# Electron Supporting Information

## Ln(II) and Ca(II) $NC_{sp3}N$ pincer type diarylmethanido complexes – promising catalysts for C−C and C−E (E = Si, P, N, S) bond formation

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**Content**

**Table S1.** Crystal data and structures refinement details for complexes **2**, **3**, **4**, and **4**$^{THF}$.

| Compound | **2** | **3** | **4** | **4**$^{THF}$ |
|---|---|---|---|---|
| Empirical Formula | $C_{38}H_{50}N_4Yb$ | $C_{38}H_{50}N_4Sm$ | $C_{38}H_{50}CaN_4$ | $C_{46}H_{66}CaN_4O_2$ |
| Formula Weight | 735.86 | 713.17 | 602.90 | 747.10 |
| Crystal System | Triclinic | Monoclinic | Triclinic | Triclinic |
| Space Group | *P-1* | $P2_1/c$ | *P-1* | *P-1* |
| *a*, Å | 8.9354(4) | 12.20130(10) | 8.9015(3) | 12.3169(6) |
| *b*, Å | 10.2031(5) | 14.20510(10) | 10.2113(4) | 17.7302(9) |
| *c*, Å | 19.6163(8) | 20.2786(2) | 19.5830(8) | 21.2620(11) |
| $\alpha$, deg | 97.942(4) | 90 | 97.879(3) | 107.8160(10) |
| $\beta$, deg | 99.558(4) | 98.9410(10) | 99.594(3) | 99.7490(10) |
| $\gamma$, deg | 99.523(4) | 90 | 99.571(3) | 90.3430(10) |
| *V*, Å$^3$ | 1713.85(14) | 3471.99(5) | 1705.65(11) | 4348.4(4) |
| *Z* | 2 | 4 | 2 | 4 |
| $d_{calcd}$, g/cm$^3$ | 1.426 | 1.364 | 1.174 | 1.141 |
| Absorption coefficient, mm$^{-1}$ | 2.759 | 1.772 | 0.215 | 0.184 |
| $F_{000}$ | 752 | 1472 | 652 | 1624 |
| Crystal size, mm | 0.30 x 0.20 x 0.03 | 0.40 x 0.40 x 0.10 | 0.29 x 0.23 x 0.20 | 0.58 x 0.36 x 0.18 |
| θ range for data collection, deg | 2.86-30.03 | 3.04-30.03 | 2.97-27.56 | 2.31-28.67 |
| Index ranges | -12<=h<=12<br>-14<=k<=14<br>-27<=l<=27 | -17<=h<=17<br>-20<=k<=20<br>-28<=l<=28 | -11<=h<=11<br>-13<=k<=13<br>-25<=l<=25 | -16 <= h <= 16<br>-23 <= k <= 23<br>-28 <= l <= 28 |
| Reflections collected | 36918 | 84557 | 26185 | 55120 |
| Independent reflections | 10025 | 10133 | 7880 | 22189 |
| $R_{int}$ | 0.0793 | 0.0346 | 0.0811 | 0.0338 |
| Completeness to $\theta$, % | 99.8 | 99.8 | 99.7 | 99.6 |
| Data / restraints / parameters | 10025 / 0 / 406 | 10133 / 0 / 408 | 7880 / 0 / 408 | 22189 / 0 / 995 |
| $S(F^2)$ | 1.014 | 1.060 | 1.041 | 1.025 |
| Final *R* indices ($I > 2\sigma(I)$) | R1 = 0.0454<br>wR2 = 0.0832 | R1 = 0.0198<br>wR2 = 0.0468 | R1 = 0.0722<br>wR2 = 0.1609 | R1 = 0.0459<br>wR2 = 0.1063 |
| *R* indices (all data) | R1 = 0.0623<br>wR2 = 0.0879 | R1 = 0.0242<br>wR2 = 0.0491 | R1 = 0.1194<br>wR2 = 0.1863 | R1 = 0.0700<br>wR2 = 0.1170 |
| Largest diff. peak and hole, e/Å$^3$ | 1.86 / -1.50 | 0.99 / -0.44 | 1.07 / -0.46 | 0.76 / -0.41 |

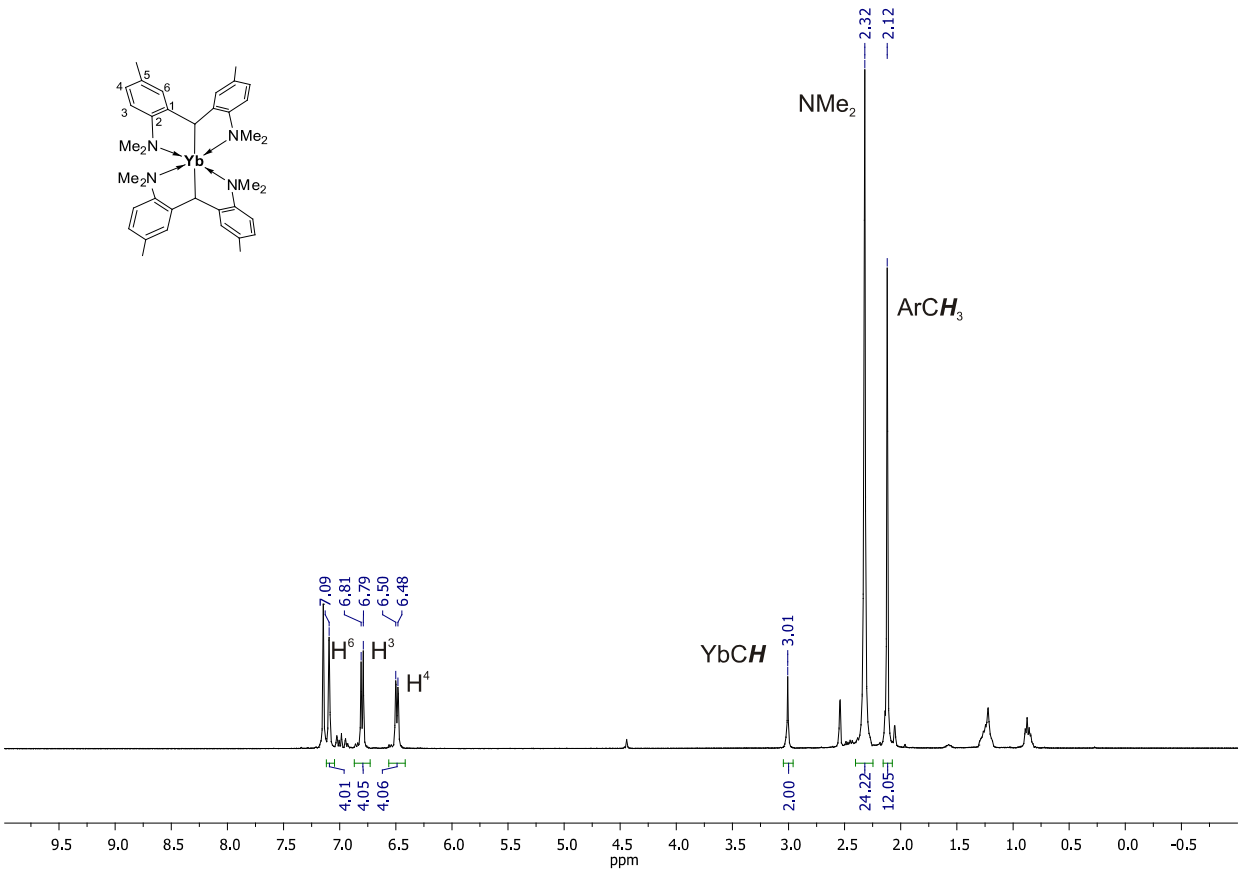


**Fig. S1.** $^{1}$H NMR spectrum of [2,2'-(4-Me$C_6H_3$N$Me_2$)$_2$CH]$_2$Yb (**2**) (400 MHz, $C_6D_6$, 293 K).

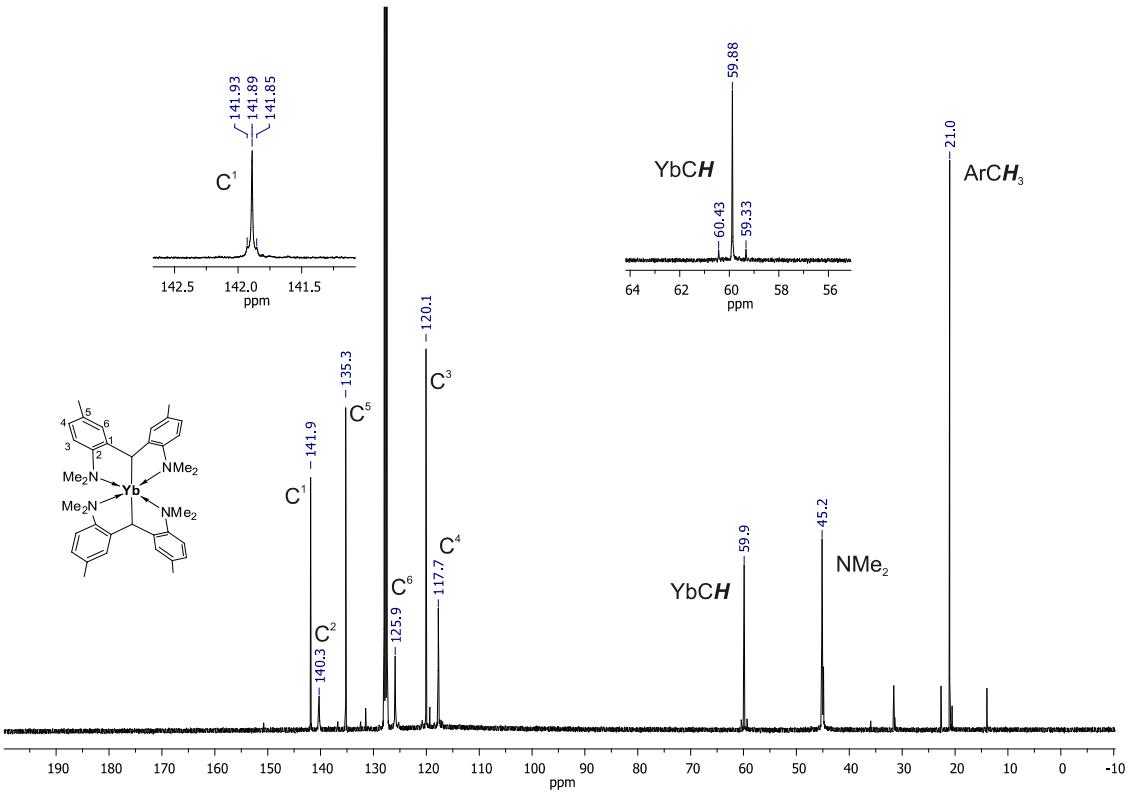


**Fig. S2.** $^{13}$C{$^{1}$H} NMR spectrum of [2,2'-(4-Me$C_6H_3$N$Me_2$)$_2$CH]$_2$Yb (**2**) (100 MHz, $C_6D_6$, 293 K).

