Electronic Supplementary Information (ESI)

Vanadium(V) Arylimido Alkylidene *N*-Heterocyclic Carbene Complexes Containing Fluorinated Alkoxide or Halogenated Phenoxide Ligands for the Syndiospecific ROMP of Cyclic Olefins.

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Table of Contents

1. Additional results for ring-opening metathesis polymerization (ROMP) of norbornene (NBE)

Table S1. Living ROMP of NBE by V(CHSiMe$_3$)(N-2,6-Cl$_2$C$_6$H$_3$)(OC$_6$X$_5$)(NHC) [X = F (**1**), Cl (**2**)]; NHC = IXy; 1,3-bis(2,6-dimethylphenyl)imidazole-2-ylidene].[a]

cat.	time/ min	yield/ %	TON[b]	TOF[b]/ h^{-1} (s^{-1})	M_n[c]×10^{-4}	M_w/M_n[c]	*cis*[d]/ %
1	1	41	2180	131000 (36.3)	39.4	1.59	92
1	3	60	3190	63700 (17.7)	65.6	2.01	91
1	5	70	3720	44600 (12.4)	73.5	2.19	90
1	7	79	4190	36000 (10.0)	87.9	2.27	90
1	10	88	4670	28000 (7.79)	93.2	2.32	90
2	1	29	1540	92400 (25.7)	17.9	1.55	96
2	3	47	2500	49900 (13.9)	40.5	1.87	95
2	5	56	2970	35700 (9.91)	58.3	2.00	95
2	7	65	3450	29600 (8.22)	67.8	2.11	95
2	10	70	3720	22300 (6.20)	85.7	2.18	94

[a]Reaction conditions: vanadium 0.20 μmol, NBE 100 mg (1.06 mmol), benzene total 9.6 mL (initial NBE conc. 0.11 mmol/mL). [b]TON (turnovers) = NBE reacted (mmol)/vanadium (mmol), TOF = TON/time. [c]GPC data in THF *vs* polystyrene standards (*Mn* in g/mol). [d]*Cis* percentage (%) estimated by ^{1}H NMR spectra.

Table S2. ROMP of NBE using V(CHSiMe$_3$)(N-2,6-Cl$_2$C$_6$H$_3$)(OC$_6$X$_5$)(NHC) [X = F (**1**), Cl (**2**)].[a]

cat.	time/ min	temp./ °C	yield/ %	TON[b]	TOF[b]/ h^{-1} (s^{-1})	M_n[c]×10^{-4}	M_w/M_n[c]	*cis*[d]/ %
1	1	25	61	2160	130000 (36.0)	34.6	1.51	92
1	3	25	83	2940	58800 (16.3)	58.3	1.66	90
1	5	25	96	3400	40800 (11.3)	77.7	1.75	88
1	1	50	58	2050	123000 (34.2)	46.1	1.58	77
1	3	50	81	2870	57300 (15.9)	83.4	1.84	76
1	5	50	89	3150	37800 (10.5)	96.5	2.08	73
2	1	25	44	1560	93500 (26.0)	17.6	1.43	96
2	3	25	69	2440	48900 (13.6)	34.1	1.57	95
2	5	25	79	2800	33600 (9.32)	39.9	1.63	94
2	1	50	38	1350	80700 (22.4)	18.7	1.55	89
2	3	50	61	2160	43200 (12.0)	35.4	1.68	89
2	5	50	68	2410	28900 (8.02)	52.5	1.72	88

[a]Reaction conditions: vanadium 0.30 μmol, NBE 100 mg (1.06 mmol), benzene total 9.6 mL (initial NBE conc. 0.11 mmol/mL). [b]TON (turnovers) = NBE reacted (mmol)/vanadium (mmol), TOF = TON/time. [c]GPC data in THF *vs* polystyrene standards (*Mn* in g/mol). [d]*Cis* percentage (%) estimated by ^{1}H NMR spectra.

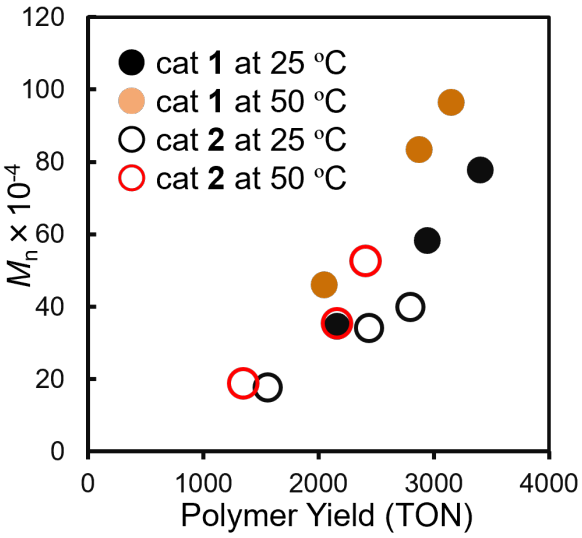

Figure S1. Plot of M_n values vs polymer yields (TON, turnover numbers based on polymer yields). The detailed data are shown in **Table S2**.

2. Selected NMR spectra of the polymers.

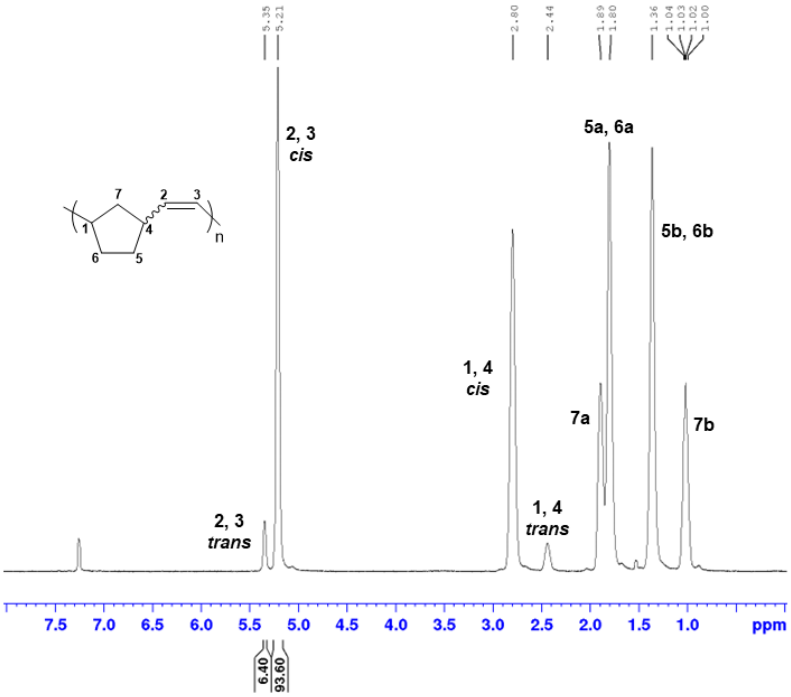

Figure S2. ^{1}H NMR spectrum ($CDCl_3$ at 25°C) of ring opened poly(NBE) prepared by V(N-2,6-$Cl_2C_6H_3$)(CHSiMe_3)(OC_6F_5)(NHC) (**1**) at 25°C (run 3).

