

Reactions of A Cerium(III) Amide with Heteroallenes: Insertion, Silyl-migration and De-insertion

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Experimental Procedures

General Methods. Unless otherwise indicated all reactions and manipulations were performed under an inert atmosphere (N_2) using standard Schlenk techniques or in a Vacuum Atmospheres, Inc. Nexus II drybox equipped with a molecular sieves 13X / Q5 Cu-0226S catalyst purifier system. Glassware was oven-dried overnight at 150 °C prior to use. 1H , ^{19}F , and ^{13}C NMR spectra were obtained at 300K on a Bruker DMX-300 Fourier transform NMR spectrometer operating at 1H frequency of 300 MHz. 1H and ^{19}F variable temperature NMR measurements were carried out at 300MHz and 282 MHz. Chemical shifts were recorded in units of parts per million referenced against residual proteo solvent peaks (1H) deuteuro solvent peaks (^{13}C) or fluorobenzene (^{19}F , -113.15 ppm). Elemental analyses were performed at the University of California, Berkeley, Microanalytical Facility using a Perkin-Elmer Series II 2400 CHNS analyzer. The infrared spectra were obtained from 400-4000 cm^{-1} using a Perkin Elmer 1600 series infrared spectrometer. High resolution mass spectrometry (HRMS) data were collected on a Waters LC-TOF mass spectrometer (model LCT-XE Premier) using electrospray ionization (ESI) in positive or negative mode, depending on the analyte.

Materials. Toluene, fluorobenzene, hexanes, and *n*-pentane were purchased from Fisher Scientific. The solvents were sparged for 20 min with dry N_2 and dried using a commercial two-column solvent purification system comprising columns packed with Q5 reactant and neutral alumina respectively (for hexanes and *n*-pentane), or two columns of neutral alumina (for toluene and fluorobenzene). Deuterated solvents were purchased from Cambridge Isotope Laboratories, Inc. and stored over molecular sieves overnight prior to use. $Ce[N(SiMe_3)Ph^F]_3$ (-Ph^F = 2, 3, 4, 5, 6-pentafluorophenyl) was prepared according to reported procedure.¹ Carbon disulfide, *N*, *N*'-

diisopropylcarbodiimide and 1-adamantyl isocyanate were purchased from ACROS and used as received. 1-adamantyl isothiocyanate was purchased from TCI and used as received.

X-Ray Crystallography. X-ray reflection intensity data were collected on a Bruker APEXII CCD area detector employing graphite-monochromated Mo-K α radiation ($\lambda = 0.71073$ Å) at a temperature of 143(1) K. In all cases, rotation frames were integrated using SAINT,² producing a listing of unaveraged F^2 and $\sigma(F^2)$ values which were then passed to the SHELXTL³ program package for further processing and structure solution on a Dell Pentium 4 computer. The intensity data were corrected for Lorentz and polarization effects and for absorption using TWINABS⁴ or SADABS.⁵ The structures were solved by direct methods (SHELXS-97).⁶ Refinement was by full-matrix least squares based on F^2 using SHELXL-97.⁶ All reflections were used during refinements. The weighting scheme used was $w = 1/[\sigma^2(F_o^2) + (0.0907P)^2 + 0.3133P]$ where $P = (F_o^2 + 2F_c^2)/3$. Non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined using a riding model.

Synthetic Details and Characterization

Synthesis of $\text{Ce}[\text{S}_2\text{CN}(\text{SiMe}_3)\text{Ph}^{\text{F}}]_3(\text{O}=\text{PPh}_3)_2$ (2**).** To a vial containing $\text{Ce}[\text{N}(\text{SiMe}_3)\text{Ph}^{\text{F}}]_3$ (0.090 g, 0.100 mmol, 1.00 equiv) suspended in 2 mL toluene, a 2 mL toluene solution containing CS_2 (0.030 g, 0.400 mmol, 4.00 equiv) was added, leading to an orange solution. After stirring for 16 h, a 1 mL toluene solution containing $\text{O}=\text{PPh}_3$ (0.056 g, 0.200 mmol, 2.00 equiv) was added, resulting in a color change to yellow. After stirring for 0.5 h, volatiles were removed under reduced pressure. The resulting off-white solids were collected on a medium porosity fritted filter, washed with 3×3 mL *n*-pentane and dried under reduced vacuum for 1 h. Yield: 0.132 g, 0.078 mmol, 78%. ^1H NMR (C_6D_6 , 300 K): δ 13.85 (s, 12H, $\text{O}=\text{PPh}_3$), 8.21 (s, 12H, $\text{O}=\text{PPh}_3$), 8.03 (t, 6H, $\text{O}=\text{PPh}_3$, $J = 6$ Hz), -1.51 (s, 27H, $-\text{SiMe}_3$). ^{19}F NMR (C_6D_6 , 300 K): δ -147.88 (dd, 6F, *o*-F, $J_1 = 23$ Hz, $J_2 = 6$ Hz), -157.74 (t, 3F, *p*-F, $J = 23$ Hz), -165.40 (td, 6F, *m*-F, $J_1 = 23$ Hz, $J_2 = 6$ Hz). Elemental analysis found (calculated) for $\text{C}_{66}\text{H}_{57}\text{CeF}_{15}\text{N}_3\text{O}_2\text{P}_2\text{S}_6\text{Si}_3$: C, 47.22 (46.97), H, 3.36 (3.40), N, 2.74 (2.49), S, 11.28 (11.40). Single crystals suitable for an X-ray diffraction study were obtained by storing an *n*-pentane solution at -25 °C.

Synthesis of $\{[{}^i\text{Pr}(\text{SiMe}_3)\text{N}]\text{C}(\text{N}^i\text{Pr})(\text{NPh}^{\text{F}})\}_3\text{Ce}^{\text{III}}$ (3**).** To a vial containing $\text{Ce}[\text{N}(\text{SiMe}_3)\text{Ph}^{\text{F}}]_3$ (0.271 g, 0.300 mmol, 1.00 equiv) suspended in 3 mL toluene, a 2 mL toluene solution containing ${}^i\text{Pr}-\text{N}=\text{C}=\text{N}-{}^i\text{Pr}$ (0.227 g, 1.800 mmol, 6.00 equiv) was added, leading to a yellow solution. After stirring for 16 h, volatiles were removed under reduced pressure. The solid residues were extracted with 5 mL *n*-pentane and filtered through Celite packed in pipette. The clear yellow solution was then concentrated to 1 mL and stored at -25 °C to yield yellow crystals. The yellow products were collected on a medium porosity fritted filter and dried under reduced vacuum for 1 h. Yield: 0.311 g, 0.243 mmol, 81%. ^1H NMR (toluene- d_8 , 300 K): δ 9.10 (s), 8.56 (br), 8.46 (br), 7.86 (s), 7.18 (br), 6.84 (br), 4.30 (s), 3.47 (s), 3.25 (br), 2.68 (s), 2.42(s),

2.28 (s), 1.28 (br), -1.91 (s), -3.79 (s), -4.54 (s), -7.93 (s), -8.46 (s), -9.97 (s). ^{19}F NMR (toluene- d_8 , 300 K): δ -154.65 (br, *o*-F), -155.01 (br, *o*-F), -158.29 (br, *o*-F), -167.30 (t, *m*-F, $J = 21$ Hz), -167.56 (t, *m*-F, $J = 21$ Hz), -167.92 (t, *m*-F, $J = 23$ Hz), -168.11 (t, *p*-F, $J = 23$ Hz), -168.66 (t, *p*-F, $J = 21$ Hz). Elemental analysis found (calculated) for $\text{C}_{48}\text{H}_{72}\text{CeF}_{15}\text{N}_9\text{Si}_3$: C 45.06 (44.88), H, 5.55 (5.65), N 9.8 (9.81). Single crystals suitable for X-ray diffraction study were obtained by storing an *n*-pentane solution at -25 °C.

Reaction of ($t\text{Bu}_2\text{bipy}$)Ce[N(SiMe $_3$)Ph F] $_3$ (1- $t\text{Bu}_2\text{bipy}$) with $^i\text{Pr-N=C=N-}^i\text{Pr}$.

($t\text{Bu}_2\text{bipy}$)Ce[N(SiMe $_3$)Ph F] $_3$ was generated quantitatively *in situ* by adding $t\text{Bu}_2\text{bipy}$ (0.027 g, 0.100 mmol, 1.00 equiv) into a toluene slurry containing Ce[N(SiMe $_3$)Ph F] $_3$ (0.090 g, 0.100 mmol, 1.00 equiv). After stirring for 5 min, $^i\text{Pr-N=C=N-}^i\text{Pr}$ (0.076 g, 0.600 mmol, 6.00 equiv) were added to the orange solution and let stirred overnight (16 h). The volatiles were removed for a reaction aliquot and ^1H and ^{19}F NMR was taken in C_6D_6 indicating no reaction between the above two compounds (Figure S9–10).

Hydrolysis of $\{[{}^i\text{Pr}(\text{SiMe}_3)\text{N}]\text{C}(\text{N}^i\text{Pr})(\text{NPh}^F)\}_3\text{Ce}^{\text{III}}$ (3) with $\text{py}\cdot\text{HCl}$. To a 2 mL THF slurry containing pyridine hydrochloride (0.069 g, 0.600 mmol, 6.00 equiv), a yellow THF solution containing $\{[{}^i\text{Pr}(\text{SiMe}_3)\text{N}]\text{C}(\text{N}^i\text{Pr})(\text{NPh}^F)\}_3\text{Ce}^{\text{III}}$ (0.128g, 0.100 mmol, 1.00 equiv) was added. The slurry was stirred overnight (16 h), leading to a colorless solution. After removing the volatiles under reduced pressure, the mixture was extracted with 5 mL *n*-pentane. The *n*-pentane solution was filtered through Celite packed in a pipet filter and concentrated to 1 mL. Storage of resulting *n*-pentane solution at -25 °C led to the precipitation of white solids. The products were collected on a medium porosity fritted filter and dried under reduced vacuum for 1 h. Yield of $(\text{NH}^i\text{Pr})_2\text{C}(=\text{NPh}^F)$: 0.083 g, 0.269 mmol, 90%. ^1H NMR (300Hz, C_6D_6 , 300 K): δ 3.50 (m, 2H, $-\underline{\text{C}}\text{H}(\text{CH}_3)_2$), 3.22(s, 2H, NH), 0.83(d, 12H, $J = 6.0$ Hz, $-\text{C}\underline{\text{H}}(\text{CH}_3)_2$). ^{19}F NMR (282 Hz, C_6D_6 ,

300 K): δ -153.46 (dd, *o*-F, $J_1 = 20$ Hz, $J_2 = 5.6$ Hz), -165.57 (td, *m*-F, $J_1 = 20$ Hz, $J_2 = 5.6$ Hz), -164.61 (tt, *p*-F, $J_1 = 23$ Hz, $J_2 = 5.6$ Hz). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 Hz, C_6D_6 , 300 K): δ 43.88 (s), 23.23 (s). These characterization data matches with previous reports for $(\text{NH}^i\text{Pr})_2\text{C}(=\text{NPh}^F)$.⁷

Reaction of 1 with CO_2 . In a 100 mL Schlenk tube, a 3 mL THF solution containing $\text{Ce}[\text{N}(\text{SiMe}_3)\text{Ph}^F]_3$ (0.027 g, 0.030 mmol, 1.00 equiv) was added in the box, followed by internal standard 1-fluorobenzene (8.50 μL , 0.030 mmol, 3.00 equiv) through micro-pipette. The Schlenk tube was attached to Schlenk line. Upon frozen of solvent with liquid N_2 , the headspace was evacuated and refilled with CO_2 using Schlenk techniques. The reaction was let thaw and stir at room temperature overnight. The product was identified by GC-MS as $\text{Ph}^F-\text{N}=\text{C}=\text{O}$. ^{19}F NMR (282 Hz, THF-*h*₈, 300 K): δ -144.49 (d, *o*-F, $J = 20$ Hz), -159.55 (t, *p*-F, $J = 21$ Hz), -164.83 (t, *m*-F, $J = 20$ Hz). Yield was estimated by NMR integration compared to the internal standard, 70 %. IR (THF solution): 2337 cm^{-1} .

