SUPPORTING INFORMATION

The use of organolithium reagents for the synthesis of 4-aryl-2-phenylpyridines and their corresponding iridium(III) complexes

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S1. NMR spectra of reported compounds

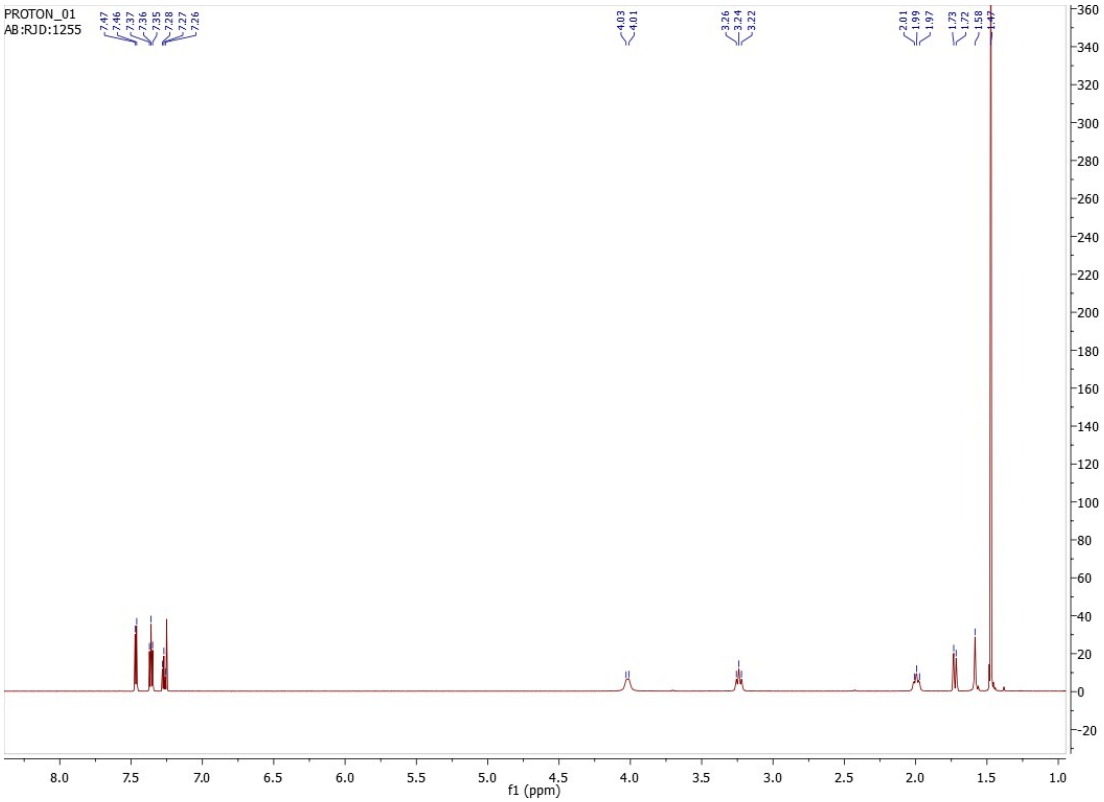

Figure S1.1. ^{1}H NMR spectrum of **1**, recorded in $CDCl_3$.

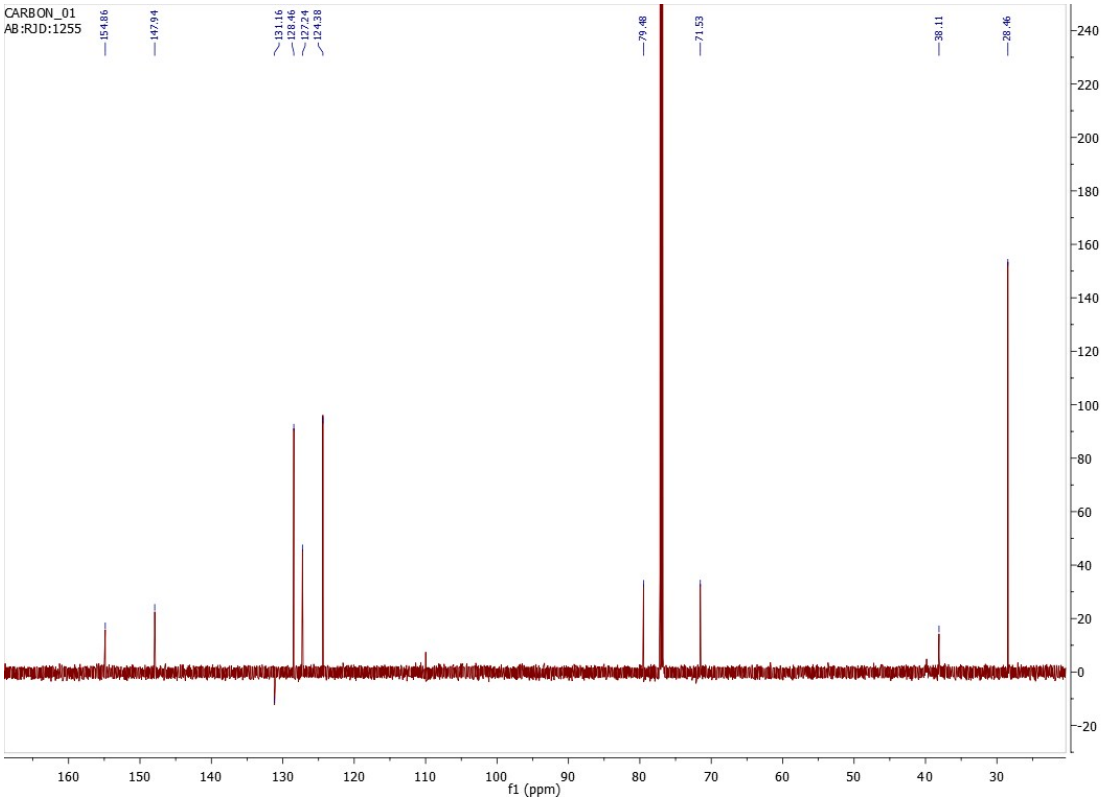

Figure S1.2. ^{13}C NMR spectrum of **1**, recorded in $CDCl_3$.

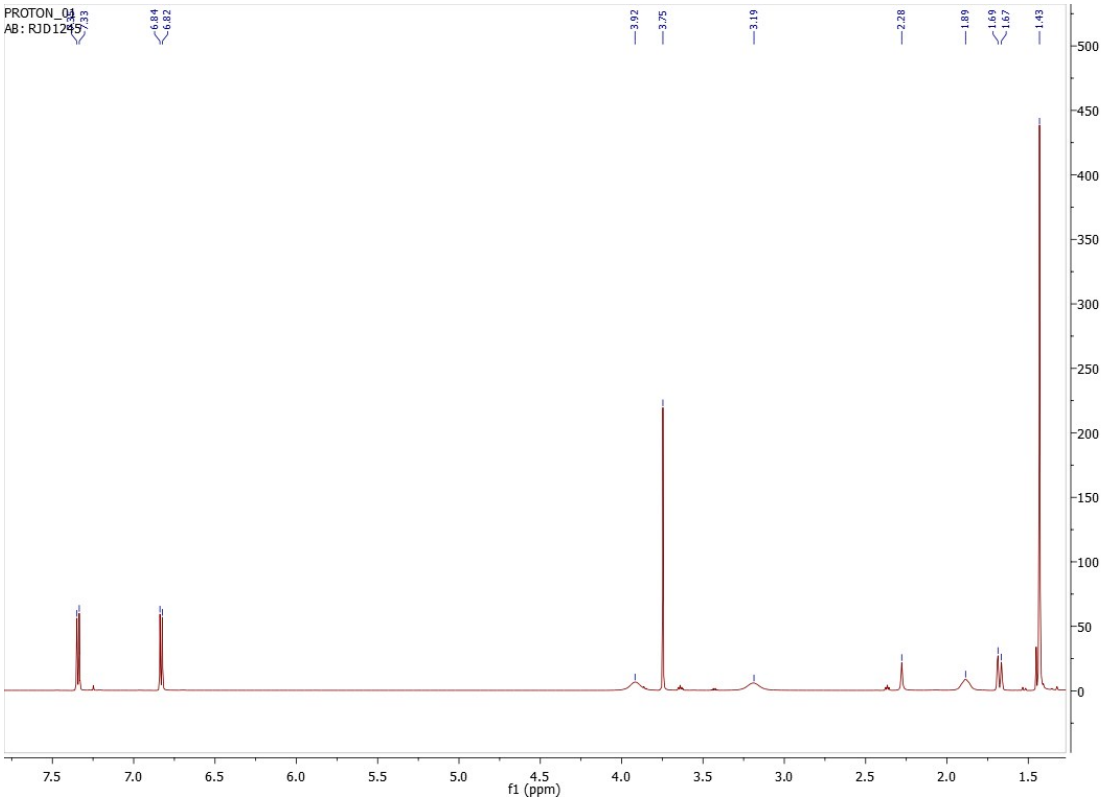

Figure S1.3. ^{1}H NMR spectrum of **2**, recorded in $CDCl_3$.

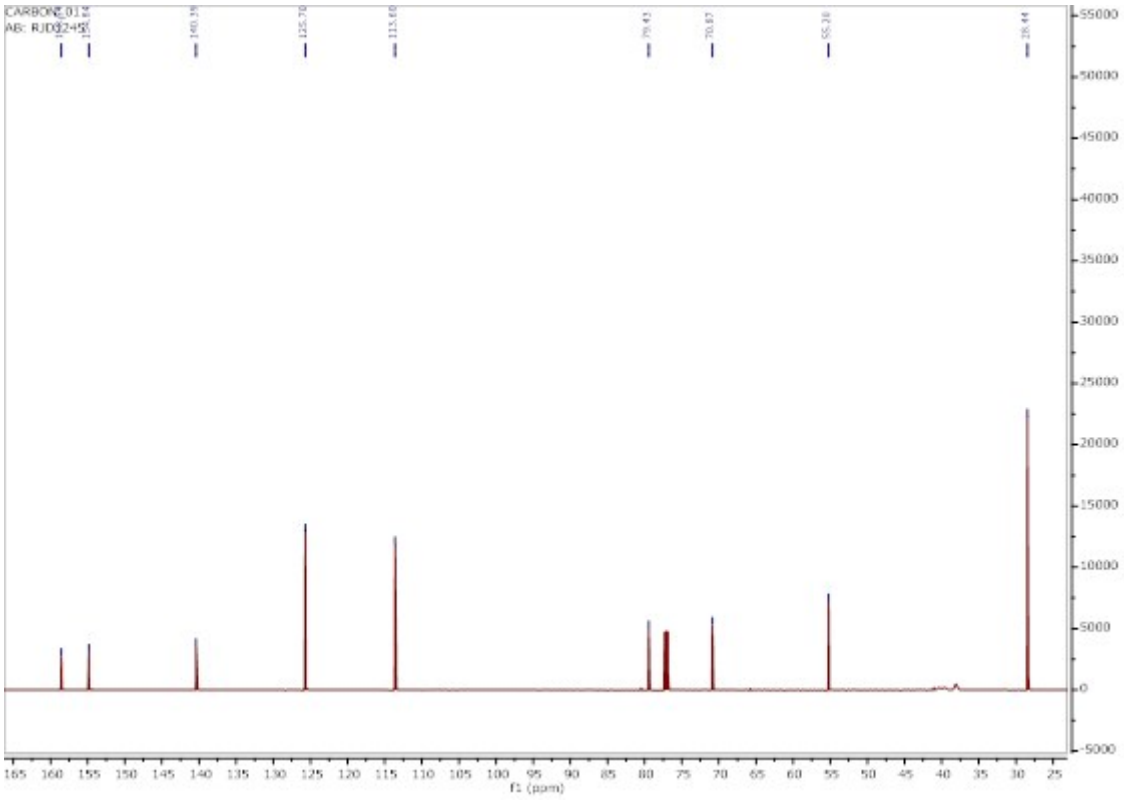

Figure S1.4. ^{13}C NMR spectrum of **2**, recorded in $CDCl_3$.

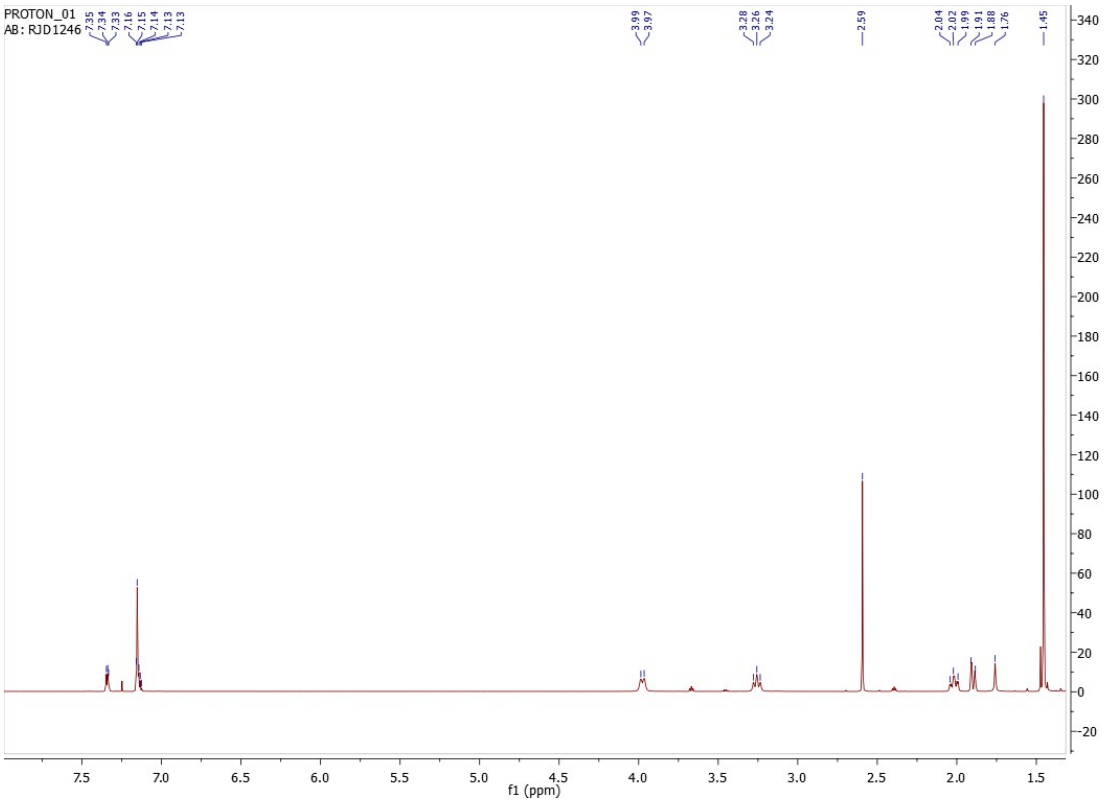

Figure S1.5. ^{1}H NMR spectrum of **3**, recorded in $CDCl_3$.

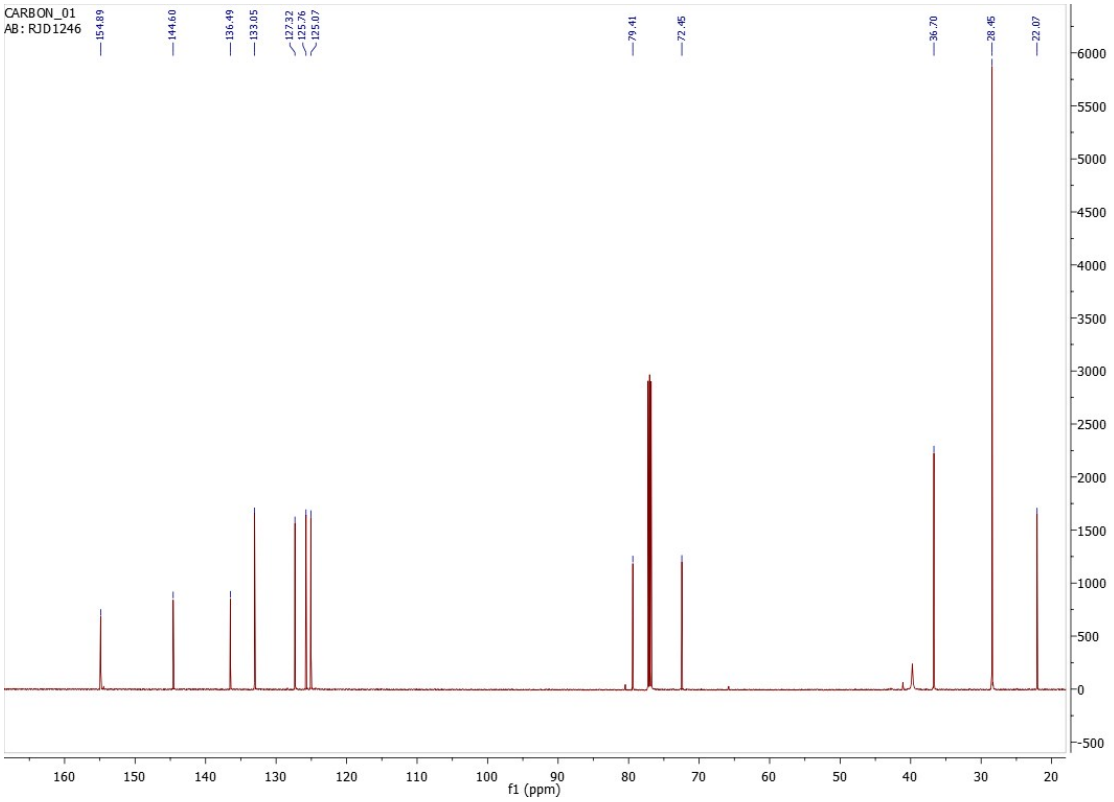

Figure S1.6. ^{13}C NMR spectrum of **3**, recorded in $CDCl_3$.

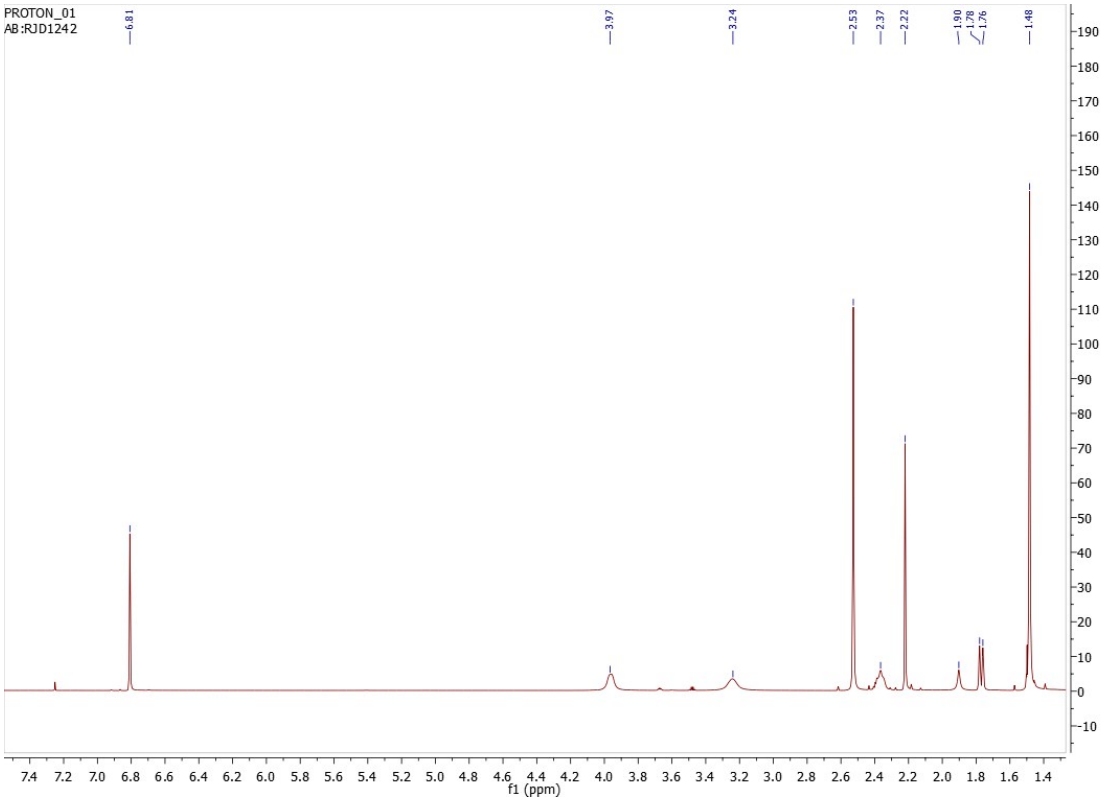

Figure S1.7. ^{1}H NMR spectrum of **4**, recorded in $CDCl_3$.

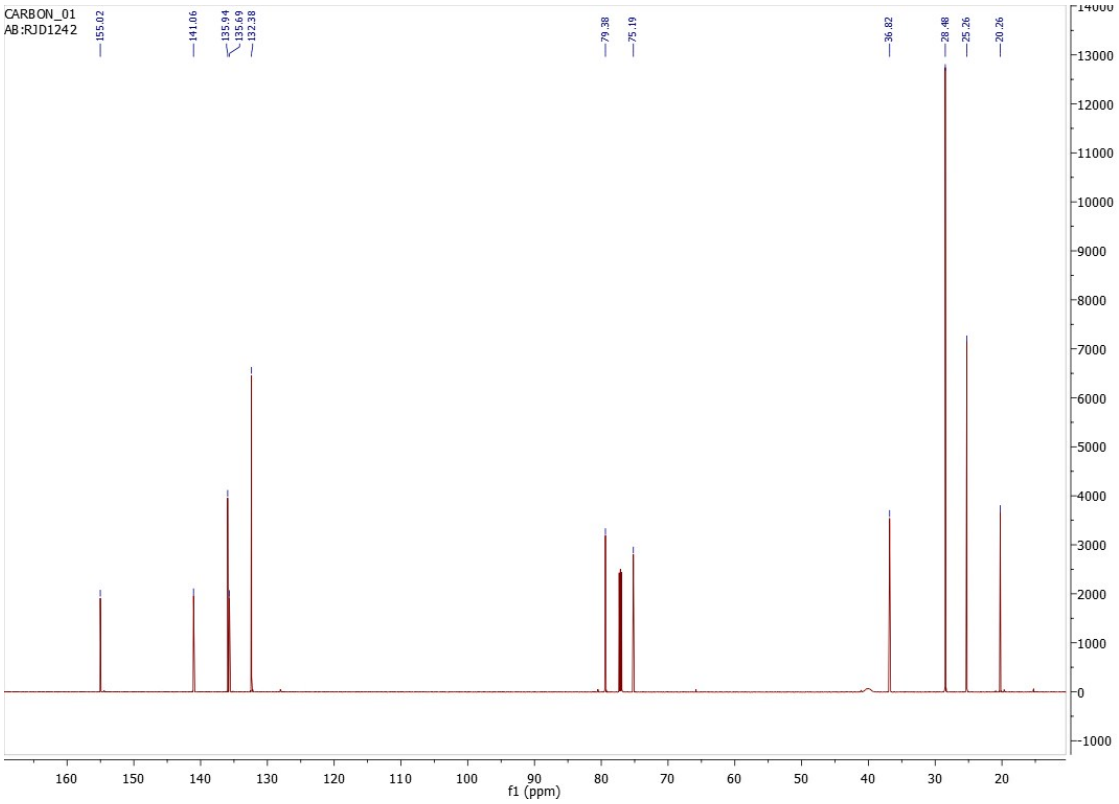

Figure S1.8. ^{13}C NMR spectrum of **4**, recorded in $CDCl_3$

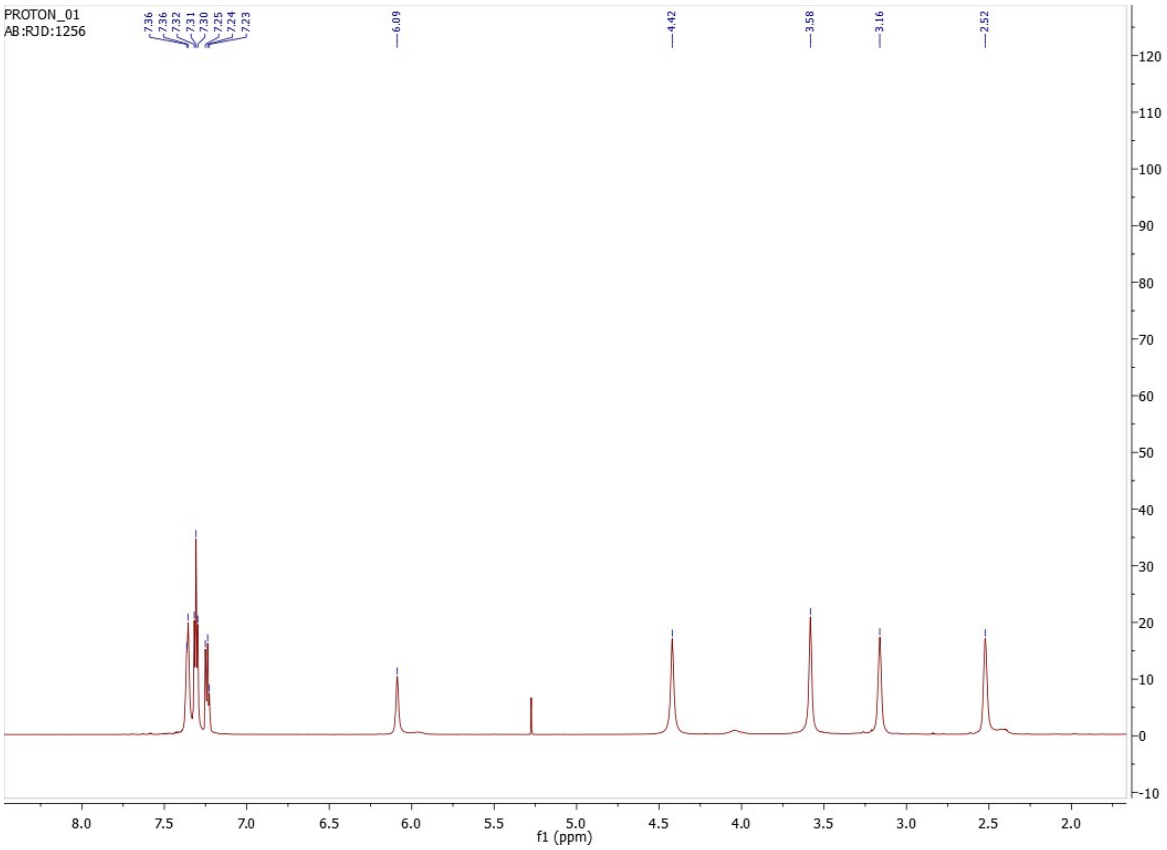

Figure S1.9. ^{1}H NMR spectrum of **5**, recorded in $CDCl_3$.

