Supplemental Information for

Accessible gold clusters using calix[4]arene N-heterocyclic carbene and phosphine ligands

Michael M. Nigra,[a] Alexander J. Yeh,[a] Alexander Okrut,[a] Antonio G. DiPasquale,[b] Sheila W. Yeh,[c] Andrew Solovyov,[*,a] and Alexander Katz[*,a]

[a]*Department of Chemical and Biomolecular Engineering, University of California, Berkeley, California 94720, United States*

[b]*X-ray Crystallographic Facility, University of California, Berkeley, California 94720, United States*

[b]*Chevron Technology Research Center, 100 Chevron Way, Richmond, California 94802, United States*

Corresponding authors emails: **solovyov@berkeley.edu* and *askatz@berkeley.edu*

Synthesis of calixarene ligands with NMR and ESI-MS characterization

Experimental

All compounds were handled under a dry nitrogen atmosphere. Solvents were dried and distilled by standard methods. Sodium hydride 60% in oil was purchased from Aldrich. *t*-butylcalix[4]arene, dibromoalkanes, 1-R-imidazoles and phenylsilane were purchased from Aldrich. Calixarenes **2**[1], **1**[2], Ph_2POCH_2OTs[3], **6a**[7], **6b**[4], **7a,b**[5,6], **T1**[8], **H1**[5,6] were synthesized using published procedures. ^1H, ^{13}C, ^{31}P NMR spectra were recorded either on a Bruker DRX-500, AVQ-400, AV-300, AV-600 instrument at UC Berkeley NMR facility. The ^1H NMR data are referenced to residual solvent resonance and ^{31}P NMR data are referenced relative to dimethylphosphate. Analytical thin-layer chromatography was performed on precoated silica gel plates (Selecto), and silica gel (Selecto 60) was used for column chromatography. MS spectra were recorded at the UC Berkeley Mass Spectrometry Facility.

General procedure of Bromoalkylation of dialkylcalix[4]arenes 1,2
A solution of dialkylcalixarenes **1,2** (1.58 mmol) in 30 ml of DMF were reacted with NaH (4.74 mmol). The resulting solution was stirred for 2 h at r.t. After a cloudy solution formed, di-bromoalkane (4.74 mmol) was added dropwise and stirring was continued for 1h at r.t. The reaction mixture was poured into 100 ml of ice water and extracted with 100 ml of DCM. DCM layer was washed with water and dried over Na_2SO_4. Evaporation gave a white solid that was purified using column chromatography.

***5,11,17,23-Tetra-tert-butyl-25,27-Dibromopropoxy-26,28-dimethoxy-calix[4]arene (*3) Column chromatography with n-hexane-chloroform (1:0.6) and washing with methanol afforded white solid: yield 41%; ^1H NMR ($CDCl_3$) δ 7.24, 7.15, 7.11, 6.94, 6.61, 6.47 (six br s, 8H, ArH), 4.34, 4.10, 3.95, 3.89, 3.77, 3.66, 2.99, 2.45 (eight br m, 26H, $ArCH_2Ar$+OMe+OCH_2+ CH_2Br+CH_2), 1.00, 1.30, 1.41 (three br s, 36H, C_4H_9-*t*); ^{13}C NMR ($CDCl_3$) δ ; 145.36, 144.27, 135.86, 135.38, 132.51, 131.87, 127.34, 126.07, 125.70, 125.43, 125.11, 124.33, 37.96, 34.15, 33.67, 31.73, 31.37, 31.15, 30.80, 30.72; +EI MS m/z 918 $[M]^+$, 838 $[M-HBr]^+$.

Dibromo-calix[4]arene-dimer (5) Column chromatography with n-hexane-chloroform (1:0.25) and washing with methanol afforded white solid: yield 47%; ^1H NMR ($CDCl_3$) δ 6.78-6.83 (br m, 16H, ArH), 4.41, 4.43 (two d, 4H+4H, ^2J = 13Hz, $ArCH_2Ar$), 3.96 (m, 4H, OCH_2), 3.87(m, 12H, OCH_2), 3.46 (m, 4H, CH_2Br), 3.15 (d, 8H, ^2J = 13Hz, $ArCH_2Ar$), 2.06-2.16 (br m, 20H, CH_2), 1.08, 1.09, 1.12 (three s, 72H, C_4H_9-*t*), 1.04 (t, 12H, CH_3); ^{13}C NMR ($CDCl_3$) δ 153.70, 153.42, 153.38, 144.45, 144.30, 133.95, 133.81, 133.68, 125.02, 124.93, 76.97, 75.20, 74.13, 34.69, 33.85, 33.57, 31.50, 31.47, 31.13, 31.05, 29.70, 29.04, 26.63, 23.45, 10.41; ; +ESI HR MS calcd for $C_{112}H_{156}O_8Br_2\ Na_1$ 1810.0059, found 1810.0095.

General procedure of calixarene imidazolium bromides C2, C3, D1 synthesis
The starting bromocalixarenes **3,4,5** were vacuumed in high vacuum for 3h. The residue was flushed two times with dry argon. A mixture of bromocalixarenes **3,4,5 (**0.59 mmol) and 1-

Alkyl-imidazol (11.8 mmol) was heated at 110 ^{0}C in minimal amount (3-5 ml) of freshly distilled over Na toluene. The reaction was monitored by TLC. After disappearance of high R_f spot of bromocalixarene on TLC plate (hexane/chloroform mixture as an eluent) in 18h, a reaction mixture was evaporated and dried in high vacuum for 24h. The residue was treated with n-hexane (for reactions with 1-Butylimidazol) or n-hexane-benzene mixture (10:0.5) (for reaction with Phenylimidazol). After 24h, organic solution was separated and white solid formed was crystallized from toluene. The same general procedure was used for synthesis of C1.

***5,11,17,23-Tetra-tert-butyl-25,27-Dipropoxy-26,28-Bis[1-Phenyl-3-propoxy-imidazolium]calix[4]arene dibromide* (C2).** Crystallization from toluene afforded white crystals: yield 73%; ^{1}H NMR ($CDCl_3$) δ 11.05 (s, 2H, NCHN), 7.85 (s, 2H, CHN), 7.81 (d, 4H, ^3J = 7.5 Hz, ArH-Im), 7.67 (s, 2H, CHN), 7.50 (m, 6H, ArH-Im), 7.11 (s, 4H, ArH), 6.49 (s, 4H, ArH), 4.83 (t, 4H, ^3J = 8.0 Hz, Im-CH_2), 4.38 (d, 4H, ^2J = 12.5 Hz, ArCH_2Ar), 4.08 (t, 4H, ^3J = 8.0 Hz, OCH_2), 3.74 (t, 4H, ^3J = 6.5 Hz, OCH_2), 3.15 (d, 4H, ^2J = 12.5 Hz, ArCH_2Ar), 2.38 (m, 4H, CH_2), 2.19 (m, 4H, CH_2), 1.95 (m, 4H, CH_2), 1.34 (s, 18H, C_4H_9-*t*), 1.10 (t, 6H, ^3J = 7.5 Hz, $CH_2C\mathbf{H}_3$), 0.85 (s, 18H, C_4H_9-*t*); ^{13}C NMR ($CDCl_3$) δ 154.12, 152.38, 145.15, 144.00, 135.57, 134.72, 132.00, 130.46, 130.01, 125.52, 124.47, 123.29, 122.03, 120.38, 77.65, 73.91, 50.49, 34.10, 33.60, 31.74, 31.18, 31.05, 27.40, 26.81, 23.83, 11.01; +ESI HR MS calcd for $C_{76}H_{98}O_4N_4Br_1$ 1209.6766, found 1209.6765.

***5,11,17,23-Tetra-tert-butyl-25,27-Dimethoxy-26,28-Bis[1-Phenyl-3-propoxy-imidazolium]calix[4]arene dibromide* (C3).** Crystallization from toluene afforded white crystals: yield 69%; ^{1}H NMR ($CDCl_3$) δ 11.11 (s, 2H, NCHN), 8.11 (br s, 2H, ArH), 7.82 (m, 6H, ArH), 7.43-7.54 (br m, 6H, ArH), 7.37 (m, 1H, ArH), 7.26 (m, 1H, ArH), 7.15 (m, 2H, ArH), 7.06 (br s, 4H, ArH), 6.50 (br s, 4H, ArH), 4.94 (br s, 4H, CH_2), 3.88, 4.01, 4.17 (three br s, 10H, CH2+OCH3), 3.16 (br s, 4H, CH_2), 2.65 (br s, 4H, CH_2), 1.27 (s, 18H, C_4H_9-*t*), 0.87 (br s, 18H, C_4H_9-*t*); ^{13}C NMR ($CDCl_3$) δ 152.99, 145.14, 144.67, 137.83, 135.89, 134.94, 134.50, 131.88, 130.45, 130.08, 129.87, 128.99, 128.18, 127.49, 125.25, 123.95, 121.95, 121.87, 121.78, 121.47, 121.00, 48.66, 34.06, 33.59, 31.65, 31.10; +ESI HR MS calcd for $C_{70}H_{86}O_4N_4Br_1$ 1125.5827, found 1125.5829.

***t*-Butyl-Calix[4]arene-dimer-n-Butyldiimidazolium dibromide (D1).** Crystallization from *n*-hexane mixture afforded white solid: yield 58%; ^{1}H NMR ($CDCl_3$) δ10.85 (s, 1H, NCHN), 7.50 (s, 1H, NCHN), 7.08 (m, 3H, ArH), 6.93 (s, 1H, ArH), 6.83 (s, 8H, ArH), 6.75, 6.77 (two s, 8H, ArH), 4.35-4.43 (br m, 16H, CH_2N+ArCH_2Ar), 3.96 (m, 8H, OCH_2), 3.82 (m, 8H, OCH_2), 3.12, 3.15 (two d, ^2J = 13.5 Hz, 8H, ArCH_2Ar), 1.41, 1.78, 1.93, 2.06 (four m, 28H, CH_2), 1.06, 1.13 (two s, 36H+36H, C_4H_9-*t*), 0.95-1.05 (br m, 18H, CH3); ^{13}C NMR ($CDCl_3$) δ 153.70, 153.12, 152.86, 144.59, 144.52, 144.46, 137.54, 133.99, 133.78, 133.43, 133.28, 125.12, 125.05, 124.91, 122.02, 121.53, 74.93, 73.40, 49.92, 49.87, 46.81, 33.87, 33.80, 33.08, 32.20, 31.50, 31.40, 31.13, 27.42, 26.91, 26.80, 23.45, 19.74, 19.51, 13.51, 10.61; +ESI HR MS calcd for $C_{126}H_{180}O_8N_4$ 1877.3790, found 1877.3822.

***25,27-Bis[Diphenylphosphorylmethoxy]-26,28-Dimetoxy-calix[4]arene* (7b)** Column chromatography with chloroform-ethylacetate (1:1) afforded white solid: yield 63%; ^{1}H NMR

(C_6D_6) δ 7.82 (m, 10H, ArH), 7.71 (m, 5H ArH), 7.47, 7.51 (two d, ^3J = 8.4, 7.2, Hz, 2H, ArH), 6.90-7.08 (br m, 37H, ArH), 6.64 (t, 2H, ^3J = 7.8 Hz, ArH), 6.49 (d, 1H, ^3J = 7.8 Hz, ArH), 6.45 (d, 1H, ^3J = 7.2, Hz, ArH), 6.38 (m, 6H, ArH), 4.48 (d, 4H, ^2J = 13.2 Hz, $ArCH_2Ar$), 4.26, 4.27 (two s, 8H, CH_2P), 4.15 (d, 2H, ^2J = 13.2 Hz, $ArCH_2Ar$), 4.07 (d, 2H, ^2J = 12.6 Hz, $ArCH_2Ar$), 3.62 (d, 2H, ^2J = 12.6 Hz, $ArCH_2Ar$), 3.47 (s, 6H, OCH_3-cone), 3.83 (s, 3H, OCH_3-alt), 3.07 (d, 4H, ^2J = 13.2 Hz, $ArCH_2Ar$), 2.98 (d, 2H, ^2J = 13.8 Hz, $ArCH_2Ar$), 2.59 (s, 3H, OCH_3-alt); ^{13}C NMR ($CDCl_3$) δ 158.69, 156.30, 136.75, 132.78, 132.60, 132.22, 131.51, 131.45, 131.35, 131.29, 130.65, 129.96, 129.21, 128.87, 128.82, 128.74, 128.66, 128.15, 127.49, 122.91, 122.47, 122.30, 73.61, 73.05, 60.52, 30.40; ^{31}P NMR (C_6D_6) δ 21.76, 21.90; +ESI HR MS calcd for $C_{56}H_{50}O_6Na1P2$ 903.2975, found 903.2982.

25,27-Bis[Diphenylphosphinomethoxy]-26,28-Dimetoxy-calix[4]arene (H1)

Flash column chromatography with DCM distilled afforded white solid: yield 79%; ^{1}H NMR ($CDCl_3$) δ 6.85-7.70 (br m, 56H, ArH), 6.48 (t, 2H, ^3J = 7.8 Hz, ArH), 6.27 (m, 3H, ArH), 6.22 (m, 3H, ArH), 4.58 (s, 8H, CH_2P), 4.27 (d, 4H, ^2J = 13.2 Hz, $ArCH_2Ar$), 3.95 (d, 2H, ^2J = 12.6 Hz, $ArCH_2Ar$), 3.73 (m, 2H, $ArCH_2Ar$), 3.66 (s, 3H, OCH_3-alt), 3.60 (d, 2H, ^2J = 12.6 Hz, $ArCH_2Ar$), 3.53 (s, 6H, OCH_3-cone), 3.14 (d, 4H, ^2J = 13.2 Hz, $ArCH_2Ar$), 3.08 (d, 2H, ^2J = 12.6 Hz, $ArCH_2Ar$), 2.65 (s, 3H, OCH3-alt)"; ^{13}C NMR ($CDCl_3$) δ 158.76, 136.96, 136.47, 133.92, 133.15, 133.03, 132.81, 132.56, 130.34, 128.95, 128.75, 128.66, 128.53, 128.49, 127.75, 127.67, 127.37, 60.70, 30.94; ^{31}P NMR (C_6D_6) δ -20.67, -20.25; +ESI HR MS calcd for $C_{56}H_{51}O_4P2$ 849.3257, found 849.3280.

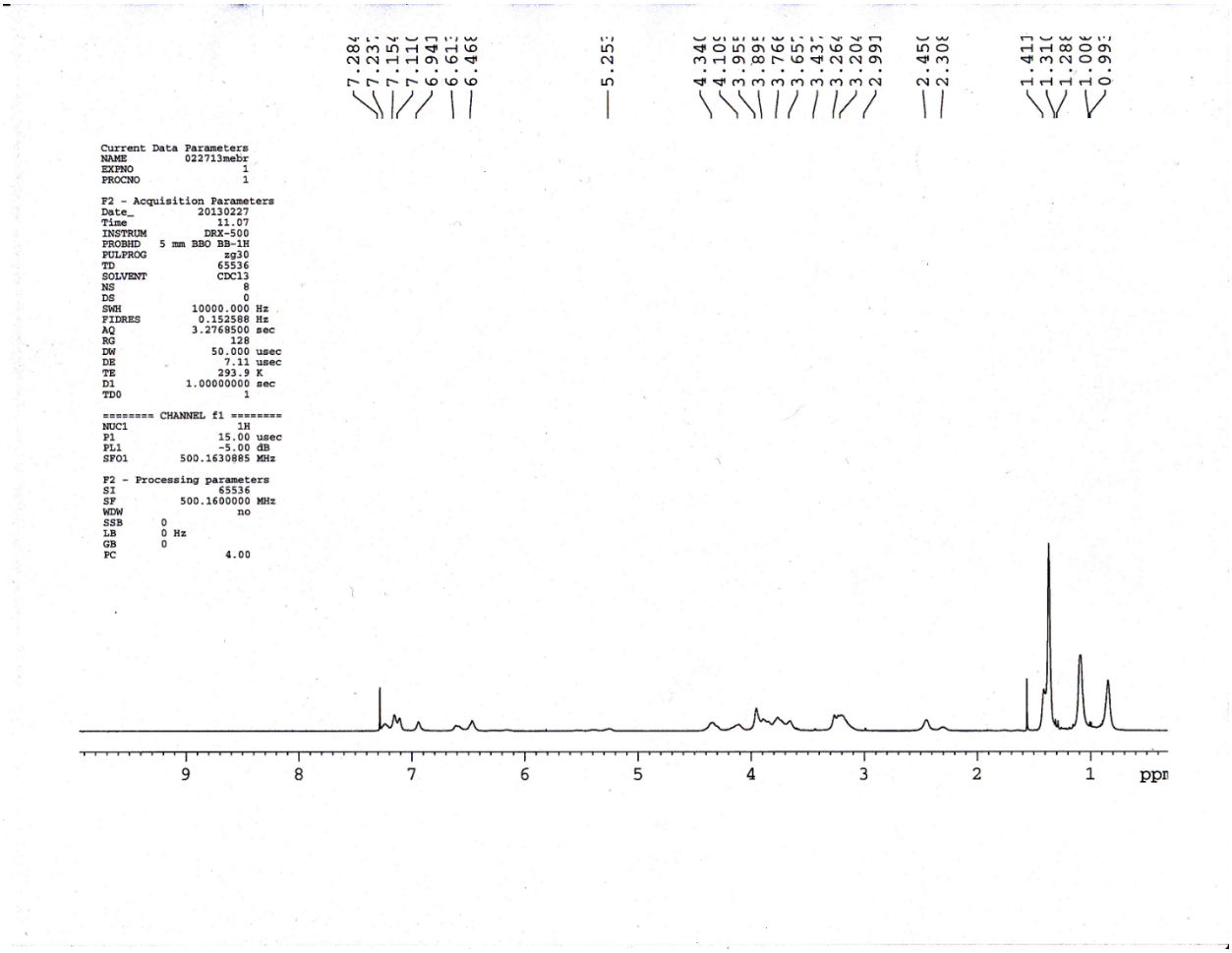


Fig. S1 ^{1}H NMR spectra of **3** ($CDCl_3$)

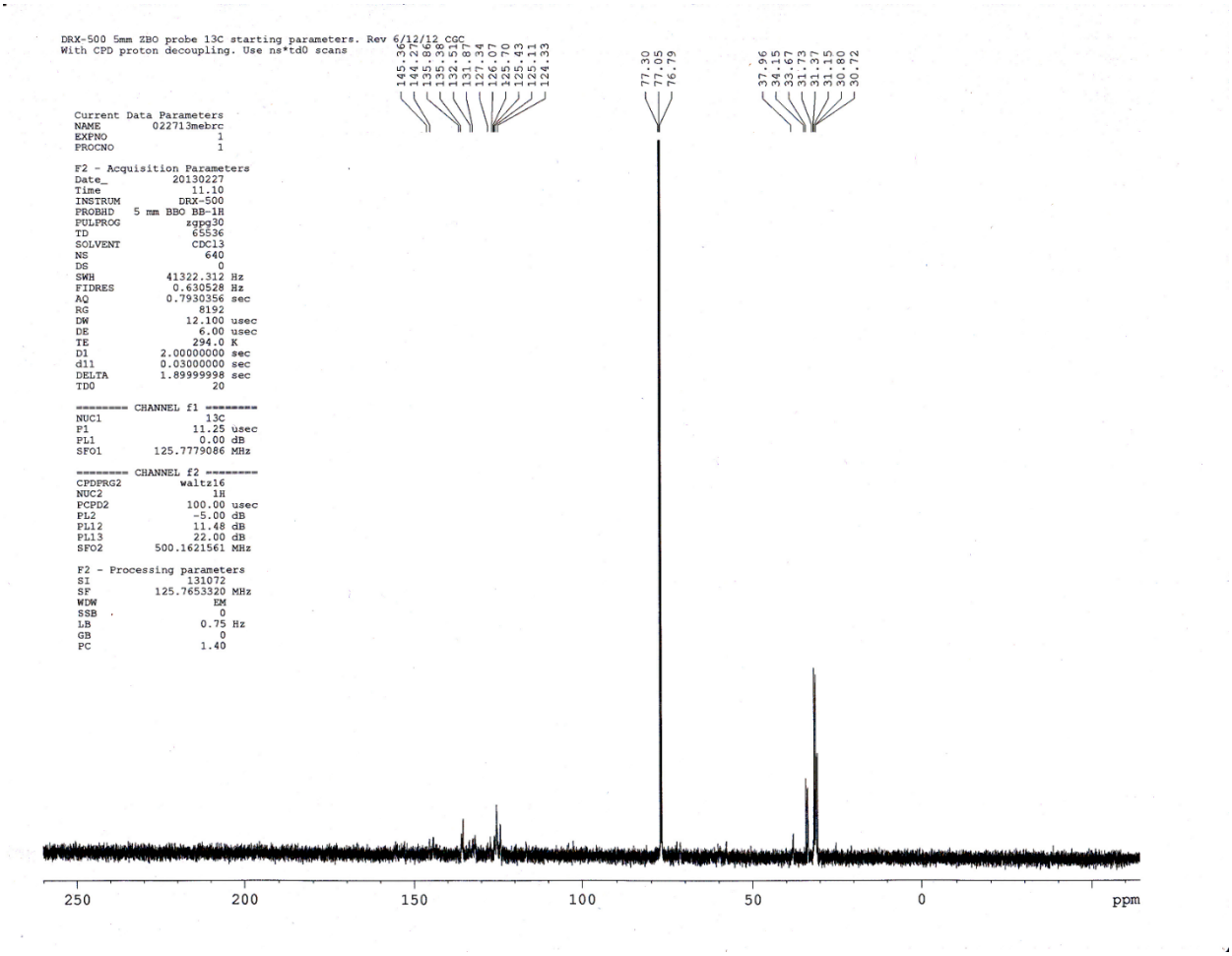


Fig. S2 ^{13}C NMR spectra of **3** ($CDCl_3$)

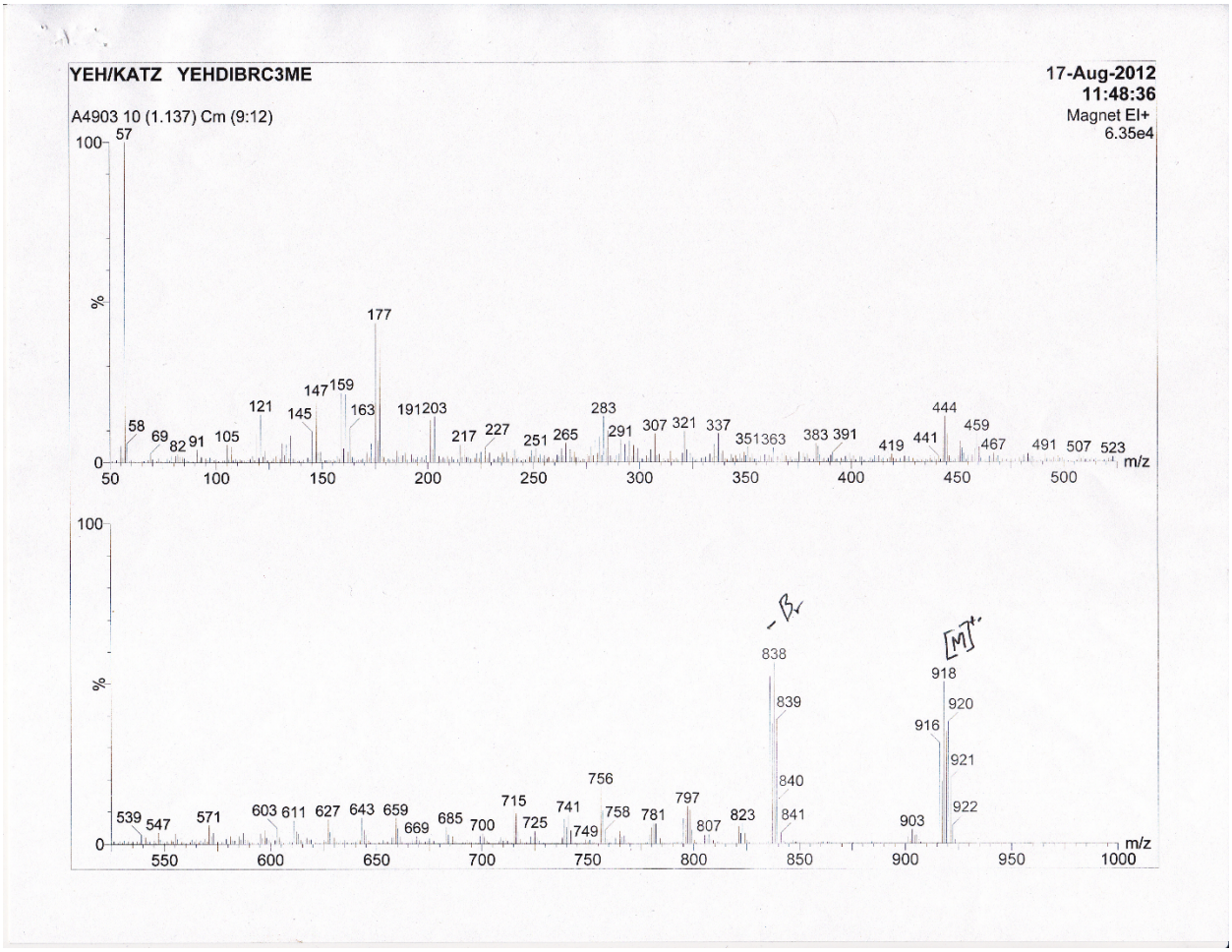


Fig. S3 +ESI MS spectra of **3**

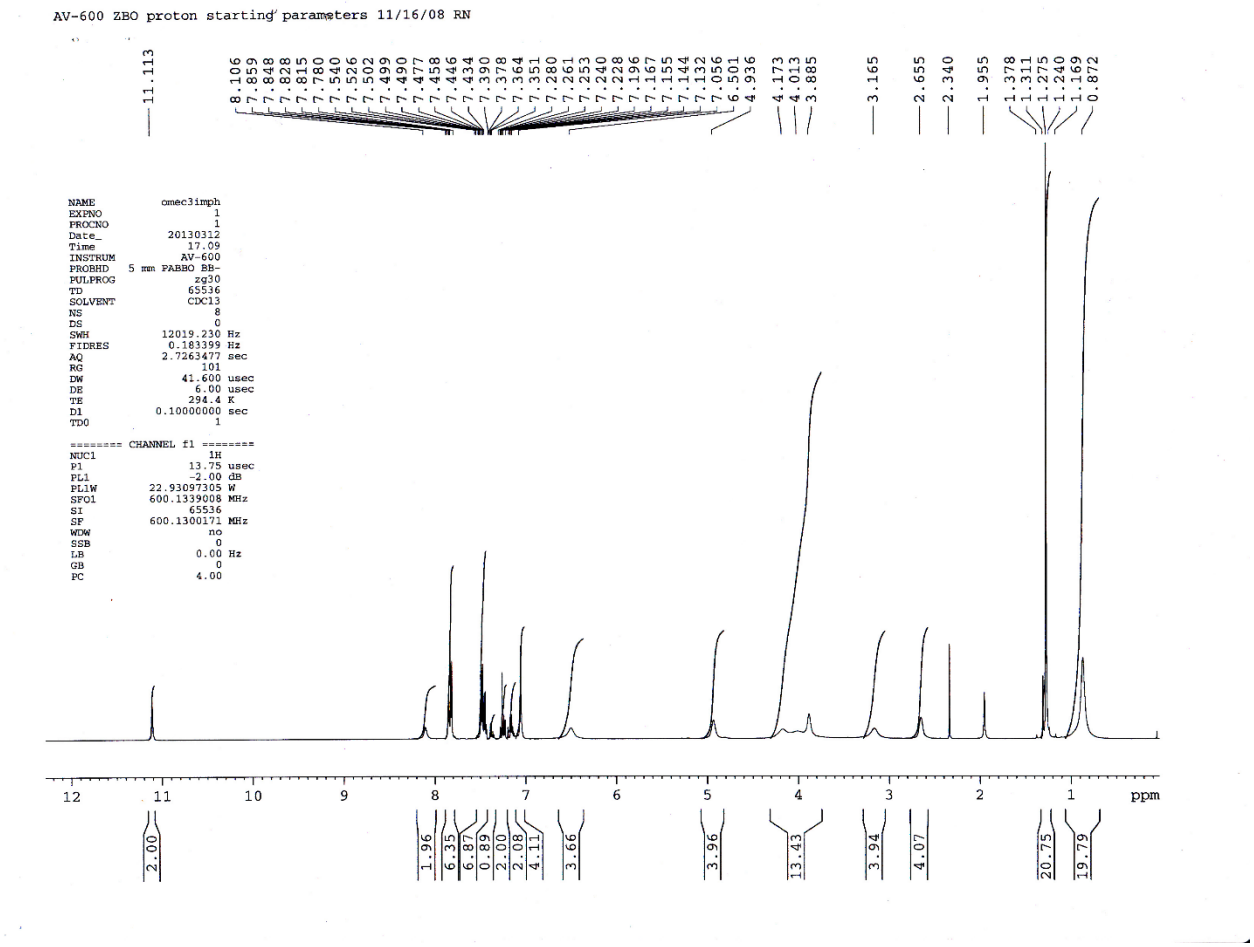


Fig. S4 ^{1}H NMR spectra of **C3** ($CDCl_3$)

