Supporting Information for

User-Friendly Aerobic Reductive Alkylation of Iridium(III) Porphyrin Chloride with Potassium Hydroxide: Scope and Mechanism

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List of Contents

I. Conditions Optimization

The optimization reactions followed the general procedures described in the experimental section with the changes of atmosphere, water loading, solvents, temperatures, reaction time bases, and loadings (1-bromopentane (**2a**), KOH).

(1) Atmosphere and solvent effects

Ir(ttp)(CO)Cl (**1**; 10 mg, 0.011 mmol), KOH (12.1 mg, 0.22 mmol), and **2a** (16.6 mg, 0.11 mmol) were added to benzene (1 mL). For the reaction conducted under N_2, the mixture was degassed for three freeze-pump-thaw cycles, filled with N_2. The mixture was heated at 120 ^oC for 5 h. Ir(ttp)-*n*-pentyl (**3a**) was isolated with 87% yield under N_2 and 83% yield under air.

Ir(ttp)(CO)Cl (**1**; 10 mg, 0.011 mmol), KOH (12.1 mg, 0.22 mmol), and **2a** (16.6 mg, 0.11 mmol) were added to benzene (1 mL) or THF (1 mL). The mixture was heated at 120 ^oC under air for 5 h. Ir(ttp)-*n*-pentyl (**3a**) was isolated in 85%, 76% yield in C_6H_6 and THF, respectively.

(2) Water loading effects

Ir(ttp)(CO)Cl (**1**; 10 mg, 0.011 mmol), KOH (12.1 mg, 0.22 mmol), **2a** (16.6 mg, 0.11 mmol), and H_2O (n equiv) were added to benzene (1 mL). Isolated yield of Ir(ttp)-*n*-pentyl (**3a**) with H_2O (200 equiv): 91%; H_2O (100 equiv): 90%; with H_2O (0 equiv): 84%.

(3) Temperature and time effects

Ir(ttp)(CO)Cl (**1**; 10 mg, 0.011 mmol), KOH (12.1 mg, 0.22 mmol), and **2a** (16.6 mg, 0.11 mmol) were added to benzene (1 mL). Isolated yield of Ir(ttp)-*n*-pentyl (**3a**) for the reaction at 80 ^oC for 5 h: < 10%; at 120 ^oC for 5 h: 84%; at 120 ^oC for 9 h: 83%; at 150 ^oC for 3 h: 73%.

(4) Base and base loading effects

Ir(ttp)(CO)Cl (**1**; 10 mg, 0.011 mmol), base (20 equiv), and **2a** (16.6 mg, 0.11 mmol) were added to benzene (1 mL). Isolated yield of Ir(ttp)-*n*-pentyl (**3a**) with the base of K_2CO_3 (30.4 mg, 0.22 mmol): < 10%; KOH (12.1 mg, 0.22 mmol): 84%; no base: 0%.

Ir(ttp)(CO)Cl (**1**; 10 mg, 0.011 mmol), KOH (m equiv), and **2a** (16.6 mg, 0.11 mmol) were added to benzene (1 mL). The mixture was heated at 120 ^{o}C. Isolated yield of Ir(ttp)-*n*-pentyl (**3a**) with 0 equiv KOH for 5 h: 0%; 1.1 equiv KOH for 12 h: 10%; 5 equiv KOH for 12 h: 79%; 10 equiv KOH for 8 h: 80%; 20 equiv KOH for 5 h: 84%.

(5) Alkyl halide loading effects

Ir(ttp)(CO)Cl (**1**; 10 mg, 0.011mmol), KOH (12.1 mg, 0.22 mmol), and **2a** (k equiv) were added benzene (1 mL). The mixture was heated at 120 ^{o}C for 5 h. Isolated yield of Ir(ttp)-*n*-pentyl (**3a**) with 2 equiv **2a**: 68%; 5 equiv **2a**: 80%; 10 equiv **2a**: 84%.

II. X-ray Crystallographic Data

Table S1 Crystallographic data and structure refinement for **3a**, **3e**, **3i** and **3k**

		Ir(ttp)-*n*-pentyl (**3a**)	Ir(ttp)-*n*-octyl (**3e**)	Ir(ttp)-*c*-pentyl (**3i**)	Ir(ttp)-adamantyl (**3k**)
Empirical formula		$C_{53}H_{48}IrN_4$	$C_{56}H_{53}IrN_4$	$C_{54}H_{47}Cl_2IrN_4$	$C_{58}H_{51}IrN_4$
Formula weight		933.15	974.22	1015.06	996.23
Temperature (K)		296.2	173.2	172.2	173.2
Wavelength (Å)		0.71073	0.71073	0.71073	0.71073
Crystal system		Monoclinic	Triclinic	Triclinic	Monoclinic
space group		$P2_1/n$	P^{-1}	$P2_1/n$	$P2_1/c$
Unit cell dimensions	a (Å)	15.451(8)	10.4399(3)	15.5148(6)	10.8114(4)
	b (Å)	12.705(6)	14.3879(4)	18.2080(8)	16.7568(6)
	c (Å)	22.893(12)	16.0385(4)	16.0602(7)	25.0862(9)
	α (deg.)	90	66.2380(10)	90	90
	β (deg.)	100.330(9)	78.2120(10)	107.5671(11)	95.283(2)
	γ (deg.)	90	83.3700(10)	90	90
Volume($Å^3$)		4421(4)	2156.91(10)	4325.3(3)	4525.4(3)
Z		4	2	4	4
Calculated density (g/cm^3)		1.402	1.500	1.559	1.462
Abs coeff (mm^{-1})		3.059	3.139	3.254	2.994
F(000)		1884	988	2040	2016
Crystal size(mm)		0.40 x 0.30 x 0.20	0.40 x 0.30 x 0.20	0.40 x 0.30 x 0.20	0.40 x 0.30 x 0.20
θ range for data collection(deg)		1.48 to 25.25 .	1.41 to 25.25	2.24 to 25.25	1.46 to 25.25
Limiting indices		-17<=h<=18	-12<=h<=12	-18<=h<=18	-10<=h<=12
		-15<=k<=12	-17<=k<=17	-21<=k<=21	-20<=k<=18
		-27<=l<=27	-19<=l<=18	-19<=l<=19	-30<=l<=27
No. of reflections collected / unique		33224 / 7989 [R(int) = 0.0595]	33042 / 7813 [R(int) = 0.0277]	84813 / 7831 [R(int) = 0.0245]	53035 / 8122 [R(int) = 0.0266]
Completeness to theta = 25.25		100.0 %	99.8 %	99.7 %	99.2 %
Absorp correction		multi-scan	multi-scan	multi-scan	multi-scan
Max. and min.		0.7456 and	0.7456 and	0.7456 and	0.7456 and

transmn	0.5042	0.5849	0.4297	0.6118
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/ restraints / parameters	7989 / 0 / 523	7813 / 24 / 596	7831 / 0 / 550	8122 / 7 / 568
Goodness-of-fit on F^2	1.017	1.187	1.057	1.066
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0353$	$R_1 = 0.0197$	$R_1 = 0.0236$	$R_1 = 0.0243$
	$wR_2 = 0.0741$	$wR_2 = 0.0535$	$wR_2 = 0.0574$	$wR_2 = 0.0559$
Final R indices (all data)	$R_1 = 0.0704$	$R_1 = 0.0219$	$R_1 = 0.0257$	$R_1 = 0.0343$
	$wR_2 = 0.0868$	$wR_2 = 0.0597$	$wR_2 = 0.0590$	$wR_2 = 0.0620$
Largest diff. peak and hole (e $Å^3$)	0.804 and -0.797	0.759 and -0.634	1.427 and -1.681	1.711 and -0.711