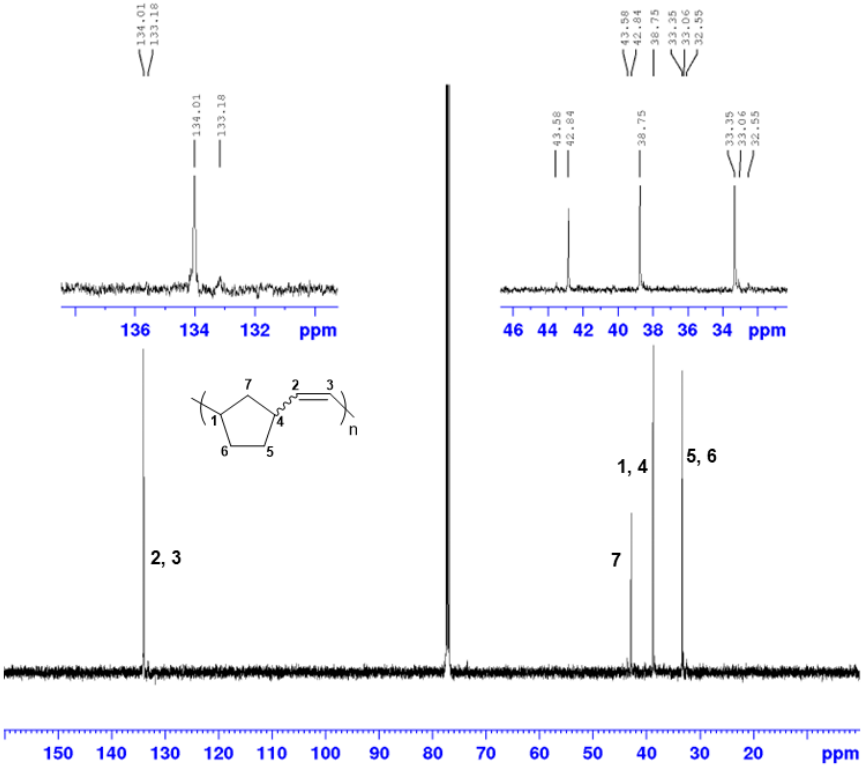

Figure S3. ^{13}C NMR spectrum ($CDCl_3$ at 25°C) of ring opened poly(NBE) prepared by V(N-2,6-$Cl_2C_6H_3$)(CHSiMe_3)(OC_6F_5)(NHC) (**1**) at 25°C (run 3).

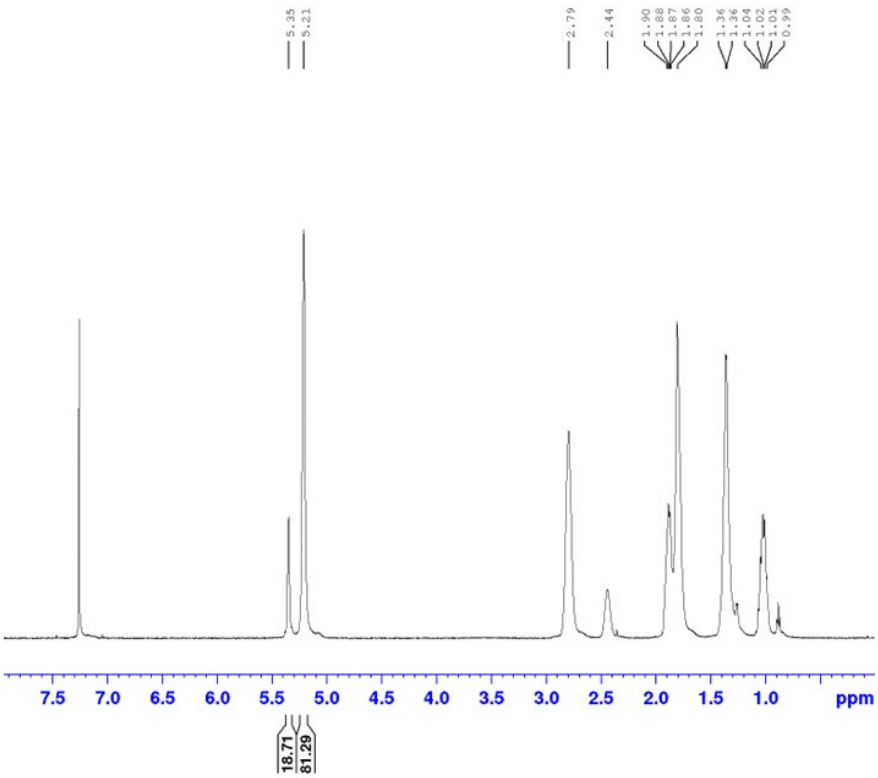

Figure S4. ^{1}H NMR spectrum ($CDCl_3$ at 25°C) of ring opened poly(NBE) prepared by V(N-2,6-$Cl_2C_6H_3$)(CHSiMe_3)(OC_6F_5)(NHC) (**1**) at 50°C (run 2).

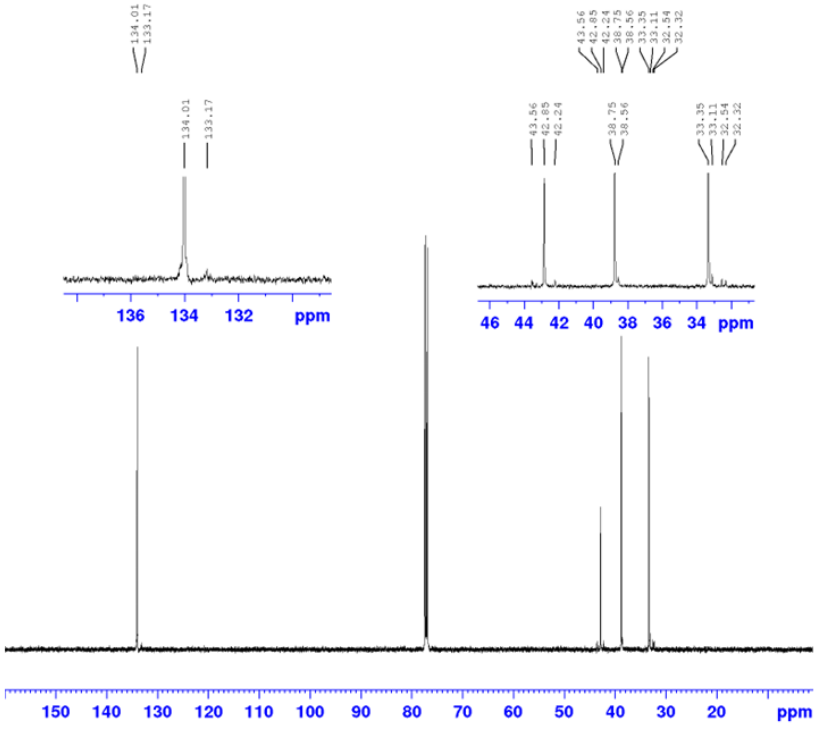

Figure S5. ^{13}C NMR spectrum ($CDCl_3$ at 25°C) of ring opened poly(NBE) prepared by V(N-2,6-$Cl_2C_6H_3$)(CHSiMe_3)(OC_6F_5)(NHC) (**1**) at 50°C (run 2).

