Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Titanium complexes with unsymmetrical imidazolin-2-iminato ligands

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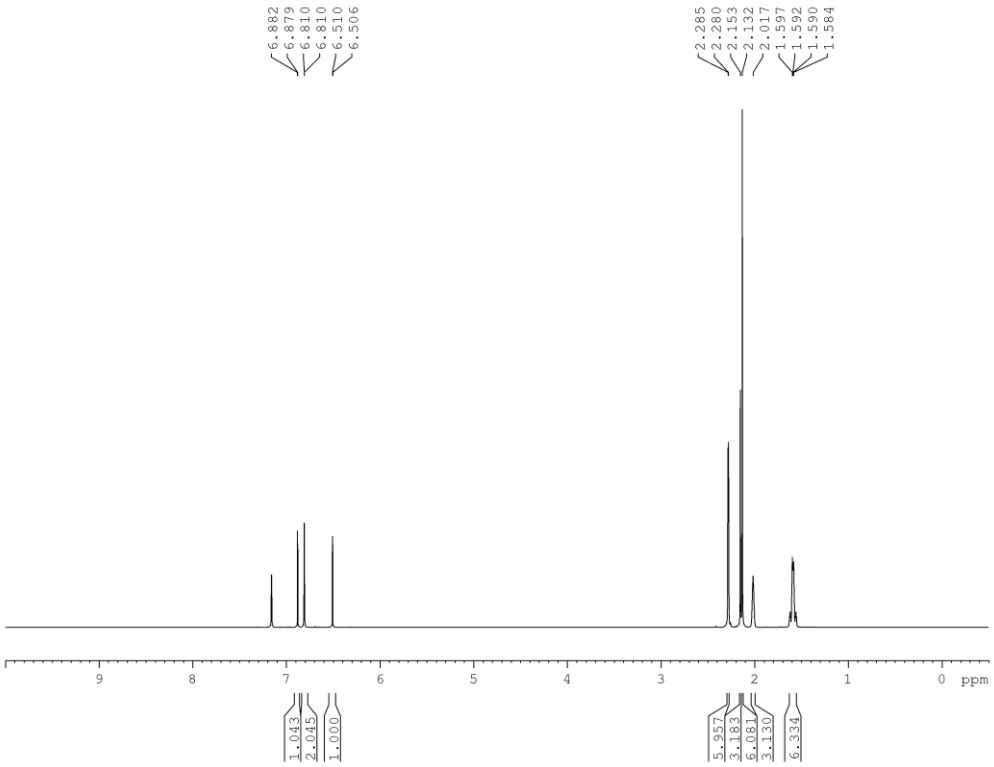
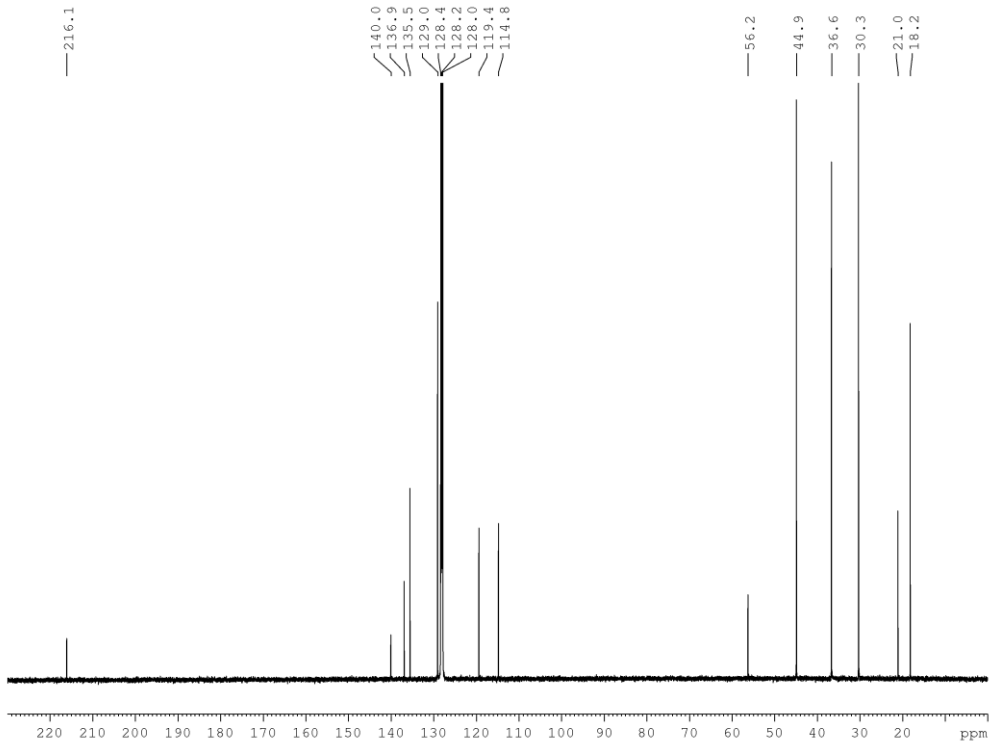
1. Spectra

1.1 1-(Adamantyl)-3-(2,4,6-trimethylphenyl)-imidazolin-2-ylidene (1a)

^{1}H NMR (500 MHz, C_6D_6) of **1a**:

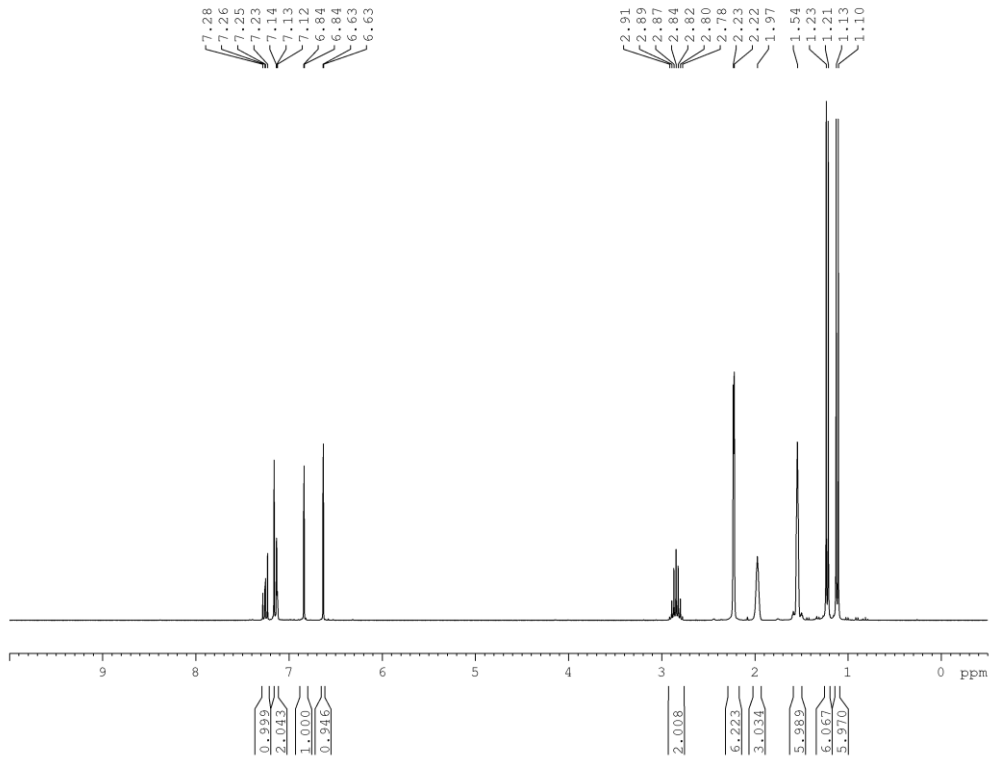


^{13}C NMR (126 MHz, C_6D_6) of **1a**:

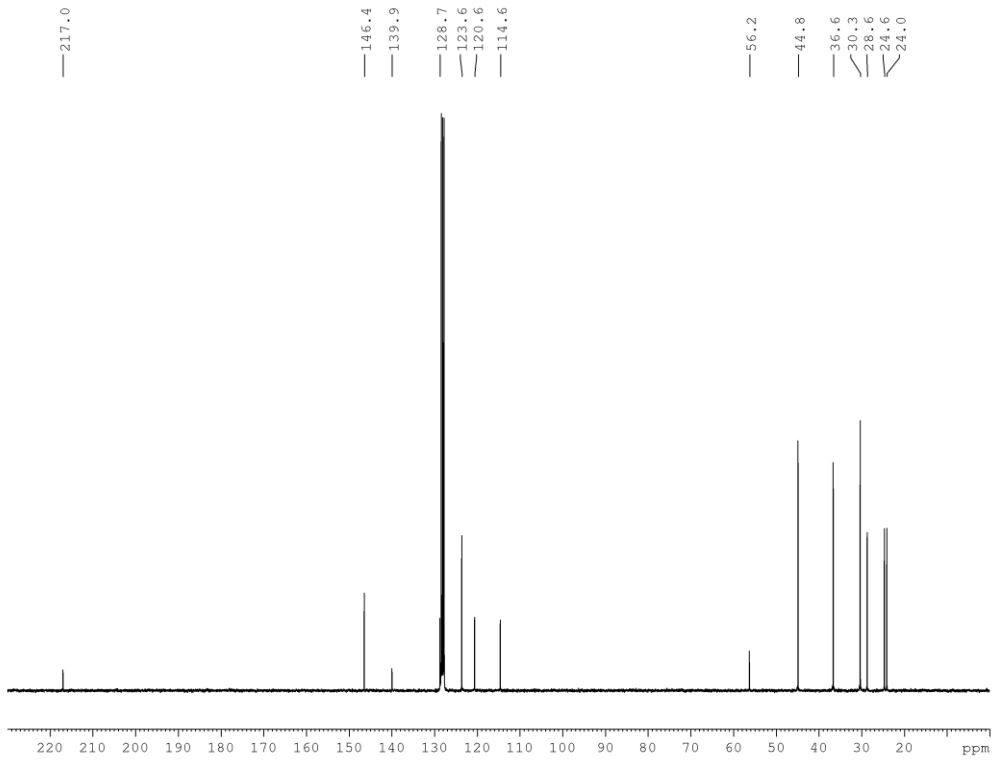


1.2 1-(Adamantyl)-3-(2,6-diisopropylphenyl)-imidazolin-2-ylidene (1b)

^{1}H NMR (300 MHz, C_6D_6) of **1b**:

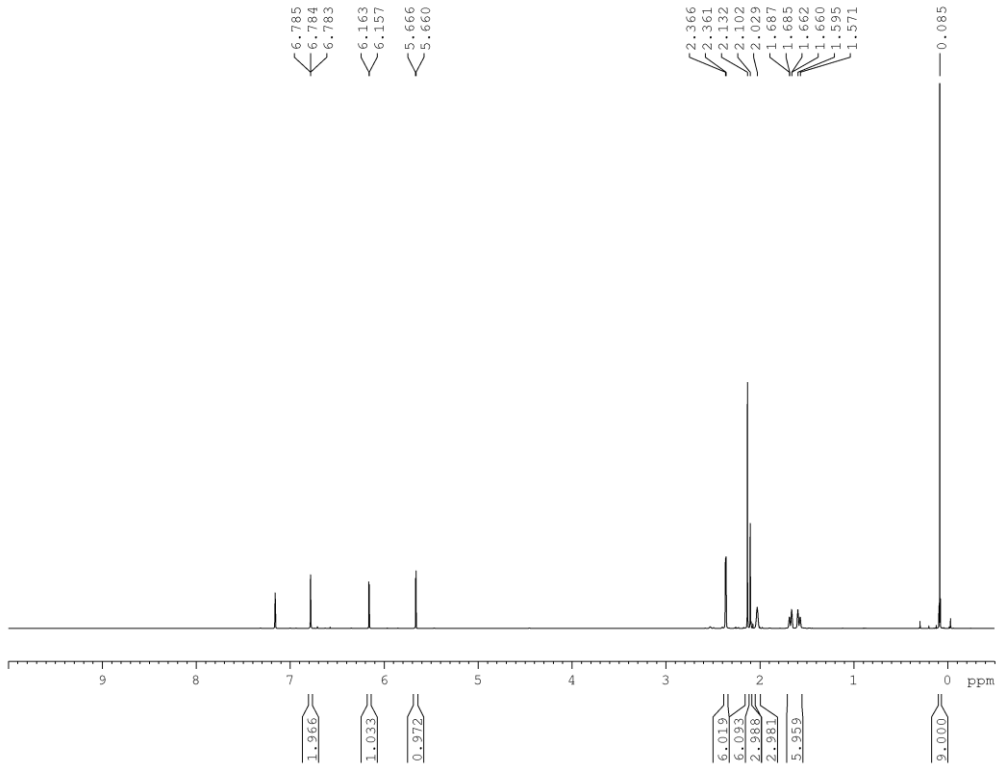


^{13}C NMR (75 MHz, C_6D_6) of **1b**:

