Synthesis of an electrodeficient dipyridylbenzene-like terden-tate ligand: cyclometallating ligand for highly emitting iridi-um(III) and platinum(II) complexes.

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Crystal Structures Determinations and Refinements.

Single crystals of compounds compound **8**, were picked up from the mother liquor, coated with a parafin mixture, collected with nylon loops and mounted on goniometer heads. Measurements were made at 200 K on a Enraf-Nonius 4 circles kappa goniometer equipped with an Incoatec high brilliance microsource with Montel optics monochromated Mo-Kα radiation (λ = 0.71073 Å). The detector was a Bruker APEXII and an Oxford Cryosystem cryostream cooler was used. The crystal data and details of the data collections are given in Error! Reference source not found.. The data were integrated and corrected for Lorentz and polarization effects using Eval14[1], corrected for absorption using SADABS[2] and finaly merged using Xprep[3]. Crystallographic structures were solved using direct methods implemented by Superflip.[4] Refinement was performed using ShelxL-2013[5] run under Olex2[6]. C, Cl, F, Ir, N, O, and Br atoms were refined anisotropically by the full matrix least-squares method on F^2. H atoms were set geometrically.

Supplementary data is available on request from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, quoting the deposition number CCDC- 2252294. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or fax: +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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[1] Duisenberg, A. J. M., Kroon-Batenburg, L. M. J. & Schreurs, A. M. M. (2003). *J. Appl. Cryst*. **36**, 220-229.
[2] Bruker (2004). *SADABS.* Bruker AXS Inc., Madison, Wisconsin, USA.
[3] Bruker (2005). *XPREP.* Bruker AXS Inc., Madison, Wisconsin, USA.
[4] Palatinus, L. & Chapuis, G. (2007). *J. Appl. Cryst.* **40**, 786-790.
[5] Sheldrick, G. M. (2015). *Acta Cryst.* C**71**, 3-8.
[6] Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341

Table S 1 : Crystal data and structure refinement.

Compound	**8**
Formula	$C_{29}H_{24}ClIrN_4$. 0.5($C_2H_4Cl_2$). 1.64(CH_4O)
F_w	758.24
T [K]	200
Morphology	needle
Color	yellow
Crystal size [mm]	0.04 x 0.09 x 0.4
Crystal system	triclinic
Space group	P -1
a [Å]	8.8948(18)
b [Å]	13.069(3)
c [Å]	16.615(3)
α [°]	105.07(3)
β [°]	104.99(3)
γ [°]	98.81(3)
Unit-cell volume [Å^3]	1750.5(7)
Z	2
D_x [g·cm^{-3}]	1.439
μ [mm^{-1}]	3.996
Radiation [Å]	MoKα (λ = 0.71073)
Θ range for data collection/°	1.340 to 27.500
Index ranges	-11 ≤ h ≤ 11, -16 ≤ k ≤ 16, -21 ≤ l ≤ 21
Total reflections	40254
Unique reflections	7967
Used reflections (I>3σ(I))	6867
Refined parameters	422
Rint.	0.0487
R^a	0.0358
R(w)	0.0877
Goodness of fit	2.02
$\Delta\rho_{min}/\Delta\rho_{max}$ (e·Å^{-3})	-0.84/1.13

