Electronic Supplementary Material (ESI) for Dalton Transactions.

Supplementary Information

Synthesis, structure and reactivity of Pd and Ir complexes based on new lutidine-derived NHC/phosphine mixed pincer ligands

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1. VT-^{1}H NMR and ^{1}H-^{1}H-EXSY Spectra of 4a(Cl)

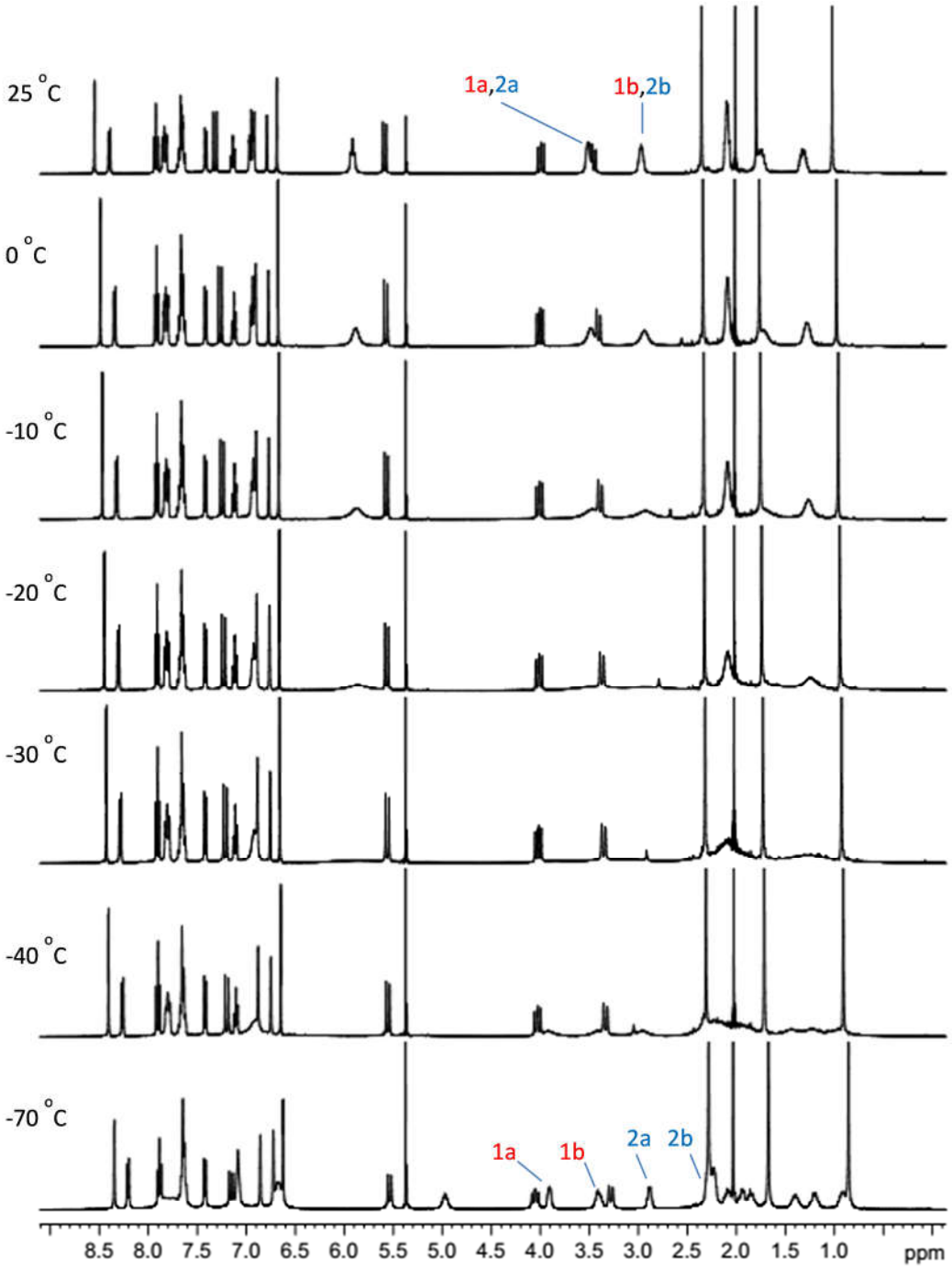

Figure S1. VT-^{1}H NMR spectra of **4a(Cl)** (400 MHz, CD_2Cl_2). [$\Delta G^{\ddagger}_{244}$ = 10.9 kcal mol^{-1}]

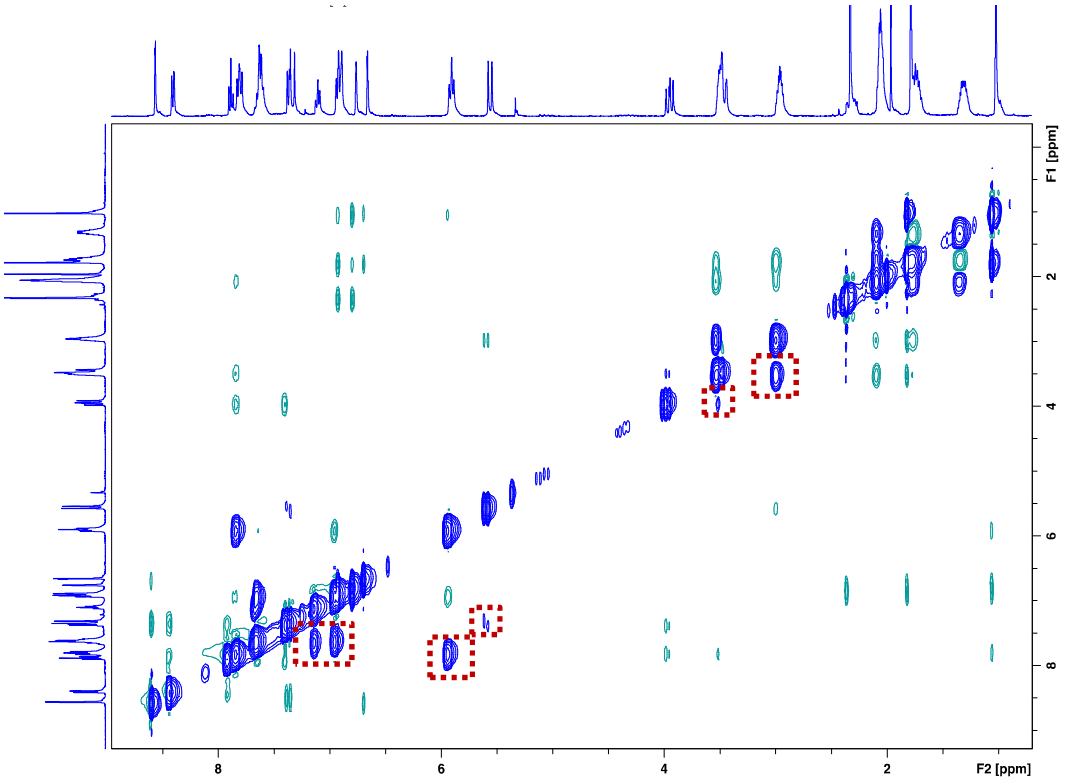

Figure S2a. ^{1}H-^{1}H NOESY spectrum of **4a(Cl)** (400 MHz, CD_2Cl_2, 50 ^{o}C) (Blue signals: exchange cross-peaks; green signals: NOE cross-peaks).