Synthesis of Ad-N=C=N-Ph^F (5):

From reaction of Ad-N=C=O with 1. To a vial containing $\text{Ce}[\text{N}(\text{SiMe}_3)\text{Ph}^F]_3$ (0.090 g, 0.100 mmol, 1.00 equiv) suspended in 2 mL toluene, a 2 mL toluene solution containing $\text{O}=\text{C}=\text{N}-\text{Ad}$ (0.053 g, 0.300 mmol, 3.00 equiv) was added, leading to a colorless solution. After stirring for 16 h, volatiles were removed under reduced pressure. The white solid residues were extracted with 5 mL *n*-pentane and filtered through Celite packed in pipette. The clear *n*-pentane solution was then concentrated to 1 mL and stored at -25 °C to yield colorless crystalline solids. The products were collected on a medium porosity fritted filter and dried under reduced vacuum for 1 h. Yield of $\text{Ph}^F-\text{N}=\text{C}=\text{N}-\text{Ad}$: 0.094 g, 0.275 mmol, 92%. ^1H NMR (300Hz, C_6D_6 , 300 K): δ 1.78 (s, 9H), 1.37 (s, 6H). ^{19}F NMR (282 Hz, C_6D_6 , 300 K): δ -150.40 (d, *o*-F, $J = 23$ Hz), -164.01 (t, *p*-F, $J = 23$ Hz), -164.61 (td, *m*-F, $J_1 = 23$ Hz, $J_2 = 6$ Hz). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 Hz, C_6D_6 , 300 K):

δ 58.67 (s), 44.83 (s), 36.15 (s), 30.32(s). IR (thin film): 2909, 2156, 1533, 1507, 1058, 993, 978, 957 cm^{-1} ; m.p. 103-104 $^{\circ}\text{C}$. High resolution mass spectra (ESI^{-}) observed (calculated) for $[\text{M}+\text{OH}]^{-}$: 359.1197 (359.1183).

From reaction of Ad-N=C=S with 1. To a vial containing $\text{Ce}[\text{N}(\text{SiMe}_3)\text{Ph}^{\text{F}}]_3$ (0.090 g, 0.100 mmol, 1.00 equiv) suspended in 2 mL toluene, a 2 mL toluene solution containing $\text{S}=\text{C}=\text{N}-\text{Ad}$ (0.058 g, 0.300 mmol, 3.00 equiv) was added, leading to a yellow solution. After stirring for 16 h, volatiles were removed under reduced pressure. The white solid residues were extracted with 5 mL *n*-pentane and filtered through Celite packed in pipette. The clear *n*-pentane solution was then concentrated to 1 mL and stored at -25 $^{\circ}\text{C}$ to yield colorless crystalline solids. The products were collected on a medium porosity fritted filter and dried under reduced vacuum for 1 h. Yield of $\text{Ph}^{\text{F}}-\text{N}=\text{C}=\text{N}-\text{Ad}$: 0.052 g, 0.152 mmol, 51%.

X-ray Crystal Structures

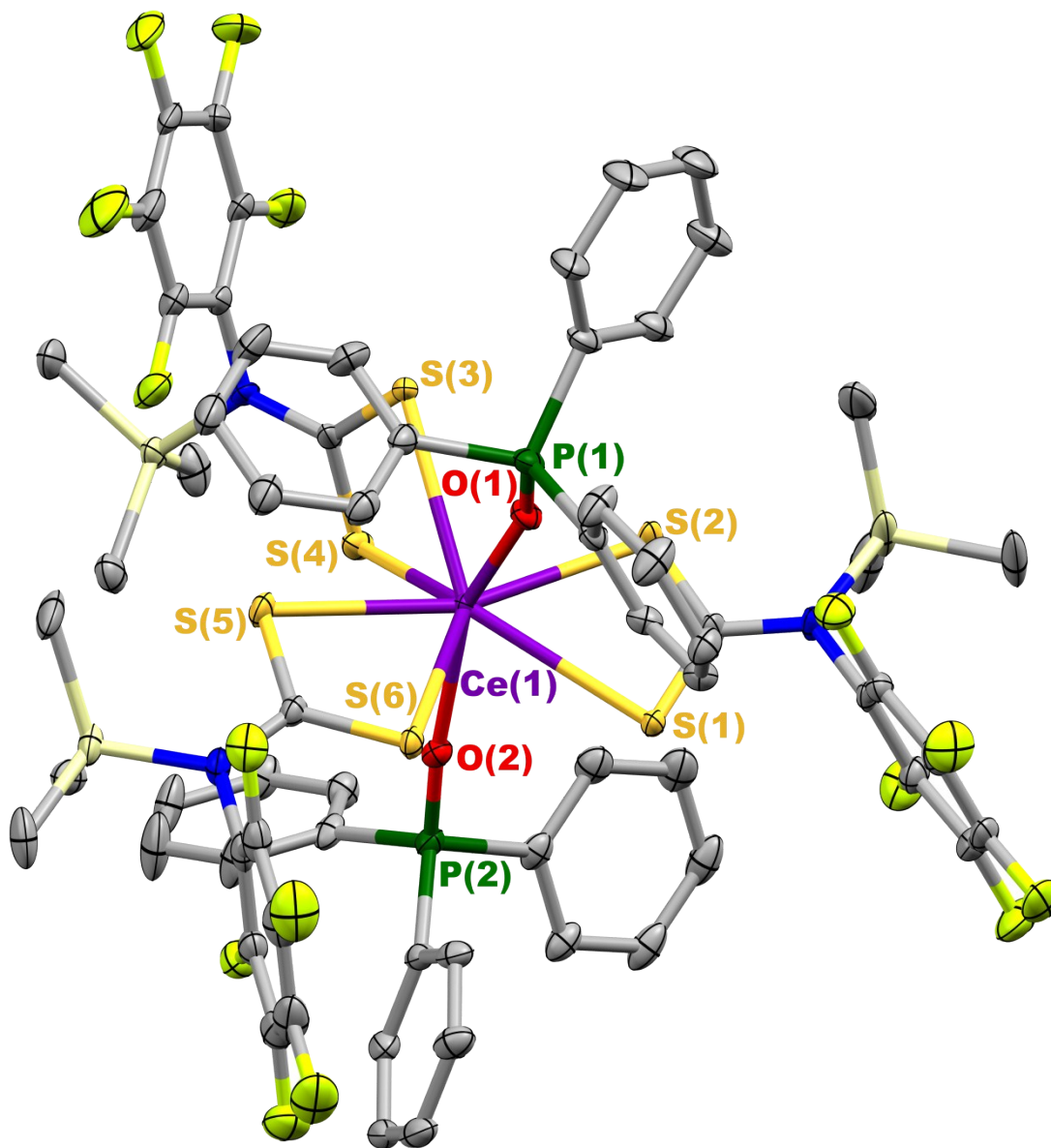


Figure S1. Thermal ellipsoid plot of $\text{Ce}[\text{S}_2\text{CN}(\text{SiMe}_3)\text{Ph}^{\text{F}}]_3(\text{O}=\text{PPh}_3)_2$ (**2**) at the 30% probability level.

Selected bond length (\AA) and angles (deg): $\text{Ce}(1)\text{-O}(1)$ 2.369(3), $\text{Ce}(1)\text{-O}(2)$ 2.370(2), $\text{Ce}(1)\text{-S}(1)$ 3.0340(8), $\text{Ce}(1)\text{-S}(2)$ 2.9506(10), $\text{Ce}(1)\text{-S}(3)$ 3.0083 (8), $\text{Ce}(1)\text{-S}(4)$ 2.9915(9), $\text{Ce}(1)\text{-S}(5)$ 2.9390(9), $\text{Ce}(1)\text{-S}(6)$ 2.9882(9); $\text{S}(1)\text{-Ce}(1)\text{-S}(2)$ 59.65(2), $\text{S}(3)\text{-Ce}(1)\text{-S}(4)$ 59.12(3), $\text{S}(5)\text{-Ce}(1)\text{-S}(6)$ 60.37(2).