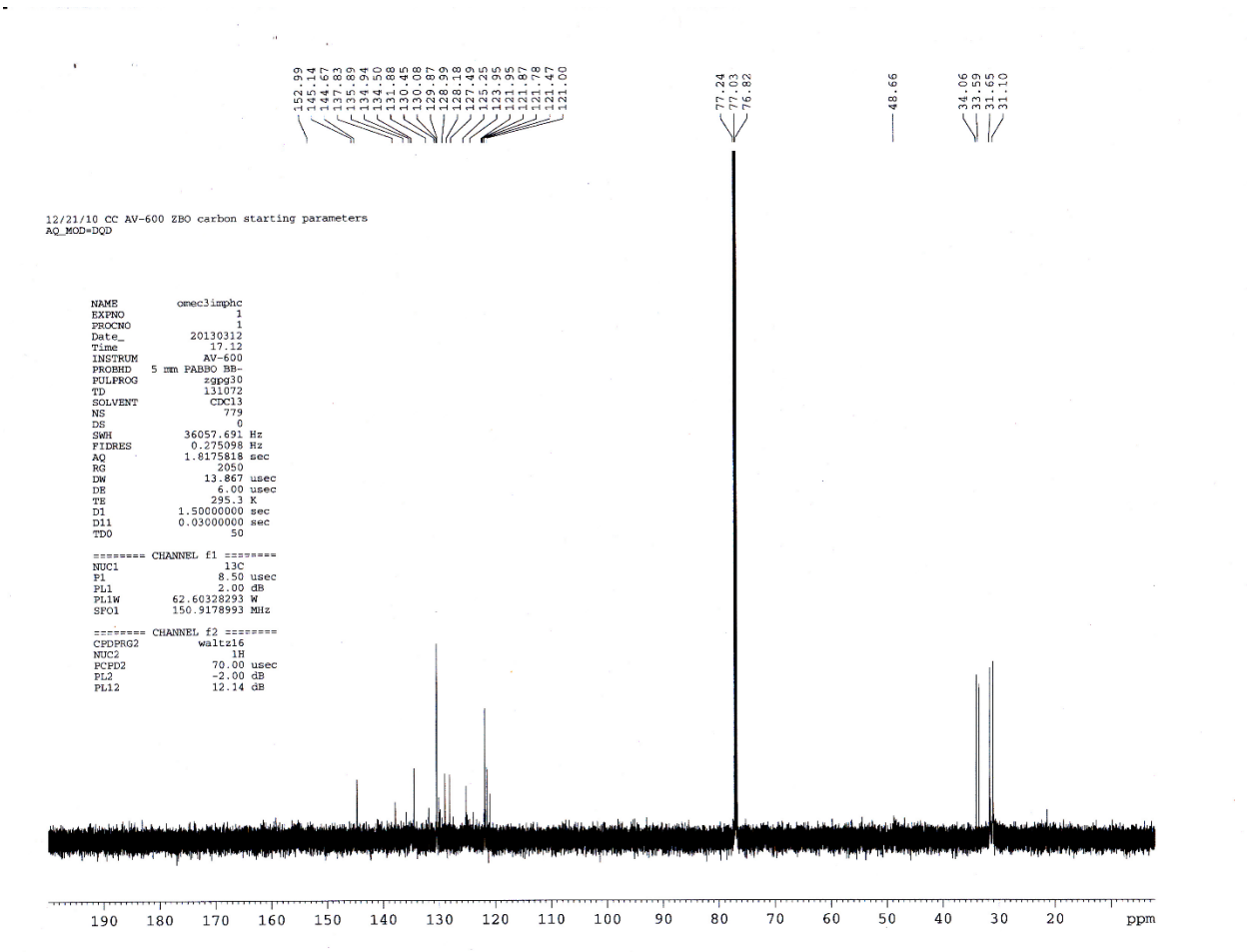


Fig. S5 ^{13}C NMR spectra of **C3** ($CDCl_3$)

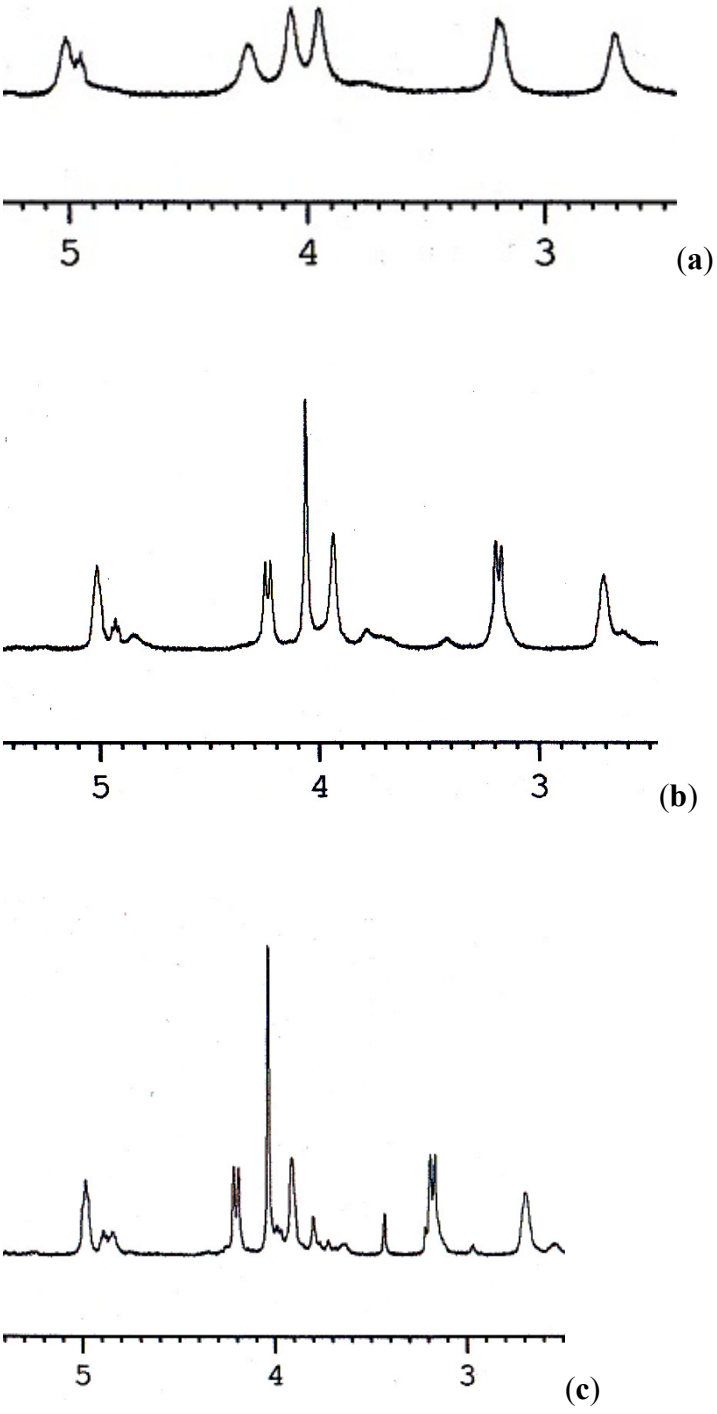


Fig. S6 ^{1}H NMR spectra of **C3** (methylene bridges region) ($CDCl_3$) at 273K (**a**), 253K (**b**), 223K(**c**)

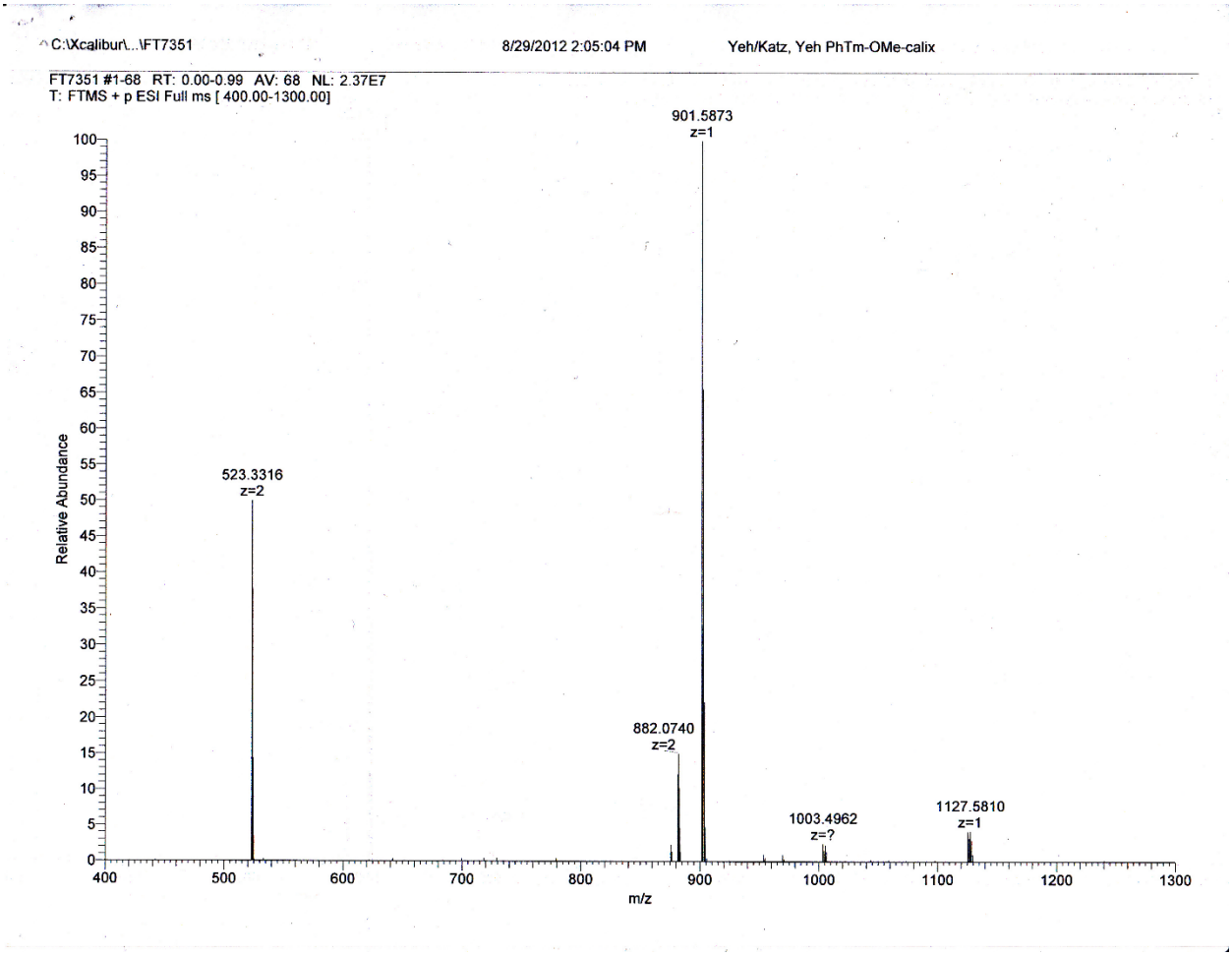


Fig. S7 +ESI MS spectra of **C3**

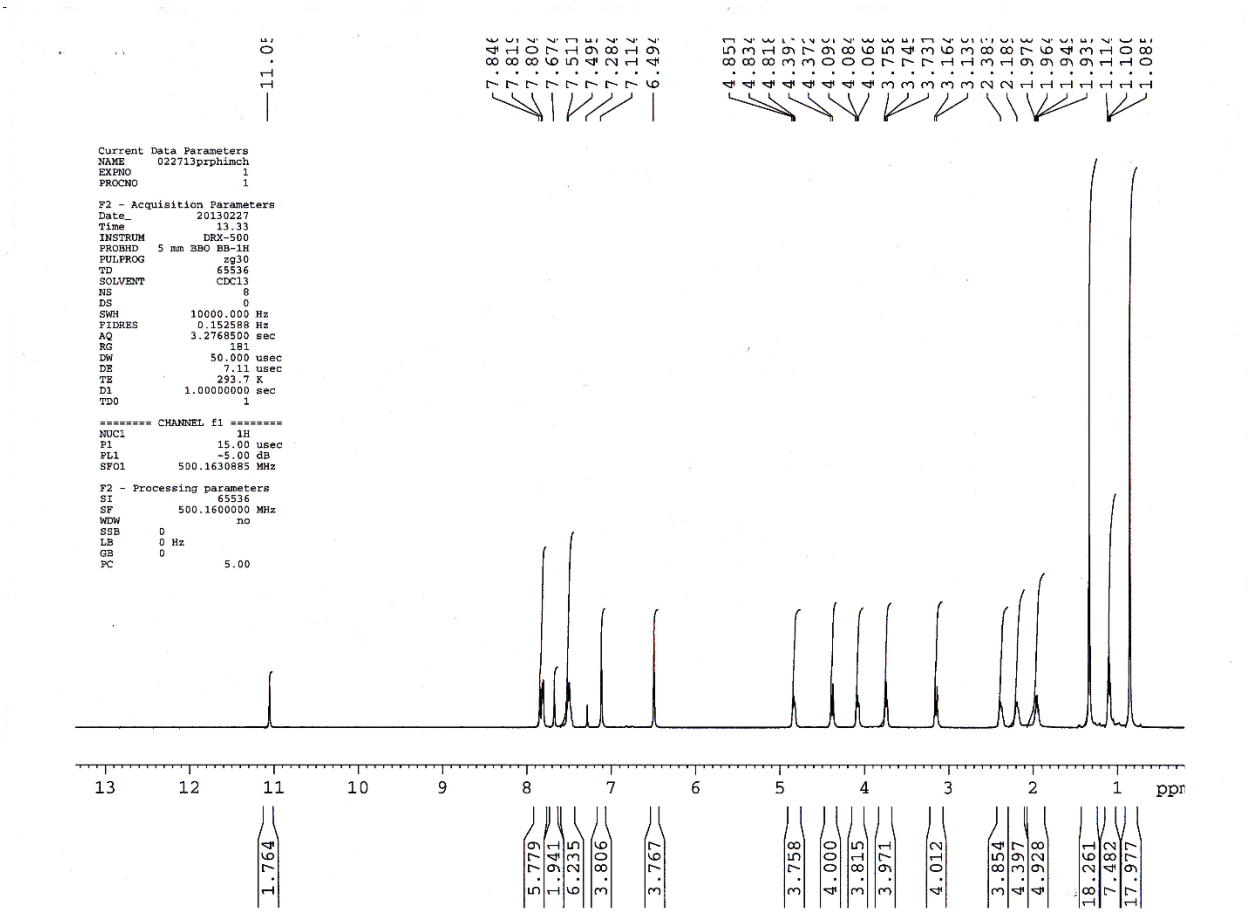


Fig. S8 ^{1}H NMR spectra of **C2** ($CDCl_3$)

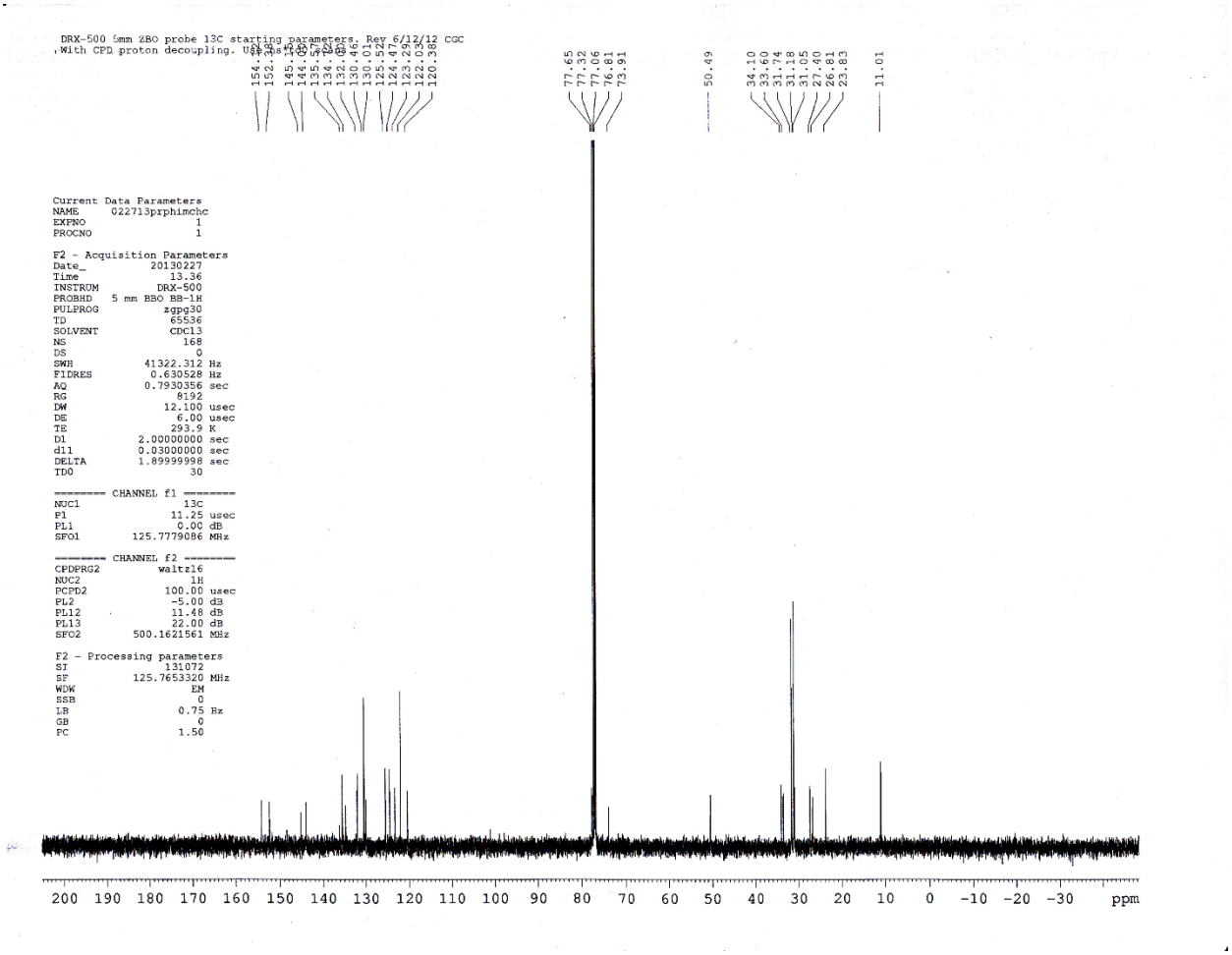


Fig. S9 ^{13}C NMR spectra of **C2** ($CDCl_3$)

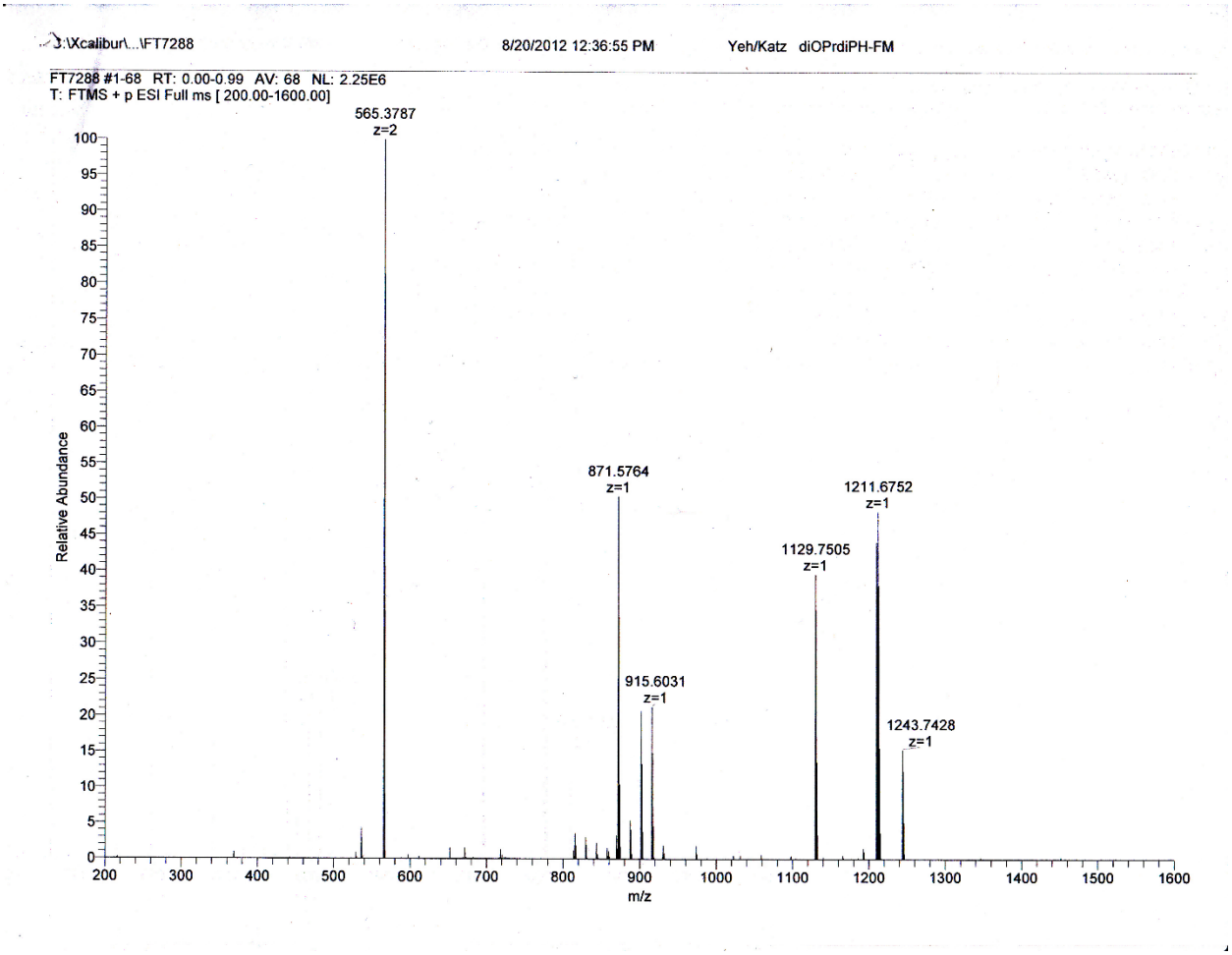


Fig. S10 +ESI MS spectra of **C2**

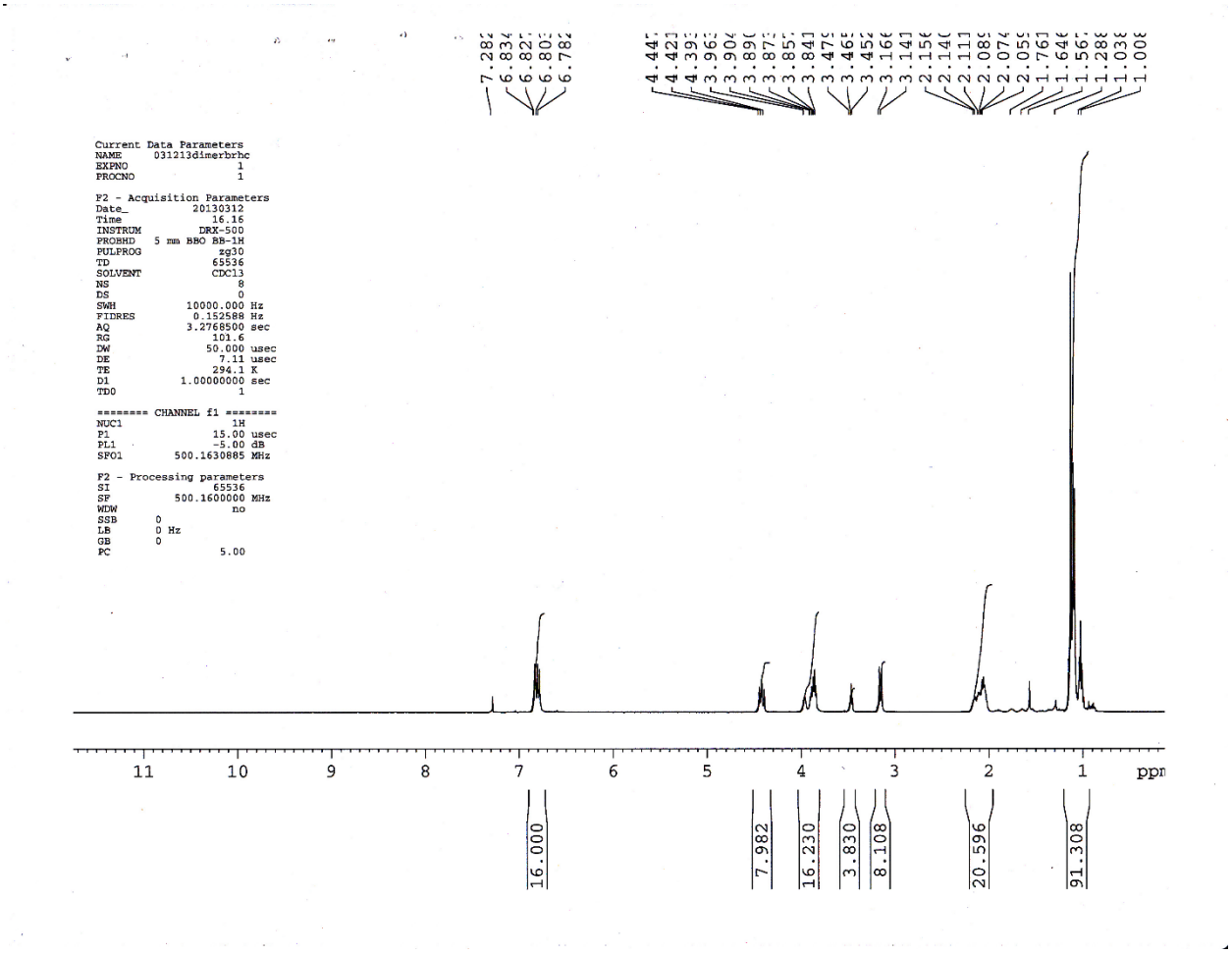


Fig. S11 ^{1}H NMR spectra of **5** ($CDCl_3$)

