Electronic Supplementary Information (ESI)

for

Facile *In Situ* Generation of Highly Active (Arylimido)Vanadium(V)-Alkylidene Catalysts for Ring-Opening Metathesis Polymerization (ROMP) of Cyclic Olefins by Immediate Phenoxy Ligand Exchange

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Contents

1. General experimental procedure, synthesis and identification of $V(CHSiMe_3)(NC_6F_5)(O\text{-}2,6\text{-}{}^iPr_2C_6H_3)(PMe_3)_2$ (**1**) including selected NMR spectra.

2. Basic polymerization procedure of ROMP of cyclic olefins, and additional data for ROMP of norbornene (NBE) for optimization of reaction conditions, in the presence of 1-hexene.

3. Selected NMR data in some reaction chemistry.

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1. General experimental procedure, synthesis and identification of $V(CHSiMe_3)(NC_6F_5)$-$(O$-$2,6$-$^iPr_2C_6H_3)(PMe_3)_2$ (1) including NMR spectra.

General Procedures. All experiments were carried out under a nitrogen atmosphere in a vacuum atmospheres drybox. Anhydrous grade, benzene, and *n*-hexane (Kanto Chemical Co., Inc.) were transferred into a bottle containing molecular sieves (a mixture of 3A 1/16, 4A 1/8, and 13X 1/16) in the drybox under N_2, and were passed through an alumina short column under a N_2 stream prior to use. Norbornene (TCI) was used after distillation in the presence of Na. Cyclopentene (Aldrich), cycloheptene (TCI) were dried in the presence of molecular sieves, and pass alumina short column prior to use. $V(NC_6F_5)Cl_3(dme)$ was prepared according to the analogous procedure for synthesis of the other (arylimido)vanadium(V) trichloride complexes[1] and stabilized in dme.[2]

All NMR spectra were recorded on a Bruker AV500 spectrometer (500.13 MHz for ^1H, 125.77 MHz for ^{13}C, 470.59 MHz for ^{19}F, 202.47 MHz for ^{31}P, 131.55 MHz for ^{51}V). All spectra were obtained in the solvent indicated at 25 °C unless otherwise noted. Chemical shifts are given in ppm and are referenced to $SiMe_4$ (δ 0.00 ppm, ^1H, ^{13}C). Coupling constants are given in Hz. Chemical shift was determined with reference to chloroform (7.26 ppm for ^1H, 77.16 ppm for ^{13}C) and benzene-d_6 (7.16 ppm for ^1H, 128.06 ppm for ^{13}C). Molecular weights and the molecular weight distributions of the resultant polymers were measured by gel-permeation chromatography (GPC). HPLC grade THF was used for GPC and was degassed prior to use. GPC was performed at 40 °C on a Shimadzu SCL-10A using a RID-10A detector (Shimadzu Co. Ltd.) in THF (containing 0.03 wt % of 2,6-di-*tert*-butyl-*p*-cresol, flow rate 1.0 mL/min). GPC columns (ShimPAC GPC-806, 804 and 802, 30 cm × 8.0 mm diameter, spherical porous gel made of styrene/ divinylbenzene copolymer, ranging from $<10^2$ to 2×10^7 MW) were calibrated versus polystyrene standard samples.

Synthesis and identification of $V(CHSiMe_3)(NC_6F_5)(O$-$2,6$-$^iPr_2C_6H_3)(PMe_3)_2$ (1).

(i) Synthesis of $V(NC_6F_5)(CH_2SiMe_3)_3$. Into a THF solution containing $LiCH_2SiMe_3$ (203 mg, 2.16 mmol, 3.0 equiv.), $V(NC_6F_5)Cl_3(dme)$ (311 mg, 0.72 mmol) was added at -30 °C. The reaction mixture was warmed slowly to room temperature and stirred for 1 h. A small amount of CH_2Cl_2 (ca. 1 mL) was added after the prescribed time, and the solution was then removed in *vacuo*. The resultant residue was extracted with *n*-hexane (ca. 30 mL). The *n*-hexane extract was then removed in *vacuo* to give deep brown oil. Yield: 110 mg (30 %). The product was characterized by NMR spectra. ^1H NMR (C_6D_6): δ 2.25 (br, 6H, -CH_2SiMe_3), -0.08 (s, 27H, -CH_2SiMe_3). ^{13}C NMR: 144.7, 142.9, 139.6, 138.9, 137.7, 136.9, 135.8, 98.4 (b), 1.6. ^{19}F NMR: δ -148.1 (d, J = 23.5 Hz), -161.4 (t, J = 25.8 Hz), -164.2 (t, J = 21.1 Hz). ^{51}V NMR: δ 1198.4 ($\Delta\nu_{1/2}$ = 199 Hz). Anal. Calcd. for $V(CH_2SiMe_3)_3(NC_6F_5)$, $C_{18}H_{33}F_5NSi_3V$: C, 43.80; H, 6.74; N, 2.84. Found: C, 44.08; H, 6.54; N, 2.94.

(ii) Synthesis of $V(NC_6F_5)(CH_2SiMe_3)_2(O$-$2,6$-$^iPr_2C_6H_3)$. Into an *n*-hexane solution (30 mL) containing $V(NC_6F_5)(CH_2SiMe_3)_3$ (110 mg, 0.22 mmol) was added $2,6$-$^iPr_2C_6H_3OH$ (40 mg, 0.22 mmol, 1.0 equiv.) at -30 °C. The reaction mixture was warmed slowly to room temperature, and the mixture was stirred for 12 h. The solution was then removed in *vacuo* to give deep brown oil. (130 mg, 98%). ^{1}H NMR(C_6D_6): δ 7.04 (d, J = 10 Hz, 2H, -*Ar*), 6.95 (t, J = 10 Hz, 1H, -*Ar*), 3.68 (m, 2H, -*CH*(CH_3)$_2$), 3.13 (d, J = 4.0 Hz, 2H, -*CH*$_2$SiMe$_3$), 2.61 (d, J = 4.0 Hz, 2H, -*CH*$_2$SiMe$_3$), 1.28 (d, J = 4.0 Hz, 12H, -CH(*CH*$_3$)$_2$), 0.10 (s, 18H, -CH$_2$Si*Me*$_3$); ^{13}C NMR: δ 137.7, 123.9, 123.2, 26.8, 23.2, 1.1; ^{19}F NMR: δ -148.9 (dd, J = 23.5 Hz, J = 4.7 Hz), -159.0 (t, J = 21.2 Hz), -163.8 (dt, J = 23.5 Hz, J = 4.7 Hz); ^{51}V NMR: δ 630 ($\Delta\nu_{1/2}$ = 443 Hz). It was difficult to obtain the analytically pure sample probabluy due to difficulty to remove impurities and/or *n*-hexane completely, and the resiltant oil (mixture) is sutable for isolation of $V(CHSiMe_3)(NC_6F_5)(O\text{-}2,6\text{-}{}^{i}Pr_2C_6H_3)(PMe_3)_2$ as pure microcrystalline in the next step.

