Through-conjugation of Phosphaalkyne ('C≡P') moieties mediated by a bimetallic scaffold.

M. C. Leech I. R. Crossley*

Department of Chemistry, University of Sussex, Falmer, Brighton, UK

Electronic Supplementary Information

General Experimental details.

All manipulations were performed under inert atmospheres (N_2 or Argon) using standard Schlenk-line and glove-box techniques. Solvents were dried by refluxing over molten alkali metals (hydrocarbons) or CaH_2 (chlorinated) and stored over potassium mirrors or 4 Å molecular sieves (CH_2Cl_2, THF) in ampoules under argon. Reagents were obtained from standard commercial vendors; $Me_3SiC{\equiv}P$[S1] and [{Ru(dppe)$_2$}$_2${μ-(C≡C)$_2$C$_6$H$_4$-1,4}Cl$_2$] (**1**)[S2] were prepared by literature methods. NMR spectra were recorded on a VNMRS 400 MHz spectrometer, reference to external Me_4Si, (^{1}H, ^{13}C, ^{29}Si) and 85 % H_3PO_4 (^{31}P) respectively. Carbon spectra were assigned with recourse to the 2D (HSQC, HMBC) spectra. UV/Vis spectra were recorded on a Thermo Spectronic UV300 instrument, IR spectra were recorded on a Perkin Elmer Spectrum One instrument. Mass spectra were recorded by Dr A. A. Sada of the departmental service and elemental analyses were obtained by Mr S. Boyer, London Metropolitan University Analytical Service.

Synthetic Procedures

[{Ru(dppe)$_2$}$_2$(μ-C≡C)$_2$C$_6$H$_4$-*p*}(η^1-P≡CSiMe$_3$)$_2$].[OTf]$_2$ (2.OTf$_2$)

[{RuCl(dppe)$_2$}$_2$(C≡C-C$_6$H$_4$-C≡C)] (**1**, 0.231 g, 0.1 mmol) was combined with AgOTf (0.061 g, 0.2 mmol) in dichloromethane solution (15 cm^3) and the resulting suspension stirred for 10 min. prior to the addition of a toluene solution of $Me_3SiC{\equiv}P$ (0.03 M; 6.5 mL, 0.2 mmol). After stirring for 2 h., the mixture was filtered and the resulting orange solution freed of volatiles under reduced pressure. The resulting residue was dissolved in CH_2Cl_2, filtered through Celite® and the resulting solution taken to dryness to yield **2.(OTf)$_2$** as a yellow solid. Yield: 0.123 g, 50.3 % ^{1}H NMR (CD_2Cl_2, 303 K, 399.5 MHz): δ_H 7.76-7.69 [16H, m (br), C_6H_5], 7.42 [16H, m, C_6H_5], 7.21 [16 H, J_{HH} = 7.6 Hz, C_6H_5], 7.13 [16 H, J_{HH} = 7.6 Hz, C_6H_5], 7.10-7.04 [16H, m (br), C_6H_5], 6.73 [4H, s, C_6H_4], 2.89 [16H, m, dppe], −0.08 [18H, br, J_{SiH} = 7 Hz, $SiMe_3$]. ^{13}C{^{1}H}-NMR (CD_2Cl_2, 303 K, 100.46 MHz): δ_C 189.8 [d, J_{CP} = 87.6 Hz, C≡P], 134.7 [quint (br), J_{CP} = 2.3 Hz, *m*-C_6H_5], 133.4 [quint (br), J_{CP} = 2.3 Hz, *m*-C_6H_5], 131.5 [s, C_6H_5], 131.4 [d, J_{CP} = 16 Hz, *p*-C_6H_5], 130.4 [m (br), C_6H_4], 129.0 [quint (br), J_{CP} = 2.3 Hz, *o*-C_6H_5], 128.8 [quint (br), J_{CP} = 2.3 Hz, *o*-C_6H_5], 125.2 [m (br), *ipso*-C_6H_4], 116.9 [m (br), Ru-C≡C], 31.2 [tt, J_{CP} = 11.9, 11.6 Hz, C_2H_4], 0.63 [s, $Si(CH_3)_3$]. ^{31}P{^{1}H} NMR (CD_2Cl_2, 303 K, 161.71 MHz): δ_P 111.4 [2P, quint, J_{PP} = 32.5 Hz, C≡P], 42.2 [8P, d, J_{PP} = 32.5 Hz, dppe]. ^{29}Si NMR (CD_2Cl_2, 303 K, 79.37 MHz): δ_{Si} −12.9 [$Si(CH_3)_3$]. ^{19}F NMR (CD_2Cl_2, 303 K, 375.78 MHz): δ_{Si} −78.9 [CF_3]. IR: ν_{max}/cm^{-1}: 1261.5 (C≡P), 2054.1 (C≡C). UV/Vis: λ_{max}/nm (ε): 230 (155000), 260 (106200), 350 (49300). Anal. Calc. For $C_{124}H_{118}P_{10}Ru_2Si_2S_2O_6F_6$: C; 60.79 %, H; 4.85 %. Found: C; 60.55 %, H; 5.00 %

[{Ru(dppe)$_2$}$_2$(μ-C≡C)$_2$C$_6$H$_4$-*p*}(η^1-C≡P)$_2$] (3)

In thf (15 cm^3) solution, **2.[OTf]$_2$** (0.158 g, 0.06 mmol) was combined with KO^{t}Bu (0.017 g, 0.15 mmol) and the mixture stirred for 1h. The solvent volume was reduced to ca 50 % to ensure complete precipitation of KOTf, and the mixture filtered. The volatiles were removed under reduced pressure, and residual tBuOH removed azeotropically by sequential addition / evaporation of benzene, to afford **3** as a yellow solid. Yield: 0.080 g, 62 %. ^{1}H-NMR (CD_2Cl_2, 303 K, 399.5 MHz): 7.66-7.61 [16H, m (br), *m*-C_6H_5], 7.55-7.50 [16H, m (br), *m*-C_6H_5], 7.30-7.20 [16H, 2 x t, J_{HH} = 6.4 Hz, *p*-C_6H_5], 7.08 [16H, t, J_{HH} = 7.0 Hz, *o*-C_6H_5], 7.00 [16H,

t, J_{HH} = 7.0 Hz, *o*-C_6H_5], 6.57 [4H, s, C_6H_4], 2.92 [8H, (br), C_2H_4], 2.69 [8H, (br), C_2H_4]. $^{13}C\{^1H\}$-NMR (CD_2Cl_2, 303K, 100.46 MHz): δ_C 281.8 [m (br), C≡P], 138.0 [quint, J_{CP} = 10.0 Hz, *ipso*-C_6H_5], 136.1 [quint, J_{CP} = 10.1 Hz, *ipso*-C_6H_5], 135.4 [quint (br), J_{CP} = 2.1 Hz, *m*-C_6H_5], 135.1 [quint (br), J_{CP} = 2.1 Hz, *m*-C_6H_5], 129.4 [s, C_6H_5], 129.8 [s, C_6H_4, CH], 129.6 [br, *p*-C_6H_5], 129.4 [br, *p*-C_6H_5], 127.7 [quint (br), J_{CP} = 1.9 Hz, *o*-C_6H_5], 127.4 [quint (br), J_{CP} = 1.9 Hz, *o*-C_6H_5], 126.0 [s, *ipso*-C_6H_4], 120.7 [s, Ru-C≡**C**], 31.8 [tt, J_{CP} = 12.2, 11.8 Hz, C_2H_4]. ^{31}P NMR (CD_2Cl_2, 303 K, 161.71 MHz): δ_P 159.7 [2P, m, C≡P], 50.7 [8P, s, dppe]. IR: ν_{max}/cm^{-1}: 1247.2 (C≡P), 2057.1 (C≡C). UV/Vis: λ_{max}/nm (ε): 230 (103900), 250 (73900), 370 (41200). ESI MS (*m/z*): Calcd for $C_{116}H_{100}P_{10}Ru_2$ 2006.3337 ($[M]^+$). Found 2007.4279 ($[MH]^+$).

Crystallography.

Diffraction data were obtained on an Agilent Excalibur with CCD plate detector using Cu-Kα radiation (λ =1.54184) and solved using either SHELX-97[S3] within Olex 2.0.[S4]

Compound 2^{2+} (CCDC 1811689): *Crystal Data*: $C_{122}H_{118}P_{10}Ru_2Si_2$, M_w = 2152.18, triclinic, *P -1* (no 2), *a* = 14.3964(4) Å, *b* = 19.4639(5) Å, *c* = 23.3880(5) Å, α = 95.011(2), β = 90.319(2), γ = 91.956(2)°, *V* = 6524.4(3) Å^3. *Z* = 2. D_c 1.035 Mg m^{-3}, μ(Cu-Kα) = 3.516 mm^{-1}, *T* = 173(2) K, 23612 independent reflections, full-matrix F^2 refinement. R_1 = 0.061, wR_2 = 0.1837 on 18345 independent absorption corrected reflections [$I > 2\sigma(I)$; $2\theta_{max}$ = 136.5°], 1369 parameters.

Computational Details. Calculations were performed using Gaussian 09W, Revision C.01,[S5] running on an Intel i5-2500 (quad, 3.3 GHz), equipped with 8 GB RAM, or Gaussian 09 Revision D.01,[S6] running on the Sussex High Performance Cluster. Results were visualised using GaussView 5.0; orbital contributions and UV/Vis spectra were calculated using GaussSum.[S7] Geometries were optimised with the hybrid density functional B3LYP, using the RECP basis set Lanl2dz for Ru and 6-31G** for all other atoms. Stationary points were characterised by frequency calculations and confirmed as minima on the basis of no imaginary frequencies. Calculated vibrational frequencies were scaled (0.9608). Excited states were calculated using TD-DFT with the B3LYP functional, using the LANL2DZ basis for ruthenium, and 3-21G* on all atoms; no solvent model was used.

The supplemental file RuCP-bridged.xyz contains the computed Cartesian coordinates of compounds $\mathbf{2^{2+}}$ and **3**. The file may be opened as a text file to read the coordinates, or opened directly by a molecular modelling program such as Mercury (version 3.3 or later, http://www.ccdc.cam.ac.uk/pages/Home.aspx) for visualization and analysis.

Electrochemistry Details. Cyclic Voltammagrams were obtained under anaerobic conditions (MBraun Glove Box) at (298 K) for solutions in CH_2Cl_2 (0.1 mM) with 0.1 M [^{n}Bu$_4$N]PF$_6$ electrolyte, using a three-electrode set-up, comprising platinum disk working electrode (1 mm diameter), platinum wire counter electrode and silver wire pseudoreference. Data were recorded using a PalmSens EmStat3+ Blue potentiostat, and the PSTrace software package. Potentials are reported

relative to the ferrocene/ferrocinium (FcH/FcH^+) couple, referenced to the Fc^*H/Fc^*H^+ couple of a doped sample (−0.560 V relative to FcH/FcH^+).

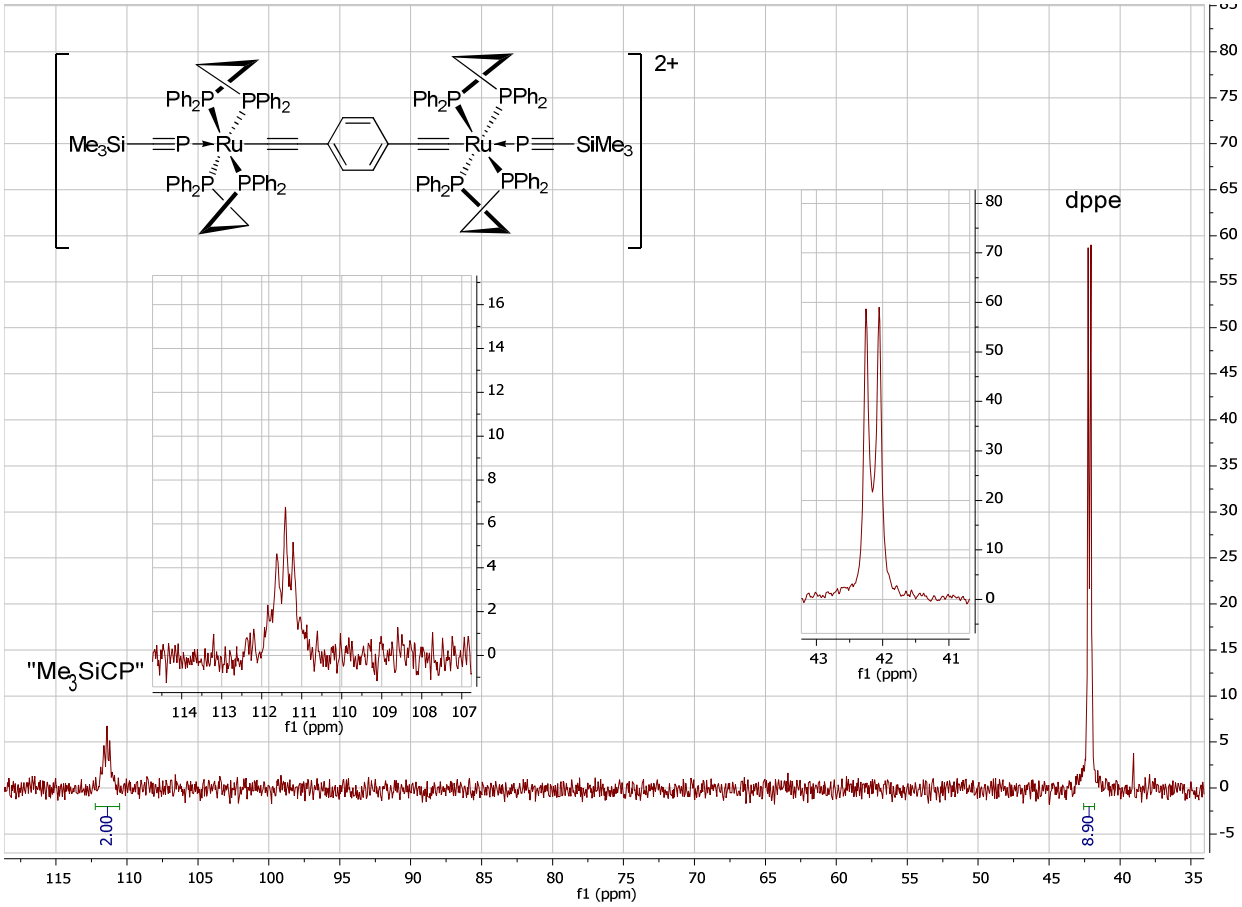

Figure S1: $^{31}P\{^1H\}$ NMR spectrum (CD_2Cl_2, 303K, 161.71 MHz) for compound **2.[OTf]$_2$**

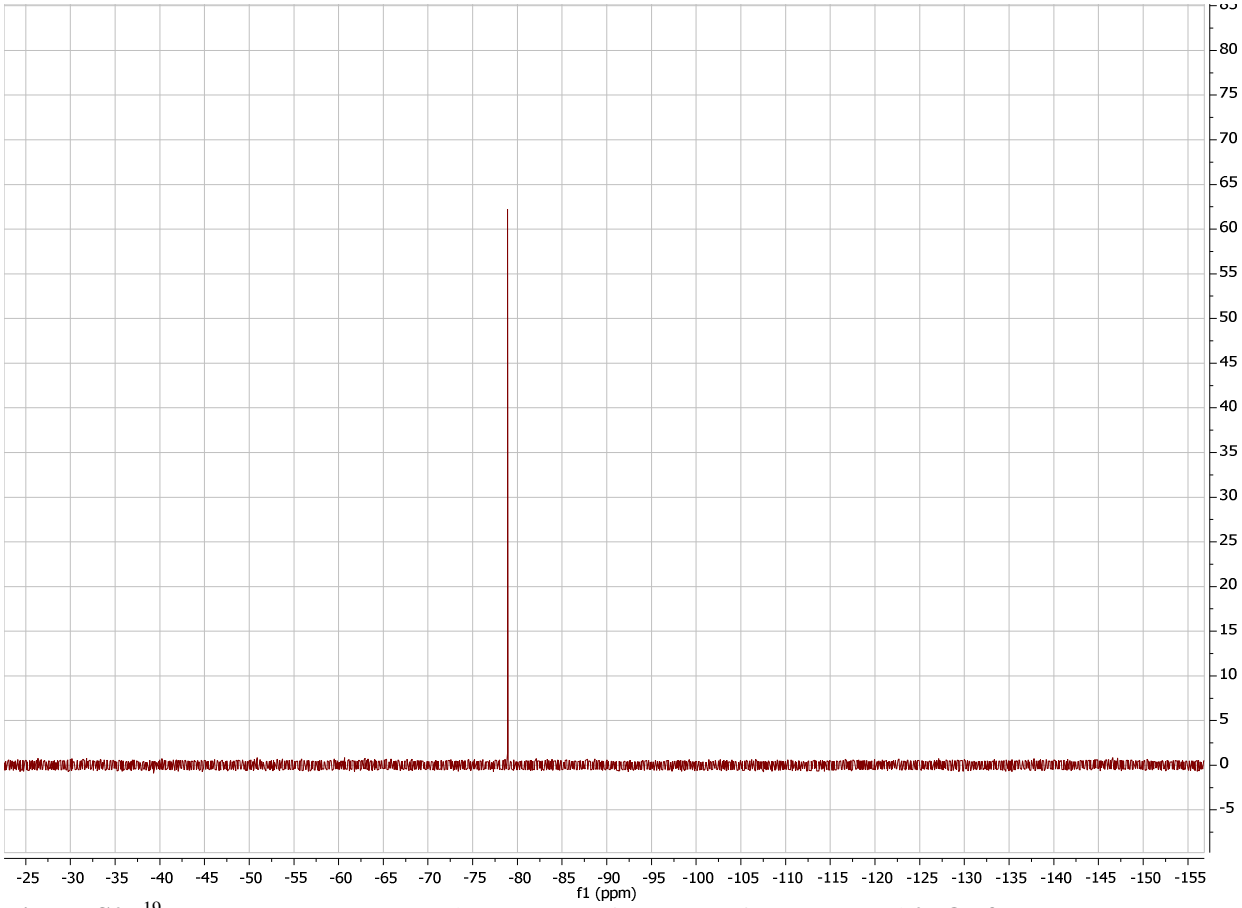

Figure S2: ^{19}F NMR spectrum (CD_2Cl_2, 303 K, 375.87 MHz) for compound **2.[OTf]$_2$**

