Supporting Information

Vanadium complexes bearing 8-Anilide-5,6,7-trihydroquinoline ligands for ethylene (co-)polymerization

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1. General Procedure

All water and oxygen-sensitive experiments were performed in the glovebox filled with nitrogen or using Schlenk technology. Toluene was refluxed on sodium under nitrogen atmosphere and further stored with 4Å molecular sieves. Dichloromethane, tetrahydrofuran and n-hexane were. Tetrahydrofuran complexes of vanadium trichloride ($VCl_3(THF)_3$) were prepared according to the literature.[1] triisopropoxyvanadium(v) oxide ($VO(O^iPr)_3$) and diethylaluminium chloride ($AlEt_2Cl$) were purchased from Aladdin. Ethyl trichloroacetate (ETA) were purchased from Aladdin. Other reagents were purchased from Macklin.

The molecular weights (M_w) were tested at 150 °C, using 1,2,4-trichlorobenzene as the eluent (equipment model: PL-GPC220). Polystyrene standard sample was used for

calibration. The ^{1}H NMR and ^{13}C NMR spectra of polyethylenes and copolymers were measured at 120 °C in o-$C_6D_4Cl_2$ by using an AVANCE 400 spectrometer. Elemental analyses of the vanadium complexes were carried out by the Varian EL microanalyzer, and all samples were dried under vacuum before being tested. A differential scanning calorimeter (METTLER DSC 3) was used to determine the melting points (T_m) of polyethylenes. The samples were heated and cooled twice (10 °C/min), and the values of the second curve were collected. The FTIR spectra of complexes were measured by a FTIR spectrometer (equipment model: BRUKER Vertex-70).

2. X-ray diffraction study

A crystal was sealed in oil under a microscope in the glovebox. Data collections of complex **V2, V3', V5, V7** were performed at 180K, 300 K and 100K on a Bruker APEX CCD area detector using graphite-monochromated Mo Kα radiation (λ= 0.71073 Å). Data collections of complex **V4** were performed at 100 K on a Hybrid Pixel Array Detector using graphite-monochromated Cu Kα radiation (λ= 1.54184 Å). The determination of crystal class and unit cell parameters was carried out by the SMART program package. The raw frame data were processed using SAINT and SADABS to yield the reflection data file. The structure was solved by using the SHELXTL program. The hydrogen atoms were placed at the calculated positions and were included in the structure calculation without further refinement of the parameters. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC numbers of vanadium complexes **V2, V3', V4, V5** and **V7** are 2234775-2234779.

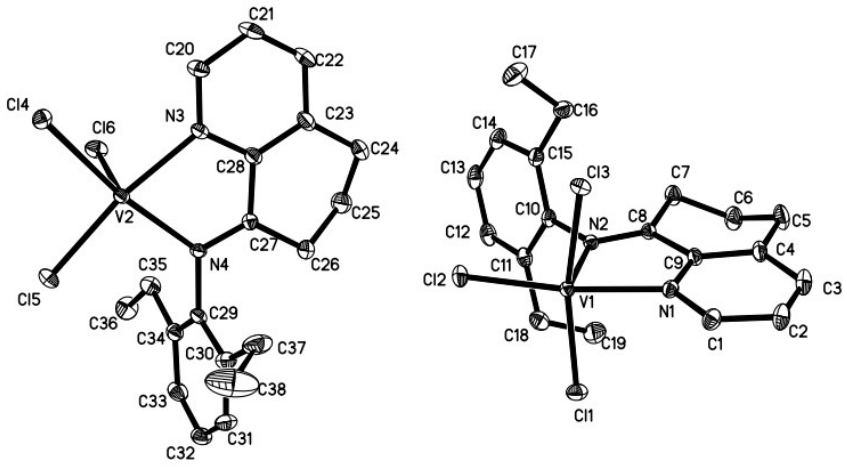

Figure S1. The molecular structure of complex **V2**.

Table S1 Summary of crystallographic data for complex **V2, V3'** and **V4**.

Complex	**V2**	**V3'**	**V4**
Formula	$C_{38}H_{44}N_4Cl_6V_2$	$C_{25}H_{34}N_2OCl_3V$	$C_{21}H_{25}BrCl_3N_2OV$
Formula weight	871.35	535.83	558.63
Crystal system	triclinic	monoclinic	trigonal
Space group	P-1	$P2_1/c$	R-3
a (Å)	10.0194(4)	18.2129(7)	35.6823(3)
b (Å)	15.2773(6)	10.5086(4)	35.6823(3)
c (Å)	16.1948(7)	17.5705(7)	13.3003(2)
α(°)	109.4430(10)	90	90
β(°)	90.0210(10)	112.4430(10)	90
γ(°)	98.8120(10)	90	120
Volume ($Å^3$)	2306.46(16)	3108.2(2)	14665.5(3)
Z	2	4	18
Calculated density (g/cm^3)	1.255	1.145	1.139
Absorption coefficient(mm^{-1})	0.781	0.594	6.33
F(0 0 0)	896.0	1120.0	5076
θ_{max} (°)	30.571	29.593	75.764

Collected reflections	101146	80117	31779
Unique reflections	14126	8719	6633
R_{int}	0.0698	0.0684	0.0457
Goodness-of-fit (GOF)	1.019	1.031	1.063
R_1	0.0777	0.0824	0.0427
wR_2	0.1504	0.1911	0.0996
Largest difference in peak and hole (e A^{-3})	0.99/-0.62	0.56/-0.58	0.98/-0.56

Table S2 Summary of crystallographic data for complex **V5** and **V7**.

Complex	**V5**	**V7**
Formula	$C_{23}H_{31}N_2O_3V$	$C_{27}H_{39}N_2O_3V$
Formula weight	434.44	490.54
Crystal system	tetragonal	orthorhombic
Space group	$I4_1/a$	Pbca
a (Å)	29.341(2)	18.683(3)
b (Å)	29.341(2)	14.963(2)
c (Å)	10.4047(14)	19.074(3)
α(°)	90	90
β(°)	90	90
γ(°)	90	90
Volume ($Å^3$)	8957.3(17)	5332.2(14)
Z	16	8
Calculated density (g/cm^3)	1.289	1.222
Absorption coefficient(mm^{-1})	0.468	0.401
F(0 0 0)	3680	2096
θ_{max} (°)	27.597	27.559
Collected reflections	26591	30584
Unique reflections	5175	6132
R_{int}	0.0346	0.0712
Goodness-of-fit (GOF)	1.058	1.045
R_1	0.0419	0.0803
wR_2	0.0847	0.1381
Largest difference in peak and hole (e A^{-3})	0.37/-0.42	0.81/-0.72

