

Electronic Supplementary Information

First-row early transition metal complexes with a highly sterically demanding triisopropylphenyl amino triphenolate ligand: synthesis and applications

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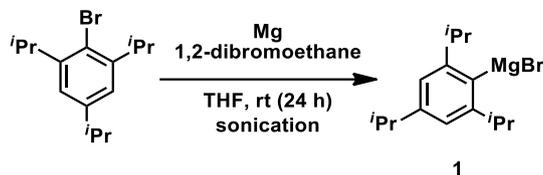
Materials and Methods

All air- and moisture-sensitive manipulations, including basic Schlenk and glovebox techniques, were performed using oven-dried or flame-dried glassware under an N₂ atmosphere. Air- and moisture-insensitive reactions were carried out under ambient conditions and were magnetically stirred. Benzene, benzene-d₆, Et₂O, toluene and THF were distilled from deep purple sodium benzophenone ketyl. Acetonitrile was dried over P₂O₅ and vacuum-distilled. Methanol was degassed with nitrogen bubbling for 1 hour and dried over activated 3 Å molecular sieves. Chloroform-*d*₁ and all other chemicals were used as received. All deuterated solvents were purchased from Aldrich (USA) and Cambridge Isotope Laboratories (USA). The NMR spectra were recorded on a DRX 500 spectrometer (Bruker, USA) operating at 500 and 125 MHz for ¹H and ¹³C acquisition, respectively. Chemical shifts were referenced to the residual proton solvent peaks (¹H: CDCl₃, δ 7.26 / C₆D₆, δ 7.16 / MeOD, δ 3.31) and ¹³C solvent signals (CDCl₃, δ 77.16 / C₆D₆, δ 128.06).¹ Signals are described as follows: chemical shift in ppm, multiplicity identified as s = singlet, br = broad, d = doublet, t = triplet and m = multiplet; coupling constants in Hz; integration. Purified compounds were further dried under high vacuum (0.01–0.05 Torr). Infrared spectra were obtained as thin films formed by evaporation of solutions on KBr windows using a Bruker Alpha system. Electronic absorption spectra were measured with a Cary 6000i ultraviolet–visible–near infrared (UV-VIS-NIR) system (Agilent, USA).

Experimental Section

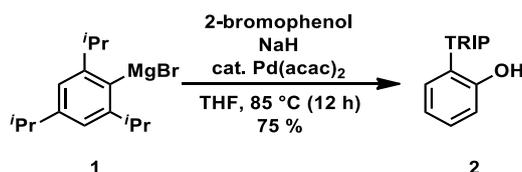
Synthesis of the ligand

(2, 4, 6-Triisopropylphenyl)magnesium bromide (**1**)²



In a nitrogen-filled glovebox, magnesium powder (2.57 g, 106 mmol, 3.0 equiv.) and 2-bromo-1, 3, 5-triisopropylbenzene (10.0 g, 35.3 mmol, 1.0 equiv.) were added to a 350 mL heavy wall round bottom flask. Dry THF (60 mL) was added to the flask and 0.1 mL of 1, 2-dibromoethane was subsequently added as an activator. The flask was taken out from the glovebox and was subsequently sonicated at 23 °C for 24 h using a temperature-controlled sonicator. After the sonication, the flask was taken into the glovebox. The resulting solution of (2, 4, 6-triisopropylphenyl)magnesium bromide was filtered through a pad of Celite and 3 × 20 mL of THF was used for washing the flask. The obtained solution was used directly in the next step. The Grignard reagent **1** was also synthesized by the traditional method (stirring under reflux condition).

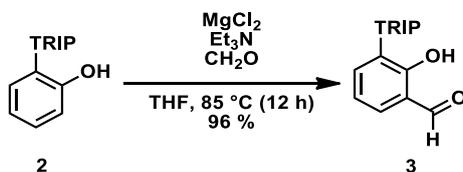
2',4',6'-Triisopropyl-2-biphenylol (**2**)³



2-Bromophenol (4.70 g, 27.2 mmol, 1.0 equiv.) was added to a mixture of sodium hydride (0.782 g, 32.6 mmol, 1.2 equiv.) and THF (40 mL) at 0 °C in a 350 mL heavy wall round bottom flask, and the mixture was stirred at 23 °C for 10 min. Pd(acac)₂ (248 mg, 0.815 mmol, 0.03 equiv.) and the solution of **1** (120 mL, 10.86 g, 0.29 M) were added to the mixture, separately, and the resulting mixture was heated at 80 °C for 12 h. After cooling the solution to 0 °C, water (40 mL) was carefully added to quench the residual Grignard reagent and sodium hydride. Aqueous hydrochloric acid (2.0 M, 10 mL) was added and the resulting mixture was filtered through a pad of Celite. The organic phase was separated by subsequent extraction of the aqueous phase with Et₂O (3 × 20 mL). The volatiles of the combined organic solution were removed *in vacuo*. The residual solid was collected and then sublimed at 80 ~ 110 °C under dynamic vacuum to afford **2** as a colorless solid (6.01 g, 75%).

¹H NMR (500 MHz, CDCl₃, 23 °C, δ): 7.29 (td, *J* = 7.8, 1.5 Hz, 1H), 7.12 (s, 2H), 7.04 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.00 (dd, *J* = 8.2, 1.0 Hz, 1H), 6.96 (td, *J* = 7.4, 1.1 Hz, 1H), 4.63 (s, 1H), 2.95 (sept, *J* = 7.0 Hz, 1H), 2.59 (sept, *J* = 6.9 Hz, 2H), 1.31 (d, *J* = 7.0 Hz, 6H), 1.09 (dd, *J* = 25.0, 6.9 Hz, 12H). ¹³C NMR (125 MHz, CDCl₃, 23 °C, δ): 153.3, 149.7, 148.6, 130.8, 129.3, 129.0, 126.1, 121.7, 120.4, 114.9, 34.5, 30.6, 24.6, 24.2, 24.1. Anal. Calcd. for C₂₁H₂₈O: C, 84.99; H, 9.41; found: C, 85.08; H, 9.52.

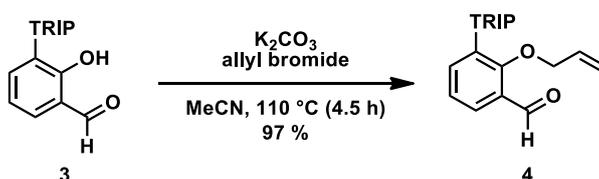
2-Hydroxy-2',4',6'-triisopropyl-3-biphenylcarbaldehyde (**3**)⁴



Dry paraformaldehyde (4.59 g, 153 mmol, 3.25 equiv.), MgCl_2 (14.6 g, 153 mmol, 3.25 equiv.) and **2** (13.9 g, 47.0 mmol, 1.0 equiv.) were added to a 350 mL heavy wall round bottom flask. Dry THF (300 mL) and distilled triethylamine (15.5 g, 153 mmol, 3.25 equiv.) were added consecutively to the flask. The resulting mixture was heated for 12 h at $85\text{ }^\circ\text{C}$. The reaction mixture was cooled to room temperature and aqueous HCl (2.0 M) and water were added. The resulting phases were separated and the aqueous phase was extracted with hexanes ($3 \times 50\text{ mL}$). The organic layer was filtered through a pad of Celite. The combined organic layers were dried to afford **3** as a colorless solid (14.5 g, 96 %).

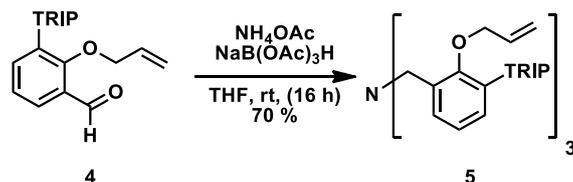
^1H NMR (500 MHz, CDCl_3 , $23\text{ }^\circ\text{C}$, δ): 11.10 (s, 1H), 10.0 (s, 1H), 7.60 (dd, $J = 7.7, 1.8\text{ Hz}$, 1H), 7.36 (dd, $J = 7.3, 1.7\text{ Hz}$, 1H), 7.1 (t, $J = 7.5\text{ Hz}$, 1H), 7.1 (s, 2H), 2.94 (sept, $J = 7.0\text{ Hz}$, 1H), 2.51 (sept, $J = 6.8\text{ Hz}$, 2H), 1.31 (d, $J = 7.0\text{ Hz}$, 6H), 1.09 (dd, $J = 29.6, 6.9\text{ Hz}$, 12H). ^{13}C NMR (125 MHz, CDCl_3 , $23\text{ }^\circ\text{C}$, δ): 196.9, 159.6, 148.7, 147.0, 139.0, 133.0, 130.6, 129.9, 121.0, 120.7, 119.6, 34.4, 30.9, 24.5, 24.2, 24.0. Anal. Calcd. for $\text{C}_{22}\text{H}_{28}\text{O}_2$: C, 81.60; H, 8.33; found: C, 81.44; H, 8.70.

2-(Allyloxy)-2',4',6'-triisopropyl-3-biphenylcarbaldehyde (**4**)⁵



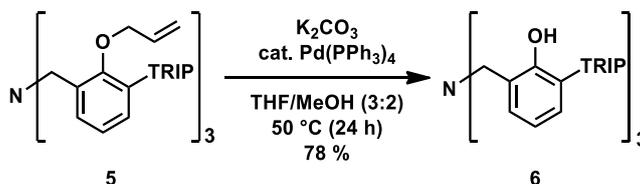
K_2CO_3 (6.42 g, 46.5 mmol, 1.2 equiv.) and **3** (12.6 g, 38.7 mmol, 1.0 equiv.) were added to a 350 mL heavy wall round bottom flask. Dry acetonitrile (200 mL) was added to the flask, followed by addition of allyl bromide (5.62 g, 46.5 mmol, 1.2 equiv.). The resulting mixture was heated for 4.5 hours at $110\text{ }^\circ\text{C}$. The reaction mixture was cooled to room temperature. HCl (aq., 2.0 M) was added and the organic layer was extracted with ethyl acetate ($3 \times 30\text{ mL}$). The combined organic layers were dried to afford **4** as a yellow solid (13.6 g, 97 %).

^1H NMR (500 MHz, CDCl_3 , $23\text{ }^\circ\text{C}$, δ): 10.46 (d, $J = 0.8\text{ Hz}$, 1H), 7.87 (dd, $J = 7.7, 2.0\text{ Hz}$, 1H), 7.39 (dd, $J = 7.5, 1.8\text{ Hz}$, 1H), 7.24 (t, $J = 7.5\text{ Hz}$, 1H), 7.07 (s, 2H), 5.65–5.56 (m, 1H), 5.05–4.97 (m, 2H), 4.03 (dt, $J = 5.8, 1.3\text{ Hz}$, 2H), 2.95 (sept, $J = 6.9\text{ Hz}$, 1H), 2.58 (sept, $J = 6.8\text{ Hz}$, 2H), 1.31 (d, $J = 6.9\text{ Hz}$, 6H), 1.11 (dd, $J = 66.9, 6.8\text{ Hz}$, 12H). ^{13}C NMR (125 MHz, CDCl_3 , $23\text{ }^\circ\text{C}$, δ): 191.0, 163.3, 160.1, 149.1, 146.9, 138.6, 135.0, 132.9, 131.5, 129.9, 127.3, 123.9, 121.2, 118.2, 75.01, 34.4, 30.9, 25.5, 24.2, 23.3. Anal. Calcd. for $\text{C}_{25}\text{H}_{32}\text{O}_2$: C, 82.45; H, 8.75; found: C, 82.37; H, 8.85.

Tris{[2-(allyloxy)-2',4',6'-triisopropyl-3-biphenyl]methyl}amine (5)⁶

Ammonium acetate (0.963 g, 12.5 mmol, 1.0 equiv.) and **4** (13.7 g, 37.5 mmol, 3.0 equiv.) were added to a 350 mL heavy wall round bottom flask. Dry THF (280 mL) was added to the flask followed by addition of sodium triacetoxyborohydride (11.9 g, 56.2 mmol, 4.5 equiv.). The resulting mixture was stirred in the sealed flask at room temperature for 16 h. Saturated sodium bicarbonate was added to the flask and the organic layer was extracted with ethyl acetate (3 × 30 mL). The combined organic layers were dried. The dried solid was washed with pentane (5 × 3 mL). The washed solid was dried to afford **5** as a colorless solid (9.3 g 70 %).

¹H NMR (500 MHz, CDCl₃, 23 °C, δ): 7.74 (dd, *J* = 7.6, 1.7 Hz, 3H), 7.17 (t, *J* = 7.4 Hz, 3H), 7.05 (s, 6H), 7.04 (d, *J* = 1.7 Hz, 3H), 5.53–5.40 (m, 3H), 4.92–4.85 (m, 6H), 3.88 (d, *J* = 5.5 Hz, 6H), 3.78 (s, 6H), 2.93 (sept, *J* = 6.9 Hz, 3H), 2.62 (sept, *J* = 6.9 Hz, 6H), 1.29 (d, *J* = 7.2 Hz, 18H), 1.09 (dd, *J* = 33.1, 6.8 Hz, 36H). ¹³C NMR (125 MHz, CDCl₃, 23 °C, δ): 155.7, 148.2, 146.9, 134.2, 133.7, 133.4, 133.3, 130.6, 129.4, 123.5, 120.8, 116.7, 73.4, 52.6, 34.4, 30.8, 25.7, 24.3, 23.3. Anal. Calcd. for C₇₅H₉₉NO₃: C, 84.29; H, 9.35; N, 1.32; found: C, 84.77; H, 9.39; N, 1.32.

Tris{[2-(hydroxy)-2',4',6'-triisopropyl-3-biphenyl]methyl}amine (6)⁵

K₂CO₃ (3.63 g, 26.2 mmol, 3.0 equiv.), Pd(PPh₃)₄ (0.707 g, 0.07 equiv.), and **5** (9.29 g, 8.74 mmol, 1.0 equiv.) were added to a 350 mL heavy wall round bottom flask. Dry THF (90 mL) and methanol (60 mL) were added to the flask. The resulting mixture was stirred in the sealed flask at 50 °C for 24 h. Distilled water was then added to the flask and the organic layer was extracted with pentane (4 × 30 mL). The combined organic layers were filtered through a pad of Celite. The layers were then filtered through a pad of silica. The combined organic layers were dried to afford **6** as a colorless solid (6.43 g, 78 %).