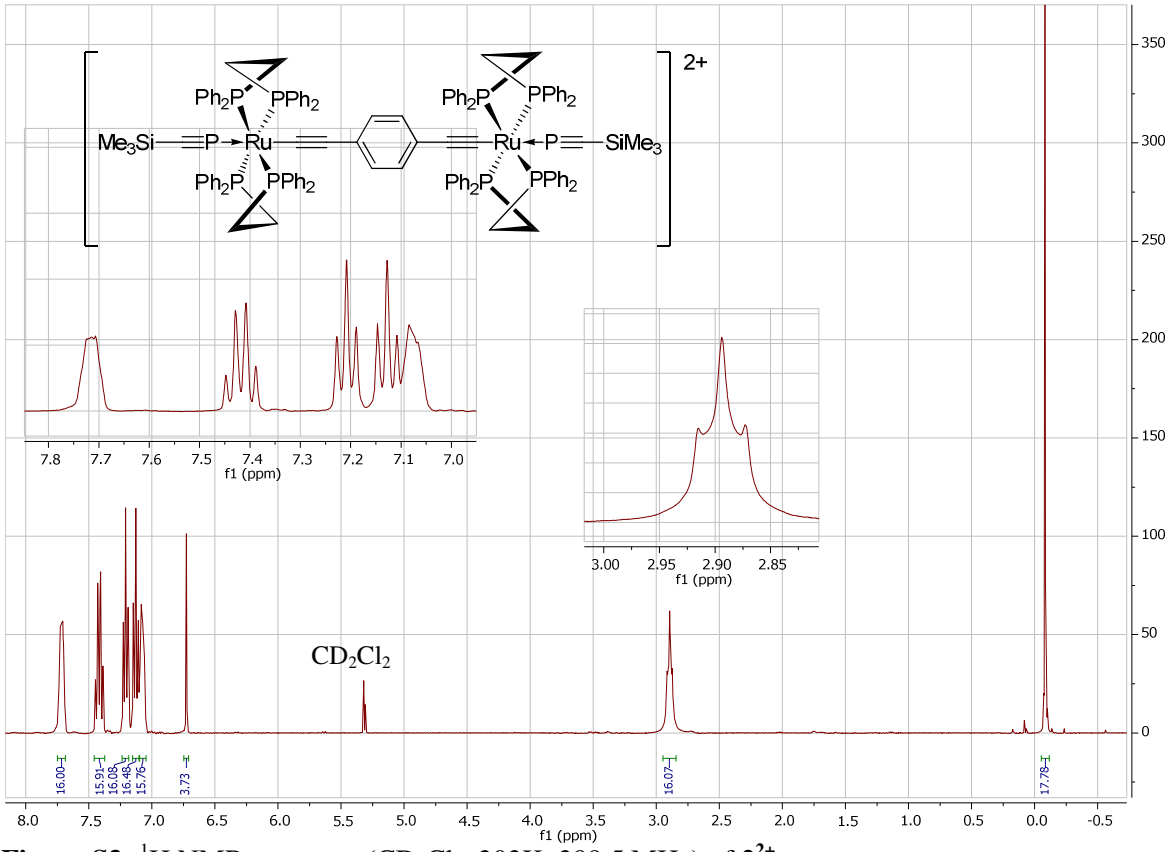

Figure S3: ^{1}H NMR spectrum (CD_2Cl_2, 303K, 399.5 MHz) of **2^{2+}**

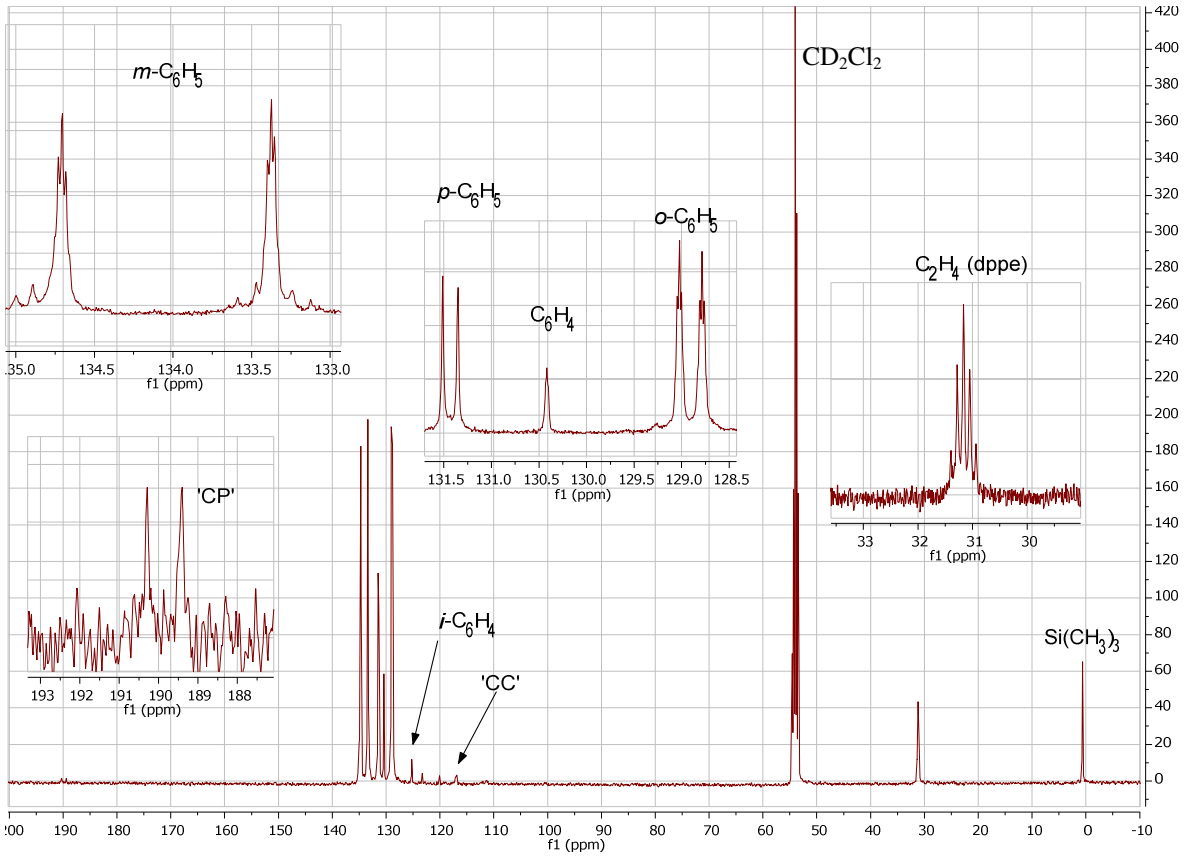

Figure S4: $^{13}C\{^{1}H\}$ NMR spectrum (CD_2Cl_2, 303K, 100.46 MHz) for compound $\mathbf{2}^{2+}$

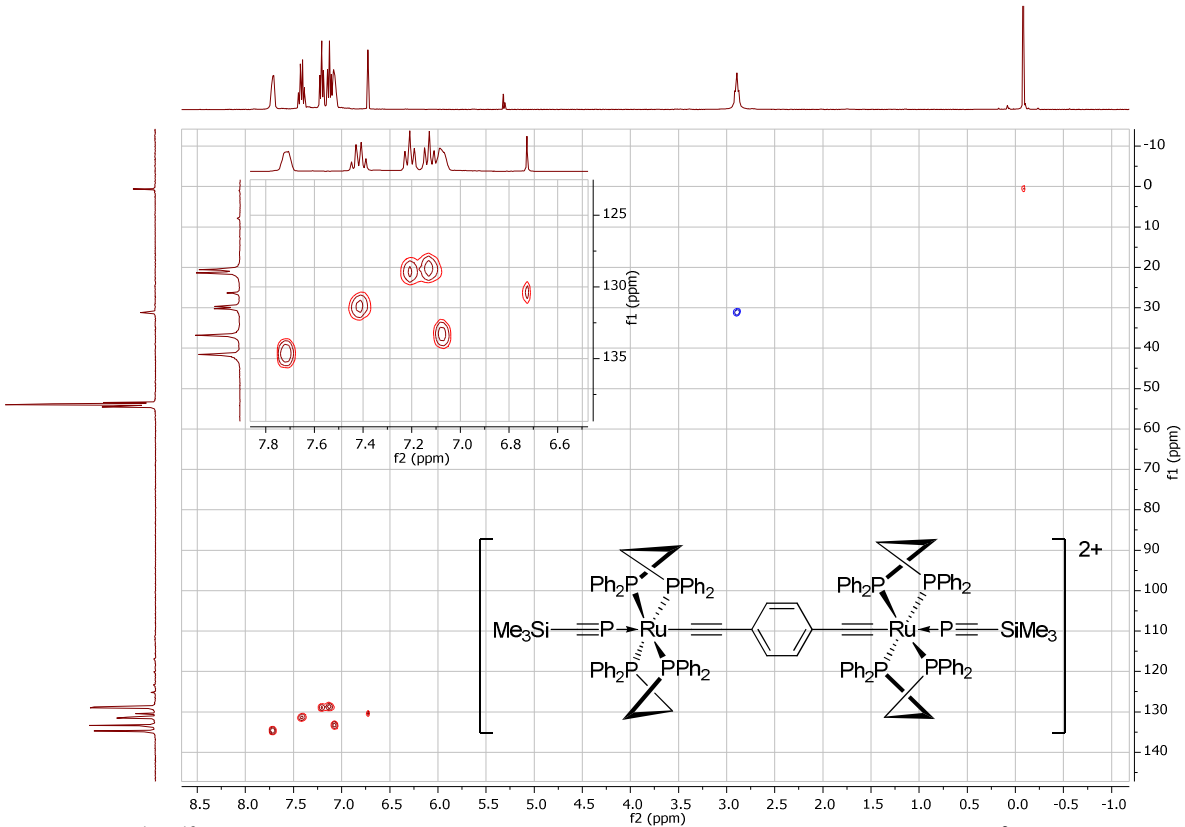

Figure S5: ^{1}H-^{13}C HSQC trace (CD_2Cl_2, 303K, 399.5, 100.46 MHz)for compound $\mathbf{2}^{2+}$; CH_2 blue; CH/CH_3 red

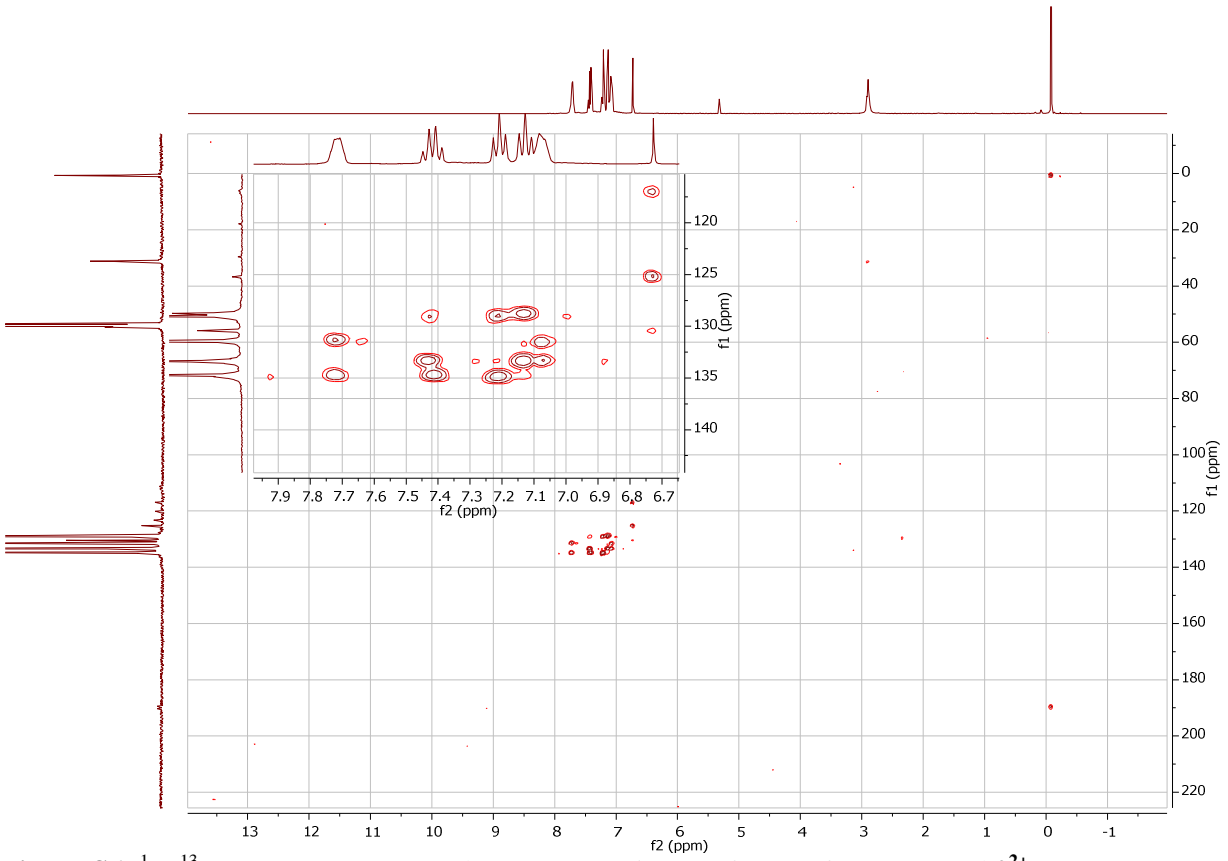

Figure S6: ^{1}H-^{13}C HMBC trace (CD_2Cl_2, 303K, 399.5, 100.46 MHz) for compound $\mathbf{2}^{2+}$

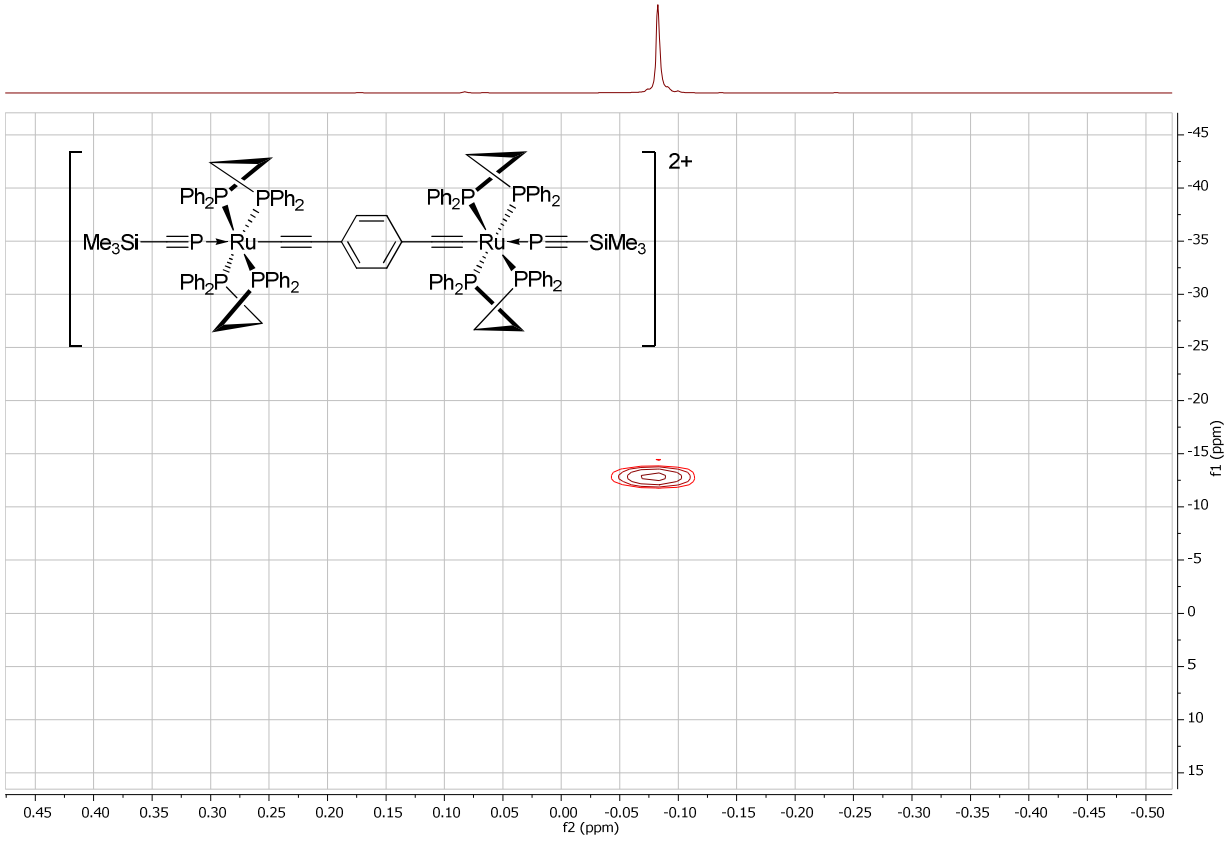

Figure S7: ^{1}H-^{29}Si HMBC trace (CD_2Cl_2, 303K, 399.5, 75.37 MHz) for compound $\mathbf{2}^{2+}$

