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Supporting Information

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Cationic Polyhydrido Rare Earth Metal Complexes. Synthesis, Structure, and Catalysis for *cis*-1,4-Selective Polymerization of 1,3-Cyclohexadiene

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Experimental Section:

General Methods. All manipulations of air and moisture-sensitive compounds were performed under a dry nitrogen atmosphere by use of standard Schlenk techniques or an Mbraun glovebox. Argon (Takachiho Chemical Industrial Co., Ltd.) was purified by being passed through a Dryclean column (4 A molecular sieves, Nikka Seiko Co.) and a Gasclean CC-XR column (Nikka Seiko Co.). Anhydrous THF, hexane, benzene, and toluene were refluxed and distilled from sodium/benzophenone under dry nitrogen, and degassed by the freeze-pump-thaw cycles, and dried over fresh Na chips in the glovebox. 1,3-cyclohexadiene (CHD) was purchased from TCI, dried over CaH_2, vacuum-transferred, and degassed by two freeze-pump-thaw cycles. $[Ph_3C][B(C_6F_5)_4]$, $[PhMe_2NH][B(C_6F_5)_4]$, and $B(C_6F_5)_3$ were purchased from Tosoh Finechem Corporation and used without purification. $LnCl_3$ (M = Y, Tm, Dy, Ho, Er, Gd, Lu) were purchased from Strem. $LiCH_2SiMe_3$ (1.0 M solution in pentane) and $C_5Me_4H(SiMe_3)$ were purchased from Aldrich, and used as received. $(C_5Me_4SiMe_3)Ln(CH_2SiMe_3)_2(THF)$, $(C_5Me_4SiMe_3)_4Y_4H_8$ and $(C_5Me_4SiMe_3)_4Ln_4H_8(THF)$ were synthesized as reported previously.[1-5] Deuterated solvents chlorobenzene-d_5 (99 atom% D) and benzene-d_6 (99.6 atom% D), chloroform-d_1 (99.8 atom% D) and 1,1,2,2,-tetrachloroethane-d_2 (99.6 atom% D) were obtained from Cambridge Isotope.

Samples of rare earth metal complexes for NMR spectroscopic measurements were prepared in the glovebox using J. Young valve NMR tubes. NMR (^1H, ^{11}B, $^{13}C\{^1H\}$, ^{19}F, ^{19}Si) spectra were recorded on a JNM-EX 270 or a JNM-Alpha 600 spectrometer. Elemental analyses were performed by Chemical Analysis Team, D&S Center in RIKEN. The NMR data of poly(CHD) were obtained on a JEOL JNM-EX 270 (FT, 300 MHz for ^1H; 75.5 MHz for $^{13}C\{^1H\}$) spectrometer at 120 °C with 1,1,2,2-$C_2D_2Cl_4$ as solvent. The molecular weight and the molecular weight distributions of the polymer samples were determined at 140 °C by high temperature gel permeation chromatography (HT-GPC) on a HLC-8121GPC/HT apparatus (Tosoh Corporation). 1,2-Dichlorobenzene (DCB) was employed as the eluent at a flow rate of 1.0 mL/min. The calibration was made by polystyrene standard EasiCal PS-1 (PL Ltd). The DSC measurements were performed on a Perkin-Elmer Pyris Diamond Differential Scanning Calorimeter at a rate of 20 °C/min.

$(C_5Me_4SiMe_3)_4Y_4H_8$ (1a).[5] A benzene solution (2 mL) of $Y_4(C_5Me_4SiMe_3)_4H_7\{C_6H_5CH(CH_3)\}$ (0.040 g, 0.03 mmol), which was prepared by reaction of $Y_4(C_5Me_4SiMe_3)_4H_8(THF)$ with 1 equiv of styrene (see supporting information in ref. 2), in a 50-mL Schlenk flask equipped with a J. Young valve was frozen in liquid nitrogen, pumped, and backfilled with H_2. The mixture was allowed to warm to room temperature and stirred for 2 days. For complete conversion, a second charge of H_2 was carried out in an identical way and the solution mixture was then further stirred for 2 days. Removal of the volatiles under reduced pressure afforded **1a** quantitatively (0.036 g, 0.03 mmol). A single crystal suitable for X-ray analysis was grown in a concentrated hexane solution at room temperature. IR (nujol): ν = 1405, 1324, 1260, 1244, 1130, 918, 838, 756, 684, 630 cm^{-1}; ^{1} H NMR (300 MHz, C_6D_6, 22 °C): δ = 0.48 (s, 36H, $C_5Me_4Si\mathit{Me}_3$), 2.20 (s, 24H, C_5Me_4), 2.37 (s, 24H, C_5Me_4), 5.26 (m, 8H, YH); ^{13}C NMR (75 MHz, C_6D_6, 22 °C): δ = 2.45 (s, 12C, $C_5Me_4Si\mathit{Me}_3$), 11.89 (s, 8C, $C_5\mathit{Me}_4$), 14.54 (s, 8C, $C_5\mathit{Me}_4$), 117.66 (s, 4C, *ipso*-C_5Me_4), 126.34 (s, 8C, C_5Me_4), 129.20 (s, 8C, C_5Me_4). Anal. Calcd for $C_{48}H_{92}Si_4Y_4$: C, 50.70; H, 8.15. Found: C, 50.05; H, 8.01.

$(C_5Me_4SiMe_3)_4Y_4H_8(THF)$ (1b).[1,2] A toluene solution of $(C_5Me_4SiMe_3)Y(CH_2SiMe_3)_2(THF)$ (0.79 g, 1.50 mmol) in a 300-mL Schlenk flask equipped with a J. Young valve was frozen in liquid nitrogen, pumped, and refilled with H_2. The mixture was allowed to warm to room temperature and stirred for 2 h. For complete conversion, a second charge of H_2 was carried out in an identical way and the solution mixture was then further stirred for 2 h. After removal of the solvent under vacuum, the resulting pale yellow residue was extracted with hexane and filtered in the glove box. Slow evaporation of the solvent under reduced pressure precipitated **1b** as a pale yellow crystalline powder (1.38 g, 1.14 mmol, 76 % yield). A single crystal suitable for X-ray analysis was grown in a concentrated hexane solution at room temperature. IR (nujol): ν = 1405, 1340, 1322, 1260, 1244, 1130, 848, 838, 756, 684, 630 cm^{-1}; ^1H NMR (270 MHz, C_6D_6, 22 °C): δ = 0.53 (s, 36H, $C_5Me_4Si\mathit{Me}_3$), 1.40 (br, 4H, THF), 2.25 (s, 24H, C_5Me_4), 2.33 (s, 24H, C_5Me_4), 3.61 (br, 4H, THF), 4.32 (quintet, $J_{Y\text{-}H}$ = 15.26 Hz, 8H, YH); ^1H NMR (270 MHz, C_4D_8O, 22 °C): δ = 0.29 (s, 36H, $C_5Me_4Si\mathit{Me}_3$), 2.05 (s, 24H, C_5Me_4), 2.16 (s, 24H, C_5Me_4), 3.75 (quintet, $J_{Y\text{-}H}$ = 14.26 Hz, 8H, YH); ^{13}C NMR (75 MHz, C_6D_6, 22 °C): δ = 3.13 (s, 12C, $C_5Me_4Si\mathit{Me}_3$), 12.67 (s, 8C, $C_5\mathit{Me}_4$), 15.44 (s, 8C, $C_5\mathit{Me}_4$), 25.22 (s, 2C, THF), 70.71 (s, 2C, THF), 114.77 (s, 4C, *ipso*-C_5Me_4), 124.48 (s, 8C, C_5Me_4), 127.07 (s, 8C, C_5Me_4); ^{13}C NMR (75 MHz, C_4D_8O, 22 °C): δ = 3.35 (s, 12C, $C_5Me_4Si\mathit{Me}_3$), 13.12 (s, 8C, $C_5\mathit{Me}_4$), 16.04 (s, 8C, $C_5\mathit{Me}_4$), 113.62 (s, 4C, *ipso*-

C_5Me_4), 123.15 (s, 8C, C_5Me_4), 127.39 (s, 8C, C_5Me_4); ^{89}Y NMR (19 MHz, C_4D_8O, 22 °C): δ = 380 (br); Anal. Calcd for $C_{52}H_{100}OSi_4Y_4$: C, 51.65; H, 8.33. Found: C 49.61; H, 8.33.