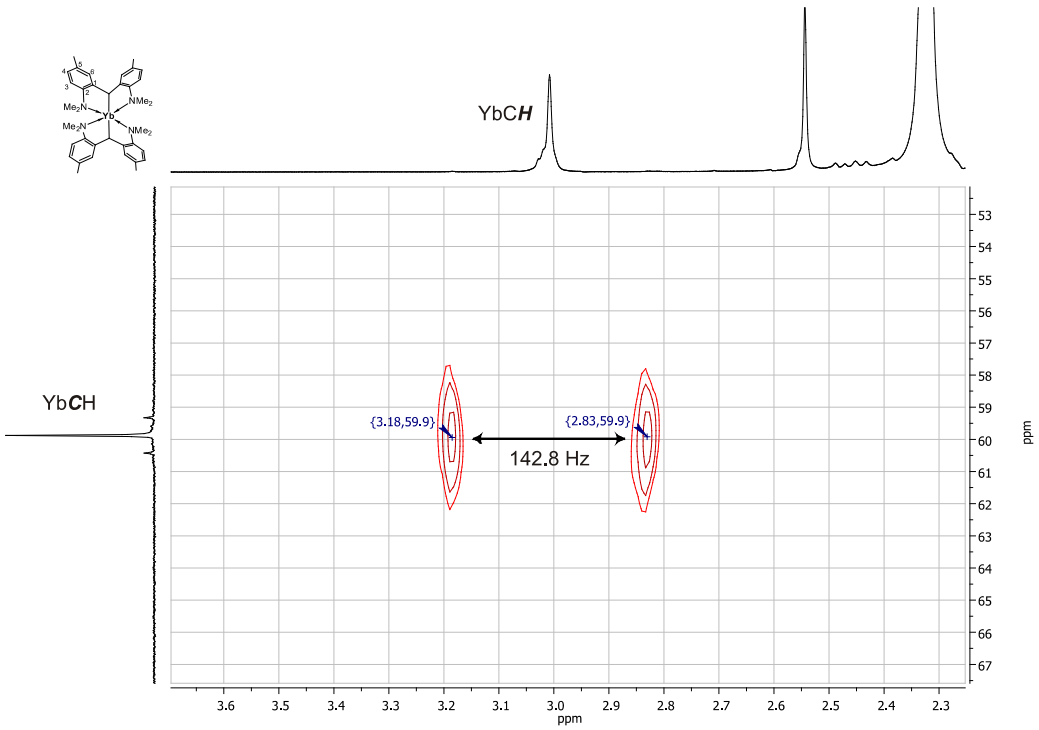


**Fig. S3.** $^{13}C–^{1}H$ HSQC without $^{1}H$ decoupling NMR spectrum of [2,2'-(4-$MeC_6H_3NMe_2)_2CH]_2Yb$ (**2**) (400 MHz, $C_6D_6$, 293 K).

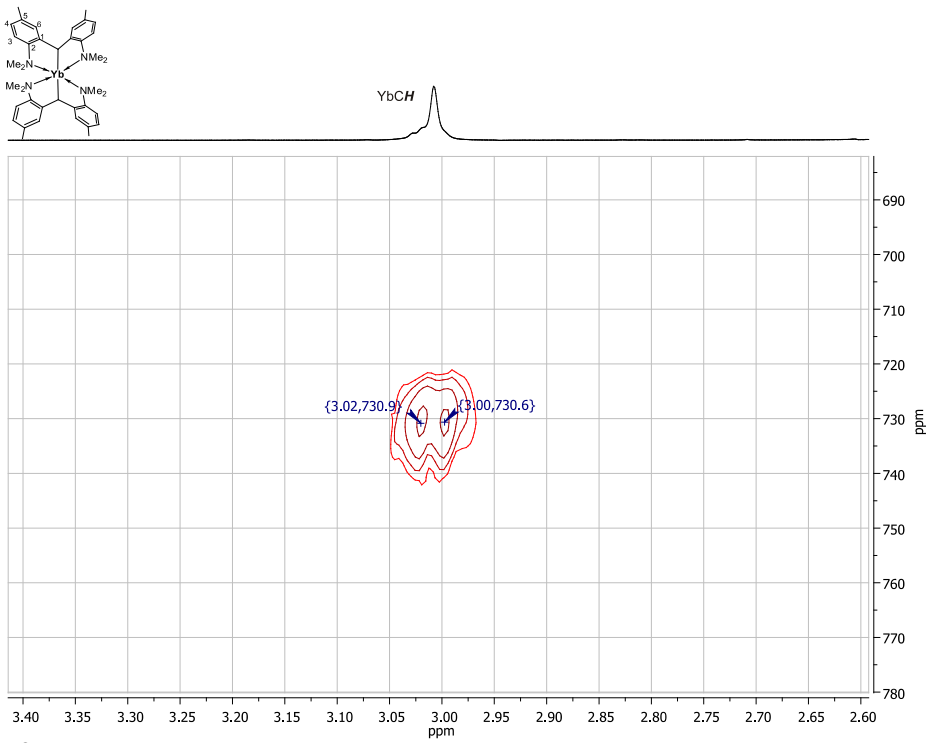


**Fig. S4.** $^{179}Yb–^{1}H$ HSQC without $^{1}H$ decoupling NMR spectrum of [2,2'-(4-$MeC_6H_3NMe_2)_2CH]_2Yb$ (**2**) (400 MHz, $C_6D_6$, 293 K).

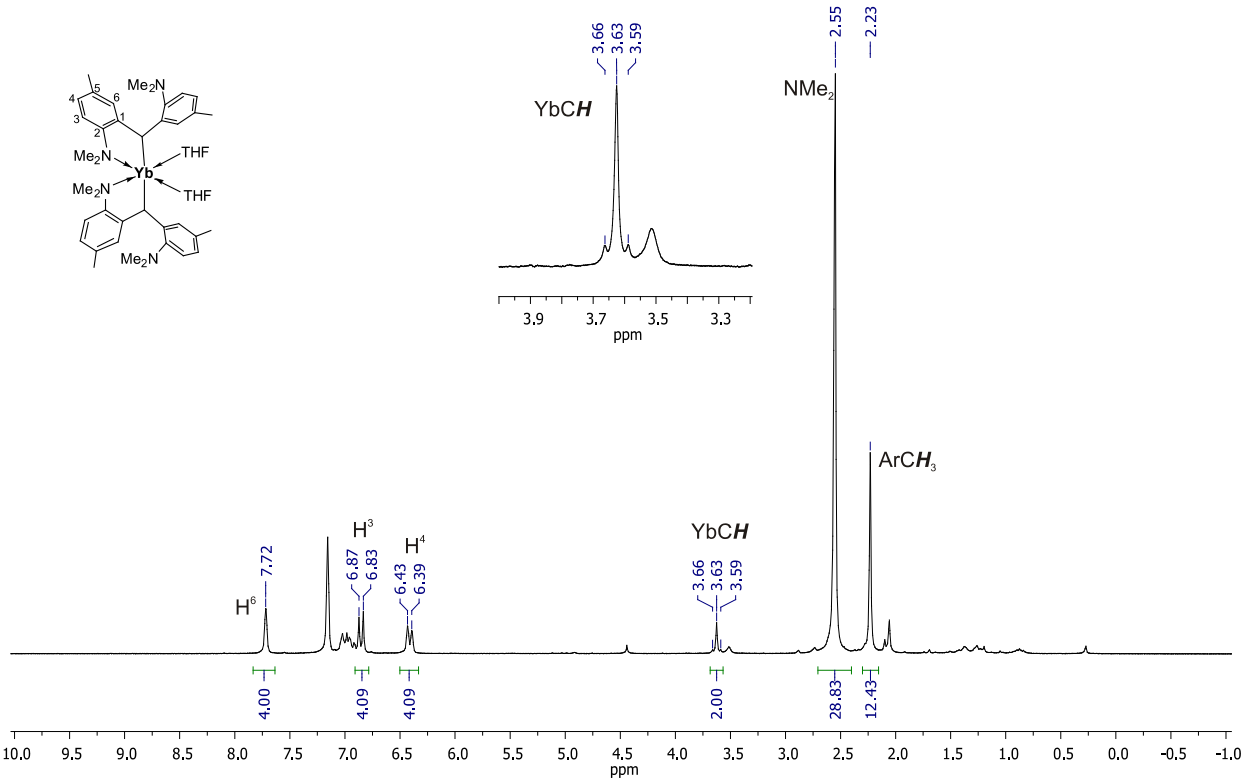


**Fig. S5.** $^1$H NMR spectrum of $[2,2'\text{-}(4\text{-}MeC_6H_3NMe_2)_2CH]_2Yb(THF)_n$ (**2**$^{THF}$) (200 MHz, $C_6D_6$/THF-$D_8$ 5/1, 293 K).

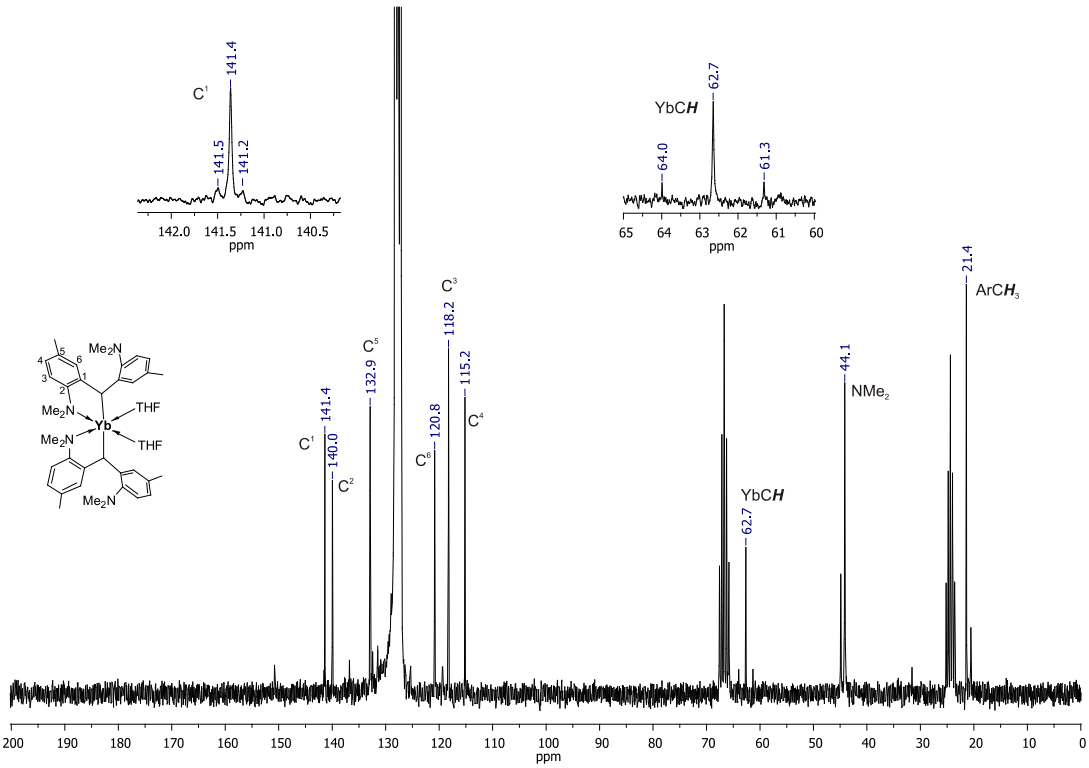


**Fig. S6.** $^{13}C\{^1H\}$ NMR spectrum of $[2,2'\text{-}(4\text{-}MeC_6H_3NMe_2)_2CH]_2Yb(THF)_n$ (**2**$^{THF}$) (50 MHz, $C_6D_6$/THF-$D_8$ 5/1, 293 K).

