

Supporting Information
for the
Communication Entitled

**Electronic Ligan Effect Enhancement in the Stereoselective Living
Coordinative Polymerization of α -Olefins by α,α,α -Trifluoroacetamidinate-
modified Group 4 Metal CPAM^{CF₃} Initiators**

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Details for the synthesis and characterization of compounds **3** – **8**, polymerization procedures and polymer characterization (27 pages).

Experimental Details

General considerations

All manipulations were performed under an inert atmosphere of N₂ using standard Schlenk-line or glove-box techniques. All non-halogenated solvents were dried (Na/benzophenone for pentane and diethyl ether, and Na for toluene) and distilled under N₂ prior to use. Benzene-*d*₆, toluene-*d*₈ and 1-hexene were dried over Na/K alloy and vacuum transferred prior to being used. Celite was oven dried at 150 °C for several days before use. Cooling for the reactions was performed in the internal freezer (-25 °C) of the glove box used. (η^5 -C₅Me₅)ZrCl₃, (η^5 -C₅Me₅)HfCl₃, NaN(SiMe₃)₂, and [PhNMe₂H][B(C₆F₅)₄] were purchased from Strem Chemicals and used as received. Carbon tetrachloride, triethylamine, tert-butyl amine, ethylamine (2M in THF) and triphenylphosphine were all purchased from Sigma Aldrich and used as received. Polymer grade propene was purchased from Matheson Trigas, and passed over activated Q5 and molecular sieves. GPC analyses were performed using a Viscotek GPC system equipped with a column oven and a differential refractometer both maintained at 45 °C and four columns also maintained at 45 °C. THF was used as the eluent at a flow rate of 1.0 mL/min. M_n, M_w, and M_w/M_n values were obtained using the Viscotek OmniSEC software and ten polystyrene standards (M_n=580 Da to 3150 kDa) (Polymer Laboratories). ¹H NMR spectra were recorded at either 400MHz or 500 MHz with benzene-*d*₆ or toluene-*d*₈. ¹⁹F NMR spectra were recorded at 376 MHz using trifluoroacetic acid as an external reference at -76.55 ppm. For polymer samples, ¹³C {¹H} NMR spectra were recorded at 200 MHz using 1,1,2,2-tetrachloroethane-*d*₂ at 85 °C. Elemental analyses (C, H, and N) were performed by Midwest Microlabs, LLC.

Synthesis of new compounds

N(^tBu)C(CF₃)N(Et)H (**5**)

To a solution of 34.3 g (0.131 mol) triphenylphosphine (PPh₃) and 5.0 g (0.044 mol) trifluoroacetic acid in 100 ml of carbon tetrachloride (CCl₄), cooled to 0° C using an ice bath, 5.3 g (0.052 mol) of triethylamine was added and the mixture stirred for 30 minutes, whereupon 3.8 g (0.052 mol) of tert-butylamine was then added. The ice-bath was removed and the reaction mixture refluxed for 3 hours, leading to a gradual conversion of the colorless solution to a yellow slurry. After cooling to room-temperature, 100 ml of pentane was added to precipitate the solid by-products and the reaction mixture was filtered using a Büchner funnel, and the collected solids rinsed with additional amounts of pentane until the washings were nearly colorless. The combined filtrate was then cooled to 0° C and 52 ml of ethylamine (2 M THF solution) added. After stirring overnight, the reaction mixture was filtered once again to remove the solid by-products and then the volatiles were removed from the filtrate under reduced pressure to provide a crude yellow product that was further purified by bulb-to-bulb distillation (70 °C, 50 mmHg) to yield pure **5** as a colorless liquid. Yield, 6.7 g (77%). For **5**: ¹H NMR (400 MHz, CDCl₃, 25 °C), δ (ppm) 1.15 (3H, t, ³J_{HH} = 7.2 Hz, CH₂CH₃), 1.34 (9H, s, C(CH₃)₃), 3.40 (2H, qq, ³J_{HH} = 7.2, ⁵J_{HF} = 2 Hz, CH₂CH₃), 4.40 (1H, br s, NH) (see Figure S1). ¹³C {¹H} NMR (125.77 MHz, C₆D₆, 25 °C), δ (ppm) 141.42 (q, ²J_{CF} = 27.7 Hz, ^tBuNCNEt), 117.73 (q, ¹J_{CF} = 291.8 Hz, CF₃), 68.14 (C(CH₃)₃), 43.70 (CH₂CH₃), 28.39 (C(CH₃)₃), 17.96 (CH₂CH₃) (see Figure S2). ¹⁹F {¹H} NMR (376 MHz, CDCl₃, 25 °C) δ (ppm) -66.5 (CF₃) (see Figure S3).

[Na(OEt)_{0.5}][N(^tBu)C(CF₃)N(Et)] (6)

To a solution of 0.730 g (0.372 mmol) of **5** in 100 ml of Et₂O, cooled to -25 °C, a solution of NaN(SiMe₃)₂ (0.683 g, 0.372 mmol) in 10 ml of Et₂O, also cooled to -25 °C, was added dropwise and the reaction mixture stirred. After 4 h, the mixture had turned blood-orange in color, at which time, all volatiles were removed under reduced pressure to give a dark red, oily solid which was then taken up in a minimal amount of pentane and cooled to -25 °C. After 18 h, **6** was isolated as a dark-red, crystalline material. Yield, 0.402 g (41%). For **6**: ¹H NMR (400 MHz, C₆D₆, 25 °C) δ (ppm) 1.09 (3H, t, ³J_{HH} = 6.8 Hz, O(CH₂CH₃)₂), 1.19 (3H, t, ³J_{HH} = 7.2 Hz, CH₂CH₃), 1.41 (9H, s, C(CH₃)₃), 3.26 (2H, q, ³J_{HH} = 7.2 Hz, CH₂CH₃), 3.56 (2H, q, ³J_{HH} = 6.8 Hz, O(CH₂CH₃)₂) (see Figure S4). ¹³C{¹H} NMR (125.77 MHz, C₆D₆, 25 °C) δ (ppm) 153.72 (q, ²J_{CF} = 21.4 Hz, ^tBuNCNEt), 122.49 (q, ¹J_{CF} = 286.76 Hz, CF₃), 66.13 (OCH₂CH₃), 51.21 (C(CH₃)₃), 43.81 (CH₂CH₃), 32.01 (C(CH₃)₃), 19.77 (CH₂CH₃), 15.55 (OCH₂CH₃) (see Figure S5). ¹⁹F{¹H} NMR (376 MHz, C₆D₆, 25 °C) δ (ppm) -66.6 (Δ_{v1/2} = 526 Hz, CF₃) (see Figure S6).

Cp*Zr[N(^tBu)C(CF₃)N(Et)]Cl₂ (7)

To a solution of 0.43 g (2.19 mmol) of **5** in 10 ml of Et₂O, cooled to -25 °C, a solution of NaN(SiMe₃)₂ (0.40 g, 2.19 mmol) in 10 ml of toluene, also cooled to -25 °C, was added dropwise. After stirring for 30 min at room temperature, the reaction mixture became orange in color, at which point, it was cooled again to -25 °C and 0.73 g (2.19 mmol) of Cp*ZrCl₃ was added as a solid. The reaction mixture was stirred for 30 min and then all volatiles were removed under reduced pressure to give an oily yellow-brown solid. The crude product was taken up into a minimum volume of pentane, filtered, and the filtrate reduced in volume and then cooled at -25 °C to provide **7** as a pale yellow, crystalline material. Yield, 0.47 g (43%). For **7**: ¹H NMR (400 MHz, C₆D₆, 25 °C), δ (ppm) 1.56 (3H, t, J = 7.1 Hz, CH₂CH₃), 1.33 (9H, s, C(CH₃)₃), 1.96 (15H, s, C₅(CH₃)₅), 3.30 (qq, ³J_{HH} = 7.1 Hz, ⁵J_{HF} = 2.4 Hz, CH₂CH₃) (see Figure S7). ¹³C NMR (125.77 MHz, toluene-*d*₈, 25 °C) δ (ppm) 157.72 (q, ²J_{CF} = 31.4 Hz, ^tBuNCNEt), 127.04 (C₅(CH₃)₅), 117.55 (q, ¹J_{CF} = 291.8 Hz, CF₃), 55.69 (C(CH₃)₃), 44.45 (q, ⁴J_{CF} = 3.8 Hz, CH₂CH₃), 32.55 (q, ⁵J_{CF} = 3.8 Hz, C(CH₃)₃) 17.00 (q, ⁵J_{CF} = 2.5 Hz, CH₂CH₃), 12.79 (C₅(CH₃)₅) (see Figure S8). ¹⁹F NMR (376 MHz, C₆D₆, 25 °C) δ (ppm) -59.3 (CF₃) (see Figure S9). Anal. Calcd. for C₁₈H₂₉F₃N₂Cl₂Zr: C, 43.89; H 5.73; N, 5.69. Found: C, 43.63; H, 5.62; N, 5.52.

Cp*Hf[N(^tBu)C(CF₃)N(Et)]Cl₂ (8)

To a solution of 0.43 g (2.19 mmol) of **5** in 10 ml of Et₂O, cooled to -25 °C, a solution of NaN(SiMe₃)₂ (0.40 g, 2.19 mmol) in 10 ml of toluene, also cooled to -25 °C, was added dropwise. After stirring for 30 min at room temperature, the reaction mixture became orange in color, at which point, it was cooled again to -25 °C and 0.92 g (2.20 mmol) of Cp*HfCl₃ was added as a solid. The reaction mixture was stirred for 1 h and then all volatiles were removed under reduced pressure to give an oily beige-brown solid. The crude product was taken up into a minimum volume of pentane, filtered, and the filtrate reduced in volume and then cooled at -25 °C to provide **8** as a white, crystalline material. Yield, 0.46 g (36%). ¹H NMR (400 MHz, C₆D₆, 25 °C) δ (ppm) 1.56 (3H, t, ³J_{HH} = 6.8 Hz, CH₂CH₃), 1.32 (9H, s, C(CH₃)₃), 2.03 (15H, s, C₅(CH₃)₅), 3.32 (br d, CH₂CH₃) (see Figure S10). ¹³C{¹H} NMR (125.77 MHz, C₆D₆, 25 °C) δ (ppm) 157.88 (q, ²J_{CF} = 32.7 Hz, ^tBuNCNEt), 124.76 (C₅(CH₃)₅), 121.20 (q, ¹J_{CF} = 289.3 Hz, CF₃), 55.73 (C(CH₃)₃), 44.25 (q, ⁴J_{CF} = 3.8 Hz, CH₂CH₃), 32.97 (q, ⁵J_{CF} = 2.5 Hz, C(CH₃)₃) 17.25 (q, ⁵J_{CF} = 2.5 Hz, CH₂CH₃),

12.88 (C₅(CH₃)₅) (see Figure S11). ¹⁹F{¹H} NMR (376.1 MHz, C₆D₆, 25 °C) δ (ppm) -56.7 (CF₃) (see Figure S12). Anal. Calcd for C₁₈H₂₉F₃N₂Cl₂Hf: C, 37.29; H 5.04; N, 4.83. Found: C, 36.94; H, 5.04; N, 4.87.

Cp*Zr[N(ⁱBu)C(CF₃)N(Et)]Me₂ (3)

To a solution of 0.19 g (0.379 mmol) of **7** in 20 ml of Et₂O, cooled to -25 °C, 0.35 ml of a 2.48 M solution of MeMgBr in Et₂O was added dropwise. After stirring at room temperature for 30 min, the volatiles were removed under reduced pressure and the crude product was taken up into a minimum amount of pentane and the mixture filtered. Removal of the volatiles from the filtrate under reduced pressure provided **3** as a bright yellow oil. For **3**: ¹H NMR (400 MHz, C₆D₆, 25 °C) δ (ppm) 0.28 (6H, s, Zr(CH₃)₂), 1.02 (3H, t, J = 6.8 Hz, CH₂CH₃), 1.19 (9H, s, C(CH₃)₃), 1.87 (15H, s, C₅(CH₃)₅), 3.07 (qq, ³J_{HH} = 6.8 Hz, ⁵J_{HF} = 2.4 Hz, CH₂CH₃) (see Figure S13). ¹⁹F NMR (376.1 MHz, C₆D₆, 25 °C), δ (ppm) -59.7 (CF₃) (see Figure S14).