$(C_5Me_4SiMe_3)_4Y_4H_8(THF)_2$ (1c). Recrystallization of **1b** in a saturated THF solution afforded colorless crystals of **1c**. IR (nujol): ν =1350, 1300, 1250, 1205, 840, 754, 684, 650 cm^{-1}; ^{1}H NMR (270 MHz, C_6D_6, 22 °C): δ = 0.53 (s, 36H, $C_5Me_4Si\mathit{Me}_3$), 1.42 (br, 8H, THF), 2.25 (s, 24H, C_5Me_4), 2.33 (s, 24H, C_5Me_4), 3.59 (br, 8H, THF), 4.25 (quintet, $J_{Y\text{-}H}$ = 15.18 Hz, 8H, YH); ^{13}C NMR (75 MHz, C_6D_6, 22 °C): δ = 3.15 (s, 12C, $C_5Me_4Si\mathit{Me}_3$), 12.71 (s, 8C, $C_5\mathit{Me}_4$), 15.50 (s, 8C, $C_5\mathit{Me}_4$), 25.49(s, 4C, THF), 69.72(s, 4C, THF), 114.52 (s, 4C, *ipso*-C_5Me_4), 124.29 (s, 8C, C_5Me_4), 126.93 (s, 8C, C_5Me_4); Anal. Calcd for $C_{52}H_{100}O_2Si_4Y_4$: C, 52.49; H, 8.50. Found: C, 44.14–47.00; H, 8.24–8.16.

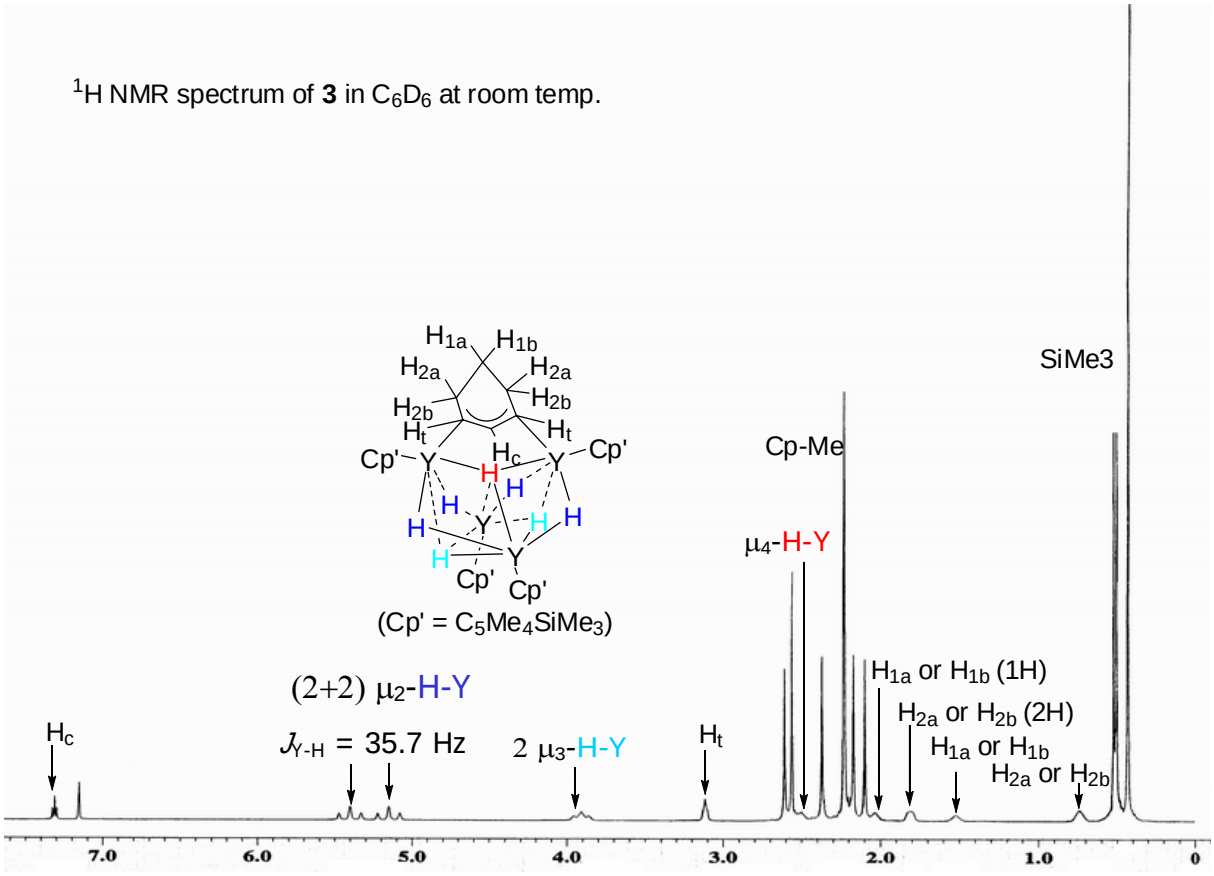
$[(C_5Me_4SiMe_3)_4Y_4H_7][B(C_6F_5)_4]$ (2a). A mixture of $Y_4(C_5Me_4SiMe_3)_4H_8$ (0.058 g, 0.053 mmol) and $[Ph_3C][B(C_6F_5)_4]$ (0.049 g, 0.053 mmol) in 10 mL chlorobenzene was stirred for 6 h. After the solvent was removed in vacuum, the resulting colorless residue was washed with hexane. Drying under vacuum and recrystallization in chlorobenzene/hexane gave colorless crystals (0.064 g, 64 %). IR (nujol): ν = 1641, 1514, 1409, 1321, 1226, 1180, 1126, 1105, 1088, 1059, 980, 883, 837, 773, 756, 683, 662, 630, 610, 572 cm^{-1}; ^{1}H NMR (300 MHz, C_6D_6, 25 °C, TMS): δ = 0.34 (s, 36H, $C_5Me_4Si\mathit{Me}_3$), 1.96 (s, 24H, C_5Me_4), 2.18 (s, 24H, C_5Me_4), 4.62 (br, 7H, YH). ^{1}H NMR (300 MHz, C_6D_5Cl, 25 °C, TMS): δ = 0.35 (s, 36H, $C_5Me_4Si\mathit{Me}_3$), 1.97 (s, 24H, C_5Me_4), 2.25 (s, 24H, C_5Me_4), 4.62 (br, 7H, YH). ^{13}C{^{1}H} NMR (75.5 MHz, C_6D_5Cl, 25 °C, TMS) δ = 2.9 (s, 12C, $C_5Me_4Si\mathit{Me}_3$), 11.6 (s, 8C, $C_5\mathit{Me}_4$), 15.0 (s, 8C, $C_5\mathit{Me}_4$), 120.5 (s, 4C, *ipso*-C_5Me_4), 128.3 (s, 8C, C_5Me_4), 131.6 (s, 8C, C_5Me_4). ^{11}B NMR (192.6 MHz, C_6D_5Cl, 25 °C, $BF_3{\cdot}Et_2O$) δ = –16.5 (s, 1B, $B(C_6F_5)_4$). ^{19}F NMR (564.7 MHz, C_6D_5Cl, 25 °C, CCl_3F) δ = –166.57 (br, 8F, *meta*-$B(C_6F_5)_4$), –162.90 (br, 4F, *para*-$B(C_6F_5)_4$), –131.76 (br, 8F, *ortho*-$B(C_6F_5)_4$). ^{29}Si NMR (119.2 MHz, C_6D_5Cl, 25 °C, TMS) δ = –8.0 ($C_5Me_4SiMe_3$). ^{1}H NMR (300 MHz, C_6D_5Cl, –40 °C, TMS): δ = 0.37 (s, 36H, $C_5Me_4Si\mathit{Me}_3$), 1.41 (br, 1H, YH), 1.95 (br s, 24H, C_5Me_4), 2.27 (br s, 24H, C_5Me_4), 3.32 (br m, 2H, YH), 5.30 (t, 4H, $J_{Y\text{-}H}$ = 36.0 Hz, YH); ^{11}B NMR (192.6 MHz, C_6D_5Cl, –40 °C, $BF_3{\cdot}Et_2O$) δ = –16.4 (s, 1B, $B(C_6F_5)_4$). ^{19}F NMR (564.7 MHz, C_6D_5Cl, –40 °C, CCl_3F) δ = –166.05 (br, 8F, *meta*-$B(C_6F_5)_4$), –162.65 (br, 4F, *para*-$B(C_6F_5)_4$), –131.64 (br, 8F, *ortho*-$B(C_6F_5)_4$). Elemental analysis of $[(C_5Me_4SiMe_3)_4Y_4H_7][B(C_6F_5)_4]{\cdot}$hexane calcd. (%) for $C_{78}H_{105}B_1F_{20}Si_4Y_4$: C 49.27, H 5.57; found: C 49.62, H 5.28.

