Electronic supplementary information

for

Alkyl backbone variations in common β-diketiminate ligands and applications to *N*-heterocyclic silylene chemistry

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1 Experimental Section

1.1 General considerations

All manipulations were carried out using standard Schlenk and glove box techniques under a dry argon or dinitrogen atmosphere unless described below (for organic condensation reactions and aqueous organic workup steps). Benzene, toluene, diethyl ether, THF, *n*-hexane and *n*-pentane were either dried and distilled under inert gas over $LiAlH_4$, sodium or potassium, or taken from an MBraun solvent purification system and degassed prior to use. ^{1}H, ^{7}Li, $^{13}C\{^{1}H\}$, and $^{31}P\{^{1}H\}$ NMR spectra were recorded on a Bruker AV 300, Bruker AVII 400 or Bruker AV III 500 spectrometer in deuterated chloroform or benzene and were referenced to the residual ^{1}H or $^{13}C\{^{1}H\}$ resonances of the solvent used, or external aqueous LiCl or H_3PO_4 solutions, respectively. Chemical shifts are given in ppm. Abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, sept = septet, br = broad, m = multiplet. IR spectra were obtained on a Shimadzu IR Affinity spectrometer with ATR attachment. Mass spectrometry was performed on Micromass LCT instrument (for electrospray ionization) at the University of St. Andrews mass spectrometry facility. Melting points were determined using a Gallenkamp apparatus in sealed glass capillaries under argon and are uncorrected. Yields or conversions in solution were determined by integration of ^{1}H NMR spectra against an internal standard (such as hexamethylbenzene). Elemental analyses on some compounds were performed by the Elemental Analysis Service at London Metropolitan University. *n*-butylsodium[1], benzylpotassium[2] and (SIDip)$SiBr_2$ [= (SIPr)$SiBr_2$][3] were synthesised as described in the literature. [Li(NEt_2)] was obtained by treating $HNEt_2$ with one equivalent of *n*BuLi in *n*-hexane. All other reagents were used as received.

1.2 Syntheses

Organic condensation reactions using a Dean-Stark trap were in most cases carried out in air with non-dried solvents. It can be beneficial (e.g., for the synthesis of **1a**) to perform these under nitrogen as described for the synthesis of **2c** (via Dean-Stark condensation) below. Workups were performed in air. Condensation reactions using PPSE were carried out with dried solvents and reagents under dinitrogen gas using Schlenk techniques. All reactions were stirred. The aqueous part of the work-up was conducted in air. Please note that the given yields for the β-diketimine proligands are isolated yields with higher *in-situ* yields and that in most cases the procedure is not fully optimised. A more optimised procedure with a higher yield is presented for compound **2a** below.

Synthesis of ^{EtDip}nacnacH 1a

To a round bottom flask was added 2,6-diisopropylaniline (19.6 g, 20.9 mL, 111 mmol, 2.0 equiv.), 3,5-heptanedione (7.10 g, 7.50 mL, 55.4 mmol) and *p*-toluenesulfonic acid hydrate (11.6 g, 60.9 mmol, 1.1 equiv.) and xylenes (mixture of isomers, 220 mL). A Dean-Stark trap was then attached, and the solution was stirred and heated under reflux for 2 days. Subsequently, the majority of the solvent was distilled off via the Dean-Stark trap, and the residue was washed with hexane (100 mL). The residue was then dissolved in dichloromethane (150 mL) and vigorously stirred with a saturated solution of Na_2CO_3 (100 mL) for one hour. The organic layer was separated off and the aqueous phase was further extracted with dichloromethane (1 × 30 mL). The organic phases were combined, and all volatiles were removed *in vacuo*. Washing with ice cold methanol (200 mL) afforded pure β-diketimine **1a** as a light-yellow solid which was dried *in vacuo*. Additional crops of **1a** were obtained from the concentration of the resultant supernatant solution and subsequent storage at -40 °C. The crystalline solid was dried under vacuum and analysed as pure **1a**. Yield = 16.1 g (65 %). ^{1}H NMR (400.3 MHz, $CDCl_3$, 297 K) δ = 1.07 (t, J_{HH} = 7.3 Hz, 6H, NCCH$_2$C*H*$_3$), 1.10 (d, J_{HH} = 6.9 Hz, 12H, Ar-*o*-CH(C*H*$_3$)$_2$), 1.22 (d, J_{HH} = 7.5 Hz, 12H, Ar-*o*-CH(C*H*$_3$)$_2$), 2.06 (q, J_{HH} = 7.5 Hz, 4H, NCC*H*$_2$CH$_3$), 3.12 (sept, J_{HH} = 7.5 Hz, 4H, Ar-*o*-C*H*(CH$_3$)$_2$), 4.95 (s, 1H, NCC*H*CN), 7.11 (s, 6H, Ar-*H*), 12.12 (s, 1H, N-*H*); ^{13}C{^{1}H} DEPTQ NMR (100.7 MHz, $CDCl_3$, 297 K): δ = 11.9 (NCCH$_2$*C*H$_3$), 23.2 (Ar-*o*-CH(*C*H$_3$)$_2$), 24.7 (Ar-*o*-CH(*C*H$_3$)$_2$), 26.4 (Ar-*o*-*C*H(CH$_3$)$_2$), 28.2 (NCC*H*$_2$CH$_3$), 88.3 (NC(CH$_2$CH$_3$)*C*H), 123.1 (Ar-*C*), 125.0 (Ar-*C*), 140.5 (Ar-*C*), 142.7 (Ar-*C*), 166.2 (N*C*CH*C*N); ^{1}H NMR (400.1 MHz, C_6D_6, 300 K) δ = 1.10 (d, J_{HH} = 6.9 Hz, 12H, Ar-*o*-CH(C*H*$_3$)$_2$), 1.20 (t, J_{HH} = 7.6 Hz, 6H, NCCH$_2$C*H*$_3$), 1.24 (d, J_{HH} = 6.9 Hz, 12H, Ar-*o*-CH(C*H*$_3$)$_2$), 2.20 (q, J_{HH} = 7.6 Hz, 4H, NCC*H*$_2$CH$_3$), 3.27 (sept, J_{HH} = 6.9 Hz, 4H, Ar-*o*-C*H*(CH$_3$)$_2$), 4.76 (s, 1H, NCC*H*CN), 7.09 (m, 2H, Ar-*H*), 7.18 (m, 4H, Ar-*H*), 12.53 (s, 1H, N-*H*); ^{13}C{^{1}H} NMR (100.6 MHz, C_6D_6, 300 K): δ = 13.6 (NCCH$_2$*C*H$_3$), 23.4 (Ar-*o*-CH(*C*H$_3$)$_2$), 24.4 (Ar-*o*-CH(*C*H$_3$)$_2$), 27.3 (Ar-*o*-*C*H(CH$_3$)$_2$), 29.0 (NC*C*H$_2$CH$_3$), 85.7 (NC*C*HCN), 121.4 (Ar-*C*), 123.0 (Ar-*C*), 139.5 (Ar-*C*), 149.8 (Ar-*C*), 167.4 (N*C*CH*C*N); M.p.: 118-123 °C. IR (ATR), $\tilde{\nu}$/cm^{-1}: 3059w, 2959m, 2868w, 1616s, 1535s, 1256m, 1433m, 1173m, 1055s, 798s, 685m.

Synthesis of ^{EtDip}nacnacH 1a via PPSE condensation

A Schlenk flask with a reflux condenser was charged with phosphorus pentoxide, P_4O_{10} (18.1 g, 63.9 mmol, 3.1 equiv.), hexamethyldisiloxane (52.5 mL, 247 mmol, 12 equiv.) and dichloromethane (40 mL). The reaction mixture was heated to reflux for 1.5 h under a stream of nitrogen gas and then cooled to room temperature. All volatiles were removed *in vacuo*, affording a colourless, viscous syrup of PPSE, which was used *in situ* for the subsequent transformation. 3,5-Heptanedione (2.50 mL, 20.6 mmol, 1.0 equiv.) and 2,6-diisopropylaniline (8.13 mL, 43.3 mmol, 2.1 equiv.) were added to

the flask in quick succession under a flow of nitrogen. The reaction mixture was then heated to 170 °C for 24 h. After that, the reaction solution was cooled to 95 °C and an aqueous solution of NaOH (100 mL of a ca. 2 M solution) was slowly poured down the condenser (CAUTION: exothermic reaction!), with vigorous stirring, affording an oily solid. The solid was extracted with dichloromethane (2 × 40 mL), the organic layer was separated, and the aqueous phase was washed with dichloromethane (2 × 30 mL). The organic phases were combined, and the volatiles were removed under reduced pressure to yield crude **1a**. The crude product was taken up in methanol (40 mL), resulting in the precipitation of a yellow crystalline solid at -40 °C that was dried under vacuum to afford pure **1a**. Yield: 3.37 g (56 %). The NMR spectroscopic values matched those reported above.

Synthesis of ^{EtAr}cacnacH 1b-d

General procedure: To a round bottom flask was added substituted aniline (73.8 mmol, 2.0 equiv.), 3,5-heptanedione (4.73 g, 36.9 mmol, 1.0 equiv.), *p*-toluenesulfonic acid hydrate (7.37 g, 38.8 mmol, 1.1 equiv.) and toluene (150 mL). A Dean-Stark trap and condenser were attached, and the solution was stirred and heated under reflux overnight. Subsequently, most of the solvent was distilled off via the Dean-Stark trap, and the residue was washed with hexane (100 mL). The residue was then dissolved in dichloromethane (150 mL) and vigorously stirred with a saturated aqueous Na_2CO_3 solution (100 mL) for one hour. The organic layer was separated off and the aqueous phase was further extracted with dichloromethane (1 × 30 mL). The combined organic phases were dried over a small quantity of $MgSO_4$ only and all volatiles were removed in vacuo. Treating the residue with ice cold methanol (150 mL) afforded pure β-diketimine as an off-white to yellow powder which was dried *in vacuo*. Additional crops of each β-diketimine were obtained from the concentration of the resultant supernatant methanol solution and subsequent storage at -40 °C.

^{EtDep}nacnacH 1b

Ar = Dep, using 2,6-diethylaniline (11.0 g, 73.8 mmol). Isolated yield: 6.85 g (48 %). ^{1}H NMR (400.3 MHz, $CDCl_3$, 296.5 K) δ = 1.03 (t, J_{HH} = 7.6 Hz, 6H, NCCH$_2$C*H*$_3$), 1.16 (t, J_{HH} = 7.5 Hz, 12H, Ar-*o*-CH$_2$C*H*$_3$), 2.01 (q, J_{HH} = 7.6 Hz, 4H, NCC*H*$_2$CH$_3$), 2.42 (dq, J_{HH} = 15.1, 8.2 Hz, 4H, Ar-*o*-C*H*$_2$CH$_3$), 2.60 (dq, J_{HH} = 15.0, 7.5 Hz, 4H, Ar-*o*-C*H*$_2$CH$_3$), 4.92 (s, 1H, NCC*H*CN), 7.06 (m, 6H, Ar-*H*), 12.26 (br s, 1H, N-*H*); ^{13}C{^{1}H} NMR (100.7 MHz, $CDCl_3$, 298 K): δ = 12.1 (NCCH$_2$*C*H$_3$), 14.5 (Ar-*o*-CH$_2$*C*H$_3$), 24.7 (Ar-*o*-*C*H$_2$CH$_3$), 26.6 (NC*C*H$_2$CH$_3$), 88.9 (NC*C*HCN), 124.6 (Ar-*C*), 125.78 (Ar-*C*), 137.9 (Ar-*C*), 142.2 (Ar-*C*), 166.2 (N*C*CH*C*N); IR (ATR), $\tilde{\nu}$/cm^{-1}: 2963w, 2934m, 2874w, 1612s, 1447s, 1267m, 1172m, 1076m, 1063s, 760s, 748m; M.p.: 29-31 °C.

^{EtMes}nacnacH 1c

Ar = Mes, using 2,4,6-trimethylaniline (9.98 g, 73.8 mmol). Yield: 9.64 g (72 %). ^{1}H NMR (400.1 MHz, $CDCl_3$, 298 K) δ = 1.02 (t, J_{HH} = 7.6 Hz, 6H, NCCH$_2$CH_3), 2.00 (q, J_{HH} = 7.5 Hz, 4H, NCCH_2CH$_3$), 2.11 (s, 12H, Ar-*o*-CH_3), 2.26 (s, 6H, Ar-*p*-CH_3), 4.89 (s, 1H, NCC*H*CN), 6.85 (s, 4H, Ar-*H*), 12.23 (br s, 1H, N-*H*); ^{13}C{^{1}H} NMR (125.7 MHz, $CDCl_3$, 294 K): δ = 12.5 (NCCH$_2$*C*H$_3$), 18.6 (Ar-*o*-*C*H$_3$), 20.9 (Ar-*p*-*C*H$_3$), 26.6 (NC*C*H$_2$CH$_3$), 89.3 (NC*C*HCN), 128.5 (Ar-*C*), 131.9 (Ar-*C*), 133.4 (Ar-*C*), 141.1 (Ar-*C*), 166.4 (N*C*CH*C*N); IR (ATR), ν~/cm^{-1}: 2970w, 2934m, 2914w, 1618s, 1491s, 1474m, 1458m, 1256s, 1186m, 1076m, 1051s, 853s, 799m; M.p.: 35-40 °C.

^{EtXyl}nacnacH 1d

Ar = Xyl, using 2,6-dimethylaniline (8.94 g, 73.8 mmol). Yield: 9.27 g (75 %). ^{1}H NMR (400.1 MHz, $CDCl_3$, 298 K) δ = 1.04 (t, J_{HH} = 7.6 Hz, 6H, NCCH$_2$CH_3), 2.02 (q, J_{HH} = 7.5 Hz, 4H, NCCH_2CH$_3$), 2.17 (s, 12H, Ar-*o*-CH_3), 4.93 (s, 1H, NCC*H*CN), 6.94-6.97 (m, 2H, Ar-*H*), 7.04-7.05 (m, 4H, Ar-*H*), 12.30 (br s, 1H, N-*H*); ^{1}H NMR (400.1 MHz, C_6D_6, 298 K) δ = 1.09 (t, J_{HH} = 7.6 Hz, 6H, NCCH$_2$CH_3), 2.07 (q, J_{HH} = 7.6 Hz, 4H, NCCH_2CH$_3$), 2.22 (s, 12H, Ar-*o*-CH_3), 4.98 (s, 1H, NCC*H*CN), 6.99 (m, 2H, Ar-*H*), 7.09 (m, 4H, Ar-*H*), 12.30 (br s, 1H, N-*H*); ^{13}C{^{1}H} NMR (125.7 MHz, $CDCl_3$, 294 K): δ = 12.4 (NCCH$_2$*C*H$_3$), 18.6 (Ar-*o*-*C*H$_3$), 26.7 (NC*C*H$_2$CH$_3$), 89.5 (NC*C*HCN), 124.2 (Ar-*C*), 127.9 (Ar-*C*), 132.2 (Ar-*C*), 143.7 (Ar-*C*), 166.2 (N*C*CH*C*N); IR (ATR), ν~/cm^{-1}: 2972w, 2930m, 2916w, 1616s, 1489s, 1458m, 1458m, 1263s, 1244m, 1177m, 1078m, 1065s, 758s, 685m; M.p.: 60-65 °C.

Synthesis of ^{iPrMes}nacnacH 2c via Dean-Stark condensation

A round bottom flask was charged with 2,4,6-trimethylaniline (16.0 g, 118 mmol, 4 equiv.), 2,6-dimethyl-3,5-heptanedione (4.62 g, 29.5 mmol, 1 equiv.), *p*-toluenesulfonic acid hydrate (11.2 g, 59.0 mmol, 2 equiv.) and xylene (mixture of isomers, 100 mL). A Dean-Stark trap and reflux condenser were attached and a nitrogen inlet with oil bubbler was fitted. The flask was placed in an oil bath and nitrogen gas was passed through the apparatus for a few minutes to displace most of the air. The mixture was then heated and stirred for one day at 100 °C before heating under reflux for six days to remove the water keeping the set-up under nitrogen gas (very low to no nitrogen gas flow). Subsequently, most of the xylene was removed by distillation via the Dean-Stark trap and volatiles were removed under vacuum. The residue was then dissolved in dichloromethane (100 mL) and stirred with a saturated solution of Na_2CO_3 (50 mL) for 0.5 h. The organic layer was separated, and the aqueous phase was washed with dichloromethane (1 × 30 mL). The combined organic phases were dried over a small amount of $MgSO_4$ only and all volatiles were removed *in vacuo*. (An ^{1}H NMR spectrum of the crude oily product confirmed the existence of both substitution products **2c** and

some **3c**.) Excess 2,4,6-trimethylaniline was now distilled off ($T \approx 70$-100 °C, $p \approx 0.1$ mbar) and the main products **2c** and **3c** were separated and purified by column chromatography (on Merck silica gel, Geduran Si 60 (40-63µm), 15 × 3 cm, eluent: 10:1 hexane:ethyl acetate, R_f from TLC: 0.88 (**2c**), 0.66 (**3c**)). The solvent was removed, and the resulting oil was dissolved in dry diethyl ether, transferred to a weighed Schlenk flask, and the solvent was removed under vacuum followed by drying under vacuum, to afford the dry product as a sticky light-brown oil. After storing the neat light brown oil of **2c** for months in a vial or flask few large colourless crystals could be obtained that were suitable for single crystal X-ray diffraction. Yield of **2c**: Yield: 5.40 g (47 %). ^{1}H NMR (400.1 MHz, $CDCl_3$, 295 K) δ = 1.08 (d, J_{HH} = 6.8 Hz, 12H, NCCH(CH_3)$_2$, 2.12 (s, 12H, Ar-*o*-CH_3), 2.27 (s, 6H, Ar-*p*-CH_3), 2.36 (sept, J_{HH} = 6.7 Hz, 2H, NCCH(CH$_3$)$_2$), 4.93 (s, 1H, NCCHCN), 6.86 (s, 4H, Ar-H), 12.26 (s, 1H, NH); ^{13}C{^{1}H} (100.6 MHz, $CDCl_3$, 295 K) δ = 19.3 (NCCH(CH_3)$_2$), 21.0 (NCCH(CH$_3$)$_2$), 22.1 (Ar-CH$_3$), 32.0 (Ar-CH$_3$), 92.8 (NCCHCN), 129.9 (Ar-C), 132.9 (Ar-C), 136.1 (Ar-C), 138.2 (Ar-C), 172.0 (NCCHCN); *m/z* 391 ([M+H]$^+$, 100%), 288 (7%), 274 (25%), 188 (6%), 136 (12%). IR (ATR), $\tilde{\nu}$/cm^{-1}: 2968w, 2934m, 2916w, 1618s, 1491s, 1474m, 1458m, 1256s, 1186m, 1076m, 1051s, 853s, 708m.

Synthesis of *i*PrC(=NMes)CH(=O)*i*Pr 3c

A round bottom flask was added 2,4,6-trimethylaniline (1.83 g, 13.5 mmol, 1 equiv.), 2,6-dimethyl-3,5-heptanedione (2.00 g, 12.8 mmol, 1 equiv.) and *p*-toluenesulfonic acid hydrate (2.51 g, 13.2 mmol, 1 equiv.), and toluene (30 mL) was added. A Dean-Stark trap was attached, and the solution was stirred and heated under reflux for 24 h. Subsequently, the toluene was removed by distillation. The residue was then dissolved in dichloromethane (75 mL) and stirred with a saturated solution of Na_2CO_3 (50 mL) for 0.5 h. The organic layer was then separated, and the aqueous phase was washed with dichloromethane (1 × 30 mL). The combined organic phases were dried over a small amount of $MgSO_4$ only, and the volatiles were removed *in vacuo*. Colourless crystals of the product were obtained from storage of the afforded yellowish oil at 5 °C. Yield: 1.20 g (34 %). ^{1}H NMR (400.1 MHz, $CDCl_3$, 294 K) δ = 1.02 (d, J_{HH} = 6.5 Hz, 6H, CH(CH_3)$_2$), 1.15 (d, J_{HH} = 6.9 Hz, 6H, CH(CH_3)$_2$), 2.16 (s, 6H, Ar-*o*-CH_3), 2.26 (sept, J_{HH} = 6.8 Hz, 1H, CH(CH$_3$)$_2$), 2.28 (s, 3H, Ar-*p*-CH_3), 2.56 (sept, J_{HH} = 6.9 Hz, 1H, CH(CH$_3$)$_2$), 5.22 (s, 1H, NC(iPr)CHCO), 6.89 (s, 2H, Ar-H), 12.12 (s, 1H, N-H); ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, 295 K) δ = 18.3 (OCCH(CH$_3$)$_2$), 20.0 ((OCCH(CH$_3$)$_2$)), 20.9 (Ar-*o*-CH$_3$), 21.8 (Ar-*p*-CH$_3$), 29.1 (NCCH(CH$_3$)$_2$), 40.0 (OCCH(CH$_3$)$_2$), 88.6 (OCCHCN), 128.9 (Ar-C), 133.6 (Ar-C), 135.7 (Ar-C), 136.6 (Ar-C), 173.9 (CNHAr), 203.4 (C=O); IR (ATR), $\tilde{\nu}$/cm^{-1}: 2965w, 2922m, 2866w, 1560s, 1458m, 1358m, 1383m, 1244s; *m/z* 274 ([M+H]$^+$, 100%), 256 (4%), 188 (5%), 134 (3%); M.p.: 70-74 °C.

Synthesis of ^{iPrDip}nacnacH 2a

The following synthetic procedure is a modified version of that recently reported,[4] and has been slightly optimised during several syntheses using fewer equivalents of PPSE and providing sufficient quantities of the correct PPSE isomer.

A Schlenk flask with condenser was charged with phosphorus pentoxide, P_4O_{10} (20.0 g, 70.4 mmol, 2.3 equiv.), hexamethyldisiloxane (46.8 mL, 220 mmol, 7.2 equiv.) and dichloromethane (50 mL). The reaction mixture was heated to reflux for 1.5 h under a stream of nitrogen and then cooled to room temperature. All volatiles were removed *in vacuo*, affording a colourless, viscous syrup of PPSE, which was used *in situ* for the subsequent transformation. 2,6-Dimethyl-3,5-heptanedione (4.98 mL, 30.0 mmol) and 2,6-diisopropylaniline (11.3 mL, 60.0 mmol) were added to the flask in quick succession under a flow of nitrogen. The reaction mixture was then heated to 170 °C and stirred. After 24 h, the reaction solution was cooled to 95 °C and an aqueous solution of NaOH (100 mL of a ca. 2 M solution) was slowly poured down the condenser (CAUTION: exothermic reaction), with vigorous stirring, affording an oily solid. The solid was extracted with dichloromethane (2 × 40 mL), the organic layer was separated, and the aqueous phase was washed with dichloromethane (2 × 30 mL). The organic phases were combined, and the volatiles were removed under reduced pressure to yield the crude product. The crude product was taken up in methanol (40 mL), resulting in the precipitation of a yellow crystalline solid at -40 °C. The solid was then dried under vacuum and analysed to be pure **2a**. Yield: 12.3 g (86 %). The NMR spectroscopic values matched those previously reported.[4]

Synthesis of ^{iPrAr}nacnacH 2b-c and (^{iPrDep}nacnac)PO_2 4b,c via PPSE condensation

General procedure: A Schlenk flask with condenser was charged with phosphorus pentoxide, P_4O_{10} (22.1 g, 77.9 mmol, 4.5 equiv.), hexamethyldisiloxane (47.8 mL, 225 mmol, 12.6 equiv.) and dichloromethane (50 mL). The reaction mixture was heated under reflux for 1.5 h under a gentle stream of nitrogen and then cooled to room temperature. All volatiles were removed *in vacuo*, affording a colourless, viscous syrup of PPSE, which was used *in situ* for the subsequent reaction. 2,6-Dimethyl-3,5-heptanedione (3.00 mL, 17.4 mmol) and the substituted aniline (2.4 equiv.) were added to the flask in quick succession under a flow of nitrogen and the reaction mixture was heated to 170 °C. After 20 h, the reaction solution was cooled to 95 °C and an aqueous solution of NaOH (100 mL of a ca. 2 M solution) was slowly poured down the condenser (CAUTION: exothermic reaction), with vigorous stirring, affording an oily solid. The solid was extracted with dichloromethane (2 × 40 mL), the organic layer was separated, and the aqueous phase was washed with dichloromethane (2 × 30 mL). The organic phases were combined, and the volatiles were removed under reduced pressure to yield the crude product.

^{iPrDep}nacnacH 2b and (^{iPrDep}nacnac)PO_2 4b

Ar = Dep, 2,6-diethylaniline (6.90 mL, 41.9 mmol). The crude product with a mixture of **2b** and **4b** can be converted to **2b** by a simple workup (aqueous NaOH, dichloromethane, vigorous stirring) and crystallisation from methanol or hexane. The ^{1}H NMR and ^{31}P NMR spectroscopic data of the mixture with **2b** and **4b** (integration: 1/0.2) and the isolated **2b** has been determined. Yield (**2b**): 3.89 g (53 %, 9.30 mmol).

Data for ^{iPrDep}nacnacH **2b**: ^{1}H NMR (499.9 MHz, $CDCl_3$, 298 K) δ = 1.08 (d, J_{HH} = 6.8 Hz, 12H, NCCH(CH_3)$_2$, 1.20 (t, J_{HH} = 7.6 Hz, 12H, Ar-*o*-CH_2CH_3), 2.38 (sept, J_{HH} = 6.6 Hz, NCC*H*(CH_3)$_2$), 2.48 (dq, J_{HH} = 15.0, 7.5 Hz, 4H, Ar-*o*-C$H_2$$CH_3$), 2.67 (dq, J_{HH} = 15.0, 7.5 Hz, 4H, Ar-*o*-C$H_2$$CH_3$), 4.98 (s, 1H, NCC*H*CN), 7.07-7.12 (m, 6H, Ar*H*), 12.34 (s, 1H, N-*H*). ^{13}C{^{1}H} (125.7 MHz, $CDCl_3$, 298 K) δ = 14.3 (NCCH(CH_3)$_2$), 21.8 (NC*C*H(CH_3)$_2$), 24.3 (Ar-*o*-CH_2*C*H_3), 30.6 (Ar-*o*-*C*$H_2$$CH_3$), 83.4 (NC*C*HCN), 124.2 (Ar-*C*), 125.5 (Ar-*C*), 137.8 (Ar-*C*), 141.9 (Ar-*C*), 170.7 (N*C*CH*C*N); IR (ATR), ν~/cm^{-1}: 2963m, 2934w, 2874w, 1612s, 1489s, 1447m, 1373m, 1267s, 1173m, 1076m, 1062s, 758s, 669m.

Data for (^{iPrDep}nacnac)PO_2 **4b** (obtained as part of a mixture): ^{1}H NMR (202.4 MHz, C_6D_6, 298 K) δ = 1.16 (d, J_{HH} = 6.8 Hz, 12H, NCCH(CH_3)$_2$, 1.29 (t, J_{HH} = 7.5 Hz, 12H, Ar-*o*-CH_2CH_3), 2.46 (sept, J_{HH} = 6.6 Hz, NCC*H*(CH_3)$_2$), 2.53 (dq, J_{HH} = 15.1, 7.6 Hz, 4H, Ar-*o*-C$H_2$$CH_3$), 3.05 (dq, J_{HH} = 15.1, 7.5 Hz, 4H, Ar-*o*-C$H_2$$CH_3$), 5.88 (s, 1H, NCC*H*CN), 6.97 (d, 2H, Ar-*H*) 7.22 (m, 4H, Ar*H*), 7.35 (m, 2H, Ar*H*); ^{31}P{^{1}H} NMR (202.4 MHz, C_6D_6, 298 K) δ = -18.8 (s).

^{iPrMes}nacnacH 2c and (^{iPrMes}nacnac)PO_2 4c

Ar = Mes, 2,4,6-trimethylaniline (5.88 mL, 41.9 mmol). The crude product was treated with *n*-hexane (40 mL) whereupon ^{iPrMes}nacnacH **2c** dissolved immediately and ^{iPrMes}nacnacPO_2 **4c** precipitated as a white powder which was isolated by filtration and dried under vacuum. Yield: 2.02 g (29 %) of **4c**. Pure ^{iPrMes}nacnacH **2c** was isolated as a light brown oil after the removal of the solvent *in vacuo*. Yield: 3.50 g (51 %) of **2c**. After storing an oily sample of **2c** at room temperature for several months, one large colourless crystal suitable for single crystal X-ray diffraction was obtained. The NMR spectroscopic values of **2c** matched those reported above.

Data for (^{iPrMes}nacnac)PO_2 **4c**: ^{1}H NMR (400.1 MHz, $CDCl_3$, 295 K) δ = 1.18 (d, J_{HH} = 6.9 Hz, 12H, NCCH(CH_3)$_2$, 2.28 (s, 6H, Ar-*p*-CH_3), 2.36 (s, 12H, Ar-*o*-CH_3), 2.52 (sept, J_{HH} = 6.9 Hz, 2H. NCC*H*(CH_3)$_2$), 5.93 (s, 1H, NCC*H*CN), 6.93 (br s, 4H, Ar*H*); ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, 295 K) δ = 19.3 (NCCH(*C*H_3)$_2$), 21.0 (NC*C*H(CH_3)$_2$), 22.1 (Ar-*C*H_3), 32.0 (Ar-*C*H_3), 92.8 (NC*C*HCN), 129.9 (Ar-*C*), 132.9 (Ar-*C*), 136.1 (d, unresolved, Ar-*C*), 138.2 (Ar-*C*), 178.0 (N*C*CH(CH_3)$_2$); ^{31}P{^{1}H} (162.0 MHz, $CDCl_3$, 294 K) δ = -18.6 (s).

Synthesis of ^{PhDip}nacnacH 5

A Schlenk flask with condenser was charged with phosphorus pentoxide, P_4O_{10} (10.0 g, 35.2 mmol, 3.1 equiv.), hexamethyldisiloxane (29.0 mL, 136 mmol, 12 equiv.) and dichloromethane (40 mL). The reaction mixture was heated to reflux for 1.5 h under a gentle stream of nitrogen and was then cooled to room temperature. All volatiles were removed *in vacuo*, affording a colourless, viscous syrup of PPSE, which was used *in situ* for the subsequent reaction. 1,3-Diphenylpropanedione (2.50 g, 11.1 mmol) and 2,6-diisopropylaniline (4.40 mL, 23.3 mmol, 2.1 equiv.) were added to the flask in quick succession under a flow of nitrogen. The reaction mixture was then heated to 170 °C. After 24 h, the reaction solution was cooled to 95 °C and an aqueous solution of NaOH (100 mL of a 1.5 M solution) was slowly poured down the condenser (CAUTION: exothermic reaction), with vigorous stirring, affording an oily solid. The solid was extracted with dichloromethane (2 × 40 mL), the organic layer was separated, and the aqueous phase was washed with dichloromethane (2 × 30 mL). The organic phases were combined, and all volatiles were removed under reduced pressure to yield the crude product. The crude product was extracted with methanol (40 mL), resulting in the precipitation of a crystalline solid at -40 °C. The solid was then dried under vacuum to afford **5** as a bright orange powder. Yield: 3.37 g (56 %). The NMR spectroscopic values matched those reported previously.[5]

Proligand recycling

Valuable ^{RAr}nacnacH proligands can be recycled if the further chemistry and reaction constituents do not involve special risks or special waste disposal. Reaction residues containing ^{RAr}nacnac-complexes can be collected in labelled waste bottles containing water and washed in with small quantities of alcohol for hydrolysis. For some proligands, it is advantageous to allow hydrolysis to complete before significant exposure to air occurs. The collected residues can be worked up by removing volatile organics, followed by an aqueous work-up (dichloromethane, aqueous Na_2CO_3 solution, collecting the organic phase, drying/filtering with a small amount of $MgSO_4$ and removing all volatiles) similar to those described as reaction workups. The crude products can typically be precipitated using cold methanol or recrystallized using alcohols or *n*-hexane (low temperature) typically allowing an estimated 50-90 % of proligand to be recovered.

Synthesis of [(^{iPrDip}nacnac)Li] 6a

Method 1: To a J. Young NMR tube containing a solution of ^{iPrDip}nacnacH **2a** (18 mg, 37.9 µmol, 1equiv.) was added [Li(NEt_2)] (3.15 mg, 39.8 µmol, 1.05 equiv.) in C_6D_6 (0.6 mL). The full conversion of **2a** was observed after keeping the reaction mixture at 60 °C for two days. Stacked spectra of the reaction process can be seen in Figure S52.

Method 2: To a cold (-78 °C) solution of ^{iPrDip}nacnacH **2a** (3.00 g, 6.33 mmol, 1 equiv.) in *n*-hexane (40 mL) was added *n*BuLi (3.96 mL of 1.6 M solution in hexanes, 6.33 mmol, 1 equiv.) and the resultant solution was stirred at this temperature for 0.5 h. The mixture was warmed to room temperature and stirred for an additional 2 hours affording a precipitate. The first crop of [(^{iPrDip}nacnac)Li] **6a** was isolated by filtration of the reaction solution as a yellow powder. The filtrate was concentrated to approximately 15 mL and subsequent crops of **6a** were afforded by storage of this solution at -40 °C. Yield: 2.72 g (90 %). ^{1}H NMR (499.9 MHz, C_6D_6, 298 K) δ = 1.03 (d, J_{HH} = 6.8 Hz, 12H, NCCH(CH_3)$_2$),1.19 (d, J_{HH} = 6.6 Hz, 12H, Ar-*o*-CH(CH_3)$_2$), 1.20 (d, J_{HH} = 6.6 Hz, 12H, Ar-*o*-CH(CH_3)$_2$), 2.66 (sept, J_{HH} = 6.8 Hz, 2H, NCC*H*(CH$_3$)$_2$), 3.23 (sept, J_{HH} = 6.9 Hz, 4H, Ar-*o*-C*H*(CH$_3$)$_2$), 4.85 (s, 1H, NCC*H*CN), 7.10-7.13 (s, 4H, Ar*H*); ^{7}Li{^{1}H} NMR (156.0 MHz, C_6D_6, 298 K) δ = 1.34 (s); ^{13}C{^{1}H} (125.7 MHz, C_6D_6, 298 K) δ = 23.0 (NCCH(*C*H$_3$)$_2$), 23.6 (Ar-*o*-CH(*C*H$_3$)$_2$), 24.9 (Ar-*o*-CH(*C*H$_3$)$_2$), 27.2 (Ar-*C*H(CH$_3$)$_2$), 31.9 (NC*C*H(CH$_3$)$_2$), 82.4 (NC*C*HCN), 122.8 (Ar-*C*), 123.2 (Ar-*C*), 128.0 (Ar-*C*), 140.8 (Ar-*C*), 147.7(Ar-*C*), 173.4 (N*C*CH*C*N).

Synthesis of [(^{EtDip}nacnac)Li] 6b

To a cold (-78 °C) solution of ^{EtDip}nacnacH **1a** (3.00 g, 6.72 mmol, 1 equiv.) in *n*-hexane (40 mL) was added *n*BuLi (4.2 mL of 1.6 M solution in hexanes, 6.72 mmol, 1 equiv.) and the resultant solution was stirred at this temperature for 0.5 h. The mixture was warmed to room temperature and stirred for an additional two hours forming a precipitate. The first crop of [(^{EtDip}nacnac)Li] **6b** was isolated by filtration of the reaction solution as a yellow powder. The filtrate was concentrated to approximately 15 mL and subsequent crops of **6b** were afforded by storage of this solution at -40 °C. Yield: 2.07 g (68 %). ^{1}H NMR (499.9 MHz, C_6D_6, 298 K) δ = 1.10 (d, J_{HH} = 6.9 Hz, 12H, Ar-*o*-CH(CH_3)$_2$), 1.14 (t, J_{HH} = 7.6 Hz, 6H, NCCH$_2$CH_3) 1.18 (d, J_{HH} = 6.9 Hz, 12H, Ar-*o*-CH(CH_3)$_2$), 2.19 (q, J_{HH} = 7.6 Hz, 4H, NCCH_2CH$_3$), 3.14 (sept, J_{HH} = 6.9 Hz, 4H, Ar-*o*-C*H*(CH$_3$)$_2$), 4.96 (s, 1H, NCC*H*CN), 7.11-7.14 (m, 4H, Ar-*H*), 7.17 (m, 2H, Ar-*H*); ^{7}Li{^{1}H} NMR (155.5 MHz, C_6D_6, 298 K) δ = 0.89 (s); ^{13}C{^{1}H} NMR (125.7 MHz, C_6D_6, 298 K): δ = 13.2 (NCCH$_2$*C*H$_3$), 23.6 (Ar-*o*-CH(*C*H$_3$)$_2$), 24.1 (Ar-*o*-CH(*C*H$_3$)$_2$), 27.7 (Ar-*o*-*C*H(CH$_3$)$_2$), 28.3 (NCCH_2CH$_3$), 87.3 (NC*C*HCN), 122.9 (Ar-*C*), 123.1 (Ar-*C*), 140.6 (Ar-*C*), 148.3 (Ar-*C*), 168.5 (N*C*CH*C*N).

Synthesis of [(^{iPrDip}nacnac)Na] 7a

Method 1: To a J. Young NMR tube containing a solution of ^{iPrDip}nacnacH **2a** (15 mg, 31.6 µmol) and an internal standard (hexamethylbenzene, 9.24 µmol, ca. 0.3 equiv.) was added [Na{N(SiMe$_3$)$_2$}] (6.37 mg, 34.8 µmol, 1.1 equiv.) in C_6D_6 (0.6 mL). The reaction process was observed via ^{1}H NMR spectroscopy, and stacked spectra can be seen in Figure S53. This showed that essentially full

conversion to compound **7a** was achieved after heating the reaction mixture at 60 °C for five days; an *in-situ* yield of only 76 % was determined by integration against the internal standard.

Method 2: To a cold (-78 °C) mixture of freshly made *n*BuNa (400 mg, 5.00 mmol, 1.1 equiv.) and ^{iPrDip}nacnacH **2a** (2.16 g, 4.54 mmol, 1 equiv.) was added *n*-hexane (40 mL) and the resultant mixture was stirred at this temperature for 15 minutes before warming to room temperature. The resulting brown mixture was stirred for an additional 2 h, was allowed to settle, was filtered, and the solvent was removed *in vacuo*. The solid residue was washed with *n*-hexane (ca. 5 ml) and dried under vacuum to give a pale brown solid of [(^{iPrDip}nacnac)Na] **7a**. Yield: 1.44 g (64 %). ^{1}H NMR (499.9 MHz, C_6D_6, 298 K) δ = 1.06 (d, J_{HH} = 6.8 Hz, 12H, NCCH(CH_3)$_2$), 1.23 (d, J_{HH} = 6.6 Hz, 24H, Ar-*o*-CH(CH_3)$_2$), 2.59 (sept, J_{HH} = 6.7 Hz, 2H, NCCH(CH$_3$)$_2$), 3.30 (sept, J_{HH} = 6.9 Hz, 4H, Ar-*o*-CH(CH$_3$)$_2$), 4.57 (s, 1H, NCCHCN), 7.02-7.08 (m, 2H, Ar-*H*), 7.14 (s, 2H, Ar-*H*), 7.17 (m, 2H, Ar-*H*). ^{13}C{^{1}H} NMR (100.6 MHz, C_6D_6, 295 K) δ = 23.1 (NCCH(*C*H$_3$)$_2$), 23.6 (Ar-*o*-CH(*C*H$_3$)$_2$), 25.0 (ArCH(*C*H$_3$)$_2$), 26.9 (Ar*C*H(CH$_3$)$_2$), 32.7 (NC*C*H(CH$_3$)$_2$), 80.0 (NC*C*HCN), 121.2 (Ar-C), 123.1 (Ar-*C*), 139.6 (Ar-*C*), 149.3 (Ar-*C*), 171.9 (N*C*CH*C*N).

Synthesis of [(^{EtDip}nacnac)Na] 7b

Method 1: To a J. Young NMR tube containing a solution of ^{EtDip}nacnacH **1a** (14.1 mg, 31.6 µmol, 1 equiv.) and hexamethylbenzene (9.24 µmol, ca. 0.3 equiv.) was added [Na{N(SiMe$_3$)$_2$}] (6.38 mg, 34.8 µmol, 1.1 equiv.) in C_6D_6 (0.6 mL). The reaction process was observed via ^{1}H NMR spectroscopy, and stacked spectra can be seen in Figure S56. The full conversion to [(^{EtDip}nacnac)Na] **7b** was observed after heating the reaction mixture at 60 °C overnight.

Method 2: To a cold (-78 °C) mixture of freshly made *n*BuNa (400 mg, 5.00 mmol, 1.1 equiv.) and ^{EtDip}nacnacH **1a** (2.03 g, 4.54 mmol, 1 equiv.) was added *n*-hexane (40 mL) and the resulting mixture was stirred at this temperature for 15 minutes. The mixture was warmed to room temperature and stirred for an additional 2 h. The resultant brown mixture was allowed to settle, was filtered, and the solvent was removed *in vacuo*. The solid residue was washed with *n*-hexane (ca. 5 ml) and dried *in vacuo* to give a pale brown solid of [(^{EtDip}nacnac)Na] **7b**. Yield: 1.64 g (77 %). ^{1}H NMR (400.0 MHz, C_6D_6, 298 K) δ = 1.09 (d, J_{HH} = 6.9 Hz, 12H, Ar-*o*-CH(CH_3)$_2$), 1.18 (t, J_{HH} = 7.6 Hz, 6H, NCCH$_2$CH_3), 1.23 (d, J_{HH} = 6.9 Hz, 12H, Ar-*o*-CH(CH_3)$_2$), 2.17 (q, J_{HH} = 7.6 Hz, 4H, NCCH_2CH$_3$), 3.26 (sept, J_{HH} = 6.7 Hz, 4H, Ar-*o*-CH(CH$_3$)$_2$), 4.73 (s, 1H, NCCHCN), 7.04-7.11 (m, 6H, Ar-*H*). ^{13}C{^{1}H} NMR (100.7 MHz, C_6D_6, 300 K): δ = 13.6 (NCCH$_2$*C*H$_3$), 23.4 (Ar-*o*-CH(*C*H$_3$)$_2$), 24.4 (Ar-*o*-CH(*C*H$_3$)$_2$), 27.3 (Ar-*o*-*C*H(CH$_3$)$_2$), 28.9 (NC*C*H$_2$CH$_3$), 85.7 (NC*C*HCN), 121.4 (Ar-*C*), 123.0 (Ar-*C*), 142.5 (Ar-*C*), 149.8 (Ar-*C*), 167.4 (N*C*CH*C*N).

Synthesis of [(^{iPrDip}nacnac)K] 8a

Method 1: To a J. Young NMR tube containing a solution of ^{iPrDip}nacnacH **2a** (15 mg, 31.6 µmol) and an internal standard (hexamethylbenzene, 9.80 µmol, ca. 0.3 equiv.) was added [K{N(SiMe$_3$)$_2$}] (6.94 mg, 34.8 µmol, 1.1 equiv.) in C_6D_6. The full conversion of **2a** and formation of **8a** was observed after heating the reaction mixture at 60 °C for five days.