3. NMR of the vanadium complexes

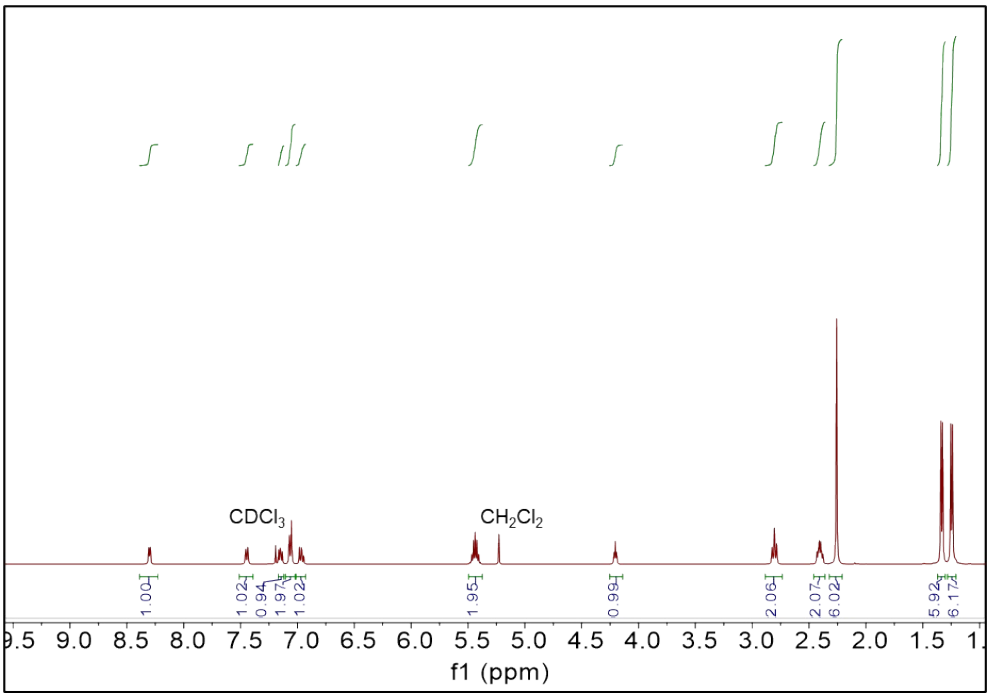

Figure S2. The ^{1}H NMR spectra of complexes **V5**.

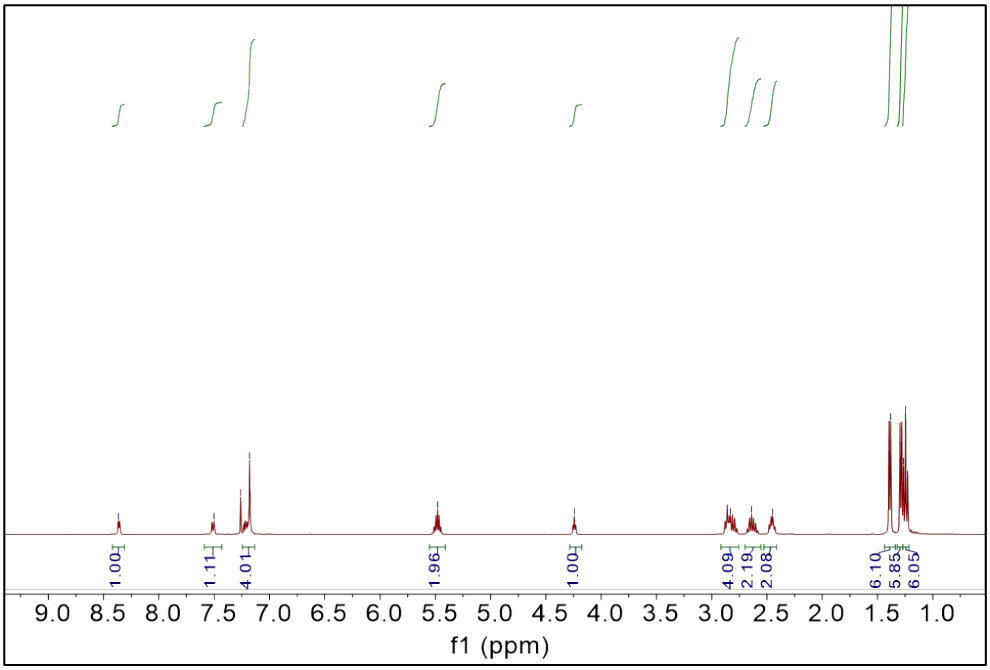

Figure S3. The ^{1}H NMR spectra of complexes **V6**.

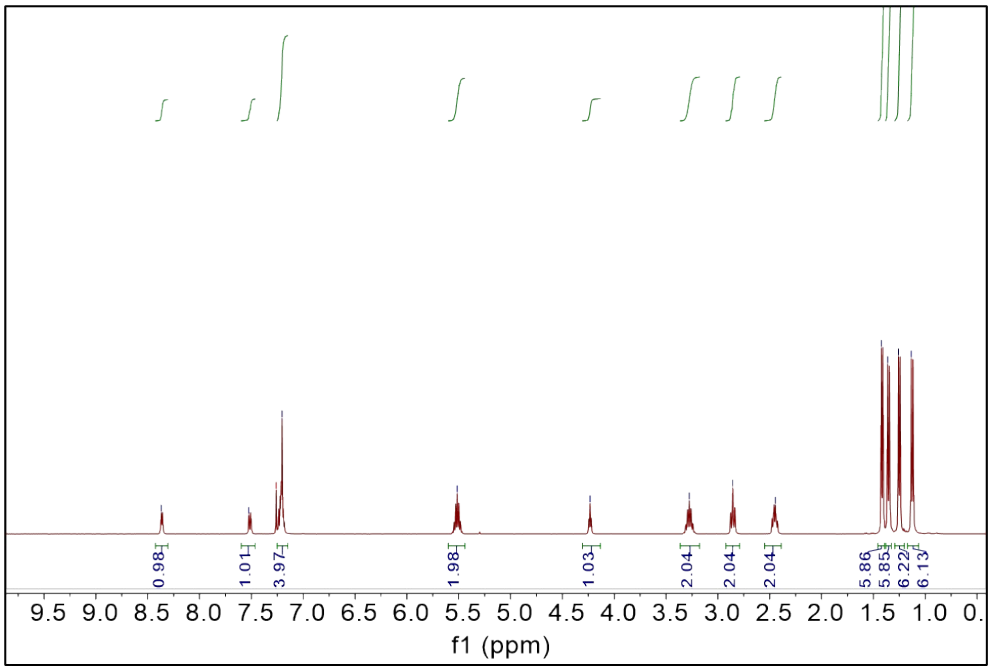

Figure S4. The ^{1}H NMR spectra of complexes **V7**.