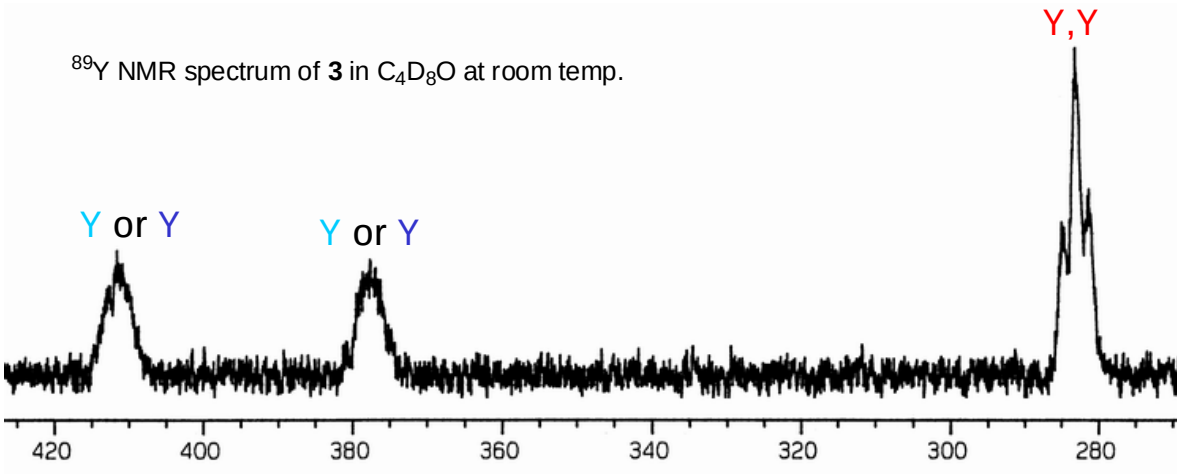
$[(C_5Me_4SiMe_3)_4Y_4H_7(THF)][B(C_6F_5)_4]$ (2b). A mixture of $(C_5Me_4SiMe_3)_4Y_4H_8(THF)$ (0.060 g, 0.050 mmol) and $[Ph_3C][B(C_6F_5)_4]$ (0.046 g, 0.050 mmol) in 10 mL chlorobenzene was stirred for 6 h to give a colorless solution. After the solvent was removed in vacuum the resulting colorless residue was washed with hexane. Drying under vacuum gave a white powder (0.088 g, 93 %). ^{1}H NMR (300 MHz, C_6D_5Cl, 25 °C, TMS): δ = 0.30 (s, 9H, $C_5Me_4Si\mathit{Me}_3$), 0.34 (s, 9H, $C_5Me_4Si\mathit{Me}_3$), 0.37 (s, 18H, $C_5Me_4Si\mathit{Me}_3$), 1.45 (br, 1H, YH), 1.81 (s, 6H, C_5Me_4), 1.85 (br, 4H, β-CH_2-THF), 2.01 (s, 6H, C_5Me_4), 2.05 (s, 6H, C_5Me_4), 2.08 (s, 6H, C_5Me_4), 2.16 (s, 6H, C_5Me_4), 2.23 (s, 6H, C_5Me_4), 2.27 (s, 6H, C_5Me_4), 2.39 (s, 6H, C_5Me_4), 3.24 (q, 1H, $J_{Y\text{-}H}$ = 21.0 Hz, YH), 3.53 (q, 1H, $J_{Y\text{-}H}$ = 25.2 Hz, YH), 3.81 (br, 4H, α-CH_2-THF), 4.98 (t, 2H, $J_{Y\text{-}H}$ = 37.5 Hz, YH), 5.40 (t, 2H, $J_{Y\text{-}H}$ = 36.9 Hz, YH). ^{13}C{^{1}H} NMR (75.5 MHz, C_6D_5Cl, 25 °C, TMS) δ = 1.8 (s, 6C, $C_5Me_4Si\mathit{Me}_3$), 1.9 (s, 3C, $C_5Me_4Si\mathit{Me}_3$), 5.3 (s, 3C, $C_5Me_4Si\mathit{Me}_3$), 11.8 (s, 4C, $C_5\mathit{Me}_4$), 11.9 (s, 2C, $C_5\mathit{Me}_4$), 12.1 (s, 2C, $C_5\mathit{Me}_4$), 15.0 (s, 6C, $C_5\mathit{Me}_4$), 15.6 (s, 2C, $C_5\mathit{Me}_4$), 25.1 (s, 2C, *β*-$\mathit{C}H_2$-THF), 70.9 (s, 2C, *α*-$\mathit{C}H_2$-THF), 121.0 (s, 2C, C_5Me_4), 121.8 (s, 2C, C_5Me_4), 125.6 (s, 2C, C_5Me_4), 126.7 (s, 2C, C_5Me_4), 127.2 (s, 4C, C_5Me_4), 127.8 (s, 2C, C_5Me_4), 131.1 (s, 2C, C_5Me_4), 131.5 (s, 2C, C_5Me_4), 132.2 (s, 2C, C_5Me_4). ^{11}B NMR (192.6 MHz, C_6D_5Cl, 25 °C, $BF_3{\cdot}Et_2O$) δ = –16.5 (s, 1B, $B(C_6F_5)_4$). ^{19}F NMR (564.7 MHz, C_6D_5Cl, 25 °C, CCl_3F) δ = –166.78 (br, 8F, *meta*-$B(C_6F_5)_4$), –162.97 (t, 4F, $J_{F\text{-}F}$ = 10.4 Hz, *para*-$B(C_6F_5)_4$), –132.19 (br, 8F, *ortho*-$B(C_6F_5)_4$). ^{29}Si NMR (119.2 MHz, C_6D_5Cl, 25 °C, TMS) δ = –9.5 (br, 2Si, $C_5Me_4SiMe_3$), –8.6 (s, 1Si, $C_5Me_4SiMe_3$), δ = –6.8 (s, 1Si, $C_5Me_4SiMe_3$).

$[(C_5Me_4SiMe_3)_4Y_4H_7(THF)_2][B(C_6F_5)_4]$ (2c). a) To a benzene solution (3 mL) of $[(C_5Me_4SiMe_3)_4Y_4H_7][B(C_6F_5)_4]$ (**2a**) (0.035 g, 0.018 mmol) 2 equiv of THF (0.003 g, 0.019 mmol) were added at room temperature. After stirring for 15 min and drying under vacuum a white powder **2c** (0.037 g, 100 %) was obtained. b) A mixture of $(C_5Me_4SiMe_3)_4Y_4H_8(THF)_2$ (0.056 g, 0.044 mmol) and $[Ph_3C][B(C_6F_5)_4]$ (0.040 g, 0.044 mmol) in 10 mL chlorobenzene was stirred for 6 h to give a colorless solution. After the solvent was removed in vacuum the resulting colorless residue was washed with hexane. Drying under vacuum gave a white powder (0.078 g, 91 %). Single crystals suitable for X-ray analysis were grown in chlorobenzene/benzene at room temperature. IR (nujol): ν = 1641, 1513, 1409, 1323, 1275, 1267, 1246, 1172, 1130, 1105, 1086, 1058, 1032, 1003, 980, 884, 837, 773, 756, 682, 662, 631, 610, 602, 572 cm^{-1}; ^{1}H NMR (300 MHz, C_6D_5Cl, 25 °C, TMS): δ = 0.34 (s, 18H, $C_5Me_4Si\mathit{Me}_3$), 0.40 (s, 18H, $C_5Me_4Si\mathit{Me}_3$), 1.95 (br, 8H, β-CH_2-THF), 1.99 (s, 12H, C_5Me_4), 2.14 (s, 12H, C_5Me_4), 2.15 (s, 12H, C_5Me_4), 2.35 (s, 12H, C_5Me_4), 2.83 (br, 1H, YH), 3.14 (m, 2H, YH), 3.99 (br, 8H, α-CH_2-THF), 5.41 (d of d, 4H, $J_{Y\text{-}H}$ = 39.6, 36.8 Hz, YH). ^{13}C{^{1}H} NMR (75.5 MHz, C_6D_5Cl, 25 °C, TMS) δ = 1.5 (s, 6C, $C_5Me_4Si\mathit{Me}_3$), 2.4 (s, 6C, $C_5Me_4Si\mathit{Me}_3$), 12.1 (s, 4C, $C_5\mathit{Me}_4$), 12.5(s, 4C, $C_5\mathit{Me}_4$), 14.9 (s, 4C, $C_5\mathit{Me}_4$), 16.1 (s, 4C, $C_5\mathit{Me}_4$), 25.2 (s, 4C, *β*-$\mathit{C}H_2$-THF), 71.0 (s, 4C, *α*-$\mathit{C}H_2$-THF), 118.4 (s, 2C, *ipso*-C_5Me_4), 119.0 (s, 2C, *ipso*-C_5Me_4), 124.9 (s, 4C, C_5Me_4), 127.0 (s, 4C, C_5Me_4), 130.2 (s, 4C, C_5Me_4), 130.6 (s, 4C, C_5Me_4). ^{11}B NMR (192.6 MHz, C_6D_5Cl, 25 °C, $BF_3{\cdot}Et_2O$) δ = –16.6 (s, 1 B, $B(C_6F_5)_4$). ^{19}F NMR (564.7 MHz, C_6D_5Cl, 25 °C, CCl_3F) δ = -166.83 (t, 8F, *meta*-$B(C_6F_5)_4$, $J_{F\text{-}F}$ = 19.8 Hz), -163.02 (t, 4F, *para*-$B(C_6F_5)_4$, $J_{F\text{-}F}$ = 19.8 Hz), -132.24 (br, 8F, *ortho*-$B(C_6F_5)_4$); ^{29}Si NMR (119.2 MHz, C_6D_5Cl, 25 °C, TMS) δ = –11.9 ($C_5Me_4SiMe_3$), –11.0 ($C_5Me_4SiMe_3$). Elemental analysis calcd. (%) for $C_{80}H_{107}B_1O_2F_{20}Si_4Y_4$: C 49.04, H 5.50; found: C 49.31, H 5.31.