¹H NMR (500 MHz, CDCl₃, 23 °C, δ): 7.22 (dd, *J* = 7.7, 1.6 Hz, 3H), 7.06 (s, 6H), 6.94 (dd, *J* = 7.5, 1.6 Hz, 3H), 6.85 (t, *J* = 7.6 Hz, 3H), 6.68 (s, 3H), 3.84 (s, 6H), 2.93 (sept, *J* = 6.9 Hz, 3H), 2.56 (sept, *J* = 6.8 Hz, 6H), 1.30 (d, *J* = 6.6 Hz, 18H), 1.01 (dd, *J* = 6.9, 5.1 Hz, 36H). ¹³C NMR (125 MHz, CDCl₃, 23 °C, δ): 153.2, 148.9, 148.1, 130.7, 130.2, 129.9, 126.6, 122.8, 121.3, 119.5, 53.9, 34.5, 30.6, 24.6, 24.2, 24.0. Anal. Calcd. for C₆₆H₈₇NO₃: C, 83.77; H, 9.63; N, 1.21; found: C, 84.12; H, 9.31; N, 1.49.

Synthesis of metal complexes

6-Ti⁷

6 (100.0 mg, 0.106 mmol, 1.0 equiv.) was added to a 20 mL vial followed by addition of 6 mL of dry benzene. Ti(O*i*Pr)₄ (35.3 μ L, 0.117 mmol, 1.1 equiv.) was added to the vial. The mixture was stirred at 23 °C for 12 h. The solution was filtered through a pad of Celite and volatiles were removed *in vacuo* to obtain **6-Ti** as a colorless solid (94.1 mg, 85 %). X-ray quality single crystals were grown by the vapor diffusion (C₆H₆/pentane) at a -40 °C over several days. ¹H NMR (500 MHz, C₆D₆, 23 °C, δ): 7.16 (s, 3H), 7.14–7.12 (m, 6H) 6.94 (d, *J* = 1.50 Hz, 1H), 6.92 (d, *J* = 1.53 Hz, 2H), 6.88 (t, *J* = 7.40 Hz, 3H) 4.16 (d, *J* = 13.76 Hz, 3H), 3.98 (sept, *J* = 6.18 Hz, 1H), 2.91–2.80 (m, 6H), 2.66 (d, *J* = 13.9 Hz, 3H), 2.55 (sept, *J* = 6.83 Hz, 3H), 1.34 (d, *J* = 6.70 Hz, 9H), 1.27 (d, *J* = 6.97 Hz, 9H), 1.26 (d, *J* = 6.97 Hz, 9H), 1.24 (d, *J* = 6.83 Hz, 9H), 1.08 (d, *J* = 6.83 Hz, 9H), 1.07 (d, *J* = 6.97 Hz, 9H), 0.58 (d, *J* = 6.18 Hz, 3H), 0.54 (d, *J* = 6.18 Hz, 3H). ¹³C NMR (125 MHz, C₆D₆, 23 °C, δ): 161.0, 148.1, 147.2, 147.2, 133.6, 131.4, 124.6, 120.6, 120.4, 120.4, 80.4, 58.1, 34.9, 31.2, 31.1, 25.5, 24.7, 24.6, 24.5, 24.4, 24.4, 24.3. IR (KBr, cm⁻¹): 3054 (s (br), C–H), 2958 (s, C–H), 2927 (s, C–H), 2866 (s, C–H), 1445 (s), 1433 (s), 1241(s), 1011(m), 874 (s), 709 (m), 858 (m). Anal. Calcd. for C₆₉H₉₁TiNO₄·(H₂O)_{1.3}: C, 77.47; H, 8.82; N, 1.31; found: C, 77.37; H, 8.74; N, 1.32.

6-V

Et₃N (89.0 μ L, 6.0 equiv.) and **6** (100.0 mg, 0.106 mmol, 1.0 equiv.) were added to a 20 mL vial. Dry toluene (10 mL) was added to the vial. The mixture was stirred at 23 °C for 30 min. VCl₃(THF)₃⁸ (39.6 mg, 0.106 mmol, 1.0 equiv.) was then added to the vial. The resulting mixture was stirred at 60 °C for 12 h. The solvents were removed *in vacuo*. The solid residue was extracted with pentane (4 \times 3 mL). The mixture was filtered through a pad of Celite, and dried *in vacuo* to afford **6-V** as a yellow solid (93.2 mg, 83 %). X-ray quality single crystals were grown from a pentane solution at -40 °C over several days. Anal. Calcd. For C₇₀H₉₂VNO₄·(n-pentane)_{1.2}: C, 79.44; H, 9.33; N, 1.22; found: C, 79.98; H, 8.83; N, 1.44. Solution magnetic moment (C₆D₆): 2.66 μ _B. IR (KBr, cm⁻¹): 2958 (s, C–H), 2930 (s, C–H), 2868 (s, C–H), 1594 (m), 1430 (m), 1360 (s), 1243 (m), 1070(m), 861 (m), 756 (s).

6-Cr

NaH (7.9 mg, 3.1 equiv.) and **6** (100.0 mg, 0.106 mmol, 1.0 equiv.) were added to a 20 mL vial. Dry THF (10 mL) was added to the vial. The resulting mixture was stirred at 23 °C for 30 min. CrCl₃(THF)₃⁹ (39.8 mg, 0.106 mmol, 1.0 equiv.) was then added to the vial. The mixture was stirred at 60 °C for 24 h. The solvents were removed *in vacuo*. The solid residue was extracted with pentane (4 \times 3 mL). The extracted solution was removed *in vacuo* to afford **6-Cr** as a green solid (75.6 mg, 67 %). X-ray quality single crystals were grown from a saturated pentane solution at -40 °C over several days. Anal. Calcd. For C₇₀H₉₂CrNO₄·H₂O: C, 77.74; H, 8.76; N, 1.30; found: C, 77.42; H, 8.86; N, 1.31. Solution magnetic moment (C₆D₆): 3.76 μ _B. IR (KBr, cm⁻¹): 2958 (s (br), C–H), 2927 (s, C–H), 2868 (s, C–H), 1589 (s), 1430 (m), 1360 (s), 1274(m), 1043(m), 859 (s), 752 (s).

6-Mn

NaH (7.9 mg, 0.329 mmol, 3.1 equiv.) and **6** (100.0 mg, 0.106 mmol, 1.0 equiv.) were added to a 20 mL vial. Dry THF (10 mL) was added to the vial. The resulting mixture was stirred at 23 °C for 30 min. Mn(acac)₃ (37.4 mg, 0.106 mmol, 1.0 equiv.) was then added to the vial. The resulting mixture was stirred at 60 °C for 12 h. The solvent was removed *in vacuo*. The solid residue was extracted with diethyl ether (4 × 3 mL). The mixture was filtered through a pad of Celite, and dried *in vacuo* to afford **6-Mn** as a green solid (33.8 mg, 26 %). X-ray quality single crystals were grown from a saturated diethyl ether solution at -40 °C over several days. Anal. Calcd. For C₇₅H₉₉MnNNa₂O₆·(H₂O)_{0.6}: C, 73.70; H, 8.26; N, 1.15; found: C, 73.33; H, 8.15; N, 1.07. Solution magnetic moment (C₆D₆): 6.00 μ_B. IR (KBr, cm⁻¹): 2960 (s, C-H), 2927 (s, C-H), 2868 (s, C-H), 1585 (s), 1503 (m), 1428 (m), 1276 (m), 1070(m), 940 (s), 853 (m), 750 (s).

General procedure for the sulfoxidation reactions catalyzed by 6-Ti^{7b}

The reactions were carried out in an N₂-purged glove box using oven-dried screw-cap NMR tubes. Aqueous H₂O₂ (34.5%; 0.15 mmol) was added to a 600- μ L solution of the corresponding thioanisoles (0.15 mmol), the catalyst 6-Ti (0.0015 mmol) and the internal standard (1,2-dichloroethane) in each solvent. The concentrations of thioanisole, sulphoxide and sulphone were measured by integrating the methyl group signals relative to the internal standard.

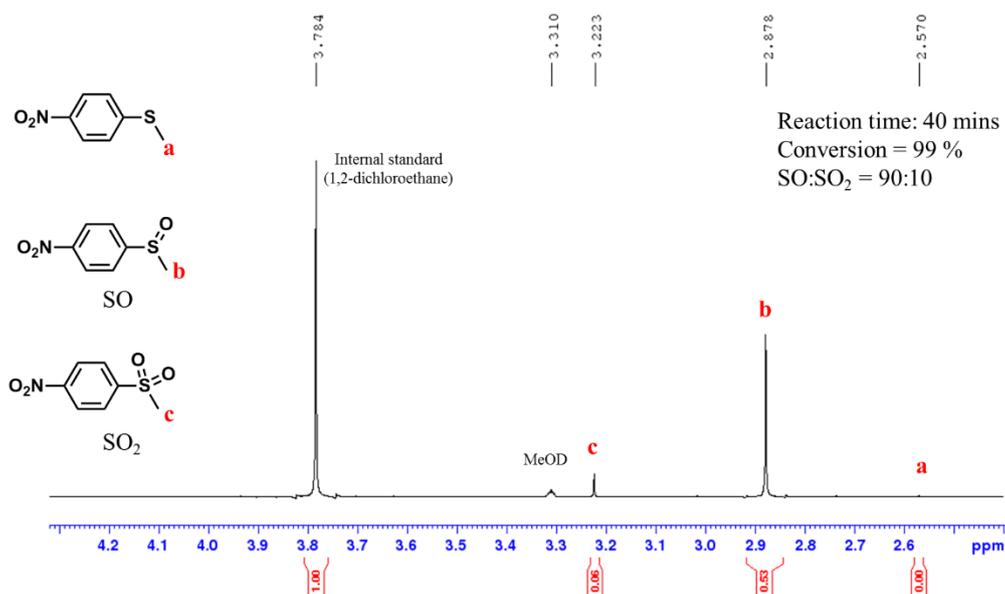


Figure S1. ¹H NMR spectrum for ¹H NMR yield of methyl phenyl sulfoxide in MeOD (Entry 2 in Table 2)

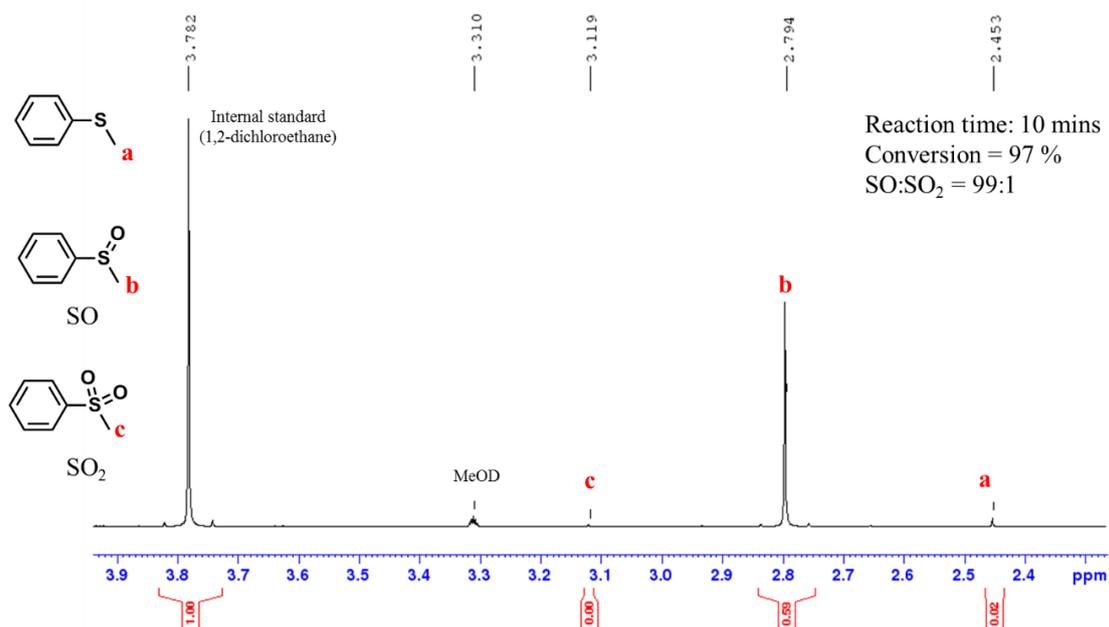


Figure S2. ¹H NMR spectrum for ¹H NMR yield of 4-nitrophenyl methyl sulfoxide in MeOD (Entry 6 in Table 2)

Polymerization of ethylene catalyzed by 6-Cr

Materials

All polymerisations were carried out under an N₂ atmosphere using a glove box, or by using standard Schlenk techniques, unless otherwise stated. All solvents were dried and distilled prior to use according to standard methods. Methylaluminoxane (MAO, 10 wt% in toluene) was purchased from Albemarle Corporation (USA). Methylcyclohexane was purchased from Alfa-Aesar (USA). The MeOH and aqueous HCl solution (34.5 wt%) were purchased from Samchun Pure Chemical Co. (Korea).

Instruments

Molecular weights and PDIs of PE were determined by high-temperature gel permeation chromatography on a PL-GPC 220 instrument with a refractive index detector (Agilent), calibrated with polystyrene standards at 160°C and 1,2,4-trichlorobenzene as the eluent. Melting points of the polymer were determined by differential scanning calorimetry with a DSC-1 instrument (Mettler-Toledo, USA) in standard DSC run mode. The polymer sample was first heated to 200°C to remove thermal history, and a second heating cycle was used to collect the DSC thermogram data at a ramping rate of 10°C min⁻¹. The ¹³C NMR spectra of the PE samples were recorded on a Bruker Avance III 600 instrument at 130°C in an 80:20 v/v solution of C₂H₂Cl₄/C₂D₂Cl₄ in the presence of Cr(III) acetylacetonate, to reduce the relaxation time of the aliphatic carbons. The ¹³C NMR spectra were referenced relative to the solvent signal (74.05 ppm).

General procedure for ethylene polymerisation

Polymerisation reactions were carried out in a 125-mL Parr reactor equipped with a pressure controller. In a glove box, the reactor was charged with solvent (47 mL) and the desired amount of dry MAO. The Cr complex (0.005 mmol) was dissolved in 3 mL of reaction solvent in a separate vial. After the reactor was assembled, it was removed from the glove box. Once the desired temperature was achieved, the reactor was charged with the catalyst solution and ethylene at a constant pressure. Time zero for the reaction was considered as the moment when the catalyst solution was injected into the reactor with ethylene gas. After the reaction was completed, it was terminated by stopping the ethylene feed and adding MeOH (10 mL) to the reactor. The reactor was dismantled in an ice bath. The product mixture was quenched with a mixture of MeOH (450 mL) and dilute aqueous HCl (5 mL) to precipitate the solid product, which was isolated by filtration, dried in a vacuum oven at 60°C, and characterized by DSC and GPC.