(iii) Synthesis of $V(CHSiMe_3)(NC_6F_5)(O\text{-}2,6\text{-}{}^{i}Pr_2C_6H_3)(PMe_3)_2$. Into an *n*-hexane solution (20 mL) containing $V(NC_6F_5)(CH_2SiMe_3)_2(O\text{-}2,6\text{-}{}^{i}Pr_2C_6H_3)$ (130 mg, 0.22 mmol) was added PMe_3 (84 mg, 0.22 mmol, excessive, 5 equiv.) at -30 ºC. The reaction mixture was warmed slowly to room temperature and was then kept in oil bath at 70 ºC for 12 h. The solution was passed through a Celite pad, and the filtercake was washed with *n*-hexane. The combined solution (filtrate and wash) was placed in a rotary evaporator to remove the volatiles. The residue was then dissolved in small amount of *n*-pentane and placed in the freezer (-30 ºC). Dark red crystalline solids were collected. (59 mg, 42%). ^{1}H NMR (C_6D_6): δ 17.12 (s, 1H, -V=*CH*SiMe$_3$), 7.17 (d, J = 10 Hz, 2H, -*Ar*), 6.93 (t, J = 10 Hz, 2H, -*Ar*), 3.71 (br, 2H, -C*H*(CH_3)$_2$), 1.34 (br, 12H, -CH(*CH*$_3$)$_2$), 0.86 (br, 18H, P*Me*$_3$), 0.31(s, 9H, -CHSi*Me*$_3$); ^{13}C NMR: δ 346.2, 163.3, 144.3, 142.4, 139.1, 137.1, 135.6, 135.2, 123.3, 118.4, 27.0, 24.2, 16.2, 2.0; ^{19}F NMR: -153.0 (d, J = 23.4 Hz), -165.7 (t, J = 20.4 Hz), -167.4 (t, J = 21.8 Hz); ^{31}P NMR: δ -13.3 (br); ^{51}V NMR: δ 1.00 (s, $\Delta\nu_{1/2}$ = 382 Hz); Anal. Calcd. for $V(CHSiMe_3)(NC_6F_5)(O\text{-}2,6\text{-}{}^{i}Pr_2C_6H_3)(PMe_3)_2$, $C_{28}H_{45}F_5NOP_2SiV$: C, 51.93; H, 7.00; N, 2.16. Found: C, 52.18; H, 7.01; N, 2.09.

1. For example, (a) D. D. Devore, J. D. Lichtenhan, F. Takusagawa and E. A. Maatta, *J. Am. Chem. Soc.*, 1987, **109**, 7408-7416; (b) J. -K. F. Buijink, J. H. Teubin, H. Kooijman and A. L. Spek, *Organometallics*, 1994, **13**, 2922-2924.

2. NMR data for $V(NC_6F_5)Cl_3$, K. A. Rufanov, J. Kipke and J. Sundermeyer, *Dalton Trans.*, 2011, **40**, 1990–1997.

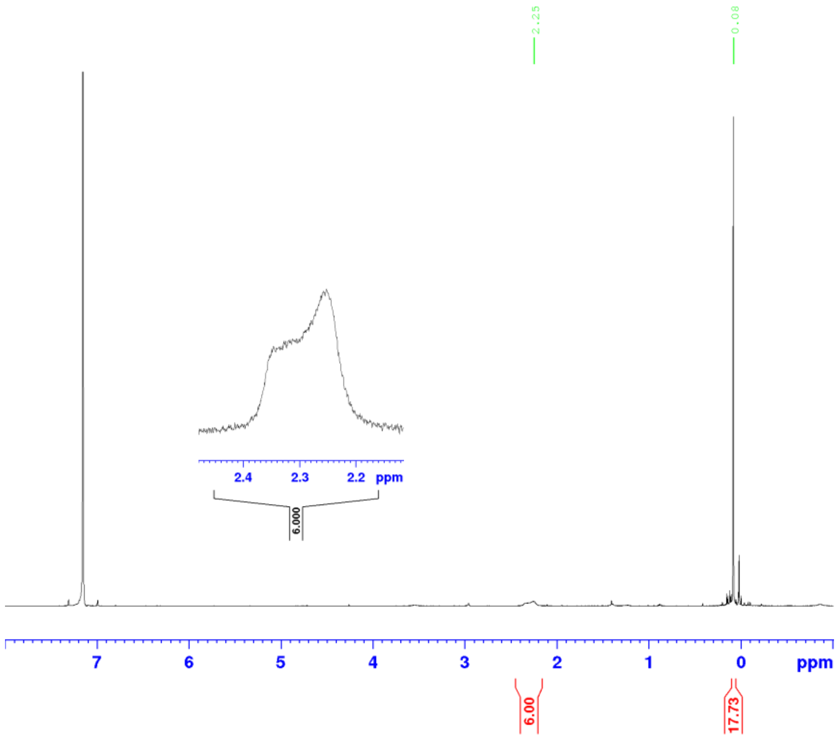


Figure S1-1. ^{1}H NMR spectrum (in C_6D_6) for $V(NC_6F_5)(CH_2SiMe_3)_3$.

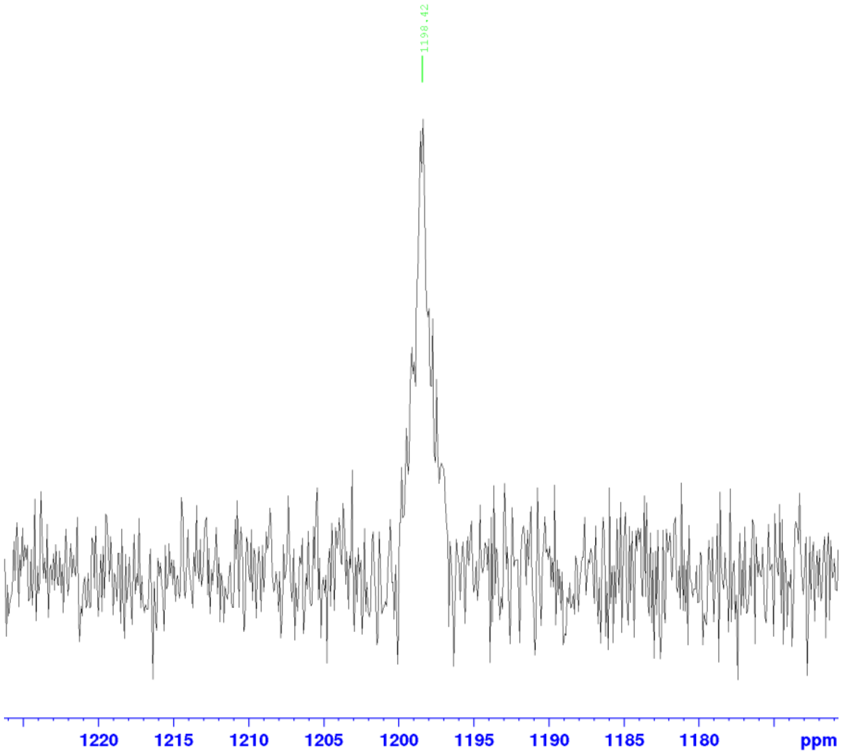


Figure S1-2. ^{51}V NMR spectrum (in C_6D_6) for $V(NC_6F_5)(CH_2SiMe_3)_3$.