$(C_5Me_4SiMe_3)_4Y_4H_7(C_6H_9)$ (3). 1,3-cyclohexadiene (0.040 g, 0.50 mmol) was added to a benzene solution of **1b** (0.605 g, 0.50 mmol), and the resulting yellow solution was stirred for 1 h. After all volatiles were removed under vacuum, the residue

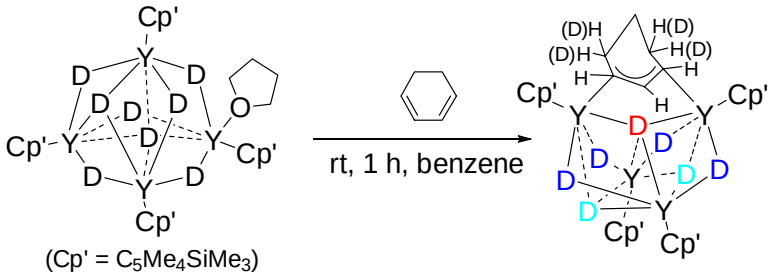
was dissolved in hexane (20 mL) and the solution volume was reduced, and decanted to precipitate **3** (0.584 g, 0.48 mmol, 96 % yield) as a yellow powder. Yellow single crystals suitable for X-ray analysis were grown in a concentrated hexane solution at –30 °C. IR (nujol): ν = 1520, 1400, 1330, 1250, 1135, 895, 846, 722, 680 cm^{-1}; ^{1}H NMR (400 MHz, C_6D_6, 22 °C): δ = 0.44 (s, 18H, $C_5Me_4SiMe_3$), 0.51 (s, 9H, $C_5Me_4SiMe_3$), 0.53 (s, 9H, $C_5Me_4SiMe_3$), 0.74 (m, 2H, YCHC*H*HCH$_2$-), 1.52 (m, 1H, YCHCH$_2$C*H*H-), 1.81 (m, 2H, YCHCH*H*CH$_2$), 2.03 (m, 1H, YCHCH$_2$CH*H*-), 2.10 (s, 6H, C_5Me_4), 2.17 (s, 6H, C_5Me_4), 2.24 (s, 18H, C_5Me_4), 2.37 (s, 6H, C_5Me_4), 2.50 (br, 1H, YH), 2.57 (s, 6H, C_5Me_4), 2.61 (s, 6H, C_5Me_4), 3.12 (m, 2H, YC*H*CH$_2$CH$_2$-), 3.91 (m, 2H, YH), 5.15 (t, $J_{Y\text{-}H}$ = 35.7 Hz, 2H, YH), 5.40 (t, $J_{Y\text{-}H}$ = 35.7 Hz, 2H, YH), 7.31 ppm (t, $J_{H\text{-}H}$ = 7.10 Hz, 1H, *H*CYCHCH$_2$CH$_2$-); ^{13}C NMR (150 MHz, C_6D_6, 22 °C): δ = 1.91 (s, 3C, $C_5Me_4SiMe_3$), 2.03 (s, 3C, $C_5Me_4SiMe_3$), 2.68 (s, 6C, $C_5Me_4SiMe_3$), 11.94 (s, 2C, C_5Me_4), 12.21 (s, 2C, C_5Me_4), 12.43 (s, 2C, C_5Me_4), 12.62 (s, 2C, C_5Me_4), 15.09 (s, 2C, C_5Me_4), 15.85 (s, 2C, C_5Me_4), 15.97 (s, 2C, C_5Me_4), 16.18 (s, 2C, C_5Me_4), 20.77 (s, 1C, YCHCH$_2$*C*H$_2$-), 21.38 (s, 2C, YCH*C*H$_2$CH$_2$-), 67.79 (d, 2C, $J_{Y\text{-}C}$ = 9.5 Hz, Y*C*HCH$_2$CH$_2$-), 114.96 (s, 2C, *ipso*-C_5Me_4), 117.34 (s, 1C, *ipso*-C_5Me_4), 117.37(s, 1C, *ipso*-C_5Me_4), 124.28(s, 2C, C_5Me_4), 124.68 (s, 2C, C_5Me_4), 124.76 (s, 2C, C_5Me_4), 125.00 (s, 2C, C_5Me_4), 126.32 (s, 2C, C_5Me_4), 127.09 (s, 2C, C_5Me_4), 129.34 (s, 2C, C_5Me_4), 129.72 (s, 2C, C_5Me_4), 165.07 (s, 1C, H*C*YCHCH$_2$CH$_2$-); ^{1}H NMR (600 MHz, C_4D_8O, 22 °C): δ = 0.23 (s, 18H, $C_5Me_4SiMe_3$), 0.30 (s, 18H, $C_5Me_4SiMe_3$), 0.52 (m, 2H, YCHC*H*HCH$_2$-), 1.43 (m, 1H, YCHCH$_2$C*H*H-), 1.73 (m, 2H, YCHCH*H*CH$_2$-), 1.99 (m, 1H, YCHCH$_2$CH*H*-), 2.04 (s, 6H, C_5Me_4), 2.10 (s, 6H, C_5Me_4), 2.14 (m, 1H, YH), 2.15 (s, 6H, C_5Me_4), 2.19 (s, 12H, C_5Me_4), 2.21 (s, 6H, C_5Me_4), 2.37 (s, 6H, C_5Me_4), 2.43 (s, 6H, C_5Me_4), 2.89 (m, 2H, YC*H*CH$_2$CH$_2$-), 3.75 (m, 2H, YH), 4.82 (t, $J_{Y\text{-}H}$ = 35.2 Hz, 2H, YH), 5.04 (t, $J_{Y\text{-}H}$ = 35.2 Hz, 2H, YH), 7.05 (t, $J_{H\text{-}H}$ = 8.3 Hz, 1H, *H*CYCHCH$_2$CH$_2$-); ^{13}C NMR (150 MHz, C_4D_8O, 22 °C): δ = 2.39 (s, 3C, $C_5Me_4SiMe_3$), 2.56 (s, 3C, C$_5$Me4Si*Me*$_3$), 2.77 (s, 6C, $C_5Me_4SiMe_3$), 12.47 (s, 2C, C_5Me_4), 12.74 (s, 2C, C_5Me_4), 12.76 (s, 2C, C_5Me_4), 12.92 (s, 2C, C_5Me_4), 15.24 (s, 2C, C_5Me_4), 16.03 (s, 2C, C_5Me_4), 16.11 (s, 2C, C_5Me_4), 16.46 (s, 2C, C_5Me_4), 21.29 (s, 1C, YCHCH$_2$*C*H$_2$-), 21.96 (s, 2C, YCH*C*H$_2$CH$_2$-), 67.19 (s, 2C, Y*C*HCH$_2$CH$_2$-), 114.68 (s, 2C, *ipso*-C_5Me_4), 116.94 (s, 2C, *ipso*-C_5Me_4), 124.30 (s, 2C, C_5Me_4), 124.60 (s, 2C, C_5Me_4), 124.65 (s, 2C, C_5Me_4), 124.96 (s, 2C, C_5Me_4), 126.48 (s, 2C, C_5Me_4), 127.10 (s, 2C, C_5Me_4), 129.30 (s, 2C, C_5Me_4), 129.75 (s, 2C, C_5Me_4), 165.91 (s, 1C, H*C*YCHCH$_2$CH$_2$-); ^{89}Y NMR (19 MHz, C_4D_8O, 22 °C): δ = 282.6 (br, 2Y), 376.6 (m, 1Y), 410.01 (m, 1Y). Anal. Calcd for $C_{54}H_{100}Si_4Y_4$: C, 53.28; H, 8.28. Found: C, 51.30; H, 8.22. Scanned ^{1}H and ^{89}Y NMR spectra of **3** are given below.