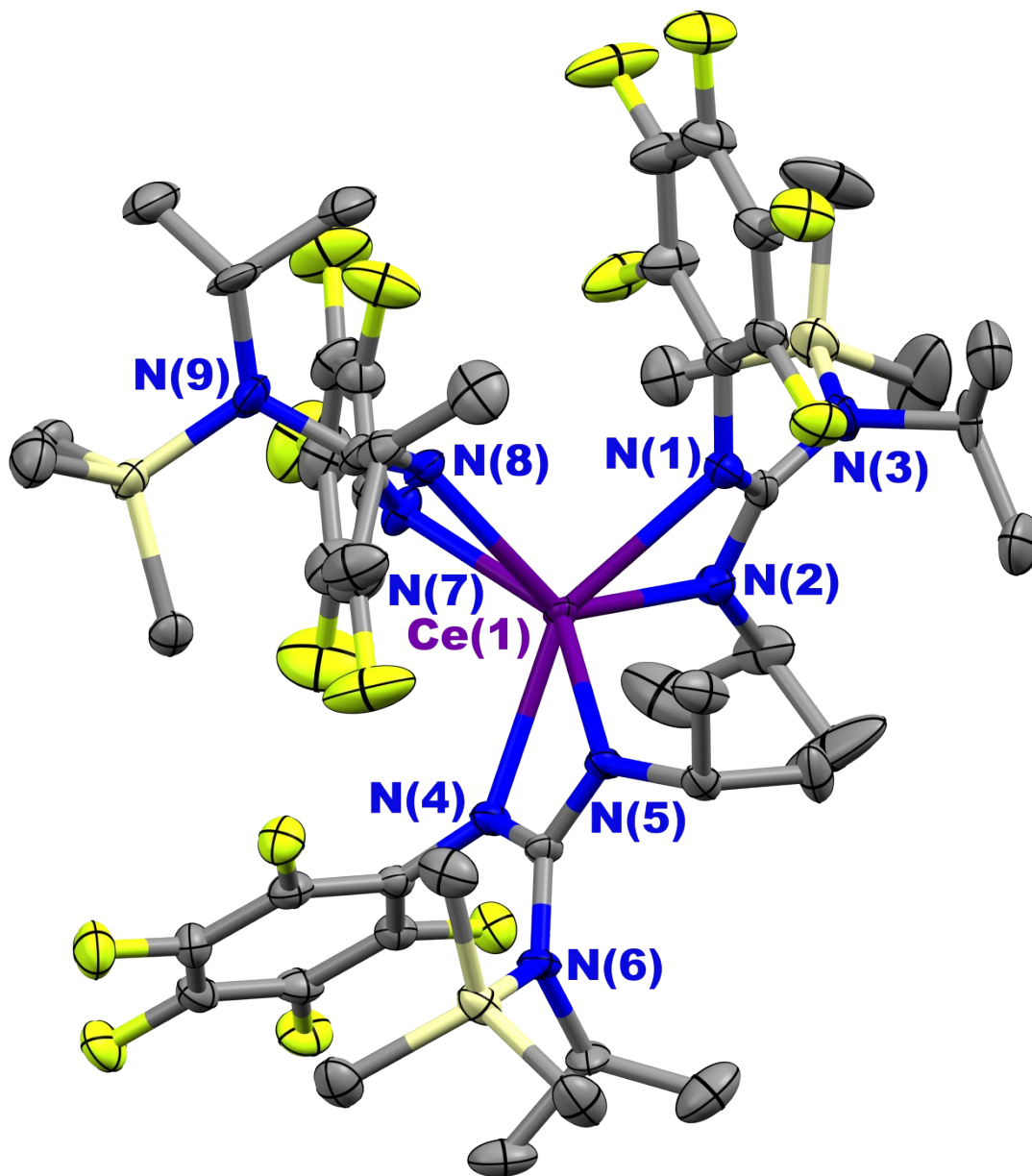


Figure S2. Thermal ellipsoid plot of $\{[{}^i\text{Pr}(\text{SiMe}_3)\text{N}]\text{C}(\text{N}^i\text{Pr})(\text{NPh}^F)\}_3\text{Ce}^{\text{III}}$ (**3**) at the 30% probability level. Selected bond length (Å) and angles (deg): Ce(1)–N(1) 2.497(3), Ce(1)–N(2) 2.440(3), Ce(1)–N(4) 2.488(3), Ce(1)–N(5) 2.506(3), Ce(1)–N(7) 2.454(3), Ce(1)–N(8) 2.494(3); N(1)–Ce(1)–N(2) 53.83(12), N(4)–Ce(1)–N(5) 53.05(9), N(7)–Ce(1)–N(8) 53.57(11).

NMR Spectra

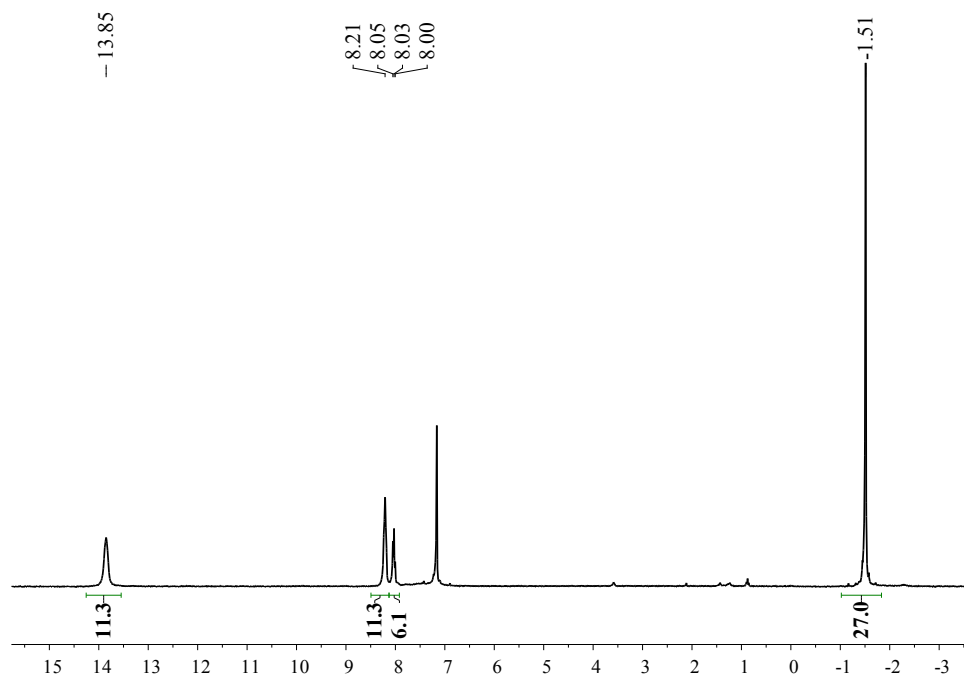


Figure S3. ^1H NMR data for $\text{Ce}[\text{S}_2\text{CN}(\text{SiMe}_3)\text{Ph}^{\text{F}}]_3(\text{O}=\text{PPh}_3)_2$ (**2**) in C_6D_6 .

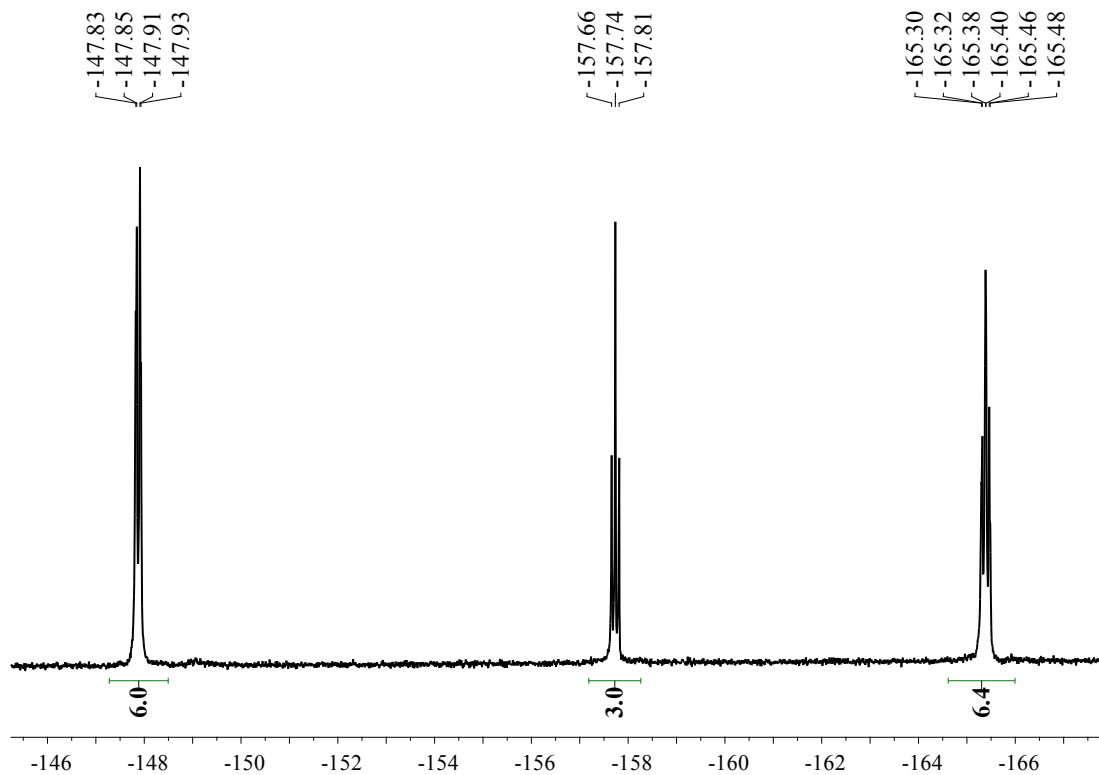


Figure S4. ^{19}F NMR data for $\text{Ce}[\text{S}_2\text{CN}(\text{SiMe}_3)\text{Ph}^{\text{F}}]_3(\text{O}=\text{PPh}_3)_2$ (**2**) in C_6D_6 .

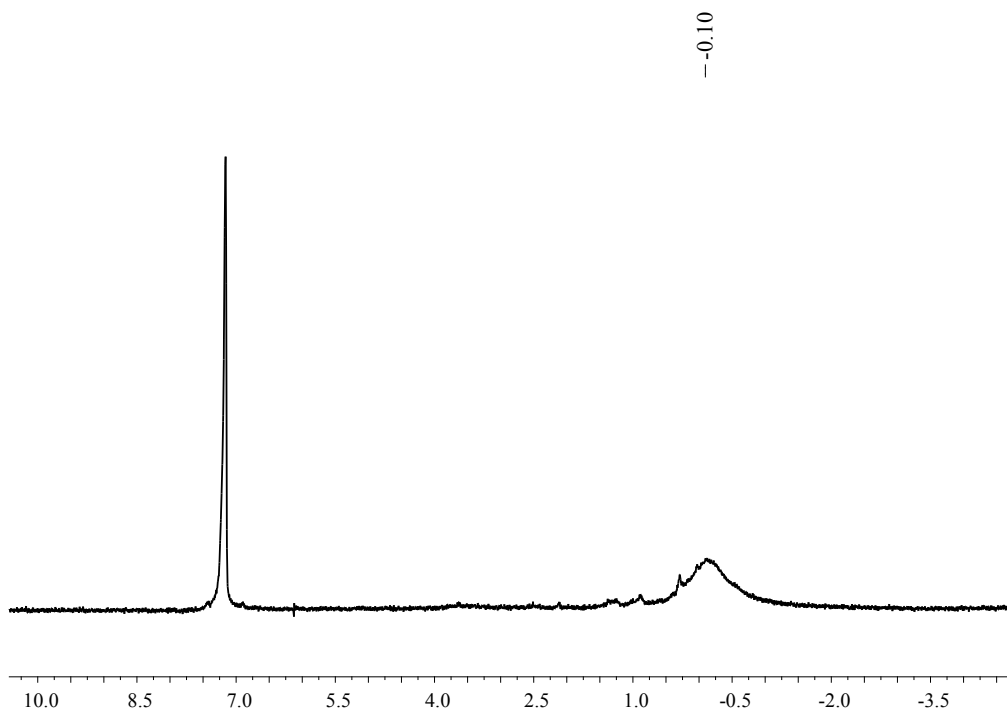


Figure S5. ^1H NMR data for aliquot of $\text{Ce}[\text{N}(\text{SiMe}_3)\text{Ph}^{\text{F}}]_3$ (**1**) reaction with CS_2 in C_6D_6 . A broad $-\text{SiMe}_3$ peak centered at -0.10 ppm was observed.

