ELECTRONIC SUPPORTING INFORMATION

Scandium, Titanium and Vanadium Complexes Supported by PCP-type Pincer Ligands: Synthesis, Structure, and Styrene Polymerization Activity

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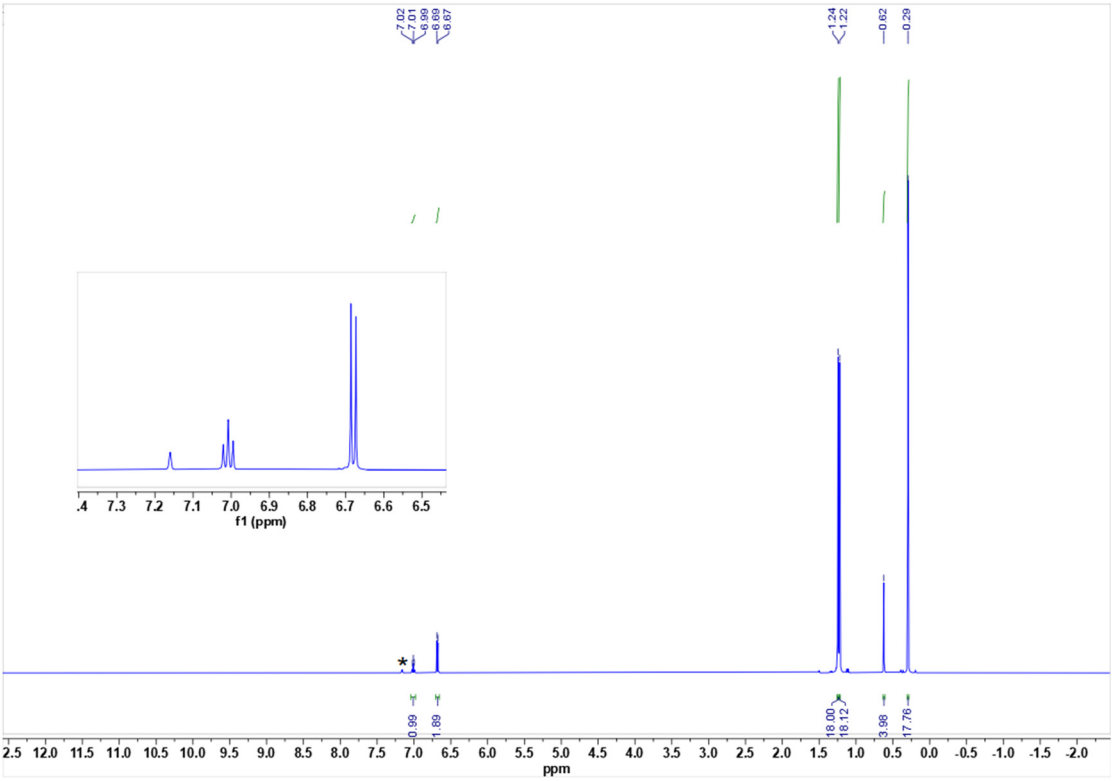

Figure S1. ^{1}H NMR spectra of complex **1-Sc** (C_6D_6, rt, *···C_6D_6)

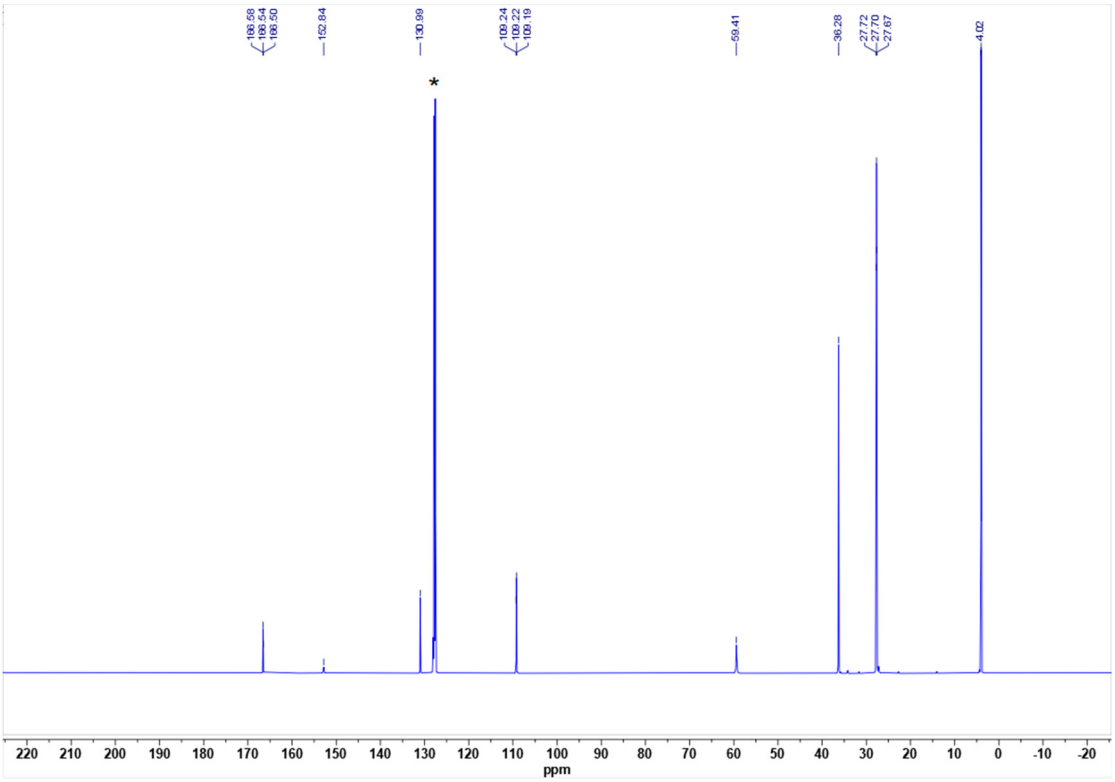

Figure S2. ^{13}C NMR spectra of complex **1-Sc** (C_6D_6, rt, *···C_6D_6)

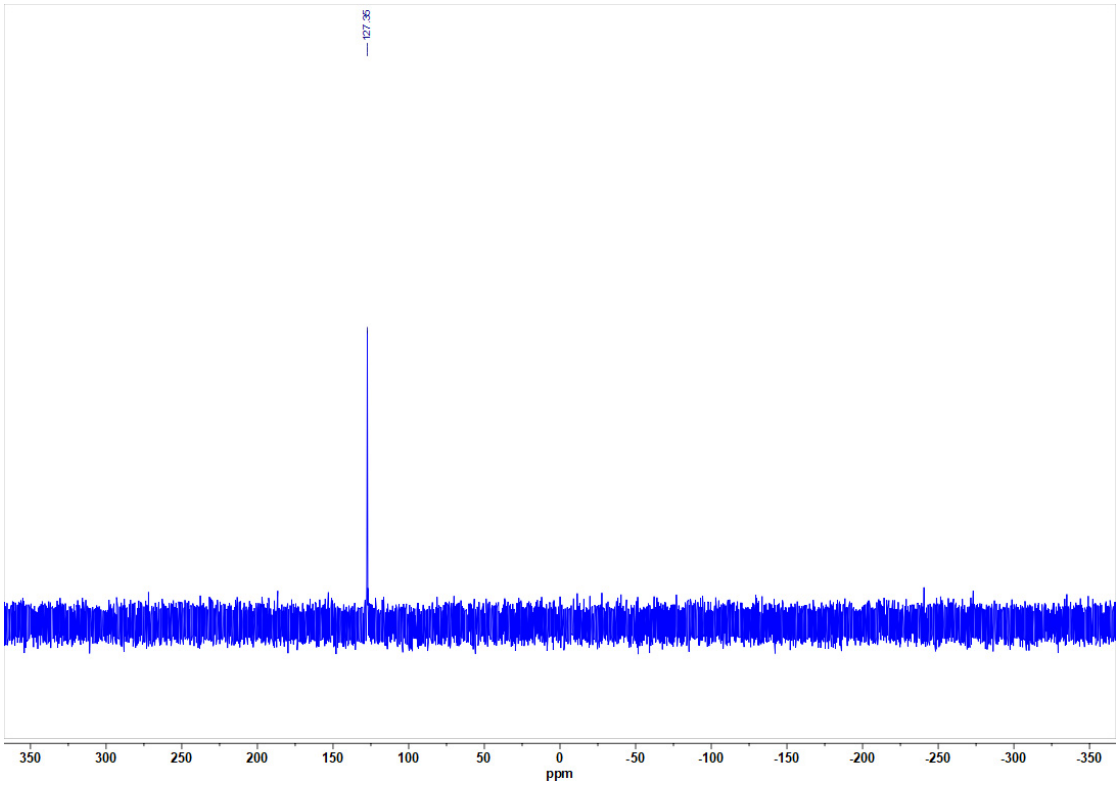

Figure S3. ^{31}P NMR spectra of complex **1-Sc** (C_6D_6, rt, *···C_6D_6)