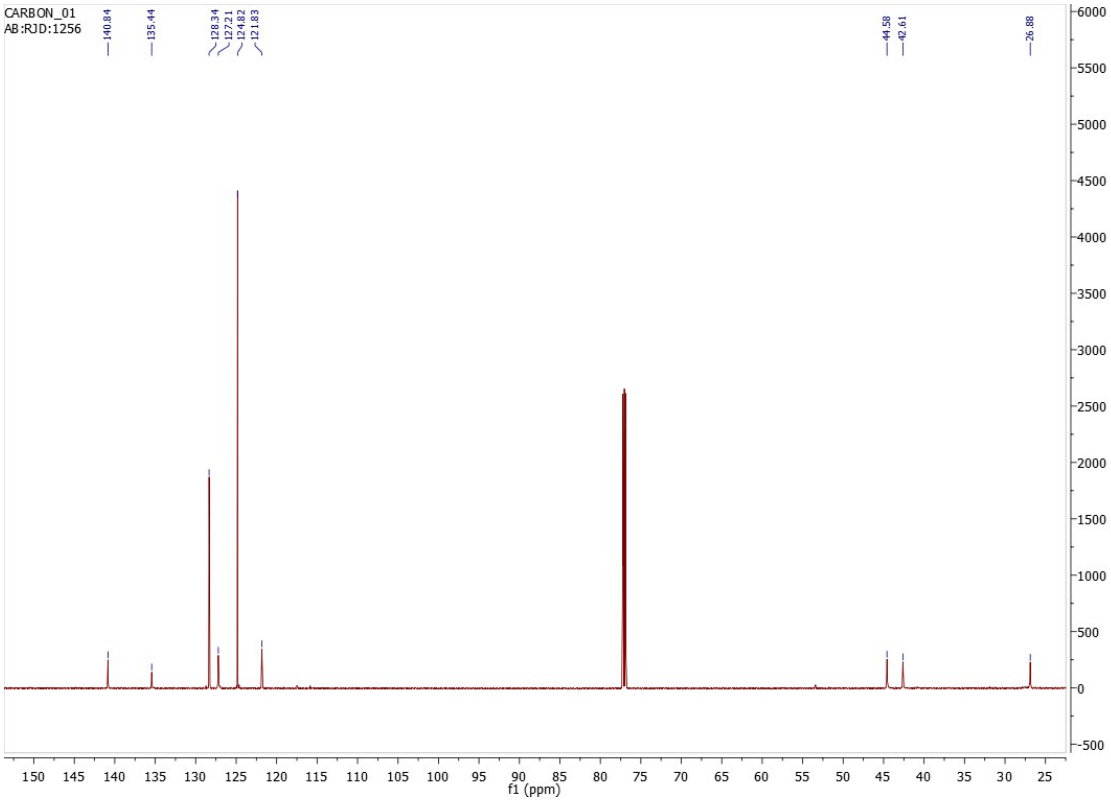

Figure S1.10. ^{13}C NMR spectrum of **5**, recorded in $CDCl_3$.

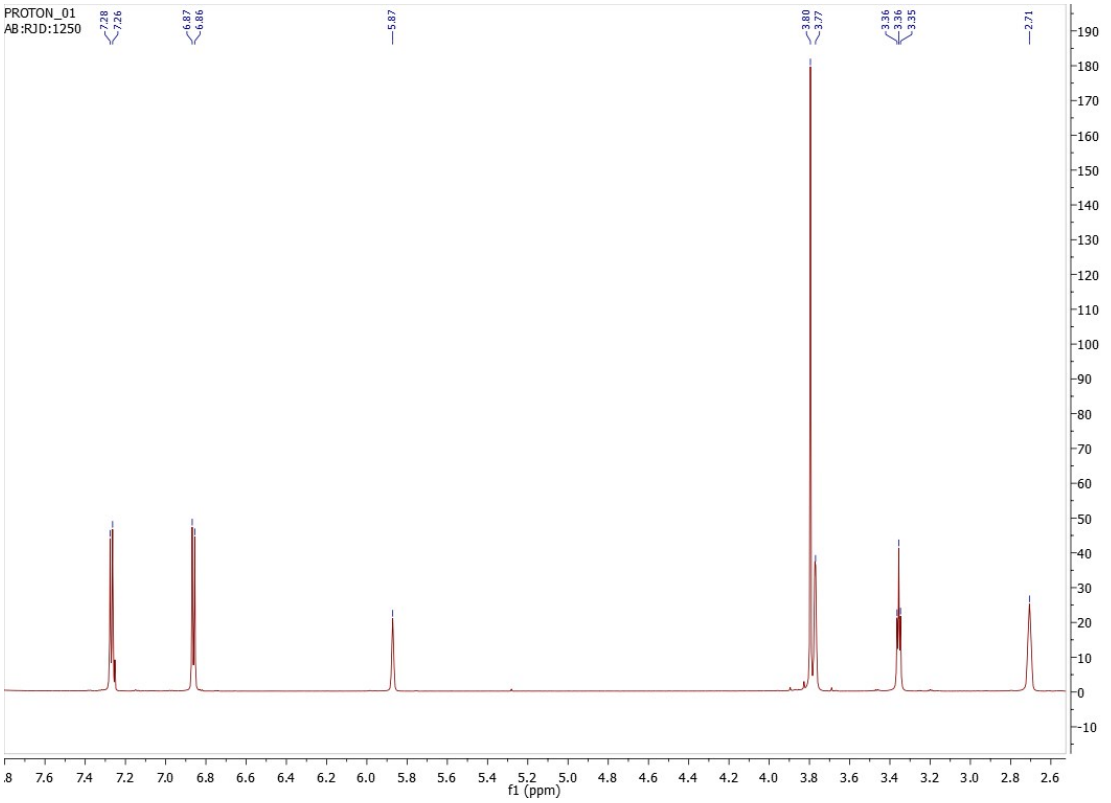

Figure S1.11. ^{1}H NMR spectrum of **6**, recorded in $CDCl_3$.

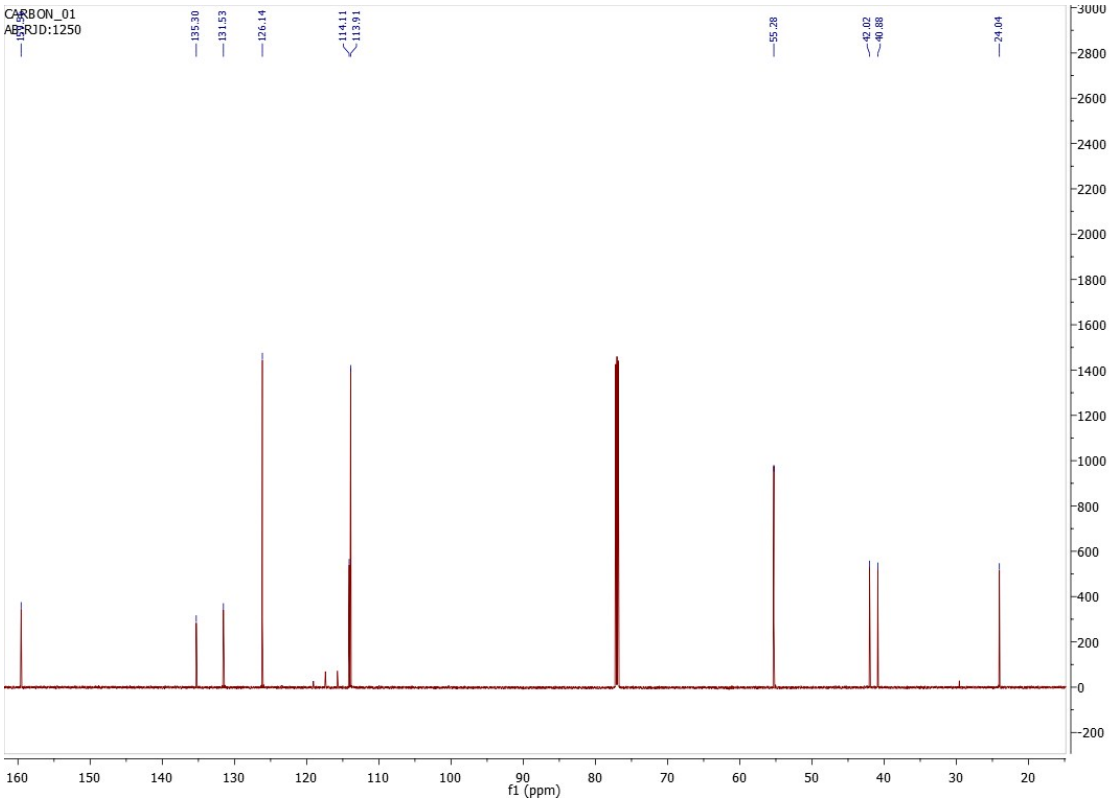

Figure S1.12. ^{13}C NMR spectrum of **6**, recorded in $CDCl_3$.

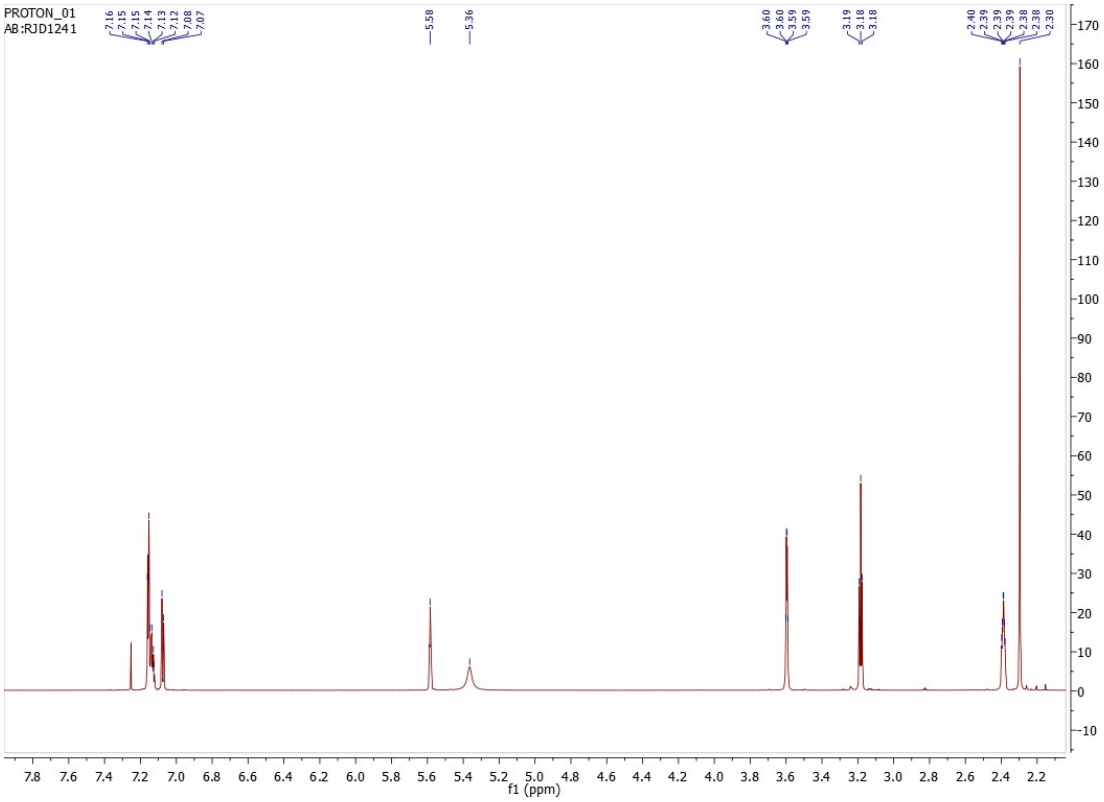

Figure S1.13. ^{1}H NMR spectrum of **7**, recorded in $CDCl_3$.

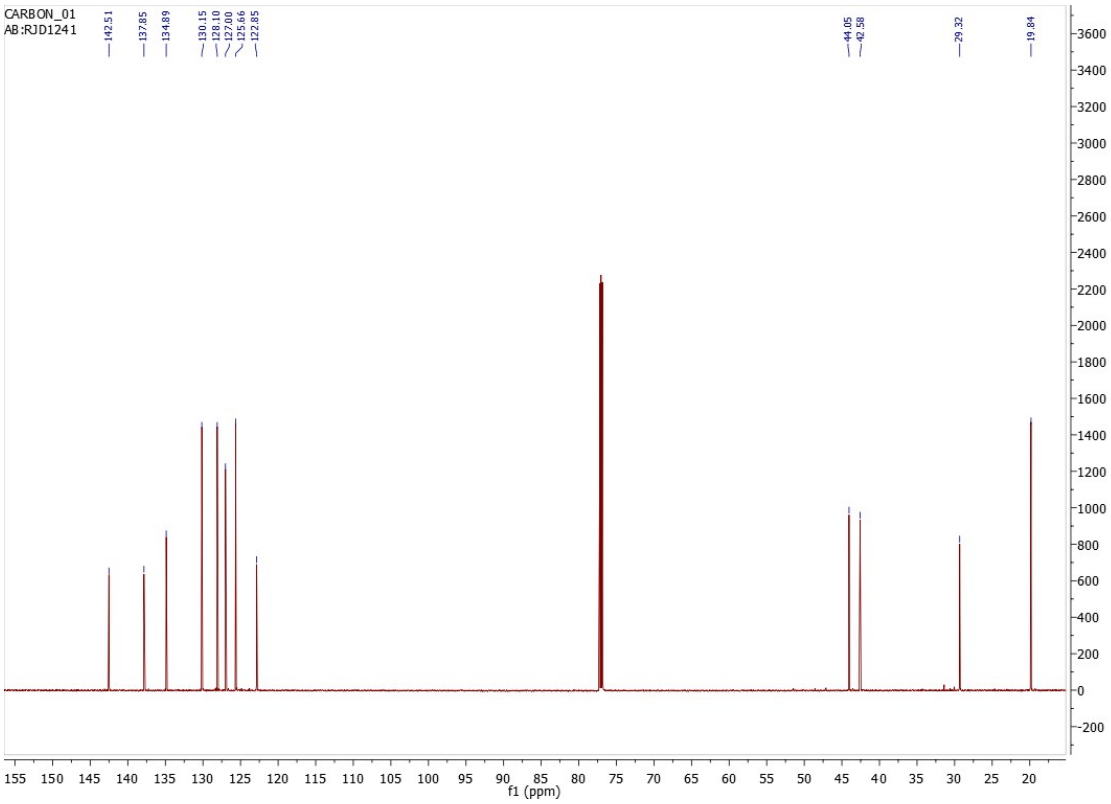

Figure S1.14. ^{13}C NMR spectrum of **7**, recorded in $CDCl_3$.

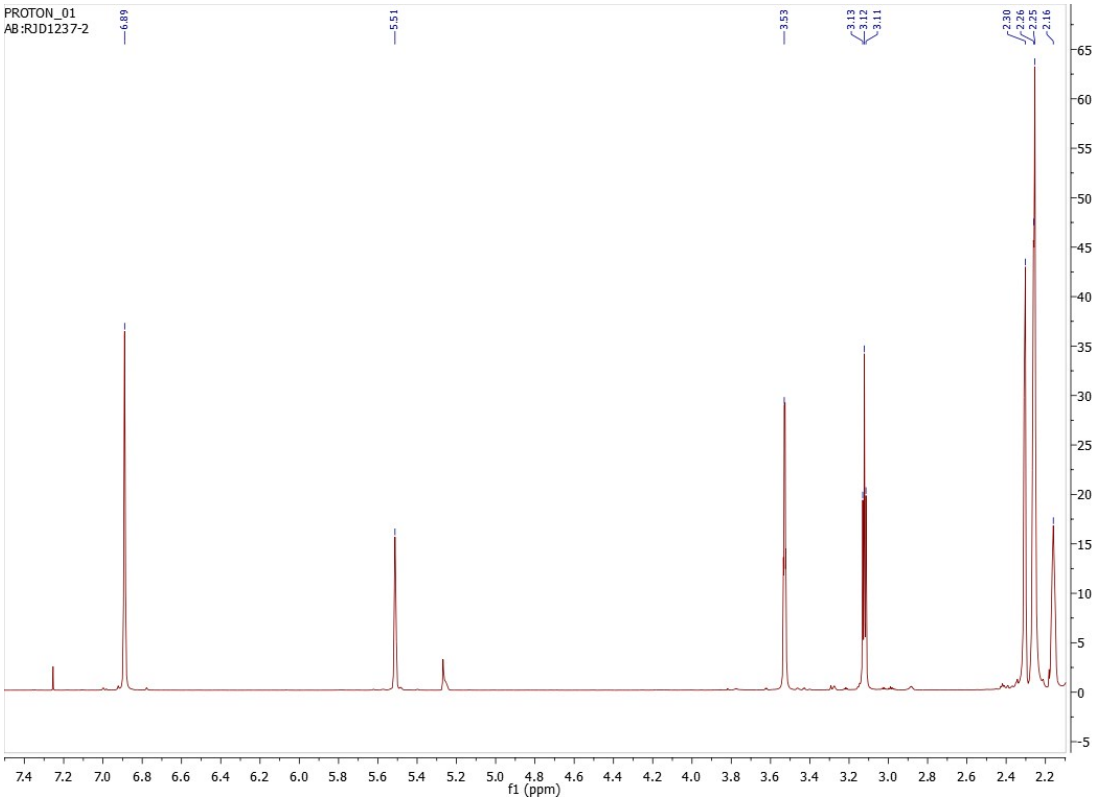

Figure S1.15. ^{1}H NMR spectrum of **8**, recorded in $CDCl_3$.

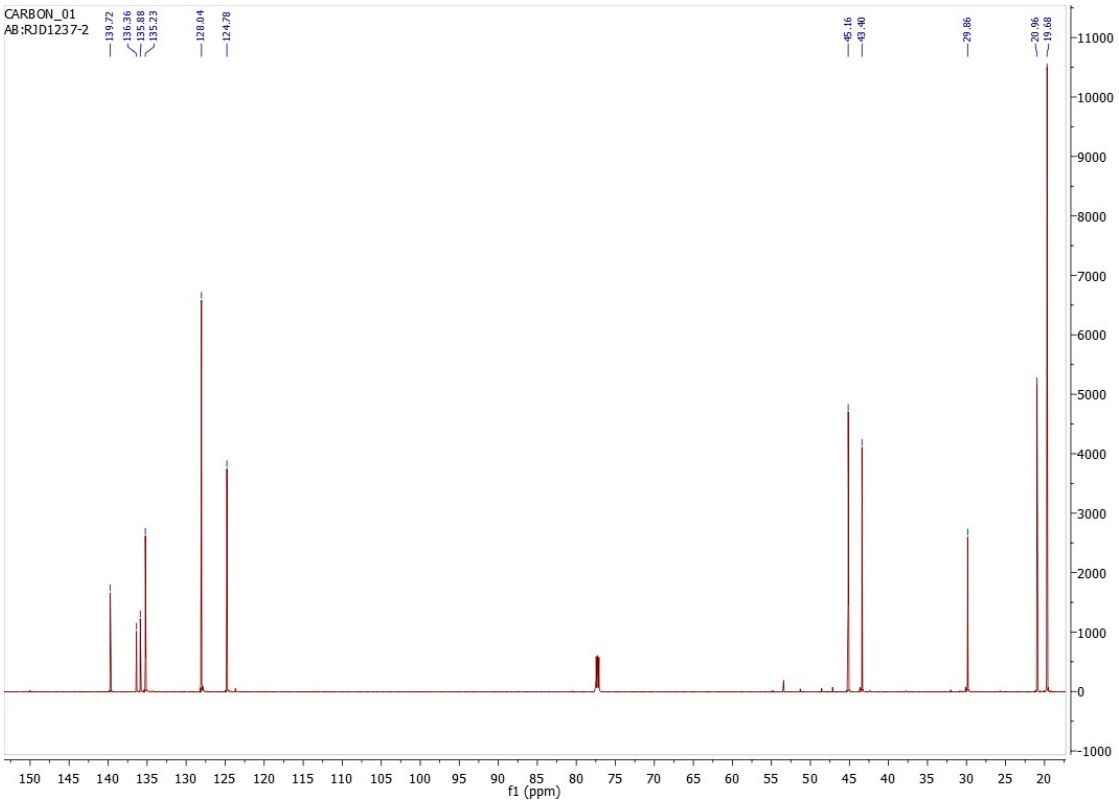

Figure S1.16. ^{13}C NMR spectrum of **8**, recorded in $CDCl_3$.

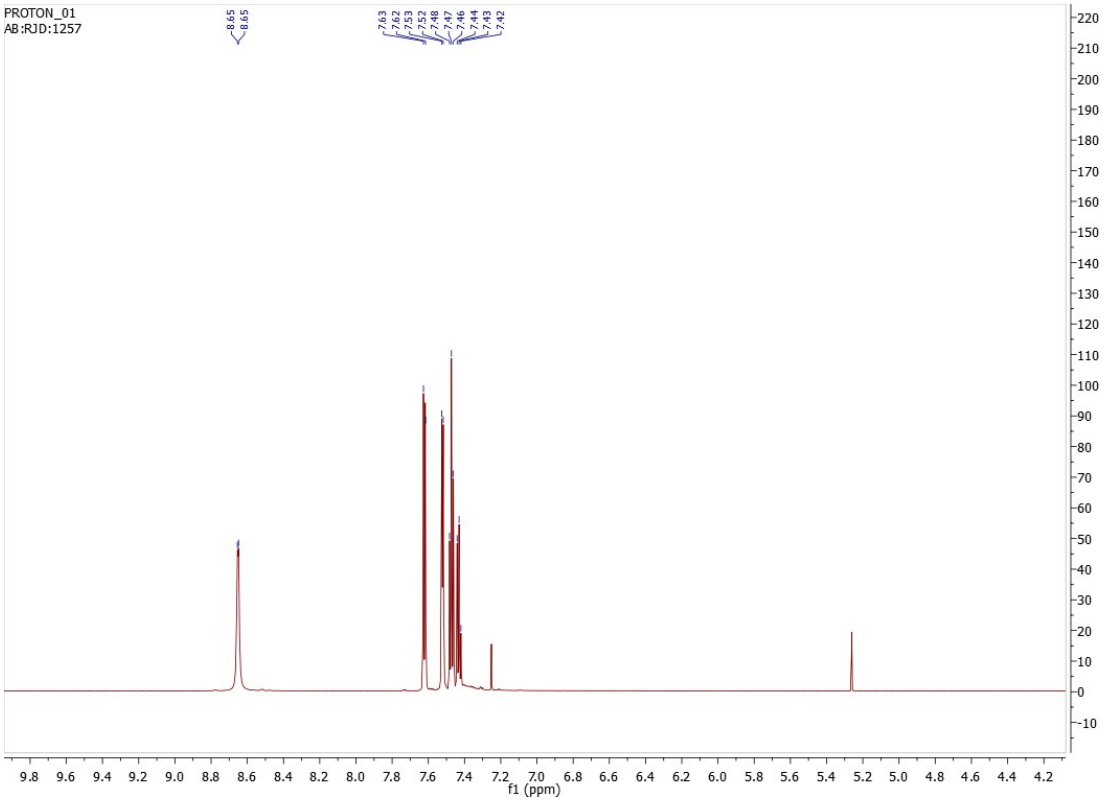

Figure S1.17. ^{1}H NMR spectrum of **9**, recorded in $CDCl_3$.