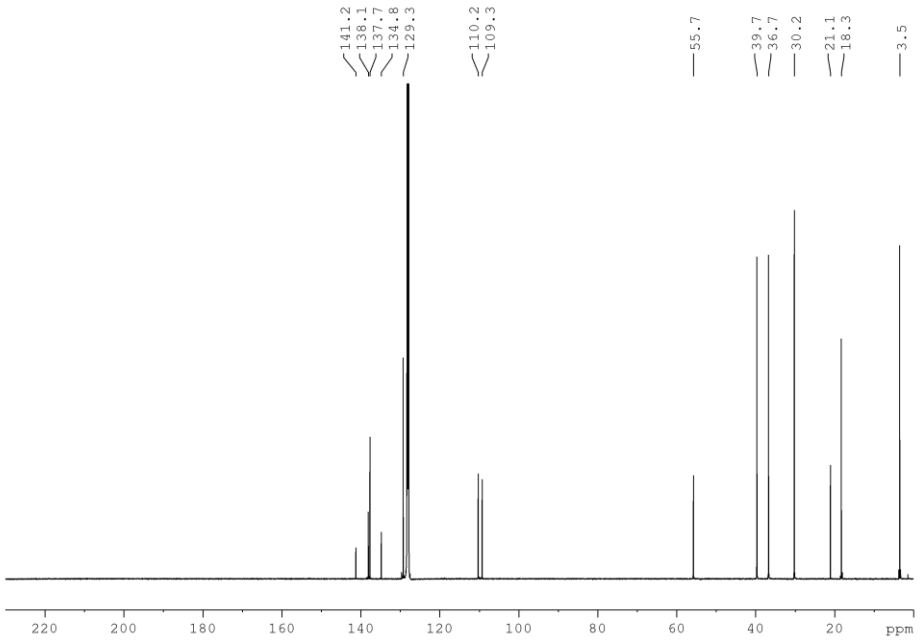


1.3 [Im^{AdMes}NSiMe$_3$] (2a)

^{1}H NMR (500 MHz, C_6D_6) of **2a**:

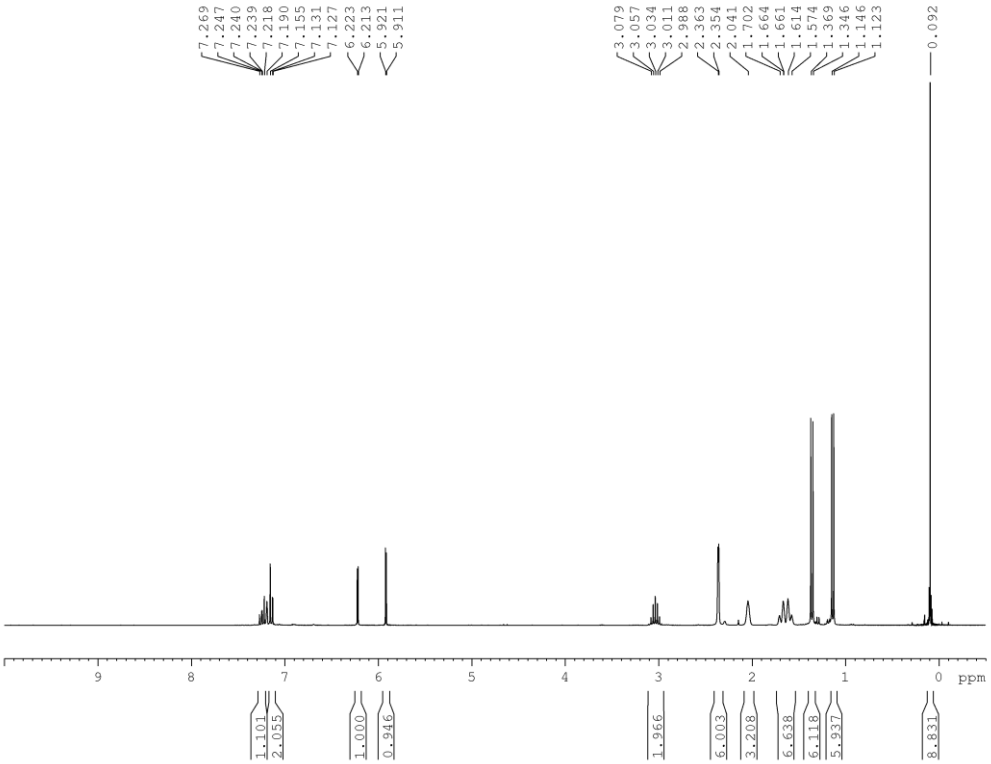


^{13}C NMR (126 MHz, C_6D_6) of **2a**:

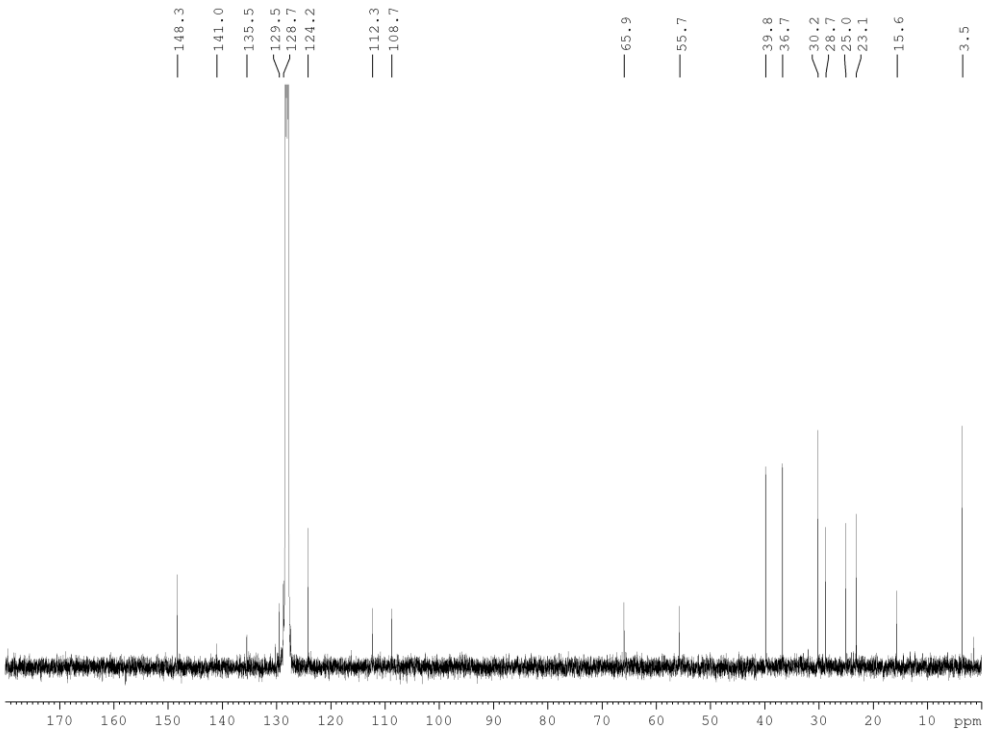


1.4 [Im^{AdDipp}NSiMe$_3$] (2b)

^{1}H NMR (400 MHz, C_6D_6) of **2b**:

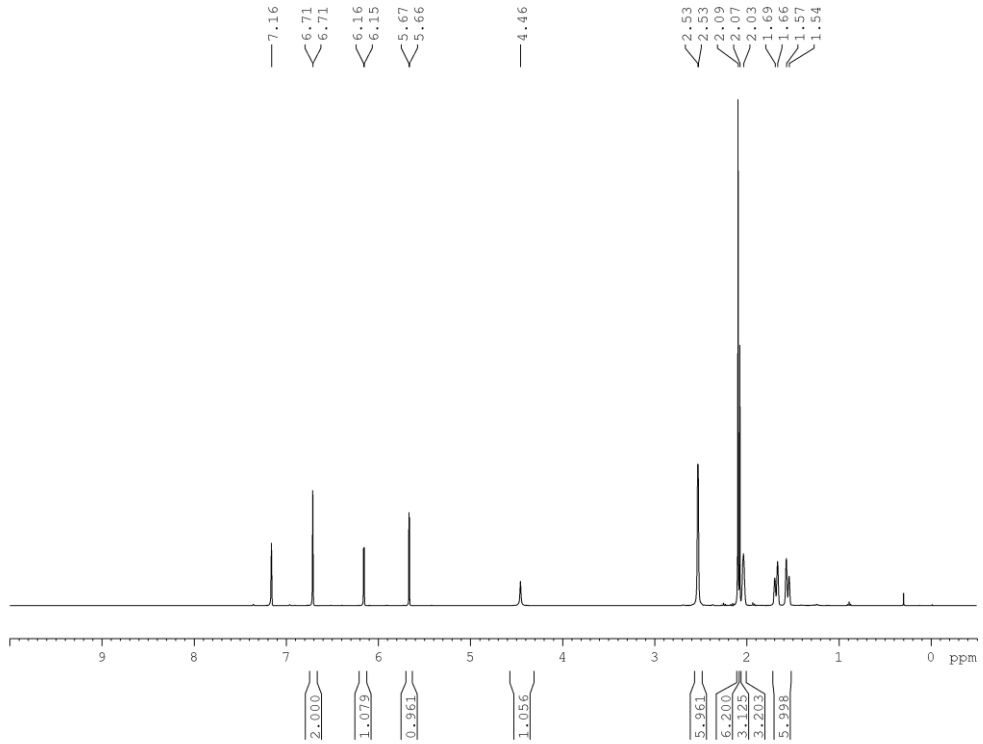


^{13}C NMR (100 MHz, C_6D_6) of **2b**:

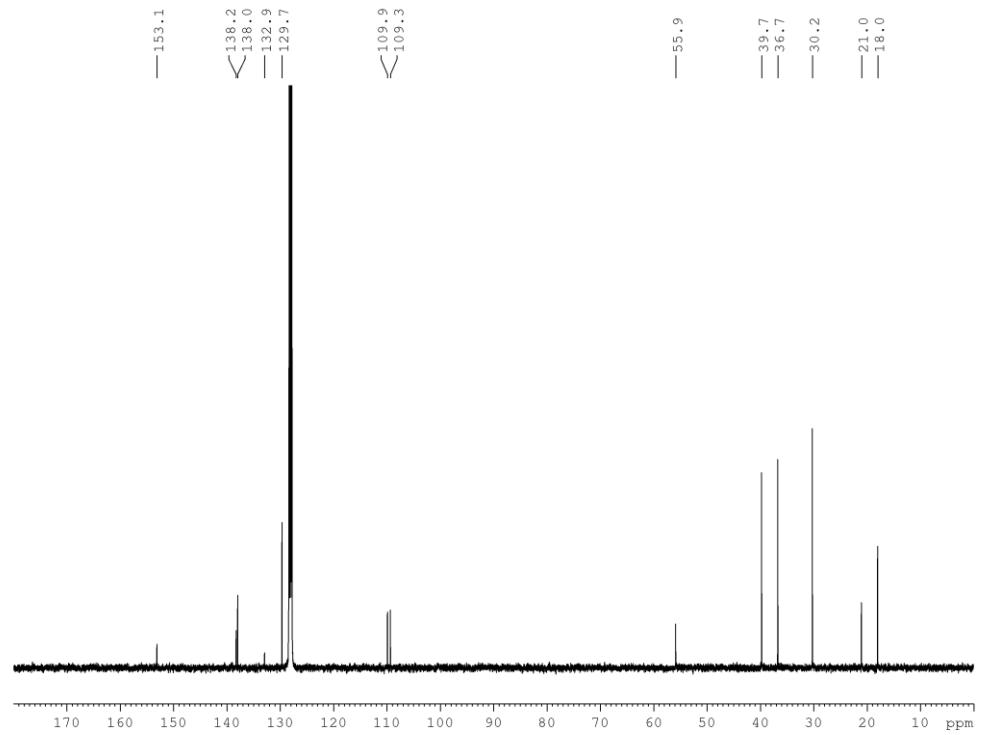


1.5 [Im^{AdMes}NH] (3a)

^{1}H NMR (400 MHz, C_6D_6) of **3a**:

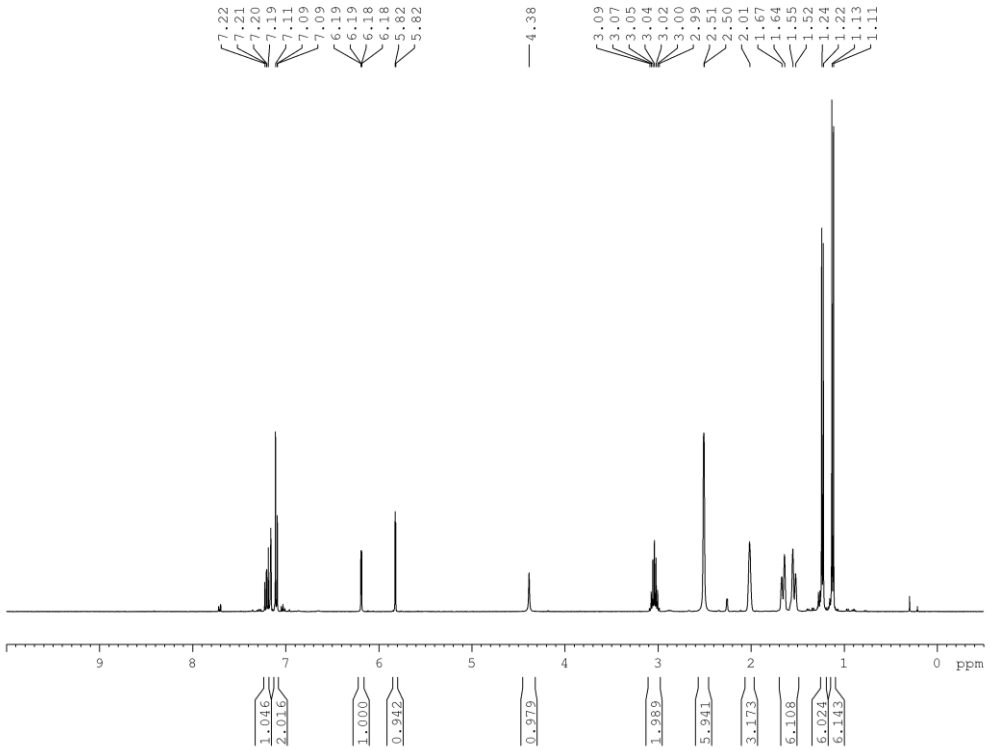


^{13}C NMR (100 MHz, C_6D_6) of **3a**:

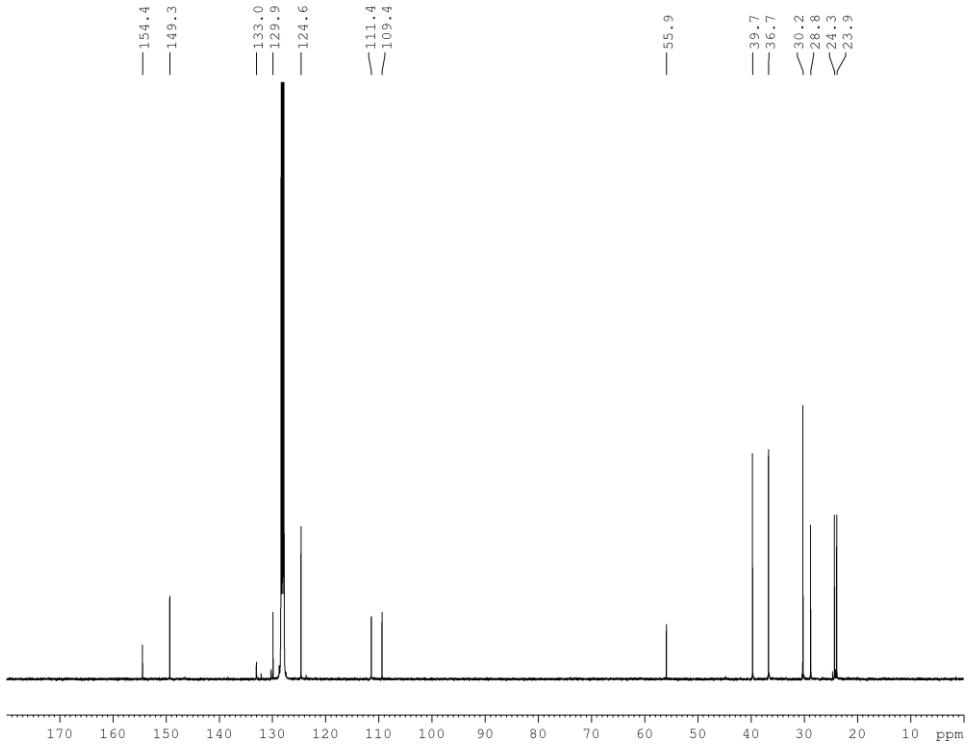


1.6 [Im^{AdDipp}NH] (3b)

^{1}H NMR (400 MHz, C_6D_6) of **3b**:

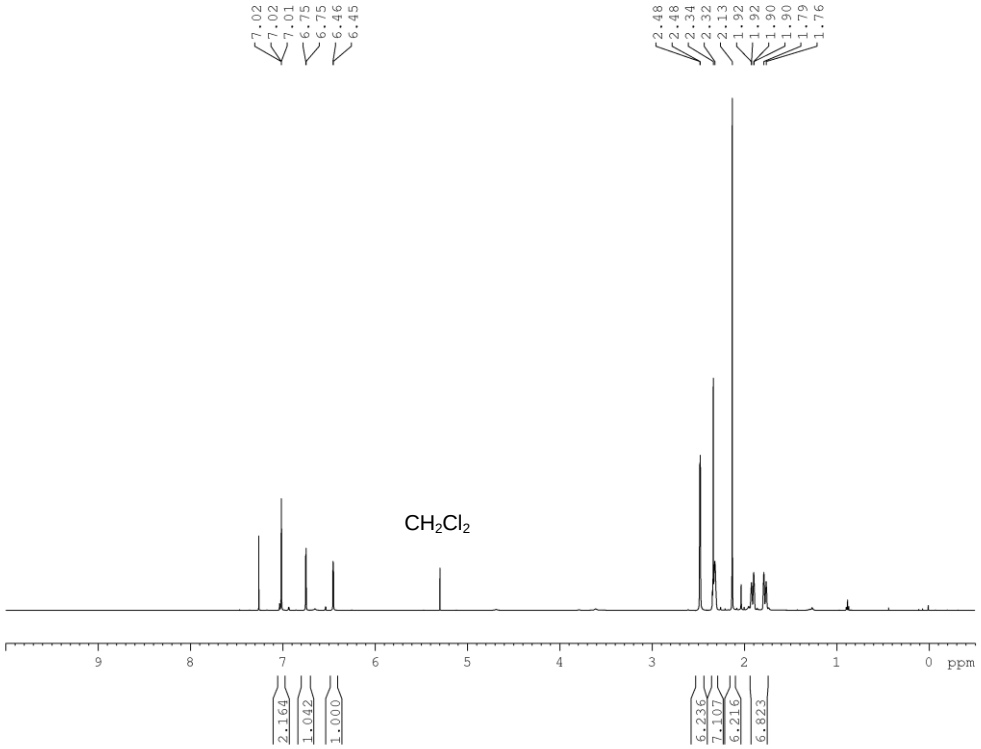


^{13}C NMR (100 MHz, C_6D_6) of **3b**:

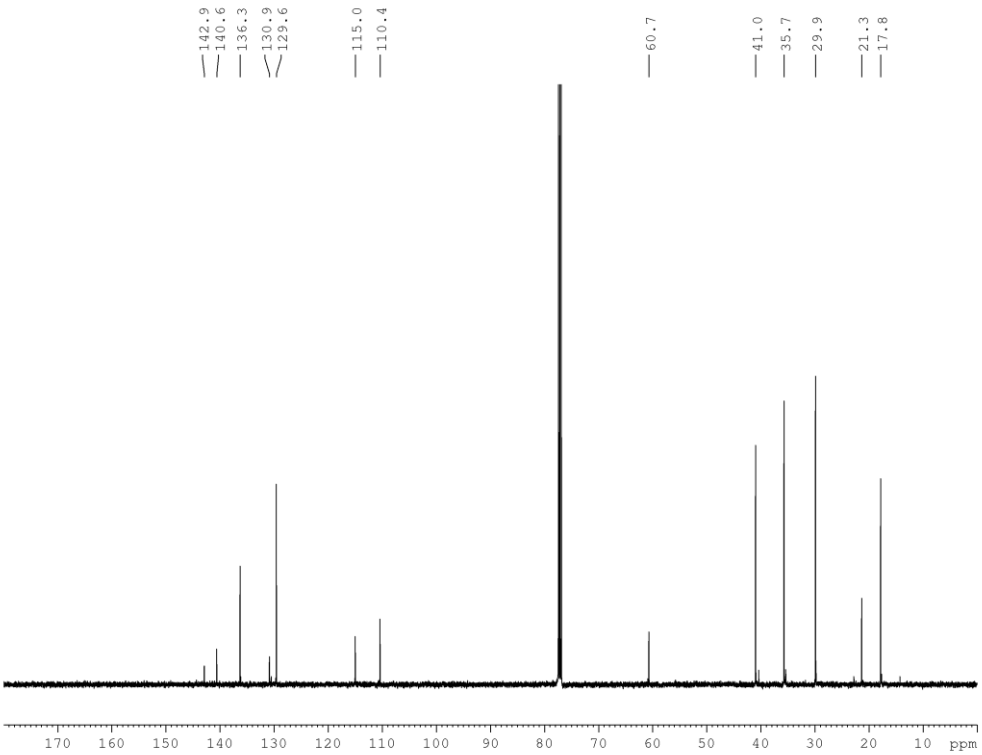


1.7 [(Im^{AdMes}N)TiCl$_3$] (4a)

^{1}H NMR (500 MHz, $CDCl_3$) of **4a**:

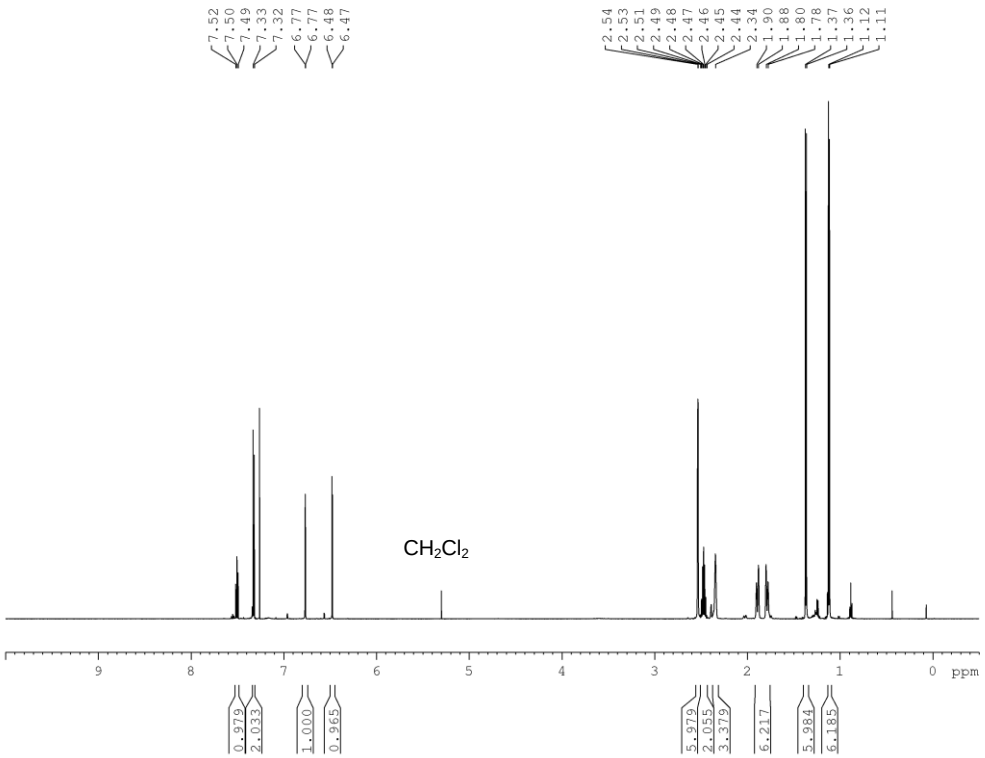


^{13}C NMR (126 MHz, $CDCl_3$) of **4a**:

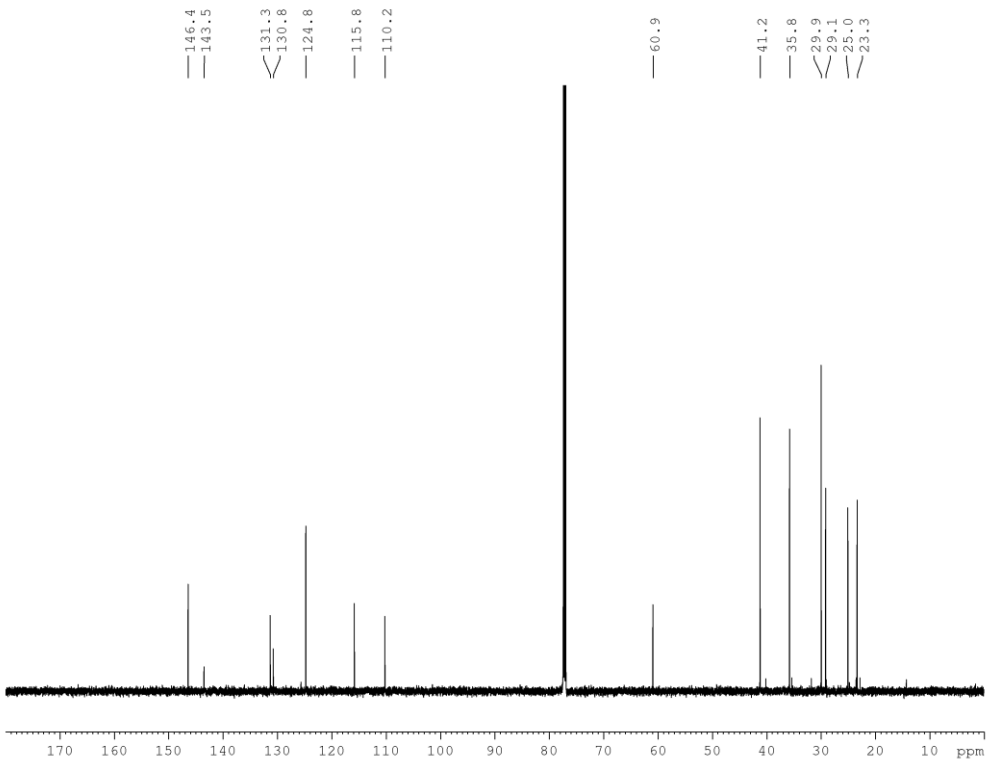


1.8 [(Im^{AdDipp}N)TiCl$_3$] (4b)

^{1}H NMR (600 MHz, $CDCl_3$) of **4b**:

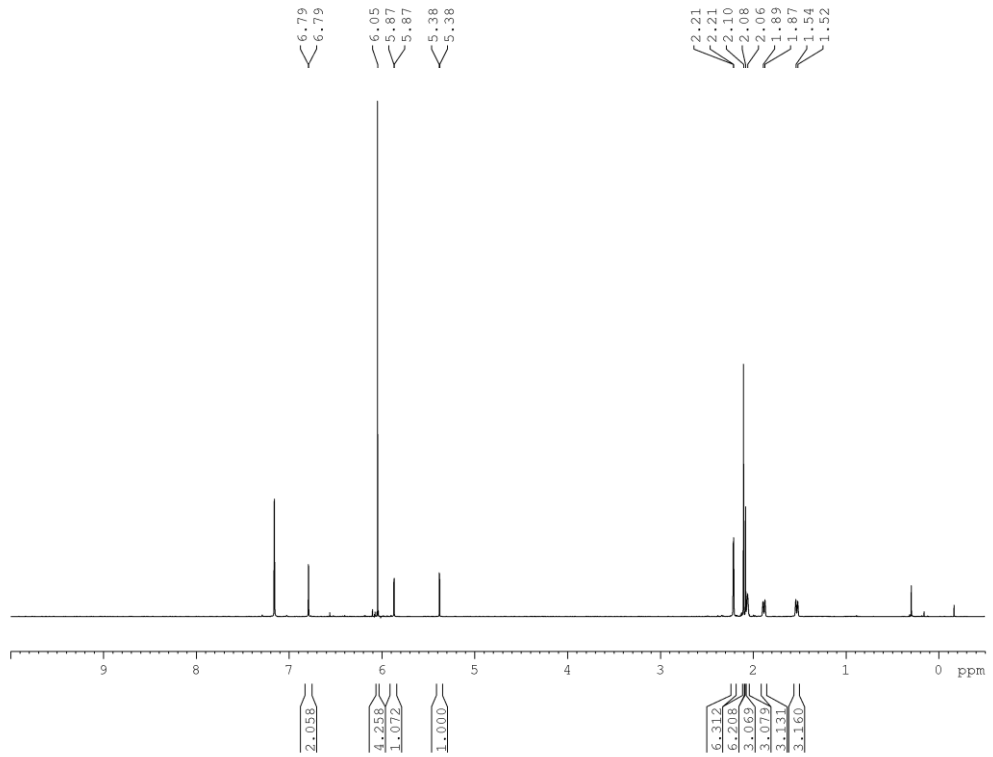


^{13}C NMR (151 MHz, $CDCl_3$) of **4b**:

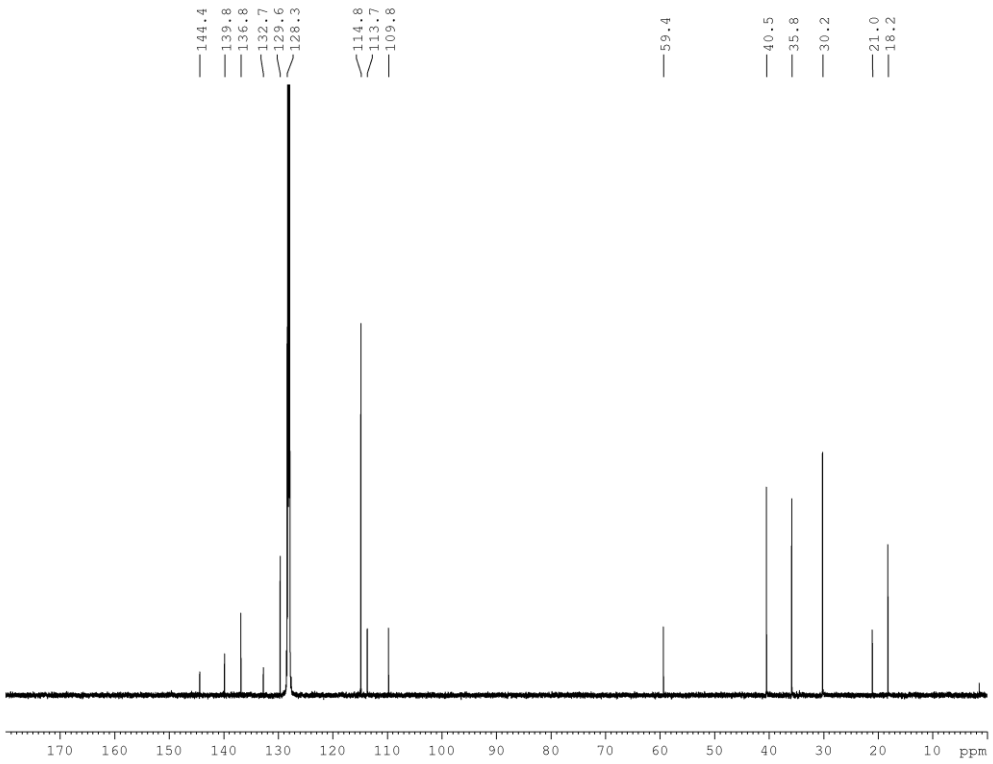


1.9 [Cp(Im^{AdMes}N)TiCl$_2$] (5a)

^{1}H NMR (600 MHz, C_6D_6) of **5a**:

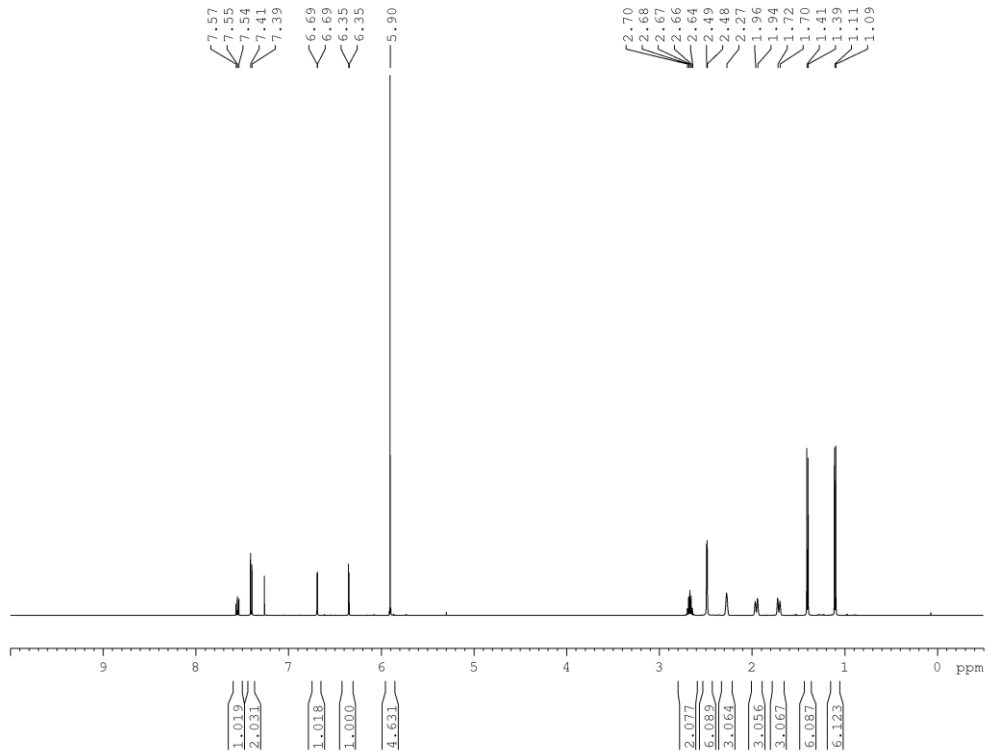


^{13}C NMR (151 MHz, C_6D_6) of **5a**:

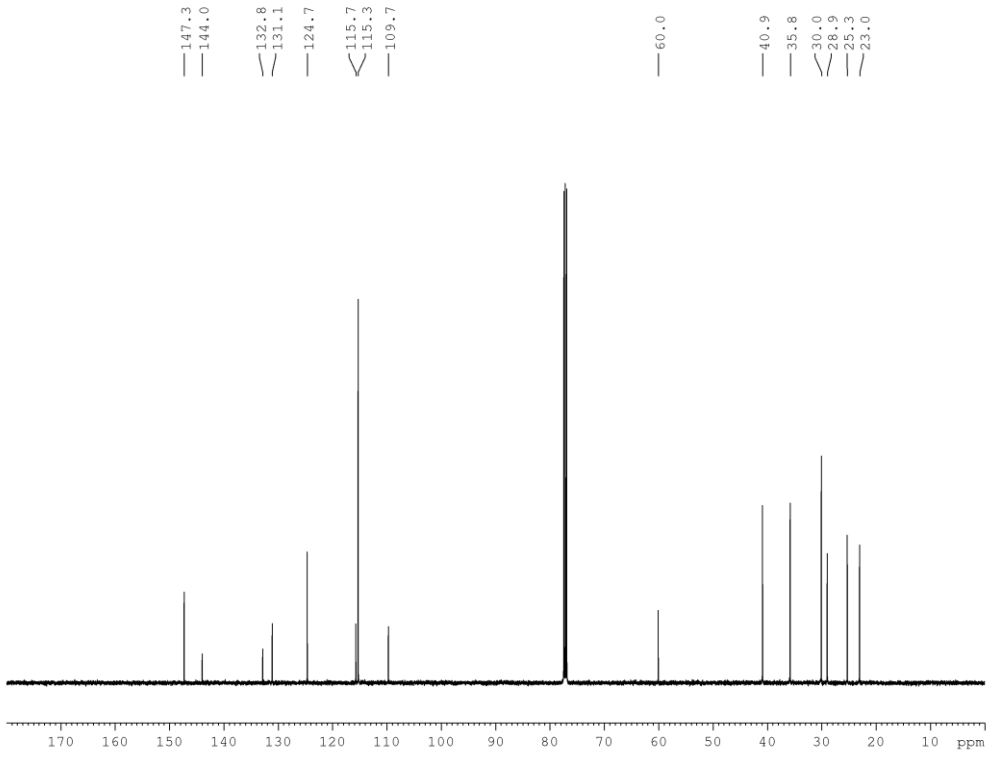


1.10 [Cp(Im^{AdDipp}N)TiCl$_2$] (5b)

^{1}H NMR (500 MHz, $CDCl_3$) of **5b**:

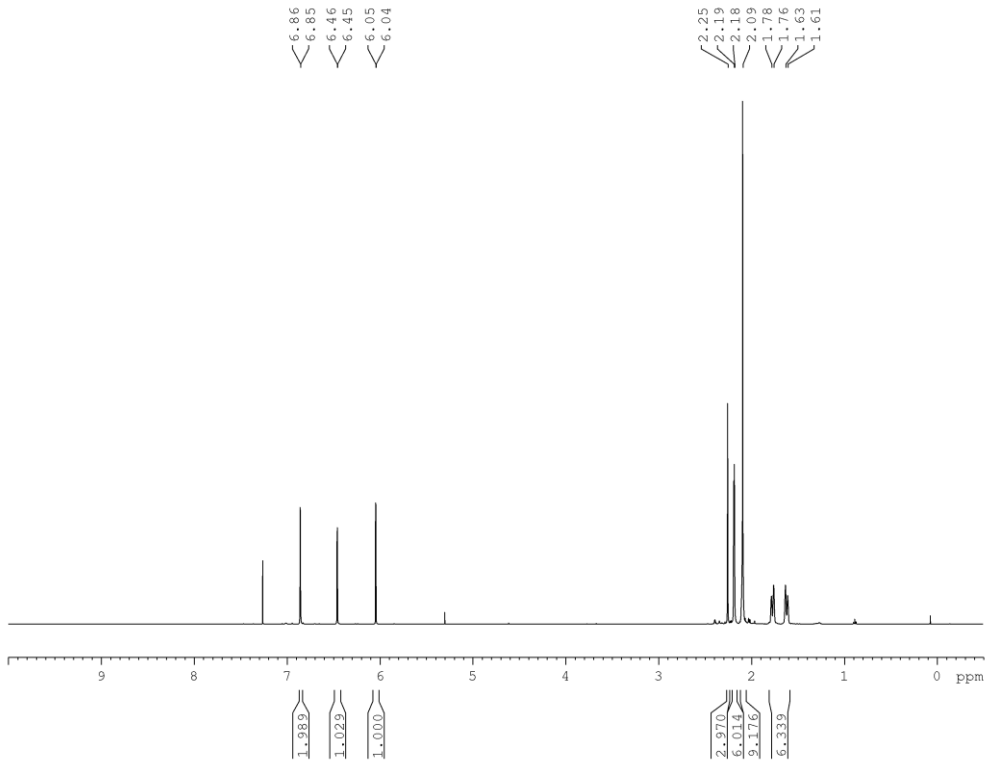


^{13}C NMR (126 MHz, $CDCl_3$) of **5b**:

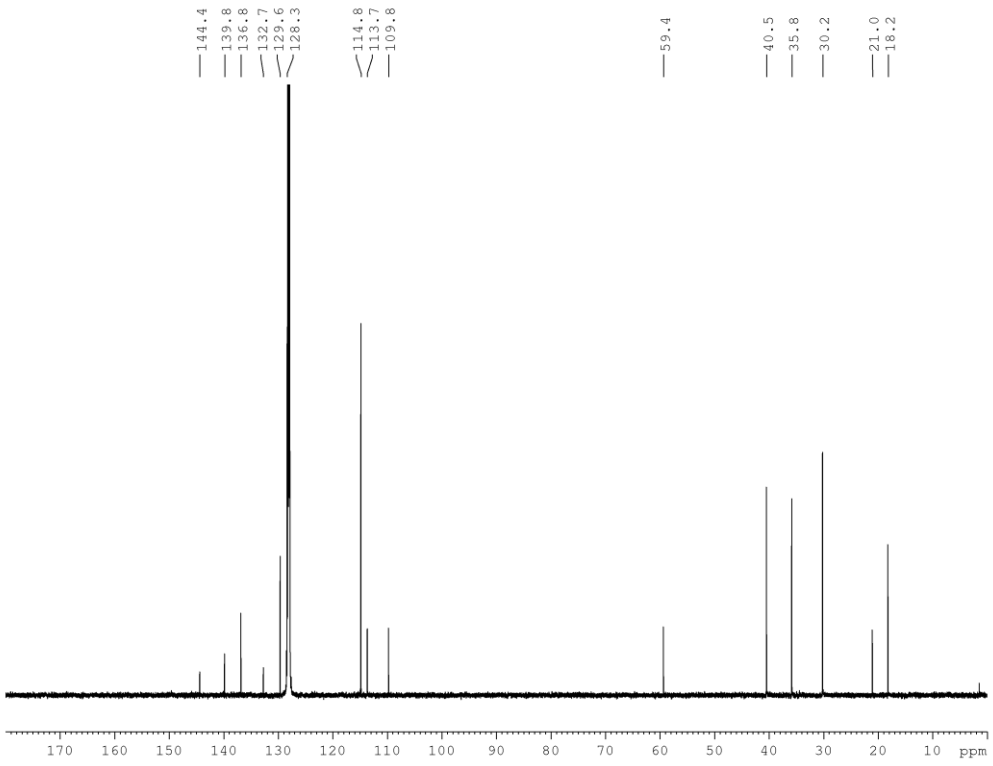


1.11 [(Im^{AdMes}N)$_2$TiCl$_2$] (6a)

