Supplementary Information

Planar-chiral 1,1'-diamioferrocenes

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Experimental Section

A Compound Synthesis

General considerations

All reactions involving air-sensitive compounds were performed in an inert atmosphere (argon or dinitrogen) by using standard Schlenk techniques or a conventional glovebox. Starting materials were procured from standard commercial sources and used as received. Tosyl azide,[S1] $[(Me_3Si)_2N]_2Pb$[S2] and $[GeCl_2(1,4\text{-dioxane})]$[S3] were synthesised by adapted versions of the published procedures. NMR spectra were recorded at ambient temperature with Varian NMRS-500 and MR-400 spectrometers operating at 500 and 400 MHz, respectively, for ^1H. Elemental analyses were carried out with a HEKAtech Euro EA-CHNS elemental analyser at the Institute of Chemistry, University of Kassel, Germany.

Optimised procedures for the synthesis of known starting materials:

Large-scale synthesis of $fc(NHSiMe_3)_2$ starting from ferrocene

The synthesis of this compound has so far been described on a fairly small scale (ca. 1.6 – 2.1 g) by using the following sequence: ferrocene $\rightarrow$ $fcLi_2$ $\rightarrow$ $fcBr_2$ $\rightarrow$ $fc(N_3)_2$ $\rightarrow$ $fc(NH_2)_2$ $\rightarrow$ $fc(NHSiMe_3)_2$.[S4] We have developed a convenient protocol which gives rapid access to much larger batches (up to at least 30 g) of the product in an overall yield of 47 %, which is substantially higher than that reported for the established procedure (at most 30 % with respect to ferrocene, depending mainly on the protocol used for the preparation of $fc(NH_2)_2$).[S4,S5] In our sequence, $fc(N_3)_2$ is obtained not via $fcBr_2$, but directly from $fcLi_2$, which is reacted with tosyl azide.[S6] The crude product obtained by our procedure is contaminated with Ph_3PO (< 10 %), which may be removed by extraction and crystallisation. However, this was not necessary for our purposes. In a typical experiment, a solution of *n*BuLi in hexane (161 mL, 1.59 M, 256 mmol) was added to a stirred suspension of ferrocene (20.00 g, 107.5 mmol) in a mixture of *n*-hexane (200 mL) and TMEDA (24.98 g, 215.0 mmol). Stirring was discontinued after 30 min and the flask was kept at complete rest for 15 h. The orange-red crystalline solid was isolated by removing the supernatant via cannula. THF (250 mL) was added to the solid and the stirred suspension was immersed in a cooling bath kept at −80 °C. The following operations were performed under exclusion of light. Tosyl azide (40.3 g, 204.3 mmol) was added in one portion. The cooling bath was removed after 15 min and stirring was continued for 3 h. Water (50 mL) was added to the dark red suspension. The volume of the mixture was reduced to ca. 50 mL under vacuum. Diethyl ether (400 mL) was added. The mixture was stirred vigorously for 15 minutes. NaCl (10 g) was added and the mixture was stirred for an additional 15 minutes. Stirring was stopped and the mixture was stored until a greyish solid appeared (ca. 15 min). The organic layer was decanted off and the residue was extracted with diethyl ether (4 × 200 mL). The combined organic layers were dried with $MgSO_4$. The drying agent was filtered off and the filtrate was slowly added to a stirred suspension of PPh_3 (59.2 g, 226 mmol) in diethyl ether (100 mL). Gas evolution was observed after a short induction period. The rate of addition was adjusted in such a way that gas evolution took place in a controlled manner. Stirring was discontinued after 3 h. The following operations were performed without exclusion of light and under aerobic conditions. The solid was filtered off, washed with diethyl ether (4 × 100 mL) and dried under vacuum, affording $fc(NPPh_3)_2$ (57.77 g, 78.47 mmol) as a burgundy red, microcrystalline solid in 73 % yield with respect to ferrocene. Spectroscopic data were consistent with those reported in the literature.[S6,S7] The complete amount of $fc(NPPh_3)_2$ thus obtained was suspended in toluene (350 mL) and subjected to hydrolysis. Water was added (6.0 mL, 0.33 mol), followed by NaOH (0.71 g, 18 mmol). After degassing, the stirred mixture was heated to reflux for 15 h under dinitrogen and was subsequently allowed to cool to ambient temperature. $MgSO_4$ (30 g, 0.25 mol) was added and the mixture was stirred for 15 minutes. Insoluble material was removed by filtration through a short pad of Celite and was then washed with toluene (2 ×15 mL). The stirred filtrate containing $fc(NH_2)_2$ was immersed in a cooling bath kept at −40 °C. Me_3SiCl (29.66 g, 273 mmol) was added, followed by NEt_3 (27.62 g, 273 mmol). The cooling bath was removed. After 2 h *n*-hexane (150 mL) was added. The beige solid (mainly triethylammonium chloride and Ph_3PO) was filtered off and then washed with *n*-hexane (3 × 20 mL). The filtrate and washing solutions were combined and volatile components were removed under vacuum. The product was extracted with ice-cold *n*-hexane (100 mL). The extract was filtered through a short pad of Celite, which was subsequently washed with cold *n*-hexane (2 × 50 mL). The filtrate and washing solutions were combined and volatile components were removed under vacuum, leaving the crude product (20.1 g) as an orange-brown solid (purity ca. 90 %; NMR spectroscopic data consistent with those reported in the literature),[S4] which contained Ph_3PO as main contaminant (< 10 %, see Fig. S12) according to an NMR spectroscopic analysis. This corresponds to a yield of ca. 18.0 g (47 % with respect to ferrocene). The crude product was used for the synthesis of compound **2** without further purification.

Synthesis of $fc(NH_2)_2$ from $fc(NPPh_3)_2$

Water (1.0 mL, 55 mmol) was added to a suspension of $fc(NPPh_3)_2$ (10.00 g, 13.6 mmol; synthesised as described above) in toluene (100 mL), followed by NaOH (0.2 g, 5 mmol). After degassing, the stirred mixture was heated to reflux for 15 h under dinitrogen and was subsequently allowed to cool to ca. 80 °C. Insoluble material was removed by filtration through a short pad of Celite. The Celite pad was washed with THF (2 × 25 ml). The filtrate and washing solutions were combined and then cooled with an ice bath. HCl (11.3 mL, 3 M in 1,4-dioxane, 34 mmol) was added to the stirred solution, affording $fc(NH_3Cl)_2$ as a precipitate, which was filtered off and then washed with THF (3 × 10 mL). The yellow solid was suspended in THF (30 mL). NEt_3 (3.44 g, 34 mmol) was added, which led to the formation of a suspension of colourless triethylammonium chloride in an orange solution of $fc(NH_2)_2$. After 30 min the solid was removed by filtration through a short pad of Celite and was then washed with THF (3 × 5 ml). The filtrate and washing solutions were combined. Volatile components were removed under vacuum, affording the product as an orange solid. Yield 2.38 g (81 %). Spectroscopic data were consistent with those reported in the literature.[S5]

Procedures for the synthesis of new compounds (in the order of their compound numbers):

Synthesis of 1a

A dark green solution of $C_{10}H_8Li$ was prepared from naphthalene (900 mg, 7.02 mmol) and lithium granules (58 mg, 8.42 mmol) in THF (30 mL) by sonicating for 10 min, followed by stirring with a glass stirring bar for 10 h. Excess lithium was removed by cannula filtration and the filtrate was added to finely ground **2** (2.000 g, 1.75 mmol). The mixture was stirred for 1 h and was subsequently placed in an ice bath. Me_3SiCl (1.52 g, 14.0 mmol) was added to the stirred orange-grey suspension. The ice bath was removed and stirring was continued for 2 h. Volatile components were removed under vacuum. Toluene (30 mL) was added to the oily residue. Insoluble components were filtered off and washed with toluene (2 × 5 mL). The combined toluene solutions were cooled to 0 °C with an ice bath and hydrochloric acid (2.0 mL, 32 %, 20 mmol) was added to the stirred solution, which resulted in the formation of a light yellow precipitate. The ice bath was removed and stirring was continued for 0.5 h. The resulting hydrochloride **1a**H_2Cl_2 was filtered off, dried under vacuum, washed with toluene (3 × 5 mL) and was subsequently suspended in THF (15 mL). NEt_3 (640 mg, 6.31 mmol) was added to liberate the product under formation of triethylammonium chloride, which was filtered off after 30 min and washed with diethyl ether (2 ×3 mL). The filtrate and washing solutions were combined and volatile components were removed under vacuum. The product was obtained as a bright orange oil. Yield 865 mg (86 %). Satisfactory microanalytical data could not be obtained due to the oily nature of the compound.

HR-APCI-DIP(+): *m/z* calcd. for $[C_{13}H_{21}FeN_2Si]^+$ 289.0823; found 289.0818 $[M + H]^+$.

^1H NMR (400 MHz, C_6D_6): δ = 3.89, 3.78, 3.72 (3 m, 3 × 1 H, cyclopentadienyl H), 3.69 (br., 4 H, cyclopentadienyl H), 1.97 (br., 4 H, NH_2), 0.29 ppm (s, 9 H, $SiMe_3$).

$^{13}C\{^1H\}$ NMR (101 MHz, C_6D_6): δ = 109.4, 104.7 (2 × $C_{ipso}N$), 69.9, 67.0, 64.6, 64.3, 64.1, 61.3 (6 × cyclopentadienyl CH), 60.2 ($C_{ipso}Si$), 59.4 (cyclopentadienyl CH), 0.4 ppm ($SiMe_3$).

Synthesis of 1b

A dark green solution of $C_{10}H_8Li$ was prepared from naphthalene (900 mg, 7.02 mmol) and lithium granules (58 mg, 8.42 mmol) in THF (30 mL) by sonicating for 10 min, followed by stirring with a glass stirring bar for 10 h. Excess lithium was removed by cannula filtration and the filtrate was added to finely ground **2** (2.000 g, 1.75 mmol). The mixture was stirred for 1 h and the orange-grey suspension was subsequently added slowly to a stirred solution of Ph_2PCl (2.39 g, 10.8 mmol) in THF (10 mL). Volatile components were removed under vacuum after 2 h. Toluene (20 mL) was added to the residue and the solid was removed by filtration. The solvent was removed from the filtrate under vacuum, leaving an orange oil, which was dissolved in THF (30 mL). The solution was cooled to 0 °C. HCl in dioxane (8.2 mL of a 3 M solution, 25 mmol) was added, which resulted in the formation of a light yellow precipitate. Diethyl ether (15 mL) was added after 15 h. The precipitate was separated off by centrifugation (20 min, 2000 rpm). The solid was triturated with THF (15 mL) under sonication and again separated off by centrifugation. This procedure was repeated with THF (3 × 15 mL) and diethyl ether (2 × 10 mL). Drying of the solid under vacuum afforded the hydrochloride **1b**H_2Cl_2 as a light yellow powder (1.640 mg), which was suspended in THF (20 mL). NEt_3 (885 mg, 8.78 mmol) was added to liberate the product under formation of triethylammonium chloride, which was filtered off after 30 min and then washed with THF (2 × 5 mL). The filtrate and washing solutions were combined and volatile components were removed under vacuum. The oily orange residue was taken up in warm methanol (ca. 10 mL). The solution was stored for 2 h at 0 °C, affording the product as an orange crystalline methanol solvate (**1b**·CH_3OH). For the synthesis of **10b** (vide infra), it was necessary to remove the methanol. For this purpose, the methanol solvate was dissolved in a minimal amount of toluene. The solution was reduced to dryness under vacuum, affording **1b** as an orange microcrystalline solid. Yield 895 mg (59 %).

$C_{22}H_{21}N_2FeP·CH_3OH$ (432.28): calcd. C 63.91, H 5.83, N 6.48 %; found C 64.31, H 5.58, N 5.71 %.

HR-APCI-DIP(+): *m*/*z* calcd. for $[C_{22}H_{22}FeN_2P]^+$ 401.0870; found 401.0865 $[M + H]^+$.

^{1}H NMR (400 MHz, CD_2Cl_2): δ = 7.60 (m, 2 H, Ph) 7.40, 7.25 (2 m, 2 × 4 H, Ph), 4.13, 3.99, 3.79, 3.76 (4 m, 4 ×1 H, cyclopentadienyl H), 3.54 (br., 2 H, cyclopentadienyl H), 3.46 (m, 1 H, cyclopentadienyl H), 2.83, 2.39 ppm (2 br., 2 × 2 H, NH_2).

$^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2): δ = 140.6 (d, $^1J_{CP}$ = 9.7 Hz, phenyl C_{ipso}), 137.8 (d, $^1J_{CP}$ = 6.6 Hz, phenyl C_{ipso}), 135.7 (d, J_{CP} = 21.0 Hz, phenyl CH), 132.5 (d, J_{CP} = 17.5 Hz, phenyl CH), 129.8 (d, J_{CP} = 1.1 Hz, phenyl CH), 128.7 (m, 2 × phenyl CH), 128.3 (phenyl CH), 110.4 (d, $^2J_{CP}$ = 23.0 Hz, $C_{ipso}N$), 105.9 ($C_{ipso}N$), 67.7 (d, J_{CP} = 2.3 Hz, cyclopentadienyl CH), 66.4 (d, J_{CP} = 1.2 Hz, cyclopentadienyl CH), 65.6, 65.5 (2 × cyclopentadienyl CH), 64.8 (d, J_{CP} = 3.7 Hz, cyclopentadienyl $C_{ipso}P$), 62.3 (d, J_{CP} = 3.2 Hz, cyclopentadienyl CH), 61.5 (d, J_{CP} = 2.0 Hz, cyclopentadienyl CH), 60.3 ppm (cyclopentadienyl CH).

$^{31}P\{^1H\}$ NMR (202 MHz, CD_2Cl_2): δ = –25.6 ppm.

Synthesis of 1c

A dark green solution of $C_{10}H_8Li$ was prepared from naphthalene (672 mg, 5.24 mmol) and lithium granules (65 mg, 9.36 mmol) in THF (15 mL) by sonicating for 10 min, followed by stirring with a glass stirring bar for 10 h. Excess lithium was removed by cannula filtration and the filtrate was added to finely ground **2** (1.500 g, 1.31 mmol). The mixture was stirred for 1 h and was subsequently placed in an ice bath. *n*Bu_3SnCl (3.600 g, 11.00 mmol) was added to the stirred orange-grey suspension. The ice bath was removed and stirring was continued for 16 h. Volatile components were removed under vacuum. Toluene (30 mL) was added to the residue. Insoluble components were filtered off through a pad of Celite and washed with toluene (10 mL). The volume of the combined toluene solutions was reduced to ca. 10 mL under vacuum. Degassed water (10 mL) was added. The mixture was placed in a heated oil bath (100 °C) and was stirred vigorously for 72 h at this temperature. The bath was removed and the mixture was allowed to cool down to ambient temperature. The organic phase was separated off and volatile components were removed under vacuum. The residue was taken up in *n*-hexane (15 mL) and was then subjected to purification by column chromatography (silica gel). Unreacted *n*Bu_3SnCl and remaining byproducts of the hydrolysis were removed by elution with *n*-hexane. The product was subsequently eluted with ethyl acetate. The solvent was removed under vacuum, which afforded the product as a bright orange oil, which contained trace amounts of residual *n*Bu_3SnCl as impurity according to

^{119}Sn NMR spectroscopy. Yield 1.126 g (86 %). Satisfactory microanalytical data could not be obtained due to the oily nature of the compound.

HR-ESI(+): *m/z* calcd. for $[C_{22}H_{38}FeN_2Sn]^+$ 506.1406; found 506.1401 $[M]^+$.

^{1}H NMR (400 MHz, C_6D_6): δ= 3.97, 3.85, 3.80, 3.78, 3.75, 3.73 (7 m, 7 × 1 H, cyclopentadienyl H), 2.12, 1.94 (2 br., 2 × 2 H, NH_2), 1.74 – 1.66 (m, 6 H, CH_2), 1.47 – 1.38 (m, 6 H, CH_2), 1.18 – 1.14 (m, 6 H, CH_2), 0.98 – 0.94 ppm (m, 9 H, CH_3).

$^{13}C\{^1H\}$ NMR (101 MHz, C_6D_6): δ = 109.2, 104.5 (2 × $C_{ipso}N$), 70.8, 67.8, 64.5, 64.1, 63.9, 61.3 (6 × cyclopentadienyl CH), 60.3 ($C_{ipso}Sn$), 59.6 (cyclopentadienyl CH), 29.8 ($^3J_{SnC}$ = 19 Hz, $SnCH_2CH_2\mathit{C}H_2$), 27.9 ($^2J_{SnC}$ = 58 Hz, $SnCH_2\mathit{C}H_2$), 14.0 (CH_3), 10.6 ppm ($^1J_{^{117}SnC}$ = 330 Hz, $J_{^{119}SnC}$ = 345 Hz, $SnCH_2$).

^{119}Sn NMR (186 MHz, C_6D_6): δ = –21.7 ppm ($^2J_{^{119}SnC}$ = 58 Hz, $^1J_{^{119}SnC}$ = 340 Hz).

Synthesis of 1d

A solution of hydroxylammonium chloride (160 mg, 2.30 mmol) in water (10 mL) was added to a solution of **5d** (570 mg, 1.10 mmol) in THF (10 mL). The dark red mixture was stirred for 30 minutes, which resulted in the formation of a yellow suspension. Diethyl ether (15 mL) was added, followed by hydrochloric acid (0.1 mL, 32 %, 1 mmol). The mixture was shaken vigorously. The organic layer was separated off. The aqueous layer was washed with diethyl ether (3 × 5 mL) and was subsequently mixed with a solution of NEt_3 (435 mg, 4.3 mmol) in diethyl ether (15 mL). The bright yellow organic layer was separated off. The aqueous phase was extracted with diethyl ether (3 × 5 mL). The combined organic layers were dried with $MgSO_4$. The drying agent was filtered off. Volatile components were removed from the filtrate under vacuum, which afforded the product as a yellow microcrystalline solid. Yield 284 mg (76 %).

$C_{10}H_{11}FeIN_2$ (341.96): calcd. C 35.12, H 3.24, N 8.19 %; found C 35.46, H 3.48, N 8.18 %.

HR-APCI-DIP(+): *m/z* calcd. for $[C_{10}H_{11}FeIN_2]^+$ 341.9316; found 341.9311 $[M]^+$.

^{1}H NMR (400 MHz, C_6D_6): δ = 3.97, 3.73, 3.70, 3.64, 3.61, 3.39, 3.36, 3.36 (7 m, 7 × 1 H, cyclopentadienyl CH), 2.08 ppm (br., 4 H, NH_2).

$^{13}C\{^1H\}$ NMR (101 MHz, C_6D_6): δ = 106.8, 105.8 (2 × CN), 69.8, 66.1, 66.1, 64.3, 63.9, 61.9, 57.1 (7 × cyclopentadienyl CH), 42.0 ppm (CI).

Synthesis of 2

A suspension of $LiN(SiMe_3)_2$ (24.10 g, 144.0 mmol) in THF (50 mL) was slowly added to a stirred suspension of $PbCl_2$ (20.06 g, 72.1 mmol) in THF (20 mL), resulting in a mildly exothermic reaction. Stirring was continued for 2 h. Volatile components were removed under vacuum, affording a suspension of LiCl in $[(Me_3Si)_2N]_2Pb$. Crude $fc(NHSiMe_3)_2$ (obtained as described above; 28.42 g, ca. 92 % purity, 73 mmol) was added, followed by toluene (5 mL). The mixture was stirred for 15 h, resulting in a solution of $fc[(NSiMe_3)_2Pb:]$ in equilibrium with its dimer **A**,[S8] with the latter predominating by far due to the high concentration used. $LiN(SiMe_3)_2$ (17.00 g, 101.6 mmol) was added, followed by toluene (250 mL). The mixture was stirred for 1 h. The stirring bar was removed. The mixture was heated to 70 °C, then kept at complete rest at this bath temperature for 15 h and was subsequently allowed to cool to room temperature slowly. The supernatant was decanted off and the residue was washed with toluene (2 × 10 mL). This afforded a solid containing **2** as large dark red crystals together with finely divided LiCl and trace amounts of elemental lead. The latter two components were removed by a procedure reminiscent of washing rice. *n*-Hexane (15 mL) was added and the finely divided components were suspended by gentle shaking and swirling. The suspension was rapidly, but carefully, decanted off so that crystalline **2** was left behind. This procedure was typically repeated 10 – 15 times. When performed on a small scale (1 – 2 g), the separation may be conveniently achieved with a porosity class 0 glass filter, which selectively holds back crystalline **2**. Yield 25.10 g (60 % with respect to $fc(NHSiMe_3)_2$ and 28 % with respect to ferrocene).

$C_{32}H_{50}N_4Fe_2Li_2Pb_2Si_4$ (1143.11): calcd. C 33.62, H 4.41, N 4.90 %; found C 33.06, H 4.53, N 4.42 %.

^1H NMR (500 MHz, C_6D_6): $\delta = 4.71, 4.17, 4.14, 4.10, 4.08, 3.47, 3.44$ (7 m, 7 × 1 H, cyclopentadienyl H), 0.49, 0.00 ppm (2 s, 2 × 9 H, $SiMe_3$).

$^{13}C\{^1H\}$ NMR (126 MHz, C_6D_6): $\delta = 125.4, 125.0$ (CN/CLi; due to broad signals and the low solubility of **2**, the signal-to-noise ratio remained very low even after 295000 scans and an assignment was not possible with certainty), 109.7 (CN), 72.5, 71.6, 71.5, 69.9, 69.7, 67.4, 64.5 (7 × cyclopentadienyl CH), 3.3, 1.5 ppm (2 × $SiMe_3$).

^7Li NMR (194 MHz, C_6D_6): $\delta = 3.4$ ppm ($\nu_{½} = 20$ Hz).

Synthesis of 5c

Benzaldehyde (1.24 g, 11.7 mmol) and molecular sieve (0.5 g, 4 Å) were added to a solution of **1c** (1.600 g, 3.17 mmol) in toluene (20 mL). The solution was decanted off after 3 d and the molecular sieve was extracted with toluene (10 × 5 mL). The solution and extracts were combined. Volatile components were removed under vacuum (finally at 50 °C), leaving the product as an intensively red oil. Yield 2.314 g (99 %). Satisfactory microanalytical data could not be obtained due to the oily nature of the compound.

HR-ESI(+): *m*/*z* calcd. for $[C_{36}H_{47}FeN_2Sn]^+$ 683.2111; found 683.2113 $[M + H]^+$.

^1H NMR (400 MHz, C_6D_6): $\delta = 8.36$, 8.33 (2 s, 2 × 1 H, NCH), 7.67 – 7.63 (m, 4 H, Ph), 7.10 – 7.03 (m, 6 H, Ph), 4.65 (m, 1 H, cyclopentadienyl H), 4.61 (m, 2 H, cyclopentadienyl H), 4.38, 4.27, 4.22, 4.14 (4 m, 4 × 1 H, cyclopentadienyl H), 1.82 – 1.75, 1.49 – 1.42 (2 m, 2 × 6 H, CH_2), 0.98 – 0.94 ppm (m, 9 H, CH_3).

$^{13}C\{^1H\}$ NMR (101 MHz, C_6D_6): $\delta = 157.4$, 157.1 (2 × NCH), 137.7, 137.5, 130.2, 130.1, 128.7, 128.7, 128.4, 128.2 (8 × Ph), 111.2, 105.9 (2 × $C_{ipso}N$), 75.4 ($J_{SnC} = 37$ Hz, cyclopentadienyl CH), 73.8 ($C_{ipso}Sn$), 71.9 ($J_{SnC} = 36$ Hz, cyclopentadienyl CH), 69.2, 68.7, 64.9, 64.2 (4 × cyclopentadienyl CH), 61.1 ($J_{SnC} = 26$ Hz, cyclopentadienyl CH), 30.0 ($^3J_{SnC} = 19$ Hz, $SnCH_2CH_2CH_2$), 28.0 ($^2J^{119}{}_{SnC} = 60$ Hz, $^2J^{117}{}_{SnC} = 57$ Hz, $SnCH_2CH_2$), 14.1 (CH_3), 11.3 ppm ($^1J^{117}{}_{SnC} = 335$ Hz, $^1J^{119}{}_{SnC} = 350$ Hz, $SnCH_2$).

^{119}Sn NMR (186 MHz, C_6D_6): $\delta = -23.1$ ppm.

Synthesis of 5d

A solution of iodine (798 mg, 3.14 mmol) in dichloromethane (50 mL) was added dropwise to a stirred solution of **5c** (2.100 g, 3.08 mmol) in dichloromethane (40 mL) cooled to –40 °C. The cooling bath was removed and the mixture was stirred for 5 h. Volatile components were removed under vacuum. Diethyl ether (50 mL) was added to the reddish oily residue and HCl in diethyl ether (6 mL of a 2 M solution, 12 mmol) was added with stirring, which resulted in the formation of a dark violet precipitate. The precipitate was separated off by centrifugation (10 min, 2000 rpm), washed with diethyl ether (5 × 15 mL) and was subsequently suspended in a mixture of diethyl ether (20 mL) and THF (10 mL). NEt_3 (1.81 g, 17.9 mmol) was added to liberate the product under formation of triethyl ammonium chloride, which was separated off by centrifugation (10 min, 2000 rpm). Volatile components of the solution were removed under vacuum, affording the product as a deep red oil, which solidified after several days at room temperature. Yield: 1.212 g (76 %). Single crystals were obtained from a concentrated solution in *n*-hexane.

$C_{24}H_{19}N_2FeI$ (518.17): calcd. C 55.63, H 3.70, N 5.41 %; found C 56.03, H 3.99, N 5.67 %.

HR-APCI-DIP(+): *m*/*z* calcd. for $[C_{24}H_{20}FeIN_2]^+$ 519.0021; found 519.0015 $[M + H]^+$.

^1H NMR (400 MHz, CD_2Cl_2): $\delta = 8.55$, 8.52 (2 s, 2 × 1 H, NCH), 7.70 – 7.66 (m, 4 H, Ph), 7.44 – 7.40 (m, 2 H, Ph), 7.38 –7.30 (m, 4 H, Ph), 4.58, 4.57, 4.52, 4.44, 4.40 (5 m, 5 × 1 H, cyclopentadienyl H), 4.30 ppm (m, 2 H, cyclopentadienyl H).

