Supplementary Information

Catalyst-free insertion of carbon monoxide into terminal Mg-C(sp_3) bonds

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1. Experimental methods and data

General Considerations

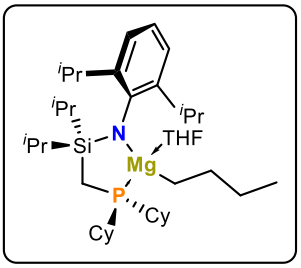
All experimental procedures and manipulations, expect preparation of samples for chromatography, were carried out under a dry oxygen free argon 5.0 atmosphere using standard Schlenk techniques or in an MBraun inert atmosphere glovebox containing an atmosphere of dry argon 5.0. THF and diethyl ether were dried by distillation over a mixture of sodium and benzophenone, degassed by applying dynamic vacuum while sonication for 15 minutes and stored over activated 4 Å mol sieves. All other solvents were dried over activated 4 Å mol sieves and degassed by applying dynamic vacuum while sonication for 15 minutes. C_6D_6 and THF-d_8 were dried, degassed by three cycles of freeze-pump-thaw and stored over a potassium mirror or over activated 4 Å mol sieves, respectively. Synthesis of DippN(H)Li,[1] $^{Ph/Pr}$DippNK,[2] $^{Cy/Pr}$DippNK,[3] were performed according to literature procedures, with slight procedural modifications implemented as needed. Phenyl silane ($PhSiH_3$) was subjected to three freeze-pump-thaw cycles and was stored over 4 Å molecular sieve. All other reagents were used as received. For all experiments utilizing carbon monoxide (CO), grade 3.6 was used.

NMR spectra were recorded on a Bruker AV 400 Spectrometer. The spectra were processed in the MestReNova 15.1.0-38027 software suite. The ^{1}H, and $^{13}C\{^{1}H\}$ NMR spectra were referenced to the residual solvent signals as internal standards. $^{29}Si\{^{1}H\}$ NMR spectra were externally calibrated to $SiMe_4$. $^{31}P\{^{1}H\}$ NMR spectra were externally calibrated to H_3PO_4. The coupling constants *J* are given in Hz. For signal multiplicities, the following abbreviations were used: s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, hept = heptet, sept = septet, m = multiplet, b = broad and combinations thereof.

Elemental analyses (C, H, N) were performed with a combustion analyzer (elementar vario EL, Bruker).

Infrared spectra were measured with the Alpha FT-IR from Bruker containing a platinum diamond ATR device. The compounds were measured as solids or dissolved in toluene and repeatedly applied onto the ATR crystal by pipetting and evaporating the solvent, all within an MBraun Labmaster dp inert atmosphere glovebox containing a dry, oxygen-free atmosphere of high-purity argon.

^{Cy}LMg^{n}Bu·THF, 1-Cy.



In-situ ^{Cy}LH synthesis. A 250 mL round-bottom Schlenk flask was charged with 10.00 g of ^{Cy}LK (18.52 mmol, 1.00 equiv.) and 2.60 g of Et_3NHCl (18.89 mmol, 1.02 equiv.). The solid mixture was cooled to –78 °C with rapid stirring, and suspended in 150 mL of THF, again under rapid stirring. The mixture was stirred for 16 h while gradually warming to room temperature. Afterwards, all volatiles were removed under reduced pressure, yielding a red-orange oil. The crude product was extracted with hexane (3 × 40 mL) into a 250 mL Schlenk tube, and the combined extracts were concentrated *in vacuo*. The presence of ^{Cy}LH, and small amounts of residual THF, was confirmed by ^{1}H NMR in C_6D_6, which was used in the next step without further purification.

Synthesis of ^{Cy}LMg^{n}Bu. The above isolated red-orange oil was dissolved in 150 mL of toluene and cooled to –78 °C. To the vigorously stirred solution, 18.52 mL of Mg^{n}Bu$_2$ (1 M in Et_2O, 18.52 mmol, 1.00 equiv.) was added quickly. The reaction mixture was stirred for 16 h, gradually warming to room temperature. All volatiles were then removed *in vacuo*, and the resulting pale-yellow solid was washed with hexane (3 × 10 mL) and dried in *vacuo* to afford 8.88 g of **1-Cy** (15.25 mmol, 82 %) as a colourless solid.

N.B. Colourless crystals of **1-Cy**, suitable for single crystal X-Ray diffraction analysis, were obtained from a concentrated hexane solution at room temperature.

^{1}H NMR (400 MHz, C_6D_6) δ (ppm) = -0.12 – -0.06 (m, 2H, MgC*H*$_2$(CH$_2$)$_2$CH$_3$), 0.93 (d, $^2J_{HP}$ = 8.8 Hz, 2H, Si-C*H*$_2$-P), 1.06 – 1.11 (m, 4H, Mg-*THF*), 1.12 – 1.18 (m, 8H, Si-^{i}Pr-C*H*$_3$, P-Cy-C*H*), 1.20 – 1.26 (m, 7H, Mg(CH$_2$)$_3$C*H*$_3$, P-Cy-C*H*), 1.26 – 1.42 (m, 17H, Dipp-^{i}Pr-C*H*$_3$, Si-^{i}Pr-C*H*$_3$, P-Cy-C*H*), 1.46 (d, $^3J_{HH}$ = 6.9 Hz, 6H, Dipp-^{i}Pr-CH$_3$), 1.61 – 1.87 (m, 12H, MgCH$_2$(C*H*$_2$)$_2$CH$_3$, P-Cy-C*H*), 1.87 – 2.01 (m, 4H, P-Cy-C*H*), 3.15 – 3.26 (m, 4H, Mg-*THF*), 4.08 (p, $^3J_{HH}$ = 6.9 Hz, 2H, Dipp-^{i}Pr-C*H*), 7.01 (t, $^3J_{HH}$ = 7.5 Hz, 1H, Dipp-C*H*$_{para}$), 7.18 (d, $^3J_{HH}$ = 7.5 Hz, 2H, Dipp-C*H*$_{meta}$).

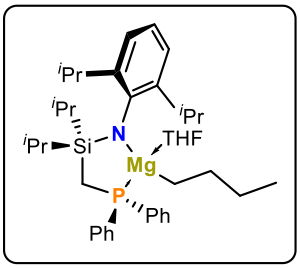
^{13}C{^{1}H} NMR (101 MHz, C_6D_6) δ (ppm) = 0.4 (d, $^1J_{CP}$ = 13.1 Hz, Si-*C*H$_2$-P), 10.4 (d, $^2J_{CP}$ = 27.6 Hz, Mg*C*H$_2$(CH$_2$)$_2$CH$_3$), 14.5 (s, Mg(CH$_2$)$_2$*C*H$_3$), 16.9 (s, Dipp-^{i}Pr-*C*H$_3$), 19.6 (s, Si-^{i}Pr-*C*H$_3$), 20.1 (s, Si-^{i}Pr-*C*H$_3$), 25.0 (s, Mg-*THF*), 25.2 (s, Dipp-^{i}Pr-*C*H$_3$), 26.0 (s, Si-^{i}Pr-*C*H), 26.8 (s, P-Cy-*C*H), 27.3 (s, *C*$_{alkyl}$), 27.8 (d, $^2J_{CP}$ = 8.9 Hz, *C*$_{alkyl}$), 28.1 (d, $^1J_{CP}$ = 11.6 Hz, P-Cy-*C*H), 30.1 (d, $^3J_{CP}$ = 3.3 Hz, P-Cy-*C*H), 31.3 (d, $^2J_{CP}$ = 8.0 Hz, P-Cy-*C*H), 32.7 (s, P-Cy-CH), 33.8 (s, Mg(CH$_2$)$_2$*C*H$_3$), 34.6 (s, P-Cy-CH), 69.2 (s, Mg-*THF*), 119.5 (s, Dipp-*C*H$_{para}$), 123.6 (s, Dipp-*C*H$_{meta}$), 144.3 (s, Dipp-C$_{ortho}$), 152.0 (s, Dipp-*C*).

^{29}Si{^{1}H} NMR (79 MHz, C_6D_6) δ (ppm) = -9.5 (d, $^2J_{SiP}$ = 6.1 Hz, *Si*^{i}Pr$_2$).

^{31}P{^{1}H} NMR (162 MHz, C_6D_6) δ (ppm) = -13.4 (s, Cy$_2$*P*-Mg).

Analc. calcd. for $C_{39}H_{70}MgNOPSi$: C, 71.58 %; H, 11.09 %; N, 2.14 %; found: C, 70.37 %, H, 11.18 %; N, 2.39 %.

^{Ph}LMg^{n}Bu·THF, 1-Ph.



In-situ ^{Ph}LH synthesis. The procedure used for ^{Cy}LH described above was used, employing 3.00 g of ^{Ph}LK (5.68 mmol, 1.00 equiv.) and 0.94 g of Et_3NHCl (6.83 mmol, 1.20 equiv.), in 50 mL of THF. The presence of ^{PhiPr}DippNH, and small amounts of residual THF, was confirmed by ^{1}H NMR in C_6D_6, and used in the following step without further purification.

Synthesis of ^{Ph}LMg^{n}Bu. The procedure used for ^{Ph}LH described above was used, employing 5.68 mL of $MgBu_2$ (1 M in Et_2O, 5.68 mmol, 1.00 equiv.). The resulting pale-yellow solid was washed with hexane (3 × 10 mL) and dried in *vacuo* to afford 3.12 g of **1-Ph** (4.86 mmol, 86 %) as a colourless solid. Additional **1-Ph** was obtained by concentrating the combined washing solutions, allowing for crystallization of **1-Ph** over the course of one week at room temperature (combined yield: 3.32 g, 91%).

N.B. Colourless crystals of **1-Ph**, suitable for single crystal X-Ray diffraction analysis, were obtained from a concentrated hexane solution at room temperature.

^{1}H NMR (400 MHz, C_6D_6) δ (ppm) = 0.16 – 0.22 (m, 2H, MgC*H*$_2$(CH$_2$)$_2$CH$_3$), 0.95 – 1.01 (m, 4H, Mg-*THF*), 1.08 – 1.23 (m, 20H, Dipp-^{i}Pr-CH$_3$, Si-^{i}Pr-C*H*$_3$, Si-^{i}Pr-C*H*), 1.28 (t, $^3J_{HH}$ = 7.2 Hz, 3H, Mg(CH$_2$)$_3$C*H*$_3$), 1.38 (d, $^3J_{HH}$ = 6.9 Hz, 6H, Dipp-^{i}Pr-C*H*$_3$), 1.73 (d, $^2J_{HP}$ = 10.4 Hz, 2H, Si-C*H*$_2$-P), 1.81 (h, $^3J_{HH}$ = 7.2 Hz, 2H, Mg(CH$_2$)$_2$C*H*$_2$CH$_3$), 1.92 – 2.02 (m, 2H, MgCH$_2$C*H*$_2$CH$_2$CH$_3$), 3.01 – 3.14 (m, 4H, Mg-*THF*), 3.99 (p, $^3J_{HH}$ = 6.9 Hz, 2H, Dipp-^{i}Pr-C*H*), 6.97 (t, $^3J_{HH}$ = 7.5 Hz, 1H, Dipp-C*H*$_{para}$), 7.01 – 7.06 (m, 2H, P-Ph-C*H*$_{para}$), 7.08 – 7.15 (m, 6H, Dipp-C*H*$_{meta}$, P-Ph-C*H*$_{meta}$), 7.59 – 7.69 (m, 4H, P-Ph-C*H*$_{ortho}$).

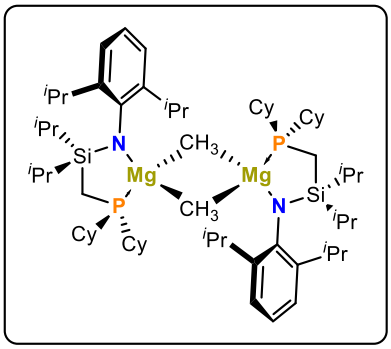
^{13}C{^{1}H} NMR (101 MHz, C_6D_6) δ (ppm) = 9.7 (d, $^1J_{CP}$ = 12.2 Hz, Si-*C*H$_2$-P), 10.2 (d, $^2J_{CP}$ = 25.4 Hz, Mg*C*H$_2$(CH$_2$)$_2$CH$_3$), 14.6 (s, Mg(CH$_2$)$_3$*C*H$_3$), 16.9 (s, Dipp-^{i}Pr-*C*H$_3$), 19.4 (s, Si-^{i}Pr-*C*H$_3$), 19.8 (s, Si-^{i}Pr-*C*H$_3$), 24.9 – 25.0 (m, Dipp-^{i}Pr-*C*H$_3$, Mg-*THF*), 25.5 (s, Si-^{i}Pr-*C*H), 27.7 (s, Dipp-^{i}Pr-*C*H), 32.6 (s, Mg(CH$_2$)$_2$*C*H$_2$CH$_3$), 33.7 (s, MgCH$_2$*C*H$_2$CH$_2$CH$_3$), 69.1 (s, 2C, Mg-*THF*), 119.5 (s, Dipp-*C*H$_{para}$), 123.5 (s, Dipp-*C*H$_{meta}$), 128.9 (d, $^3J_{CP}$ = 8.25 Hz, P-Ph-*C*H$_{meta}$), 129.6 (s, P-Ph-*C*H$_{para}$), 133.0 (d, $^2J_{CP}$ = 15.7 Hz, P-Ph-*C*H$_{ortho}$), 137.6 (d, J_{CP} = 10.3 Hz, P-Ph-*C*), 144.3 (s, Dipp-*C*$_{ortho}$), 151.7 (d, $^3J_{CP}$ = 2.3 Hz, Dipp-*C*).

^{29}Si{^{1}H} NMR (79 MHz, C_6D_6) δ (ppm) = -8.6 (d, $^2J_{SiP}$ = 8.5 Hz, *Si*^{i}Pr$_2$).

^{31}P{^{1}H} NMR (162 MHz, C_6D_6) δ (ppm) = -24.1 (s, Ph$_2$*P*-Mg).

Analc. calcd. for $C_{39}H_{58}MgNOPSi$: C, 73.16%; H, 9.13 %; N, 2.19 %; found: C, 73.07 %; H, 9.07 %; N, 2.25 %.

(^{Cy}LMgMe)$_2$, 2.



A 100 mL Schlenk flask was charged with 1.02 g ^{Cy}LK (1.89 mmol, 1.00 equiv.) and and 20 mL THF. The solution was cooled to -78 °C, and 0.91 mL of a MeMgBr solution (2.4 M, 2.17 mmol, 1.15 equiv.) was added dropwise. The solution was stirred for 16 hours, while slowly warming to room temperature. The suspension was subsequently filtered, and all volatiles were removed from filtrate *in vacuo*. The residue was washed with pentane (3 x 10 mL). After drying *in vacuo*, 0.87 g of **2** (1.61 mmol, 85 %) were obtained as a colourless solid.

N.B. Colourless crystals of **2**, suitable for single crystal X-Ray diffraction analysis, were obtained from a concentrated pentane solution at room temperature.

^{1}H NMR (400 MHz, C_6D_6 / THF-d_8) δ (ppm) = -0.76 (bs, 6H, MgC*H*$_3$), 0.94 (d, $^1J_{CP}$ = 9.5 Hz, 4H, Si-C*H*$_2$-P), 1.08 – 1.18 (m, 24H, Si-^{i}Pr-C*H*$_3$, Mg-*THF*), 1.15 – 1.30 (m, 16H, P-Cy-C*H*), 1.34 (bs, 26H, Dipp-^{i}Pr-C*H*$_3$, Si-^{i}Pr-C*H*$_3$, Si-^{i}Pr-C*H*), 1.45 (d, $^3J_{HH}$ = 6.8 Hz, 24H, Dipp-^{i}Pr-C*H*$_3$), 1.57 – 1.66 (m, 4H, P-Cy-C*H*), 1.68 – 1.85 (m, 12H, P-Cy-C*H*), 1.87 – 1.95 (m, 4H, P-Cy-C*H*), 1.97 – 2.08 (m, 4H, P-Cy-C*H*), 3.42 (s, 8H, Mg-*THF*) 4.08 (bs, 4H, Dipp-^{i}Pr-C*H*), 7.01 (t, $^3J_{HH}$ = 7.5 Hz, 2H, Dipp-C*H*$_{para}$), 7.19 (d, $^3J_{HH}$ = 8.0 Hz, 2H, Dipp-C*H*$_{meta}$).

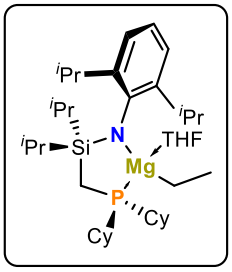
^{13}C{^{1}H} NMR (101 MHz, C_6D_6 / THF-d_8) δ (ppm) = -14.1 – -13.6 (m, Mg*C*H$_3$), -0.5 (s, Si-*C*H$_2$-P), 16.6 (s, Si-^{i}Pr-*C*H), 19.4 (s, Si-^{i}Pr-*C*H$_3$, Mg-*THF*), 20.1 (s, Si-^{i}Pr-*C*H$_3$), 24.8 – 25.3 (m, Dipp-^{i}Pr-*C*H$_3$, Si-^{i}Pr-*C*H$_3$), 26.4 – 26.9 (m, Dipp-^{i}Pr-*C*H$_3$, P-Cy-*C*H), 27.3 (s, P-Cy-*C*H), 22.7 (d, $^2J_{CP}$ = 9.5 Hz, P-Cy-*C*H), 28.0 (d, $^1J_{CP}$ = 11.9 Hz, P-Cy-*C*H), 30.0 (d, $^1J_{CP}$ = 2.9 Hz, P-Cy-*C*H), 31.2 (d, $^2J_{CP}$ = 6.0 Hz, P-Cy-*C*H), 34.3 (d, $^2J_{CP}$ = 6.1 Hz, P-Cy-*C*H), 69.4 (s, Mg-*THF*), 120.1 (s, Dipp-*C*H$_{para}$), 123.6 (s, Dipp-*C*H$_{meta}$), 144.5 (s, Dipp-*C*$_{ortho}$), 150.9 (s, Dipp-*C*).

^{29}Si{^{1}H} NMR (79 MHz, C_6D_6 / THF-d_8) δ (ppm) = -9.7 (bs, ^{i}Pr$_2$*Si*).

^{31}P{^{1}H} NMR (162 MHz, C_6D_6 / THF-d_8) δ (ppm) = -13.7 (s, Ph$_2$*P*-Mg).

Analc. calcd. for $C_{36}H_{66}MgNOPSi$ (for the monomeric THF-coordinated species): C, 70.62 %; H, 10.87 %; N, 2.29 %; found: C, 61.71 %; H, 9.43 %; N, 2.01 %.

^{Cy}LMgEt·THF, 3.



The procedure for ^{Cy}LMgMe described above was used, employing 3.59 g of ^{Cy}LK (6.64 mmol, 1.00 equiv.) and 2.30 mL EtMgBr (3.0 M in Et_2O, 6.90 mmol, 1.04 equiv.) in 40 mL THF. The reaction residue, following filtration and solvent removal, was washed with cold pentane (3 x 5 mL) and dried *in vacuo*, to give 3.45 g of **3** (6.23 mmol, 93.7 %) as a colourless solid.

N.B. Colourless crystals of **3**, suitable for single crystal X-Ray diffraction analysis, were obtained from a concentrated THF solution layered with pentane at room temperature.

^{1}H NMR (400 MHz, C_6D_6) δ (ppm) = -0.07 (q, $^3J_{HH}$ = 8.2 Hz, 2H, MgC*H*$_2$CH$_3$), 0.94 (d, $^2J_{HP}$ = 8.8 Hz, 2H, Si-C*H*$_2$-P), 1.07 – 1.13 (m, 4H, Mg-*THF*), 1.13 – 1.18 (m, 8H, Si-^{i}Pr-C*H*$_3$, P-Cy-C*H*), 1.18 – 1.29 (m, 8H, Si-^{i}Pr-C*H*$_3$, P-Cy-C*H*), 1.31 (d, $^3J_{HH}$ = 6.9 Hz, 6H, Dipp-^{i}Pr-C*H*$_3$), 1.33 – 1.40 (m, 10H, Si-^{i}Pr-C*H*$_3$, P-Cy-C*H*), 1.45 (d, $^3J_{HH}$ = 6.9 Hz, 6H, Dipp-^{i}Pr-C*H*$_3$), 1.65 (d, $^3J_{HH}$ = 12.3 Hz, 3H, P-Cy-C*H*), 1.71 (t, $^3J_{HH}$ = 8.2 Hz, 3H, MgCH$_2$C*H*$_3$), 1.74 – 1.82 (m, 7H, P-Cy-C*H*), 1.85 – 2.00 (m, 4H, P-Cy-C*H*), 3.24 (t, $^3J_{HH}$ = 6.2 Hz, 4H, Mg-*THF*), 4.08 (p, $^3J_{HH}$ = 6.9 Hz, 2H, Dipp-^{i}Pr-C*H*), 7.00 (t, $^3J_{HH}$ = 7.5 Hz, 1H, Dipp-C*H*$_{para}$), 7.18 (d, $^3J_{HH}$ = 7.6 Hz, 2H, Dipp-C*H*$_{meta}$).

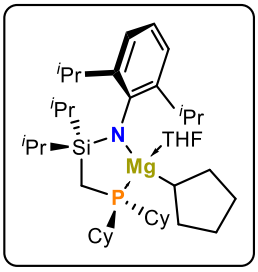
^{13}C{^{1}H} NMR (101 MHz, C_6D_6) δ (ppm) = 0.4 (d, $^1J_{CP}$ = 13.0 Hz, Si-*C*H$_2$-P), 1.0 (bs, Mg*C*H$_2$CH$_3$), 14.6 (s, MgCH$_2$*C*H$_3$), 16.9 (s, *C*$_{alkyl}$), 19.6 (s, *C*$_{alkyl}$), 20.1 (s, *C*$_{alkyl}$), 25.0 (s, Mg-*THF*), 25.2 (s, Dipp-^{i}Pr-*C*H$_3$), 26.0 (s, Dipp-^{i}Pr-*C*H$_3$), 26.7 (s, Dipp-^{i}Pr-*C*H), 27.3 (s, P-Cy-*C*H), 27.8 (d, J_{CP} = 8.9 Hz, P-Cy-*C*H), 28.1 (d, J_{CP} = 11.7 Hz, P-Cy-*C*H), 30.1 (d, J_{CP} = 3.3 Hz, P-Cy-*C*H), 31.3 (d, J_{CP} = 8.1 Hz, P-Cy-*C*H), 34.6 (s, P-Cy-*C*H), 69.2 (s, Mg-*THF*), 119.4 (s, Dipp-*C*H$_{para}$), 123.6 (s, Dipp-*C*H$_{meta}$), 144.3 (s, Dipp-*C*$_{ortho}$), 152.0 (s, Dipp-*C*).

^{29}Si{^{1}H} NMR (79 MHz, C_6D_6) δ (ppm) = -9.6 (d, $^2J_{SiP}$ = 6.3 Hz, *Si*^{i}Pr$_2$).

^{31}P{^{1}H} NMR (162 MHz, C_6D_6) δ (ppm) = -13.4 (s, Ph$_2$*P*-Mg).

Analc. calcd. for $C_{37}H_{68}MgNOPSi$: C, 70.96 %; H, 10.94 %; N, 2.24 %; found: C, 68.61 %; N, 10.83 %; H, 2.35 %.

^{Cy}LMg(^{cy}Pent)·THF, 4.



A 100 mL round-bottom flask was loaded with 0.42 g magnesium turnings (17.07 mmol, 2.30 equiv.) and suspended in 20 mL dry diethyl ether. An iodine crystal was added, and the suspension was stirred until the solution turned colourless. The supernatant was removed and 30 mL diethyl ether was added. While stirring vigorously 0.93 mL of cyclopentylbromide (98 %, 8.52 mmol, 1.15 equiv.) were added at room temperature. The reaction solution was brought to reflux and stirred for 2 hours. The Grignard suspension was cooled down to room temperature and filtered directly onto a stirring solution of 4.00 g $^{Cy\mathit{i}Pr}$DippNK (7.41 mmol, 1.00 equiv.) in 30 mL THF at -78 °C. After complete addition, the reaction was left to stir overnight, whilst slowly warming up room temperature. The solution was separated by filtration, and all volatiles were removed *in vacuo*. The obtained residue was washed twice with cold pentane (2 x 10 mL) and again dried *in vacuo*, to yield 4.12 g **4** (6.93 mmol, 94 %) as a colourless solid.

N.B. Colourless crystals of **4**, suitable for single crystal X-Ray diffraction analysis, were obtained from a concentrated pentane solution at room temperature.

^{1}H NMR (400 MHz, C_6D_6) δ (ppm) = -0.01 (tt, $^{3}J_{HH}$ = 7.0, 13.3 Hz, 1H, MgC*H*), 0.95 (d, $^{2}J_{HP}$ = 8.8 Hz, 2H, Si-CH_2-P), 1.08 – 1.26 (m, 16H, Mg-*THF*, Mg(c-C$_5H_9$), P-Cy-C*H*), 1.28 (d, $^{3}J_{HH}$ = 6.8 Hz, 6H, Dipp-$^{\mathit{i}}$Pr-CH_3), 1.29 – 1.40 (m, 10H, Si-$^{\mathit{i}}$Pr-CH_3, Si-$^{\mathit{i}}$Pr-C*H*, P-Cy-C*H*), 1.46 (d, $^{3}J_{HH}$ = 6.8 Hz, 6H, Dipp-$^{\mathit{i}}$Pr-CH_3), 1.59 – 1.69 (m, 4H, Mg(c-C$_5H_9$)), 1.75 – 1.83 (m, 8H, P-Cy-C*H*), 1.85 – 1.96 (m, 4H, P-Cy-C*H*), 1.96 – 2.06 (m, 2H, Mg(c-C$_5H_9$)), 2.26 – 2.39 (m, 2H, Mg(c-C$_5H_9$)), 3.27 (bs, 4H, Mg-*THF*), 4.07 (p, $^{3}J_{HH}$ = 6.8 Hz, 4H, Dipp-$^{\mathit{i}}$Pr-C*H*), 7.01 (t, $^{3}J_{HH}$ = 7.4 Hz, 1H, Dipp-CH_{para}), 7.18 (d, $^{3}J_{HH}$ = 7.6 Hz, 2H, Dipp-CH_{meta}).

