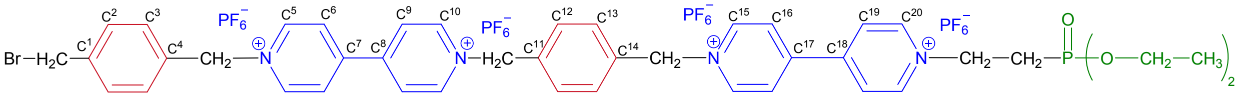
To a solution of **P1** (0.60 g, 1.50 mmol) in 30 mL acetone was added 1,4-bis (bromomethyl)benzene (0.40 g, 1.52 mmol). The mixture was heated at 50 °C for 16h. The resulting solid was filtered, washed with acetone and diethyl ether and dried in vacuo to give 0.53 g (53%) of compound as pale yellow powder identified as **P2.2Br**. This result solid was dissolved in 7 mL of water, and 4 mL of a saturated aqueous solution of NH_4PF_6 was added dropwise. The resulting solid was filtered, washed with cold water and diethyl ether and dried in vacuo. mp 172-174 °C; ^1H NMR (300 MHz, CD_3CN) δ 1.27 (t, $^3J_{HH}$ = 7.0 Hz, 6H, OCH_2-$\underline{CH_3}$), 2.57 (dt, $^2J_{PH}$ = 18.2 Hz, $^3J_{HH}$ = 7.3 Hz, 2H, CH_2-$\underline{CH_2}$-P), 4.07 (dq, $^3J_{PH}$ = 14.4 Hz , $^3J_{HH}$ = 7.1 Hz, 4H, O$\underline{CH_2}$-CH_3), 4.63 (s, 2H, Br-CH_2), 4.88 (dt, $^3J_{PH}$ = 16.6 Hz, $^3J_{HH}$ = 7.2 Hz, 2H, $\underline{CH_2}$-CH_2-P), 5.84 (s, 2H, C^4-CH_2), 7.51, 7.58 (2d, $^3J_{HH}$ = 8.2 Hz, 4H, H^2 and H^3), 8.42 (d, $^3J_{HH}$ = 6.7 Hz, 4H, H^6 and H^9), 8.99, 9.00 (2d, $^3J_{HH}$ = 6.9 Hz, 4H, H^5 and H^{10}); ^{13}C NMR (75 MHz, CD_3CN) δ 15.67 (d, $^3J_{PC}$ = 5.9 Hz, OCH_2-$\underline{CH_3}$), 26.55 (d, $^1J_{PC}$ = 140.9 Hz, CH_2-$\underline{CH_2}$-P), 32.53 (Br-CH_2), 56.66 (d, $^2J_{PC}$ = 3.1 Hz, $\underline{CH_2}$-CH_2-P), 62.32 (d, $^2J_{PC}$ = 6.4 Hz, O$\underline{CH_2}$-CH_3), 64.29 (C^4-$\underline{CH_2}$), 127.01, 127.56 (C^6 and C^9), 129.73, 130.20 (C^2 and C^3), 132.68 (C^4), 140.45 (C^1), 145.66, 146.13 (C^5 and C^{10}), 150.29 (C^7 and C^8); $^{31}P\{^1H\}$ NMR (122 MHz, CD_3CN) δ 24.06; ESI m/z 650.9 $[M-PF_6]^+$; IR (neat): ν 2987 (OCH_3), 1640 (C=N) cm^{-1}.

Synthesis of (P3)



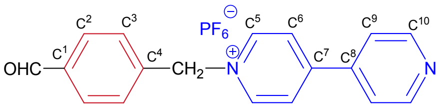
To a solution of **P2.2Br⁻** (0.20 g, 0.30 mmol) in 20 mL acetonitrile was added 4,4'-Bipyridine (0.20 g, 1.28 mmol). The mixture was heated at 50 °C for 14h. The resulting solid was filtered, washed with acetone and diethyl ether and dried in vacuo to give 0.22 g (89%) of compound as pale yellow powder. This result solid was dissolved in 5 mL of water, and 3 mL of a saturated aqueous solution of NH_4PF_6 was added dropwise. The resulting solid was filtered, washed with cold water and diethyl ether and dried in vacuo. ^1H NMR (300 MHz, CD_3CN) δ 1.27 (t, $^3J_{HH}$ = 7.1 Hz, 6H, OCH_2-$\underline{CH_3}$), 2.57 (dt, $^2J_{PH}$ = 18.2 Hz, $^3J_{HH}$ = 7.3 Hz, 2H, CH_2-$\underline{CH_2}$-P), 4.07 (dq, $^3J_{PH}$ = 14.2 Hz, $^3J_{HH}$ = 7.1 Hz, 4H, O$\underline{CH_2}$-CH_3), 4.88 (dt, $^3J_{PH}$ = 16.5 Hz, $^3J_{HH}$ = 7.2 Hz, 2H, $\underline{CH_2}$-CH_2-P), 5.81 (s, 2H, C^{10}-CH_2), 5.88 (s, 2H, C^7-CH_2), 7.60 (s, 4H, H^8 and H^9), 7.81 (d, $^3J_{HH}$ = 6.3 Hz, 2H, H^2), 8.36 (d, $^3J_{HH}$ = 7.0 Hz, 2H, H^5), 8.42, 8.44 (2d, $^3J_{HH}$ = 7.0 Hz, 4H, H^{12} and H^{15}), 8.85 (d, $^3J_{HH}$ = 6.3 Hz, 2H, H^1), 8.87 (d, $^3J_{HH}$ = 7.0 Hz, 2H, H^6), 8.99, 9.00 (2d, $^3J_{HH}$ = 7.0 Hz, 4H, H^{11} and H^{16}); ^{13}C NMR (75.47 MHz, CD$_3$CN): δ 15.67 (d, $^3J_{PC}$ = 5.9 Hz, OCH$_2$-$\underline{\mathrm{CH}_3}$), 26.55 (d, $^1J_{PC}$ = 140.8 Hz, CH$_2$-$\underline{\mathrm{CH}_2}$-P), 56.65 (d, $^2J_{PC}$ = 3.1 Hz, $\underline{\mathrm{CH}_2}$-CH$_2$-P), 62.35 (d, $^2J_{PC}$ = 6.4 Hz, O$\underline{CH_2}$-CH$_3$), 63.43 (C^{10}-$\underline{\mathrm{CH}_2}$), 64.04 (C^7-$\underline{\mathrm{CH}_2}$), 121.92 (C^2), 126.36 (C^5), 127.02, 127.57 (C^{12} and C^{15}), 130.18, 130.32 (C^8 and C^9), 134.21, 134.75 (C^7 and C^{10}), 141.25 (C^3), 145.06 (C^6), 145.72, 146.13 (C^{11}and C^{16}), 150.30, 150.41 (C^{13} and C^{14}), 151.05 (C^1), 154.69 (C^4); ^{31}P NMR (122 MHz, CD$_3$CN) δ 23.71; ESI m/z 871.6 [M-PF$_6$]$^+$.

Synthesis of (P4)



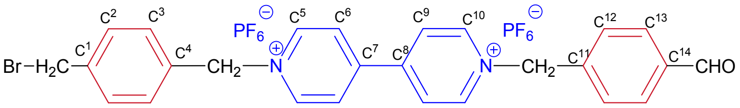
A solution of **P3** (0.20 g, 0.20 mmol) and 1,4-bis (bromomethyl)benzene (0.16 g, 0.62 mmol) in 20 mL of acetone was heated at 37°C for 14h. After filtration, the filtrate was evaporated under vacuum and the residue was watched with diethyl ether (20 mL X 3). The solid was dried under vacuum to give 0.22 g (82 %) as a yellow solid. ^{1}H NMR (300 MHz, CD$_3$CN) δ 1.27 (t, $^3J_{HH}$ = 7.0 Hz, 6H, OCH$_2$-$\underline{CH_3}$), 2.58 (dt, $^2J_{PH}$ = 18.0 Hz, $^3J_{HH}$ = 7.2 Hz, 2H, CH$_2$-$\underline{CH_2}$-P), 4.08 (dq, $^3J_{PH}$ = 14.2 Hz, $^3J_{HH}$ = 7.1 Hz, 4H, O$\underline{CH_2}$-CH$_3$), 4.69 (s, 2H, Br-CH$_2$), 4.89 (dt, $^3J_{PH}$ = 14.8 Hz, $^3J_{HH}$ = 7.3 Hz, 2H, $\underline{CH_2}$-CH$_2$-P), 5.84 (s, 2H, C^4-CH$_2$), 5.88 (s, 2H, C^{11}-CH$_2$ and C^{14}-CH$_2$), 7.51, 7.57 (2d, $^3J_{HH}$ = 8.2 Hz, 4H, H^2 and H^3), 7.63 (s, 4H, H^{12} and H^{13}), 8.42, 8.44 (2d, $^3J_{HH}$ = 6.4 Hz, 8H, H^6, H^9, H^{16}and H^{19}), 8.93-9.08 (m, 8H, H^5, H^{10}, H^{15} and H^{20}); ^{13}C NMR (75.47 MHz, CD$_3$CN): δ 15.67 (d, $^3J_{PC}$ = 5.9 Hz, OCH$_2$-$\underline{\mathrm{CH}_3}$), 26.54 (d, $^1J_{PC}$ = 140.8 Hz, CH$_2$-$\underline{\mathrm{CH}_2}$-P), 32.57 (Br-CH$_2$), 56.63 (d, $^2J_{PC}$ = 3.0 Hz, $\underline{\mathrm{CH}_2}$-CH$_2$-P), 62.40 (d, $^2J_{PC}$ = 6.4 Hz, O$\underline{CH_2}$-CH$_3$), 64.02 (C^{11}-$\underline{\mathrm{CH}_2}$ and C^{14}-$\underline{\mathrm{CH}_2}$), 64.27 (C^4-$\underline{\mathrm{CH}_2}$), 127.03, 127.58 (C^5, C^{10}, C^{15} and C^{20}), 129.75, 130.20 (C^2 and C^3), 130.37 (C^{12} and C^{13}), 132.69 (C^4), 134.35 (C^{11} and C^{14}), 140.39 (C^1), 145.70, 146.11 (C^5, C^{10}, C^{15} and C^{20}), 150.32, 150.42, 150.52, 150.55 (C^7, C^8, C^{17} and C^{18}); ^{31}P NMR (122 MHz, CD$_3$CN) δ 23.73; ESI m/z 528.3 [M-2PF$_6$]$^{2+}$, 303.7 [M-3PF$_6$]$^{3+}$

Synthesis of 1-(4-formylbenzyl)-[4,4'-bipyridin]-1-ium* hexafluorophosphate *(P5) [2]



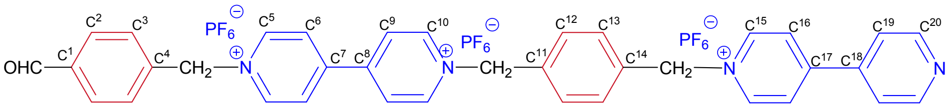
A mixture of 4-(bromomethyl)benzaldehyde (1.00 g, 5.05 mmol) and 4,4’-bipyridine (0.90 g, 5.76 mmol) in 12 mL acetone was heated at 40 °C for 6h. The resulting solid was filtered, washed with acetone and diethyl ether and dried in vacuo to yield 1.45 g (81%) as a yellow solid. The solid was dissolved in 40 mL of water and 2 mL of a saturated aqueous solution of NH_4PF_6 was added dropwise. The resulting solid was filtered, washed with cold water and diethyl ether and dried in vacuo. mp 278°C; ^{1}H NMR (400 MHz, CD_3CN): δ 5.88 (s, 2H, CH_2), 7.66 (d, 2H, $^3J_{HH}$ = 8.1 Hz, H^3), 7.81 (d, 2H, $^3J_{HH}$ = 6.2 Hz, H^9), 8.01 (d, 2H, $^3J_{HH}$ = 8.3 Hz, H^2), 8.38 (d, 2H, $^3J_{HH}$ = 6.8 Hz, H^6), 8.87 (d, 2H, $^3J_{HH}$ = 6.2 Hz, H^{10}), 8.89 (d, 2H, $^3J_{HH}$ = 6.9 Hz, H^5), 10.06 (s, 1H, CHO); ^{13}C NMR (101 MHz, CD_3CN): δ 63.51 (CH_2), 121.85 (C^9), 126.42 (C^6), 129.63 (C^3), 130.29 (C^2), 137.33 (C^1), 138.90 (C^4), 141.08 (C^8), 145.23 (C^5), 151.19 (C^{10}), 154.88 (C^7), 192.11 (CHO); ESI m/z 275.0 [M-PF_6]$^+$; IR (neat): *v* 1702 (C=O), 1641 (C=N) cm^{-1}.

Synthesis of (P6)



A solution of 1,4-bis (bromomethyl)benzene (0.50 g, 1.89 mmol) and **P5** (0.60 g, 1.43 mmol) in 20 mL of acetone was heated at 40°C for 14h. The resulting solid was isolated by filtration, washed with acetone and diethyl ether and dried in vacuo to yield 0.56 g (57%) as a yellow solid. The solid was dissolved in 10 mL of water and 1 mL of a saturated aqueous solution of NH_4PF_6 was added dropwise. The resulting solid was filtered, washed with cold water and diethyl ether and dried in vacuo. ^{1}H NMR (300 MHz, CD_3CN): δ 4.63 (s, 2H, Br-CH_2), 5.84 (s, 2H, C^4-CH_2), 5.93 (s, 2H, C^{11}-CH_2), 7.51 (d, $^3J_{HH}$ = 8.0 Hz, 2H, H^3), 7.58 (d, $^3J_{HH}$ = 8.2 Hz, 2H, H^2), 7.68 (d, $^3J_{HH}$ = 8.1 Hz, 2H, H^{12}), 8.02 (d, $^3J_{HH}$ = 8.2 Hz, 2H, H^{13}), 8.42 (d, $^3J_{HH}$ = 6.2 Hz, 4H, H^6 and H^9), 8.95-9.05 (m, 4H, H^5 and H^{10}), 10.07 (s, 1H, CHO); ^{13}C NMR (75 MHz, CD_3CN) δ 32.53 (Br-CH_2), 64.10 (C^{11}-$\underline{CH_2}$), 64.29 (C^4-$\underline{CH_2}$), 127.60, 127.67 (C^6 and C^9), 129.75 (C^3), 129.84 (C^{12}), 130.20 (C^2), 130.32 (C^{13}), 132.66 (C^4), 137.42 (C^{14}), 138.49 (C^{11}), 140.43 (C^1), 145.65, 145.88 (C^5 and C^{10}), 150.36, 150.63 (C^7 and C^8), 192.12 (CHO); IR (neat): *v* 1696 (C=O), 1637 (C=N) cm^{-1}; ESI m/z 605.1 [M-PF_6]$^+$

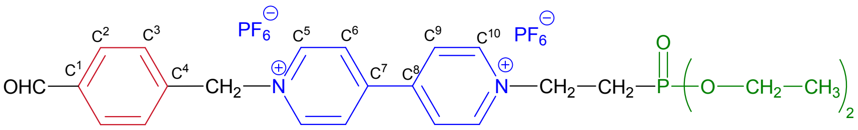
Synthesis of (P7)



A solution of **P6** (0.40 g, 0.58 mmol) and 4,4'-bipyridine (0.40 g, 1.60 mmol) in 10 mL of acetone was heated at 40°C for 16h. After filtration, the filtrate is evaporated under vacuum and the residue was watched with diethyl ether (20 mL X 4). The solid was dried under vacuum to give 0.40 g (71 %) as a yellow solid identified as **P7**. ^{1}H NMR (300 MHz, CD_3CN): δ 5.80 (s, 2H, C^{14}-CH_2), 5.87 (s, 2H, C^{11}-CH_2), 5.93 (s, 2H, C^4-CH_2), 7.59 (s, 4H, H^{12} and H^{13}), 7.67 (d, $^3J_{HH}$ = 8.3 Hz, 2H, H^3), 7.81 (d, $^3J_{HH}$ = 6.2 Hz, 2H, H^{19}), 8.03 (d, $^3J_{HH}$ =

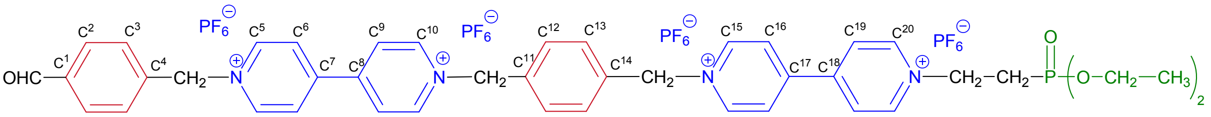
8.3 Hz, 2H, H^2), 8.35 (d, $^3J_{HH}$ = 6.9 Hz, 2H, H^{16}), 8.41 (d, $^3J_{HH}$ = 6.6 Hz, 4H, H^6 and H^9), 8.85 (d, $^3J_{HH}$ = 7.0 Hz, 2H, H^{15}), 8.87 (d, $^3J_{HH}$ = 6.2 Hz, 2H, H^{20}), 8.97, 9.00 (2d, $^3J_{HH}$ = 7.1 Hz, 4H, H^5 and H^{10}), 10.07 (s, 1H, CHO); ^{13}C NMR (75.47 MHz, CD_3CN): δ 63.41 (C^{14}-$\underline{CH_2}$), 64.04 (C^{11}-$\underline{CH_2}$), 64.11 (C^4-$\underline{CH_2}$), 121.88 (C^{19}), 126.35 (C^{16}), 127.61, 127.67 (C^6 and C^9), 129.83 (C^3), 130.16 (C^2), 130.16, 130.31 (C^{12} and C^{13}), 134.17, 134.75 (C^{11} and C^{14}), 137.43 (C^1), 138.48 (C^4), 141.15 (C^{18}), 145.05 (C^{15}), 145.71, 145.89 (C^5 and C^{10}), 150.47, 150.56 (C^7 and C^8), 151.11 (C^{20}), 154.77 (C^{17}), 192.10 (CHO); ESI m/z 825.2 $[M-PF_6]^+$, 340.2 $[M-2PF_6]^{2+}$

Synthesis of (1V) [2]



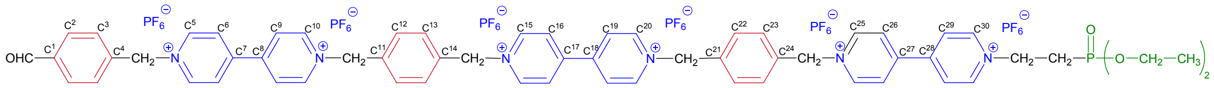
A solution of 4-(bromomethyl)benzaldehyde (0.24 g, 1.21 mmol) and **P1** (0.35 g, 0.87 mmol) in 8 mL acetonitrile was heated at 80 °C for 16h. The resulting solid was filtered, washed with acetonitrile and diethyl ether and dried in vacuo to yield 0.38 g (73%) as a yellow solid. This result solid was dissolved in 10 mL of water, and 5 mL of a saturated aqueous solution of NH_4PF_6 was added dropwise. The resulting solid was filtered, washed with cold water and diethyl ether and dried in vacuo. mp 167 °C; ^{1}H NMR (300 MHz, CD_3CN) δ 1.27 (t, $^3J_{HH}$ = 7.1 Hz, 6H, OCH_2-$\underline{CH_3}$), 2.59 (dt, $^2J_{PH}$ = 18.3 Hz, $^3J_{HH}$ = 7.3 Hz, 2H, CH_2-$\underline{CH_2}$-P), 4.08 (dq, $^3J_{PH}$ = 14.1 Hz , $^3J_{HH}$ = 7.1 Hz, 4H, O$\underline{CH_2}$-CH_3), 4.89 (dt, $^3J_{PH}$ = 14.9 Hz, $^3J_{HH}$ = 7.3 Hz, 2H, $\underline{CH_2}$-CH_2-P), 5.95 (s, 2H, C^4-CH_2), 7.69 (d, $^3J_{HH}$ = 8.2 Hz, 2H, H^3), 8.02 (d, $^3J_{HH}$ = 8.3 Hz, 2H, H^2), 8.53-8.40 (m, 4H, H^6 and H^9), 9.10-8.97 (m, 4H, H^5 and H^{10}), 10.06 (s, 1H, CHO); ^{13}C NMR (75 MHz, CD_3CN) δ 15.66 (d, $^3J_{PC}$ = 6.0 Hz, OCH_2-$\underline{CH_3}$), 26.53 (d, $^1J_{PC}$ = 140.7 Hz, CH_2-$\underline{CH_2}$-P), 56.63 (d, $^2J_{PC}$ = 3.0 Hz, $\underline{CH_2}$-CH_2-P), 62.36 (d, $^2J_{PC}$ = 6.4 Hz, O$\underline{CH_2}$-CH_3), 64.08 (C^4-$\underline{CH_2}$), 127.03 (C^9), 127.64 (C^6), 129.81 (C^3), 130.32 (C^2), 137.37 (C^1), 138.55 (C^4), 145.90, 146.12 (C^{10}, C^5), 150.27, 150.51 (C^8, C^7), 192.19 (CHO); $^{31}P\{^1H\}$ NMR (122 MHz, CD_3CN) δ 23.19; ESI m/z 585.5 $[M-PF_6]^+$; IR (neat): ν 1696 (C=O), 1637 (C=N) cm^{-1}.

Synthesis of (2V)



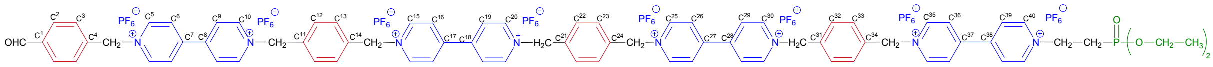
A solution of **P3** (0.50 g, 0.49 mmol) and 4-(bromomethyl)benzaldehyde (0.12 g, 0.60 mmol) in 10 mL of acetonitrile was heated at 80°C for 14h. After filtration, the filtrate is evaporated under vacuum and the residue was watched with diethyl ether (10 mL X 4). The solid was dried under vacuum to give 0.46 g (73%) as a yellow solid identified as **2V**. ^{1}H NMR (400 MHz, CD$_3$CN) δ 1.27 (t, $^3J_{HH}$ = 7.1 Hz, 6H, OCH$_2$-CH_3), 2.58 (dt, $^2J_{PH}$ = 18.3 Hz, $^3J_{HH}$ = 7.3 Hz, 2H, CH$_2$-$\underline{CH_2}$-P), 4.08 (dq, $^3J_{PH}$ = 14.1 Hz , $^3J_{HH}$ = 7.1 Hz, 4H, O$\underline{CH_2}$-CH$_3$), 4.88 (dt, $^3J_{PH}$ = 14.9 Hz, $^3J_{HH}$ = 7.3 Hz, 2H, $\underline{CH_2}$-CH$_2$-P), 5.89 (s, 4H, C^{11}-CH$_2$ and C^{14}-CH$_2$), 5.94 (s, 2H, C^4-CH$_2$), 7.63 (s, 4H, H^{12} and H^{13}), 7.68 (d, $^3J_{HH}$ = 8.3 Hz, 2H, H^3), 8.02 (d, $^3J_{HH}$ = 8.3 Hz, 2H, H^2), 8.40-8.51 (m, 8H, H^6, H^9, H^{16} and H^{19}), 8.98-9.04 (m, 8H, H^5, H^{10}, H^{15}, and H^{20}), 10.07 (s, 1H, CHO); ^{13}C NMR (101 MHz, CD$_3$CN) δ 15.67 (d, $^3J_{PC}$ = 5.9 Hz, OCH$_2$-$\underline{CH_3}$), 26.56 (d, $^1J_{PC}$ = 140.9 Hz, CH$_2$-$\underline{CH_2}$-P), 56.67 (d, $^2J_{PC}$ = 3.1 Hz, $\underline{CH_2}$-CH$_2$-P), 62.33 (d, $^2J_{PC}$ = 6.4 Hz, O$\underline{CH_2}$-CH$_3$), 64.03, 64.10(C^4-$\underline{CH_2}$, C^{11}-$\underline{CH_2}$ and C^{14}-$\underline{CH_2}$), 127.02, 127.58, 127.62, 127.67 (C^6, C^9, C^{16} and C^{19}), 129.84 (C^3), 130.32 (C^2), 130.41 (C^{12} and C^{13}), 134.33, 134.36 (C^{11} and C^{14}), 137.43 (C^1), 138.49 (C^4), 145.72, 145.89, 146.13 (C^5, C^{10}, C^{15}and C^{20}), 150.30, 150.42, 150.48, 150;60 (C^7, C^8, C^{17} and C^{18}), 192.12 (CO); ^{31}P NMR (162 MHz, CD$_3$CN) δ 23.58; ESI m/z 1135.1 [M-PF$_6$]$^+$; IR (neat): *v* 1698 (CO), 1638 (C=N) cm^{-1}.