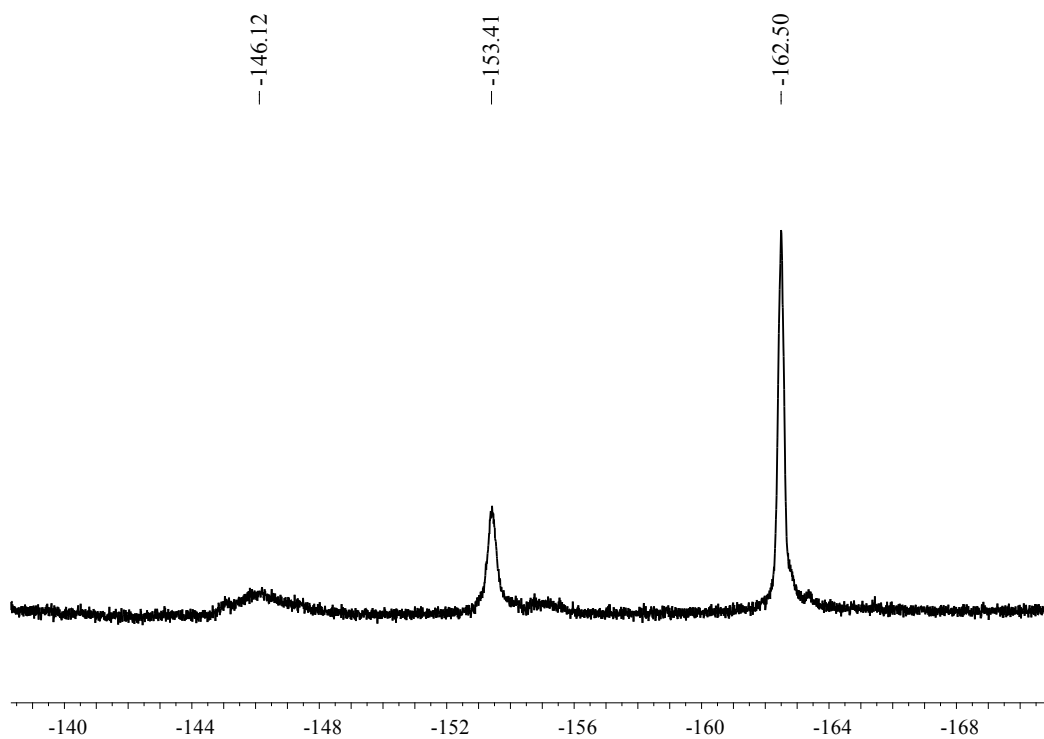


Figure S6. ^{19}F NMR data for aliquot of $\text{Ce}[\text{N}(\text{SiMe}_3)\text{Ph}^{\text{F}}]_3$ (**1**) reaction with CS_2 in C_6D_6 . A set of three broad resonances attributable to $-\text{Ph}^{\text{F}}$ group was observed.

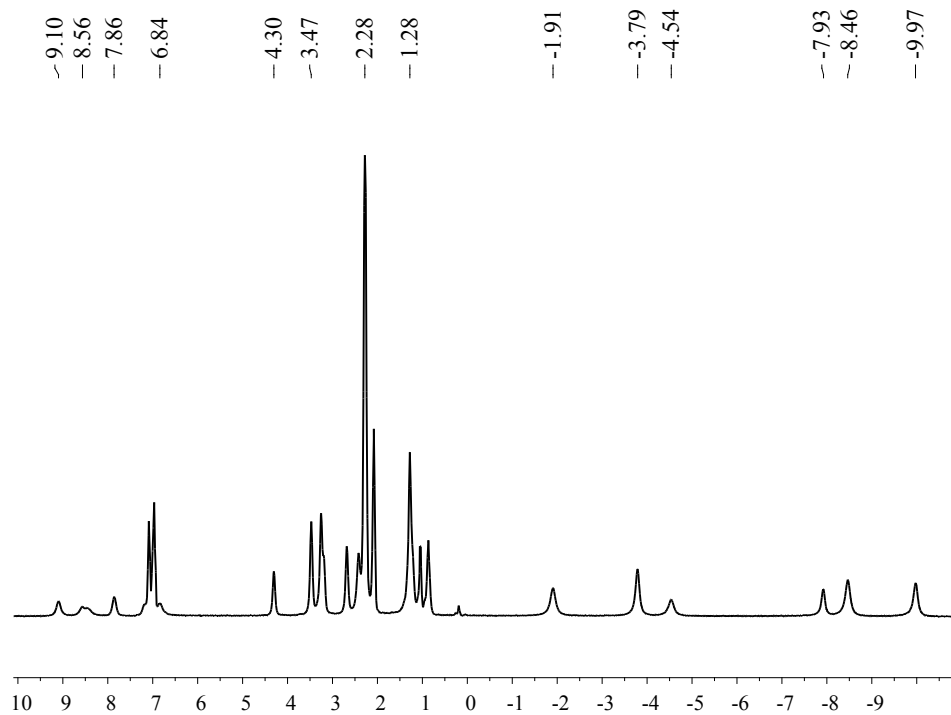


Figure S7. ^1H NMR data for $\{[{}^i\text{Pr}(\text{SiMe}_3)\text{N}]\text{C}(\text{N}^i\text{Pr})(\text{NPh}^{\text{F}})\}_3\text{Ce}^{\text{III}}$ (**3**) in toluene- d_8 .

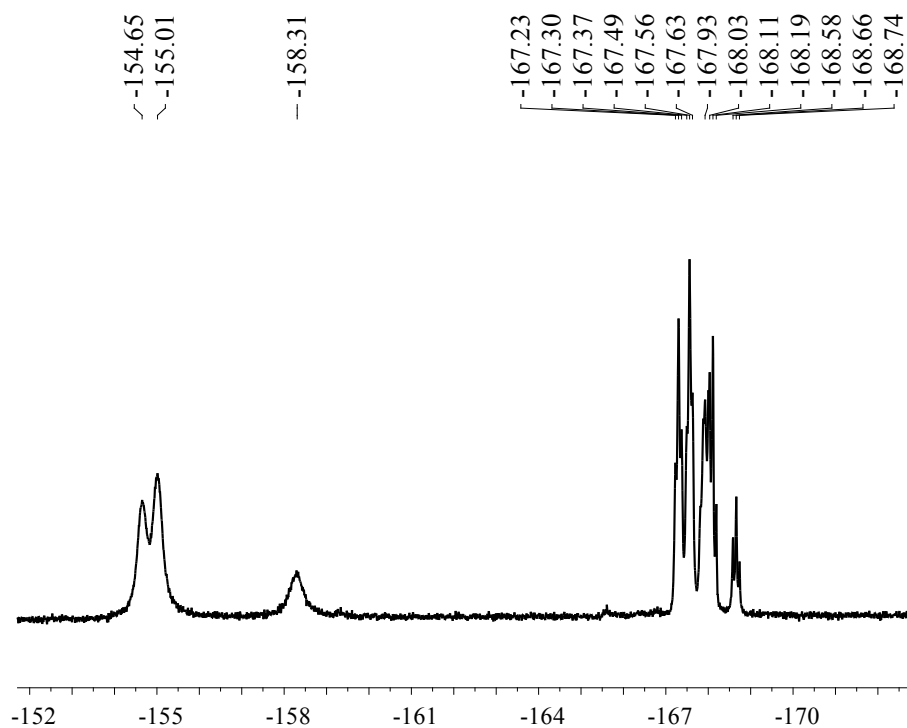


Figure S8. ^{19}F NMR data for $\{[{}^i\text{Pr}(\text{SiMe}_3)\text{N}]\text{C}(\text{N}^i\text{Pr})(\text{NPh}^{\text{F}})\}_3\text{Ce}^{\text{III}}$ (**3**) in toluene- d_8 .

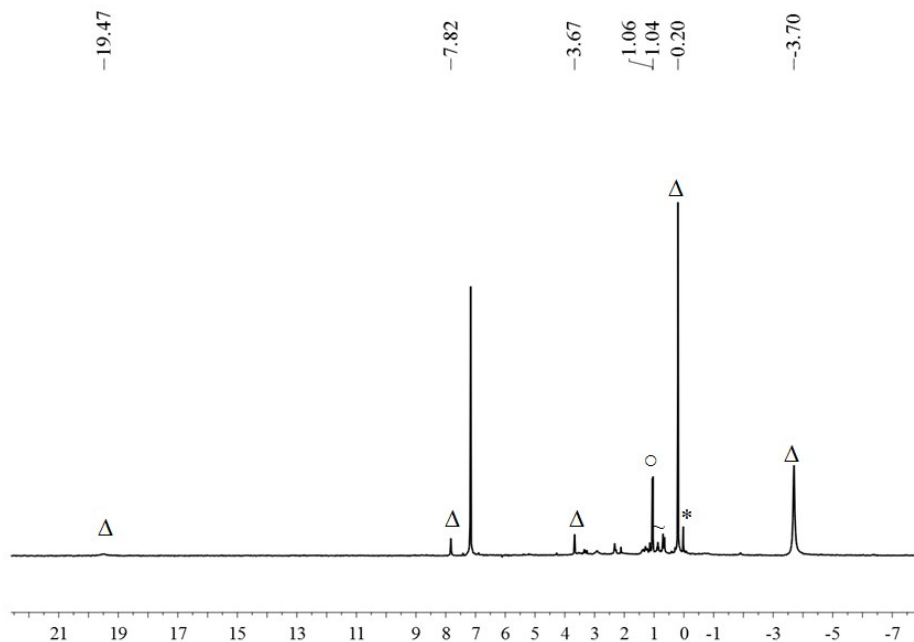


Figure S9. ^1H NMR of reaction aliquots of $(^i\text{Bu}_2\text{bipy})\text{Ce}[\text{N}(\text{SiMe}_3)\text{Ph}^{\text{F}}]_3$ (**1- $^i\text{Bu}_2\text{bipy}$**) with $^i\text{Pr}-\text{N}=\text{C}=\text{N}-^i\text{Pr}$ in toluene overnight, suggesting no reaction. The NMR was obtained in C_6D_6 . $(^i\text{Bu}_2\text{bipy})\text{Ce}[\text{N}(\text{SiMe}_3)\text{Ph}^{\text{F}}]_3$ and residue $^i\text{Pr}-\text{N}=\text{C}=\text{N}-^i\text{Pr}$ indicated by Δ and \circ , respectively. Protonated ligand (indicated by $*$) and solvent residue (*n*-pentane, indicated by \sim) were also evident in the spectra.

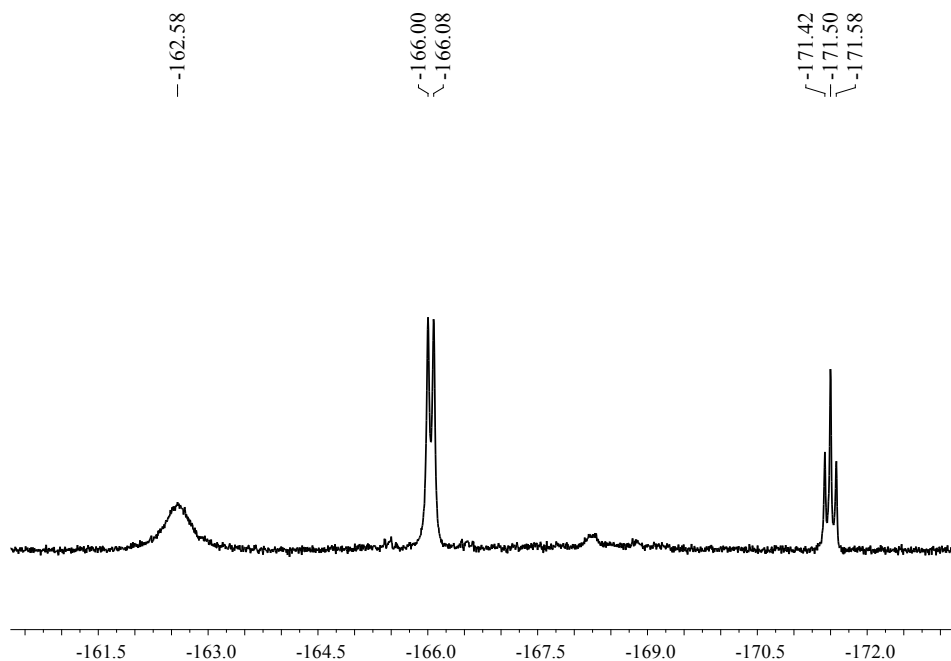


Figure S10. ^{19}F NMR of reaction aliquots of $(^i\text{Bu}_2\text{bipy})\text{Ce}[\text{N}(\text{SiMe}_3)\text{Ph}^{\text{F}}]_3$ (**1- $^i\text{Bu}_2\text{bipy}$**) with $^i\text{Pr}-\text{N}=\text{C}=\text{N}-^i\text{Pr}$ in toluene overnight, suggesting no reaction. The NMR was obtained in C_6D_6 and only $(^i\text{Bu}_2\text{bipy})\text{Ce}[\text{N}(\text{SiMe}_3)\text{Ph}^{\text{F}}]_3$ was observed.