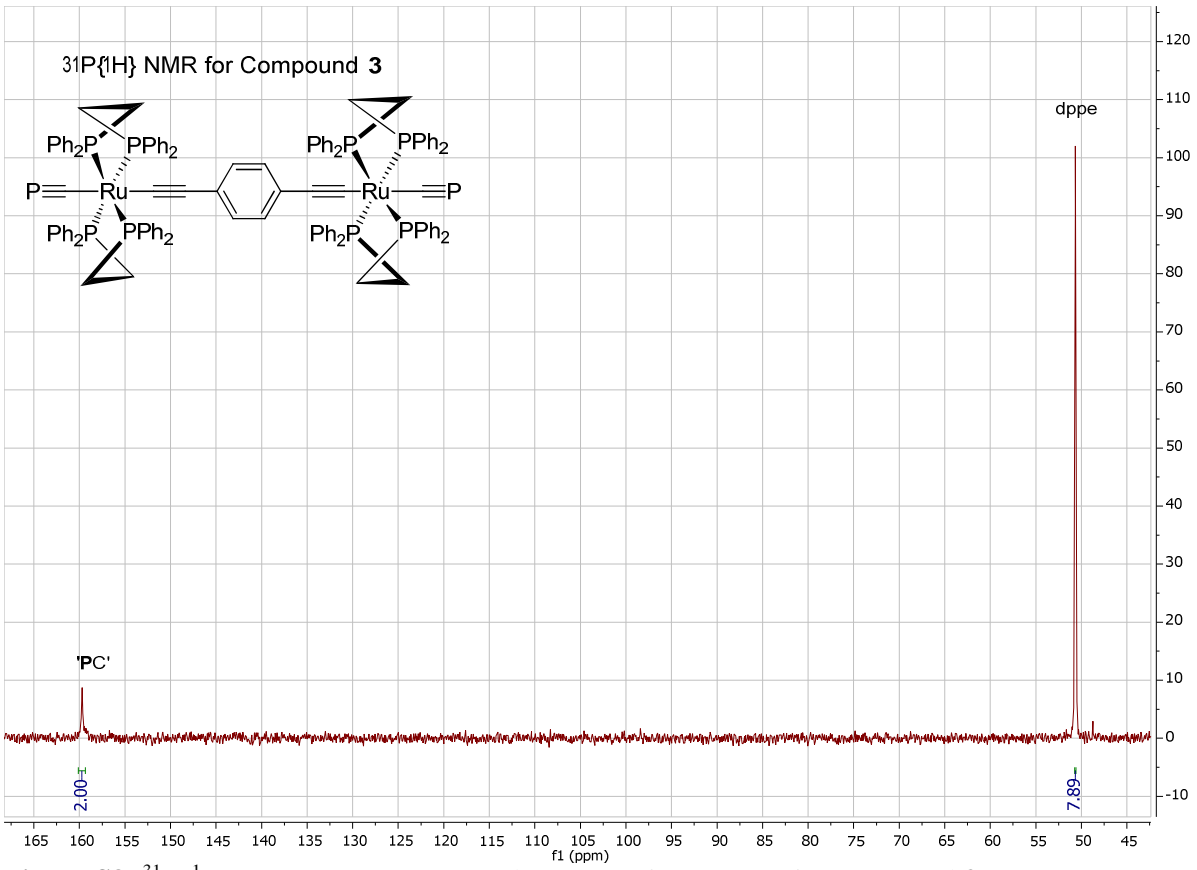

Figure S8: $^{31}P\{^{1}H\}$ NMR spectrum (CD_2Cl_2, 303K, 161.71 MHz) for compound **3**

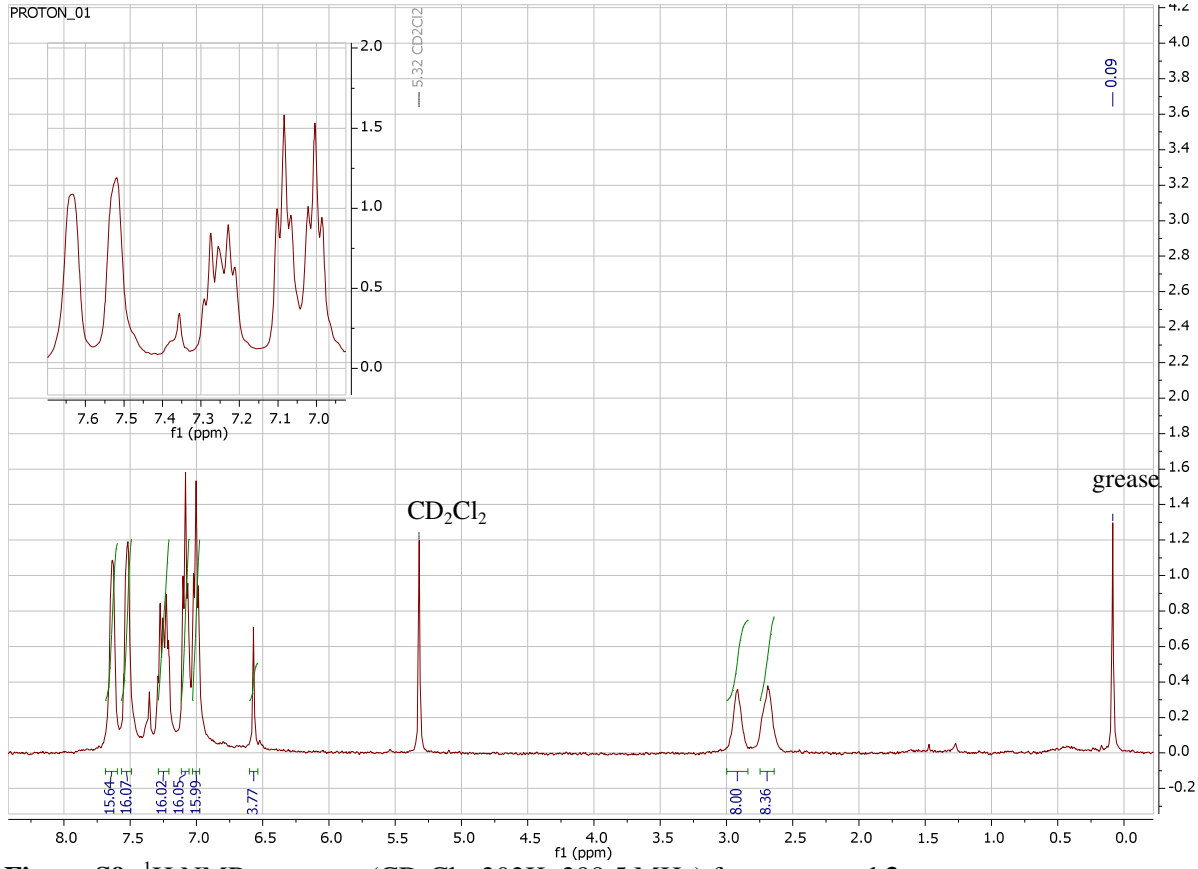

Figure S9: ^{1}H NMR spectrum (CD_2Cl_2, 303K, 399.5 MHz) for compound **3**

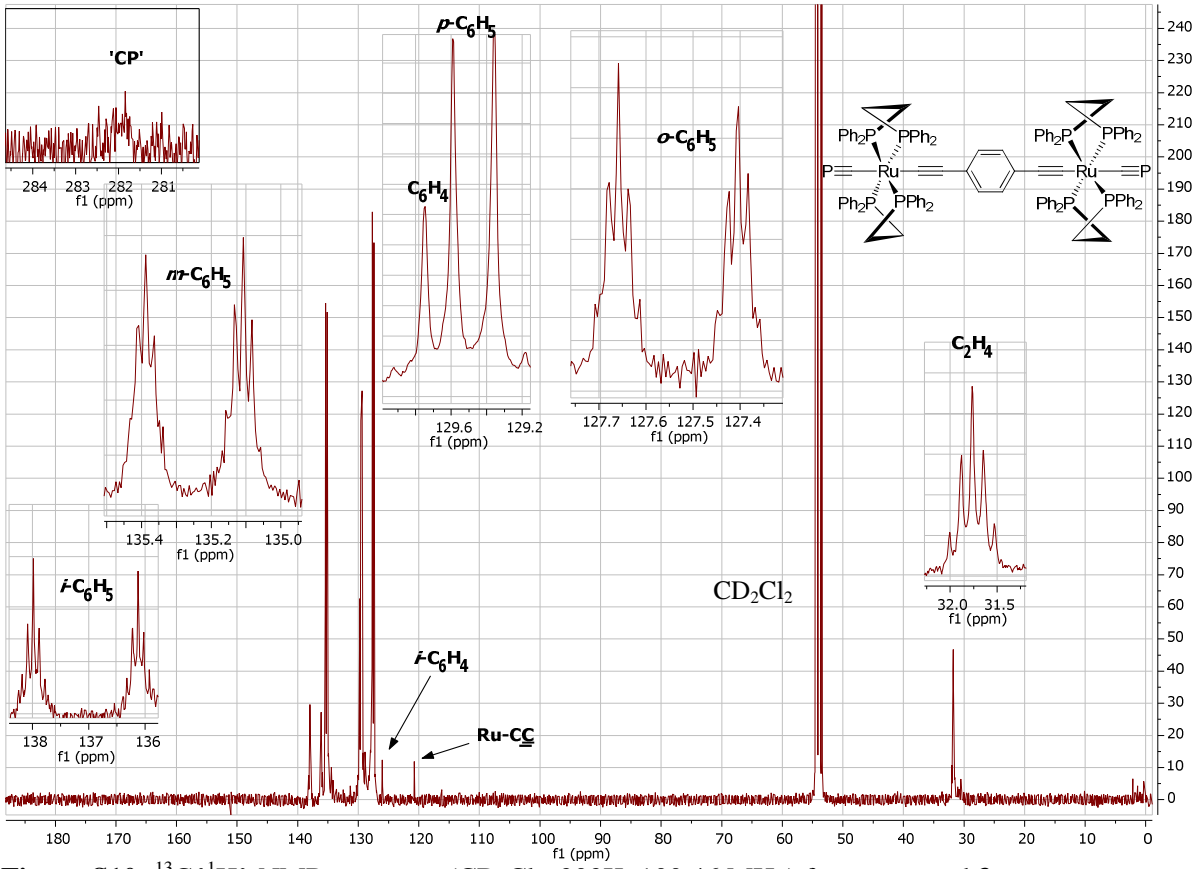

Figure S10: $^{13}C\{^{1}H\}$ NMR spectrum (CD_2Cl_2, 303K, 100.46 MHz) for compound **3**

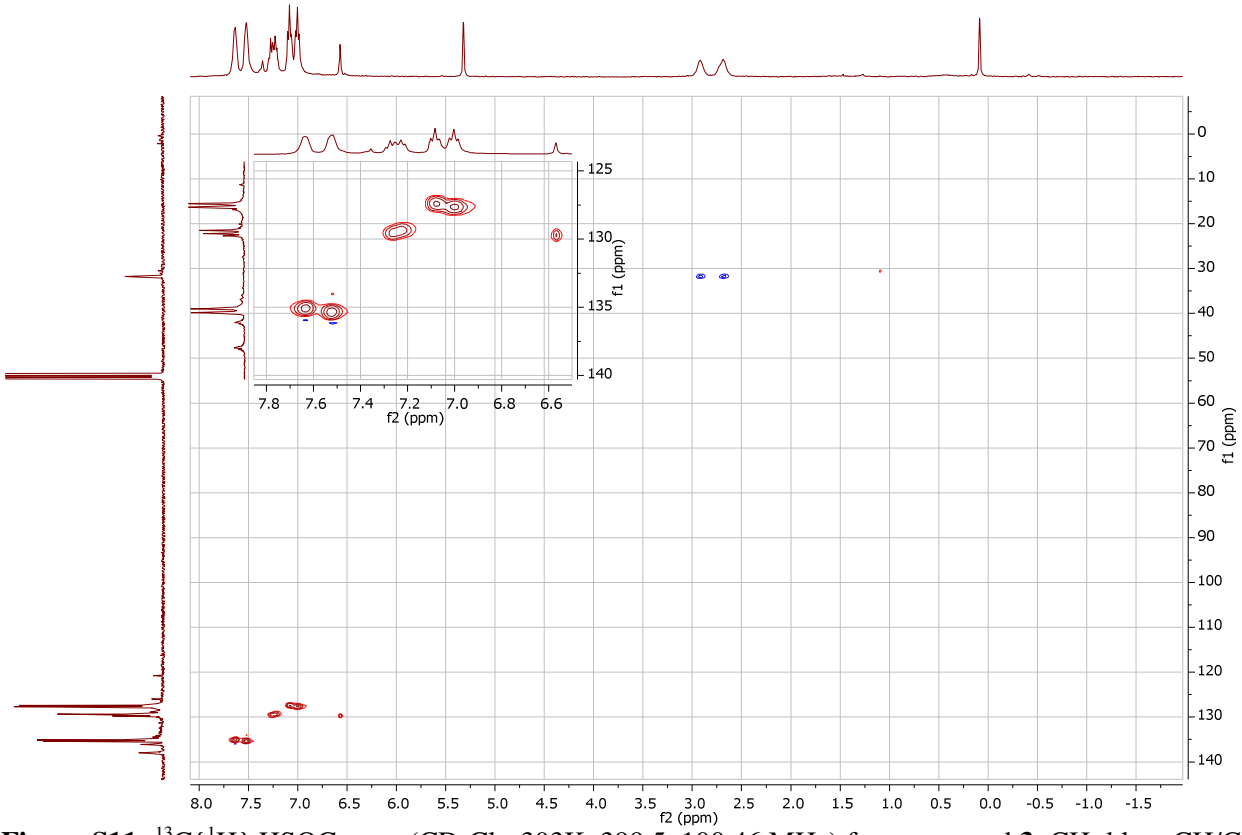

Figure S11: $^{13}C\{^{1}H\}$ HSQC trace (CD_2Cl_2, 303K, 399.5, 100.46 MHz) for compound **3**; CH_2 blue; CH/CH_3 red.

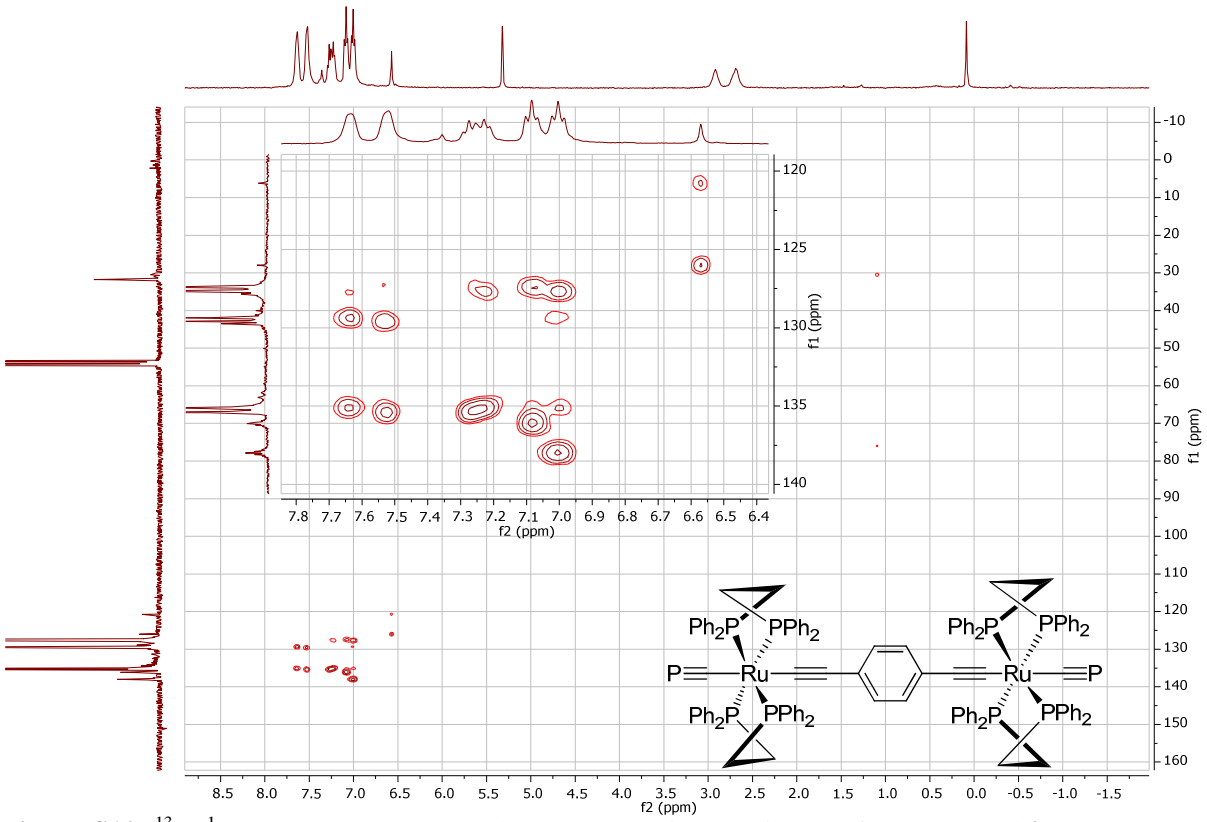

Figure S12: $^{13}C\{^{1}H\}$ HMBC trace (CD_2Cl_2, 303K, 399.5, 100.46 MHz) for compound **3**

