Electronic Supplementary Information (ESI)

for

Cis-Specific Ring-Opening Metathesis Polymerisation (ROMP) of Cyclic Olefins by

(Pentafluorophenylimido)vanadium(V)-Alkylidene, $V(CHSiMe_3)(NC_6F_5)[OC(CF_3)_3](PMe_3)_2$.

Kotohiro Nomura* and Sapanna Chaimongkolkunasin

Department of Chemistry, Faculty of Science and Engineering, Tokyo Metropolitan University, 1-1 Minami Osawa, Hachioji, Tokyo 192-0397, Japan.

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*Corresponding Authors, tel.&fax: +81-42-677-2547, e-mail: ktnomura@tmu.ac.jp (K.N.)

1. Selected NMR spectra for synthesis of $V(CHSiMe_3)(NC_6F_5)[OC(CF_3)_3](PMe_3)_2$ (1).

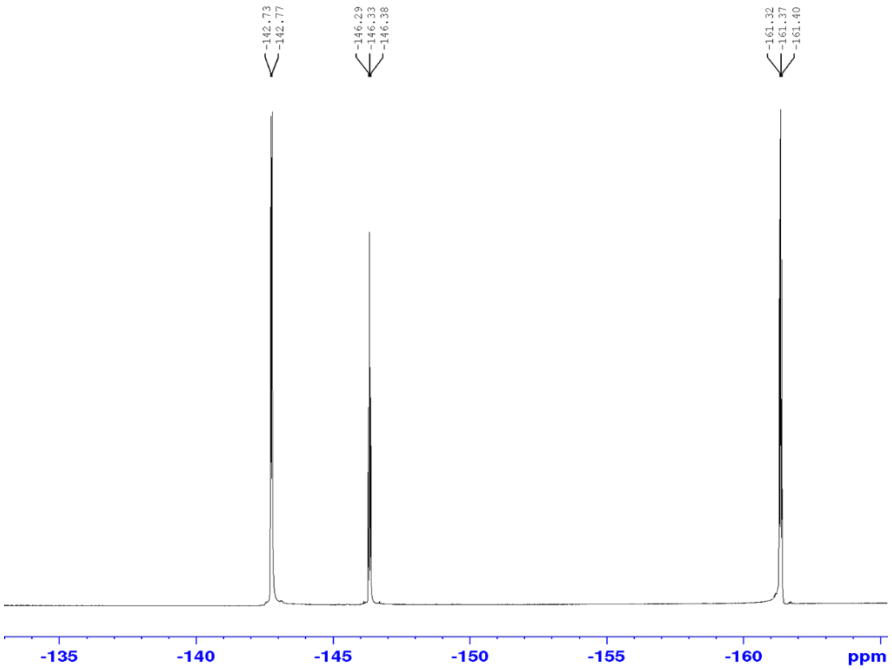


Figure S1-1. ^{19}F NMR spectrum of $V(NC_6F_5)Cl_3$ (in C_6D_6 at 25 ºC).

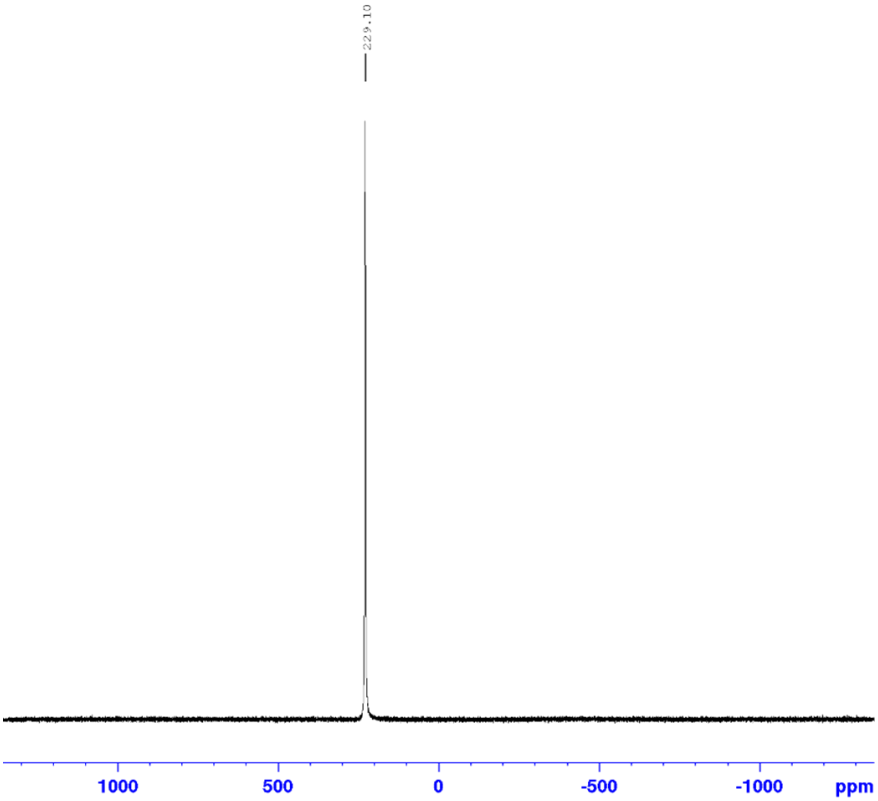


Figure S1-2. ^{51}V NMR spectrum of $V(NC_6F_5)Cl_3$ (in C_6D_6 at 25 ºC).