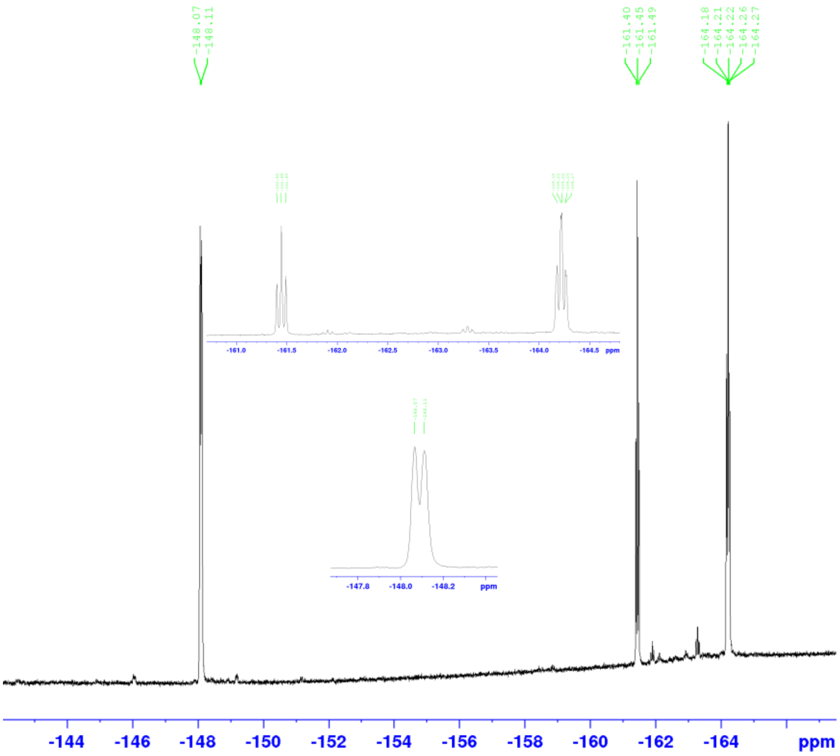


Figure S1-3. ^{19}F NMR spectrum (in C_6D_6) for $V(NC_6F_5)(CH_2SiMe_3)_3$.

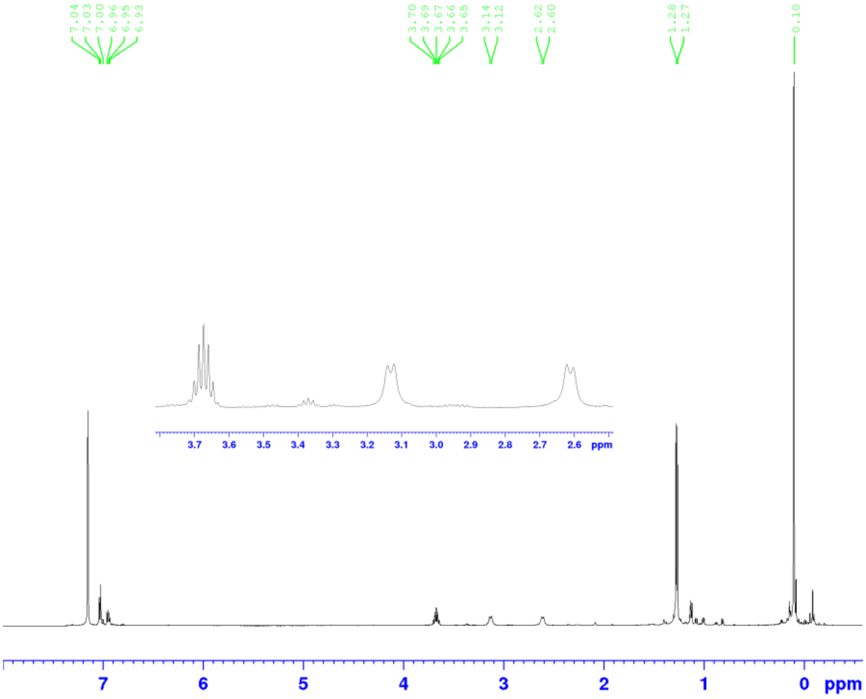


Figure S1-4. ^{1}H NMR spectrum (in C_6D_6) for $V(NC_6F_5)(CH_2SiMe_3)_2(O\text{-}2,6\text{-}{}^{i}Pr_2C_6H_3)$.

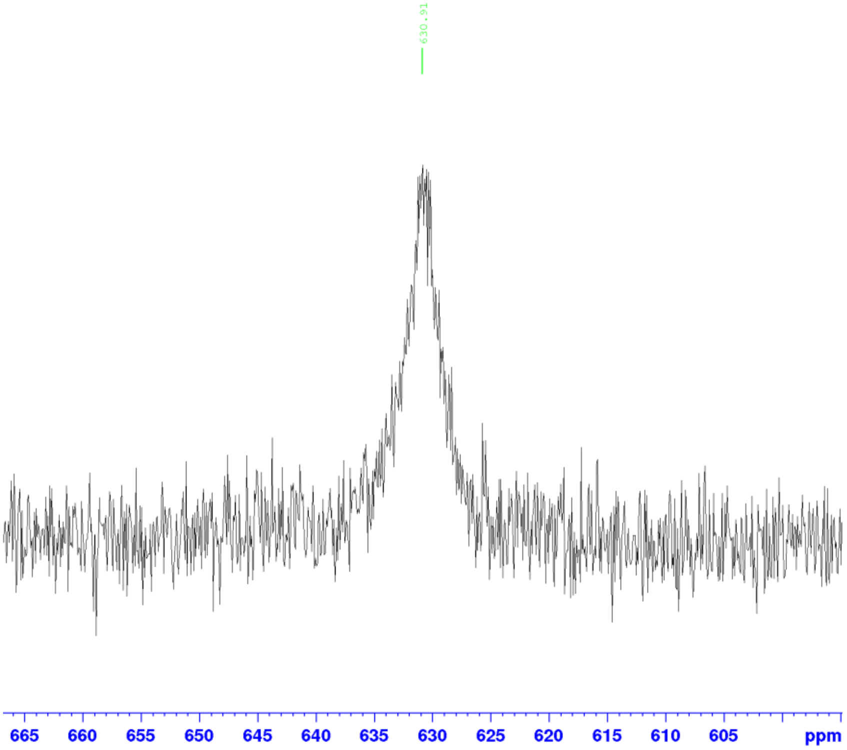


Figure S1-5. ^{51}V NMR spectrum (in C_6D_6) for $V(NC_6F_5)(CH_2SiMe_3)_2(O\text{-}2,6\text{-}^{i}Pr_2C_6H_3)$.

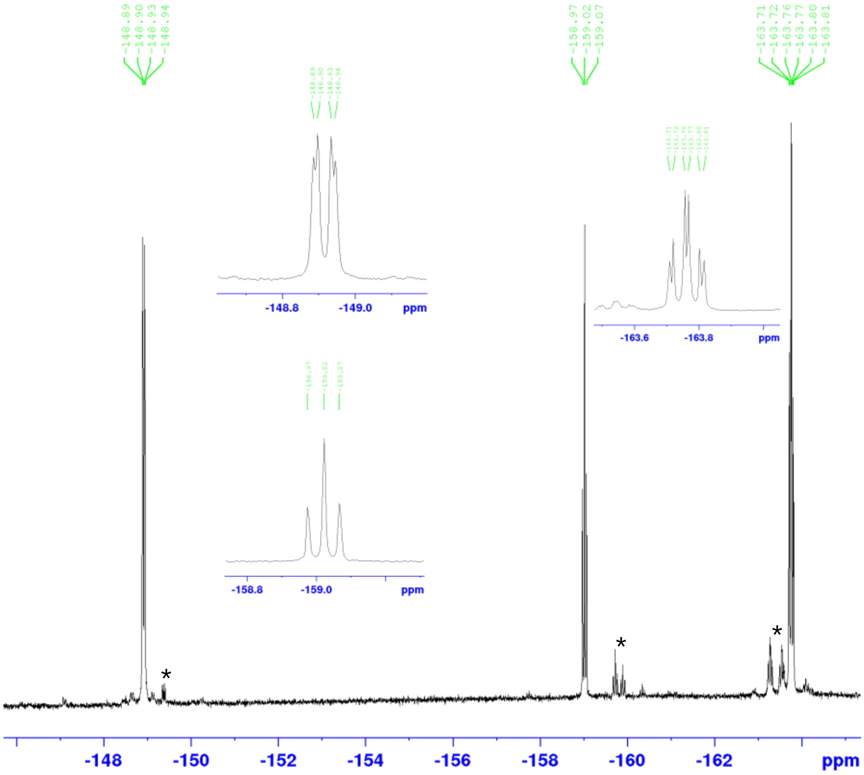


Figure S1-6. ^{19}F NMR spectrum (in C_6D_6) for $V(NC_6F_5)(CH_2SiMe_3)_2(O\text{-}2,6\text{-}^{i}Pr_2C_6H_3)$. Resonances marked with * would be impurities that are difficult to separate at this step.