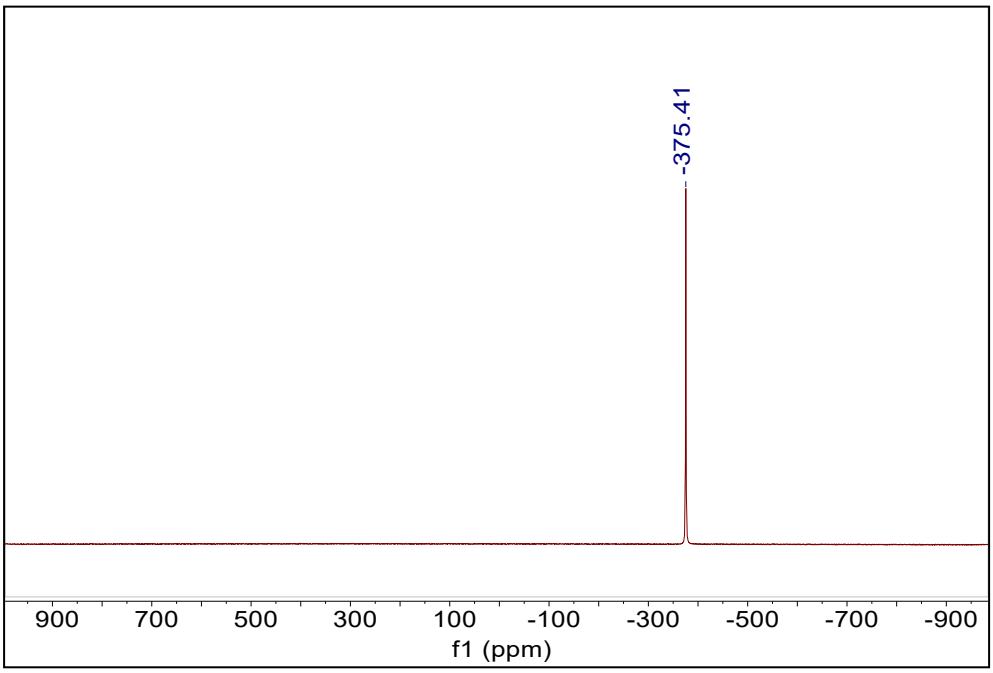

Figure S5. The ^{51}V NMR spectra of complexes **V5**.

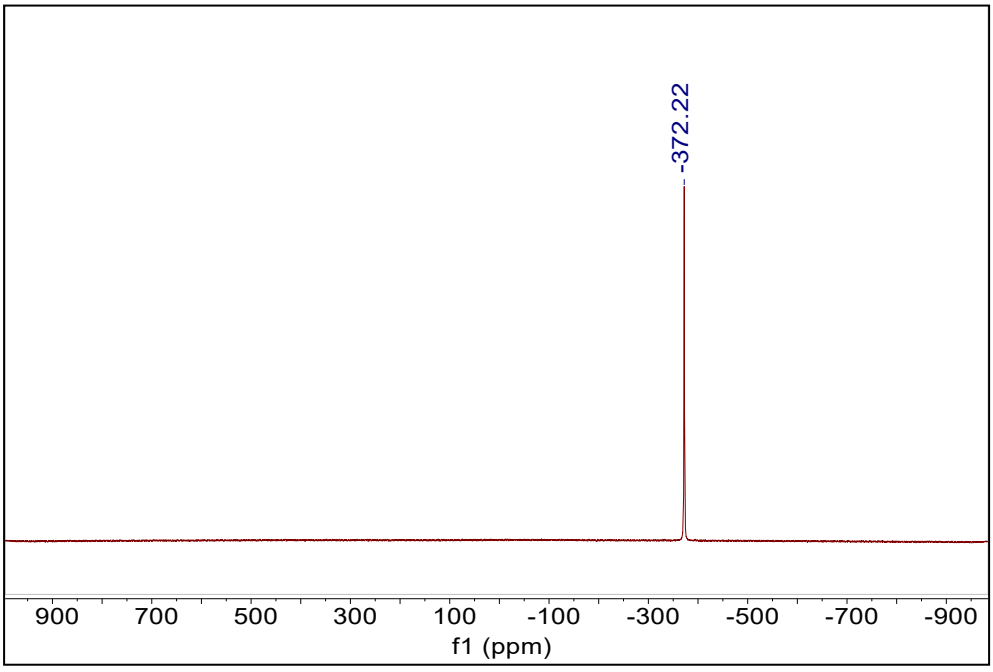

Figure S6. The ^{51}V NMR spectra of complexes **V6**.

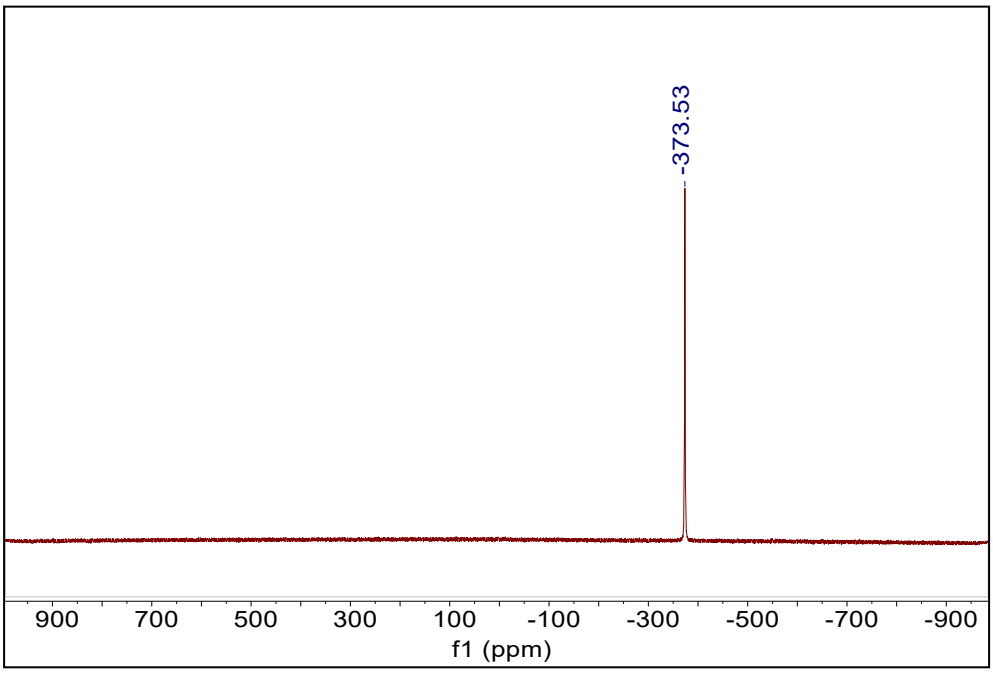

Figure S7. The ^{51}V NMR spectra of complexes **V7**.

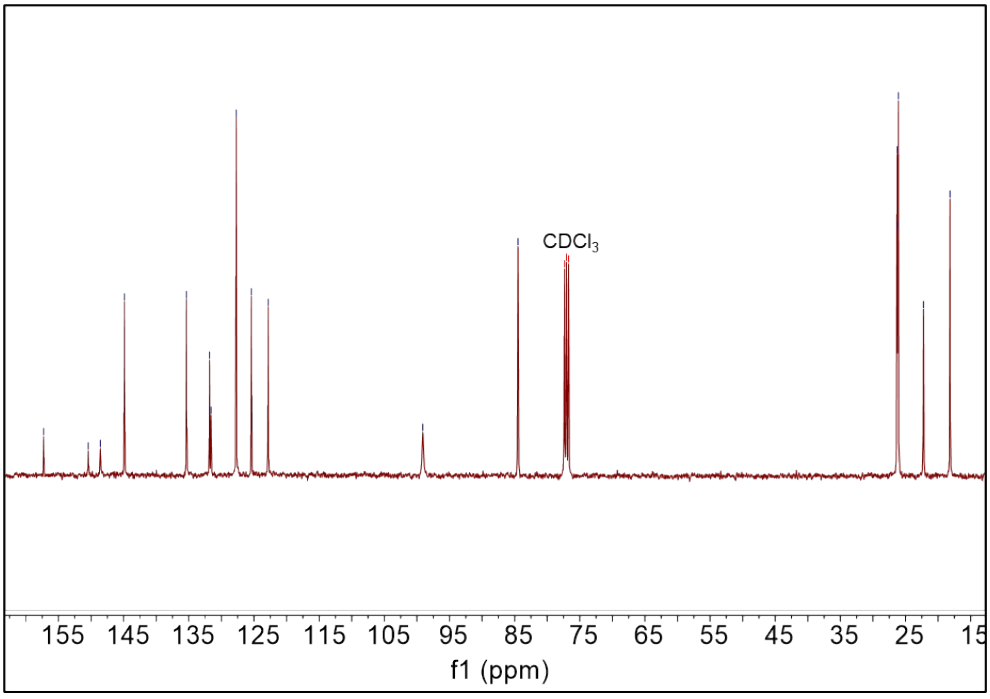

Figure S8. The ^{13}C NMR spectra of complexes **V5**.

