Synthesis of Stable Pentacoordinate Silicon(IV)-NHC Adducts: An Entry to Anionic N-Heterocyclic Carbene Ligands

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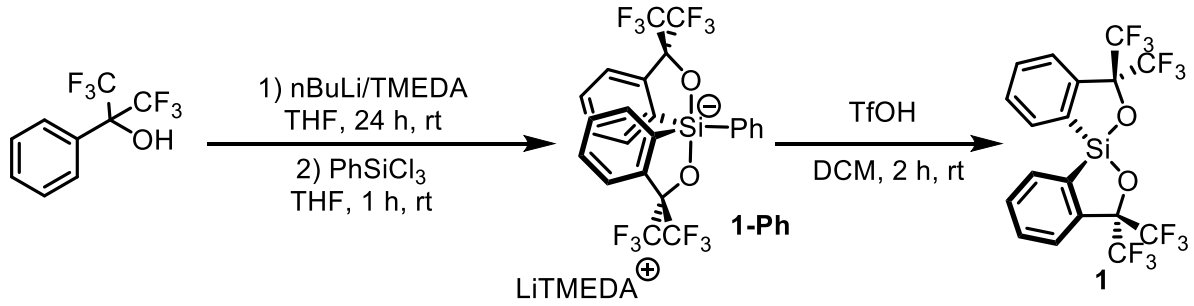
I. General informations

Unless otherwise noted, reactions were carried out under an argon atmosphere in oven-dried glassware using Schlenk line techniques. All the solvents were distilled prior to be used. Dichloromethane and pentane were distilled over CaH_2, THF was distilled over sodium/benzophenone, toluene was distilled over sodium, tetramethylethylenediamine (TMEDA) over potassium hydroxide. Sodium hydride 60% dispersion, was washed three times with distilled pentane, dried and stored in the glove box. Reagents and chemicals were purchased from commercial sources and used as received. Melting points were determined on a melting point apparatus SMP3 (Stuart scientific) and are uncorrected. HRMS were registered on a micrOTOF Brucker with ESI source. ^{1}H, ^{19}F, ^{31}P NMR spectra were recorded at room temperature at 300, 282, 121 MHz on a Brucker AVANCE 300 nanobay spectrometer. ^{1}H, ^{19}F, ^{13}C, ^{31}P and ^{29}Si NMR spectra were recorded at room temperature at 400, 376, 100, 161 and 79.49 MHz respectively, on a Brucker AVANCE 400 spectrometer. ^{1}H, ^{19}F, ^{13}C, ^{29}Si, ^{31}P ^{77}Se, ^{7} Li NMR were recorded, unless otherwise noted, at room temperature at 600, 564, 150, 119, 242, 114.45 and 233.23 MHz respectively, on a Brucker AVANCE III 600 spectrometer. Chemical shifts (δ) are reported in ppm and coupling constants (*J*) are given in Hertz (Hz). Abbreviations used for peak multiplicity are: s (singlet); bs (broad singlet); d (doublet); t (triplet); q (quartet), td (triplet of doublet), dt (doublet of triplet); m (multiplet). Calibration tol-d_8: 2.08; CD_2Cl_2: 5.32; $CDCl_3$: 7.26; THF-d_8: 3.58, 1.72.

For compounds **3a**, **3b**, **4c**, **6c** and **6d** single crystals were selected, mounted and transferred into a cold nitrogen gas stream. Intensity data was collected with Bruker Kappa-APEX2 systems using micro-source Cu-Kα or fine-focus sealed tube Mo-Kα radiation. Unit-cell parameters determination, data collection strategy, integration and absorption correction were carried out with the Bruker APEX2 suite of programs. The structures were solved with SHELXT-2014 and refined by full-matrix least-squares methods with SHELXL-2014 using the WinGX suite. For **7c** , a single crystal of each compound was selected, mounted onto a cryoloop, and transferred in a cold nitrogen gas stream. Intensity data were collected with a BRUKER Kappa-APEXII diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). Data collection were performed with APEX2 suite (BRUKER). Unit-cell parameters refinement, integration and data reduction were carried out with SAINT program (BRUKER). SADABS (BRUKER) was used for scaling and multi-scan absorption corrections. In the WinGX suite of programs,[1] the structure were solved with SHELXT-14 program[2] and refined by full-matrix least-squares methods using SHELXL-14.[2]

II. Synthesis of Martin's spirosilane 1



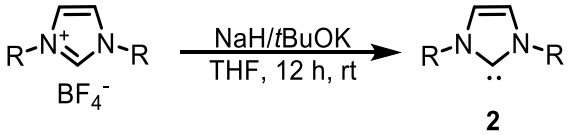
To a stirred solution of *n*BuLi (2.5 M in hexane, 110.0 mmol, 44 mL, 2.25 eq.), distilled TMEDA (5.0 mmol, 749 µL, 0.1 eq.) was added at RT. After 30 min the mixture was cooled down to 0°C and then a solution of 1,1,1,3,3,3-hexafluoro-2-phenyl-2-propanol (50.0 mmol, 12 g, 1.0 eq.) in THF (15 mL) was added dropwise over 20 min. The reaction mixture was stirred for 24 h at room temperature and then was cooled again to 0°C and $PhSiCl_3$ (26 mmol, 4.16 mL, 0.52 eq.) was added dropwise over 15 min. The reaction mixture was stirred for 4 h and quenched with 10 mL of HCl (0.5 M) and diluted with 150 mL of diethyl ether and washed with water. The organic layer was dried over $MgSO_4$ and evaporated under reduced pressure. The silicate **1-Ph [LiTMEDA]** was obtained by precipitation after solubilisation of the crude product in the minimal amount of dichloromethane and addition of pentane, filtration and drying under vacuum for 6h afford silicate **1-Ph [LiTMEDA]** as a light- yellow solid (10.2 g, 81%).

^{1}H NMR (400 MHz, acetone-d_6): δ 8.43 (d, J = 7.29 Hz, 2H, CH_{Ar}), 7.76 (dd, 2H, CH_{Ar}), 7.44 (d, J = 7.70 Hz, 1H, CH_{Ar}), 7.34 (m, 2H, CH_{Ar}), 7.26 (m, 2H, CH_{Ar}), 6.97 (m, 4H, CH_{Ar}), 3.13 (m, 4H, NCH_2), 2.71 (m, 12H, NCH_3). **^{19}F{^{1}H} NMR** (376 MHz, acetone-d_6): δ -74.44 (q, 6F), -75.74 (q, 6F).

Triflic acid (1.7 mL, 19.6 mmol, 7.0 eq.) was added dropwise to a solution of **1-Ph [LiTMEDA]** (2.0 g, 2.8 mmol, 1.0 eq.) in dichloromethane (70 mL). The reaction mixture was stirred for 13 h at room temperature and then was cooled down to 0°C, quenched with distilled water and diluted with diethyl ether. After washing with distilled water, the organic layer was dried over $MgSO_4$ and evaporated under reduced pressure. The crude product recrystallized in pentane to afford spirosilane **1** as off-white crystals. (1.0 g, 70%). **^{1}H NMR** (400 MHz, tol-d_8): δ 7.55 (d, J = 8.0 Hz, 2H, CH_{Ar}), 7.34 (d, J = 6.4 Hz, 2H, CH_{Ar}), 7.05 (dd, J = 7.5, 1.3 Hz, 2H, CH_{Ar}), 6.93 (dd, J = 7.4, 1.1 Hz, 2H, CH_{Ar}); **^{19}F{^{1}H} NMR** (376 MHz, tol-d_8): δ -75.9 (q, J = 8.6 Hz, 6F), -76.24 (q, J = 8.7 Hz, 6F). **^{13}C{^{1}H} NMR** (100 MHz, tol-d_8): 142.0, 133.4, 133.4, 131.5, 122.6 (q, $^1J_{C\text{-}F}$ = 285 Hz, CF$_3$), 83.14 (sept, $^2J_{C\text{-}F}$ = 31.8 Hz, C(CF$_3$)$_2$) **^{29}Si{^{1}H} NMR (119 MHz, $CDCl_3$)**: δ 7.5. NMR data are consistent with those found in literature[3].

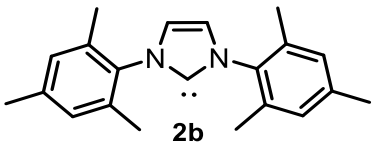
III. Synthesis of Carbenes

III.1 General Procedure[4]



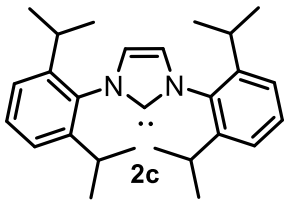
In a flame-dried Schlenk tube, imidazolium salt (8.3 mmol, 1.0 eq.), NaH (398 mg, 16.6 mmol, 2.0 eq.) and *t*BuOK (93.13 mg, 0.83 mmol, 0.1 eq.), were added followed by the addition of THF (41.5 mL). The reaction was stirred for 12 h, after that time the agitation was stopped and the solution was decanted. The liquid phase was transferred in another flame dried Schlenk tube using a filtrating canula. The remaining solid was washed with THF and the liquid phase was transferred. After concentration of the liquid phase, pentane (20 mL) was added and a precipitate appeared. The solid was filtered off using a filtrating cannula, washed with pentane (20 mL) and filtered again. The free carbene **2** was dried under vacuum for 4 h, then stored in the glove box

1,3-Bis(2,4,6-trimethylphenyl)imidazol-2-ylidene (2b)



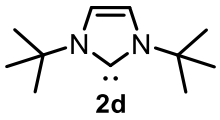
Carbene **2b** (IMes) was synthesized following the general procedure. Yield: 84%. **^{1}H NMR** (400 MHz, tol-d_8): 6.77 (s, 4H, CH_{Ar}), 6,5 (s, 2H, C$H_{imidazol}$), 2.16 (s, 6H, *p*-CH_3), 2.11 (s, 12H, *o,m*-CH_3); **^{13}C{^{1}H} NMR** (100 MHz, tol-d_8): 219.7, 139.2, 137.0, 135.3, 129.0, 120.4, 21.0, 18.0. NMR data are consistent with those found in literature [4].

1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (2c)



Carbene **2c** (IPr) following the general procedure. Yield: 78%. **^{1}H NMR** (400 MHz, tol-d_8): 7.25 (q, 2H, *p*-CH_{Ar}), 7.14 (d, *J* = 7.7Hz, 4H, *o,m*-CH_{Ar}), 6.64 (s, 2H, C$H_{imidazol}$), 2.91 (m, 4H, CH(CH_3)$_2$), 1.24 (d, *J* = 6.9Hz, 12H, CHCH_3), 1.17 (d, *J* = 7.0 Hz, 12H, CHCH_3); **^{13}C{^{1}H} NMR** (100 MHz, tol-d_8): 220.7, 146.2, 138.9, 123.5, 121.5, 28.7, 24.7, 23.6. NMR data are consistent with those found in literature [4].

1,3-bis(2,6-di-tert-butyl)imidazol-2-ylidene (2d)

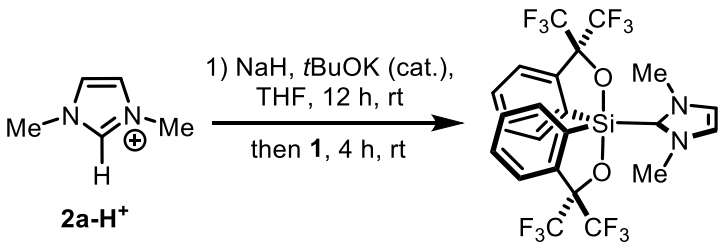


2d

Carbene **2d** (I*t*Bu) was synthesized following the general procedure. Yield: 61%. **^{1}H NMR** (400 MHz, tol-d_8): 6.75 (s, 2H, C$H_{imidazol}$), 1.47 (s, 18H, C(CH_3)$_3$); **^{13}C{^{1}H} NMR** (100 MHz, tol-d_8): 213.1, 114.8, 55.7, 31.4. NMR data are consistent with those found in literature [5].

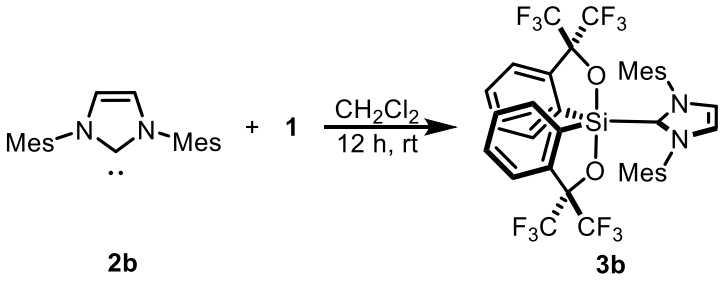
IV. Synthesis of Adducts

IV.1 Synthesis of adduct 3a



In a flame-dried Schlenk tube under argon, imidazolium salt **2a-H^{+}** (218 mg, 0.97 mmol, 1.0 eq.), NaH (46 mg, 1.95 mmol, 2.0 eq.) and *t*BuOK (10.88 mg, 0.097 mmol, 0.1 eq.), were added followed by the addition of THF (1.9 mL). The reaction was stirred for 12 h then **1** (500 mg, 0.97 mmol, 1.0 eq.) was added and the reaction mixture was stirred for 4 h. After this time the solvent was evaporated and the white solid was dissolved in the minimal amount of dichloromethane and was passed over a short pad of silica (R_f: 0.96), washed three times with 15 mL of dichloromethane. The solvent was evaporated and a white solid was obtained. 496 mg, 84%. Melting Point: 255-263°C. **HRMS-ESI** Mass calculated for $C_{23}H_{16}F_{12}N_2NaO_2Si$: 631.0682; found: 631.0691. **^{1}H NMR** (600 MHz, CD_2Cl_2): 8.26 (d, *J* = 7.4 Hz, 2H, CH_{Ar}), 7.63 (d, *J* = 7.6 Hz, 2H, CH_{Ar}), 7.55 (td, *J* = 7.2, 1.0 Hz, 2H, CH_{Ar}), 7.50 (td, *J* = 7.5, 1.4 Hz, 2H, CH_{Ar}), 6.80 (s, 2H, C$H_{imidazol}$), 3.74 (s, 6H, CH_3); **^{19}F{^{1}H} NMR** (564 MHz, CD_2Cl_2): -75.93 (q, *J* = 9.2 Hz, 6F), -77.10 (q, *J* = 9.2 Hz, 6F); **^{13}C{^{1}H} NMR** (150 MHz, CD_2Cl_2): 160.1, 142.1, 138.2, 138.1, 131.0, 130.2, 124.7, 124.4 (q, $^{1}J_{C\text{-}F}$ = 287 Hz, *C*F_3), 124.2 (q, $^{1}J_{C\text{-}F}$ = 287 Hz, *C*F_3), 122.3, 82.1 (sept, $^{2}J_{C\text{-}F}$ = 29.6 Hz, *C*$(CF_3)_2$), 37.6; **^{29}Si{^{1}H} NMR** (119 MHz, CD_2Cl_2): -83.54.

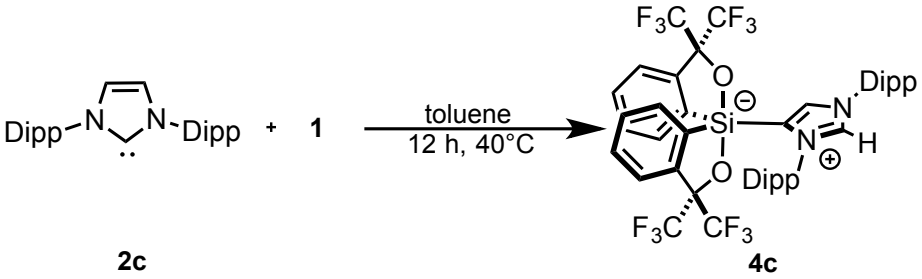
IV.2 Synthesis of NHC-Si adduct 3b



2b **3b**

In a flame-dried Schlenk tube, **2b** (304 mg, 1.0 mmol, 1.0 eq.) and **1** (461 mg, 0.9 mmol, 0.9 eq.) and CH_2Cl_2 (19.6 mL) were added. The reaction was stirred for 12 h, after the mixture was filtered through a pad of silica (R_f: 0.96), washed with dichloromethane (3x20 mL). The filtrate was evaporated and a pale yellow solid was obtained. 568 mg, 77%. Melting Point: 205-215°C. **HRMS-ESI** Mass calculated for $C_{39}H_{33}F_{12}N_2O_2Si$: 817.2114; found: 817.2138. **^{1}H NMR** (400MHz, tol-d_8): 7.57 (d, *J* = 7.7 Hz, 2H, CH_{Ar}), 7.24 (d, *J* = 7.6 Hz, 2H, CH_{Ar}), 7.06 (td, *J* = 7.5, 1.4 Hz, 2H, CH_{Ar}), 6.92 (td, *J* = 7.3, 1.1 Hz, 2H, CH_{Ar}), 6.86 (bs, 2H, CH_{Ar}), 6.21 (bs, 2H, CH_{Ar}), 5.72 (bs, 2H, C$H_{imidazol}$), 2.14 (s, 6H, CH_3), 2.11 (s, 6H, CH_3), 1.14 (s, 6H, CH_3); **^{19}F{^{1}H} NMR** (376 MHz, tol-d_8): -71.82 (q, *J* = 10.7 Hz, 6F), -73.56 (q, *J* = 10.6 Hz, 6F); **^{13}C{^{1}H} NMR**(100 MHz, tol-d_8): 160.1, 141.6, 140.1, 140.0, 138.8, 136.7, 136.2, 133.7, 129.6, 129.4, 129.0, 128.7, 125.1 (q, $^1J_{C\text{-}F}$ = 287 Hz, *C*F_3), 124.2 (q, $^1J_{C\text{-}F}$ = 290 Hz, *C*F_3), 123.5, 123.2, 82.6 (sept, $^2J_{C\text{-}F}$ = 28.9 Hz, *C*$(CF_3)_2$), 18.5 (q, *J* = 3.3 Hz), 16.5 (q, $^9J_{C\text{-}F}$ = 3.3 Hz); **^{29}Si{^{1}H} NMR** (119 MHz, CD_2Cl_2): -81.82

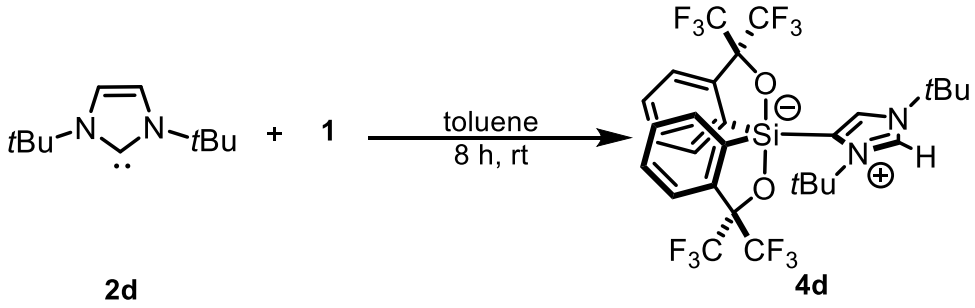
IV.3 Abnormal adduct 4c



2c **4c**

In a flame-dried Schlenk tube under argon, IPr (389mg, 1.0 mmol, 1.0 eq.), **1** (461mg, 0.9 mmol, 0.9 eq) and distilled toluene (0.05 M) were added, and the solution was stirred for 12 h at 40°C. After this time the solvent was evaporated and the withe solid was dissolved in the minimal amount of dichloromethane and was passed over a silica pad (R_f: 0.93), that was washed five times with 20mL of dichloromethane. The solvent was evaporated and the abnormal adduct **4c** was obtained as a white solid, 631 mg, yield: 70%. 226.5-230°C **HRMS-ESI** Mass calculated for $C_{45}H_{43}F_{12}N_2O_2Si$: 899.2891; found: 899.2909.**^{1}H NMR** (600 MHz, CD_2Cl_2) δ 7.98 (d, *J* = 7.26 Hz, 2H, CH_{Ar}), 7.91 (d, *J* = 1.74Hz, 1H, C$H_{imidazol}$), 7.54 (t, *J* = 7.82 Hz, 1H, CH_{Ar}), 7.50 (d, *J* = 7.7 Hz 2H, CH_{Ar}), 7.46 (t, *J* = 7.74Hz, 1H, CH_{Ar}), 7.41 (m, 2H, CH_{Ar}), 7.34 (dd, *J* = 7.91, 1.34, 2H, CH_{Ar}), 7.29 (m, 5H, CH_{Ar}), 7.18 (d, *J* = 6.9 Hz, 1H, CH_{Ar}), 7.03 (dd, *J* = 7.69, 1.58, 1H, CH_{Ar}), 7.02(d, 7.8 Hz, 1H, C$H_{imidazol}$), 2.94 (m, *J* = 6.62Hz, 1H, CH(CH_3)$_2$), 2.40 (m, *J* = 6.87 Hz, 1H, CH(CH_3)$_2$), 2.33 (m, *J* = 6.71 Hz 1H, CH(CH_3)$_2$), 2.25 (m, *J* = 6.97 Hz, 1H, CH(CH_3)$_2$), 1.35 (d, *J* = 6.5 Hz, 3H, CH_3), 1.24 (d, *J* = 6.78 Hz, 3H, CH_3), 1.15 (t, *J* = 6.62 Hz, 6H, CH_3), 1.02 (d, *J* = 6.86 Hz, 3H, CH_3), 0.97 (d, *J* = 6.76 Hz, 3H, CH_3), 0.77 (d, *J* = 6.82 Hz, 3H, CH_3), 0.59 (d, *J* = 6.53 Hz, 3H, CH_3). **^{19}F{^{1}H} NMR** (564 MHz, CD_2Cl_2) δ -74.47 (q, *J* = 9.8, 9.74 Hz 6F), -75.45 (q, *J* = 9.82, 9.7 Hz, 6F). **^{13}C{^{1}H} NMR** (150 MHz, CD_2Cl_2): 148.0, 146.0, 146.0, 145.9, 145.8, 145.3, 142.4, 141.1, 137.6, 136.8, 133.4, 132.4, 132.1, 131.4, 130.3, 129.4, 129.3, 129.2, 128.6, 125.7, 125.5, 125.1, 125.0, 124.6, 124.6 (q, $^1J_{C\text{-}F}$ = 287 Hz, CF$_3$), 124.3, 124.3 (q, $^1J_{C\text{-}F}$ = 289 Hz, CF$_3$), 124.1, 82.0 (sept, $^2J_{C\text{-}F}$ = 28.8 Hz, C(CF_3)$_2$), 29.6, 29.1, 29.0, 28.6, 28.5, 27.3, 26.8, 24.7, 24.5, 24.4, 24.1, 24.0, 23.8, 22.6, 21.6, 21.1; **^{29}Si{^{1}H} NMR** (119 MHz, CD_2Cl_2) δ -81.96.