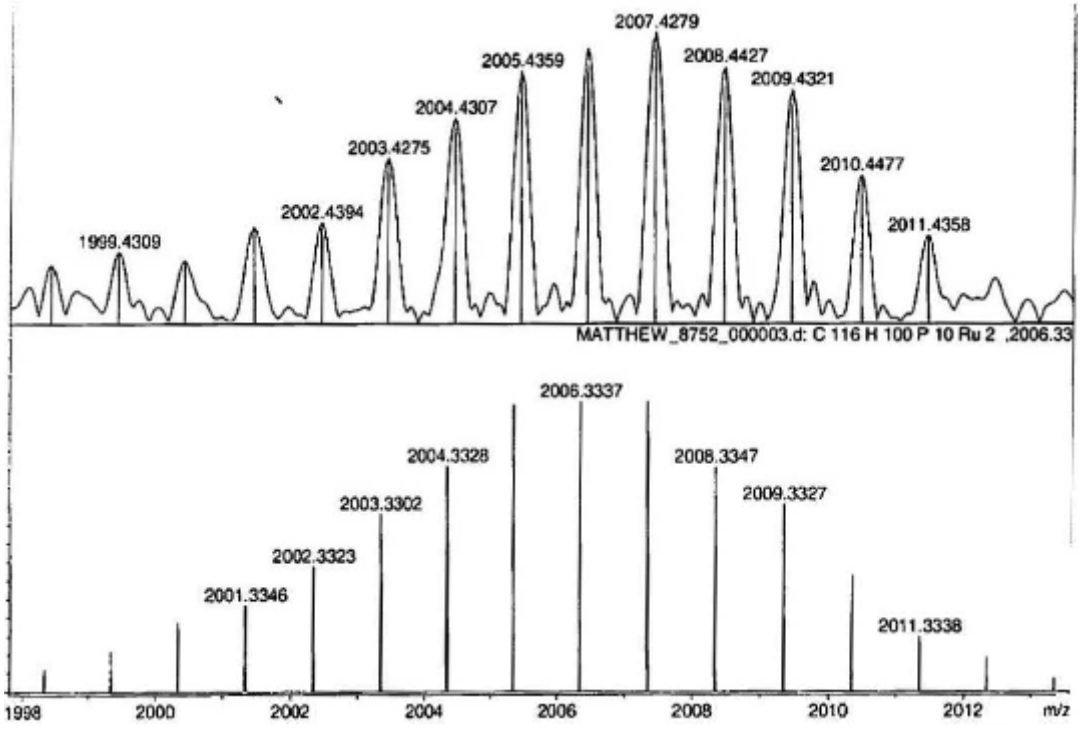

Figure S13: Experimental (top, observed $[MH]^+$) and simulated (bottom, for $[M]^+$) high-res mass spectrum for compound **3** (Mr = 2006.35 for $[M]^+$).

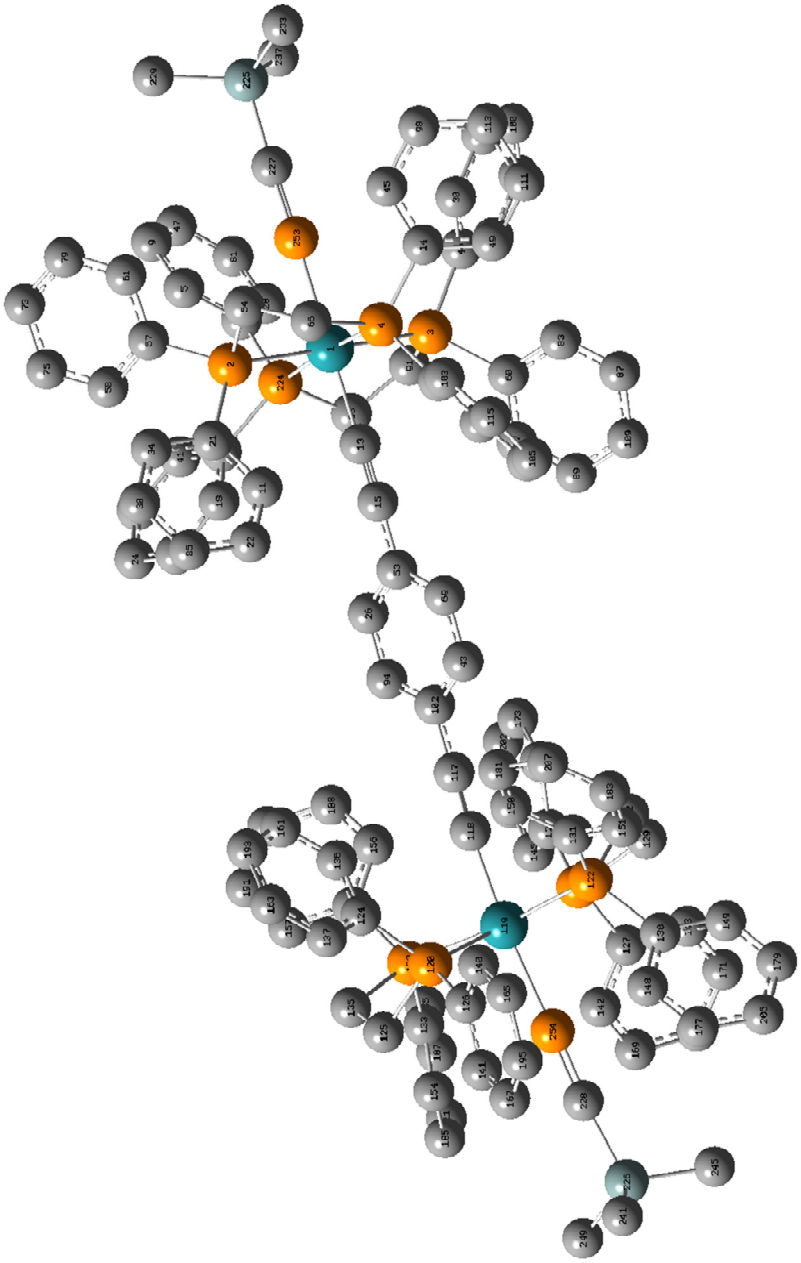

Figure S14: Optimized geometry of $\mathbf{2}^{2+}$. Selected geometric parameters [Å,°]: P≡C 1.548, PC-Si, 1.860, Ru-CP 2.363, RuCC 2.036, C≡C 1.230, C-Ar 1.431; C-P-Ru 178.17, P-Ru-C 175.08, Ru-C-C 175.67, C-C-Ar 178.74.

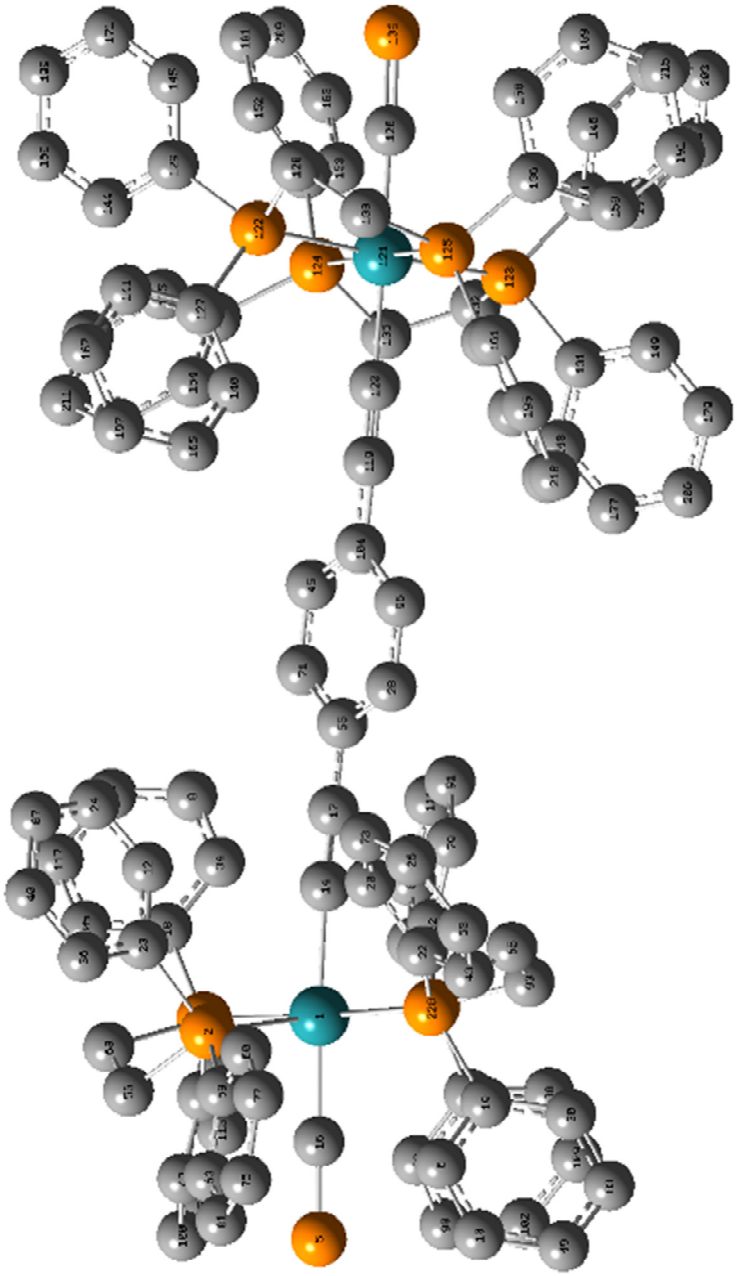

Figure S15: Optimized geometry of **3**. Selected geometric parameters [Å,°]: P≡C 1.587, Ru-CP 2.044, Ru-CC 2.114, C≡C 1.235, CC-Ar 1.429; P-C-Ru 178.17, C-Ru-C 177.20, Ru-C-C 176.03, C-C-Ar 178.77

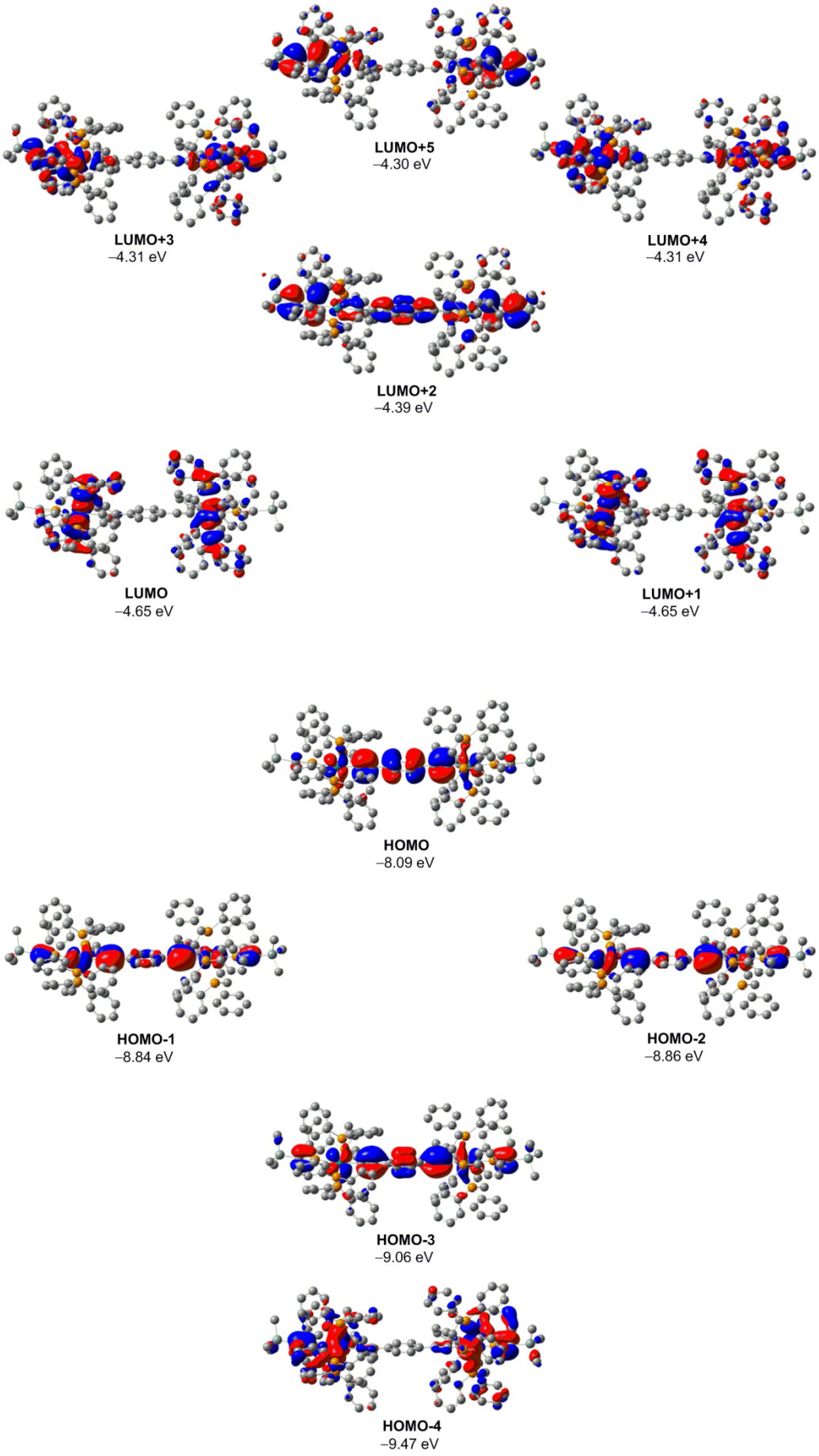

Figure S16: Selected Molecular Orbitals of $\mathbf{2}^{2+}$

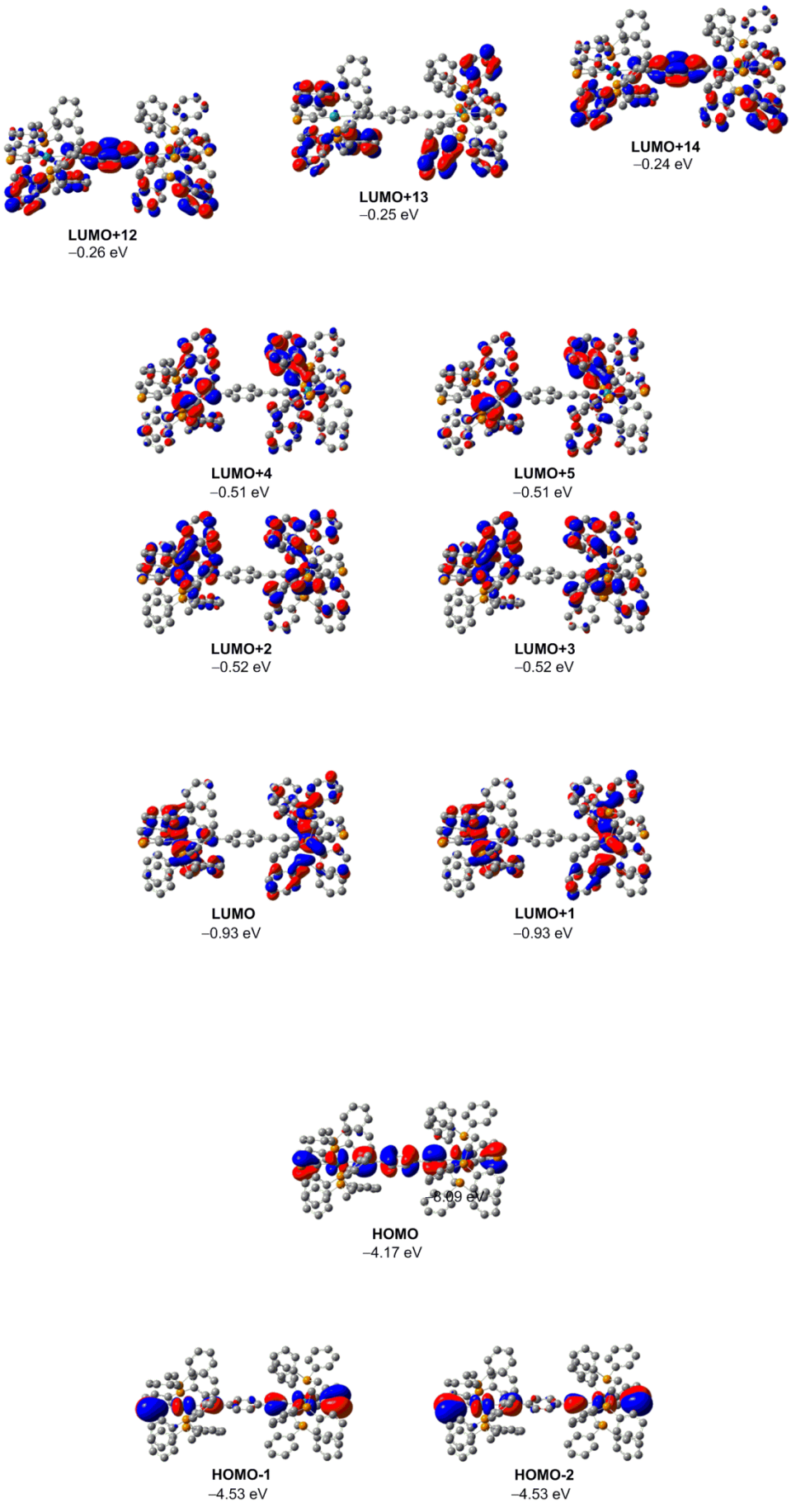

Figure S17: Selected Molecular Orbitals of **3**.

Table S1. Composition of selected molecular orbitals for $\mathbf{2}^{2+}$.