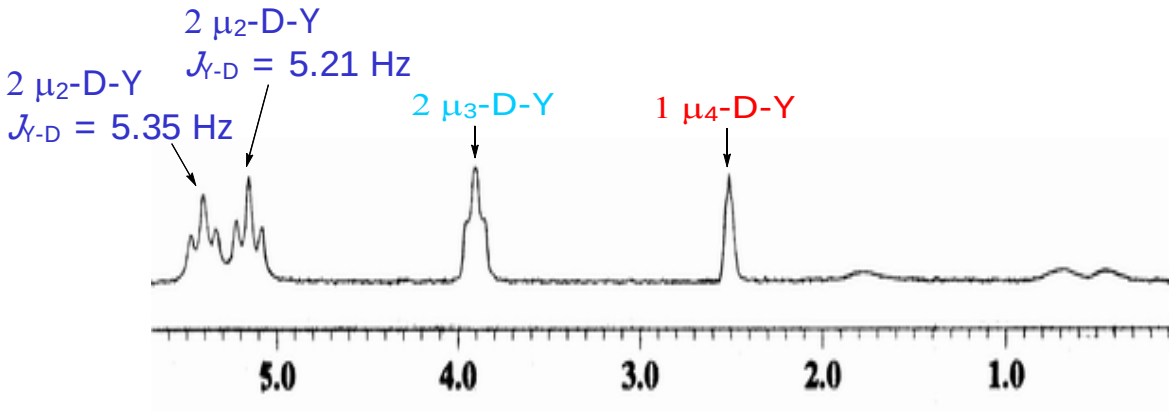




[($C_5Me_4SiMe_3$)Y]$_4$(μ-D)$_7$(μ-C_6H_8D) (3-*d*): **3–*d*** was prepared analogously to **3** by reaction of ($C_5Me_4SiMe_3$)$_4$Y$_4$D$_8$(THF) with CHD. IR (nujol): ν = 1500, 1330, 1250, 930, 895, 846, 752 cm^{-1}; ^{1}H NMR (300 MHz, C_6D_6, 22 °C): δ = 0.43 (s, 18H, $C_5Me_4SiMe_3$), 0.51 (s, 9H, $C_5Me_4SiMe_3$), 0.53 (s, 9H, $C_5Me_4SiMe_3$), 0.70 (m, xH, YCHC*H*DCH$_2$), 1.51 (m, 1H, YCHCDHC*H*H), 1.79 (m, xH, YCHCD*H*CH$_2$), 2.03 (m, 1H, YCHCDHCH*H*-), 2.10 (s, 6H, C_5Me_4), 2.18 (s, 6H, C_5Me_4), 2.23 (s, 6H, C_5Me_4), 2.24 (s, 12H, C_5Me_4), 2.38 (s, 6H, C_5Me_4), 2.57 (s, 6H, C_5Me_4), 2.61 (s, 6H, C_5Me_4), 3.12 (m, 2H, YC*H*CDHCH$_2$-), 7.31 ppm (t, J_{H-H} = 7.34 Hz, 1H, *H*CYCHCDHCH$_2$-); ^{13}C NMR (75 MHz, C_6D_6, 22 °C): δ = 1.93 (s, 3C, $C_5Me_4SiMe_3$), 2.04 (s, 3C, $C_5Me_4SiMe_3$), 2.70 (s, 6C, $C_5Me_4SiMe_3$), 11.93 (s, 2C, C_5Me_4), 12.21 (s, 2C, C_5Me_4), 12.44 (s, 2C, C_5Me_4), 12.60 (s, 2C, C_5Me_4), 15.08 (s, 2C, C_5Me_4), 15.85 (s, 2C, C_5Me_4), 15.99 (s, 2C, C_5Me_4), 16.19 (s, 2C, C_5Me_4), 20.64 (s, 1C, YCHCDHCH_2-), 21.34 (s, 2C, YCHC*D*HCH$_2$-), 67.63 (m, 2C, Y*C*HCDHCH$_2$-), 114.79 (s, 2C, *ipso*-C_5Me_4), 117.15 (s, 2C, *ipso*-C_5Me_4), 124.07 (s, 2C, C_5Me_4), 124.46 (s, 2C, C_5Me_4), 124.53 (s, 2C, C_5Me_4), 124.77 (s, 2C, C_5Me_4), 126.14 (s, 2C, C_5Me_4), 126.89 (s, 2C, C_5Me_4), 129.13 (s, 2C, C_5Me_4), 129.51 (s, 2C, C_5Me_4), 165.07 (s, 1C, H*C*YCHCH$_2$CH$_2$-); ^{2}H NMR (61 MHz, C_6H_6, 22 °C): δ = 0.3–0.9 and 1.6–1.9 (vbr, 1D, C_6H_9D), 2.51 (br s, 1D, Y*D*), 3.91 (br m, 2D, Y*D*), 5.15 (t, J_{Y-D} = 5.35 Hz, 2D, Y*D*), 5.41 ppm (t, J_{Y-D} = 5.21 Hz, 2D, Y*D*). A scanned ^{2}H NMR spectrum of **3-d** is given below.

^{2}H NMR spectrum of **3-d** in C_6H_6 at room temp.





A typical procedure for the regio- and stereoselective polymerization of 1,3-cyclohexadiene by use of an *in-situ* generated cationic polyhydrido rare earth metal species (Table 2, entry 3): In the glove box, a toluene solution (1 mL) of

$[Ph_3C][B(C_6F_5)_4]$ (0.037 g, 0.040 mmol) was added to a toluene solution (1 mL) of $(C_5Me_4SiMe_3)_4Y_4H_8(THF)$ (0.048 g, 0.040 mmol) in a 10-mL flask. The mixture was stirred at room temperature for 5 min, and then 1,3-cyclohexadiene (0.80 g, 0.010 mol) was added under vigorous stirring. The polymerization solution became heterogeneous at rt as a orange precipitate formed after 5 h. After 15 h, the flask was taken outside of the glove box and methanol was added to terminate the polymerization. The mixture was poured into methanol (200 mL, containing 1 % butylhydroxytoluene (BHT)) to precipitate the polymer product. The white polymer powder was collected by filtration, and dried *in vacuo* at 60 °C to a constant weight (0.40 g, 50%). The product obtained is soluble in dichlorobenzene and 1,1,2,2-tetrachloroethane at 120 °C.

X-Ray Crystallographic Study. A crystal was sealed in a thin-walled glass capillary under a microscope in the glove box. Data collections were performed at –100 °C on a Bruker SMART APEX diffractometer with a CCD area detector using graphite-monochromated Mo K_α radiation (λ = 0.71069 Å). The determination of crystal class and unit cell was carried out by SMART program package.[5] The raw frame data were processed using SAINT[6] and SADABS[7] to yield the reflection data file. The structures were solved by using SHELXTL program.[8] Refinements were performed on F^2 anisotropically for all the non-hydrogen atoms by the full-matrix least-squares method. The analytical scattering factors for neutral atoms were used throughout the analysis. The hydrido atoms were located by difference Fourier syntheses and their coordinates and isotropic parameters were refined. Other hydrogen atoms were placed at the calculated positions and were included in the structure calculation without further refinement of the parameters. In **2a** disorder was found for the Cp' ligands connected to Y2 and Y4. The silyl and carbon atoms in the $SiMe_3$ groups (Si2, Si3, Si5, Si6, C22, C24, C49, C50) were treated with 50% occupancy. The hexane molecule was refined isotropically. The residual electron densities were of no chemical significance. In **2c** disorder was found for the lattice solvent. The disordered benzene molecule was separated in two parts (C81A-C86A and C81B-C86B) and was treated with 50 % occupancy. The residual electron densities were of no chemical significance. In **3** disorder was found for the Cp' ligands coordinated to Y3 and Y4. The silyl and carbon atoms in the $SiMe_3$ groups (Si3, Si4, Si5, Si6, C40, C42, C52, C54) were treated with 50% occupancy. The residual electron densities were of no chemical significance. CCDC-617797 (**1c**), -617794 (**2a**), -617795 (**2c**), -617796 (**3**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (+44)-1223-336033; or deposit@ccdc.cam.ac.uk)

