

CHEMISTRY

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Supporting Information

Heterolytic Si–H Bond Cleavage at a Molybdenum-Oxido-Based Lewis Pair

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Supplementary figures

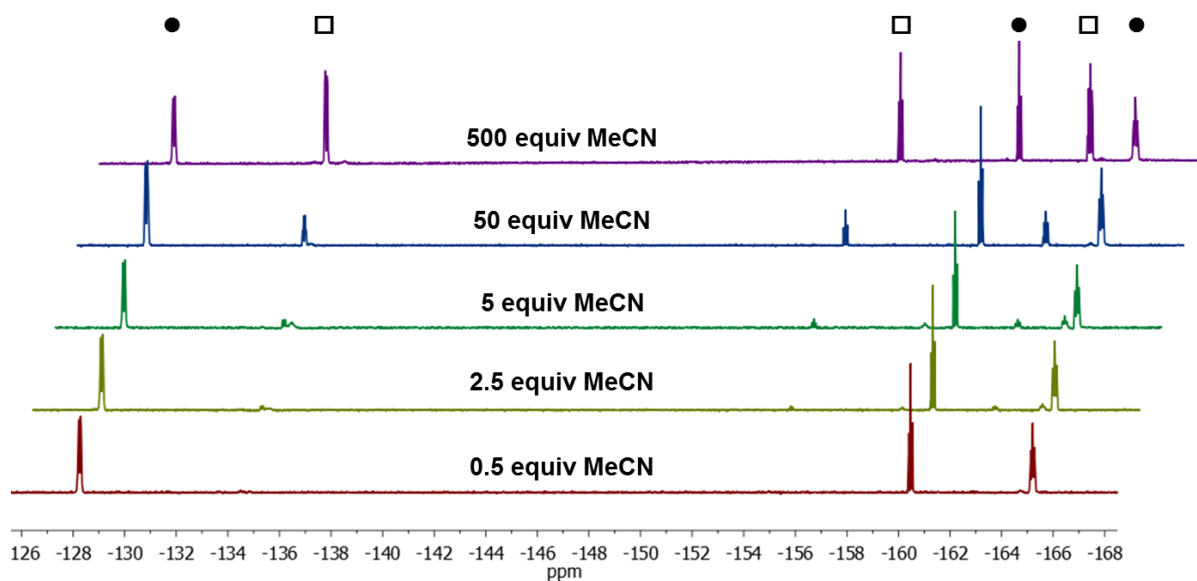


Figure S1. ^{19}F NMR spectra of the concentration dependent equilibrium of **2** (●) with $\text{MeCN}\cdot\text{B}(\text{C}_6\text{F}_5)_3$ (□) in C_6D_6 .

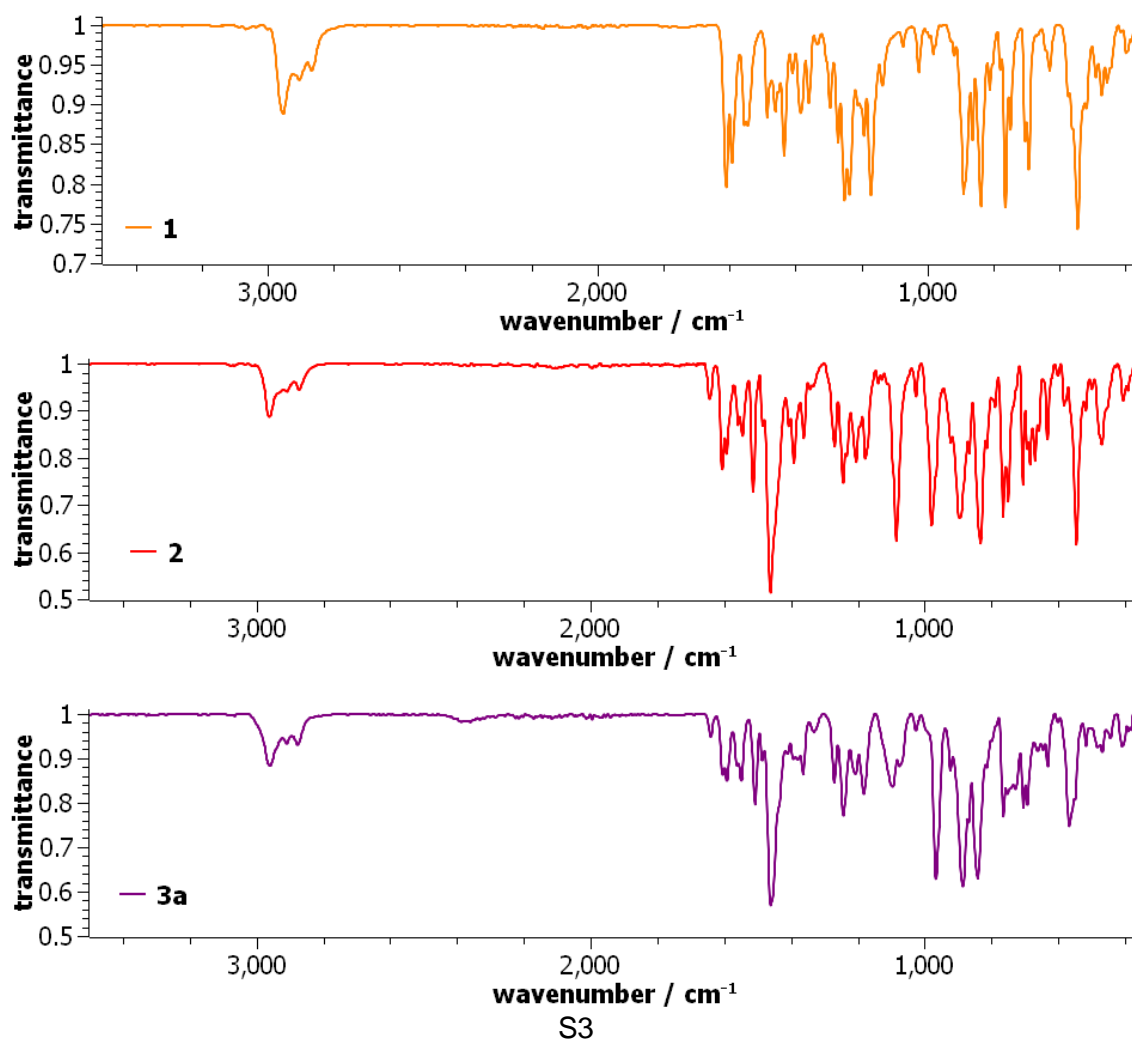


Figure S2. IR spectra of compounds **1**,^[1] **2** and **3a** in the region from 350 to 3500 cm^{-1} .

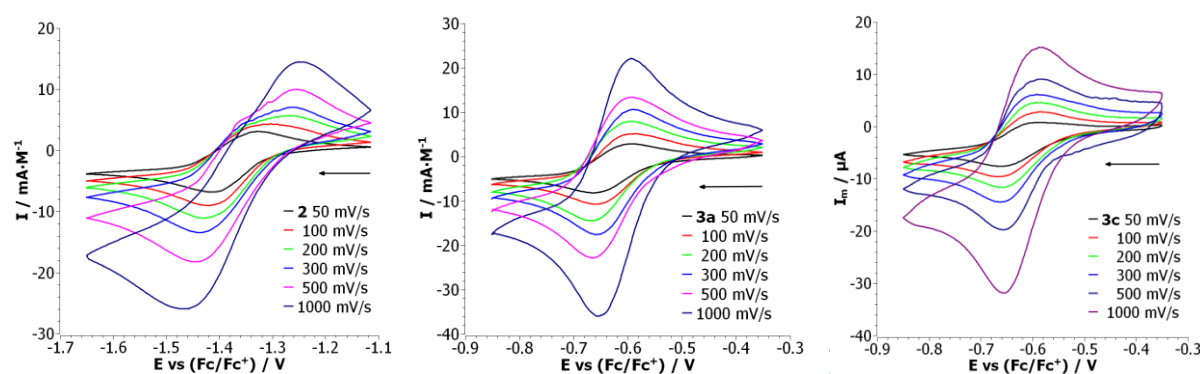


Figure S3. Scan rate dependence of the redox couples assigned to Mo(VI)/Mo(V) for complex **2** (left), **3a** (middle) and **3c** (right).

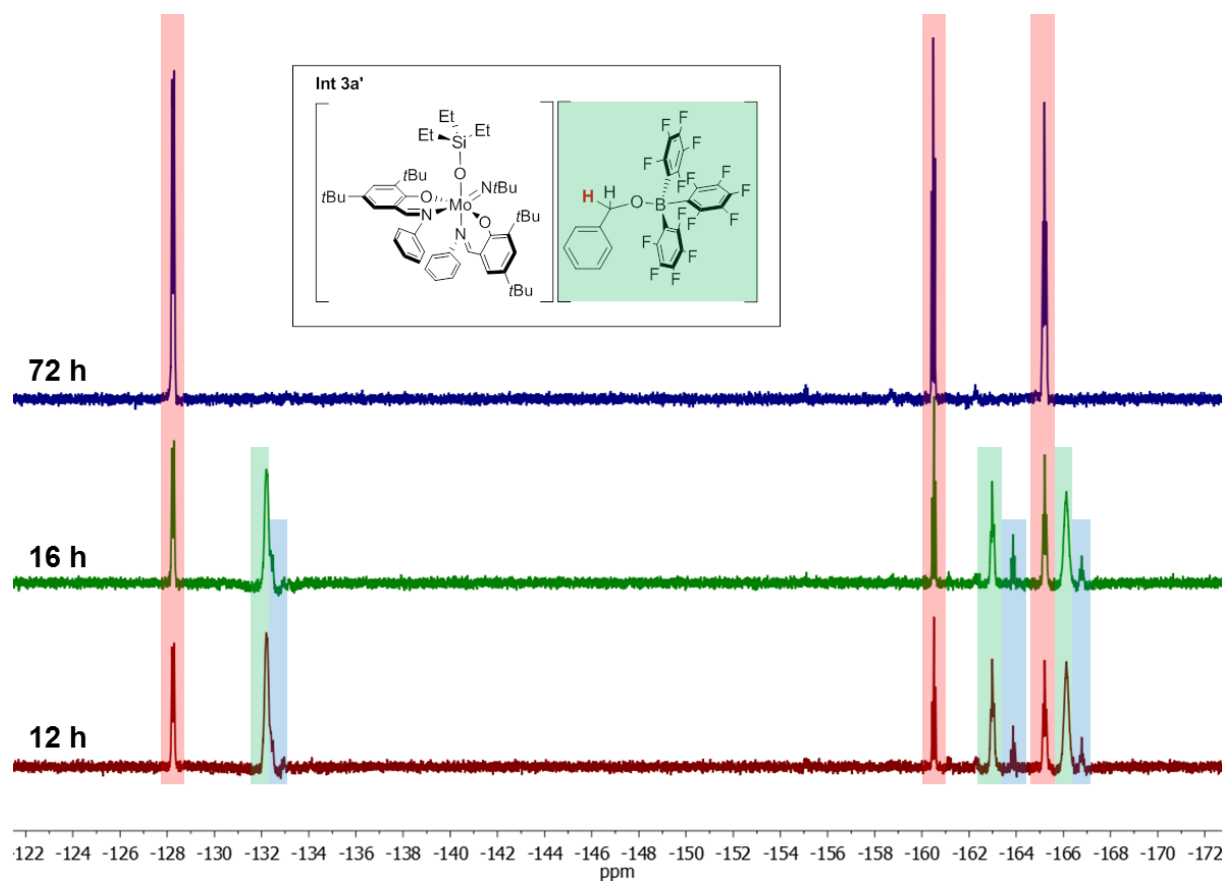


Figure S4. ^{19}F NMR spectra of the reaction of **3a** with benzaldehyde in C_6D_6 . The red boxes mark the resonances for the Lewis adduct **2**, the blue boxes mark residual $[\text{HB}(\text{C}_6\text{F}_5)_3]^-$ from **3a** and the resonances in the green boxes correspond to the anion of the intermediate species **Int 3a'**.

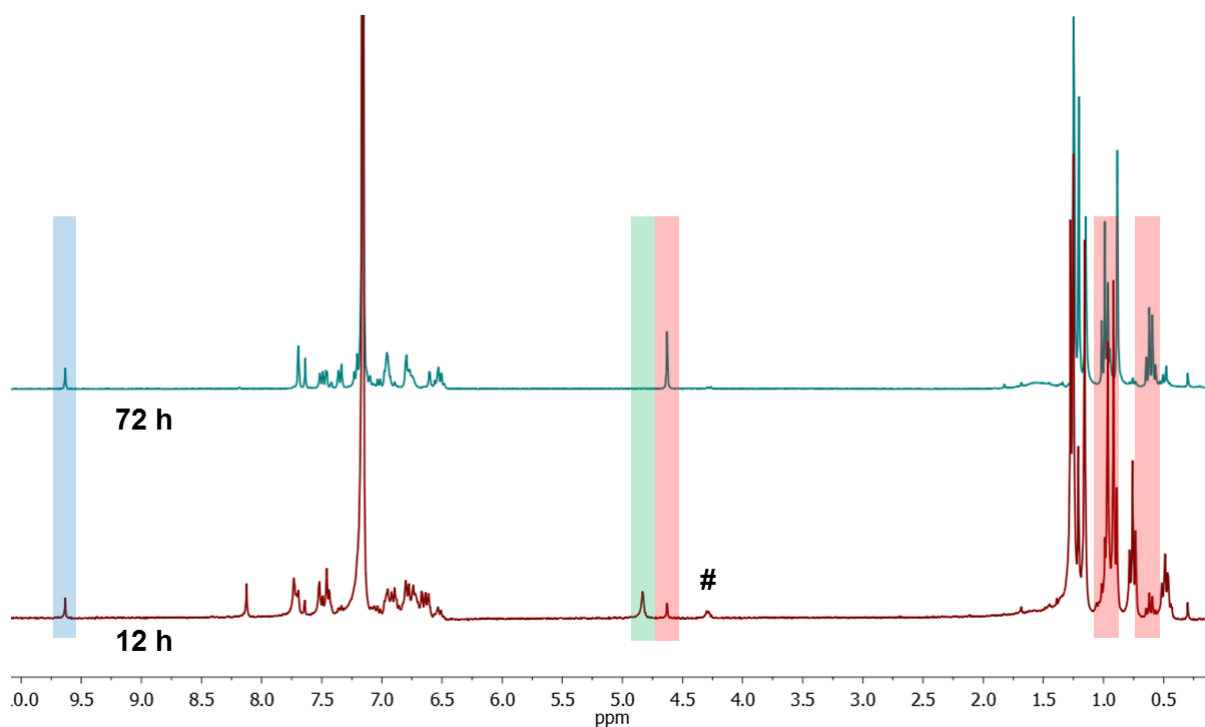


Figure S5. ^1H NMR spectra of the reaction of **3a** with benzaldehyde in C_6D_6 . The red boxes correspond to Bn-OSiEt_3 , the blue box refers to residual benzaldehyde and the # symbols correspond to Bn-OH impurity. The resonance in the green box corresponds to the intermediate species **Int 3a'**.

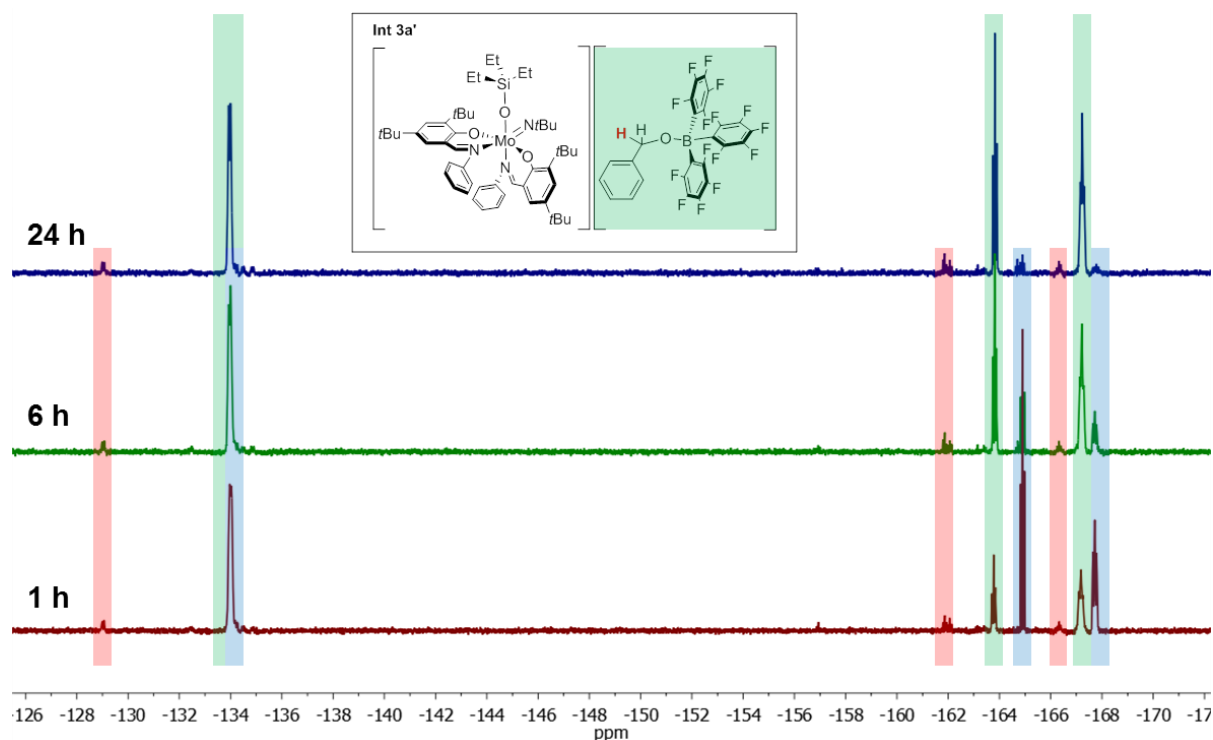


Figure S6. ^{19}F NMR spectra of the reaction of **3a** with benzaldehyde in CD_2Cl_2 . The blue boxes mark the resonances for the $[\text{HB}(\text{C}_6\text{F}_5)_3]^-$ anion of the initial complex **3a** and the resonances in the green boxes correspond to the intermediate species **Int 3a'**, consistent to literature.^[2] Lewis adduct **2** is only formed in minute quantities, marked with the red boxes.