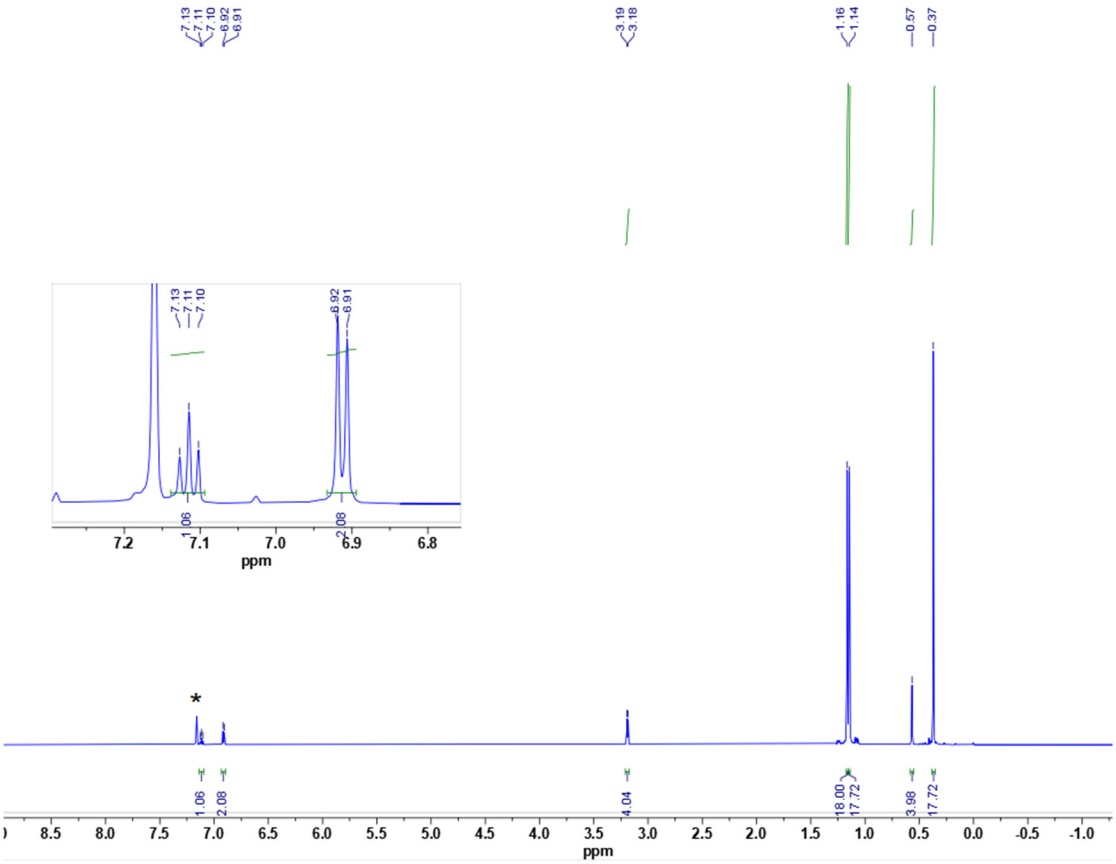

Figure S4. ^{1}H NMR spectra of complex **2-Sc** (C_6D_6, rt, *···C_6D_6)

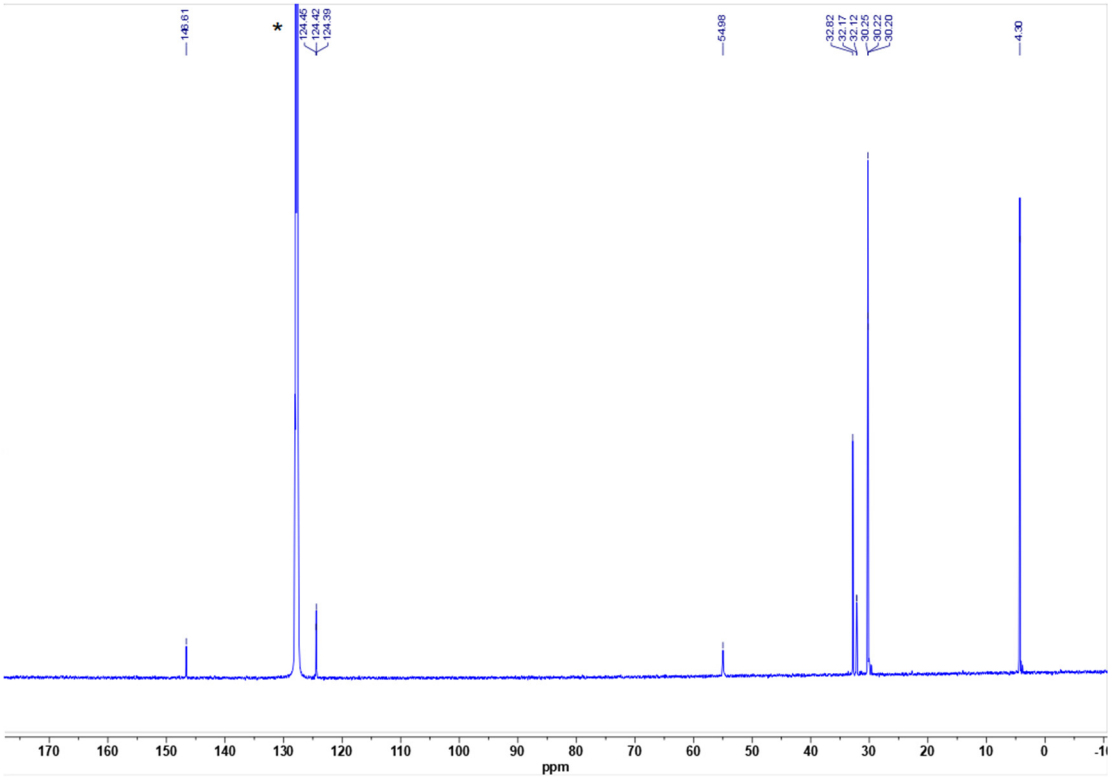

Figure S5. ^{13}C NMR spectra of complex **2-Sc** (C_6D_6, rt, *···C_6D_6)