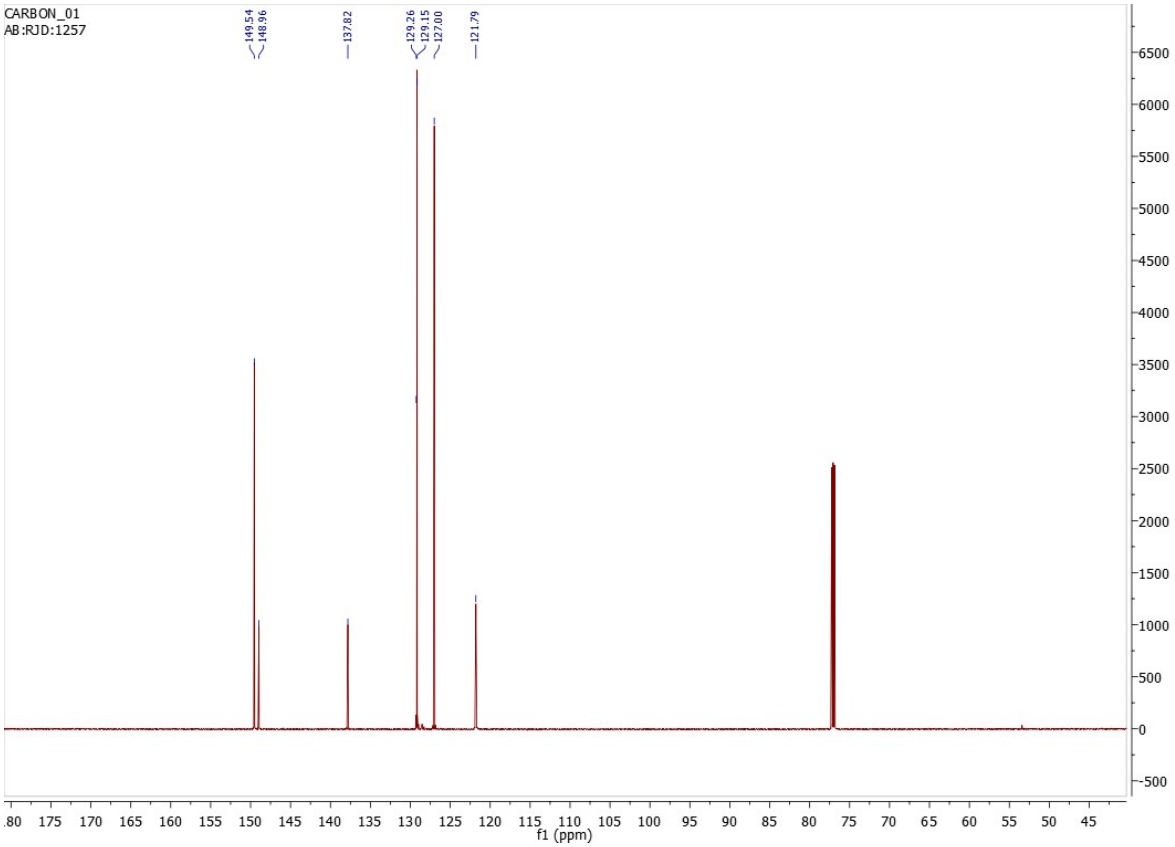

Figure S1.18. ^{13}C NMR spectrum of **9**, recorded in $CDCl_3$.

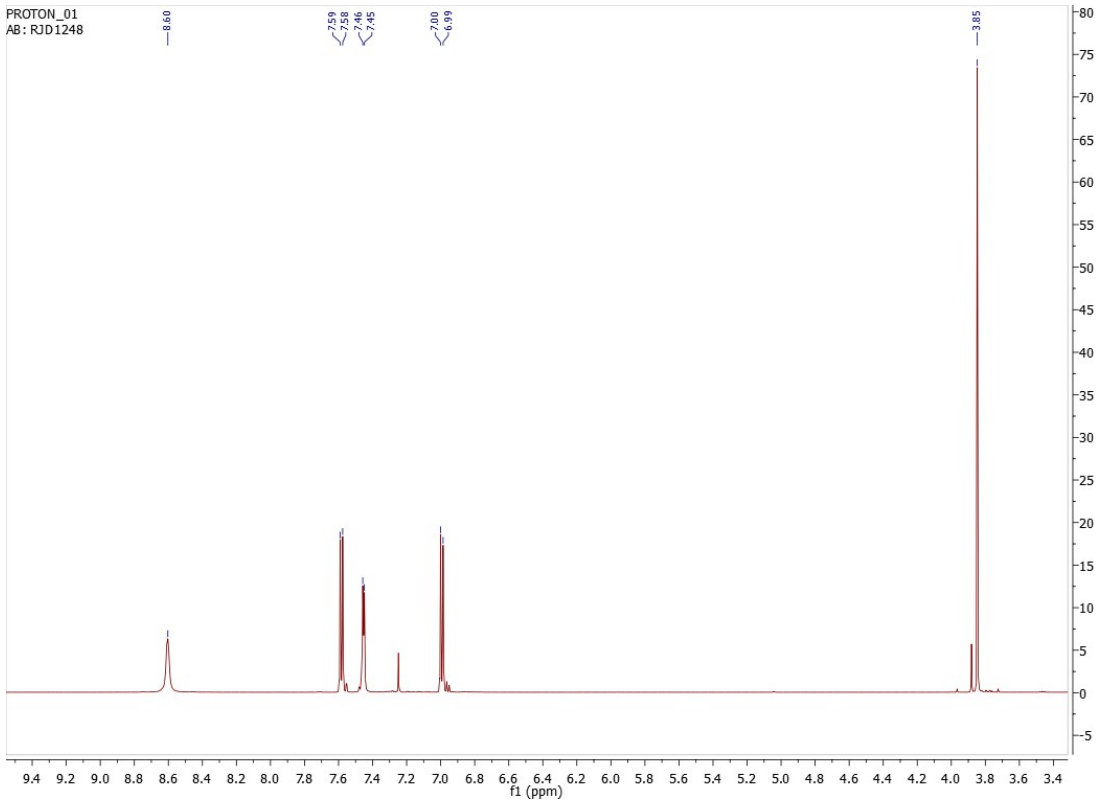

Figure S1.19. ^{1}H NMR spectrum of **10**, recorded in $CDCl_3$.

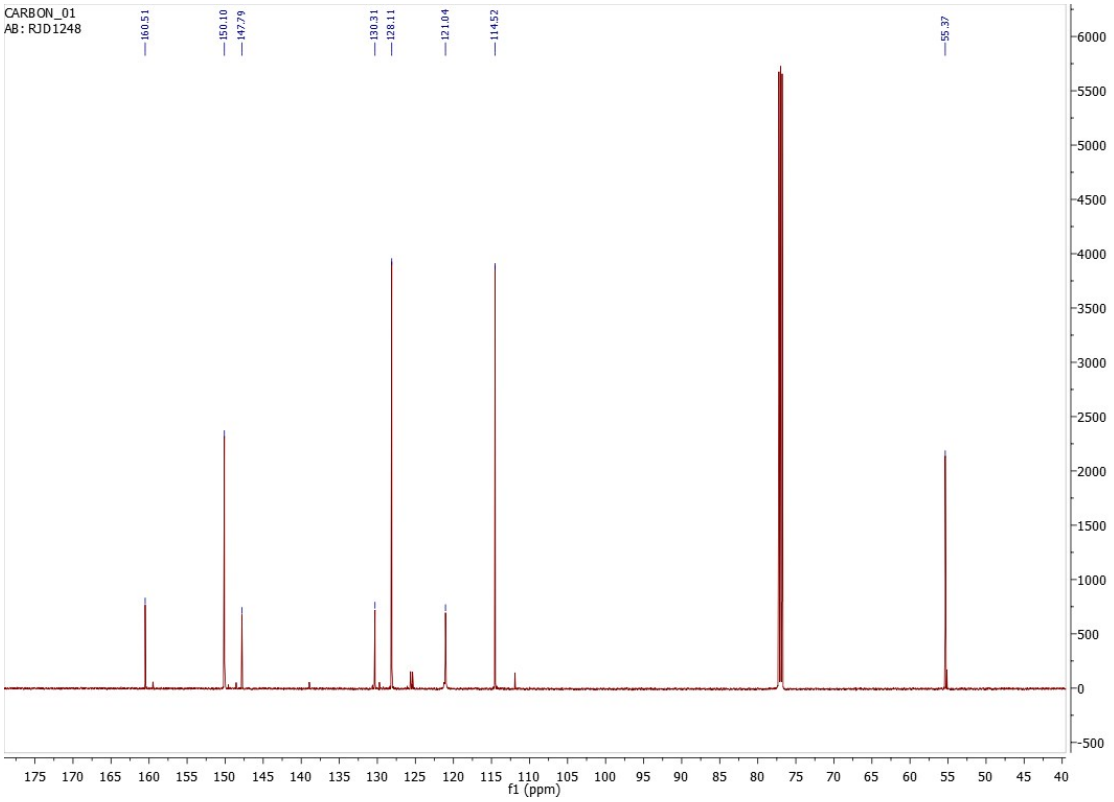

Figure S1.20. ^{13}C NMR spectrum of **10**, recorded in $CDCl_3$.

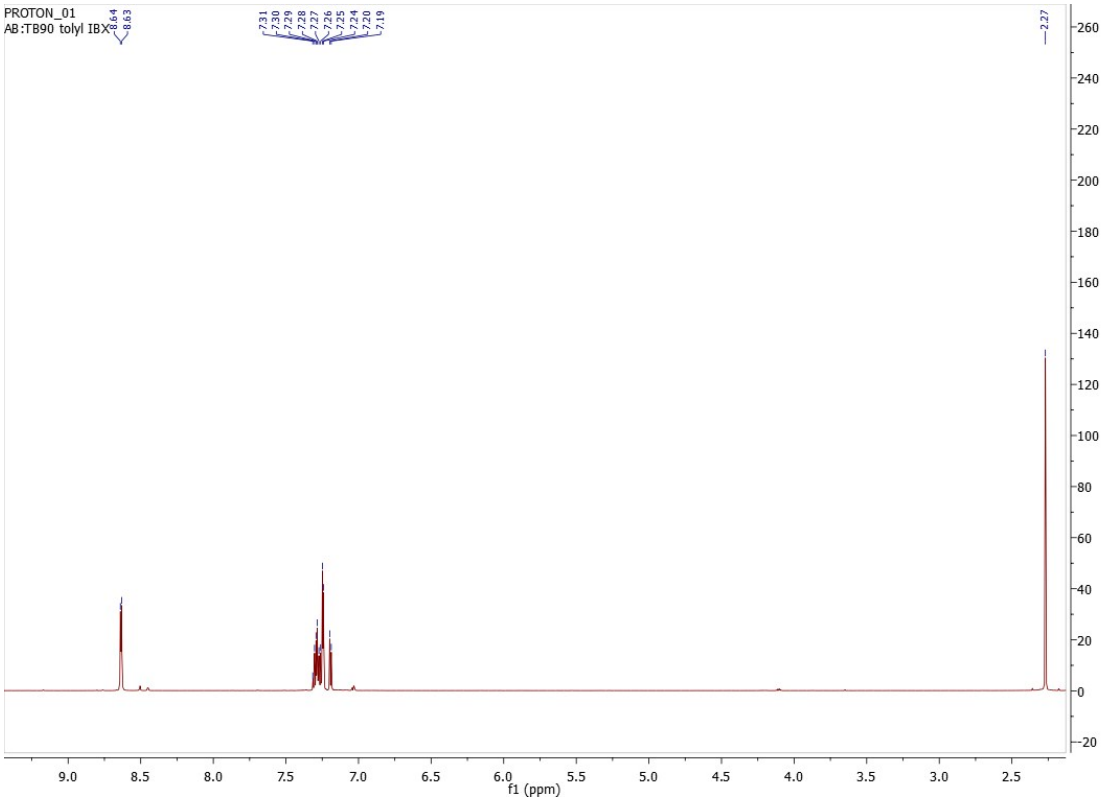

Figure S1.21. ^{1}H NMR spectrum of **11**, recorded in $CDCl_3$.

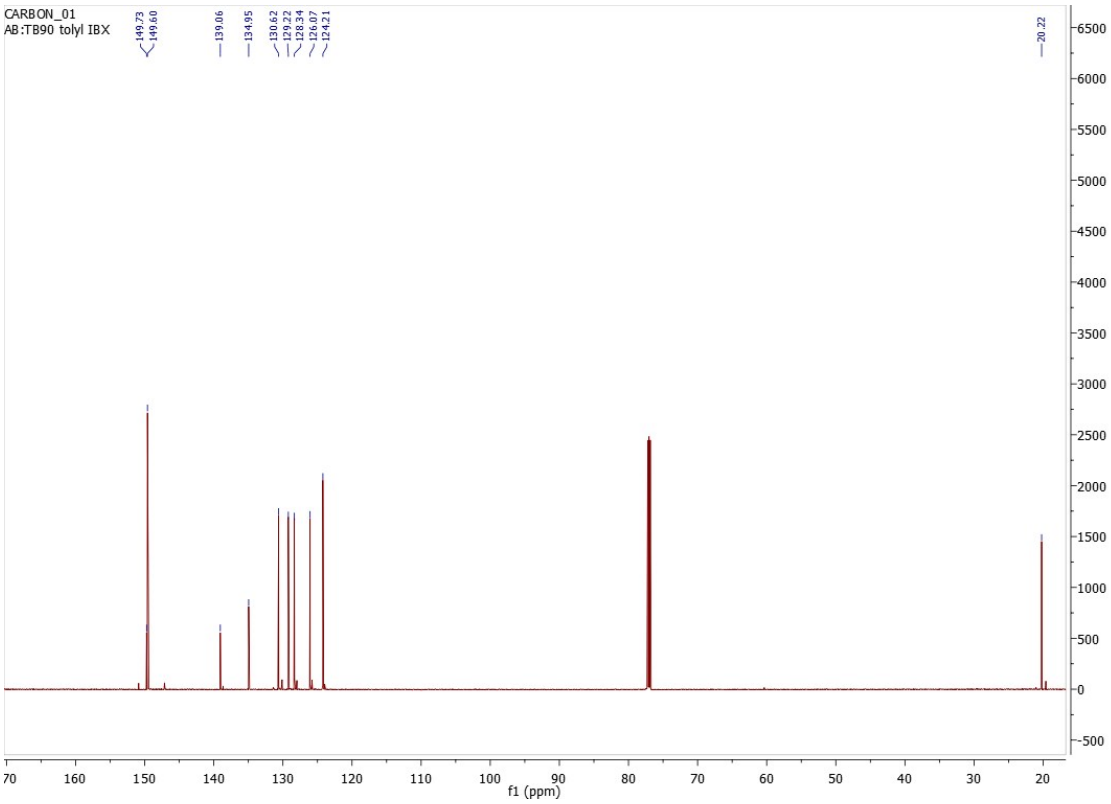

Figure S1.22. ^{13}C NMR spectrum of **11**, recorded in $CDCl_3$.

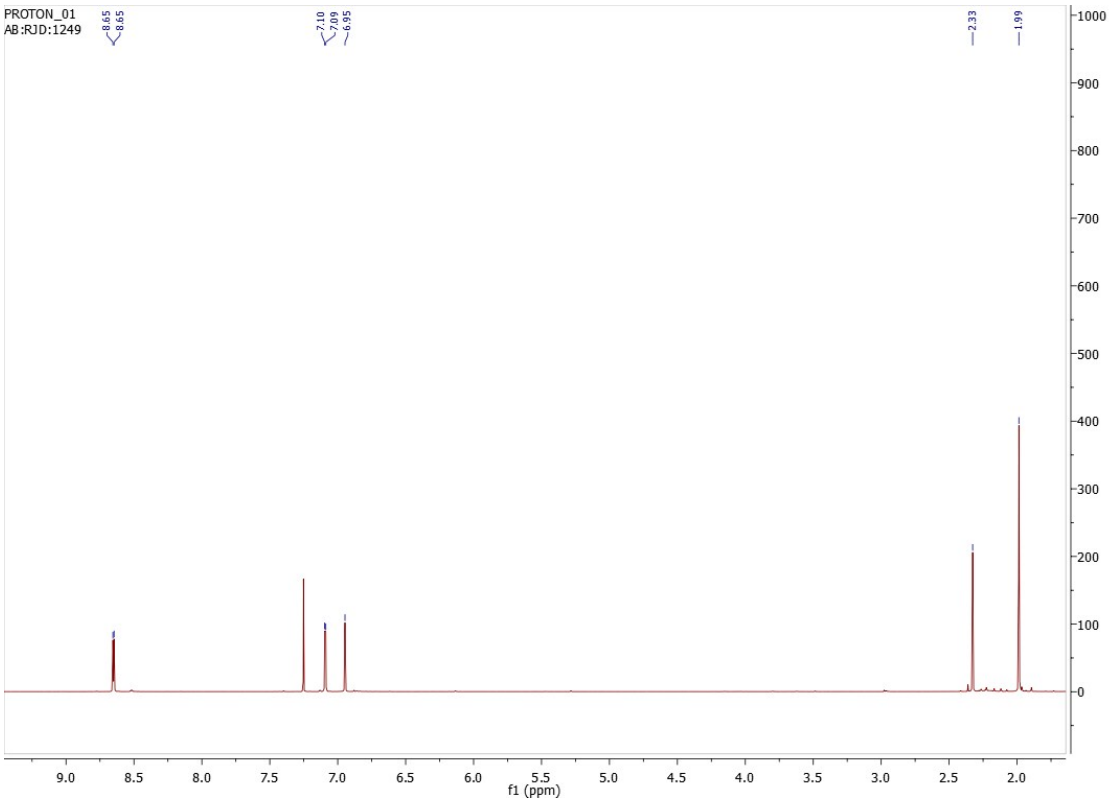

Figure S1.23. ^{1}H NMR spectrum of **12**, recorded in $CDCl_3$.

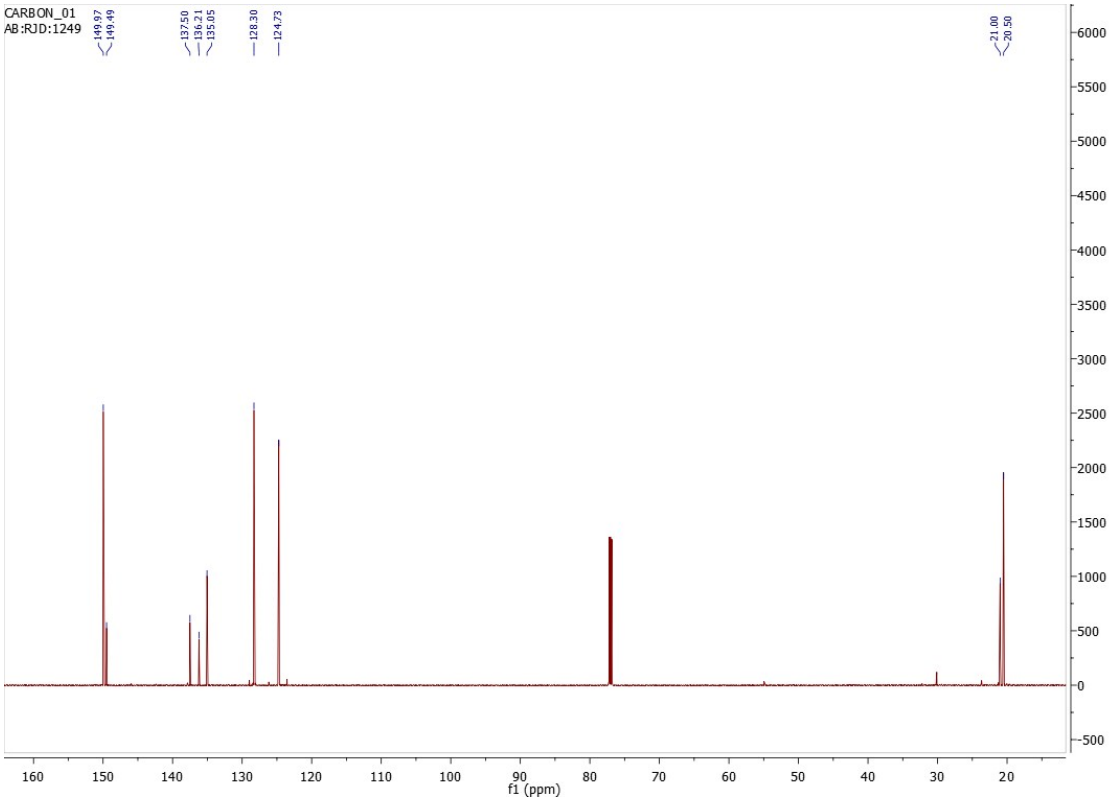

Figure S1.24. ^{13}C NMR spectrum of **12**, recorded in $CDCl_3$.

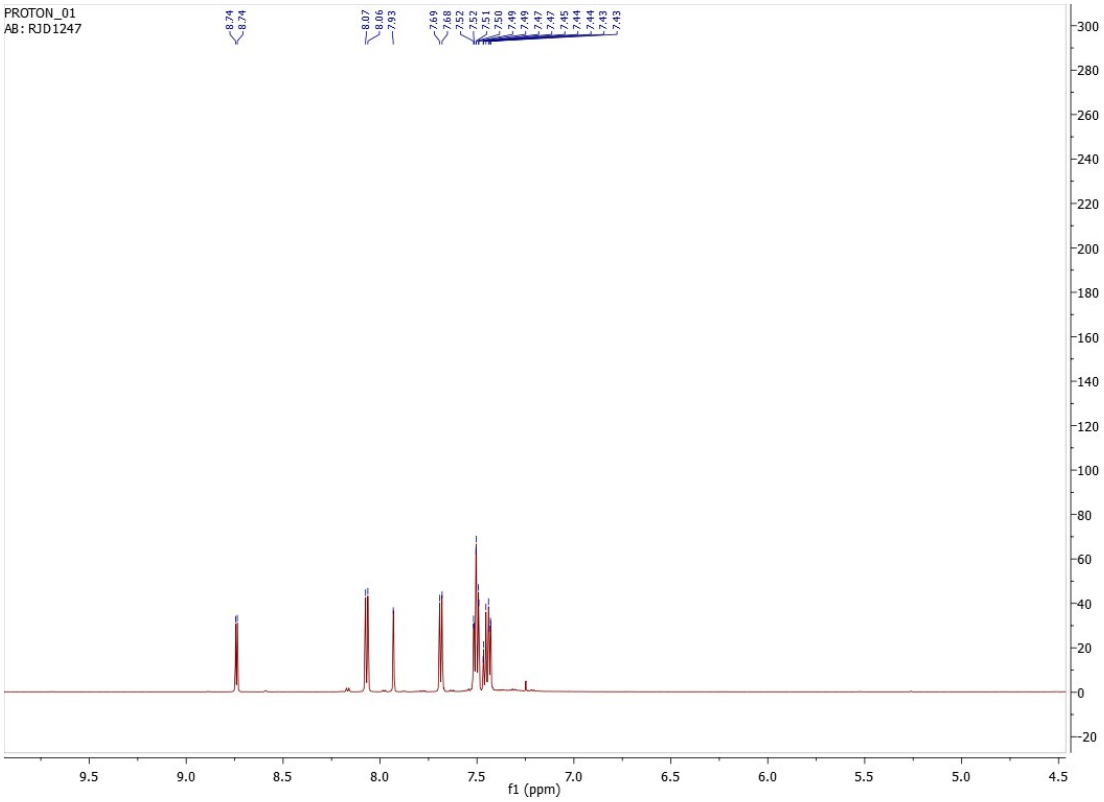

Figure S1.25. ^{1}H NMR spectrum of **L^{1}H**, recorded in $CDCl_3$.