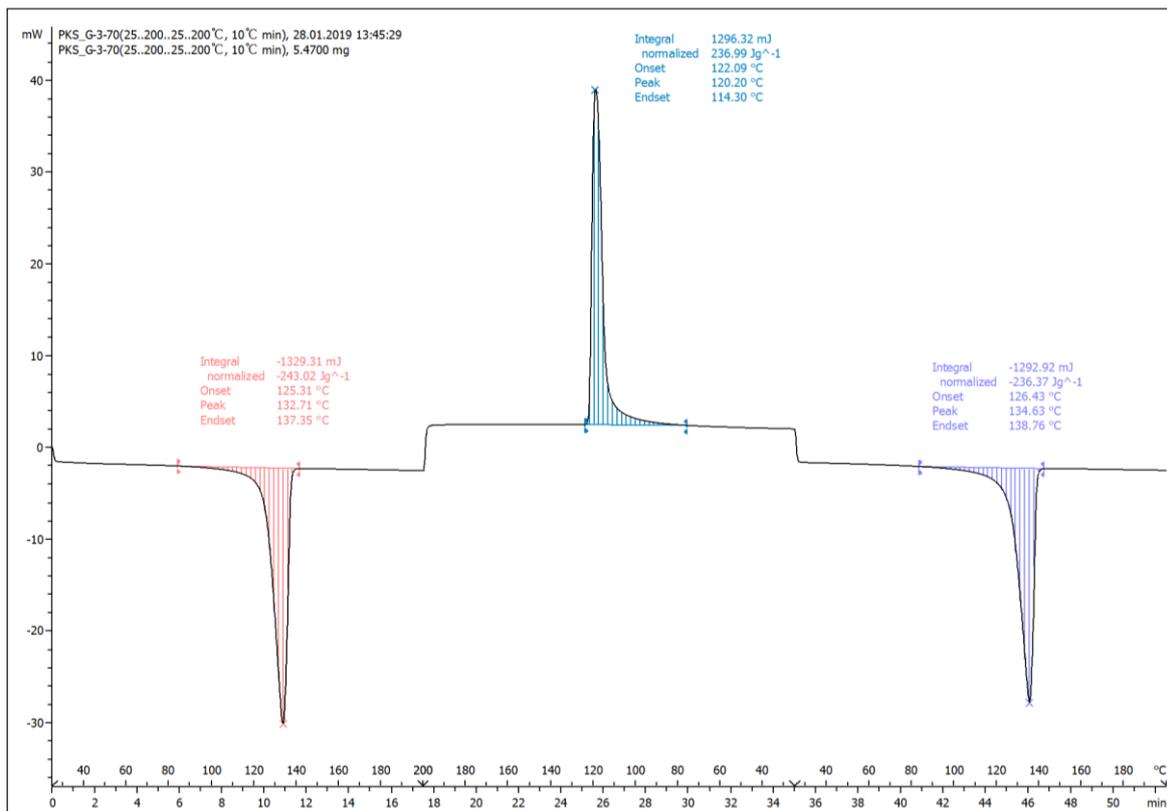


Figure S3. DSC thermogram of polyethylene (entry 1 in Table 3)

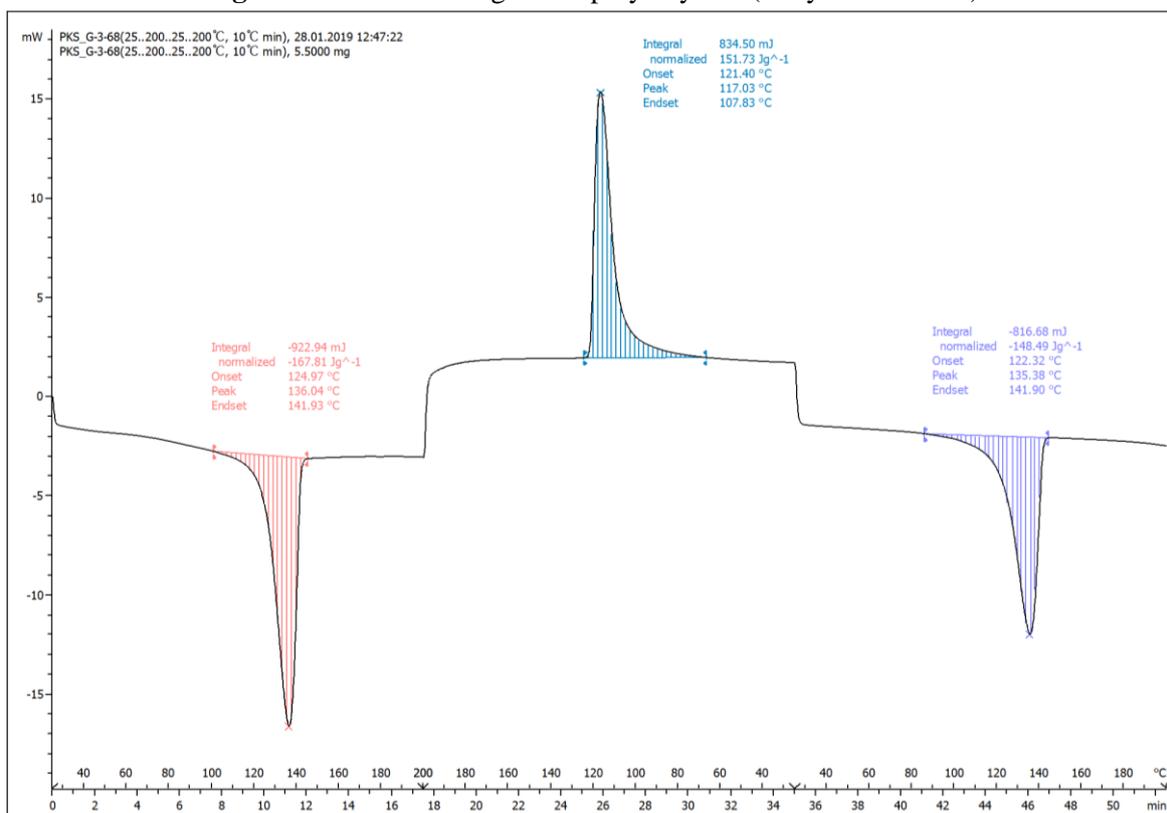
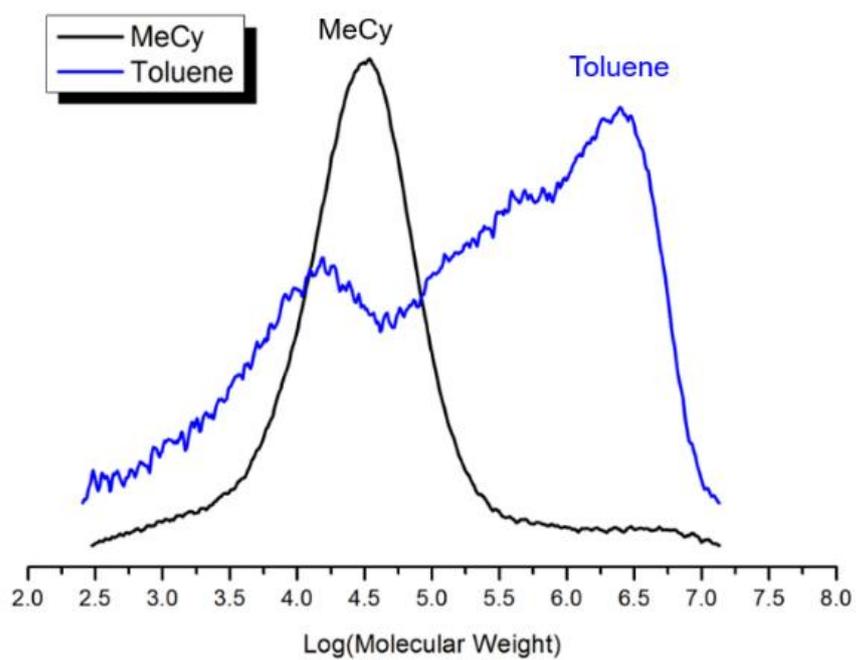


Figure S4. DSC thermogram of polyethylene (entry 3 in Table 3)

(a)



(b)

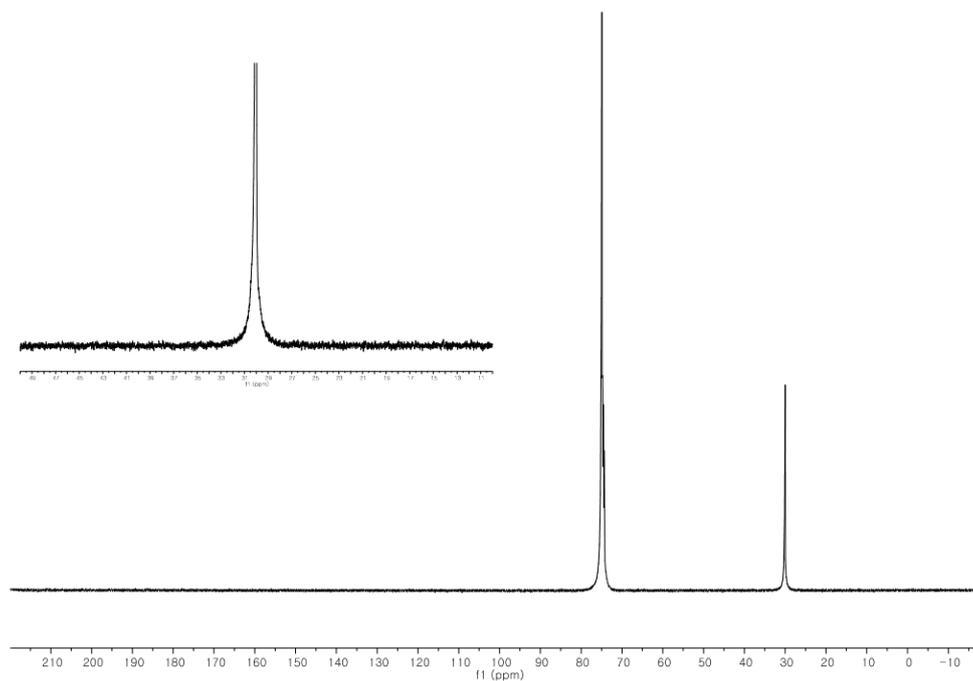


Figure S5. (a) GPC traces of polyethylene samples (entries 1 and 3 in Table 3), (b) ^{13}C NMR spectrum of polyethylene (entry 1).

X-ray Crystallographic Analysis

CCDC 1894388-1834412 contains the supplementary crystallographic data for **6**, **6-Ti**, **6-V**, **6-Cr**, and **6-Mn**. These data can be obtained free of charge via www.ccdc.cam.ac.uk/cgi-bin/catreq.cgi (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

General information

A suitable crystal was coated with Paratone-N oil and the diffraction data were measured at 100 K using either synchrotron radiation on the 2D beamline at the Pohang Accelerator Laboratory, Korea (for **6**, **6-V** and **6-Mn**) or using graphite-monochromated Mo K α ($\lambda = 0.71073 \text{ \AA}$) radiation on a Bruker Venture CMOS diffractometer (for **6-Ti** and **6-Cr**). Using Olex2 software,¹⁰ the structure was solved by the ShelXT structure solution program¹¹ using intrinsic phasing, and refined by the ShelXL refinement package¹² using least squares minimisation. All of the nonhydrogen atoms were refined anisotropically and all hydrogen atoms were added to their ideal positions.

A clear colorless plate-shaped crystal of **6** (0.08 x 0.05 x 0.02 mm³) was picked up with paraton oil and the diffraction data measured at 100 K with synchrotron radiation on a 2D beamline at the Pohang Accelerator Laboratory, Korea.

A clear light colorless hexagonal prism-shaped crystal of **6-Ti** (0.150 x 0.100 x 0.03 mm³) was picked up with paraton oil and the diffraction data measured on a Bruker APEX-II CCD diffractometer. The crystal was kept at 100 K during data collection.

A clear light navy plate-shaped crystal of **6-V** (0.120 x 0.110 x 0.02 mm³) was picked up with paraton oil and the diffraction data measured on a Bruker APEX-II CCD diffractometer. The crystal was kept at 100 K during data collection.

A clear light green plate-shaped crystal of **6-Cr** (0.150 x 0.150 x 0.05 mm³) was picked up with paraton oil and the diffraction data measured on a Bruker APEX-II CCD diffractometer. The crystal was kept at 100 K during data collection.

A clear light green plate-shaped crystal of **6-Mn** (0.150 x 0.04 x 0.02 mm³) was picked up with paraton oil and the diffraction data measured at 100 K with synchrotron radiation on a 2D beamline at the Pohang Accelerator Laboratory, Korea.

Crystal data and structure refinement for 6

Identification code	6
Empirical formula	C ₇₀ H ₉₅ NO ₄
Formula weight	1014.46
Temperature/K	100
Crystal system	monoclinic
Space group	P2 ₁ /c
a/Å	22.089(4)
b/Å	9.862(2)
c/Å	27.858(6)
α/°	90
β/°	93.81(3)
γ/°	90
Volume/Å ³	6055(2)
Z	4
ρ _{calc} /cm ³	1.113
μ/mm ⁻¹	0.067
F(000)	2216.0
Crystal size/mm ³	0.08 × 0.05 × 0.02
Radiation	synchrotron (λ = 0.70000)
2Θ range for data collection/°	2.93 to 49.426
Index ranges	-25 ≤ h ≤ 25, -11 ≤ k ≤ 11, -32 ≤ l ≤ 32
Reflections collected	37868
Independent reflections	10276 [R _{int} = 0.0627, R _{sigma} = 0.0640]
Data/restraints/parameters	10276/0/700
Goodness-of-fit on F ²	0.792
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0621, wR ₂ = 0.1976
Final R indexes [all data]	R ₁ = 0.0945, wR ₂ = 0.2247
Largest diff. peak/hole / e Å ⁻³	0.41/-0.37

X-ray crystal structure of **6**

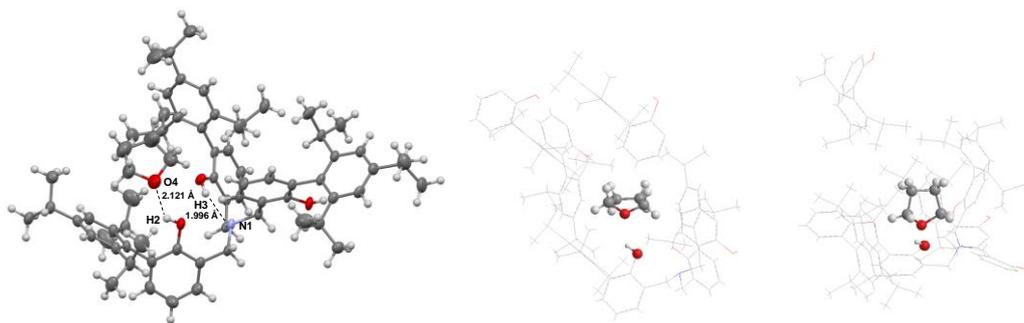


Figure S6. X-ray crystal structures of **6** with thermal ellipsoids at the 50% probability level. Selected bond lengths (Å) for **6**: H2–O4 2.121, H3–N1 1.996.