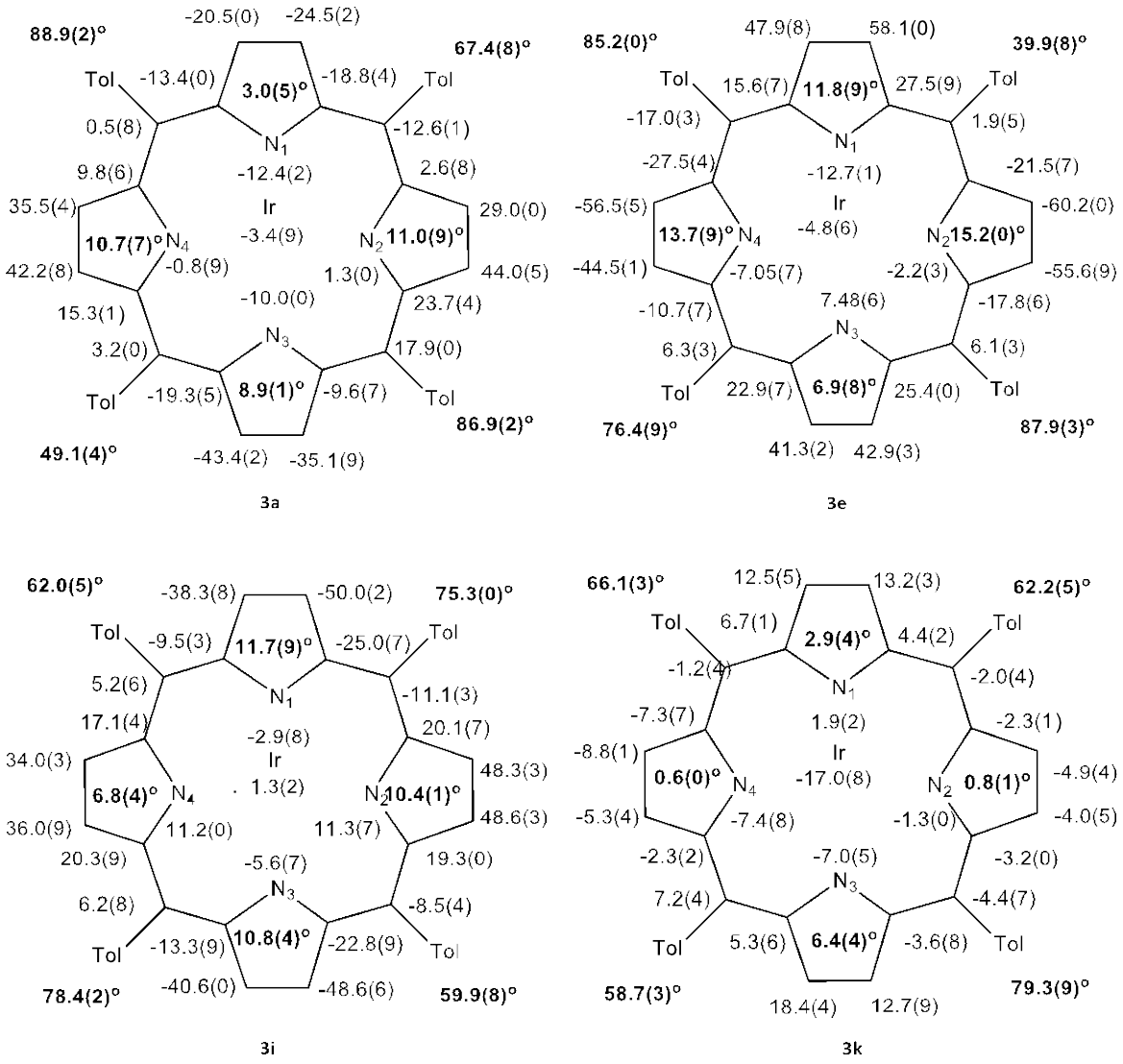
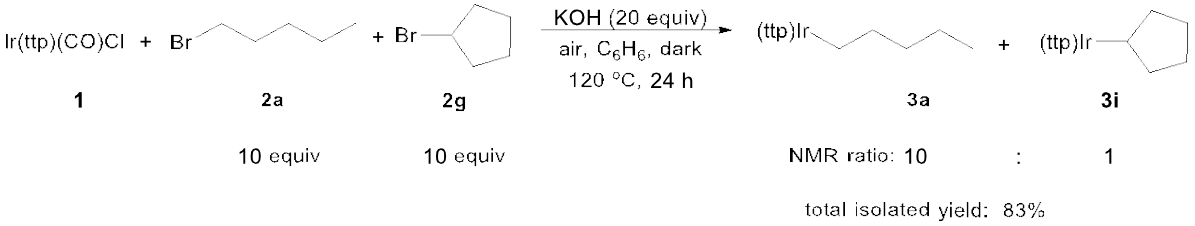


Fig. S1 The conformation of porphyrins showing the displacement of core atoms and of iridium atom from the 24-atom least-squares plane of porphyrin core (in pm; negative values correspond to displacement towards the alkyl group). Absolute values of the angles between pyrrole rings and the least-squares plane, and angles between phenyl substituents and the least-squares plane, are shown in bold.

