Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Synthesis of bi-metallic complexes bridged 2,6-bis(benzimidazol-2-yl) pyridine derivatives and their catalytic properties in transfer hydrogenation

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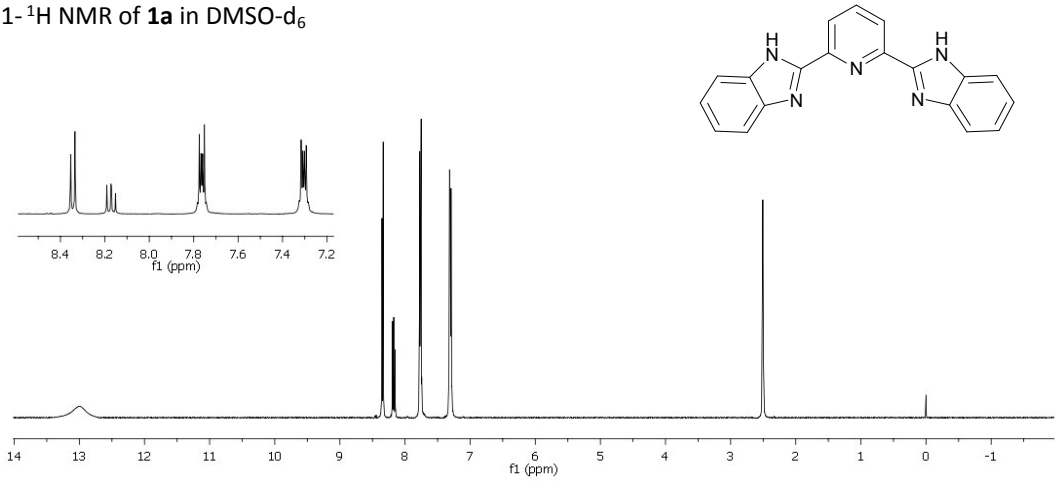
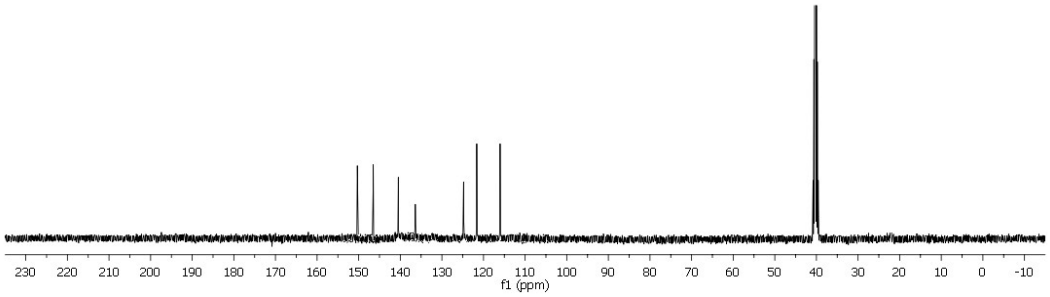
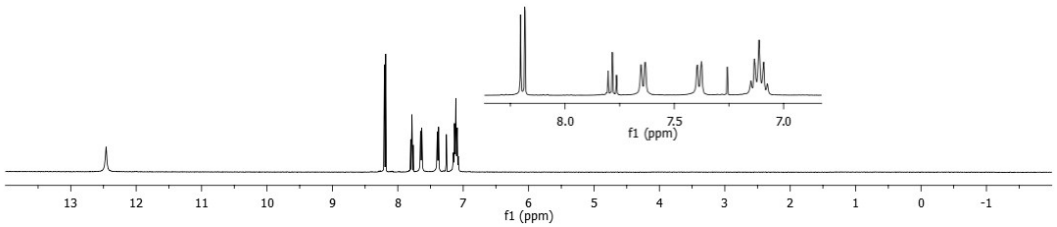


