Supplementary Material (ESI) for Chemical Communications
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Supporting Information for:

Synthesis of a New Olefin Polymerization Catalyst Supported by an sp^3-C Donor via Insertion of a Ligand-appended Alkene into the Hf-C Bond of a Neutral Pyridylamidohafnium trimethyl Complex

*Gregory J. Domski, Joseph B. Edson, Ivan Keresztes, Emil B. Lobkovsky, and Geoffrey W. Coates**

Department of Chemistry and Chemical Biology, Baker Laboratory, Cornell University, Ithaca, NY 14853-1301

General methods. All manipulations of air- and/or water-sensitive compounds were carried out under dry nitrogen using a Braun UniLab drybox or standard Schlenk techniques. ^{1}H NMR spectra of ligands and complexes were recorded using either a Varian Mercury (300 MHz) or Varian Inova (500 MHz) spectrometer. $^{13}C\{^{1}H\}$ 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 and referenced versus residual non-deuterated solvent shifts. The gradient selected HMBC, gradient selected COSY, HSQC, and NOESY spectra were recorded on a Varian INOVA 600 MHz spectrometer operating at 599.757 MHz for ^{1}H observation using a Varian inverse ^{1}H-$\{^{13}C,^{15}N\}$ triple-resonance probehead with triple-axis gradients. The gradient selected COSY spectrum was acquired using the gCOSY sequence as supplied with Vnmrj 2.1B/Chempack 4.1 with a sweep width of 5.4 kHz. A total of 512 points were collected in the indirectly detected dimension with 1 scan and 5.4k points per increment. The resulting matrix was zero filled to 2k x 2k complex data points and sinebell window functions were applied in both dimensions prior to Fourier transformation. The NOESY spectrum was acquired using the NOESY sequence as supplied with Vnmrj 2.1B/Chempack 4.1 with a sweep width of 5.4 kHz. A total of 400 complex points were collected in the indirectly detected dimension with 8 scans and 811 points per increment. The resulting matrix was zero

filled to 2k x 2k complex data points an unshifted Gaussian window function was applied in both dimensions prior to Fourier transformation. The multiplicity edited adiabatic HSQC spectrum was acquired with the HSQCAD sequence supplied with Chempack. Sweep widths were 5.4 kHz and 30.2 kHz in ^{1}H and ^{13}C dimensions, respectively. A total of 256 complex points were collected in the indirectly detected dimension with 4 scans and 811 points per increment. The resulting matrix was zero filled to 2k x 2k complex data points and an unshifted Gaussian window function was applied in the ^{1}H dimension prior to Fourier transformation. The gradient selected adiabatic HMBC spectrum was acquired in phase sensitive mode with the gHMBCAD sequence supplied with Chempack. The one bond J-filter was disabled. Sweep widths were 5.4 kHz and 36.2 kHz in ^{1}H and ^{13}C dimensions respectively. A total of 500 complex points were collected in the indirectly detected dimension with 4 scans and 1.6k points per increment. The resulting matrix was zero filled to 2k x 4k complex data points a squared sinebell window function was applied in the ^{1}H dimension prior to Fourier transformation. The polymer samples were dissolved in 1,1,2,2-tetrachloroethane-d_2 in a 5 mm O.D. tube, and spectra were collected at 135 °C in the case of iPP and at 75 °C in the case of poly(1-hexene). Molecular weights (M_n and M_w) and polydispersities (M_w/M_n) were determined by high temperature gel permeation chromatography (GPC). Analyses were performed with 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 calibrated using monomodal polyethylene standards in the case of PP or monomodal polystyrene standards in the case of poly(1-hexene) (from Polymer Standards Service). Polymers were usually placed in a 140 °C oven for 24 h prior to molecular weight measurements. Polymer melting points (T_m) and glass

transition temperatures (T_g) 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 TA Q series software. Mass spectral analyses were conducted at the School of Chemical Sciences Mass Spectrometry Laboratory at the University of Illinois at Urbana-Champaign or they 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. *N*-Bromosuccinimide (NBS), 2-methyl-1-bromonaphthalene, benzoyl peroxide (BPO), $AgNO_3$, triphenylmethylphosphonium bromide ($[Ph_3PMe]^+Br^-$), BuLi (1.6 M in hexanes), trimethyl borate ($B(OMe)_3$), dimethoxyethane (anhydrous), 1-naphthaleneboronic acid, 2-acetyl-6-bromopyridine, $Pd(OAc)_2$, PPh_3, Me_3Al (2.0 M in toluene), and MeMgBr (3.0 M in Et_2O), were purchased from Aldrich and used as received. 2,6-Diisopropylaniline was donated by Lonza and purified according to the procedure outlined by Nagai and Yamaguchi.[i] Magnesium turnings, $HfCl_4$ (99.9+%, sublimed grade) and tris(pentafluorophenyl)borane ($B(C_6F_5)_3$) were purchased from Strem and used as received. Toluene, hexanes, and pentane were purified over columns of alumina and copper (Q5). Tetrahydrofuran was purified over columns of alumina. To record the NMR spectra of the pyridylamidohafnium dimethyl complexes, the C_6D_6 was dried over sodium/benzophenone ketyl by refluxing for three days

prior to vacuum transfer. The solvent was then degassed by at least three freeze/pump/thaw cycles and stored in the glovebox over molecular seives. Propylene (Matheson, Ultra High Purity) was purified over columns of Selexorb COS alumina donated by Coastal Chemical Company and copper Q5 purchased from Engelhard Corporation.

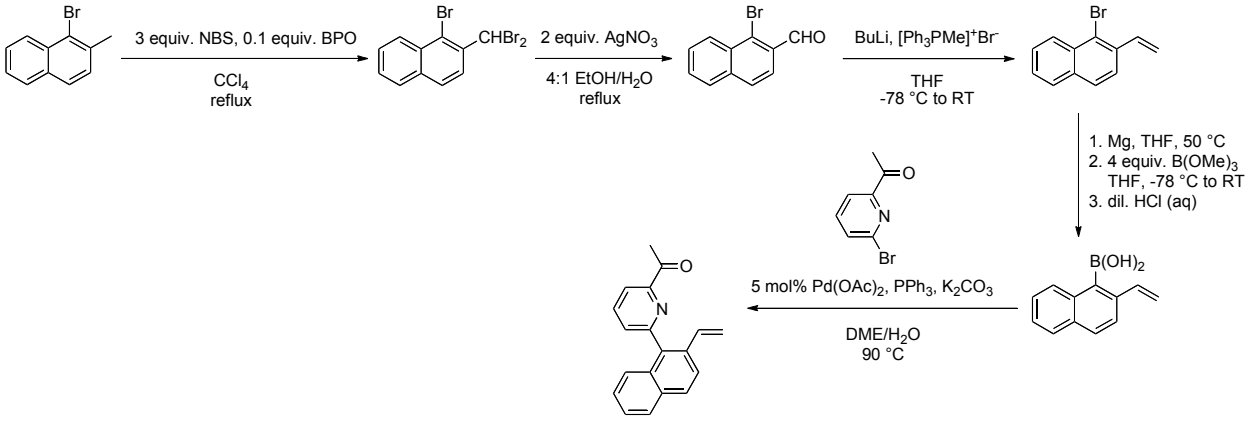
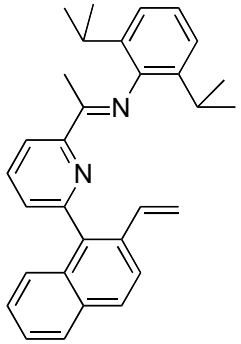


Figure S1. Synthesis of 1-(6-(2-vinylnaphthalen-1-yl)pyridin-2-yl)ethanone.

1-(6-(2-Vinylnaphthalen-1-yl)pyridin-2-yl)ethanone. Following the procedure of Demir and Reis,[ii] 1-bromo-2-(dibromomethyl)naphthalene was prepared via radical bromination of 1-bromo-2-methylnaphthalene (3.6 mL, 23 mmol) with NBS (12.0 g, 67.4 mmol) and BPO (0.75 g, 3.1 mmol) in 68% yield. Hydrolysis of 1-bromo-2-(dibromomethyl)naphthalene (4.00 g, 10.6 mmol) was conducted in EtOH and DI H_2O (500 mL of a 4:1 v/v mixture) in the presence of $AgNO_3$ (3.59 g, 21.1 mol) to furnish 1-bromonaphthalene-2-carbaldehyde in 90% yield. The aldehyde was converted to 1-bromo-2-vinylnaphthalene via the Wittig protocol outlined by Tanaka and coworkers.[iii] Methyltriphenylphosphonium bromide (11.9 g, 33.4 mmol) was suspended in 200 mL of THF and cooled to -78 °C. To this suspension was added BuLi (19.4 mL of a 1.6 M solution in hexanes). The reaction mixture was allowed to stir at -78 °C for two hours after which a solution of 1-bromo-2-naphthalenecarbaldehyde (6.65 g, 28.3 mmol) in 100