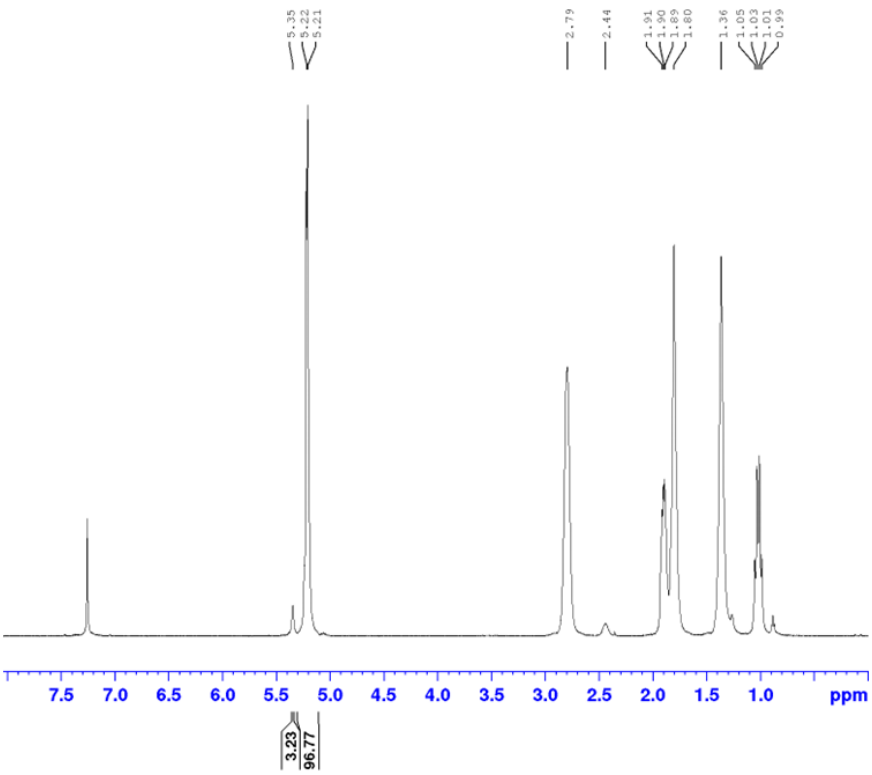

Figure S6. ^{1}H NMR spectrum ($CDCl_3$ at 25°C) of ring opened poly(NBE) prepared by V(N-2,6-$Cl_2C_6H_3$)(CHSiMe_3)(OC_6Cl_5)(NHC) (**2**) at 25°C (run 7).

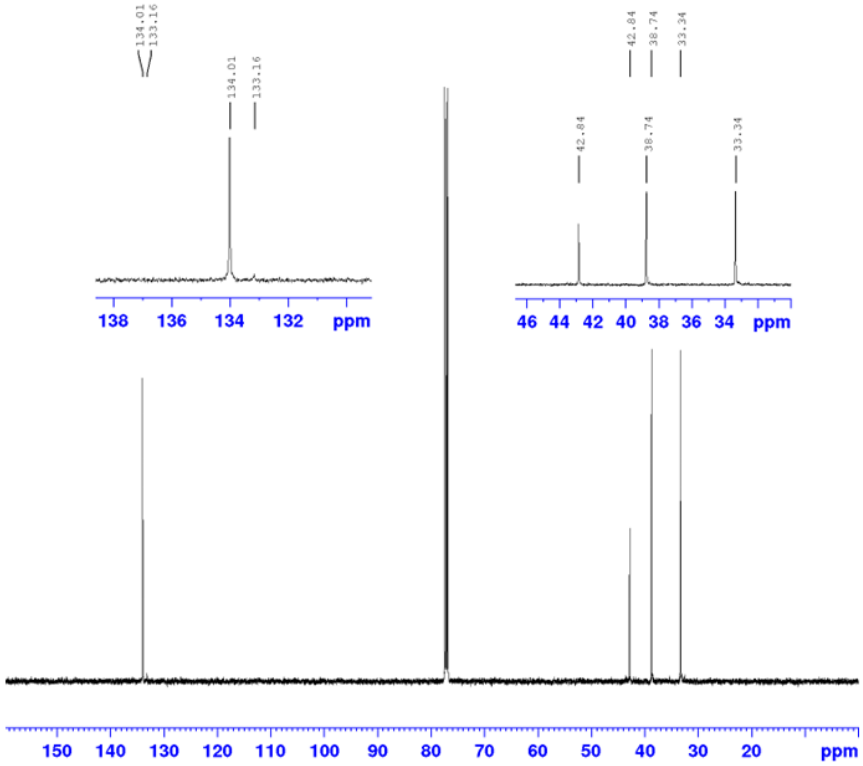

Figure S7. ^{13}C NMR spectrum ($CDCl_3$ at 25°C) of ring opened poly(NBE) prepared by V(N-2,6-$Cl_2C_6H_3$)(CHSiMe_3)(OC_6Cl_5)(NHC) (**2**) at 25°C (run 7).

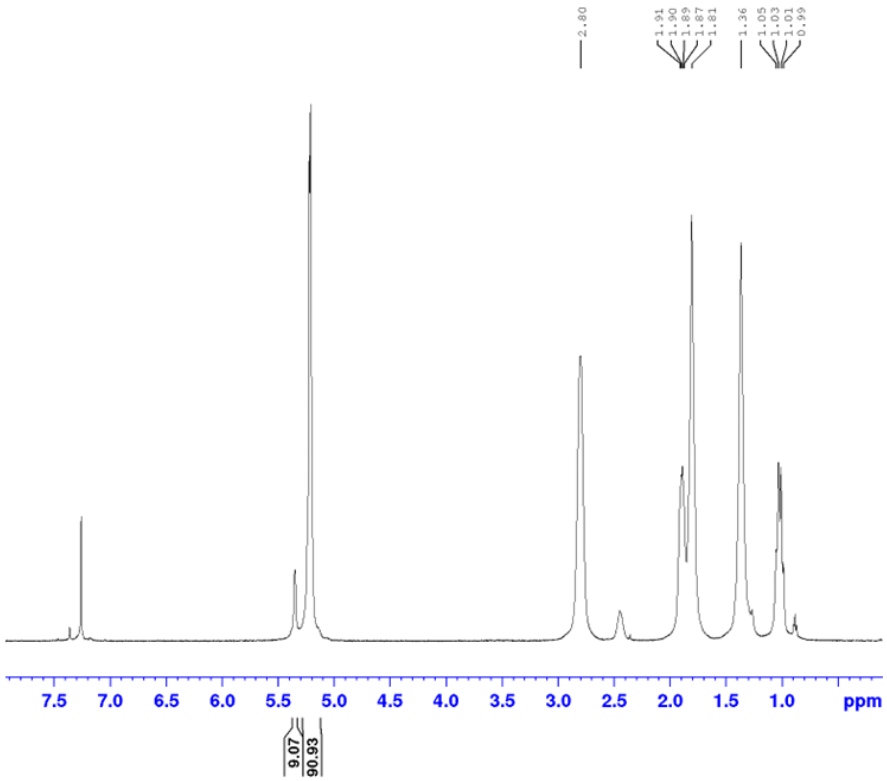

Figure S8. ^{1}H NMR spectrum ($CDCl_3$ at 25°C) of ring opened poly(NBE) prepared by V(N-2,6-$Cl_2C_6H_3$)(CHSiMe_3)(OC_6Cl_5)(NHC) (**2**) at 50°C (run 10).

