Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supporting Information

Capturing the interplay between spin-orbit coupling and non-Condon effects on the photoabsorption spectra of Ru and Os dyes

Theo Keane[ab], Thomas W. Rees[c†], Etienne Baranoff[c] , Basile F. E. Curchod[d]

[a] Department of Chemistry, University of Sheffield, Brook Hill, Sheffield, S3 7HF, UK;
E-mail: t.keane@shef.ac.uk

[b] School of Natural and Environmental Sciences, Newcastle University, Newcastle uponTyne, NE1 7RU, UK.

[c] School of Chemistry, University of Birmingham, Edgbaston, Birmingham B15 2TT, UK.

[d] Department of Chemistry, Durham University, South Road, Durham DH1 3LE, UK.
E-mail: basile.f.curchod@durham.ac.uk

[†] Current address: MOE Key Laboratory of Bioinorganic and Synthetic Chemistry,
School of Chemistry, Sun Yat-Sen University, Guangzhou, 510275, P. R. China

1 Instrumentation

Infra-red spectra were recorded neat as thin films on a Perkin Elmer "Spectrum" spectrometer. The intensity of each band is described as s (strong), m (medium) or w (weak) where appropriate.

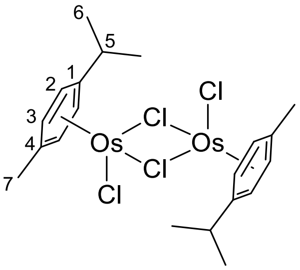
^{1}H NMR ^{19}F NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ unless specified otherwise, on a Bruker AVIII400 (400 and 100 MHz), or a BrukerAVIII300 (300 MHz). Chemical shifts are reported as δ values (ppm) referenced to the following solvent signals: $CHCl_3$, δ_H 7.26; $CDCl_3$, δ_C 77.0. Multiplicity of signals and coupling constants were obtained by processing on MestReNova.

Mass spectra were recorded on a Micromass ZABspec spectrometer utilizing electrospray ionization with a MeOH or MeCN mobile phase and are reported as (*m/z* (%)).

UV-Vis spectra were recorded on a Cary-5000 spectrometer in CH_2Cl_2 solution.

2 Synthesis of 1-Os

Dichloro(*p*-cymene)osmium(II) dimer



A 10 mL microwave reactor vial fitted with a septum, was charged with sodium hexachloroosmate dihydrate (200 mg, 412 µmol, 1eq.) and *α*-phellandrene (0.5 mL). The apparatus was then evacuated and filled with argon. EtOH (2.5 mL) and H_2O (0.1 mL) were added and the resulting mixture was degassed with argon for 20 min before heating to 100 ^{o}C and stirring for 3 h in a microwave reactor. After cooling to rt the resulting suspension was cooled to 5 ^{o}C overnight. The resulting orange precipitate was collected by vacuum filtration, washed with ice-cold EtOH (2 x 10 mL) and diethyl ether (2 x 10 mL), and dried under vacuum to yield an orange solid, (93.0 mg, 118 µmol, 57%).

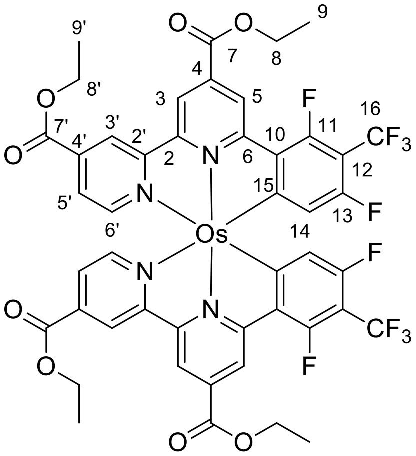
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.18 (d, *J* = 5.7 Hz, 2H, H^3), 6.02 (d, *J* = 5.7 Hz, 2H, H^2), 2.78 (sep, *J* = 6.9 Hz, 1H, H^5), 2.20 (s, 3H, H^7), 1.28 (d, *J* = 6.9 Hz, 6H, H^6);
^{13}C NMR (100 MHz, $CDCl_3$) δ 92.6 (C^4), 89.3 (C^1), 74.2 (C^3), 72.6 (C^2), 31.5 (C^5), 22.6 (C^6), 19.6 (C^7);

IR(film, cm^{-1}): 3045s (C-H), 2961s (C-H), 2925s (C-H), 2868s (C-H), 1448s (C=C), 1387s (C-H), 876s (Os-Cl);

MS (TOF ES$^+$): *m/z* (%): 755.2 (100) [M+H]$^+$;

HRMS (ES$^+$): [M+H]$^+$ calcd. For $C_{20}H_{28}Cl_3{}^{190}Os{}^{192}Os$, 755.0456; found, 755.0424.

Osmium(II) bis(diethyl-6-(2,4-difluoro-3-(trifluoromethyl)phenyl)-2-2'-bipyridine-4,4'-dicarboxylate) (1-Os)



Standard procedure: A 2 neck round bottom flask fitted with stirrer, condenser and stopcock was charged with **Ligand**[1] (97.2 mg, 202 µmol, 4 eq.) and dichloro(*p*-cymene)osmium(II) dimer (41 mg, 50.6 mmol, 1 eq.). The apparatus was evacuated and filled with argon before the addition of *n*PrCN (10 mL) and *N*-ethylmorpholine (0.2 mL). The resulting orange solution was degassed with argon for 20 min before heating and stirring at 120 °C, for 16 h under argon and reduced light. After cooling to rt solvent was removed under reduced pressure and the crude black solid was dried under high vacuum. Ethylene glycol (10 mL) was added and the resulting mixture degassed for 20 min with argon. The reaction mixture was then heated and stirred at 200 °C for 2 h under argon and reduced light. The crude black mixture was combined with H_2O (50 mL) and CH_2Cl_2 (50 mL). The organic phase was separated and the aqueous phase extracted with further portions of CH_2Cl_2 (3 x 50 mL). The organic phases were combined, dried ($MgSO_4$) and solvent removed under reduced pressure. The crude product was purified by column chromatography on silica (Hexane:EtOAc 7:3 *v/v*) to yield a black solid (5.8 mg, 5.05 µmol, 5.7%). *Rf* = 0.24 (Hexane:EtOAc 7:3 *v/v*, on silica).