mL of THF that had been cooled to -78 °C was added slowly via cannula to the ylide solution. After complete addition, the reaction mixture was allowed to warm to room temperature. The reaction was quenched by the addition of DI H_2O. The organic layer was separated, and the aqueous layer was extracted with Et_2O (3 x 100 mL). The ethereal extracts were combined with the organic layer, and the combined organics were washed with DI H_2O (2 x 200 mL), saturated $NaHCO_3$ (aq) (1 x 100 mL), and brine (1 x 100 mL). The organics were then dried over Na_2SO_4, filtered and concentrated via rotary evaporation. The resultant brown residue was purified via flash chromatography (SiO_2, 9:1 hexanes/EtOAc) to furnish the desired product as a yellow crystalline solid in 39% yield based on the aldehyde. To prepare the boronic acid,[iv] 1-bromo-2-vinylnaphthalene (1.30 g, 5.58 mmol) was converted to the corresponding Grignard reagent by reaction with Mg turnings (0.15 g, 6.1 mmol) in THF at 50 °C for three hours. The solution containing 1-naphthalene-2-vinylmagnesium bromide was cooled to -78 °C and added via cannula to a solution of $B(OMe)_3$ (2.5 mL, 22 mmol) in THF at -78 °C. The reaction mixture was allowed to warm to room temperature and stir overnight. After stirring overnight, 2 mL of HCl (conc.) in 20 mL of DI H_2O was added to the reaction mixture and it was allowed to stir for an hour. The organic layer was separated and the aqueous layer was extracted with Et_2O (3 x 100 mL). The combined organics were washed with DI H_2O (3 x 100 mL) and then concentrated via rotary evaporation. The yellow oily solid was dried over P_2O_5 under reduced pressure and used as the crude product in the next step. Following the Suzuki coupling protocol described by Huo,[v] 1-naphthalene-2-vinylboronic acid from the previous step (ca 1.1 g, 5.5 mmol) was dissolved in DME and combined with 2-acetyl-6-bromopyridine (0.88 g, 4.4 mmol), and PPh_3 (0.30 g, 1.2 mmol). To this solution was added K_2CO_3 (6.6 mL of a 2.0 M aqueous solution). The solution was degassed by sparging with N_2 for 15 minutes, and then $Pd(OAc)_2$ (0.06 g, 0.3 mmol) was

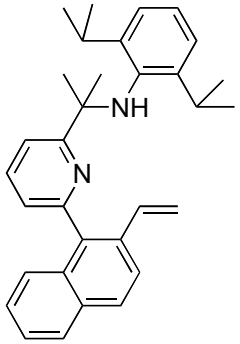
added to the reaction mixture. The reaction mixture was heated to 90 °C and allowed to stir overnight. After cooling, the organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (3 x 100 mL). The combined organics were washed with $NaHCO_3$ (1 x 100 mL), DI H_2O (2 x 100 mL), and brine (1 x 100 mL), then dried over Na_2SO_4, filtered, and concentrated via rotary evaporation. The resultant brown residue was purified via flash chromatography (SiO_2, 9:1 hexanes/EtOAc) to furnish 0.83 g (69% based on ketone) of the desired product as a white crystalline solid. ^{1}H NMR (C_6D_6, 500 MHz): δ 8.02 (dd, J_{HH} = 7.81 Hz, 0.98 Hz, 1H, Ar*H*), 7.68-7.63 (m, 3H, Ar*H*), 7.40 (d, J_{HH} = 8.30 Hz, 1H, Ar*H*), 7.23 (td, J_{HH} = 7.45 Hz, 1.63 Hz, 1H, Ar*H*), 7.18-7.15 (m, 1H, Ar*H*), 7.09 (t, J_{HH} = 7.81 Hz, 1H, Ar*H*), 6.94 (dd, J_{HH} = 7.33 Hz, 0.98 Hz, 1H, Ar*H*), 6.60 (dd, J_{HH} = 17.58 Hz, 10.74 Hz, 1H, *H*C=CH_2), 5.65 (dd, J_{HH} = 17.58 Hz, 0.98 Hz, 1H, HC=C*H*(H)), 5.07 (dd, J_{HH} = 11.23 Hz, 0.98 Hz, 1H, HC=C*H*(H)), 2.50 (s, 3H, (C*H*$_3$)C=O). ^{13}C{^{1}H} NMR (C_6D_6, 125 MHz): δ 199.65 (*C*=O), 157.96, 154.45, 137.21, 137.04, 135.67, 133.99, 133.93, 133.34, 129.92, 129.44, 128.73, 127.19, 126.87, 126.54, 123.44, 120.31, 116.04 (H_2C=CH), 26.01 ((H$_3$*C*)C=O) MS-EI (*m/z*): 273.1 (M^+). HRMS-EI (*m/z*): calcd for $C_{19}H_{15}NO$, 273.1154; found, 273.1162.



(*E*)-2,6-Diisopropyl-*N*-(1-(6-(2-vinylnaphthalen-1-yl)pyridin-2-yl)ethylidene)aniline.

The title compound was prepared via the condensation of 1-(6-(2-vinylnaphthalen-1-yl)pyridin-2-yl)ethanone (0.40 g, 1.5 mmol) with 2,6-diisopropylaniline (0.28 mL, 1.5 mmol) as described

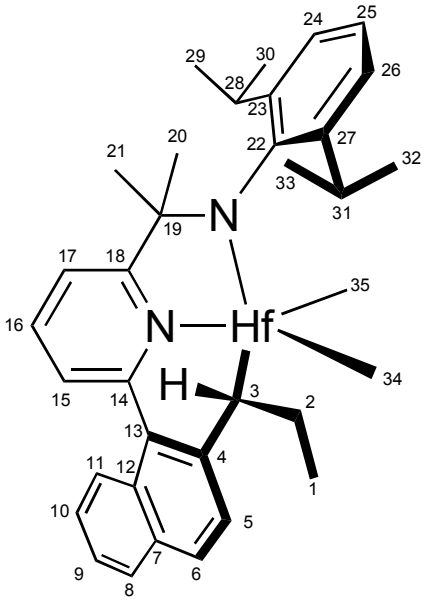
previously[vi] to furnish the desired compound as a yellow powder (0.54 g, 86%). ^{1}H NMR (C_6D_6, 500 MHz): δ 8.59 (dd, J_{HH} = 7.81 Hz, 0.98 Hz, 1H, Ar*H*), 7.71-7.63 (m, 3H, Ar*H*), 7.57 (d, J_{HH} = 8.79 Hz, 1H, Ar*H*), 7.29 (t, J_{HH} = 7.81 Hz, 1H, Ar*H*), 7.21-7.08 (m, 5H, Ar*H*), 7.02 (dd, J_{HH} = 7.32 Hz, 0.98 Hz, 1H, Ar*H*), 6.75 (dd, J_{HH} = 23.58 Hz, 11.23 Hz, 1H, *H*C=CH_2), 5.65 (dd, J_{HH} = 17.58 Hz, 0.98 Hz, 1H, HC=C*H*(H)), 5.01 (dd, J_{HH} = 11.23 Hz, 0.98 Hz, 1H, HC=C*H*(H)), 2.95 (sept, J_{HH} = 6.84 Hz, 2H, C*H*(CH_3)$_2$), 2.26 (s, 3H, (H_3C)C=N), 1.21 (d, J_{HH} = 6.84 Hz, 6 H, CH(C*H*$_3$)$_2$), 1.08 (d, J_{HH} = 6.84 Hz, 6H, CH(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (C_6D_6, 125 MHz): δ 168.15 ((H_3C)*C*=N), 157.84, 157.24, 147.50, 137.62, 136.98, 136.31, 135.97, 134.02, 133.97, 133.51, 129.28, 128.65, 128.11, 127.19, 127.14, 126.45, 124.59, 123.84, 123.46, 120.11, 115.80 (H_2C=CH), 29.12 (*C*H(CH_3)$_2$), 23.90 (CH(*C*H_3)$_2$), 23.23 (CH(*C*H_3)$_2$), 17.78 ((H_3C)C=N). MS-EI (*m/z*): 432.2 (M^+). HRMS-EI (*m/z*): calcd for $C_{31}H_{32}N_2$, 432.2566; found, 432.2554.



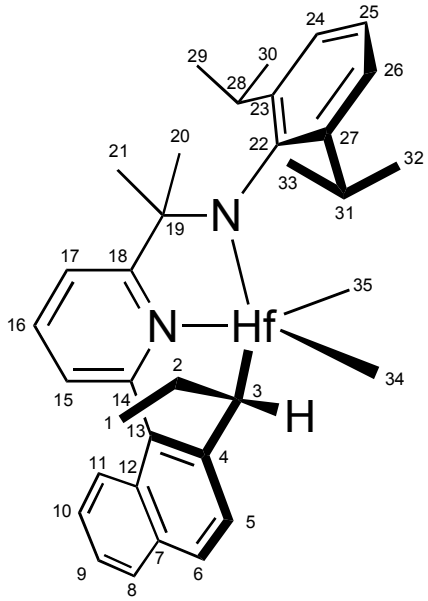
2,6-Diisopropyl-*N*-(2-(6-(2-vinylnaphthalen-1-yl)pyridin-2-yl)propan-2-yl)aniline.