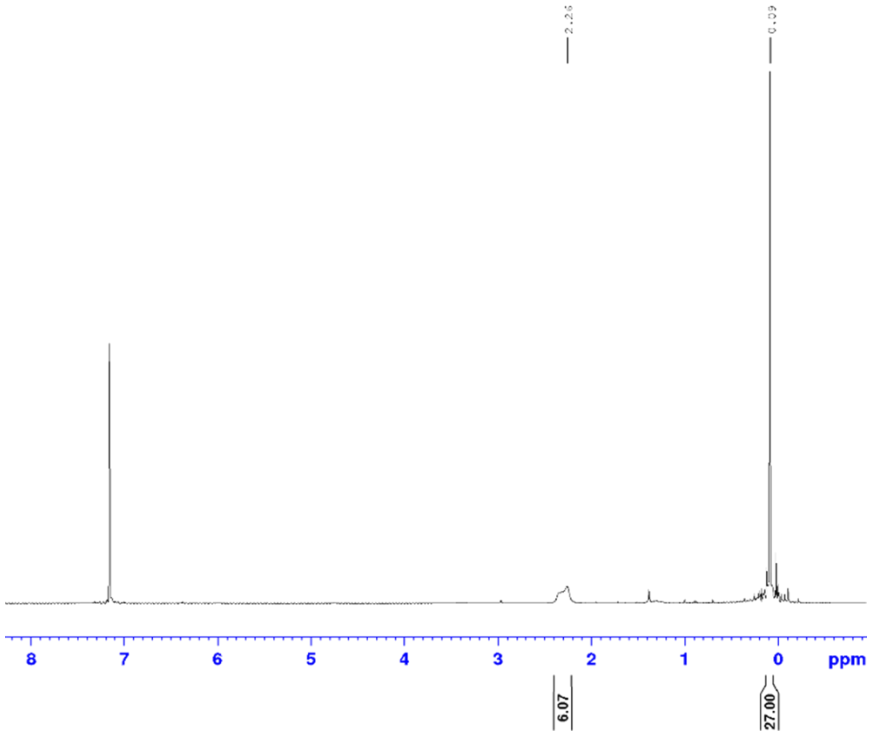


Figure S1-3. ^{1}H NMR spectrum of $V(NC_6F_5)(CH_2SiMe_3)_3$ (in C_6D_6 at 25 ºC).

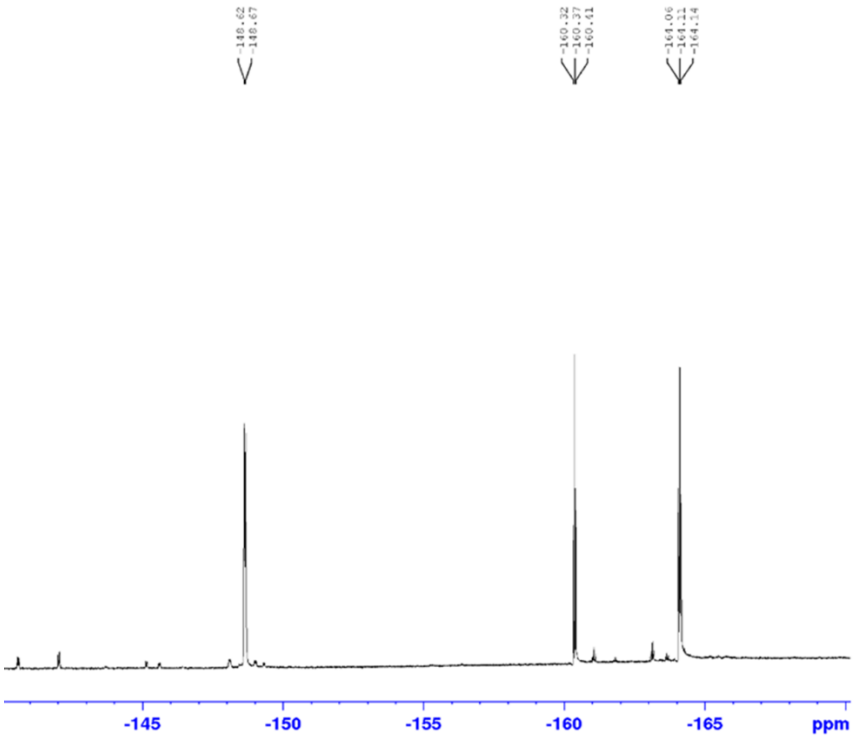


Figure S1-4. ^{19}F NMR spectrum of $V(NC_6F_5)(CH_2SiMe_3)_3$ (in C_6D_6 at 25 ºC).

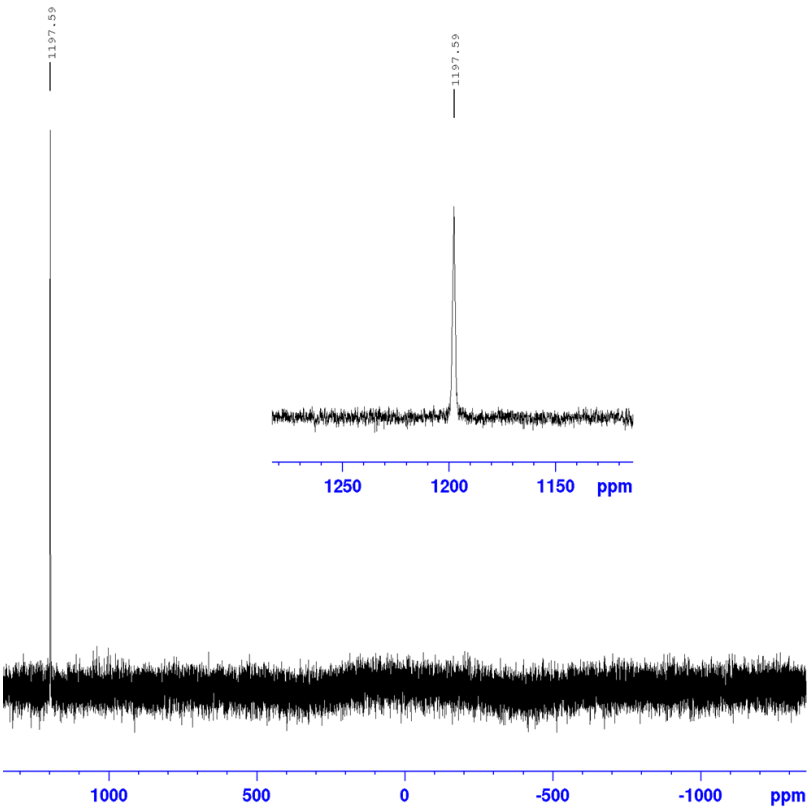
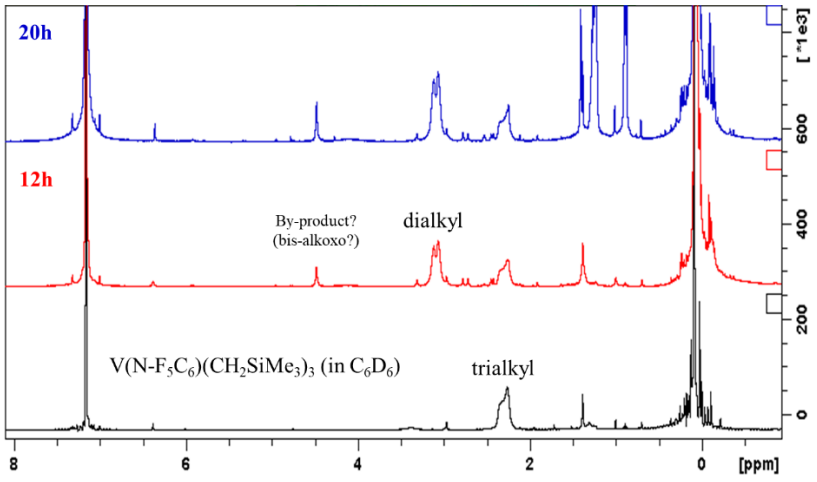


Figure S1-5. ^{51}V NMR spectrum of $V(NC_6F_5)(CH_2SiMe_3)_3$ (in C_6D_6 at 25 ºC).