Microwave procedure: A 10 mL microwave reactor vial fitted with a septum, was charged with **Ligand**[1] (100 mg, 208 µmol, 4eq.) and dichloro(*p*-cymene)osmium(II) dimer (41.2 mg, 52.0 µmol, 1 eq.). The apparatus was then evacuated and filled with argon. EtOH (2.5 mL) and *N*-ethylmorpholine (0.1 mL) were added and the resulting mixture was degassed with argon for 20 min before heating to 100 °C and stirring for 14 h in a microwave reactor. After cooling to rt solvent was removed under reduced pressure and the crude black solid was purified by column chromatography on silica (Hexane:CH_2Cl_2 7:1 *v/v*) to yield a black solid (31.0 mg, 27.0 µmol, 26%). *Rf* = 0.24 (Hexane:EtOAc 7:3 *v/v*, on silica).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.99 (s, 2H, H^3), 8.97 (d, *J* = 1.4 Hz, 2H, H^5), 8.89 (dd, *J* =1.6, 0.6 Hz, 2H, $H^{3'}$), 7.33 (dd, *J* = 5.9, 0.6 Hz, 2H, $H^{6'}$), 7.29 (dd, *J* = 5.9, 1.6 Hz, 2H, $H^{5'}$), 5.32 (d, *J* = 10.3 Hz, 2H, H^{14}), 4.64 (q, *J* = 7.1 Hz, 4H, H^8), 4.43 (q, *J* = 7.1 Hz, 4H, $H^{8'}$), 1.59 (t, *J* = 7.1 Hz, 6H, H^9), 1.39 (t, *J* = 7.1 Hz, 6H, $H^{9'}$);

^{19}F NMR (282 MHz, $CDCl_3$) δ –55.02 (dd, *J* = 29.2, 16.1 Hz, 6F, F^{16}), –112.61 (qd, *J* = 22.4, 4.5 Hz, 2F, F^{11}), –113.54 (qd, *J* = 22.8, 4.6 Hz, 2F, F^{13});

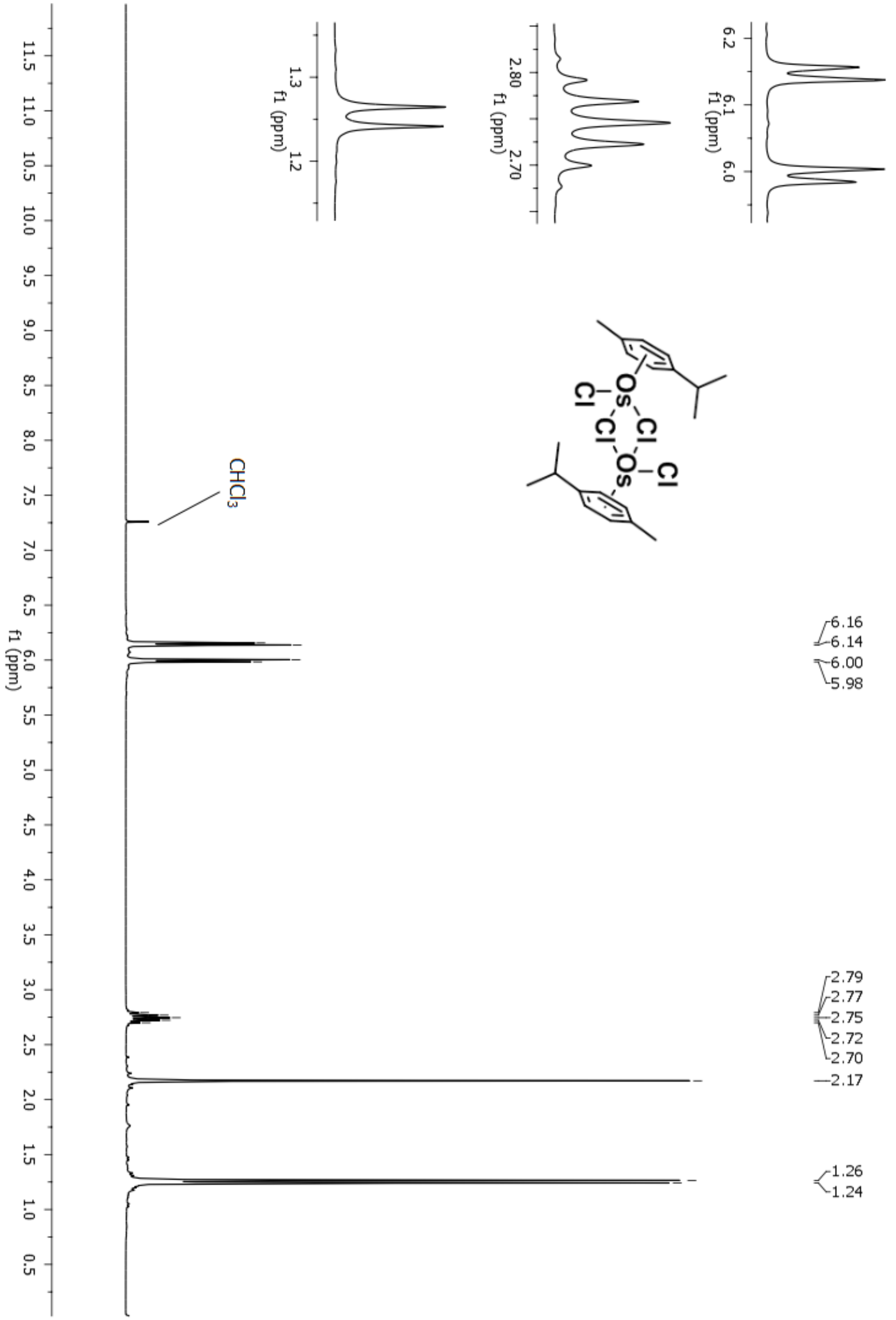
^{13}C NMR (100 MHz, $CDCl_3$) δ 179.27 (d, *J* = 6.5 Hz, C^{15}), 164.89 (s, $C^{7'}$), 163.57 (s, C^7), 160.80 (d, *J* = 265.5 Hz, C^{11}), 158.78 (d, *J* = 270.7 Hz, C^{13}), 158.45 (d, *J* = 6.3 Hz, C^6), 157.63 (s, C^2), 149.89 (s, C^6), 149.74 (s, $C^{2'}$), 135.61 (s, C^4), 130.83 (s, $C^{4'}$), 128.43 (s, $C^{5'}$), 125.36 (s, $C^{3'}$), 122.90 (q, *J* = 272.2 Hz), 122.43 (s, C^5), 119.62 (d, *J* = 19.9 Hz, C^{10}), 117.87 (s, C^3), 116.03 (d, *J* = 14.5 Hz, C^{14}), 62.56 (s, $C^{8'}$), 62.26 (s, C^8), 14.71 (s, C^9), 14.42 (s, $C^{9'}$);