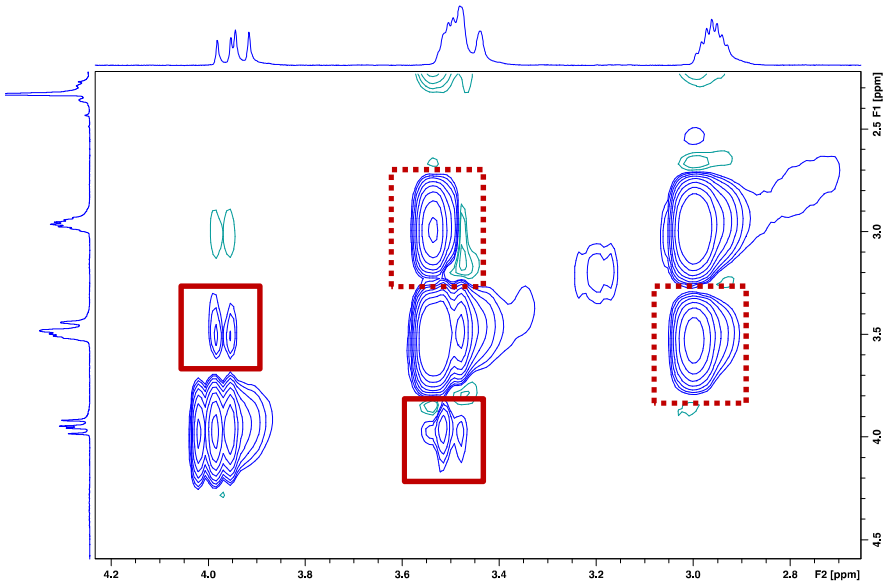

Figure S2b. Region of the ^{1}H-^{1}H NOESY spectrum of **4a(Cl)** (400 MHz, CD_2Cl_2, 50 ^{o}C) (Blue signals: exchange cross-peaks; green signals: NOE cross-peaks. Signals marked with solid line squares: exchange cross-peaks due to CH_2P protons, signals marked with dotted line squares: olefin exchange cross-peaks due to olefinic protons).

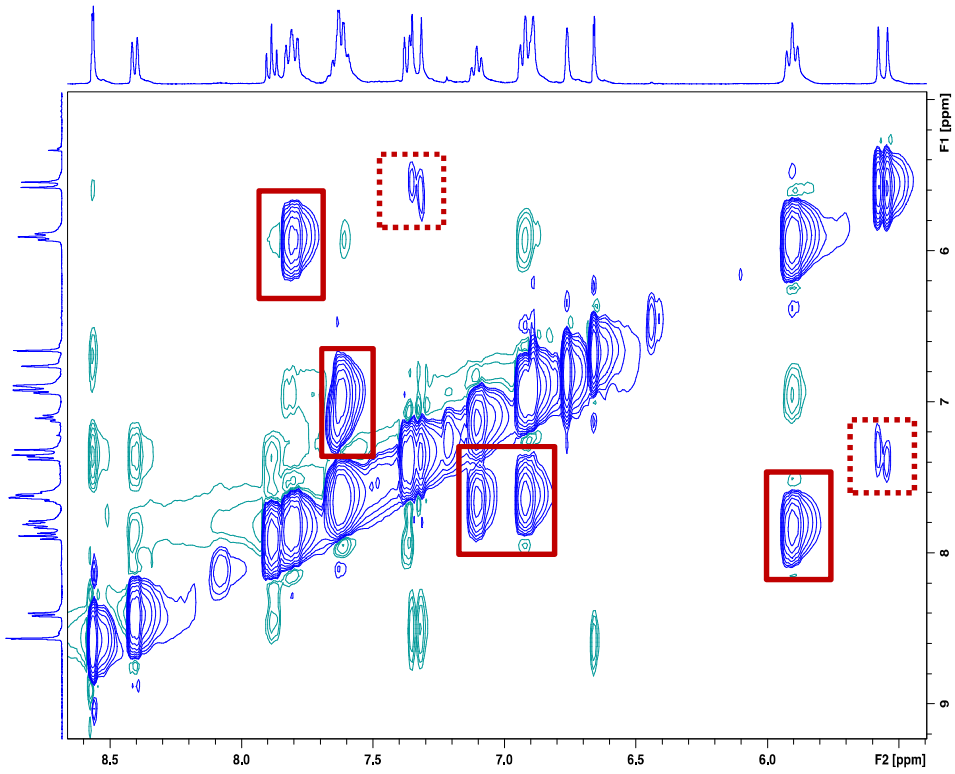

Figure S2c. Region of the ^{1}H-^{1}H NOESY spectrum of **4a(Cl)** (400 MHz, CD_2Cl_2, 50 ^{o}C) (Blue signals: exchange cross-peaks; green signals: NOE cross-peaks. Signals marked with solid line squares: exchange cross-peaks due to PPh_2 protons, signals marked with dotted line squares: exchange cross-peaks due to CH_2N protons).

2. VT-^{1}H NMR Spectra of 5a(Cl) and 6a(Cl)

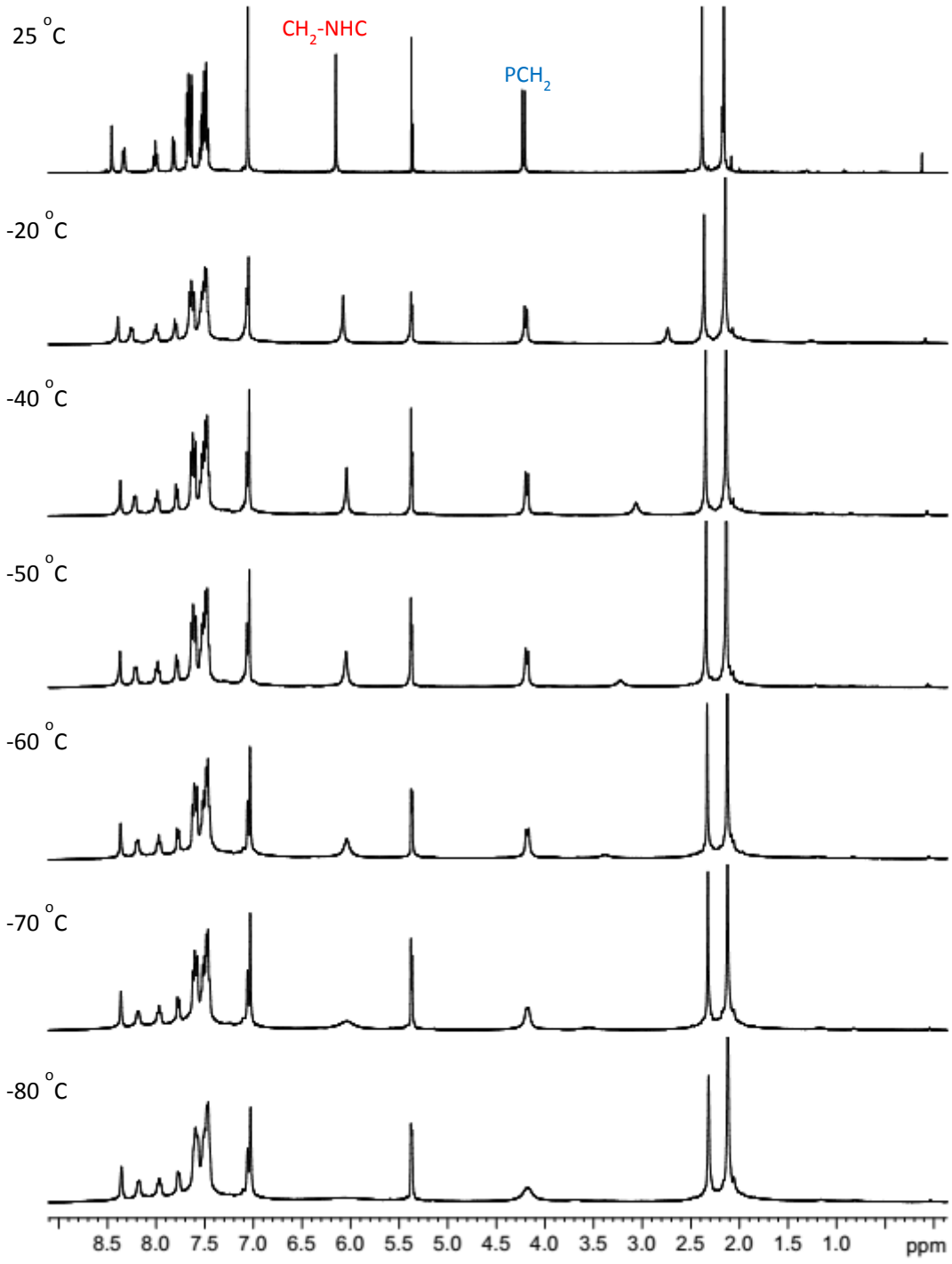

Figure S3. VT-^{1}H NMR spectra of **5a(Cl)** (400 MHz, CD_2Cl_2).