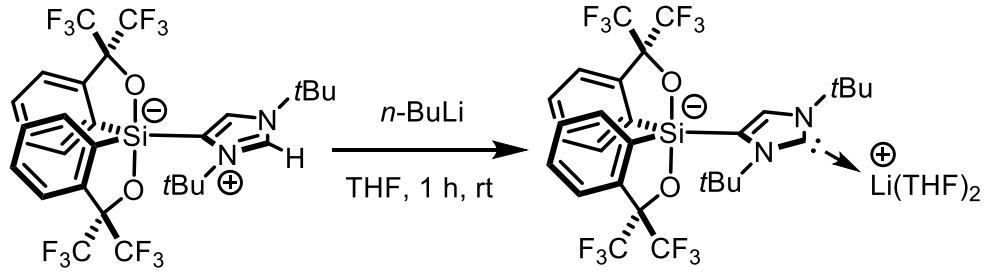
IV.4 Abnormal adduct 4d



2d **4d**

In a flame-dried Schlenk tube under argon, I*t*Bu (774 mg, 4.3 mmol, 1.1eq.), **1** (2.0 g, 3.9 mmol, 1.0 eq) and distilled toluene (0.05 M) were added, and the solution was stirred for 8 h. After this time the solvent was evaporated and the white solid was dissolved in the minimal amount of dichloromethane and was passed over a short pad of silica (R_f: 0.86), that was washed five times with 20 mL of dichloromethane. The solvent was evaporated and the abnormal adduct **4d** was obtained as a white solid, 2.1 g, yield: 77%. **^{1}H NMR** (400 MHz, CD_2Cl_2): 8.30 (d, *J* = 7.2 Hz, 2H, CH_{Ar}), 7.82 (d, *J* = 2.0 Hz, 1H, C$H_{imidazol}$), 7.57 (d, *J* = 7.8 Hz, 2H, CH_{Ar}), 7.50 (td, *J* = 7.3, 1.2 Hz, 2H, CH_{Ar}), 7.42 (td, *J* = 7.5, 7.4, 1.4 Hz, 2H, CH_{Ar}), 6.98 (d, *J* = 2.0 Hz, 1H, C$H_{imidazol}$), 1.51 (s, 9H, C(CH_3)$_3$), 1.45 (s, 9H, C(CH_3)$_3$);**^{19}F{^{1}H} NMR** (376 MHz, CD_2Cl_2): -75.27 (q, *J* = 9.6 Hz, 6F), -75.62 (q, *J* = 9.6 Hz, 6F); **^{13}C{^{1}H} NMR** (100 MHz, CD_2Cl_2): 147.3, 142.2, 141.3, 137.9, 129.9, 129.7, 128.4, 126.5, 124,7 (q, $^{1}J_{C\text{-}F}$ = 287 Hz, *C*F_3), 124.5 (q, $^{1}J_{C\text{-}F}$ = 290 Hz, *C*F_3), 124.4, 82.1 (sept, $^{2}J_{C\text{-}F}$ = 28.9 Hz, *C*$(CF_3)_2$), 61.9, 58.7, 31.0, 29.9; **^{29}Si{^{1}H} NMR** (119 MHz, CD_2Cl_2): -79.0

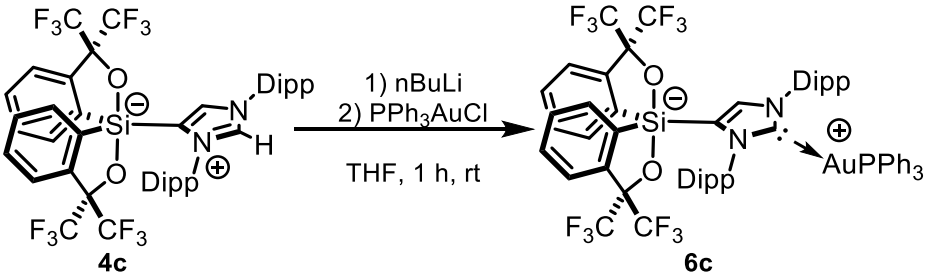
IV.5 Abnormal I*t*Bu lithium complex 5d



4d **5d**

In a flame-dried Schlenk under argon abnormal adduct **4d** (692 mg, 1.0 mmol, 1.0 eq) and distilled THF (10 mL, 0.1 M) were added. After total solubilisation, *n*BuLi (2.5 M, 396 µL, 1.1 eq) was added dropwise at room temperature and the reaction was allowed to stir for 1 h. The solvent was evaporated, and the lithium complex **5d** was obtained quantitatively as a red solid. **^{1}H NMR** (400 MHz, CD_2Cl_2): 8.29 (d, *J* = 8.1 Hz, 2H, CH_{Ar}), 7.56 (d, *J* = 7.8 Hz, 2H, CH_{Ar}), 7.50 (td, *J* = 7.3, 1.2 Hz, 2H, CH_{Ar}), 7.42 (td, *J* = 7.5, 7.4, 1.4 Hz, 2H, CH_{Ar}), 6.97 (s, 1H, C$H_{imidazol}$), 3.68 (m, 8H, CH_2 THF), 1.8 (m, 8H, CH_2 THF) 1.51 (s, 9H, C(CH_3)$_3$), 1.45 (s, 9H, C(CH_3)$_3$); **^{19}F{^{1}H} NMR** 376 MHz, CD_2Cl_2): -75.28 (q, *J* = 9.5 Hz, 6F), -75.64 (q, *J* = 9.5 Hz, 6F); **^{13}C{^{1}H} NMR** (150 MHz, CD_2Cl_2): 147.2, 142.2, 141.3, 137.8, 129.9, 129.7, 128.4, 126.5, 124,7 (q, $^{1}J_{C\text{-}F}$ = 288 Hz, CF_3), 124.5 (q, $^{1}J_{C\text{-}F}$ = 288 Hz, CF_3), 124.4, 82.1 (sept, $^{2}J_{C\text{-}F}$ = 28.9 Hz, $C(CF_3)_2$), 68.2, 61.9, 58.7, 31.0, 29.9, 26.0; **^{29}Si{^{1}H} NMR** (79 MHz, CD_2Cl_2): -79.33; **^{7}Li{^{1}H} NMR** (155 MHz, CD_2Cl_2): 1.34.

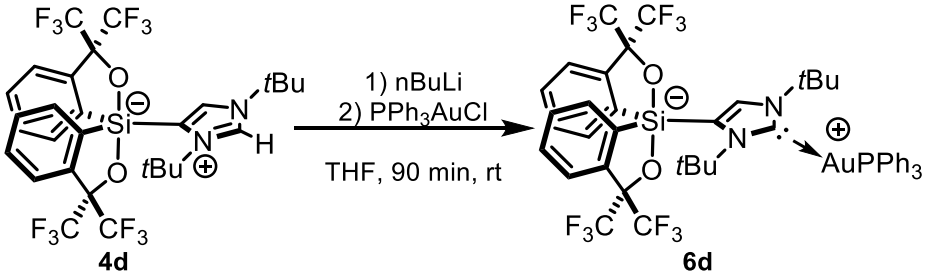
IV.6 Abnormal IPr Gold(I) complex 6c



4c **6c**

In a flame-dried Schlenk tube under argon, abnormal adduct **4c** (100 mg, 0.11 mmol, 1.0 eq) was dissolved in distilled THF (1.6 mL, 0.07 M). *n*Buli (2.5 M, 48.4 μL, 1.1eq) was added dropwise at room temperature and the solution was allowed to stir for 30 minute before adding PPh_3AuCl (54.4 mg, 0.11 mmol, 1.0 eq) at once. The reaction was stirred for another hour. The solvent was concentrated, and distilled pentane was added to trigger the precipitation of the product. After filtration, the solid was washed with pentane then was dried under vacuum. Gold complex **6c** was obtained as a white solid, 106 mg, 71%. **^{1}H NMR** (600 MHz, CD_2Cl_2): 8.11 (d, *J* = 7.1 Hz, 2H, CH_{Ar}), 7.47-7.41 (m, 6H, CH_{Ar}), 7.37 (t, *J* = 7.8 Hz, 1H, CH_{Ar}), 7.31 (td, *J* = 7.9, 2.5 Hz, 6H, CH_{Ar}), 7.27-7.22 (m, 6H, CH_{Ar}), 7.17 (d, *J* = 7.8 Hz, 1H, CH_{Ar}), 7.12 (d, *J* = 7.8 Hz, 1H, CH_{Ar}), 6.94 (dd, *J* = 13, 8.1 Hz, 6H, CH_{Ar}), 2.71 (m, *J* = 6.8 Hz, 1H, C*H*$(CH_3)_2$), 2.58 (m, *J* = 6.8 Hz, 2H, C*H*$(CH_3)_2$), 2.4 (m, *J* = 6.8 Hz, 1H, C*H*$(CH_3)_2$), 1.10-1.04 (m, 15H, CH_3), 0.99 (dd, *J* = 6.9, 4.6 Hz, 6H, CH_3), 0.72 (d, *J* = 6.7 Hz, 3H, CH_3); **^{13}C{^{1}H} NMR** (150 MHz, CD_2Cl_2): 190.4 (d, $^{2}J_{CP}$ = 126 Hz, N*C*N), 147, 146.9, 146.8, 146.6, 145, 144, 140.9, 137.9, 137.5, 134.6, 134.2 (d, $^{2}J_{CP}$ = 13.7 Hz, *o*-C_6H_3), 132.5 (d, $^{4}J_{CP}$ = 2.6 Hz, *p*-C_6H_3), 130.5, 129.6 (d, $^{3}J_{CP}$ = 11.2 Hz, *m*-C_6H_3), 128.8 (d, $^{1}J_{CP}$ = 57.8 Hz, *i*-C_6H_3), 128.6, 128.5, 126.2 (q, $^{1}J_{C\text{-}F}$ = 287 Hz, *C*F_3), 124.5 (q, $^{1}J_{C\text{-}F}$ = 290 Hz, *C*F_3), 124.3, 124.2, 124.2, 123.9, 123.5 (bs, *C*H_{Imid}), 28.8, 28.7, 28.7, 28.6, 27.1, 26.4, 24.7, 24.3, 24.2, 24.2, 23.1, 22.6; **^{19}F{^{1}H} NMR** (376 MHz, CD_2Cl_2): -73.31 (q, *J* = 10 Hz, 9F), -74.92 (q, *J* = 10 Hz, 6F); **^{31}P{^{1}H} NMR** (161 MHz, CD_2Cl_2): 39.98; **^{29}Si{^{1}H} NMR**: the signal was not detected.

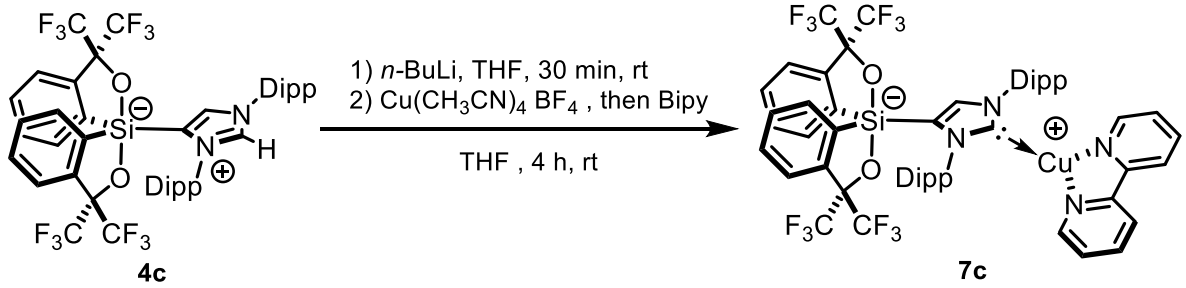
IV.7 Abnormal I*t*Bu Gold(I) complex 6d



4d **6d**

In a flame-dried Schlenk tube under argon, abnormal adduct **4d** (100 mg, 0.14 mmol, 1.0 eq) was dissolved in distilled THF (2 mL, 0.07 M). *n*Buli (2 M, 79.2 µL, 1.1 eq) was added dropwise at room temperature and the solution was allowed to stir for 30 min before adding PPh_3AuCl (71.2 mg, 0.14 mmol, 1.0 eq) at once. The reaction was stirred for another hour and then the solvent was concentrated, and distilled pentane was added to trigger the precipitation of the product. After filtration, the solid was washed with pentane then was dried under vacuum. Gold complex **6d** was obtained as 129 mg, 80%. **^{1}H NMR** (400 MHz, CD_2Cl_2): 8.21 (bd, J = 27.4 Hz, 2H, CH_{Ar}), 7.52 (m, 17H, CH_{Ar}), 7.42 (m, 2H, CH_{Ar}), 7.35 (td, J = 7.4, 1.4 Hz, 2H, CH_{Ar}), 6.85 (s, 1H, C$H_{imidazol}$), 1.81 (s, 9H, C(CH_3)$_3$), 1.61 (s, 9H, C(CH_3)$_3$); **^{13}C{^{1}H} NMR** (150 MHz, CD_2Cl_2): 143.0, 134.3 (d, J_{CP} = 13.4 Hz), 132.5 (d, J_{CP} = 2.6 Hz), 129.9 (d, J_{CP} = 11.5 Hz), 129.5, 129.2, 126.2, 124.1 (bs, CH$_{Imid}$), 60.3, 57.7, 34.4, 32.5; **^{19}F{^{1}H} NMR** (376 MHz, CD_2Cl_2): -75.23 (q, 9F), -75.89 (q, 3F); **^{31}P{^{1}H} NMR** (161 MHz, CD_2Cl_2): 39.86; **^{29}Si{^{1}H} NMR** (79 MHZ, CD_2Cl_2): -76.54.

IV.8 Abnormal IPr Copper(I) complex 7c



In a flame dried Schlenk tube under argon, abnormal adduct **4c** (75 mg, 0.083 mmol, 1.0 eq) was dissolved in distilled THF (1.2 mL, 0.07 M). *n*Buli (2.5 M, 36.5 µL, 1.1 eq) was added dropwise at room temperature and the solution was allowed to stir for 30 minute. Then $Cu(CH_3CN)_4BF_4$ (24.2 mg, 0.083 mmol, 1.0 eq) was added, the mixture was allowed to stir for five minutes before addition of 2,2'-bipyridine (13 mg, 0.083 mmol, 1.0 eq), the reaction was allowed to stir for 3 h. The solvent was evaporated under vacuum, the solid then, was solubilised in the minimum amount of distilled CH_2Cl_2 and stored -30°C for 8h. Copper complex **7c** was obtained as orange cubic crystal. 62.6 mg, yield: 67%. **^{1}H NMR** (600 MHz, CD_2Cl_2): 7.96 (dd, *J* = 6.8, 1.9 Hz, 2H, CH_{Ar}), 7.87 (d, *J* = 7.9 Hz, 2H, CH_{Ar}), 7.81 (td, *J* = 7.9, 7.76, 1.69 Hz, 2H, CH_{Ar}), 7.58 (t, 7.8 Hz, 1H, CH_{Ar}), 7.48 (t, *J* = 7.7 Hz, 1H, CH_{Ar}), 7.44 (m, 3H, CH_{Ar}), 7.37 (dd, *J* = 7.8, 1.4 Hz, 1H, CH_{Ar}), 7.32 (dd, *J* = 7.8 1.4 Hz, 1H, CH_{Ar}), 7.21 (m, 5H, CH_{Ar}), 7.12 (ddd, *J* = 7.5, 5.1, 1.16 Hz, 2H, CH_{Ar}), 7.01 (dd, *J* = 7.6, 1.63 Hz, 1H, CH_{Ar}), 6.30 (ddd, *J* = 5.0, 1.6, 0.9 Hz, 2H, CH_{Ar}), 3.10 (m, 1H, C*H*$(CH_3)_2$), 2.68 (m, 1H, C*H*$(CH_3)_2$), 2.62 (m, 1H, C*H*$(CH_3)_2$), 2.48 (m, 1H, C*H*$(CH_3)_2$), 1.26 (d, *J* = 6.6 Hz, 3H, CH_3), 1.20 (d, *J* = 6.8 Hz, 3H, CH_3), 1.03 (d, *J* = 6.8 Hz, 3H, CH_3), 0.97 (d, *J* = 6.8 Hz, 3H, CH_3), 0.94 (t, *J* = 8.2, 6.9 Hz, 6H, CH_3), 0.87 (d, *J* = 6.76 Hz, 3H, CH_3), 0.54 (d, *J* = 6.5 Hz, 3H, CH_3); **^{13}C{^{1}H} NMR** (150 MHz, CD_2Cl_2): 182.8 (N*C*N), 152.1, 150.8, 147.6, 147.5, 147.2, 147.2, 145.2, 143.6, 140.8, 140.4, 139.3, 137.6, 137.6, 131.6, 129.8, 129.0, 128.6, 128.2, 126.0, 124.8(q, $^1J_{C\text{-}F}$ = 288 Hz, *C*F_3), 124.6, 124.6 (q, $^1J_{C\text{-}F}$ = 290 Hz, *C*F_3), 124.6, 124.3, 124.1, 123.7, 120.9, 81.7 (sept, $^2J_{C\text{-}F}$ = 28.9 Hz, *C*$(CF_3)_2$), 28.6, 28.5, 28.5, 28.2, 27.7, 27.4, 24.5, 24.5, 24.1, 24.0, 23.2, 22.1; **^{19}F{^{1}H} NMR** (564 MHz, CD_2Cl_2): -73.88 (q, *J* = 9.8, 9.7 Hz, 6F), -75.42 (q, *J* = 10.0, 9.7 Hz, 6F); **^{29}Si{^{1}H} NMR** (119 MHZ, CD_2Cl_2): -80.6.