NMR spectra

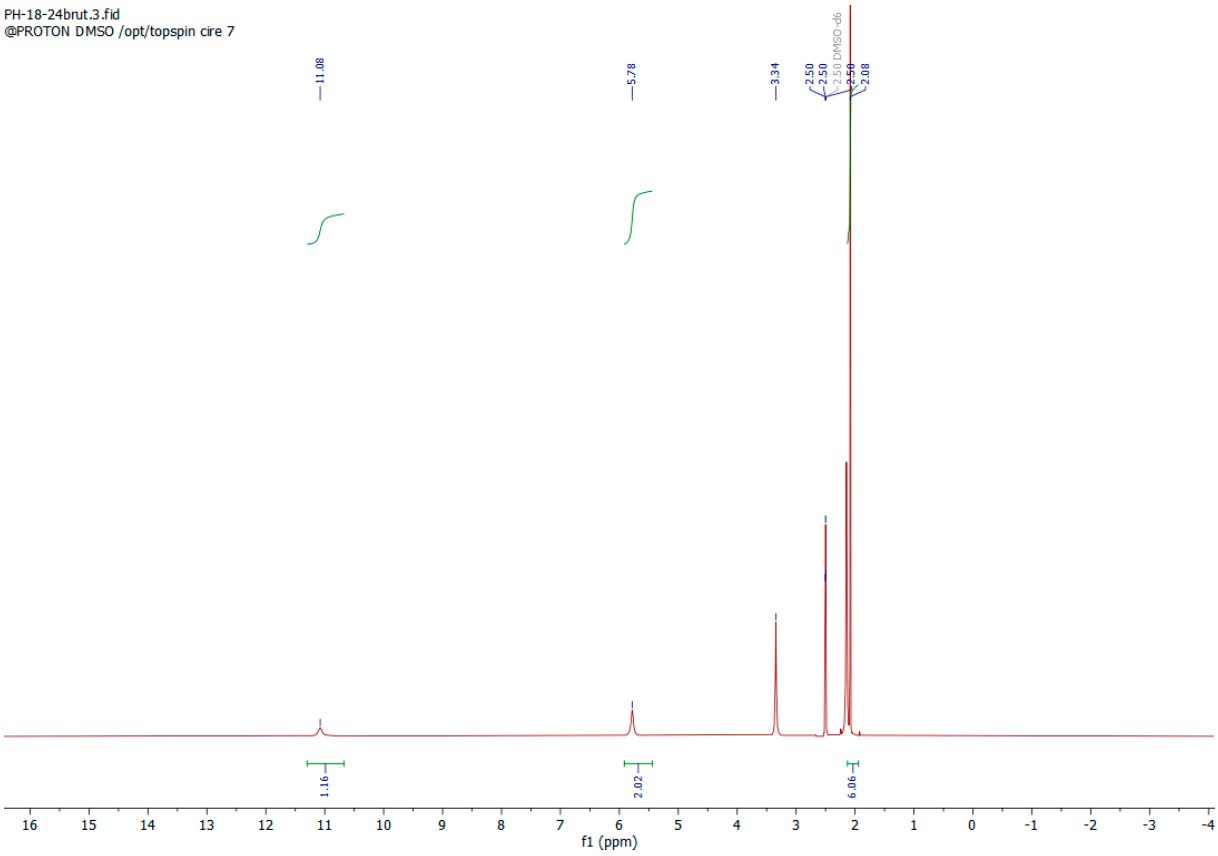

*Figure S 1 : ^{1}H NMR Compound **1** in DMSO, 400 MHz*

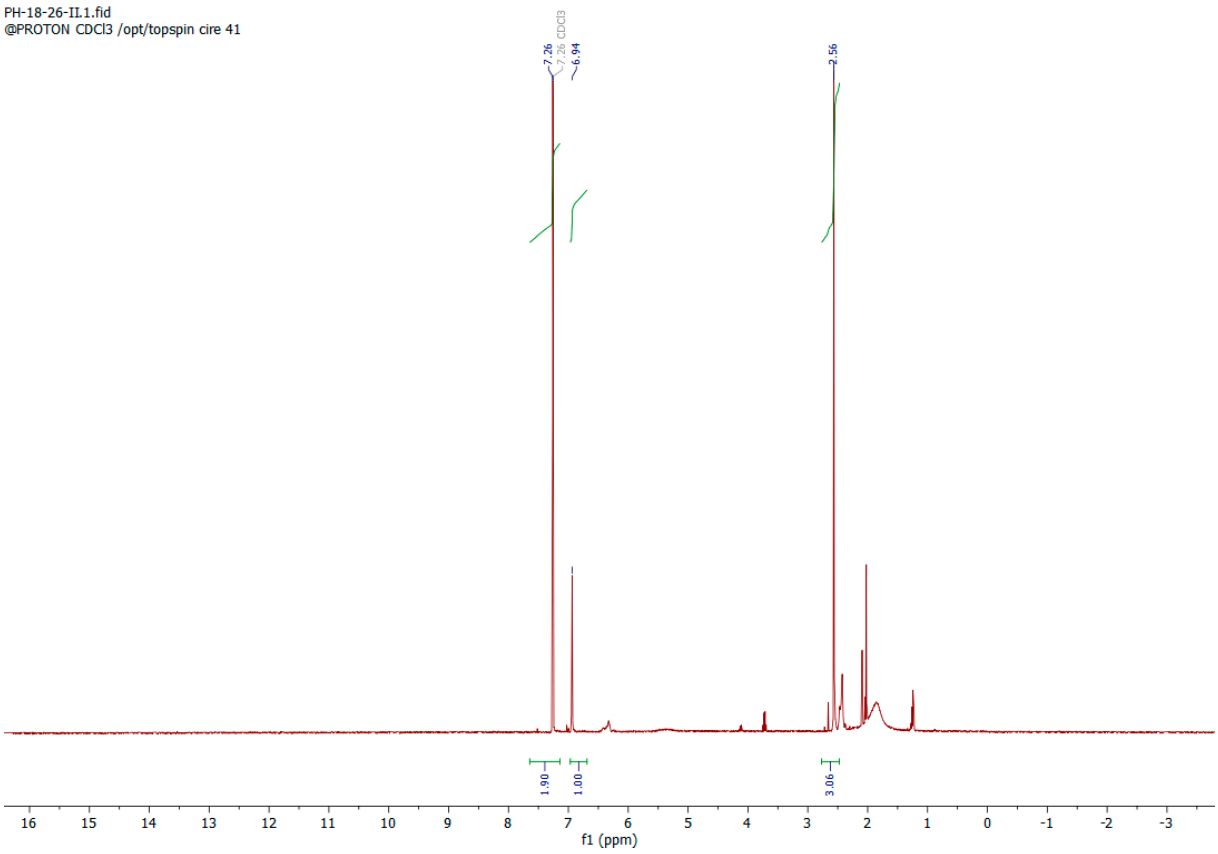

*Figure S 2 : ^{1}H NMR Compound **2** in $CDCl_3$, 400 MHz*