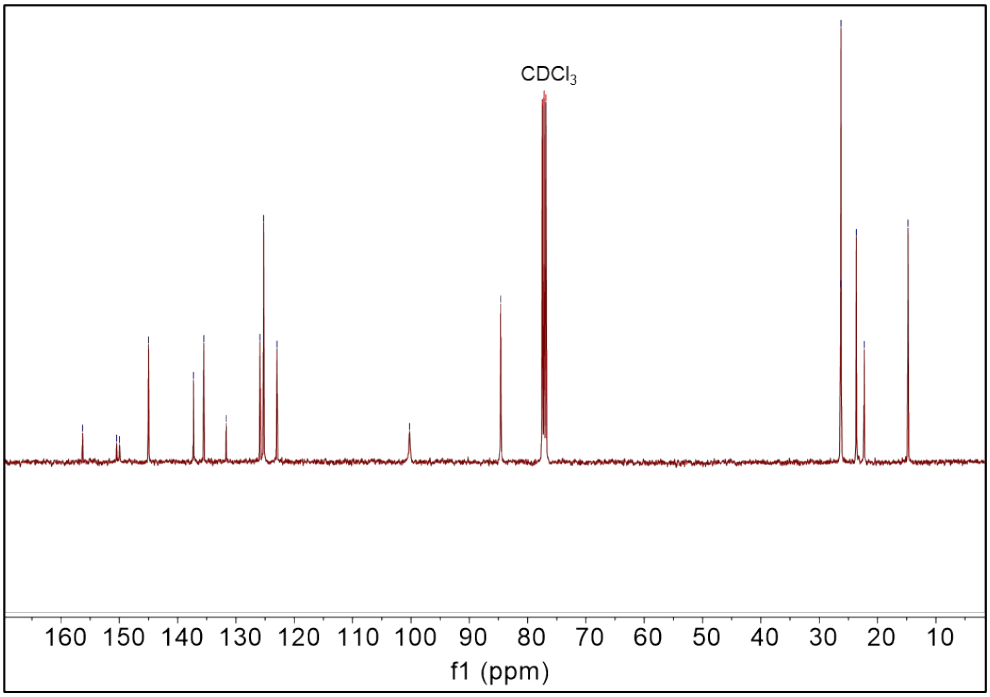

Figure S9. The ^{13}C NMR spectra of complexes **V6**.

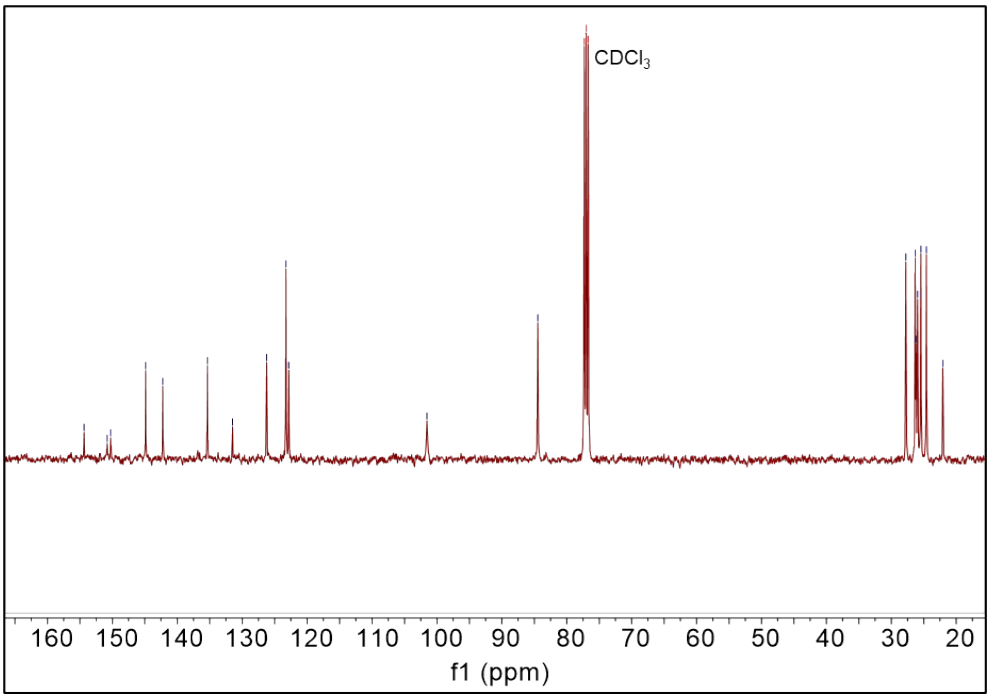

Figure S10. The ^{13}C NMR spectra of complexes **V7**.

4. NMR of the obtained polymers

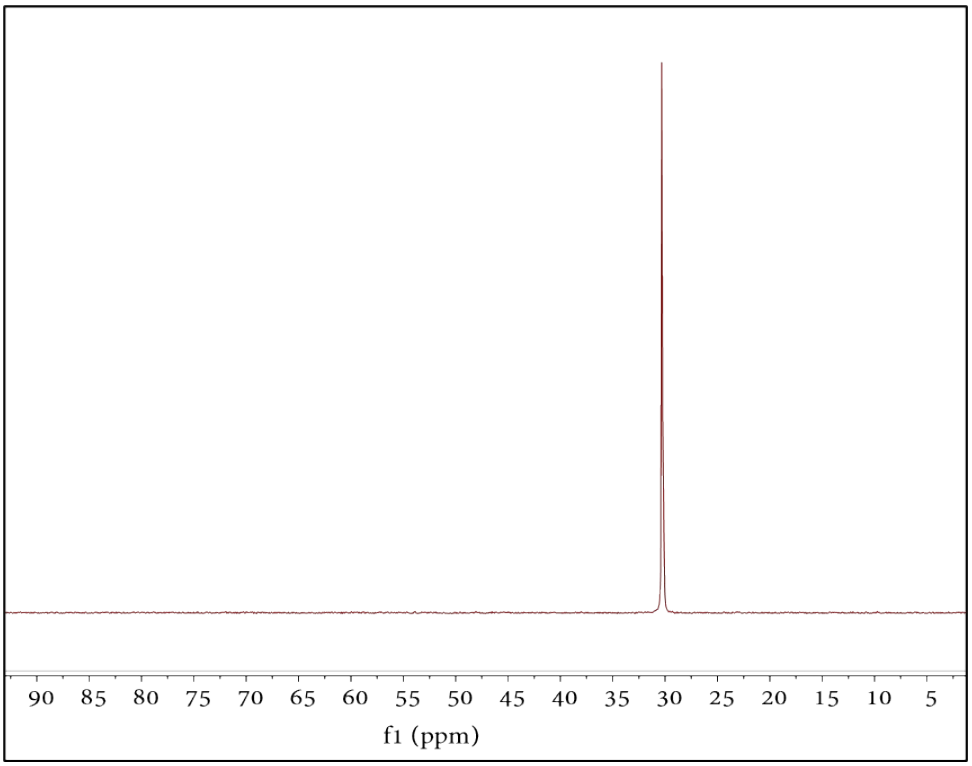

Figure S11. ^{13}C NMR of the obtained polyethylene (Table 1, Entry 6).