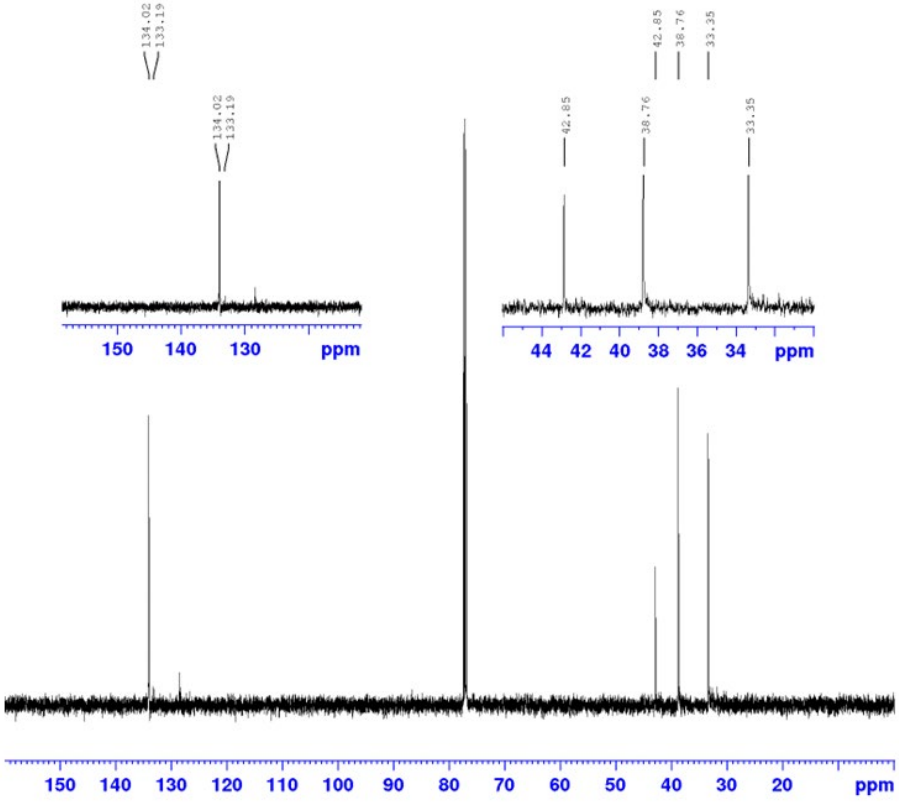

Figure S9. ^{13}C NMR spectrum ($CDCl_3$ at 25°C) of ring opened poly(NBE) prepared by V(N-2,6-$Cl_2C_6H_3$)(CHSiMe_3)(OC_6Cl_5)(NHC) (**2**) at 50°C (run 10).

Hydrogenation of ring-opened poly(NBE)s.

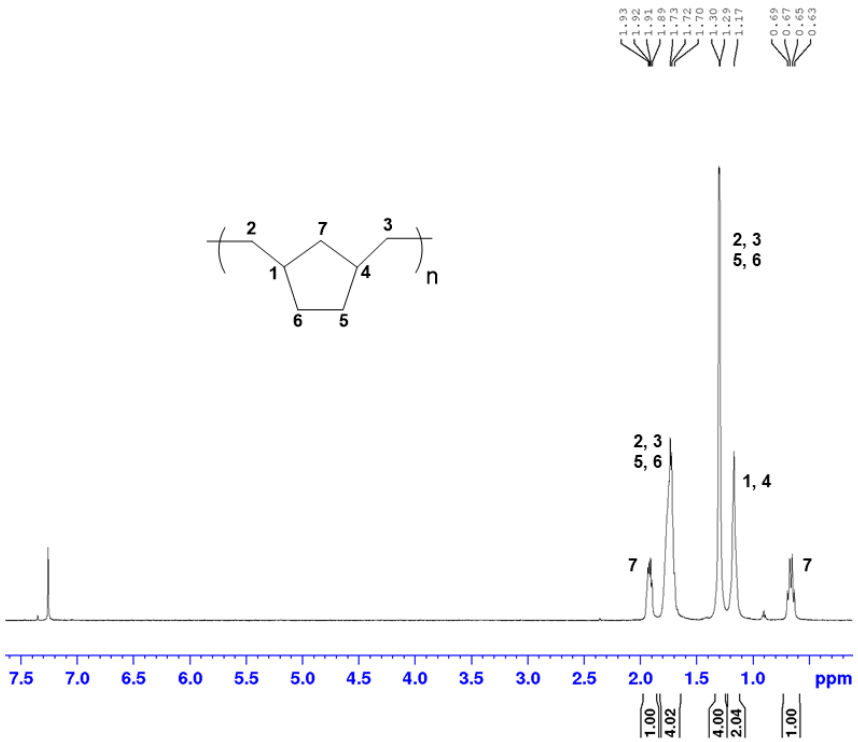

Figure S10. ^{1}H NMR spectrum ($CDCl_3$ at 50°C) of hydrogenated ring opened poly(NBE) prepared by V(N-2,6-$Cl_2C_6H_3$)($CHSiMe_3$)(OC_6Cl_5)(NHC) (**2**) at 25°C (run 19).