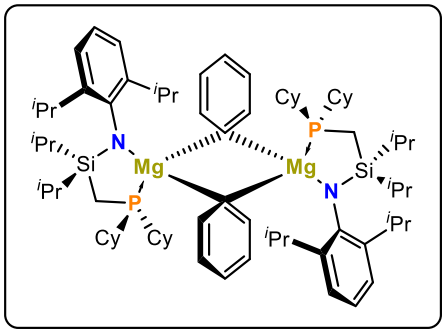
^{13}C{^{1}H} NMR (101 MHz, C_6D_6) δ (ppm) = 1.0 (d, $^{1}J_{CP}$ = 13.2 Hz, Si-CH_2-P), 16.9 (s, C_{alkyl}), 19.6 (s, C_{alkyl}), 20.1 (s, C_{alkyl}), 24.2 (s, MgC*H*), 24.5 (s, C_{alkyl}), 25.2 (s, Dipp-$^{\mathit{i}}$Pr-CH_3), 25.3 (s, C_{alkyl}), 26.0 (s, C_{alkyl}), 26.8 (s, Dipp-$^{\mathit{i}}$Pr-*C*H), 27.4 (s, Mg(c-C_5H_9)), 27.9 (d, $^{2}J_{CP}$ = 8.7 Hz, P-Cy-*C*H), 28.1 (d, $^{1}J_{CP}$ = 11.7 Hz, P-Cy-*C*H), 28.5 (s, C_{alkyl}), 30.1 (d, $^{3}J_{CP}$ = 2.7 Hz, P-Cy-*C*H), 31.4 (d, $^{1}J_{CP}$ = 13.2 Hz, P-Cy-*C*H), 34.8 (s, P-Cy-*C*H), 35.3 (s, P-Cy-*C*H), 69.3 (s, Mg-*THF*), 119.5 (s, Dipp-*C*H$_{para}$), 123.6 (s, Dipp-*C*H$_{meta}$), 144.4 (s, Dipp-C_{ortho}), 152.1 (s, Dipp-*C*).

^{29}Si{^{1}H} NMR (79 MHz, C_6D_6) δ (ppm) = -9.1 (d, $^{2}J_{SiP}$ = 6.5 Hz, *Si*$^{\mathit{i}}$Pr$_2$).

^{31}P{^{1}H} NMR (162 MHz, C_6D_6) δ (ppm) = -13.3 (s, Cy$_2$*P*-Mg).

Analc. calcd. for $C_{37}H_{68}MgNOPSi$: C, 72.10 %; H, 10.89 %; N, 2.10 %; found: C, 70.53 %; N, 10.81 %; H, 2.45 %.

(^{Cy}LMgPh)$_2$, 5.



The procedure for ^{Cy}LMg(^{cy}Pent) described above was used, employing 0.16 g magnesium turnings (6.62 mmol, 2.38 equiv.), 0.34 mL bromobenzene (3.20 mmol, 1.15 equiv.), and 1.50 g ^{Cy}*i*^{Pr}DippNK (2.79 mmol, 1.00 equiv.), in 30 mL THF at -78 °C. The obtained residue was washed twice with cold pentane (2 x 10 mL), and dryied *in vacuo*, affording 1.54 g of **5** (2.28 mmol, 82 %) as a colourless solid.

N.B. Colourless crystals of **5**, suitable for single crystal X-Ray diffraction analysis, were obtained from a concentrated benzene solution at room temperature.

^{1}H NMR (400 MHz, C_6D_6 / THF-d_8) δ (ppm) = 0.95 (d, $^2J_{HP}$ = 9.0 Hz, 4H, Si-C*H*$_2$-P), 1.09 (d, $^3J_{HH}$ = 6.8 Hz, 12H, Si-*i*Pr-C*H*$_3$), 1.13 (d, $^3J_{HH}$ = 6.9 Hz, 12H, Dipp-*i*Pr-C*H*$_3$), 1.15 – 1.30 (m, 16H, Si-*i*Pr-C*H*$_3$, Si-*i*Pr-C*H*, P-Cy-C*H*), 1.35 (d, $^3J_{HH}$ = 7.0 Hz, 12H, Dipp-*i*Pr-C*H*$_3$), 1.56 – 1.79 (m, 12H, P-Cy-C*H*), 1.81 – 2.00 (m, 8H, P-Cy-C*H*), 4.05 (hept, $^3J_{HH}$ = 7.2 Hz, 4H, Dipp-*i*Pr-C*H*$_3$), 6.91 (t, $^3J_{HH}$ = 7.5 Hz, 2H, Dipp-C*H*$_{para}$), 7.08 (d, $^3J_{HH}$ = 7.5 Hz, 4H, Dipp-C*H*$_{meta}$), 7.10 – 7.12 (m, 2H, Mg-Ph-C*H*$_{para}$), 7.20 (t, $^3J_{HH}$ = 7.2 Hz, 4H, Mg-Ph-C*H*$_{meta}$), 7.66 (d, $^3J_{HH}$ = 6.1 Hz, 4H, Mg-Ph-C*H*$_{ortho}$).

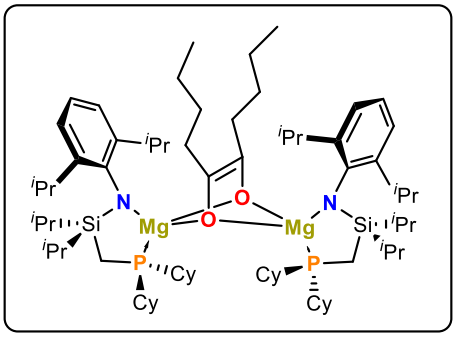
^{13}C{^{1}H} NMR (101 MHz, C_6D_6 / THF-d_8) δ (ppm) = 1.6 (d, $^1J_{CP}$ = 12.3 Hz, Si-*C*H$_2$-P), 17.8 (d, $^3J_{CP}$ = 2.0 Hz,Si-*i*Pr-*C*H), 19.7 (s, Si-*i*Pr-*C*H$_3$), 20.2 (s, Si-*i*Pr-*C*H$_3$), 24.9 (s, Dipp-*i*Pr-*C*H$_3$), 26.4 (s, Dipp-*i*Pr-*C*H$_3$), 26.7 (s, P-Cy-*C*H), 27.5 (s, Dipp-*i*Pr-*C*H), 27.8 (d, $^2J_{CP}$ = 8.9 Hz, P-Cy-*C*H), 28.0 (d, $^1J_{CP}$ = 11.9 Hz, P-Cy-*C*H), 30.0 (d, $^3J_{CP}$ = 2.6 Hz, P-Cy-*C*H), 31.3 (d, $^2J_{CP}$ = 7.7 Hz, P-Cy-*C*H), 34.8 (s, P-Cy-*C*H), 119.7 (s, Dipp-*C*H$_{para}$), 123.5 (s, Dipp-*C*H$_{meta}$), 124.9 (s, Mg-Ph-*C*H$_{para}$), 126.4 (s, Mg-Ph-*C*H$_{meta}$), 141.0 (s, Mg-Ph-*C*H$_{ortho}$), 144.4 (s, Dipp-*C*$_{ortho}$), 151.6 (s, Dipp-*C*), 167.4 (d, $^2J_{CP}$ = 24.3 Hz, Mg-Ph-*C*).

^{29}Si{^{1}H} NMR (79 MHz, C_6D_6 / THF-d_8) δ (ppm) = -9.3 (d, $^2J_{SiP}$ = 6.1 Hz, *Si*^{i}Pr$_2$).

^{31}P{^{1}H} NMR (162 MHz, C_6D_6 / THF-d_8) δ (ppm) = -13.1 (s, Cy$_2$*P*-Mg).

Analc. calcd. for $C_{37}H_{60}MgNPSi$: C, 73.79 %; H, 10.04 %; N, 2.33 %; found: C, 70.45 %; H, 10.50 %; N, 2.49 %.

(^{Cy}LMg)$_2$(μ-C$_2$O$_2$)^{n}Bu$_2$, 6-Cy.



A 100 mL Fisher-Porter bottle was loaded with 1.8 g of **1-Cy** (2.75 mmol, 1.00 equiv.) and dissolved in 30 mL toluene. The solution was subjected to three freeze-pump-thaw cycles and subsequently pressurized with 2 atm of carbon monoxide. The reaction mixture was left to stir for 24 h at room temperature, whereby no further change in gas pressure was observed, indicating complete consumption of **1-Cy**. The reaction solution was then transferred into a 50 mL Schlenk tube and the solvent was removed *in vacuo*. The resulting orange-red residue was dissolved in 15 mL pentane and subsequently concentrated to 3 mL of volume. The concentrate was stored in a freezer at -32 °C, leading to the formation of colourless crystals after ten days, suitable for single crystal X-Ray diffraction analysis. The supernatant was decanted, and the crystalline product was washed three times with 5 mL cold pentane. Additional product was obtained by storing the combined washings and supernatant solution at -32 °C. After drying the combined solids *in vacuo*, **6-Cy** was obtained as a colourless solid (631 mg, 517 µmol, 38 %).

N.B. Conducted the reaction on an NMR scale, in a Teflon-sealed NMR tubes, indicates the complete and selective conversion to **6-Cy**. We attribute the relatively low isolated yield to the high solubility of this species.

^{1}H NMR (400 MHz, C_6D_6) δ (ppm) = 0.81 (d, $^2J_{HP}$ = 10.9 Hz, 4H, Si-CH_2-P), 0.92 – 0.97 (m, 12H, Si-^{i}Pr-CH_3), 1.00 (t, $^3J_{HH}$ = 6.9 Hz, 6H, Mg(μ-C$_2$O$_2$)(CH$_2$)$_3$CH_3), 1.10 – 1.31 (m, 36H, Mg(μ-C$_2$O$_2$)(CH$_2$(CH_2)$_2$CH$_3$)$_2$, P-Cy-CH, Si-^{i}Pr-CH), 1.34 (d, $^3J_{HH}$ = 6.8 Hz, 12H, Dipp-^{i}Pr-CH_3), 1.36 – 1.38 (m, 4H, CH_{alkyl}), 1.40 (d, $^3J_{HH}$ = 6.8 Hz, 12H, Dipp-^{i}Pr-CH_3), 1.65 (d, $^3J_{HH}$ = 12.1 Hz, 4H, P-Cy-CH), 1.70 – 1.85 (m, 20H, Mg(μ-C$_2$O$_2$)(CH_2(CH$_2$)$_2$CH$_3$)$_2$, P-Cy-CH), 1.86 – 1.95 (m, 4H, P-Cy-CH), 1.97 – 2.07 (m, 4H, P-Cy-CH), 3.75 (hept, $^3J_{HH}$ = 6.8 Hz, 4H, Dipp-^{i}Pr-CH), 7.02 (dd, $^3J_{HH}$ = 6.8, 8.2 Hz, 2H, Dipp-CH_{para}), 7.12 (d, $^3J_{HH}$ = 7.5 Hz, 4H, Dipp-CH_{meta}).

^{13}C{^{1}H} NMR (101 MHz, C_6D_6) δ (ppm) = -2.0 (d, $^1J_{CP}$ = 9.5 Hz, Si-CH$_2$-P), 14.5 (s, Mg(μ-C$_2$O$_2$)(CH$_2$)$_3$CH$_3$), 15.0 (s, Si-^{i}Pr-CH), 19.6 (s, Si-^{i}Pr-CH$_3$), 20.2 (s, Si-^{i}Pr-CH$_3$), 22.7 (s, Mg(μ-C$_2$O$_2$)CH$_2$(CH$_2$)$_2$CH$_3$), 23.9 (s, Mg(μ-C$_2$O$_2$)CH$_2$(CH$_2$)$_2$CH$_3$), 25.2 (s, Dipp-^{i}Pr-CH$_3$), 26.4 (s, Dipp-^{i}Pr-CH$_3$), 26.5 (s, P-Cy-CH), 27.7 (s, P-Cy-CH), 27.8 (s, Dipp-^{i}Pr-CH), 28.0 (s, P-Cy-CH), 28.1 (s, P-Cy-CH), 29.2 (s, Dipp-^{i}Pr-CH$_3$), 29.9 (s, P-Cy-CH), 30.1 – 30.3 (m, P-Cy-CH), 30.3 (s, P-Cy-CH), 34.5 (s, Mg(μ-C$_2$O$_2$)(CH$_2$(CH$_2$)$_2$CH$_3$)$_2$), 34.6 (d, $^1J_{CP}$ = 5.0 Hz, P-Cy-CH), 120.6 (s, Dipp-CH$_{para}$), 123.6 (s, Dipp-CH$_{meta}$), 139.7 (s, Mg(μ-C_2O$_2$)), 144.5 (s, Dipp-C_{ortho}), 151.4 (s, Dipp-C).

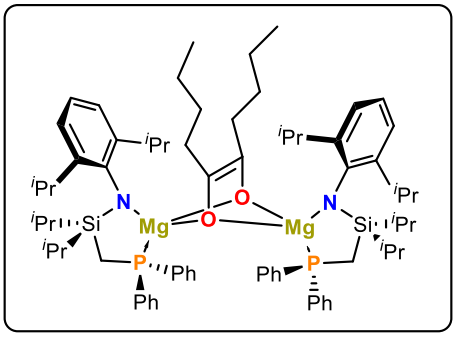
^{29}Si{^{1}H} NMR (79 MHz, C_6D_6) δ (ppm) = -8.6 (d, $^2J_{SiP}$ = 3.8 Hz, Si^{i}Pr$_2$).

$^{31}P\{^{1}H\}$ NMR (162 MHz, C_6D_6) δ (ppm) = -14.7 (s, Cy_2P-Mg)

Analc. calcd. for $C_{72}H_{128}Mg_2N_2O_2P_2Si_2$: C, 70.85 %; H, 10.57 %; N, 2.30 %; found: 71.30 %; H, 10.14 %; N, 2.28 %.

N.B. Conducted the reaction on an NMR scale, in a Teflon-sealed NMR tubes, indicates the complete and selective conversion to **6-Cy**. We attribute the relatively low isolated yield to the high solubility of this species.

(^{Ph}LMg)$_2$(μ-C_2O_2)^{n}Bu$_2$, 6-Ph.



The procedure for (^{Cy}LMg)$_2$(μ-C_2O_2)^{n}Bu$_2$ described above was used, employing 1.0 g of **1-Ph** (1.56 mmol, 1.00 equiv.) and 20 mL toluene. The concentrated pentane solution attained following product extraction was stored at -32 °C, leading to the formation of colourless crystals after two weeks, which were suitable for single crystal X-Ray diffraction analysis. The supernatant was decanted, and the crystalline product was carefully washed three times with 2 mL cold pentane. A second crop is isolated following storage of the combined extracts at -32 °C for a further week. After drying the combined solids *in vacuo*, **6-Ph** was obtained as an off-white solid (257 mg, 215 μmol, 28 %).

^{1}H NMR (400 MHz, C_6D_6) δ (ppm) = 0.86 (d, $^{3}J_{HH}$ = 7.5 Hz, 12H, Si-^{i}Pr-CH_3), 0.92 – 1.05 (m, 18H, Si-^{i}Pr-CH3, Mg(μ-C_2O_2)((CH$_2$)$_3$CH_3)$_2$), 1.09 – 1.20 (m, 10H, Si-^{i}Pr-CH, Mg(μ-C_2O_2)(CH$_2$(CH_2)$_2$CH$_3$)$_2$), 1.24 (d, $^{3}J_{HH}$ = 6.7 Hz, 12H, Dipp-^{i}Pr-CH_3), 1.32 (p, $^{3}J_{HH}$ = 7.4 Hz, 2H, Si-^{i}Pr-CH), 1.43 (d, $^{3}J_{HH}$ = 6.8 Hz, 12H, Dipp-^{i}Pr-CH_3), 1.55 (d, $^{2}J_{HP}$ = 12.1 Hz, 4H, Si-CH_2-P), 2.02 (dd, $^{3}J_{HH}$ = 6.5, 10.1 Hz, 4H, Mg(μ-C_2O_2)(CH_2(CH$_2$)$_2$CH$_3$)$_2$), 3.73 (hept, $^{3}J_{HH}$ = 6.8 Hz, 4H, Dipp-^{i}Pr-CH), 6.84 (t, $^{3}J_{HH}$ = 7.1 Hz, 8H, P-Ph-CH_{meta}), 6.93 (t, $^{3}J_{HH}$ = 7.2 Hz, 4H, P-Ph-CH_{para}), 7.02 (t, $^{3}J_{HH}$ = 7.4 Hz, 2H, Dipp-CH_{para}), 7.13 (d, $^{3}J_{HH}$ = 7.5 Hz, 4H, Dipp-CH_{meta}), 7.54 (t, $^{3}J_{HH}$ = 8.5 Hz, 8H, P-Ph-CH_{ortho}).

$^{13}C\{^{1}H\}$ NMR (101 MHz, C_6D_6) δ (ppm) = 14.3 (bs, Si-CH$_2$-P, Mg(μ-C_2O_2)((CH$_2$)$_3$CH_3)$_2$), 15.5 (s, Si-^{i}Pr-CH), 19.5 (s, Si-^{i}Pr-CH$_3$), 19.8 (s, Si-^{i}Pr-CH$_3$), 23.9 (s, Si-^{i}Pr-CH), 25.0 (s, Dipp-^{i}Pr-CH$_3$), 25.9 (s, Dipp-^{i}Pr-CH$_3$), 28.1 (s, Si-^{i}Pr-CH), 28.5 (s, Dipp-^{i}Pr-CH$_3$), 30.3 (s, Mg(μ-C_2O_2)(CH$_2$(CH$_2$)$_2$CH$_3$)$_2$), 120.5 (s, Dipp-CH$_{para}$), 123.6 (s, Dipp-CH$_{meta}$), 128.8 – 129.5 (m, P-Ph-CH$_{meta}$), 130.1 (s, P-Ph-CH$_{para}$), 133.5 – 134.2 (m, P-Ph-CH_{ortho}), 135.0 (d, $^{1}J_{CP}$ = 18.6 Hz, P-Ph-C), 140.4 (s, Mg(μ-C_2O_2)), 143.9 (s, Dipp-C_{ortho}), 151.2 (s, Dipp-C).

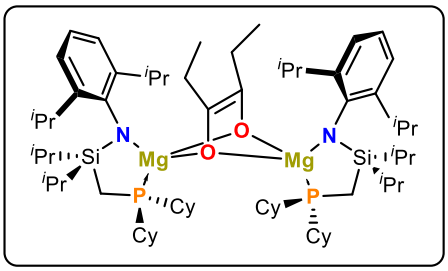
^{29}Si{^{1}H} NMR (79 MHz, C_6D_6) δ (ppm) = -6.6 (d, $^{3}J_{HH}$ = 2.5 Hz, *Si*^{i}Pr$_2$), -6.5 (d, $^{2}J_{SiP}$ = 2.6 Hz, *Si*^{i}Pr$_2$).

^{31}P{^{1}H} NMR (162 MHz, C_6D_6) δ (ppm) = -23.6 (s, Ph$_2$*P*-Mg).

Analc. calcd. for $C_{72}H_{104}Mg_2N_2O_2P_2Si_2$: C, 72.29 %; H, 8.76 %; N, 2.34 %; found: 72.11 %; H, 8.98 %; N, 2.37 %.

N.B. Conducted the reaction on an NMR scale, in a Teflon-sealed NMR tubes, indicates the complete and selective conversion to **6-Cy**. We attribute the relatively low isolated yield to the high solubility of this species.

(^{Cy}LMg)$_2$(*μ*-C$_2$O$_2$)Et$_2$, 7-Cy.



A 50 mL pressure Schlenk tube was loaded with 300 mg **3** (481 µmol, 1.00 equiv.) and dissolved in 3 mL toluene. The solution was subjected to three freeze-pump-thaw cycles and subsequently pressurized with 2 bar of carbon monoxide (excess equiv.). After 24 h stirring at room temperature, all volatiles were removed *in vacuo*. The obtained orange-brown oil was treated with 2 mL cold pentane and the obtained pale-brown microcrystalline precipitate was isolated by filtration. After washing with 1 mL pentane, 73 mg of **7** (63 µmol, 13 %) were obtained as a colourless solid.

N.B. Though colourless crystals of **7** could be isolated, they were not suitable for single crystal X-Ray diffraction analysis.

^{1}H NMR (400 MHz, C_6D_6) δ (ppm) = 0.80 (d, $^{3}J_{HH}$ = 10.7 Hz, 4H, Si-C*H*$_2$-P), 0.92 – 0.99 (m, 18H, Mg(*μ*-C$_2$O$_2$)(CH$_2$C*H*$_3$)$_2$, Si-^{i}Pr-C*H*$_3$), 1.16 – 1.27 (m, 32H, Si-^{i}Pr-C*H*$_3$, Si-^{i}Pr-C*H*, P-Cy-C*H*), 1.34 (d, $^{3}J_{HH}$ = 6.8 Hz, 12H, Dipp-^{i}Pr-C*H*$_3$), 1.40 (d, $^{3}J_{HH}$ = 6.8 Hz, 12H, Dipp-^{i}Pr-C*H*$_3$), 1.60 – 1.70 (m, 6H, P-Cy-C*H*), 1.70 – 1.83 (m, 18H, Mg(*μ*-C$_2$O$_2$)(C*H*$_2$CH$_3$)$_2$, P-Cy-C*H*), 1.85 – 1.94 (m, 4H, P-Cy-C*H*), 1.95 – 2.06 (m, 4H, P-Cy-C*H*), 3.74 (p, $^{3}J_{HH}$ = 6.8 Hz, 4H, Dipp-^{i}Pr-C*H*), 7.04 (t, $^{3}J_{HH}$ = 7.8 Hz, 2H, Dipp-C*H*$_{para}$), 7.15 (d, $^{3}J_{HH}$ = 7.4 Hz, 4H, Dipp-C*H*$_{meta}$).

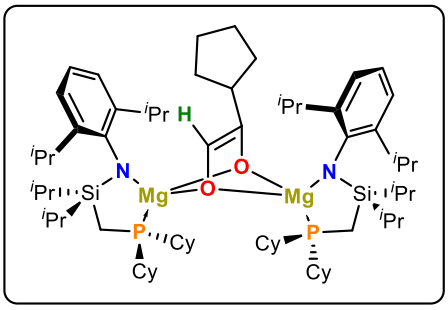
^{13}C{^{1}H} NMR (101 MHz, C_6D_6) δ (ppm) = -2.0 (d, $^{1}J_{CP}$ = 9.6 Hz, Si-*C*H$_2$-P), 11.3 (s, Mg(C$_2$O$_2$)(CH$_2$*C*H$_3$)$_2$), 15.0 (s, Si-^{i}Pr-*C*H), 19.6 (s, Si-^{i}Pr-*C*H$_3$), 20.1 (s, Si-^{i}Pr-*C*H$_3$), 23.0 (s, Mg(C$_2$O$_2$)(*C*H$_2$CH$_3$)$_2$), 24.1 (s, P-Cy-*C*H), 25.2 (s, Dipp-^{i}Pr-*C*H$_3$), 26.3 (s, Dipp-^{i}Pr-*C*H$_3$), 26.5 (s, P-Cy-*C*H), 27.7 (s, Dipp-^{i}Pr-*C*H), 28.0 (d, $^{1}J_{CP}$ = 12.1 Hz, P-Cy-*C*H), 29.9 (s, P-Cy-*C*H), 30.2 (d, $^{2}J_{CP}$ = 5.6 Hz, P-Cy-*C*H), 34.6 (d, $^{2}J_{CP}$ = 5.2 Hz, P-Cy-*C*H), 120.5 (s, Dipp-*C*H$_{para}$), 123.7 (s, Dipp-*C*H$_{meta}$), 140.1 (s, Mg(*C*$_2$O$_2$)), 144.5 (s, Dipp-*C*$_{ortho}$), 151.4 (s, Dipp-*C*).

^{29}Si{^{1}H} NMR (79 MHz, C_6D_6) δ (ppm) = -8.6 (m, *Si*^{i}Pr$_2$).

$^{31}P\{^{1}H\}$ NMR (162 MHz, C_6D_6) δ (ppm) = -14.7 (s, Cy_2P-Mg).

Analc. calcd. for $C_{68}H_{120}Mg_2N_2O_2P_2Si_2$: C, 70.14 %; H, 10.39 %; N, 2.41 %; found: 67.21 %; H, 9.96 %; N, 2.46 %.

$(^{Cy}LMg)_2(\mu\text{-}C_2O_2)(H)(^{cy}Pent)$, 8-Cy.



The procedure for $(^{Cy}LMg)_2(\mu\text{-}C_2O_2)Et_2$ described above was used, employing 300 mg **4** (452 µmol, 1.00 equiv.) in 3 mL toluene. The obtained intense red coloured oil was treated with 2 mL cold pentane and dried thoroughly *in vacuo* again. 251 mg of **7** (63 µmol, 94.5 %) were obtained as a pale red solid, which were not subjected to further purification methods.

^{1}H NMR (400 MHz, C_6D_6) δ (ppm) = 0.92 – 1.05 (m, 8H, Si-C*H*$_2$-P, C*H*$_{alkyl}$), 1.06 – 1.15 (m, 14H, Si-*i*Pr-C*H*$_3$, C*H*$_{alkyl}$), 1.15 – 1.20 (m, 30H, C*H*$_{alkyl}$), 1.25 – 1.31 (m, 15H, Si-*i*Pr-C*H*, P-Cy-C*H*, Dipp-*i*Pr-C*H*$_3$), 1.45 – 1.52 (m, 12H, Dipp-*i*Pr-C*H*$_3$), 1.50 – 1.60 (m, 4H, P-Cy-C*H*), 1.62 – 2.02 (m, 8H, P-Cy-C*H*), 3.23 (bs, 1H, Mg(μ-C_2O_2)(H)(-c-C_5H_9-C*H*)), 4.02 (hept, $^{3}J_{HH}$ = 6.9 Hz, 4H, Dipp-*i*Pr-C*H*), 6.07 (s, 1H, Mg(μ-C_2O_2)(*H*)(c-C_5H_9)), 6.94 – 7.07 (m, 2H, Dipp-C*H*$_{para}$), 7.10 – 7.14 (m, 2H, Dipp-C*H*$_{meta}$), 7.15 – 7.18 (m, 2H, Dipp-C*H*$_{meta}$).