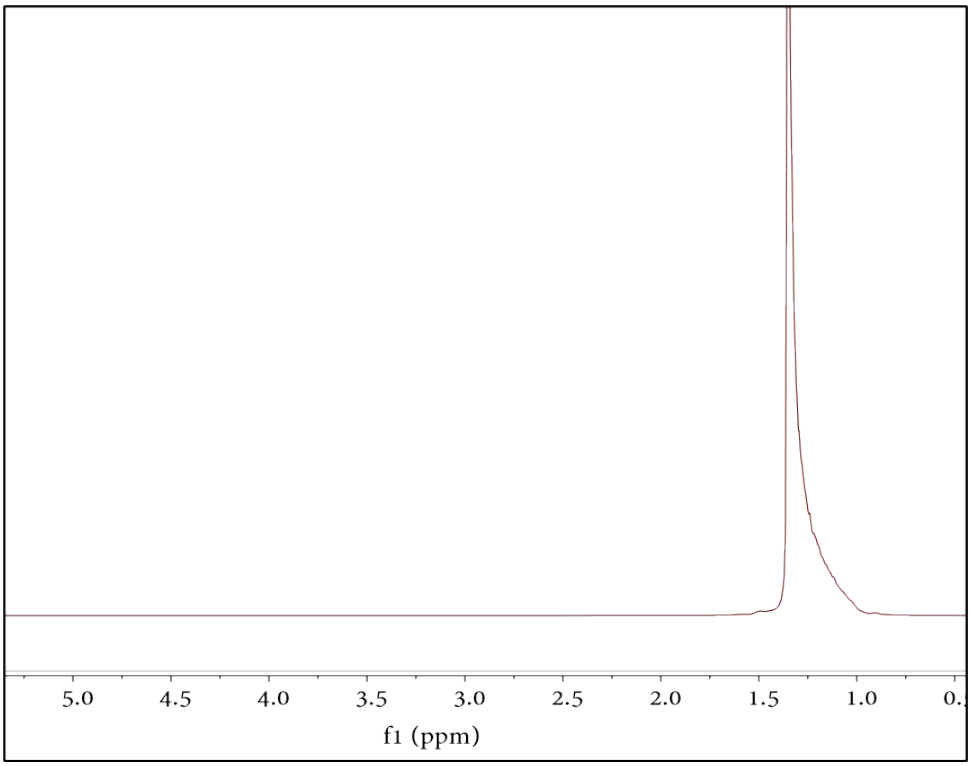

Figure S12 ^{1}H NMR of the obtained polyethylene (Table 1, Entry 6).

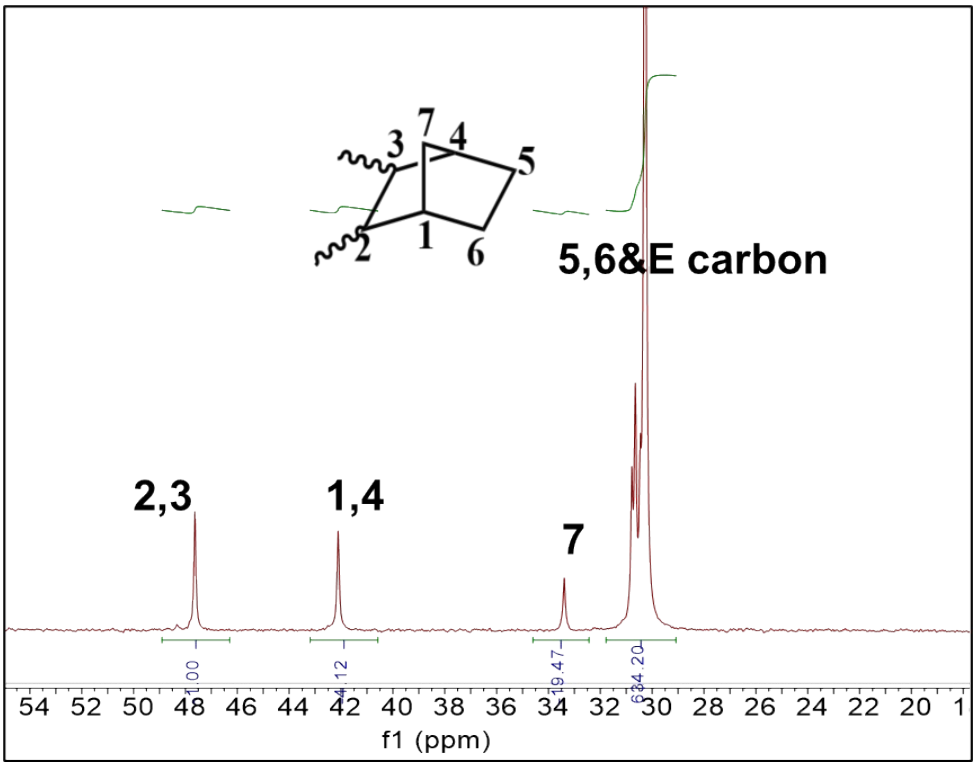

Figure S13. ^{13}C NMR of the obtained copolymer (Table 3, Entry 1).