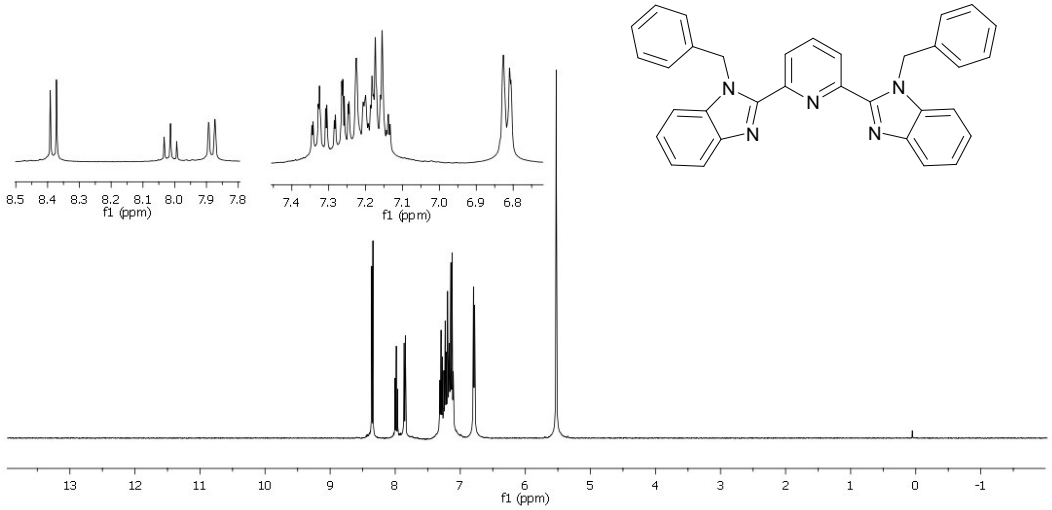
2- ^{13}C NMR of **1a** in DMSO-d_6



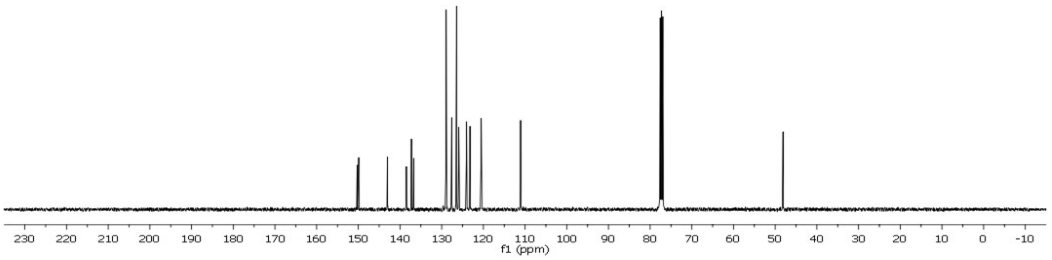
3-^{1}H NMR of **1a** in $CDCl_3$



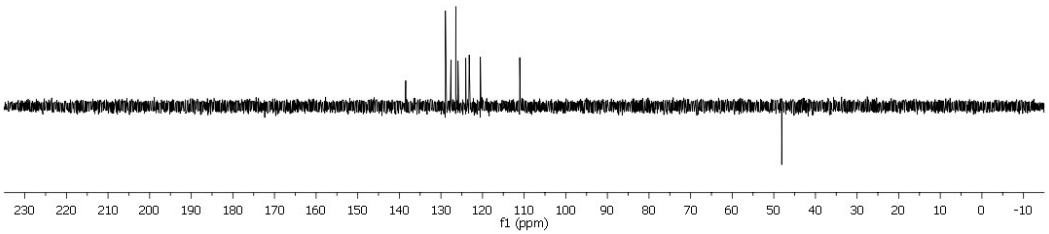
4- ^{1}H NMR of **1b**



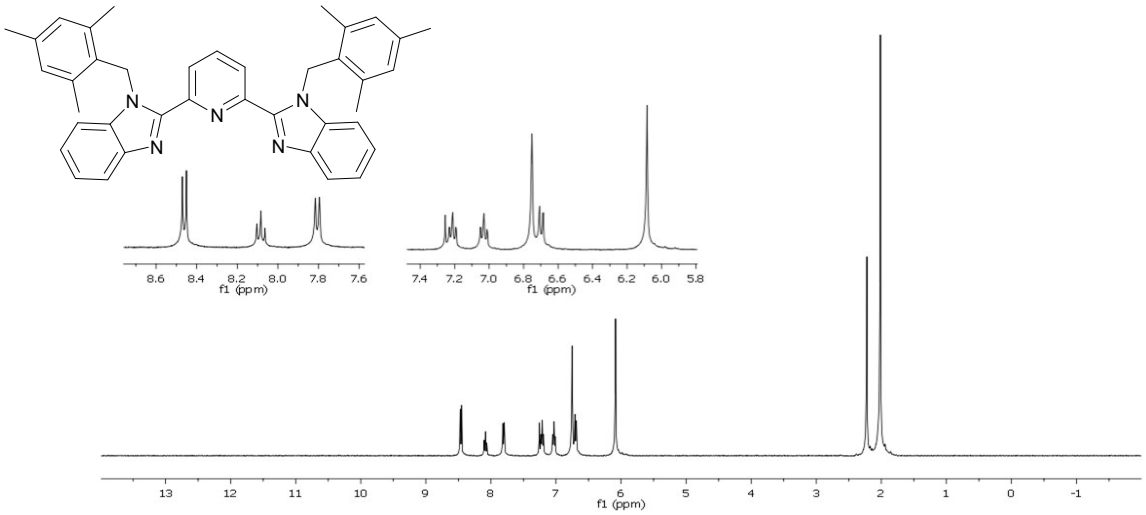
5- ^{13}C NMR of **1b**



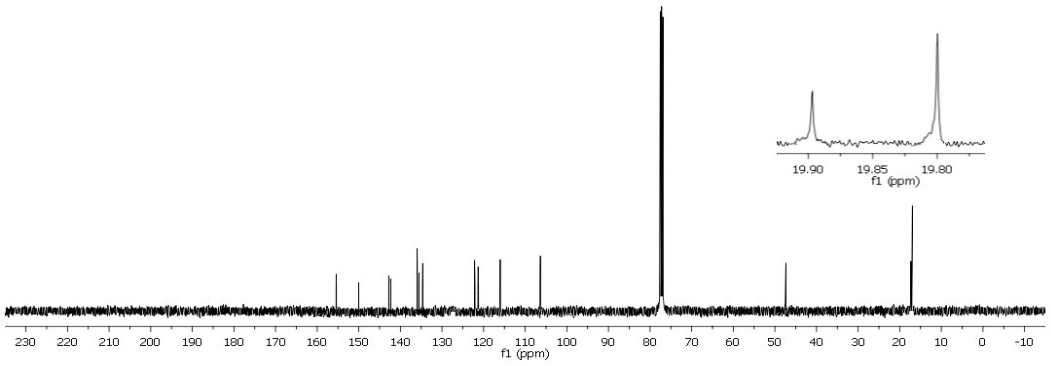
6- DEPT-135 of **1b**



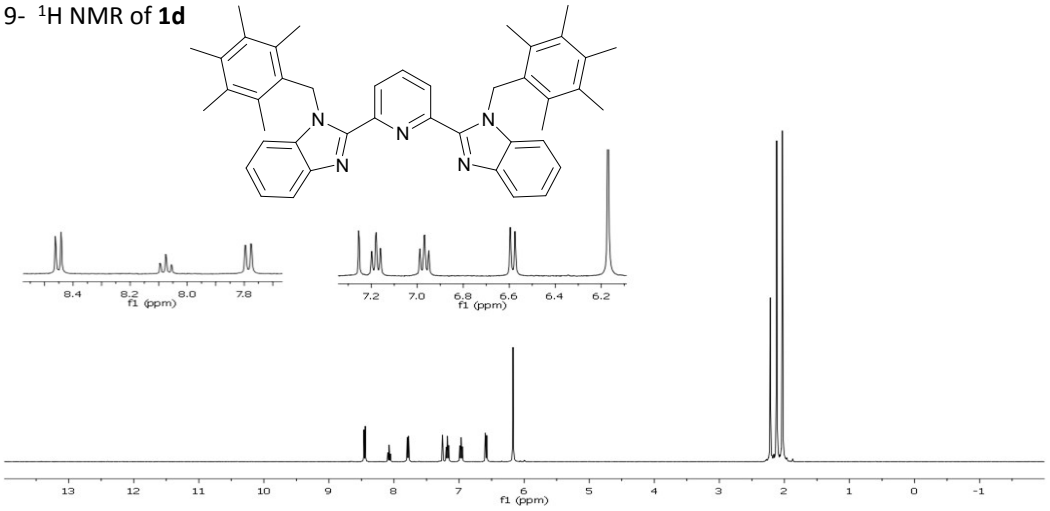
7- ^{1}H NMR of **1c**



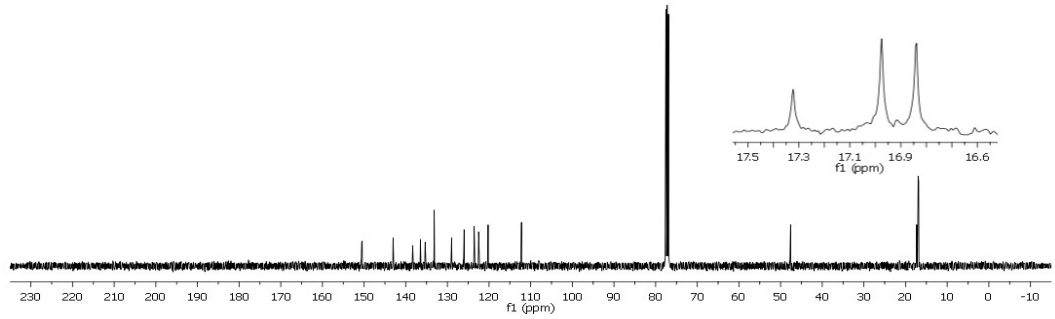
8- ^{13}C NMR of **1c**



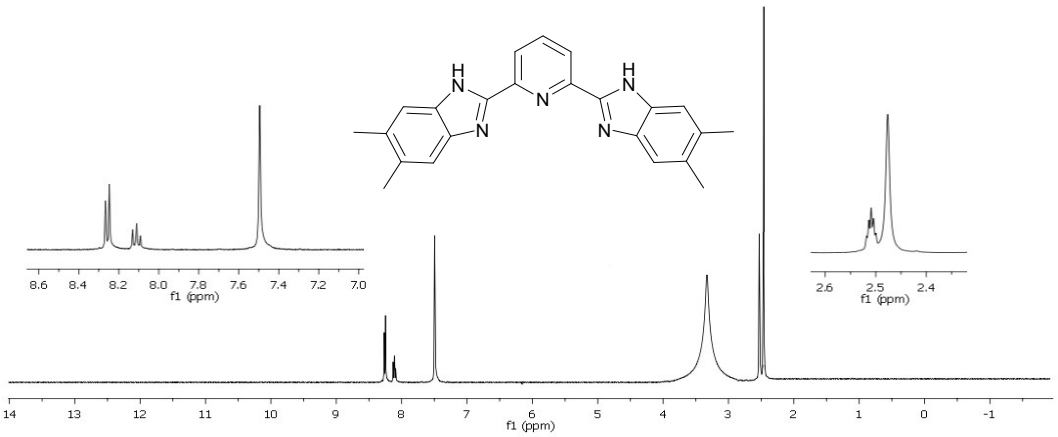
9- ^{1}H NMR of **1d**



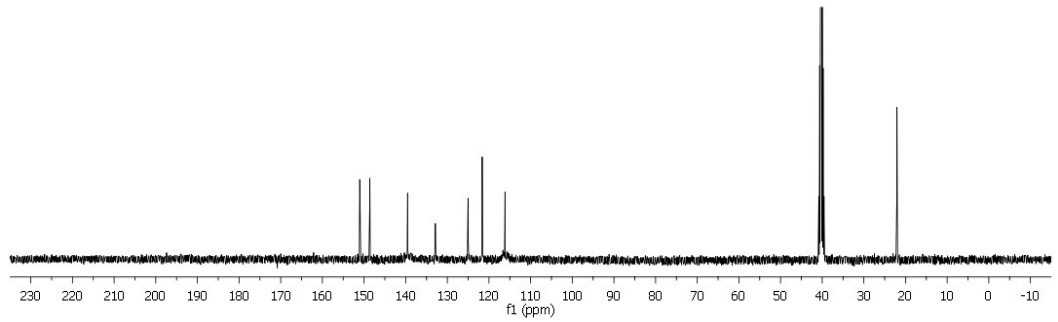
10- ^{13}C NMR of **1d**



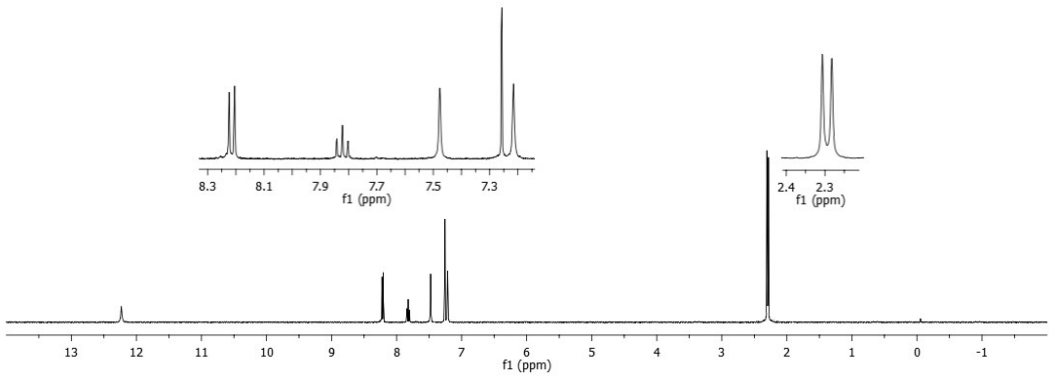
11- ^{1}H NMR of **2a** in DMSO-d_6



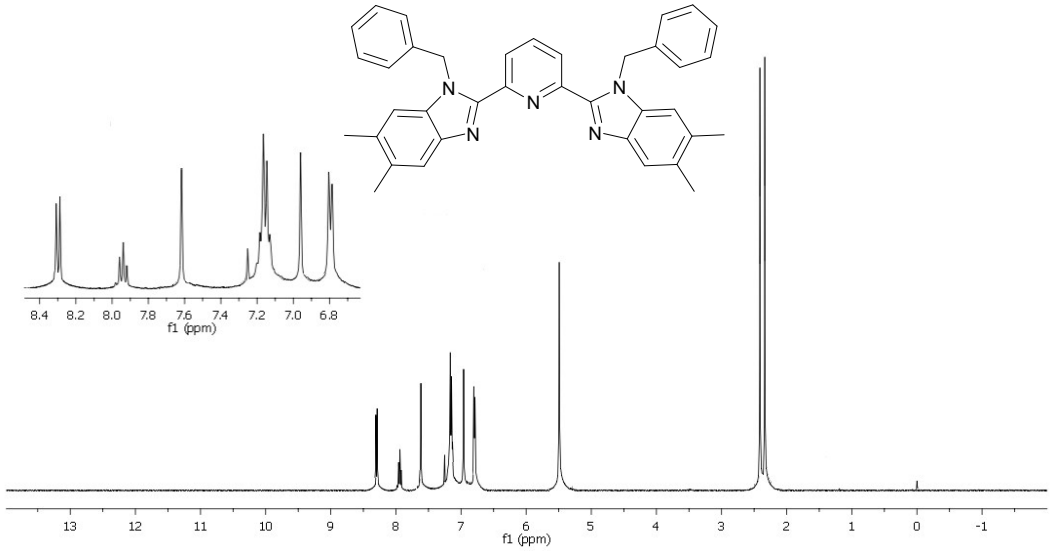
12- ^{13}C NMR of **2a** in DMSO-d_6



13- ^{1}H NMR of **2a** in $CDCl_3$



14- ^{1}H NMR of **2b**



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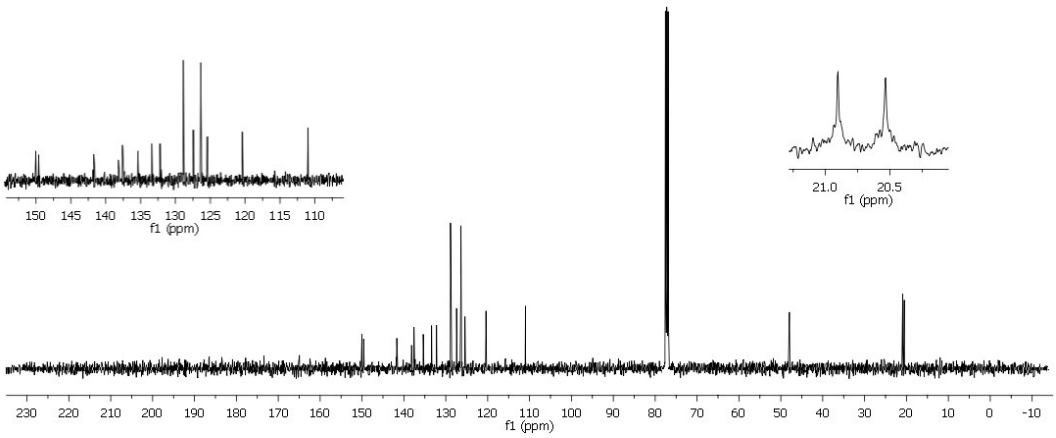
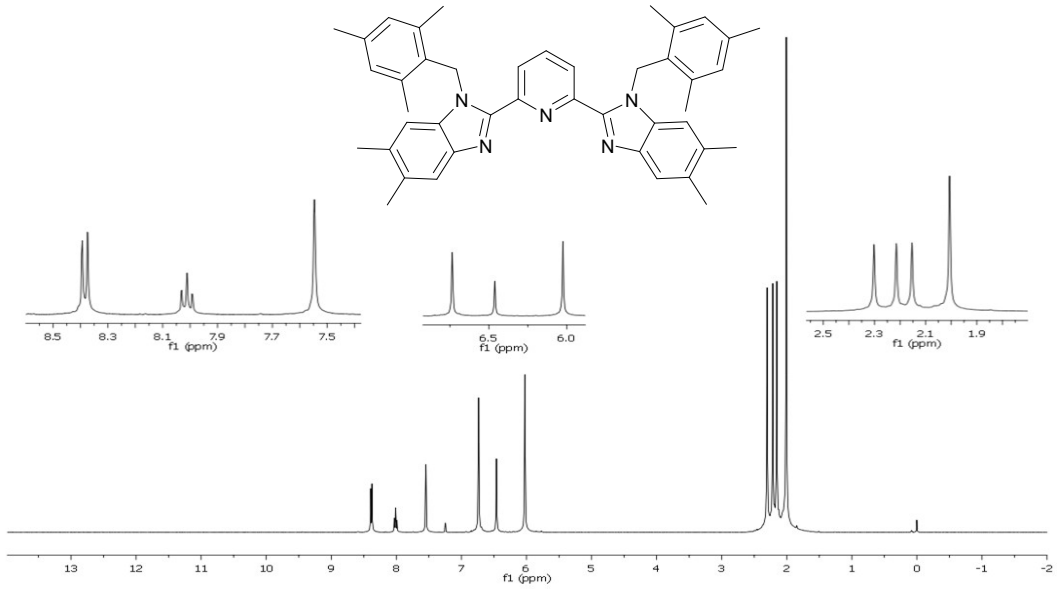


16- ^{1}H NMR of **2c**



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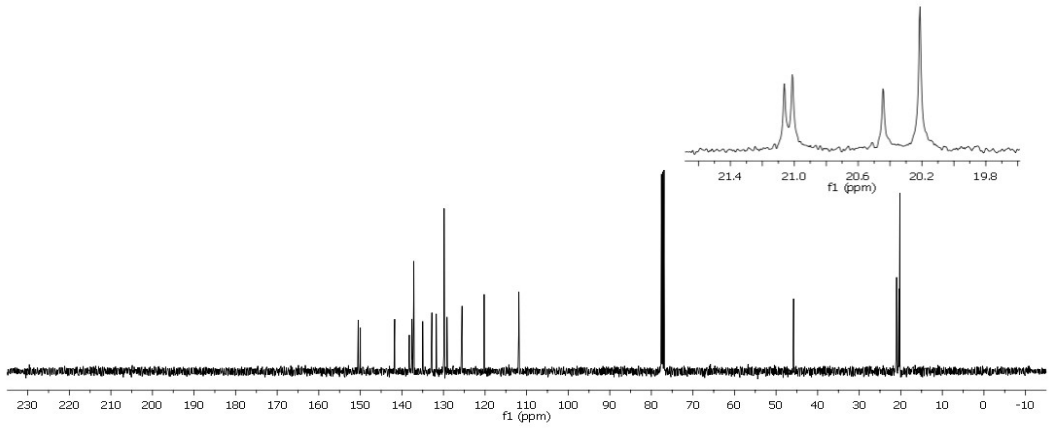
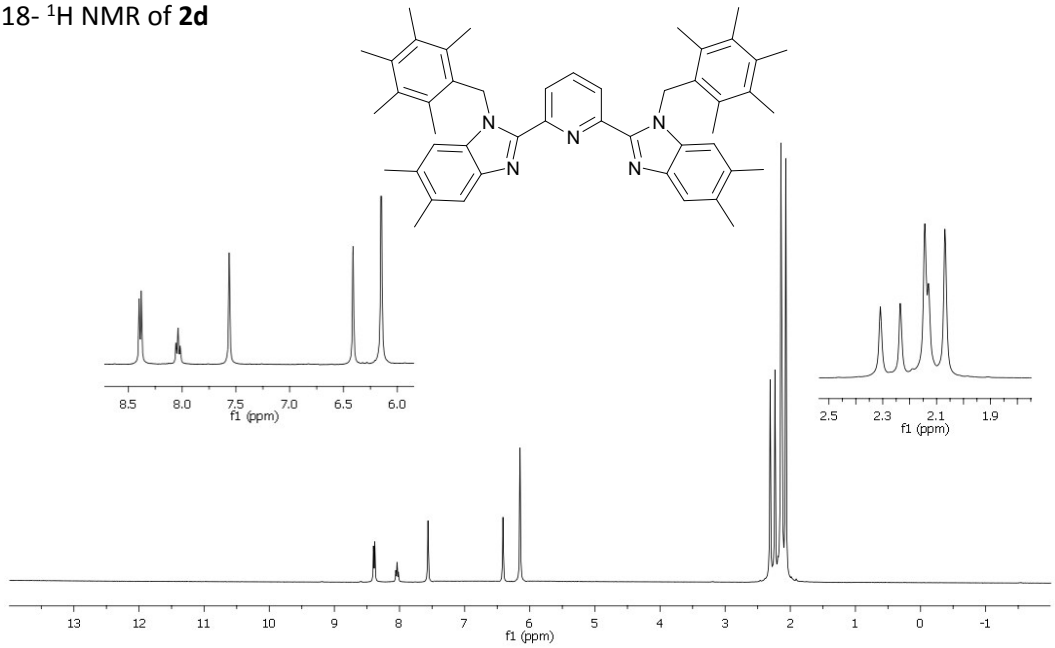


18- ^{1}H NMR of **2d**



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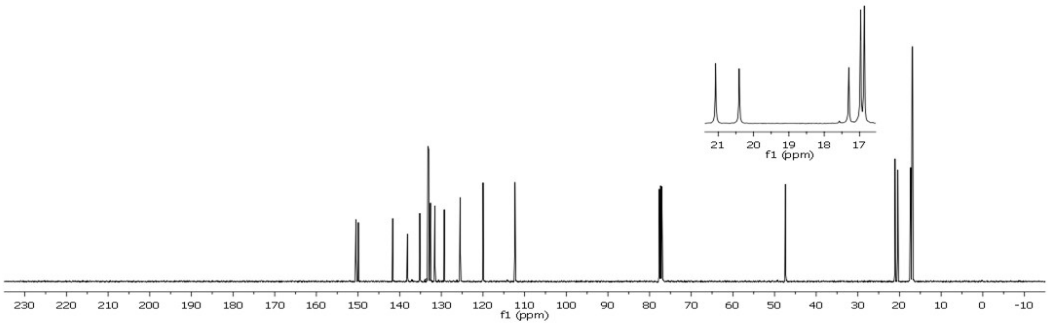

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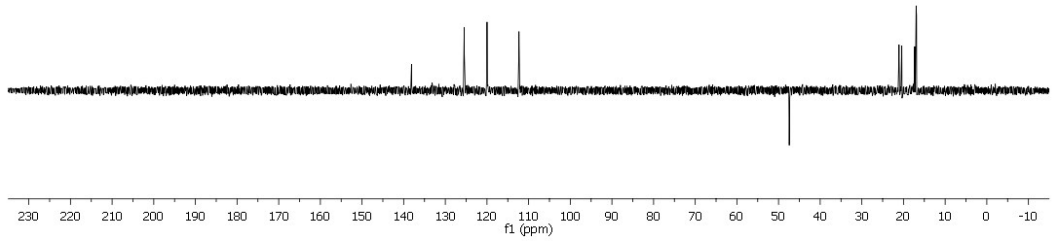

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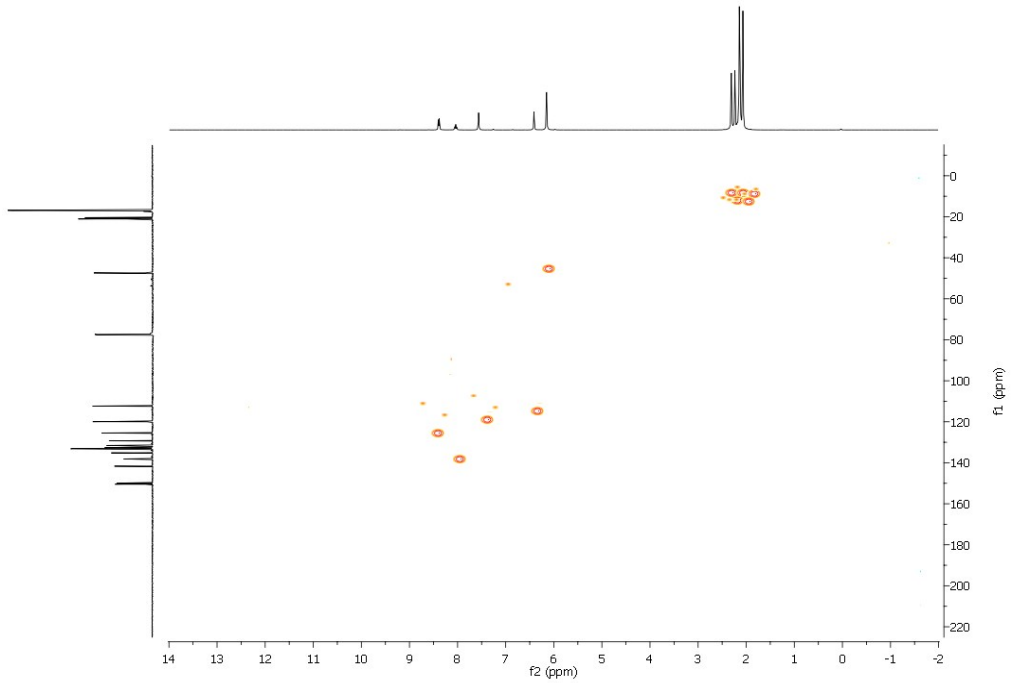

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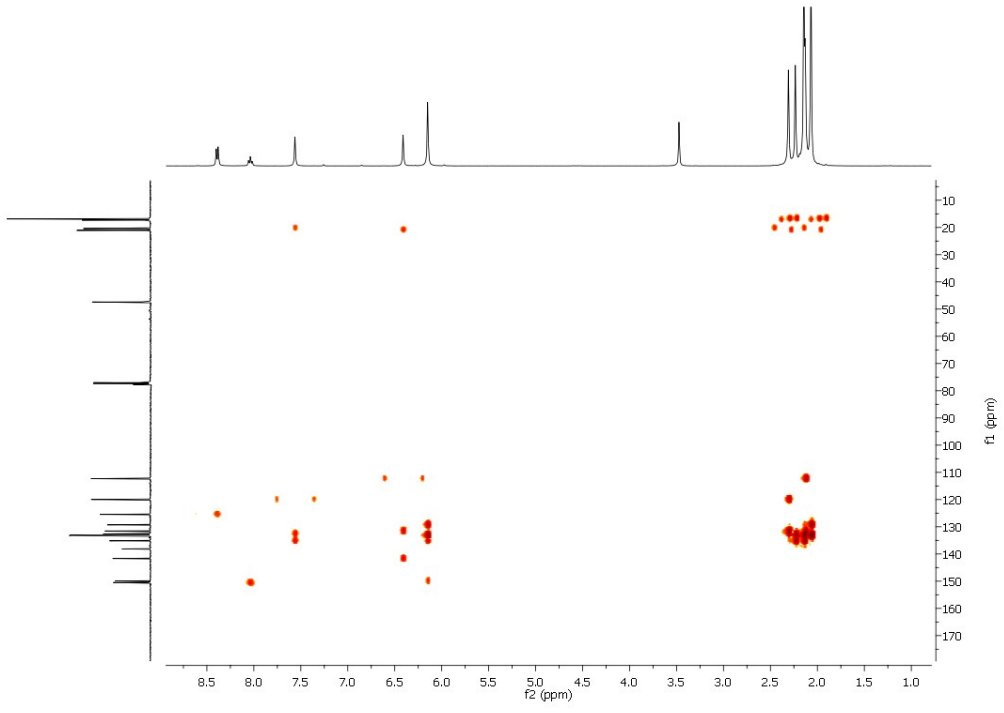
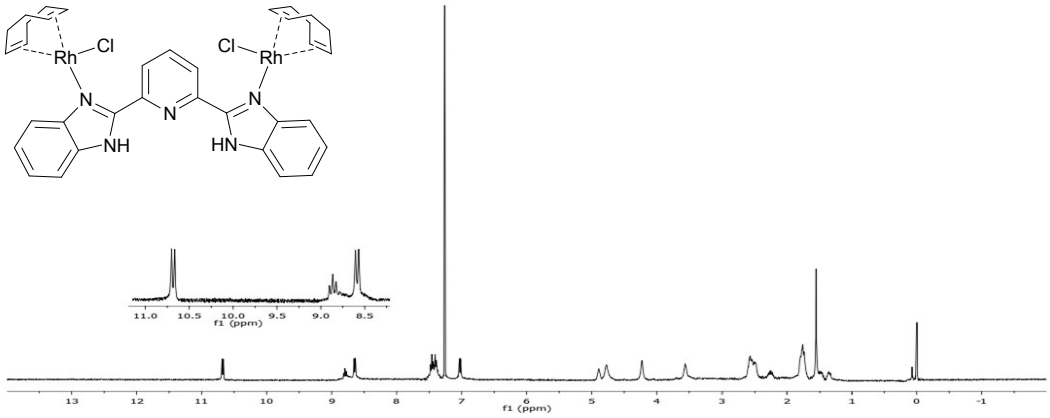


23- ^{1}H NMR of **3a**



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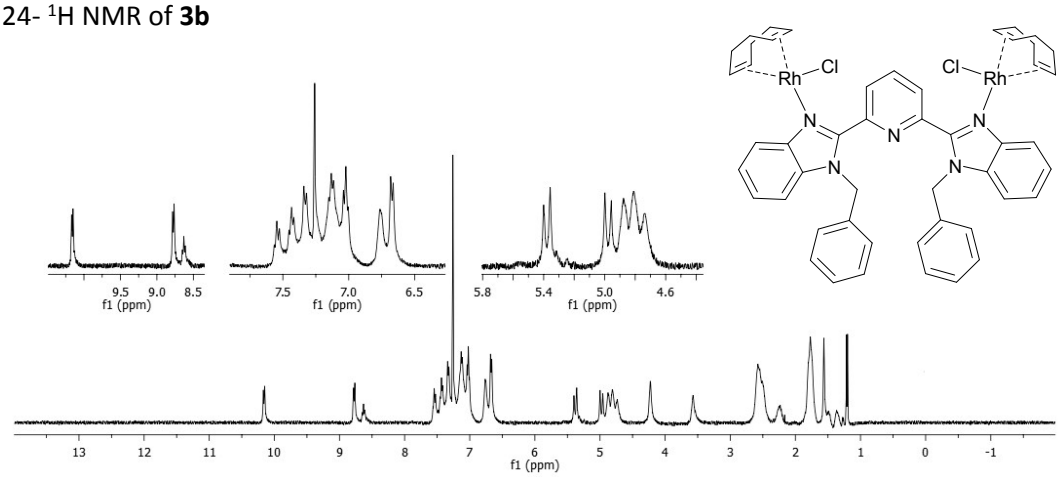

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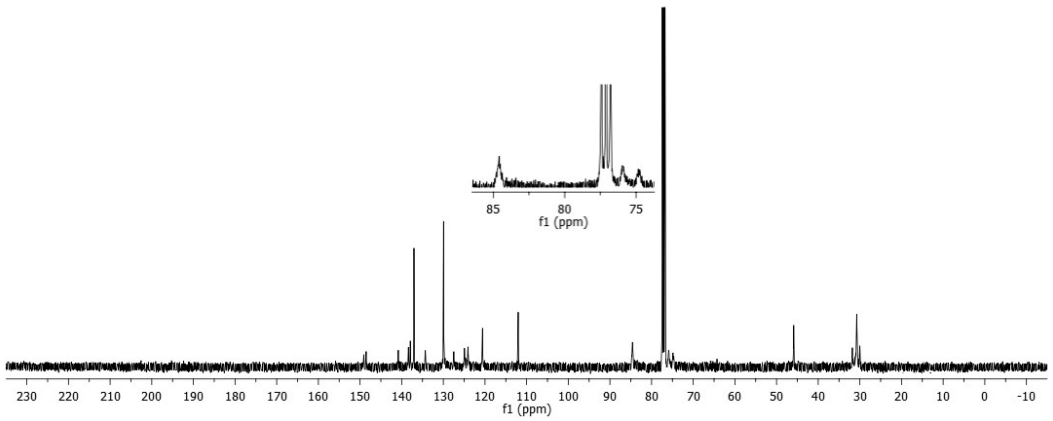

