Supporting Information for:

Fluorinated Bis(phenoxyketimine)titanium Complexes for the Living, Isoselective Polymerization of Propylene: Multiblock Isotactic Polypropylene Copolymers via Sequential Monomer Addition

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General Methods. All manipulations of air- and/or water-sensitive compounds were carried out under dry nitrogen using an MBraun Unilab drybox or standard Schlenk line techniques. ^{1}H and ^{19}F NMR spectra of ligands and complexes were recorded using a Varian Inova (500 MHz) spectrometer and were referenced versus residual non-deuterated solvent shifts (^{1}H) or versus a hexafluorobenzene external standard (^{19}F). ^{13}C NMR spectra of ligands, complexes, and polymers were recorded on a Varian Inova (500 MHz) spectrometer equipped with a ^{1}H/BB switchable with Z-pulse field gradient probe referenced versus residual non-deuterated solvent signals. The polymer samples were dissolved in 1,1,2,2-tetrachloroethane-d_2 in a 5 mm O.D. tube, and spectra were recorded at 135 °C. For quantitative analysis, an inverse decoupling sequence was used with a 30° pulse width, 2.0 s acquisition time, and 10 s delay time. Molecular weights (M_n and M_w) and molecular weight distributions (M_w/M_n) were determined by high temperature gel permeation chromatography (GPC). Analyses were performed using a Waters Alliance GPCV 2000 GPC equipped with a Waters DRI detector and viscometer. The column set (four Waters HT 6E and one Waters HT2) was eluted with 1,2,4-trichlorobenzene containing 0.01 wt. % di-*tert*-butylhydroxytoluene (BHT) at 1.0 mL/min at 140 °C. Data were measured relative to a polyethylene calibration curve (Polymer Standards Service). Polymers were usually placed in a 140 °C oven for 24 h prior to molecular weight measurements. Polymer melting points (T_ms) and glass transition temperatures (T_gs) were measured by differential scanning calorimetry (DSC) using a TA Instruments Q1000 calorimeter equipped with an automated sampler. Analyses were performed in crimped aluminum pans under nitrogen and data were collected from the second heating run at a heating rate of 10 °C/min from –100 to 200 °C, and processed with the TA Q series software. Mass spectra were acquired using a JEOL GCMate II mass spectrometer operating at 3000 resolving power for high resolution measurements in positive ion mode and an electron ionization potential of 70 eV. Samples were introduced via a GC inlet using an Agilent HP 6890N GC equipped with a 30 m (0.25 μm i.d.) HP-5ms capillary GC column. The carrier gas was helium with a flow rate of 1 mL/min. Samples were introduced into the GC using a split/splitless injector at 230 °C with a split ratio of 10:1.

Materials. Toluene and pentane were purified over columns of alumina and copper (Q5) prior to use. Tetrahydrofuran (THF) and methylene chloride were purified over a column of alumina and degassed by three freeze-pump thaw cycles and stored under nitrogen. Benzene-d_6 was distilled from sodium benzophenone ketyl under nitrogen, degassed, and stored over 4Å molecular sieves under nitrogen. Chloroform-*d* was stirred over CaH_2 for several days, degassed by three freeze-pump thaw cycles, vacuum distilled, and stored under nitrogen. Propylene (Matheson, ultra high purity) was purified over columns of alumina COS and copper Q5. Ethylene (Matheson, Matheson purity) was purified over columns of copper Q5 and 4Å molecular sieves. Methylaluminoxane (Akzo Nobel PMAO-IP, 13 wt. % Al in toluene) was dried in vacuo to remove residual trimethylaluminum and used as a solid white powder. Anhydrous 1,2-dichloroethane, $TiCl_4$ (1.0 M solution in toluene), 2,3,4,5,6-pentafluoroaniline, 2,4-dimethylphenol, 2-benzyl-4-methylphenol, 2-bromo-4-methylphenol, 2-chloro-4-methylphenol, 4-chloro-2-methylphenol, 4-fluoro-2-methylphenol, 2-hydroxy-5-methoxybenzaldehyde, and 5,6,7,8-tetrahydro-1-naphthol were purchased from commercial sources and used as received. The synthesis of PKI ligand **L1** and the corresponding complex **1** has been reported.[1]

General procedure for phenoxyketimine ligand synthesis. Phenoxyketimine ligands were synthesized as previously described.[2] Phosphorus pentachloride (5.0 mmol) was added to a methylene chloride solution (20 mL) of the desired amide (5.0 mmol) under a stream of nitrogen. The resultant suspension was stirred at room temperature under nitrogen for 4-6 hours. The solvent was removed in vacuo and the resulting white imidoyl chloride was dried to remove residual $POCl_3$. The crude imidoyl chloride was dissolved in anhydrous 1,2-dichloroethane (5 mL) and transferred via cannula to a Schlenk tube containing aluminum chloride (6.0 mmol) and 1,2-dichloroethane (5 mL). A solution of the desired phenol (5.0 mmol in 5 mL 1,2-dichloroethane) was then added resulting in a color change from light brown to deep orange-red. The reaction was heated at 75 °C under nitrogen overnight. After cooling, the reaction was poured into water (40 mL) and the organic layer was collected and washed with aqueous sodium carbonate solution followed by brine. The organic layer was then dried over sodium sulfate and

filtered. The solvent was removed in vacuo to give the crude ligand as a yellow to orange-red oil. When possible ligands were purified by column chromatography or recystallization.

2-Chloro-4-methyl-6-[phenyl(pentafluorophenylimino)methyl]phenol (L2). *N*-Pentafluorophenylbenzamide (0.77 g, 2.7 mmol) and 2-chloro-4-methylphenol (0.32 mL, 2.7 mmol) were reacted as described above to give the crude product as an orange oil. Recrystallization from methanol at -20 °C produced an orange crystalline solid (0.13 g, 12%). ^{1}H NMR ($CDCl_3$, 500 MHz): 13.51 (s, 1H, O*H*), 7.36-7.44 (m, 4H, Ph*H*), 7.16, 7.15 (s, 1H each, Ar*H*), 6.73 (m, 1H, Ph*H*), 2.14 (s, 3H, ArCH_3). ^{13}C NMR ($CDCl_3$, 125MHz): 181.3 (N=*C*-Ph), 156.1 (Ar*C*-OH), 136.1, 134.2, 131.9, 130.4, 128.8, 128.3, 127.0, 122.6, 120.0 (Ar*C* or Ph*C*), 20.6 (Ar*C*H$_3$). The three Ar_FC-F and Ar_FC_{ipso} signals are hidden. ^{19}F NMR ($CDCl_3$, 470 MHz): -151.6, -162.5, -165.1 (m, Ar_FF). HRMS EI (*m*/*z*): calc. for $C_{20}H_{11}ClF_5NO$, 411.0449; found, 411.0440.

2-Bromo-4-methyl-6-[phenyl(pentafluorophenylimino)methyl]phenol (L3). *N*-Pentafluorophenylbenzamide (2.37 g, 8.24 mmol) and 2-bromo-4-methylphenol (1.0 mL, 8.3 mmol) were reacted as described above to give the crude product as an orange oil. Recrystallization from methanol at -20 °C produced an orange crystalline solid (0.42 g, 11%). ^{1}H NMR ($CDCl_3$, 500 MHz): 13.64 (s, 1H, O*H*), 7.54 (m, 1H, Ar*H*), 7.36-7.42 (m, 3H, Ph*H*), 7.15 (m, 2H, Ph*H*), 6.78 (m, 1H, Ar*H*), 2.14 (s, 3H, ArCH_3). ^{13}C NMR ($CDCl_3$, 125MHz): 181.2 (N=*C*-Ph), 157.0 (Ar*C*-OH), 139.1 (Ar*C*), 138.6 (Ar_FC-F, m, J_{CF} = 250 Hz), 138.3 (Ar_FC-F, m, J_{CF} = 250 Hz), 137.8 (Ar_FC-F, m, J_{CF} = 250 Hz), 134.1, 132.7, 130.4, 128.9, 128.8, 127.0 (Ar*C* or Ph*C*), 123.1 (Ar_FC_{ipso}, m), 119.8, 111.9 (Ar*C*), 20.4 (Ar*C*H$_3$). ^{19}F NMR ($CDCl_3$, 470 MHz): -151.6, -162.5, -165.1 (m, Ar_FF). HRMS EI (*m*/*z*): calc. for $C_{20}H_{11}BrF_5NO$, 454.9944; found, 454.9943.

2-(2-Bromo-4-methylphenoxy)tetrahydro-2*H*-pyran. An oven-dried, Schenk-adapted tube was charged with 2-bromo-4-methylphenol (2.0 mL, 16.5 mmol), 3,4-dihydro-2*H*-pyran (2.2 mL, 24.1 mmol), pyridinium toluene-*p*-sulfonate (0.43 g, 1.65 mmol) and methylene chloride (20 mL) under N_2. The reaction was stirred overnight at room temperature. Brine (20 mL) was added and the organic phase

was separated, dried over Na_2SO_4, filtered and solvent removed in vacuo to yield a colorless oil (4.48 g, 100%). The crude product was used without further purification. ^{1}H NMR (C_6D_6, 500 MHz): 7.27 (d, 1H, J = 1.5 Hz, Ar*H*), 7.06 (d, 1H, J = 8.5 Hz, Ar*H*), 6.77 (dd, 1H, J = 1.5, 8.5 Hz, Ar*H*), 5.27 (t, 1H, J = 2.5 Hz, ArOC*H*), 3.77, 3.35, 2.01 (m, 1H each, ArOTHP-*H*), 1.92 (s, 1H, ArCH_3), 1.78, 1.53 (m, 1H each, ArOTHP-*H*), 1.35 (m, 2H, ArOTHP-*H*), 1.20 (m, 1H, ArOTHP-*H*). ^{13}C NMR (C_6D_6, 125MHz): 152.3 (Ar*C*-OTHP), 134.3, 132.8, 129.4, 117.2, 113.6 (Ar*C*), 97.2 (ArO*C*H), 61.7, 30.8, 25.9 (ArOTHP-*C*), 20.5 (Ar*C*H_3), 18.9 (ArOTHP-*C)*. HRMS EI (*m*/*z*): calc. for $C_{12}H_{15}BrO_2$, 270.0255; found, 270.0244.

5-Methylbiphenyl-2-ol. An oven-dried, Schenk-adapted tube was charged with 2-(2-bromo-4-methylphenoxy)tetrahydro-2*H*-pyran (3.90 g, 14.4 mmol) and $Pd(PPH_3)_4$ (0.83 g, 0.72 mmol) in anhydrous dimethoxyethane (15 mL) under N_2. The solution was degassed for 20 minutes by sparging with N_2: this solution was transferred via cannula to a flask containing a degassed solution of phenylboronic acid (2.11 g, 17.3 mmol) and 2.0 M aqueous Na_2CO_3 (14.4 mL, 28.8 mmol) in dimethoxyethane (15 mL). Under an active N_2 purge, a reflux condenser was attached and reaction was heated to reflux and stirred under N_2 for 16 hours. After cooling, 30 mL of ethyl acetate was added and the solution was dried over Na_2SO_4, filtered and solvent removed in vacuo to yield a black oil. To the crude oil was added HCl (0.3 mL) in methanol (1 mL) and ethyl acetate (1 mL). The solution was heated at 40 °C for 4 hours. After cooling the solvent was removed in vacuo and the crude product was purified by flash chromatography (hexanes/ethyl acetate 20:1) to yield a colorless oil that solidified as a white solid upon drying in vacuo (2.12 g, 80%). ^{1}H NMR (C_6D_6, 300 MHz): 7.31-7.34 (m, 2H, Ar*H*), 7.12-7-17 (m, 2H, Ar*H*), 7.05-7.09 (m, 1H,, Ar*H*), 6.97 (m, 1H, Ar*H*), 6.85-6.88 (m, 1H, Ar*H*), 6.79 (d, 1H, J = 6 Hz, Ar*H*), 4.62 (s, 1H, ArO*H*), 2.11 (s, 3H, ArCH_3). ^{13}C NMR (C_6D_6, 125MHz): 151.4 (Ar*C*-OH), 138.5, 131.5, 130.2, 130.1, 129.8, 129.5, 128.8, 127.9, 116.6 (Ar*C* or Ph*C*), 20.8 (Ar*C*H_3). HRMS EI (*m*/*z*): calc. for $C_{13}H_{12}O$, 184.0888; found, 184.0893.

5-Methyl-3-[phenyl(pentafluorophenylimino)methyl)biphenyl-2-ol (L4). *N*-

Pentafluorophenylbenzamide (2.25 g, 7.83 mmol) and 5-methylbiphenyl-2-ol (1.37 g, 7.44 mmol) were reacted as described above to give the crude product as a yellow solid. Repeated recrystallizations from methanol at -20 °C was necessary to obtain the product as small yellow needles (0.12 g, 4%). ^{1}H NMR ($CDCl_3$, 500 MHz): 13.41 (s, 1H, O*H*), 7.63 (m, 2H, Ph*H*), 7.34-7.46 (m, 7H, Ar*H* or Ph*H*), 7.20 (m, 2H, Ph*H*), 6.82 (m, 1H, Ar*H*), 2.19 (s, 3H, ArCH_3). ^{13}C NMR ($CDCl_3$, 125MHz): 181.7 (N=*C*-Ph), 157.9 (Ar*C*-OH), 138.6 (Ar_FC-F, m, J_{CF} = 250 Hz), 138.1 (Ar_FC-F, m, J_{CF} = 250 Hz), 137.8 (Ar_FC-F, m, J_{CF} = 250 Hz), 137.7, 137.3, 134.8, 132.6, 131.0, 130.1, 129.7, 128.7, 128.4, 127.7, 127.5, 127.0 (Ar*C* or Ph*C*), 123.6 (Ar_FC_{ipso}, m), 119.2 (Ar*C*), 20.7 (Ar*C*H_3). ^{19}F NMR ($CDCl_3$, 470 MHz): -152.4, -163.8, -166.0 (m, Ar_FF). HRMS EI (*m*/*z*): calc. for $C_{26}H_{16}F_5NO$, 453.1152; found, 453.1131.

2-Benzyl-4-methyl-6-[phenyl(pentafluorophenylimino)methyl)phenol (L5). *N*-Pentafluorophenylbenzamide (1.49 g, 5.17 mmol) and 2-benzyl-4-methylphenol (0.98 g, 4.9 mmol) were reacted as described above to give the crude product as a brown oil. Recrystallization from methanol/toluene 9:1 at -20 °C produced a yellow crystalline solid (0.64 g, 28%). ^{1}H NMR ($CDCl_3$, 500 MHz): 13.22 (s, 1H, O*H*), 7.32-7.42 (m, 7H, Ph*H*), 7.20-7.26 (m, 3H, Ph*H*), 7.12, 6.72 (s, 1H each, Ar*H*), 4.10 (s, 2H, ArCH_2Ph), 2.12 (s, 3H, ArCH_3). ^{13}C NMR ($CDCl_3$, 125MHz): 181.6 (N=*C*-Ph), 158.6 (Ar*C*-OH), 140.8 (Ph*C*), 138.6 (Ar_FC-F, m, J_{CF} = 250 Hz), 138.0 (Ar_FC-F, m, J_{CF} = 250 Hz), 137.7 (Ar_FC-F, m, J_{CF} = 250 Hz), 137.0, 134.9, 131.4, 130.3, 130.0, 129.3, 128.63, 128.59, 127.4, 127.0, 126.3 (Ar*C* or Ph*C*), 123.8 (Ar_FC_{ipso}, m), 118.7 (Ar*C*), 35.7 (Ar*C*H_2Ph), 20.7 (Ar*C*H_3). ^{19}F NMR ($CDCl_3$, 470 MHz): -152.3, -164.0, -166.2 (m, Ar_FF). HRMS EI (*m*/*z*): calc. for $C_{27}H_{18}F_5NO$, 467.1309; found, 467.1324.

2-[Phenyl(pentafluorophenylimino)methyl]-5,6,7,8-tetrahydro-1-naphthol (L6). *N*-Pentafluorophenylbenzamide (1.01 g, 3.52 mmol) and 5,6,7,8-tetrahydro-1-naphthol (0.50 g, 3.3 mmol) were reacted as described above to give the crude product as a yellow solid. Recrystallization from methanol produced a light yellow crystalline solid (0.34 g, 25%). ^{1}H NMR ($CDCl_3$, 500 MHz): 13.41 (s, 1H, O*H*), 7.34-7.49 (m, 3H, Ph*H*), 7.18 (m, 2H, Ph*H*), 6.65 (dd, 2H, J = 8.0 Hz, 132 Hz, Ar*H*), 2.77 (m,

4H, ArCH_2-), 1.83 (m, 4H, ArCH$_2$CH_2-). ^{13}C NMR ($CDCl_3$, 125MHz): 181.3 (N=*C*-Ph), 160.9 (Ar*C*-OH), 145.6 (Ar*C*), 138.8 (Ar$_F$*C*-F, m, J_{CF} = 244 Hz), 137.9 (Ar$_F$*C*-F, m, J_{CF} = 250 Hz), 137.8 (Ar$_F$*C*-F, m, J_{CF} = 250 Hz), 135.0, 129.9, 129.8, 128.5, 127.1, 126.5 (Ar*C* or Ph*C*), 123.9 (Ar$_F$*C*$_{ipso}$, m), 119.6, 116.1 (Ar*C*), 30.5, 23.0, 22.7 (Ar-(*C*H$_2$)$_4$-Ar). ^{19}F NMR ($CDCl_3$, 470 MHz): -152.6, -164.3, -166.4 (m, Ar$_F$F). HRMS EI (*m*/*z*): calc. for $C_{23}H_{16}F_5NO$, 417.1152; found, 417.1151.