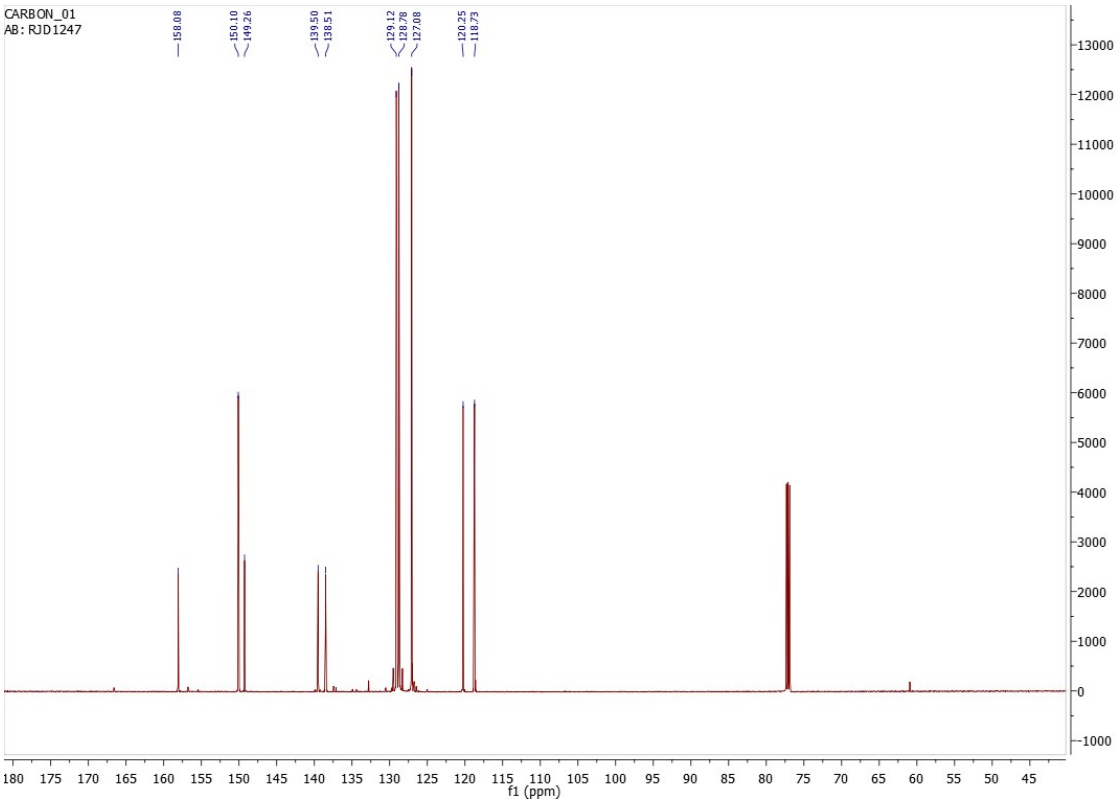

Figure S1.26. ^{13}C NMR spectrum of **L^{1}H**, recorded in $CDCl_3$.

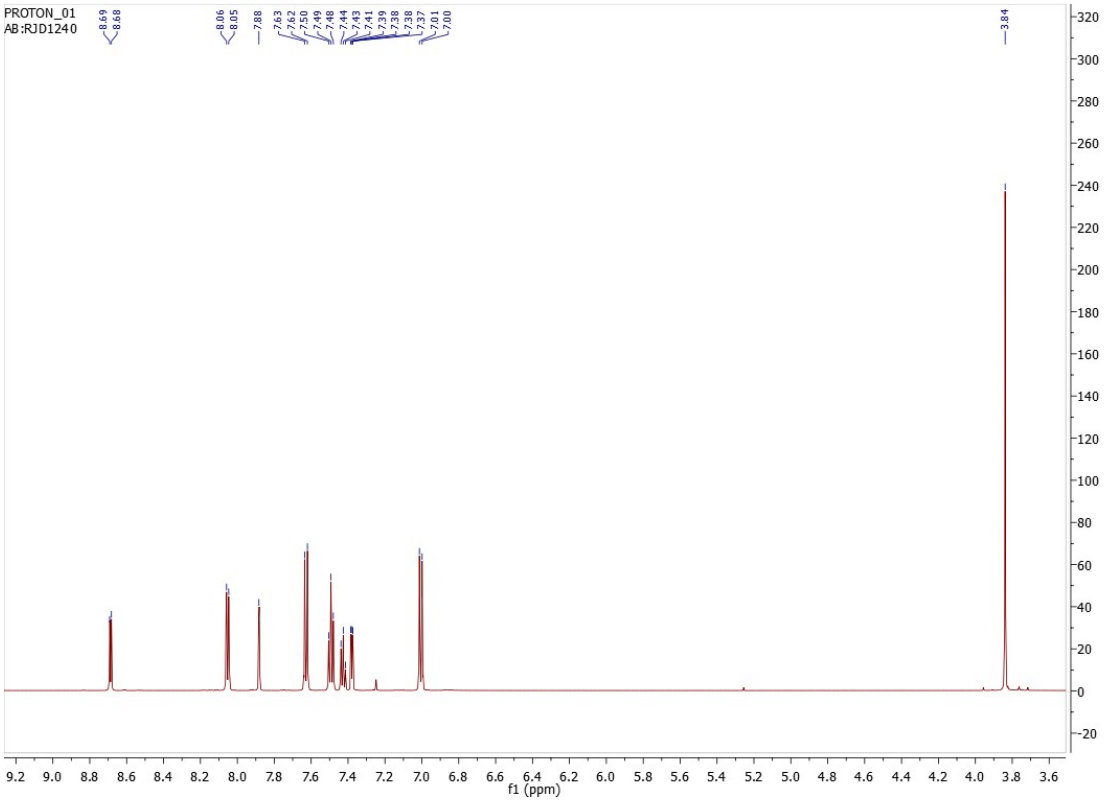

Figure S1.27. ^{1}H NMR spectrum of **L^{2}H**, recorded in $CDCl_3$.

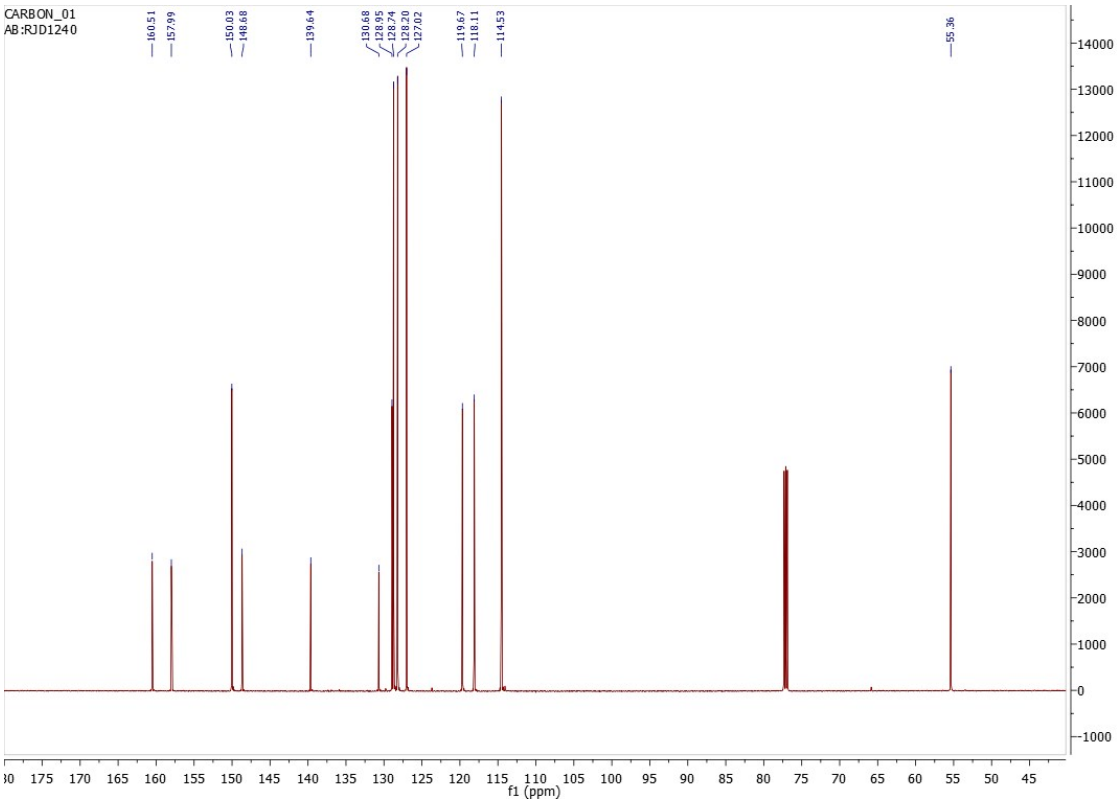

Figure S1.28. ^{13}C NMR spectrum of **L^{2}H**, recorded in $CDCl_3$.

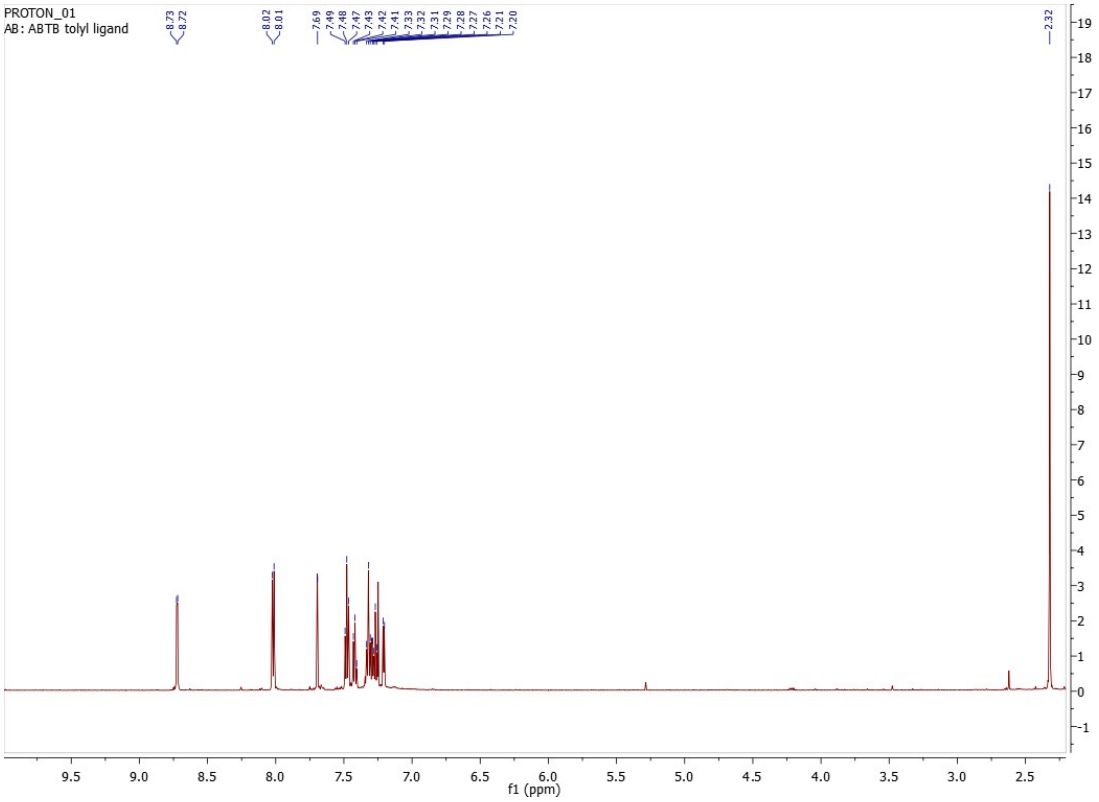

Figure S1.29. ^{1}H NMR spectrum of **L^{3}**H, recorded in $CDCl_3$.

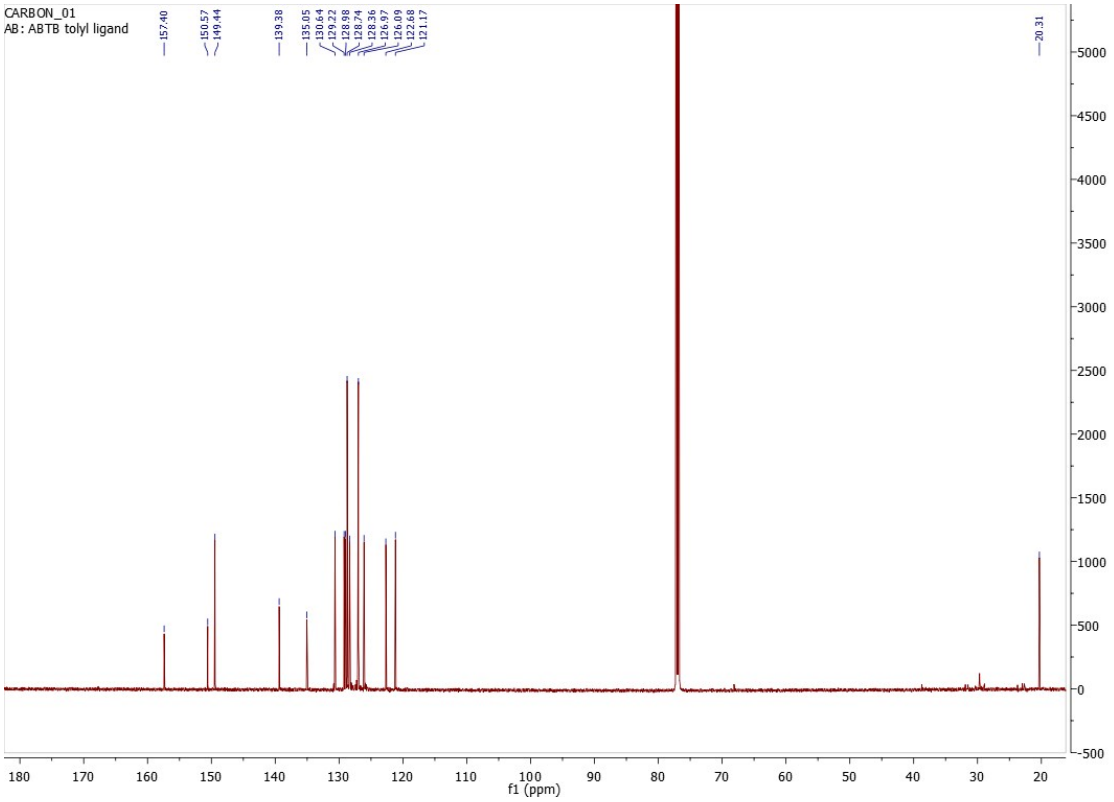

Figure S1.30. ^{13}C NMR spectrum of $\mathbf{L^3}H$, recorded in $CDCl_3$.

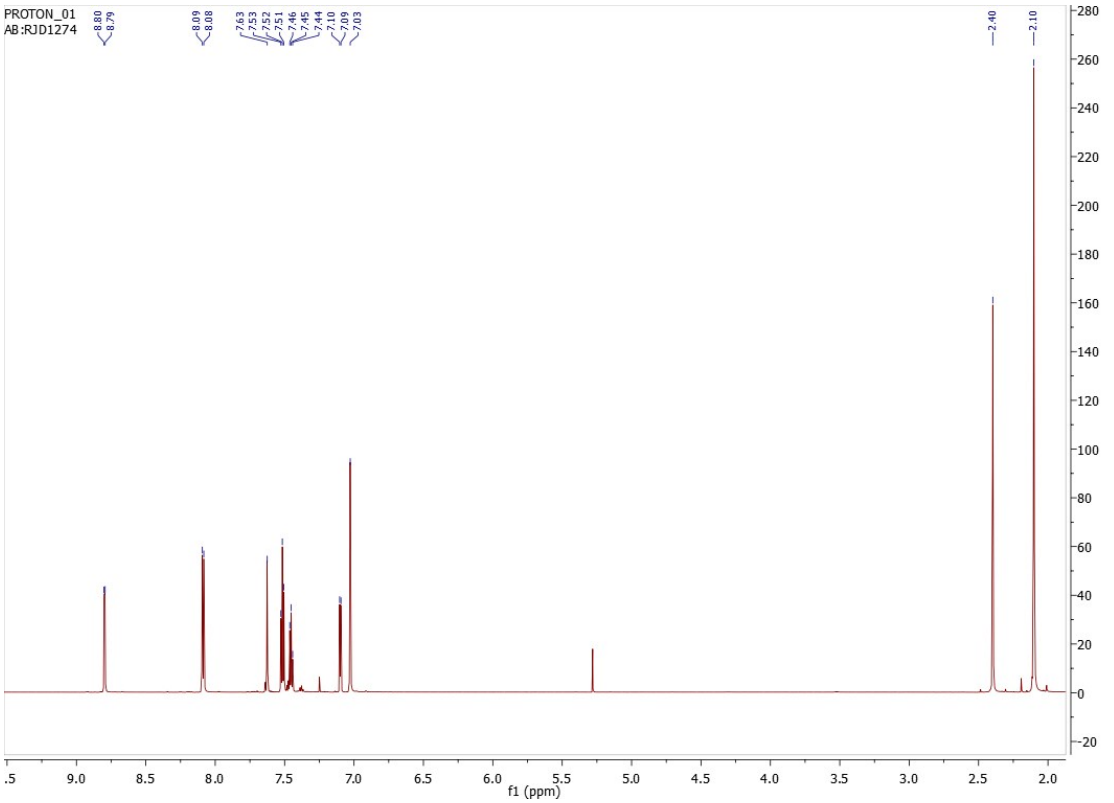

Figure S1.31. ^{1}H NMR spectrum of $\mathbf{L^4}H$, recorded in $CDCl_3$.

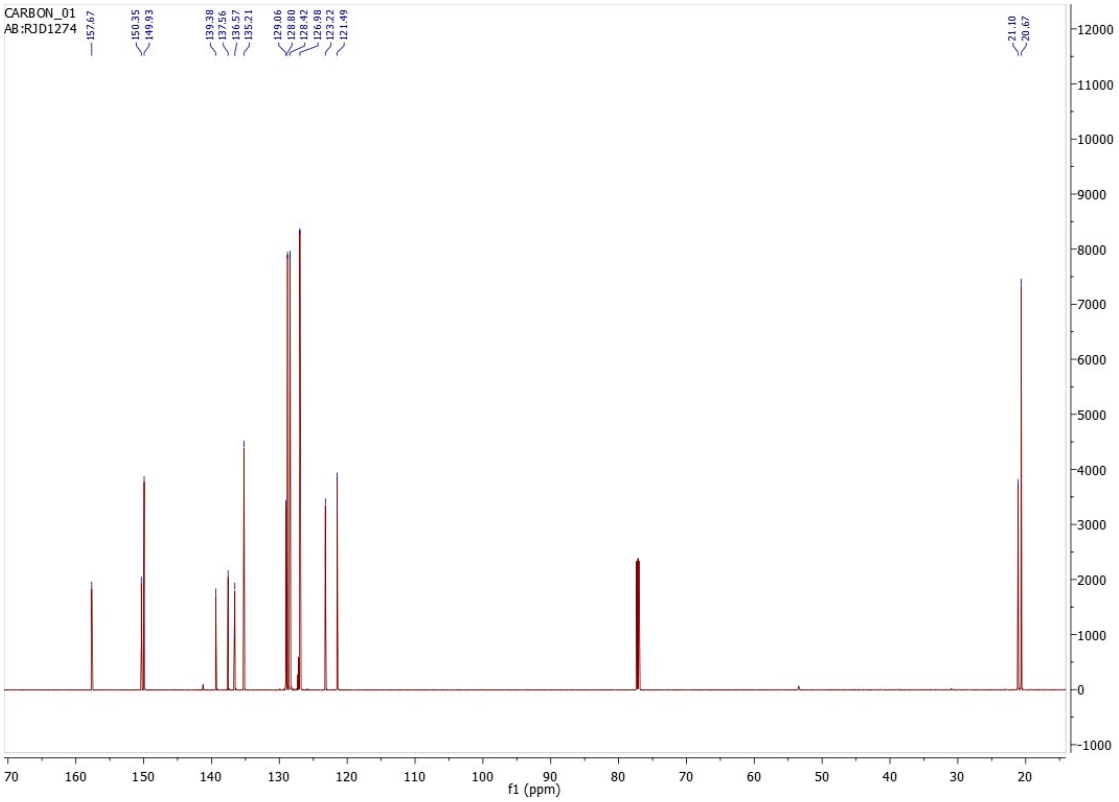

Figure S1.32. ^{13}C NMR spectrum of $\mathbf{L^4}H$, recorded in $CDCl_3$.

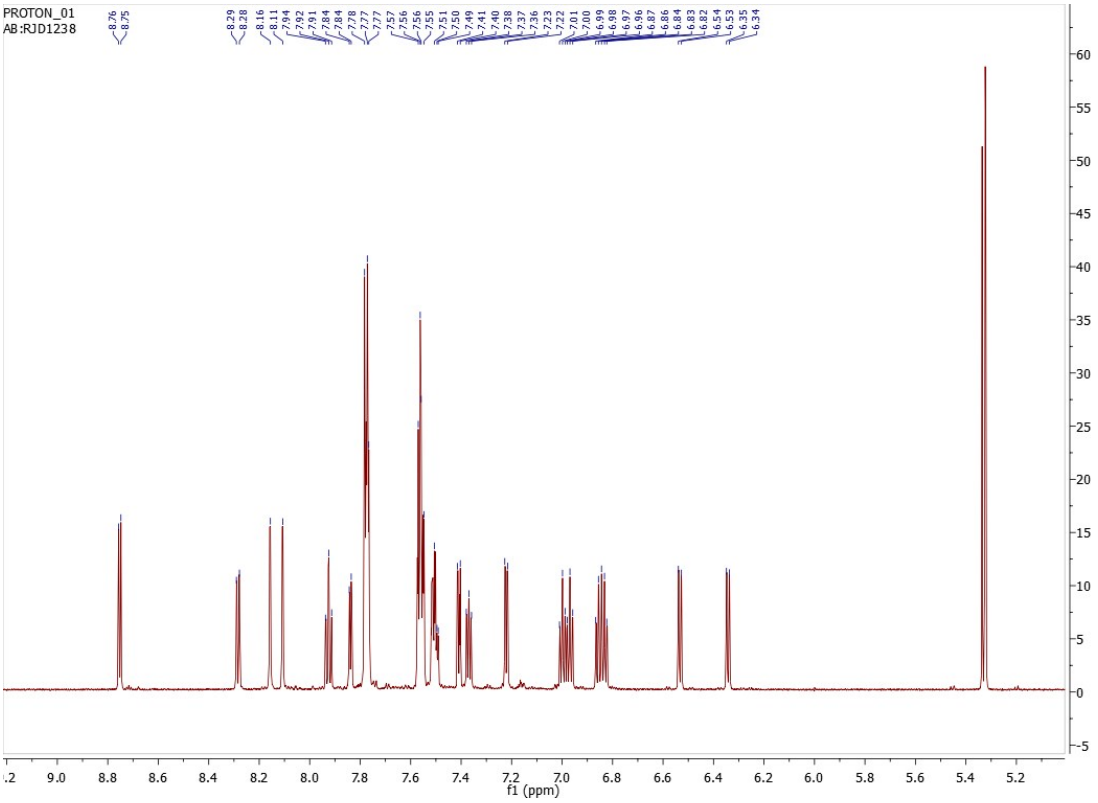

Figure S1.33. ^{1}H NMR spectrum of **Ir1**, recorded in CD_2Cl_2.