^{1}H NMR (500 MHz, $CDCl_3$) of **6a**:

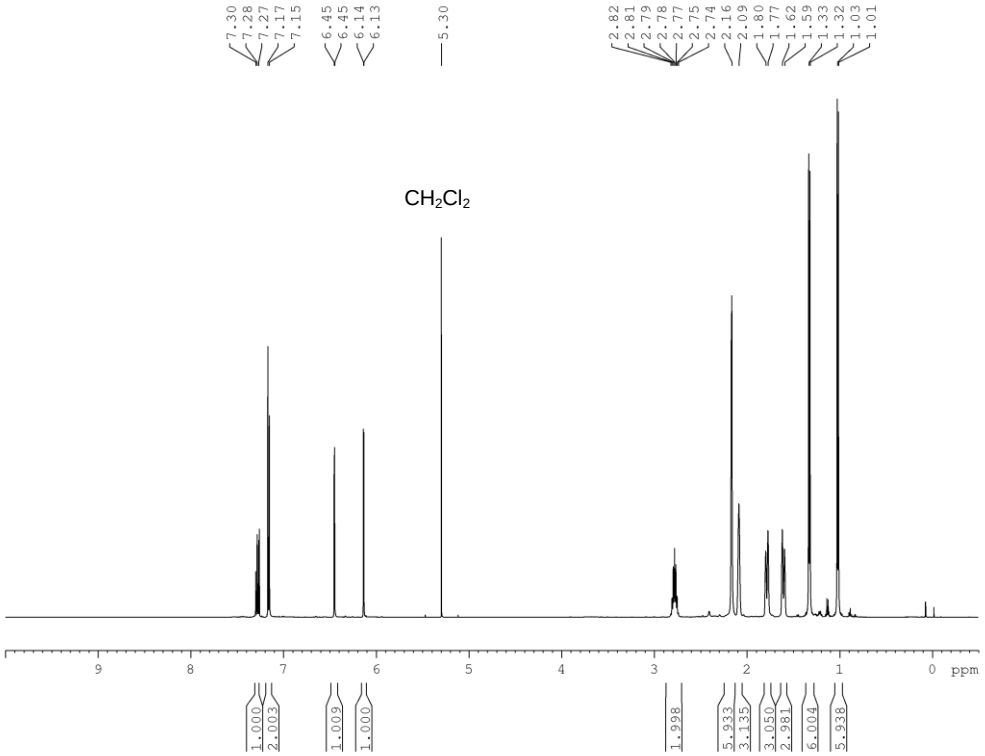


^{13}C NMR (126 MHz, $CDCl_3$) of **6a**:

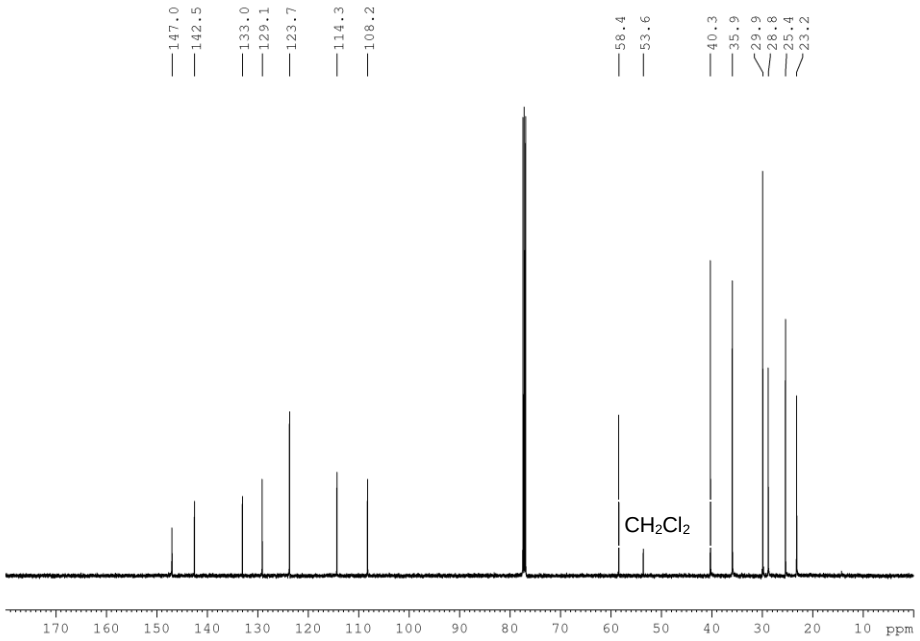


1.12 [(Im^{AdDipp}N)$_2$TiCl$_2$] (6b)

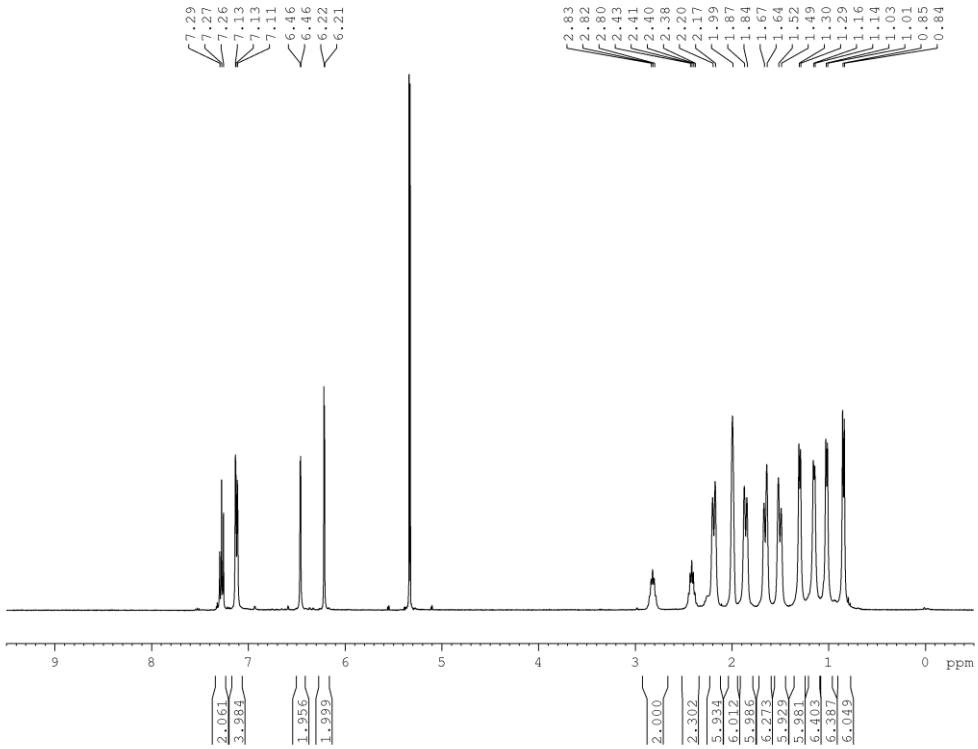
^{1}H NMR (500 MHz, $CDCl_3$) of **6b**:



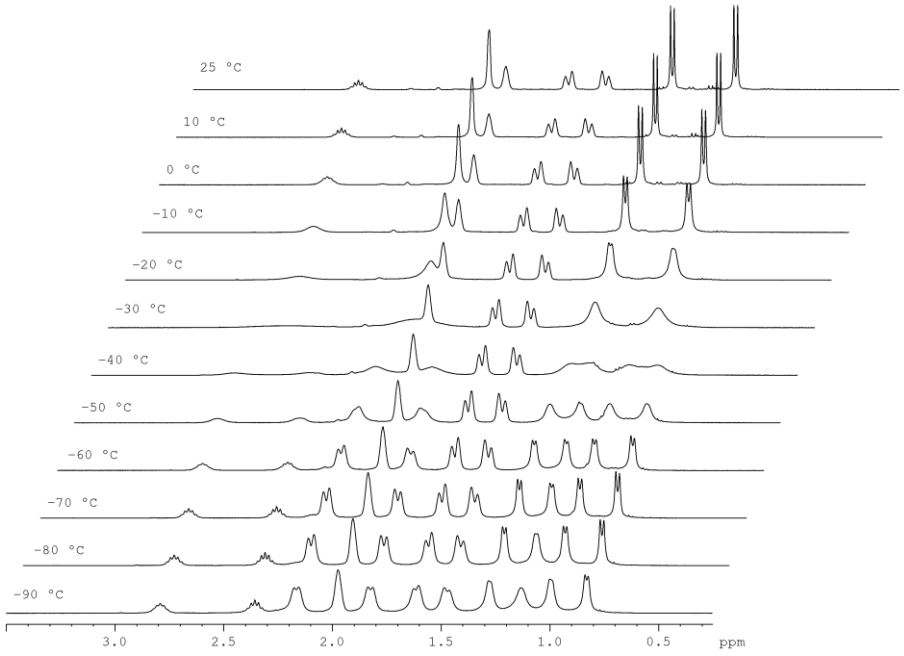
^{13}C NMR (126 MHz, $CDCl_3$) of **6b**:



^{1}H NMR (400 MHz, CD_2Cl_2) of **6b** at –70 °C:



^{1}H NMR (400 MHz, CD_2Cl_2) of **6b** at variable temperatures; zoom-in to the aliphatic region:



2. X-Ray Crystal Structure Determinations

For a summary of crystal data, see Tables S4.1 - 4.6. Crystals were mounted on either MiTiGen or Hampton mounts in perfluorinated inert oil. Intensity measurements were performed at 100 K using a Rigaku XtaLAB Synergy S Single Source with mirror-focussed CuKα radiation or a Rigaku XtaLAB Synergy S Single Source with mirror-focused MoKα radiation. Additional measurements were performed using an Oxford Diffraction Xcalibur Eos diffractometer with MoKα radiation. Data reduction was performed with the CrysAlisPRO software.[A] Absorption corrections were based on multi-scans, analytical methods or face-indexation using a gaussian grid. The structures solved using either direct methods in SHELXS[B] or intrinsic phasing in SHELXT[C] and were refined anisotropically on F2 using the program SHELXL[D] in OLEX2.[E] The hydrogen atoms were, unless otherwise noted, included either as constituents of idealized rigid methyl groups allowed to rotate but not tip, or using a riding model starting from calculated positions. The implementation of BYPASS[F] in OLEX2 had to be used for compound **4b**. One figure was created using the program Mercury[G].

CCDC 2174864-2174874 contain the supplementary crystallographic data for this paper. These data are provided free of charge by the Cambridge Crystallographic Data Centre.

References:

[A] Rigaku Oxford Diffraction, CrysAlisPRO Software System, Rigaku Corporation, Oxford, UK.

[B] G. M. Sheldrick, *Acta Cryst.* **2007**, *A64*, 112-122.

[C] G. M. Sheldrick, *Acta Cryst*. **2015**, *A71*, 3–8.

[D] G. M. Sheldrick, *Acta Cryst*. **2015**, *C71*, 3–8.

[E] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Cryst*. **2009**, *42*, 339–341.

[F] P. van der Sluis, A. L. Spek, *Acta Cryst.* **1990**, *A46*, 194-201.

[G] C. F. Macrae, I. Sovago, S. J. Cottrell, P. T. A. Galek, P. McCabe, E. Pidcock, M. Platings, G. P. Shields, J. S. Stevens, M. Towler et al., *J. Appl. Crystallogr.* **2020**, *53*, 226.

2.1 1-(Adamantyl)-3-(2,4,6-trimethylphenyl)-imidazolin-2-ylidene (1a)

Identification code	mk31mk	
CCDC Number:	2174864	
Empirical formula	$C_{22}H_{28}N_2$	
Formula weight	320.46	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Instrument (scan mode)	XtaLAB Synergy, Single source HyPix (ω scan)	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 13.5173(4) Å	α= 90°
	b = 10.3836(2) Å	β= 95.869(2)°
	c = 12.8450(4) Å	γ = 90°
Volume	1793.45(8) Å^3	
Z	4	
Density (calculated)	1.187 Mg/m^3	
Absorption coefficient	0.069 mm^{-1}	
F(000)	696	
Crystal habitus	plate (colourless)	
Crystal size	0.279 x 0.211 x 0.143 mm^3	
Theta range for data collection	2.478 to 44.855°	
Index ranges	-26<=h<=26, -20<=k<=20, -25<=l<=25	
Reflections collected	134137	
Independent reflections	14658 [R(int) = 0.0485]	
Completeness to theta = 25.242°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.88245	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	14658 / 0 / 220	
Goodness-of-fit on F^2	1.066	
Final R indices [I>2sigma(I)]	R1 = 0.0441, wR2 = 0.1296	
R indices (all data)	R1 = 0.0624, wR2 = 0.1381	
Largest diff. peak and hole	0.606 and -0.314 e.Å^{-3}	
Crystallisation Details:	Toluol/n-Hexan -40°C	

Solution: SHELXT-2014/5 (G. M. Sheldrick, Acta Cryst., 2015, A71, 3-8)

Refinement: SHELXL-2018/3 (G. M. Sheldrick, Acta Cryst. (2008), A64, 112-122)

Interface: OLEX2 v1.2 (O. V. Dolomanov et al., J. Appl. Cryst., 2009, 42, 339-341)

Measurement and Refinement Details: -

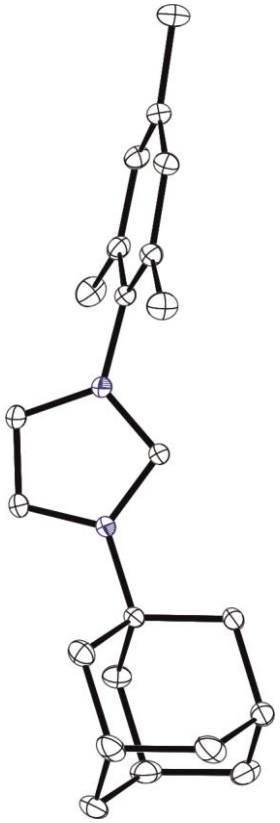


Figure S1: Molecular structure of **1a** with thermal displacement parameters drawn at 50% probabillity. All hydrogens are omitted for clarity. Selected bond lenghts [Å] and angles [°]: C1-N1 1.3739(5), C1-N2 1.3651(5), N1-C4 1.4313(5), N2-C13 1.4711(6), N1-C1-N2 102.05(3).

