Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Gold Dipyrrin-Bisphenolates: A Combined Experimental and DFT Study of Metal-Ligand Interactions

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A. ^{1}H NMR spectra

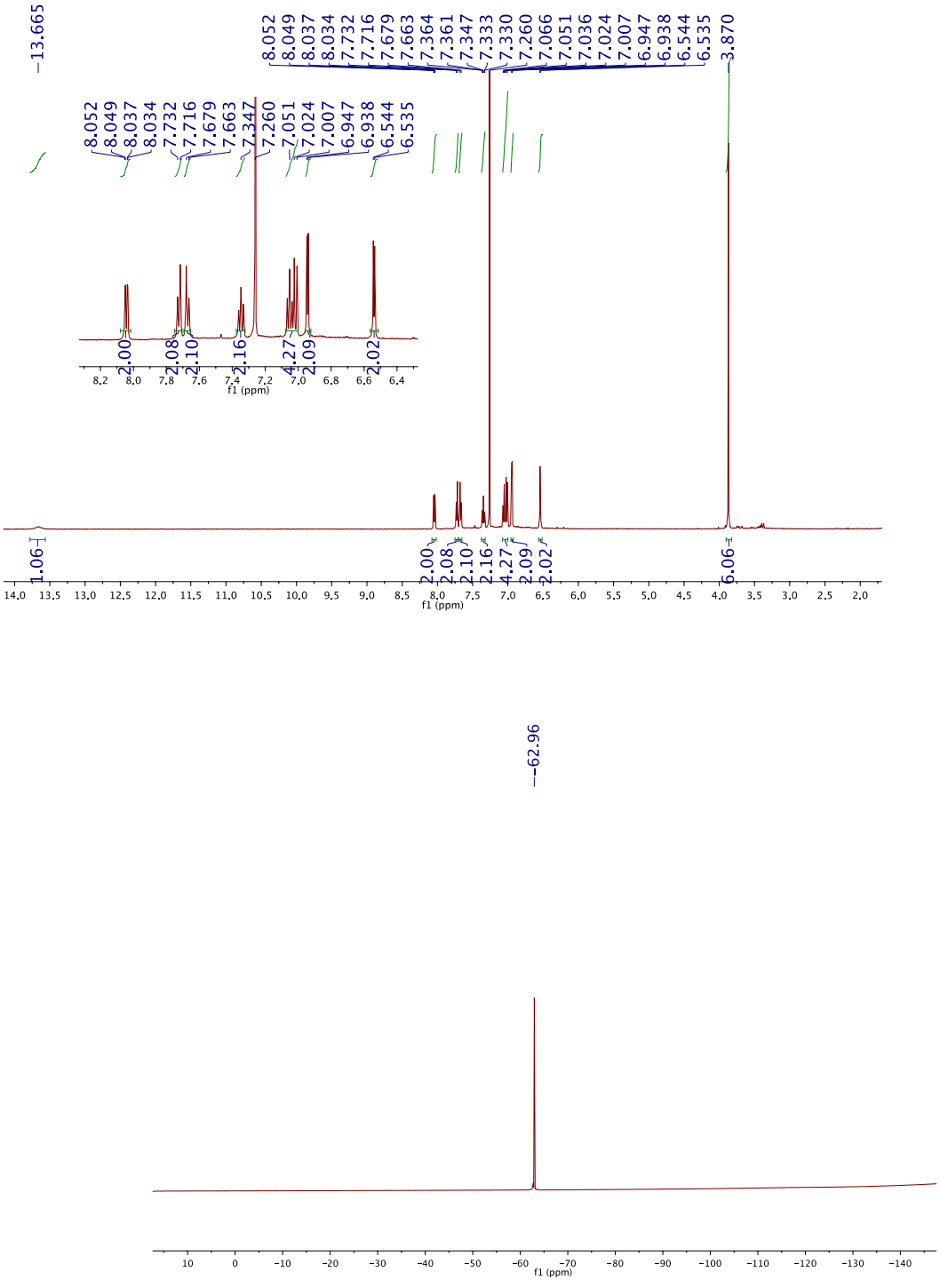

Figure S1. ^{1}H (500 MHz, $CDCl_3$) and ^{19}F (564 MHz, acetone-d_6) NMR spectra of **H_3[CF_3DPPOMe]**.

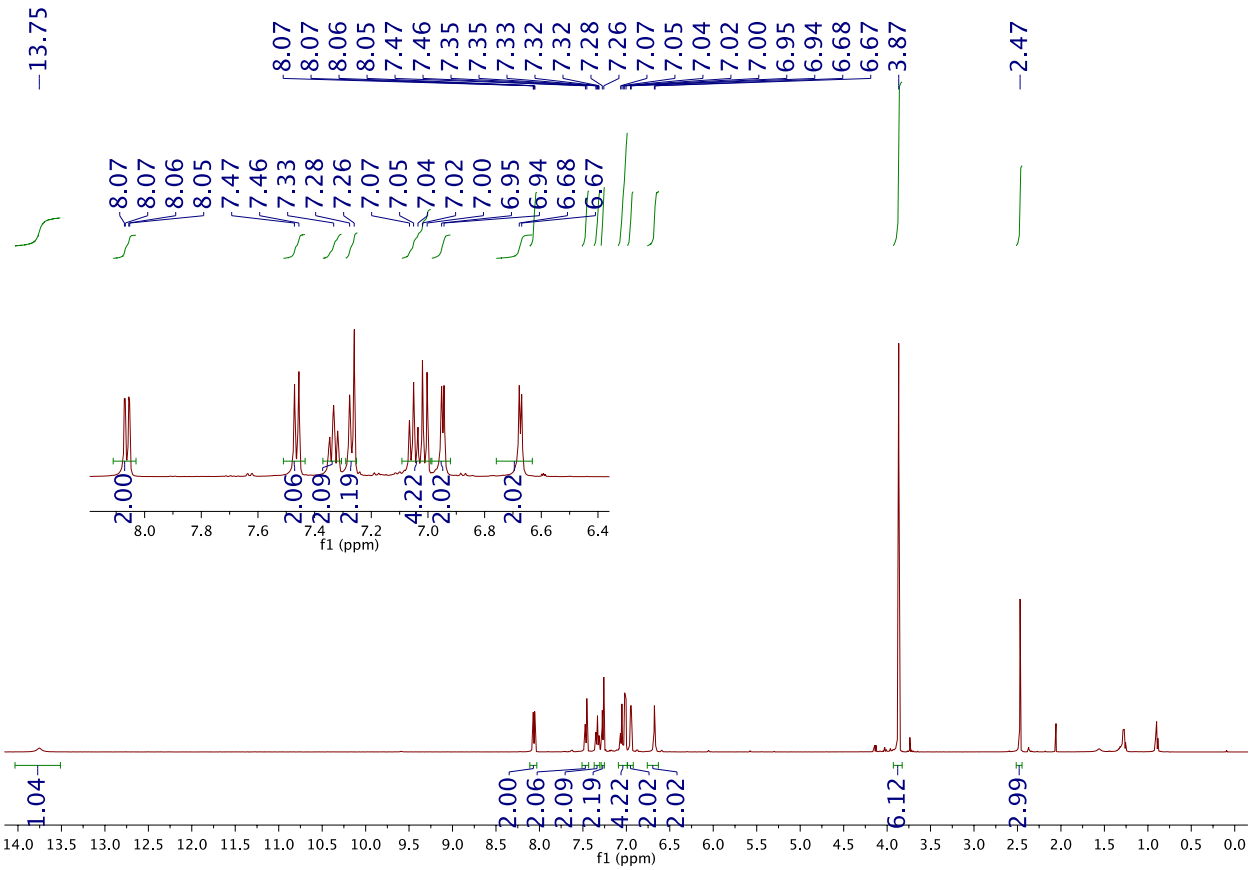

Figure S2. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **H_3[MeDPPOMe].**

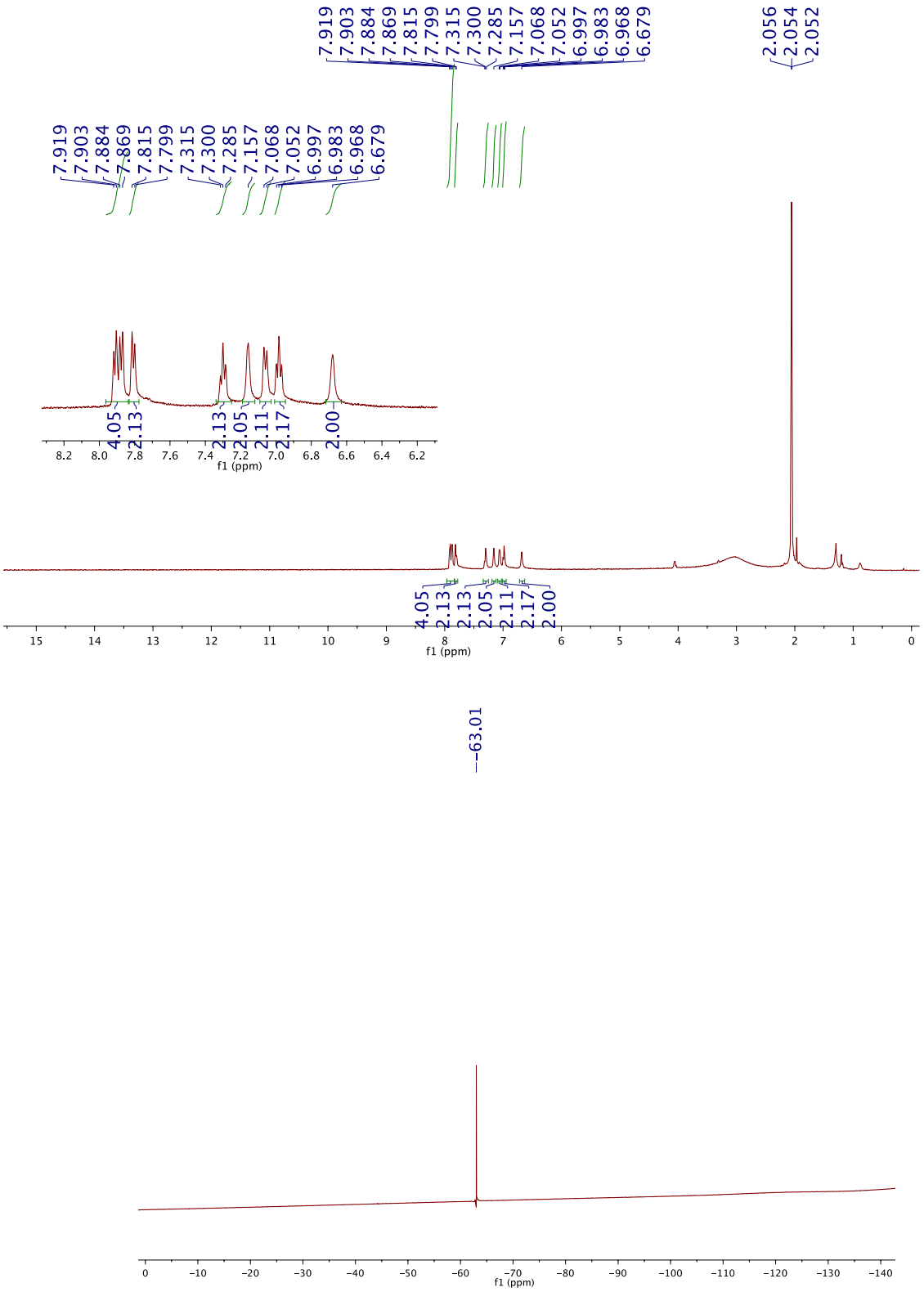

Figure S3. ^{1}H (500 MHz, acetone-d_6) and ^{19}F (564 MHz, acetone-d_6) NMR spectra of **H_3[CF_3DPP].**