V. NMR Spectra

Figure S1: ^{1}H NMR (400 MHz, tol-d_8) of **1**

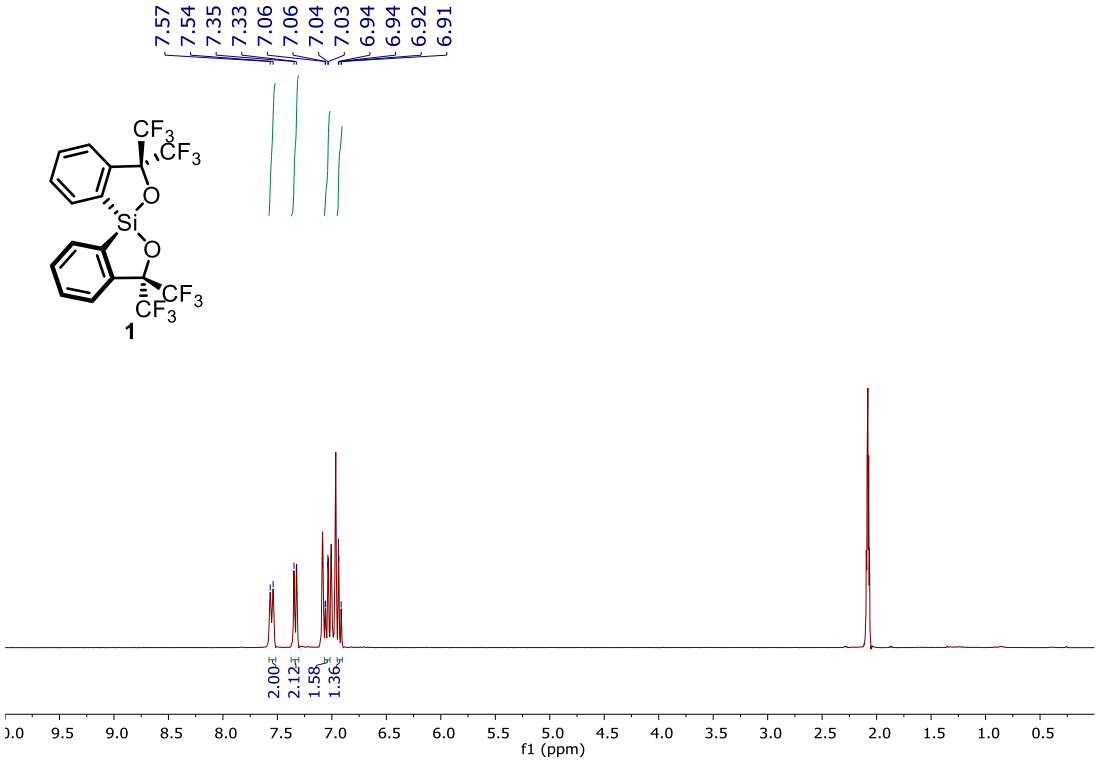


Figure S2: $^{19}F\{^{1}H\}$ (400 MHz, NMR tol-d_8) of **1**

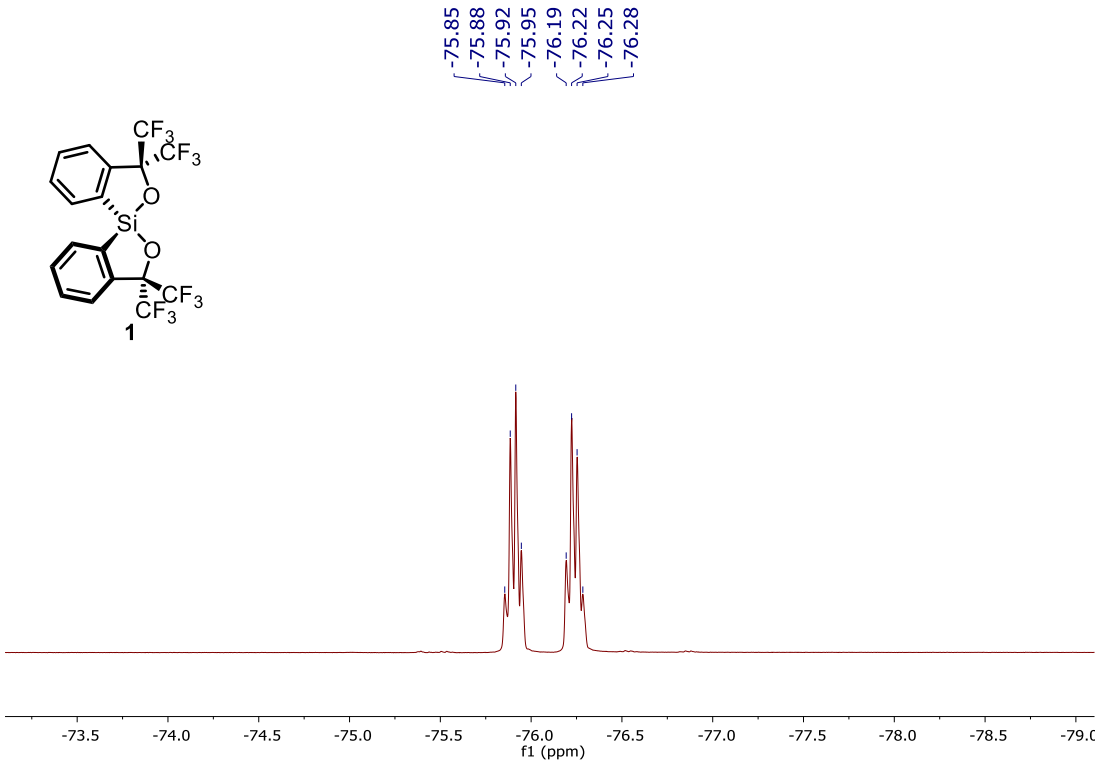


Figure S3: $^{13}C\{^{1}H\}$ NMR (400 MHz, tol-d_8) of **1**

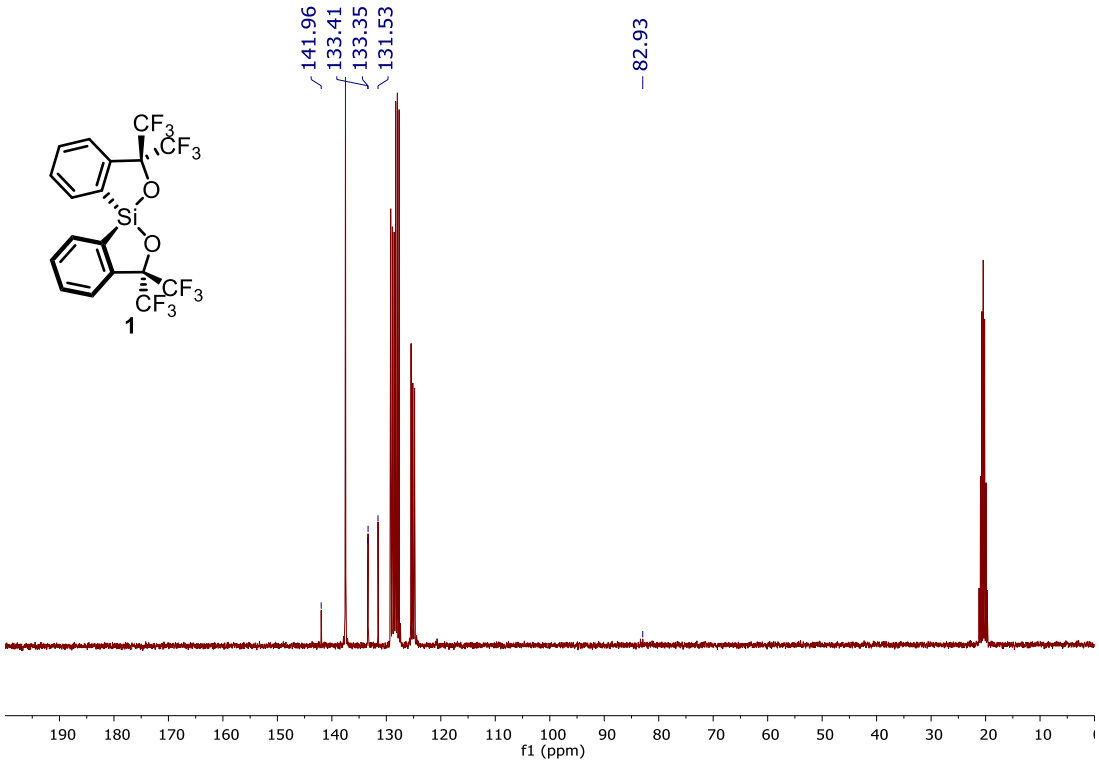


Figure S4: ^{1}H NMR (400 MHz, tol-d_8) of **2b**

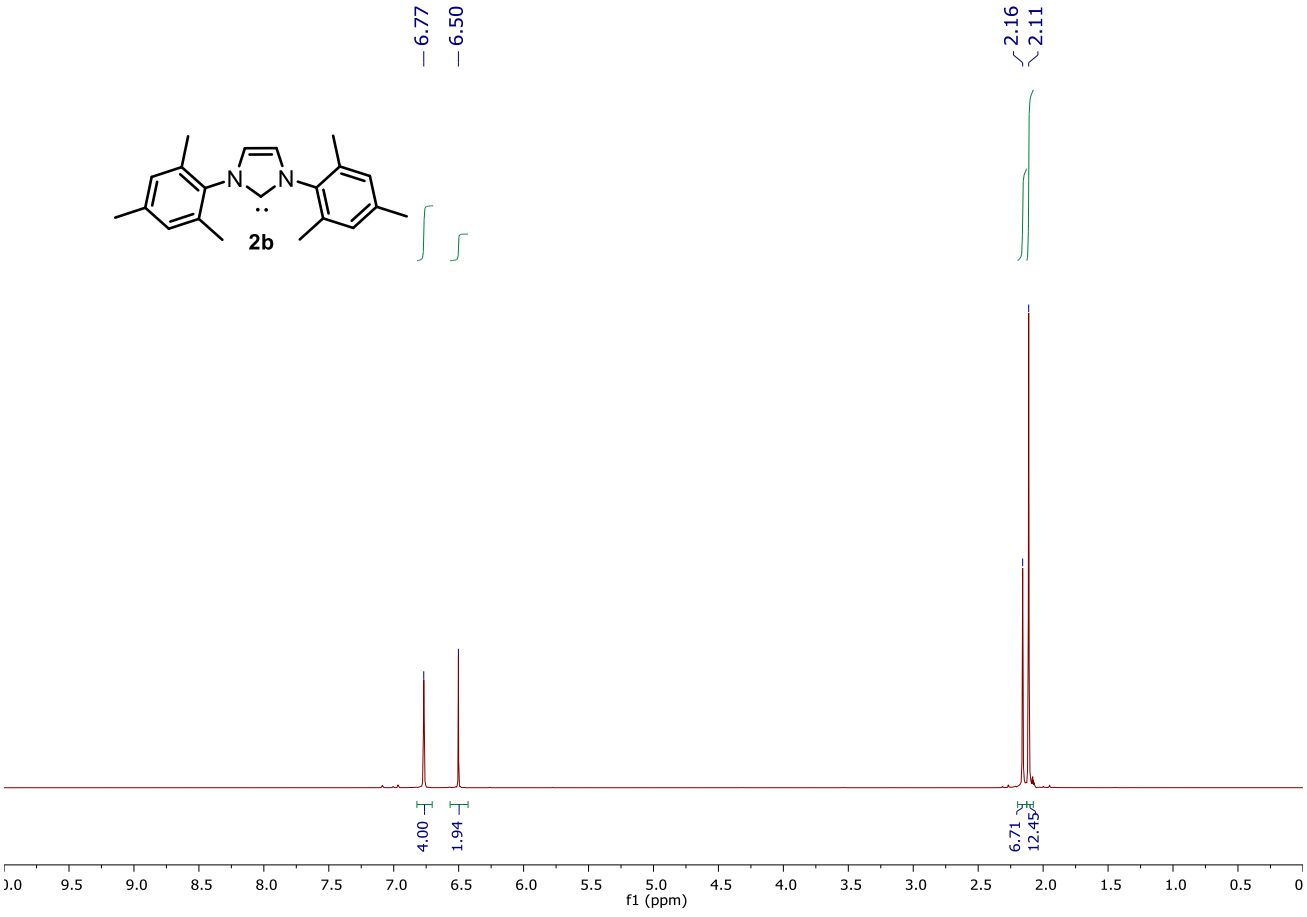


Figure S5: $^{13}C\{^{1}H\}$ NMR (400 MHz, tol-d_8) of **2b**

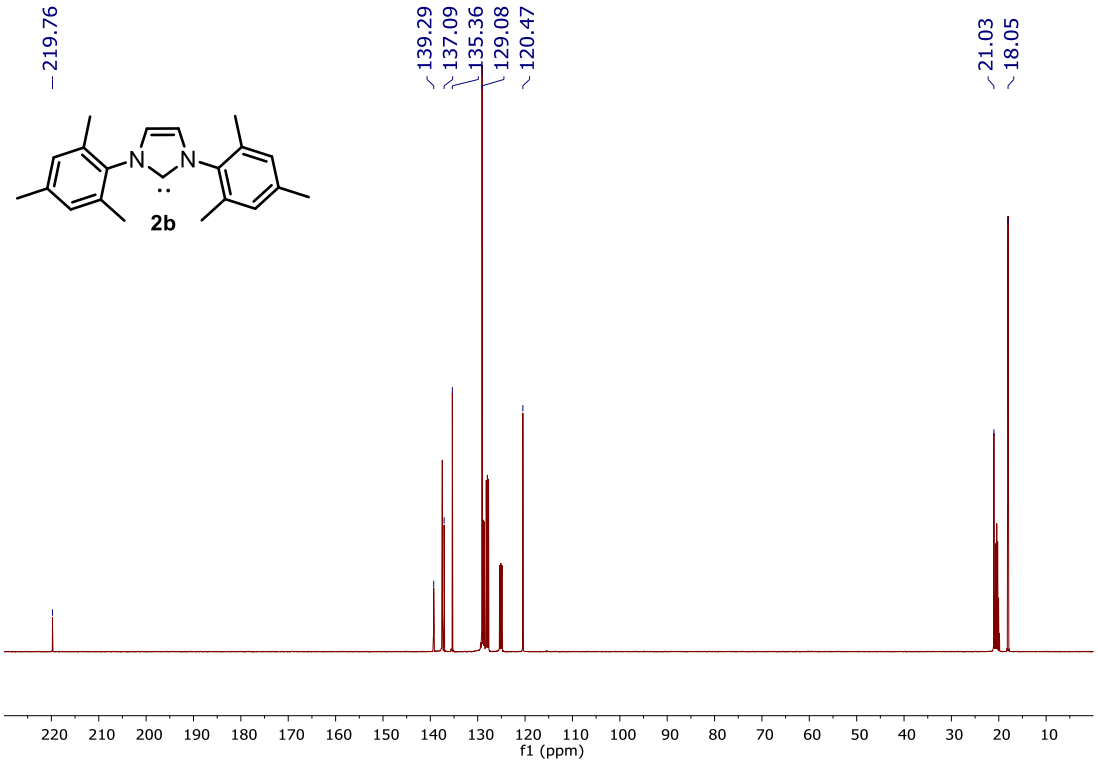


Figure S6: ^{1}H NMR (400 MHz, tol-d_8) of **2c**

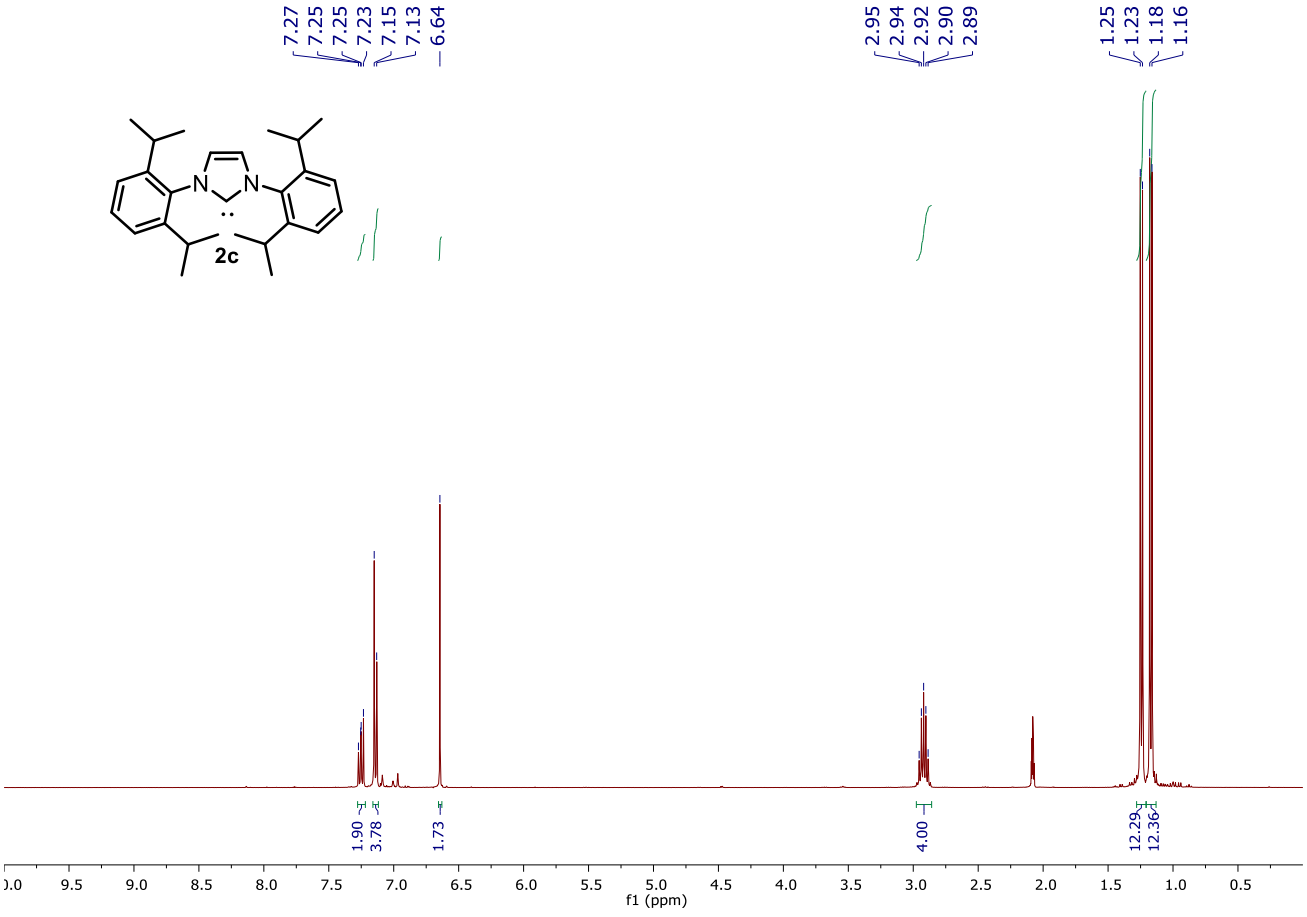


Figure S7: $^{13}C\{^{1}H\}$ NMR (400 MHz, tol-d_8) of **2c**

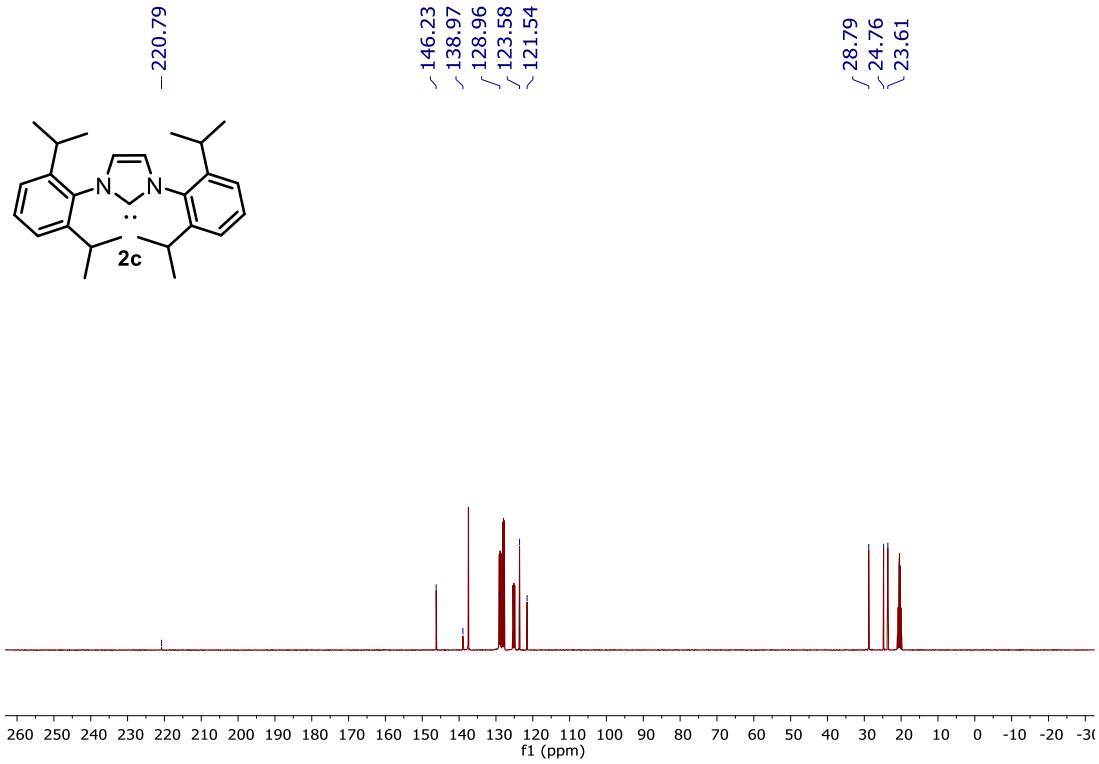


Figure S8: ^{1}H NMR (400 MHz, tol-d_8) of **2d**