Following the procedure for alkylation of pyridylimines,[7] the title compound was prepared by combining (*E*)-2,6-diisopropyl-*N*-(1-(6-(2-vinylnaphthalen-1-yl)pyridin-2-yl)ethylidene)aniline (0.81 g, 1.9 mmol) and Me_3Al (1.88 mL of a 2.0 M solution in toluene) in toluene (ca. 20 mL) and heating the resultant solution to 110 °C with stirring for 18 hours. After allowing the reaction to cool, DI H_2O was added carefully under a stream of N_2. The organic layer was separated and the aqueous layer was extracted with Et_2O (3 x 100 mL). The combined organics were washed

with DI H_2O (2 x 100 mL) and brine (1 x 100 mL), dried over Na_2SO_4, filtered and concentrated via rotary evaporation to furnish a colorless oil. The oil was further dried *in vacuo*, and crystallized on standing to furnish the desired product as a white crystalline solid (0.76 g, 90%). ^{1}H NMR (C_6D_6, 500 MHz): δ 7.72 (d, J_{HH} = 8.79 Hz, 1H, Ar*H*), 7.66-7.61 (m, 3H, Ar*H*), 7.24-7.19 (m, 4H, Ar*H*), 7.12 (s, 2H, Ar*H*), 6.94 (dd, J_{HH} = 6.83 Hz, 1.47 Hz, 1H, Ar*H*), 6.81 (dd, J_{HH} = 17.58 Hz, 11.23 Hz, 1H, *H*C=CH_2), 5.69 (apparent d, J_{HH} = 17.58 Hz, 1H, HC=C*H*(H)), 5.12 (apparent d, J_{HH} = 11.23 Hz, 1H, HC=C*H*(H)), 4.63 (s, 1H, $(CH_3)_2$C-N*H*), 3.47 (sept, J_{HH} = 6.84 Hz, 2H, C*H*$(CH_3)_2$), 1.53 (s, 6H, $(CH_3)_2$C-NH), 1.11 (d, J_{HH} = 6.84 Hz, 12H, CH$(CH_3)_2$). ^{13}C{^{1}H} NMR (C_6D_6, 125 MHz): 169.19, 157.39, 147.42, 141.35, 138.13, 136.84, 136.06, 134.05, 133.75, 133.59, 129.13, 128.68, 127.20, 127.03, 126.43, 125.55, 124.52, 123.81, 123.41, 117.83, 115.57, 59.82, 29.90, 28.93, 24.62. MS-EI (*m/z*): 448.3 (M^+). HRMS-EI (*m/z*): calcd for $C_{32}H_{36}N_2$, 448.28749; found, 448.287853.



rac-**2a** (major)



rac-**2b** (minor)

Synthesis of *rac*-2a,b. A hexanes solution of 2,6-diisopropyl-*N*-(2-(6-(2-vinylnaphthalen-1-yl)pyridin-2-yl)propan-2-yl)aniline (0.46 g, 1.0 mmol) was cooled to 0 °C. To this solution was added BuLi (0.68 mL of a 1.6 M solution in hexanes); the previously colorless solution became green and a white precipitate formed. The reaction was allowed to stir for one hour at 0 °C, and then the volatiles were removed in vacuo. The resultant pale green solid was treated with pentane to furnish a white precipitate. The supernatant was removed, and the precipitate was dried *in vacuo*, and then redissolved in toluene and added to a suspension of $HfCl_4$ (0.36 g, 1.1 mmol) in toluene. The resulting mixture was heated to 110 °C and allowed to stir for 6 hours for metalation as previously described.[8] The reaction mixture gradually changed from brown to orange and then finally to pale yellow. After cooling, MeMgBr (1.27 mL of a 3.0 M solution in Et_2O) was added to the reaction mixture and the reaction was allowed to stir overnight. The volatiles were removed *in vacuo*, and the resultant brown residue was extracted with toluene, and filtered through Celite to furnish an orange solution. The volatiles were removed *in vacuo* to furnish the crude product as an orange foam-like solid. Characterization of the crude product via ^{1}H NMR spectroscopy revealed a 15:85 mixture of the pyridylamidohafnium trimethyl complex (**1**) and a diastereomeric mixture of the pyridylamidohafnium dimethyl complex (*rac*-**2a,b**) which resulted from intramolecular insertion of the vinyl moiety in a 2,1-fashion. The crude product was redissolved in toluene, and then heated to 80 °C for 12 hours. The volatiles were removed to furnish the product as an orange resinous solid (0.39 g, 57%). Single crystals of suitable quality for structural determination via X-ray crystallography were grown from a saturated, pentane-layered toluene solution at -30 °C. The ^{1}H and ^{13}C{^{1}H} NMR data for the diastereomeric mixture are tabulated below. The resonances for *rac*-**2a** (major) and *rac*-**2b** (minor) were assigned with the aid of *g*COSY,

*g*HMBC, *g*HSQC, and NOESY experiments. ^{1}H NMR (C_6D_6, 300 MHz): δ 7.77-7.55 (m; H5, 6, 9, 11 (major); H6, 9, 11 (minor)), 7.38 (d, J_{HH} = 8.62 Hz, H5 (minor)), 7.29-7.12 (m; H8, 10, 24, 26 (major and minor) and H16 (minor)), 7.10 (td, J_{HH} = 7.97 Hz, 0.88 Hz, H16 (major)), 6.94 (dd, J_{HH} = 7.60 Hz, 0.88 Hz, H15 (minor)), 6.82 (dd, J_{HH} = 7.60 Hz, 0.88 Hz, H15 (major)), 6.58 (dd, J_{HH} = 8.25 Hz, 0.88 Hz, H17 (minor), 6.53 (dd, J_{HH} = 8.18 Hz, 0.88 Hz, 1H, H17 (major)), 4.02 (two overlapped sept, J_{HH} = 6.72 Hz, H28 (major and minor)), 3.69 (sept, J_{HH} = 6.72 Hz, H31 (major)), 3.68 (sept, J_{HH} = 6.72 Hz, H31 (minor)), 2.84-2.48 (m, H2^{a,b}, 3 (major); H3 (minor)), 2.14-2.01 (m, H2^{a} (minor)), 1.48-0.96 (apparent multiplet, H1, 20, 21, 29, 30, 32, 33 (major); H1, 2^{b}, 20, 21, 29, 30, 32, 33 (minor)), 0.11 (s, 3H, H34 (major)), 0.08 (s, 3H, H34 (minor)), -0.33 (s, 3H, H35 (minor)), -0.35 (s, 3H, H35 (major)). ^{13}C{^{1}H} NMR (C_6D_6, 125 MHz): δ 173.91 (C18 (minor)), 173.25 (C18 (major)), 154.20 (C14 (minor)), 153.64 (C14 (major)), 150.85 (C27 (minor)), 150.32 (C27 (major)), 149.93 (C23 (minor)), 149.51 (C23 (major)), 140.61 (C16 (major)), 140.49 (C16 (minor)), 139.95 (C22 (major)), 139.61 (C4 (minor)), 138.84 (C4 (major)), 138.59 (C22 (minor)), 134.98 (C5 (minor)), 133.42 (C7 (minor)), 132.91 (C6 (major)), 132.46 (C6 (minor)), 132.21 (C12 (minor)), 131.90 (C7 (major)), 129.79 (C13 (minor)), 129.67 (C8 (minor)), 129.62 (C8 (major)), 127.94 (C13 (major)), 127.86 (C10 (major)), 127.78 (C10 (minor)), 127.32 (C25 (minor)), 127.10 (C25 (major)), 126.04 (C12 (major)), 125.81 (C5 (major)), 125.50 (C24 (minor)), 125.33 (C24 (major)), 125.25 (C9 (minor)), 125.13 (C26 (minor)), 125.05 (C26 (major)), 124.65 (C9 (major)), 124.02 (C15 (minor)), 123.92 (C15 (major)), 123.01 (C11 (minor)), 122.87 (C11 (major)) 119.51 (C17 (minor)), 118.99 (C17 (major)), 86.82 (C3 (minor)), 82.08 (C3 (major)), 72.13 (C19 (major)), 72.00 (C19 (minor)), 61.24 (C34 (major)), 58.10 (C34 (minor)), 47.45 (C35 (major)), 46.36 (C35 (minor), 34.28 (C20 (major)), 34.18 (C20 (minor)), 29.33 (C31 (major)), 29.01 (C31 (minor)),

28.57 (C28 (major)), 28.01 (C21 (major)), 27.82 (C32 (major)), 27.81 (C30 (major)), 27.71 (C30 (minor)), 27.66 (C21 (minor)), 27.17 (C32 (minor)), 26.98 (C2 (minor)), 25.23 (C29 (minor)), 25.18 (C29 (major)), 24.73 (2 *C*, C2 (major); C33 (minor)), 24.55 (C33 (major)), 21.78 (C28 (minor)), 20.02 (C1 (minor)), 18.34 (C1 (major)).