Synthesis of (3V)



A mixture of **P4** (0.15 g, 0.11 mmol) and **P5** (0.05 g, 0.11 mmol) in 8 mL of acetonitrile was heated at 60°C for 16 h. The resulting solid was filtered and dried in vacuo to give 0.15 g (74%) of compound **3V** as yellow powder. ^{1}H NMR (300 MHz, CD$_3$CN) δ 1.26 (t, $^3J_{HH}$ = 7.1 Hz, 6H, OCH$_2$-$\underline{CH_3}$), 2.62 (dt, $^2J_{PH}$ = 18.5 Hz, $^3J_{HH}$ = 7.4 Hz, 2H, CH$_2$-$\underline{CH_2}$-P), 4.08 (dq, $^3J_{PH}$ = 14.2 Hz, $^3J_{HH}$ = 7.1 Hz, 4H, O$\underline{CH_2}$-CH$_3$), 4.90 (dt, $^3J_{PH}$ = 14.9 Hz, $^3J_{HH}$ = 7.4 Hz, 2H, $\underline{CH_2}$-CH$_2$-P), 5.89 (s, 8H, C^{11}-CH$_2$, C^{14}-CH$_2$, C^{21}-CH$_2$ and C^{24}-CH$_2$), 5.96 (s, 2H, C^4-CH$_2$), 7.62 (s, 8H, H^{12}, H^{13}, H^{22} and H^{23}), 7.68 (d, $^3J_{HH}$ = 8.2 Hz, 2H, H^3), 8.01 (d, $^3J_{HH}$ = 8.3 Hz, 2H, H^2), 8.40-8.53 (m, 12H, H^6, H^9, H^{16}, H^{19}, H^{26}, H^{29}), 8.99-9.11 (m, 12H, H^5, H^{10}, H^{15}, H^{20}, H^{25}, H^{30}), 10.04 (s, 1H, CHO); ^{13}C NMR (75.47 MHz, CD$_3$CN): δ 15.62 (d, $^3J_{PC}$ = 5.9 Hz, OCH$_2$-$\underline{CH_3}$), 26.46 (d, $^1J_{PC}$ = 141.2 Hz, CH$_2$-$\underline{CH_2}$-P), 56.31 (d, $^2J_{PC}$ = 2.8 Hz, $\underline{CH_2}$-CH$_2$-P), 62.84 (d, $^2J_{PC}$ = 6.4 Hz, O$\underline{CH_2}$-CH$_3$), 63.96 (C^{11}-$\underline{CH_2}$, C^{14}-CH_2, C^{21}-$\underline{CH_2}$ and C^{24}-$\underline{CH_2}$), 64.04 (C^4-$\underline{CH_2}$), 127.11, 127.55, 127.63 (C^6, C^9, C^{16}, C^{19}, C^{26} and C^{29}), 129.84 (C^3), 130.40 (C^2, C^{12}, C^{13}, C^{22} and C^{23}), 134.34 (C^{11}, C^{14}, C^{21} and C^{24}), 137.28 (C^1), 138.69 (C^4), 145.74, 145.93, 146.11 (C^5, C^{10}, C^{15}, C^{20}, C^{25} and C^{30}), 150.30, 150.39, 150.50 (C^7, C^8, C^{17}, C^{18}, C^{27} and C^{28}), 192.65 (CHO); ^{31}P NMR (122 MHz, CD$_3$CN) δ 24.83; IR (neat): *v* 1697 (CHO), 1640 (C=N); ESI m/z 1685.3 [M-PF$_6$]$^+$, 770.2 [M-2PF$_6$]$^{2+}$

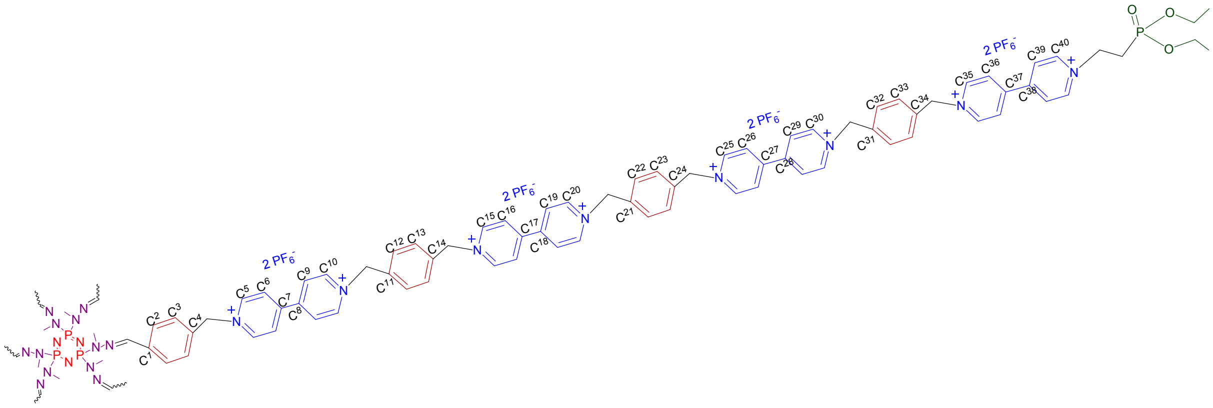
Synthesis of (4V)



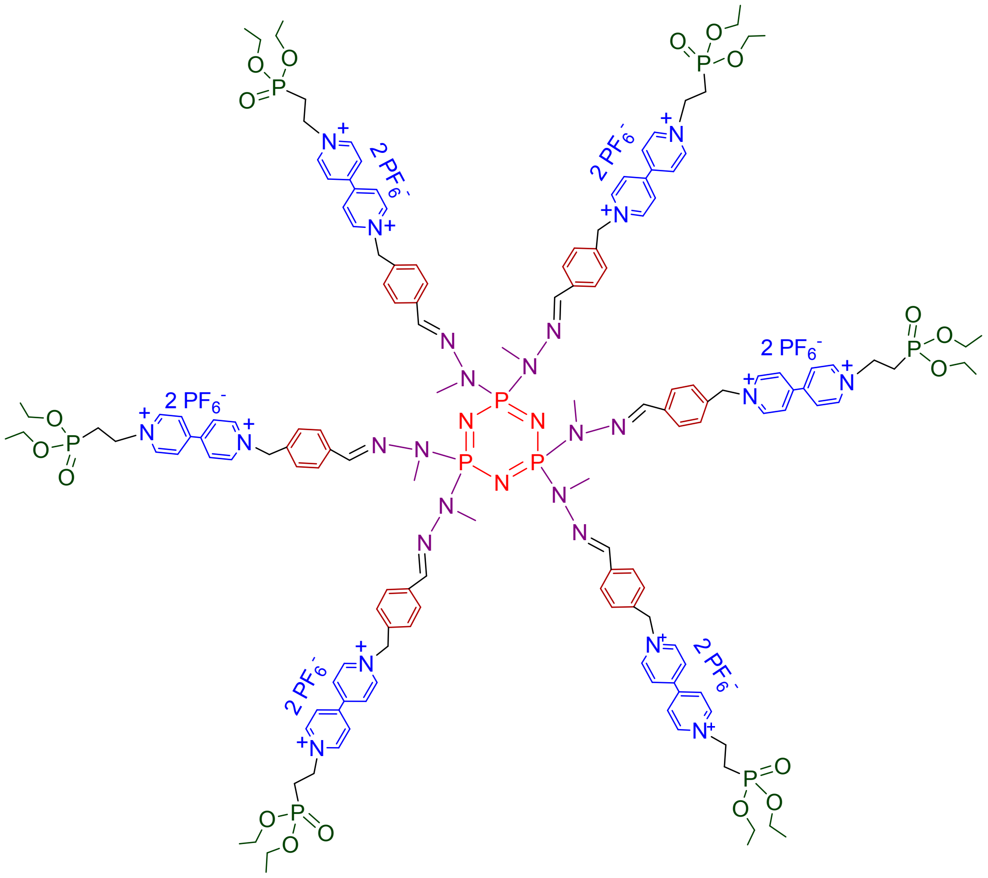
A mixture of **P4** (0.20 g, 0.29 mmol) and **P7** (0.29 g, 0.29 mmol) in 15 mL of acetonitrile was heated at 60°C for 16 h. The resulting solid was filtered and dried in vacuo to give 0.49 g (71%) of compound **3V** as yellow powder. ^{1}H NMR (300 MHz, CD_3CN) δ 1.26 (t, $^{3}J_{HH}$ = 7.0 Hz, 6H, $OCH_2\text{-}\underline{CH_3}$), 2.62 (dt, $^{2}J_{PH}$ = 18.6 Hz, $^{3}J_{HH}$ = 7.3 Hz, 2H, $CH_2\text{-}\underline{CH_2}\text{-}P$), 4.08 (dq, $^{3}J_{PH}$ = 14.2 Hz, $^{3}J_{HH}$ = 7.1 Hz, 4H, $O\underline{CH_2}\text{-}CH_3$), 4.90 (dt, $^{3}J_{PH}$ = 14.8 Hz, $^{3}J_{HH}$ = 7.3 Hz, 2H, $\underline{CH_2}\text{-}CH_2\text{-}P$), 5.89 (s, 12H, $C^{11}\text{-}CH_2$, $C^{14}\text{-}CH_2$, $C^{21}\text{-}CH_2$, $C^{24}\text{-}CH_2$, $C^{31}\text{-}CH_2$ and $C^{34}\text{-}CH_2$), 5.95 (s, 2H, $C^{4}\text{-}CH_2$), 7.61 (s, 12H, H^{12}, H^{13}, H^{22}, H^{23}, H^{32} and H^{33}), 7.68 (d, $^{3}J_{HH}$ = 8.2 Hz, 2H, H^{3}), 8.01 (d, $^{3}J_{HH}$ = 8.2 Hz, 2H, H^{2}), 8.45 (d, $^{3}J_{HH}$ = 6.3 Hz, 16H, H^{6}, H^{9}, H^{16}, H^{19}, H^{26}, H^{29}, H^{36} and H^{39}), 9.04 (d, $^{3}J_{HH}$ = 6.0 Hz, 16H, H^{5}, H^{10}, H^{15}, H^{20}, H^{25}, H^{30}, H^{35} and H^{40}), 10.05 (s, 1H, CHO); ^{13}C NMR (75.47 MHz, CD_3CN): δ 15.60 (d, $^{3}J_{PC}$ = 6.0 Hz, $OCH_2\text{-}\underline{CH_3}$), 26.37 (d, $^{1}J_{PC}$ = 141.3 Hz, $CH_2\text{-}\underline{CH_2}\text{-}P$), 56.27 (d, $^{2}J_{PC}$ = 2.8 Hz, $\underline{CH_2}\text{-}CH_2\text{-}P$), 62.88 (d, $^{2}J_{PC}$ = 6.5 Hz, $O\underline{CH_2}\text{-}CH_3$), 63.97, 64.03 ($C^{11}\text{-}\underline{CH_2}$, $C^{14}\text{-}\underline{CH_2}$, $C^{21}\text{-}\underline{CH_2}$, $C^{24}\text{-}\underline{CH_2}$, $C^{31}\text{-}\underline{CH_2}$ and $C^{34}\text{-}\underline{CH_2}$), 64.23 ($C^{4}\text{-}\underline{CH_2}$), 127.11, 127.53, 127.62 (C^{5}, C^{10}, C^{15}, C^{20}, C^{25}, C^{30}, C^{35} and C^{40}), 129.84 (C^{3}), 130.19 (C^{2}), 129.40 (C^{12}, C^{13}, C^{22}, C^{23}, C^{32} and C^{33}), 134.33 (C^{11}, C^{14}, C^{21}, C^{24}, C^{31} and C^{34}), 137.26 (C^{1}), 138.71 (C^{4}), 145.73, 145.92, 146.10 (C^{5}, C^{10}, C^{15}, C^{20}, C^{25}, C^{30}, C^{35} and C^{40}), 150.31, 150.44, 150.51 (C^{7}, C^{8}, C^{17}, C^{18}, C^{27}, C^{28}, C^{37} and, C^{38}), 192.76 (CHO); ^{31}P NMR (122 MHz, CD_3CN) δ 23.73; ESI m/z 2236.4 $[M\text{-}PF_6]^{+}$, 1045.3 $[M\text{-}2PF_6]^{2+}$.

S1c: Synthesis and characterization of the viologen-dendrimers asterisks

The numbering used for ^{1}H and ^{13}C NMR is as follows:

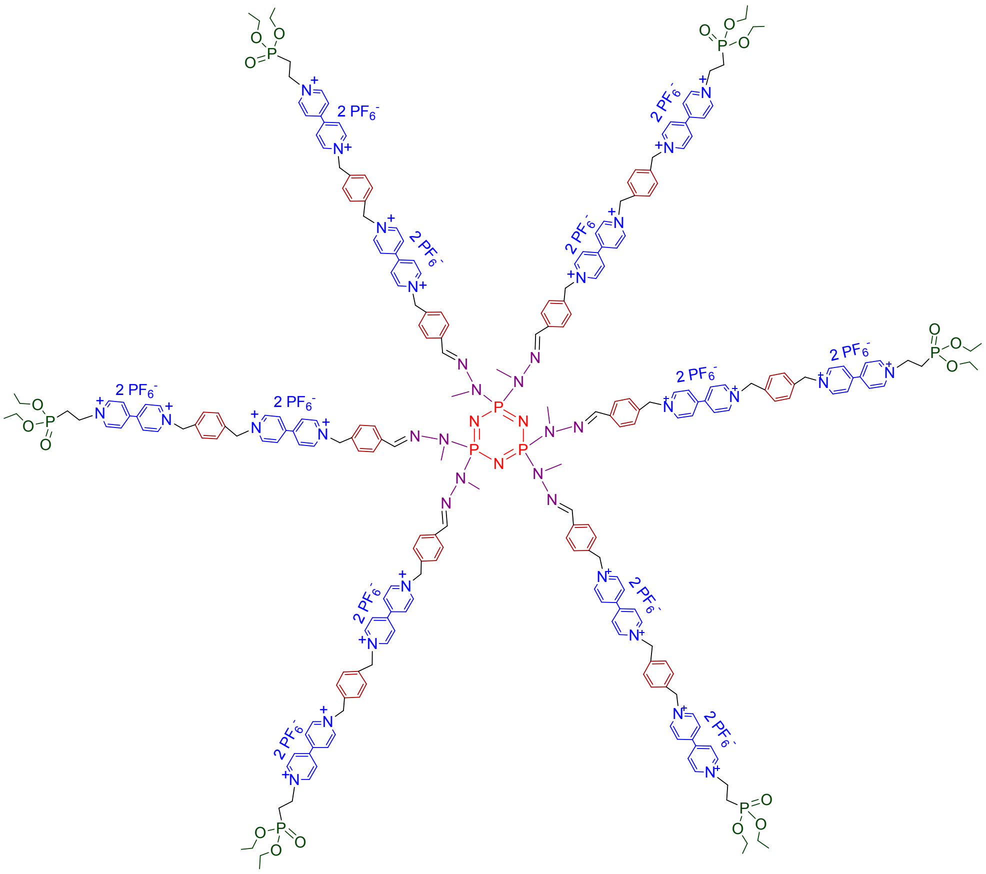


Synthesis of D1V



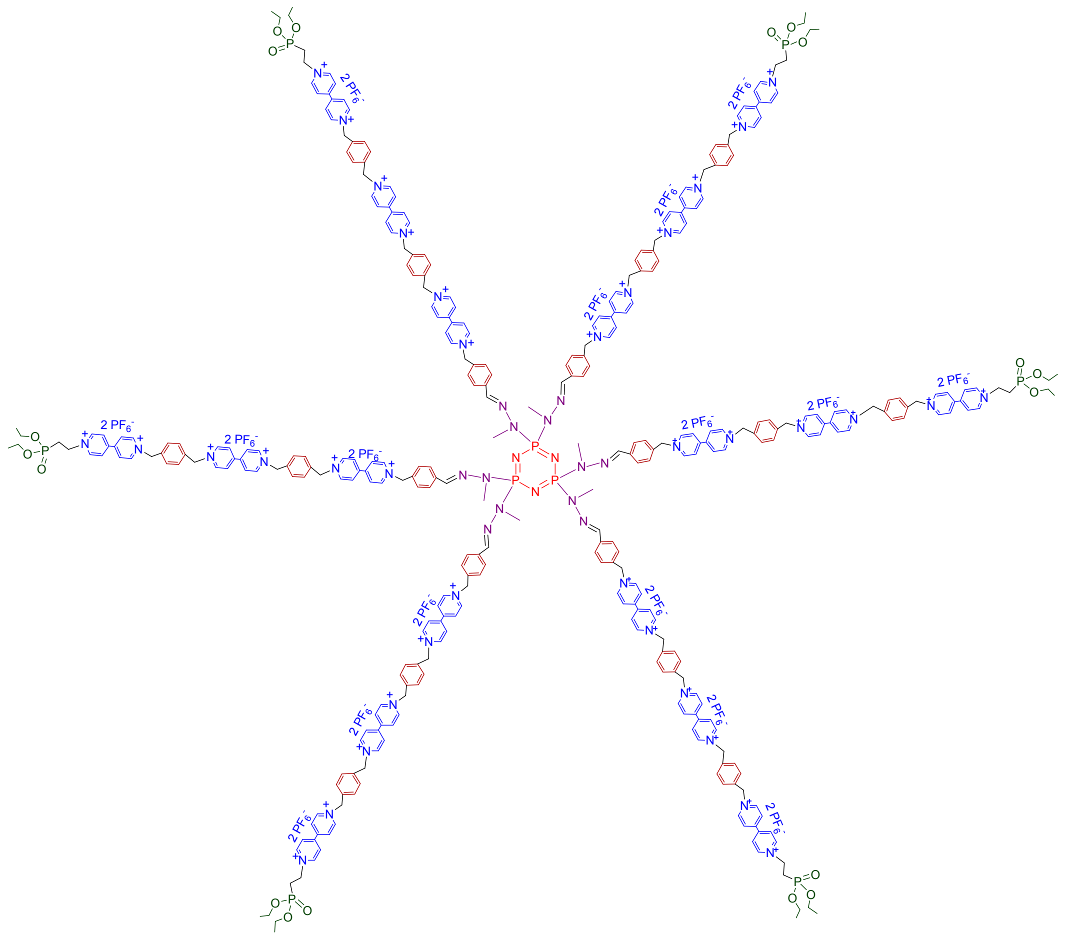
To a solution of **1V** (0.75 g, 1.03 mmol) in acetonitrile (10 mL) was added $N_3P_3[N(Me)NH_2]_6$ (0.069 g, 0.17 mmol). The mixture was stirred overnight. The solvent was removed in vacuo to yield (0.63 g, 77%) as an orange solid. ^1H NMR (300 MHz, CD_3CN) δ 1.26 (t, $^3J_{HH}$ = 7.1 Hz, 36H, $OCH_2\text{-}\underline{CH_3}$), 2.57 (dt, $^2J_{PH}$ = 18.3 Hz, $^3J_{HH}$ = 7.3 Hz, 12H, $CH_2\text{-}\underline{CH_2}\text{-}P$), 3.29 (s.br, 18H, $CH_3\text{-}N$), 4.07 (dq, $^3J_{PH}$ = 8.2 Hz, $^3J_{HH}$ = 7.1 Hz, 24H, $O\underline{CH_2}\text{-}CH_3$), 4.88 (dt, $^3J_{PH}$ = 14.9 Hz, 7.3 Hz, 12H, $\underline{CH_2}\text{-}CH_2\text{-}P$), 5.81 (s, 12H, $C^4\text{-}CH_2$), 7.46 (d, $^3J_{HH}$ = 8.3 Hz, 12H, H^3), 7.71 (d, $^3J_{HH}$ = 8.3 Hz, 12H, H^2), 7.72 (s, 6H, CH=N), 8.52-8.33 (m, 24H, H^6 and H^9), 8.96 (d, $^3J_{HH}$ = 7.1 Hz, 12H, H^5), 9.00 (d, $^3J_{HH}$ = 7.1 Hz, 12H, H^{10}); ^{13}C NMR (75 MHz, CD_3CN) δ 15.67 (d, $^3J_{PC}$ = 5.9 Hz, $OCH_2\text{-}\underline{CH_3}$), 26.53 (d, $^1J_{PC}$ = 140.8 Hz, $CH_2\text{-}\underline{CH_2}\text{-}P$), 31.94 (d, $^2J_{PC}$ = 8.7 Hz, $N\text{-}CH_3$), 56.60 (d, $^2J_{PC}$ = 3.1 Hz, $\underline{CH_2}\text{-}CH_2\text{-}P$), 62.39 (d, $^2J_{PC}$ = 6.4 Hz, $O\underline{CH_2}\text{-}CH_3$), 64.43 ($CH_2$), 126.98 ($C^9$), 127.09 ($C^2$), 127.43 ($C^6$), 129.82 ($C^3$), 132.21 ($C^1$), 136.30 (d, $^3J_{PC}$ = 13.0 Hz, CH=N), 137.84 (C^4), 145.55 , 146.11 (C^5 and C^{10}), 150.22, 150.31 (C^7 and C^8); ^{31}P NMR (122 MHz, CD_3CN) δ 17.16, 23.74; ESI m/z 1414.8 $[M\text{-}3PF_6]^{3+}$; IR (neat): *ν* 1638 (C=N) cm^{-1}.

Synthesis of D2V



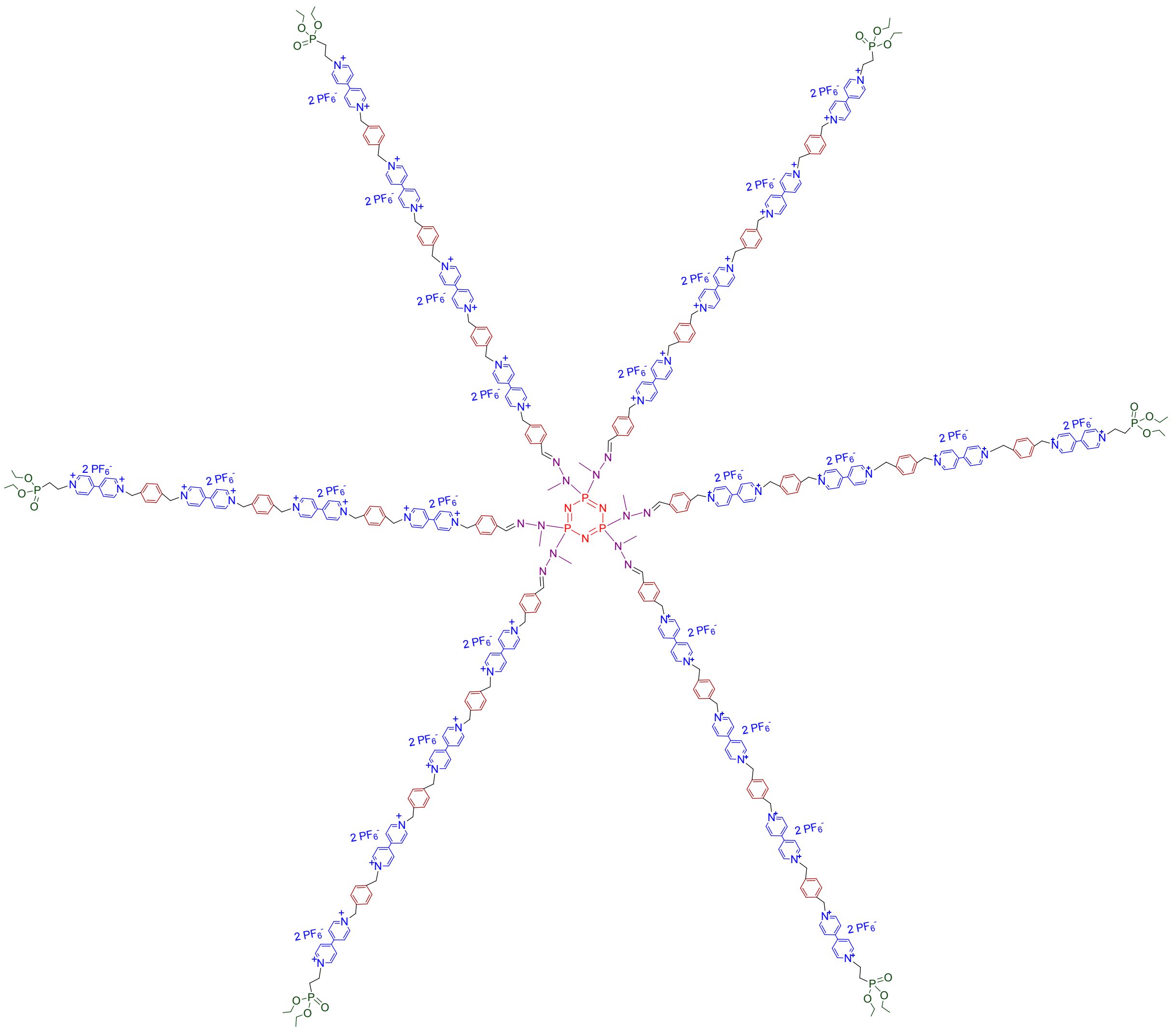
To a solution of **2V** (0.10 g, 0.078 mmol) in acetonitrile (6 mL) was added $N_3P_3[N(Me)NH_2]_6$ (0.0053 g, 0.0128 mmol). The mixture was stirred for 16h. The solvent was removed in vacuo to yield 0.10 g (95%) as a yellow solid; ^{1}H NMR (400 MHz, CD_3CN) δ 1.27 (t, $^3J_{HH}$ = 7.1 Hz, 36H, OCH_2-$\underline{CH_3}$), 2.59 (dt, $^2J_{PH}$ = 18.3 Hz, $^3J_{HH}$ = 7.3 Hz, 12H, CH_2-$\underline{CH_2}$-P), 3.30 (d, $^3J_{PH}$ = 8.9 Hz, 18H, CH_3-N), 4.08 (dq, $^3J_{PH}$ = 14.2 Hz, $^3J_{HH}$ = 7.1 Hz, 24H, O$\underline{CH_2}$-CH_3), 4.89 (dt, $^3J_{PH}$ = 14.9 Hz, $^3J_{HH}$ = 7.3 Hz, 12H, $\underline{CH_2}$-CH_2-P), 5.82 (s, 12H, C^4-CH_2), 5.90 (s, 24H, C^{11}-CH_2 and C^{14}-CH_2), 7.46 (d, $^3J_{HH}$ = 7.0 Hz, 12H, H^3), 7.63 (s, 24H, H^{12} and H^{13}), 7.71 (d, $^3J_{HH}$ = 8.3 Hz, 12H, H^2), 7.73 (s, 6H, CH=N), 8.37-8.48 (m, 48H, H^6, H^9, H^{16} and H^{19}), 8.94-9.05 (m, 48H, H^5, H^{10}, H^{15} and H^{20}); ^{13}C NMR (101 MHz, CD_3CN) δ 15.68 (d, $^3J_{PC}$ = 5.9 Hz, OCH_2-$\underline{CH_3}$), 26.55 (d, $^1J_{PC}$ = 140.7 Hz, CH_2-$\underline{CH_2}$P), 31.94 (d, $^2J_{PC}$ = 7.2 Hz, N-CH_3), 56.65 (d, $^2J_{PC}$ = 2.9 Hz, $\underline{CH_2}$-CH_2P), 62.38 (d, $^2J_{PC}$ = 6.4 Hz, O$\underline{CH_2}$-CH_3), 64.02 (C^{11}-$\underline{CH_2}$ and C^{14}-$\underline{CH_2}$), 64.42 (C^4-$\underline{CH_2}$), 127.09 (C^2), 127.03, 127.45, 127.57 (C^6, C^9, C^{16} and C^{19}), 129.83 (C^3), 130.34 (C^{12} and C^{13}), 132.18 (C^1), 134.35 (C^{11} and C^{14}), 136.32 (d, $^3J_{PC}$ = 15.1 Hz, CH=N), 137.86 (C^4), 145.54, 145.69, 145.72, 146.12 (C^5, C^{10}, $C^{15}$and C^{20}), 150.32, 150.42, 150.54, 151;12 (C^7, C^8, C^{17} and C^{18}); ^{31}P NMR (122 MHz, CD_3CN) δ 17.17, 23.75; ESI m/z 1850.7 $[M-4PF_6]^{4+}$; IR (neat): v 1638 (C=N) cm^{-1}.

Synthesis of D3V



To a solution of **3V** (0.08 g, 0.05 mmol) in acetonitrile (6 mL) was added $N_3P_3[N(Me)NH_2]_6$ (0.0033 g, 0.0074 mmol). The mixture was stirred for 16h. The solvent was removed in vacuo to yield 0.086 g (90 %) as a yellow solid; ^{1}H NMR (300 MHz, CD_3CN) δ 1.26 (t, $^3J_{HH}$ = 7.0 Hz, 36H, OCH_2-$\underline{CH_3}$), 2.62 (dt, $^2J_{PH}$ = 18.5 Hz, $^3J_{HH}$ = 7.3 Hz, 12H, CH_2-$\underline{CH_2}$-P), 3.27 (s, 18H, CH_3-N), 4.08 (dq, $^3J_{PH}$ = 14.2 Hz, $^3J_{HH}$ = 7.1 Hz, 28H, O$\underline{CH_2}$-CH_3), 4.90 (dt, $^3J_{PH}$ = 14.8 Hz, $^3J_{HH}$ = 7.3 Hz, 12H, $\underline{CH_2}$-CH_2-P), 5.82 (s, 12H, C^4-CH_2), 5.89 (s, 48H, C^{11}-CH_2, C^{14}-CH_2, C^{21}-CH_2 and C^{24}-CH_2), 7.45 (d, $^3J_{HH}$ = 8.2 Hz, 12H, H^3), 7.62 (s, 48H, H^{12}, H^{13}, H^{22} and H^{23}), 7.71 (d, $^3J_{HH}$ = 8.1 Hz, 12H, H^2), 7.72 (s, 6H, CH=N), 8.40-8.51 (m, 72H, H^6, H^9, H^{16}, H^{19}, H^{26}, H^{29}), 8.99-9.10 (m, 72H, H^5, H^{10}, H^{15}, H^{20}, H^{25}, H^{30}); ^{13}C NMR (75.47 MHz, CD_3CN): δ 15.61 (d, $^3J_{PC}$ = 6.0 Hz, OCH_2-$\underline{CH_3}$), 26.34 (d, $^1J_{PC}$ = 141.5 Hz, CH_2-$\underline{CH_2}$-P), 31.92 (N-CH_3), 56.22 (d, $^2J_{PC}$ = 2.7 Hz, $\underline{CH_2}$-CH_2P), 63.04 (d, $^2J_{PC}$ = 6.5 Hz, O$\underline{CH_2}$-CH_3), 63.98 (C^{11}-$\underline{CH_2}$, C^{14}-$\underline{CH_2}$, C^{21}-$\underline{CH_2}$ and C^{24}-$\underline{CH_2}$), 64.36 (C^4-$\underline{CH_2}$), 127.18 (C^2), 127.11, 127.42, 127.51 (C^6, C^9, C^{16}, C^{19}, C^{26} and C^{29}), 129.78 (C^3), 130.41 (C^{12}, C^{13}, C^{22} and C^{23}), 132.37 (C^1), 134.30, 134.34 (C^{11}, C^{14}, C^{21} and C^{24}), 136.72 (CH=N), 137.61 (C^4), 145.58, 145.73, 146.09 (C^5, C^{10}, C^{15}, C^{20}, C^{25} and C^{30}), 150.25, 150.31, 150.38 (C^7, C^8, C^{17}, C^{18}, C^{27} and C^{28}); ^{31}P NMR (122 MHz, CD_3CN) δ 17.46, 24.74.