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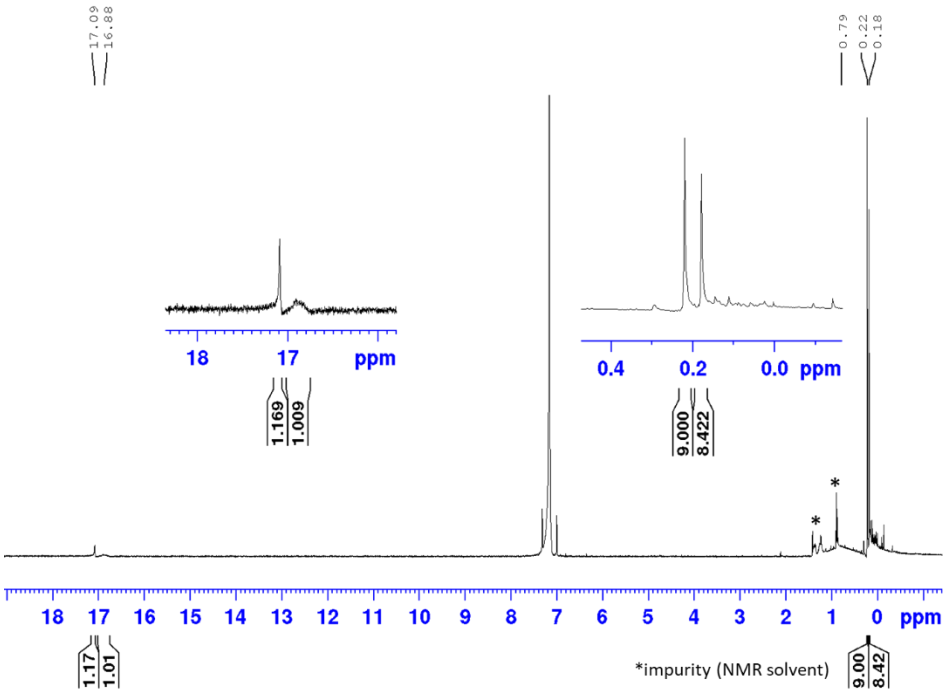

Figure S1-7. ^{1}H NMR spectrum of $V(CHSiMe_3)(NC_6F_5)[OC(CF_3)_3](PMe_3)_2$ (in C_6D_6 at 25 ºC).

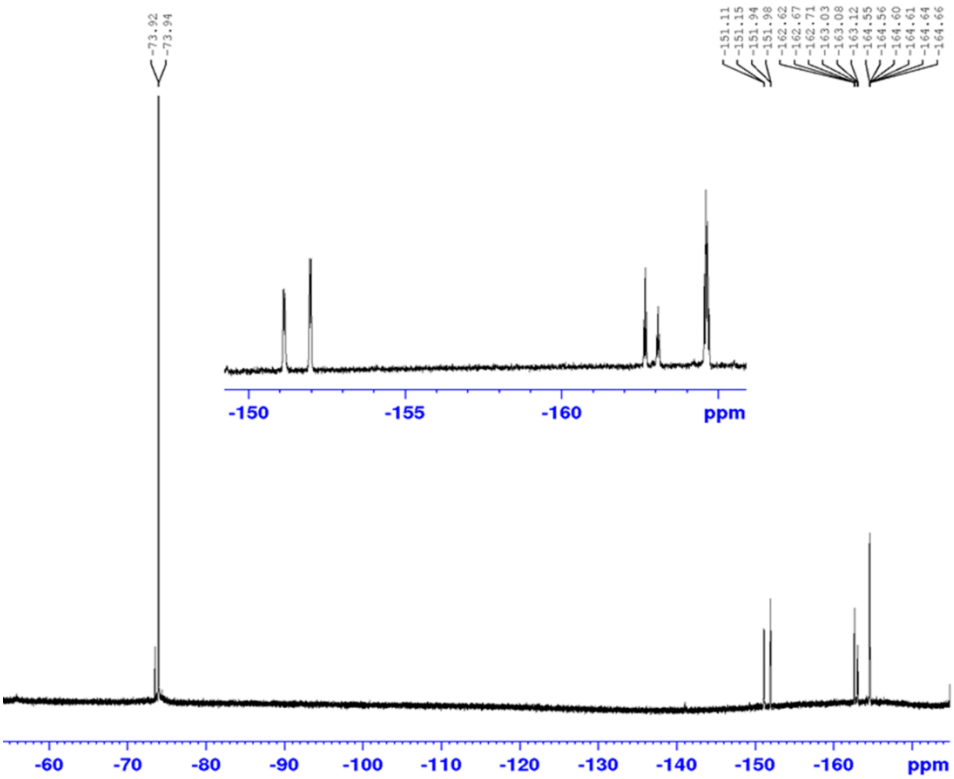

Figure S1-8. ^{19}F NMR spectrum of $V(CHSiMe_3)(NC_6F_5)[OC(CF_3)_3](PMe_3)_2$ (in C_6D_6 at 25 ºC).

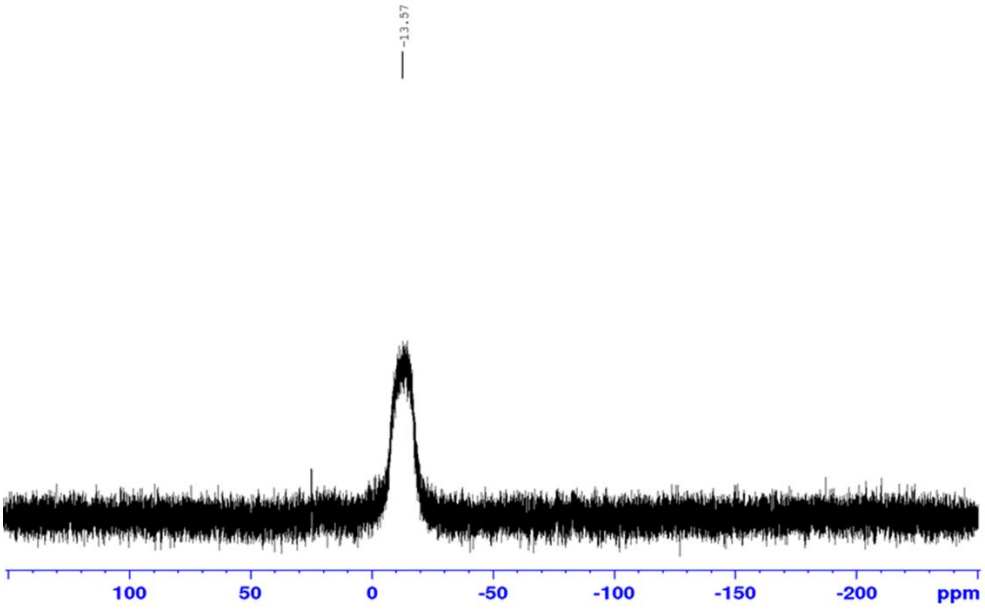

Figure S1-9. ^{31}P NMR spectrum of $V(CHSiMe_3)(NC_6F_5)[OC(CF_3)_3](PMe_3)_2$ (in C_6D_6 at 25 ºC).