2.2 1-(Adamantyl)-3-(2,6-diisopropylphenyl)-imidazolin-2-ylidene (1b)

Identification code	mk28mk	
CCDC Number:	2174865	
Empirical formula	$C_{25}H_{34}N_2$	
Formula weight	362.54	
Temperature	100(2) K	
Wavelength	1.54184 Å	
Instrument (scan mode)	XtaLAB Synergy, Single source, HyPix (ω scan)	
Crystal system	Orthorhombic	
Space group	*Pnma*	
Unit cell dimensions	a = 10.4134(2) Å	α= 90°
	b = 12.3697(2) Å	β= 90°
	c = 16.5809(2) Å	γ = 90°
Volume	2135.80(6) $Å^3$	
Z	4	
Density (calculated)	1.127 Mg/m^3	
Absorption coefficient	0.490 mm^{-1}	
F(000)	792	
Crystal habitus	plate (colourless)	
Crystal size	0.347 x 0.100 x 0.089 mm^3	
Theta range for data collection	4.460 to 77.393°	
Index ranges	-11<=h<=13, -15<=k<=15, -20<=l<=20	
Reflections collected	39788	
Independent reflections	2337 [R(int) = 0.0431]	
Completeness to theta = 67.684°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.47134	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2337 / 0 / 141	
Goodness-of-fit on F^2	1.044	
Final R indices [I>2sigma(I)]	R1 = 0.0398, wR2 = 0.0995	
R indices (all data)	R1 = 0.0417, wR2 = 0.1013	
Largest diff. peak and hole	0.216 and -0.194 $e.Å^{-3}$	
Crystallisation Details:	toluene/*n*-hexane -30 °C	

Solution: SHELXT-2014/5 (G. M. Sheldrick, Acta Cryst., 2015, A71, 3-8)

Refinement: SHELXL-2018/3 (G. M. Sheldrick, Acta Cryst., 2008, A64, 112-122)

Interface: OLEX2 v1.2 (O. V. Dolomanov et al., J. Appl. Cryst., 2009, 42, 339-341)

Measurement and Refinement Details: -

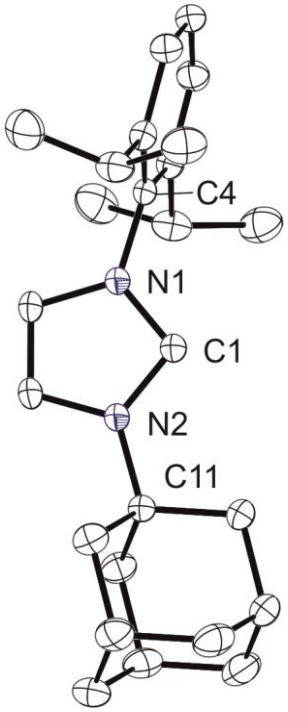


Figure S2: Molecular structure of **1b** with thermal displacement parameters drawn at 50% probabillity. All hydrogens are omitted for clarity. Selected bond lenghts [Å] and angles [°]: C1-N1 1.3709(18), C1-N2 1.3627(18), N1-C4 1.4352(17), N2-C11 1.4765(17), N1-C1-N2 101.48(11).

2.3 [($Im^{AdMes}NSiMe_3$] (2a)

Identification code	mk17mk	
CCDC Number:	2174866	
Empirical formula	$C_{25}H_{37}N_3Si$	
Formula weight	407.66	
Temperature	103(1) K	
Wavelength	0.71073 Å	
Instrument (scan mode)	Oxford Diffraction Xcalibur, Eos (ω scan)	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 9.7011(4) Å	α= 90°
	b = 24.1407(8) Å	β= 99.776(4)°
	c = 10.2311(4) Å	γ = 90°
Volume	2361.24(16) Å^3	
Z	4	
Density (calculated)	1.147 Mg/m^3	
Absorption coefficient	0.115 mm^{-1}	
F(000)	888	
Crystal habitus	irregular (colourless)	
Crystal size	0.701 x 0.591 x 0.469 mm^3	
Theta range for data collection	2.291 to 36.316°	
Index ranges	-16<=h<=16, -40<=k<=40, -17<=l<=17	
Reflections collected	121520	
Independent reflections	11433 [R(int) = 0.0726]	
Completeness to theta = 25.242°	100.0 %	
Absorption correction	Gaussian	
Max. and min. transmission	0.961 and 0.942	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	11433 / 0 / 268	
Goodness-of-fit on F^2	1.040	
Final R indices [I>2sigma(I)]	R1 = 0.0457, wR2 = 0.1173	
R indices (all data)	R1 = 0.0601, wR2 = 0.1258	
Largest diff. peak and hole	0.671 and -0.236 e.Å^{-3}	
Crystallisation Details:	*n*-hexane at -27 °C	

Solution: SHELXT-2014/5 (G. M. Sheldrick, Acta Cryst., 2015, A71, 3-8)

Refinement: SHELXL-2018/3 (G. M. Sheldrick, Acta Cryst. (2008), A64, 112-122)

Interface: OLEX2 v1.2 (O. V. Dolomanov et al., J. Appl. Cryst., 2009, 42, 339-341)

Measurement and Refinement Details: -

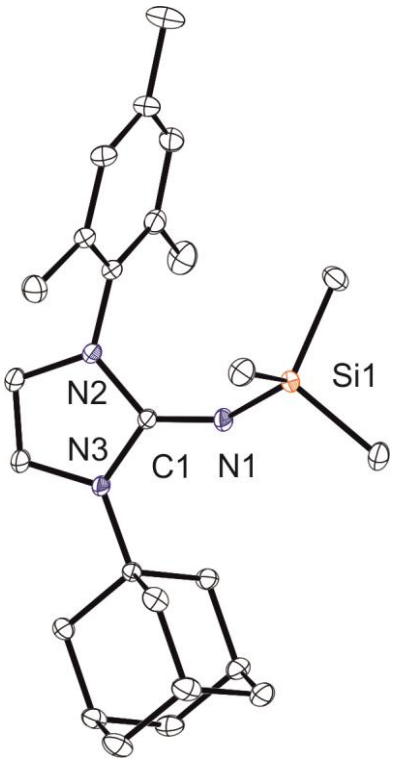


Figure S3: Molecular structure of **2a** with thermal displacement parameters drawn at 50% probabillity. All hydrogens are omitted for clarity. Selected bond lenghts [Å] and angles [°]: C1-N1 1.2782(10), N1-Si1 1.6823(7), N2-C1-N3 103.99(6), C1-N1-Si1142.68(7).

2.4 [Im^{AdMes}NH] (3a)

Identification code	mk18mk	
CCDC Number:	2174867	
Empirical formula	$C_{22}H_{29}N_3$	
Formula weight	335.48	
Temperature	100(2) K	
Wavelength	1.54184 Å	
Instrument (scan mode)	XtaLAB Synergy, Single source, HyPix (ω scan)	
Crystal system	Orthorhombic	
Space group	*Pbca*	
Unit cell dimensions	a = 16.6873(2) Å	α= 90°
	b = 11.37240(10) Å	β= 90°
	c = 19.4505(2) Å	γ = 90°
Volume	3691.21(7) Å^3	
Z	8	
Density (calculated)	1.207 Mg/m^3	
Absorption coefficient	0.545 mm^{-1}	
F(000)	1456	
Crystal habitus	fragment of trapezoid (colourless)	
Crystal size	0.108 x 0.101 x 0.099 mm^3	
Theta range for data collection	4.547 to 77.613°	
Index ranges	-21<=h<=21, -14<=k<=11, -24<=l<=24	
Reflections collected	41369	
Independent reflections	3865 [R(int) = 0.0255]	
Completeness to theta = 67.684°	100.0 %	
Absorption correction	Gaussian	
Max. and min. transmission	1.000 and 0.793	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3865 / 0 / 233	
Goodness-of-fit on F^2	1.043	
Final R indices [I>2sigma(I)]	R1 = 0.0408, wR2 = 0.1015	
R indices (all data)	R1 = 0.0429, wR2 = 0.1038	
Largest diff. peak and hole	0.280 and -0.283 e.Å^{-3}	
Crystallisation Details:	cooling of hot *n*-hexane solution to room temperature	

Solution: SHELXT-2014/5 (G. M. Sheldrick, Acta Cryst., 2015, A71, 3-8)

Refinement: SHELXL-2018/3 (G. M. Sheldrick, Acta Cryst., 2008, A64, 112-122)

Interface: OLEX2 v1.2 (O. V. Dolomanov et al., J. Appl. Cryst., 2009, 42, 339-341)

Measurement and Refinement Details: N-H hydrogen was refined freely.

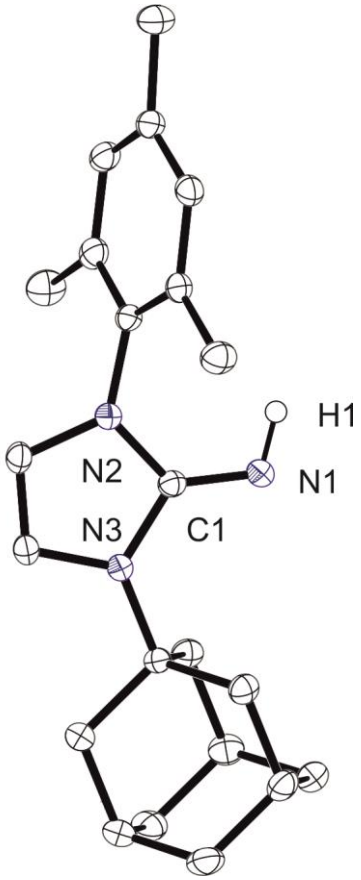


Figure S4: Molecular structure of **3a** with thermal displacement parameters drawn at 50% probabillity. All hydrogens are omitted for clarity. Selected bond lenghts [Å] and angles [°]: C1-N1 1.2966(14), N2-C1-N3 104.55(9).

2.5 [Im^{AdDipp}NH] (3b)

Identification code	mk15mk	
CCDC Number:	2174868	
Empirical formula	$C_{25}H_{35}N_3$	
Formula weight	377.56	
Temperature	100(2) K	
Wavelength	1.54184 Å	
Instrument (scan mode)	XtaLAB Synergy, Single source, HyPix (ω scan)	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 13.8605(1) Å	α= 90°
	b = 6.5130(1) Å	β= 98.599(1)°
	c = 24.0076(2) Å	γ = 90°
Volume	2142.89(4) Å^3	
Z	4	
Density (calculated)	1.170 Mg/m^3	
Absorption coefficient	0.521 mm^{-1}	
F(000)	824	
Crystal habitus	lath (colourless)	
Crystal size	0.352 x 0.067 x 0.039 mm^3	
Theta range for data collection	3.225 to 77.449°	
Index ranges	-17<=h<=17, -6<=k<=8, -30<=l<=30	
Reflections collected	47042	
Independent reflections	4470 [R(int) = 0.0319]	
Completeness to theta = 67.684°	100.0 %	
Absorption correction	Gaussian	
Max. and min. transmission	1.000 and 0.784	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4470 / 0 / 261	
Goodness-of-fit on F^2	1.038	
Final R indices [I>2sigma(I)]	R1 = 0.0378, wR2 = 0.0967	
R indices (all data)	R1 = 0.0401, wR2 = 0.0998	
Largest diff. peak and hole	0.265 and -0.212 e.Å^{-3}	
Crystallisation Details:	*n*-hexane -40 °C	

Solution: SHELXT-2014/5 (G. M. Sheldrick, Acta Cryst., 2015, A71, 3-8)

Refinement: SHELXL-2018/3 (G. M. Sheldrick, Acta Cryst., 2008, A64, 112-122)

Interface: OLEX2 v1.2 (O. V. Dolomanov et al., J. Appl. Cryst., 2009, 42, 339-341)

Measurement and Refinement Details: N-H hydrogen was refined freely.

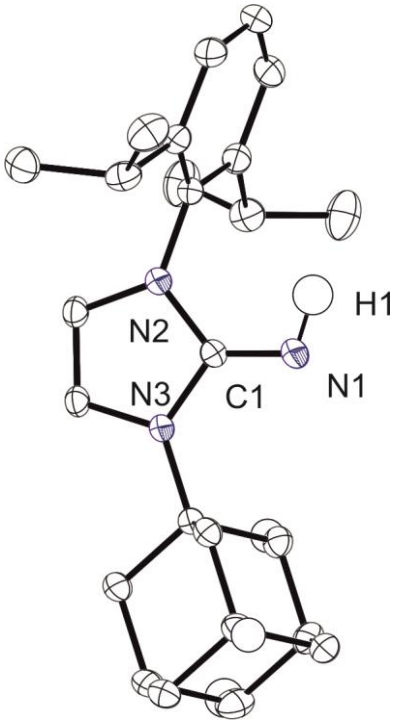


Figure S5: Molecular structure of **3b** with thermal displacement parameters drawn at 50% probabillity. All hydrogens are omitted for clarity. Selected bond lenghts [Å] and angles [°]: C1-N1 1.2891(13), N2-C1-N3 104.78(8).

