ELECTRONIC SUPPLEMENTARY INFORMATION

Non-symmetric, potentially redox non-innocent imino NHC pyridine 'pincers' via a zinc ion template-assisted synthesis

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Contents

1. X-ray Crystallography

Table S1. Summary of crystal data, data collection and refinement for the different compounds.

	16C	**18**	**19**
Chemical formula	C_{18} H_{21} Br Cl_2 N_2 Zn	C_{60} H_{68} Fe N_8 Br	C_{60} H_{68} Fe N_8
CCDC Number	1530405	1530406	1530407
Formula Mass (g/mol)	481.55	1036.98	957.07
Crystal system	trigonal	orthorhombic	triclinic
a (Å)	14.1615(3)	23.9792(10)	11.2073(14)
b (Å)	14.1615(3)	29.3525(12)	13.8988(19)
c (Å)	22.7112(7)	18.8532(8)	20.840(3)
α	90	90	96.111(3)
β	90	90	96.654(3)
γ	120	90	100.812(3)
V ($Å^3$)	3944.5(2)	13269.8(10)	3139.7(7)
Temperature (K)	173(2)	173(2)	173(2)
Space group	*P* 3_1 2 1	A b a 2	*P* -1
Formula units / cell, Z	6	8	2
Absorption coef. μ (mm^{-1})	2.658	0.867	0.279
No. of reflections measured	6054	17156	15358
No. of independent reflections	3750	9672	10488
R_{int}	0.0939	0.0820	0.0696
Final R_1 values *(I > 2σ(I))*	0.0675	0.0497	0.0982
Final *wR(F^2)* values (*I > 2σ(I)*)	0.1679	0.0804	0.2210
Final R_1 values (all data)	0.952	0.0908	0.1314
Final *wR(F^2)* values (all data)	0.1044	0.104	0.2331
Goodness of fit on F^2	0.952	0.875	1.048

2. NMR Spectra

2.1. Compound 12

^{1}H NMR (400.13 MHz, $CDCl_3$)

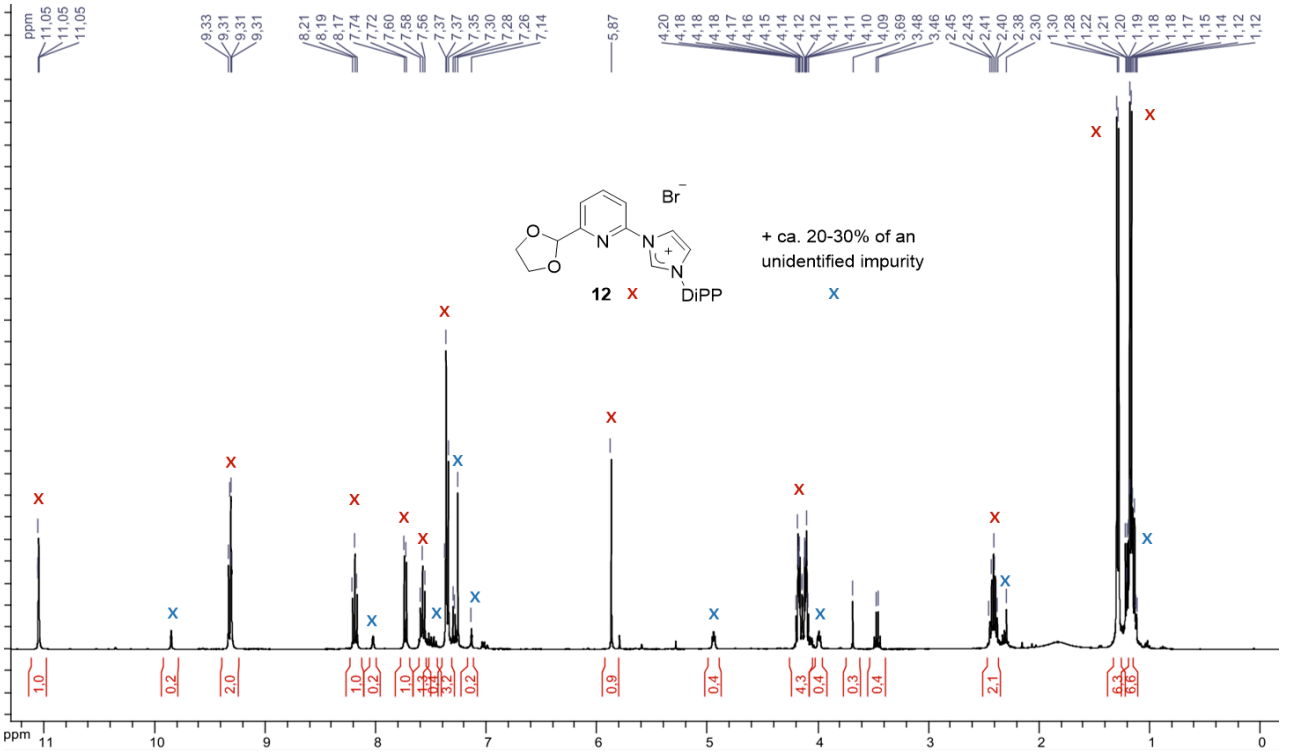

Figure S2.1 ^{1}H NMR spectrum of **12** in $CDCl_3$ along with *ca*. 20-30% of an unidentified side-product probably arising from ring-opening of the 1,3-dioxolane protecting group (see main text). Residual protio solvent from $CDCl_3$ at δ 7.26.

^{13}C{^{1}H} NMR (75.49 MHz, $CDCl_3$)

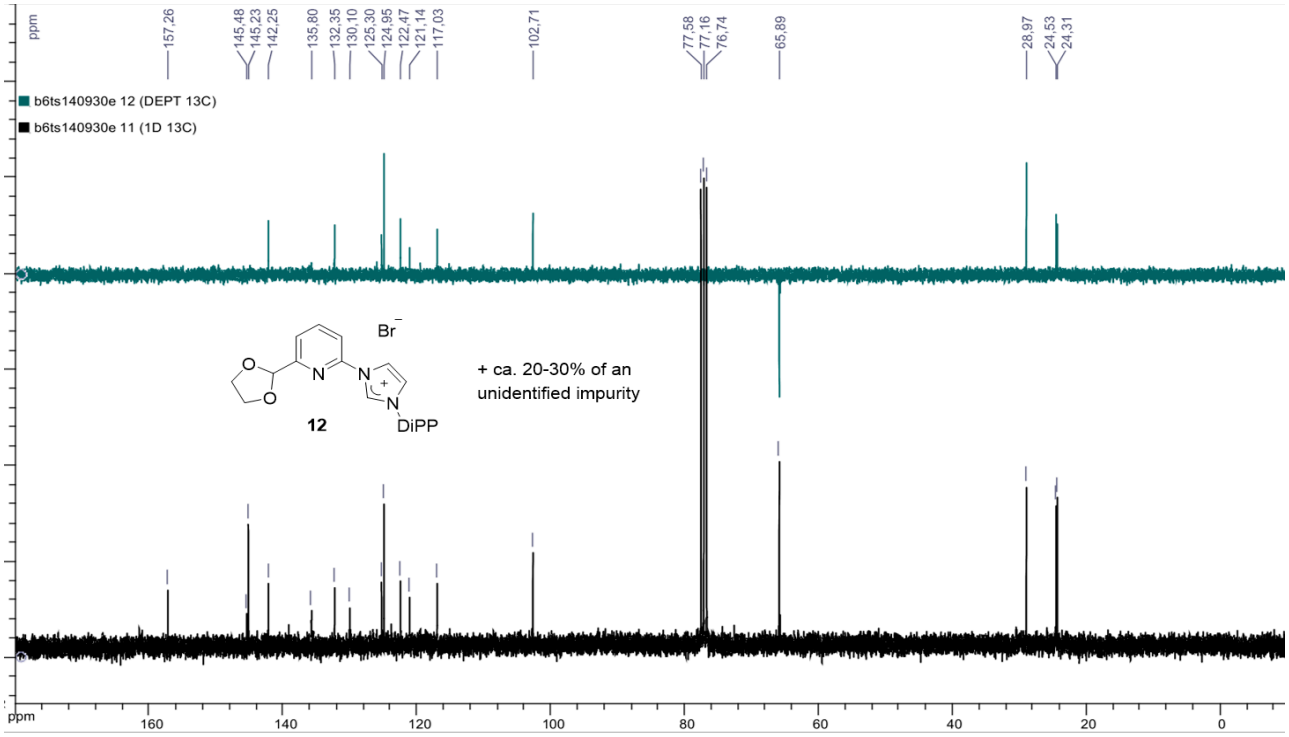

Figure S2.2 ^{13}C{^{1}H} (bottom) and ^{13}C-DEPT (top) NMR spectra of **12** in $CDCl_3$ along with *ca*. 20-30% of an unidentified side-product (see main text). Residual protio solvent from $CDCl_3$ at δ 77.16.