Synthesis of D4V



To a solution of **4V** (0.094 g, 0.039 mmol) in acetonitrile (6 mL) was added $N_3P_3[N(Me)NH_2]_6$ (0.0027 g, 0.0066 mmol). The mixture was stirred for 16h. The solvent was removed in vacuo to yield 0.093 g (99 %) as a yellow solid; ^{1}H NMR (400 MHz, CD_3CN) δ 1.23 (t, $^3J_{HH}$ = 7.0 Hz, 36H, OCH_2-$\underline{CH_3}$), 2.64 (dt, $^2J_{PH}$ = 18.5 Hz, $^3J_{HH}$ = 7.3 Hz, 12H, CH_2-$\underline{CH_2}$-P), 3.24 (s, 18H, CH_3-N), 4.07 (dq, $^3J_{PH}$ = 14.2 Hz, $^3J_{HH}$ = 7.1 Hz, 24H, O$\underline{CH_2}$-CH_3), 4.90 (dt, $^3J_{PH}$ = 14.9 Hz, $^3J_{HH}$ = 7.4 Hz, 12H, $\underline{CH_2}$-CH_2-P), 5.79 (s, 12H, C^4-CH_2), 5.87 (s, 72H, C^{11}-CH_2, C^{14}-CH_2, C^{21}-CH_2, C^{24}-CH_2, C^{31}-CH_2 and C^{34}-CH_2), 7.39-7.50 (m, 12H, H^3), 7.59 (s, 72H, H^{12}, H^{13}, H^{22}, H^{23}, H^{32} and H^{33}),7.68 (s, 6H, CH=N), 7.69-7.74 (m, 12H, H^2), 8.36-8.52 (m, 96H, H^6, H^9, H^{16}, H^{19}, H^{26}, H^{29}, H^{36} and H^{39}), 8.92- 9.13 (m, 96H, H^5, H^{10}, H^{15}, H^{20}, H^{25}, H^{30}, H^{35} and H^{40}); ^{13}C NMR (101 MHz, CD_3CN): δ 15.58 (d, $^3J_{PC}$ = 5.9 Hz, OCH_2-$\underline{CH_3}$), 26.26 (d, $^1J_{PC}$ = 141.6 Hz, CH_2-$\underline{CH_2}$-P), 31.82 (N-CH_3), 56.12 (d, $^2J_{PC}$ = 2.8 Hz, $\underline{CH_2}$-CH_2-P), 63.24 (d, $^2J_{PC}$ = 6.5 Hz, O$\underline{CH_2}$-CH_3), 4.00 (C^{11}-$\underline{CH_2}$, C^{14}-$\underline{CH_2}$, C^{21}-$\underline{CH_2}$, C^{24}-$\underline{CH_2}$, C^{31}-$\underline{CH_2}$ and C^{34}-$\underline{CH_2}$), 64.36 (C^4-$\underline{CH_2}$), 127.21 (C^3), 127.10, 127.37, 127.45 (C^5,

C^{10}, C^{15}, C^{20}, C^{25}, C^{30}, C^{35} and C^{40}), 129.73 (C^{2}), 130.39 (C^{12}, C^{13}, C^{22}, C^{23}, C^{32} and C^{33}),132.40 (C^{1}), 134.24, 134.28 (C^{11}, C^{14}, C^{21}, C^{24}, C^{31} and C^{34}), 137.07 (CH=N), 137.61 (C^{4}), 145.19, 145.54, 145.69, 146.03 (C^{5}, C^{10}, C^{15}, C^{20}, C^{25}, C^{30}, C^{35} and C^{40}), 150.25, 150.33, 150.36 (C^{7}, C^{8}, C^{17}, C^{18}, C^{27}, C^{28}, C^{37} and, C^{38}); ^{31}P NMR (122 MHz, CD_3CN) δ 17.38, 25.41.

S1d:Typical example of preparation of gold nanoparticules DnV@Au)

AuNPs were synthesized by the reduction of $HAuCl_4.3H_2O$ in the presence of **DnV**. In a typical synthesis, a solution of $HAuCl_4.3H_2O$ (5.8 mg, 170.69 10^{-4} mmol) in ethanol (1 mL) was added to a solution of **D1V** (5.0 mg, 85.39 mmol) in acetonitrile (3 mL) the mixture was sonicated for 30 min at 25°C. $NaBH_4$ (0.2 mL, 85.9 mM) was freshly prepared with deionized water and added to reaction mixture while stirring. The solution immediately turned purplish red.

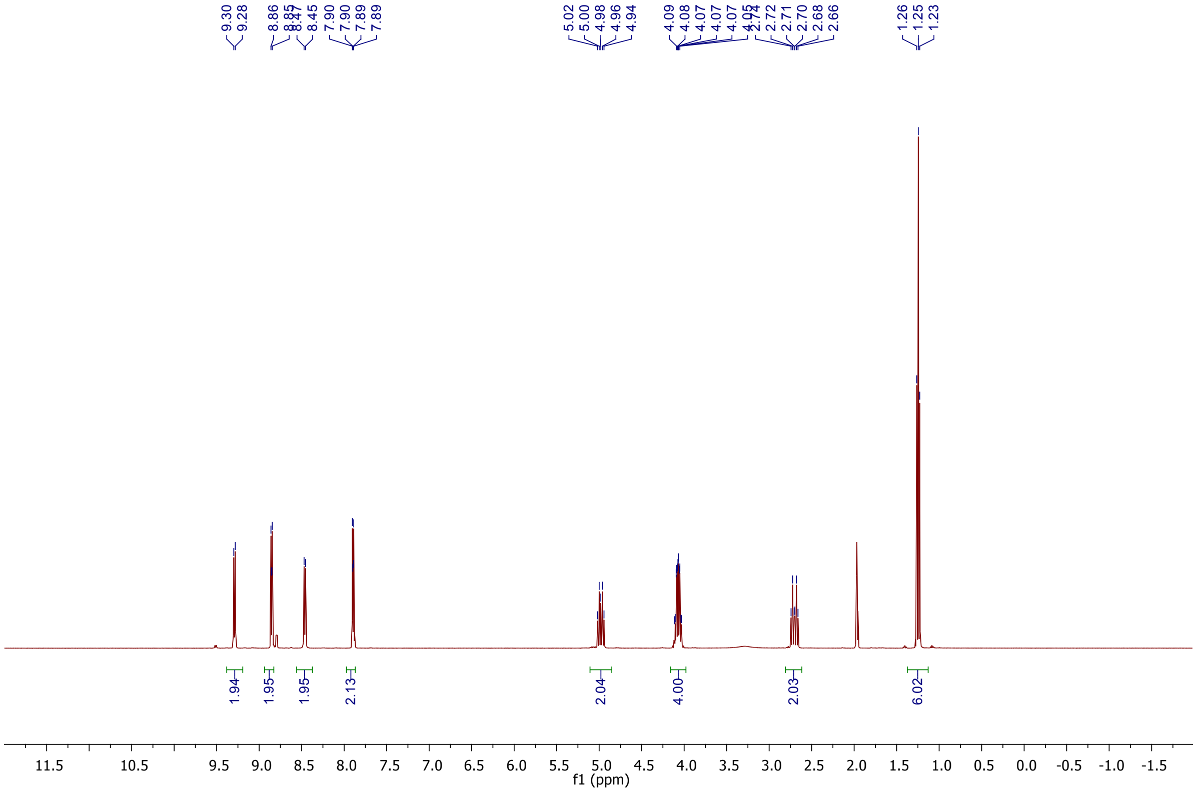
References:

1 (a) R. Kraemer, C. Galliot, J. Mitjaville, A.-M. Caminade and J. P. Majoral, *Heteroat. Chem.*, 1996, **7**, 149-154; (b) C. Galliot, A.-M. Caminade, F. Dahan and J. P. Majoral, *Angew. Chem. Int. Ed. Eng.*, 1993, **32**, 1477-1479.

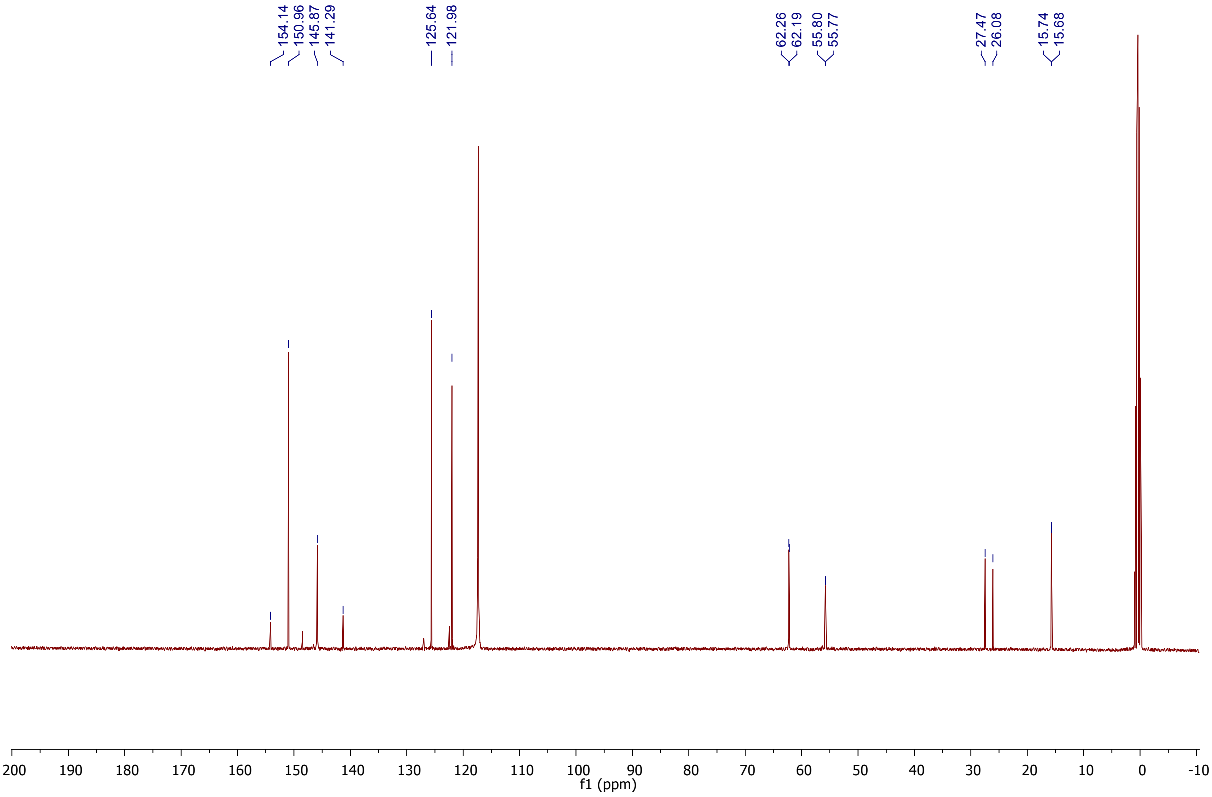
2 N. Katir, J. P. Majoral, A. El Kadib, A.-M. Caminade and M. Bousmina, *Eur. J. Org. Chem.*, 2012, **2012**, 269-273.

S2: NMR spectroscopy of compounds

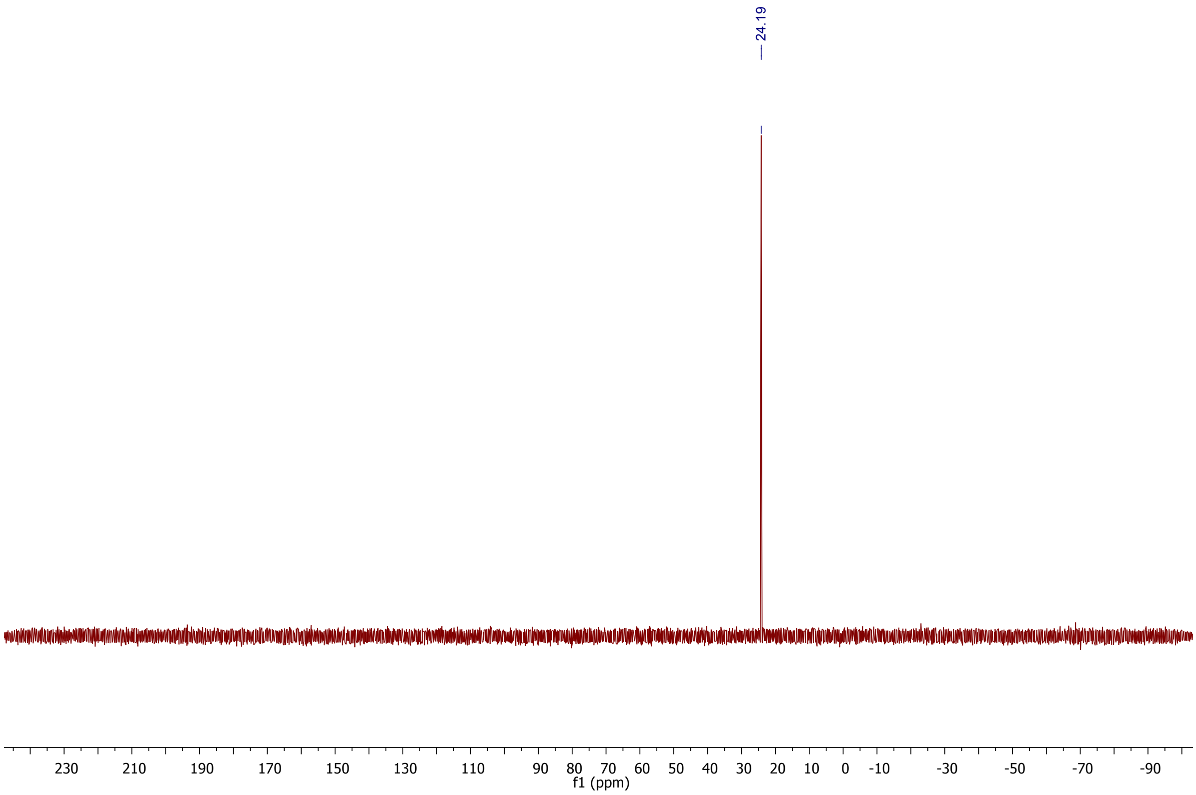
1H NMR P1



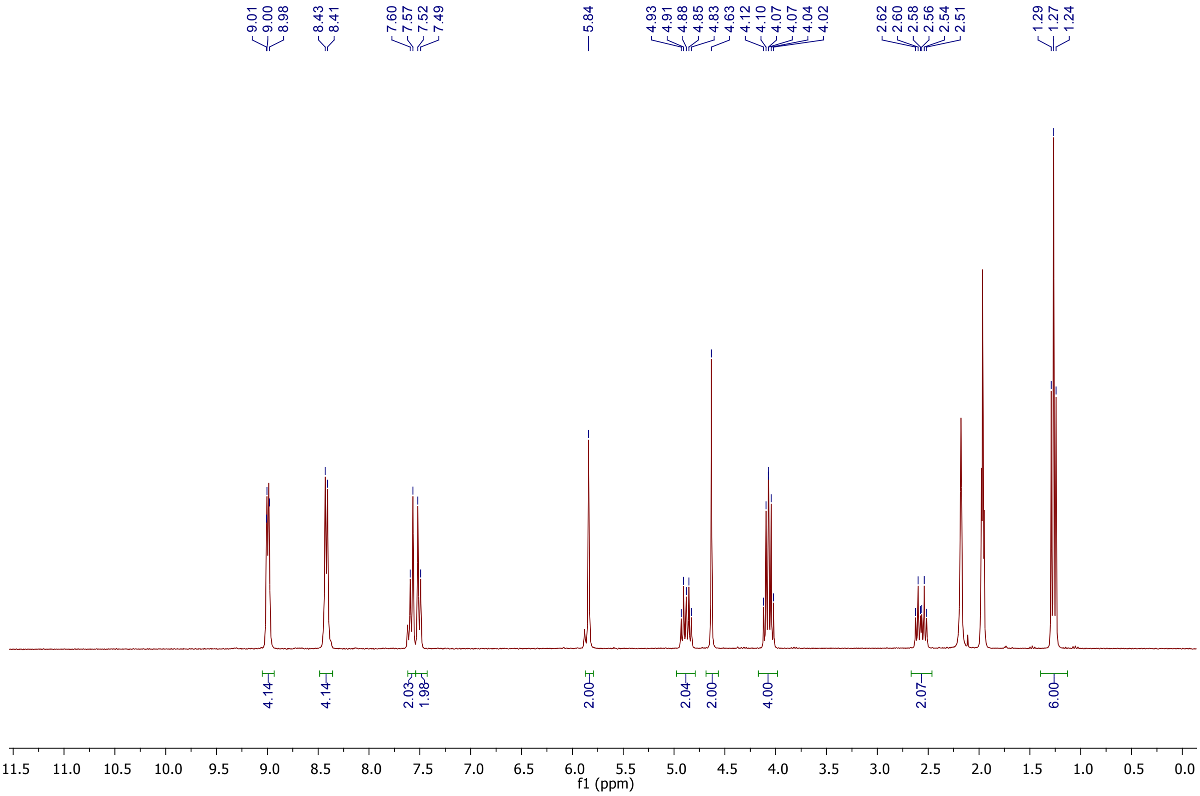
13C NMR P1



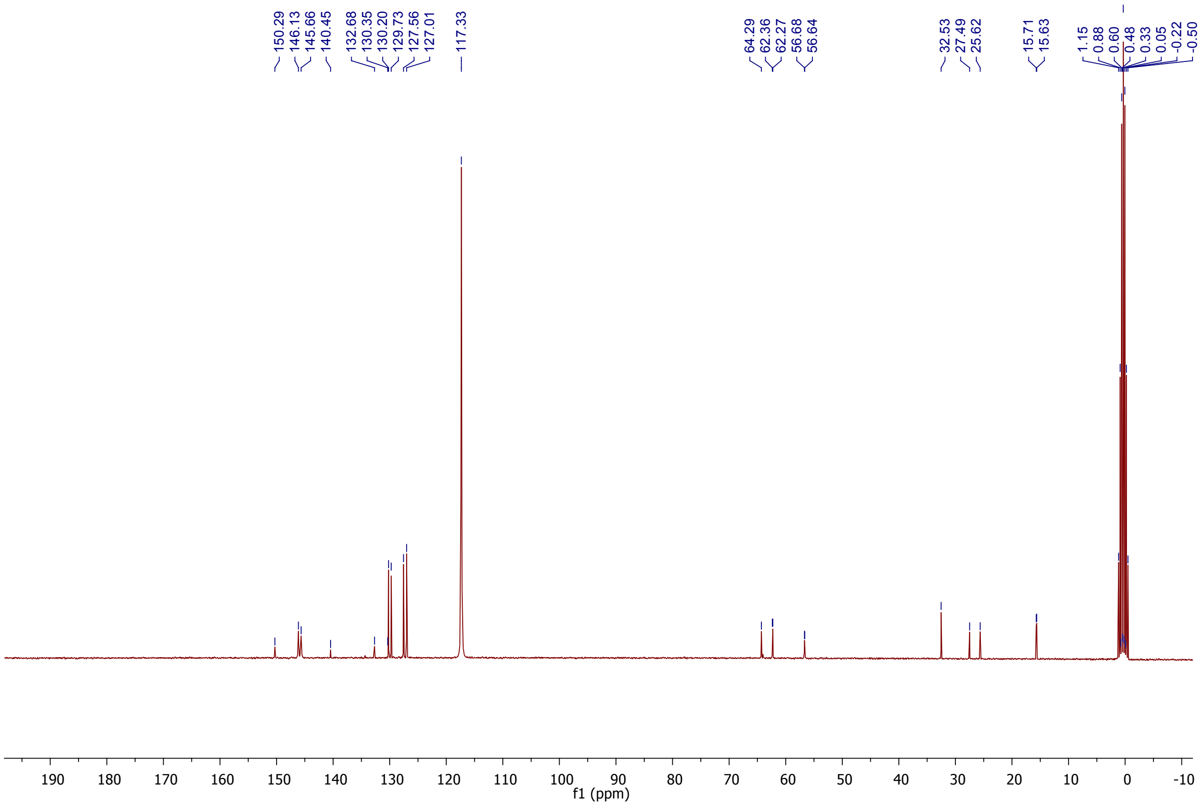
31P NMR P1



1H NMR P2



13C NMR P2



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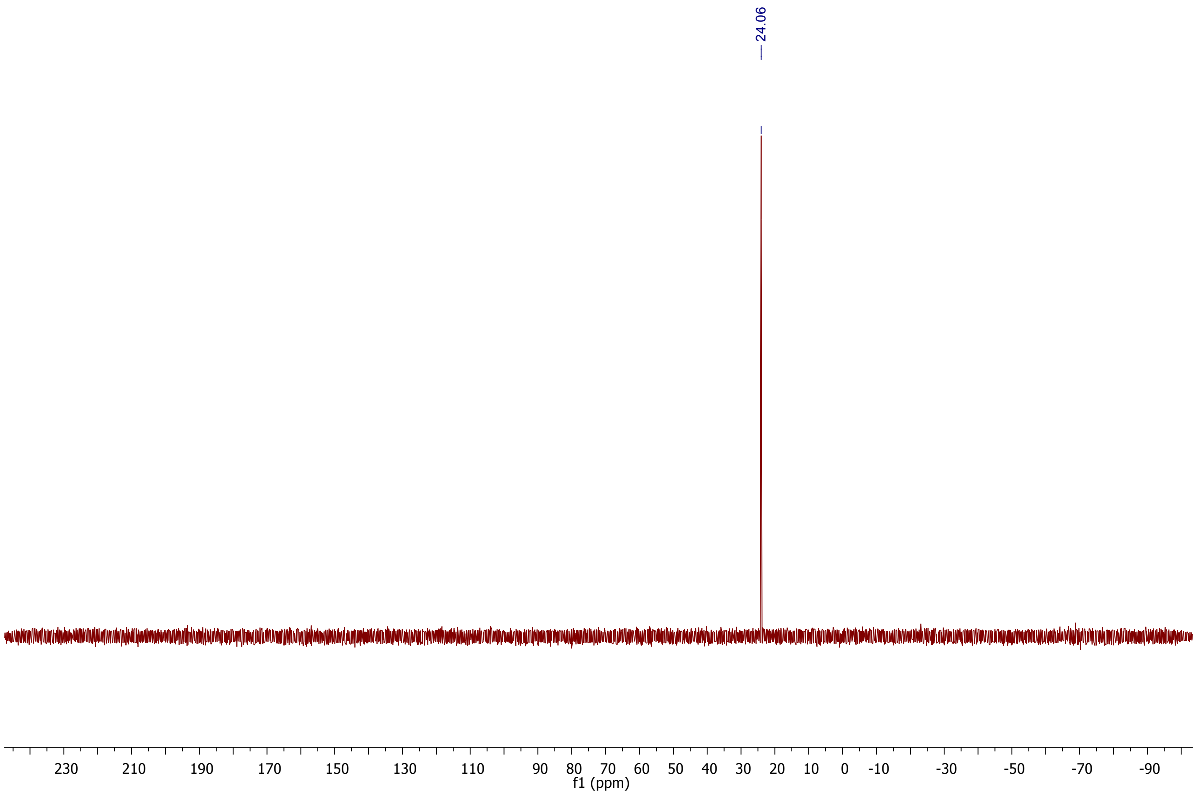
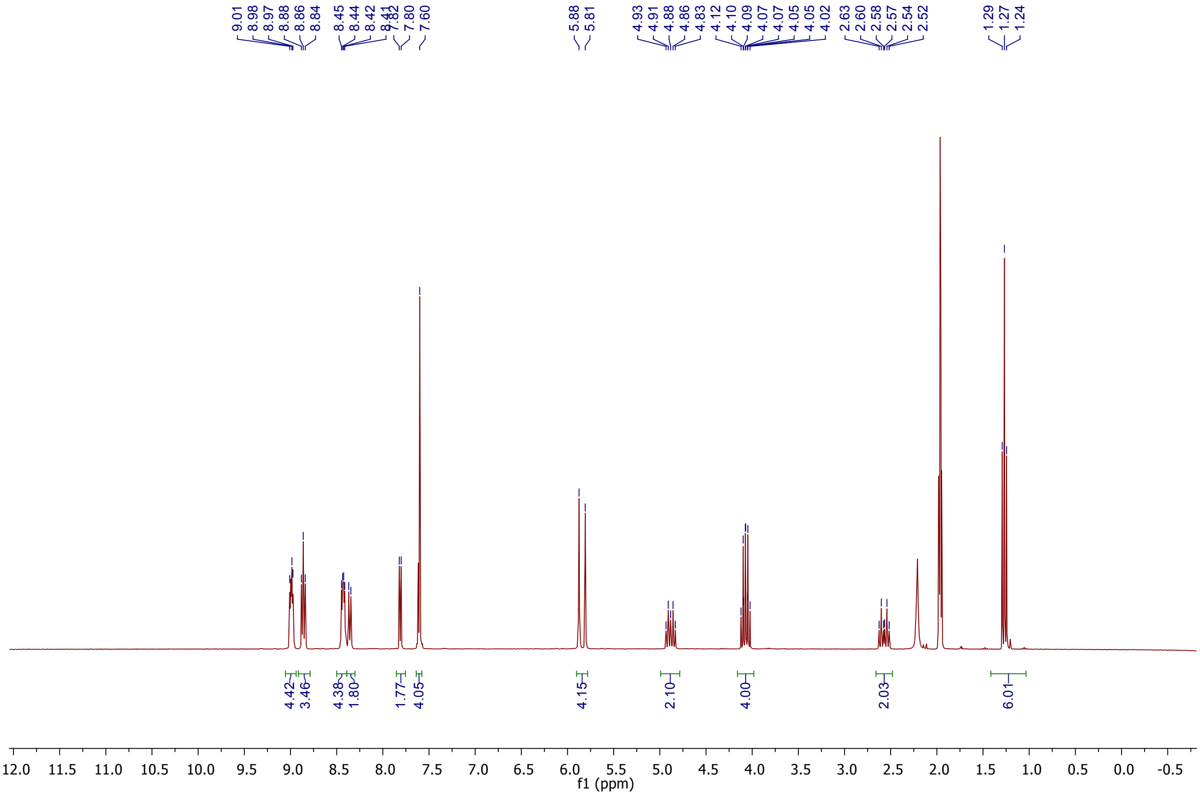
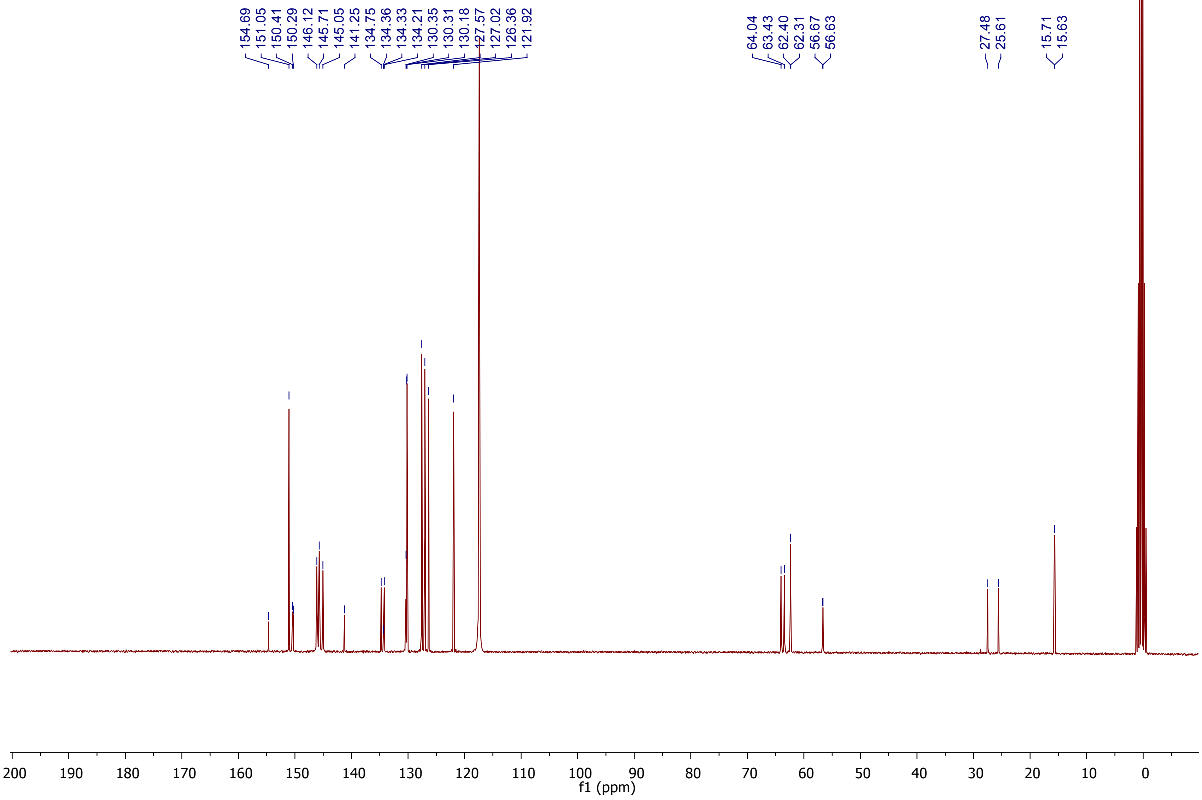