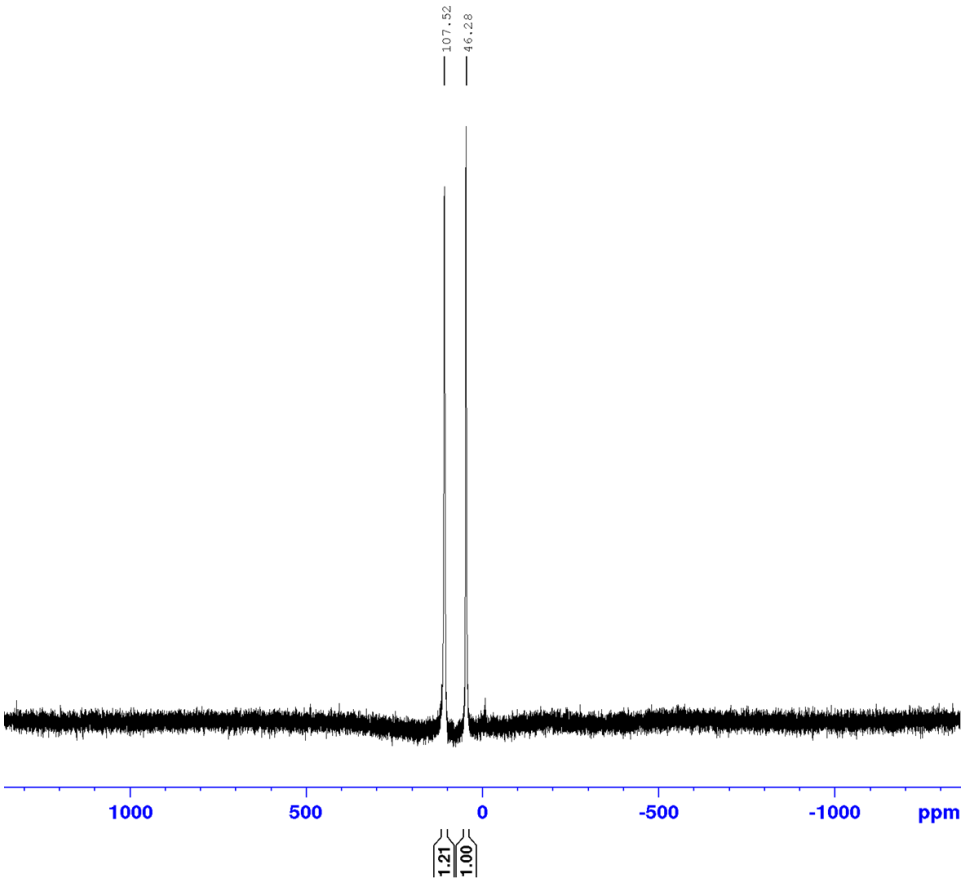

Figure S1-10. ^{51}V NMR spectrum of $V(CHSiMe_3)(NC_6F_5)[OC(CF_3)_3](PMe_3)_2$ (in C_6D_6 at 25 ºC).

2. Additional data for ROMP of norbornene (NBE) and cycloheptene (CHPE).

Table S2-1. Ring opening metathesis polymerisation (ROMP) of norbornene (NBE) by $V(CHSiMe_3)(NR)[OC(CF_3)_3](PMe_3)_2$ [R = C_6F_5 (**1**), 2,6-$Cl_2C_6H_3$ (**2**)], $V(CHSiMe_3)(NR)(OC_6Cl_5)$-$(PMe_3)_2$ [R = 2,6-$Cl_2C_6H_3$ (**3**), C_6H_5 (**4**), 2,6-$Me_2C_6H_3$ (**5**)]. [a]

run	cat. (μmol)	PMe_3 equiv	NBE	temp. / ºC	time / min	TON[b]	TOF[c] / sec^{-1}	conv. / %	M_n[d] $\times 10^{-4}$	M_w/M_n[d]	*cis*[e] / %
1	**1** (0.3)	--	0.44	25	3	4250	23.6	60.1	179	1.53	98
2	**1** (0.3)	3.0	0.44	25	3	4740	26.3	67.1	191	1.77	
S1	**1** (0.3)	10.0	0.44	25	3	1490	8.28	21.2			
S2	**1** (0.3)	20.0	0.44	25	3	1660	9.22	23.5			
S3	**1** (0.3)	--	0.44	25	5	4350	14.5	61.6	236	1.55	
3	**1** (0.3)	--	0.44	25	10	4570	7.62	64.7	244	1.64	98
S3	**1** (0.3)	--	0.44	25	15	4780	5.31	67.6	249	1.61	98
4	**1** (0.3)	--	0.44	50	3	trace					
S4	**1** (0.3)	3.0	0.44	50	3	trace					
5	**1** (0.3)	10.0	0.44	50	3	7010	38.9	99.2	200	1.56	
S5	**1** (0.3)	--	0.44	80	3	trace					
S6	**1** (0.3)	30	0.44	80	3	2480	13.8	35.1			
S7	**1** (0.3)	50	0.44	80	3	4280	23.8	60.6			
6	**1** (2.0)	--	0.22	25	3	4074	45.3	96.1	133	1.74	98
7	**1** (1.0)	--	0.22	25	3	6280	34.9	74.1	174	1.91	98
8	**1** (1.0)	--	0.22	25	5	8040	26.8	94.8	188	2.03	98
9	**1** (1.0)	--	0.22	25	7	8360	19.9	98.6	189	2.03	98
10	**2** (0.3)	--	0.44	25	3	3120	17.3	44.2	140	1.43	98
11	**2** (0.3)	3.0	0.44	25	3	4350	24.2	61.6	155	1.63	98
S8	**2** (0.3)	--	0.44	25	10	6440	10.7	91.1	191	1.40	
12	**2** (0.3)	--	0.44	25	15	7040	7.82	99.6	188	1.55	
13	**3** (0.1)	--	0.44	25	3	19500	108	92.0	132	1.60	39
14	**4** (0.1)	--	0.44	25	3	5300	29.4	25.0	114	1.81	51
15	**5** (0.1)	--	0.44	25	3	3500	19.4	16.5	62.5	1.12	49

[a]Conditions: cat. 0.3 or 1.0 (or 2.0) μmol, NBE 2.12 mmol in benzene (total 4.8 mL, initial NBE 0.44 M) or 8.48 mmol in benzene (total 38.5 mL). [b]TON (turnover) = NBE reacted (mmol)/vanadium (mmol). [c]TOF = TON/time. [d]GPC data in THF *vs* polystyrene standards (g/mol). [e]*Cis* percentage (%) estimated by ^{1}H NMR spectra.