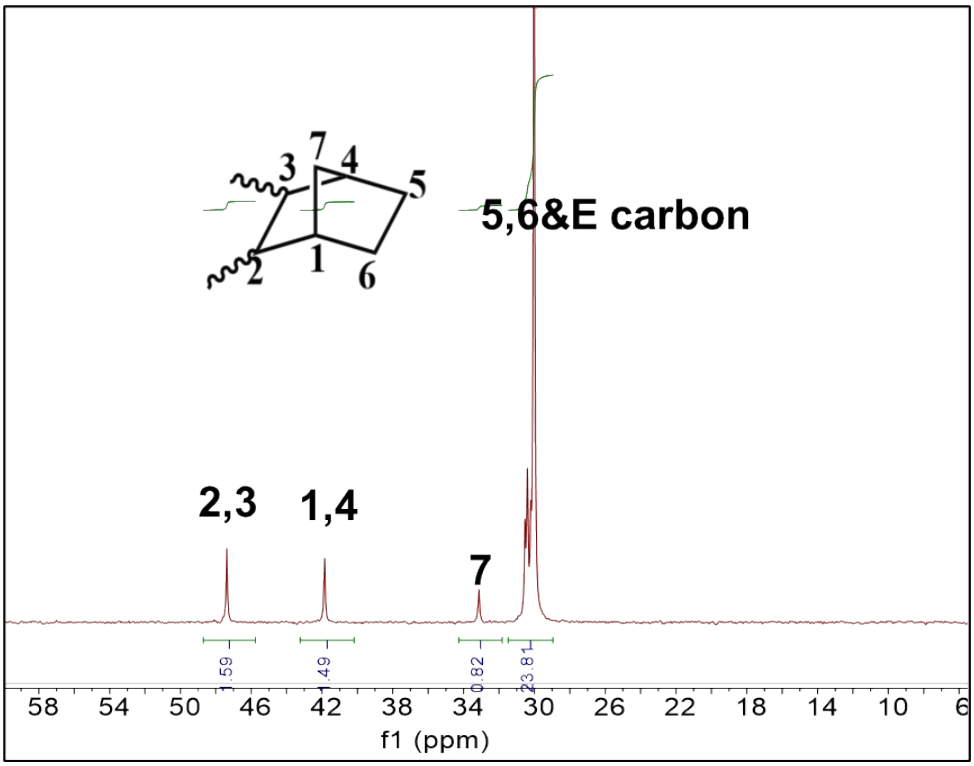

Figure S14. ^{13}C NMR of the obtained copolymer (Table 3, Entry 2).

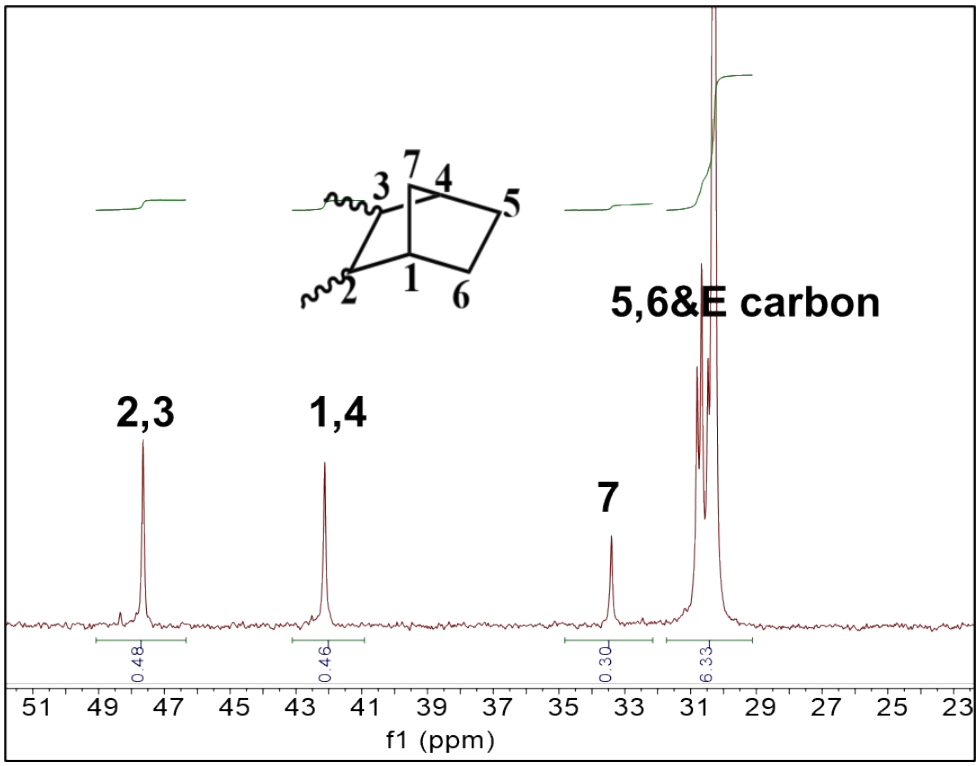

Figure S15. ^{13}C NMR of the obtained copolymer (Table 3, Entry 3).

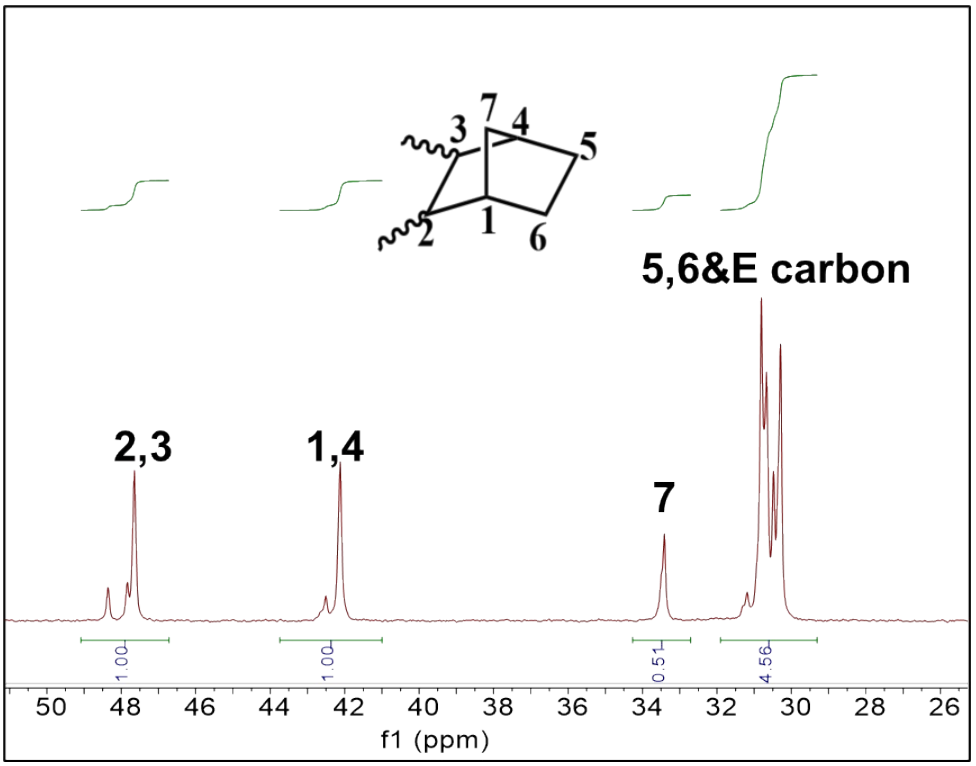

Figure S16. ^{13}C NMR of the obtained copolymer (Table 3, Entry 4).