Method 2: To a cold (0 °C) stirred slurry of benzyl potassium (302 mg, 2.32 mmol, 1.1 equiv.) in toluene (40 mL) was added a toluene (30 mL) solution of ^{iPrDip}nacnacH **2a** (1.00 g, 2.11 mmol, 1 equiv.) and the bright orange reaction mixture was vigorously stirred at room temperature for 1 hour. The resultant brownish solution was allowed to settle and filtered. Volatiles of the yellow filtrate were removed under vacuum resulting in a foamy paste, which was washed with *n*-hexane (ca. 5 ml) and dried *in vacuo* to give a pale-yellow solid of [(^{iPrDip}nacnac)K] **8a**. Yield: 0.86 g (80 %). ^{1}H NMR (400.1 MHz, C_6D_6, 298 K) δ = 1.01 (d, J_{HH} = 6.8 Hz, 12H, NCCH(C*H*$_3$)$_2$), 1.28 (d, J_{HH} = 6.9 Hz, 24H, Ar-*o*-CH(C*H*$_3$)$_2$), 2.56 (sept, J_{HH} = 6.7 Hz, 2H, NCC*H*(CH$_3$)$_2$), 3.39 (sept, J_{HH} = 6.9 Hz, 4H, Ar-o-C*H*(CH$_3$)$_2$), 4.65 (s, 1H, NCC*H*CN), 6.98-7.03 (m, 5H, Ar-*H*), 7.12 (s, 1H, Ar-*H*), 7.13 (s, 3H, Ar-*H*), 7.15 (s, 2H, Ar-*H*); ^{13}C{^{1}H} NMR (100.6 MHz, C_6D_6, 298 K) δ = 23.6 (NCCH(*C*H$_3$)$_2$), 24.1 (Ar-*o*-CH(*C*H$_3$)$_2$), 25.4 (Ar-*o*-CH(*C*H$_3$)$_2$), 27.0 (Ar-*o*-*C*H(CH$_3$)$_2$), 33.5 (NC*C*H(CH$_3$)$_2$), 80.4 (NC*C*HCN), 120.8 (Ar-*C*), 139.6 (Ar-*C*), 149.8 (Ar-*C*), 176.6 (N*C*CH*C*N).

Synthesis of [(^{EtDip}nacnac)K] 8b

To a cold (0 °C) stirred slurry of benzyl potassium (805 mg, 6.18 mmol, 1.1 equiv.) in toluene (40 mL) was added a toluene (20 mL) solution of ^{EtDip}nacnacH (2.51 g, 5.62 mmol, 1 equiv.) and the bright orange reaction mixture was vigorously stirred at room temperature for 1 hour. The resultant brown solution was allowed to settle and filtered. Volatiles of the yellow filtrate were removed under vacuum resulting in foamy pasta, which was washed with *n*-hexane (ca. 5 ml) and dried under vacuum to give a pale-yellow solid of [(^{EtDip}nacnac)K] **8b**. Yield: 2.73 g (91 %). ^{1}H NMR (400.1 MHz, C_6D_6, 300 K) δ = 1.04 (d, J_{HH} = 6.9 Hz, 12H, Ar-*o*-CH(C*H*$_3$)$_2$), 1.24 (t, J_{HH} = 7.6 Hz, 6H, NCCH$_2$C*H*$_3$), 1.26 (d, J_{HH} = 6.9 Hz, 12H, Ar-*o*-CH(C*H*$_3$)$_2$), 2.24 (q, J_{HH} = 7.6 Hz, 4H, NCC*H*$_2$CH$_3$), 3.37 (sept, J_{HH} = 6.9 Hz, 4H, Ar-*o*-C*H*(CH$_3$)$_2$), 4.83 (s, 1H, NCC*H*CN), 6.99-7.05 (m, 2H, Ar-*H*), 7.14 (s, 4H, Ar-*H*); ^{13}C{^{1}H} NMR (100.7 MHz, C_6D_6, 298 K): δ = 13.9 (NCCH$_2$*C*H$_3$), 23.5 (Ar-*o*-CH(*C*H$_3$)$_2$), 24.5 (Ar-*o*-CH(*C*H$_3$)$_2$), 27.1 (Ar-*o*-*C*H(CH$_3$)$_2$), 29.2 (NCC*H*$_2$CH$_3$), 86.1 (NC*C*HCN), 120.7 (Ar-*C*), 123.3 (Ar-*C*), 139.2 (Ar-*C*), 149.9 (Ar-*C*), 165.2 (N*C*CH*C*N).

Comments on the deprotonation of ^{iPrDip}nacnacH 2a with alkali metal amide bases

The rate of deprotonation of **2a** followed the trend [Li(NEt$_2$)] > [K{N(SiMe$_3$)$_2$}] > /≈ [Na{N(SiMe$_3$)$_2$}] and spectra for some *in-situ* NMR spectroscopic studies are provided in Figures

S50-S52. Full conversion of **2a** to the lithium complex **6a** can be achieved with [Li(NEt$_2$)] at 60 °C for two days. The *in-situ* yields of 76 % (**7a**) and 100 % (**8a**) were obtained from the reactions of **2a** with [Na{N(SiMe$_3$)$_2$}] and [K{N(SiMe$_3$)$_2$}], respectively. (Please note that [K{N(SiMe$_3$)$_2$}] is more soluble than Na{N(SiMe$_3$)$_2$}] in deuterated benzene at room temperature).

Reactions of ^{RDip}nacnacH, R = Me, Et, iPr, with [Na{N(SiMe$_3$)$_2$}]

To a J. Young NMR tube containing a solution of ^{RDip}NacnacH (31.6 µmol, 1 equiv.) in C_6D_6 (0.6 mL) with an internal standard (hexamethylbenzene, 9.80 µmol, ca. 0.3 equiv.) was added [Na{N(SiMe$_3$)$_2$}] (6.37 mg, 34.8 µmol, 1.1 equiv.) and the reaction progress was monitored by ^{1}H NMR spectroscopy at room temperature or 60 °C (see Figures S51, S53, and S54). The rate of the deprotonation reaction followed the trend: ^{MeDip}nacnacH > ^{EtDip}nacnacH **1a** > ^{iPrDip}nacnacH **2a**.

Synthesis of (^{EtDip}nacnac)SiBr 9

Benzene (35 mL) was added to a cold (ca. 10 °C) stirring mixture of [(^{EtDip}nacnac)Li] **6b** (502 mg, 1.06 mmol, 1 equiv.) and (SIDip)SiBr$_2$ (312 mg, 1.10 mmol, 1.04 equiv.) and the resultant deep red solution was stirred for 4 h. The resultant orange-red reaction mixture was allowed to settle and filtered. All volatiles of the orange filtrate were removed under vacuum resulting in an orange residue, which was dissolved in *n*-pentane (15 mL) and stored at -40 °C to afford **9** as orange block-like crystals. Yield: 252 mg (43 %). ^{1}H NMR (499.9 MHz, C_6D_6, 298 K) δ = 0.84 (t, J_{HH} = 7.6 Hz, 6H, NCCH$_2$C*H*$_3$) 1.02 (d, J_{HH} = 6.9 Hz, 12H, Ar-*o*-CH(C*H*$_3$)$_2$), 1.21 (d, J_{HH} = 6.9 Hz, 12H, Ar-*o*-CH(C*H*$_3$)$_2$), 1.25 (d, J_{HH} = 6.9 Hz, 12H, Ar-*o*-CH(C*H*$_3$)$_2$), 1.55 (d, J_{HH} = 6.9 Hz, 12H, Ar-*o*-CH(C*H*$_3$)$_2$), 2.00 (dq, J_{HH} = 14.8, 6.6 Hz, 4H, NCC*H*$_2$CH$_3$), 3.10 (sept, J_{HH} = 6.9 Hz, 2H, Ar-*o*-C*H*(CH$_3$)$_2$), 4.03 (sept, J_{HH} = 6.9 Hz, 2H, Ar-*o*-C*H*(CH$_3$)$_2$), 5.72 (s, 1H, NCC*H*CN), 7.05-7.07 (m, 2H, Ar-*H*), 7.15-7.19 (m, 4H, Ar-*H*); ^{29}Si{^{1}H} NMR (99.3 MHz, C_6D_6, 298 K) δ = -7.4 (s); ^{13}C{^{1}H} NMR (125.7 MHz, C_6D_6, 298 K): δ = 12.1 (NCCH$_2$*C*H$_3$), 23.9 (Ar-*o*-CH(*C*H$_3$)$_2$), 24.7 (Ar-*o*-CH(*C*H$_3$)$_2$), 27.6 (Ar-*o*-*C*H(*C*H$_3$)$_2$), 28.5 (Ar-*o*-*C*H(CH$_3$)$_2$), 29.0 (Ar-*o*-*C*H(CH$_3$)$_2$), 101.0 (NC*C*HCN), 124.2 (Ar-*C*H), 125.4 (Ar-*C*H), 128.2 (Ar-*C*H), 144.6 (Ar-*C*), 147.4 (Ar-*C*), 171.7 (Ar-*C*). Anal. Calcd for $C_{31}H_{45}BrN_2Si{\cdot}0.5C_5H_{12}$: C, 68.22; H, 8.72; N, 4.75. Found: C, 68.97; H, 8.44; N, 4.89. M.p.: 181-184 °C.

Synthesis of (^{EtDip}nacnac')Si 10

Toluene (15 mL) was added to a solid mixture of (^{EtDip}nacnac)SiBr **9** (100 mg, 0.180 mmol, 1 equiv.) and [K{N(SiMe$_3$)$_2$}] (38.0 mg, 0.190 mmol, 1.05 equiv.) at room temperature, and the resulting orange mixture was stirred at room temperature for two hours. The volatiles were removed under vacuum resulting in a yellowish residue, which was extracted with *n*-hexane (5 mL) and then toluene

(5 mL). A yellowish crystalline solid was obtained from the above hexane (as large hexagonal plates) and toluene extracts at -40 °C and analysed as **10**. Yellow crystals suitable for single crystal X-ray diffraction analysis were obtained from a concentrated benzene-d_6 solution. Yield = 35.2 mg (36 %). Additionally, the full conversion to **10** was observed within an hour at room temperature when conducting the reaction with **9** (10 mg, 0.018 mmol, 1 equiv.) and [K{N(SiMe$_3$)$_2$}] (3.8 mg, 0.019 mmol, 1.05 equiv.) in C_6D_6 (0.6 mL). ^{1}H-NMR (400.1 MHz, C_6D_6, 298 K): δ = 0.85 (t, J_{HH} = 7.1 Hz, 3H, NCCH$_2$C*H*$_3$), 1.21 (d, J_{HH} = 6.3 Hz, 6H, Ar-*o*-CH(C*H*$_3$)$_2$), 1.30 (d, J_{HH} = 7.9 Hz, 6H, Ar-*o*-CH(C*H*$_3$)$_2$), 1.34 (d, J_{HH} = 7.3 Hz, 6H, Ar-*o*-CH(C*H*$_3$)$_2$), 1.36 (d, J_{HH} = 7.3 Hz, 6H, Ar-*o*-CH(C*H*$_3$)$_2$), 1.62 (d, J_{HH} = 8.0 Hz, 3H, =CHC*H*$_3$), 1.79 (q, J_{HH} = 7.0 Hz, 2H, NCC*H*$_2$CH$_3$), 3.56 (sept, J_{HH} = 7.4 Hz, 2 H, Ar-*o*-C*H*(CH$_3$)$_2$), 3.68 (sept, J_{HH} = 6.5 Hz, 2 H, Ar-*o*-C*H*(CH$_3$)$_2$), 3.84 (q, J_{HH} = 7.4 Hz, 1 H, =C*H*CH$_3$), 5.68 (s, 1H, NCC*H*CN), 7.09 (m, 2H, Ar-C*H*), 7.23 (m, 4H, Ar-C*H*). ^{13}C{^{1}H} NMR (100.6 MHz, C_6D_6, 295 K): δ = 11.1 (NCCH$_2$*C*H$_3$), 11.4 (=CH*C*H$_3$), 23.0 (Ar-*o*-CH(*C*H$_3$)$_2$), 24.2 (Ar-*o*-CH(*C*H$_3$)$_2$), 25.0 (Ar-*o*-CH(*C*H$_3$)$_2$), 25.2 (Ar-*o*-CH(*C*H$_3$)$_2$), 26.3 (NC*C*H$_2$CH$_3$), 28.2 (Ar-*o*-*C*H(CH$_3$)$_2$), 28.3 (Ar-*o*-*C*H(CH$_3$)$_2$), 93.5 (=*C*HCH$_3$), 100.0 (NC*C*HCN), 123.8 (Ar-*C*H), 124.3 (Ar-*C*H), 136.8 (Ar-*o*-*C*), 136.9 (Ar-*o*-*C*), 141.0 (N*C*=CHCH$_3$), 143.9 (N*C*CH*C*N), 147.8 (Ar-*C*). ^{29}Si{^{1}H} NMR (99.3 MHz, C_6D_6, 298 K) δ = 87.9 (s). IR (ATR), $\tilde{\nu}$/cm^{-1}: 2961m, 2922m, 2866m, 1588w, 1641s, 1460s, 1246s, 1043m, 800s, 754m. The sample sent for elemental analysis was slightly low in C,H,N, but agrees well when a small contamination of salt (e.g. KBr) is modelled, e.g. Anal. Calcd for **10**$_6$(KBr): C, 75.58; H, 9.00; N, 5.69. Found: C, 75.54; H, 8.93; N, 5.36. M.p.: 170-172 °C.

2 NMR Spectroscopy

NMR spectra were recorded in deuterated benzene (or deuterated chloroform) and further details are given in the figure captions. In some samples, resonances of residual solvent and silicone grease (as impurities) may be present; for example silicone grease (literature values in deuterated benzene: ^{1}H: 0.29 ppm, ^{13}C{^{1}H}: 1.38, marked as orange circles), toluene (^{1}H: 2.11, 7.02, 7.13 ppm, ^{13}C{^{1}H}: 21.10, 125.68, 128.56, 129.33, 137.91), and *n*-hexane (^{1}H: 0.89, 1.24, ^{13}C{^{1}H}: 14.32, 23.04, 31.96).[4]

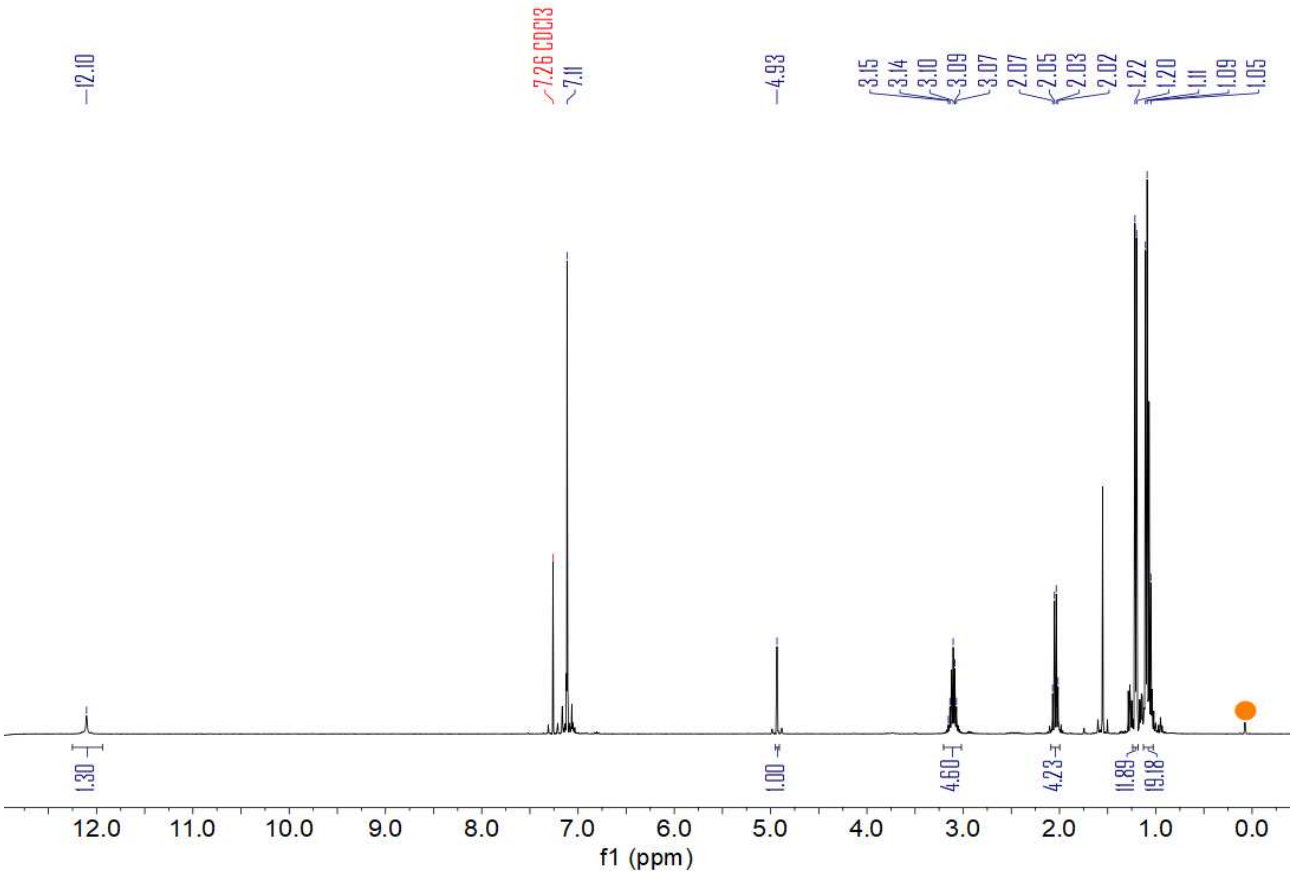


Figure S1. ^{1}H NMR spectrum (400.3 MHz, $CDCl_3$, 297 K) of ^{EtDip}nacnacH **1a**. The orange circle denotes the chemical shift of silicone grease.

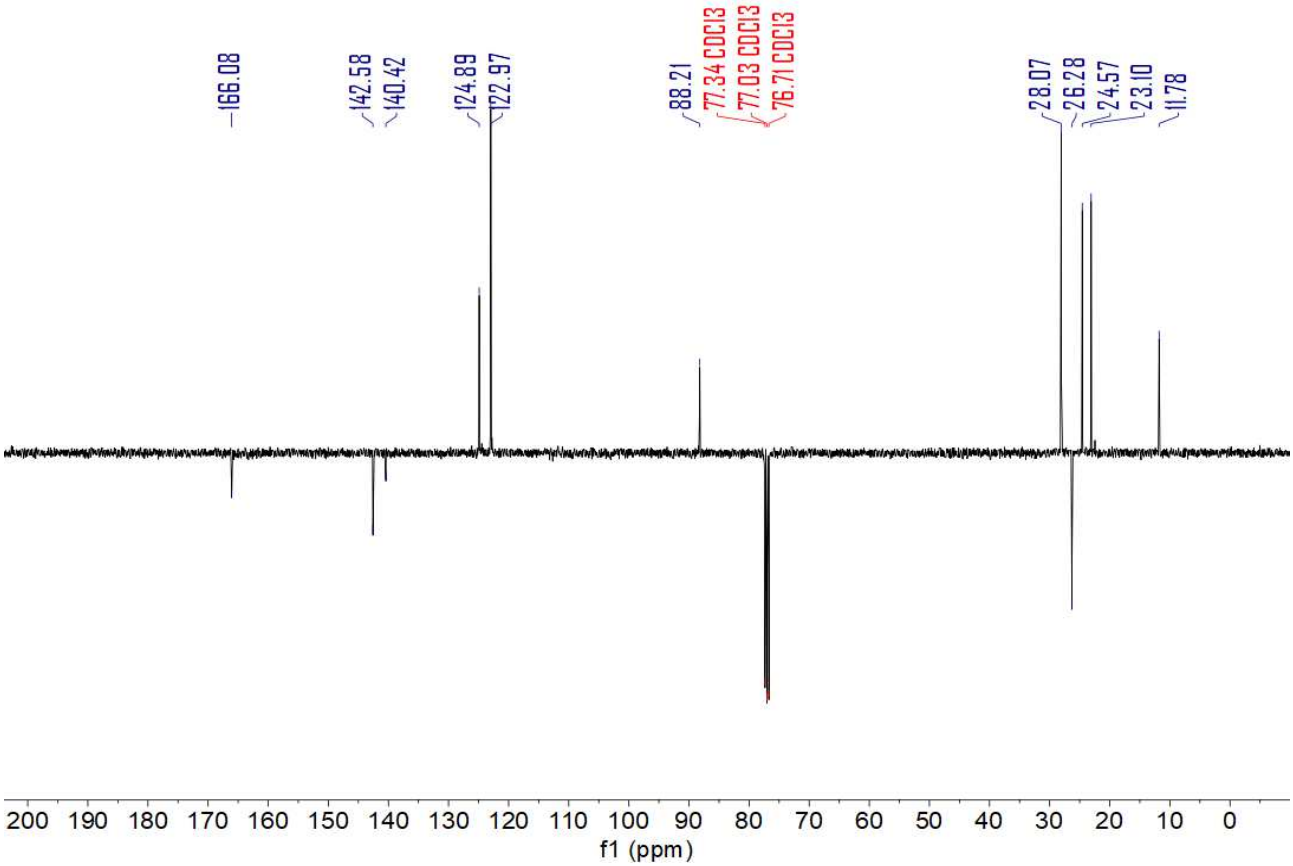


Figure S2. ^{13}C{^{1}H} DEPTQ NMR spectrum (100.7 MHz, $CDCl_3$, 297 K) of ^{EtDip}nacnacH **1a**.

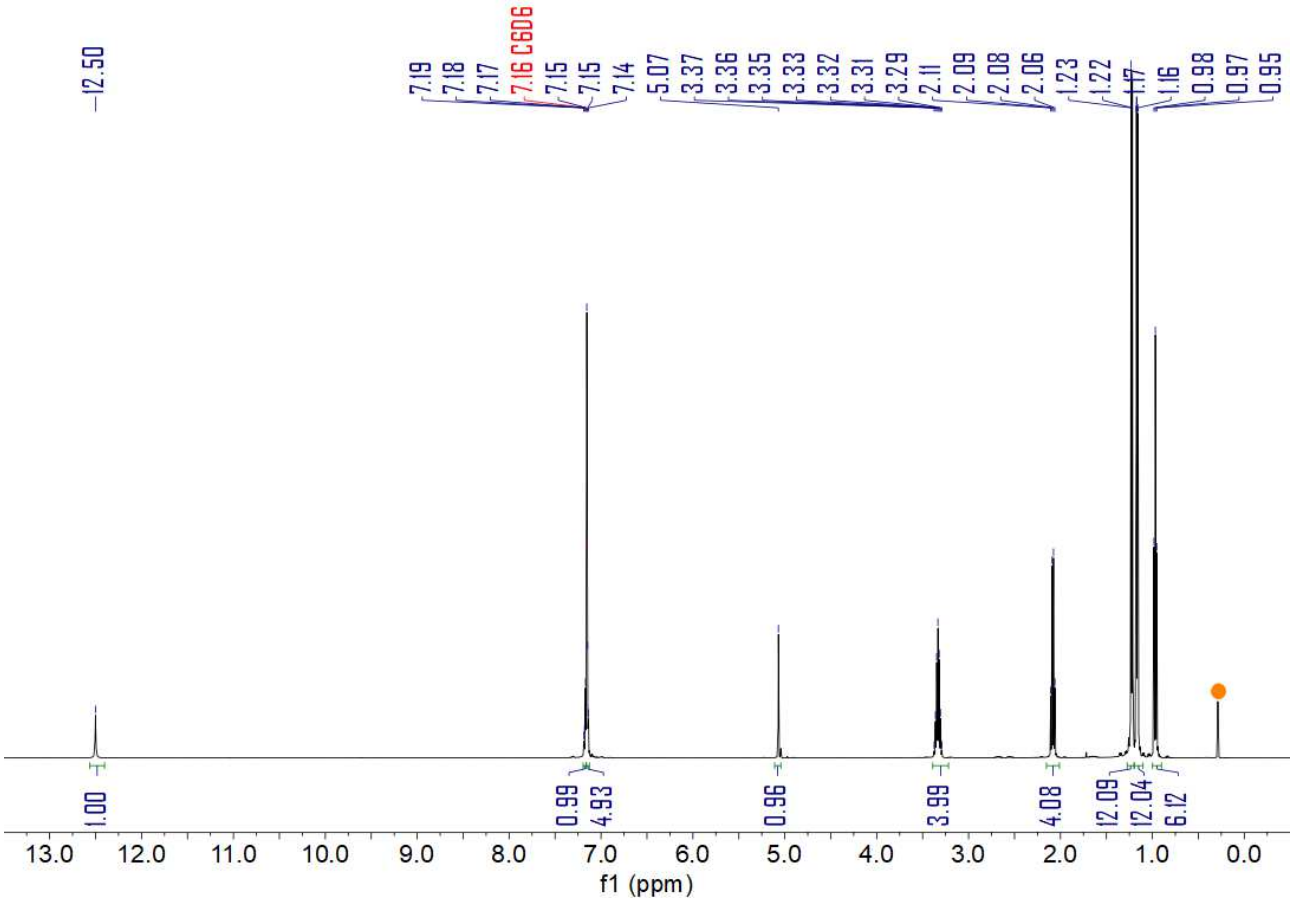


Figure S3. ^{1}H NMR spectrum (400.1 MHz, C_6D_6, 300 K) of ^{EtDip}nacnacH **1a**. The orange circle denotes the chemical shift of silicone grease.

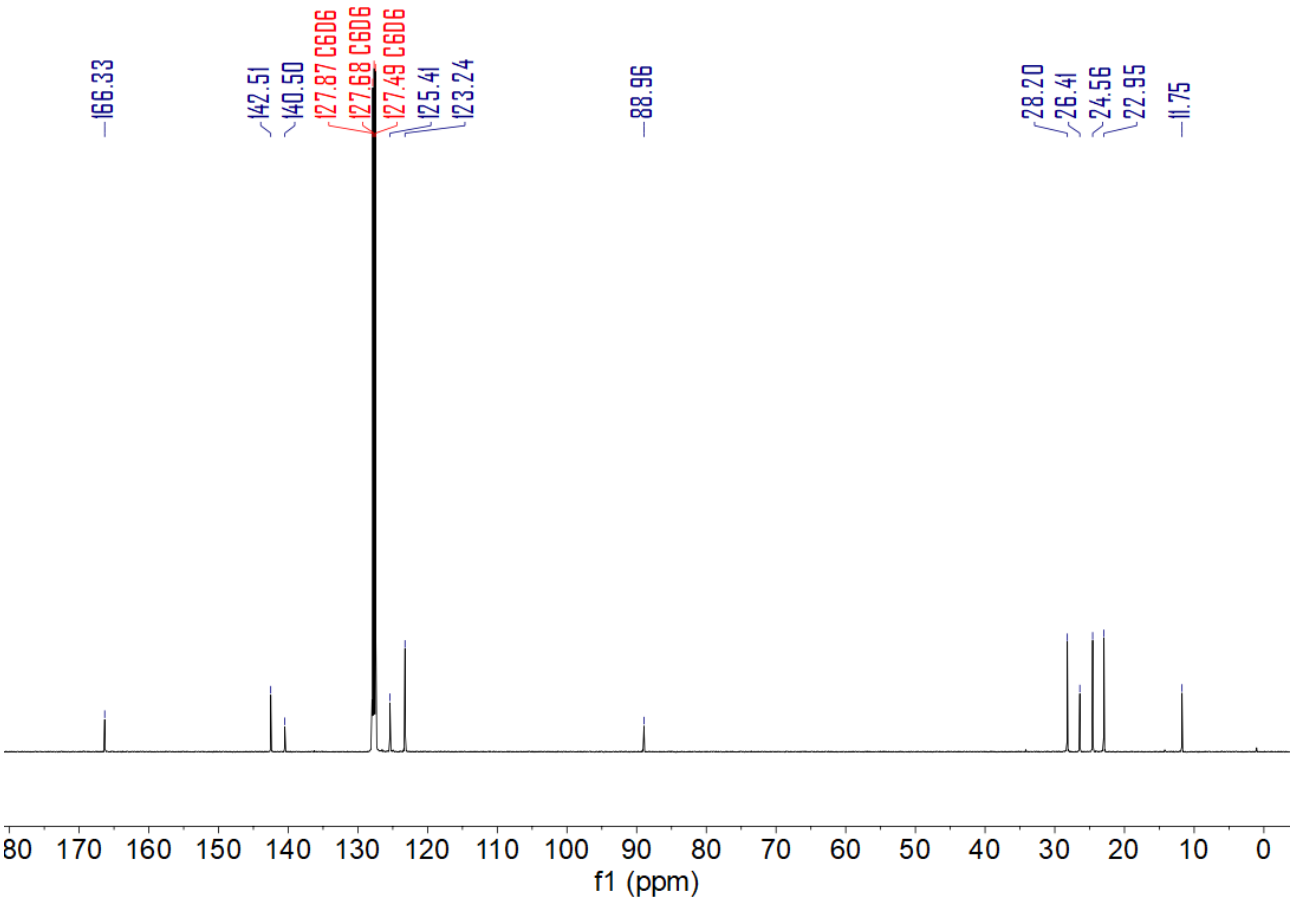


Figure S4. $^{13}C\{^{1}H\}$ NMR spectrum (100.6 MHz, C_6D_6, 300 K) of ^{EtDip}nacnacH **1a**.

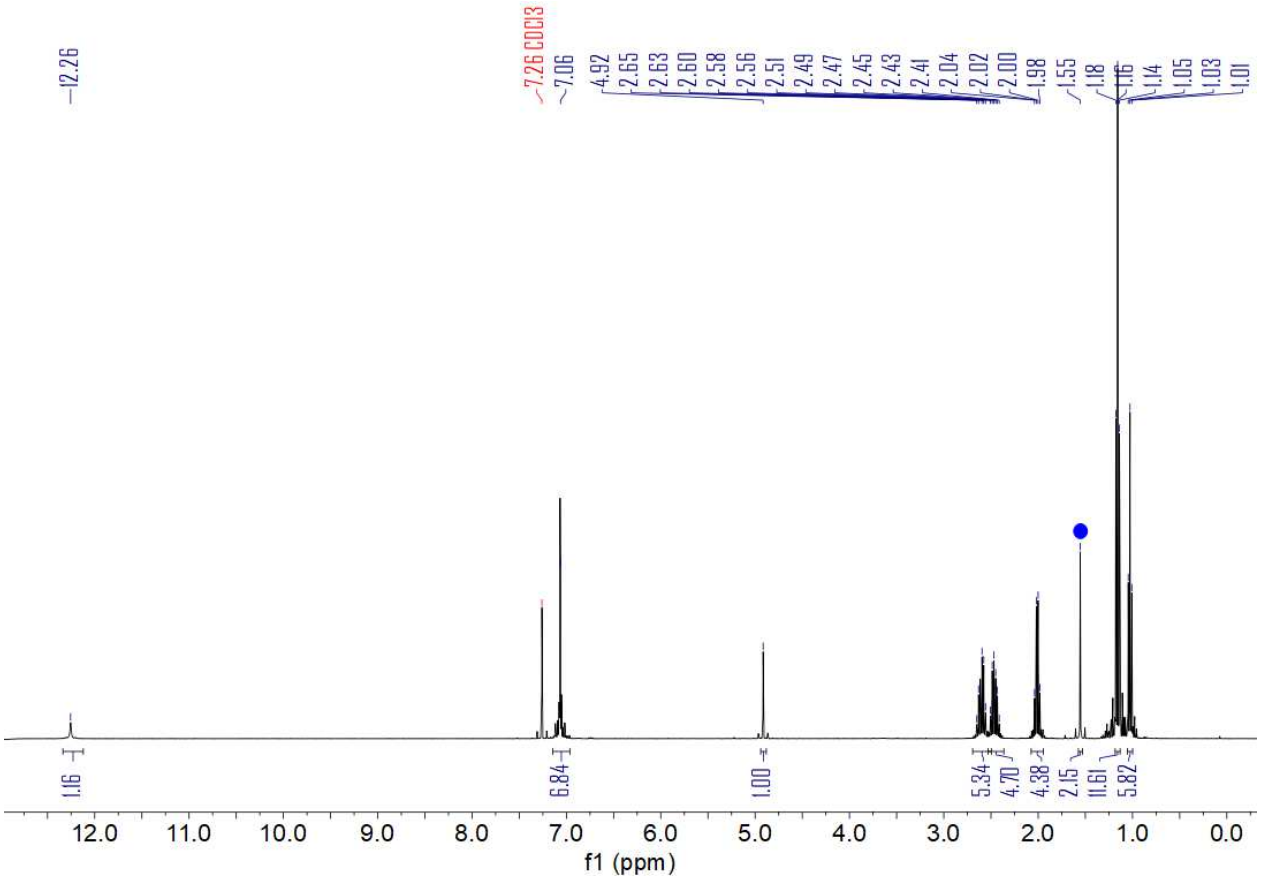


Figure S5. ^{1}H NMR spectrum (400.1 MHz, $CDCl_3$, 298 K) of ^{EtDep}nacnacH **1b**. The blue circle denotes the resonance of water.

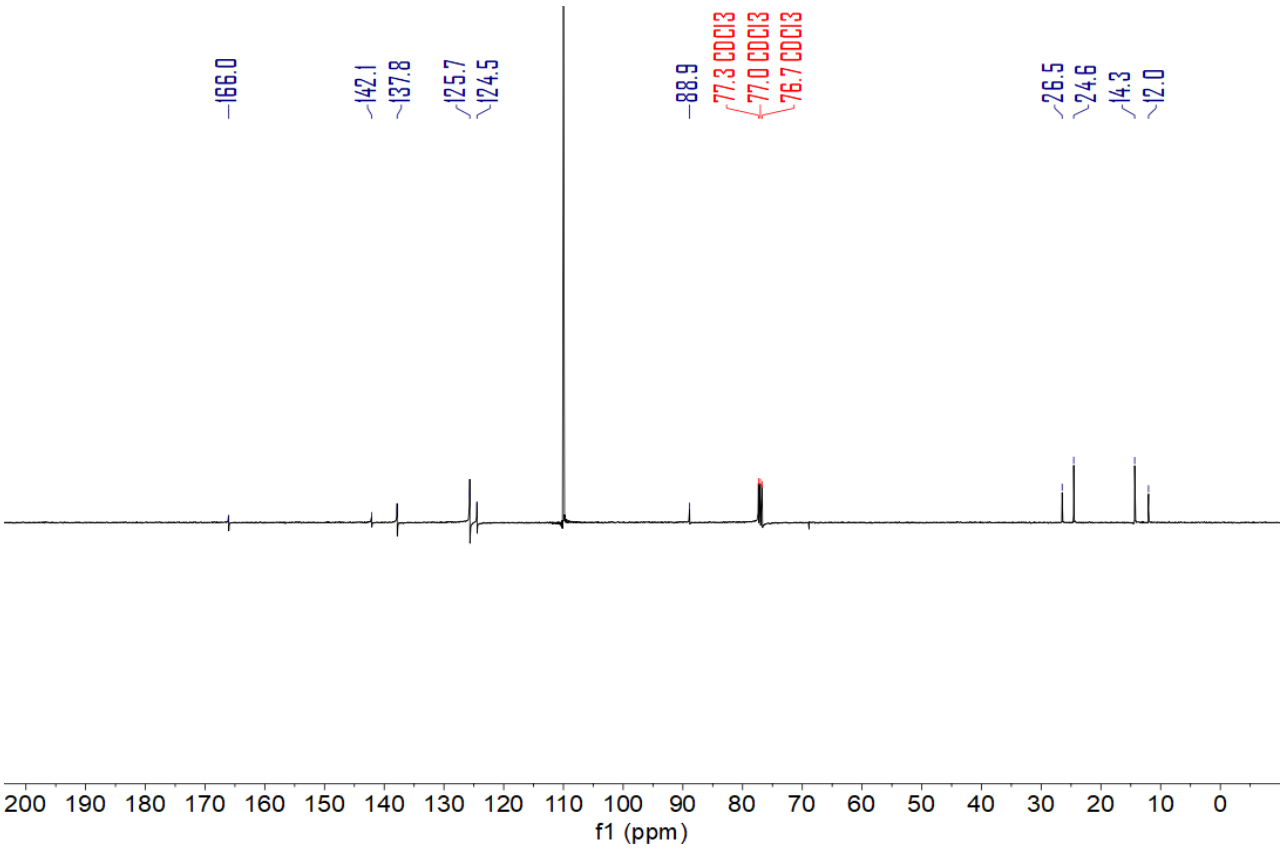


Figure S6. $^{13}C\{^{1}H\}$ (UDEFT) NMR (100.7 MHz, $CDCl_3$, 298 K) of ^{EtDep}nacnacH **1b**.

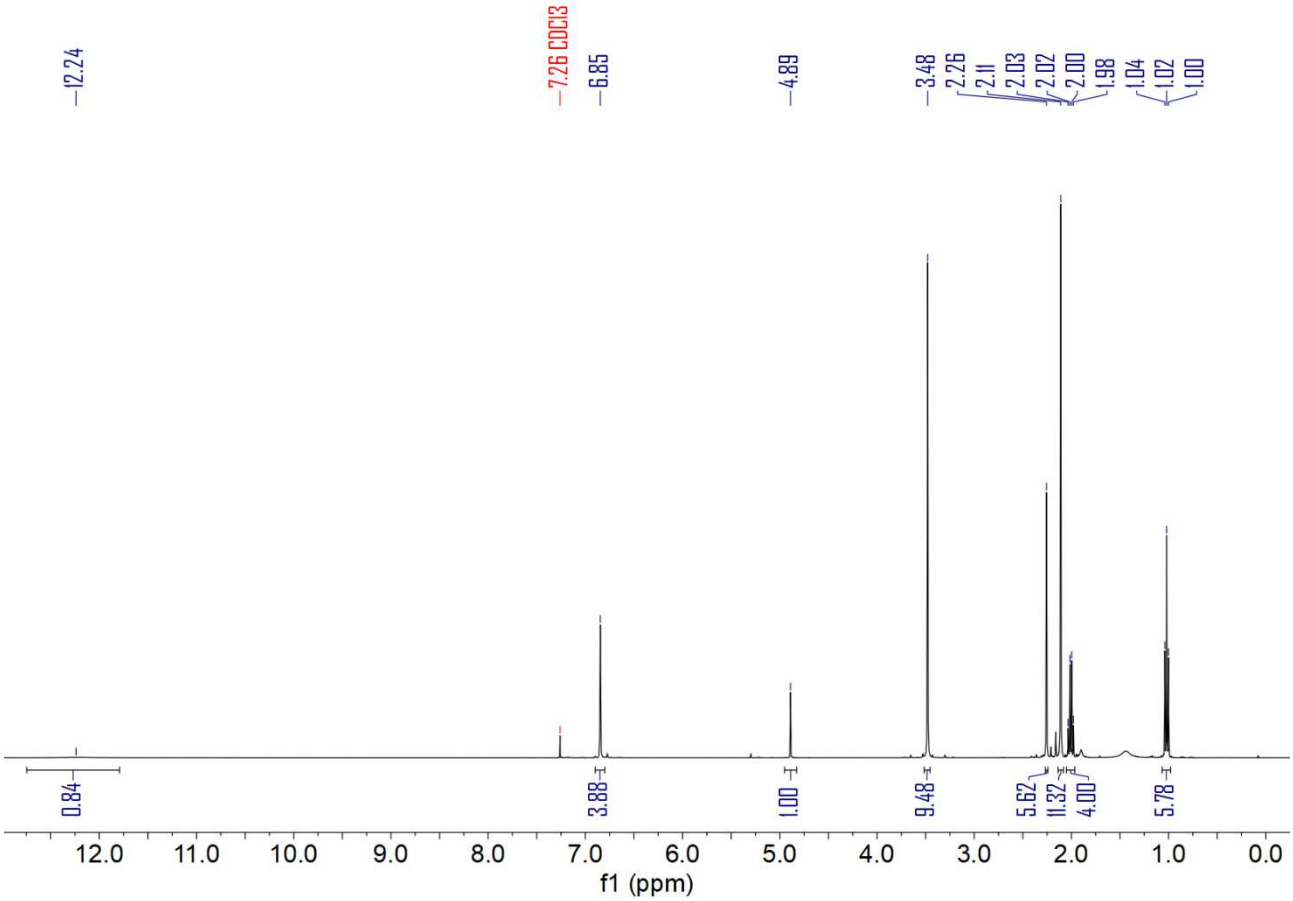


Figure S7. ^{1}H NMR spectrum (400.1 MHz, $CDCl_3$, 294 K) of ^{EtMes}nacnacH **1c**.

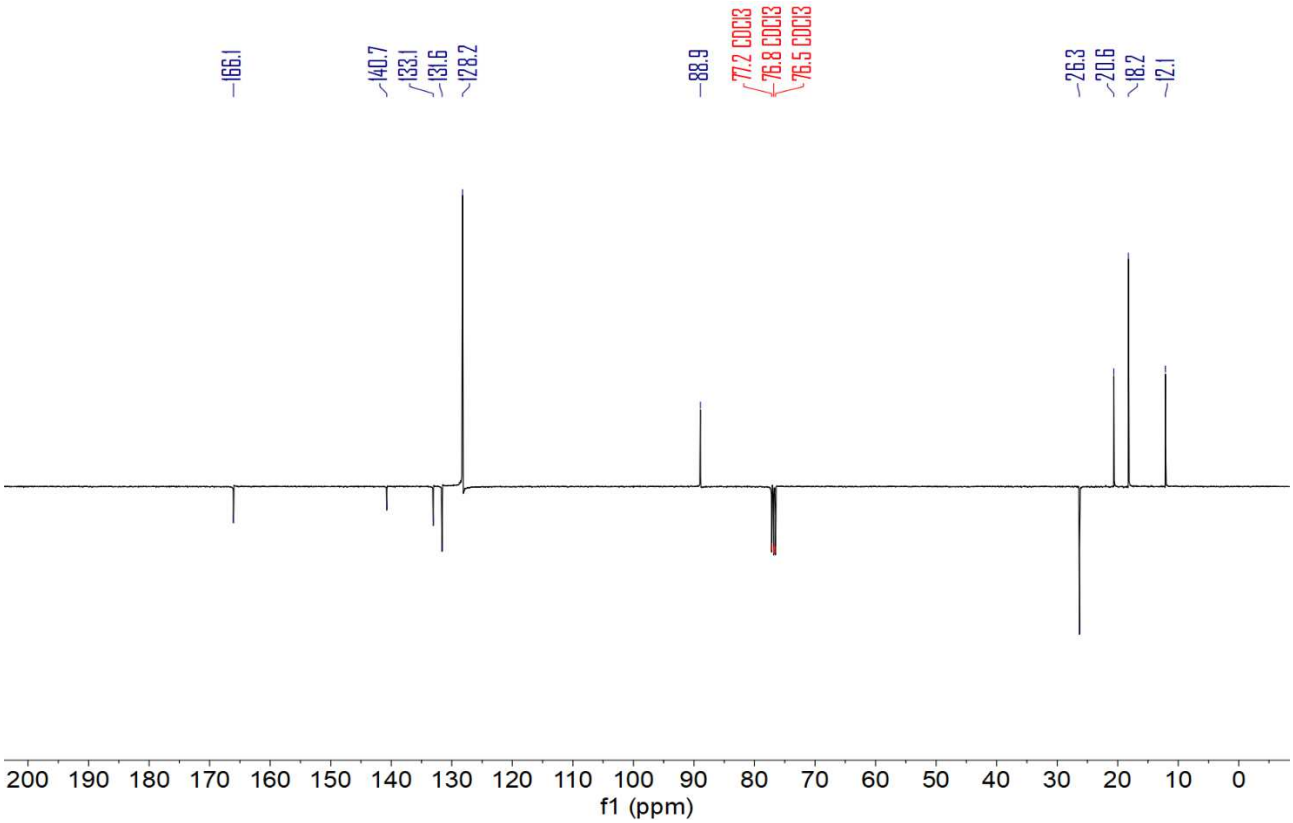


Figure S8. ^{13}C{^{1}H} DEPTQ NMR spectrum (100.6 MHz, $CDCl_3$, 294 K) of ^{EtMes}nacnacH **1c**.