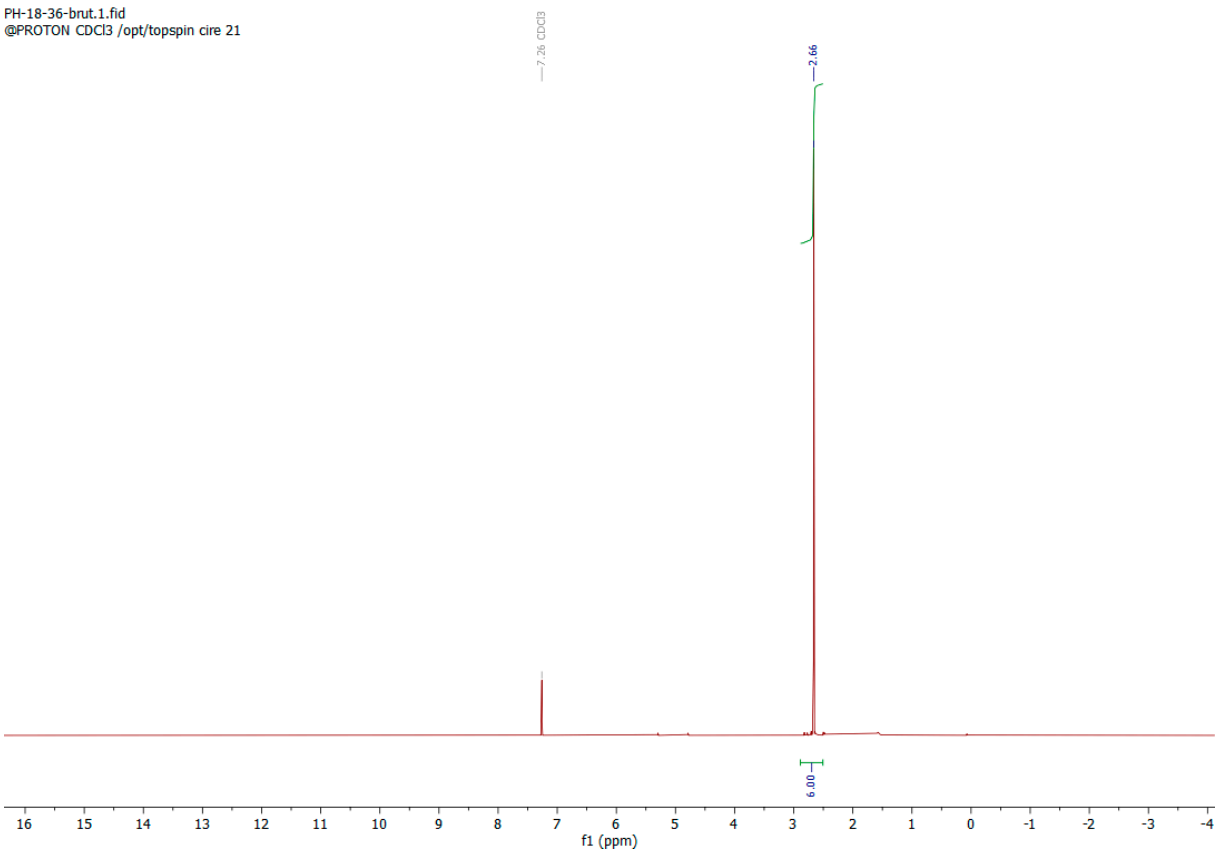

*Figure S 3 : ^{1}H NMR Compound **3** in $CDCl_3$, 400 MHz*

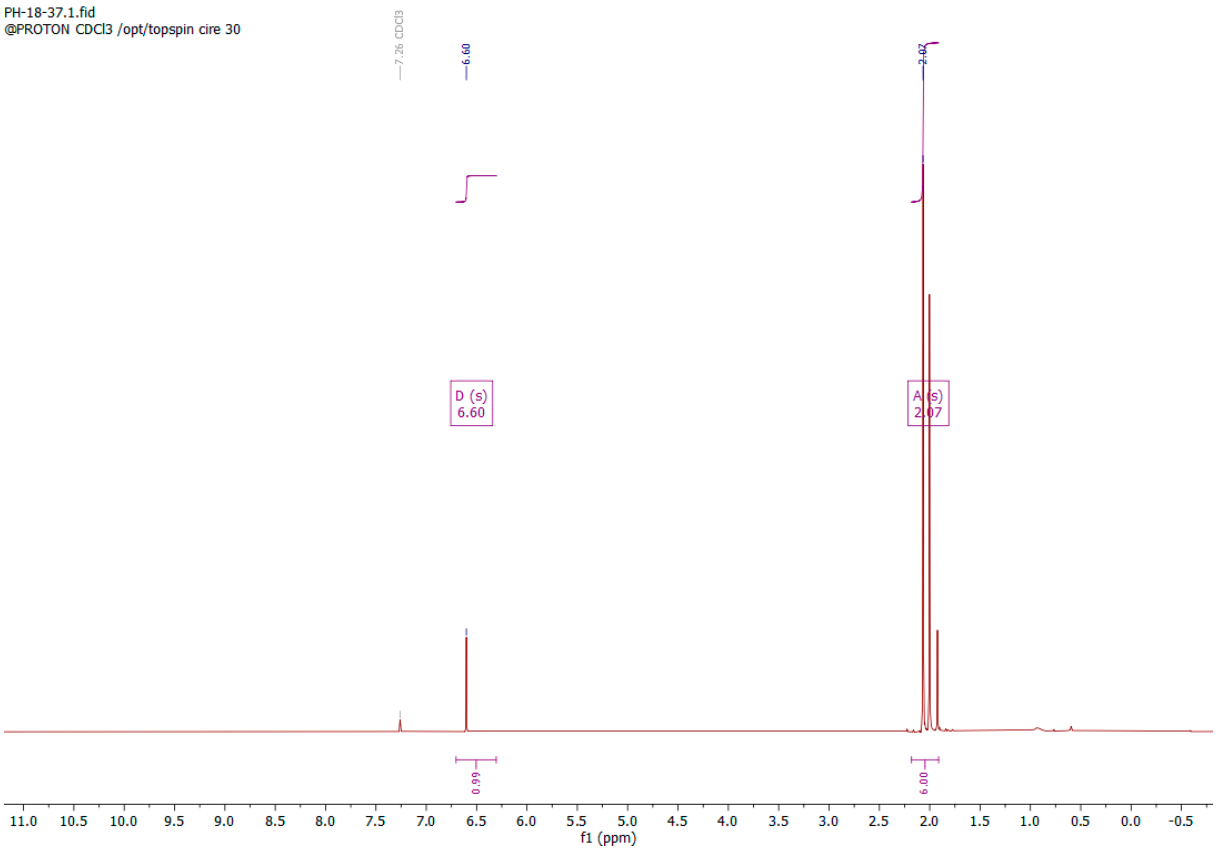