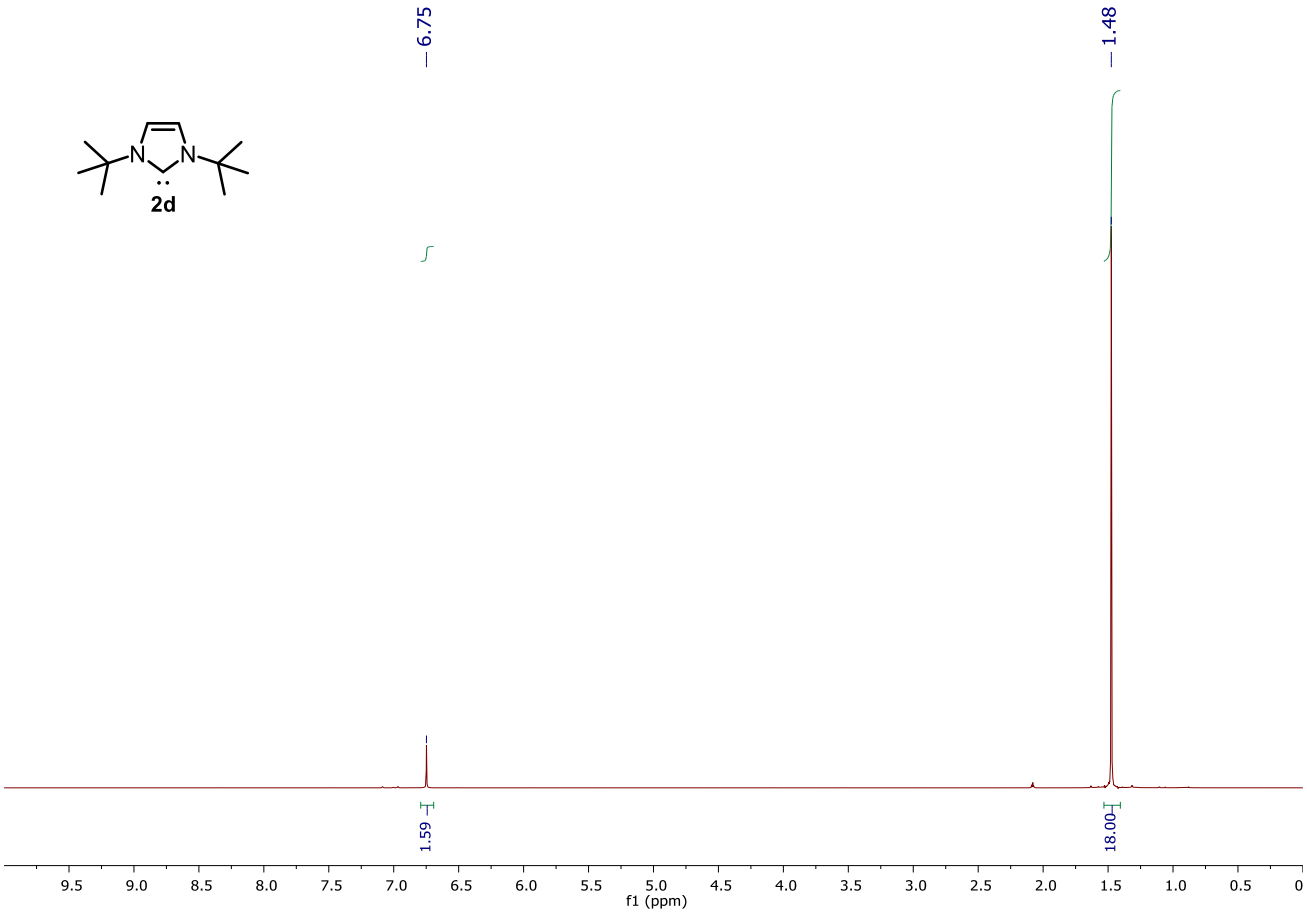


Figure S9: $^{13}C\{^{1}H\}$ NMR (400 MHz, tol-d_8) of **2d**

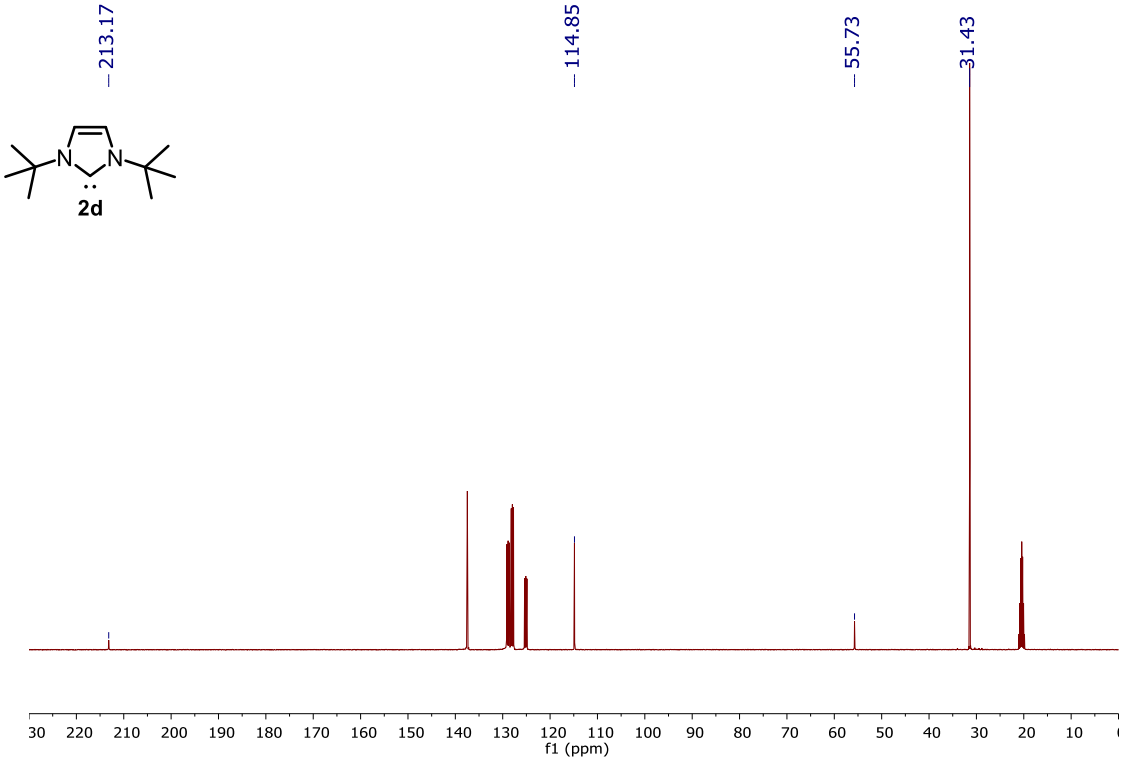


Figure S10: ^{1}H NMR (600 MHz, CD_2Cl_2) of **3a**

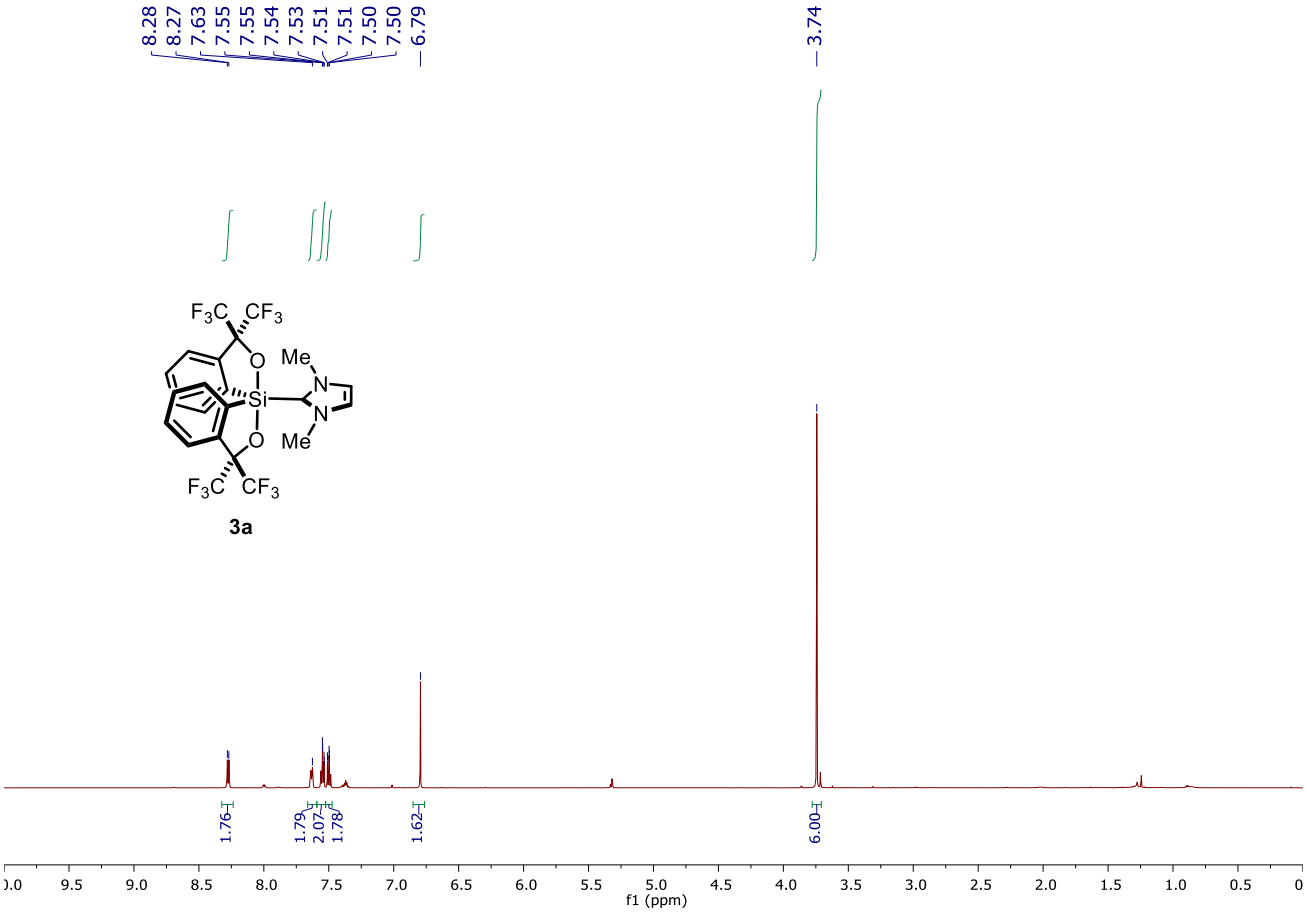


Figure S11: $^{19}F\{^{1}H\}$ NMR (564 MHz, CD_2Cl_2) of **3a**

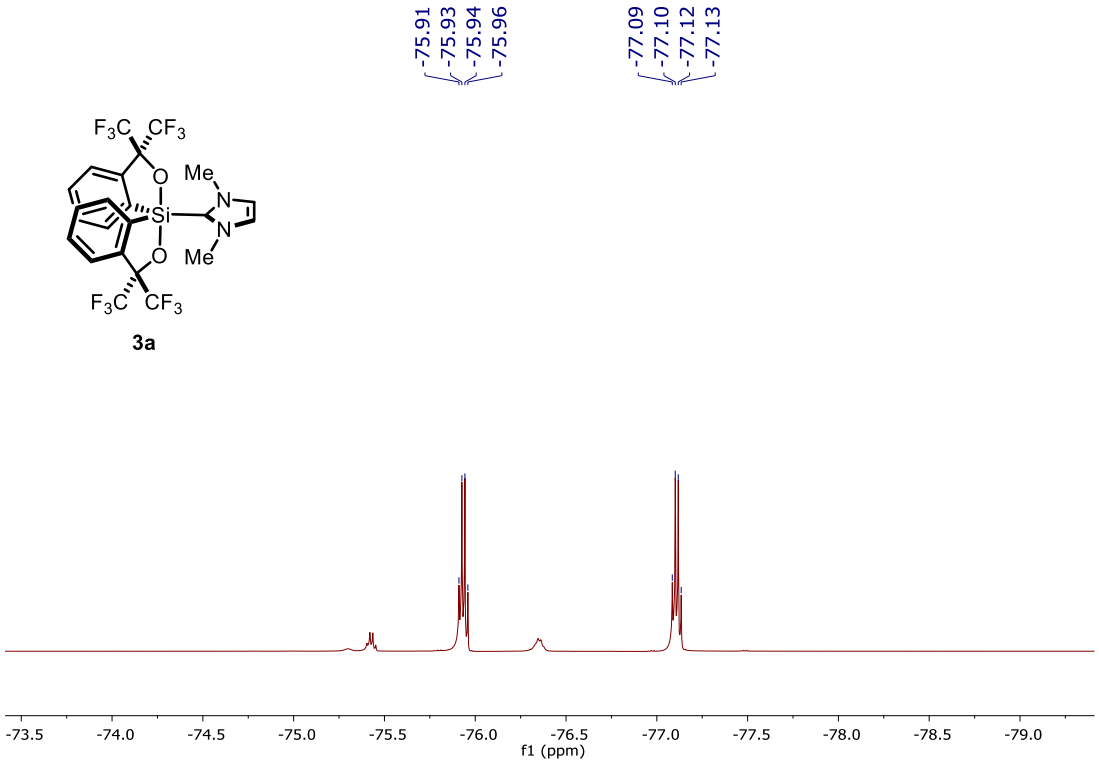


Figure S12: $^{13}C\{^{1}H\}$ NMR (150 MHz, CD_2Cl_2) of **3a**

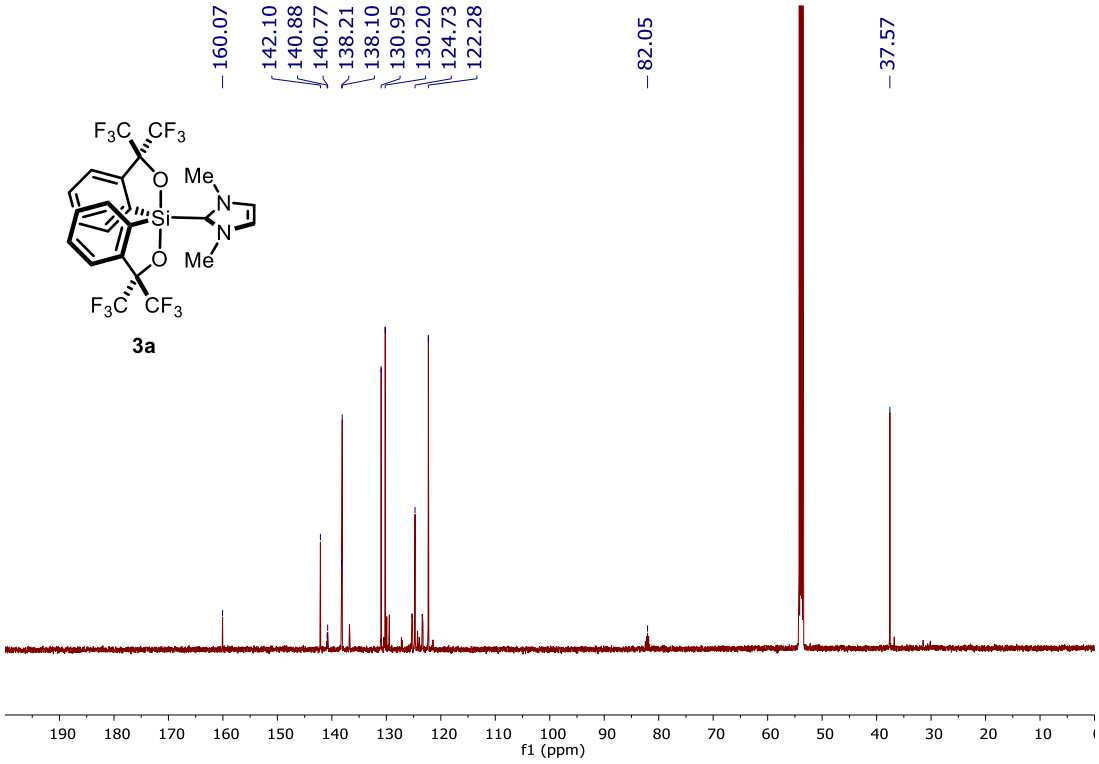


Figure S13: $^{29}Si\{^{1}H\}$ NMR (119 MHz, CD_2Cl_2) of **3a**

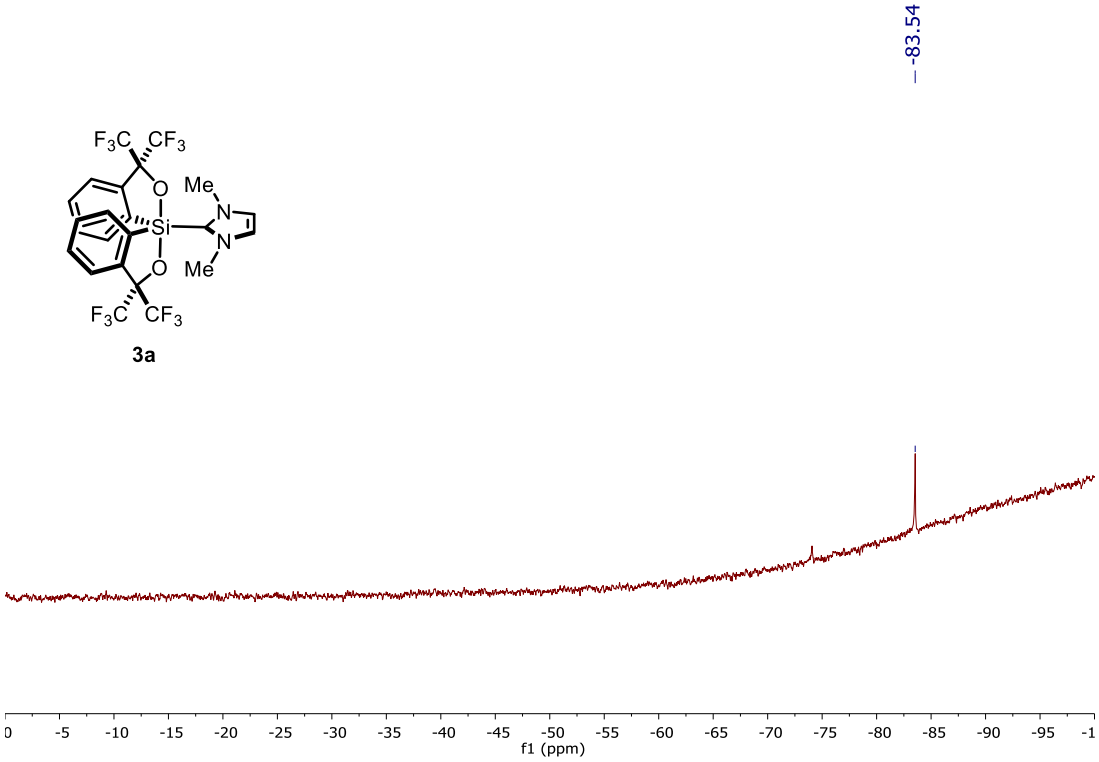


Figure S14: ^{1}H NMR (400 MHz, tol-d_8) of **3b**

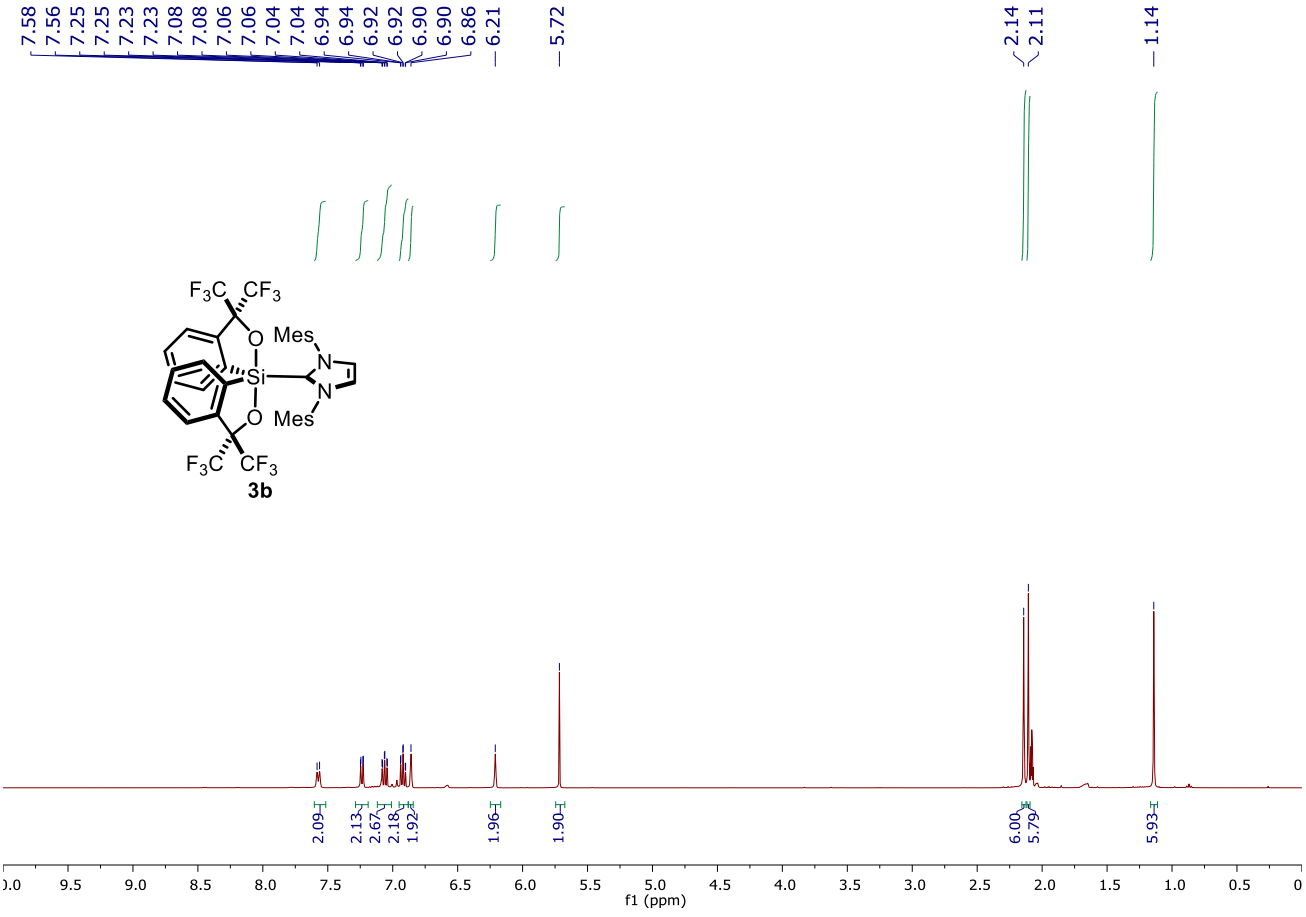


Figure S15: $^{19}F\{^{1}H\}$ NMR (376 MHz, tol-d_8) of **3b**

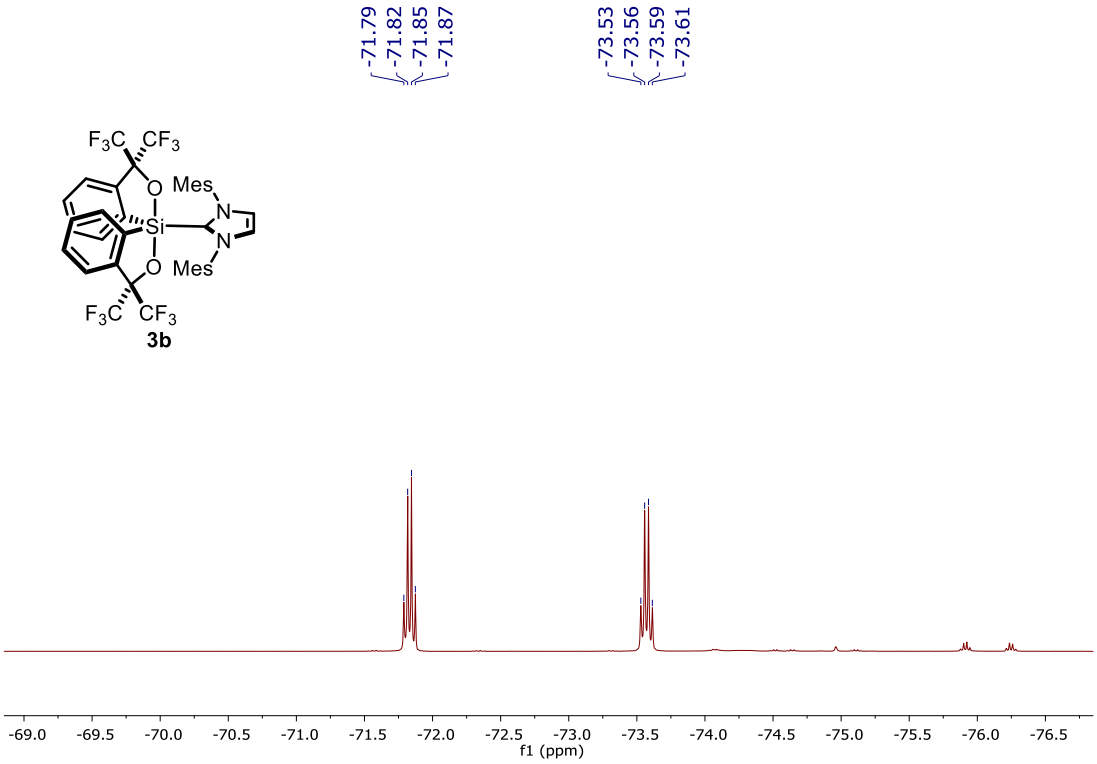