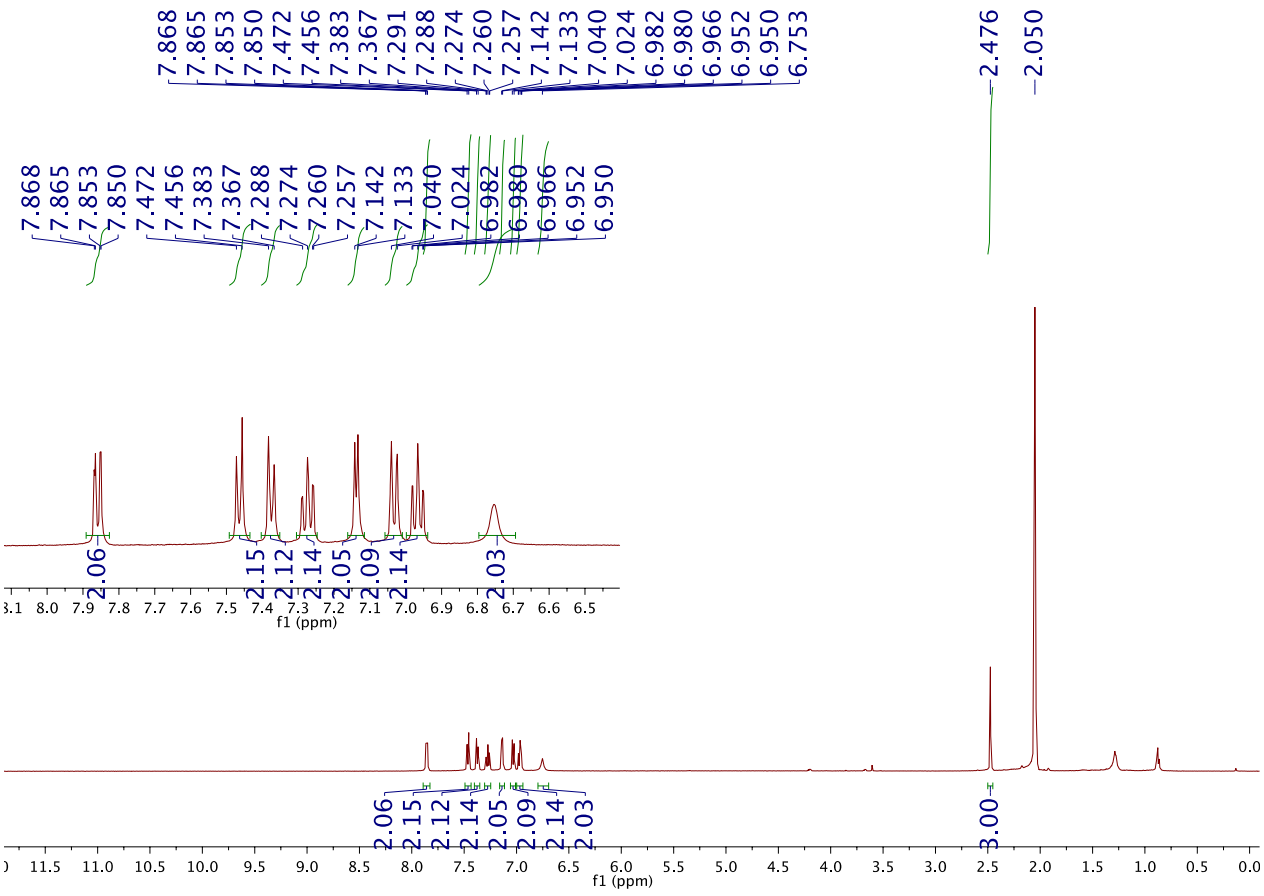

Figure S4. ^{1}H NMR (500 MHz, acetone-d_6) spectrum of **H$_3$[MeDPP].**

(* represents solvent impurity)

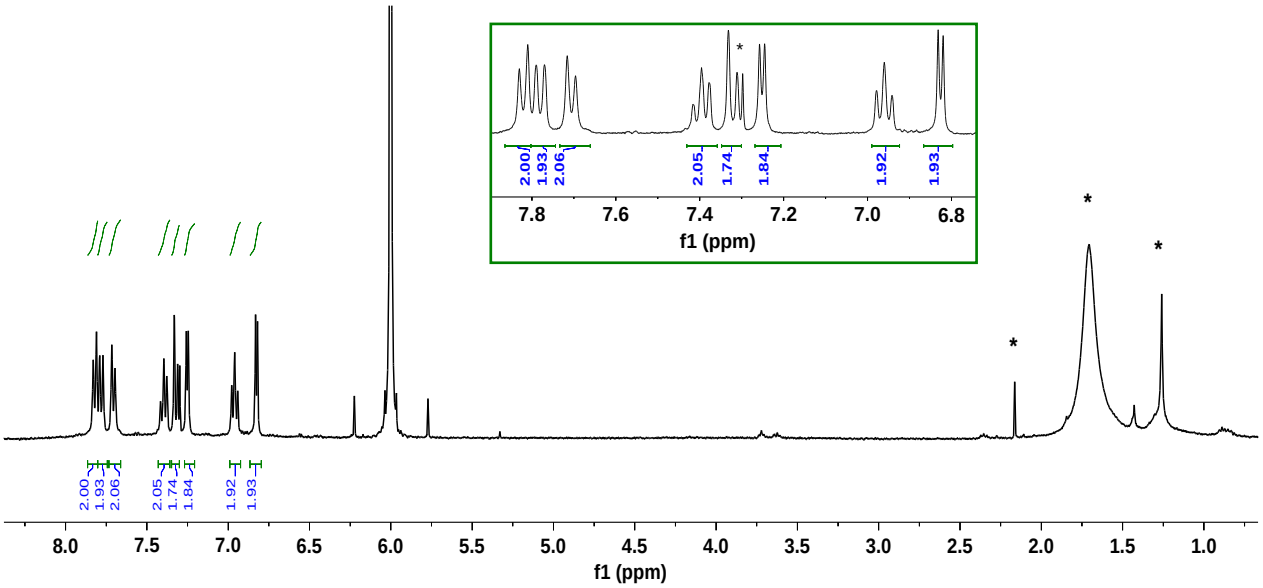

Figure S5.1. ^{1}H NMR (400 MHz, 1,1,2,2-tetrachloroethane-d_2) spectrum of **Au[CF$_3$DPP]**. Insert: Aromatic region.

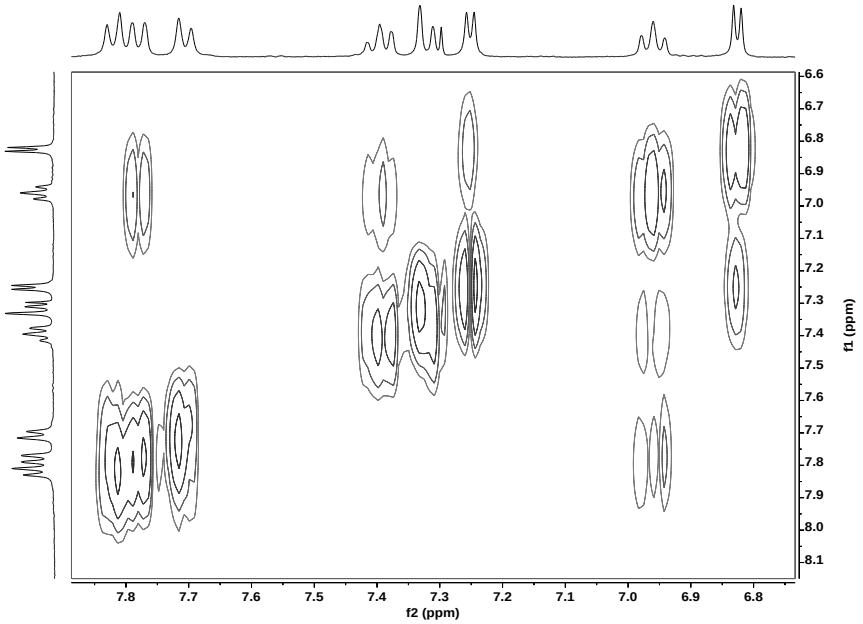

Figure S5.2. COSY (400 MHz, 1,1,2,2-tetrachloroethane-d_2) of **Au[CF$_3$DPP]**.

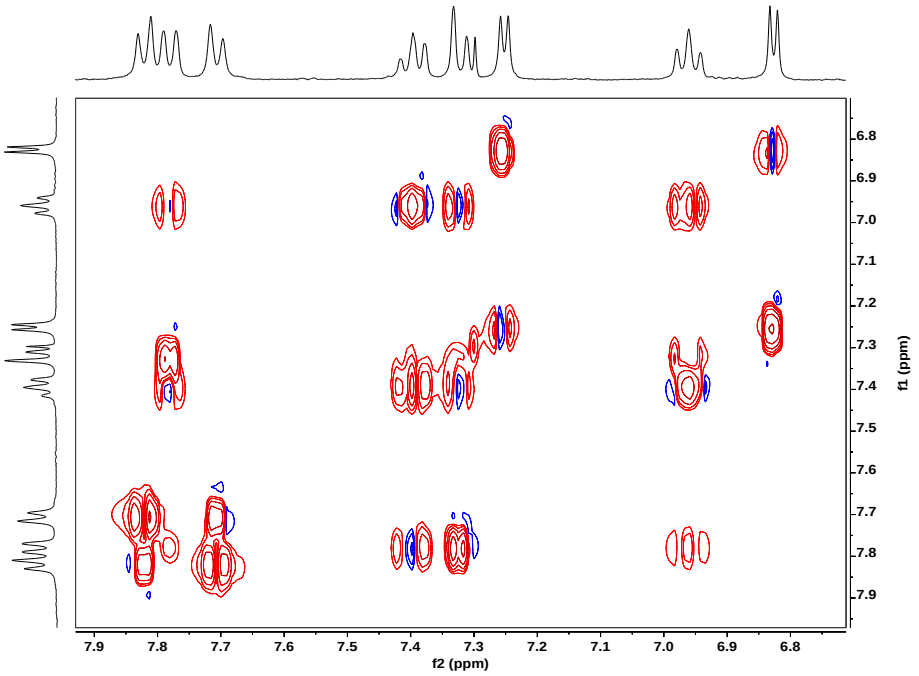

Figure S5.3. TOCSY (400 MHz, 1,1,2,2-tetrachloroethane-d_2) of **Au[CF$_3$DPP]**.