Cp*Hf[N(ⁱBu)C(CF₃)N(Et)]Me₂ (4)

To a solution of 0.22 g (0.379 mmol) of **8** in 20 ml of Et₂O cooled to -25 °C, 0.35 ml of a 2.48 M solution of MeMgBr in Et₂O was added dropwise. After stirring at room temperature for 30 min, the volatiles were removed under reduced pressure and the crude product was taken up into a minimum amount of pentane and the mixture filtered. Removal of the volatiles from the filtrate under reduced pressure provided **4** as a dark-yellow oil. Yield 0.19 g (93%). ¹H NMR (400 MHz, C₆D₆, 25 °C) δ (ppm) 0.08 (6H, s, Hf(CH₃)₂), 1.06 (3H, t, ³J_{HH} = 7.1 Hz, CH₂CH₃), 1.23 (9H, s, C(CH₃)₃), 1.96 (15H, s, C₅(CH₃)₅), 3.13 (qq, ³J_{HH} = 7.1 Hz, ⁵J_{HF} = 2.4 Hz, CH₂CH₃) (see Figure S15). ¹³C{¹H} NMR (125.77 MHz, C₆D₆, 25 °C) δ (ppm) 157.82 (q, ²J_{CF} = 30.2 Hz, ⁱBuNCNEt), 119.81 (q, ¹J_{CF} = 291.8 Hz, CF₃), 119.98 (C₅(CH₃)₅), 55.48 (Hf(CH₃)₂), 54.41 (C(CH₃)₃), 42.54 (q, ⁴J_{CF} = 3.8 Hz, CH₂CH₃), 33.09 (q, ⁵J_{CF} = 1.3 Hz, C(CH₃)₃) 18.15 (CH₂CH₃), 12.17 (C₅(CH₃)₅) (see Figure S16). ¹⁹F{¹H} NMR (376.1 MHz, C₆D₆, 25 °C) δ (ppm) -59.7 (CF₃) (see Figure S17).

General procedure for the polymerization of propene.

To a solution of the pre-initiator (0.020 mmol) in 0.5 mL of PhCl at -10 °C, was added a solution of [PhNMe₂H][B(C₆F₅)₄] (0.026 mmol) in 0.5 ml of PhCl and then the resulting mixture was diluted with 19 mL of PhCl and cooled to -10 °C in a Schlenk flask. The flask was charged to 5 psi with propene gas with stirring. Both the pressure and stirring was maintained at -10 °C for the duration of the polymerization, where upon it was quenched with the addition of 1.0 mL of methanol and the crude product precipitated into 600 mL of acidic methanol. The polymer was then collected by filtration and dried under vacuum. The isolated polyolefins were then characterized by DSC, GPC, ¹H and ¹³C NMR.

General procedure for the polymerization of 1-hexene.

To a solution of the pre-initiator (0.020 mmol) in 0.5 mL of PhCl at -10 °C, was added a solution of [PhNMe₂H][B(C₆F₅)₄] (0.026 mmol) in 0.5 ml of PhCl and then the resulting mixture was diluted with 19 mL of PhCl and cooled to -10 °C in a Schlenk flask, whereupon 200 eq of 1-hexene was added all at once. The reaction mixture was stirred at -10 °C for the duration of the polymerization time where upon it was quenched with 1.0 mL of methanol and precipitated into 600 mL acidic methanol to isolate the polymer. The polymer was collected and dried under

vacuum. The resulting polymers were characterized by DSC, GPC, ^1H and ^{13}C NMR. For kinetic analysis of 1-hexene polymerization, the general procedure was followed, however, aliquots were taken at timed intervals and quenched with silica gel. After removal of the volatiles, the crude polymer product for each aliquot was analyzed by GPC.

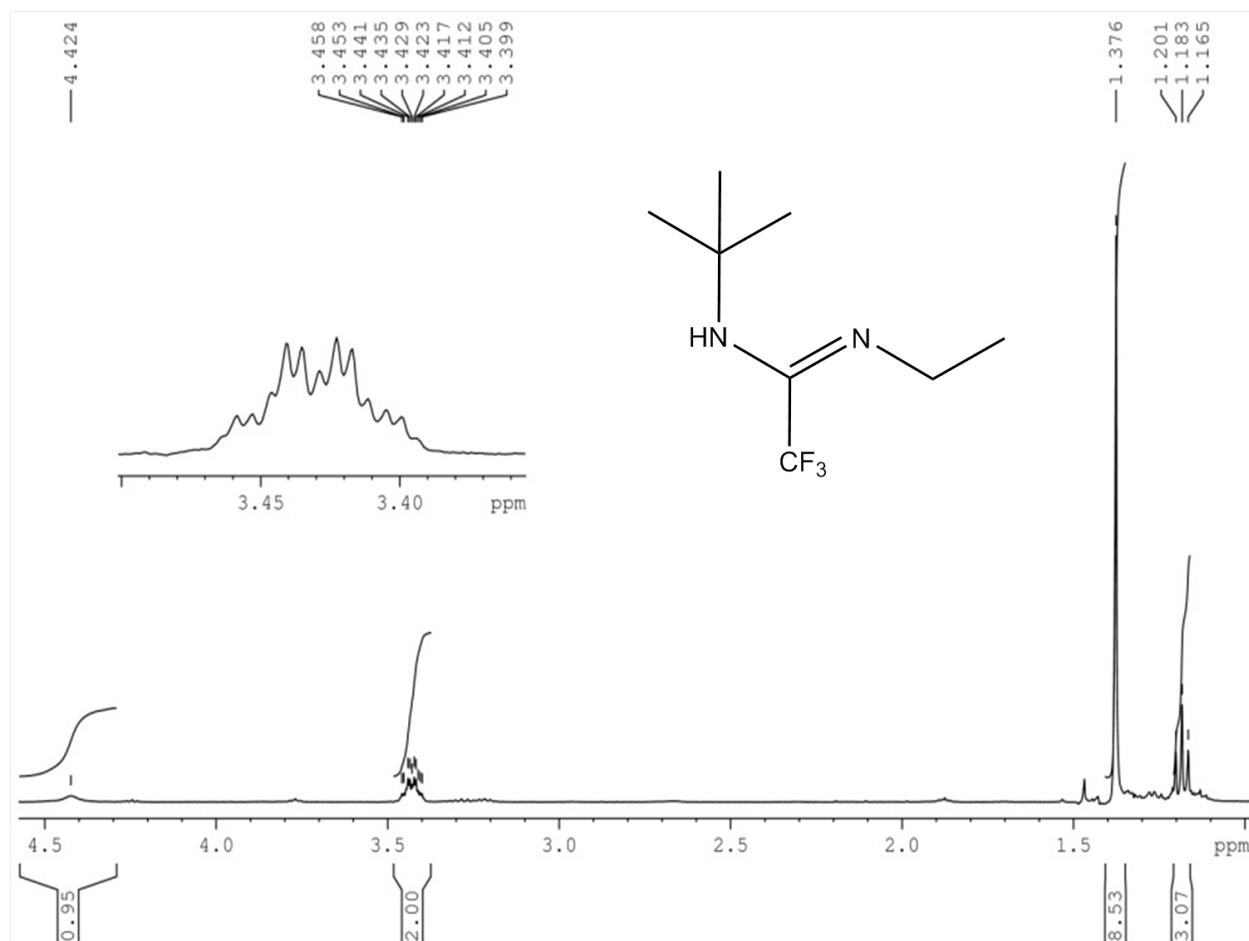


Figure S1. ^1H NMR (400 MHz, CDCl_3 , 25 $^\circ\text{C}$) spectrum of **5**; Inset shows the quartet of quartets evidenced by the CH_2 of the ethyl group.

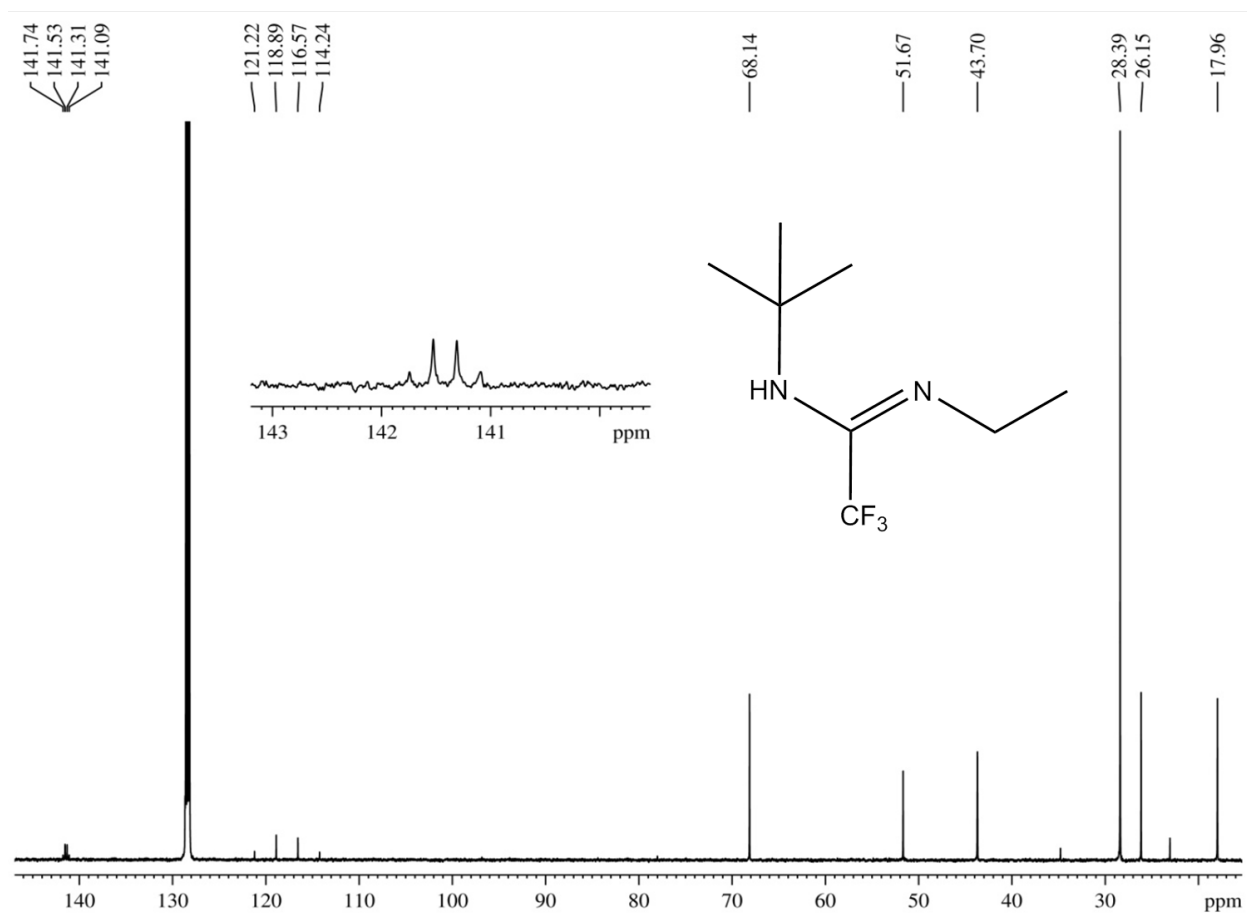


Figure S2. $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3 , 25 °C) spectrum of **5**; inset shows the quartet of the NC(CF₃)N which experiences $^2J_{\text{C-F}}$ coupling. The peaks at 68.14 and 26.15 ppm are due to residual THF.