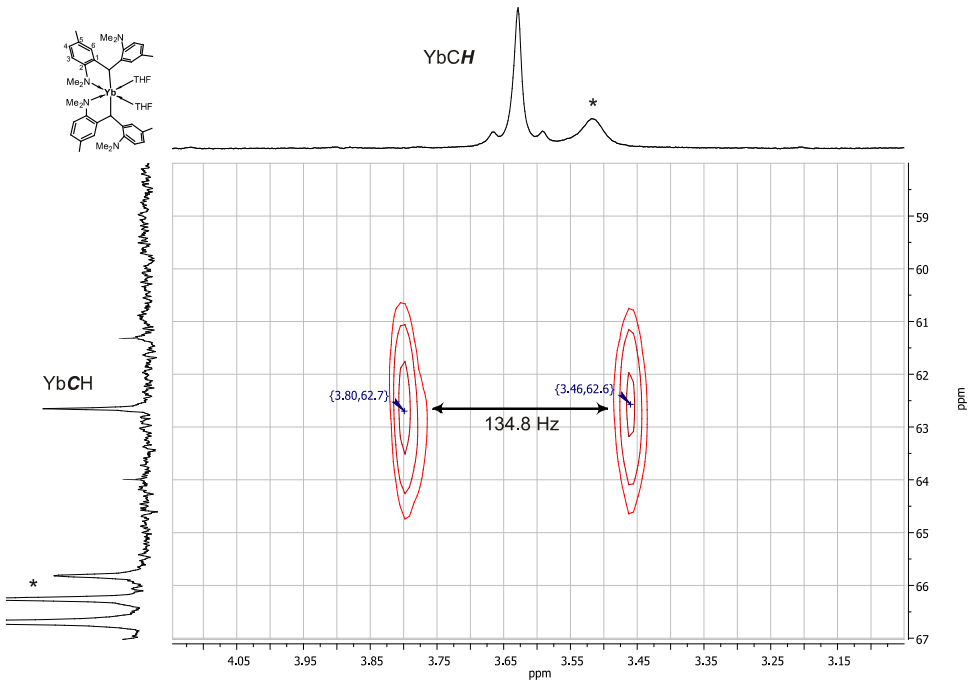


**Fig. S7.** $^{13}C–^{1}H$ HSQC without $^{1}H$ decoupling NMR spectrum of [2,2'-(4-$MeC_6H_3NMe_2)_2CH]_2Yb(THF)_n$ (**2**$^{THF}$) (400 MHz, $C_6D_6$/THF-$D_8$ 5/1, 293 K); * - signals of residual protons and $^{13}C$ of THF-$D_8$.

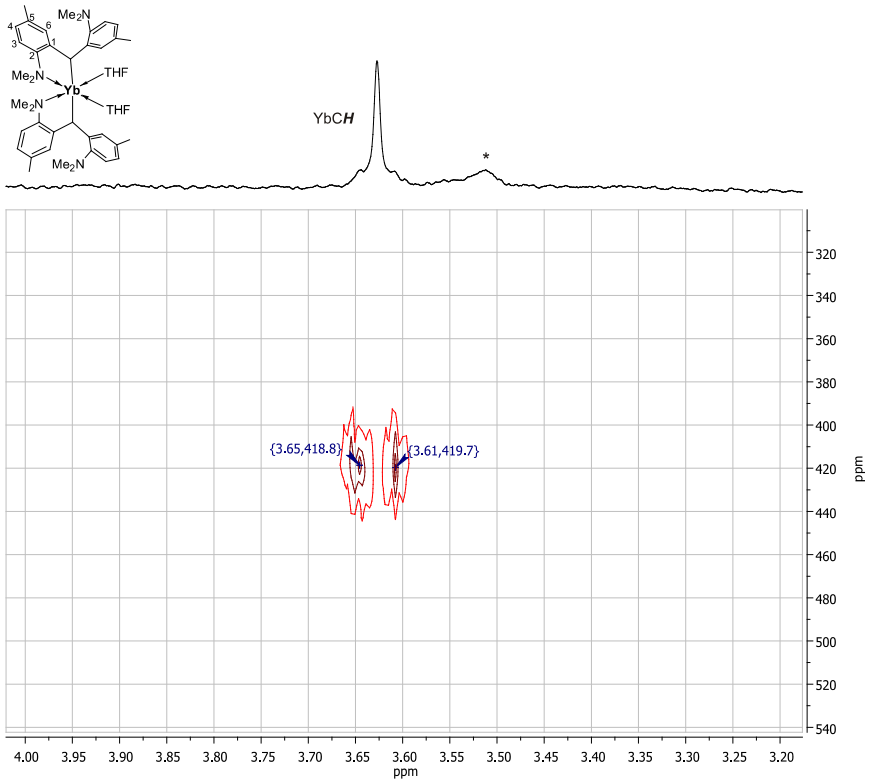


**Fig. S8.** $^{179}Yb–^{1}H$ HSQC without $^{1}H$ decoupling NMR spectrum of [2,2'-(4-$MeC_6H_3NMe_2)_2CH]_2Yb(THF)_n$ (**2**$^{THF}$) (400 MHz, $C_6D_6$/THF-$D_8$ 5/1, 293 K); * - signals of residual protons of THF-$D_8$.

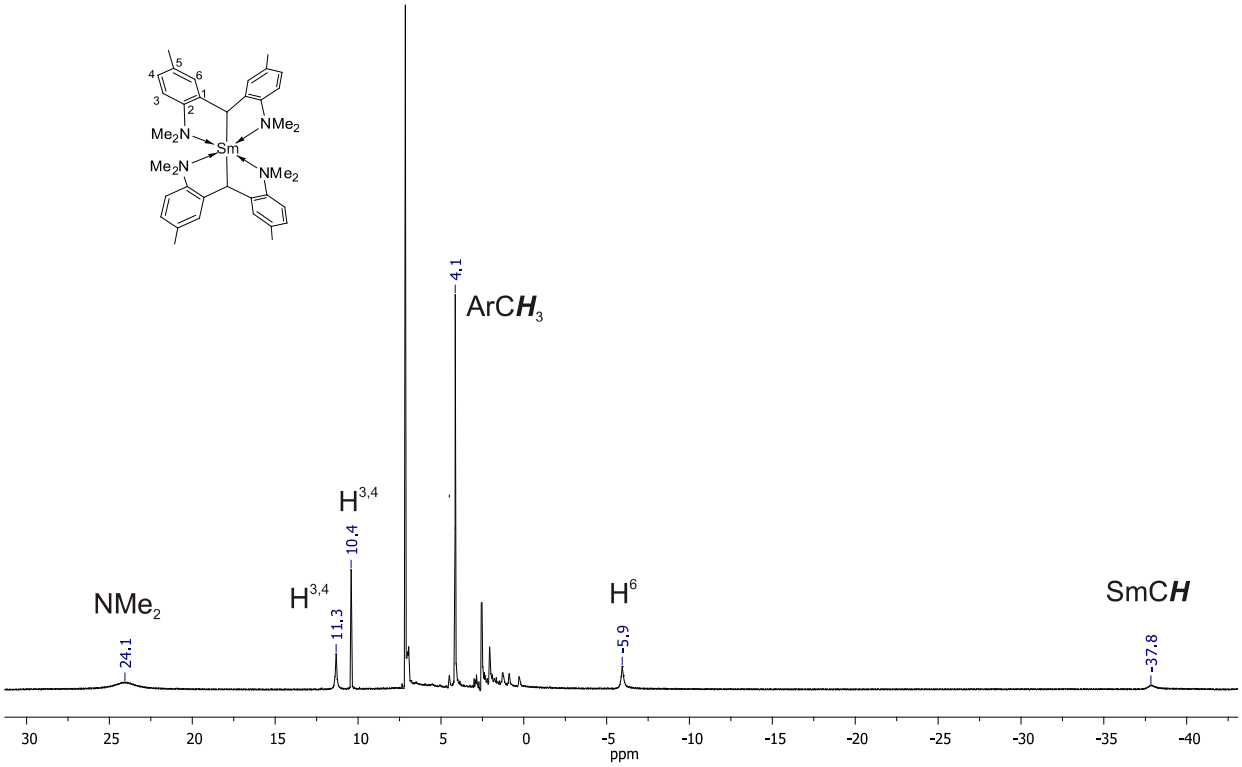


**Fig. S9.** $^{1}$H NMR spectrum of [2,2'-(4-Me$C_6H_3$N$Me_2$)$_2$CH]$_2$Sm (**3**) (400 MHz, $C_6D_6$, 293 K).

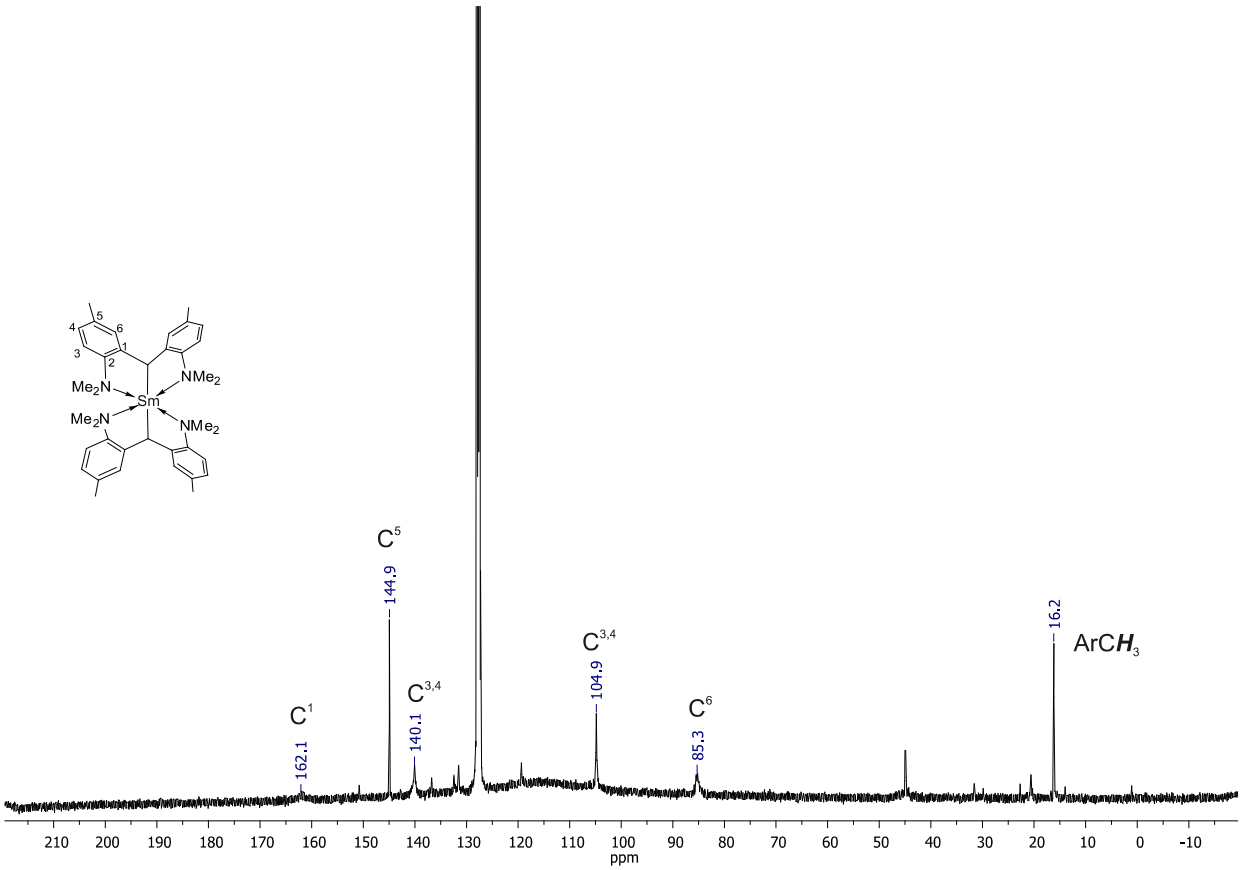


**Fig. S10.** $^{13}$C{$^{1}$H} NMR spectrum of [2,2'-(4-Me$C_6H_3$N$Me_2$)$_2$CH]$_2$Sm (**3**) (100 MHz, $C_6D_6$, 293 K).