2.2. Compound 13

^{1}H NMR (400.13 MHz, $CDCl_3$)

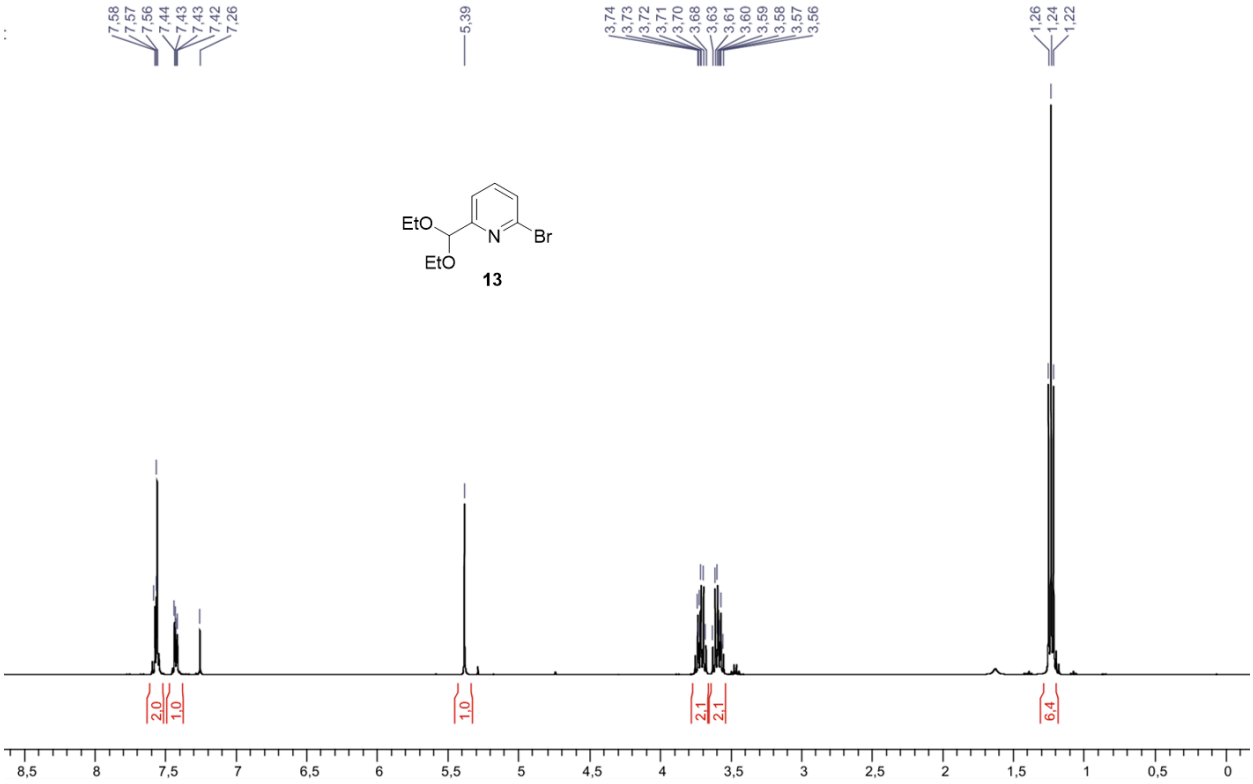

Figure S2.3 ^{1}H NMR spectrum of **13** in $CDCl_3$ (residual protio solvent from $CDCl_3$ at δ 7.26).

^{13}C{^{1}H} NMR (100.62 MHz, $CDCl_3$)

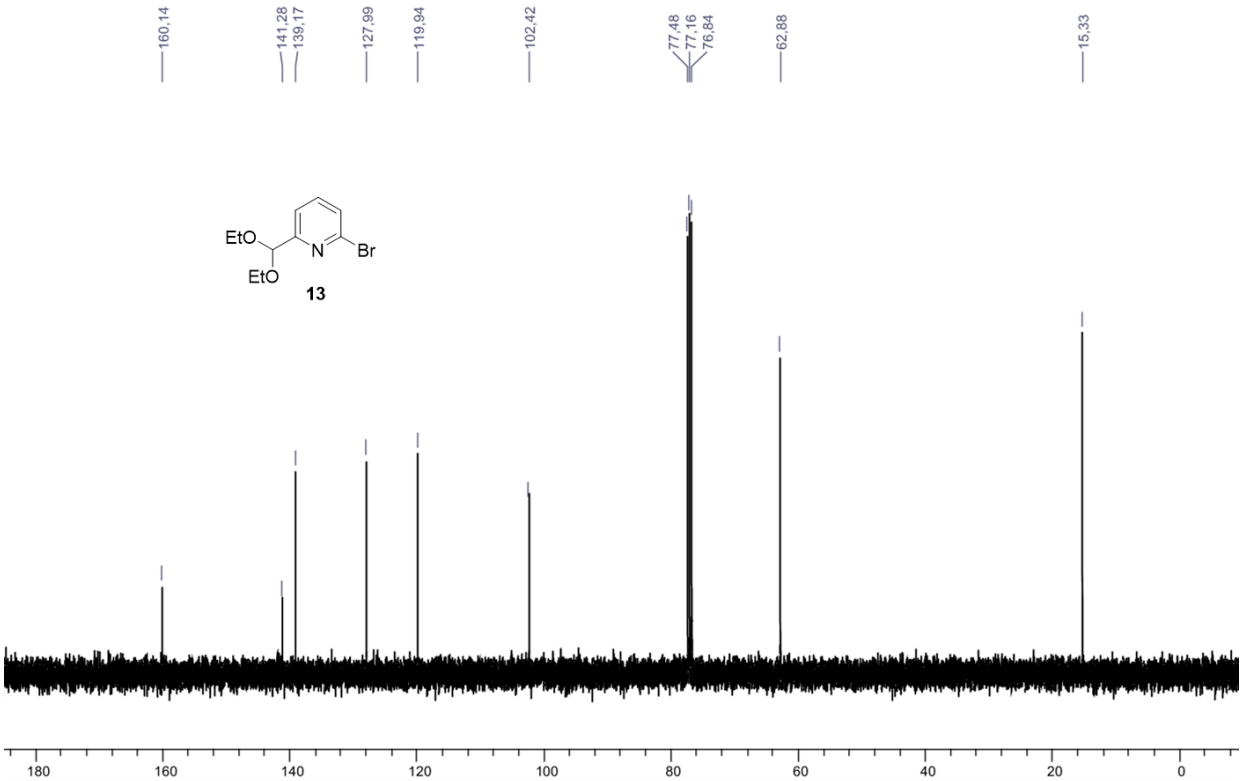

Figure S2.4 ^{13}C{^{1}H} NMR spectrum of **13** in $CDCl_3$ (residual protio solvent at δ 77.16).

2.3. Compound 15

^{1}H NMR (400.13 MHz, $CDCl_3$)

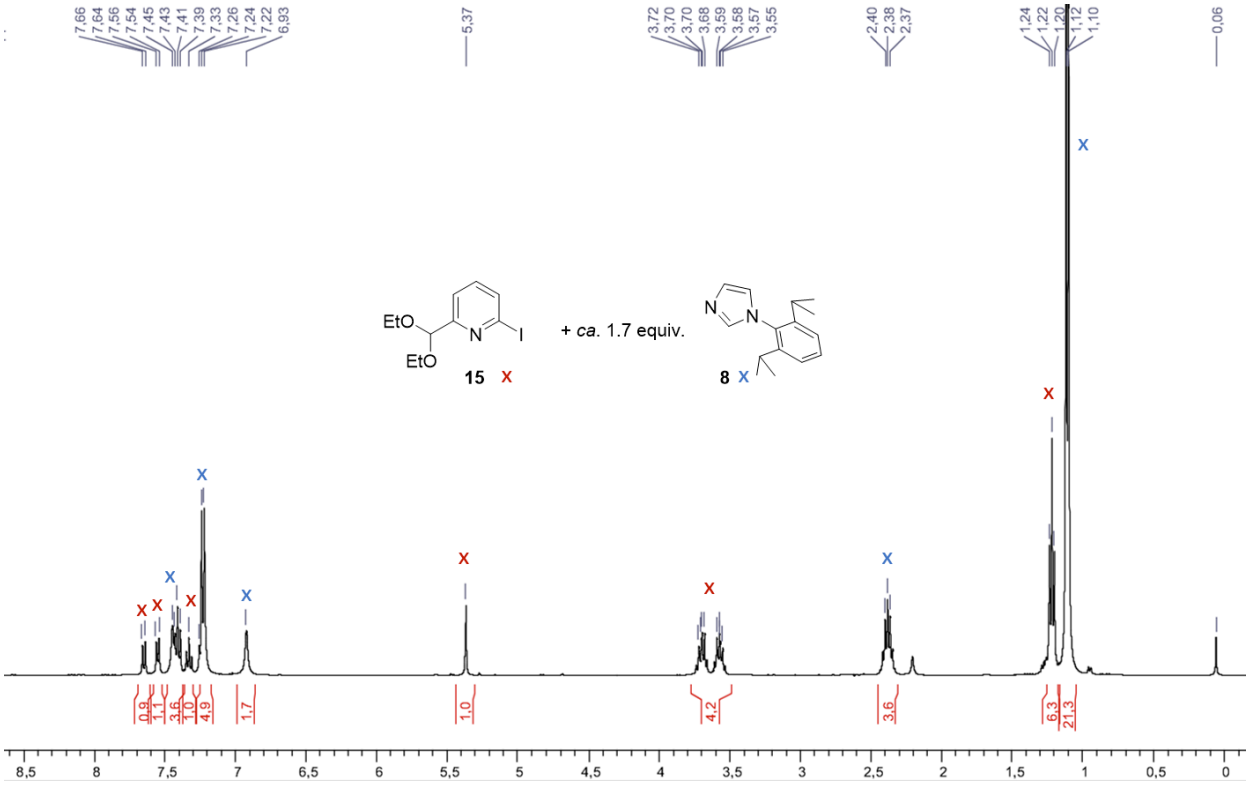

Figure S2.5 ^{1}H NMR spectrum of **15** in $CDCl_3$ along with *ca*. 1.7 equiv. of **8** (residual protio solvent from $CDCl_3$ at δ 7.26).