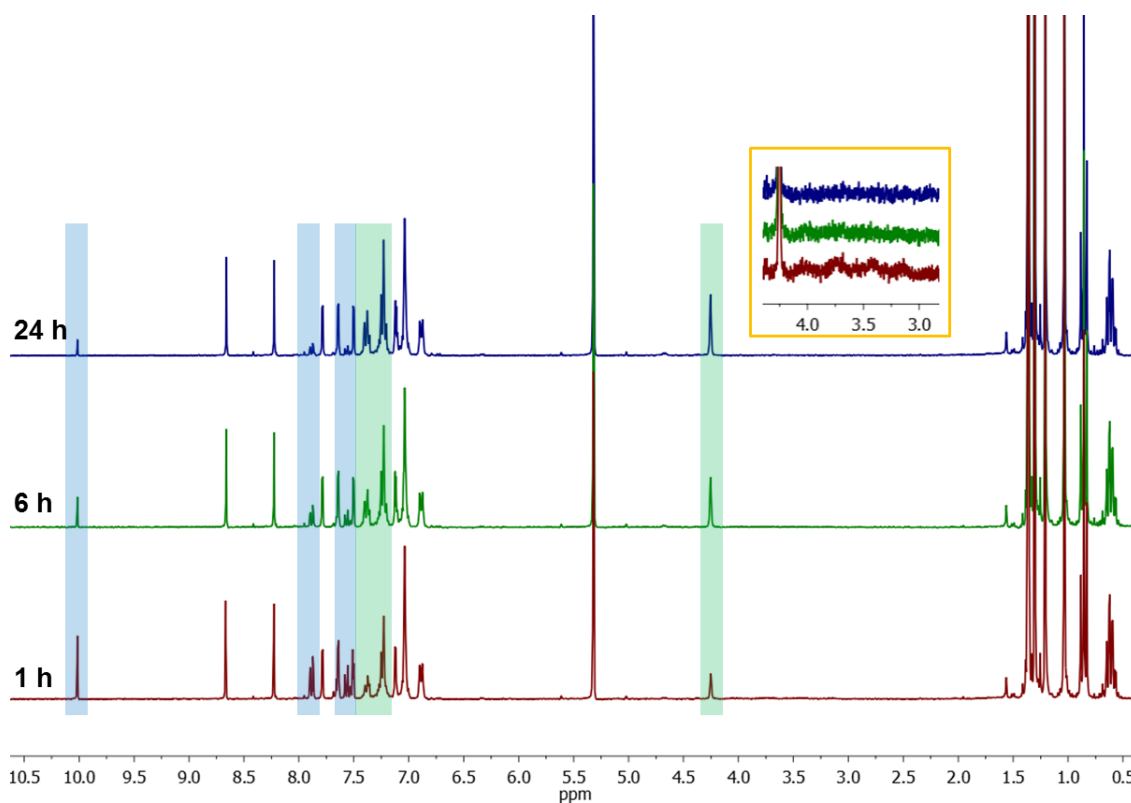


Figure S7. ^1H NMR spectra of the reaction of **3a** with benzaldehyde in CD_2Cl_2 . The resonances in the green boxes correspond to the intermediate species **Int 3a'**, the blue boxes refer to residual benzaldehyde and the yellow box shows the decrease of the B–H resonance. No formation of complex **2** or Bn-O-SiEt_3 is observed within 24 h of reaction time, after 72 h, the conversion is $\sim 5\%$.

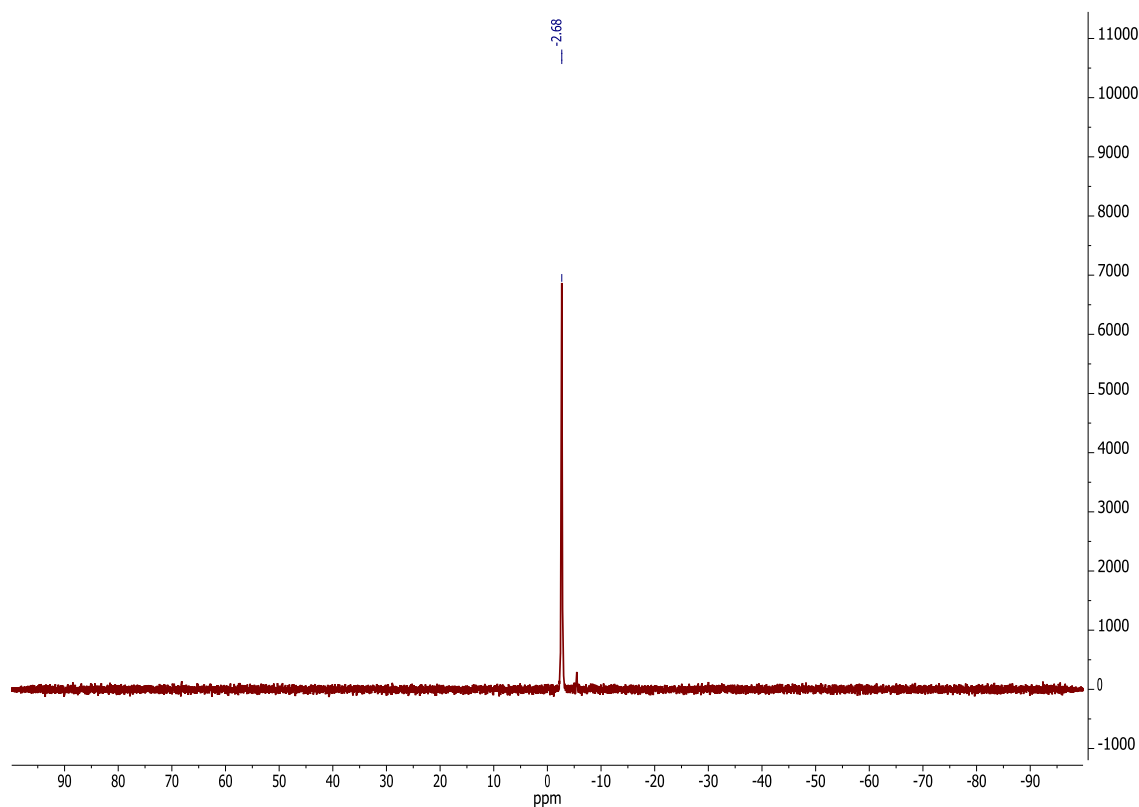


Figure S8. ^{11}B NMR spectrum of **Int 3a'** from the reaction of **3a** with benzaldehyde in CD_2Cl_2 after 24 h.

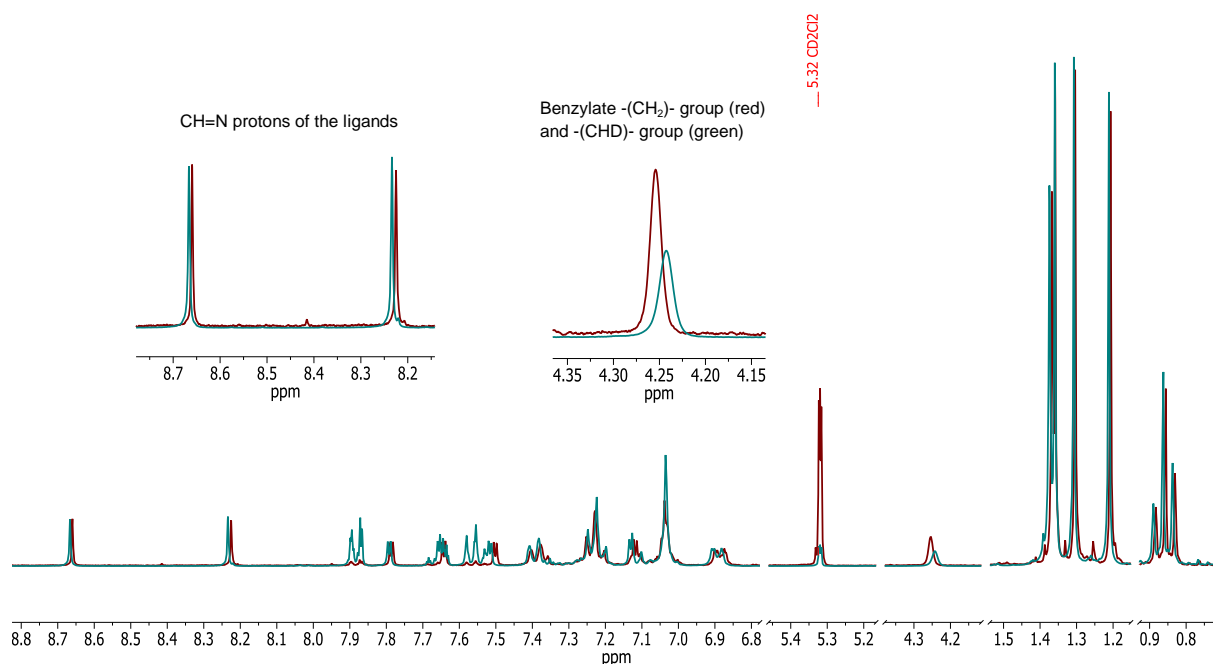


Figure S9. Superimposed ^1H NMR spectra of **Int 3a'** and **Int 3a'-d₁** showing the different peak areas for the benzylate methylene group; Red: **Int 3a'**, $-(\text{CH}_2)-$ group integrates for two protons, Green: **Int 3a'-d₁**, $-(\text{CHD})-$ group integrates for one proton. Additional signals in the spectrum of **Int 3a'-d₁** correspond to excess benzaldehyde.

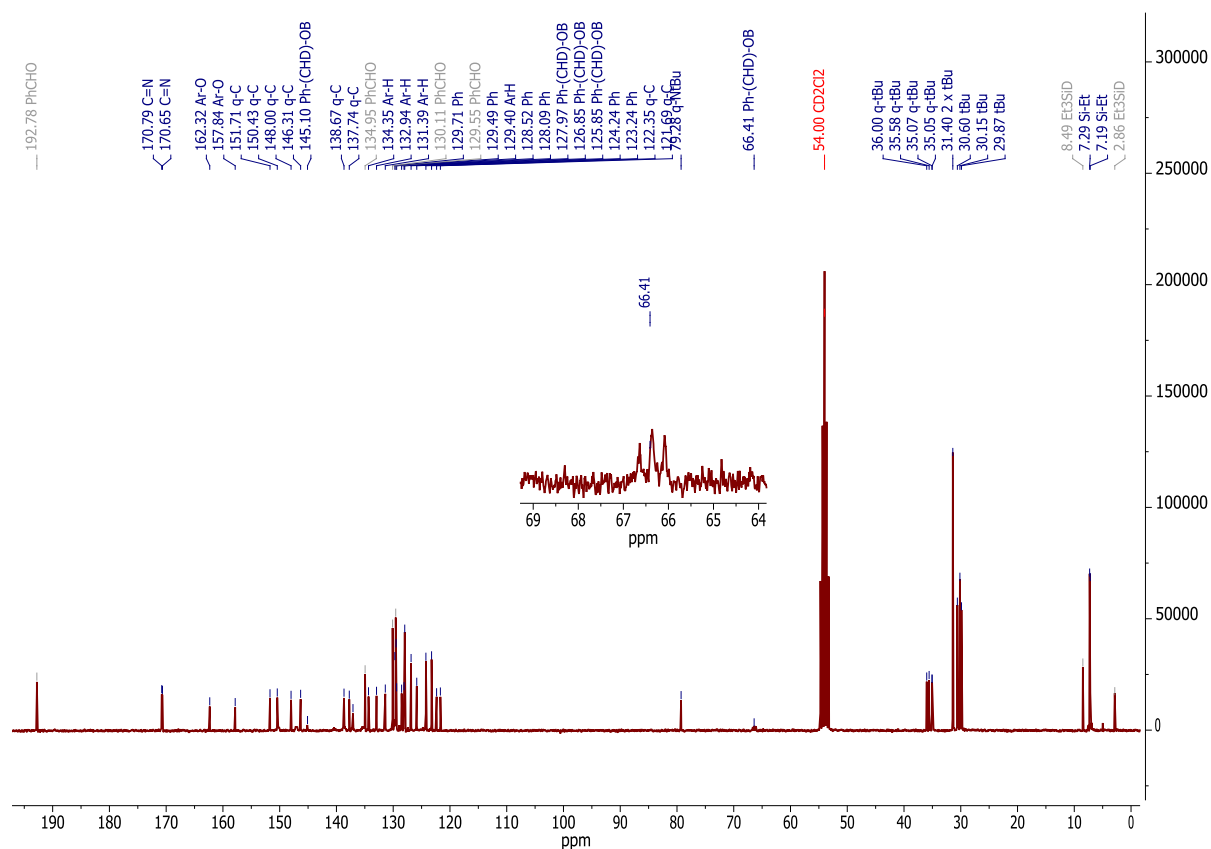


Figure S10. ^{13}C NMR spectrum of **Int 3a'-d₁** showing the characteristic triplet for the $-(\text{CHD})-$ group arising from $^1\text{J}_{(\text{C-D})}$ coupling. The mixture also contains excess Et_3SiD and PhCHO as a result of *in situ* measurements.

NMR and MS spectra of the compounds

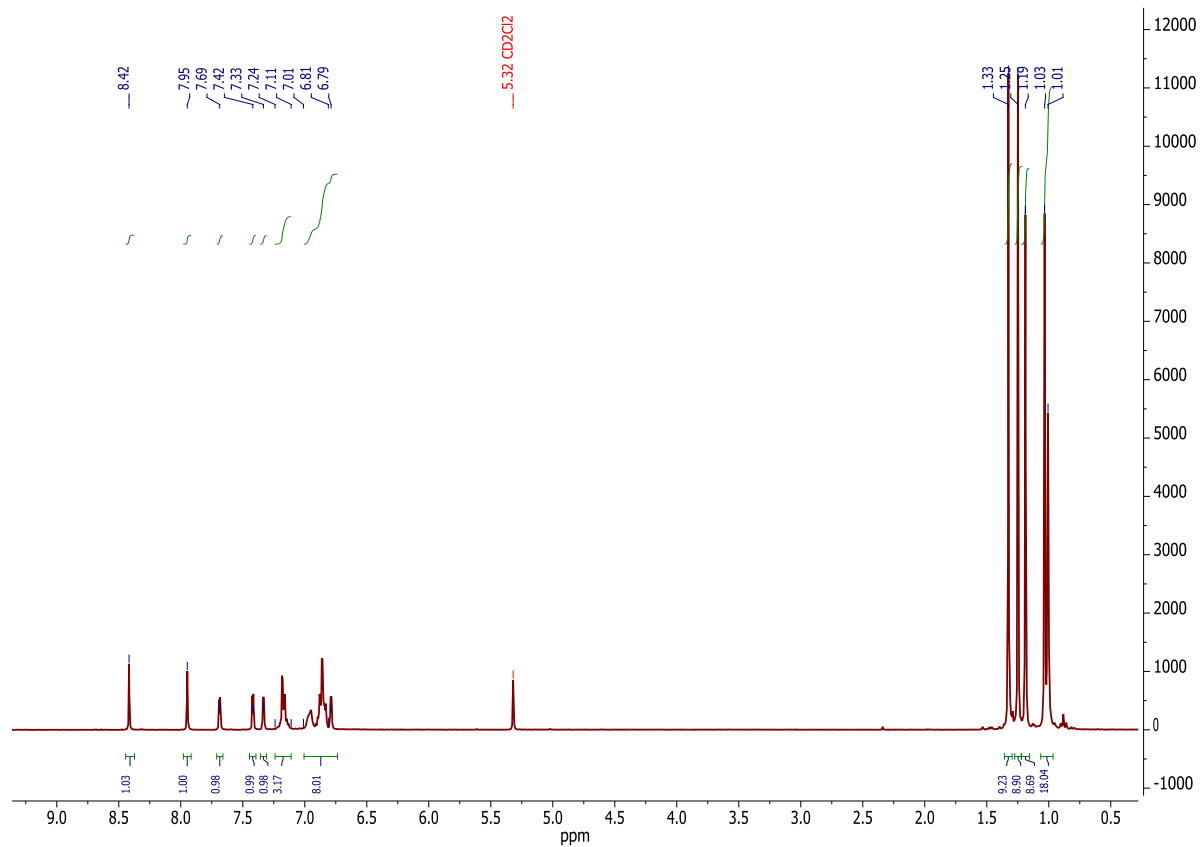


Figure S11. ^1H NMR spectrum of complex **2** in CD_2Cl_2 .

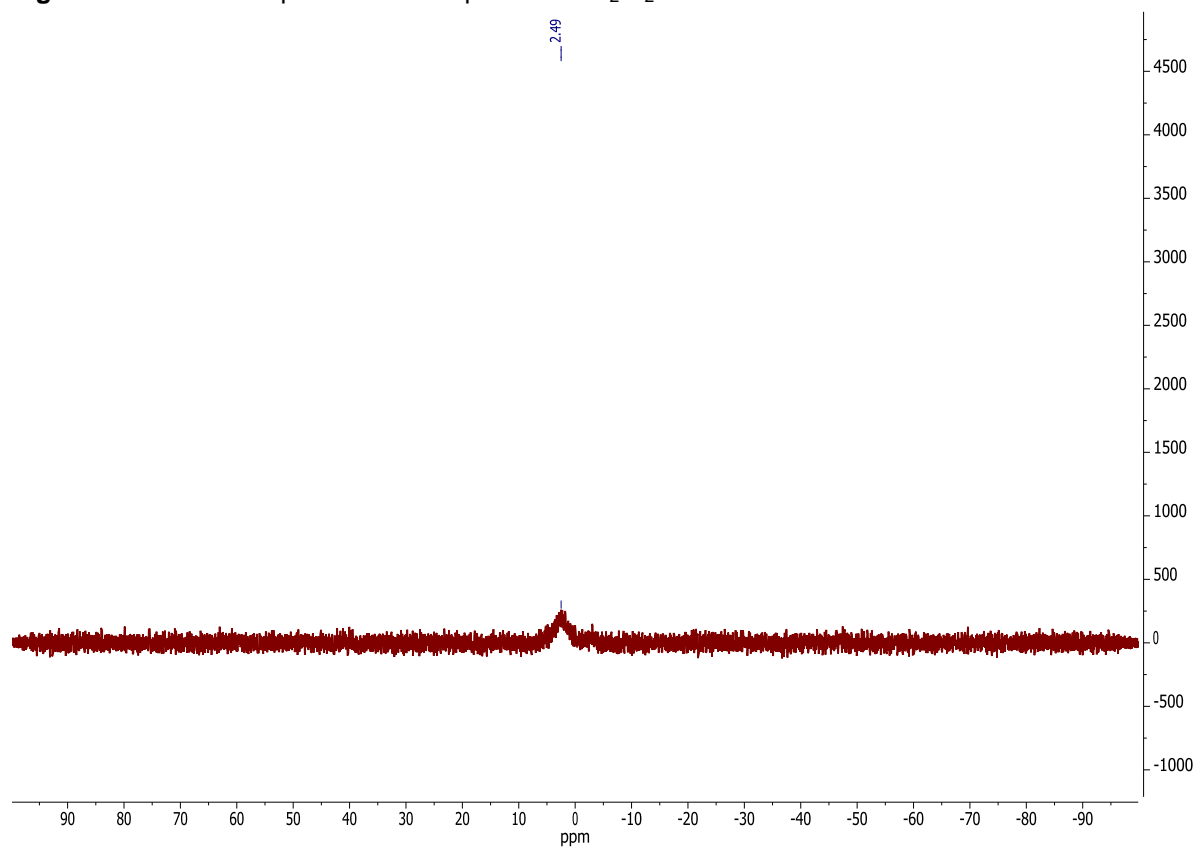


Figure S12. ^{11}B NMR spectrum of complex **2** in CD_2Cl_2 .