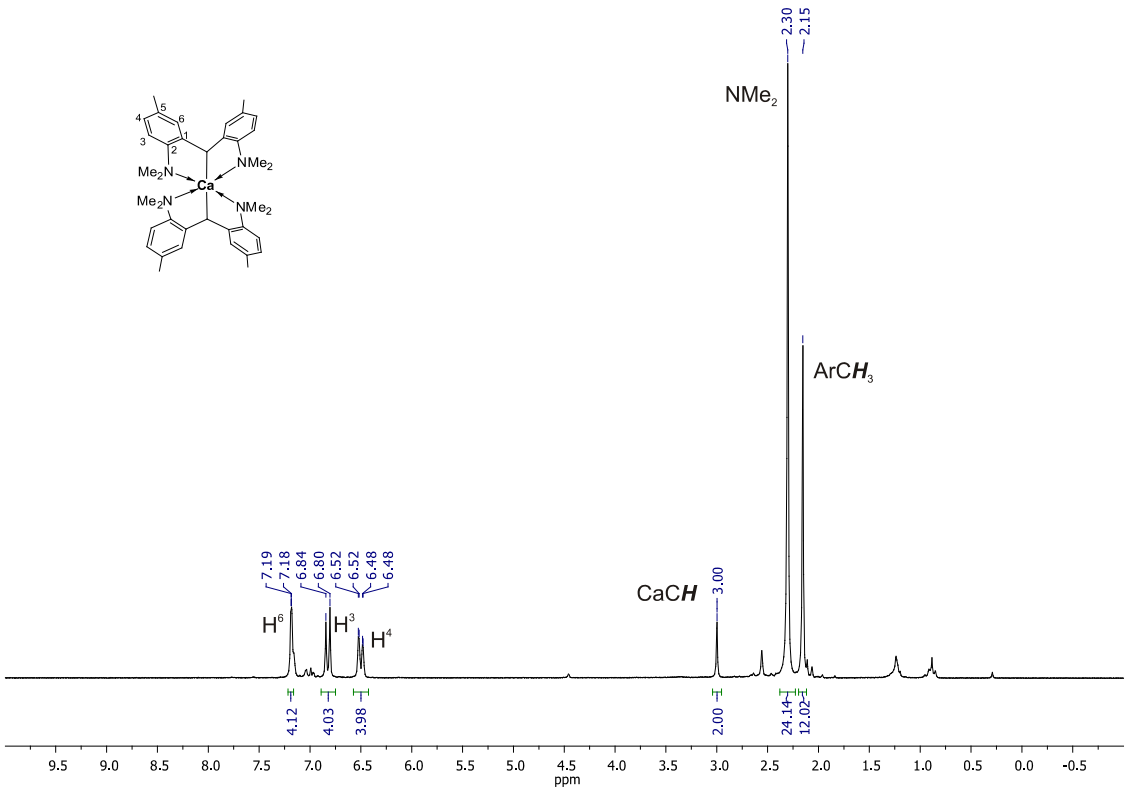


**Fig. S11.** $^{1}$H NMR spectrum of [2,2'-(4-Me$C_6H_3$N$Me_2$)$_2$CH]$_2$Ca (**4**) (200 MHz, $C_6D_6$, 293 K).

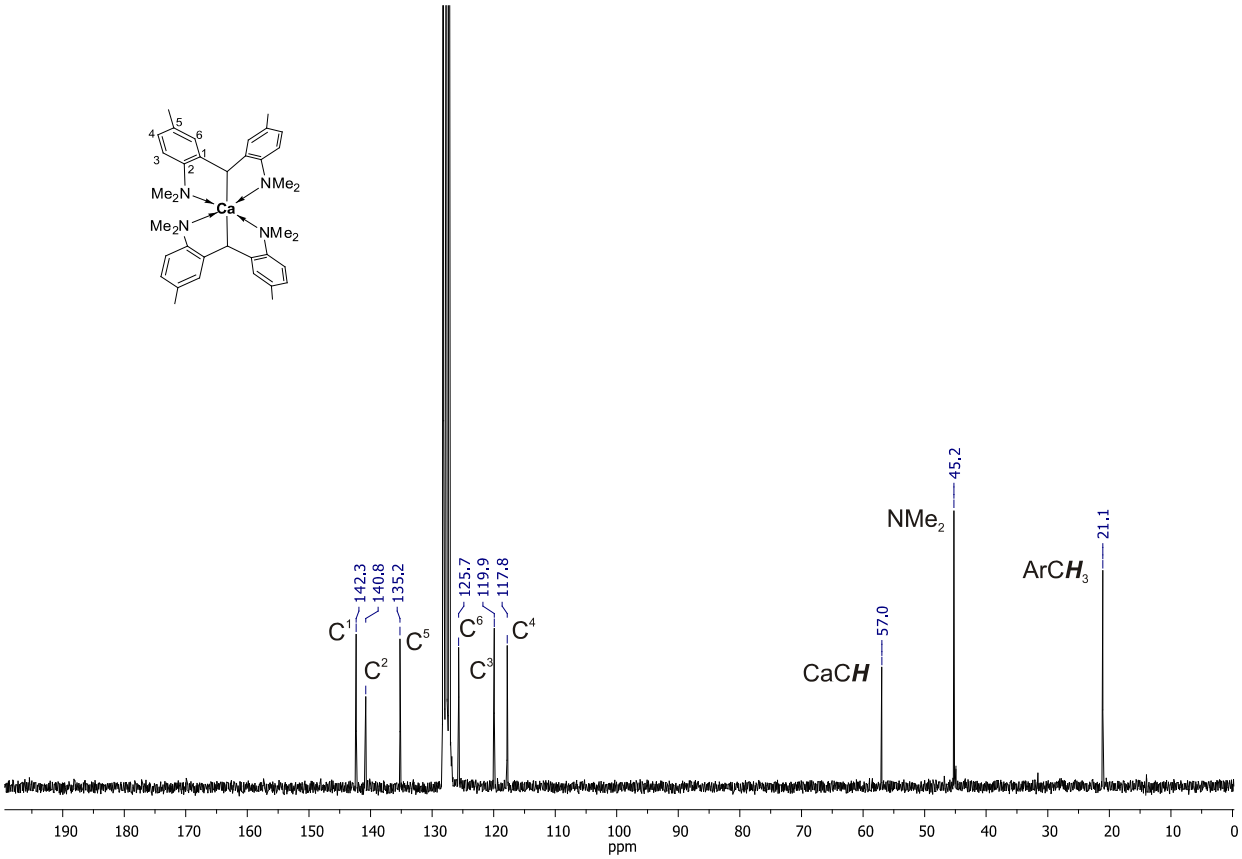


**Fig. S12.** $^{13}$C{$^{1}$H} NMR spectrum of [2,2'-(4-Me$C_6H_3$N$Me_2$)$_2$CH]$_2$Ca (**4**) (50 MHz, $C_6D_6$, 293 K).

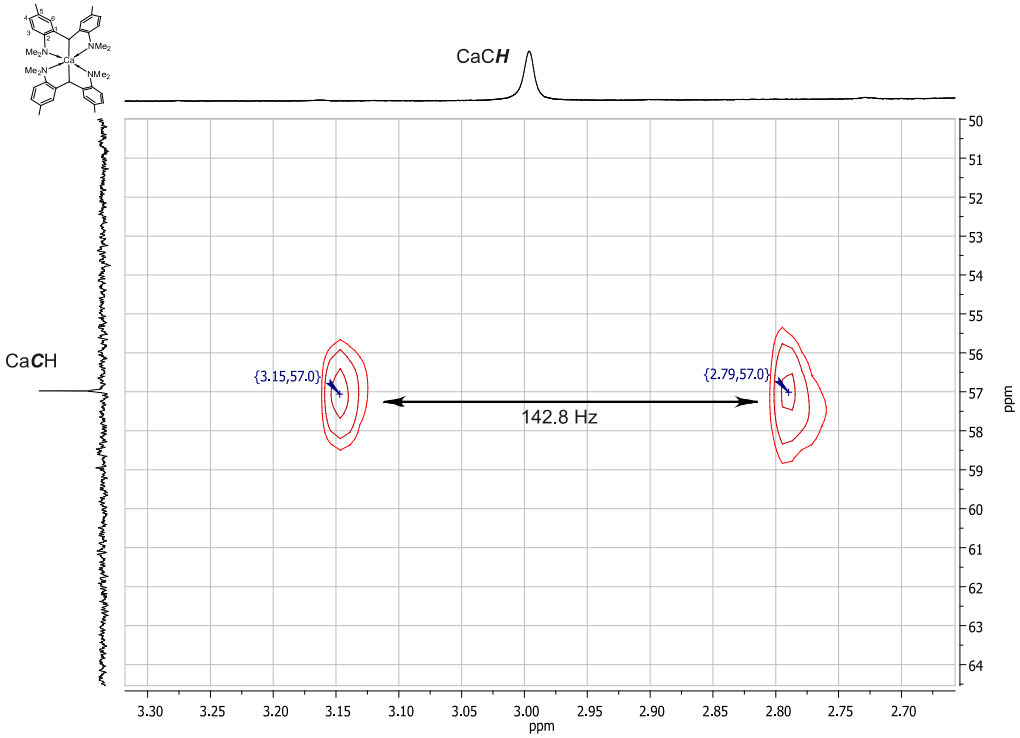


**Fig. S13.** $^{13}C–^{1}H$ HSQC without $^{1}H$ decoupling NMR spectrum of [2,2'-(4-$MeC_6H_3NMe_2)_2CH]_2Ca$ (**4**) (400 MHz, $C_6D_6$, 293 K).