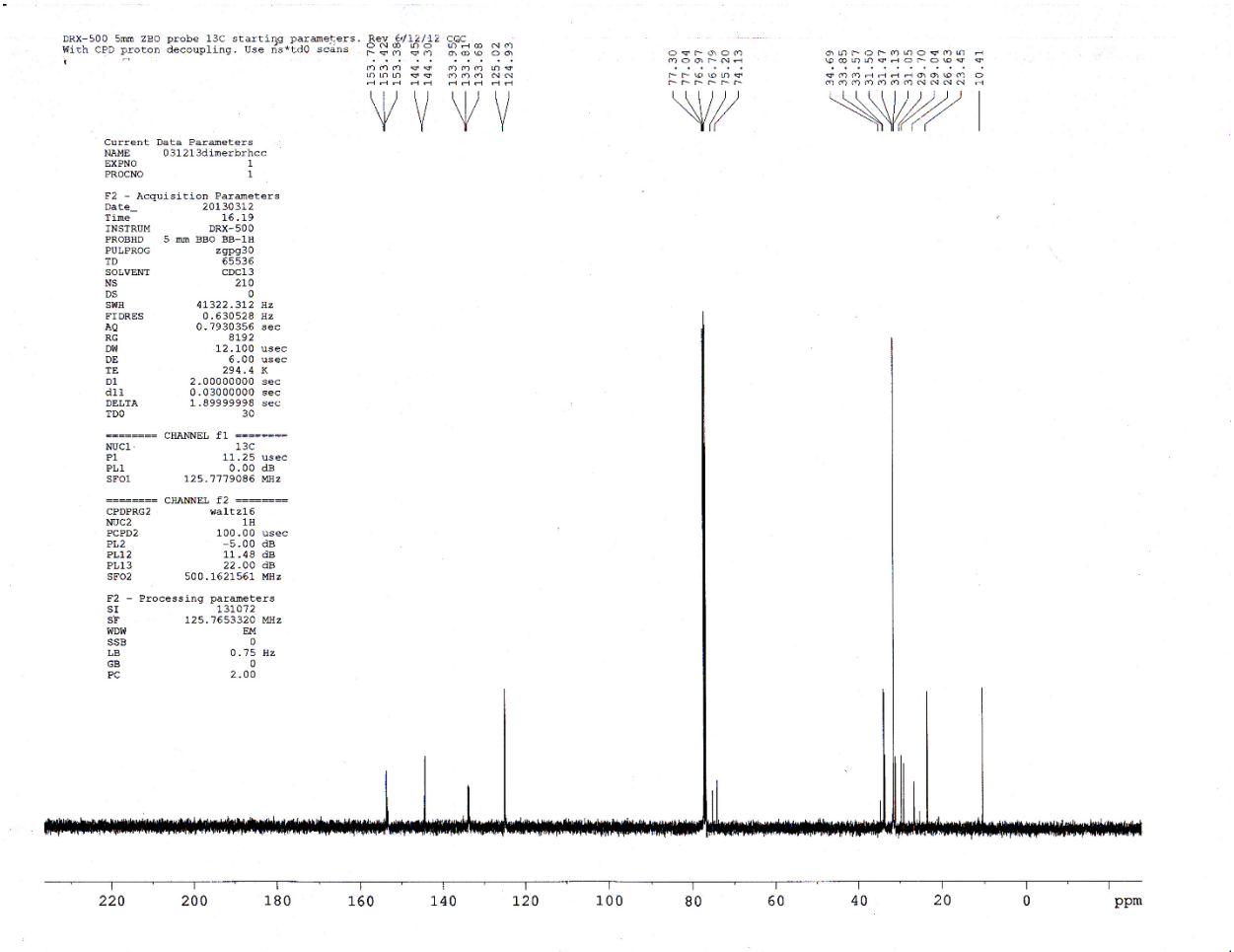


Fig. S12 ^{13}C NMR spectra of **5** ($CDCl_3$)

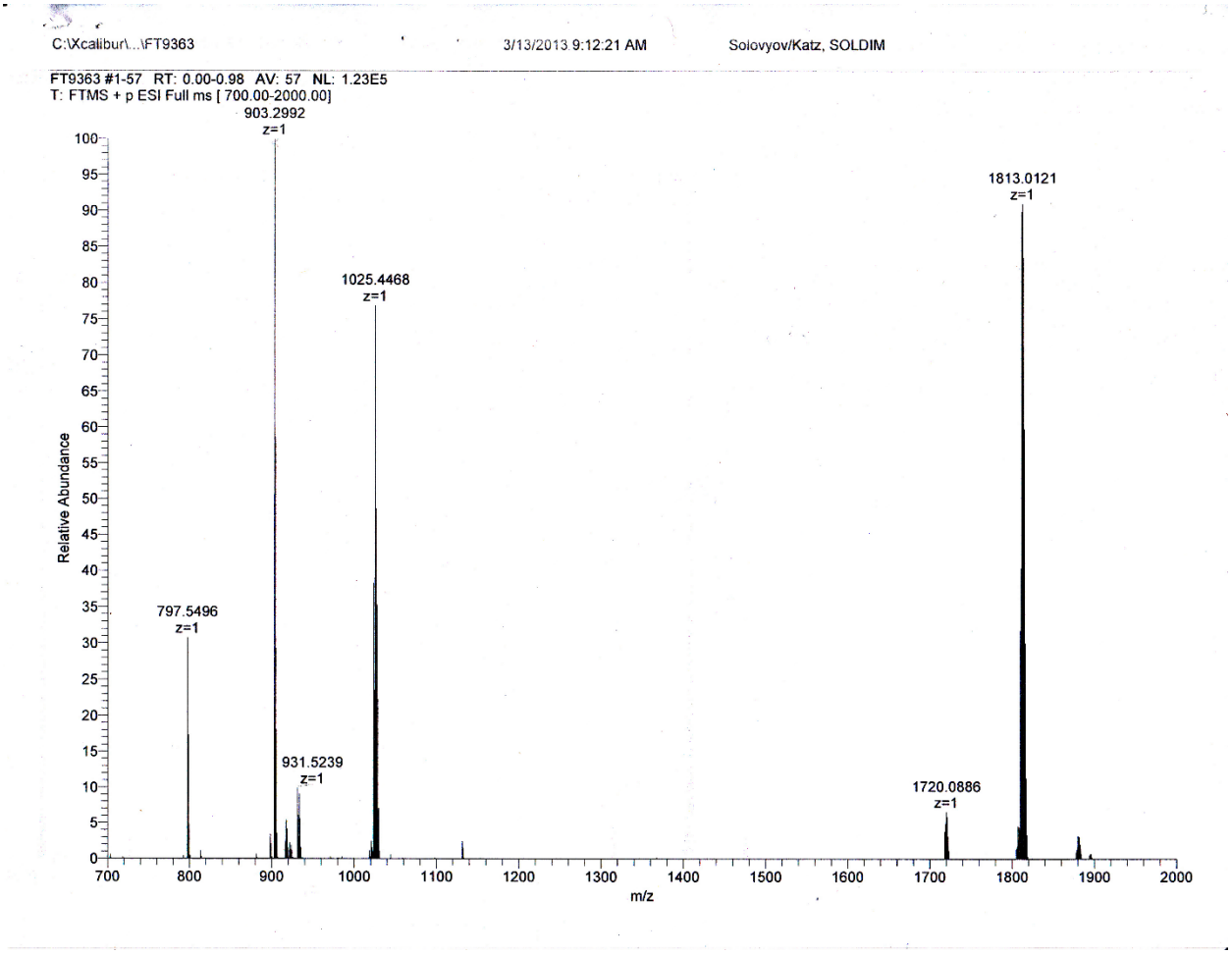


Fig. S13 +ESI MS spectra of **5**

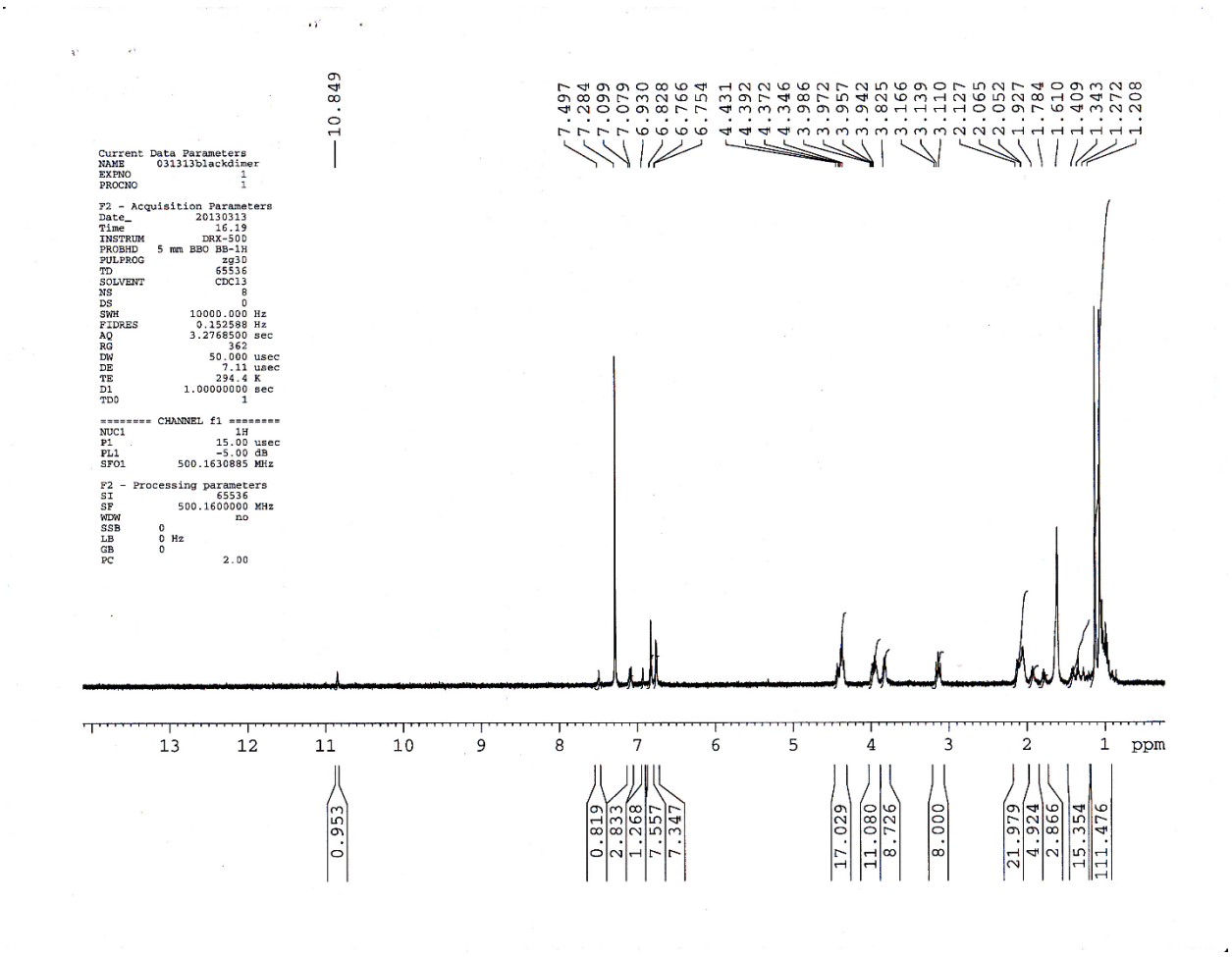


Fig. S14 ^{1}H NMR spectra of **D1** ($CDCl_3$)

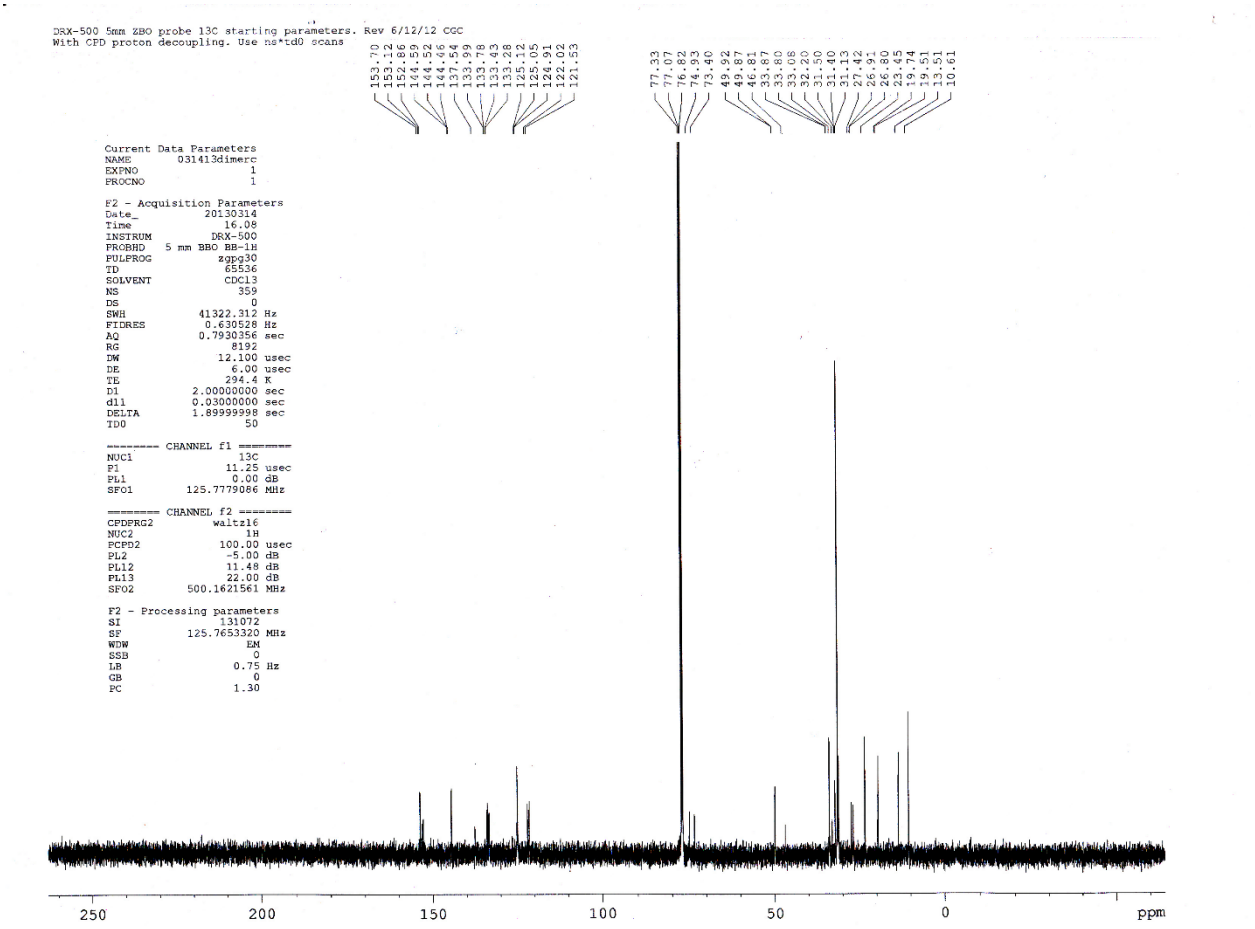


Fig. S15 ^{13}C NMR spectra of **D1** ($CDCl_3$)

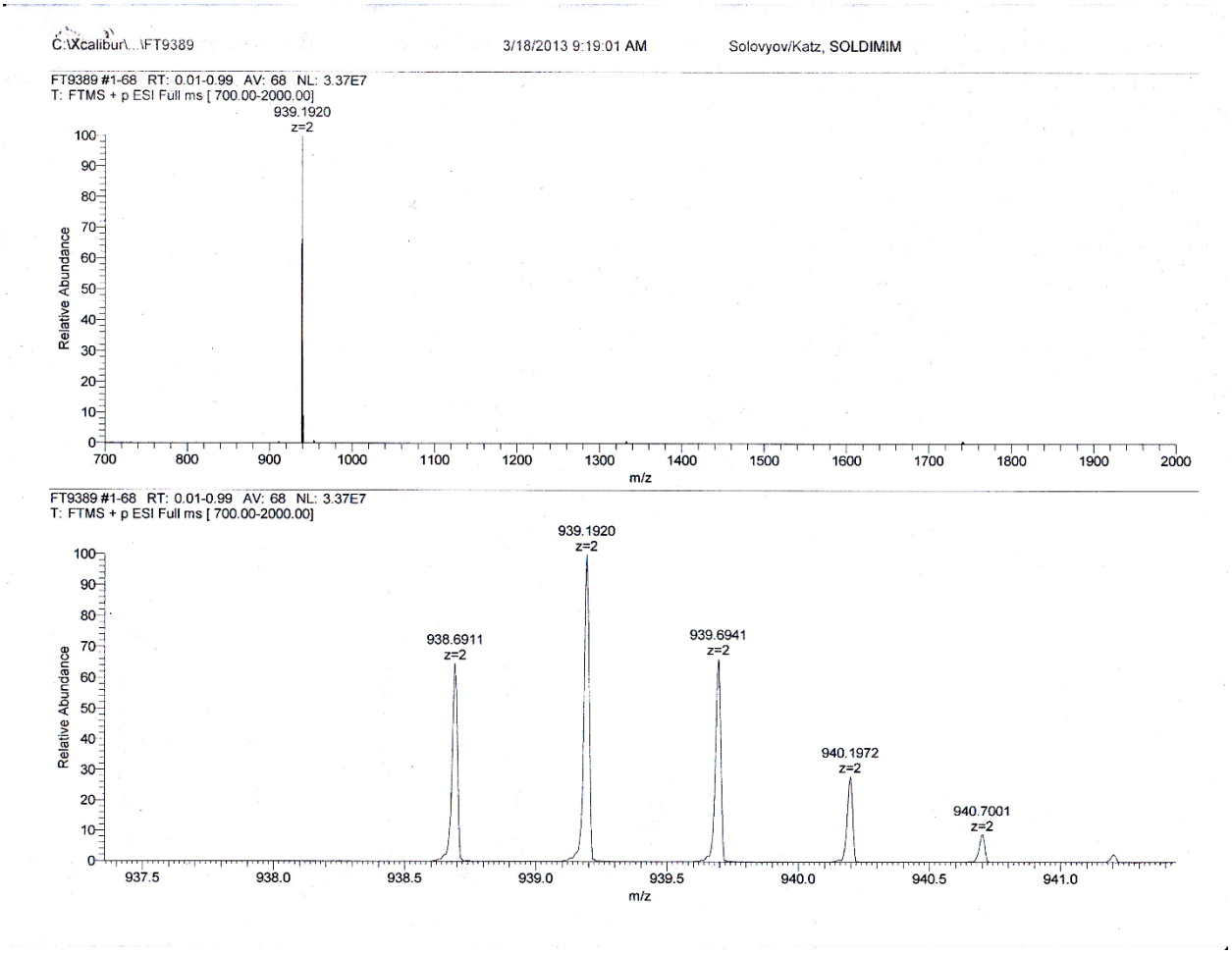


Fig. S16 +ESI MS spectra of **D1**

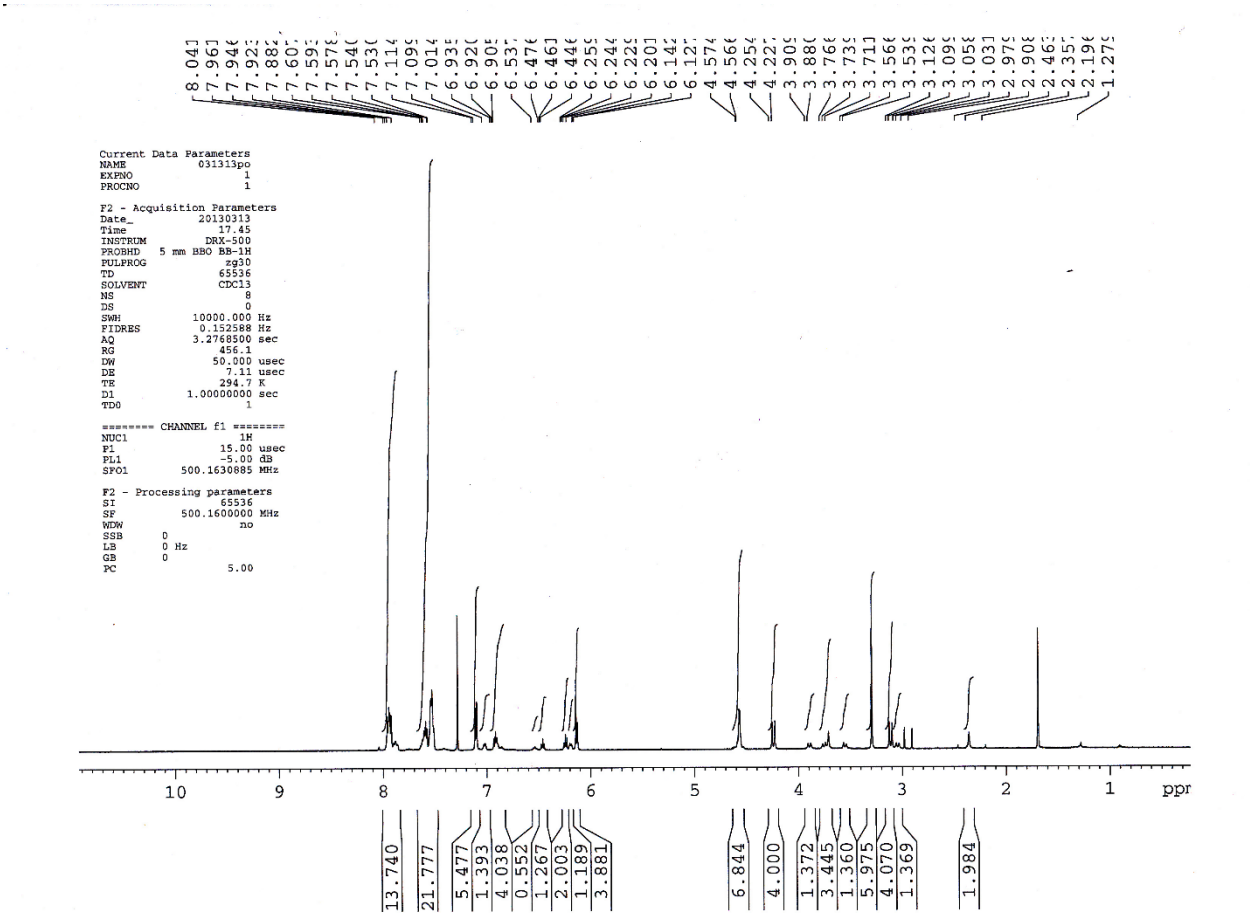


Fig. S17 ^{1}H NMR spectra of **7b** ($CDCl_3$)