[1] O. Tardif, M. Nishiura, Z. Hou, *Organometallics* **2003**, *22*, 1171–1173.
[2] D. Cui, O. Tardif, Z. Hou, *J. Am. Chem. Soc.* **2004**, *126*, 1312–1313.
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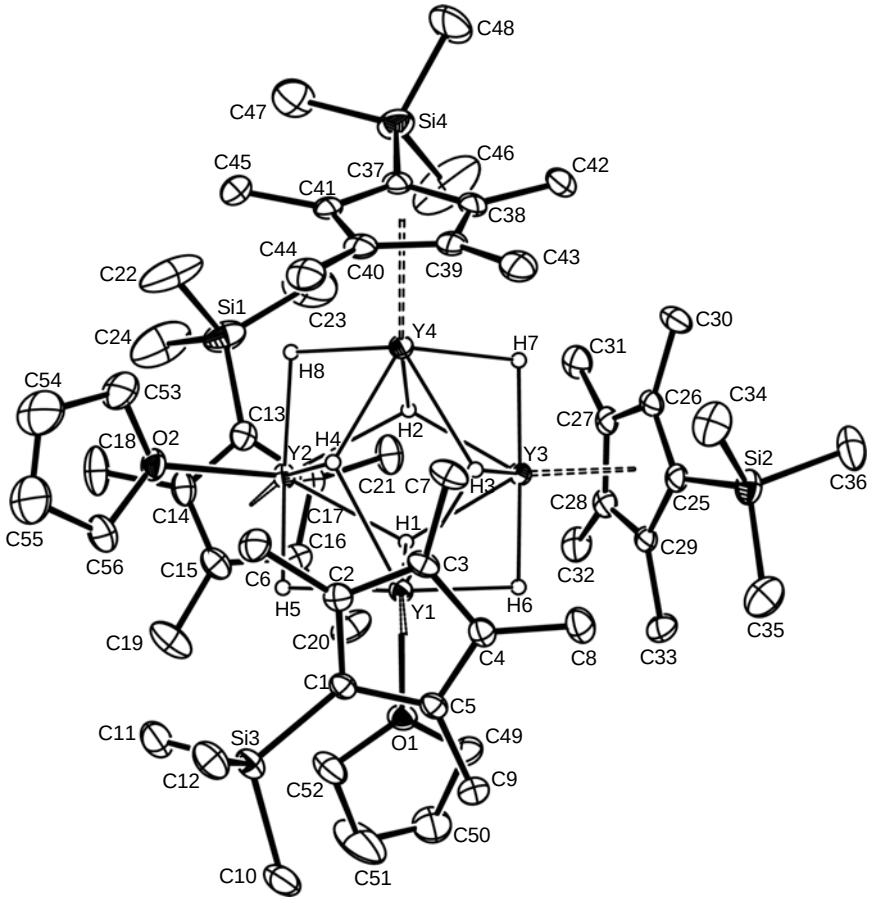
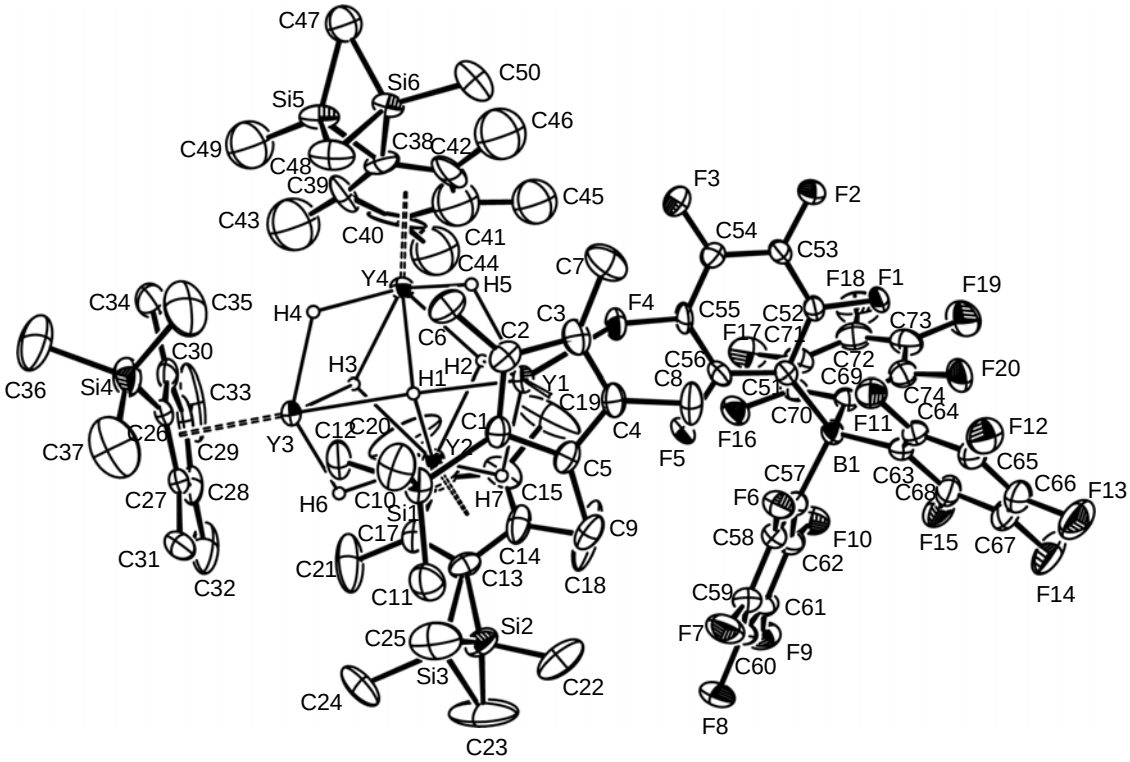
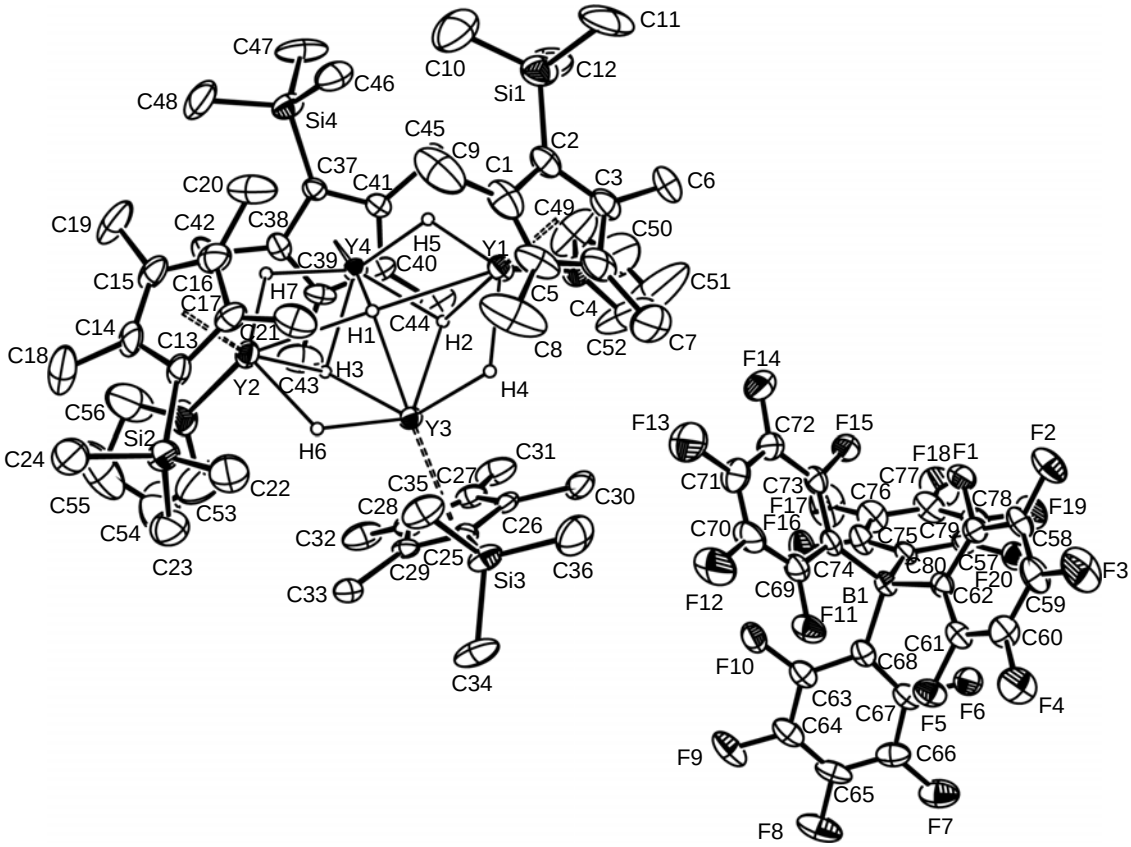
[6] SMART Software Users Guide, version 4.21; Bruker AXS, Inc.: Madison, WI, 1997.
[7] SAINT+, Version 6.02; Bruker AXS, Inc.: Madison, WI 1999.
[8] Sheldrick, G. M. SADABS; Bruker AXS, Inc.: Madison, WI, 1998.
[9] Sheldrick, G. M. SHELXTL, Version 5.1; BUKER AXS, INC.: Madison, WI, 1998.