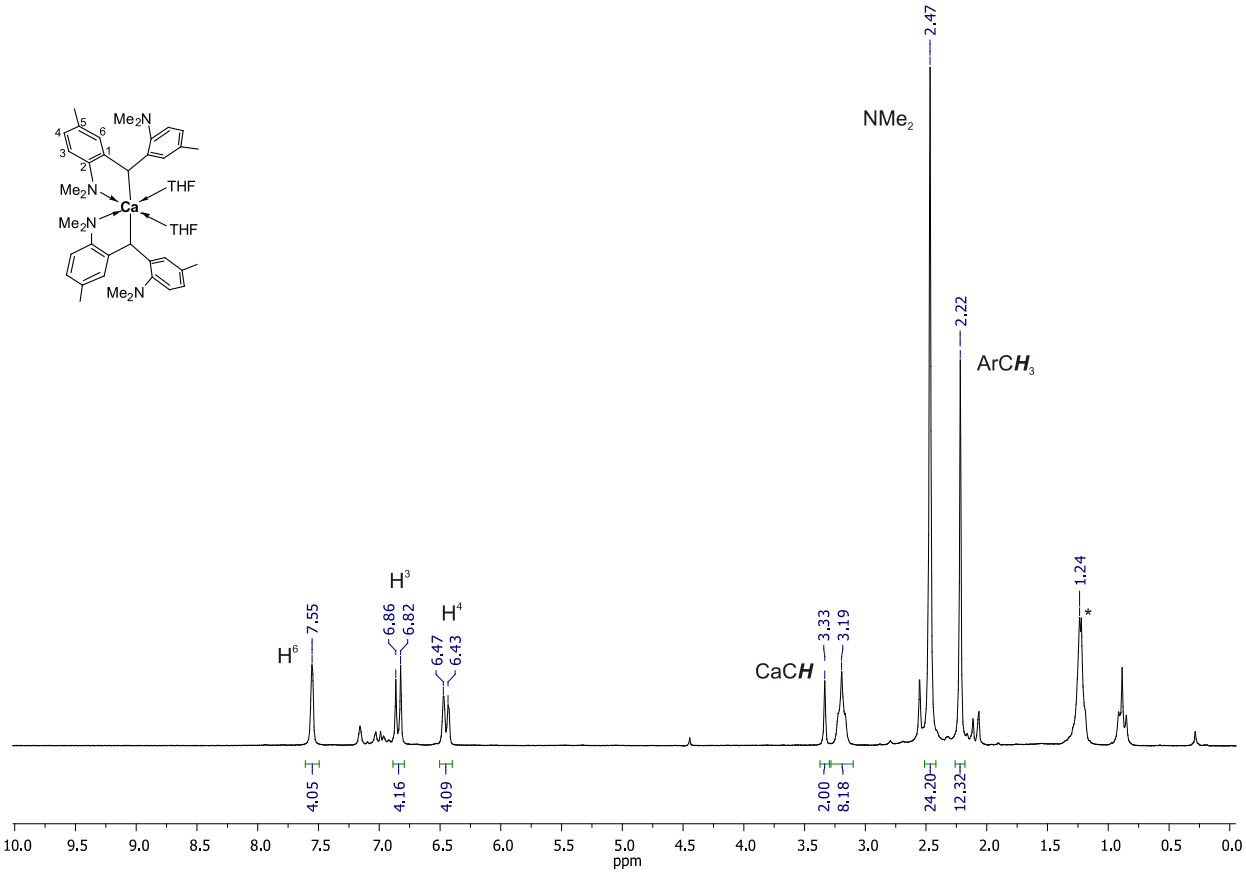


**Fig. S14.** $^{1}H$ NMR spectrum of [2,2'-(4-$MeC_6H_3NMe_2)_2CH]_2Ca(THF)_2$ (**4**$^{THF}$) (200 MHz, $C_6D_6$, 293 K); * - signal of β-$CH_2$ THF protons overlaps with solvated hexane.

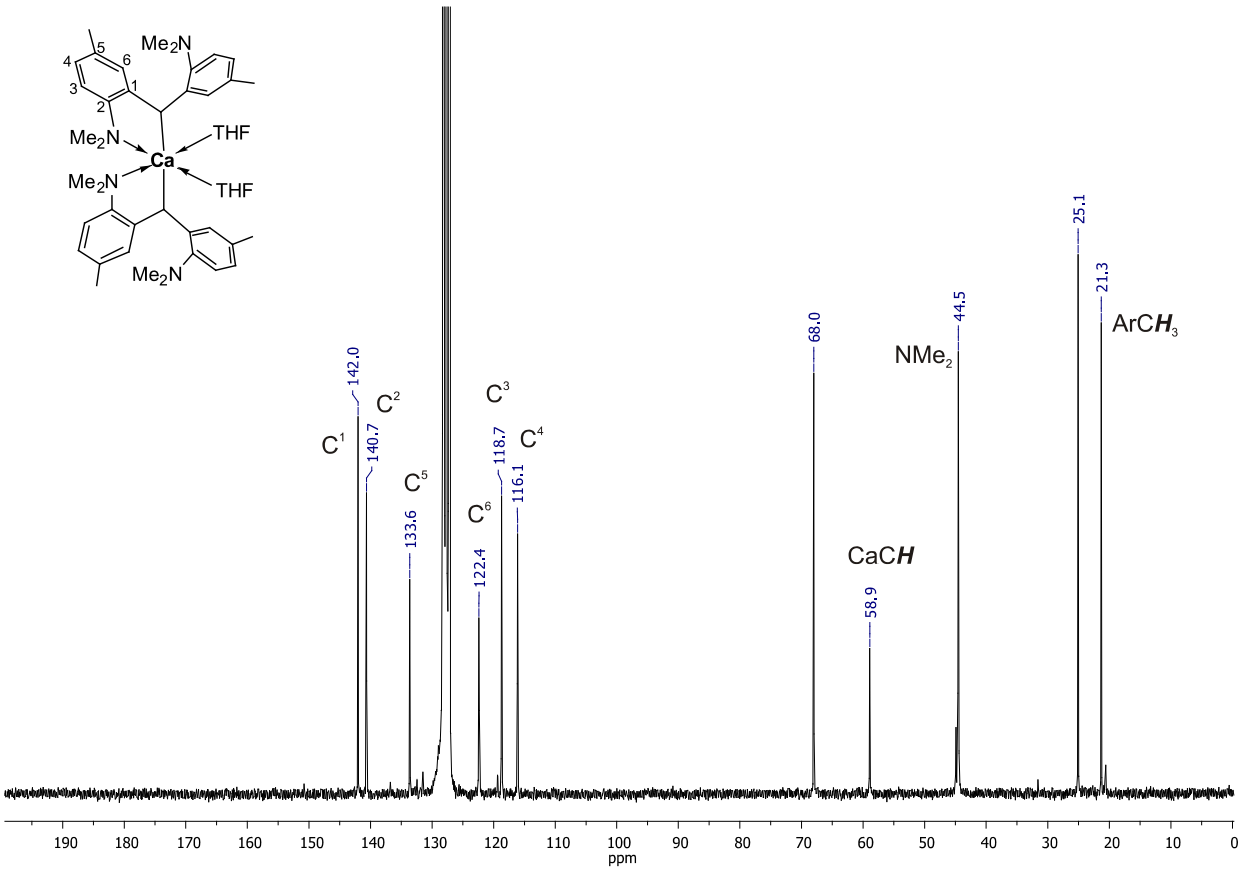


**Fig. S15.** $^{13}C\{^{1}H\}$ NMR spectrum of $[2,2'\text{-}(4\text{-}MeC_6H_3NMe_2)_2CH]_2Ca(THF)_2$ (**4**$^{THF}$) (100 MHz, $C_6D_6$, 293 K)

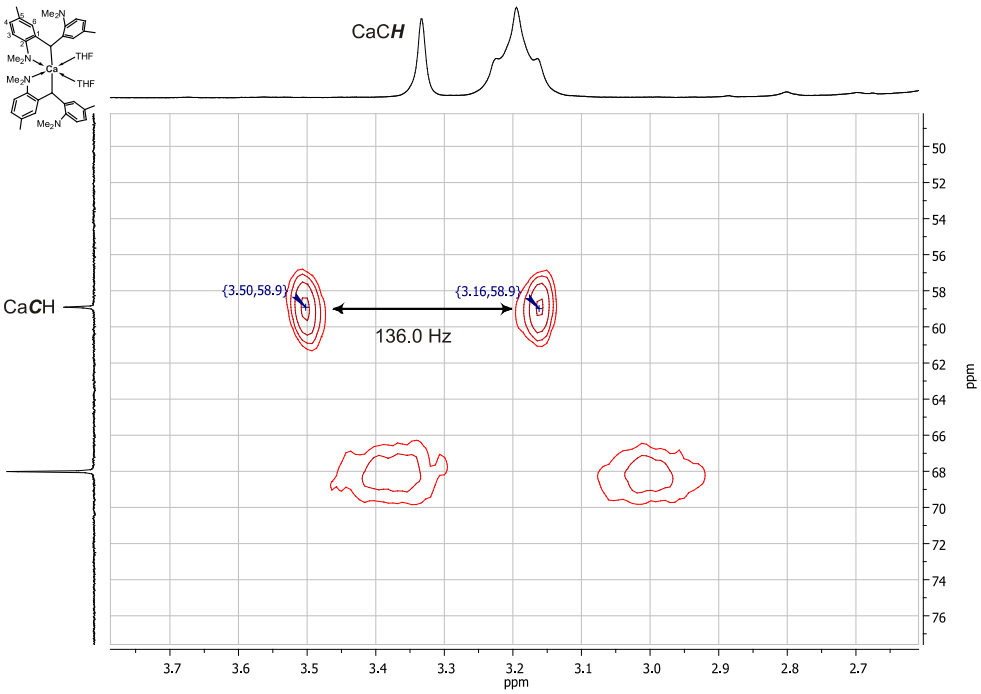


**Fig. S16.** $^{13}C–^{1}H$ HSQC without $^{1}H$ decoupling NMR spectrum of $[2,2'\text{-}(4\text{-}MeC_6H_3NMe_2)_2CH]_2Ca(THF)_2$ (**4**$^{THF}$) (400 MHz, $C_6D_6$, 293 K).

**Characterization of $PhCH_2CH(Ph)SiH_2Ph$.** Hydrosilylation product of *cis*- or *trans*-stilbenes by $PhSiH_3$ was isolated after column chromatography purification (silica gel, $C_6H_6$/Hexane 1/1) as colorless oily product. Elemental analysis calculated for $C_{20}H_{20}Si$ (288.46 g·mol$^{-1}$): C, 83.28; H, 6.99. Found: C, 83.40; H, 7.08. GC-MS: [$M^+$]: 289.1 m/z. $^1$H NMR (400 MHz, $CDCl_3$, 293 K): 2.89 (m, 1H, CH), 3.23 (d, $^3J_{HH}$ = 7.9 Hz, 2H, $CH_2$), 4.45 (m, $^1J_{SiH}$ = 198 Hz, 2H, SiH), 7.11 (m, 4H, CH Ph), 7.16 (m, 2H, CH Ph), 7.25 (m, 4H, CH Ph), 7.34 (m, 2H, CH Ph), 7.41 (m, 3H, CH Ph) ppm. $^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$, 293 K): 34.3 (s, with $^{29}$Si satellites, $^1J_{SiC}$ = 50.3 Hz, Si*C*H), 37.7 (s, *C*$H_2$), 125.5 (s, *p*-CH Ph), 126.0 (s, *p*-CH Ph), 127.9 (s, CH Ph), 128.1 (s, CH Ph), 128.2 (s, CH Ph), 128.4 (s, CH Ph), 128.7 (s, CH Ph), 129.9 (s, CH Ph), 131.1 (s, *ipso*-C SiPh), 135.8 (s, *ortho*-*C*H SiPh), 141.2 (s, *ipso*-C Ph), 142.2 (s, *ipso*-C Ph) ppm. $^{29}$Si{$^1$H} NMR (79.5 MHz, $CDCl_3$, 293 K): −23.6 (s) ppm.