$^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2): δ = 160.4, 159.8 (2 × NCH), 137.2, 137.1, 131.2, 131.0, 129.1, 129.1, 128.7, 128.6 (8 × Ph), 107.3, 105.6 (2 × $C_{ipso}N$), 75.3, 72.1, 71.1, 69.5, 68.2, 67.0, 59.1 ppm (7 × cyclopentadienyl CH). The CI signal was not detected.

Synthesis of 6a

Pivaldehyde (370 mg, 4.30 mmol) and 4 Å molecular sieve (200 mg) were added to a solution of **1a** (410 mg, 1.42 mmol) in toluene (15 mL). The mixture was stirred slowly for 2 d. Volatile components were subsequently removed under vacuum. The residue was extracted with THF (10 mL) and the extract was filtered to remove insoluble material. Li[AlH_4] (104 mg, 2.76 mmol) was added to the filtrate. The stirred mixture was heated to 70 °C bath temperature for 1 h and was subsequently cooled with an ice bath. Degassed water (0.5 mL) was added. The solid was filtered off and then washed with THF (2 × 5 mL). The filtrate and washing solutions were combined. Volatile components were removed under vacuum, leaving the product as an orange oil. Yield 431 mg (72 %). Satisfactory microanalytical data could not be obtained due to the oily nature of the compound.

HR-APCI-DIP(+): *m*/*z* calcd. for $[C_{23}H_{41}FeN_2Si]^+$ 429.2388; found 429.2382 $[M + H]^+$.

^1H NMR (400 MHz, C_6D_6): δ = 4.13, 4.06, 3.96, 3.91 (4 m, 4 × 1 H, cyclopentadienyl H), 3.85 (m, 2 H, cyclopentadienyl H), 3.79 (m, 1 H, cyclopentadienyl H), 2.78 – 2.66 (m, 4 H, CH_2), 2.41, 2.11 (2 br., 2 × 1 H, NH), 0.94, 0.91 (2 s, 2 × 9 H, CMe_3), 0.36 ppm (s, 9 H, $SiMe_3$).

$^{13}C\{^1H\}$ NMR (101 MHz, C_6D_6): δ = 116.1, 111.6 (2 × $C_{ipso}N$), 69.1, 66.5, 64.4, 63.7 (4 × CH), 60.2, 59.9 (2 × CH_2), 58.5 (CH), 57.6 ($C_{ipso}Si$), 56.5, 55.9 (2 × CH), 31.5, 31.4 (2 × $\mathit{C}Me_3$), 27.9, 27.8 (2 × $C\mathit{Me}_3$), 0.4 ppm ($SiMe_3$).

Synthesis of 6b

Pivaldehyde (775 mg, 9.00 mmol) and 4 Å molecular sieves (200 mg) were added to a solution of **1b** (901 mg, 2.25 mmol) in THF (10 mL). The mixture was stirred for 48 h. Insoluble material was removed by filtration. Volatile components were removed from the filtrate under vacuum. The orange residue was dissolved in THF (20 mL). Li[AlH_4] was added (167 mg, 4.40 mmol) to the solution. The slowly stirred mixture was heated to 70 °C bath temperature for 1 h and was subsequently cooled with an ice bath. Degassed water (0.5 mL) was added dropwise. Volatile components were removed under vacuum. Toluene (5 mL) was added to the residue. The solid was filtered off and then washed with toluene (3 × 1 mL). The filtrate and washing solutions were combined. Volatile components were removed under vacuum, leaving the product as an orange oil. Yield 680 mg (56 %). Satisfactory microanalytical data could not be obtained due to the oily nature of the compound.

HR-APCI-DIP(+): *m/z* calcd. for $[C_{32}H_{42}FeN_2P]^+$ 541.2435; found 541.2430 $[M + H]^+$.

^{1}H NMR (500 MHz, C_6D_6): 7.73 (br, 2 H, Ph), 7.46 (m, 2 H, Ph), 7.09 (m, 3 H, Ph), 7.03 (m, 2 H, Ph), 6.97 (m, 1 H, Ph), 4.12, 4.06, 3.86, 3.84, 3.80, 3.65 (7 m, 7 × 1 H, cyclopentadienyl H), 3.15 (br., 2 H, NH), 2.79 – 2.70 (m, 2 H, CH_2) 2.56 – 2.42 (m, 2 H, CH_2), 1.92 (m, 2 H, NH), 0.86, 0.85 ppm (2 s, 2 × 9 H, *t*Bu).

$^{13}C\{^1H\}$ NMR (101 MHz, C_6D_6): δ = 140.8 (d, $^1J_{CP}$ = 9.7 Hz, phenyl C_{ipso}), 138.3 (d, $^1J_{CP}$ = 6.6 Hz, phenyl C_{ipso}), 135.9 (d, J_{CP} = 21.3 Hz, phenyl CH), 132.5 (d, J_{CP} = 16.9 Hz, phenyl CH), 129.4 (br., phenyl CH), 128.5 – 128.4 (m, 3 × phenyl CH), 116.9 (d, $^2J_{CP}$ = 20.0 Hz, $Cp_{ipso}N$), 112.4 ($Cp_{ipso}N$), 66.6 (cyclopentadienyl CH), 65.7 (d, J_{CP} = 1.7 Hz, cyclopentadienyl CH), 65.0, 64.6 (2 br., 2 × cyclopentadienyl CH), 62.0 (d, $^1J_{CP}$ = 4.2 Hz, cyclopentadienyl $C_{ipso}P$), 60.1, 59.6 (2 × CH_2), 57.0 (d, J_{CP} = 0.8 Hz, cyclopentadienyl CH), 56.8 (d, J_{CP} = 3.1 Hz, cyclopentadienyl CH), 55.9 (cyclopentadienyl CH), 31.6, 31.6 (2 × $\mathit{C}CH_3$), 27.8, 27.8 ppm (2 × $C\mathit{C}H_3$).

$^{31}P\{^1H\}$ NMR (202 MHz, C_6D_6): δ = –24.4 ppm.

Synthesis of 7a

$NH_4[BF_4]$ (92 mg, 0.88 mmol) and triethyl orthoformate (993 mg, 6.70 mmol) were added to a solution of **6a** (376 mg, 0.88 mmol) in toluene (6 mL). The stirred mixture was heated to 110 °C bath temperature for 1 h and was subsequently allowed to cool to room temperature. Volatile components were removed under vacuum. Dichloromethane (5 mL) was added to the residue. The solid was filtered off and then washed with dichloromethane (2 × 2 mL). The filtrate and washing solutions were combined. Diethyl ether (10 mL) was added and the mixture was sonicated for 5 min. The supernatant was decanted off. The remaining orange solid was extracted with diethyl ether (2 × 10 mL) under sonication and was subsequently dried under vacuum. Yield 322 mg (70 %).

$C_{24}H_{39}N_2BF_4FeSi$ (526.32): calcd. C 54.77, H 7.47, N 5.32 %; found C 54.84, H 7.50, N 5.10 %.

HR-APCI-DIP(+): *m/z* calcd. for $[C_{24}H_{39}FeN_2Si]^+$ 439.2232; found 439.2226 $[M]^+$.

^{1}H NMR (400 MHz, CD_2Cl_2): δ = 8.38 (s, 1 H, N_2CH), 4.70 (br., 1 H, cyclopentadienyl H), 4.61 (m, 1 H, cyclopentadienyl H), 4.59 (br., 1 H, cyclopentadienyl H), 4.46 (br., 2 H, cyclopentadienyl H), 4.42 (br., 1 H, cyclopentadienyl H), 4.32 (br., 1 H, cyclopentadienyl H), 4.19 (d, J_{HH} = 13.9 Hz, 1 H, CH_2), 4.07 (d, J_{HH} = 14.1 Hz, 1 H, CH_2), 3.53 (d, J_{HH} = 14.1 Hz, 1 H, CH_2), 3.28 (d, J_{HH} = 13.9 Hz, 1 H, CH_2), 1.05, 1.03 (2 s, 2 × 9 H, CMe_3), 0.29 ppm ($SiMe_3$).

$^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2): δ= 164.6 (N_2CH), 98.1, 93.9 (2 × $C_{ipso}N$), 78.1, 74.9, 72.8 (3 × cyclopentadienyl CH), 72.2 ($C_{ipso}Si$), 71.9 (cyclopentadienyl CH), 71.2, 71.0 (2 × CH_2), 70.9, 69.3, 68.1 (3 × cyclopentadienyl CH), 33.1, 32.9 (2 × CMe_3), 27.5, 27.3 (2 × CMe_3), –0.6 ppm ($SiMe_3$).

Synthesis of 7b

$NH_4[BF_4]$ (50 mg, 0.48 mmol) and triethyl orthoformate (889 mg, 6.00 mmol) were added to a solution of **6b** (250 mg, 0.46 mmol) in toluene (6 mL). The stirred mixture was heated to 110 °C bath temperature for 2 h and was subsequently allowed to cool to room temperature. Volatile components were removed under vacuum. Toluene (4 mL) and diethyl ether (2 mL) were added to the residue and the mixture was sonicated for 10 min. The supernatant was decanted off and the remaining orange solid was dried under vacuum. Yield 164 mg (56 %).

$C_{33}H_{40}N_2BF_4FeP$ (638.31): calcd. C 62.09, H 6.32, N 4.39 %; found C 62.20, H 6.50, N 4.03 %.

HR-APCI-DIP(+): *m/z* calcd. for $[C_{33}H_{40}N_2FeP]^+$ 541.2279; found 551.2273 $[M – BF_4]^+$.

^1H NMR (400 MHz, CD_2Cl_2): δ= 8.42 (s, 1 H, N_2CH), 7.49 – 7.35 (m, 10 H, Ph), 4.82 (s, 1 H, cyclopentadienyl H), 4.65 (m, 2 H, cyclopentadienyl H), 4.59, 4.39, 4.19, 4.12 (4 m, 4 × 1 H, cyclopentadienyl H), 4.08 (d, J_{HH} = 14.2 Hz, 1 H, CH_2), 3.73 (d, J_{HH} = 14.3 Hz, 1 H, CH_2), 3.64 (d, J_{HH} = 14.2 Hz, 1 H, CH_2), 2.80 (d, J_{HH} = 14.3 Hz, 1 H, CH_2), 1.08, 0.84 ppm (2 s, 2 × 9 H, CMe_3).

$^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2): δ= 165.3 (N_2CH), 137.1 (d, $^1J_{CP}$ = 8.6 Hz, phenyl C_{ipso}), 135.1 (d, $^1J_{CP}$ = 8.9 Hz, phenyl C_{ipso}), 134.5 (d, J_{CP} = 19.7 Hz, phenyl CH), 134.3 (d, J_{CP} = 20.5 Hz, phenyl CH), 130.2, 130.2 (2 × phenyl CH), 129.4 (d, J_{CP} = 7.3 Hz, phenyl CH), 129.2 (d, J_{CP} = 7.4 Hz, phenyl CH), 98.8 (d, $^2J_{CP}$ = 23.5 Hz, $C_{ipso}N$), 95.1 ($C_{ipso}N$), 78.8 (d, $^1J_{CP}$ = 15.9 Hz, cyclopentadienyl $C_{ipso}P$), 76.7 (d, J_{CP} = 4.1 Hz, cyclopentadienyl CH), 74.7 (d, J_{CP} = 7.8 Hz, cyclopentadienyl CH), 74.0, 73.4, 73.3 (3 × cyclopentadienyl CH), 72.0 (d, J_{CP} = 2.0 Hz, cyclopentadienyl CH), 71.8 (CH_2), 70.5 (d, J_{CP} = 2.9 Hz, CH_2) 68.7 (cyclopentadienyl CH), 33.5, 33.3 (2 × CMe_3), 28.0, 27.8 ppm (2 × CMe_3).

$^{31}P\{^1H\}$ NMR (202 MHz, CD_2Cl_2): δ= –28.3 ppm.

Synthesis of 8a

$LiN(SiMe_3)_2$ (16 mg, 96 μmol) was added to a suspension of **7a** (50 mg, 95 μmol) in C_6D_6 (0.4 mL). The mixture was swirled gently for 10 min. Insoluble material was removed with a filter pipette (Celite) and then washed with C_6D_6 (0.1 mL). The filtrate and washing solution were collected in an NMR tube. The sample was subjected to immediate NMR spectroscopic analysis. No spectroscopic changes were detected after several days, indicating that the carbene is stable at room temperature in solution.

^1H NMR (400 MHz, C_6D_6): $\delta = 4.44$, 4.21 (2 d, $J_{HH} = 13.0$ Hz, 2 × 1 H, CH_2), 4.11, 4.06, 4.03 (3 m, 3 × 1 H, cyclopentadienyl H), 3.94 – 3.90 (m, 3 H, cyclopentadienyl H), 3.85 (m, 1 H, cyclopentadienyl H), 3.54 (d, $J_{HH} = 13.2$ Hz, 1 H, CH_2), 3.36 (d, $J_{HH} = 13.0$ Hz, 1 H, CH_2), 1.12, 1.09 (2 s, 2 × 9 H, CMe_3), 0.26 ppm (s, 9 H, $SiMe_3$).

$^{13}C\{^1H\}$ NMR (101 MHz, C_6D_6): $\delta = 269.4$ ($C_{carbene}$), 107.9, 103.5 (2 × $C_{ipso}N$), 75.3, (cyclopentadienyl CH), 73.6, 73.4 (2 × CH_2), 71.9, 70.7 (2 × cyclopentadienyl CH), 69.7 ($C_{ipso}Si$), 69.6, 69.2, 68.8, 67.7 (4 × cyclopentadienyl CH), 33.7, 33. 6 (2 × $\mathit{C}Me_3$), 29.2, 29.0 (2 × $C\mathit{Me}_3$), 0.1 ppm ($SiMe_3$).

Synthesis of 8b

$LiN(SiMe_3)_2$ (13 mg, 78 μmol) was added to a suspension of **7b** (50 mg, 78 μmol) in C_6D_6 (0.4 mL). The mixture was swirled gently for 10 min. Insoluble material was removed with a filter pipette (Celite) and then washed with C_6D_6 (0.1 mL). The filtrate and washing solution were collected in an NMR tube. The sample was subjected to immediate NMR spectroscopic analysis. No spectroscopic changes were detected after several days, indicating that the carbene is stable at room temperature in solution.

^1H NMR (400 MHz, C_6D_6): $\delta = 7.54 – 7.41$ (m, 4 H, Ph), 7.10 – 7.01 (m, 6 H, Ph), 4.43 (m, 1 H, cyclopentadienyl H), 4.31 (d, $J_{HH} = 13.2$ Hz, CH_2), 4.23 (d, $J_{HH} = 13.5$ Hz, CH_2), 4.12, 4.02, 3.89 (3 m, 3 × 1 H, cyclopentadienyl H), 3.86 – 3.79 (m, 3 H, cyclopentadienyl H), 3.66 (d, $J_{HH} = 13.2$ Hz, CH_2), 3.05 4.23 (d, $J_{HH} = 13.5$ Hz, CH_2), 1.15, 1.00 ppm (2 s, 2 × 9 H, CMe_3).

$^{13}C\{^1H\}$ NMR (101 MHz, C_6D_6): $\delta = 268.8$ (br., $C_{carbene}$), 139.5 (d, $^1J_{CP} = 12.1$ Hz, phenyl C_{ipso}), 138.1 (d, $^1J_{CP} = 11.8$ Hz, phenyl C_{ipso}), 134.5 (d, $J_{CP} = 19.5$ Hz, phenyl CH), 134.4 (d, $J_{CP} = 20.1$ Hz, phenyl CH) 128.8 (br., 2 × phenyl CH), 128.6 (d, $J_{CP} = 6.6$ Hz, phenyl CH), 128.5 (d, $J_{CP} = 6.7$ Hz, phenyl CH), 108.6 (d, $^2J_{CP} = 26.0$ Hz, $C_{ipso}N$), 104.3 ($C_{ipso}N$), 75.9 (d, $J_{CP} = 10.8$ Hz, cyclopentadienyl $C_{ipso}P$), 73.8 (d, $J_{CP} = 4.5$ Hz, cyclopentadienyl CH), 73.5

(cyclopentadienyl CH), 73.5 (N*C*H$_2$), 72.2 (d, J_{CP} = 2.2 Hz, N*C*H$_2$), 70.8 (d, J_{CP} = 2.6 Hz, cyclopentadienyl CH), 70.7, 70.3, 69.8, 67.7 (4 × cyclopentadienyl CH), 33.6, 33.5 (2 × *C*Me$_3$), 29.1, 29.0 ppm (2 × C*Me*$_3$).
^{31}P{^{1}H} NMR (202 MHz, C_6D_6): $\delta = -22.9$ ppm.

Synthesis of 9a

LiN(SiMe$_3$)$_2$ (26 mg, 155 μmol) was added to a suspension of **7a** (80 mg, 152 μmol) in toluene (5 mL). The mixture was stirred for 10 min. [Rh(μ-Cl)(COD)]$_2$ (37 mg, 75 μmol) was added. Volatile components were removed under vacuum after 5 h. The residue was subjected to purification by column chromatography (silica gel). Traces of unreacted [Rh(μ-Cl)(COD)]$_2$ were removed by elution with dichloromethane. The product was subsequently eluted with dichlormethane–ethyl acetate (10:1). It was obtained as a yellow, crystalline solid by recrystallization from toluene. Yield 43 mg (41 %). An analytical sample of the methanol solvate was obtained by recrystallization from methanol. $C_{32}H_{50}ClFeN_2RhSi\cdot CH_3OH$ (717.09): cald. C 55.27, H 7.59, N 3.91 %; found C 54.41, H 8.26, N 3.59 %.
HRMS/ESI(+): *m*/*z* calcd. for $[C_{32}H_{50}FeN_2RhSi]^+$ 649.2148; found 649.2142 $[M - Cl]^+$.
^{1}H NMR (400 MHz, C_6D_6): δ = 6.81 (d, J_{HH} = 13.4 Hz, 1 H, NCH$_2$), 6.20 (d, J_{HH} = 14.0 Hz, 1 H, NCH$_2$), 5.36 (br., 2 H, COD CH), 4.81 (d, J_{HH} = 14.0 Hz, 1 H, NCH$_2$), 4.31 (br., 1 H, cyclopentadienyl CH), 4.26 (d, J_{HH} = 13.4 Hz, 1 H, NCH$_2$), 4.03 (m, 1 H, cyclopentadienyl CH), 4.00 (t, J_{HH} = 2.5 Hz, 1 H, cyclopentadienyl CH), 3.86 (m, 1 H, cyclopentadienyl CH), 3.85 – 3.80 (m, 2 H, cyclopentadienyl CH), 3.77 – 3.65 (m, 2 H, COD CH), 3.75 – 3.67 (m, 2 H, CH), 2.48 – 2.20, 1.87 – 1.62 (2 m, 2 × 4 H, COD CH$_2$), 1.21, 1.06 (2 s, 2 × 9 H, CMe$_3$), 0.12 ppm (s, 9 H, SiMe$_3$).
^{13}C{^{1}H} NMR (101 MHz, C_6D_6): δ = 227.7 (d, $^1J_{CRh}$ = 47.3 Hz, N$_2$C), 103.2, 99.0 (2 br., 2 × C$_{ipso}$N), 93.8 (d, J_{CRh} = 7.2 Hz, COD CH), 93.7 (d, J_{CRh} = 7.7 Hz, COD CH), 77.5, 73.2 (2 × cyclopentadienyl CH), 72.5 (2 × NCH$_2$), 71.4, 71.4, 70.1, 68.7 (4 × cyclopentadienyl CH), 68.6 (C$_{ipso}$Si), 68.5 (d, J_{CRh} = 7.9 Hz, COD CH), 68.4 (d, J_{CRh} = 7.7 Hz, COD CH), 68.2 (cyclopentadienyl CH) 33.5 (COD CH$_2$), 33.1 (*C*Me$_3$), 32.6 (COD CH$_2$), 32.5 (*C*Me$_3$), 30.1 (C*Me*$_3$), 29.8 (COD CH$_2$), 29.7 (C*Me*$_3$), 28.8 (COD CH$_2$), 0.3 ppm (SiMe$_3$).

Synthesis of 9b

[Rh(μ-Cl)(COD)]$_2$ (19 mg, 39 μmol) was added to a C_6D_6 solution (0.5 mL) of **8b**, prepared as described above from LiN(SiMe$_3$)$_2$ (13 mg, 78 μmol) and **7b** (50 mg, 78 μmol). NMR spectroscopic monitoring of the reaction indicated the swift formation of two complexes (possibly *C*- and *P*-coordinated isomers) at room temperature. Subsequent heating to 70 °C bath temperature for 24 h selectively furnished a single product (thermodynamic control). Volatile components were removed under vacuum. Recrystallization of the solid residue from toluene (3 mL) at –40 °C afforded the product as yellow platelets. Yield 26 mg (42 %). $C_{41}H_{51}ClFeN_2PRh$ (797.05): cald. C 61.78, H 6.45, N 3.51 %; found C 61.72, H 6.56, N 3.37 %.

^1H NMR (400 MHz, C_6D_6): δ = 7.66 (d, J_{HH} = 13.3 Hz, 1 H, NCH_2), 7.43 (d, J_{HH} = 13.6 Hz, 1 H, NCH_2), 7.46 – 7.34 (m, 4 H, Ph), 7.13 – 7.02 (m, 6 H, Ph), 5.34 (br., 2 H, COD CH), 4.24 (m, 1 H, CH), 4.01 – 3.97 (br., 3 H, CH), 3.86, 3.81, 3.74, 3.70 (4 m, 4 × 1 H, CH), 3.69 (d, J_{HH} = 13.3 Hz, 1 H, NCH_2), 3.67 – 3.60 (br., 1 H, CH), 3.02 (d, J_{HH} = 13.6 Hz, 1 H, NCH_2), 2.62 – 2.52 (m, 1 H) , 2.34 – 2.22 (m, 3 H, COD CH_2), 2.10 – 2.02 (br, 1 H, COD CH_2), 1.90 – 1.75 (m, 3 H, COD CH_2), 1.29, 1.18 ppm (2 s, 2 × 9 H, CMe_3).

$^{13}C\{^1H\}$ NMR (101 MHz, C_6D_6): δ = 229.8 (d, $^1J_{CRh}$ = 48.4 Hz, N_2C), 138.1 (d, J_{CP} = 10.6 Hz, phenyl C_{ipso}), 136.8 (d, $^1J_{CP}$ = 10.8 Hz, phenyl C_{ipso}), 134.7 (d, J_{CP} = 20.4 Hz, phenyl CH), 134.1 (d, J_{CP} = 19.1 Hz, phenyl CH), 129.5, 129.1 (2 × phenyl CH), 128.8 (d, J_{CP} = 7.2 Hz, phenyl CH), 128.5 (d, J_{CP} = 6.8 Hz, phenyl CH), 103.6 (d, $^2J_{CP}$ = 23.5 Hz, $C_{ipso}N$), 99.8 ($C_{ipso}N$), 94.6 (d, J_{CRh} = 7.3 Hz, COD CH), 93.9 (d, J_{CRh} = 7.5 Hz, COD CH), 75.6 (d, J_{CP} = 3.5 Hz, cyclopentadienyl CH), 75.5 (d, $^1J_{CP}$ = 11.9 Hz. cyclopentadienyl $C_{ipso}P$), 73.7 (d, J_{CP} = 8.0 Hz, cyclopentadienyl CH), 72.4, (cyclopentadienyl CH), 72.0 (NCH_2), 71.9, (m, COD CH), 71.5 (d, J_{CP} = 2.3 Hz), 71.4 (2 × cyclopentadienyl CH), 71.1 – 71.9 (m, COD CH), 70.6 (NCH_2) 70.2, 68.1 (2 × cyclopentadienyl CH), 33.6, 33.2 (2 × COD CH_2), 33.1, 32.5 (2 × $\mathit{C}Me_3$), 29.9 (COD CH_2), 29.7, 29.6 (2× $C\mathit{Me}_3$), 29.2 (COD CH_2) ppm.

$^{31}P\{^1H\}$ NMR (202 MHz, C_6D_6): δ = –28.0 ppm.

Synthesis of 10a

NEt_3 (99 mg, 0.98 mmol) and Me_3SiCl (109 mg, 1.00 mmol) were added sequentially to a stirred solution of **1a** (140 mg, 0.49 mmol) in dichloromethane (2 mL) at –40 °C bath temperature. The cooling bath was removed and the mixture was stirred for 5 h. Volatile components were removed under vacuum. *n*-Hexane (5 mL) was added to the residue. Insoluble material was removed by filtration through a short Celite pad and was subsequently washed with *n*-hexane (2 × 2 mL). The filtrate and washing solutions were combined. The solvent was removed under vacuum, affording the product as a light orange oil. Yield 177 mg

(84 %). Satisfactory microanalytical data could not be obtained due to the oily nature of the compound.

^{1}H NMR (400 MHz, C_6D_6): δ = 4.14, 3.91, 3.81 (3 br., 3 × 1 H, cyclopentadienyl H), 3.77 (br. 3 H, cyclopentadienyl H), 3.74 (br., 1 H, cyclopentadienyl H), 2.28, 2.03 (2 br., 2 × 1H, NH), 0.33, 0.17, 0.14 ppm (3 s, 3 × 9 H, $SiMe_3$).

^{13}C{^{1}H} NMR (101 MHz, C_6D_6): δ = 109.2, 105.1 (2 × C_{ipso}N), 69.6, 68.3, 65.7, 65.3, 64.3, 61.6 (6 × cyclopentadienyl CH), 59.2 (C_{ipso}Si), 59.0 (cyclopentadienyl CH), 0.1 (two closely spaced signals), 0.0 ppm (3 × $SiMe_3$).