*Figure S 4 : ^{1}H NMR Compound **4** in $CDCl_3$, 400 MHz*

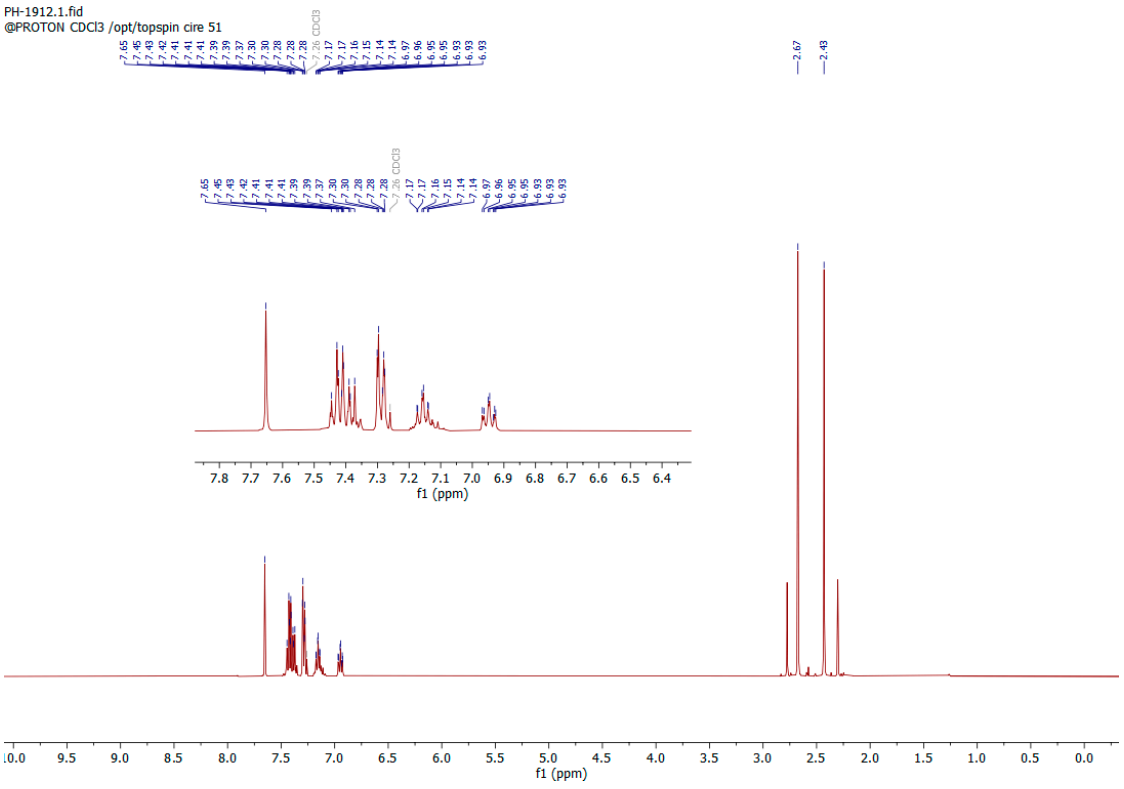

*Figure S 5^{1}H NMR Compound **5** in $CDCl_3$, 400 MHz*

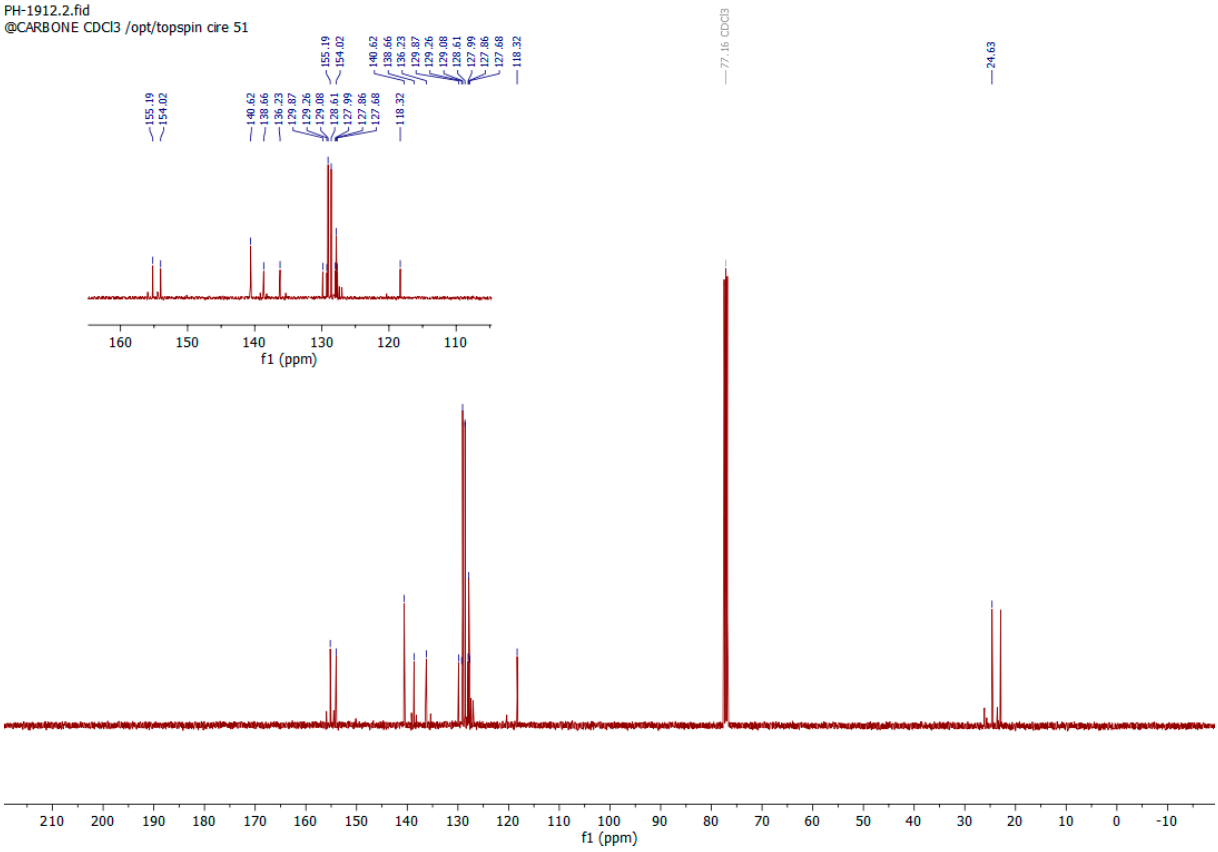