4-Chloro-2-methyl-6-[phenyl(pentafluorophenylimino)methyl]phenol (L7). *N*-Pentafluorophenylbenzamide (3.69 g, 12.9 mmol) and 4-chloro-2-methylphenol (1.83 g, 12.9 mmol) were reacted as described above to give the crude product as a yellow oil. Recrystallization from methanol at -20 °C produced a yellow crystalline solid (0.46 g, 9%). ^{1}H NMR ($CDCl_3$, 500 MHz): 13.26 (s, 1H, O*H*), 7.35-7.44 (m, 3H, Ph*H*), 7.27 (m, 1H, Ar*H*), 7.16 (m, 2H, Ph*H*), 6.84 (m, 1H, Ar*H*), 2.31 (s, 3H, ArCH_3). ^{13}C NMR ($CDCl_3$, 125MHz): 181.0 (N=*C*-Ph), 159.7 (Ar*C*-OH), 138.6 (Ar$_F$*C*-F, m, J_{CF} = 250 Hz), 138.3 (Ar$_F$*C*-F, m, J_{CF} = 250 Hz), 137.8 (Ar$_F$*C*-F, m, J_{CF} = 250 Hz), 135.7, 134.1, 130.5, 129.8, 129.7, 128.9, 127.0 (Ar*C* or Ph*C*), 123.4 (Ar$_F$*C*$_{ipso}$, m), 122.8, 119.3 (Ar*C*), 16.0 (Ar*C*H$_3$). ^{19}F NMR ($CDCl_3$, 470 MHz): -151.7, -162.7, -165.2 (m, Ar$_F$F). HRMS EI (*m*/*z*): calc. for $C_{20}H_{11}ClF_5NO$, 411.0449; found, 411.0447.

4-Fluoro-2-methyl-6-[phenyl(pentafluorophenylimino)methyl]phenol (L8). *N*-Pentafluorophenylbenzamide (1.52 g, 5.29 mmol) and 4-fluoro-2-methylphenol (0.63 g, 5.1 mmol) were reacted as described above to give the crude product as an orange oil. The crude product was flash chromatographed (silica gel, hexanes/ethyl acetate 20:1) to yield a yellow oil. Recrystallization from methanol at -20 °C produced a yellow crystalline solid (0.10 g, 5%). ^{1}H NMR ($CDCl_3$, 500 MHz): 13.05 (s, 1H, O*H*), 7.35-7.43 (m, 3H, Ph*H*), 7.17 (m, 2H, Ph*H*), 7.07 (dd, 1H, J = 3.0 Hz, 8.0 Hz, Ar*H*), 6.56 (dd, 1H, J = 3.0 Hz, 9.5 Hz, Ar*H*), 2.33 (s, 3H, ArCH_3). ^{13}C NMR ($CDCl_3$, 125MHz): 181.0 (N=*C*-Ph), 159.7 (Ar*C*-OH), 154.4 (ArC-F, d, J_{CF} = 234 Hz), 138.6 (Ar$_F$*C*-F, m, J_{CF} = 250 Hz), 138.2 (Ar$_F$*C*-F, m, J_{CF} = 250 Hz), 137.8 (Ar$_F$*C*-F, m, J_{CF} = 250 Hz), 134.3, 130.4 (Ph*C*), 129.5 (Ar*C*, d, J_{CF} = 6.8 Hz), 128.8, 127.0 (Ph*C*), 123.5 (Ar$_F$*C*$_{ipso}$, m), 123.4 (Ar*C*, d, J_{CF} = 22.8 Hz), 118.2 (Ar*C*, d, J_{CF} = 7.6 Hz), 115.6

(Ar*C*, d, J_{CF} = 24.3 Hz), 16.2 (Ar*C*H_3). ^{19}F NMR ($CDCl_3$, 470 MHz): -128.5 (m, ArF), -152.4, -163.5, -165.9 (m, Ar_FF). HRMS EI (*m*/*z*): calc. for $C_{20}H_{11}F_6NO$, 395.0745; found, 395.0758.

4-Methoxy-2-methylphenol. An Schenk-adapted tube was charged with 2-hydroxy-5-methoxybenzaldehyde (0.94 g, 6.19 mmol) and potassium hydroxide (1.75 g, 31.2 mmol) in di(ethylene gycol) (40 mL). Hydrazine hydrate (2.1 mL, 43.3 mmol) was added via syringe and a reflux condenser was attached. The reaction was brought to reflux for 15 hours. After cooling, 1.0 M HCl (40 mL) was slowly added followed by methylene chloride (40 mL). The organic phase was separated, washed with copious amounts of water, dried over Na_2SO_4, filtered and solvent removed in vacuo to yield a white crystalline solid (0.56 g, 65%). The crude product was used directly for the synthesis of ligand **L9**. ^{1}H NMR (C_6D_6, 500 MHz): 6.69 (d, 1H, J = 3.0 Hz, Ar*H*), 6.56 (dd, 1H, J = 3.0, 8.5 Hz, Ar*H*), 6.47 (d, 1H, J = 8.5 Hz, Ar*H*), 4.83 (s, 1H, ArO*H*), 3.35 (s, 3H, ArOCH_3), 2.11 (s, 3H, ArCH_3). ^{13}C NMR (C_6D_6, 125MHz): 154.3 (Ar*C*-OH), 148.8 (Ar*C*-OMe), 125.9, 117.4, 116.1, 112.5 (Ar*C*), 55.7 (ArO*C*H_3), 16.7 (Ar*C*H_3). HRMS EI (*m*/*z*): calc. for $C_8H_{10}O_2$, 138.0681; found, 138.0675.

4-Methoxy-2-methyl-6-[phenyl(pentafluorophenylimino)methyl]phenol (L9). *N*-Pentafluorophenylbenzamide (1.05 g, 3.66 mmol) and 4-methoxy-2-methylphenol (0.50 g, 3.6 mmol) were reacted as described above to give the crude product as a yellow oil. The crude product was flash chromatographed (silica gel, hexanes/ethyl acetate 20:1) to yield a yellow oil. Recrystallization from methanol at -20 °C produced a yellow crystalline solid (0.13 g, 9%). ^{1}H NMR ($CDCl_3$, 500 MHz): 12.85 (s, 1H, O*H*), 7.32-7.40 (m, 3H, Ph*H*), 7.16 (m, 2H, Ph*H*), 6.96 (d, 1H, J = 3 Hz, Ar*H*), 6.35 (d, 1H, J = 3 Hz, Ar*H*), 3.56 (s, 3H, ArOCH_3), 2.31 (s, 3H, ArCH_3). ^{13}C NMR ($CDCl_3$, 125MHz): 181.4 (N=*C*-Ph), 155.6 (Ar*C*-OH), 151.0 (Ar*C*-OCH_3), 138.6 (Ar_F*C*-F, m, J_{CF} = 250 Hz), 138.1 (Ar_F*C*-F, m, J_{CF} = 250 Hz), 137.8 (Ar_F*C*-F, m, J_{CF} = 250 Hz), 134.8, 130.1, 128.6, 127.0 (Ar*C* or Ph*C*), 123.9 ($Ar_F C_{ipso}$, m), 123.7, 118.2, 116.5, 114.2 (Ar*C* or Ph*C*), 55.9 (ArO*C*H_3), 16.3 (Ar*C*H_3). ^{19}F NMR ($CDCl_3$, 470 MHz): -151.9, -163.4, -165.5 (m, Ar_FF). HRMS EI (*m*/*z*): calc. for $C_{21}H_{14}F_5NO_2$, 407.0945; found, 407.0943.

2,4-Dimethyl-6-[1-(pentafluorophenylimino)ethyl]phenol (L10). *N*-Pentafluorophenylethanamide

(2.53 g, 11.2 mmol) and 2,4-dimethylphenol (1.35 mL, 11.2 mmol) were reacted as described above to give the crude product as a green oil. The crude product was flash chromatographed (silica gel, hexanes/ethyl acetate 20:1) to yield a yellow solid. Recrystallization from methanol at -20 °C produced fine yellow needles (0.27 g, 7%). ^{1}H NMR ($CDCl_3$, 500 MHz): 13.30 (s, 1H, O*H*), 7.30, 7.14 (s, 1H each, Ar*H*), 2.36 (s, 3H, N=C-CH_3), 2.29, 2.26 (s, 3H each, ArCH_3). ^{13}C NMR ($CDCl_3$, 125MHz): 178.3 (N=*C*-CH_3), 158.2 (Ar*C*-OH), 139.0 (Ar_F*C*-F, m, J_{CF} = 250 Hz), 138.4 (Ar_F*C*-F, m, J_{CF} = 250 Hz), 138.2 (Ar_F*C*-F, m, J_{CF} = 250 Hz), 136.8, 127.4, 127.2 (Ar*C*), 122.5 (Ar_F*C*$_{ipso}$, m), 118.2 (Ar*C*), 20.8 (Ar*C*H_3), 19.3 (N=C-*C*H_3), 16.0 (Ar*C*H_3). ^{19}F NMR ($CDCl_3$, 470 MHz): -152.6, -163.0, -165.0 (m, Ar_FF). HRMS EI (*m*/*z*): calc. for $C_{16}H_{12}F_5NO$, 329.0839; found, 329.0855.

2,4-Dimethyl-6-[2-methyl-1-(pentafluorophenylimino)propyl]phenol (L11). 2-Methyl-*N*-pentafluorophenylpropanamide (3.12 g, 12.3 mmol) and 2,4-dimethylphenol (1.40 mL, 11.7 mmol) were reacted as described above to give the crude product as a yellow oil. The crude product was flash chromatographed (alumina, hexanes/ethyl acetate 98:2) to yield a light yellow solid (0.67 g, 16%). ^{1}H NMR ($CDCl_3$, 500 MHz): 13.45 (s, 1H, O*H*), 7.49, 7.13 (s, 1H each, Ar*H*), 3.15 (septet, 1H, J = 7.5 Hz, N=C-C*H*$(CH_3)_2$), 2.30, 2.26 (s, 3H each, ArCH_3), 1.40 (d, 6H, J = 7.5 Hz, N=C-CH(CH_3)$_2$). ^{13}C NMR ($CDCl_3$, 125MHz): 185.8 (N=*C*-$CH(CH_3)_2$), 159.1 (Ar*C*-OH), 138.5 (Ar_F*C*-F, m, J_{CF} = 250 Hz), 138.2 (Ar_F*C*-F, m, J_{CF} = 250 Hz), 138.0 (Ar_F*C*-F, m, J_{CF} = 250 Hz), 136.6, 127.9, 127.4, 126.3 (Ar*C*), 122.4 (Ar_F*C*$_{ipso}$, m), 116.3 (Ar*C*), 35.2 (N=C-*C*$H(CH_3)_2$), 21.0, 20.8, 16.3 (N=C-CH(*C*H_3)$_2$ or Ar*C*H_3). ^{19}F NMR ($CDCl_3$, 470 MHz): -153.7, -164.6, -165.7 (m, Ar_FF). HRMS EI (*m*/*z*): calc. for $C_{18}H_{16}F_5NO$, 357.1152; found, 357.1151.

2-[Cyclohexyl(pentafluorophenylimino)methyl)-4,6-dimethylphenol (L12). *N*-Pentafluorophenylcyclohexanecarboxamide (1.33 g, 4.53 mmol) and 2,4-dimethylphenol (0.55 mL, 4.6 mmol) were reacted as described above to give the crude product as a green oil. Recrystallization from pentane at -20 °C produced a light yellow crystalline solid (0.27 g, 15%). ^{1}H NMR ($CDCl_3$, 500 MHz): 13.43 (s, 1H, O*H*), 7.52, 7.11 (s, 1H each, Ar*H*), 2.85 (m, 1H, N=C-Cy*H*), 2.30, 2.24 (s, 3H each,

ArC*H*$_3$), 1.68-1.88 (m, 7H, Cy*H*), 1.18-1.23 (m, 3H, Cy*H*). ^{13}C NMR ($CDCl_3$, 125MHz): 184.5 (N=*C*-Cy), 158.9 (Ar*C*-OH), 138.4 (Ar_F*C*-F, m, $^1J_{CF}$ = 250 Hz), 138.0 (Ar_F*C*-F, m, $^1J_{CF}$ = 250 Hz), 136.8 (Ar_F*C*-F, m, $^1J_{CF}$ = 250 Hz), 136.3, 127.9, 127.3, 126.3 (Ar*C*), 122.7 ($Ar_F C_{ipso}$, m), 117.2 (Ar*C*), 47.0, 30.4, 26.8, 25.9 (N=C-Cy*C*) 21.1, 16.0 (Ar*C*H$_3$). ^{19}F NMR ($CDCl_3$, 470 MHz): -152.9, -164.1, -165.0 (m, Ar_FF). HRMS EI (*m*/*z*): calc. for $C_{21}H_{20}F_5NO$, 397.1465; found, 397.1466.

2-[Cycloheptyl(pentafluorophenylimino)methyl)-4,6-dimethylphenol (L13). *N*-Pentafluorophenylcycloheptanecarboxamide (2.04 g, 6.63 mmol) and 2,4-dimethylphenol (0.79 mL, 6.6 mmol) were reacted as described above to give the crude product as a yellow oil. The crude product was flash chromatographed (silica gel, hexanes/ethyl acetate 20:1) to yield a yellow oil. Recrystallization from methanol/toluene 3:1 at -20 °C produced a bright yellow crystalline solid (0.43 g, 16%). ^{1}H NMR ($CDCl_3$, 500 MHz): 13.48 (s, 1H, O*H*), 7.37, 7.11 (s, 1H each, Ar*H*), 2.82 (m, 1H, N=C-Cycloheptyl*H*), 2.29, 2.25 (s, 3H each, ArC*H*$_3$), 1.97-2.05 (m, 2H, Cycloheptyl*H*), 1.78-1.89 (m, 4H, Cycloheptyl*H*), 1.34-1.58 (m, 6H, Cycloheptyl*H*). ^{13}C NMR ($CDCl_3$, 125MHz): 186.3 (N=*C*-Cycloheptyl), 159.2 (Ar*C*-OH), 138.7 (Ar_F*C*-F, m, J_{CF} = 250 Hz), 138.1 (Ar_F*C*-F, m, J_{CF} = 250 Hz), 138.0 (Ar_F*C*-F, m, J_{CF} = 250 Hz), 136.2, 127.9, 126.2 (Ar*C*), 122.5 ($Ar_F C_{ipso}$, m), 116.0 (Ar*C*), 47.2, 32.2, 29.0, 28.3 (N=C-Cycloheptyl*C*) 21.1, 16.3 (Ar*C*H$_3$). ^{19}F NMR ($CDCl_3$, 470 MHz): -153.3, -163.6, -165.0 (m, Ar_FF). HRMS EI (*m*/*z*): calc. for $C_{22}H_{22}F_5NO$, 411.1622; found, 411.1632.

2,4-Dimethyl-6-(2,2,2-trifluoro-1-(pentafluorophenylimino)ethyl)phenol (L14). 2,2,2-Trifluoro-*N*-pentafluorophenylethanimidoyl chloride (1.92 g, 6.46 mmol), prepared according to the procedure described by Uneyama and coworkers,[3] and 2,4-dimethylphenol (0.79 mL, 6.6 mmol) were reacted in the Friedel-Crafts reaction as described above to give the crude product as a brown oil. The crude product was flash chromatographed (silica gel, hexanes/ethyl acetate 20:1) to yield an orange oil. Recrystallization from pentane at -20 °C produced large orange crystals (1.77 g, 72%). ^{1}H NMR ($CDCl_3$, 500 MHz): 12.13 (s, 1H, O*H*), 7.33, 7.23 (s, 1H each, Ar*H*), 2.30, 2.26 (s, 3H each, ArC*H*$_3$). ^{13}C NMR ($CDCl_3$, 125MHz): 161.9 (N=*C*-CF_3, q, J_{CF} = 30 Hz), 159.4 (Ar*C*-OH), 138.7 (Ar_F*C*-F, m, J_{CF} =

250 Hz), 138.6 (Ar*C*), 138.1 (Ar_F*C*-F, m, J_{CF} = 250 Hz), 137.8 (Ar_F*C*-F, m, J_{CF} = 250 Hz), 128.1, 128.0 (Ar*C*), 127.2 (Ar*C*-C=N, q, J_{CF} = 4.5 Hz), 121.4 (Ar_FC_{ipso}, m), 118.6 (N=C-*C*F_3, q, J_{CF} = 290 Hz), 113.3 (Ar*C*), 20.9, 16.2 (Ar*C*H_3). ^{19}F NMR ($CDCl_3$, 470 MHz): -64.0 (s, N=C-C*F*$_3$), -153.7, -162.1, -164.9 (m, Ar_FF). HRMS EI (*m*/*z*): calc. for $C_{16}H_9F_8NO$, 383.0556; found, 383.0553.

2,4-Dimethyl-6-[naphthalen-2-yl(pentafluorophenylimino)methyl]phenol (L15). *N*-Pentafluorophenylnaphthalene-2-carboxamide (1.80 g, 5.34 mmol) and 2,4-dimethylphenol (0.64 mL, 5.3 mmol) were reacted as described above to give the crude product as a red-brown oil. Recrystallization from methanol at -20 °C produced a yellow crystalline solid (0.61 g, 26%). ^{1}H NMR ($CDCl_3$, 500 MHz): 13.12 (s, 1H, O*H*), 7.81-7.87 (m, 3H, Ar*H*), 7.67 (s, 1H, Ar*H*), 7.52-7.59 (m, 2H, Ar*H*), 7.27 (d, 1H, J = 8 Hz, Ar*H*), 7.15, 6.64 (s, 1H each, Ar*H*), 2.33, 2.07 (s, 3H each, ArC*H*$_3$). ^{13}C NMR ($CDCl_3$, 125MHz): 181.6 (N=*C*-Ar), 158.9 (Ar*C*-OH), 138.7 (Ar_F*C*-F, m, J_{CF} = 250 Hz), 137.9 (Ar_F*C*-F, m, J_{CF} = 250 Hz), 137.7 (Ar_F*C*-F, m, J_{CF} = 250 Hz), 137.4, 133.6, 132.5, 132.4, 130.8, 128.8, 128.6, 128.1, 127.7, 127.3, 127.24, 127.19, 126.7, 124.2 (Ar*C*), 123.8 (Ar_FC_{ipso}, m), 118.5 (Ar*C*), 20.6, 16.0 (Ar*C*H_3). ^{19}F NMR ($CDCl_3$, 470 MHz): -152.0, -163.4, -165.4 (m, Ar_FF). HRMS EI (*m*/*z*): calc. for $C_{25}H_{16}F_5NO$, 441.1152; found, 441.1150.