^{13}C{^{1}H} NMR (100.62 MHz, $CDCl_3$)

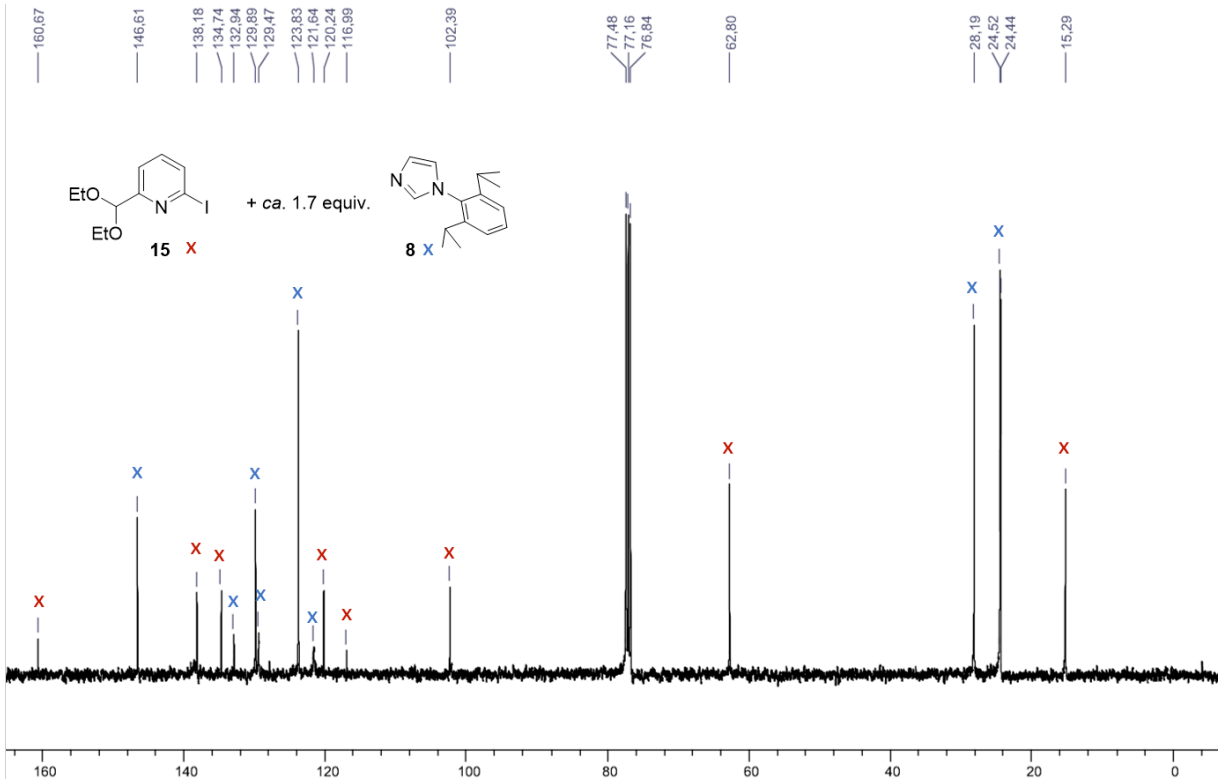

Figure S2.6 ^{13}C{^{1}H} NMR spectrum of **15** in $CDCl_3$ along with *ca*. 1.7 equiv. of **8** (residual protio solvent at δ 77.16).

2.4. Compound 10B

^{1}H NMR (400.13 MHz, $CDCl_3$)

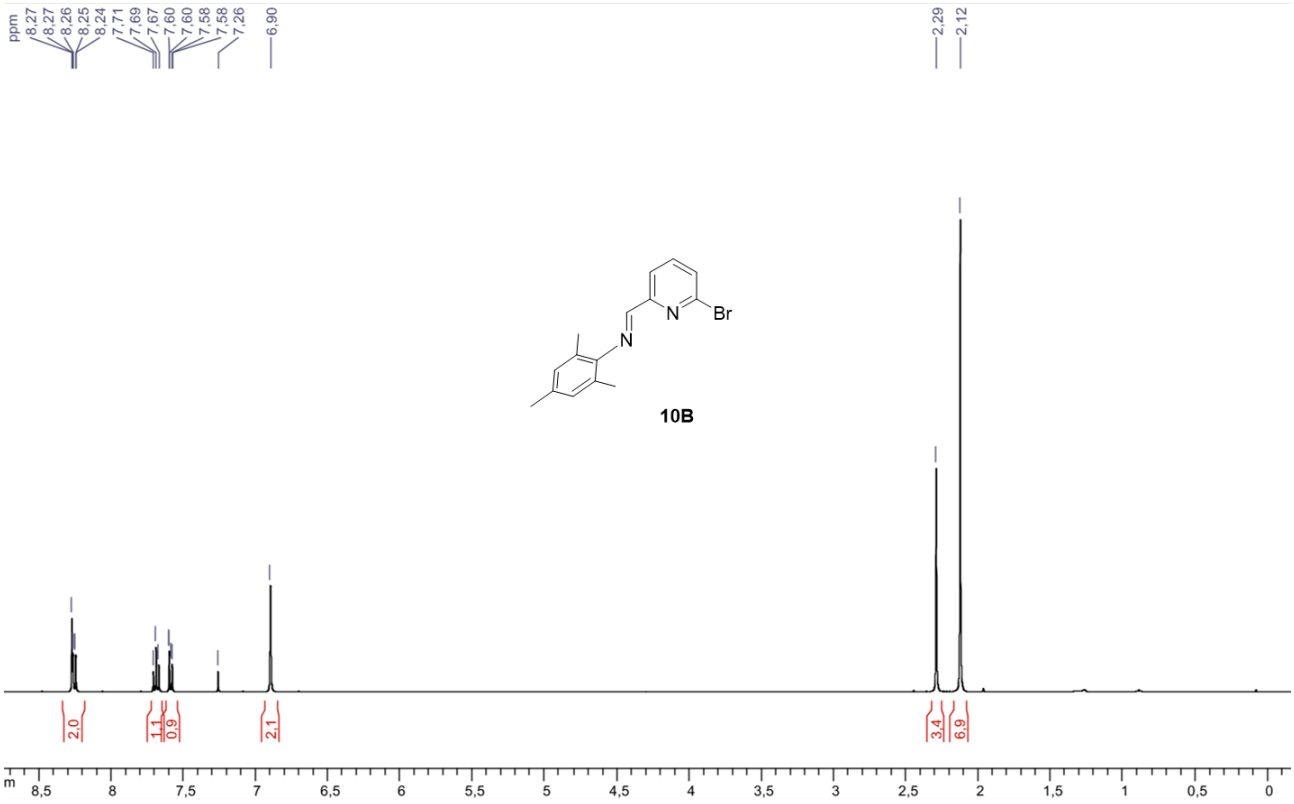

Figure S2.7 ^{1}H NMR spectrum of **10B** in $CDCl_3$ (residual protio solvent from $CDCl_3$ at δ 7.26).

^{13}C{^{1}H} NMR (100.62 MHz, $CDCl_3$)

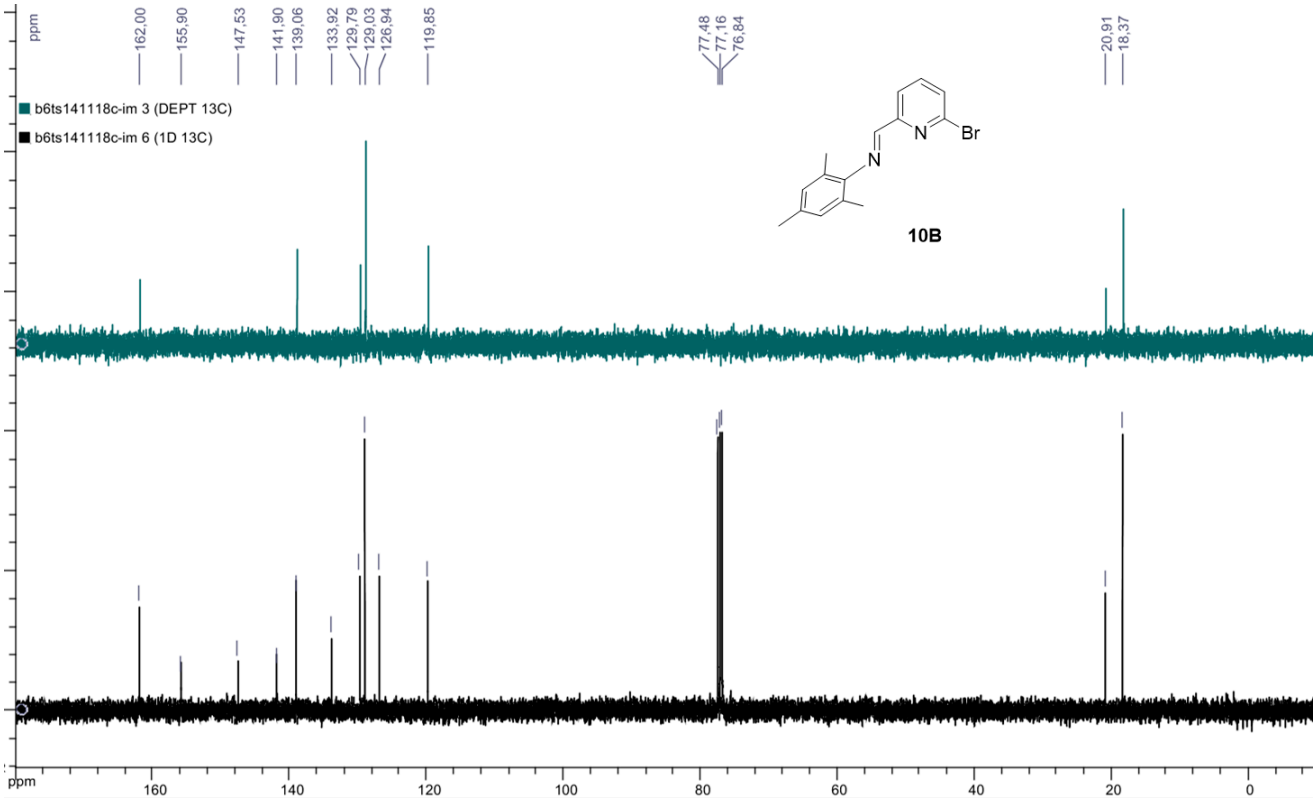

Figure S2.8 ^{13}C{^{1}H} (bottom) and ^{13}C-DEPT (top) NMR spectra of **10B** in $CDCl_3$ (residual protio solvent from $CDCl_3$ at δ 77.16).