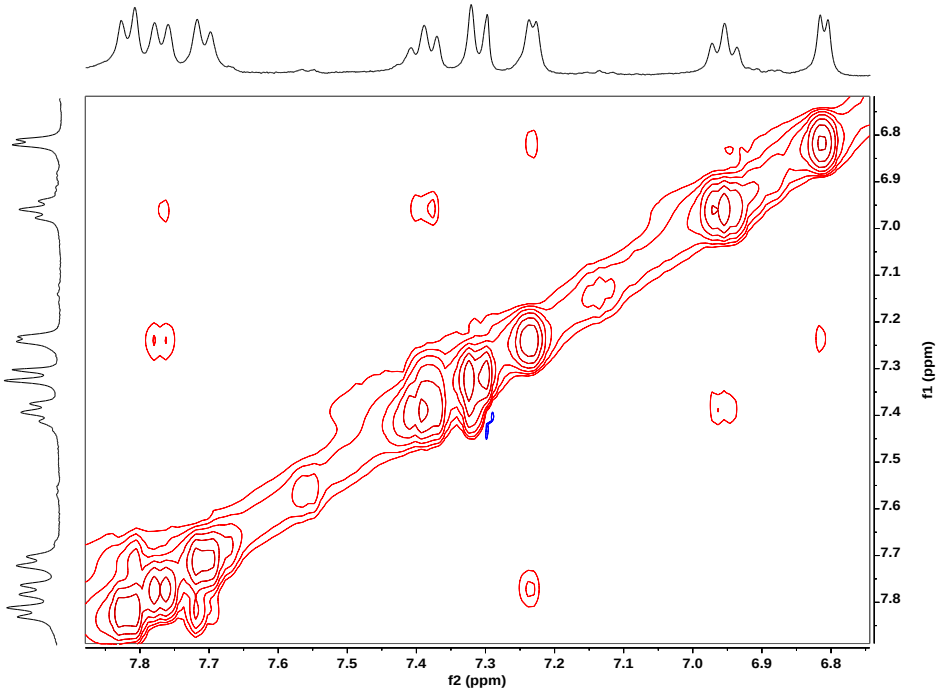

Figure S5.4. NOESY (400 MHz, 1,1,2,2-tetrachloroethane-d_2) of **Au[CF$_3$DPP]**.

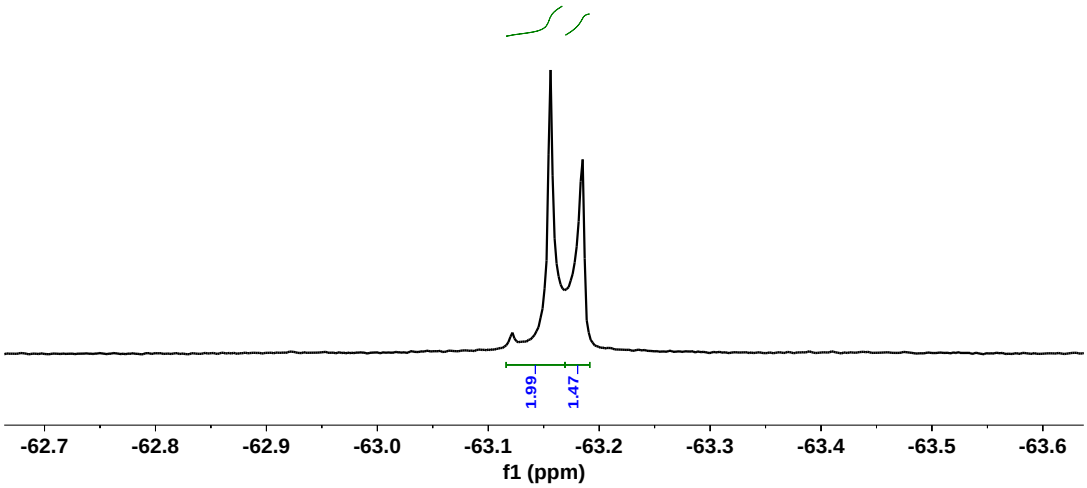

Figure S5.5. ^{19}F NMR (376 MHz, 1,1,2,2-tetrachloroethane-d_2) spectrum of **Au[CF$_3$DPP]**.

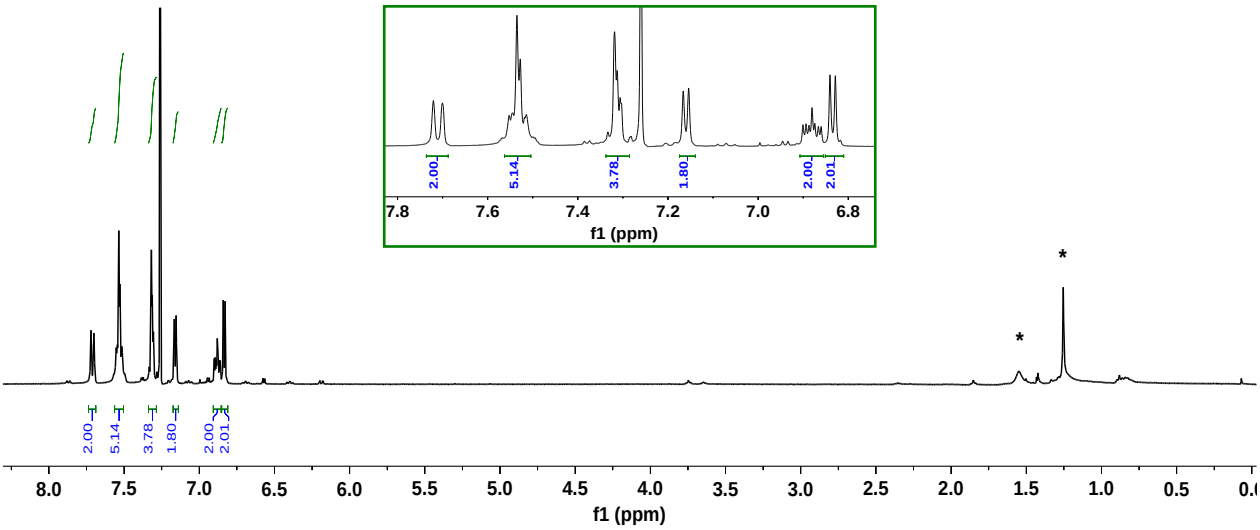

Figure S6.1. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **Au[HDPP**]. Insert:Aromatic region.

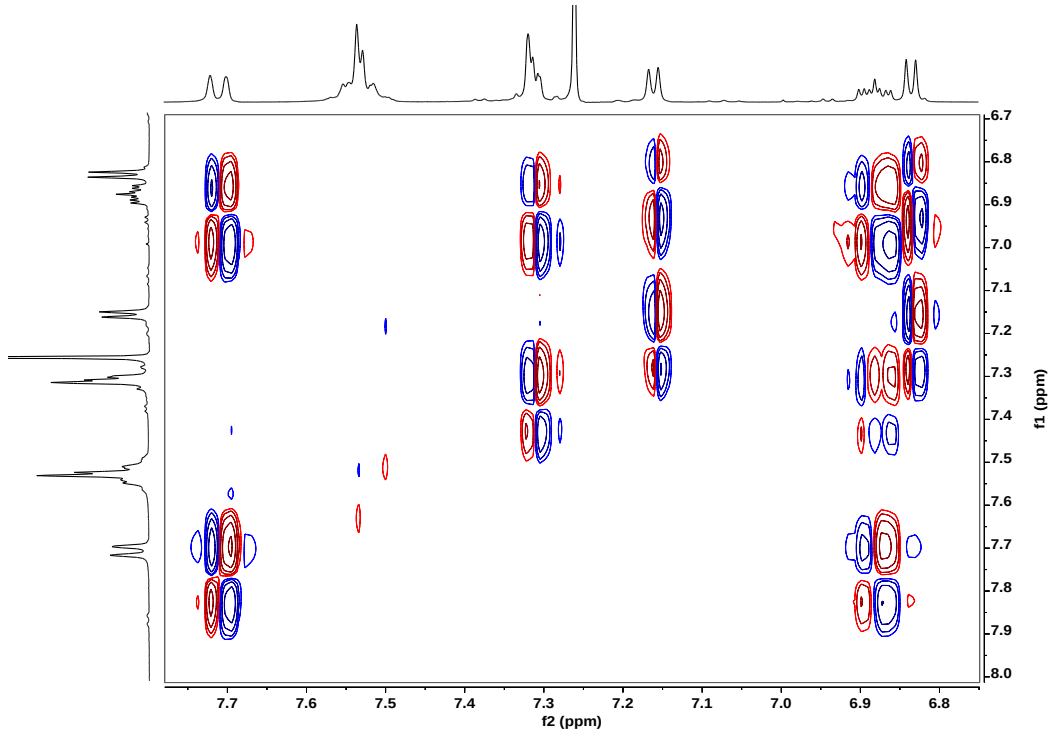

Figure S6.2. dqCOSY (400 MHz, $CDCl_3$) of **Au[HDPP]**.

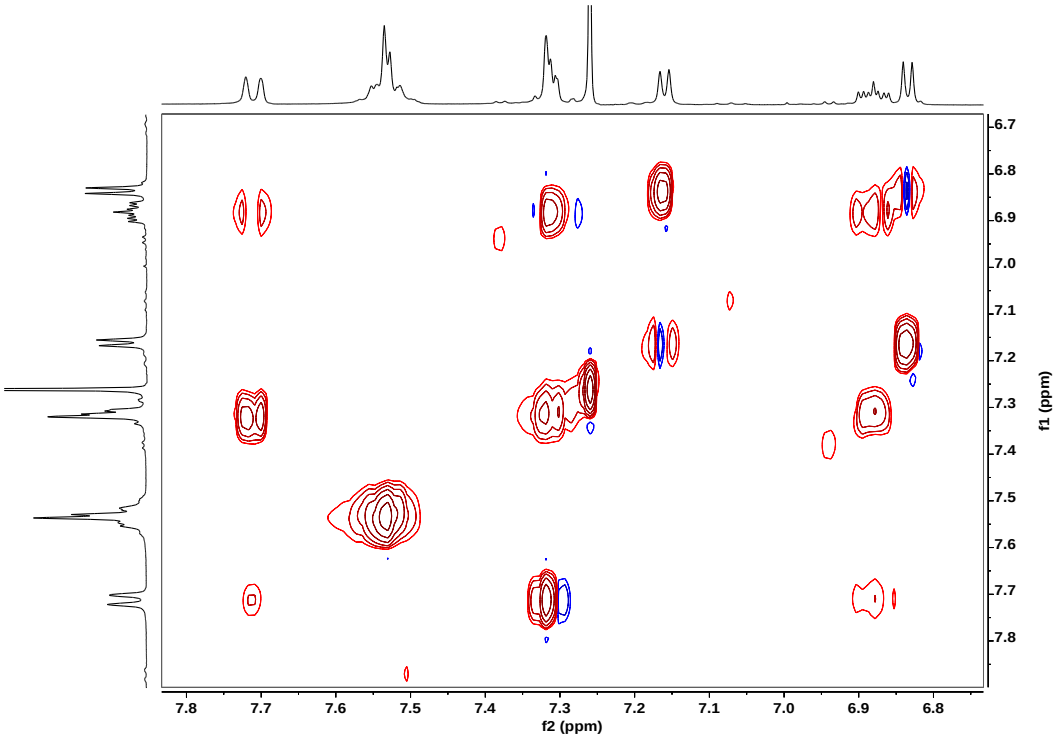

Figure S6.3. TOCSY (400 MHz, $CDCl_3$) of **Au[HDPP]**.