2,4-Dimethyl-6-[naphthalen-1-yl(pentafluorophenylimino)methyl]phenol (L16). *N*-Pentafluorophenylnaphthalene-1-carboxamide (1.79 g, 5.30 mmol) and 2,4-dimethylphenol (0.64 mL, 5.3 mmol) were reacted as described above to give the crude product as a yellow solid. Recrystallization from methanol at -20 °C produced a yellow crystalline solid (1.2 g, 50%). ^{1}H NMR ($CDCl_3$, 500 MHz): 13.33 (s, 1H, O*H*), 7.87 (d, 1H, J = 8.5 Hz, Ar*H*), 7.82 (d, 1H, J = 8.5 Hz, Ar*H*), 7.69 (d, 1H, J = 8.5 Hz, Ar*H*), 7.40-7.49 (m, 4H, Ar*H*), 7.14, 6.50 (s, 1H each, Ar*H*), 2.37, 1.99 (s, 3H each, ArC*H*$_3$). ^{13}C NMR ($CDCl_3$, 125MHz): 181.5 (N=*C*-Ar), 158.8 (Ar*C*-OH), 138.7 (Ar_F*C*-F, m, J_{CF} = 250 Hz), 137.7 (Ar_F*C*-F, m, J_{CF} = 250 Hz), 137.6 (Ar_F*C*-F, m, J_{CF} = 250 Hz), 137.5, 133.2, 132.5, 130.5, 130.2, 129.8, 128.6, 127.4, 127.3, 127.2, 126.9, 125.5, 125.2, 124.8 (Ar*C*), 123.6 (Ar_FC_{ipso}, m), 118.8 (Ar*C*), 20.5, 16.0 (Ar*C*H_3). ^{19}F NMR ($CDCl_3$, 470 MHz): -151.2, -163.5, -165.6 (m, Ar_FF). HRMS EI (*m*/*z*): calc. for

$C_{25}H_{16}F_5NO$, 441.1152; found, 441.1167.

2-[4-Methoxyphenyl(pentafluorophenylimino)methyl]-4,6-dimethylphenol (L17). 4-Methoxy-*N*-pentafluorophenylbenzamide (2.31 g, 7.28 mmol) and 2,4-dimethylphenol (0.87 mL, 7.3 mmol) were reacted as described above to give the crude product as a brown oil. Recrystallization from methanol at -20 °C produced an orange crystalline solid (0.41 g, 13%). ^{1}H NMR ($CDCl_3$, 500 MHz): 13.13 (s, 1H, O*H*), 7.13 (s, 1H, Ar*H*), 7.09 (d, 2H, J = 8.5 Hz, Ar*H*), 6.85 (d, 2H, J = 9.0 Hz, Ar*H*), 6.71 (s, 1H, Ar*H*), 3.81 (s, 3H, ArOCH_3), 2.30, 2.13 (s, 3H each, ArCH_3). ^{13}C NMR ($CDCl_3$, 125MHz): 181.5 (N=*C*-Ar), 160.6 (Ar*C*-OCH_3), 158.9 (Ar*C*-OH), 138.8 (Ar_FC-F, m, J_{CF} = 250 Hz), 137.9 (Ar_FC-F, m, J_{CF} = 250 Hz), 137.8 (Ar_FC-F, m, J_{CF} = 250 Hz), 137.2, 130.8, 128.9, 127.2, 127.1, 127.0 (Ar*C*), 124.1 (Ar_FC_{ipso}, m), 118.6, 113.9 (Ar*C*), 20.7, 16.0 (Ar*C*H_3). ^{19}F NMR ($CDCl_3$, 470 MHz): -152.1, -163.8, -165.7 (m, Ar_FF). HRMS EI (*m*/*z*): calc. for $C_{22}H_{16}F_5NO_2$, 421.1101; found, 421.1097.

2-[Mesityl(pentafluorophenylimino)methyl]-4,6-dimethylphenol (L18). 2,4,6-Trimethyl-*N*-pentafluorophenylbenzamide (1.93 g, 5.87 mmol) and 2,4-dimethylphenol (0.70 mL, 5.8 mmol) were reacted as described above to give the crude product as a yellow oil. The crude product was flash chromatographed (silica gel, hexanes/ethyl acetate 20:1) to yield a yellow oil. Repeated recrystallization from methanol/toluene 4:1 at -20 °C was necessary to obtain the product as a yellow crystalline solid (0.12 g, 5%). ^{1}H NMR ($CDCl_3$, 500 MHz): 13.44 (s, 1H, O*H*), 7.11 (s, 1H, Ar*H*), 6.79 (s, 2H, Mes*H*), 6.53 (s, 1H, Ar*H*), 2.30 (s, 3H, ArCH_3), 2.26 (s, 3H, Mes-CH_3), 2.10 (s, 3H, ArCH_3), 2.02 (s, 6H, Mes-CH_3). ^{13}C NMR ($CDCl_3$, 125MHz): 182.1 (N=*C*-Mes), 158.7 (Ar*C*-OH), 139.2, 137.3, 135.4, 131.4, 129.5, 128.7, 127.5, 127.2, 118.5 (Ar*C* or Mes*C*), 21.4, 20.7, 19.9, 16.0 (Ar*C*H_3 or Mes*C*H_3). The three Ar_FC-F and Ar_FC_{ipso} signals are hidden. ^{19}F NMR ($CDCl_3$, 470 MHz): -150.2, -163.1, -165.7 (m, Ar_FF). HRMS EI (*m*/*z*): calc. for $C_{24}H_{20}F_5NO$, 433.1465; found, 433.1454.

2,4-Dimethyl-6-[pentafluorophenyl(pentafluorophenylimino)methyl]phenol (L19). 2,3,4,5,6-Pentafluoro-*N*-pentafluorophenylbenzamide (1.55 g, 4.10 mmol) and 2,4-dimethylphenol (0.49 mL, 4.1 mmol) were reacted as described above to give the crude product as a yellow solid. The crude solid was

washed with pentane and the filtrate was collected and solvent removed in vacuo to give a yellow solid. Recrystallization from methanol at -20 °C afforded the product as a bright yellow crystalline solid (0.12 g, 6%). ^{1}H NMR ($CDCl_3$, 500 MHz): 12.54 (s, 1H, O*H*), 7.21 (s, 1H, Ar*H*), 6.56 (s, 1H, Ar*H*), 2.30, 2.19 (s, 3H each, ArCH_3). ^{13}C NMR ($CDCl_3$, 125MHz): 167.0 (N=*C*-Ar_F), 158.9 (Ar*C*-OH), 143.1 (Ar_F*C*-F, m, J_{CF} = 250 Hz), 142.9 (Ar_F*C*-F, m, J_{CF} = 250 Hz), 139.0 (Ar_F*C*-F, m, J_{CF} = 250 Hz), 138.8 (Ar_F*C*-F, m, J_{CF} = 250 Hz), 138.7 (Ar*C*), 138.0 (Ar_F*C*-F, m, J_{CF} = 250 Hz), 137.9 (Ar_F*C*-F, m, J_{CF} = 250 Hz), 128.3, 128.2, 127.9 (Ar*C*), 122.2 (Ar_FC_{ipso}, m), 117.1 (Ar*C*), 109.0 (Ar_FC_{ipso}, m), 20.7, 16.0 (Ar*C*H_3). ^{19}F NMR ($CDCl_3$, 470 MHz): -139.6, -150.5, -152.1, -160.5, -160.8, -163.9 (m, Ar_FF). HRMS EI (*m*/*z*): calc. for $C_{21}H_9F_{10}NO$, 481.0524; found, 481.0527.

General procedure for titanium dichloride complex synthesis. Phenoxyketimine complexes were synthesized by a modified previously reported procedure.[2, 4] To a stirred solution of the PKI ligand (1.00 mmol) in THF (ca. 10 mL) was added *n*-butyllithium (1.6 M in hexanes, 1.05 mmol) by syringe at -78 °C. The deprotonated ligand solution is warmed to room temperature and stirred for about 20 minutes. This solution was transferred via cannula to a THF solution of $TiCl_4$ (1.0 M in toluene, 0.50 mmol) at -78 °C. After warming to room temperature the dark red solution was stirred overnight. After solvent removal in vacuo, the residues were taken up in CH_2Cl_2 and filtered through a plug of celite. The solution was concentrated in vacuo and layered with pentane in order to crystallize the desired complex.

Bis(2-chloro-4-methyl-6-[phenyl(pentafluorophenylimino)methyl]phenolato)titanium dichloride (2). Ligand **L2** (0.10 g, 0.21 mmol) was reacted as described above to give **2** as an orange-red crystalline solid (0.06 g, 54%). ^{1}H NMR ($CDCl_3$, 500 MHz): 7.28-7.40 (m, 4H, Ph*H*), 7.23 (m, 1H, Ph*H*), 7.07, 6.55 (m, 1H each, Ar*H*), 2.11 (s, 3H, ArCH_3). ^{13}C NMR ($CDCl_3$, 125MHz): 180.9 (N=*C*-Ar), 157.1 (Ar*C*-OTi), 137.7, 135.6, 134.1, 131.6, 130.6, 128.8, 126.2, 126.1, 125.7, 125.0, 122.3 (Ar*C* or Ph*C*), 20.7 (Ar*C*H_3). The Ar_F*C*-F and Ar_FC_{ipso} signals are hidden. ^{19}F NMR ($CDCl_3$, 470 MHz): -140.7, -148.7, -160.8, -163.4, -167.7 (m, Ar_FF). Anal. calc. for $C_{40}H_{20}Cl_4F_{10}N_2O_2Ti$: C, 51.10; H, 2.14; N, 2.98. Anal. found: C, 50.72; H, 2.13; N, 2.77.

Bis(2-bromo-4-methyl-6-[phenyl(pentafluorophenylimino)methyl]phenolato)titanium dichloride (3). Ligand **L3** (0.23 g, 0.51 mmol) was reacted as described above to give **3** as a dark red crystalline solid (0.13 g, 51%). ^{1}H NMR ($CDCl_3$, 500 MHz): 7.55 (m, 1H, Ar*H*), 7.28-7.40 (m, 3H, Ph*H*), 7.22, 7.07 (m, 1H each, Ph*H*), 6.60 (m, 1H each, Ar*H*), 2.11 (s, 3H, ArCH_3). ^{13}C NMR ($CDCl_3$, 125MHz): 181.0 (N=*C*-Ar), 157.9 (Ar*C*-OH), 140.8 (Ph*C* or Ar*C*), 140.0 (Ar_FC-F, m, J_{CF} = 250 Hz), 139.5 (Ar_FC-F, m, J_{CF} = 250 Hz), 138.0 (Ar_FC-F, m, J_{CF} = 250 Hz), 136.9 (Ar_FC-F, m, J_{CF} = 250 Hz), 135.6, 134.9, 132.1, 130.6, 128.8, 128.7, 126.2, 125.7 (Ar*C* or Ph*C*), 125.1 (Ar_FC_{ipso}, m), 124.8, 111.8 (Ph*C* or Ar*C*), 20.6 (Ar*C*H$_3$). ^{19}F NMR ($CDCl_3$, 470 MHz): -140.5, -148.5, -160.7, -163.0, -167.6 (m, Ar_FF). Anal. calc. for $C_{40}H_{20}Br_2Cl_2F_{10}N_2O_2Ti$: C, 46.68; H, 1.96; N, 2.72. Anal. found: C, 46.91; H, 2.02; N, 2.60.

Bis(5-methyl-3-[phenyl(pentafluorophenylimino)methyl)biphenyl-2-olato)titanium dichloride (4). Ligand **L4** (0.09 g, 0.20 mmol) was reacted as described above to give **4** as a brown-red crystalline solid (0.04 g, 35%). ^{1}H NMR ($CDCl_3$, 500 MHz): 7.73 (d, 2H, J = 7.5 Hz, Ph*H*), 7.43-7.46 (m, 3H, Ph*H*), 7.22-7.34 (m, 4H, Ph*H* or Ar*H*), 7.18, 7.00 (m, 1H each, Ph*H*), 6.60 (m, 1H, Ar*H*), 2.15 (s, 3H, ArCH_3). ^{13}C NMR ($CDCl_3$, 125MHz): 180.9 (N=*C*-Ar), 159.3 (Ar*C*-OTi), 138.7, 136.2, 135.4, 134.9, 131.3, 130.2, 129.7, 129.3, 128.6, 128.5, 128.48, 127.9, 126.1, 125.6, 124.8 (Ar*C* or Ph*C*), 21.0 (Ar*C*H$_3$). The Ar_FC-F and Ar_FC_{ipso} signals are hidden. ^{19}F NMR ($CDCl_3$, 470 MHz): -142.2, -148.9, -159.7, -163.4, -168.1 (m, Ar_FF). Anal. calc. for $C_{52}H_{30}Cl_2F_{10}N_2O_2Ti$: C, 61.02; H, 2.95; N, 2.74. Anal. found: C, 60.57; H, 3.20; N, 2.59.

Bis(2-benzyl-4-methyl-6-[phenyl(pentafluorophenylimino)methyl)phenolato)titanium dichloride (5). Ligand **L5** (0.10 g, 0.21 mmol) was reacted as described above to give **5** as a dark red crystalline solid (0.06 g, 54%). ^{1}H NMR ($CDCl_3$, 500 MHz): 7.27-7.40 (m, 7H, Ph*H*), 7.18-7.22 (m, 2H, Ph*H*), 7.14 (m, 1H, Ph*H*), 7.07, 6.47 (s, 1H each, Ar*H*), 3.77 (dd, 2H, J = 15, 364 Hz, ArCH_2Ph), 2.04 (s, 3H, ArCH_3). ^{13}C NMR ($CDCl_3$, 125MHz): 181.1 (N=*C*-Ar), 159.8 (Ar*C*-OTi), 140.0 (Ar_FC-F, m, J_{CF} = 250 Hz), 139.8, 138.8 (Ph*C* or Ar*C*), 138.8 (Ar_FC-F, m, J_{CF} = 250 Hz), 137.6 (Ar_FC-F, m, J_{CF} = 250 Hz), 136.7 (Ar_FC-F, m, J_{CF} = 250 Hz), 136.1, 133.5, 131.1, 130.4, 130.2, 129.5, 128.8, 128.56, 128.54,

126.5, 126.0 (Ar*C* or Ph*C*), 125.5 (Ar_FC_{ipso}, m), 124.1 (Ar*C*), 35.3 (Ar*C*H_2Ph), 20.9 (Ar*C*H_3). ^{19}F NMR ($CDCl_3$, 470 MHz): -141.0, -147.1, -160.5, -164.5, -167.3 (m, Ar_FF). Anal. calc. for $C_{54}H_{34}Cl_2F_{10}N_2O_2Ti$: C, 61.67; H, 3.26; N, 2.66. Anal. found: C, 61.40; H, 2.98; N, 2.67.

Bis(2-[phenyl(pentafluorophenylimino)methyl]-5,6,7,8-tetrahydro-1-naphtholato)titanium dichloride (6). Ligand **L6** (0.15 g, 0.21 mmol) was reacted as described above to give **6** as a light orange powder (0.05 g, 27%). ^{1}H NMR ($CDCl_3$, 500 MHz): 7.25-7.35 (m, 3H, Ph*H*), 7.18, 7.12 (m, 1H each, Ph*H*), 6.59 (dd, 2H, J = 9.0, 21.5 Hz, Ar*H*), 2.66-2.80 (m, 3H, Ar-(CH_2)$_4$-Ar), 2.08 (m, 1H, Ar-(CH_2)$_4$-Ar), 1.65-1.76 (m, 4H, Ar-(CH_2)$_4$-Ar). ^{13}C NMR ($CDCl_3$, 125MHz): 180.5 (N=*C*-Ar), 162.1 (Ar*C*-OTi), 149.1 (Ar*C*), 140.1 (Ar_FC-F, m, J_{CF} = 250 Hz), 138.9 (Ar_FC-F, m, J_{CF} = 250 Hz), 137.5 (Ar_FC-F, m, J_{CF} = 250 Hz), 136.8 (Ar_FC-F, m, J_{CF} = 250 Hz), 136.2, 132.1, 130.2, 128.5, 126.5, 126.4, 126.0, 125.9 (Ar*C* or Ph*C*), 125.9 (Ar_FC_{ipso}, m), 122.7, 121.8 (Ar*C* or Ph*C*), 30.4, 23.3, 22.4, 22.2 (Ar-(*C*H_2)$_4$-Ar). ^{19}F NMR ($CDCl_3$, 470 MHz): -140.9, -146.7, -161.4, -164.5, -167.2 (m, Ar_FF). Anal. calc. for $C_{46}H_{30}Cl_2F_{10}N_2O_2Ti$: C, 58.07; H, 3.18; N, 2.94. Anal. found: C, 57.82; H, 2.95; N, 2.85.

Bis(4-chloro-2-methyl-6-[phenyl(pentafluorophenylimino)methyl]phenolato)titanium dichloride (7). Ligand **L7** (0.28 g, 0.69 mmol) was reacted as described above to give **7** as a red crystalline solid (0.20 g, 61%). ^{1}H NMR ($CDCl_3$, 500 MHz): 7.31-7.41 (m, 4H, Ar*H* or Ph*H*), 7.18, 7.10 (m, 1H each, Ph*H*), 6.66 (m, 1H, Ar*H*), 2.08 (s, 3H, ArCH_3). ^{13}C NMR ($CDCl_3$, 125MHz): 180.8 (N=*C*-Ar), 160.8 (Ar*C*-OTi), 139.8 (Ar_FC-F, m, J_{CF} = 250 Hz), 139.1 (Ar_FC-F, m, J_{CF} = 250 Hz), 137.8 (Ar*C*), 137.7 (Ar_FC-F, m, J_{CF} = 250 Hz), 136.7 (Ar_FC-F, m, J_{CF} = 250 Hz), 135.2, 132.0, 130.9, 129.0, 128.95, 128.9, 126.3, 126.2, 125.8 (Ar*C* or Ph*C*), 125.1 (Ar_FC_{ipso}, m), 124.7 (Ph*C* or Ar*C*), 15.7 (Ar*C*H_3). ^{19}F NMR ($CDCl_3$, 470 MHz): -141.1, -147.4, -160.0, -164.1, -166.8 (m, Ar_FF). Anal. calc. for $C_{40}H_{20}Cl_4F_{10}N_2O_2Ti$: C, 51.10; H, 2.14; N, 2.98. Anal. found: C, 50.65; H, 1.93; N, 2.85.