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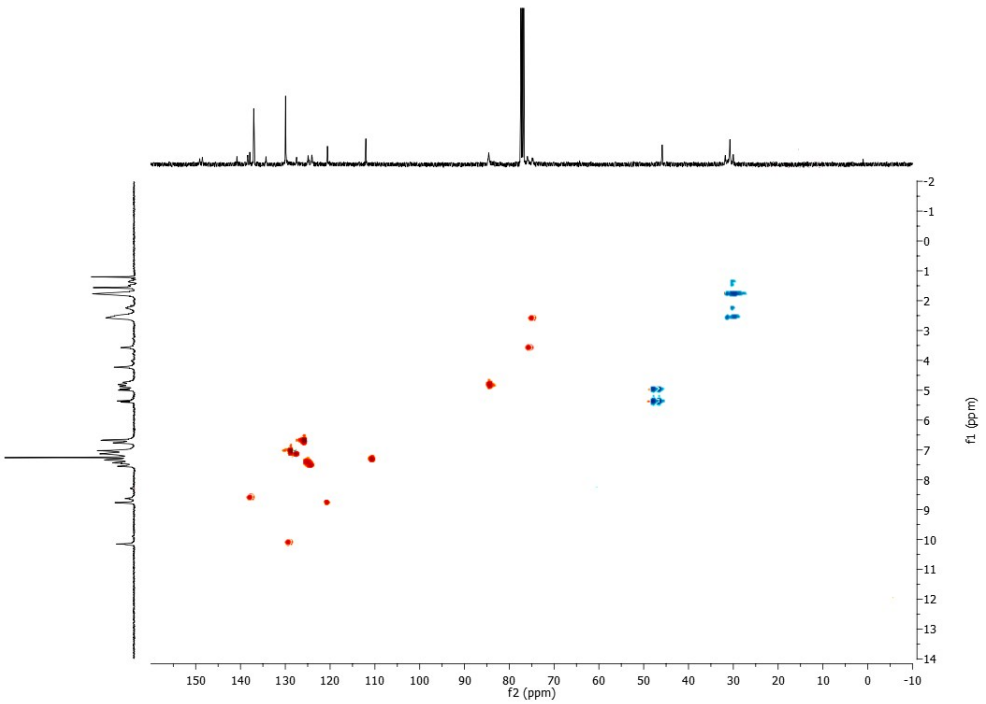
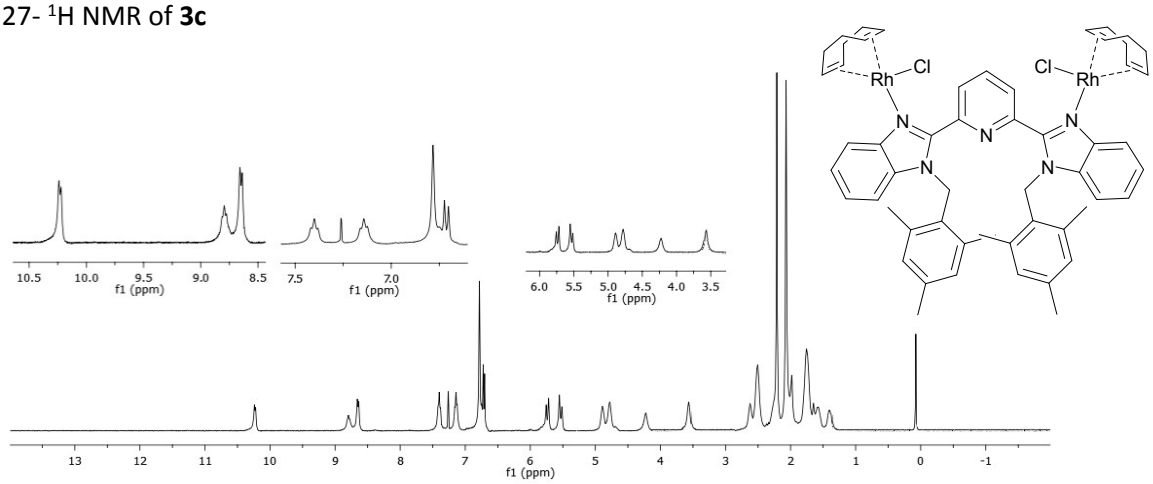
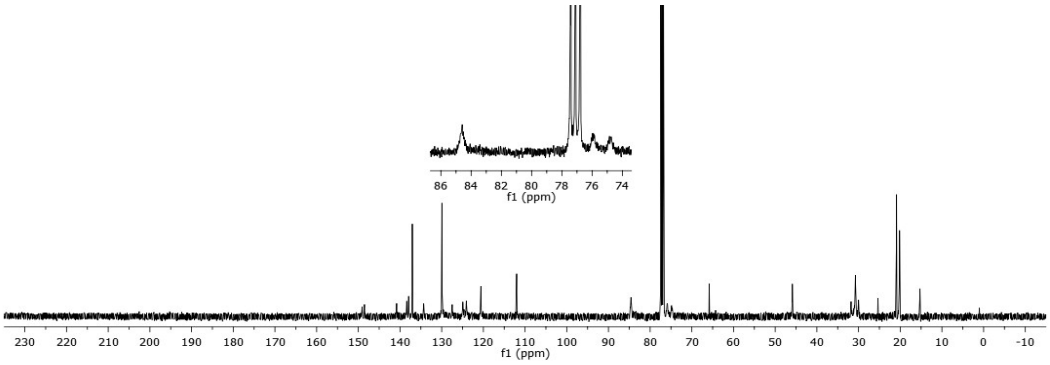


27- ^{1}H NMR of **3c**



28- ^{13}C NMR of **3c**



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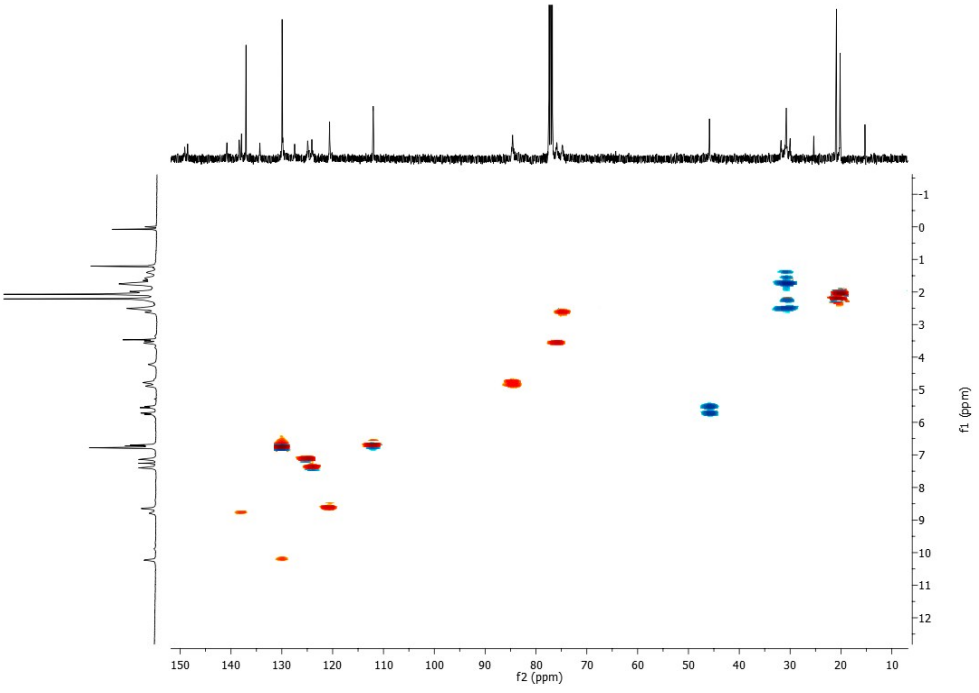
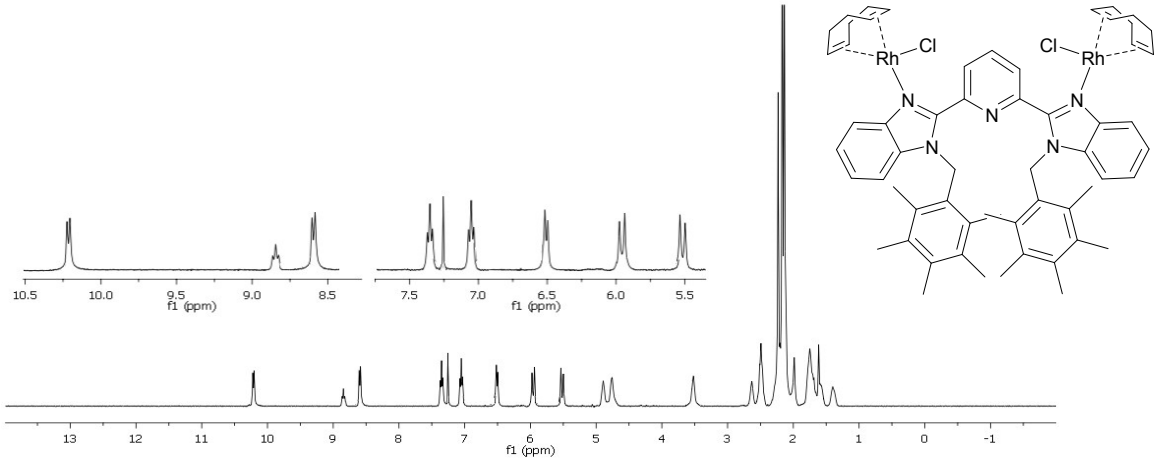
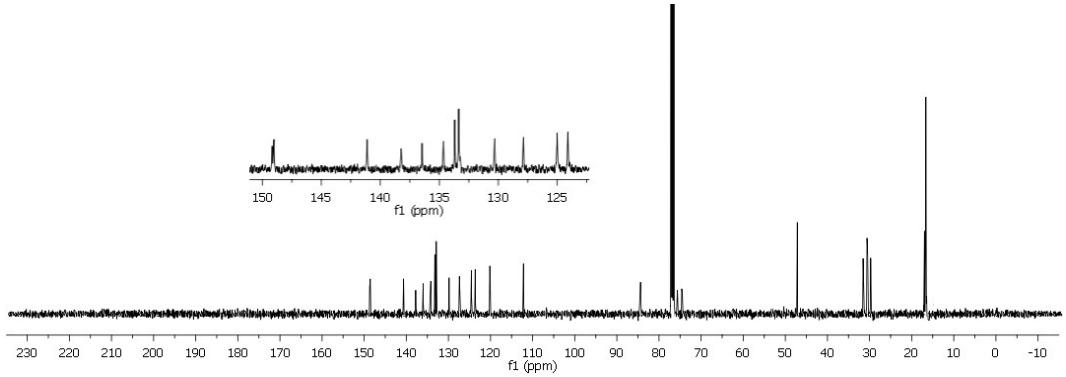


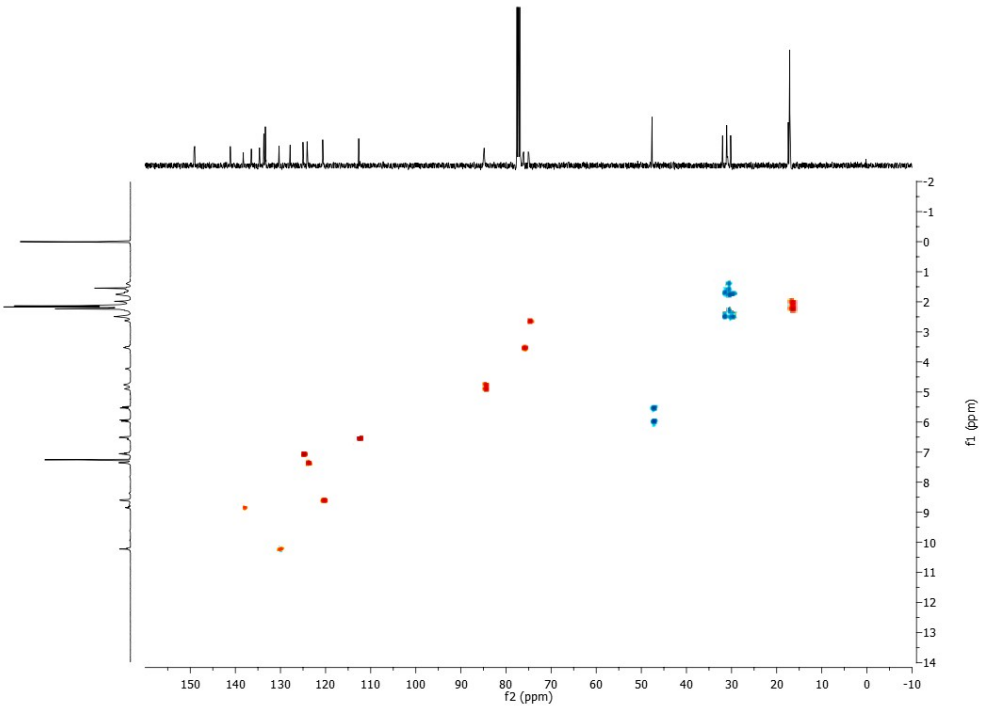
30- ^{1}H NMR of **3d**



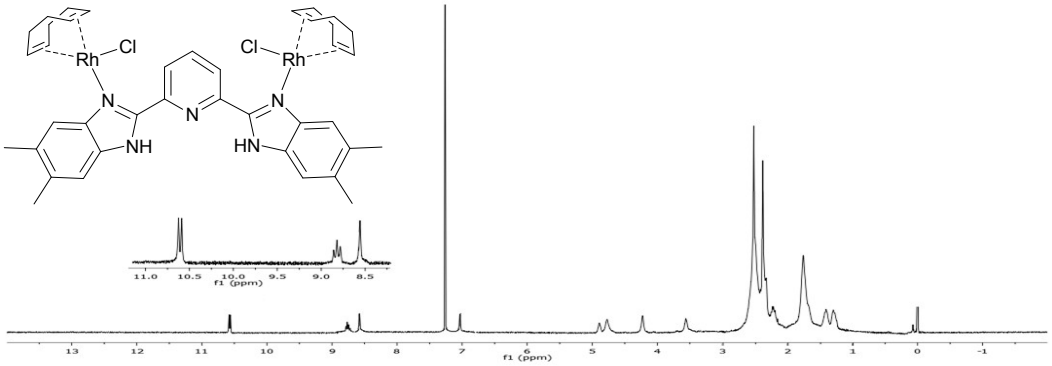
31- ^{13}C NMR of **3d**



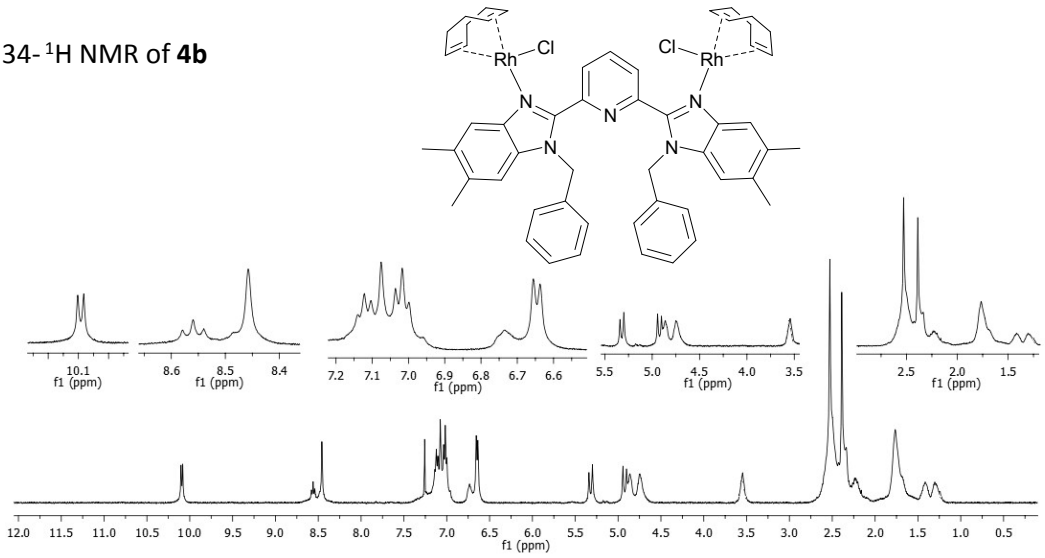
32- HSQC NMR of **3d**



33- ^{1}H NMR of **4a**



34- ^{1}H NMR of **4b**



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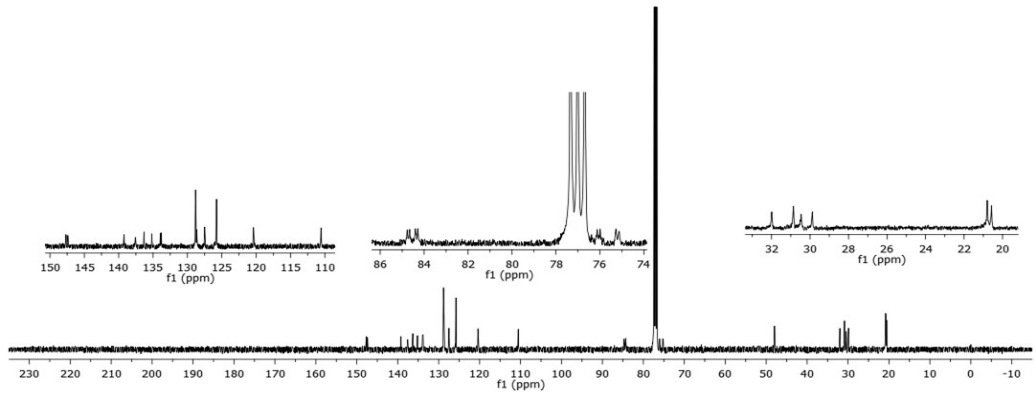

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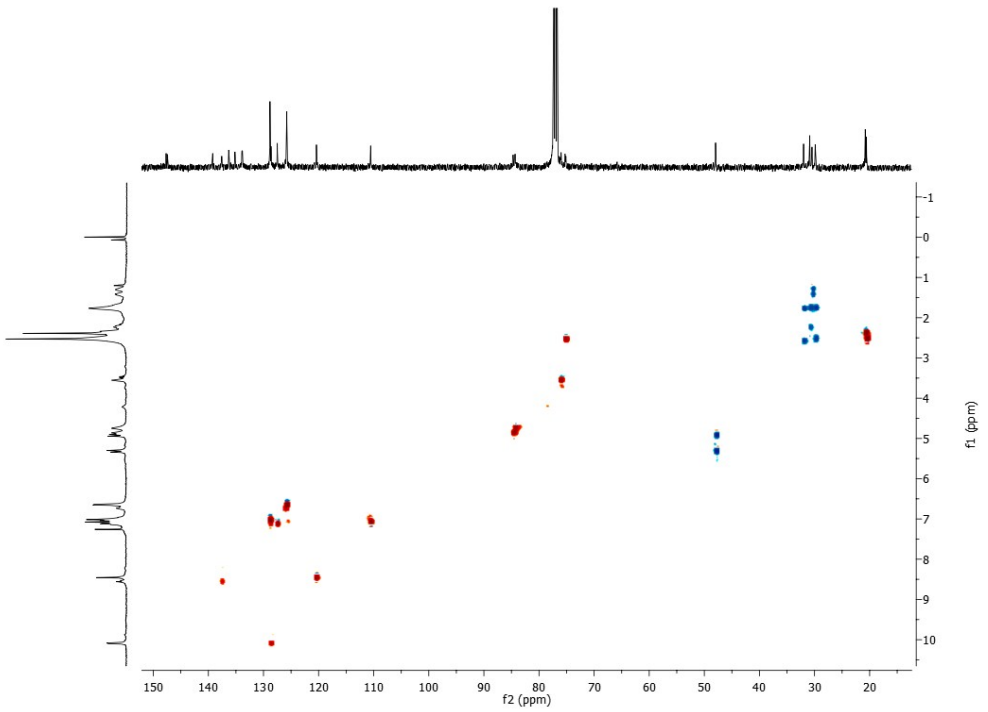
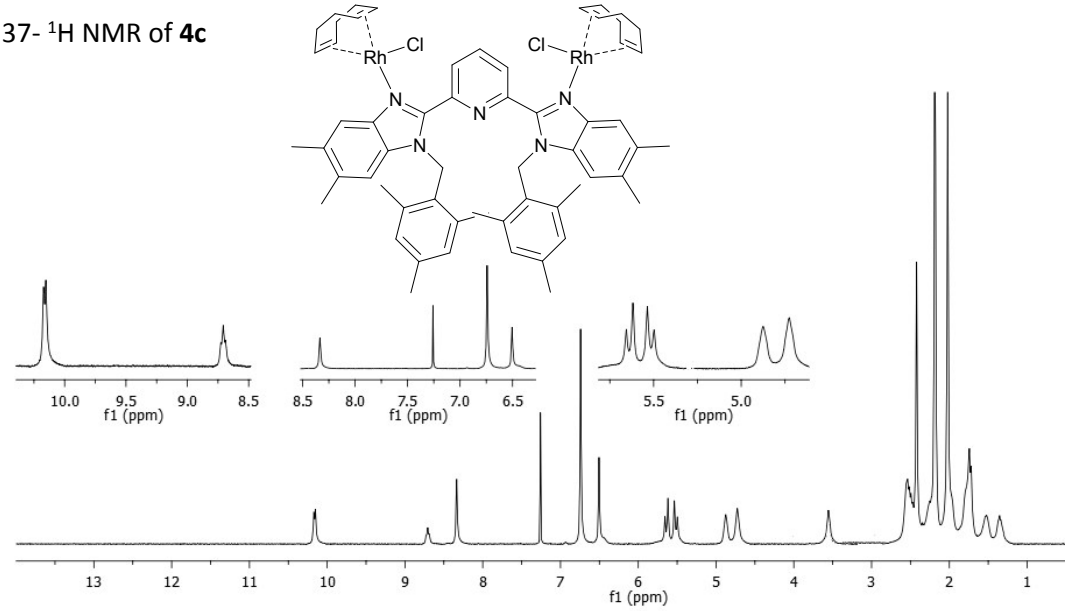
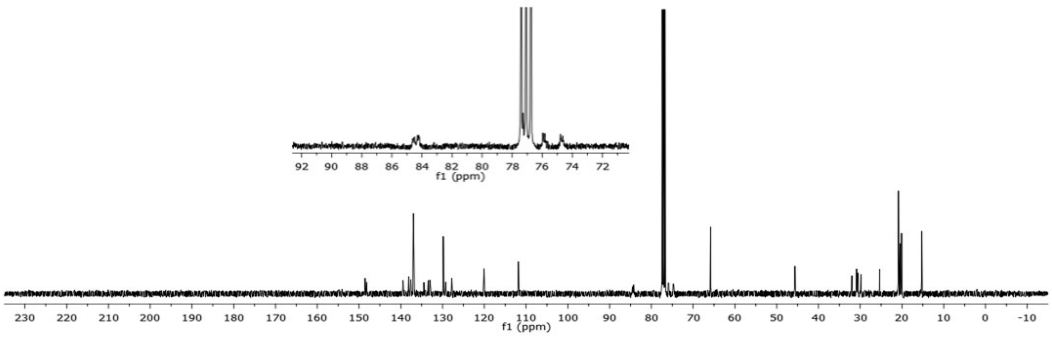