III. Mechanistic Investigation Reactions

1. Competition reaction of 1-bromopentane (**2a**) and 1-bromocyclopentane (**2g**).



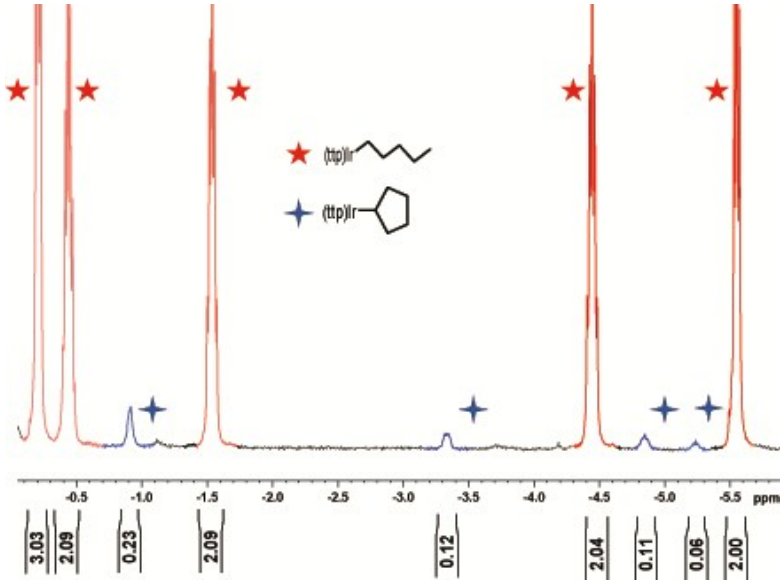
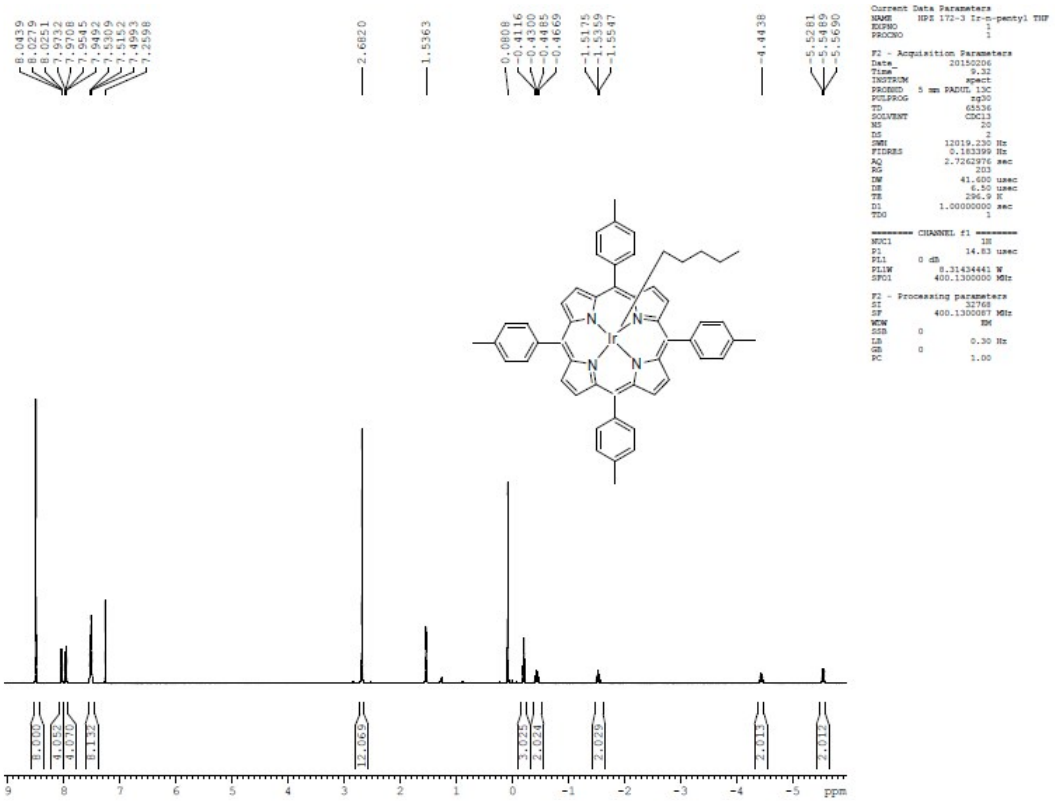


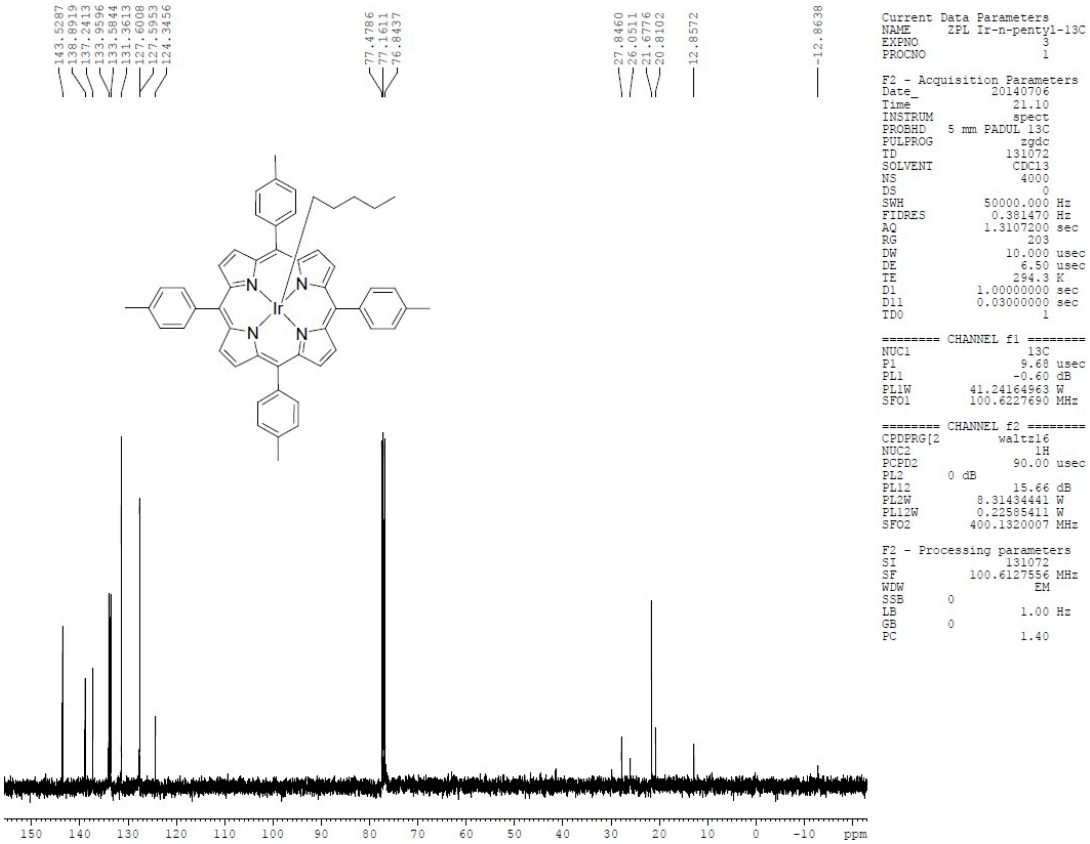
Fig. S2 Integrations of proton signals of **3a**, **3i** by ^{1}H NMR spectrum