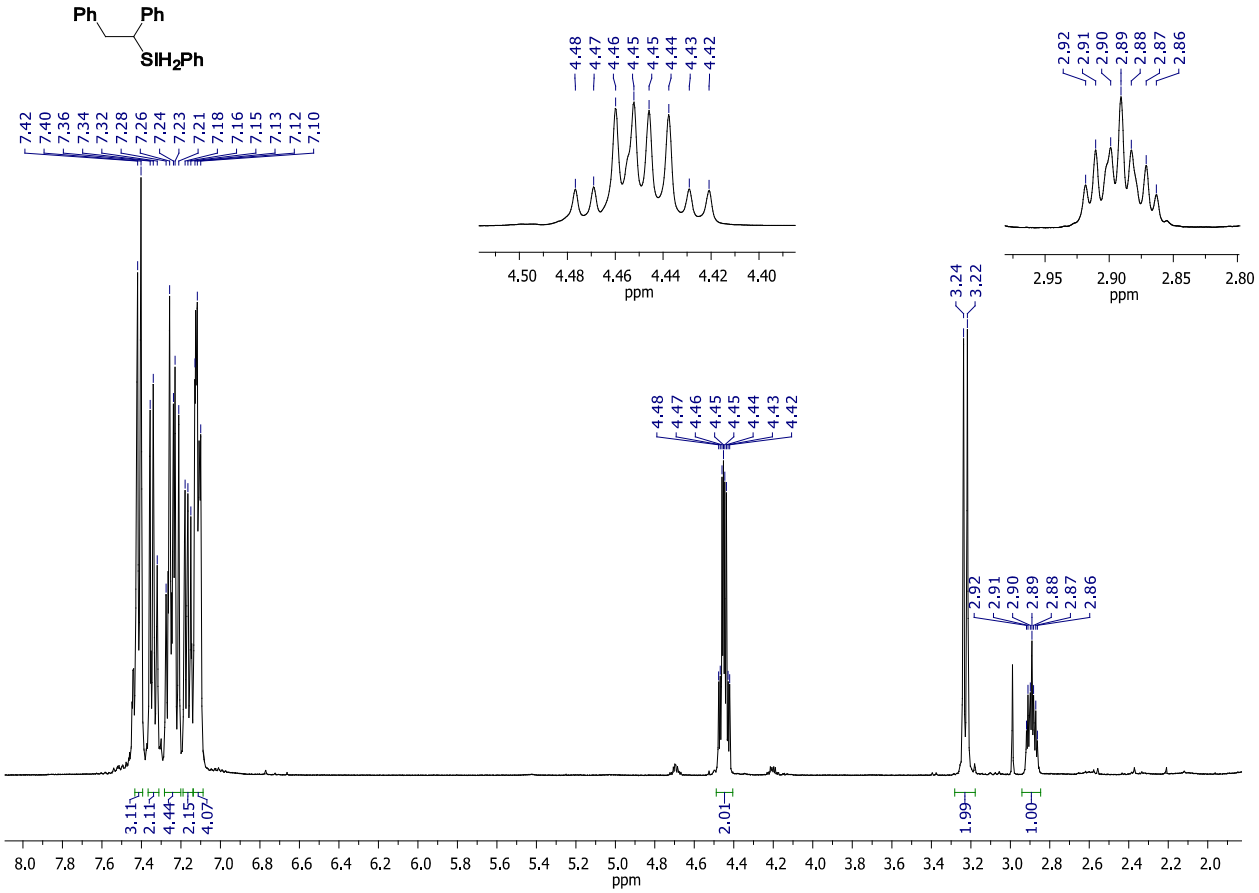


**Fig. S17.** $^1$H NMR spectrum of $PhCH_2CH(Ph)SiH_2Ph$ (400 MHz, $CDCl_3$, 293 K).

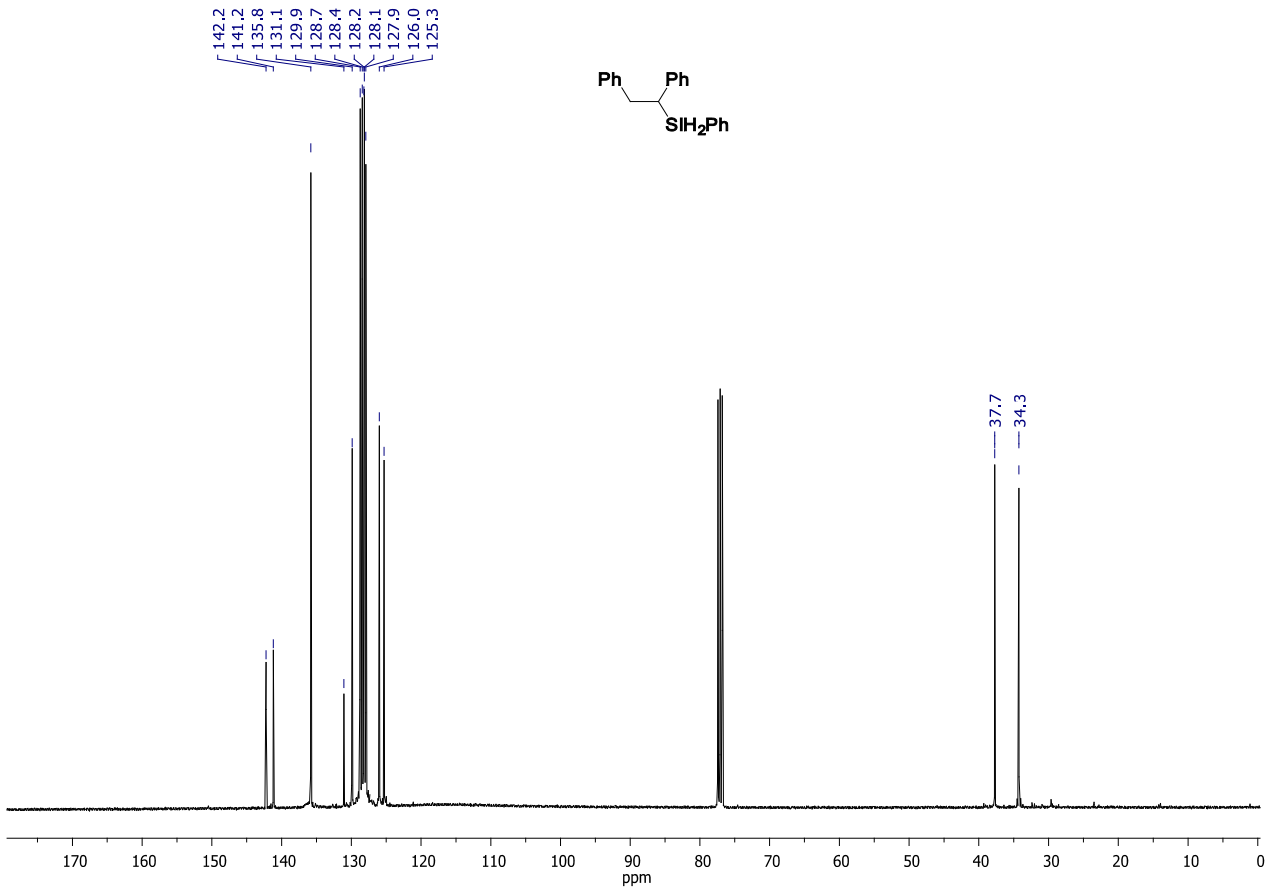


**Fig. S18.** $^{13}C\{^{1}H\}$ NMR spectrum of $PhCH_2CH(Ph)SiH_2Ph$ (100 MHz, $CDCl_3$, 293 K).

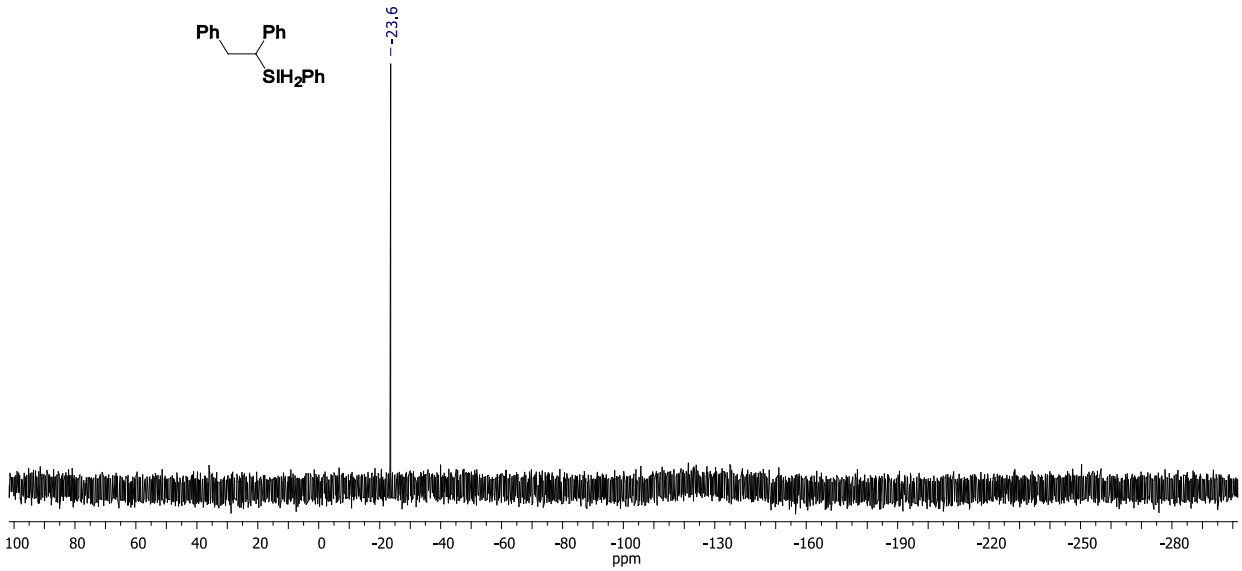


**Fig. S19.** $^{29}Si\{^{1}H\}$ NMR spectrum of $PhCH_2CH(Ph)SiH_2Ph$ (79.5 MHz, $CDCl_3$, 293 K).

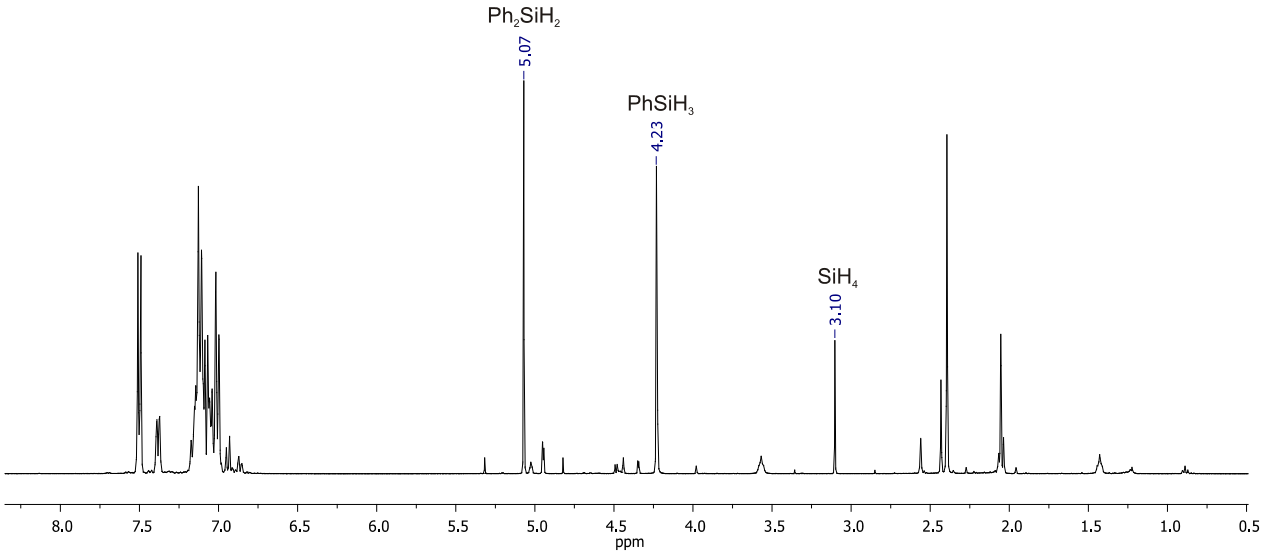


**Fig. S20.** $^{1}$H NMR spectrum of $PhSiH_3$ disproportionation reaction catalyzed by **4**$^{THF}$ ([$PhSiH_3$]:[**4**$^{THF}$] = 50:1, 70 °C, 72 h) (400 MHz, $C_6D_6$, 293 K).