2.5. Compound 10C

^{1}H NMR (400.13 MHz, $CDCl_3$)

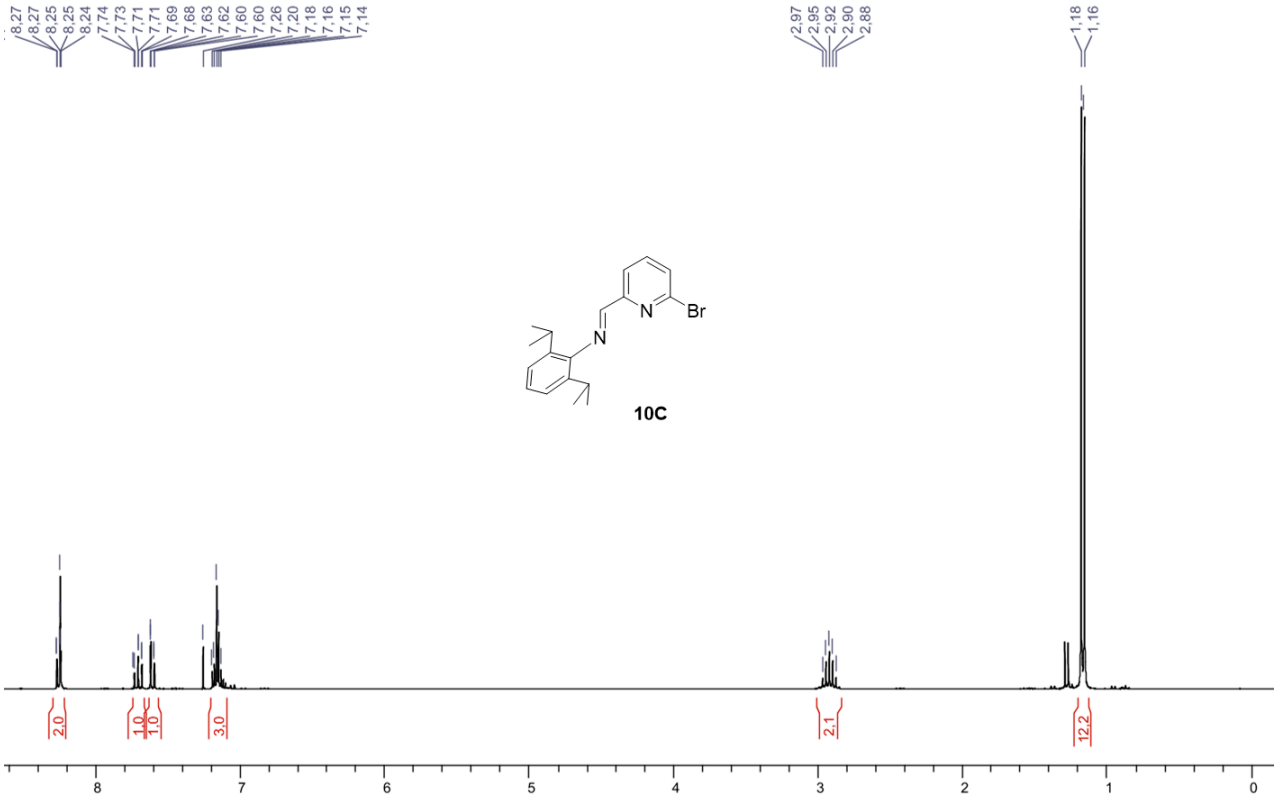

Figure S2.9 ^{1}H NMR spectrum of **10C** in $CDCl_3$ (residual protio solvent from $CDCl_3$ at δ 7.26).

^{13}C{^{1}H} NMR (100.62 MHz, $CDCl_3$)

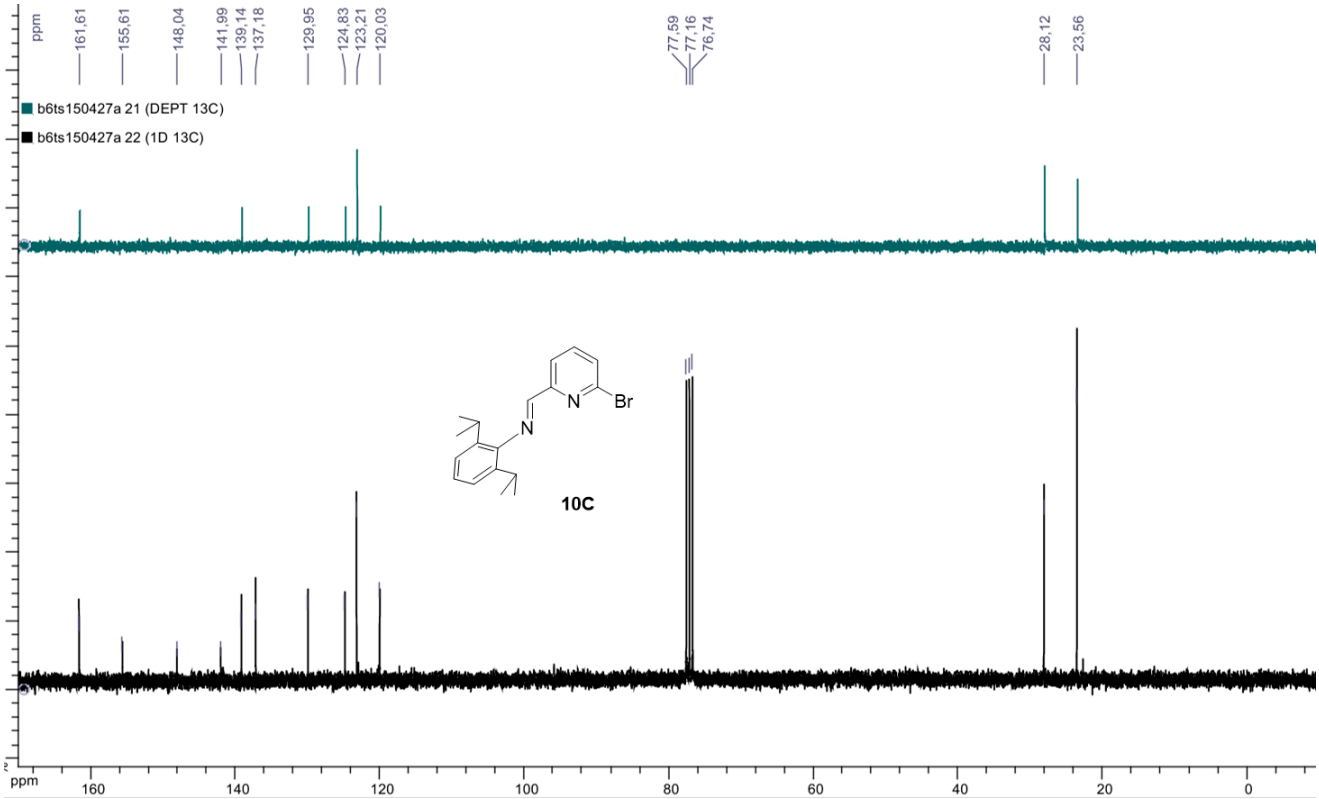

Figure S2.10 ^{13}C{^{1}H} (bottom) and ^{13}C-DEPT (top) NMR spectra of **10C** in $CDCl_3$ (residual protio solvent from $CDCl_3$ at δ 77.16).

2.6. Compound 16B

^{1}H NMR (400.13 MHz, DMSO-d_6)

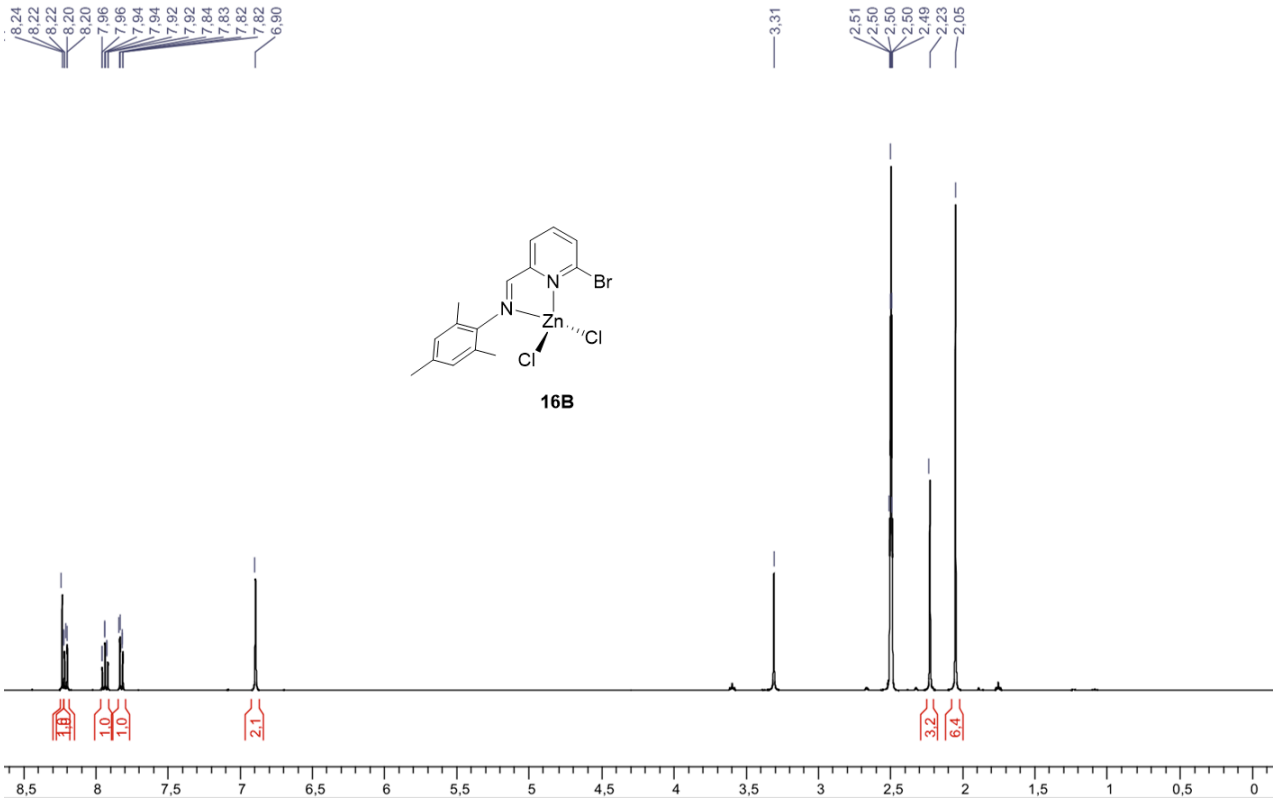

Figure S2.11 ^{1}H NMR spectrum of **16B** in DMSO-d_6 (residual protio solvent and residual water from wet DMSO-d_6 at δ 2.50 and 3.31 respectively).