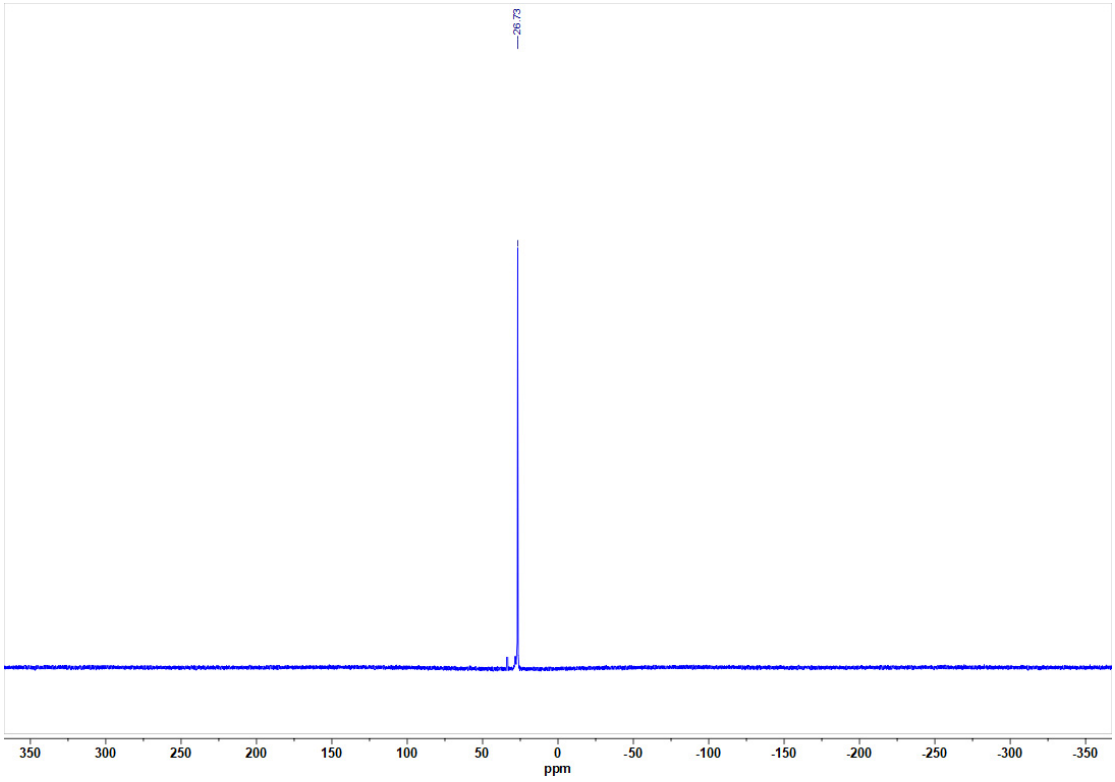

Figure S6. ^{31}P NMR spectra of complex **2-Sc** (C_6D_6, rt, *···C_6D_6)