Synthesis of 10b

NEt_3 (257 mg, 2.54 mmol) and Me_3SiCl (277 mg, 2.55 mmol) were added sequentially to a stirred solution of **1b** (500 mg, 1.25 mmol) in dichloromethane (20 mL) at –40 °C bath temperature. The cooling bath was removed and the mixture was stirred for 3 h. Volatile components were removed under vacuum. *n*-Hexane (10 mL) was added to the residue. Insoluble material was removed by filtration through a short Celite pad and was subsequently washed with hexane (2 × 5 mL). The filtrate and washing solutions were combined. The solvent was removed under vacuum, affording the product as a bright orange oil. Yield 530 mg (78 %). Satisfactory microanalytical data could not be obtained due to the oily nature of the compound.

^{1}H NMR (400 MHz, C_6D_6): δ = 7.77 – 7.70, 7.46 – 7.35 (2 m, 2 × 2 H, Ph), 7.13 – 6.94 (m, 6 H, Ph), 4.24, 4.01, 3.87, 3.79 (4 m, 4 × 1 H, cyclopentadienyl H), 3.71 (m, 2 H, cyclopentadienyl H), 3.65 (m, 1 H, cyclopentadienyl H), 2.99 (d, J_{HP} = 5.0 Hz, NH), 1.81, (s, 1 H, NH), 1.11, 1.10 ppm (2 s, 2 × 9 H, $SiMe_3$).

^{13}C{^{1}H} NMR (101 MHz, C_6D_6): δ = 140.9 (d, $^1J_{CP}$ = 9.5 Hz, phenyl C_{ipso}P), 138.5 (d, $^1J_{CP}$ = 6.8 Hz, phenyl C_{ipso}P), 135.9 (d, J_{CP} = 21.1 Hz, phenyl CH), 132.5 (d, J_{CP} = 17.0 Hz, phenyl CH), 129.3 (d, J_{CP} = 1.1 Hz, phenyl CH), 128.5, 128.4, 128.4 (3 × phenyl CH), 111.7 (d, $^2J_{CP}$ = 23.2 Hz, C_{ipso}N), 106.7 (C_{ipso}N), 68.1 (d, J_{CP} = 1.5 Hz, cyclopentadienyl CH), 67.2 (d, J_{CP} = 1.4 Hz, cyclopentadienyl CH), 66.5, 66.2, (2 × cyclopentadienyl CH), 63.1 (d, J_{CP} = 2.0 Hz, cyclopentadienyl C_{ipso}P), 62.8 (d, J_{CP} = 2.9 Hz, cyclopentadienyl CH), 61.5 (d, J_{CP} = 1.0 Hz, cyclopentadienyl CH), 60.5 (cyclopentadienyl CH), 0.4, 0.3 ppm (2 × $SiMe_3$).

^{29}Si{^{1}H} NMR (99 MHz, C_6D_6): δ = 2.9, 2.0 ppm.

^{31}P{^{1}H} NMR (202 MHz, C_6D_6): δ = –25.4 ppm.

Synthesis of 11

$LiN(SiMe_3)_2$ (1.32 g, 7.91 mmol) was added to a solution of **10b** (2.051 g, 3.77 mmol) in toluene (6 mL). The solution was stirred for 15 min and was subsequently stored for 5 h at room temperature, during which time the product started to crystallize. *n*-Hexane (2 mL) was added and the flask was stored at –40 °C for 16 h. The cold mother liquor was separated from the crystalline product with a pipette and the product was dried under vacuum. Yield 1.679 g (78 %). NMR spectroscopic data indicate the presence of different aggregates in solution. The data given below refer to the main component.

$C_{28}H_{35}FeLi_2N_2PSi_2 \cdot C_7H_8$ (648.61): calcd. C 77.18, H 7.61, N 4.50 %; found C 76.21, H 7.78, N 4.12 %.

^1H NMR (500 MHz, C_6D_6): δ = 7.82, 7.48, 7.18 – 7.06 (3 m, 10 H, Ph), 4.02 (m, 2 H, cyclopentadienyl H), 3.99, 3.88 (2 m, 2 × 1 H, cyclopentadienyl H), 3.73 (m, 2 H, cyclopentadienyl H), 3.67 (m, 1 H, cyclopentadienyl H), 0.51, 0.04 ppm (2 s, 2 × 9 H, $SiMe_3$).

$^{13}C\{^1H\}$ NMR (101 MHz, C_6D_6): δ = 138.3 (d, $^1J_{CP}$ = 1.7 Hz, phenyl C_{ipso}), 136.4 (d, $^1J_{CP}$ = 7.8 Hz, phenyl C_{ipso}), 134.7 (d, J_{CP} = 16.5 Hz, phenyl CH), 133.3 (d, J_{CP} = 16.5 Hz, phenyl CH), 129.3, 129.0, 128.6, 128.6 (4 × phenyl CH), 121.1 (d, $^2J_{CP}$ = 27.7 Hz, cyclopentadienyl $C_{ipso}N$), 117.9 ($C_{ipso}N$), 71.1 (d, J_{CP} = 3.3 Hz, cyclopentadienyl CH), 67.6 (cyclopentadienyl CH), 67.2 (d, J_{CP} = 3.4 Hz, cyclopentadienyl CH), 66.6 (d, J_{CP} = 2.7 Hz, cyclopentadienyl CH), 66.4 (d, $^1J_{CP}$ = 20.8 Hz, cyclopentadienyl $C_{ipso}P$), 65.9 (cyclopentadienyl CH), 64.3 (d, J_{CP} = 1.6 Hz, cyclopentadienyl CH), 60.7 (cyclopentadienyl CH), 3.9 (d, J_{CP} = 5.8 Hz), 2.6 ppm (2 × $SiMe_3$).

^7Li NMR (194 MHz, C_6D_6): δ = 2.6 (br., main signal), 2.0, 1.0, 0.2, –0.6 ppm (4 × br.).

$^{31}P\{^1H\}$ NMR (202 MHz, C_6D_6): δ = 23.5 – 24.1 (m), 25.0 – 26.0 (m) ppm.

Synthesis of 12

$[(Me_3Si)_2N]_2Pb$ (79 mg, 0.15 mmol) was added to a solution of **10a** (65 mg, 0.15 mmol) in C_6D_6 (0.4 mL) contained in an NMR tube. The sample was subjected to NMR spectroscopic analysis after 15 h, which revealed a quantitative reaction.

^1H NMR (400 MHz, C_6D_6): δ = 4.02, 3.90, 3.84, 3.80, 3.78 (5 m, 5 × 1 H, cyclopentadienyl H), 3.77 – 3.73 (m, 2 H, cyclopentadienyl H), 0.34, 0.24, 0.18 ppm (3 s, 3 × 9 H, $SiMe_3$).

$^{13}C\{^1H\}$ NMR (101 MHz, C_6D_6): δ = 120.6, 115.9 (2 × $C_{ipso}N$), 73.5, 72.8, 71.4, 69.9 (4 × cyclopentadienyl CH), 69.6 ($C_{ipso}Si$), 68.0, 65.3, 65.1 (3 × cyclopentadienyl CH), 4.3, 3.3, 2.0 ppm (3 × $SiMe_3$).

The ^{207}Pb NMR signal could not be observed. No spectroscopic changes were detected after several days, indicating that, in contrast to fc[(NSiMe$_3$)$_2$Pb:], plumbylene **12** does not undergo dimerization.

Synthesis of 13

[(Me$_3$Si)$_2$N]$_2$Pb (200 mg, 0.38 mmol) was added to a stirred solution of **10b** (200 mg, 0.37 mmol) in toluene (5 mL). Volatile components were removed under vacuum after 18 h, leaving the product as a brick red solid, which was recrystallized from toluene. Yield 254 mg (92 %).

$C_{28}H_{35}FeN_2PPbSi_2$ (749.79): calcd. C 44.85, H 4.71, N 3.74 %; found C 45.15, H 4.92, N 3.71 %.

^{1}H NMR (400 MHz, C_6D_6): δ = 7.71, 7.30 (2 m, 2 × 2 H, Ph), 7.10 (m, 3 H, Ph), 7.02 (m, 2 H, Ph), 6.92 (m, 1 H, Ph), 4.51, 4.36, 3.84, 3.70, 3.60, 3.54, 3.33, (7 m, 7 × 1 H, cyclopentadienyl H), 0.36, 0.35 ppm (2 s, 2 × 9 H, SiMe$_3$).

^{13}C{^{1}H} NMR (101 MHz, C_6D_6): δ = 138.7 (d, $^1J_{CP}$ = 15.2 Hz, phenyl C$_{ipso}$), 136.6 (d, J_{CP} = 14.1 Hz, phenyl CH), 131.7 (d, J_{CP} = 11.9 Hz, phenyl CH), 131.5 (d, J_{CP} = 2.2 Hz, phenyl CH), 130.3 (d, $^1J_{CP}$ = 27.5 Hz, phenyl C$_{ipso}$), 129.5 (d, J_{CP} = 1.6 Hz, phenyl CH), 129.1 (d, J_{CP} = 10.2 Hz, phenyl CH), 128.7 (d, J_{CP} = 8.3 Hz, phenyl CH), 112.1 (C$_{ipso}$N), 73.4 (cyclopentadienyl CH), 71.0 (d, J_{CP} = 6.0 Hz, cyclopentadienyl CH), 70.6 (d, J_{CP} = 4.5 Hz, cyclopentadienyl CH), 66.9, 66.6 (2 × cyclopentadienyl CH), 65.8 (d, J_{CP} = 3.0 Hz, cyclopentadienyl CH), 63.7 (cyclopentadienyl CH), 62.0 (d, $^1J_{CP}$ = 44.2 Hz, cyclopentadienyl C$_{ipso}$P), 3.3 (d, J_{CP} = 1.8 Hz, SiMe$_3$), 2.9 ppm (d, J_{CP} = 1.4 Hz, SiMe$_3$).

^{29}Si{^{1}H} NMR (99 MHz, C_6D_6): δ = 4.4, 2.3 ppm (d, J_{SiP} = 2.6 Hz).

^{31}P{^{1}H} NMR (202 MHz, C_6D_6): δ = 42.2 ppm ($^1J_{PbP}$ = 1934 Hz).

^{207}Pb NMR (105 MHz, C_6D_6): δ = 3050 ppm ($^1J_{PbP}$ = 1916 Hz).

Synthesis of 14

LiN(SiMe$_3$)$_2$ (223 mg, 133 µmol) was added to a solution of **10b** (360 mg, 66 µmol) in THF (5 mL), resulting in the formation of **11**. The solution was stirred for 3 h. SnCl$_2$ (125 mg, 66 µmol) was added and the mixture was stirred for an additional 5 h. Volatile components were removed under vacuum. The oily residue was taken up in *n*-hexane (10 mL). The solid (LiCl) was filtered off using a filter pipette (Celite). The solution was concentrated under vacuum to a volume of ca. 2 mL and was then stored at –40 °C for 1 week, affording the product as dark orange plates. The cold supernatant was removed with a pipette and the product was dried under vacuum. Yield 338 mg (77 %).

$C_{28}H_{35}FeN_2PSi_2Sn$ (661.30): calcd. C 50.86, H 5.33, N 4.24 %; found C 50.23, H 5.66, N 4.10 %.

^{1}H NMR (400 MHz, C_6D_6): δ= 7.73 (m, 2 H, Ph), 7.29 (m, 2 H, Ph), 7.08 (m, 3 H, Ph), 6.96 (m, 3 H, Ph), 4.62, 4.25, 3.89, 3.79, 3.65, 3.63, 3.30 (7 m, 7 × 1 H, cyclopentadienyl H), 0.42, 0.38 ppm (2 s, 2 × 9 H, $SiMe_3$).

$^{13}C\{^1H\}$ NMR (101 MHz, C_6D_6): δ= 135.9 (d, J_{CP} = 13.1 Hz, phenyl CH), 133.4 (d, $^1J_{CP}$ = 22.6 Hz, phenyl C_{ipso}), 131.7 (br., phenyl CH), 131.6 (d, J_{CP} = 11.6 Hz, phenyl CH), 129.7 (d, J_{CP} = 1.9 Hz, phenyl CH), 129.2 (d, $^1J_{CP}$ = 33.0 Hz, phenyl C_{ipso}P), 129.1 (d, J_{CP} = 10.3 Hz, phenyl CH), 128.8 (d, J_{CP} = 8.8 Hz, phenyl CH), 110.9 (d, J_{CP} = 3.3 Hz, cyclopentadienyl C_{ipso}N), 72.9 (cyclopentadienyl CH), 70.1 (d, J_{CP} = 4.6 Hz, cyclopentadienyl CH), 68.6 (d, J_{CP} = 6.7 Hz, cyclopentadienyl CH), 67.4 (cyclopentadienyl CH), 66.0 (br., cyclopentadienyl CH), 66.0, 64.3 (2 × cyclopentadienyl CH), 58.5 (d, $^1J_{CP}$ = 47.9 Hz, cyclopentadienyl C_{ipso}P), 3.4 (d, J_{CP} = 2.3 Hz, $SiMe_3$), 3.0 ppm (d, J_{CP} = 2.9 Hz, $SiMe_3$). One cyclopentadienyl C_{ipso}N signal was not detected.

$^{31}P\{^1H\}$ NMR (202 MHz, C_6D_6): δ= 10.2 ppm ($^1J_{^{117}SnP}$ = 1360 Hz, $^1J_{^{119}SnP}$ = 1422 Hz).

$^{119}Sn\{^1H\}$ NMR (186 MHz, C_6D_6): δ= 187 ppm ($^1J_{^{119}SnP}$ = 1419 Hz).

Synthesis of 15

$LiN(SiMe_3)_2$ (207 mg, 124 µmol) was added to a solution of **10b** (335 mg, 62 µmol) in toluene (5 mL), resulting in the formation of **11**. The solution was stirred for 3 h. [$GeCl_2$(1,4-dioxane)] (143 mg, 62 µmol) and THF (1 mL) were added and the mixture was stirred for an additional 2 h. Volatile components were removed under vacuum. The oily residue was taken up in *n*-hexane (10 mL). The solid (LiCl) was filtered off using a filter pipette (Celite). The solution was concentrated under vacuum to a volume of ca. 0.5 mL. After crystallisation of the product, the supernatant was removed with a pipette and the crystalline solid dried under vacuum. Yield 235 mg (62 %).

$C_{28}H_{35}FeN_2PSi_2Ge$ (615.22): calcd. C 54.66, H 5.73, N 4.55 %; found C 54.85, H 5.83, N 4.51 %.

^{1}H NMR (400 MHz, C_6D_6): δ= 7.73 (m, 2 H, Ph), 7.33 (m, 2 H, Ph), 7.07 (m, 3 H, Ph), 6.94 (m, 3 H, Ph), 4.58, 4.25, 3.98, 3.82, 3.73, 3.66, 3.20 (7 m, 7 × 1 H, cyclopentadienyl H), 0.46, 0.39 ppm (2 s, 2 × 9 H, $SiMe_3$).

$^{13}C\{^1H\}$ NMR (101 MHz, C_6D_6): δ = 135.4 (d, J_{CP} = 13.2 Hz, phenyl CH), 132.8 (d, $^1J_{CP}$ = 22.1 Hz, phenyl C_{ipso}), 131.7 (d, J_{CP} = 11.6 Hz, phenyl CH), 131.5 (d, J_{CP} = 2.0 Hz, phenyl CH_{para}), 129.7 (br., phenyl CH_{para}), 129.2 (d, J_{CP} = 11.0 Hz, phenyl CH), 128.7 (d, J_{CP} = 9.8 Hz, phenyl CH), 126.2 (d, $^1J_{CP}$ = 41.0 Hz, phenyl C_{ipso}), 108.6 (d, J_{CP} = 5.1 Hz, cyclopentadienyl $C_{ipso}N$), 72.8 (cyclopentadienyl CH), 70.6 (d, J_{CP} = 3.9 Hz, cyclopentadienyl CH), 68.1 (cyclopentadienyl CH), 68.0 (d, J_{CP} = 6.5 Hz, cyclopentadienyl CH), 66.3 (d, J_{CP} = 4.5 Hz, cyclopentadienyl CH), 66.1, 64.9 (2 × cyclopentadienyl CH), 58.3 (d, $^1J_{CP}$ = 46.3 Hz, cyclopentadienyl $C_{ipso}P$), 3.4 (d, J_{CP} = 2.3 Hz, $SiMe_3$), 3.0 ppm (d, J_{CP} = 2.9 Hz, $SiMe_3$). One cyclopentadienyl $C_{ipso}N$ signal was not detected.

$^{31}P\{^1H\}$ NMR (202 MHz, C_6D_6): δ = −14.9 ppm.

B X-Ray Crystallography

For each data collection a single crystal was mounted on a micro-mount and all geometric and intensity data were taken from this sample. Data collections were carried out at 100(2) K. In the case of **5d**, **7b**·C_6H_6, **9a** and **14** this was done with a Stoe IPDS2 diffractometer equipped with a 2-circle goniometer and an area detector by using MoK_α radiation (λ = 0.71073 Å). In all other cases data collection was carried out with a Stoe StadiVari diffractometer equipped with a 4-circle goniometer and a DECTRIS Pilatus 200K detector by using CuK_α radiation (λ = 1.54186 Å), except for **2**, where MoK_α radiation (λ = 0.71073 Å) was used. The data sets were corrected for absorption, Lorentz and polarisation effects. The structures were solved by direct methods (SHELXT) and refined using alternating cycles of least-squares refinements against F^2 (SHELXL2014/7).[S9] C-bonded H atoms were included in the models in calculated positions, heteroatom-bonded H atoms have been found in the difference Fourier lists. All H atoms were treated with the 1.2 fold or 1.5 fold isotropic displacement parameter of their bonding partner. Experimental details for each diffraction experiment are given in Table S1. CCDC 2108485 – 2108495 contain the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

Table S1 X-ray crystallographic details.

	2	[**3**(THF)]$_3$	**1b**·MeOH	**7a**·CH_2Cl_2	**7b**·C_6H_6	**9a**
Chemical formula	$C_{32}H_{50}Fe_2Li_2N_4Pb_2Si_4$	$C_{60}H_{99}Fe_3Li_9N_6O_3Si_6$	$C_{23}H_{25}FeN_2OP$	$C_{25}H_{41}BCl_2F_4FeN_2Si$	$C_{39}H_{46}BF_4FeN_2P$	$C_{32}H_{50}ClFeN_2RhSi$
Formula mass	1143.08	1351.00	432.27	611.25	716.41	685.04
Crystal system	monoclinic	triclinic	orthorhombic	monoclinic	monoclinic	triclinic
Space group	$P2_1/n$	P-1	$Pccn$	$P2_1$	$P2_1/c$	P-1
a /Å	9.0630(4)	12.5721(8)	18.4207(10)	10.3039(3)	22.2413(8)	10.0905(5)
b /Å	12.3037(6)	16.4696(14)	31.6063(12)	12.9444(4)	9.0687(3)	18.0609(9)
c /Å	17.6508(9)	20.0781(16)	7.5560(3)	11.8996(3)	19.5393(7)	18.3689(9)
α /°	90	107.662(6)	90	90	90	96.230(4)
β /°	91.172(4)	94.249(6)	90	108.155(2)	113.594(3)	98.922(4)
γ /°	90	96.501(6)	90	90	90	94.876(4)
V /Å^3	1967.80(16)	3910.0(5)	4399.2(3)	1508.13(8)	3611.6(2)	3269.9(3)
Z	2	2	8	2	4	4
Crystal size /mm	9.402	5.590	6.295	6.379	0.513	1.090
μ /mm^{-1}	1096	1428	1808	640	1504	1432
F(000)	0.15 × 0.11 × 0.09	0.25 × 0.22 × 0.16	0.35 × 0.14 × 0.03	0.20 × 0.13 × 0.06	0.10 × 0.07 × 0.04	0.15 × 0.08 × 0.01
Absorption correction	multi-scan	multi-scan	multi-scan	multi-scan	integration	multi-scan
$T_{\min}$ / $T_{\max}$	0.1364 / 0.2281	0.1202 / 0.4053	0.2392 / 1.0000	0.1016 / 0.6309	0.9473 / 0.9857	0.5078 / 0.9662
θ range /°	2.018 – 27.491	3.562 – 71.010	2.796 – 70.628	3.909 – 70.903	2.086 – 26.498	2.054 – 26.847
No. of reflections measured	9066	29514	9188	14649	16456	25921
Independent reflections [R_{int}]	4489 [0.0281]	14270 [0.0248]	3994 [0.0248]	5387 [0.0154]	7453 [0.1093]	13789 [0.0641]
Parameters	214	794	261	334	439	703
Final R_1 (wR_2) [$I > 2\sigma(I)$]	0.0245 (0.0584)	0.0699 (0.1799)	0.0502 (0.1291)	0.0287 (0.0749)	0.0896 (0.1793)	0.0543 (0.1363)
Final R_1 (wR_2) [all data]	0.0311 (0.0616)	0.0769 (0.1860)	0.0620 (0.1387)	0.0298 (0.0757)	0.1679 (0.2377)	0.0891 (0.1573)
Goodness of fit	1.035	1.037	1.060	1.041	1.180	1.102
Residual electron density /eÅ^{-3}	–1.199 / 1.561	–1.338 / 1.924	–0.503 / 0.543	–0.371 / 0.519	–0.448 / 0.732	–1.193 / 1.597
CCDC number	2108485	2108486	2108487	2108488	2108489	2108490

Table S1 (continued) X-ray crystallographic details.

	9b·2 MeOH	**13**	**14**	**15**	**5d**
Chemical formula	$C_{43}H_{59}ClFeN_2O_2PRh$	$C_{28}H_{35}FeN_2PPbSi_2$	$C_{28}H_{35}FeN_2PSi_2Sn$	$C_{28}H_{35}FeGeN_2PSi_2$	$C_{24}H_{19}FeIN_2$
Formula mass	861.10	749.77	661.27	615.19	518.16
Crystal system	triclinic	triclinic	monoclinic	monoclinic	triclinic
Space group	P-1	P-1	$P2_1/n$	$P2_1/n$	P-1
a /Å	12.726(2)	10.3749(9)	14.6357(8)	14.8150(5)	11.3314(5)
b /Å	12.903(3)	11.2394(14)	10.9872(4)	11.1150(2)	13.1595(6)
c /Å	13.744(2)	15.5017(12)	18.1148(10)	18.0884(6)	14.7468(7)
α /°	107.385(14)	106.545(8)	90	90	109.107(4)
β /°	90.842(13)	93.996(7)	104.104(4)	104.095(3)	100.846(4)
γ /°	106.663(15)	108.683(8)	90	90	98.487(4)
V /Å^3	2050.9(7)	1615.5(3)	2825.1(2)	2888.92(15)	1988.20(17)
Z	2	2	4	4	4
Crystal size /mm	7.341	14.919	1.559	6.770	2.323
μ /mm^{-1}	900	736	1344	1272.0	1024.0
F(000)	0.15 × 0.11 × 0.05	0.18 × 0.12 × 0.03	0.19 × 0.12 × 0.07	0.15 × 0.12 × 0.09	0.30 × 0.15 × 0.06
Absorption correction	multi-scan	multi-scan	multi-scan	multi-scan	multi-scan
T_{min} / T_{max}	0.1503 / 0.6416	0.0774 / 0.5610	0.7251 / 0.9142	0.1383 / 0.5590	0.4294 / 0.8619
θ range /°	3.648 – 70.832	4.391 – 70.923	1.610 – 25.685	4.710 – 69.495	1.511 – 25.702
No. of reflections measured	15206	13110	13349	13583	14234
Independent reflections [R_{int}]	7424 [0.0467]	5933 [0.0165]	5295 [0.0263]	5299 [0.0188]	7467 [0.0220]
Parameters	470	322	322	316	505
Final R_1 (wR_2) [$I > 2\sigma(I)$]	0.0587 (0.1533)	0.0211 (0.0542)	0.0292 (0.0699)	0.0309 (0.0820)	0.0267 (0.0673)
Final R_1 (wR_2) [all data]	0.0728 (0.1657)	0.0226 (0.0549)	0.0398 (0.0822)	0.0331 (0.0838)	0.0311 (0.0686)
Goodness of fit	1.029	1.053	1.113	1.057	1.076
Residual electron density /eÅ^{-3}	–0.768 / 1.462	–0.979 / 1.110	–0.775 / 0.686	–0.657 / 0.426	–0.490 / 0.825
CCDC number	2108491	2108492	2108493	2108494	2108495

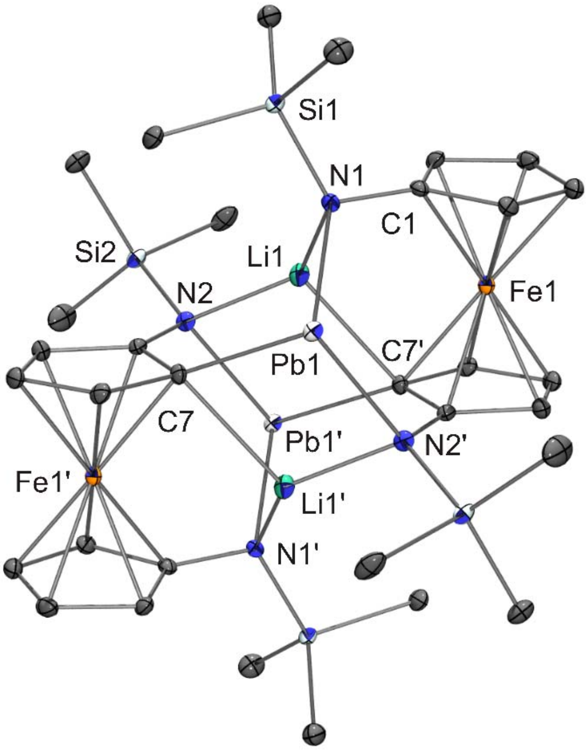

Fig. S1 Solid state molecular structure of **2** (ORTEP with 30 % probability ellipsoids). H atoms have been omitted for clarity. Selected interatomic distances [Å] and angles [°]: C1–N1 1.428(4), C7–Pb1 2.366(4), C7–Li1 2.351(7), N1–Si1 1.743(3), N1–Pb1 2.316(3), N1–Li1 1.972(7), N2–Si2 1.743(3), N2–Pb1 2.383(3), N2–Li1 1.978(7), Li1–Pb1 3.094(6), Li1–Pb1’ 2.964(7); N2–Pb1–C7 91.52(11), N1–Pb1–C7 90.66(12), N1–Pb1–N2 100.70(10).