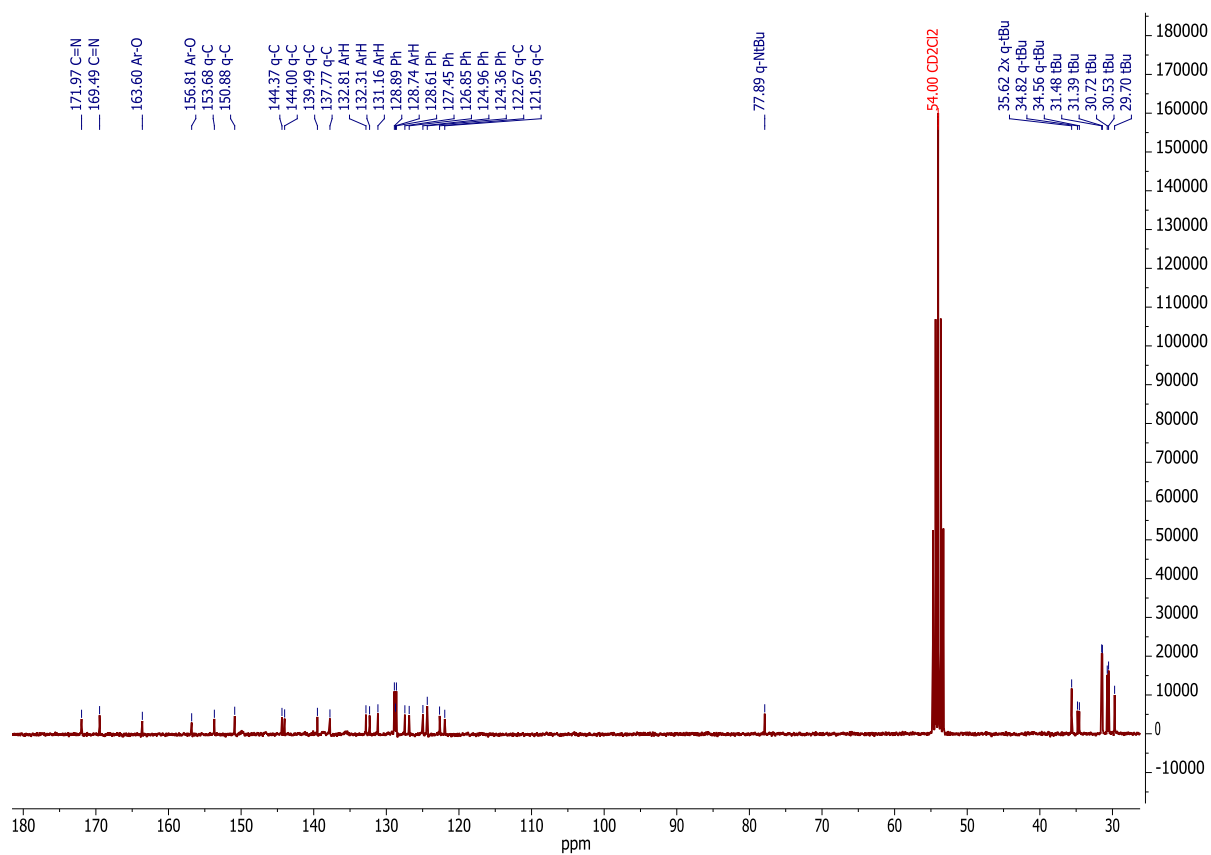


Figure S13. ^{13}C NMR spectrum of complex **2** in CD_2Cl_2 .

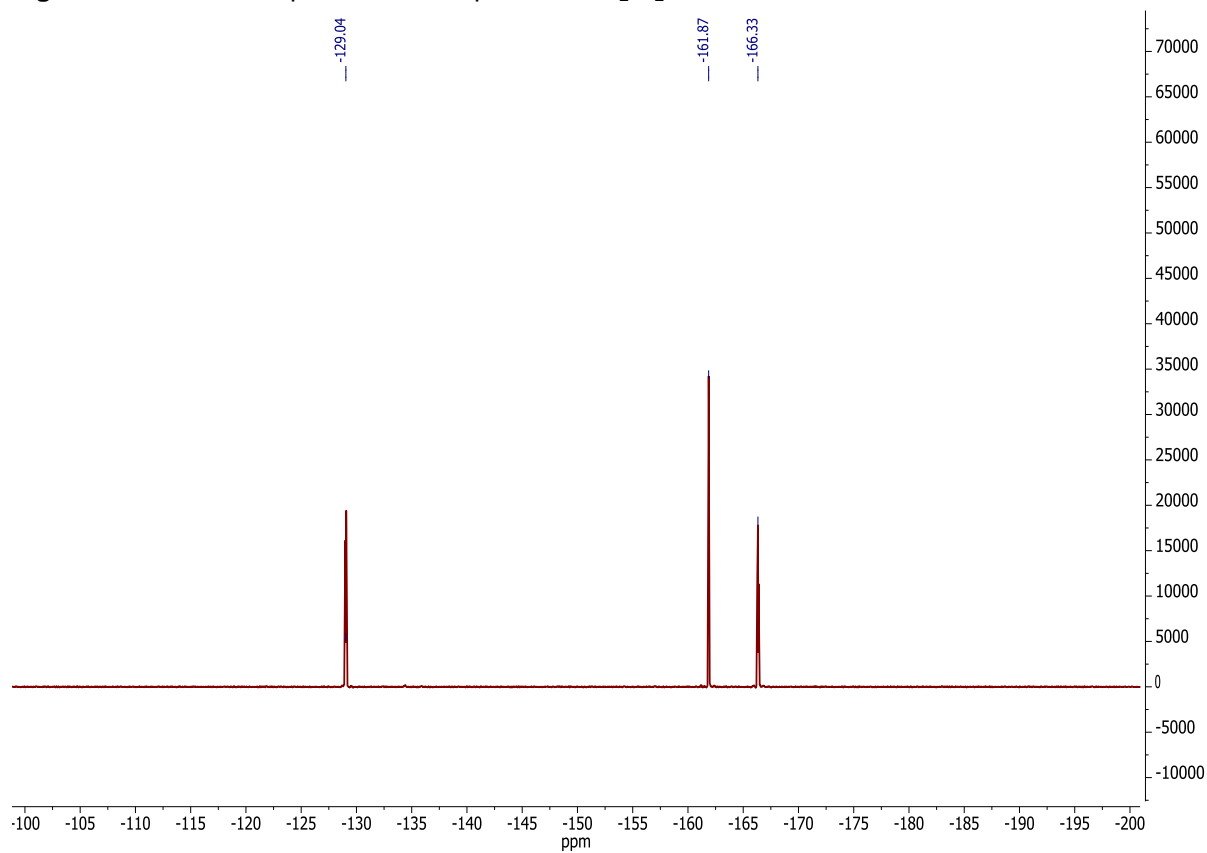


Figure S14. ^{19}F NMR spectrum of complex **2** in CD_2Cl_2 .

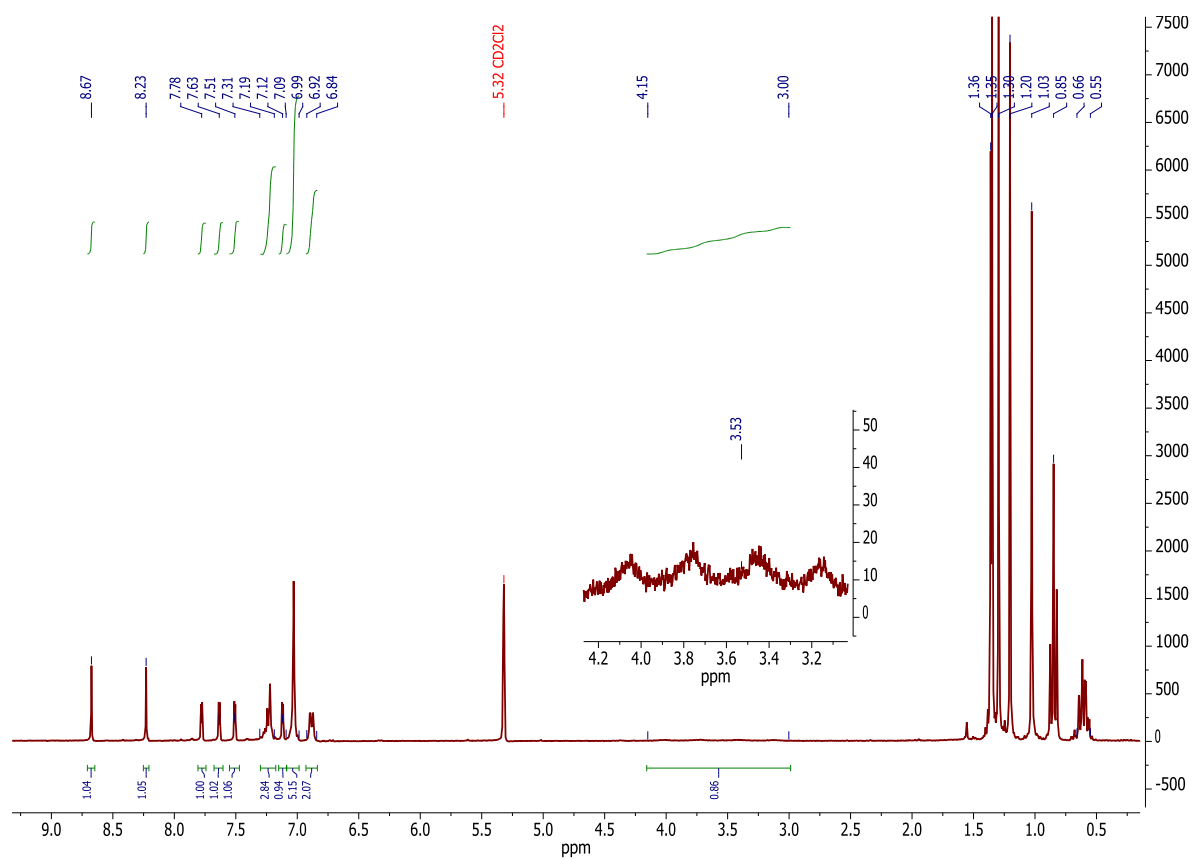


Figure S15. ¹H NMR spectrum of complex **3a** in CD₂Cl₂.

¹¹B NMR (96 MHz, Methylene Chloride-d₂) δ -25.44 (d, J = 89.9 Hz).

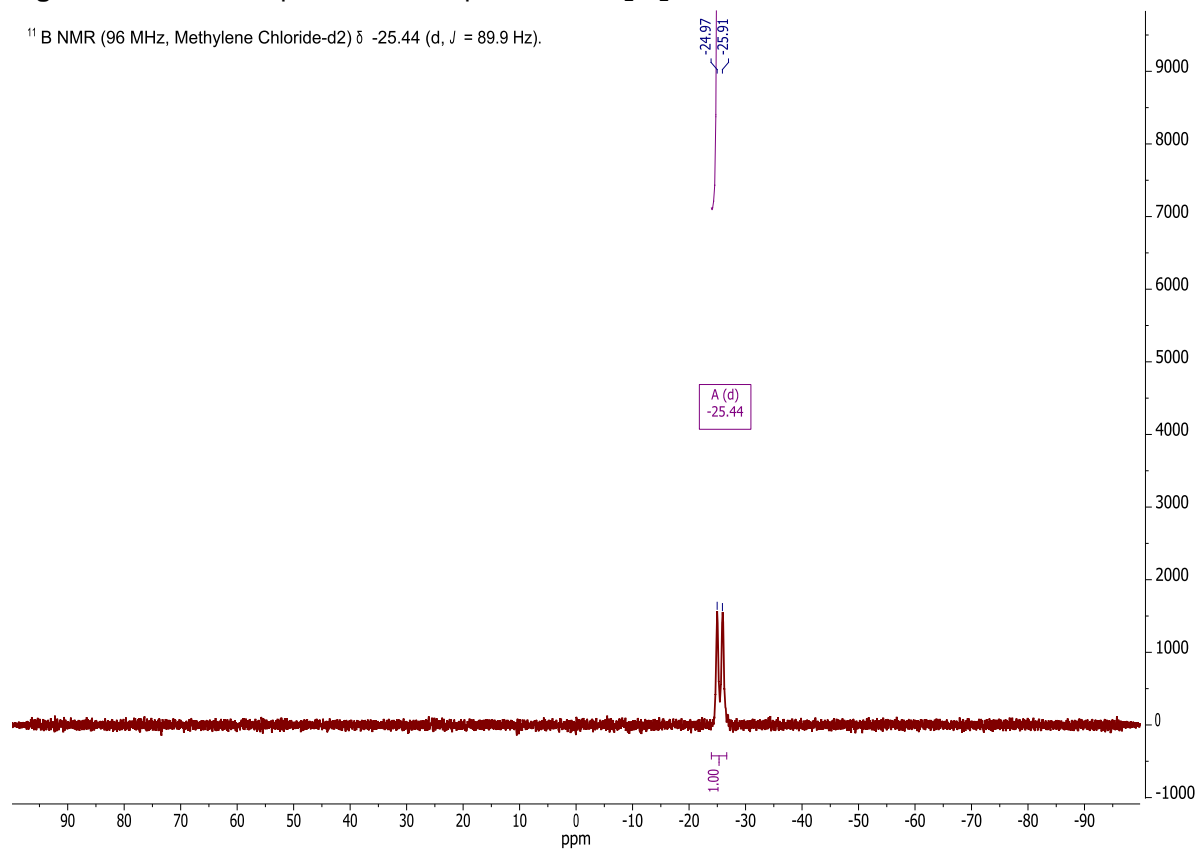


Figure S16. ¹¹B NMR spectrum of complex **3a** in CD₂Cl₂.

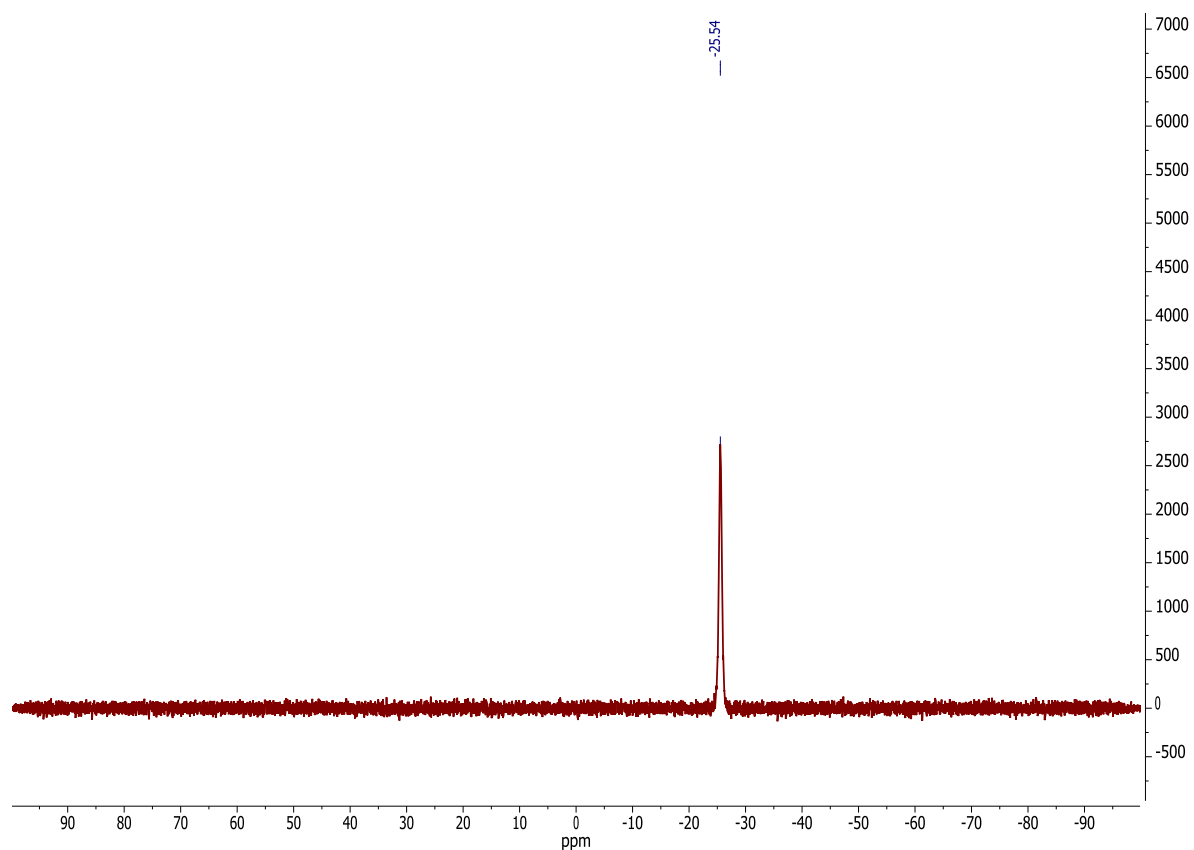


Figure S17. ^{11}B NMR spectrum of complex **3a-d₁** in CD_2Cl_2 .

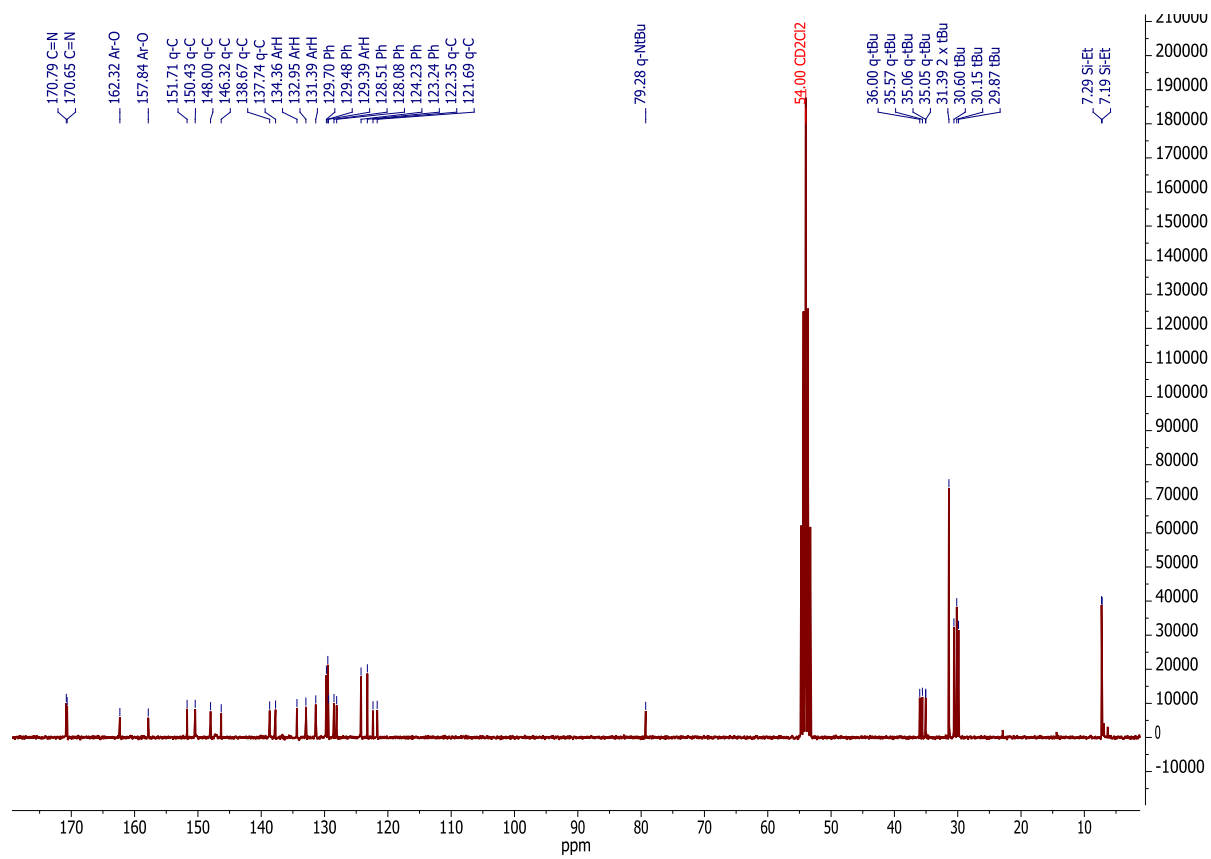


Figure S18. ^{13}C NMR spectrum of complex **3a** in CD_2Cl_2 .