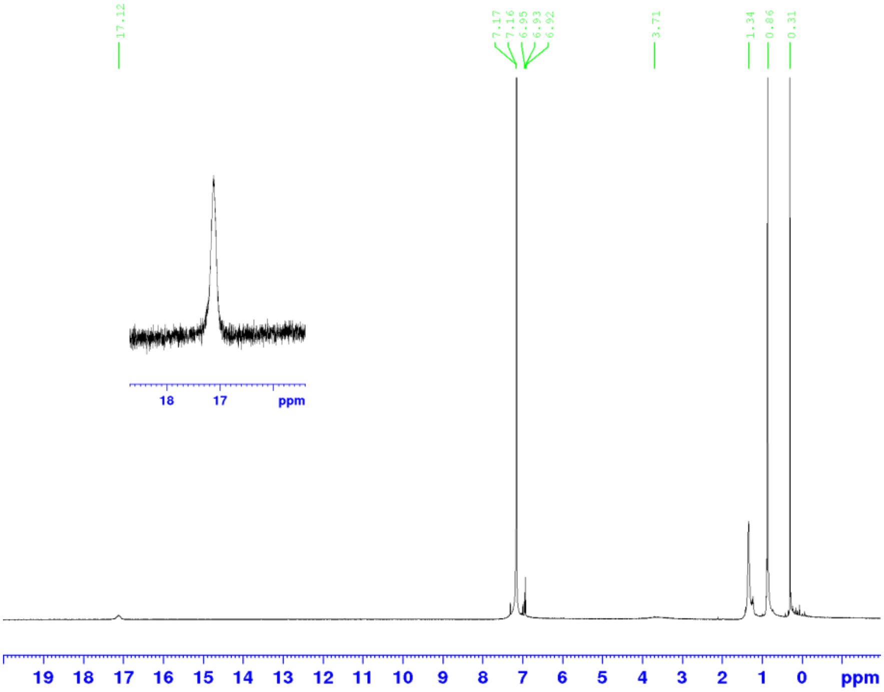


Figure S1-7. ^{1}H NMR spectrum (in C_6D_6) for $V(CHSiMe_3)(NC_6F_5)(O\text{-}2,6\text{-}{}^i Pr_2C_6H_3)(PMe_3)_2$ (**1**).

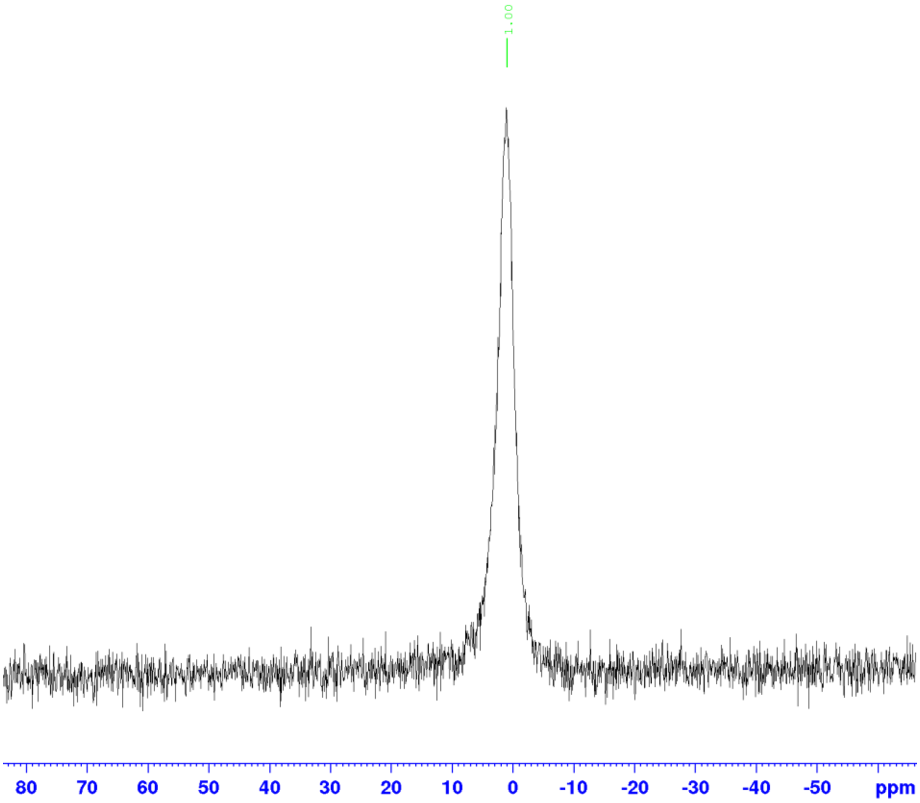


Figure S1-8. ^{51}V NMR spectrum (in C_6D_6) for $V(CHSiMe_3)(NC_6F_5)(O\text{-}2,6\text{-}{}^i Pr_2C_6H_3)(PMe_3)_2$ (**1**).

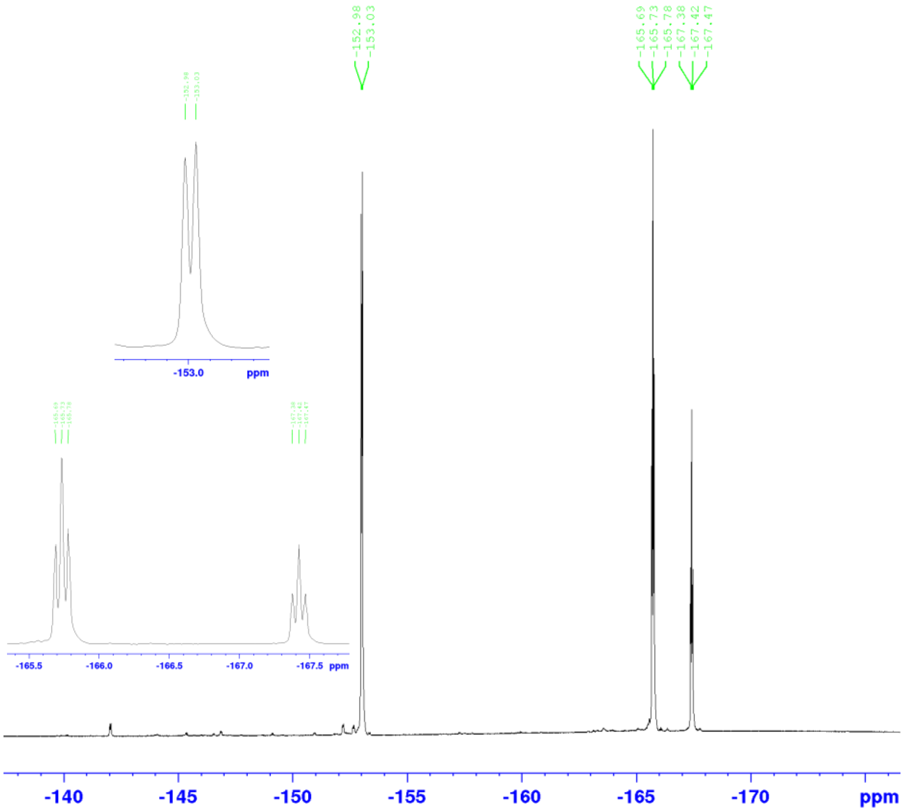


Figure S1-9. ^{19}F NMR spectrum (in C_6D_6) for $V(CHSiMe_3)(NC_6F_5)(O\text{-}2,6\text{-}^iPr_2C_6H_3)(PMe_3)_2$ (**1**).