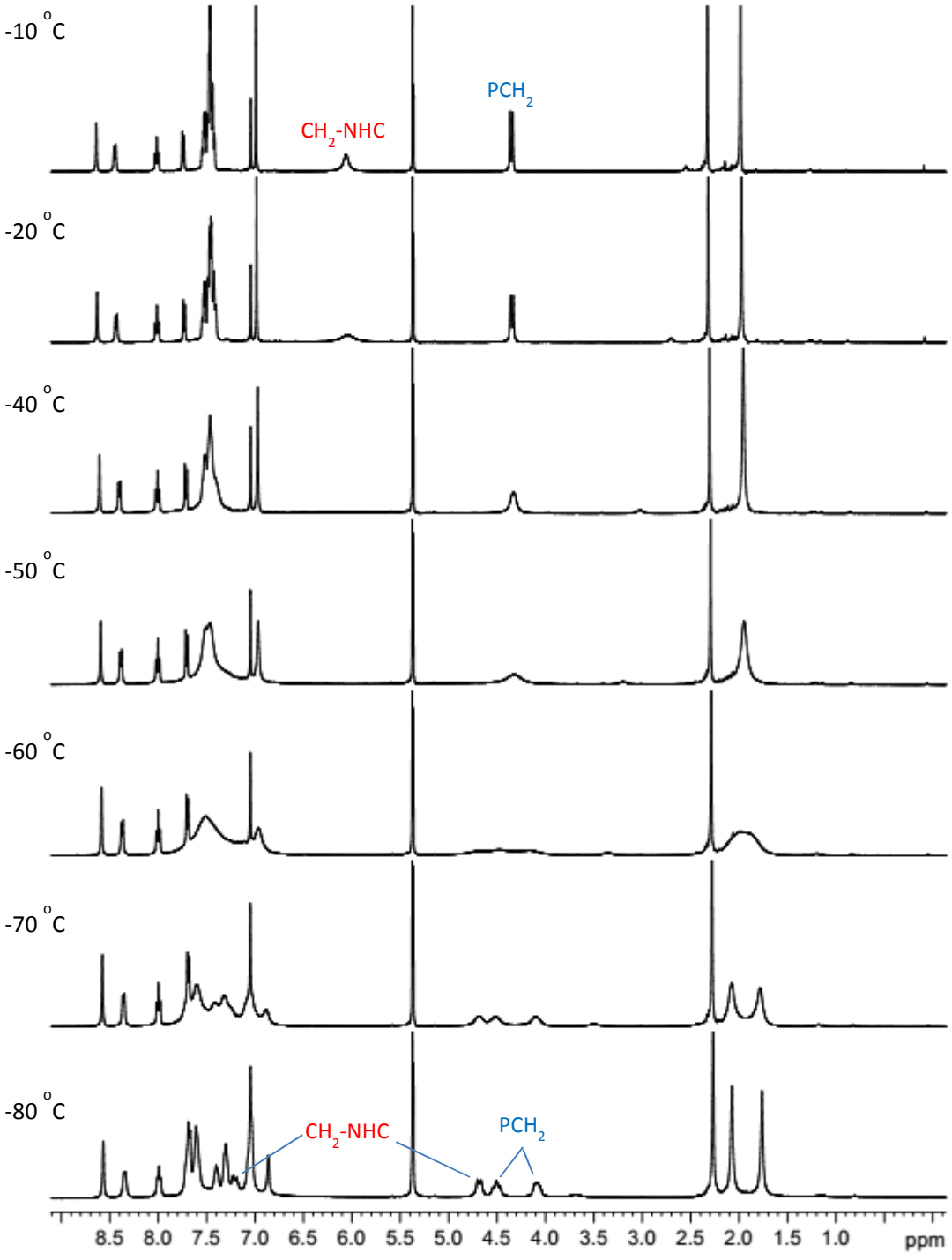

Figure S4. VT-^{1}H NMR spectra of **6a(Cl)** (400 MHz, CD_2Cl_2). [$\Delta G^{\ddagger}_{214}$ = 10.0 kcal mol^{-1}]

3. X-Ray Structure Analysis of 1a(Cl), 2a, 4b(BAr_F) and 7a(Cl)

Crystals of suitable size for X-ray diffraction analysis, obtained using liquid diffusion techniques, were coated with dry perfluoropolyether and mounted on glass fibers and fixed in a cold nitrogen stream (T = 213 K) to the goniometer head. Crystallographic data collection were performed on a Bruker-Nonius X8Apex-II CCD diffractometer, using monochromatic radiation λ(Mo K_α) = 0.71073 Å, by means of ω and φ scans with a width of 0.50 degree. The data were reduced (SAINT)[1] and corrected for absorption effects by the multi-scan method (SADABS).[2] The structures were solved by direct methods (SIR-2002)[3] and refined against all F^2 data by full-matrix least-squares techniques (SHELXTL-6.12)[4] minimizing $w[F_o^2-F_c^2]^2$. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were included from calculated positions and refined riding on their respective carbon atoms with isotropic displacement parameters. The details of X-Ray single-crystal diffraction experiments are given below in Tables S1 to S4 in the Supporting Information, and molecular structures are shown in Figures S1 to S4. CCDC 1486492 [**1a(Cl**)], 1486493 [**2a**], 1486494 [**4b(BAr$_F$**)] and 1486495 [**7a(Cl)**], contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[1] Bruker. APEX2. Bruker AXS Inc., Madison, Wisconsin, USA, 2007.

[2] Bruker Advanced X-ray Solutions, Bruker AXS Inc., Madison, Wisconsin, USA, 2001.

[3] C. M. Burla, M. Camalli, B. Carrozzini, G. L. Cascarano, C. Giacovazzo, G. Polipori and R. Spagna, SIR2002: the program, *J. Appl. Cryst.*, 2003, **36**, 1103.

[4] C. M. Burla, M. Camalli, B. Carrozzini, G. L. Cascarano, C. Giacovazzo, G. Polipori and R. Spagna, SIR2002: the program, *J. Appl. Cryst.*, 2003, **36**, 1103.

X-Ray data for 1a(Cl)

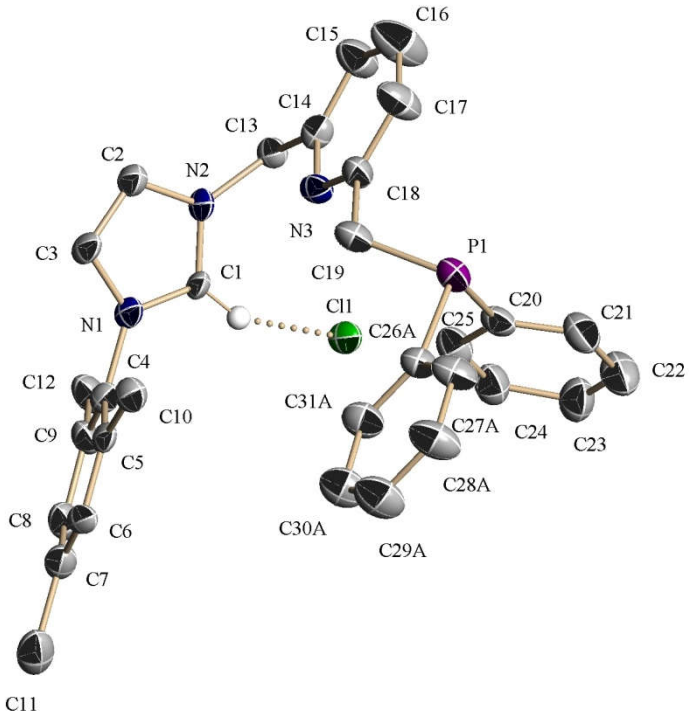

Figure S5. ORTEP view of molecular structure of **1a(Cl)** with thermal ellipsoids drawn at the 30% level. Most of the hydrogen atoms are omitted for clarity.

Table S1. Crystal data and structure refinement for **1a(Cl)**.