Figure S16: $^{13}C\{^{1}H\}$ NMR (100 MHz, tol-d_8) of **3b**

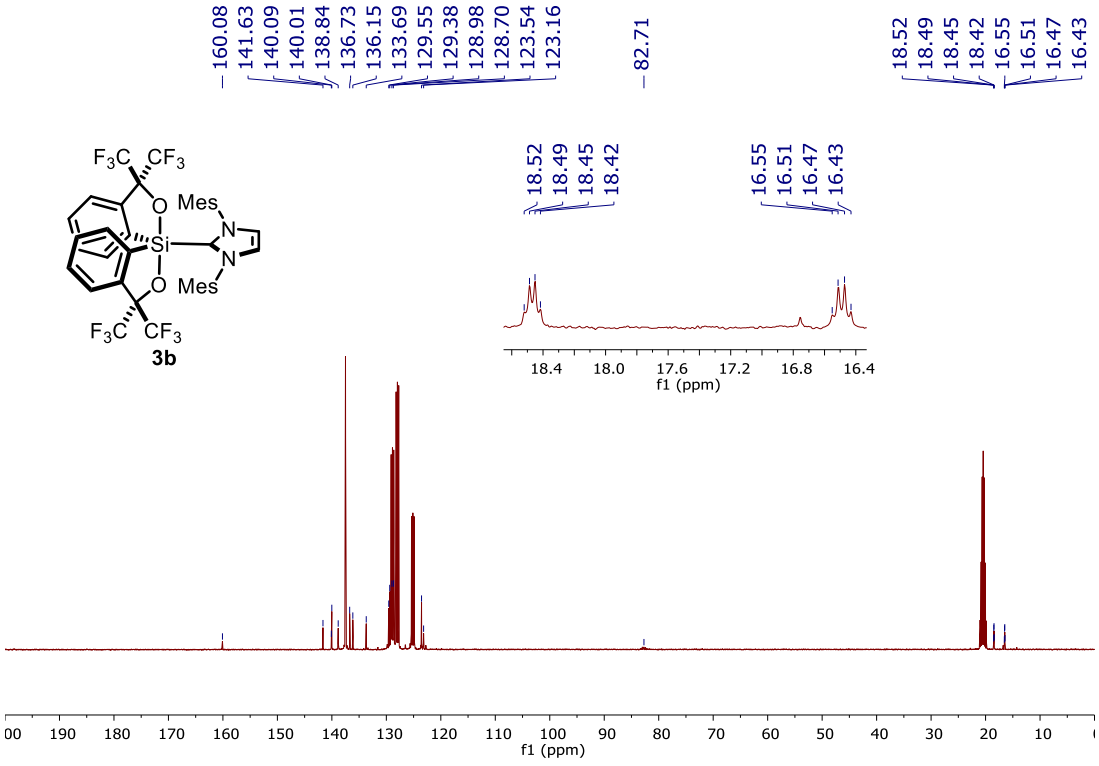


Figure S17: $^{29}Si\{^{1}H\}$ NMR (119 MHz, CD_2Cl_2) of **3b**

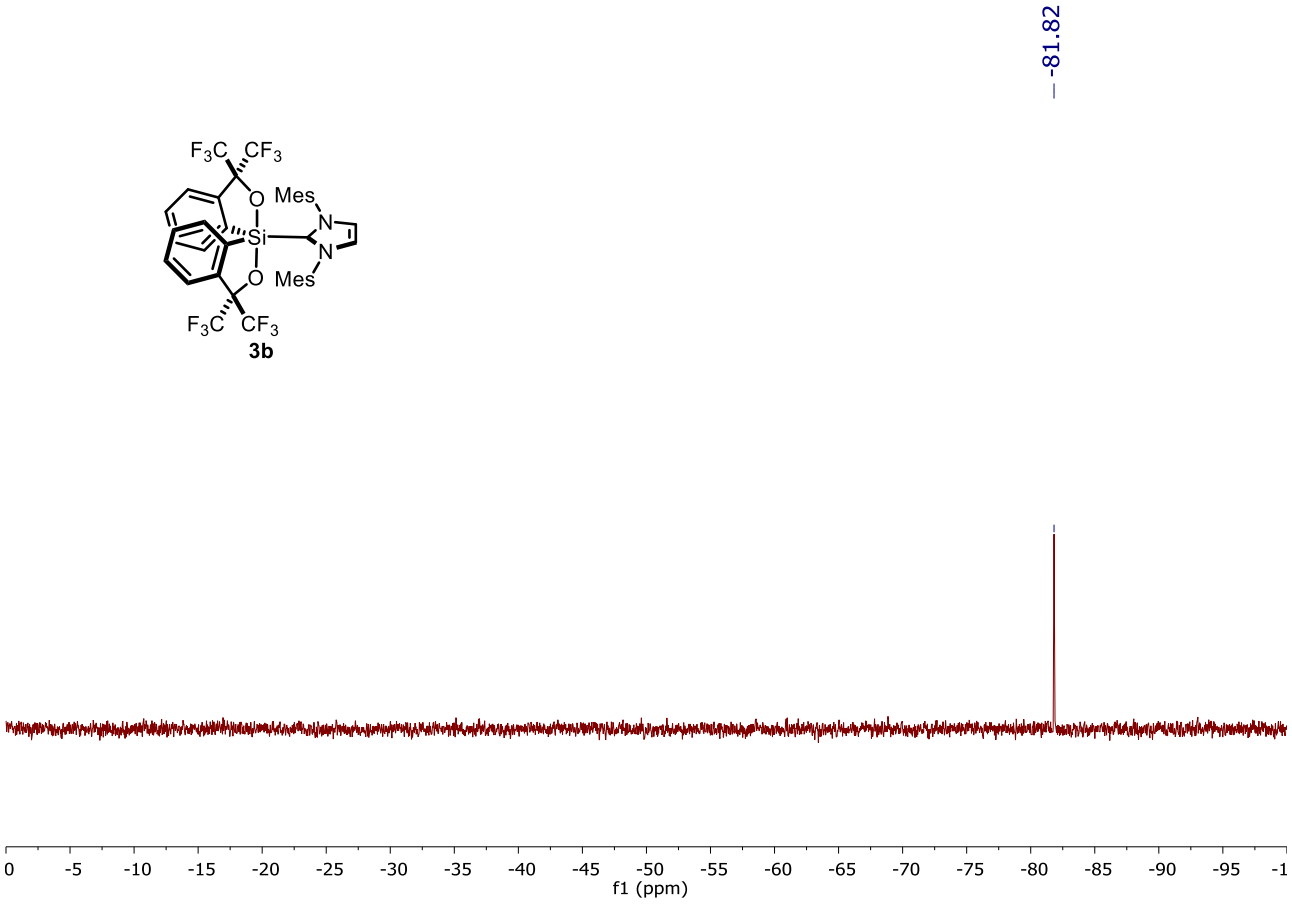


Figure S18: ^{1}H NMR (600 MHz CD_2Cl_2) of **4c**

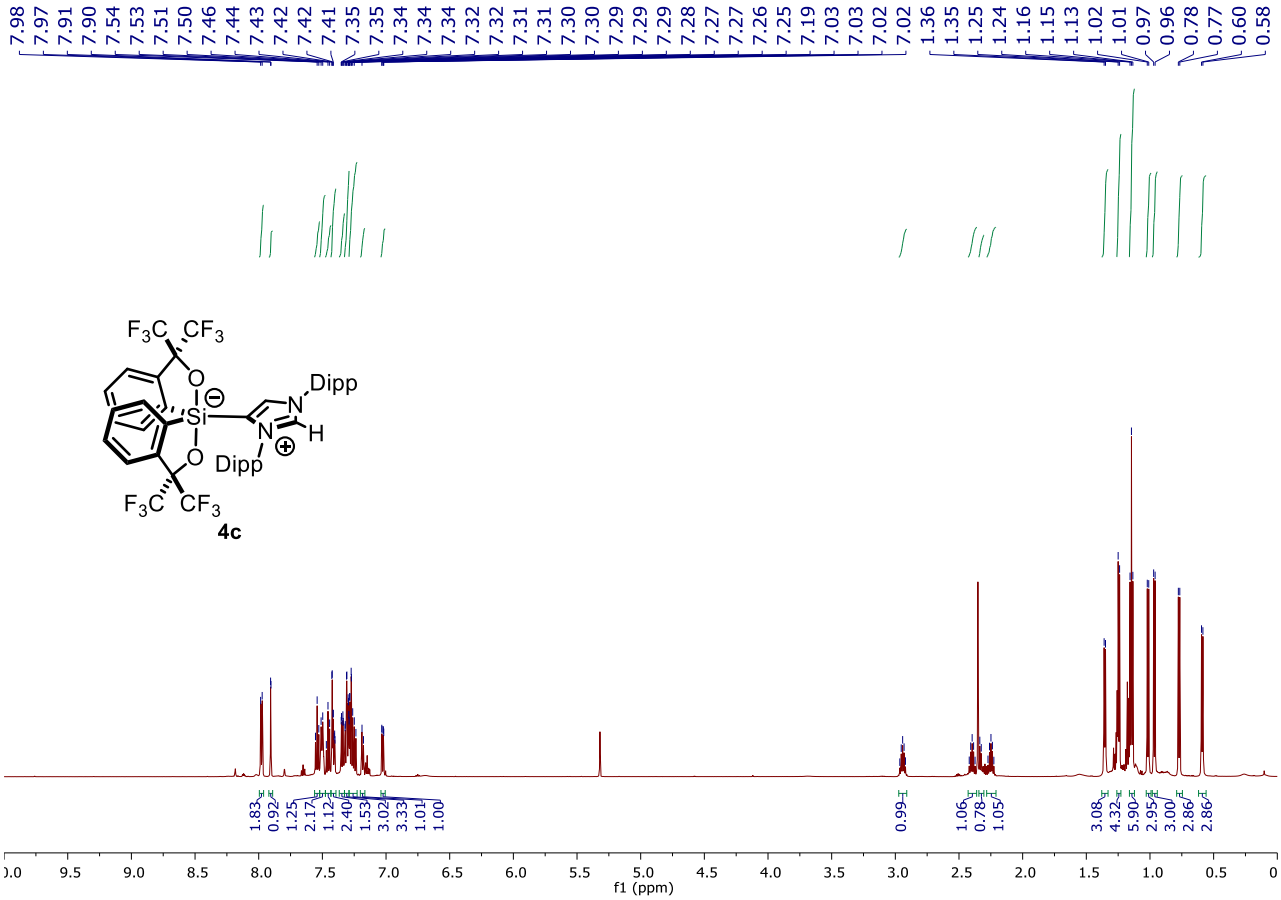


Figure S19: $^{19}F\{^{1}H\}$ NMR (564 MHz, CD_2Cl_2) of **4c**

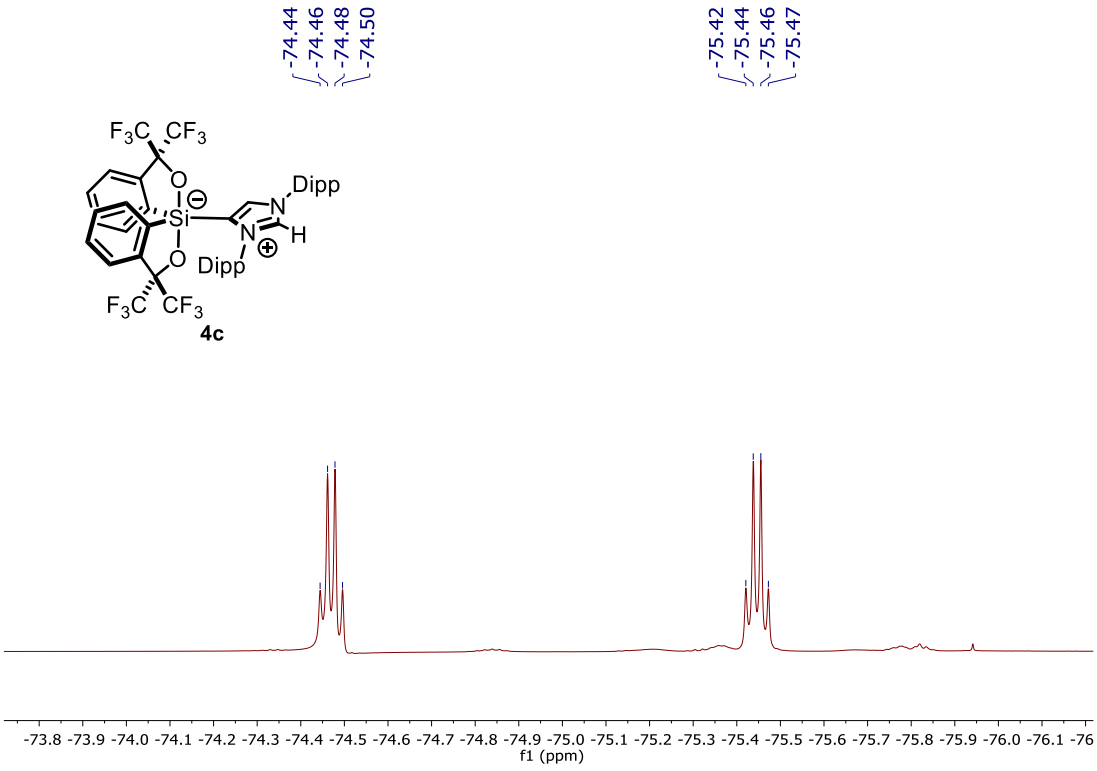


Figure S20: $^{13}C\{^{1}H\}$ NMR (150 MHz, CD_2Cl_2) of **4c**

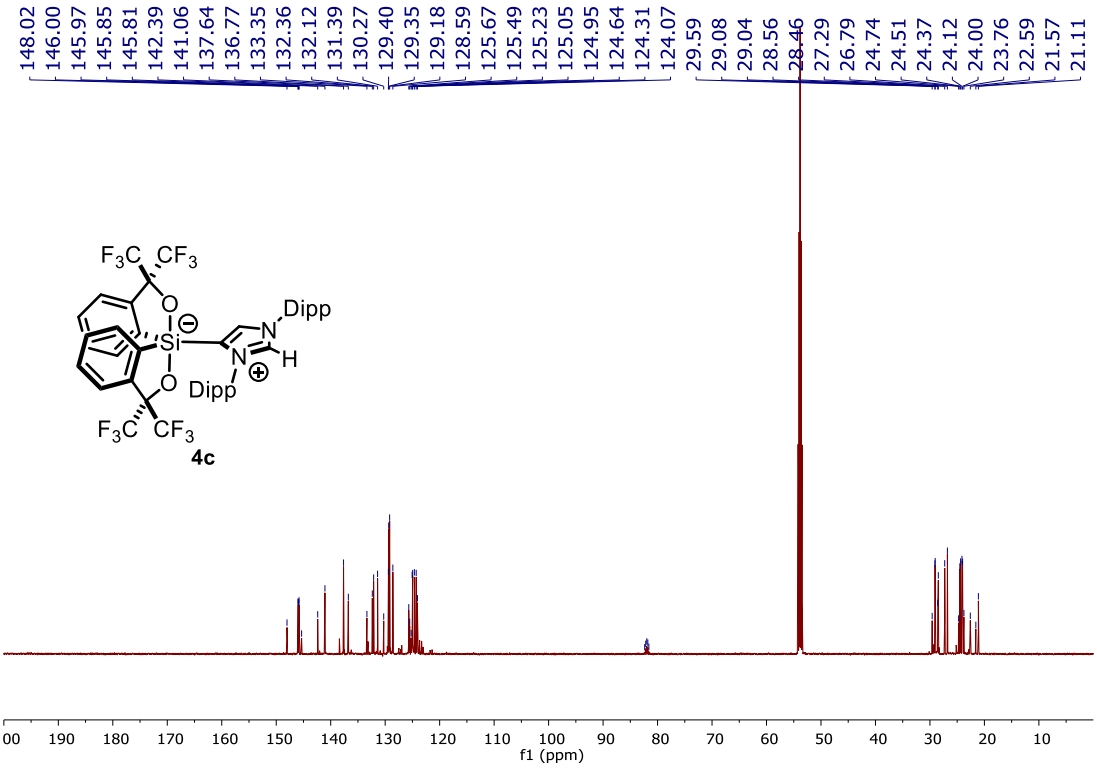


Figure S21: $^{29}Si\{^{1}H\}$ NMR (119 MHz, CD_2Cl_2) of **4c**

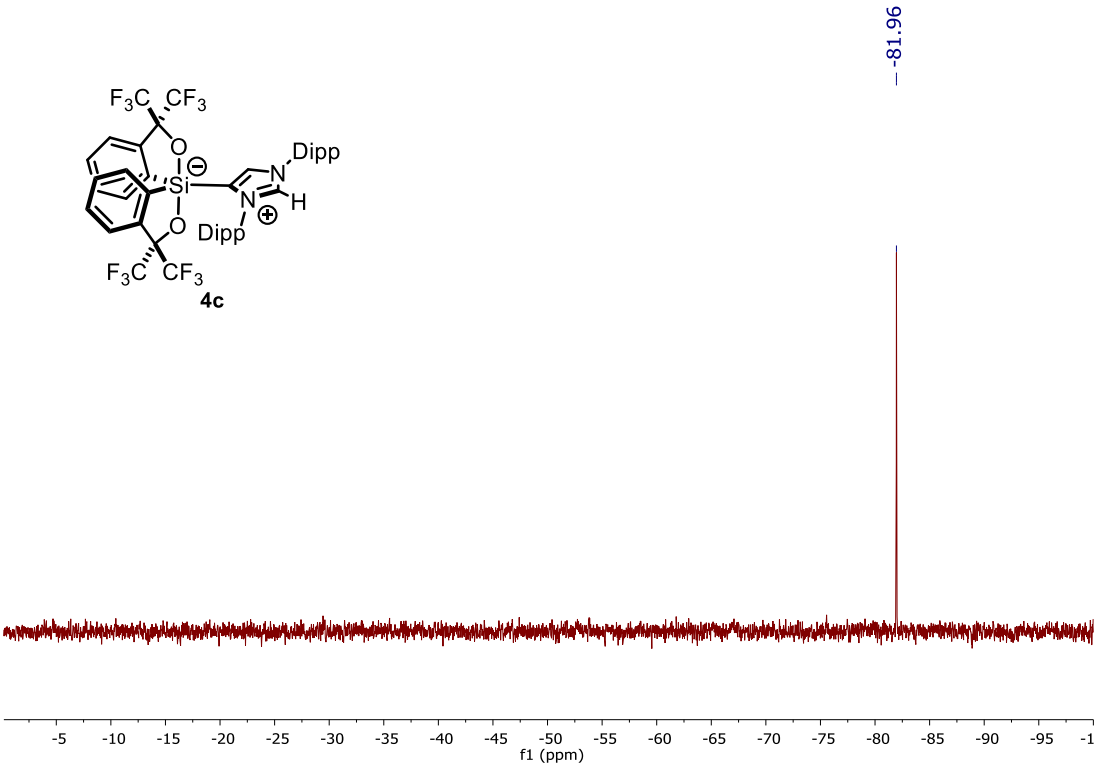


Figure S22: ^{1}H NMR (400 MHz CD_2Cl_2) of **4d**

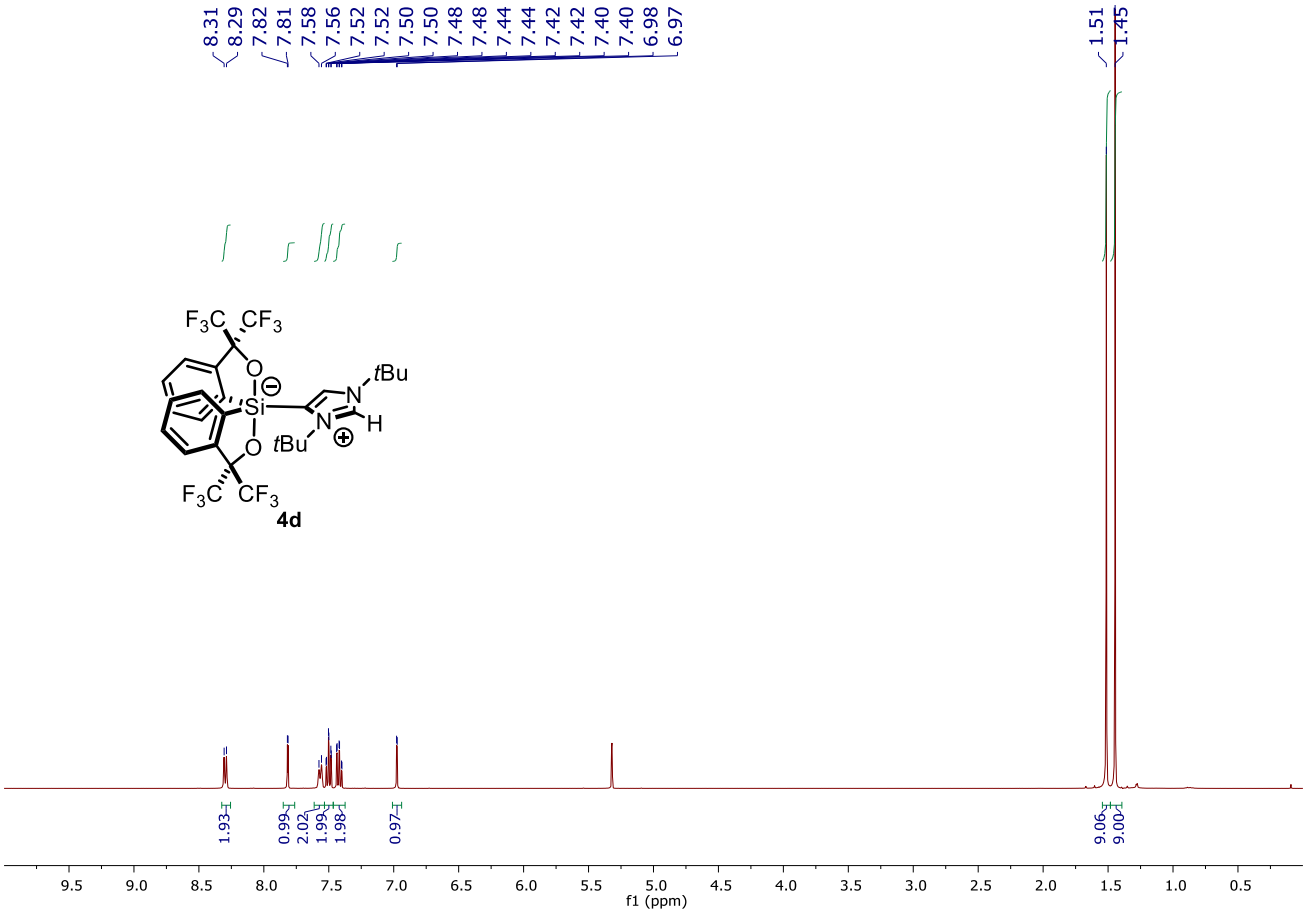


Figure S23: $^{19}F\{^{1}H\}$ NMR (376 MHz, CD_2Cl_2) of **4d**