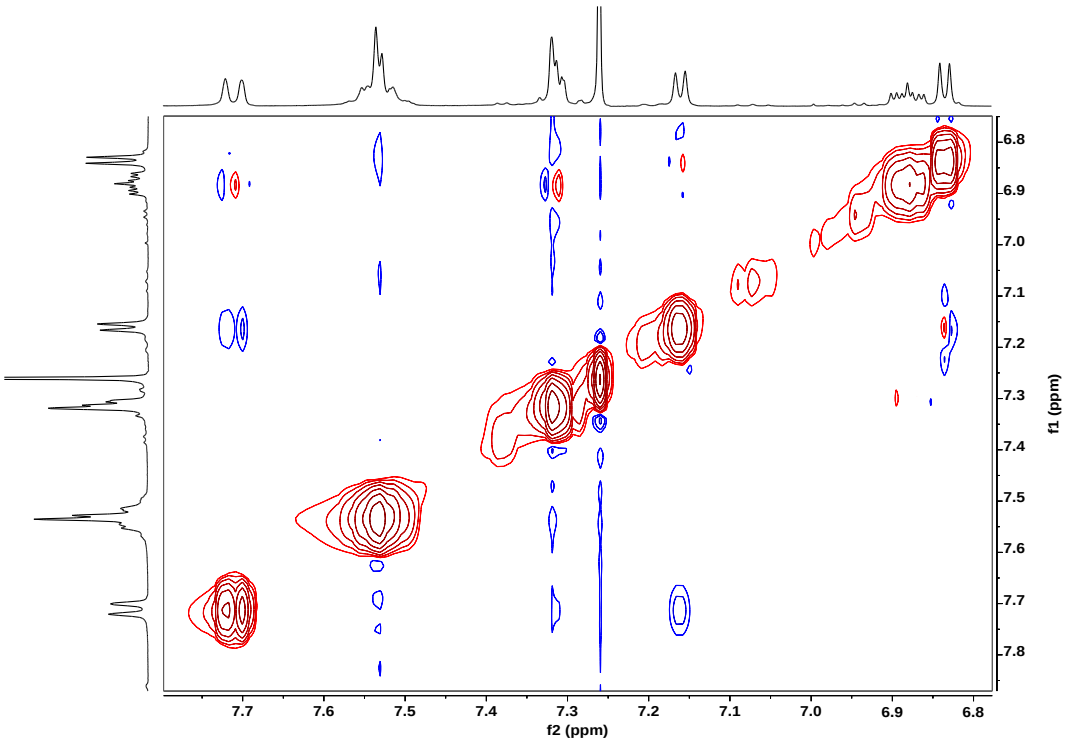

Figure S6.4. NOESY (400 MHz, $CDCl_3$) of **Au[HDPP].**

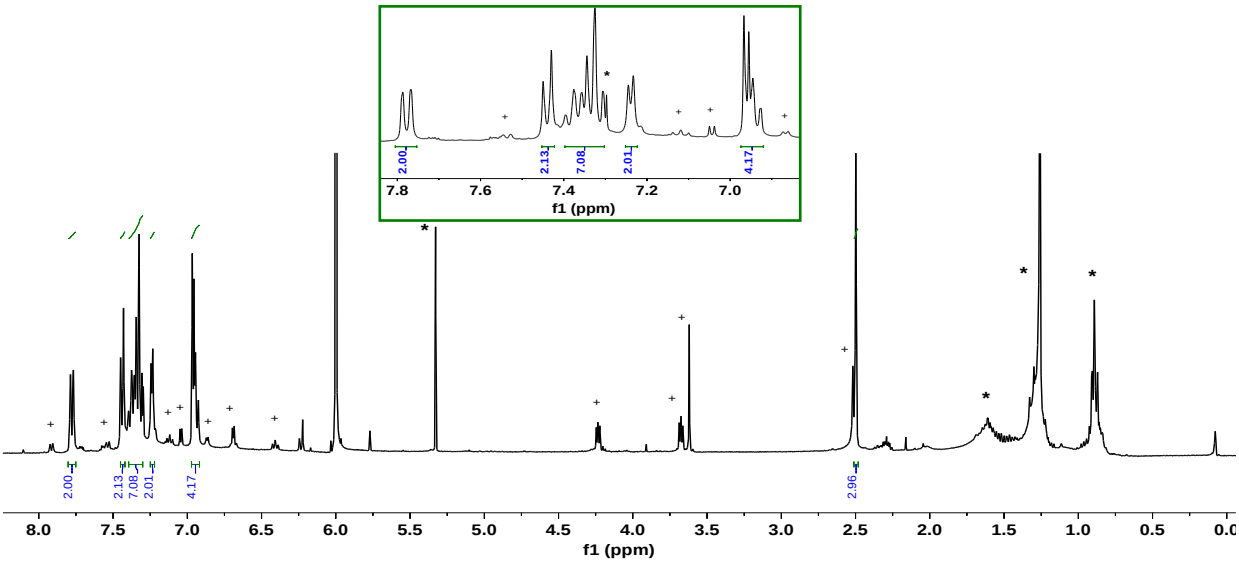

Figure S7.1. ^{1}H NMR (400 MHz, 1,1,2,2-tetrachloroethane-d_2) spectrum of **Au[MeDPP]**. Insert: Aromatic region; + represents a gold dipyrrin dimer impurity.

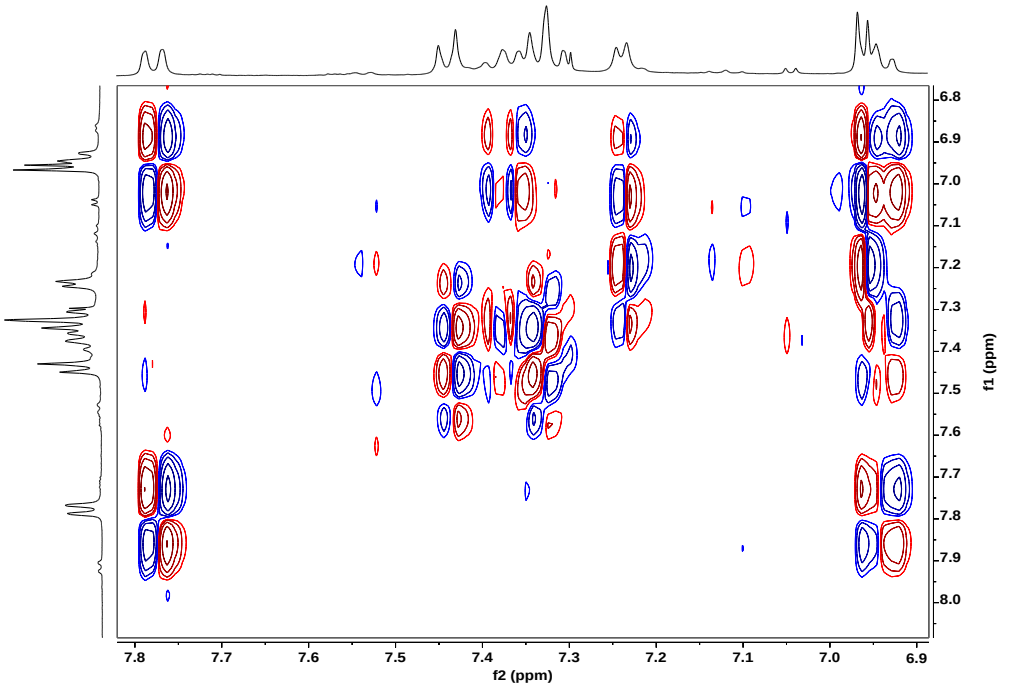

Figure S7.2. dqCOSY (400 MHz, 1,1,2,2-tetrachloroethane-d_2) of **Au[MeDPP]** (aromatic region).

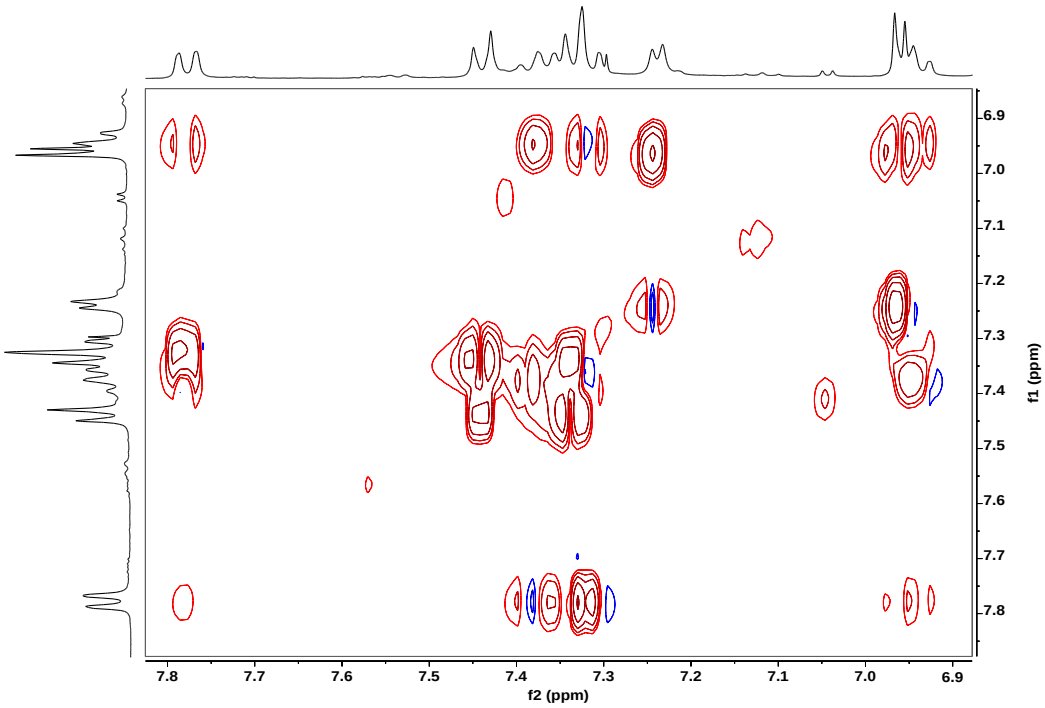

Figure S7.3. TOCSY (400 MHz, 1,1,2,2-tetrachloroethane-d_2) of **Au[MeDPP]** (aromatic region).