Table S2-2. Ring opening metathesis polymerisation (ROMP) of cycloheptene (CHPE) and cis-cyclooctene (COE) by V(CHSiMe$_3$)(NR)[OC(CF$_3$)$_3$](PMe$_3$)$_2$ [R = C$_6$F$_5$ (**1**), 2,6-Cl$_2$C$_6$H$_3$ (**2**)], V(CHSiMe$_3$)(N-2,6-Cl$_2$C$_6$H$_3$)(OC$_6$Cl$_5$)(PMe$_3$)$_2$ (**3**). [a]

run	cat. (μmol)	monomer	B(C$_6$F$_5$)$_3$	time / min	TON[b]	TOF[c] / h^{-1}	conv. / %	M_n[d] ×10^{-4}	M_w/ M_n[d]	*cis*[e] / %
16	**1** (4.0)	CHPE	--	10	18	109	0.7	5.87	1.19	
17	**1** (4.0)	CHPE	--	30	70	140	2.8	6.40	1.42	>99
18	**1** (2.0)	CHPE	1.0 B(C$_6$F$_5$)$_3$	10	192	1150	3.8	12.1	1.30	>99
19	**1** (2.0)	CHPE	1.0 B(C$_6$F$_5$)$_3$	30	769	1540	15.4	15.8	1.82	>99
20	**1** (2.0)	CHPE	3.0 PMe$_3$	10	104	624	2.1	2.86	1.10	>99
21	**1** (2.0)	CHPE	3.0 PMe$_3$	30	270	541	5.4	28.1	1.60	>99
S9	**2** (4.0)	CHPE	--	10	--					
22	**2** (4.0)	CHPE	--	30	--					
23	**3** (1.0)[f]	CHPE	--	10	2100	12600	21.0	56.3	1.54	29
26	**1** (10.0)	COE	--	30	--					
27	**1** (10.0)	COE	1.0 B(C$_6$F$_5$)$_3$	30	--					
28	**3** (1.0)[f]	COE	--	30	799	1600	8.0	9.55	1.15	

[a]Conditions: CHPE 10 mmol in benzene (total 4.8 mL), COE 10.0 mmol in benzene (total 1.8 mL). [b]TON (turnover) = CHPE or COE reacted (mmol)/vanadium (mmol). [c]TOF = TON/time. [d]GPC data in THF *vs* polystyrene standards (g/mol). [e]*Cis* percentage (%) estimated by ^{1}H NMR spectra. [f]Cited from reference: S. Chaimongkolkunasin and K. Nomura, *Organometallics*, 2018, **37**, 2064-2074.

Table S2-3. Ring opening metathesis polymerisation (ROMP) of cycloheptene (CHPE) by $V(CHSiMe_3)(NC_6F_5)[OC(CF_3)_3](PMe_3)_2$ (**1**): ROMPs under scale up conditions. [a]

run	time / min	temp. / ºC	TON[b]	TOF[c] / h^{-1}	conv. / %	M_n[d] $\times 10^{-4}$	M_w/M_n[d]	*cis*[e] / %
29	15	25	180	720	1.4	8.25	1.21	98
30	30	25	498	996	4.0	14.9	1.34	>99
31	60	25	1970	1970	15.8	26.6	1.63	>99
32	240	25	3430	857	27.4	59.2	1.93	
S10	30	50	227	454	1.8	11.3	1.71	>99
S11	60	50	338	338	2.7	16.9	1.90	>99

[a]Conditions: complex **1** 4.0 μmol, CHPE 50 mmol in benzene (total 24 mL). [b]TON (turnover) = CHPE reacted (mmol)/vanadium (mmol). [c]TOF = TON/time. [d]GPC data in THF *vs* polystyrene standards (g/mol). [e]*Cis* percentage (%) estimated by ^{1}H NMR spectra.

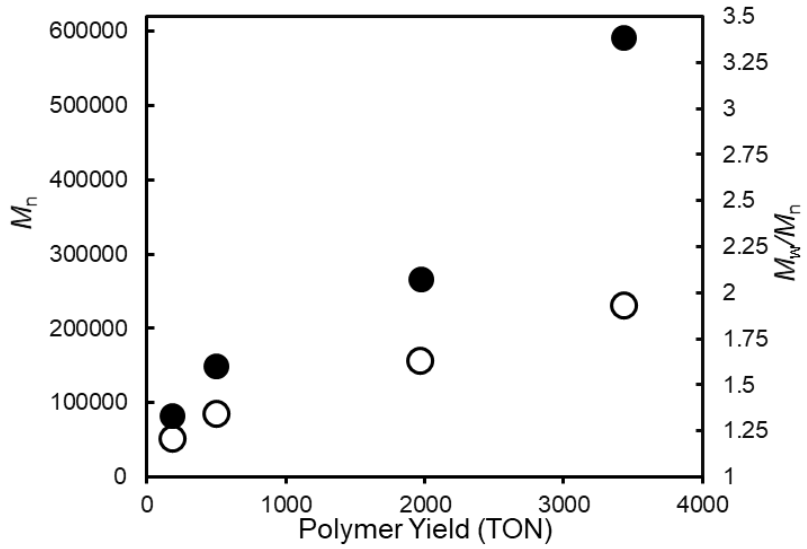

Figure S2-1. Plots of M_n, M_w/M_n vs polymer yield (TON) in ring opening metathesis polymerisation (ROMP) of cycloheptene (CHPE) using $V(CHSiMe_3)(NC_6F_5)[OC(CF_3)_3](PMe_3)_2$ (**1**). Detailed conditions and data are shown in Table 3 (and Table S2-3).