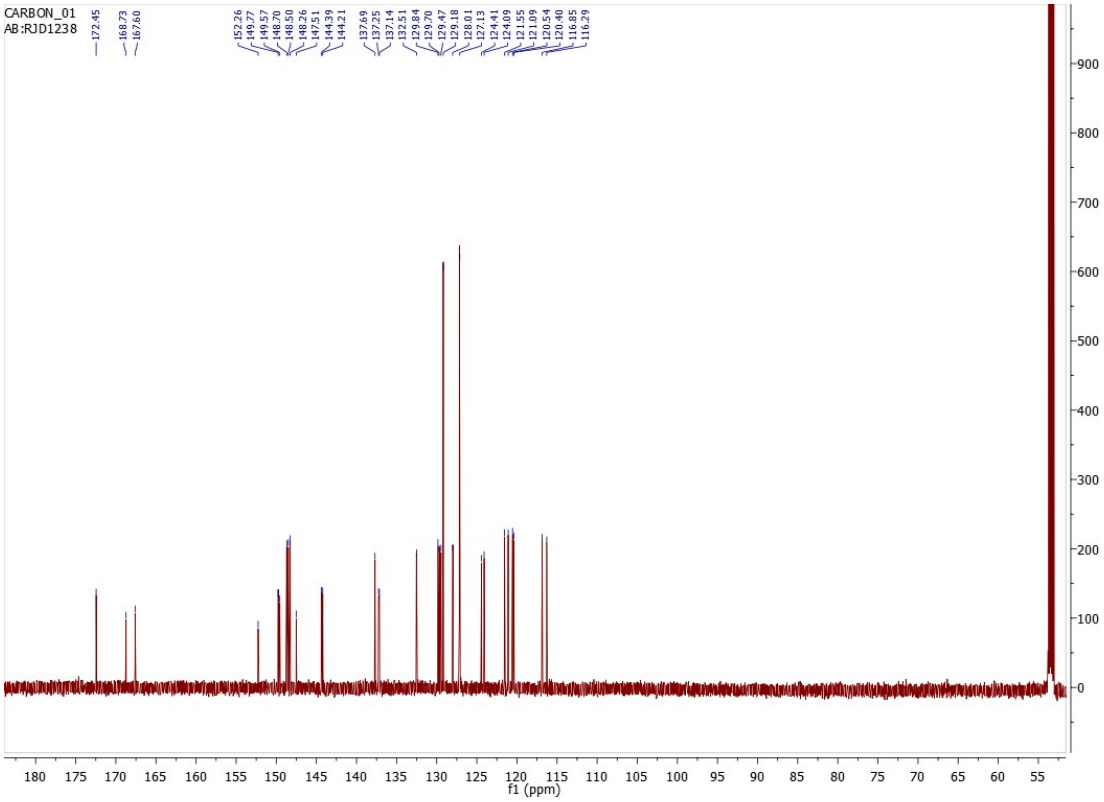

Figure S1.34. ^{13}C NMR spectrum of **Ir1**, recorded in CD_2Cl_2.

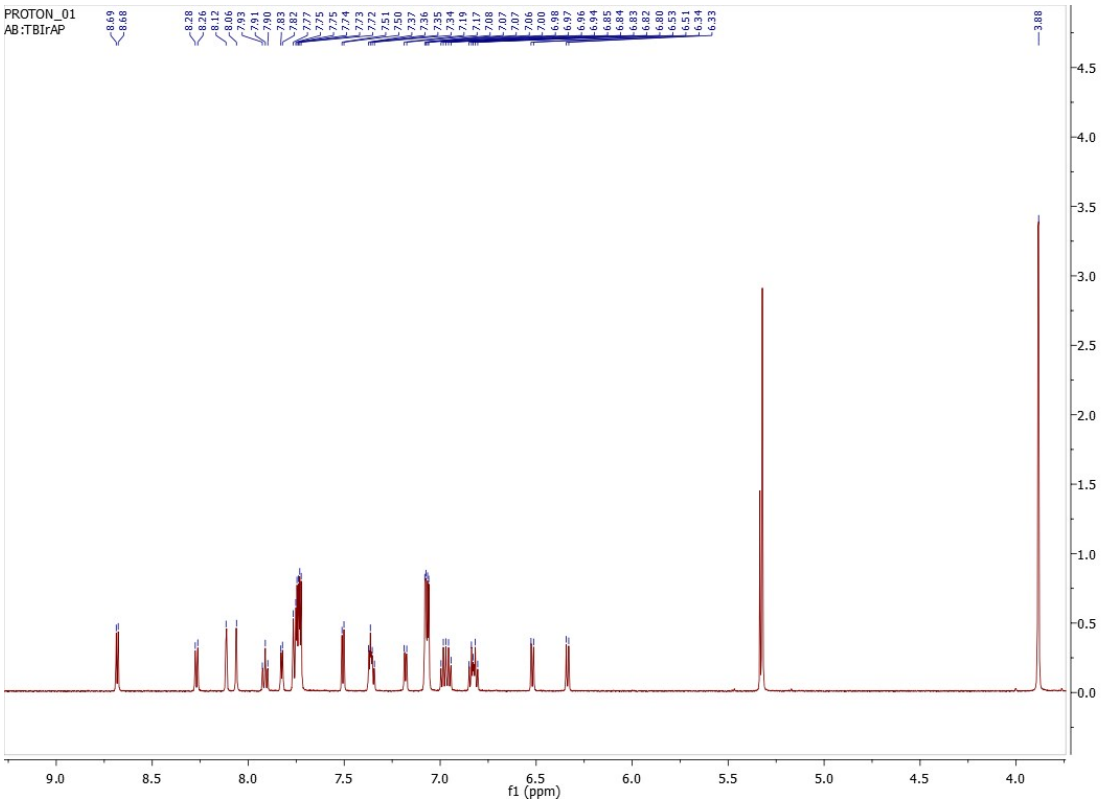

Figure S1.35. ^{1}H NMR spectrum of **Ir2**, recorded in CD_2Cl_2.

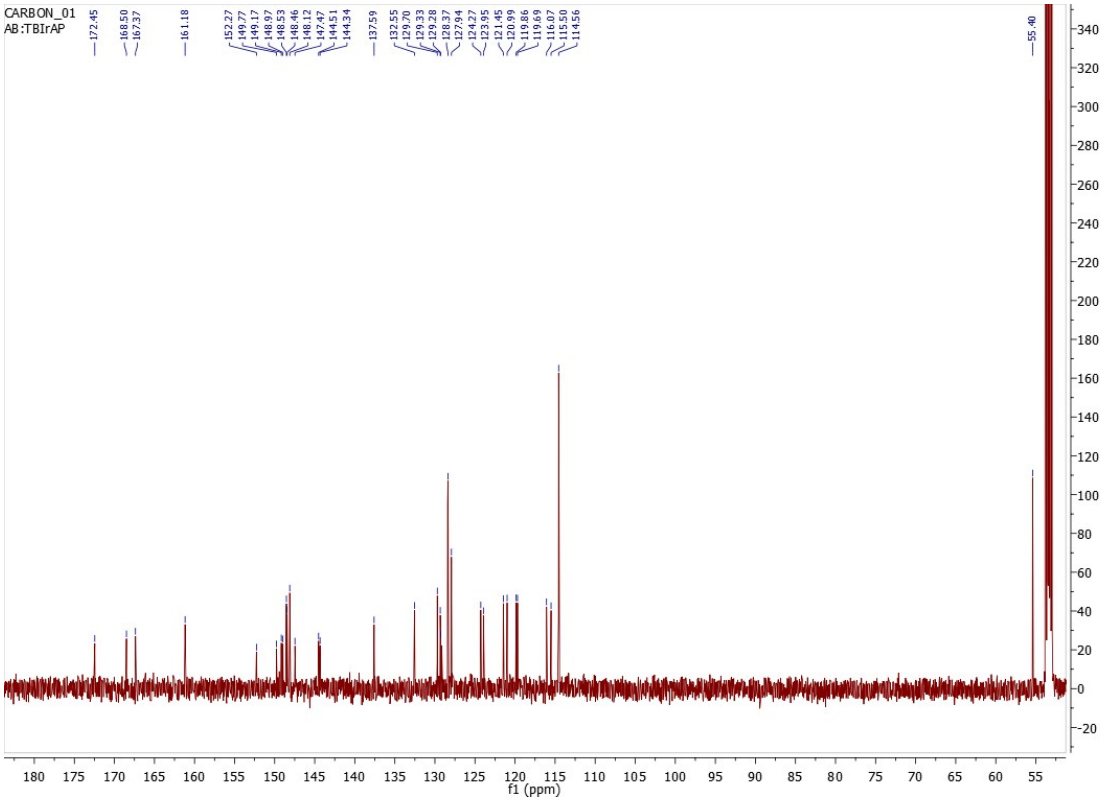

Figure S1.36. ^{13}C NMR spectrum of **Ir2**, recorded in CD_2Cl_2.

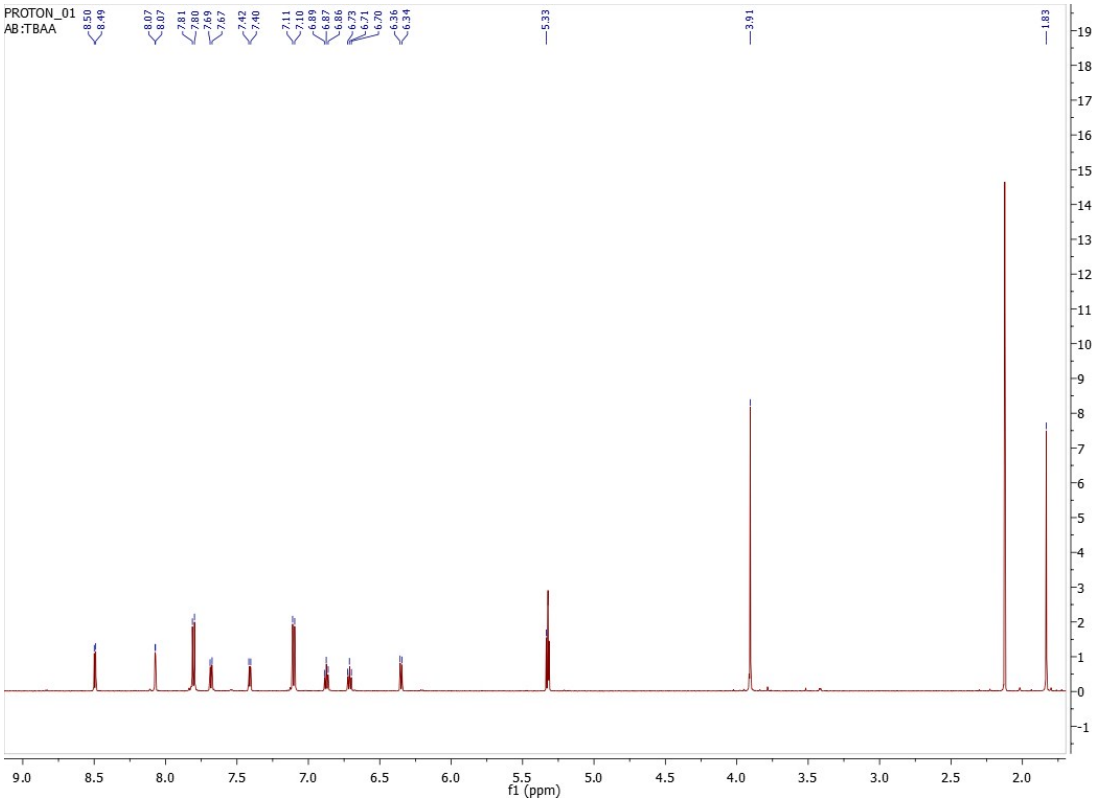

Figure S1.37. ^{1}H NMR spectrum of **Ir3**, recorded in CD_2Cl_2.

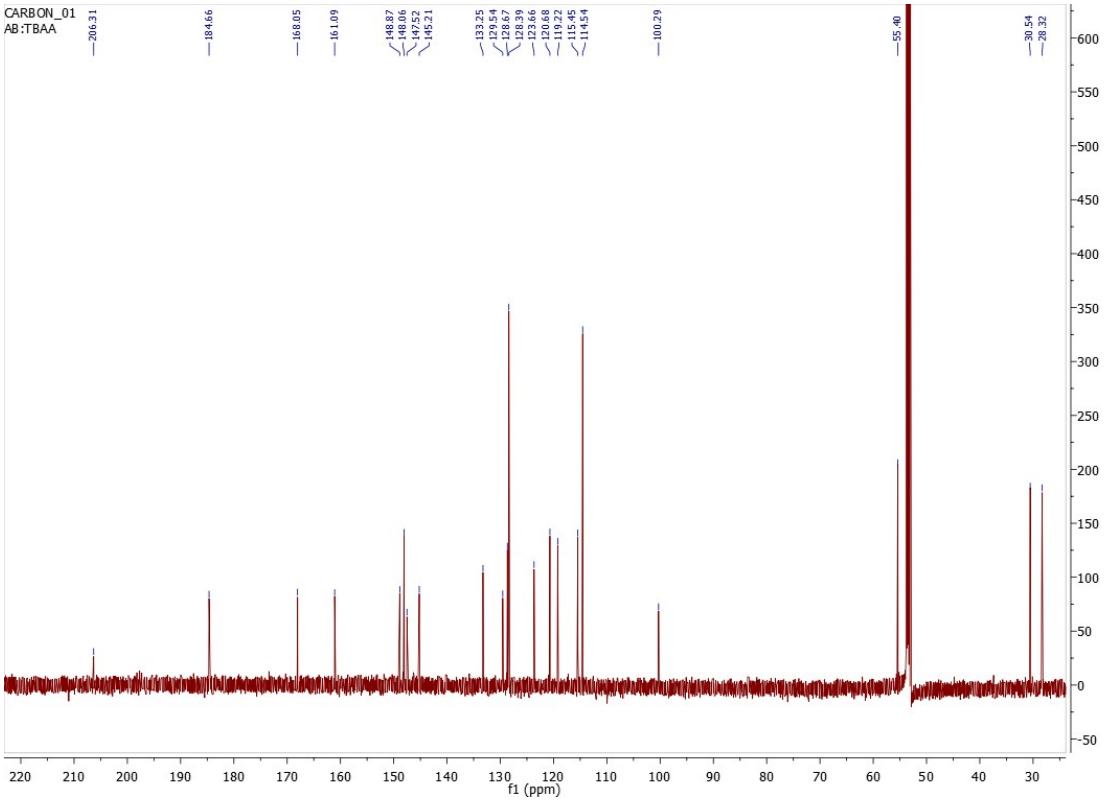

Figure S1.38. ^{13}C NMR spectrum of **Ir3**, recorded in CD_2Cl_2.

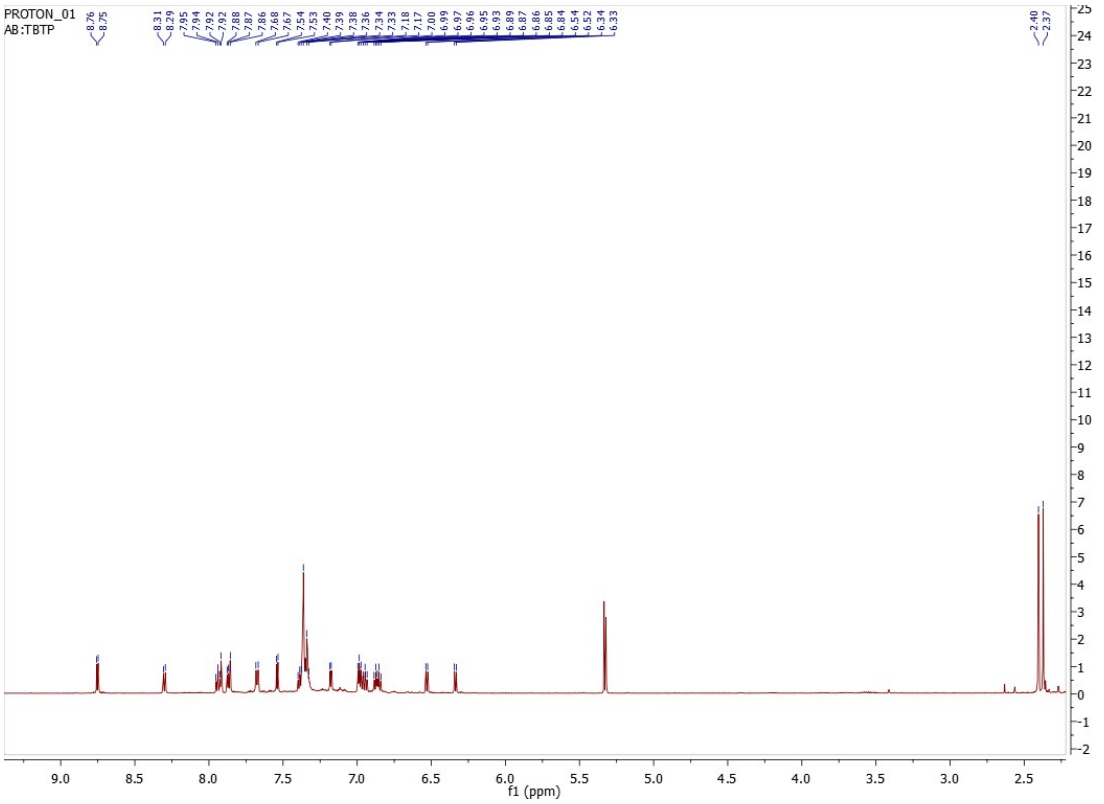

Figure S1.39. ^{1}H NMR spectrum of **Ir4**, recorded in CD_2Cl_2.

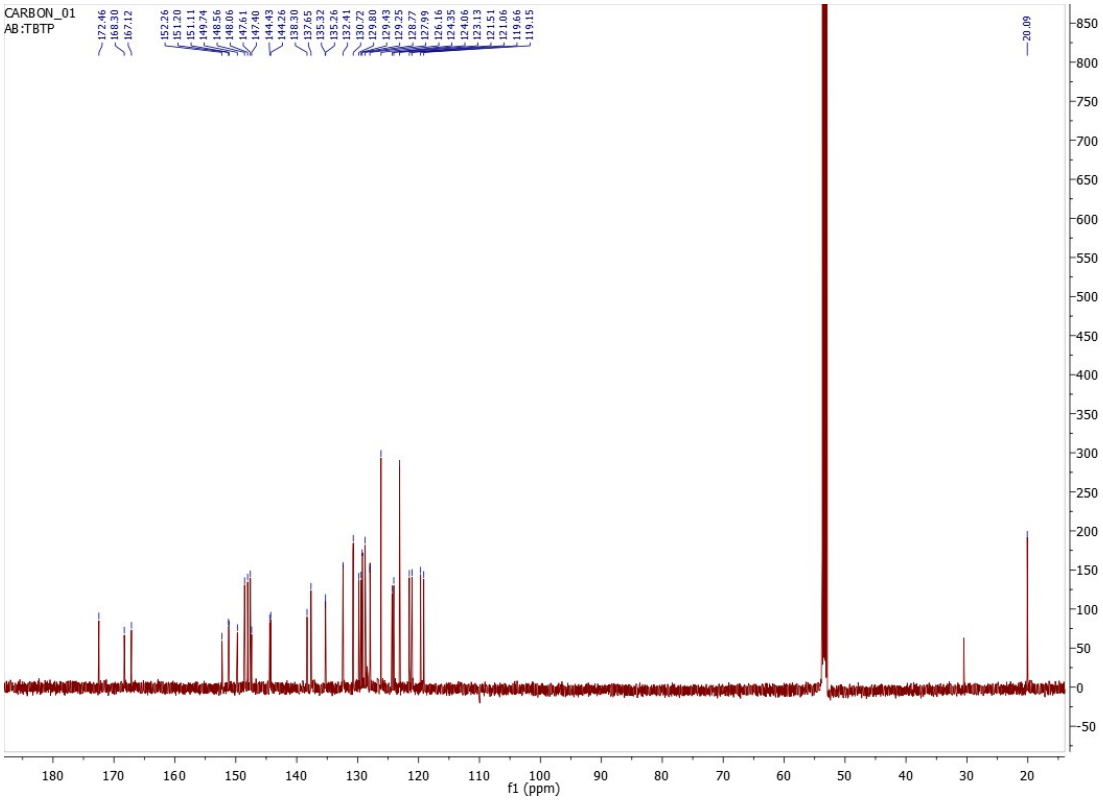

Figure S1.40. ^{13}C NMR spectrum of **Ir4**, recorded in CD_2Cl_2.

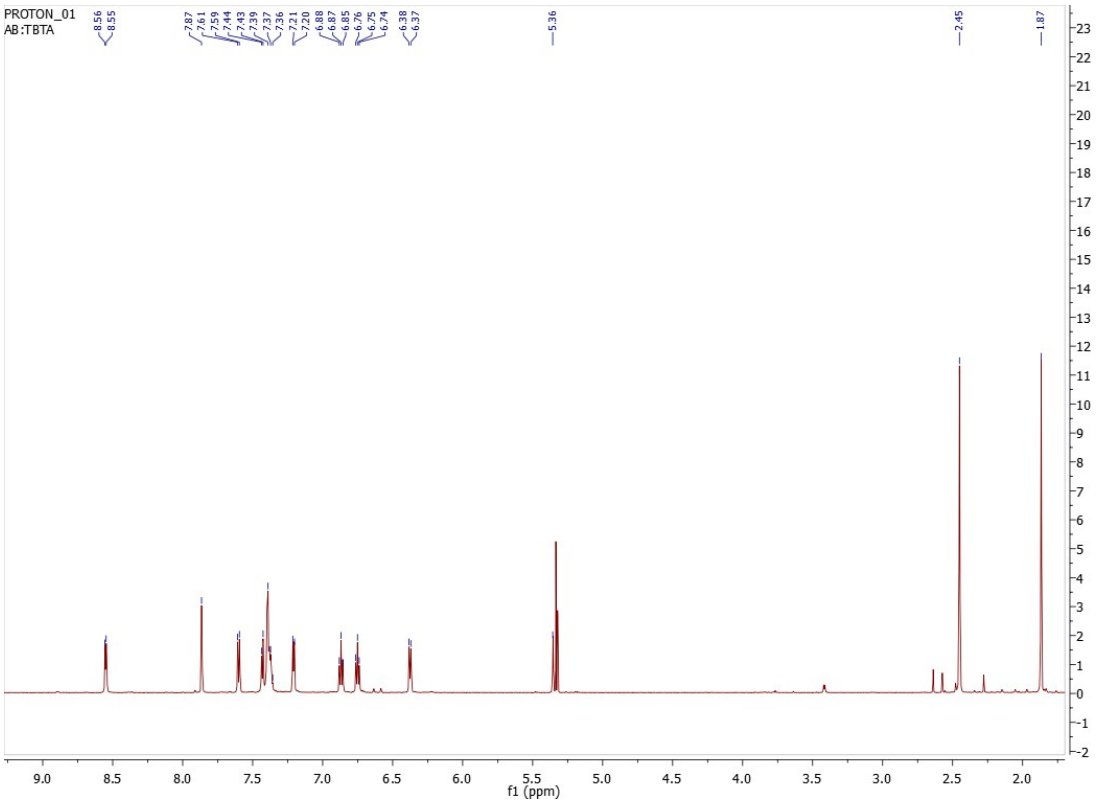

Figure S1.41. ^{1}H NMR spectrum of **Ir5**, recorded in CD_2Cl_2.

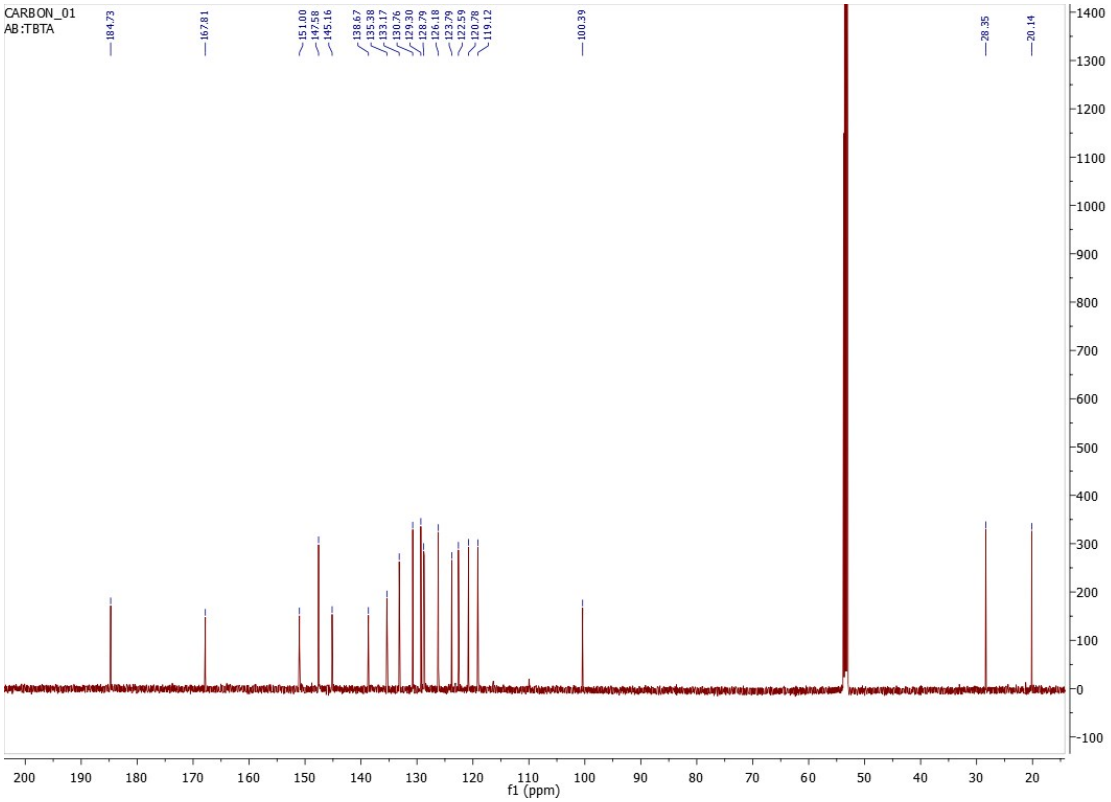

Figure S1.42. ^{13}C NMR spectrum of **Ir5**, recorded in CD_2Cl_2.