IV. NMR Spectra

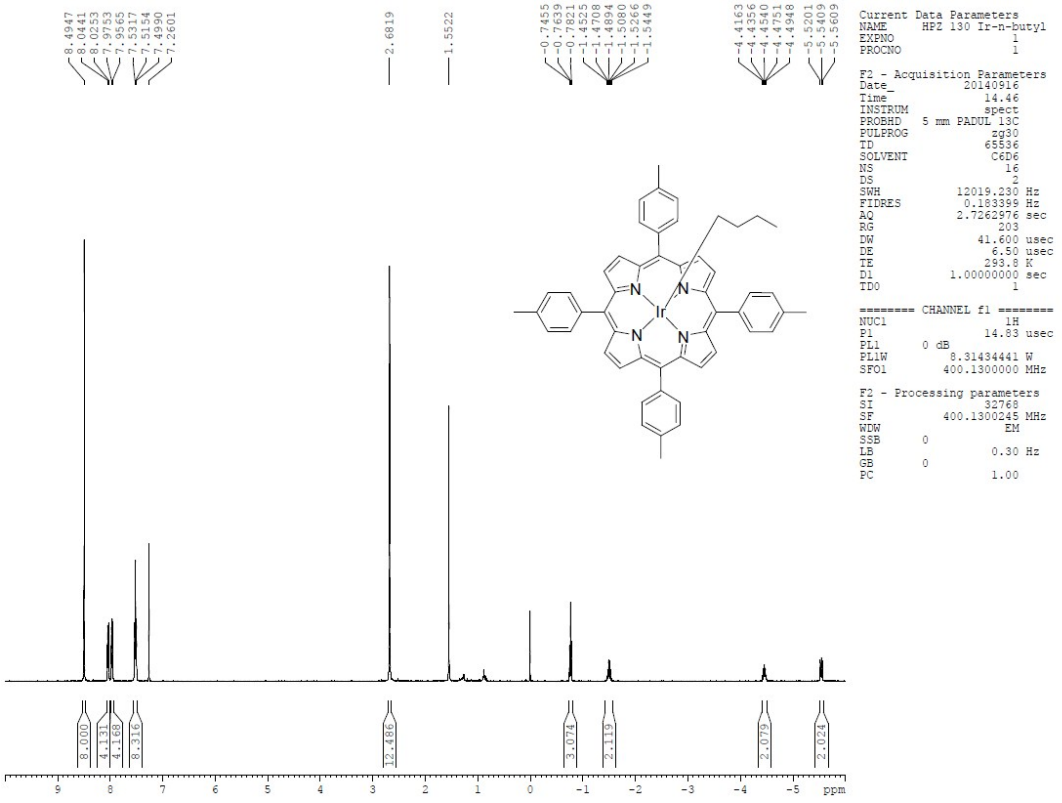
^{1}H NMR spectrum of Ir(ttp)-*n*-pentyl (**3a**)



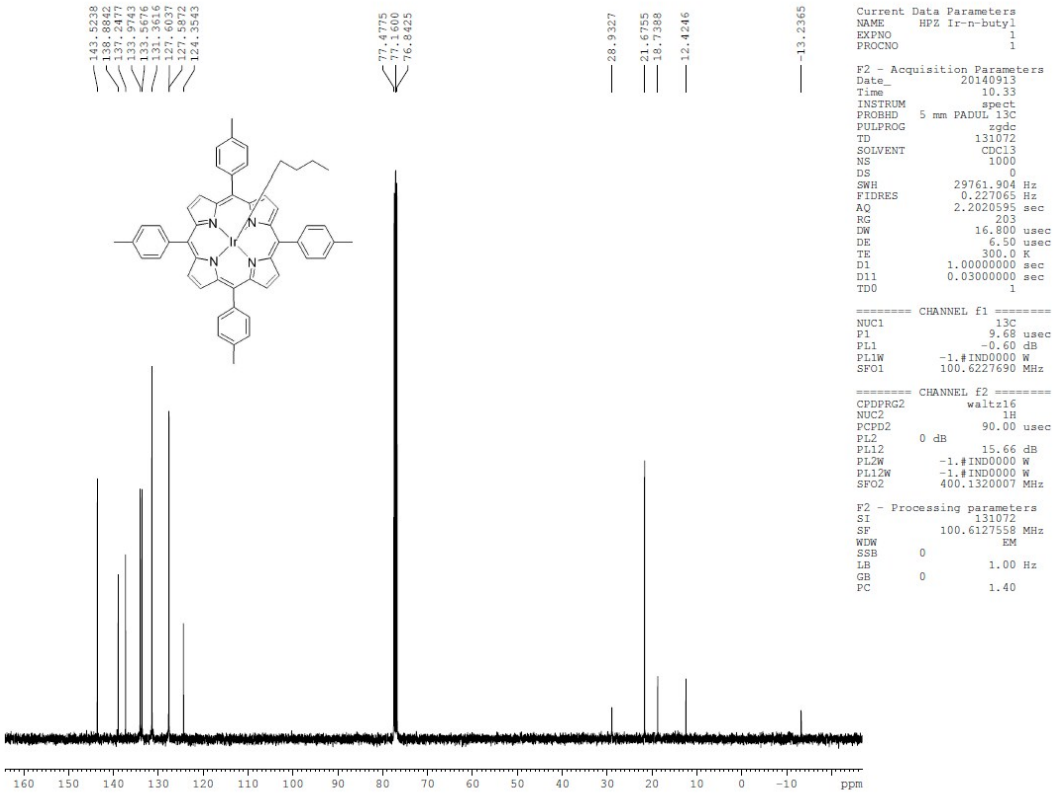
^{13}C NMR spectrum of Ir(ttp)-*n*-pentyl (**3a**)



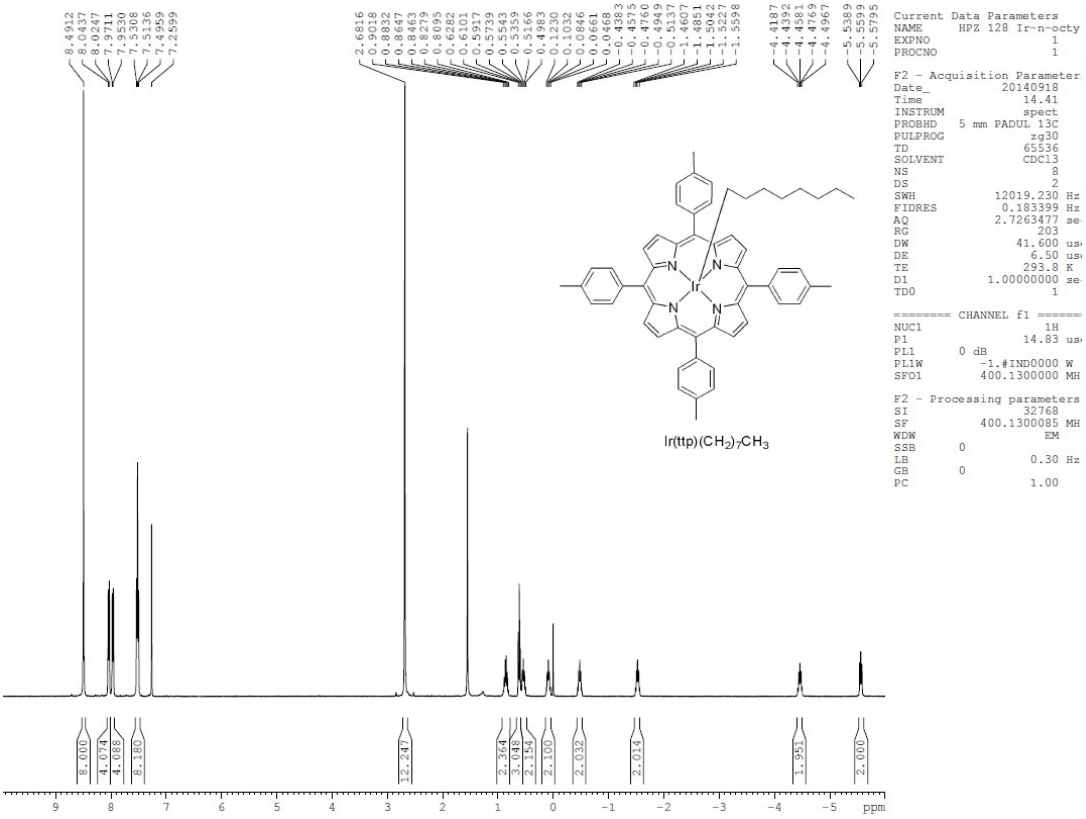
^{1}H NMR spectrum of Ir(ttp)-*n*-butyl (**3c**)