^{13}C{^{1}H} NMR (100.62 MHz, DMSO-d_6)

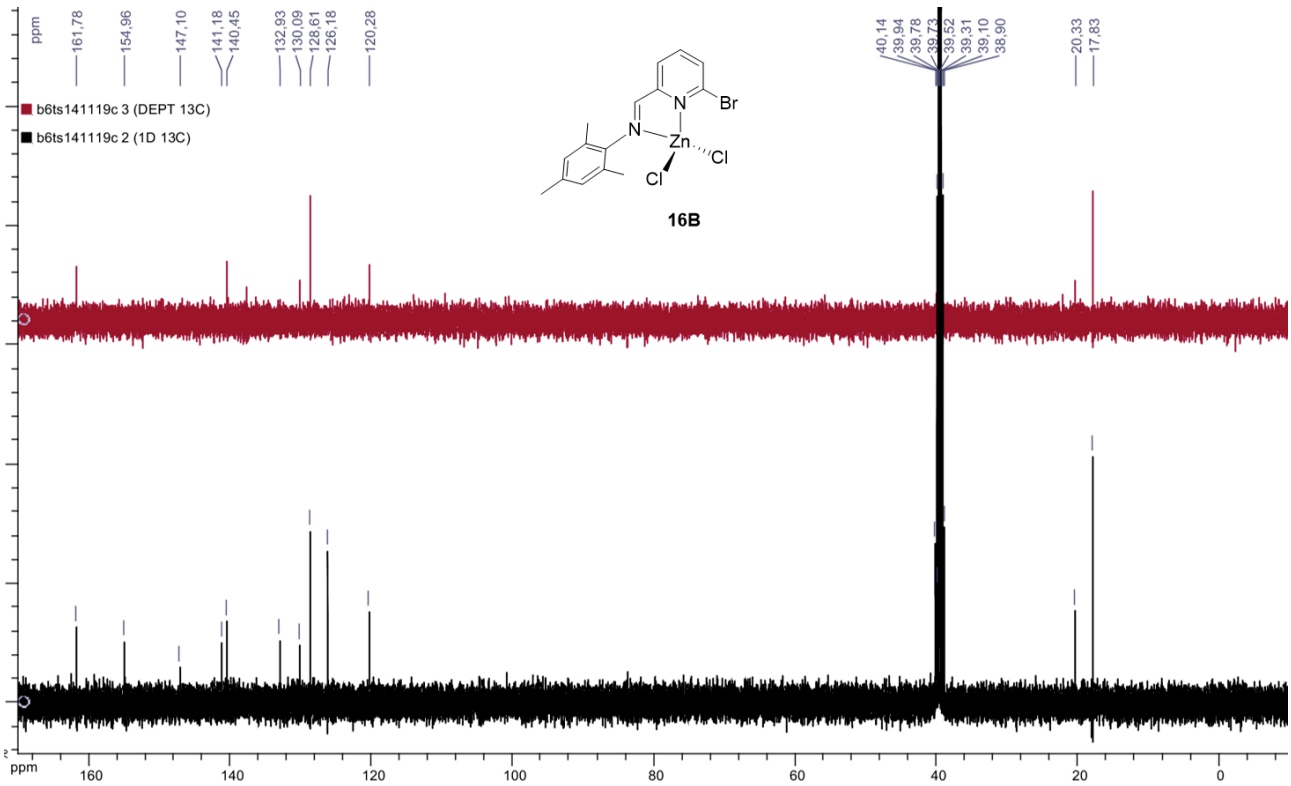

Figure S2.12 ^{13}C{^{1}H} (bottom) and ^{13}C-DEPT (top) NMR spectra of **16B** in DMSO-d_6 (residual protio solvent at δ 39.52).

2.7. Compound 16C

^{1}H NMR (400.13 MHz, DMSO-d_6)

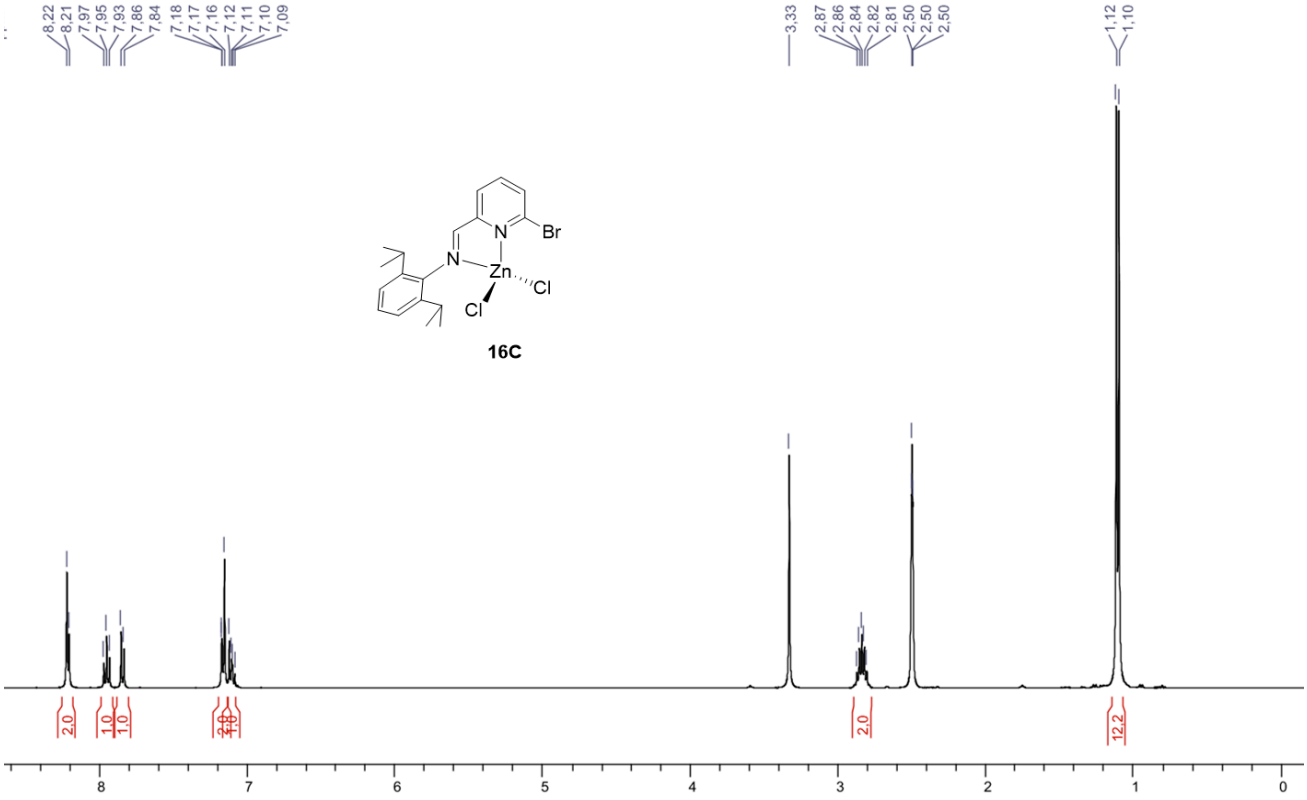

Figure S2.13 ^{1}H NMR spectrum of **16C** in DMSO-d_6 (residual protio solvent and residual water from wet DMSO-d_6 at δ 2.50 and 3.33 respectively).

^{13}C{^{1}H} NMR (100.62 MHz, DMSO-d_6)

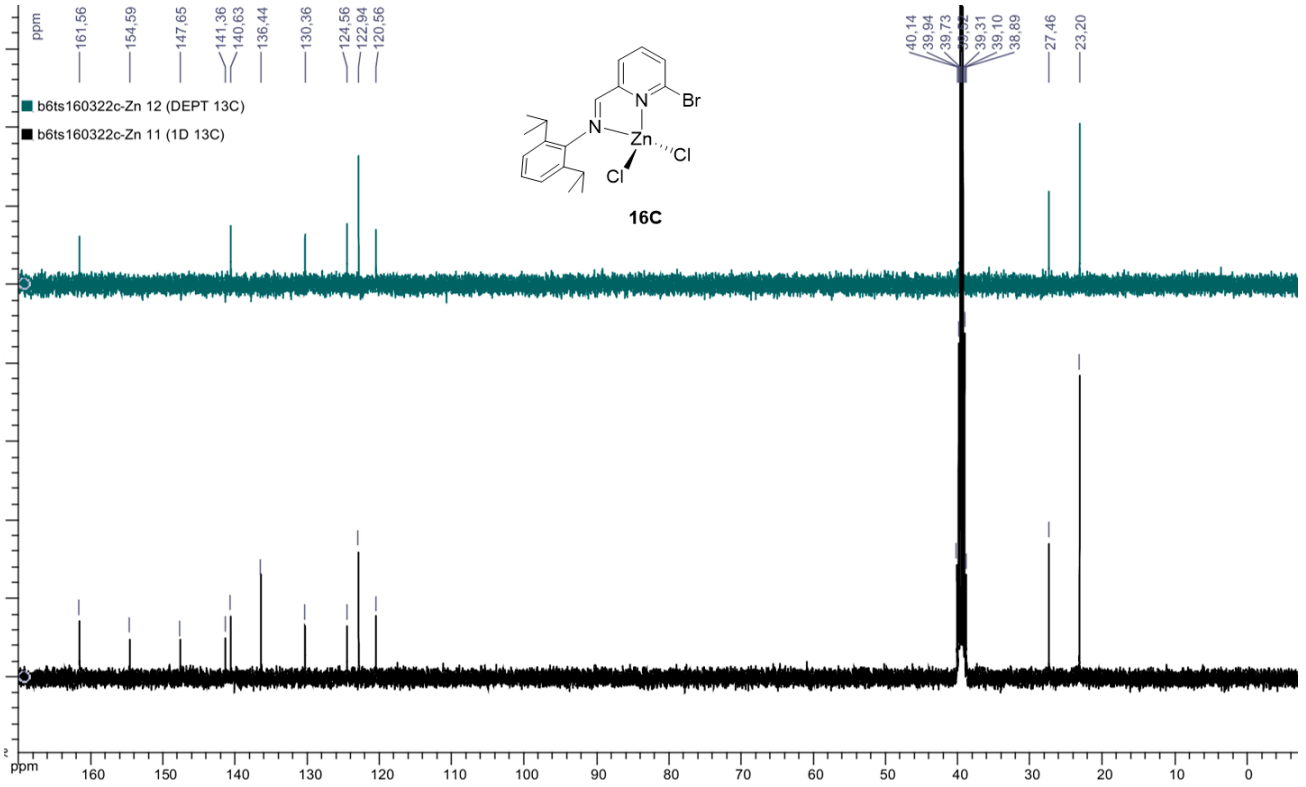

Figure S2.14 ^{13}C{^{1}H} (bottom) and ^{13}C-DEPT (top) NMR spectra of **16C** in DMSO-d_6 (residual protio solvent at δ 39.52).