1H NMR P3



13C NMR P3



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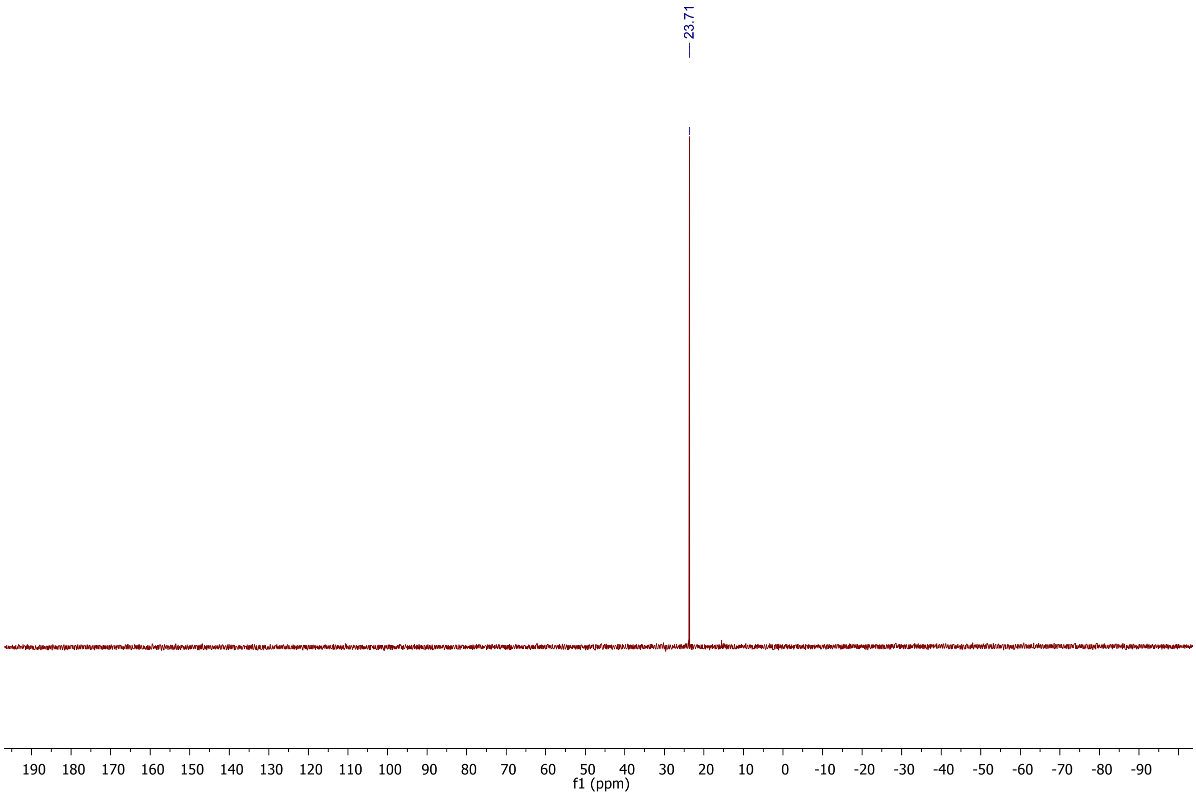
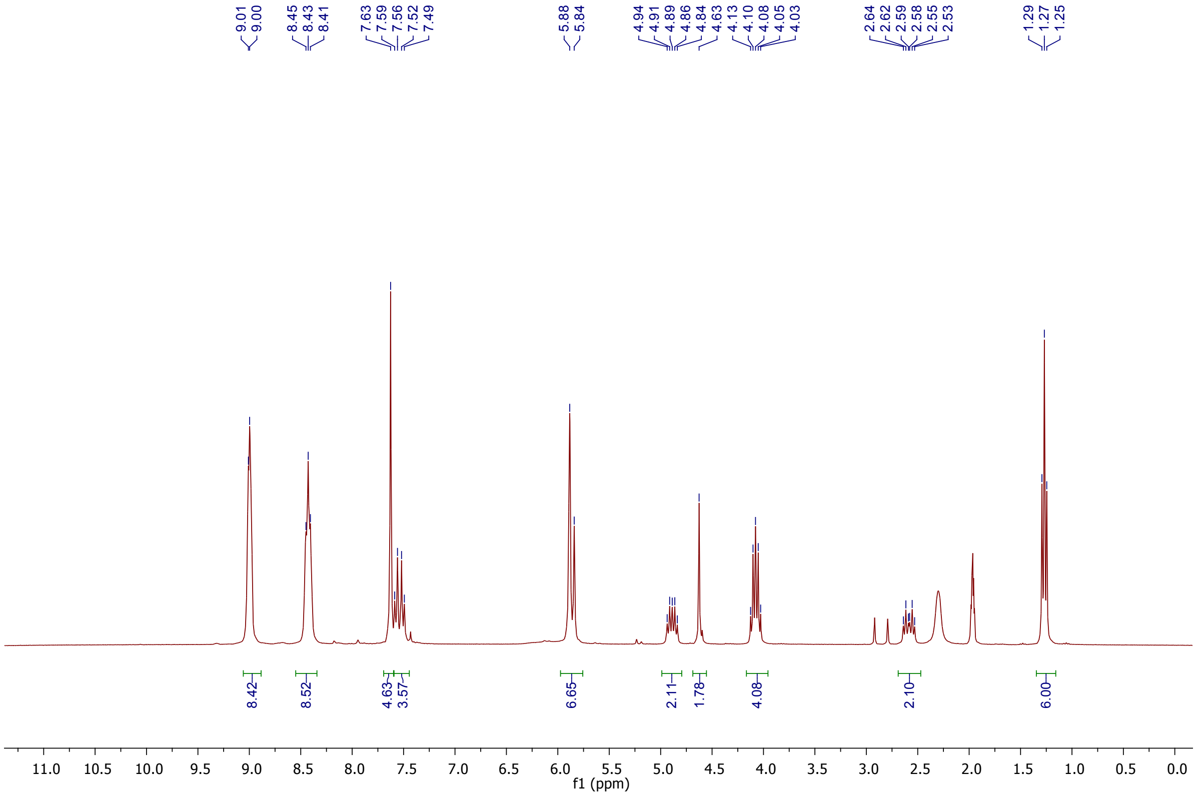
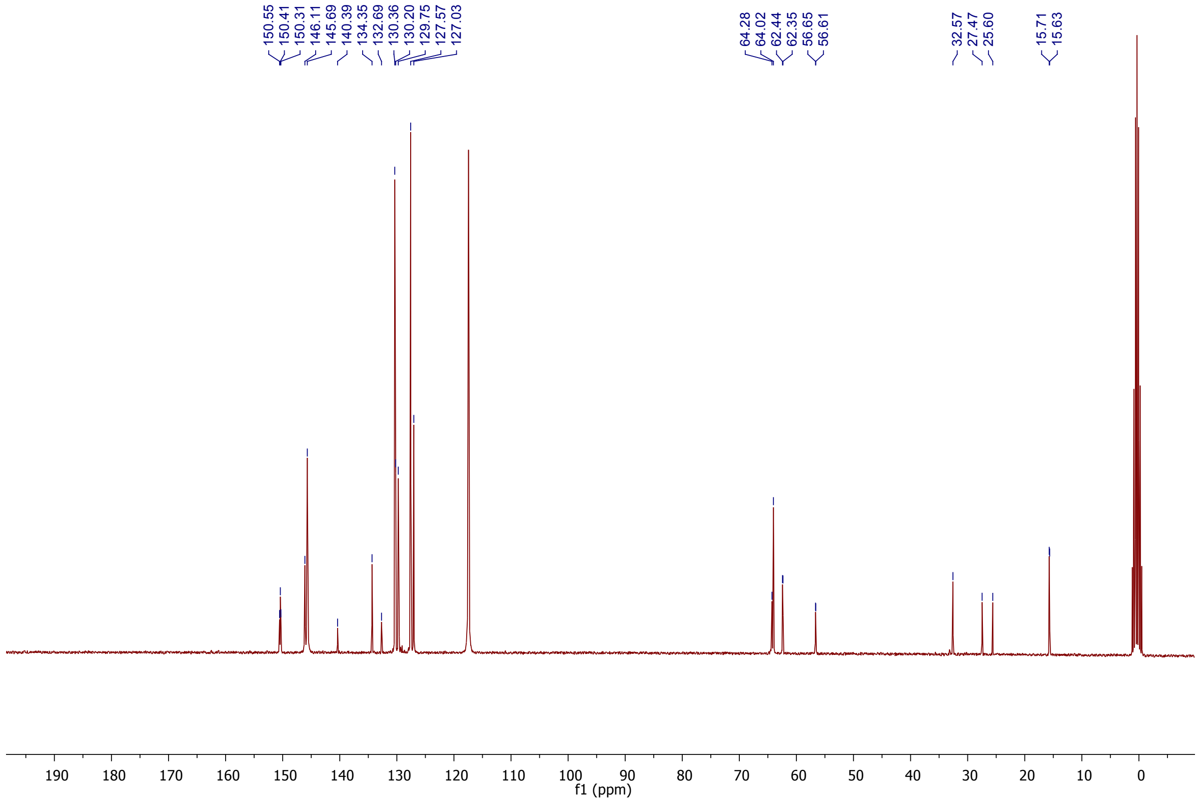


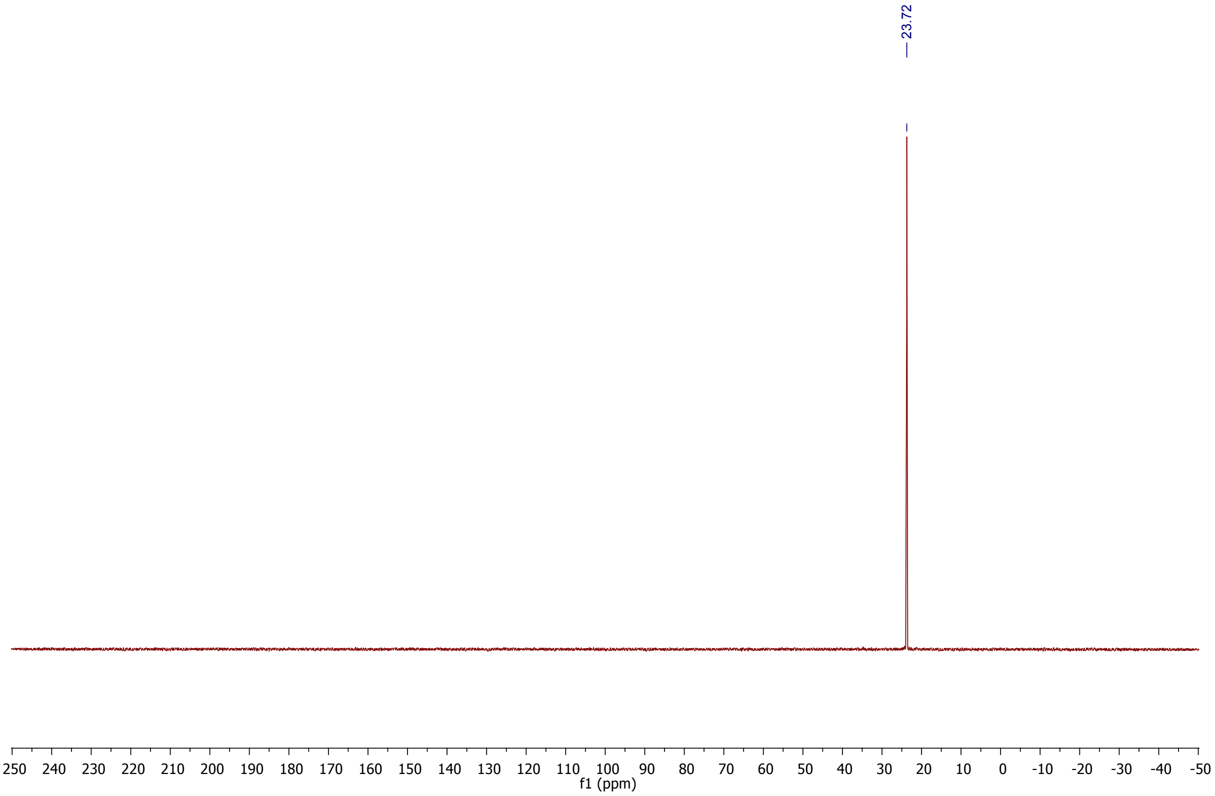
1H NMR P4



13C NMR P4



31P NMR P4



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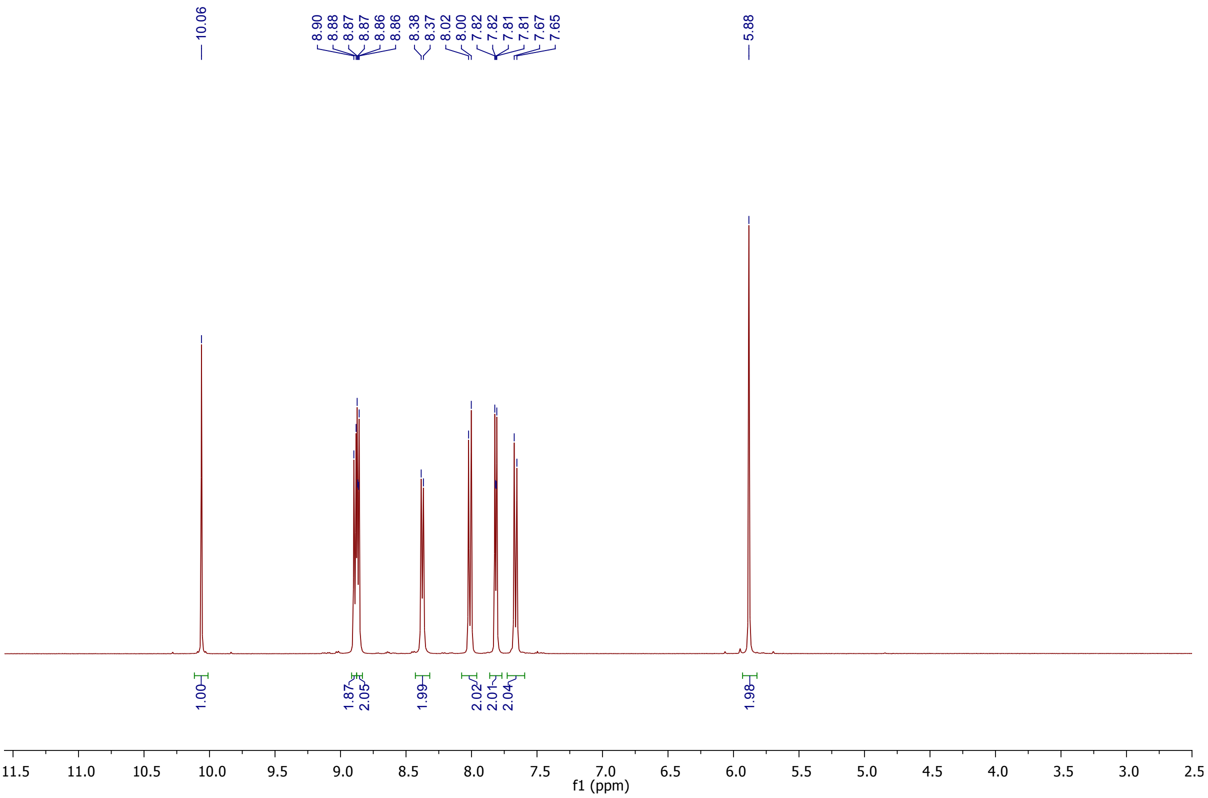
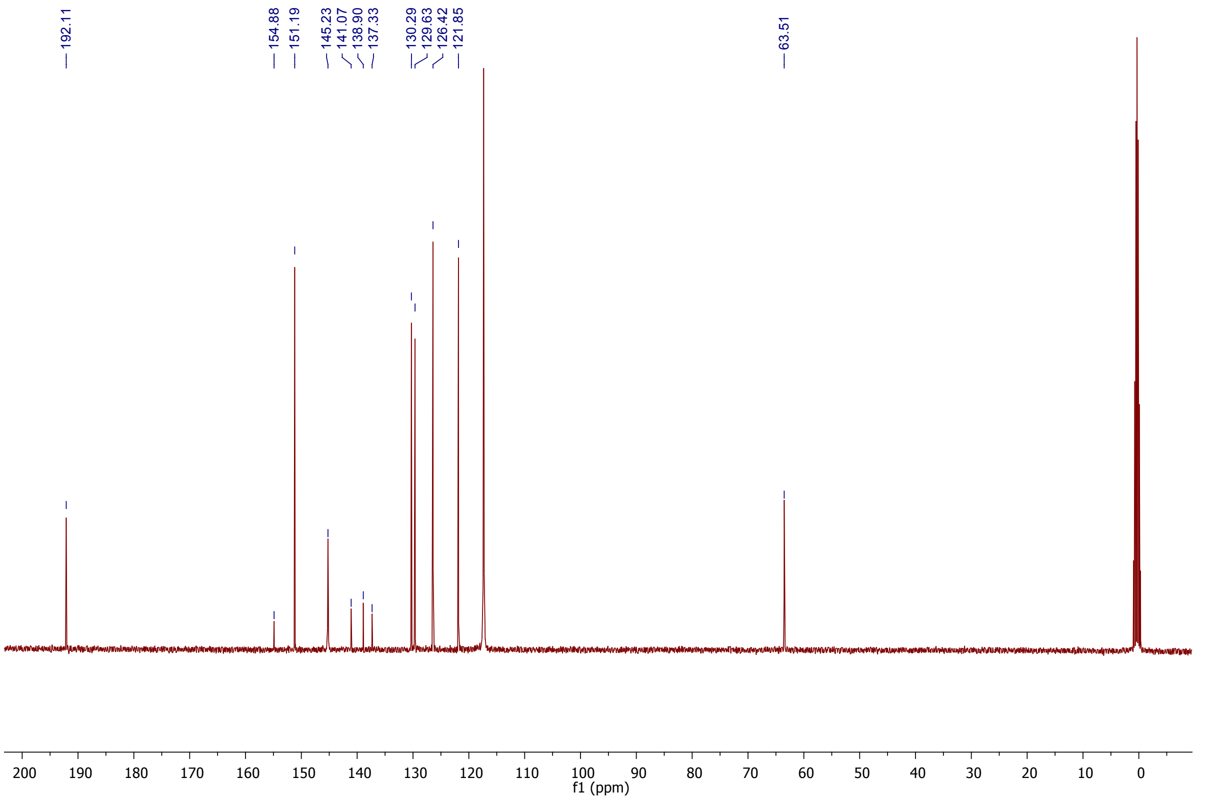


13C NMR P5



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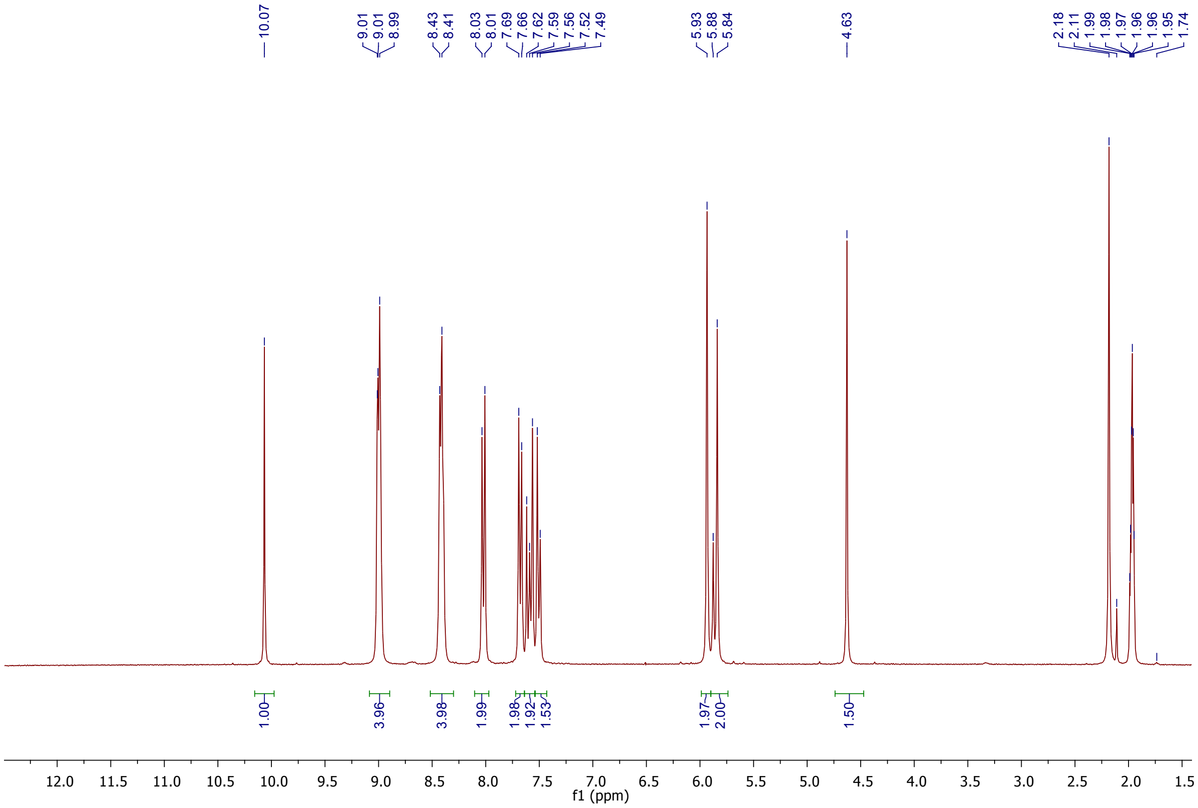
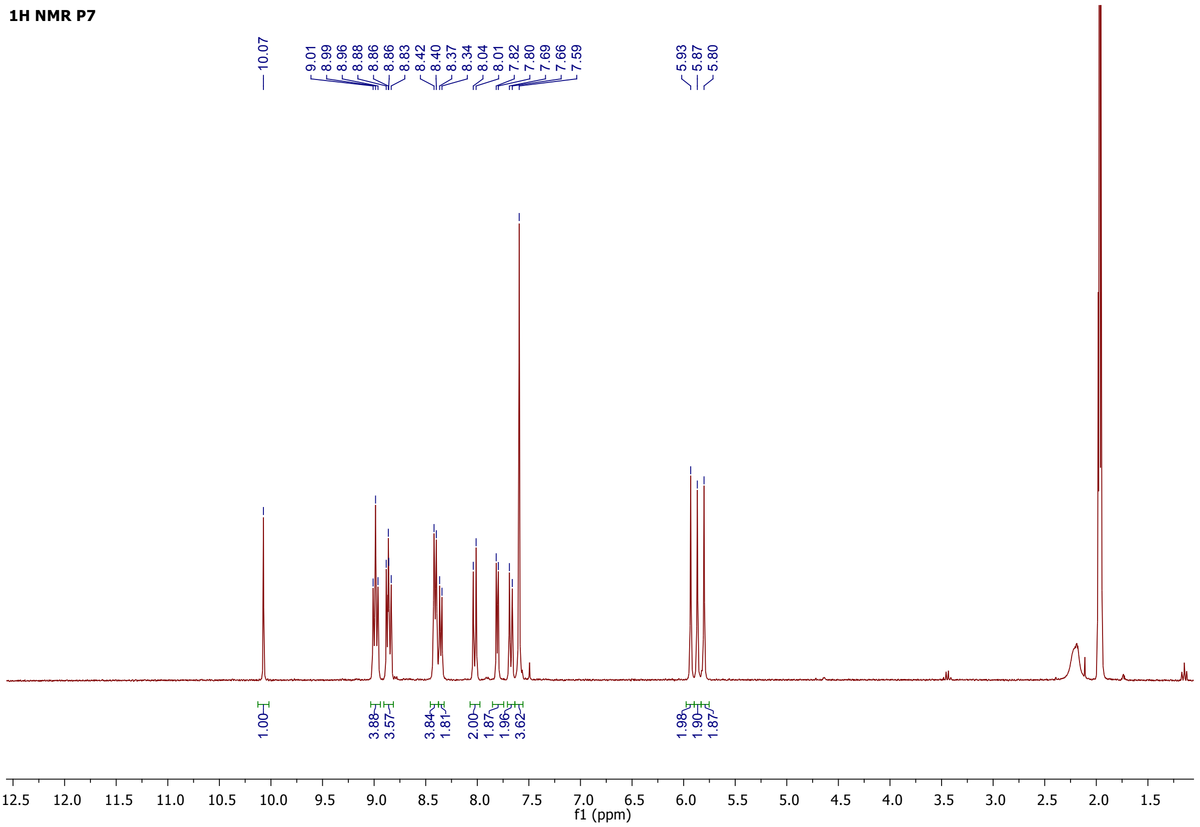
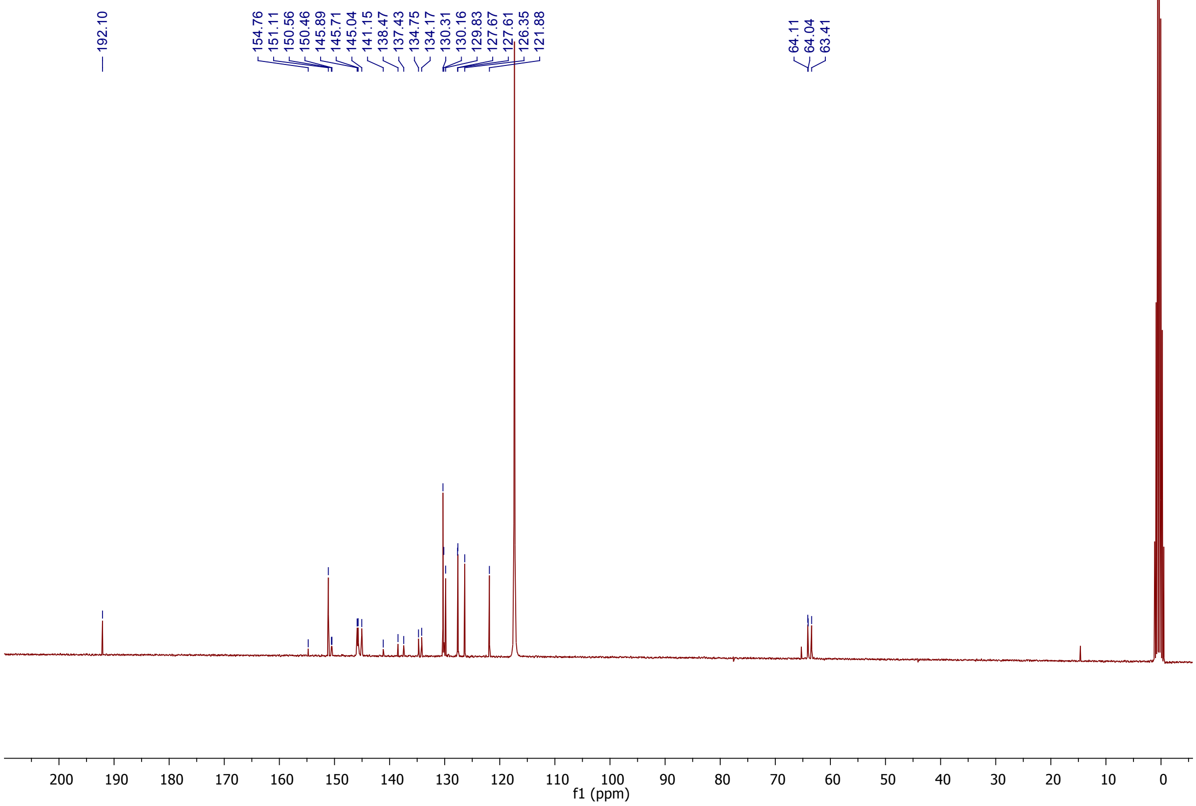