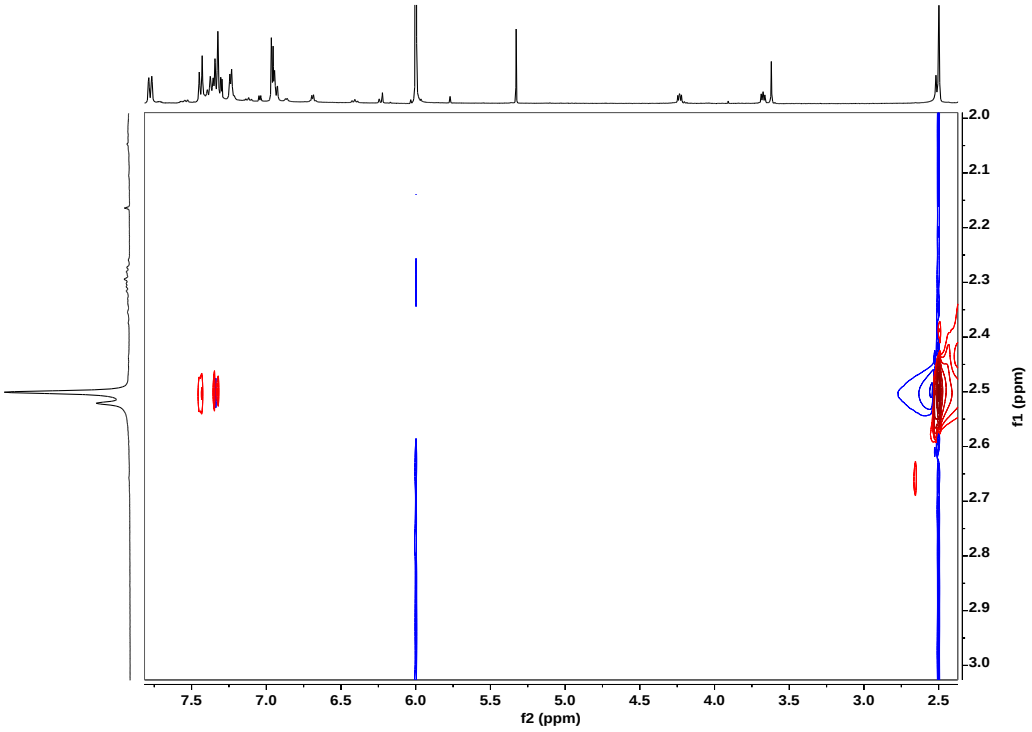

Figure S7.4. TOCSY (400 MHz, 1,1,2,2-tetrachloroethane-d_2) of **Au[MeDPP]** showing correlation between -*p*CH_3 and phenyl protons.

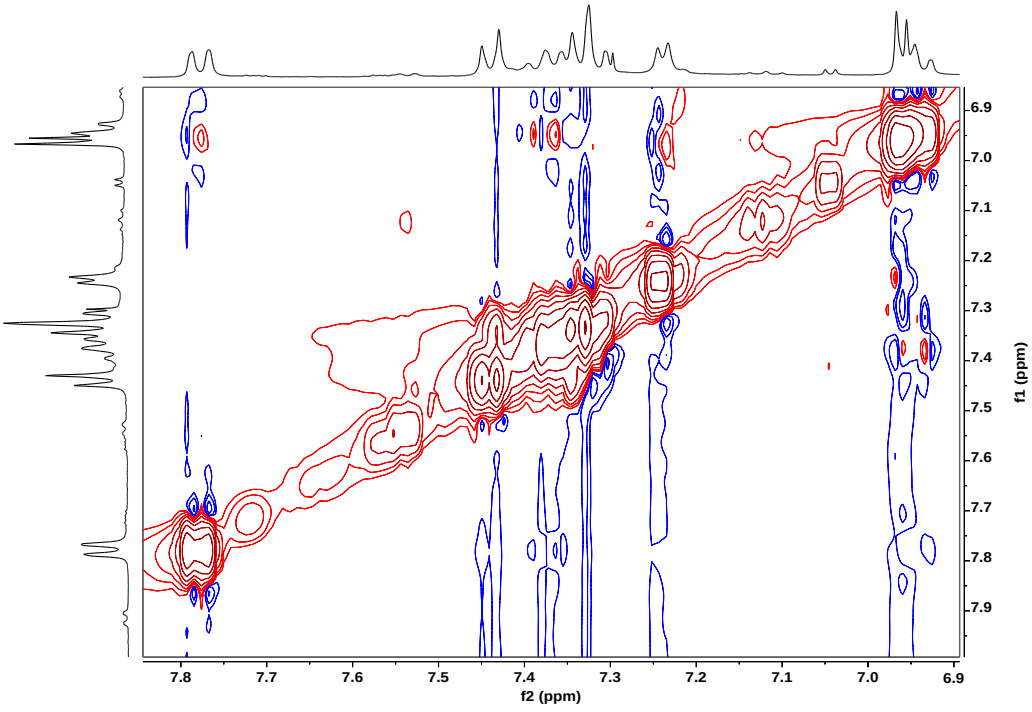

Figure S7.5. NOESY (400 MHz, 1,1,2,2-tetrachloroethane-d_2) of **Au[MeDPP](**aromatic region).