2.8. Compound 5B

^{1}H NMR (500.13 MHz, CD_2Cl_2)

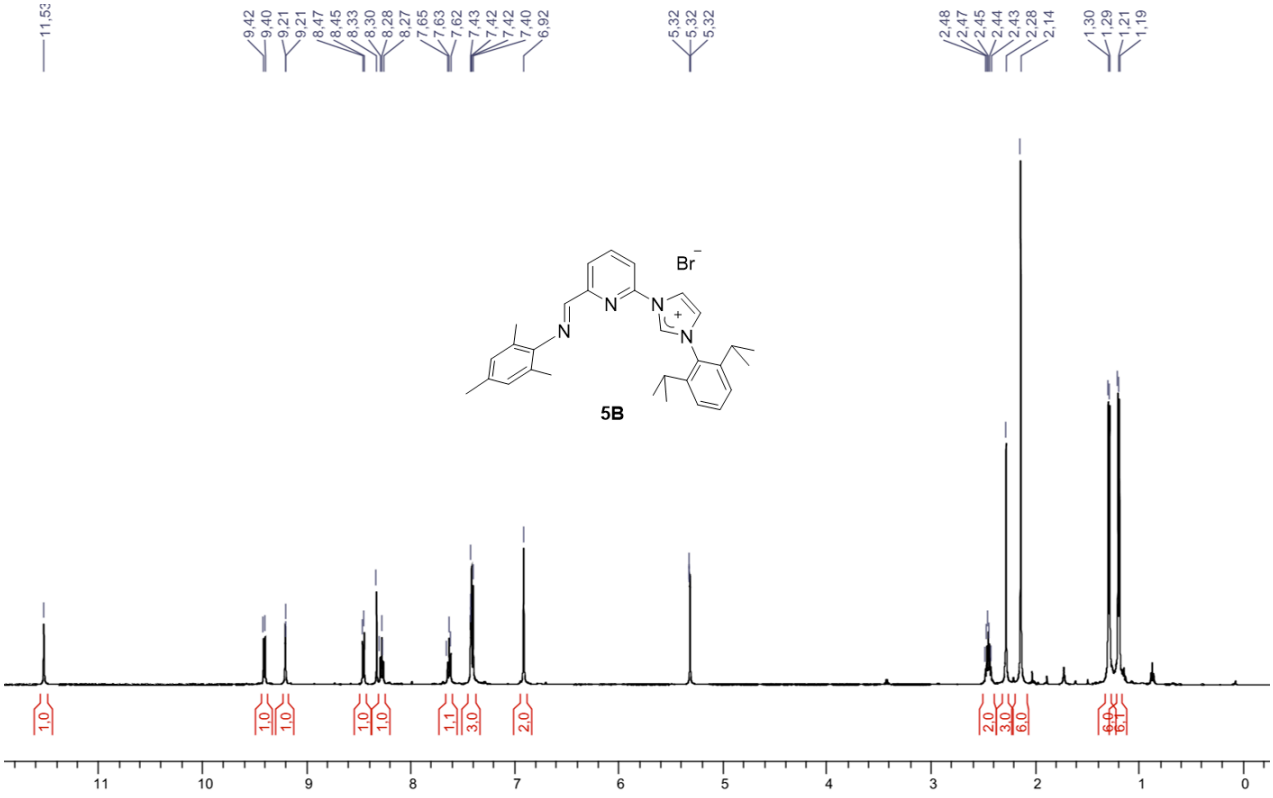

Figure S2.15 ^{1}H NMR spectrum of **5B** in CD_2Cl_2 (residual protio solvent from CD_2Cl_2 at δ 5.32).

^{13}C{^{1}H} NMR (125.77 MHz, CD_2Cl_2)

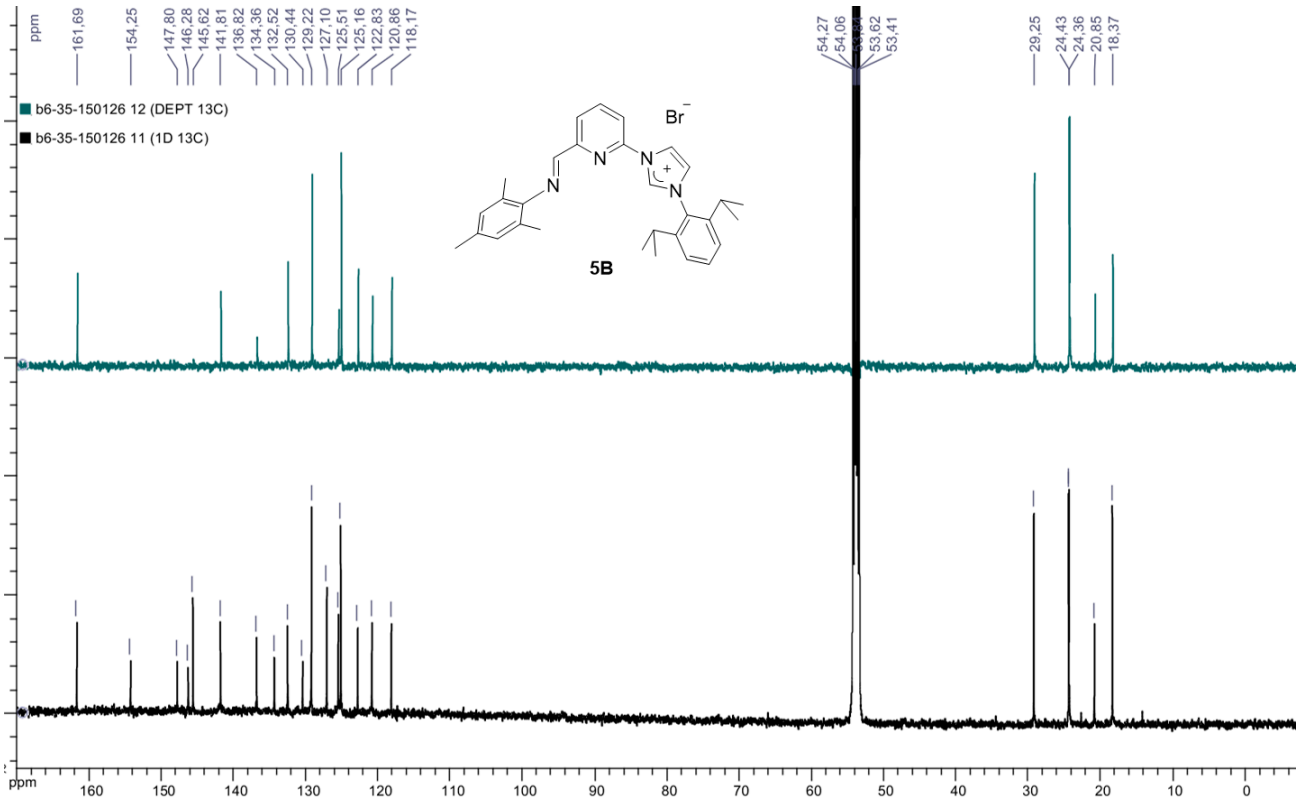

Figure S2.16 ^{13}C{^{1}H} (bottom) and ^{13}C-DEPT (top) NMR spectra of **5B** in CD_2Cl_2 (residual protio solvent from CD_2Cl_2 at δ 53.84).

2.9. Compound 5C

^{1}H NMR (500.13 MHz, CD_2Cl_2)