37- ^{1}H NMR of **4c**



38- ^{13}C NMR of **4c**



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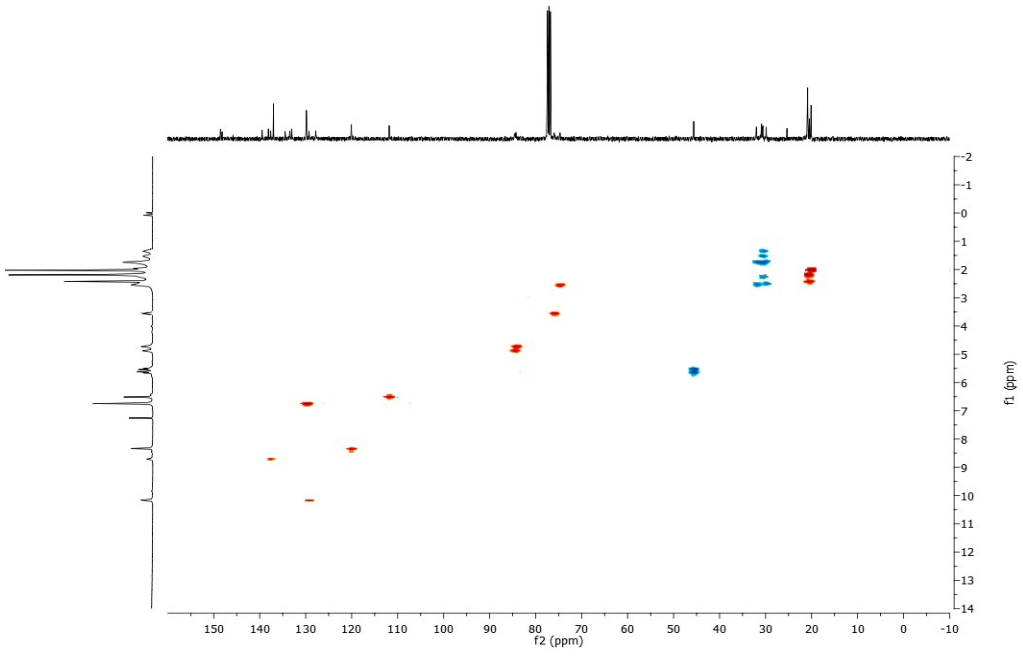
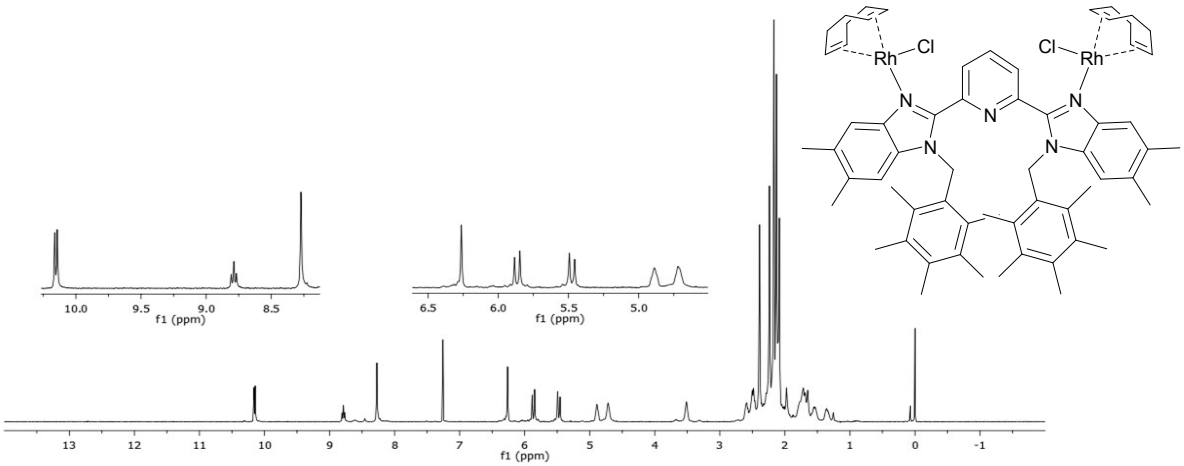


40- ^{1}H NMR of **4d**



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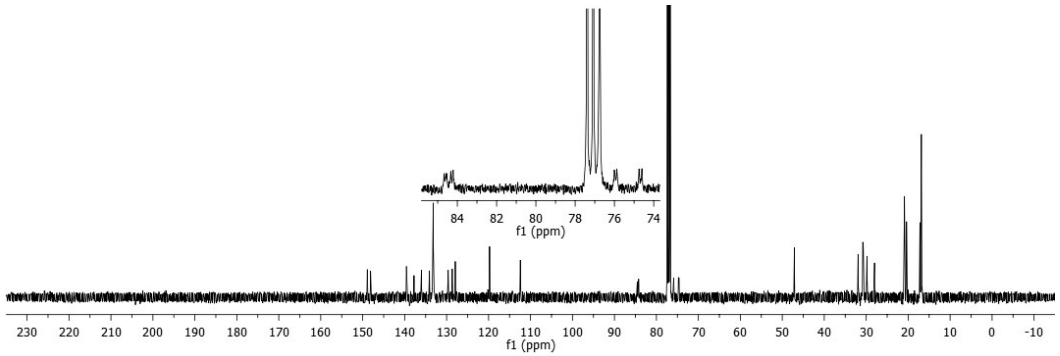

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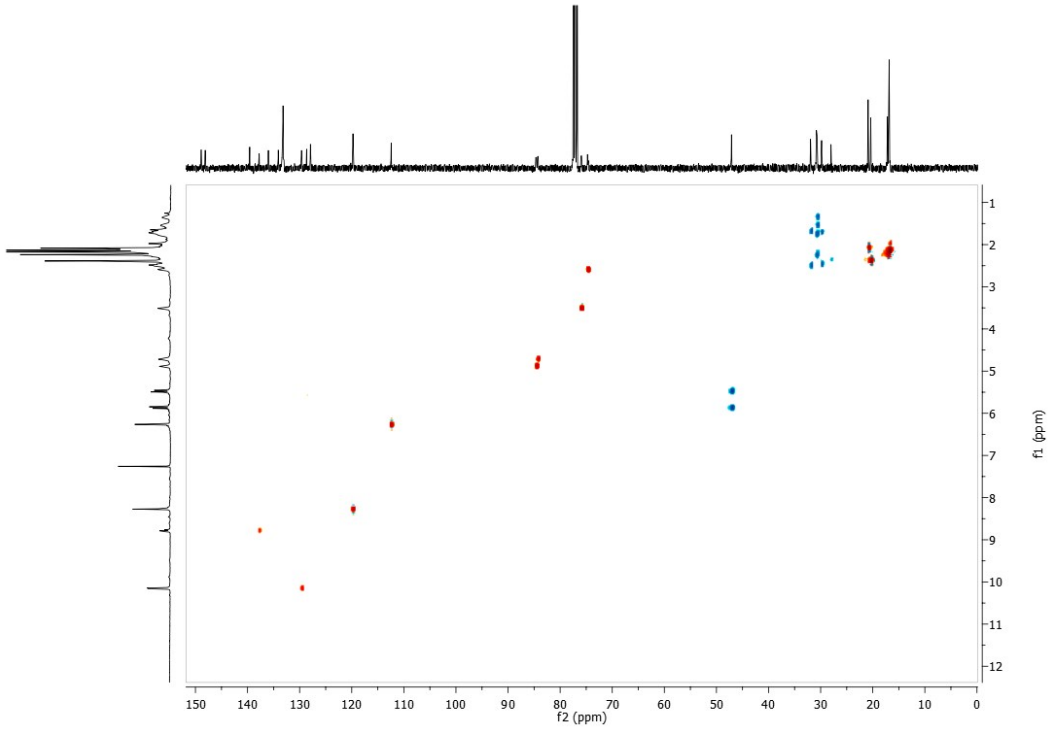
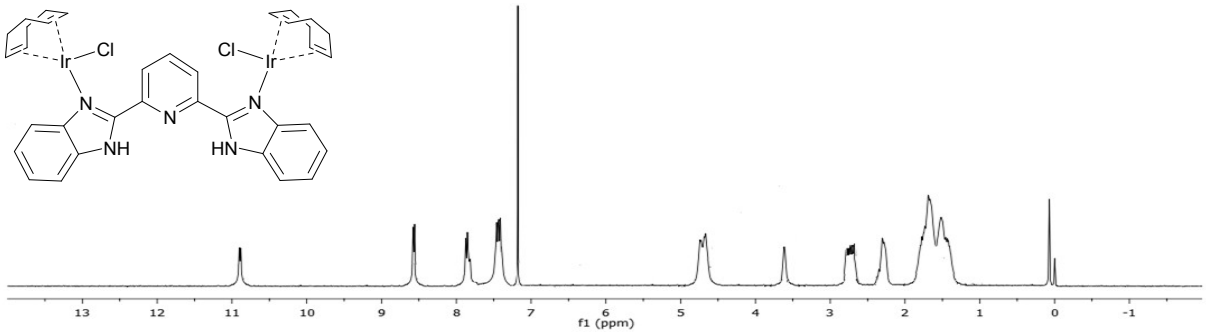


43- ^{1}H NMR of **5a**



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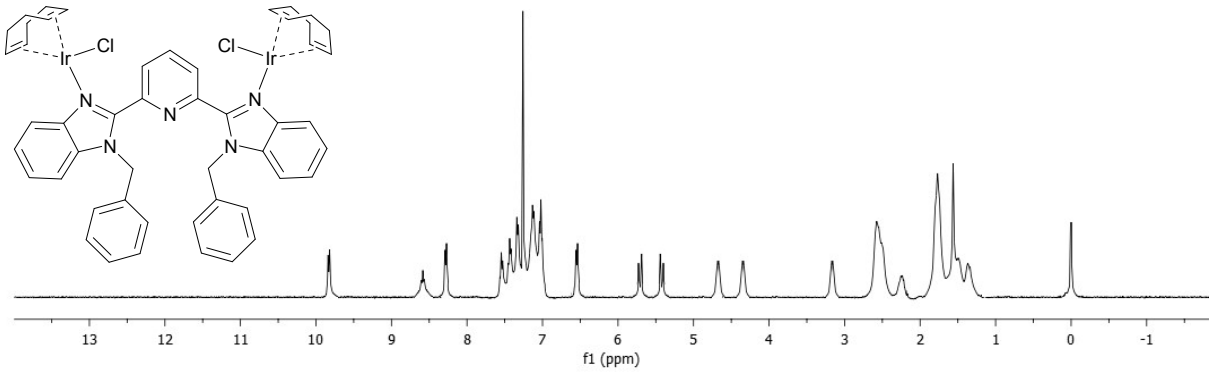
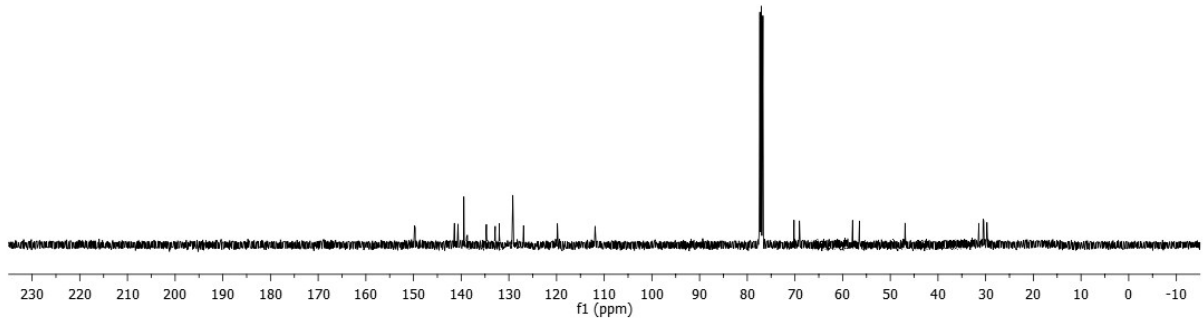
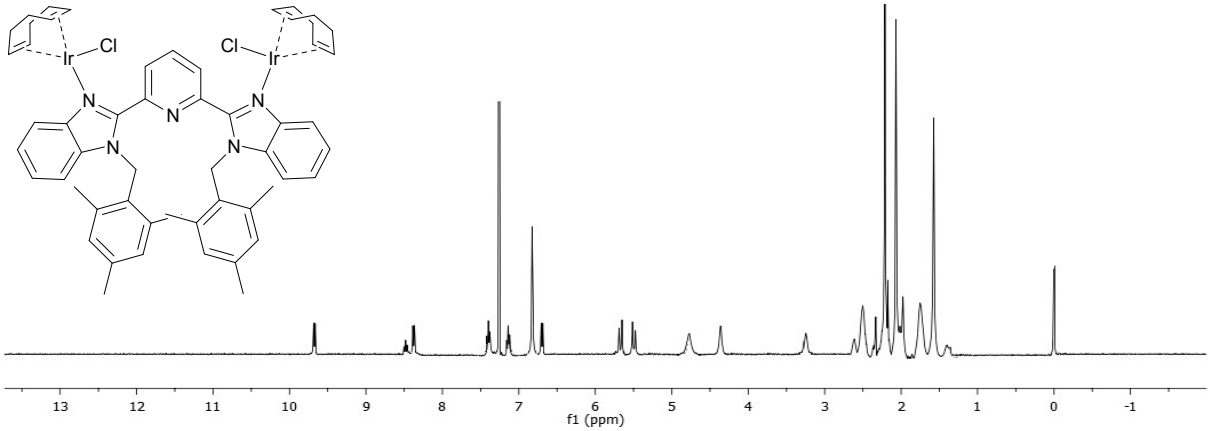


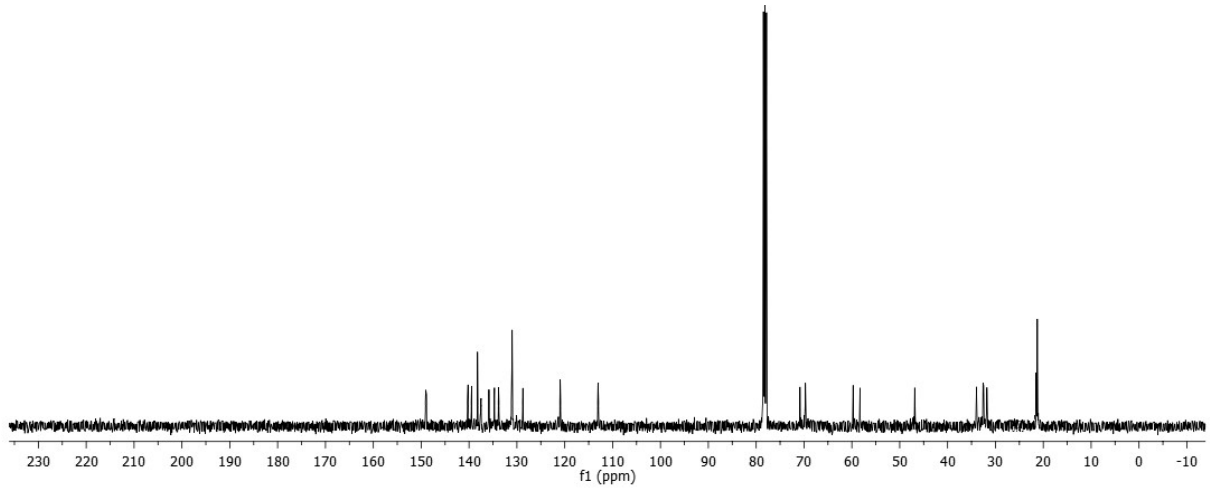
45- ^{13}C NMR of **5b**



46- ^{1}H NMR of **5c**



47- ^{13}C NMR of **5c**



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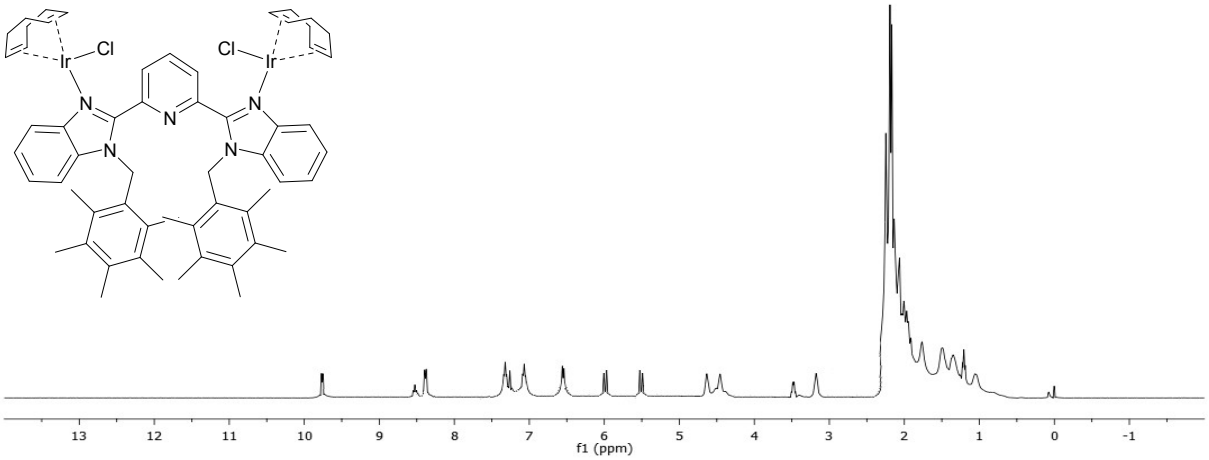