Empirical formula	$C_{31}H_{31}ClN_3P$	
	$[C_{31}H_{31}N_3P^+, Cl^-]$	
Formula weight	512.01	
Temperature	193(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P $2_1/c$	
Unit cell dimensions	*a* = 8.8606(15) Å	α = 90°
	b = 27.202(4) Å	β = 110.027(6)°
	c = 12.531(2) Å	γ = 90°
Volume	2837.6(8) $Å^3$	
Z	4	
Density (calculated)	1.198 Mg/m^3	
Absorption coefficient	0.215 mm^{-1}	
F(000)	1080	
Crystal size	0.20 x 0.10 x 0.05 mm^3	
Theta range for data collection	1.88 to 23.50°.	
Index ranges	-9<=h<=9, -29<=k<=30, -7<=l<=14	
Reflections collected	17580	
Independent reflections	4176 [R(int) = 0.0930]	
Completeness to theta = 23.50°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9893 and 0.9583	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4176 / 258 / 353	
Goodness-of-fit on F^2	1.009	
Final R indices [I>2sigma(I)]	R1 = 0.0977, wR2 = 0.2374	
R indices (all data)	R1 = 0.1966, wR2 = 0.2702	
Extinction coefficient	0.009(2)	
Largest diff. peak and hole	1.263 and -0.347 $e.Å^{-3}$	

$R1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$, $wR2 = [\Sigma(w(F_o^2-F_c^2)^2)/\Sigma(w(F_o^2)^2)]^{½}$

X-Ray data for 2a

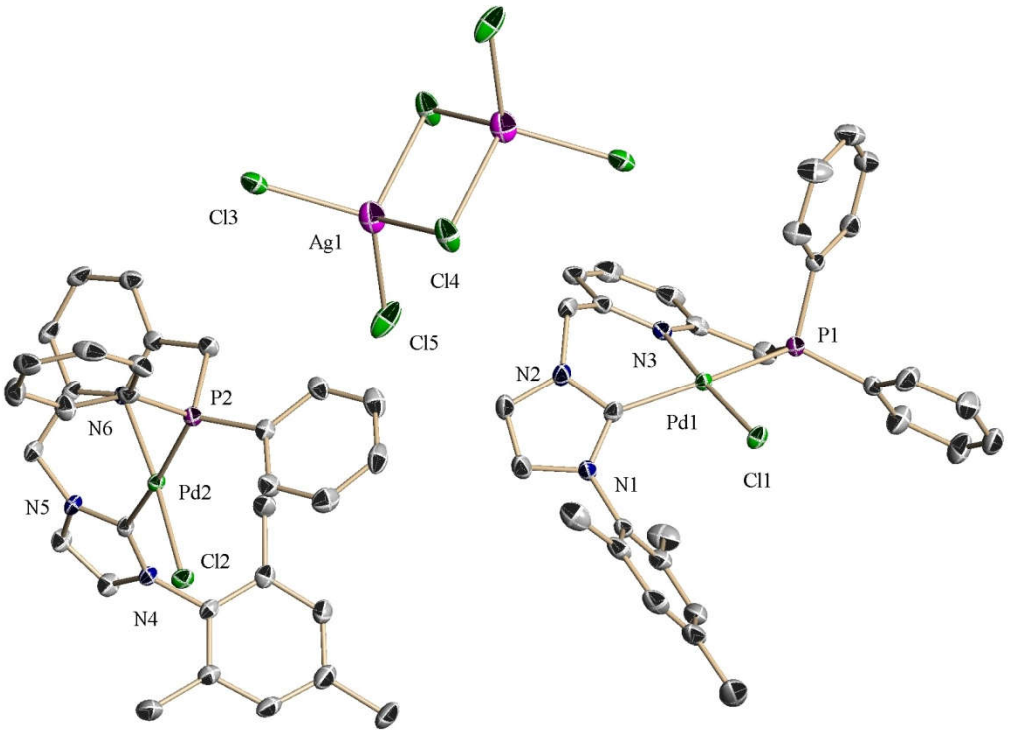

Figure S6. ORTEP view of molecular structure of complex salt **2a** with thermal ellipsoids drawn at the 30% level. Most of the hydrogen atoms are omitted for clarity.

Table S2. Crystal data and structure refinement for **2a**.

Empirical formula	$C_{63}H_{62}AgCl_7N_6P_2Pd_2$	
	$[2(C_{31}H_{30}ClN_3PPd), 0.5(Ag_2Cl_6), CH_2Cl_2]$	
Formula weight	1533.95	
Temperature	193(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	$P\bar{1}$	
Unit cell dimensions	*a* = 11.9582(4) Å	α = 76.776(2)°.
	b = 14.6903(5) Å	β = 84.078(2)°.
	c = 18.8464(6) Å	γ = 79.620(2)°.
Volume	3163.56(18) $Å^3$	
Z	2	
Density (calculated)	1.610 Mg/m^3	
Absorption coefficient	1.260 mm^{-1}	
F(000)	1540	
Crystal size	0.20 x 0.20 x 0.05 mm^3	
Theta range for data collection	2.00 to 25.25°.	
Index ranges	-13<=h<=14, -17<=k<=17, -22<=l<=21	
Reflections collected	40011	
Independent reflections	11449 [R(int) = 0.0306]	
Completeness to theta = 25.25°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9397 and 0.7867	
Refinement method	Full-matrix-block least-squares on F^2	
Data / restraints / parameters	11449 / 45 / 736	
Goodness-of-fit on F^2	1.065	
Final R indices [I>2sigma(I)]	R1 = 0.0541, wR2 = 0.1513	
R indices (all data)	R1 = 0.0694, wR2 = 0.1596	
Largest diff. peak and hole	3.525 and -1.550 $e.Å^{-3}$	

$R1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$, $wR2 = [\Sigma(w(F_o^2-F_c^2)^2)/\Sigma(w(F_o^2)^2)]^{½}$

X-Ray data for 4b(BAr_F)

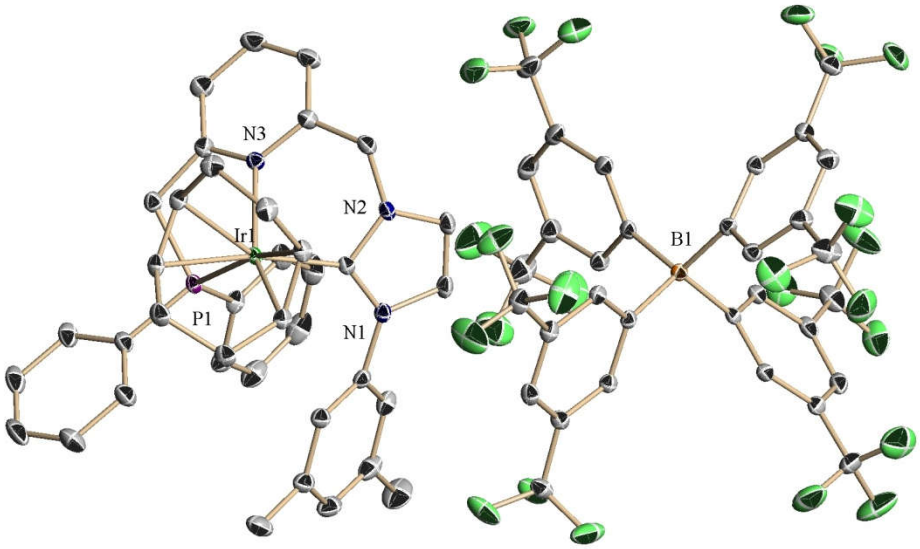

Figure S7. ORTEP view of molecular structure of complex salt **4b(BAr_F)** with thermal ellipsoids drawn at the 30% level. Most of the hydrogen atoms are omitted for clarity.

Table S3. Crystal data and structure refinement for **4b(BAr$_F$)**.

Empirical formula	$C_{71}H_{54}BCl_2F_{24}IrN_3P$	
	$[C_{32}H_{12}BF_{24}, C_{38}H_{40}IrN_3P, CH_2Cl_2]$	
Formula weight	1710.05	
Temperature	193(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	$P\bar{1}$	
Unit cell dimensions	a = 12.6720(3) Å	α = 102.5910(10)°
	b = 15.6405(3) Å	β = 90.3940(10)°
	c = 18.3012(3) Å	γ = 100.2620(10)°
Volume	3479.42(12) Å^3	
Z	2	
Density (calculated)	1.632 Mg/m^3	
Absorption coefficient	2.128 mm^{-1}	
F(000)	1696	
Crystal size	0.40 x 0.40 x 0.20 mm^3	
Theta range for data collection	2.04 to 25.25°.	
Index ranges	-15<=h<=15, -18<=k<=18, -21<=l<=21	
Reflections collected	49057	
Independent reflections	12593 [R(int) = 0.0210]	
Completeness to theta = 25.25°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.6756 and 0.4832	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	12593 / 309 / 984	
Goodness-of-fit on F^2	1.056	
Final R indices [I>2sigma(I)]	R1 = 0.0287, wR2 = 0.0751	
R indices (all data)	R1 = 0.0308, wR2 = 0.0762	
Largest diff. peak and hole	1.379 and -0.934 e.Å^{-3}	