B. Mass spectra

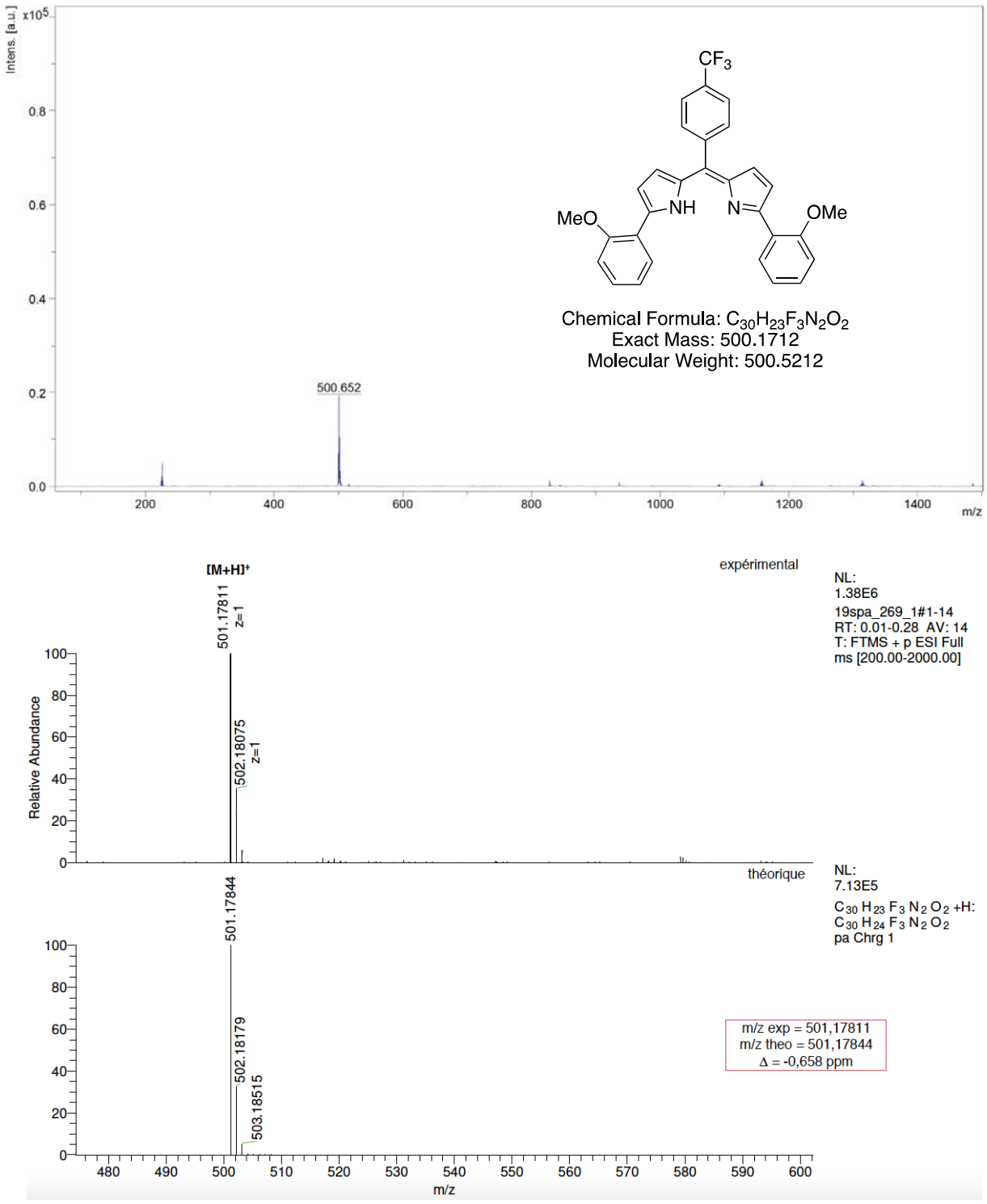

Figure S8. MALDI/TOF LRMS and ESI HRMS mass spectra of **H_3[CF_3DPPOMe]**

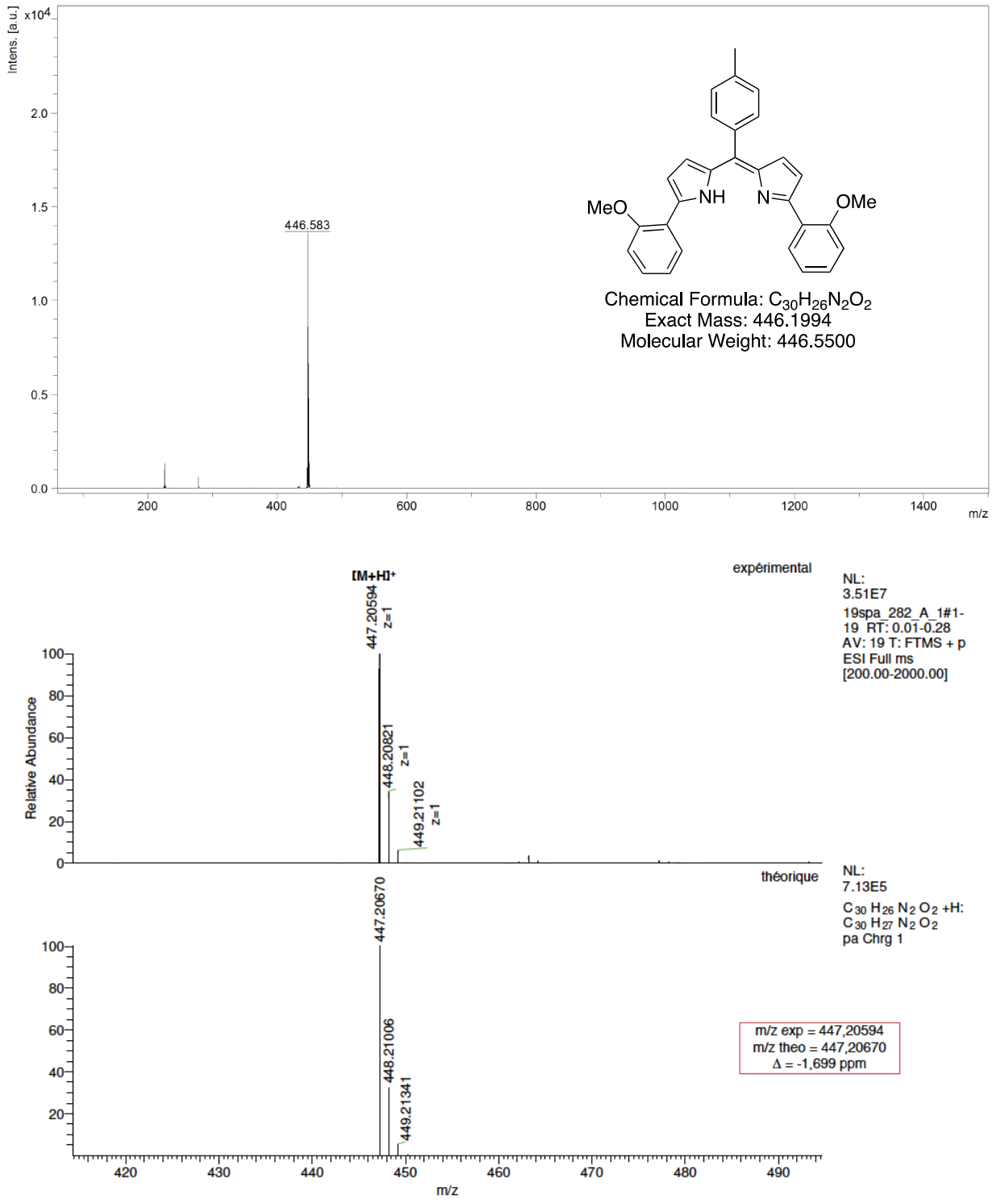

Figure S9. MALDI/TOF LRMS and ESI HRMS mass spectra of **H_3[MeDPPOMe].**

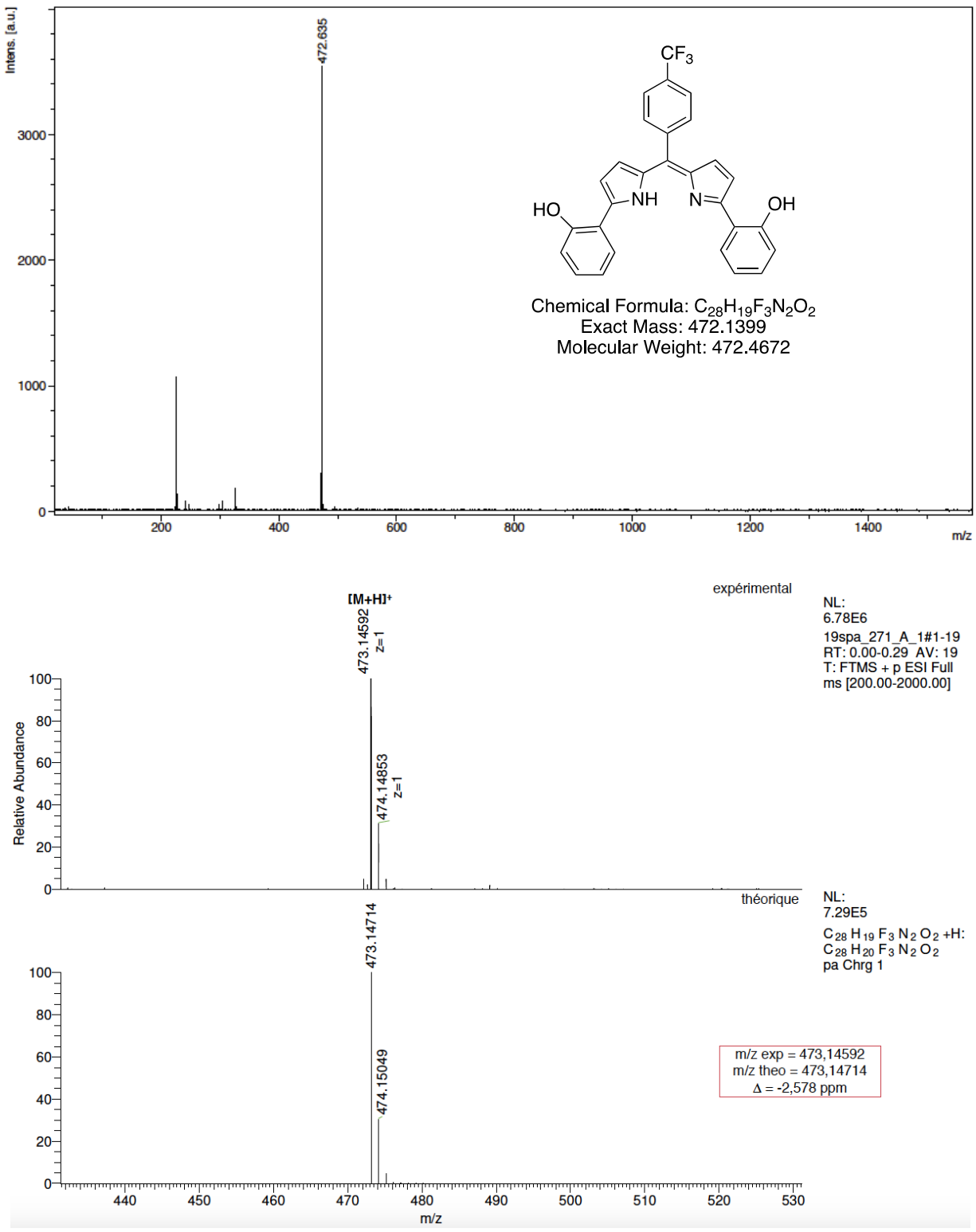

Figure S10. MALDI/TOF LRMS and ESI HRMS mass spectra of **H_3[CF_3DPP].**

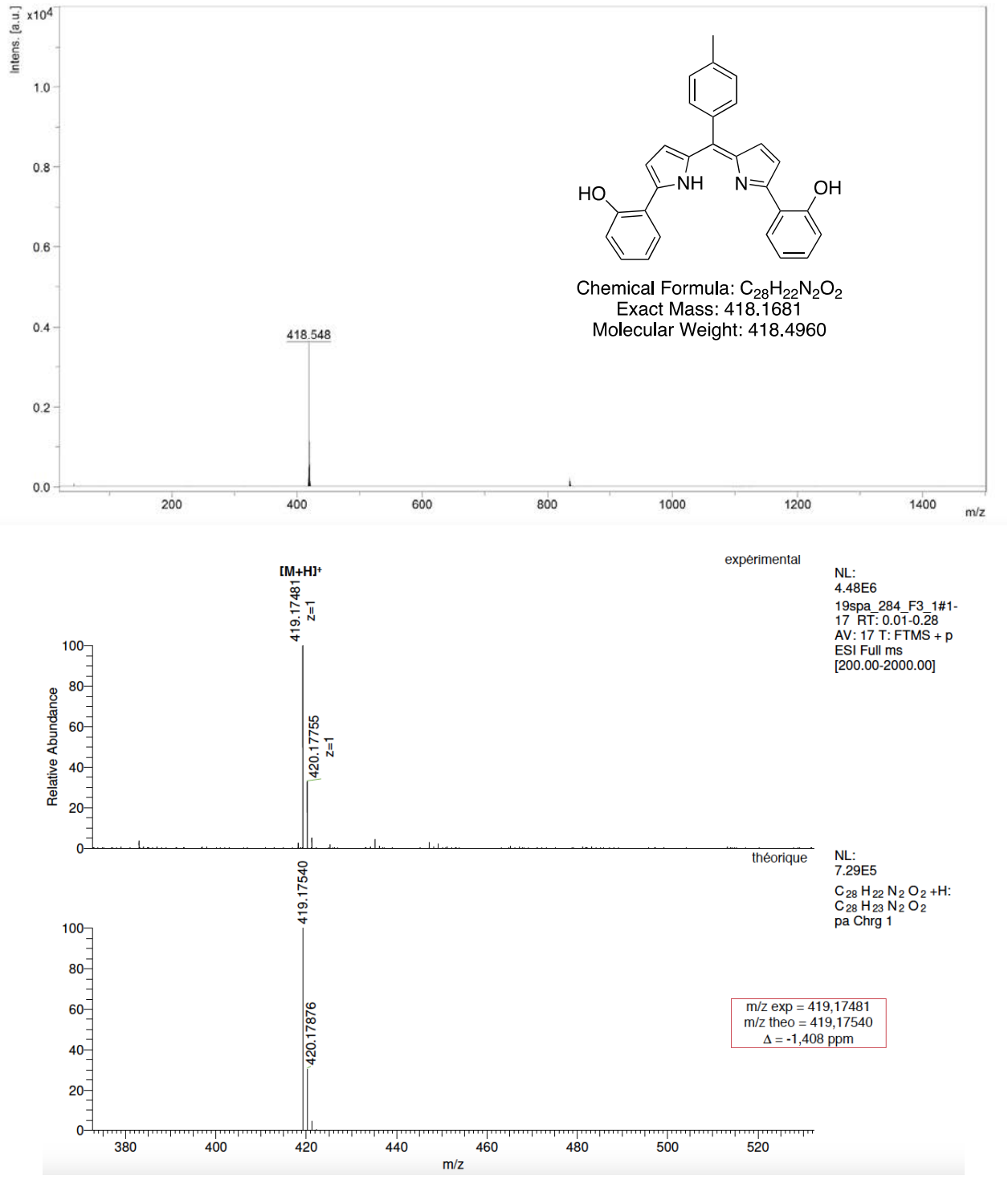

Figure S11. MALDI/TOF LRMS and ESI HRMS mass spectra of **H_3[MeDPP].**

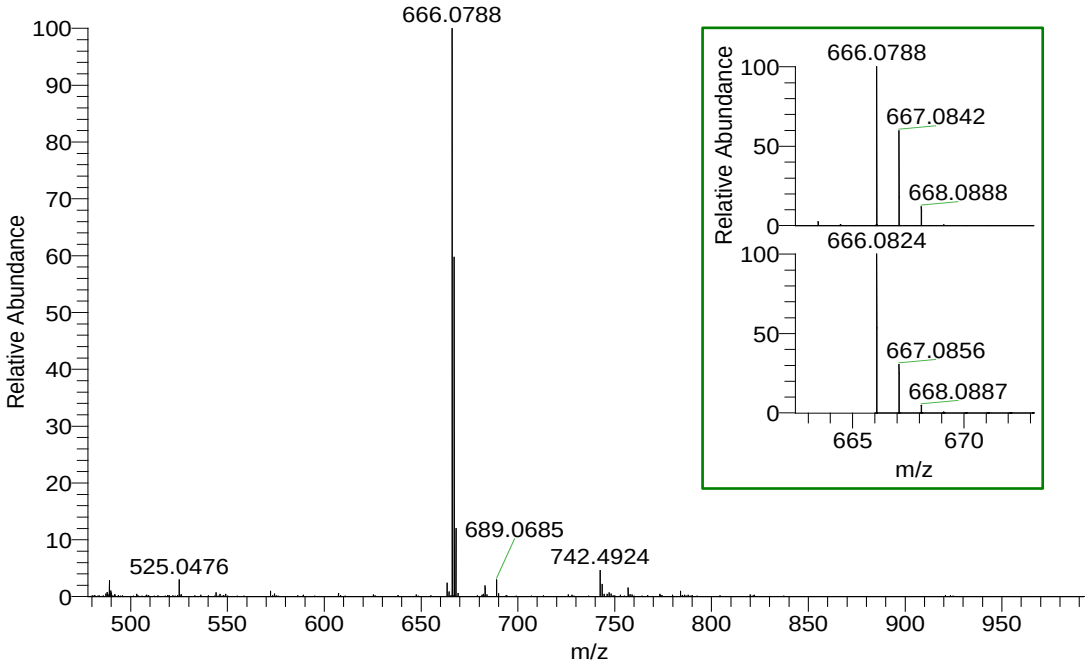

Figure S12. Positive-mode ESI mass spectrum of **Au[CF$_3$DPP].** Insert: Detail of the molecular ion peak (top) and simulation (bottom).