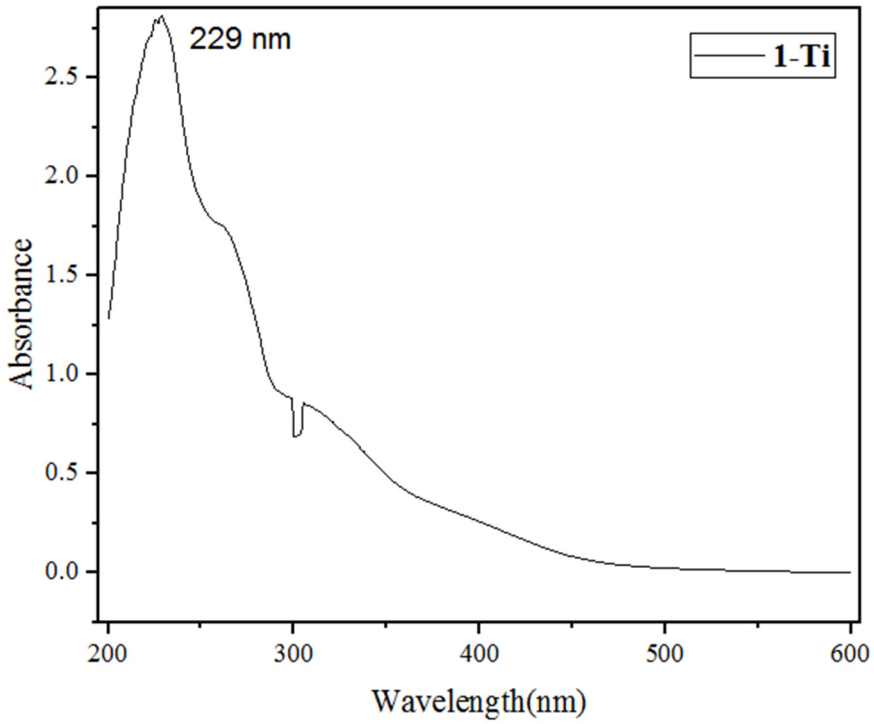

Figure S7. UV-Vis spectra of **1-Ti**

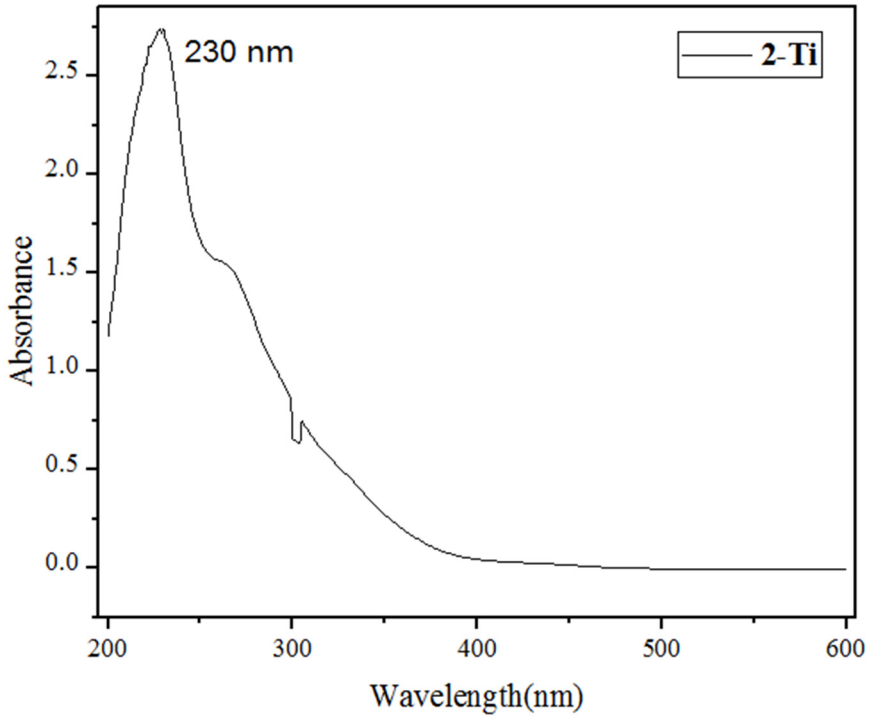

Figure S8. UV-Vis spectra of **2-Ti**

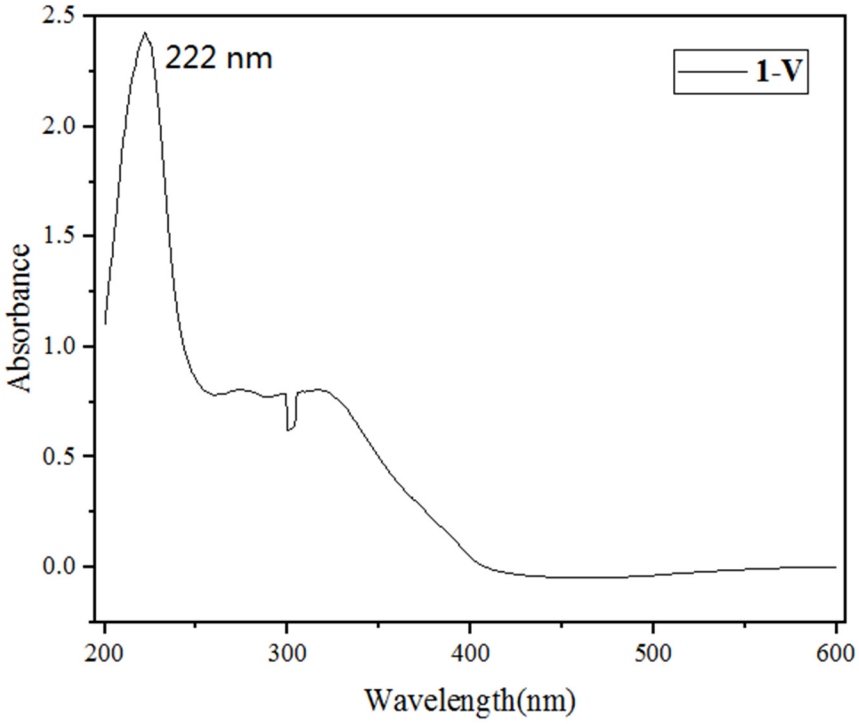

Figure S9. UV-Vis spectra of **1-V**

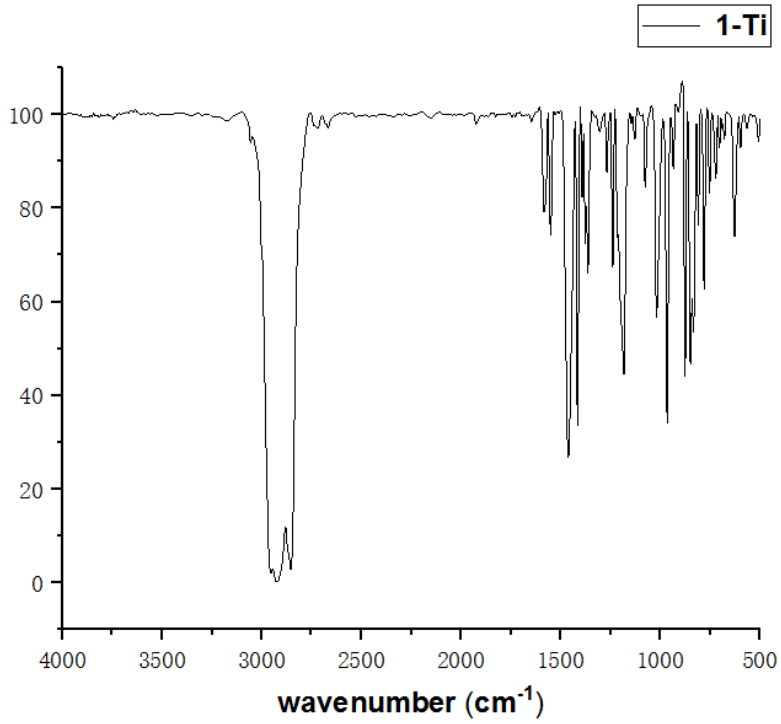

Figure S10. Infrared spectra of **1-Ti**

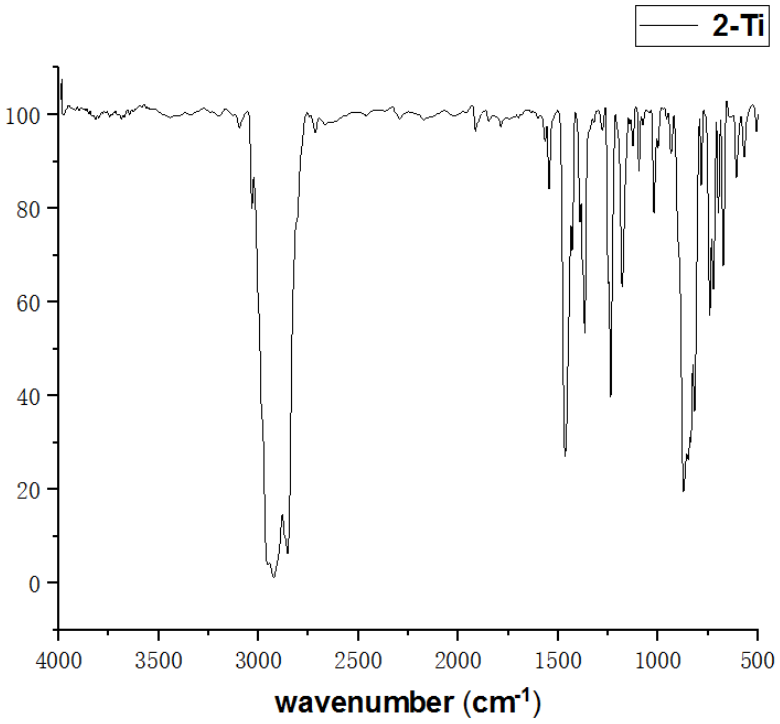

Figure S11. Infrared spectra of **2-Ti**

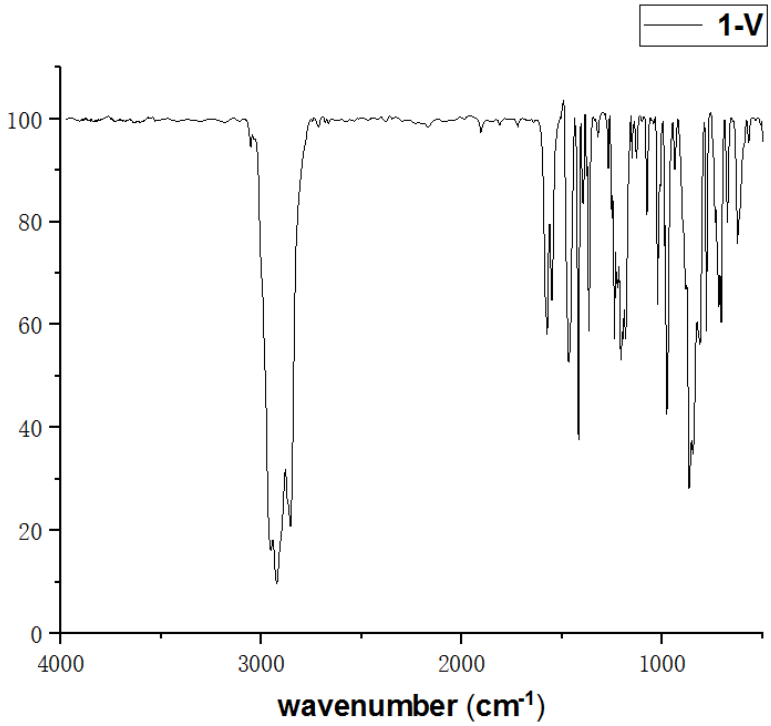

Figure S12. Infrared spectra of **1-V**

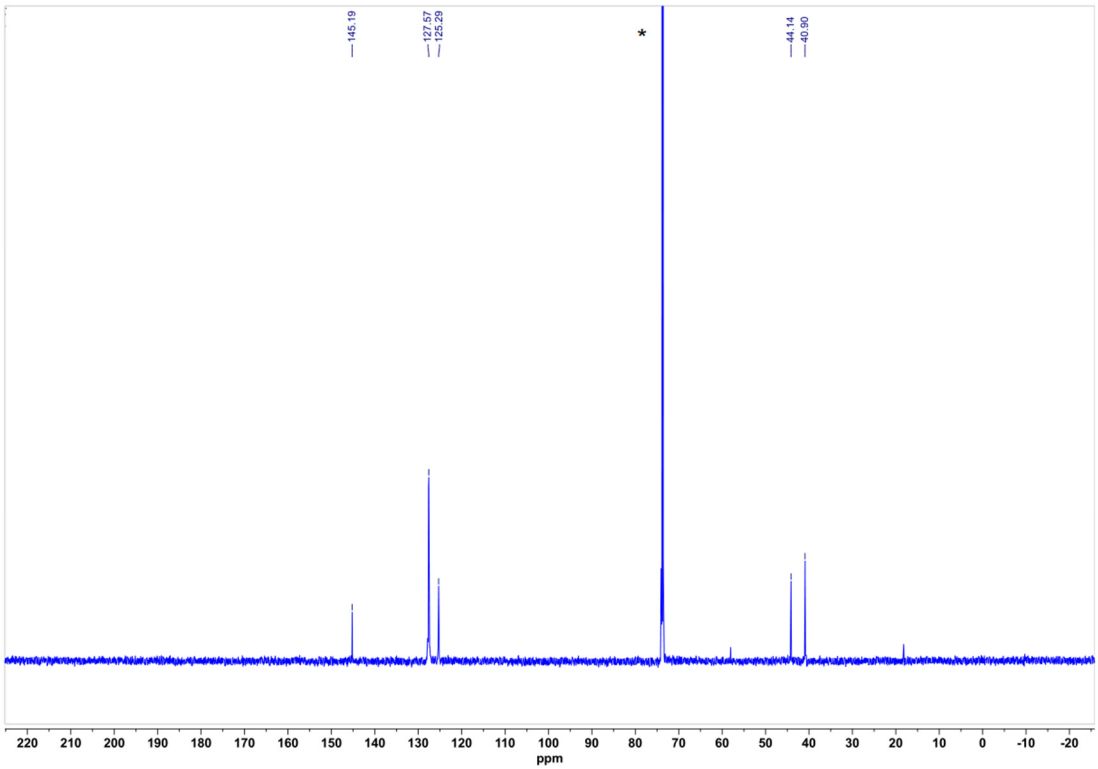

Figure S13. ^{13}C NMR (120 °C, *···1,1,2,2-tetrachloroethane-d_2) of sPS obtained with complex **1-Sc**