X-ray crystal structure of triisopropylphenyl amino triphenolate (TRIP-ATP). TRIP-ATP (**6**) was crystallized in THF solution at -20°C . Interestingly, a THF molecule crystallized inside a pocket surrounded by four TRIP-ATP ligands through one strong hydrogen bond with one hydroxyl group (the $\text{O}_{\text{THF}}\cdots\text{H}-\text{O}$ distance is 2.121 Å) (Figure S6). The other phenol interacts with the nitrogen atom (the $\text{N}\cdots\text{H}-\text{O}$ distance is 1.996 Å) at the same side of the phenol group interacting with the THF molecule. The last phenol is located at another side, possibly due to steric hindrance of the TRIP group.

Crystal data and structure refinement for 6-Ti

Identification code	6-Ti
Empirical formula	C ₉₀ H ₁₁₂ NO ₄ Ti
Formula weight	1319.70
Temperature/K	100
Crystal system	trigonal
Space group	R-3
a/Å	23.4039(2)
b/Å	23.4039(2)
c/Å	24.9083(5)
α/°	90
β/°	90
γ/°	120
Volume/Å ³	11815.5(3)
Z	6
ρ _{calc} /cm ³	1.113
μ/mm ⁻¹	0.158
F(000)	4278.0
Crystal size/mm ³	0.15 × 0.1 × 0.03
Radiation	MoKα (λ = 0.71073)
2θ range for data collection/°	2.59 to 72.854
Index ranges	-39 ≤ h ≤ 38, -32 ≤ k ≤ 33, -38 ≤ l ≤ 41
Reflections collected	38020
Independent reflections	12774 [R _{int} = 0.0436, R _{sigma} = 0.0588]
Data/restraints/parameters	12774/54/321
Goodness-of-fit on F ²	1.059
Final R indexes [I >= 2σ (I)]	R ₁ = 0.0784, wR ₂ = 0.2231
Final R indexes [all data]	R ₁ = 0.1226, wR ₂ = 0.2583
Largest diff. peak/hole / e Å ⁻³	2.15/-0.63

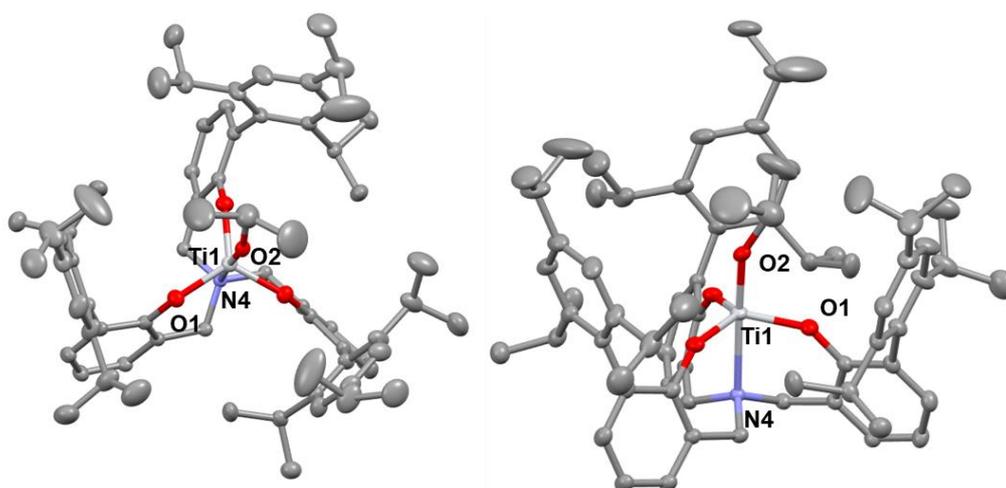


Figure S7. X-ray crystal structures of **6-Ti** thermal ellipsoids at the 50% probability level. Hydrogen atoms were omitted for clarity (Top view and side view).

Crystal data and structure refinement for 6-V

Identification code	6-V
Empirical formula	C ₇₀ H ₉₂ NO ₄ V
Formula weight	1062.38
Temperature/K	100
Crystal system	monoclinic
Space group	C2/c
a/Å	37.206(7)
b/Å	14.294(3)
c/Å	24.650(5)
α/°	90
β/°	95.33(3)
γ/°	90
Volume/Å ³	13053(5)
Z	8
ρ _{calc} /cm ³	1.081
μ/mm ⁻¹	0.197
F(000)	4592.0
Crystal size/mm ³	0.12 × 0.11 × 0.02
Radiation	synchrotron (λ = 0.7000)
2θ range for data collection/°	3.054 to 49.426
Index ranges	-42 ≤ h ≤ 43, -16 ≤ k ≤ 16, -28 ≤ l ≤ 28
Reflections collected	19755
Independent reflections	10736 [R _{int} = 0.0148, R _{sigma} = 0.0256]
Data/restraints/parameters	10736/12/714
Goodness-of-fit on F ²	1.057
Final R indexes [I >= 2σ (I)]	R ₁ = 0.0862, wR ₂ = 0.2447
Final R indexes [all data]	R ₁ = 0.0901, wR ₂ = 0.2498
Largest diff. peak/hole / e Å ⁻³	1.54/-0.76

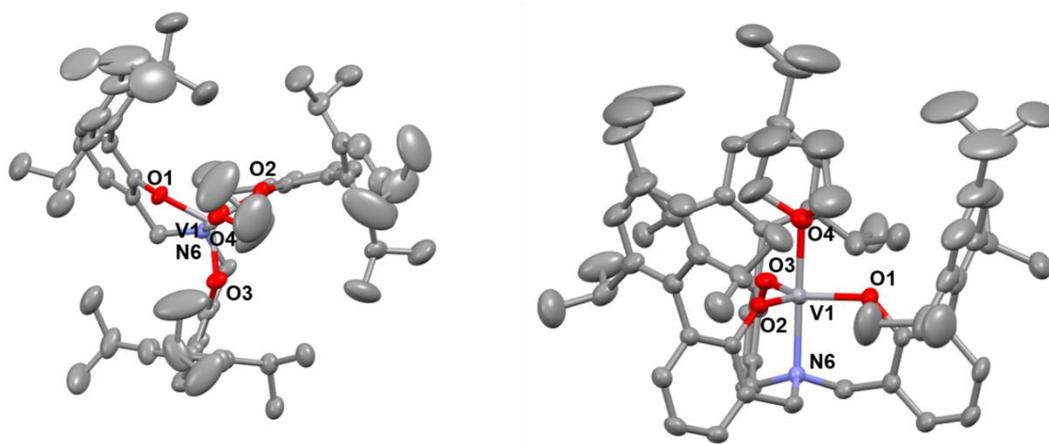


Figure S8. X-ray crystal structures of **6-V** thermal ellipsoids at the 50% probability level. Hydrogen atoms were omitted for clarity (Top view and side view).

Crystal data and structure refinement for 6-Cr

Identification code	6-Cr
Empirical formula	C _{72.5} H ₉₈ CrNO ₄
Formula weight	1099.51
Temperature/K	100
Crystal system	Triclinic
Space group	P-1
a/Å	14.1640(11)
b/Å	14.4132(11)
c/Å	18.4865(14)
α/°	108.161(3)
β/°	91.379(3)
γ/°	110.604(3)
Volume/Å ³	3318.4(4)
Z	2
ρ _{calc} /cm ³	1.100
μ/mm ⁻¹	0.218
F(000)	1192.0
Crystal size/mm ³	0.15 × 0.15 × 0.05
Radiation	MoKα (λ = 0.71073)
2θ range for data collection/°	2.346 to 49.426
Index ranges	-16 ≤ h ≤ 16, -16 ≤ k ≤ 16, -21 ≤ l ≤ 21
Reflections collected	108134
Independent reflections	11295 [R _{int} = 0.0344, R _{sigma} = 0.0175]
Data/restraints/parameters	11295/12/724
Goodness-of-fit on F ²	1.031
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0499, wR ₂ = 0.1315
Final R indexes [all data]	R ₁ = 0.0555, wR ₂ = 0.1369
Largest diff. peak/hole / e Å ⁻³	0.49/-0.49

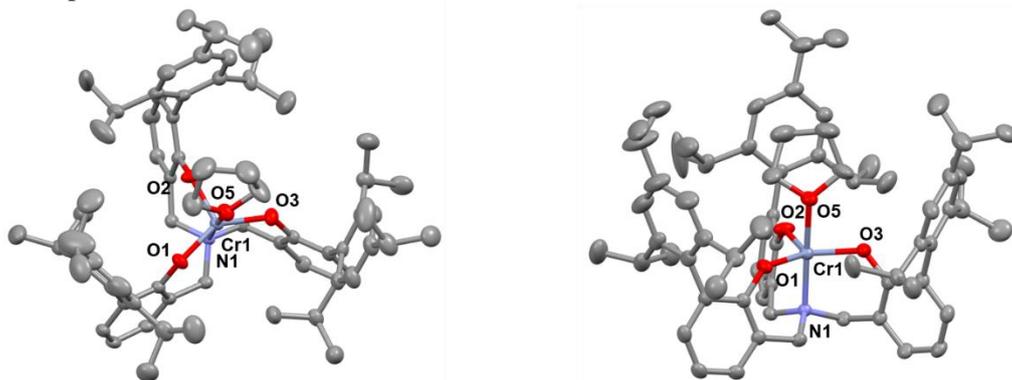


Figure S9. X-ray crystal structures of **6-Cr** thermal ellipsoids at the 50% probability level. Hydrogen atoms were omitted for clarity (Top view and side view).

Crystal data and structure refinement for 6-Mn

Identification code	6-Mn
Empirical formula	C ₇₅ H _{99.06} MnNNa ₂ O ₆
Formula weight	1211.52
Temperature/K	100.0
Crystal system	orthorhombic
Space group	Pbca
a/Å	18.612(4)
b/Å	27.311(6)
c/Å	30.616(6)
α/°	90
β/°	90
γ/°	90
Volume/Å ³	15562(5)
Z	8
ρ _{calc} /cm ³	1.034
μ/mm ⁻¹	0.226
F(000)	5208.0
Crystal size/mm ³	0.15 × 0.04 × 0.02
Radiation	synchrotron (λ = 0.70000)
2θ range for data collection/°	2.964 to 52.744
Index ranges	-23 ≤ h ≤ 23, -34 ≤ k ≤ 34, -38 ≤ l ≤ 38
Reflections collected	60522
Independent reflections	15909 [R _{int} = 0.0618, R _{sigma} = 0.0491]
Data/restraints/parameters	15909/27/840
Goodness-of-fit on F ²	1.066
Final R indexes [I >= 2σ (I)]	R ₁ = 0.0682, wR ₂ = 0.2089
Final R indexes [all data]	R ₁ = 0.1038, wR ₂ = 0.2275
Largest diff. peak/hole / e Å ⁻³	0.76/-0.48

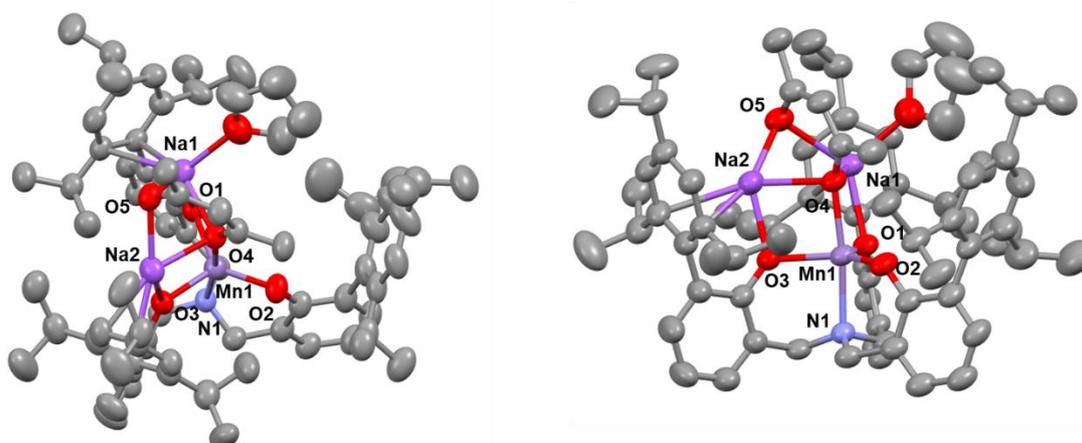


Figure S10. X-ray crystal structures of **6-Mn** thermal ellipsoids at the 50% probability level. Hydrogen atoms were omitted for clarity(Top view and side view).

Table S1. Selected bond angles [°] for **6-Ti**, **6-V**, **6-Cr**, and **6-Mn**.^a

	O-M-O'	N _{anchor} -M-L _{axial}	Geometry index (τ)
6-Ti	118.03	173.78	0.93
6-V	119.96	179.26	0.99
6-Cr	119.79	176.58	0.95
6-Mn	119.96	172.42	0.87

^aSee Figure S11 for atom labeling. O-M-O' values are the average values.