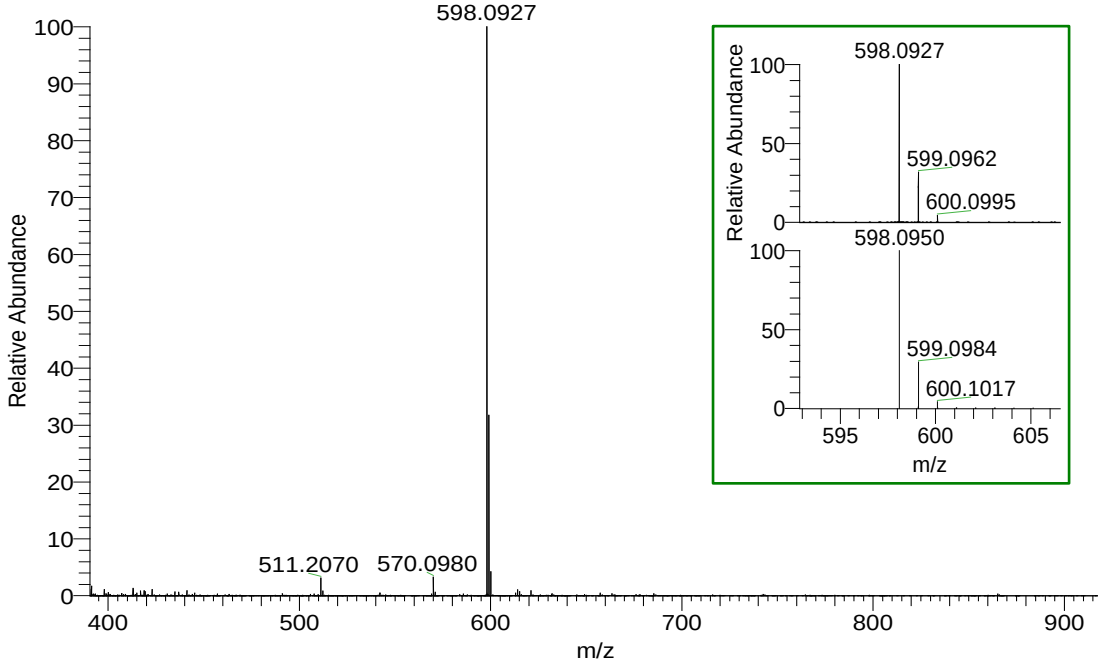

Figure S13. Positive-mode ESI mass spectrum of **Au[HDPP]**. Insert: Detail of the molecular ion peak (top) and simulation (bottom).

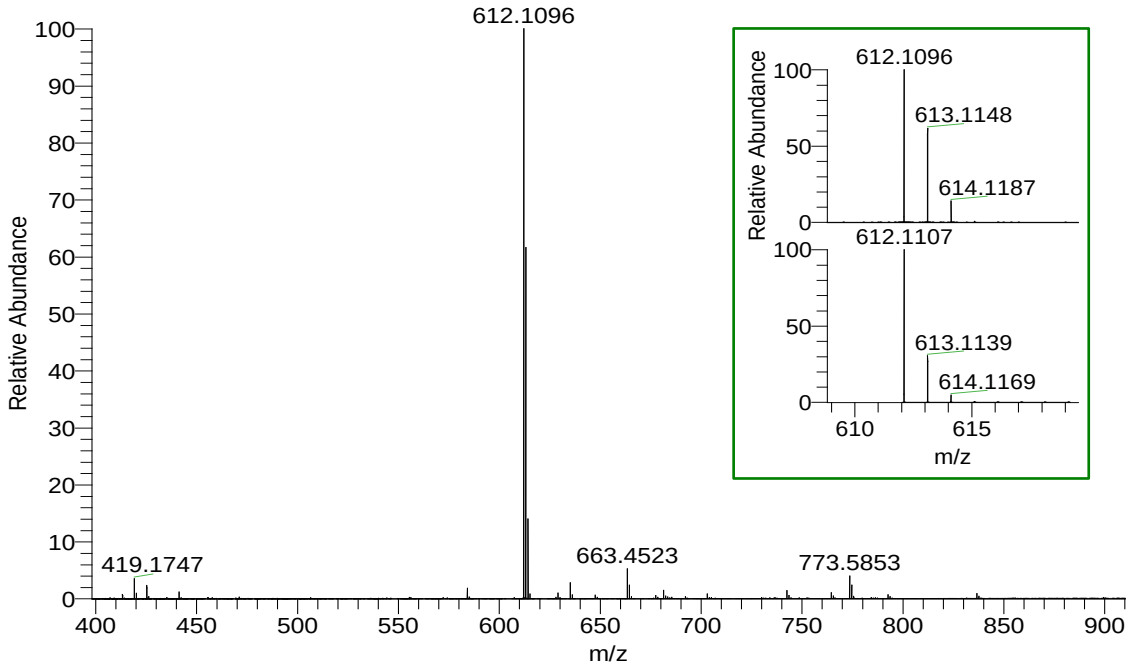

Figure S14. Positive-mode ESI mass spectrum of **Au[MeDPP]**. Insert: Detail of the molecular ion peak (top) and simulation (bottom).

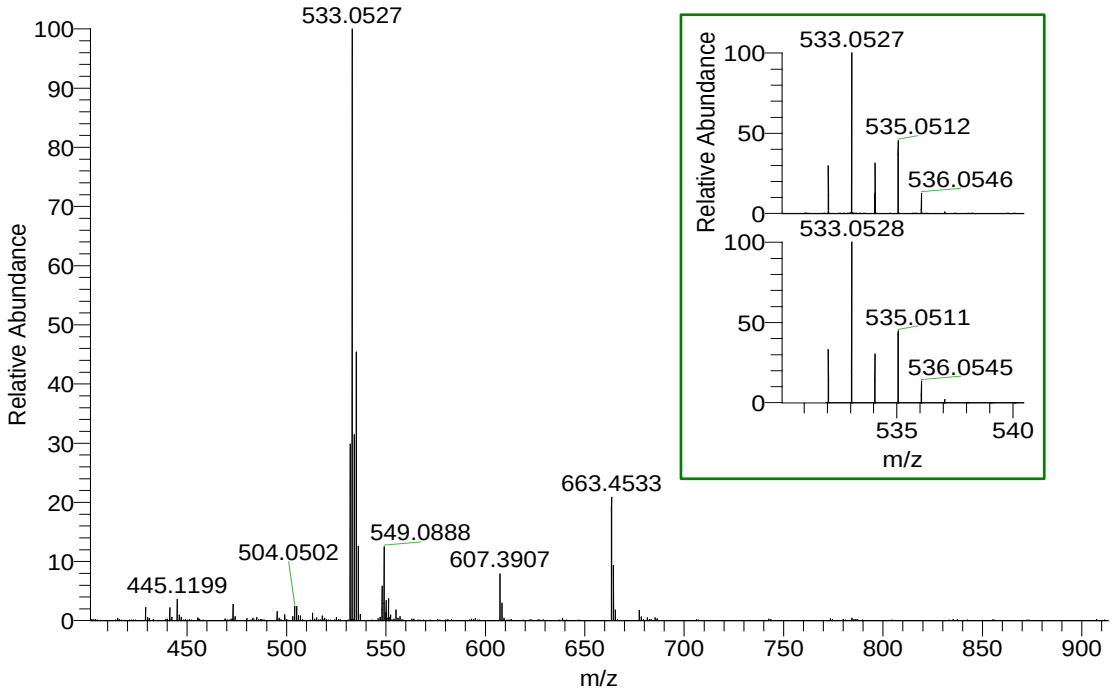

Figure S15. Positive-mode ESI mass spectrum of **Cu[CF$_3$DPP].** Insert: Detail of the molecular ion peaks (top) and simulation (bottom) for $[M]^+$ and $[M+H]^+$ mixture.

C. Redox potentials

Table 1. Redox potentials (V vs SCE) for Au[XDPP] (X = CF_3, H and CH_3) in benzonitrile with 0.1M TBAP. Scan rate: $0.1Vs^{-1}$.

Dipyrrin	$E_{1/2ox1}$	$E_{1/2ox2}$	$E_{1/2red1}$	$E_{1/2red2}$
Au[CF_3DPP]	0.98	1.42	-0.86	-
Au[HDPP]	0.96	1.43	-0.89	-
Au[MeDPP]	0.95	1.42	-0.91	

Table 2. Redox potentials (V vs SCE) for Au[XDPP] (X = CF_3, H and CH_3) in CH_2Cl_2 with 0.1M TBAP. Scan rate: $0.1Vs^{-1}$.

Dipyrrin	$E_{1/2ox1}$	$E_{1/2ox2}$	$E_{1/2red1}$	$E_{1/2red2}$
Au[CF_3DPP]	1.01	1.43	-0.86	-
Au[HDPP]	0.96	1.41	-0.91	-
Au[MeDPP]	0.97	1.42	-0.88	-

Table 3. Redox potentials (V vs SCE) for Cu[CF_3DPP] in benzonitrile and CH_2Cl_2 with 0.1M TBAP. Scan rate: $0.05Vs^{-1}$.

Solvent	$E_{1/2ox1}$	$E_{1/2ox2}$	$E_{1/2red1}$	$E_{1/2red2}$
Benzonitrile	0.75	-	-0.23	-
CH_2Cl_2	irrev	0.79	-0.20	-

D. Optimized OLYP/ZORA-STO-TZ2P coordinates (Å)

1 Au(DPP), S = 0, C_2

Au	0.000000000	0.000000000	-1.181949000
C	0.000000000	0.000000000	2.218165000
C	0.000000000	0.000000000	3.720415000
C	0.000000000	0.000000000	6.529848000
C	0.297044000	1.167982000	5.828208000
C	0.298294000	1.168417000	4.433502000
C	1.228561000	-0.203363000	1.574928000
C	2.494722000	-0.421254000	2.183640000
C	2.593010000	-0.393765000	-2.598728000
C	2.751162000	-0.431075000	-0.070787000
C	3.271906000	-0.478543000	-3.838555000
C	3.345707000	-0.501502000	-1.389669000
C	3.423935000	-0.558852000	1.182039000
C	4.639415000	-0.660703000	-3.900171000
C	4.746884000	-0.684874000	-1.502574000
C	5.390924000	-0.764491000	-2.720651000
C	-0.297044000	-1.167982000	5.828208000
C	-0.298294000	-1.168417000	4.433502000
C	-1.228561000	0.203363000	1.574928000
C	-2.494722000	0.421254000	2.183640000
C	-2.593010000	0.393765000	-2.598728000
C	-2.751162000	0.431075000	-0.070787000
C	-3.271906000	0.478543000	-3.838555000
C	-3.345707000	0.501502000	-1.389669000
C	-3.423935000	0.558852000	1.182039000
C	-4.639415000	0.660703000	-3.900171000
C	-4.746884000	0.684874000	-1.502574000
C	-5.390924000	0.764491000	-2.720651000
H	0.000000000	0.000000000	7.617486000
H	0.528444000	2.084553000	6.366225000
H	0.529838000	2.082721000	3.893163000
H	2.670679000	-0.466593000	3.248829000
H	2.672072000	-0.394002000	-4.739952000
H	4.480668000	-0.736488000	1.316137000
H	5.128313000	-0.721250000	-4.870139000
H	5.339619000	-0.763869000	-0.598338000
H	6.467660000	-0.904520000	-2.759482000
H	-0.528444000	-2.084553000	6.366225000
H	-0.529838000	-2.082721000	3.893163000
H	-2.670679000	0.466593000	3.248829000