Bis(4-fluoro-2-methyl-6-[phenyl(pentafluorophenylimino)methyl]phenolato)titanium dichloride (8). Ligand **L8** (0.13 g, 0.32 mmol) was reacted as described above to give **8** as a dark purple-red crystalline solid (0.05 g, 36%). ^{1}H NMR ($CDCl_3$, 500 MHz): 7.30-7.40 (m, 4H, Ar*H* or Ph*H*), 7.20, 7.12

(m, 1H each, Ph*H*), 6.38 (dd, 1H, J = 3, 9 Hz Ar*H*), 2.09 (s, 3H, ArCH_3). ^{13}C NMR ($CDCl_3$, 125MHz): 180.9 (N=*C*-Ph), 158.7 (Ar*C*-OTi), 155.9 (ArC-F, d, J_{CF} = 240 Hz), 139.8 (Ar_F*C*-F, m, J_{CF} = 250 Hz), 139.1 (Ar_F*C*-F, m, J_{CF} = 250 Hz), 137.7 (Ar_F*C*-F, m, J_{CF} = 250 Hz), 136.8 (Ar_F*C*-F, m, J_{CF} = 250 Hz), 135.4, 130.8 (Ph*C*), 129.2 (Ar*C*, d, J_{CF} = 7.5 Hz), 128.9 (Ar*C*, d, J_{CF} = 9.1 Hz), 126.2, 125.8, 125.7, 125.5 (Ph*C*), 125.2 (Ar_FC_{ipso}, m), 123.9 (Ar*C*, d, J_{CF} = 8.3 Hz), 117.8 (Ar*C*, d, J_{CF} = 25 Hz), 15.9 (Ar*C*H_3). ^{19}F NMR ($CDCl_3$, 470 MHz): -123.0, -141.1, -147.5, -160.2, -164.2, -167.0 (m, Ar_FF). Anal. calc. for $C_{40}H_{20}Cl_2F_{12}N_2O_2Ti$: C, 52.95; H, 2.22; N, 3.09. Anal. found: C, 52.42; H, 1.98; N, 2.86.

Bis(4-methoxy-2-methyl-6-[phenyl(pentafluorophenylimino)methyl]phenolato)titanium dichloride (9). Ligand **L9** (0.09 g, 0.21 mmol) was reacted as described above to give **9** as a dark purple-red crystalline solid (0.04 g, 37%). ^{1}H NMR ($CDCl_3$, 500 MHz): 7.27-7.36 (m, 3H, Ph*H*), 7.21, 7.12 (m, 1H each, Ph*H*), 6.97, 6.12 (m, 1H each, Ar*H*), 3.50 (s, 3H, ArOCH_3), 2.07 (s, 3H, ArCH_3). ^{13}C NMR ($CDCl_3$, 125MHz): 180.8 (N=*C*-Ar), 157.5 (Ar*C*-OTi), 153.1 (Ar*C*-OCH_3), 139.9 (Ar_F*C*-F, m, J_{CF} = 250 Hz), 138.9 (Ar_F*C*-F, m, J_{CF} = 250 Hz), 137.6 (Ar_F*C*-F, m, J_{CF} = 250 Hz), 136.8 (Ar_F*C*-F, m, J_{CF} = 250 Hz), 136.0, 130.5, 128.64, 128.59, 128.0, 126.4, 125.9 (Ar*C* or Ph*C*), 125.5 (Ar_FC_{ipso}, m), 125.5, 124.1, 116.0 (Ph*C* or Ar*C*), 55.8 (ArO*C*H_3), 15.9 (Ar*C*H_3). ^{19}F NMR ($CDCl_3$, 470 MHz): -141.1, -147.2, -161.0, -164.7, -167.4 (m, Ar_FF). Anal. calc. for $C_{42}H_{26}Cl_2F_{10}N_2O_4Ti$: C, 54.16; H, 2.81; N, 3.01. Anal. found: C, 53.88; H, 2.84; N, 2.89.

Bis(2,4-dimethyl-6-[1-(pentafluorophenylimino)ethyl]phenolato)titanium dichloride (10). Ligand **L10** (0.23 g, 0.69 mmol) was reacted as described above to give **10** as a brown-red crystalline solid (0.16 g, 61%). ^{1}H NMR (C_6D_6, 300 MHz): 6.94, 6.76 (s, 1H each, Ar*H*), 2.05, 2.02, 1.65 (s, 3H each, ArCH_3 or N=C-CH_3). ^{13}C NMR ($CDCl_3$, 125MHz): 178.3 (N=*C*-Ar), 159.3 (Ar*C*-OTi), 140.4 (Ar_F*C*-F, m, J_{CF} = 250 Hz), 140.0 (Ar_F*C*-F, m, J_{CF} = 250 Hz), 139.3 (Ar_F*C*-F, m, J_{CF} = 250 Hz), 138.9 (Ar*C*), 138.1 (Ar_F*C*-F, m, J_{CF} = 250 Hz), 137.4 (Ar_F*C*-F, m, J_{CF} = 250 Hz), 131.2, 128.8, 126.9 (Ar*C*), 124.5 (Ar_FC_{ipso}, m), 123.2 (Ar*C*), 21.9, 21.1, 15.7 (N=C-*C*H_3 or Ar*C*H_3). ^{19}F NMR ($CDCl_3$, 470 MHz): -144.9, -149.3, -161.2, -164.0, -166.5 (m, Ar_FF). Anal. calc. for $C_{32}H_{22}Cl_2F_{10}N_2O_2Ti$: C, 49.57; H, 2.86; N, 3.61. Anal.

found: C, 49.09; H, 2.87; N, 2.51.

Bis(2,4-dimethyl-6-[2-methyl-1-(pentafluorophenylimino)propyl]phenolato)titanium dichloride (11). Ligand **L11** (0.15 g, 0.42 mmol) was reacted as described above to give **11** as a dark red crystalline solid from toluene/pentane (0.07 g, 41%). ^{1}H NMR ($CDCl_3$, 500 MHz): 7.59, 7.19 (s, 1H each, Ar*H*), 3.00 (s, 1H, J = 7.5 Hz, N=C-C*H*$(CH_3)_2$), 2.32, 2.03 (s, 3H each, ArCH_3), 1.40 (d, 6H, J = 7.5Hz, N=C-CH(CH_3)$_2$). ^{13}C NMR ($CDCl_3$, 125MHz): 185.5 (N=*C*-Ar), 160.4 (Ar*C*-OTi), 140.2 (Ar_F*C*-F, m, J_{CF} = 250 Hz), 139.1 (Ar_F*C*-F, m, J_{CF} = 250 Hz), 138.2 (Ar_F*C*-F, m, J_{CF} = 250 Hz), 138.1 (Ar*C*), 137.4 (Ar_F*C*-F, m, J_{CF} = 250 Hz), 130.0, 129.2, 127.1 (Ar*C*), 123.8 ($Ar_F C_{ipso}$, m), 120.9 (Ar*C*), 36.9 (N=C-*C*H$(CH_3)_2$), 21.7, 21.4 (N=C-CH(*C*H_3)$_2$), 21.2, 16.0 (Ar*C*H_3). ^{19}F NMR ($CDCl_3$, 470 MHz): -143.8, -148.1, -161.6, -164.2, -166.5 (m, Ar_FF). Anal. calc. for $C_{36}H_{30}Cl_2F_{10}N_2O_2Ti$: C, 52.01; H, 3.64; N, 3.37. Anal. found: C, 52.70; H, 3.87; N, 3.19.

Bis(2-[cyclohexyl(pentafluorophenylimino)methyl)-4,6-dimethylphenolato)titanium dichloride (12). Ligand **L12** (0.25 g, 0.63 mmol) was reacted as described above to give **12** as a red crystalline solid (0.17 g, 59%). ^{1}H NMR ($CDCl_3$, 500 MHz): 7.72, 7.18 (s, 1H each, Ar*H*), 2.61 (m, 1H, Cy*H*), 2.33, 2.03 (s, 3H each, ArCH_3), 1.66-1.80 (m, 6H, Cy*H*), 1.25, 0.95 (m, 2H each, Cy*H*). ^{13}C NMR ($CDCl_3$, 125MHz): 184.1 (N=*C*-Ar), 160.4 (Ar*C*-OTi), 140.2 (Ar_F*C*-F, m, J_{CF} = 250 Hz), 139.1 (Ar_F*C*-F, m, J_{CF} = 250 Hz), 138.0 (Ar*C*), 138.0 (Ar_F*C*-F, m, J_{CF} = 250 Hz), 137.2 (Ar_F*C*-F, m, J_{CF} = 250 Hz), 129.8, 129.4, 126.9 (Ar*C*), 123.8 ($Ar_F C_{ipso}$, m), 121.7 (Ar*C*), 49.5, 31.1, 30.9, 30.8, 27.1, 25.7 (Cy*C*), 21.3, 16.1 (Ar*C*H_3). ^{19}F NMR ($CDCl_3$, 470 MHz): -143.8, -147.8, -161.4, -164.2, -166.4 (m, Ar_FF). Anal. calc. for $C_{42}H_{38}Cl_2F_{10}N_2O_2Ti$: C, 55.34; H, 4.20; N, 3.07. Anal. found: C, 55.50; H, 4.48; N, 2.84.

Bis(2-[cycloheptyl(pentafluorophenylimino)methyl)-4,6-dimethylphenolato)titanium dichloride (13). Ligand **L13** (0.26 g, 0.64 mmol) was reacted as described above to give **13** as a brown-red crystalline solid (0.11 g, 37%). ^{1}H NMR ($CDCl_3$, 500 MHz): 7.41, 7.17 (s, 1H each, Ar*H*), 2.75 (m, 1H, Cycloheptyl*H*), 2.32, 2.02 (s, 3H each, ArCH_3), 1.71-1.80 (m, 5H, Cycloheptyl*H*), 1.10-1.53 (m, 7H, Cycloheptyl*H*). ^{13}C NMR ($CDCl_3$, 125MHz): 185.8 (N=*C*-Ar), 160.4 (Ar*C*-OTi), 140.3 (Ar_F*C*-F, m, J_{CF}

= 250 Hz), 139.0 (Ar_FC-F, m, J_{CF} = 250 Hz), 138.0 (Ar*C*), 138.0 (Ar_FC-F, m, J_{CF} = 250 Hz), 137.2 (Ar_FC-F, m, J_{CF} = 250 Hz), 129.9, 129.7, 126.9 (Ar*C*), 124.1 (Ar_FC_{ipso}, m), 121.0 (Ar*C*), 48.6, 32.8, 32.6, 29.6, 29.0, 28.8, 28.1 (Cycloheptyl*C*), 21.3, 15.9 (Ar*C*H_3). ^{19}F NMR ($CDCl_3$, 470 MHz): -143.8, -148.3, -161.4, -164.4, -166.5 (m, Ar_FF). Anal. calc. for $C_{44}H_{42}Cl_2F_{10}N_2O_2Ti$: C, 56.25; H, 4.51; N, 2.98. Anal. found: C, 56.27; H, 4.62; N, 2.69.

Bis(2,4-dimethyl-6-(2,2,2-trifluoro-1-(pentafluorophenylimino)ethyl)phenolato)titanium dichloride (14). Ligand **L14** (0.32 g, 0.83 mmol) was reacted as described above to give **14** as a dark brown-red crystalline solid (0.12 g, 33%). ^{1}H NMR ($CDCl_3$, 500 MHz): 7.44, 7.37 (s, 1H each, Ar*H*), 2.36, 2.05 (s, 3H each, ArCH_3). ^{13}C NMR ($CDCl_3$, 125MHz): 164.7 (N=*C*-CF_3, q, J_{CF} = 29 Hz), 162.9 (Ar*C*-OTi), 140.8, 131.8 (Ar*C*), 129.0 (Ar*C*-C=N, q, J_{CF} = 5.3 Hz), 126.8 (Ar*C*), 119.2 (N=C-*C*F_3, q, J_{CF} = 290 Hz), 118.1 (Ar*C*), 21.3, 15.8 (Ar*C*H_3). The Ar_FC-F and Ar_FC_{ipso} signals are hidden. ^{19}F NMR ($CDCl_3$, 470 MHz): -59.6 (s, 3F, N=C-C*F*$_3$), -148.2 (br s, 2F, Ar_FF), -160.3 (m, Ar_FF), -164.3, -166.8 (br s, 1F each, Ar_FF). Despite repeated attempts, this compound proved to be too sensitive for transport for elemental analysis.

Bis(2,4-dimethyl-6-[naphthalen-2-yl(pentafluorophenylimino)methyl]phenolato)titanium dichloride (15). Ligand **L15** (0.46 g, 1.04 mmol) was reacted as described above to give **15** as a red crystalline solid (0.29 g, 55%). ^{1}H NMR (C_6D_6, 500 MHz): 7.74 (dd, 1H, J = 7, 206 Hz, Ar*H*), 7.25-7.49 (m, 4H, Ar*H*), 6.97-7.15 (m, 2H, Ar*H*), 6.67 (s, 1H, Ar*H*), 6.57 (d, 1H, J = 10 Hz, Ar*H*), 2.11, 1.56 (s, 3H each, ArCH_3). ^{13}C NMR (C_6D_6, 125MHz): 181.6 (N=*C*-Ar), 161.7 (Ar*C*-OTi), 141.1 (Ar_FC-F, m, J_{CF} = 250 Hz), 140.0 (Ar*C*), 139.5 (Ar_FC-F, m, J_{CF} = 250 Hz), 138.4 (Ar_FC-F, m, J_{CF} = 250 Hz), 137.5 (Ar_FC-F, m, J_{CF} = 250 Hz), 134.6, 134.1, 133.9, 133.3, 132.7, 131.1, 129.0, 128.7, 128.1, 127.3 (Ar*C*), 126.5 (Ar_FC_{ipso}, m), 126.3, 124.5, 124.1, 123.5 (Ar*C*), 20.5, 15.9 (Ar*C*H_3). ^{19}F NMR ($CDCl_3$, 470 MHz): -141.3, -147.3, -161.0, -164.7, -167.3 (m, Ar_FF). Anal. calc. for $C_{50}H_{30}Cl_2F_{10}N_2O_2Ti$: C, 60.08; H, 3.03; N, 2.80. Anal. found: C, 59.85; H, 3.31; N, 2.74.

Bis(2,4-dimethyl-6-[naphthalen-1-yl(pentafluorophenylimino)methyl]phenolato)titanium

dichloride (16). Ligand **L16** (0.53 g, 1.20 mmol) was reacted as described above to give **16** as a red crystalline solid (0.36 g, 60%). ^{1}H NMR ($CDCl_3$, 500 MHz): 7.77-7.83 (m, 2H, Ar*H*), 7.67 (m, 1H, Ar*H*), 7.33-7.48 (m, 4H, Ar*H*), 7.11, 6.31 (s, 1H each, Ar*H*), 2.04, 1.90 (s, 3H each, ArCH_3). ^{13}C NMR ($CDCl_3$, 125MHz): 181.6 (N=*C*-Ar), 160.1 (Ar*C*-OTi), 140.5 (Ar_F*C*-F, m, J_{CF} = 250 Hz), 140.1 (Ar_F*C*-F, m, J_{CF} = 250 Hz), 139.5 (Ar*C*), 137.5 (Ar_F*C*-F, m, J_{CF} = 250 Hz), 136.6 (Ar_F*C*-F, m, J_{CF} = 250 Hz), 133.5, 133.0, 132.8, 131.1, 130.8, 129.9, 128.3, 127.5, 127.3, 126.5, 126.4 (Ar*C*), 125.3 (Ar_FC_{ipso}, m), 124.5, 124.3, 124.2 (Ar*C*), 20.6, 15.4 (Ar*C*H_3). ^{19}F NMR ($CDCl_3$, 470 MHz): -139.7, -145.8, -161.6, -164.6, -168.0 (m, Ar_FF). Anal. calc. for $C_{50}H_{30}Cl_2F_{10}N_2O_2Ti$: C, 60.08; H, 3.03; N, 2.80. Anal. found: C, 60.26; H, 3.31; N, 2.65.

Bis(2-[4-methoxyphenyl(pentafluorophenylimino)methyl]-4,6-dimethylphenolato)titanium dichloride (17). Ligand **L17** (0.30 g, 0.70 mmol) was reacted as described above to give **17** as a red crystalline solid (0.15 g, 43%). ^{1}H NMR ($CDCl_3$, 500 MHz): 7.17 (s, 1H, Ar*H*), 7.08, 7.01 (m, 1H each, Ar*H*), 6.79 (m, 2H, Ar*H*), 6.48 (s, 1H, Ar*H*), 3.78 (s, 3H, ArOCH_3), 2.10, 2.06 (s, 3H each, ArCH_3). ^{13}C NMR ($CDCl_3$, 125MHz): 180.9 (N=*C*-Ar), 160.6 (Ar*C*-OTi), 140.0 (Ar_F*C*-F, m, J_{CF} = 250 Hz), 139.3 (Ar*C*), 138.8 (Ar_F*C*-F, m, J_{CF} = 250 Hz), 137.6 (Ar_F*C*-F, m, J_{CF} = 250 Hz), 136.8 (Ar_F*C*-F, m, J_{CF} = 250 Hz), 133.0, 130.7, 128.42, 128.4, 128.2, 128.0, 126.3 (Ar*C*), 125.6 (Ar_FC_{ipso}, m), 124.2, 114.2, 113.5 (Ar*C*), 55.5 (ArO*C*H_3), 20.8, 15.6 (Ar*C*H_3). ^{19}F NMR ($CDCl_3$, 470 MHz): -141.6, -147.4, -161.5, -164.9, -167.7 (m, Ar_FF). Anal. calc. for $C_{44}H_{30}Cl_2F_{10}N_2O_4Ti$: C, 55.08; H, 3.15; N, 2.92. Anal. found: C, 54.98; H, 3.21; N, 2.81.

Bis(2-[mesityl(pentafluorophenylimino)methyl]-4,6-dimethylphenolato)titanium dichloride (18). Ligand **L18** (0.10 g, 0.24 mmol) was reacted as described above to give **18** as a light brown-red crystalline solid (0.05 g, 44%). ^{1}H NMR ($CDCl_3$, 500 MHz): 7.12, 6.79, 6.64, 6.52 (s, 1H each, Ar*H*), 2.21, 2.10, 2.07, 1.96, 1.92 (s, 3H each, ArCH_3). ^{13}C NMR ($CDCl_3$, 125MHz): 183.8 (N=*C*-Ar), 159.6 (Ar*C*-OTi), 140.9 (Ar_F*C*-F, m, J_{CF} = 250 Hz), 140.6 (Ar_F*C*-F, m, J_{CF} = 250 Hz), 139.5, 138.8 (Ar*C*), 137.6 (Ar_F*C*-F, m, J_{CF} = 250 Hz), 137.2 (Ar*C*), 136.8 (Ar_F*C*-F, m, J_{CF} = 250 Hz), 134.3, 132.3, 131.51,

131.49, 129.2, 128.4, 126.1 (Ar*C*), 125.0 (Ar_FC_{ipso}, m), 124.8 (Ar*C*), 21.2, 20.9, 20.8, 19.1, 15.3 (Ar*C*H_3). ^{19}F NMR ($CDCl_3$, 470 MHz): -137.3, -145.1, -161.9, -165.3, -168.5 (m, Ar_FF). Anal. calc. for $C_{48}H_{38}Cl_2F_{10}N_2O_2Ti$: C, 58.61; H, 3.89; N, 2.85. Anal. found: C, 58.16; H, 3.90; N, 2.70.