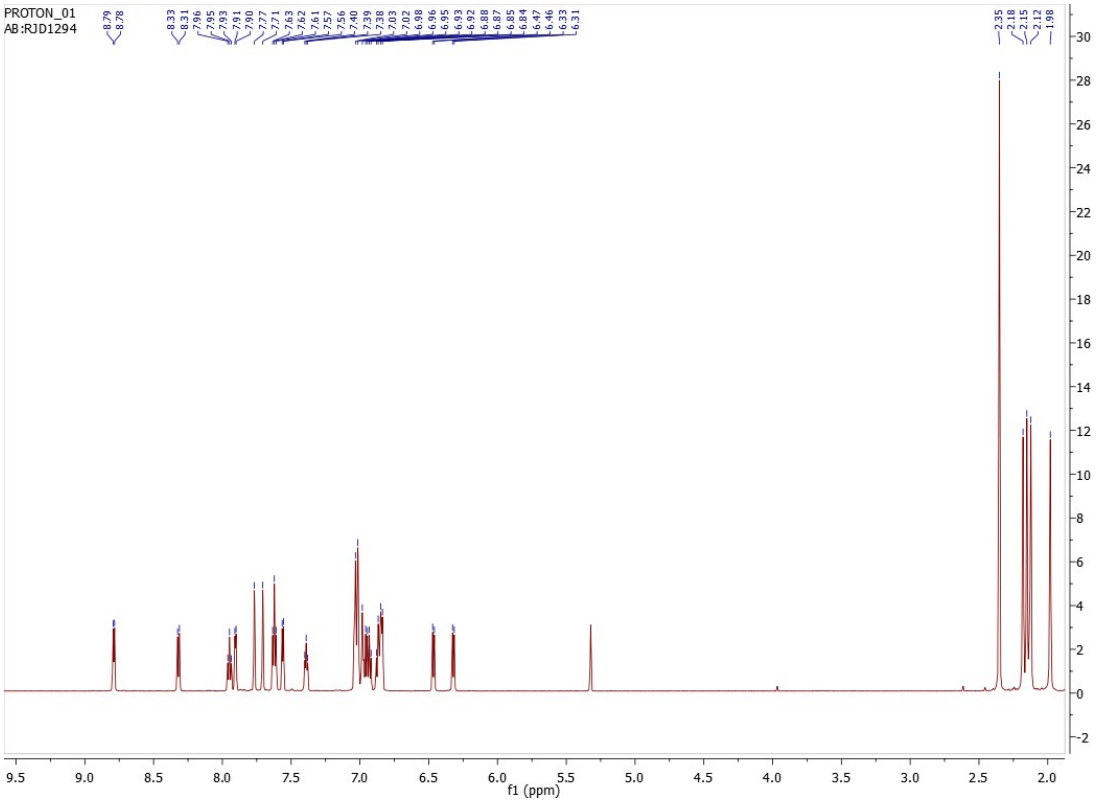

Figure S1.43. ^{1}H NMR spectrum of **Ir6**, recorded in CD_2Cl_2.

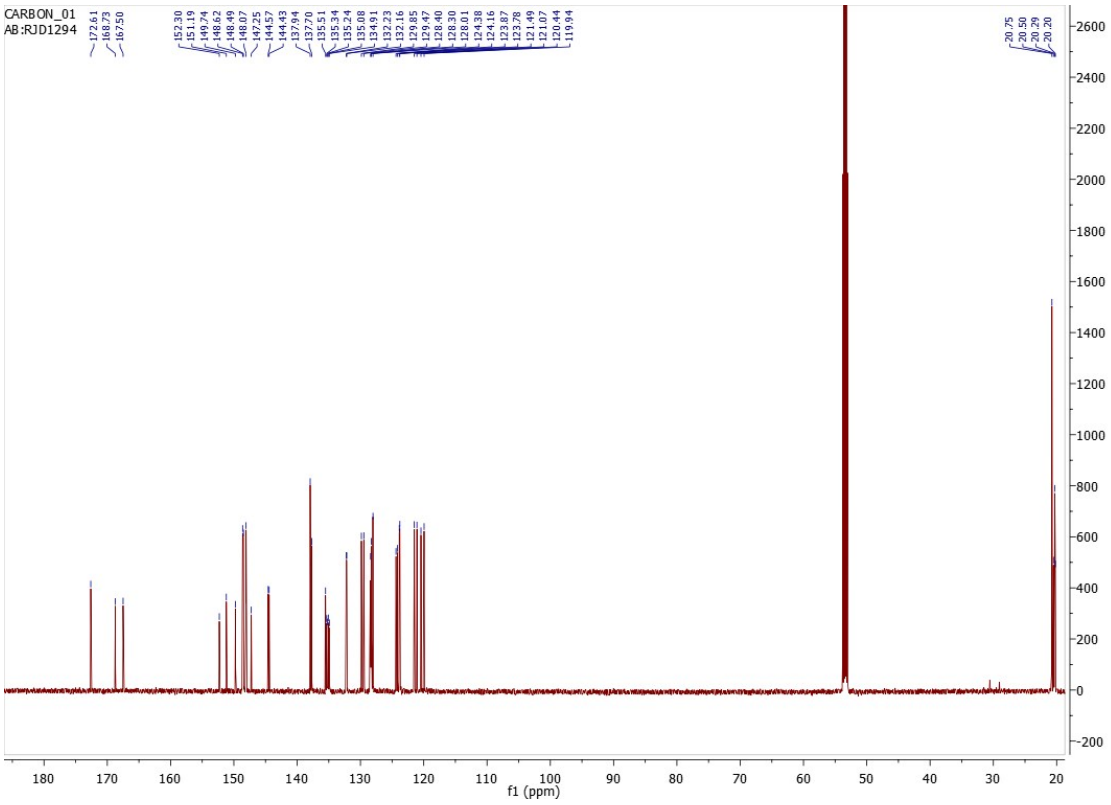

Figure S1.44. ^{13}C NMR spectrum of **Ir6**, recorded in CD_2Cl_2.

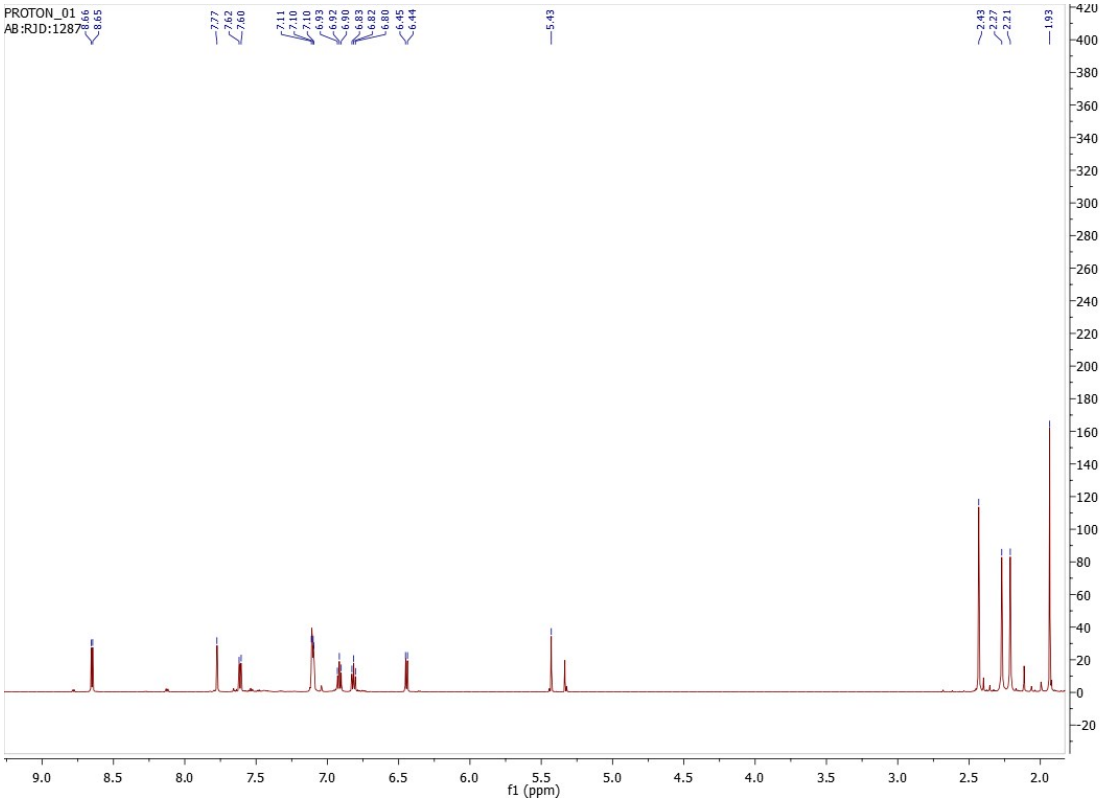

Figure S1.45. ^{1}H NMR spectrum of **Ir7**, recorded in CD_2Cl_2.

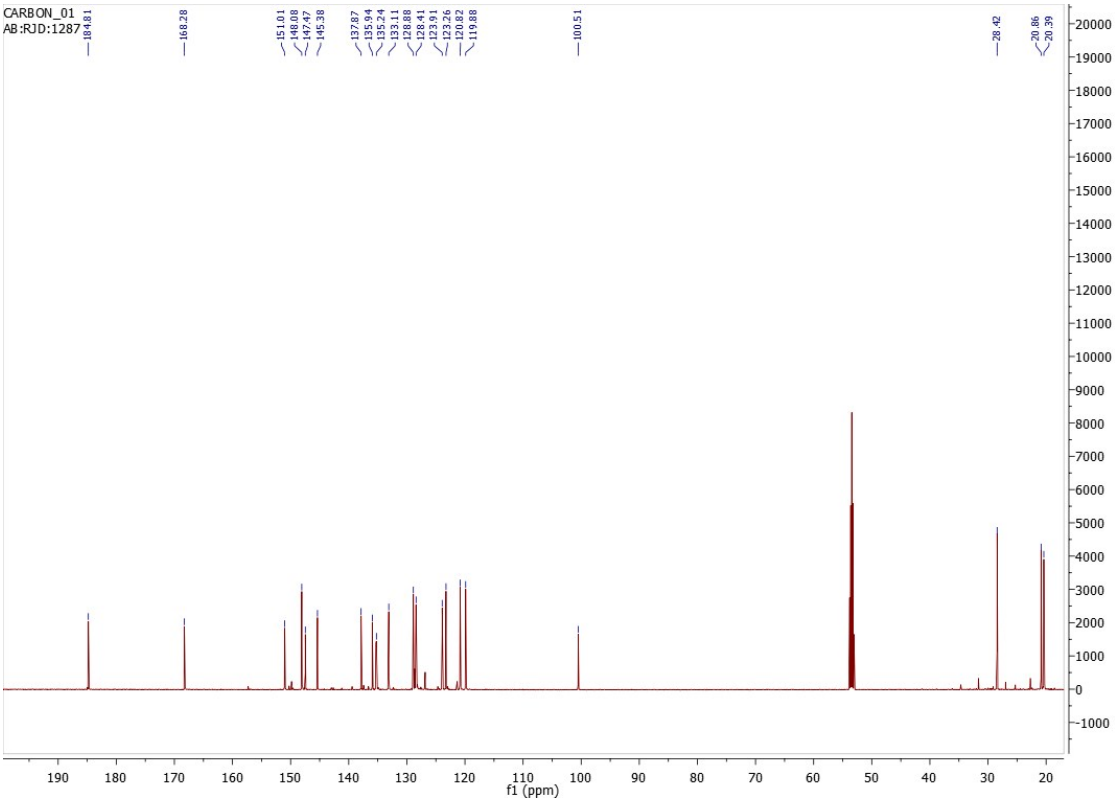

Figure S1.46. ^{13}C NMR spectrum of **Ir7**, recorded in CD_2Cl_2.

S2. Crystallographic data

Table S2.1. Crystal and Refinement Data for 4, $[7+H]^+[TFA]^-$ and $Ir1 \cdot 2CH_3OH$

Compound	4	$[7+H]^+[TFA]^-$	$Ir1 \cdot 2CH_3OH$
Code	15srv133	15srv059	15srv040
Empirical formula	$C_{19}H_{29}NO_3$	$C_{12}H_{16}N^+ \times F_3C_2O_2^-$	$C_{40}H_{28}IrN_3O_4$ x 2 CH_3OH
Formula weight	319.43	287.28	838.94
Temperature/K	120.0	120.0	120.0
Crystal system	orthorhombic	triclinic	triclinic
Space group	$P2_12_12_1$	P-1	P-1
a/Å	11.4540(8)	6.3784(3)	11.2366(4)
b/Å	20.9192(15)	9.4630(6)	12.7646(6)
c/Å	22.0993(16)	12.6226(6)	13.7741(6)
α/°	90.00	105.666(5)	102.782(4)
β/°	90.00	99.952(4)	108.667(4)
γ/°	90.00	106.901(5)	107.287(4)
Volume/Å^3	5295.2(7)	675.27(6)	1674.30(12)
Z	12	2	2
ρ_{calc}g/cm^3	1.202	1.413	1.664
μ/mm^{-1}	0.080	0.121	4.037
F(000)	2088.0	300.0	836.0
Crystal size/mm^3	0.25 × 0.24 × 0.16	0.42 × 0.23 × 0.15	0.22 × 0.13 × 0.04
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ =

			0.71073)
2Θ range for data collection/°	4 to 58	4.78 to 57.98	3.94 to 58
Index ranges	-15 ≤ h ≤ 15, -28 ≤ k ≤ 28, -30 ≤ l ≤ 30	-8 ≤ h ≤ 8, -12 ≤ k ≤ 12, -17 ≤ l ≤ 17	-15 ≤ h ≤ 15, -17 ≤ k ≤ 16, -17 ≤ l ≤ 18
Reflections collected	110590	8762	18500
Independent reflections	14082 [R_{int} = 0.0939, R_{sigma} = 0.0654]	3601 [R_{int} = 0.0271, R_{sigma} = 0.0360]	8900 [R_{int} = 0.0678, R_{sigma} = 0.1079]
Data/restraints/parameters	14082/0/643	3601/0/210	8900/0/447
Goodness-of-fit on F^2	1.029	1.035	1.029
Final R indexes [I>=2σ (I)]	R_1 = 0.0539, wR_2 = 0.1005	R_1 = 0.0463, wR_2 = 0.1105	R_1 = 0.0532, wR_2 = 0.1031
Final R indexes [all data]	R_1 = 0.0844, wR_2 = 0.1112	R_1 = 0.0600, wR_2 = 0.1202	R_1 = 0.0746, wR_2 = 0.1132
Largest diff. peak/hole / e $Å^{-3}$	0.26/-0.30	0.41/-0.40	1.96/-1.81

Table S2.2. Crystal and Refinement Data for Ir3·CH_2Cl_2, Ir5 and Ir7

Compound	Ir3·CH_2Cl_2	Ir5	Ir7
Code	15srv109	15srv101	15srv156
Empirical formula	$C_{41}H_{35}IrN_2O_4$ x CH_2Cl_2	$C_{41}H_{35}IrN_2O_2$	$C_{45}H_{43}IrN_2O_2$
Formula weight	896.84	779.91	836.01
Temperature/K	120.0	120.0	120.0
Crystal system	triclinic	triclinic	triclinic
Space group	P-1	P-1	P-1
a/Å	9.3800(6)	13.818(3)	12.5811(8)
b/Å	14.4932(9)	14.101(3)	13.1174(8)
c/Å	14.9593(9)	19.071(4)	13.6793(9)
α/°	69.040(10)	94.29(3)	112.105(2)
β/°	74.260(10)	98.66(3)	116.5260(10)
γ/°	71.550(10)	118.08(3)	90.323(2)
Volume/$Å^3$	1772.57(19)	3195.6(11)	1829.9(2)
Z	2	4	2
$\rho_{calc}g/cm^3$	1.680	1.621	1.517
μ/mm^{-1}	3.964	4.218	3.689
F(000)	892.0	1552.0	840.0
Crystal size/mm^3	0.08 × 0.08 × 0.04	0.16 × 0.16 × 0.14	0.27 × 0.04 × 0.02
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	2.96 to 58	3.32 to 58	3.42 to 55
Index ranges	-12 ≤ h ≤ 12, -19 ≤ k	-18 ≤ h ≤ 18, -19 ≤ k	-16 ≤ h ≤ 16, -17 ≤ k

	≤ 19, -20 ≤ l ≤ 20	≤ 19, -26 ≤ l ≤ 26	≤ 17, -17 ≤ l ≤ 17
Reflections collected	27616	52905	23849
Independent reflections	9378 [R_{int} = 0.0561, R_{sigma} = 0.0670]	16967 [R_{int} = 0.0464, R_{sigma} = 0.0491]	8380 [R_{int} = 0.0668, R_{sigma} = 0.0832]
Data/restraints/parameters	9378/3/473	16967/0/837	8380/0/459
Goodness-of-fit on F^2	1.035	1.050	1.078
Final R indexes [I>=2σ (I)]	R_1 = 0.0377, wR_2 = 0.0738	R_1 = 0.0380, wR_2 = 0.0842	R_1 = 0.0497, wR_2 = 0.1066
Final R indexes [all data]	R_1 = 0.0556, wR_2 = 0.0790	R_1 = 0.0533, wR_2 = 0.0912	R_1 = 0.0731, wR_2 = 0.1146
Largest diff. peak/hole / e $Å^{-3}$	1.86/-1.44	2.07/-1.33	2.23/-2.30

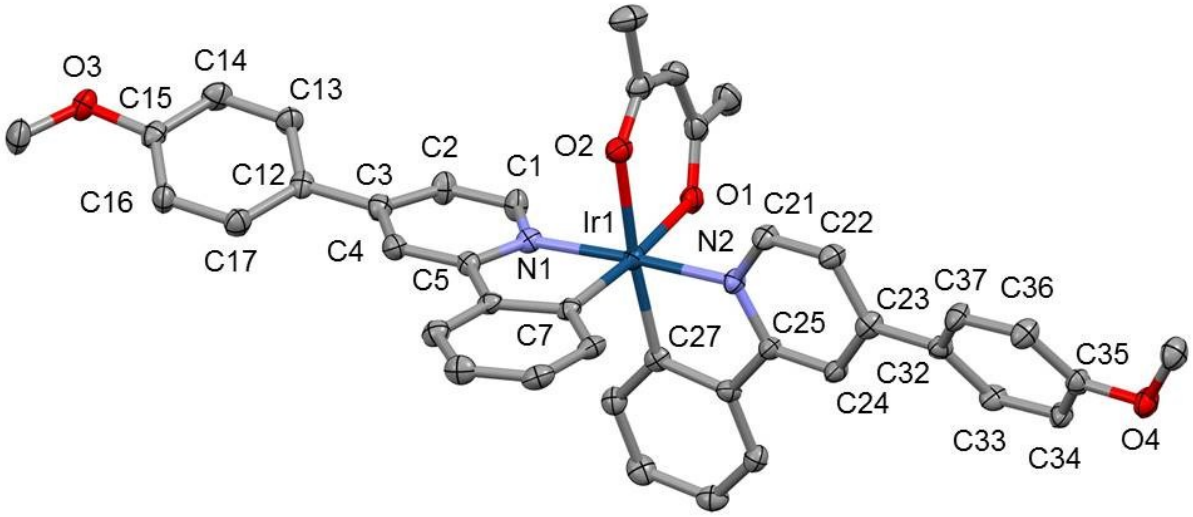

Figure S2.1. Crystal structure of **Ir3**; hydrogen atoms and solvent molecules have been removed for clarity. Thermal ellipsoids are displayed at 50 % probability.

Table S2.3. Selected bond lengths for **4**.

Atom	Atom	Length/Å		Atom	Atom	Length/Å		Atom	Atom	Length/Å
O1	C6	1.336(2)		O1A	C7A	1.478(2)		O2B	C6B	1.211(2)
O1	C7	1.485(2)		O2A	C6A	1.225(2)		O3B	C3B	1.434(2)
O2	C6	1.220(2)		O3A	C3A	1.426(2)		N1B	C1B	1.456(2)
O3	C3	1.428(2)		N1A	C1A	1.474(2)		N1B	C5B	1.466(2)
N1	C1	1.463(2)		N1A	C5A	1.467(2)		N1B	C6B	1.356(2)
N1	C5	1.462(2)		N1A	C6A	1.346(2)		C1B	C2B	1.522(2)
N1	C6	1.353(2)		C1A	C2A	1.523(2)		C2B	C3B	1.539(2)
C1	C2	1.525(2)		C2A	C3A	1.529(2)		C3B	C4B	1.533(2)
C2	C3	1.533(3)		C3A	C4A	1.543(2)		C3B	C11B	1.545(2)
C3	C4	1.531(3)		C3A	C11A	1.550(2)		C4B	C5B	1.518(2)
C3	C11	1.550(2)		C4A	C5A	1.525(2)		C7B	C8B	1.514(3)
C4	C5	1.520(3)		C7A	C8A	1.512(3)		C7B	C9B	1.512(3)
C7	C8	1.519(3)		C7A	C9A	1.523(3)		C7B	C10B	1.519(3)
C7	C9	1.510(3)		C7A	C10A	1.514(3)		C11B	C12B	1.418(2)
C7	C10	1.514(3)		C11A	C12A	1.416(2)		C11B	C16B	1.415(2)
C11	C12	1.418(3)		C11A	C16A	1.413(2)		C12B	C13B	1.392(3)
C11	C16	1.406(3)		C12A	C13A	1.396(2)		C12B	C17B	1.522(2)
C12	C13	1.397(3)		C12A	C17A	1.521(2)		C13B	C14B	1.385(3)
C12	C17	1.517(3)		C13A	C14A	1.377(3)		C14B	C15B	1.376(3)
C13	C14	1.381(3)		C14A	C15A	1.382(3)		C14B	C18B	1.507(3)
C14	C15	1.373(3)		C14A	C18A	1.507(3)		C15B	C16B	1.393(3)
C14	C18	1.514(3)		C15A	C16A	1.394(3)		C16B	C19B	1.518(3)

C15	C16	1.396(3)		C16A	C19A	1.518(3)				
C16	C19	1.523(3)		O1B	C6B	1.358(2)				
O1A	C6A	1.350(2)		O1B	C7B	1.474(2)				

Table S2.4. Selected bond angles for **4**.