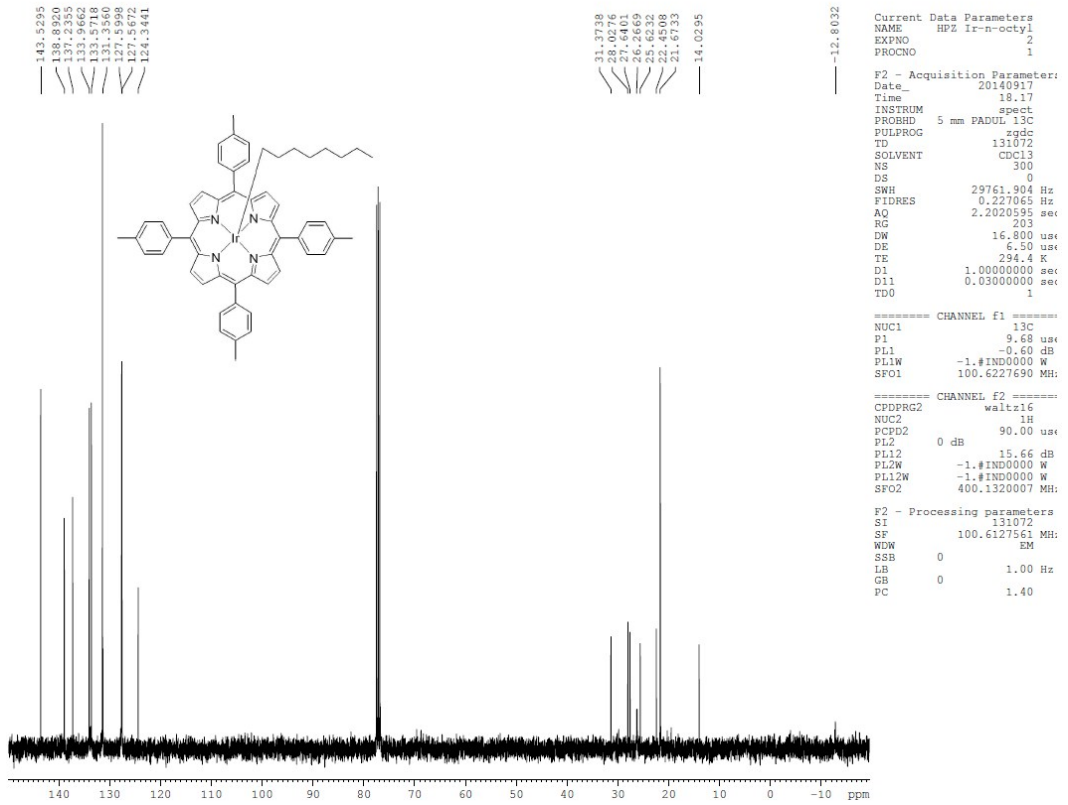
^{13}C NMR spectrum of Ir(ttp)-*n*-butyl (**3c**)



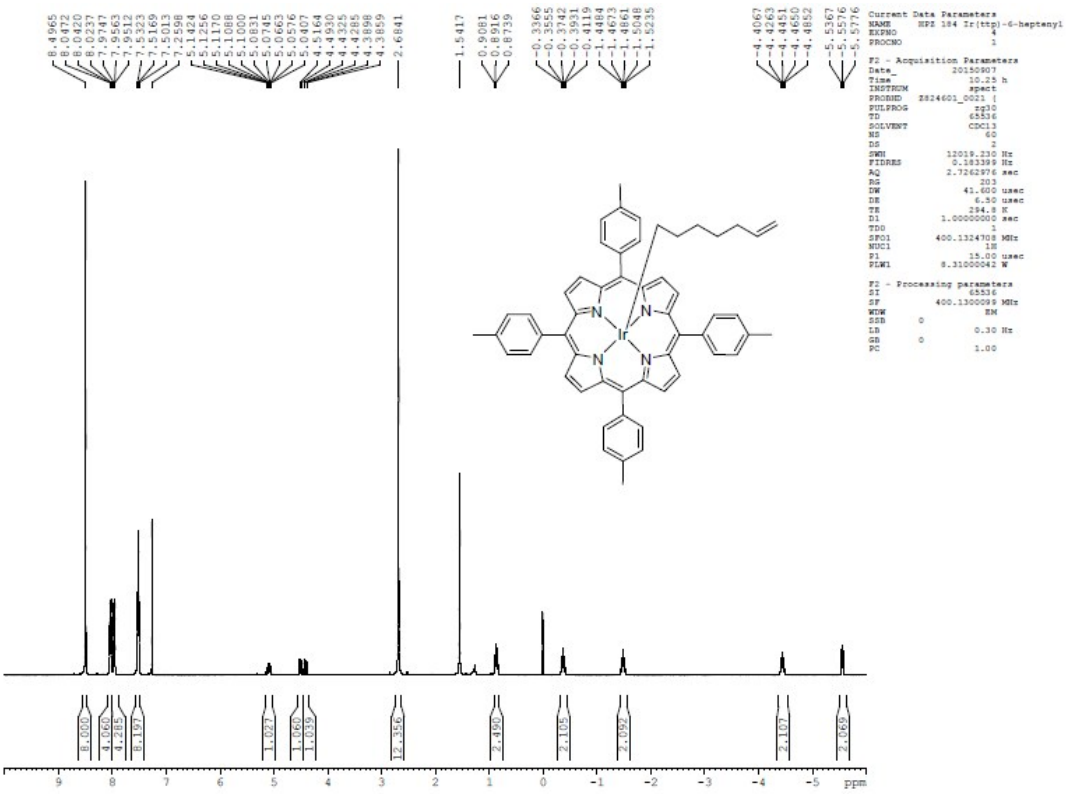
^{1}H NMR spectrum of Ir(ttp)-*n*-octyl (**3e**)



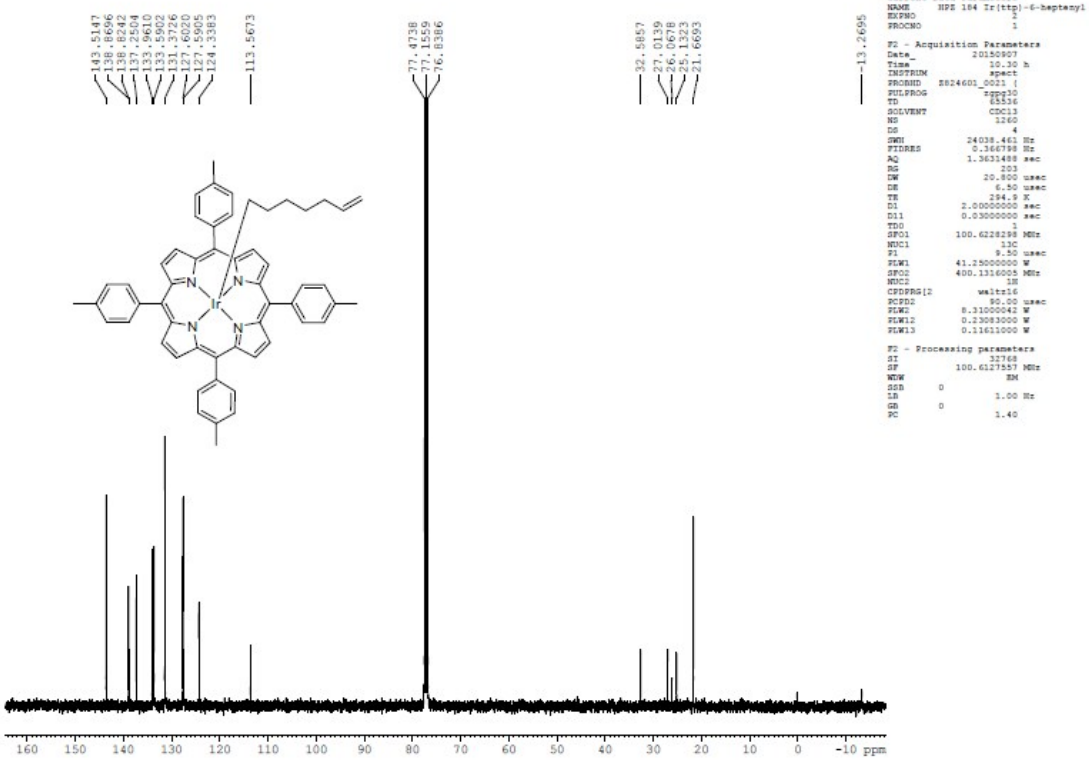
^{13}C NMR spectrum of Ir(ttp)-*n*-octyl (**3e**)