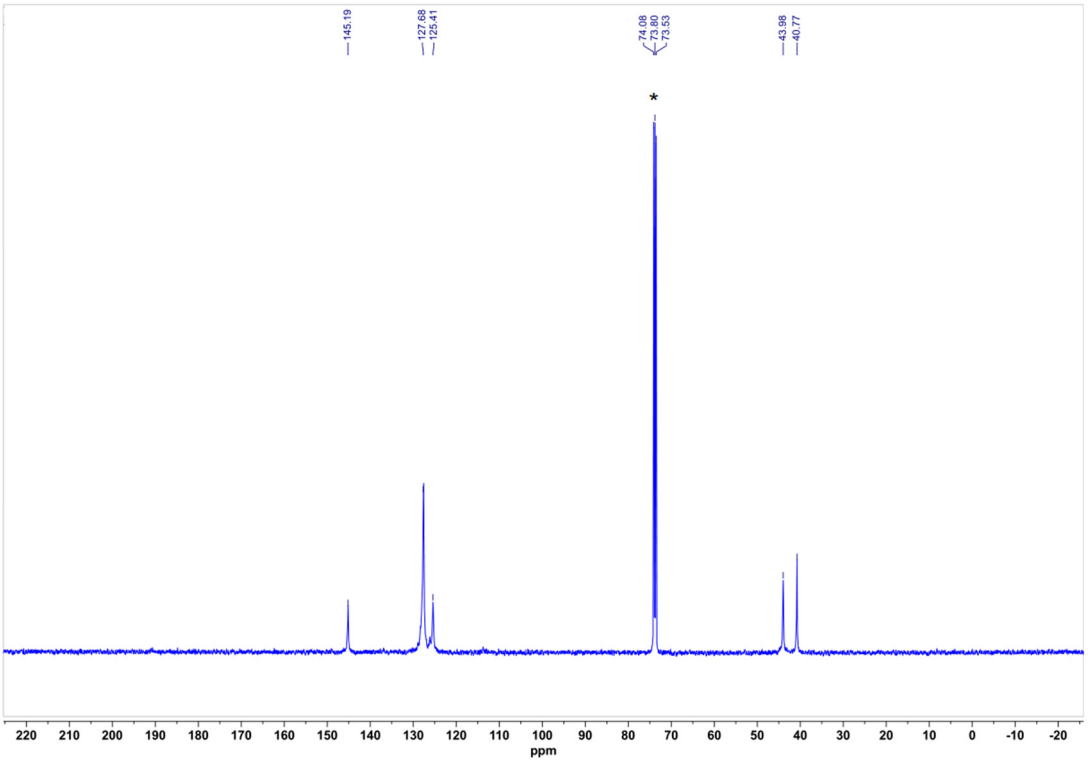

Figure S14. ^{13}C NMR (120 °C**,** *···1,1,2,2-tetrachloroethane-d_2) of sPS obtained with complex **2-Sc**

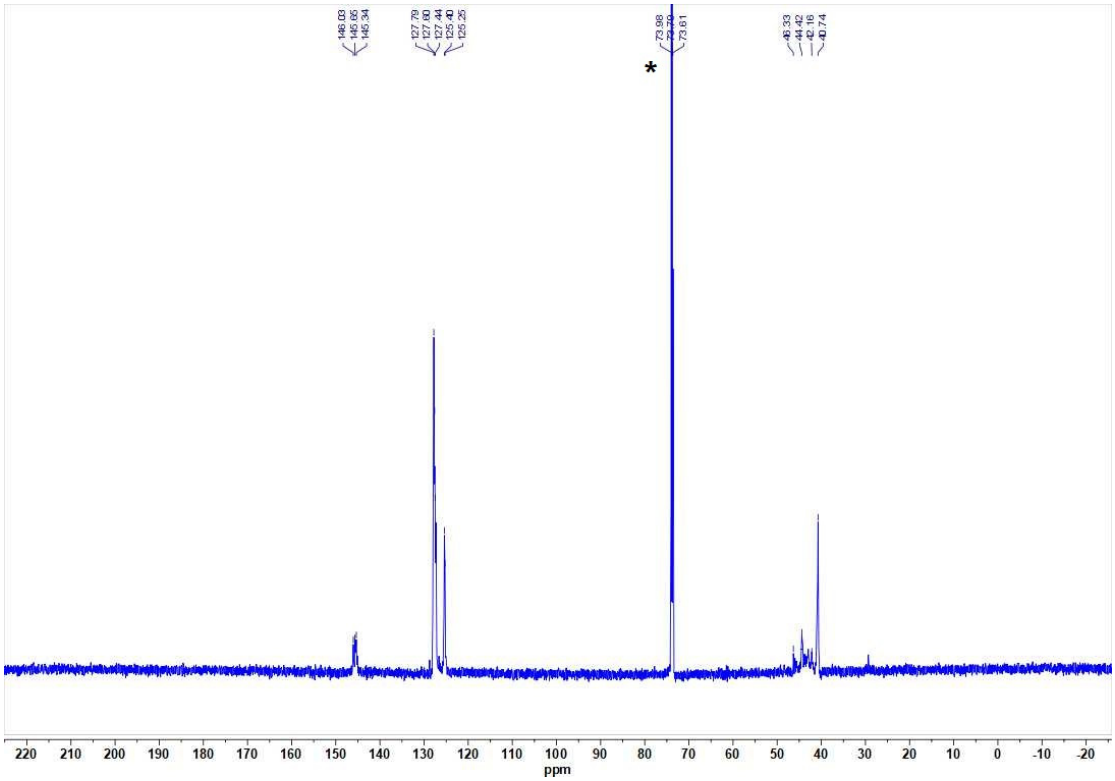

Figure S15. ^{13}C NMR (120 ^{o}C**,** *···1,1,2,2-tetrachloroethane-d_2) of aPS (atactic polystyrene) obtained with complex **1-Ti**

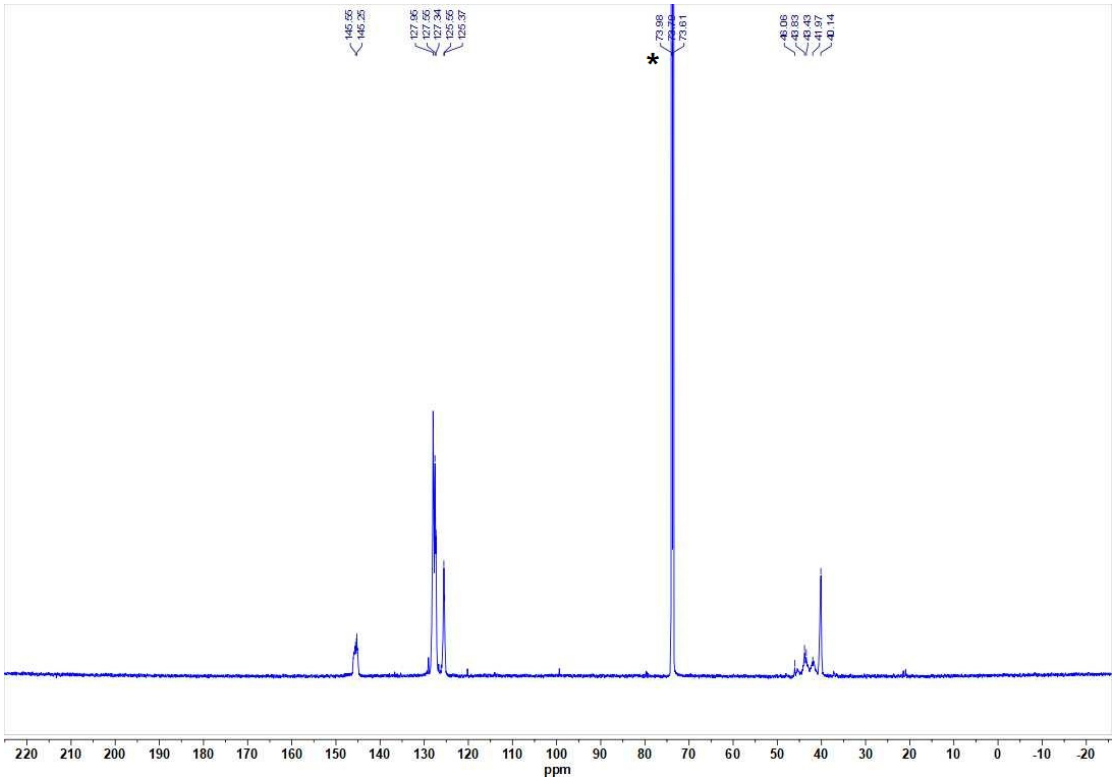

Figure S16. ^{13}C NMR (120 ^{o}C, *···1,1,2,2-tetrachloroethane-d_2) of aPS (atactic polystyrene) obtained with complex **1-V**