IR(film, cm^{-1}): 3052w (C-H), 2968s (C-H), 2927s (C-H), 2855s (C-H), 2027s (Os-C), 1961s (Os-C), 1721s (C=O), 1704s (C=O), 1606s (C=C), 1537s (C=C), 1465s (C-H), 1448s (C-H), 1432s (C-H), 1366s (C-H), 1303 (C-O);

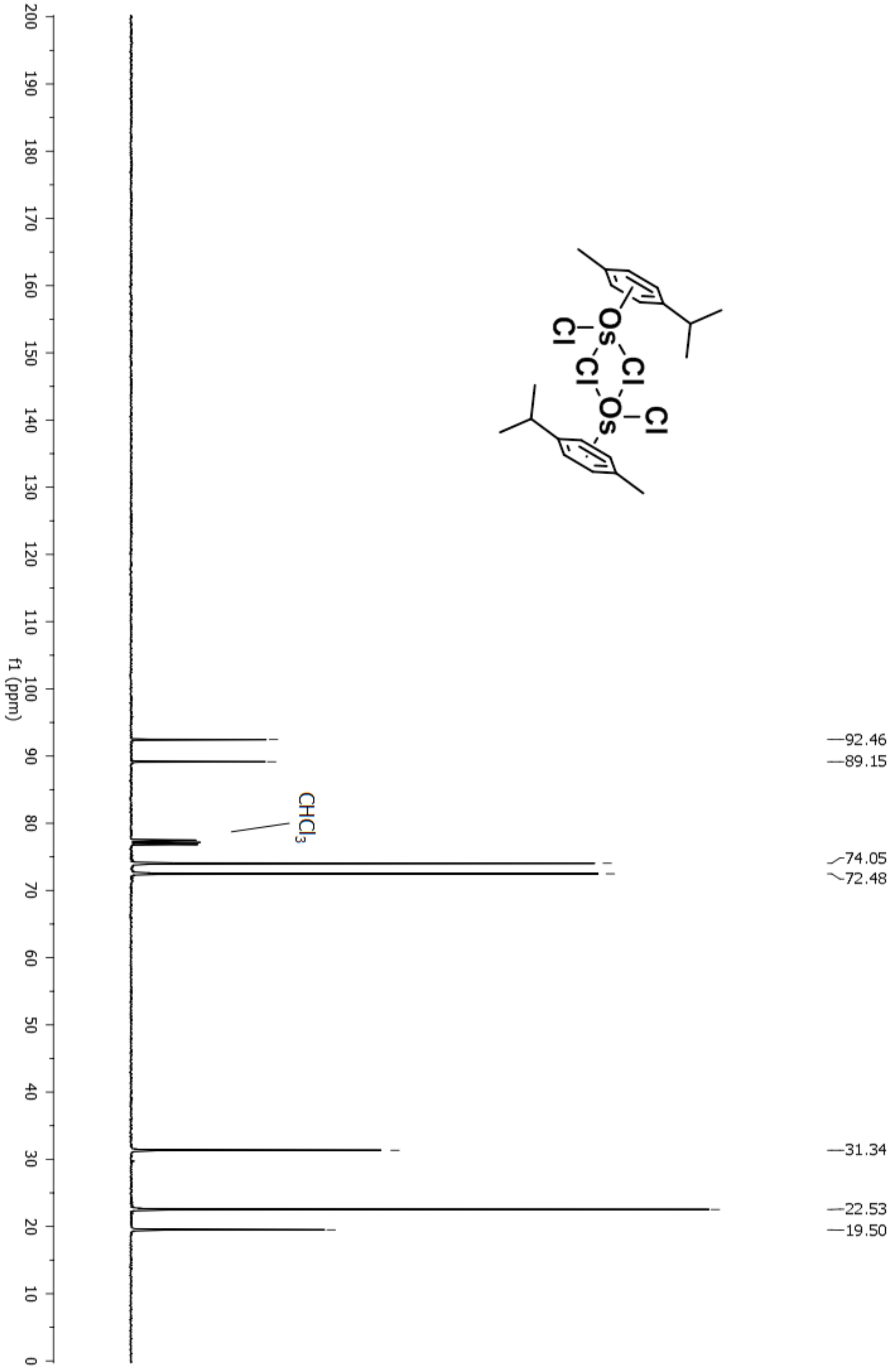
MS (TOF ES$^+$): *m/z* (%): 1150.6 (100) $[M+H]^+$