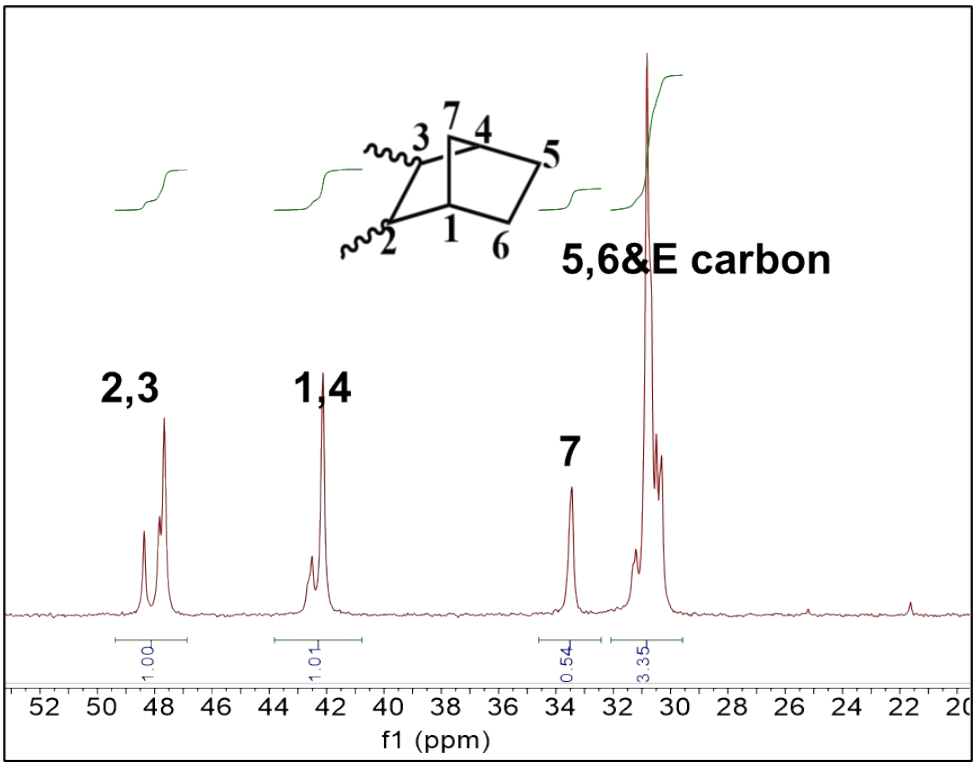

Figure S17. ^{13}C NMR of the obtained copolymer (Table 3, Entry 5).

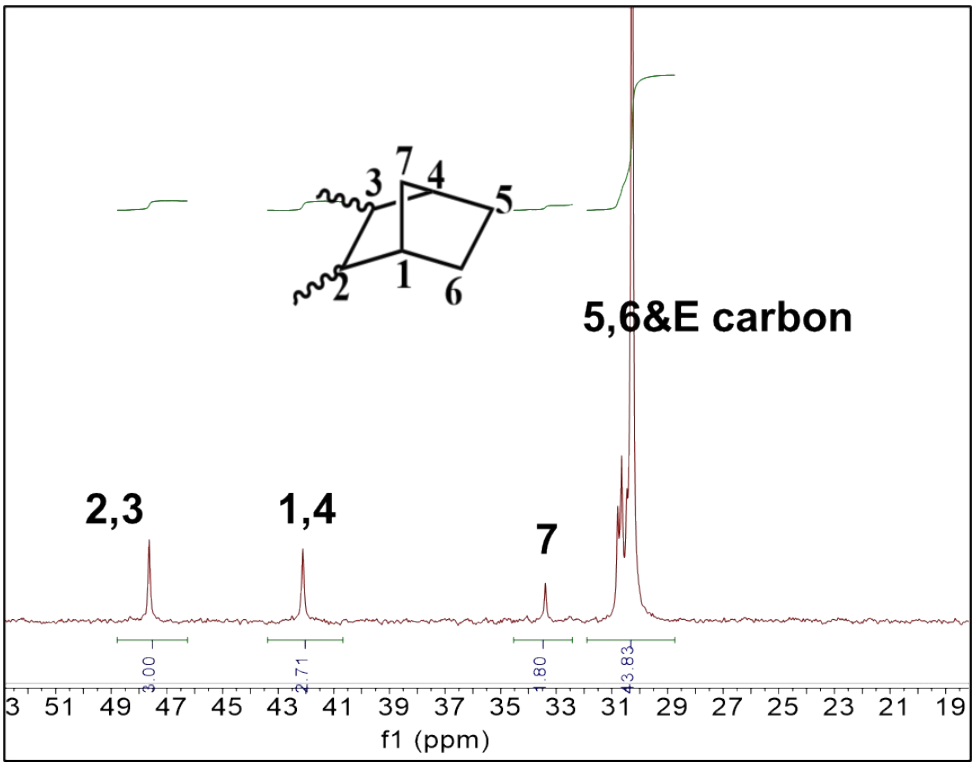

Figure S18. ^{13}C NMR of the obtained copolymer (Table 3, Entry 6).

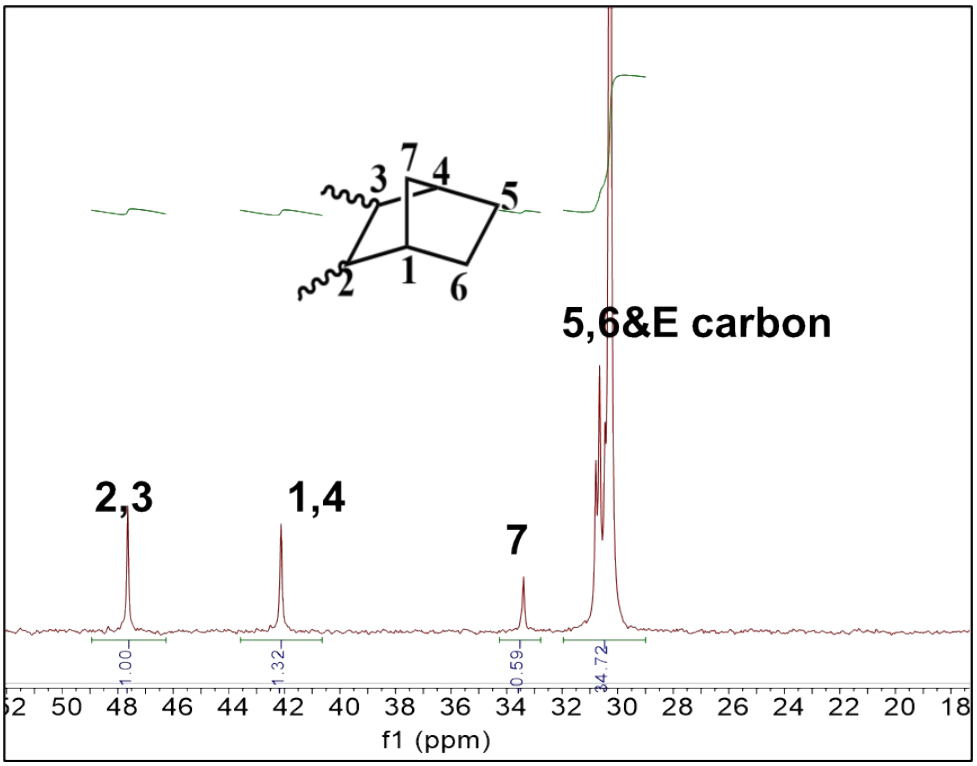

Figure S19. ^{13}C NMR of the obtained copolymer (Table 3, Entry7).