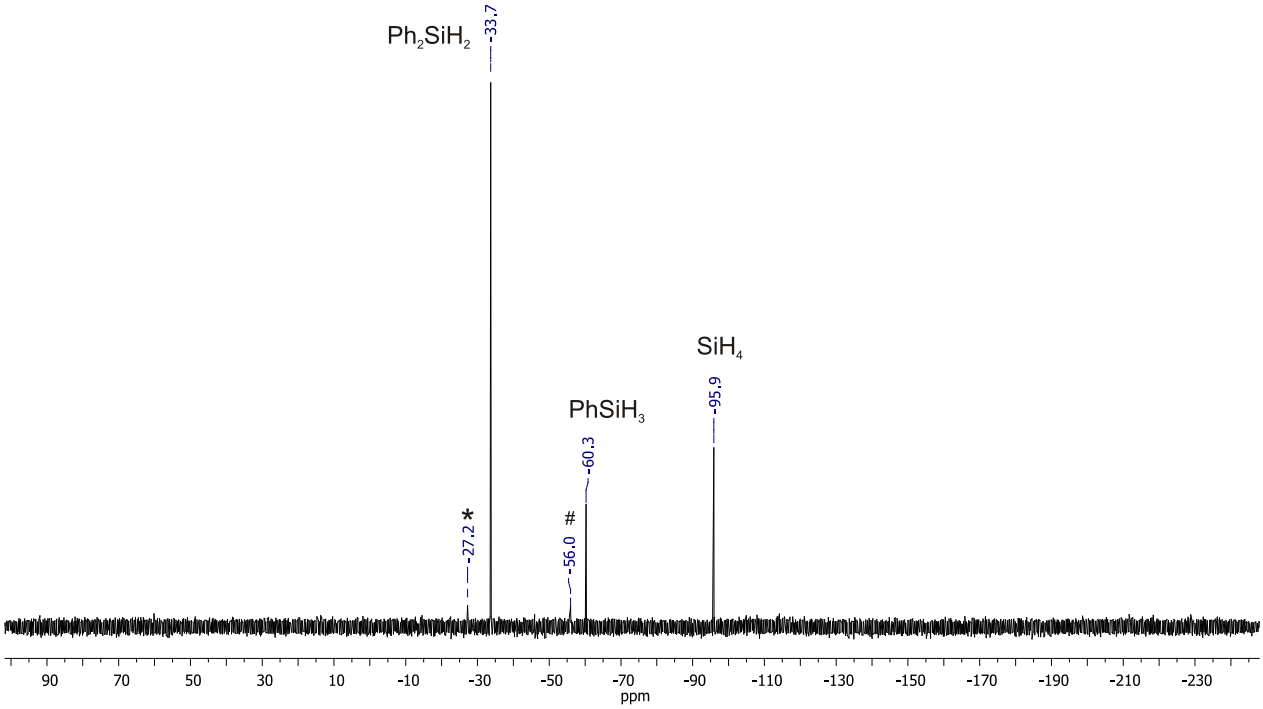


**Fig. S21.** $^{29}$Si{$^{1}$H} NMR spectrum of $PhSiH_3$ disproportionation reaction catalyzed by **4**$^{THF}$ ([$PhSiH_3$]:[**4**$^{THF}$] = 50:1, 70 °C, 72 h) (79.5 MHz, $C_6D_6$, 293 K). * – signal of 2,2'-(4-$MeC_6H_3NMe_2)_2CHSiH_2Ph$; $^{\#}$ – signal if 2,2'-(4-$MeC_6H_3NMe_2)_2CHSiH_3$.