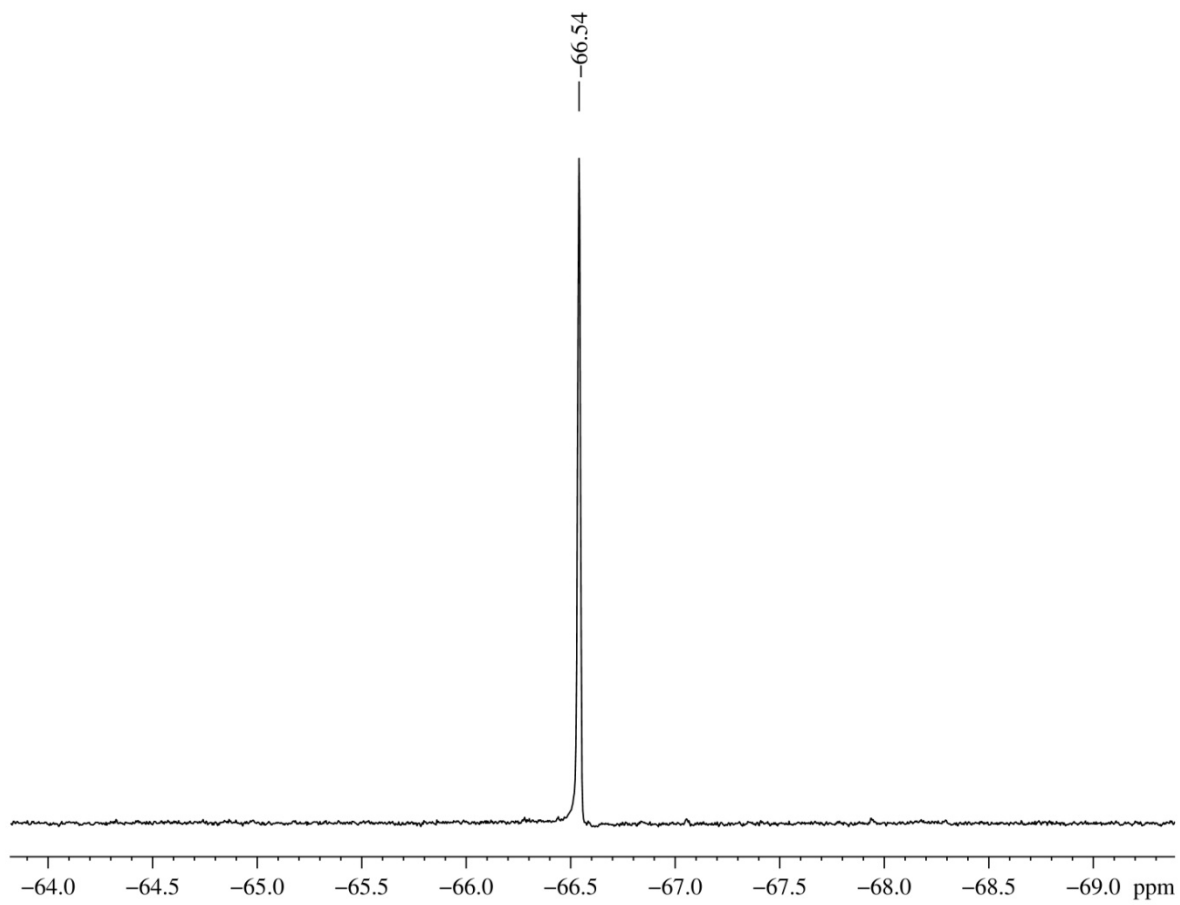


Figure S3. $^{19}\text{F}\{^1\text{H}\}$ NMR (376 MHz, CDCl_3 , 25 °C) spectrum of **5**.

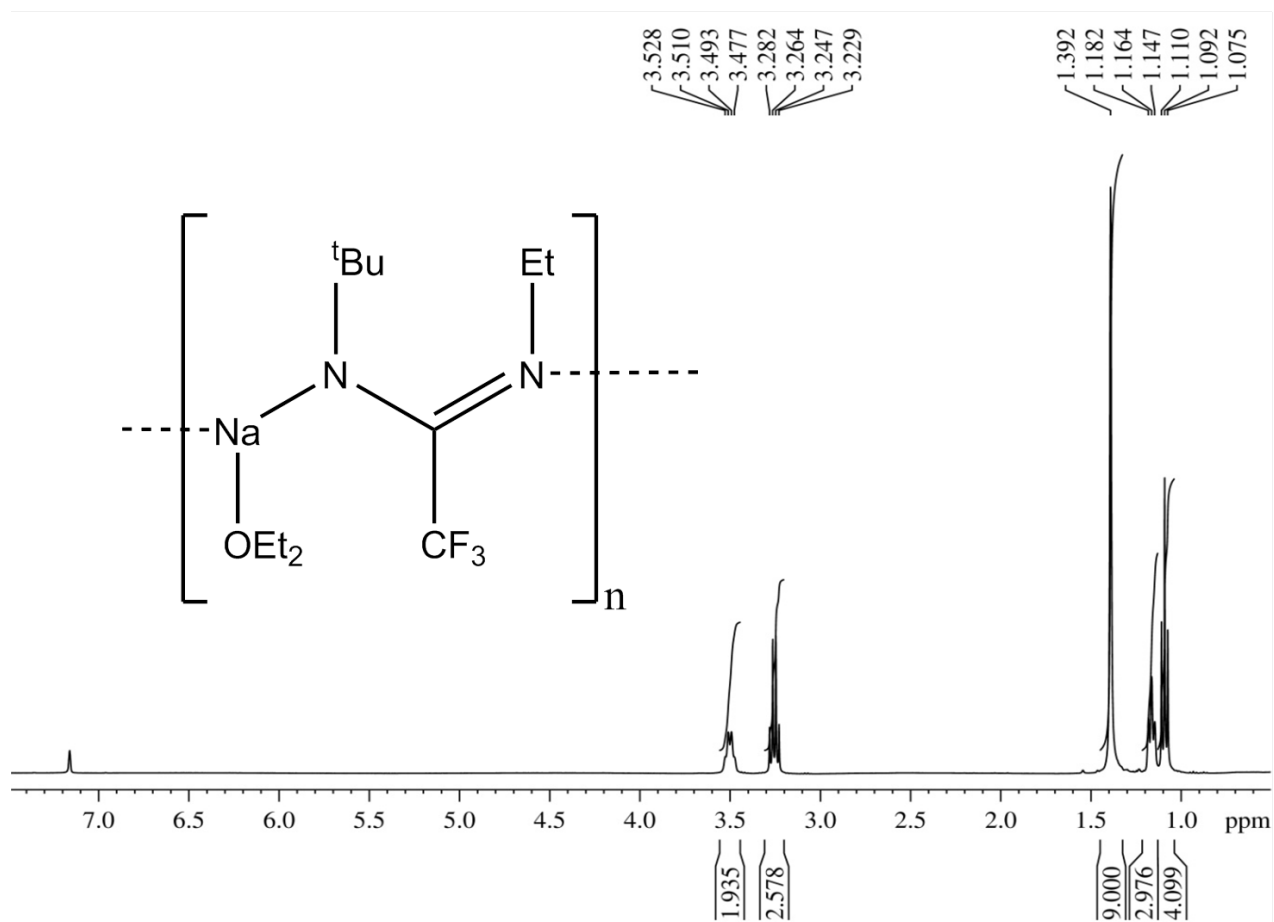


Figure S4. ¹H NMR (400 MHz, C₆D₆, 25 °C) spectrum of **6**.

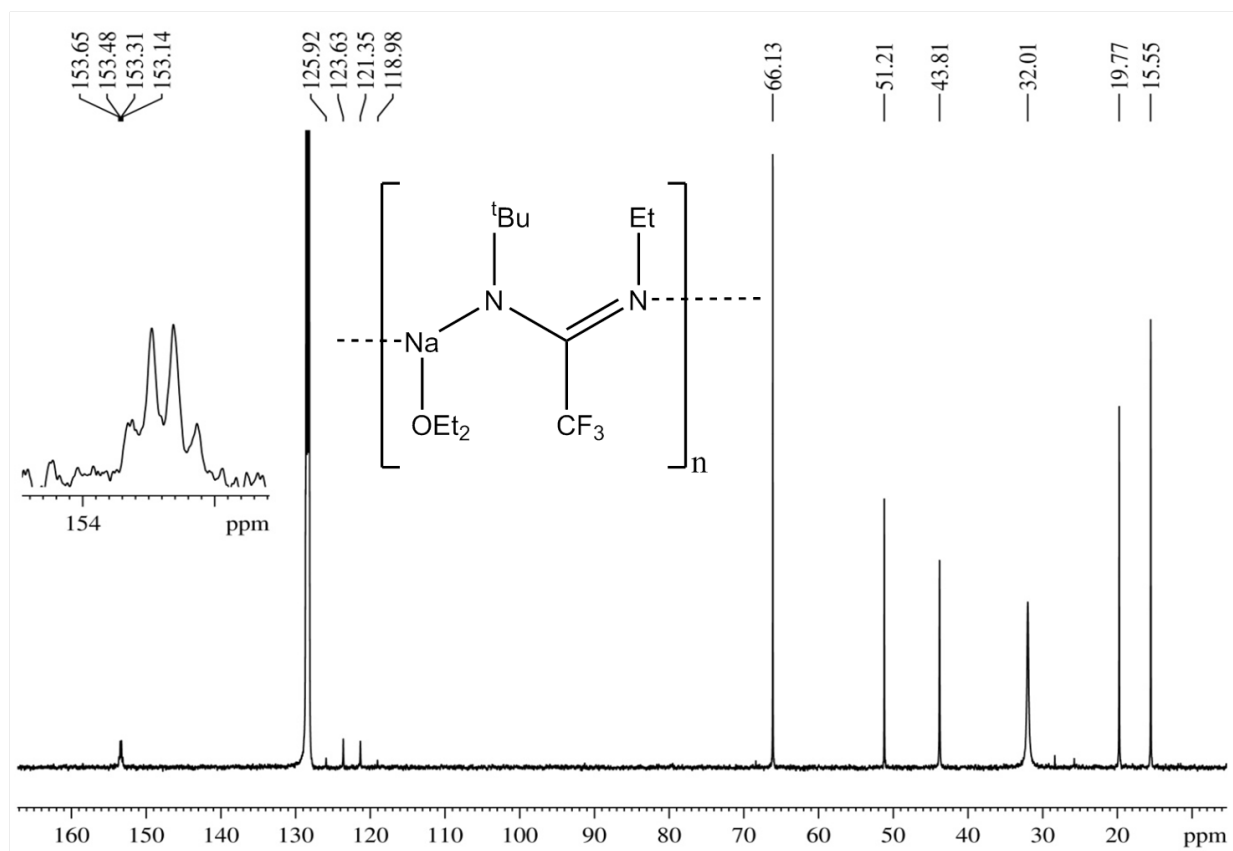


Figure S5. $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, C_6D_6 , 25 °C) spectrum of **6**; inset shows the quartet of the $\text{NC}(\text{CF}_3)\text{N}$ which experiences $^2J_{\text{C-F}}$ coupling.