H	-2.672072000	0.394002000	-4.739952000
H	-4.480668000	0.736488000	1.316137000
H	-5.128313000	0.721250000	-4.870139000
H	-5.339619000	0.763869000	-0.598338000
H	-6.467660000	0.904520000	-2.759482000
N	1.431381000	-0.221302000	0.194528000
N	-1.431381000	0.221302000	0.194528000
O	1.279642000	-0.221908000	-2.701473000
O	-1.279642000	0.221908000	-2.701473000

2 Au(DPP), S = 0, C_{2v}

Au	0.000000000	0.000000000	-0.895595000
C	0.000000000	0.000000000	2.506117000
C	0.000000000	0.000000000	4.008957000
C	0.000000000	0.000000000	6.819175000
C	0.000000000	1.204804000	6.117241000
C	0.000000000	1.205544000	4.722439000
C	0.000000000	-1.204804000	6.117241000
C	0.000000000	-1.205544000	4.722439000
C	1.245112000	0.000000000	1.862773000
C	2.529319000	0.000000000	2.472417000
C	2.623674000	0.000000000	-2.309770000
C	2.785044000	0.000000000	0.218204000
C	3.308753000	0.000000000	-3.549030000
C	3.383700000	0.000000000	-1.100440000
C	3.469157000	0.000000000	1.471309000
C	4.688084000	0.000000000	-3.610627000
C	4.796948000	0.000000000	-1.213286000
C	5.446563000	0.000000000	-2.430908000
C	-1.245112000	0.000000000	1.862773000
C	-2.529319000	0.000000000	2.472417000
C	-2.623674000	0.000000000	-2.309770000
C	-2.785044000	0.000000000	0.218204000
C	-3.308753000	0.000000000	-3.549030000
C	-3.383700000	0.000000000	-1.100440000
C	-3.469157000	0.000000000	1.471309000
C	-4.688084000	0.000000000	-3.610627000
C	-4.796948000	0.000000000	-1.213286000
C	-5.446563000	0.000000000	-2.430908000
H	0.000000000	0.000000000	7.906800000
H	0.000000000	2.149112000	4.182497000
H	0.000000000	2.150328000	6.655291000
H	0.000000000	-2.149112000	4.182497000
H	0.000000000	-2.150328000	6.655291000

H	2.703321000	0.000000000	-4.450699000
H	2.709476000	0.000000000	3.537909000
H	4.540585000	0.000000000	1.606172000
H	5.180779000	0.000000000	-4.580596000
H	5.394544000	0.000000000	-0.308710000
H	6.532317000	0.000000000	-2.469662000
H	-2.703321000	0.000000000	-4.450699000
H	-2.709476000	0.000000000	3.537909000
H	-4.540585000	0.000000000	1.606172000
H	-5.180779000	0.000000000	-4.580596000
H	-5.394544000	0.000000000	-0.308710000
H	-6.532317000	0.000000000	-2.469662000
N	1.448705000	0.000000000	0.482358000
N	-1.448705000	0.000000000	0.482358000
O	1.299314000	0.000000000	-2.414134000
O	-1.299314000	0.000000000	-2.414134000

3 Au(DPP)$^-$, *S* = ½, C_2

Au	0.000000000	0.000000000	-1.204435000
C	0.000000000	0.000000000	2.209587000
C	0.000000000	0.000000000	3.702916000
C	0.000000000	0.000000000	6.530551000
C	0.389560000	-1.139211000	5.824167000
C	0.393155000	-1.136675000	4.430147000
C	1.245081000	-0.194694000	1.568302000
C	2.536498000	-0.139685000	2.163849000
C	2.598578000	-0.665504000	-2.615469000
C	2.766572000	-0.480229000	-0.068734000
C	3.317822000	-0.770809000	-3.837742000
C	3.349483000	-0.690343000	-1.385746000
C	3.467304000	-0.301071000	1.157289000
C	4.686916000	-0.963341000	-3.879922000
C	4.747789000	-0.889238000	-1.481089000
C	5.417001000	-1.030995000	-2.685341000
C	-0.389560000	1.139211000	5.824167000
C	-0.393155000	1.136675000	4.430147000
C	-1.245081000	0.194694000	1.568302000
C	-2.536498000	0.139685000	2.163849000
C	-2.598578000	0.665504000	-2.615469000
C	-2.766572000	0.480229000	-0.068734000
C	-3.317822000	0.770809000	-3.837742000
C	-3.349483000	0.690343000	-1.385746000
C	-3.467304000	0.301071000	1.157289000
C	-4.686916000	0.963341000	-3.879922000

C	-4.747789000	0.889238000	-1.481089000
C	-5.417001000	1.030995000	-2.685341000
H	0.000000000	0.000000000	7.619054000
H	0.689762000	-2.037411000	6.361544000
H	0.696558000	-2.028520000	3.888583000
H	2.729845000	-0.718472000	-4.750875000
H	2.738408000	0.052814000	3.208797000
H	4.541405000	-0.299541000	1.285069000
H	5.189793000	-1.065146000	-4.840998000
H	5.325661000	-0.944320000	-0.563899000
H	6.492941000	-1.191933000	-2.696281000
H	-0.689762000	2.037411000	6.361544000
H	-0.696558000	2.028520000	3.888583000
H	-2.729845000	0.718472000	-4.750875000
H	-2.738408000	-0.052814000	3.208797000
H	-4.541405000	0.299541000	1.285069000
H	-5.189793000	1.065146000	-4.840998000
H	-5.325661000	0.944320000	-0.563899000
H	-6.492941000	1.191933000	-2.696281000
N	1.426918000	-0.432220000	0.206441000
N	-1.426918000	0.432220000	0.206441000
O	1.290711000	-0.567625000	-2.734267000
O	-1.290711000	0.567625000	-2.734267000

4 Au(DPP)$^{+}$, *S* = ½, C_2

Au	0.000000000	0.000000000	-1.181588000
C	0.000000000	0.000000000	2.223357000
C	0.000000000	0.000000000	3.721766000
C	0.000000000	0.000000000	6.527058000
C	0.158125000	-1.195601000	5.826902000
C	0.164271000	-1.197884000	4.432648000
C	1.227402000	-0.190501000	1.564457000
C	2.515019000	-0.345369000	2.177620000
C	2.573294000	-0.460565000	-2.603142000
C	2.747555000	-0.438234000	-0.078455000
C	3.240180000	-0.606090000	-3.847271000
C	3.333459000	-0.551718000	-1.377833000
C	3.435449000	-0.500355000	1.184410000
C	4.597108000	-0.819824000	-3.898775000
C	4.735634000	-0.772269000	-1.492618000
C	5.356394000	-0.902345000	-2.710698000
C	-0.158125000	1.195601000	5.826902000
C	-0.164271000	1.197884000	4.432648000
C	-1.227402000	0.190501000	1.564457000

C	-2.515019000	0.345369000	2.177620000
C	-2.573294000	0.460565000	-2.603142000
C	-2.747555000	0.438234000	-0.078455000
C	-3.240180000	0.606090000	-3.847271000
C	-3.333459000	0.551718000	-1.377833000
C	-3.435449000	0.500355000	1.184410000
C	-4.597108000	0.819824000	-3.898775000
C	-4.735634000	0.772269000	-1.492618000
C	-5.356394000	0.902345000	-2.710698000
H	0.000000000	0.000000000	7.614132000
H	0.276346000	-2.132720000	6.365230000
H	0.282084000	-2.135958000	3.896404000
H	2.639058000	-0.536324000	-4.748309000
H	2.695907000	-0.332344000	3.242439000
H	4.498057000	-0.637946000	1.316971000
H	5.086974000	-0.924572000	-4.863735000
H	5.334803000	-0.844049000	-0.593314000
H	6.428129000	-1.071055000	-2.758801000
H	-0.276346000	2.132720000	6.365230000
H	-0.282084000	2.135958000	3.896404000
H	-2.639058000	0.536324000	-4.748309000
H	-2.695907000	0.332344000	3.242439000
H	-4.498057000	0.637946000	1.316971000
H	-5.086974000	0.924572000	-4.863735000
H	-5.334803000	0.844049000	-0.593314000
H	-6.428129000	1.071055000	-2.758801000
N	1.418150000	-0.251220000	0.192739000
N	-1.418150000	0.251220000	0.192739000
O	1.278420000	-0.244369000	-2.696570000
O	-1.278420000	0.244369000	-2.696570000

5 Cu(DPP), *S* = 1, C_2

Cu	0.000000000	0.000000000	-1.147756000
C	0.000000000	0.000000000	2.203197000
C	0.000000000	0.000000000	3.705114000
C	0.000000000	0.000000000	6.517993000
C	0.021966000	-1.204496000	5.815629000
C	0.024029000	-1.204859000	4.420780000
C	1.231740000	-0.179702000	1.548654000
C	2.513460000	-0.335529000	2.184187000
C	2.519022000	-0.486928000	-2.580655000
C	2.734796000	-0.415023000	-0.066322000
C	3.190594000	-0.639976000	-3.836182000
C	3.319275000	-0.534455000	-1.368290000

C	3.438378000	-0.480352000	1.193958000
C	4.550472000	-0.812481000	-3.908482000
C	4.721763000	-0.713628000	-1.503732000
C	5.330745000	-0.848036000	-2.730561000
C	-0.021966000	1.204496000	5.815629000
C	-0.024029000	1.204859000	4.420780000
C	-1.231740000	0.179702000	1.548654000
C	-2.513460000	0.335529000	2.184187000
C	-2.519022000	0.486928000	-2.580655000
C	-2.734796000	0.415023000	-0.066322000
C	-3.190594000	0.639976000	-3.836182000
C	-3.319275000	0.534455000	-1.368290000
C	-3.438378000	0.480352000	1.193958000
C	-4.550472000	0.812481000	-3.908482000
C	-4.721763000	0.713628000	-1.503732000
C	-5.330745000	0.848036000	-2.730561000
H	0.000000000	0.000000000	7.605583000
H	0.037156000	-2.149924000	6.353501000
H	0.039800000	-2.148575000	3.881476000
H	2.570669000	-0.605704000	-4.727514000
H	2.689556000	-0.332771000	3.250614000
H	4.501360000	-0.620288000	1.328212000
H	5.031586000	-0.920670000	-4.878547000
H	5.338525000	-0.744871000	-0.612385000
H	6.407565000	-0.981342000	-2.791558000
H	-0.037156000	2.149924000	6.353501000
H	-0.039800000	2.148575000	3.881476000
H	-2.570669000	0.605704000	-4.727514000
H	-2.689556000	0.332771000	3.250614000
H	-4.501360000	0.620288000	1.328212000
H	-5.031586000	0.920670000	-4.878547000
H	-5.338525000	0.744871000	-0.612385000
H	-6.407565000	0.981342000	-2.791558000
N	1.406273000	-0.229272000	0.178260000
N	-1.406273000	0.229272000	0.178260000
O	1.241844000	-0.313101000	-2.610449000
O	-1.241844000	0.313101000	-2.610449000