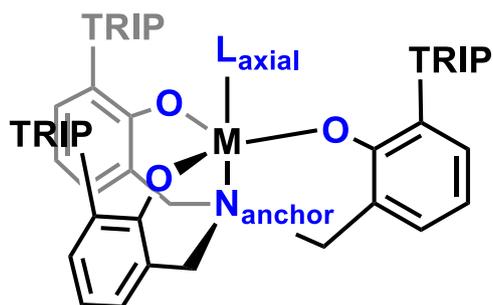
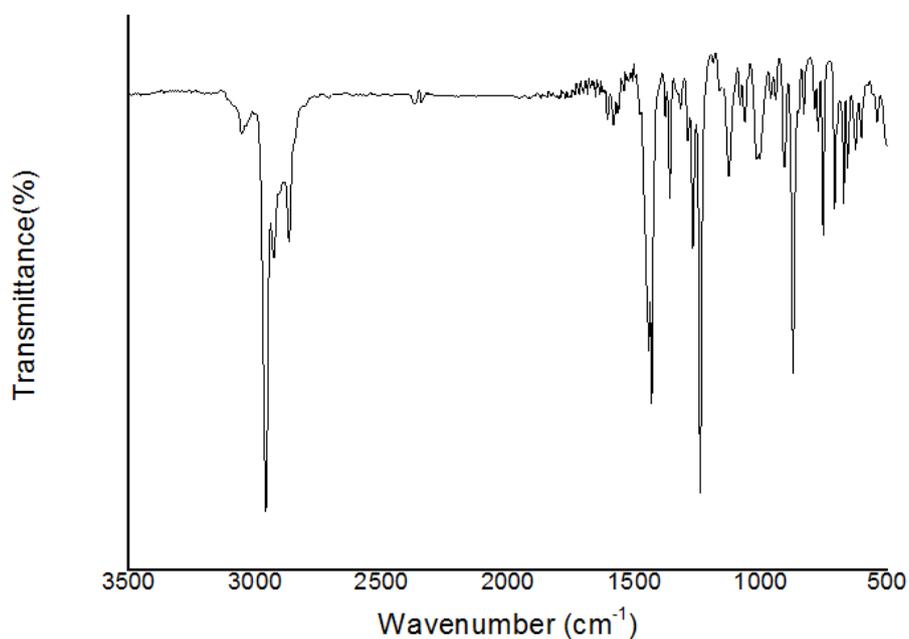


Figure S11. Schematic drawing of complexes with atom labels used in Table S1.

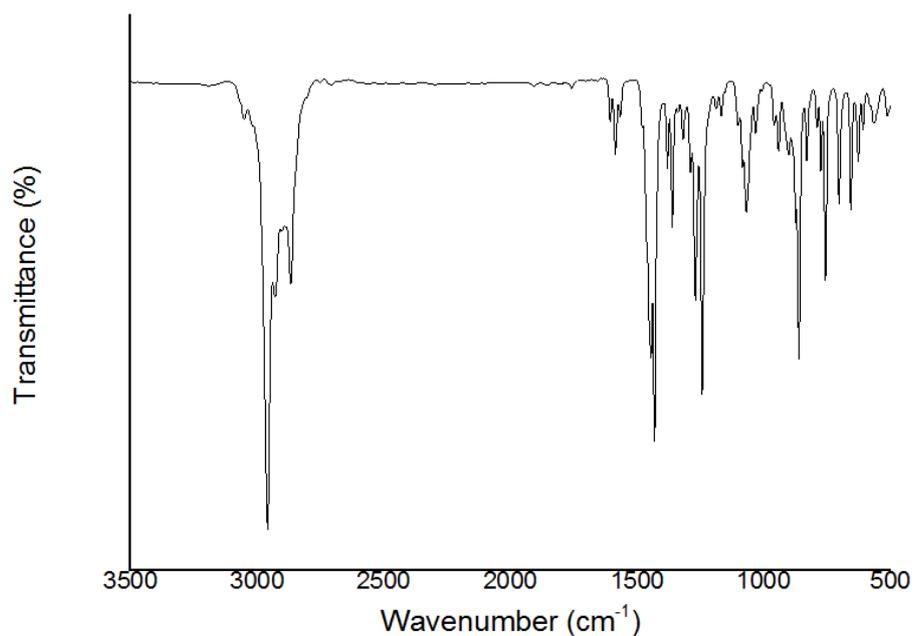
IR spectra of metal complexes

IR spectrum of **6-Ti**



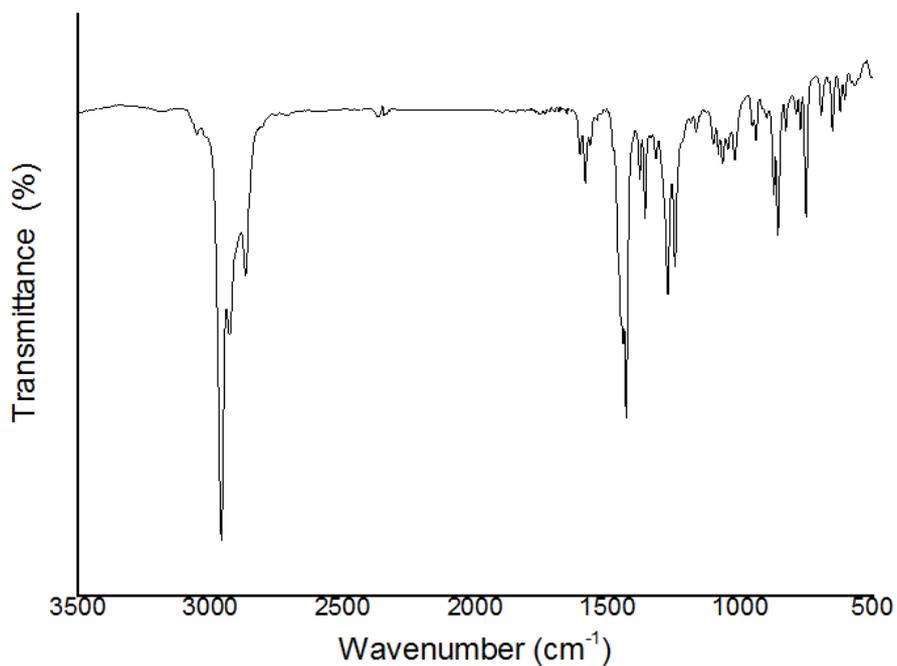
IR (KBr, cm^{-1}): 3054 (s (br), C–H), 2958 (s, C–H), 2927 (s, C–H), 2866 (s, C–H), 1445 (s), 1433 (s), 1241(s), 1011(m), 874 (s), 709 (m), 858 (m).

IR spectrum of **6-V**



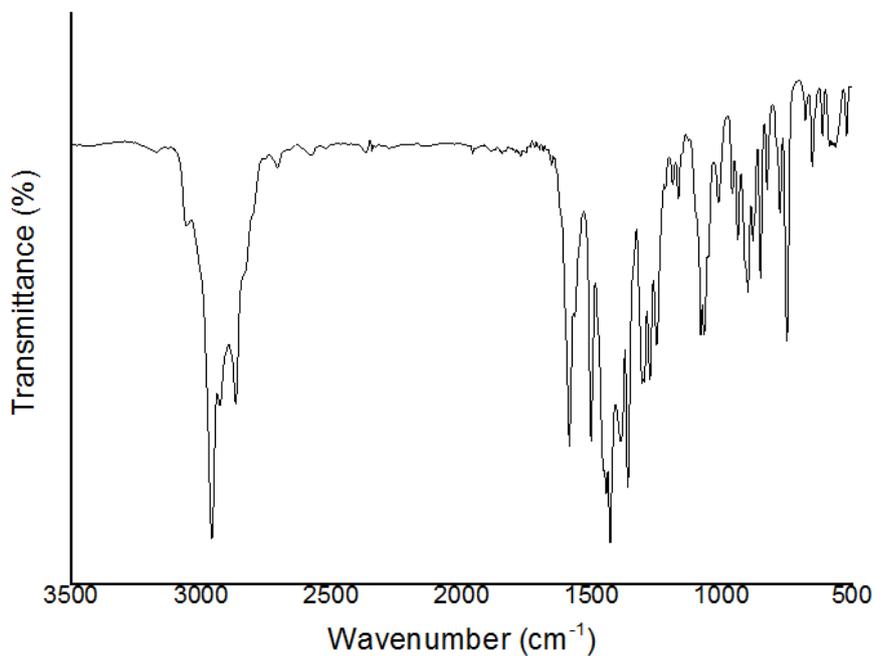
IR (KBr, cm^{-1}): 2958 (s, C–H), 2930 (s, C–H), 2868 (s, C–H), 1594 (m), 1430 (m), 1360 (s), 1243 (m), 1070(m), 861 (m), 756 (s).

IR spectrum of **6-Cr**



IR (KBr, cm^{-1}): 2958 (s (br), C-H), 2927 (s, C-H), 2868 (s, C-H), 1589 (s), 1430 (m), 1360 (s), 1274(m), 1043(m), 859 (s), 752 (s).

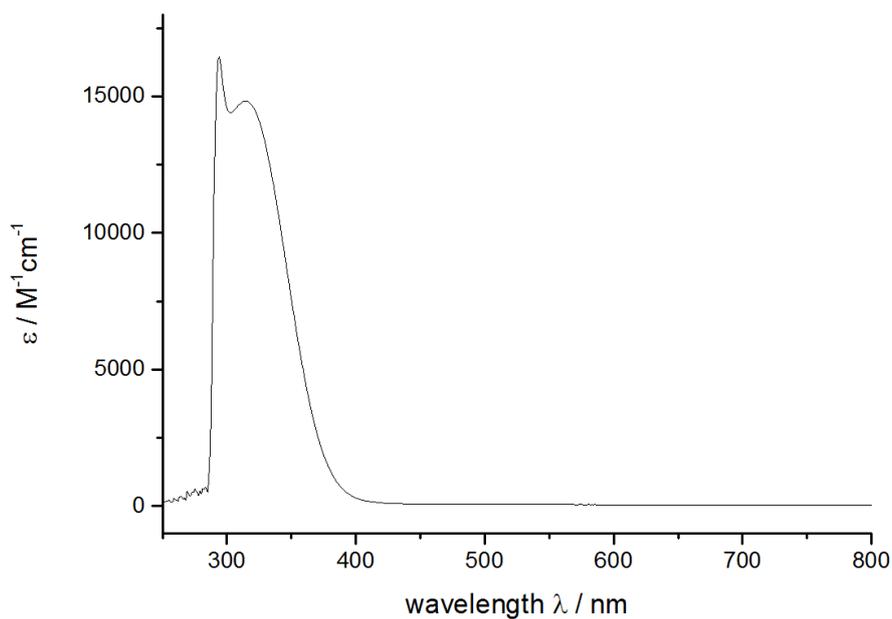
IR spectrum of **6-Mn**



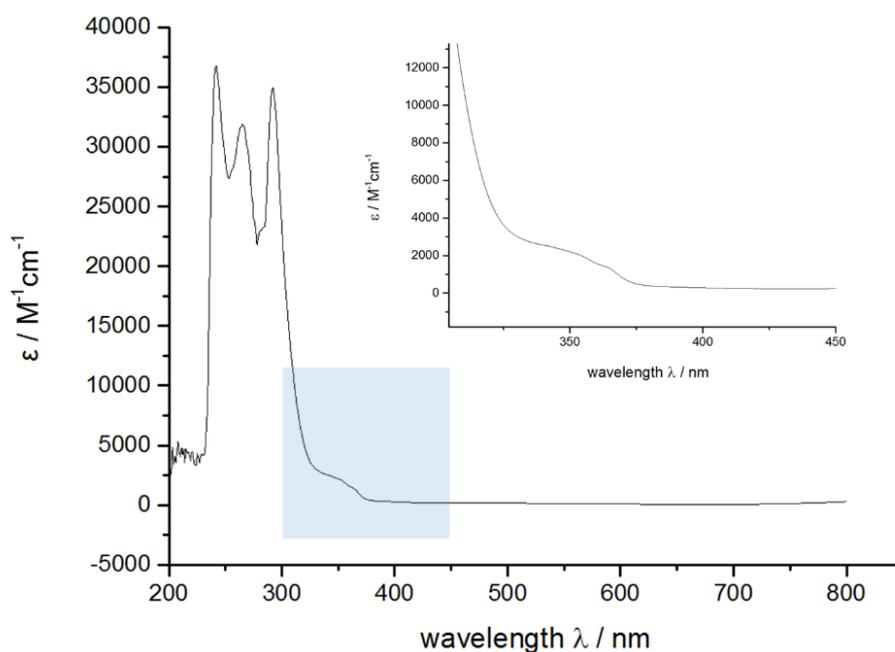
IR (KBr, cm^{-1}): 2960 (s, C-H), 2927 (s, C-H), 2868 (s, C-H), 1585 (s), 1503 (m), 1428 (m), 1276 (m), 1070(m), 940 (s), 853 (m), 750 (s).

UV-Vis spectra of metal complexes

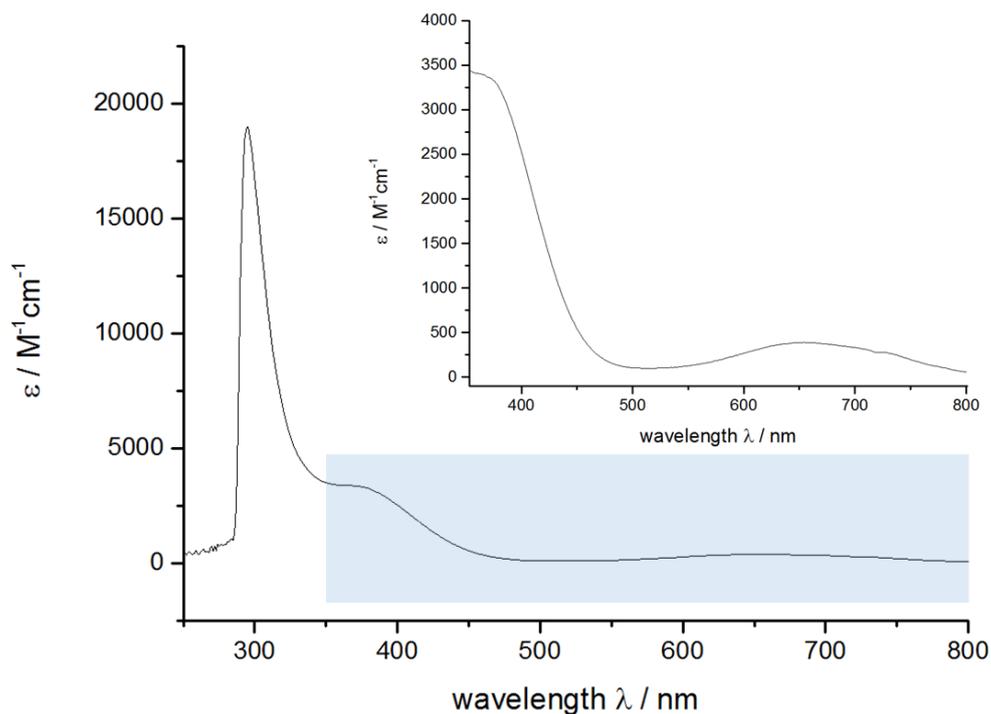
Electronic adsorption spectrum of **6-Ti**, recorded in THF.



Electronic adsorption spectrum and its magnified section of **6-V**, recorded in THF.