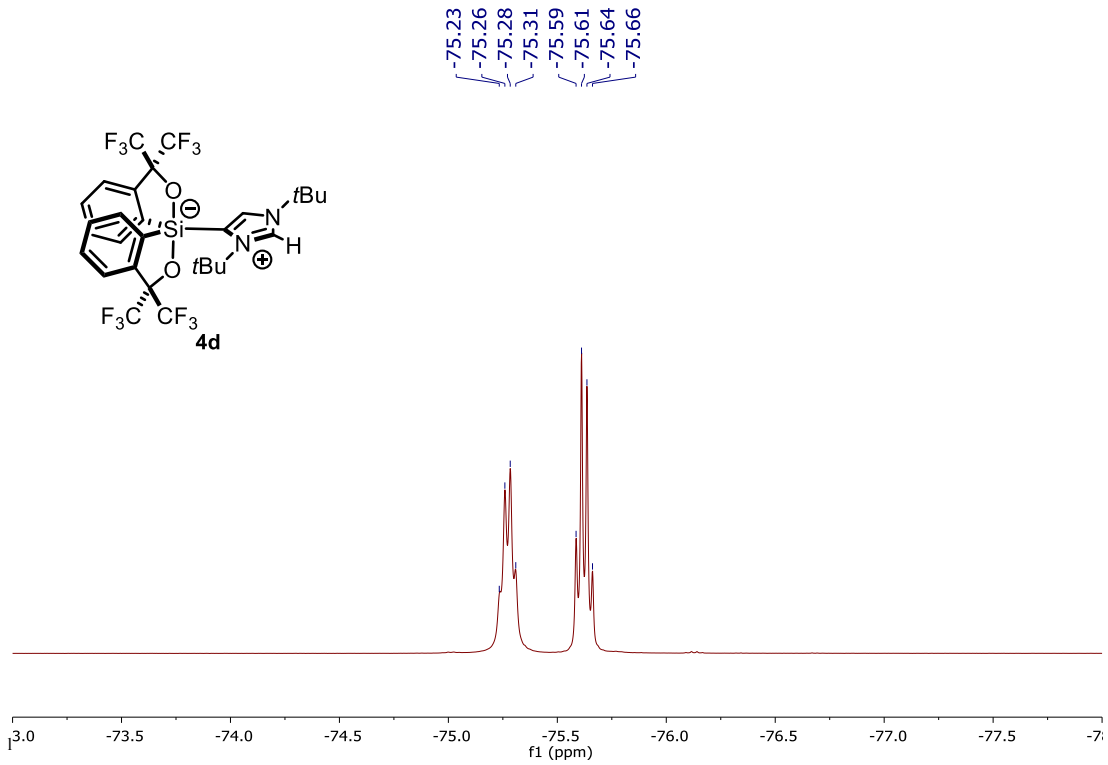


Figure S24: $^{13}C\{^{1}H\}$ NMR (100 MHz, CD_2Cl_2) of **4d**

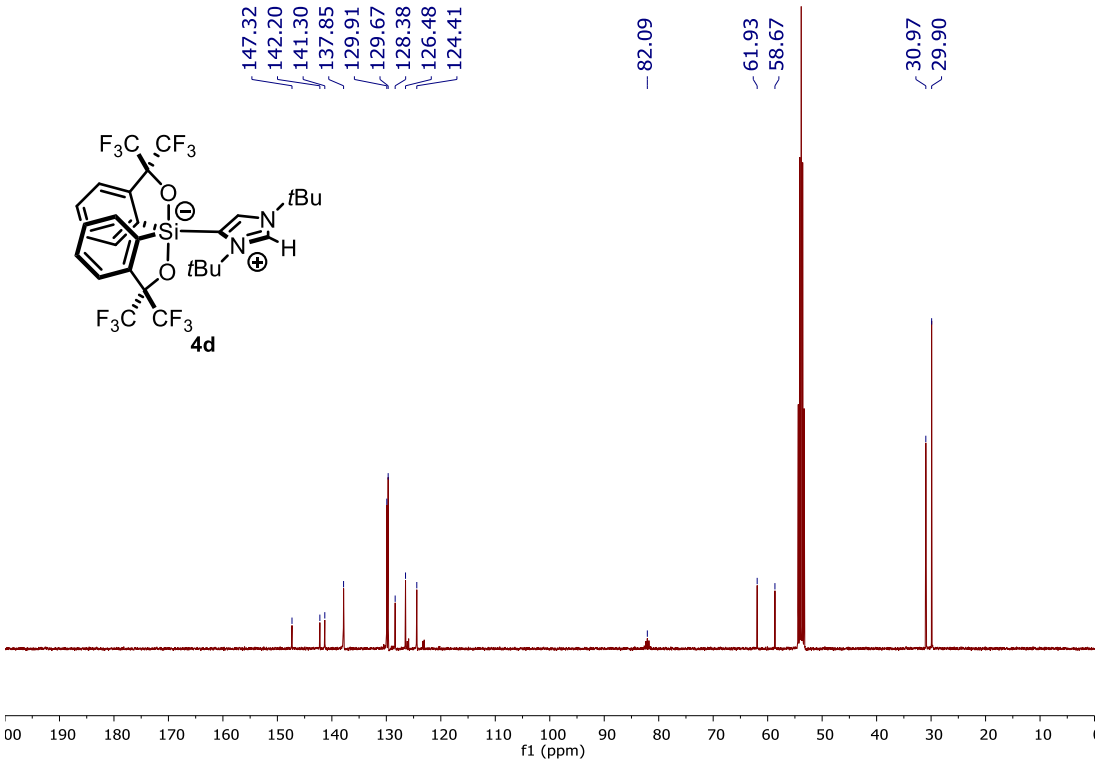


Figure S25: $^{29}Si\{^{1}H\}$ NMR (119 MHz, CD_2Cl_2) of **4d**

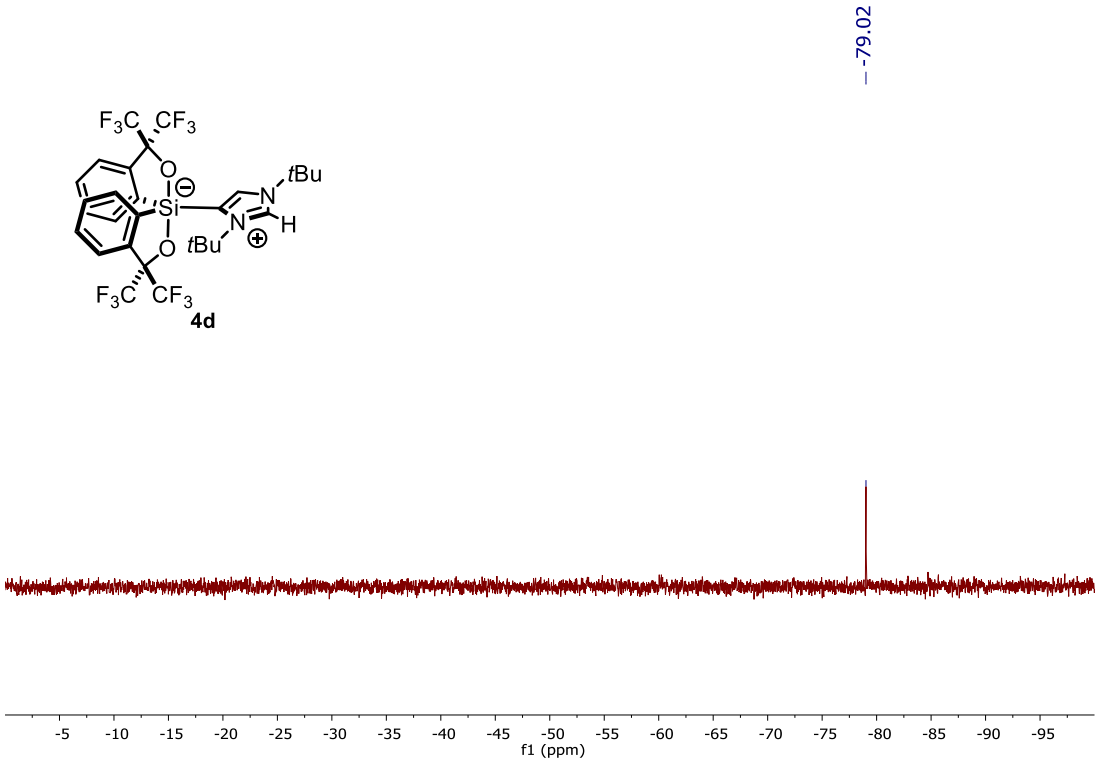


Figure S26: ^{1}H NMR (600 MHz CD_2Cl_2) of **5d**

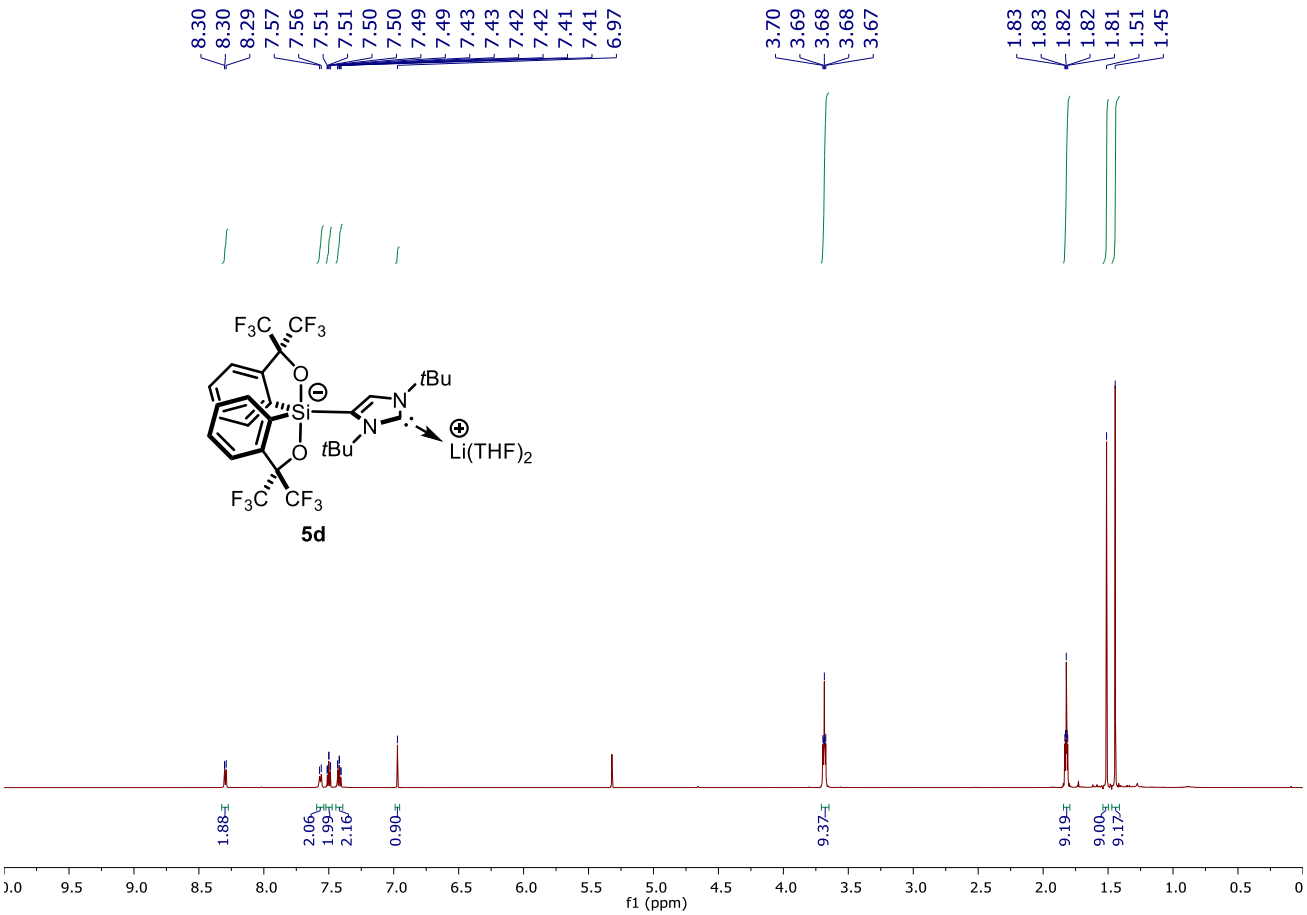


Figure S27: $^{19}F\{^{1}H\}$ NMR (564 MHz, CD_2Cl_2) of **5d**

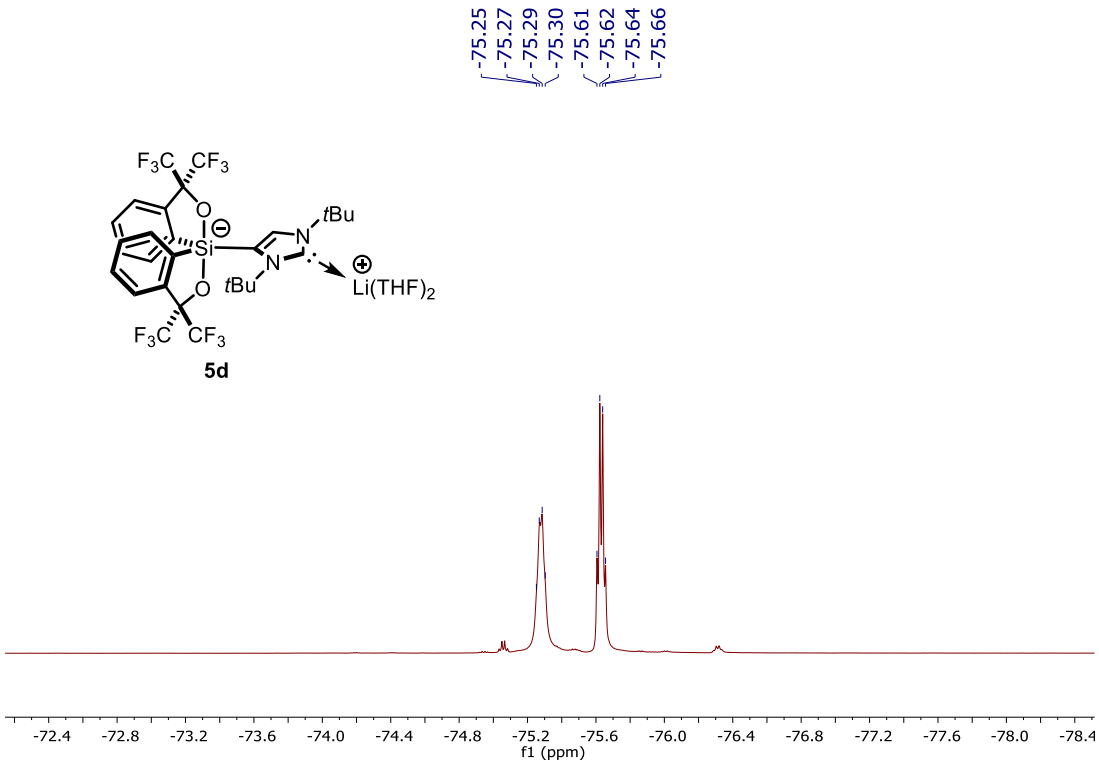


Figure S28: $^{13}C\{^{1}H\}$ NMR (150 MHz, CD_2Cl_2) of **5d**

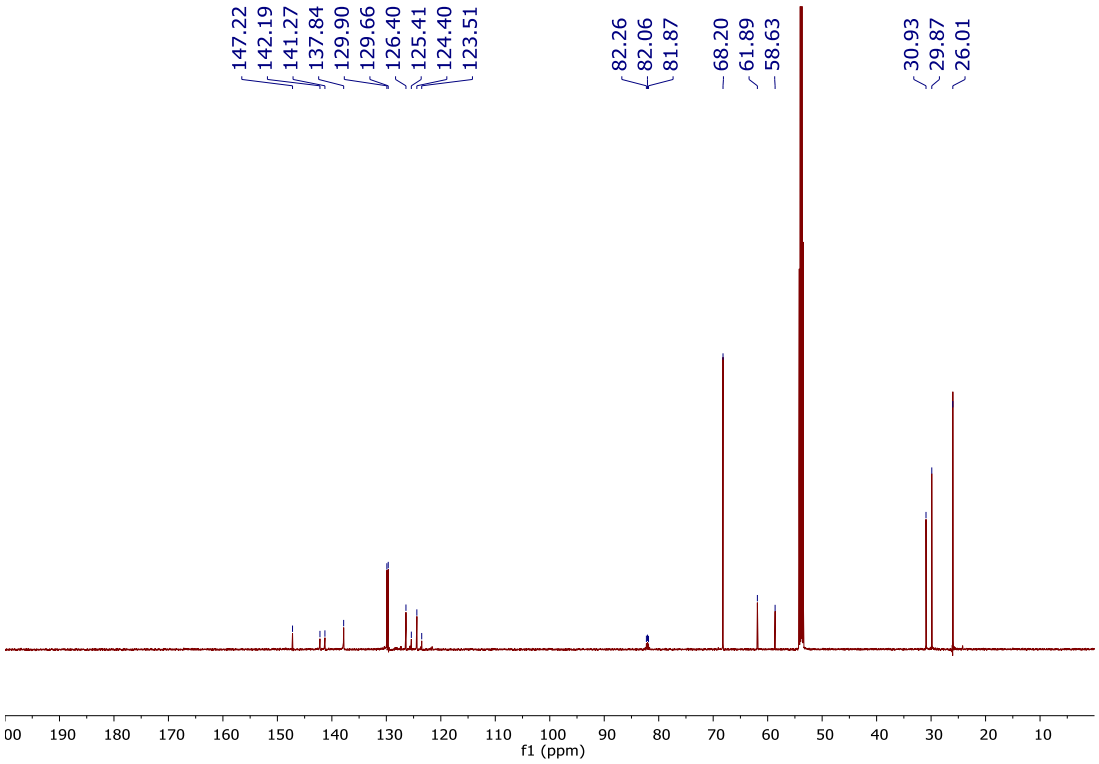


Figure S29: $^{29}Si\{^{1}H\}$ NMR (79 MHz, CD_2Cl_2) of **5d**

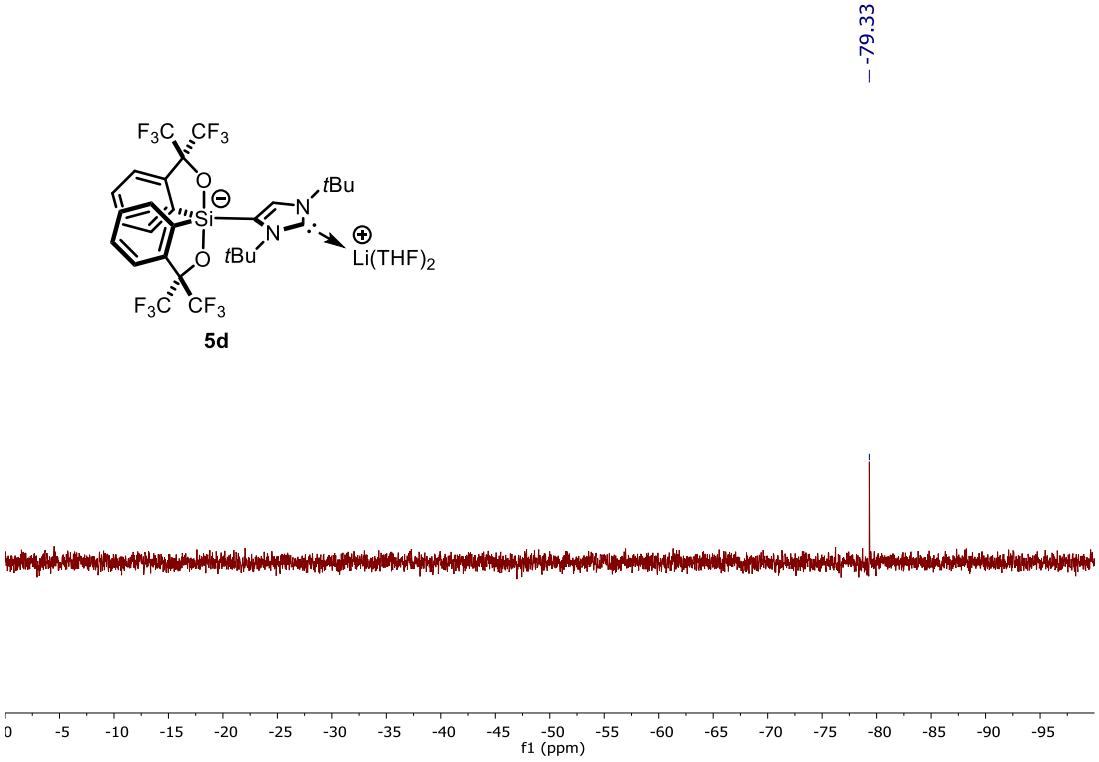


Figure S30: $^{7}Li\{^{1}H\}$ NMR (155 MHz, CD_2Cl_2) of **5d**; (LiCl 1M in D_2O as external standard)