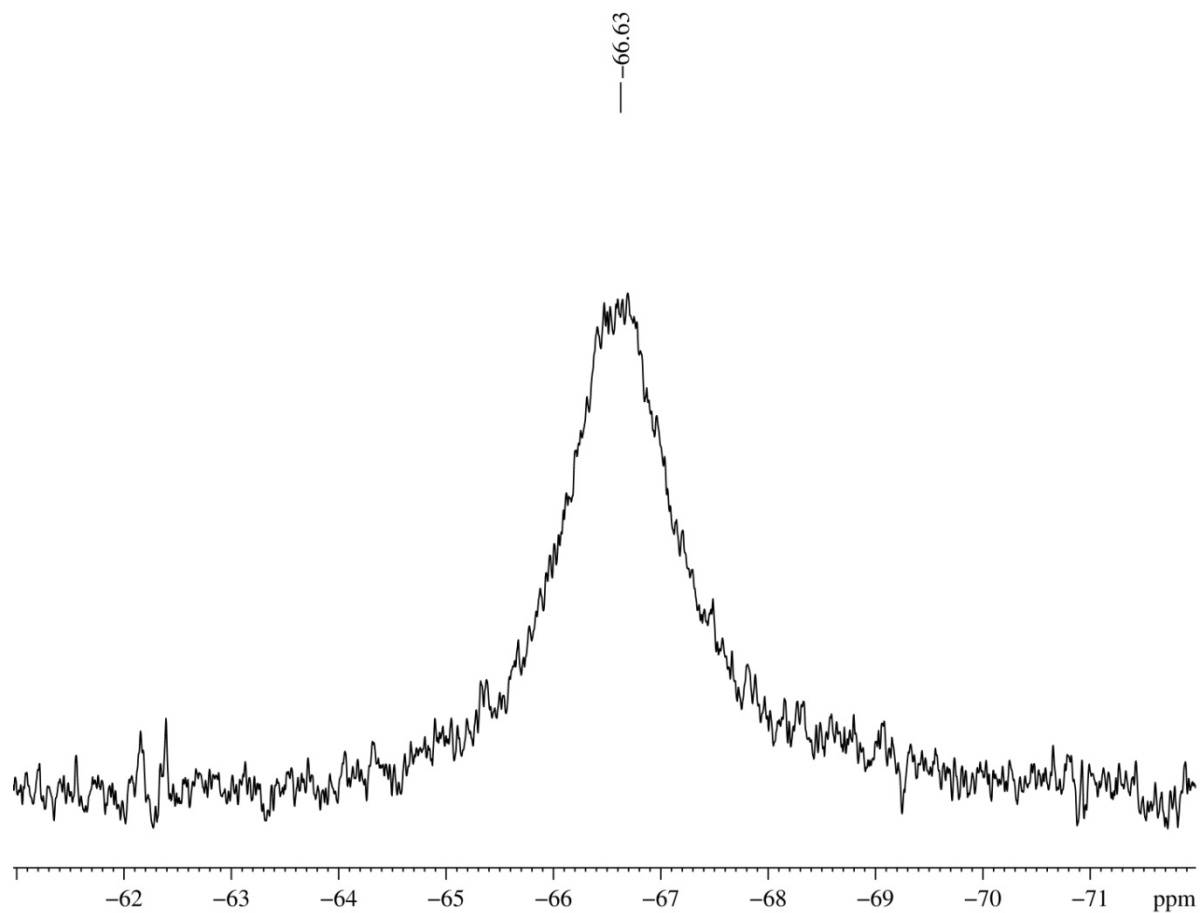


Figure S6. $^{19}\text{F}\{^1\text{H}\}$ NMR (376 MHz, C_6D_6 , 25 °C) spectrum of **6**.

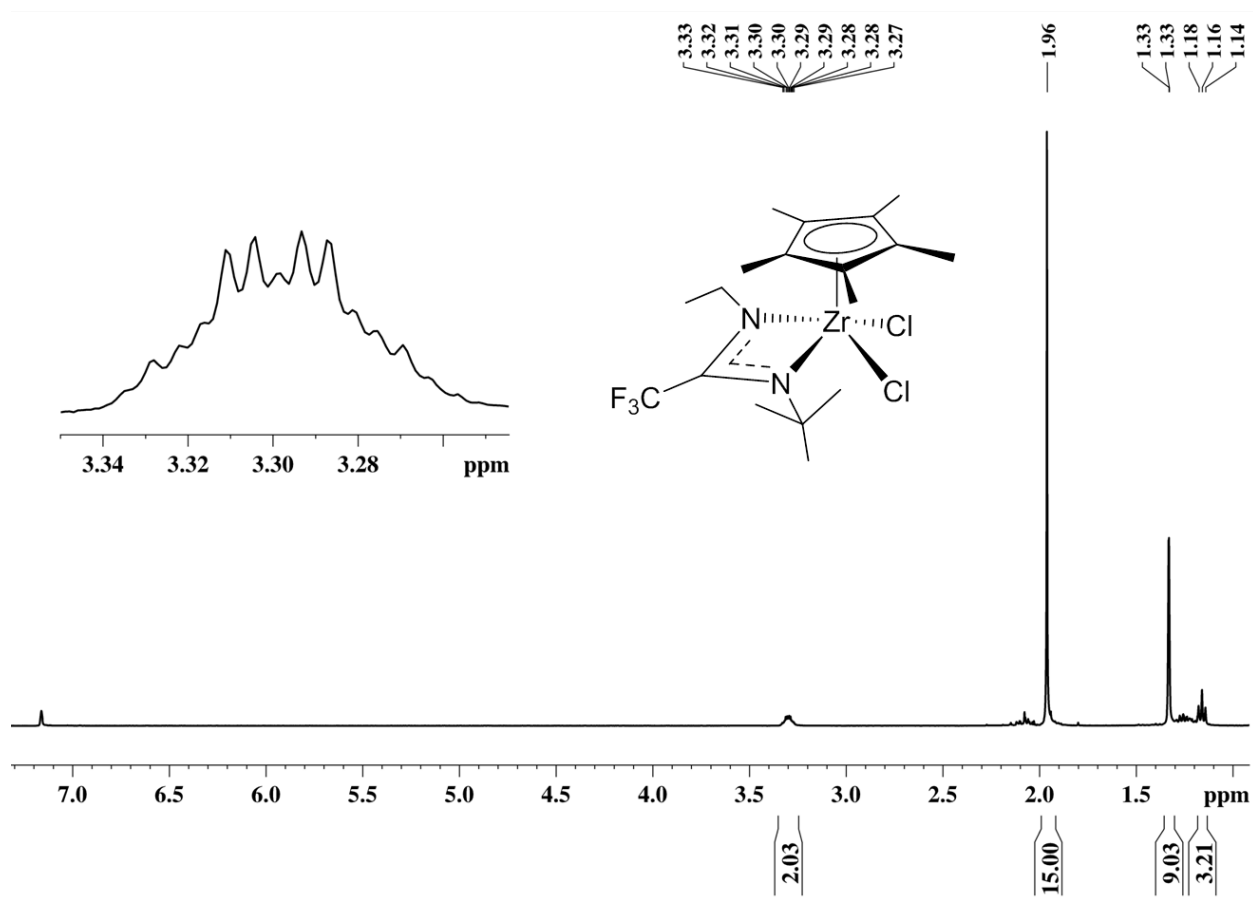


Figure S7. ^1H NMR (400 MHz, C_6D_6 , 25 $^\circ\text{C}$) spectrum of **7**, *inset* shows the quartet of quartets for the CH_2 of the ethyl group.

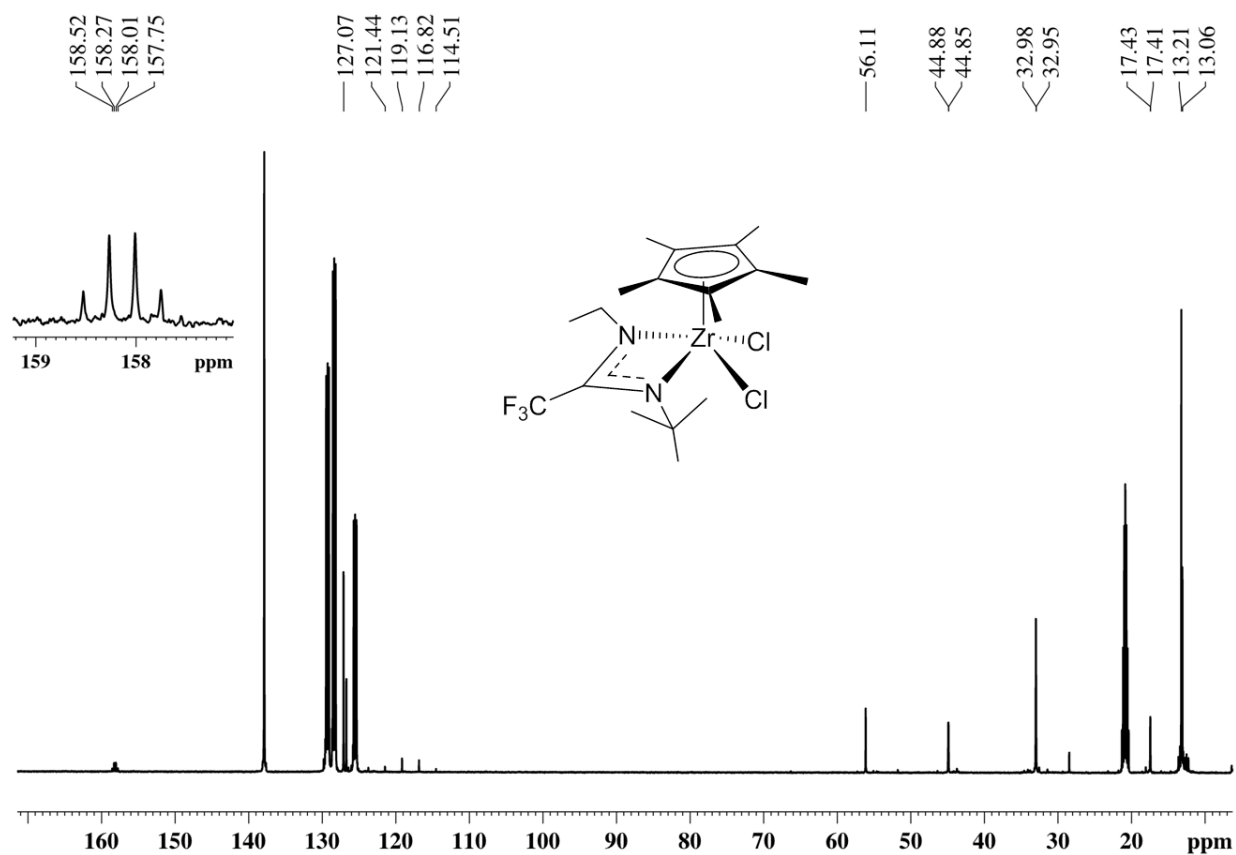


Figure S8. $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, tol-D_8 , 25 °C) spectrum of **7**; Inset highlights the $\text{NC}(\text{CF}_3)\text{N}$ resonance.

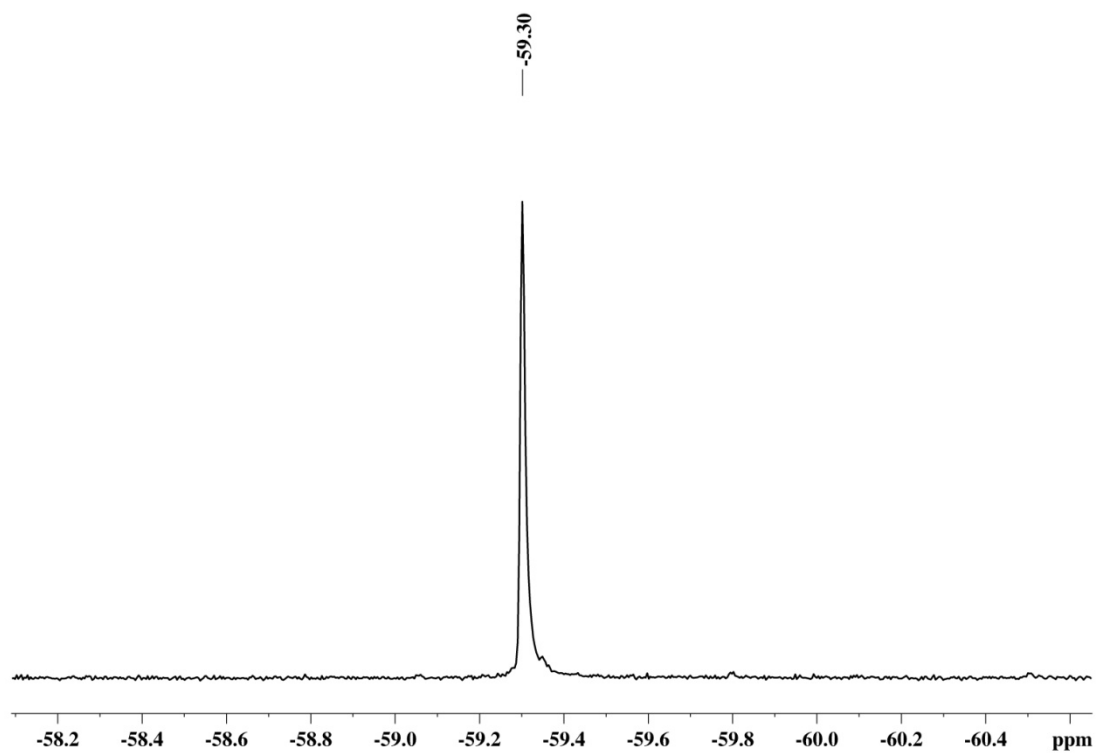


Figure S9. $^{19}\text{F}\{^1\text{H}\}$ NMR (376 MHz, CDCl_3 , 25 °C) spectrum of **7**.