2.6 [($Im^{AdMes}NH$)$TiCl_3$] (4a)

Identification code	mk23mk	
CCDC Number:	2174869	
Empirical formula	$C_{22}H_{28}Cl_3N_3Ti$	
Formula weight	488.72	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Instrument (scan mode)	XtaLAB Synergy, Single source, HyPix (ω scan)	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 9.6555(2) Å	α= 90°
	b = 23.9142(3) Å	β= 98.744(2)°
	c = 10.2854(2) Å	γ = 90°
Volume	2347.33(7) $Å^3$	
Z	4	
Density (calculated)	1.383 Mg/m^3	
Absorption coefficient	0.720 mm^{-1}	
F(000)	1016	
Crystal habitus	irregular (orange)	
Crystal size	0.370 x 0.269 x 0.100 mm^3	
Theta range for data collection	2.731 to 41.154°	
Index ranges	-17<=h<=17, -44<=k<=44, -19<=l<=19	
Reflections collected	209853	
Independent reflections	15591 [R(int) = 0.0354]	
Completeness to theta = 25.242°	99.8 %	
Absorption correction	Gaussian	
Max. and min. transmission	1.000 and 0.272	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	15591 / 0 / 265	
Goodness-of-fit on F^2	1.051	
Final R indices [I>2sigma(I)]	R1 = 0.0268, wR2 = 0.0751	
R indices (all data)	R1 = 0.0329, wR2 = 0.0774	
Largest diff. peak and hole	0.626 and -0.215 $e.Å^{-3}$	
Crystallisation Details:	DCM/*n*-hexane	

Solution: SHELXT-2014/5 (G. M. Sheldrick, Acta Cryst., 2015, A71, 3-8)

Refinement: SHELXL-2018/3 (G. M. Sheldrick, Acta Cryst. (2008), A64, 112-122)

Interface: OLEX2 v1.2 (O. V. Dolomanov et al., J. Appl. Cryst., 2009, 42, 339-341)

Measurement and Refinement Details: -

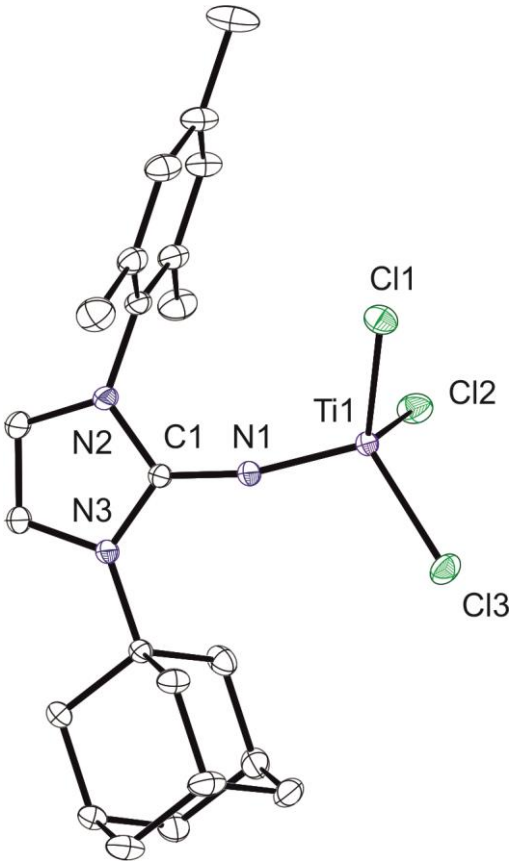


Figure S6: Molecular structure of **4a** with thermal displacement parameters drawn at 50% probabillity. All hydrogens are omitted for clarity. Selected bond lenghts [Å] and angles [°]: C1-N1 1.3265(7), N1-Ti1 1.7347(5), N2-C1-N3 107.41(4), C1-N1-Ti1 162.58(5), Cl1-Ti-Cl2 111.50(2), N1-C1-N2 124.07(5), N1-C1-N3 128.50(5).

2.7 [($Im^{AdDipp}N$)$TiCl_3$] CH_2Cl_2·Solv (4b)

Identification code	mk26mk	
CCDC Number:	2174870	
Empirical formula	$C_{26}H_{36}Cl_5N_3Ti$	
Formula weight	615.73	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Instrument (scan mode)	XtaLAB Synergy, Single source, HyPix (ω scan)	
Crystal system	Triclinic	
Space group	$P\bar{1}$	
Unit cell dimensions	a = 9.8202(4) Å	α= 63.091(5)°
	b = 13.2868(6) Å	β= 81.445(4)°
	c = 14.4204(7) Å	γ = 76.358(4)°
Volume	1628.59(15) $Å^3$	
Z	2	
Density (calculated)	1.256 Mg/m^3	
Absorption coefficient	0.691 mm^{-1}	
F(000)	640	
Crystal habitus	fragment of block (orange)	
Crystal size	0.18 x 0.10 x 0.05 mm^3	
Theta range for data collection	2.137 to 32.385°	
Index ranges	-14<=h<=14, -19<=k<=19, -21<=l<=20	
Reflections collected	43682	
Independent reflections	9833 [R(int) = 0.0215]	
Completeness to theta = 25.242°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.88732	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	9833 / 0 / 320	
Goodness-of-fit on F^2	1.030	
Final R indices [I>2sigma(I)]	R1 = 0.0581, wR2 = 0.1560	
R indices (all data)	R1 = 0.0667, wR2 = 0.1618	
Largest diff. peak and hole	2.297 and -1.603 $e.Å^{-3}$	
Crystallisation Details:	dichloromethane/*n*-hexane -30 °C	

Solution: SHELXT-2014/5 (G. M. Sheldrick, Acta Cryst., 2015, A71, 3-8)
Refinement: SHELXL-2018/3 (G. M. Sheldrick, Acta Cryst. (2008), A64, 112-122)
Interface: OLEX2 v1.2 (O. V. Dolomanov et al., J. Appl. Cryst., 2009, 42, 339-341)

Measurement and Refinement Details: A solvent mask was calculated and 66 electrons were found in a volume of 231 $Å^3$ in 1 void per unit cell. This is consistent with the presence of 0.5[CH_2Cl_2], 0.25[C_6H_{14}] per Asymmetric Unit which account for 67 electrons per unit cell. A reason why the molecules could not be refined satisfactorly might be their disorder along a canal. Additionally modulation could be a reason, as ‘smeared’ reflexes were observed along the c* axis.

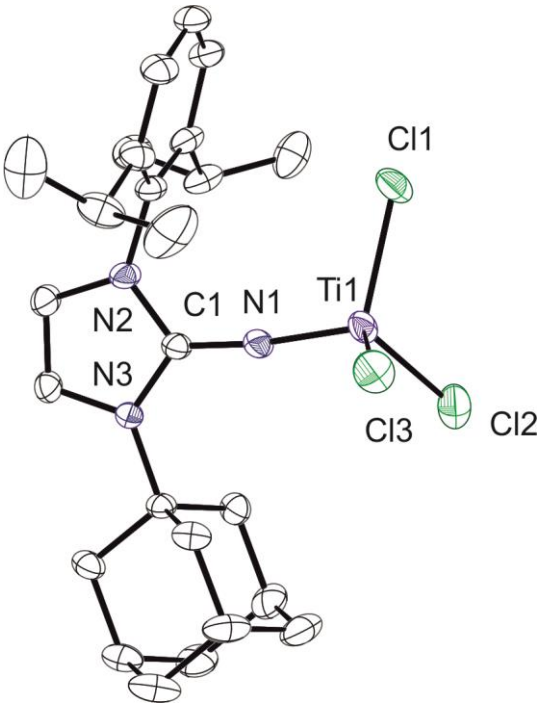


Figure S7: Molecular structure of **4b**·CH_2Cl_2·Solv. with thermal displacement parameters drawn at 50% probabillity. All hydrogens, one molecule of CH_2Cl_2 and disordered solvent molecules are omitted for clarity. Selected bond lenghts [Å] and angles [°]: C1-N1 1.330(3), N1-Ti 1.7316(17), N2-C1-N3 106.89(17), C1-N1-Ti1 173.04(16), Cl1-Ti1-Cl2 109.17(3), N1-C1-N2 124.33(17), 128.75(18).

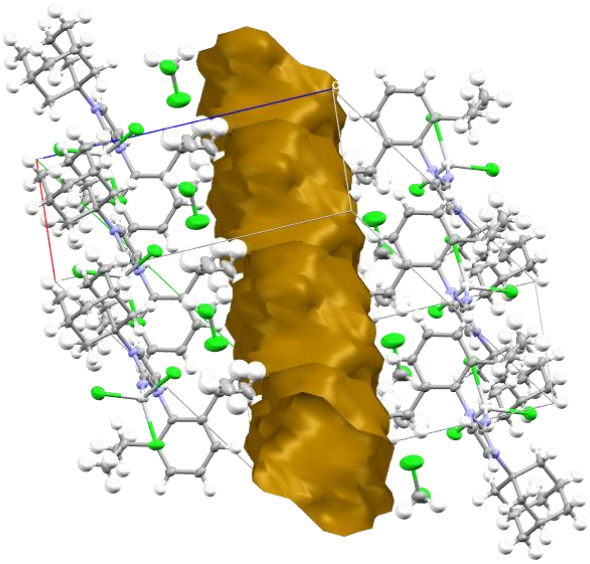


Figure S8: Depiction of the solvent accessible voids in the structure of **4b** in Mercury.

2.8 [Cp(Im^{AdMes}N)TiCl$_2$] (5a)

Identification code	mk22mk	
CCDC Number:	2174871	
Empirical formula	$C_{27}H_{33}Cl_2N_3Ti$	
Formula weight	518.36	
Temperature	100(2) K	
Wavelength	1.54184 Å	
Instrument (scan mode)	XtaLAB Synergy, Single source, HyPix (ω scan)	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 9.97590(10) Å	α= 90°
	b = 11.30190(10) Å	β= 90°
	c = 22.11580(10) Å	γ = 90°
Volume	2493.48(4) Å^3	
Z	4	
Density (calculated)	1.381 Mg/m^3	
Absorption coefficient	5.029 mm^{-1}	
F(000)	1088	
Crystal habitus	trapezoid (orange)	
Crystal size	0.228 x 0.126 x 0.072 mm^3	
Theta range for data collection	3.998 to 77.473°	
Index ranges	-12<=h<=10, -14<=k<=14, -27<=l<=28	
Reflections collected	53498	
Independent reflections	5264 [R(int) = 0.0323]	
Completeness to theta = 67.684°	100.0 %	
Absorption correction	Gaussian	
Max. and min. transmission	1.000 and 0.670	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5264 / 0 / 302	
Goodness-of-fit on F^2	1.033	
Final R indices [I>2sigma(I)]	R1 = 0.0218, wR2 = 0.0504	
R indices (all data)	R1 = 0.0227, wR2 = 0.0513	
Absolute structure parameter	0.434(5)	
Largest diff. peak and hole	0.242 and -0.226 e.Å^{-3}	
Crystallisation Details:	toluene/*n*-hexane room temperature	

Solution: SHELXT-2014/5 (G. M. Sheldrick, Acta Cryst., 2015, A71, 3-8)

Refinement: SHELXL-2018/3 (G. M. Sheldrick, Acta Cryst., 2008, A64, 112-122)

Interface: OLEX2 v1.2 (O. V. Dolomanov et al., J. Appl. Cryst., 2009, 42, 339-341)

Measurement and Refinement Details: Refined as a 2-component inversion twin.

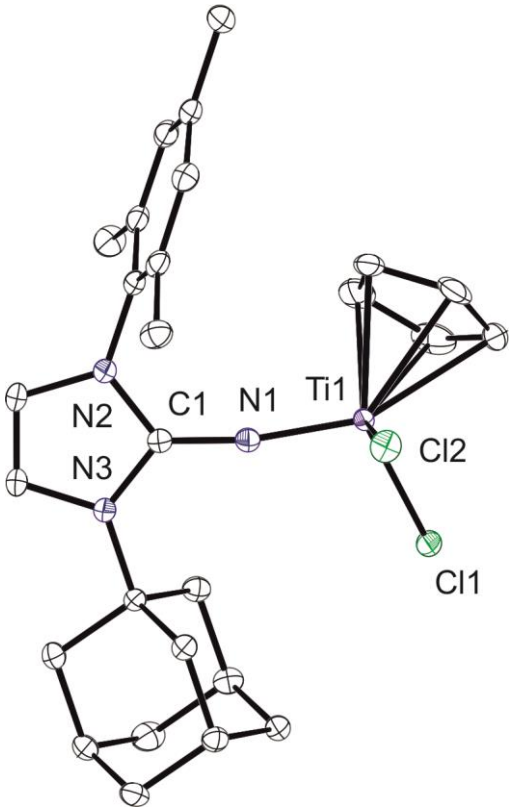


Figure S9: Molecular structure of **5a** with thermal displacement parameters drawn at 50% probabillity. All hydrogens are omitted for clarity. Selected bond lenghts [Å] and angles [°]: C1-N1 1.319(2), N1-Ti1 1.7758(16), Ti1-Cl1 2.3135(5), Ti1-Cl2 2.3156(5), Ti1-$C_5H_5^{Centroid}$ 2.0562(9), N2-C1-N3 105.99(15), C1-N1-Ti1 170.26(14), Cl1-Ti1-Cl2 101.87(2), N1-C1-N2 125.66(16), N1-C1-N3 128.31(16).