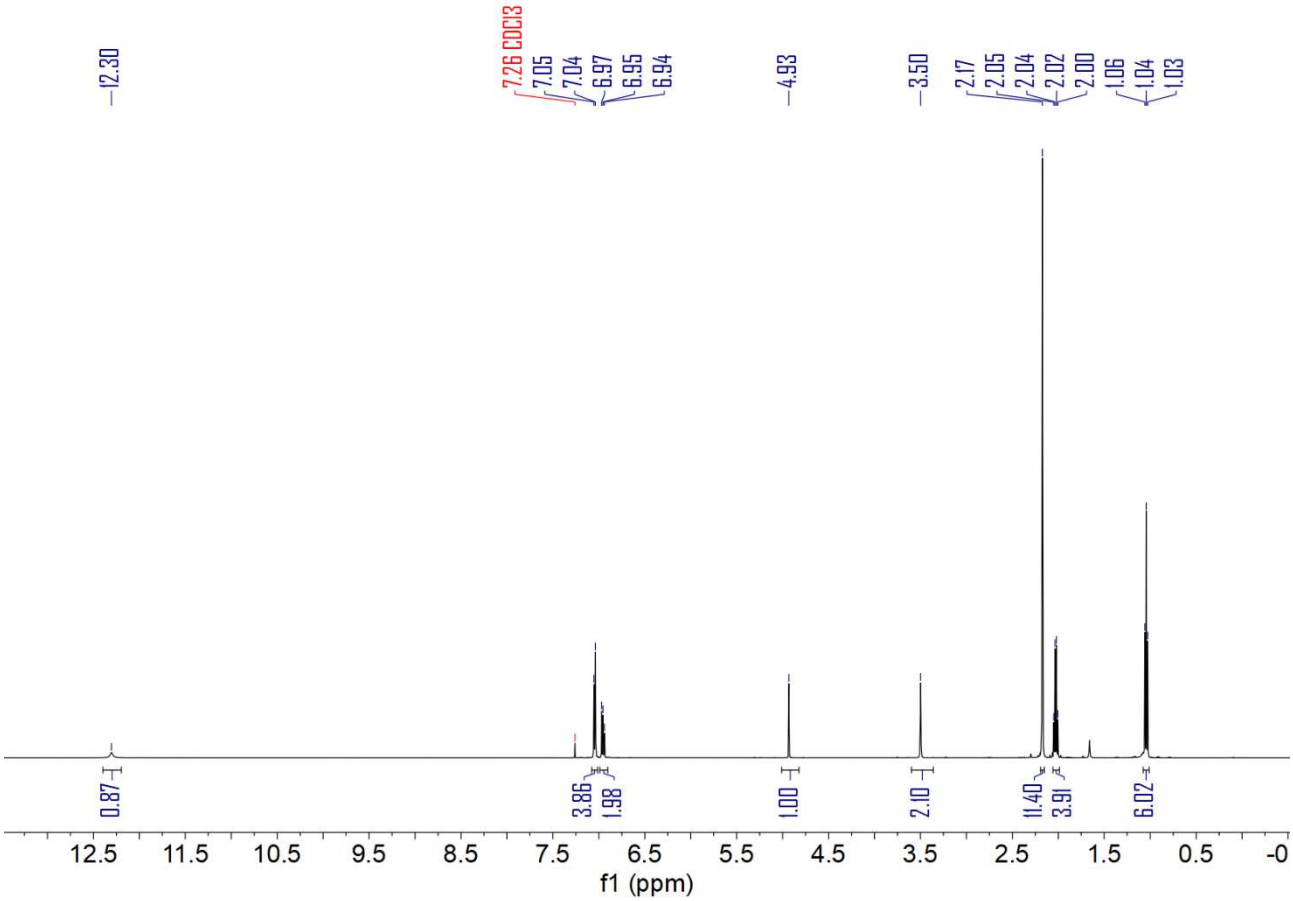


Figure S9. ^{1}H NMR spectrum (499.9 MHz, $CDCl_3$, 295 K) of ^{EtXyl}nacnacH **1d**.

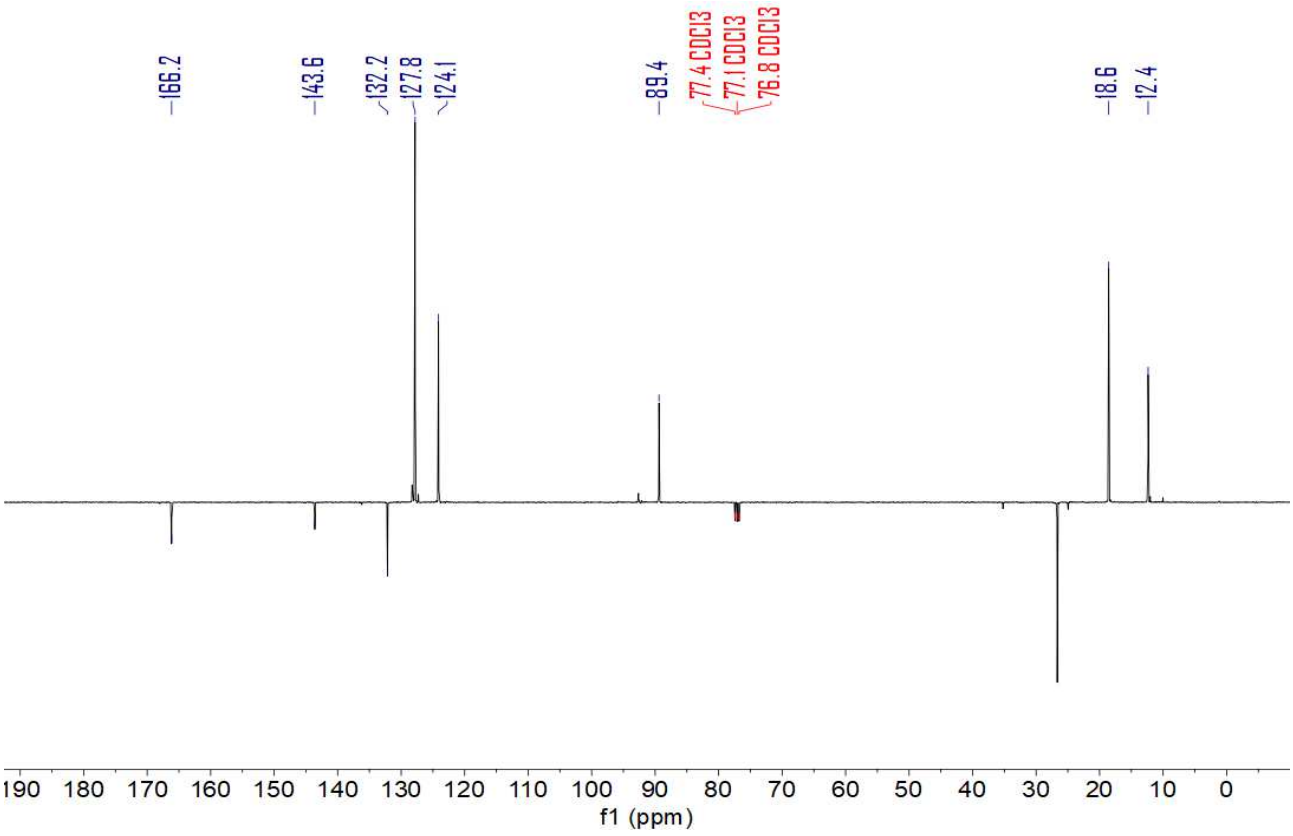


Figure S10. ^{13}C{^{1}H} DEPTQ NMR spectrum (100.7 MHz, $CDCl_3$, 297 K) of ^{EtXyl}nacnacH **1d**.

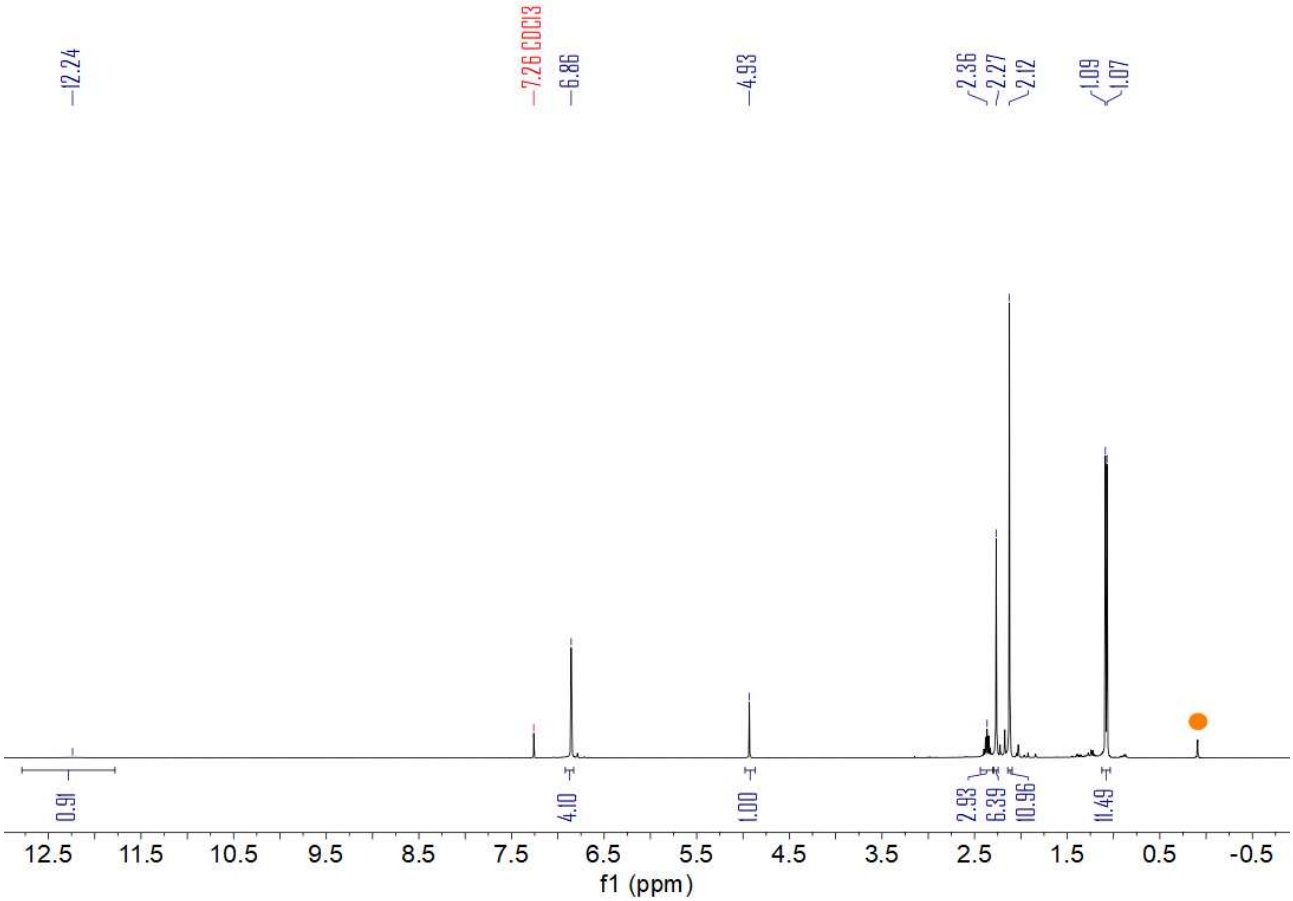


Figure S11. ^{1}H NMR spectrum (400.1 MHz, $CDCl_3$, 295 K) of ^{iPrMes}nacnacH **2c**. The orange circle denotes the chemical shift of silicone grease.

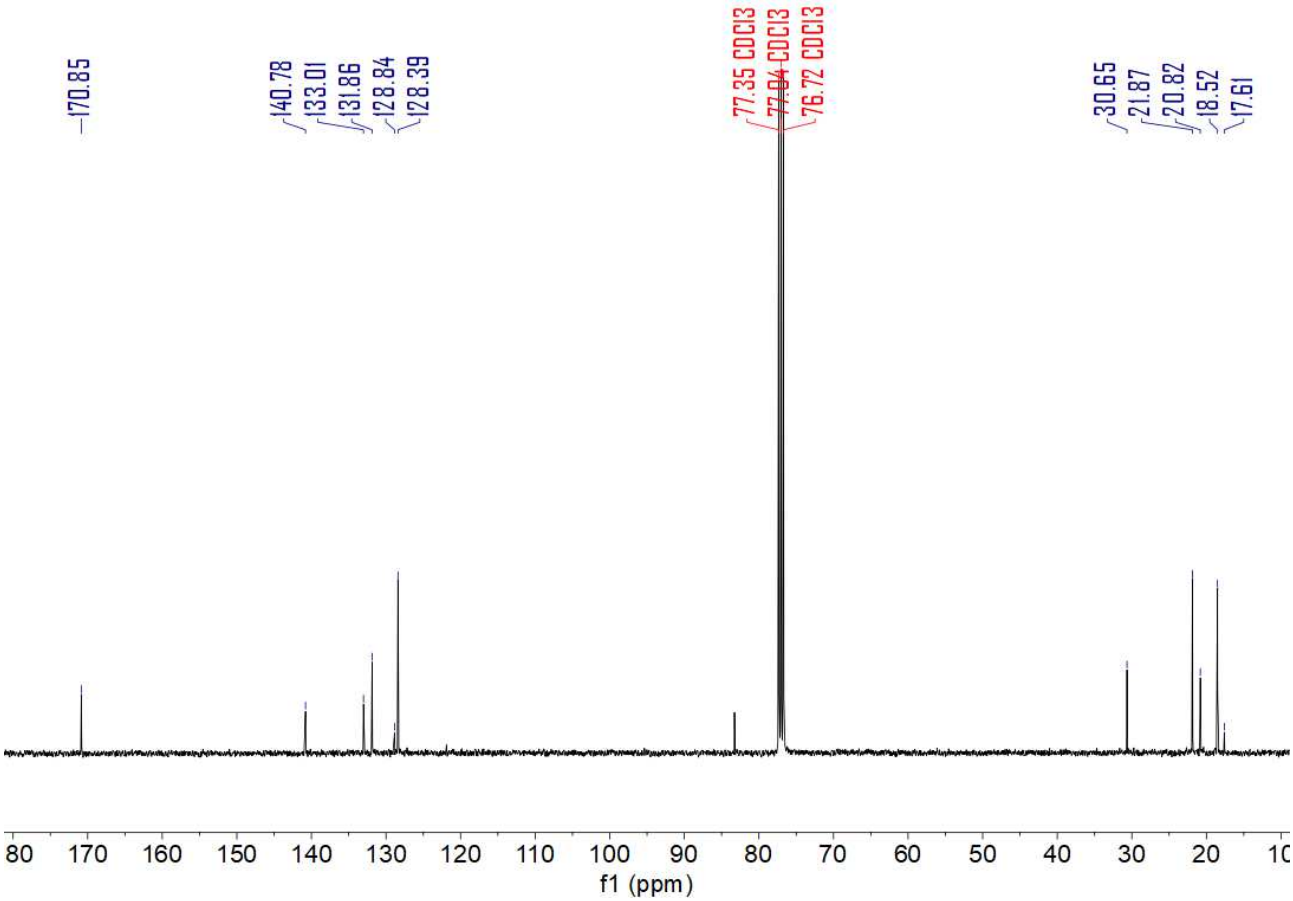


Figure S12. $^{13}C\{^{1}H\}$ NMR spectrum (100.6 MHz, $CDCl_3$, 295 K) of ^{iPrMes}nacnacH **2c**.

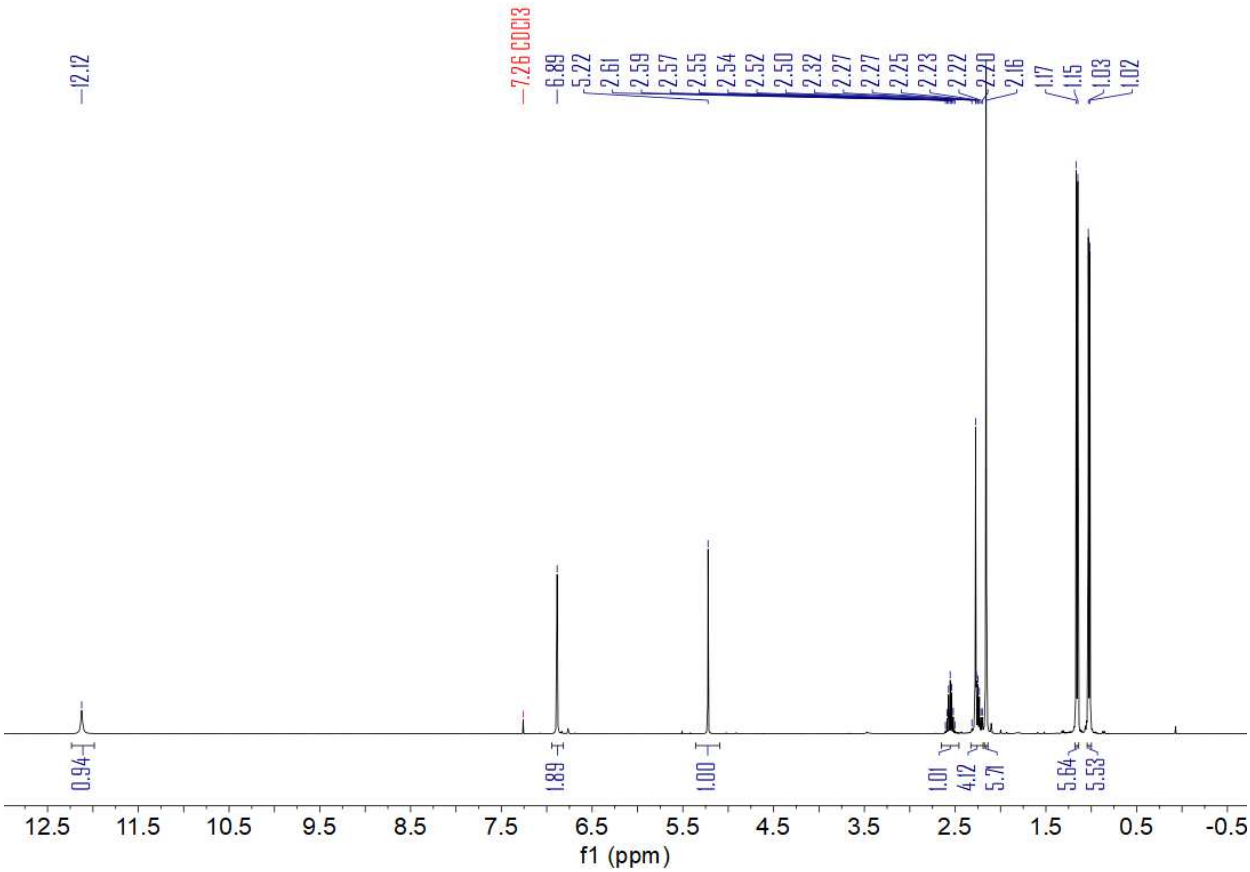


Figure S13. ^{1}H NMR spectrum (400.1 MHz, $CDCl_3$, 294 K) of *i*PrC(NHMes)CHC(=O)*i*Pr **3c**.

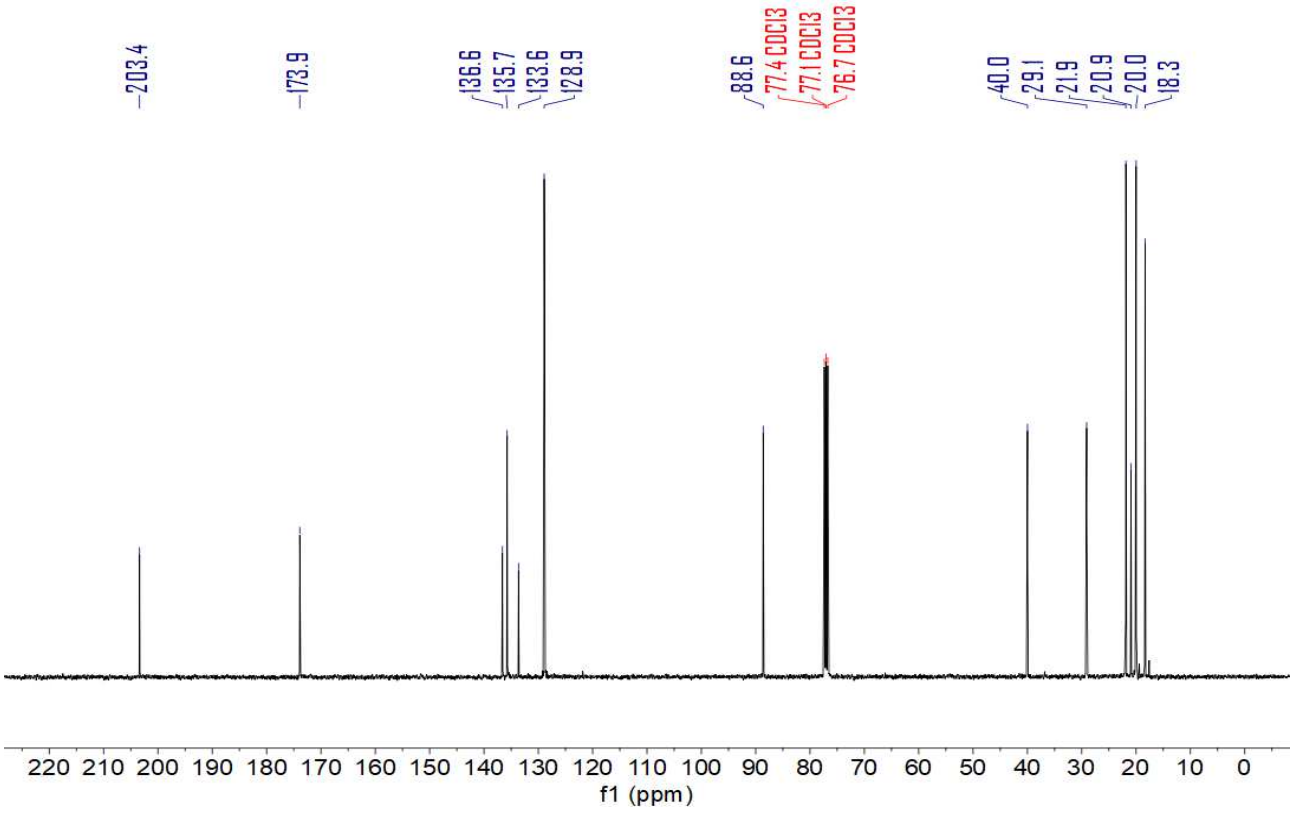


Figure S14. $^{13}C\{^{1}H\}$ NMR spectrum (100.6 MHz, $CDCl_3$, 295 K) of *i*PrC(NHMes)CHC(=O)*i*Pr **3c**.

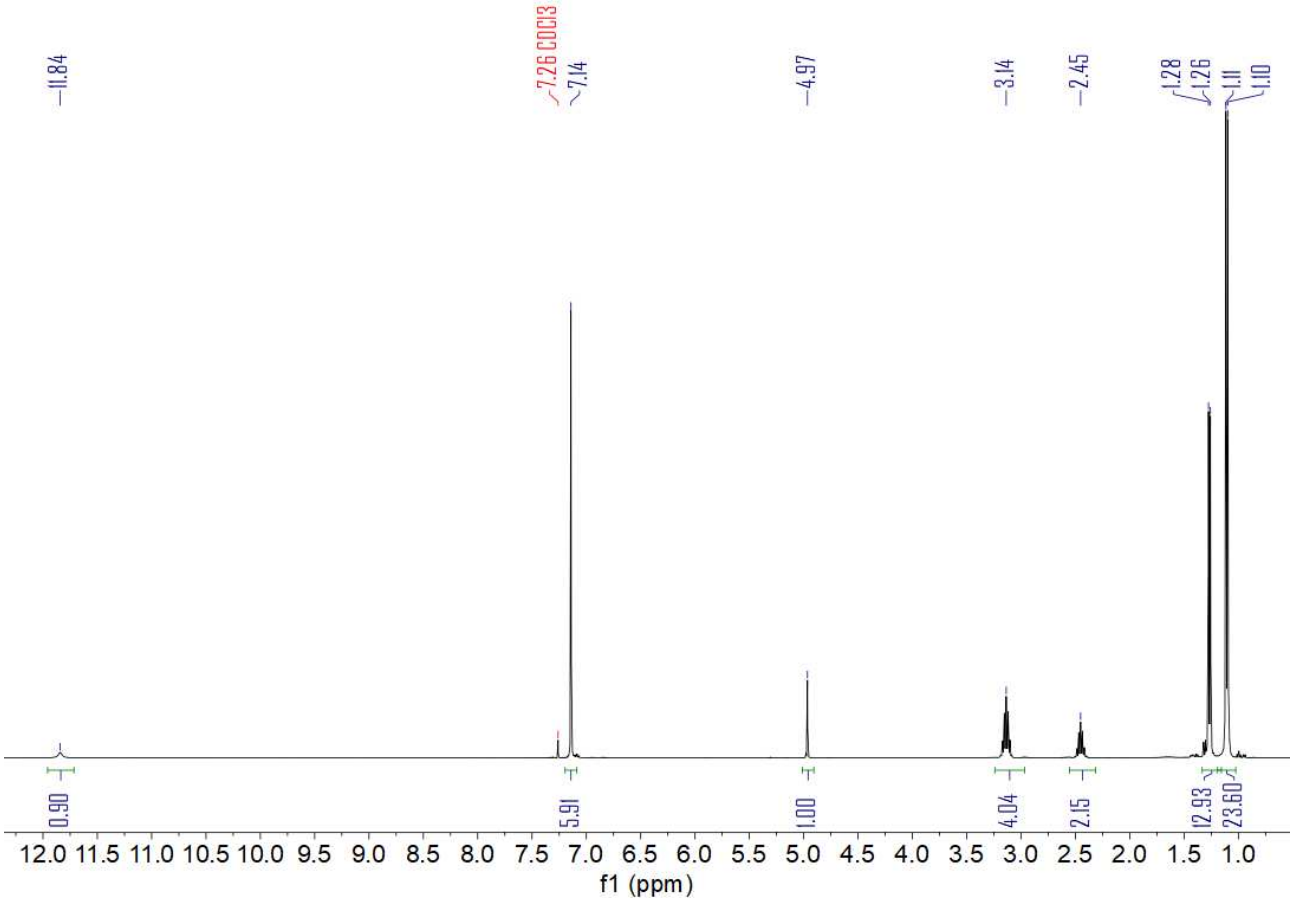


Figure S15. ^{1}H NMR spectrum (400.1 MHz, $CDCl_3$, 295 K) of ^{iPrDip}nacnacH **2a**.

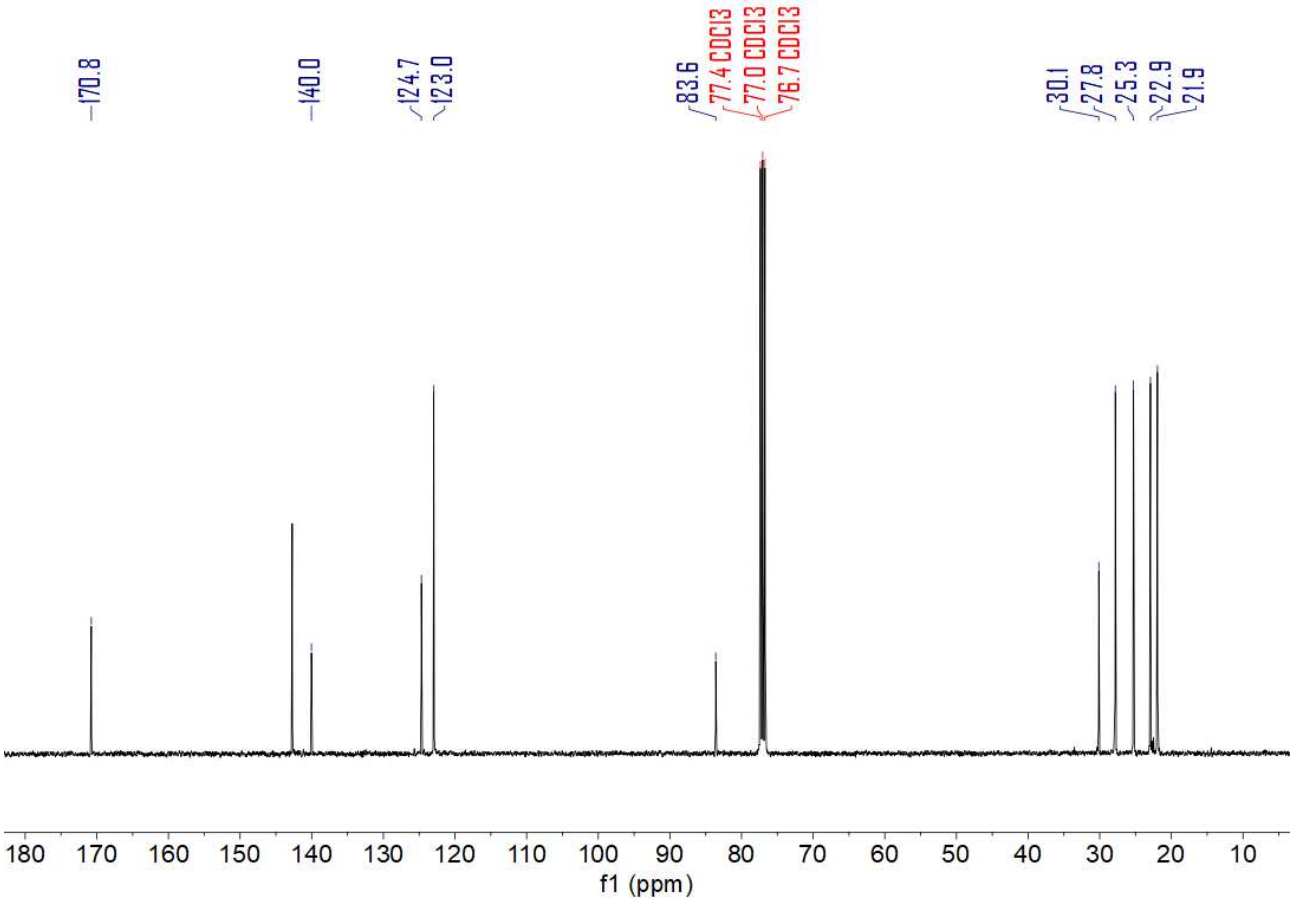


Figure S16. $^{13}C\{^{1}H\}$ NMR spectrum (100.6 MHz, $CDCl_3$, 295 K) of ^{iPrDip}nacnacH **2a**.

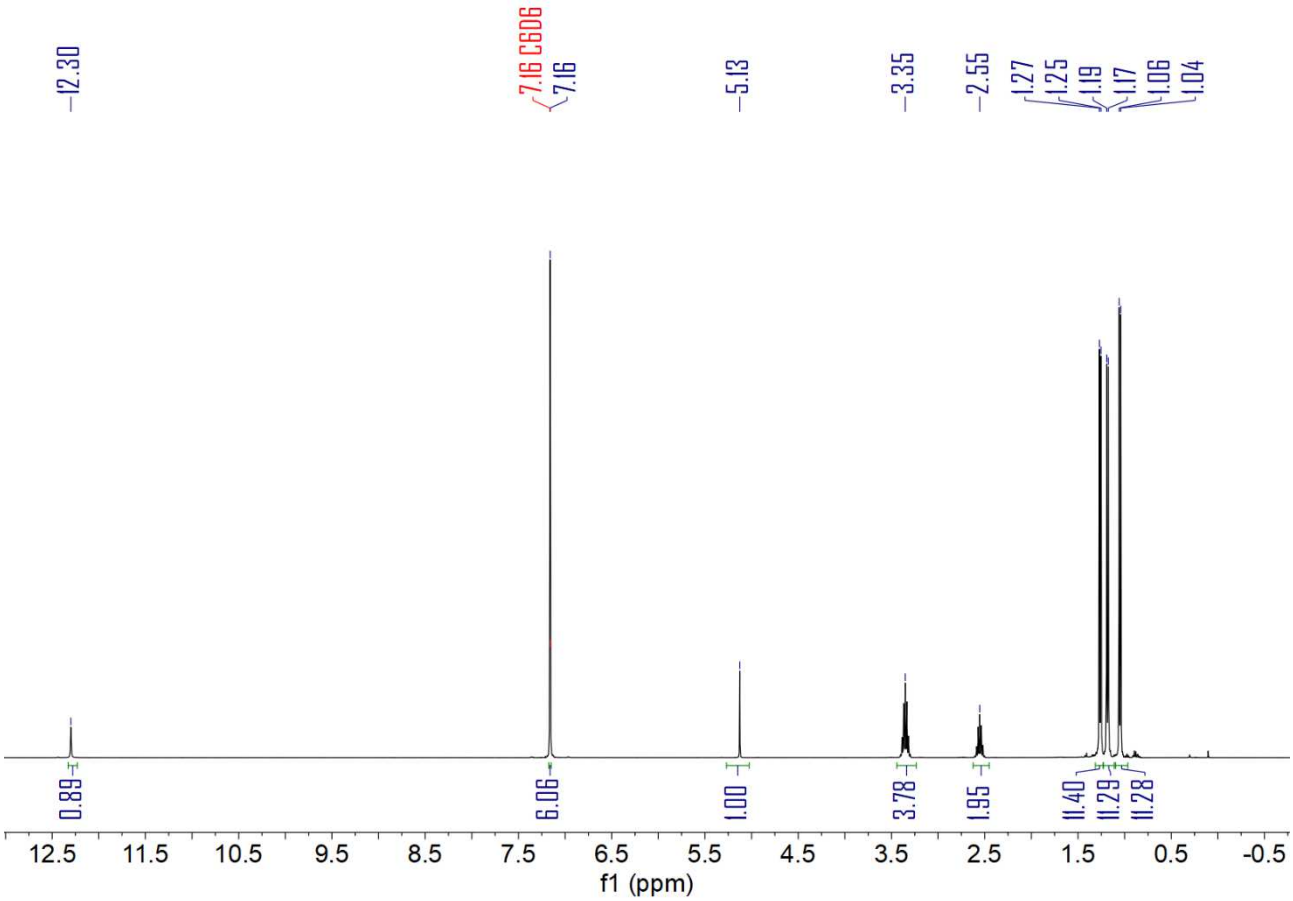


Figure S17. ^{1}H NMR spectrum (400.1 MHz, C_6D_6, 294 K) of ^{iPrDip}nacnacH **2a**.

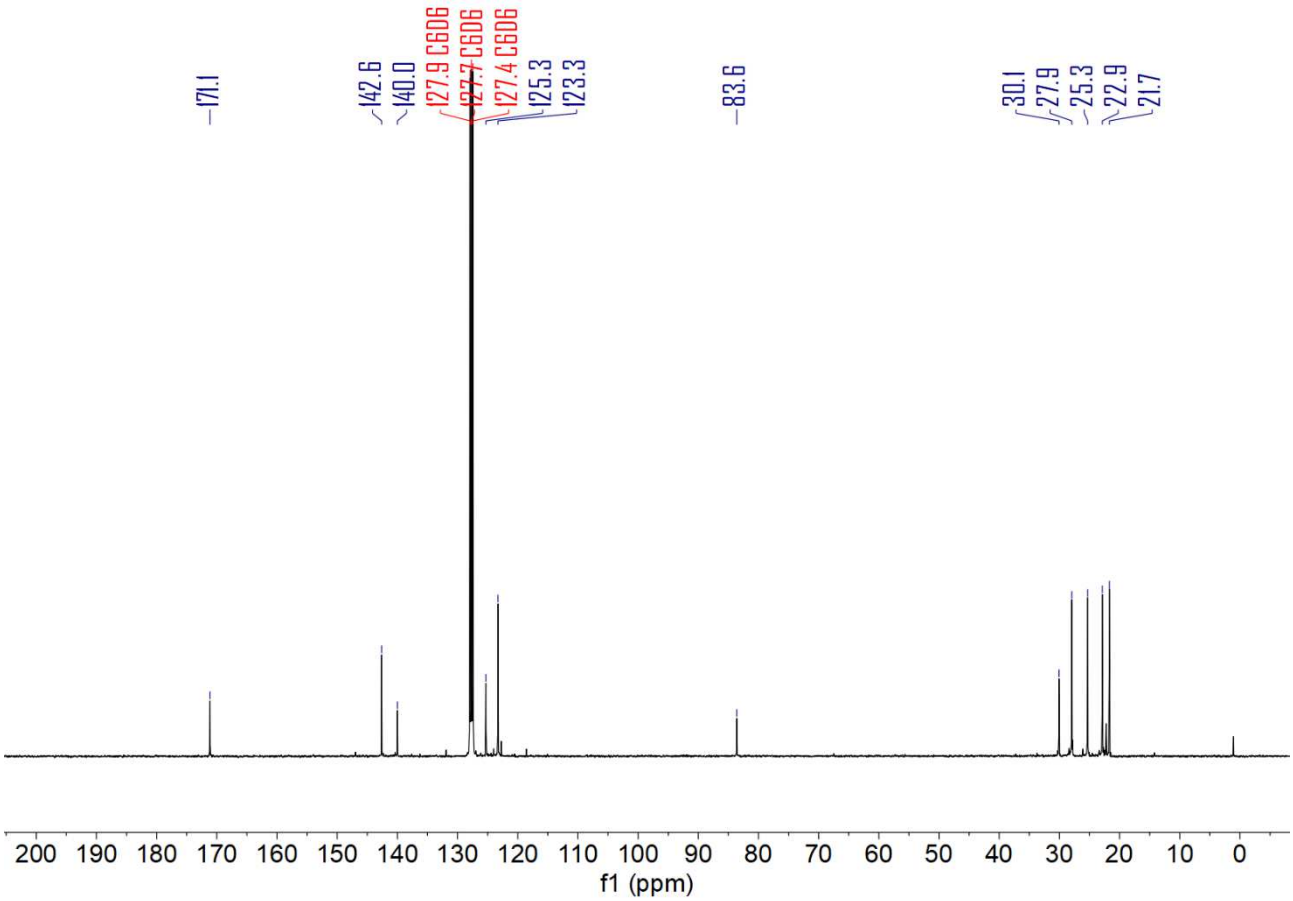


Figure S18. $^{13}C\{^{1}H\}$ NMR spectrum (100.6 MHz, C_6D_6, 294 K) of ^{iPrDip}nacnacH **2a**.

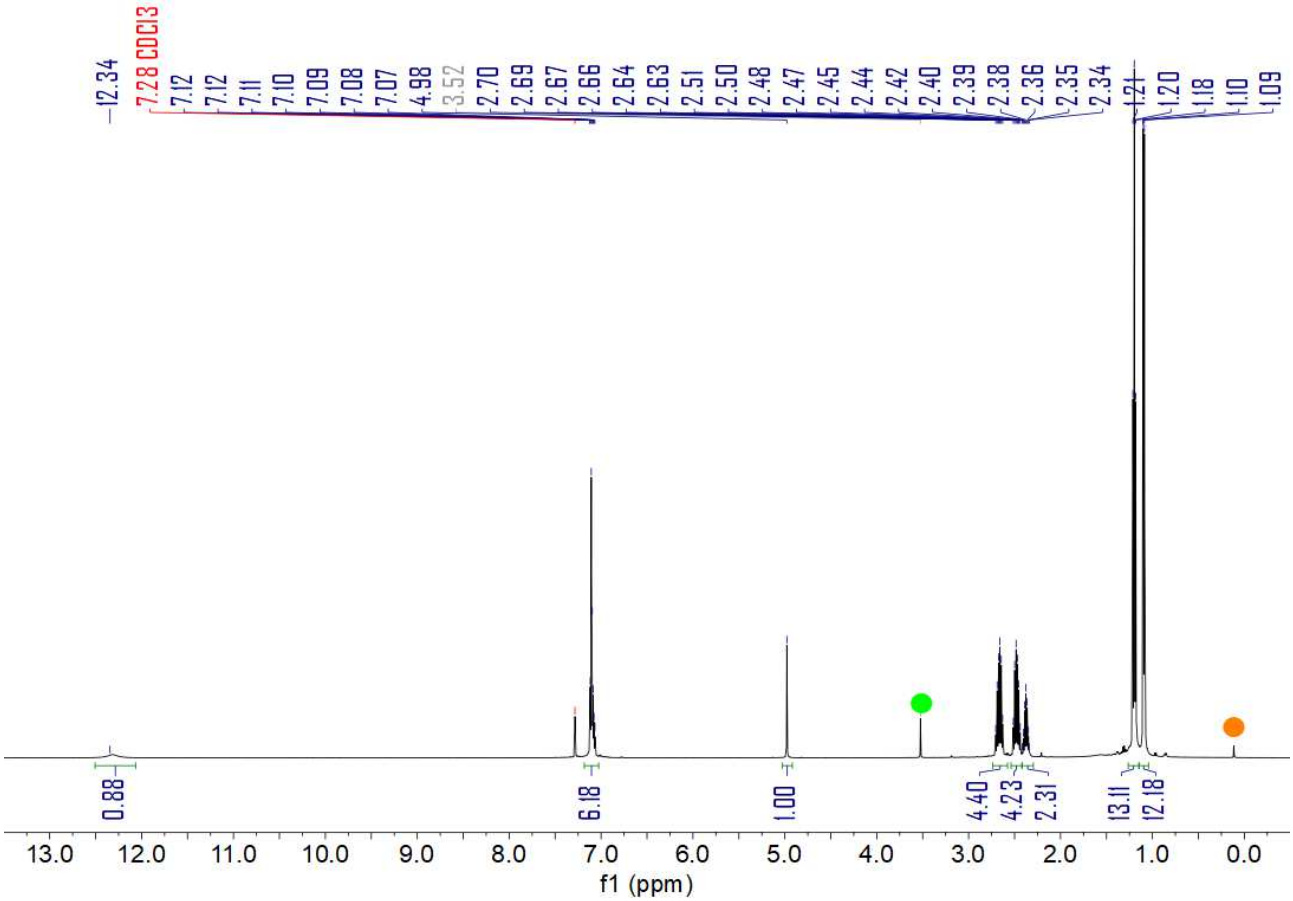


Figure S19. ^{1}H NMR spectrum (499.9 MHz, $CDCl_3$, 298 K) of ^{iPrDep}nacnacH **2b**. The green circle denotes the resonance of methanol. The orange circle denotes the chemical shift of silicone grease.