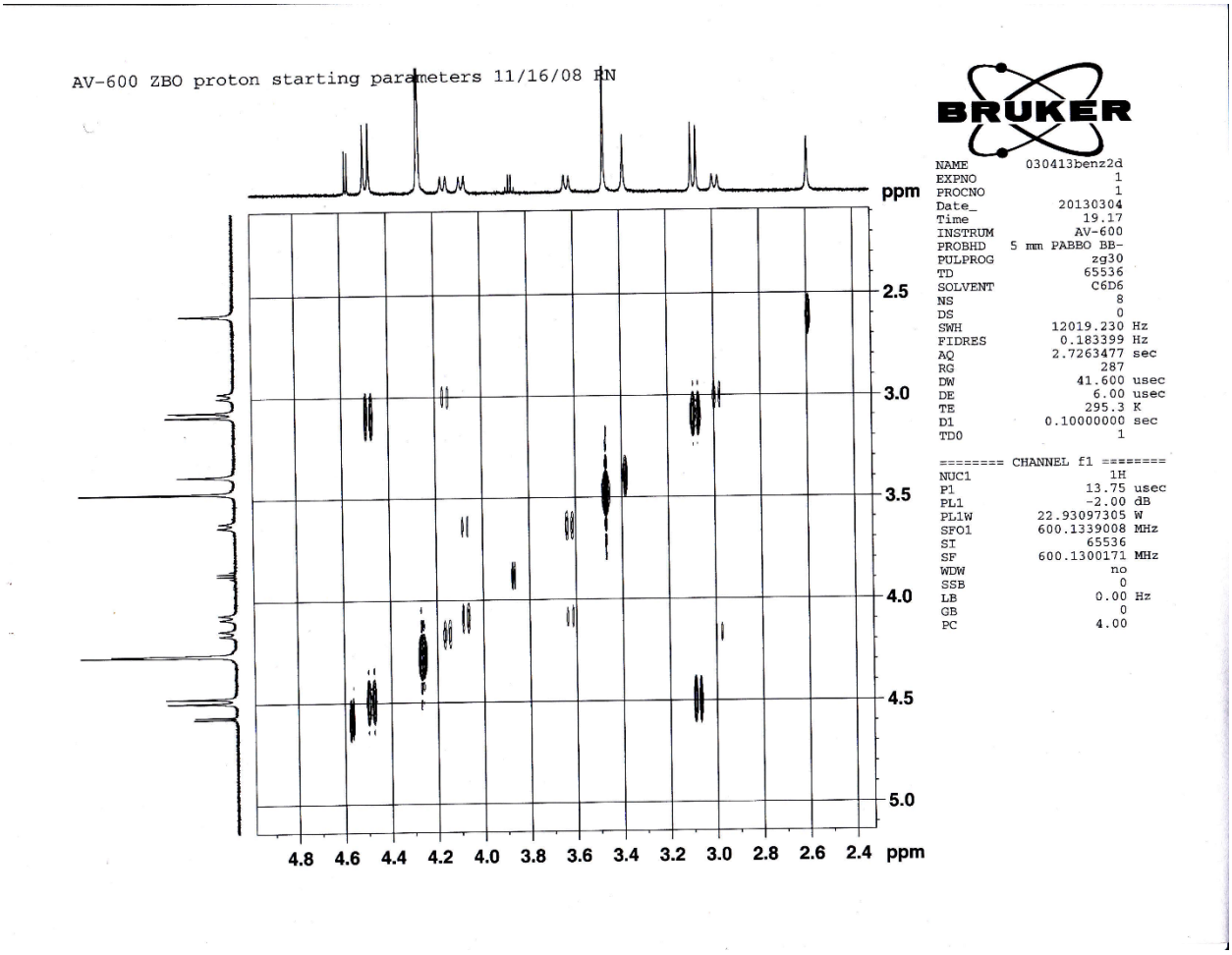


Fig. S18 ^{1}H-^{1}H 2D COSY NMR spectra of **7b** (methylene region) (C_6D_6)

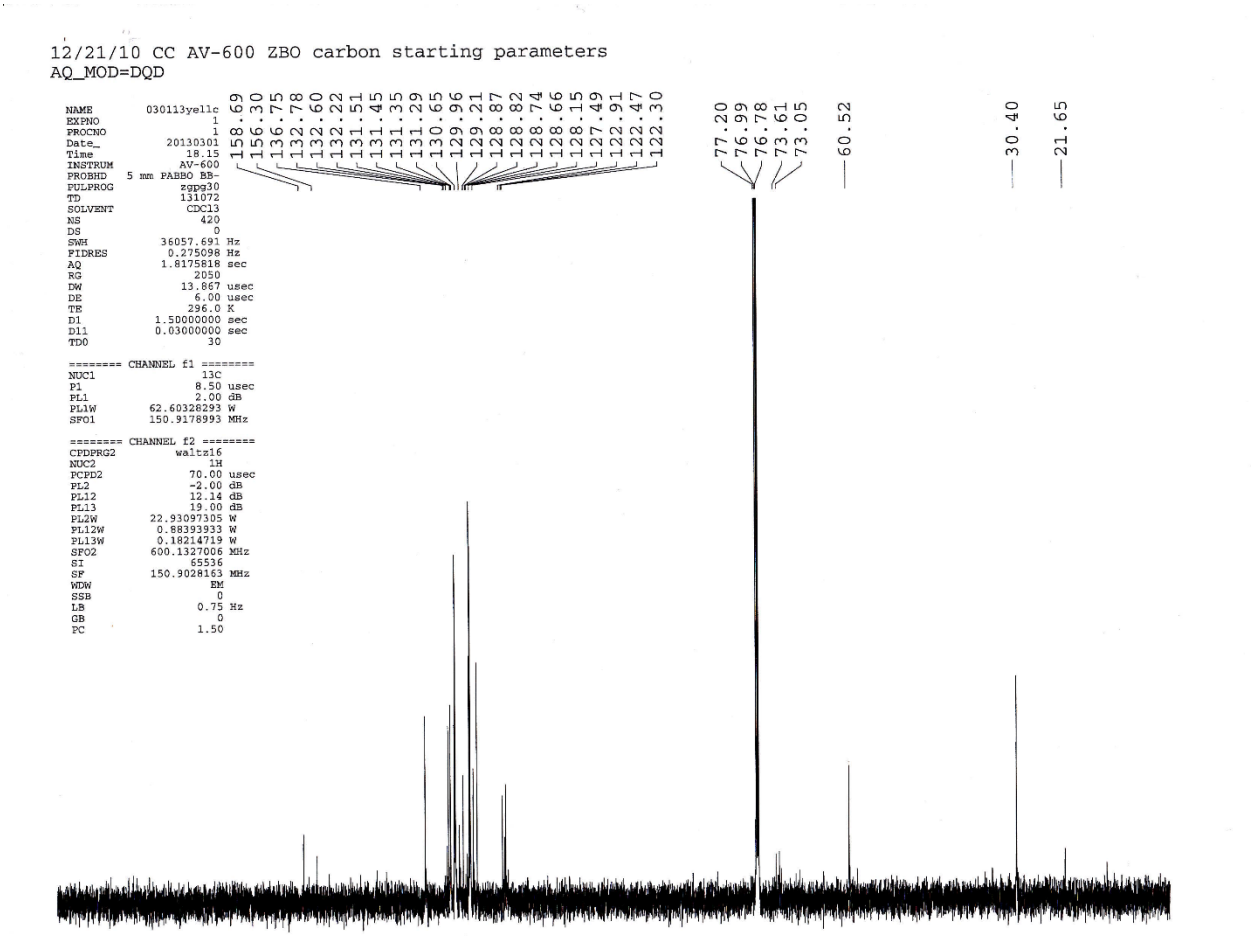


Fig. S19 ^{13}C NMR spectra of **7b** ($CDCl_3$)

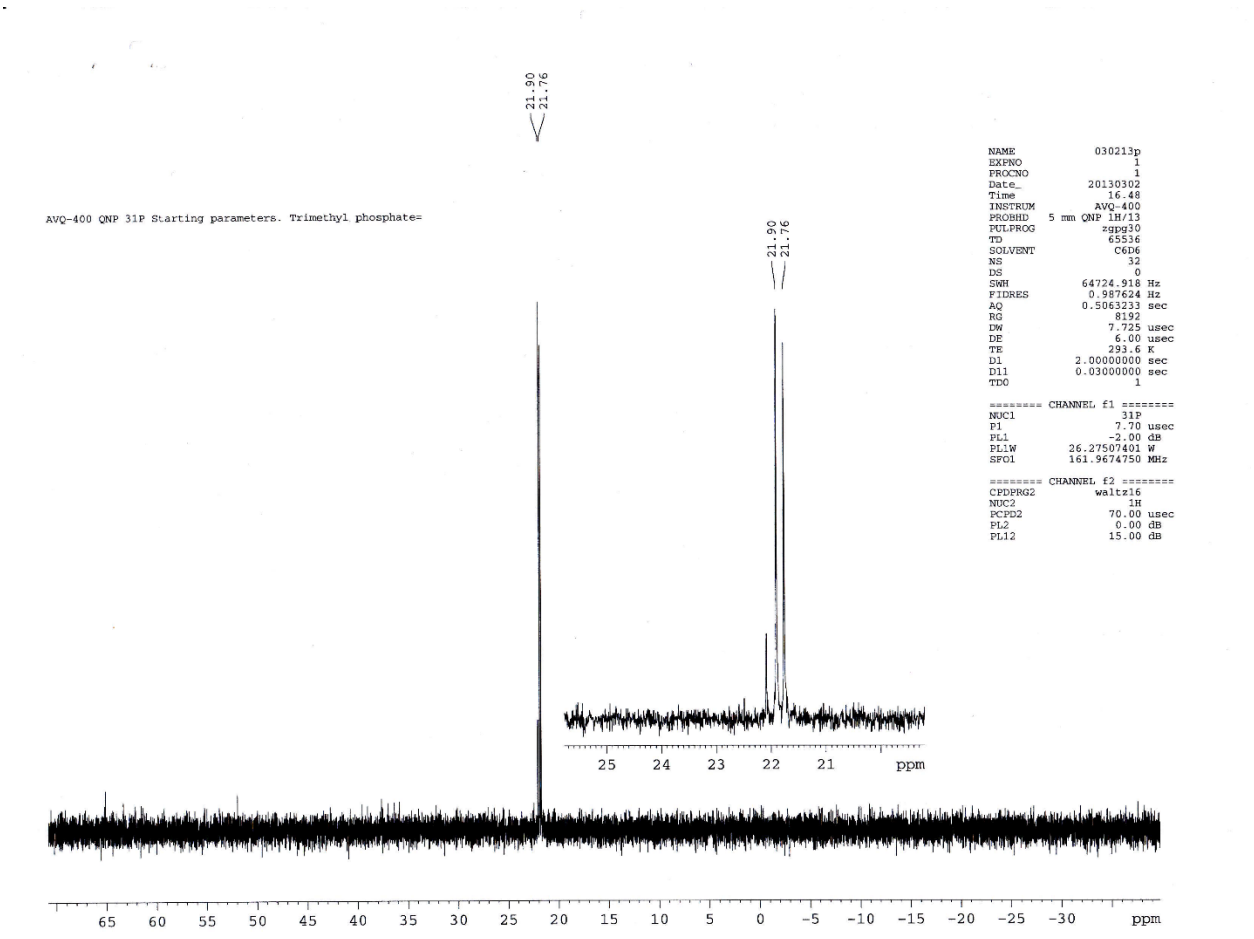


Fig. S20 ^{31}P NMR spectra of **7b** (C6D6)

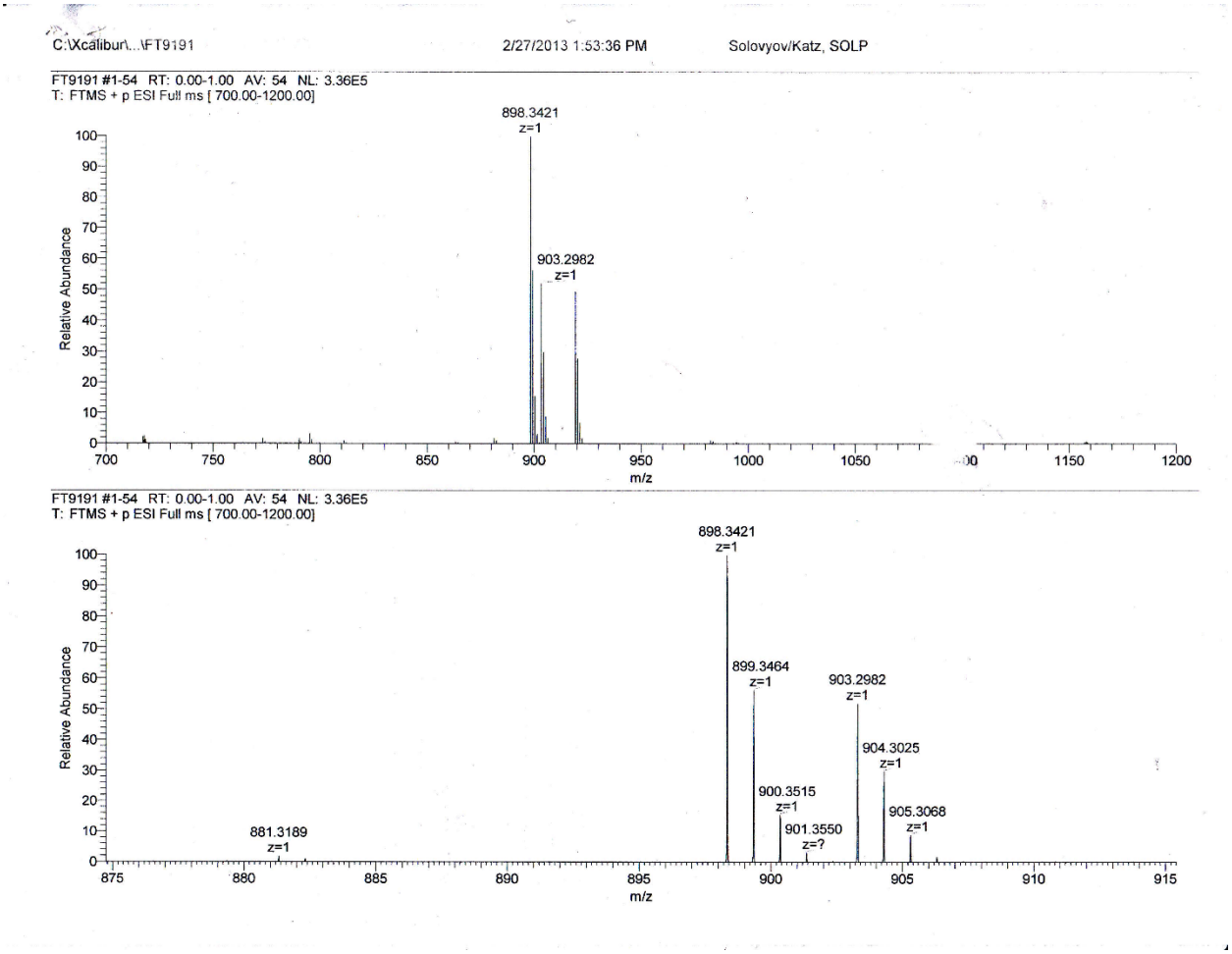


Fig. S21 +ESI MS spectra of **7b**

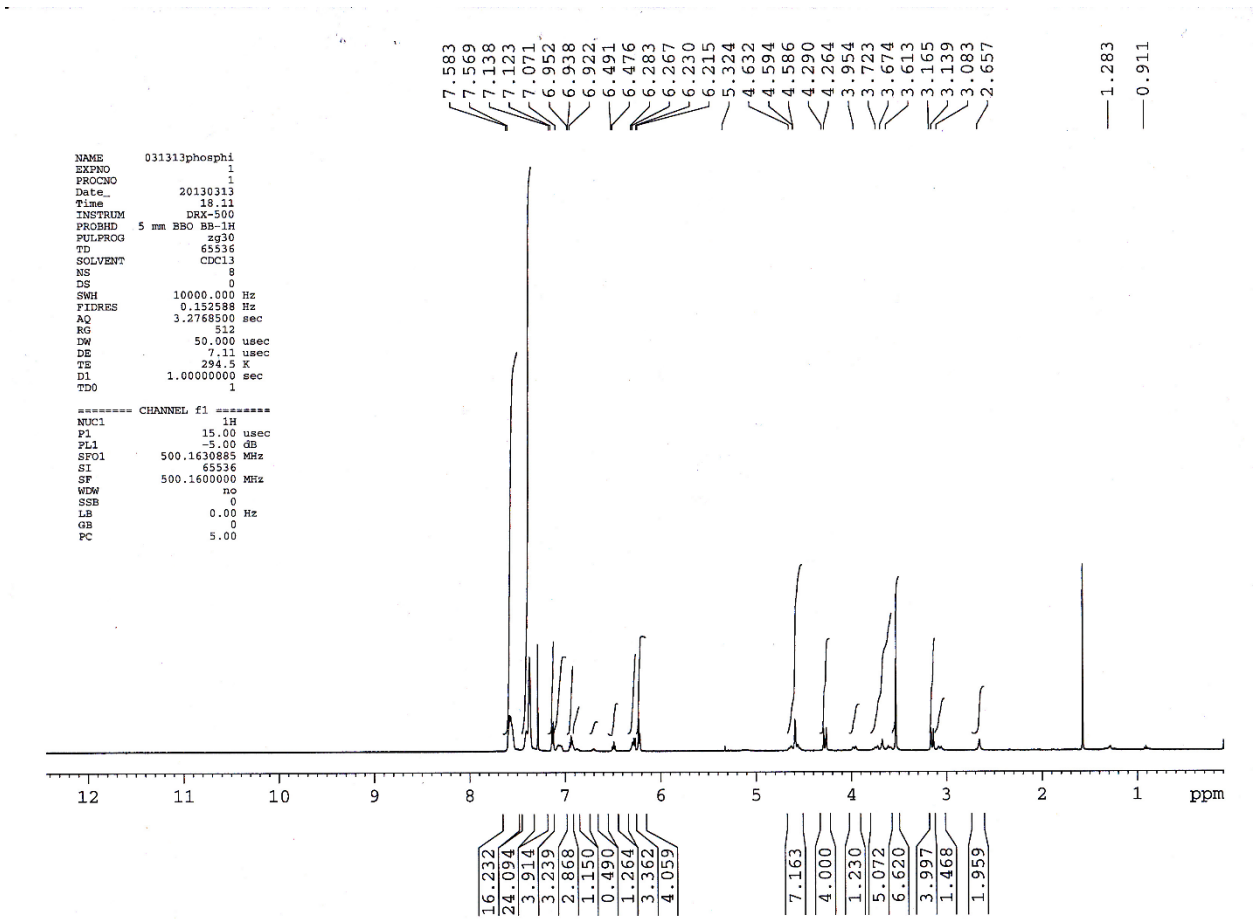
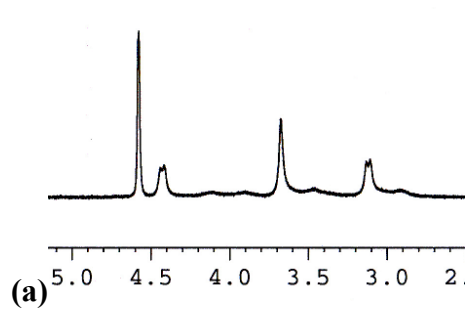
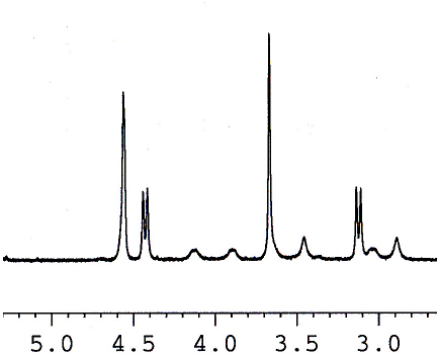


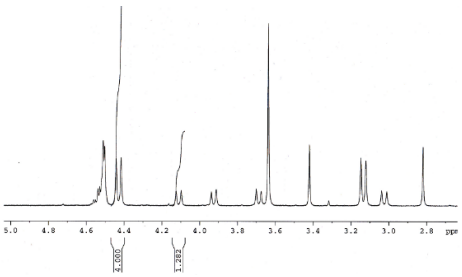
Fig. S22 ^{1}H NMR spectra of **H1** ($CDCl_3$)



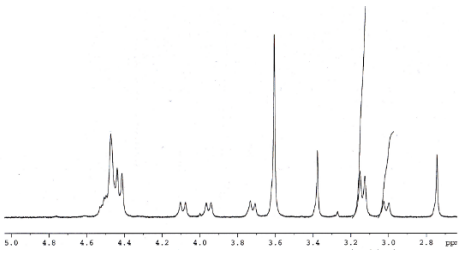
(a)



(b)



(c)



(d)

Fig. S23 ^{1}H NMR spectra of **H1** (methylene bridges region) (toluene-d_8) at 323K (**a**), 303K (**b**), 253K(**c**), 213K (**d**)

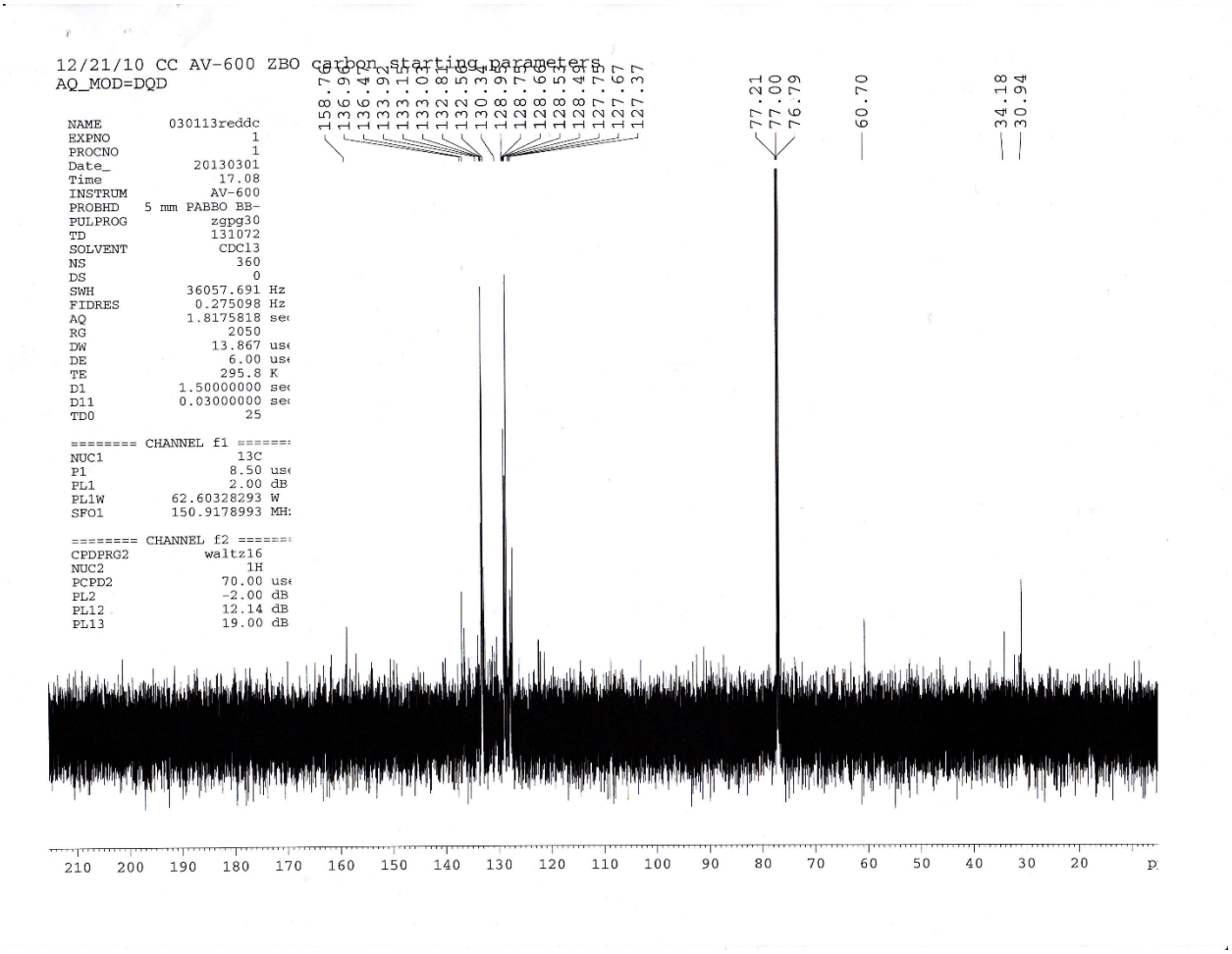


Fig. S24 ^{13}C NMR spectra of **H1** ($CDCl_3$)

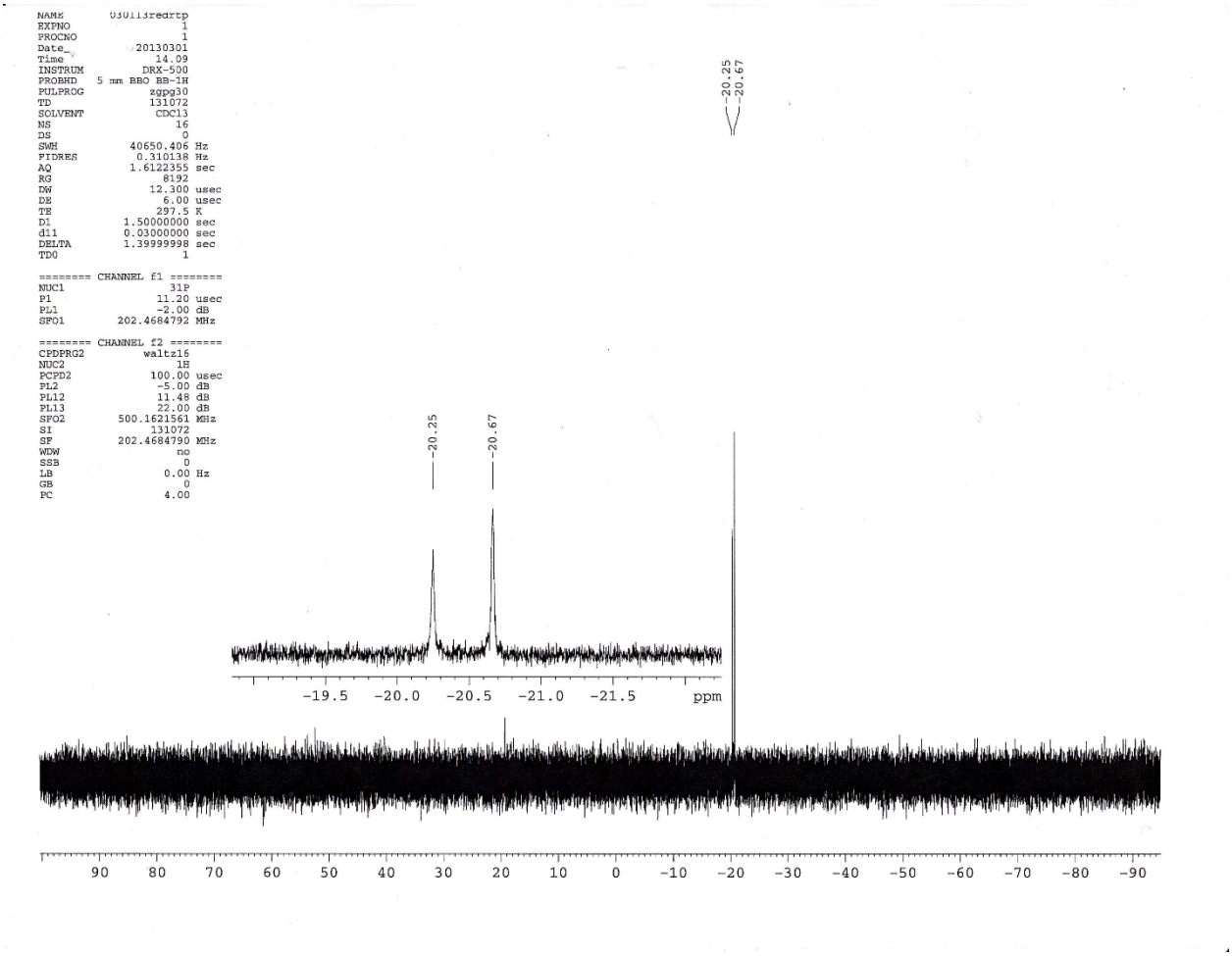


Fig. S25 ^{31}P NMR spectra of **H1** ($CDCl_3$)