*Figure S 6 : ^{13}C NMR compound **5** in $CDCl_3$, 101 MHz*

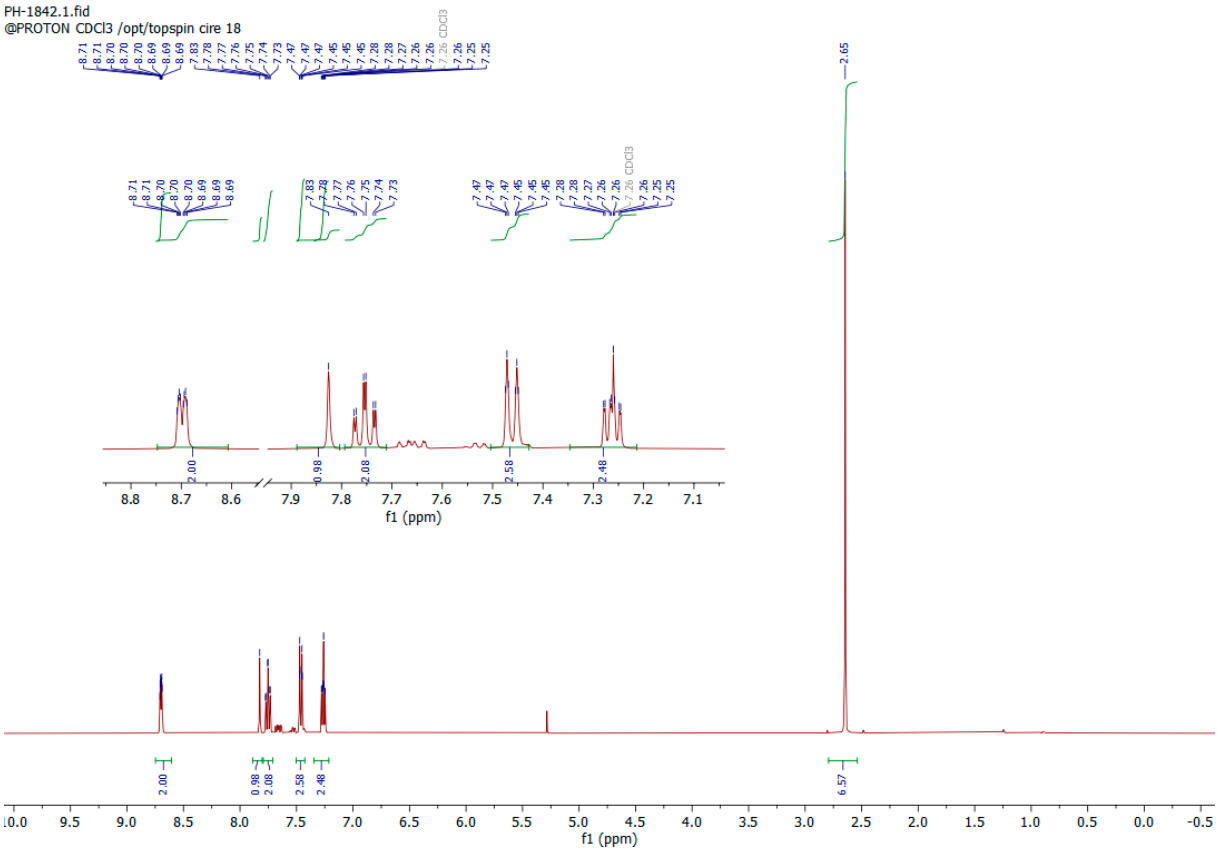

*Figure S 7 : ^{1}H NMR Compound **6** in $CDCl_3$, 400 MHz*

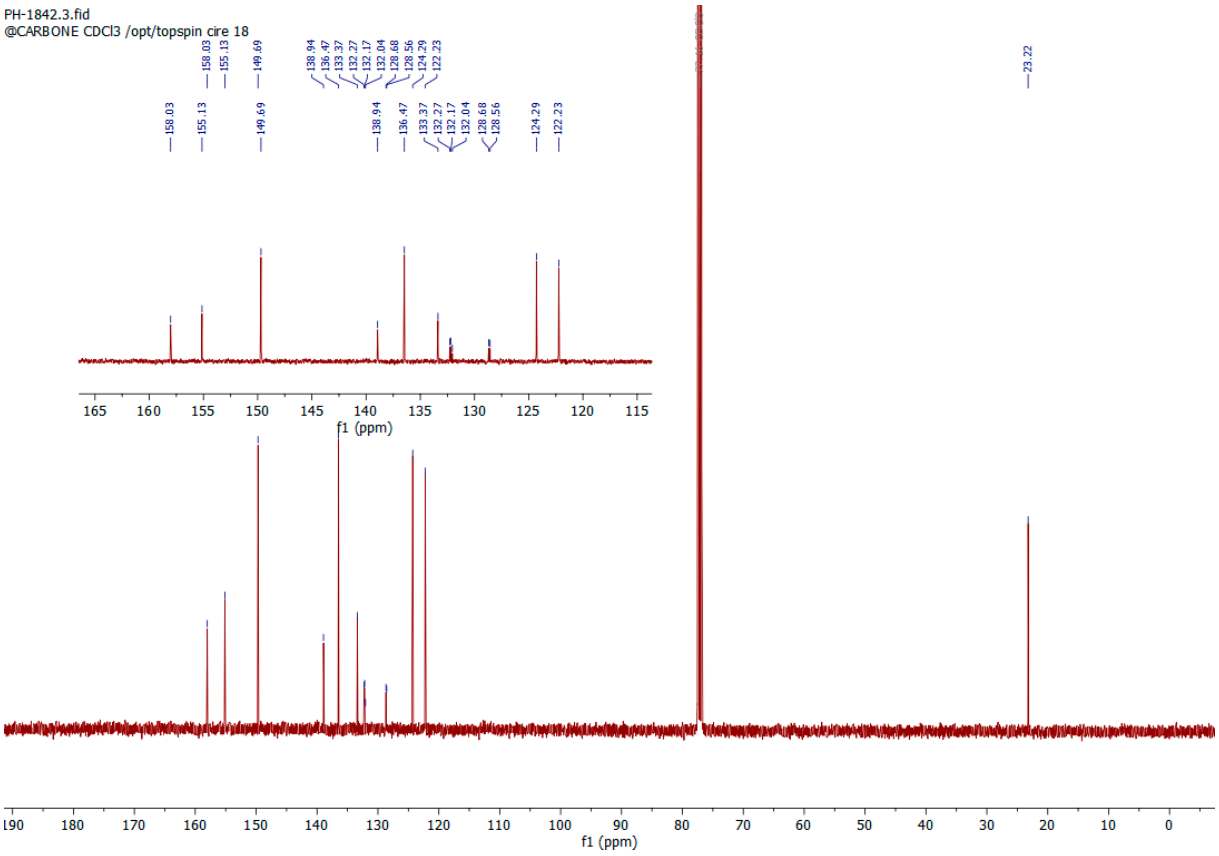