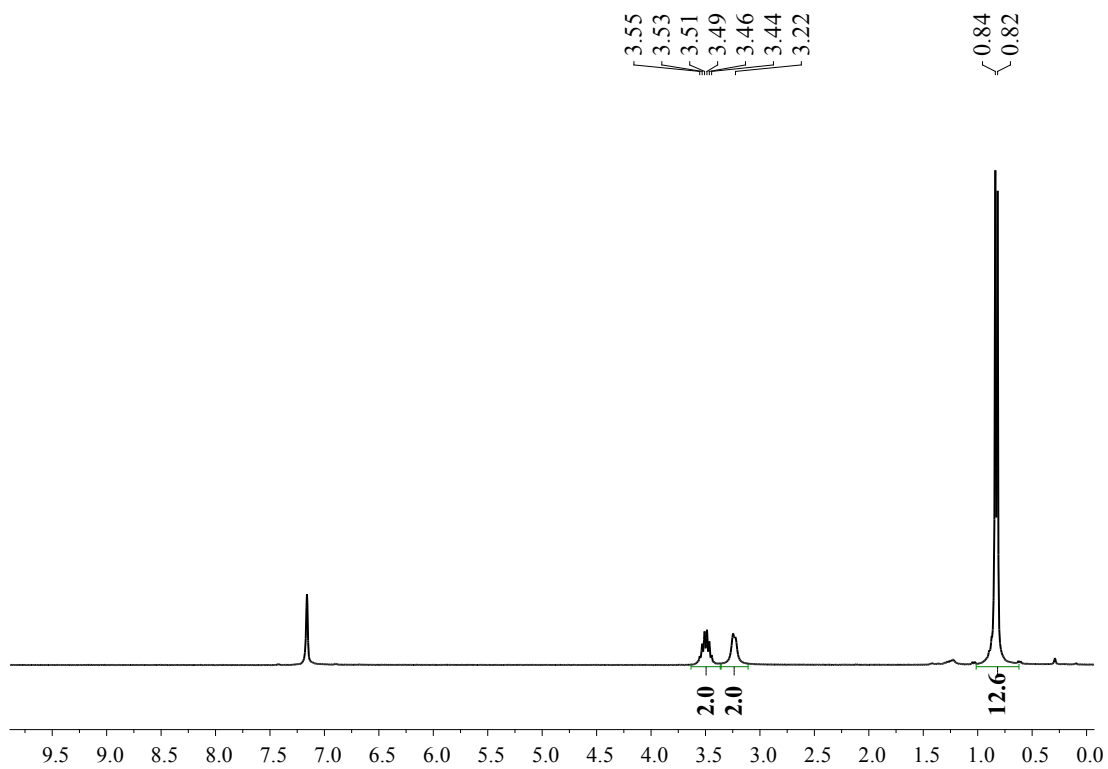


Figure S11. ^1H NMR data for $(\text{NH}^i\text{Pr})_2\text{C}(=\text{NPh}^F)$ (hydrolysis product of **3**) in C_6D_6 .

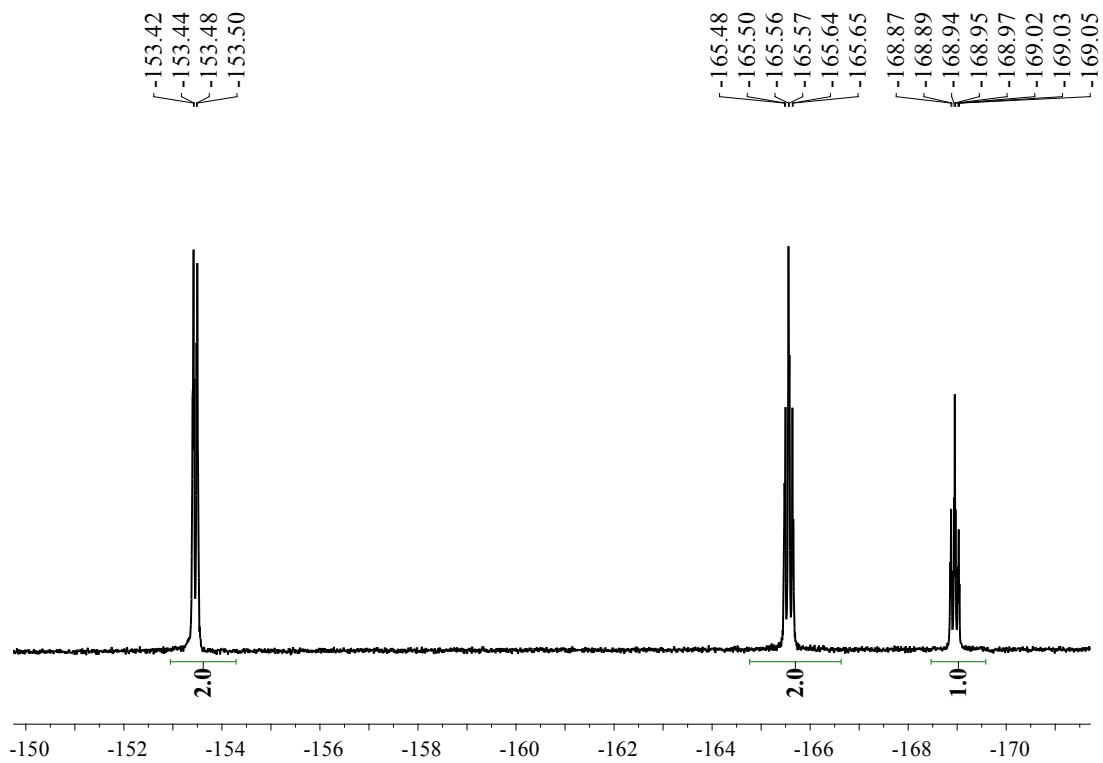


Figure S12. ^{19}F NMR data for $(\text{NH}^i\text{Pr})_2\text{C}(=\text{NPh}^F)$ (hydrolysis product of **3**) in C_6D_6 .

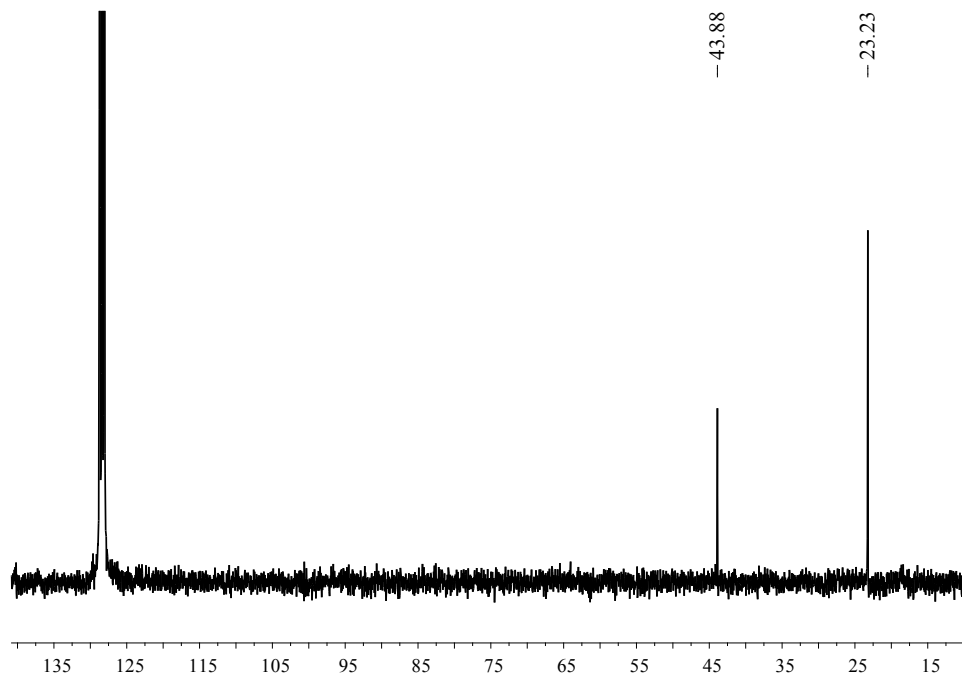


Figure S13. ^{13}C NMR data for $(\text{NH}'\text{Pr})_2\text{C}(\text{=NPh}^{\text{F}})$ (hydrolysis product of **3**) in C_6D_6 .

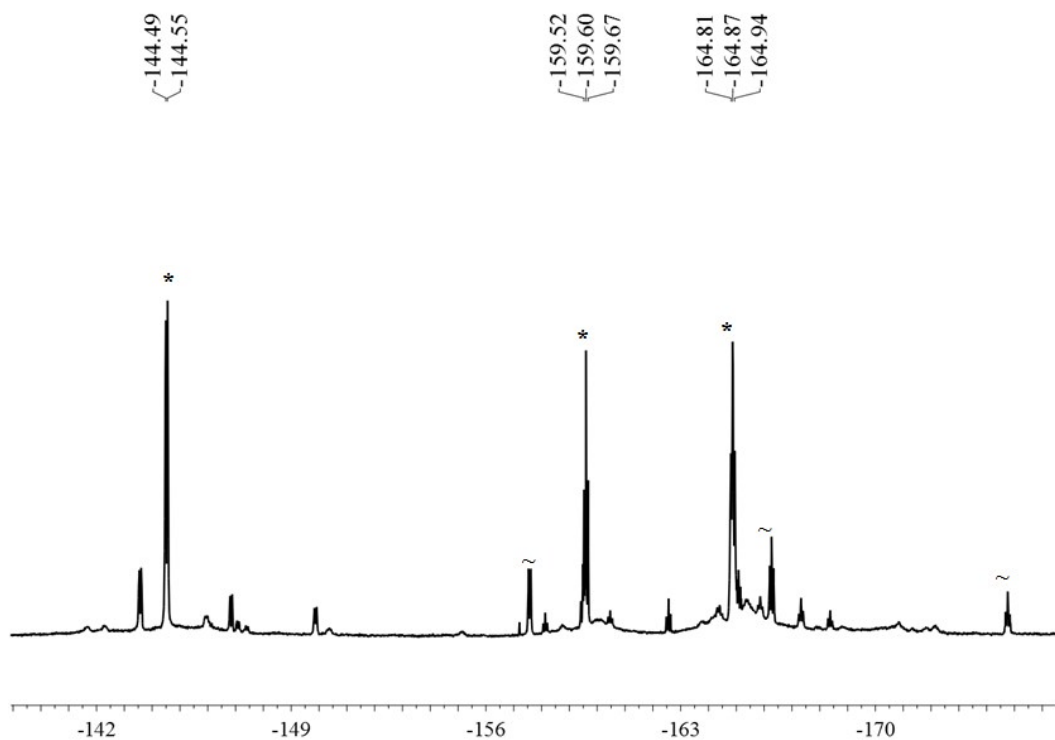


Figure S14. ^{19}F NMR data obtained in C_6D_6 for reaction aliquot of **1** with CO_2 . The desired product $\text{Ph}^{\text{F}}\text{-N}=\text{C}=\text{O}$ (**4**) is indicated by *. $\text{HN}(\text{SiMe}_3)\text{Ph}^{\text{F}}$, the hydrolysis product from **1** is indicated by ~.