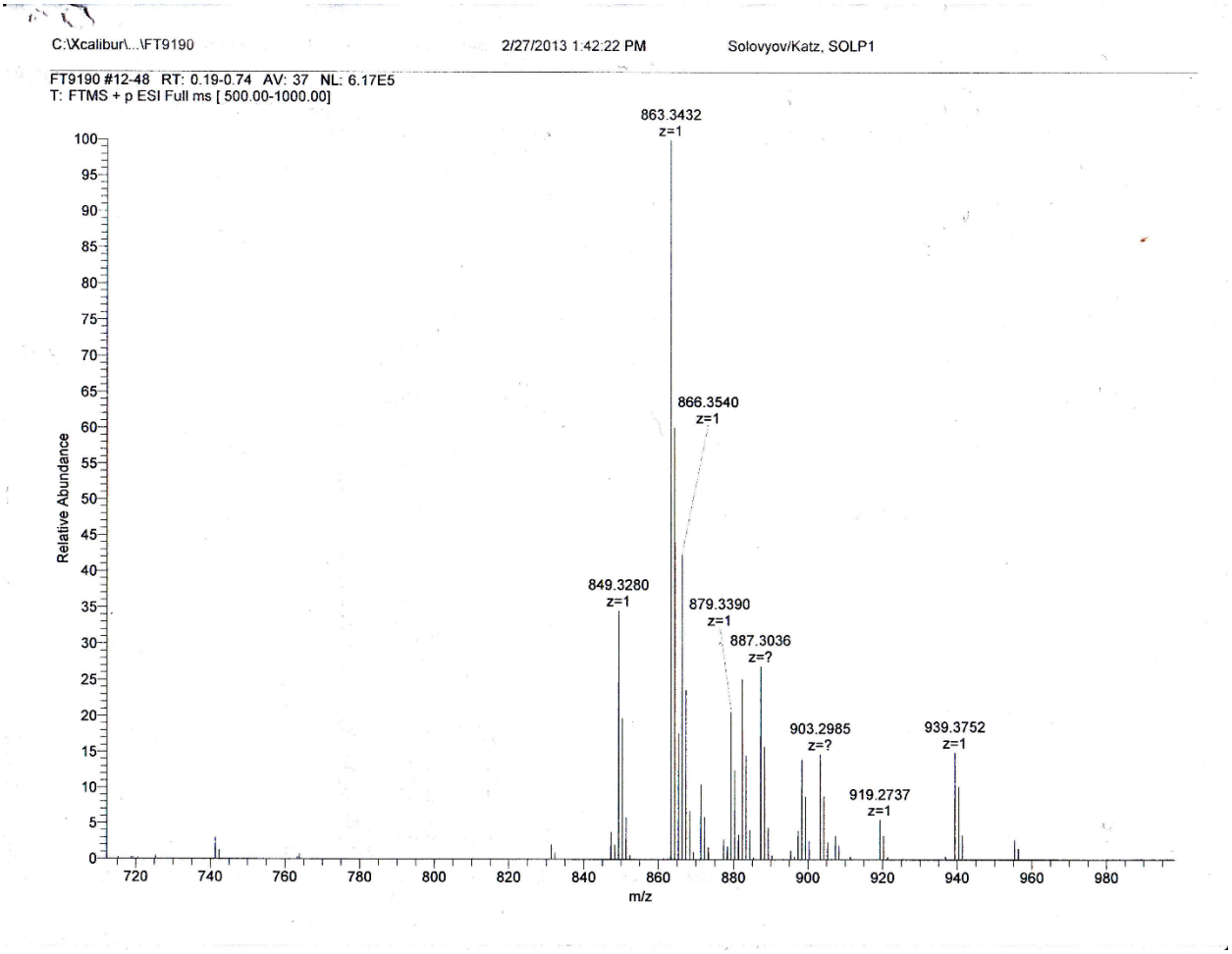


Fig. S26 +ESI MS spectra of **H1**

Synthesis of Au-calixarene complexes with NMR and ESI-MS characterization

Synthesis and characterization of H1G:

300 mg (0.35 mmol) ligand were dissolved in 10 mL dichloromethane and 210 mg (0.71 mmol). Me_2SAuCl were added in the dark. The mixture was stirred in the dark for 45 min. The solution was then filtered through celite and the solvent was evaporated. The obtained product was filtered a second time through celite and the solvent was evaporated. The product was purified via column chromatography (Selecto , dichloromethane : ethylacetate = 2 : 1). ^{1}H NMR (600 MHz, toluene-d8) δ 7.47 (m, 8H, C_6H_5P), 7.10 (m, 12H, C_6H_5P), 6.91 (m, 6H, ArH), 6.31 (m, 6H, ArH), 4.33 (s, 4H, CH_2P), 4.09 (d, 4H, ^{2}J=13.2 Hz, $ArCH_2Ar$), 3.67 (s, 6H, OCH_3), 2.99 (d, 4H, ^{2}J=13.2 Hz, $ArCH_2Ar$); ^{31}P NMR (toluene-d8) δ 24.22, 24.44; HR MS TOF $C_{56}H_{50}Au_2Cl_2O_4P_2Na^+$ m/z calculated: 1335.1785, observed: 1335.1819 Single crystals were obtained through slow evaporation of a acetonitrile:DCM solution (4:1) of **H1G**.

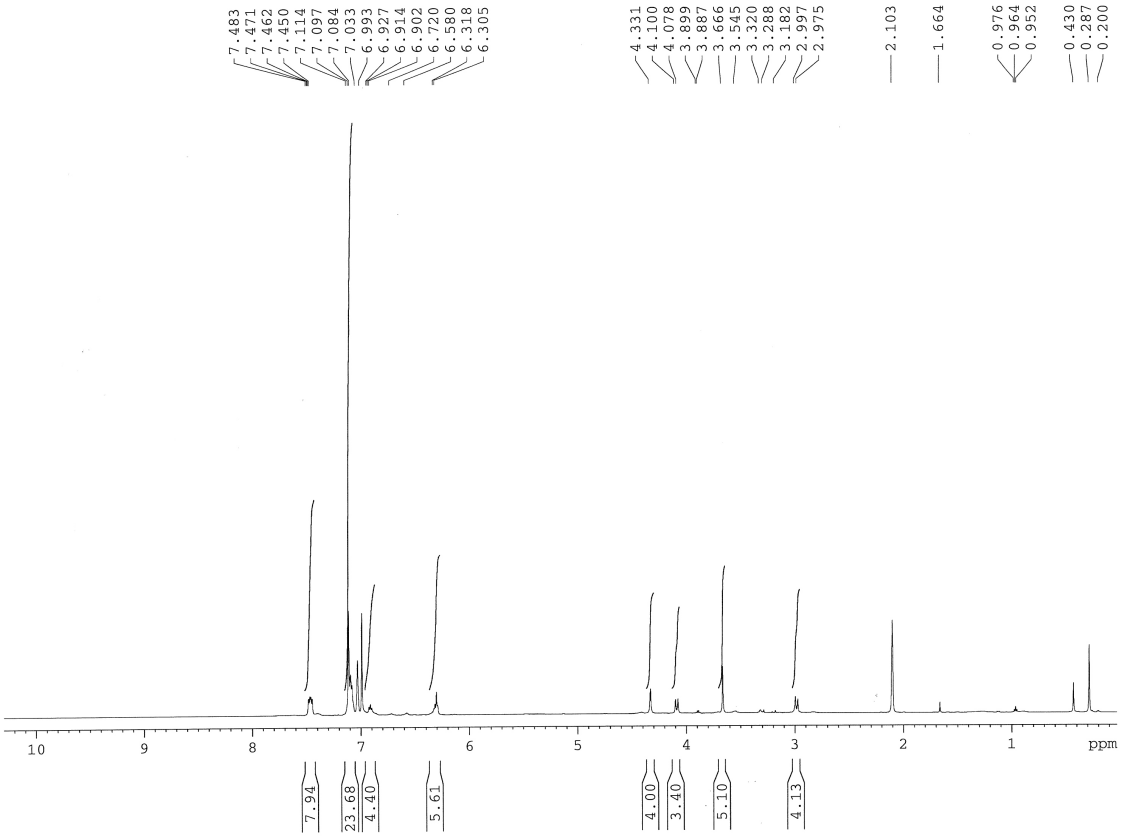


Fig. S27 ^{1}H NMR of **H1G** in toluene-d_8 solvent

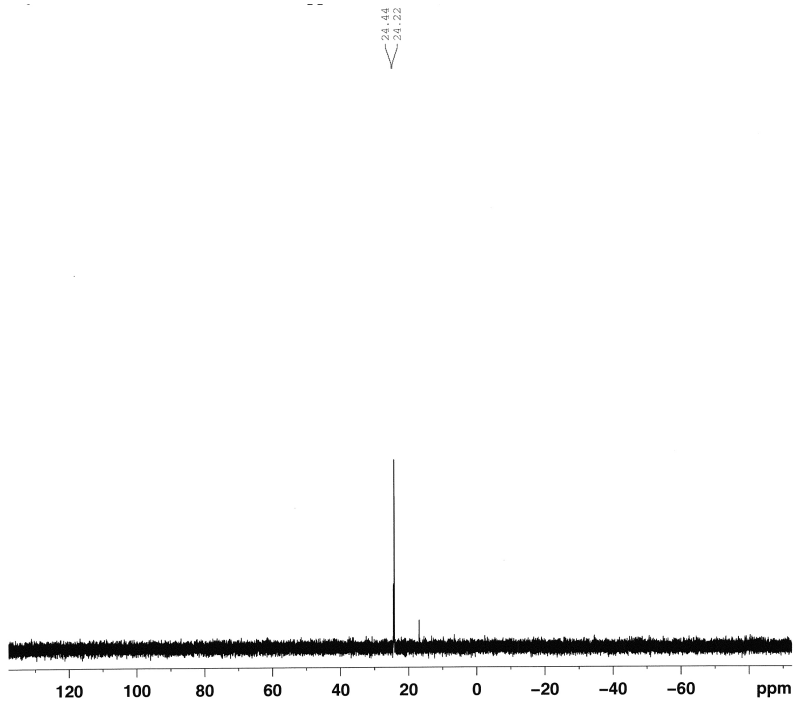


Fig. S28 ^{31}P NMR of **H1G** in toluene-d_8 solvent.

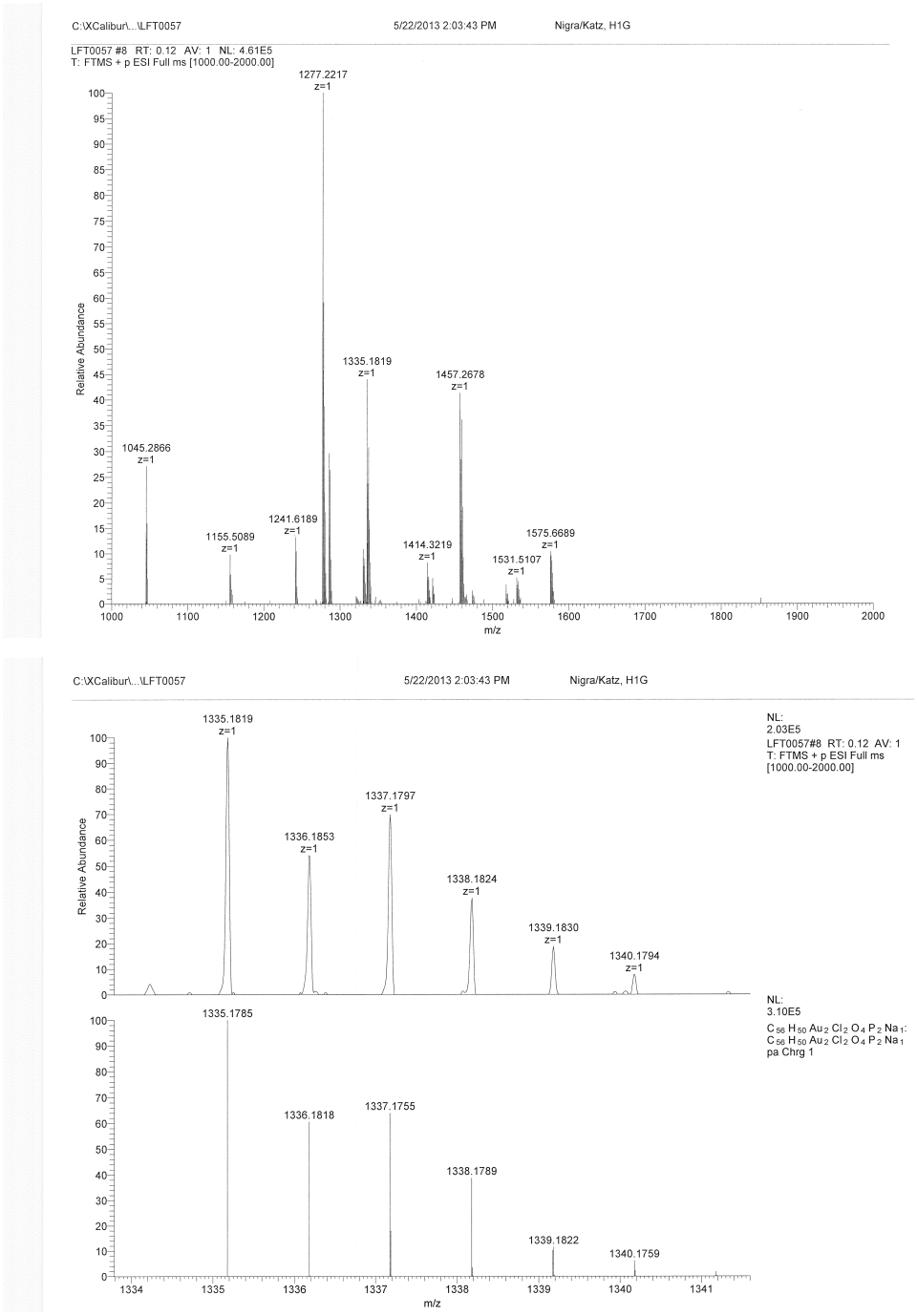


Fig. S29 ESI-MS (+) of **H1G.** Full range spectrum (top), relevant region zoom (middle) simulated spectrum (bottom)

Single-crystal X-ray measurements were completed at the UC Berkeley College of Chemistry X-ray crystallography facility. CCDC # contains the supplementary crystallographic data **H1G**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via

www.ccdc.cam.ac.uk/data_request/cif Fig. S30 illustrates the 2 molecules of **H1G** located in the unit cell in overlay of the two molecules.

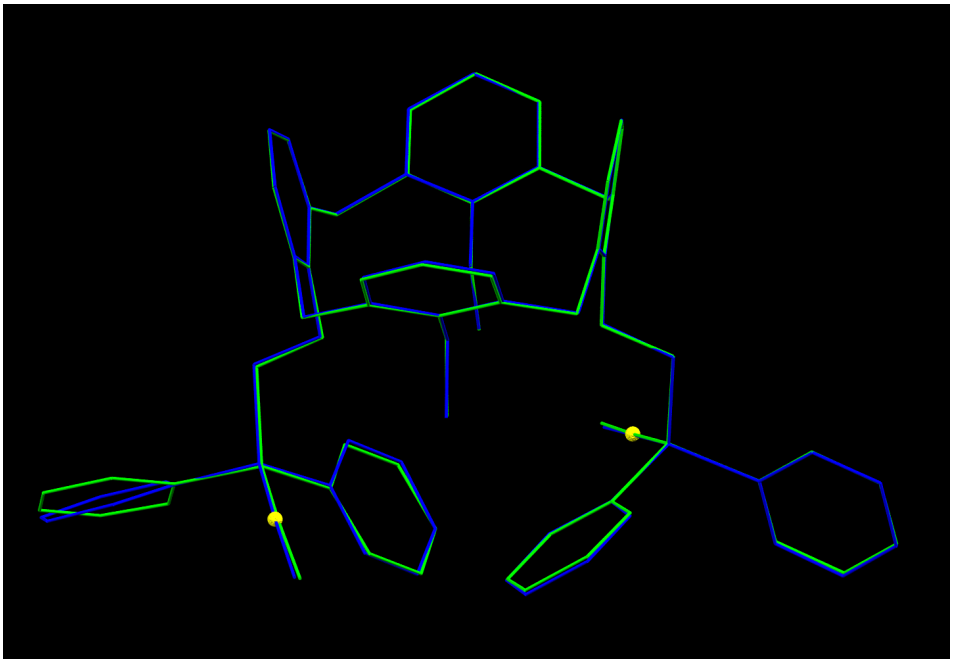


Fig. S30 RMS optimized overlay of the two independent molecules (green = molecule 1; blue = inverted molecule 2) from the X-ray crystal structure of **H1G**. Au atoms highlighted as yellow spheres.

Synthesis and characterization of T1G:

The synthesis and characterization rigorously followed the procedures developed by Katz *et al*. in *Nature Chemistry*, 2010, 2, 1062-1068. Characterization data was identical to the data published.

Synthesis and characterization of C1G

100 mg (0.08 mmol) ligand were dissolved in 10 mL dichloromethane and 40 mg (0.17 mmol) Ag_2O were added in the dark. The solution was stirred for 15 h and was subsequently filtered through celite. 47 mg (0.16 mmol) Me_2SAuCl were added to the obtained colorless solution. The mixture was stirred in the dark for 1 h. The solution was then filtered through celite and the solvent was evaporated. The obtained product was purified via column chromatography (Selecto , dichloromethane : ethylacetate = 5 : 1). The product is a white powder. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.04 (s, 2H, ImH), 6.97 (s, 2H, ImH), 6.89 (m, 4H, ArH), 6.67 (m, 4H, ArH), 4.35 (d, 4H, ^{2}J=12.4 Hz, $ArCH_2Ar$), 4.28 (t, 4H, ^{3}J=7.6 Hz, NCH_2), 4.17 (t, 4H, ^{3}J=7.2 Hz, OCH_2), 3.94 (t, 4H, ^{3}J=7.6 Hz, NCH_2), 3.76 (t, 4H, ^{3}J=7.2 Hz, OCH_2), 3.13 (d, 4H, ^{2}J=12.4 Hz, $ArCH_2Ar$), 2.13 (m, 4H, CH_2), 1.97 (m, 8H, CH_2), 1.84 (m, 4H, CH_2), 1.37 (m, 4H, CH_2), 1.16 (s, 18H, t-C_4H_9), 1.05 (m, 6H, CH_3), 1.00 (s, 18H, t-C_4H_9), 0.96 (m, 6H, CH_3); HR MS TOF $C_{72}H_{104}Au_2Cl_2N_4O_4Na^+$, calculated: 1575.6658, actual: 1575.6695

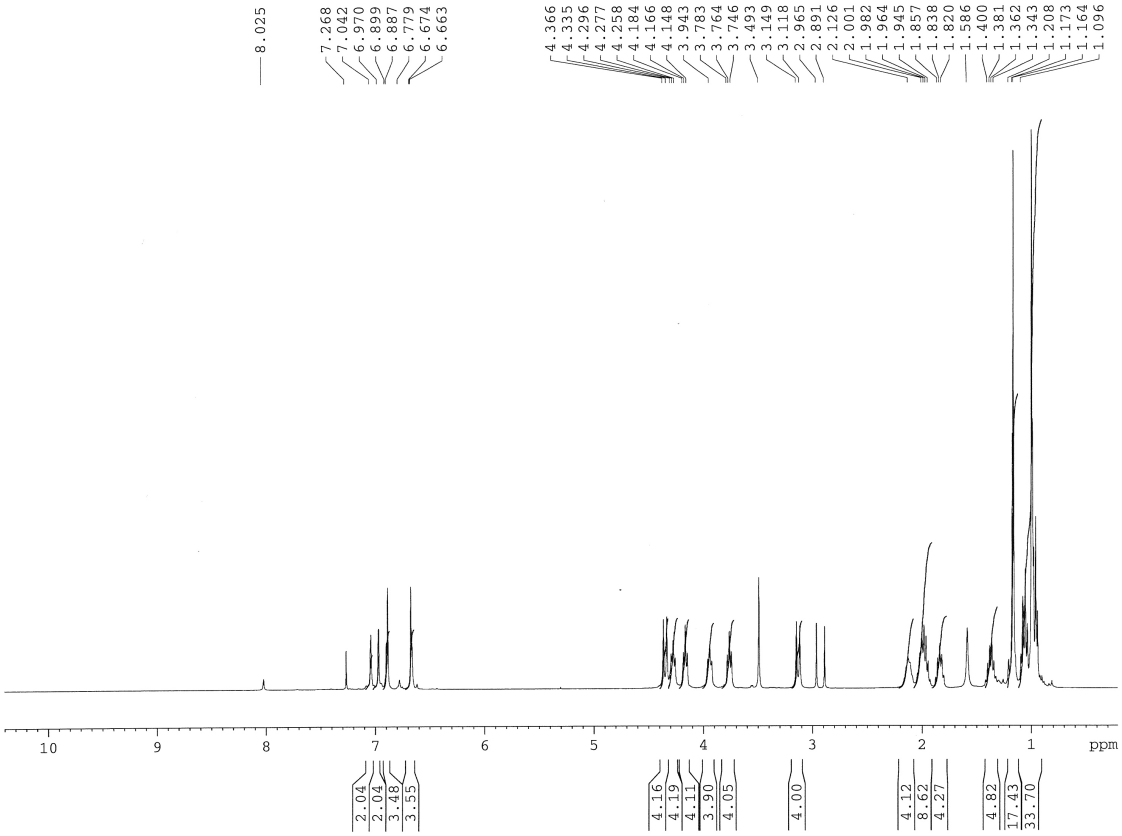


Fig. S31 ^{1}H NMR of **C1G** ($CDCl_3$)

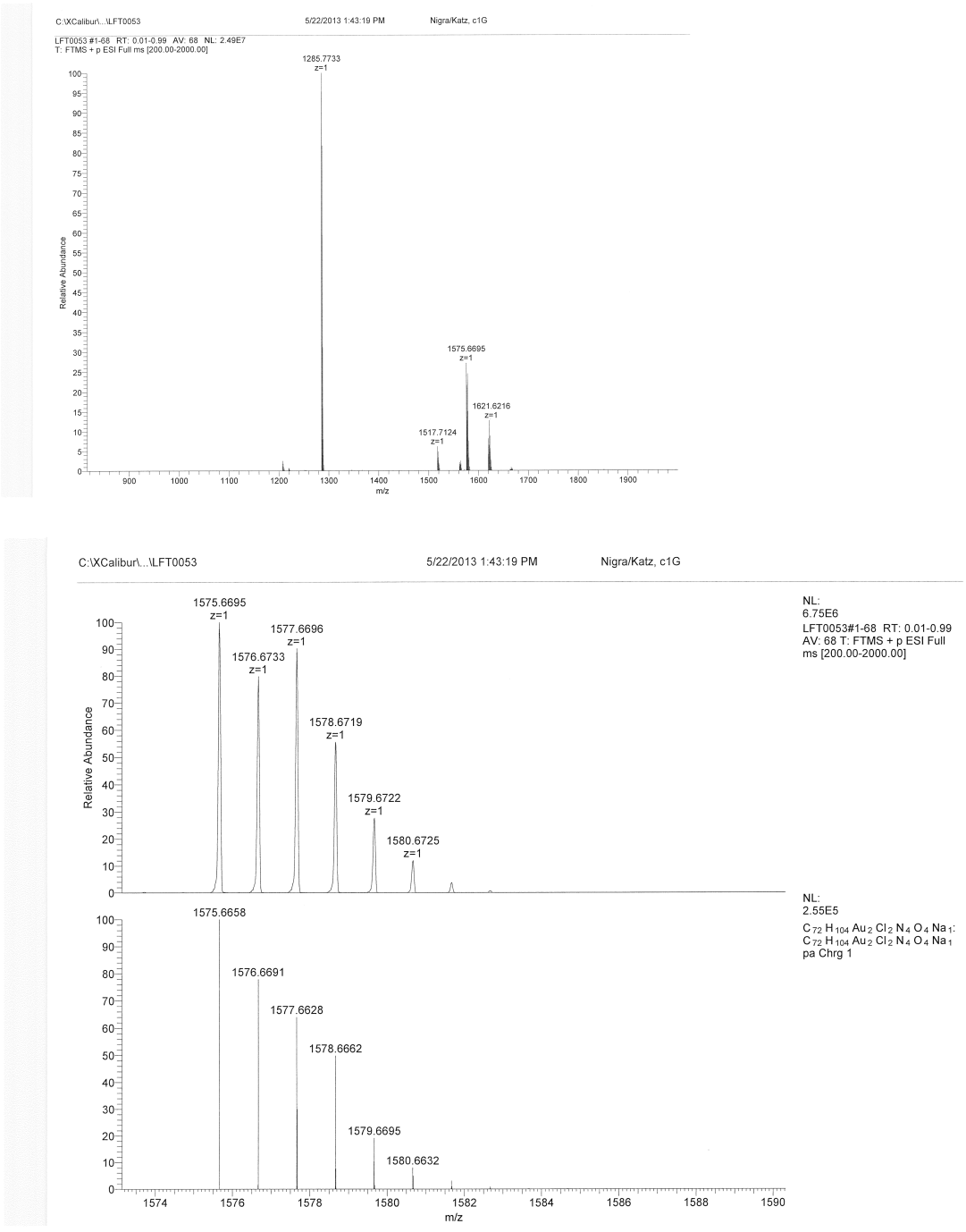


Fig. S32 ESI-MS (+) of **C1G**. Full range spectrum (top), relevant region zoom (middle) simulated spectrum (bottom)

Synthesis and characterization of C2G:

125 mg (0.097 mmol) ligand C1 were dissolved in 10 mL dichloromethane and 40 mg (0.17 mmol) Ag_2O were added in the dark. The solution was stirred for 15 h and was subsequently filtered through celite. 57 mg (0.19 mmol) Me_2SAuCl were added to the obtained colorless solution. The mixture was stirred in the dark for 1 h. The solution was then filtered through celite and the solvent was evaporated. The obtained product was purified via column chromatography (Selecto , dichloromethane : ethylacetate = 5 : 1). The product is a white powder.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (m, 4H, C_6H_5), 7.45 (m, 6H, C_6H_5), 7.26 (s, 2H, ImH), 7.20 (m, 2H, ImH), 7.00 (s, 4H, ArH), 6.60 (s, 4H, ArH), 4.50 (m, 4H+4H, $ArCH_2Ar$+NCH_2), 4.10 (m, 4H, OCH_2), 3.75 (m, 4H, OCH_2), 3.20 (d, 4H, ^{2}J=12.4 Hz, $ArCH_2Ar$), 2.25 (m, 4H, CH_2), 2.15 (m, 4H, CH_2), 1.95 (m, 4H, CH_2), 1.25 (s, 18H, t-C_4H_9), 1.10 (t, 6H, ^{3}J=7.2 Hz, CH_3), 0.95 (s, 18H, t-C_4H_9); HR MS TOF $C_{76}H_{96}Au_2Cl_1N_4O_4$, calculated: 1557.6646, actual: 1577.6646.