*Figure S 8 : ^{13}C NMR compound **6** in $CDCl_3$, 101 MHz*

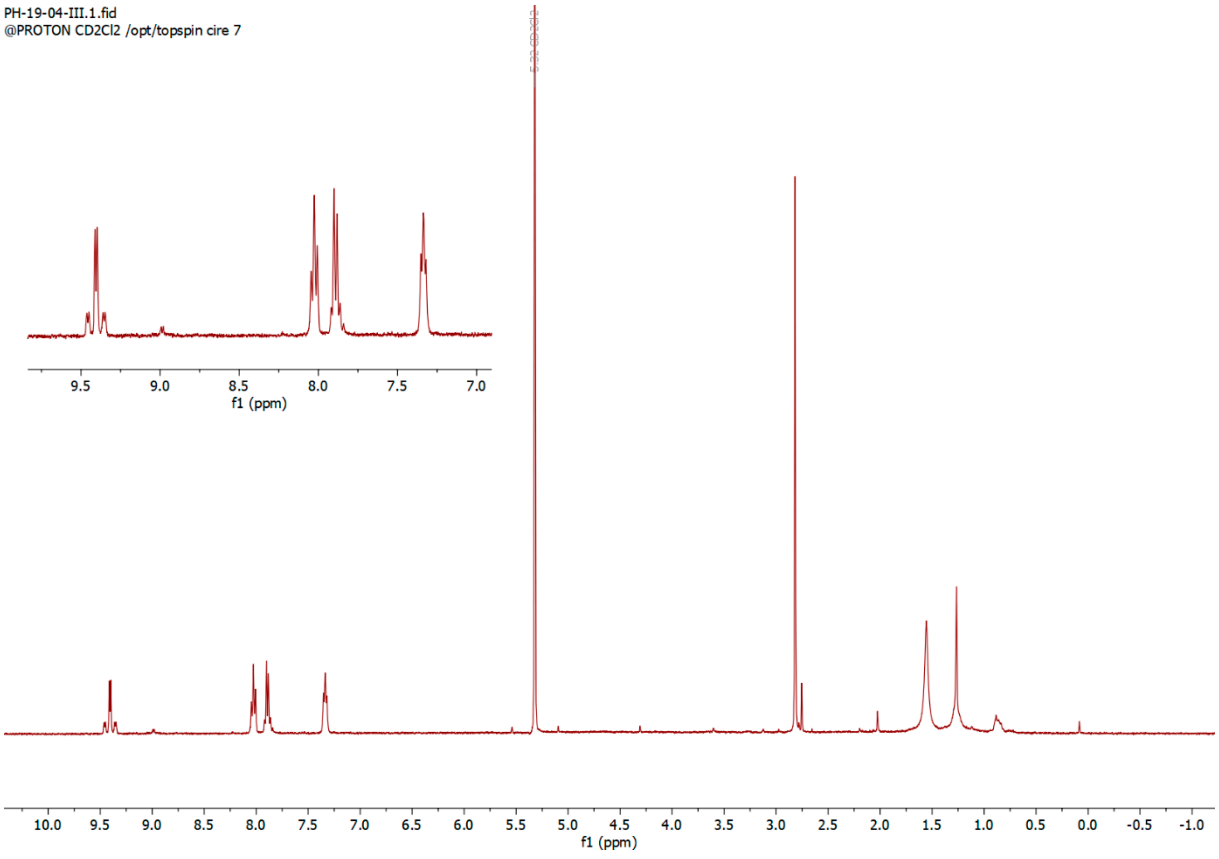

*Figure S 9 : ^{1}H NMR complex **7** in CD_2Cl_2 400 MHz*

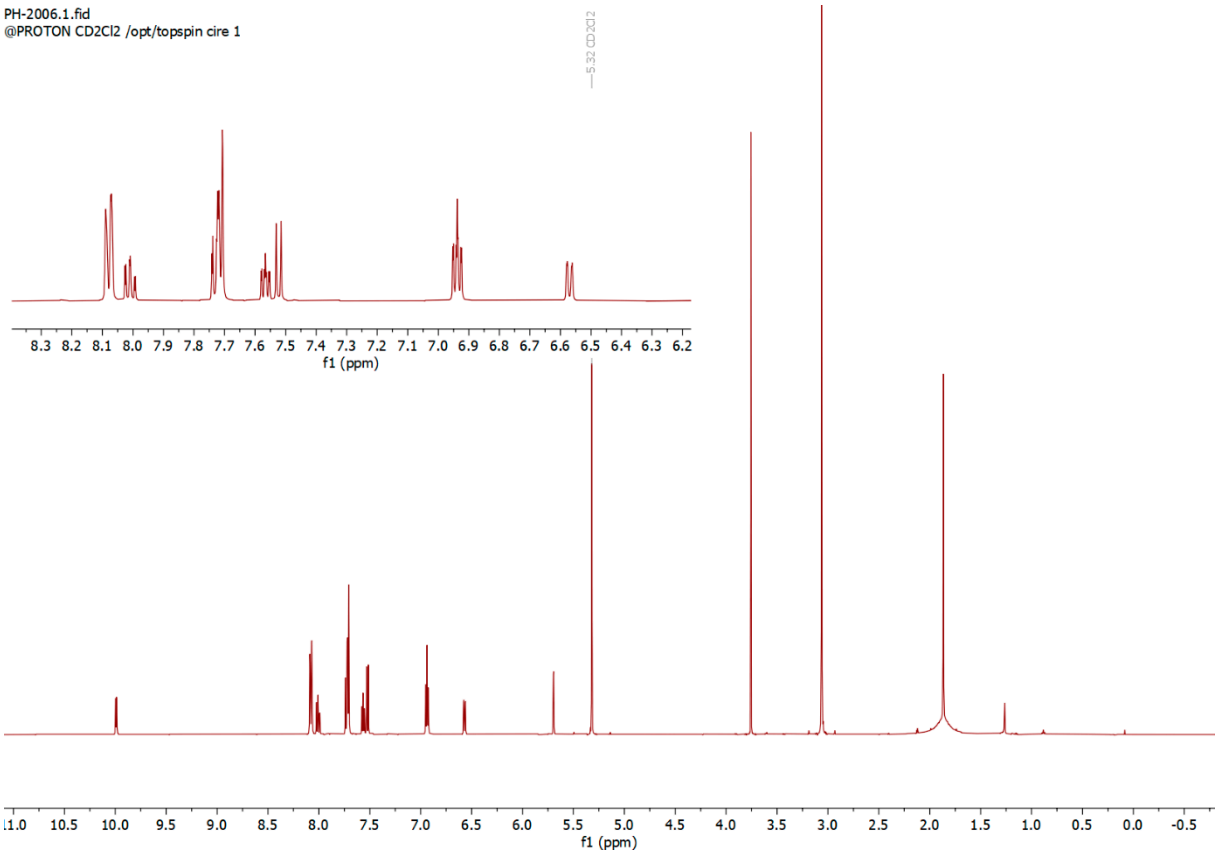