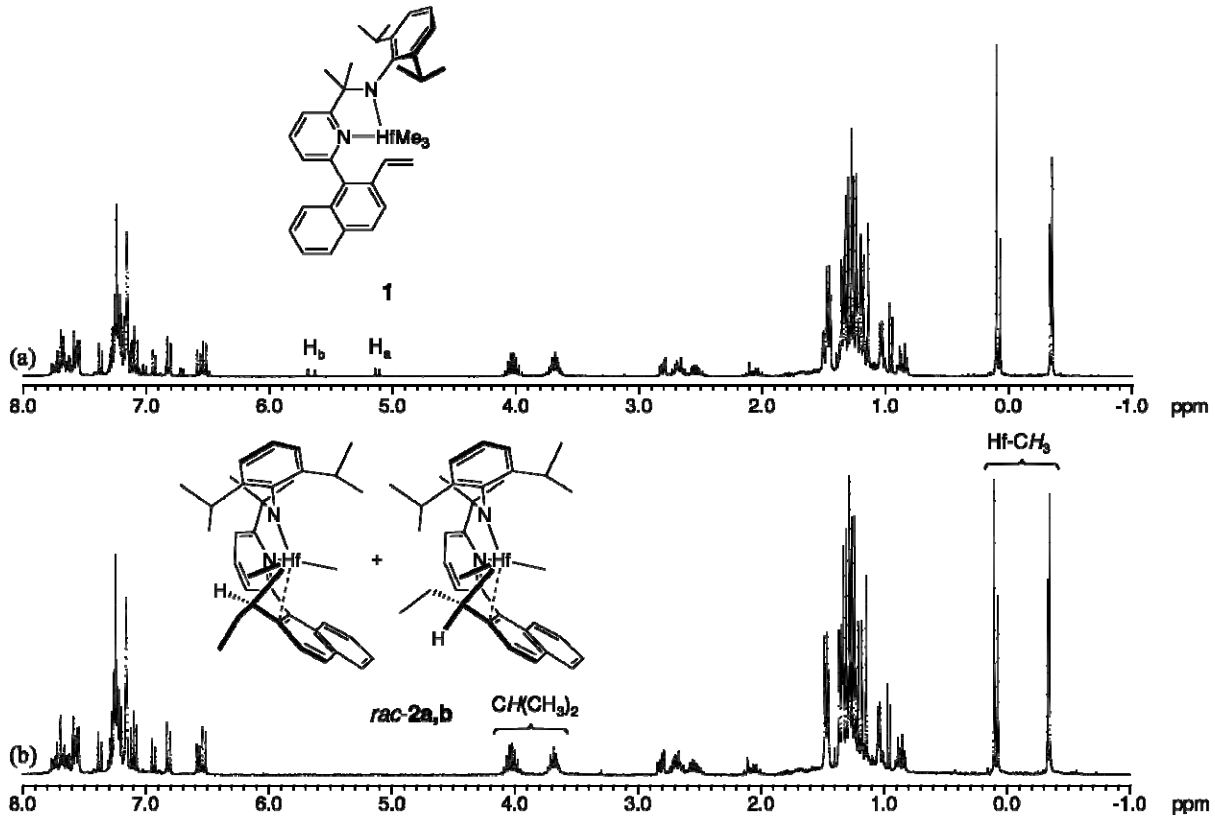


Figure S2. ^{1}H NMR spectra (300 MHz, C_6D_6, 25 °C) of (a) crude product containing a mixture (15:85) of **1** and *rac*-**2a,b**; (b) product after heating mixture for 18 hours at 80 °C showing complete conversion to *rac*-**2a,b**.

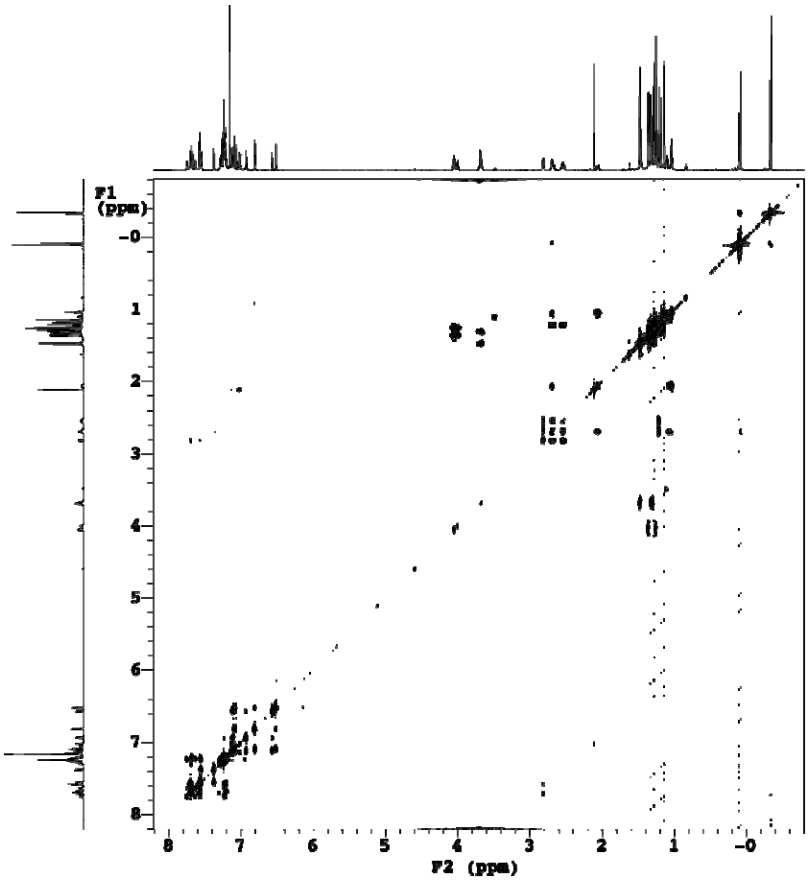

F1 (ppm)
F2 (ppm)

Figure S3. *g*COSY spectrum of *rac*-**2a,b** at 25 °C in C_6D_6.

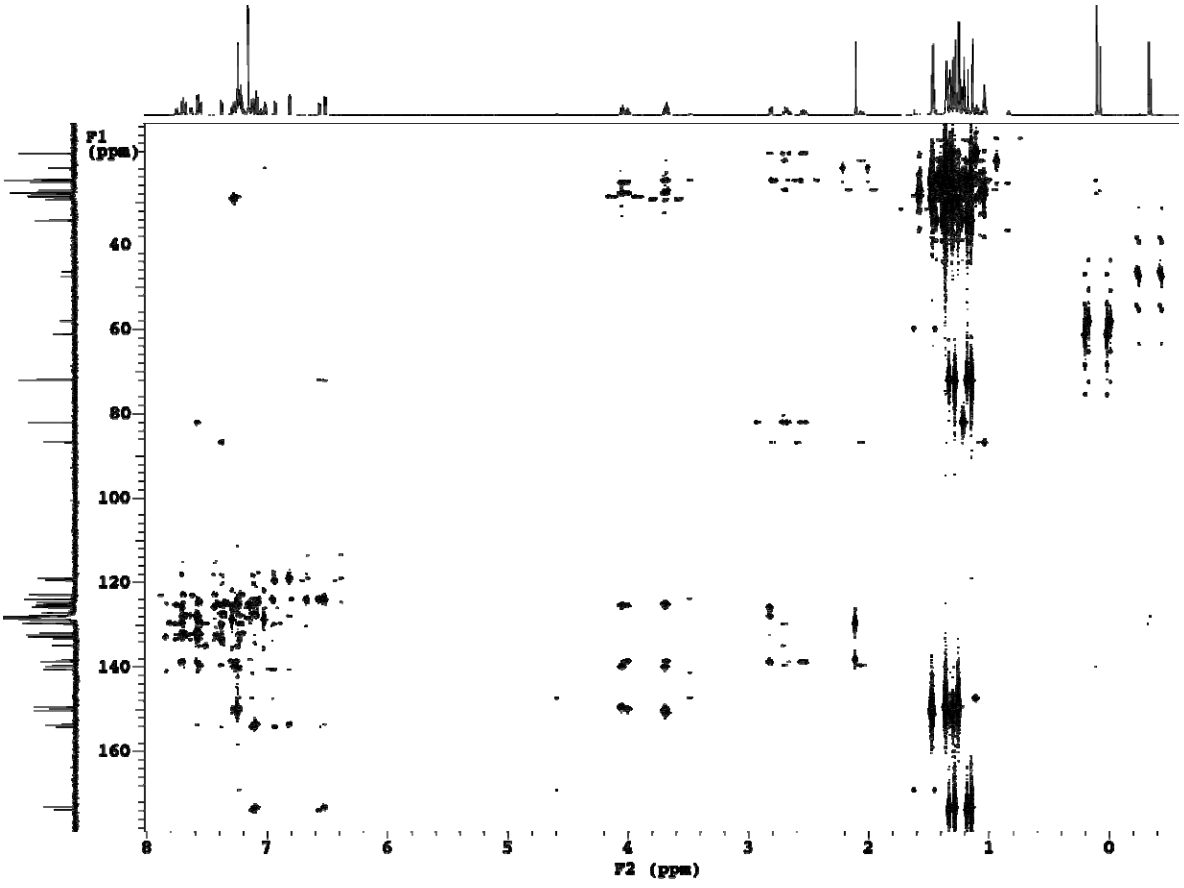


Figure S4. $^{1}H–^{13}C$ *g*HMBC spectrum of *rac*-**2a,b** at 25 °C in C_6D_6.