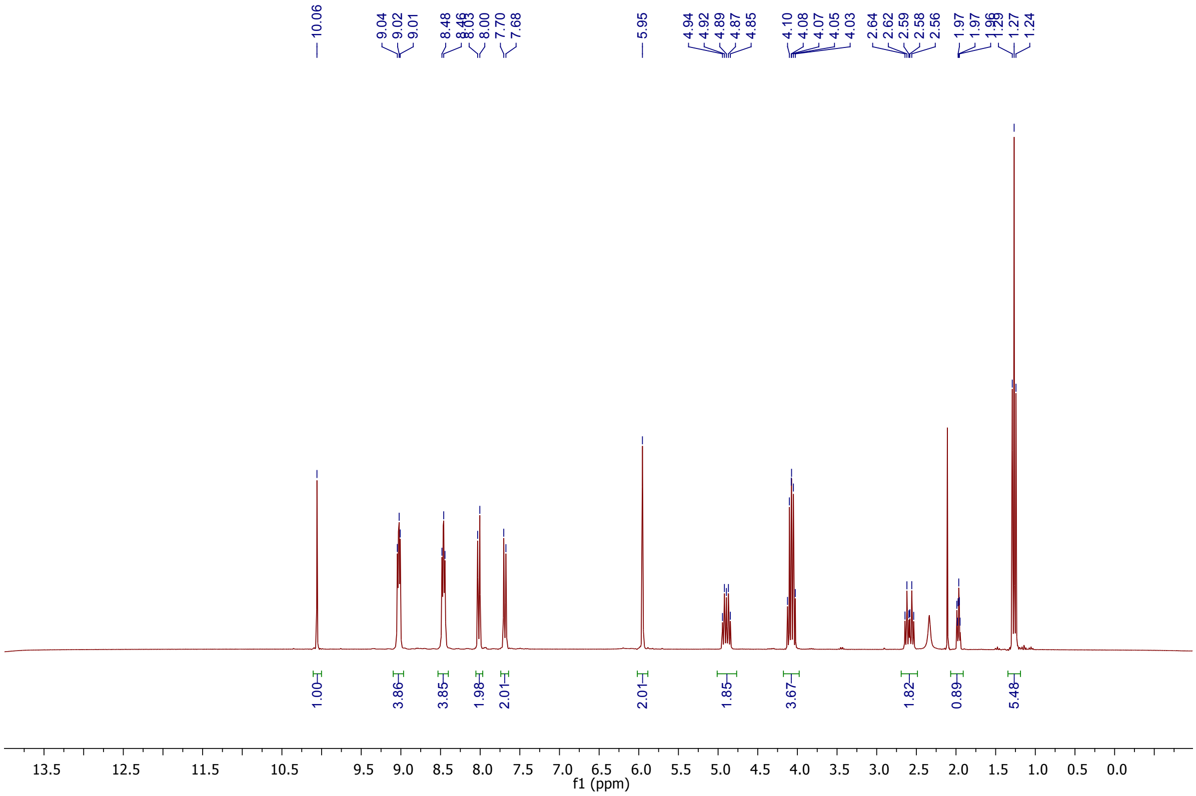
1H NMR P7



13C NMR P7



1H NMR 1V



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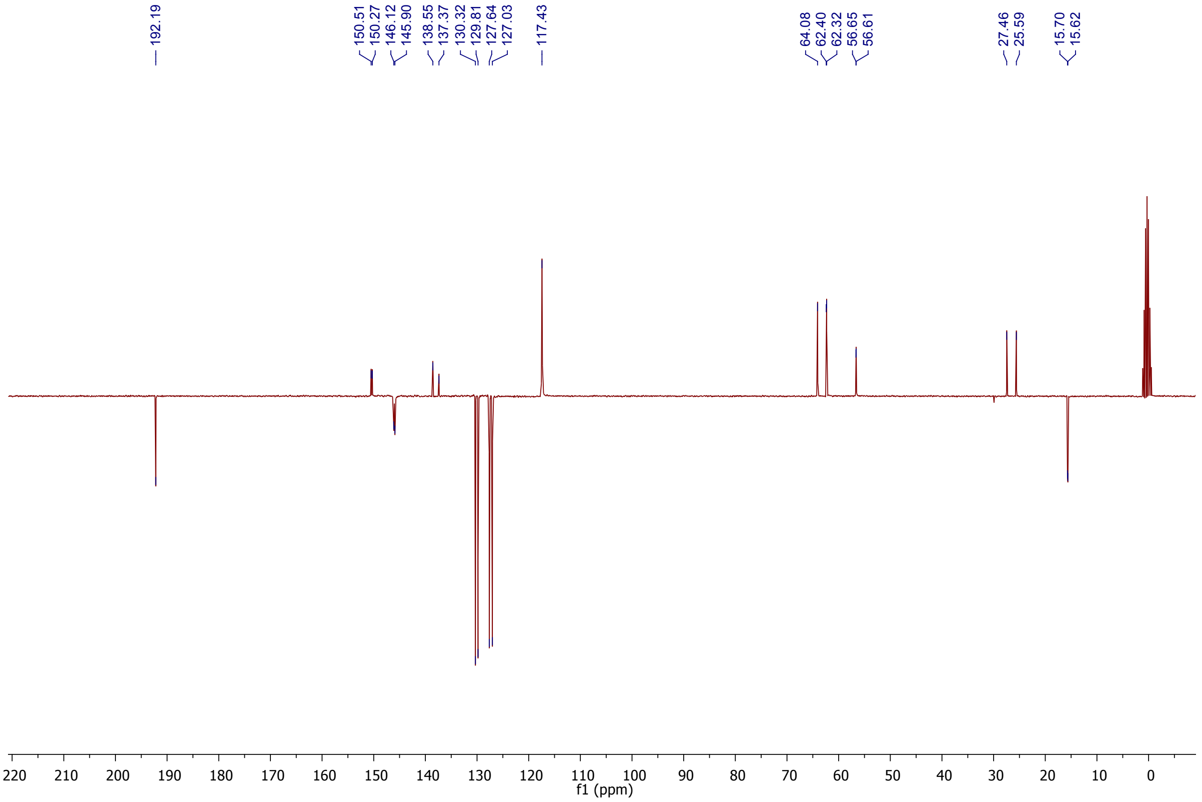
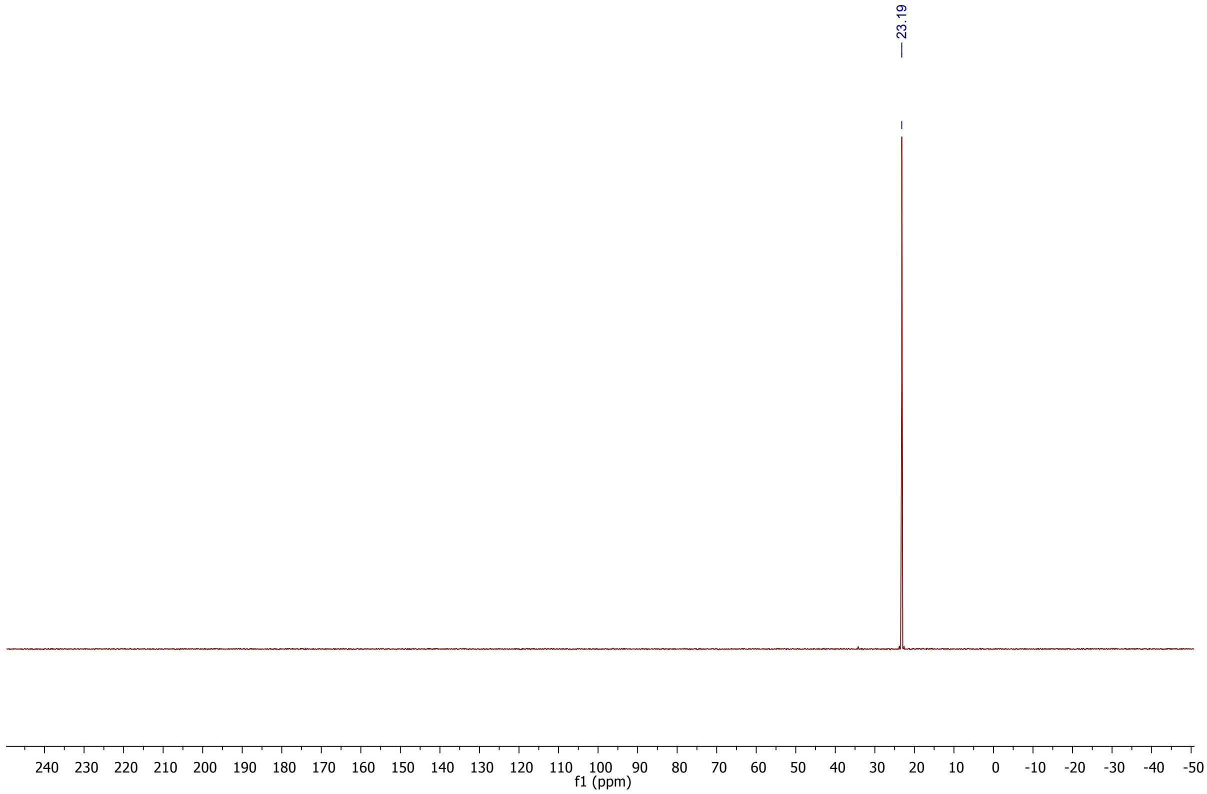
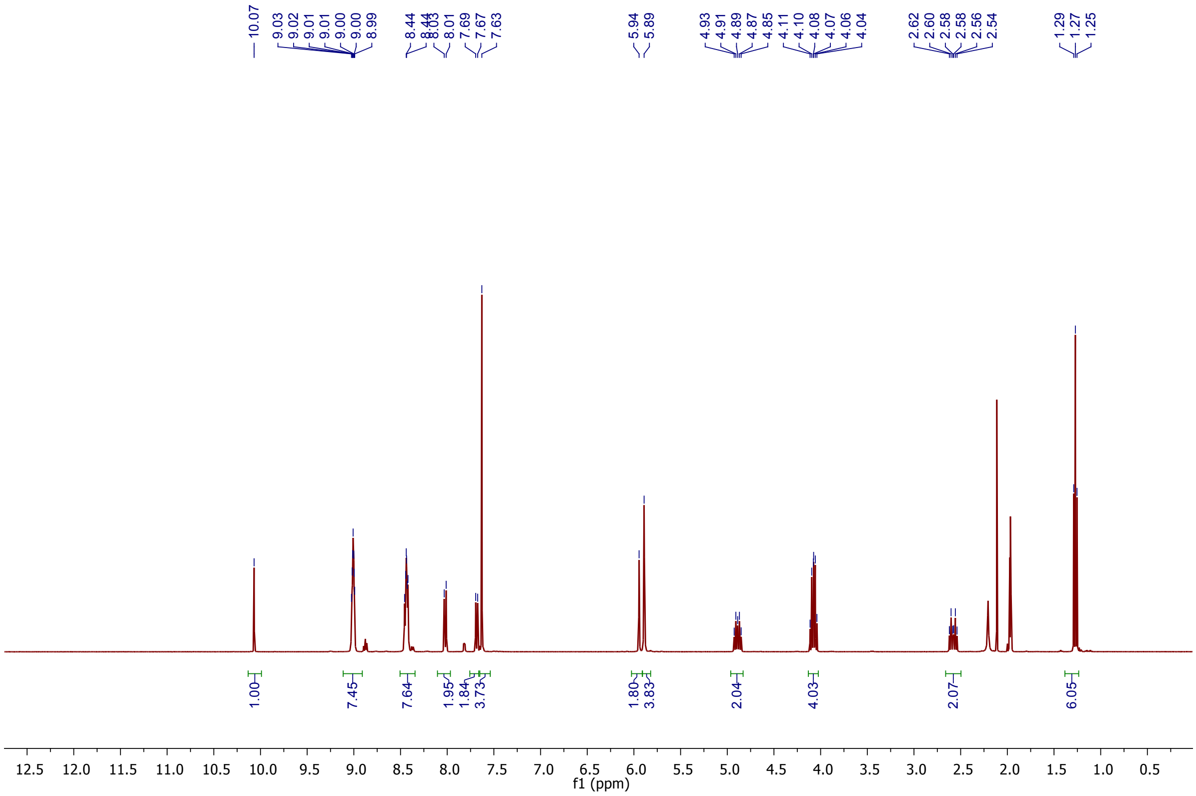


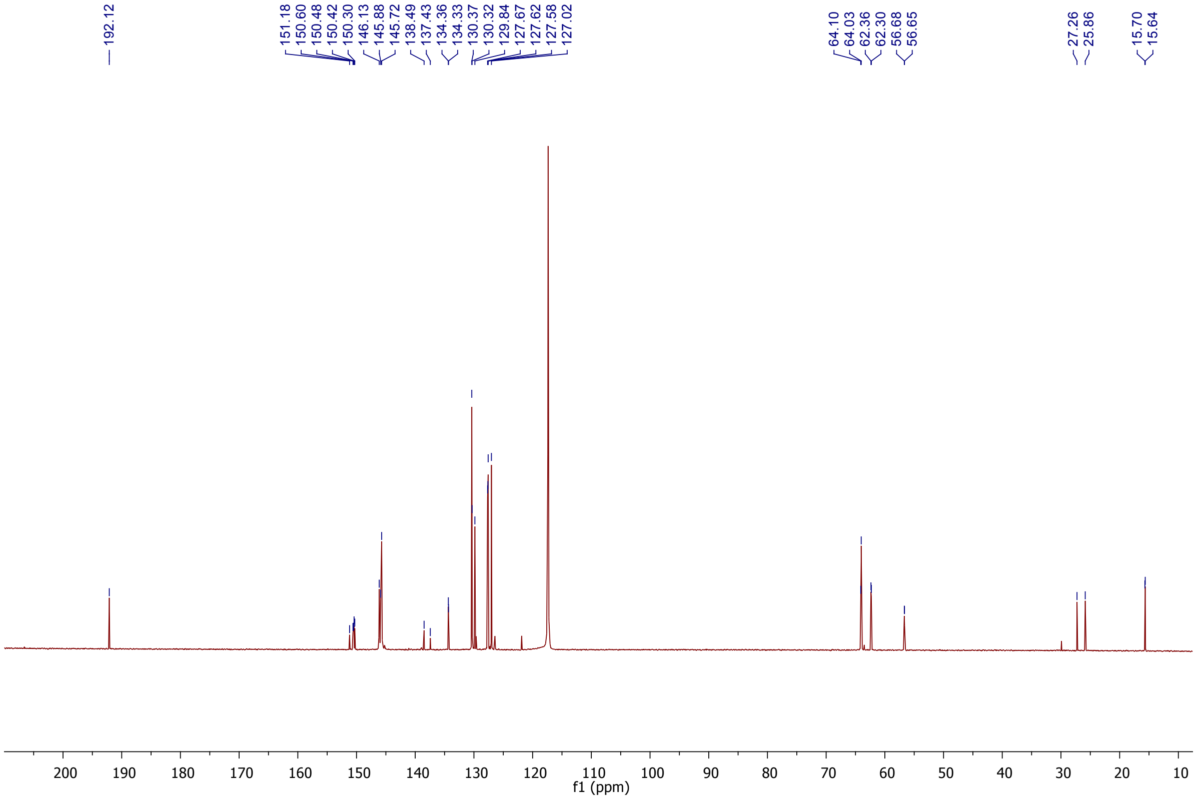
31P NMR 1V



1H NMR 2V



13C NMR 2V



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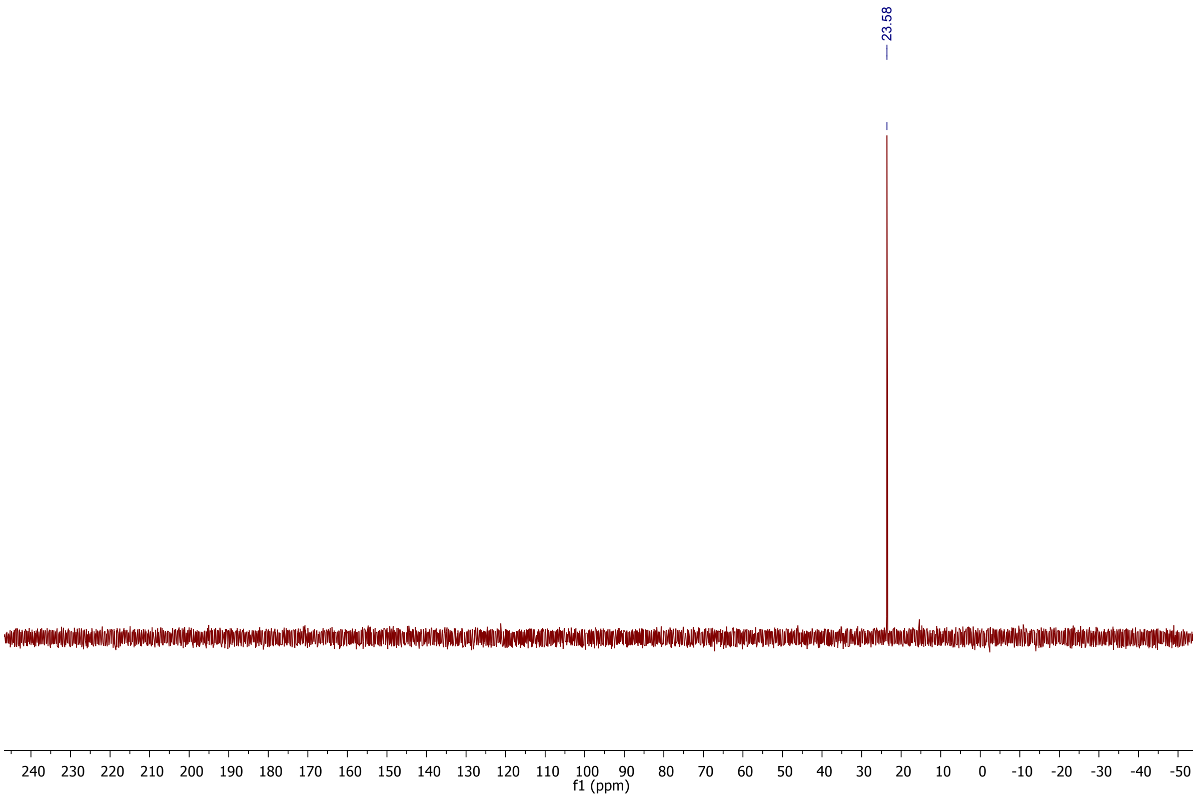
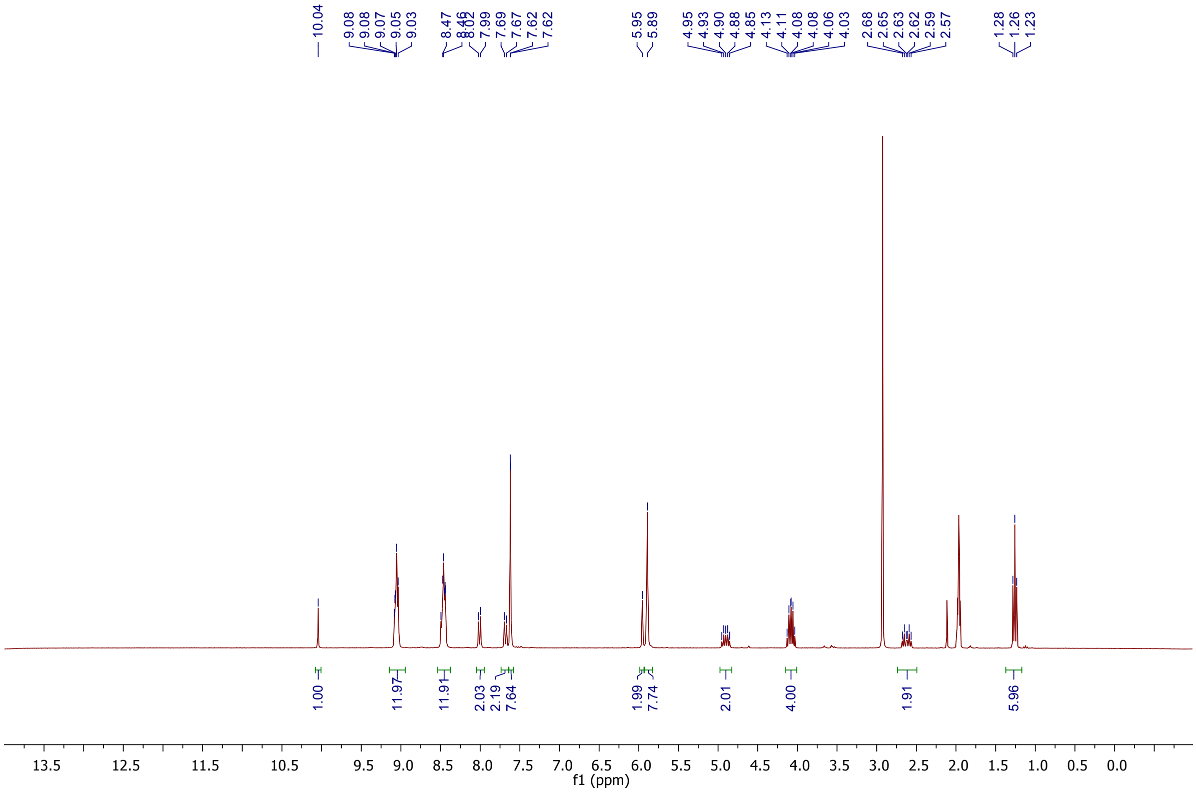
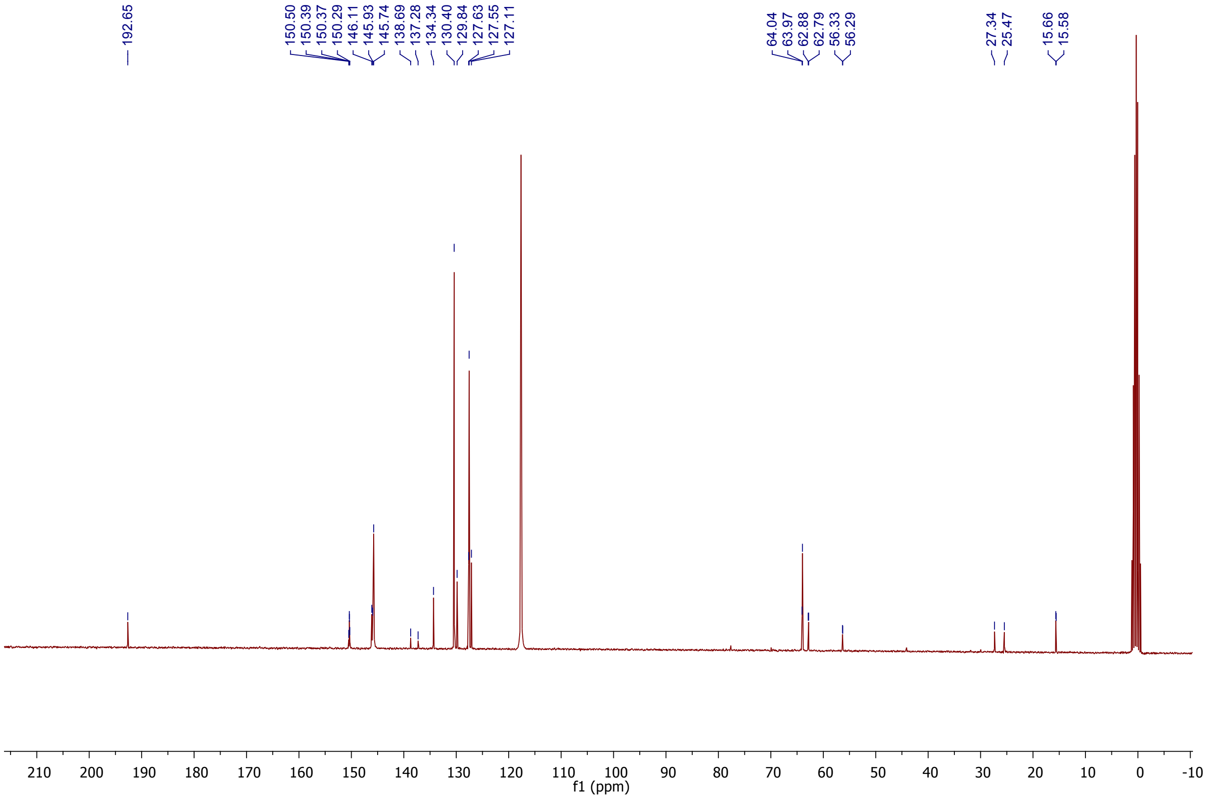


1H NMR 3V



13C NMR 3V



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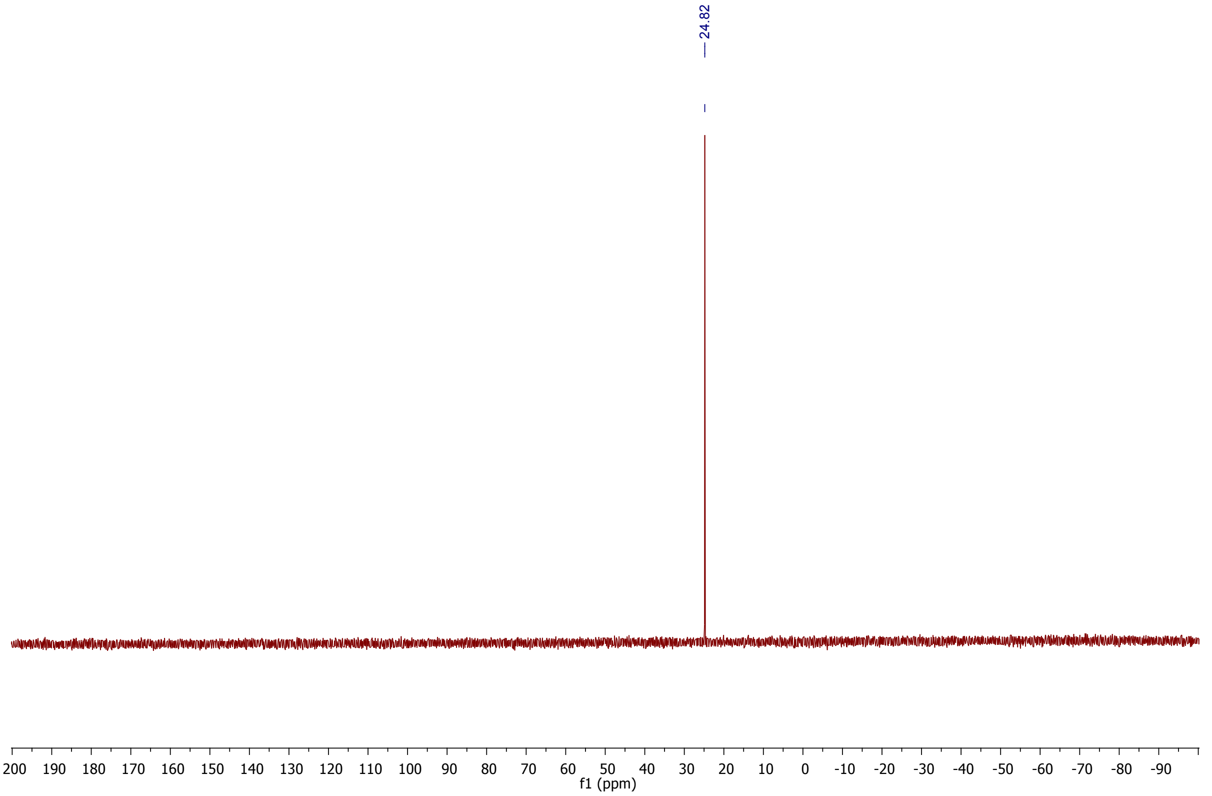

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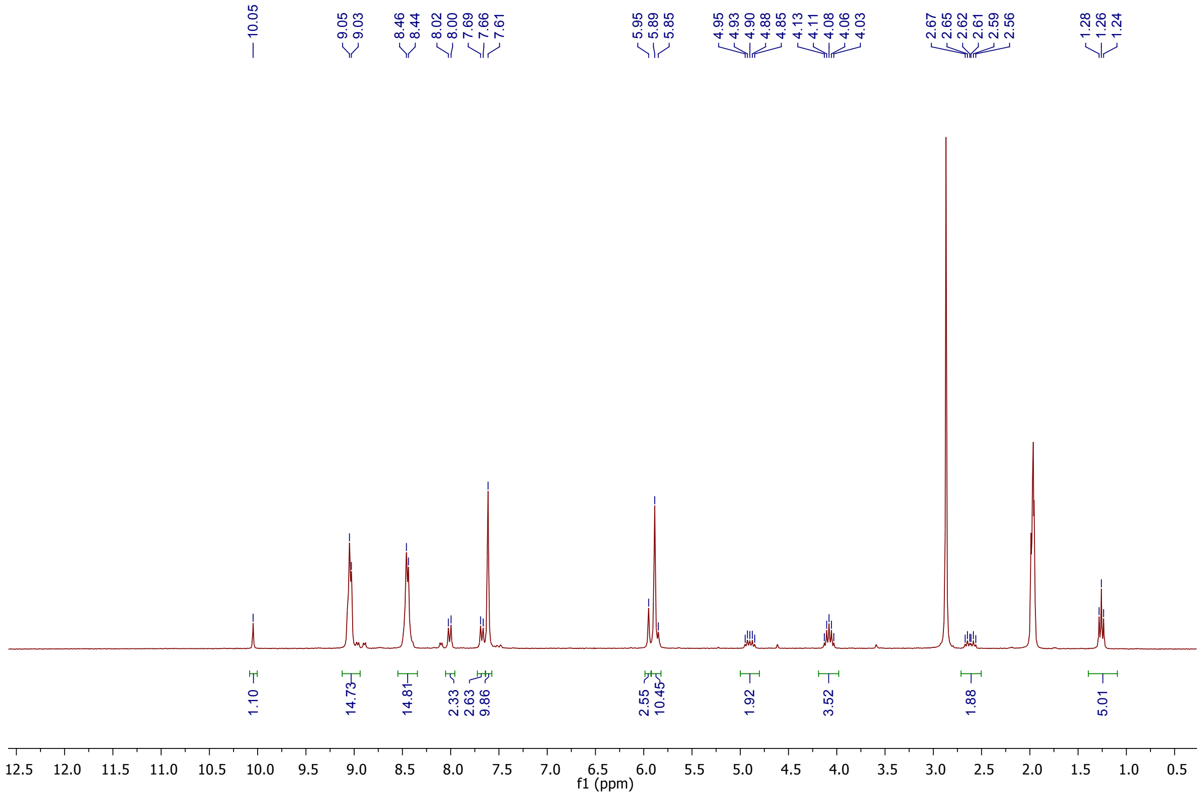