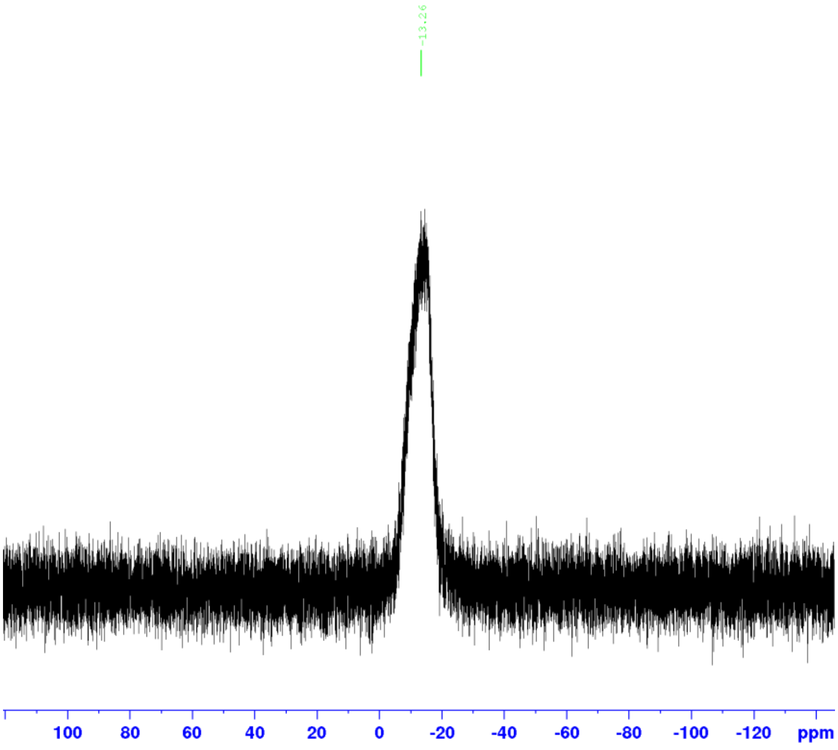
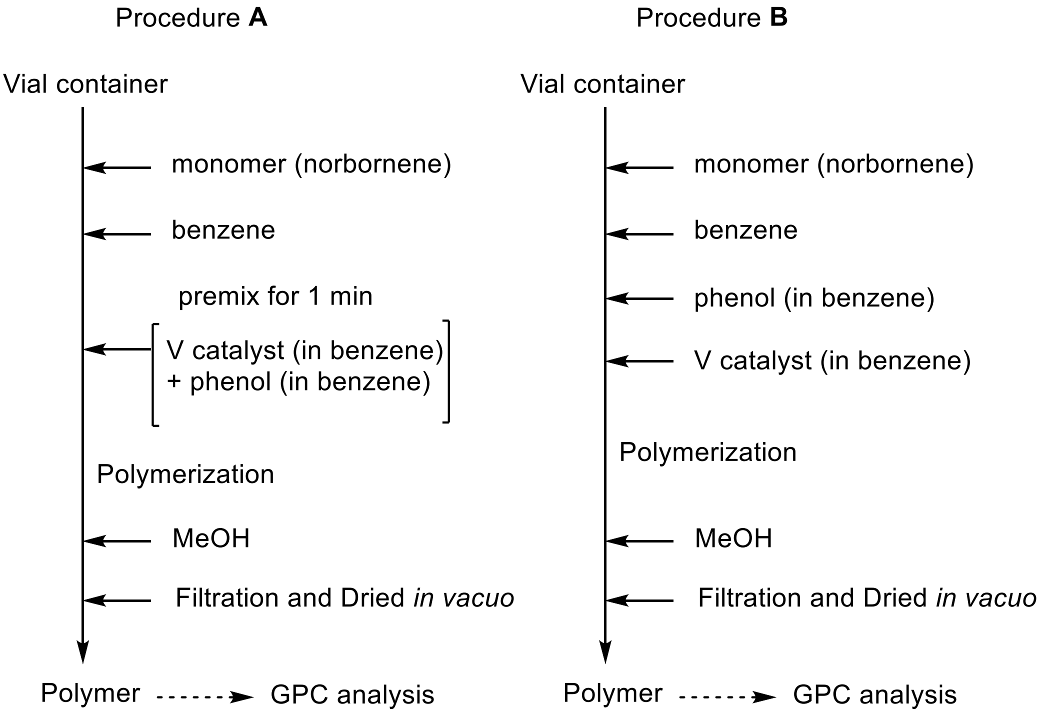


Figure S1-10. ^{31}P NMR spectrum (in C_6D_6) for $V(CHSiMe_3)(NC_6F_5)(O\text{-}2,6\text{-}^iPr_2C_6H_3)(PMe_3)_2$ (**1**).

2. Basic polymerization procedure of ROMP of cyclic olefins, and additional data for ROMP of norbornene (NBE).

ROMP of norbornene (NBE). Typical reaction procedure (Procedure A, Scheme S1) is as follows. Into a vial (10 mL scale) containing a stirred benzene solution (0.5 mL) of prescribed amount of phenol, benzene solution (0.5 mL) containing prescribed amount of $V(CHSiMe_3)(NC_6F_5)(O\text{-}2,6\text{-}{}^i Pr_2C_6H_3)(PMe_3)_2$ (**1**) was added. The solution was kept stirring at 25 ºC (for 1 minute), and the solution was then added into a vial (10 mL scale) containing norbornene dissolved in benzene. The mixture was stirred for a prescribed time at 25 ºC. The polymerization was then quenched by the addition of excess PhCHO, and the solution was stirred for an additional 1 h at room temperature. The mixture was then poured into methanol (ca. 100 mL). The resultant solid was collected by filtration, washed with methanol, and then dried in *vacuo* at room temperature.



Scheme S1. Polymerization procedure employed for ring-opening metathesis polymerization (ROMP) of norbornene (NBE): Procedure A was chosen in this study (ROMP of cyclic olefins).

Table S2-1. Optimization of the reaction procedure.[a]

1 (μmol)	phenol	procedure[b]	premix[c] / min	time / min	polymer / mg	conv.[d] / %	TON[e]	TOF[f] min^{-1}
0.1	C_6F_5OH	B	--	1	34	17.0	3610	3620
0.1	C_6F_5OH	A	1.0	1	207	>100	>21200	>21200
0.05	C_6F_5OH	A	1.0	1	173	86.7	36800	36700
0.05	C_6F_5OH	A[g]	1.0	1	218	54.5	46300	46300
0.05	C_6F_5OH	A[g]	1.0	1	201	50.4	42700	42700

[a]Reaction conditions: **1** and 1.0 equiv of phenol, norbornene (NBE) 2.12 mmol, benzene 4.8 mL (total), at 25 °C, [b]Procedure shown in Scheme S1. [c]The ligand exchange reaction (premix) was conducted in benzene 0.1 mM (vanadium). [d]Conversion of NBE. [e]TON (turnovers) = NBE reacted (μmol)/vanadium complex charged (μmol). [f]TOF = (TON)/time. [g]NBE 4.24 mmol, benzene 9.6 mL (total).