2.9 [Cp(Im^{AdDipp}N)TiCl$_2$] (5b)

Identification code	mk27mk	
CCDC Number:	2174872	
Empirical formula	$C_{30}H_{39}Cl_2N_3Ti$	
Formula weight	560.44	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Instrument (scan mode)	XtaLAB Synergy, Single source, HyPix (ω scan)	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 10.3898(2) Å	α= 90°
	b = 19.4721(2) Å	β= 101.575(2)°
	c = 13.9922(2) Å	γ = 90°
Volume	2773.21(7) Å^3	
Z	4	
Density (calculated)	1.342 Mg/m^3	
Absorption coefficient	0.526 mm^{-1}	
F(000)	1184	
Crystal habitus	fragment of trapezoid (orange)	
Crystal size	0.221 x 0.207 x 0.148 mm^3	
Theta range for data collection	2.240 to 38.315°	
Index ranges	-17<=h<=17, -33<=k<=33, -24<=l<=24	
Reflections collected	193977	
Independent reflections	14793 [R(int) = 0.0306]	
Completeness to theta = 25.242°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.89211	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	14793 / 0 / 329	
Goodness-of-fit on F^2	1.070	
Final R indices [I>2sigma(I)]	R1 = 0.0307, wR2 = 0.0836	
R indices (all data)	R1 = 0.0358, wR2 = 0.0856	
Largest diff. peak and hole	0.842 and -0.715 e.Å^{-3}	
Crystallisation Details:	dichloromethane/*n*-hexane room temperature	
Solution:	SHELXT-2014/5 (G. M. Sheldrick, Acta Cryst., 2015, A71, 3-8)	
Refinement:	SHELXL-2018/3 (G. M. Sheldrick, Acta Cryst. (2008), A64, 112-122)	
Interface:	OLEX2 v1.2 (O. V. Dolomanov et al., J. Appl. Cryst., 2009, 42, 339-341)	
Measurement and Refinement Details:	-	

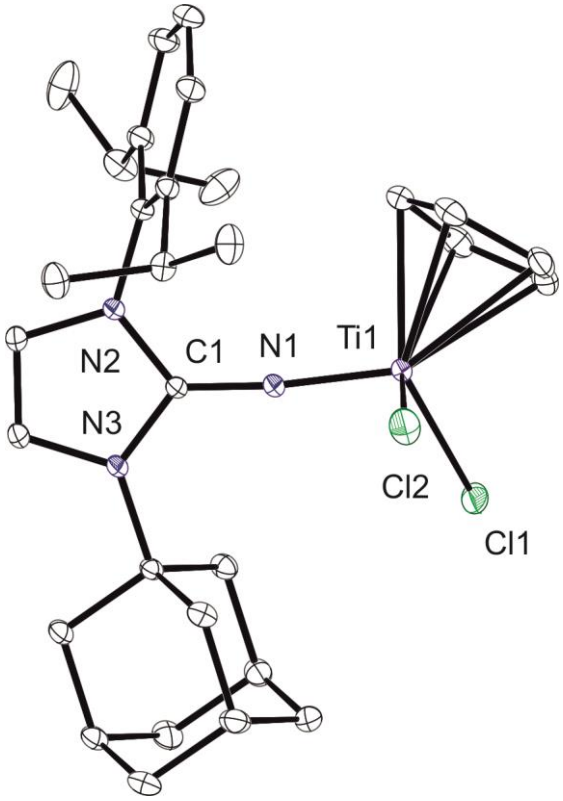


Figure S10: Molecular structure of **5b** with thermal displacement parameters drawn at 50% probabillity. All hydrogens are omitted for clarity. Selected bond lenghts [Å] and angles [°]:C1-N1 1.3189(8), N1-Ti1 1.7760(5), Ti1-Cl1 2.3074(3), Ti1-Cl2 2.3117(2),Ti1-$C_5H_5^{Centroid}$ 2.0689(4), N2-C1-N3 106.13(5), C1-N1-Ti1 170.86(5), Cl1-Ti1-Cl2 102.873(11), N1-C1-N2 125.75(6), N1-C1-N3 128.10(6).

2.10 $[(Im^{AdMes}N)_2TiCl_2]\cdot 0.5CH_2Cl_2$ (6a)

Identification code	mk19mk	
CCDC Number:	2174873	
Empirical formula	$C_{44.5}H_{57}Cl_3N_6Ti$	
Formula weight	830.21	
Temperature	100(2) K	
Wavelength	1.54184 Å	
Instrument (scan mode)	XtaLAB Synergy, Single source, HyPix (ω scan)	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 13.24640(4) Å	α= 90°
	b = 13.47847(4) Å	β= 101.0795(3)°
	c = 24.79338(8) Å	γ = 90°
Volume	4344.13(2) $Å^3$	
Z	4	
Density (calculated)	1.269 Mg/m^3	
Absorption coefficient	3.655 mm^{-1}	
F(000)	1756	
Crystal habitus	irregular (orange)	
Crystal size	0.253 x 0.110 x 0.098 mm^3	
Theta range for data collection	3.534 to 77.822°	
Index ranges	-16<=h<=16, -17<=k<=17, -31<=l<=28	
Reflections collected	94547	
Independent reflections	9180 [R(int) = 0.0312]	
Completeness to theta = 67.684°	100.0 %	
Absorption correction	Gaussian	
Max. and min. transmission	1.000 and 0.531	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	9180 / 6 / 596	
Goodness-of-fit on F^2	1.069	
Final R indices [I>2sigma(I)]	R1 = 0.0450, wR2 = 0.1290	
R indices (all data)	R1 = 0.0462, wR2 = 0.1308	
Largest diff. peak and hole	1.180 and -0.885 $e.Å^{-3}$	
Crystallisation Details:	CH_2Cl_2/*n*-hexane at room temperature	

Solution: SHELXT-2014/5 (G. M. Sheldrick, Acta Cryst., 2015, A71, 3-8)

Refinement: SHELXL-2018/3 (G. M. Sheldrick, Acta Cryst., 2008, A64, 112-122)

Interface: OLEX2 v1.2 (O. V. Dolomanov et al., J. Appl. Cryst., 2009, 42, 339-341)

Measurement and Refinement Details: The CH_2Cl_2 fragment is disordered over an inversion center and occupies a special position. Therefore, its occupancy was set at 0.5 and refined accordingly. Additionally the mesityl group on one ligand is disordered and was refined accordingly resulting in a 60/40 occupancy.

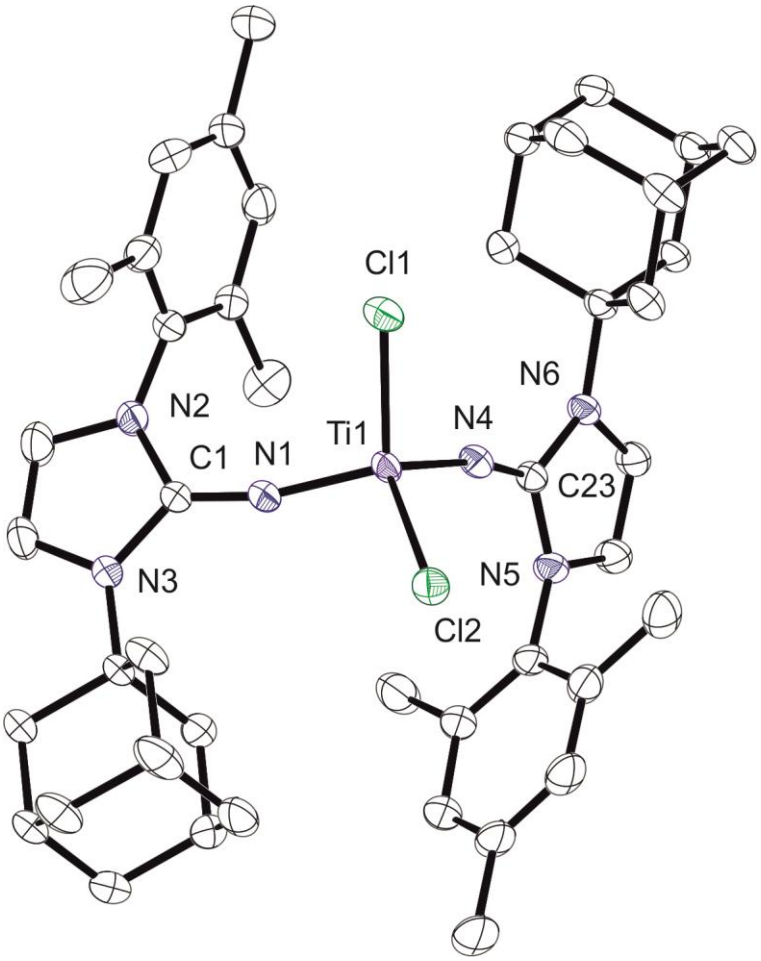


Figure S11: Molecular structure of the main component of **6a**·0.5CH_2Cl_2 with thermal displacement parameters drawn at 50% probabillity. All hydrogens, 0.5 molecules of CH_2Cl_2 and the minor component of the disordered mesityl group at N5 are omitted for clarity. Selected bond lenghts [Å] and angles [°]: C1-N1 1.304(2), C23-N4 1.302(2), N1-Ti1 1.7951(15), N4-Ti1 1.7867(16), Ti1-Cl1 2.2938(5),Ti1-Cl2 2.3160(5), N2-C1-N3 105.89(14), N5-C23-N6 105.69(15), C1-N1-Ti1 166.51(13), C23-N4-Ti1 166.94(13), Cl1-Ti1-Cl2 109.49(2), N1-Ti1-N4 113.57(8).

2.11 $[(Im^{AdDipp}N)_2TiCl_2]\cdot CH_2Cl_2$ (6b)

Identification code	mk24mk2	
CCDC Number:	2174874	
Empirical formula	$C_{51}H_{70}Cl_4N_6Ti$	
Formula weight	956.83	
Temperature	100(2) K	
Wavelength	1.54184 Å	
Instrument (scan mode)	XtaLAB Synergy, Single source, HyPix (ω scan)	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 16.9882(3) Å	α= 90°
	b = 18.0462(2) Å	β= 116.512(2)°
	c = 18.3671(3) Å	γ = 90°
Volume	5038.71(15) Å^3	
Z	4	
Density (calculated)	1.261 Mg/m^3	
Absorption coefficient	3.694 mm^{-1}	
F(000)	2032	
Crystal habitus	needle (orange)	
Crystal size	0.135 x 0.080 x 0.051 mm^3	
Theta range for data collection	2.907 to 77.812°	
Index ranges	-21<=h<=21, -19<=k<=22, -23<=l<=23	
Reflections collected	122767	
Independent reflections	10633 [R(int) = 0.0647]	
Completeness to theta = 67.684°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.58339	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	10633 / 6 / 567	
Goodness-of-fit on F^2	1.076	
Final R indices [I>2sigma(I)]	R1 = 0.0561, wR2 = 0.1599	
R indices (all data)	R1 = 0.0606, wR2 = 0.1649	
Largest diff. peak and hole	0.813 and -1.177 e.Å^{-3}	
Crystallisation Details:	dichloromethane/*n*-hexane room temperature	

Solution: SHELXT-2014/5 (G. M. Sheldrick, Acta Cryst., 2015, A71, 3-8)

Refinement: SHELXL-2018/3 (G. M. Sheldrick, Acta Cryst., 2008, A64, 112-122)

Interface: OLEX2 v1.2 (O. V. Dolomanov et al., J. Appl. Cryst., 2009, 42, 339-341)

Measurement and Refinement Details: Data had to be cut due to sample decay.

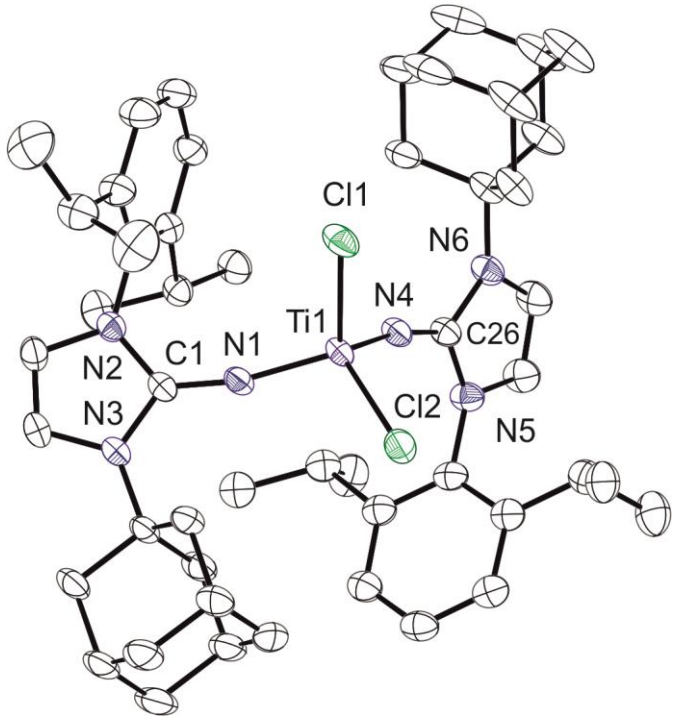


Figure S12: Molecular structure of the main component of **6b**·CH_2Cl_2 with thermal displacement parameters drawn at 50% probabillity. All hydrogens and one molecule of CH_2Cl_2 are omitted for clarity. Selected bond lenghts [Å] and angles [°]: C1-N1 1.304(3), C26-N4 1.302(3), N1-Ti1 1.7994(18), N4-Ti1 1.8067(18), Ti1-Cl1 2.2836(6), Ti1-Cl2 2.3042(6), N2-C1-N3 105.69(18), N5-C26-N6 105.24(18), C1-N1-Ti1 167.14(17), C26-N4-Ti1 167.64(17), Cl1-Ti1-Cl2 105.19(3), N1-Ti1-N4 116.99(9).