3 NMR

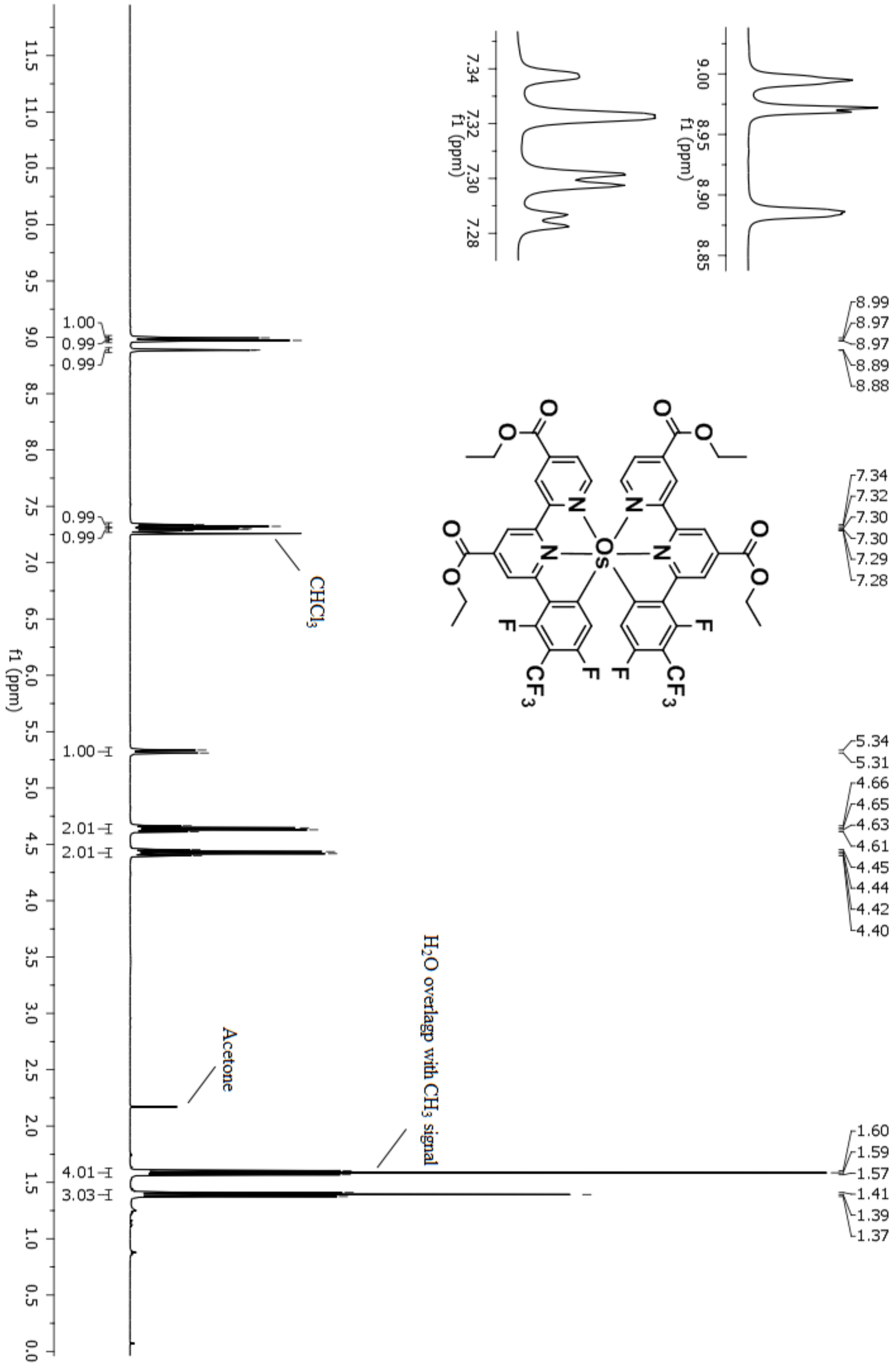
Osmium(II) *para*-cymene dichloride dimer ^1H NMR in $CDCl_3$