*Figure S 10 : ^{1}H NMR complex **8** in CD_2Cl_2 500 MHz*

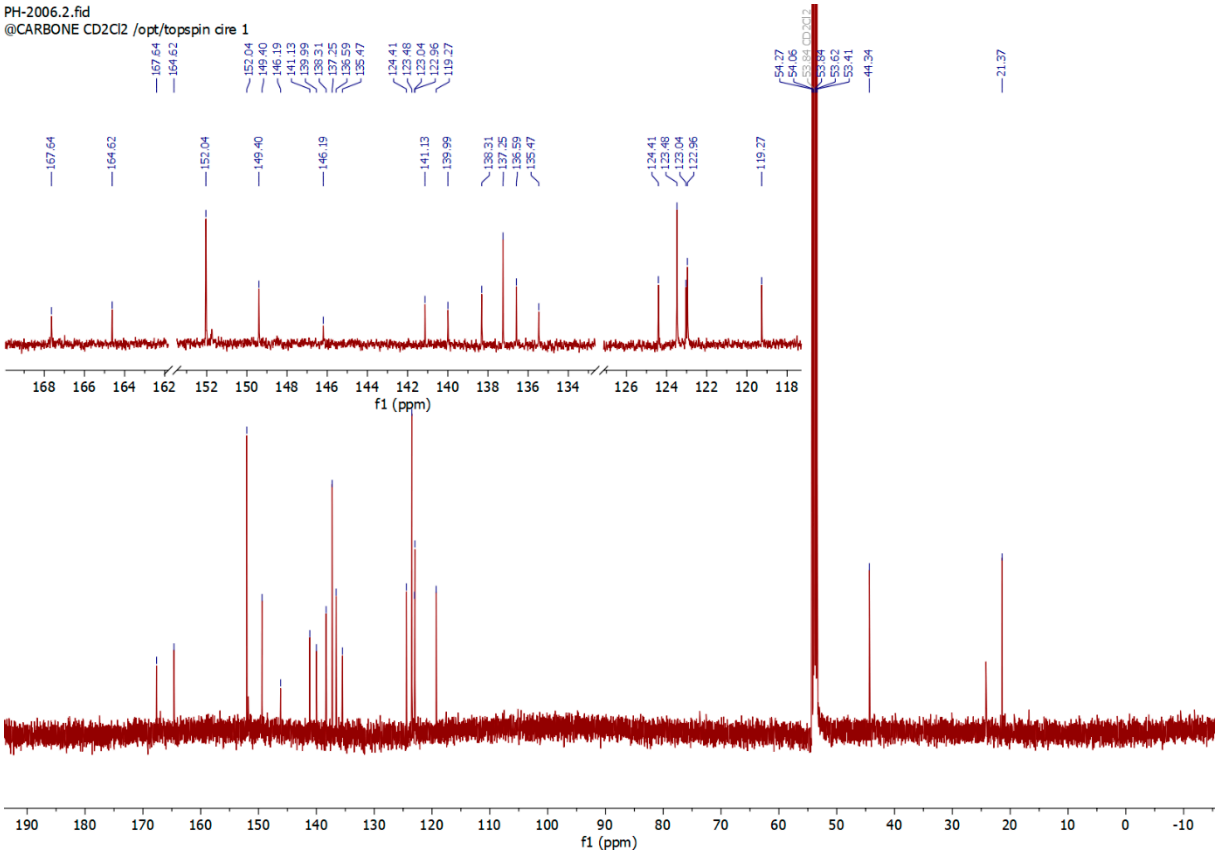

*Figure S 11 : ^{13}C complex 8 complex **8** in CD_2Cl_2 126 MHz*