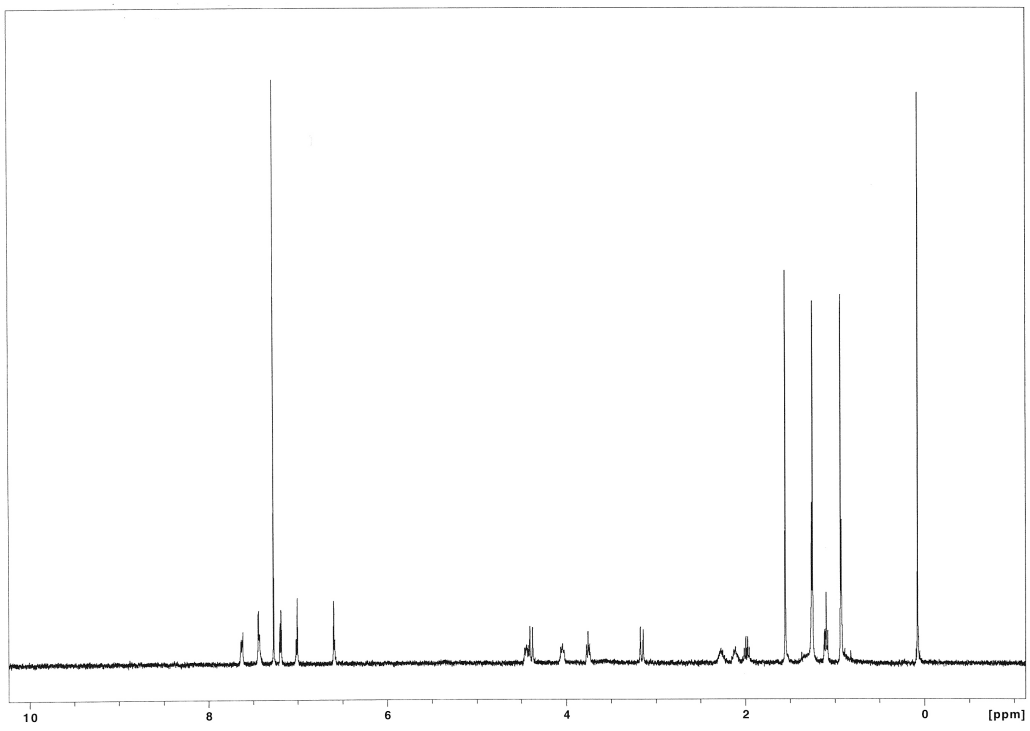


Fig. S33 ^{1}H NMR data for **C2G**. ($CDCl_3$)

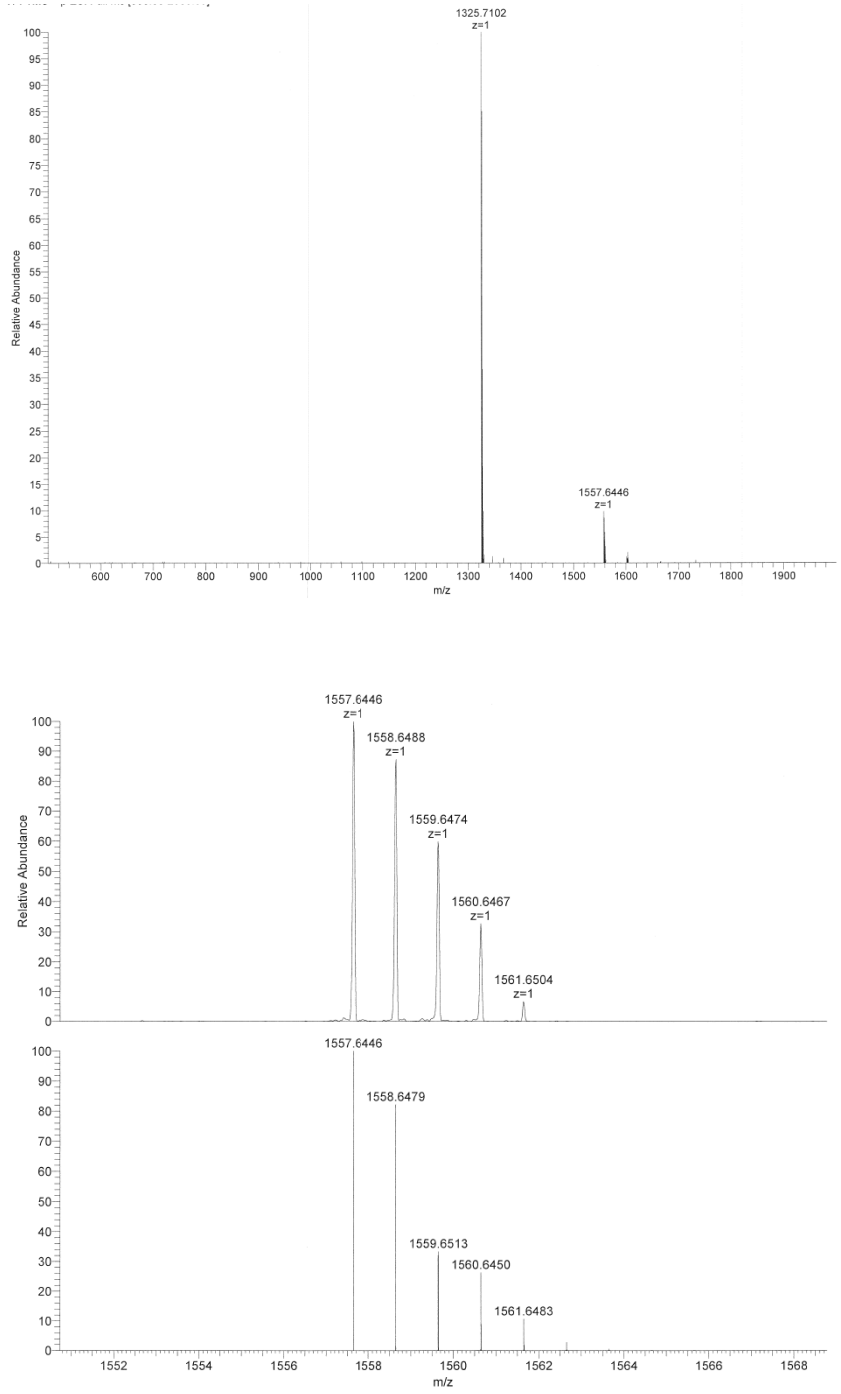


Fig. S34 ESI-MS (+) data for **C2G**. Full range spectrum (top), relevant region zoom (middle) simulated spectrum (bottom)

Synthesis and Characterization of C3G

94 mg (0.08 mmol) ligand were dissolved in 10 mL dichloromethane and 22 mg (0.09 mmol) Ag_2O were added in the dark. The solution was stirred for 15 h and was subsequently filtered through celite. 46 mg (0.15 mmol) Me_2SAuCl were added to the obtained colorless solution. The mixture was stirred in the dark for 1 h. The solution was then filtered through celite and the solvent was evaporated. The obtained product was purified via column chromatography (Selecto , dichloromethane : ethylacetate = 5 : 1). ^1H NMR (400 MHz, $CDCl_3$) δ 7.63 (m, 4H, C_6H_5), 7.47 (m, 6H, C_6H_5), 7.27 (s, 2H, ImH), 7.22 (s, 2H, ImH), 7.13 (br s, 4H, ArH), 6.49 (br s, 4H, ArH), 2.56, 3.19, 3.90, 4.07, 4.28, 4.66 (six br s, 26H, CH_2+OCH_3), 1.34 (s, 18H, t-C_4H_9), 1.05, 0.86 (two br s, 18H, t-C_4H_9); HR ES MS: $C_{70}H_{84}Au_2Cl_1N_4O_4^+$ m/z calculated 1473.5507, actual 1473.5518

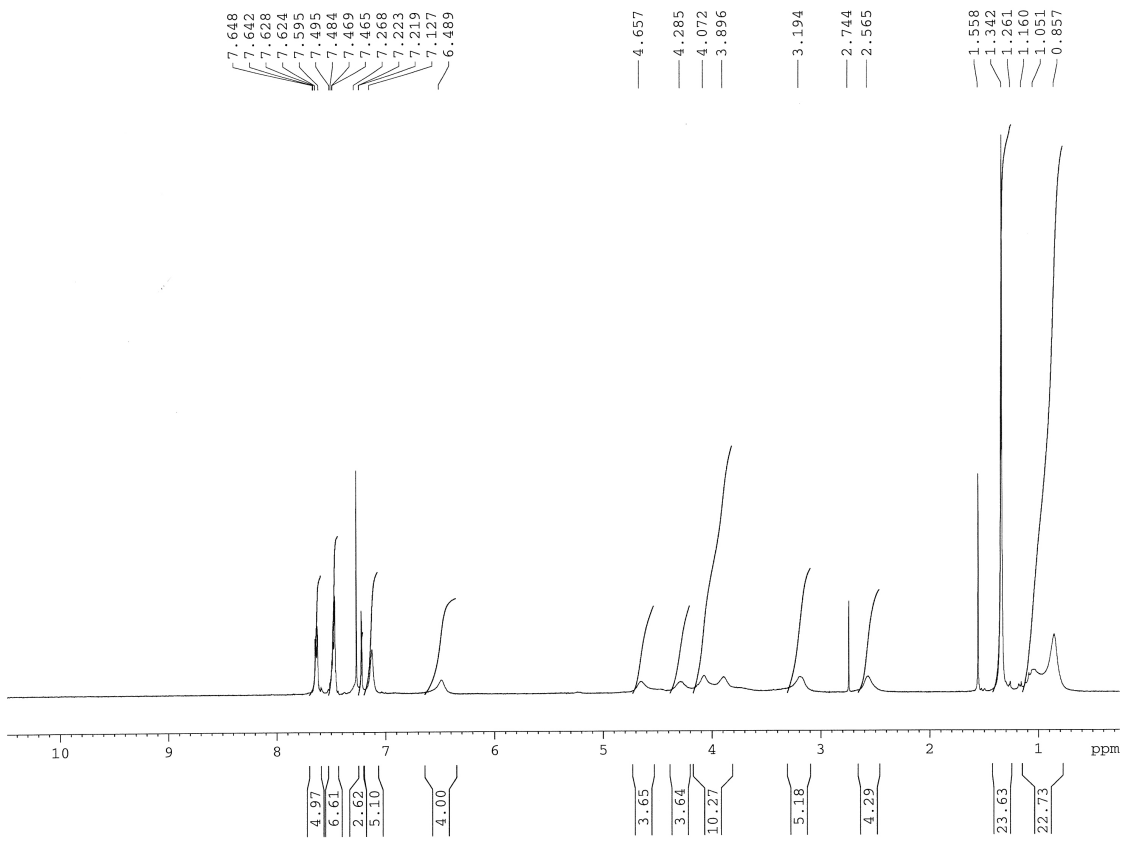


Fig. S35 ^1H NMR of **C3G** ($CDCl_3$)

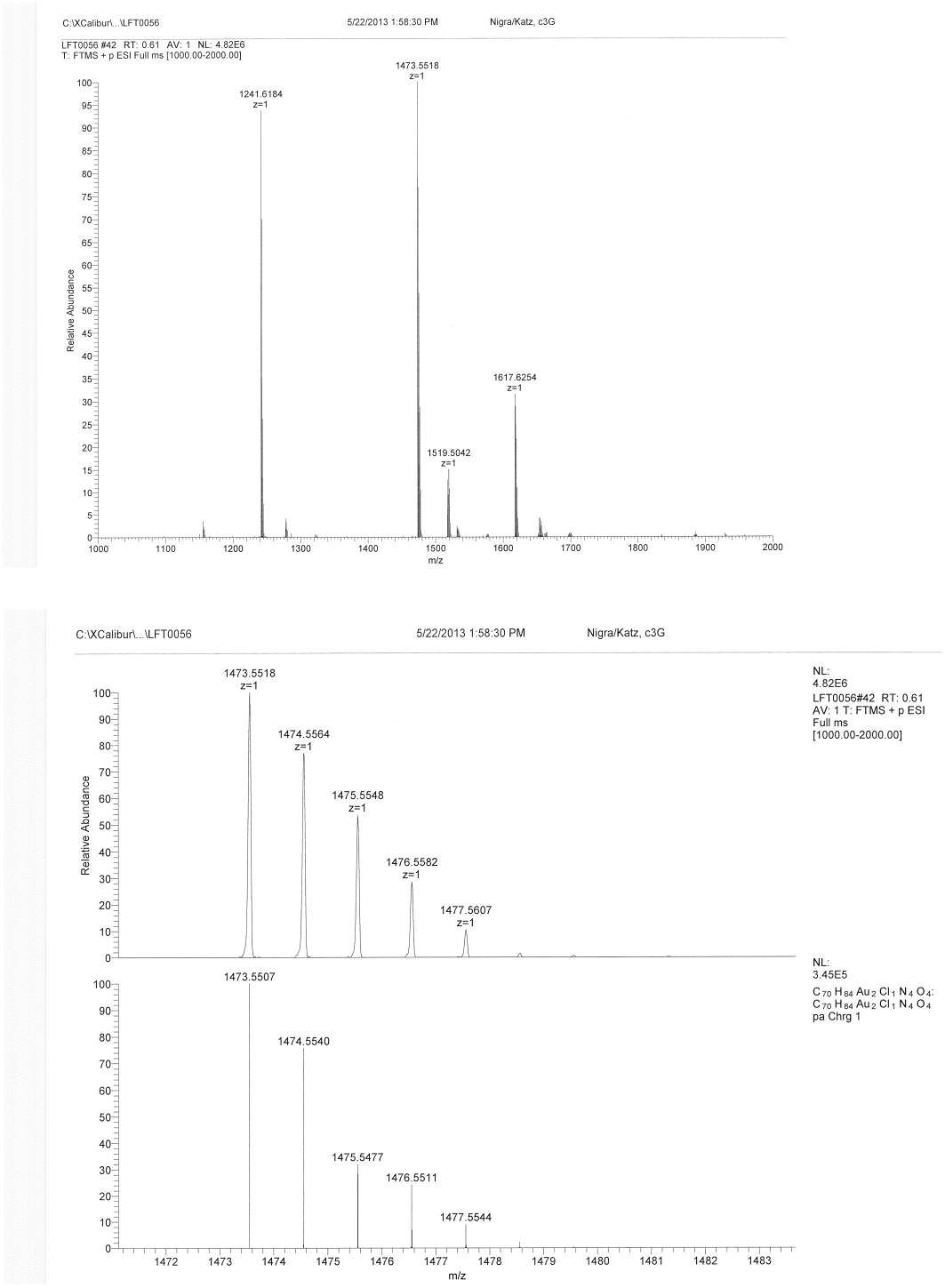


Fig. S36 ESI-MS (+) of **C3G.** Full range spectrum (top), relevant region zoom (middle) simulated spectrum (bottom)

Synthesis and Characterization of D1G

235 mg (0.11 mmol) ligand were dissolved in 10 mL dichloromethane and 32 mg (0.14 mmol) Ag_2O were added in the dark. The solution was stirred for 15 h and was subsequently filtered through celite. 68 mg (0.23 mmol) Me_2SAuCl were added to the obtained colorless solution. The mixture was stirred in the dark for 1 h. The solution was then filtered through celite and the solvent was evaporated. The obtained product was purified via column chromatography (Selecto G60, dichloromethane : ethylacetate = 5 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.88 (d, 2H, ^{3}J=2.0 Hz, ImH), 6.86 (s, 8H, ArH), 6.82 (d, 2H, ^{3}J=2.0 Hz, ImH), 6.69, 6.72 (two s, 4H+4H, ArH), 4.34, 4.38 (two d, 4H+4H, ^{2}J=12.4 Hz, $ArCH_2Ar$), 4.14 (m, 8H, CH_2), 3.83 (m, 16H, CH_2), 3.12, 3.13 (two d, 4H+4H, ^{2}J=12.4 Hz, $ArCH_2Ar$), 1.97, 2.04, 2.11 (three m, 18H, CH_2), 1.81 (m, 4H, CH_2), 1.34 (m, 8H, CH_2), 1.15 (s, 36H, t-C_4H_9), 1.02 (s, 36H, t-C_4H_9), 0.95 (m, 18H, CH_3); $C_{126}H_{178}Au_2Cl_2N_4O_8Na^+$, calculated: 2365.27 actual: 2365.24.

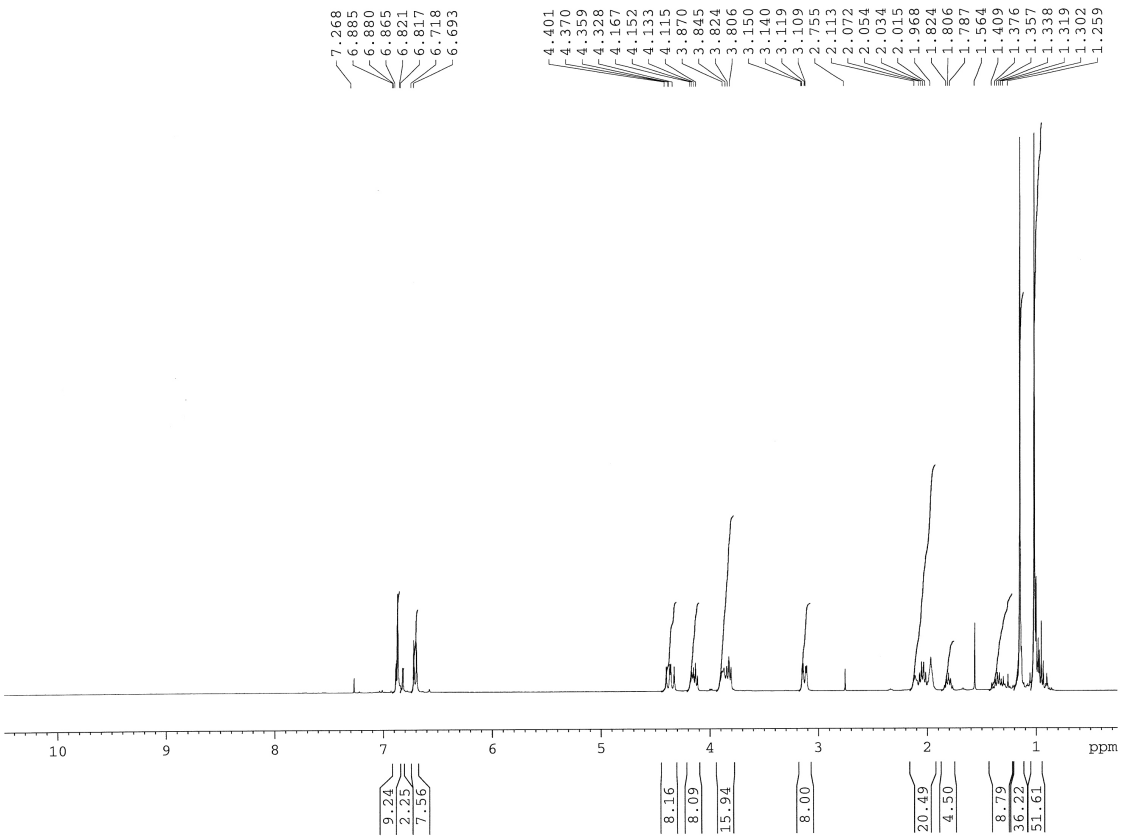


Fig. S37 ^{1}H NMR of **D1G** ($CDCl_3$)

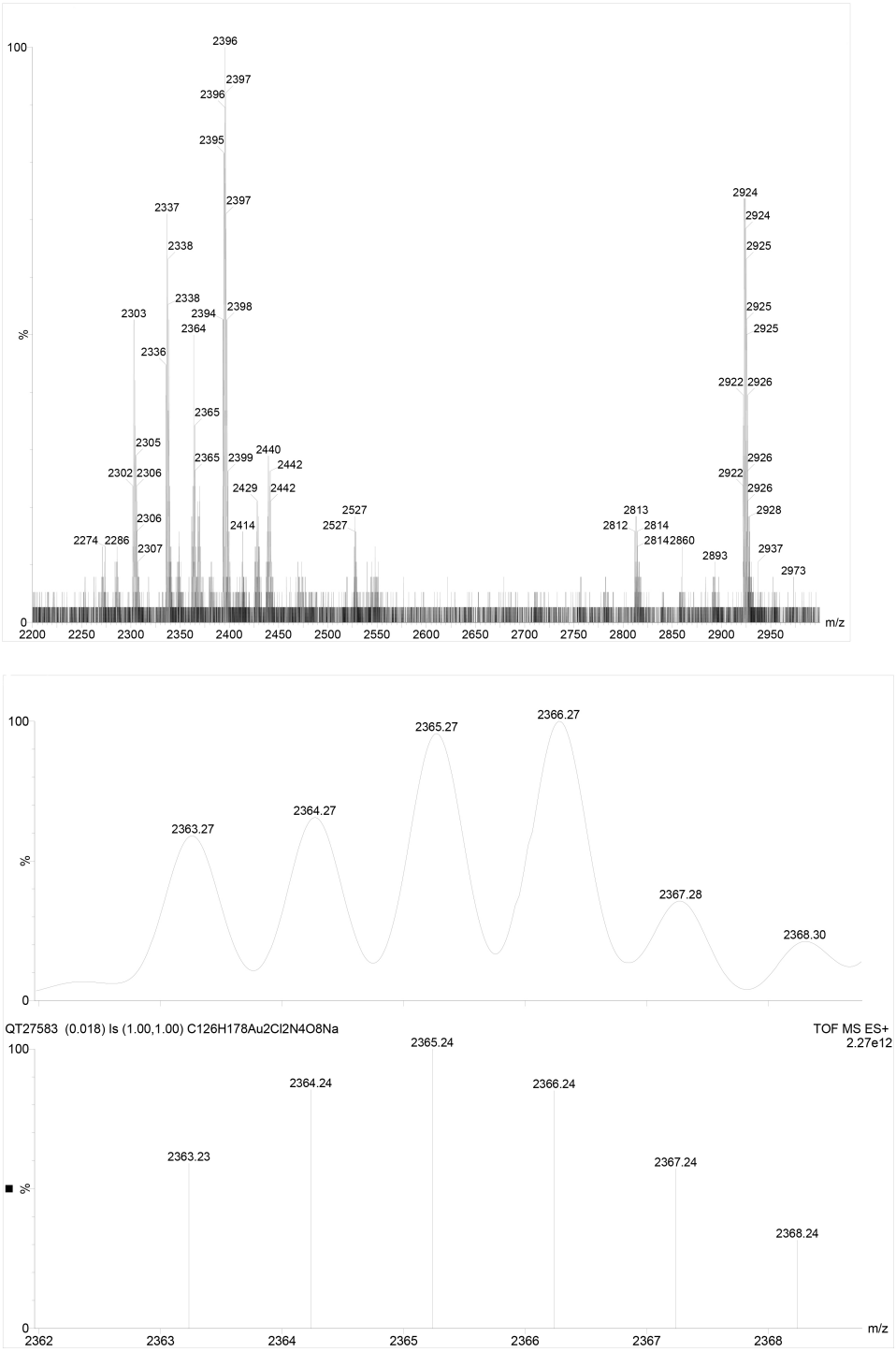


Fig. S38 ESI-MS (+) of **D1G** Full range spectrum (top), relevant region zoom (middle) simulated spectrum (bottom).