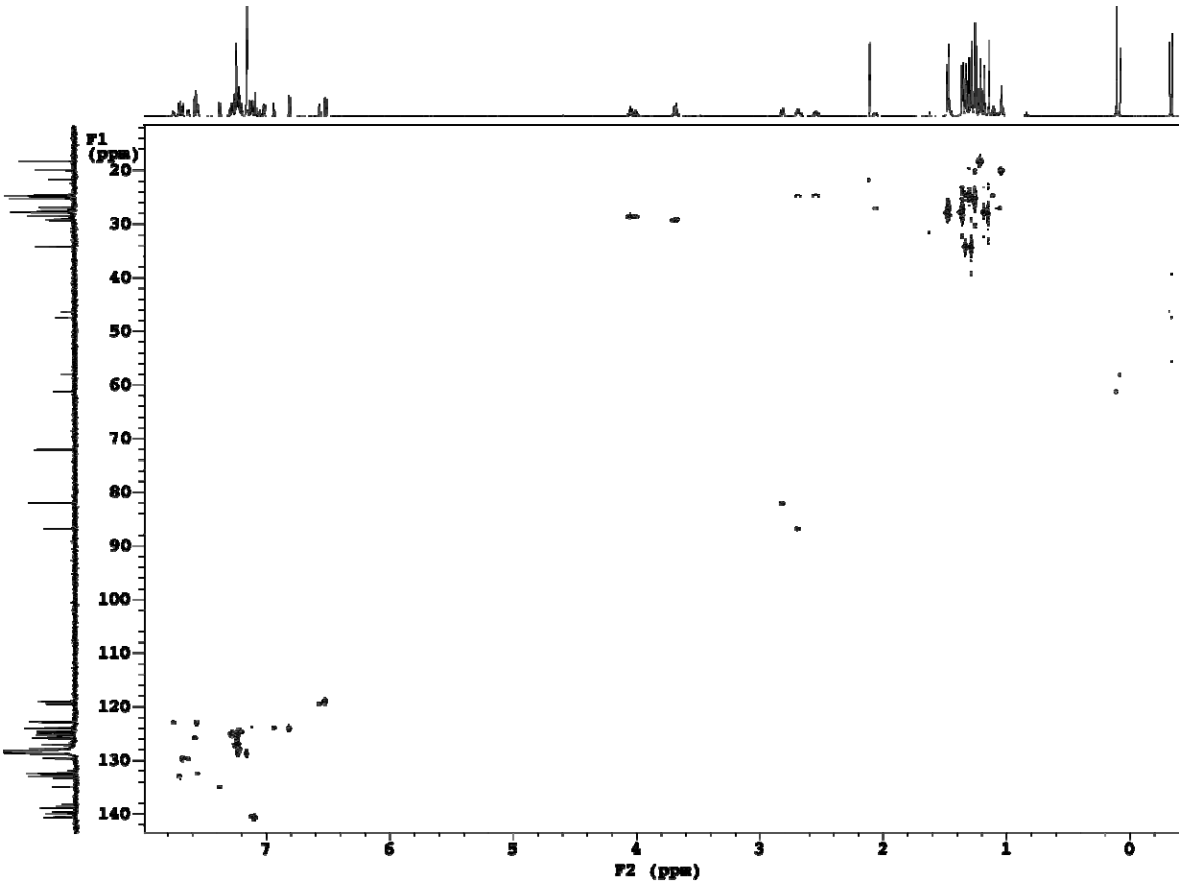


Figure S5. $^{1}H–^{13}C$ *g*HSQC spectrum of *rac*-**2a,b** at 25 °C in C_6D_6. Negative peaks are denoted with a single contour.

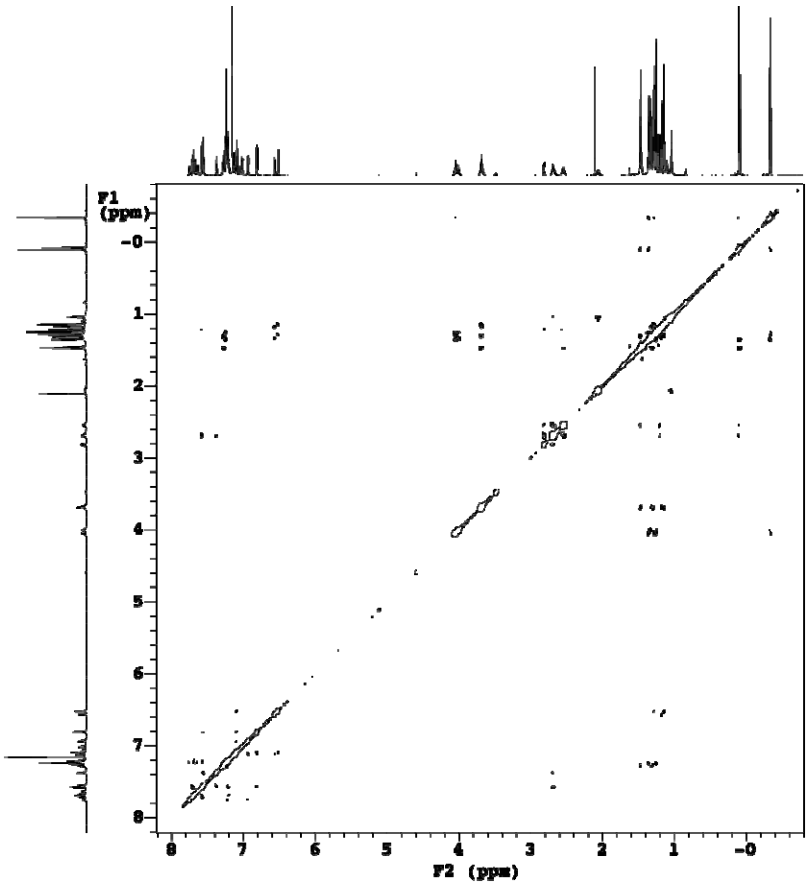


Figure S6. NOESY NMR spectrum of *rac*-**2a,b** in C_6D_6 at 25 °C. Negative peaks are denoted with a single contour.

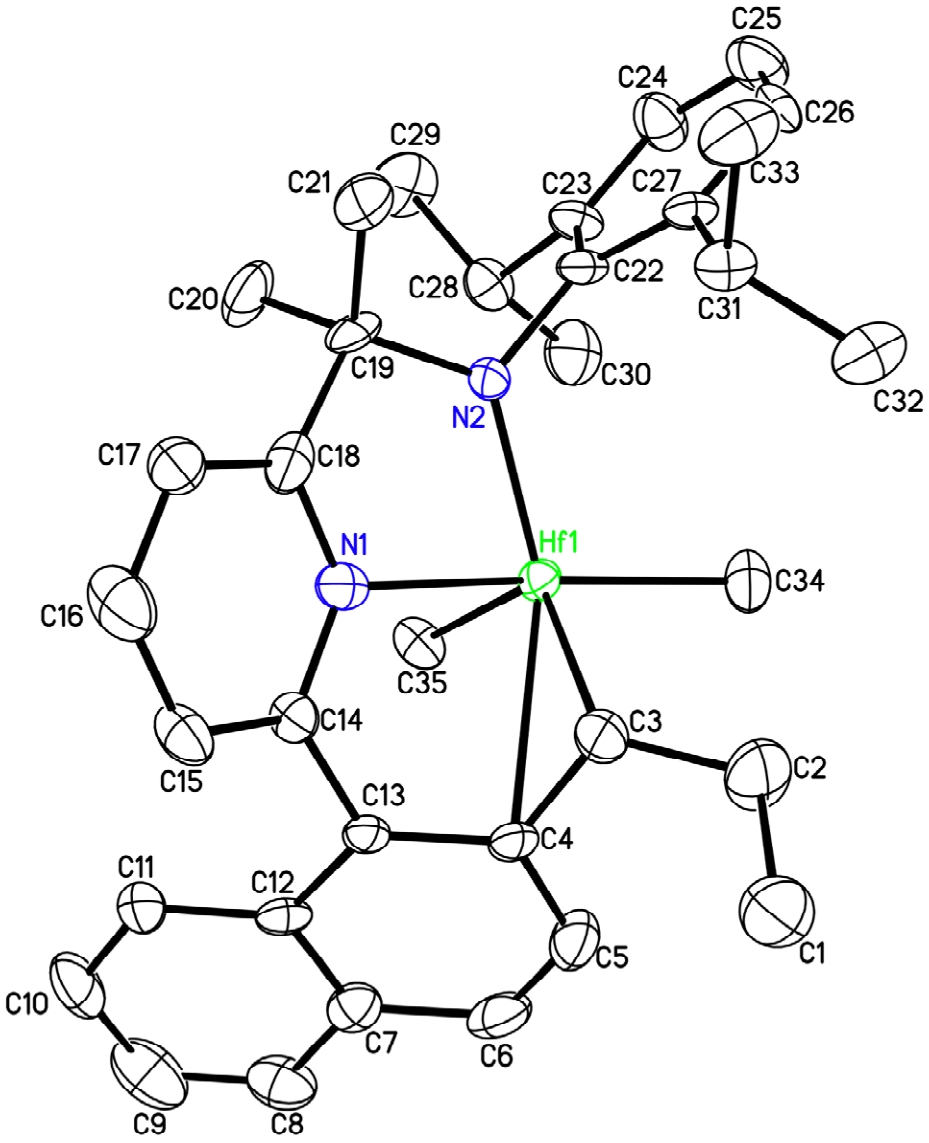


Figure S7. ORTEP diagram of *rac*-**2a**. Thermal ellipsoids are depicted at the 40% probability level.