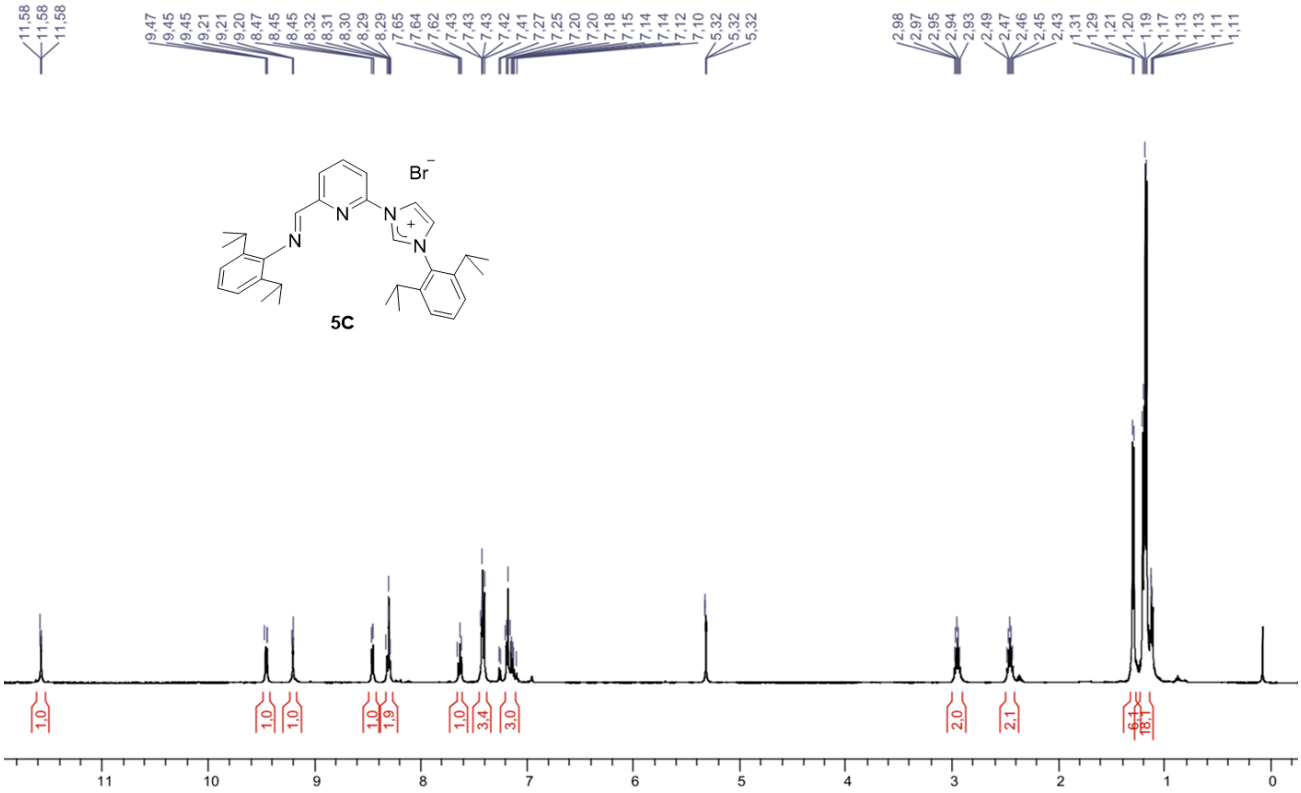

Figure S2.17 ^{1}H NMR spectrum of **5C** in CD_2Cl_2 (residual protio solvent from CD_2Cl_2 at δ 5.32).

^{13}C{^{1}H} NMR (125.77 MHz, CD_2Cl_2)

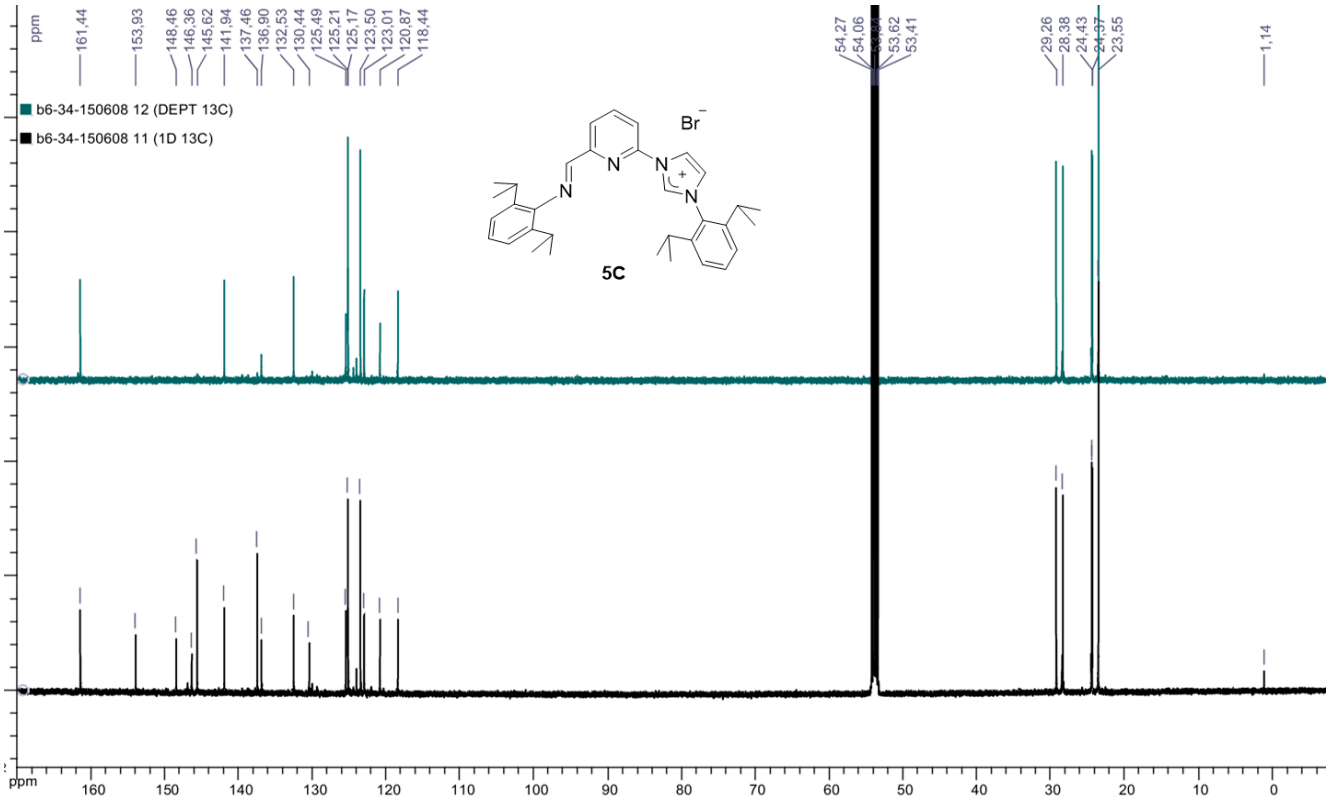

Figure S2.18 ^{13}C{^{1}H} (bottom) and ^{13}C-DEPT (top) NMR spectra of **5C** in CD_2Cl_2 (residual protio solvent from CD_2Cl_2 at δ 53.84).

2.10. Compound 4B

^{1}H NMR (500.13 MHz, C_6D_6)

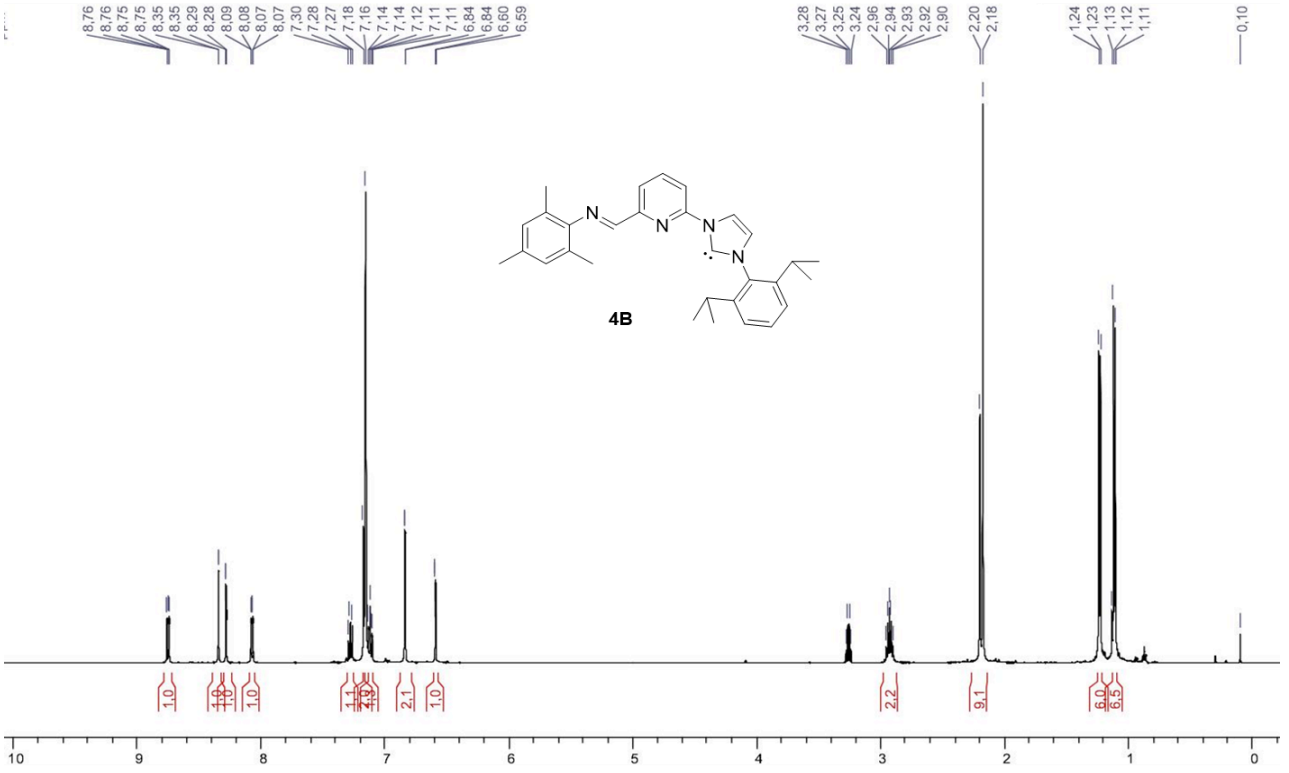

Figure S2.19 ^{1}H NMR spectrum of **4B** in C_6D_6 (residual protio solvent from C_6D_6 at δ 7.16). Traces of diethylether can be noticed at δ 3.26 and 1.12.