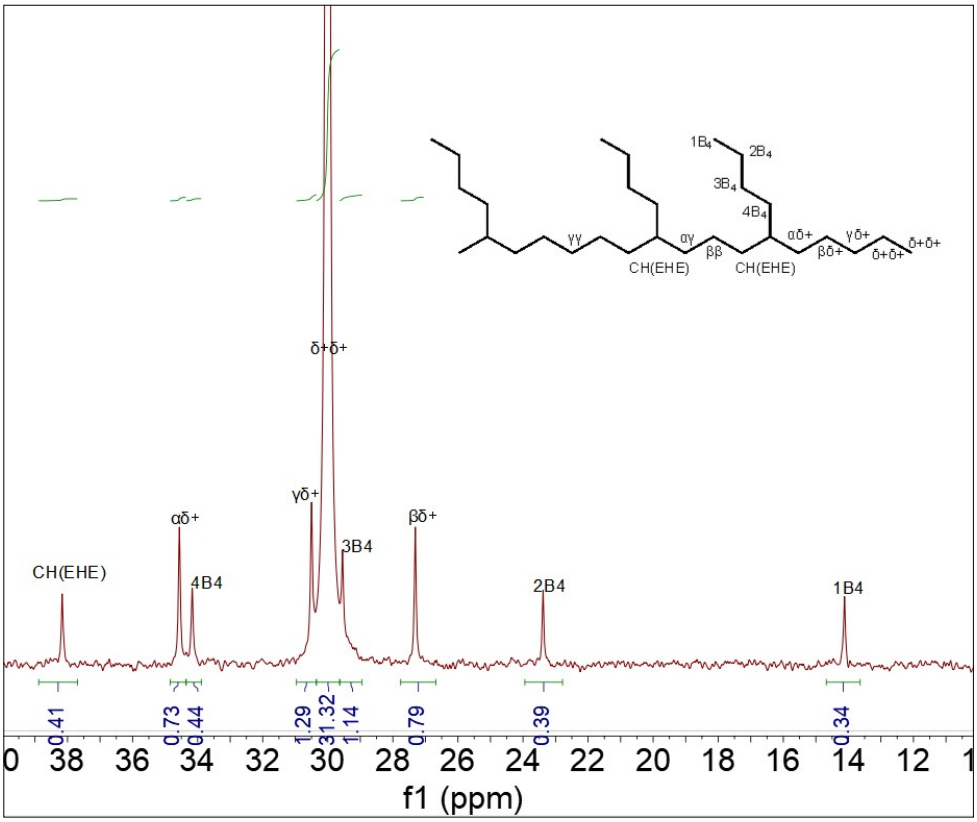

Figure S20. ^{13}C NMR of the obtained copolymer (Table 3, Entry8).

5. Comparison with reported pentavalent vanadium complexes

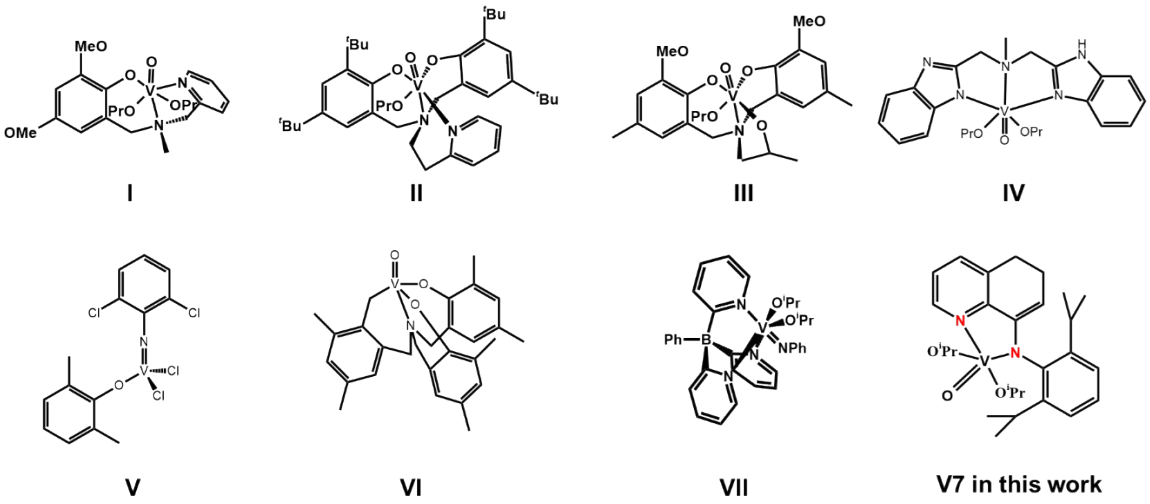

Table S3 Ethylene polymerization data reported in literatures.

Entry	Catalyst	The optimal polymerization temperature (°C)	Pressure (bar)	Time (min)	Activity (10^6 g mol(V)$^{-1}$ h^{-1})
1	I	50	4	5	66.2

2	**II**	**50**	**4**	**5**	**34.1**
3	**III**	**50**	**6**	**5**	**31.2**
4	**IV**	**/**	**4**	**30**	**41.5**
5	**V**	**0**	**8**	**10**	**55.8**
6	**VI**	**80**	**1**	**15**	**96.5**
7	**VII**	**90**	**10**	**60**	**0.1**
8	**V7 in this work**	**50**	**4**	**5**	**82.8**

Entry	Catalyst	Polymerization temperature (°C)	Pressure (bar)	C_{NBE} (mol/L)	Time (min)	Activity (10^6 g mol(V)$^{-1}$ h^{-1})	NBE incorporation (mol%)
1	**I**	**50**	**5**	**0.5**	**5**	**329**	**18.0**
2	**II**	**50**	**4**	**0.5**	**5**	**40.8**	**22.4**
3	**III**	**50**	**4**	**0.5**	**5**	**16.4**	**15.7**
4	**IV**	**50-66**	**4**	**0.47**	**20**	**11.6**	**15.5**
5	**V**	**0**	**8**	**0.5**	**10**	**49.9**	**9.4**
6	**V7 in this work**	**50**	**4**	**0.5**	**5**	**105.6**	**22.1**

Table S4 Date on copolymerization of ethylene and norbornene reported in literatures.

Reference

I: *J. B. Wang, L. P. Lu, J. Y. Liu and Y. S. Li, Dalton transactions, 2014, 43, 12926-12934.*

II: *J. B. Wang, L. P. Lu, J. Y. Liu, H. l. Mu and Y. S. Li, Journal of Molecular Catalysis A: Chemical, 2015, 398, 289-296.*

III: *J. Q. Wu, J. S. Mu, S. W. Zhang and Y. S. Li, Journal of Polymer Science Part A: Polymer Chemistry, 2010, 48, 1122-1132.*

IV: *A. K. Tomov, V. C. Gibson, D. Zaher, M. R. Elsegood and S. H. Dale, Chemical communications, 2004, 17(17), 1956-1957.*

V: *N. Diteepeng, X. Y. Tang, X. H. Hou, K. Nomura, Dalton transactions, 2015, 44,*

12273-12281.

VI: *C. Redshaw, M. A. Rowan, D. M. Homden, S. H. Dale, M. R. Elsegood, S. Matsui and S. Matsuura,* Chemical communications*, 2006, 3329-3331.*

VII: *J. Qian and R. J. Comito, Organometallics, 2021, 40, 1817-1821.*