Table S1. Crystal data and structure refinement for *rac*-**2a**.

Identification code	gd10	
Empirical formula	C35 H44 Hf N2	
Formula weight	671.21	
Temperature	203(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	Pna2(1)	
Unit cell dimensions	a = 20.2668(9) Å	α= 90°
	b = 10.4810(5) Å	β= 90°
	c = 14.6117(7) Å	γ = 90°
Volume	3103.8(3) $Å^3$	
Z	4	
Density (calculated)	1.436 Mg/m^3	
Absorption coefficient	3.385 mm^{-1}	
F(000)	1360	
Crystal size	0.20 x 0.10 x 0.05 mm^3	
Theta range for data collection	2.01 to 28.32°.	
Index ranges	-25<=h<=27, -11<=k<=13, -19<=l<=15	
Reflections collected	17243	
Independent reflections	6188 [R(int) = 0.0725]	
Completeness to theta = 28.32°	99.6 %	
Absorption correction	Semi-empirical from equivalents	

Max. and min. transmission	0.8490 and 0.5508
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6188 / 1 / 343
Goodness-of-fit on F^2	0.969
Final R indices [I>2sigma(I)]	R1 = 0.0450, wR2 = 0.0844
R indices (all data)	R1 = 0.0758, wR2 = 0.0971
Absolute structure parameter	-0.002(15)
Largest diff. peak and hole	1.155 and -1.235 e.$Å^{-3}$

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for *rac*-**2a**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Hf(1)	11074(1)	8125(1)	4369(1)	24(1)
N(1)	12174(3)	7821(5)	4081(3)	28(2)
N(2)	11498(3)	7290(5)	5494(4)	26(1)
C(1)	11462(5)	12536(7)	3735(7)	59(3)
C(2)	11139(3)	11341(7)	4206(9)	58(3)
C(3)	11482(4)	10125(7)	3965(5)	39(2)
C(4)	11451(3)	9674(6)	3004(5)	30(2)
C(5)	10914(4)	9989(8)	2404(6)	43(2)
C(6)	10848(4)	9473(8)	1583(6)	44(2)
C(7)	11300(4)	8545(7)	1234(6)	34(2)
C(8)	11226(4)	7989(8)	368(6)	48(2)
C(9)	11654(5)	7117(9)	52(6)	67(3)
C(10)	12181(4)	6750(8)	611(6)	50(2)
C(11)	12269(4)	7276(7)	1454(5)	41(2)
C(12)	11846(3)	8198(6)	1794(4)	26(2)
C(13)	11900(3)	8797(6)	2670(5)	25(2)
C(14)	12422(3)	8345(6)	3314(5)	27(2)
C(15)	13104(3)	8447(7)	3188(5)	38(2)
C(16)	13500(4)	7928(9)	3857(6)	54(3)
C(17)	13236(3)	7387(8)	4631(5)	40(2)
C(18)	12556(3)	7339(7)	4737(5)	35(2)
C(19)	12178(3)	6741(7)	5517(5)	32(2)
C(20)	12153(4)	5273(7)	5309(6)	49(2)
C(21)	12547(4)	6928(8)	6411(5)	47(2)
C(22)	11100(3)	7114(7)	6327(5)	29(2)
C(23)	10656(3)	6078(7)	6431(5)	30(2)
C(24)	10291(4)	5948(7)	7226(6)	44(2)
C(25)	10337(4)	6828(8)	7901(6)	46(2)
C(26)	10738(4)	7898(7)	7801(5)	36(2)
C(27)	11129(3)	8062(6)	7031(5)	26(2)
C(28)	10510(3)	5124(7)	5663(5)	36(2)
C(29)	10616(4)	3733(7)	5976(7)	55(3)
C(30)	9800(4)	5313(8)	5323(6)	52(3)
C(31)	11525(3)	9290(6)	6962(5)	30(2)
C(32)	11069(4)	10418(7)	6826(6)	43(2)
C(33)	11965(4)	9513(8)	7810(6)	50(2)
C(34)	10063(3)	8865(7)	4755(5)	41(2)
C(35)	10796(4)	6641(7)	3338(5)	37(2)

Table S3. Bond lengths [Å] and angles [°] for a *rac*-**2a**.

Hf(1)-N(2)	2.050(6)
Hf(1)-C(35)	2.238(8)
Hf(1)-C(34)	2.261(6)
Hf(1)-N(1)	2.292(5)
Hf(1)-C(3)	2.329(7)
Hf(1)-C(4)	2.684(7)
N(1)-C(18)	1.332(8)
N(1)-C(14)	1.346(8)
N(2)-C(22)	1.472(8)
N(2)-C(19)	1.495(8)
C(1)-C(2)	1.572(11)
C(2)-C(3)	1.494(10)
C(3)-C(4)	1.483(10)
C(4)-C(13)	1.383(9)
C(4)-C(5)	1.436(10)
C(5)-C(6)	1.323(12)
C(6)-C(7)	1.430(11)
C(7)-C(8)	1.401(12)
C(7)-C(12)	1.422(10)
C(8)-C(9)	1.343(12)
C(9)-C(10)	1.398(12)
C(10)-C(11)	1.362(11)
C(11)-C(12)	1.384(10)
C(12)-C(13)	1.431(9)
C(13)-C(14)	1.492(9)
C(14)-C(15)	1.398(9)
C(15)-C(16)	1.378(11)
C(16)-C(17)	1.373(11)
C(17)-C(18)	1.389(10)
C(18)-C(19)	1.508(10)
C(19)-C(21)	1.517(10)
C(19)-C(20)	1.569(10)
C(22)-C(23)	1.419(9)
C(22)-C(27)	1.431(10)
C(23)-C(24)	1.383(10)
C(23)-C(28)	1.532(10)
C(24)-C(25)	1.353(11)
C(25)-C(26)	1.392(10)
C(26)-C(27)	1.386(10)
C(27)-C(31)	1.520(9)
C(28)-C(29)	1.543(10)
C(28)-C(30)	1.536(10)
C(31)-C(32)	1.514(10)
C(31)-C(33)	1.544(10)
N(2)-Hf(1)-C(35)	110.4(3)
N(2)-Hf(1)-C(34)	109.0(2)
C(35)-Hf(1)-C(34)	100.3(3)
N(2)-Hf(1)-N(1)	71.35(19)
C(35)-Hf(1)-N(1)	91.4(2)
C(34)-Hf(1)-N(1)	167.1(2)
N(2)-Hf(1)-C(3)	116.0(2)
C(35)-Hf(1)-C(3)	122.9(3)
C(34)-Hf(1)-C(3)	94.4(3)
N(1)-Hf(1)-C(3)	74.5(2)
N(2)-Hf(1)-C(4)	137.3(2)
C(35)-Hf(1)-C(4)	89.5(3)
C(34)-Hf(1)-C(4)	103.6(2)
N(1)-Hf(1)-C(4)	70.74(19)
C(3)-Hf(1)-C(4)	33.5(2)
C(18)-N(1)-C(14)	122.5(6)
C(18)-N(1)-Hf(1)	119.1(4)
C(14)-N(1)-Hf(1)	117.4(4)
C(22)-N(2)-C(19)	116.1(5)
C(22)-N(2)-Hf(1)	119.1(4)
C(19)-N(2)-Hf(1)	124.7(4)
C(3)-C(2)-C(1)	112.5(7)
C(4)-C(3)-C(2)	118.4(8)
C(4)-C(3)-Hf(1)	86.5(4)
C(2)-C(3)-Hf(1)	122.9(5)
C(13)-C(4)-C(5)	115.9(7)
C(13)-C(4)-C(3)	121.2(6)
C(5)-C(4)-C(3)	122.4(6)
C(13)-C(4)-Hf(1)	92.7(4)
C(5)-C(4)-Hf(1)	112.1(5)
C(3)-C(4)-Hf(1)	60.0(4)
C(6)-C(5)-C(4)	122.4(7)
C(5)-C(6)-C(7)	122.5(7)
C(8)-C(7)-C(12)	119.7(7)
C(8)-C(7)-C(6)	122.4(7)
C(12)-C(7)-C(6)	117.9(7)
C(9)-C(8)-C(7)	121.6(8)
C(8)-C(9)-C(10)	118.7(8)
C(11)-C(10)-C(9)	121.1(8)
C(10)-C(11)-C(12)	121.7(8)
C(11)-C(12)-C(7)	117.0(7)
C(11)-C(12)-C(13)	125.4(6)
C(7)-C(12)-C(13)	117.6(6)
C(4)-C(13)-C(12)	123.8(6)
C(4)-C(13)-C(14)	117.1(6)
C(12)-C(13)-C(14)	118.7(6)
N(1)-C(14)-C(15)	120.7(6)
N(1)-C(14)-C(13)	112.9(5)
C(15)-C(14)-C(13)	126.4(6)
C(16)-C(15)-C(14)	116.9(7)
C(17)-C(16)-C(15)	121.4(7)
C(16)-C(17)-C(18)	119.6(7)
N(1)-C(18)-C(17)	118.9(7)
N(1)-C(18)-C(19)	114.0(6)
C(17)-C(18)-C(19)	127.1(7)
N(2)-C(19)-C(18)	106.9(5)
N(2)-C(19)-C(21)	115.1(6)
C(18)-C(19)-C(21)	110.3(6)
N(2)-C(19)-C(20)	110.0(5)