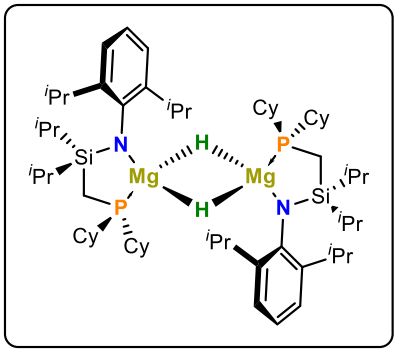
$^{13}C\{^{1}H\}$ NMR (101 MHz, C_6D_6) δ (ppm) = 0.2 (d, $^{1}J_{CP}$ = 11.2 Hz, Si-*C*H$_2$-P), 0.9 (d, $^{1}J_{CP}$ = 11.1 Hz, Si-*C*H$_2$-P), 14.3 (s, Si-*i*Pr-*C*H), 16.7 (s, *C*$_{alkyl}$), 17.0 (s, *C*$_{alkyl}$), 19.6 (s, Si-*i*Pr-*C*H$_3$), 19.7 (s, Si-*i*Pr-*C*H$_3$), 20.1 (s, Si-*i*Pr-*C*H$_3$), 20.2 (s, Si-*i*Pr-*C*H$_3$), 24.8 (s, Dipp-*i*Pr-*C*H$_3$), 24.9 (s, Dipp-*i*Pr-*C*H$_3$), 25.5 (s, Dipp-*i*Pr-*C*H$_3$), 26.2 (s, *C*$_{alkyl}$), 27.6 (s, Dipp-*i*Pr-*C*H$_3$), 27.7 (s, *C*$_{alkyl}$), 27.8 – 28.0 (m, *C*$_{alkyl}$) 28.1 (s, *C*$_{alkyl}$), 28.2 (s, *C*$_{alkyl}$), 29.8 (s, *C*$_{alkyl}$), 30.0 (s, *C*$_{alkyl}$), 31.0 (d, $^{2}J_{CP}$ = 7.7 Hz, P-Cy-*C*H), 34.4 (d, $^{1}J_{CP}$ = 5.0 Hz, P-Cy-*C*H), 34.5 (d, $^{1}J_{CP}$ = 4.4 Hz, P-Cy-*C*H), 39.7 (s, Mg(μ-C_2O_2)(H)(-c-C_5H_9-*C*H)), 119.5 (s, Dipp-*C*H$_{para}$), 119.7 (s, Dipp-*C*H$_{para}$), 123.1 – 123.6 (s, Dipp-*C*H$_{meta}$), 127.0 (s, Mg(μ-O*C*(H)C(*c*-C_5H_9)O)), 139.5 (s, Mg(μ-OC(H)*C*(*c*-C_5H_9)O)), 144.2 – 144.6 (m, Dipp-*C*$_{ortho}$), 151.5 (d, $^{3}J_{CP}$ = 2.4 Hz, Dipp-*C*), 151.6 (d, $^{3}J_{CP}$ = 2.1 Hz, Dipp-*C*).

$^{29}Si\{^{1}H\}$ NMR (79 MHz, C_6D_6) δ (ppm) = -9.9 (d, $^{2}J_{SiP}$ = 4.8 Hz, *Si*^{i}Pr$_2$), -9.6 (d, $^{2}J_{SiP}$ = 5.1 Hz, *Si*^{i}Pr$_2$).

$^{31}P\{^{1}H\}$ NMR (162 MHz, C_6D_6) δ (ppm) = -14.1 (s, Ph_2P-Mg), -13.6 (s, Ph_2P-Mg).

Analc. calcd. for $C_{68}H_{120}Mg_2N_2O_2P_2Si_2$: C, 70.54 %; H, 10.28 %; N, 2.41 %; found: 68.79 %; H, 10.18 %; N, 2.41 %.

(^{Cy}LMgH)$_2$, 9.



Method A: A 50 mL Schlenk tube was loaded with 150 mg **6-Cy** (123 µmol, 1.00 equiv.) and dissolved in 1 mL C_6D_6. To this solution, 32 µL $PhSiH_3$ (258 µmol, 2.10 equiv.) was added, and the reaction was stirred for 2 days at 60 °C. The reaction was monitored in one day intervals via NMR spectroscopy and was stopped until no further formation of **9** was observed (see Figs. S81 and S82). On cooling and storage at ambient temperature for 12h, colourless crystals of **9**, suitable for single crystal X-Ray diffraction analysis, were obtained (85 mg,161 µmol, 65 %).

Method B: To a solution of 5.00 g **1-Cy** (8.59 mmol, 1.00 equiv) in 40 mL toluene was added 2.12 mL $PhSiH_3$ (17.17 mmol, 2.00 equiv.). The solution was heated to 60 °C and the reaction was stirred at this temperature for two days. The colourless suspension was subsequently evaporated to dryness *in vacuo*, and the obtained residue was washed three times with pentane (3 x 10 mL). Removal of all volatiles *in vacuo* yielded 3.45 g of **9** (6.65 mmol, 76.4 %) as a colourless solid.

N.B. Colourless crystals of **9**, suitable for single crystal X-Ray diffraction analysis, were obtained from a concentrated pentene solution at room temperature.

^{1}H NMR (400 MHz, C_6D_6) δ (ppm) = 0.77 (d, $^2J_{HP}$ = 10.9 Hz, 4H, Si-C*H*$_2$-P), 0.97 (d, $^3J_{HH}$ = 6.4 Hz, 12H, Si-^{i}Pr-C*H*$_3$), 1.10 – 1.33 (m, 36H, Si-^{i}Pr-C*H*$_3$, Si-^{i}Pr-C*H*, P-Cy-C*H*), 1.39 (d, $^3J_{HH}$ = 6.8 Hz, 12H, Dipp-^{i}Pr-C*H*$_3$), 1.43 (d, $^3J_{HH}$ = 7.0 Hz, 12H, Dipp-^{i}Pr-C*H*$_3$), 1.56 – 1.68 (m, 8H, P-Cy-C*H*), 1.71 – 1.84 (m, 16H, P-Cy-C*H*), 3.89 (p, $^3J_{HH}$ = 7.0 Hz, 4H, Dipp-^{i}Pr-C*H*), 4.01 (t, $^2J_{HP}$ = 11.2 Hz, 2H, Mg*H*), 6.96 (t, $^3J_{HH}$ = 7.5 Hz, 2H, Dipp-C*H*$_{para}$), 7.13 (d, $^3J_{HH}$ = 7.6 Hz, 4H, Dipp-C*H*$_{meta}$).

^{1}H NMR (400 MHz, THF-d_8) δ (ppm) = 0.79 (s, 4H, Si-C*H*$_2$-P), 0.82 (d, $^3J_{HH}$ = 6.8 Hz, 12H, Si-^{i}Pr-C*H*$_3$), 0.99 (p, $^3J_{HH}$ = 6.5 Hz, 4H, Si-^{i}Pr-C*H*), 1.05 (d, $^3J_{HH}$ = 6.8 Hz, 12H, Si-^{i}Pr-C*H*$_3$), 1.14 (d, $^3J_{HH}$ = 7.4 Hz, 24H, Dipp-^{i}Pr-C*H*$_3$), 1.22 – 1.47 (m, 20H, P-Cy-C*H*), 1.73 (bs, 8H, P-Cy-C*H*), 1.78 – 1.88 (m, 8H, P-Cy-C*H*), 1.90 – 1.98 (m, 8H, P-Cy-C*H*), 3.75 (p, $^3J_{HH}$ = 6.8 Hz, 4H, Dipp-^{i}Pr-C*H*), 3.87 (bs, 2H, Mg*H*), 6.63 (t, $^3J_{HH}$ = 7.5 Hz, 2H, Dipp-C*H*$_{para}$), 6.84 (d, $^3J_{HH}$ = 7.5 Hz, 4H, Dipp-C*H*$_{meta}$).

^{13}C{^{1}H} NMR (101 MHz, THF-d_8) δ (ppm) = 1.2 (d, $^1J_{CP}$ = 14.3 Hz, Si-*C*H$_2$-P), 16.8 (d, $^3J_{CP}$ = 2.2 Hz, Si-^{i}Pr-*C*H), 19.9 (s, Si-^{i}Pr-*C*H$_3$), 20.3 (s, Si-^{i}Pr-*C*H$_3$), 25.0 (s, Dipp-^{i}Pr-*C*H$_3$), 27.4 (s, Dipp-^{i}Pr-*C*H), 27.5 (s, Dipp-^{i}Pr-C*H*$_3$), 27.9 (s, P-Cy-*C*H), 28.7 (dd, $^1J_{CP}$ = 10.2, 12.2 Hz, P-Cy-*C*H), 30.6 (d, $^3J_{CP}$ = 3.6 Hz, P-Cy-*C*H), 31.3 (d, $^2J_{CP}$ = 5.8 Hz, P-Cy-*C*H), 36.0

(s, P-Cy-*C*H), 119.9 (s, Dipp-*C*H$_{para}$), 123.7 (s, Dipp-*C*H$_{meta}$), 145.3 (s, Dipp-*C*$_{ortho}$), 152.5 (s, Dipp-*C*).

^{29}Si{^{1}H} NMR (79 MHz, THF-d$_8$) δ (ppm) = -8.5 (d, $^{2}J_{SiP}$ = 7.0 Hz, *Si*^{i}Pr$_2$).

^{31}P{^{1}H} NMR (162 MHz, C$_6$D$_6$) δ (ppm) = -12.5 (s, Cy$_2$*P*-Mg).

^{31}P{^{1}H} NMR (162 MHz, THF-d$_8$) δ (ppm) = -17.4 (s, Cy$_2$*P*-Mg).

Analc. calcd. for $C_{62}H_{112}Mg_2N_2P_2Si_2$: C, 70.77 %; H, 10.73 %; N, 2.66 %; found: 70.97 %; H, 10.87 %; N, 3.00 %.

3. NMR spectra

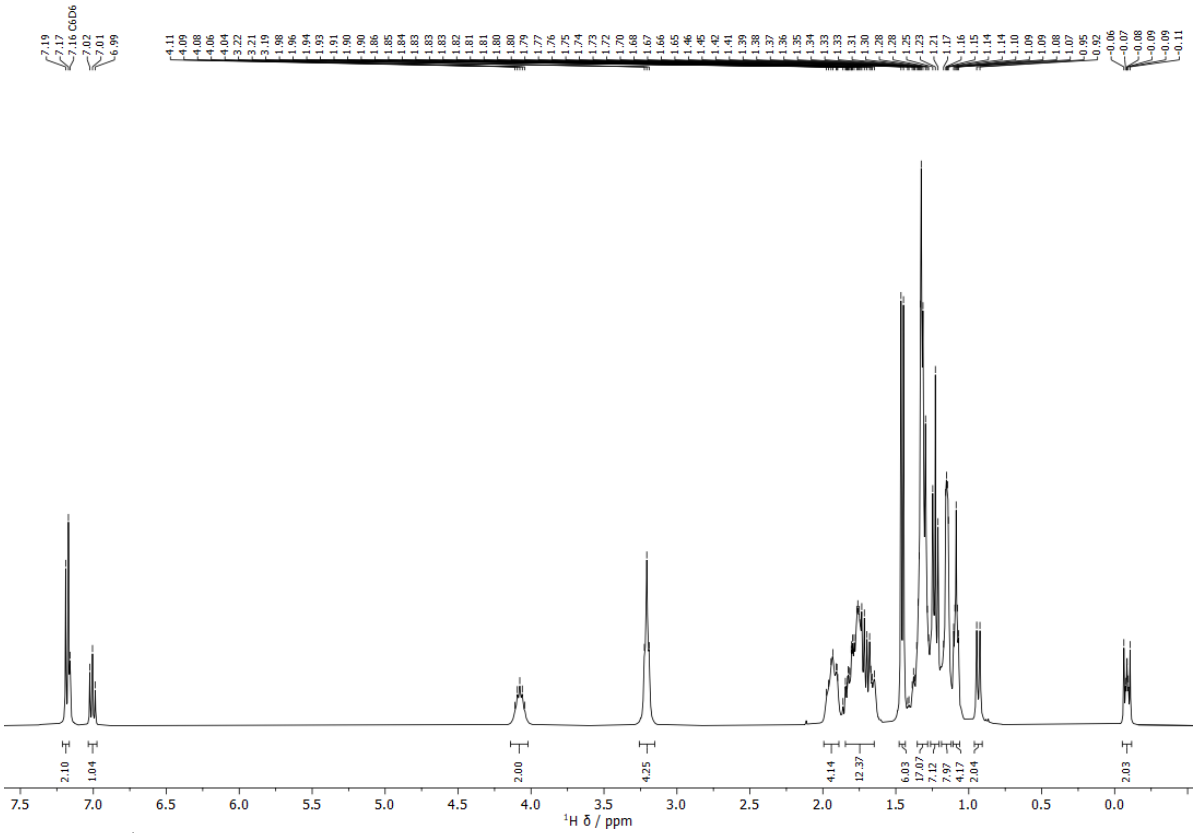


Figure S1. ^{1}H NMR spectrum (400.13 MHz, 295.1 K, C_6D_6) of **1-Cy**.

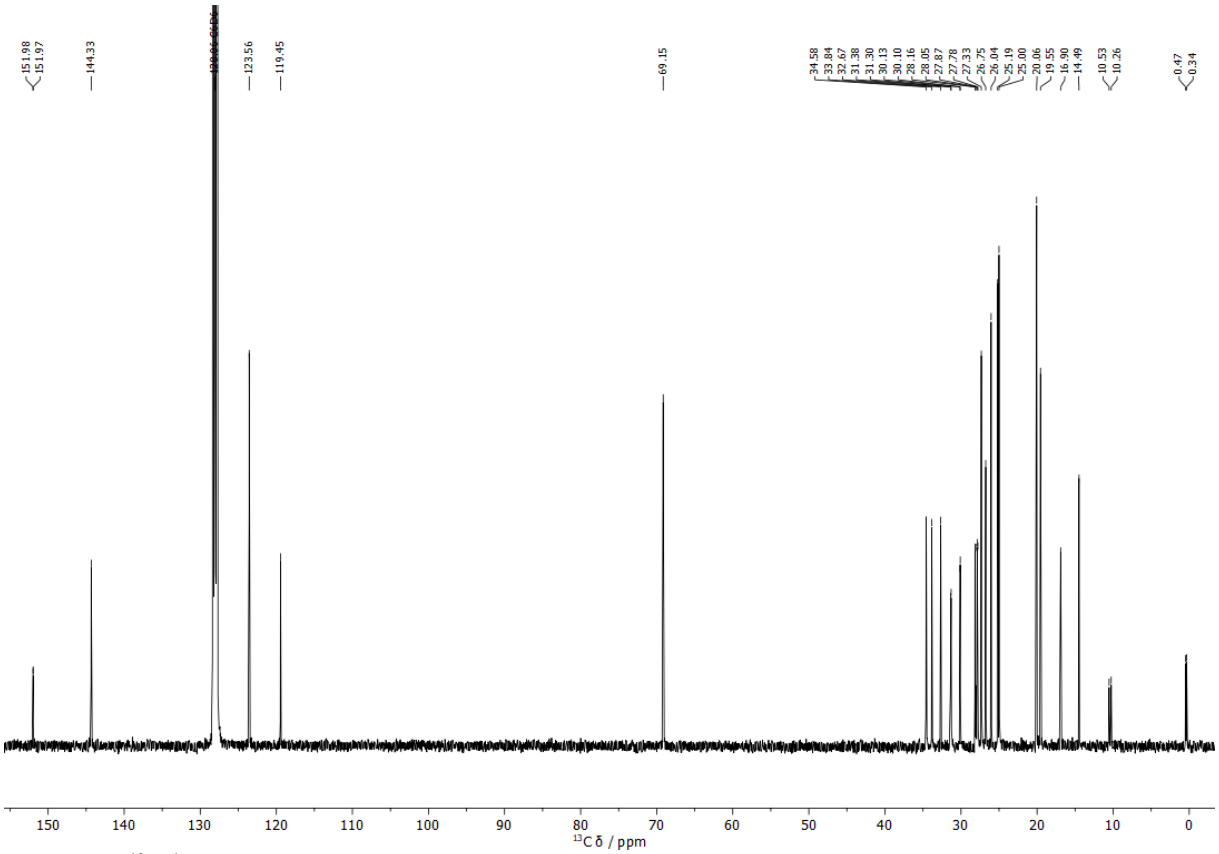


Figure S2. $^{13}C\{^{1}H\}$ NMR spectrum (100.62 MHz, 296.2 K, C_6D_6) of **1-Cy**.

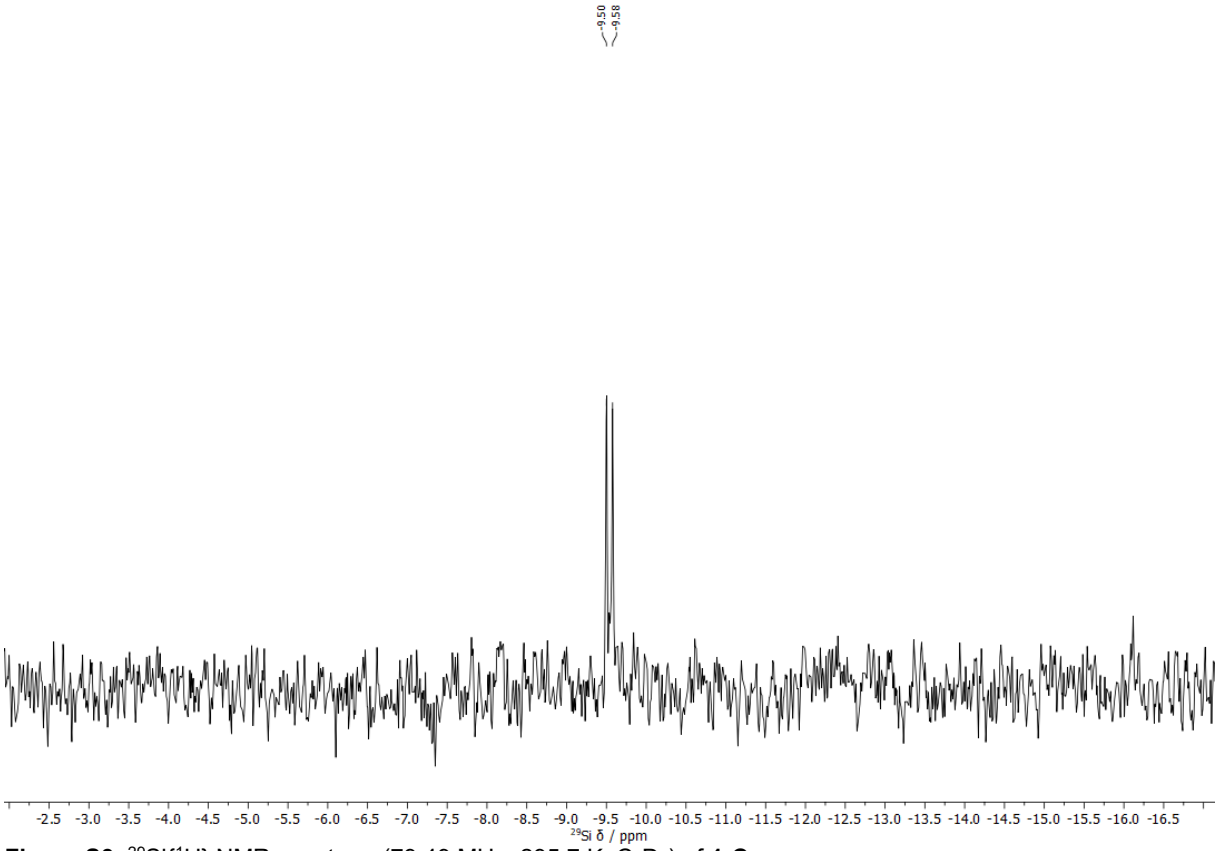


Figure S3. $^{29}Si\{^{1}H\}$ NMR spectrum (79.49 MHz, 295.7 K, C_6D_6) of **1-Cy**.

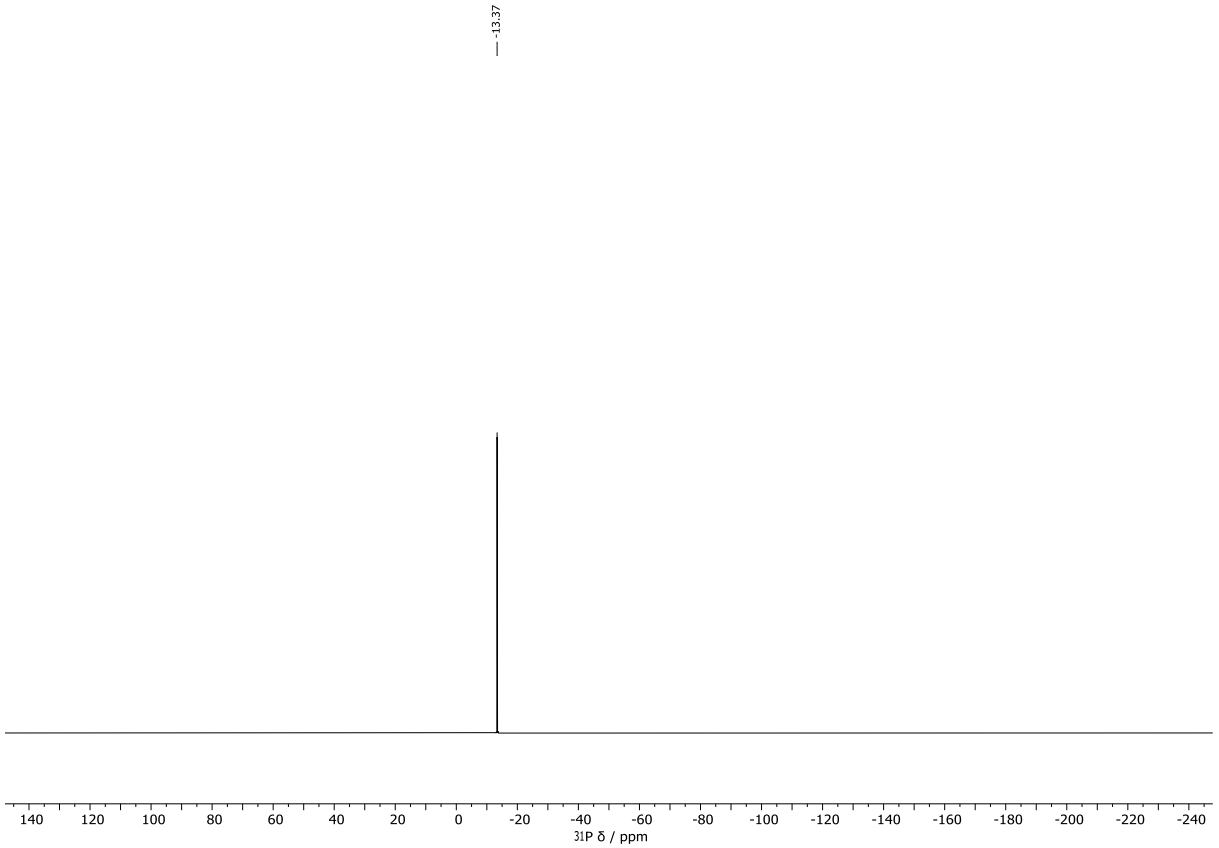


Figure S4. $^{31}P\{^{1}H\}$ NMR spectrum (161.97 MHz, 296.1 K, C_6D_6) of **1-Cy**.

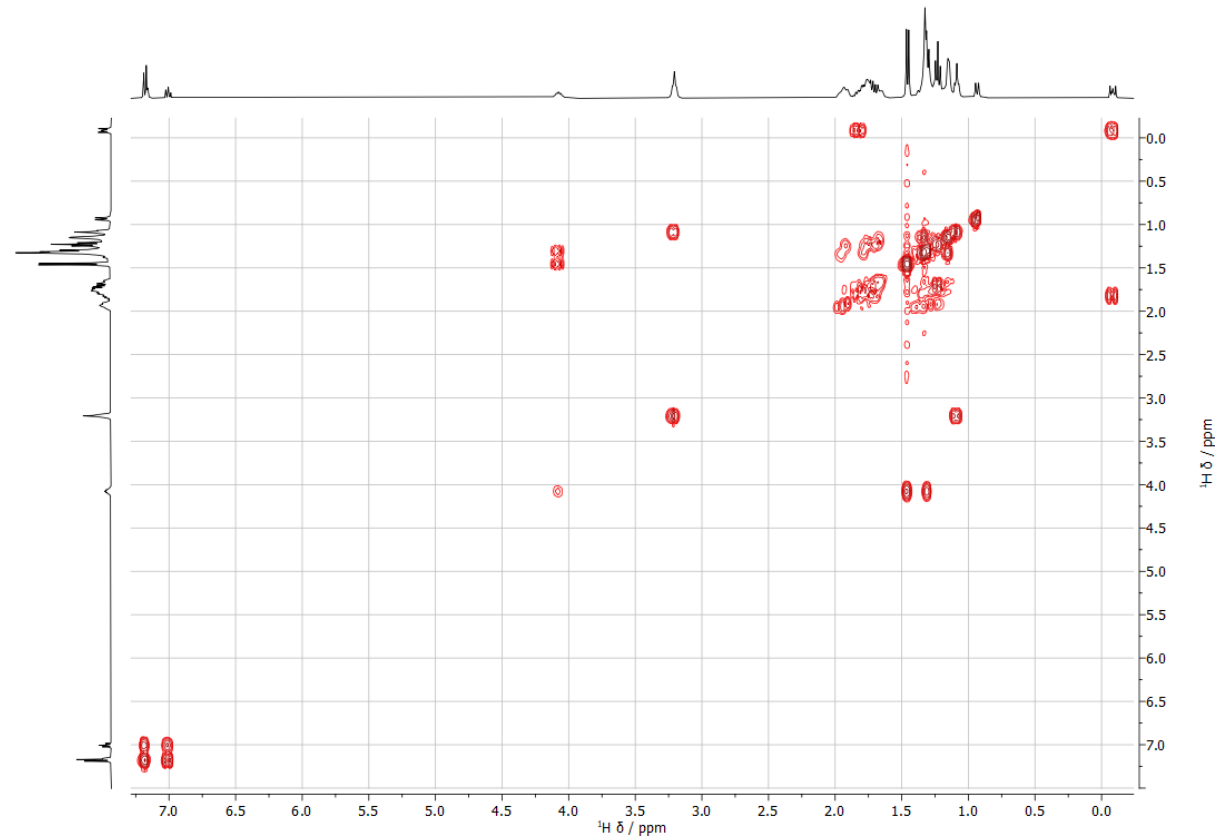


Figure S5. COSY NMR spectrum (400.13 / 400.13 MHz, 295.6 K, C_6D_6) of **1-Cy**.