Orbital	Energy / eV	% Ru	%RC≡P	%C≡C	%Ar	%dppe
L+40	-3.05	0	2	0	0	98
L+39	-3.05	2	2	0	6	90
L+38	-3.07	4	2	2	1	92
L+37	-3.07	6	2	2	0	92
L+36	-3.1	2	2	0	0	98
L+35	-3.11	2	2	0	5	92
L+34	-3.14	6	2	2	0	91
L+33	-3.14	6	2	2	0	92
L+32	-3.17	8	4	0	2	86
L+31	-3.18	8	4	0	0	90
L+30	-3.23	0	2	0	0	98
L+29	-3.23	0	2	0	0	97
L+28	-3.27	12	6	4	0	77
L+27	-3.27	12	6	4	1	76
L+26	-3.4	2	4	0	0	93
L+25	-3.4	2	4	0	0	94
L+24	-3.42	0	2	0	1	96
L+23	-3.42	0	2	0	0	96
L+22	-3.53	2	2	0	3	92
L+21	-3.53	2	0	0	0	98
L+20	-3.56	2	2	0	1	96
L+19	-3.56	2	2	0	0	98
L+18	-3.64	2	4	2	6	86
L+17	-3.64	2	0	0	0	96
L+16	-3.66	2	8	2	5	84
L+15	-3.69	0	6	0	0	94
L+14	-3.74	0	0	2	7	88
L+13	-3.76	0	0	0	1	98
L+12	-3.79	2	10	2	8	78
L+11	-3.81	2	8	0	0	90
L+10	-3.84	2	2	4	7	86
L+9	-3.85	2	2	0	0	96
L+8	-3.87	2	0	8	18	70
L+7	-4.2	12	60	2	0	26
L+6	-4.21	12	58	4	0	26
L+5	-4.3	14	58	2	0	26
L+4	-4.31	24	22	8	0	48
L+3	-4.31	20	32	6	0	44
L+2	-4.39	8	60	6	9	18
L+1	-4.65	32	0	0	0	69
LUMO	**-4.65**	**32**	**0**	**0**	**0**	**69**
HOMO	**-8.09**	**14**	**4**	**44**	**32**	**6**
H-1	-8.84	32	10	46	3	8
H-2	-8.86	32	12	42	4	10

H-3	-9.06	34	14	36	8	8
H-4	-9.47	14	20	2	0	62
H-5	-9.48	14	16	2	0	68
H-6	-9.57	20	30	2	2	46
H-7	-9.6	12	16	4	1	68
H-8	-9.74	6	16	4	7	66
H-9	-9.75	2	22	6	1	68
H-10	-9.78	4	6	2	31	58

Table S2. Composition of selected molecular orbitals for **3**.

Orbital	Energy / eV	% Ru	%C≡P	%C≡C	%Ar	%dppe
L+20	-0.12	0	0	0	2	96
L+19	-0.12	0	0	0	0	100
L+18	-0.16	2	2	2	7	86
L+17	-0.17	2	2	0	0	96
L+16	-0.2	2	2	2	3	94
L+15	-0.2	2	0	0	0	98
L+14	-0.24	2	2	8	21	66
L+13	-0.25	2	0	0	0	98
L+12	-0.26	0	2	8	15	74
L+11	-0.33	0	0	0	0	98
L+10	-0.35	0	2	2	5	90
L+9	-0.4	2	2	0	0	94
L+8	-0.41	2	2	0	2	96
L+7	-0.42	0	2	0	0	98
L+6	-0.43	2	2	2	4	92
L+5	-0.51	2	2	0	0	98
L+4	-0.51	2	2	0	1	96
L+3	-0.52	4	0	0	0	96
L+2	-0.52	4	0	0	0	96
L+1	-0.93	24	0	0	0	76
LUMO	**-0.93**	**24**	**0**	**0**	**0**	**76**
HOMO	**-4.17**	**26**	**14**	**34**	**22**	**4**
H-1	-4.53	38	44	12	1	6
H-2	-4.53	36	42	15	2	4
H-3	-4.68	34	48	8	3	4
H-4	-5.06	8	52	16	12	12
H-5	-5.49	2	28	44	3	22
H-6	-5.51	4	26	42	4	26
H-7	-5.68	8	24	38	8	22
H-8	-5.93	80	0	0	0	20
H-9	-5.93	80	2	0	0	20
H-10	-6.19	12	6	2	1	78
H-11	-6.2	12	10	2	0	74
H-12	-6.25	2	2	0	86	10
H-13	-6.26	10	14	6	13	58
H-14	-6.27	8	50	16	1	26
H-15	-6.29	10	42	14	1	34
H-16	-6.32	8	8	6	1	78
H-17	-6.46	12	8	2	2	76
H-18	-6.47	2	2	0	0	92
H-19	-6.49	8	2	0	2	88
H-20	-6.52	4	2	4	0	92

Table S3. First 200 excited states for $\mathbf{2}^{2+}$ derived from TD-DFT.

No.	E /cm^{-1}	λ / nm	Osc. Strength	Major contributions
1	23034.55	434.1305	0.0021	HOMO->LUMO (83%)
2	23045.03	433.9330	0.0111	HOMO->L+1 (83%)
3	25713.94	388.8941	0.0001	HOMO->L+3 (66%)
4	25729.26	388.6625	0.0005	HOMO->L+4 (65%)
5	26155.93	382.3224	0.0003	H-2->LUMO (28%), H-1->L+1 (32%)
6	26155.93	382.3224	0.0014	H-2->L+1 (28%), H-1->LUMO (33%)
7	27439.17	364.4425	0.4642	HOMO->L+2 (86%)
8	28009.41	357.0229	0.0002	HOMO->L+5 (63%), HOMO->L+7 (17%)
9	28225.57	354.2887	0.0048	H-2->L+4 (26%), H-1->L+3 (32%)
10	28236.86	354.1470	0.0000	H-2->L+3 (29%), H-1->L+4 (33%)
11	28523.19	350.5919	0.1105	HOMO->L+6 (65%)
12	28678.05	348.6988	0.0001	H-13->L+1 (12%), H-12->L+1 (11%), H-11->LUMO (23%)
13	28717.57	348.2189	0.0127	H-13->LUMO (13%), H-12->LUMO (12%), H-11->L+1 (24%)
14	28842.59	346.7096	0.0001	HOMO->L+5 (15%), HOMO->L+7 (59%)
15	30122.60	331.9767	0.0256	H-2->L+5 (30%), H-1->L+2 (46%)
16	30162.12	331.5417	0.0000	H-2->L+2 (42%), H-1->L+5 (32%)
17	30542.81	327.4093	0.0097	H-3->L+1 (55%), HOMO->LUMO (11%)
18	30553.30	327.2969	0.0055	H-3->LUMO (55%), HOMO->L+1 (11%)
19	31554.24	316.9146	0.2208	HOMO->L+8 (60%), HOMO->L+10 (31%)
20	31613.12	316.3244	0.0000	HOMO->L+9 (83%)
21	31693.78	315.5194	0.5160	HOMO->L+8 (31%), HOMO->L+10 (49%)
22	31952.68	312.9628	0.0005	HOMO->L+11 (74%)
23	31991.40	312.5840	0.2350	HOMO->L+12 (56%)
24	32434.20	308.3166	0.0003	HOMO->L+13 (88%)
25	32477.75	307.9031	0.0833	HOMO->L+12 (17%), HOMO->L+14 (54%)
26	32650.36	306.2754	0.0001	H-3->L+2 (12%), H-2->L+6 (14%), H-1->L+7 (17%)
27	32722.14	305.6035	0.0014	H-2->LUMO (43%), H-1->L+1 (43%)
28	32722.14	305.6035	0.0005	H-2->L+1 (43%), H-1->LUMO (43%)
29	32839.90	304.5077	0.0388	HOMO->L+12 (11%), HOMO->L+14 (37%)
30	33117.35	301.9565	0.0085	H-3->L+3 (42%), HOMO->L+4 (12%)
31	33123.00	301.9050	0.0001	H-3->L+4 (41%), HOMO->L+3 (12%)
32	33360.13	299.7590	0.0000	HOMO->L+15 (67%), HOMO->L+17 (18%)
33	33448.85	298.9639	0.0211	HOMO->L+16 (71%), HOMO->L+18 (11%)
34	33810.19	295.7688	0.0012	HOMO->L+15 (15%), HOMO->L+17 (68%)
35	33864.23	295.2969	0.0181	H-1->L+2 (24%), H-1->L+8 (21%)
36	33911.01	294.8895	0.0597	HOMO->L+18 (60%)
37	33979.57	294.2945	0.0004	H-2->L+2 (22%), H-2->L+8 (18%)
38	34111.84	293.1533	0.0740	H-5->LUMO (39%), H-4->L+1 (34%)
39	34112.65	293.1464	0.0741	H-5->L+1 (36%), H-4->LUMO (32%)
40	34181.21	292.5584	0.0044	H-3->L+6 (24%)
41	34214.28	292.2757	0.0156	H-3->L+7 (19%), HOMO->L+18 (20%)
42	34672.40	288.4138	0.0010	HOMO->L+21 (87%)
43	34727.25	287.9583	0.0301	HOMO->L+22 (81%)
44	34794.19	287.4043	0.0000	HOMO->L+19 (87%)
45	34797.42	287.3776	0.0057	HOMO->L+20 (82%)

46	35202.31	284.0723	0.0716	H-7->LUMO (10%), H-6->L+1 (11%)
47	35210.38	284.0072	0.0383	H-7->L+1 (27%), H-6->LUMO (29%)
48	35278.13	283.4618	0.0738	H-7->LUMO (20%), H-6->L+1 (23%)
49	35338.62	282.9765	0.0718	H-11->L+4 (13%)
50	35669.31	280.3531	0.0000	HOMO->L+23 (58%), HOMO->L+25 (11%)
51	35678.18	280.2833	0.0011	H-2->L+4 (31%), H-1->L+3 (28%), HOMO->L+24 (15%), HOMO->L+26 (16%)
52	35691.09	280.1820	0.0003	H-2->L+3 (39%), H-1->L+4 (32%), HOMO->L+23 (11%)
53	35714.48	279.9985	0.0129	H-2->L+4 (12%), H-1->L+3 (11%), HOMO->L+24 (59%)
54	35744.32	279.7647	0.0075	H-5->L+2 (12%), H-1->L+5 (11%), HOMO->L+23 (13%)
55	35824.98	279.1349	0.0125	H-5->L+5 (14%), H-4->L+2 (16%), H-2->L+5 (13%)
56	35891.11	278.6205	0.0025	HOMO->L+25 (58%)
57	35902.41	278.5329	0.0082	HOMO->L+24 (16%), HOMO->L+26 (50%), HOMO->L+28 (10%)
58	36164.54	276.5140	0.0055	H-3->L+2 (37%), H-1->L+7 (10%)
59	36285.52	275.5920	0.0510	H-3->L+5 (15%), H-2->L+5 (18%), H-1->L+6 (16%)
60	36363.76	274.9991	0.0002	HOMO->L+26 (15%), HOMO->L+28 (69%)
61	36366.18	274.9808	0.0016	HOMO->L+25 (14%), HOMO->L+27 (66%)
62	36565.40	273.4826	0.1027	H-5->L+4 (12%), H-4->L+3 (11%), H-1->L+10 (17%)
63	36566.20	273.4766	0.0134	H-5->L+3 (10%), H-2->L+10 (21%), H-1->L+9 (14%)
64	36649.28	272.8567	0.0004	H-2->L+2 (10%), H-2->L+6 (10%), H-2->L+8 (24%), H-1->L+5 (15%)
65	36704.93	272.4429	0.0300	H-2->L+9 (24%), H-1->L+8 (11%), H-1->L+10 (23%)
66	36755.75	272.0663	0.0241	H-5->L+3 (13%), H-4->L+4 (16%), H-2->L+10 (16%), H-1->L+9 (21%)
67	36830.76	271.5122	0.0087	HOMO->L+41 (55%)
68	36844.47	271.4112	0.0152	H-9->L+1 (34%), H-8->LUMO (33%)
69	36850.92	271.3636	0.0254	H-9->LUMO (37%), H-8->L+1 (33%)
70	36910.61	270.9248	0.0570	H-2->L+7 (11%)
71	36960.61	270.5583	0.0017	H-1->L+7 (13%), HOMO->L+31 (21%)
72	37016.26	270.1515	0.0227	HOMO->L+29 (10%), HOMO->L+32 (39%)
73	37042.88	269.9574	0.0004	HOMO->L+31 (44%)
74	37170.32	269.0319	0.0150	H-3->L+5 (10%), H-2->L+11 (12%), HOMO->L+32 (11%)
75	37207.42	268.7636	0.0033	H-2->L+7 (31%), H-1->L+6 (30%)
76	37217.10	268.6937	0.0014	H-2->L+6 (23%), H-2->L+8 (14%), H-1->L+7 (12%)
77	37331.63	267.8694	0.0001	H-2->L+12 (18%), H-1->L+7 (15%), H-1->L+11 (13%)
78	37339.70	267.8115	0.0128	H-10->LUMO (10%), H-1->L+12 (10%)
79	37362.28	267.6496	0.0031	HOMO->L+30 (73%)
80	37422.77	267.2170	0.0070	HOMO->L+29 (54%), HOMO->L+32 (14%)
81	37506.65	266.6194	0.0894	
82	37534.88	266.4188	0.1179	
83	37651.03	265.5970	0.0033	H-2->L+14 (33%), H-1->L+13 (41%)
84	37671.19	265.4548	0.0545	H-2->L+13 (36%), H-1->L+14 (40%)
85	37715.55	265.1426	0.0001	H-5->LUMO (34%), H-4->L+1 (35%)
86	37728.46	265.0519	0.0144	H-5->L+1 (33%), H-4->LUMO (31%)
87	37814.76	264.4470	0.0018	H-7->L+4 (21%), H-6->L+3 (21%)
88	37818.79	264.4188	0.0874	H-7->L+3 (18%), H-6->L+4 (21%)
89	37886.54	263.9460	0.0721	HOMO->L+34 (12%)
90	37958.33	263.4468	0.0718	HOMO->L+33 (18%)

91	38005.91	263.1169	0.0157	HOMO->L+34 (64%)
92	38007.53	263.1058	0.0227	HOMO->L+33 (57%)
93	38101.09	262.4597	0.0024	H-15->L+1 (21%), H-14->LUMO (15%)
94	38126.90	262.2820	0.0099	H-15->LUMO (21%), H-14->L+1 (19%)
95	38206.75	261.7339	0.0021	H-2->L+16 (26%), H-1->L+15 (28%)
96	38223.68	261.6179	0.0011	H-2->L+15 (28%), H-1->L+16 (31%)
97	38272.08	261.2871	0.0165	H-7->L+6 (13%), H-3->L+6 (23%)
98	38301.92	261.0835	0.0022	H-7->L+7 (14%), H-6->L+6 (11%), H-3->L+7 (24%)
99	38398.71	260.4254	0.0003	HOMO->L+35 (78%)
100	38399.52	260.4200	0.0006	HOMO->L+36 (84%)
101	38435.81	260.1740	0.0167	H-17->L+1 (25%), H-16->LUMO (25%)
102	38439.84	260.1467	0.0125	H-17->LUMO (25%), H-16->L+1 (24%)
103	38599.54	259.0704	0.0056	H-18->LUMO (20%)
104	38625.35	258.8973	0.0108	H-18->L+1 (19%), H-15->LUMO (11%), HOMO->L+38 (23%)
105	38666.49	258.6219	0.0006	H-2->L+18 (11%), H-1->L+17 (13%), HOMO->L+37 (36%)
106	38668.91	258.6057	0.0055	H-7->L+1 (17%), H-6->LUMO (14%), H-2->L+17 (11%), H-1->L+18 (11%)
107	38669.71	258.6003	0.0056	H-7->LUMO (14%), H-6->L+1 (12%), HOMO->L+37 (36%)
108	38689.07	258.4709	0.0149	HOMO->L+38 (49%)
109	38782.63	257.8474	0.0005	H-2->L+18 (20%), H-1->L+17 (18%)
110	38783.44	257.8420	0.0270	H-2->L+17 (14%), H-1->L+18 (21%)
111	38811.67	257.6545	0.0204	H-13->LUMO (32%), H-12->LUMO (20%)
112	38819.73	257.6009	0.0003	H-13->L+1 (28%), H-12->L+1 (18%)
113	38881.03	257.1948	0.0034	H-10->L+5 (10%), H-9->L+2 (19%), H-8->L+5 (11%), H-3->L+8 (12%)
114	38941.52	256.7953	0.0052	H-10->L+2 (13%), H-9->L+5 (12%)
115	38960.07	256.6730	0.0199	H-20->L+1 (18%), H-19->LUMO (16%)
116	38960.88	256.6677	0.0057	H-20->LUMO (19%), H-19->L+1 (17%)
117	39117.35	255.6410	0.0000	H-3->L+8 (32%), HOMO->L+39 (24%)
118	39123.00	255.6041	0.0022	H-23->LUMO (16%), H-22->L+1 (15%), H-20->L+1 (12%), H-19->LUMO (13%), HOMO->L+40 (12%)
119	39124.61	255.5936	0.0146	H-23->L+1 (17%), H-22->LUMO (16%), H-20->LUMO (12%), H-19->L+1 (13%), HOMO->L+39 (11%)
120	39189.94	255.1675	0.0078	H-3->L+8 (12%), HOMO->L+39 (50%)
121	39201.24	255.0940	0.0038	HOMO->L+40 (66%)
122	39298.02	254.4657	0.0064	H-22->L+1 (11%), H-21->LUMO (26%)
123	39301.25	254.4448	0.0001	H-21->L+1 (20%), H-2->L+10 (12%)
124	39330.29	254.2570	0.0057	H-3->L+10 (15%), H-2->L+10 (21%), H-1->L+9 (16%)
125	39332.70	254.2413	0.0020	H-3->L+9 (21%), H-2->L+9 (31%), H-1->L+10 (20%)
126	39436.75	253.5706	0.0134	H-9->L+4 (23%), H-8->L+3 (19%)
127	39447.24	253.5032	0.0010	H-9->L+3 (22%), H-8->L+4 (16%)
128	39511.76	253.0892	0.0000	H-25->L+1 (17%), H-24->LUMO (16%)
129	39515.79	253.0634	0.0917	H-25->LUMO (17%), H-24->L+1 (16%)
130	39564.19	252.7538	0.0003	H-27->LUMO (11%), H-26->L+1 (12%), H-25->LUMO (15%), H-24->L+1 (11%)
131	39580.32	252.6508	0.0017	H-27->L+1 (16%), H-26->LUMO (16%)
132	39647.26	252.2242	0.0004	H-3->L+12 (11%), H-2->L+12 (13%), H-1->L+11 (11%)
133	39680.33	252.0140	0.0370	H-2->L+11 (12%), H-2->L+19 (16%), H-1->L+20 (19%)
134	39698.08	251.9014	0.0146	H-3->L+11 (17%), H-2->L+11 (15%)