C(18)-C(19)-C(20)	106.1(6)	C(26)-C(27)-C(31)	117.4(7)
C(21)-C(19)-C(20)	108.0(6)	C(22)-C(27)-C(31)	124.2(6)
C(23)-C(22)-C(27)	118.7(6)	C(23)-C(28)-C(29)	111.9(7)
C(23)-C(22)-N(2)	122.1(6)	C(23)-C(28)-C(30)	109.5(6)
C(27)-C(22)-N(2)	119.0(6)	C(29)-C(28)-C(30)	110.4(6)
C(24)-C(23)-C(22)	120.3(7)	C(32)-C(31)-C(27)	110.4(6)
C(24)-C(23)-C(28)	116.6(6)	C(32)-C(31)-C(33)	109.8(6)
C(22)-C(23)-C(28)	122.9(6)	C(27)-C(31)-C(33)	112.4(6)
C(25)-C(24)-C(23)	120.6(7)		
C(24)-C(25)-C(26)	120.8(7)		
C(27)-C(26)-C(25)	121.2(7)		
C(26)-C(27)-C(22)	118.3(6)		

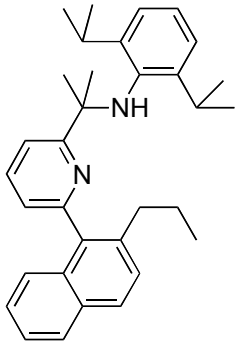
Symmetry transformations used to generate equivalent atoms:

Table S4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for *rac*-**2a**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2 a^{*2} U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Hf(1)	24(1)	24(1)	22(1)	0(1)	-2(1)	3(1)
N(1)	40(3)	21(3)	23(3)	-3(2)	-2(2)	-3(2)
N(2)	31(3)	23(3)	24(3)	4(2)	8(2)	5(2)
C(1)	79(6)	41(5)	56(6)	0(5)	8(5)	-5(5)
C(2)	68(5)	33(4)	74(9)	11(6)	22(6)	0(4)
C(3)	38(4)	38(4)	41(5)	9(3)	15(3)	4(4)
C(4)	32(4)	26(4)	31(4)	14(3)	7(3)	4(3)
C(5)	33(4)	41(5)	54(6)	5(4)	4(4)	12(4)
C(6)	42(4)	47(5)	44(5)	20(4)	-9(4)	6(4)
C(7)	32(4)	30(4)	40(5)	5(4)	0(3)	-4(3)
C(8)	46(5)	66(6)	33(5)	5(4)	-9(4)	-9(4)
C(9)	75(6)	89(8)	36(5)	-16(5)	5(5)	-16(6)
C(10)	62(5)	50(5)	38(5)	-16(4)	18(4)	1(4)
C(11)	55(5)	34(4)	35(5)	4(4)	13(4)	13(4)
C(12)	36(3)	20(3)	23(3)	7(3)	-4(3)	-7(3)
C(13)	25(3)	26(4)	25(4)	10(3)	5(3)	1(3)
C(14)	19(3)	34(4)	27(4)	-1(3)	-2(3)	-1(3)
C(15)	28(4)	57(5)	29(4)	-5(4)	4(3)	-3(4)
C(16)	26(4)	93(7)	43(5)	-5(5)	1(4)	-1(5)
C(17)	28(4)	59(5)	31(5)	1(3)	-5(3)	8(4)
C(18)	33(4)	32(4)	41(4)	-7(3)	-7(3)	9(3)
C(19)	28(3)	39(4)	28(4)	9(3)	-13(3)	9(3)
C(20)	47(4)	30(4)	70(7)	12(4)	7(4)	16(4)
C(21)	43(4)	61(6)	37(5)	1(4)	-10(4)	20(4)
C(22)	33(3)	35(4)	19(3)	9(3)	-1(3)	4(3)
C(23)	37(4)	31(4)	23(4)	5(3)	3(3)	-6(3)
C(24)	50(4)	40(5)	41(5)	0(4)	15(4)	-4(4)
C(25)	52(5)	50(5)	36(5)	7(4)	16(4)	-6(4)
C(26)	52(4)	38(5)	19(4)	-5(3)	9(3)	9(4)
C(27)	34(4)	23(4)	22(3)	9(3)	-3(3)	-4(3)
C(28)	36(4)	36(4)	35(4)	-3(4)	4(3)	-3(3)
C(29)	79(6)	21(4)	67(7)	2(4)	0(5)	-12(4)
C(30)	54(5)	44(5)	58(6)	-11(4)	-2(4)	-2(4)
C(31)	32(4)	27(4)	31(4)	3(3)	-4(3)	-9(3)
C(32)	48(4)	31(5)	50(5)	3(4)	-20(4)	-9(4)
C(33)	63(5)	33(5)	53(5)	-1(4)	-27(4)	-5(4)
C(34)	37(4)	42(5)	45(5)	-9(4)	3(3)	9(4)
C(35)	36(4)	45(5)	31(4)	-2(4)	6(3)	-2(4)

Table S5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for *rac*-**2a**.

	x	y	z	U(eq)
H(1A)	11229	13301	3920	88
H(1B)	11436	12444	3075	88
H(1C)	11921	12599	3918	88
H(2A)	11151	11456	4872	70
H(2B)	10675	11283	4020	70
H(3A)	11949	10184	4155	47
H(5A)	10598	10584	2602	51
H(6A)	10491	9725	1215	53
H(8A)	10867	8232	0	58
H(9A)	11600	6760	-533	80
H(10A)	12479	6130	400	60
H(11A)	12626	7005	1815	50
H(15A)	13283	8852	2670	46
H(16A)	13961	7944	3782	65
H(17A)	13515	7053	5086	48
H(20A)	11918	5131	4740	73
H(20B)	11926	4838	5803	73
H(20C)	12598	4944	5256	73
H(21A)	12568	7831	6554	71
H(21B)	12991	6593	6352	71
H(21C)	12318	6481	6898	71
H(24A)	10010	5243	7298	52
H(25A)	10095	6716	8444	55
H(26A)	10743	8520	8264	44
H(28A)	10814	5300	5149	43
H(29A)	11066	3630	6193	83
H(29B)	10539	3161	5466	83
H(29C)	10311	3534	6467	83
H(30A)	9740	6191	5130	78
H(30B)	9493	5119	5813	78
H(30C)	9717	4749	4809	78
H(31A)	11815	9226	6419	36
H(32A)	10794	10273	6292	65
H(32B)	11329	11185	6736	65
H(32C)	10791	10520	7362	65
H(33A)	12206	10306	7737	74
H(33B)	12274	8812	7872	74
H(33D)	11691	9563	8353	74
H(34A)	9886	8356	5252	62
H(34D)	9772	8810	4230	62
H(34B)	10099	9748	4949	62
H(35D)	10629	5891	3650	56
H(35A)	11182	6410	2980	56
H(35B)	10458	6977	2935	56



Methanolysis of *rac*-2a,b. To a solution of *rac*-**2a,b** (25 mg) in C_6D_6 which had been stored in a J. Young NMR tube was added several drops of MeOH, the tube was shaken vigorously and the orange solution became colorless almost immediately. The volatiles were removed *in vacuo*. The residue was taken up in C_6D_6 and flashed through a small plug of Celite to isolate 2,6-diisopropyl-*N*-(2-(6-(2-propylnaphthalen-1-yl)pyridin-2-yl)propan-2-yl)aniline. ^{1}H NMR (C_6D_6, 500 MHz): δ 7.72-7.69 (m, 2H, Ar*H*), 7.56-7.54 (m, 1H, Ar*H*), 7.31 (d, J_{HH} = 8.54 Hz, 1H, Ar*H*), 7.26-7.22 (m, 3H, Ar*H*), 7.12 (apparent s, 1H, Ar*H*), 6.95 (t, J_{HH} = 4.28 Hz, 1H, Ar*H*), 4.56 (s, 1H, $(CH_3)_2$C-N*H*), 3.49 (sept, J_{HH} = 6.71 Hz, 2H, C*H*$(CH_3)_2$), 2.66-2.52 (m, 2H, $C_{Napthyl}CH_2CH_2CH_3$), 1.75-1.50 (m, 2H, $C_{Naphthyl}CH_2CH_2CH_3$), 1.62 (s, 3H, $(CH_3)_2$C-NH), 1.45 (s, 3H, $(CH_3)_2$C-NH), 1.11 (d, J_{HH} = 6.71 Hz, 6H, CH$(CH_3)_2$), 1.09 (d, J_{HH} = 6.71 Hz, 6H, CH$(CH_3)_2$), 0.84 (t, J_{HH} = 7.32 Hz, 3H, $C_{Naphthyl}CH_2CH_2CH_3$). MS-EI (*m/z*): 464.3 (M^+).