Atom	**Atom**	**Atom**	**Angle/°**		**Atom**	**Atom**	**Atom**	**Angle/°**
C6	O1	C7	120.11(14)		O1A	C7A	C10A	111.71(15)
C5	N1	C1	115.12(14)		C8A	C7A	C9A	109.97(16)
C6	N1	C1	124.24(15)		C8A	C7A	C10A	112.53(17)
C6	N1	C5	117.96(14)		C10A	C7A	C9A	110.61(17)
N1	C1	C2	111.38(14)		C12A	C11A	C3A	119.26(15)
C1	C2	C3	112.65(15)		C16A	C11A	C3A	122.91(16)
O3	C3	C2	110.38(15)		C16A	C11A	C12A	117.80(16)
O3	C3	C4	106.32(16)		C11A	C12A	C17A	125.90(16)
O3	C3	C11	105.16(14)		C13A	C12A	C11A	119.20(16)
C2	C3	C11	111.53(14)		C13A	C12A	C17A	114.74(16)
C4	C3	C2	109.07(15)		C14A	C13A	C12A	123.19(17)
C4	C3	C11	114.18(15)		C13A	C14A	C15A	116.85(17)
C5	C4	C3	111.92(16)		C13A	C14A	C18A	121.53(17)
N1	C5	C4	110.09(15)		C15A	C14A	C18A	121.60(17)
O1	C6	N1	111.94(15)		C14A	C15A	C16A	122.82(17)
O2	C6	O1	123.99(16)		C11A	C16A	C19A	125.67(17)
O2	C6	N1	124.01(16)		C15A	C16A	C11A	119.61(17)
O1	C7	C8	110.20(16)		C15A	C16A	C19A	114.70(16)
O1	C7	C9	110.54(15)		C6B	O1B	C7B	120.70(14)
O1	C7	C10	101.91(15)		C1B	N1B	C5B	114.00(14)
C9	C7	C8	112.47(17)		C6B	N1B	C1B	125.33(14)
C9	C7	C10	110.52(18)		C6B	N1B	C5B	119.48(15)

C10	C7	C8	110.71(19)		N1B	C1B	C2B	109.36(14)
C12	C11	C3	120.08(16)		C1B	C2B	C3B	111.31(15)
C16	C11	C3	122.40(16)		O3B	C3B	C2B	105.49(14)
C16	C11	C12	117.52(16)		O3B	C3B	C4B	105.48(14)
C11	C12	C17	126.20(17)		O3B	C3B	C11B	110.90(14)
C13	C12	C11	119.26(17)		C2B	C3B	C11B	113.72(14)
C13	C12	C17	114.51(17)		C4B	C3B	C2B	109.28(14)
C14	C13	C12	123.03(18)		C4B	C3B	C11B	111.49(14)
C13	C14	C18	121.25(18)		C5B	C4B	C3B	112.00(15)
C15	C14	C13	116.80(17)		N1B	C5B	C4B	111.21(15)
C15	C14	C18	121.93(18)		O2B	C6B	O1B	124.43(16)
C14	C15	C16	122.95(18)		O2B	C6B	N1B	125.24(17)
C11	C16	C19	126.65(17)		N1B	C6B	O1B	110.33(15)
C15	C16	C11	119.83(17)		O1B	C7B	C8B	110.03(15)
C15	C16	C19	113.49(16)		O1B	C7B	C9B	111.56(15)
C6A	O1A	C7A	121.71(14)		O1B	C7B	C10B	102.10(15)
C5A	N1A	C1A	114.96(14)		C8B	C7B	C10B	110.31(17)
C6A	N1A	C1A	119.09(14)		C9B	C7B	C8B	111.91(17)
C6A	N1A	C5A	124.19(14)		C9B	C7B	C10B	110.53(18)
N1A	C1A	C2A	111.09(15)		C12B	C11B	C3B	120.68(16)
C1A	C2A	C3A	112.06(15)		C16B	C11B	C3B	121.97(15)
O3A	C3A	C2A	106.20(14)		C16B	C11B	C12B	117.33(16)
O3A	C3A	C4A	105.49(14)		C11B	C12B	C17B	126.13(16)

Table S2.4 continued. Selected bond angles for **4**.

Atom	Atom	Atom	Angle/°		Atom	Atom	Atom	Angle/°
O3A	C3A	C11A	109.87(14)		C13B	C12B	C11B	119.69(17)
C2A	C3A	C4A	108.29(14)		C13B	C12B	C17B	114.06(16)
C2A	C3A	C11A	111.01(14)		C14B	C13B	C12B	122.93(18)
C4A	C3A	C11A	115.46(14)		C13B	C14B	C18B	121.58(18)
C5A	C4A	C3A	110.50(15)		C15B	C14B	C13B	116.66(17)
N1A	C5A	C4A	109.38(14)		C15B	C14B	C18B	121.73(18)
O2A	C6A	O1A	124.09(16)		C14B	C15B	C16B	123.20(18)
O2A	C6A	N1A	124.60(16)		C11B	C16B	C19B	126.17(17)
N1A	C6A	O1A	111.31(15)		C15B	C16B	C11B	119.69(17)
O1A	C7A	C8A	109.67(15)		C15B	C16B	C19B	114.09(16)
O1A	C7A	C9A	101.84(14)					

Table S2.5. Selected bond lengths for [**7**+H]$^+$[TFA]$^-$.

Atom	Atom	Length/Å		Atom	Atom	Length/Å		Atom	Atom	Length/Å
F1	C22	1.3365(17)		N1	C5	1.4938(18)		C6	C11	1.4004(19)
F2	C22	1.3382(17)		C1	C2	1.501(2)		C7	C8	1.400(2)
F3	C22	1.3420(18)		C2	C3	1.438(2)		C7	C12	1.507(2)
O1	C21	1.2444(17)		C3	C4	1.393(2)		C8	C9	1.390(2)

O2	C21	1.2433(17)		C3	C6	1.4949(18)		C9	C10	1.386(2)
C21	C22	1.557(2)		C4	C5	1.492(2)		C10	C11	1.393(2)
N1	C1	1.4925(18)		C6	C7	1.4067(19)				

Table S2.6. Selected bond angles for [**7**+H]$^{+}$[TFA]$^{-}$.

Table 5 Bond Angles for 15srv059.								
Atom	**Atom**	**Atom**	**Angle/°**		**Atom**	**Atom**	**Atom**	**Angle/°**
O1	C21	C22	113.45(12)		C4	C3	C6	120.19(12)
O2	C21	O1	130.31(13)		C3	C4	C5	120.98(13)
O2	C21	C22	116.21(12)		C4	C5	N1	110.90(11)
F1	C22	F2	106.38(12)		C7	C6	C3	121.25(12)
F1	C22	F3	106.10(12)		C11	C6	C3	119.43(12)
F1	C22	C21	113.16(12)		C11	C6	C7	119.32(12)
F2	C22	F3	106.80(13)		C6	C7	C12	120.75(12)
F2	C22	C21	113.21(12)		C8	C7	C6	118.55(13)
F3	C22	C21	110.71(12)		C8	C7	C12	120.67(13)
C1	N1	C5	111.87(11)		C9	C8	C7	121.58(14)
N1	C1	C2	111.29(12)		C10	C9	C8	119.84(13)
C3	C2	C1	117.59(13)		C9	C10	C11	119.39(14)
C2	C3	C6	118.68(12)		C10	C11	C6	121.29(14)
C4	C3	C2	121.13(13)					

Table S2.7. Selected bond lengths for **Ir1**·2CH_3OH.

Atom	**Atom**	**Length/Å**		**Atom**	**Atom**	**Length/Å**		**Atom**	**Atom**	**Length/Å**
Ir1	O1	2.172(4)		C6	C7	1.422(8)		C27	C28	1.373(9)

Ir1	N1	2.033(5)		C6	C11	1.402(8)		C28	C29	1.393(8)
Ir1	N2	2.031(5)		C7	C8	1.391(8)		C29	C30	1.387(9)
Ir1	N3	2.153(5)		C8	C9	1.389(8)		C30	C31	1.393(9)
Ir1	C7	2.006(6)		C9	C10	1.397(8)		C32	C33	1.397(9)
Ir1	C27	2.020(6)		C10	C11	1.369(8)		C32	C37	1.411(8)
O1	C46	1.272(7)		C12	C13	1.388(9)		C33	C34	1.391(9)
O2	C46	1.238(7)		C12	C17	1.394(8)		C34	C35	1.383(8)
N1	C1	1.342(8)		C13	C14	1.393(8)		C35	C36	1.400(10)
N1	C5	1.394(7)		C14	C15	1.372(9)		C36	C37	1.395(8)
N2	C21	1.335(8)		C15	C16	1.387(9)		C41	C42	1.366(9)
N2	C25	1.382(7)		C16	C17	1.391(8)		C41	C46	1.525(8)
N3	C41	1.347(7)		C21	C22	1.383(8)		C42	C43	1.396(9)
N3	C45	1.349(7)		C22	C23	1.392(8)		C43	C44	1.371(10)
C1	C2	1.367(8)		C23	C24	1.389(9)		C44	C45	1.389(9)
C2	C3	1.400(8)		C23	C32	1.487(8)		O3	C1S	1.388(10)
C3	C4	1.393(8)		C24	C25	1.386(8)		C2SA	O2S	1.350(9)
C3	C12	1.502(8)		C25	C26	1.477(8)				
C4	C5	1.381(8)		C26	C27	1.427(8)				
C5	C6	1.454(8)		C26	C31	1.390(8)				

Table S2.8. Selected bond angles for **Ir1**·2CH_3OH.

Atom	Atom	Atom	Angle/°		Atom	Atom	Atom	Angle/°
N1	Ir1	O1	94.53(18)		C13	C12	C17	119.3(6)
N1	Ir1	N3	86.38(18)		C17	C12	C3	120.6(6)
N2	Ir1	O1	88.66(17)		C12	C13	C14	120.2(6)
N2	Ir1	N1	176.6(2)		C15	C14	C13	120.6(6)
N2	Ir1	N3	95.66(18)		C14	C15	C16	119.4(6)
N3	Ir1	O1	75.97(17)		C15	C16	C17	120.8(6)
C7	Ir1	O1	174.70(19)		C16	C17	C12	119.6(6)
C7	Ir1	N1	80.9(2)		N2	C21	C22	123.8(5)
C7	Ir1	N2	96.0(2)		C21	C22	C23	119.2(6)
C7	Ir1	N3	101.0(2)		C22	C23	C32	119.5(6)
C7	Ir1	C27	85.8(2)		C24	C23	C22	117.5(6)
C27	Ir1	O1	97.52(19)		C24	C23	C32	123.0(5)
C27	Ir1	N1	97.7(2)		C25	C24	C23	121.3(5)
C27	Ir1	N2	80.6(2)		N2	C25	C24	120.4(6)
C27	Ir1	N3	172.63(19)		N2	C25	C26	112.7(5)
C46	O1	Ir1	117.1(4)		C24	C25	C26	126.9(5)
C1	N1	Ir1	125.8(4)		C27	C26	C25	115.2(5)
C1	N1	C5	117.8(5)		C31	C26	C25	123.2(5)
C5	N1	Ir1	116.2(4)		C31	C26	C27	121.6(6)
C21	N2	Ir1	125.0(4)		C26	C27	Ir1	114.3(4)
C21	N2	C25	117.9(5)		C28	C27	Ir1	128.6(4)
C25	N2	Ir1	117.1(4)		C28	C27	C26	117.1(5)
C41	N3	Ir1	115.4(4)		C27	C28	C29	121.9(6)
C41	N3	C45	118.8(5)		C30	C29	C28	120.5(6)
C45	N3	Ir1	125.7(4)		C29	C30	C31	119.6(6)
N1	C1	C2	123.3(6)		C26	C31	C30	119.4(6)
C1	C2	C3	120.4(6)		C33	C32	C23	121.1(5)
C2	C3	C12	120.6(6)		C33	C32	C37	117.9(6)
C4	C3	C2	116.6(5)		C37	C32	C23	121.0(6)
C4	C3	C12	122.7(5)		C34	C33	C32	122.4(6)
C5	C4	C3	121.6(5)		C35	C34	C33	119.5(6)
N1	C5	C6	112.7(5)		C34	C35	C36	119.2(6)
C4	C5	N1	120.2(5)		C37	C36	C35	121.4(6)
C4	C5	C6	127.0(5)		C36	C37	C32	119.5(6)
C7	C6	C5	116.2(5)		N3	C41	C42	121.8(6)
C11	C6	C5	123.7(5)		N3	C41	C46	115.2(5)
C11	C6	C7	120.2(6)		C42	C41	C46	123.0(6)
C6	C7	Ir1	114.0(4)		C41	C42	C43	119.7(6)
C8	C7	Ir1	128.4(4)		C44	C43	C42	118.7(7)
C8	C7	C6	117.6(5)		C43	C44	C45	119.0(6)
C9	C8	C7	121.7(6)		N3	C45	C44	121.9(6)
C8	C9	C10	119.9(6)		O1	C46	C41	116.3(5)
C11	C10	C9	119.8(6)		O2	C46	O1	125.8(6)
C10	C11	C6	120.8(6)		O2	C46	C41	118.0(6)
C13	C12	C3	120.1(6)					

Table S2.9. Selected bond lengths for **Ir3**·CH_2Cl_2.

Atom	Atom	Length/Å		Atom	Atom	Length/Å		Atom	Atom	Length/Å
Ir1	O1	2.146(3)		C4	C5	1.391(6)		C26	C27	1.423(5)
Ir1	O2	2.148(3)		C5	C6	1.463(6)		C26	C31	1.390(6)
Ir1	N1	2.044(3)		C6	C7	1.411(5)		C27	C28	1.398(5)
Ir1	N2	2.031(3)		C6	C11	1.397(6)		C28	C29	1.398(6)
Ir1	C7	1.998(4)		C7	C8	1.398(6)		C29	C30	1.388(6)
Ir1	C27	1.995(4)		C8	C9	1.392(6)		C30	C31	1.379(6)
O1	C39	1.261(5)		C9	C10	1.391(6)		C32	C33	1.393(6)
O2	C41	1.261(5)		C10	C11	1.380(6)		C32	C37	1.389(6)
O3	C15	1.374(5)		C12	C13	1.406(6)		C33	C34	1.381(6)
O3	C18	1.434(5)		C12	C17	1.391(6)		C34	C35	1.395(6)
O4	C35	1.370(5)		C13	C14	1.377(6)		C35	C36	1.386(6)
O4	C38	1.439(5)		C14	C15	1.382(6)		C36	C37	1.386(6)
N1	C1	1.339(5)		C15	C16	1.390(6)		C39	C40	1.401(6)
N1	C5	1.362(5)		C16	C17	1.390(6)		C39	C43	1.510(6)
N2	C21	1.343(5)		C21	C22	1.381(6)		C40	C41	1.399(6)
N2	C25	1.369(5)		C22	C23	1.397(6)		C41	C42	1.512(6)
C1	C2	1.379(6)		C23	C24	1.394(6)		Cl1	C1S	1.743(4)
C2	C3	1.403(6)		C23	C32	1.487(6)		Cl2	C1S	1.757(4)
C3	C4	1.400(6)		C24	C25	1.388(5)		Cl3	C1S	1.735(4)
C3	C12	1.474(6)		C25	C26	1.469(5)				

Table S2.10. Selected bond angles for **Ir3**·CH_2Cl_2.

Atom	Atom	Atom	Angle/°		Atom	Atom	Atom	Angle/°
O1	Ir1	O2	88.64(11)		C14	C13	C12	121.4(4)
N1	Ir1	O1	92.69(12)		C13	C14	C15	120.3(4)
N1	Ir1	O2	87.15(12)		O3	C15	C14	115.8(4)
N2	Ir1	O1	91.14(12)		O3	C15	C16	124.2(4)
N2	Ir1	O2	93.84(12)		C14	C15	C16	120.0(4)
N2	Ir1	N1	176.06(14)		C17	C16	C15	119.1(4)
C7	Ir1	O1	173.70(14)		C16	C17	C12	122.1(4)
C7	Ir1	O2	90.31(14)		N2	C21	C22	123.0(4)
C7	Ir1	N1	81.05(15)		C21	C22	C23	119.9(4)
C7	Ir1	N2	95.13(15)		C22	C23	C32	120.6(4)
C27	Ir1	O1	90.83(13)		C24	C23	C22	116.9(4)
C27	Ir1	O2	174.29(14)		C24	C23	C32	122.5(4)
C27	Ir1	N1	98.55(15)		C25	C24	C23	121.2(4)
C27	Ir1	N2	80.48(14)		N2	C25	C24	120.7(4)
C27	Ir1	C7	90.83(16)		N2	C25	C26	112.5(3)
C39	O1	Ir1	123.9(3)		C24	C25	C26	126.8(4)
C41	O2	Ir1	124.9(3)		C27	C26	C25	115.2(3)
C15	O3	C18	117.2(3)		C31	C26	C25	123.5(4)
C35	O4	C38	116.3(3)		C31	C26	C27	121.2(4)
C1	N1	Ir1	125.5(3)		C26	C27	Ir1	114.5(3)
C1	N1	C5	119.3(3)		C28	C27	Ir1	128.6(3)
C5	N1	Ir1	115.1(3)		C28	C27	C26	116.8(4)
C21	N2	Ir1	124.4(3)		C27	C28	C29	121.2(4)
C21	N2	C25	118.3(3)		C30	C29	C28	120.8(4)
C25	N2	Ir1	117.1(3)		C31	C30	C29	119.1(4)
N1	C1	C2	122.8(4)		C30	C31	C26	120.7(4)
C1	C2	C3	120.1(4)		C33	C32	C23	121.9(4)
C2	C3	C12	121.9(4)		C37	C32	C23	120.4(4)
C4	C3	C2	116.0(4)		C37	C32	C33	117.7(4)
C4	C3	C12	122.1(4)		C34	C33	C32	121.5(4)
C5	C4	C3	122.0(4)		C33	C34	C35	119.9(4)
N1	C5	C4	119.8(4)		O4	C35	C34	116.1(4)
N1	C5	C6	114.1(3)		O4	C35	C36	124.5(4)
C4	C5	C6	126.1(4)		C36	C35	C34	119.4(4)
C7	C6	C5	115.5(4)		C35	C36	C37	119.8(4)
C11	C6	C5	122.8(4)		C36	C37	C32	121.6(4)
C11	C6	C7	121.7(4)		O1	C39	C40	127.4(4)
C6	C7	Ir1	114.0(3)		O1	C39	C43	114.1(4)
C8	C7	Ir1	129.0(3)		C40	C39	C43	118.4(4)
C8	C7	C6	117.0(4)		C41	C40	C39	128.0(4)
C9	C8	C7	121.4(4)		O2	C41	C40	126.6(4)
C10	C9	C8	120.2(4)		O2	C41	C42	115.5(4)
C11	C10	C9	120.0(4)		C40	C41	C42	118.0(4)
C10	C11	C6	119.6(4)		Cl1	C1S	Cl2	106.1(3)
C13	C12	C3	121.1(4)		Cl3	C1S	Cl1	115.8(4)

Table S2.10 continued. Selected bond angles for **Ir3**·CH_2Cl_2.

Atom	Atom	Atom	Angle/°		Atom	Atom	Atom	Angle/°
C17	C12	C3	121.7(4)		Cl3	C1S	Cl2	35.23(19)
C17	C12	C13	117.1(4)					

Table S2.11. Selected bond lengths for **Ir5**.

Atom	Atom	Length/Å		Atom	Atom	Length/Å		Atom	Atom	Length/Å
Ir1	O1	2.141(3)		C26	C27	1.422(6)				
Ir1	O2	2.149(3)		C26	C31	1.393(6)		C6A	C25A	1.458(6)
Ir1	N1	2.034(4)		C27	C28	1.408(6)		C7A	C8A	1.406(6)
Ir1	N2	2.034(4)		C28	C29	1.396(7)		C8A	C9A	1.381(6)
Ir1	C7	1.992(4)		C29	C30	1.377(7)		C9A	C10A	1.380(7)
Ir1	C27	1.989(4)		C30	C31	1.385(7)		C10A	C11A	1.389(6)
O1	C39	1.261(5)		C32	C33	1.395(6)		C12A	C13A	1.400(6)
O2	C41	1.270(5)		C32	C37	1.401(7)		C12A	C17A	1.405(6)
N1	C1	1.342(5)		C33	C34	1.397(7)		C13A	C14A	1.402(6)
N1	C5	1.363(5)		C33	C38	1.484(7)		C13A	C18A	1.508(6)
N2	C21	1.342(5)		C34	C35	1.366(8)		C14A	C15A	1.367(7)
N2	C25	1.362(5)		C35	C36	1.387(8)		C15A	C16A	1.381(7)
C1	C2	1.353(7)		C36	C37	1.377(7)		C16A	C17A	1.383(7)
C2	C3	1.397(7)		C39	C40	1.402(6)		C21A	C22A	1.364(6)
C3	C4	1.390(6)		C39	C43	1.519(6)		C22A	C23A	1.409(6)
C3	C12	1.481(7)		C40	C41	1.379(7)		C23A	C24A	1.397(6)
C4	C5	1.396(6)		C41	C42	1.519(6)		C23A	C32A	1.494(6)
C5	C6	1.468(6)		Ir1A	O1A	2.150(3)		C24A	C25A	1.396(6)
C6	C7	1.414(6)		Ir1A	O2A	2.151(3)		C26A	C27A	1.406(6)
C6	C11	1.394(6)		Ir1A	N1A	2.031(4)		C26A	C31A	1.399(6)
C7	C8	1.400(6)		Ir1A	N2A	2.035(4)		C27A	C28A	1.390(6)
C8	C9	1.385(6)		Ir1A	C7A	1.998(4)		C28A	C29A	1.389(6)
C9	C10	1.387(7)		Ir1A	C27A	2.004(4)		C29A	C30A	1.384(7)
C10	C11	1.382(6)		O1A	C39A	1.263(5)		C30A	C31A	1.381(6)
C12	C13	1.378(7)		O2A	C41A	1.262(5)		C32A	C33A	1.399(6)
C12	C17	1.444(7)		N1A	C1A	1.335(5)		C32A	C37A	1.392(6)
C13	C14	1.440(7)		N1A	C5A	1.364(5)		C33A	C34A	1.394(7)
C13	C18	1.469(7)		N2A	C21A	1.354(5)		C33A	C38A	1.503(7)
C14	C15	1.333(8)		N2A	C25A	1.367(5)		C34A	C35A	1.370(8)
C15	C16	1.418(8)		C1A	C2A	1.383(6)		C35A	C36A	1.384(8)
C16	C17	1.330(7)		C2A	C3A	1.404(6)		C36A	C37A	1.377(7)
C21	C22	1.381(6)		C3A	C4A	1.386(6)		C39A	C40A	1.402(7)
C22	C23	1.403(6)		C3A	C12A	1.490(6)		C39A	C43A	1.508(7)
C23	C24	1.379(6)		C4A	C5A	1.402(6)		C40A	C41A	1.394(7)
C23	C32	1.482(6)		C5A	C26A	1.470(6)		C41A	C42A	1.510(6)
C24	C25	1.392(6)		C6A	C7A	1.414(6)				
C25	C26	1.466(6)		C6A	C11A	1.401(6)				

Table S2.12. Selected bond angles for **Ir5**.

Atom	Atom	Atom	Angle/°		Atom	Atom	Atom	Angle/°
O1	Ir1	O2	87.79(12)		O1A	Ir1A	O2A	87.02(12)
N1	Ir1	O1	87.90(13)		N1A	Ir1A	O1A	94.37(13)
N1	Ir1	O2	93.55(13)		N1A	Ir1A	O2A	90.18(13)
N2	Ir1	O1	94.03(13)		N1A	Ir1A	N2A	174.21(13)
N2	Ir1	O2	89.48(13)		N2A	Ir1A	O1A	87.84(13)
N2	Ir1	N1	176.47(13)		N2A	Ir1A	O2A	95.29(13)
C7	Ir1	O1	91.47(14)		C7A	Ir1A	O1A	91.28(14)
C7	Ir1	O2	174.42(14)		C7A	Ir1A	O2A	175.60(14)
C7	Ir1	N1	80.90(16)		C7A	Ir1A	N1A	94.00(16)
C7	Ir1	N2	96.09(16)		C7A	Ir1A	N2A	80.58(15)
C27	Ir1	O1	174.76(15)		C7A	Ir1A	C27A	90.88(16)
C27	Ir1	O2	92.04(14)		C27A	Ir1A	O1A	174.70(14)
C27	Ir1	N1	97.33(16)		C27A	Ir1A	O2A	91.16(14)
C27	Ir1	N2	80.73(16)		C27A	Ir1A	N1A	80.66(15)
C27	Ir1	C7	89.19(16)		C27A	Ir1A	N2A	97.28(15)
C39	O1	Ir1	125.2(3)		C39A	O1A	Ir1A	126.1(3)
C41	O2	Ir1	125.2(3)		C41A	O2A	Ir1A	126.4(3)
C1	N1	Ir1	124.9(3)		C1A	N1A	Ir1A	124.1(3)
C1	N1	C5	119.4(4)		C1A	N1A	C5A	119.2(4)
C5	N1	Ir1	115.7(3)		C5A	N1A	Ir1A	116.2(3)
C21	N2	Ir1	124.1(3)		C21A	N2A	Ir1A	125.3(3)
C21	N2	C25	119.5(4)		C21A	N2A	C25A	118.8(4)
C25	N2	Ir1	116.4(3)		C25A	N2A	Ir1A	116.0(3)
N1	C1	C2	122.7(4)		N1A	C1A	C2A	122.6(4)
C1	C2	C3	120.1(4)		C1A	C2A	C3A	120.1(4)
C2	C3	C12	117.8(4)		C2A	C3A	C12A	119.5(4)
C4	C3	C2	117.3(4)		C4A	C3A	C2A	116.4(4)
C4	C3	C12	124.9(4)		C4A	C3A	C12A	124.1(4)
C3	C4	C5	120.7(4)		C3A	C4A	C5A	121.7(4)
N1	C5	C4	119.7(4)		N1A	C5A	C4A	119.9(4)
N1	C5	C6	113.9(4)		N1A	C5A	C26A	112.9(4)
C4	C5	C6	126.4(4)		C4A	C5A	C26A	127.2(4)
C7	C6	C5	114.8(4)		C7A	C6A	C25A	115.1(4)
C11	C6	C5	123.3(4)		C11A	C6A	C7A	121.4(4)
C11	C6	C7	122.0(4)		C11A	C6A	C25A	123.4(4)
C6	C7	Ir1	114.5(3)		C6A	C7A	Ir1A	114.5(3)
C8	C7	Ir1	128.7(3)		C8A	C7A	Ir1A	128.3(3)
C8	C7	C6	116.7(4)		C8A	C7A	C6A	117.1(4)
C9	C8	C7	121.2(4)		C9A	C8A	C7A	120.7(4)
C8	C9	C10	121.1(4)		C10A	C9A	C8A	121.6(4)
C11	C10	C9	119.5(4)		C9A	C10A	C11A	119.5(4)
C10	C11	C6	119.6(4)		C10A	C11A	C6A	119.5(4)
C13	C12	C3	122.5(5)		C13A	C12A	C3A	124.5(4)
C13	C12	C17	119.3(5)		C13A	C12A	C17A	118.5(4)
C17	C12	C3	118.1(5)		C17A	C12A	C3A	117.0(4)

Table S2.12 continued. Selected bond angles for **Ir5**.