Table S2-2. Additional polymerization data: ring opening metathesis polymerization (ROMP) of norbornene (NBE) in the presence of 1-hexene using $V(CHSiMe_3)(NC_6F_5)(O\text{-}2,6\text{-}{}^{i}Pr_2C_6H_3)(PMe_3)_2$ (**1**) – $2,6\text{-}Cl_2C_6H_3OH$ catalyst system.[a]

run	phenol	1-hexene / mol%	time / min	yield[b] / mg	conv.[c] / %	TON[d]	TOF[e] / min-^{1}	M_n[f] ×10^{-4}	M_w/ M_n[f]
1	--	--	10	291	72.8	1550	155	112	2.04
9	$2,6\text{-}Cl_2C_6H_3OH$	--	1	115	28.8	12200	12200	insoluble	
10	$2,6\text{-}Cl_2C_6H_3OH$	--	1	101	25.3	10700	10700	insoluble	
11	$2,6\text{-}Cl_2C_6H_3OH$	--	3	298	74.6	31700	10600	insoluble	
S1	$2,6\text{-}Cl_2C_6H_3OH$	10	1	73.8	36.9	7840	7840	11.46[g]	1.45[g]
S2	$2,6\text{-}Cl_2C_6H_3OH$	30	1	72.9	36.5	7740	7740	4.62[g]	1.46[g]

[a]Reaction Conditions: $V(CHSiMe_3)(NC_6F_5)(O\text{-}2,6\text{-}{}^{i}Pr_2C_6H_3)(PMe_3)_2$ (**1**) 0.10 μmol, initial NBE conc. 0.44 M [NBE 4.24 mmol and benzene 9.6 mL (runs 1,9-11) or 2.12 mmol and benzene 4.8 mL (runs S1 and 2)], 25 °C. The catalyst solution was prepared *in situ* by premixing **1** with 1.0 equiv of $2,6\text{-}Cl_2C_6H_3OH$ for 1 min at 25 °C (0.10 mmol/mL V, 200 rpm). [b]Isolated yield after precipitation into MeOH. [c]Conversion on the basis of polymer yield. [d]TON (turnovers) = monomer reacted (mmol)/vanadium complex (mmol). [e]TOF (min^{-1}) = TON/time. [f]GPC data in THF *vs* polystyrene standards. [g]GPC data in *o*-dichlorobenzene *vs* polystyrene standards.

3. Selected NMR data in some reaction chemistry.

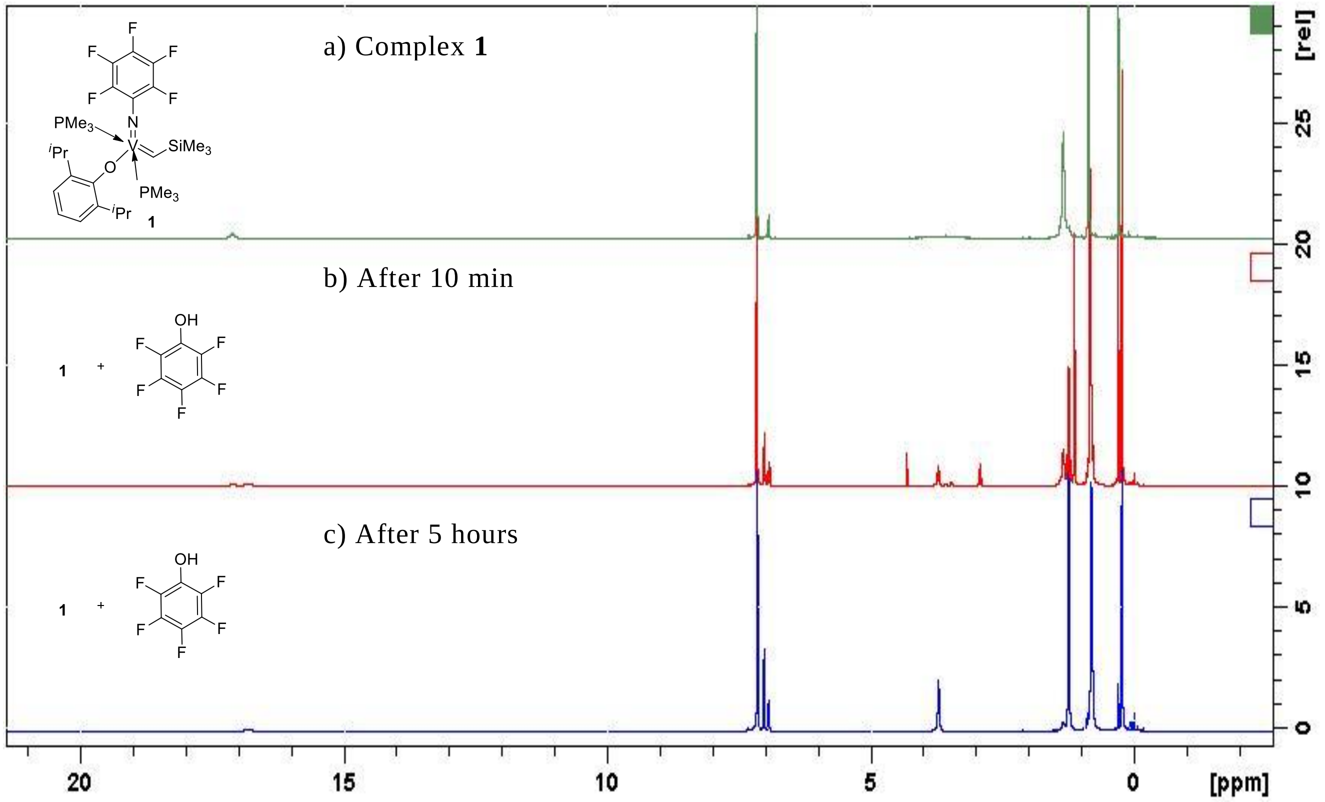


Figure S3-1. ^{1}H NMR spectra (in C_6D_6 at 25 ºC) for (a) V(CHSiMe$_3$)(NC$_6$F$_5$)(O-2,6-^{i}Pr$_2$C$_6$H$_3$)(PMe$_3$)$_2$ (**1**), and (b,c) reaction of **1** with 1.0 equiv of C_6F_5OH (b) after 10 min, (c) 5 h.