General Procedure for 1-Hexene Polymerization. In the glovebox $B(C_6F_5)_3$ (8.4 mg, 16 μmol) was placed into a scintillation vial along with 3.0 g of toluene and 0.78 g of 1-hexene. To this solution was added *rac*-**2a,b** (10.8 mg, 16 μmol) dissolved in 0.6 g of C_6D_6. The polymerization was allowed to proceed for 30 minutes after which time the vial was removed from the glovebox and the polymerization was terminated by the addition of MeOH. The volatiles were removed *in vacuo* to furnish poly(1-hexene) (0.48 g, 62%).

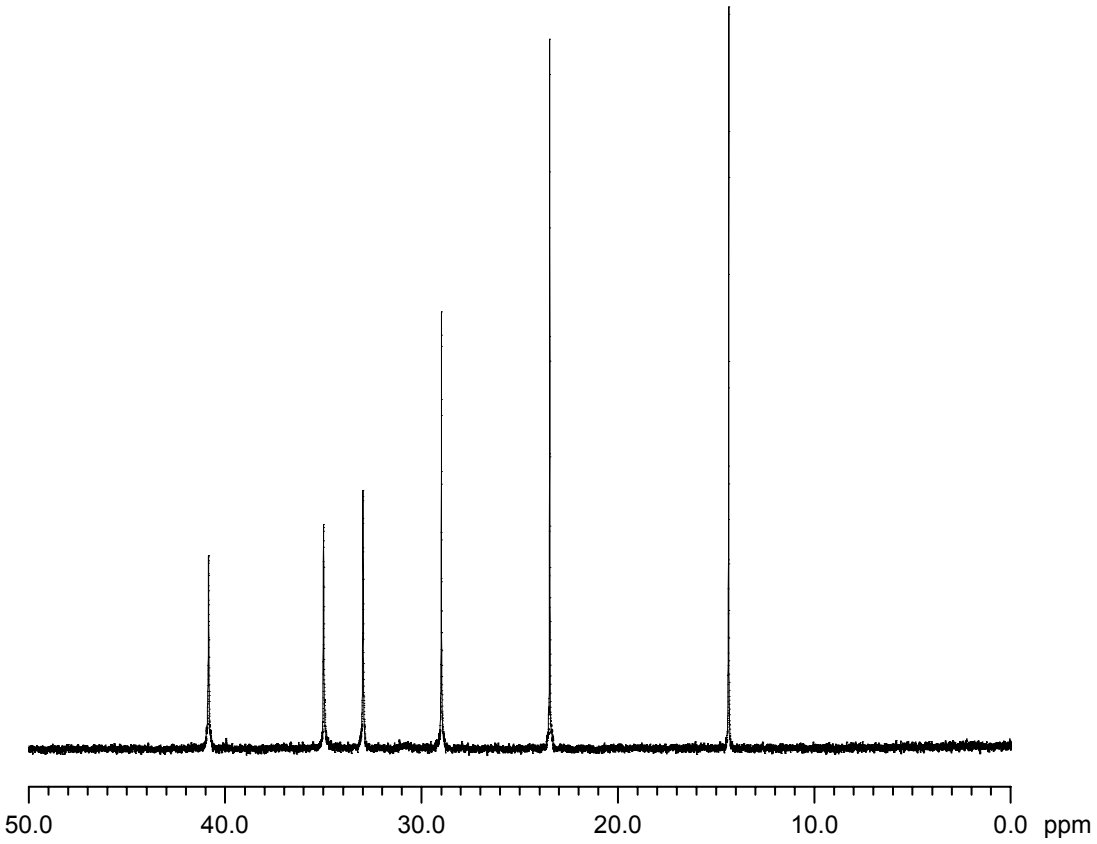


Figure S8. $^{13}C\{^{1}H\}$ NMR spectrum (125 MHz, $C_2D_2Cl_4$, 75 °C) of poly(1-hexene) produced by *rac*-**2a,b**/$B(C_6F_5)_3$ at 25 °C.

General Procedure for Propylene Polymerization. A stock solution of hafnium precatalyst was prepared by dilution of 50 μmol (33.5 mg) of *rac*-**2a,b** to 25 mL in a volumetric flask. A stock solution of $B(C_6F_5)_3$ (27.0 mg, 50 μmol) was prepared in an identical manner. In the glovebox, a 6 oz. flat-bottomed Lab-Crest pressure reaction vessel (Andrews Glass Co.) was charged with 20 mL of toluene. The reactor was sealed, and the solution was saturated under a constant feed of propylene (30 psig) for 15 minutes with continuous stirring in a 20 °C water bath. Polymerization was initiated by injection of 5 mL of the $B(C_6F_5)_3$ solution followed by 5 mL of the precatalyst solution. The polymerization was allowed to proceed under a constant feed

of propylene for the desired period of time and terminated by the addition of MeOH with simultaneous venting and discontinuation of the propylene feed. The polymer was precipitated in copious MeOH and allowed to stir overnight; it was collected via filtration and dried to constant weight *in vacuo* at 60 °C.

NMR Scale Reaction of *rac*-2a,b with $B(C_6F_5)_3$. In the glovebox, *rac*-**2a,b** (20.0 mg, 29.8 μmol) was dissolved in 0.35 mL of C_6D_6 and combined with $B(C_6F_5)_3$ (15.7 mg, 30.0 μmol) in C_6D_6 (0.35 mL). The ^{1}H NMR spectrum was recorded at 500 MHz within 15 minutes of mixing the reagents.

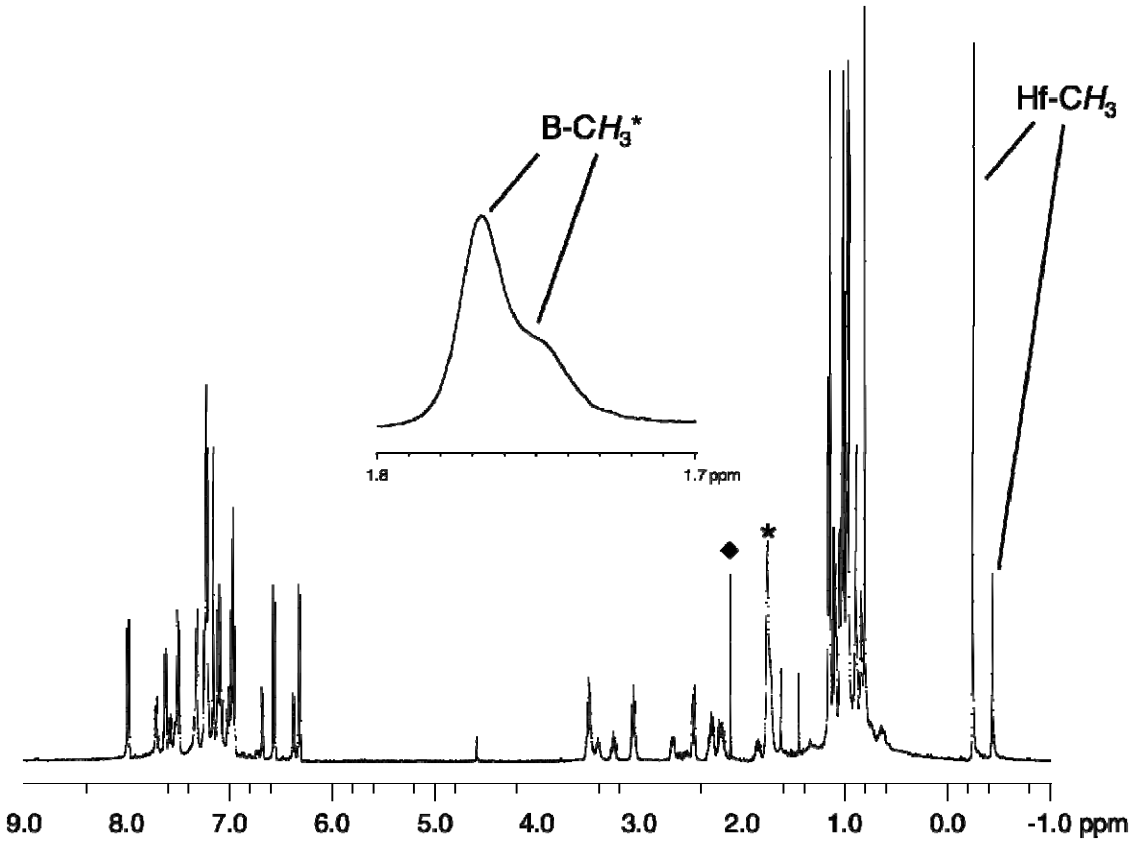


Figure S9. ^{1}H NMR spectrum of *rac*-**2a,b**/$B(C_6F_5)_3$ (500 MHz, C_6D_6, 25 °C). Toluene was added as an internal standard ($H_3CC_6H_5$ (□)).

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