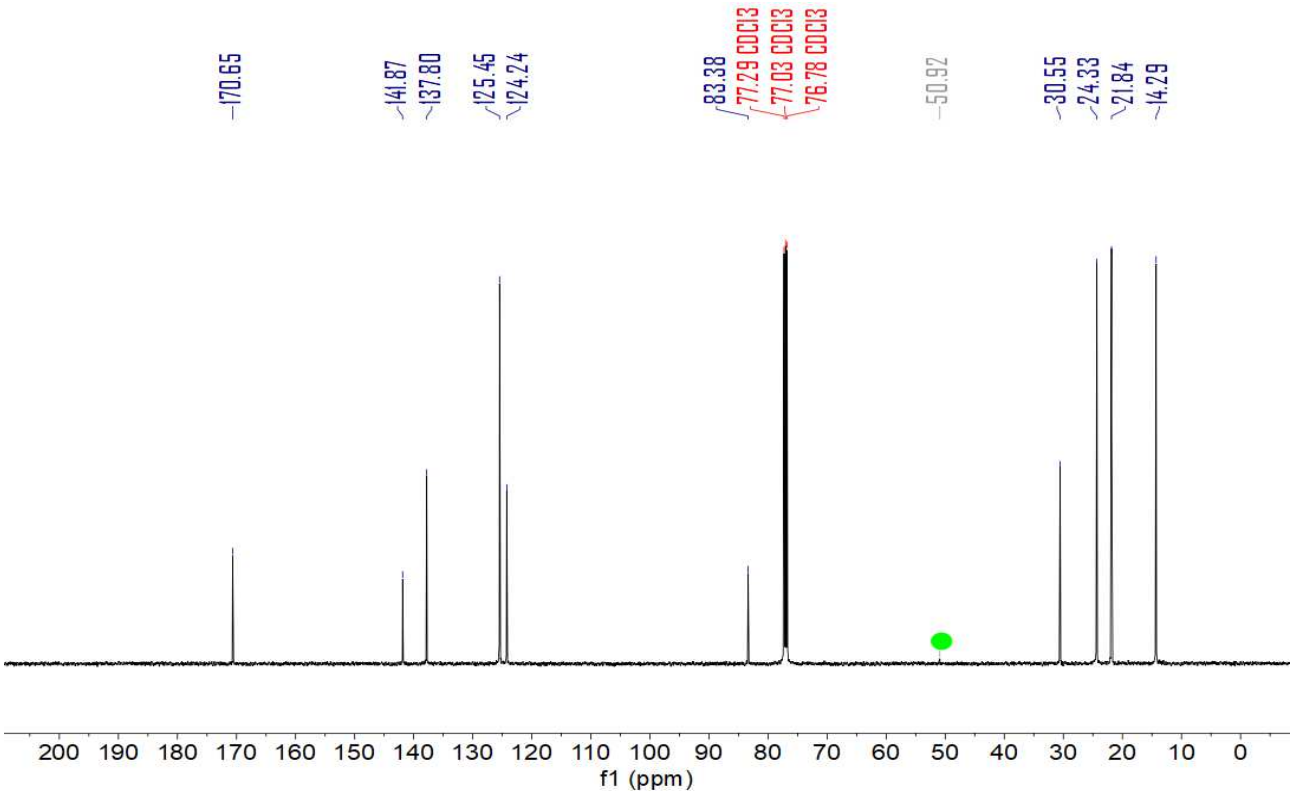


Figure S20. $^{13}C\{^{1}H\}$ NMR spectrum (125.7 MHz, $CDCl_3$, 298 K) of ^{iPrDep}nacnacH **2b**. The green circle denotes the resonance of methanol.

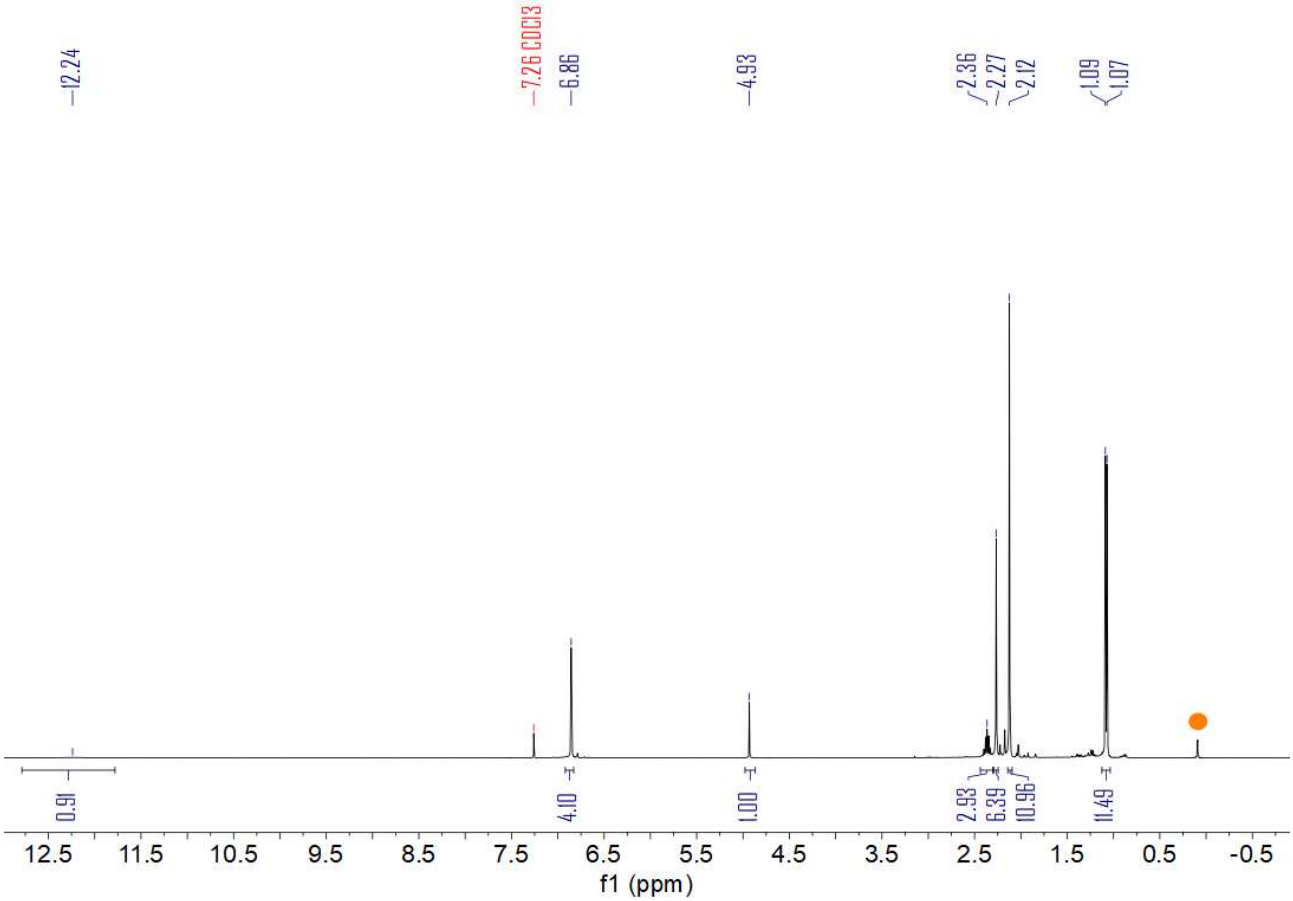


Figure S21. ^{1}H NMR spectrum (400.1 MHz, $CDCl_3$, 295 K) of ^{iPrMes}nacnacH **2c**. The orange circle denotes the chemical shift of silicone grease.

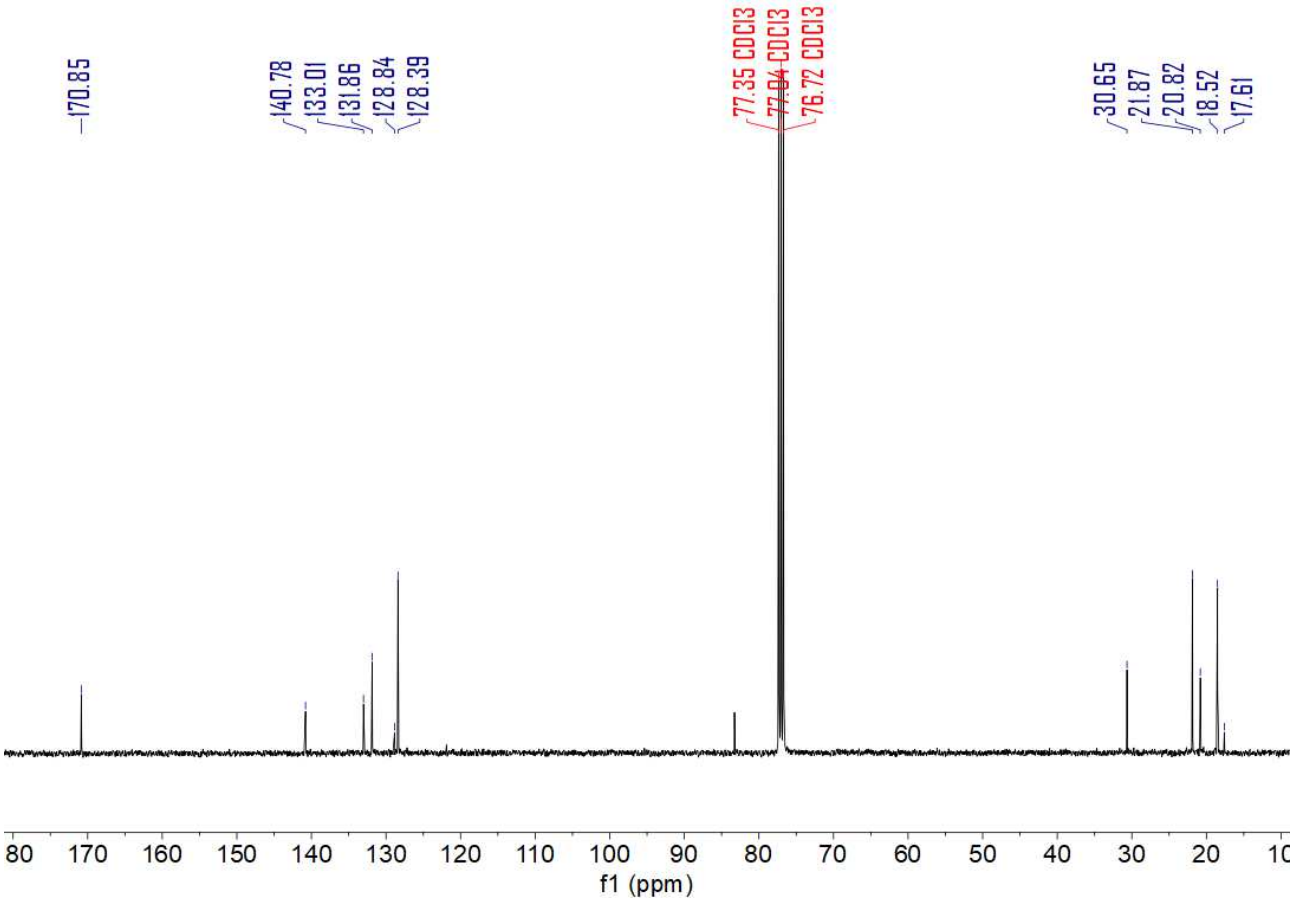


Figure S22. $^{13}C\{^{1}H\}$ NMR spectrum (100.6 MHz, $CDCl_3$, 295 K) of ^{iPrMes}nacnacH **2c.**

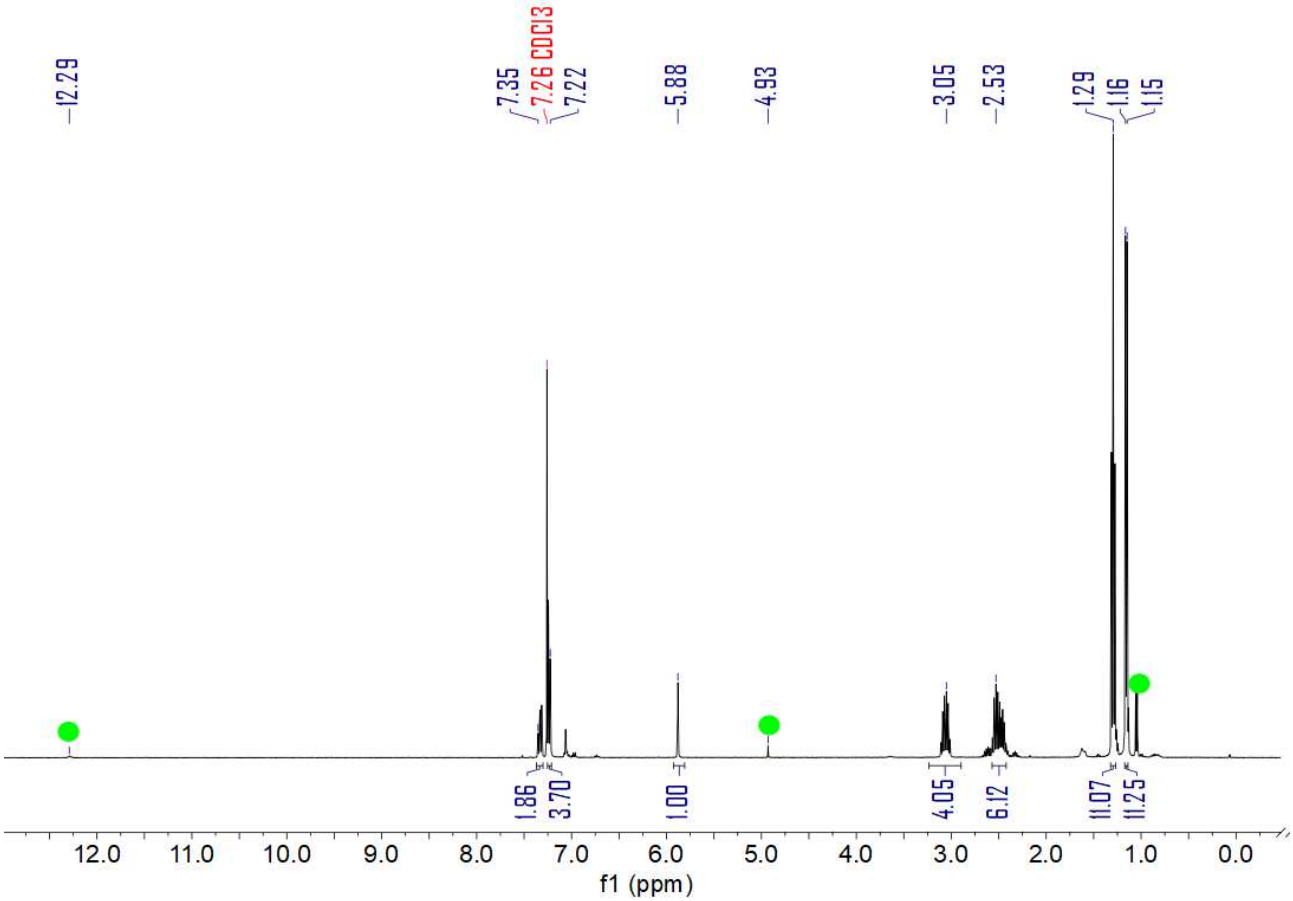


Figure S23. ^{1}H NMR spectrum (400.1 MHz, C_6D_6, 295 K) of a mixture with (^{iPrDep}nacnac)PO_2 **4b** and ^{iPrDep}nacnacH **2b** (green circles).

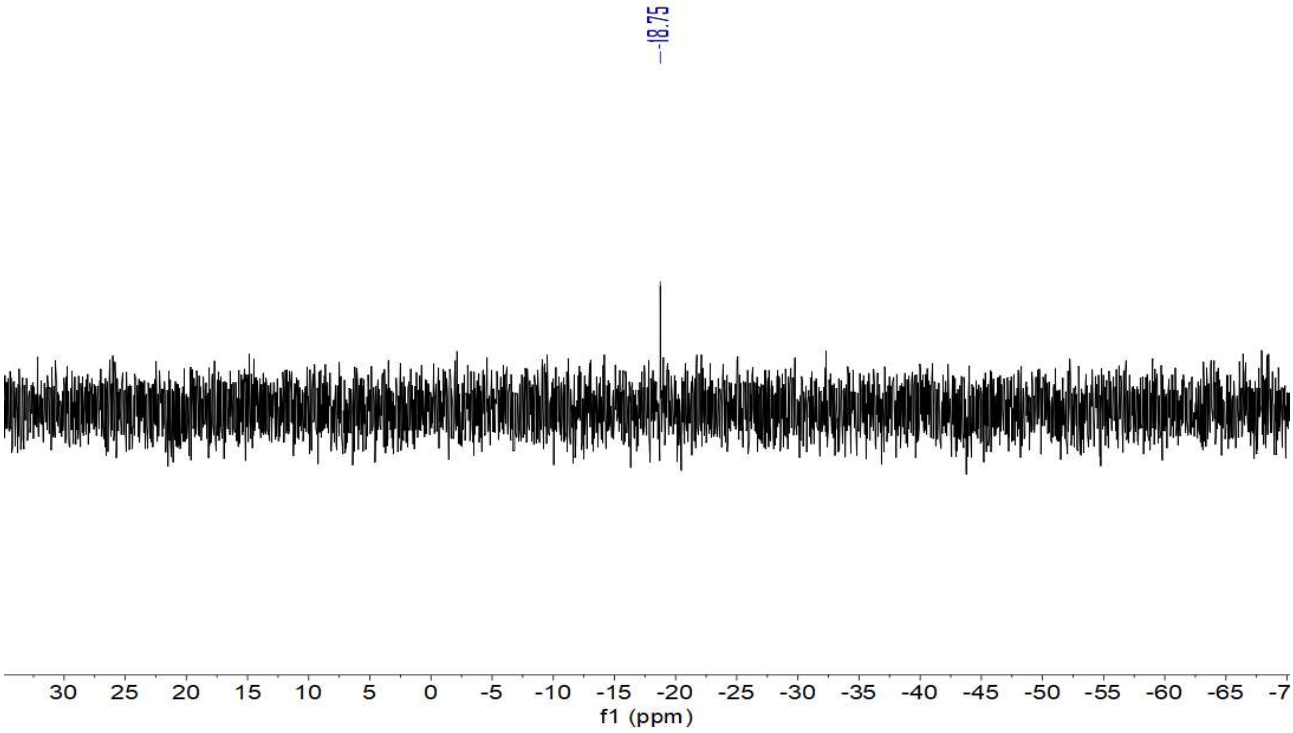


Figure S24. ^{31}P{^{1}H} NMR spectrum (202.4 MHz, C_6D_6, 298 K) of a mixture with ^{iPrDep}nacnacH **2b** and (^{iPrDep}nacnac)PO_2 **4b** (after storing the sample at room temperature for several months).

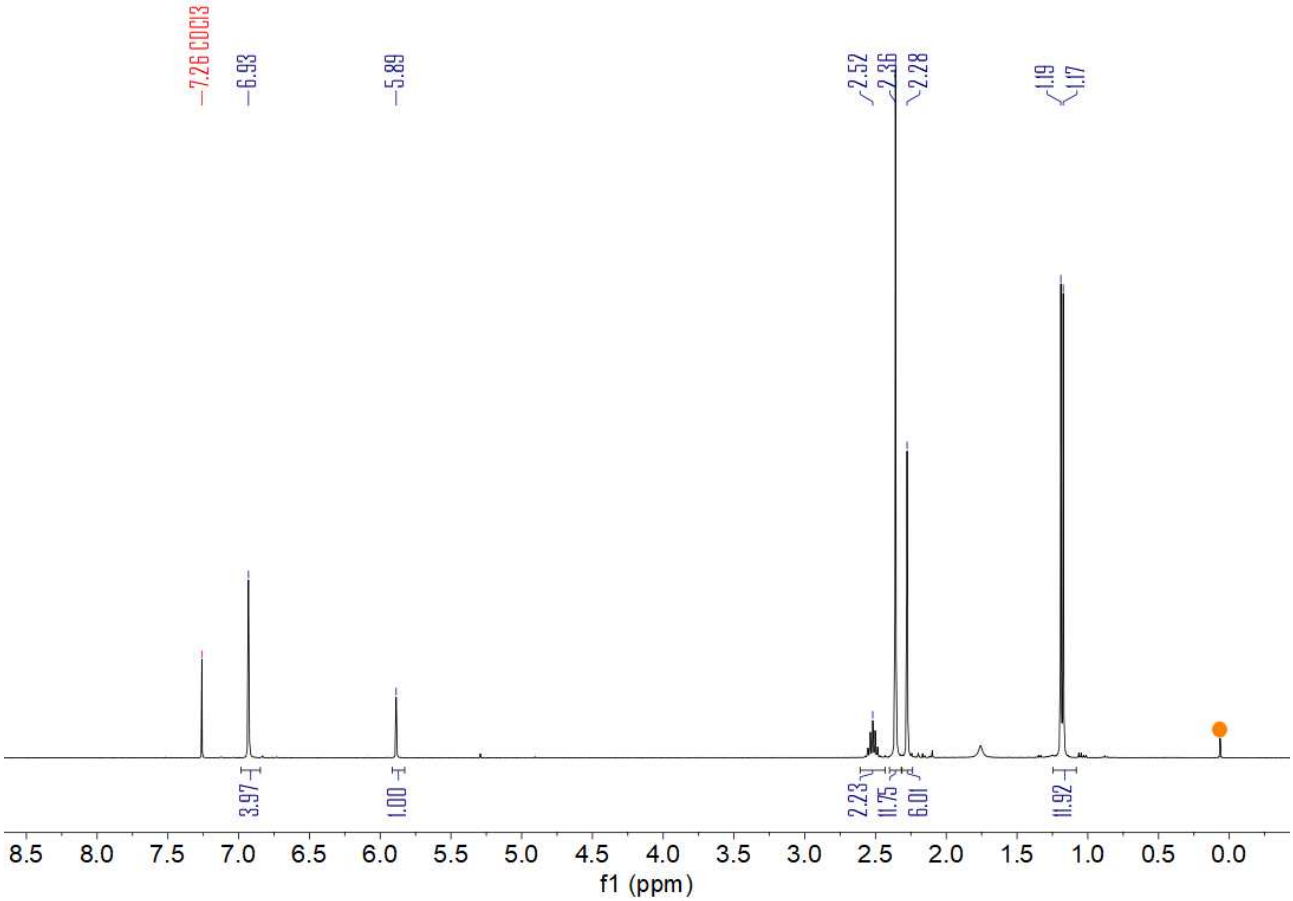


Figure S25. ^{1}H NMR spectrum (400.1 MHz, $CDCl_3$, 294 K) of (^{iPrMes}nacnac)PO_2 **4c**. The orange circle denotes the chemical shift of silicone grease.

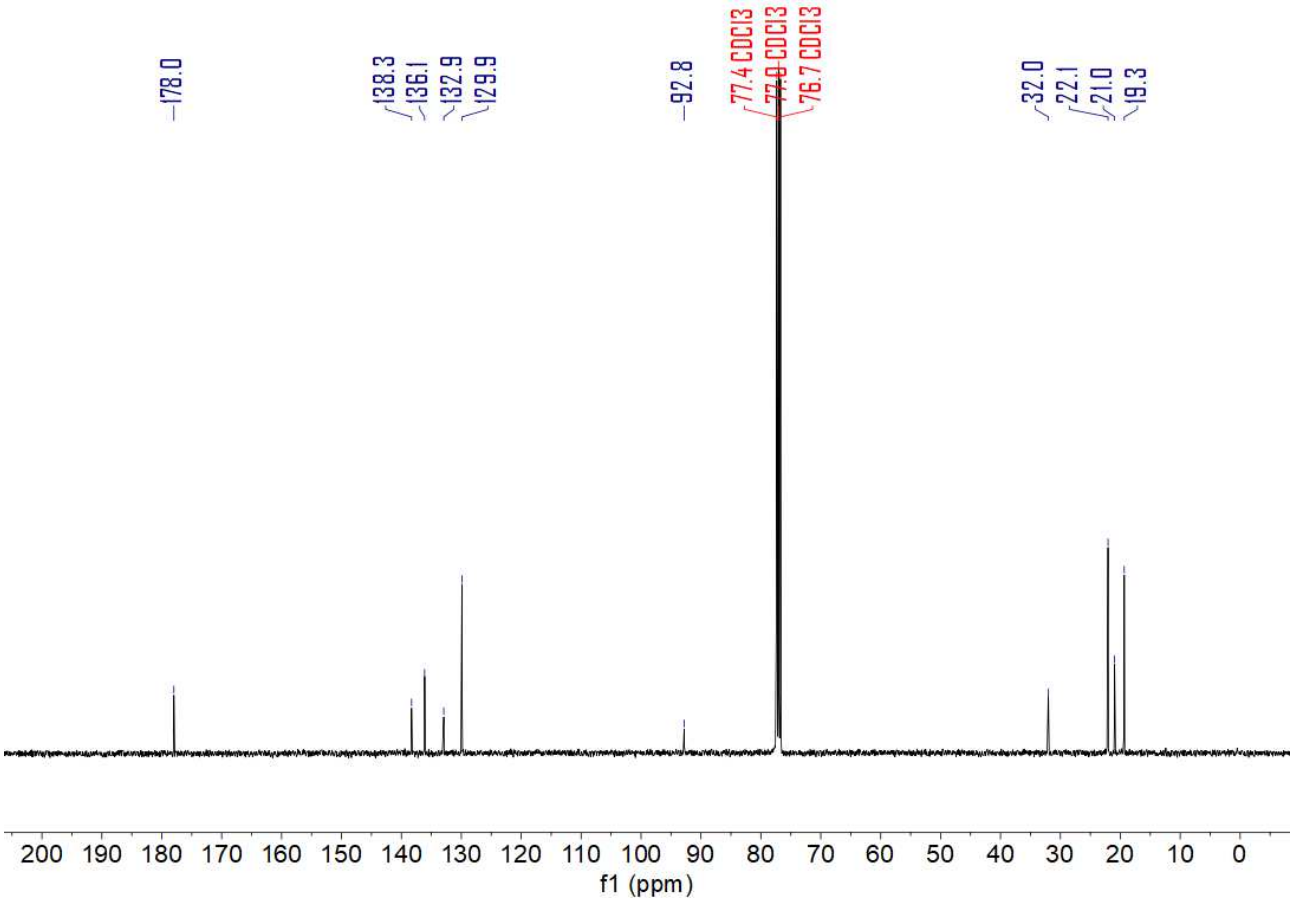


Figure S26. $^{13}C\{^{1}H\}$ NMR spectrum (100.6 MHz, $CDCl_3$, 295 K) of (^{iPrMes}nacnac)PO_2 **4c**.

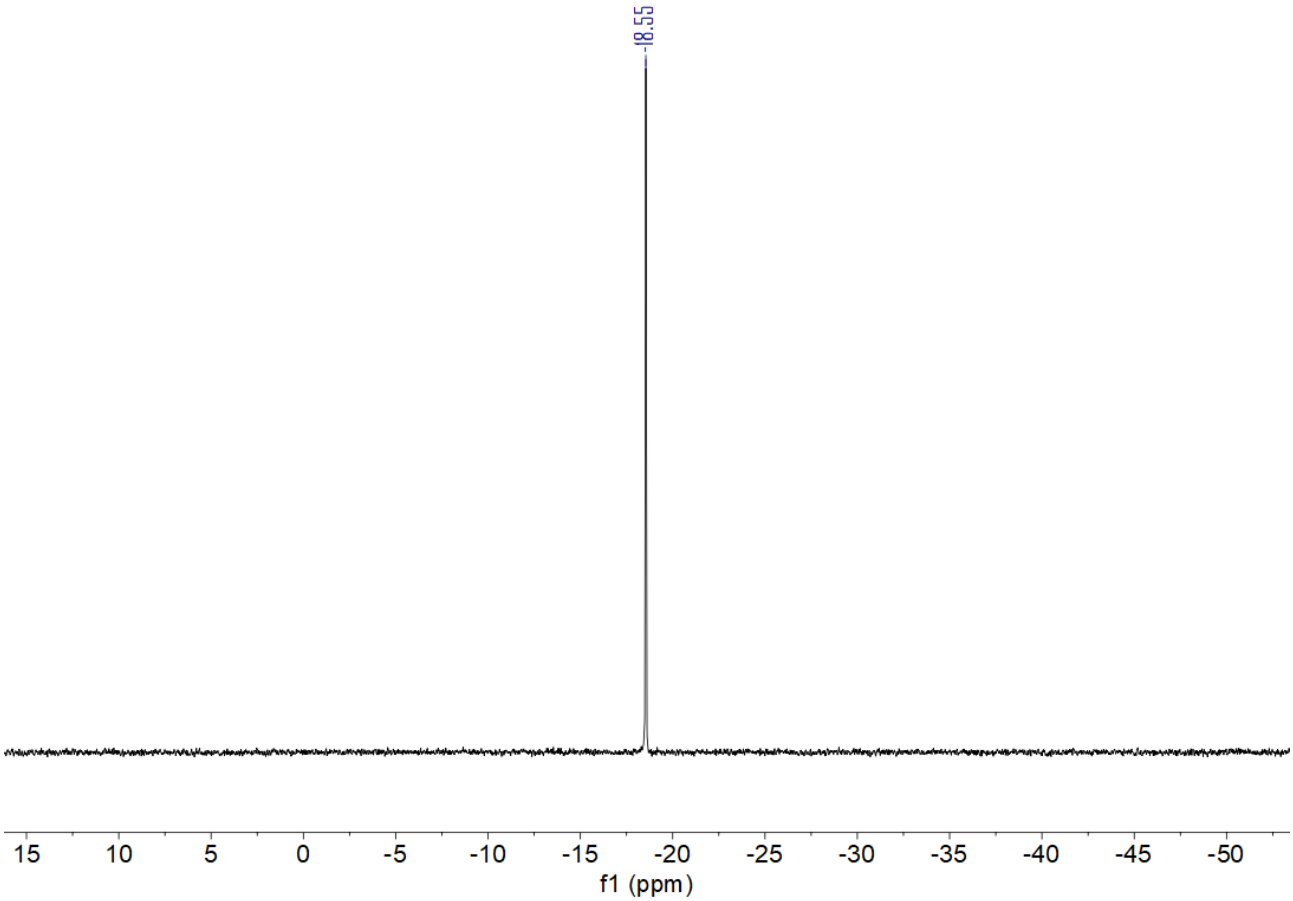


Figure S27. $^{31}P\{^{1}H\}$ NMR spectrum (162.0 MHz, $CDCl_3$, 294 K) of (^{iPrMes}nacnac)PO_2 **4c**.

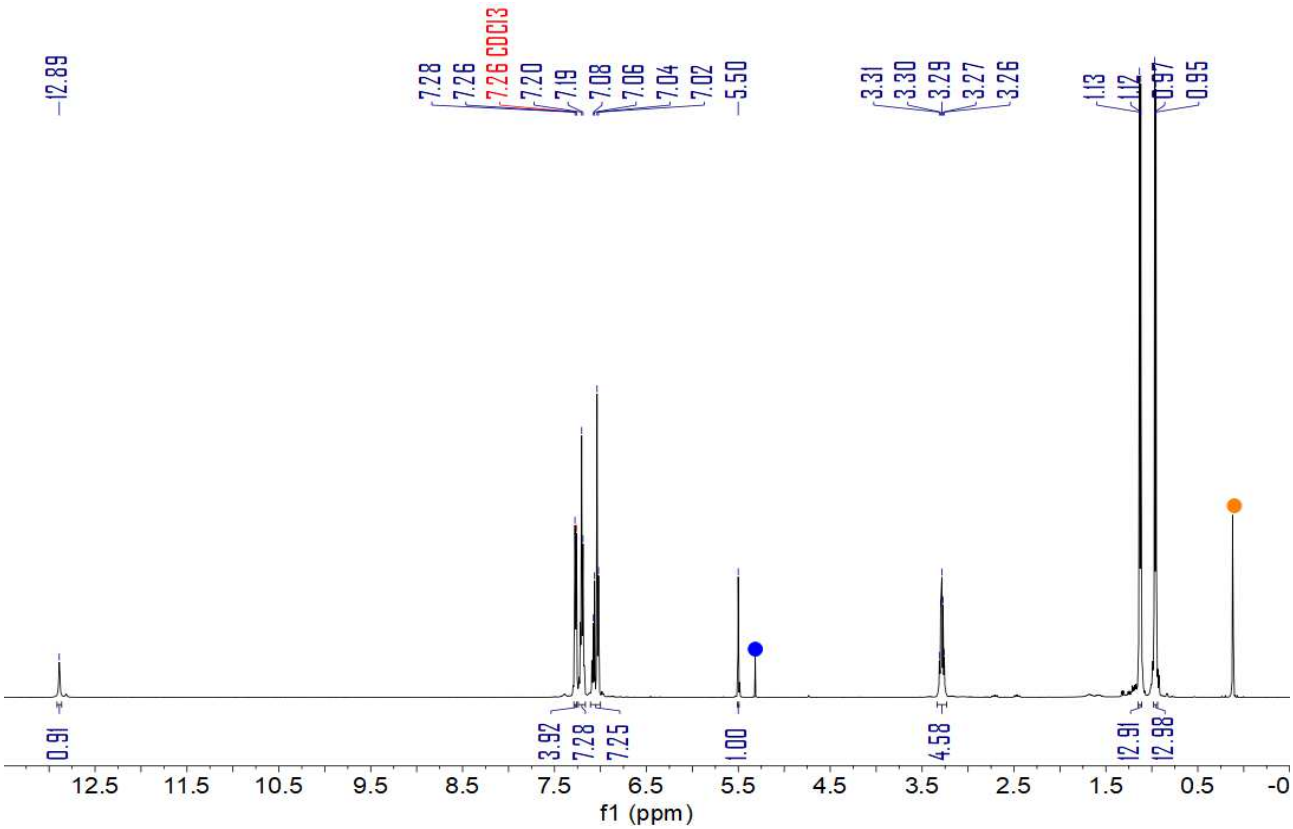


Figure S28. ^{1}H NMR spectrum (499.9 MHz, C_6D_6, 298 K) of ^{PhDip}nacnacH **5**. The blue circle denotes the resonance of DCM. The orange circle denotes the chemical shift of silicone grease.

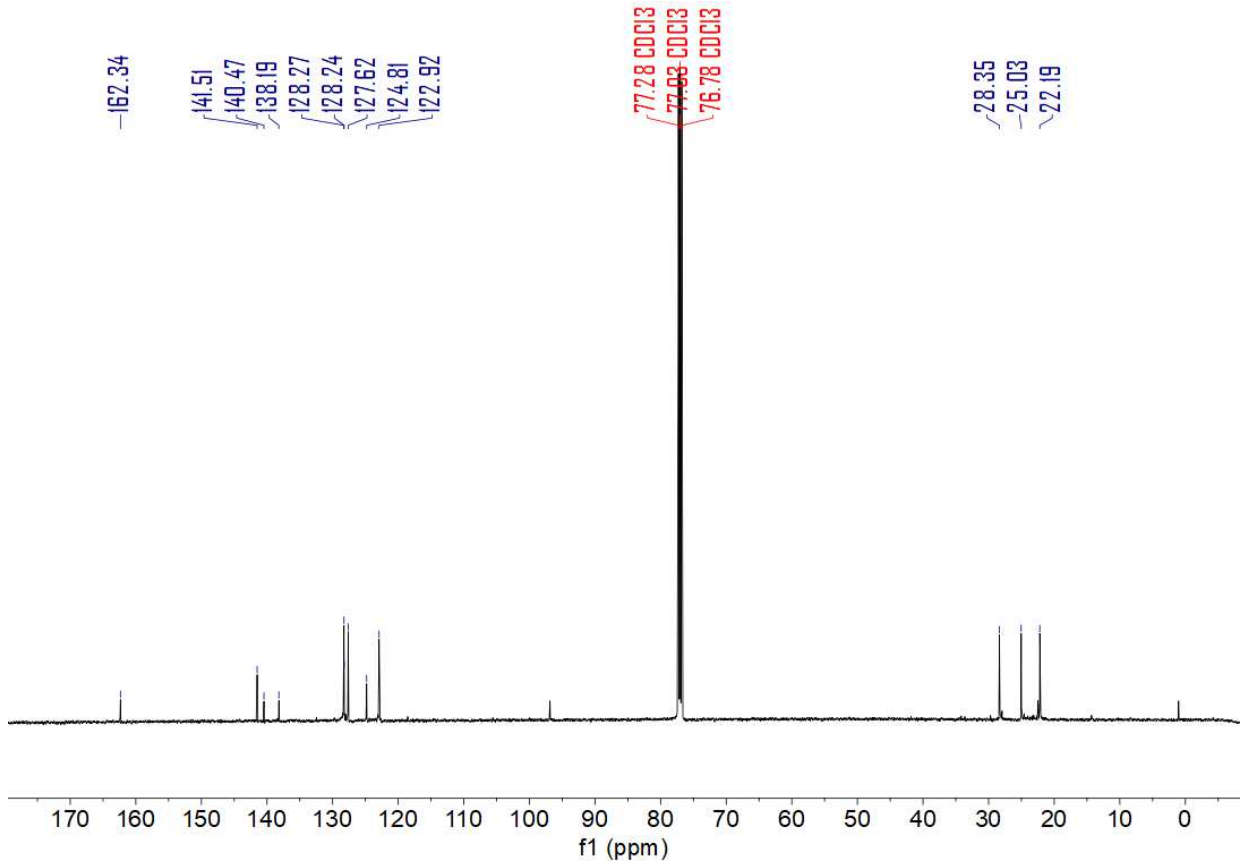


Figure S29. ^{13}C{^{1}H} NMR spectrum (125.8 MHz, $CDCl_3$, 298 K) of ^{PhDip}nacnacH **5**.

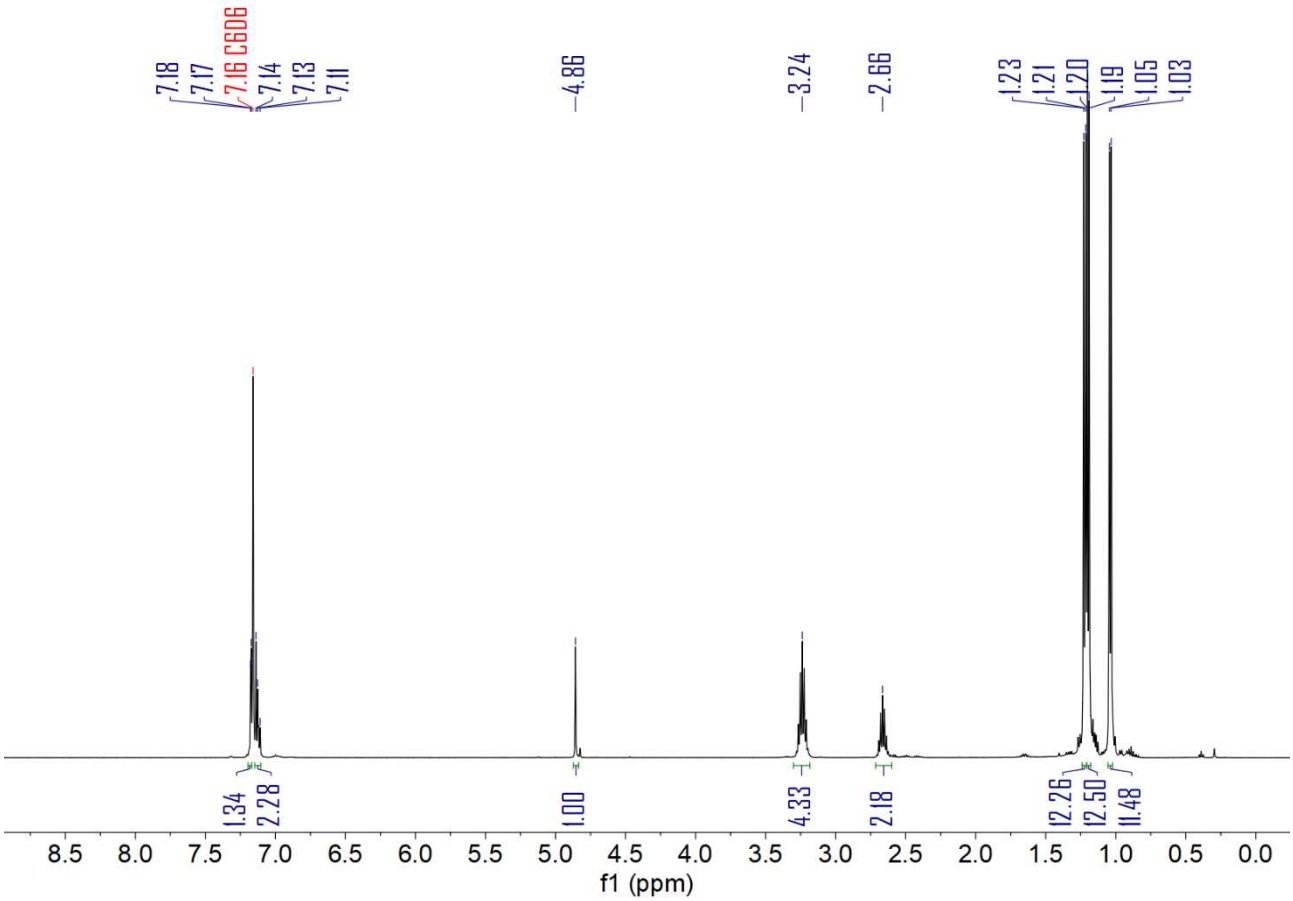


Figure S30. ^{1}H NMR spectrum (499.9 MHz, C_6D_6, 298 K) of [(^{iPrDip}nacnac)Li] **6a**.

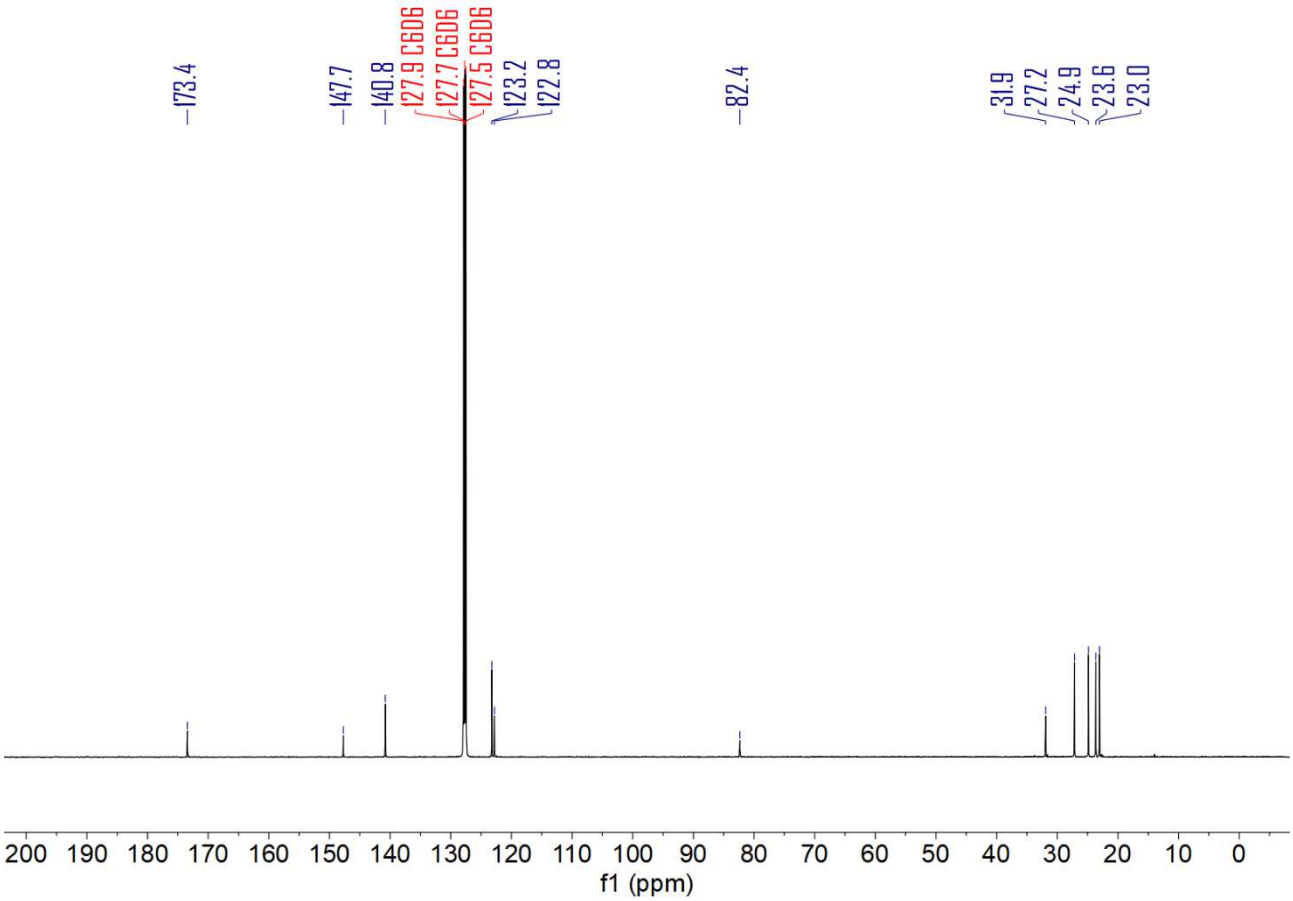


Figure S31. $^{13}C\{^{1}H\}$ NMR spectrum (125.7 MHz, C_6D_6, 298 K) of [(^{iPrDip}nacnac)Li] **6a**.