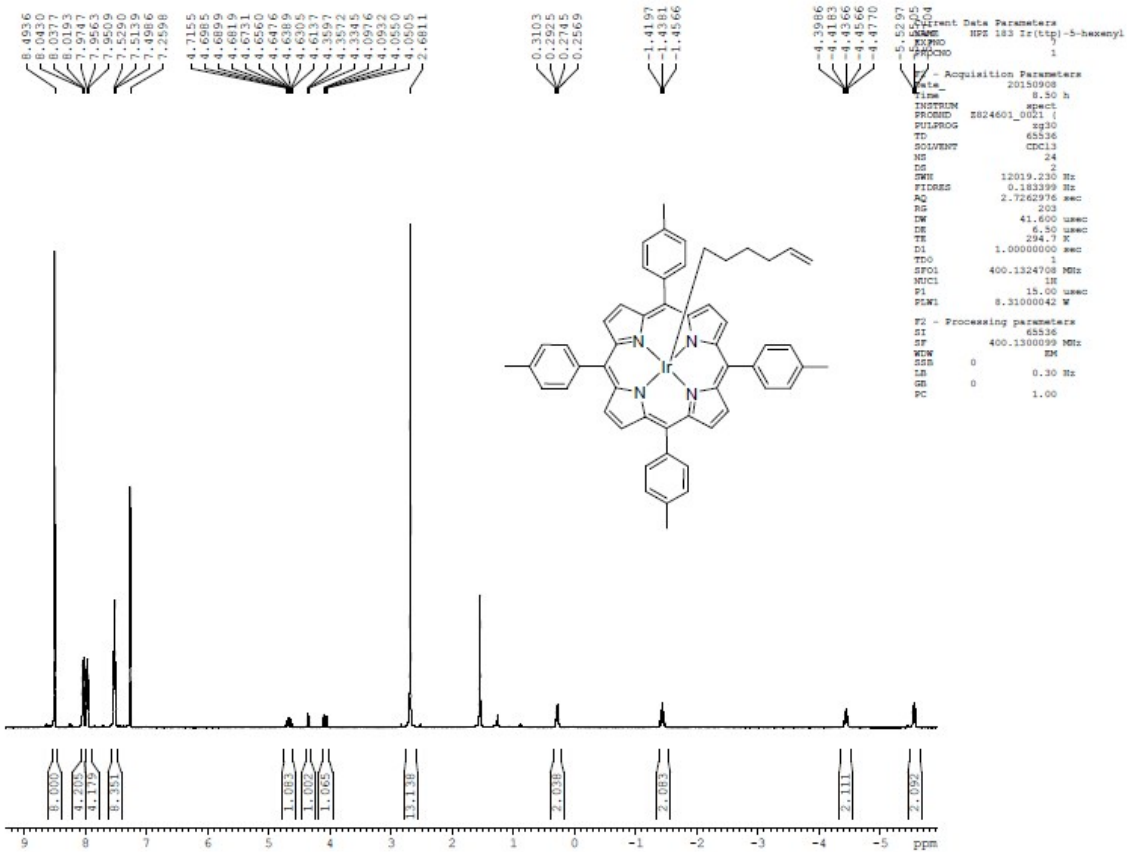
^{1}H NMR spectrum of Ir(ttp)-*6*-heptenyl (**3f**)



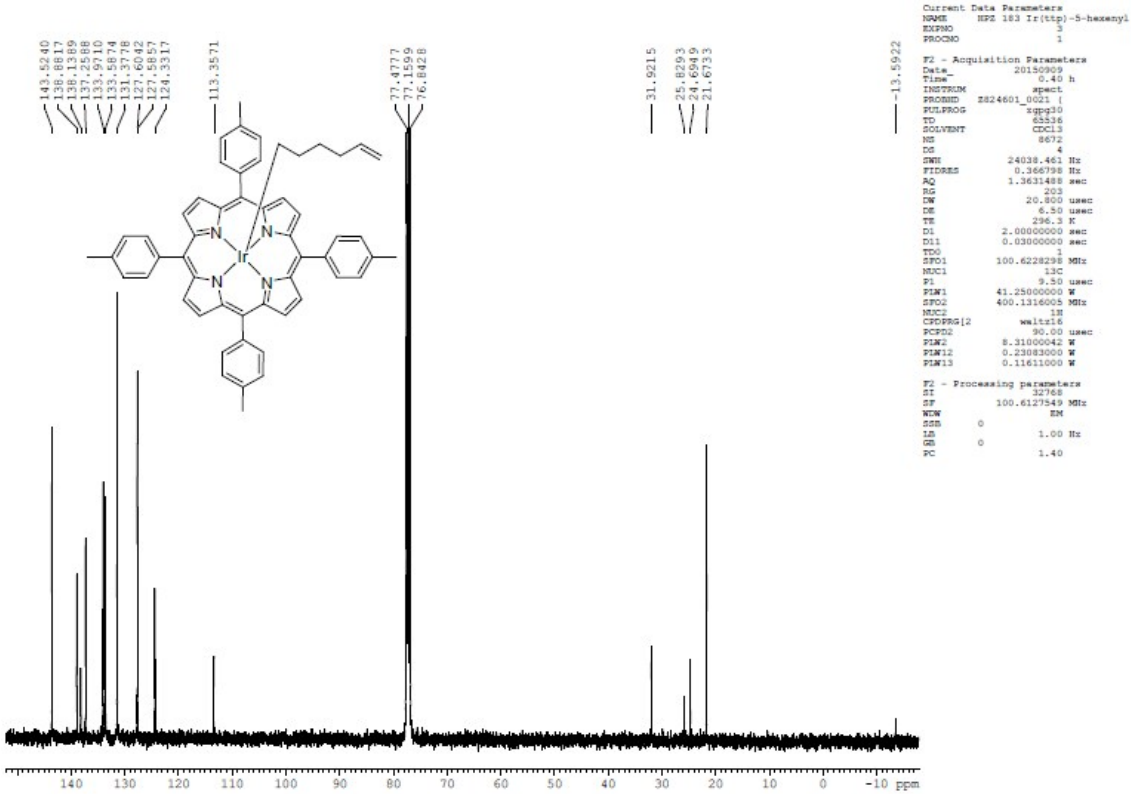
^{13}C NMR spectrum of Ir(ttp)-*6*-heptenyl (**3f**)