Atom	Atom	Atom	Angle/°		Atom	Atom	Atom	Angle/°
C12	C13	C14	118.0(5)		C12A	C13A	C14A	118.3(4)
C12	C13	C18	125.5(5)		C12A	C13A	C18A	125.0(4)
C14	C13	C18	116.5(5)		C14A	C13A	C18A	116.7(4)
C15	C14	C13	121.4(5)		C15A	C14A	C13A	122.2(5)
C14	C15	C16	120.3(5)		C14A	C15A	C16A	119.9(5)
C17	C16	C15	120.3(5)		C15A	C16A	C17A	119.2(5)
C16	C17	C12	120.7(5)		C16A	C17A	C12A	121.8(5)
N2	C21	C22	122.5(4)		N2A	C21A	C22A	123.2(4)
C21	C22	C23	119.2(4)		C21A	C22A	C23A	119.5(4)
C22	C23	C32	121.0(4)		C22A	C23A	C32A	120.9(4)
C24	C23	C22	117.5(4)		C24A	C23A	C22A	117.3(4)
C24	C23	C32	121.4(4)		C24A	C23A	C32A	121.8(4)
C23	C24	C25	121.5(4)		C25A	C24A	C23A	120.9(4)
N2	C25	C24	119.8(4)		N2A	C25A	C6A	113.7(4)
N2	C25	C26	113.3(4)		N2A	C25A	C24A	120.2(4)
C24	C25	C26	126.9(4)		C24A	C25A	C6A	126.1(4)
C27	C26	C25	115.0(4)		C27A	C26A	C5A	115.4(4)
C31	C26	C25	123.9(4)		C31A	C26A	C5A	123.3(4)
C31	C26	C27	121.1(4)		C31A	C26A	C27A	121.3(4)
C26	C27	Ir1	114.5(3)		C26A	C27A	Ir1A	114.1(3)
C28	C27	Ir1	128.6(3)		C28A	C27A	Ir1A	128.2(3)
C28	C27	C26	117.0(4)		C28A	C27A	C26A	117.5(4)
C29	C28	C27	121.0(4)		C29A	C28A	C27A	121.1(4)
C30	C29	C28	120.6(4)		C30A	C29A	C28A	120.7(4)
C29	C30	C31	120.1(4)		C31A	C30A	C29A	119.5(4)
C30	C31	C26	120.1(4)		C30A	C31A	C26A	119.8(5)
C33	C32	C23	122.4(4)		C33A	C32A	C23A	122.6(4)
C33	C32	C37	119.2(4)		C37A	C32A	C23A	118.1(4)
C37	C32	C23	118.4(4)		C37A	C32A	C33A	119.2(4)
C32	C33	C34	118.0(5)		C32A	C33A	C38A	121.9(4)
C32	C33	C38	123.3(5)		C34A	C33A	C32A	118.5(4)
C34	C33	C38	118.4(5)		C34A	C33A	C38A	119.6(5)
C35	C34	C33	122.2(5)		C35A	C34A	C33A	121.8(5)
C34	C35	C36	120.0(5)		C34A	C35A	C36A	119.6(5)
C37	C36	C35	118.9(5)		C37A	C36A	C35A	119.7(5)
C36	C37	C32	121.6(5)		C36A	C37A	C32A	121.2(5)
O1	C39	C40	127.1(4)		O1A	C39A	C40A	126.3(4)
O1	C39	C43	114.7(4)		O1A	C39A	C43A	115.3(4)
C40	C39	C43	118.1(4)		C40A	C39A	C43A	118.4(4)
C41	C40	C39	127.8(4)		C41A	C40A	C39A	128.0(4)
O2	C41	C40	126.8(4)		O2A	C41A	C40A	126.2(4)
O2	C41	C42	115.0(4)		O2A	C41A	C42A	116.1(4)
C40	C41	C42	118.2(4)		C40A	C41A	C42A	117.7(4)

Table S2.13. Selected bond lengths for **Ir7**.

Atom	Atom	Length/Å		Atom	Atom	Length/Å		Atom	Atom	Length/Å
Ir1	O1	2.143(4)		C7	C8	1.402(9)		C26	C31	1.395(9)
Ir1	O2	2.163(5)		C8	C9	1.377(10)		C27	C28	1.416(9)
Ir1	N1	2.035(5)		C9	C10	1.403(10)		C28	C29	1.392(9)
Ir1	N2	2.040(5)		C10	C11	1.377(9)		C29	C30	1.397(9)
Ir1	C7	1.973(7)		C12	C13	1.413(10)		C30	C31	1.374(9)
Ir1	C27	1.981(6)		C12	C17	1.383(10)		C32	C33	1.406(9)
O1	C41	1.263(8)		C13	C14	1.397(10)		C32	C37	1.402(9)
O2	C43	1.267(8)		C13	C18	1.498(10)		C33	C34	1.392(9)
N1	C1	1.347(8)		C14	C15	1.376(11)		C33	C38	1.523(10)
N1	C5	1.369(8)		C15	C16	1.370(10)		C34	C35	1.376(10)
N2	C21	1.345(8)		C15	C19	1.515(9)		C35	C36	1.376(10)
N2	C25	1.367(8)		C16	C17	1.419(9)		C35	C39	1.505(9)
C1	C2	1.377(9)		C17	C20	1.520(10)		C36	C37	1.398(9)
C2	C3	1.393(9)		C21	C22	1.363(9)		C37	C40	1.511(10)
C3	C4	1.372(9)		C22	C23	1.396(9)		C41	C42	1.393(10)
C3	C12	1.514(9)		C23	C24	1.396(9)		C41	C45	1.506(10)
C4	C5	1.401(8)		C23	C32	1.494(8)		C42	C43	1.373(10)
C5	C6	1.454(9)		C24	C25	1.388(8)		C43	C44	1.521(10)
C6	C7	1.437(9)		C25	C26	1.462(9)				
C6	C11	1.390(9)		C26	C27	1.415(8)				

Table S2.13. Selected bond angles for **Ir7**.

Atom	Atom	Atom	Angle/°		Atom	Atom	Atom	Angle/°
O1	Ir1	O2	88.24(18)		C15	C14	C13	122.1(7)
N1	Ir1	O1	83.88(19)		C14	C15	C19	120.2(7)
N1	Ir1	O2	94.94(19)		C16	C15	C14	118.8(6)
N1	Ir1	N2	179.3(2)		C16	C15	C19	121.0(7)
N2	Ir1	O1	95.91(19)		C15	C16	C17	121.6(7)
N2	Ir1	O2	85.77(19)		C12	C17	C16	118.6(7)
C7	Ir1	O1	89.2(2)		C12	C17	C20	123.3(6)
C7	Ir1	O2	175.4(2)		C16	C17	C20	118.0(6)
C7	Ir1	N1	81.1(2)		N2	C21	C22	123.1(6)
C7	Ir1	N2	98.2(2)		C21	C22	C23	119.6(6)
C7	Ir1	C27	91.3(3)		C22	C23	C32	122.6(6)
C27	Ir1	O1	176.3(2)		C24	C23	C22	117.1(6)
C27	Ir1	O2	91.5(2)		C24	C23	C32	120.3(6)
C27	Ir1	N1	99.8(2)		C25	C24	C23	121.2(6)
C27	Ir1	N2	80.4(2)		N2	C25	C24	119.7(6)
C41	O1	Ir1	123.7(4)		N2	C25	C26	113.9(5)
C43	O2	Ir1	124.3(4)		C24	C25	C26	126.4(6)
C1	N1	Ir1	124.5(4)		C27	C26	C25	114.0(5)
C1	N1	C5	119.7(5)		C31	C26	C25	124.6(5)
C5	N1	Ir1	115.1(4)		C31	C26	C27	121.4(6)
C21	N2	Ir1	125.2(4)		C26	C27	Ir1	115.6(5)
C21	N2	C25	118.9(5)		C26	C27	C28	116.6(6)
C25	N2	Ir1	115.4(4)		C28	C27	Ir1	127.8(5)
N1	C1	C2	122.2(6)		C29	C28	C27	121.4(6)
C1	C2	C3	119.4(6)		C28	C29	C30	120.3(6)
C2	C3	C12	121.5(6)		C31	C30	C29	119.6(6)
C4	C3	C2	118.2(6)		C30	C31	C26	120.7(6)
C4	C3	C12	120.3(6)		C33	C32	C23	119.3(6)
C3	C4	C5	121.3(6)		C37	C32	C23	121.3(6)
N1	C5	C4	119.1(6)		C37	C32	C33	119.2(5)
N1	C5	C6	114.2(5)		C32	C33	C38	121.6(6)
C4	C5	C6	126.6(6)		C34	C33	C32	119.0(6)
C7	C6	C5	114.1(6)		C34	C33	C38	119.3(6)
C11	C6	C5	124.2(6)		C35	C34	C33	122.7(7)
C11	C6	C7	121.7(6)		C34	C35	C36	117.6(6)
C6	C7	Ir1	114.7(5)		C34	C35	C39	121.0(7)
C8	C7	Ir1	129.8(5)		C36	C35	C39	121.4(7)
C8	C7	C6	115.4(6)		C35	C36	C37	122.6(6)
C9	C8	C7	123.1(6)		C32	C37	C40	122.2(6)
C8	C9	C10	119.7(6)		C36	C37	C32	118.9(6)
C11	C10	C9	119.9(6)		C36	C37	C40	118.9(6)
C10	C11	C6	120.2(6)		O1	C41	C42	128.0(6)
C13	C12	C3	120.9(6)		O1	C41	C45	114.4(7)
C17	C12	C3	118.7(6)		C42	C41	C45	117.7(7)
C17	C12	C13	120.4(6)		C43	C42	C41	127.9(7)

Table S2.13 continued. Selected bond angles for **Ir7**.

Atom	Atom	Atom	Angle/°		Atom	Atom	Atom	Angle/°
C12	C13	C18	122.3(6)		O2	C43	C42	127.2(7)
C14	C13	C12	118.4(7)		O2	C43	C44	114.5(6)
C14	C13	C18	119.2(7)		C42	C43	C44	118.2(7)

S3. DFT model validation

As a means of validating the computational models the structural accuracy were compared to with the experimental data by measuring the mean average deviation (MAD) values of the X-ray crystallography data shown in Tables S2.8-13.

Table S3.1 Bond length comparison of SDD~~, LANL2DZ/6-31G*~~ and LANL2DZ/6-31G(d) basis sets, MAD values.

Compound	Basis set (MAD values, Å)	
	SDD	LANL2DZ/6-31G(d)
Ir1	0.027	0.030
Ir3	0.031	0.033
Ir5	0.036	0.037
Ir7	0.164	0.165

S4 Orbital Contributions

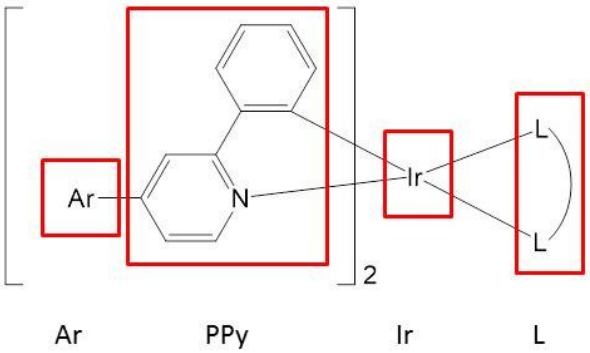

Figure S4.1. Molecular components of **Ir1-7** where Ar = phenyl (Ph), 4-anasole (C_6H_4OMe), 2-toluene (2-Tolyl) and 2-mesitylene (Mes); and L∩L = acetylacetonate (acac) or 2-picolinate (pic).

Table S4.1. Orbital contributions for $Ir(PhPPy)_2(acac)$

Molecular Orbital		**Energy (eV)**	**Molecular Components Contributions (%)**			
			Ir	L∩L	PPy	Ar
167	L+10	0.07	2	1	90	7
166	L+9	-0.03	96	1	1	1
165	L+8	-0.21	5	0	41	54
164	L+7	-0.22	2	1	45	52
163	L+6	-0.56	0	0	2	97
162	L+5	-0.56	1	0	3	96
161	L+4	-1.26	1	0	90	9
160	L+3	-1.37	4	96	0	0
159	L+2	-1.39	1	0	90	9
158	L+1	-1.94	3	0	73	23
157	LUMO	-1.94	3	1	72	23
156	HOMO	-5.24	47	5	48	0
155	H-1	-5.64	49	36	12	3
154	H-2	-5.99	67	5	22	6
153	H-3	-6.25	1	3	96	0
152	H-4	-6.51	5	1	93	2
151	H-5	-6.52	9	49	35	7
150	H-6	-6.65	4	8	75	13
149	H-7	-6.93	4	69	25	3
148	H-8	-7.01	9	2	20	69
147	H-9	-7.14	18	11	15	56
146	H-10	-7.24	0	0	0	100

Table S4.2. Orbital contributions for **Ir1**.

Molecular Orbital		**Energy (eV)**	**Molecular Components Contributions (%)**			
			Ir	L∩L	PPy	Ar
172	L+10	-0.03	4	1	87	9
171	L+9	-0.25	2	0	42	56
170	L+8	-0.28	4	1	46	49
169	L+7	-0.57	0	0	3	97
168	L+6	-0.59	1	0	3	97
167	L+5	-1.32	1	18	74	8
166	L+4	-1.33	1	38	55	6
165	L+3	-1.56	1	43	52	4
164	L+2	-1.98	3	2	72	23
163	L+1	-2.01	4	21	58	17
162	LUMO	-2.08	0	75	20	5
161	HOMO	-5.42	44	4	52	0
160	H-1	-5.98	61	13	20	5
159	H-2	-6.15	61	5	26	8
158	H-3	-6.33	4	3	91	1
157	H-4	-6.57	4	1	93	2
156	H-5	-6.70	2	4	90	4
155	H-6	-6.98	4	25	18	53
154	H-7	-7.05	4	49	16	31
153	H-8	-7.10	8	25	19	48
152	H-9	-7.25	0	0	0	100
151	H-10	-7.26	0	0	0	100

Table S4.3. Orbital contributions for **Ir2**.

Molecular Orbital		**Energy (eV)**	**Molecular Components Contributions (%)**			
			Ir	L∩L	PPy	Ar
188	L+10	0.01	82	0	18	1
187	L+9	-0.07	3	0	44	52
186	L+8	-0.15	7	2	63	28
185	L+7	-0.63	0	0	4	96
184	L+6	-0.65	1	0	4	96
183	L+5	-1.27	1	3	87	9
182	L+4	-1.29	1	45	48	6
181	L+3	-1.53	1	51	45	4
180	L+2	-1.90	4	1	75	20
179	L+1	-1.94	4	7	71	17
178	LUMO	-2.05	1	90	8	1
177	HOMO	-5.39	44	4	52	0
176	H-1	-5.88	51	10	19	20
175	H-2	-6.00	42	4	20	34
174	H-3	-6.28	1	2	88	9
173	H-4	-6.40	12	6	29	53
172	H-5	-6.48	19	4	37	41
171	H-6	-6.59	13	4	71	12
170	H-7	-6.72	10	6	78	6
169	H-8	-7.03	0	84	16	0
168	H-9	-7.35	0	1	1	99
167	H-10	-7.37	0	0	1	99

Table S4.4. Orbital contributions for **Ir3**.

Molecular Orbital		**Energy (eV)**	**Molecular Components Contributions (%)**			
			Ir	L∩L	PPy	Ar
183	L+10	0.12	1	0	78	20
182	L+9	0.00	58	1	19	22
181	L+8	-0.06	43	1	26	30
180	L+7	-0.07	3	1	58	38
179	L+6	-0.61	1	0	4	95
178	L+5	-0.62	0	0	4	96
177	L+4	-1.22	1	0	89	10
176	L+3	-1.34	1	0	89	10
175	L+2	-1.35	4	96	0	0
174	L+1	-1.85	3	1	76	20
173	LUMO	-1.86	3	1	75	20
172	HOMO	-5.21	47	5	48	0
171	H-1	-5.59	48	32	13	7
170	H-2	-5.88	53	4	20	23
169	H-3	-6.22	1	4	94	1
168	H-4	-6.25	0	23	14	63
167	H-5	-6.39	11	1	42	46
166	H-6	-6.53	16	2	64	19
165	H-7	-6.55	5	19	72	4
164	H-8	-6.80	17	31	38	14
163	H-9	-6.93	12	68	19	2
162	H-10	-7.34	0	1	2	98

Table S4.5. Orbital contributions for **Ir4**.

Molecular Orbital		**Energy (eV)**	**Molecular Components Contributions (%)**			
			Ir	L∩L	PPy	Ar
180	L+10	-0.05	4	1	88	7
179	L+9	-0.26	2	0	29	69
178	L+8	-0.29	3	1	33	64
177	L+7	-0.45	0	0	3	96
176	L+6	-0.46	1	0	3	96
175	L+5	-1.26	1	4	88	8
174	L+4	-1.29	1	40	52	6
173	L+3	-1.54	1	55	42	3
172	L+2	-1.87	4	1	80	15
171	L+1	-1.91	4	4	79	13
170	LUMO	-2.07	1	94	5	0
169	HOMO	-5.42	44	4	52	0
168	H-1	-5.99	62	13	21	4
167	H-2	-6.16	61	5	27	7
166	H-3	-6.33	5	4	91	1
165	H-4	-6.57	4	1	92	2
164	H-5	-6.70	2	4	88	6
163	H-6	-6.85	3	5	9	84
162	H-7	-6.89	5	2	6	87
161	H-8	-7.02	1	26	8	65
160	H-9	-7.06	1	48	12	40
159	H-10	-7.09	4	15	11	70

Table S4.6. Orbital contributions for **Ir5**.

Molecular Orbital		**Energy (eV)**	**Molecular Components Contributions (%)**			
			Ir	L∩L	PPy	Ar
175	L+10	0.05	2	1	92	5
174	L+9	-0.04	96	1	1	2
173	L+8	-0.23	1	0	30	68
172	L+7	-0.24	3	0	27	70
171	L+6	-0.44	0	0	3	97
170	L+5	-0.45	2	0	4	95
169	L+4	-1.20	1	0	91	8
168	L+3	-1.33	1	0	90	9
167	L+2	-1.36	4	96	1	0
166	L+1	-1.82	3	2	80	15
165	LUMO	-1.82	3	1	82	14
164	HOMO	-5.23	47	5	48	0
163	H-1	-5.64	48	38	12	2
162	H-2	-6.01	68	5	22	5
161	H-3	-6.24	1	3	96	0
160	H-4	-6.50	5	1	92	2
159	H-5	-6.52	9	47	37	7
158	H-6	-6.65	4	8	69	19
157	H-7	-6.85	4	1	7	88
156	H-8	-6.90	2	22	15	61
155	H-9	-6.93	8	52	15	25
154	H-10	-7.04	3	1	8	88

Table S4.8. Orbital contributions for **Ir7**.

Molecular Orbital		**Energy (eV)**	**Molecular Components Contributions (%)**			
			Ir	L∩L	PPy	Ar
196	L+10	-0.06	4	1	89	5
195	L+9	-0.16	0	0	3	97
194	L+8	-0.18	0	0	4	96
193	L+7	-0.28	1	0	8	91
192	L+6	-0.3	1	0	8	91
191	L+5	-1.19	2	2	93	3
190	L+4	-1.22	2	26	70	2
189	L+3	-1.51	1	69	29	1
188	L+2	-1.72	4	2	92	3
187	L+1	-1.79	3	2	92	2
186	LUMO	-2.06	1	96	3	0
185	HOMO	-5.41	44	4	52	0
184	H-1	-6.01	63	14	21	2
183	H-2	-6.19	62	5	30	3
182	H-3	-6.32	8	4	87	1
181	H-4	-6.55	1	0	40	58
180	H-5	-6.57	1	1	20	77
179	H-6	-6.59	6	2	40	52
178	H-7	-6.64	0	0	1	99
177	H-8	-6.65	0	0	3	96
176	H-9	-6.71	5	5	86	4
175	H-10	-7.05	0	84	16	0

Table S4.7. Orbital contributions for **Ir7**.

Molecular Orbital		**Energy (eV)**	**Molecular Components Contributions (%)**			
			Ir	L∩L	PPy	Ar
191	L+10	0.03	3	1	95	2
190	L+9	-0.06	97	1	0	2
189	L+8	-0.15	0	0	2	98
188	L+7	-0.16	0	0	2	98
187	L+6	-0.28	0	0	6	94
186	L+5	-0.29	1	0	6	93
185	L+4	-1.12	2	0	95	3
184	L+3	-1.23	2	0	95	3
183	L+2	-1.37	4	93	3	0
182	L+1	-1.67	4	4	91	2
181	LUMO	-1.69	3	1	95	2
180	HOMO	-5.24	47	5	48	0
179	H-1	-5.66	49	38	12	1
178	H-2	-6.04	71	6	22	1
177	H-3	-6.24	1	3	96	0
176	H-4	-6.51	6	1	85	9
175	H-5	-6.53	4	23	20	54
174	H-6	-6.55	2	0	10	88
173	H-7	-6.56	4	15	42	39
172	H-8	-6.63	0	0	0	99
171	H-9	-6.63	0	0	1	99
170	H-10	-6.74	15	27	54	4

S4 Photoluminescence Quantum Yield (PLQY) determination

The photophysical measurments of the complexes (**Ir1**-**Ir7**) were measured in degassed DCM solutions by repeated freeze-pump-thaw cycles using a turbomolecular pump until the pressure is stable in quartz cuvettes, l = 1 cm. The emission spectra of all iridium complexes were collected by exciting the samples at 410 nm. The solutions had absorbance below 0.1 to minimise inner filter effects. PLQYs were determined using Quinine sulfate in 0.1 M H_2SO_4 (ϕ_F: 0.546)[1] as the reference, the emission spectra of quinine sulfate were collected by exciting the samples at 360 nm. The PLQY of all complexes were measure in triplicates and determined by following method:

1. The UV-vis absorbance spectrum was recorded in quartz cuvette with path length l = 2cm (to improve spectrum resolution), recording the absorbance at the excitation wavelength.
2. The same sample solution was transferred to the quartz fluorescence cell (a standard 1 cm modified with a Teflon Young's tap) degassed via repeated freeze-pump-thaw cycles before the emission spectrum was recorded.
3. The fully corrected fluorescence spectrum was integrated and the integrated intensity (the area of the fluorescence spectrum) was recorded.
4. Steps 1 to 3 were repeated for five additional solutions with increasing concentrations (with absorbance ranging from 0.02 to 0.1).
5. The integrated florescence intensity was plotted verse absorbance, which resulted a linear plot with gradient X ($Grad_X$).
6. Steps 1, 3, 4 and 5 were repeated for the chosen standard (quinine sulfate).
7. Fluorescence quantum yield for each complex was calculated using the following equation

$$\Phi_X = \Phi_{ST}\left(\frac{Grad_X}{Grad_{ST}}\right)\left(\frac{\eta^2{}_X}{\eta^2{}_{ST}}\right)$$

Where ST and X denote standard and the measured complex, Φ is the fluorescence quantum yield, Grad the gradient from the plot of integrated fluorescence intensity vs. absorbance, and η the refractive index of the solvent.

References

1. W. H. Melhuish, *J. Phys. Chem.*, 1961, **65**, 229-235.