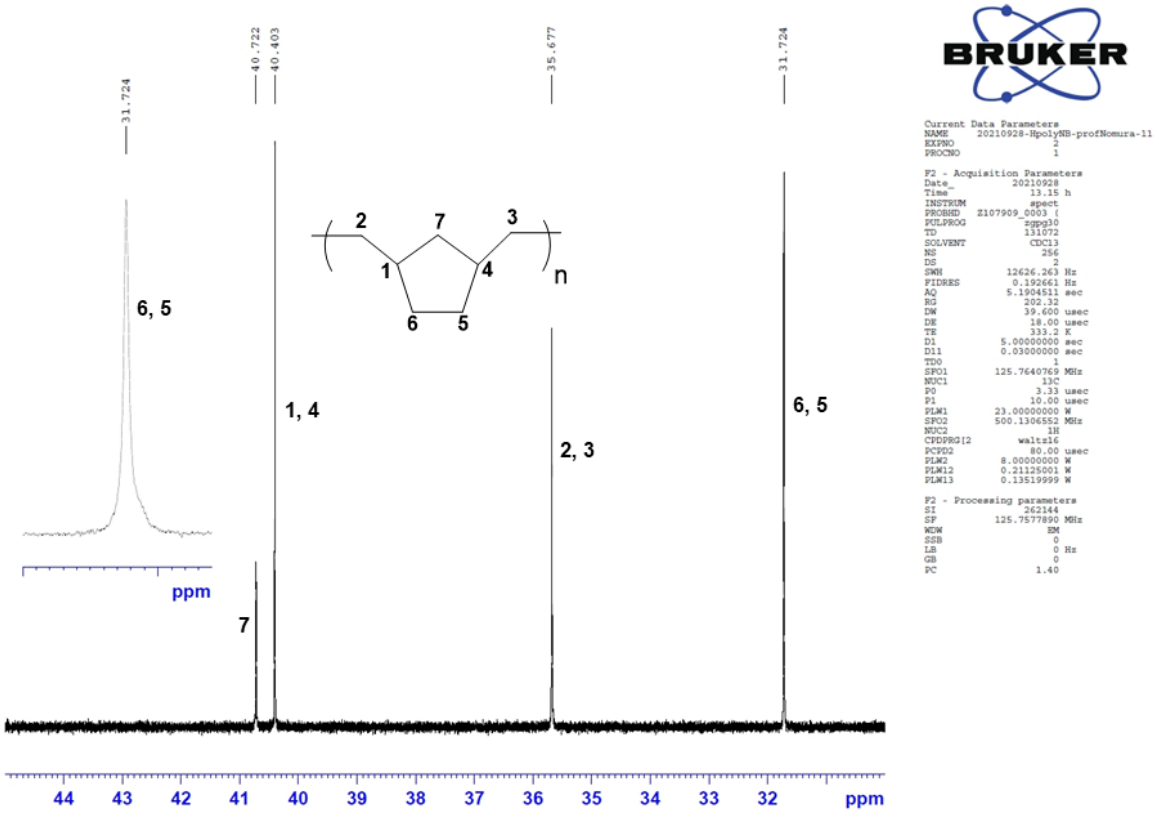

Figure S11. ^{13}C NMR spectrum (in $CDCl_3$ at 50 ºC) of hydrogenated ring opened poly(NBE) prepared by V(N-2,6-$Cl_2C_6H_3$)($CHSiMe_3$)(OC_6Cl_5)(NHC) (**2**) at 25 ºC (run 19).

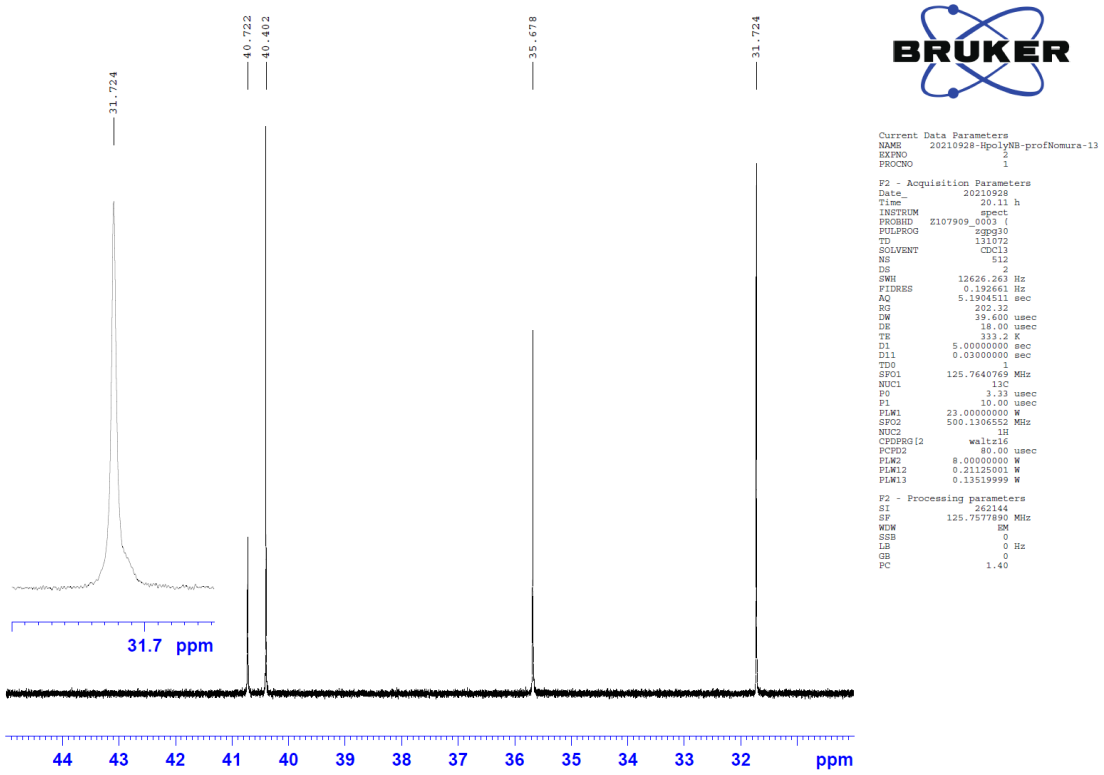

Figure S12. ^{13}C NMR spectrum (in $CDCl_3$ at 50 ºC) of hydrogenated ring opened poly(NBE) prepared by V(N-2,6-$Cl_2C_6H_3$)(CHSiMe_3)(OC_6Cl_5)(NHC) (**2**) at 50ºC (run 18).