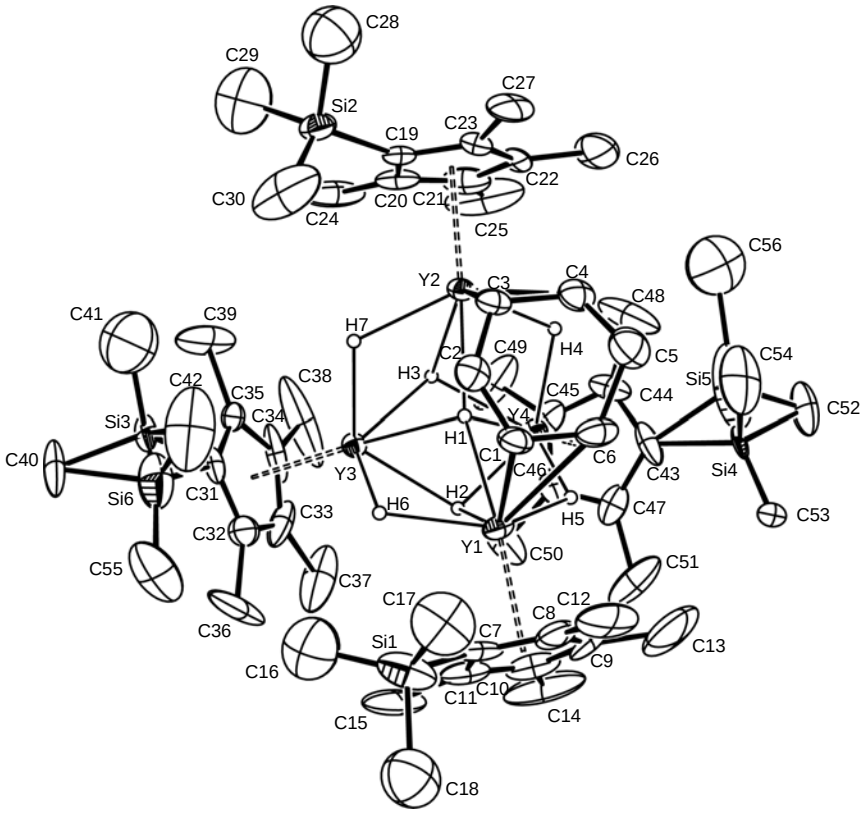
SFigure 1. ORTEP drawing of **1c**.



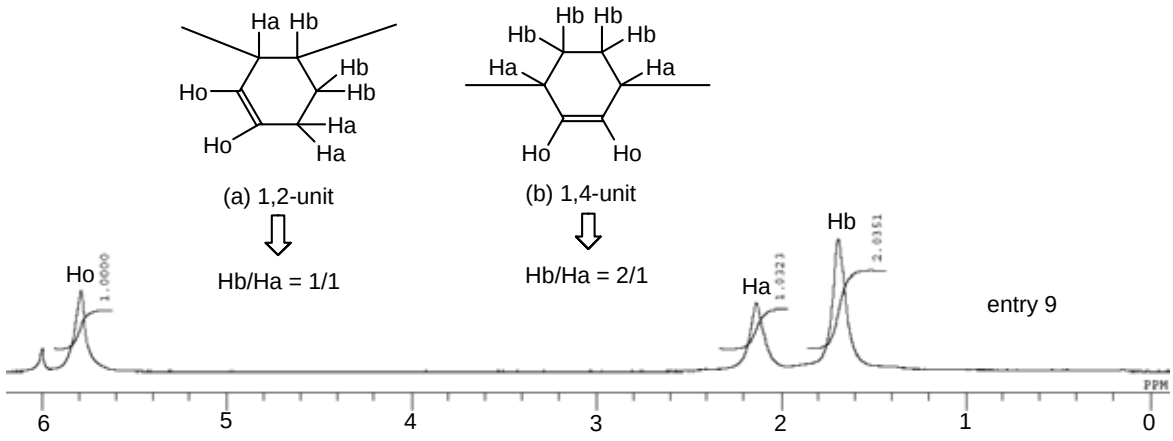
SFigure 2. ORTEP drawing of **2a**.



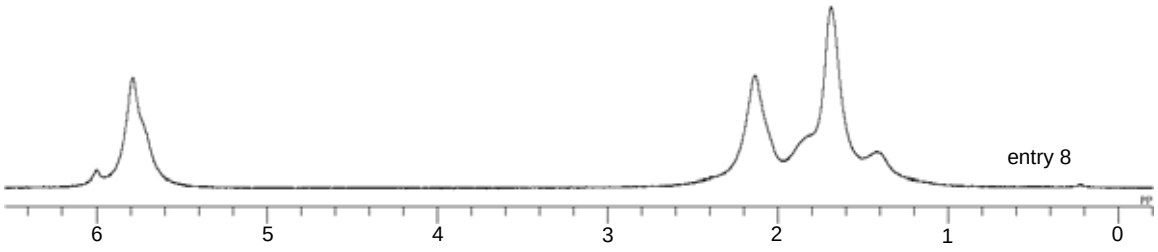
SFigure 3. ORTEP drawing of **2c**.



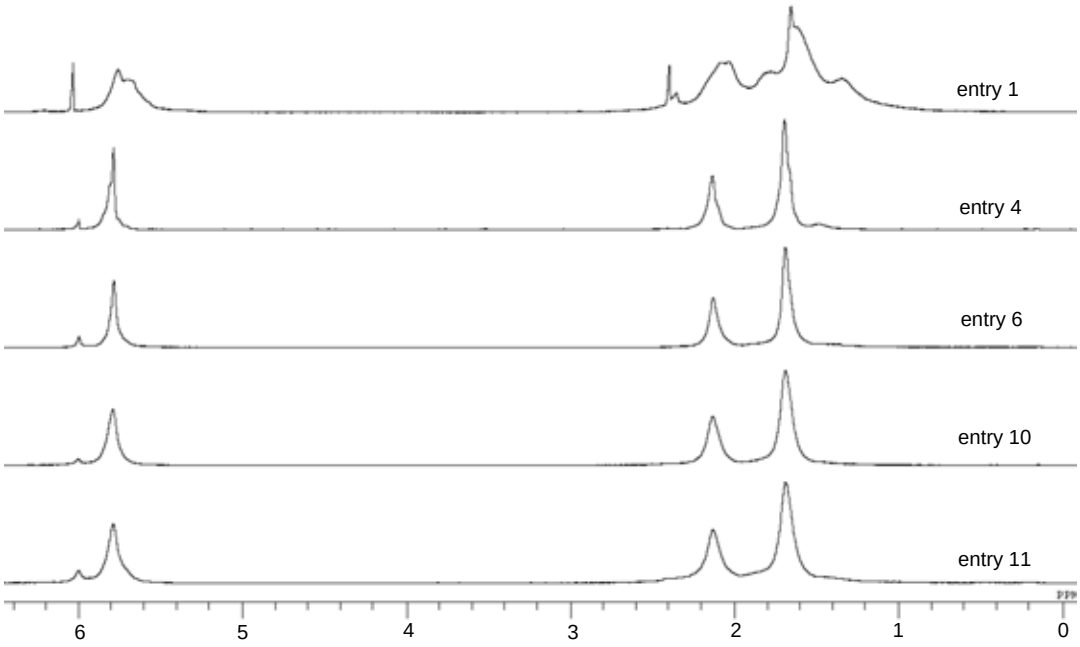
SFigure 4. ORTEP drawing of **3**.