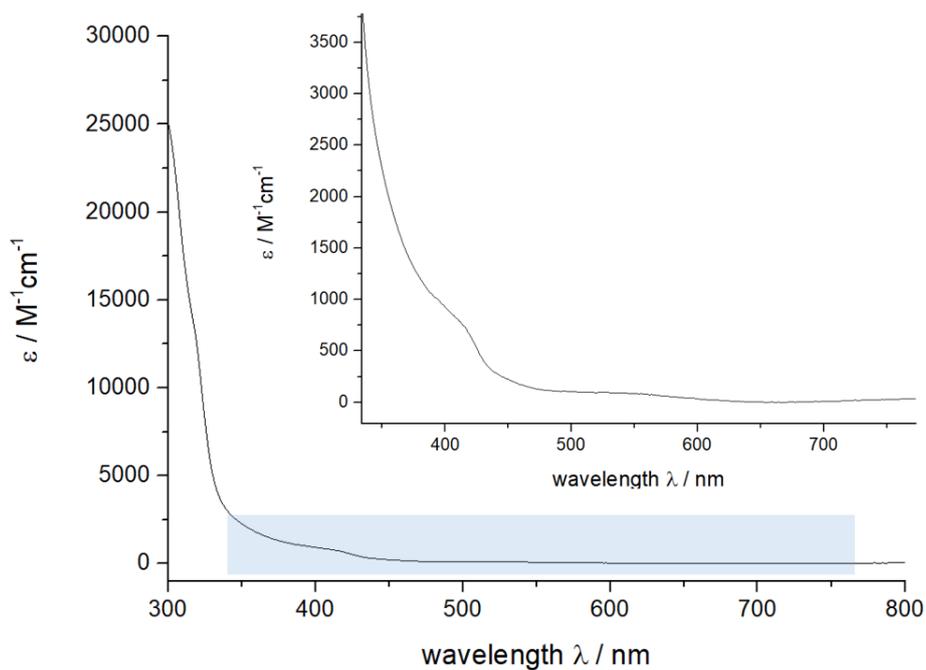


Electronic adsorption spectrum and its magnified section of **6-Cr**, recorded in THF.



UV/Vis (THF, 0.1 mM, 25 °C, nm ($\epsilon = \text{M}^{-1}\text{cm}^{-1}$)): λ (ϵ) = 295 (18990), ca. 379 (ca. 3263, shoulder), 654 (389), ca. 725 (ca. 278, shoulder).

Electronic adsorption spectrum and its magnified section of **6-Mn**, recorded in THF.



UV/Vis (THF, 0.1 mM, 25 °C, nm ($\epsilon = \text{M}^{-1}\text{cm}^{-1}$)): λ (ϵ) = ca. 415 (ca. 736, shoulder), 547 (86).

DFT Calculations

The DFT calculations were performed using Gaussian09¹³ at the clusters at Pohang University of Science and Technology (POSTECH). Geometry optimizations were carried out using the atomic coordinates from crystal structures (for **6-V** and **6-Cr**). The nature of all stationary points calculated from full optimizations was confirmed via frequency analysis, which revealed zero imaginary frequency for the ground state. All geometries were optimized using the B3PW91¹⁴ under standard convergence criteria with the following basis sets, which include SDD quasirelativistic pseudopotentials on V (10) and Cr (10), with their associated basis sets (V and Cr: (8s7p6d1f)/[6s5p3d1f])¹⁵ augmented by polarization functions (V: f, 1.751; Cr: f, 1.941),¹⁶ and 6-31G(d,p)¹⁷ on H, C, N and O. Molecular orbitals of **6-V** and **6-Cr** were generated using an isosurface value of 0.03 on the optimized structures of **6-V** and **6-Cr**, respectively.

Coordinates of optimized structures

6-V

V,0,13.9760155629,3.7180529639,11.1067913268
O,0,13.6033974986,4.6030593201,9.5003697796
O,0,14.2089930806,4.7692288887,12.63984858
O,0,14.0803893887,1.8430253012,11.1434131417
N,0,16.0692021768,3.8270872466,10.6906882252
C,0,14.3693720353,5.0979912132,8.5225630263
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C,0,15.0769434597,0.9697065037,10.9670895211
C,0,14.6400461854,6.5625867302,6.6112098373
C,0,16.4930583121,5.4819853012,12.5404912096
C,0,15.2827266262,5.2886132751,13.2436038635
C,0,17.6003831905,6.0188715327,13.1992406888
C,0,13.8429363888,6.0882576069,7.6574582099
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C,0,13.9655381185,5.4054551238,15.4130125048
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Table S2. Metric comparison between DFT optimized and X-ray determined structures of **6-V** and **6-Cr** (distance, Å).

6-V	V-O _{THF}	V-O1	V-O2	V-O3	V-N1
X-ray data	2.102	1.874	1.866	1.869	2.145
B3PW91	2.123	1.878	1.873	1.872	2.137
6-Cr	Cr-O _{THF}	Cr-O1	Cr-O2	Cr-O3	Cr-N1
X-ray data	2.041	1.879	1.857	1.891	2.069
B3PW91	2.068	1.895	1.888	1.897	2.059

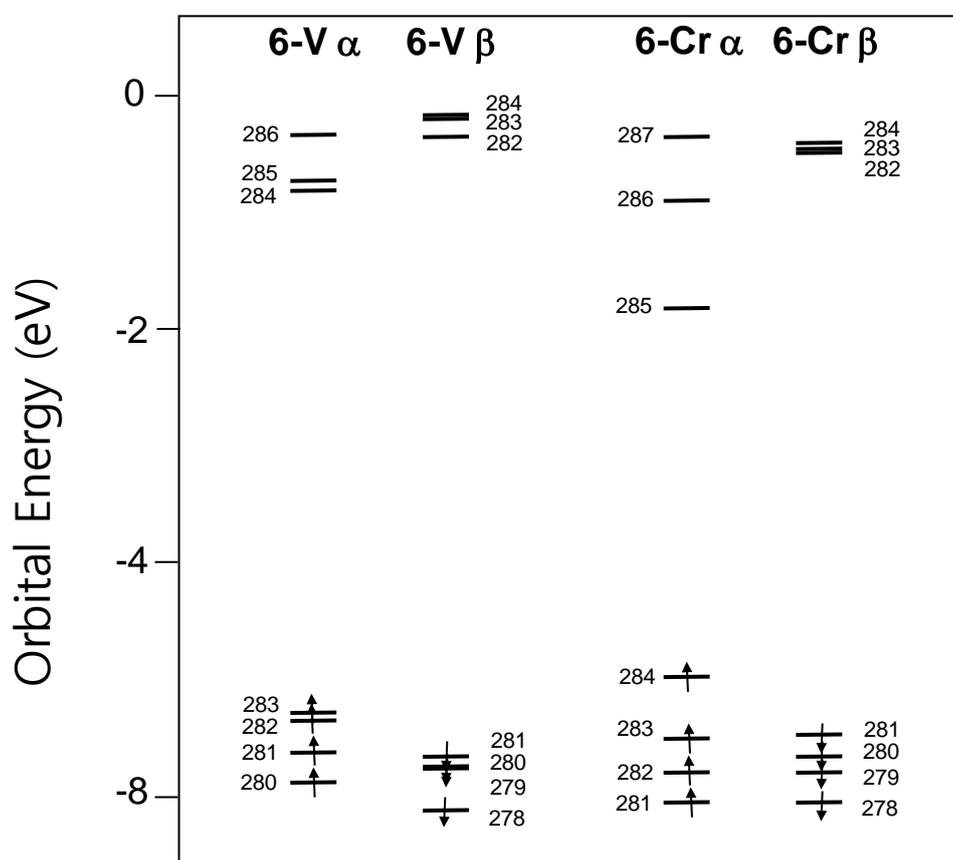


Figure S12. Computed α and β orbital energies for **6-V** and **6-Cr**.

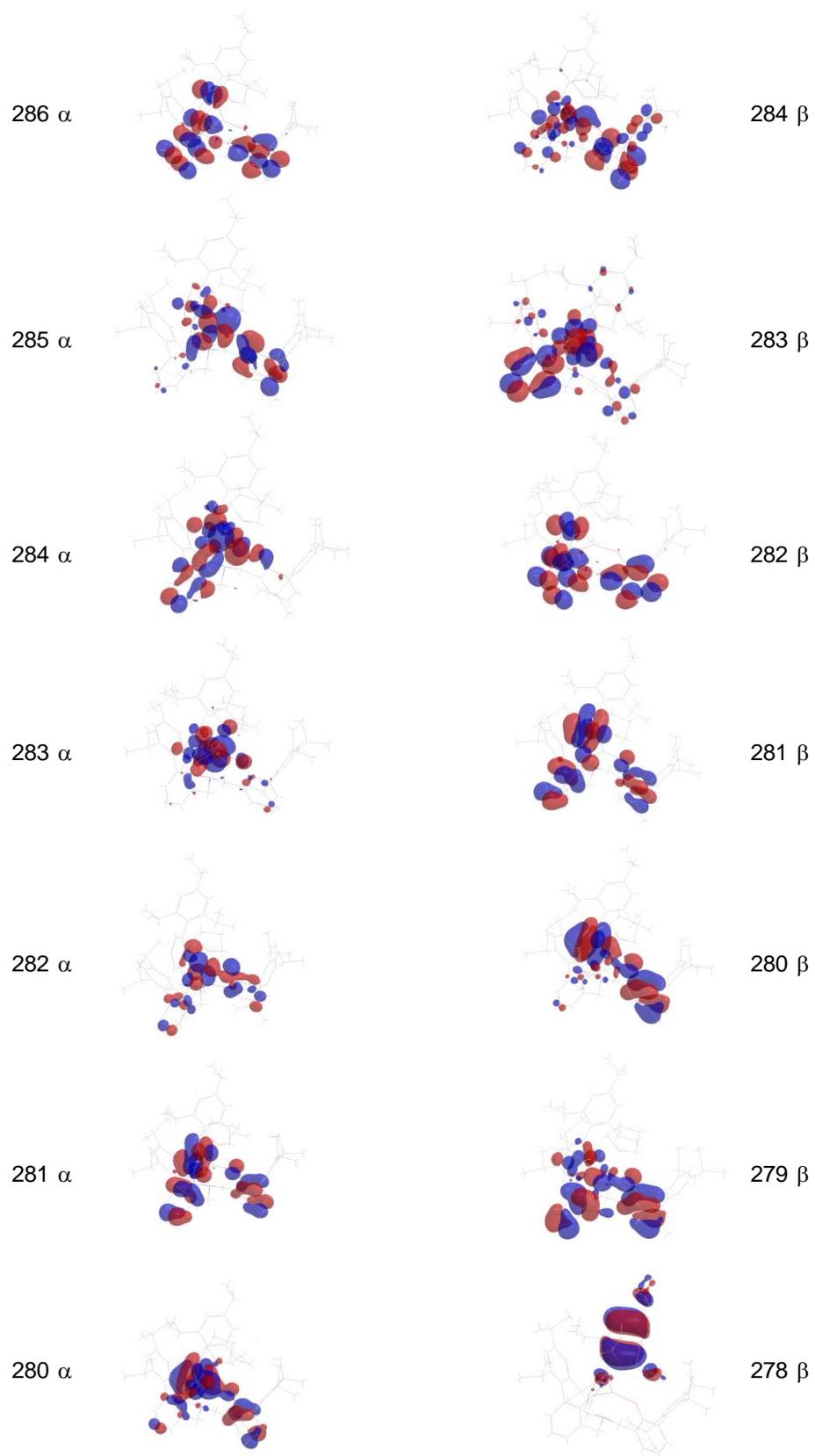


Figure S13. Computed frontier molecular orbitals (α and β) of **6-V**.

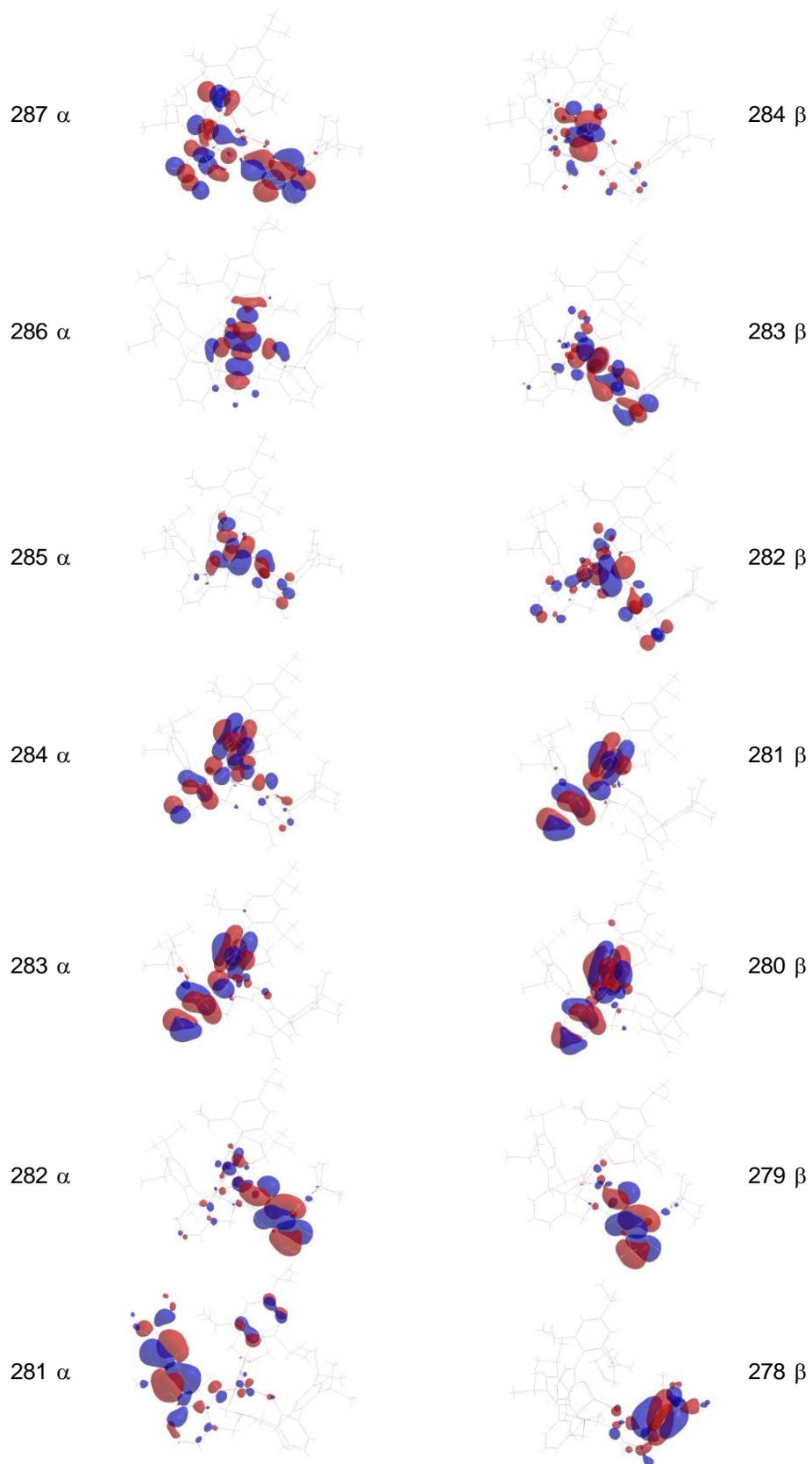
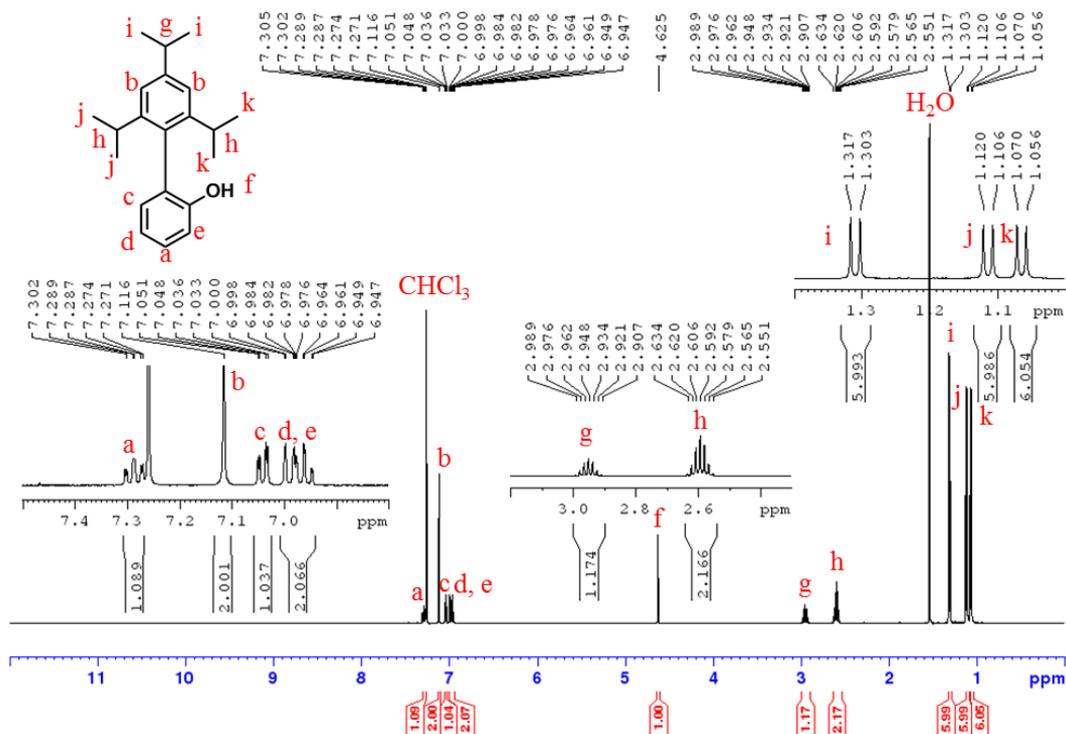