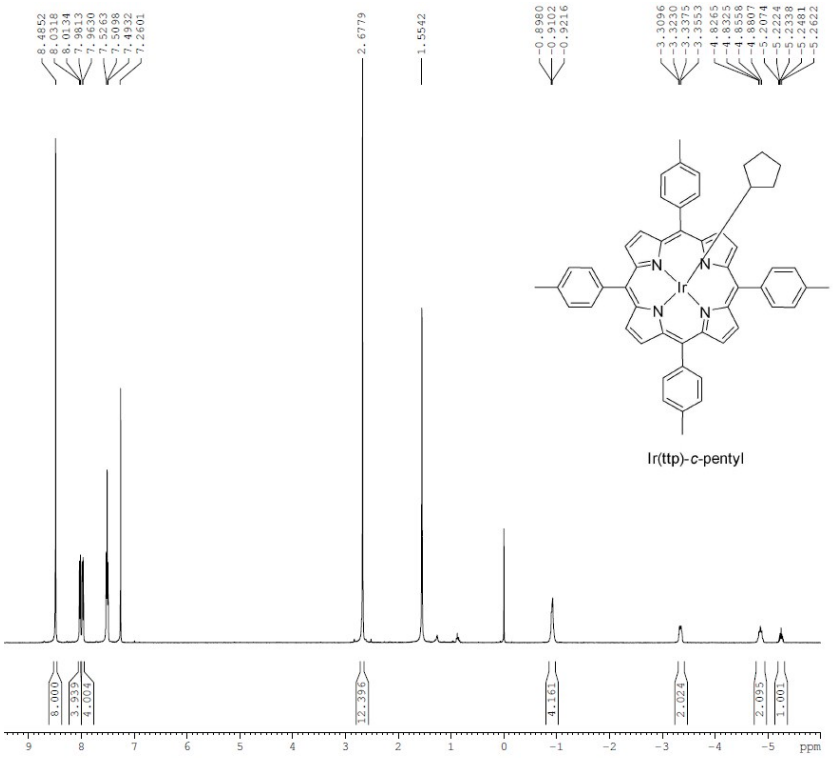
^{1}H NMR spectrum of Ir(ttp)-*5*-hexenyl (**3g**)



^{13}C NMR spectrum of Ir(ttp)-*5*-hexenyl (**3g**)



^{1}H NMR spectrum of Ir(ttp)-*c*-pentyl (**3i**)

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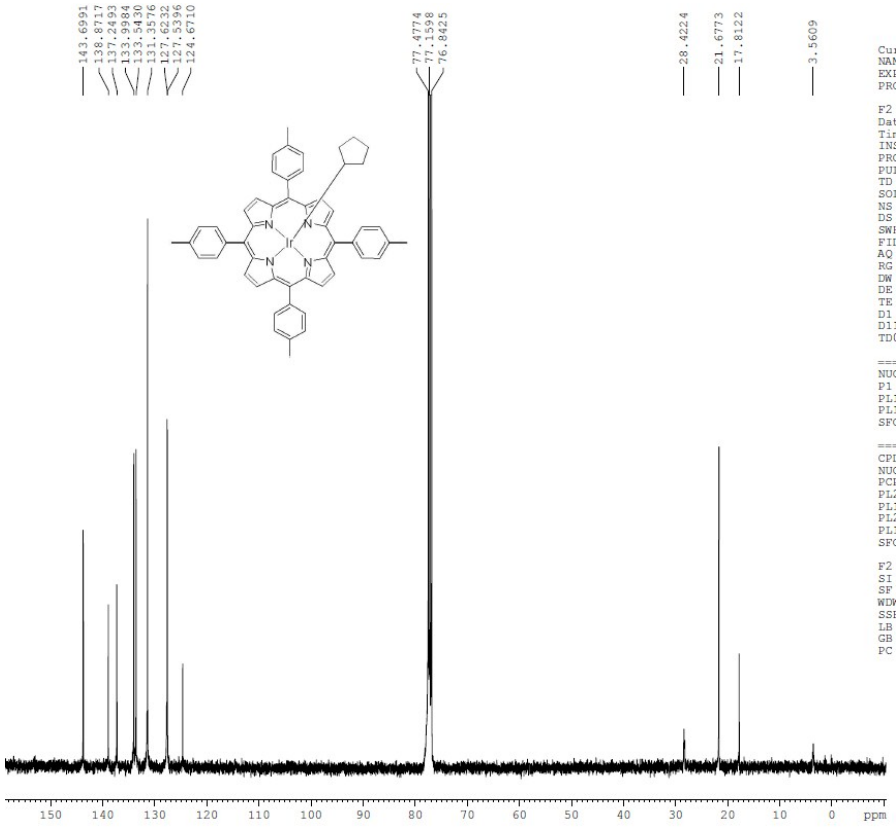
^{13}C NMR spectrum of Ir(ttp)-*c*-pentyl (**3i**)