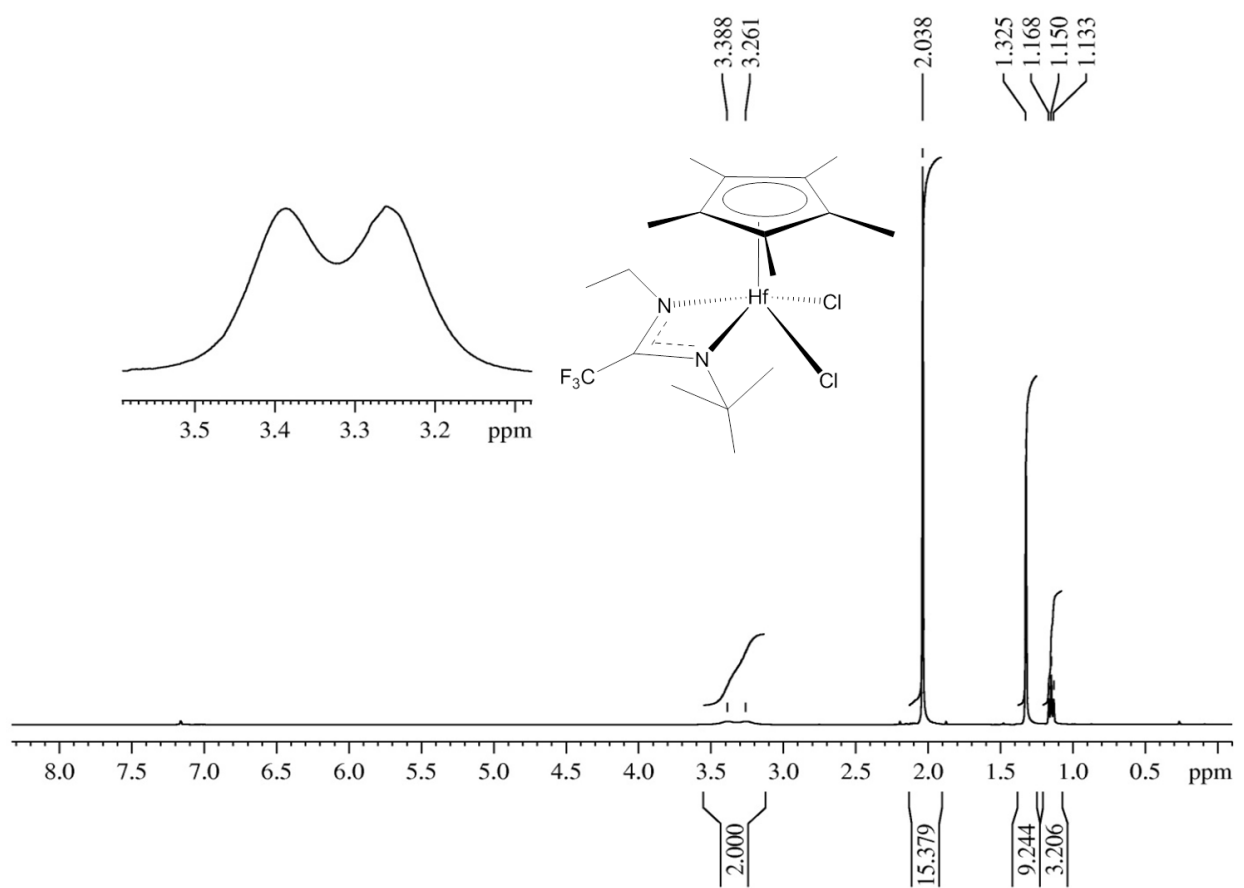


Figure S10. ^1H NMR (400 MHz, C_6D_6 , 25 $^\circ\text{C}$) spectrum of **8**; *inset* shows the CH_2 of the ethyl group.

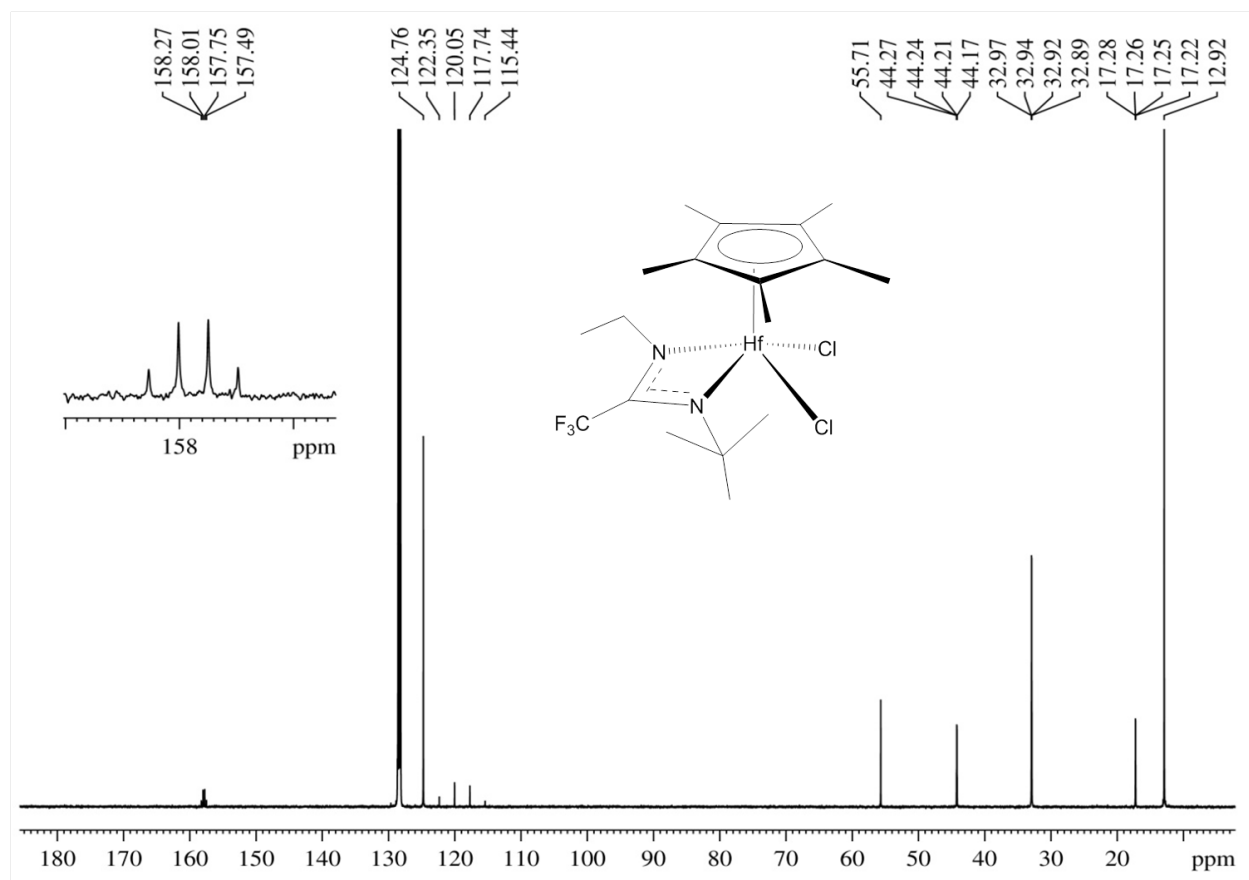


Figure S11. $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, C_6D_6 , 25 °C) spectrum of **8**; Inset highlights the $\text{NC}(\text{CF}_3)\text{N}$ resonance.

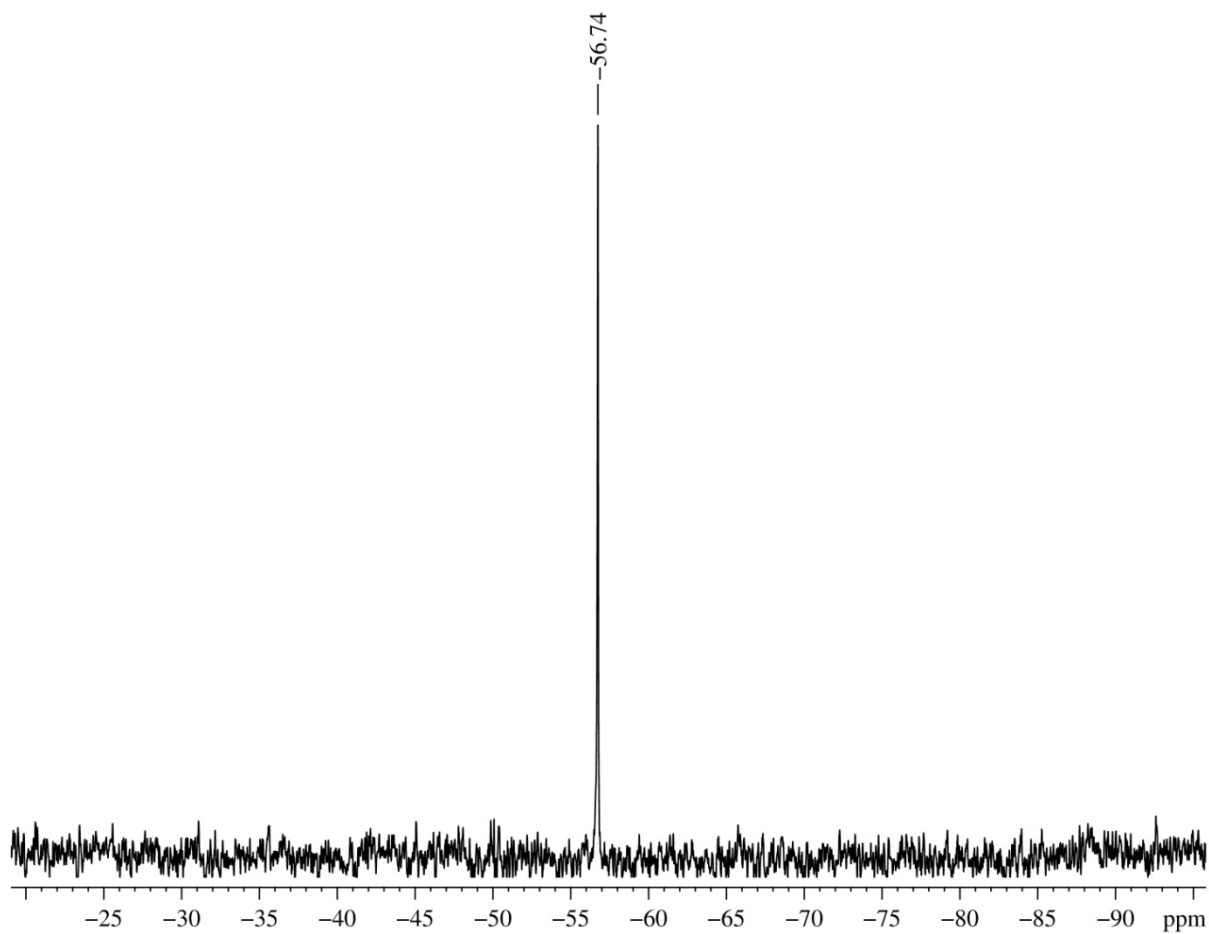


Figure S12. $^{19}\text{F}\{^1\text{H}\}$ NMR (376 MHz, C_6D_6 , 25 °C) spectrum of **8**.