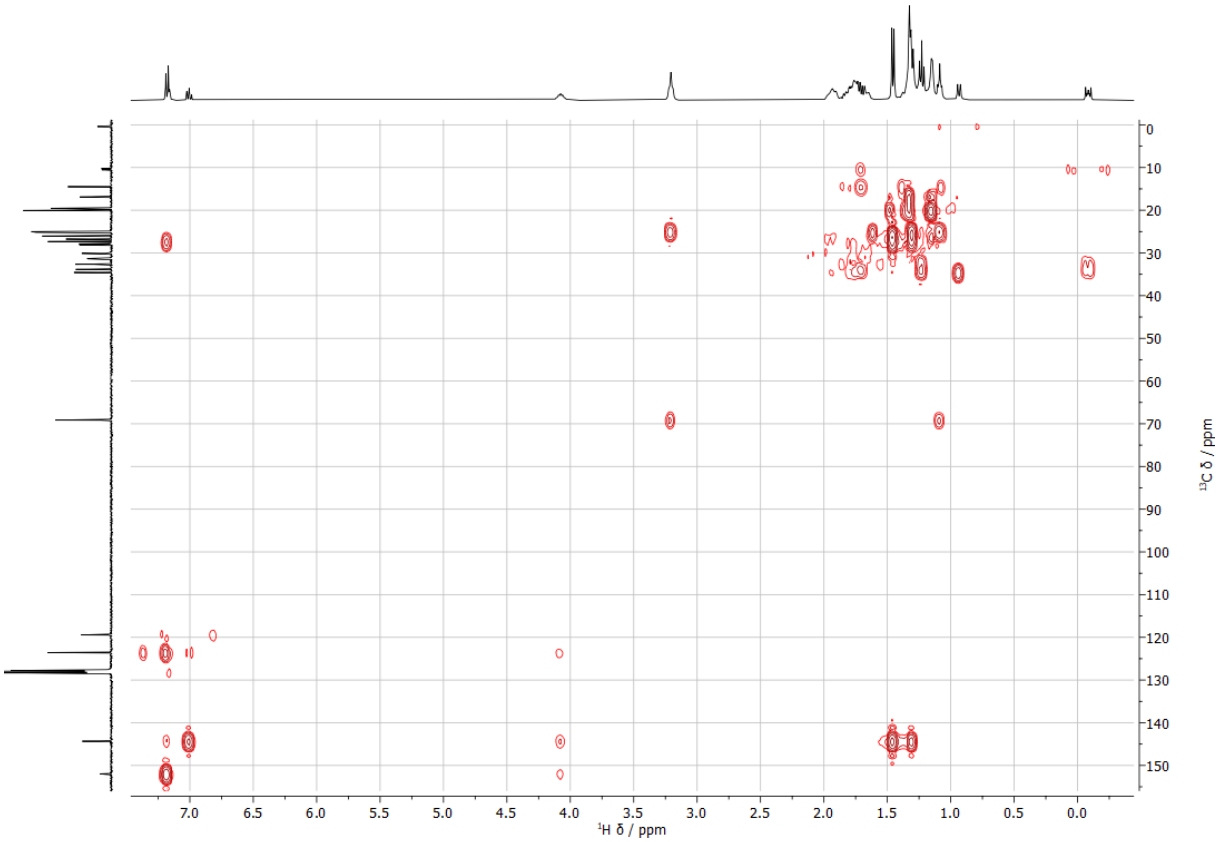


Figure S6. HMBC NMR spectrum (400.13 / 100.62 MHz, 295.5 K, C_6D_6) of **1-Cy**.

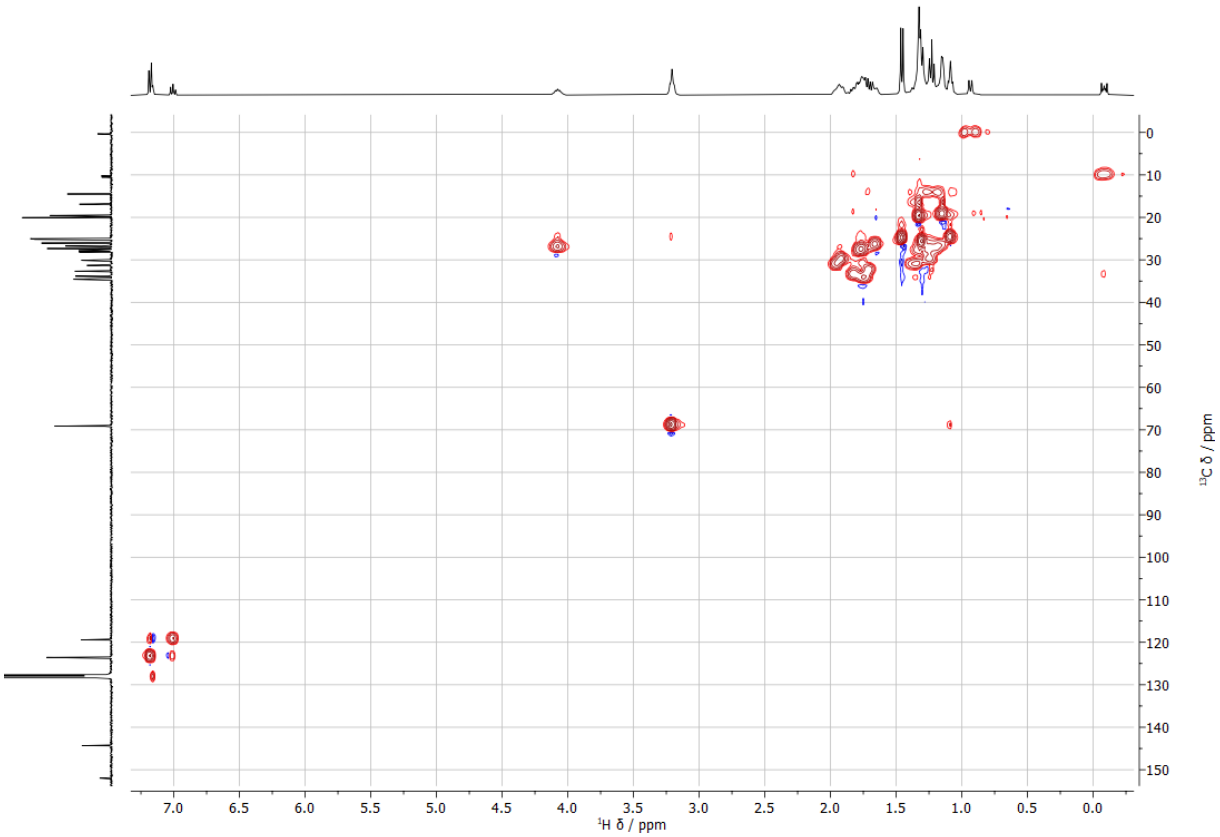


Figure S7. HSQC NMR spectrum (400.13 / 100.62 MHz, 295.5 K, C_6D_6) of **1-Cy**.

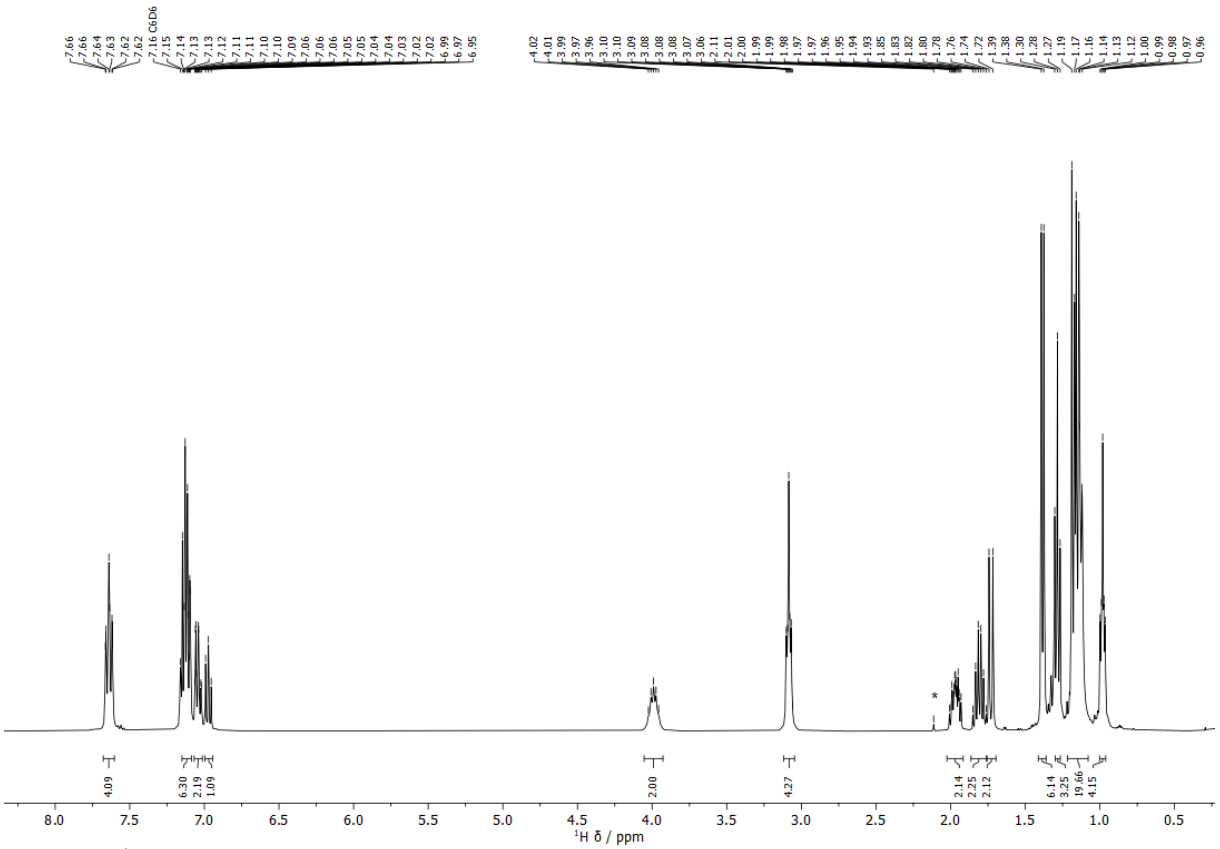


Figure S8. ^{1}H NMR spectrum (400.13 MHz, 295.1 K, C_6D_6) of **1-Ph**; * indicates small amounts of toluene.

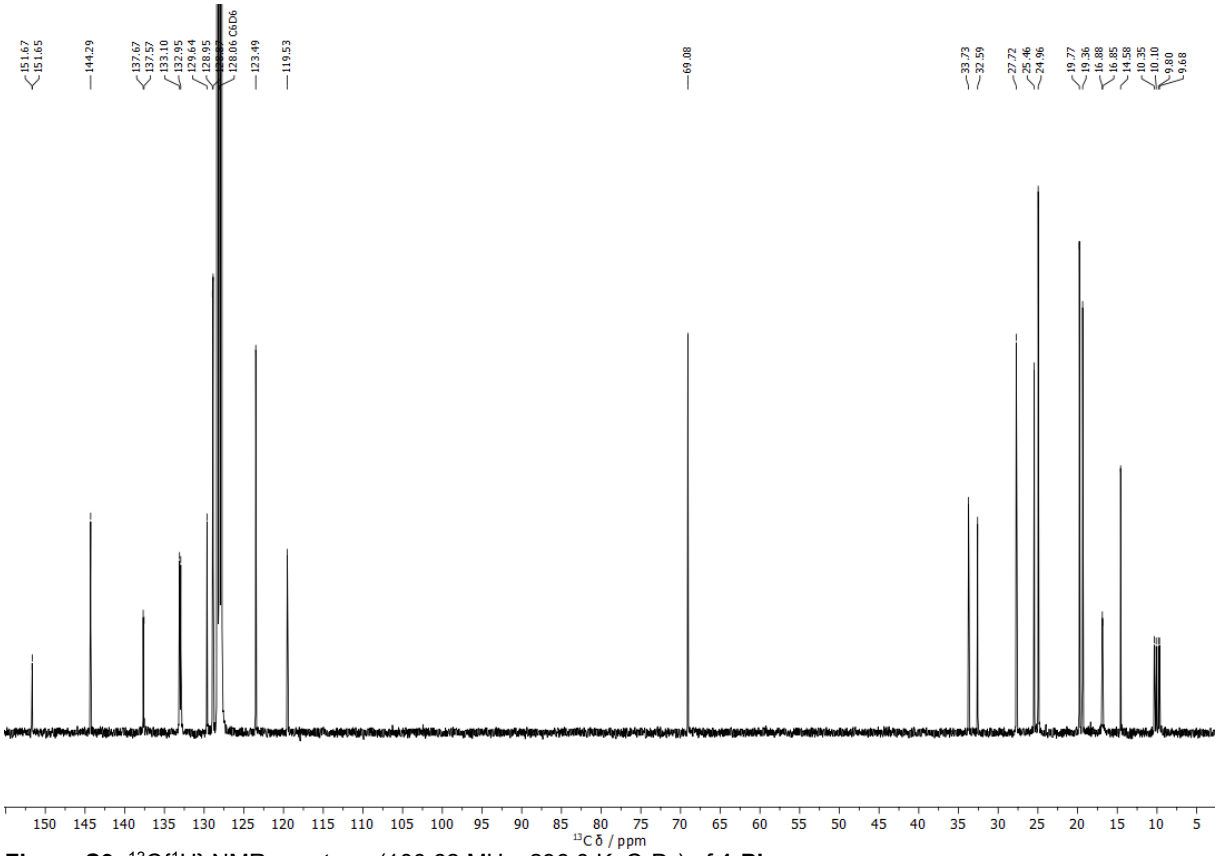


Figure S9. $^{13}C\{^{1}H\}$ NMR spectrum (100.62 MHz, 296.0 K, C_6D_6) of **1-Ph**.

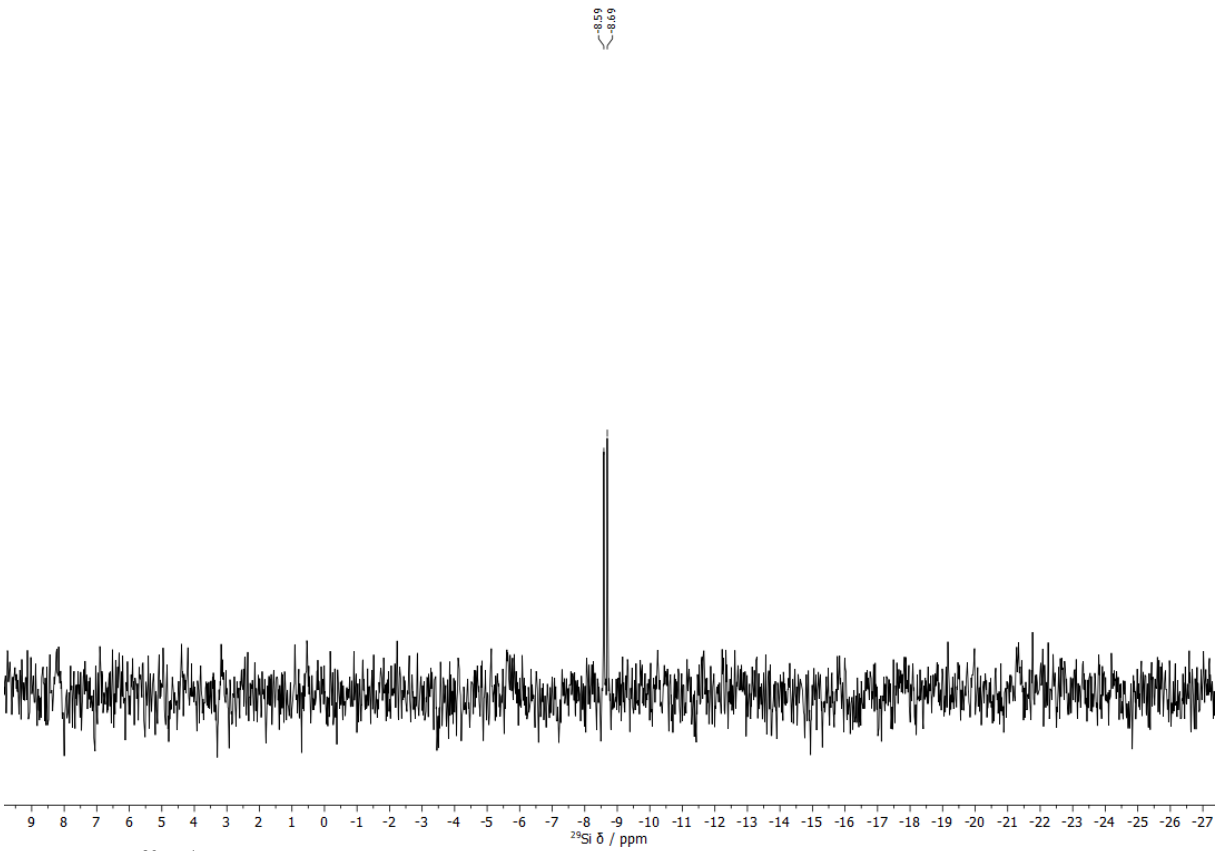


Figure S10. $^{29}Si\{^{1}H\}$ NMR spectrum (79.49 MHz, 295.5 K, C_6D_6) of **1-Ph**.

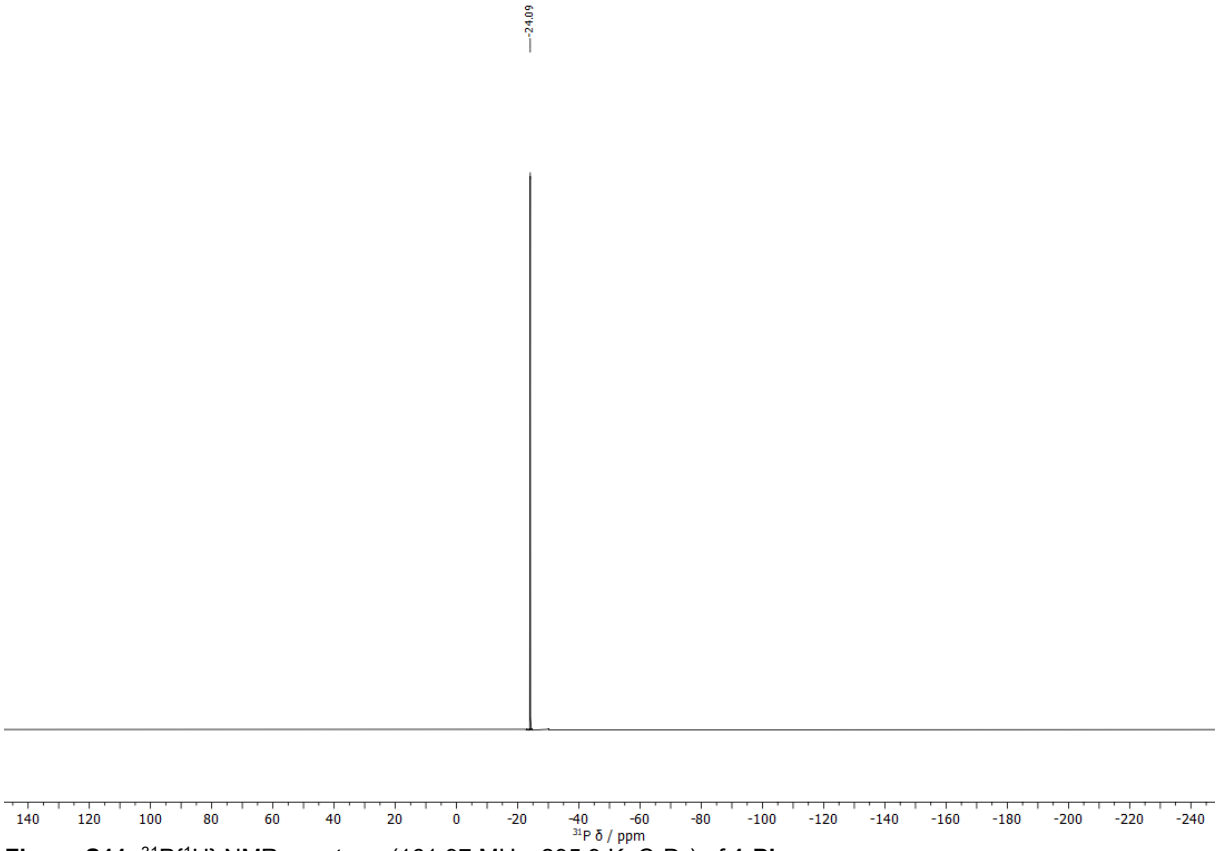


Figure S11. $^{31}P\{^{1}H\}$ NMR spectrum (161.97 MHz, 295.9 K, C_6D_6) of **1-Ph**.

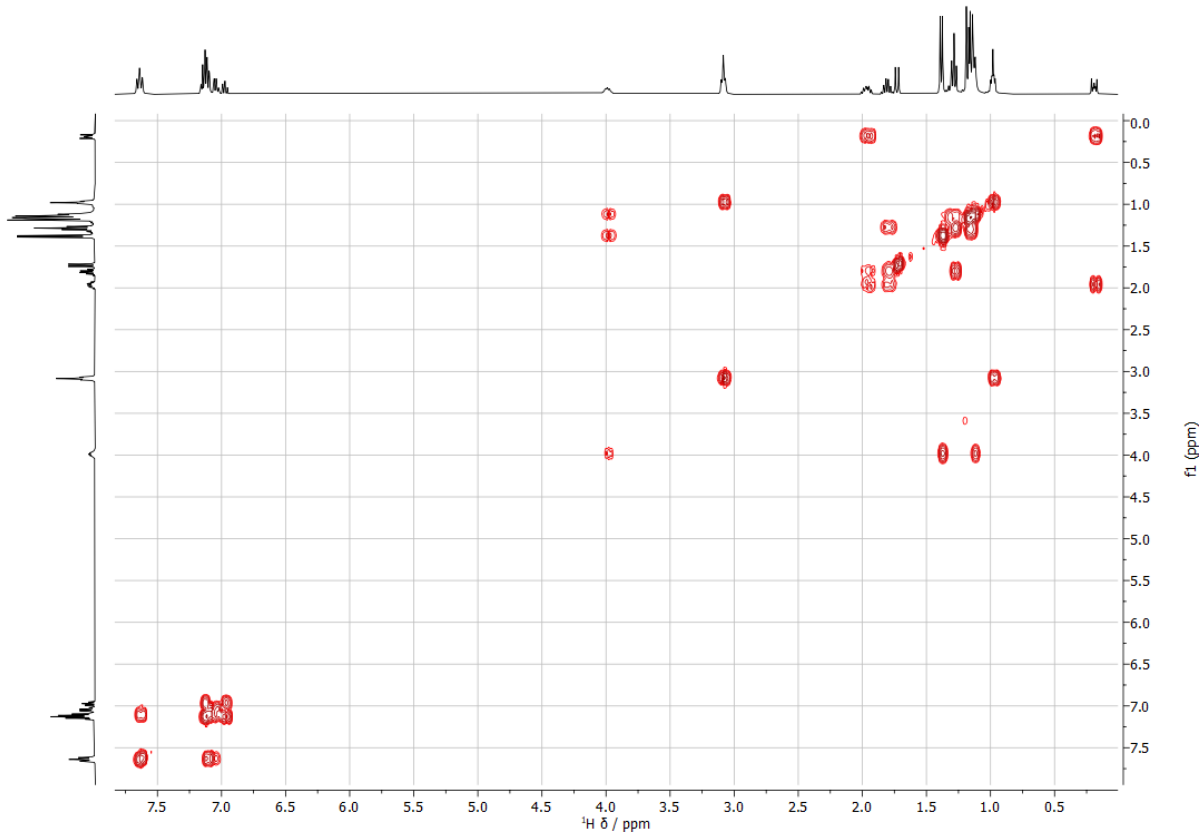


Figure S12. COSY NMR spectrum (400.13 / 400.13 MHz, 295.4 K, C_6D_6) of **1-Ph**.