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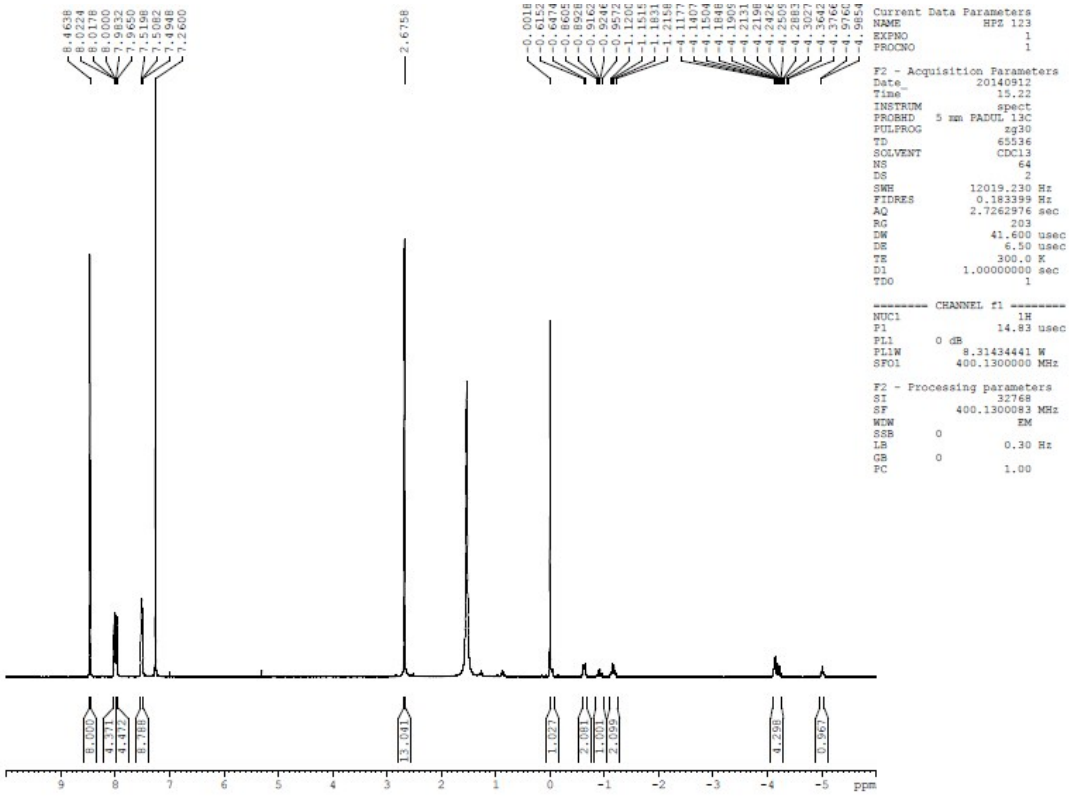
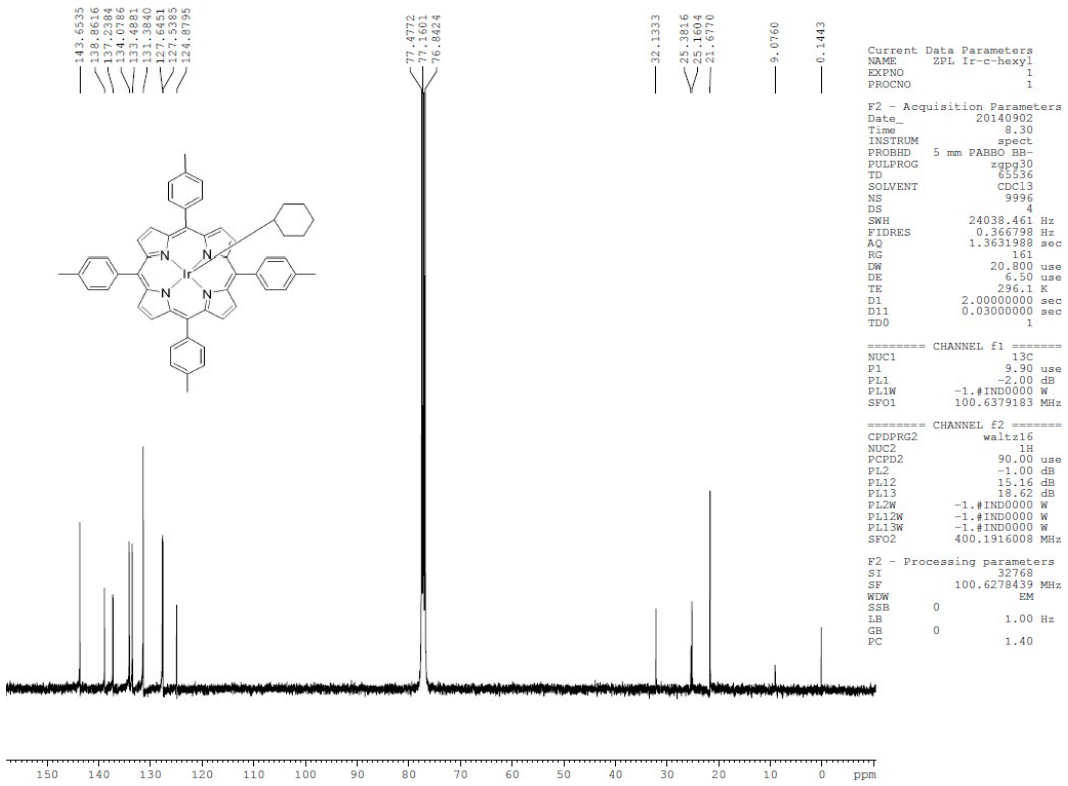
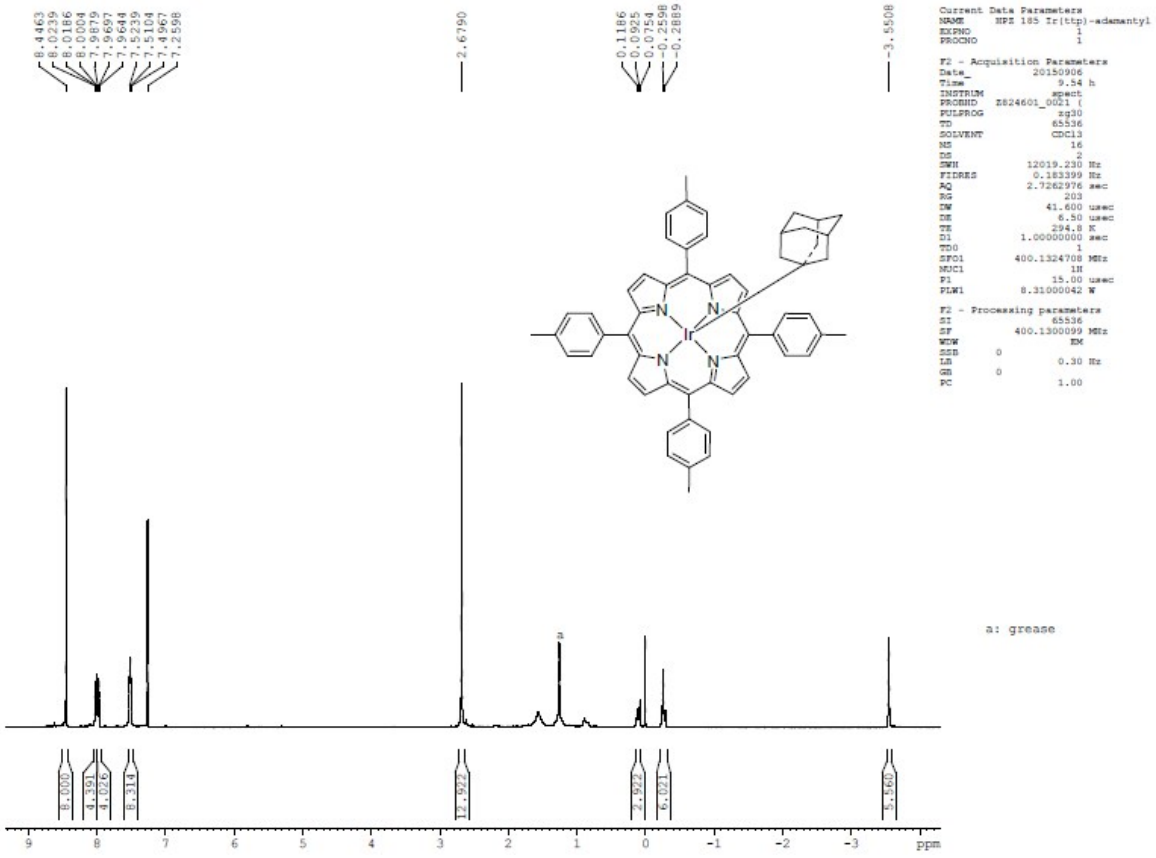
^{1}H NMR spectrum of Ir(ttp)-*c*-hexyl (**3j**)



^{13}C NMR spectrum of Ir(ttp)-*c*-hexyl (**3j**)



^{1}H NMR spectrum of Ir(ttp)-adamantyl (**3k**)



^{13}C NMR spectrum of Ir(ttp)-adamantyl (**3k**)