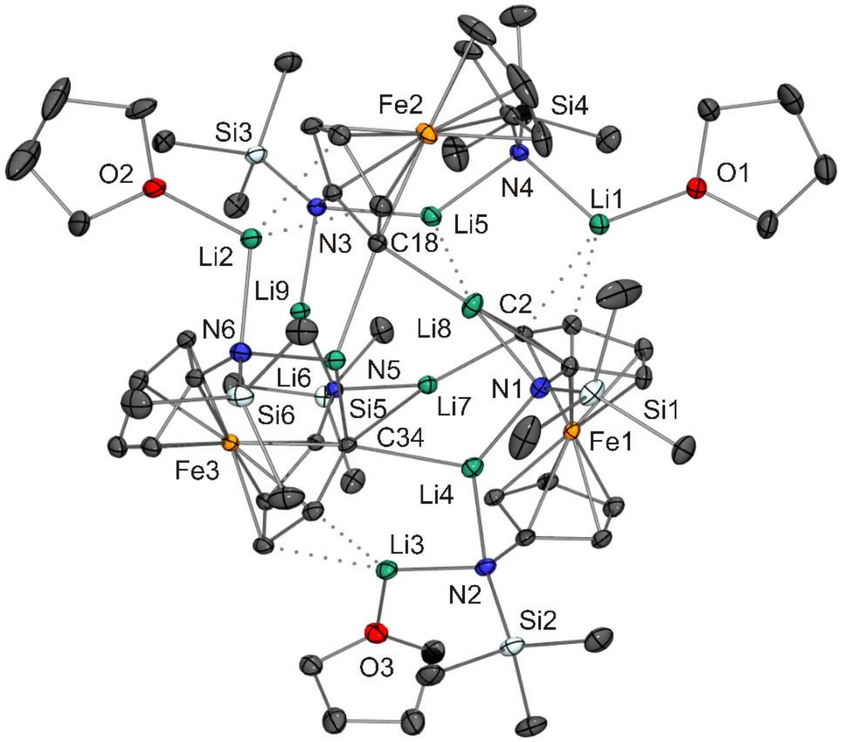

Fig. S2 Solid state molecular structure of $[\mathbf{3}(\mathrm{THF})]_3$ (ORTEP with 30 % probability ellipsoids). H atoms have been omitted for clarity. Selected interatomic distances [Å]: N1−Si1 1.694(3), N1−Li4 2.007(9), N1−Li8 1.923(8), N2−Si2 1.705(3), N2−Li3 1.970(9), N2−Li4 1.997(8), N3−Si3 1.709(4), N3−Li5 2.105(8), N3−Li9 1.997(8), N4−Si4 1.696(4), N4−Li1 1.988(9), N4−Li5 2.024(8), N5−Si5 1.709(3), N5−Li7 1.935(8), N5−Li9 1.964(8), N6−Si6 1.706(4), N6−Li6 2.050(8), N6−Li2 1.974(8), O1−Li1 1.934(9), O2−Li2 1.914(8), O3−Li3 1.947(8), C2−Li7 2.077(8), C2−Li8 2.184(9), C18−Li6 2.198(8), C18−Li8 2.066(9), C34−Li4 2.383(8), C34−Li6 2.207(8), C34−Li7 2.308(8). The THF-coordinated Li atoms are involved in cyclopentadienyl π-interactions, with the shortest Li···C contacts lying in the range between ca. 2.19 and 2.43 Å (indicated by dotted lines). The structure contains several short Li···Li contacts ≤ 3.0 Å. The shortest one (Li5···Li8 2.619(11) Å; indicated by a dotted line) is only slightly longer than twice the covalent radius of Li (2.56 Å).[S10]

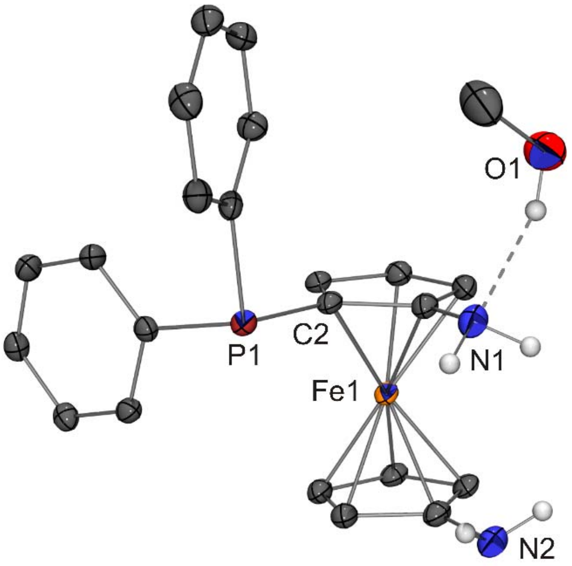

Fig. S3 Solid state molecular structure of **1b**·MeOH (ORTEP with 30 % probability ellipsoids). C-bonded H atoms have been omitted for clarity. The solvent molecule is involved in a hydrogen bond (H1···N1 2.06 Å, O1–H1···N1 145.5°), which is indicated by a dashed line.

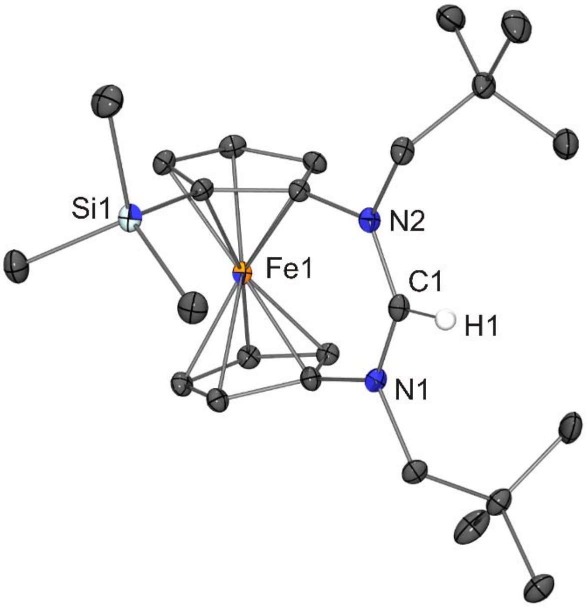

Fig. S4 Solid state molecular structure of the cation of **7a**·CH_2Cl_2 (ORTEP with 30 % probability ellipsoids). The solvent molecule and C-bonded H atoms except that of the cationic N_2CH unit have been omitted for clarity. Selected interatomic distances [Å] and angles [°]: C1–N1 1.317(4), C1–N2 1.330(4); N1–C1–N2 130.7(3).

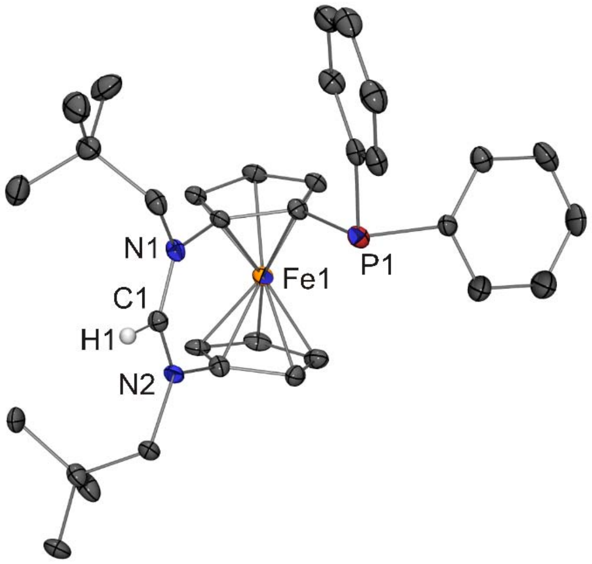

Fig. S5 Solid state molecular structure of the cation of **7b**·C_6H_6 (ORTEP with 30 % probability ellipsoids). The solvent molecule and C-bonded H atoms except that of the cationic N_2CH unit have been omitted for clarity. Selected interatomic distances [Å] and angles [°]: C1–N1 1.318(8), C1–N2 1.303(8); N1–C1–N2 131.3(6).

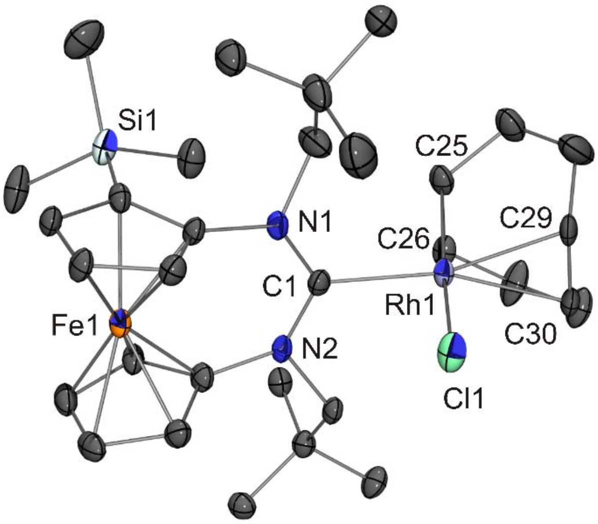

Fig. S6 Solid state molecular structure of **9a** (ORTEP with 30 % probability ellipsoids). H atoms have been omitted for clarity. Only one of the two independent molecules in the asymmetric unit is shown. Selected interatomic distances [Å] and angles [°]: C1–N1 1.356(7), C1–N2 1.355(6), C1–Rh1, 2.072(5), C25–Rh1 2.114(6), C26–Rh1 2.114(5), C29–Rh1 2.192(5), C30–Rh1 2.171(5), Cl1–Rh1 2.3636(14); N1–C1–N2 121.4(4), C1–Rh1–Cl1 84.47(14).

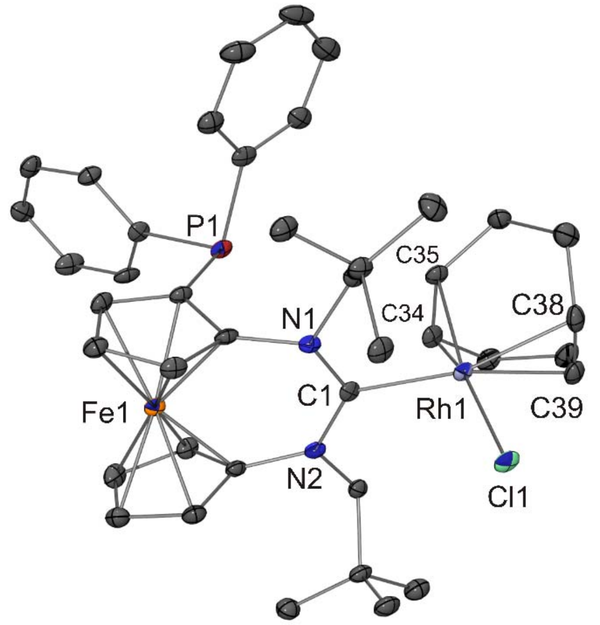

Fig. S7 Solid state molecular structure of **9b**·2 MeOH (ORTEP with 30 % probability ellipsoids). H atoms and solvent molecules have been omitted for clarity. Selected interatomic distances [Å] and angles [°]: C1–N1 1.354(6), C1–N2 1.367(6), C1–Rh1, 2.075(5), C34–Rh1 2.120(5), C35–Rh1 2.132(5), C38–Rh1 2.184(5), C39–Rh1 2.205(5), Cl1–Rh1 2.4045(12); N1–C1–N2 121.4(4), C1–Rh1–Cl1 91.22(12).

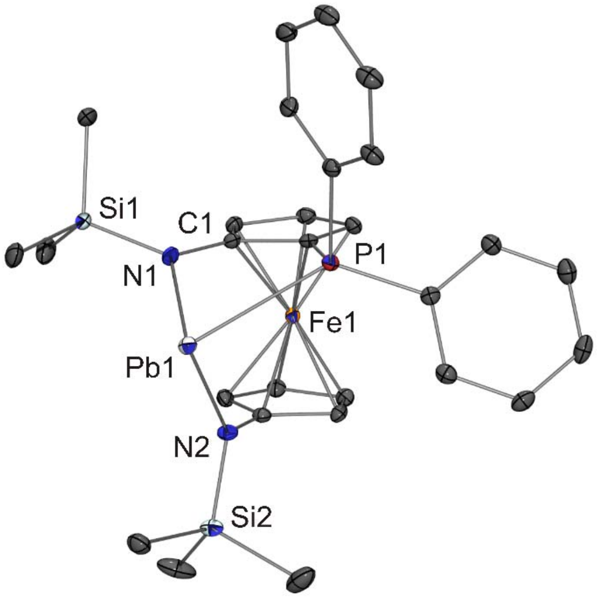

Fig. S8 Solid state molecular structure of **13** (ORTEP with 30 % probability ellipsoids). H atoms and solvent molecules have been omitted for clarity. Selected interatomic distances [Å] and angles [°]: Pb1–P1 2.8624(8), Pb1–N1 2.260(2), Pb1–N2 2.213(2), Si1–N1 1.714(3), Si2–N2 1.722(3); N1–Pb1–P1 73.51(7), N2–Pb1–P1 91.83(7), N2–Pb1–N1 95.32(9).

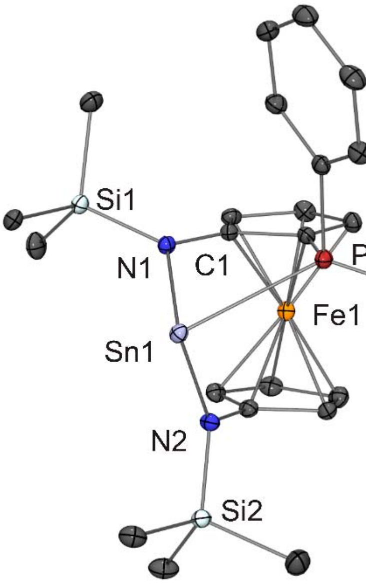

Fig. S9 Solid state molecular structure of **14** (ORTEP with 30 % probability ellipsoids). Selected interatomic distances [Å] and angles [°]: Sn1–P1 2.7526(8), Sn1–N1 2.126(3), Sn1–N2 2.084(3), Si1–N1 1.701(3), Si2–N2 1.708(3); N1–Sn1–P1 74.35(7), N2–Sn1–P1 95.05(7), N2–Sn1–N1 98.11(10).

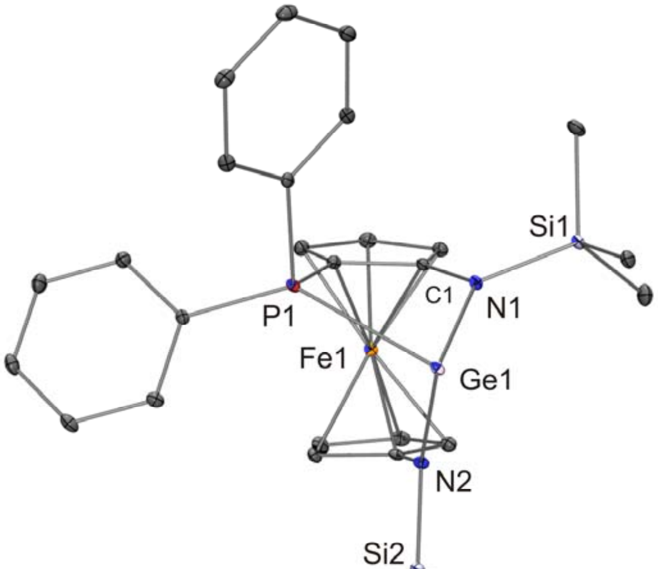

Fig. S10 Solid state molecular structure of **15** (ORTEP with 30 % probability ellipsoids). Selected interatomic distances [Å] and angles [°]: Ge1–P1 2.6497(6), Ge1–N1 1.953(2), Ge1–N2 1.916(2), Si1–N1 1.732(2), Si2–N2 1.745(2); N1–Ge1–P1 77.72(5), N2–Ge1–P1 97.76(6), N2–Sn1–N1 100.69(7).

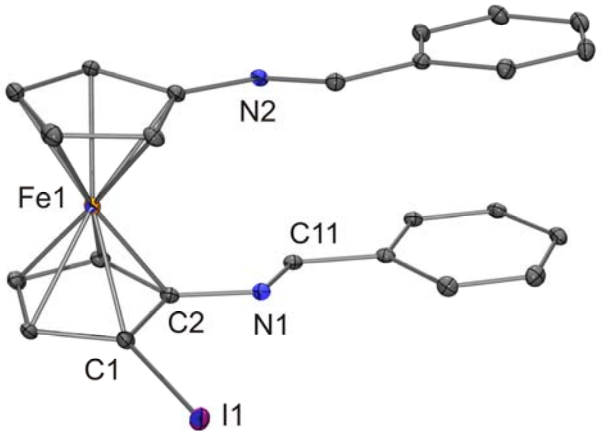

Fig. S11 Solid state molecular structure of **5d** (ORTEP with 30 % probability ellipsoids). Selected interatomic distances [Å] and angles [°]: C1–I1 2.079(3), C2–N1 1.387(4), N2–C6 1.398(4), C11–N1 1.273(4), C18–N2 1.276(4); C2–N1–C11 120.4(3), C6–N2–C18 119.0(3).

C Plots of NMR Spectra

following the order of compounds in Section A

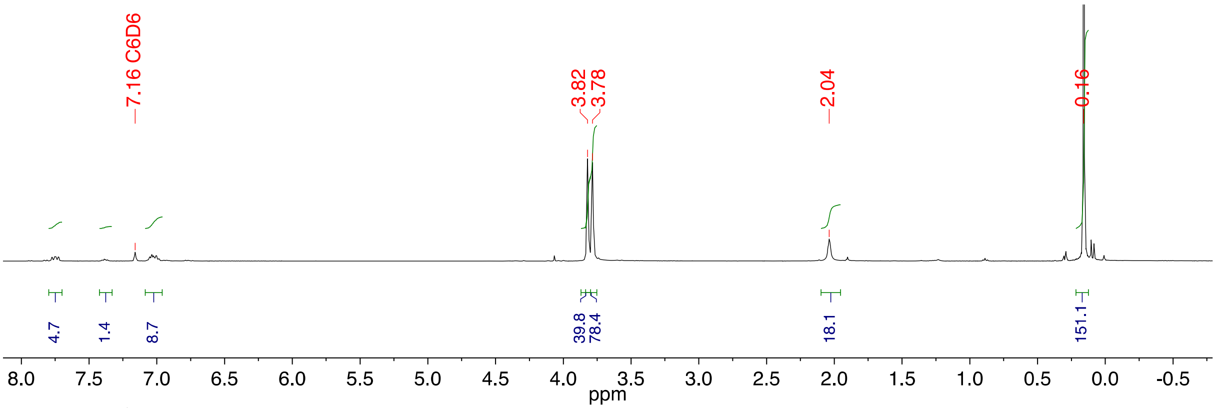

Fig. S12 ^{1}H NMR spectrum (500 MHz, C_6D_6) of crude fc($NHSiMe_3$)$_2$ containing ca. 8% of Ph_3PO.

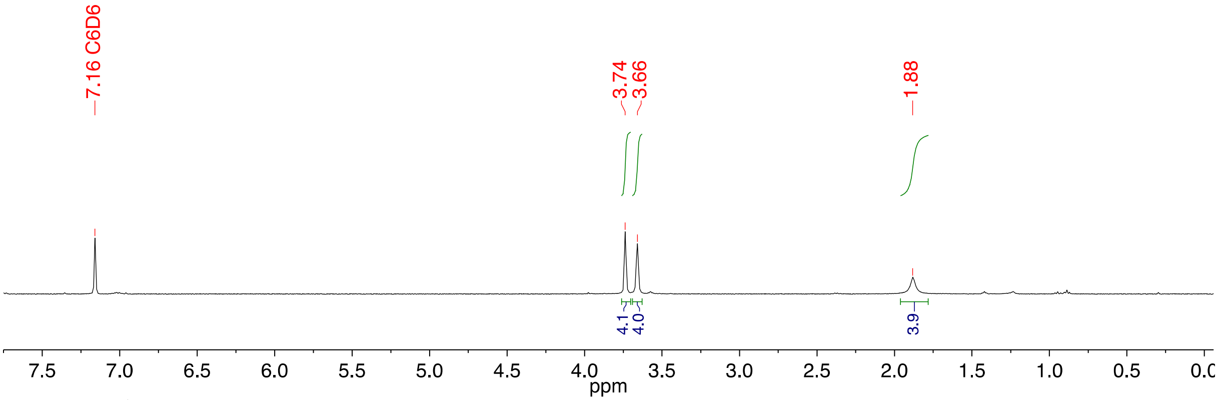

Fig. S13 ^{1}H NMR spectrum (500 MHz, C_6D_6) of fc(NH_2)$_2$ synthesised from fc($NPPh_3$)$_2$ by hydrolysis.

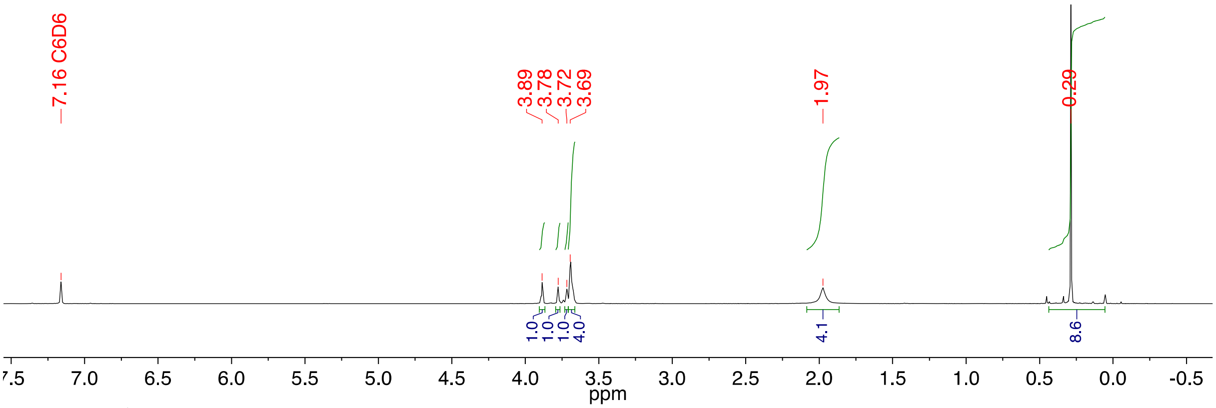

Fig. S14 ^{1}H NMR spectrum (400 MHz, C_6D_6) of **1a**.

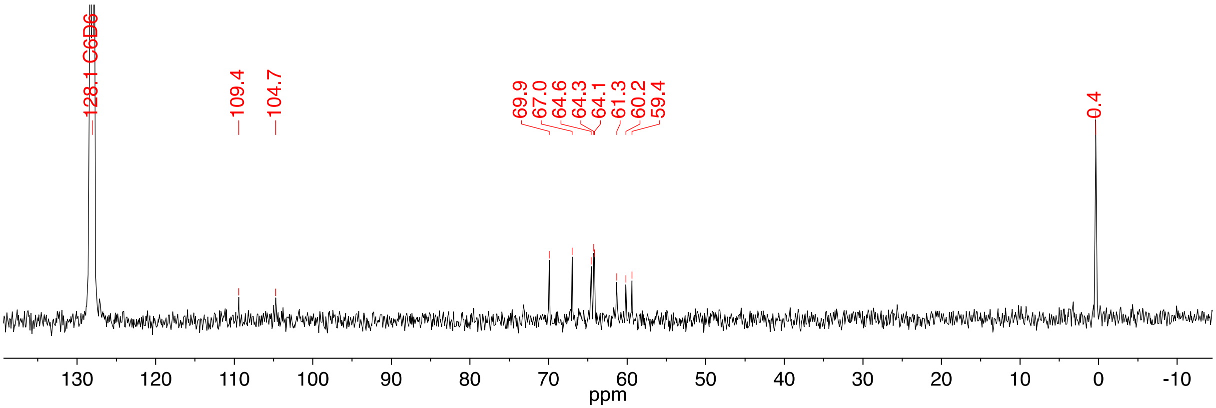

Fig. S15 $^{13}C\{^1H\}$ NMR spectrum (101 MHz, C_6D_6) of **1a**.

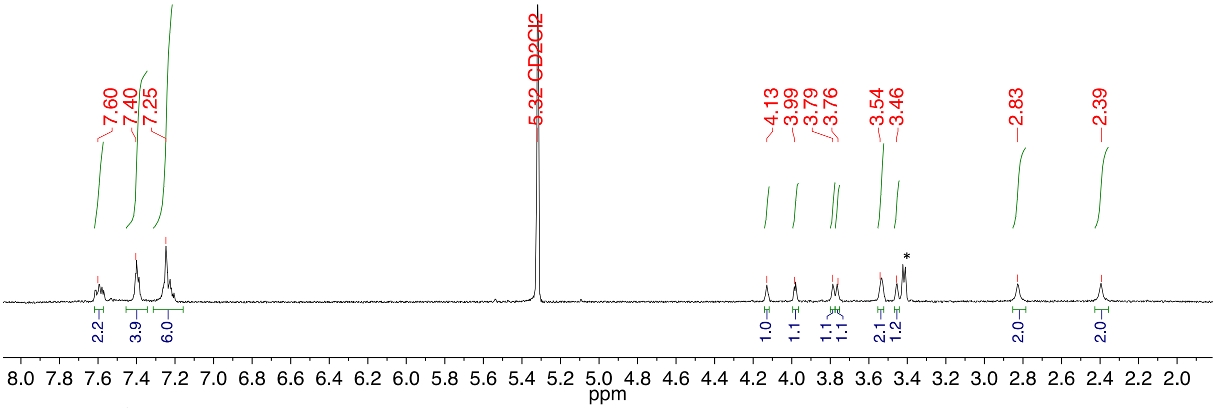

Fig. S16 ^1H NMR spectrum (400 MHz, CD_2Cl_2) of **1b**. The signal marked (*) belongs to trace amounts of methanol.