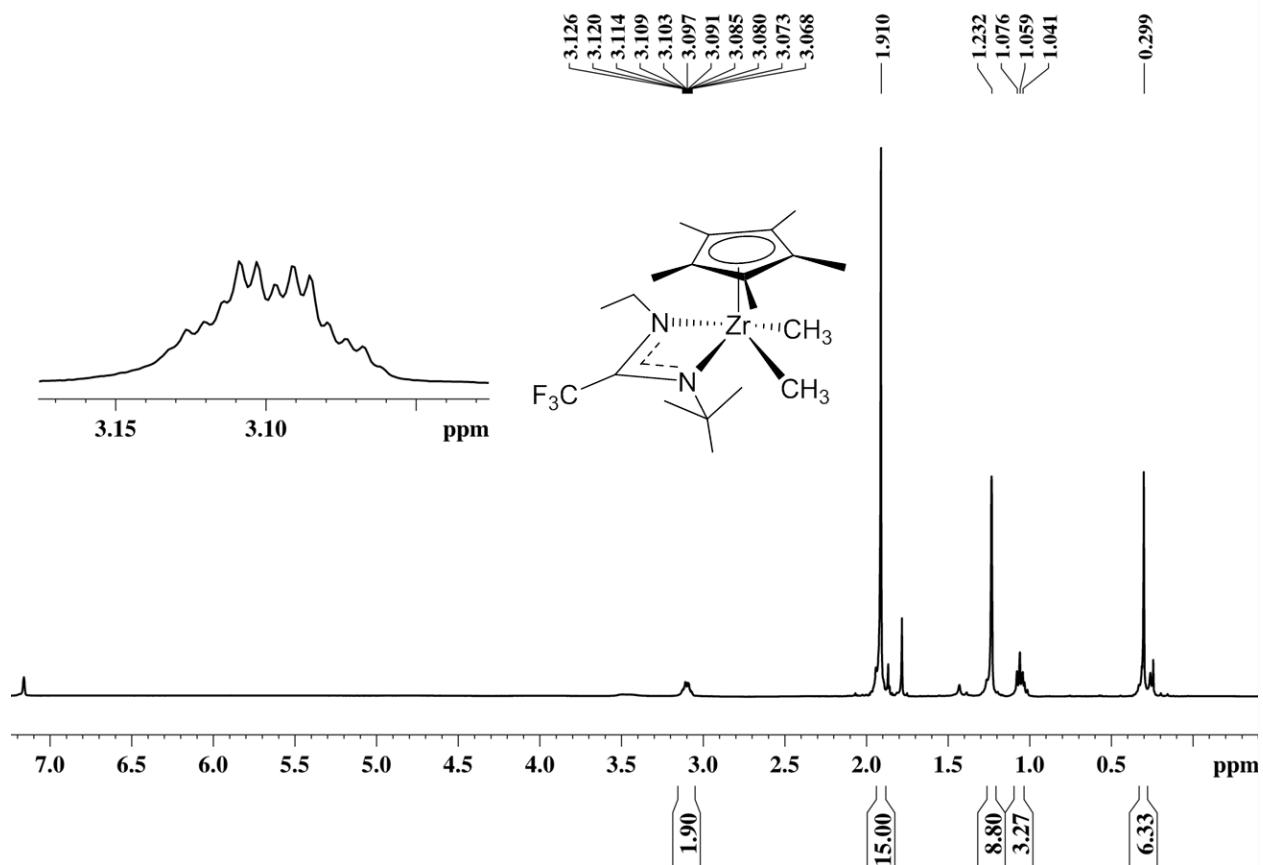


Figure S13. ¹H NMR (400 MHz, C₆D₆, 25 °C) spectrum of **3**, *inset* shows the quartet of quartets for the CH₂ of the ethyl group.

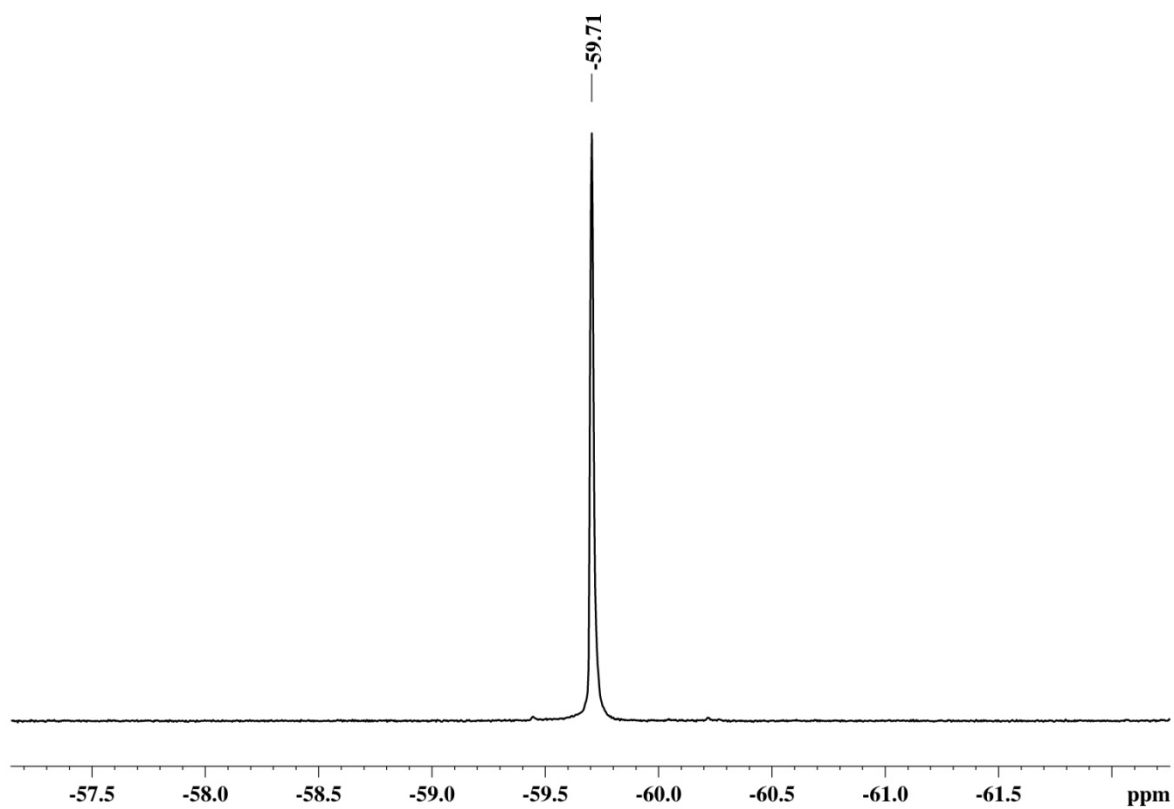


Figure S14. $^{19}\text{F}\{^1\text{H}\}$ NMR (376 MHz, CDCl_3 , 25 °C) spectrum of **3**.

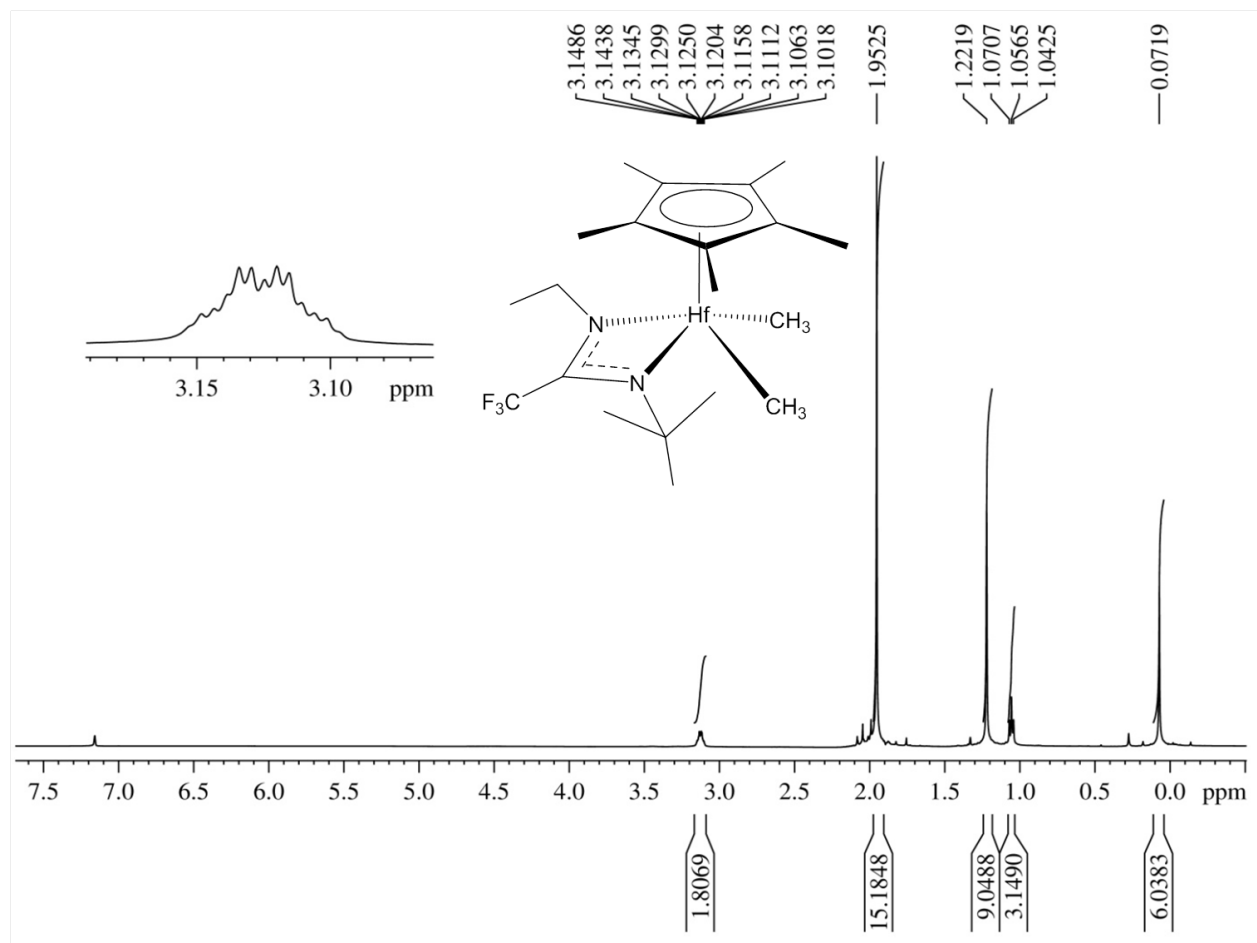


Figure S15. ¹H NMR (400 MHz, C₆D₆, 25 °C) of **4**. Inset shows the quartet of quartets for the CH₂ of the ethyl group.