3. Selected NMR spectra in the resultant polymers.

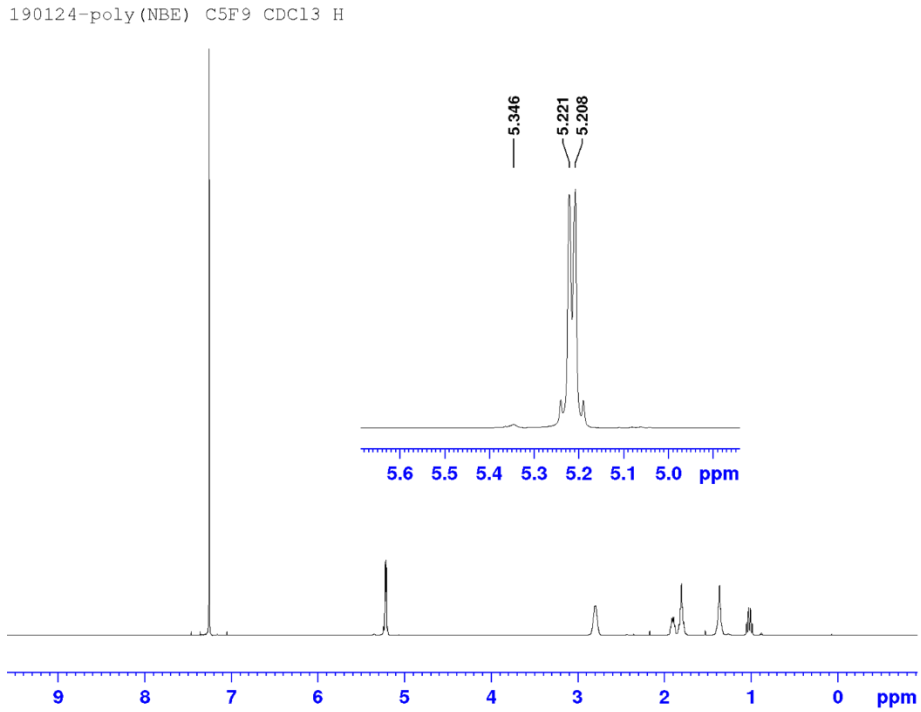

Figure S3-1. ^{1}H NMR spectrum (in $CDCl_3$ at 25 ºC) for poly(norbornene) prepared by $V(CHSiMe_3)(NC_6F_5)[OC(CF_3)_3](PMe_3)_2$ (**1**, Table 1, run 1).

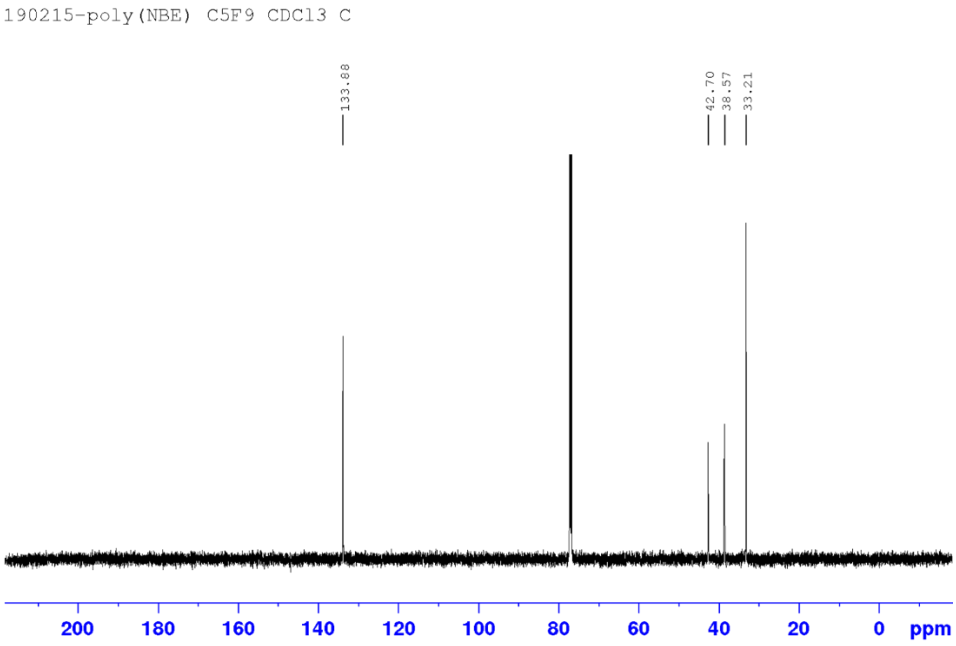

Figure S3-2. ^{13}C NMR spectrum (in $CDCl_3$ at 25 ºC) for poly(norbornene) prepared by $V(CHSiMe_3)(NC_6F_5)[OC(CF_3)_3](PMe_3)_2$ (**1**, Table 1, run 1).

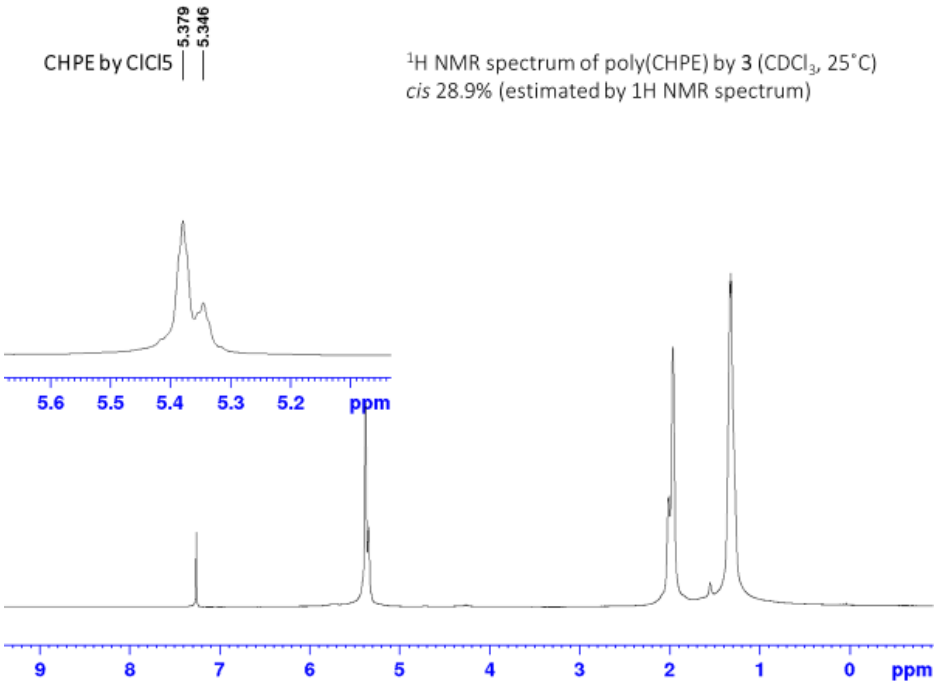

Figure S3-3. ^{1}H NMR spectrum (in $CDCl_3$ at 25 ºC) for poly(cycloheptene) prepared by $V(CHSiMe_3)(N\text{-}2,6\text{-}Cl_2C_6H_3)(OC_6Cl_5)(PMe_3)_2$ (**3**, Table 2, run 23).