R1 = $\Sigma||F_o|-|F_c||/\Sigma|F_o|$, wR2 = $[\Sigma(w(F_o^2-F_c^2)^2)/\Sigma(w(F_o^2)^2)]^{½}$

X-Ray data for 7a(Cl)

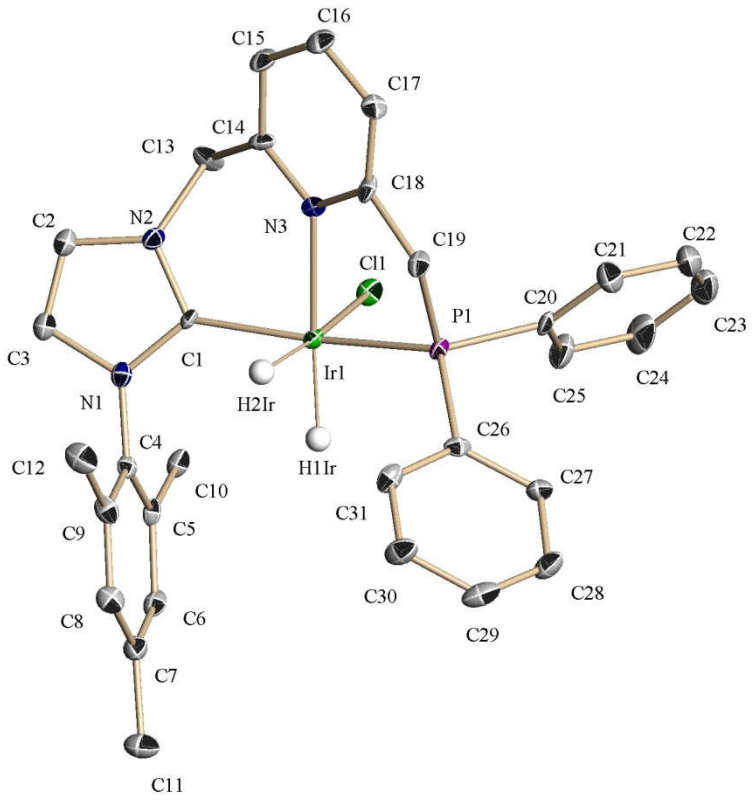

Figure S8. ORTEP view of molecular structure of complex **7a(Cl)** with thermal ellipsoids drawn at the 30% level. Most of the hydrogen atoms are omitted for clarity.

Table S4. Crystal data and structure refinement for **7a(Cl)**.

Empirical formula	$C_{33}H_{36}Cl_5IrN_3P$	
	$[C_{31}H_{32}ClIrN_3P, 2(CH_2Cl_2)]$	
Formula weight	875.07	
Temperature	193(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P b c a	
Unit cell dimensions	*a* = 11.7851(6) Å	α = 90°
	b = 14.3274(7) Å	β = 90°
	c = 41.473(2) Å	γ = 90°
Volume	7002.8(6) $Å^3$	
Z	8	
Density (calculated)	1.660 Mg/m^3	
Absorption coefficient	4.268 mm^{-1}	
F(000)	3456	
Crystal size	0.50 x 0.30 x 0.20 mm^3	
Theta range for data collection	3.59 to 25.25°.	
Index ranges	-13<=h<=14, -17<=k<=12, -49<=l<=40	
Reflections collected	84509	
Independent reflections	6299 [R(int) = 0.0293]	
Completeness to theta = 25.25°	99.4 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.4823 and 0.2241	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6299 / 129 / 419	
Goodness-of-fit on F^2	1.409	
Final R indices [I>2sigma(I)]	R1 = 0.0711, wR2 = 0.1647	
R indices (all data)	R1 = 0.0731, wR2 = 0.1653	
Largest diff. peak and hole	3.417 and -4.932 $e.Å^{-3}$	

$R1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$, $wR2 = [\Sigma(w(F_o^2-F_c^2)^2)/\Sigma(w(F_o^2)^2)]^{½}$

4. Selected ^{1}H and $^{13}C\{^{1}H\}$-NMR spectra of M-CNP complexes

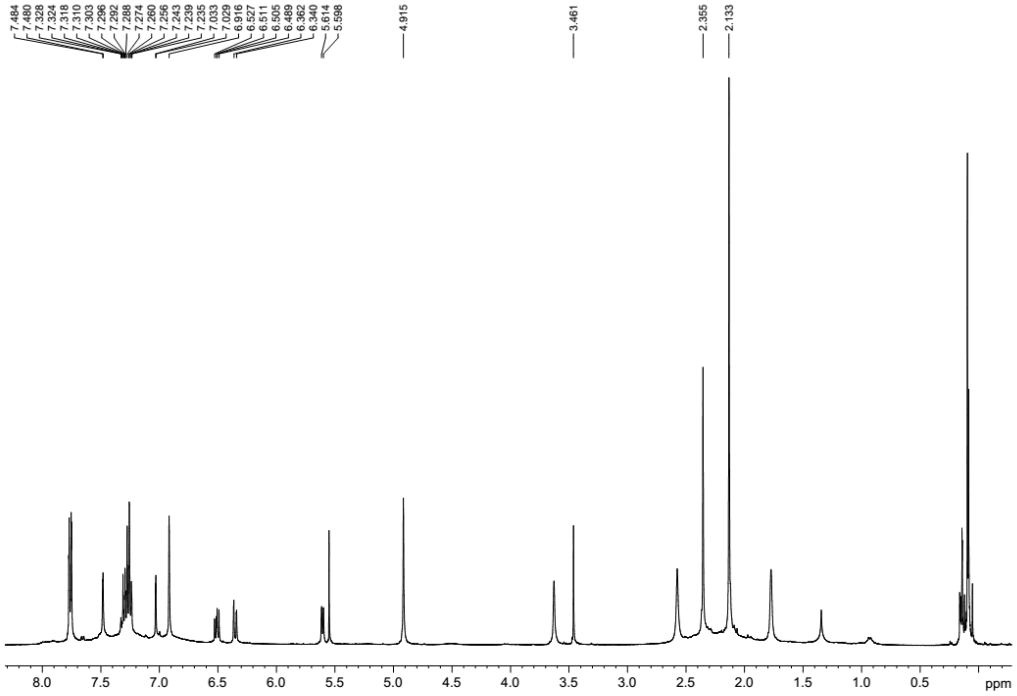

Figure S9. ^{1}H NMR spectrum of **3a** (400 MHz, THF-d_8).

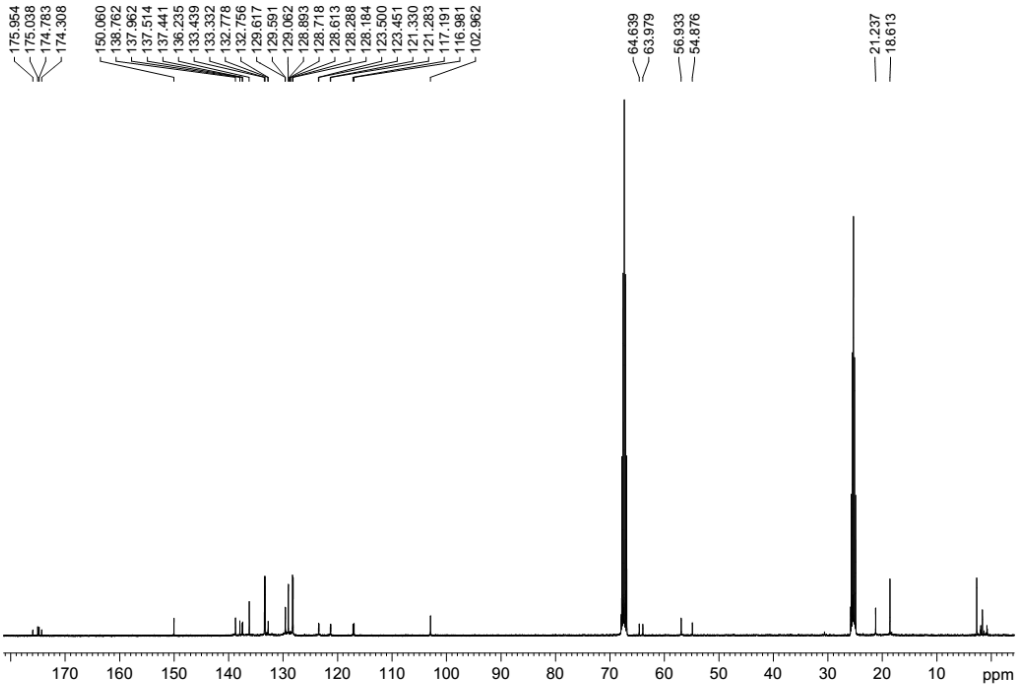

Figure S10. $^{13}C\{^{1}H\}$ NMR spectrum of **3a** (101 MHz, THF-d_8).