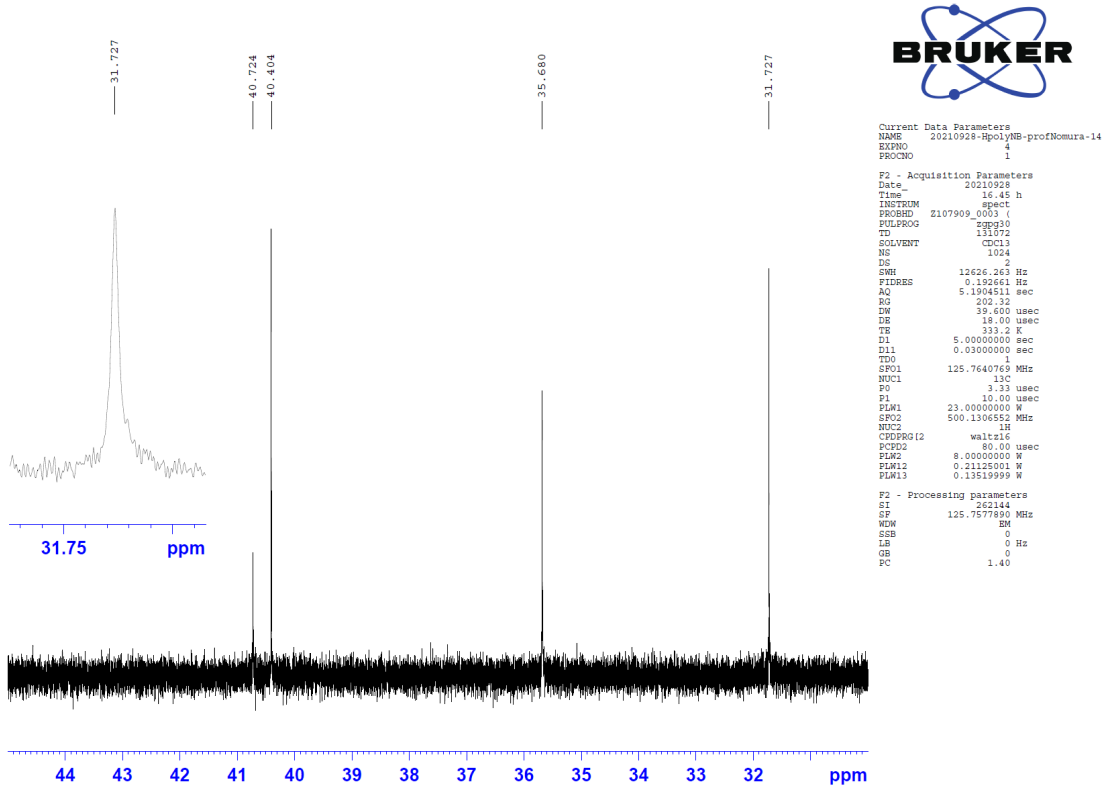

Figure S13. ^{13}C NMR spectrum (in $CDCl_3$ at 50 ºC) of hydrogenated ring opened poly(NBE) prepared by V(N-2,6-$Cl_2C_6H_3$)(CHSiMe_3)(OC_6F_5)(NHC) (**1**) at 25ºC (run 15).

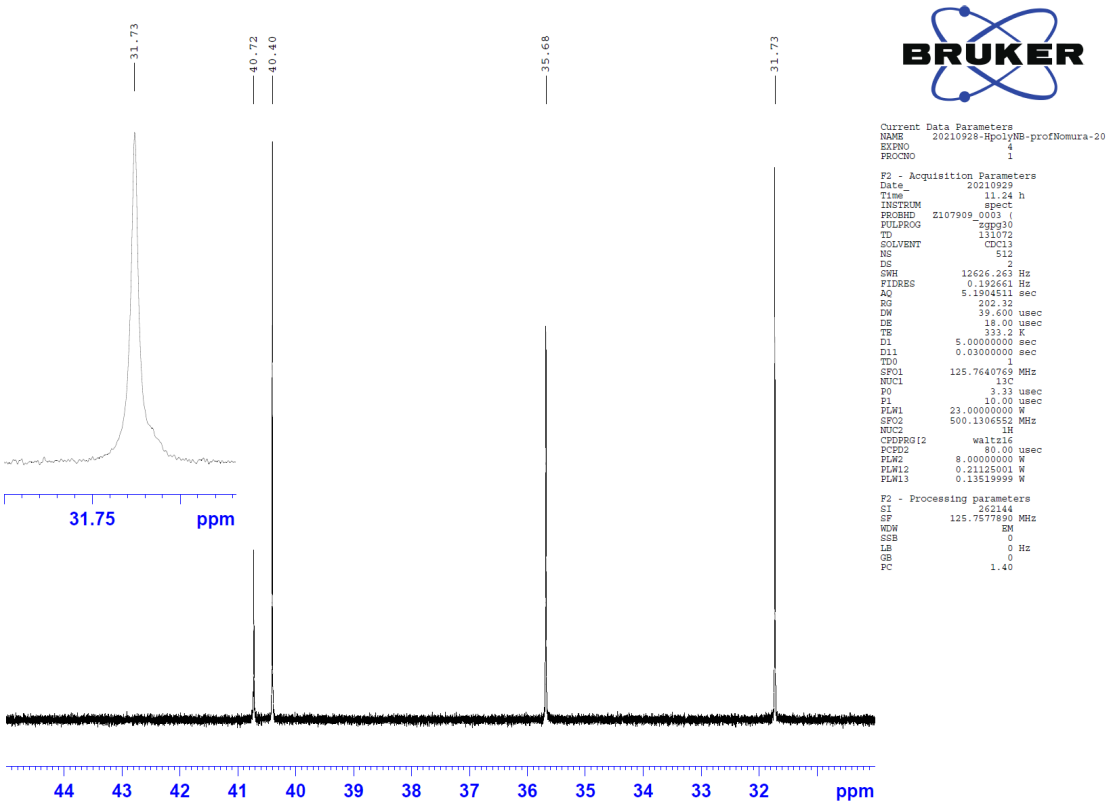

Figure S14. ^{13}C NMR spectrum (in $CDCl_3$ at 50 ºC) of hydrogenated ring opened poly(NBE) prepared by V(N-2,6-$Cl_2C_6H_3$)(CHSiMe_3)(OC_6F_5)(NHC) (**1**) at 50ºC (run 16).

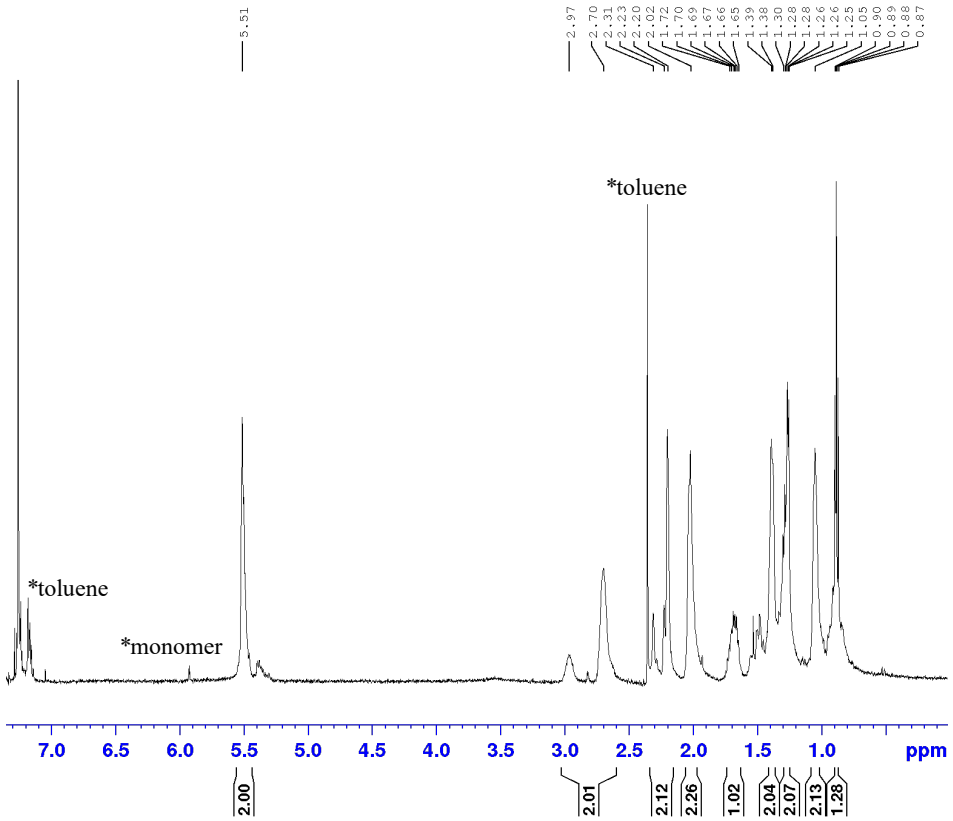

Figure S15. ^{1}H NMR spectrum (in $CDCl_3$ at 25 ºC) of ring opened poly(TCD) prepared by V(N-2,6-$Cl_2C_6H_3$)(CHSiMe_3)[$OC(CF_3)_3$](NHC) (**4**) at 25ºC (run 36).