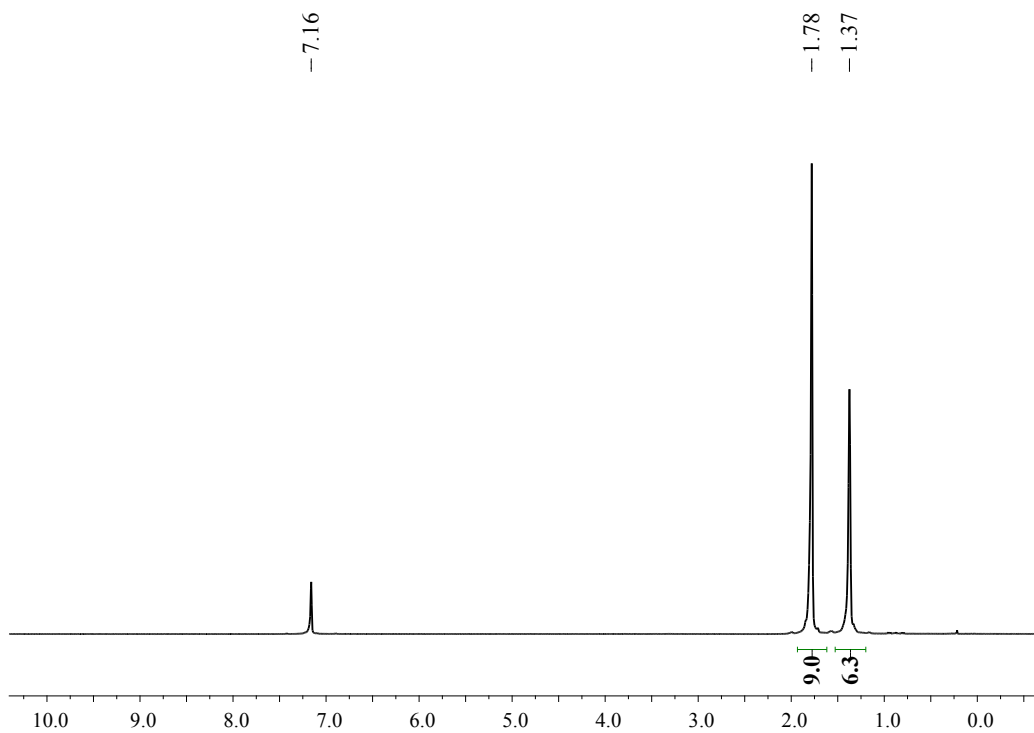


Figure S15. ^1H NMR data for $\text{Ad-N=C=N-Ph}^{\text{F}}$ (**5**) in C_6D_6 .

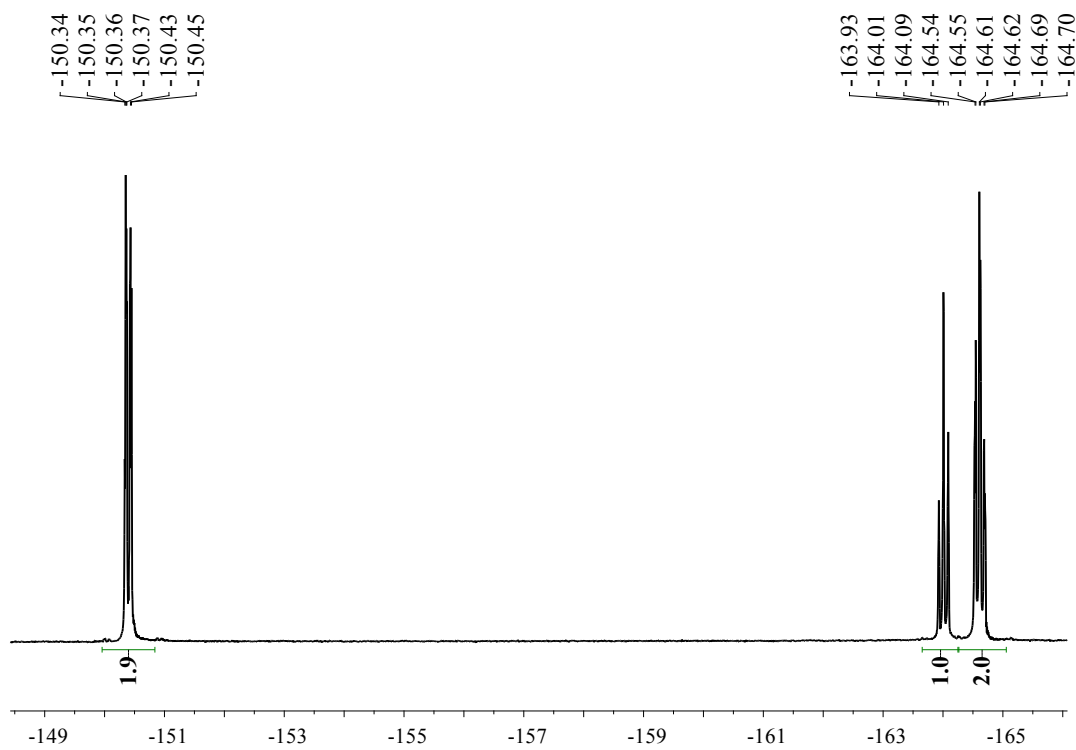


Figure S16. ^{19}F NMR data for $\text{Ad-N=C=N-Ph}^{\text{F}}$ (**5**) in C_6D_6 .

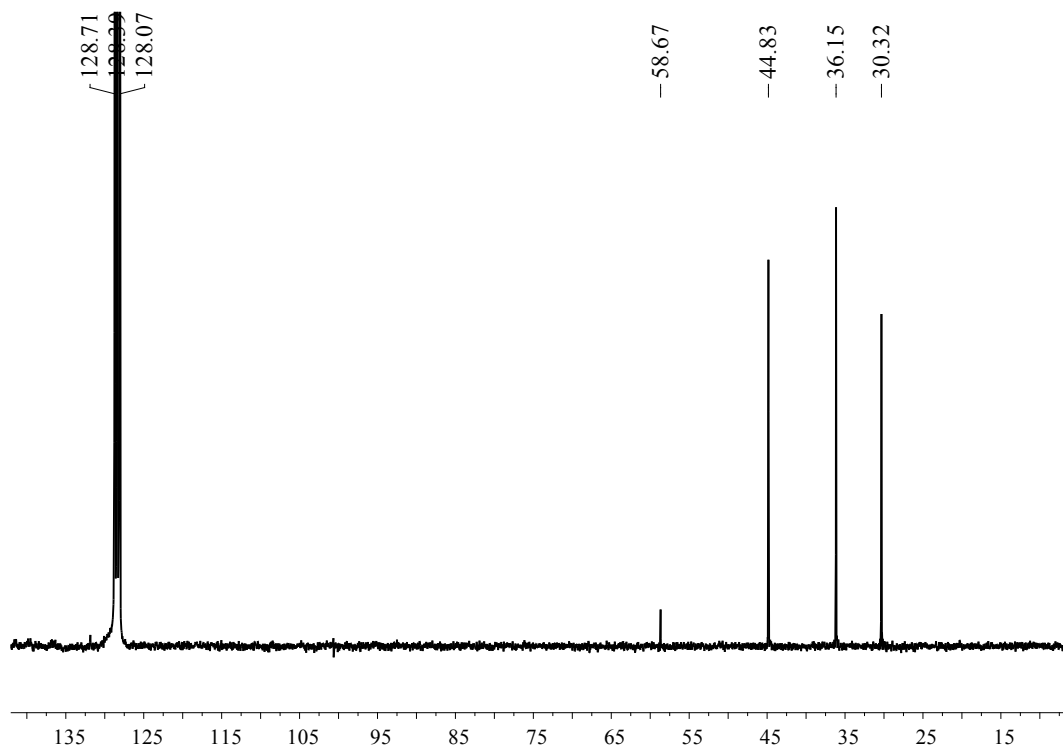


Figure S17. ^{13}C NMR data for **Ad-N=C=N-Ph^F (5)** in C_6D_6 .

VT NMR Spectra

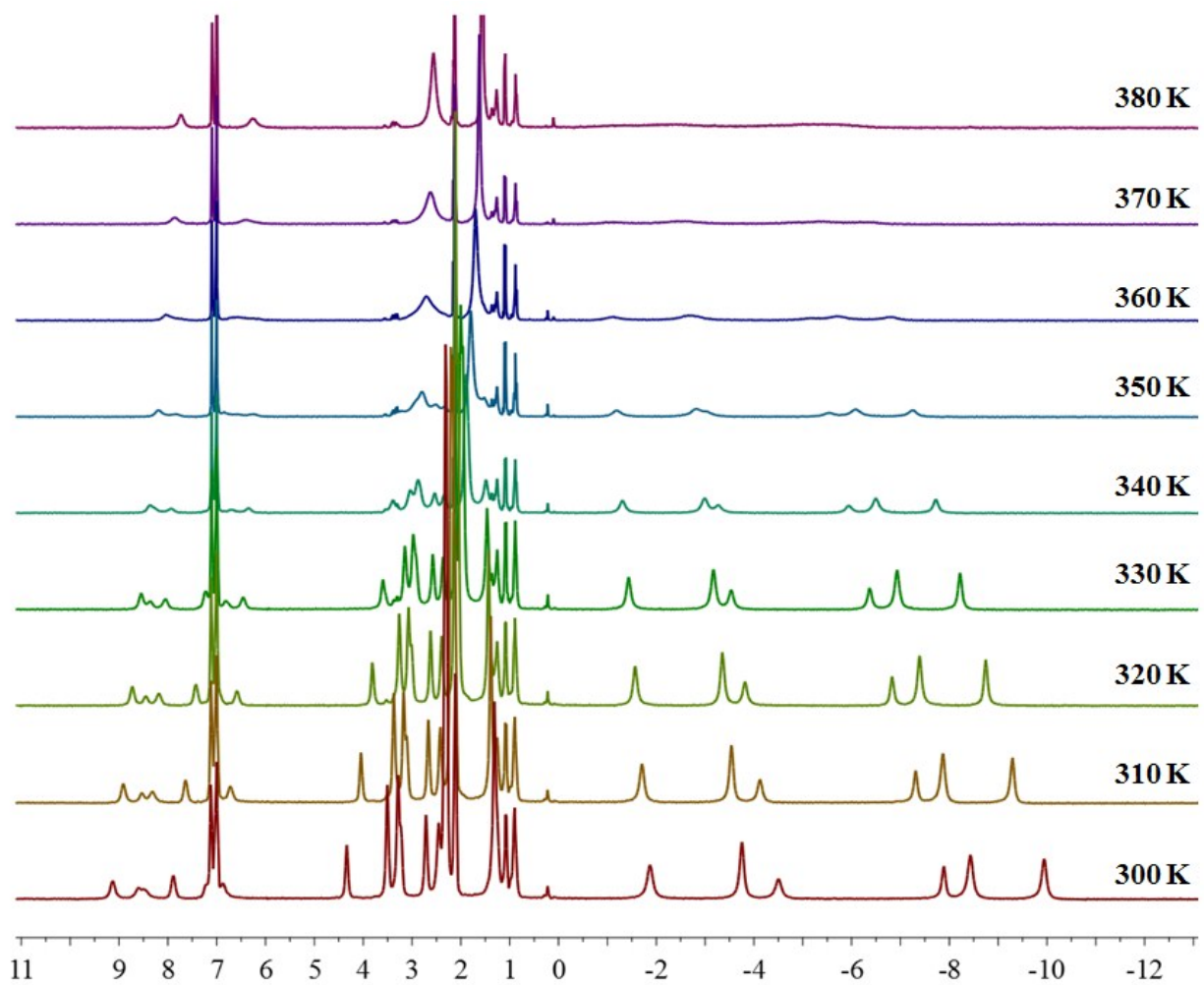


Figure S18. VT ¹H NMR data for $\{[{}^i\text{Pr}(\text{SiMe}_3)\text{N}]\text{C}(\text{N}^i\text{Pr})(\text{NPh}^F)\}_3\text{Ce}^{\text{III}}$ (**3**) in toluene-*d*₈ between 380–300 K.