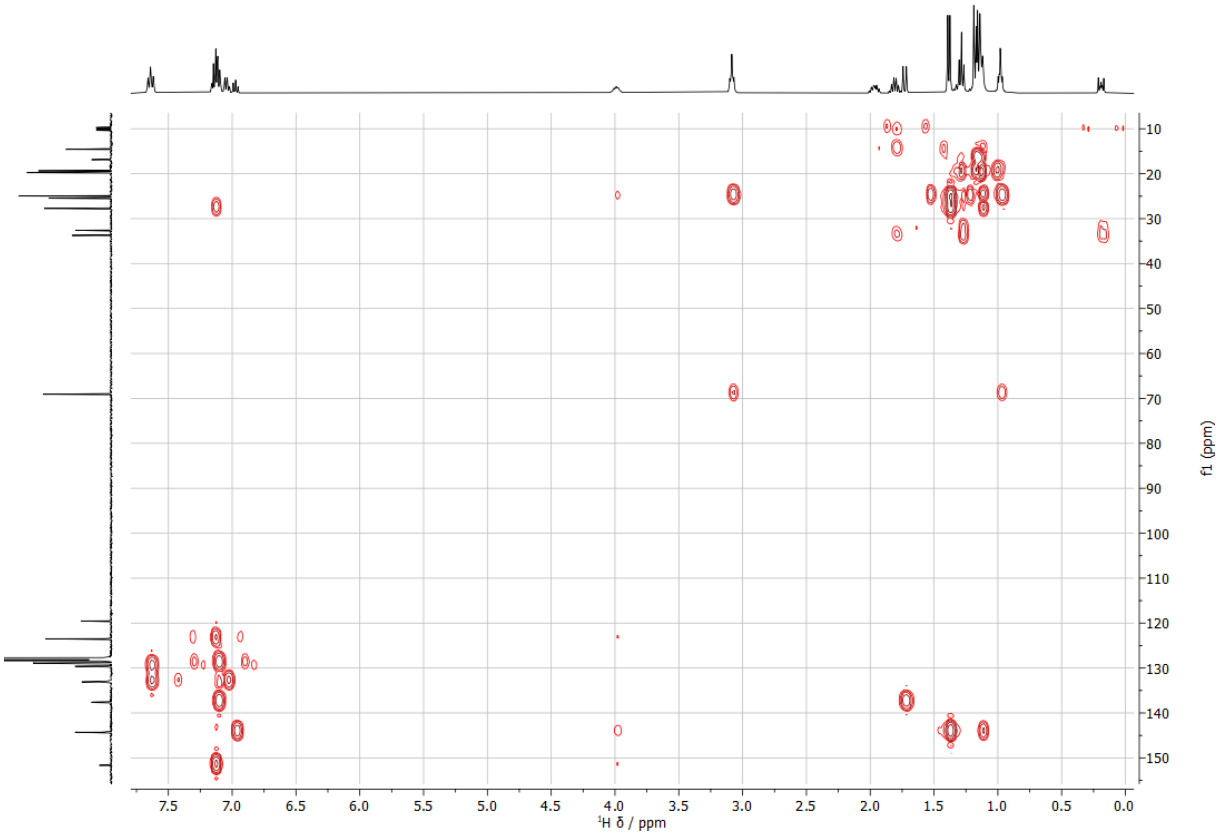


Figure S13. HMBC NMR spectrum (400.13 / 100.62 MHz, 295.3 K, C_6D_6) of **1-Ph**.

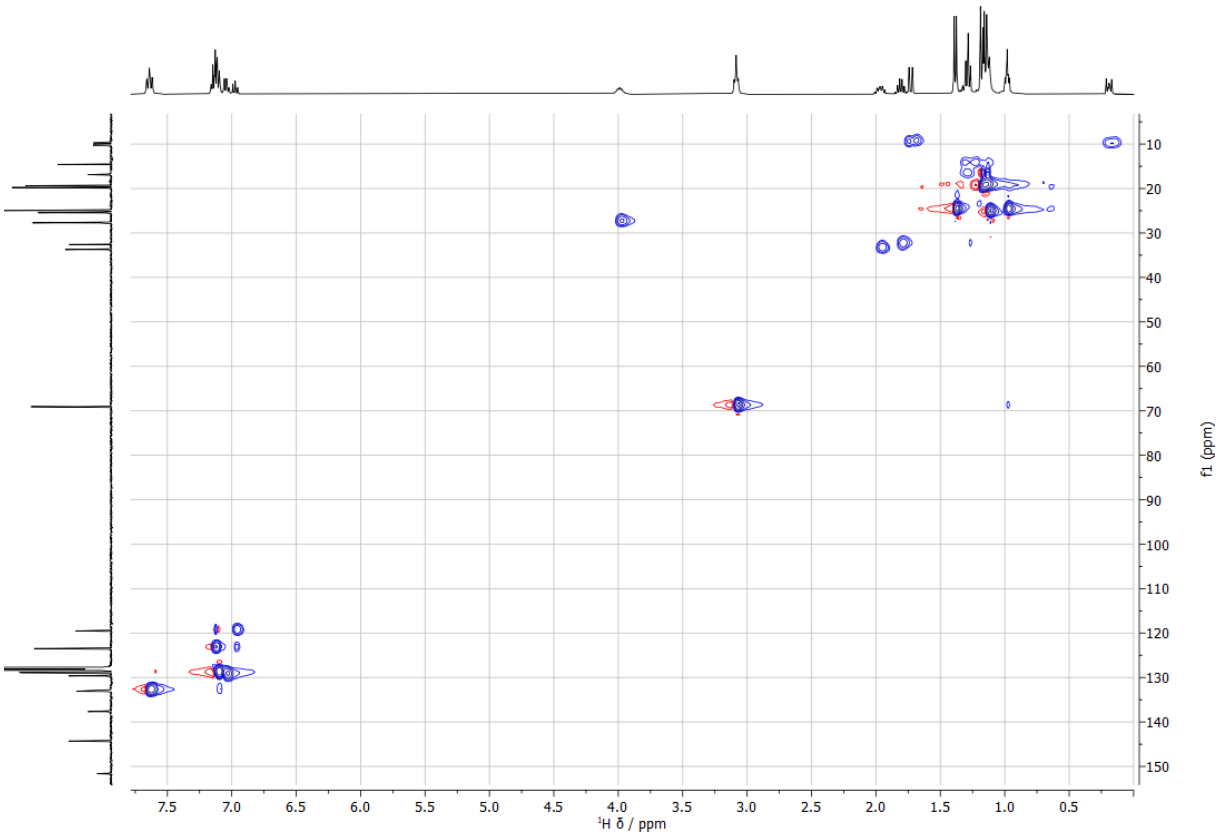


Figure S14. HSQC NMR spectrum (400.13 / 100.62 MHz, 295.4 K, C_6D_6) of **1-Ph**.

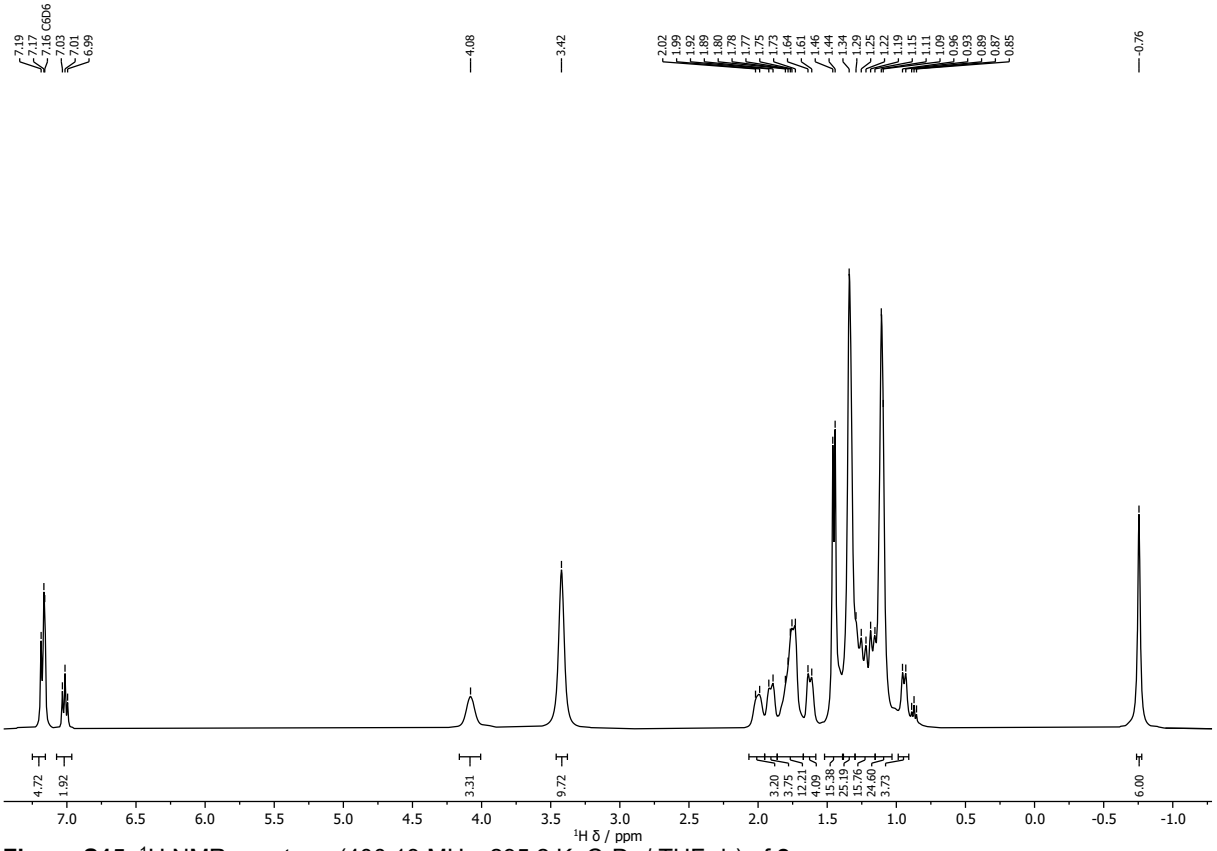


Figure S15. ^{1}H NMR spectrum (400.13 MHz, 295.2 K, C_6D_6 / THF-d_8) of **2**.

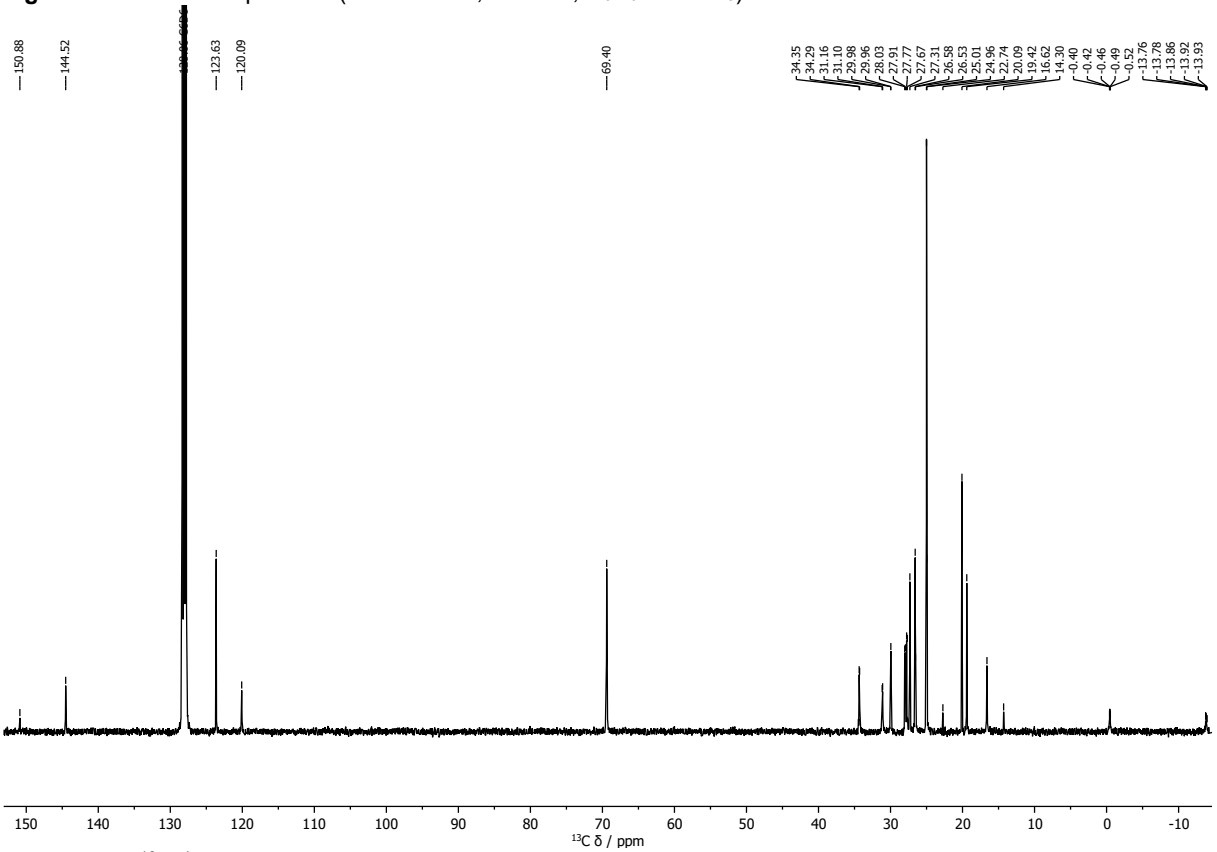


Figure S16. $^{13}C\{^{1}H\}$ NMR spectrum (100.62 MHz, 295.9 K, C_6D_6 / THF-d_8) of **2**.

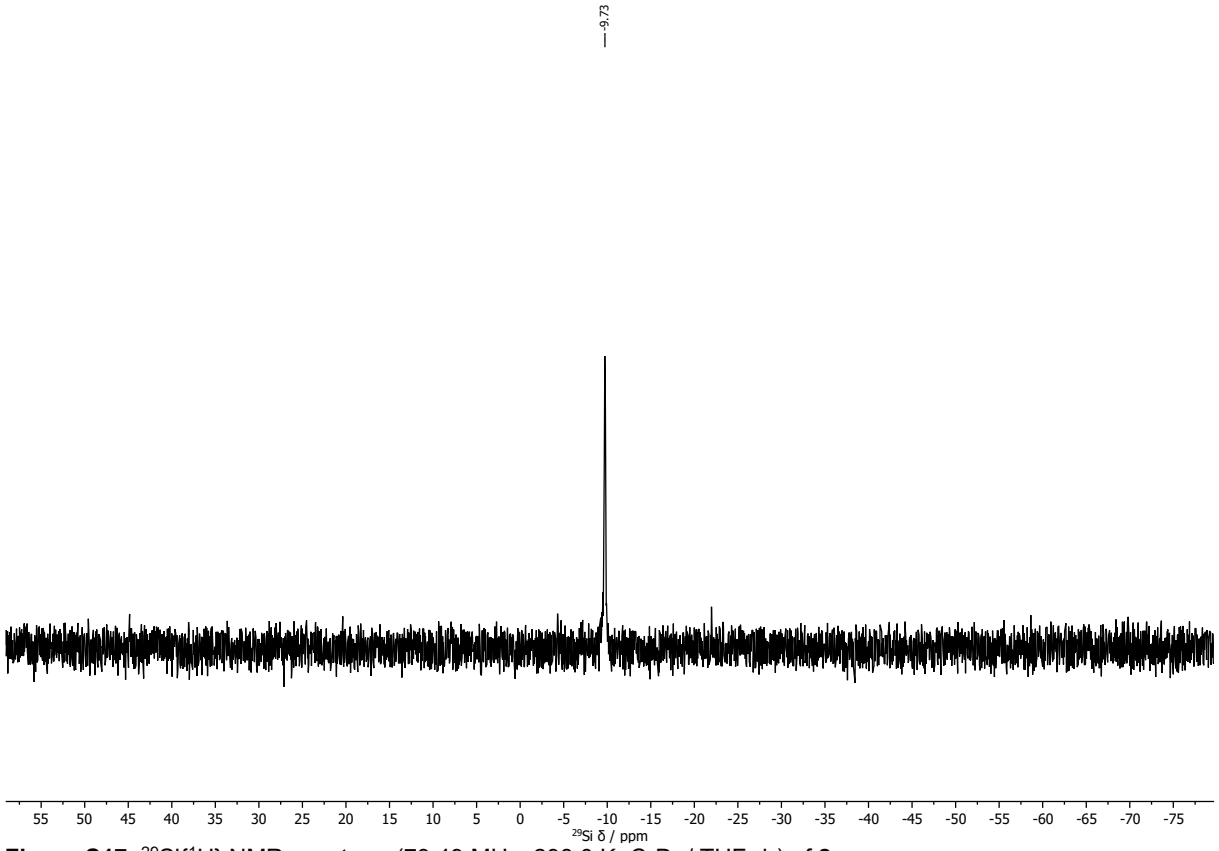


Figure S17. $^{29}Si\{^{1}H\}$ NMR spectrum (79.49 MHz, 298.0 K, C_6D_6 / THF-d_8) of **2**.

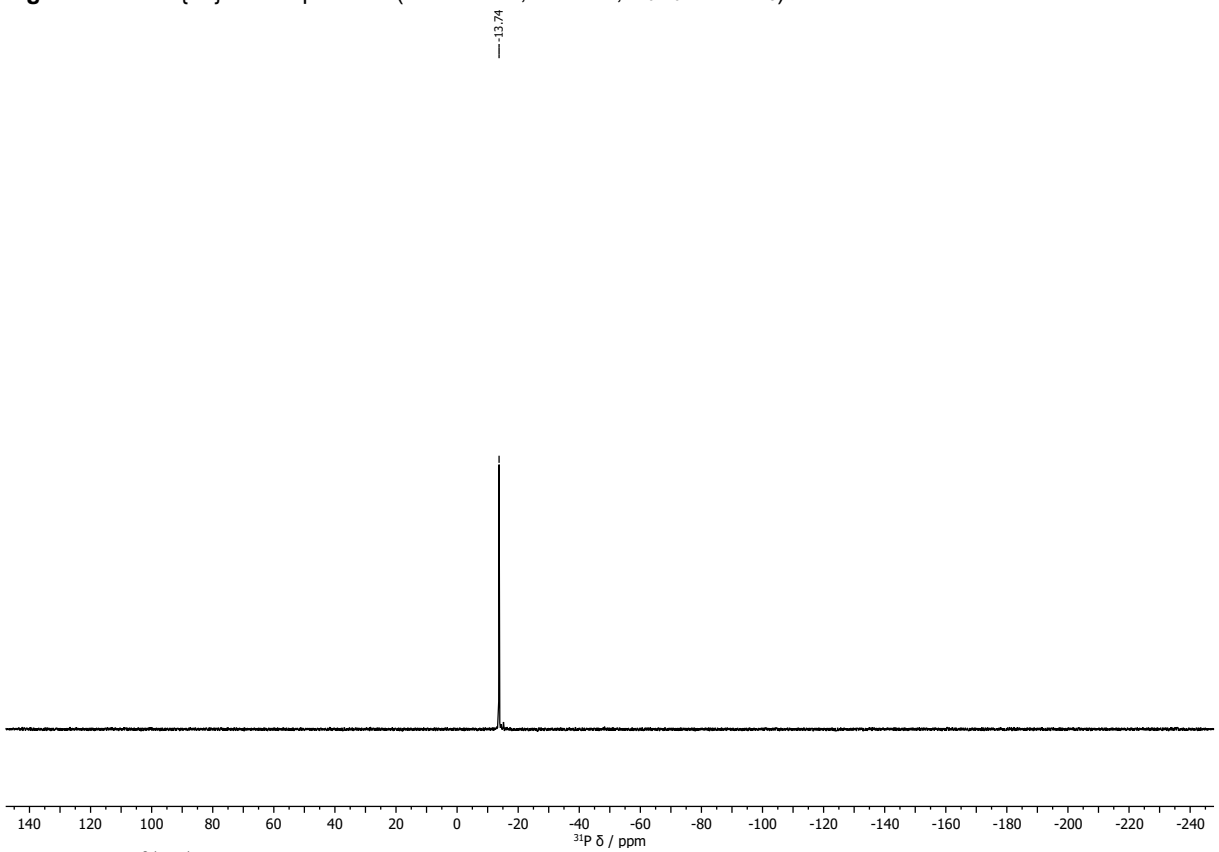


Figure S18. $^{31}P\{^{1}H\}$ NMR spectrum (161.97 MHz, 295.8 K, C_6D_6 / THF-d_8) of **2**.

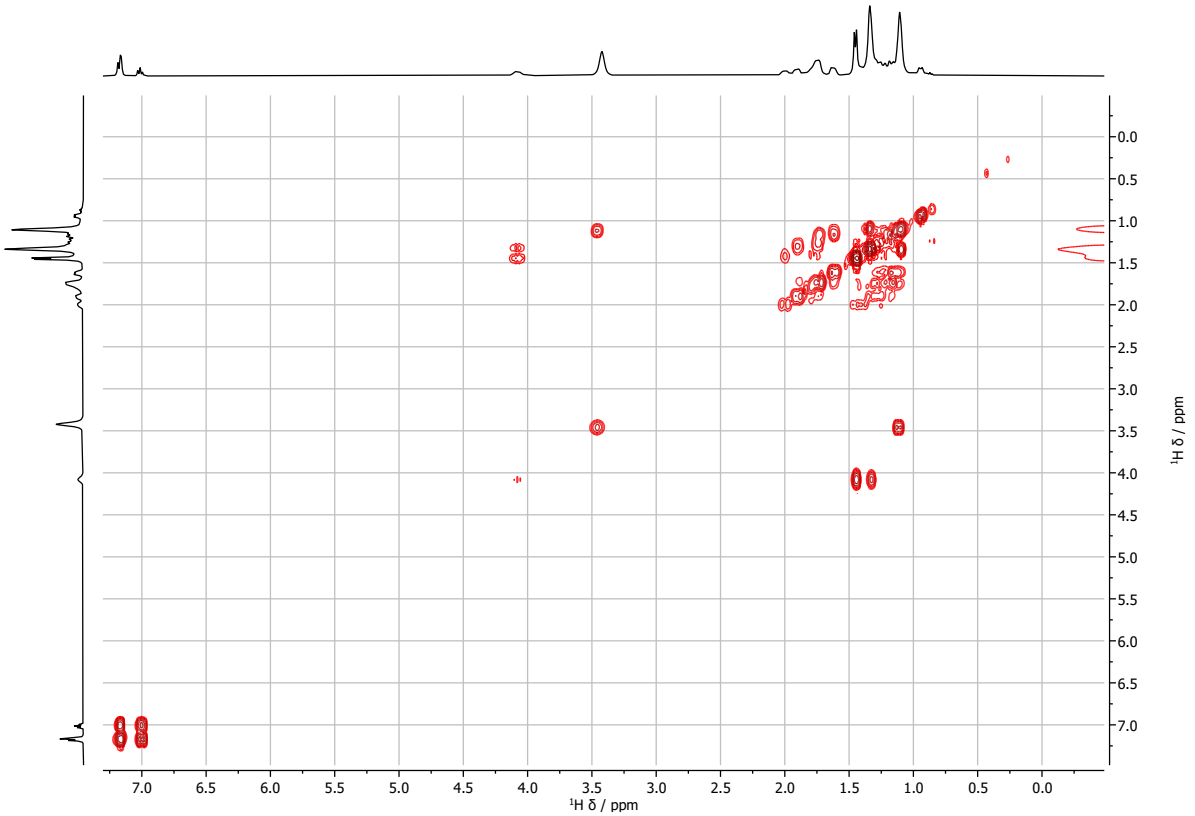


Figure S19. COSY NMR spectrum (400.13 / 400.13 MHz, 295.3 K, C_6D_6 / THF-d_8) of **2**.

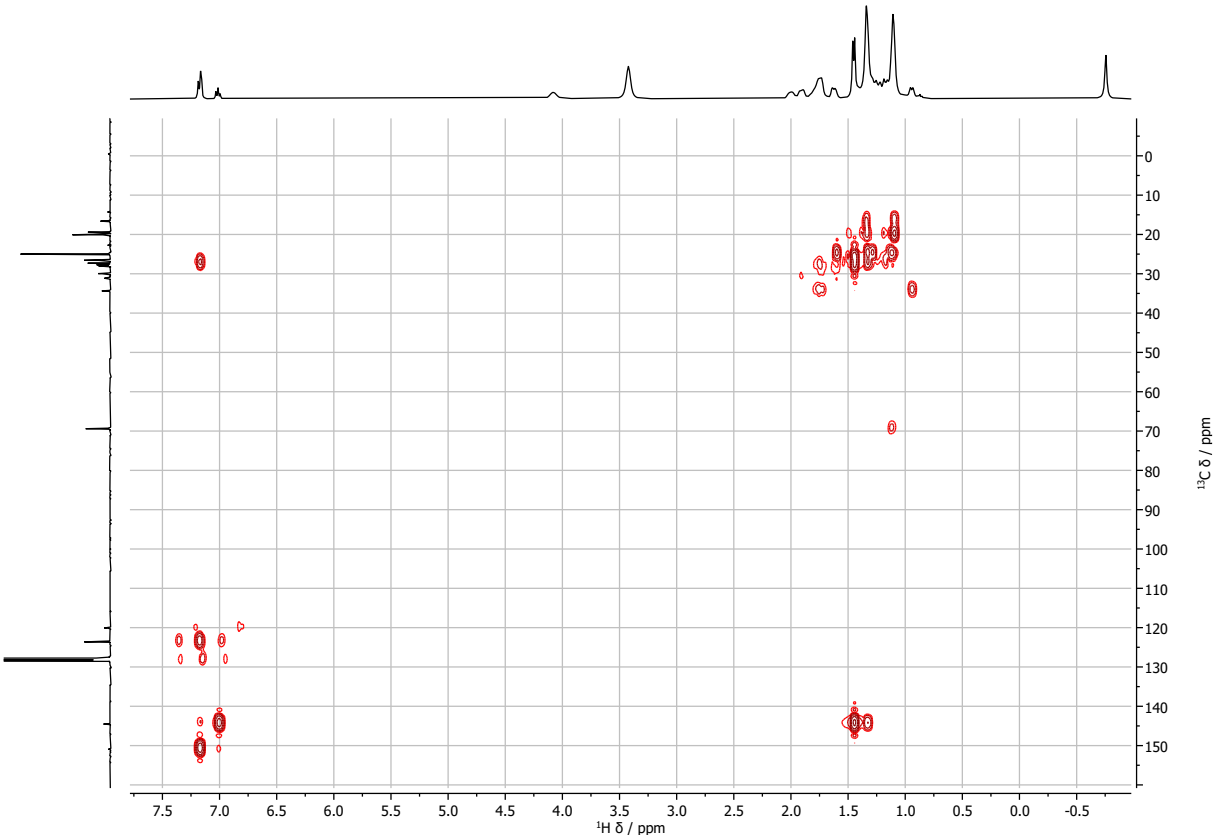


Figure S20. HMBC NMR spectrum (400.13 / 100.62 MHz, 295.2 K, C_6D_6 / THF-d_8) of **2**.