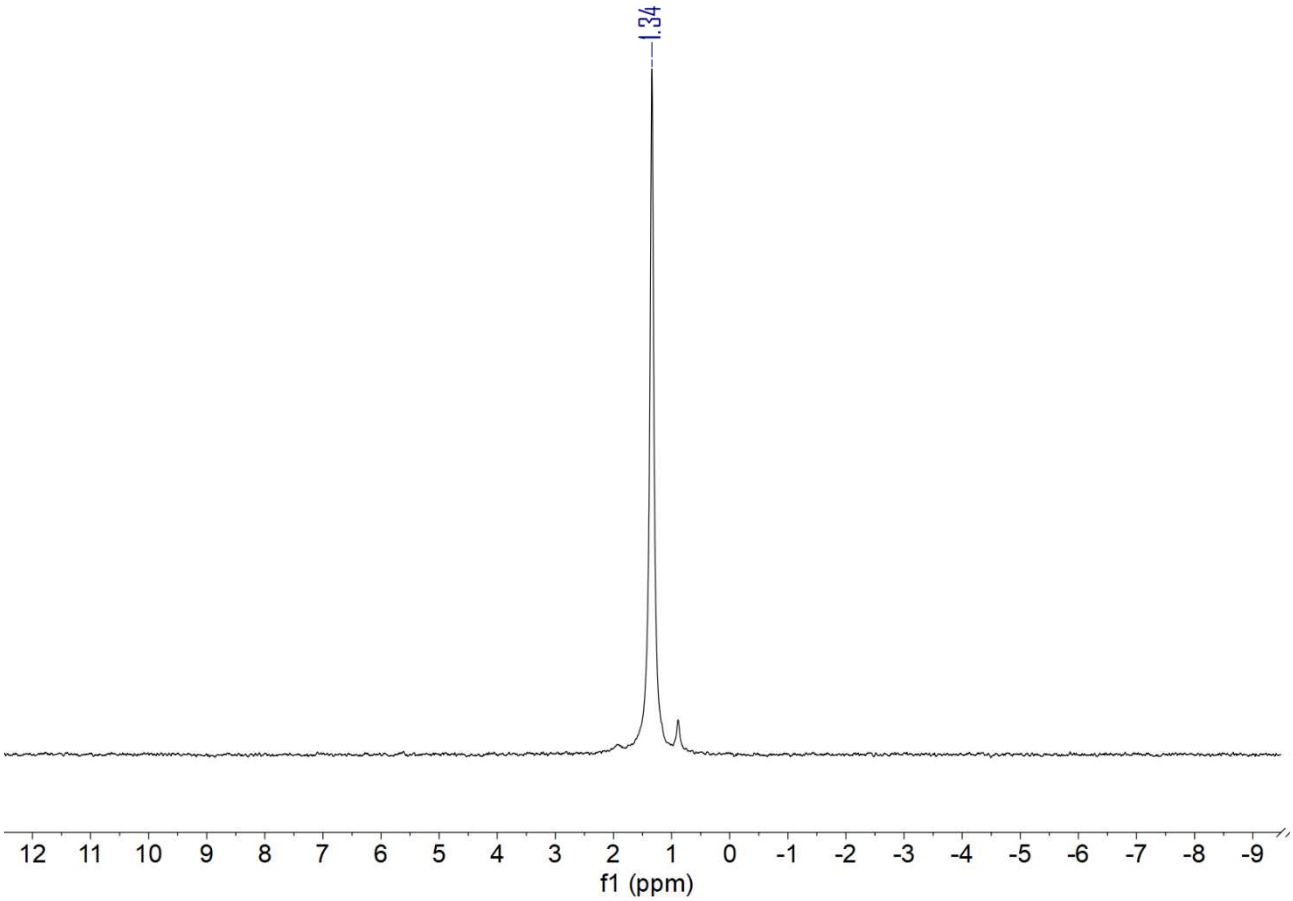


Figure S32. $^{7}Li\{^{1}H\}$ NMR (155.5 MHz, C_6D_6, 298 K) of ^{iPrDip}nacnacLi **6a**.

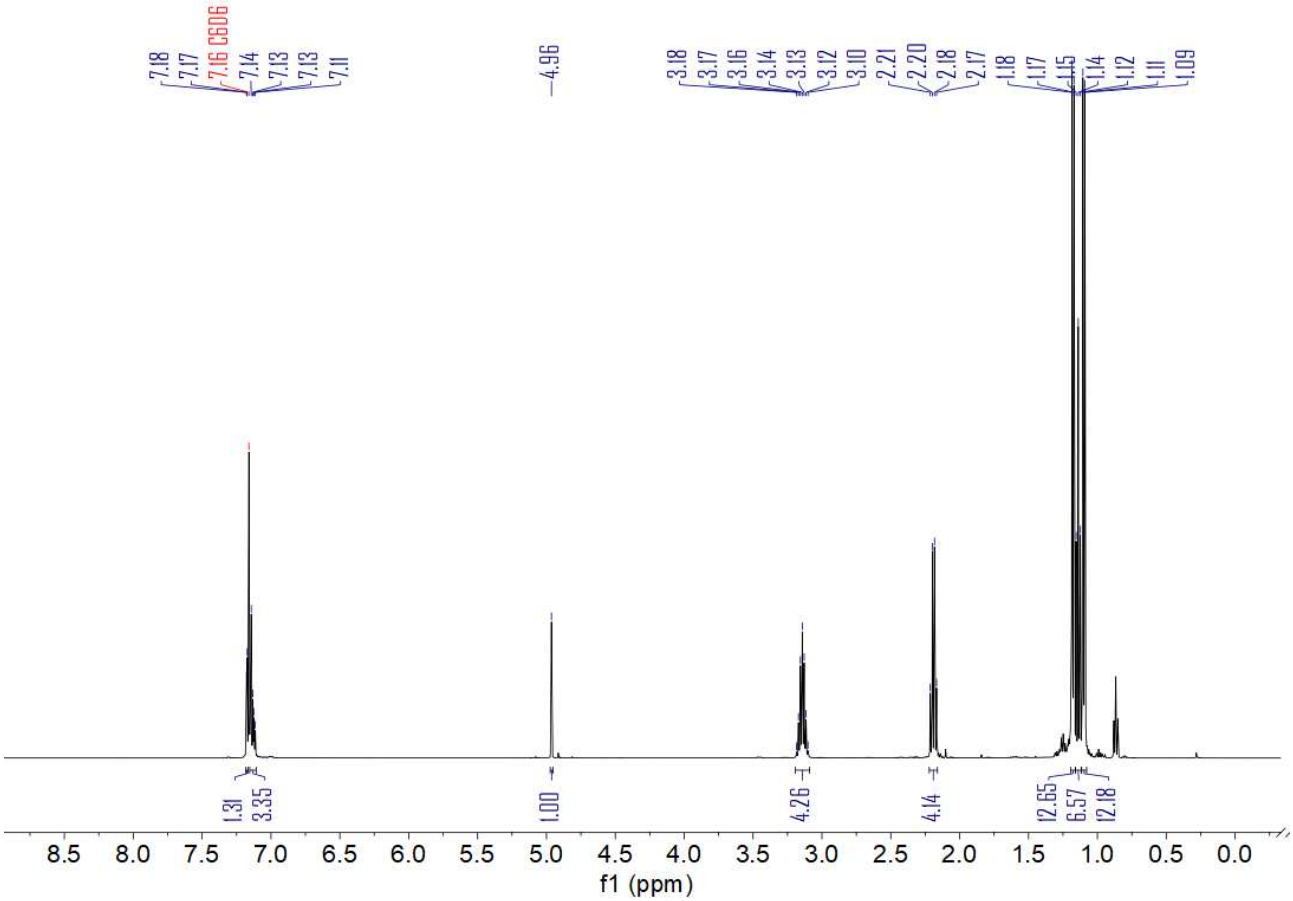


Figure S33. ^{1}H NMR spectrum (499.9 MHz, C_6D_6, 298 K) of [(^{EtDip}nacnac)Li] **6b**.

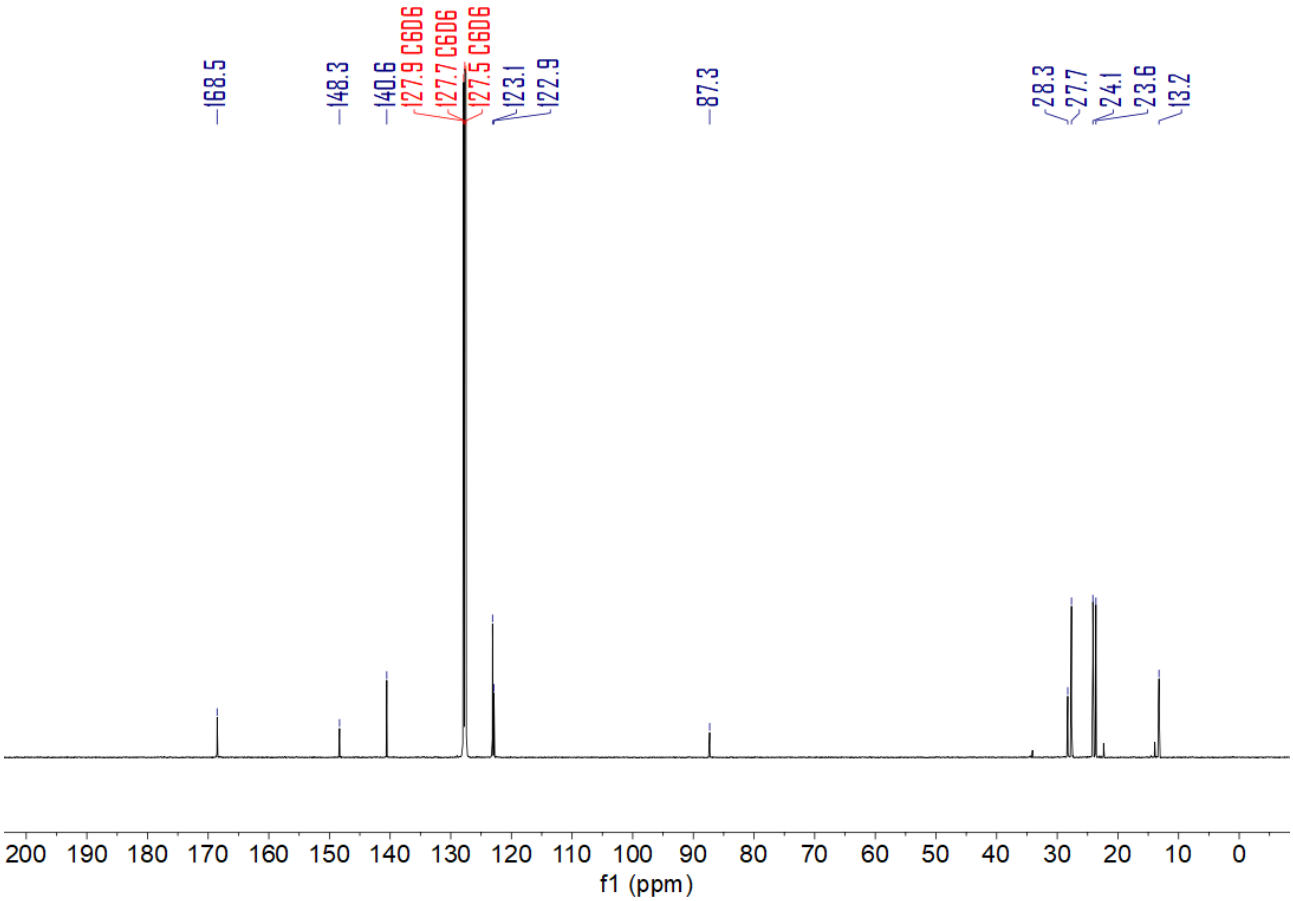


Figure S34. $^{13}C\{^{1}H\}$ NMR spectrum (125.7 MHz, C_6D_6, 298 K) of [(^{EtDip}nacnac)Li] **6b**.

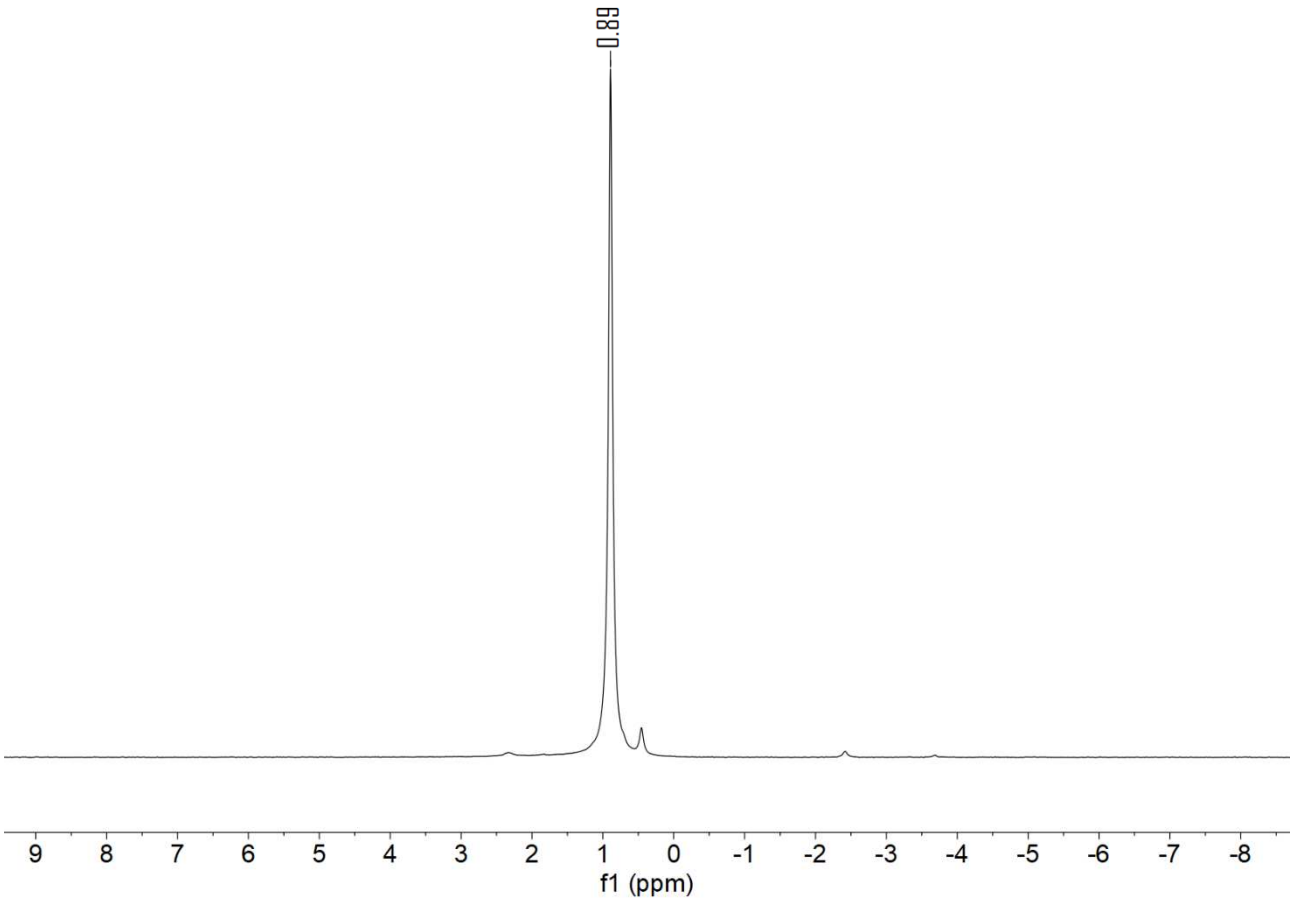


Figure S35. $^{7}Li\{^{1}H\}$ NMR Spectrum (155.5 MHz, C_6D_6, 298 K) of [(^{EtDip}nacnac)Li] **6b**.

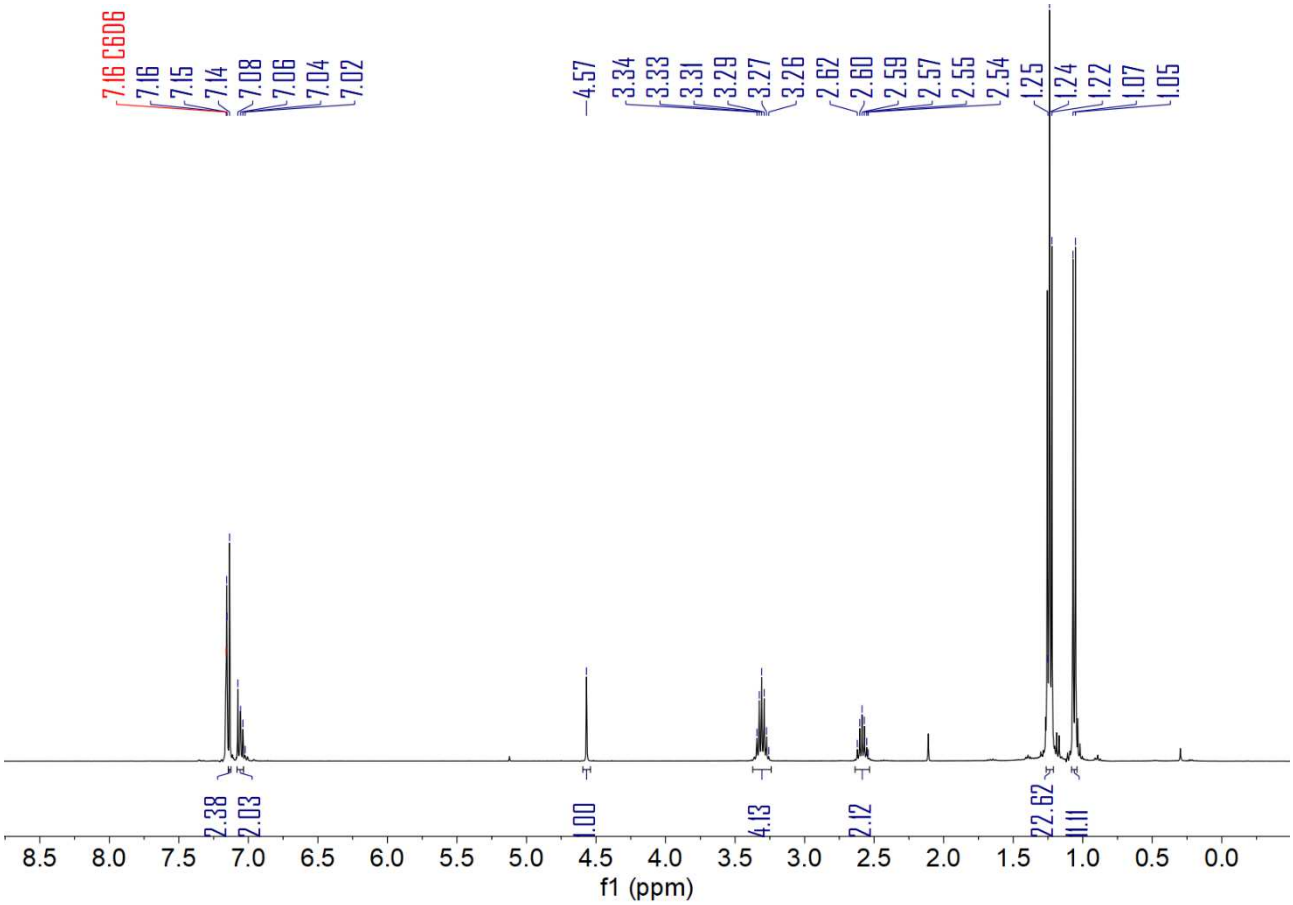


Figure S36. ^{1}H NMR spectrum (499.9 MHz, C_6D_6, 298 K) of [(^{iPrDip}nacnac)Na] **7a**.

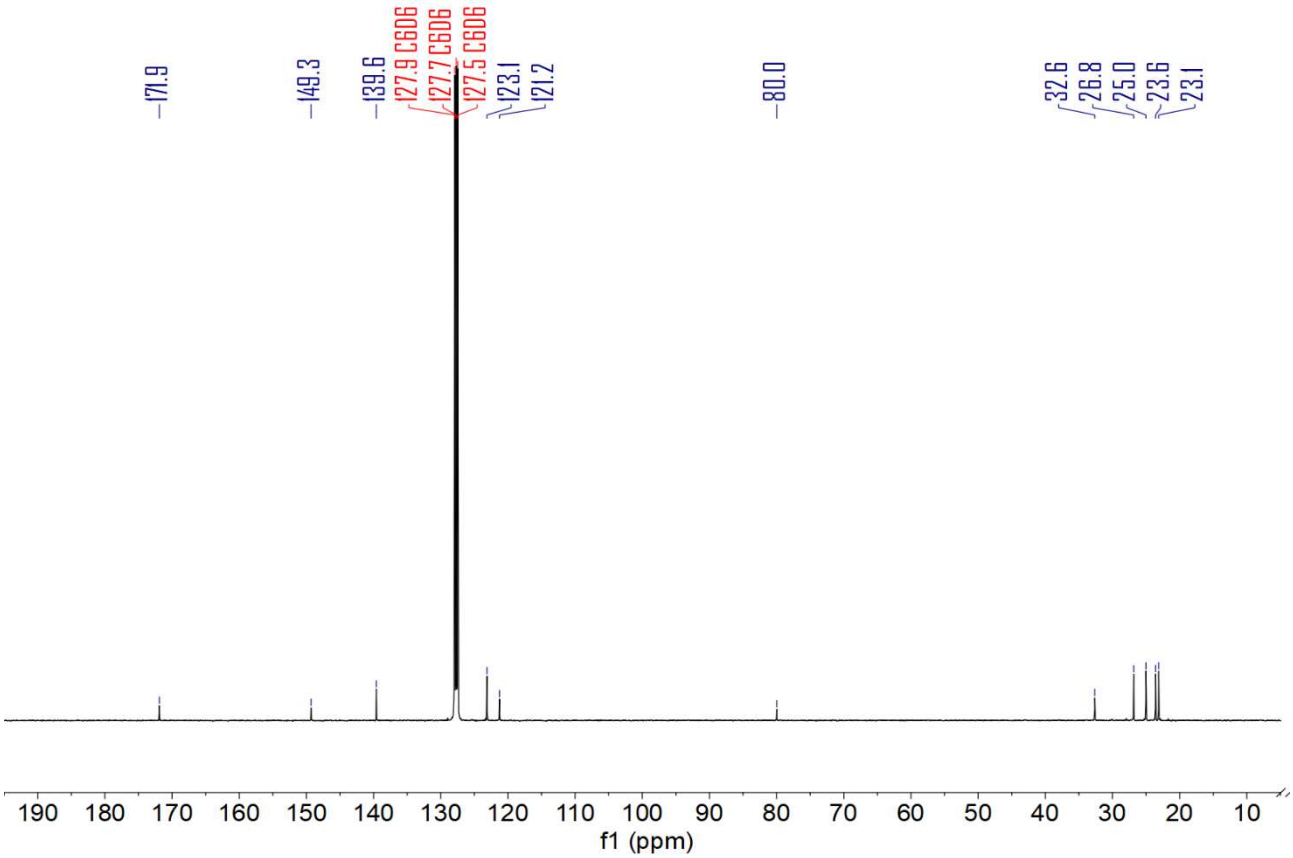


Figure S37. $^{13}C\{^{1}H\}$ NMR spectrum (100.6 MHz, C_6D_6, 295 K) of [(^{iPrDip}nacnac)Na] **7a**.

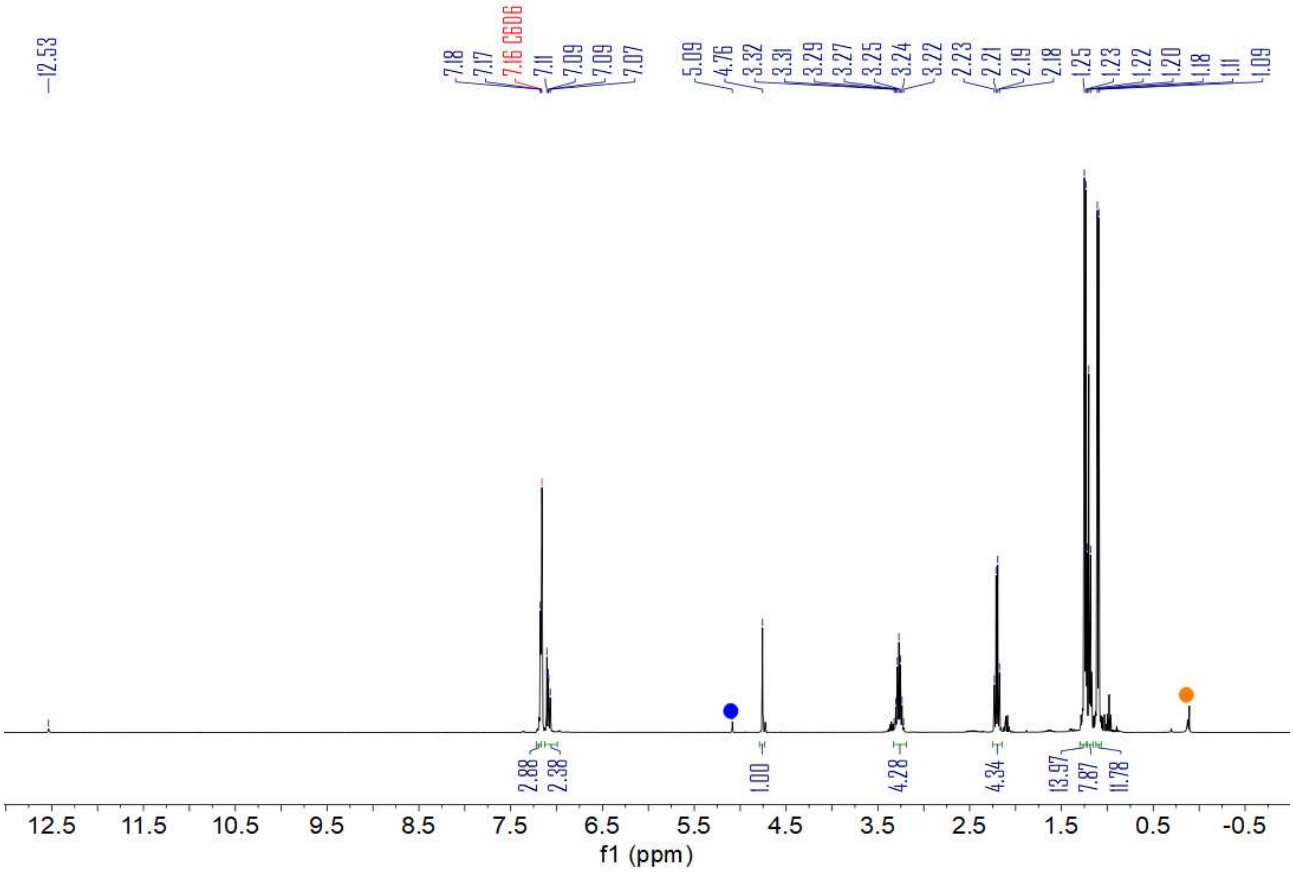


Figure S38. ^{1}H NMR spectrum (400.1 MHz, C_6D_6, 300 K) of [(^{EtDip}nacnac)Na] **7b**. The blue circle denotes the resonance of ^{EtDip}nacnacH **1a**. The orange circle denotes the chemical shift of silicone grease.

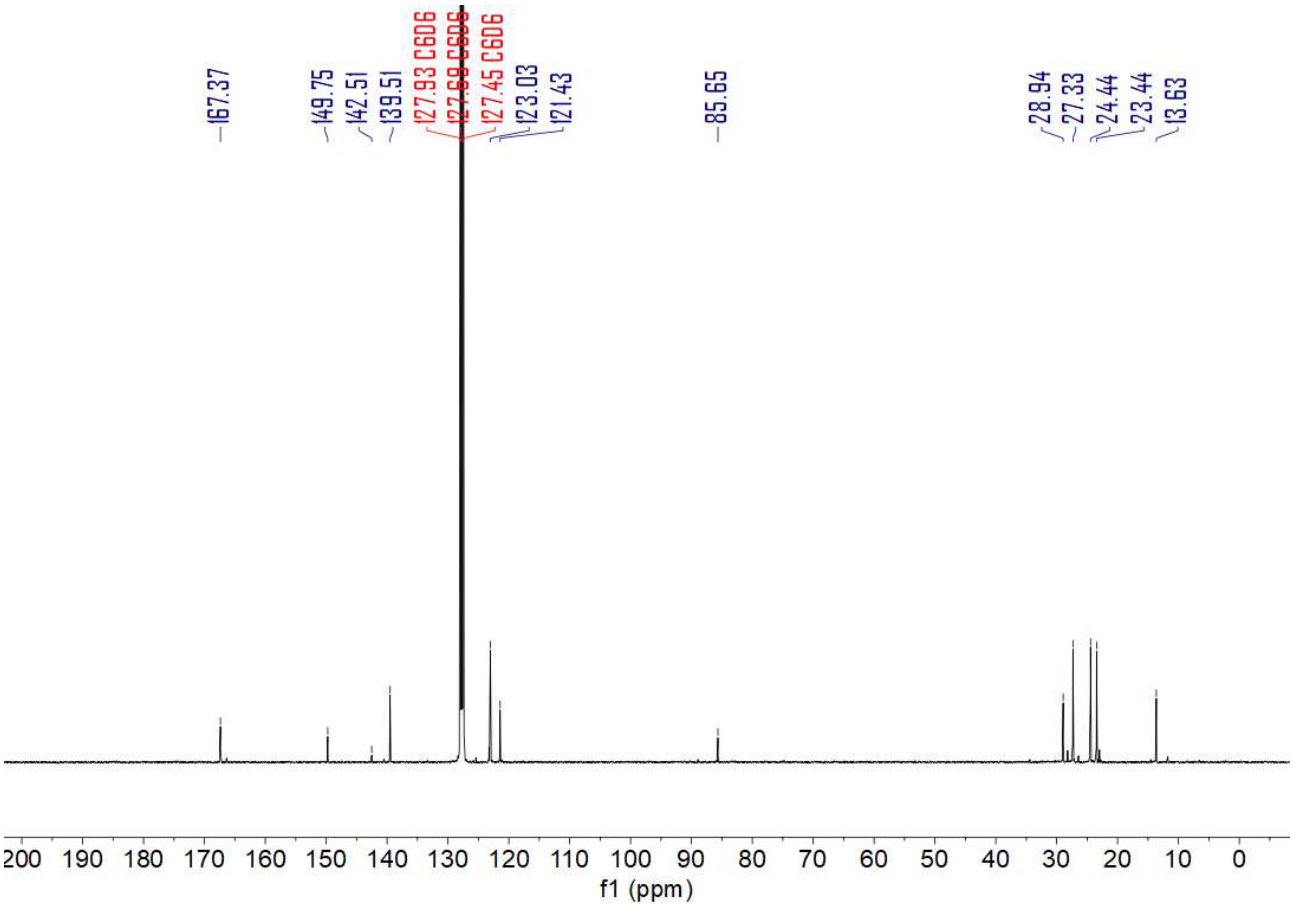


Figure S39. $^{13}C\{^{1}H\}$ NMR spectrum (101.0 MHz, C_6D_6, 300 K) of [(^{EtDip}nacnac)Na] **7b**.

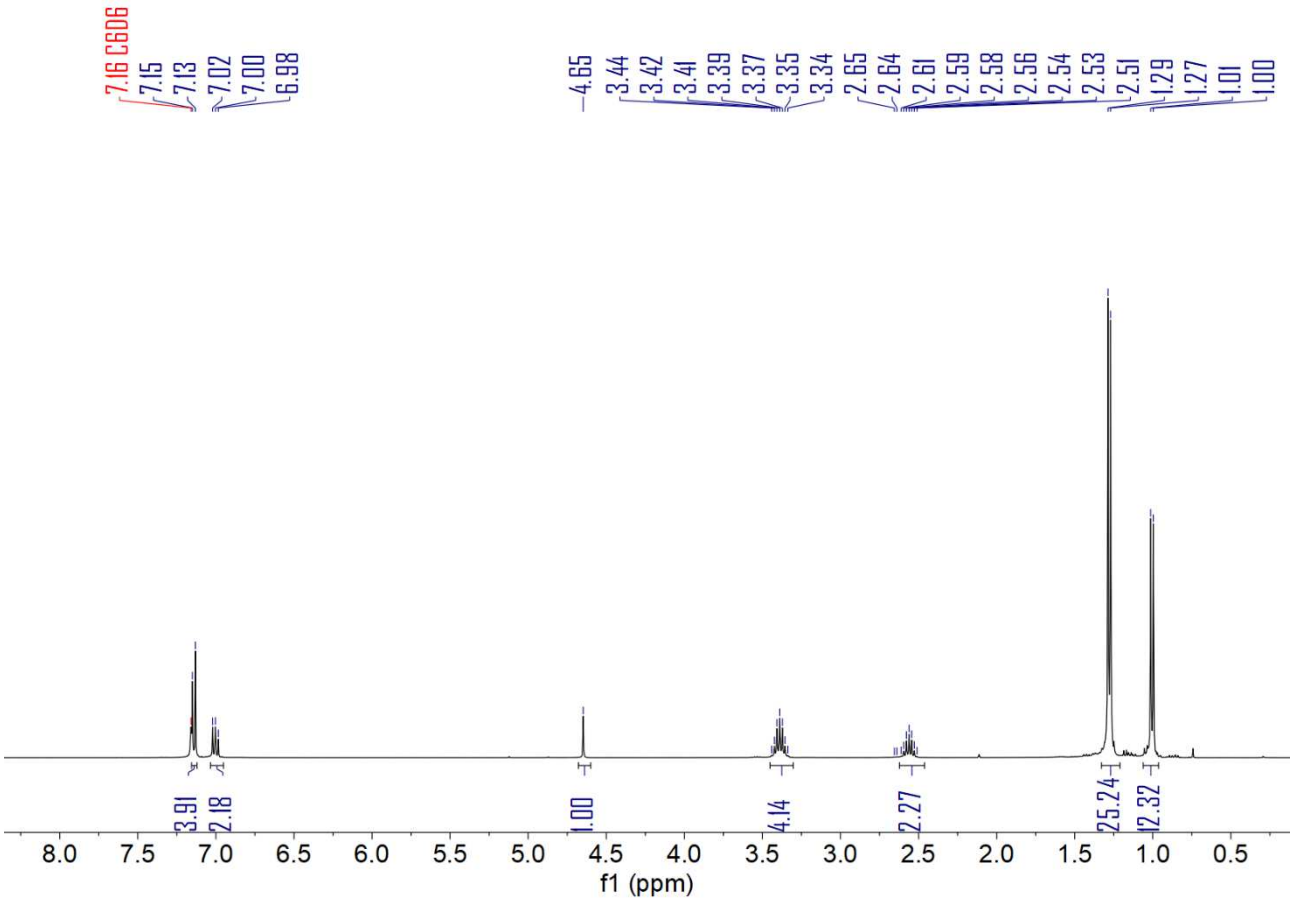


Figure S40. ^{1}H NMR spectrum (400.1 MHz, C_6D_6, 298 K) of [(^{iPrDip}nacnac)K] **8a**.

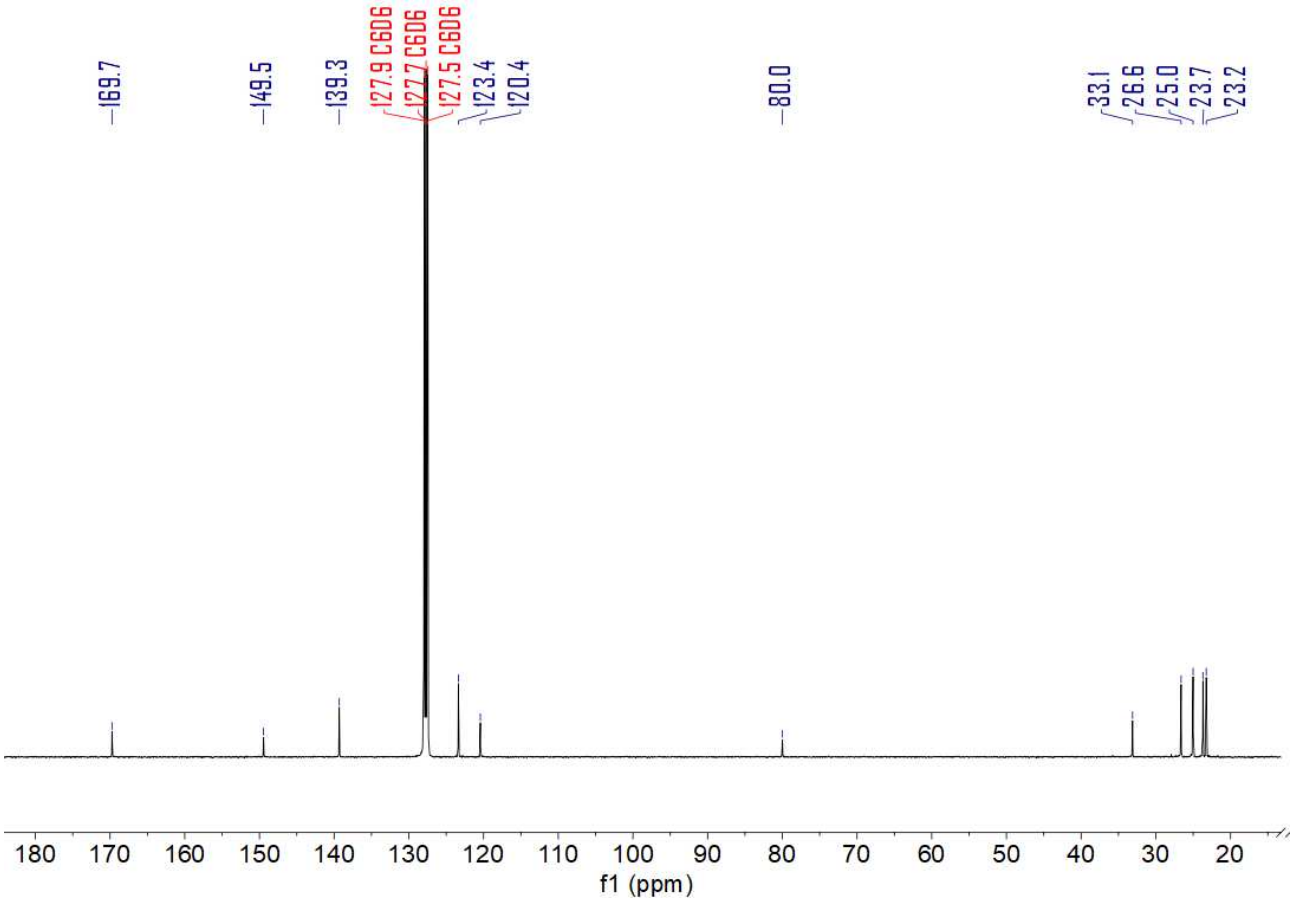


Figure S41. $^{13}C\{^{1}H\}$ NMR spectrum (100.6 MHz, C_6D_6, 298 K) of [(^{iPrDip}nacnac)K] **8a**.

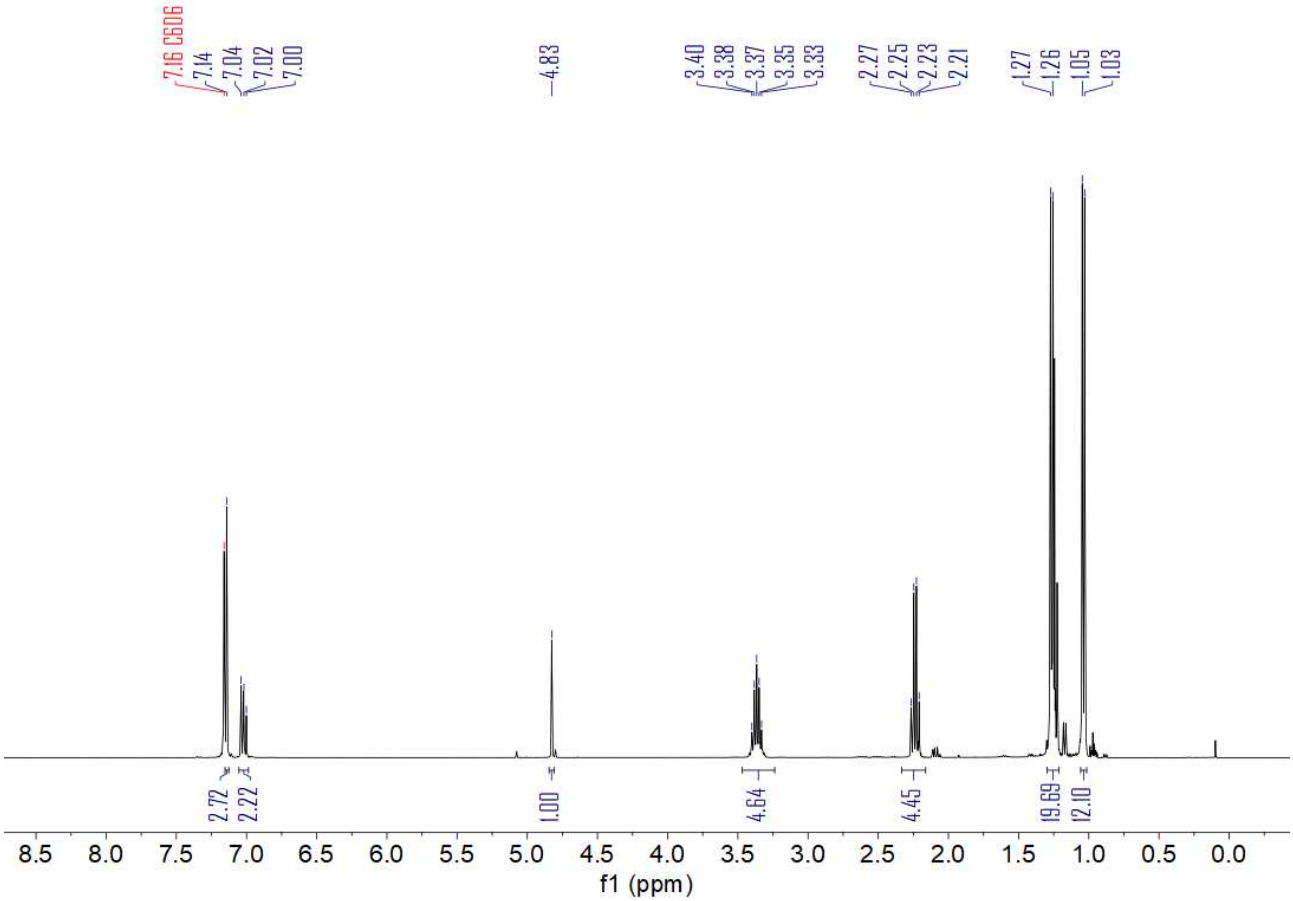


Figure S42. ^{1}H NMR spectrum (400.1 MHz, C_6D_6, 300 K) of [(^{EtDip}nacnac)K] **8b**.