Bis(2,4-dimethyl-6-[pentafluorophenyl(pentafluorophenylimino)methyl]phenolato)titanium dichloride (19). Ligand **L19** (0.12 g, 0.26 mmol) was reacted as described above to give **19** as a dark red crystalline solid (0.05 g, 38%). ^{1}H NMR ($CDCl_3$, 500 MHz): 7.30, 6.48 (s, 1H each, Ar*H*), 2.20, 2.07 (s, 3H each, ArCH_3). ^{13}C NMR ($CDCl_3$, 125MHz): 168.7 (N=*C*-Ar), 161.0 (Ar*C*-OTi), 140.9, 132.3, 129.9, 127.3 (Ar*C*), 123.8 (Ar_FC_{ipso}, m), 122.8 (Ar*C*), 110.2 (Ar_FC_{ipso}, m), 20.9, 15.5 (Ar*C*H_3). The Ar_FC-F signals are not baseline separated due to C-F coupling. ^{19}F NMR ($CDCl_3$, 470 MHz): -137.7, -139.3, -143.1, -145.5, -149.5, -158.6, -160.8, -161.1, -163.2, -165.7 (m, Ar_FF). Despite repeated attempts, this compound proved to be too sensitive for transport for elemental analysis.

General Procedure for propylene polymerization. A six-ounce Lab-Crest pressure reaction vessel (Andrews Glass) equipped with a magnetic stir bar was charged with dry PMAO-IP (150 equivalents Al per Ti) and toluene (100 mL). The reactor was then equilibrated at 0 °C and the solution was saturated with propylene (30 psig). A toluene solution (5 mL) of PKI catalyst (0.01 mmol) was injected via syringe to initiate the polymerization. A constant pressure of propylene (30 psig) was maintained throughout the polymerization. After an appropriate time (generally 6 hours) at 0 °C, the reaction was quenched with methanol (5 mL) and the reactor was vented. The polymer was precipitated in copious amounts of methanol/HCl (2% acid, 400 mL), collected, washed with methanol, and dried to constant weight.

Synthesis of iPP-*block*-PEP-*block*-iPP triblock copolymers. A six-ounce Lab-Crest pressure reaction vessel (Andrews Glass) equipped with a magnetic stir bar was charged with dry PMAO-IP (150 equivalents Al per Ti) and toluene (100 mL). The reactor was then equilibrated at 0 °C and the solution was saturated with propylene (30 psig). A toluene solution (5 mL) of **12** (0.04 mmol) was injected via syringe to initiate the polymerization. A constant pressure of propylene (30 psig) was maintained for 15-

16 hours. An aliquot of iPP was removed from the reactor via cannula and quenched with acidified methanol. The reactor was placed under ethylene pressure (32 psig), and the polymerization was continued for 14-56 minutes at 0 °C. The reactor was vented free of ethylene and propylene for approximately 10 min. An aliquot of iPP-*block*-PEP was removed from the reactor via cannula and quenched with acidified methanol. Propylene (30 psig) was reconnected and polymerization continued for an additional 15-16 hours. The polymerization was quenched with methanol (5 mL) and the reactor was vented. The polymer was precipitated in copious amounts of methanol/HCl (2% acid, 400 mL), collected, washed with methanol, and dried to constant weight.

Synthesis of iPP-*block*-PEP-*block*-iPP-*block*-PEP-*block*-iPP pentablock copolymer. An iPP-*block*-PEP-*block*-iPP triblock copolymer was made as described above. An aliquot of iPP-*block*-PEP-*block*-iPP was removed from the reactor via cannula and quenched with acidified methanol. The reactor was placed under ethylene pressure (40 psig), and the polymerization was continued for 14 minutes at 0 °C. The reactor was vented free of ethylene and propylene for approximately 10 min. An aliquot of iPP-*block*-PEP-*block*-iPP-*block*-PEP was removed from the reactor via cannula and quenched with acidified methanol. Propylene (30 psig) was reconnected and polymerization continued for an additional 15 hours. The polymerization was quenched with methanol (5 mL) and the reactor was vented. The polymer was precipitated in copious amounts of methanol/HCl (2% acid, 400 mL), collected, washed with methanol, and dried to constant weight.

Synthesis of iPP-*block*-PEP-*block*-iPP-*block*-PEP-*block*-iPP-*block*-PEP-*block*-iPP heptablock copolymer. An iPP-*block*-PEP-*block*-iPP-*block*-PEP-*block*-iPP pentablock copolymer was made as described above. An aliquot of iPP-*block*-PEP-*block*-iPP-*block*-PEP-*block*-iPP was removed from the reactor via cannula and quenched with acidified methanol. The reactor was placed under ethylene pressure (40 psig), and the polymerization was continued for 12 minutes at 0 °C. The reactor was vented free of ethylene and propylene for approximately 10 min. An aliquot of iPP-*block*-PEP-*block*-iPP-*block*-PEP-*block*-iPP-*block*-PEP was removed from the reactor via cannula and quenched with acidified

methanol. Propylene (30 psig) was reconnected and polymerization continued for an additional 15 hours. The polymerization was quenched with methanol (5 mL) and the reactor was vented. The polymer was precipitated in copious amounts of methanol/HCl (2% acid, 400 mL), collected, washed with methanol, and dried to constant weight.

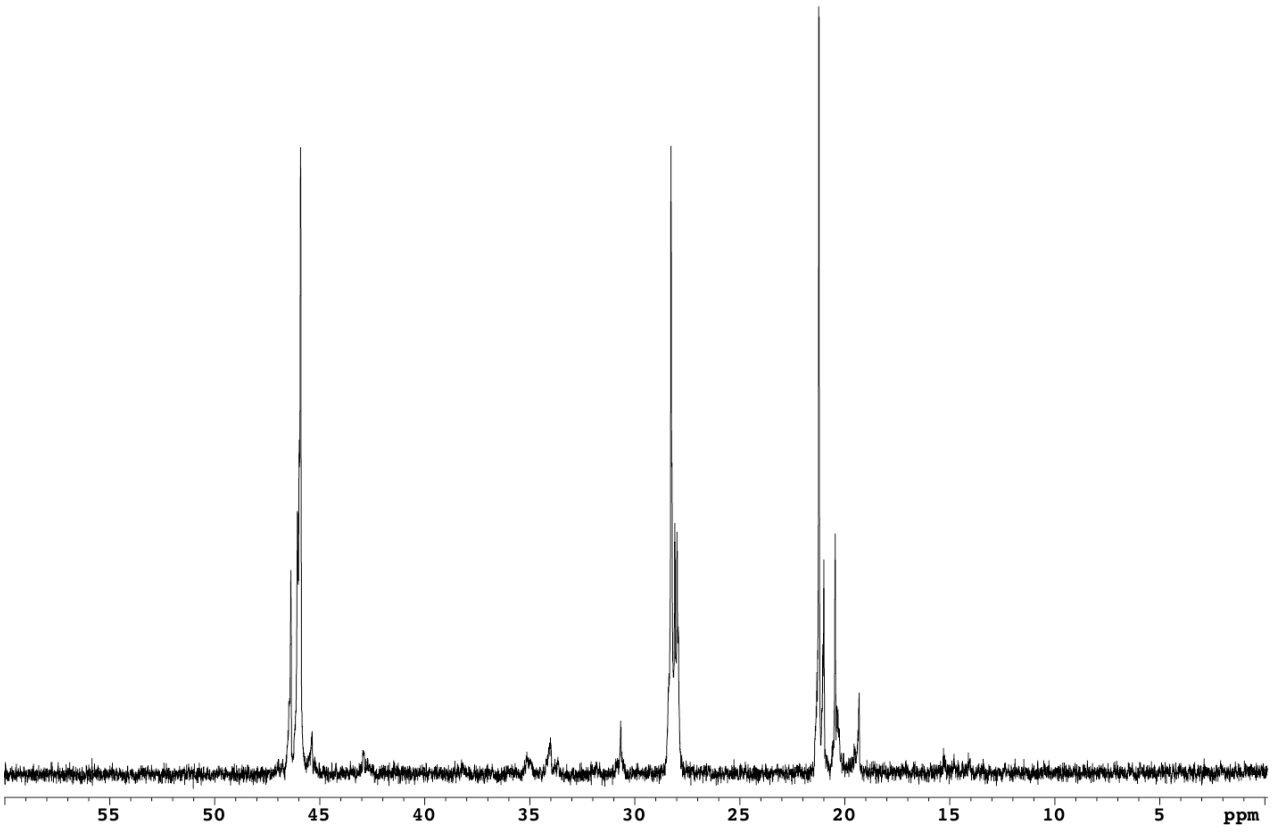

Figure 1. ^{13}C NMR (1,1,2,2-$C_2D_2Cl_4$, 125 MHz, 135 °C) of isotactic PP formed by **1**/MAO at 0 °C.

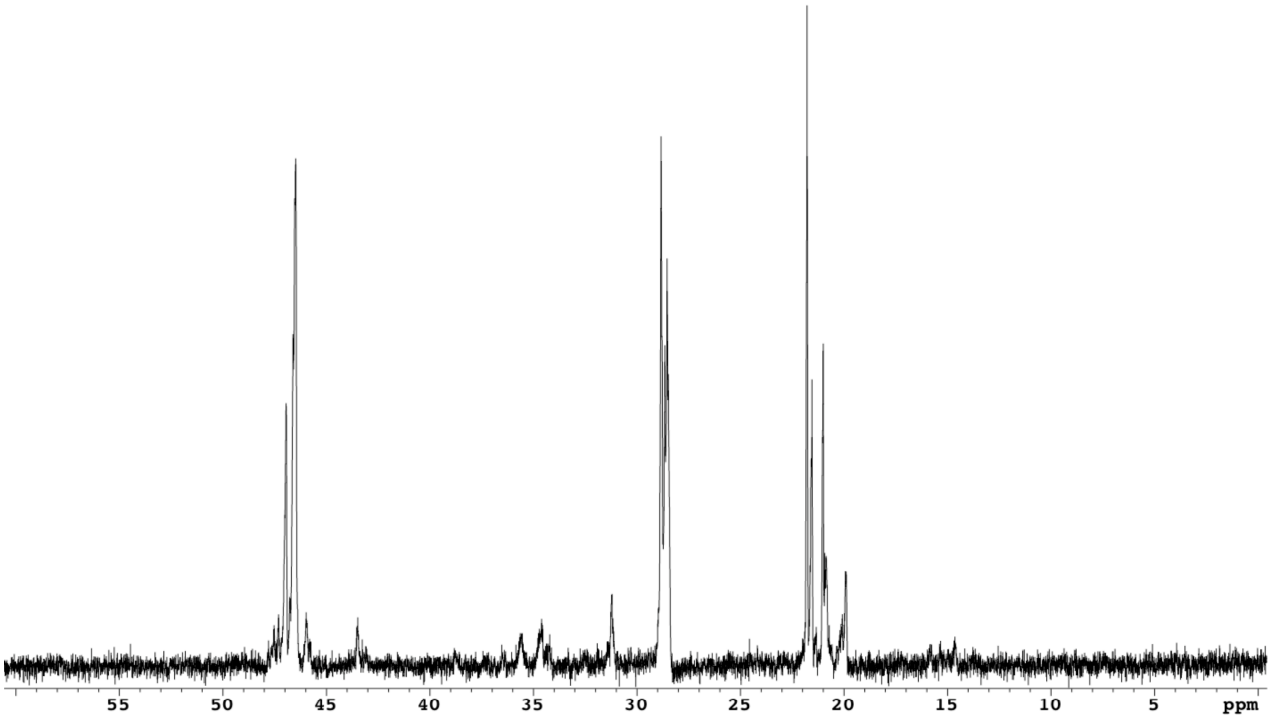

Figure 2. ^{13}C NMR (1,1,2,2-$C_2D_2Cl_4$, 125 MHz, 135 °C) of isotactic PP formed by **2**/MAO at 0 °C.

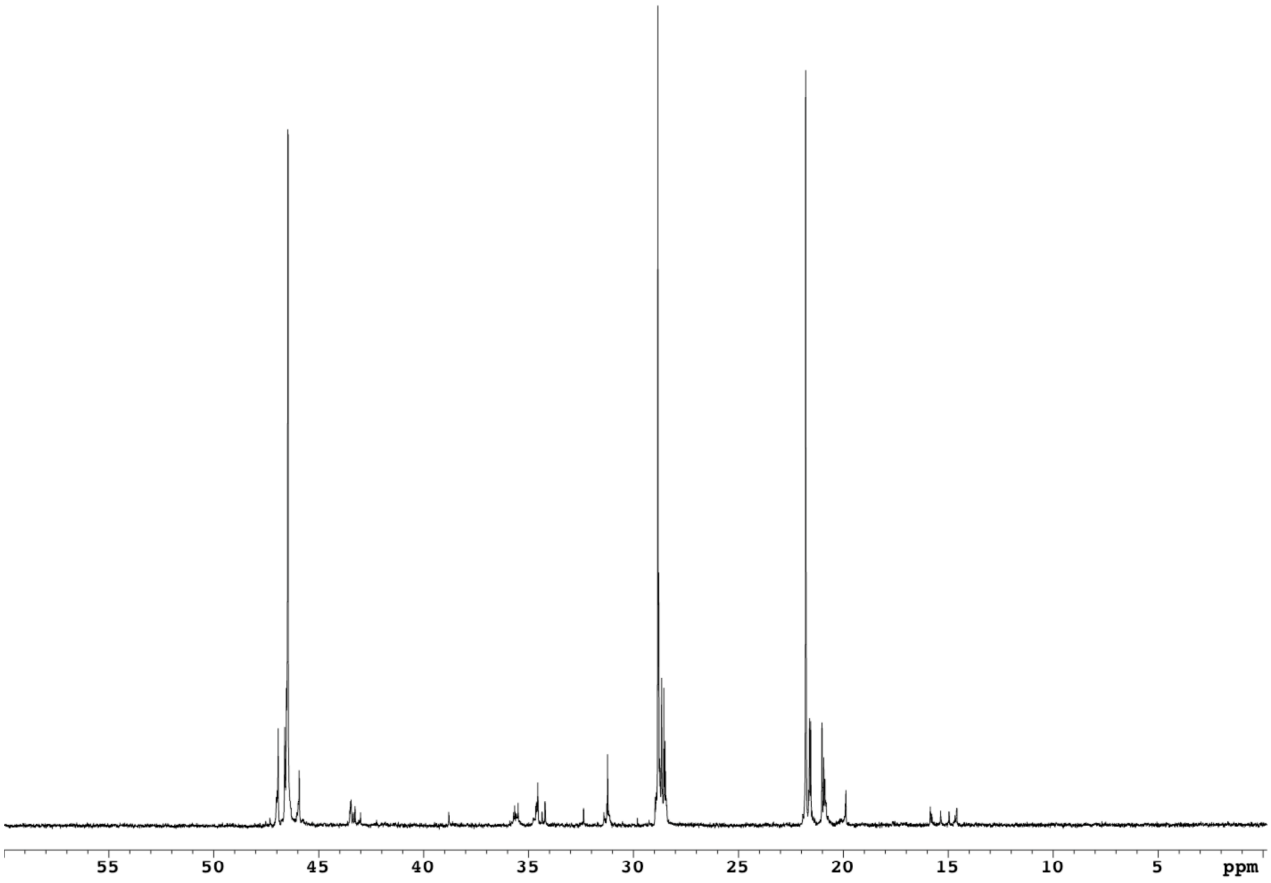

Figure 3. ^{13}C NMR (1,1,2,2-$C_2D_2Cl_4$, 125 MHz, 135 °C) of isotactic PP formed by **3**/MAO at 0 °C.

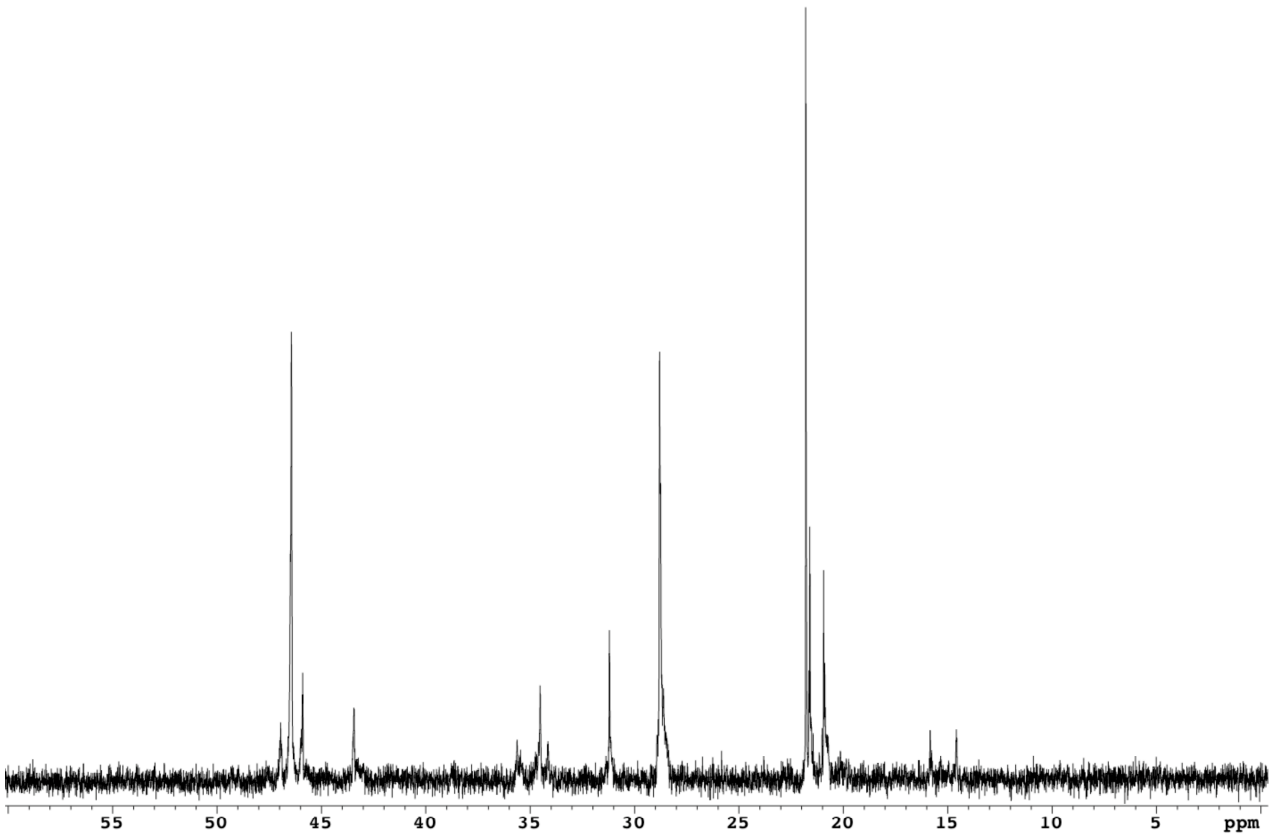

Figure 4. ^{13}C NMR (1,1,2,2-$C_2D_2Cl_4$, 125 MHz, 135 °C) of isotactic PP formed by **5**/MAO at 0 °C.