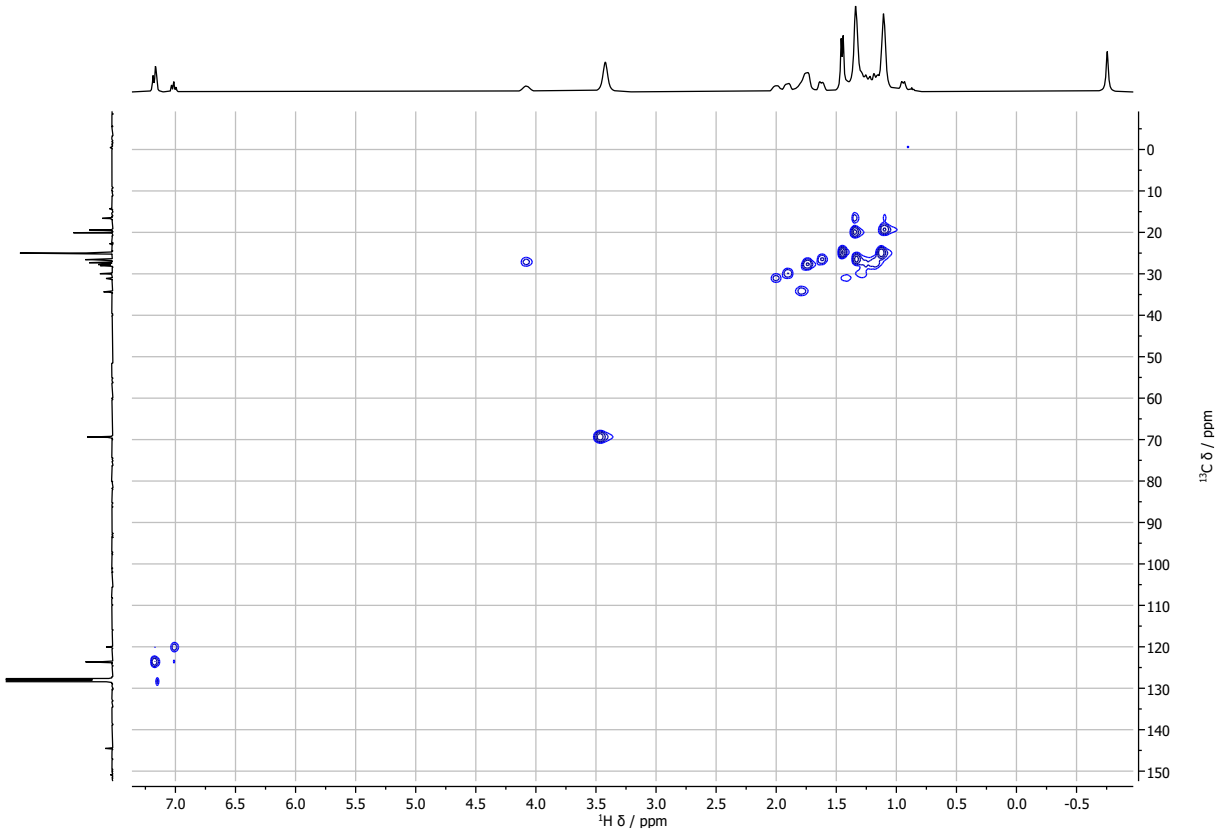


Figure S21. HSQC NMR spectrum (400.13 / 100.62 MHz, 295.2 K, C_6D_6 / THF-d_8) of **2**.

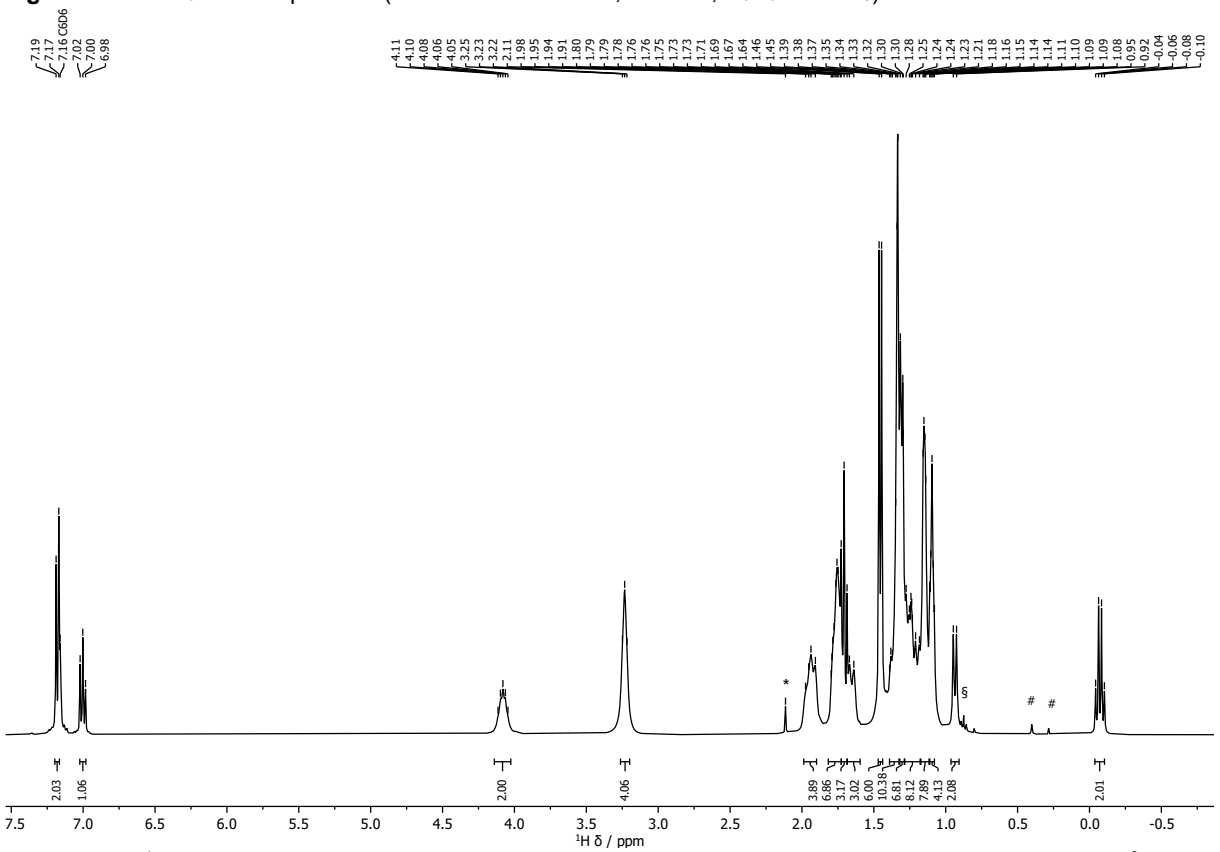


Figure S22. ^{1}H NMR spectrum (400.13 MHz, 295.4 K, C_6D_6) of **3**; * indicates small amounts of toluene, § indicates small amounts of pentane and # marks an unknown impurity.

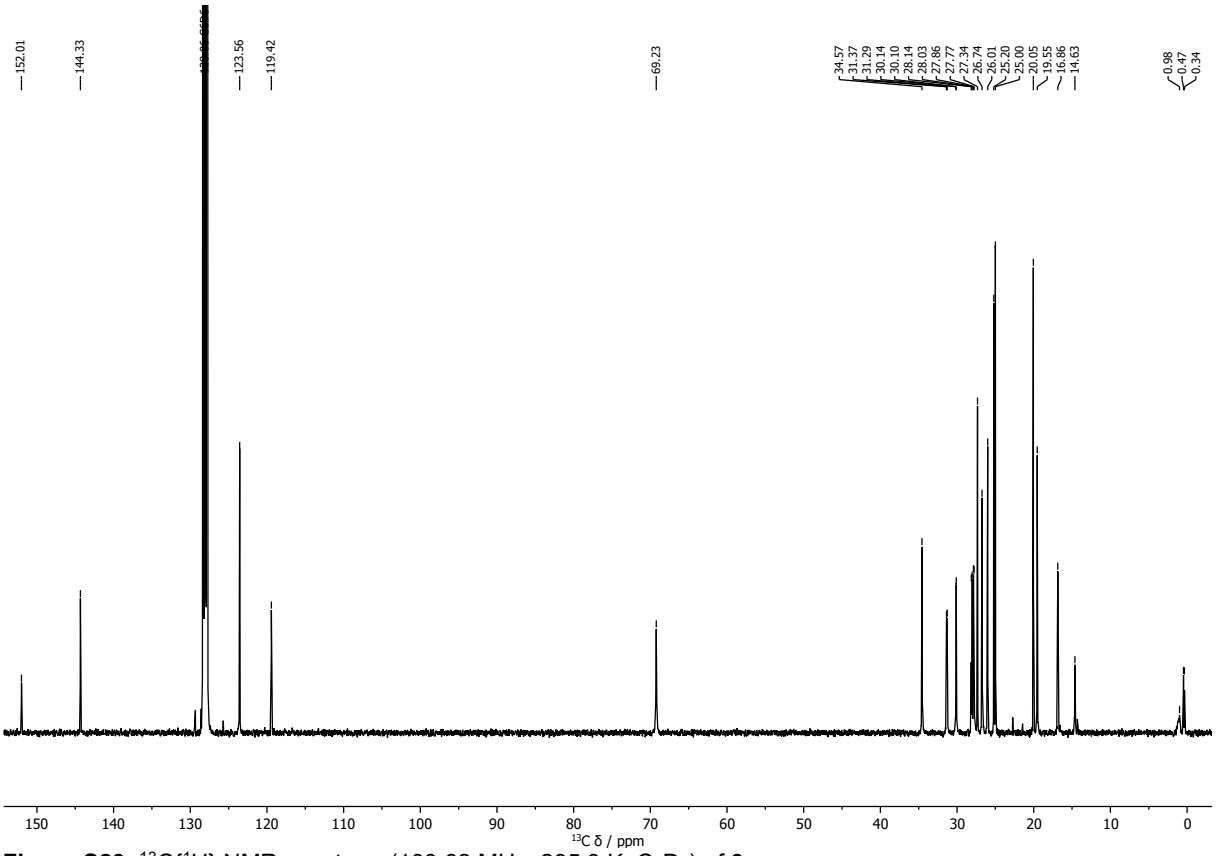


Figure S23. $^{13}C\{^{1}H\}$ NMR spectrum (100.62 MHz, 295.9 K, C_6D_6) of **3**.

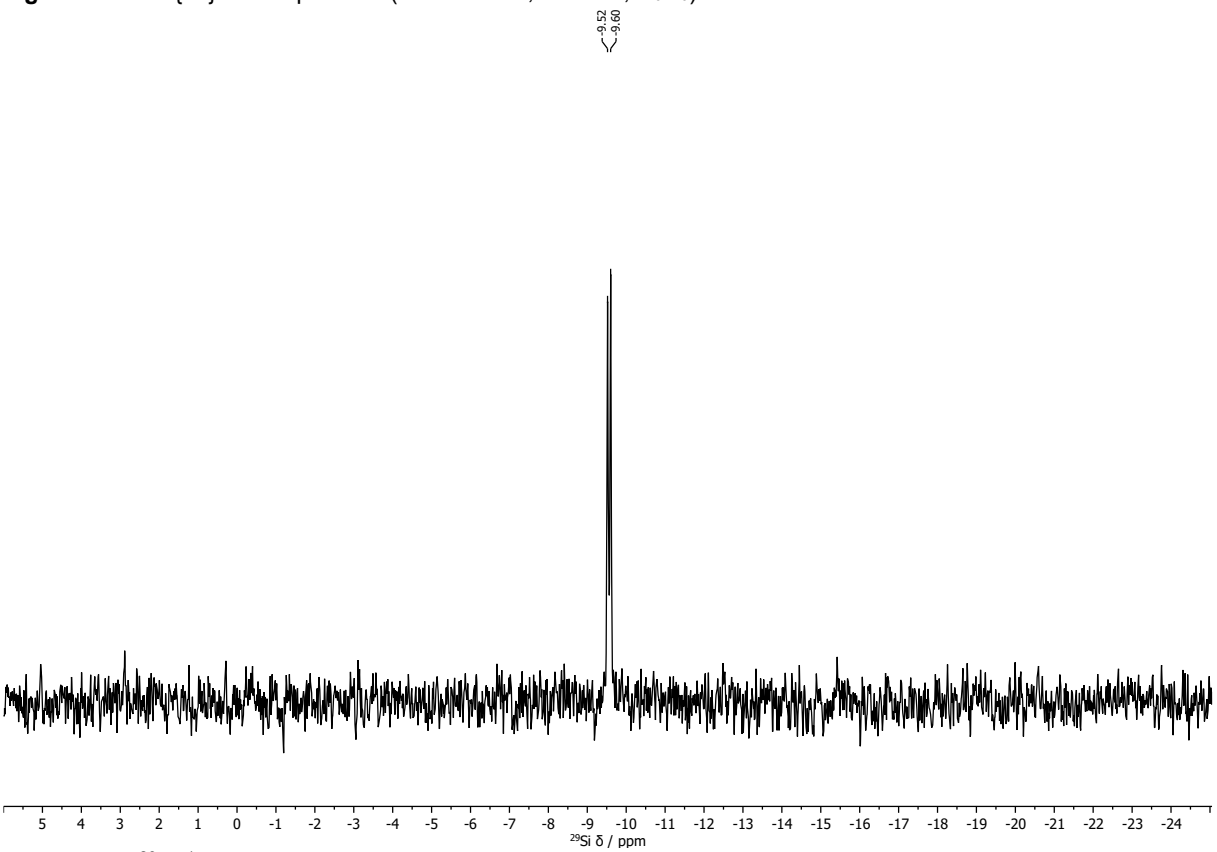


Figure S24. $^{29}Si\{^{1}H\}$ NMR spectrum (79.49 MHz, 295.3 K, C_6D_6) of **3**.

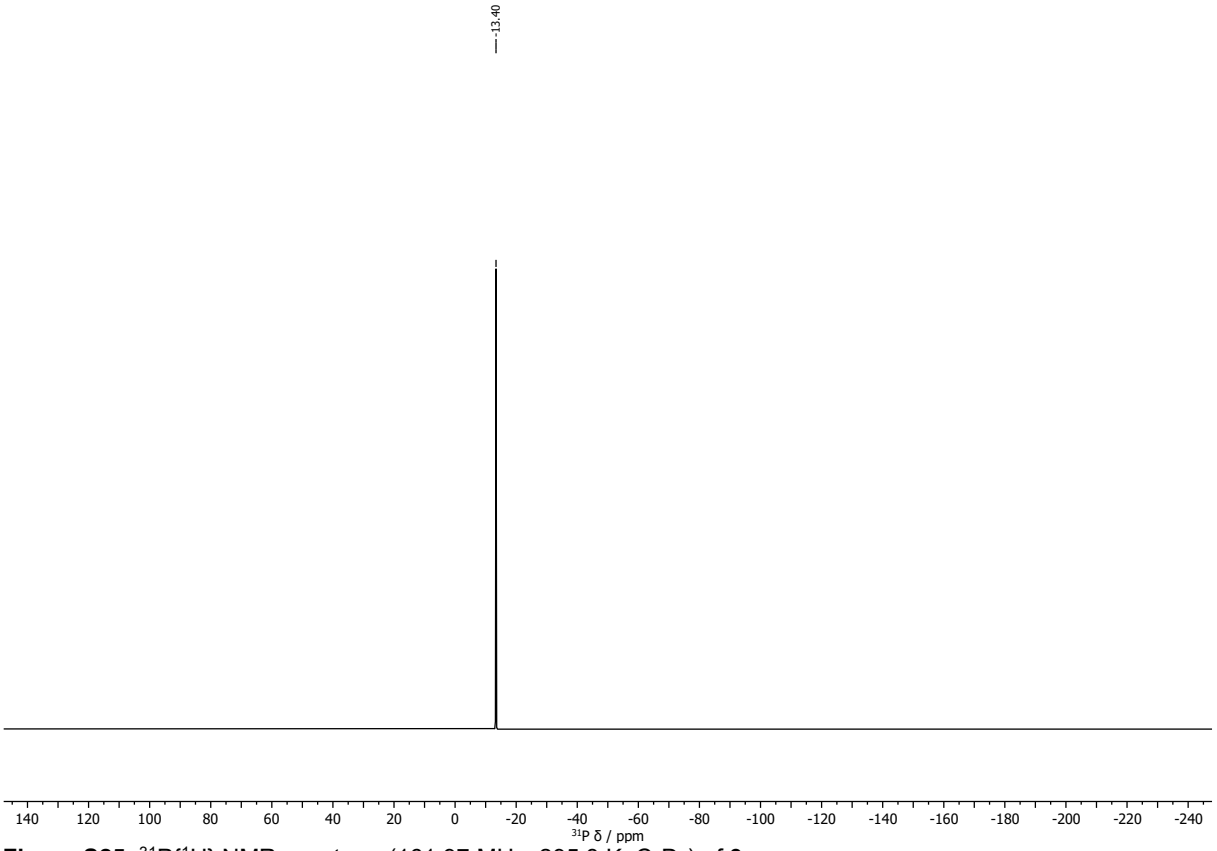


Figure S25. $^{31}P\{^{1}H\}$ NMR spectrum (161.97 MHz, 295.8 K, C_6D_6) of **3**.

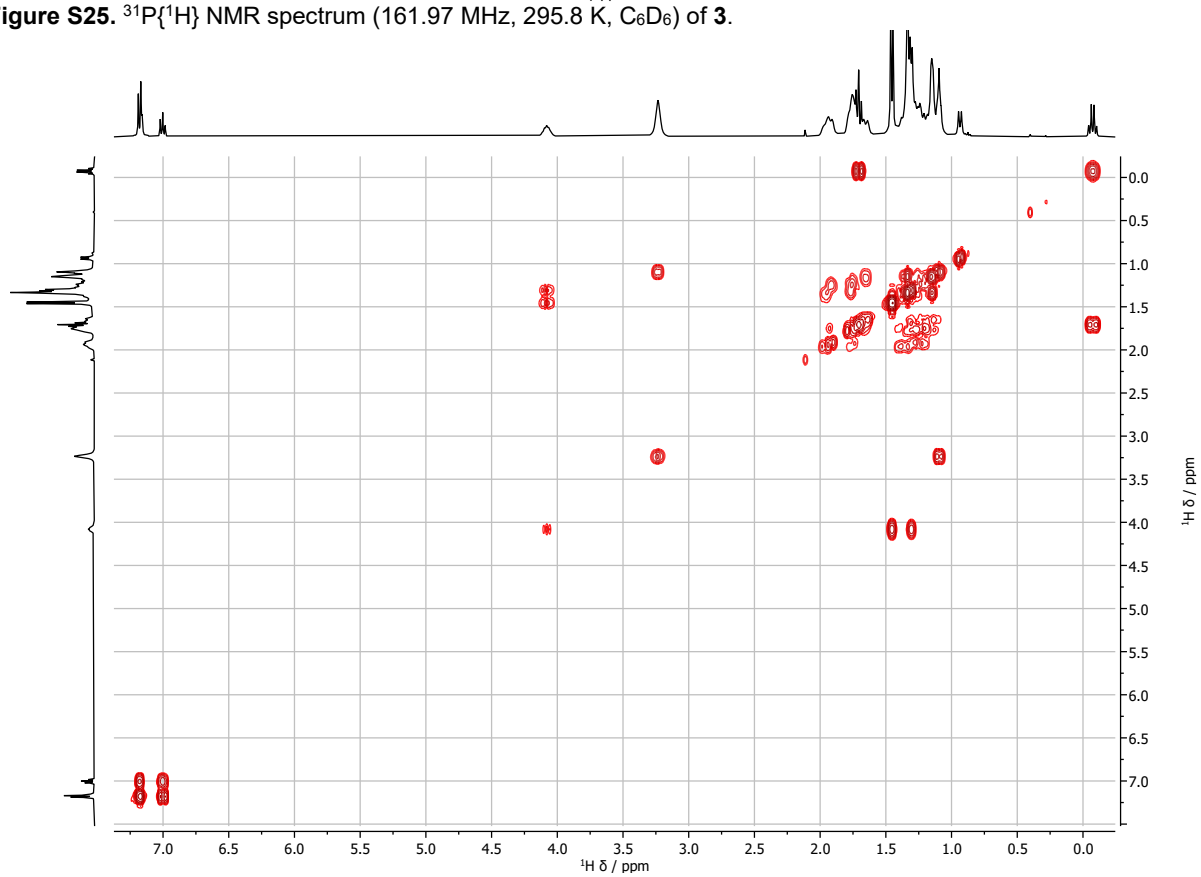


Figure S26. COSY NMR spectrum (400.13 / 400.13 MHz, 295.2 K, C_6D_6) of **3**.

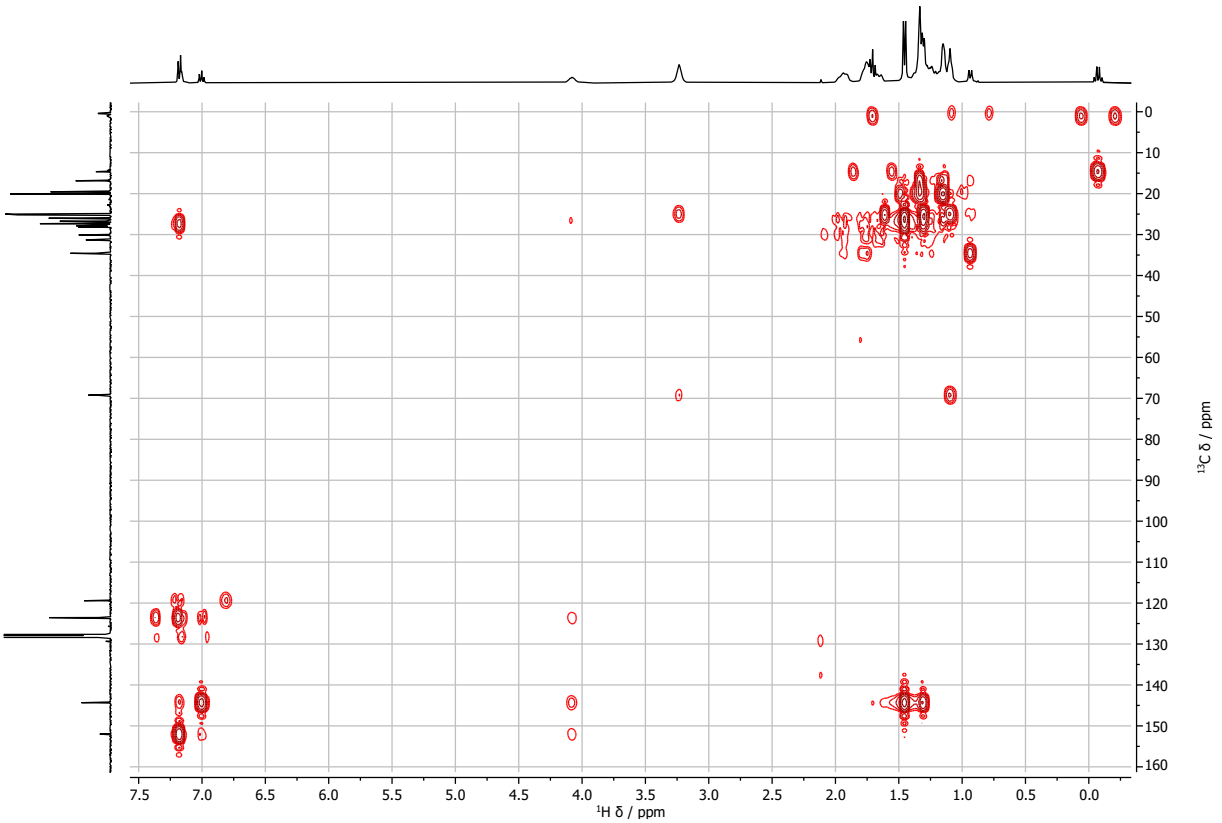


Figure S27. HMBC NMR spectrum (400.13 / 100.62 MHz, 295.1 K, C_6D_6) of **3**.

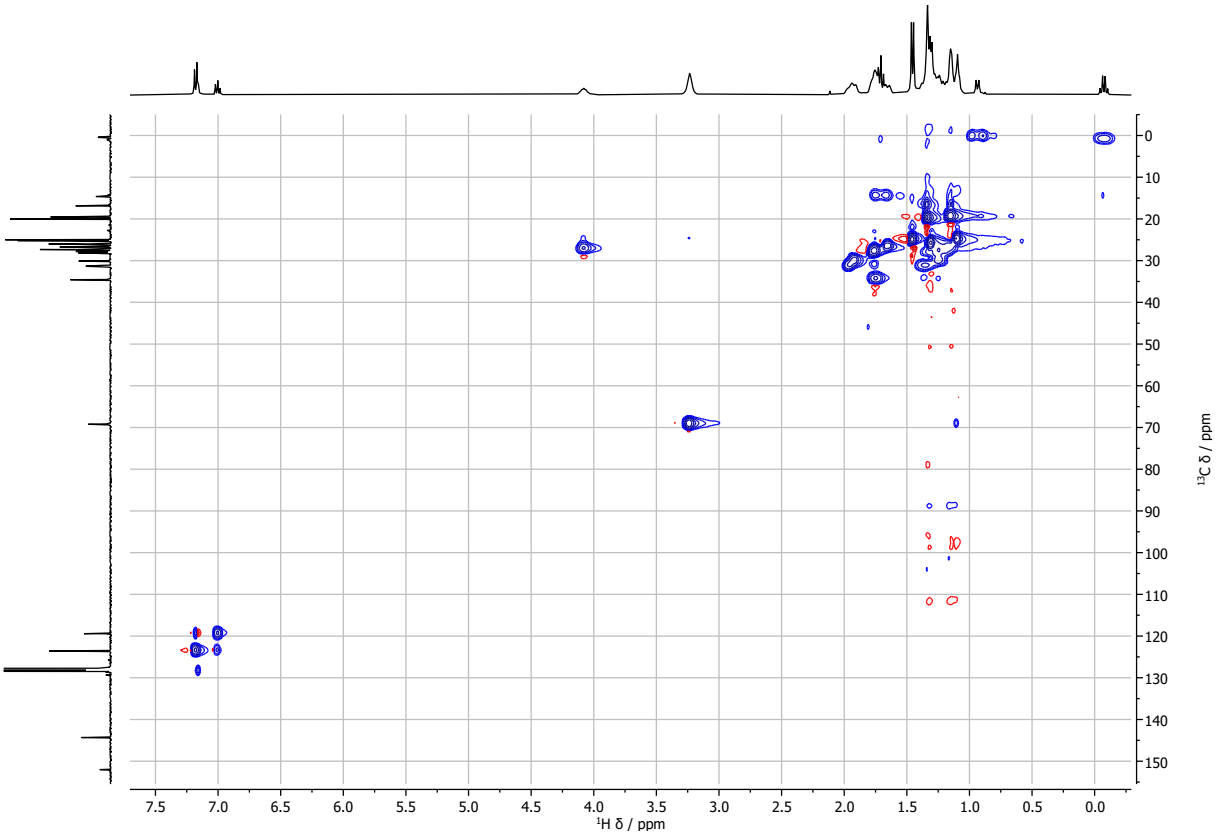


Figure S28. HSQC NMR spectrum (400.13 / 100.62 MHz, 295.2 K, C_6D_6) of **3**.