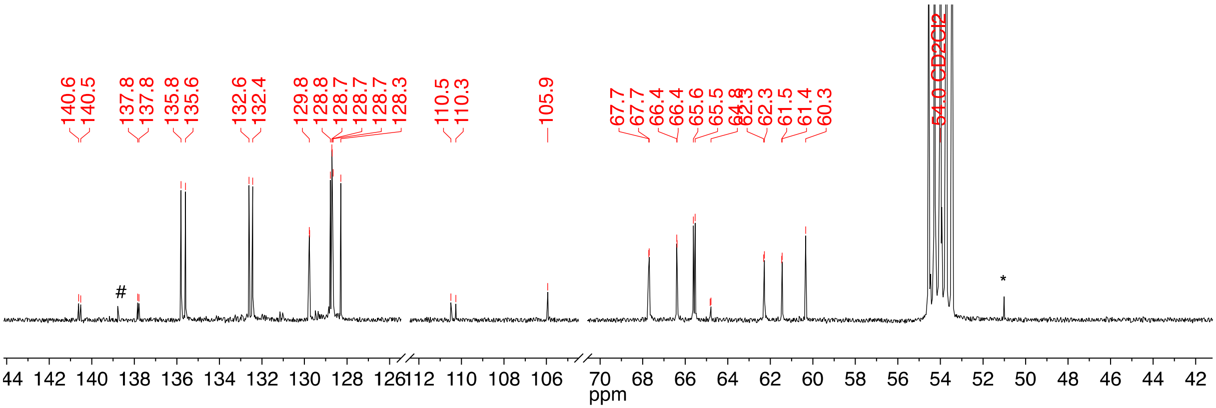

Fig. S17 $^{13}C\{^1H\}$ NMR spectrum (101 MHz, CD_2Cl_2) of **1b**. The signals marked belongs to trace amounts of methanol (*) and an unknown impurity (#).

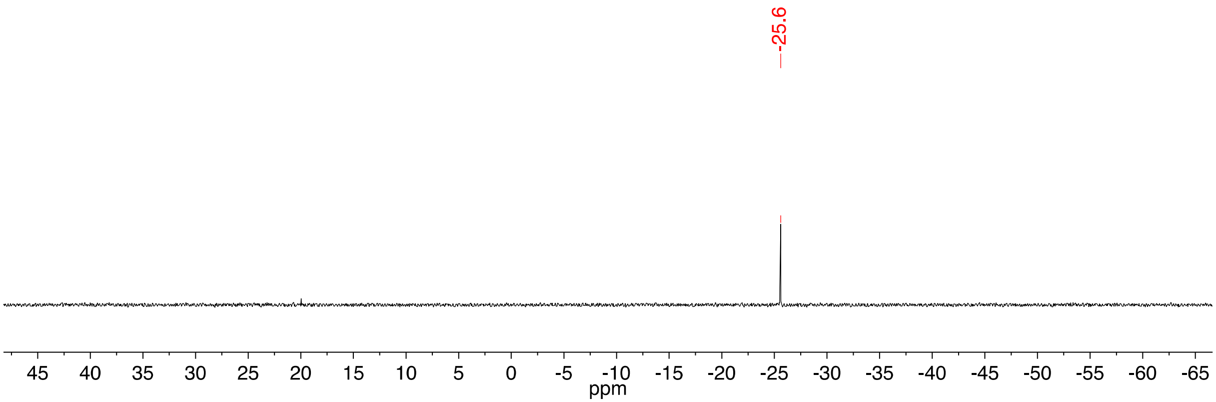

Fig. S18 $^{31}P\{^1H\}$ NMR spectrum (202 MHz, CD_2Cl_2) of **1b**.

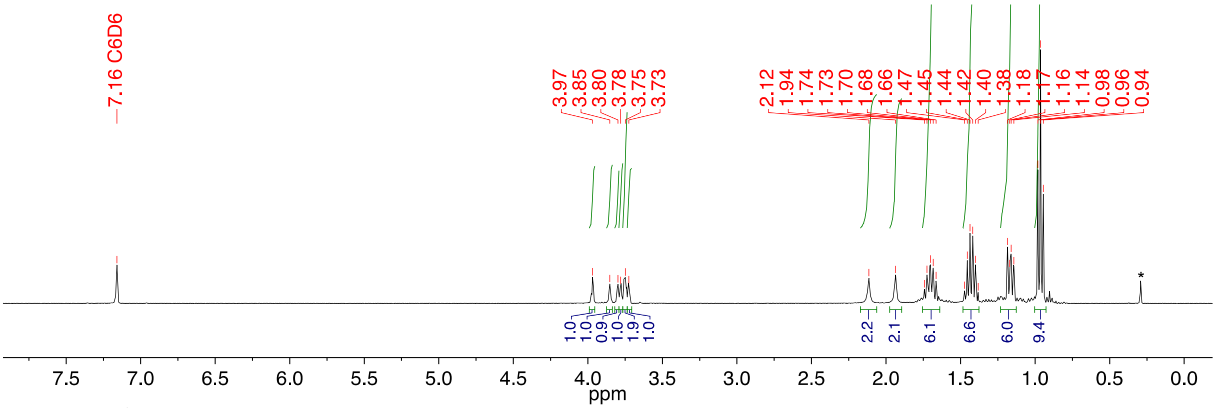

Fig. S19 ^1H NMR spectrum (400 MHz, C_6D_6) of **1c**.

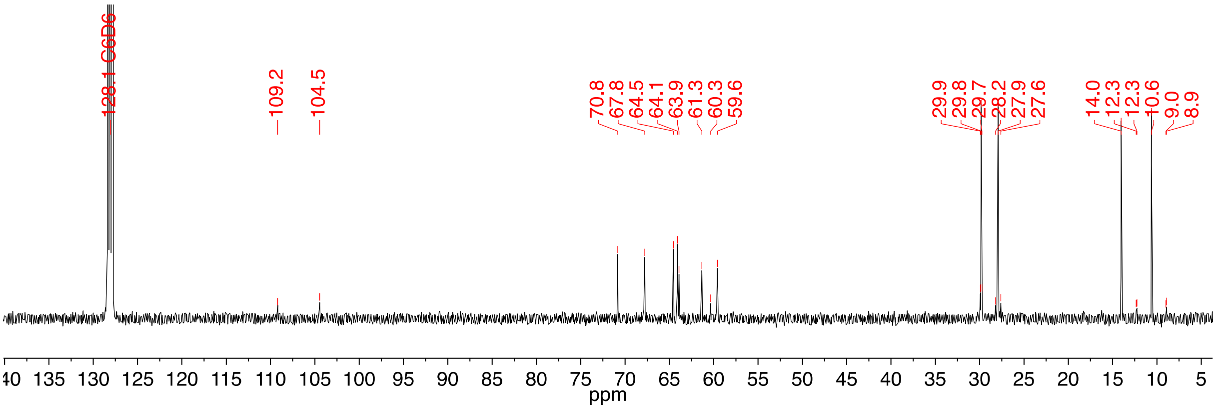

Fig. S20 $^{13}C\{^1H\}$ NMR spectrum (101 MHz, C_6D_6) of **1c**.

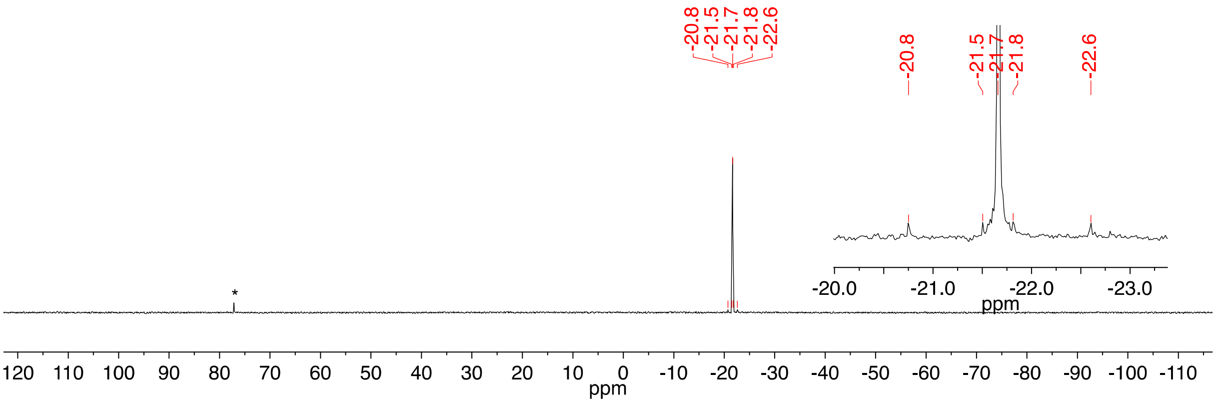

Fig. S21 ^{119}Sn NMR spectrum (186 MHz, C_6D_6) of **1c**. The signal marked (*) belongs to trace amounts of *n*Bu_3SnCl.

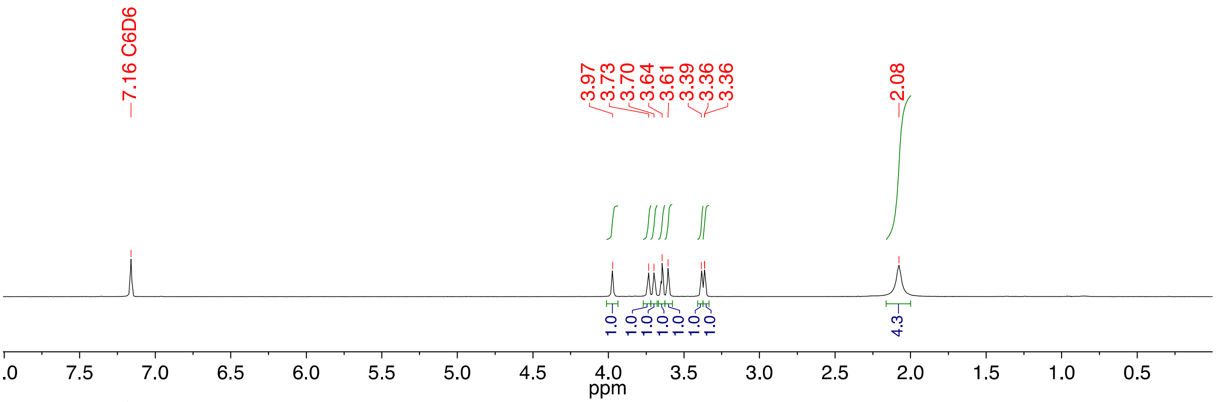

Fig. S22 ^{1}H NMR spectrum (400 MHz, C_6D_6) of **1d**.

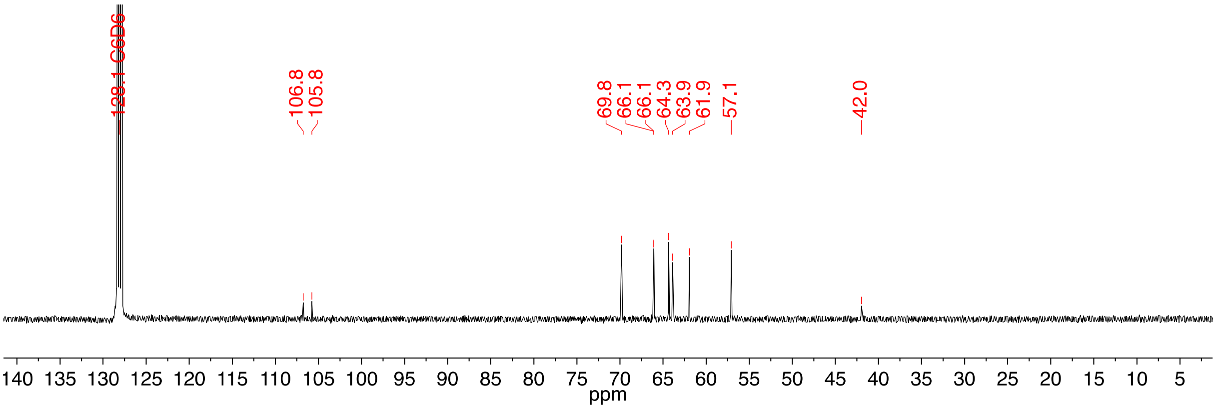

Fig. S23 ^{13}C{^{1}H} NMR spectrum (101 MHz, C_6D_6) of **1d**.

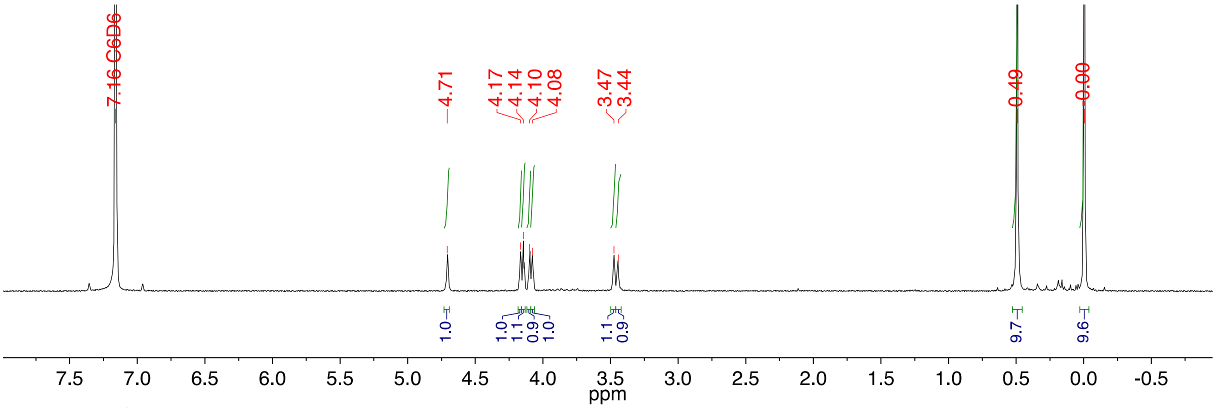

Fig. S24 ^{1}H NMR spectrum (500 MHz, C_6D_6) of **2**.

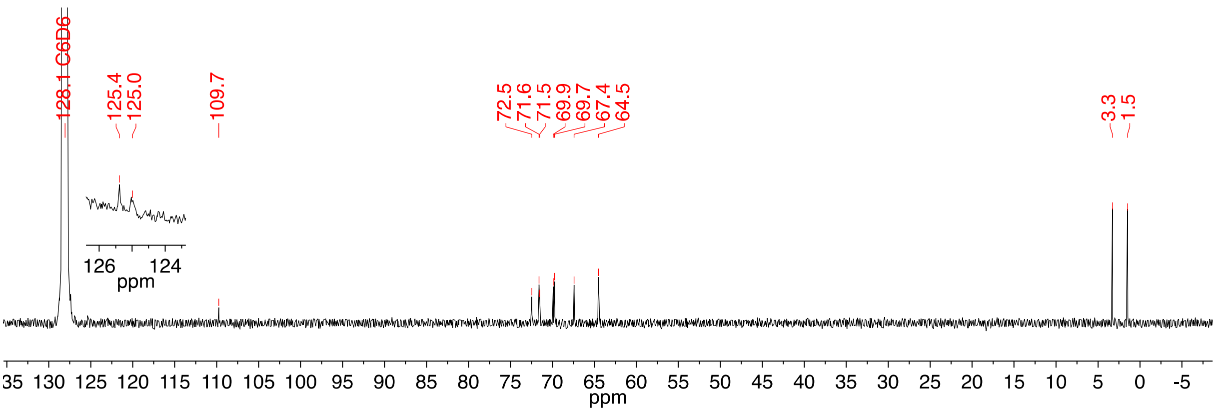

Fig. S25 ^{13}C{^{1}H} NMR spectrum (126 MHz, C_6D_6) of **2**.

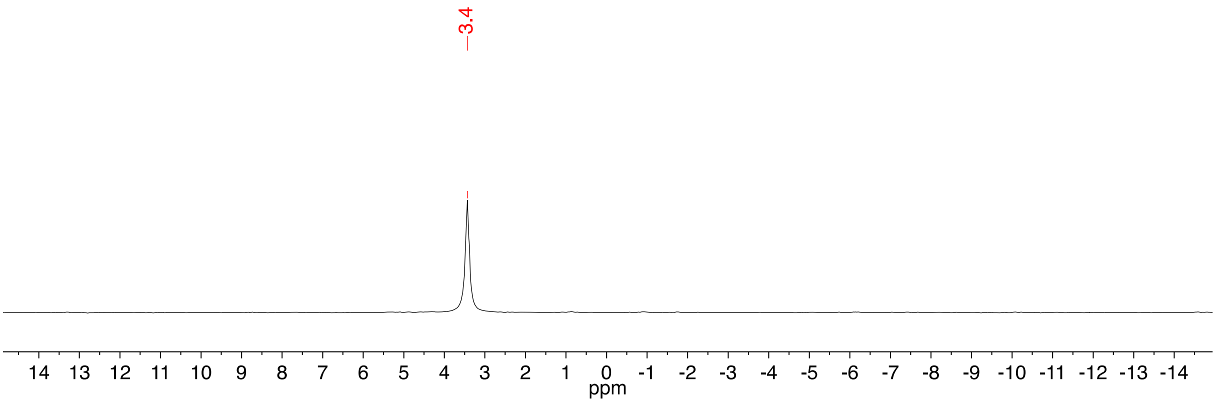

Fig. S26 ^{7}Li NMR spectrum (194 MHz, C_6D_6) of **2**.

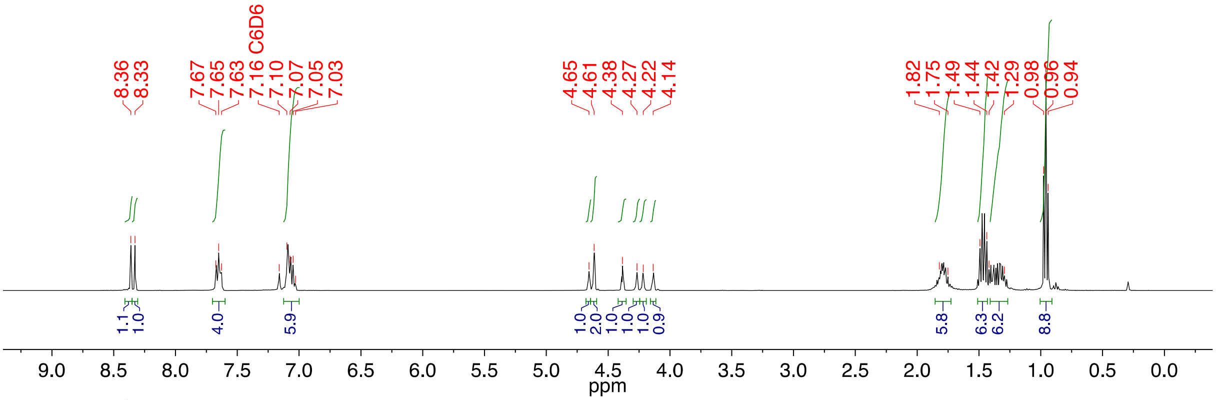

Fig. S27 ^{1}H NMR spectrum (400 MHz, C_6D_6) of **5c**.

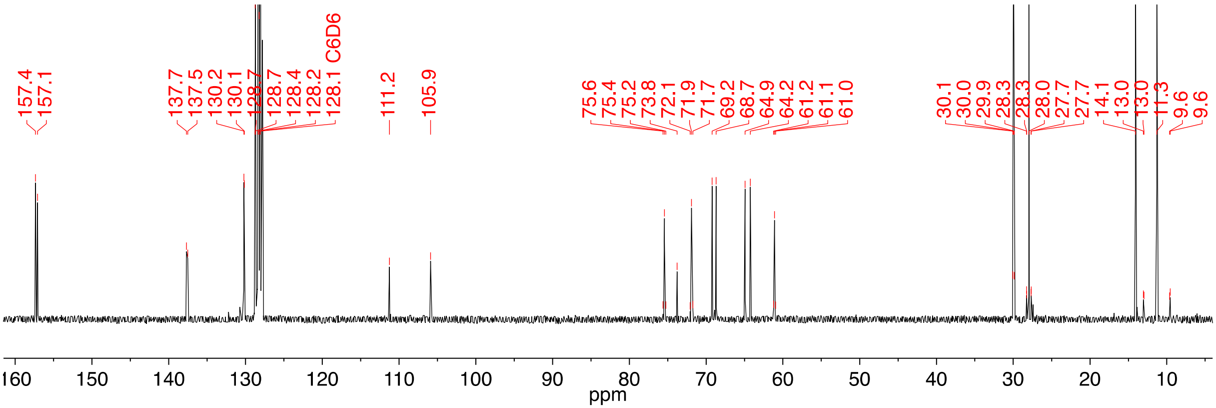

Fig. S28 $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, C_6D_6) of **5c**.

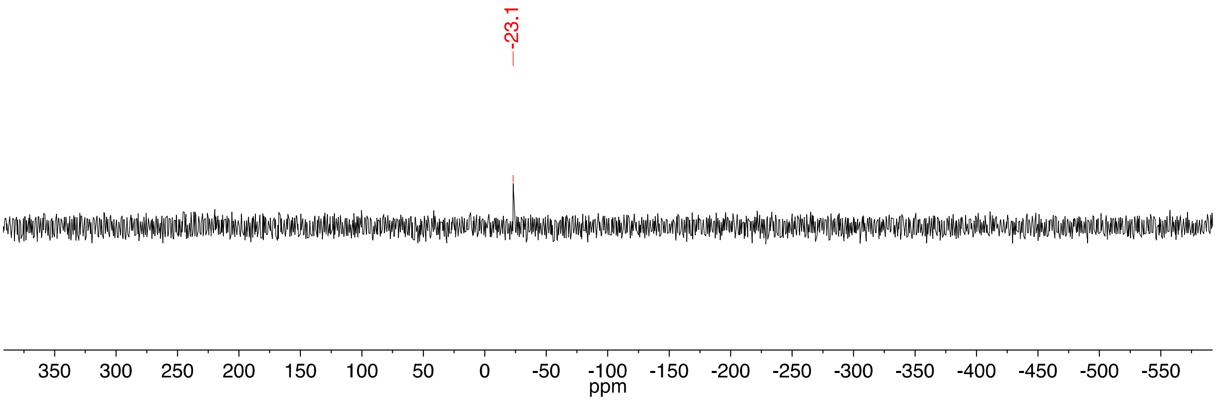

Fig. S29 ^{119}Sn NMR spectrum (186 MHz, C_6D_6) of **5c**.

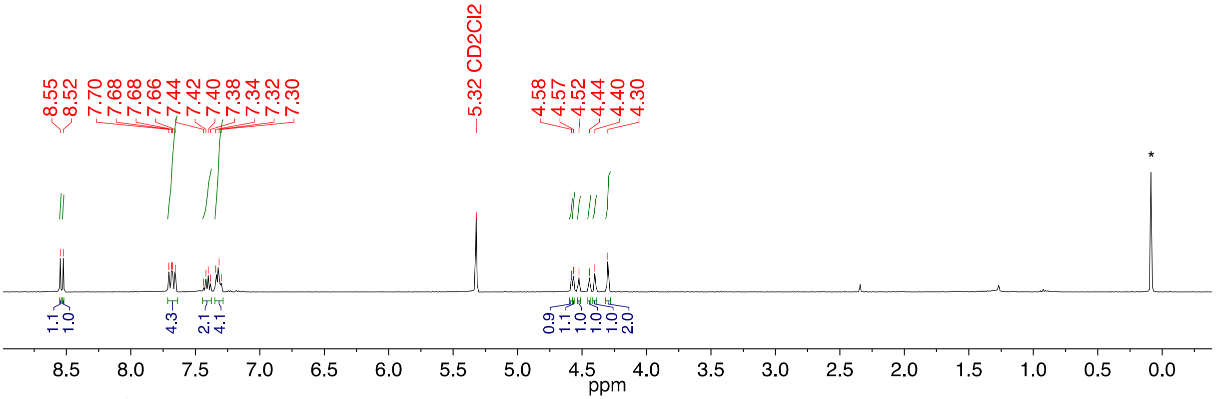

Fig. S30 ^{1}H NMR spectrum (400 MHz, CD_2Cl_2) of **5d**. The signal marked (*) belongs to silicon grease.

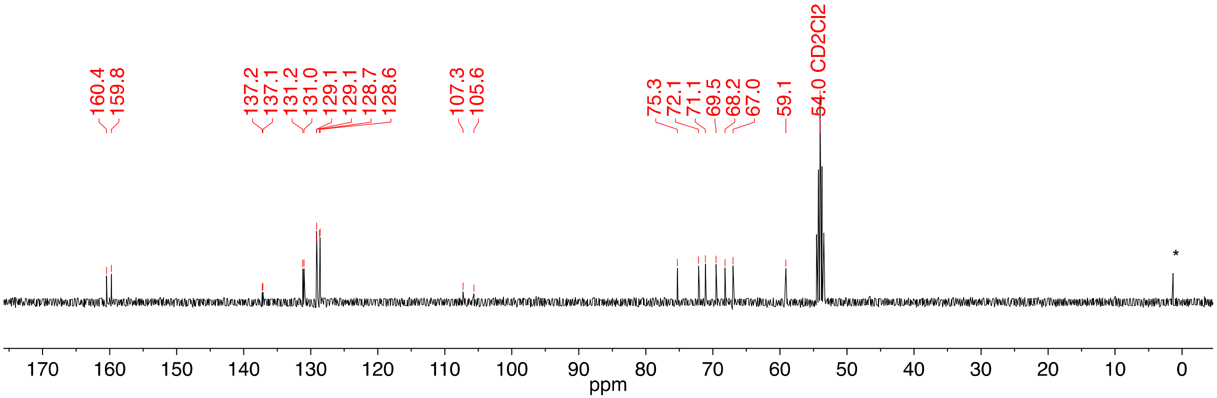

Fig. S31 ^{13}C{^{1}H} NMR spectrum (101 MHz, CD_2Cl_2) of **5d**. The signal marked (*) belongs to silicon grease.