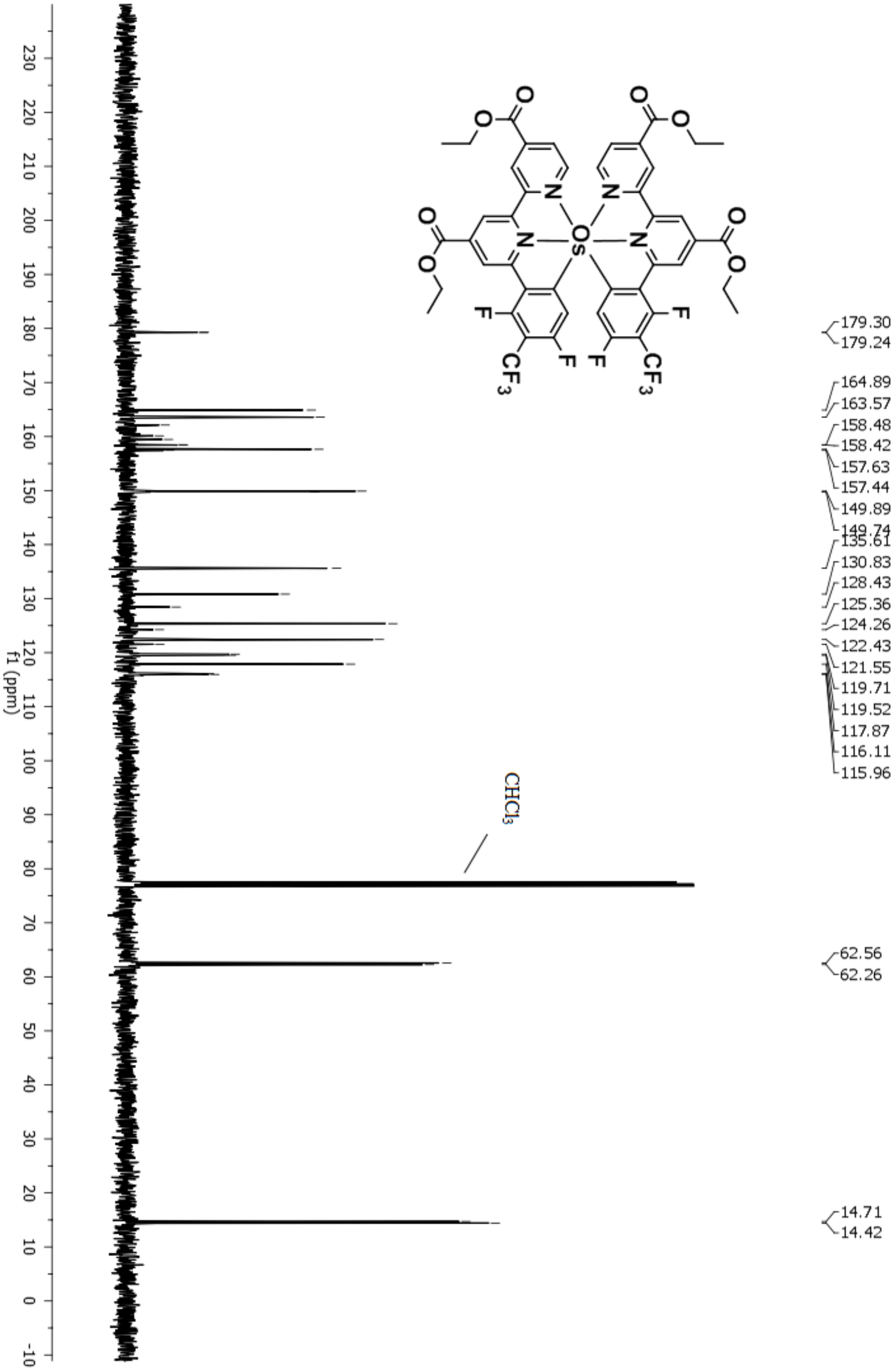
Osmium(II) *para*-cymene dichloride dimer ^{13}C NMR in $CDCl_3$