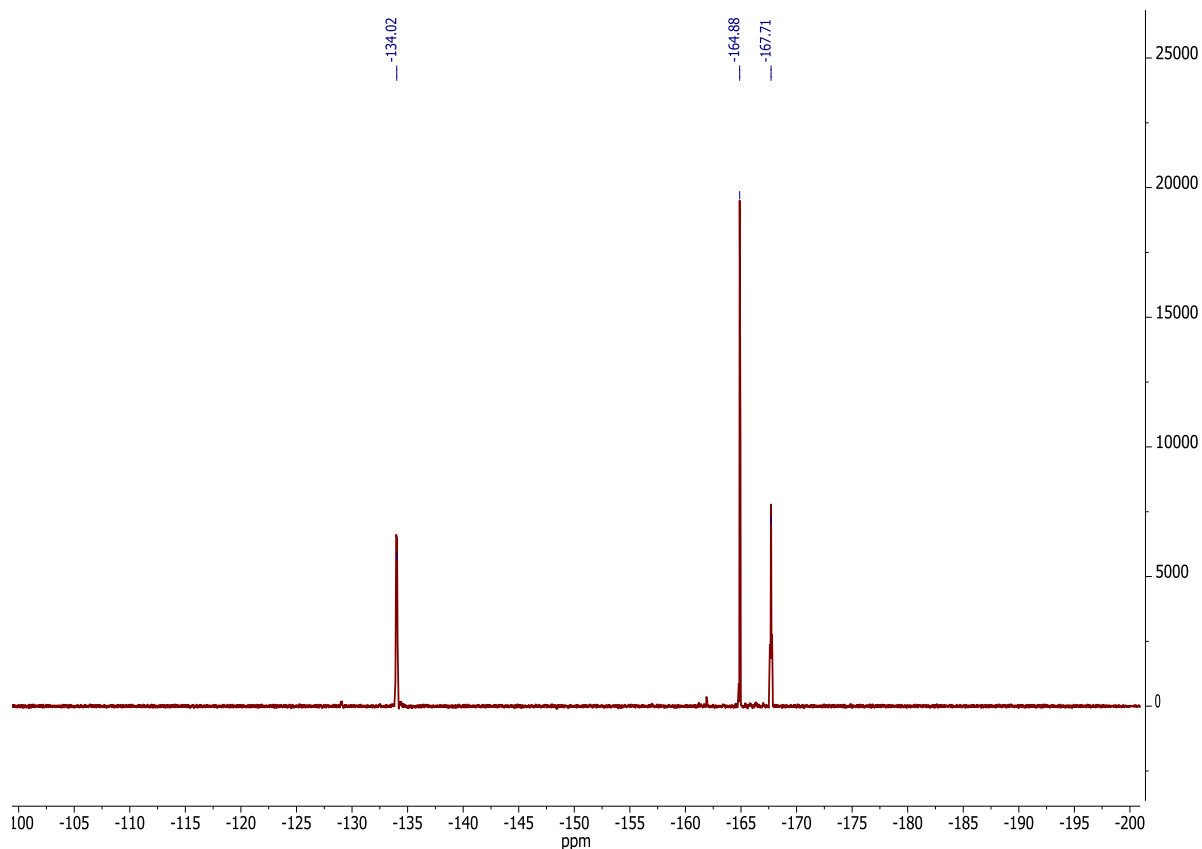


Figure S19. ^{19}F NMR spectrum of complex **3a** in CD_2Cl_2 .

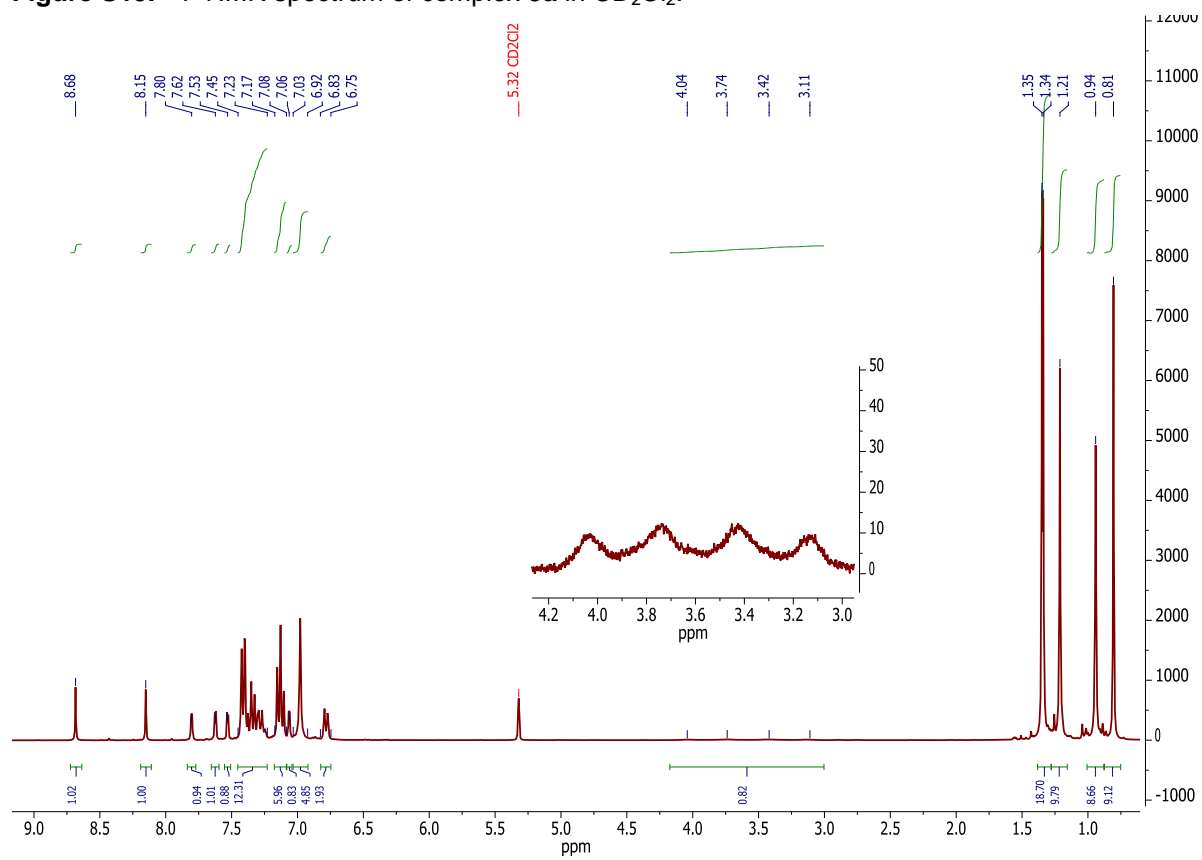


Figure S20. ^1H NMR spectrum of complex **3b** in CD_2Cl_2 .

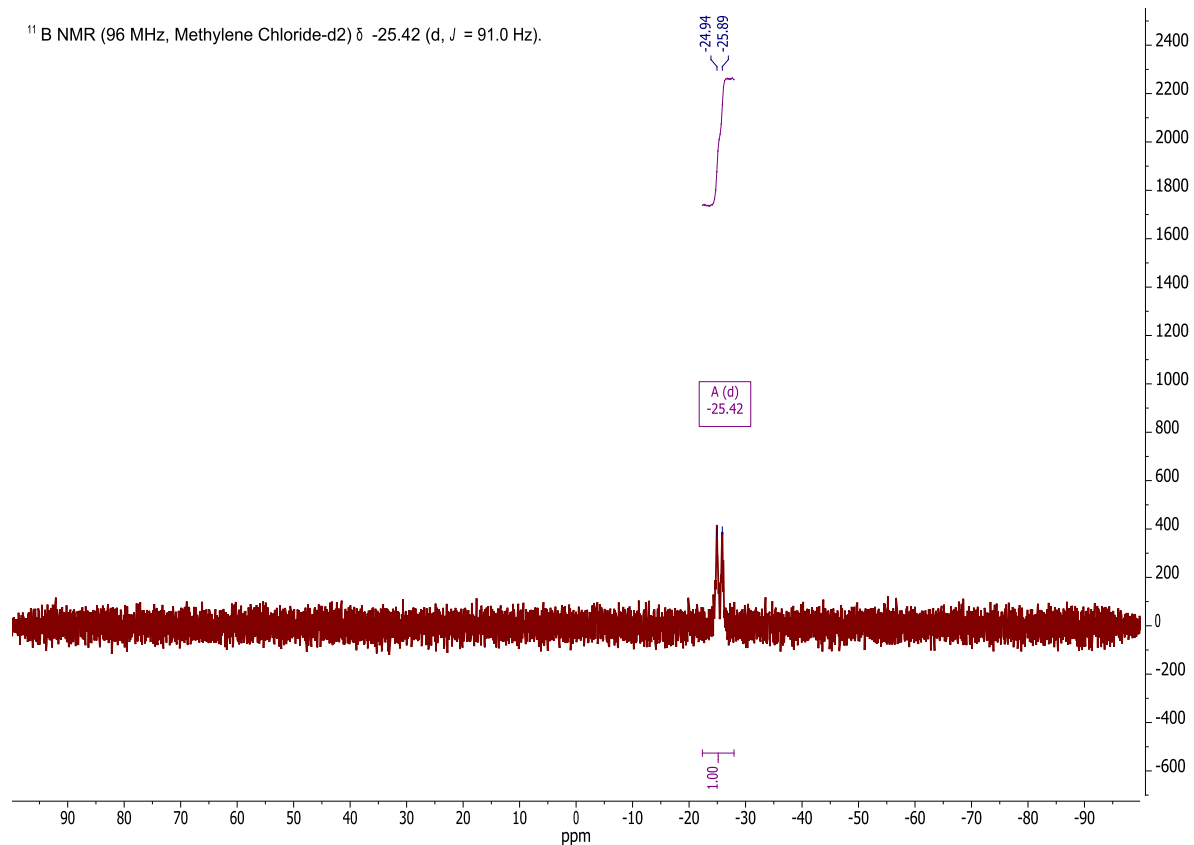


Figure S21. ^{11}B NMR spectrum of complex **3b** in CD_2Cl_2 .

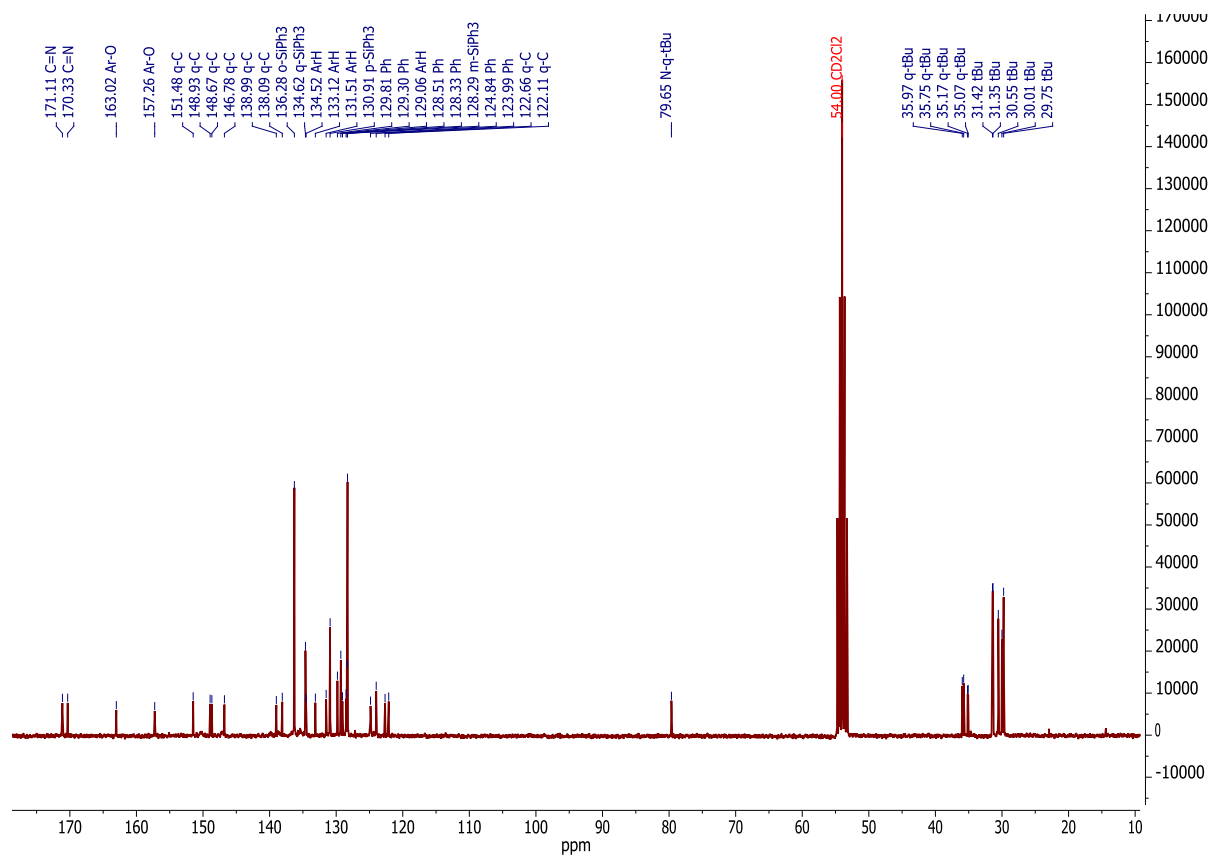


Figure S22. ^{13}C NMR spectrum of complex **3b** in CD_2Cl_2 .

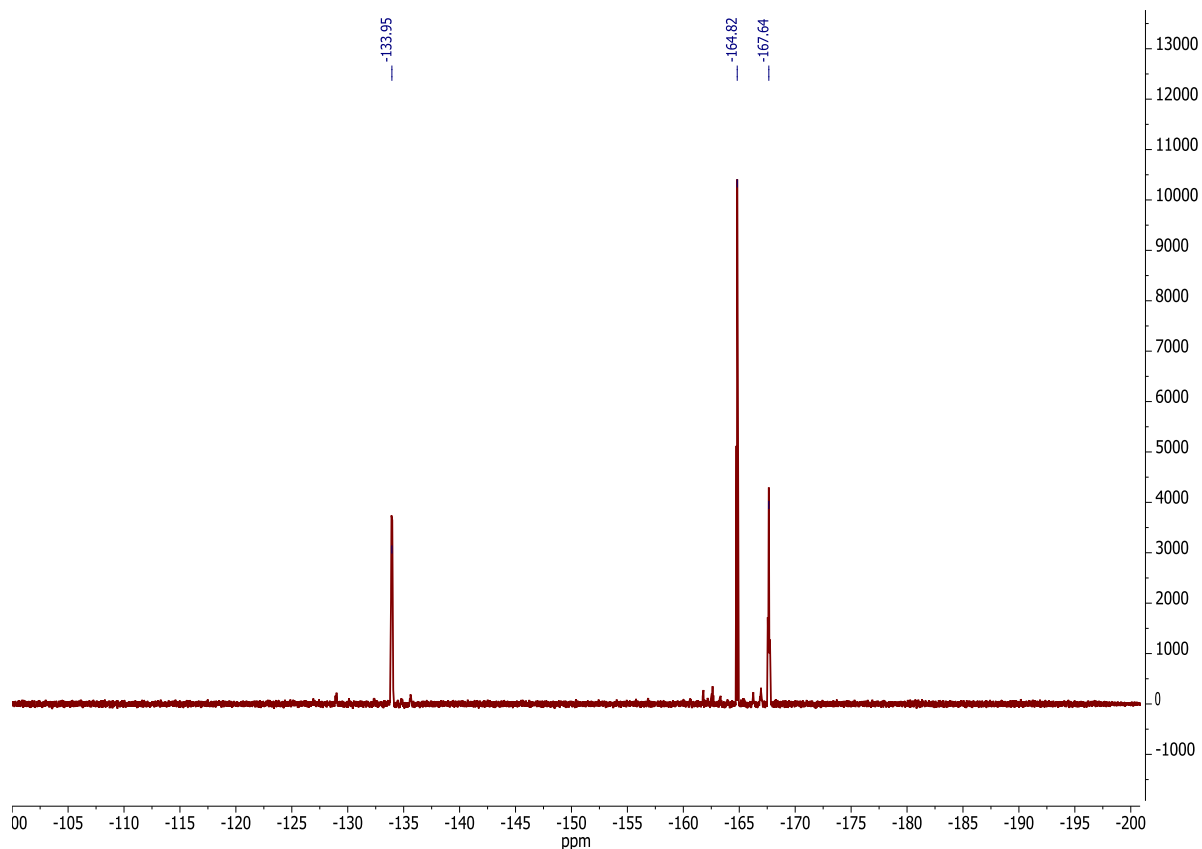


Figure S23. ^{19}F NMR spectrum of complex **3b** in CD_2Cl_2 .