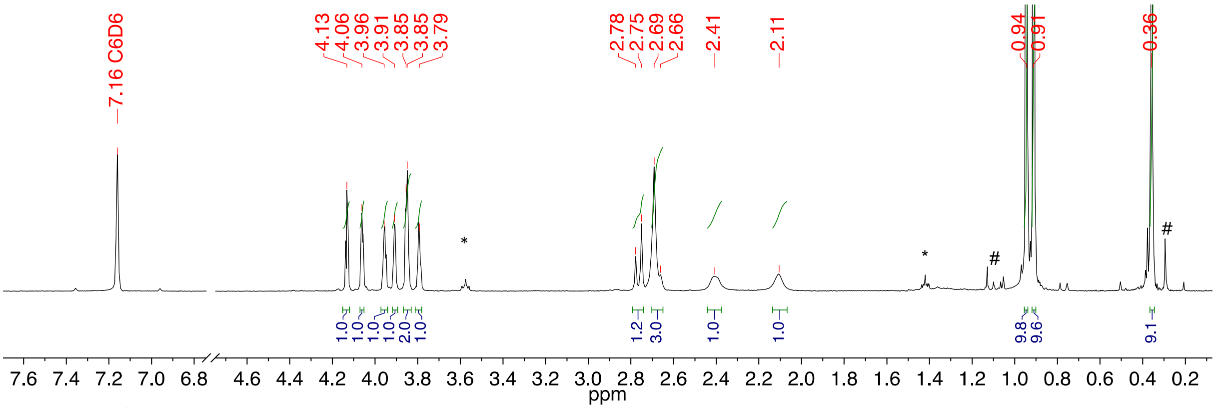

Fig. S32 ^{1}H NMR spectrum (400 MHz, C_6D_6) of **6a.** Signals marked belong to trace amounts of THF (*) and an unknown impurity (#).

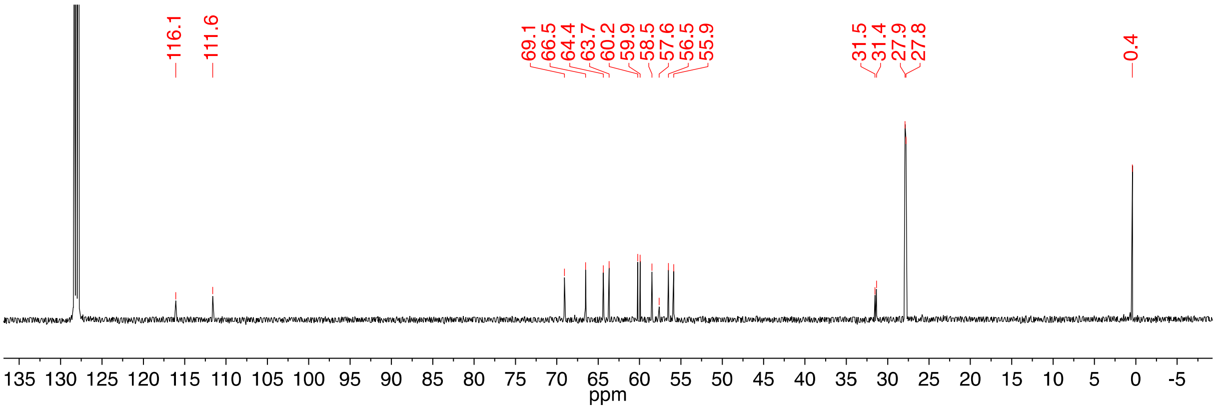

Fig. S33 $^{13}C\{^1H\}$ NMR spectrum (101 MHz, C_6D_6) of **6a**.

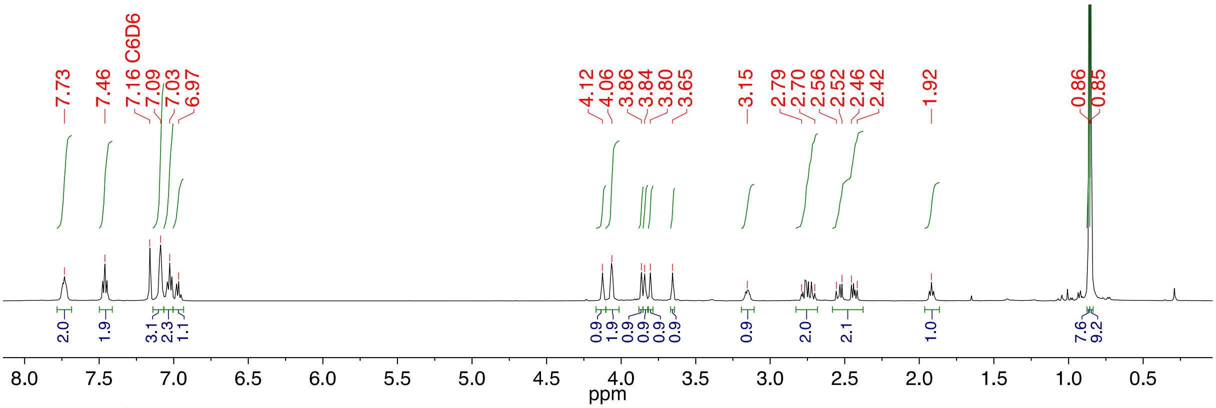

Fig. S34 ^1H NMR spectrum (500 MHz, C_6D_6) of **6b**.

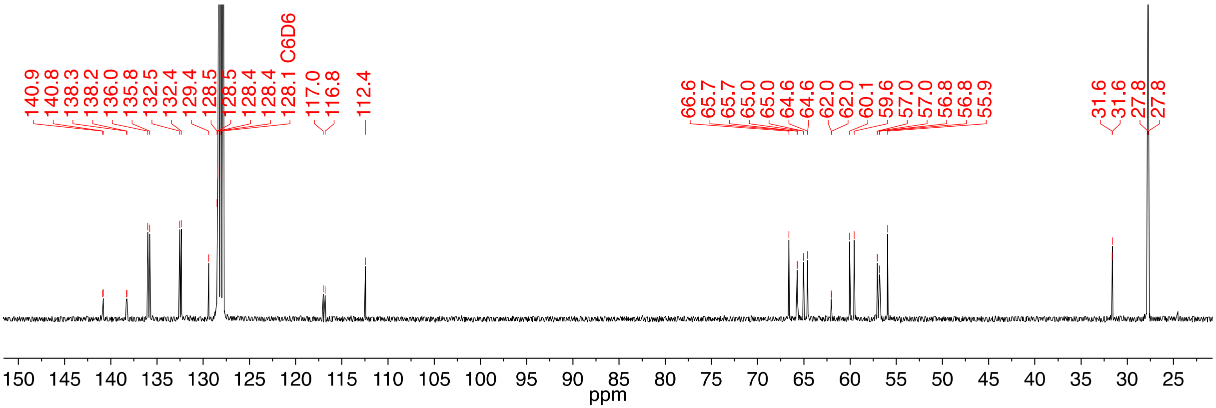

Fig. S35 $^{13}C\{^1H\}$ NMR spectrum (101 MHz, C_6D_6) of **6b**.

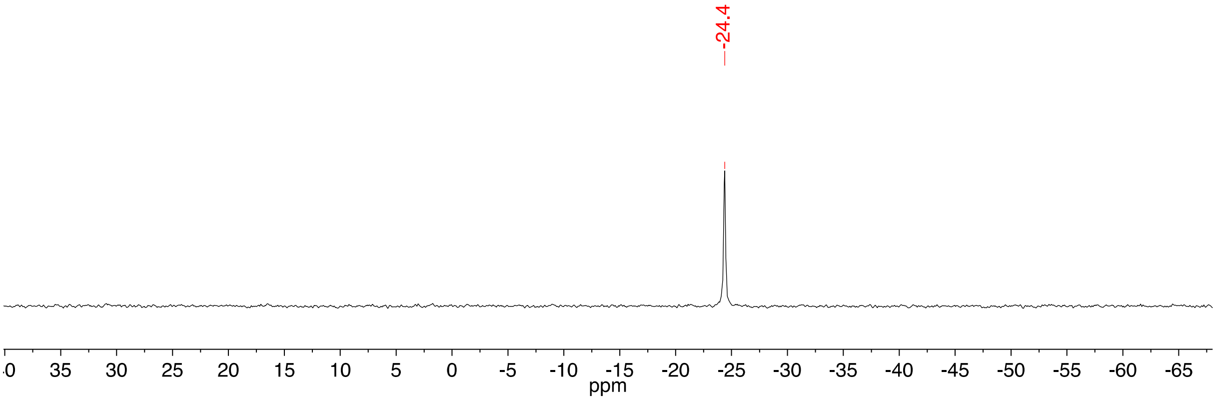

Fig. S36 $^{31}P\{^1H\}$ NMR spectrum (202 MHz, C_6D_6) of **6b**.

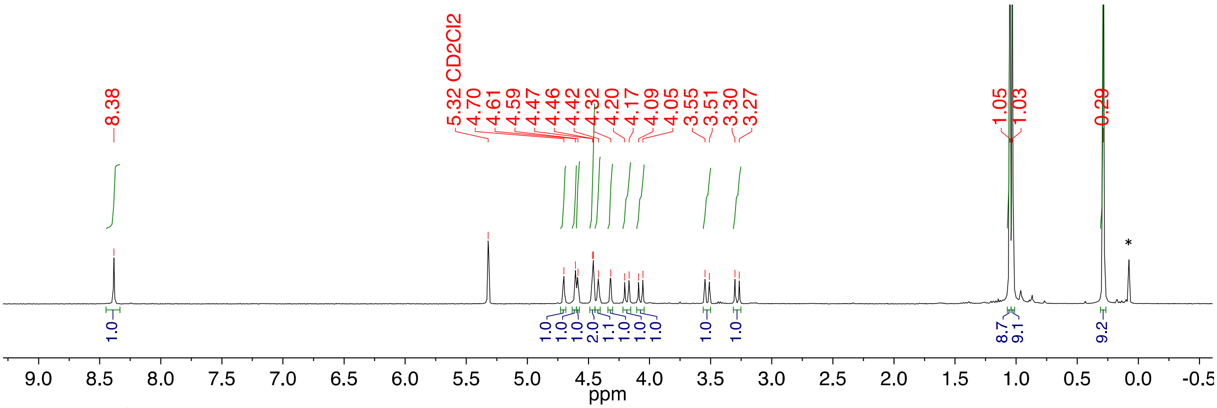

Fig. S37 ^{1}H NMR spectrum (400 MHz, CD_2Cl_2) of **7a**. The signal marked (*) belongs to silicon grease.

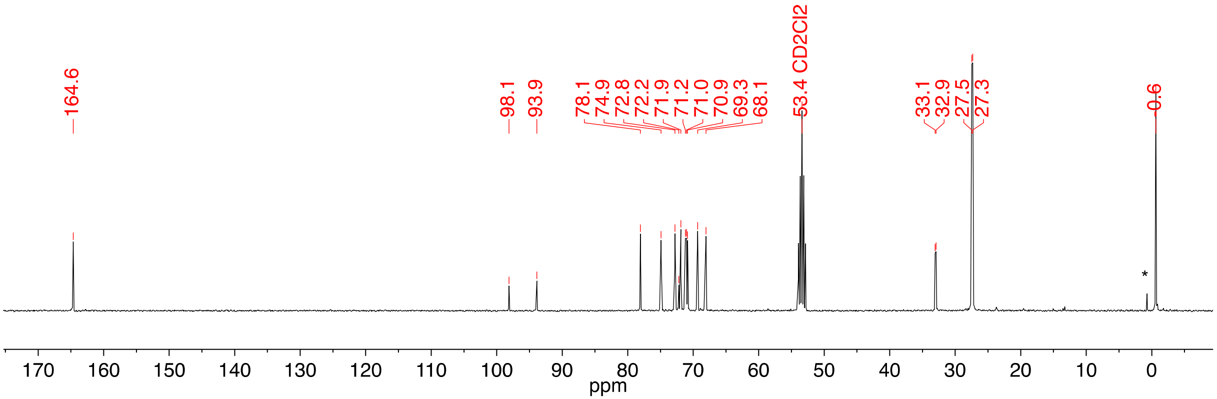

Fig. S38 $^{13}C\{^1H\}$ NMR spectrum (101 MHz, CD_2Cl_2) of **7a**. The signal marked (*) belongs to silicon grease.

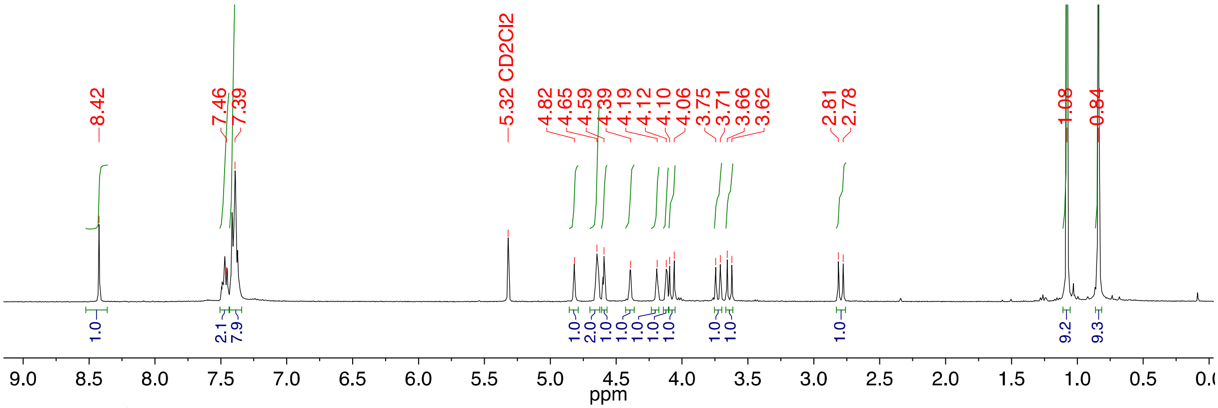

Fig. S39 ^{1}H NMR spectrum (400 MHz, CD_2Cl_2) of **7b**.

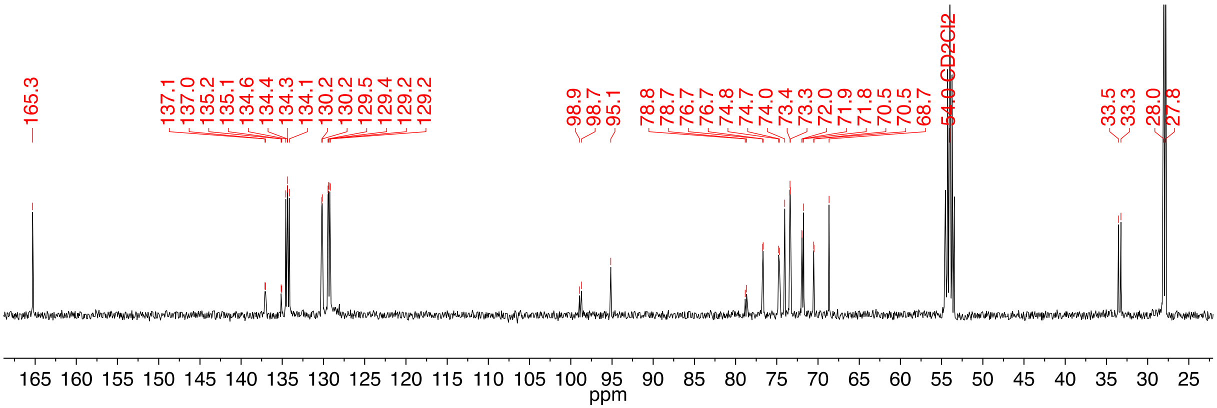

Fig. S40 $^{13}C\{^1H\}$ NMR spectrum (101 MHz, CD_2Cl_2) of **7b**.

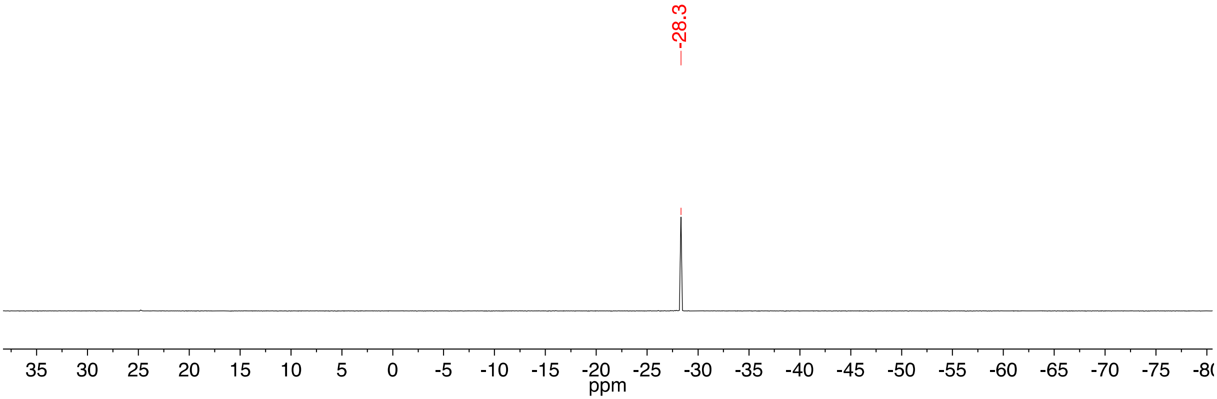

Fig. S41 $^{31}P\{^1H\}$ NMR spectrum (202 MHz, CD_2Cl_2) of **7b**.

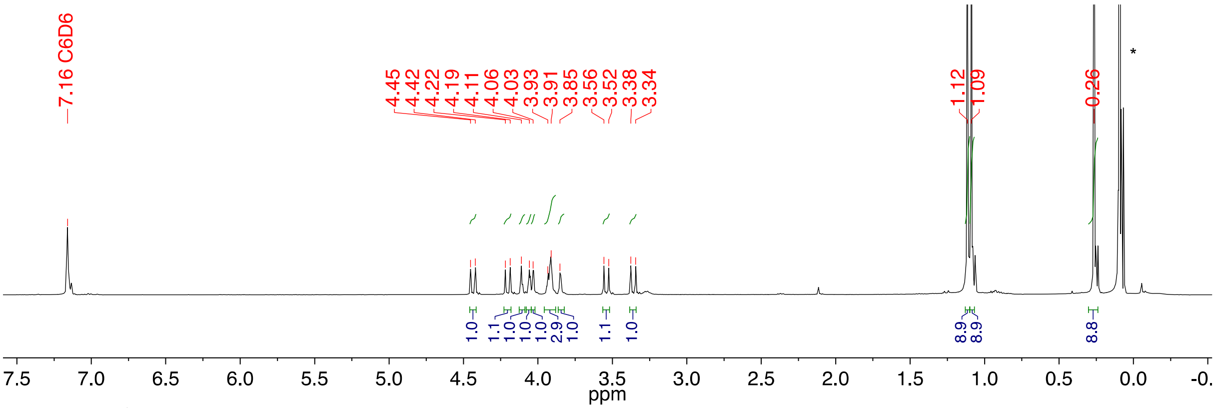

Fig. S42 ^1H NMR spectrum (400 MHz, C_6D_6) of **8a**. The signal marked (*) belongs to silicon grease; the adjacent signal is due to $(Me_3Si)_2NH$.

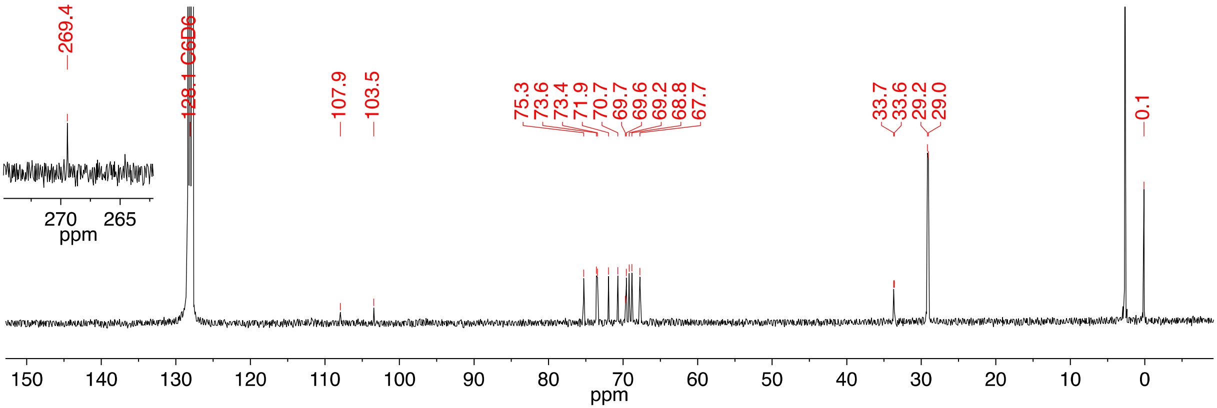

Fig. S43 $^{13}C\{H\}$ NMR spectrum (101 MHz, C_6D_6) of **8a**. The signal without peak picking is due to $(Me_3Si)_2NH$.

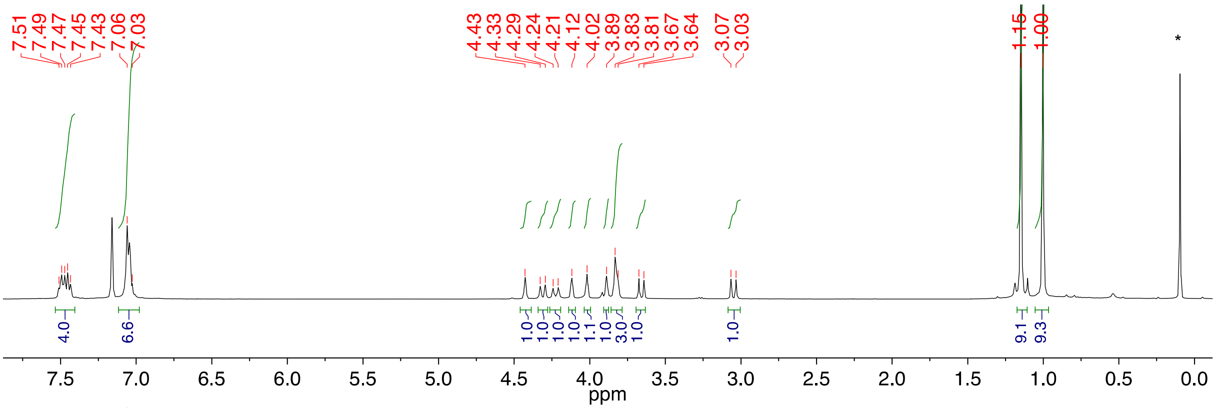

Fig. S44 ^{1}H NMR spectrum (400 MHz, C_6D_6) of **8b**. The signal marked (*) is due to $(Me_3Si)_2NH$.

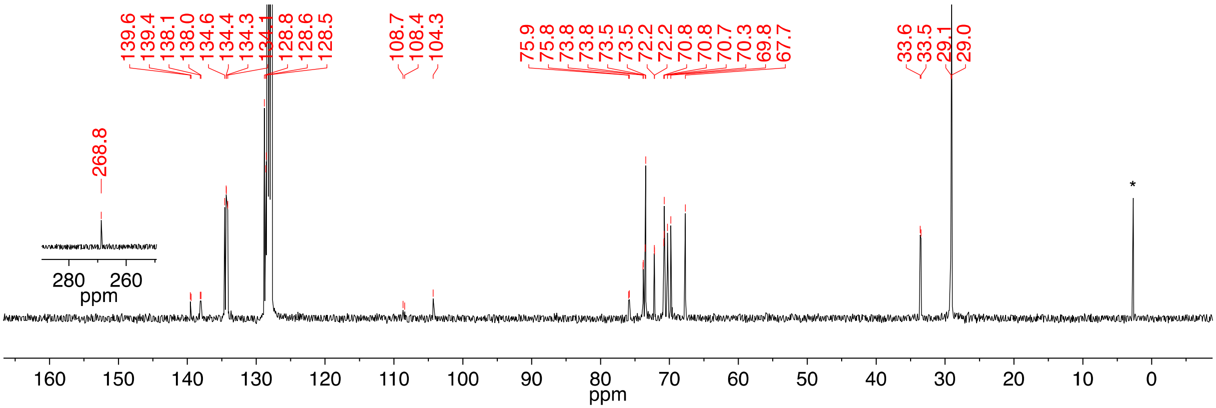

Fig. S45 $^{13}C\{H\}$ NMR spectrum (101 MHz, C_6D_6) of **8b**. The signal marked (*) is due to $(Me_3Si)_2NH$.

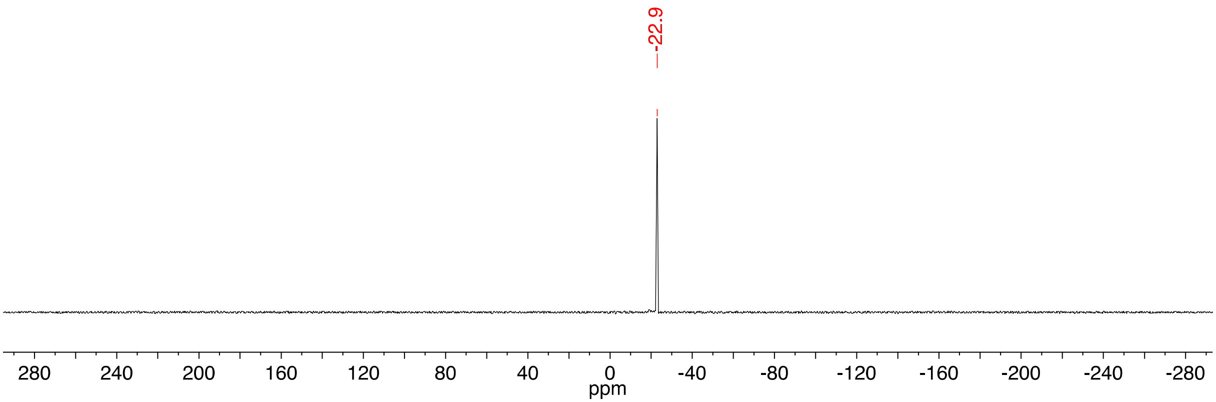

Fig. S46 $^{31}P\{H\}$ NMR spectrum (202 MHz, C_6D_6) of **8b**.