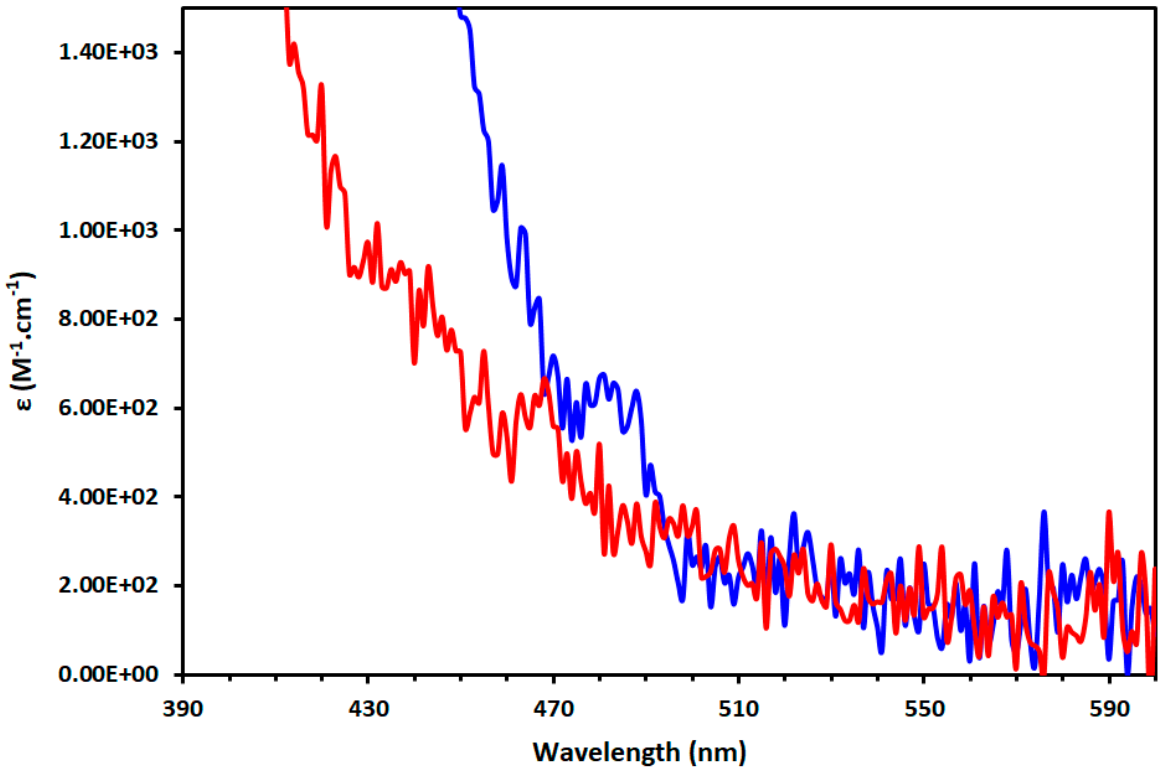

*Figure S 12 : Absorption spectra of compounds **7** (blue) and **8** (red) in CH2Cl2 at R.T. displaying the absorption band of the spin forbidden ^{1}MLCT → ^{3}MLCT.*