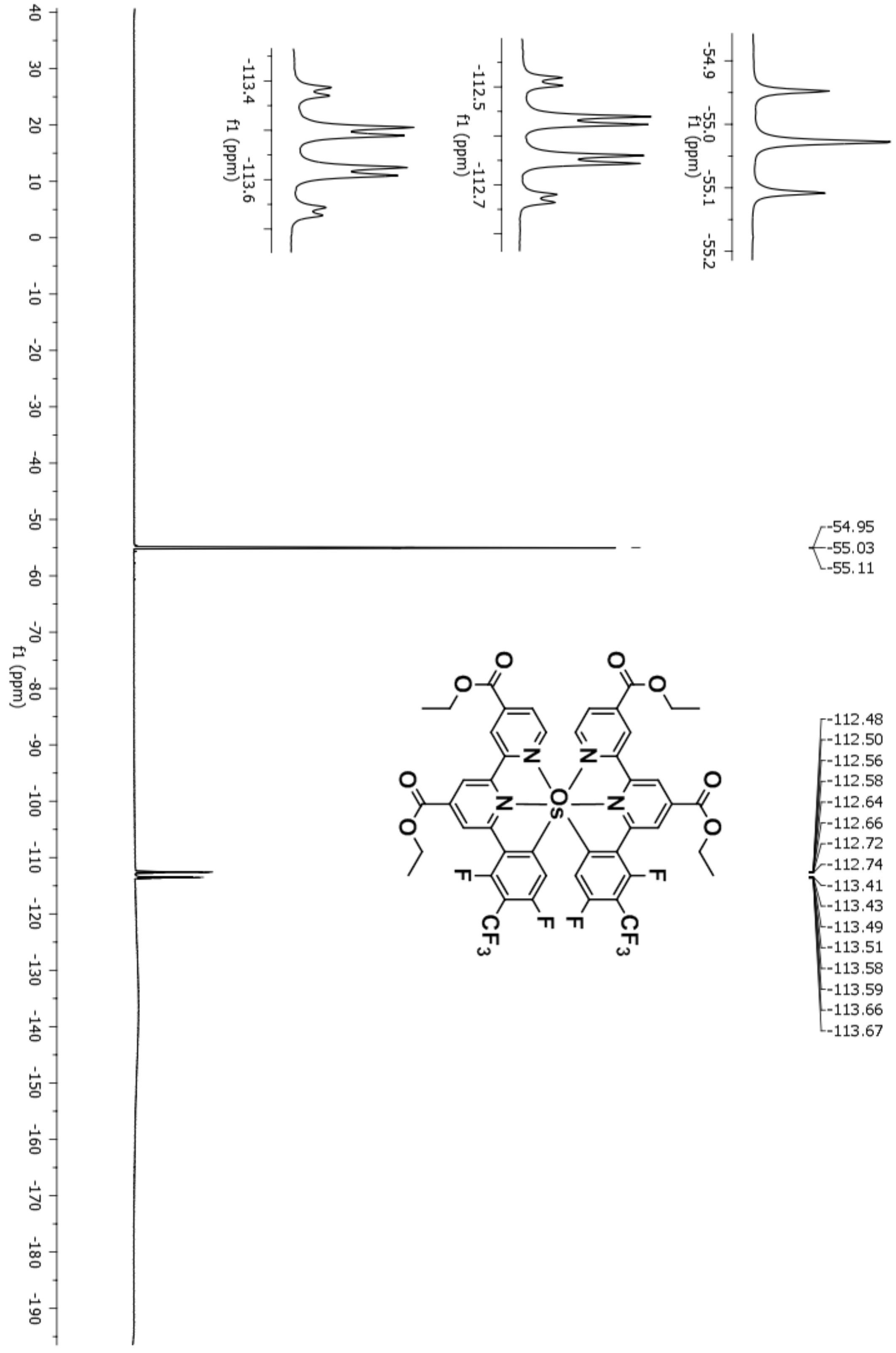
^{1}H NMR of 1-Os in $CDCl_3$



^{13}C NMR of 1-Os in $CDCl_3$



^{19}F NMR of 1-Os in $CDCl_3$



4 UV-Vis

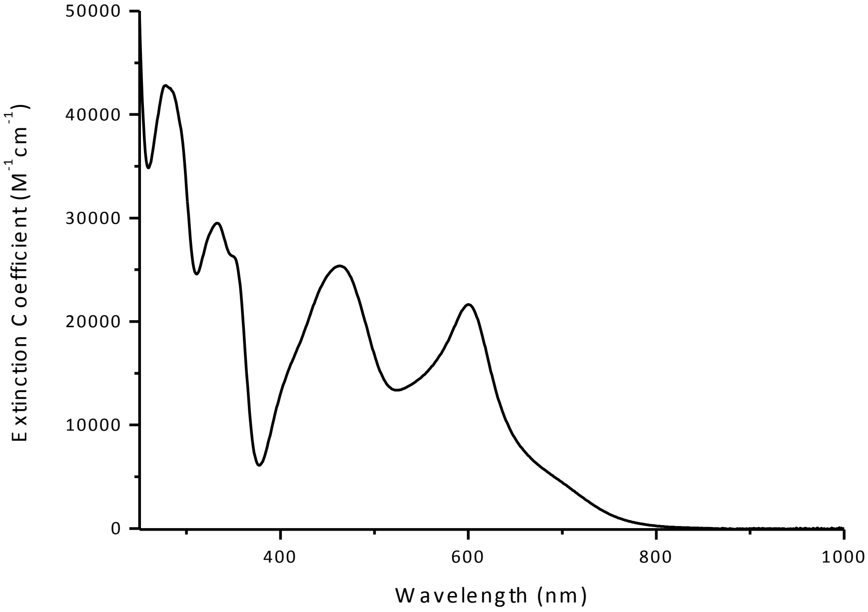


Figure 1: Absorption spectrum of 1-Ru recorded in CH_2Cl_2 at rt.

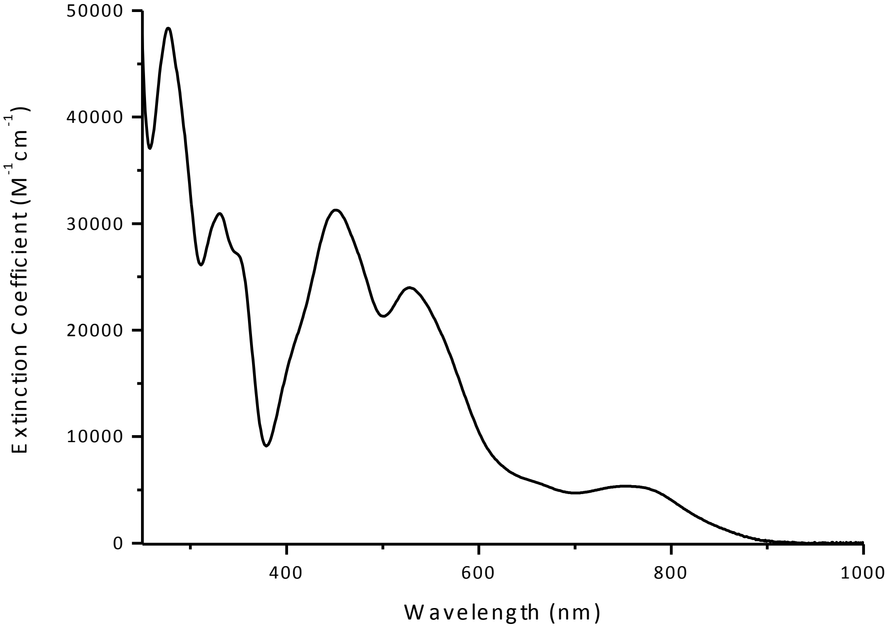


Figure 2: Absorption spectrum of 1-Os recorded in CH_2Cl_2 at rt.

5 Electron-hole correlation plots

Decomposition of the one component (1C) single-point (SP) excitations of **1-Ru** and **1-Os** in terms of fragment-to-fragment transitions (also known as electron-hole correlation plots)[2] was performed using the TheoDORE 1.7 program.[3,4] The metal centre and the aromatic rings with their substituents were chosen as the fragments. This is illustrated in Fig. 3, which also shows the labels chosen for each fragment.