135	39741.63	251.6253	0.0019	H-27->L+1 (11%), H-1->L+21 (11%)
136	39746.47	251.5947	0.0025	H-2->L+21 (27%), H-1->L+22 (32%)
137	39765.02	251.4773	0.0016	H-2->L+20 (24%), H-1->L+19 (26%)
138	39773.09	251.4263	0.0225	H-1->L+20 (10%)
139	39827.93	251.0801	0.0010	H-3->L+10 (19%), H-2->L+22 (12%), H-1->L+21 (11%)
140	39849.71	250.9429	0.0137	H-3->L+9 (54%), H-2->L+9 (10%), H-1->L+10 (15%)
141	39873.10	250.7956	0.0003	H-3->L+10 (26%)
142	39978.76	250.1328	0.0110	H-30->LUMO (12%), H-29->L+1 (10%), H-9->L+1 (15%), H-8->LUMO (13%)
143	39983.60	250.1025	0.0010	H-30->L+1 (11%), H-9->LUMO (15%), H-8->L+1 (13%)
144	40041.67	249.7398	0.0022	
145	40049.74	249.6895	0.0082	H-2->L+13 (17%), H-1->L+14 (12%)
146	40057.00	249.6443	0.0053	H-2->L+13 (20%), H-1->L+14 (12%)
147	40073.93	249.5388	0.0007	H-2->L+14 (24%), H-1->L+13 (19%)
148	40121.52	249.2428	0.0006	
149	40122.33	249.2378	0.0120	
150	40136.85	249.1476	0.0092	H-30->LUMO (13%), H-29->L+1 (11%)
151	40146.52	249.0876	0.0086	H-30->L+1 (13%), H-29->LUMO (12%)
152	40244.92	248.4785	0.0175	H-32->L+1 (14%), H-31->LUMO (18%), H-3->L+11 (10%)
153	40246.54	248.4686	0.0001	H-32->LUMO (17%), H-31->L+1 (21%)
154	40272.35	248.3093	0.0005	H-3->L+11 (14%)
155	40339.29	247.8973	0.0000	H-11->LUMO (37%), H-10->L+1 (34%)
156	40340.10	247.8923	0.0010	H-11->L+1 (39%), H-10->LUMO (36%)
157	40350.58	247.8279	0.0000	H-3->L+12 (31%)
158	40365.10	247.7388	0.0316	H-34->L+1 (20%), H-33->LUMO (26%)
159	40365.10	247.7388	0.0001	H-34->LUMO (19%), H-33->L+1 (24%)
160	40418.33	247.4125	0.0157	H-3->L+11 (10%)
161	40418.33	247.4125	0.0012	
162	40517.54	246.8067	0.0038	H-5->L+5 (39%), H-4->L+2 (32%)
163	40523.19	246.7723	0.0000	H-5->L+2 (33%), H-4->L+5 (34%)
164	40611.10	246.2381	0.0011	H-3->L+13 (67%), H-1->L+14 (10%)
165	40616.75	246.2039	0.0091	H-14->LUMO (15%), H-3->L+14 (14%)
166	40621.59	246.1745	0.0062	H-14->L+1 (18%)
167	40644.98	246.0329	0.0000	H-3->L+14 (49%)
168	40669.17	245.8865	0.0001	H-5->L+3 (31%), H-4->L+4 (23%)
169	40676.43	245.8426	0.0036	H-5->L+4 (27%), H-4->L+3 (26%)
170	40770.80	245.2736	0.0005	H-3->L+15 (26%), H-2->L+15 (16%), H-1->L+16 (10%)
171	40807.10	245.0554	0.0000	H-14->LUMO (13%), H-3->L+16 (17%), H-2->L+16 (10%)
172	40879.69	244.6203	0.0180	H-15->LUMO (15%), H-14->L+1 (12%)
173	40889.37	244.5624	0.0069	H-15->L+1 (11%)
174	40909.53	244.4418	0.0248	H-15->L+3 (11%), H-2->L+23 (11%), H-1->L+24 (12%)
175	40917.60	244.3936	0.0014	H-2->L+24 (18%), H-1->L+23 (20%)
176	40969.22	244.0857	0.0035	H-15->LUMO (13%), H-2->L+23 (12%), H-1->L+24 (13%)
177	40978.09	244.0329	0.0001	H-15->L+1 (13%)
178	41026.48	243.7450	0.0002	H-18->LUMO (27%), H-17->L+1 (23%)
179	41028.90	243.7306	0.0053	H-18->L+1 (26%), H-17->LUMO (36%), H-16->L+1 (14%)
180	41031.32	243.7163	0.0001	H-17->L+1 (11%)
181	41032.93	243.7067	0.0020	H-2->L+23 (11%), H-1->L+24 (13%)

182	41086.17	243.3909	0.0006	H-36->LUMO (11%), H-17->L+1 (10%), H-16->LUMO (22%)
183	41093.43	243.3479	0.0145	H-37->LUMO (12%), H-36->L+1 (17%), H-16->L+1 (15%)
184	41156.34	242.9759	0.0149	
185	41159.56	242.9569	0.0078	H-36->LUMO (11%)
186	41186.99	242.7951	0.0040	H-2->L+17 (14%)
187	41221.67	242.5909	0.0001	H-3->L+18 (21%), H-2->L+18 (25%), H-1->L+17 (14%)
188	41258.77	242.3727	0.0127	
189	41261.19	242.3585	0.0131	H-38->LUMO (11%), H-35->L+1 (10%)
190	41268.45	242.3159	0.0079	H-6->L+2 (14%)
191	41295.87	242.1550	0.0003	H-2->L+26 (18%), H-1->L+25 (22%)
192	41317.65	242.0273	0.0049	H-2->L+25 (12%), H-1->L+26 (13%)
193	41323.30	241.9943	0.0050	H-16->L+3 (10%), H-7->L+2 (15%), H-6->L+5 (14%), H-3->L+16 (11%)
194	41342.65	241.8809	0.0004	H-3->L+16 (17%), H-1->L+15 (11%)
195	41358.78	241.7866	0.0030	H-7->L+5 (14%)
196	41401.53	241.5370	0.0117	H-15->L+2 (12%), H-3->L+15 (10%)
197	41450.73	241.2503	0.0036	
198	41478.96	241.0861	0.0011	H-20->L+1 (12%), H-19->LUMO (17%), H-17->L+2 (14%)
199	41481.38	241.0720	0.0026	H-20->LUMO (24%), H-19->L+1 (30%)
200	41487.83	241.0345	0.0096	H-20->L+1 (20%), H-19->LUMO (19%), H-17->L+2 (11%)

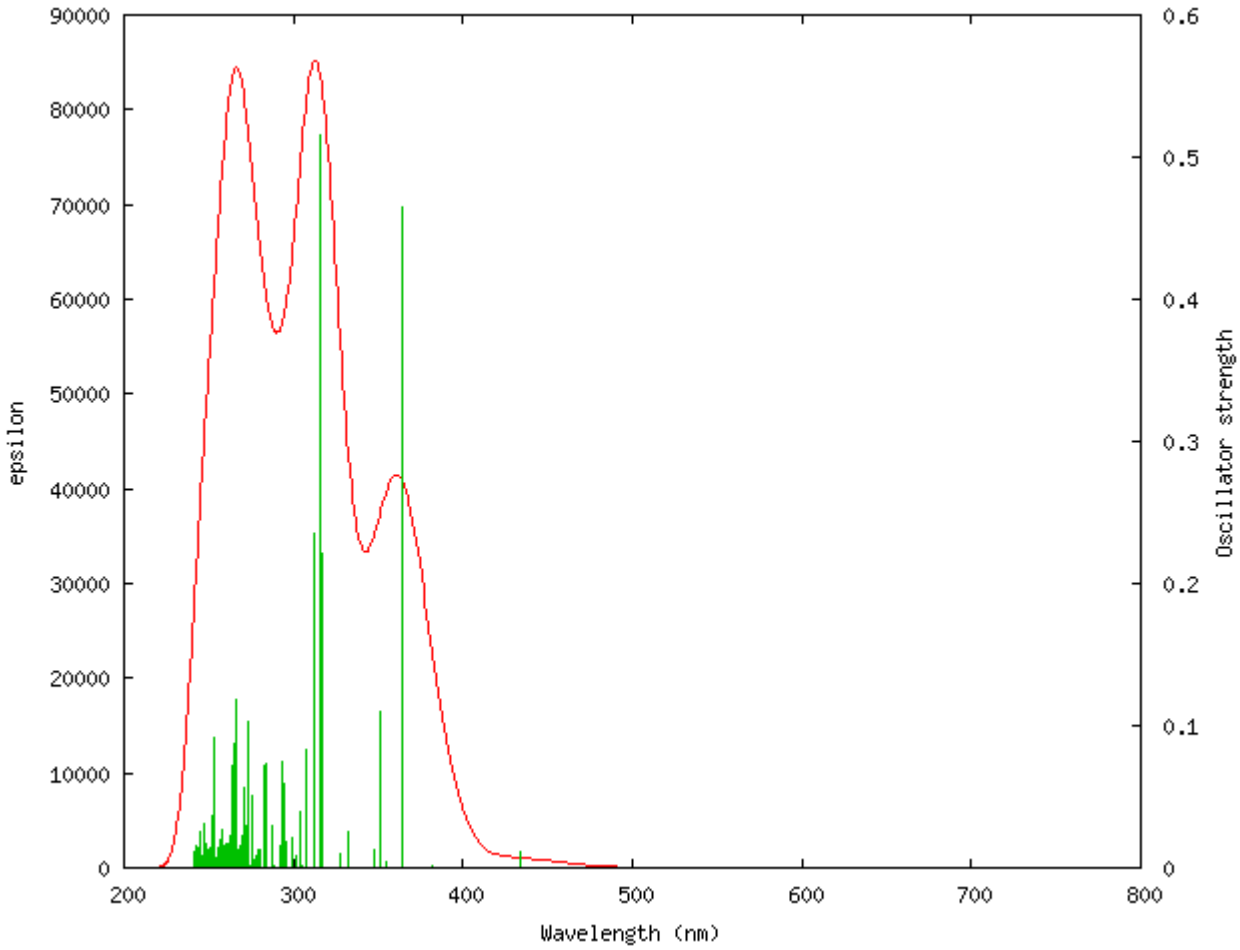

Figure S18: Simulated UV/Vis spectrum for $\mathbf{2}^{2+}$, showing calculated electronic transitions, derived from TD-DFT.

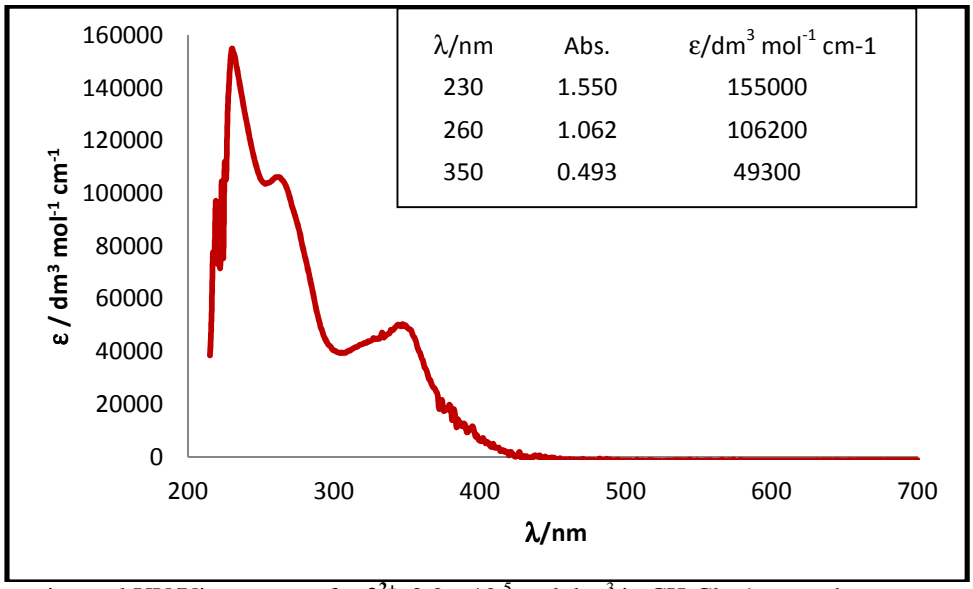

Figure S19: Experimental UV/Vis spectrum for $\mathbf{2}^{2+}$, 2.0 x 10^{-5} mol dm^{-3} in CH_2Cl_2, 1 cm path.

Table S4. First 200 excited states for **3** derived from TD-DFT.

No.	E /cm^{-1}	λ / nm	Osc. Strength	Major contributions
1	20675.36	483.6675	0.0006	H-1->L+1 (16%), HOMO->LUMO (64%)
2	20679.39	483.5732	0.0003	H-1->LUMO (16%), HOMO->L+1 (63%)
3	21860.20	457.4524	0.0035	H-3->L+1 (14%), H-2->LUMO (44%), H-1->L+1 (27%)
4	21861.00	457.4356	0.0001	H-3->LUMO (14%), H-2->L+1 (44%), H-1->LUMO (27%)
5	25959.94	385.2089	0.0012	HOMO->L+2 (73%)
6	25984.14	384.8502	0.0005	HOMO->L+3 (72%)
7	26158.35	382.2871	0.0091	H-3->L+1 (34%), H-1->L+1 (10%), HOMO->LUMO (18%), HOMO->L+4 (18%)
8	26168.84	382.1339	0.0057	H-3->LUMO (36%), H-1->LUMO (11%), HOMO->L+1 (19%), HOMO->L+5 (16%)
9	26497.92	377.3882	0.0247	HOMO->L+4 (71%)
10	26536.63	376.8376	0.0036	HOMO->L+5 (70%)
11	27268.99	366.7170	0.0407	HOMO->L+6 (46%), HOMO->L+8 (10%)
12	27308.51	366.1862	0.0009	H-2->L+3 (14%), H-1->L+2 (11%), HOMO->L+7 (11%), HOMO->L+9 (30%)
13	27442.40	364.3996	0.0389	H-2->L+2 (24%), H-1->L+3 (17%), HOMO->L+6 (34%)
14	27452.08	364.2712	0.0019	HOMO->L+8 (73%)
15	27461.75	364.1428	0.0000	HOMO->L+7 (33%), HOMO->L+9 (47%)
16	27482.73	363.8649	0.0000	H-2->L+3 (19%), H-1->L+2 (15%), HOMO->L+7 (44%)
17	27685.17	361.2042	0.0009	H-3->L+1 (12%), H-2->LUMO (47%), H-1->L+1 (37%)
18	27687.59	361.1726	0.0014	H-3->LUMO (12%), H-2->L+1 (47%), H-1->LUMO (37%)
19	28024.73	356.8277	0.0729	H-2->L+4 (25%), H-1->L+5 (15%), HOMO->L+10 (38%)
20	28061.03	356.3661	0.0002	H-2->L+5 (33%), H-1->L+4 (33%)
21	28154.59	355.1819	0.1578	H-2->L+4 (18%), H-1->L+5 (13%), HOMO->L+10 (45%)
22	28253.80	353.9347	0.0052	HOMO->L+11 (76%)
23	28615.14	349.4654	0.2142	H-9->L+1 (19%), H-8->LUMO (20%), HOMO->L+12 (41%)
24	28624.01	349.3571	0.0000	H-9->LUMO (39%), H-8->L+1 (40%)
25	28632.07	349.2587	0.2522	H-9->L+1 (20%), H-8->LUMO (21%), HOMO->L+12 (37%)
26	28755.48	347.7598	0.0006	HOMO->L+13 (81%)
27	28798.22	347.2436	0.2017	HOMO->L+14 (67%)
28	28998.25	344.8484	0.0000	H-2->L+9 (29%), H-1->L+6 (27%)
29	29024.87	344.5321	0.0624	H-2->L+6 (31%), H-1->L+9 (16%), HOMO->L+14 (12%)
30	29287.81	341.4390	0.0007	H-2->L+8 (34%), H-1->L+7 (31%)
31	29288.61	341.4296	0.0000	H-2->L+7 (36%), H-1->L+8 (30%)
32	29396.69	340.1743	0.0000	HOMO->L+15 (28%), HOMO->L+17 (51%)
33	29444.28	339.6245	0.0118	H-2->L+10 (24%), HOMO->L+16 (15%), HOMO->L+18 (23%)
34	29483.80	339.1693	0.0003	H-2->L+11 (22%), H-1->L+10 (35%)
35	29514.45	338.8171	0.1215	H-2->L+10 (20%), H-1->L+11 (13%), HOMO->L+16 (15%), HOMO->L+18 (26%)
36	29537.03	338.5580	0.0026	HOMO->L+16 (59%), HOMO->L+18 (28%)
37	29537.03	338.5580	0.0016	HOMO->L+15 (53%), HOMO->L+17 (28%)
38	29979.84	333.5575	0.0000	H-2->L+11 (21%), H-1->L+12 (51%)
39	30000.00	333.3333	0.0434	H-2->L+12 (56%), H-1->L+11 (16%)
40	30214.54	330.9664	0.0010	HOMO->L+19 (87%)
41	30228.26	330.8163	0.0188	HOMO->L+20 (82%)
42	30351.66	329.4713	0.0062	H-3->L+2 (31%), H-2->L+13 (12%), H-1->L+2 (14%), H-1->L+14