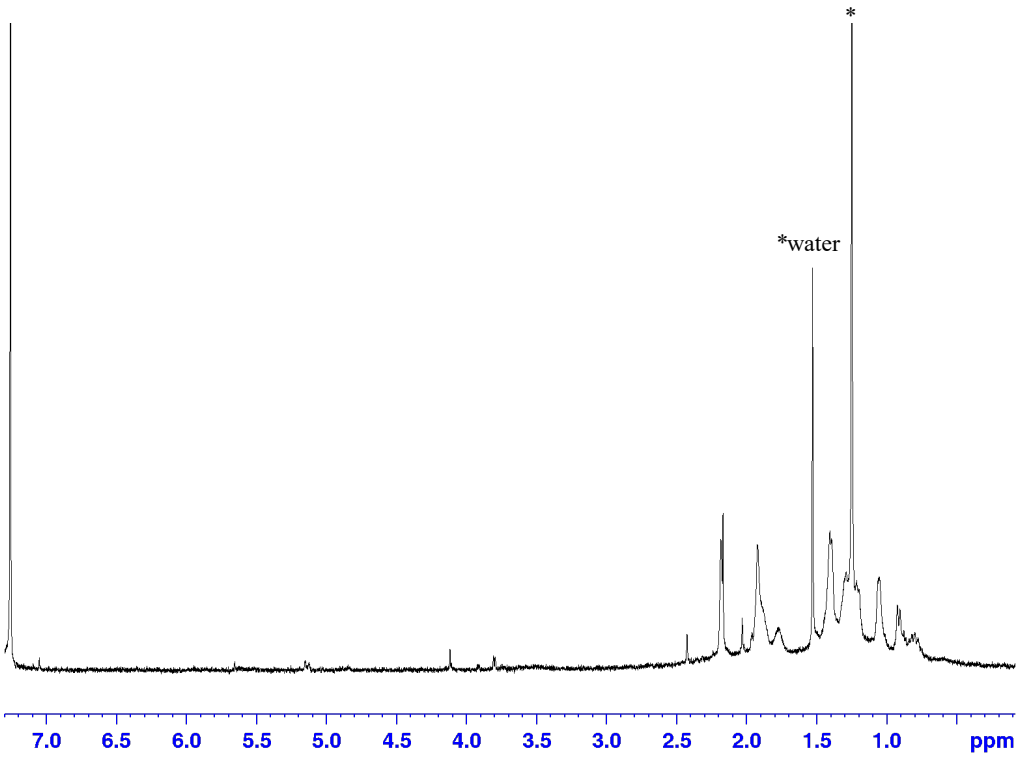

Figure S16. ^{1}H NMR spectrum (in $CDCl_3$ at 50 ºC) of hydrogenated ring opened poly(TCD) prepared by V(N-2,6-$Cl_2C_6H_3$)(CHSiMe_3)[OC(CF_3)$_3$](NHC) (**4**) at 25ºC (run 36).

3. Selected DSC thermograms of the polymers after hydrogenation.

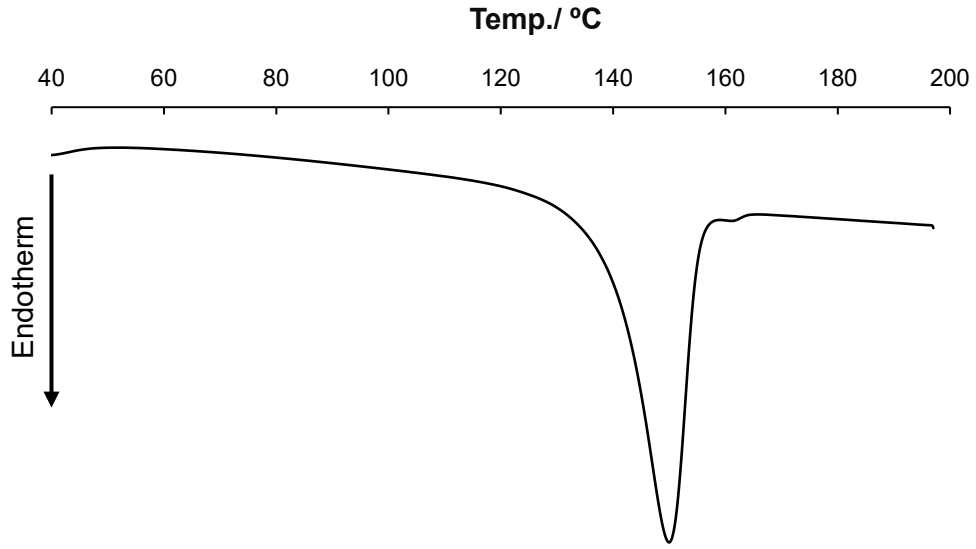

Figure S17. DSC thermogram of hydrogenated ring opened poly(NBE) prepared by V(N-2,6-$Cl_2C_6H_3$)(CHSiMe$_3$)(OC_6F_5)(NHC) (**1**) at 50ºC (run 5, T_m = 136.2ºC, *cis* 86%).

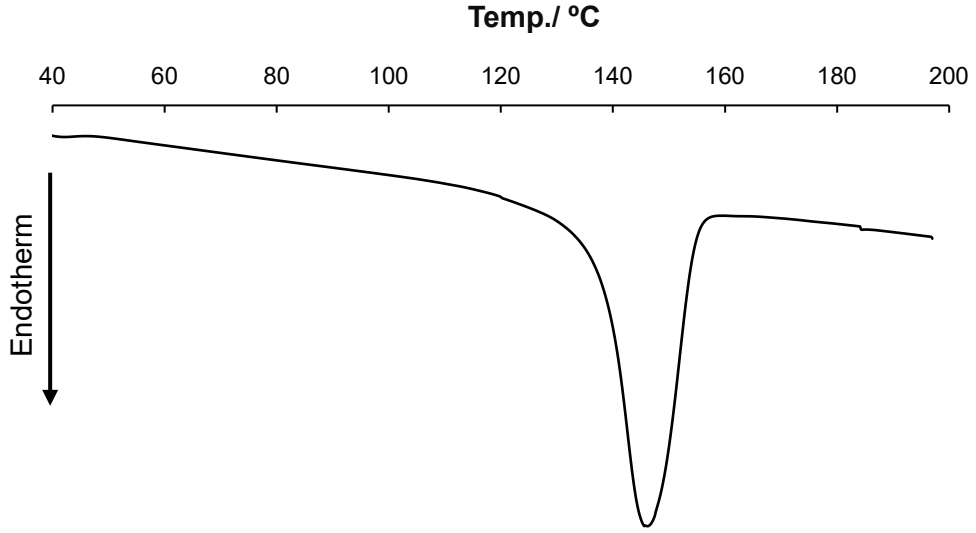

Figure S18. DSC thermogram of hydrogenated ring opened poly(NBE) prepared by V(N-2,6-$Cl_2C_6H_3$)(CHSiMe$_3$)(OC_6Cl_5)(NHC) (**2**) at 25ºC (run 9, T_m = 137.8ºC, *cis* 97%).