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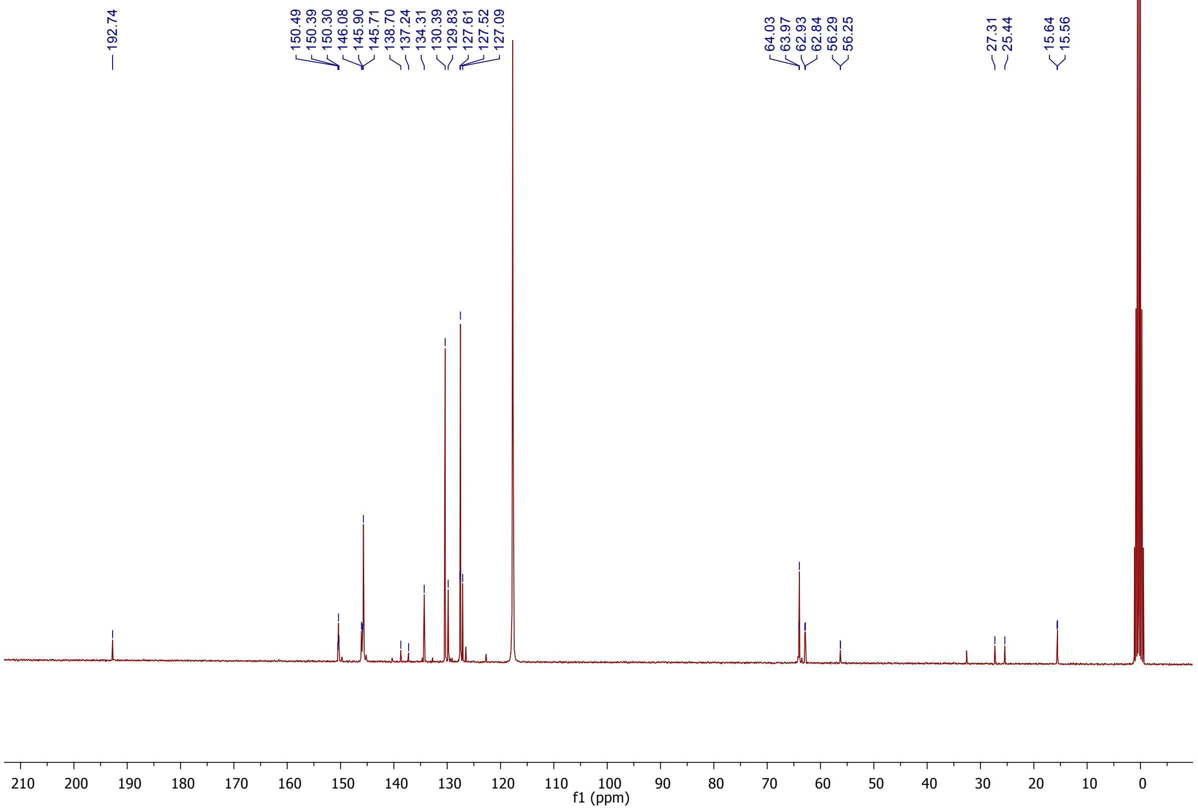

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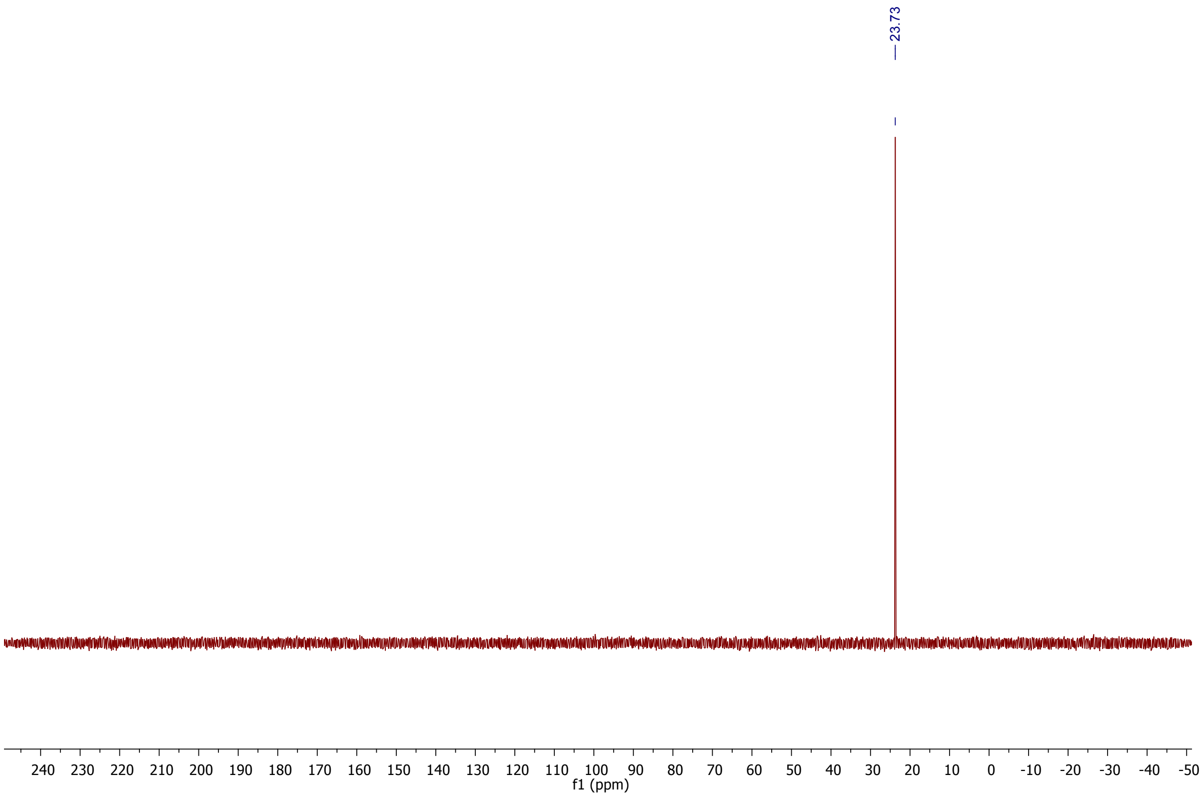
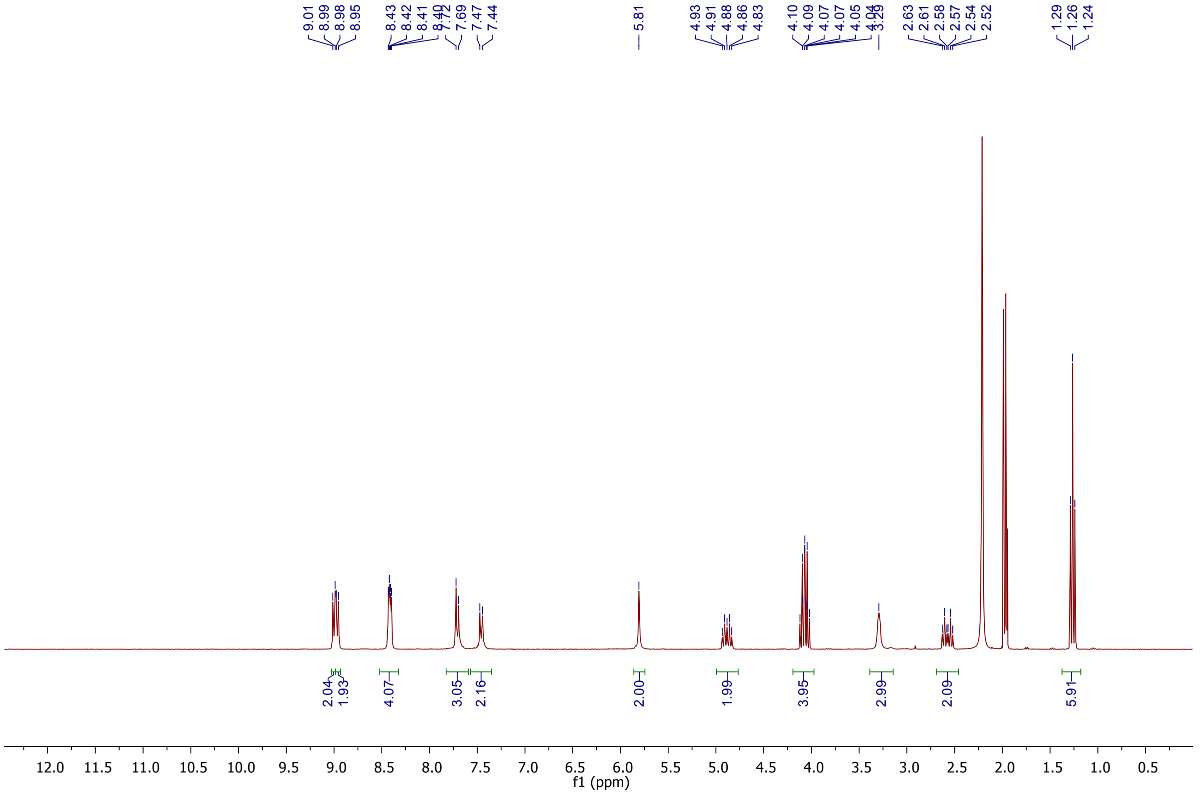
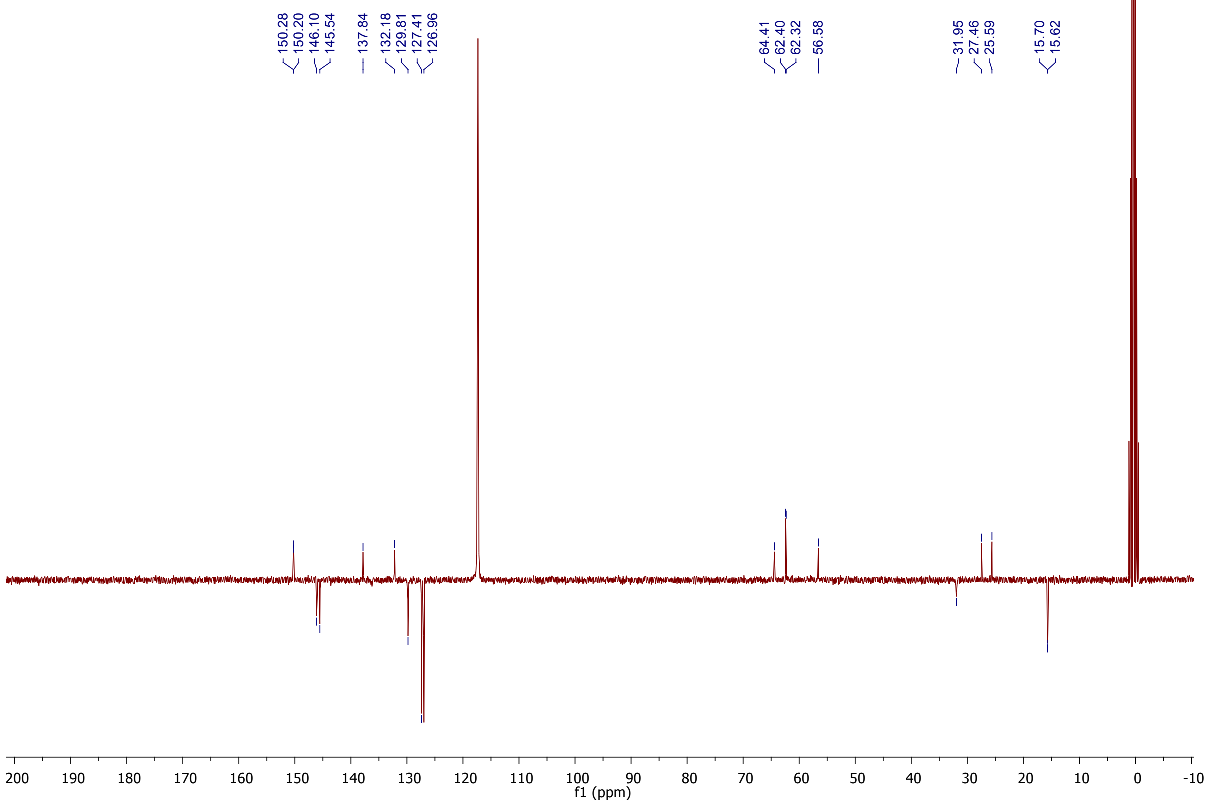


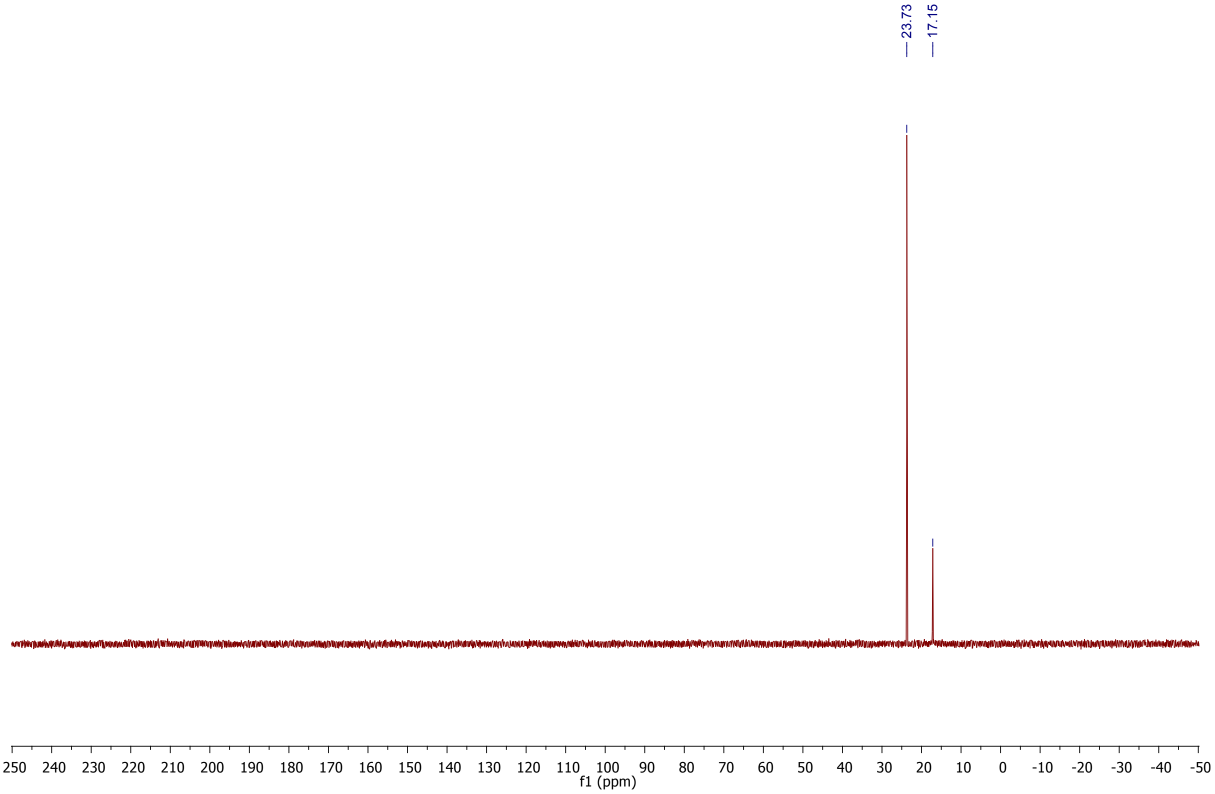
1H NMR D1V



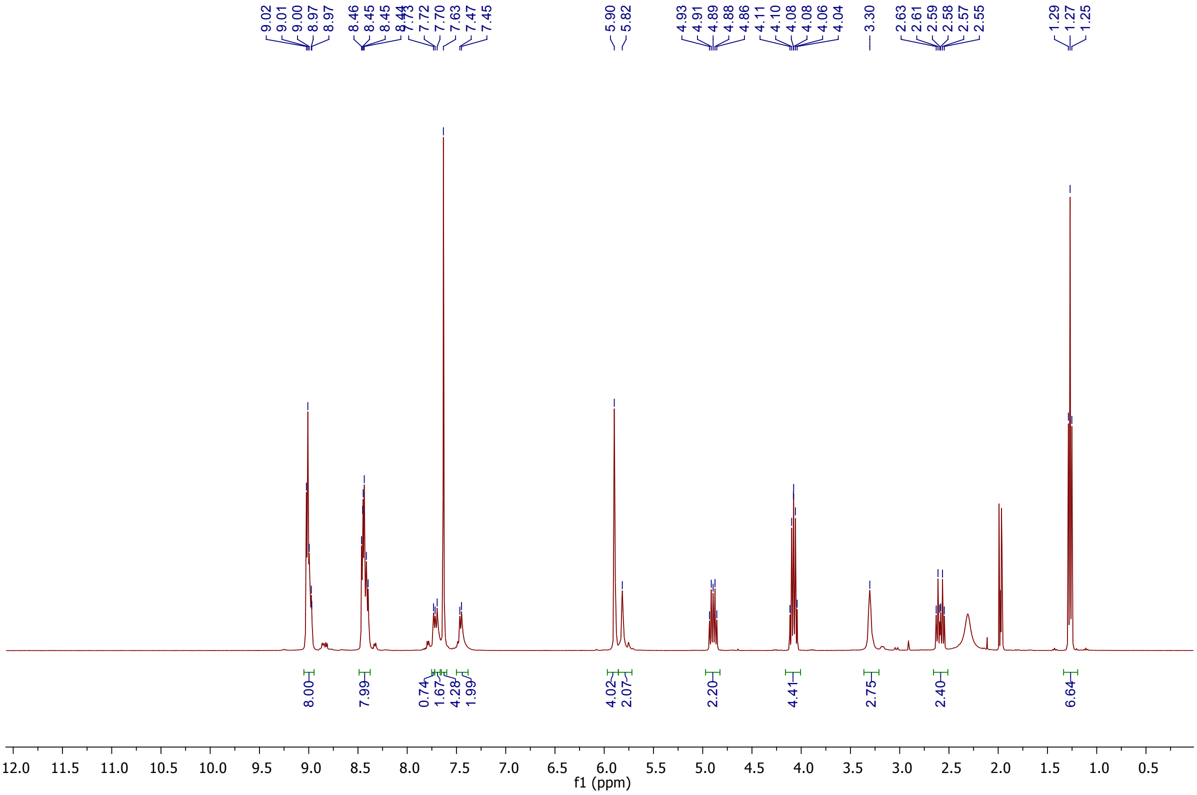
13C NMR D1V



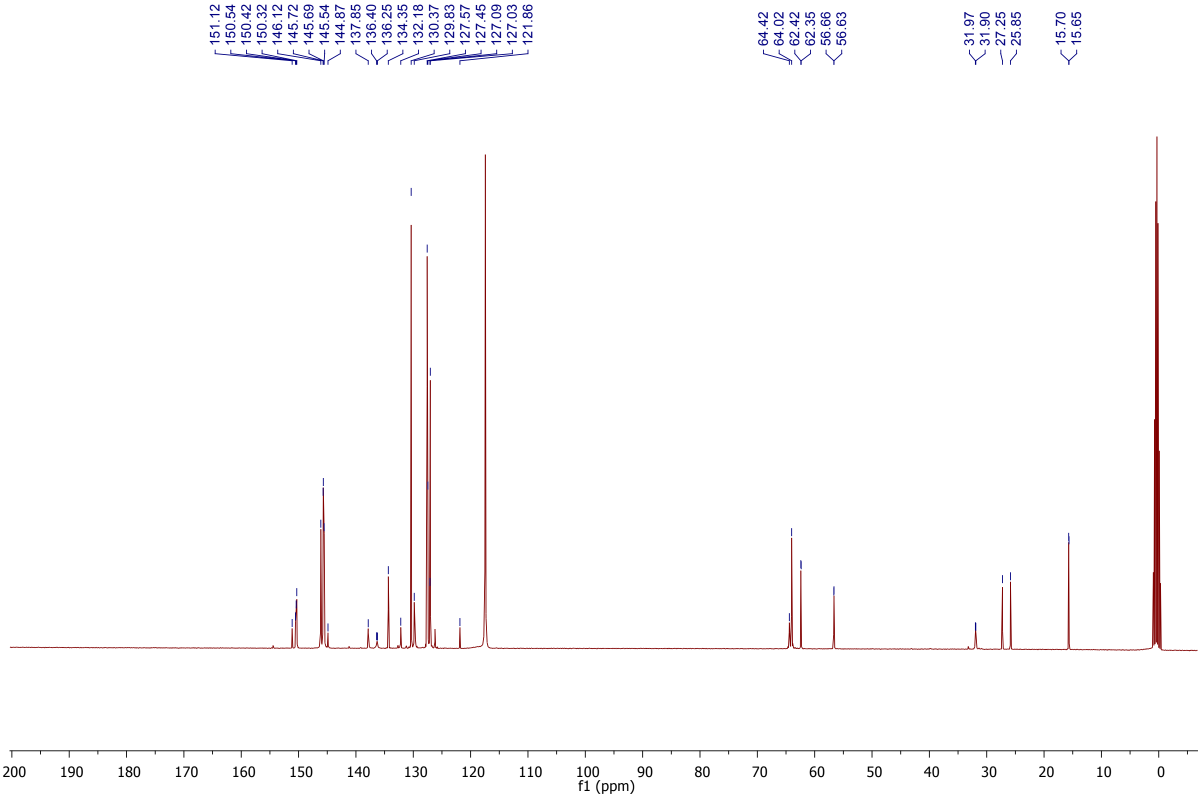
31P NMR D1V



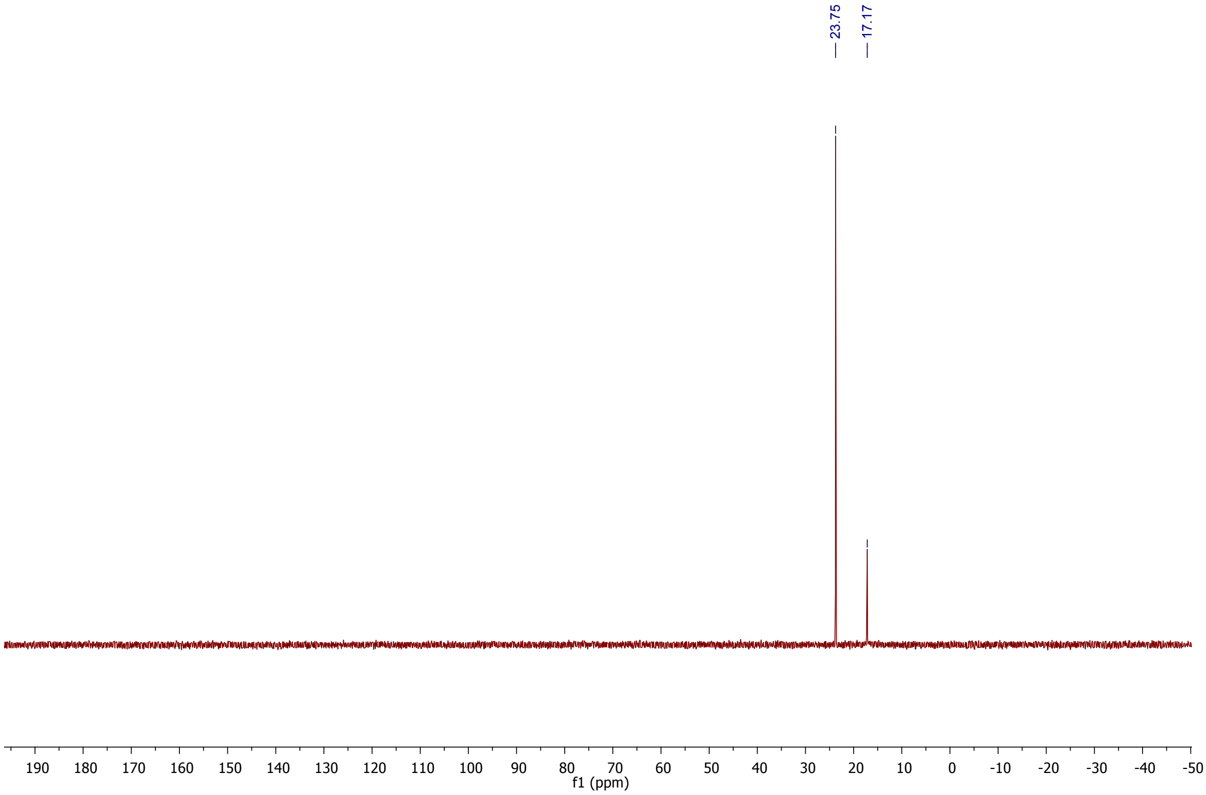
1H NMR D2V



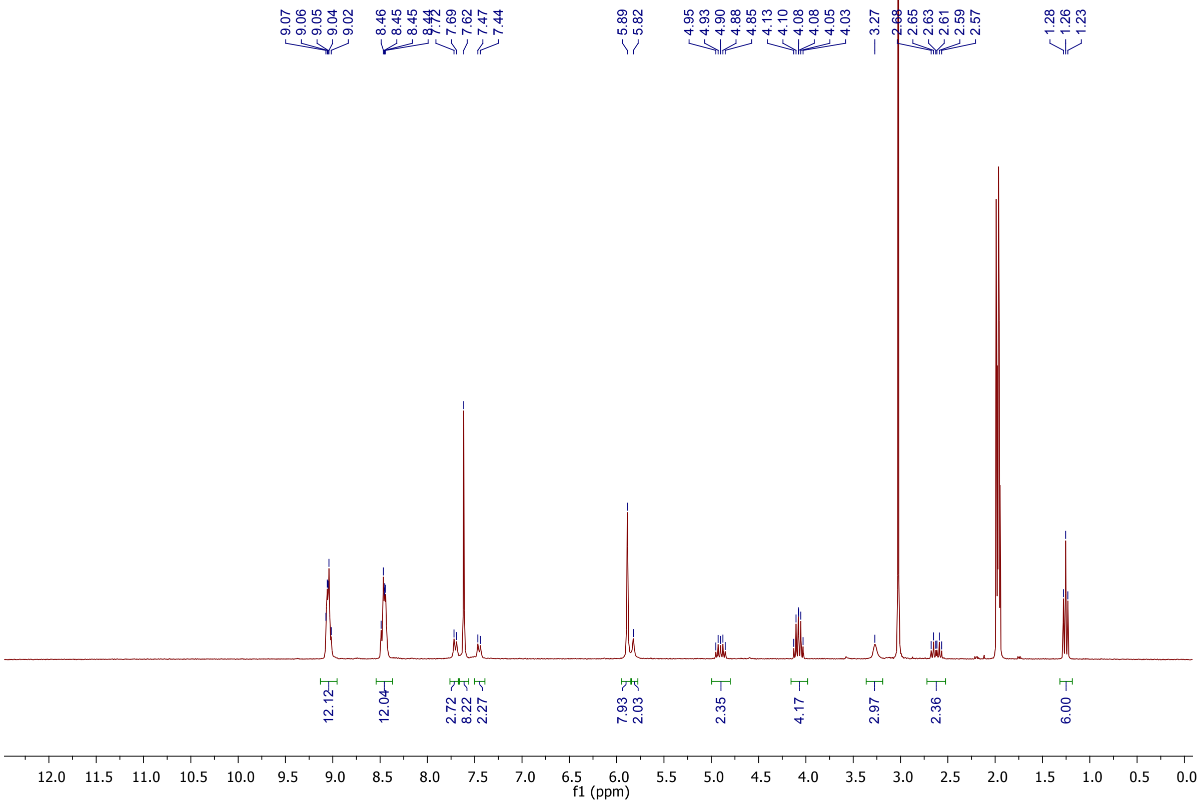
13C NMR D2V



31P NMR D2V



1H NMR D3V



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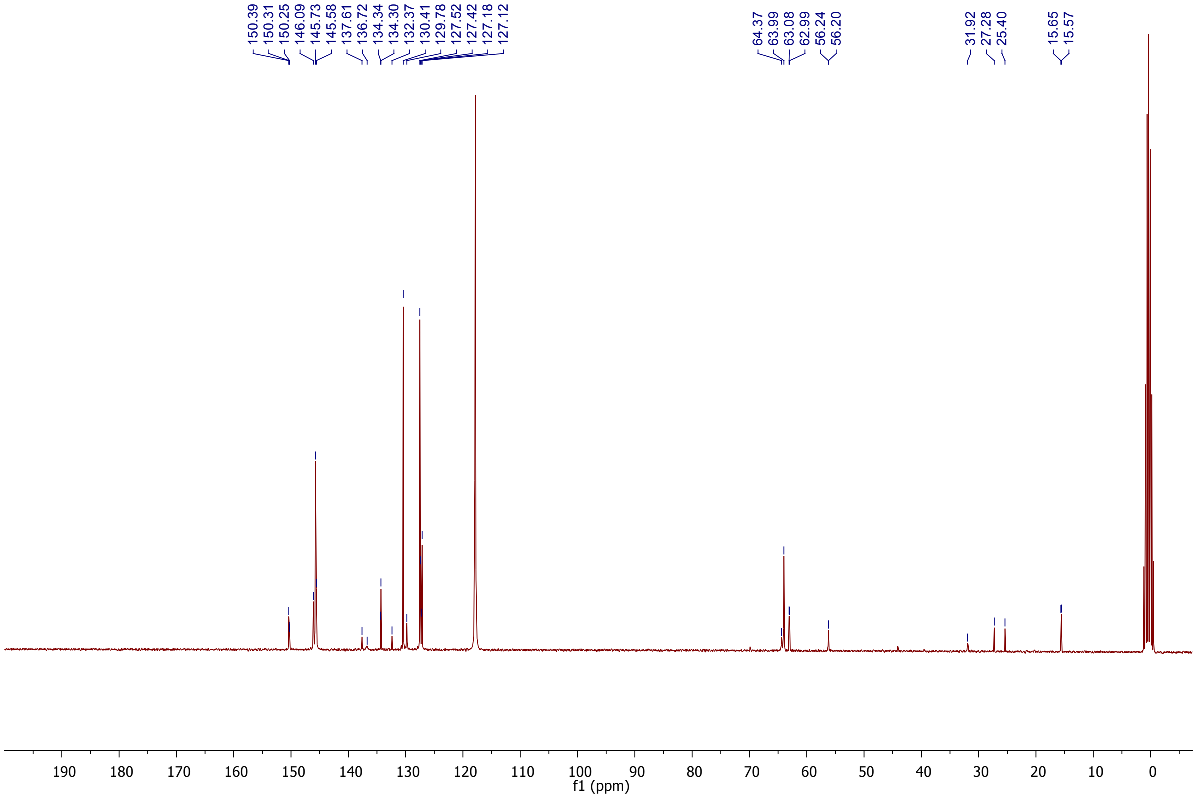