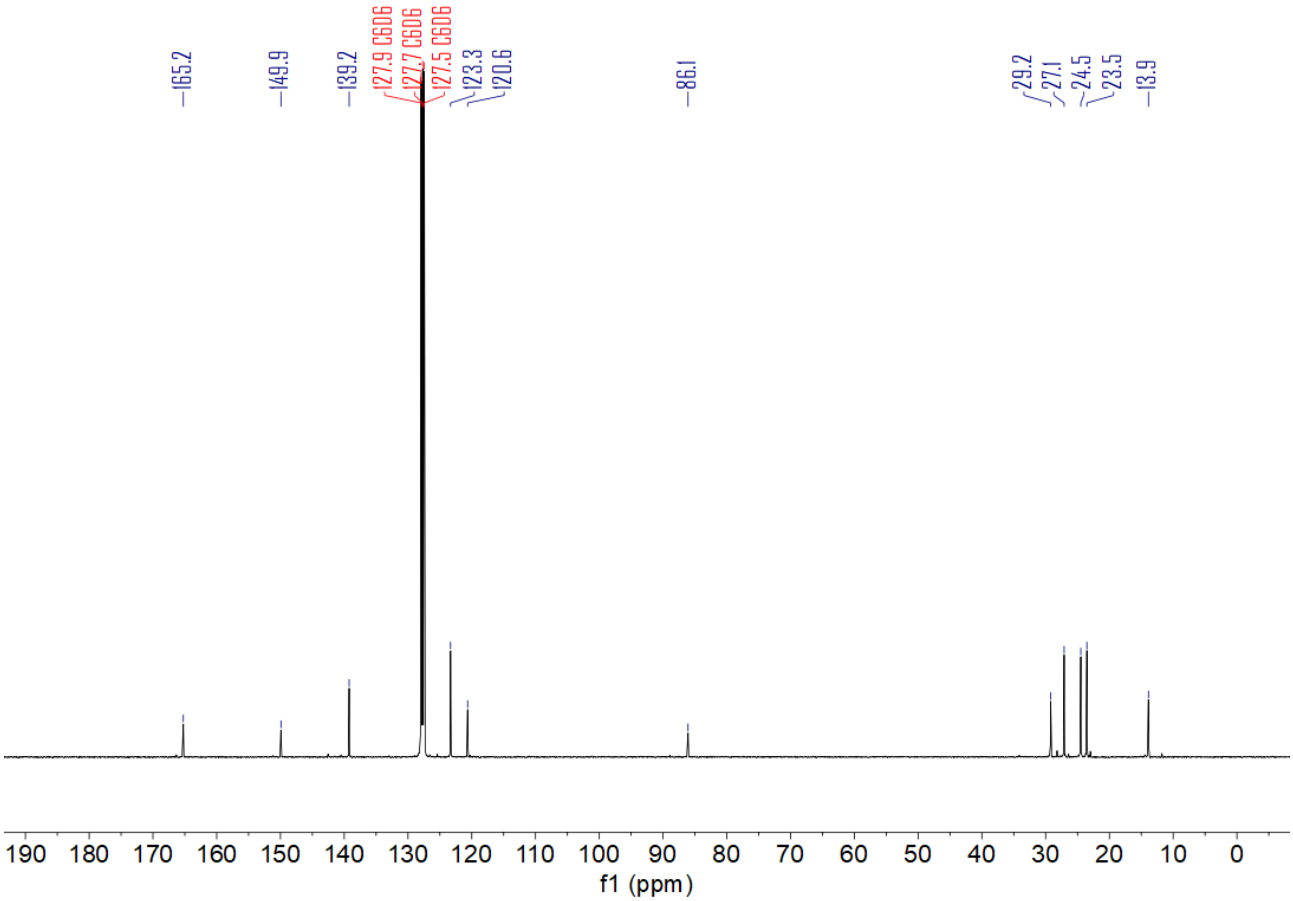


Figure S43. $^{13}C\{^{1}H\}$ NMR (100.7 MHz, C_6D_6, 300 K) of [(^{EtDip}nacnac)K] **8b**.

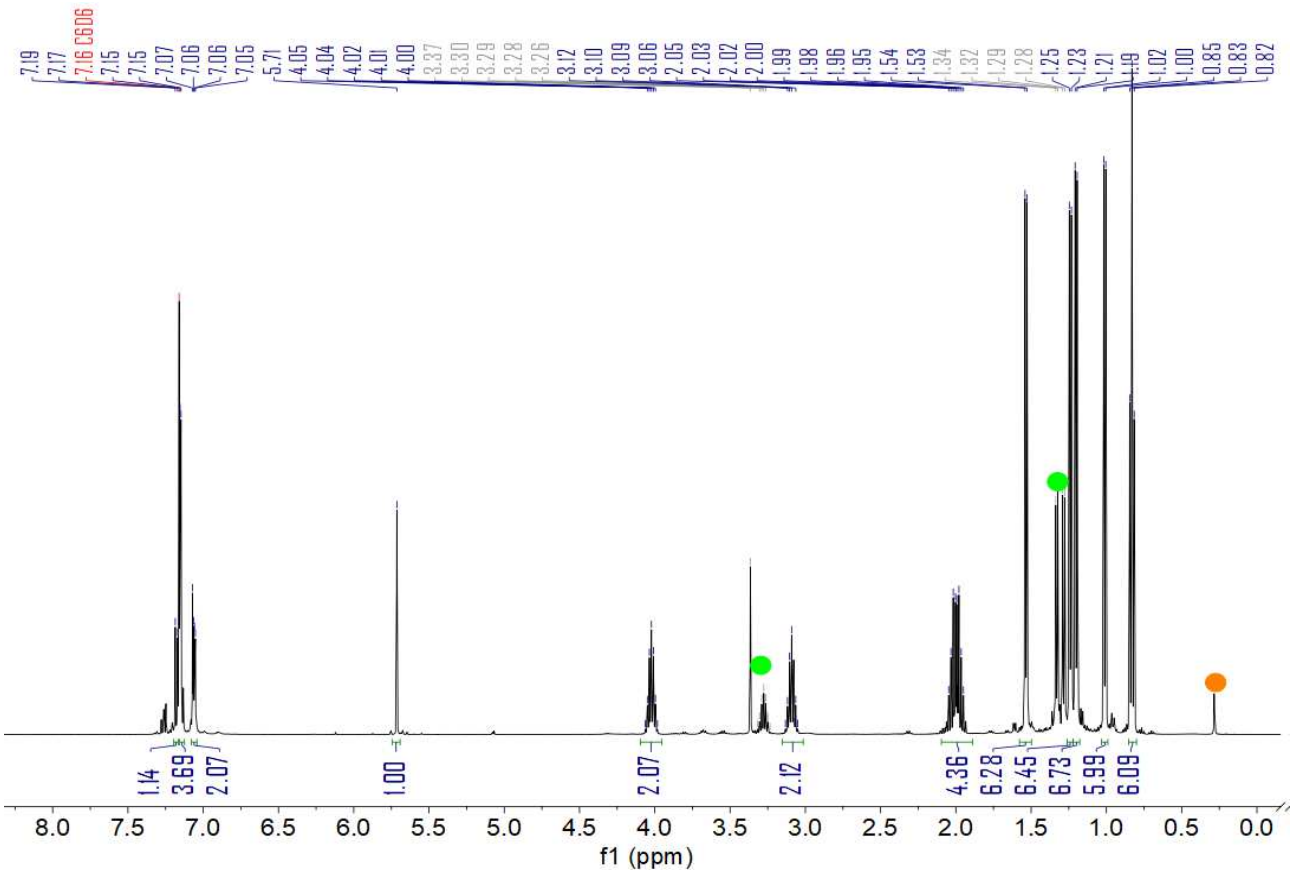


Figure S44. ^{1}H NMR spectrum (499.9 MHz, C_6D_6, 298 K) of (^{EtDip}nacnac)SiBr **9**. The green circles denote some residual resonances of uncoordinated SIDip in this sample. The orange circle denotes the chemical shift of silicone grease.

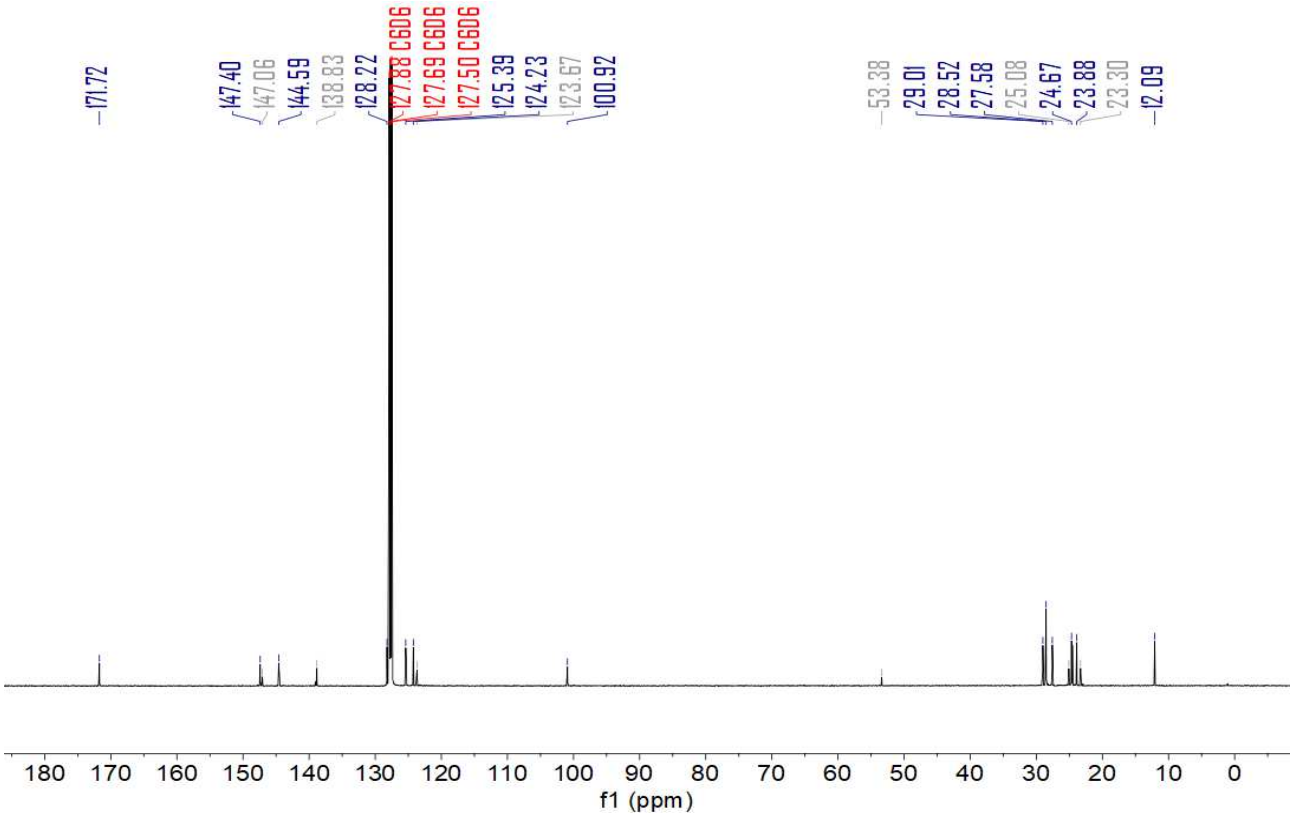


Figure S45. $^{13}C\{^{1}H\}$ NMR (100.7 MHz, C_6D_6, 300 K) of (^{EtDip}nacnac)SiBr **9**. The grey-labelled peaks denote the resonances of uncoordinated SIDip.

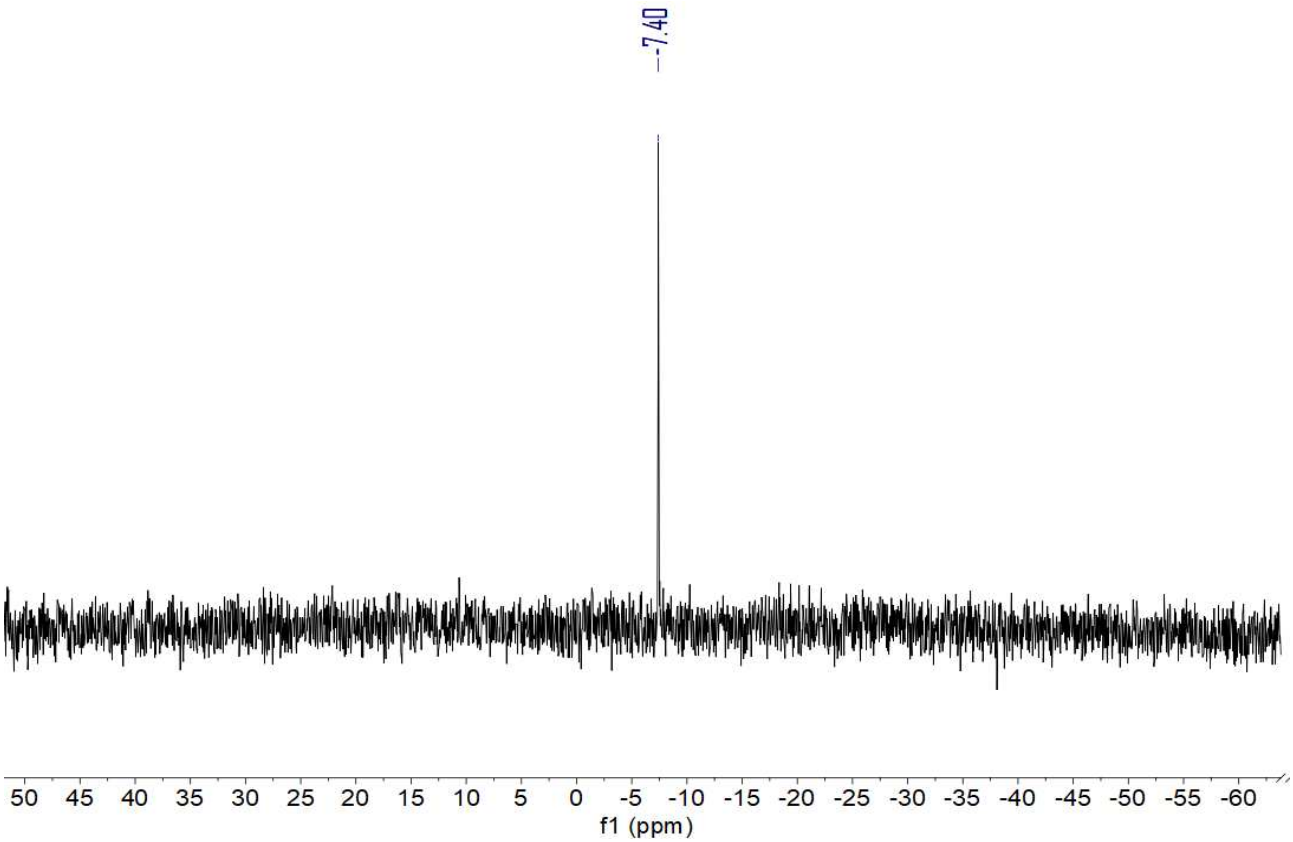


Figure S46. $^{29}Si\{^{1}H\}$ NMR spectrum (99.3 MHz, C_6D_6, 298 K) of (^{EtDip}nacnac)SiBr **9**.

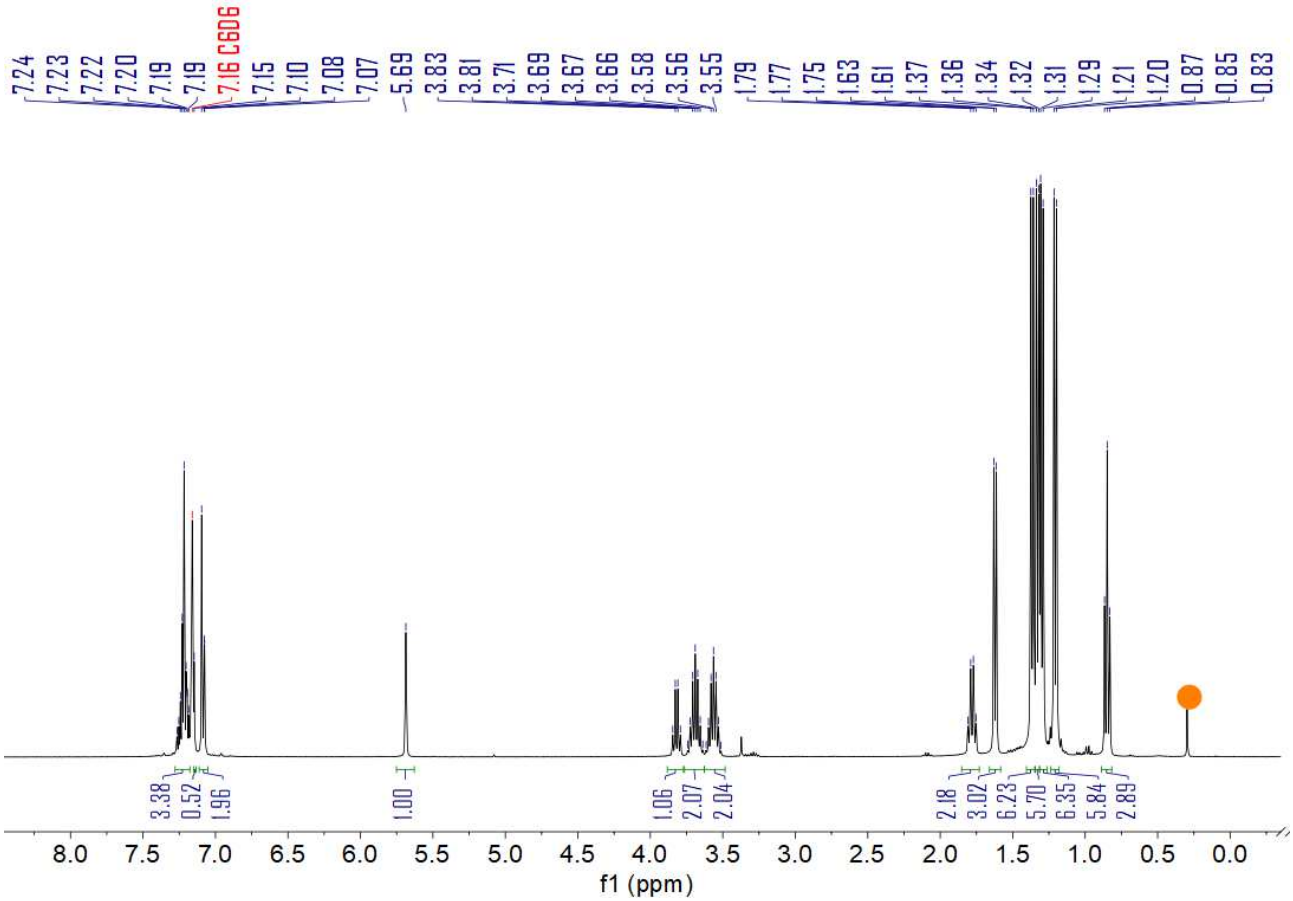


Figure S47. ^{1}H NMR spectrum (400.1 MHz, C_6D_6, 300 K) of (^{EtDip}nacnac')Si **10**. The orange circle denotes the chemical shift of silicone grease.

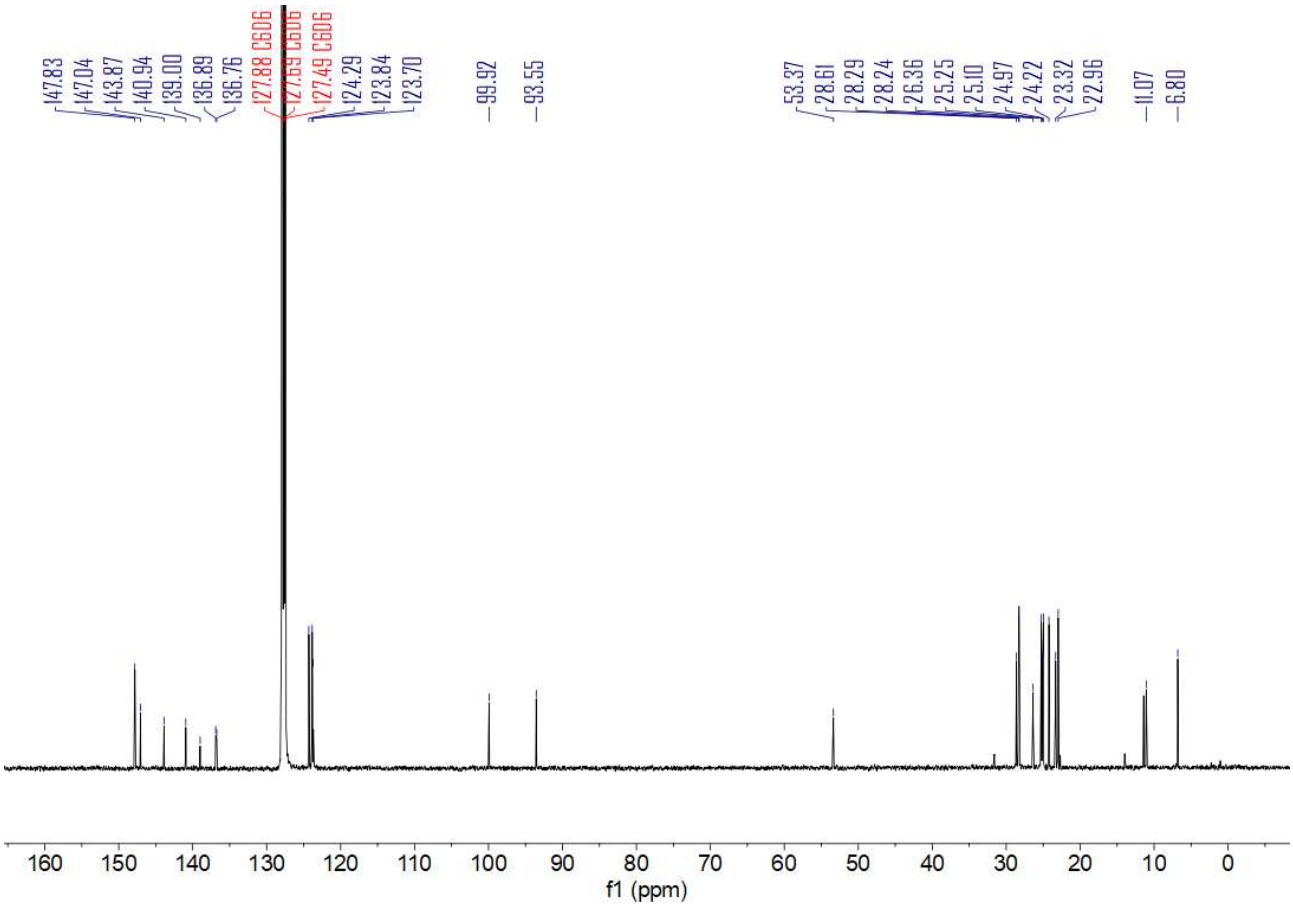


Figure S48. $^{13}C\{^{1}H\}$ NMR (100.7 MHz, C_6D_6, 300 K) of (^{EtDip}nacnac')Si **10**.

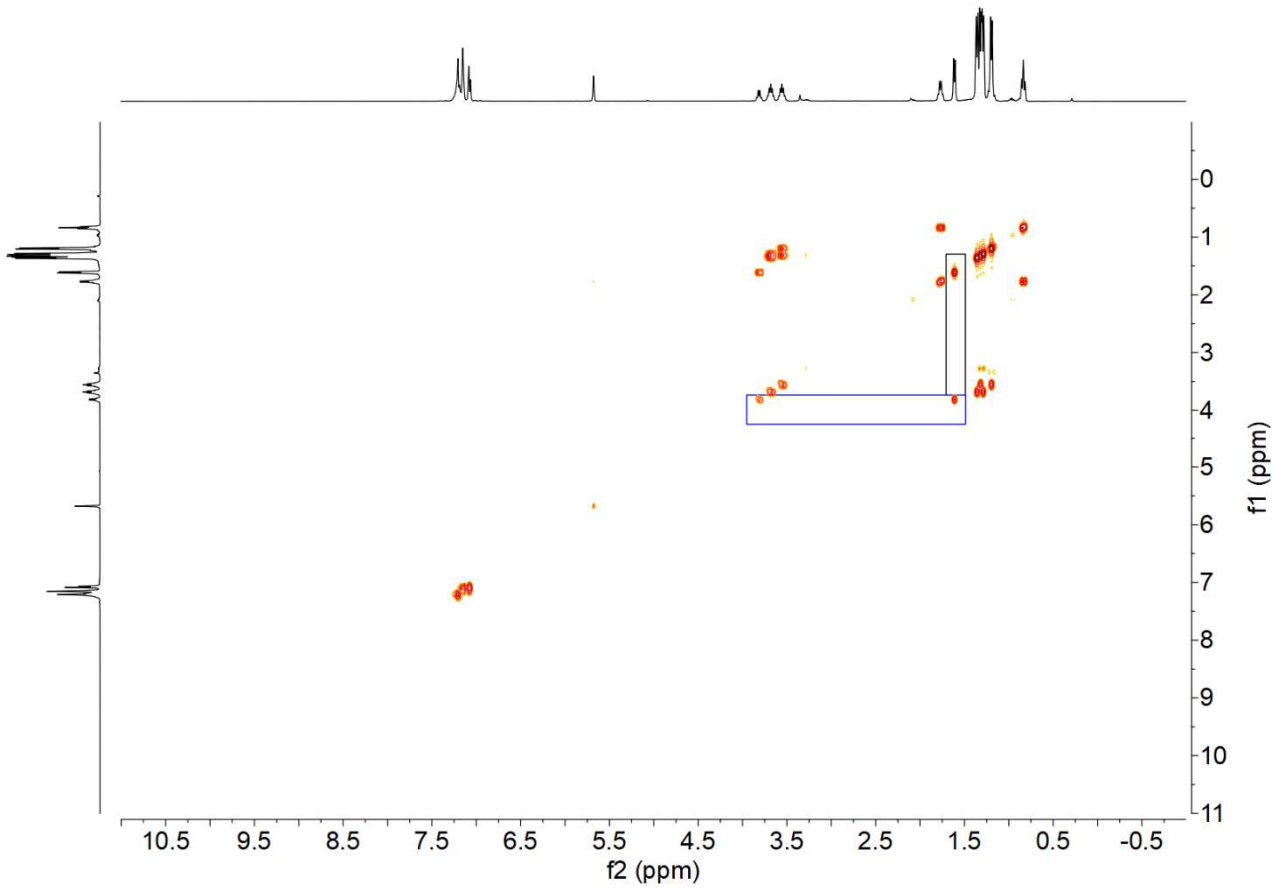


Figure S49. ^{1}H-^{1}H COSY NMR spectrum of (^{EtDip}nacnac')Si **10**. The coupling between the C*H* and CH_3 of the deprotonated Et group was marked as above.

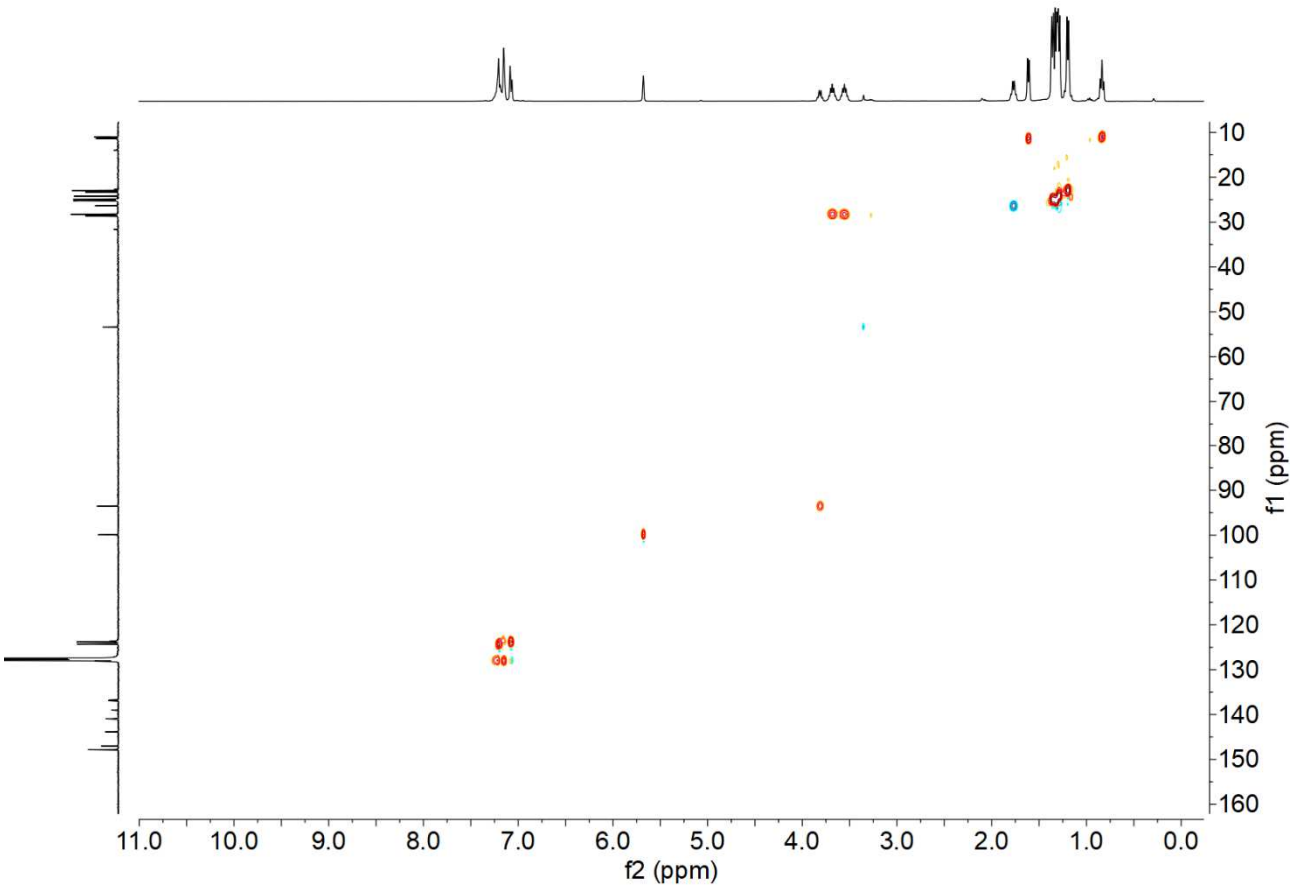


Figure S50. ^{1}H-^{13}C HSQC NMR spectrum of (^{EtDip}nacnac')Si **10**.

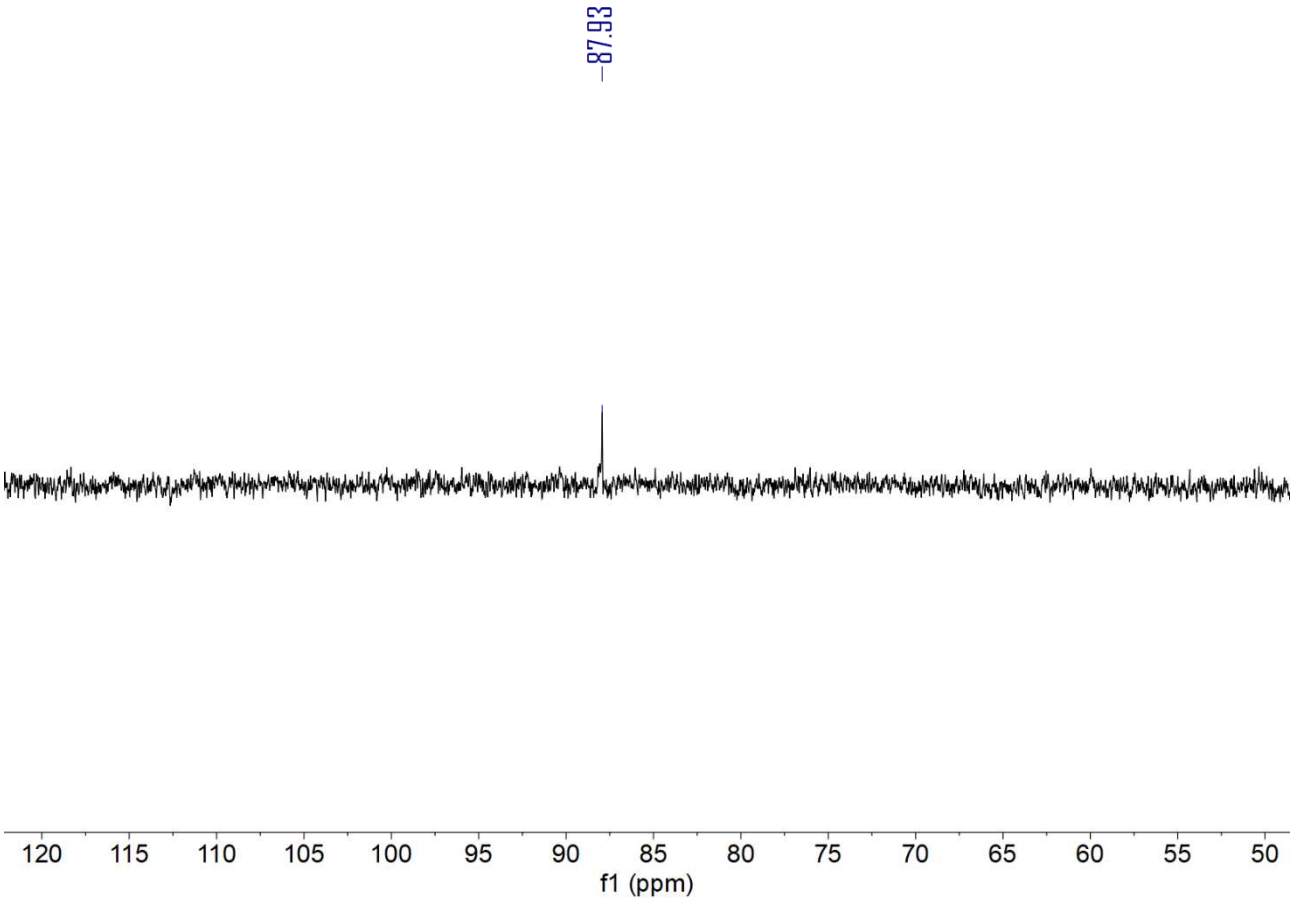


Figure S51. $^{29}Si\{^{1}H\}$ NMR spectrum (99.3 MHz, C_6D_6, 298 K) of (^{EtDip}nacnac')Si **10**.

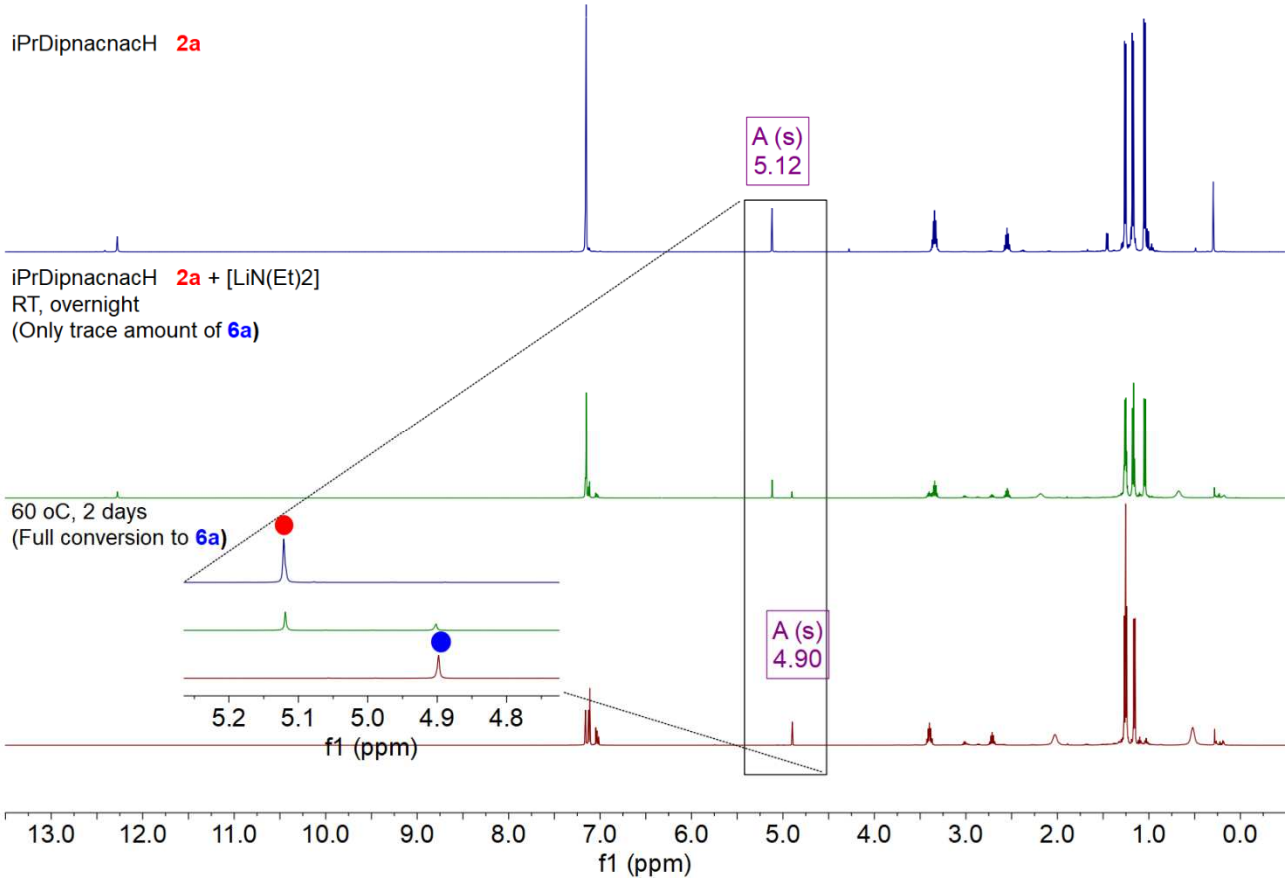


Figure S52. Stacked ^{1}H NMR spectra (499.9 MHz, C_6D_6, 298 K) of the reaction of ^{iPrDip}nacnacH **2a** (18 mg, 37.9 µmol, 1 equiv.) with [Li(NEt_2)] (3.15 mg, 39.8 µmol, 1.05 equiv.) in C_6D_6 (0.6 mL). The full conversion of **2a** was observed after heating the reaction mixture at 60 °C within 2 days. The red circle denotes the resonance of backbone-C*H* of **2a**. The blue circle denotes the resonance of backbone-C*H* of [(^{iPrDip}nacnac)Li] **6a**.

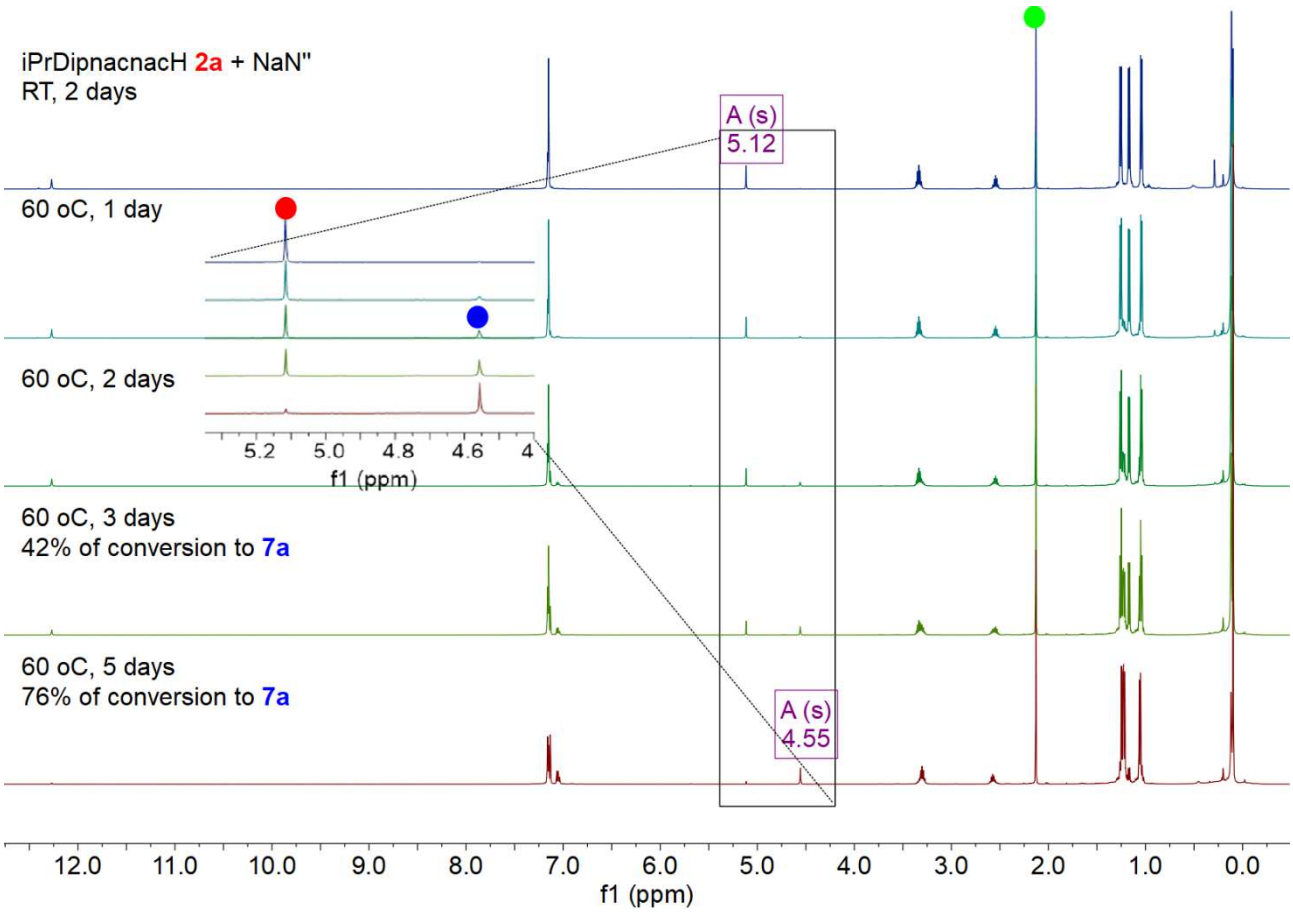


Figure S53. Stacked ^{1}H NMR spectra (499.9 MHz, C_6D_6, 298 K) of the reaction of ^{iPrDip}nacnacH **2a** (15 mg, 31.6 µmol, 1 equiv.) with [Na{N(SiMe$_3$)$_2$}] (6.37 mg, 34.8 µmol, 1.1 equiv.) in C_6D_6 (0.6 mL). Hexamethylbenzene (9.80 µmol, ca. 0.3 equiv.) was added as an internal standard. An *in-situ* yield of 76% was obtained by integrating against the internal standard after heating the reaction mixture at 60 °C for 5 days. The red circle denotes the resonance of backbone-C*H* of **2a**. The blue circle denotes the resonance of backbone-C*H* of [(^{iPrDip}nacnac)Na] **7a**. The green circle denotes the chemical shift of hexamethylbenzene.