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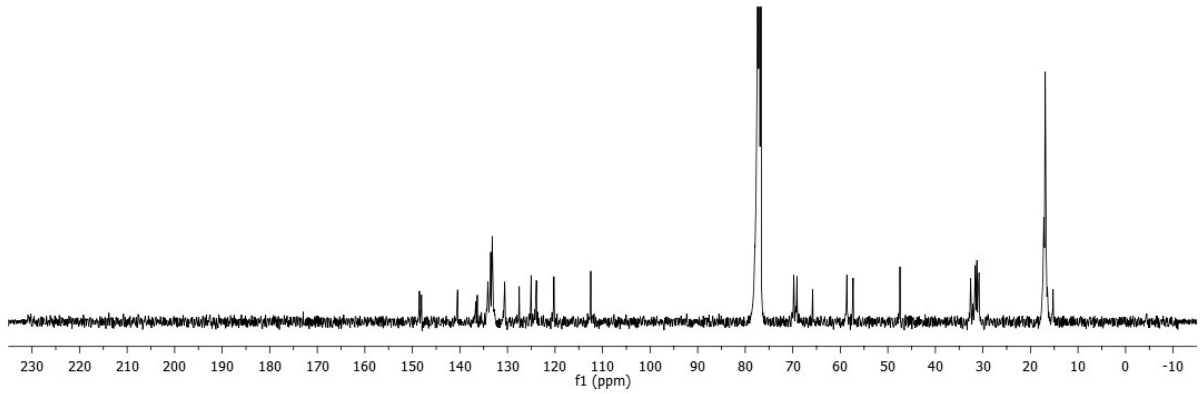
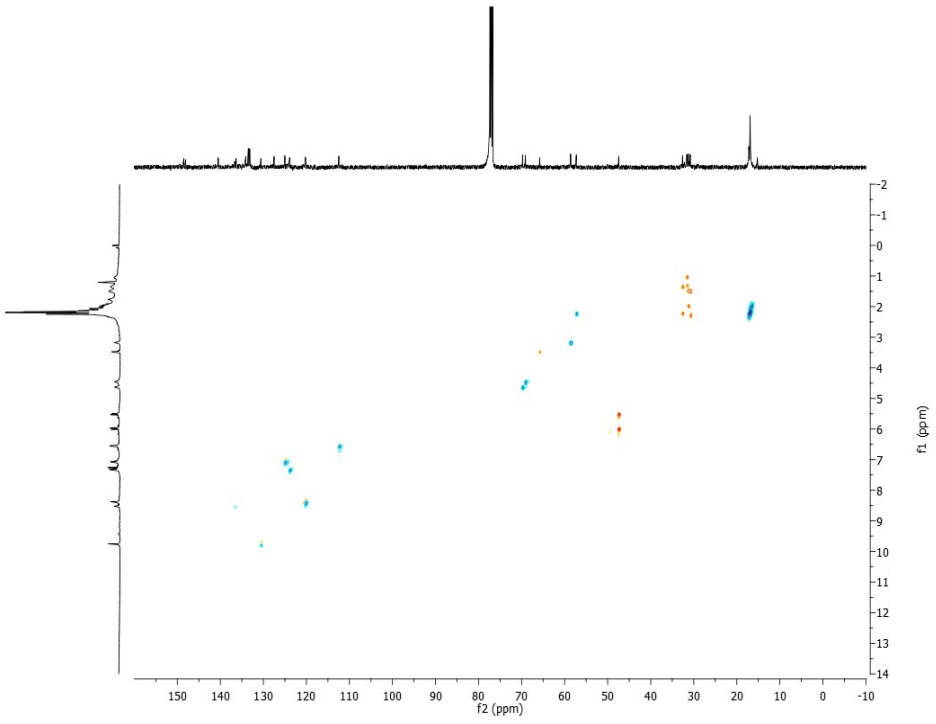
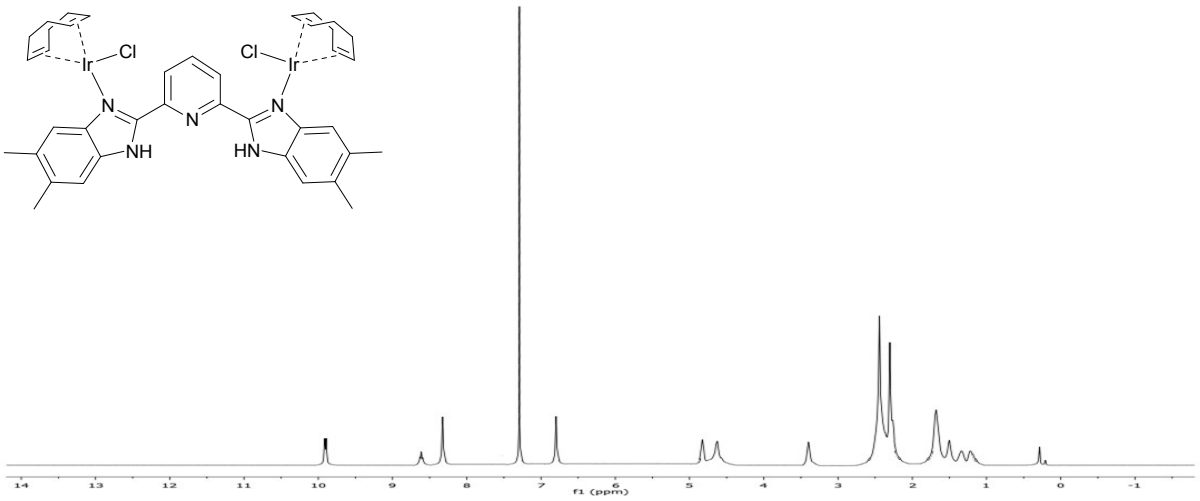