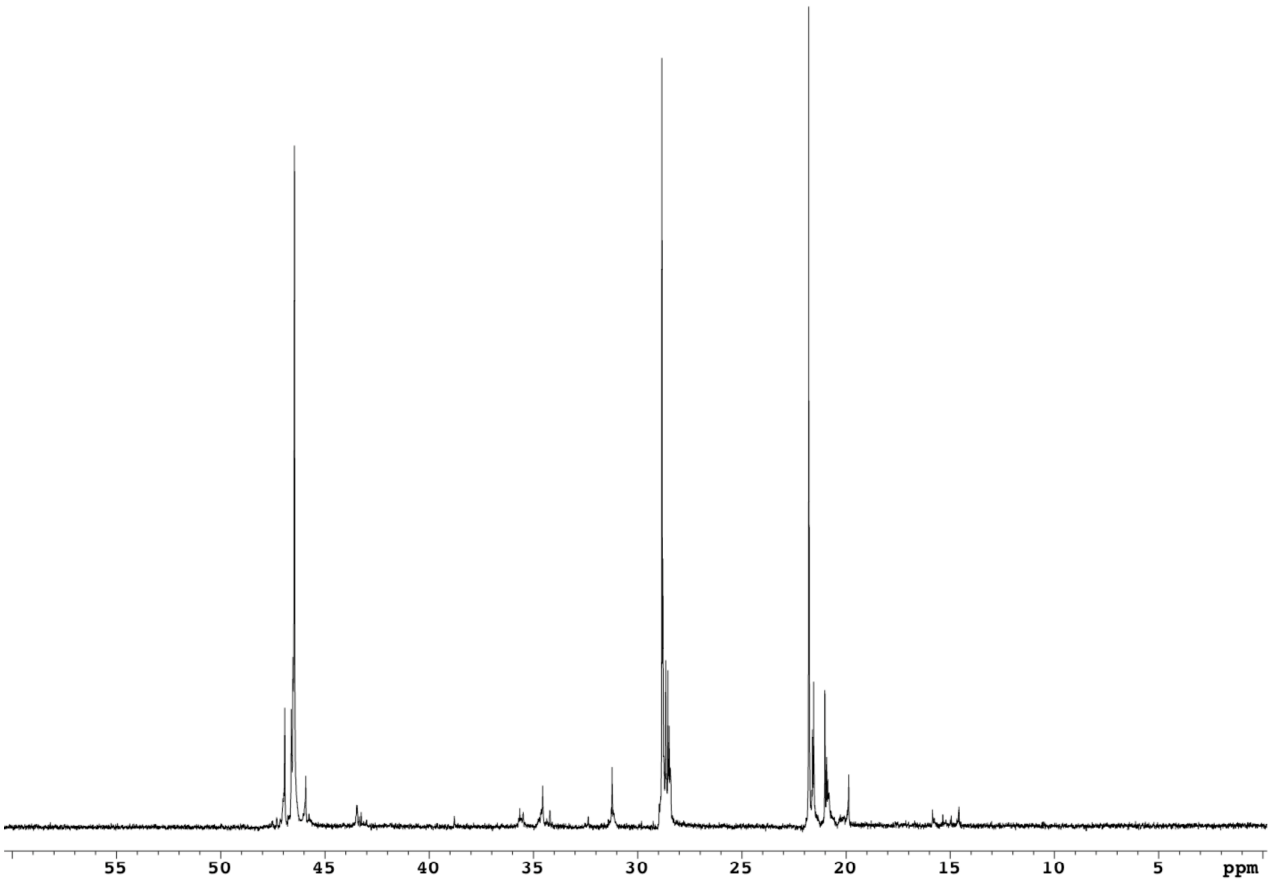

Figure 5. ^{13}C NMR (1,1,2,2-$C_2D_2Cl_4$, 125 MHz, 135 °C) of isotactic PP formed by **6**/MAO at 0 °C.

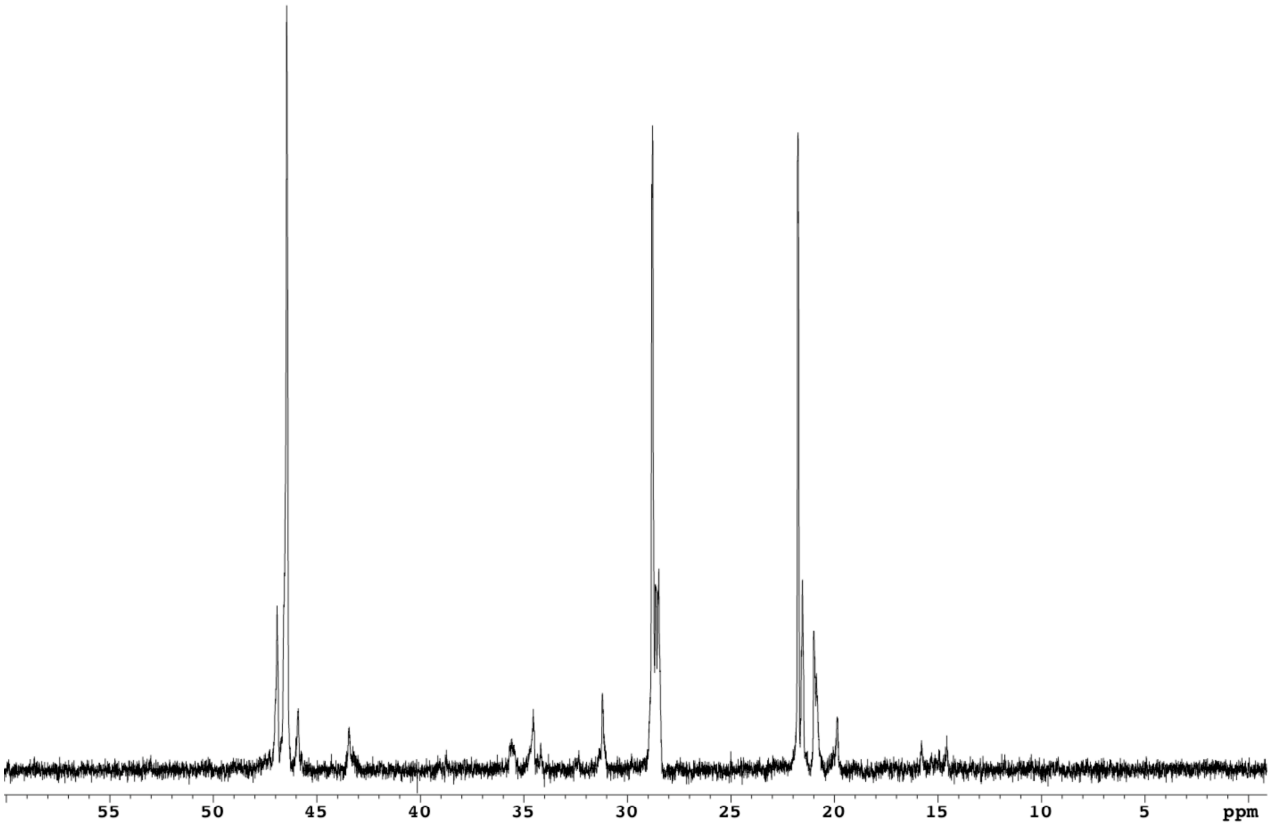

Figure 6. ^{13}C NMR (1,1,2,2-$C_2D_2Cl_4$, 125 MHz, 135 °C) of isotactic PP formed by **7**/MAO at 0 °C.

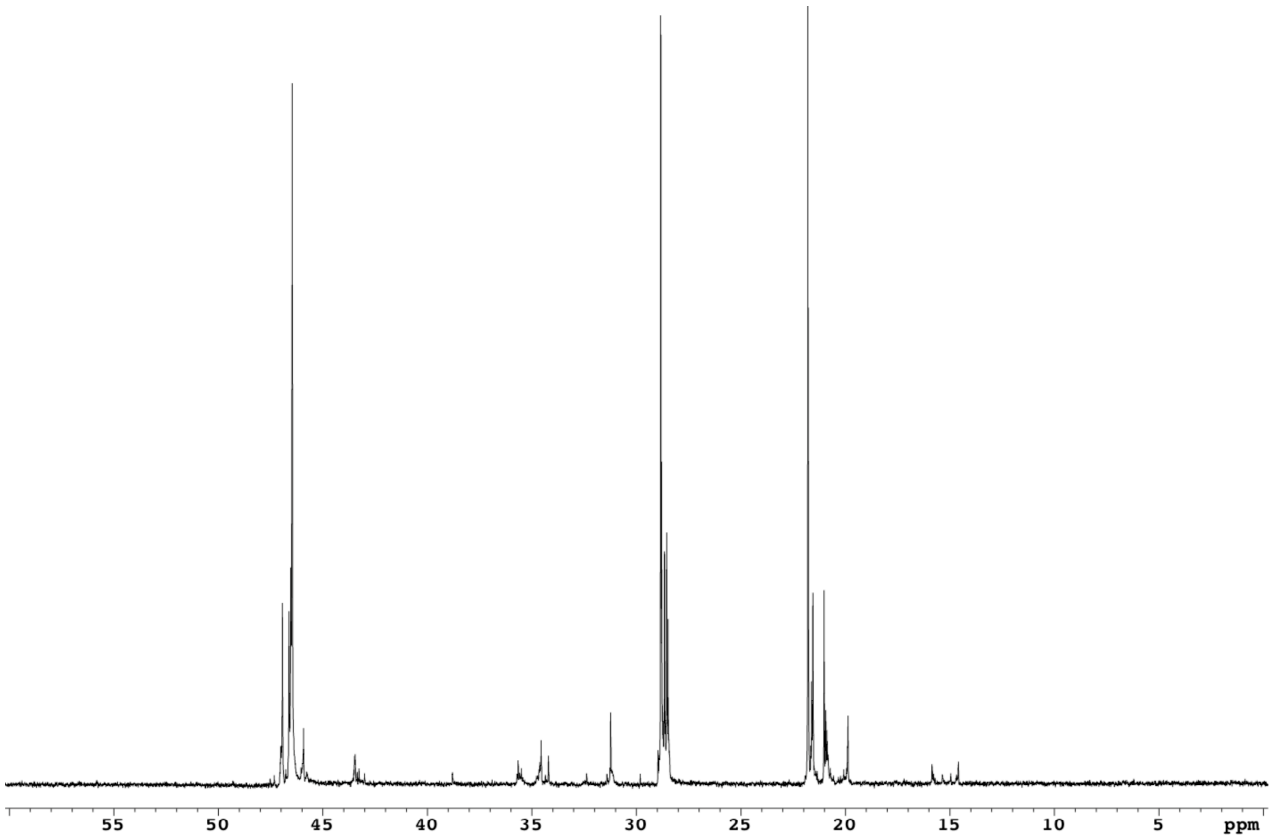

Figure 7. ^{13}C NMR (1,1,2,2-$C_2D_2Cl_4$, 125 MHz, 135 °C) of isotactic PP formed by **8**/MAO at 0 °C.

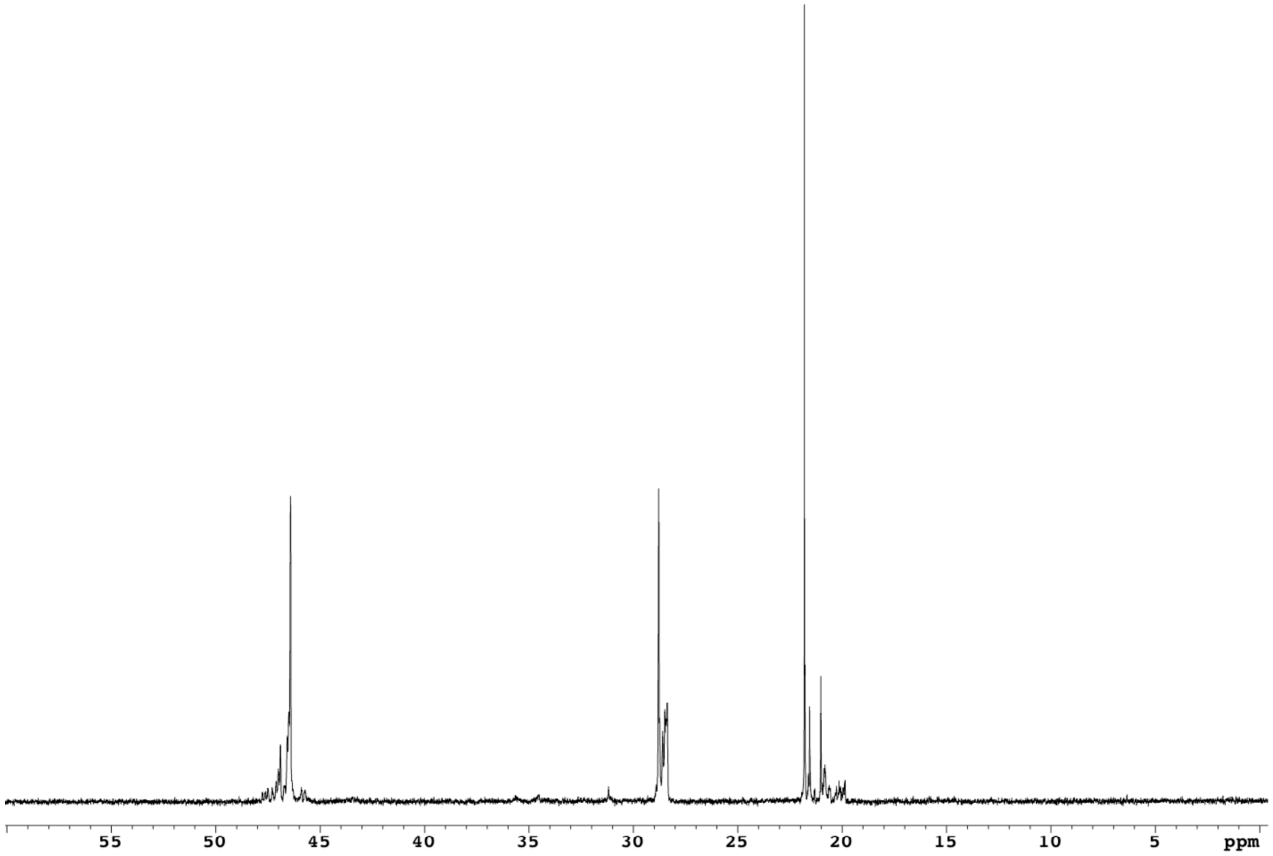

Figure 8. ^{13}C NMR (1,1,2,2-$C_2D_2Cl_4$, 125 MHz, 135 °C) of isotactic PP formed by **9**/MAO at 0 °C.

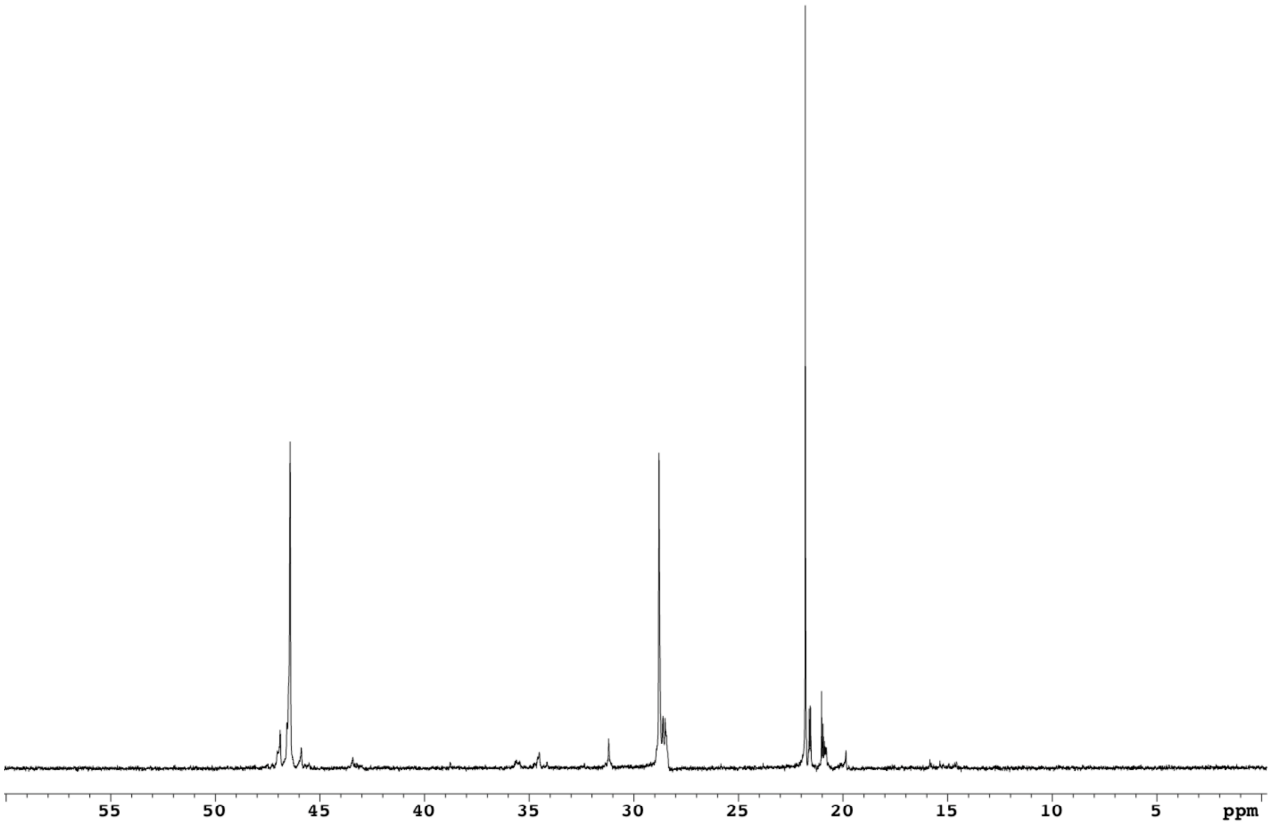

Figure 9. ^{13}C NMR (1,1,2,2-$C_2D_2Cl_4$, 125 MHz, 135 °C) of isotactic PP formed by **10**/MAO at 0 °C.