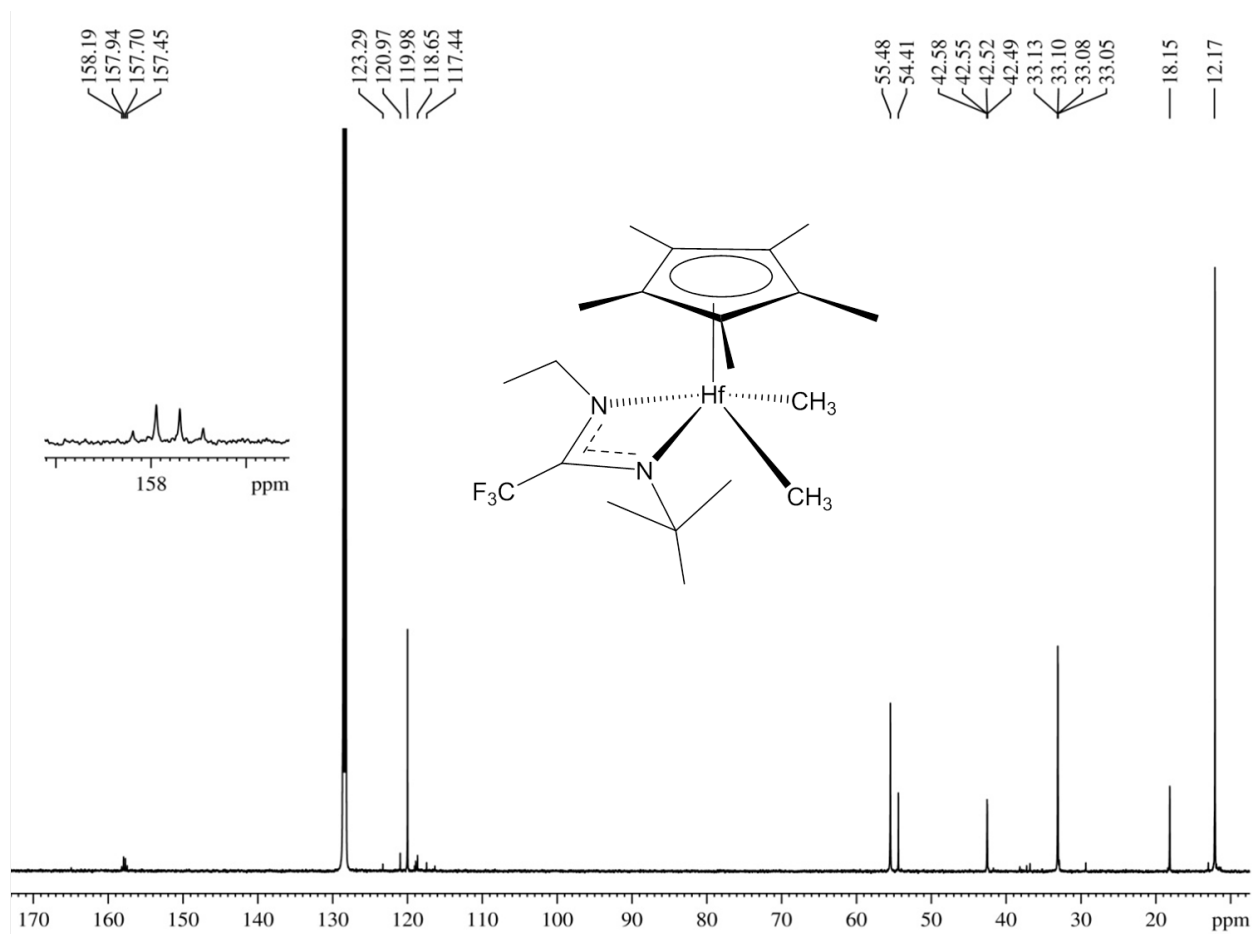


Figure S16. $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, C_6D_6 , 25 °C) spectrum of **4**; Inset highlights the $\text{NC}(\text{CF}_3)\text{N}$ resonance.

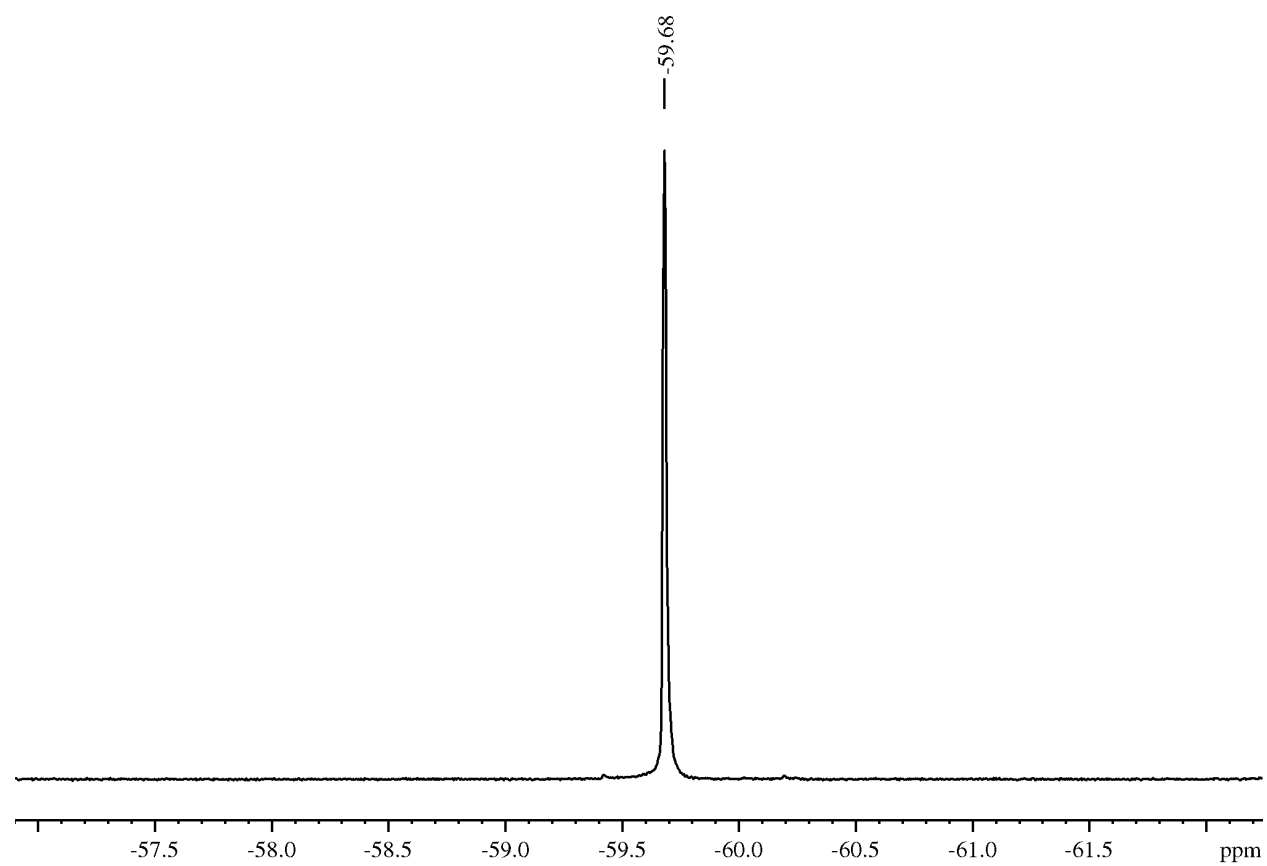


Figure S17. $^{19}\text{F}\{^1\text{H}\}$ NMR (376 MHz, C_6D_6 , 25 °C) spectrum of **4**.

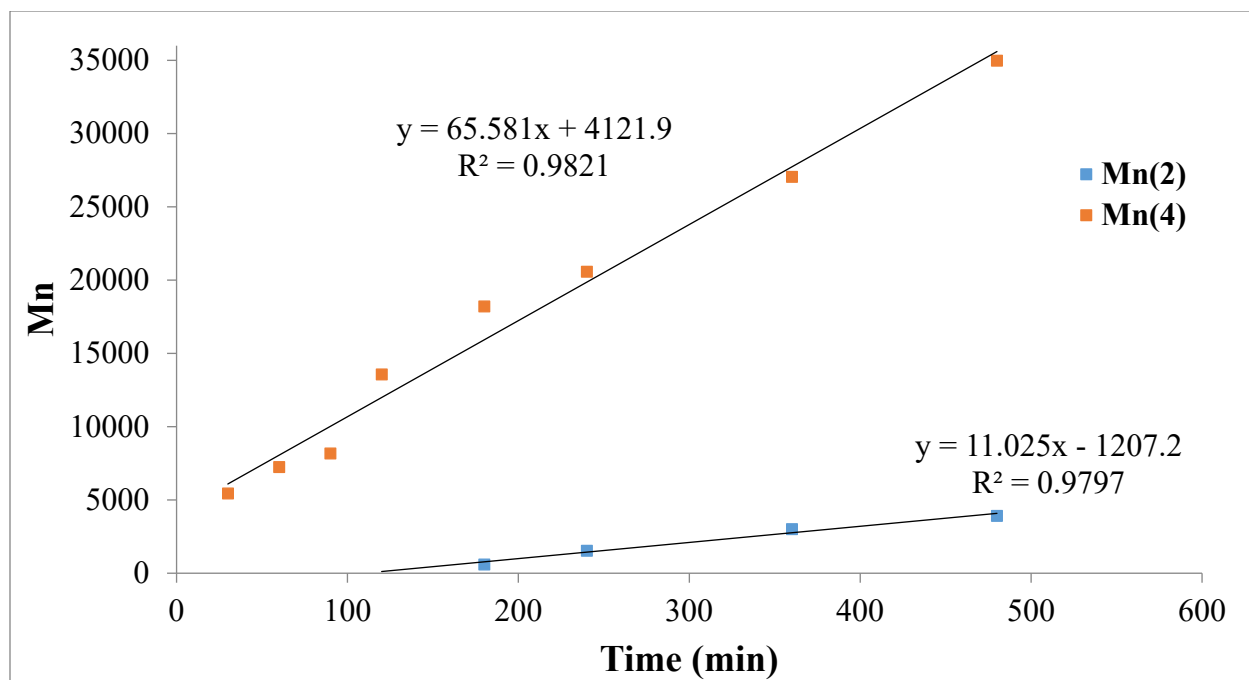


Figure S19. Linear dependence of M_n vs time for 1-hexene polymerization using CPAM^{CH₃} **2** and CPAM^{CF₃} **4**. The initial 4 time points for **2** are not shown as the mass of the polymeric product was too low to be accurately measured for these time intervals.

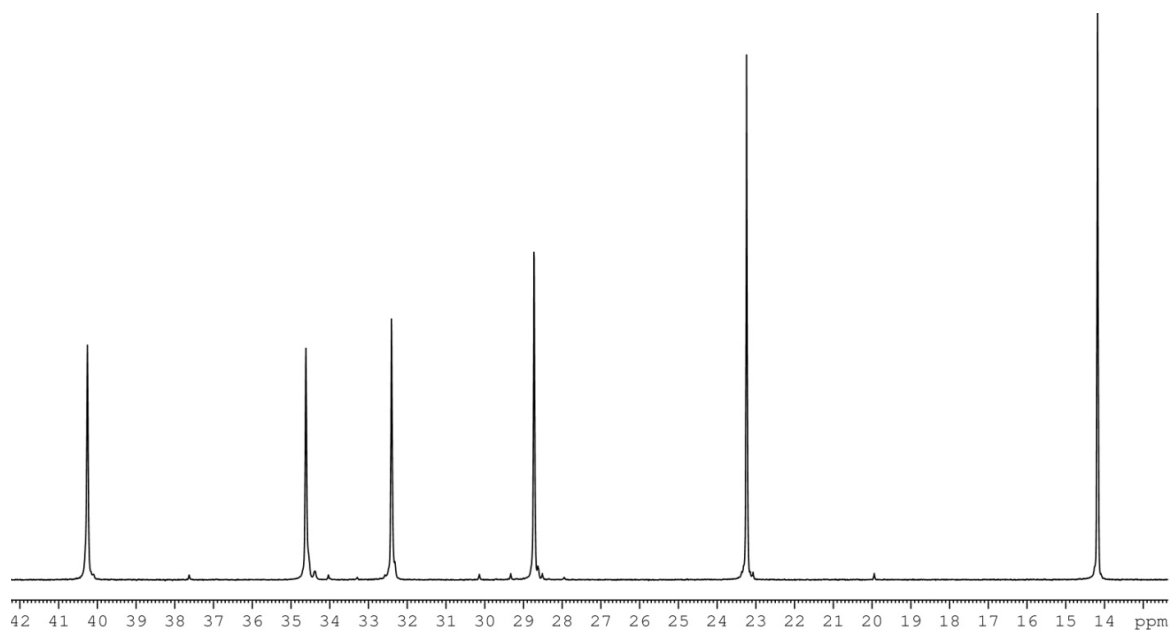


Figure S20. $^{13}\text{C}\{^1\text{H}\}$ NMR of isotactic poly(1-hexene) obtained using CPAM^{CF₃} **4**.