4. Crystal data and collection parameters for structural analysis of [V(CHSiMe$_3$)(N-2,6-X$_2$C$_6$H$_3$){OC(CF$_3$)$_3$}(NHC)] (X = F, Cl)

Table S3. Crystal data and collection parameters of [V(CHSiMe$_3$)(N-2,6-X$_2$C$_6$H$_3$){OC(CF$_3$)$_3$}(NHC)] [X = F (**3**), ,Cl (**4**); NHC = 1,3-bis(2,6-dimethylphenyl)imidazole-2-ylidene (IXy)].

	V(CHSiMe$_3$)(N-2,6-F$_2$C$_6$H$_3$)[OC(CF$_3$)$_3$]-(NHC) (**3**)	V(CHSiMe$_3$)(N-2,6-Cl$_2$C$_6$H$_3$)[OC(CF$_3$)$_3$]-(NHC) (**4**)
Formula	$C_{33}H_{33}F_{11}N_3OSiV$	$C_{33}H_{33}Cl_2F_9N_3OSiV$
Formula weight	775.65	808.55
Crystal color, Habit	black, plate	violet, block
Crystal size (mm)	0.186 × 0.185 × 0.041	0.288 × 0.227 × 0.139
Crystal system	Triclinic	monoclinic
Space group	*P*-1	$P2_1/n$
a (Å)	9.6615(4)	15.1196(5)
b (Å)	12.4091(4)	16.0398(5)
c (Å)	16.1836(5)	15.5170(5)
α (deg)	91.240(2)	
β (deg)	95.293(3)	102.341(3)
γ (deg)	111.900(3)	
V (Å^3)	1789.27(11)	3676.2(2)
Z value	2	4
D_{calcd} (g/cm^3)	1.440	1.461
F_{000}	792.0	1648.0
Temp (K)	93 (2)	93 (2)
μ (Mo K*α*) (cm^{-1})	3.99	5.25
No. of reflections measured (R_{int})	Total: 26875 Unique: 8543 (0.0273)	Total: 55266 Unique: 8811 (0.0464)
$2\theta_{max}$ (deg)	55.8	55.9
No. of observations [$I > 2.00\sigma(I)$]	8543	8811
No. of variables	594	691
$R1$ [$I > 2.00\sigma(I)$]	0.0790	0.0818
$wR2$ [$I > 2.00\sigma(I)$]	0.2180	0.2132
Goodness of Fit	1.041	1.120

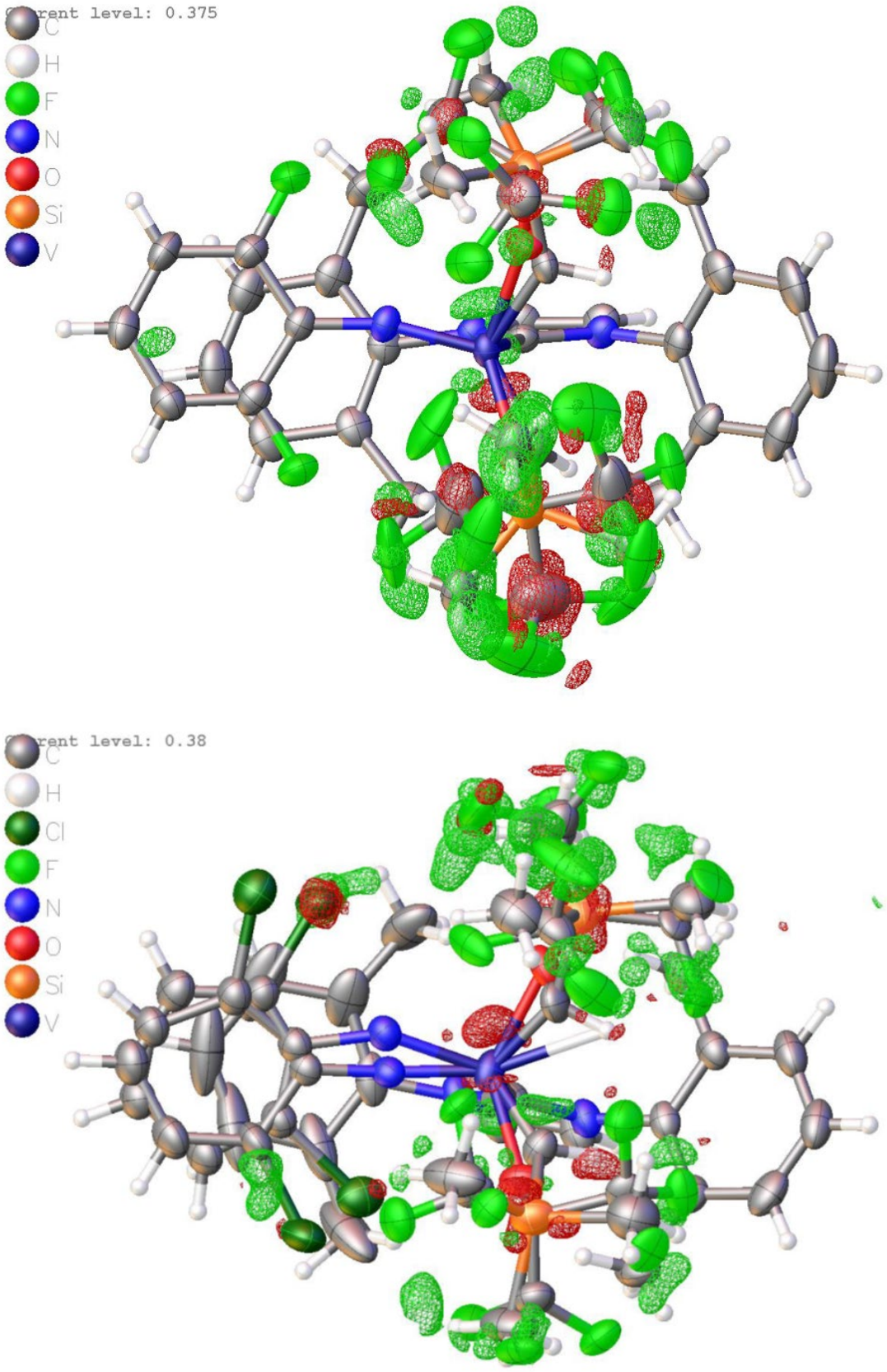

Figure S19. Electron density maps of V(N-2,6-$X_2C_6H_3$)($CHSiMe_3$)[($OC(CF_3)_3$)](NHC) [X = F (**3**, top),Cl (**4**,bottom)]. There are large residuals due to disorder hard to solve.