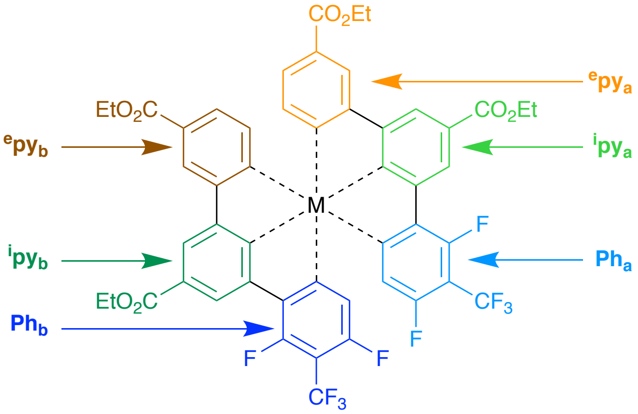


Figure 3: Fragments used in the excited-state analysis. For each NNC ligand, differentiated by subscript ‘a’ and ‘b’, the two ‘external’ functionalised pyridines are denoted $^{e}py_a$ and $^{e}py_b$, the two ‘internal’ functionalised pyridines are denoted $^{i}py_a$ and $^{i}py_b$, and the two functionalised phenyls are denoted Ph_a and Ph_b. Note that the metal center is denoted as Ru or Os as appropriate.

The electron-hole correlation plots for the first 30 electronic states of **1-Ru** and **1-Os** are shown in Fig. 4 and Fig.5, respectively, and are constructed as follows. For each excitation, a 7×7 matrix showing the percentage contribution to the total transition due to hole located on one fragment giving rise to an electron located on another fragment. The location of the hole is indicated by the column, the labels of which are found at the bottom of the figure. The location of the electron is indicated by the row, the labels of which are found on the left of the figure. For example, the percentage contribution of a transition due to metal to $^{e}py_a$ transfer can be found in the centre of the top row. The character (singlet, S, or triplet, T), index (1, 2, 3,…) and energy in electronvolts of each transition is shown above the corresponding matrix. The sums of the values for each row or column are shown on the outside of the row or column. Note that contributions below 1% are hidden to increase clarity and that nearest-integer rounding was used, thus the sum of values on the charts may not be 100.