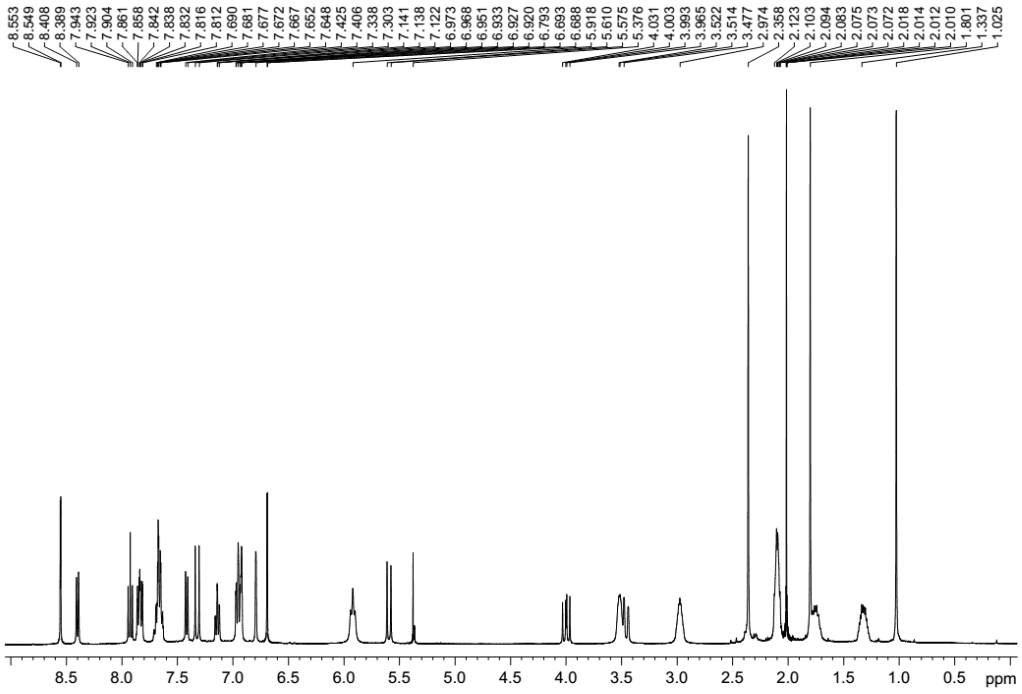

Figure S11. ^{1}H NMR spectrum of **4a(Cl)** (400 MHz, CD_2Cl_2).

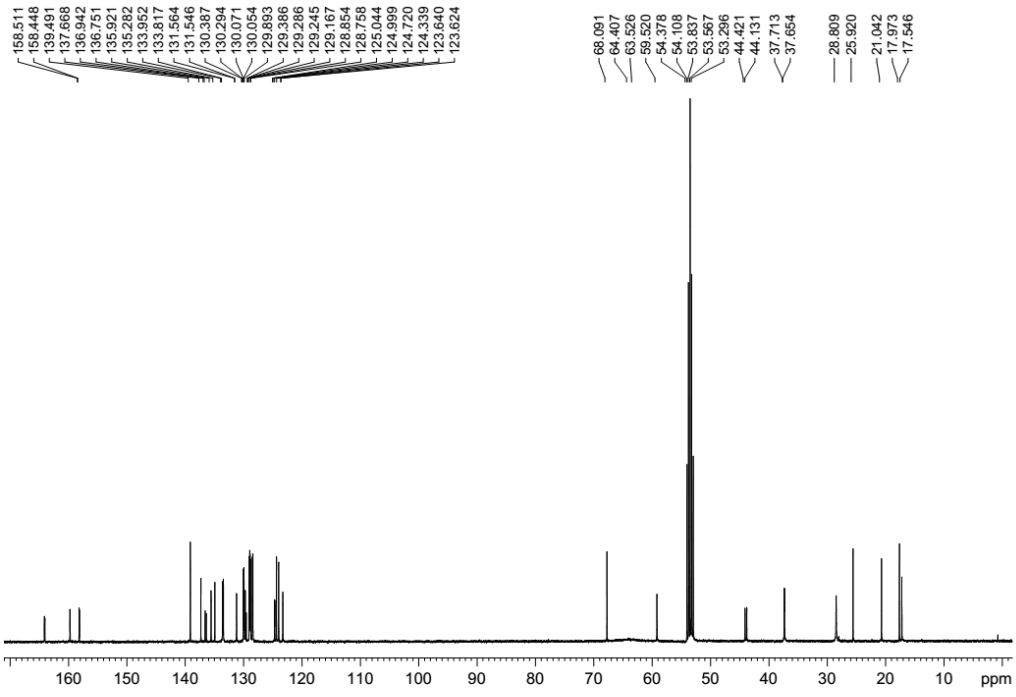

Figure S12. $^{13}C\{^{1}H\}$ NMR spectrum of **4a(Cl)** (101 MHz, CD_2Cl_2).

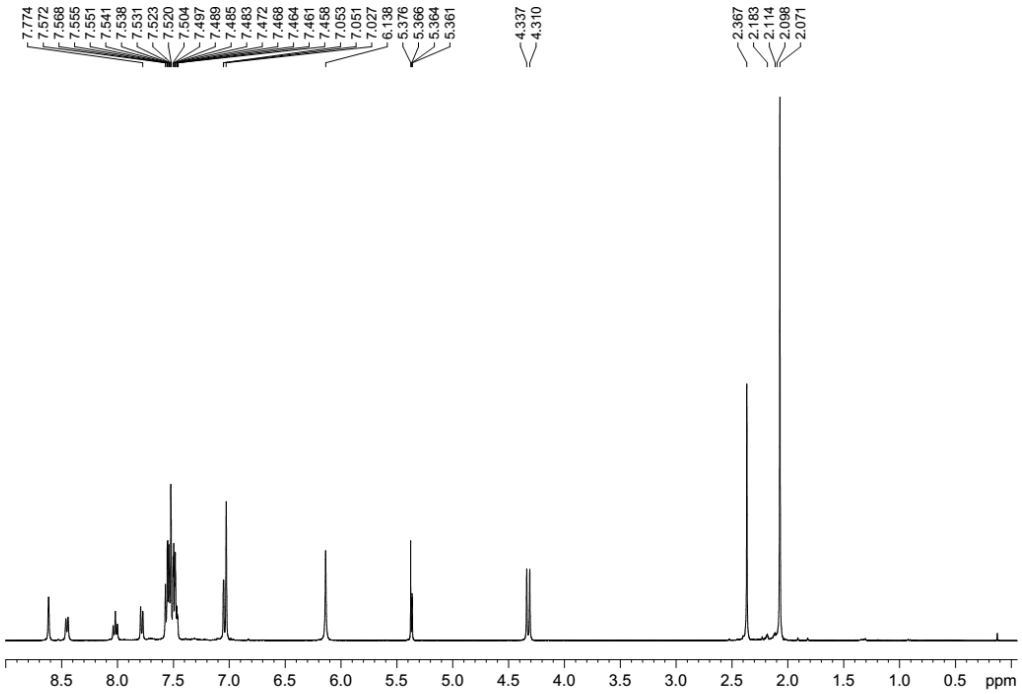

Figure S13. ^{1}H NMR spectrum of **6a(Cl)** (400 MHz, CD_2Cl_2).