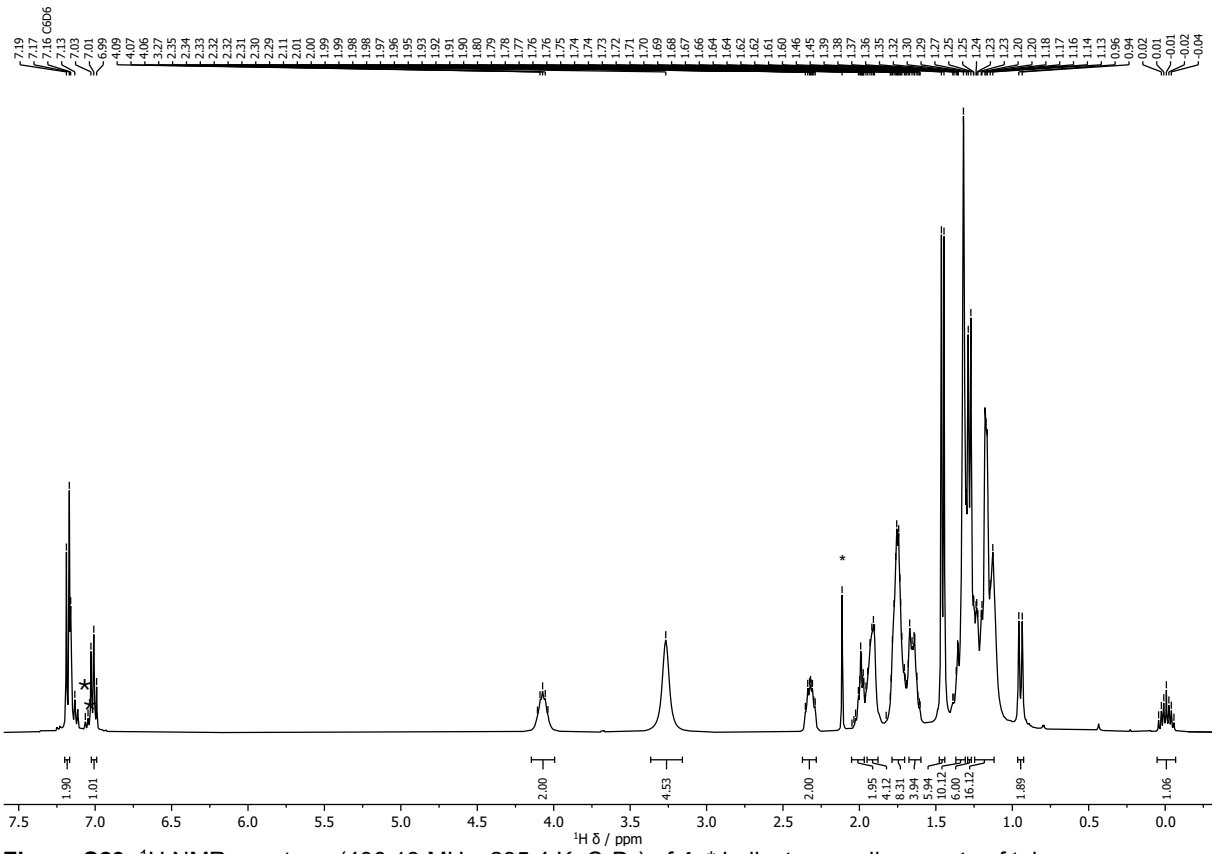


Figure S29. ^{1}H NMR spectrum (400.13 MHz, 295.4 K, C_6D_6) of **4**; * indicates small amounts of toluene.

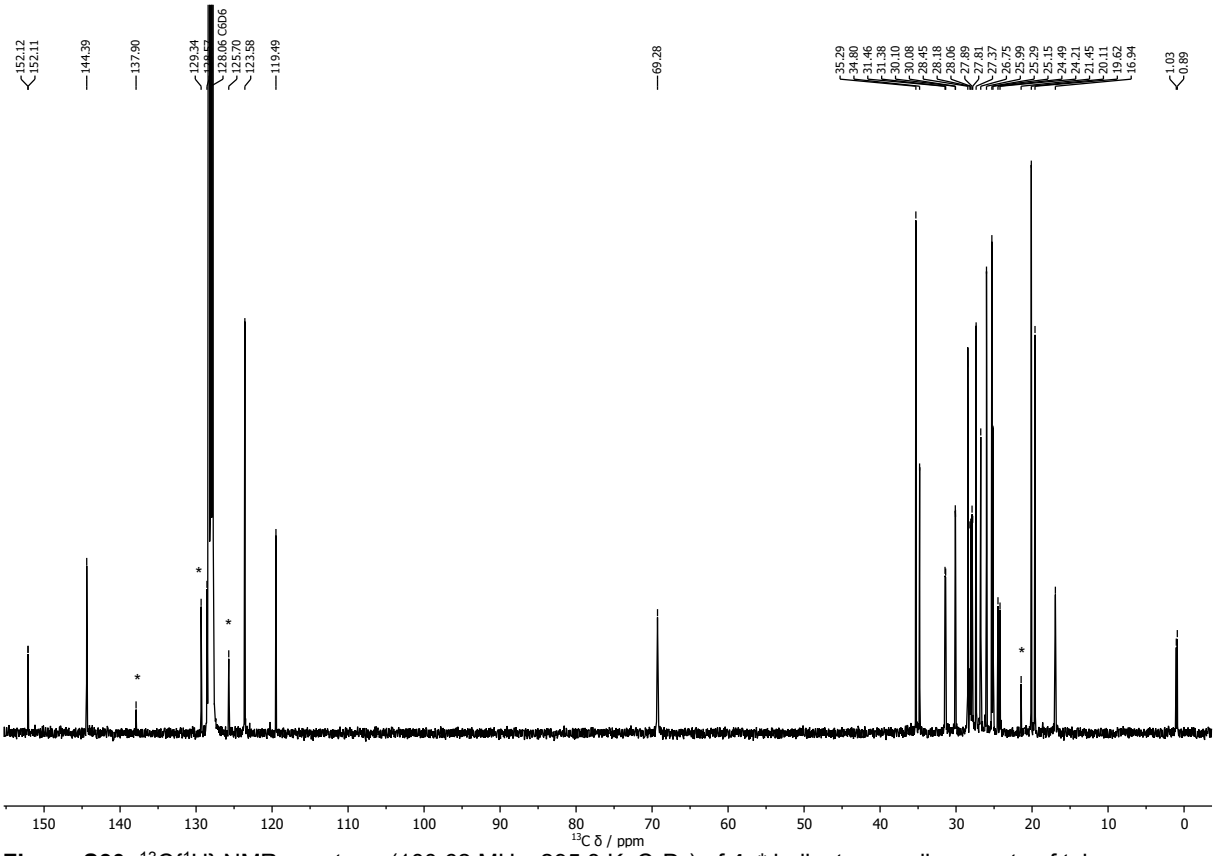


Figure S30. $^{13}C\{^{1}H\}$ NMR spectrum (100.62 MHz, 295.8 K, C_6D_6) of **4**; * indicates small amounts of toluene.

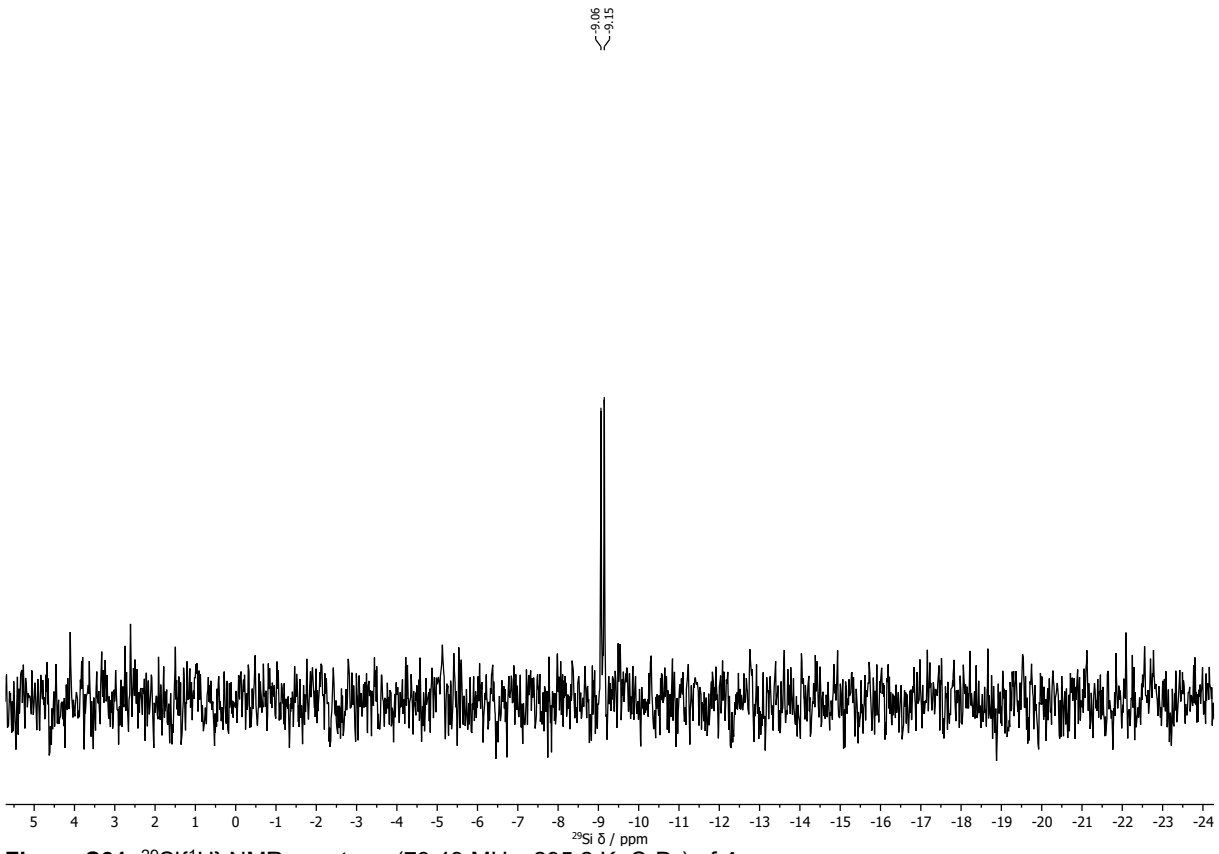


Figure S31. $^{29}Si\{^{1}H\}$ NMR spectrum (79.49 MHz, 295.2 K, C_6D_6) of **4**.

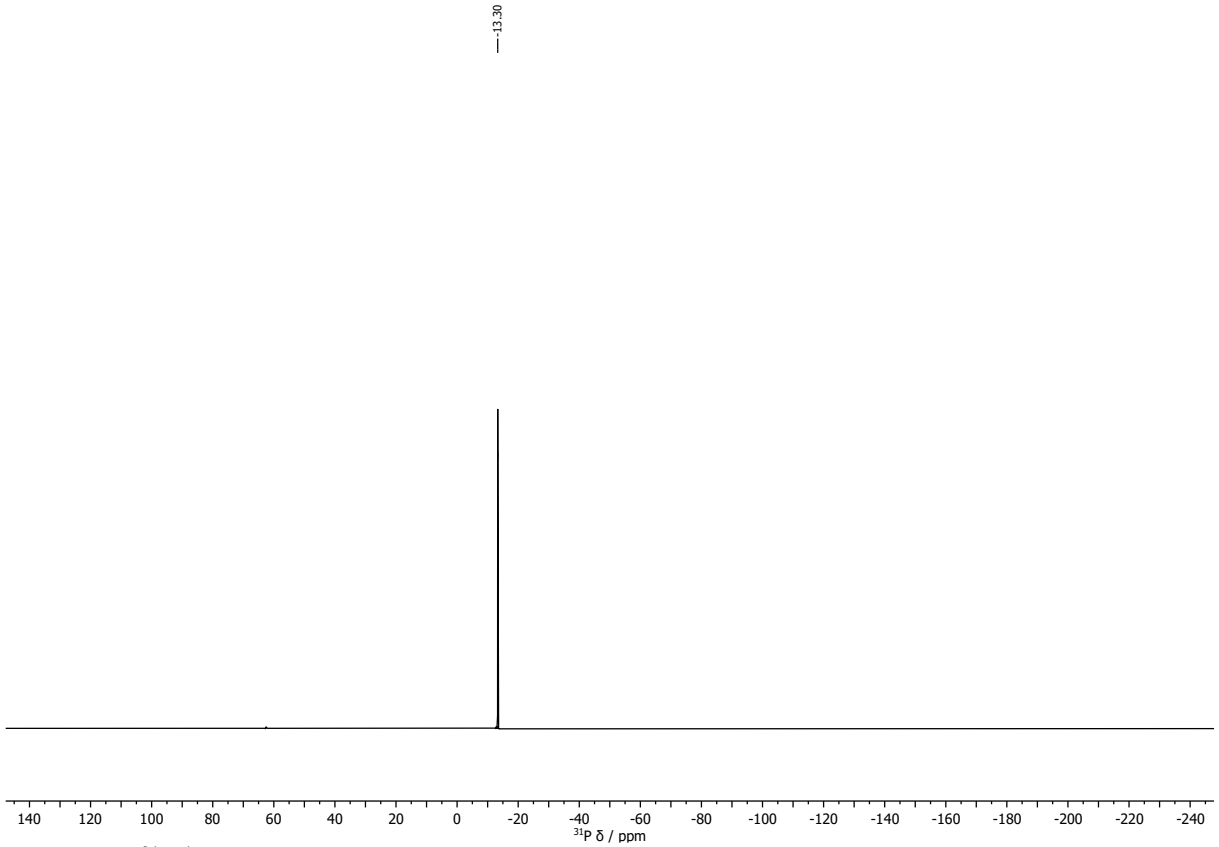


Figure S32. $^{31}P\{^{1}H\}$ NMR spectrum (161.97 MHz, 295.8 K, C_6D_6) of **4**.

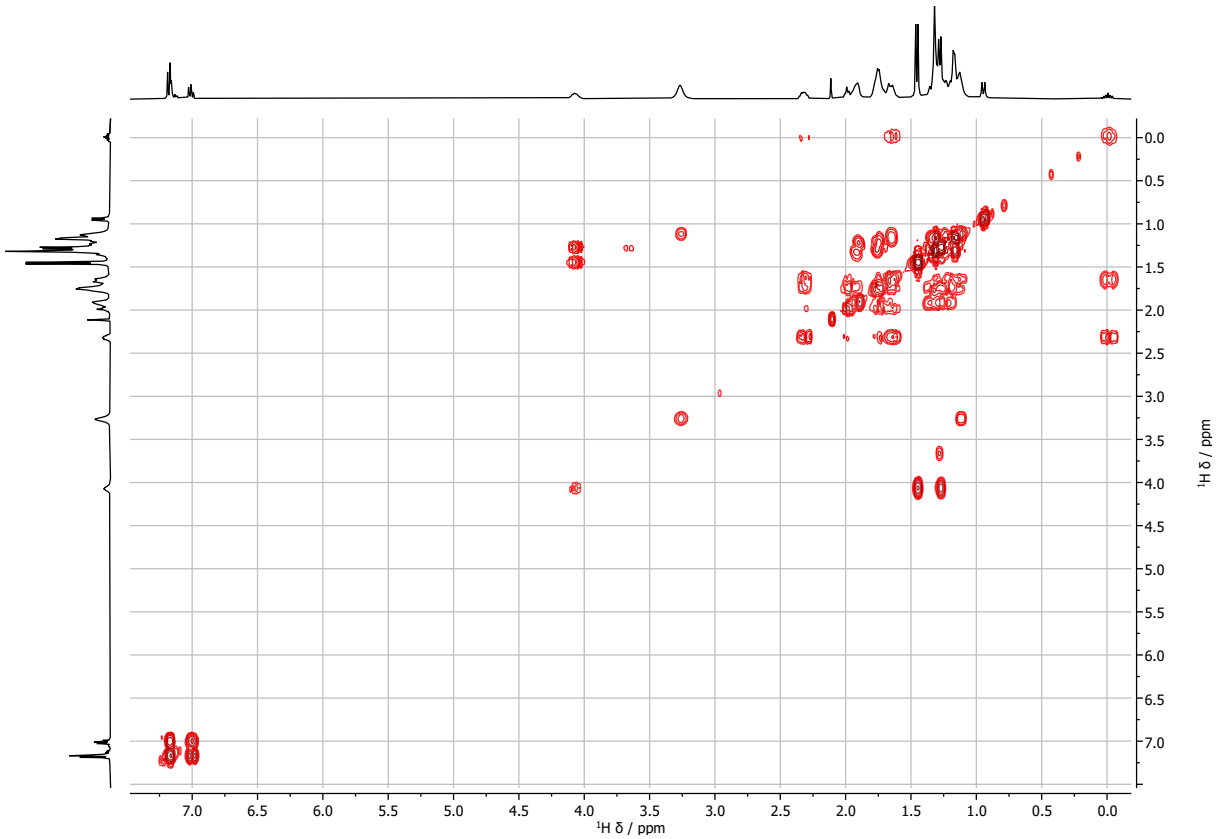


Figure S33. COSY NMR spectrum (400.13 / 400.13 MHz, 295.1 K, C_6D_6) of **4**.

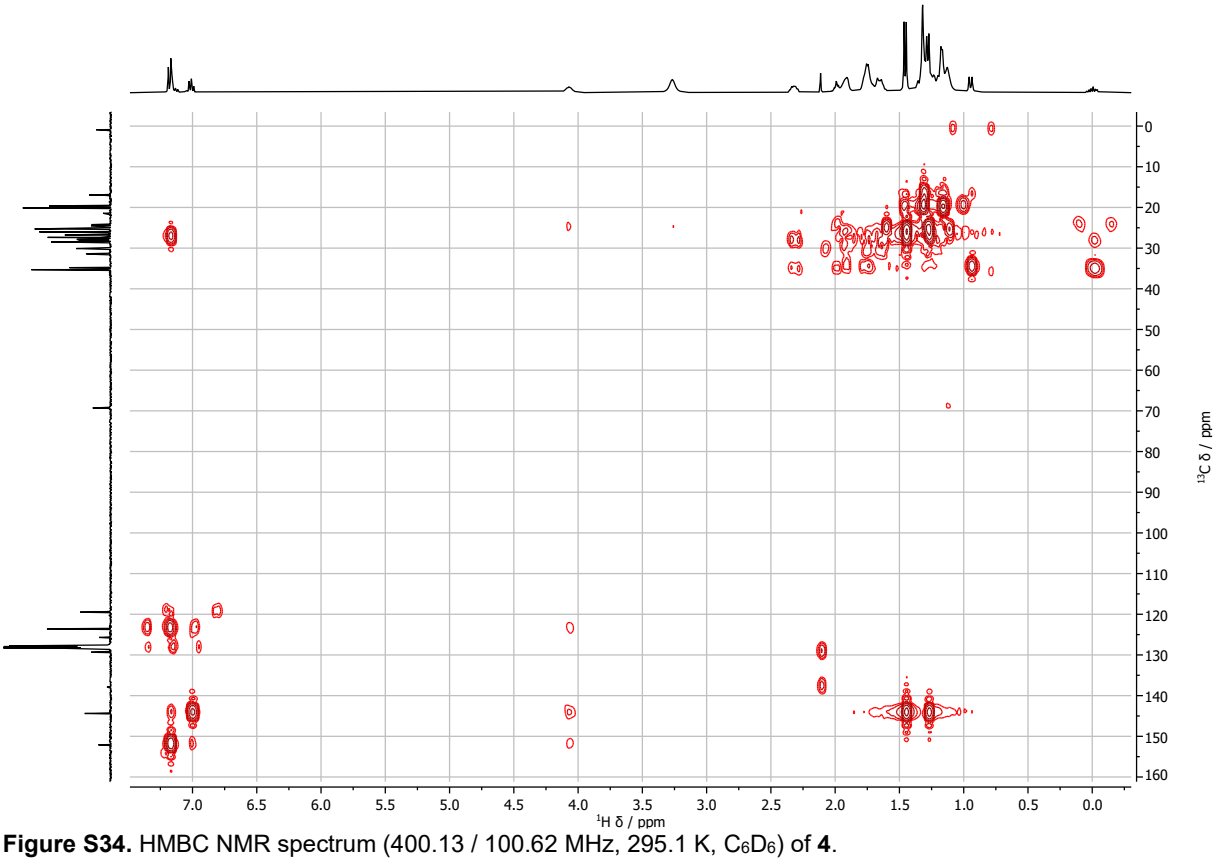


Figure S34. HMBC NMR spectrum (400.13 / 100.62 MHz, 295.1 K, C_6D_6) of **4**.

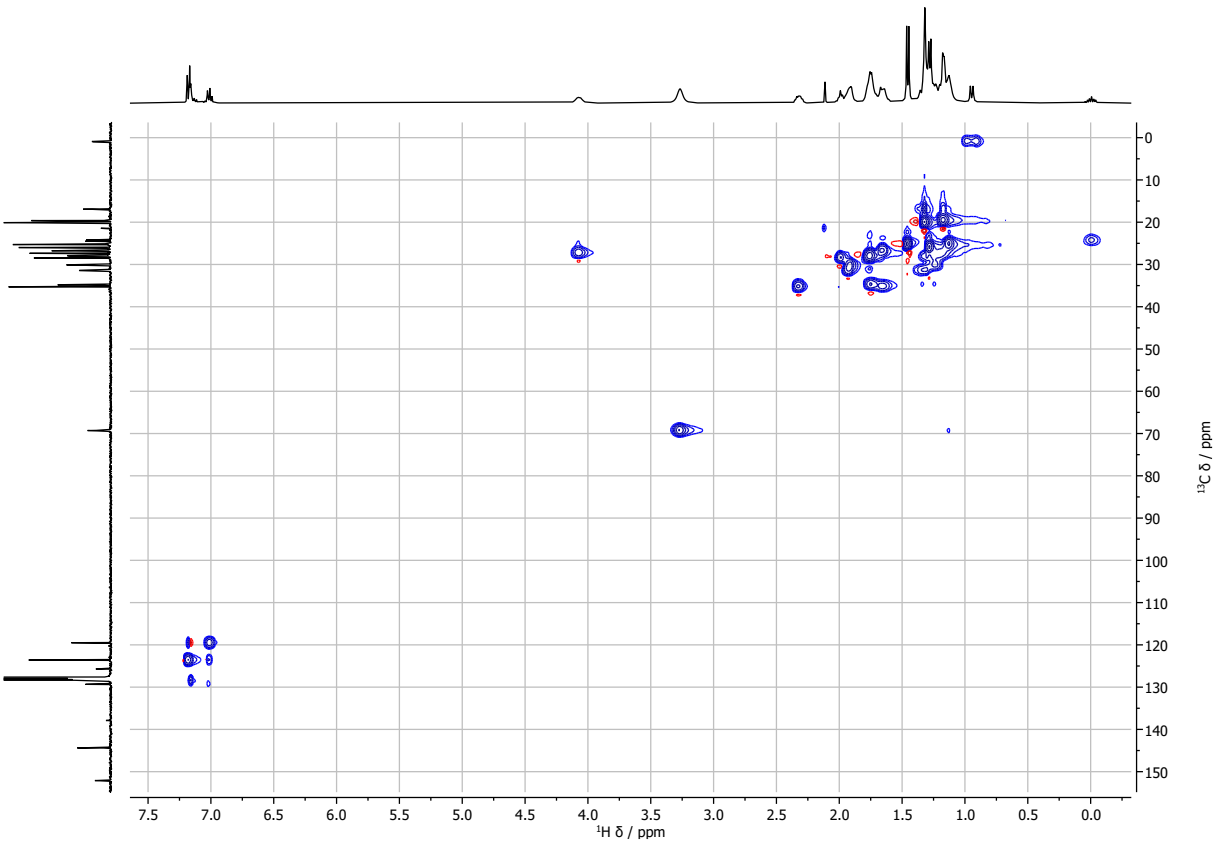


Figure S35. HSQC NMR spectrum (400.13 / 100.62 MHz, 295.4 K, C_6D_6) of **4**.