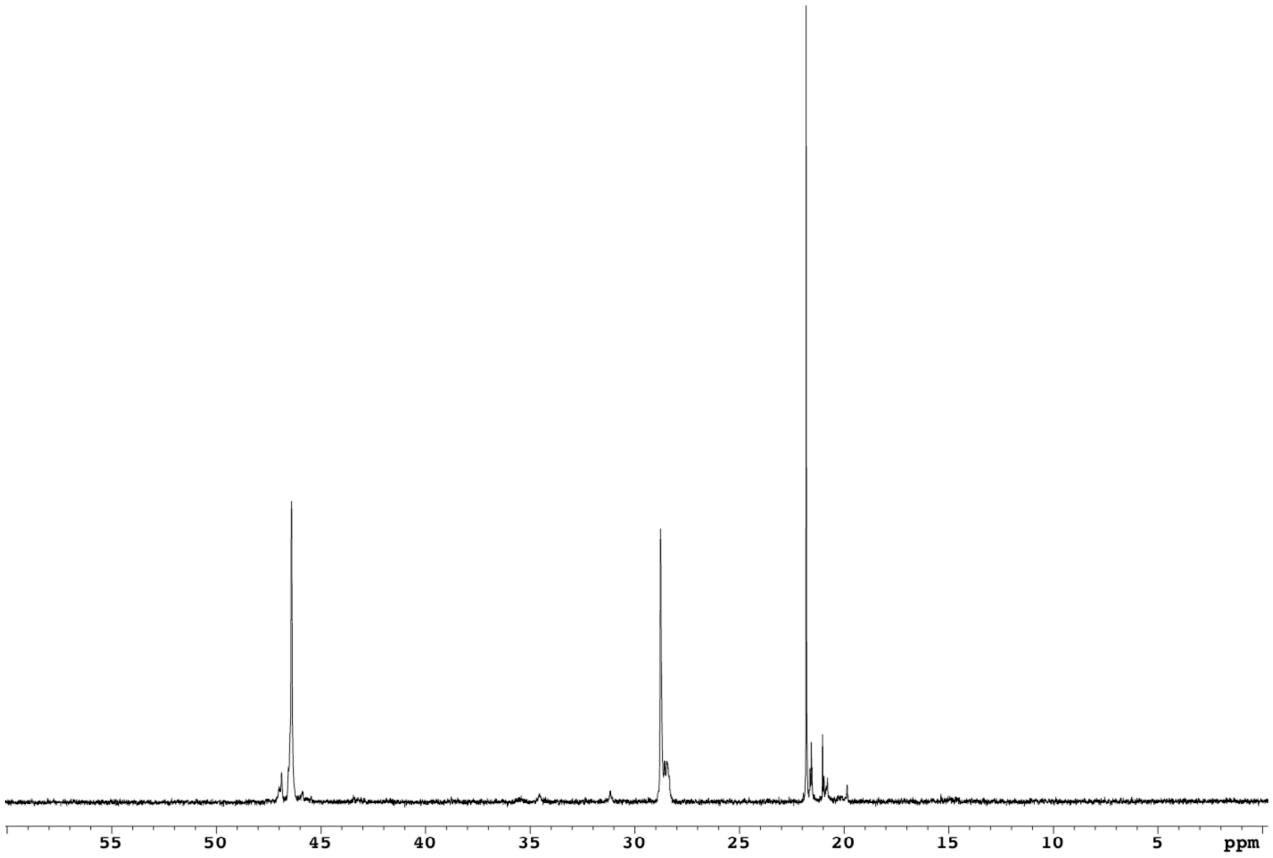

Figure 10. ^{13}C NMR (1,1,2,2-$C_2D_2Cl_4$, 125 MHz, 135 °C) of isotactic PP formed by **11**/MAO at 0 °C.

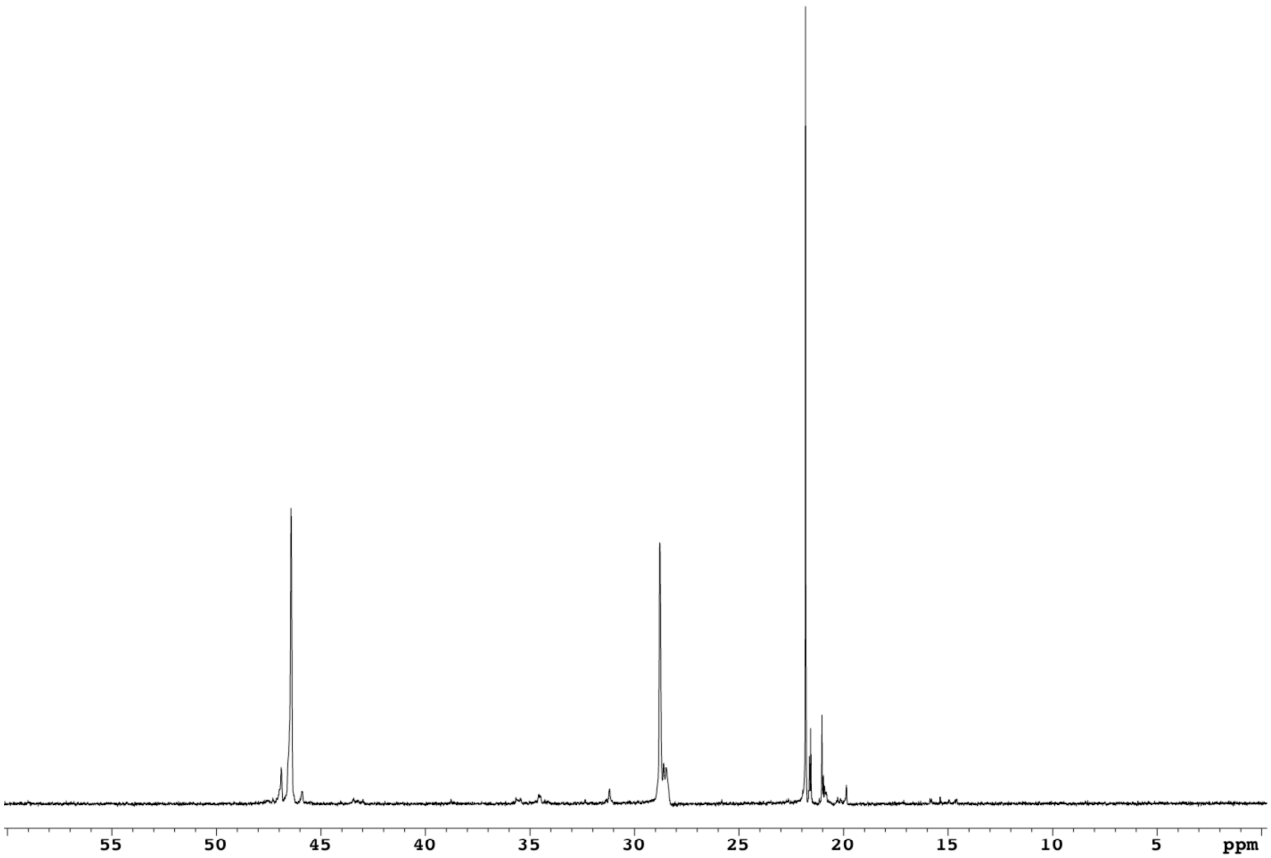

Figure 11. ^{13}C NMR (1,1,2,2-$C_2D_2Cl_4$, 125 MHz, 135 °C) of isotactic PP formed by **13**/MAO at 0 °C.

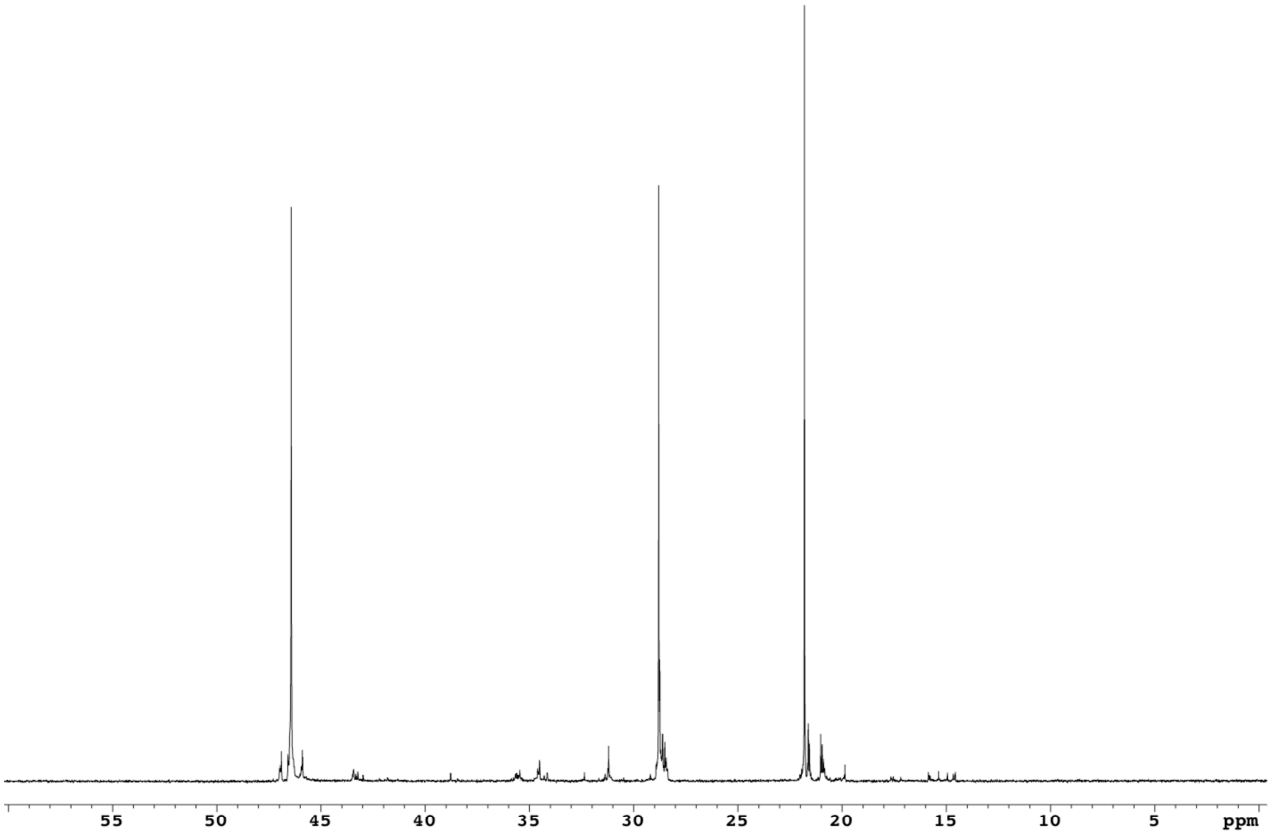

Figure 12. ^{13}C NMR (1,1,2,2-$C_2D_2Cl_4$, 125 MHz, 135 °C) of isotactic PP formed by **14**/MAO at 0 °C.

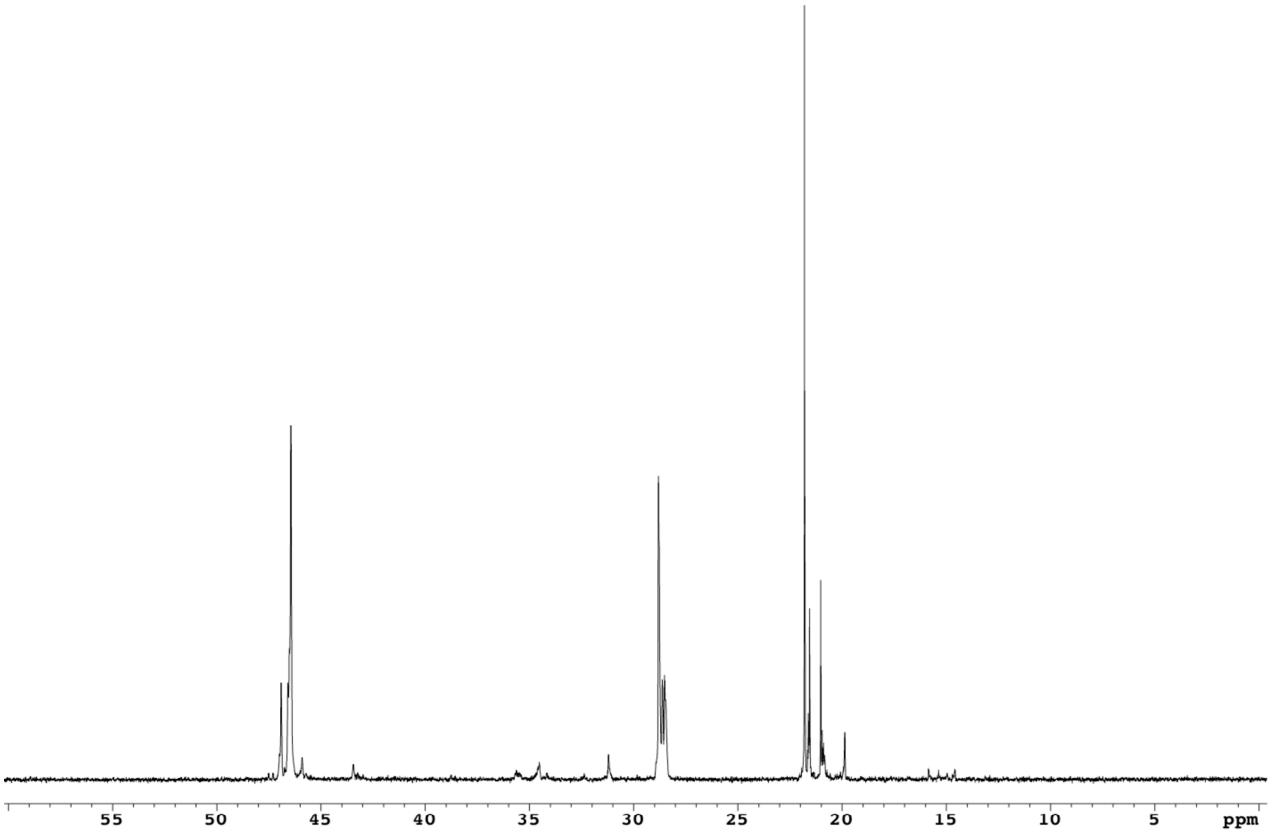

Figure 13. ^{13}C NMR (1,1,2,2-$C_2D_2Cl_4$, 125 MHz, 135 °C) of isotactic PP formed by **15**/MAO at 0 °C.

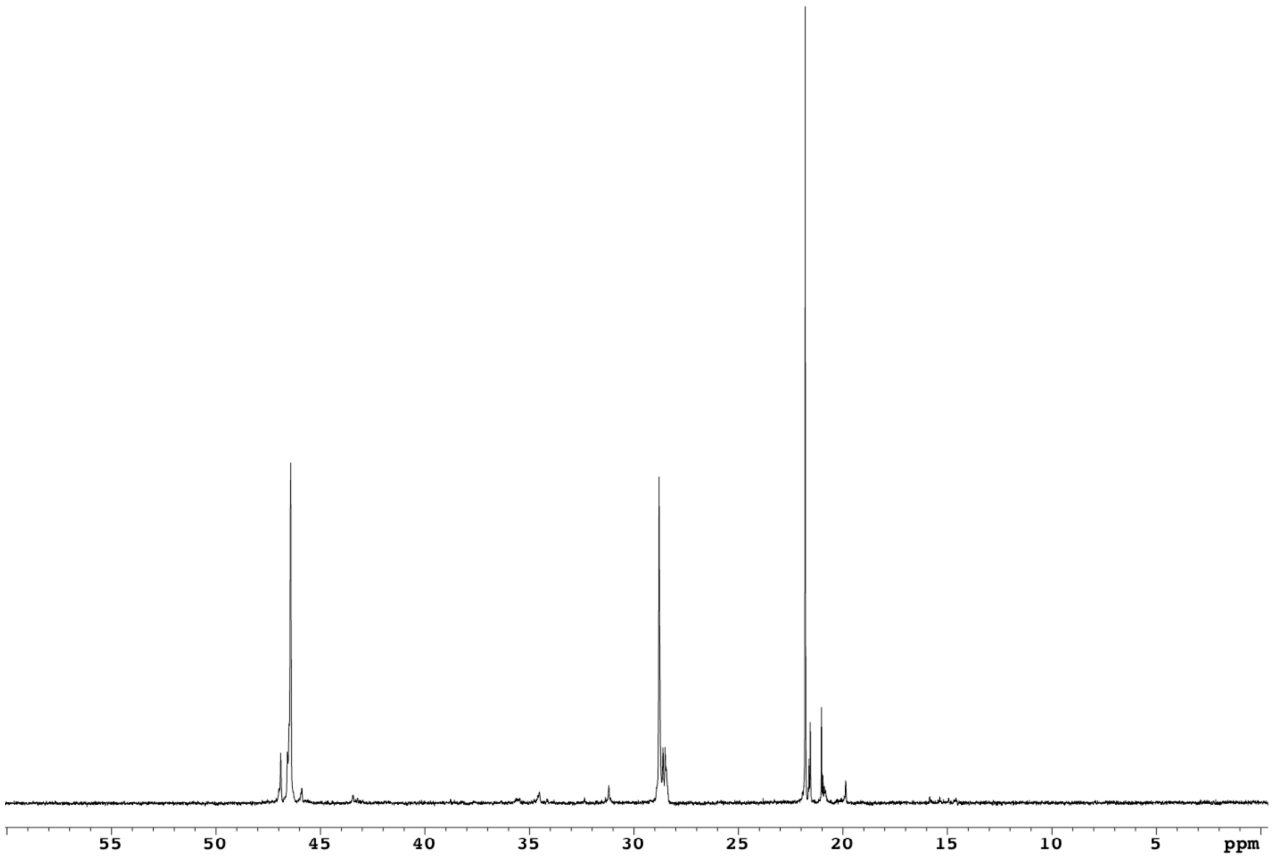

Figure 14. ^{13}C NMR (1,1,2,2-$C_2D_2Cl_4$, 125 MHz, 135 °C) of isotactic PP formed by **16**/MAO at 0 °C.