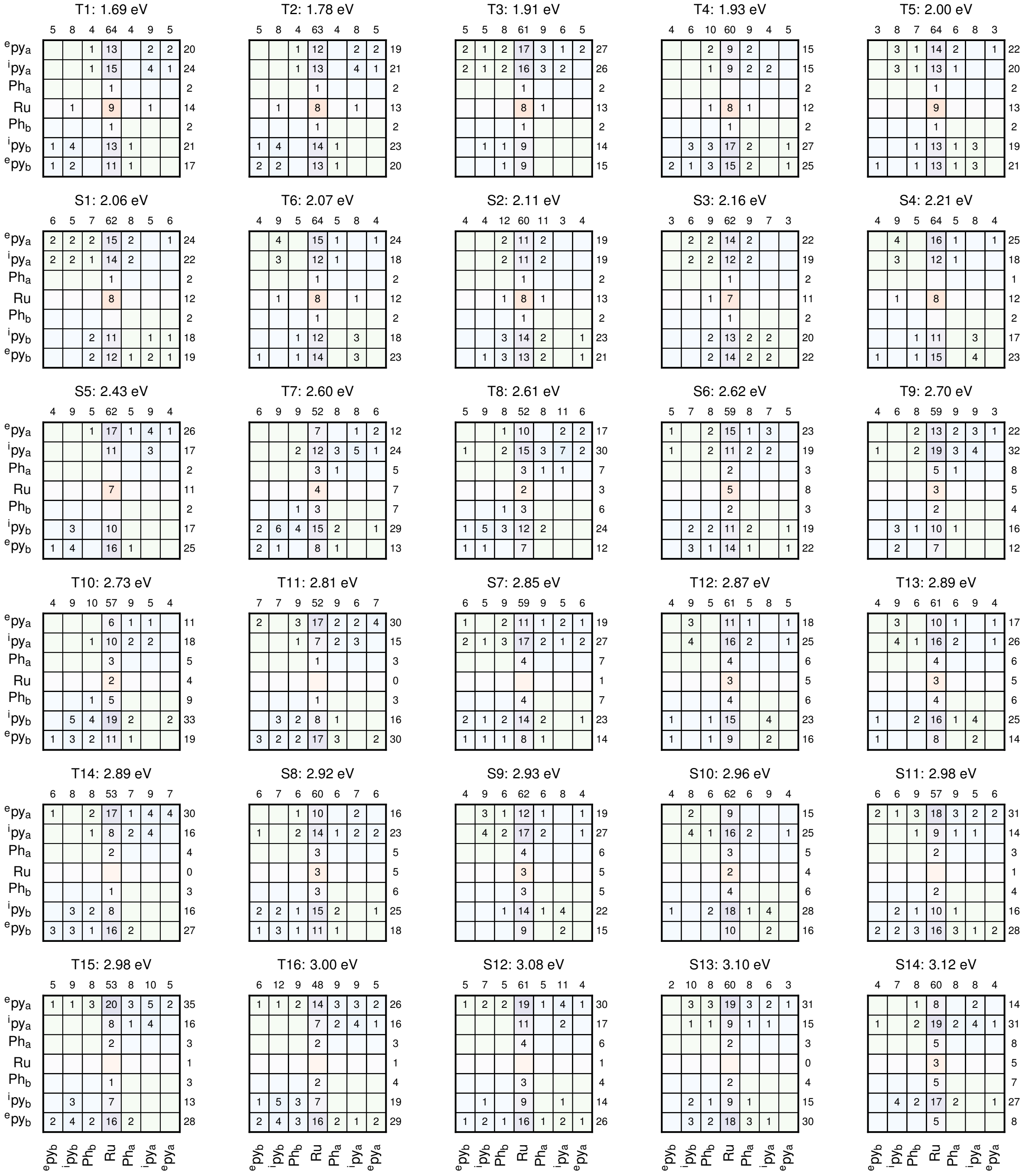


Figure 4: Electron-hole correlation plots for the first 30 excited states of 1-Ru calculated with LR-TDDFT/1C-X2C-PBE0/x2c-SV(P)all/COSMO(CH_2Cl_2). See text for a detailed explanation of how to read the diagrams.

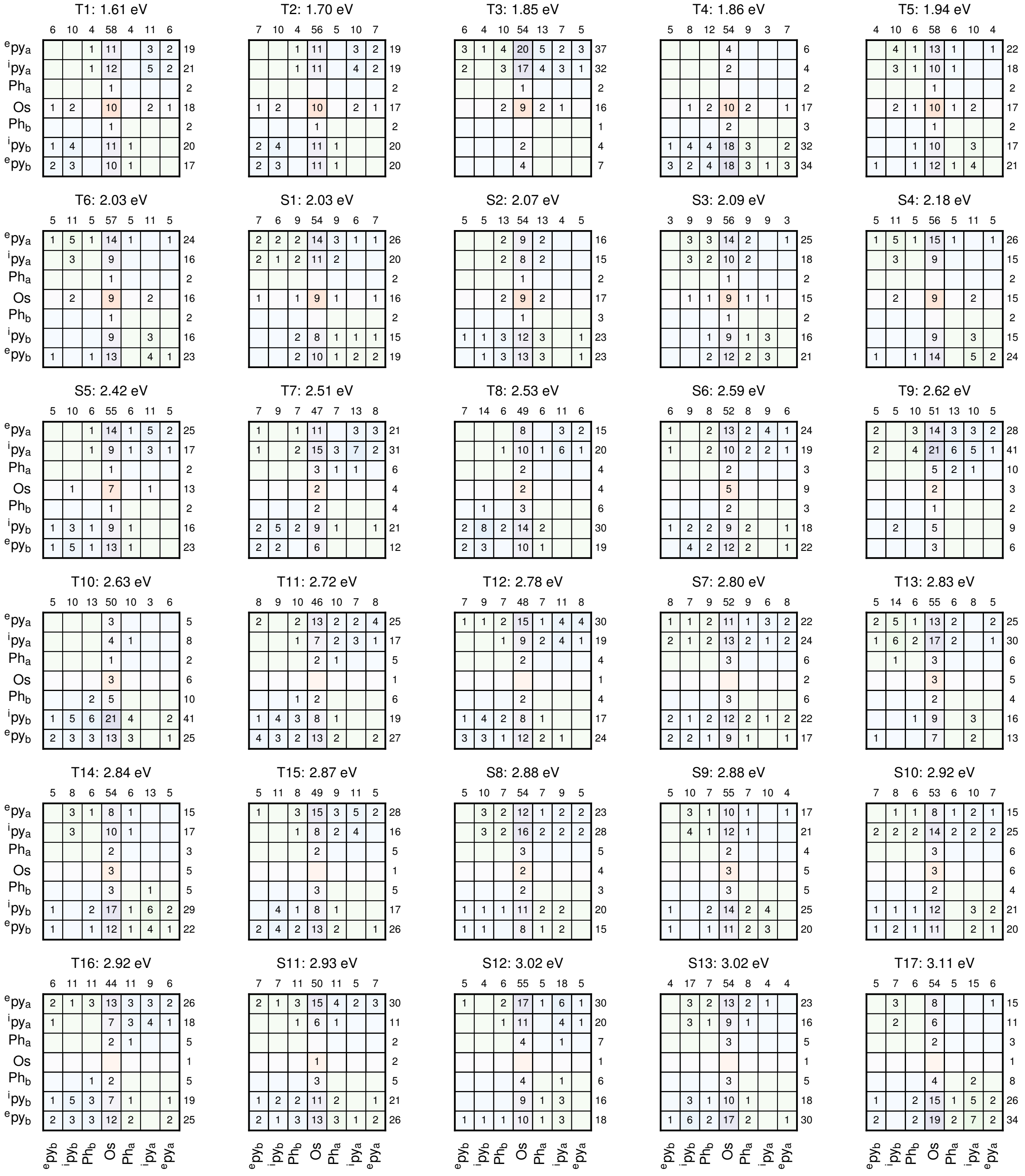


Figure 5: Electron-hole correlation plots for the first 30 excited states of 1-Os calculated with LR-TDDFT/1C-X2C-PBE0/x2c-SV(P)all/COSMO(CH_2Cl_2). See text for a detailed explanation of how to read the diagrams.

6 References

[1] T. W. Rees, J. Liao, A. Sinopoli, L. Male, G. Calogero, B. F. E. Curchod and E. Baranoff, *Inorg. Chem.*, 2017, **56**, 9903–9912.

[2] S. Tretiak and S. Mukamel, *Chem. Rev.*, 2002, **102**, 3171–3212.

[3] F. Plasser and H. Lischka, *J. Chem. Theory Comput.*, 2012, **8**, 2777–2789.

[4] F. Plasser, “TheoDORE 1.7: a package for theoretical density, orbital relaxation and exciton analysis”; available from http://theodore-qc.sourceforge.net.