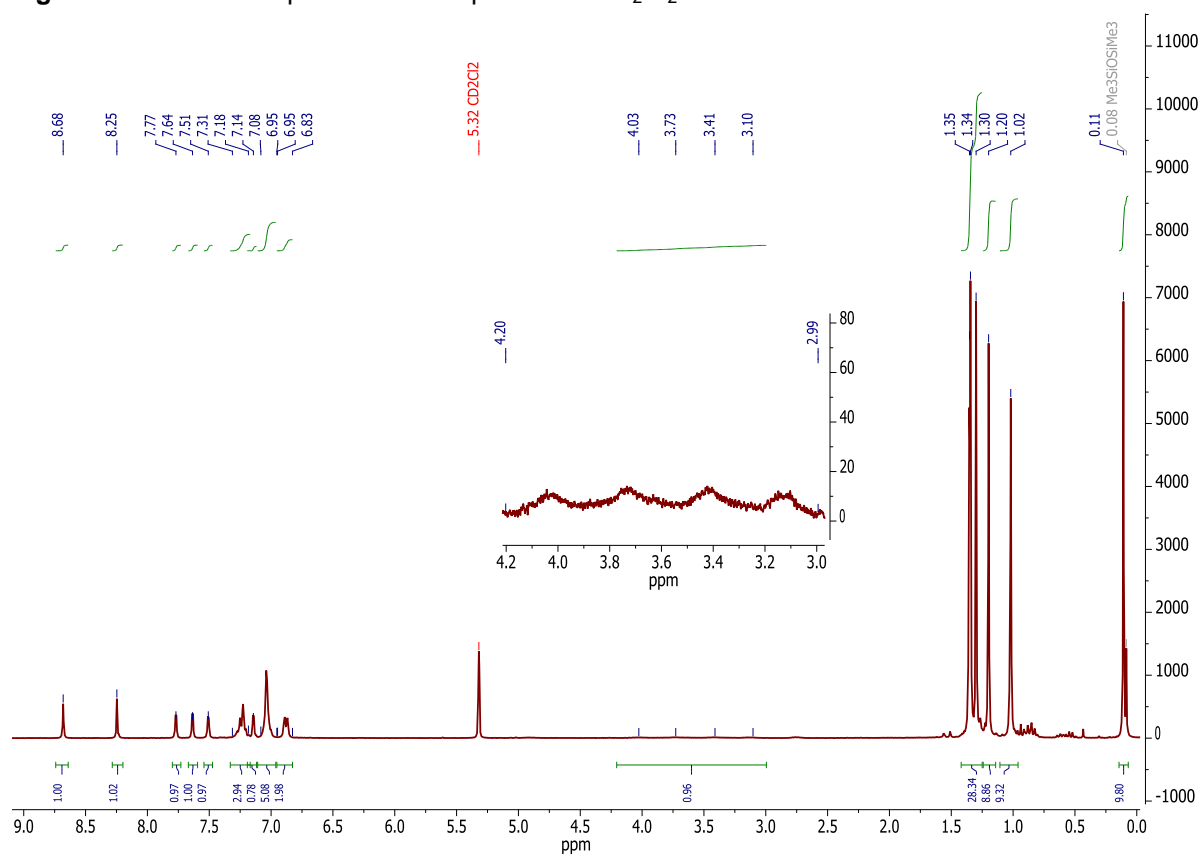


Figure S24. ^1H NMR spectrum of complex **3c** in CD_2Cl_2 .

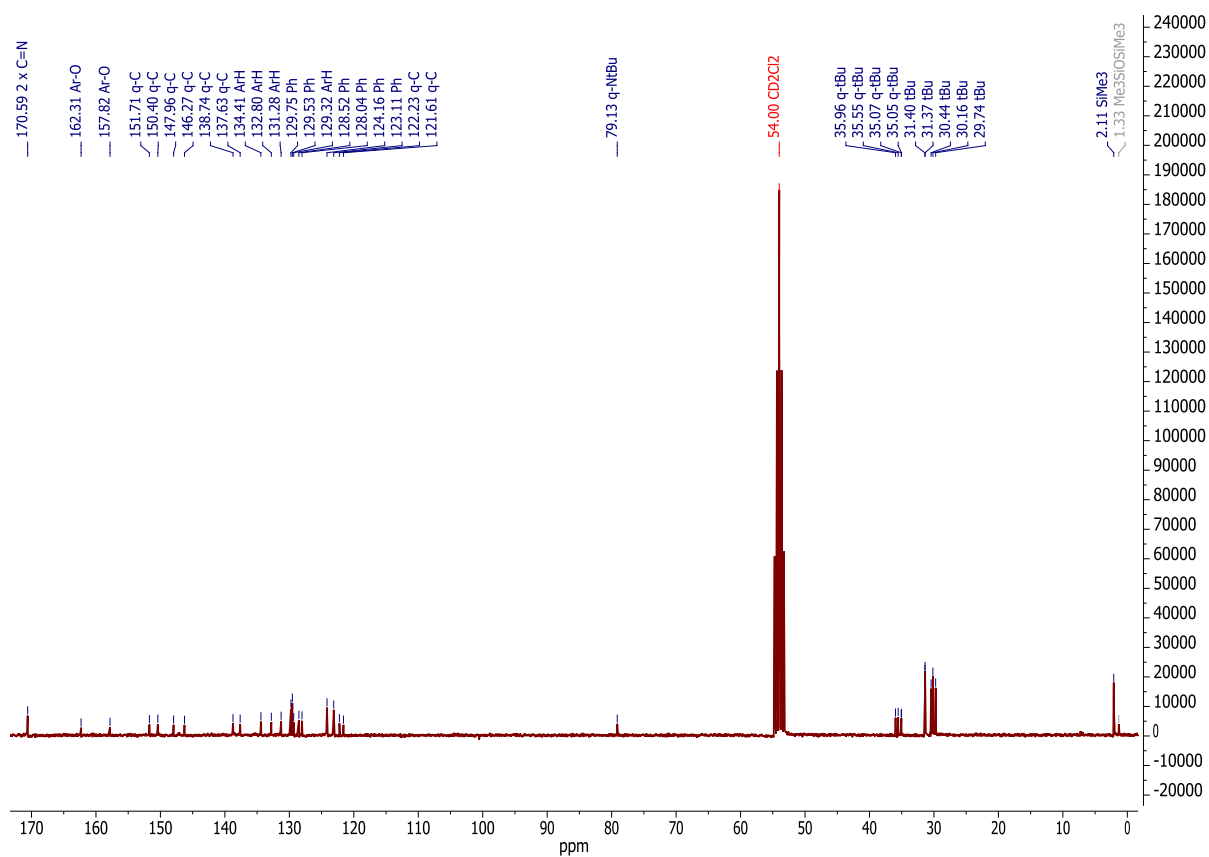


Figure S25. ^{13}C NMR spectrum of complex **3c** in CD_2Cl_2 .

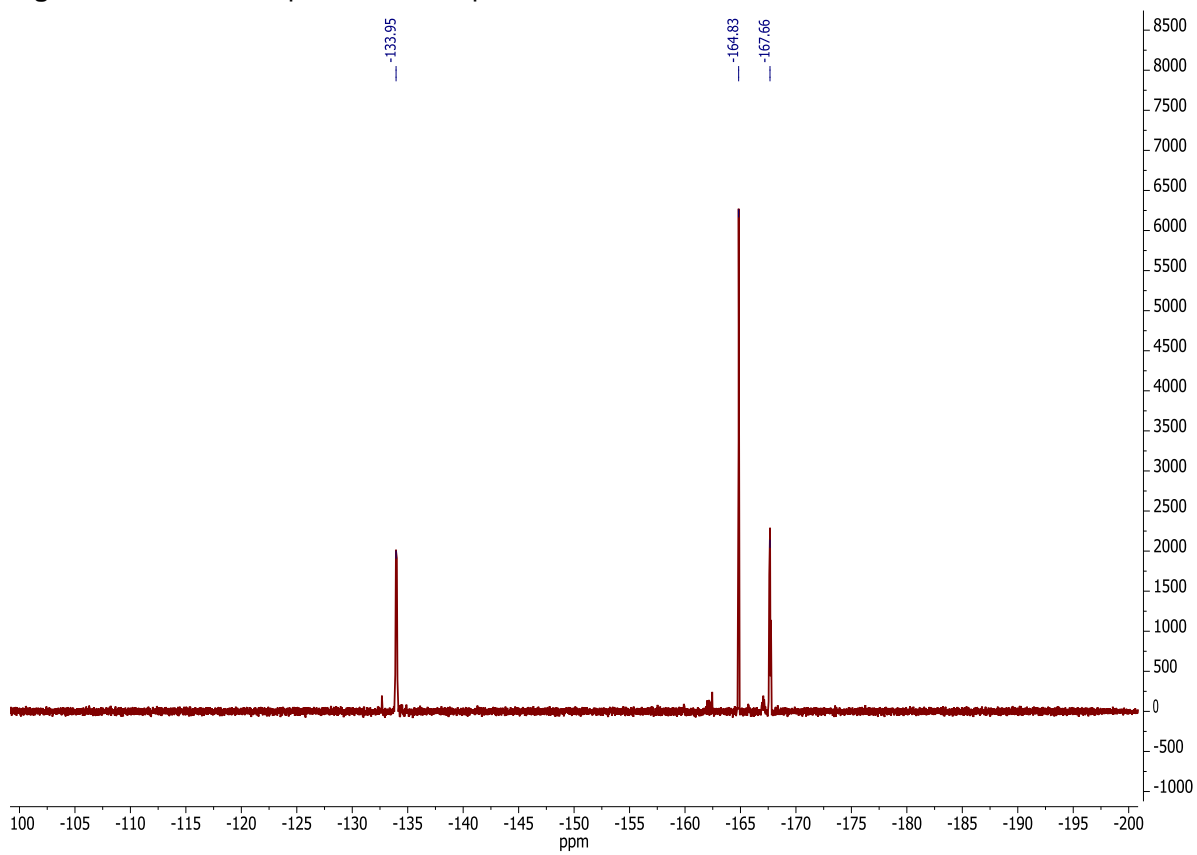


Figure S26. ^{19}F NMR spectrum of complex **3c** in CD_2Cl_2 .

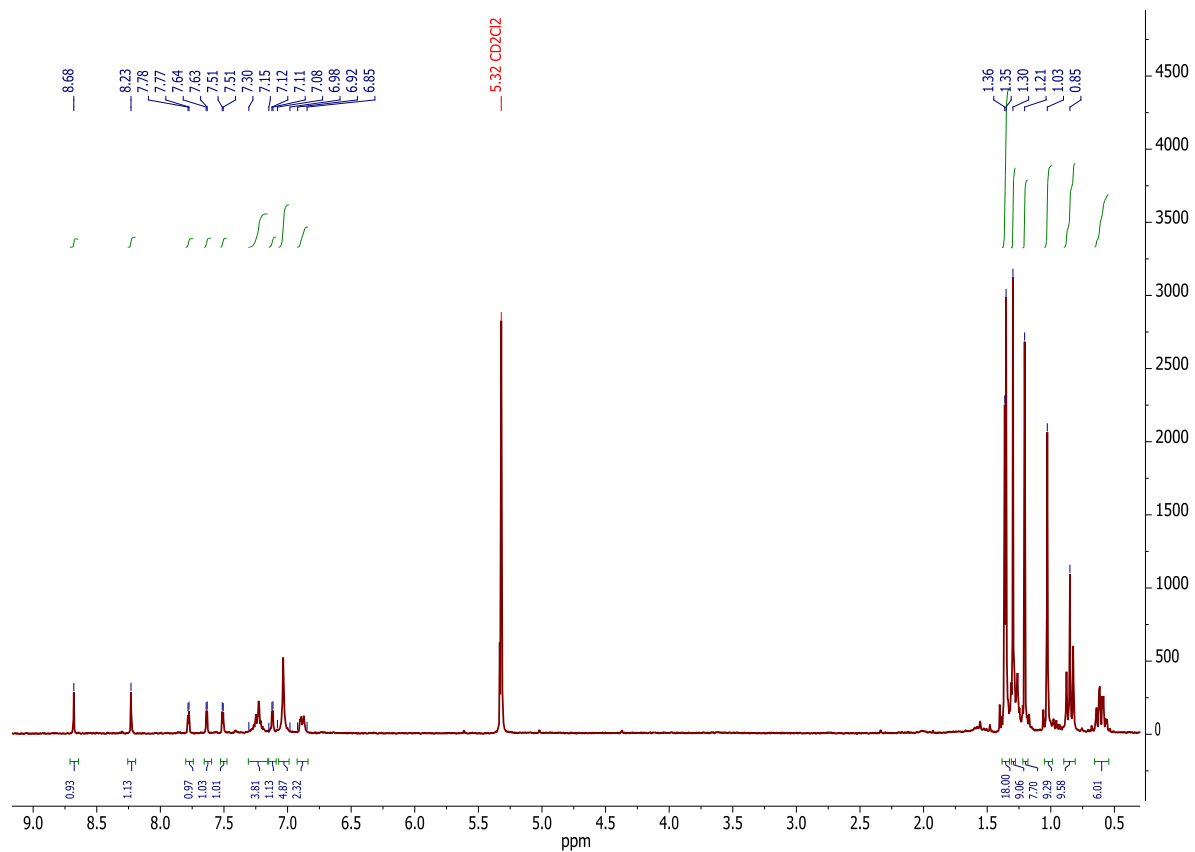


Figure S27. ¹H NMR spectrum of complex 4a in CD₂Cl₂.

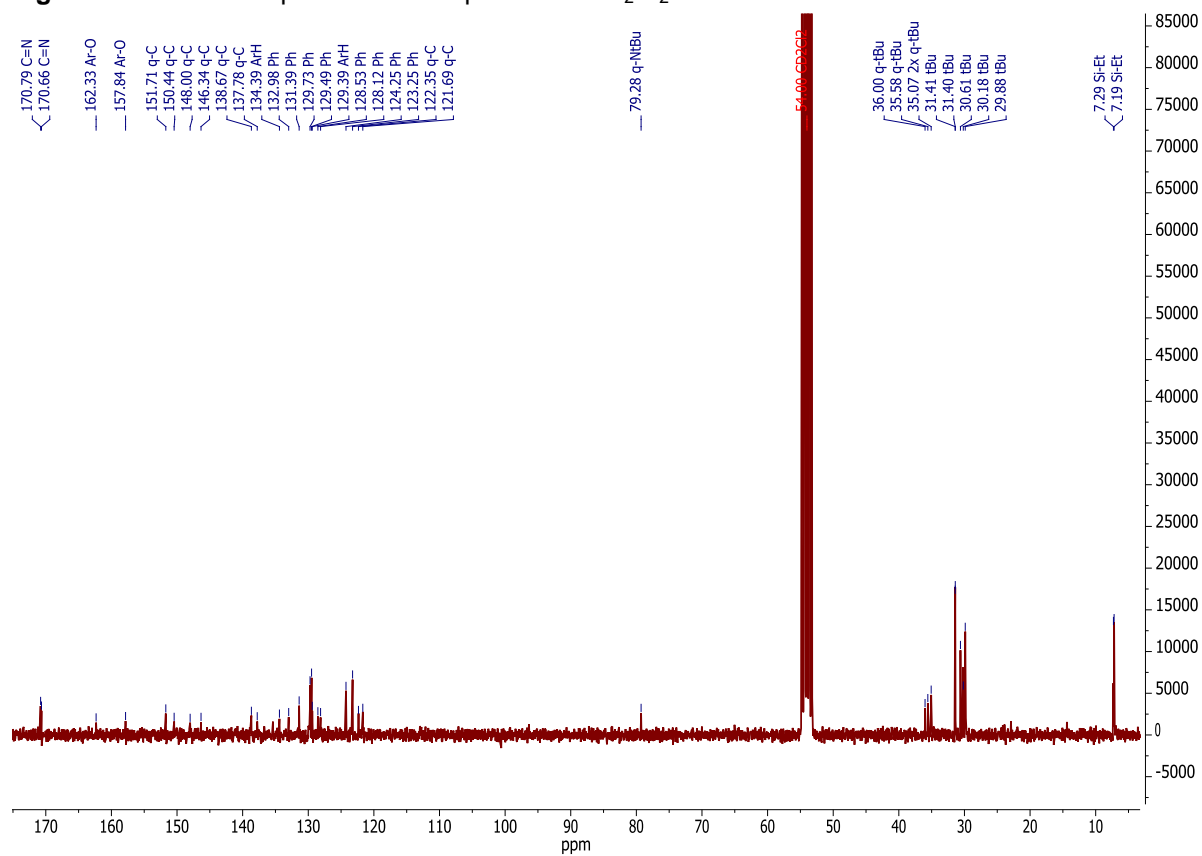


Figure S28. ¹³C NMR spectrum of complex 4a in CD₂Cl₂.

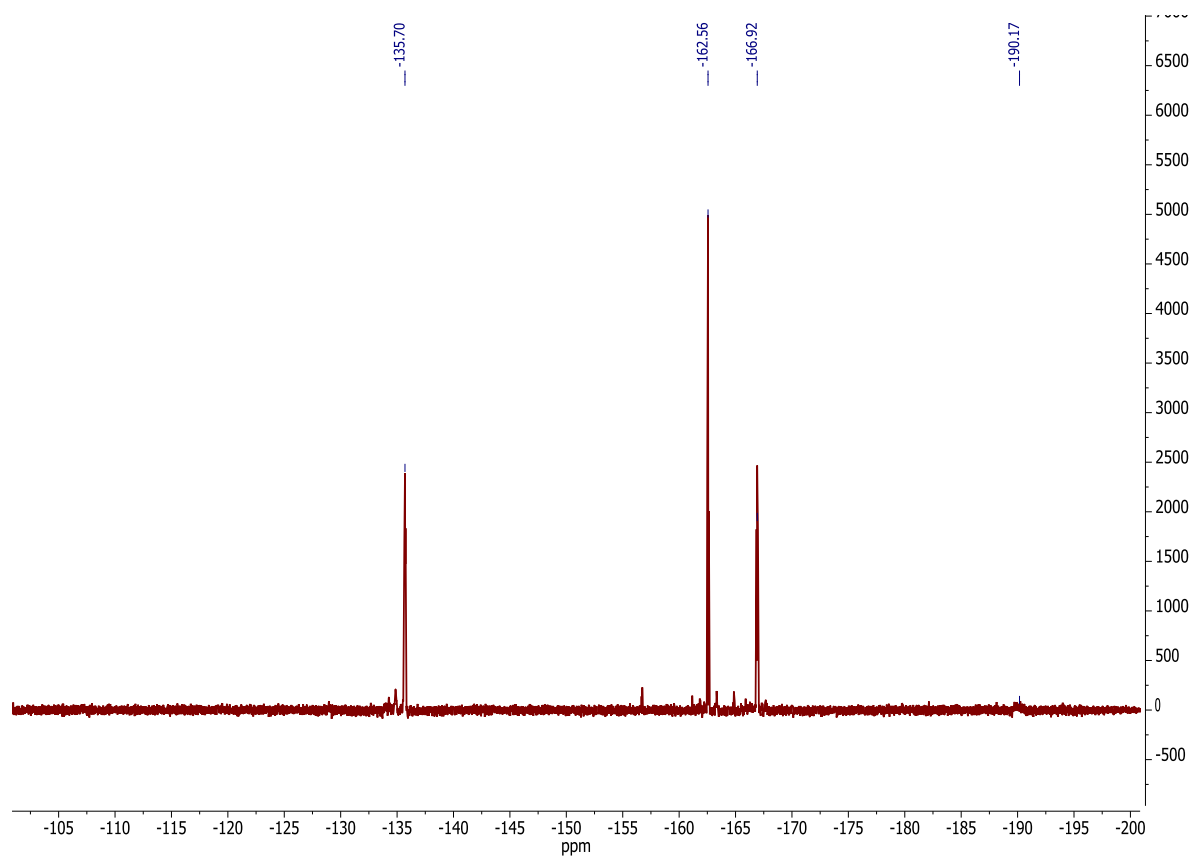


Figure S29. ^{19}F NMR spectrum of complex **4a** in CD_2Cl_2 .