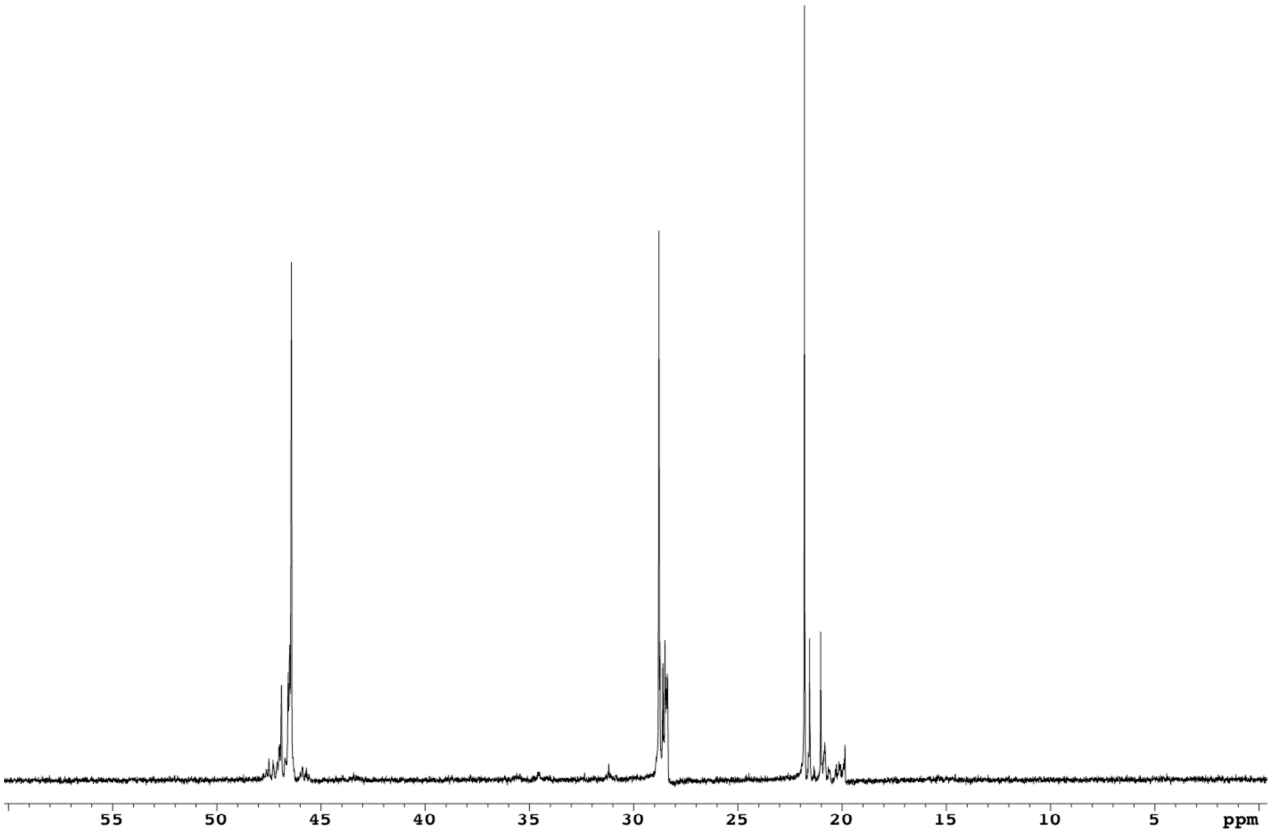

Figure 15. ^{13}C NMR (1,1,2,2-$C_2D_2Cl_4$, 125 MHz, 135 °C) of isotactic PP formed by **17**/MAO at 0 °C.

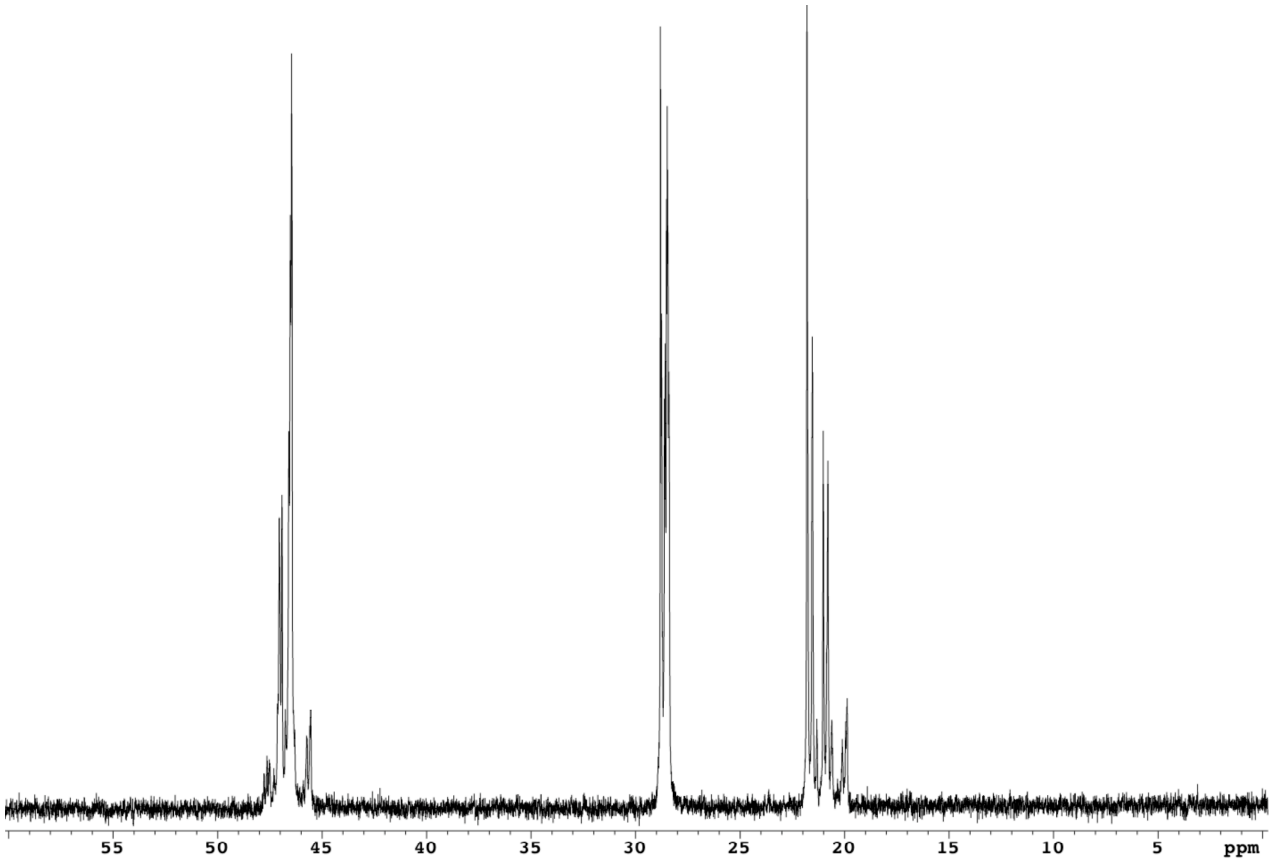

Figure 16. ^{13}C NMR (1,1,2,2-$C_2D_2Cl_4$, 125 MHz, 135 °C) of isotactic PP formed by **18**/MAO at 0 °C.

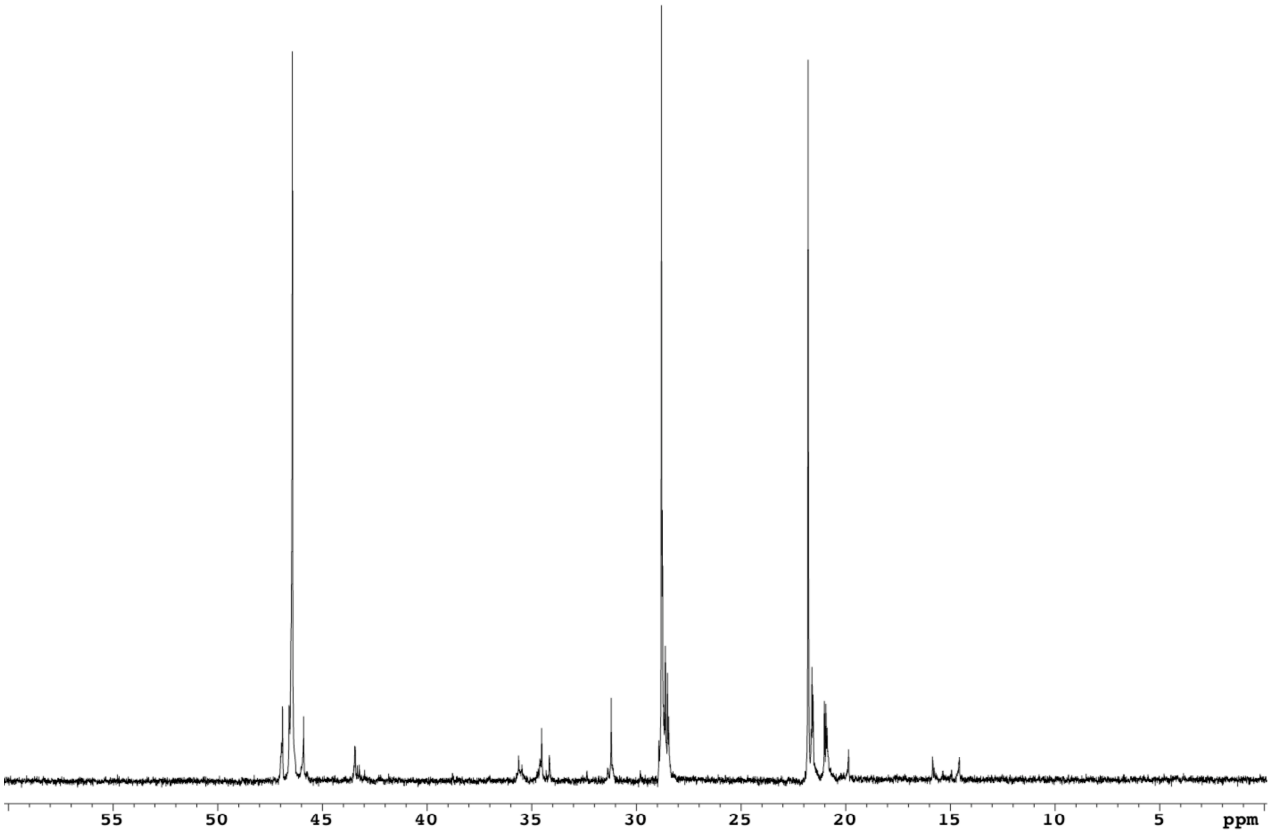

Figure 17. ^{13}C NMR (1,1,2,2-$C_2D_2Cl_4$, 125 MHz, 135 °C) of isotactic PP formed by **19**/MAO at 0 °C.

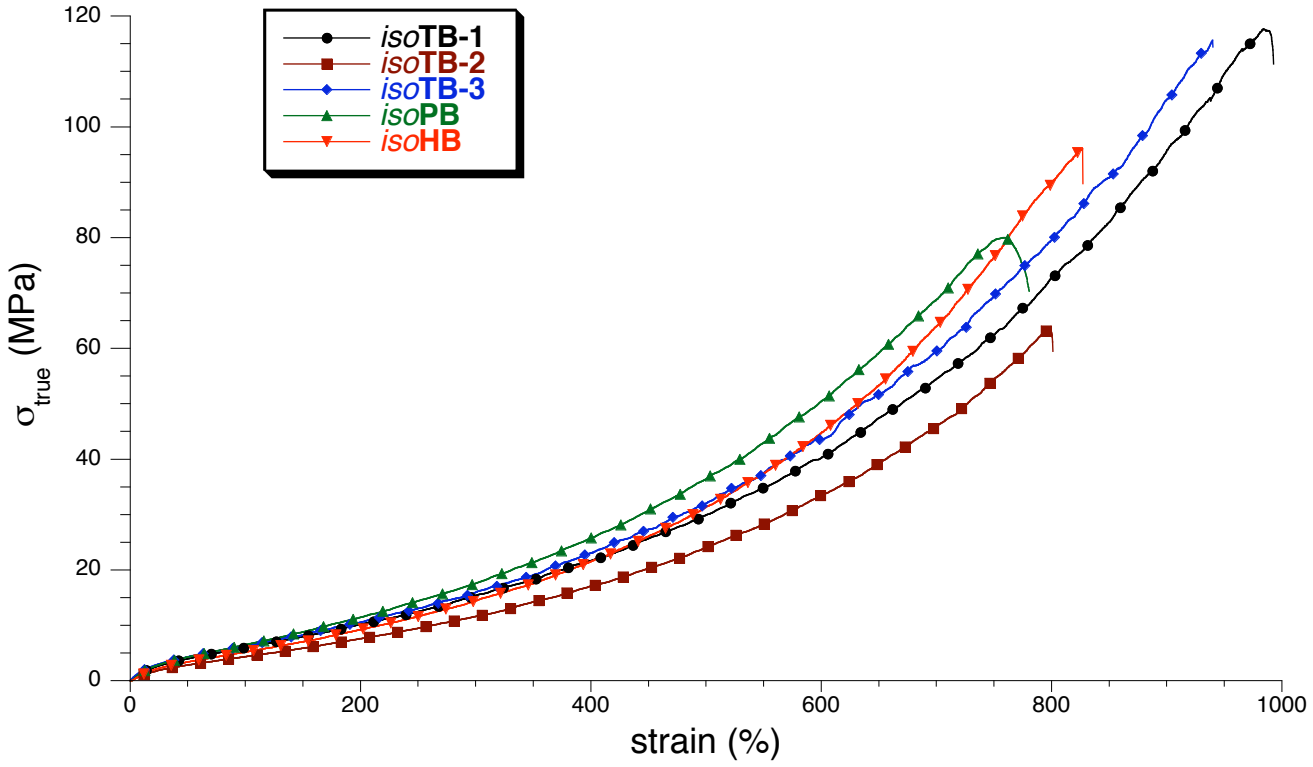

Figure 18. Tensile true stress-versus-strain curves for *iso***TB-1,** *iso***TB-2,** *iso***TB-3,** *iso***HB**, and *iso***PB**.

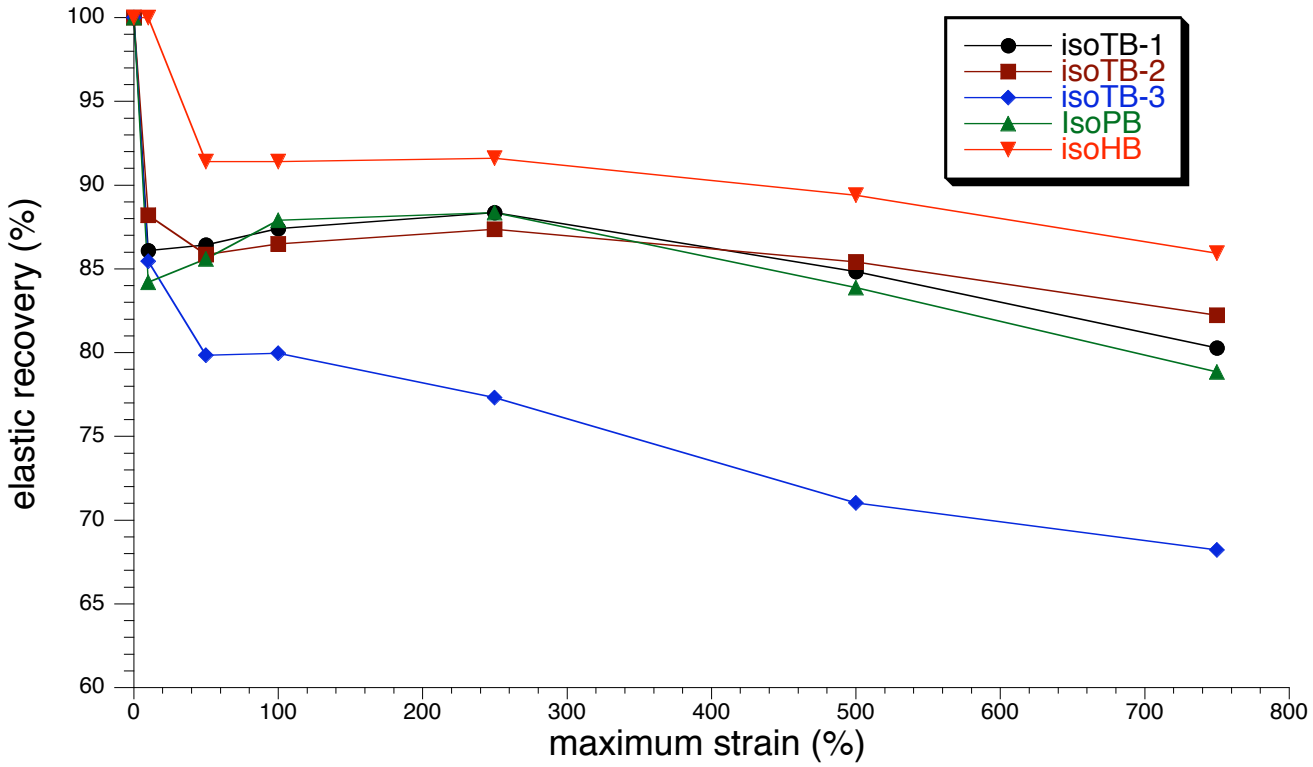

Figure 19. Elastic recovery of *iso***TB-1,** *iso***TB-2,** *iso***TB-3,** *iso***HB**, and *iso***PB** as a function of maximum tensile strain.

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