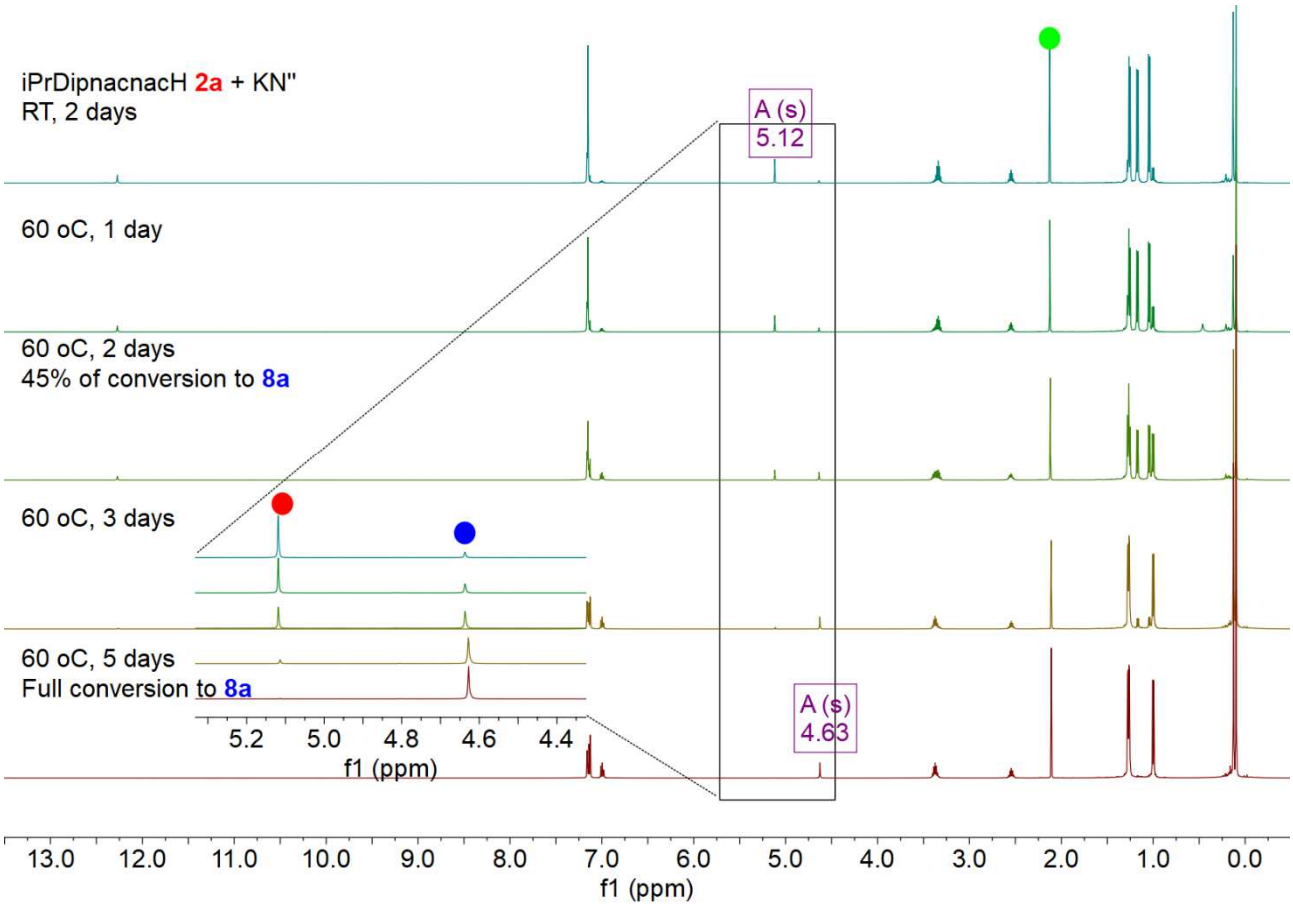


Figure S54. Stacked ^{1}H NMR spectra (499.9 MHz, C_6D_6, 298 K) of the reaction of ^{iPrDip}nacnacH **2a** (15 mg, 31.6 µmol, 1 equiv.) with [K{N(SiMe$_3$)$_2$}] (6.94 mg, 34.8 µmol, 1.1 equiv.) in C_6D_6 (0.6 mL). Hexamethylbenzene (9.80 µmol, ca. 0.3 equiv.) was added as an internal standard. *in-situ* yield (ca. 100%) of compound **8a** was achieved after heating the reaction mixture at 60 °C for 5 days. The red circle denotes the resonance of backbone-C*H* of **2a**. The blue circle denotes the resonance of backbone-C*H* of **8a**. The green circle denotes the chemical shift of hexamethylbenzene.

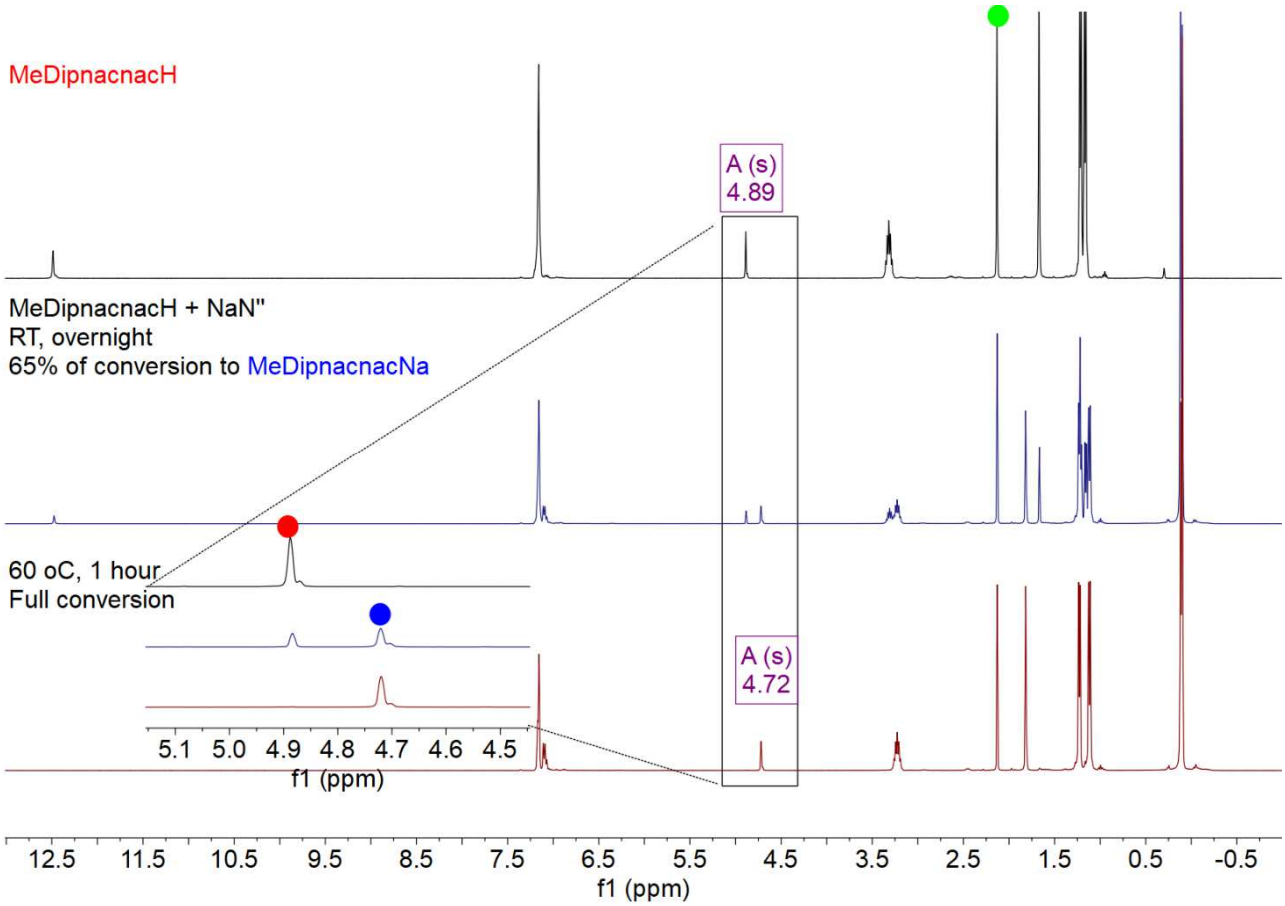


Figure S55. Stacked ^{1}H NMR spectra (400.1 MHz, C_6D_6, 294 K) of the reaction of ^{MeDip}nacnacH (13.2 mg, 31.6 µmol, 1 equiv.) with [Na{N(SiMe$_3$)$_2$}] (6.38 mg, 34.8 µmol, 1.1 equiv.) in C_6D_6 (0.6 mL). Hexamethylbenzene (9.80 µmol, ca. 0.3 equiv.) was added as an internal standard. The *in-situ* yield (ca. 100%) of compound [(^{MeDip}nacnac)Na] was achieved after heating the reaction mixture at 60 °C for one hour (following the partial room temperature conversion). The red circle denotes the resonance of backbone-C*H* of ^{MeDip}nacnacH. The blue circle denotes the resonance of backbone-C*H* of [(^{MeDip}nacnac)Na]. The green circle denotes the chemical shift of hexamethylbenzene.

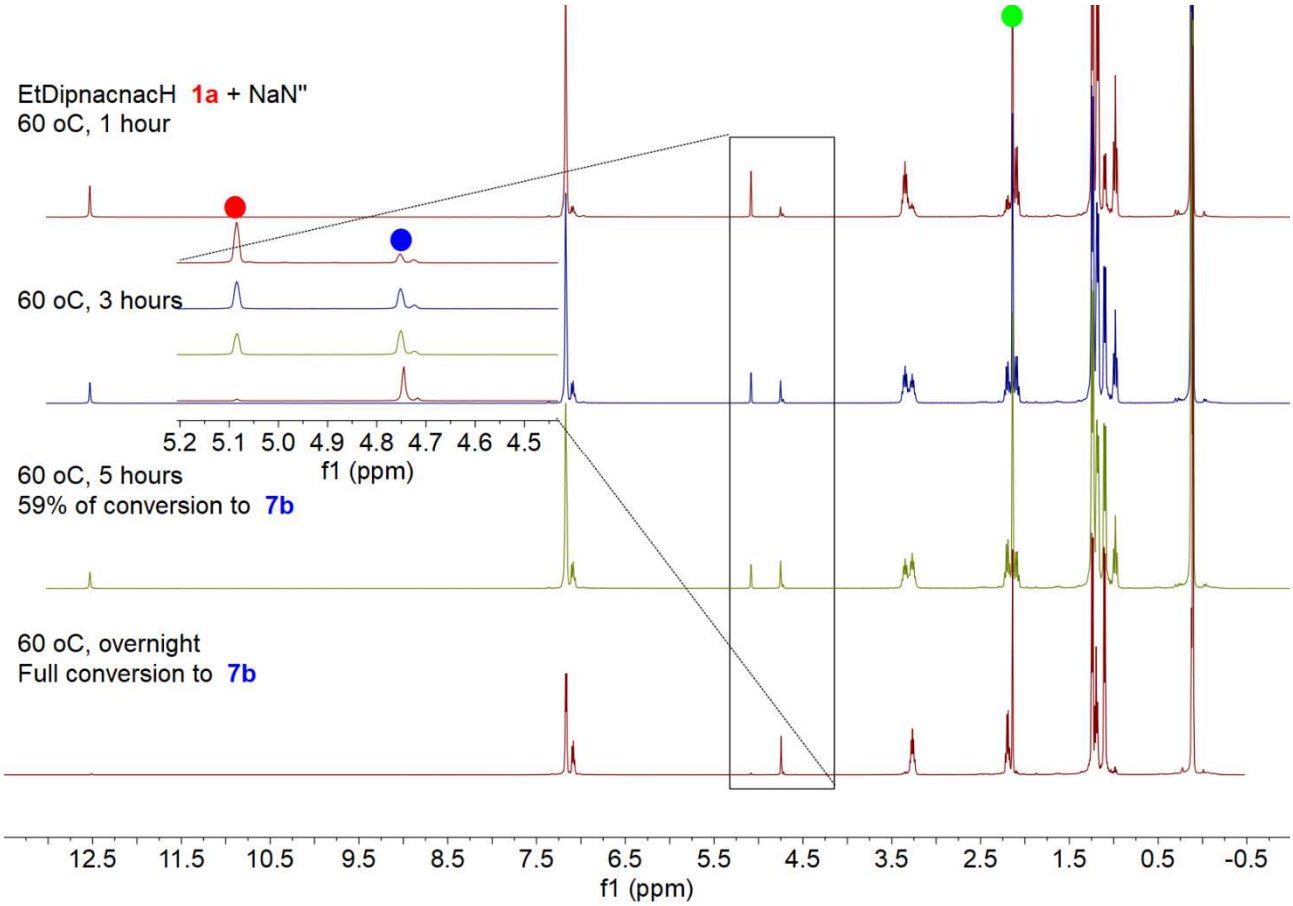
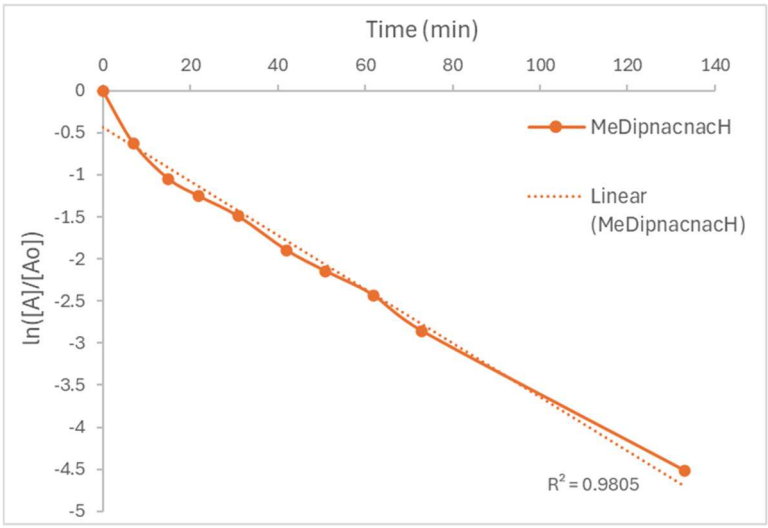
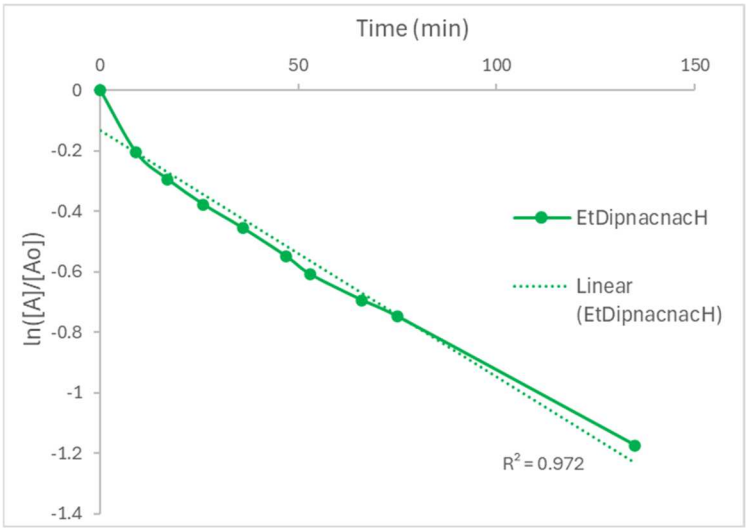


Figure S56. Stacked ^{1}H NMR spectra (400.1 MHz, C_6D_6, 294 K) of the reaction of ^{EtDip}nacnacH (14.1 mg, 31.6 µmol, 1 equiv.) with [Na{N(SiMe$_3$)$_2$}] (6.38 mg, 34.8 µmol, 1.1 equiv.) in C_6D_6 (0.6 mL). Hexamethylbenzene (9.80 µmol, ca. 0.3 equiv.) was added as an internal standard. An *in-situ* conversion (ca. 100%) of compound [(^{EtDip}nacnac)Na] **7b** was achieved after heating the reaction mixture at 60 °C overnight. The red circle denotes the resonance of backbone-C*H* of ^{EtDip}nacnacH **1a**. The blue circle denotes the resonance of backbone-C*H* of **7b**. The green circle denotes the chemical shift of hexamethylbenzene.

(a)



(b)



(c)

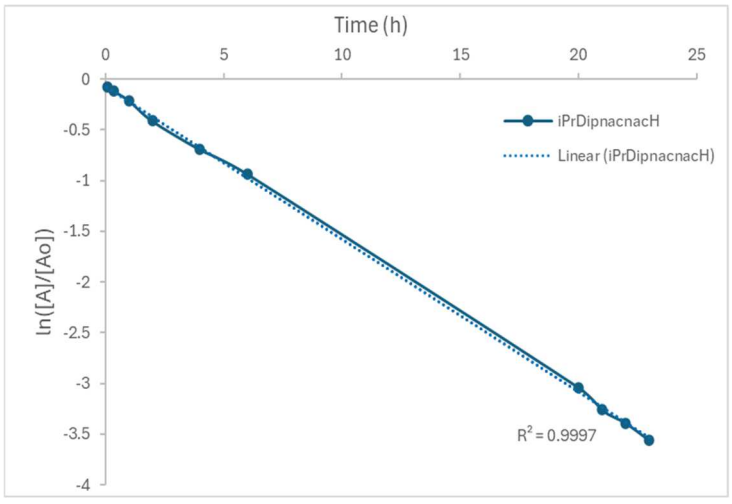


Figure S57. Pseudo first order kinetics for the reactions of (a) ^{MeDip}nacnacH (5.44 mg, 13.1 µmol, 1 equiv.), (b) ^{EtDip}nacnacH (5.81 mg, 13.1 µmol, 1 equiv.) and (c) ^{iPrDip}nacnacH (6.17 mg, 13.1 µmol, 1 equiv.) with an excess of [K{N(SiMe$_3$)$_2$}] (26.0 mg, 131 µmol, 10 equiv.), respectively. Hexamethylbenzene (2.0 mg, 12.3 µmol) was added as an internal standard. The concentration of

each compound was determined by the integration of targeting resonance from the corresponding ^{1}H NMR spectrum (499.9 MHz, C_6D_6, 298 K). The experiments of ^{MeDip}nacnacH and ^{EtDip}nacnacH with [K{N(SiMe$_3$)$_2$}] (charts a and b) were conducted at room temperature, whilst the experiment of ^{iPrDip}nacnacH with [K{N(SiMe$_3$)$_2$}] (chart c) was conducted at 60 °C. The rate constant (*k'*) for each compounds were calculated as 3.03×10^{-2} min^{-1} (a), 7.58×10^{-3} min^{-1} (b), 2.51×10^{-3} min^{-1} (c). Please note that the time recorded for the compound addition and start of the reaction ($t = 0$) is less accurate due to the practicalities of the sample preparation in the glove box.

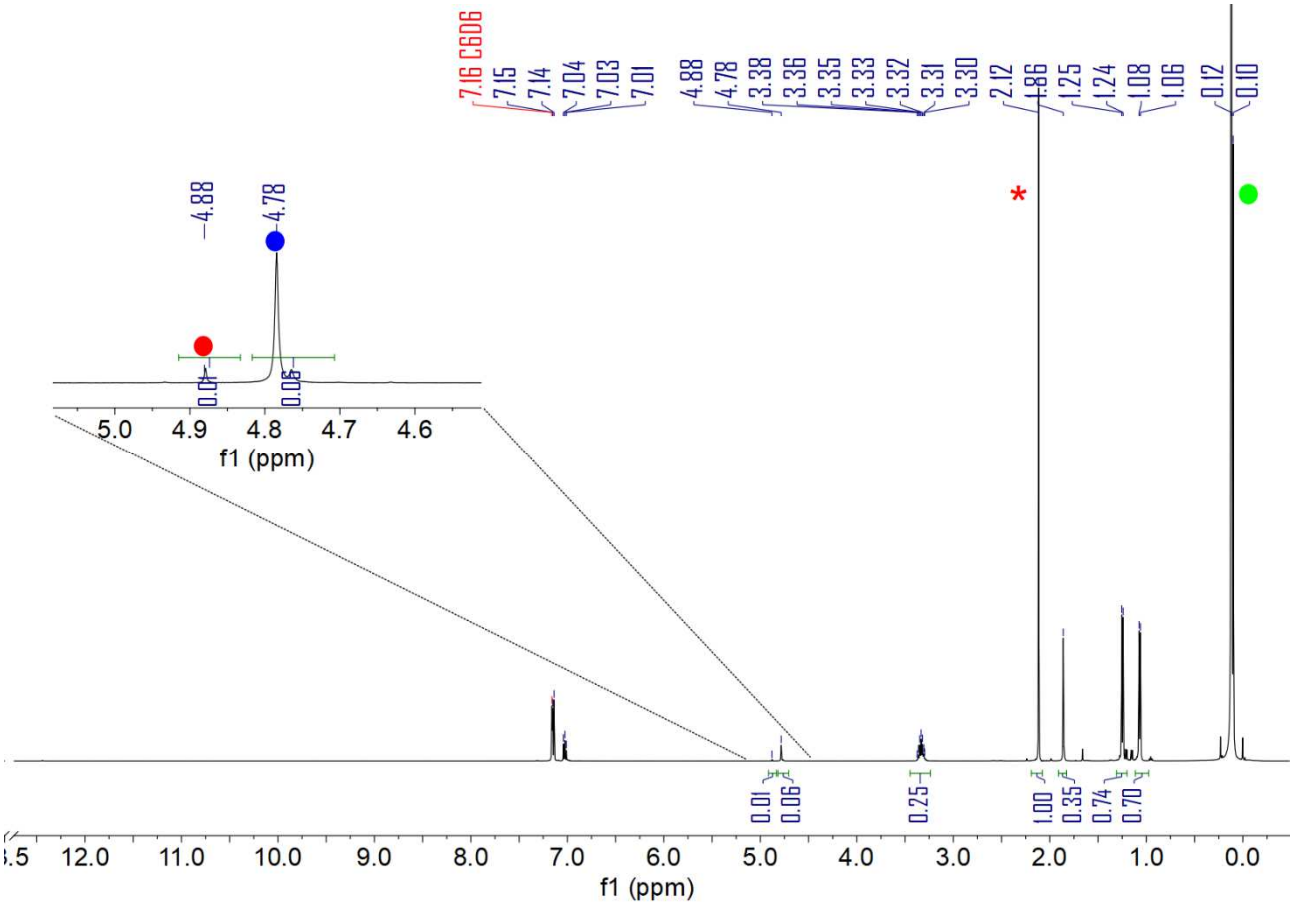


Figure S58. The example NMR spectrum of the deprotonation of ^{MeDip}nacnacH (5.44 mg, 13.1 µmol, 1 equiv.) with [K{N(SiMe$_3$)$_2$}] (26.0 mg, 131 µmol, 10 equiv.) at room temperature after *ca.* 73 minutes. Hexamethylbenzene (2.0 mg, 12.3 µmol) was added as an internal standard and marked with a red star. The red circle denotes the resonance of backbone-C*H* of ^{MeDip}nacnacH. The blue circle denotes the resonance of backbone-C*H* of [(^{MeDip}nacnac)K]. The green circle denotes the resonances of [K{N(SiMe$_3$)$_2$}] and [H{N(SiMe$_3$)$_2$}].

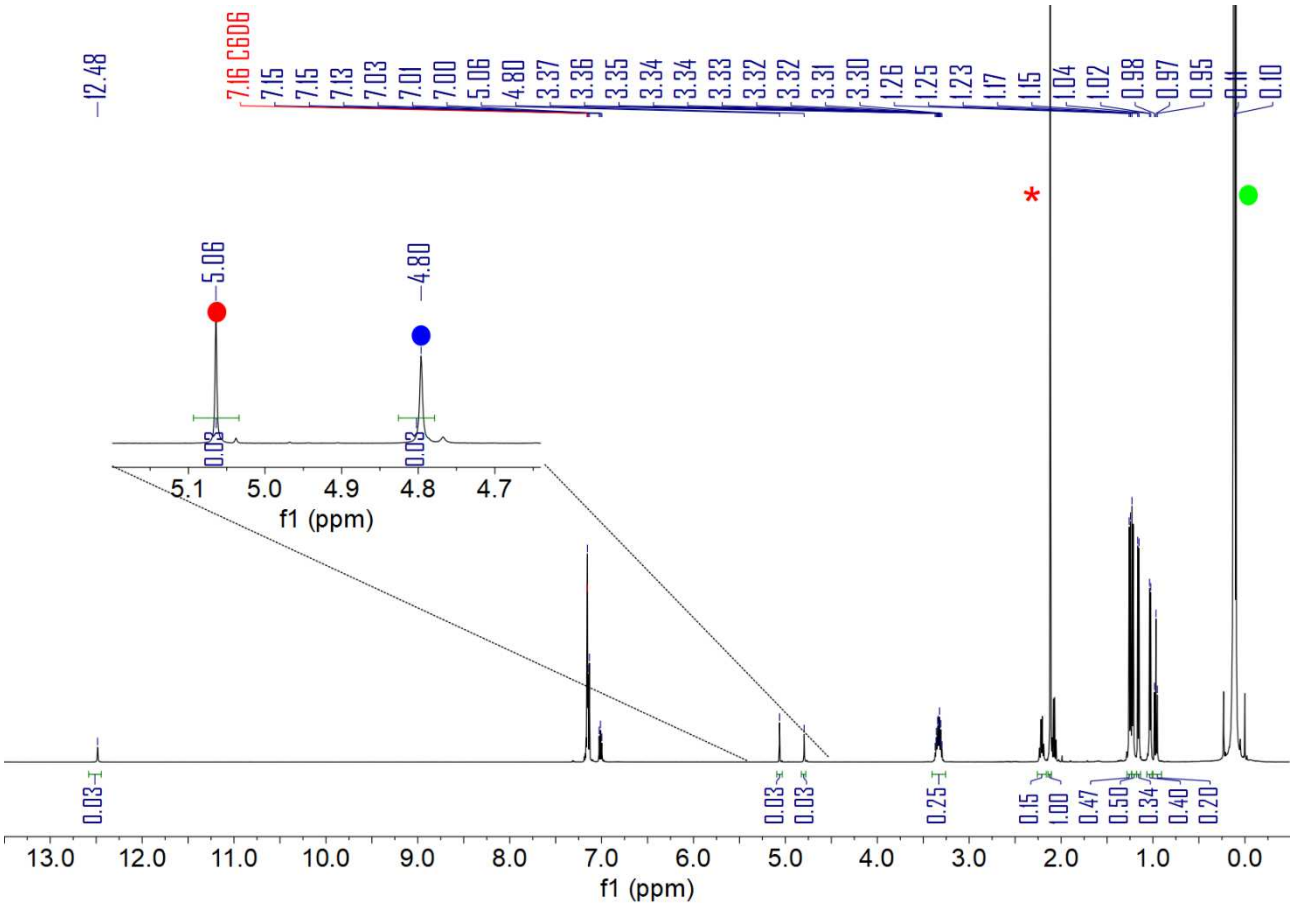


Figure S59. The example NMR spectrum of the deprotonation of ^{EtDip}nacnacH **1a** (5.81 mg, 13.1 µmol, 1 equiv.) with [K{N(SiMe$_3$)$_2$}] (26.0 mg, 131 µmol, 10 equiv.) at room temperature after *ca.* 75 minutes. Hexamethylbenzene (2.0 mg, 12.3 µmol) was added as an internal standard and marked with a red star. The red circle denotes the resonance of backbone-C*H* of ^{EtDip}nacnacH. The blue circle denotes the resonance of backbone-C*H* of [(^{EtDip}nacnac)K] **8b**. The green circle denotes the resonances of [K{N(SiMe$_3$)$_2$}] and [H{N(SiMe$_3$)$_2$}].

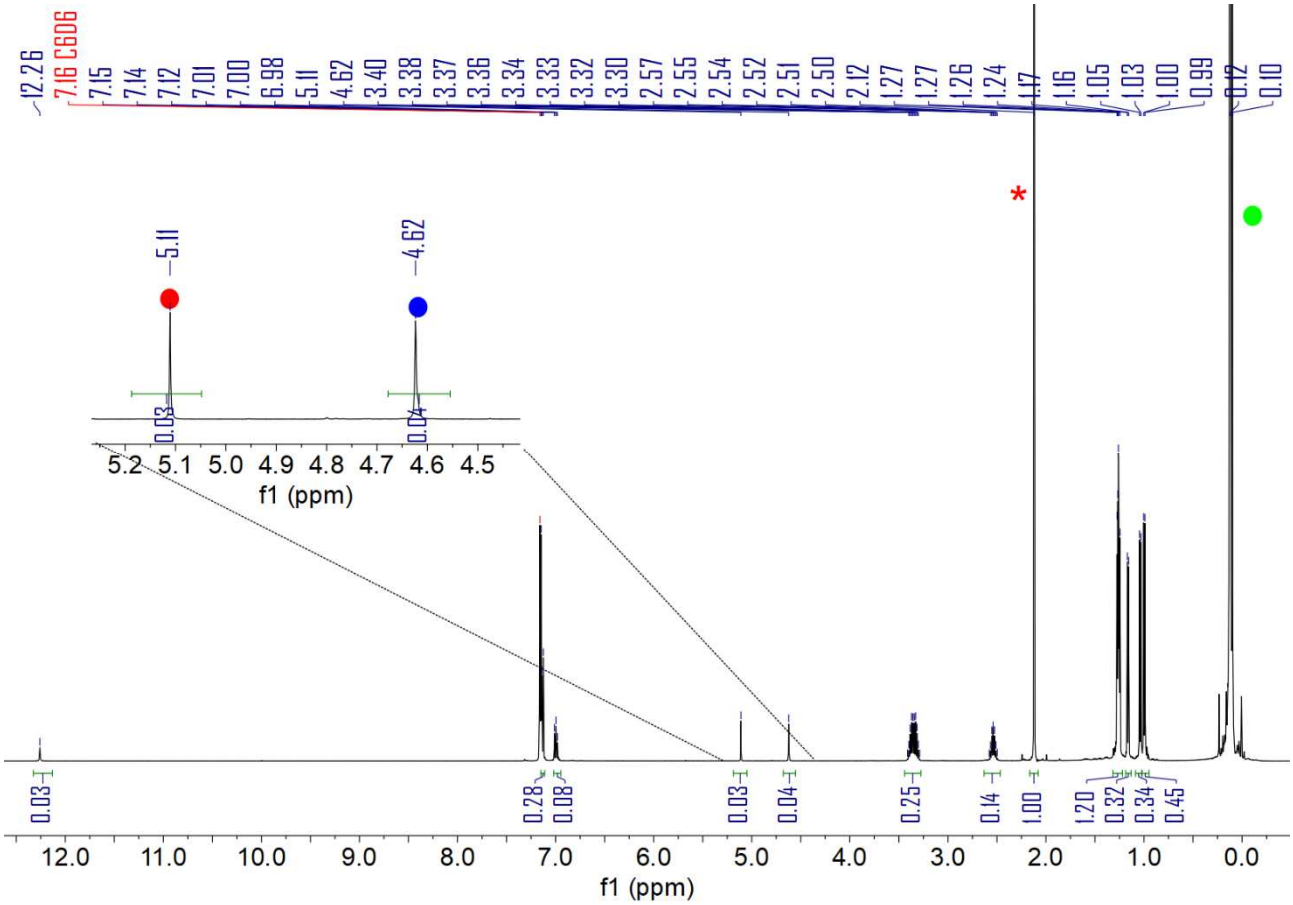


Figure S60. The example NMR spectrum of the deprotonation of ^{iPrDip}nacnacH **2a** (6.17 mg, 13.1 µmol, 1 equiv.) with [K{N(SiMe$_3$)$_2$}] (26.0 mg, 131 µmol, 10 equiv.) at 60 °C for 6 hours. Hexamethylbenzene (2.0 mg, 12.3 µmol) was added as an internal standard and marked as a red star. The red circle denotes the resonance of backbone-C*H* of ^{iPrDip}nacnacH. The blue circle denotes the resonance of backbone-C*H* of [(^{iPrDip}nacnac)K] **8a**. The green circle denotes the resonances of [K{N(SiMe$_3$)$_2$}] and [H{N(SiMe$_3$)$_2$}].

3 X-ray crystallography

Suitable crystals were mounted in paratone oil and were measured using either a Rigaku FR-X Ultrahigh brilliance Microfocus RA generator/confocal optics with XtaLAB P200 diffractometer (Mo Kα radiation), or a Rigaku MM-007HF High Brilliance RA generator/confocal optics with XtaLAB P100 or P200 diffractometers (Cu Kα radiation). Data for all compounds analysed were collected using either CrystalClear[7] (using ω steps and accumulating area detector images spanning at least a hemisphere of reciprocal space) (using ω steps and accumulating area detector images spanning at least a hemisphere of reciprocal space) or CrysAlisPro[8] (using a calculated strategy). Data were processed (including correction for Lorentz, polarization, and absorption) using either CrystalClear[7] or CrysAlisPro.[8] Structures were solved by dual-space (SHELXT)[9] or direct (SIR2004,[10] SIR2011[11]) methods, and were refined by full-matrix least-squares against F^2 using SHELXL-2018/3.[12] All non-hydrogen atoms were refined anisotropically except in selected cases of disorder as described below. Hydrogen atoms were placed in calculated positions (riding model) except in selected cases as described below. Calculations were performed using the CrystalStructure[13] or Olex2[14] interface. Details on individual crystal structure refinements are given below and selected crystallographic data is collected in Table S1. Further experimental and refinement details are given in the CIF-files. CCDC 2352325-2352336 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via https://www.ccdc.cam.ac.uk/structures/.

Table S1 Crystallographic data.

Compound reference	^{EtDip}nacnacH, **1a**	^{EtDep}nacnacH, **1b**	^{EtXyl}nacnacH, **1d**	^{iPrDep}nacnacH, **2b**	^{iPrMes}nacnacH, **2c**
Chemical formula	$C_{31}H_{46}N_2$	$C_{27}H_{38}N_2$	$C_{23}H_{30}N_2$	$C_{29}H_{42}N_2$	$C_{27}H_{38}N_4$
Formula weight	446.70	390.61	334.50	418.66	390.61
Temperature/K	173	173	173	173	173
Radiation type	Mo Kα	Mo Kα	Mo Kα	Mo Kα	Mo Kα
Crystal system	monoclinic	trigonal	monoclinic	monoclinic	triclinic
Space group	$P2_1/c$	$P\bar{3}$	$P2_1/n$	$P2_1/c$	$P\bar{1}$
a/Å	15.8308(4)	32.532(4)	11.479(2)	20.984(4)	10.2164(5)
b/Å	16.5393(4)	32.532(4)	11.1228(16)	9.1852(17)	10.7791(5)
c/Å	21.5528(6)	12.1693(17)	16.637(3)	28.454(6)	13.0555(5)
α/°	90	90	90	90	67.311(4)
β/°	91.311(2)	90	104.589(4)	103.542(6)	70.582(4)
γ/°	90	120	90	90	79.542(4)
Unit cell volume/Å^3	5641.7(3)	11154(2)	2055.7(6)	5331.8(18)	1248.66(11)
No. of formula units per unit cell, Z	8	18	4	8	2
Density (calc)/ Mg/m^3	1.052	1.047	1.081	1.043	1.039
Absorption coefficient, μ/mm^{-1}	0.060	0.060	0.063	0.060	0.060
F(000)	1968	3852	728	1840	428
Theta range/°	1.552 to 29.440	1.673 to 25.334	1.947 to 25.376	1.472 to 25.343	1.766 to 29.052
Reflections collected	121505	137427	24677	72382	16382
Independent reflections	13897	13590	3765	9722	5418
R_{int}	0.0622	0.0979	0.0281	0.1726	0.0436
Parameters, restraints	655, 14	973, 209	236, 1	605, 5	276, 1
Goodness of fit on F^2	1.012	1.015	1.023	0.788	1.050
Final R_1 values ($I > 2\sigma(I)$)	0.0759	0.0598	0.0459	0.0513	0.0616
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.1686	0.1302	0.1171	0.1085	0.1568
Final R_1 values (all data)	0.1449	0.1362	0.0564	0.1210	0.1295
Final $wR(F^2)$ values (all data)	0.1962	0.653	0.1252	0.1242	0.1823
Largest diff. peak and hole/e·Å^{-3}	0.373 and -0.212	0.22 and -0.17	0.19 and -0.19	0.25 and -0.25	0.30 and -0.25
Absolute structure parameter	-	-	-	-	-
CCDC number	2352331	2352330	2352333	2352332	2352325

Table S1 continued Crystallographic data.

Compound reference	*i*PrC(NHMes)CHC(=O)*i*Pr, **3c**	(^{iPrMes}nacnac)PO_2, **4c**	[(^{iPrDip}nacnac)Li], **6a**	[(^{iPrDip}nacnac)Li(OEt_2)], **6a(OEt_2)**	[(^{EtDip}nacnac)K(C_6H_6)], **8b(C_6H_6)**
Chemical formula	$C_{18}H_{27}NO$	$C_{27}H_{37}N_2O_2P$	$C_{33}H_{49}LiN_2$	$C_{37}H_{59}LiN_2O$	$C_{37}H_{51}KN_2$
Formula weight	273.42	452.58	480.70	554.83	554.83
Temperature/K	93	93	93	173	173
Radiation type	Mo Kα	Mo Kα	Mo Kα	Cu Kα	Cu Kα
Crystal system	monoclinic	triclinic	monoclinic	monoclinic	monoclinic
Space group	*C*2/*c*	$P\overline{1}$	$P2_1/n$	$P2_1/n$	$P2_1/n$
a/Å	25.661(11)	7.4666(3)	13.069(3)	21.02927(17)	11.5987(4)
b/Å	7.581(3)	12.1844(3)	16.031(3)	17.76700(9)	15.6955(5)
c/Å	16.993(8)	14.2288(5)	14.893(3)	22.03725(17)	18.1851(7)
α/°	90	98.309(2)	90	90	90
β/°	101.242(8)	92.873(3)	105.472(5)	117.6008(10)	93.499(3)
γ/°	90	105.787(3)	90	90	90
Unit cell volume/$Å^3$	3242(2)	1227.13(8)	3007.1(11)	7296.69(11)	3304.4(2)
No. of formula units per unit cell, *Z*	8	2	4	8	4
Density (calc)/ Mg/m^3	1.120	1.225	1062	1.010	1.131
Absorption coefficient, *μ*/mm^{-1}	0.068	0.138	0.060	0.441	1.586
F(000)	1200	488	1056	2448	1224
Theta range/°	2.444 to 25.265	2.090 to 29.767	1.845 to 25.315	2.402 to 75.493	3.723 to 66.968
Reflections collected	20480	19020	41849	86594	27280
Independent reflections	2927	5846	5466	14938	5831
R_{int}	0.0863	0.0504	0.0686	0.0193	0.0331
Parameters, restraints	191, 1	299, 0	337, 0	791, 6	371, 0
Goodness of fit on F^2	1.075	1.061	1.064	1.058	1.051
Final R_1 values ($I > 2\sigma(I)$)	0.0519	0.0575	0.0977	0.0436	0.0356
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.1298	0.1351	0.2449	0.1216	0.0955
Final R_1 values (all data)	0.0742	0.0928	0.1145	0.0484	0.0425
Final $wR(F^2)$ values (all data)	0.1484	0.172	0.2638	0.1257	0.1004
Largest diff. peak and hole/e·$Å^{-3}$	0.28 and -0.20	0.51 and -0.34	1.12 and -0.21	0.29 and -0.24	0.224 and -0.256
Absolute structure parameter	-	-	-	-	-
CCDC number	2352326	2352334	2352327	2352328	2352336

Table S1 continued Crystallographic data.

Compound reference	(^{EtDip}NacNac)SiBr, **9**	(^{EtDip}NacNac')Si, **10**
Chemical formula	$C_{31}H_{45}BrN_2Si$	$C_{31}H_{44}N_2Si$
Formula weight	553.69	472.77
Temperature/K	173	173
Radiation type	Cu Kα	Mo Kα
Crystal system	monoclinic	orthorhombic
Space group	$P2_1/n$	$Fdd2$
a/Å	9.96708(12)	42.4215(8)
b/Å	22.4804(2)	15.2419(4)
c/Å	13.98249(18)	8.7768(2)
α/°	90	90
β/°	107.1595(13)	90
γ/°	90	90
Unit cell volume/Å^3	2993.51(6)	5674.9(2)
No. of formula units per unit cell, Z	4	8
Density (calc)/ Mg/m^3	1.229	1.107
Absorption coefficient, μ/mm^{-1}	2.396	0.103
F(000)	1176	2064
Theta range/°	3.849 to 66.776	1.920 to 29.625
Reflections collected	52040	15725
Independent reflections	5256	2949
R_{int}	0.0182	0.0186
Parameters, restraints	336, 0	165, 1
Goodness of fit on F^2	1.090	1.047
Final R_1 values ($I > 2\sigma(I)$)	0.0282	0.0268
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.0756	0.0698
Final R_1 values (all data)	0.0285	0.0280
Final $wR(F^2)$ values (all data)	0.0758	0.0702
Largest diff. peak and hole/e·Å^{-3}	0.365 and -0.374	0.170 and -0.171
Absolute structure parameter	-	0.46(12)
CCDC number	2352329	2352335

^{EtDip}nacnacH 1a

The compound crystallised with two full molecules in the asymmetric unit. In molecule 2, one ethyl group (67 and 33% parts) and the one isopropyl group (57 and 43% parts for the outer methyl groups) are disordered and were modelled with two positions for each atom and freely refined using geometry restraints (DFIX, ISOR). The NH hydrogen atoms were located from the difference Fourier map and refined with a geometry restraint (DFIX).

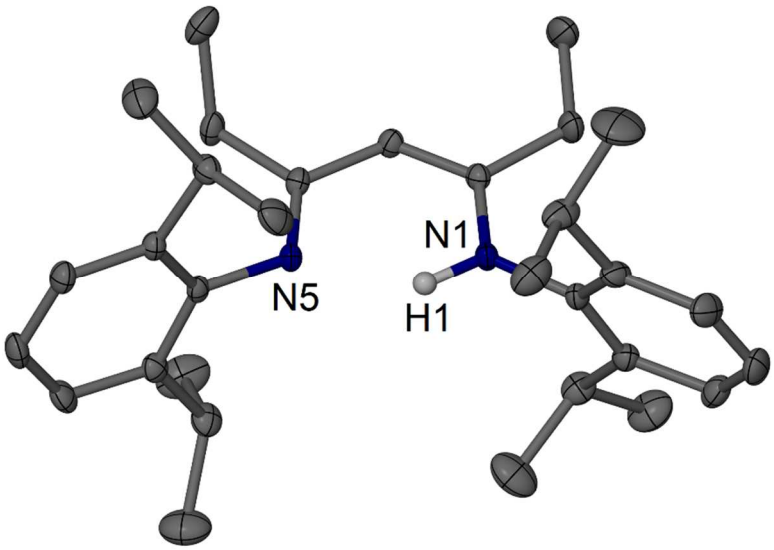


Figure S61. Molecular structure of ^{EtDip}nacnacH, **1a** (30% thermal ellipsoids). Hydrogen atoms except H1, and minor components of disorder are omitted. Selected bond lengths (Å) and angles (°): Shown molecule: N1–C2 1.352(2), C2–C3 1.362(2), C4–C3 1.439(2), N5–C4 1.301(2); C2–N1–C6 123.78(15), C4–N5 C22 119.59(14), C2–C3 C4 126.56(17); Second molecule: N41–C42 1.351(2), C42–C43 1.368(2), C44–C43 1.431(2), N45–C44 1.300(2); C42–N41–C46 123.37(15), C44–N45–C62 120.45(15), C42–C43–C44 126.68(17).