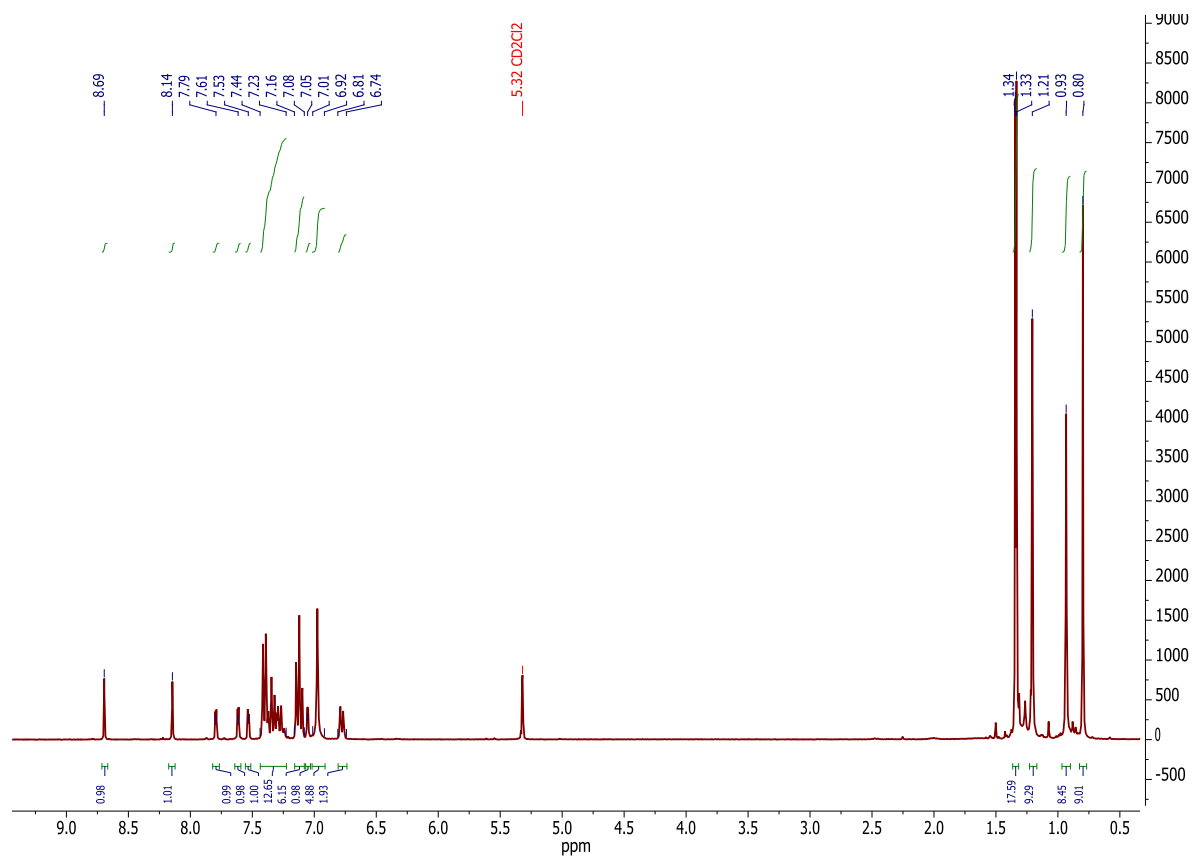


Figure S30. ^1H NMR spectrum of complex **4b** in CD_2Cl_2 .

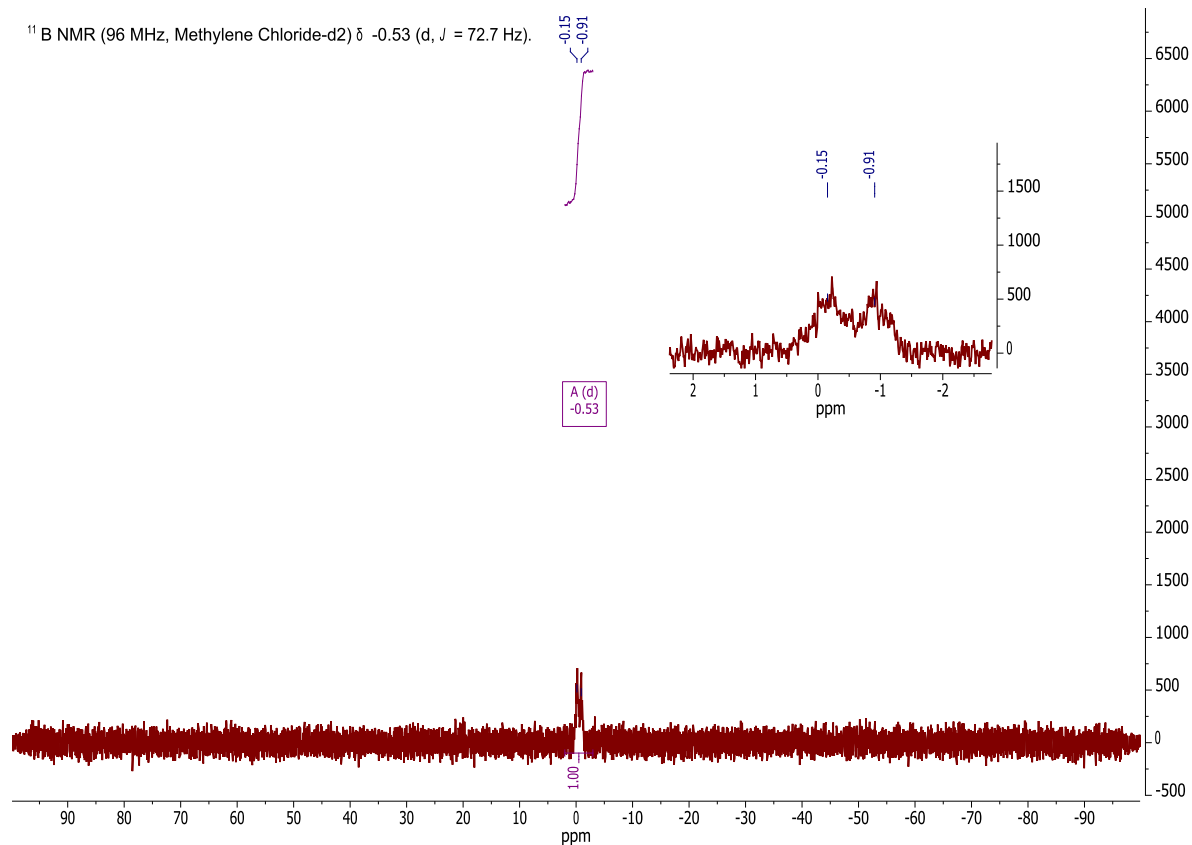


Figure S31. ^{11}B NMR spectrum of complex **4b** in CD_2Cl_2 .

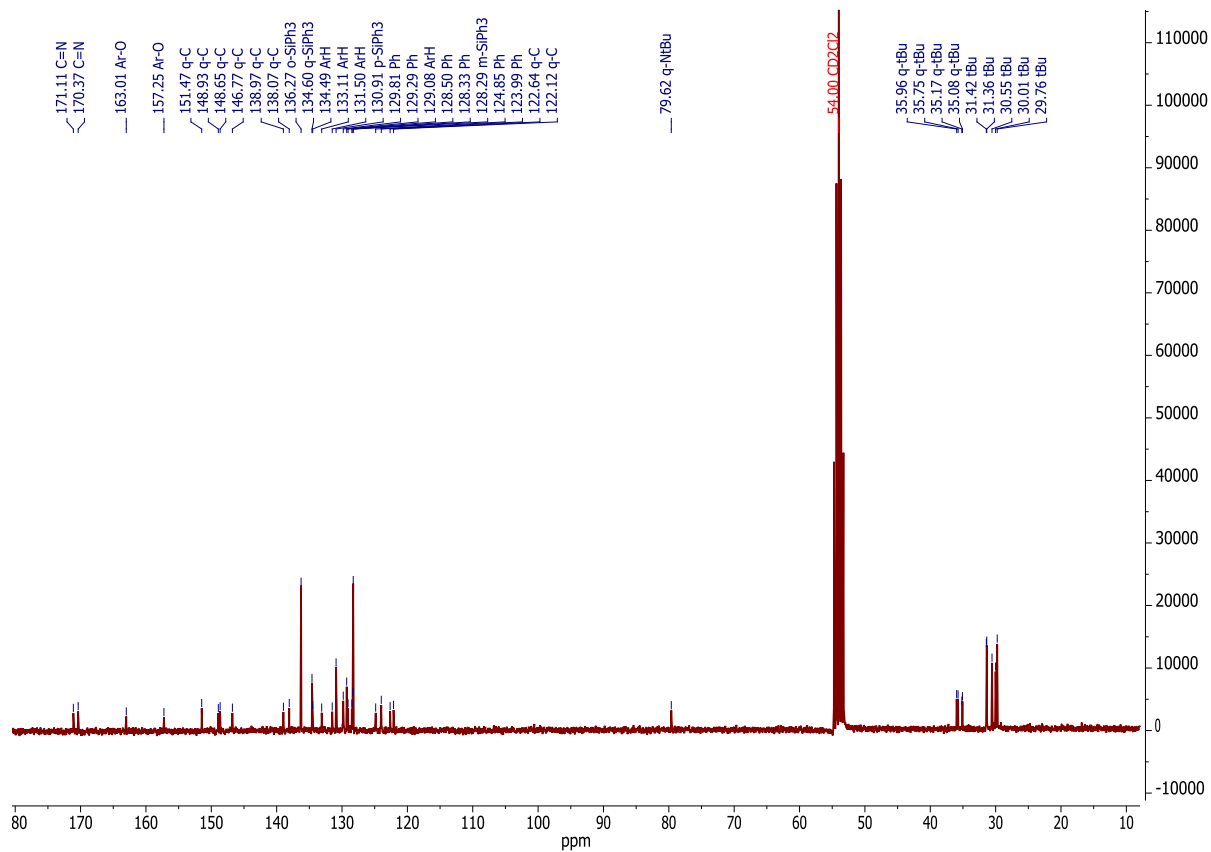


Figure S32. ^{13}C NMR spectrum of complex **4b** in CD_2Cl_2 .

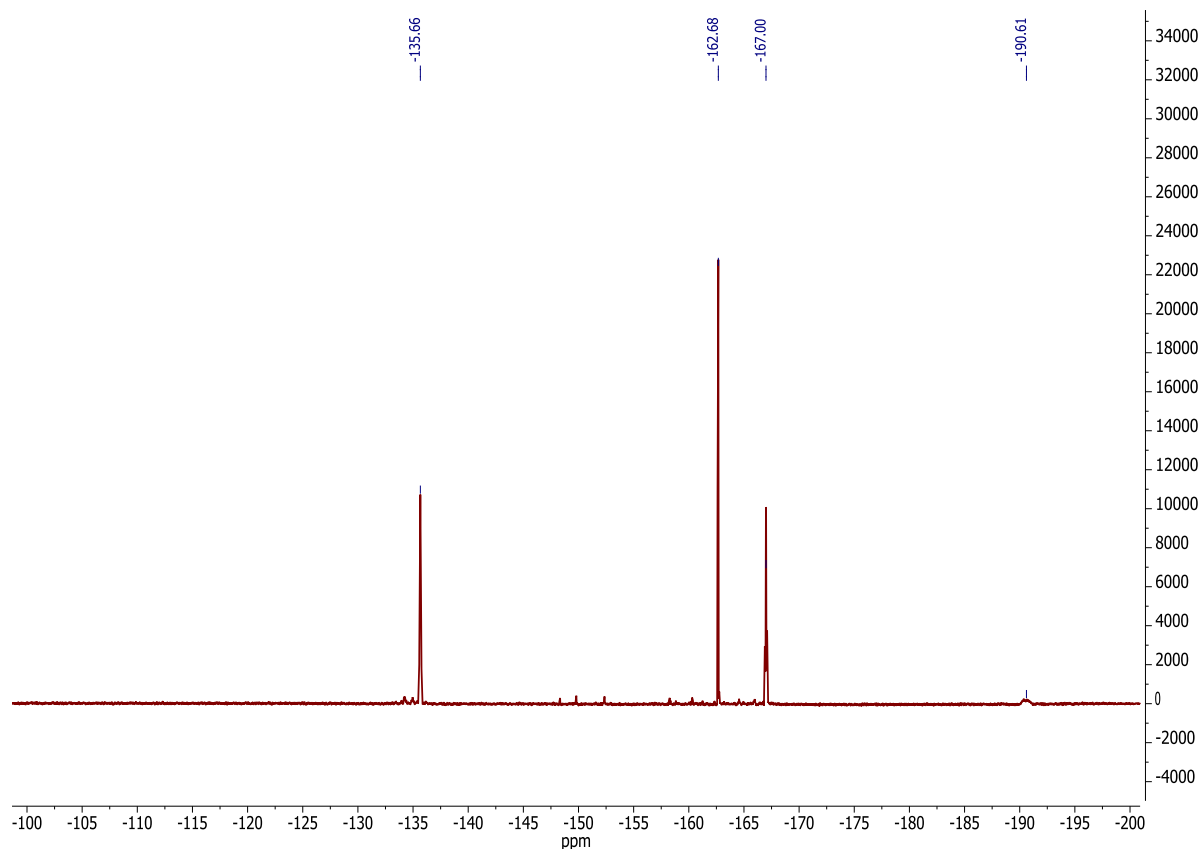


Figure S33. ^{19}F NMR spectrum of complex **4b** in CD_2Cl_2 .

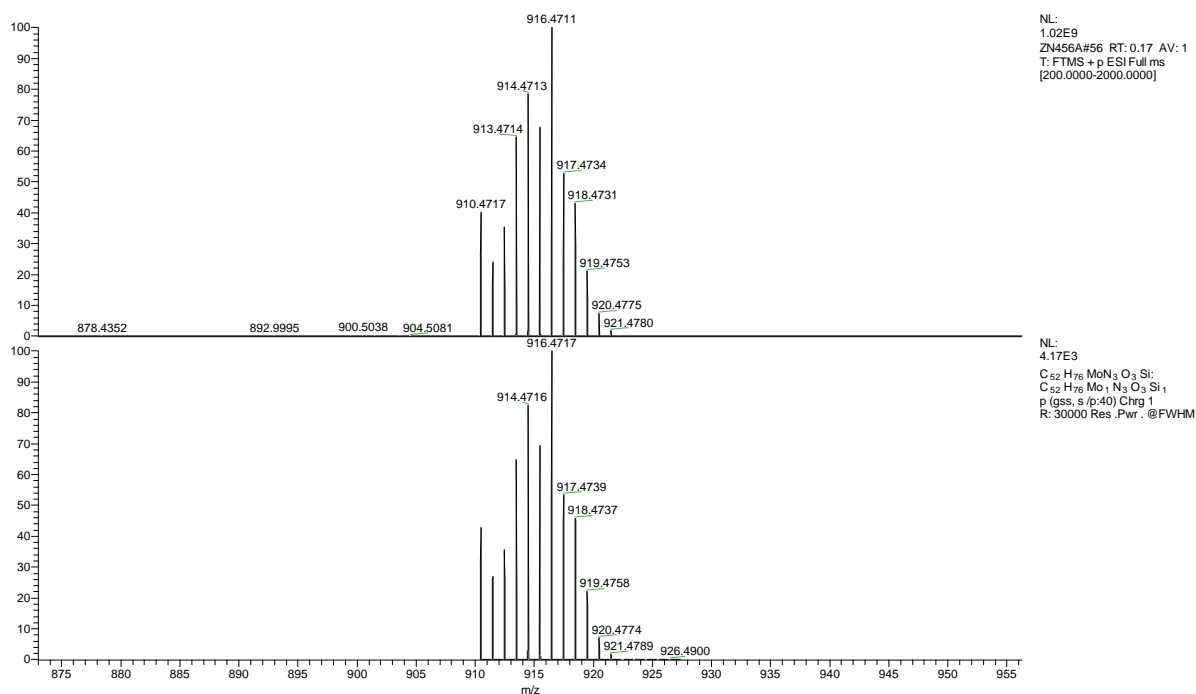


Figure S34. ESI-MS (positive mode) spectrum for **3a**, showing the peak for $[\text{Mo}(\text{OSiEt}_3)(\text{NtBu})]^+$ with the correct isotope pattern.

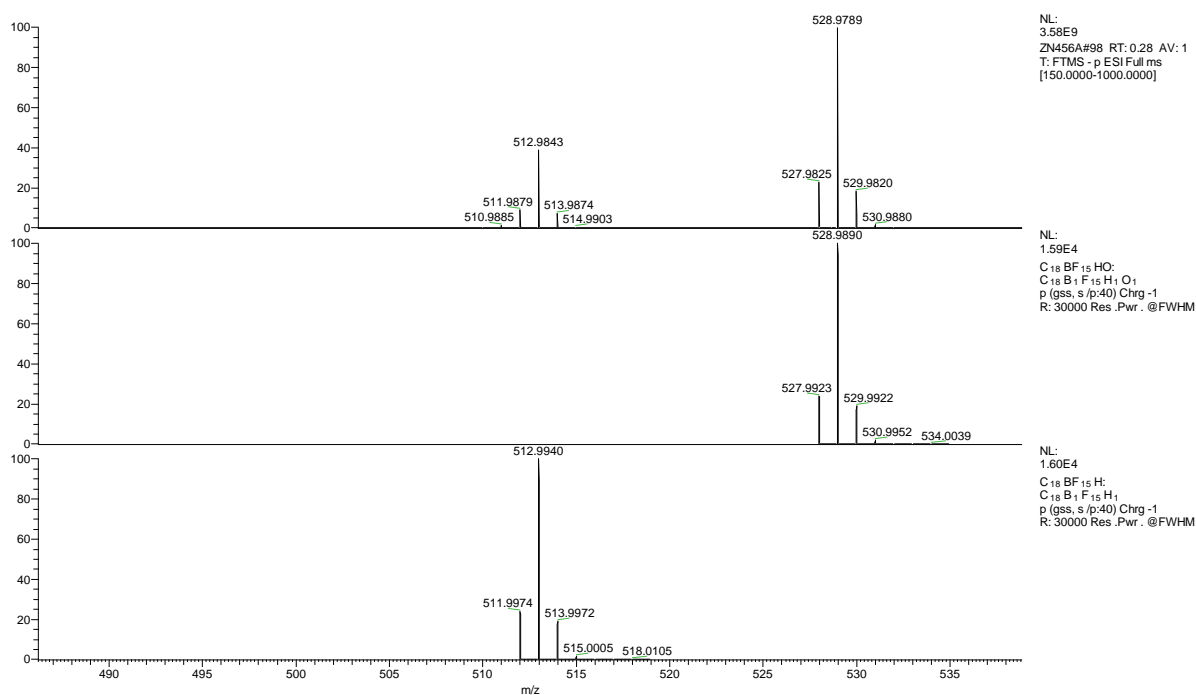


Figure S35. ESI-MS (negative mode) spectrum for **3a**, showing peaks for $[\text{HB}(\text{C}_6\text{F}_5)_3]^-$ and $[\text{HOB}(\text{C}_6\text{F}_5)_3]^-$, the latter presumably originating from a reaction with adventitious water in the sample.