				(13%)
43	30380.70	329.1564	0.0035	H-4->LUMO (68%), H-3->L+1 (10%)
44	30387.15	329.0865	0.0125	H-4->L+1 (61%)
45	30400.86	328.9381	0.0242	H-3->L+3 (37%), H-1->L+3 (18%)
46	30461.35	328.2848	0.0126	H-2->L+13 (30%), H-1->L+14 (25%)
47	30473.45	328.1545	0.0126	H-2->L+14 (40%), H-1->L+13 (28%)
48	30623.47	326.5469	0.0038	H-3->L+4 (39%), H-1->L+4 (20%)
49	30634.76	326.4266	0.0001	H-3->L+5 (40%), H-2->L+4 (11%), H-1->L+5 (25%)
50	30675.90	325.9888	0.0016	HOMO->L+21 (77%)
51	30687.19	325.8689	0.0071	HOMO->L+22 (78%)
52	30946.90	323.1341	0.0118	H-2->L+18 (44%), H-1->L+17 (32%)
53	30956.58	323.0331	0.0014	H-2->L+17 (39%), H-1->L+18 (36%)
54	31149.35	321.0340	0.0009	H-2->L+15 (30%), H-1->L+16 (26%)
55	31168.70	320.8346	0.0044	H-2->L+16 (33%), H-1->L+15 (29%)
56	31225.97	320.2463	0.0009	H-3->L+2 (23%), H-2->L+3 (39%), H-1->L+2 (27%)
57	31232.42	320.1801	0.0006	H-3->L+3 (24%), H-2->L+2 (35%), H-1->L+3 (26%)
58	31258.23	319.9157	0.0003	H-3->L+4 (18%), H-2->L+5 (20%), H-2->L+15 (10%), H-1->L+4 (13%)
59	31292.91	319.5612	0.0004	H-3->L+5 (25%), H-2->L+4 (26%), H-1->L+5 (17%)
60	31440.52	318.0609	0.0000	H-3->L+6 (37%)
61	31453.42	317.9304	0.0029	H-3->L+7 (33%), H-1->L+7 (17%)
62	31522.78	317.2309	0.0006	H-3->L+8 (34%), H-1->L+8 (23%)
63	31538.11	317.0767	0.0004	H-3->L+9 (37%), H-2->L+8 (10%), H-1->L+9 (20%)
64	31657.48	315.8811	0.0000	HOMO->L+23 (73%)
65	31719.59	315.2626	0.0163	HOMO->L+24 (80%)
66	31909.93	313.3820	0.0001	H-3->L+10 (20%), H-2->L+19 (20%), H-1->L+20 (17%)
67	31955.10	312.9391	0.0099	H-6->L+1 (10%), H-5->LUMO (10%), H-2->L+20 (24%), H-1->L+19 (20%)
68	31955.10	312.9391	0.0012	H-6->LUMO (10%), H-5->L+1 (11%), H-3->L+10 (13%)
69	32004.30	312.4580	0.0008	H-2->L+7 (10%)
70	32031.72	312.1905	0.0100	H-2->L+8 (12%), HOMO->L+33 (12%)
71	32111.57	311.4142	0.0359	H-6->L+1 (12%), H-5->LUMO (13%), H-2->L+20 (14%), H-1->L+19 (12%)
72	32130.12	311.2344	0.0015	H-6->LUMO (15%), H-5->L+1 (18%), H-3->L+10 (12%)
73	32159.97	310.9456	0.0194	H-5->LUMO (10%), H-3->L+11 (36%), H-1->L+11 (17%)
74	32180.13	310.7508	0.0024	H-3->L+8 (15%), H-2->L+9 (12%), H-2->L+21 (13%), H-1->L+22 (11%)
75	32183.36	310.7196	0.0028	H-3->L+7 (18%), H-2->L+22 (17%), H-1->L+21 (14%)
76	32239.82	310.1755	0.0050	H-3->L+8 (14%), HOMO->L+26 (14%), HOMO->L+34 (14%)
77	32269.66	309.8886	0.0353	H-2->L+22 (11%), HOMO->L+25 (22%)
78	32327.73	309.3319	0.0000	H-2->L+9 (10%), H-2->L+21 (21%), H-1->L+22 (18%)
79	32365.64	308.9696	0.0000	H-3->L+7 (10%), H-3->L+9 (11%), H-2->L+6 (29%), H-1->L+7 (11%), H-1->L+9 (16%)
80	32387.42	308.7619	0.0011	H-3->L+12 (19%), HOMO->L+26 (20%)
81	32420.49	308.4470	0.0003	H-2->L+22 (15%), H-1->L+21 (13%)
82	32514.05	307.5594	0.0015	HOMO->L+27 (10%)
83	32527.76	307.4297	0.0066	HOMO->L+25 (45%), HOMO->L+28 (17%)
84	32591.48	306.8287	0.0015	H-3->L+12 (15%), HOMO->L+26 (27%), HOMO->L+27 (20%)
85	32789.89	304.9720	0.0028	H-3->L+13 (30%), H-1->L+13 (18%), HOMO->L+28 (25%)

86	32830.22	304.5974	0.0005	H-3->L+14 (44%), H-2->L+13 (10%), H-1->L+14 (23%)
87	32848.77	304.4254	0.0031	HOMO->L+28 (26%), HOMO->L+33 (11%)
88	32875.39	304.1789	0.0000	HOMO->L+27 (39%), HOMO->L+34 (12%)
89	33019.76	302.8490	0.0008	H-3->L+10 (15%), H-3->L+12 (12%), H-2->L+11 (35%), H-1->L+10 (19%)
90	33026.21	302.7898	0.0005	H-3->L+11 (22%), H-2->L+10 (26%), H-2->L+12 (10%), H-1->L+11 (24%)
91	33153.65	301.6259	0.0059	HOMO->L+30 (59%)
92	33176.23	301.4206	0.0002	HOMO->L+29 (70%)
93	33252.05	300.7333	0.0270	H-2->L+33 (11%), HOMO->L+30 (14%), HOMO->L+37 (10%)
94	33318.19	300.1364	0.0014	H-2->L+34 (10%)
95	33418.20	299.2381	0.0029	H-3->L+15 (20%), H-1->L+15 (20%)
96	33452.88	298.9279	0.0028	H-3->L+16 (11%), H-2->L+23 (12%), H-1->L+16 (13%), H-1->L+24 (14%)
97	33552.09	298.0440	0.0000	H-3->L+14 (20%), H-2->L+13 (24%), H-1->L+14 (14%)
98	33558.54	297.9867	0.0025	H-3->L+13 (19%), H-2->L+14 (17%), H-1->L+13 (12%)
99	33569.83	297.8865	0.0100	H-3->L+17 (21%), H-1->L+17 (11%)
100	33633.55	297.3222	0.0004	H-2->L+23 (24%), H-1->L+16 (12%), H-1->L+24 (18%)
101	33636.78	297.2936	0.0015	H-2->L+24 (28%), H-1->L+23 (21%)
102	33683.56	296.8807	0.0001	H-3->L+18 (29%), H-1->L+18 (17%)
103	33797.28	295.8818	0.0103	HOMO->L+31 (46%)
104	33819.06	295.6912	0.0060	HOMO->L+32 (44%)
105	33988.44	294.2177	0.0000	H-2->L+26 (14%), H-1->L+25 (10%), HOMO->L+31 (10%)
106	34004.57	294.0781	0.0051	H-2->L+25 (14%), H-1->L+26 (10%), HOMO->L+32 (12%)
107	34126.36	293.0286	0.0003	H-3->L+15 (38%), H-2->L+16 (25%), H-1->L+15 (13%)
108	34141.68	292.8971	0.0002	H-3->L+16 (36%), H-2->L+15 (21%), H-1->L+16 (13%)
109	34215.89	292.2619	0.0157	H-3->L+19 (24%), H-2->L+20 (10%), H-1->L+19 (24%)
110	34234.44	292.1035	0.0011	H-3->L+20 (26%), H-2->L+19 (12%), H-1->L+20 (27%)
111	34241.70	292.0416	0.0051	H-4->L+2 (65%)
112	34275.57	291.7530	0.0115	H-4->L+2 (12%), H-2->L+18 (20%), H-1->L+17 (13%)
113	34277.19	291.7392	0.0065	H-4->L+3 (71%)
114	34315.10	291.4169	0.0001	H-3->L+18 (11%), H-2->L+17 (23%), H-2->L+26 (11%), H-1->L+18 (10%)
115	34328.81	291.3005	0.0012	H-4->L+4 (75%)
116	34358.65	291.0475	0.0026	H-4->L+5 (75%)
117	34426.40	290.4747	0.0110	H-3->L+17 (25%), H-2->L+18 (13%)
118	34436.89	290.3863	0.0029	H-3->L+18 (17%), H-2->L+17 (11%), HOMO->L+38 (12%)
119	34532.87	289.5792	0.0056	H-3->L+21 (19%), H-2->L+28 (12%), H-1->L+21 (20%), H-1->L+27 (12%)
120	34538.51	289.5319	0.0001	H-3->L+22 (18%), H-2->L+27 (12%), H-1->L+22 (19%), H-1->L+28 (13%)
121	34656.27	288.5481	0.0070	H-3->L+21 (13%), H-2->L+22 (11%), H-2->L+28 (24%), H-1->L+21 (10%), H-1->L+27 (18%)
122	34663.53	288.4876	0.0007	H-3->L+22 (14%), H-2->L+21 (14%), H-2->L+27 (21%), H-1->L+22 (13%), H-1->L+28 (16%)
123	34701.44	288.1725	0.0028	H-2->L+30 (20%), H-1->L+29 (14%), HOMO->L+35 (31%)
124	34732.09	287.9182	0.0012	H-2->L+29 (36%), H-1->L+30 (27%)
125	34742.57	287.8313	0.0027	H-2->L+30 (16%), H-1->L+29 (12%), HOMO->L+35 (41%)
126	34856.30	286.8922	0.0012	H-3->L+20 (41%), H-2->L+19 (23%), H-1->L+20 (13%)

127	34862.75	286.8391	0.0002	H-3->L+19 (39%), H-2->L+20 (22%), H-1->L+19 (14%)
128	35008.74	285.6430	0.0047	
129	35044.23	285.3537	0.0150	H-2->L+39 (11%)
130	35148.27	284.5090	0.0237	H-4->L+6 (62%), H-4->L+8 (23%)
131	35194.25	284.1374	0.0000	H-4->L+7 (69%), H-4->L+9 (17%)
132	35235.38	283.8057	0.0117	H-4->L+6 (14%), H-4->L+8 (41%), H-3->L+21 (15%), H-2->L+22 (10%)
133	35237.80	283.7862	0.0000	H-3->L+22 (44%), H-2->L+21 (30%), H-1->L+22 (17%)
134	35240.22	283.7667	0.0025	H-4->L+8 (23%), H-3->L+21 (29%), H-2->L+22 (20%), H-1->L+21 (11%)
135	35325.71	283.0799	0.0141	H-4->L+9 (44%), H-2->L+31 (16%), H-1->L+32 (13%)
136	35332.17	283.0282	0.0016	H-2->L+32 (37%), H-1->L+31 (33%)
137	35341.04	282.9572	0.0017	H-4->L+7 (11%), H-4->L+9 (25%), H-2->L+31 (23%), H-1->L+32 (19%)
138	35433.79	282.2165	0.0096	H-7->L+1 (39%), H-6->L+1 (11%)
139	35439.44	282.1715	0.0380	H-7->LUMO (41%), H-6->LUMO (11%)
140	35681.41	280.2580	0.0010	H-3->L+23 (35%), H-2->L+24 (19%), H-1->L+23 (34%)
141	35704.80	280.0744	0.0011	H-3->L+24 (31%), H-2->L+23 (20%), H-1->L+24 (36%)
142	35904.82	278.5141	0.0274	H-4->L+10 (77%)
143	35975.00	277.9708	0.0054	H-6->LUMO (32%), H-5->L+1 (34%)
144	35978.22	277.9459	0.0026	H-7->L+1 (11%), H-6->L+1 (34%), H-5->LUMO (36%)
145	36006.45	277.7280	0.0002	H-4->L+11 (75%)
146	36137.11	276.7238	0.0076	H-1->L+41 (11%), HOMO->L+40 (27%)
147	36148.41	276.6374	0.0005	H-1->L+40 (12%), HOMO->L+41 (25%)
148	36237.93	275.9539	0.0156	H-3->L+23 (37%), H-2->L+24 (23%), H-1->L+23 (13%)
149	36269.39	275.7146	0.0003	H-3->L+24 (44%), H-2->L+23 (23%), H-1->L+24 (12%)
150	36362.14	275.0113	0.1082	H-4->L+12 (68%)
151	36421.83	274.5606	0.0000	H-3->L+25 (35%), H-2->L+26 (10%), H-1->L+25 (24%)
152	36427.48	274.5181	0.0108	H-3->L+26 (32%), H-1->L+26 (22%)
153	36533.94	273.7181	0.0069	H-4->L+13 (58%)
154	36543.62	273.6456	0.0373	H-6->L+3 (13%), H-5->L+2 (16%), H-4->L+14 (46%)
155	36637.18	272.9468	0.0099	H-6->L+2 (26%), H-5->L+3 (33%), H-4->L+13 (11%)
156	36647.67	272.8687	0.0003	H-6->L+4 (14%), H-5->L+5 (13%), H-4->L+13 (13%), H-3->L+28 (20%), H-1->L+28 (16%)
157	36660.57	272.7726	0.0011	H-6->L+5 (18%), H-5->L+4 (25%), H-3->L+27 (16%), H-1->L+27 (13%)
158	36664.60	272.7426	0.0187	H-6->L+3 (20%), H-5->L+2 (21%), H-4->L+14 (28%)
159	36690.41	272.5508	0.0023	H-6->L+5 (14%), H-5->L+4 (17%), H-3->L+27 (19%), H-1->L+27 (15%)
160	36707.35	272.4250	0.0000	H-6->L+4 (20%), H-5->L+5 (22%), H-3->L+28 (16%), H-1->L+28 (13%)
161	36994.49	270.3105	0.0002	H-3->L+29 (43%), H-1->L+29 (23%)
162	36995.29	270.3046	0.0001	H-3->L+30 (43%), H-1->L+30 (23%)
163	37043.69	269.9515	0.0001	H-3->L+26 (29%), H-2->L+25 (31%), H-1->L+26 (19%)
164	37043.69	269.9515	0.0008	H-3->L+25 (28%), H-2->L+26 (30%), H-1->L+25 (19%)
165	37059.82	269.8340	0.0005	H-13->LUMO (32%), H-12->L+1 (32%), H-11->LUMO (13%)
166	37059.82	269.8340	0.0079	H-13->L+1 (32%), H-12->LUMO (32%), H-11->L+1 (12%)
167	37142.09	269.2363	0.0027	H-2->L+41 (11%)
168	37148.54	269.1896	0.0048	H-2->L+40 (16%)

169	37193.71	268.8627	0.0000	H-4->L+17 (13%)
170	37222.74	268.6530	0.0002	H-4->L+16 (44%)
171	37230.81	268.5948	0.0017	H-4->L+15 (61%), H-4->L+17 (11%)
172	37283.24	268.2171	0.0067	H-4->L+16 (21%), H-4->L+18 (17%), H-3->L+27 (12%), H-2->L+28 (14%)
173	37318.72	267.9620	0.0002	H-4->L+17 (28%), H-3->L+28 (28%), H-2->L+27 (22%), H-1->L+28 (13%)
174	37326.79	267.9041	0.0034	H-4->L+18 (44%), H-3->L+27 (19%), H-2->L+28 (14%)
175	37456.65	266.9753	0.0009	H-4->L+17 (29%), H-3->L+28 (10%), H-3->L+32 (14%)
176	37483.26	266.7857	0.0000	H-4->L+18 (17%), H-3->L+31 (22%)
177	37644.57	265.6425	0.0038	H-5->L+6 (29%), H-5->L+12 (19%)
178	37648.61	265.6141	0.0002	H-6->L+6 (26%), H-6->L+12 (16%)
179	37717.97	265.1256	0.0038	H-6->L+7 (12%), H-6->L+9 (22%), H-5->L+8 (38%)
180	37717.97	265.1256	0.0023	H-6->L+8 (30%), H-5->L+7 (15%), H-5->L+9 (20%)
181	37735.72	265.0009	0.0020	H-3->L+31 (15%), H-3->L+34 (22%), H-1->L+31 (10%)
182	37742.98	264.9500	0.0001	H-2->L+29 (13%)
183	37747.81	264.9160	0.0007	H-3->L+30 (15%), H-3->L+33 (10%), H-2->L+29 (22%), H-1->L+30 (16%)
184	37748.62	264.9103	0.0006	H-3->L+29 (24%), H-2->L+30 (36%), H-1->L+29 (24%)
185	37947.03	263.5252	0.0001	H-4->L+19 (71%)
186	37951.07	263.4972	0.0131	H-4->L+20 (65%)
187	38018.01	263.0332	0.0038	H-10->L+1 (10%), HOMO->L+36 (11%)
188	38034.14	262.9217	0.0092	H-6->L+7 (21%), H-5->L+6 (10%), H-5->L+10 (16%)
189	38066.41	262.6988	0.0070	H-6->L+6 (10%), H-6->L+12 (13%), H-5->L+7 (18%), H-5->L+9 (11%)
190	38080.12	262.6042	0.1442	H-11->L+1 (20%), H-10->LUMO (20%)
191	38135.77	262.2210	0.0125	HOMO->L+36 (15%)
192	38149.48	262.1268	0.0007	H-2->L+35 (79%)
193	38214.01	261.6842	0.0002	H-1->L+35 (87%)
194	38283.37	261.2100	0.0118	H-2->L+32 (20%), H-1->L+31 (14%)
195	38330.96	260.8857	0.0000	H-4->L+21 (33%), H-3->L+32 (18%), H-2->L+31 (23%), H-1->L+32 (15%)
196	38339.83	260.8254	0.0049	H-4->L+22 (63%)
197	38361.61	260.6773	0.0001	H-4->L+21 (51%), H-3->L+32 (14%), H-2->L+31 (12%)
198	38372.90	260.6006	0.0051	H-4->L+22 (22%), H-3->L+31 (16%), H-2->L+32 (13%)
199	38564.05	259.3088	0.0006	H-9->L+2 (30%), H-8->L+3 (30%)
200	38633.42	258.8433	0.0020	H-6->L+10 (20%), H-6->L+12 (20%), H-5->L+11 (41%)