^{EtDep}nacnacH 1b

The compound crystallised in the trigonal crystal system with three full molecules in the asymmetric unit. All three molecules show some disorder and this was modelled with two positions for one (molecule 1) or two (molecules 2 and 3) backbone ethyl groups and two positions for a Dep group (molecule 3, on N65) and refined using geometry restraints (DFIX, SIMU, RIGU). N-H hydrogen atoms were placed in calculated positions. This structure was affected by pseudo-merohedral twinning.

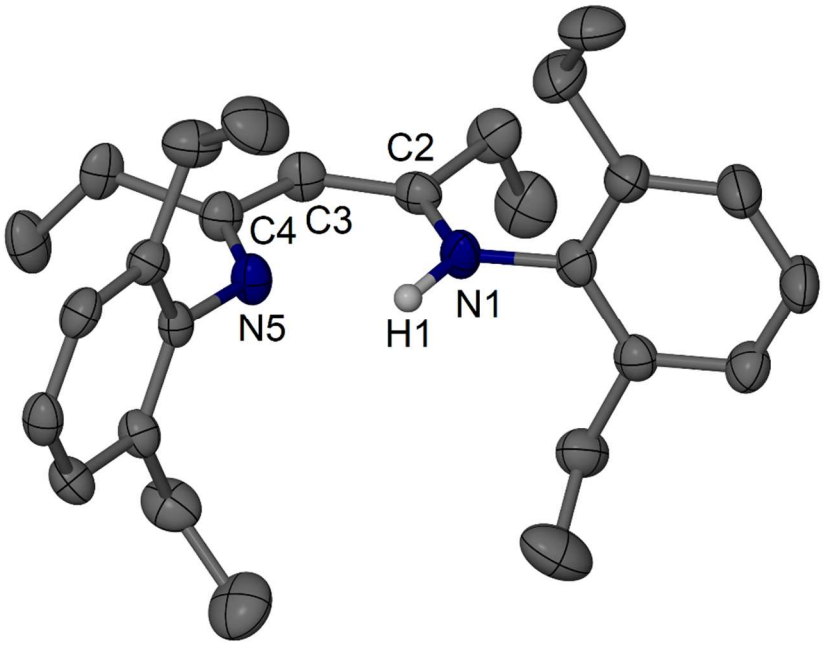


Figure S62. Molecular structure of ^{EtDep}nacnacH, **1b** (30% thermal ellipsoids). Only one independent molecule is shown. Hydrogen atoms except H1, and minor components of disorder are omitted. Selected bond lengths (Å) and angles (°) for one molecule: N1–C2 1.301(4), N5–C4 1.321(4), C2–C3 1.395(5), C3–C4 1.400(5); N1–C2–C3 121.3(3), C2–C3–C4 125.8(3), N5–C4–C3 120.0(3).

^{EtXyl}nacnacH 1d

The compound crystallised with a full molecule in the asymmetric unit. The NH hydrogen atom was located from the difference Fourier map and refined with a geometry restraint (DFIX).

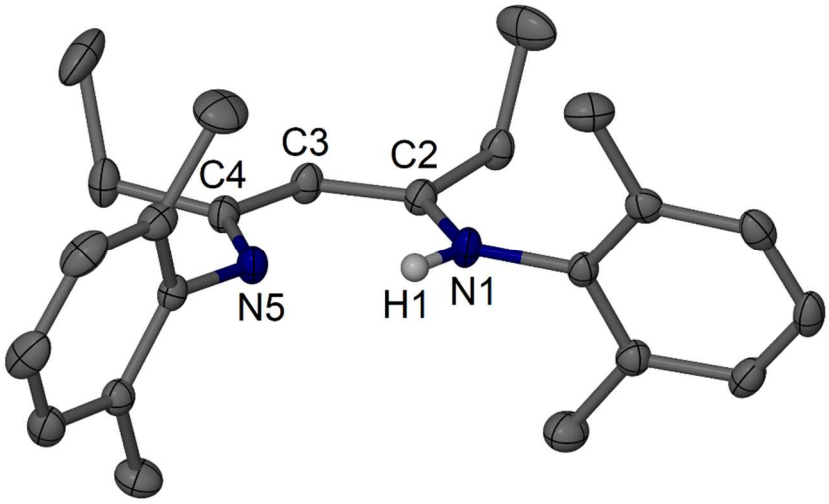


Figure S63. Molecular structure of ^{EtXyl}nacnacH, **1d** (30% thermal ellipsoids). Hydrogen atoms except H1 are omitted. Selected bond lengths (Å) and angles (°): N1–C2 1.3522(19), N5–C4 1.3016(19), C2–C3 1.372(2), C3–C4 1.428(2); N1–C2–C3 121.43(14), N5–C4–C3 120.85(13), C2–C3–C4 126.26(14).

^{iPrDep}nacnacH 2b

The compound crystallised with two full molecules in the asymmetric unit. One (molecule 1) or two (molecule 2) ethyl groups are disordered and were modelled over two positions and refined using geometry restraints (DFIX), with the minor component of disorder refined isotropically. The NH hydrogen atoms were located from the difference Fourier map and refined with a geometry restraint (DFIX).

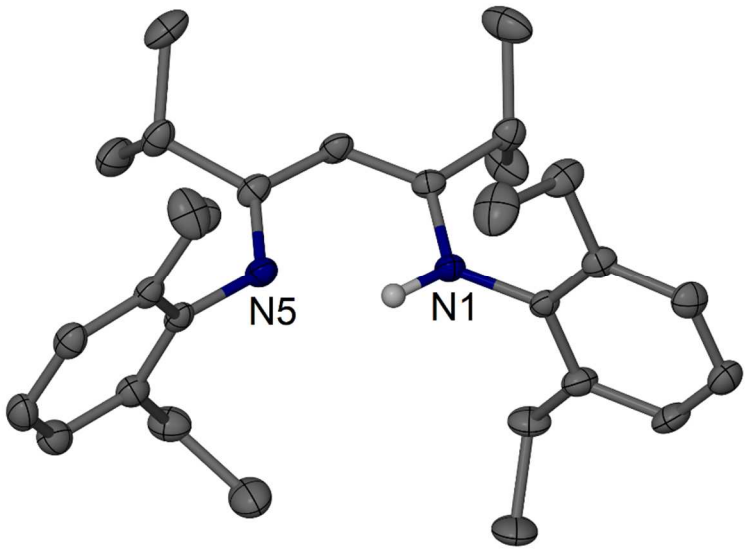


Figure S64. Molecular structure of ^{iPrDep}nacnacH, **2b** (30% thermal ellipsoids). Only one independent molecule is shown. Hydrogen atoms except H1, and minor components of disorder are omitted. Selected bond lengths (Å) and angles (°): Shown molecule: N1–C2 1.357(2), N5–C4 1.315(2), C2–C3 1.373(3), C3–C4 1.428(3); C2–N1–C6 125.78(18), C4–N5–C22 121.50(16), N1–C2–C3 120.54(19), C2–C3–C4 127.08(18), N5–C4–C3 120.63(18); Second molecule: N41–C42 1.356(2), C42–C43 1.374(3), C43–C44 1.420(3), N45–C44 1.317(2); C42–N41–C46 126.23(19), C44–N45–C62 122.52(18), N41–C42–C43 120.1(2), C42–C43–C44 126.86(19), N45–C44–C43 120.10(19).

^{iPrMes}nacnacH 2c

The compound crystallised with a full molecule in the asymmetric unit. The NH hydrogen atom was located from the difference Fourier map and refined with a geometry restraint (DFIX).

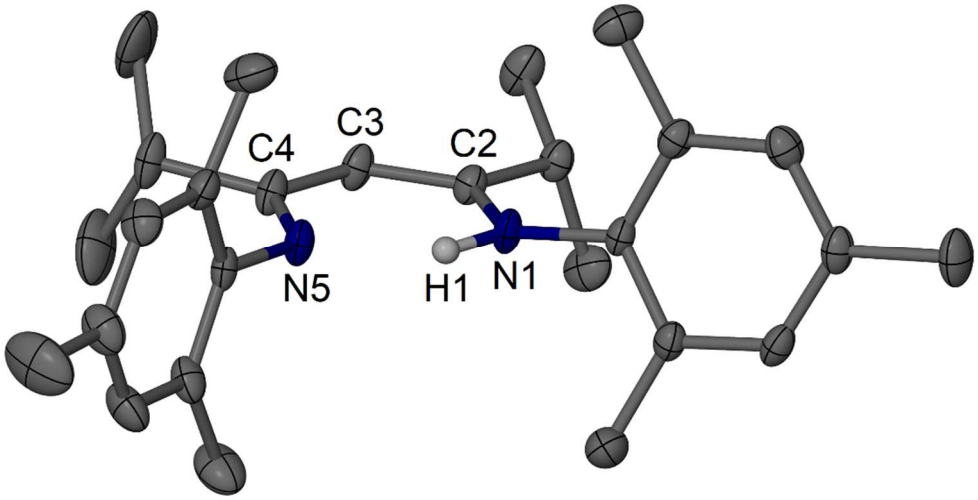
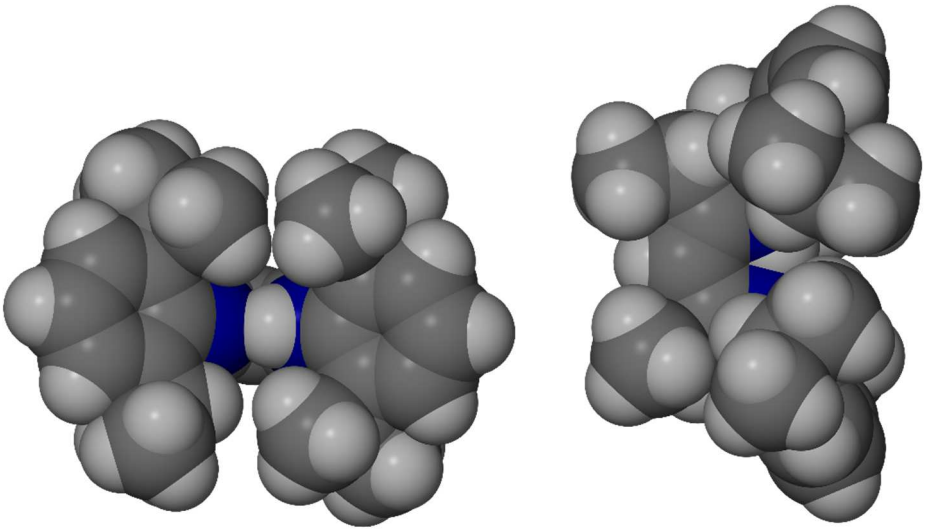
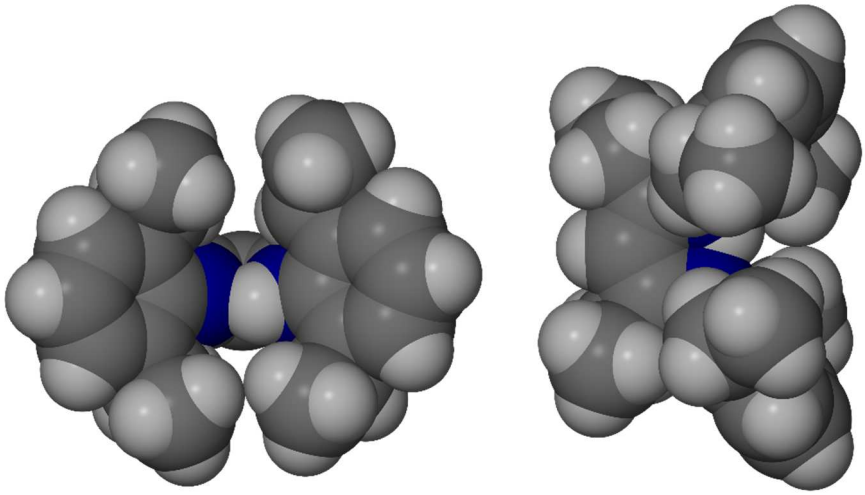


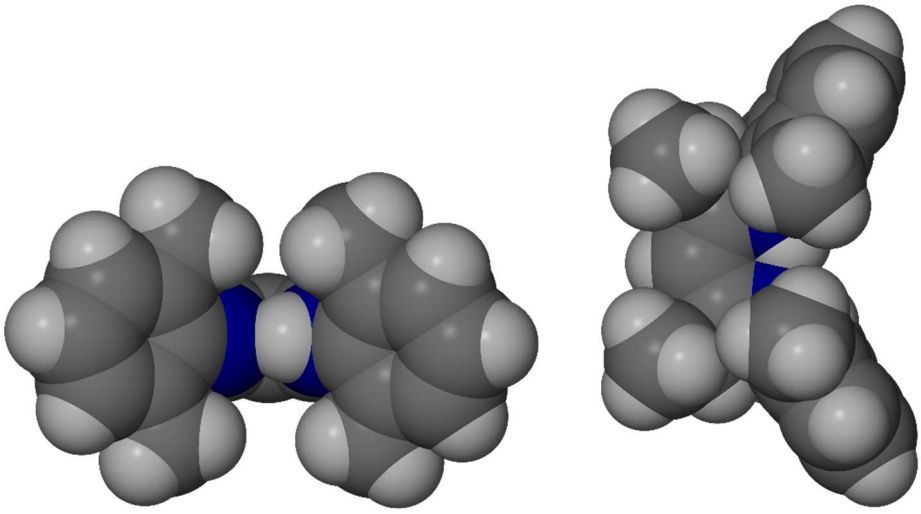
Figure S65. Molecular structure of ^{iPrMes}nacnacH, **2c** (30% thermal ellipsoids). Hydrogen atoms except H1 are omitted. Selected bond lengths (Å) and angles (°): N1–C2 1.354(2), N5–C4 1.299(2), C2–C3 1.373(3), C3–C4 1.438(3); C2–N1–C6 127.68(17), N1–C2–C3 119.33(18), C2–C3–C4 125.27(18), N5–C4–C3 119.34(17).



^{EtDip}nacnacH **1a**

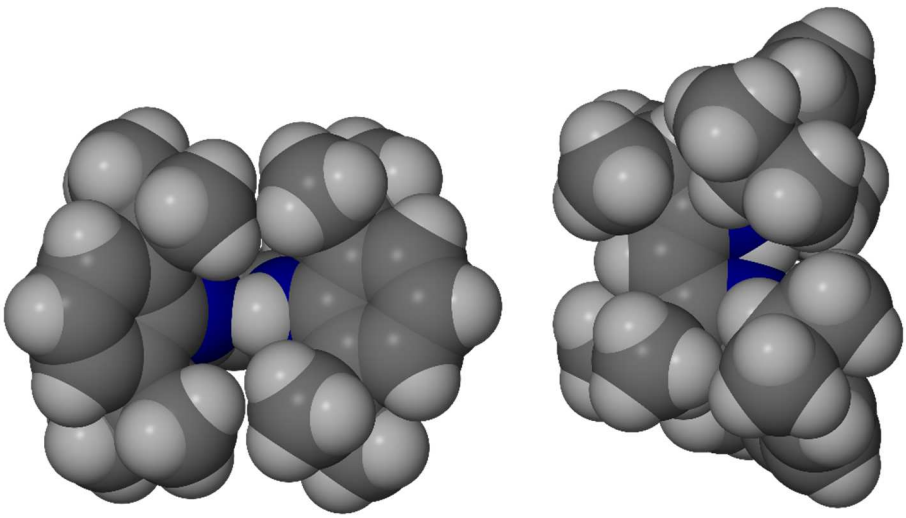


^{EtDep}nacnacH **1b**

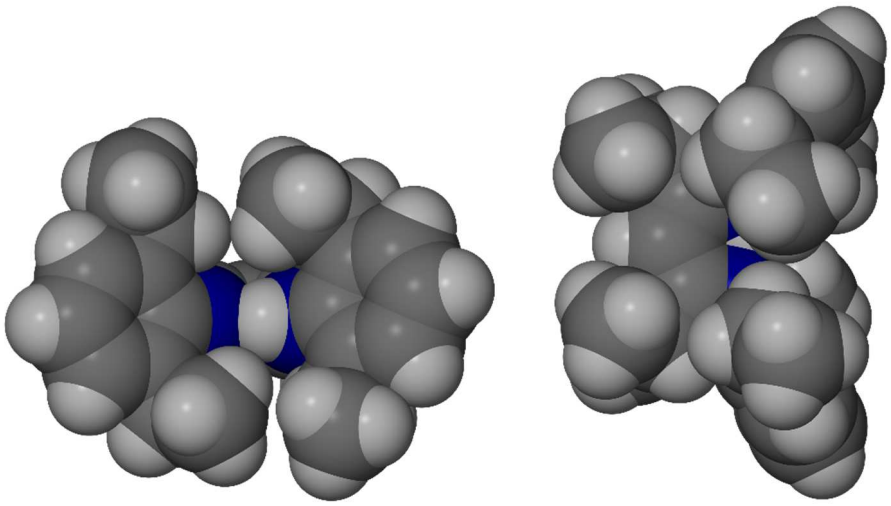


^{EtXyl}nacnacH **1d**

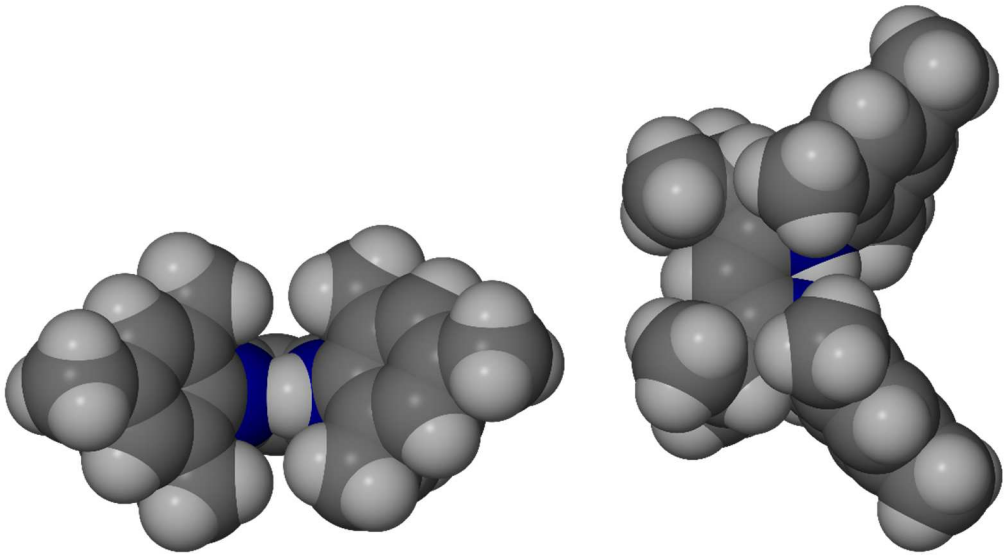
Figure S66. Space-filling models (two views) of the molecular structures of ^{EtAr}nacnacH (**1**) compounds.



^{iPrDip}nacnacH **2a**



^{iPrDep}nacnacH **2b**



^{iPrMes}nacnacH **2c**

Figure S67. Space-filling models (two views) of the molecular structures of ^{iPrAr}nacnacH (**2**) compounds. The molecular structure of ^{iPrDip}nacnacH **2a** was reported previously.[4]

***i*PrC(NHMes)CHC(=O)*i*Pr 3c**

The compound crystallised with a full molecule in the asymmetric unit. The NH hydrogen atom was located from the difference Fourier map and refined with a geometry restraint (DFIX).

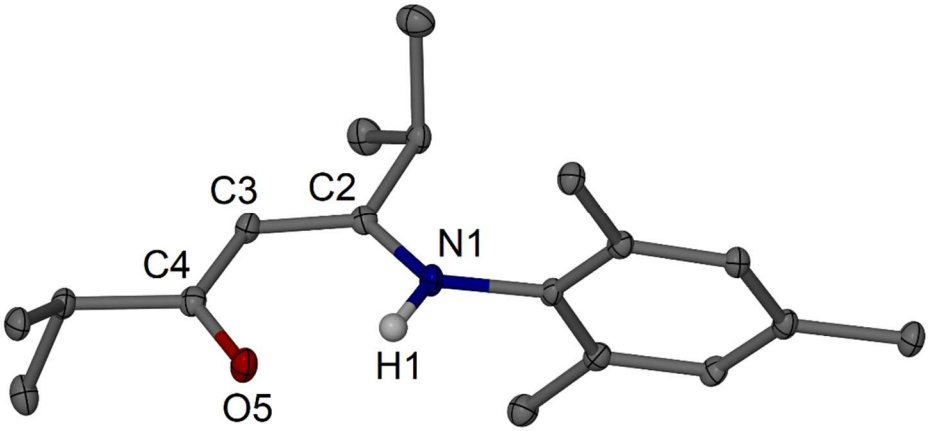


Figure S68. Molecular structure of *i*PrC(NHMes)CHC(=O)*i*Pr **3c** (30% thermal ellipsoids). Hydrogen atoms except H1 are omitted. Selected bond lengths (Å) and angles (°): O5–C4 1.247(2), N1–C2 1.343(2), N1–C6 1.438(2), C2–C3 1.386(3), C3–C4 1.420(3); N1–C2–C3 120.49(17), C2–N1–C6 127.07(16), C2–C3–C4 123.50(17), O5–C4–C3 123.34(17).

(^{iPrMes}nacnac)PO_2 4c

The compound crystallised with a full molecule in the asymmetric unit.

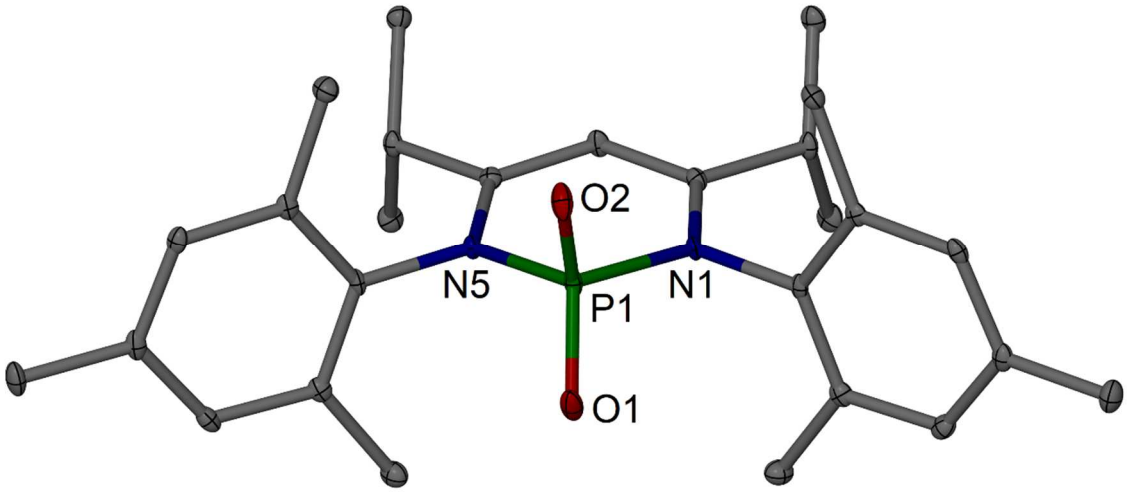


Figure S69. Molecular structure of (^{iPrMes}nacnac)PO_2 **4c** (30% thermal ellipsoids). Hydrogen atoms are omitted. Selected bond lengths (Å) and angles (°): P1–O1 1.4712(16), P1–O2 1.4720(17), P1–N5 1.7518(17), P1–N1 1.7548(17), N1–C2 1.356(3), N5–C4 1.356(3), C2–C3 1.387(3), C3–C4 1.390(3); O1–P1–O2 121.67(10), N5–P1–N1 98.47(8), O1–P1–N1 108.54(9), O2–P1–N1 108.50(9), O1–P1–N5 109.55(9), O2–P1–N5 107.62(9).

[(^{iPrDip}nacnac)Li] 6a

The compound crystallised with a full molecule in the asymmetric unit and is arranged as a weakly bound dimer in the solid state. The refined molecular structure shows a relatively high *R* value, likely due to poor crystallinity, but is otherwise well ordered.

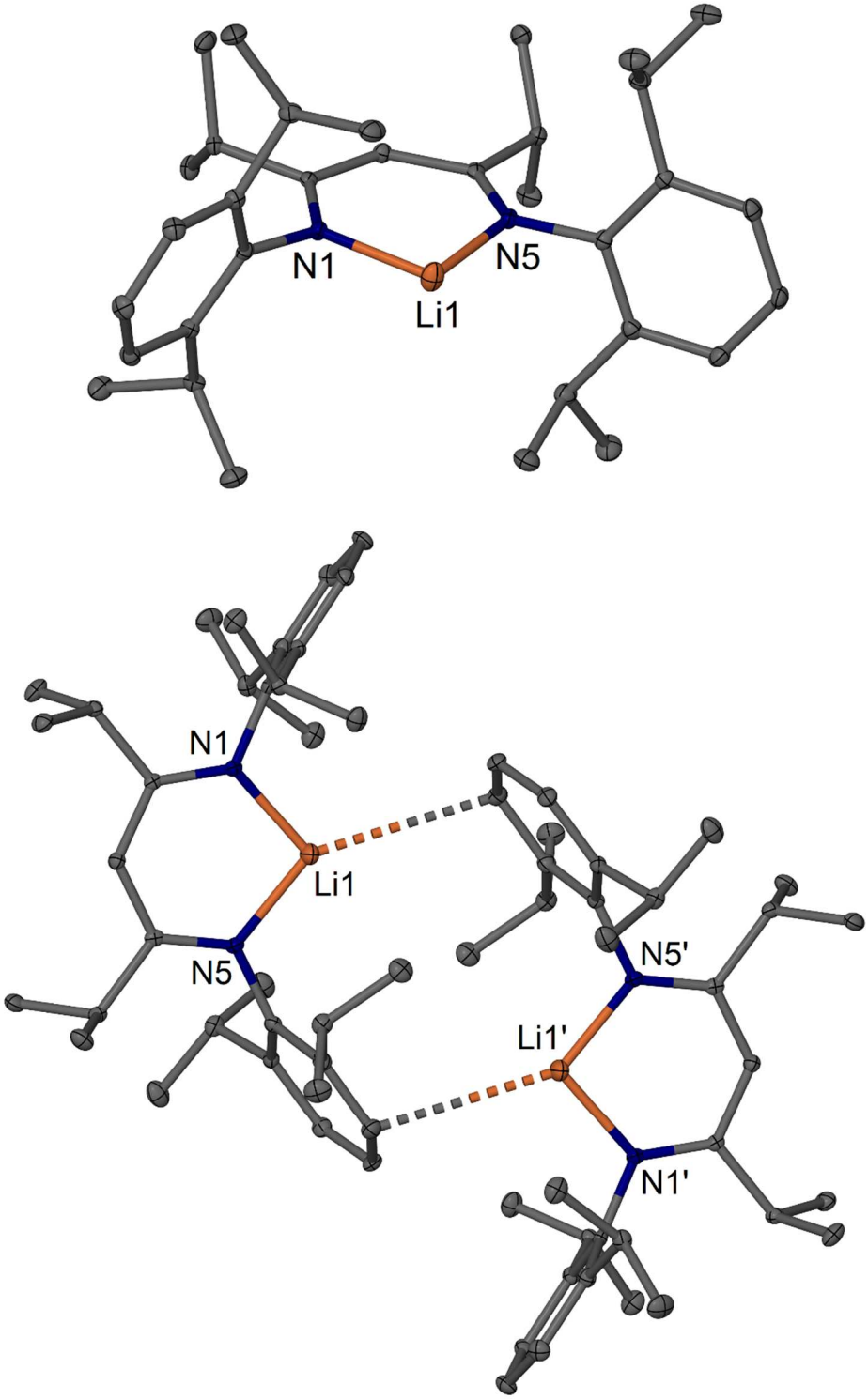


Figure S70. Molecular structure of [(^{iPrDip}nacnac)Li] **6a** (30% thermal ellipsoids). Hydrogen atoms are omitted. Selected bond lengths (Å) and angles (°): N1–Li1 1.886(4), N5–Li1 1.893(4), N1–C2 1.323(3), C2–C3 1.409(3), C3–C4 1.411(3), N5–C4 1.330(3); N1–Li1–N5 100.2(2).

(^{iPrDip}nacnac)Li(OEt$_2$)] 6a(OEt$_2$)

The compound crystallised with two full molecules in the asymmetric unit. The coordinated Et_2O ligands are disordered and were modelled over two positions for each atom and refined using geometry restraints (DFIX).

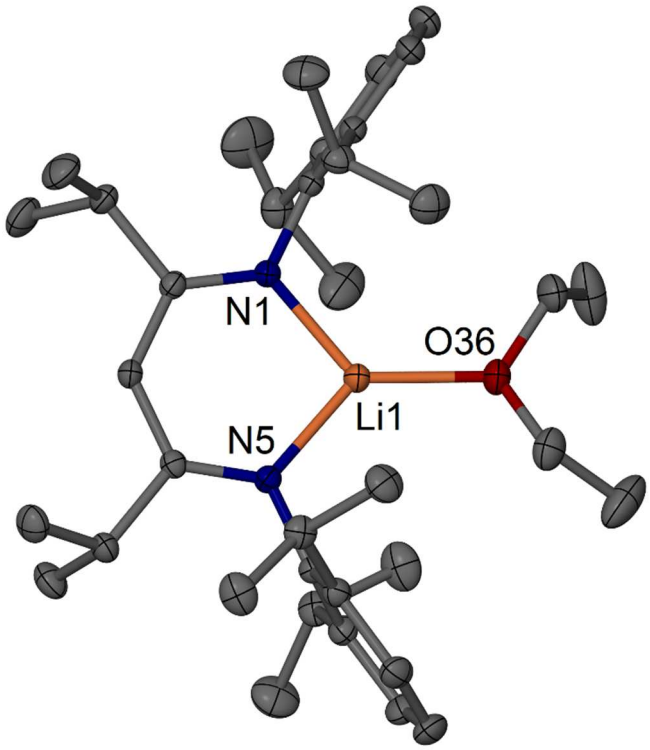


Figure S71. Molecular structure of [(^{iPrDip}nacnac)Li(OEt$_2$)] **6a(OEt$_2$)** (30% thermal ellipsoids). Only one independent molecule shown. Hydrogen atoms and minor components of disorder are omitted. Selected bond lengths (Å) and angles (°): Shown molecule: O36–Li1 1.937(2), N1–Li1 1.914(2), N5–Li1 1.920(2), N1–C2 1.3224(13), C2–C3 1.4060(14), C3–C4 1.4059(14), N5–C4 1.3243(13); N1–Li1–O36 129.26(11), N5–Li1–O36 131.49(10), N1–Li1–N5 99.09(9), C4–C3–C2 129.86(9). Second molecule: O76–Li41 2.011(2), N41–Li41 1.948(2), N45–Li41 1.930(2), N41–C42 1.3216(13), N45–C44 1.3221(13), C42–C43 1.4070(14), C43–C44 1.3996(15); N41–Li41–O76 139.96(10), N45–Li41–N41 98.42(9), N45–Li41–O76 121.38(10), C44–C43–C42 129.96(10).

[(^{EtDip}nacnac)K(C_6H_6)] 8b(C_6H_6)

The compound crystallised with a full molecule in the asymmetric unit and one unit of benzene is coordinated to the K centre. A weak contact of a Dip-*para*-CH unit to the K atom of a neighbouring molecule arranges the complex into a weakly-bound one-dimensional coordination polymer.

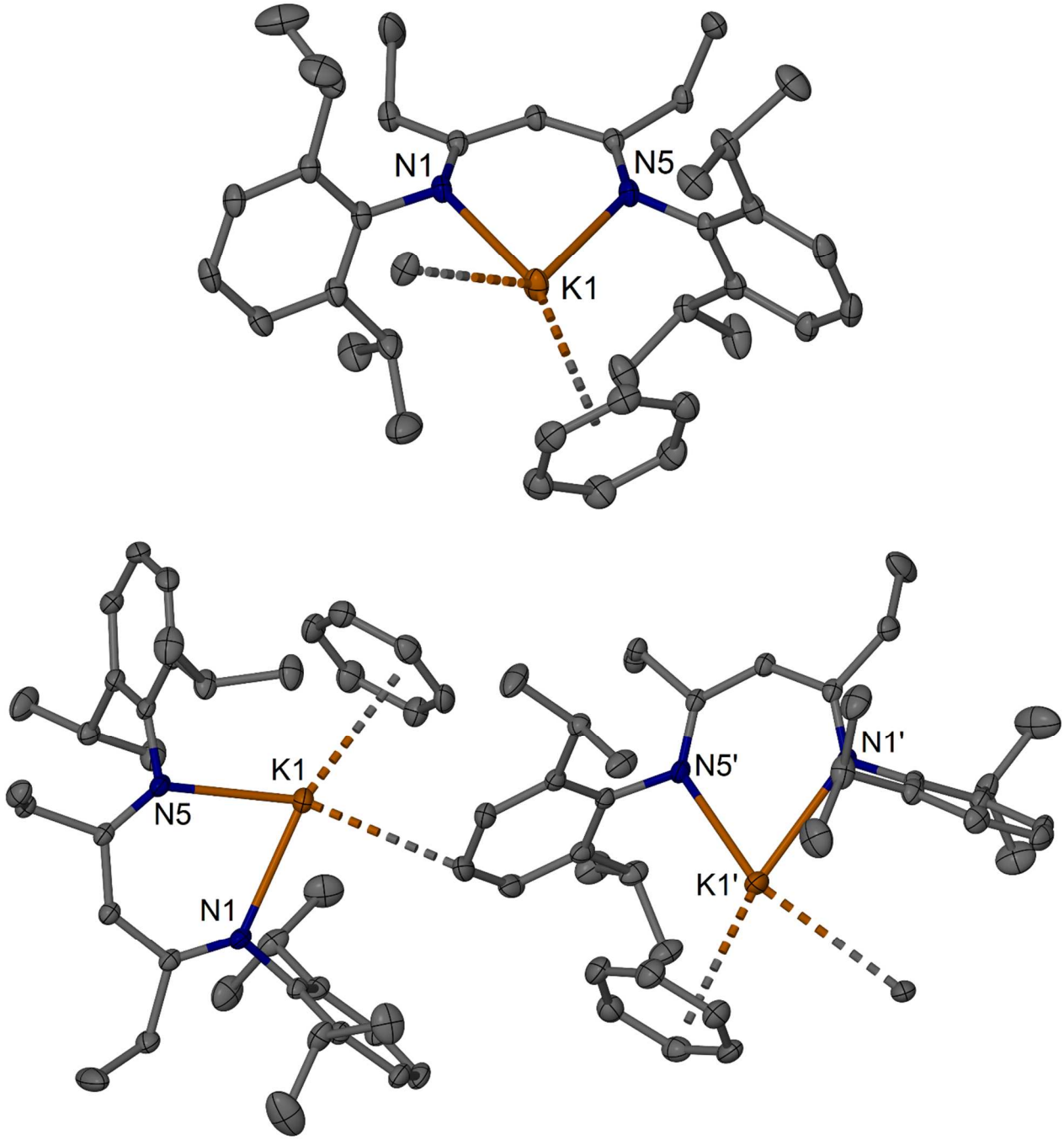


Figure S72. Molecular structure of [(^{EtDip}nacnac)K(C_6H_6)] **8b(C_6H_6)** (30% thermal ellipsoids). Hydrogen atoms are omitted. The benzene molecule includes C41-C46. Selected bond lengths (Å) and angles (°): K1–N1 2.6979(12), K1–N5 2.6613(12), K1–C41 3.2755(18), K1–C42 3.2544(17), K1–C43 3.4139(19), K1–C44 3.569(2) K1–C45 3.5739(19), K1–C46 3.4380(18), N1–C2

1.3124(18), C2–C3 1.4182(18), C4–C3 1.4057(19), N5–C4 1.3205(18); N5–K1–N1 70.67(3), C4–C3–C2 131.93(13). In addition, there is an intermolecular contact of K to a para-Dip-CH: K···H: ca. 2.83, K···C: 3.28.

(^{EtDip}NacNac)SiBr 9

The compound crystallised with a full molecule in the asymmetric unit. The coordinated bromide is disordered and was modelled over two positions, although its behaviour suggests it may be dynamically disordered.

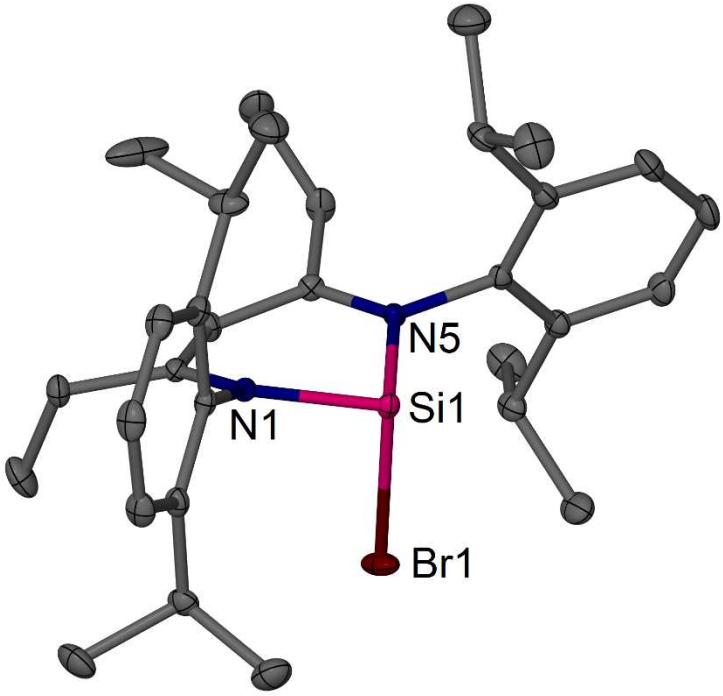


Figure S73. Molecular structure of (^{EtDip}NacNac)SiBr **9** (30% thermal ellipsoids). Hydrogen atoms and a minor component of disorder are omitted. Selected bond lengths (Å) and angles (°): Br1–Si1 2.405(2), Si1–N1 1.8406(12), Si1–N5 1.8652(12), N1–C2 1.3505(18), C2–C3 1.383(2), C3–C4 1.399(2), N5–C4 1.3323(18); N1–Si1–N5 94.53(6), N1–Si1–Br1 97.20(9), N5–Si1–Br1 94.67(8), C2–C3–C4 125.50(14), Br1–Si1···C3: ca. 83.80, Br1–Si1–(N1···N5-midpoint): ca. 98.75.

(^{EtDip}nacnac')Si 10

The compound crystallised with half a molecule in the asymmetric unit and thus, the backbone unit is disordered by symmetry. This resulted in disorder in the ethyl/ethylidene group, the inner carbon of which was modelled over two positions (Figure S74). The disordered carbon atoms were constrained to have identical thermal parameters. The structure is an inversion twin.

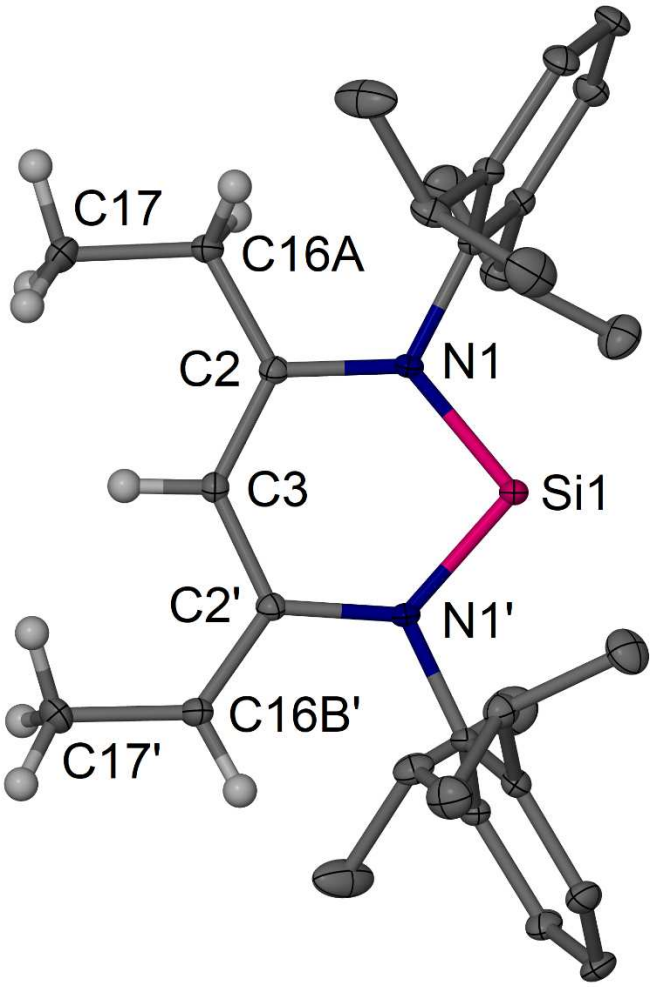


Figure S74. Molecular structure of (^{EtDip}nacnac')Si **10** (30% thermal ellipsoids). Only one set of atoms is shown for each half of the backbone unit. Only hydrogen atoms of the backbone unit are shown. Selected bond lengths (Å) and angles (°): Si1–N1 1.7358(12), Si1–N1' 1.7357(12), N1–C2 1.4157(19), C2–C3 1.4018(17), C2–C16A 1.48(2), C2–C16B 1.38(3); N1–Si1–N1' 99.23(8).

4 References

1 C. Schade, W. Bauer and P. von Ragué Schleyer, *J. Organomet. Chem.*, 1985, **295**, C25–C28.

2 L. Lochmann and J. Trekoval, *J. Organomet. Chem.*, 1987, **326**, 1–7.

3 A. C. Filippou, O. Chernov and G. Schnakenburg, *Chem. Eur. J.*, 2011, **17**, 13574–13583.

4 S. Burnett, C. Bourne, A. M. Z. Slawin, T. van Mourik, A. Stasch, *Angew. Chem. Int. Ed.* 2022, **61**, e202204472.

5 M. Arrowsmith, M. R. Crimmin, M. S. Hill and G. Kociok-Köhn, *Dalton Trans.*, 2013, **42**, 9720–9726.

6 G. R. Fulmer, A. J. M. Miller, N. H. Sherden, H. E. Gottlieb, A. Nudelman, B. M. Stoltz, J. E. Bercaw, K. I. Goldberg, *Organometallics*, 2010, **29**, 2176–2179.

7 *CrystalClear-SM Exper*t v2.1. Rigaku Americas, The Woodlands, Texas, USA, and Rigaku Corporation, Tokyo, Japan, 2015.

8 *CrysAlisPro* v1.171.38.46, v1.171.39.8d, v1.171.41.93a, v1.171.42.74a, v1.171.42.83a, v1.171.42.93a Rigaku Oxford Diffraction, Rigaku Corporation, *Tokyo,* Japan, 2015-2023.

9 G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Adv*., 2015, **71**, 3–8.

10 M. C. Burla, R. Caliandro, M. Camalli, B. Carrozzini, G. L. Cascarano, L. De Caro, C. Giacovazzo, G. Polidori, R. Spagna, *J. Appl. Crystallogr.*, 2005, **38**, 381–388.

11 M. C. Burla, R. Caliandro, M. Camalli, B. Carrozzini, G. L. Cascarano, C. Giacovazzo, M. Mallamo, A. Mazzone, G. Polidori and R. Spagna, *J. Appl. Crystallogr.*, 2012, **45**, 357–361.

12 G. M. Sheldrick, *Acta Crystallogr., Sect. C: Struct. Chem.*, 2015, **71**, 3–8.

13 *CrystalStructure* v4.3.0. Rigaku Americas, The Woodlands, Texas, USA, and Rigaku Corporation, Tokyo, Japan, 2018.

14 O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Crystallogr*., 2009, **42**, 339–341.