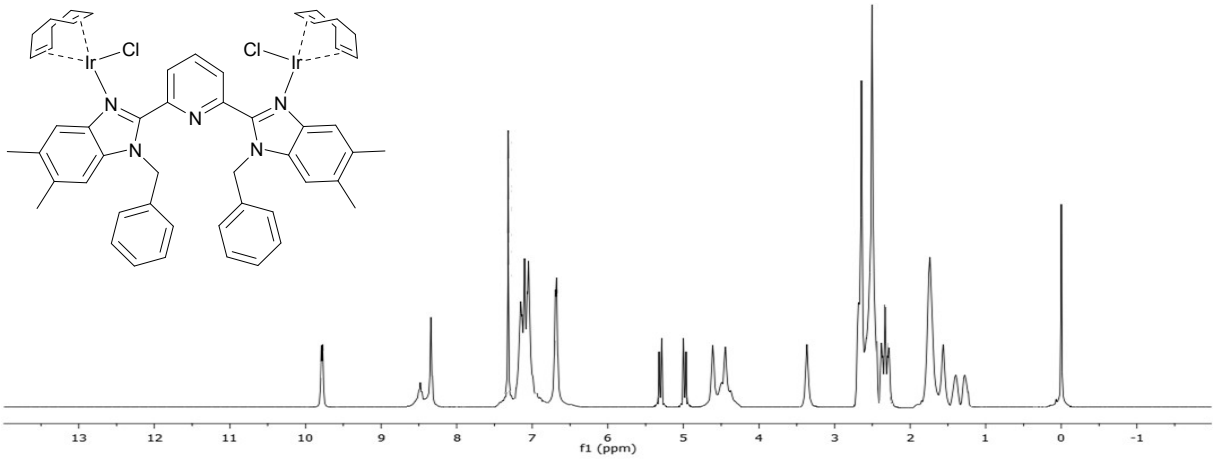
50- HSQC NMR of **5d**



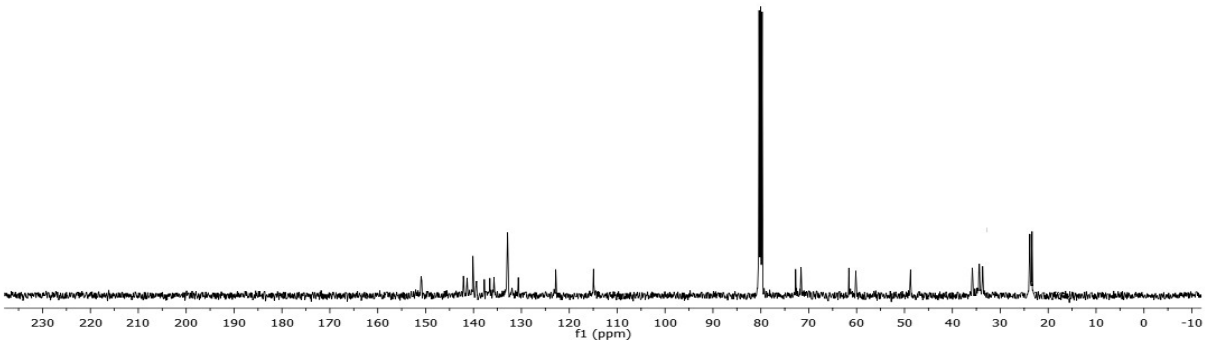
51- ^{1}H NMR of **6a**



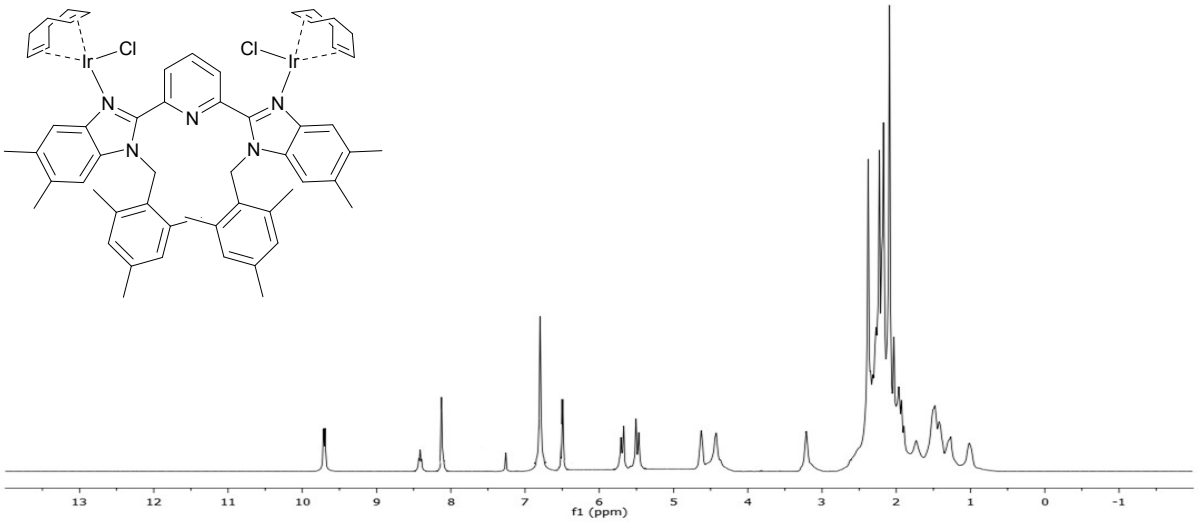
52- ^{1}H NMR of **6b**



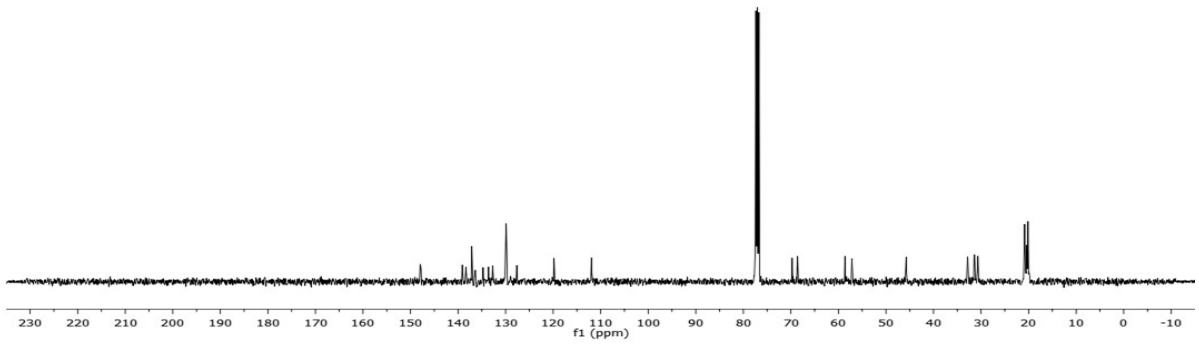
53- ^{13}C NMR of **6b**



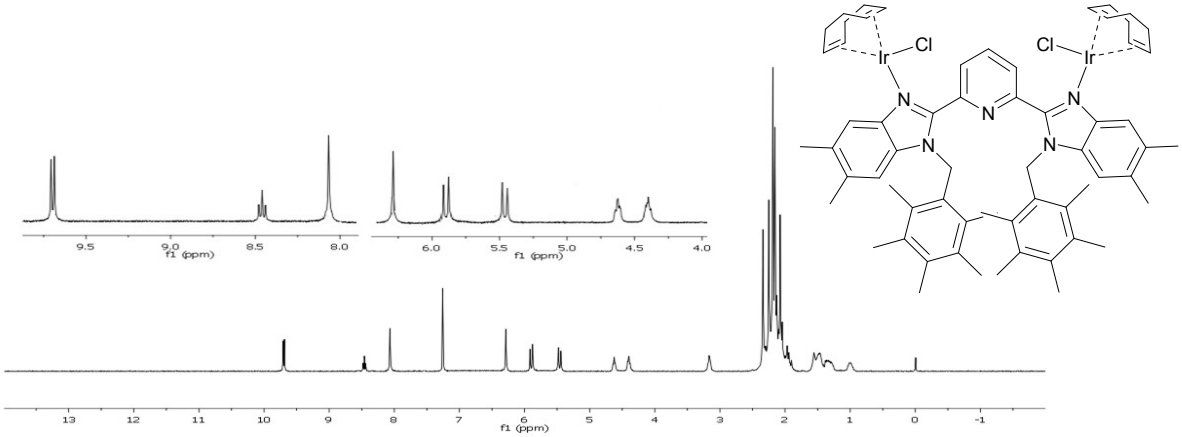
54- ^{1}H NMR of **6c**



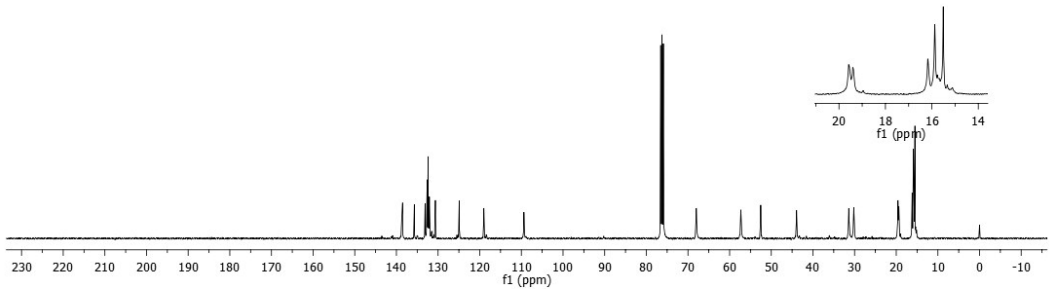
55- ^{13}C NMR of **6c**



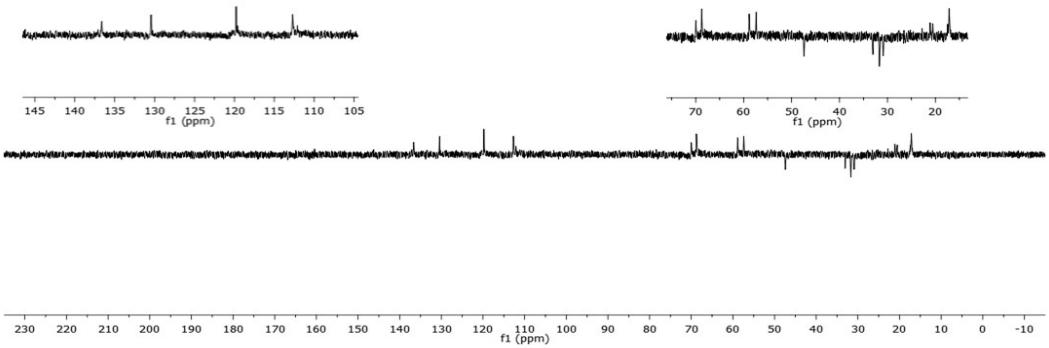
56- ^{1}H NMR of **6d**



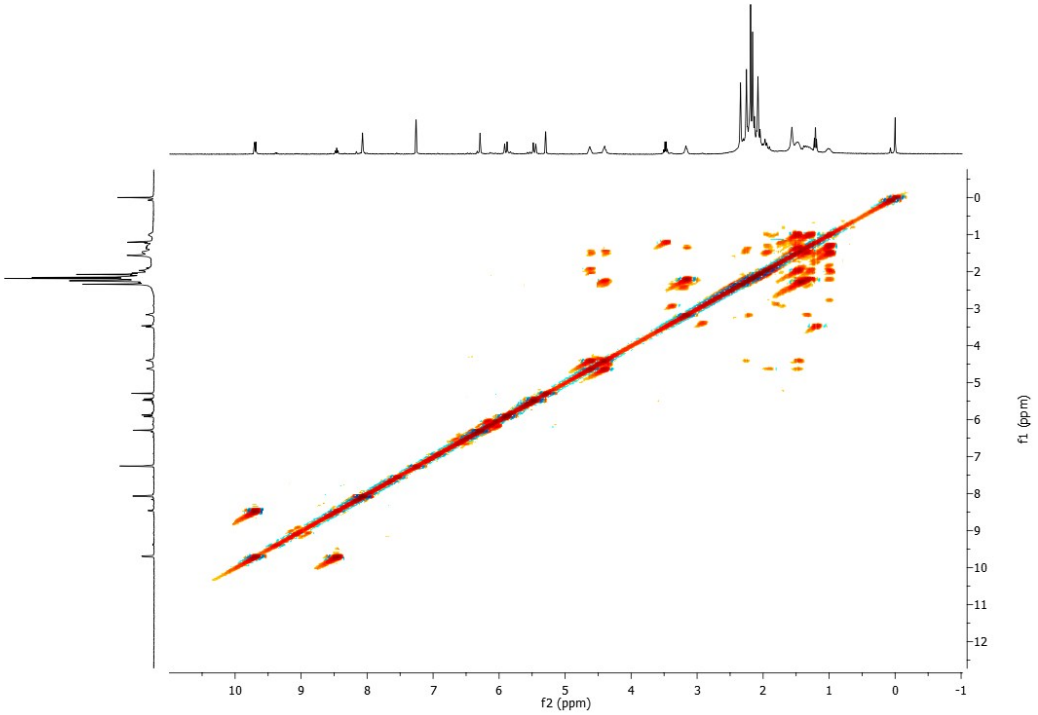
57- ^{13}C NMR of **6d**



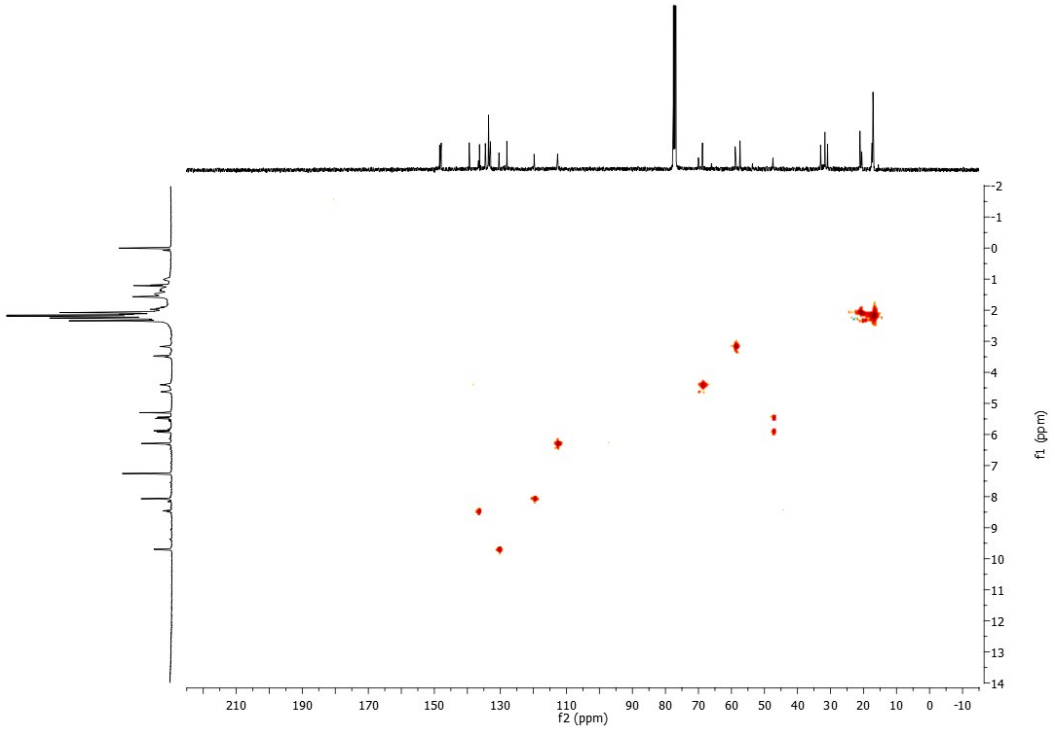
58- DEPT-135 NMR of **6d**



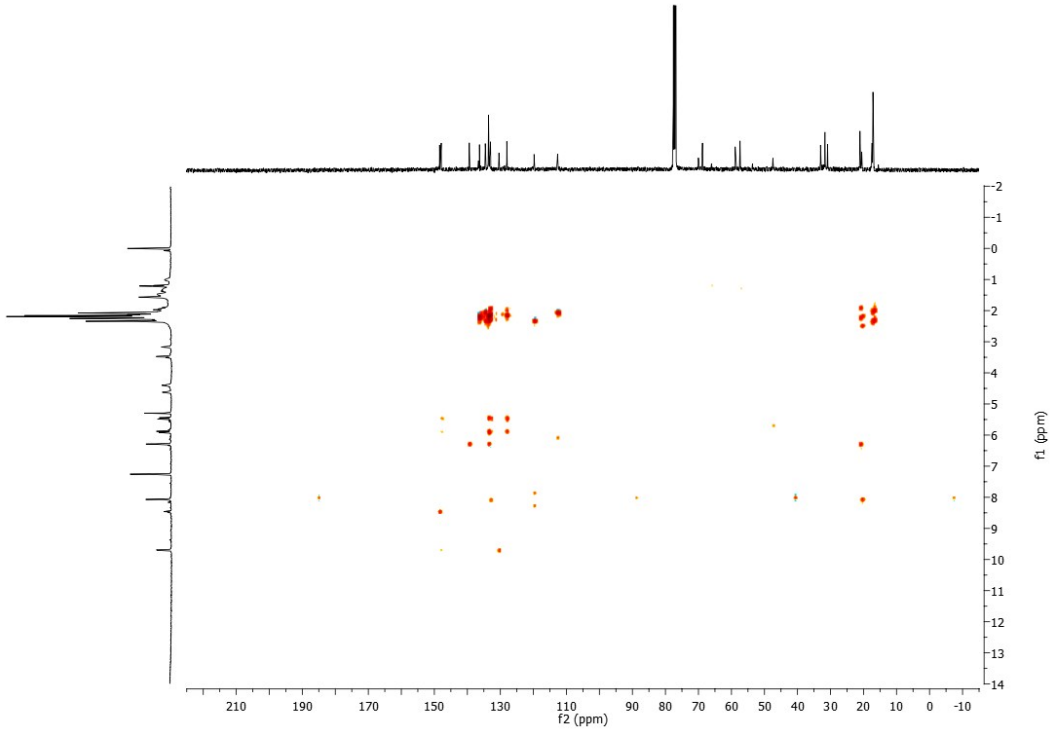
59- COSY NMR of **6d**



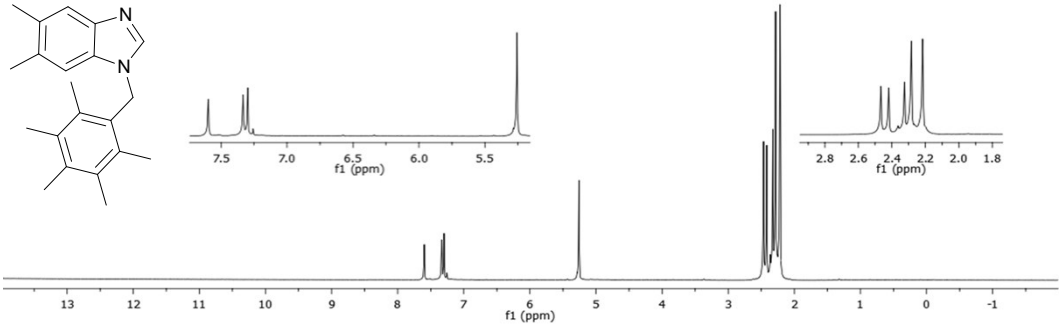
60- HMQC NMR of **6d**



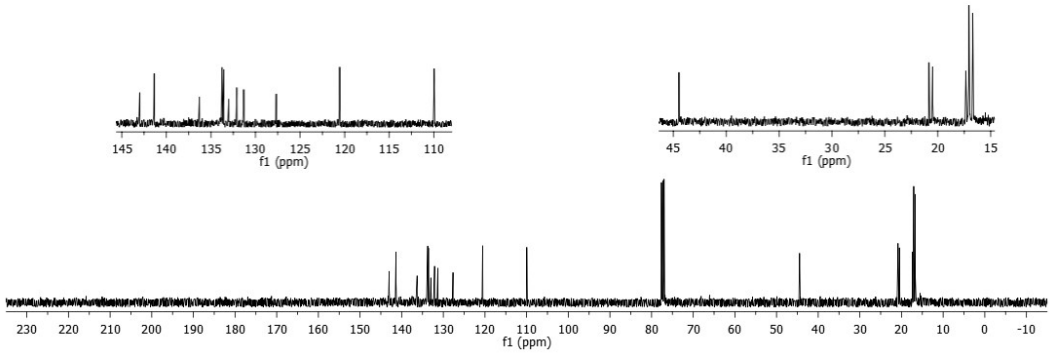
61- HMBC NMR of **6d**



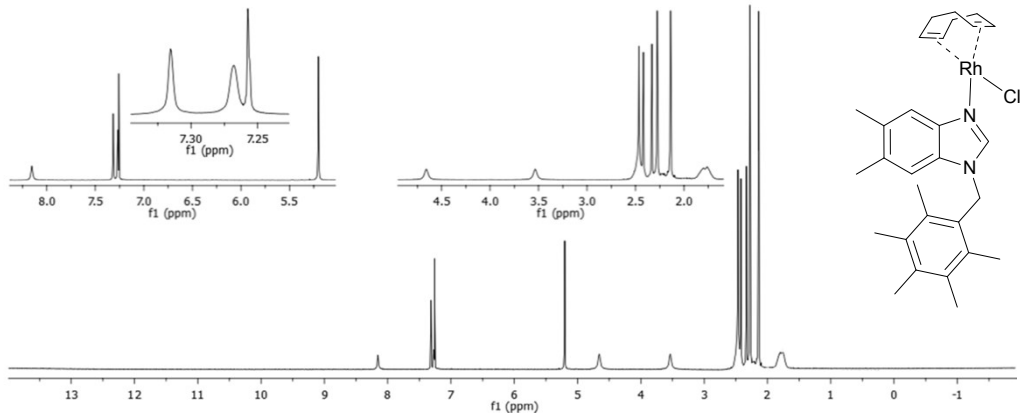
62- ^{1}H NMR of **7**



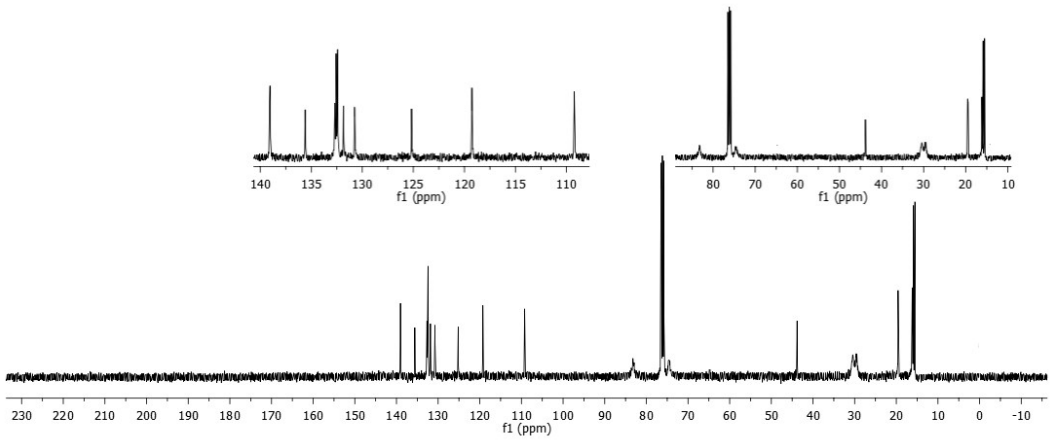
63- ^{13}C NMR of **7**



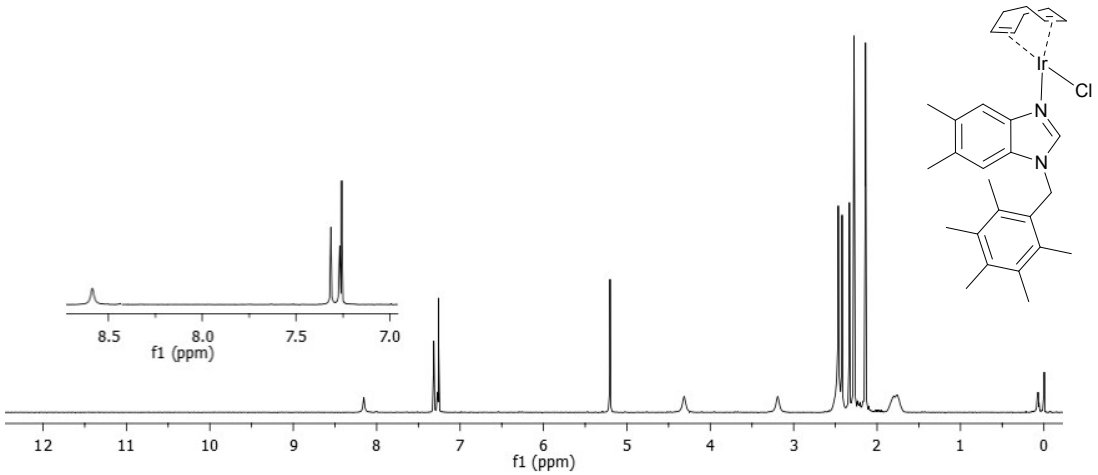
64- ^{1}H NMR of **8**



65- ^{13}C NMR of **8**

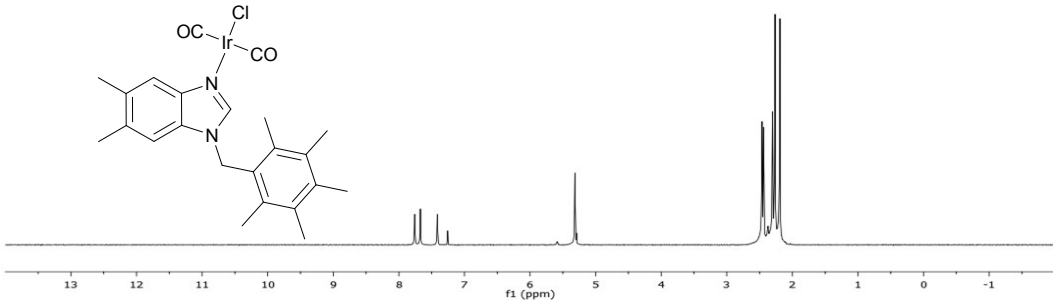


66- ^{1}H NMR of **9**

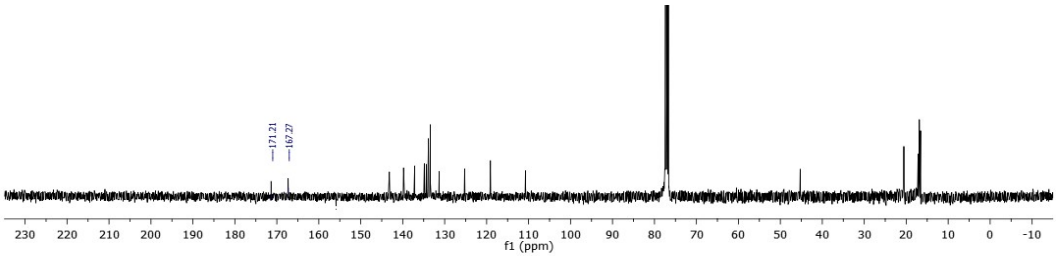


67- ^{13}C NMR of **9**

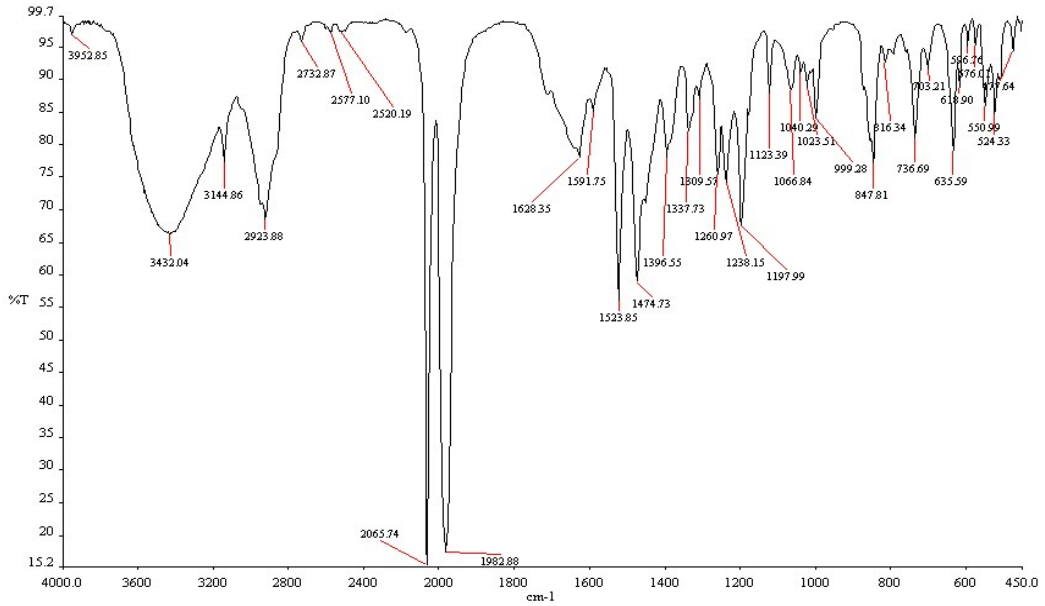
68- ^{1}H NMR of **9'**



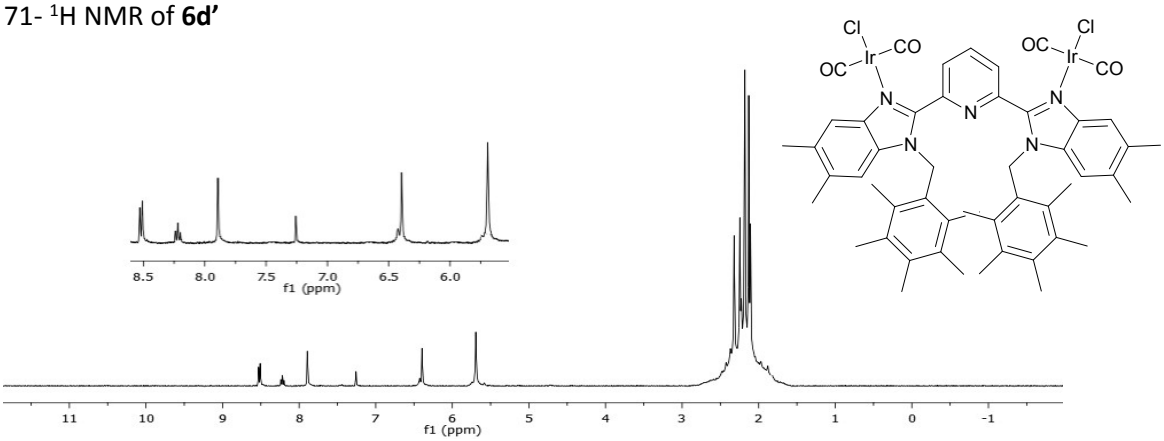
69- ^{13}C NMR of **9'**



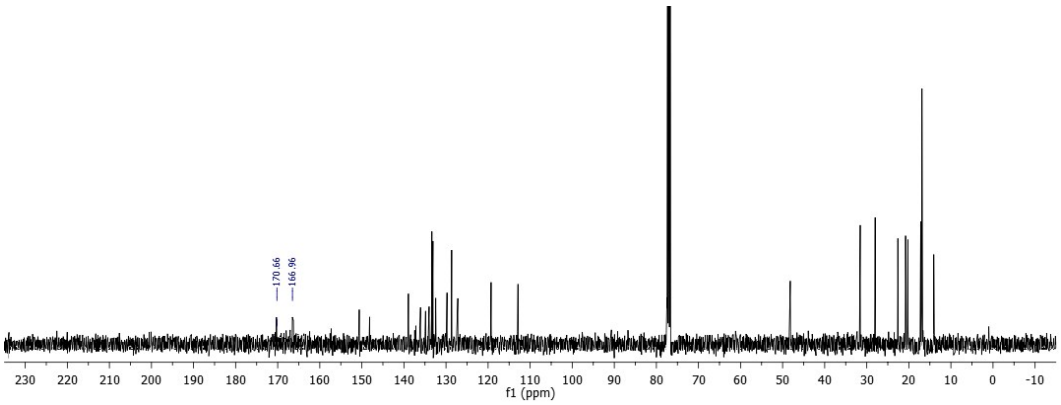
70- IR of **9'**



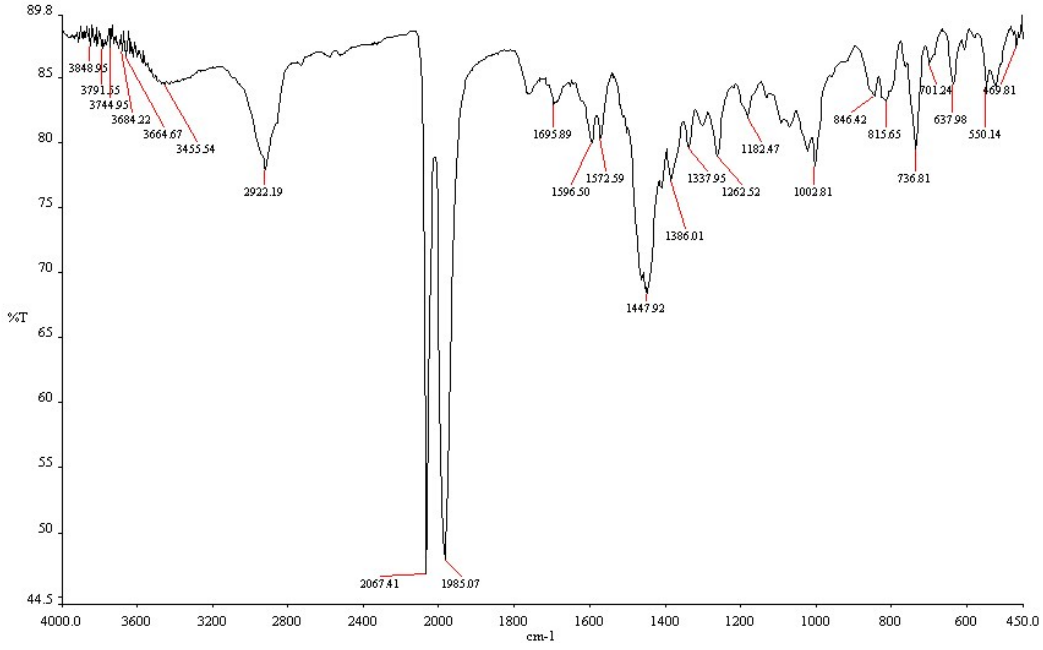
71- ^{1}H NMR of **6d'**



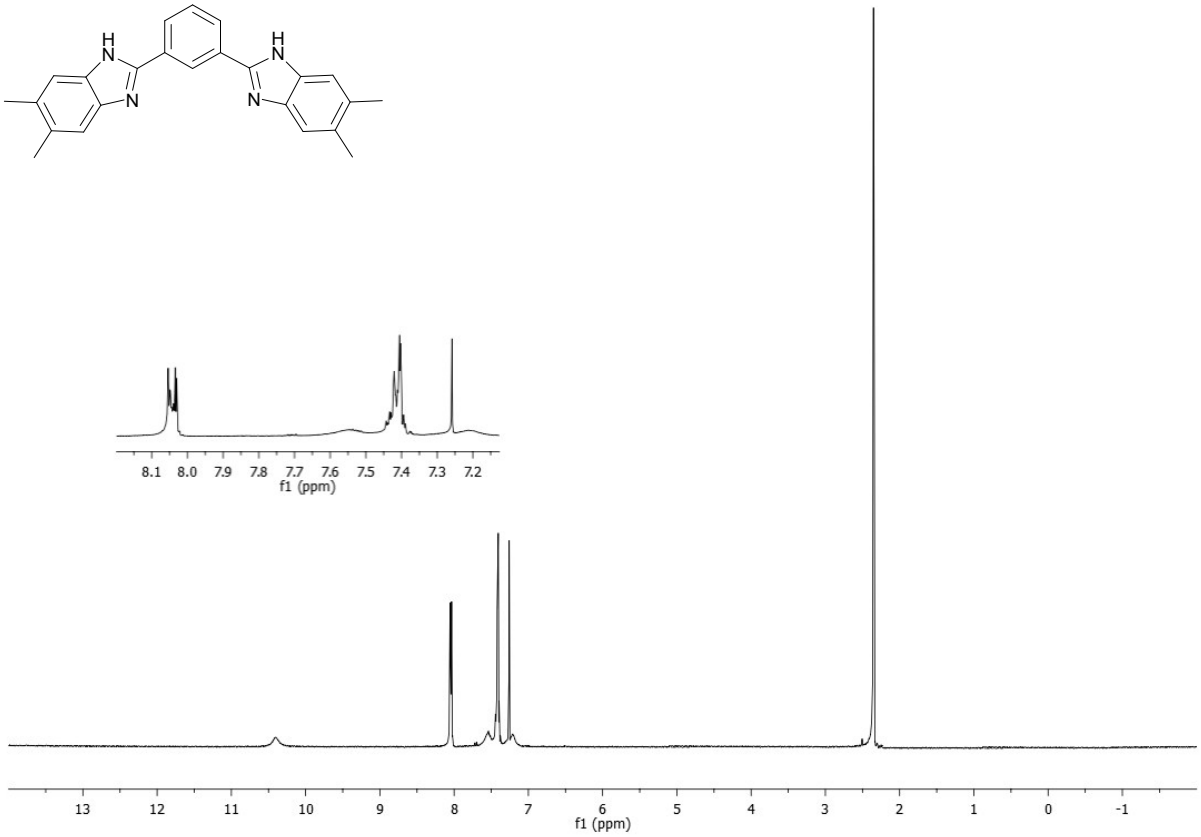
72- ^{13}C NMR of **6d'**



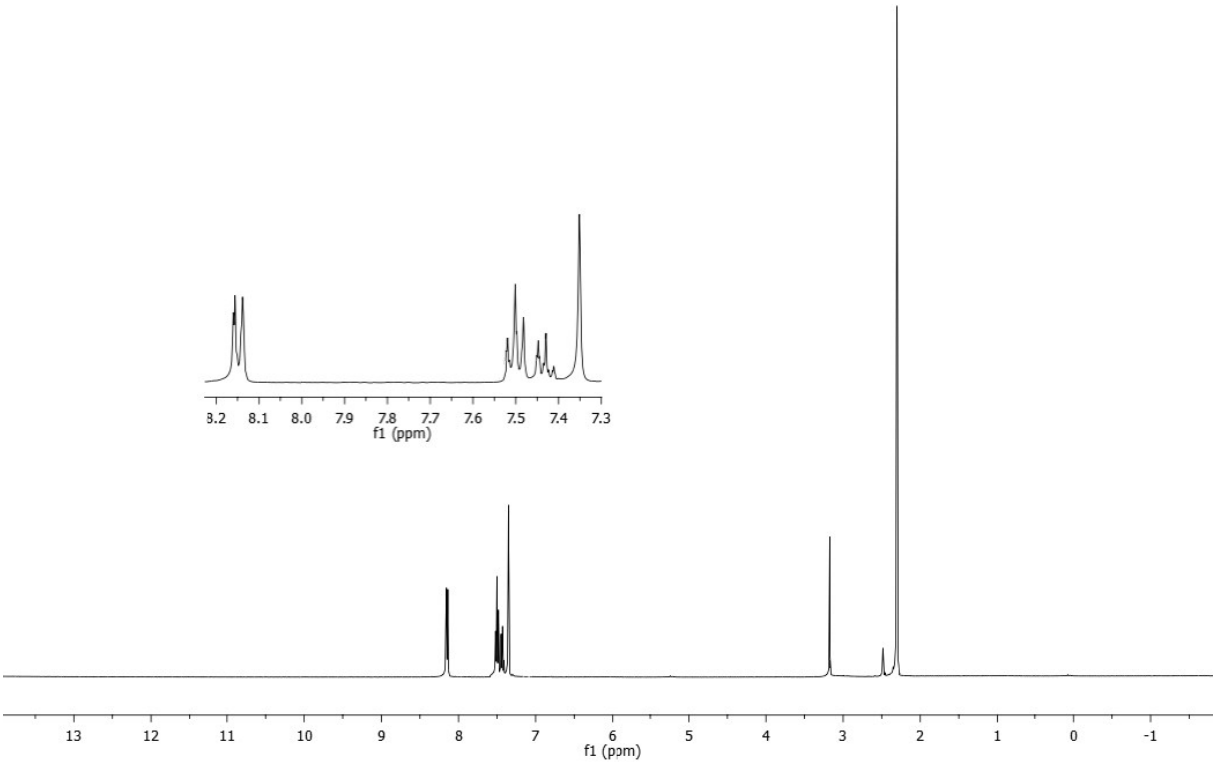
73- IR of **6d'**



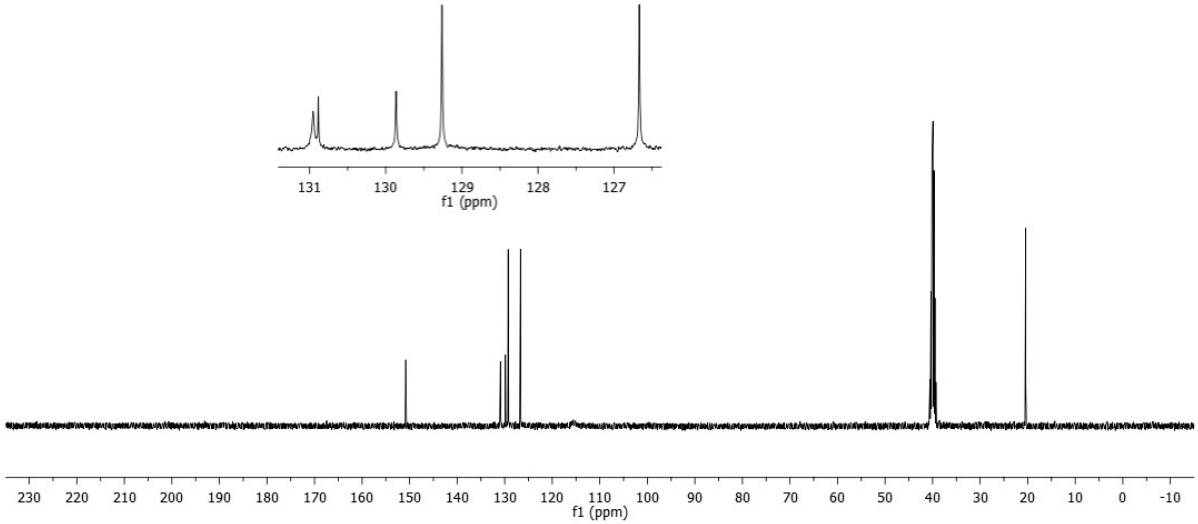
74- ^{1}H NMR of **10** in $CDCl_3$



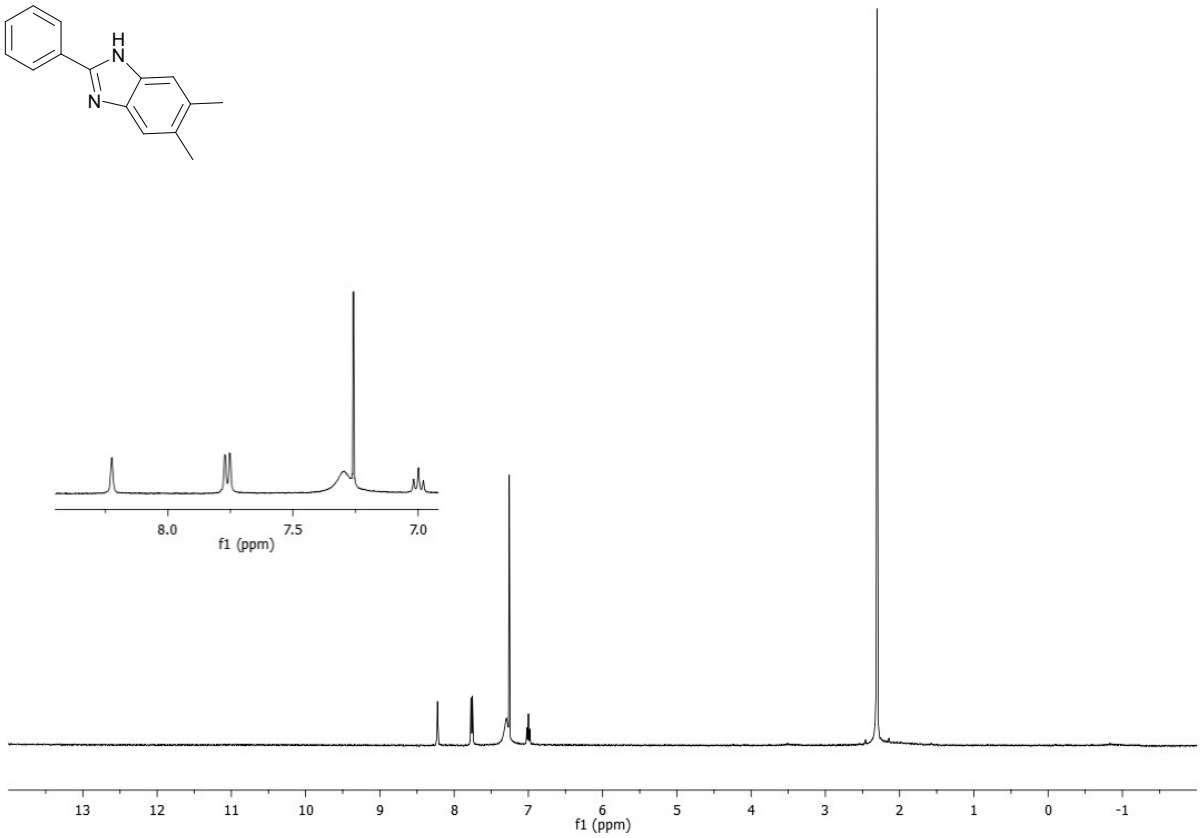