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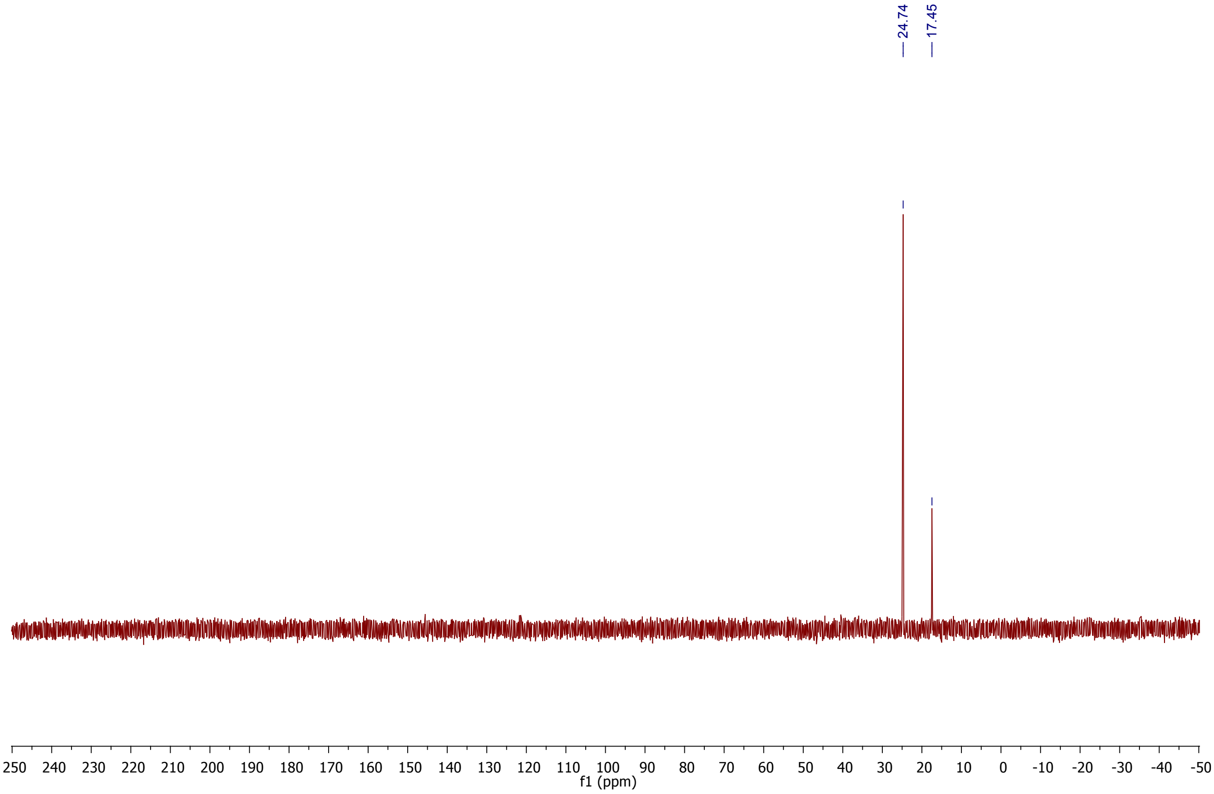
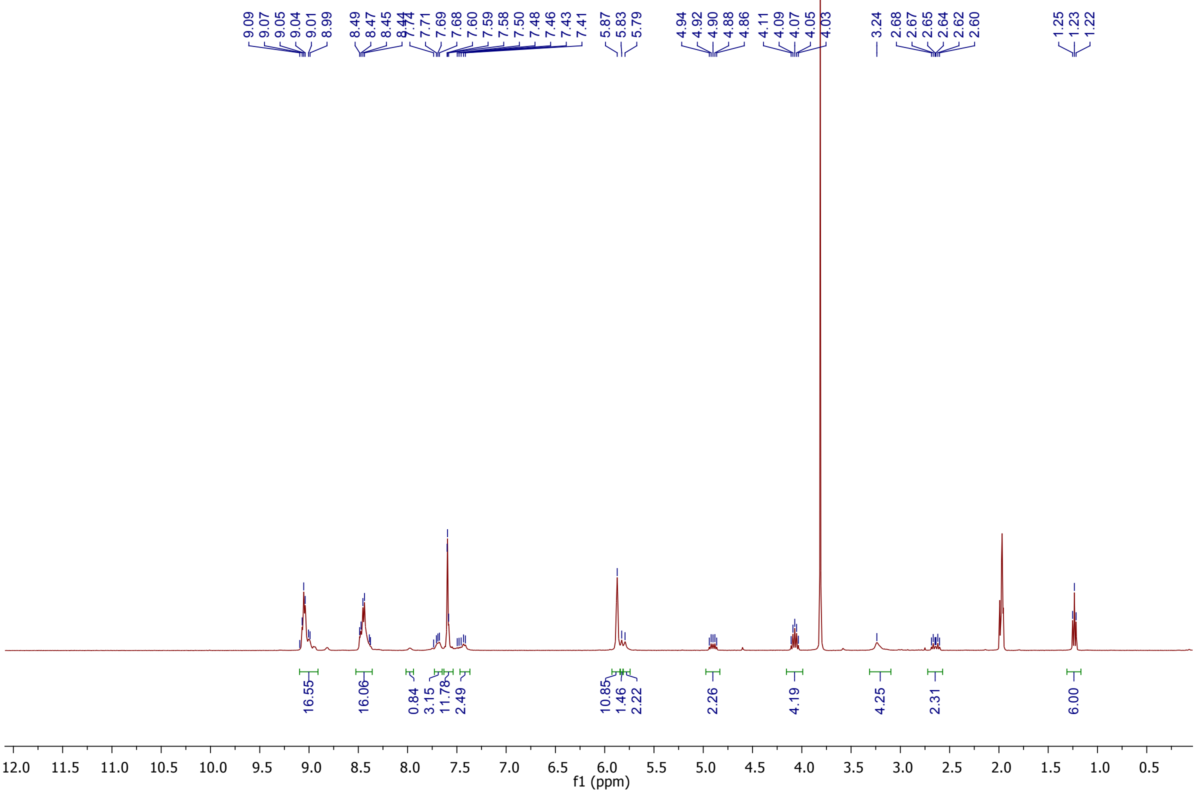
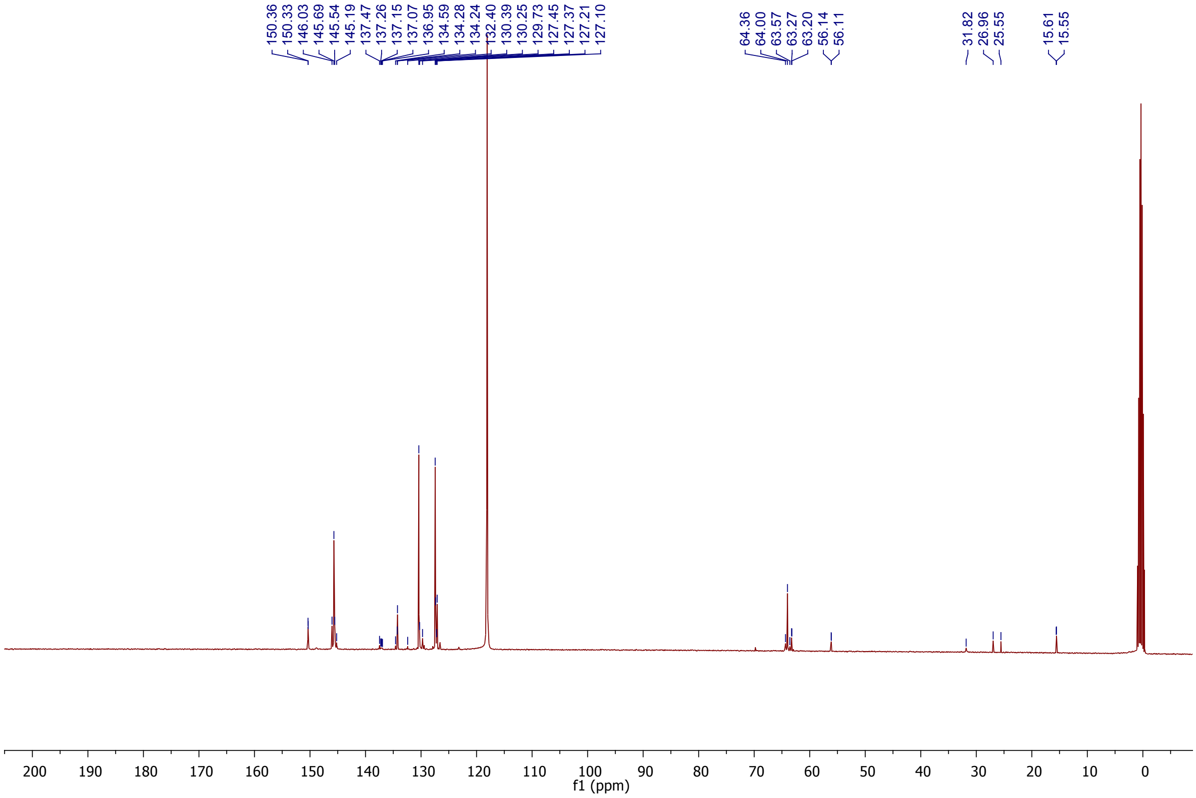


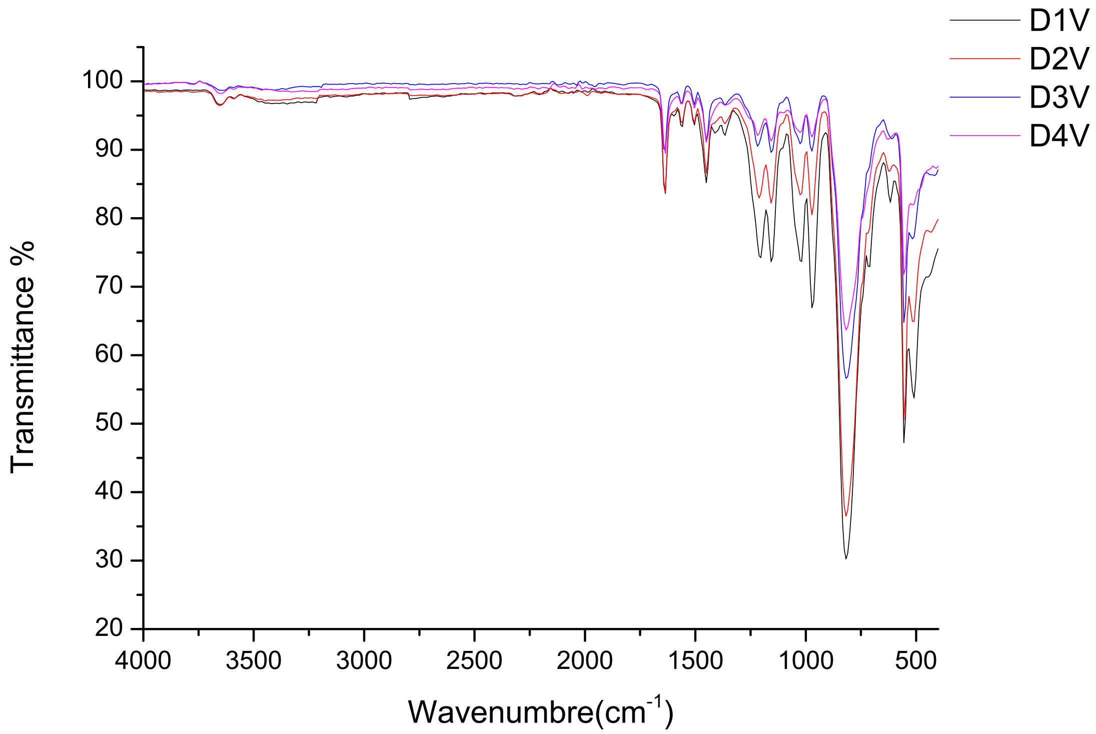
1H NMR D4V

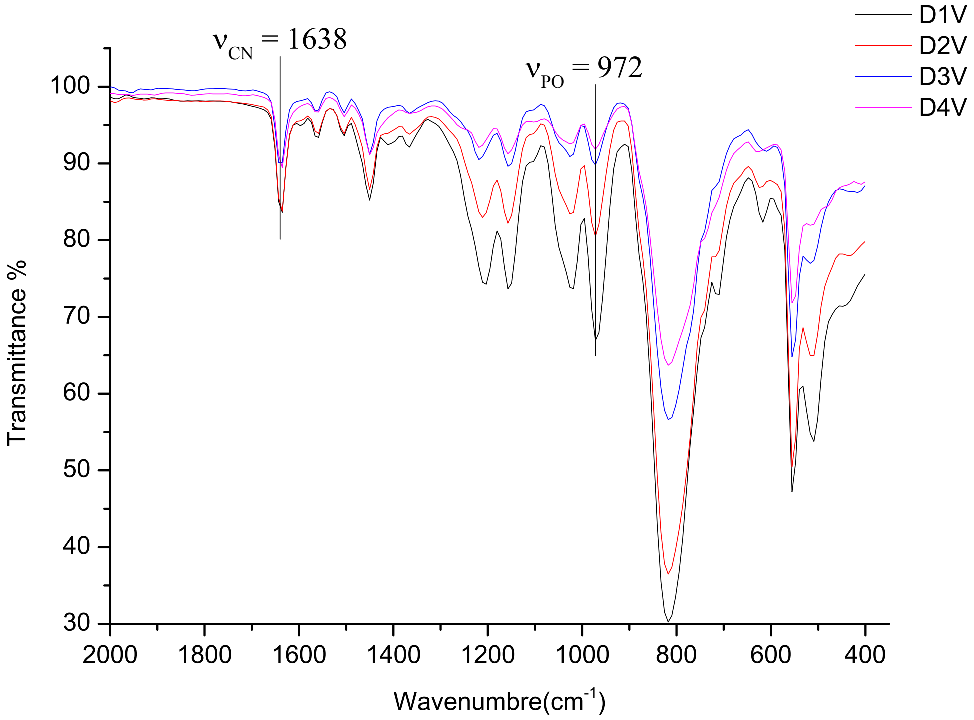


13C NMR D4V

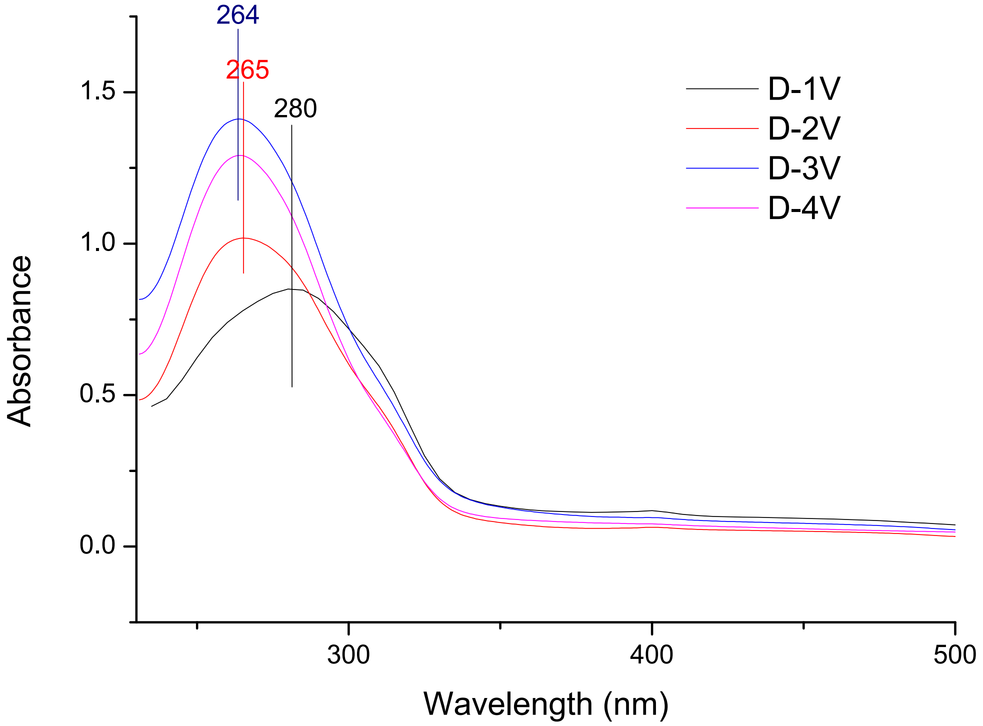


S3: FTIR of the viologen-dendrimers asterisks

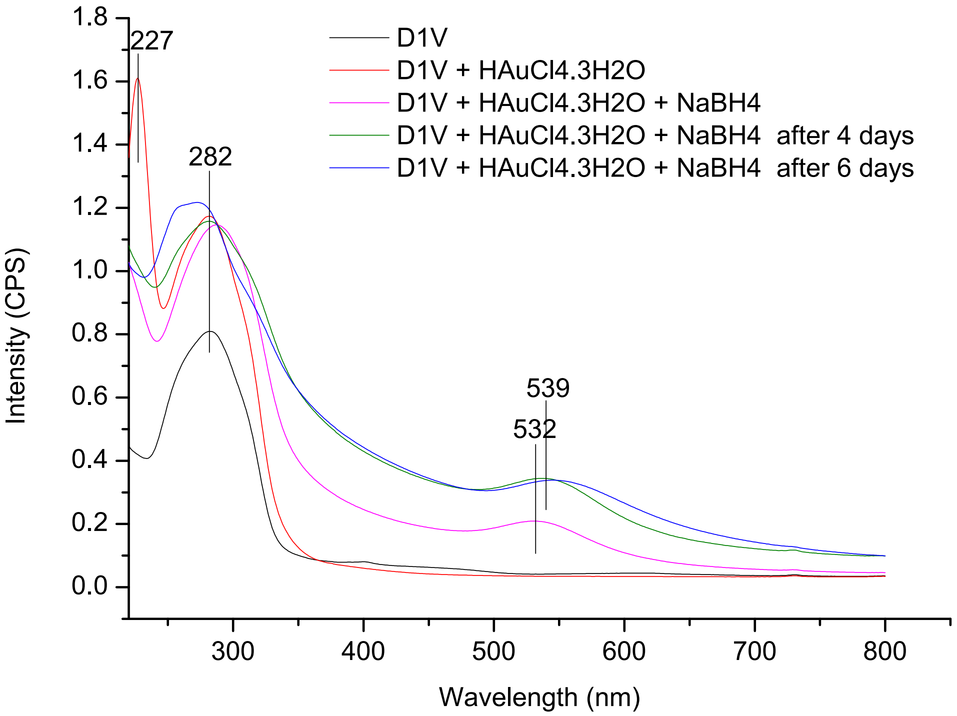


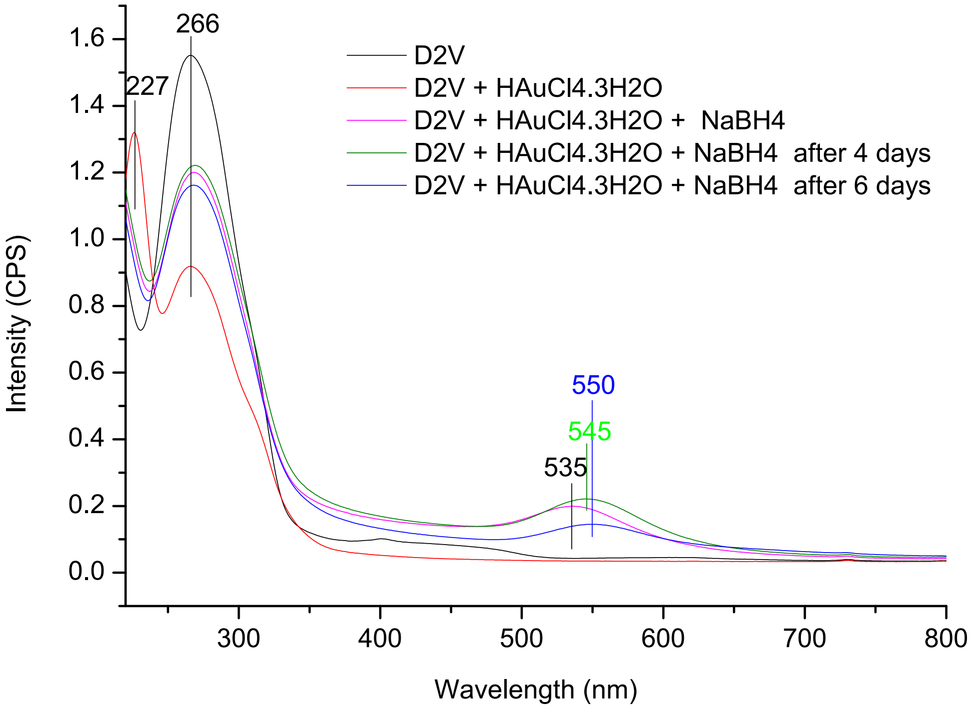


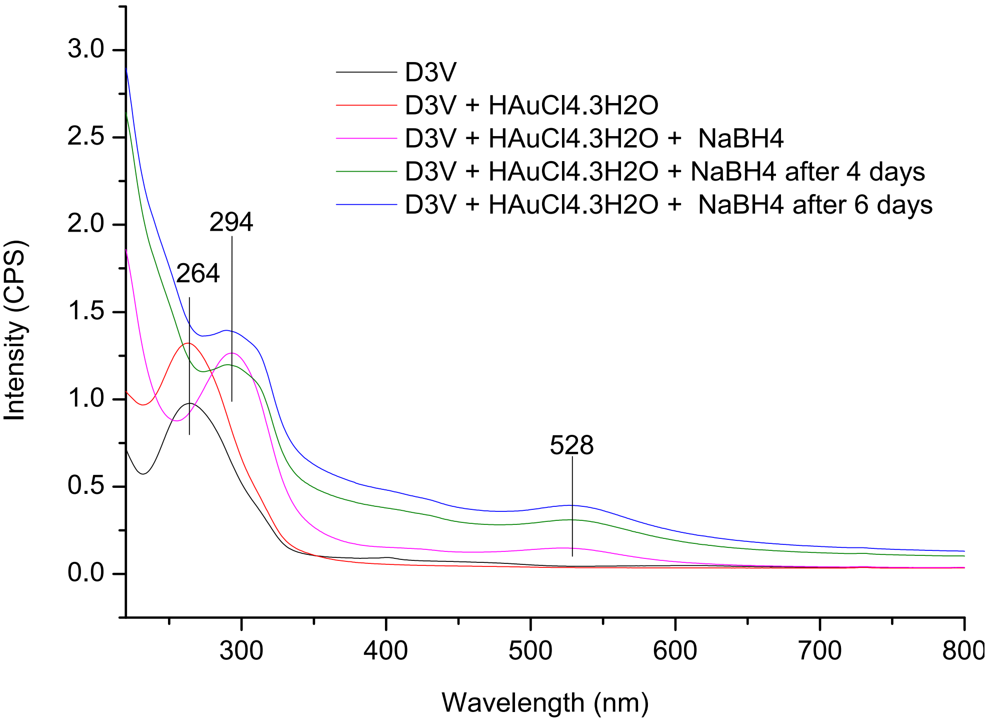
S4a: UV spectra of the viologen-dendrimers asterisks

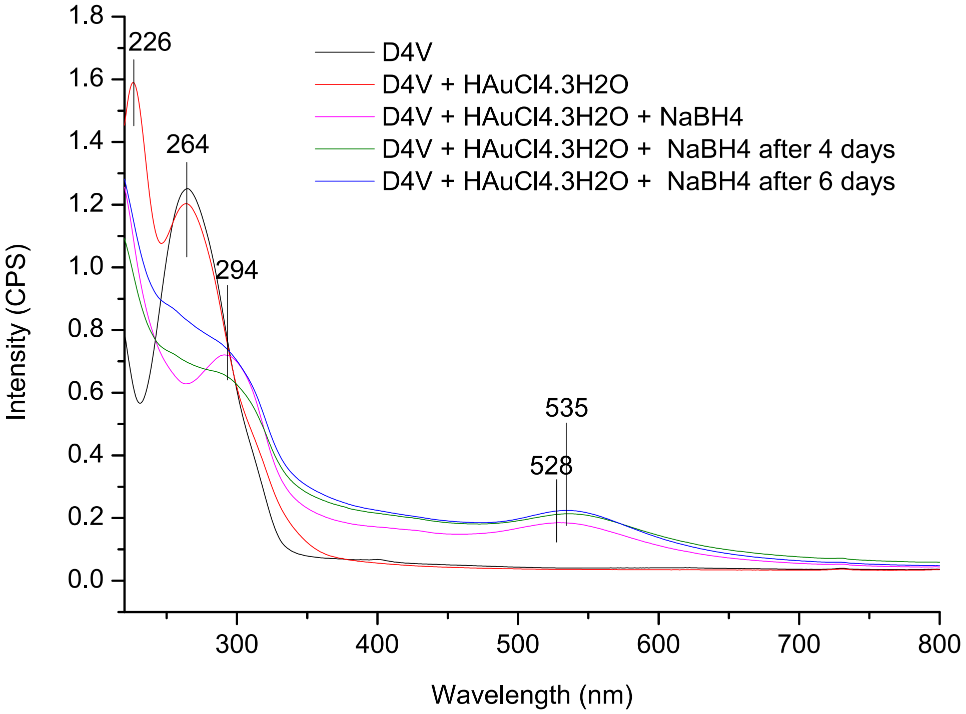


S4b: UV spectra of the viologen-dendrimers asterisks and viologen-dendrimers@AuNPs