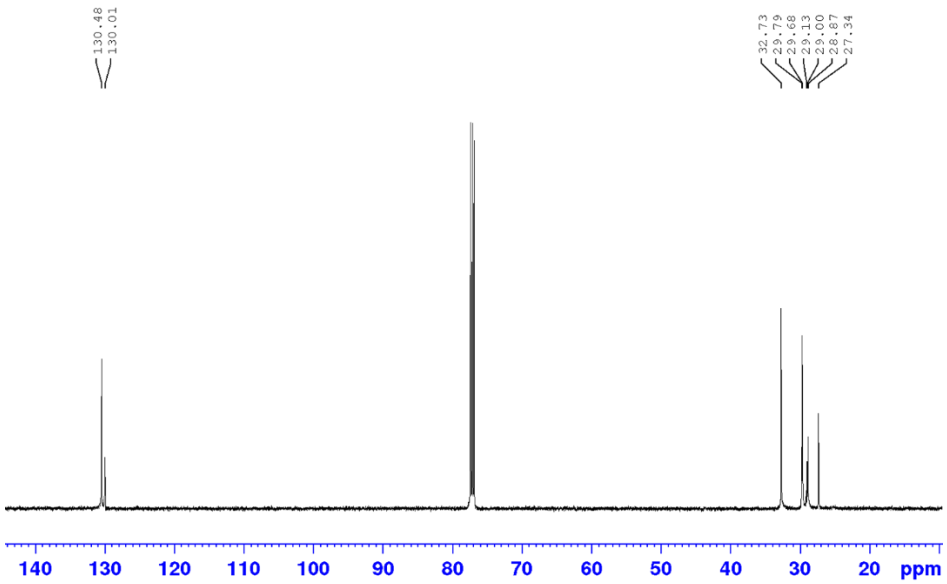

Figure S3-4. ^{13}C NMR spectrum (in $CDCl_3$ at 25 ºC) for poly(cycloheptene) prepared by $V(CHSiMe_3)(N\text{-}2,6\text{-}Cl_2C_6H_3)(OC_6Cl_5)(PMe_3)_2$ (**3**, Table 2, run 23).

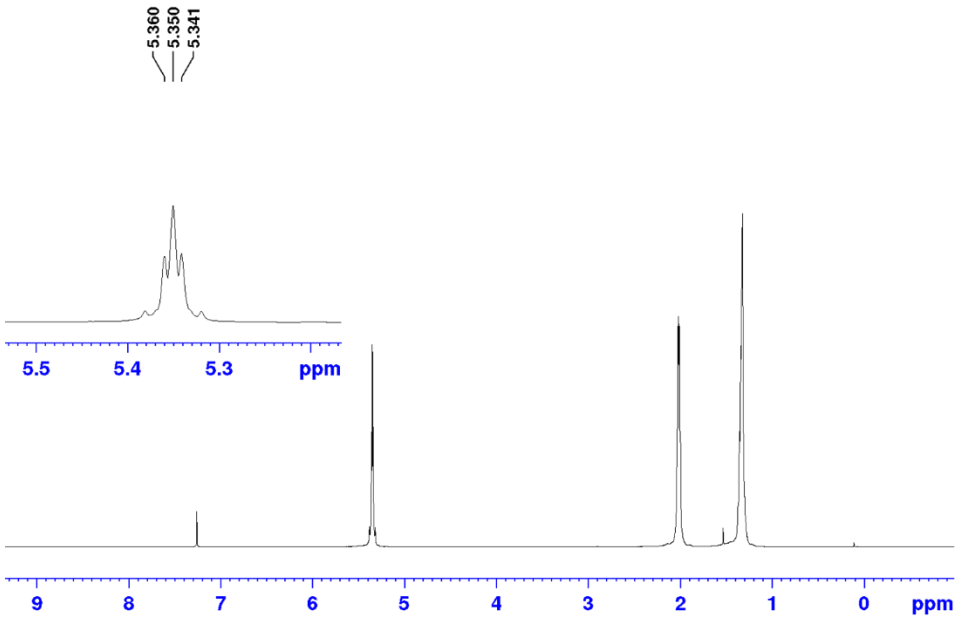

Figure S3-5. ^{1}H NMR spectrum (in $CDCl_3$ at 25 ºC) for poly(cycloheptene) prepared by $V(CHSiMe_3)(NC_6F_5)[OC(CF_3)_3](PMe_3)_2$ (**1**, Table 2, run 17).

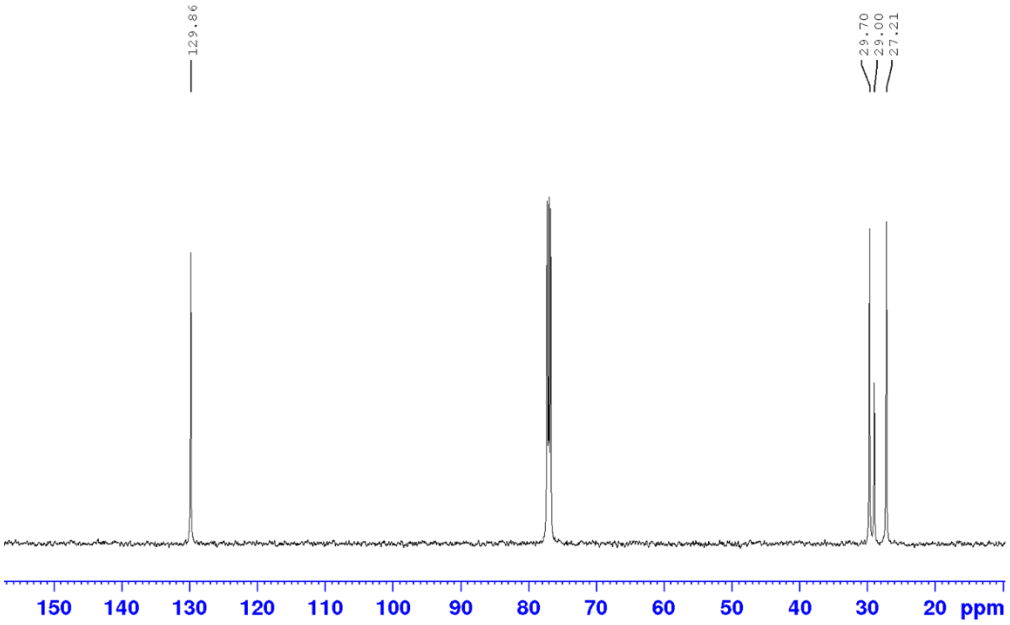

Figure S3-6. ^{13}C NMR spectrum (in $CDCl_3$ at 25 ºC) for poly(cycloheptene) prepared by $V(CHSiMe_3)(NC_6F_5)[OC(CF_3)_3](PMe_3)_2$ (**1**, Table 2, run 17).