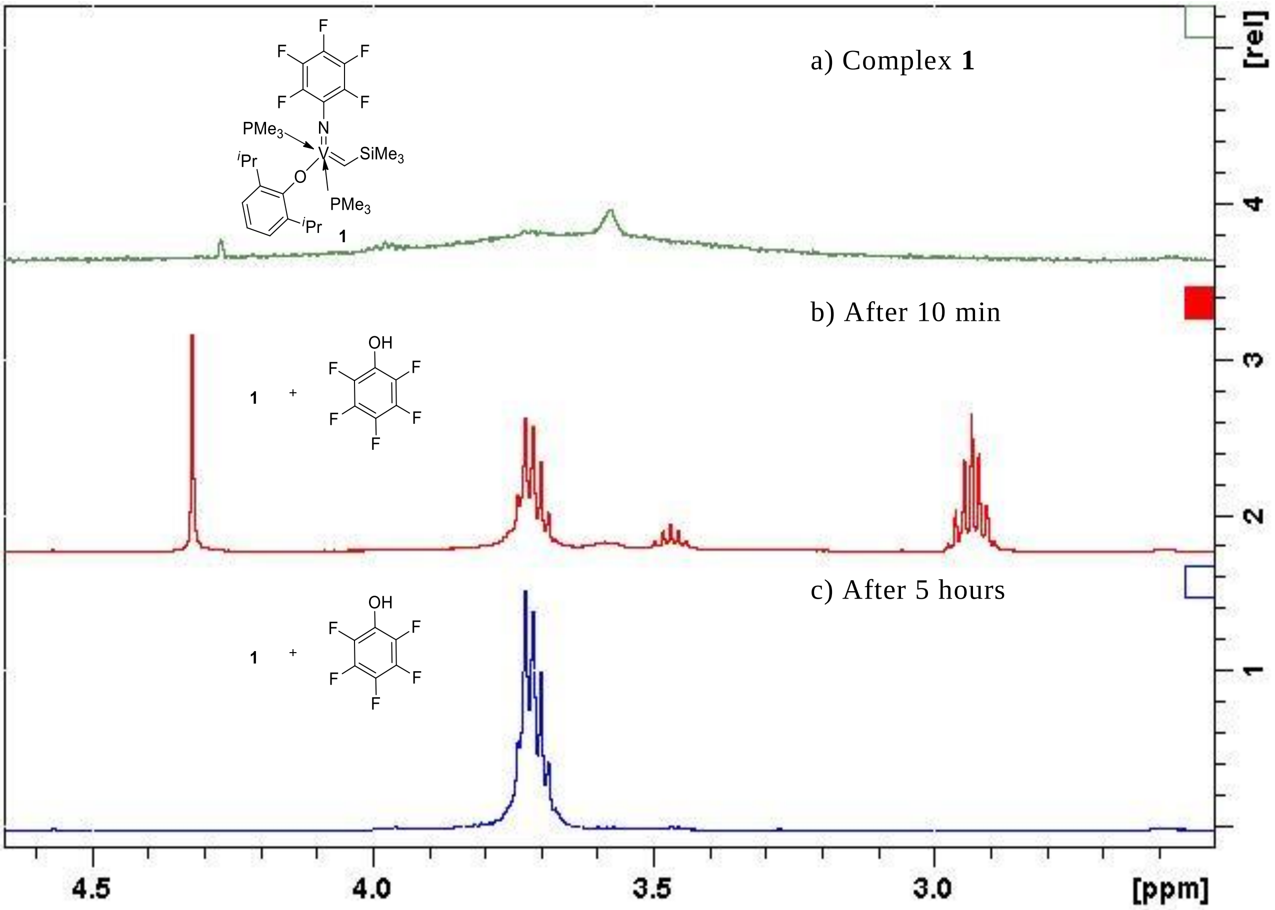


Figure S3-2. ^{1}H NMR spectra (in C_6D_6 at 25 ºC, expanded 2.6-4.6 ppm) for (a) $V(CHSiMe_3)(NC_6F_5)(O\text{-}2,6\text{-}{}^iPr_2C_6H_3)(PMe_3)_2$ (**1**), and (b,c) reaction of **1** with 1.0 equiv of C_6F_5OH (b) after 10 min, (c) 5 h.

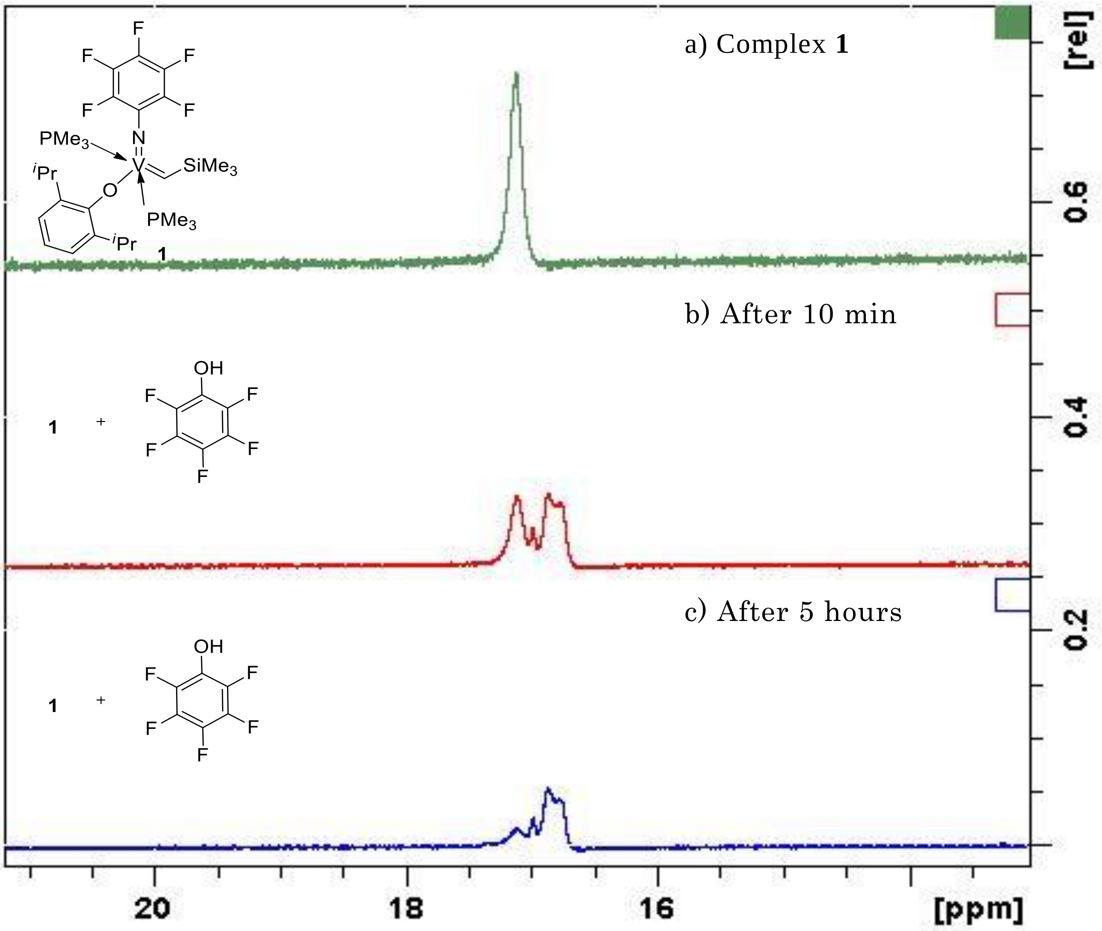


Figure S3-3. ^{1}H NMR spectra (in C_6D_6 at 25 ºC, expanded 13-21 ppm, resonances corresponding to alkylidene protons) for (a) $V(CHSiMe_3)(NC_6F_5)(O\text{-}2,6\text{-}{}^i Pr_2C_6H_3)(PMe_3)_2$ (**1**), and (b,c) reaction of **1** with 1.0 equiv of C_6F_5OH (b) after 10 min, (c) 5 h.