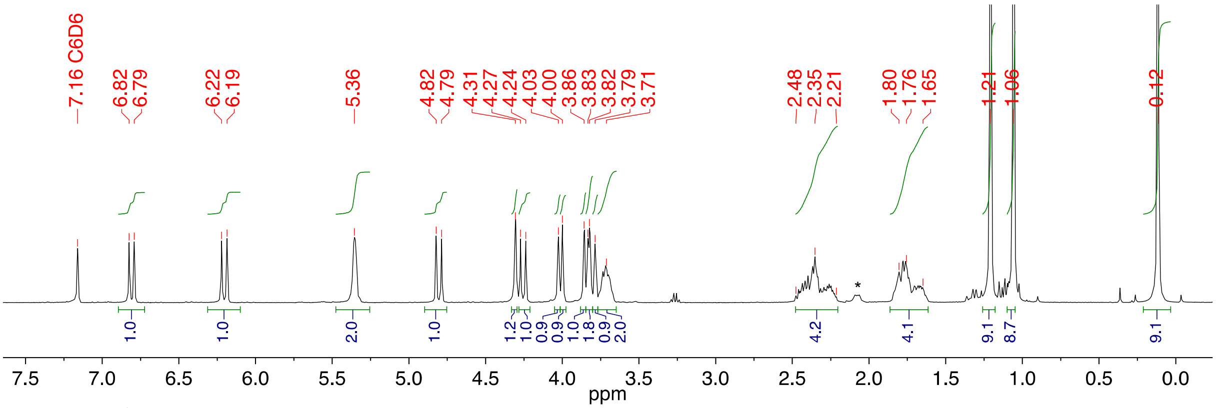

Fig. S47 ^1H NMR spectrum (400 MHz, C_6D_6) of **9a**. Signals marked (*) belong to trace amounts of $[RhCl(COD)]_2$.

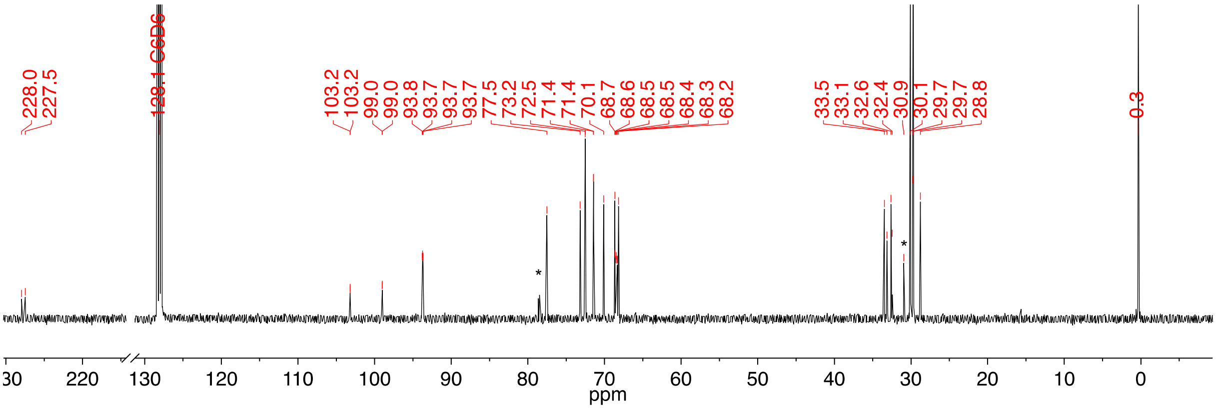

Fig. S48 $^{13}C\{H\}$ NMR spectrum (101 MHz, C_6D_6) of **9a**. Signals marked (*) belong to trace amounts of $[RhCl(COD)]_2$.

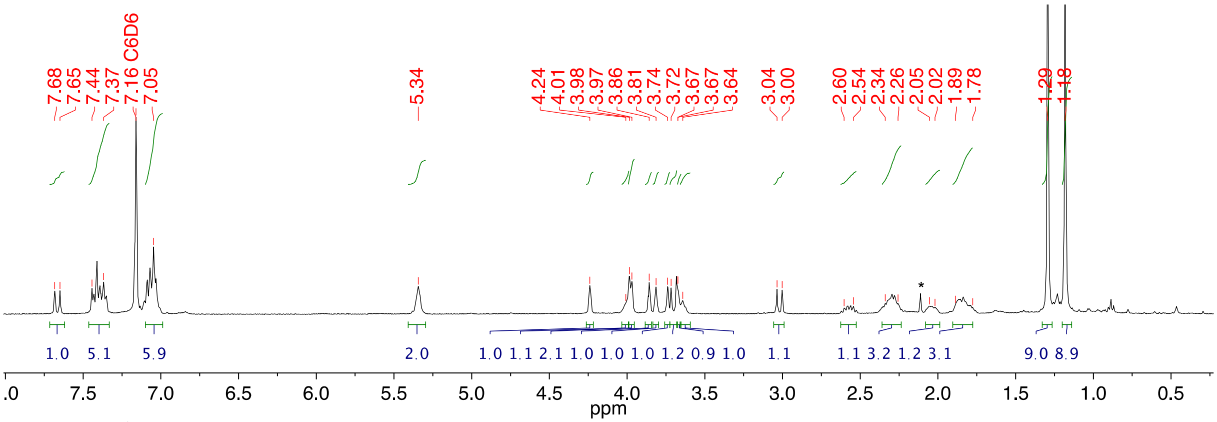

Fig. S49 ^{1}H NMR spectrum (400 MHz, C_6D_6) of **9b**. The signal marked (*) belong to trace amounts of toluene.

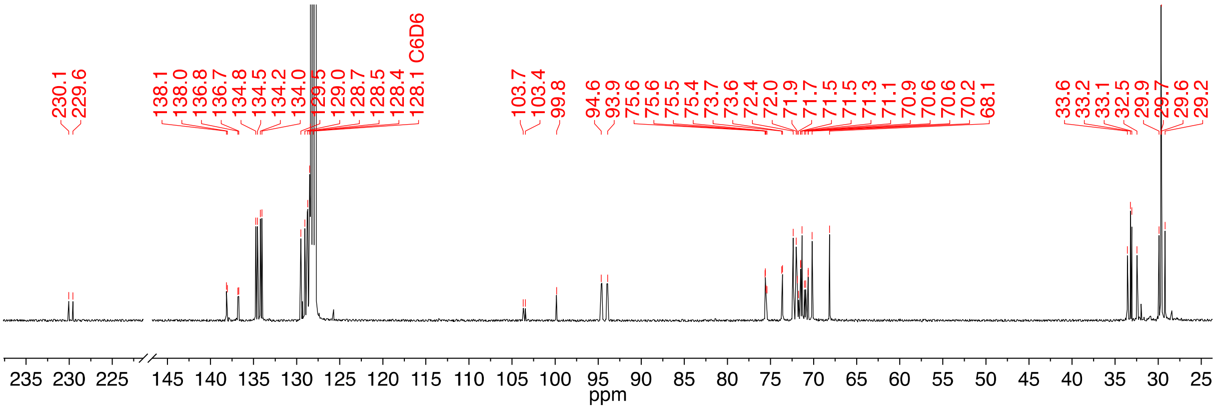

Fig. S50 $^{13}C\{^1H\}$ NMR spectrum (101 MHz, C_6D_6) of **9b**.

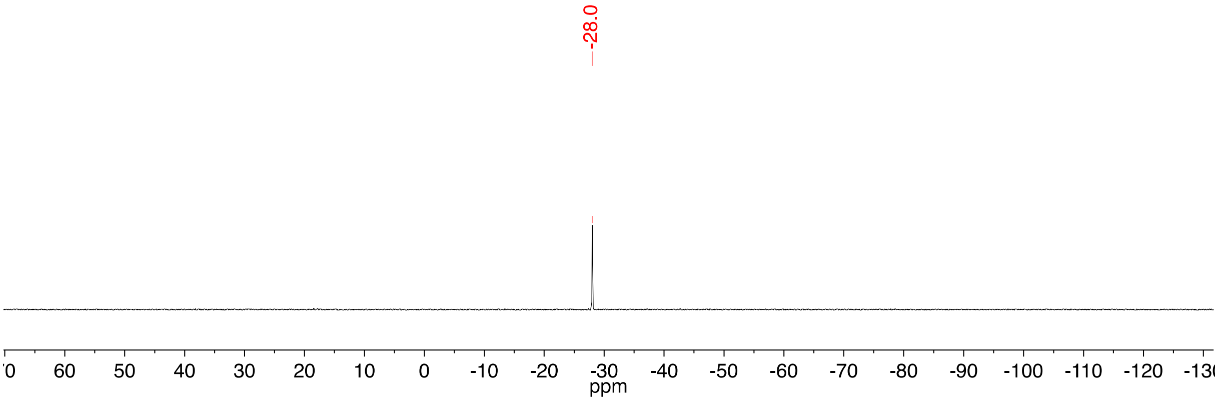

Fig. S51 $^{31}P\{^1H\}$ NMR spectrum (101 MHz, C_6D_6) of **9b**.

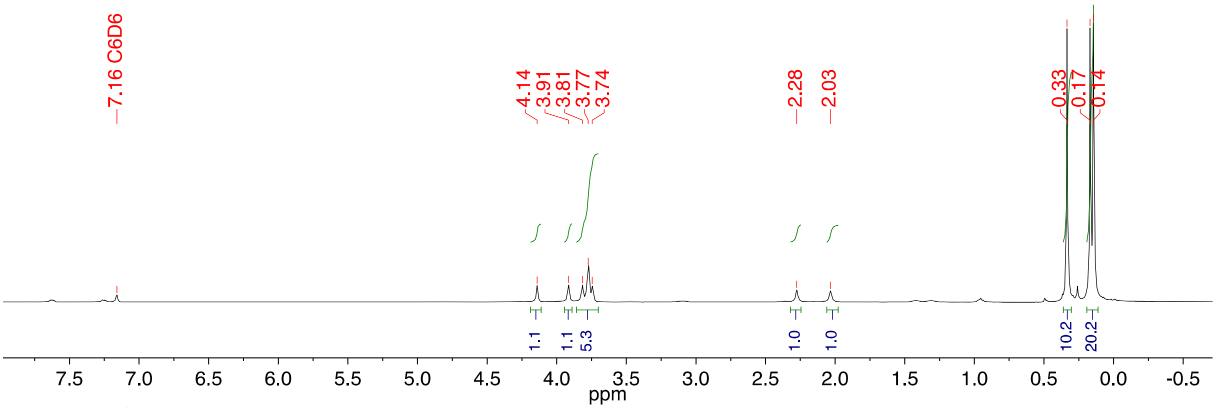

Fig. S52 ^{1}H NMR spectrum (400 MHz, C_6D_6) of **10a**.

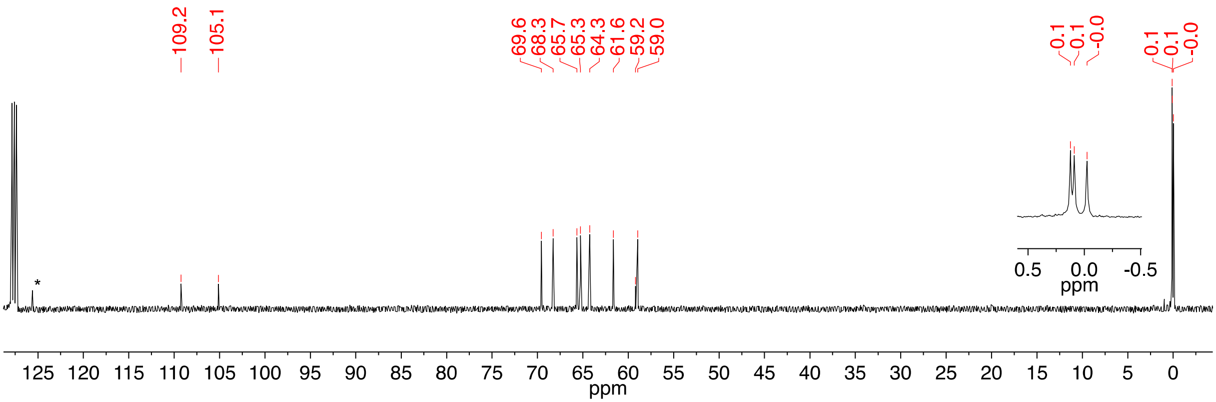

Fig. S53 $^{13}C\{^1H\}$ NMR spectrum (101 MHz, C_6D_6) of **10a**. The signal marked (*) belongs to trace amounts of naphthalene.

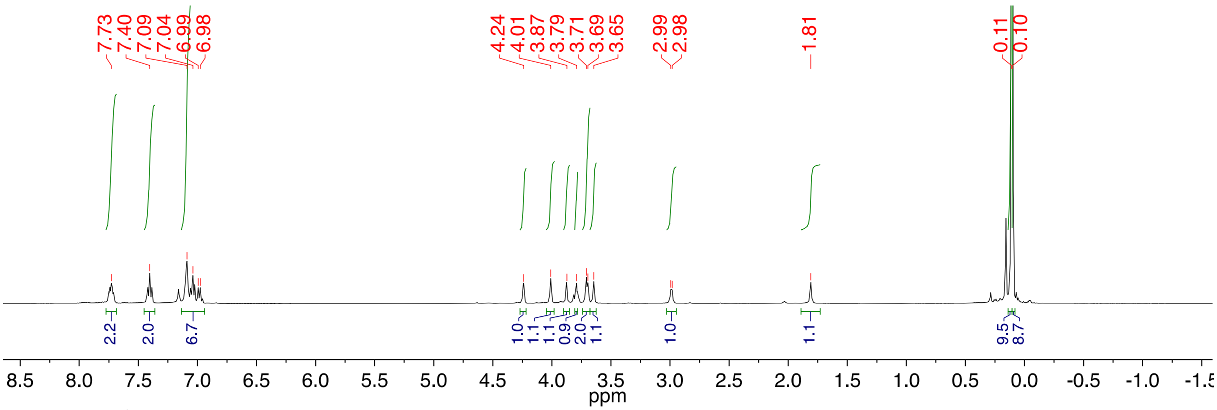

Fig. S54 ^{1}H NMR spectrum (400 MHz, C_6D_6) of **10b**.

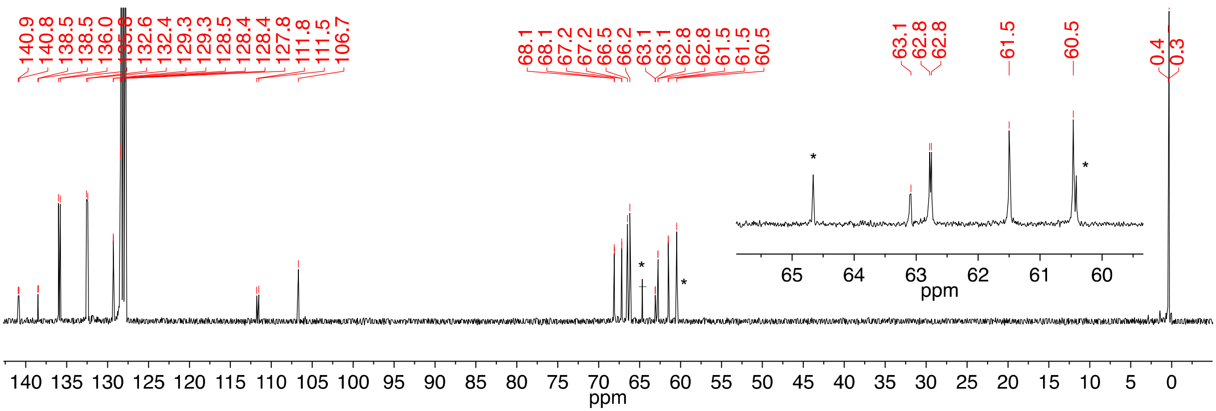

Fig. S55 $^{13}C\{^1H\}$ NMR spectrum (101 MHz, C_6D_6) of **10b**. The signals marked (*) belong to an unknown impurity.

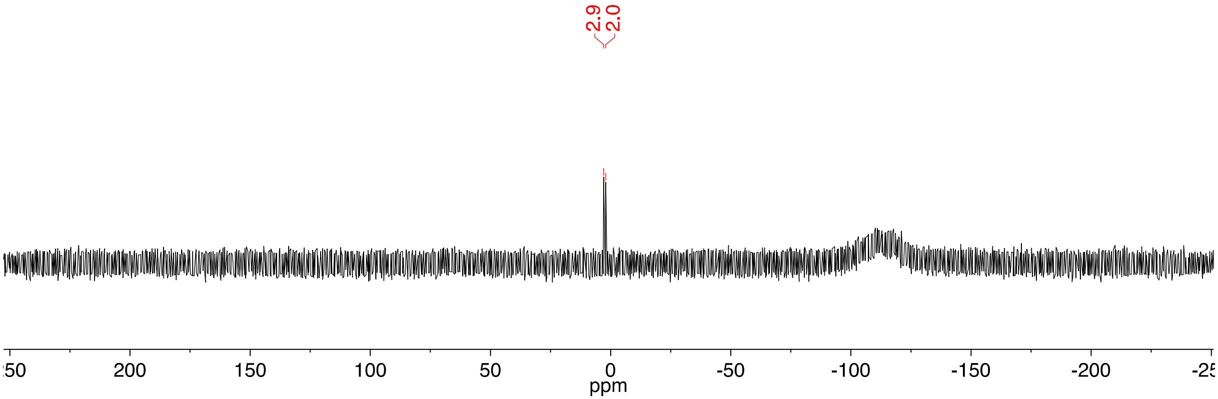

Fig. S56 $^{29}Si\{^1H\}$ NMR spectrum (99 MHz, C_6D_6) of **10b**.

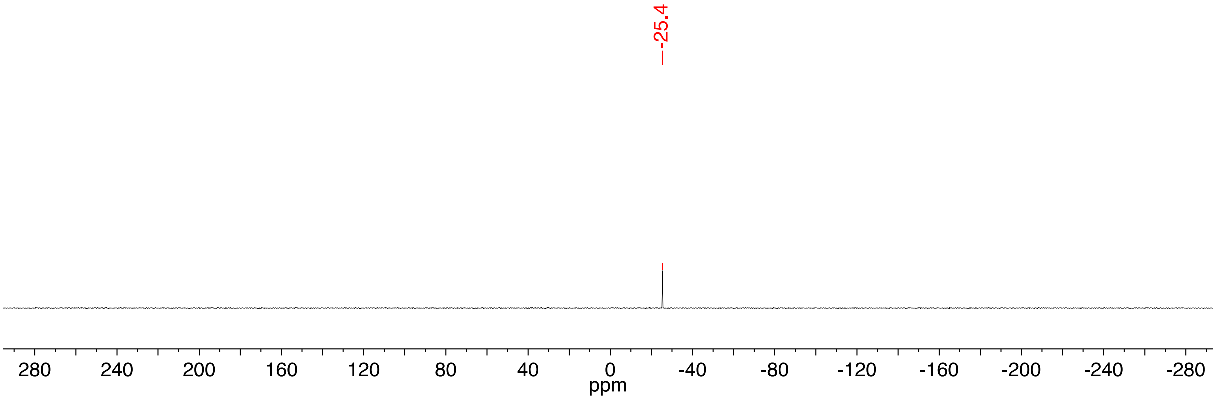

Fig. S57 $^{31}P\{^1H\}$ NMR spectrum (202 MHz, C_6D_6) of **10b**.

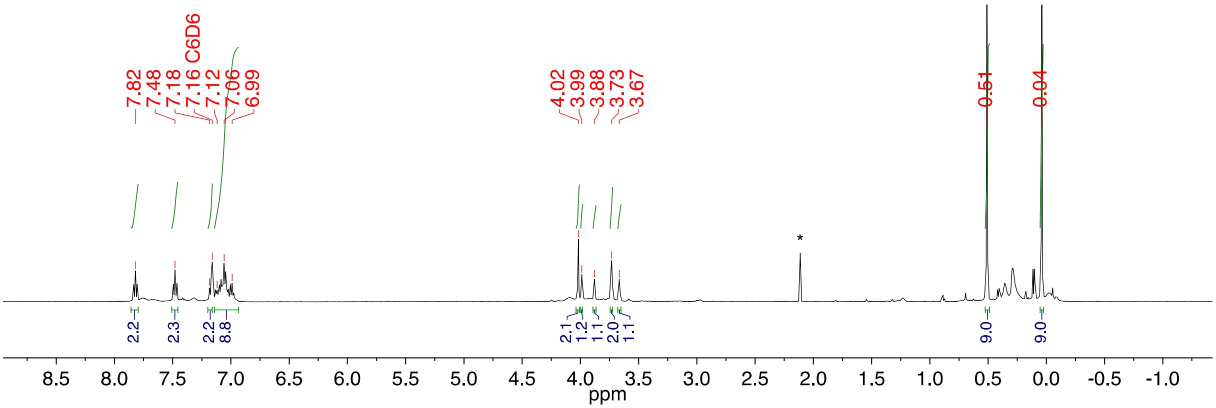

Fig. S58 ^{1}H NMR spectrum (500 MHz, C_6D_6) of **11**. The signal marked (*) belongs to small amounts of toluene.

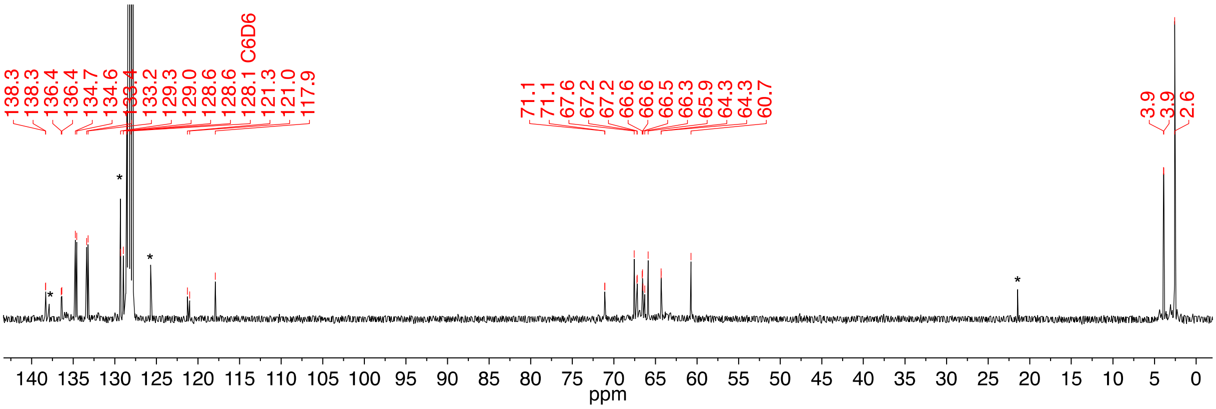

Fig. S59 ^{13}C{^{1}H} NMR spectrum (101 MHz, C_6D_6) of **11**. The signals marked (*) belong to small amounts of toluene.

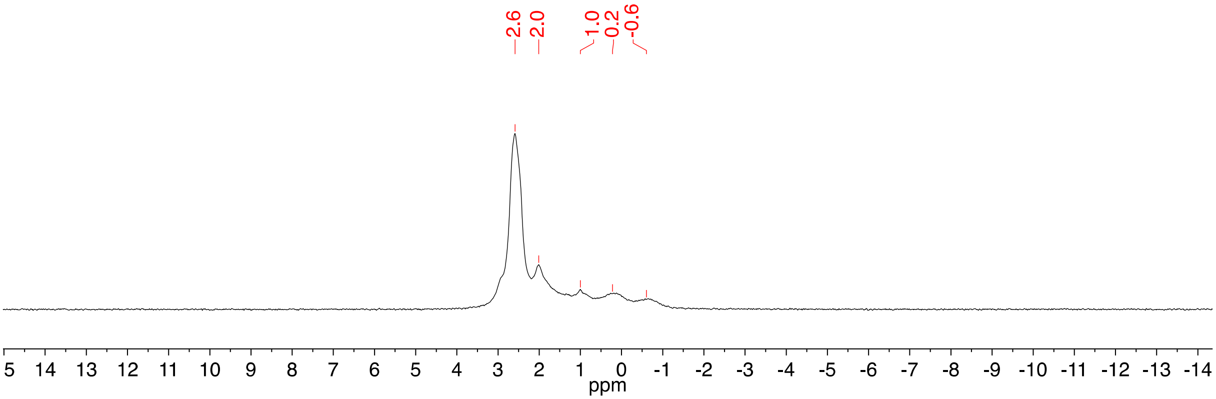

Fig. S60 ^{7}Li NMR spectrum (194 MHz, C_6D_6) of **11**.

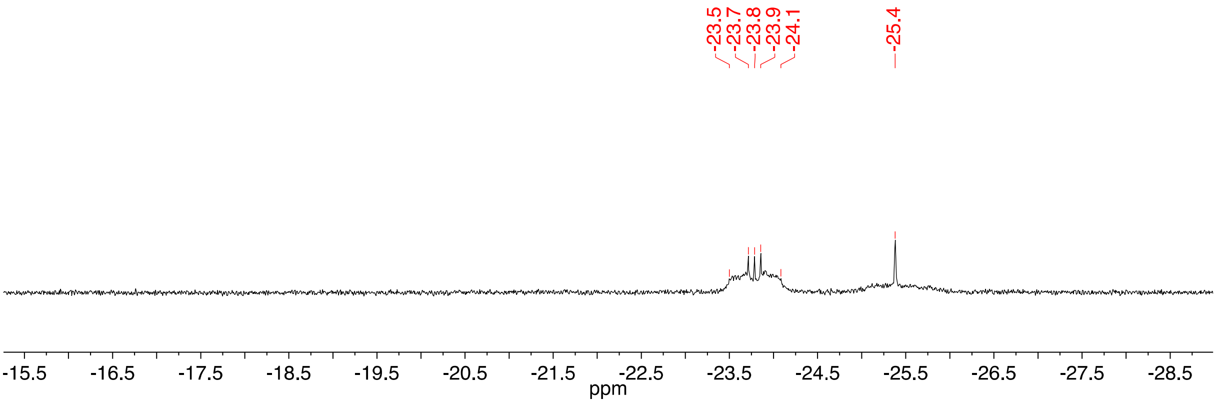

Fig. S61 $^{31}P\{^{1}H\}$ NMR spectrum (202 MHz, C_6D_6) of **11**.