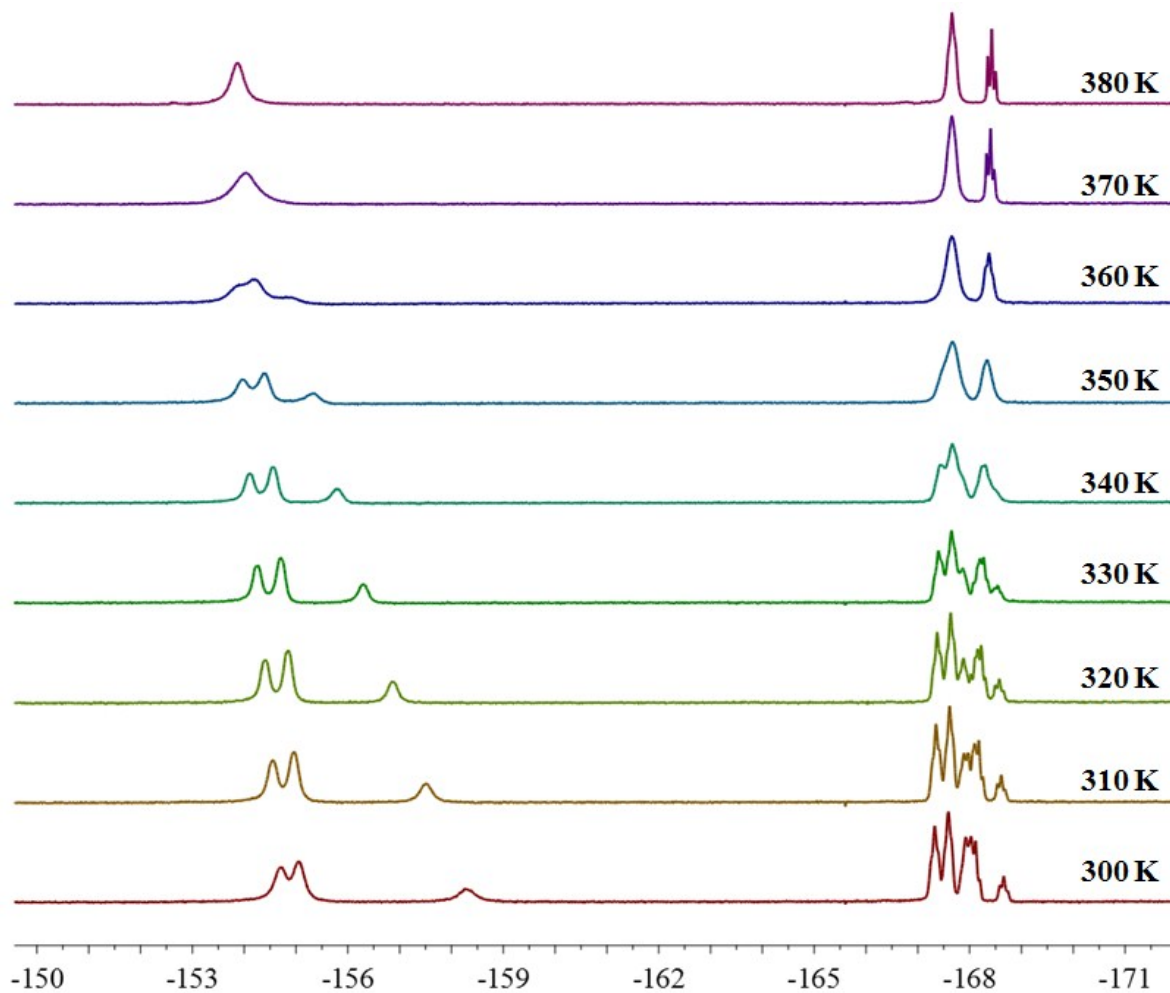
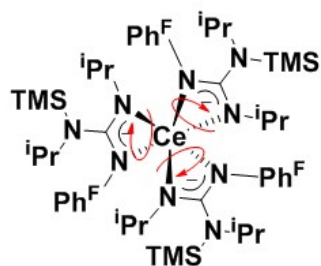


Figure S19. VT ^{19}F NMR data for $\{[\text{Pr}(\text{SiMe}_3)\text{N}]\text{C}(\text{N}^i\text{Pr})(\text{NPh}^F)\}_3\text{Ce}^{\text{III}}$ (**3**) in toluene- d_8 between 380–300 K showing a symmetry change from C_1 to C_3 on NMR timescale. The coalescence was observed at ~ 365 K. The rotational barrier (17.4 kcal/mol) was calculated based on *o*-F resonances according to following equations:

$$k_c = \frac{\pi}{\sqrt{2}} \Delta\nu_{AB} ; \quad \Delta G^\ddagger = RT \ln\left(\frac{kT}{k_c h}\right)$$



IR Spectra

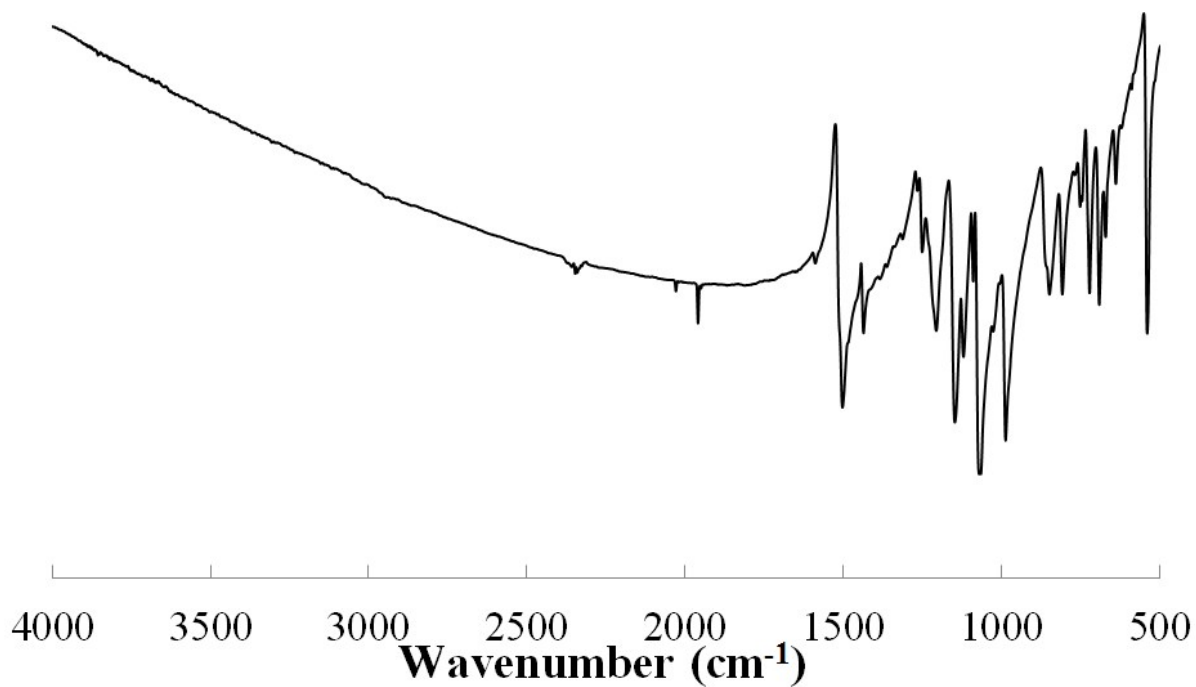


Figure S20. Infrared spectrum for $\text{Ce}[\kappa^2\text{-S}_2\text{CN}(\text{SiMe}_3)\text{Ph}^{\text{F}}]_3(\text{O}=\text{PPh}_3)_2$ (**2**) (KBr plate).

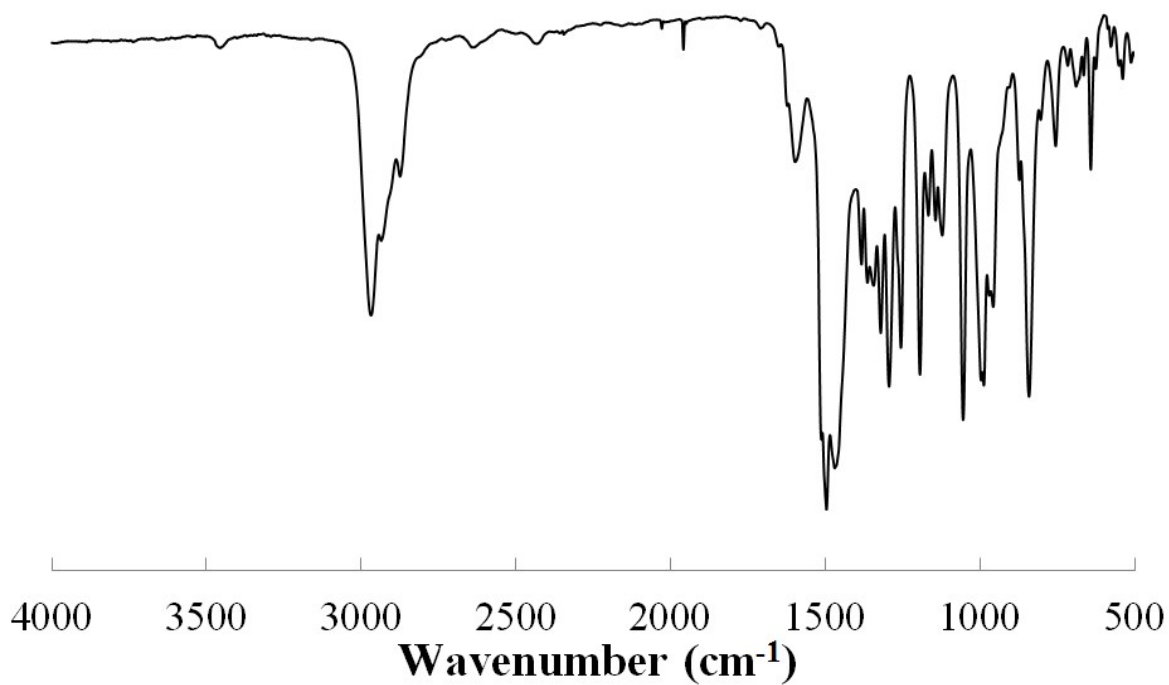


Figure S21. Infrared spectrum for $\{[\text{Pr}(\text{SiMe}_3)\text{N}]\text{C}(\text{N}^{\text{F}}\text{Pr})(\text{NPh}^{\text{F}})\}_3\text{Ce}^{\text{III}}$ (**3**) (KBr plate).