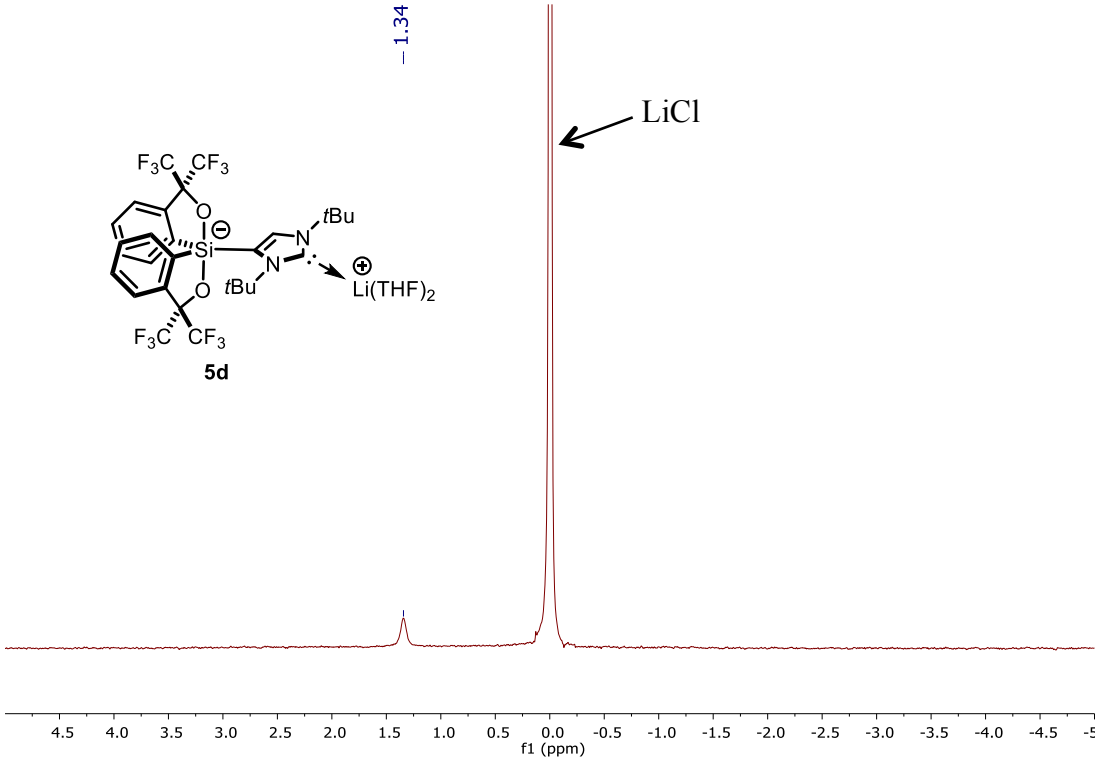


Figure S31: ^{1}H NMR (600 MHz, CD_2Cl_2) of **6c**

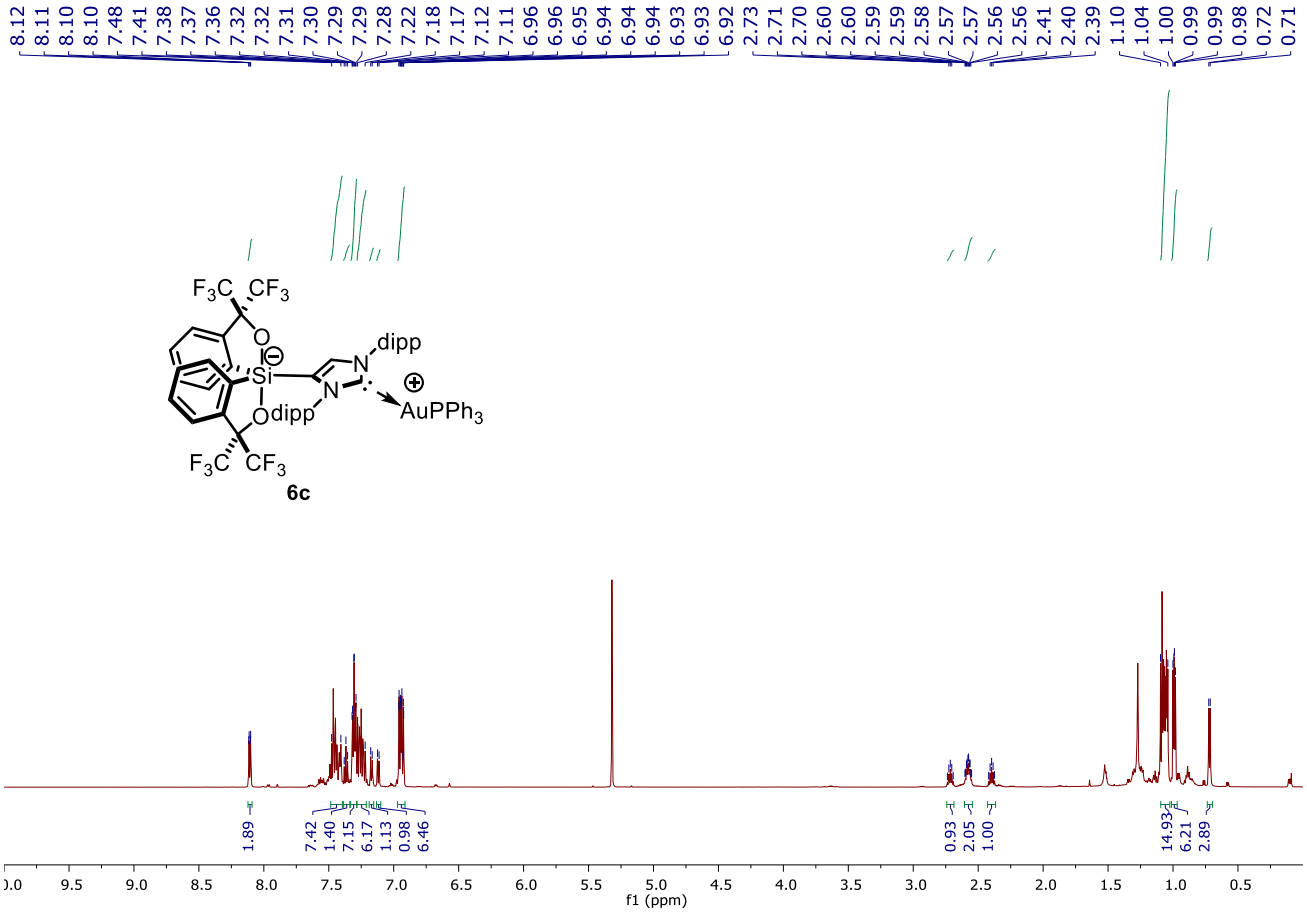


Figure S32: $^{19}F\{^{1}H\}$ NMR (564 MHz, CD_2Cl_2) of **6c**

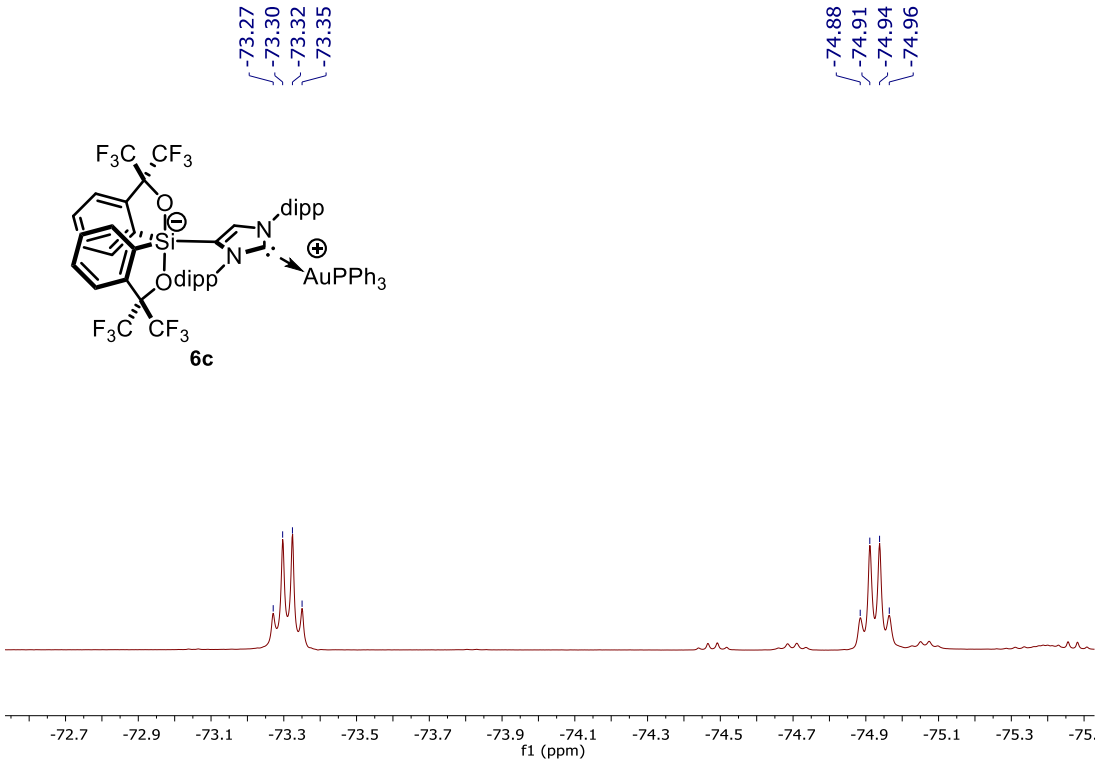


Figure S33: $^{13}C\{^{1}H\}$ NMR (150 MHz, CD_2Cl_2) of 6c

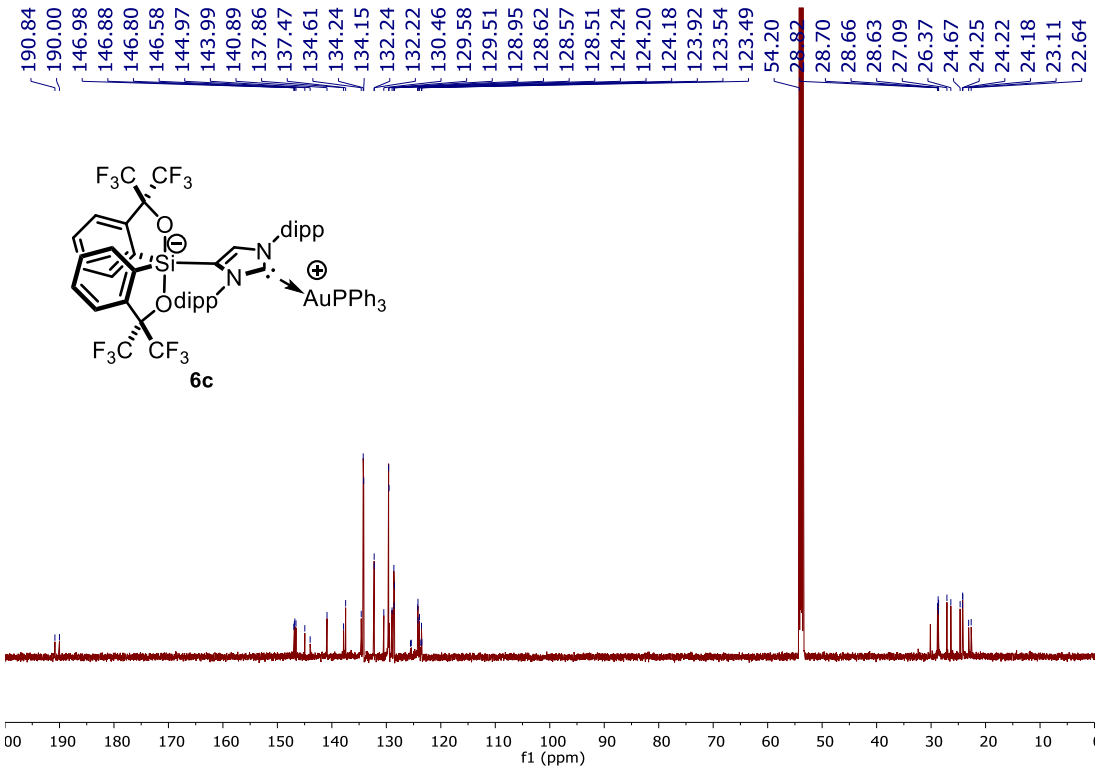


Figure S34: $^{31}P\{^{1}H\}$ NMR (161 MHz, CD_2Cl_2) of **6c**

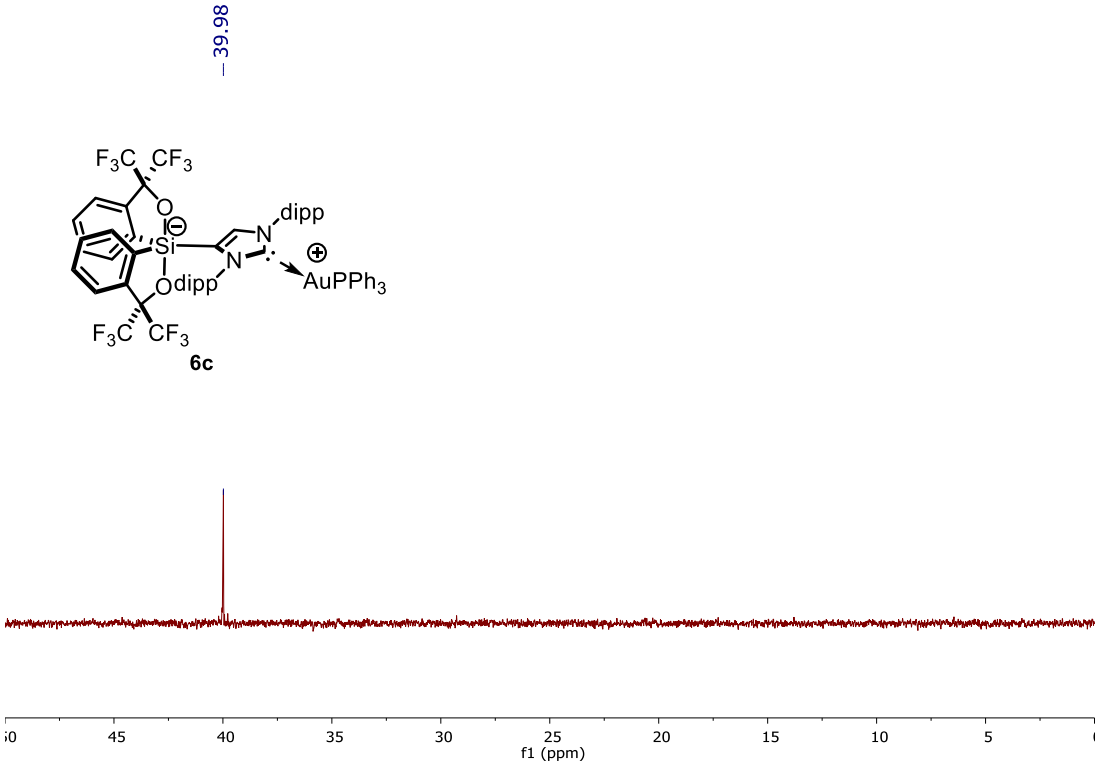


Figure S35: ^{1}H NMR (400 MHz, CD_2Cl_2) of **6d**

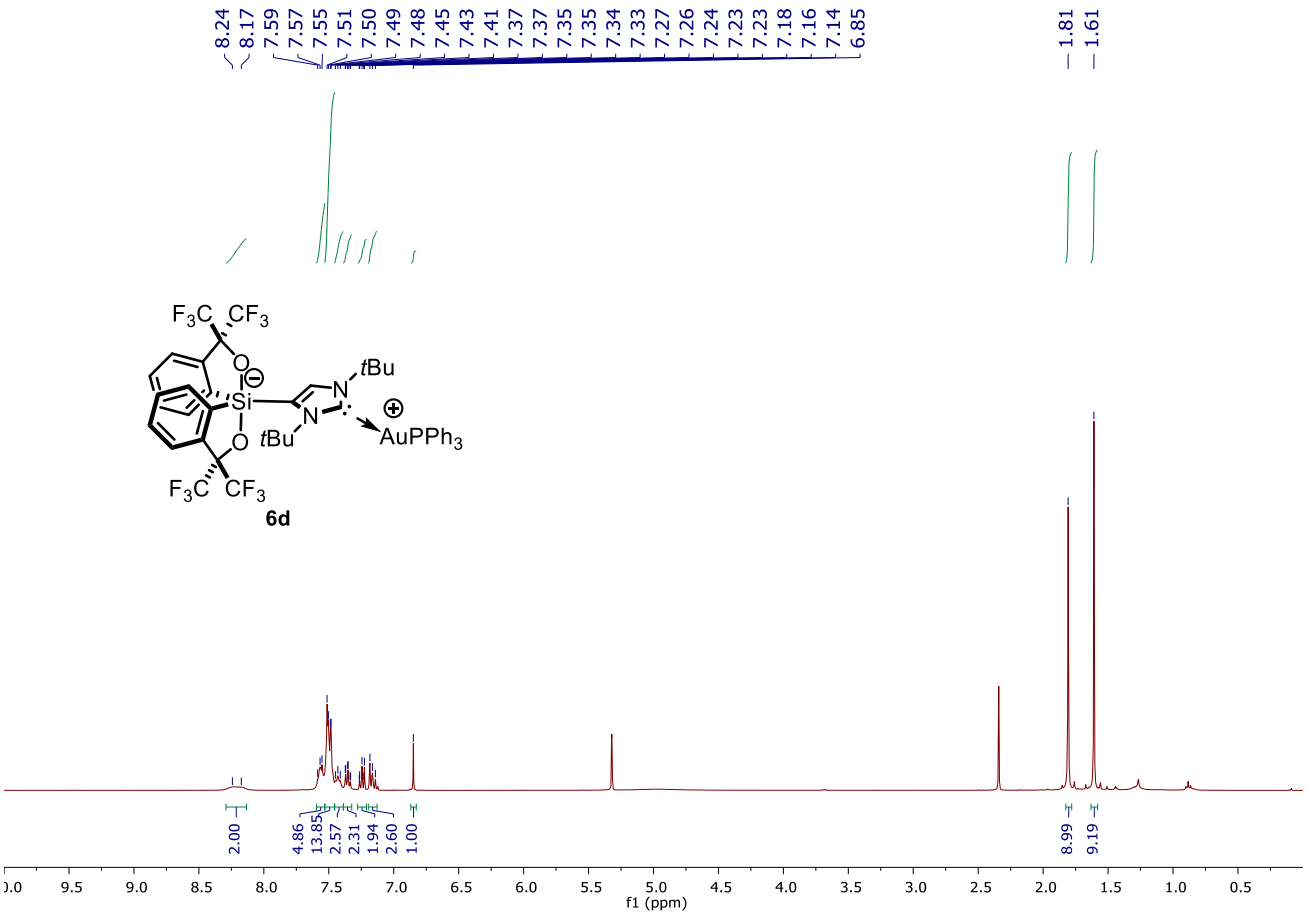


Figure S36: $^{19}F\{^{1}H\}$ NMR (376 MHz, CD_2Cl_2) of **6d**

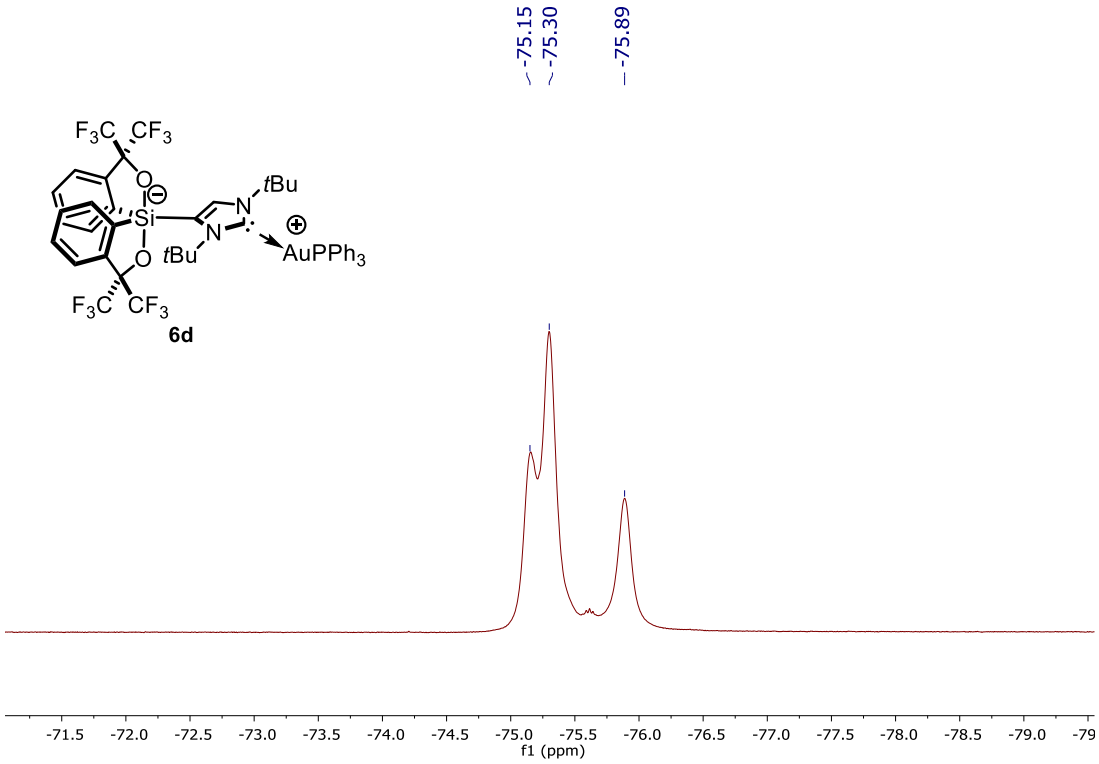


Figure S37: $^{13}C\{^{1}H\}$ NMR (100 MHz, CD_2Cl_2) of **6d**

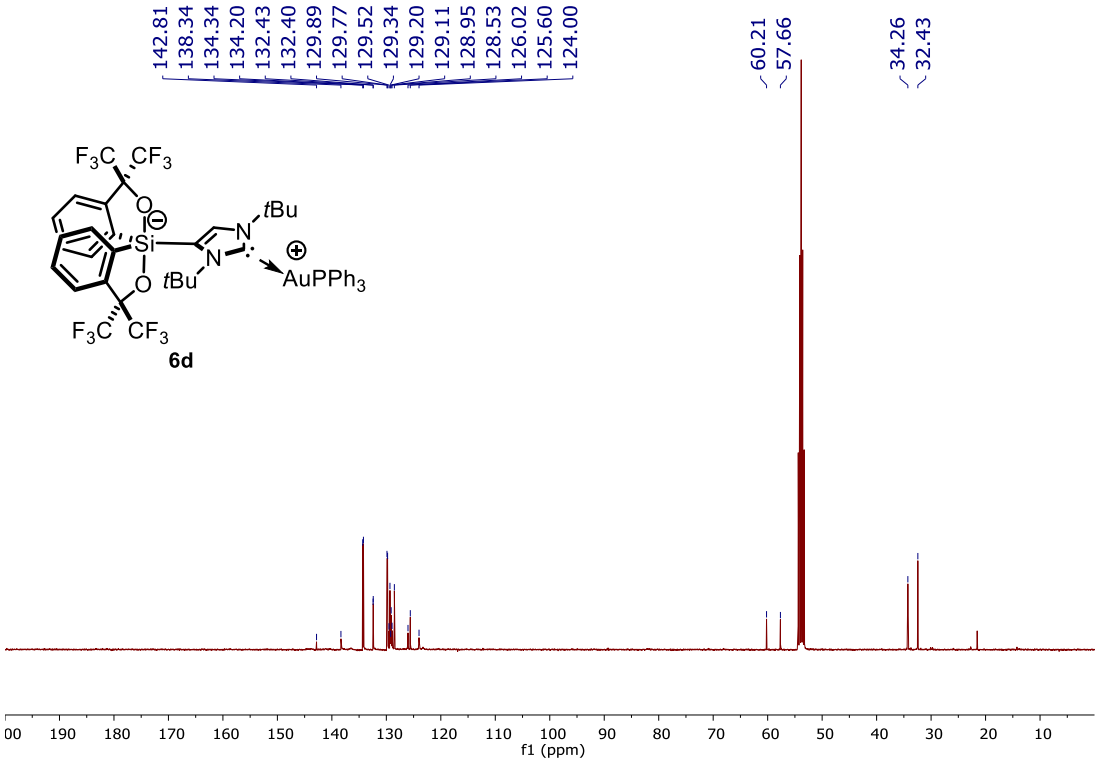


Figure S38: $^{29}Si\{^{1}H\}$ NMR (79 MHz, CD_2Cl_2) of **6d**

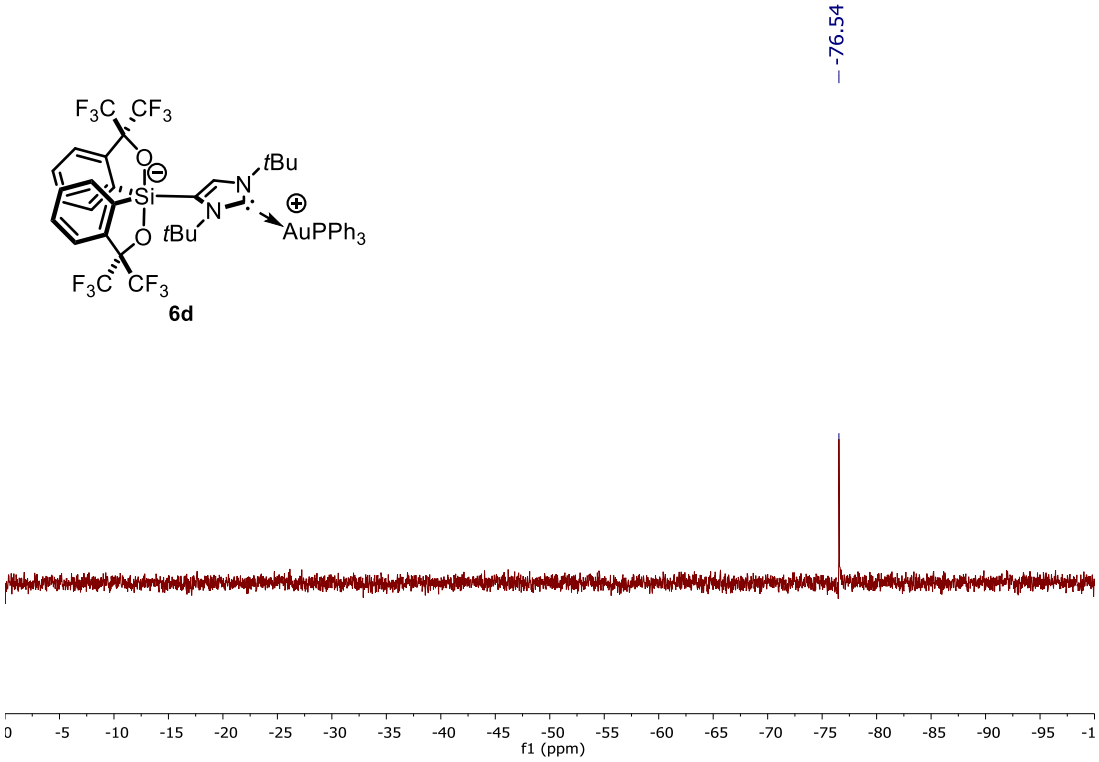


Figure S39: $^{31}P\{^{1}H\}$ NMR (162 MHz, CD_2Cl_2) of **6d**; H_3PO_4 85% in H_2O as external standard