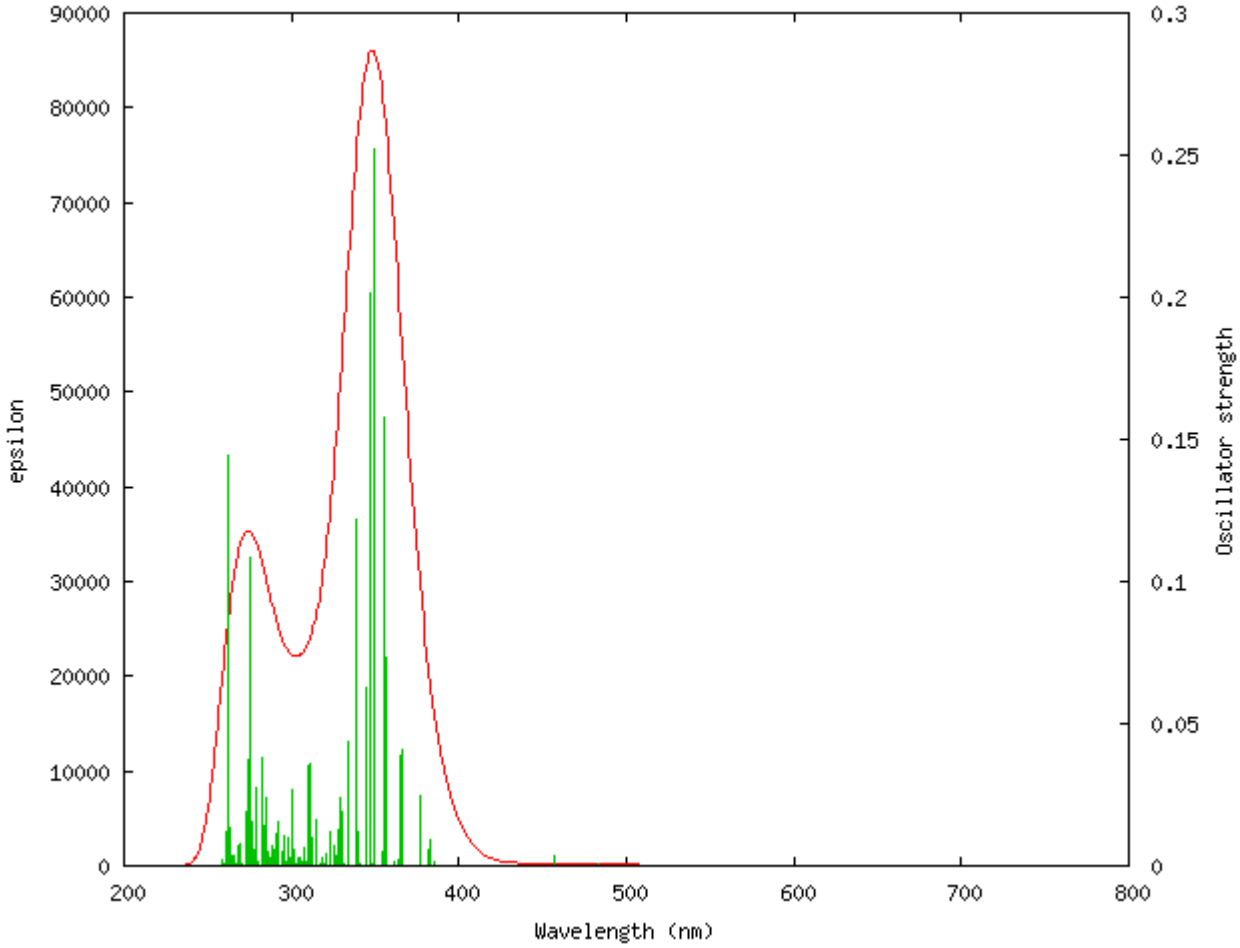

Figure S20: Simulated UV/Vis spectrum for **3**, showing calculated electronic transitions, derived from TD-DFT.

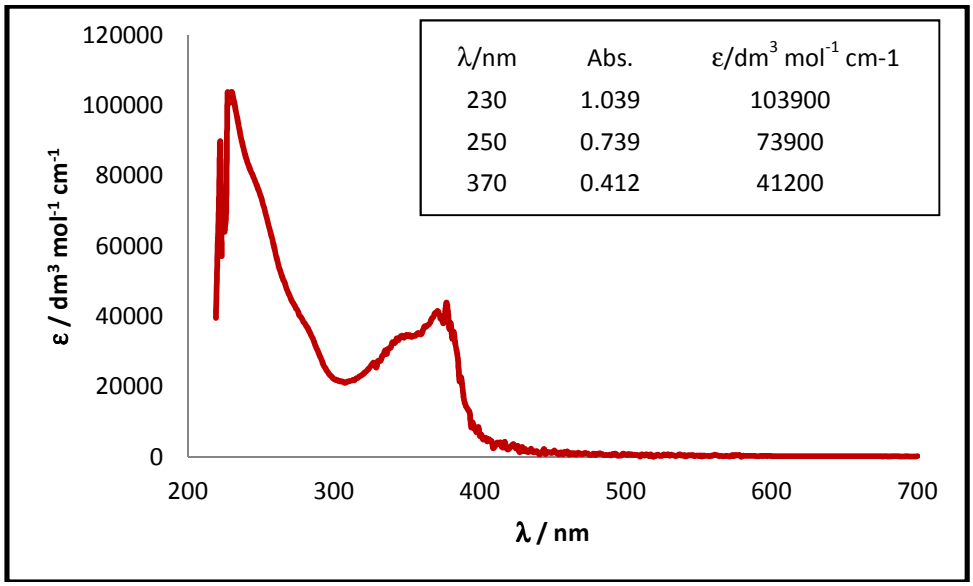

Figure S21: Experimental UV/Vis spectrum for **3**, 1.0 x 10^{-5} mol dm^{-3} in CH_2Cl_2, 1 cm path.

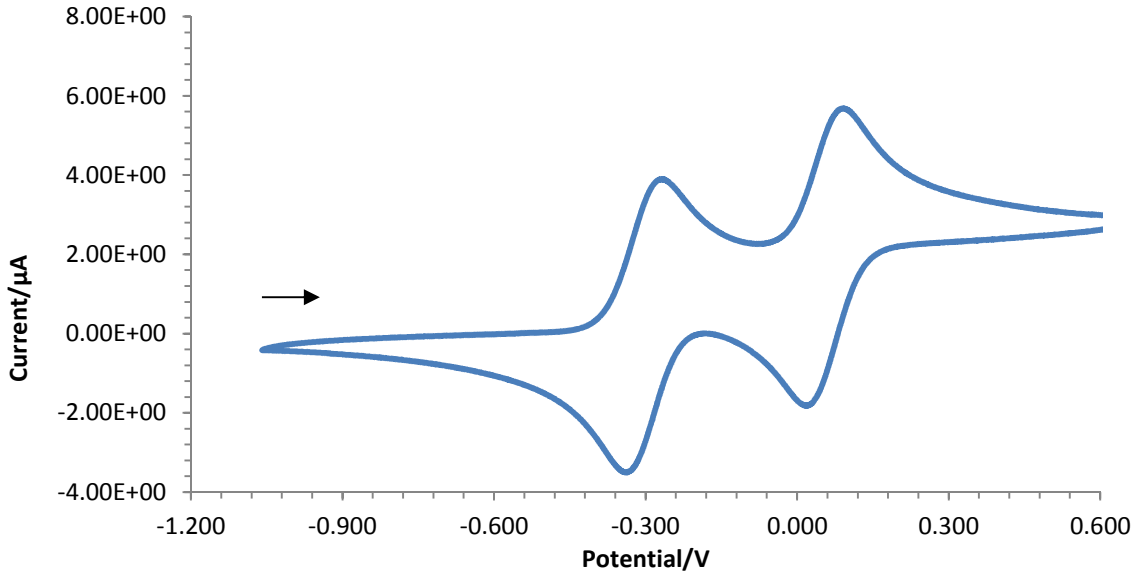

Figure S22: Cyclic Voltammagram for **1** (un-doped referenced to FcH) as solution in CH_2Cl_2 (1 mM) with $^{n}Bu_4NPF_6$ (0.1 M) supporting electrolyte; recorded at 100 mV s^{-1}.

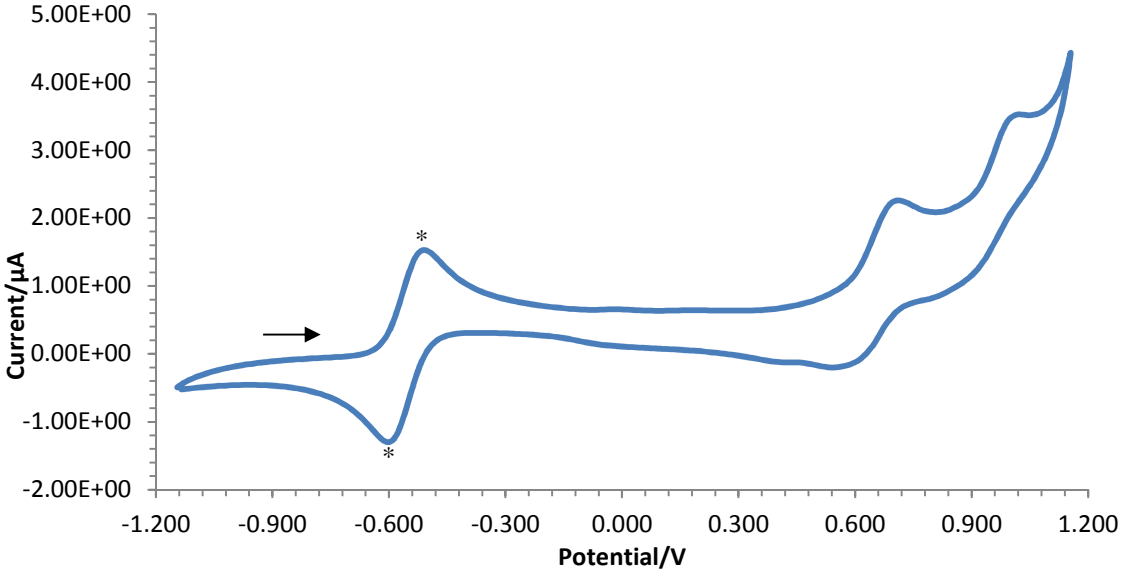

Figure S23: Cyclic Voltammagram for $\mathbf{2^{2+}}$, doped with decamethylferrocene (*), as solution in CH_2Cl_2 (1 mM) with $^{n}Bu_4NPF_6$ (0.1 M) supporting electrolyte; recorded at 100 mV s^{-1}.

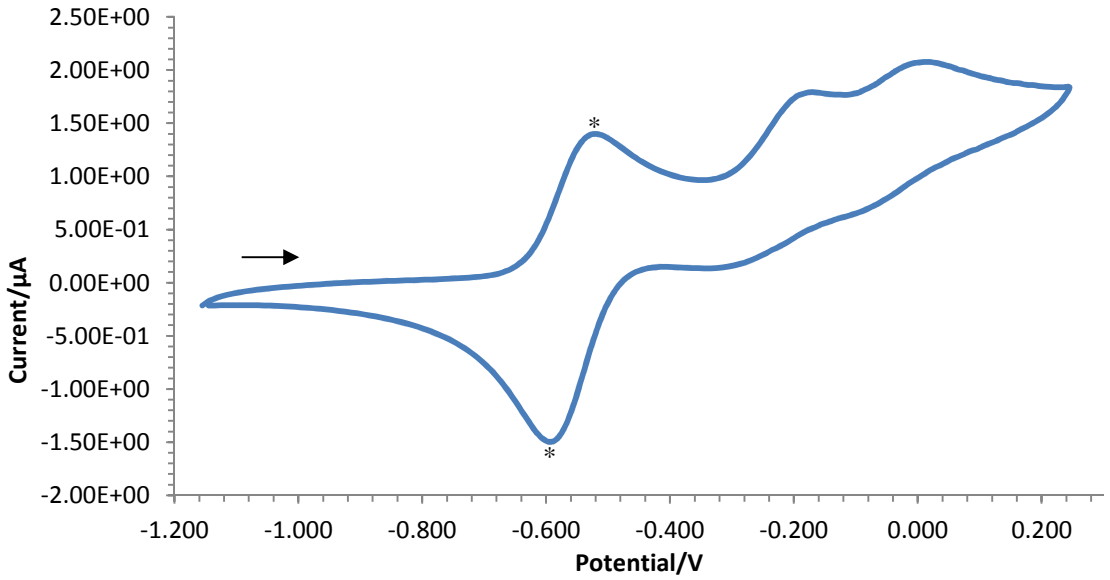

Figure S24: Cyclic Voltammagram for **3**, doped with decamethylferrocene, as solution in CH_2Cl_2 (1 mM) with $^{n}Bu_4NPF_6$ (0.1 M) supporting electrolyte; recorded at 100 mV s^{-1}. The irreversible reductive event is masked by the Fc*H couple.

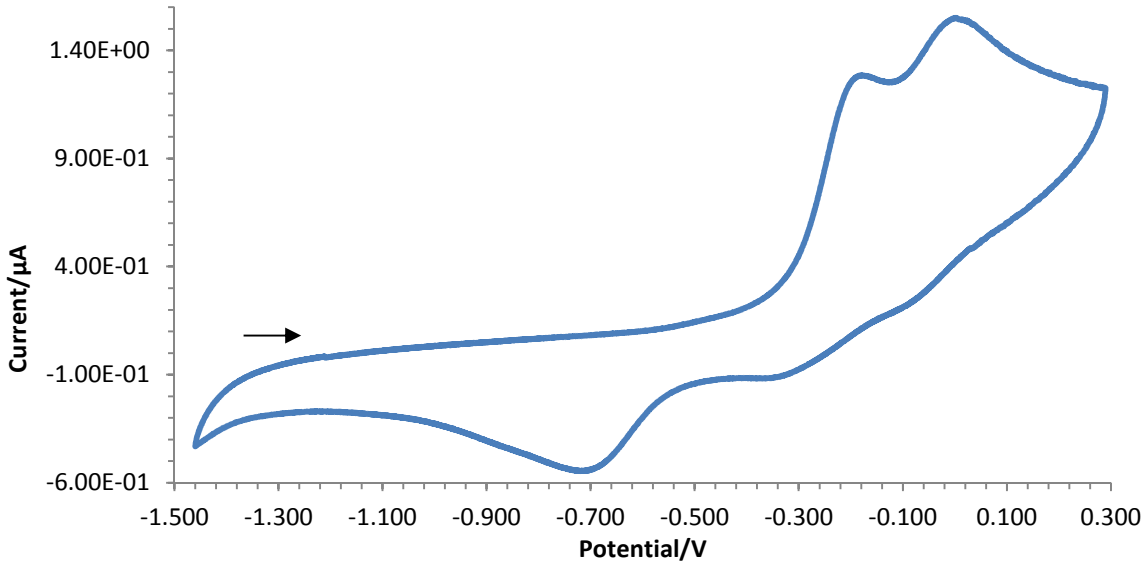

Figure S25: Cyclic Voltammagram for **3** (un-doped, referenced to FcH), as solution in CH_2Cl_2 (1 mM) with $^{n}Bu_4NPF_6$ (0.1 M) supporting electrolyte; recorded at 100 mV s^{-1}.

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[S3] Purity of **3** is demonstrated by spectroscopic data (vide supra), taken alongside the high-res mass spectrum as indicative identity; there was no evidence for residual fluorinated (e.g. $CF_3SO_3^-$) or silylated (e.g. Me_3SiO^tBu) species in ^{19}F or ^{29}Si spectra, which were devoid of signals. Attempts to obtain microanalytical data were, however, repeatedly unsuccessful, even with addition of V_2O_5 to aid combustion. Carbon content was routinely low by 5 – 10 %, with smaller disparity in hydrogen content; these data were inconsistent with the presence of NMR silent impurities (NMR active species being absent). Incomplete combustion of some phosphorus-containing species is an occasionally encountered issue, to which this is presumably attributable.

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