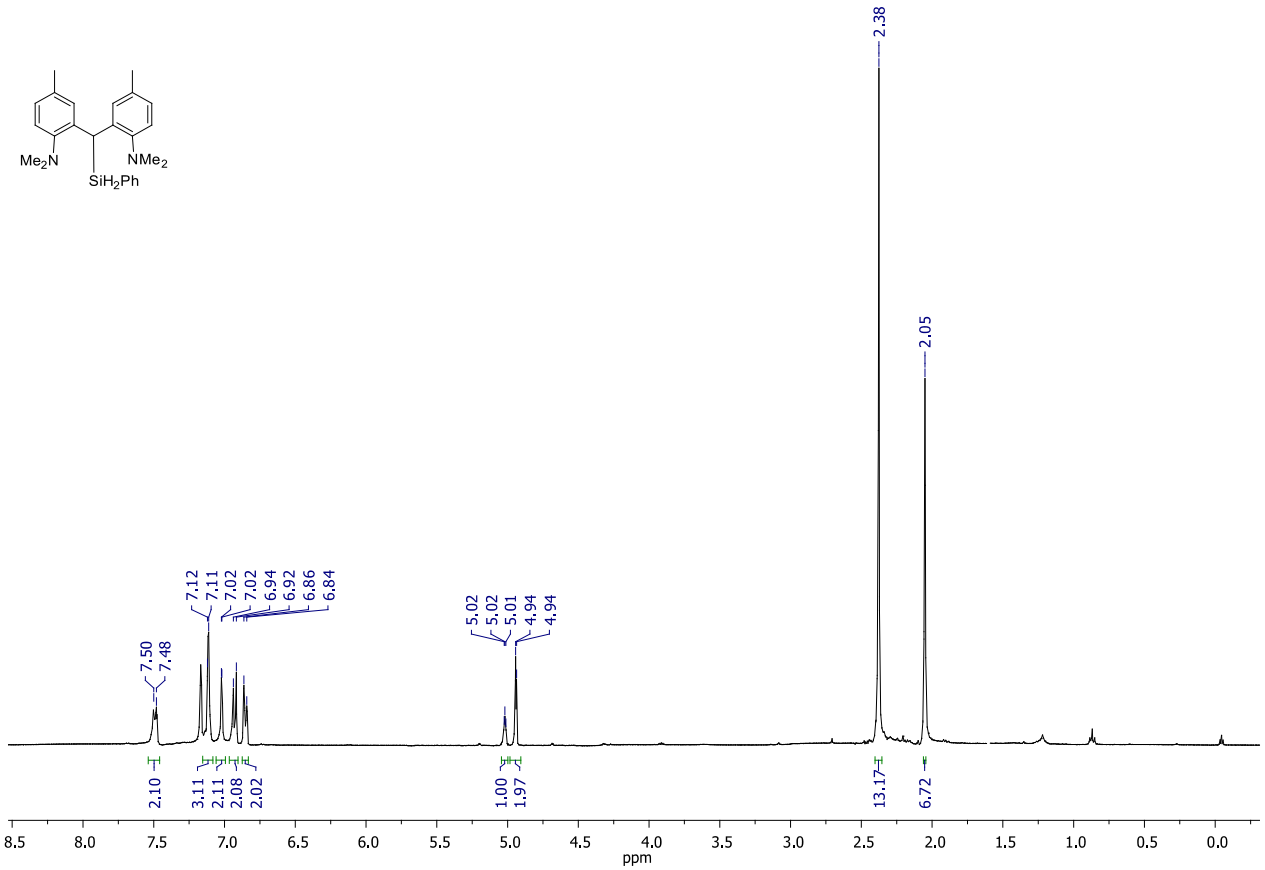


**Fig. S22.** $^{1}$H NMR spectrum of 2,2'-(4-Me$C_6H_3NMe_2$)$_2$CHSi$H_2$Ph (400 MHz, $C_6D_6$, 293 K).

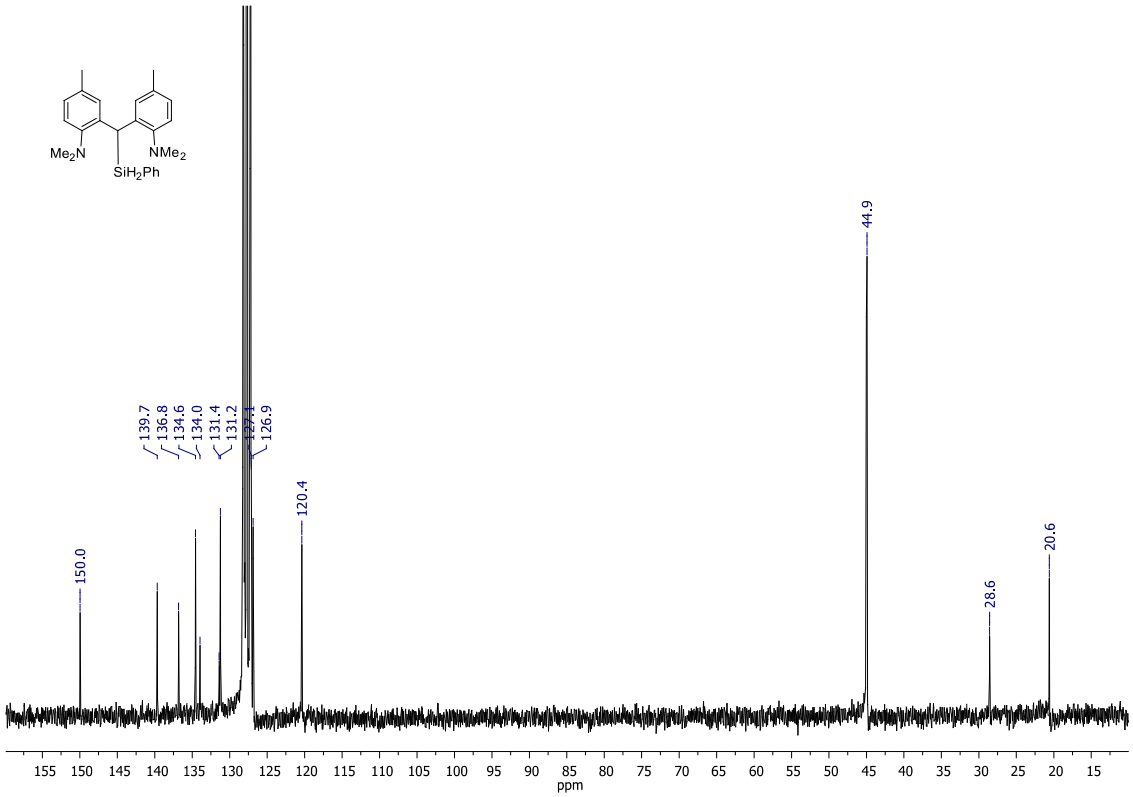


**Fig. S23.** $^{13}$C{$^{1}$H} NMR spectrum of 2,2'-(4-Me$C_6H_3NMe_2$)$_2$CHSi$H_2$Ph (50 MHz, $C_6D_6$, 293 K).

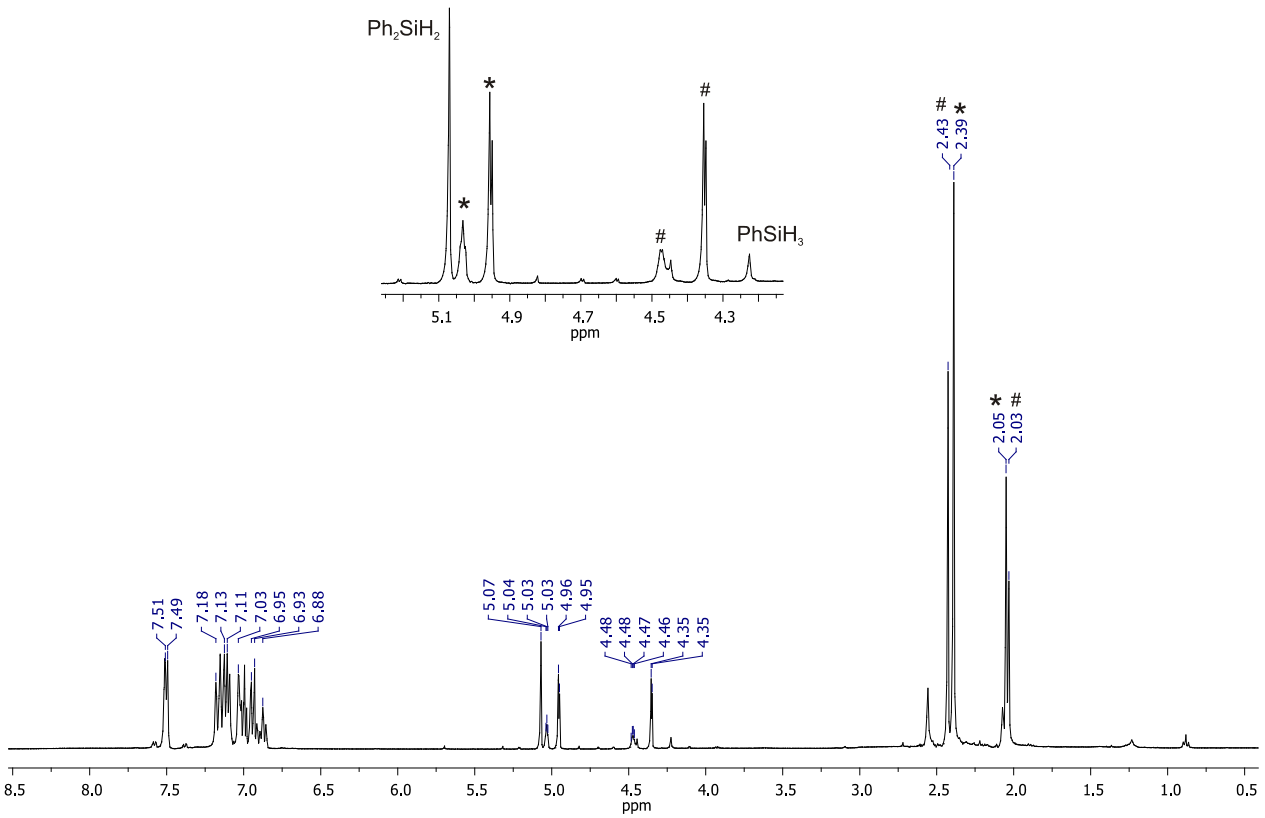


**Fig. S24.** $^{1}$H NMR spectrum of the reaction mixture of **4** and $PhSiH_3$ ([**4**]:[$PhSiH_3$] = 1:2) (400 MHz, $C_6D_6$, 293 K). * – signals of 2,2'-(4-$MeC_6H_3NMe_2$)$_2$CH$SiH_2$Ph; # – signals of 2,2'-(4-$MeC_6H_3NMe_2$)$_2$CH$SiH_3$.

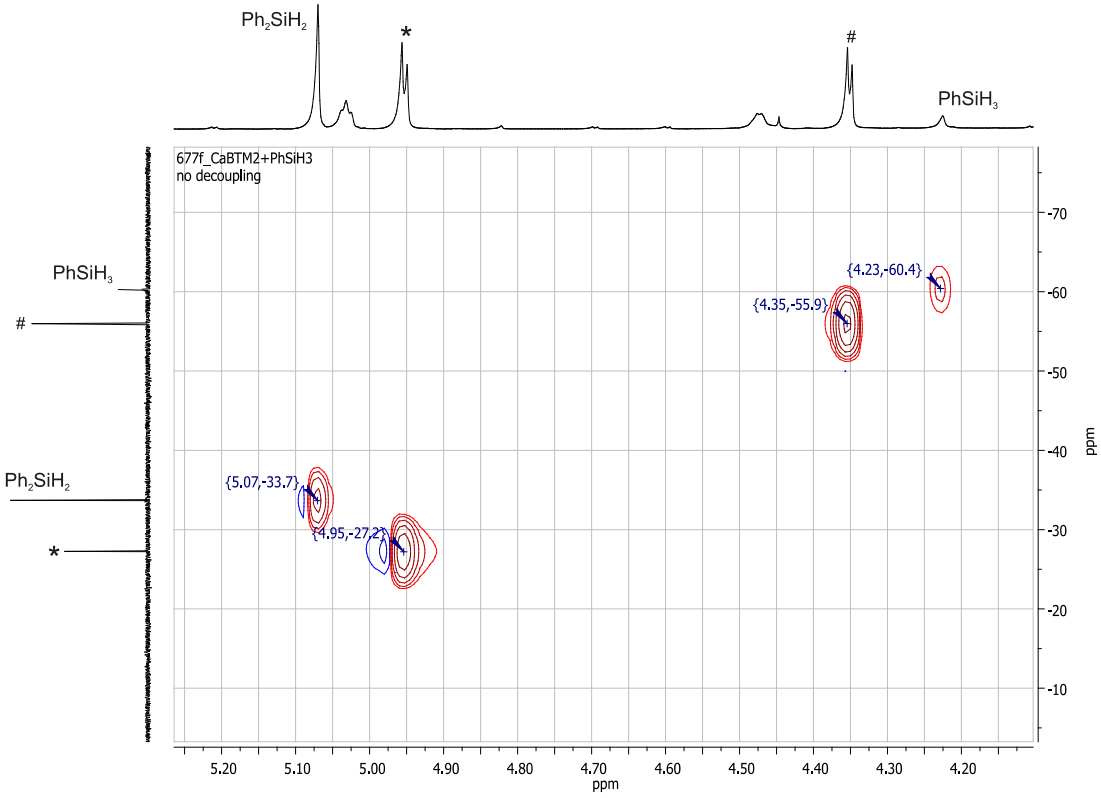

**Fig. S25.** $^{29}Si–^{1}H$ HSQC NMR spectrum of the reaction mixture of **4** and $PhSiH_3$ ([**4**]:[$PhSiH_3$] = 1:2) (400 MHz, $C_6D_6$, 293 K). * – signal of 2,2'-(4-$MeC_6H_3NMe_2)_2CHSiH_2Ph$; # – signal if 2,2'-(4-$MeC_6H_3NMe_2)_2CHSiH_3$.

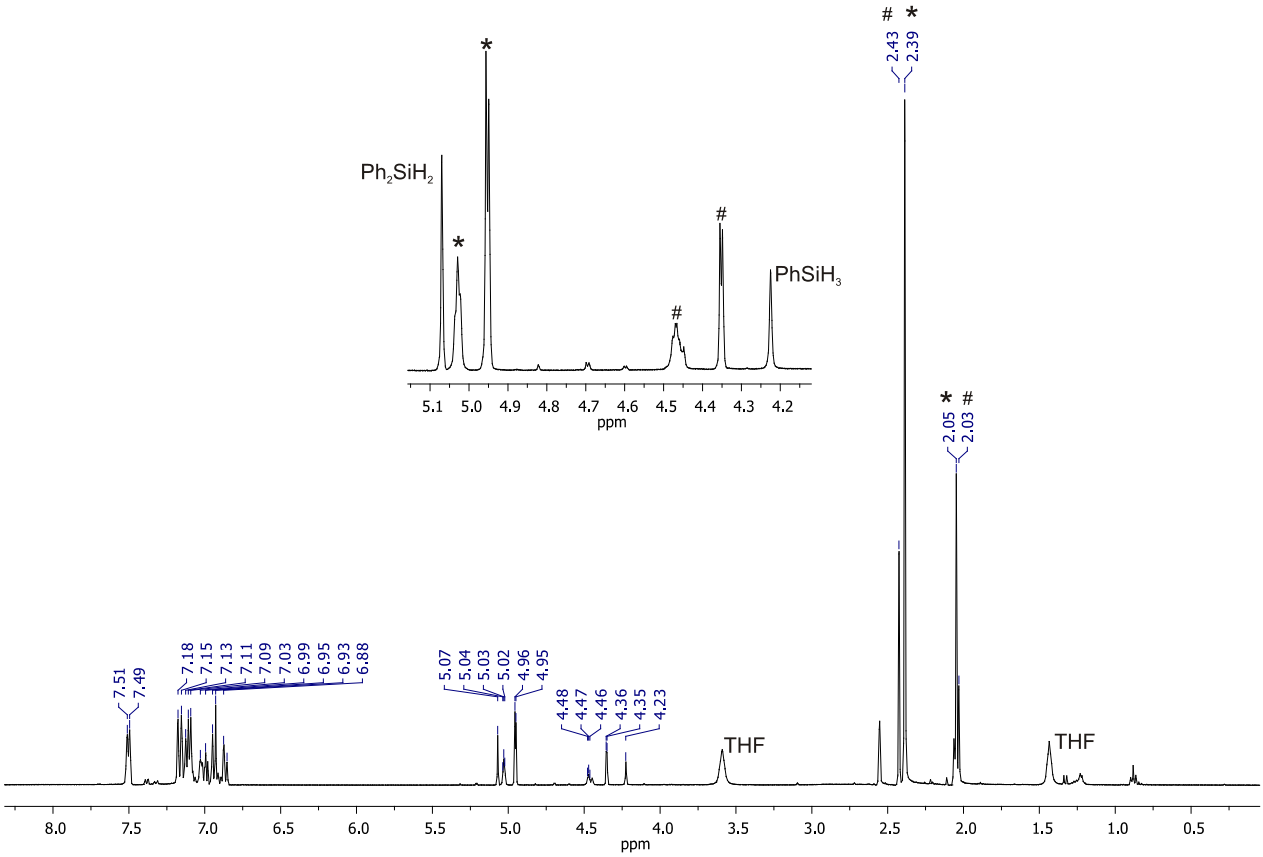


**Fig. S26.** $^{1}H$ NMR spectrum of the reaction mixture of $\mathbf{4^{THF}}$ and $PhSiH_3$ ([$\mathbf{4^{THF}}$]:[$PhSiH_3$] = 1:2) (400 MHz, $C_6D_6$, 293 K). * – signal of 2,2'-(4-$MeC_6H_3NMe_2)_2CHSiH_2Ph$; # – signal if 2,2'-(4-$MeC_6H_3NMe_2)_2CHSiH_3$.