75- ^{1}H NMR of **10** in DMSO



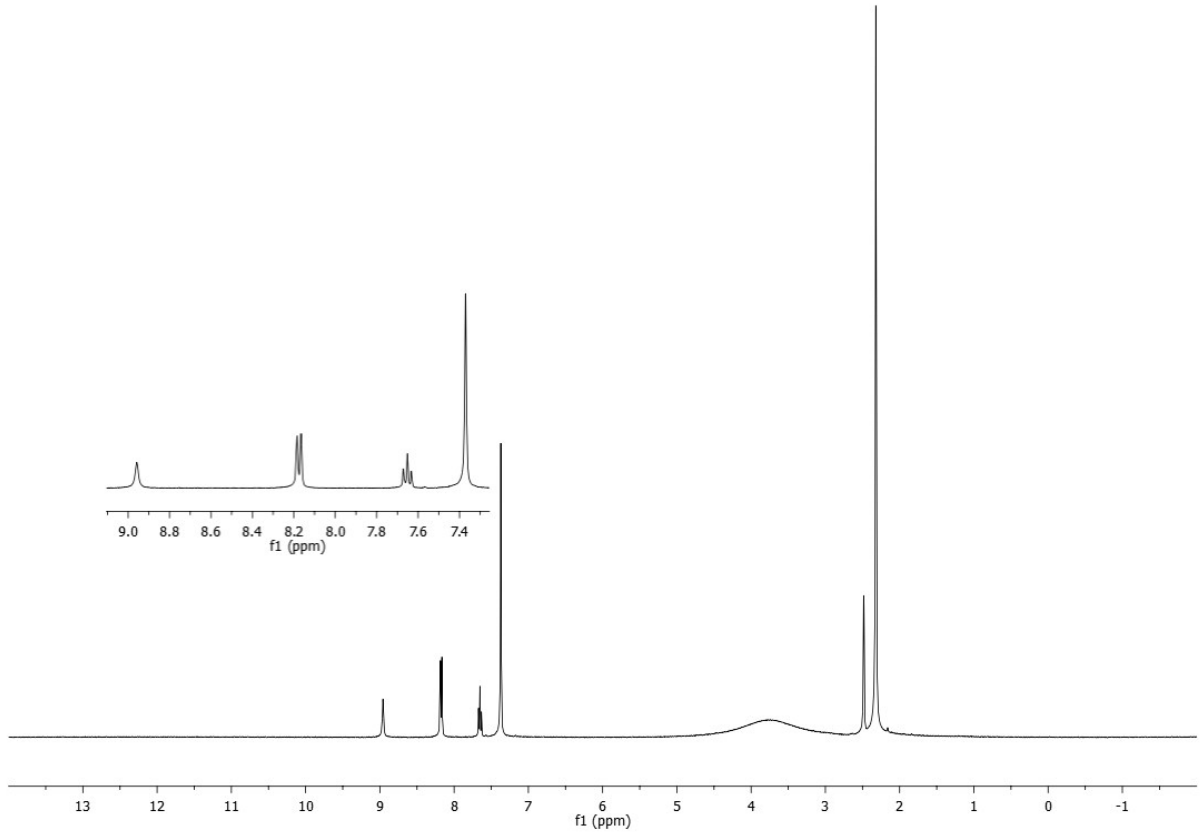
76- ^{13}C NMR of **10**



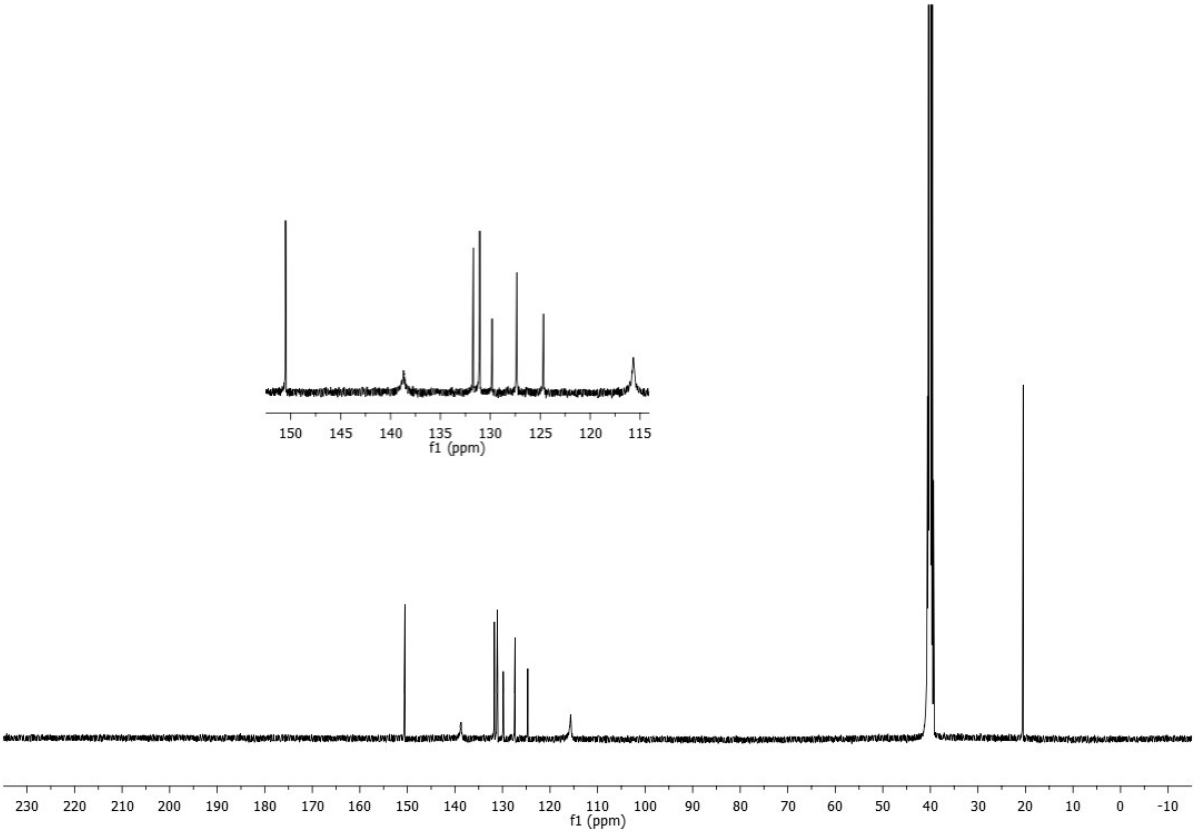
77- ^{1}H NMR of **11** in $CDCl_3$



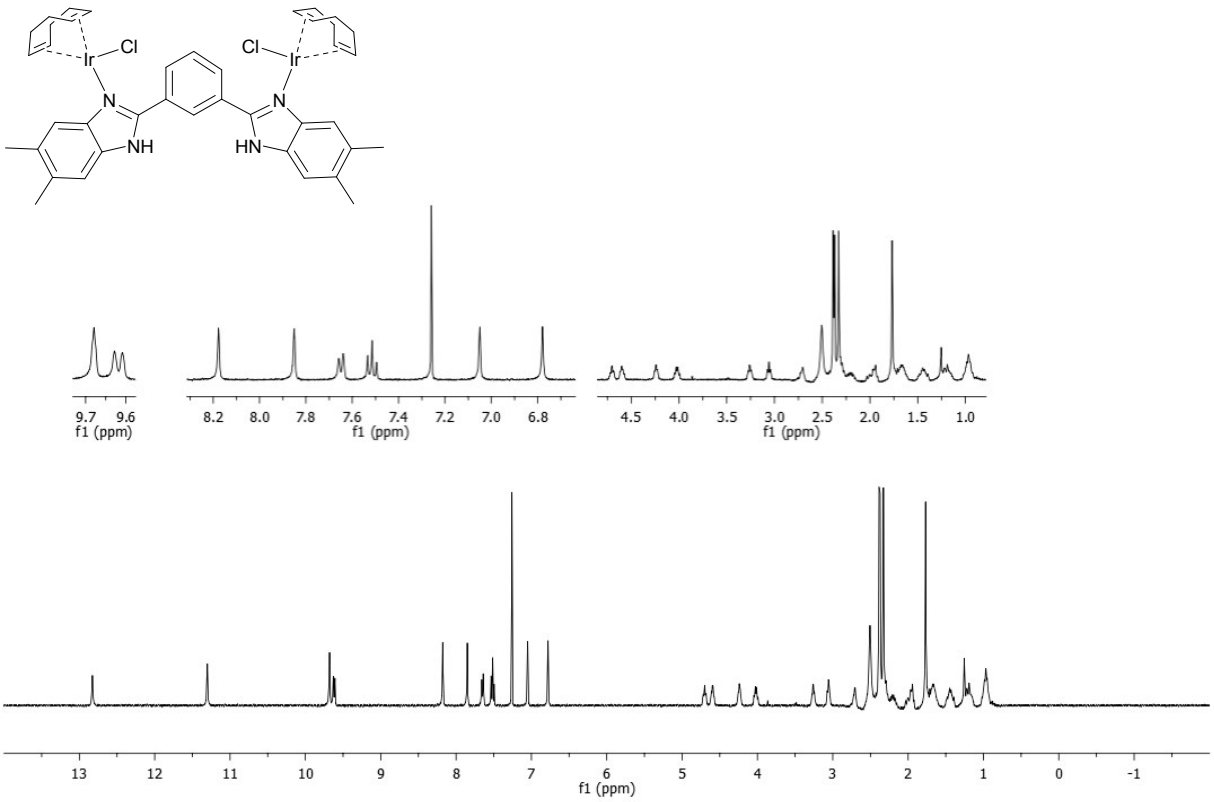
78- ^{1}H NMR of **11** in DMSO



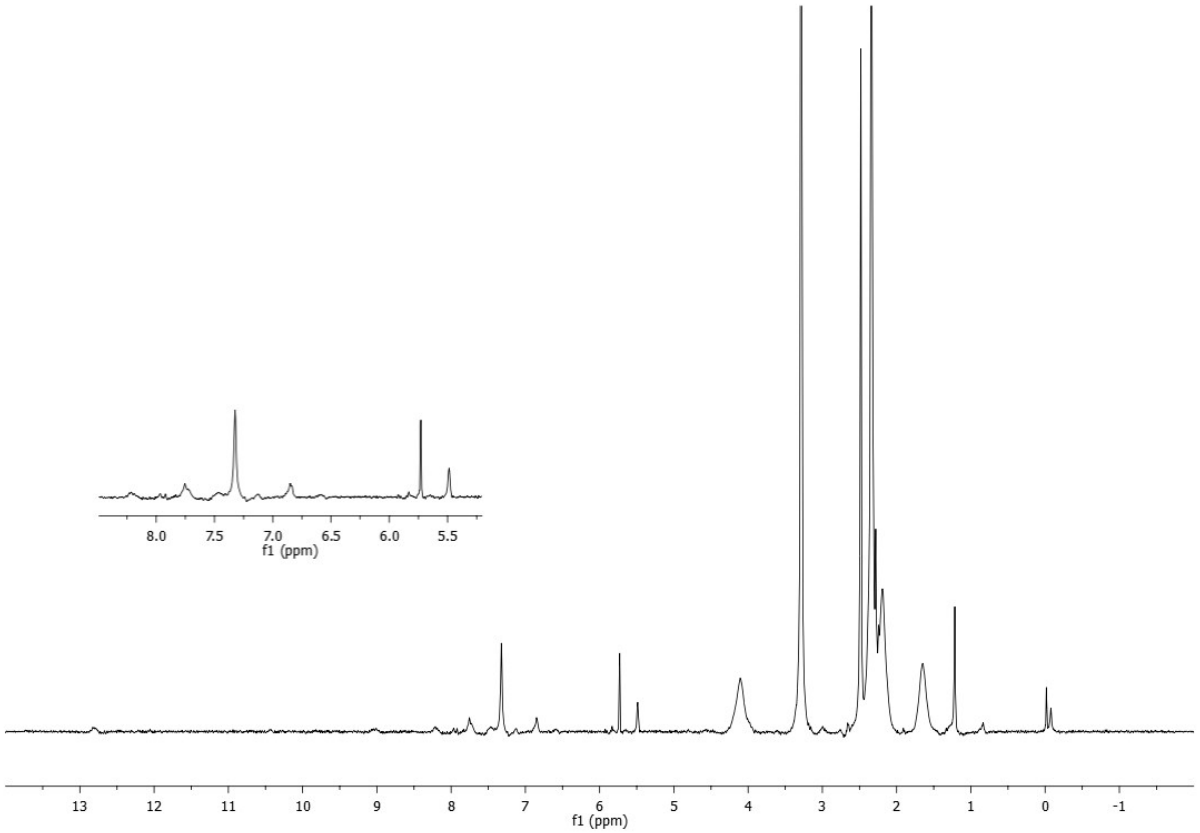
79- ^{13}C NMR of **11**



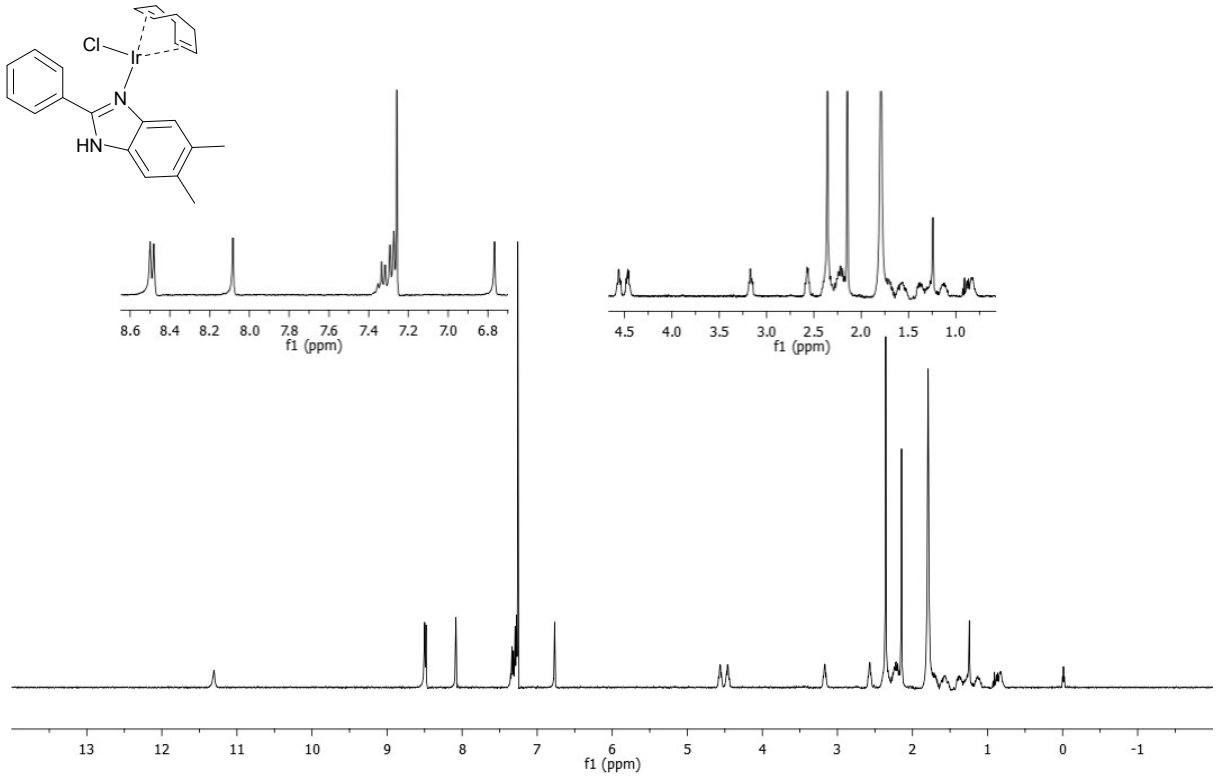
80- ^{1}H NMR of **12** in $CDCl_3$



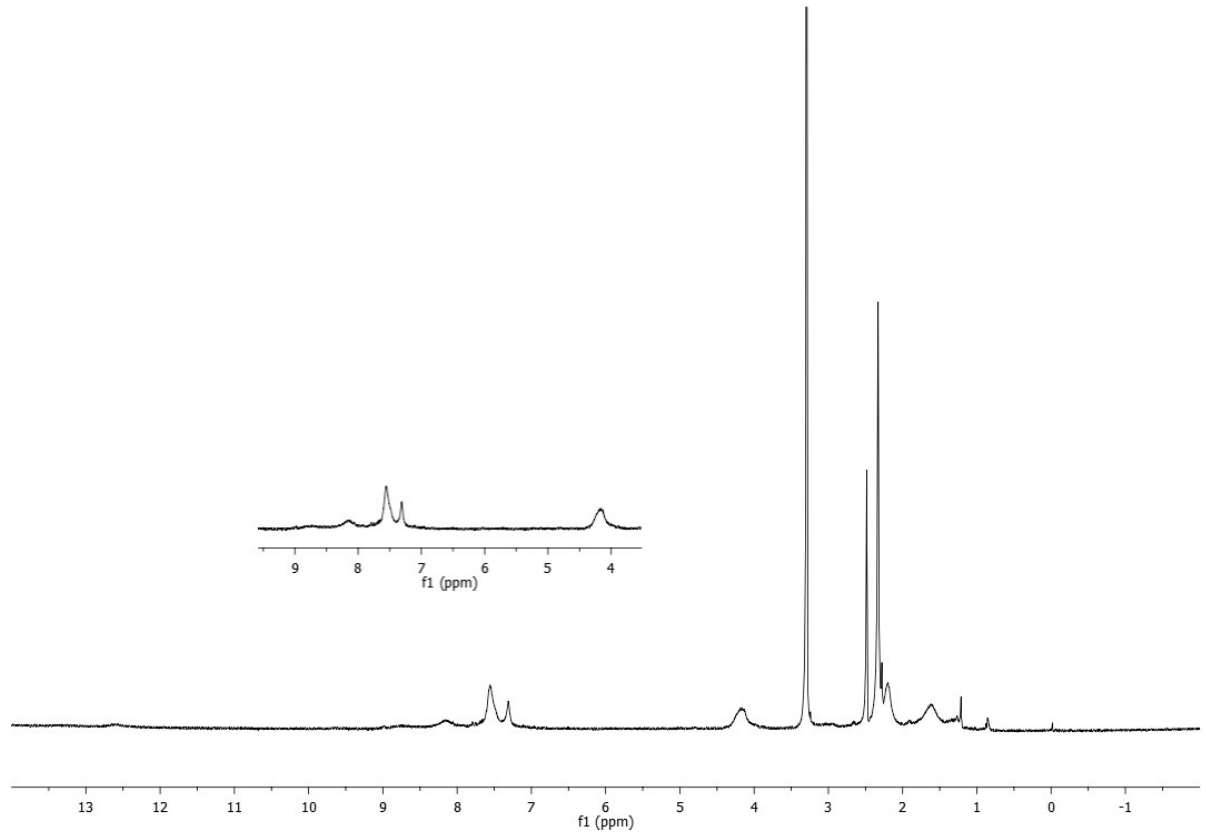
81- ^{1}H NMR of **12** in DMSO



82- ^{1}H NMR of **13** in $CDCl_3$



83- ^{1}H NMR of **13** in DMSO



84- X-Ray crystallographic data of **3d**

The crystallographic data and structure refinement summary for SGN4Rh are tabulated in Table S1. The intra- and intermolecular interactions are given in Table S2. As shown in Fig. S1, an intramolecular interaction of C3-H3···Cl1 generates six-membered ring, producing *S(6)* hydrogen ring motif. There are two intermolecular C-H···π type interactions in the crystal structure. In the first interaction, the solvent molecules interact with the molecule through a C-H···π interaction between a dichloromethane C atom and a six-membered ring component of the benzimidazole ring system (Fig. S2a). The second one is observed between C14 atom of the COD ring in the molecule at (*x, y, z*) and the pentamethylbenzyl ring (C21-C26) in the molecule at (*x,1-y,1/2+z*), as shown in Fig. S2b. In addition, there are two C-H···Cl type intermolecular interactions. As shown in Fig**.** S3, atoms C18 and C40 in the molecule at (*x, y, z*) act as C-H···Cl hydrogen-bond donors to the Cl3 atom in the molecule at (*-x,1-y,1-z*) and the Cl1 atom in the molecule at (*x,-1+y,z*), respectively, leading to a centrosymmetric $R_4^4(16)$ dimer.