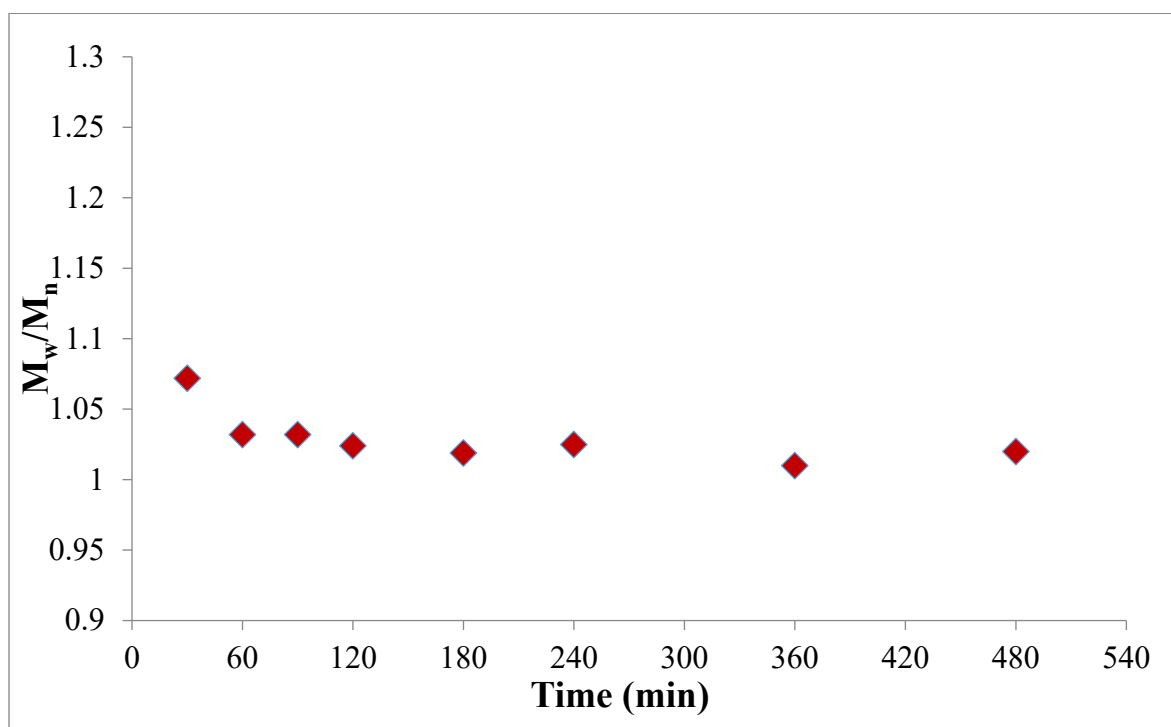


Figure S21. Time dependence of polydispersity (M_w/M_n) for on poly-1-hexene produced by 4.

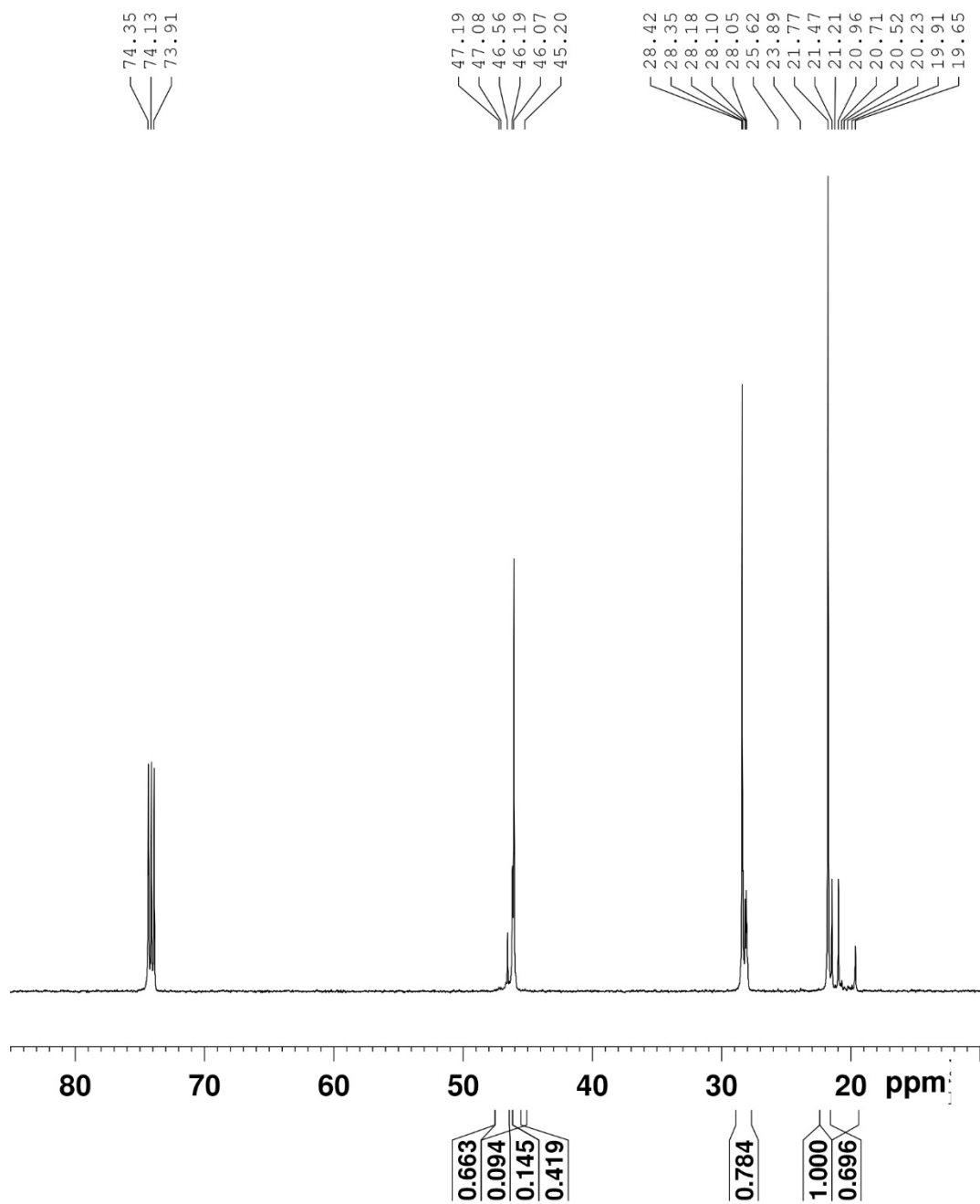


Figure S22. $^{13}\text{C}\{^1\text{H}\}$ NMR of isotactic polypropylene produced using **4**.

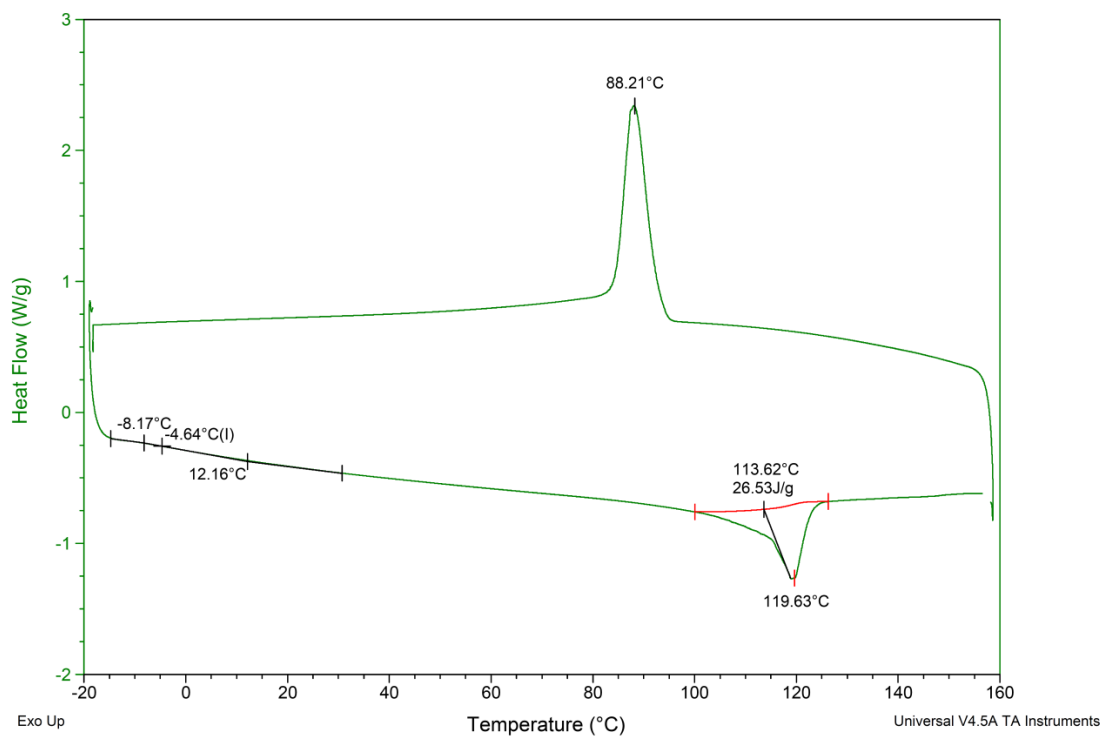


Figure S23. DSC traces (2nd heating and cooling cycle, 10 °C/min) of PP sample made from precatalyst **4**.

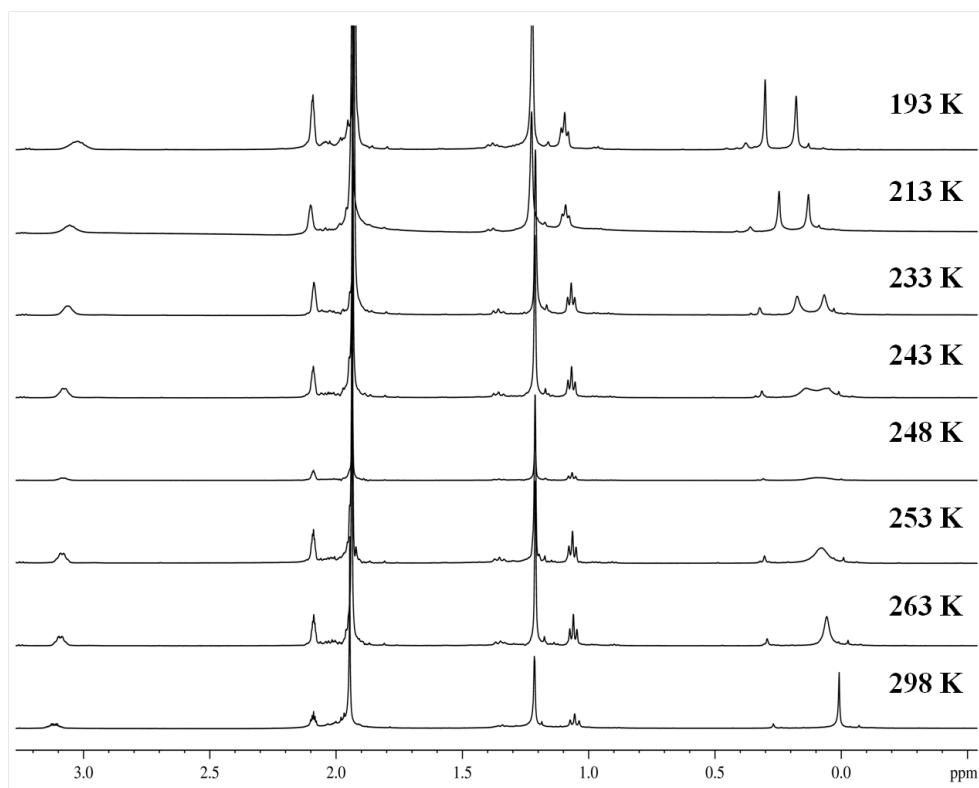


Figure S24. Variable Temperature ^1H NMR of **4**.