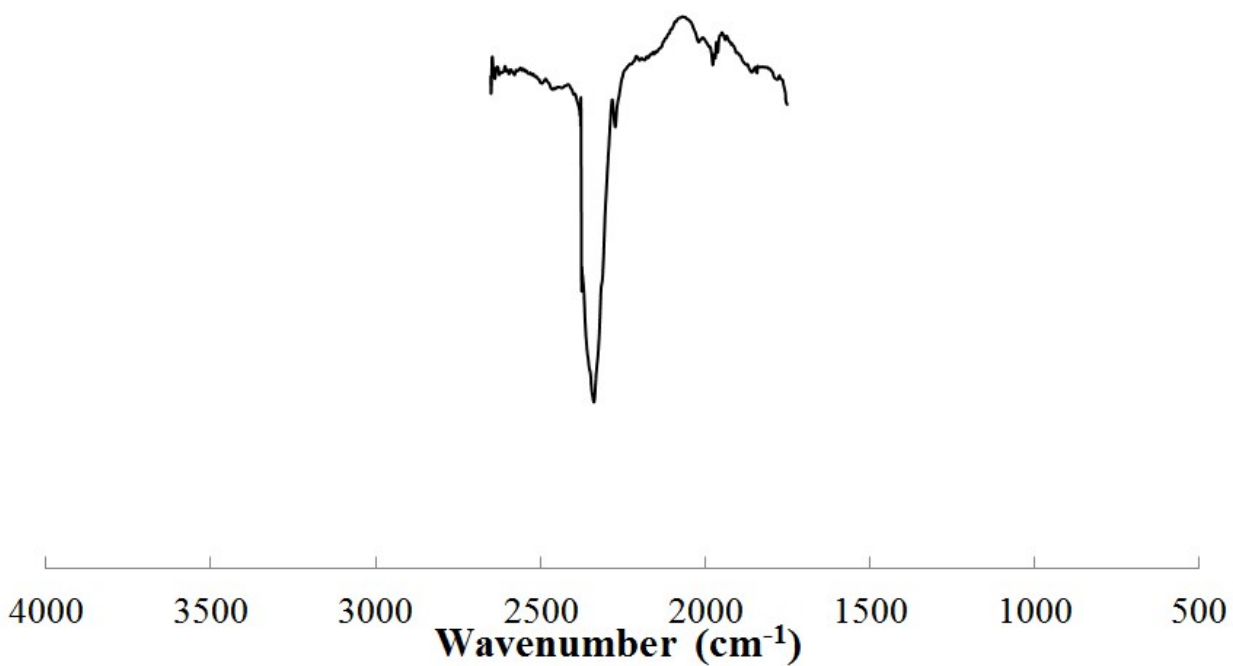


Figure S22. Infrared spectrum for reaction aliquot of **1** with CO₂ in THF solution, the spectrum region between 1650 to 2650 cm⁻¹ was shown. The absorption at 2337 cm⁻¹ indicates the presence of isocyanate species.

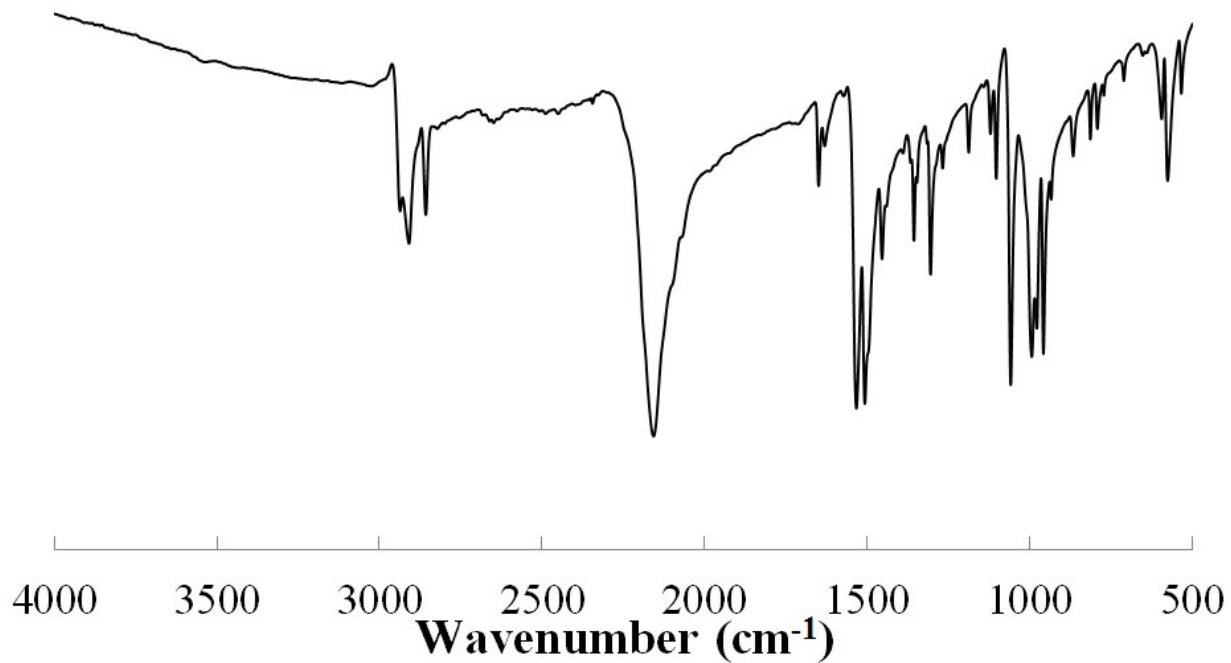


Figure S23. Infrared spectrum for Ad-N=C=N-Ph^F (**5**) (KBr plate).

Mass Spectra

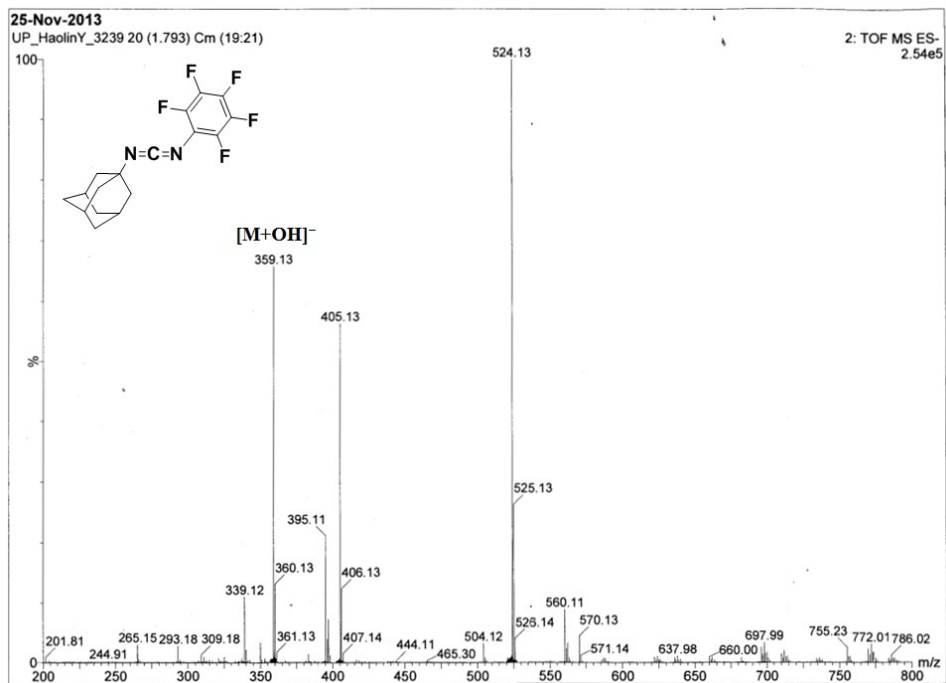


Figure S26. High resolution mass spectra of Ad-N=C=N-Ph^F (5). $[M+OH]^-$ was observed in ESI⁻ mode.

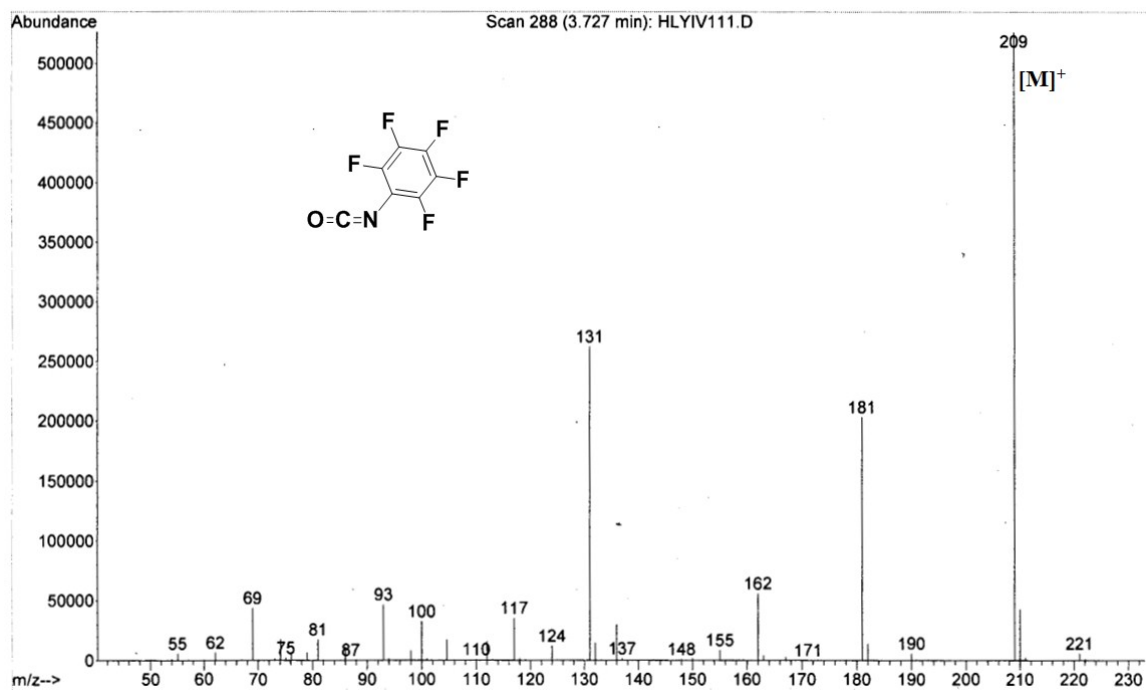


Figure S27. GC-MS spectra of Ph^F-C=N=O (4). $[M]^+$ was observed in the spectra.

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