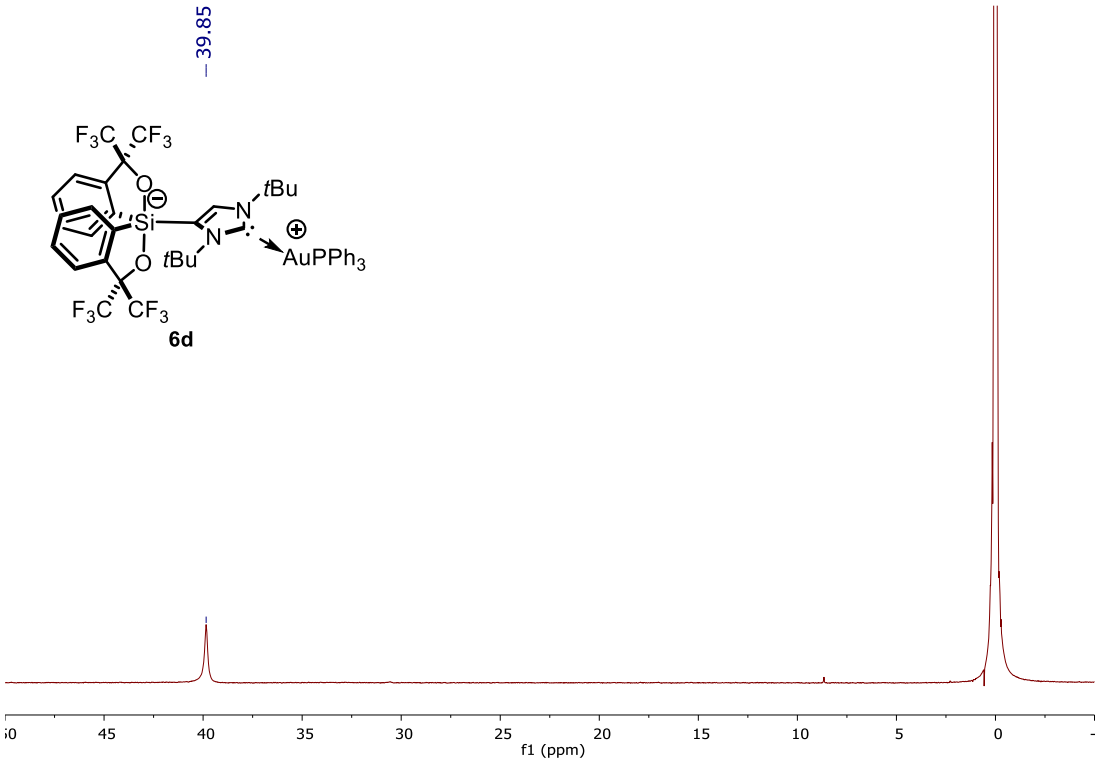


Figure S40: ^{1}H NMR (600 MHz, CD_2Cl_2) of **7c**

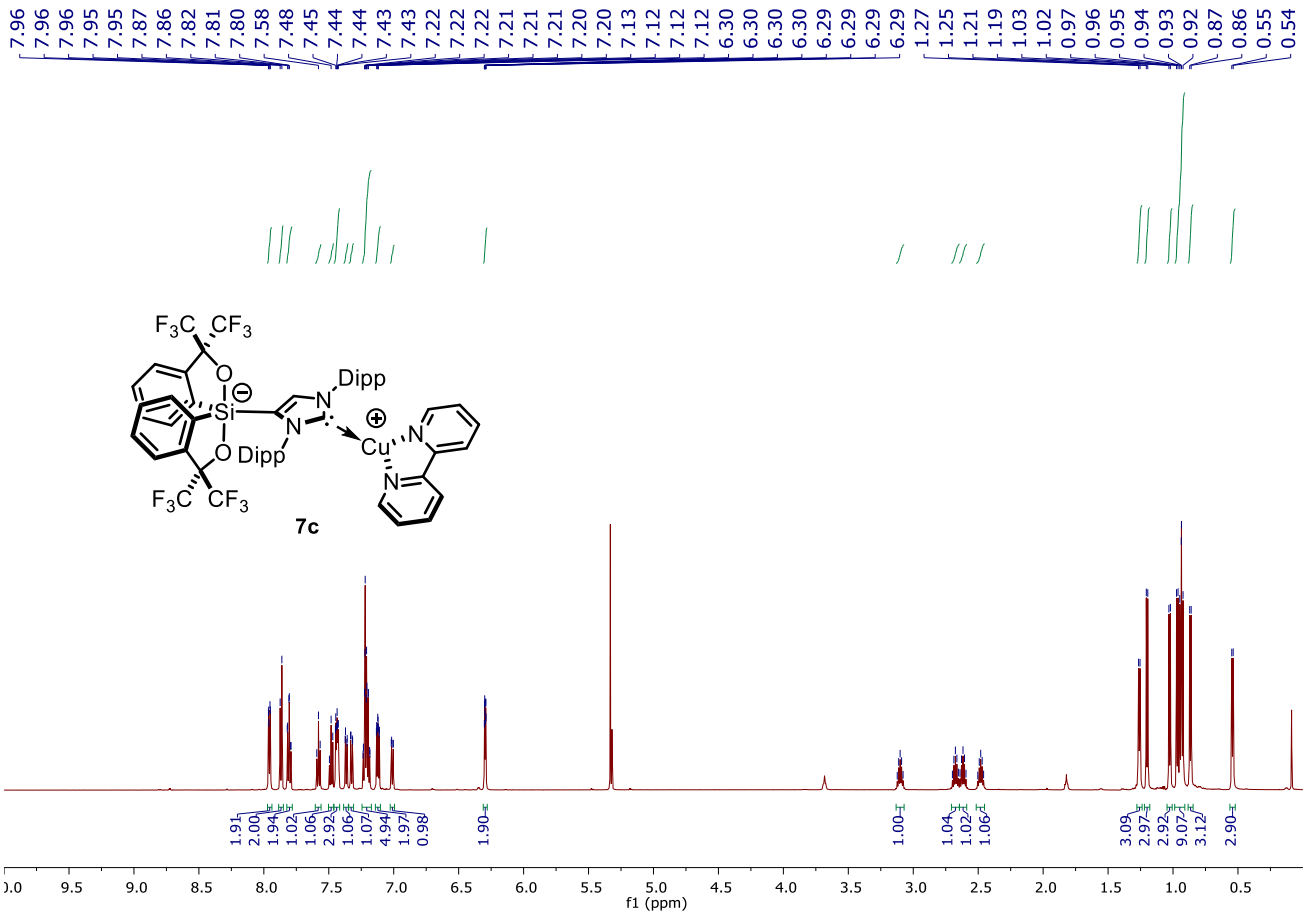


Figure S41: $^{19}F\{^{1}H\}$ NMR (564 MHz, CD_2Cl_2) of **7c**

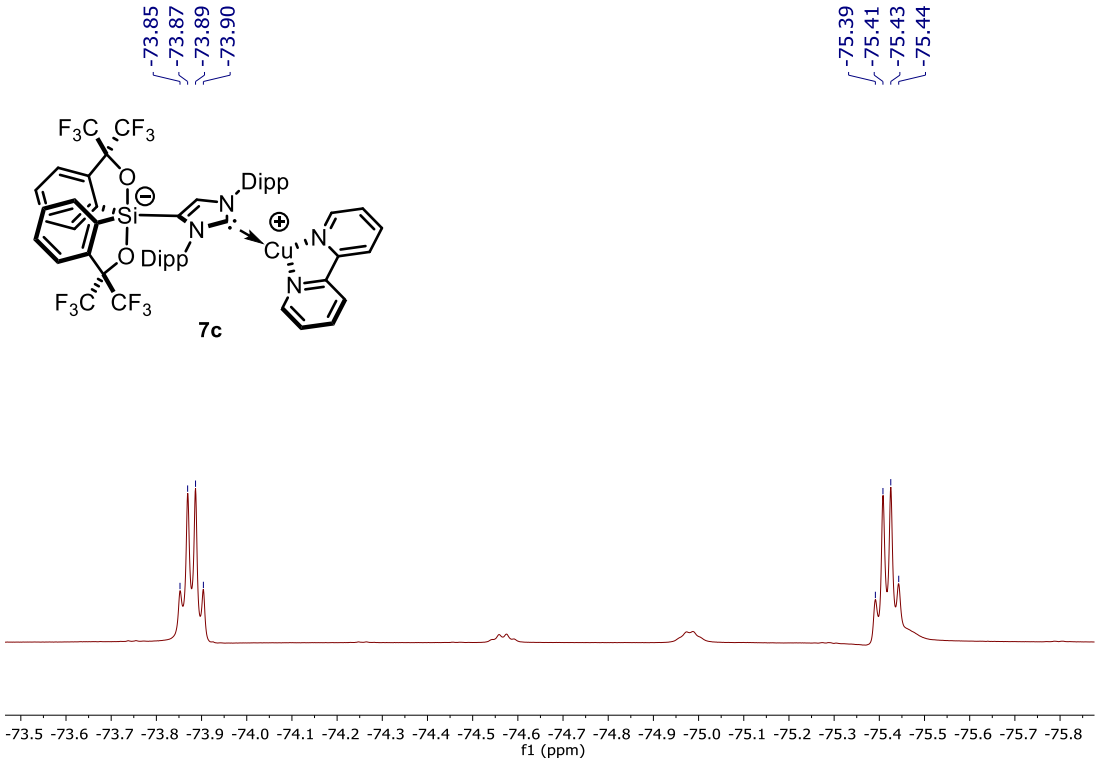


Figure S42: $^{13}C\{^{1}H\}$ NMR (150 MHz, CD_2Cl_2) of **7c**

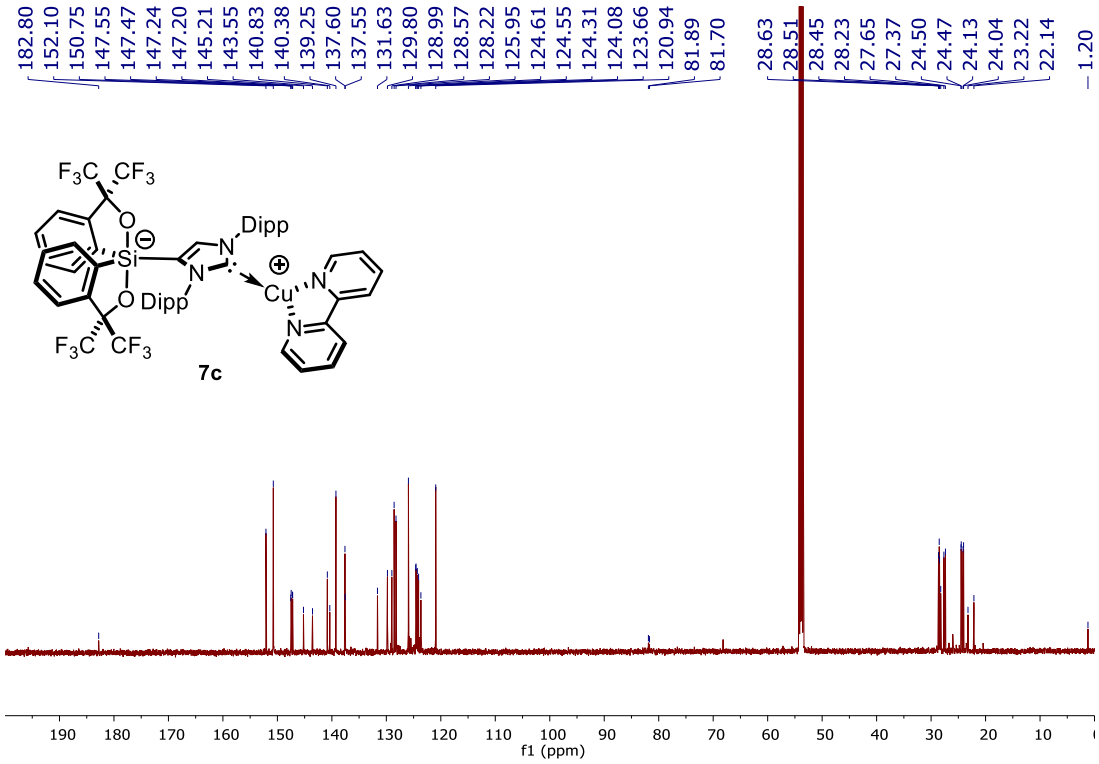
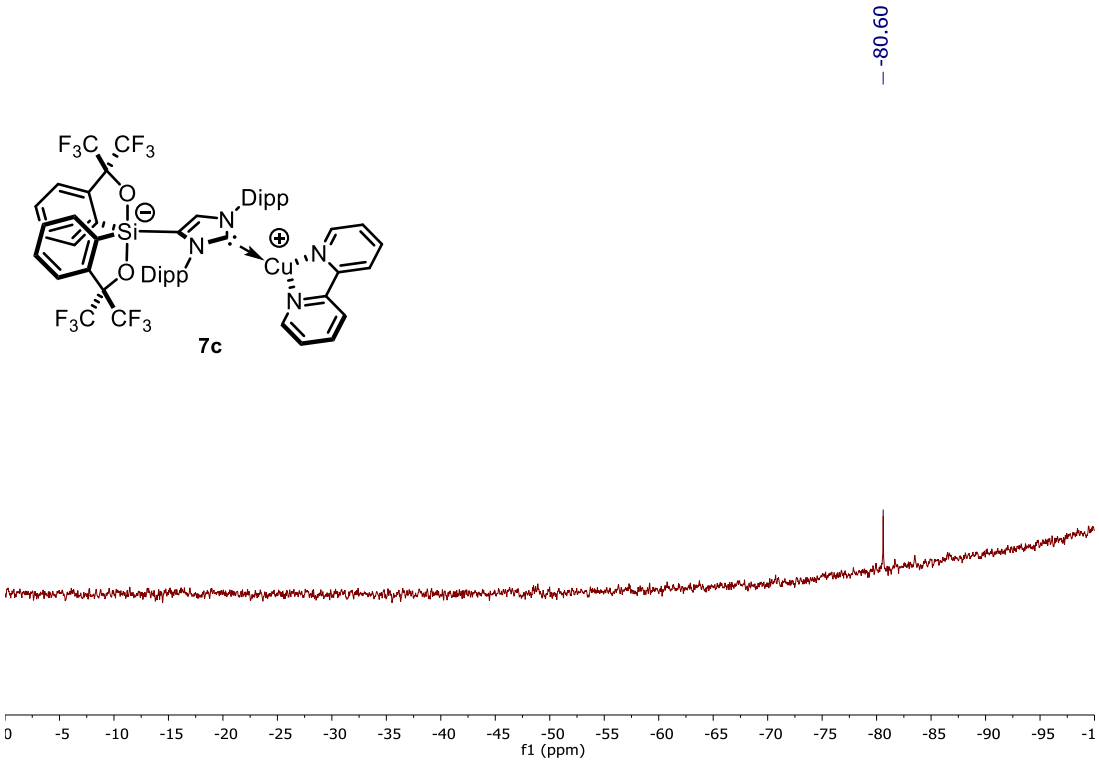


Figure S43: $^{29}Si\{^{1}H\}$ NMR (119 MHz, CD_2Cl_2) of **7c**



VI. X-RAY Data

These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Compound 3a *(CCDC number: 1523668)*

Empirical formula	$C_{23}\ H_{16}\ F_{12}\ N_2\ O_2\ Si$
Crystal system	Orthorhombic
Space group	P b c a
Unit cell dimensions	a = 12.7028(10) Å
	b = 11.9895(10) Å
	c = 31.828(3) Å
	α = 90°
	β = 90°
	γ = 90°
Volume	4847.5(7) $Å^3$
Z	8
Crystal description	colourless fragment
Crystal size	0.4 x 0.3 x 0.2 mm
Min. and max. transmission	0.93 and 0.98
Temperature	200(1) K
θ range for data collection	3.02° to 30.07°
Reflections (all / independent)	45794 / 7098
R(int)	2.21 %
Data / parameters / restraints	7098 / 363 / 0

Compound 3b *(CCDC number: 1523669)*

Empirical formula	$C_{42.5}\ H_{11}\ F_{12}\ N_2\ O_2\ Si$
Crystal system	Monoclinic
Space group	P 2_1/n
Unit cell dimensions	a = 10.9559(4) Å
	b = 40.9680(16) Å
	c = 18.0864(7) Å
	α = 90°
	β = 100.232(2)°
	γ = 90°
Volume	7988.8(5) $Å^3$
Z	8
Crystal description	colourless fragment
Crystal size	0.3 x 0.2 x 0.2 mm
Min. and max. transmission	0.75 and 0.83
Temperature	200(1) K
θ range for data collection	2.71° to 66.64°
Reflections (all / independent)	53393 / 14060
R(int)	2.33 %
Data / parameters / restraints	14060 / 1085 / 0

Compound 4c *(CCDC number: 1523670)*

Empirical formula	$C_{48.5}$ H_{48} F_{12} N_2 O_2 Si
Crystal system	Triclinic
Space group	P -1
Unit cell dimensions	a = 10.8510(3) Å
	b = 11.2578(3) Å
	c = 19.0950(5) Å
	α = 85.788(2)°
	β = 89.285(2)°
	γ = 87.827(2)°
Volume	2324.53(11) $Å^3$
Z	2
Crystal description	colourless prism
Crystal size	0.2 x 0.15 x 0.1 mm
Min. and max. transmission	0.73 and 0.75
Temperature	200(1) K
θ range for data collection	1.07° to 30.66°
Reflections (all / independent)	56212 / 14342
R(int)	1.96 %
Data / parameters / restraints	14342 / 622 / 72

Compound 6c *(CCDC number : 1575949)*

Empirical formula	$C_{63}H_{58}AuF_{12}N_2O_2PSi$
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimension	a= 12.8739 (9)
	b= 13.2923 (9)
	c= 18.6706 (14)
	α= 84.008 (3)
	β= 72.333 (3)
	γ= 76.619 (3)
Volume	2959.6 (4) $Å^3$
Z	2
Crystal description	Fragment
Crystal size	0.15 × 0.10 × 0.03 mm
Min. and max. transmission	2.49, -0.94
Temperature	200 K
θ range for data collection	1.9° to 26.4°
Reflections (all / independent)	60945, 12156
R(int)	0.044
Data / parameters / restraints	12156 / 739 / 0

Compound 7c *(CCDC number : 1575951)*

Empirical formula	$C_{55}H_{51}CuF_{12}N_4O_2Si \cdot 3(CH_2Cl_2)$
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimension	a= 15.2050 (7),
	b= 23.6591 (10),
	c= 17.7121 (8)
	α= 90
	β= 104.738 (1)
	γ= 90
Volume	6162.1 (5) $Å^3$
Z	4
Crystal description	Stick
Crystal size	0.24 × 0.13 × 0.12 mm
Min. and max. transmission	0.33, -0.25
Temperature	200 K
θ range for data collection	1.7° το 30.1°
Reflections (all / independent)	171774, 18112
R(int)	0.029
Data / parameters / restraints	18112 / 765 / 0

VII. Computational Details

All structures were optimized using Turbomole V6.5 with the B3LYP-D3 functional and the def2-SV(P) basis set. The Cartesian coordinates of all molecules have been uploaded in a separate file. Please find below a table containing the absolute energies for the singlet state of the various carbenes (optimized geometries) and for the triplet state (on the singlet state geometry).

	Abs. En. (au)		
	Singlet	Triplet	Gap (kJ/mol)
IDipp	-1158.416945	-1158.268641	389.00
IDipp-Si^- Me_4N^+	-3698.284806	-3698.133261	397.50
CAAC	-834.3118822	-834.2188282	244.08

VIII. References

(1) Farrugia, L. J. *J. Appl. Crystallogr.* **1999**, *32* (4), 837–838.
(2) Sheldrick, G. M. *Acta Crystallogr. Sect. C Struct. Chem.* **2015**, *71* (1), 3–8.
(3) Perozzi, E. F.; Michalak, R. S.; Figuly, G. D.; Stevenson, W. H.; Dess, D.; Ross, M. R.; Martin, J. C. *J. Org. Chem.* **1981**, *46* (6), 1049–1053.
(4) Bantreil, X.; Nolan, S. P. *Nat. Protoc.* **2011**, *6* (1), 69–77.
(5) Scott, N. M.; Dorta, R.; Stevens, E. D.; Correa, A.; Cavallo, L.; Nolan, S. P. *J. Am. Chem. Soc.* **2005**, *127* (10), 3516–3526.
(6) Vummaleti, S. V. C.; Nelson, D. J.; Poater, A.; Gómez-Suárez, A.; Cordes, D. B.; Slawin, A. M. Z.; Nolan, S. P.; Cavallo, L. *Chem. Sci.* **2015**, *6* (3), 1895–1904.