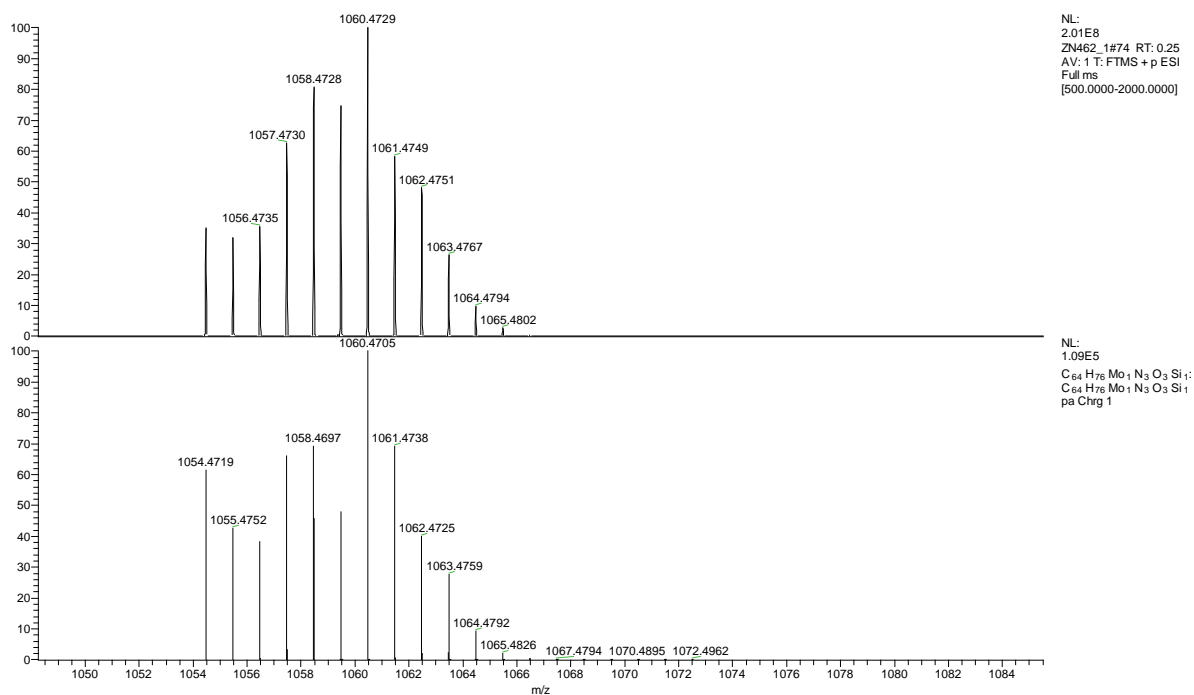


Figure S36. ESI-MS (positive mode) spectrum for **3b**, showing the peak for $[\text{Mo}(\text{OSiPh}_3)(\text{NtBu})]^+$ with the correct isotope pattern.

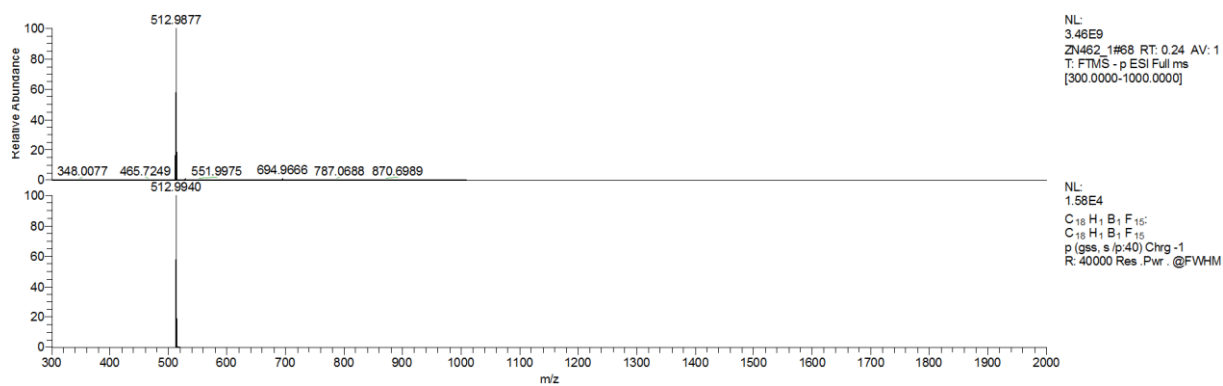


Figure S37. ESI-MS (negative mode) spectrum for **3b**, showing the peak for $[\text{HB}(\text{C}_6\text{F}_5)_3]^-$.

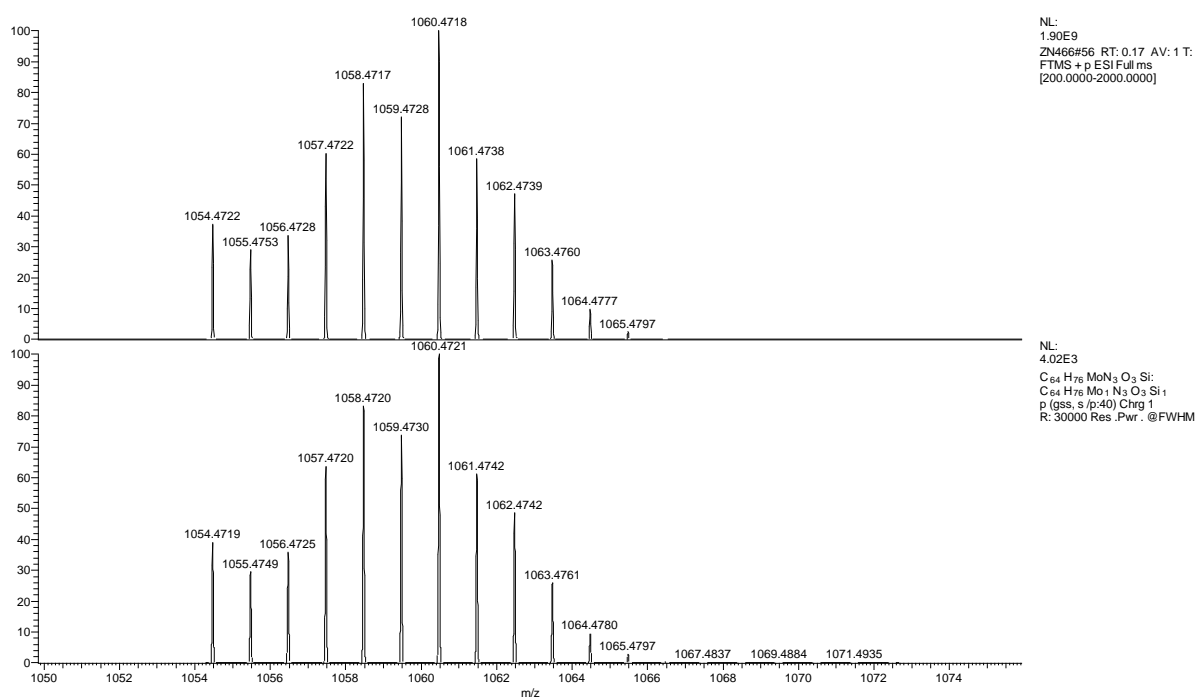


Figure S38. ESI-MS (positive mode) spectrum for **4b**, showing the peak for $[\text{Mo}(\text{OSiPh}_3)(\text{NtBu})]^+$ with the correct isotope pattern.

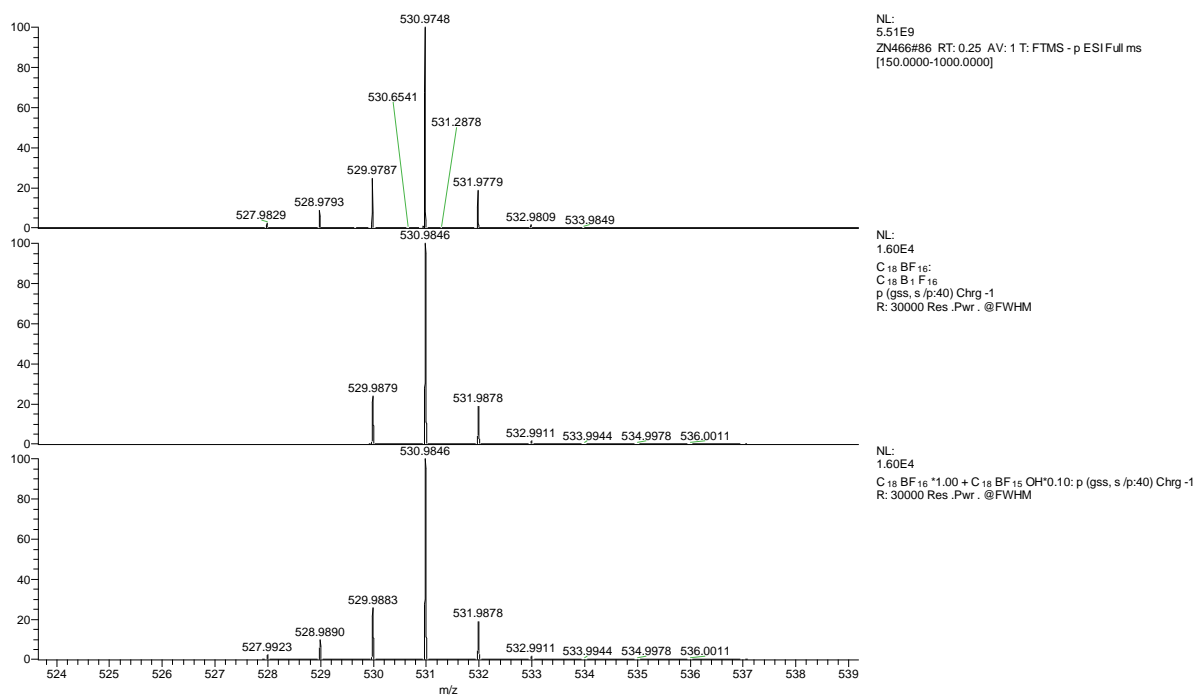


Figure S39. ESI-MS (negative mode) spectrum for **4b**, showing a peak for $[\text{FB}(\text{C}_6\text{F}_5)_3]^-$, accompanied by a small amount of $[\text{HOB}(\text{C}_6\text{F}_5)_3]^-$, the latter presumably originating from a reaction with adventitious water in the sample.

Electrochemistry data of the compounds

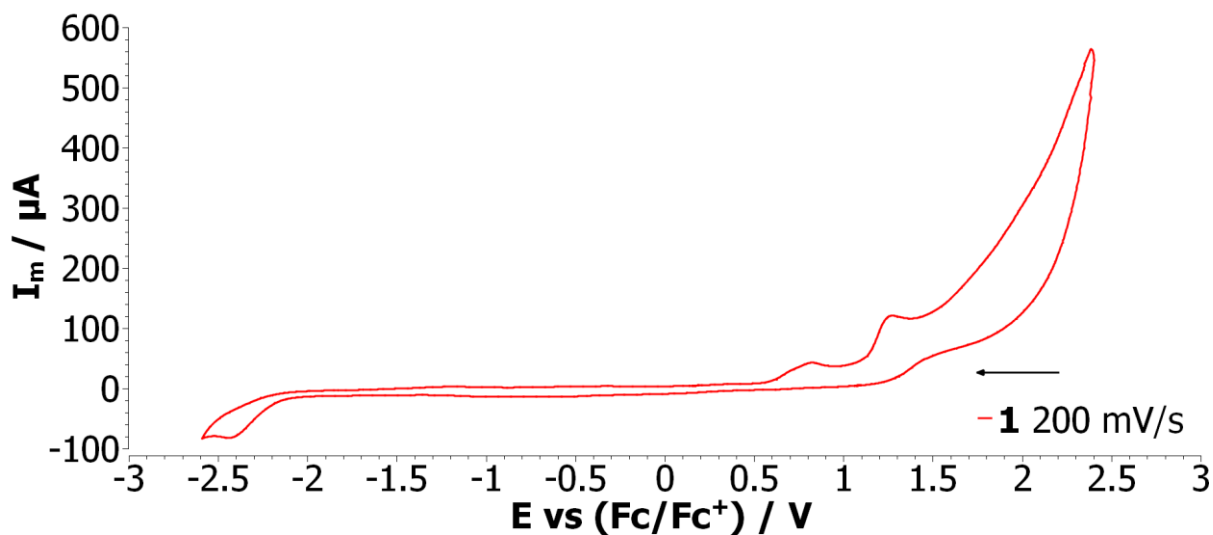


Figure S40. Full sweep-width cyclic voltammogram of complex **1**^[1] in MeCN.

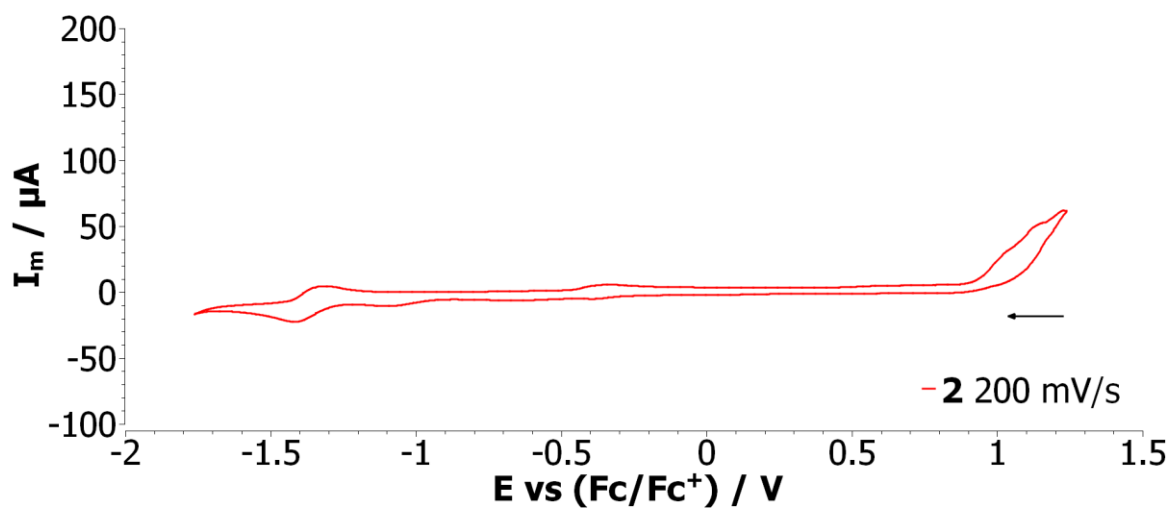


Figure S41. Full sweep-width cyclic voltammogram of complex **2** in CH_2Cl_2 .

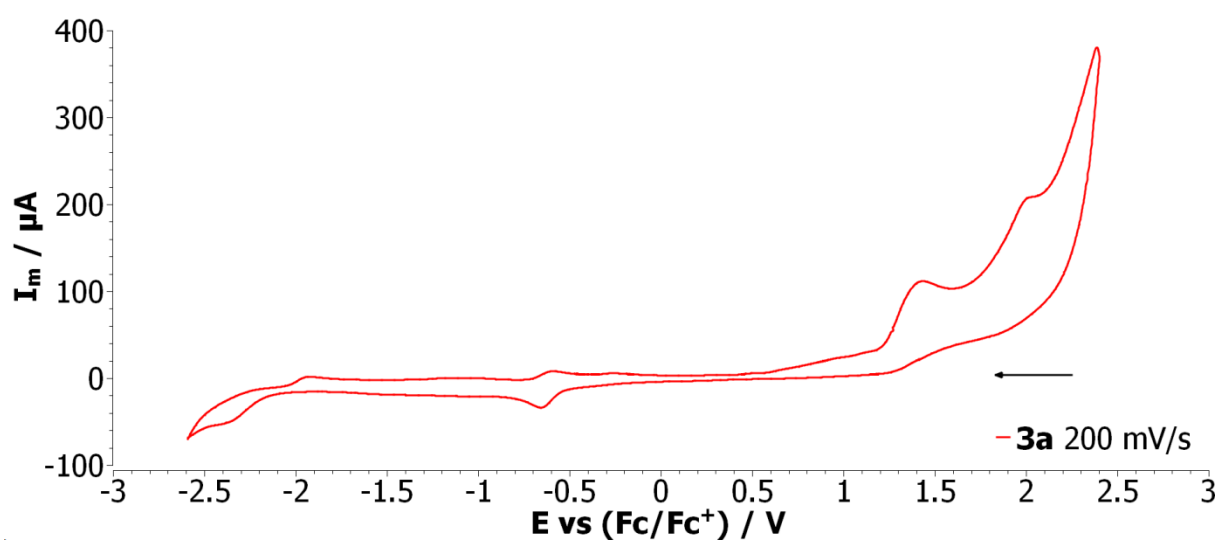


Figure S42. Full sweep-width cyclic voltammogram of complex **3a** in MeCN.

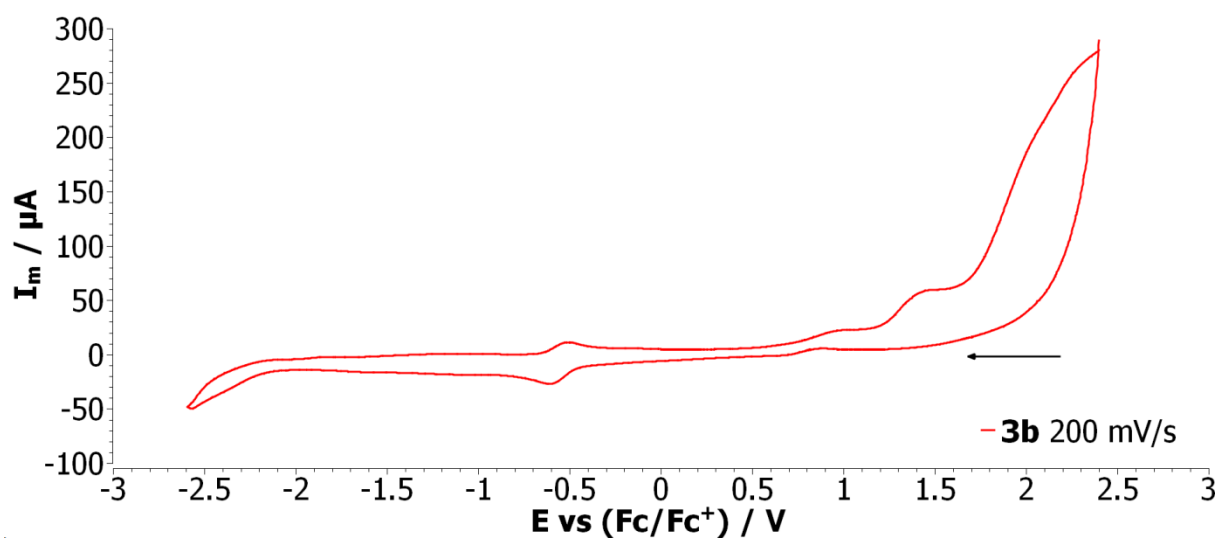


Figure S43. Full sweep-width cyclic voltammogram of complex **3b** in MeCN.