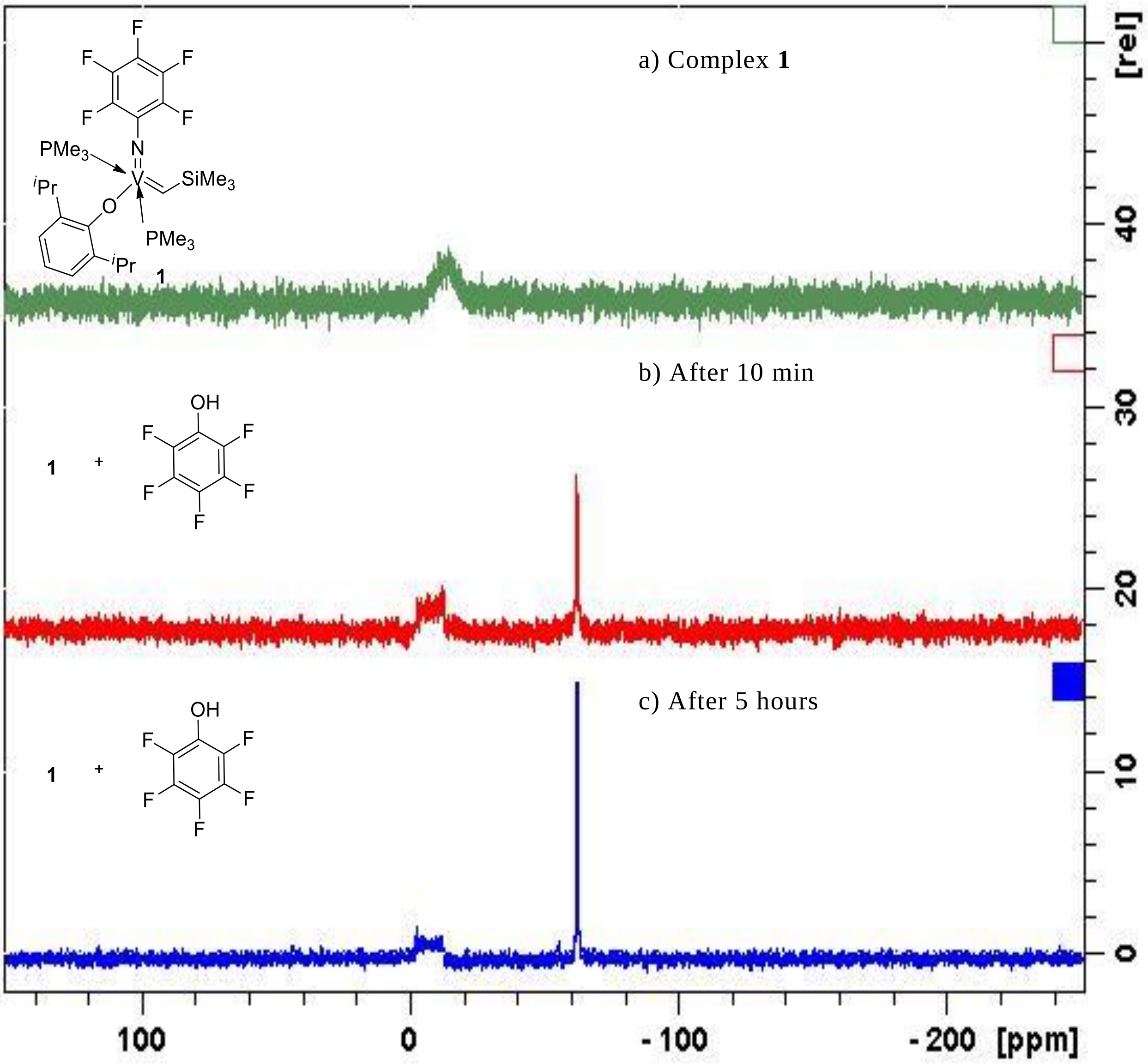


Figure S3-4. ^{31}P NMR spectra (in C_6D_6 at 25 ºC) for (a) $V(CHSiMe_3)(NC_6F_5)(O\text{-}2,6\text{-}{}^iPr_2C_6H_3)(PMe_3)_2$ (**1**), and (b,c) reaction of **1** with 1.0 equiv of C_6F_5OH (b) after 10 min, (c) 5 h.

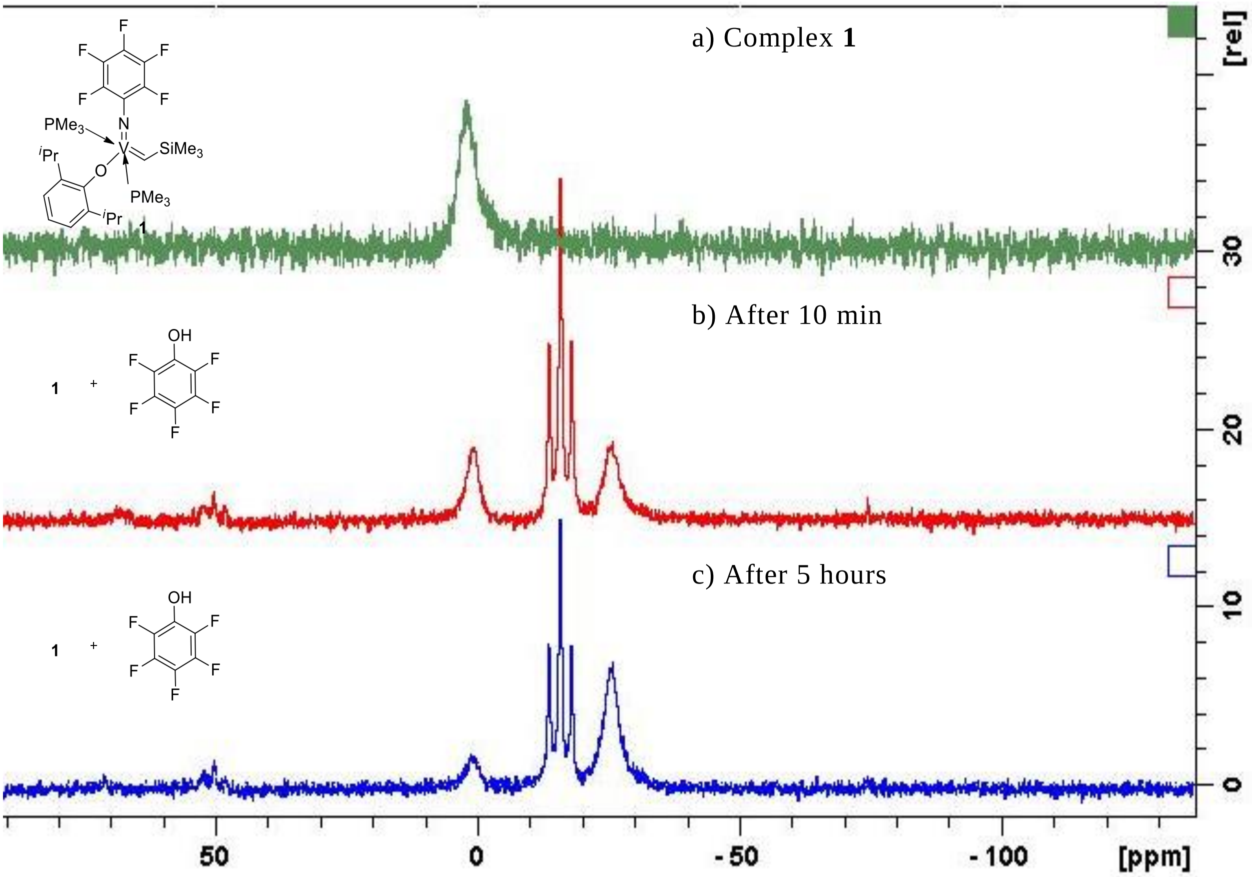


Figure S3-5. ^{51}V NMR spectra (in C_6D_6 at 25 ºC) for (a) $V(CHSiMe_3)(NC_6F_5)(O\text{-}2,6\text{-}{}^iPr_2C_6H_3)(PMe_3)_2$ (**1**), and (b,c) reaction of **1** with 1.0 equiv of C_6F_5OH (b) after 10 min, (c) 5 h.