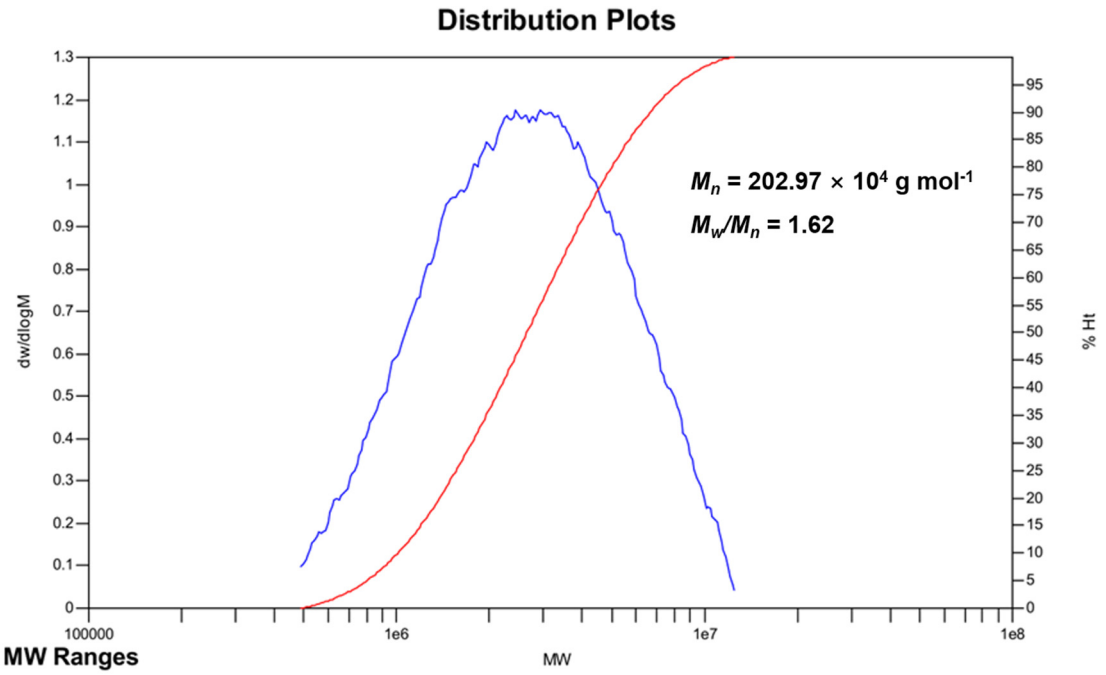

Figure S17. GPC curve of sPS sample obtained by complex **1-Sc**

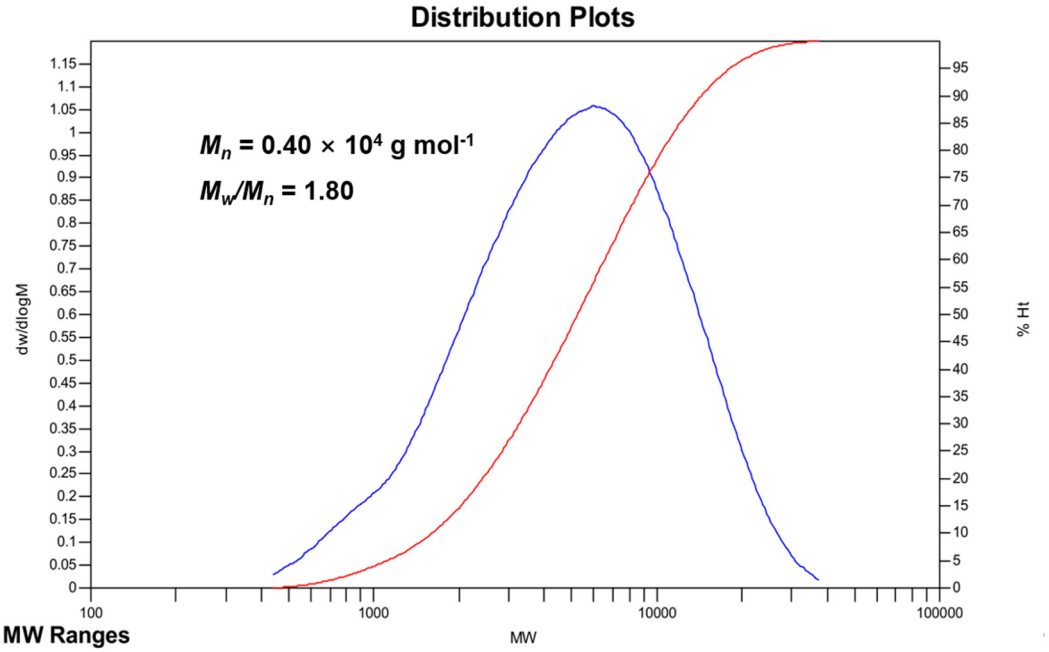

Figure S18. GPC curve of aPS (atactic polystyrene) sample obtained by complex **1-Ti**

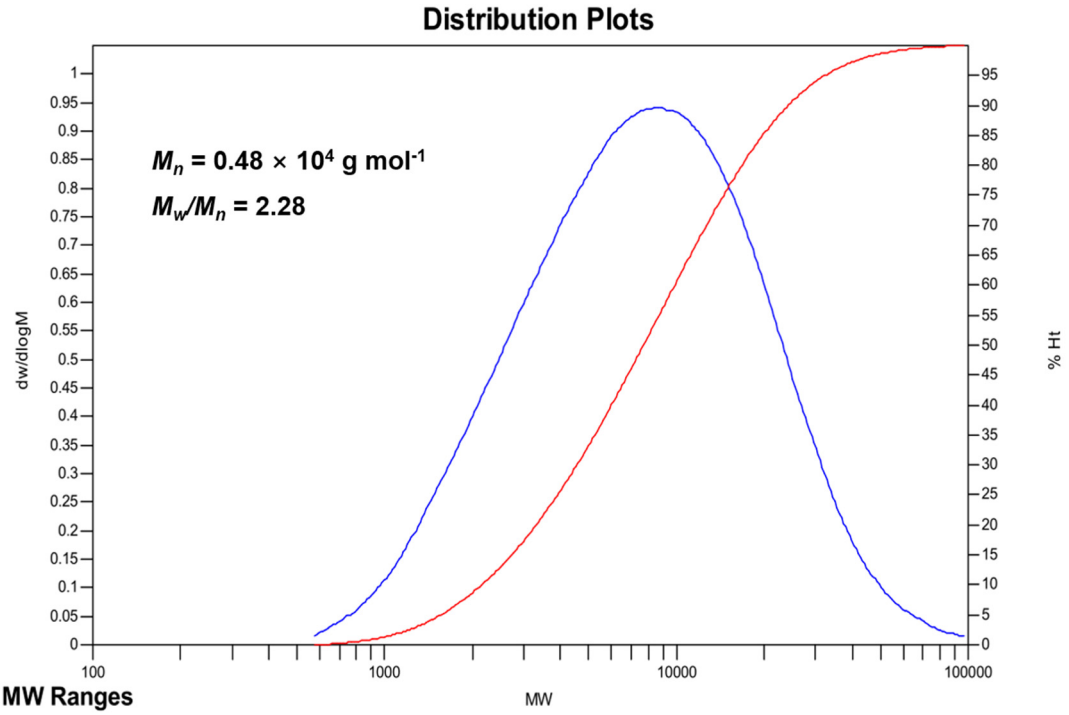

Figure S19. GPC curve of aPS (atactic polystyrene) sample obtained by complex **1-V**