Table S1. Crystallographic data and structure refinement summary for SGN4Rh.

Formula	$C_{61}\ H_{73}\ Cl_6\ N_5\ Rh_2$
Colour/shape	Yellow/ Plate
M_r	1294.76
Crystal system, space group	Monoclinic, C12/c1
Unit cell parameters	a=26.8865(12)Å, b=10.0794(4)Å, c=23.4752(15)Å, β=110.681(6)°
V ($Å^3$)	5951.8(5)
Z	4
F(000)	2664
D_x $(Mg.m^{-3})$	1.445
μ (mm^{-1})	0.866
T $(°K)$	293
$\theta_{min}/\theta_{max}$ (°)	3.0/29.2
No. of measured/unique/observed reflections	15414/6812/4524
θ_{min}, θ_{max} (°)	3.0, 29.2
R(int)	0.0268
h = min to max	-36 to 32
k = min to max	-12 to 12
l = min to max-	-18 to 29
No. of reflections/parameters/restrains	6,812/338/0
GOOF on F^2	0.992
R indices [I >2σ(I)]	$R_1 = 0.0448, wR_2 = 0.1010$
R indices (all data)	$R_1 = 0.0820$, $wR_2 = 0.1165$
$\Delta\rho_{max}$, $\Delta\rho_{min}$ $(eÅ^{-3})$	0.581, -0.581

Table S2. Intra- and intermolecular interaction geometry (Å, °).*

D-H···A	H···A	D···A	∠ D-H···A
C3-H3···Cl1	2.82	3.6424(2)	149
C40-H40B···Cg1	2.38	3.3416(2)	174
C14-H14A···Cg2^{ii}	2.90	3.7316(2)	144
C18-H18B···Cl3^{iii}	2.80	3.5749(2)	138
C40-H40A···Cl1^{iv}	2.52	3.4855(2)	176

*Cg1 and Cg2 are the centroids of the C5-C10 and C21-C26 rings, respectively. Symmetry codes: (ii) *x,1-y,1/2+z*, (iii) *-x,1-y,1-z*, (iv) *x,-1+y,z*.

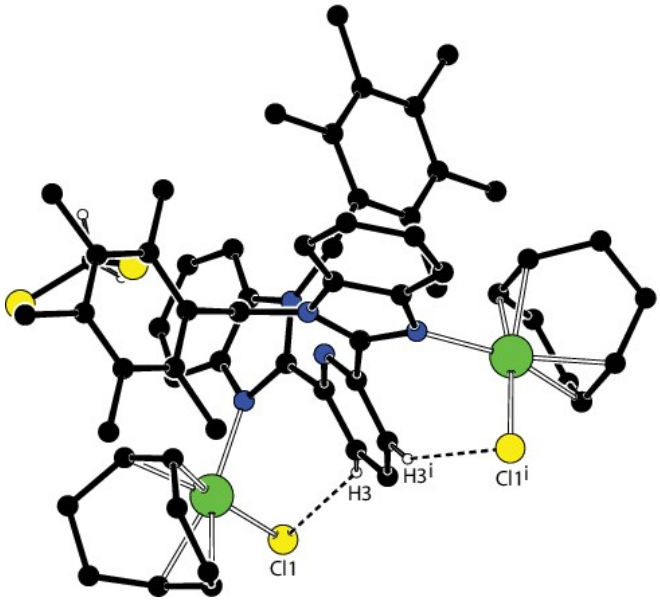


Figure S1. The molecular structure of **3d** showing the C-H···Cl type intramolecular interaction.

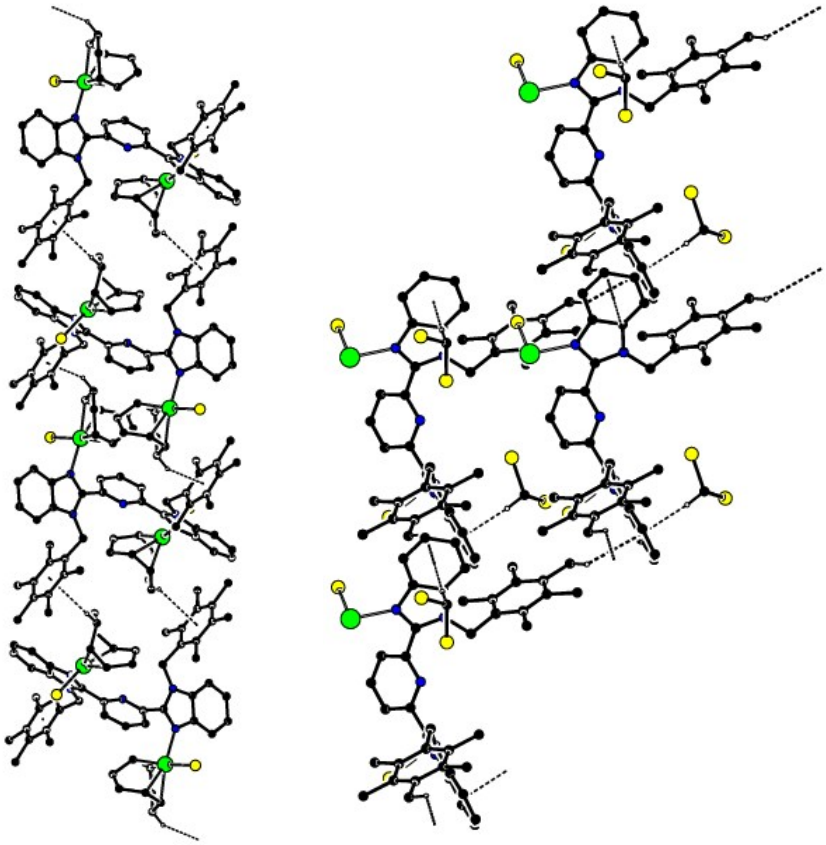


Figure S2. Part of the crystal structure, showing C-H···π interactions [left (a), right (b)].

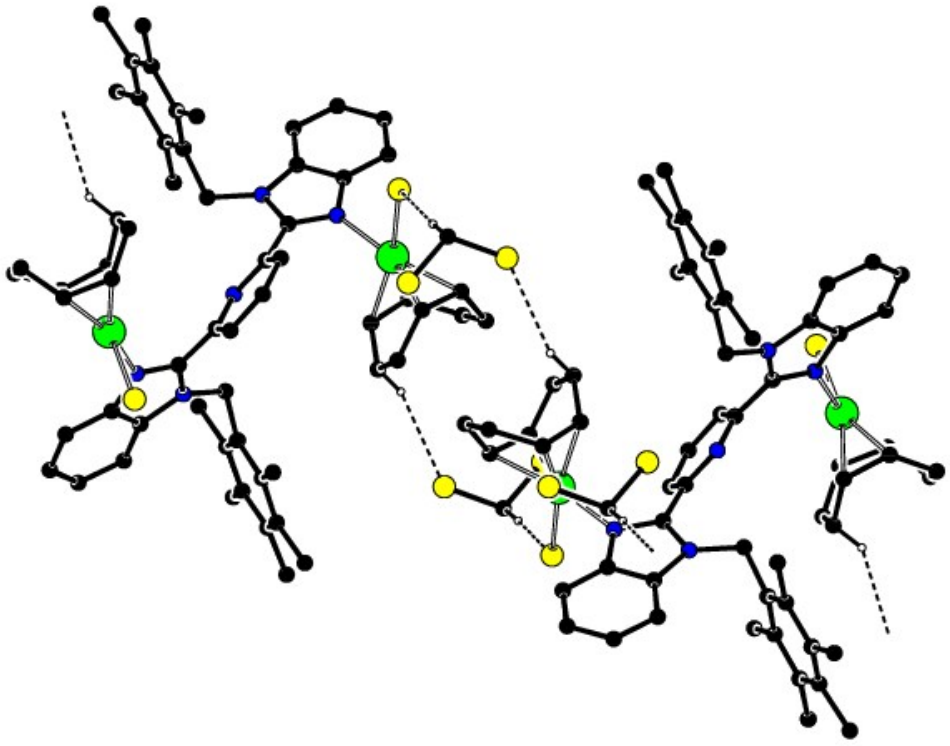


Figure S3. Part of the crystal structure, showing C-H···Cl interactions.