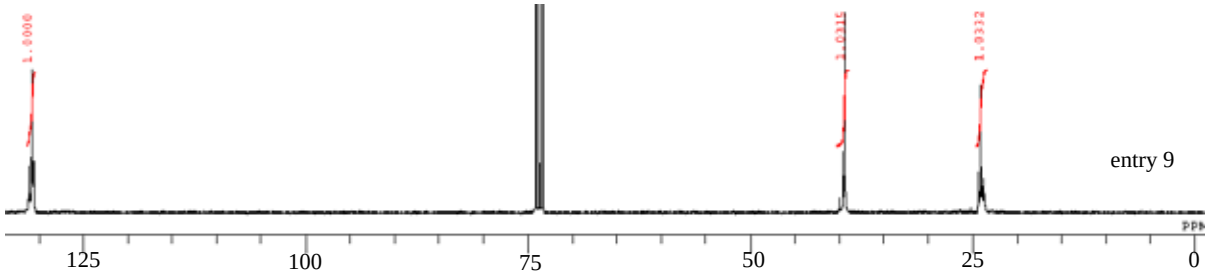
SFigure 5. ^{1}H NMR spectrum of the *cis*-1,4-linked poly(CHD) (Table 2, entry 9) (Only one single peak at ca. 1.7 ppm could be observed, as expected for the *cis*-1,4-polymer).



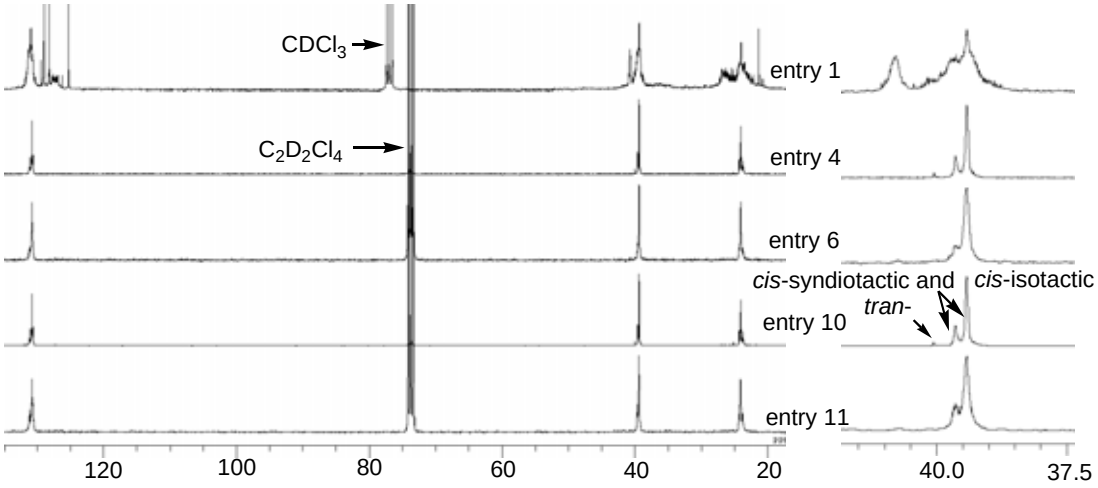
SFigure 6. ^{1}H NMR spectrum of poly(CHD) (Table 2, entry 8) (Peaks at ca. 1.35 and 1.75 ppm are expected for the trans planomers).



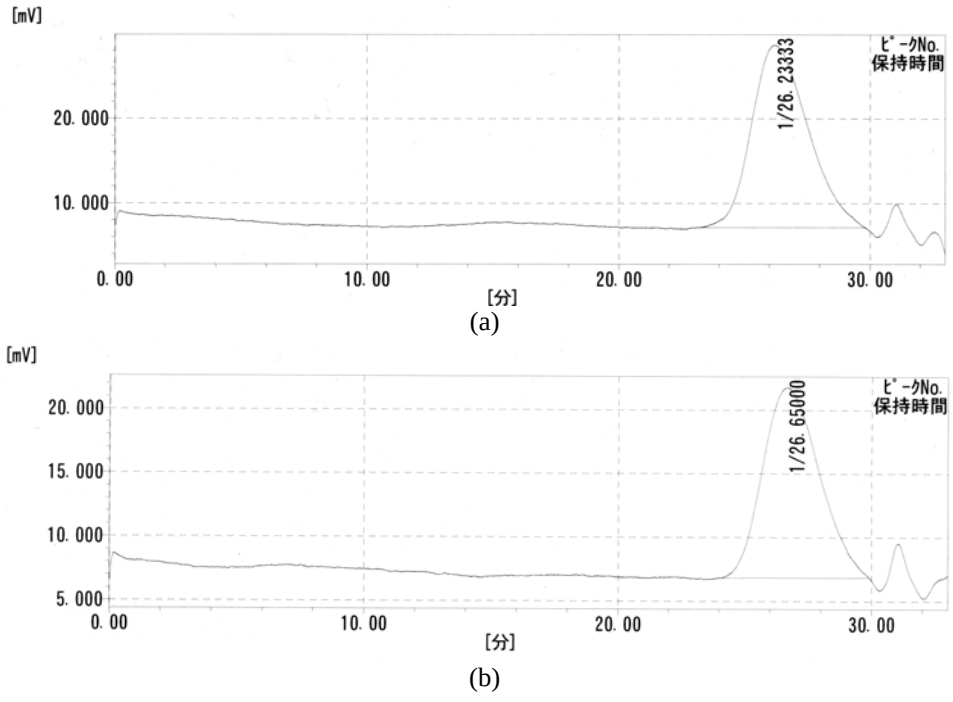
SFigure 7. ^{1}H NMR spectra of poly(CHD)s in Table 2.



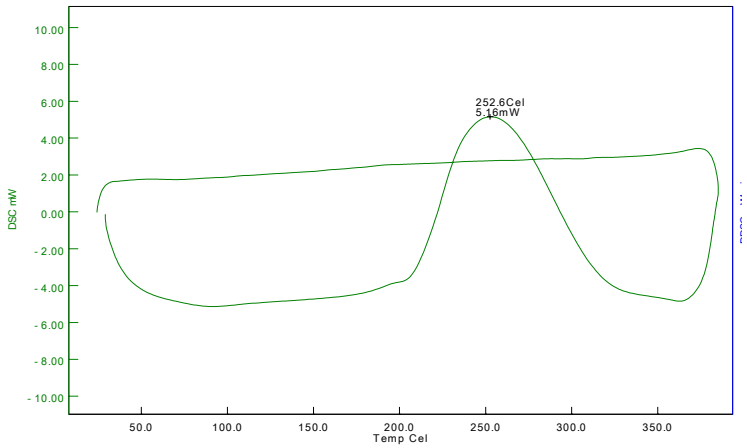
SFigure 8. ^{13}C NMR spectrum of the *cis*-1,4-linked poly(CHD) (Table 2, entry 9).



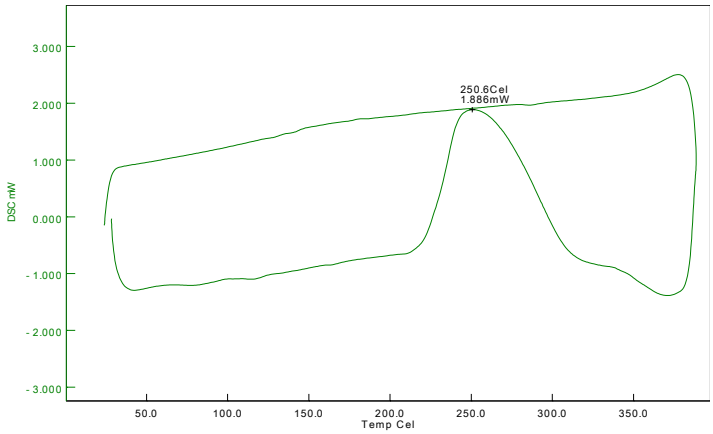
SFigure 9. ^{13}C NMR spectra of poly(CHD)s obtained in Table 2.



SFigure 10. GPC curves of the *cis*-1,4-linked poly(CHD)s in Table 2: (a) entry 3; (b) entry 9.



(a)



(b)

SFigure 11. DSC curves of the *cis*-1,4-linked poly(CHD)s in Table 2: (a) entry 3; (b) entry 9 (The DSC traces of the poly(CHD)s showed an endothermic peak around 250 °C for the first heating, however, it is difficult to find endothermic peak for the second heating, probably due to degradation in the melt).