Synthesis of Au(I) clusters by reduction of Au(I) complexes

Based on reduction procedures to synthesize calix[4]arene phosphine-bound Au clusters,[8] the following method was used to synthesize small Au clusters. A 2.0 mM suspension of an Au(I) complex (**C1G**, **C2G**, **C3G**, **D1G** or **H1G**) was suspended in anhydrous ethanol. (Aldrich) 4 eq. of sodium borohydride relative to Au atoms (Aldrich, 99.7%) was added to this suspension and stirred vigorously for 40 minutes at room temperature. The ethanol was evaporated *in vacuo*, and the resulting solid was washed with 100 mL of deionized water (18 MΩ) and then washed with 2 mL of hexane and filtered using vacuum filtration. The samples were dried overnight at room temperature under vacuum. An additional filtration was necessary for cluster **H1-red** where the sample was dissolved in dichloromethane and filtered through a syringe filter to remove the insoluble species. The solvent was then evaporated to recover the cluster. Yields for clusters are typically 20-50% of the initial Au(I) complex added.

UV-Vis characterization of Au clusters

Liquid phase UV-Vis measurements were recorded to characterize the reduced calixarene-bound Au(I) clusters. The clusters were dissolved in dichloromethane (Fisher, HPLC grade) to give a clear brown-colored solution. Absorption spectra were recorded from 700 to 350 nm with a step size of 0.5 nm and a time per data point of 0.166 s using a Varian Cary 4000 UV-Vis spectrometer at 25°C.

Transmission electron microscopy measurements of Au clusters

HAADF-STEM images were recorded using a 200kV F20 UT Tecnai electron microscope at the National Center for Electron Microscopy at Lawrence Berkeley National Laboratory. At least 200 particles were measured to obtain a particle size distribution. The samples were prepared by dissolving the cluster in dichloromethane and placing a 2-3 drops on to a ultra-thin holey carbon coated copper grid (Ted Pella)

Fluorescence binding measurements

Based on procedures published for determining the accessibility of Au clusters using 2-NT as a probe molecule,[8,9] a similar titration experiment using adsorption of 2-NT onto cluster **H1-red** was performed and followed using steady-state fluorescence. The 2-NT fluorescence emission was measured on a Hitachi F-4500 Fluorimeter operating at 950 V and with an excitation/emission slit width of 5 nm (excitation wavelength was 283 nm). A typical procedure was as follows: 0.35 mg of **H1-red** were dissolved in 3 mL of dicholoromethane and 20 μL doses of 2-NT solution (1.0 mM 2-NT in dichloromethane) were added directly to the cuvette. The cuvette was shaken for 1 minute and equilibrated for 5 minutes before steady-state

fluorescence measurements were recorded. All measurements and 2-NT titration experiments were conducted at 25°C. The peak of the 2-NT is observed at 350 nm.[8,9] Each fluorescence spectra is normalized at 308 nm, as described previously.[8,9] Each point on the titration curve represents a 20 μL dose of the 2-NT solution.

The large background fluorescence emission of all NHC-calixarene bound clusters (i.e. in the absence of any fluorophore probe molecule) was problematic from the standpoint of quantifying accessible and open surface sites via titration with 2-NT. This background fluorescence emission blocked our ability to accurately and reliably measure the binding of 2-NT to the gold surface. To exemplify this background fluorescence problem, Figure S34 shows the steady-state fluorescence emission spectra for solutions of **T1-red** and **C2-red** at a concentration of 120 μM (in Au atoms) for each cluster. The spectrum of the **C2-red** cluster shows a broad band that extends into the range where the peak fluorescence emission of 2-NT is located, at 350 nm.

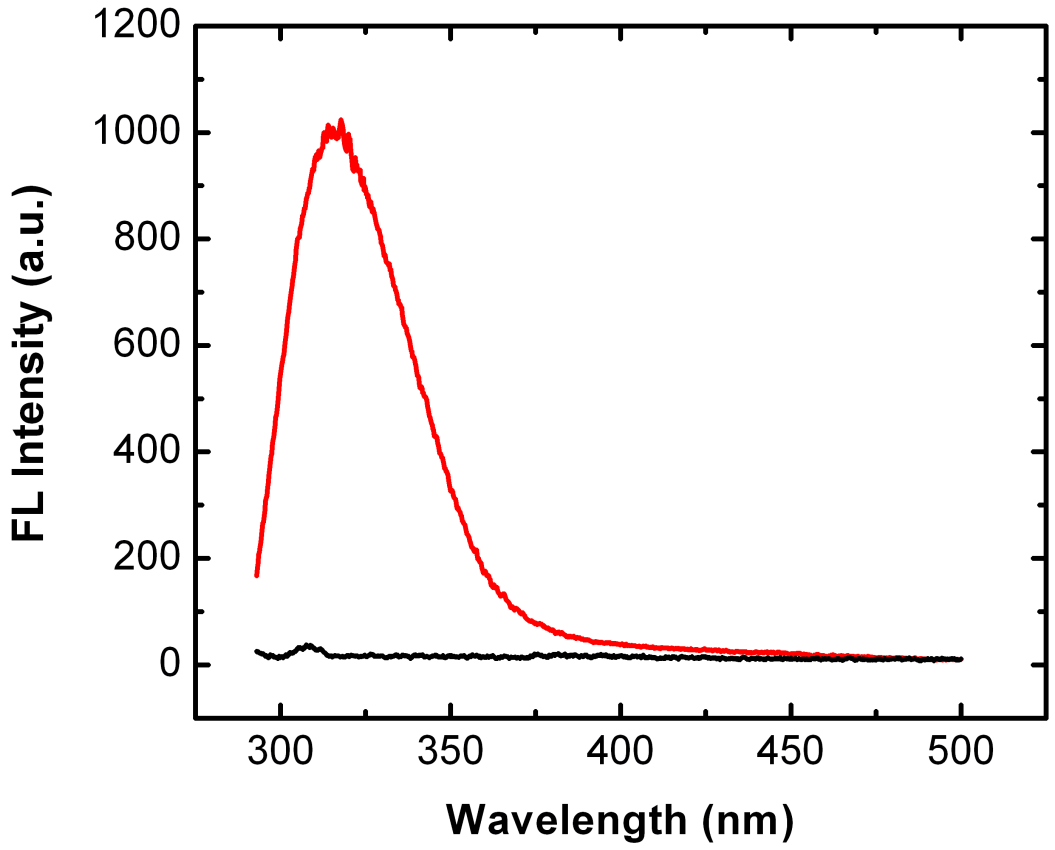


Fig. S39 FL spectra of **T1-red** (black) and **C2-red** (red) excited at 283 nm at gold atom concentrations of 120 μM.

SAMSA-Fluorescein titrations

Due to the large background fluorescence of all calixarene NHC-bound gold clusters investigated here, we developed a new method for titrating and quantifying density of accessible, open "coordinatively unsaturated" sites on gold clusters. This method replaced 2-NT with a probe molecule that emits/excites at lower energy – to avoid the overlap with background fluorescence described above and shown in Figure S34. This new method is based on a SAMSA fluorescein dye as fluorescent probe molecule, which is able to bind to the gold surface by virtue of its pendant thioester/thiol functionality. The SAMSA fluorescein was activated according to procedures described by the manufacturer (Molecular Probes). To activate the SAMSA-fluorescein, 5 mg of SAMSA fluorescein was dissolved in 0.5 mL of 0.1 M NaOH solution for 15 minutes. The solution was then neutralized with 7 uL of 6 M HCl and buffered with 0.1 mL of 0.5 M sodium phosphate buffer at pH = 7. After the SAMSA fluorescein was activated, we proceeded with the titration experiments. In the titration experiments, our approach was to dissolve a known mass of gold cluster in 3 mL of isopropanol and add 20 μL doses of 0.25 mM SAMSA fluorescein to the cluster. After the SAMSA fluorescein was added to the gold cluster, the resulting solution was shaken for 1 minute and stored in the dark for 15 minutes. Immediately following this, the steady-state fluorescence emission was measured using a Hitachi F-4500 Fluorimeter operating at 450 V and with an excitation/emission slit width of 5 nm exciting at 470 nm, and looking the peak height at 520 nm. The titrations were performed at 25°C.

To demonstrate the new approach, we used it on a cluster with a known number density of open "coordinatively unsaturated" sites, as measured by 2-NT titration. Our goal was to investigate whether or not a similar number density of open sites could be measured for both 2-NT and SAMSA fluorescein when using the same known cluster consisting of **T1-red**. Thus, 0.075 mg of cluster **T1-red** present was dissolved in 3 mL of isopropanol. When using a solution of 0.25 mM 2-NT to titrate, the expected uptake of 2-NT was measured, based on 2-NT titrations previously reported.[8]

$$(0.075 \text{ mg cluster } \mathbf{T1\text{-}red})\left(\frac{21.3 \text{ mg Au}}{100 \text{ mg cluster}}\right)\left(\frac{\text{g Au}}{1000 \text{ mg Au}}\right)\left(\frac{\text{mol Au}}{197 \text{ g Au}}\right)\left(\frac{2.7 \text{ open mol Au}}{11 \text{ mol Au}}\right)$$
$$\times\left(\frac{1 \text{ mol 2-NT}}{1 \text{ open mol Au}}\right)\left(\frac{10^6 \text{ μL}}{0.25\ (10^{-3}) \text{ mol 2-NT}}\right) = 79.6 \text{ μL}$$

Based on previously reported 2.7 open sites per Au_{11} fragment in **T1-red**,[8] 79.6 μL of 0.25 mM 2-NT solution is expected to be needed to bind all of the open sites on **T1-red**.

Using the SAMSA-fluorescein titrant with the same mass of **T1-red** and the same concentration of titrant (0.25 mM), the amount of SAMSA fluorescein needed to titrate the open sites on cluster **T1-red** was measured. The equivalence point of the SAMSA-fluorescein titration was

determined by finding the point of intersection of different slopes of fluorescence intensity versus amount of SAMSA-fluorescein added. This is based on the previously observed rationale that a fluorophore dye molecule with pendant thioester/thiol functionality emits at greater intensity when bound to a gold nanoparticle surface rather than when present in solution.[10] Linear regression was used to determine the point of intersection alluded to above.

An example titration plot using SAMSA fluorescein is shown below.

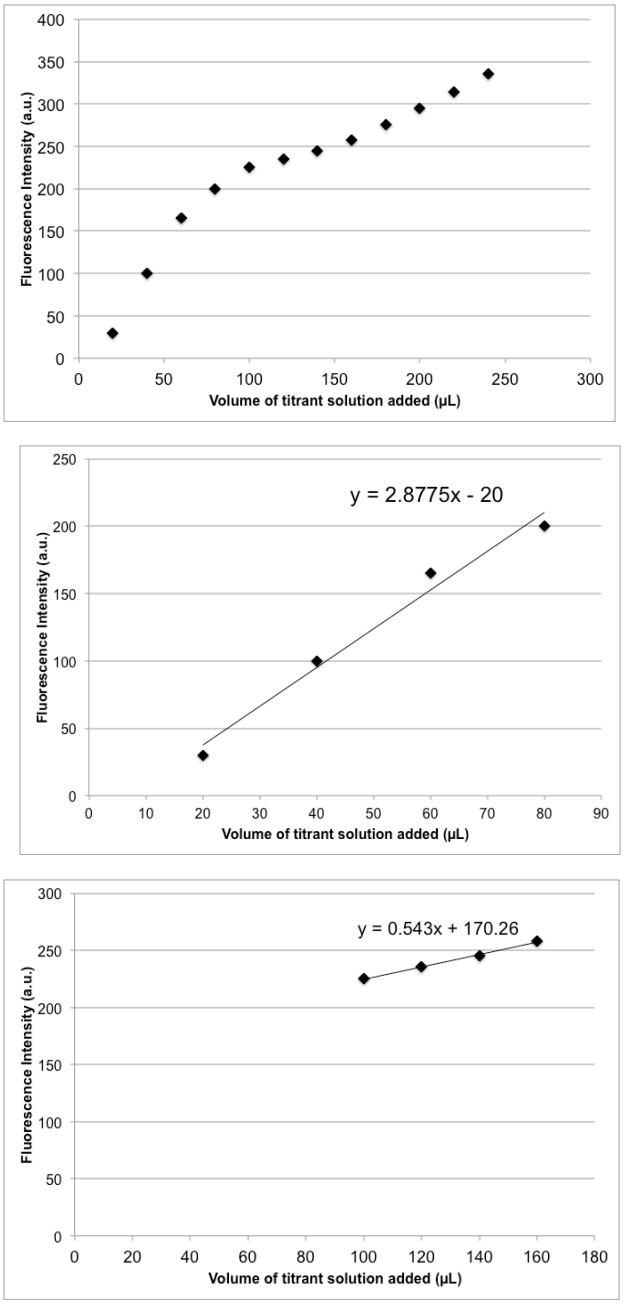


Fig. S40 SAMSA-fluorescein titration data for **T1-red**. The linear regressions are shown for the two differently sloped regions of the graph. The equivalence point was shown to be when 81 µL of 0.25 mM SAMSA solution was added for 0.075 mg of **T1-red** in this experiment.

The data in Fig. S40 illustrate a 1:1 correspondence with the amount of 2-NT needed to titrate an open site on **T1-red** and the amount of SAMSA fluorescein needed to titrate an open site on **T1-red**. The data in Figure S41 show that the amount of bound SAMSA fluorescein increases linearly with the mass of **T1-red** in solution, and that the slope of the line represents the same

accessible number density of open sites on **T1-red** when using SAMSA fluorescein as a probe molecule, relative to when using 2-NT as a probe molecule.

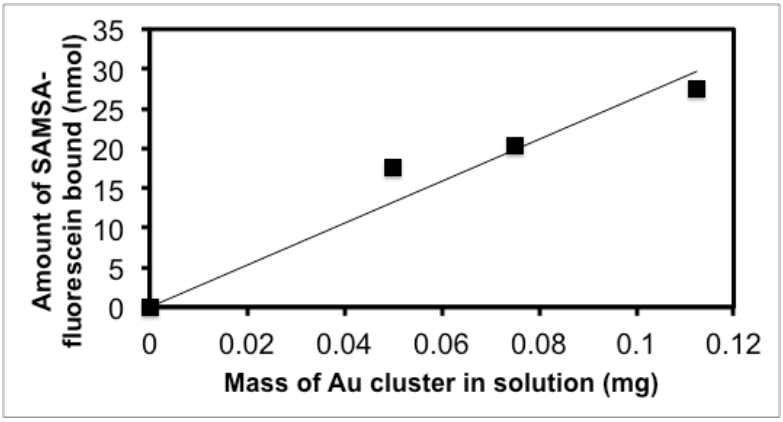


Fig. S41 Linear dependence of SAMSA fluorescein bound as a function of **T1-red** in solution.

The new procedure based on using a SAMSA fluorescein probe was also used for determining the number of open sites on **C2-red**. An example is shown in Figure S42.

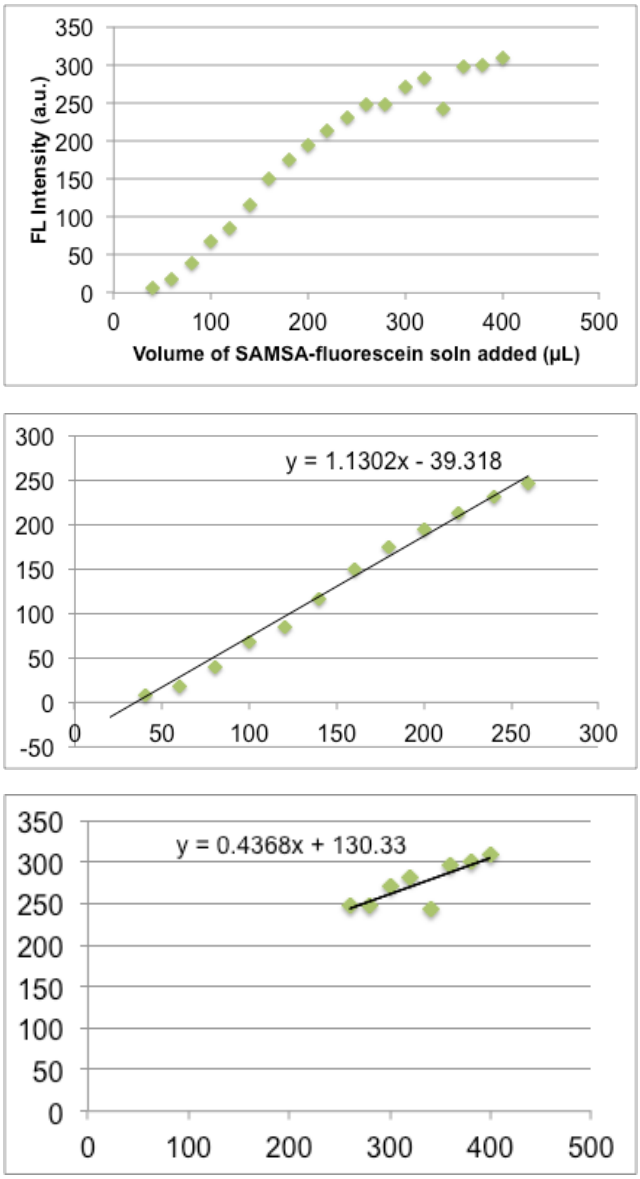


Fig. S42 SAMSA-fluorescein titration data for **C2-red**. (top) The linear regressions of the data in the top panel are shown for the two differently sloped regions of the graph. (middle and bottom) The equivalence point was shown to be when 244 µL of SAMSA solution was added for 0.8 mg of **C2-red** in this experiment.

Knowing the equivalence point, the amount of open sites on **C2-red** was calculated as shown below.

Total number of open sites titrated by SAMSA fluorescein:

$$244(10^{-6})\text{ L solution}\left(\frac{0.25(10^{-3})\text{ mol SAMSA F}}{\text{L solution}}\right)\left(\frac{\text{mol open Au sites}}{\text{mol SAMSA F}}\right)\left(\frac{197\text{ g open Au sites}}{\text{mol open Au sites}}\right)$$
$$= 1.2(10^{-5})\text{ g open Au sites}$$

Total number of surface sites on a 1.2 nm particle:

$$0.8\text{ mg C2-red}\left(\frac{\text{g C2-red}}{10^3\text{ mg }\mathbf{C2\text{-}red}}\right)\left(\frac{0.29\text{ g Au total}}{\text{g C2-red}}\right)\left(\frac{0.72\text{ g Au surface}}{\text{g Au total}}\right)$$
$$= 1.67(10^{-4})\text{g Au surface}$$

$$\frac{1.2(10^{-5})\text{g open Au sites}}{1.67(10^{-4})\text{g Au surface}} = 0.072$$

7.2% of the gold surface area of **C2-red** is accessible to SAMSA fluorescein at this data point.

Different masses of **C2-red** were used to determine the linearity of the response of the equivalence point of the titration and gold cluster mass. The results are shown in Figure S43. The equivalence point scales linearly with gold cluster mass as expected.

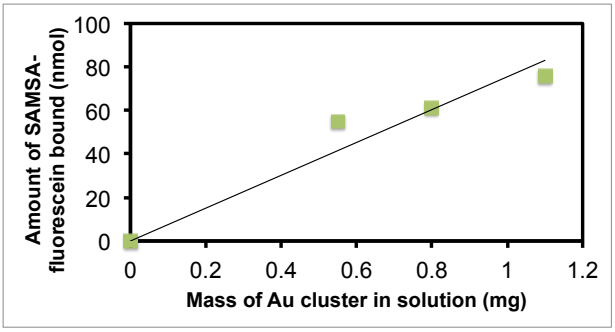


Fig. S43 Amount of SAMSA-fluorescein bound per mass of **C2-red** in solution.

The dispersion of **C2-red** was calculated using a volumetric average using the particle size distribution in Fig. 1. The volume averaged size was found to be 1.38 nm. Using a spherical model and the density of gold, the number of atoms in this particle was calculated.

$$\frac{4}{3}\pi\left(\frac{1.38(10^{-9})\text{m}}{2}\right)^3\left(\frac{1.93(10^7)\text{g Au}}{\text{m}^3}\right)\left(\frac{\text{mol Au}}{197\text{ g Au}}\right)\left(\frac{6.022(10^{23})\text{ Au atoms}}{\text{mol Au}}\right) = 81\text{ Au atoms}$$

Assuming **C2-red** consists of an 81-atom cluster, the amount of surface atoms was calculated using correlations with a full shell model. (see p. 395 of Supported Gold Nanoparticles as Oxidation Catalysts by A. Corma and H. Garcia (Chapter 12) in *Nanoparticles and Catalysis*, Wiley-VCH (2008), Volume 1, Editor: Didier Astruc). Using linear interpolation between a 55 atom cluster having 76% of the atoms on the surface and a 147 atom cluster having 63% of the atoms on the surface, an 81 atom cluster is estimated to have 72% of the gold atoms on the

surface. Using this knowledge of the dispersion, the data in Fig. S43 leads to 7.1% of the surface sites as open sites, using the slope of the line of best fit (75.5) from Fig. S43. The calculation is shown below.

$$\frac{75.5\left(10^{-9}\right)\text{mol SAMSA F}}{\text{mg C2-red}}\left(\frac{1\text{ mol open sites}}{1\text{ mol SAMSA F}}\right)\left(\frac{1000\text{ mg C2-red}}{1\text{ g C2-red}}\right)\left(\frac{100\text{ g C2-red}}{29\text{ g Au}}\right)\left(\frac{100\text{ g Au total}}{72\text{ g Au surface}}\right)\left(\frac{197\ g\ Au\ surface}{mol\ Au\ surface\ atoms}\right) = 0.071\frac{mol\ open\ sites}{mol\ Au\ surface\ atoms}$$

TGA measurements of Au clusters

TGA measurements were performed using a TA instruments Model 2950 to determine the amount of organic material present in the reduced clusters. A mixture of 20% oxygen, balance argon was passed over the sample for 10 minutes under isothermal conditions and the sample was heated to 800°C at a rate of 5°C min^{-1}.

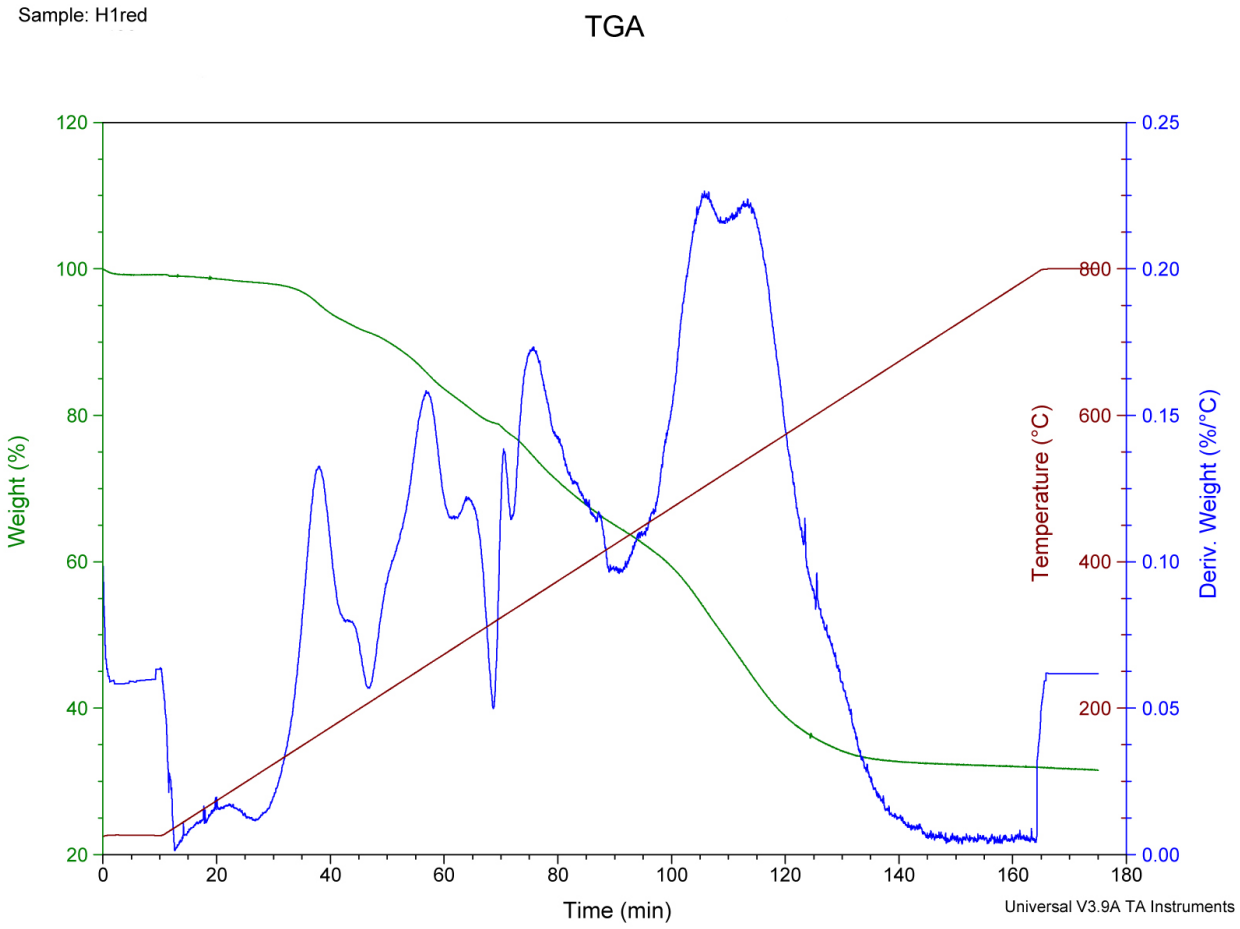


Fig. S44 TGA of **H1-red**

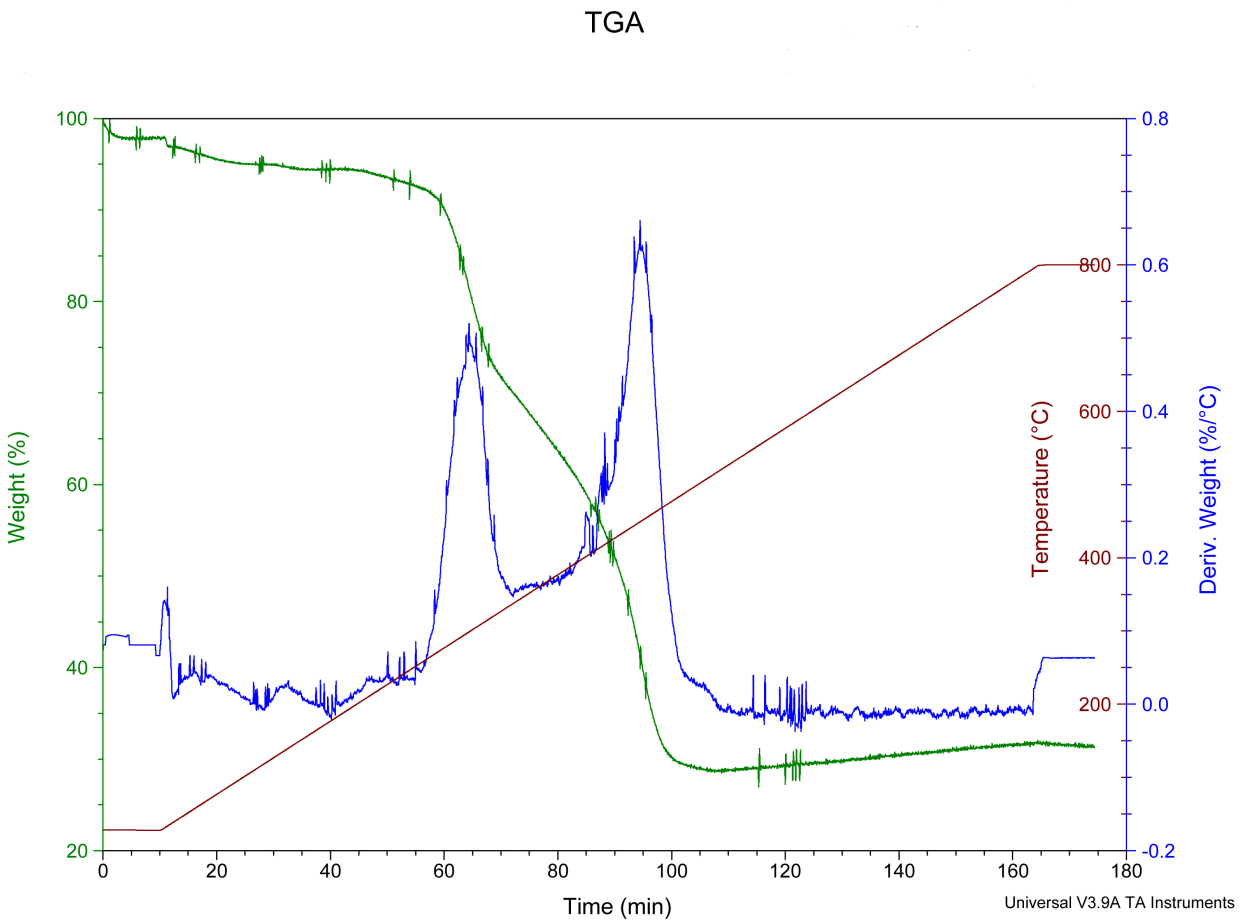


Fig. S45 TGA of **C1-red**.