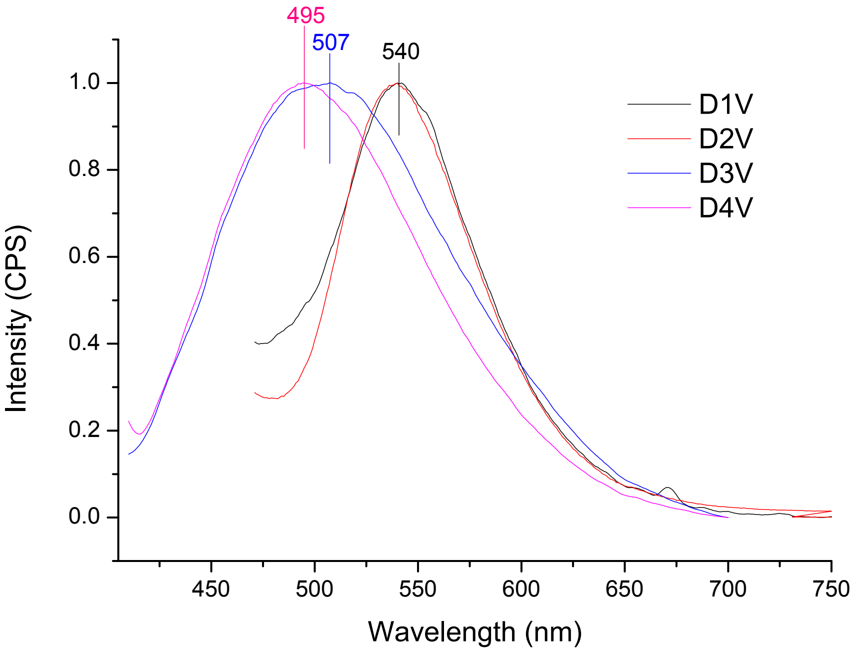



266
227
550
545
535
D2V
D2V + HAuCl4.3H2O
D2V + HAuCl4.3H2O + NaBH4
D2V + HAuCl4.3H2O + NaBH4 after 4 days
D2V + HAuCl4.3H2O + NaBH4 after 6 days
Intensity (CPS)
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
300
400
500
600
700
800
Wavelength (nm)


D3V
D3V + HAuCl4.3H2O
D3V + HAuCl4.3H2O + NaBH4
D3V + HAuCl4.3H2O + NaBH4 after 4 days
D3V + HAuCl4.3H2O + NaBH4 after 6 days
294
264
528
Intensity (CPS)
3.0
2.5
2.0
1.5
1.0
0.5
0.0
300
400
500
600
700
800
Wavelength (nm)

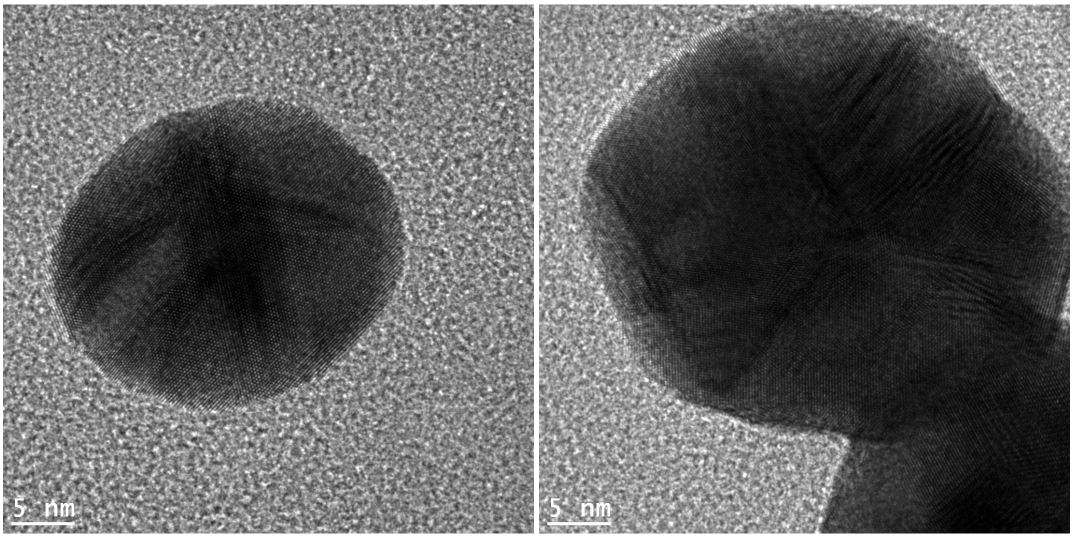

1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
Intensity (CPS)
300
400
500
600
700
800
Wavelength (nm)
226
264
294
535
528
D4V
D4V + HAuCl4.3H2O
D4V + HAuCl4.3H2O + NaBH4
D4V + HAuCl4.3H2O + NaBH4 after 4 days
D4V + HAuCl4.3H2O + NaBH4 after 6 days

S5: Fluorescence spectra of the viologen-dendrimers asterisks

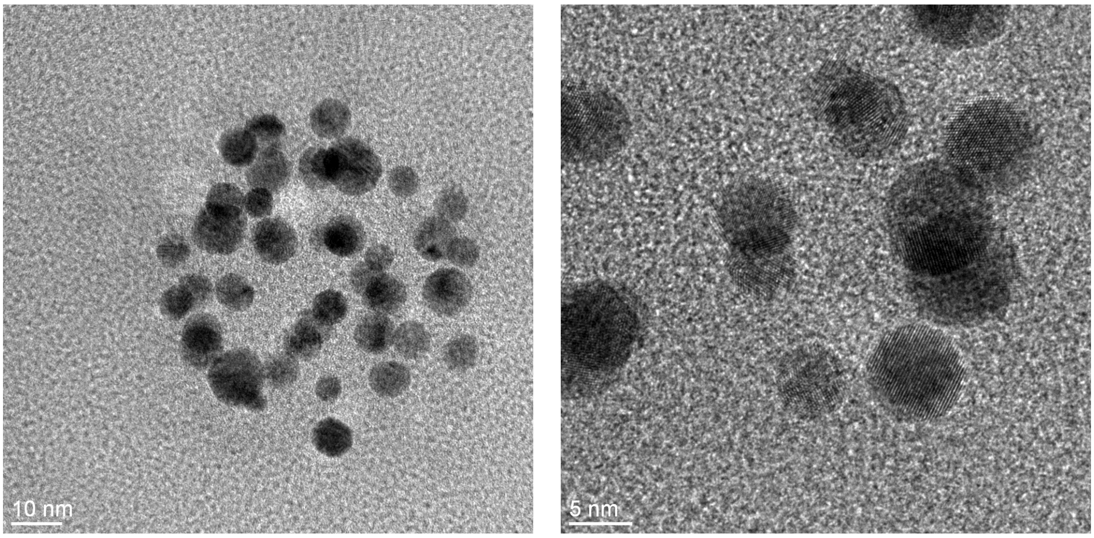


S_6: TEM analysis of DnV@Au

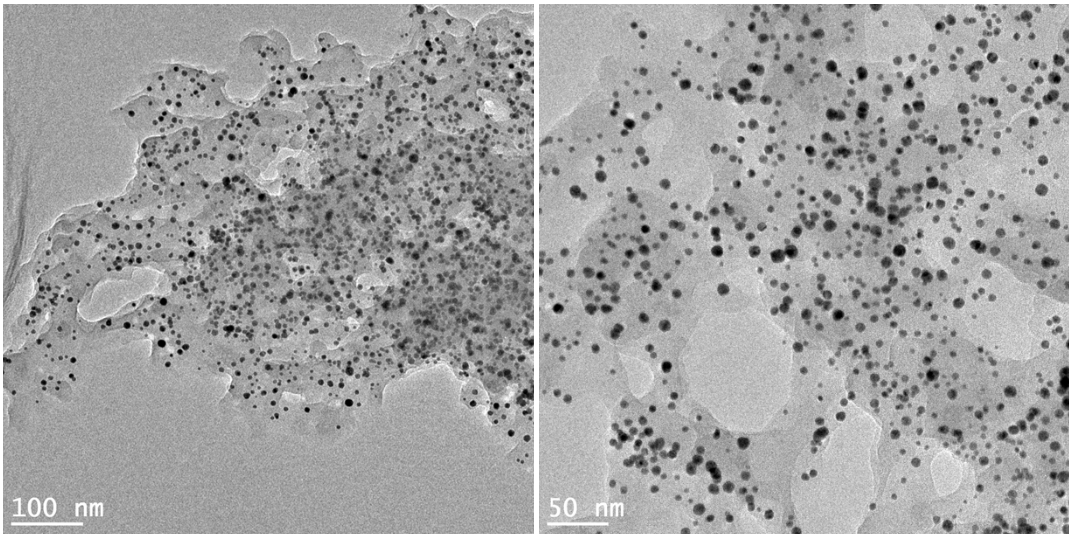
S_{6a}: TEM analysis of D1V@Au

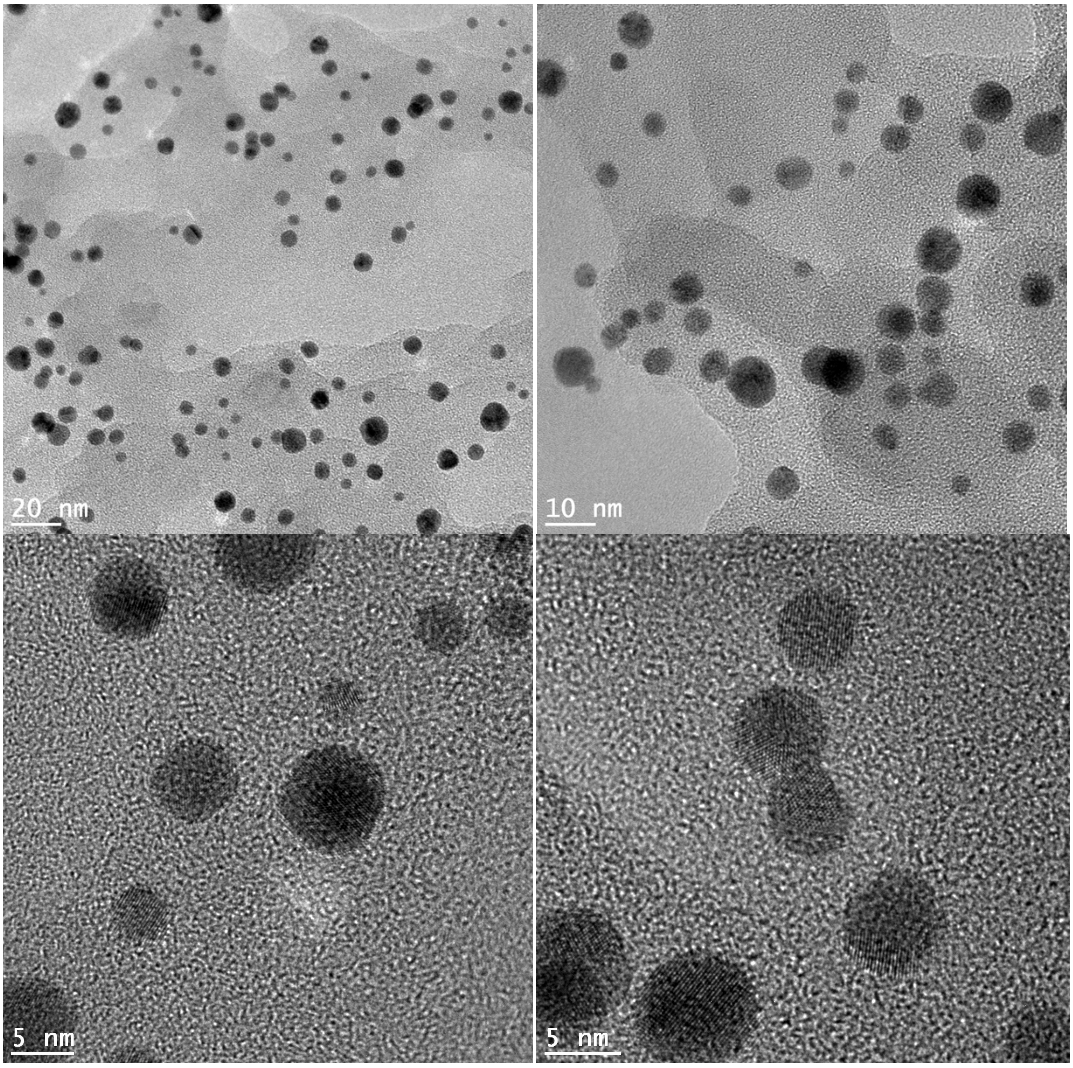


S_{6b}: TEM analysis of D2V@Au

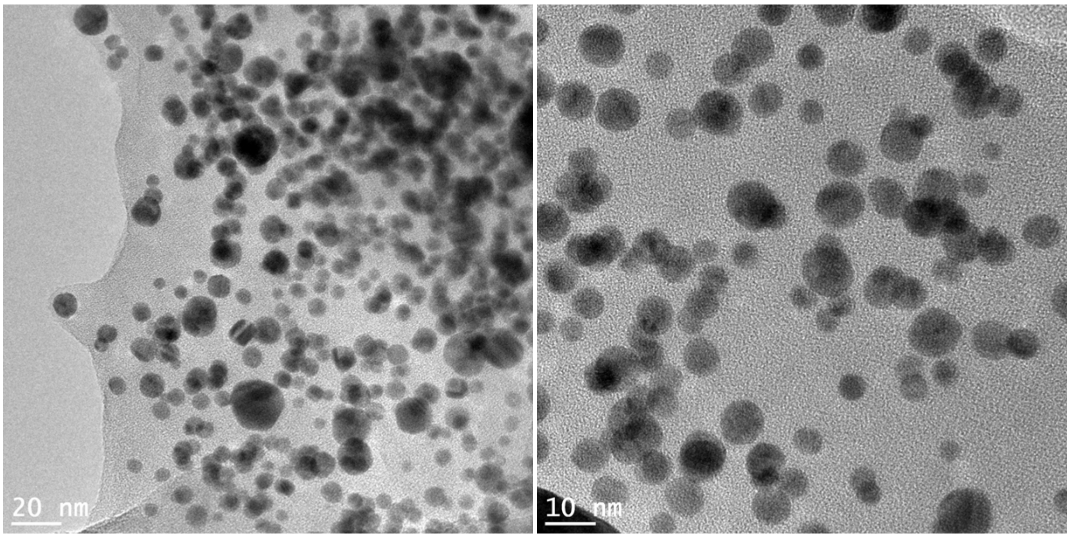


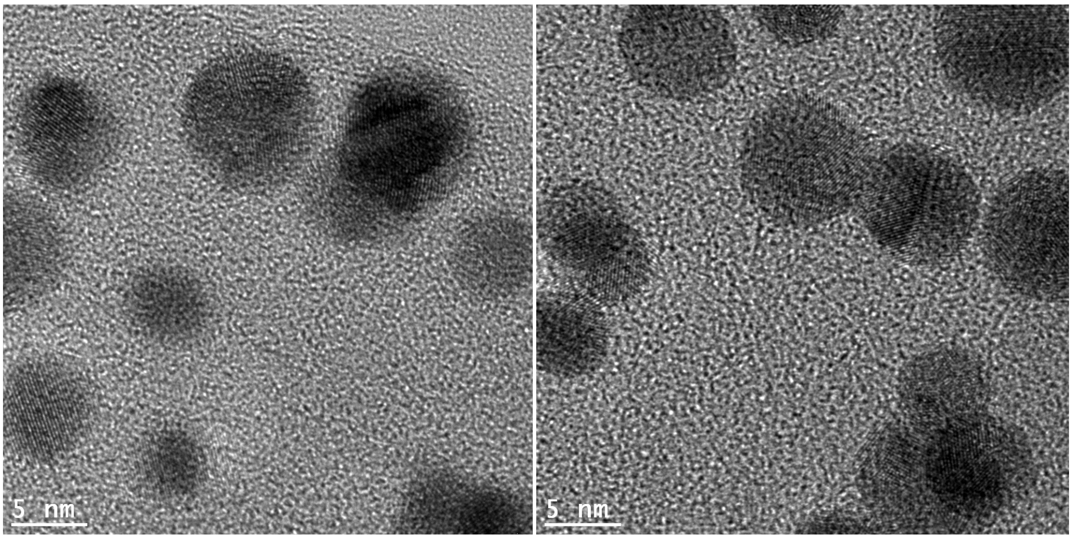
S_{6c}: TEM analysis of D3V@Au



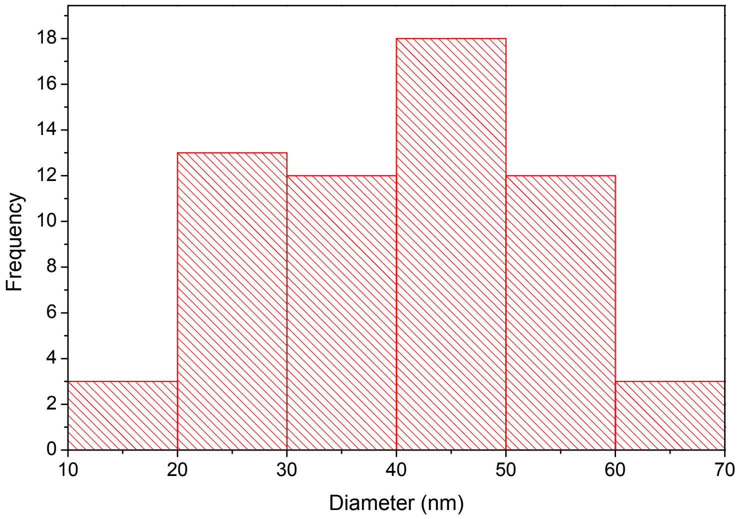


S$_{6d}$: TEM analysis of D4V@Au

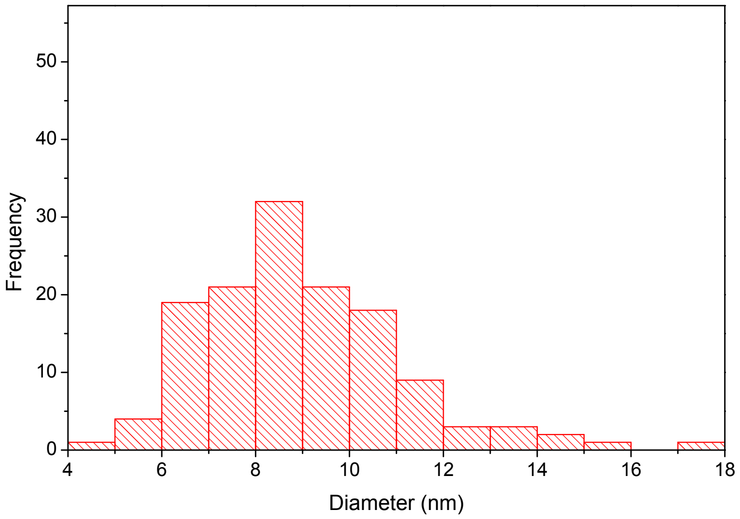




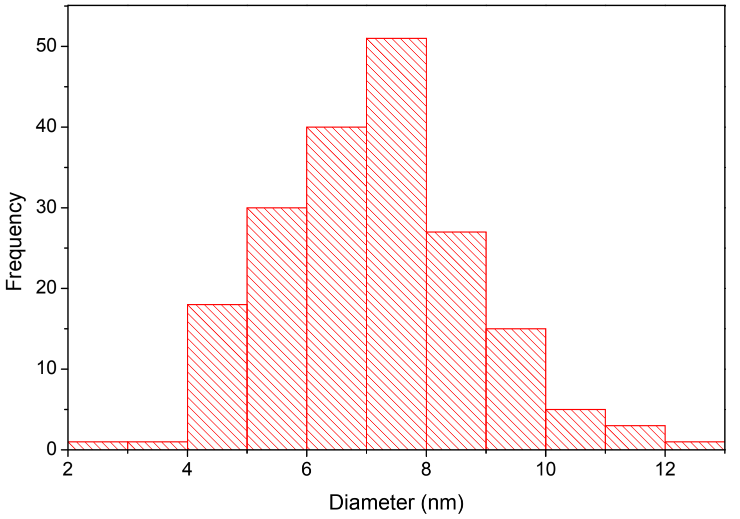
S7: Histogram size distribution of D1V@Au - D3V@Au



S7a: Graph of the calculated nanoparticles D1V@Au size distribution using HRTEM

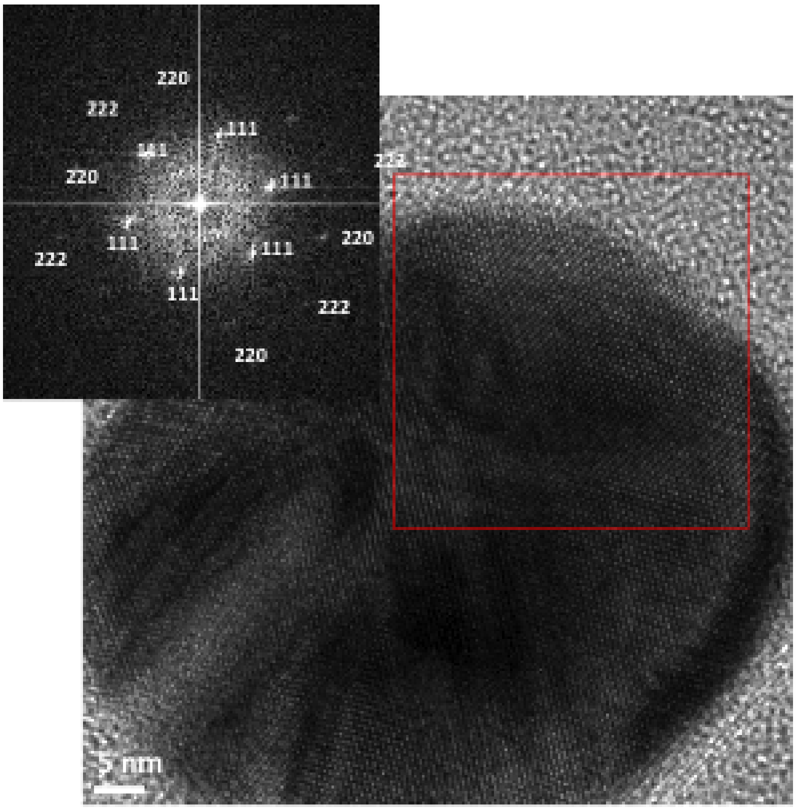


S7b: Graph of the calculated nanoparticles D2V@Au size distribution using HRTEM

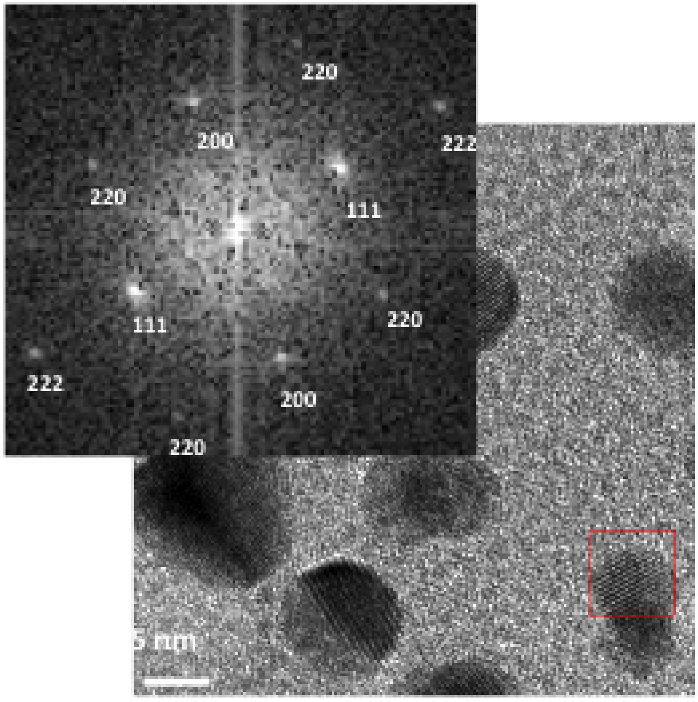


S7c: Graph of the calculated nanoparticles D3V@Au size distribution using HRTEM

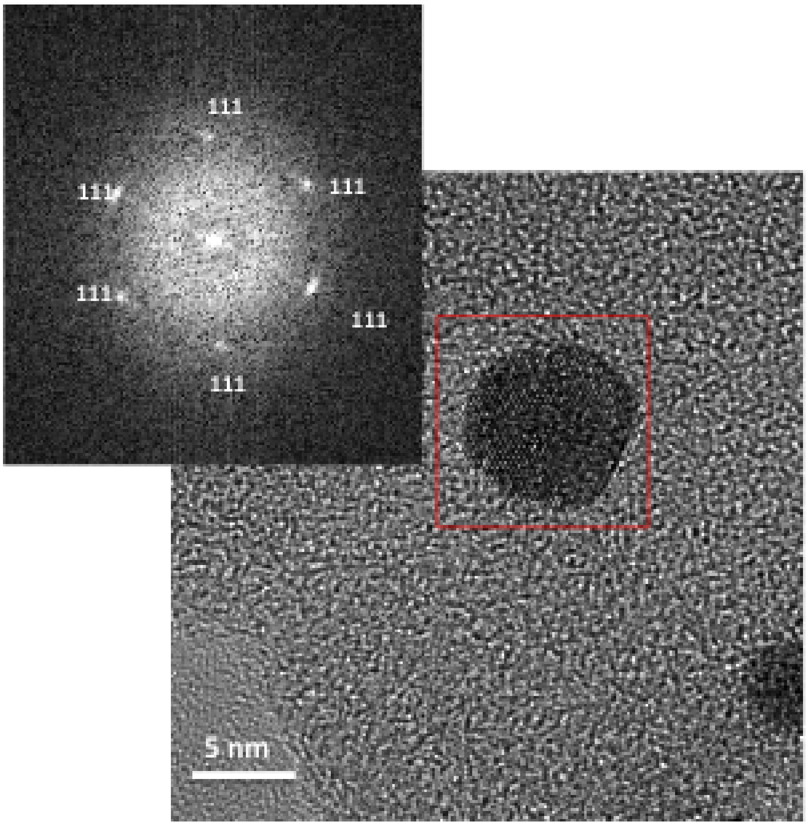
S8: SAED showing the planes of D1V@Au - D3V@Au



S8a : SAED of D1V@Au

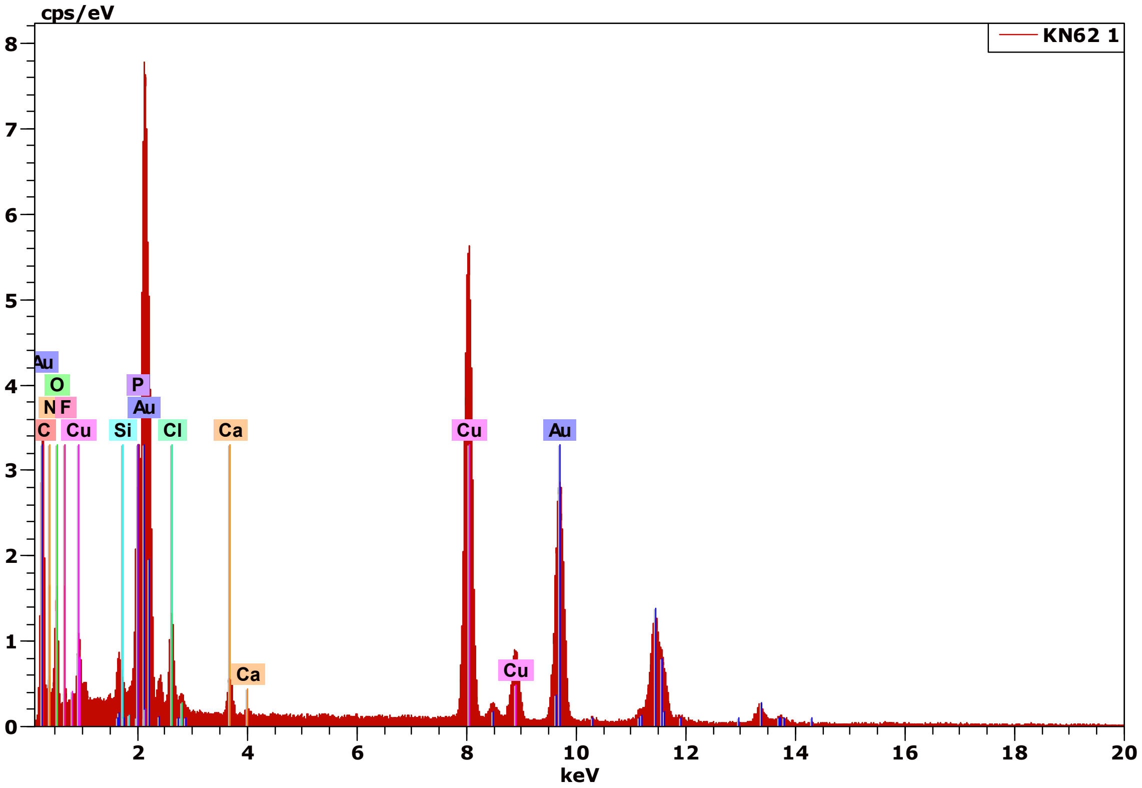


S8b : SAED of D2V@Au



S8c : SAED of D2V@Au

S9: EDX analysis of D1V@Au



S10: Schematic illustration of the mechanism for the formation of DV4@Au