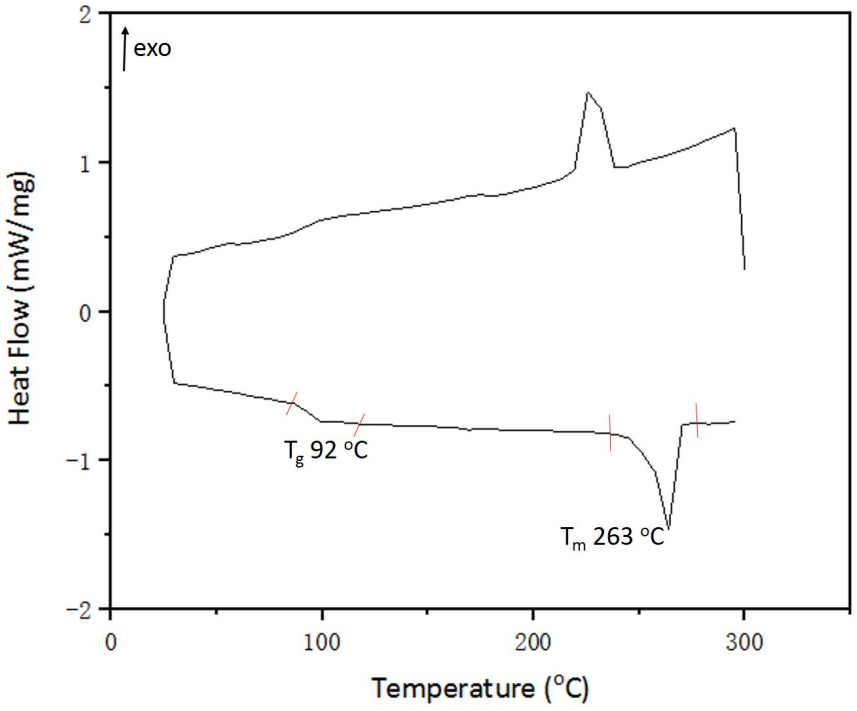

Figure S20. DSC curve of sPS obtained by complex **1-Sc**

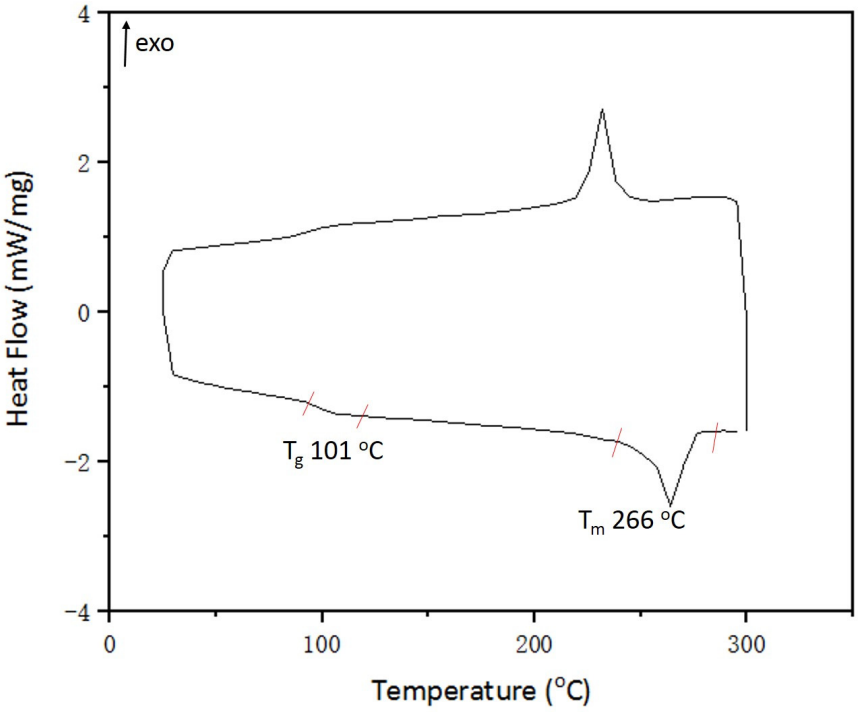

Figure S21. DSC curve of sPS obtained by complex **2-Sc**

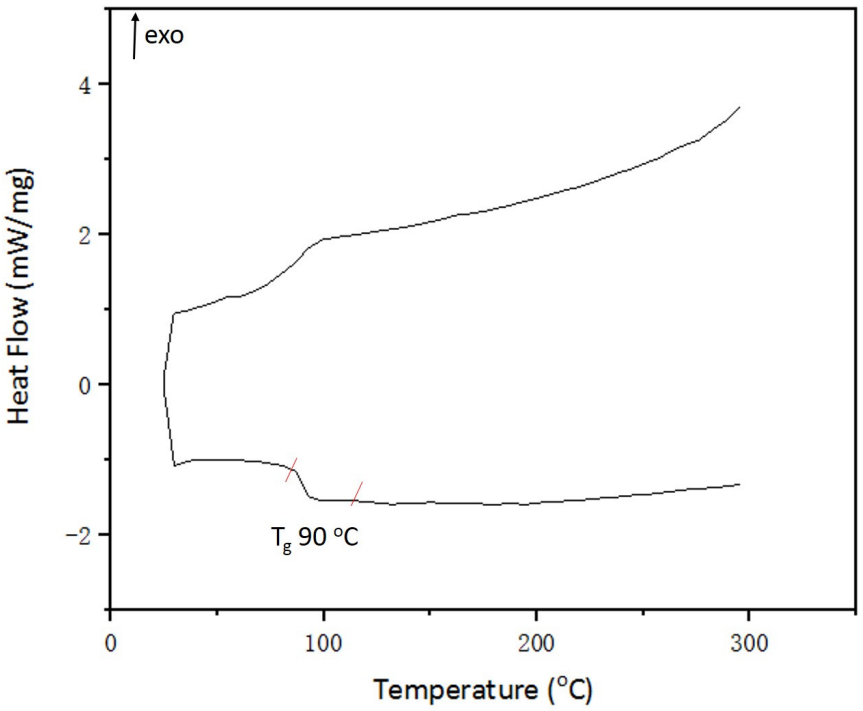

Figure S22. DSC curve of aPS (atactic polystyrene) obtained by complex **1-Ti**

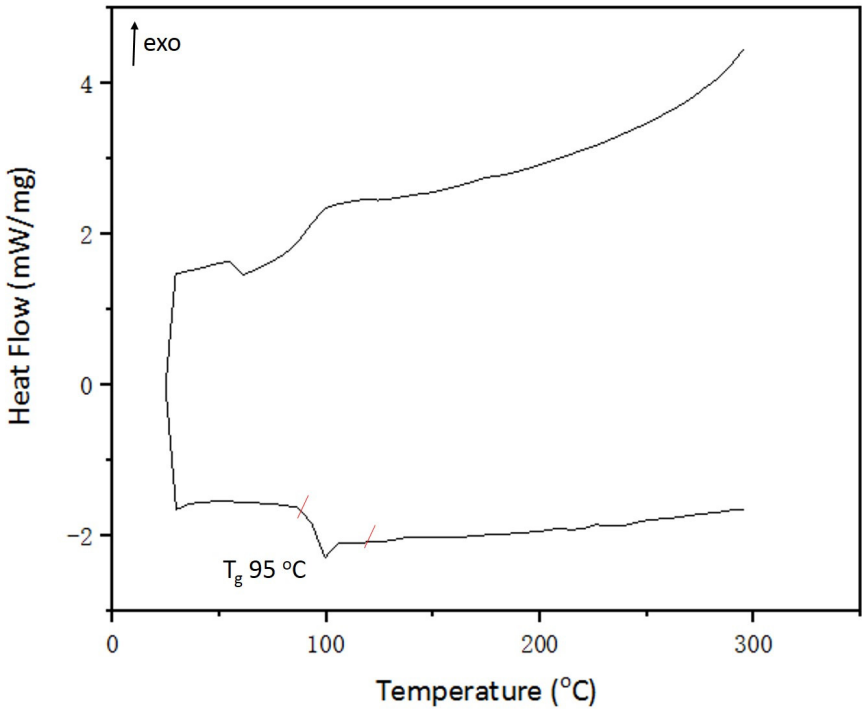

Figure S23. DSC curve of aPS (atactic polystyrene) obtained by complex **1-V**

X-ray Crystallographic Studies

Crystals for X-ray diffraction studies were obtained as described in the preparations. The crystals were manipulated in a glovebox under a microscope and were sealed in thin-walled glass capillaries. Intensity data were collected on a Rigaku Mercury CCD area detector with Mo or Cu Kα radiation. The diffracted intensities were corrected for Lorentz–polarization effects and empirical absorption corrections. All of the structures were solved using SHELXL-2018.[1] Structural refinement was performed using on F^2 anisotropically for all of the non-hydrogen atoms by the full-matrix least-squares method. Structural refinement was performed using the SHELXL option in the WINGX system,[2] or Olex2 system[3] on F^2 anisotropically for all of the non-hydrogen atoms by the full-matrix least-squares method. Analytical scattering factors for neutral atoms were used throughout the analysis. The hydrogen atoms of ligands were placed at the calculated positions, which were refined using a riding model. The analytical scattering factors for neutral atoms were used throughout the analysis. The residual electron densities were of no chemical significance.