^{13}C{^{1}H} NMR (125.77 MHz, C_6D_6)

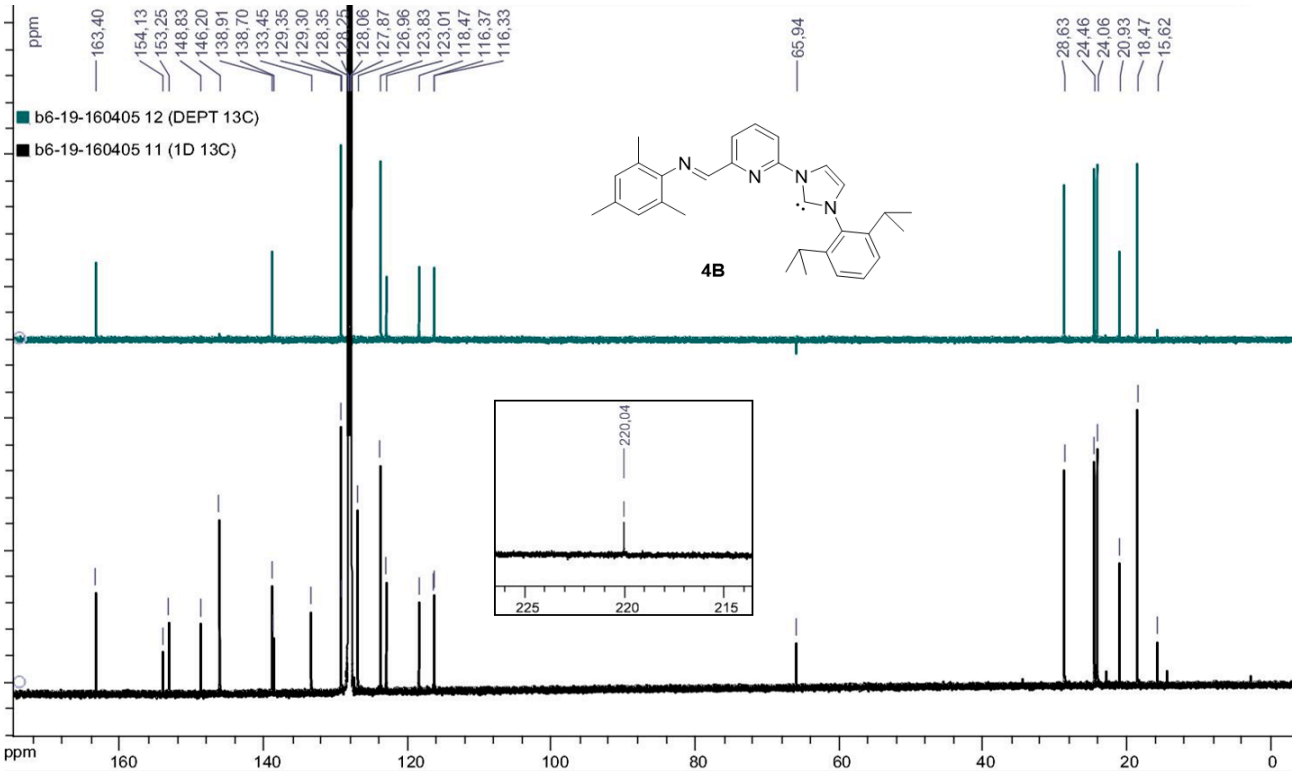

Figure S2.20 ^{13}C{^{1}H} (bottom) and ^{13}C-DEPT (top) NMR spectra of **4B** in C_6D_6 (solvent signal at δ 128.06). The inset shows the NHC carbene signal observed as a singlet at δ 220.0. Traces of diethylether can be noticed at δ 65.9 and 15.6.

2.11. Compound 4C

^{1}H NMR (500.13 MHz, C_6D_6)

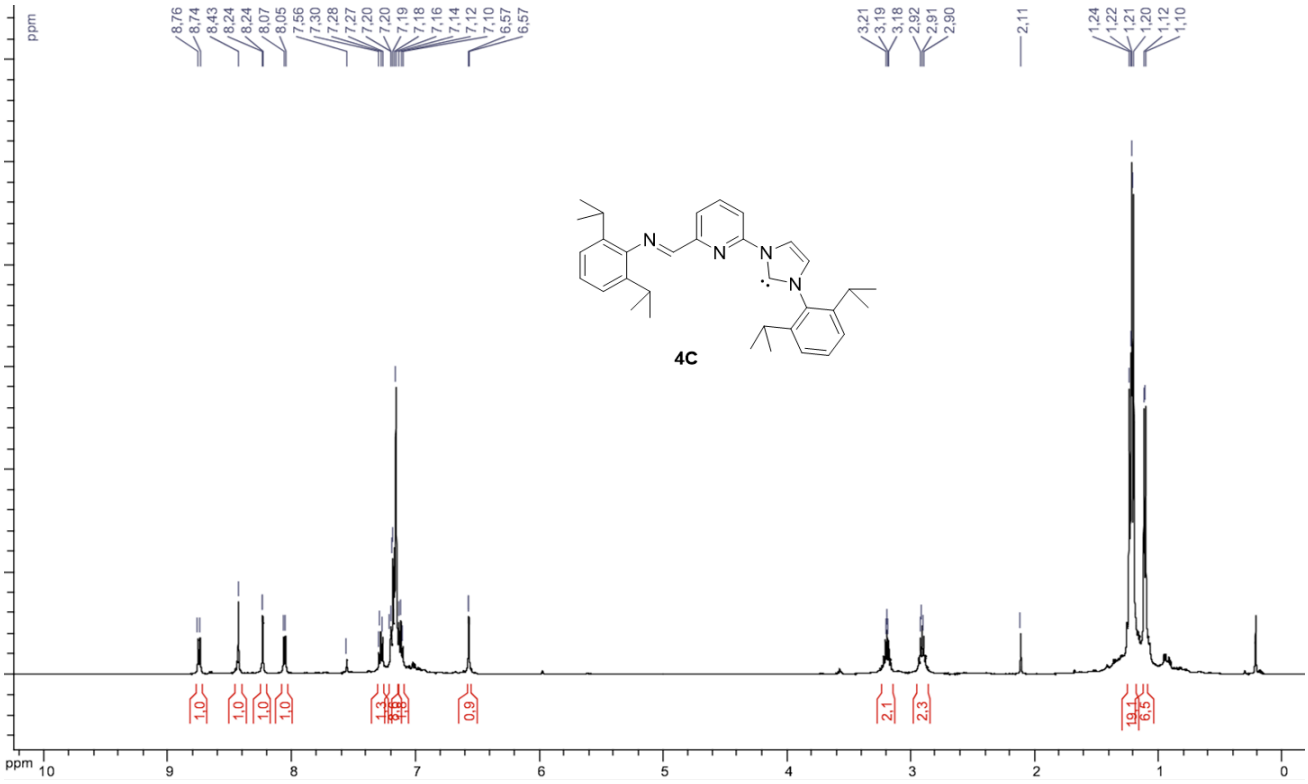

Figure S2.21 ^{1}H NMR spectrum of **4C** in C_6D_6 (residual protio solvent from C_6D_6 at δ 7.16).

^{13}C{^{1}H} NMR (125.77 MHz, C_6D_6)

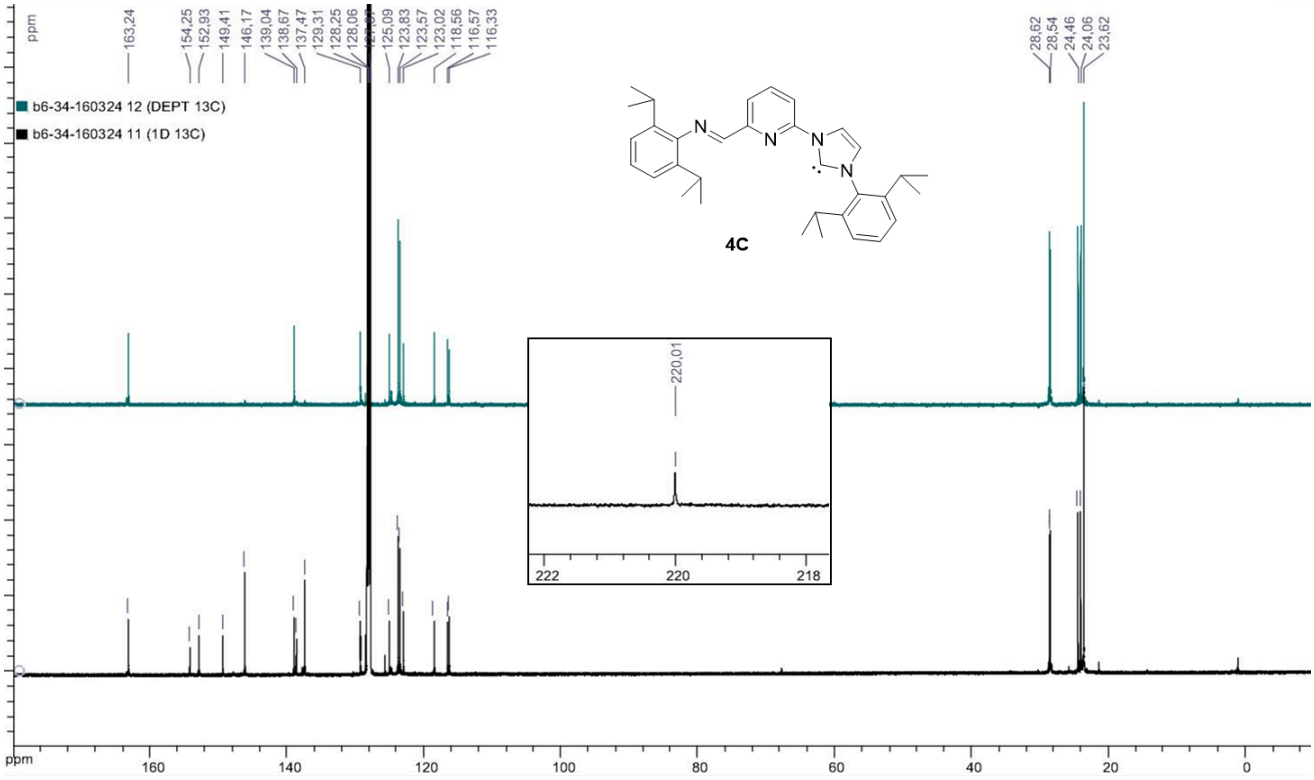

Figure S2.22 ^{13}C{^{1}H} (bottom) and ^{13}C-DEPT (top) NMR spectra of **4C** in C_6D_6 (solvent signal at δ 128.06). The inset shows the NHC carbene signal observed as a singlet at δ 220.0.