Figure S14. Computed frontier molecular orbitals (α and β) of **6-Cr**.

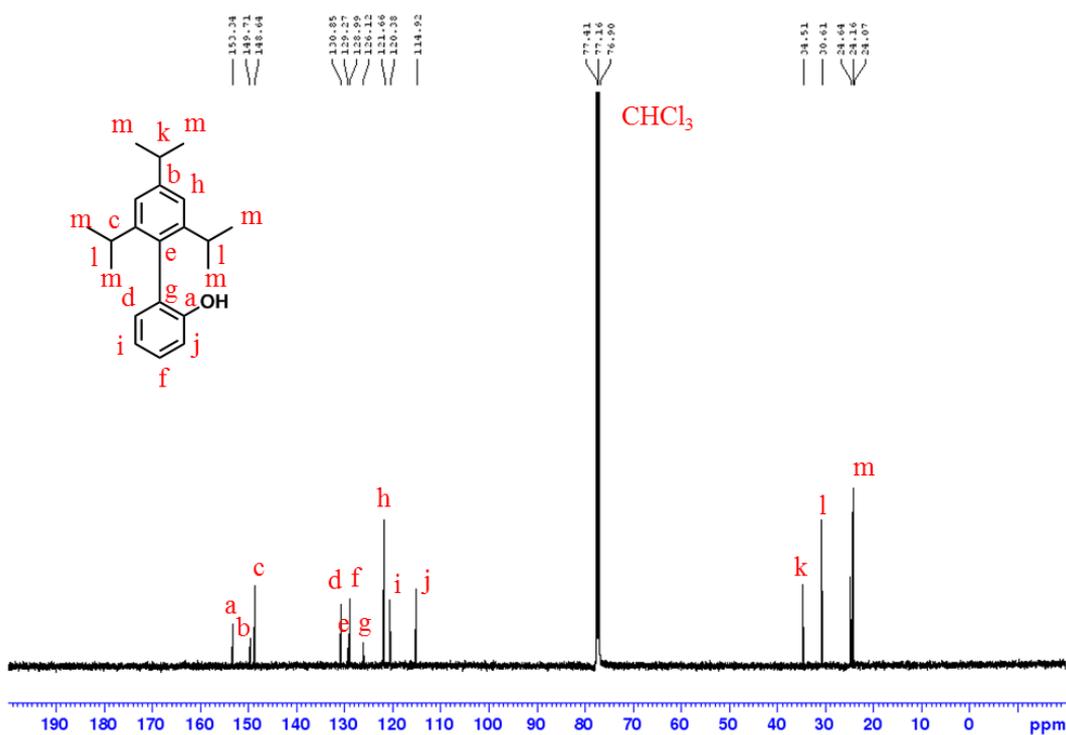
NMR Data

NMR Spectra of 1

¹H-NMR in CDCl₃

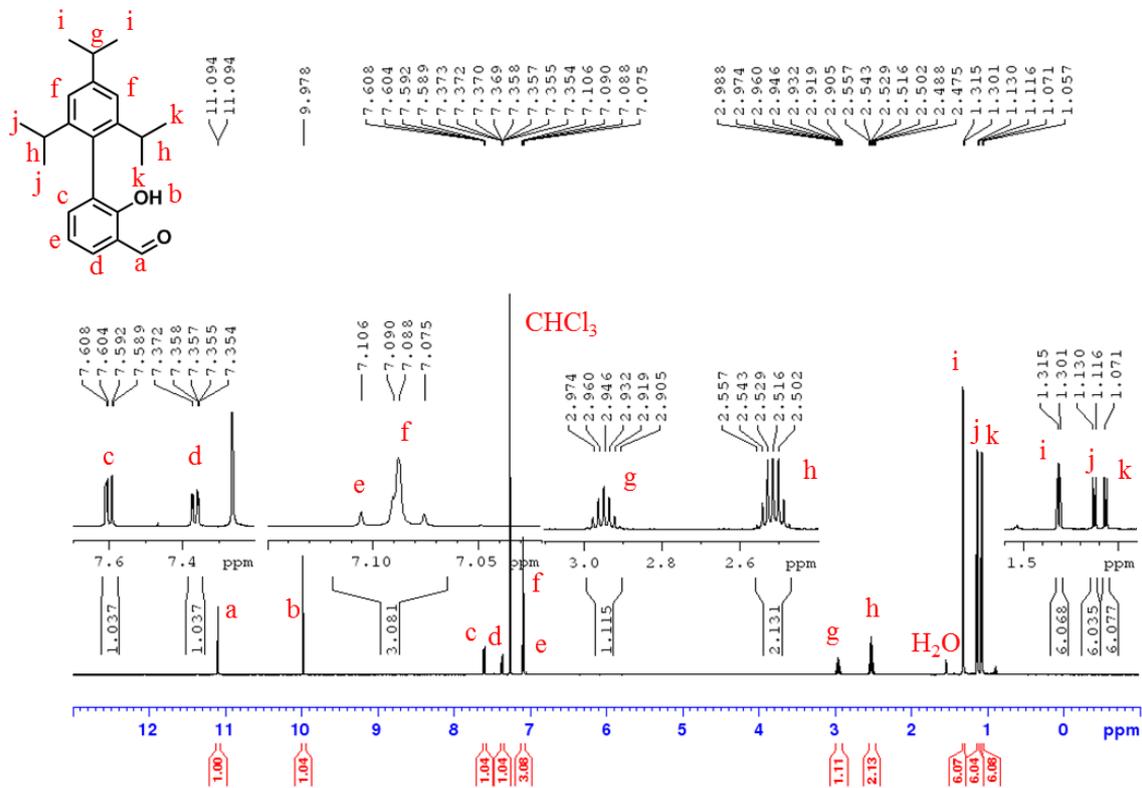


¹³C-NMR in CDCl₃

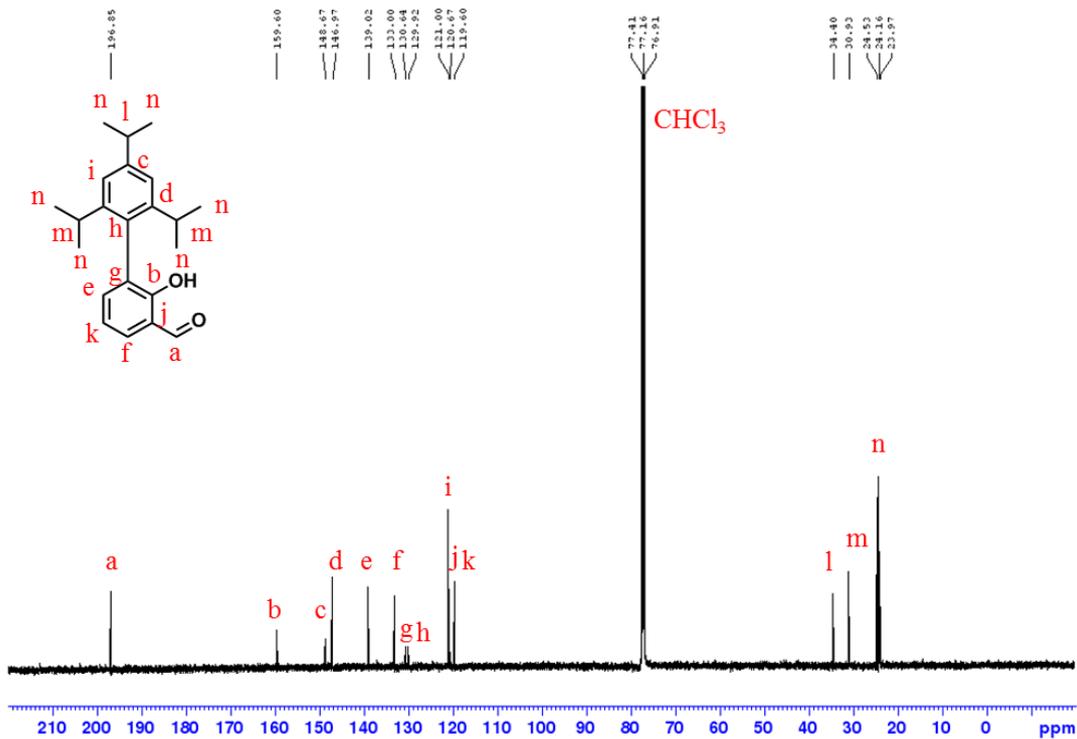


NMR Spectra of 2

¹H-NMR in CDCl₃

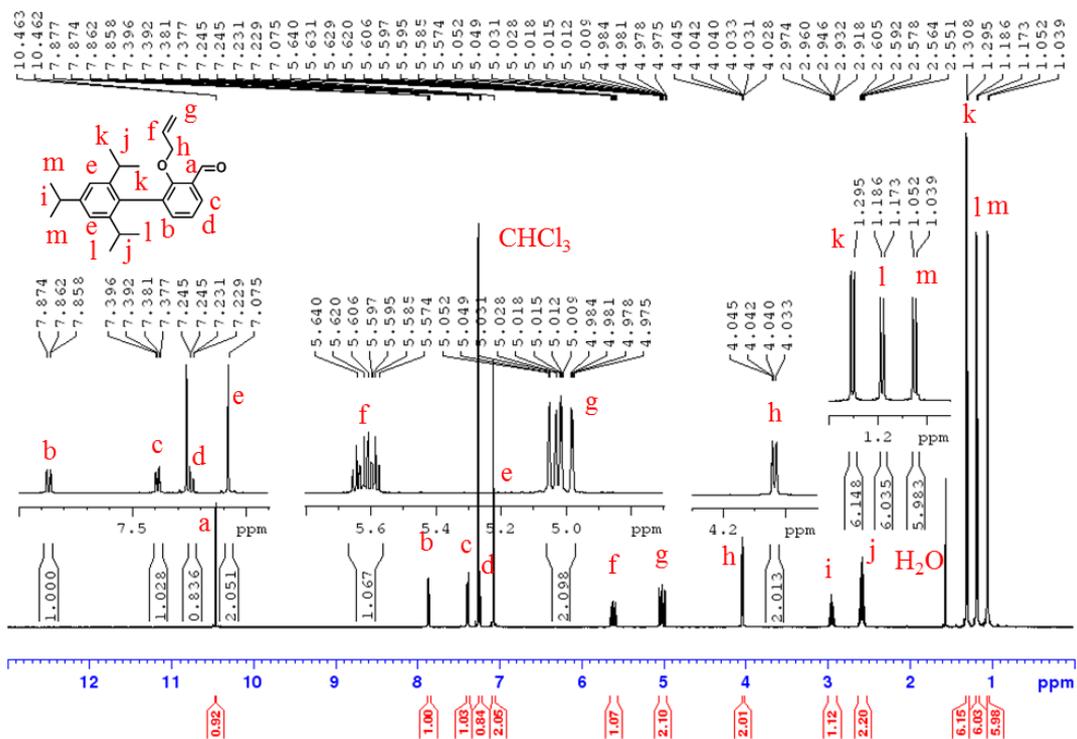


¹³C-NMR in CDCl₃

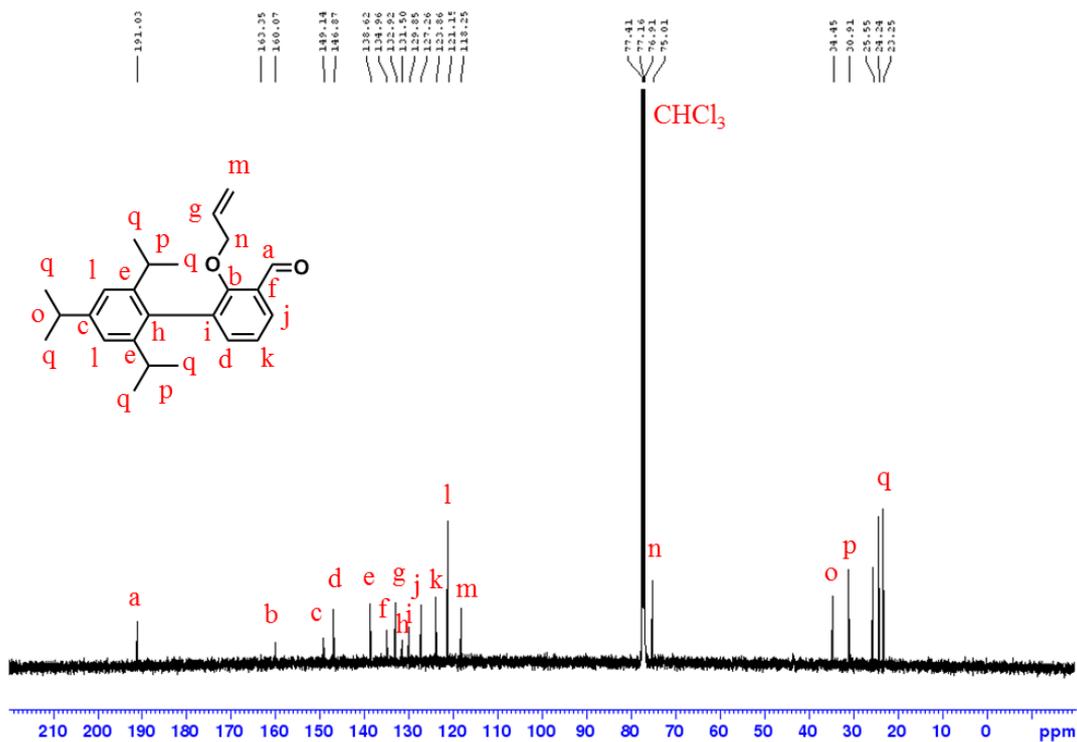


NMR Spectra of 3

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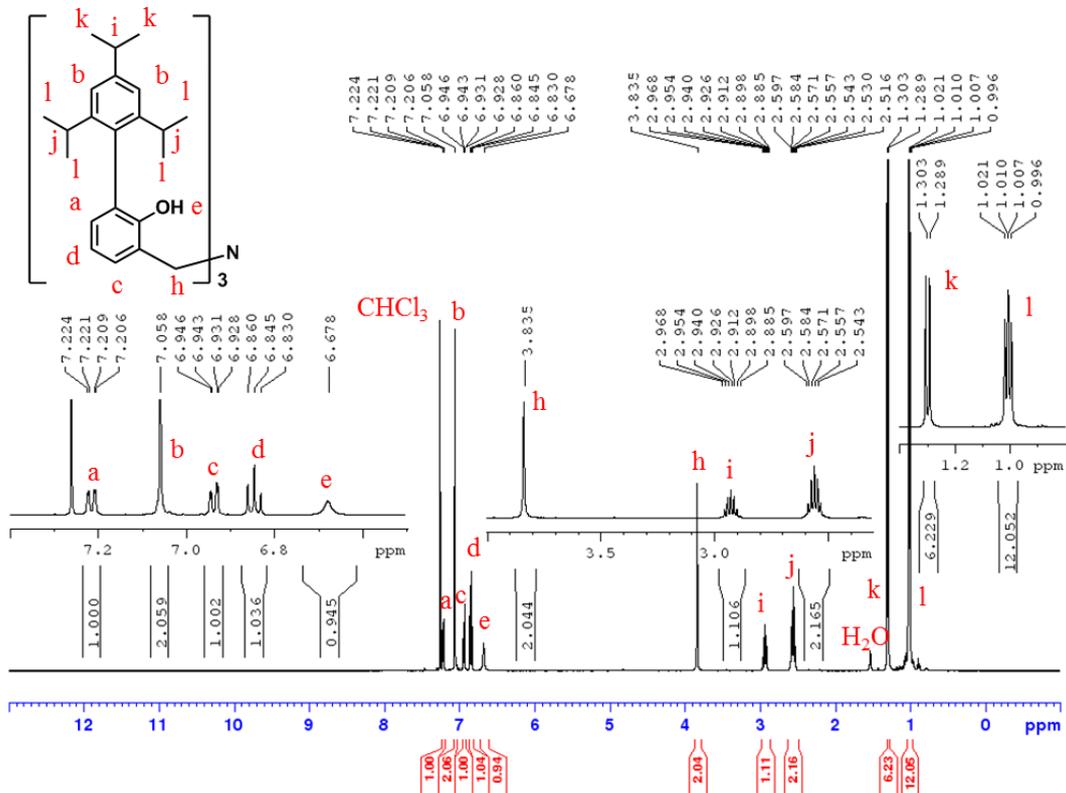