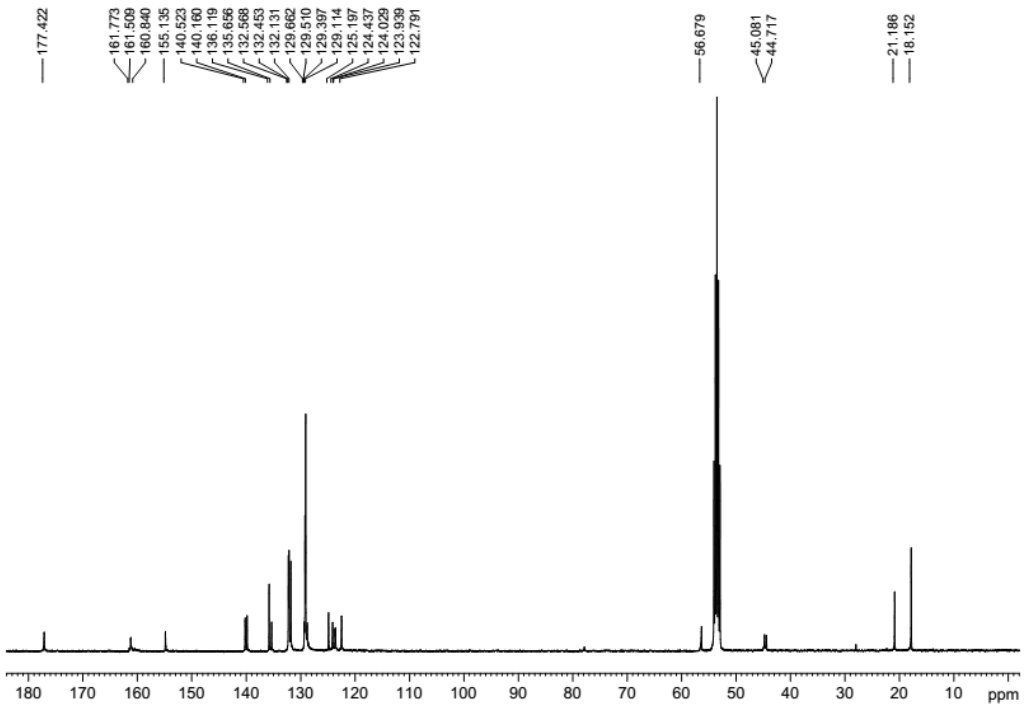

Figure S14. $^{13}C\{^{1}H\}$ NMR spectrum of **6a(Cl)** (101 MHz, CD_2Cl_2).

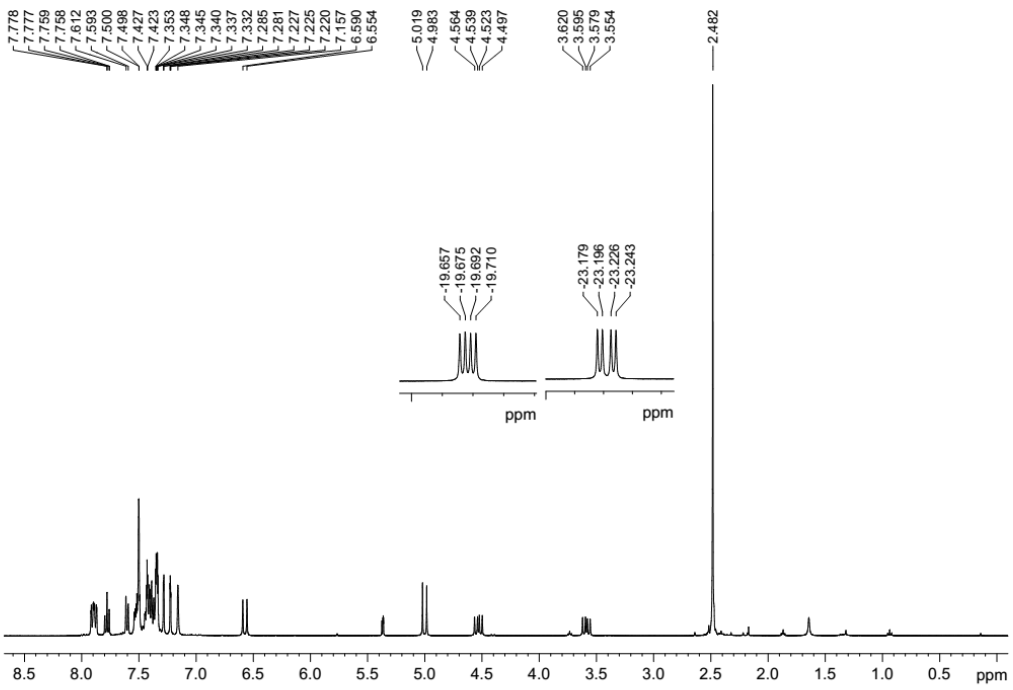

Figure S15. ^{1}H NMR spectrum of **7b(Cl)** (400 MHz, CD_2Cl_2).

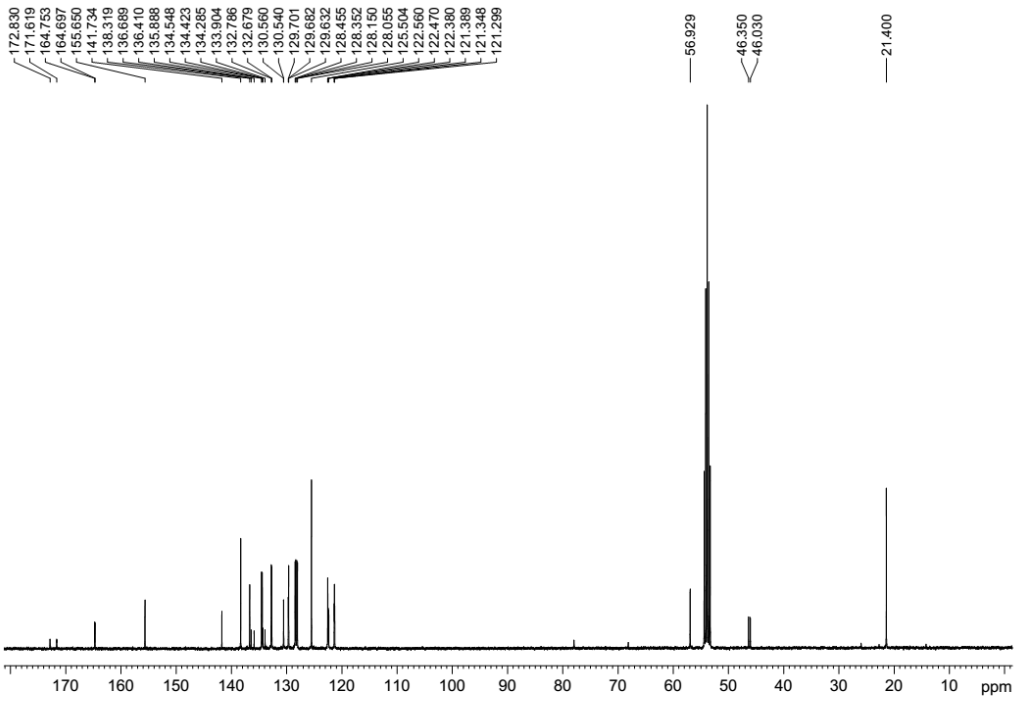

Figure S16. $^{13}C\{^{1}H\}$ NMR spectrum of **7b(Cl)** (101 MHz, CD_2Cl_2).

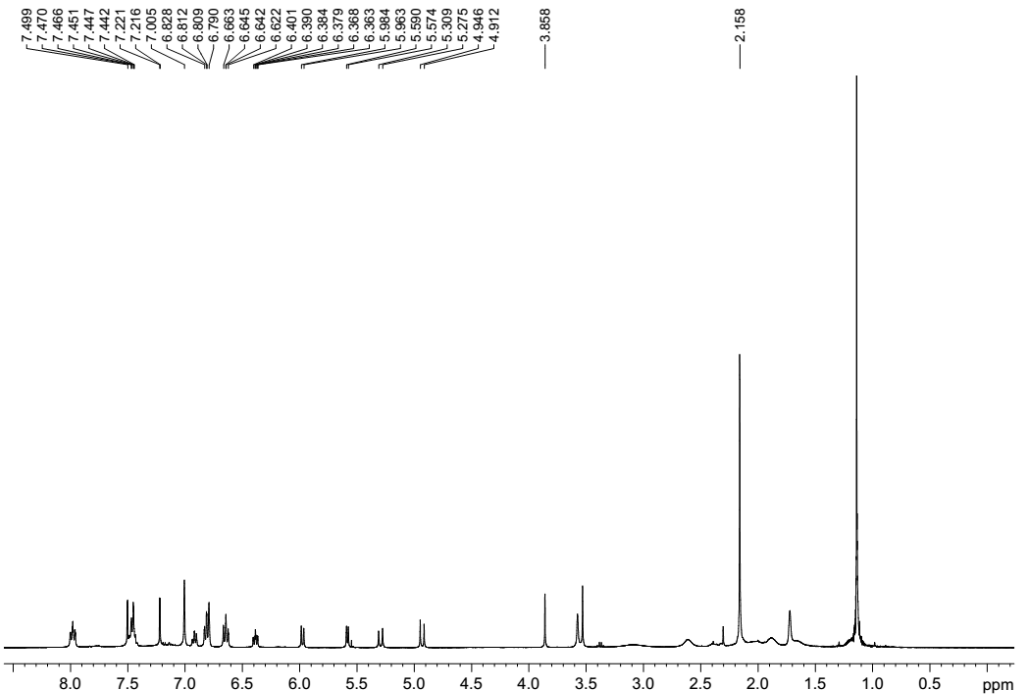

Figure S17. ^{1}H NMR spectrum of **8b** (400 MHz, THF-d_8, 273 K).