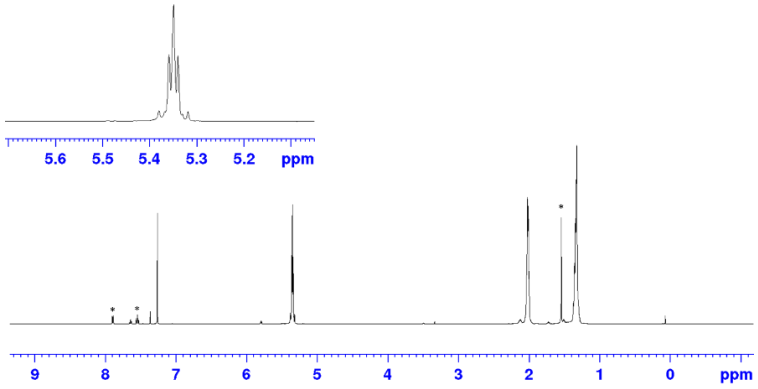

Figure S3-7. ^{1}H NMR spectrum (in $CDCl_3$ at 25 ºC) for poly(cycloheptene) prepared by $V(CHSiMe_3)(NC_6F_5)[OC(CF_3)_3](PMe_3)_2$ (**1**) in the presence of $B(C_6F_5)_3$ (Table 2, run 19). *impurities.

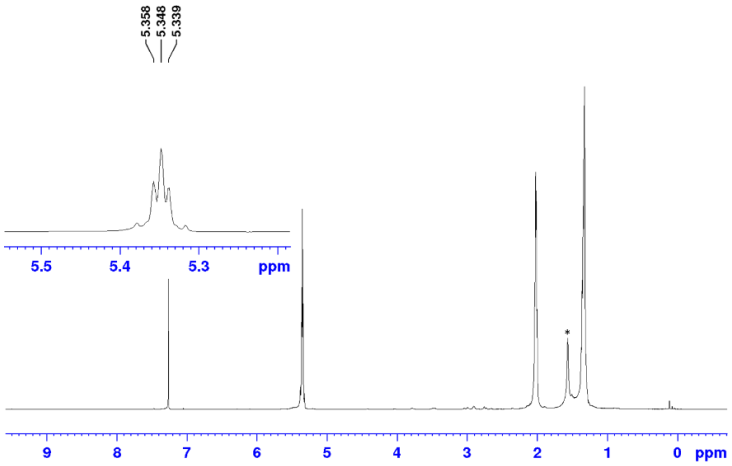

Figure S3-8. ^{1}H NMR spectrum (in $CDCl_3$ at 25 ºC) for poly(cycloheptene) prepared by $V(CHSiMe_3)(NC_6F_5)[OC(CF_3)_3](PMe_3)_2$ (**1**, Table 3, run 30). *impurities.

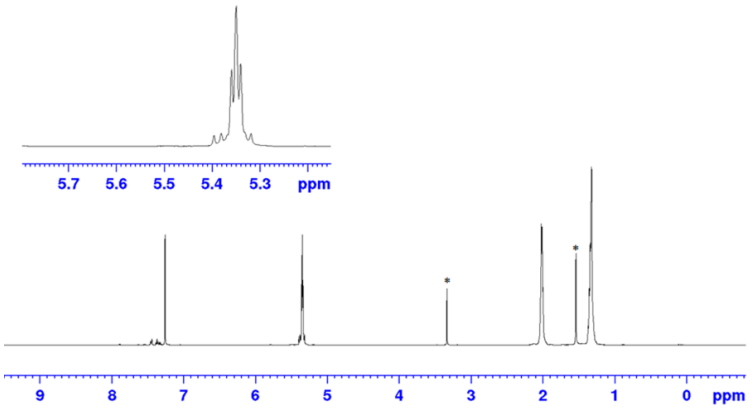

Figure S3-9. ^{1}H NMR spectrum (in $CDCl_3$ at 25 ºC) for poly(cycloheptene) prepared by $V(CHSiMe_3)(NC_6F_5)[OC(CF_3)_3](PMe_3)_2$ (**1**, Table 3, run 31). *impurities.

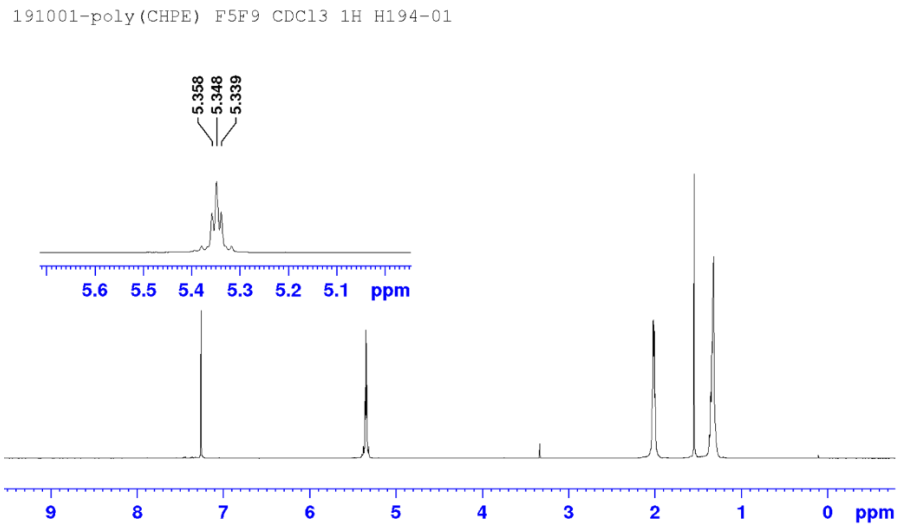

Figure S3-10. ^{1}H NMR spectrum (in $CDCl_3$ at 25 ºC) for poly(cycloheptene) prepared by $V(CHSiMe_3)(NC_6F_5)[OC(CF_3)_3](PMe_3)_2$ (**1**, Table 3, run 32). *impurities.