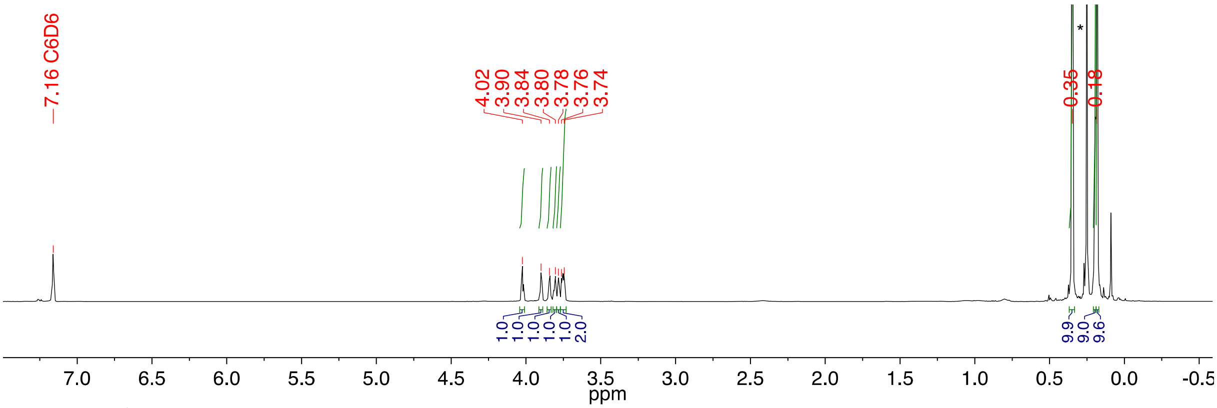

Fig. S62 ^{1}H NMR spectrum (400 MHz, C_6D_6) of **12**. The signal marked (*) belongs to $(Me_3Si)_2NH$.

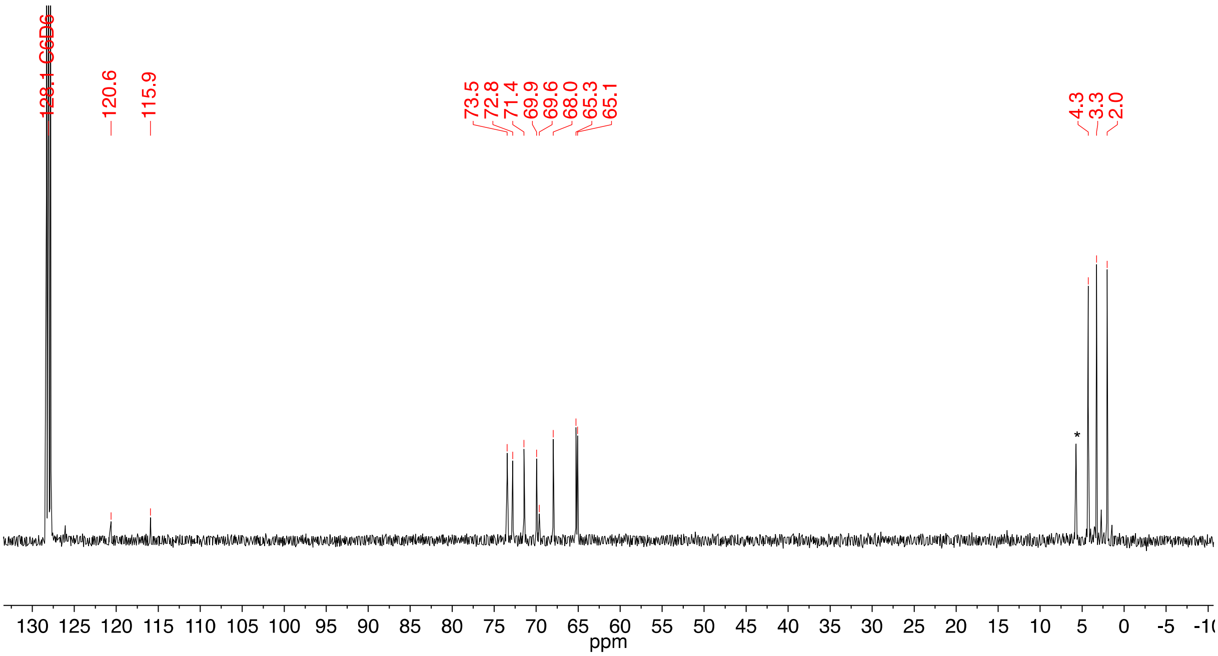

Fig. S63 $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, C_6D_6) of **12**. The signal marked (*) belongs to $(Me_3Si)_2NH$.

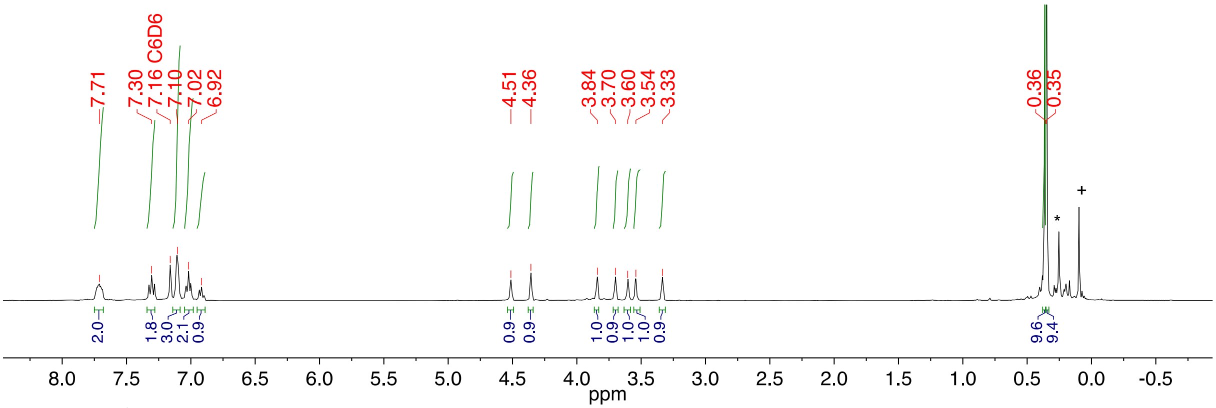

Fig. S64 ^{1}H NMR spectrum (400 MHz, C_6D_6) of **13**. The signals marked belong to $(Me_3Si)_2NH$ (*) and silicon grease (+).

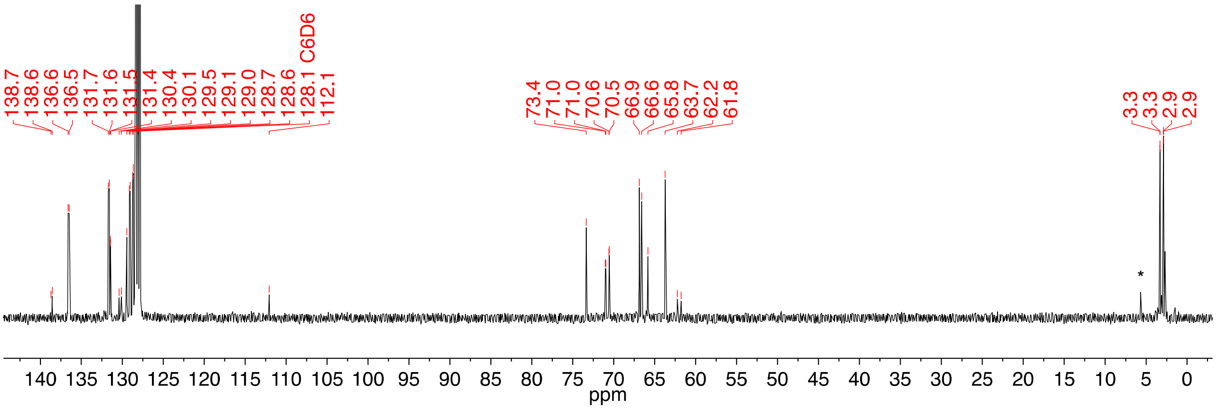

Fig. S65 ^{13}C{^{1}H} NMR spectrum (101 MHz, C_6D_6) of **13**. The signal marked (*) belongs to $(Me_3Si)_2NH$.

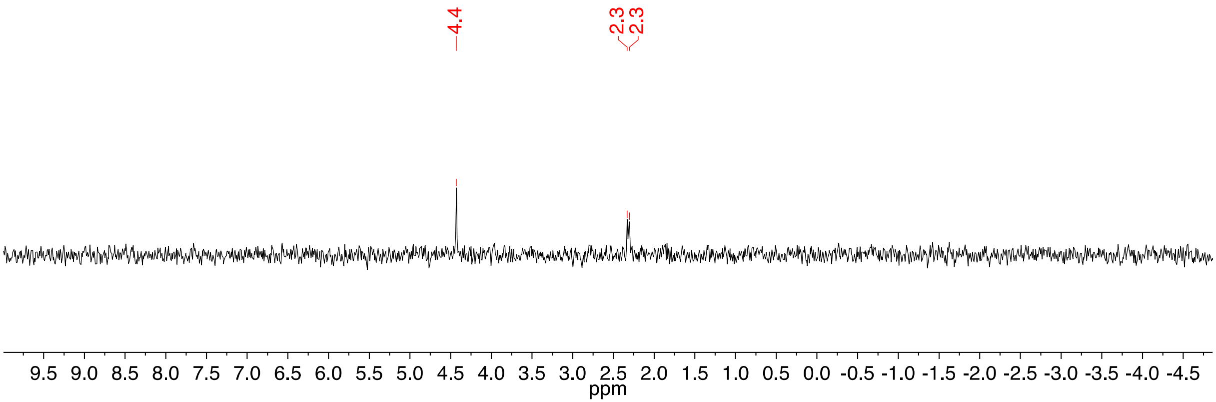

Fig. S66 ^{29}Si{^{1}H} NMR spectrum (99 MHz, C_6D_6) of **13**.

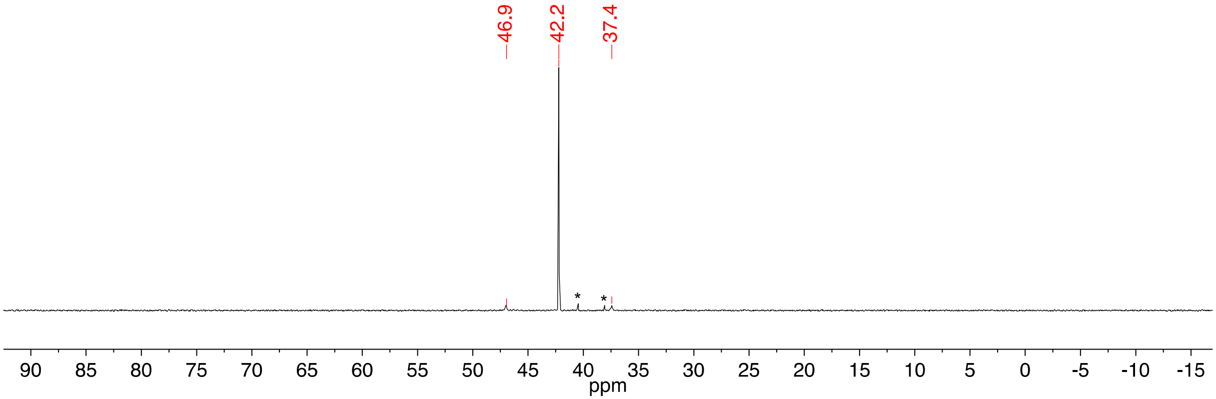

Fig S67 $^{31}P\{^1H\}$ NMR spectrum (202 MHz, C_6D_6) of **13**. The signals marked (*) belong to an unknown impurity.

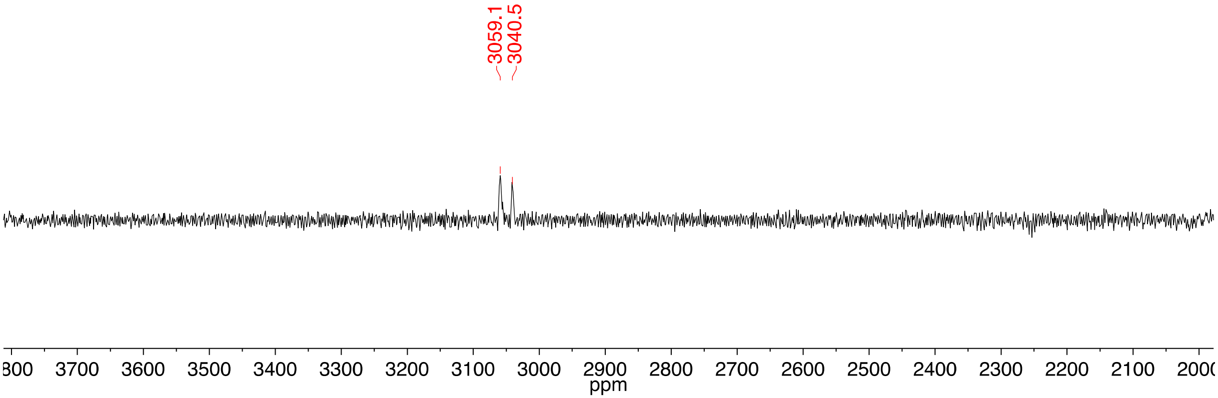

Fig. S68 $^{207}Pb\{^1H\}$ NMR spectrum (105 MHz, C_6D_6) of **13**.

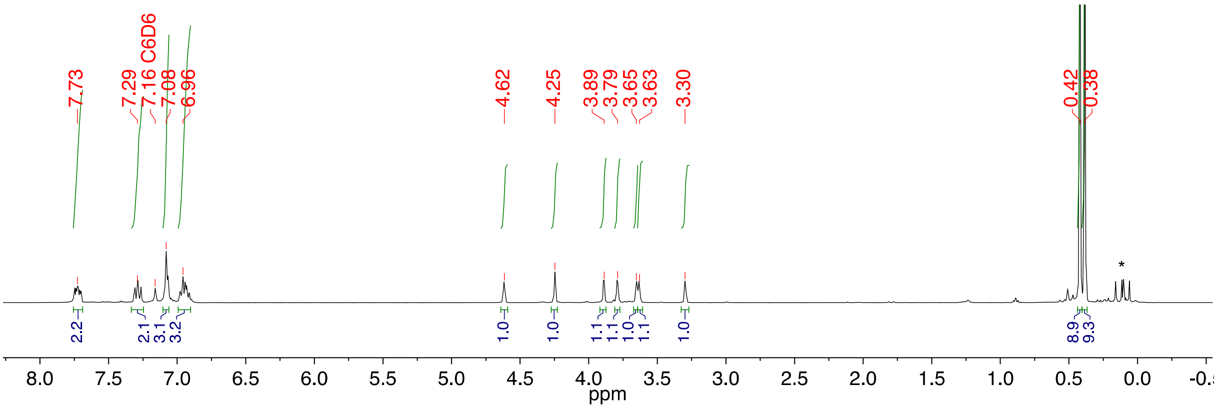

Fig. S69 ^1H NMR spectrum (400 MHz, C_6D_6) of **14**. The signal marked (*) belongs to an unknown impurity.

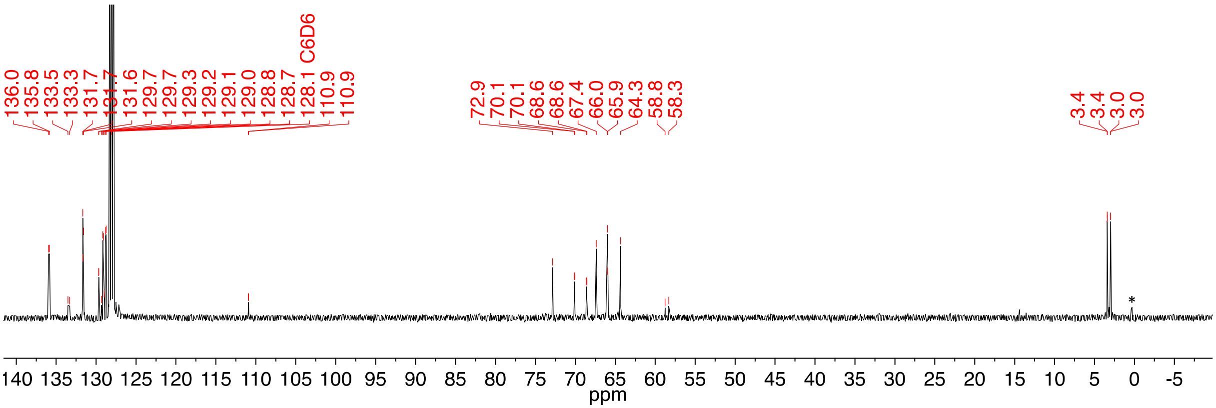

Fig. S70 $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, C_6D_6) of **14**. The signal marked (*) belongs to an unknown impurity.

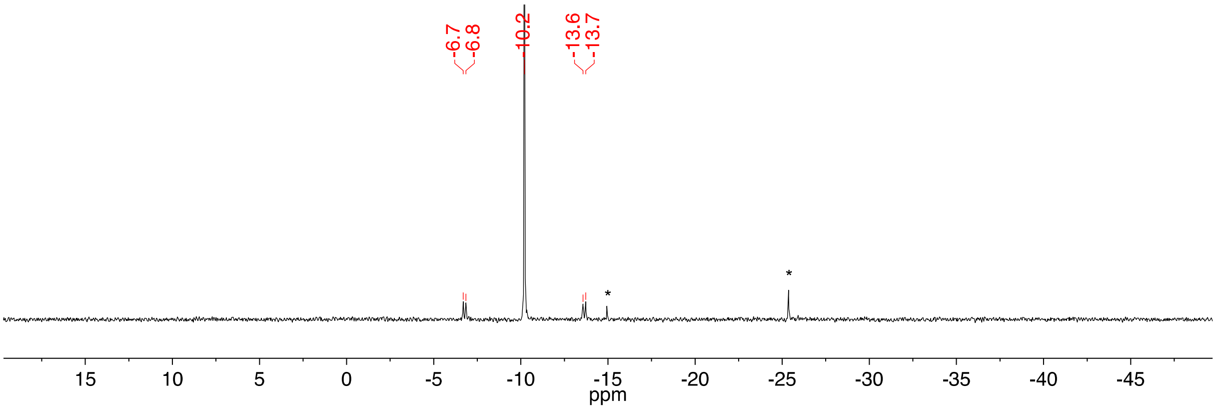

Fig. S71 $^{31}P\{^{1}H\}$ NMR spectrum (202 MHz, C_6D_6) of **14**. The signals marked (*) belong to an unknown impurity.

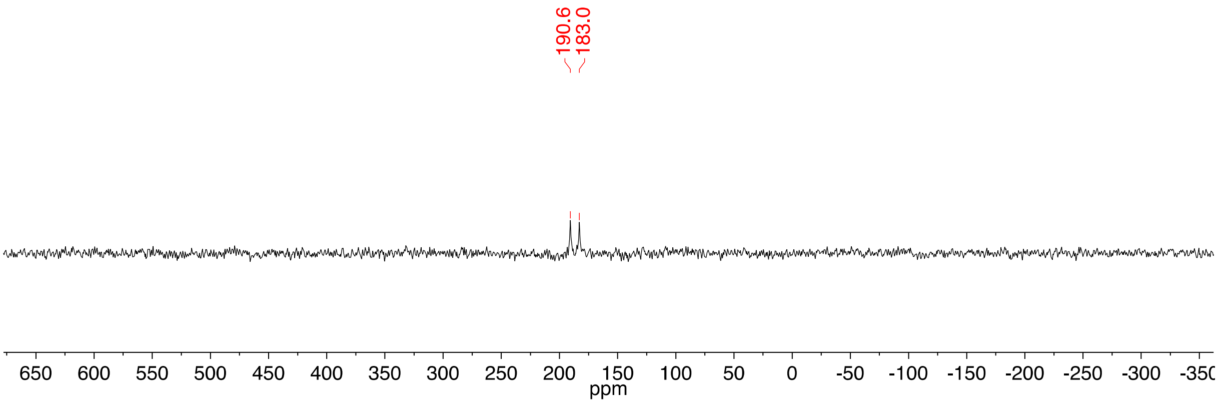

Fig. S72 $^{119}Sn\{^{1}H\}$ NMR spectrum (186 MHz, C_6D_6) of **14**.

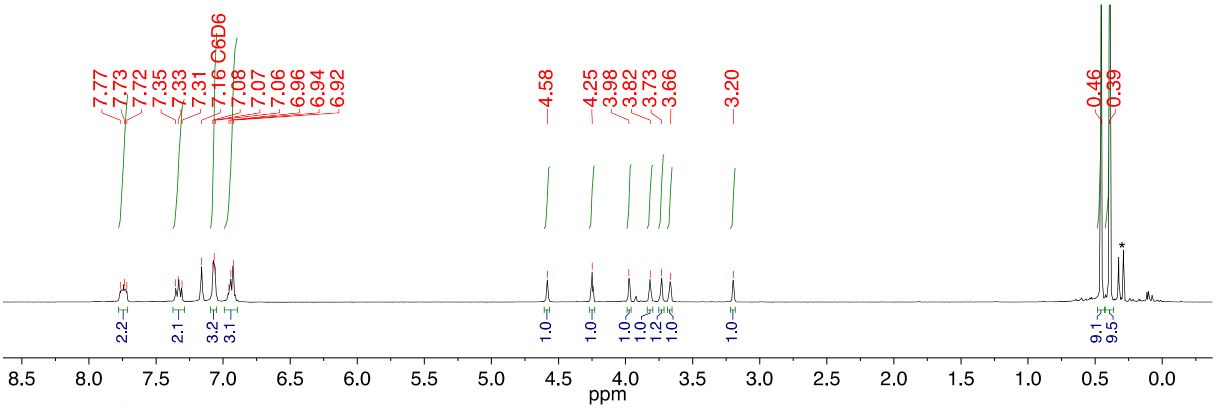

Fig. S73 ^{1}H NMR spectrum (400 MHz, C_6D_6) of **15**. The signal marked (*) belongs to an unknown impurity.

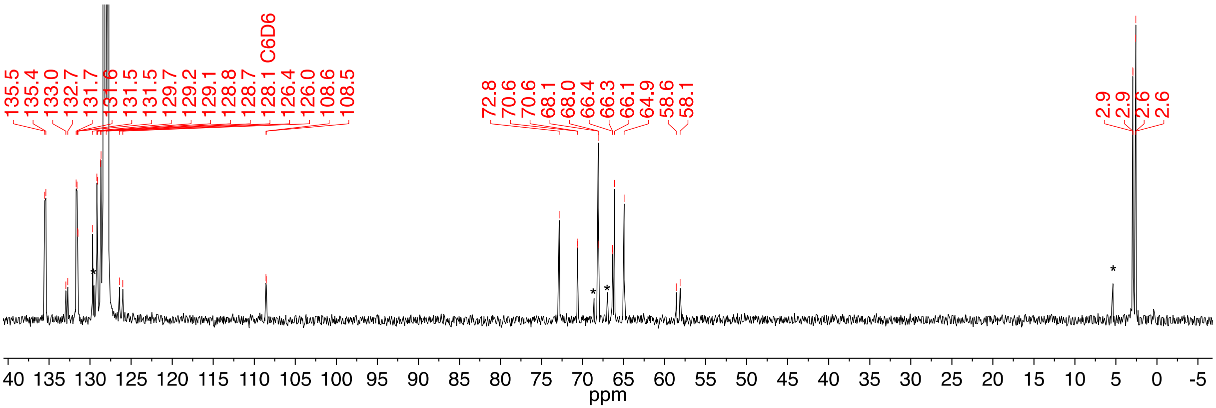

Fig. S74 $^{13}C\{^1H\}$ NMR spectrum (101 MHz, C_6D_6) of **15**. The signals marked (*) belong to an unknown impurity.

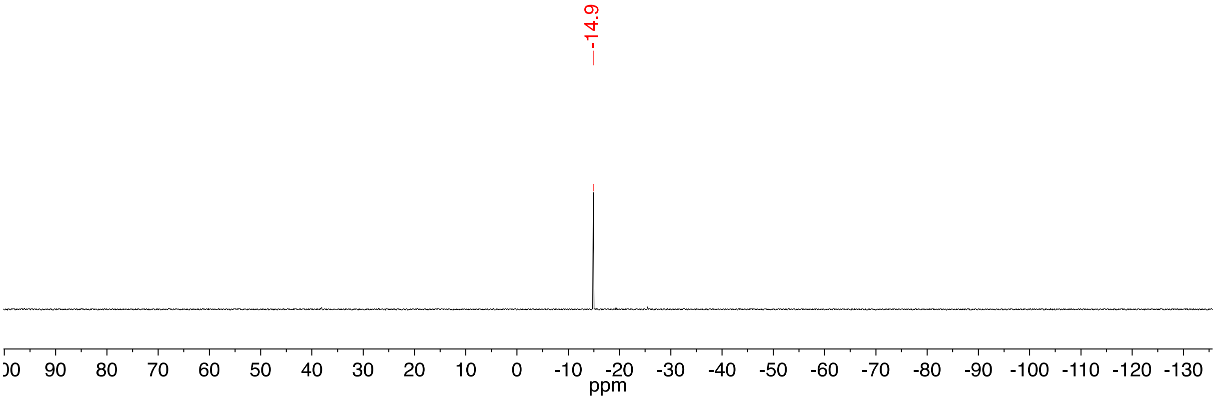

Fig. S75 $^{31}P\{^1H\}$ NMR spectrum (202 MHz, C_6D_6) of **15**.

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