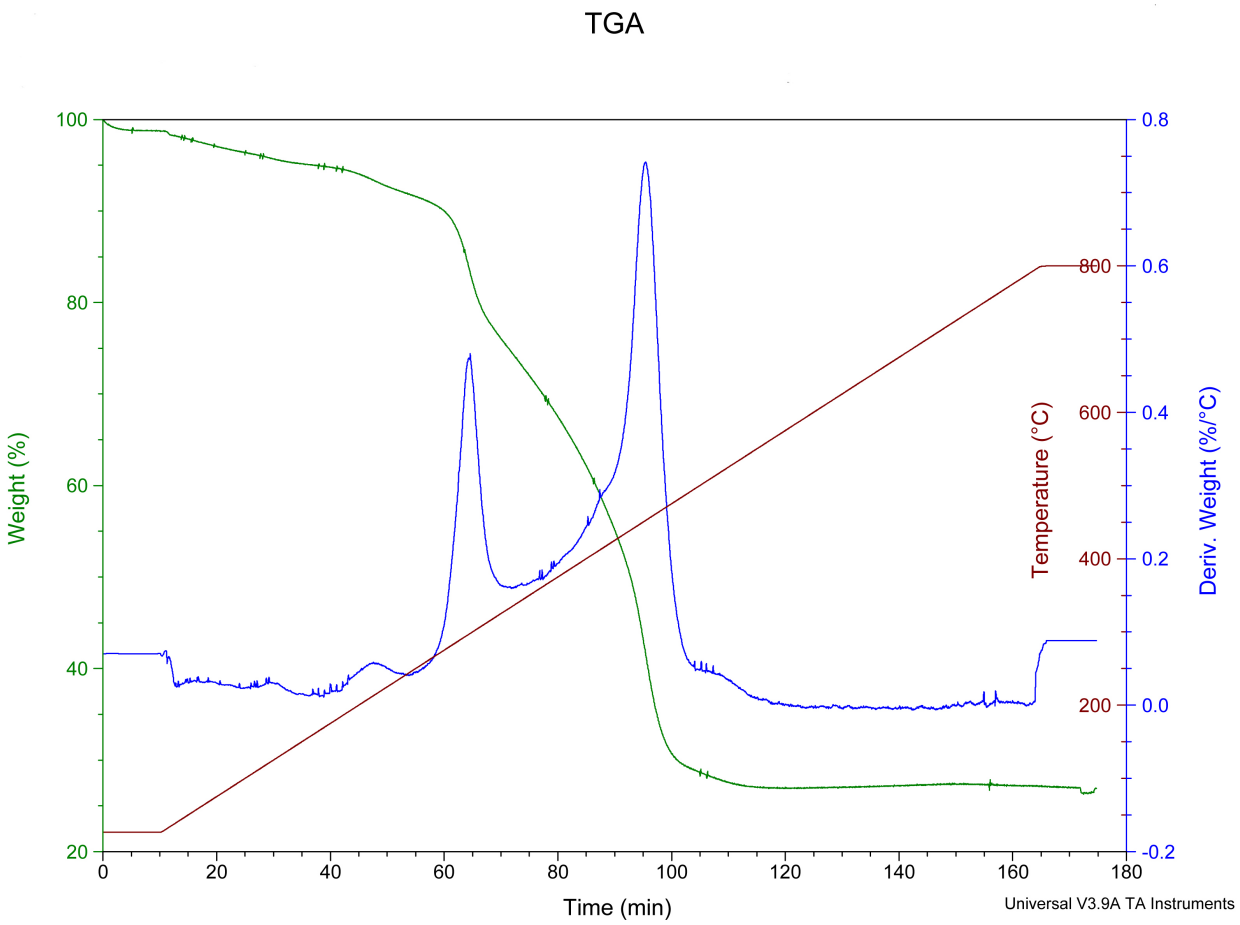


Fig. S46 TGA of **C2-red**

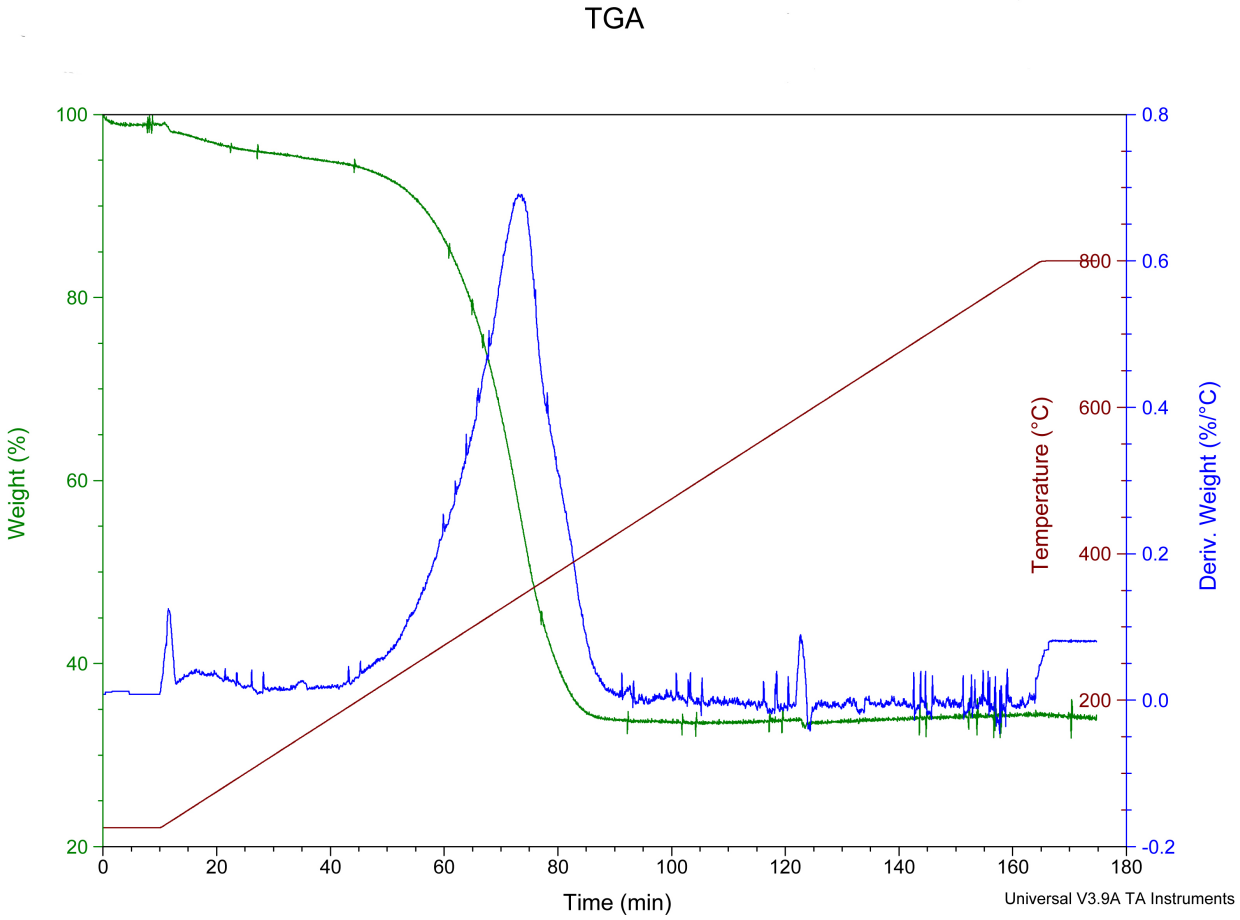


Fig. S47 TGA of **C3-red**.

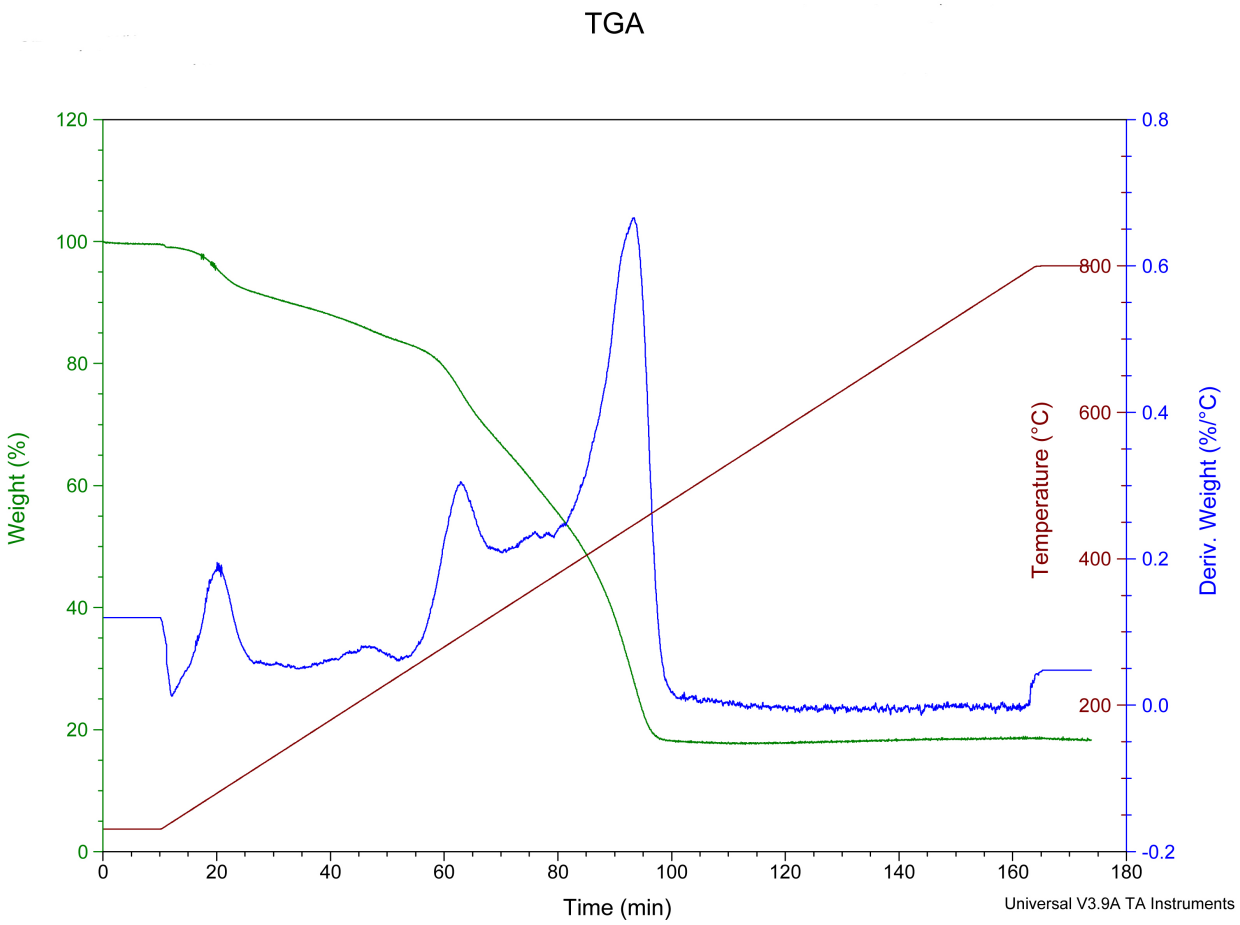


Fig. S48 TGA of **D1-red**

XPS characterization data of H1-red

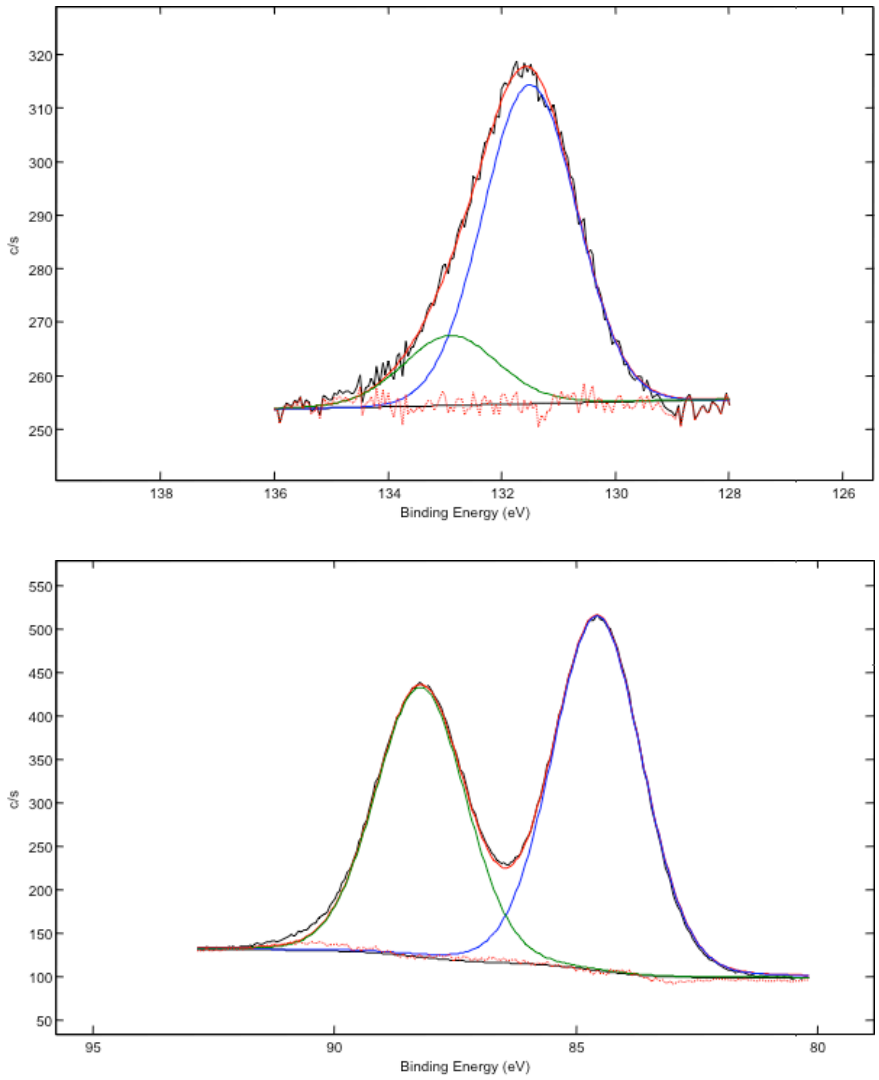


Fig. S49 (top) P 2p and (bottom) Au 4f XPS results for **H1-red**. Deconvolution of the P 2p results shows the phosphine to phosphine oxide ratio to be 4.7 ± 1.5.

ESI-TOF MS data of H1-red

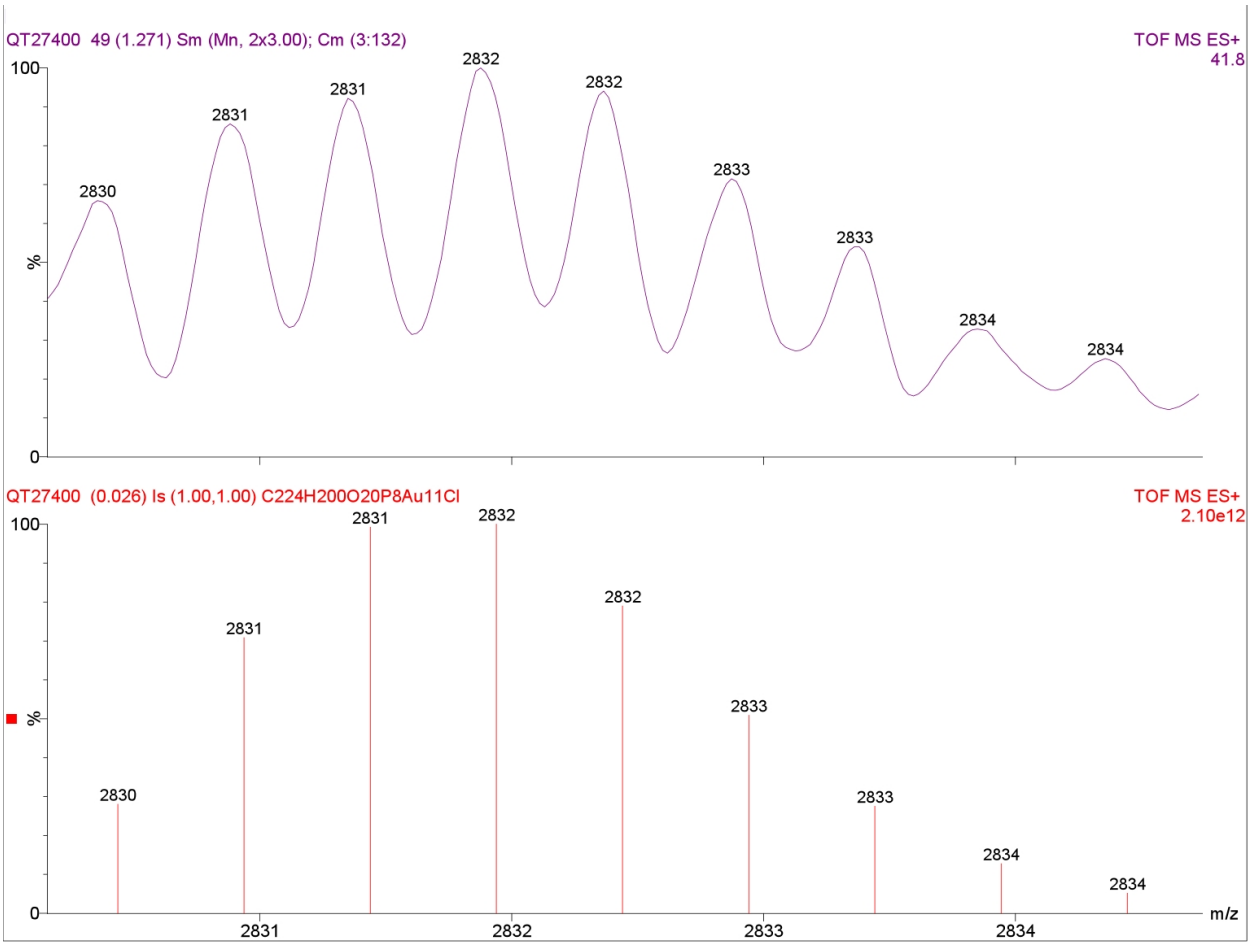


Fig. S50 ESI mass spectrum (+) showing a molecular ion fragment in **H1-red** (top) and theoretical simulation of $[Au_{11}L_4Cl]^{2+}$. L = **H1** with one of the P present as phosphine and the other P present as phosphine oxide.

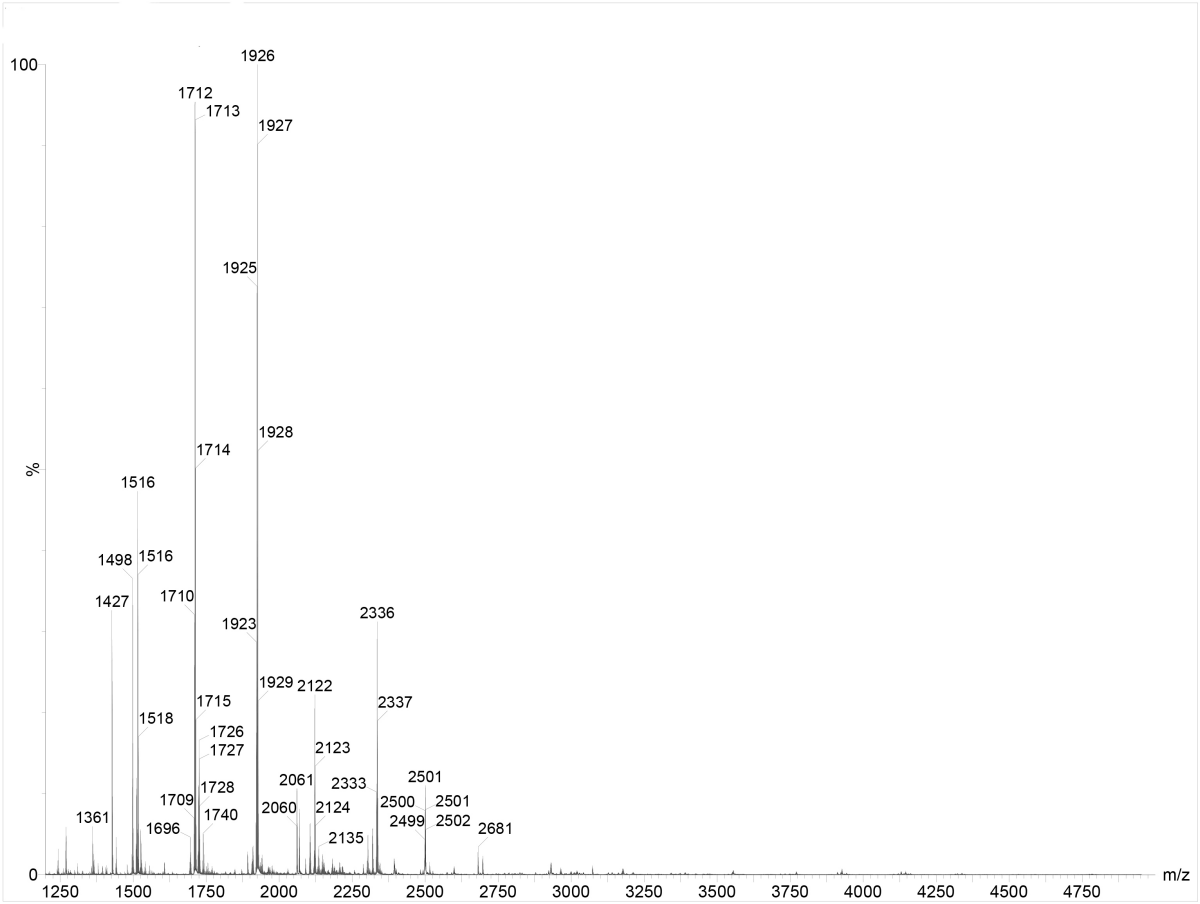


Fig. S51 Full ESI mass spectrum (+) for **H1-red**

References

1. K. Iwamoto, K. Araki and S. Shinkai, *Tetrahedron*, 1991, **47**, 4325-42.

2. P. J. Dijkstra, J. A. J. Brunink, K. E. Bugge, D. N. Reinhoudt, S. Harkema, R. Ungaro, F. Ugozzoli and E. Ghidini, *J. Am. Chem. Soc.,* 1989, **111**, 7567-75.

3. W. Wegener, *Z. Chem.,* 1971, **11**, 262-3.

4. C. D. Gutsche and K. A. See, *J. Org. Chem.,* 1992, **57**, 4527-39.

5. C. B. Dieleman, D. Matt and P. G. Jones, *J. Organomet. Chem.,* 1997, **545-546**, 461-73.

6. N. de Silva, A. Solovyov and A. Katz, *Dalton Trans.* 2010, **39**, 2194-7.

7. C.D. Gutsche, B. Dhawan, J. A. Levine. K. H. No and L. J. Bauer. *Tetrahedron,* 1983, **39** 409-26.

8. N. de Silva, J.-M. Ha, A. Solovyov, M. M. Nigra, I. Ogino, S. W. Yeh, K. A. Durkin and A. Katz, *Nat. Chem.*, 2010, **2**, 1062–8.

9. J.-M. Ha, A. Solovyov, and A. Katz, *Langmuir* 2009, **25**, 10548-53.

10. M. M. Y. Chen and A. Katz, *Langmuir*, 2002, **18**, 2413-20.