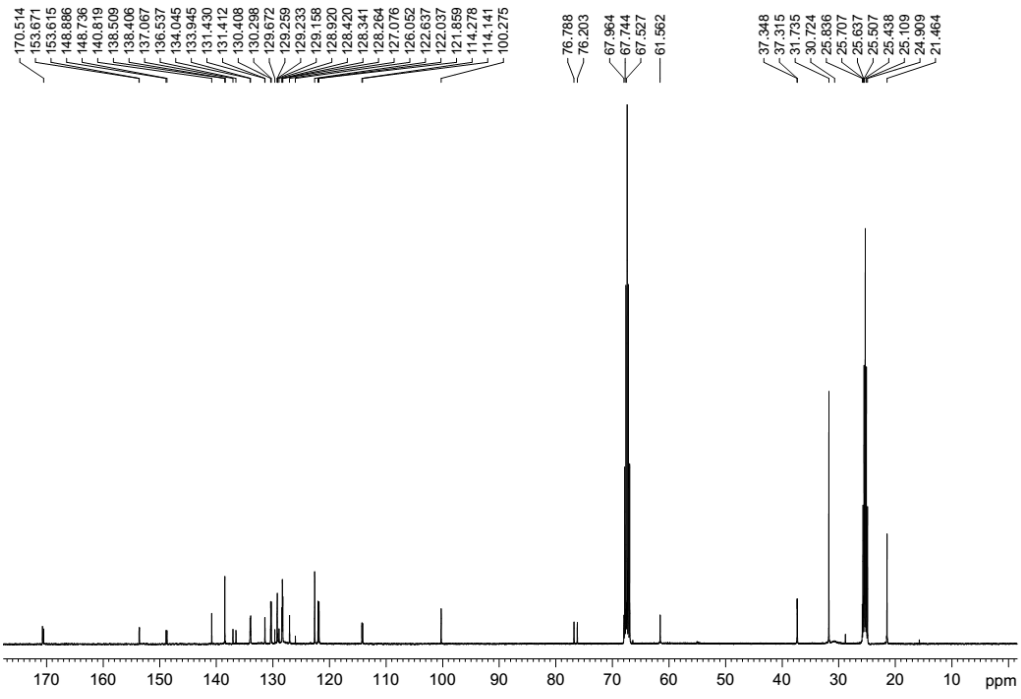

Figure S18. ^{13}C{^{1}H} NMR spectrum of **8b** (101 MHz, THF-d_8, 273 K).

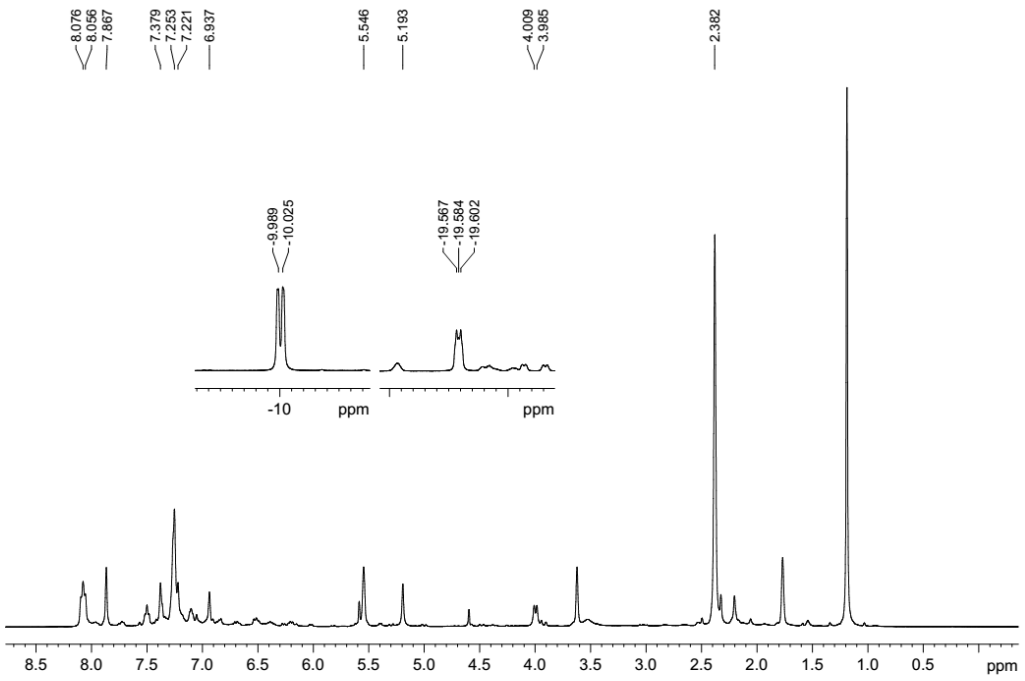

Figure S19. ^{1}H NMR spectrum of **9b** (400 MHz, THF-d_8).

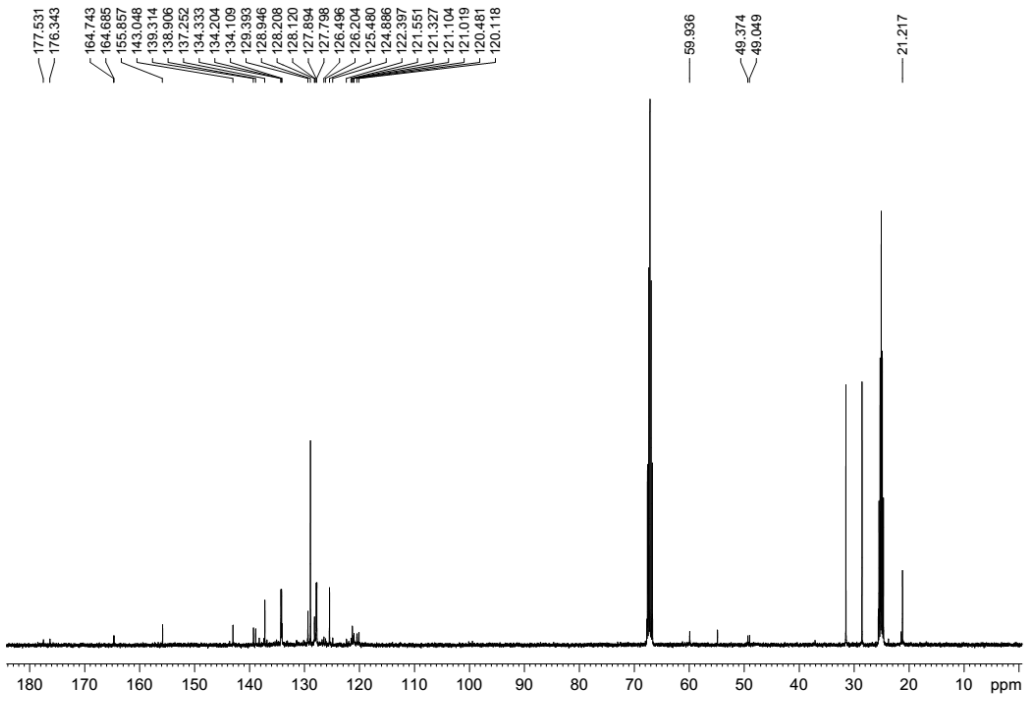

Figure S20. ^{13}C{^{1}H} NMR spectrum of **9b** (101 MHz, THF-d_8).