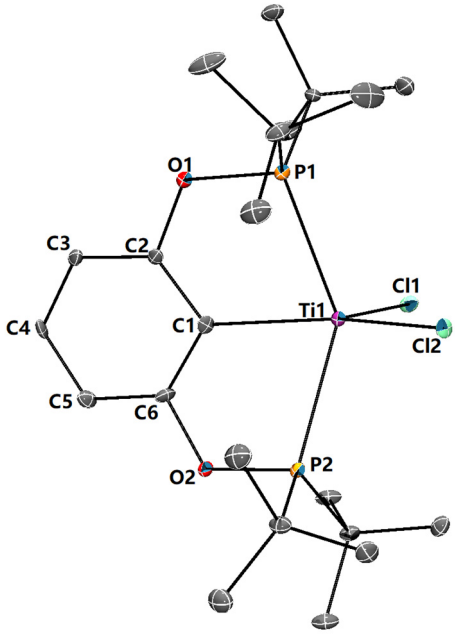

Figure S24. X-ray diffraction crystal structure of **3-Ti** with thermal ellipsoids drawn at 30% probability. Hydrogen atoms was omitted for clarity.

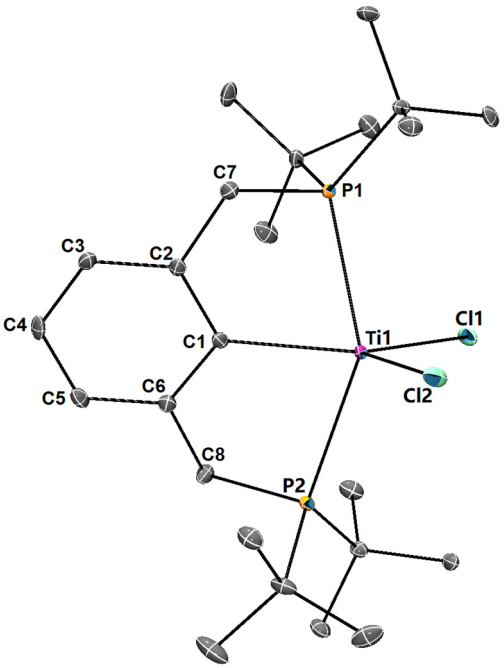

Figure S25. X-ray diffraction crystal structure of **4-Ti** with thermal ellipsoids drawn at 30% probability. Hydrogen atoms was omitted for clarity.

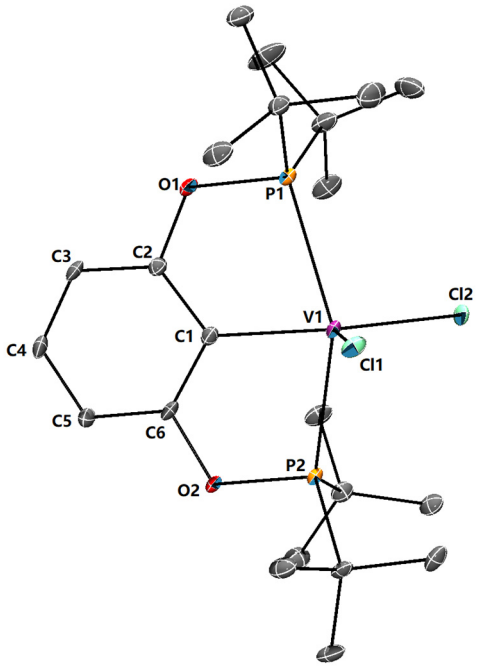

Figure S26. X-ray diffraction crystal structure of **3-V** with thermal ellipsoids drawn at 30% probability. Hydrogen atoms was omitted for clarity.

Table S1. X-Ray crystallographic data and structure refinement for 1-Sc, 1-Ti, 1-V, 2-Sc and 2-Ti.

	1-Sc	2-Sc	1-Ti	1-V	2-Ti
CCDC	2161776	2163361	2161777	2162723	2161786
formula	$C_{30}H_{61}O_2P_2ScSi_2$	$C_{32}H_{65}P_2ScSi_2$	$C_{30}H_{61}O_2P_2TiSi_2$	$C_{30}H_{61}O_2P_2VSi_2$	$C_{32}H_{65}P_2Si_2Ti$
crystal system	Orthorhombic	Monoclinic	Orthorhombic	Orthorhombic	Orthorhombic
space group	Pca21	P21/c	Pca21	Pca21	Pca21
a, Å	16.3488(9)	16.7335(7)	16.1891(2)	16.1044(4)	16.1352(2)
b, Å	13.2688(8)	13.2393(6)	13.1418(2)	13.1750(3)	13.17667(18)
c, Å	16.9093(10)	16.9263(8)	16.9923(3)	16.9968(6)	17.2700(3)
α, deg	90	90	90	90	90
β, deg	90	97.212(4)	90	90	90
γ, deg	90	90	90	90	90
V, Å^3	3668.1(4)	3720.2(3)	3615.18(10)	3606.30(18)	3671.75(9)
Z	4	4	4	4	4
D_{calcd}, g/cm^3	1.117	1.094	1.139	1.147	1.099
temp, K	100	100	100	100	100
μ, mm^{-1}(MoKa)	0.376	0.366	3.645	0.453	3.542
reflections collected	15172	19441	13919	42226	9078
independent reflections (R_{int})	7508(0.0305)	8822(0.0410)	5894(0.0323)	8658(0.0590)	6009(0.0370)
*R*1 ($I > 2\sigma(I)$)	0.0430	0.0394	0.0260	0.0384	0.0460
*wR*2 ($I > 2\sigma(I)$)	0.0946	0.0936	0.0677	0.0866	0.1249
*wR*2 (all data)	0.1014	0.1014	0.0681	0.0929	0.1257
parameters	353	335	335	353	352
GOF	1.023	1.027	1.041	0.981	1.067
absolute structure Flack	0.28(4)	-	0.004(4)	-0.06(2)	0.000(8)

Table S2. X-Ray crystallographic data and structure refinement for 3-Ti, 3-V and 4-Ti.

	3-Ti	**3-V**	**4-Ti**
CCDC	2168774	2168775	2169339
formula	$C_{22}H_{39}Cl_2O_2P_2Ti$	$C_{22}H_{39}Cl_2O_2P_2V$	$C_{24}H_{43}Cl_2P_2Ti$
crystal system	Monoclinic	Monoclinic	Monoclinic
space group	P21/n	P21/n	P21/n
a, Å	10.6740(6)	10.6403(4)	12.1470(7)
b, Å	16.1874(9)	16.2799(8)	15.8810(7)
c, Å	15.2797(10)	15.1343(8)	14.4631(11)
α, deg	90	90	90
β, deg	91.080(6)	90.332(4)	105.389(7)
γ, deg	90	90	90
V, Å^3	2639.6(3)	2621.6(2)	2690.0(3)
Z	4	4	4
D_{calcd}, g/cm^3	1.299	1.316	1.265
temp, K	100	100	100
μ, mm^{-1}(MoKa)	0.663	0.720	0.645
reflections collected	14374	31769	18427
independent reflections (R_{int})	6321(0.0919)	6664(0.0750)	6450(0.1071)
*R*1 ($I > 2\sigma(I)$)	0.0725	0.0525	0.0565
*wR*2 ($I > 2\sigma(I)$)	0.1300	0.1235	0.1369
*wR*2 (all data)	0.1688	0.1368	0.1703
parameters	274	274	274
GOF	1.048	1.029	1.045

References

1. G. M. Sheldrick, *Acta Cryst.* **2015**, *C71*, 3–8.
2. L. J. J. Farrugia, WinGX suite for small-molecule single-crystal crystallography. *J. Appl. Cryst.* **1999,** 32(4), 837–838.
3. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Cryst.* **2009**, *42*, 339-341.