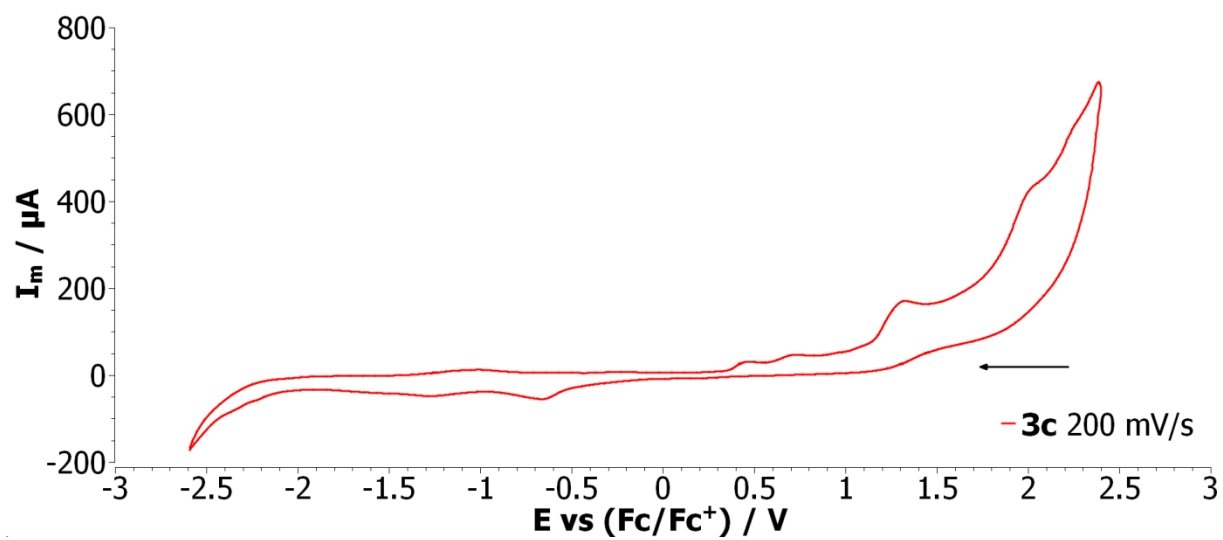


Figure S44. Full sweep-width cyclic voltammogram of complex **3c** in MeCN.

Crystallographic data for 2 and 4b

Crystal structure determination of 2. The structure was solved by direct methods (SHELXS-97)^[3] and refined by full-matrix least-squares techniques against F^2 (SHELXL-2014/6).^[4] The non-hydrogen atoms of the two complexes of the asymmetric unit were refined with anisotropic displacement parameters without any constraints. The H atoms of the phenyl rings including any adjacent CH=N groups were put at the external bisectors of the C–C–C angles at C–H distances of 0.95Å and common isotropic displacement parameters were refined for the H atoms of the same ring. The H atoms of the *tert*-butyl groups were refined with common isotropic displacement parameters for the H atoms of the same group and idealized geometries with tetrahedral angles, enabling rotation around the C–C bonds, and C–H distances of 0.98Å. For 809 parameters final R indices of $R_1 = 0.0360$ and $wR^2 = 0.0900$ (GOF = 1.028) were obtained. The largest peak in a difference Fourier map was $0.807\text{e}\text{\AA}^{-3}$.

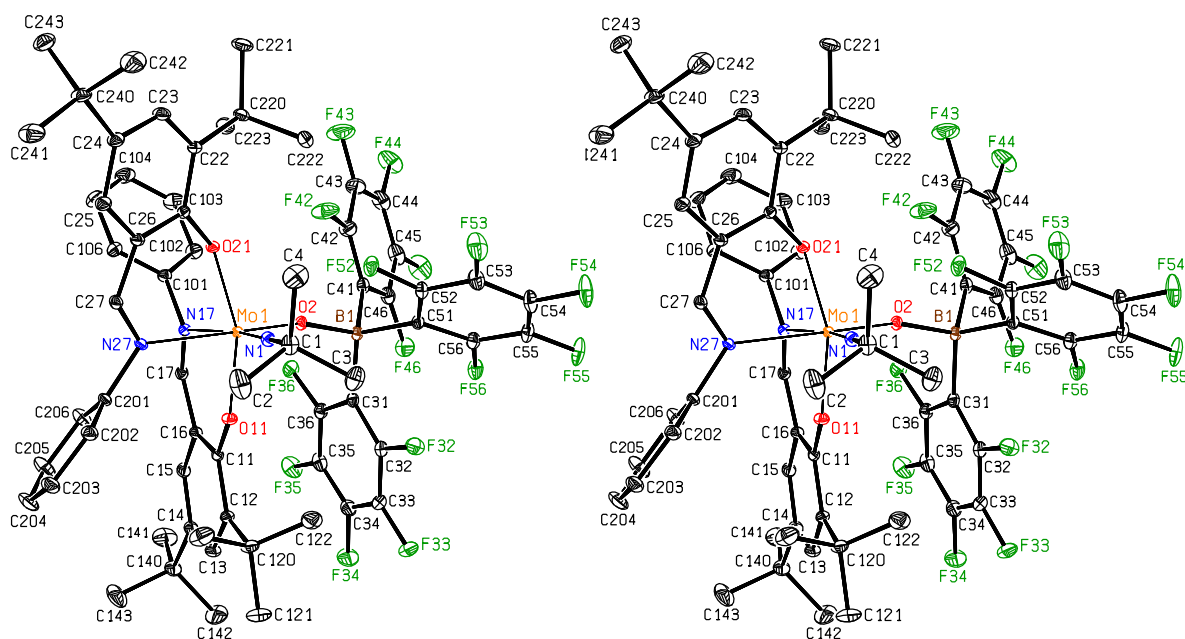


Figure S45. Stereoscopic ORTEP^[5] plot of **2** showing the atomic numbering scheme. The probability ellipsoids are drawn at the 50% probability level. The H atoms were omitted for clarity reasons.

Table S1. Crystal data and structure refinement for **2** (CCDC deposition number: 1574332)**Crystal data**

| | |
|-------------------------------------|--|
| Empirical formula | $C_{64}H_{61}BF_{15}MoN_3O_3$ |
| Formula weight | 1311.90 |
| Crystal description | block, red |
| Crystal size | 0.32 x 0.19 x 0.18mm |
| Crystal system, space group | monoclinic, $P 2_1/n$ |
| Unit cell dimensions: | |
| a | 12.0188(14)Å |
| b | 26.298(3)Å |
| c | 18.9156(19)Å |
| β | 95.221(5)° |
| Volume | 5953.8(11)Å ³ |
| Z | 4 |
| Calculated density | 1.464Mg/m ³ |
| F(000) | 2688 |
| Linear absorption coefficient μ | 0.316mm ⁻¹ |
| Absorption correction | semi-empirical from equivalents |
| Max. and min. transmission | 1.000 and 0.841 |
| Unit cell determination | 2.48° < Θ < 33.67° 9805 reflections used at 100K |

Data collection

| | |
|---------------------------------------|---------------------------------|
| Temperature | 100K |
| Diffractometer | Bruker APEX-II CCD |
| Radiation source | Incoatec microfocus sealed tube |
| Radiation and wavelength | MoK α , 0.71073Å |
| Monochromator | multilayer monochromator |
| Scan type | ϕ and ω scans |
| Θ range for data collection | 1.87 to 33.00° |
| Reflections collected / unique | 82751 / 22432 |
| Significant unique reflections | 17789 with $I > 2 \sigma(I)$ |
| R(int), R(sigma) | 0.0490, 0.0477 |
| Completeness to $\Theta = 33.0^\circ$ | 100.0% |

Refinement

| | |
|---------------------------------------|--|
| Refinement method | Full-matrix least-squares on F^2 |
| Data / parameters / restraints | 22432 / 809 / 0 |
| Goodness-of-fit on F^2 | 1.028 |
| Final R indices [$I > 2\sigma(I)$] | R1 = 0.0360, wR2 = 0.0831 |
| R indices (all data) | R1 = 0.0515, wR2 = 0.0900 |
| Extinction expression | none |
| Weighting scheme | $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ where $P = (F_o^2 + 2F_c^2)/3$ |
| Weighting scheme parameters a, b | 0.0357, 2.7963 |
| Largest Δ/σ in last cycle | 0.002 |
| Largest difference peak and hole | 0.807 and -0.546e/Å ³ |
| Structure Solution Program | SHELXS-97 (Sheldrick, 2008) |
| Structure Refinement Program | SHELXL-2014/6 (Sheldrick, 2015) |

Table S2. Selected bond lengths [Å] and angles [°] for **2**.

| | |
|--------------------|------------|
| Mo(1)–N(1) | 1.7259(12) |
| Mo(1)–O(2) | 1.8221(9) |
| Mo(1)–O(11) | 1.9583(10) |
| Mo(1)–O(21) | 1.9570(9) |
| Mo(1)–N(17) | 2.3140(12) |
| Mo(1)–N(27) | 2.2957(11) |
| O(2)–B(1) | 1.5002(16) |
| | |
| O(11)–Mo(1)–O(21) | 158.63(4) |
| N(1)–Mo(1)–N(17) | 170.36(5) |
| O(2)–Mo(1)–N(27) | 165.81(4) |
| B(1)–O(2)–Mo(1) | 162.72(9) |
| C(1)–N(1)–Mo(1) | 175.08(10) |
| C(11)–O(11)–Mo(1) | 138.36(9) |
| C(17)–N(17)–C(101) | 115.06(11) |
| C(17)–N(17)–Mo(1) | 123.44(9) |
| C(101)–N(17)–Mo(1) | 120.37(8) |
| C(21)–O(21)–Mo(1) | 134.49(8) |
| C(27)–N(27)–C(201) | 112.55(11) |
| C(27)–N(27)–Mo(1) | 121.04(9) |
| C(201)–N(27)–Mo(1) | 125.69(8) |

Crystal structure determination of 4b. The structure was solved by direct methods (SHELXS-97)^[3] and refined by full-matrix least-squares techniques against F^2 (SHELXL-2014/6).^[4] The n-pentane molecules are disordered over two orientations and were refined with site occupation factors of 0.5. The C–C bonds in these solvent molecules were restrained to 1.53 Å and the same anisotropic displacement parameters were used for the C atoms. The other non-hydrogen atoms were refined with anisotropic displacement parameters without any constraints. The H atoms of the aromatic rings as well as those of the imino groups were put at the external bisectors of the C–C–C angles at C–H distances of 0.95 Å and common isotropic displacement parameters were refined for the H atoms of the same ring including the H atom of the adjacent imino group. The H atoms of the *tert*-butyl groups were refined with common isotropic displacement parameters for the H atoms of the same group and idealized geometries with tetrahedral angles, enabling rotation around the C–C bonds, and C–H distances of 0.98 Å. The H atoms of the solvent molecules were included with idealized geometries and their isotropic displacement parameters fixed to 1.2 times U_{eq} of the C atom they are bonded to. For 1027 parameters final R indices of $R1 = 0.0434$ and $wR^2 = 0.1283$ (GOF = 1.038) were obtained. The largest peak in a difference Fourier map was $0.669e^{-3}$.

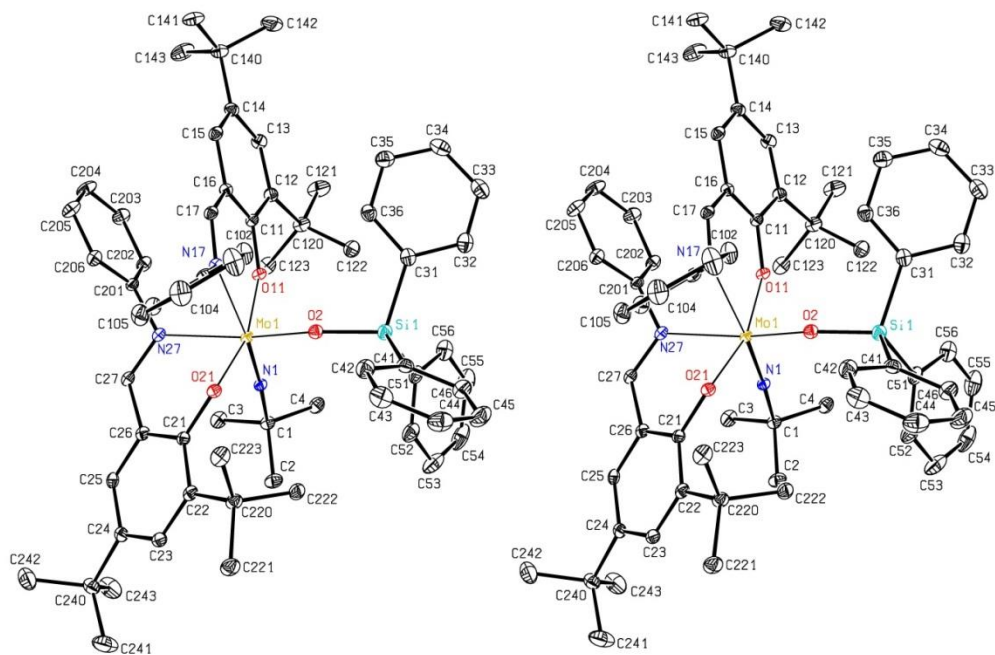


Figure S46. Stereoscopic ORTEP^[5] plot of the complex cation found in **4b** showing the atomic numbering scheme. The probability ellipsoids are drawn at the 30% probability level. The H atoms were omitted for clarity reasons.

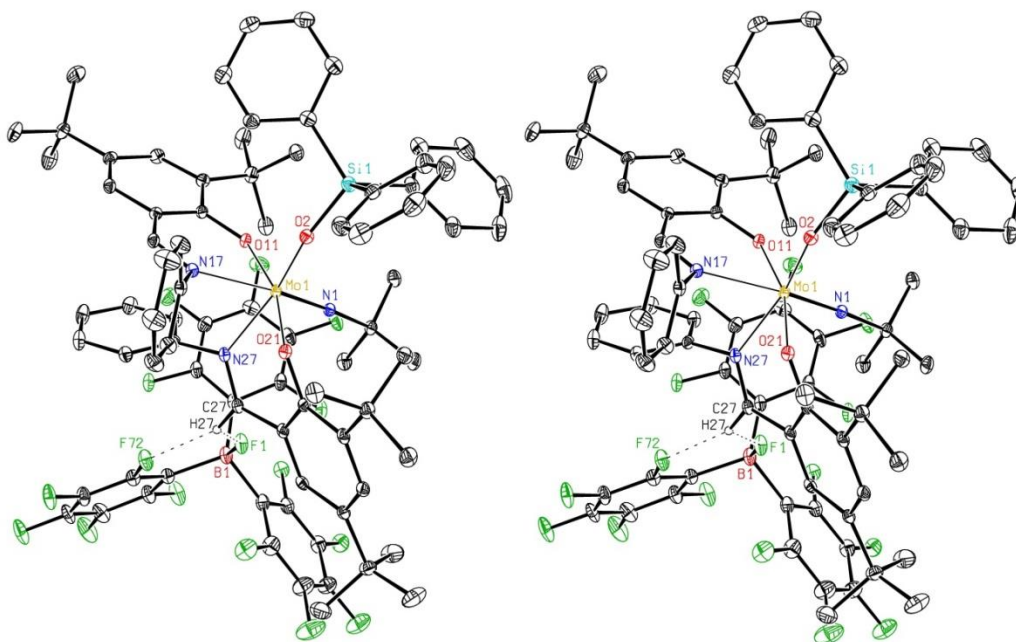


Figure S47. Stereoscopic ORTEP^[5] plot of **4b** showing the atomic numbering scheme. The probability ellipsoids are drawn at the 30% probability level. H27 is drawn with an arbitrary radius; the other H atoms were omitted for clarity.

Table S3. Crystal data and structure refinement for **4b** (CCDC deposition number: 1574333)**Crystal data**

| | |
|---------------------------------|--|
| Empirical formula | $C_{64}H_{76}MoN_3O_3Si^+ C_{18}BF_{16}^- \cdot C_5H_{12}$ |
| Formula weight | 1662.44 |
| Crystal description | plate, amber |
| Crystal size | 0.30 x 0.26 x 0.03mm |
| Crystal system, space group | monoclinic, P 2 ₁ /c |
| Unit cell dimensions: | |
| a | 13.3781(10)Å |
| b | 36.228(3)Å |
| c | 18.4909(13)Å |
| β | 97.748(3)° |
| Volume | 8880.0(12)Å ³ |
| Z | 4 |
| Calculated density | 1.243Mg/m ³ |
| F(000) | 3440 |
| Linear absorption coefficient μ | 0.241mm ⁻¹ |
| Absorption correction | semi-empirical from equivalents |
| Max. and min. transmission | 1.000 and 0.839 |
| Unit cell determination | 2.31° < Θ < 25.52° 9947 reflections used at 100K |

Data collection

| | |
|--------------------------------|---------------------------------|
| Temperature | 100K |
| Diffractometer | Bruker APEX-II CCD |
| Radiation source | Incoatec microfocus sealed tube |
| Radiation and wavelength | MoK _α , 0.71073Å |
| Monochromator | multilayer monochromator |
| Scan type | φ and ω scans |
| Θ range for data collection | 1.86 to 25.00° |
| Reflections collected / unique | 50857 / 15605 |
| Significant unique reflections | 11678 with I > 2σ(I) |
| R(int), R(sigma) | 0.0368, 0.0601 |
| Completeness to Θ = 25.0° | 99.9% |

Refinement

| | |
|-----------------------------------|--|
| Refinement method | Full-matrix least-squares on F ² |
| Data / parameters / restraints | 15605 / 1027 / 14 |
| Goodness-of-fit on F ² | 1.038 |
| Final R indices [I > 2σ(I)] | R1 = 0.0434, wR2 = 0.1170 |
| R indices (all data) | R1 = 0.0663, wR2 = 0.1283 |
| Extinction expression | none |
| Weighting scheme | w = 1/[σ ² (F _o ²)+(aP) ² +bP] where P = (F _o ² +2F _c ²)/3 |
| Weighting scheme parameters a, b | 0.0691, 1.9520 |
| Largest Δ/σ in last cycle | 0.001 |
| Largest difference peak and hole | 0.669 and -0.404e/Å ³ |
| Structure Solution Program | SHELXS-97 (Sheldrick, 2008) |
| Structure Refinement Program | SHELXL-2014/6 (Sheldrick, 2015) |

Table S4. Selected bond lengths [Å] and angles [°] for **4b**.

| | |
|--------------------|------------|
| Mo(1)–N(1) | 1.715(2) |
| Mo(1)–O(2) | 1.8975(19) |
| Mo(1)–O(11) | 1.9391(18) |
| Mo(1)–O(21) | 1.9365(18) |
| Mo(1)–N(17) | 2.315(2) |
| Mo(1)–N(27) | 2.214(2) |
| N(1)–C(1) | 1.470(4) |
| O(2)–Si(1) | 1.630(2) |
| O(11)–C(11) | 1.344(3) |
| C(17)–N(17) | 1.291(3) |
| O(21)–C(21) | 1.354(3) |
| C(27)–N(27) | 1.289(4) |
| B(1)–F(1) | 1.435(3) |
| B(1)–C(61) | 1.646(5) |
| B(1)–C(71) | 1.648(4) |
| B(1)–C(81) | 1.649(5) |
| | |
| O(11)–Mo(1)–O(21) | 163.05(8) |
| N(1)–Mo(1)–N(17) | 170.64(9) |
| O(2)–Mo(1)–N(27) | 163.49(8) |
| C(1)–N(1)–Mo(1) | 175.60(19) |
| Si(1)–O(2)–Mo(1) | 155.54(12) |
| C(11)–O(11)–Mo(1) | 143.05(17) |
| C(17)–N(17)–C(101) | 114.2(2) |
| C(17)–N(17)–Mo(1) | 125.59(18) |
| C(101)–N(17)–Mo(1) | 120.03(17) |
| C(21)–O(21)–Mo(1) | 125.99(16) |
| C(27)–N(27)–C(201) | 115.8(2) |
| C(27)–N(27)–Mo(1) | 121.15(17) |
| C(201)–N(27)–Mo(1) | 123.04(18) |

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