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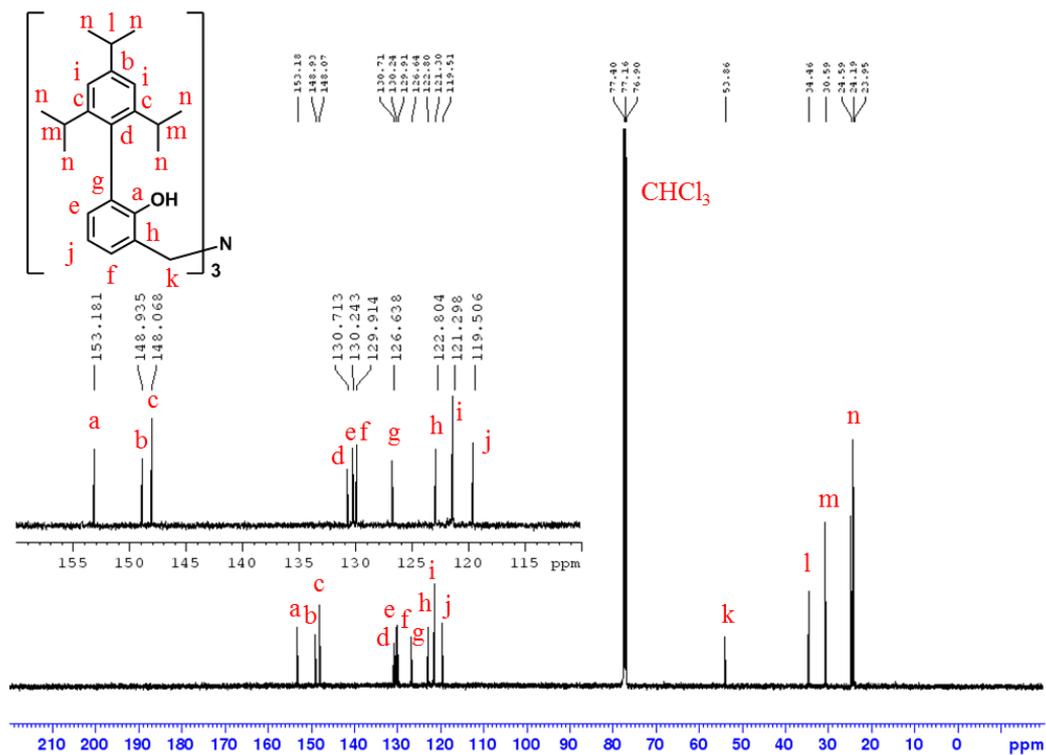


NMR Spectra of 5

¹H-NMR in CDCl₃

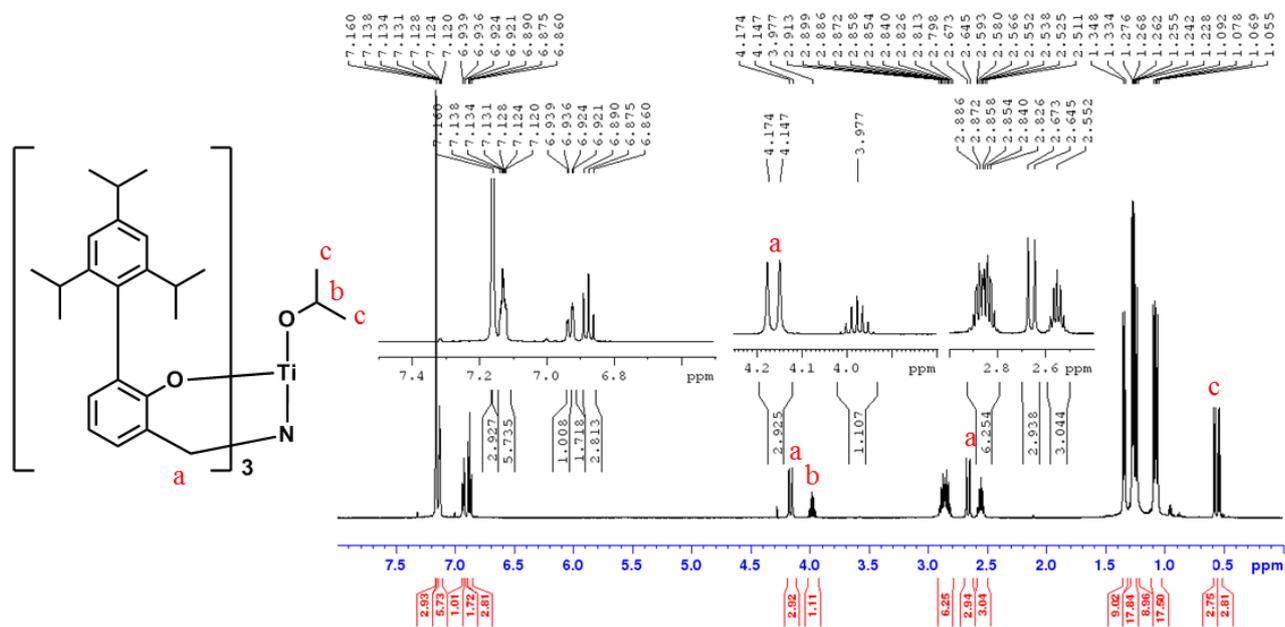


¹³C-NMR in CDCl₃

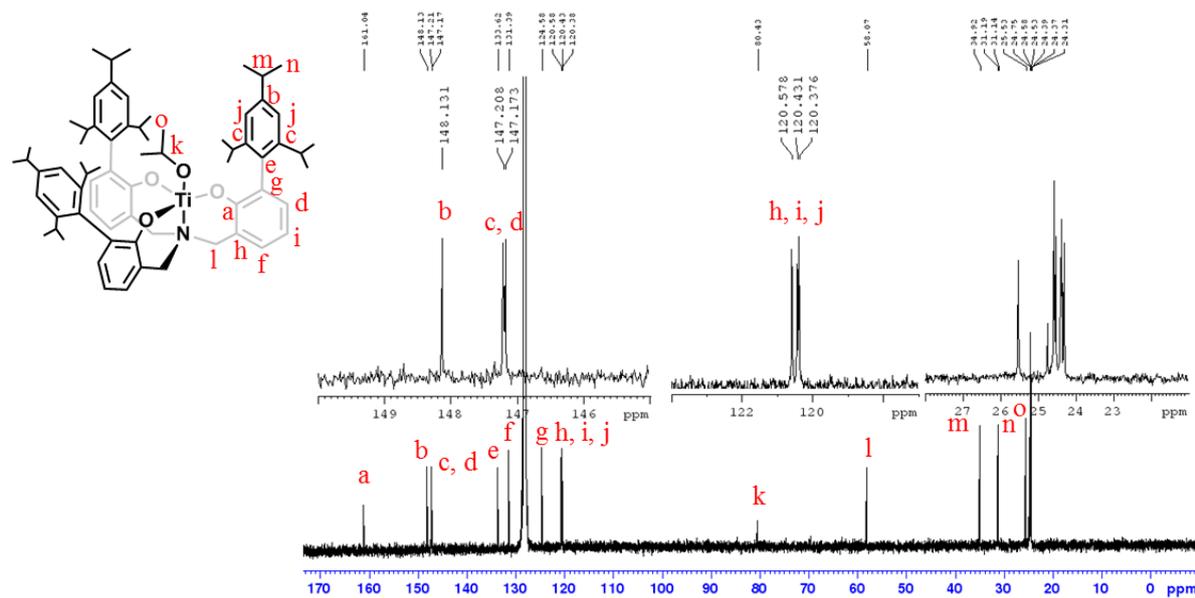


NMR Spectra of 6-Ti

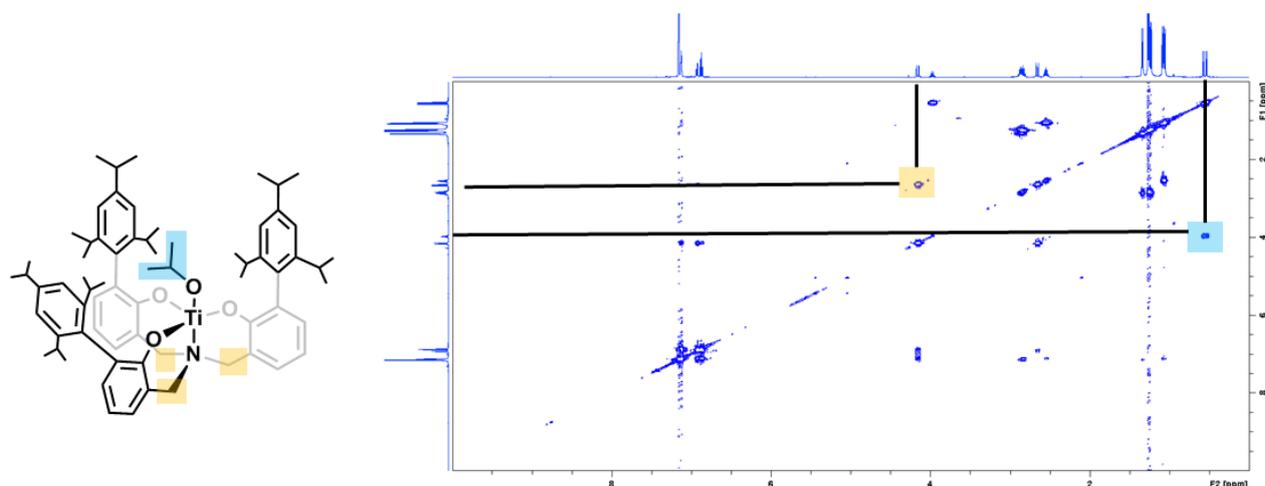
$^1\text{H-NMR}$ in C_6D_6



$^{13}\text{C-NMR}$ in C_6D_6



^1H - ^1H COSY NMR in C_6D_6



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