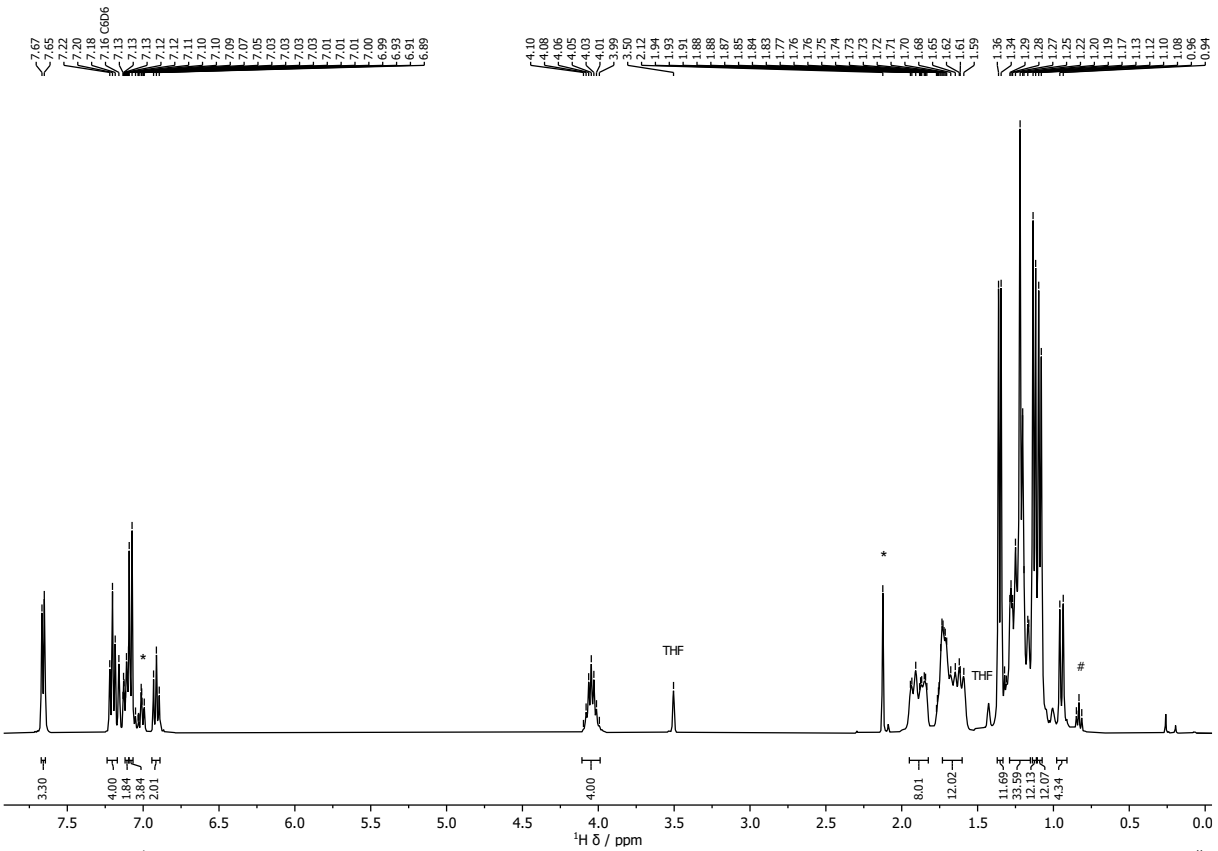


Figure S36. ^{1}H NMR spectrum (400.13 MHz, 298.0 K, C_6D_6 / THF-d_8) of **5**; * indicates small amounts of toluene, # indicates pentane.

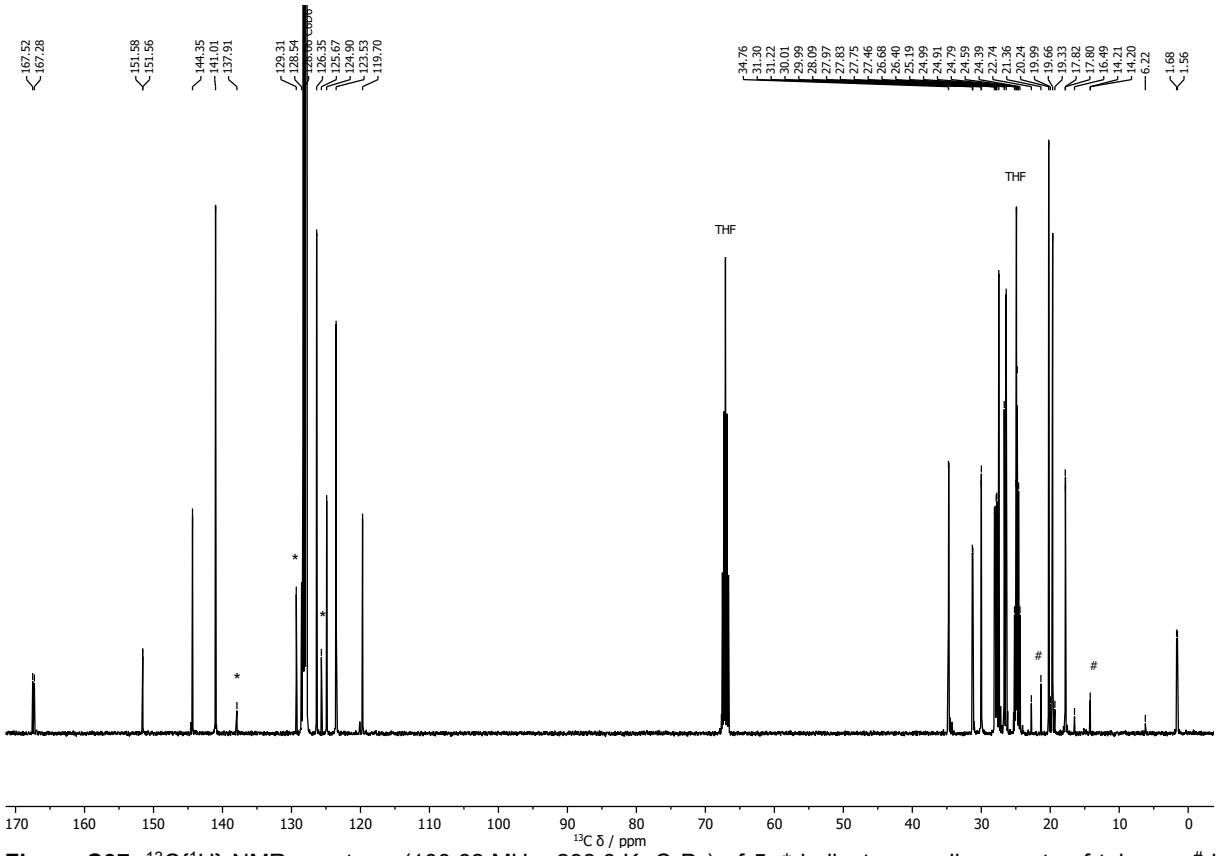


Figure S37. $^{13}C\{^{1}H\}$ NMR spectrum (100.62 MHz, 298.0 K, C_6D_6) of **5**; * indicates small amounts of toluene, # indicates small amounts of pentane.

#

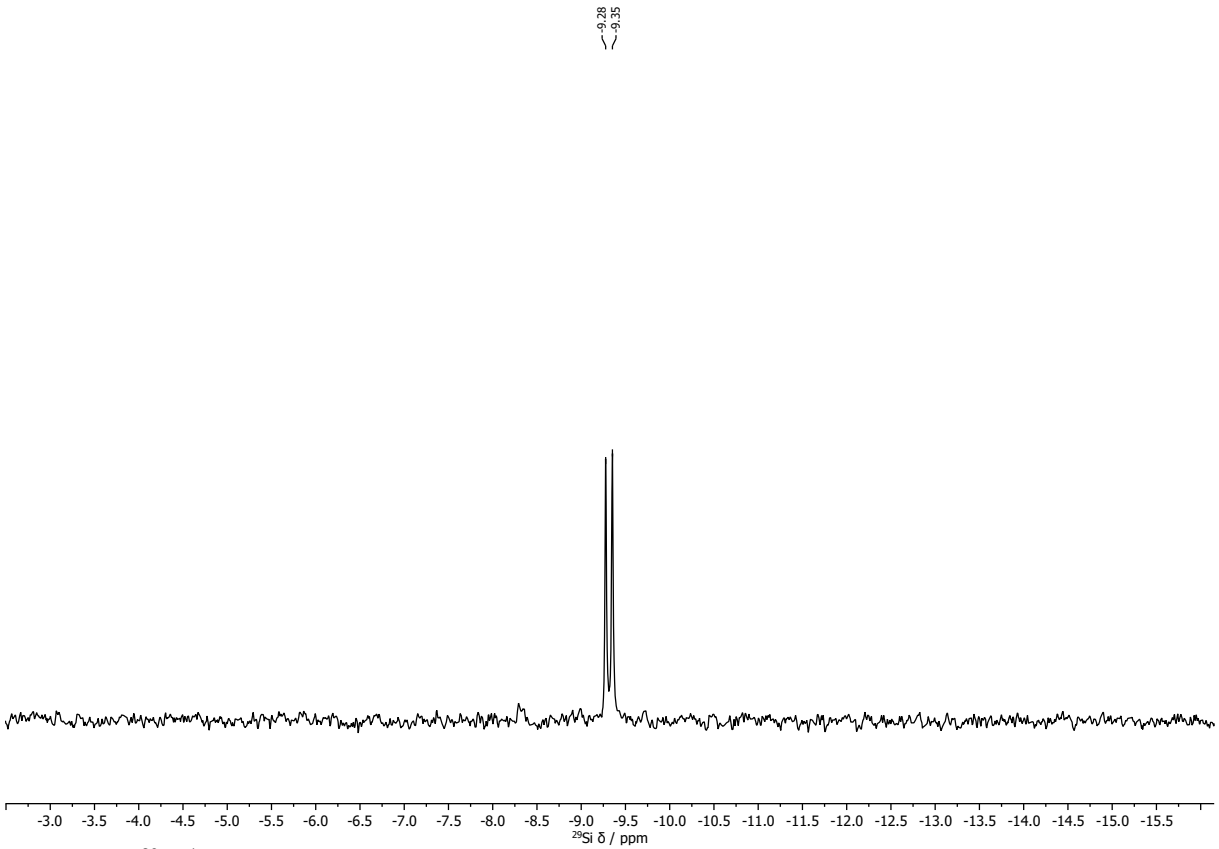


Figure S38. $^{29}Si\{^{1}H\}$ NMR spectrum (79.49 MHz, 298.0 K, C_6D_6) of **5**.

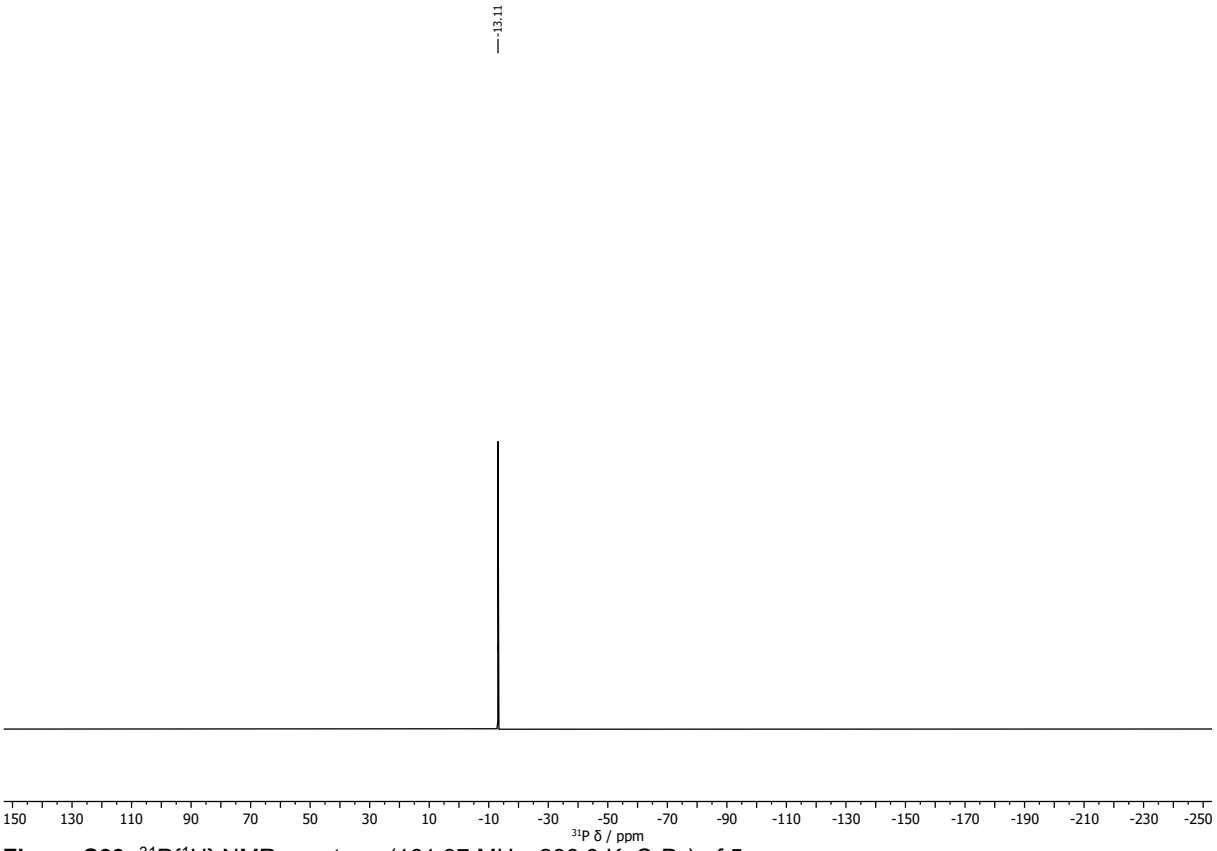


Figure S39. $^{31}P\{^{1}H\}$ NMR spectrum (161.97 MHz, 298.0 K, C_6D_6) of **5**.

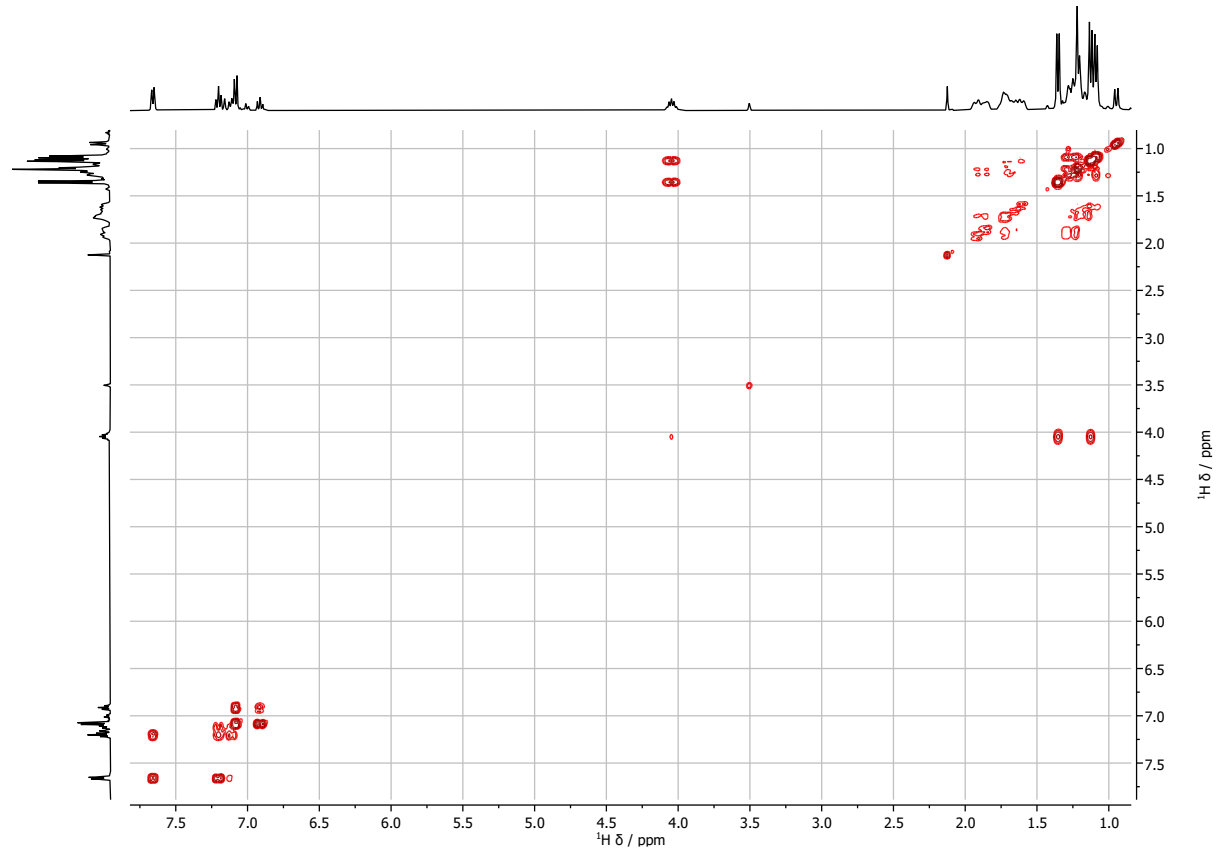


Figure S40. COSY NMR spectrum (400.13 / 400.13 MHz, 298.0 K, C_6D_6) of **5**.

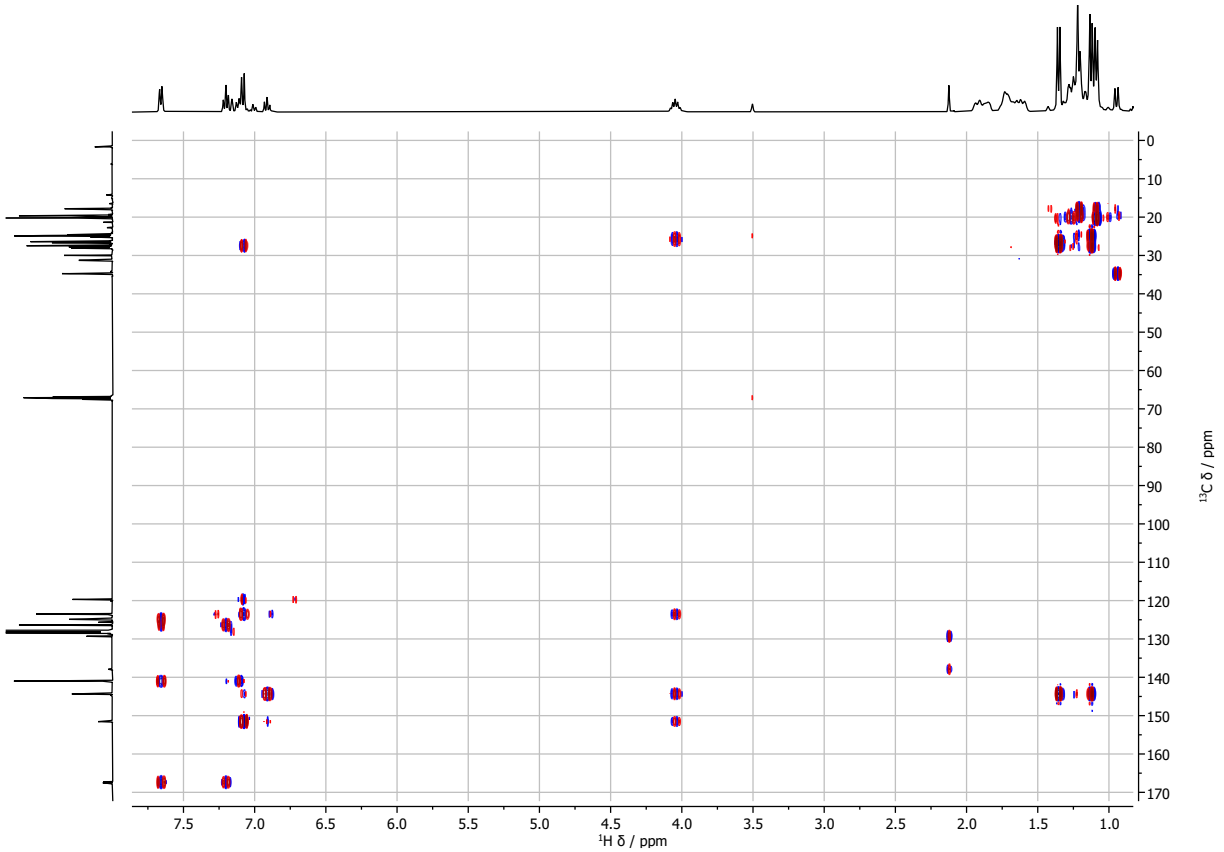


Figure S41. HMBC NMR spectrum (400.13 / 100.62 MHz, 298.0 K, C_6D_6) of **5**.

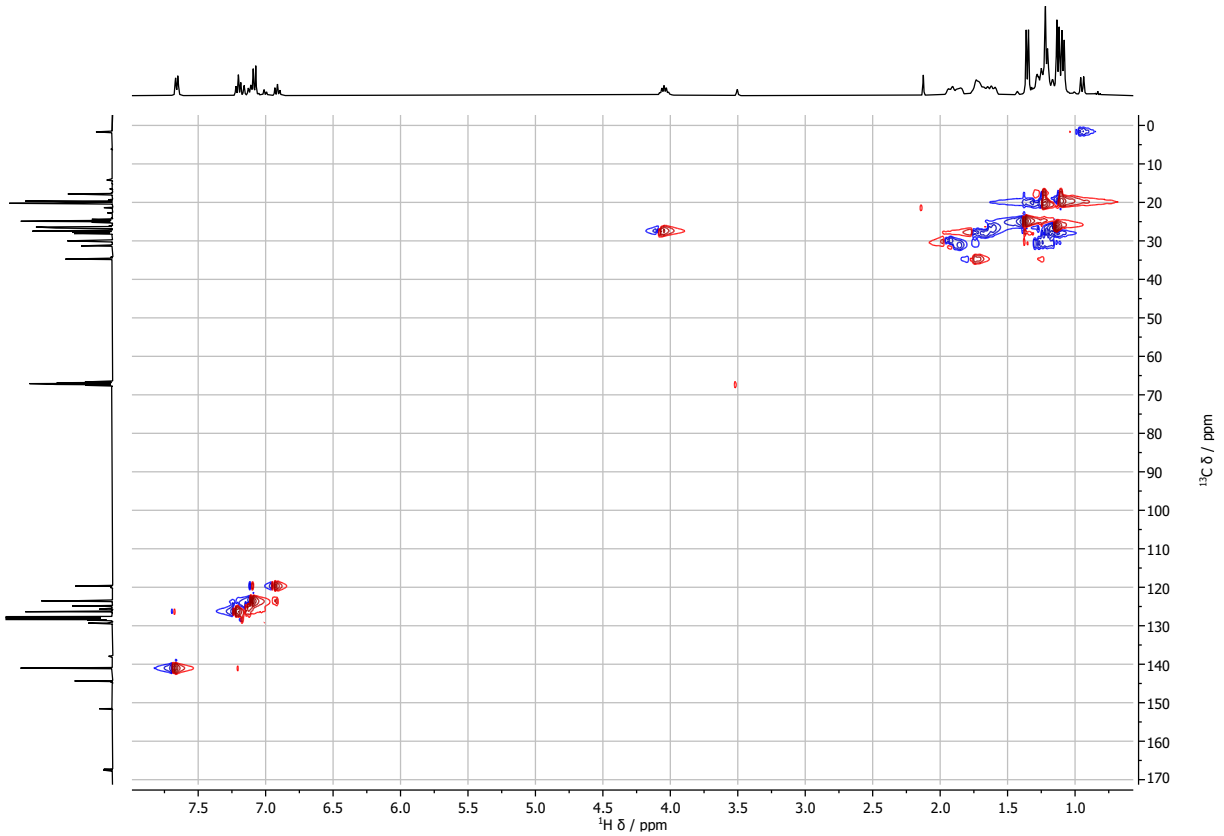


Figure S42. HSQC NMR spectrum (400.13 / 100.62 MHz, 298.0 K, C_6D_6) **5**.

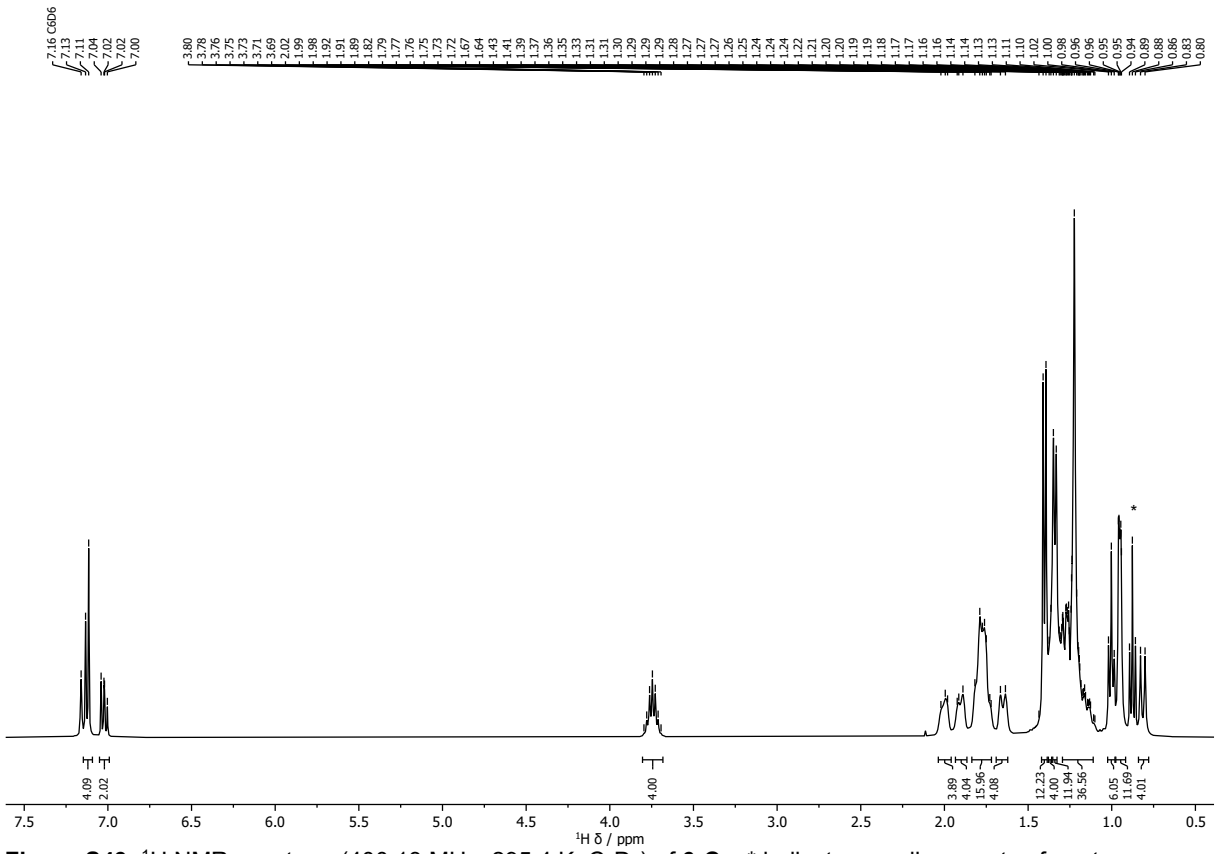


Figure S43. ^{1}H NMR spectrum (400.13 MHz, 295.4 K, C_6D_6) of **6-Cy**; * indicates small amounts of pentane.

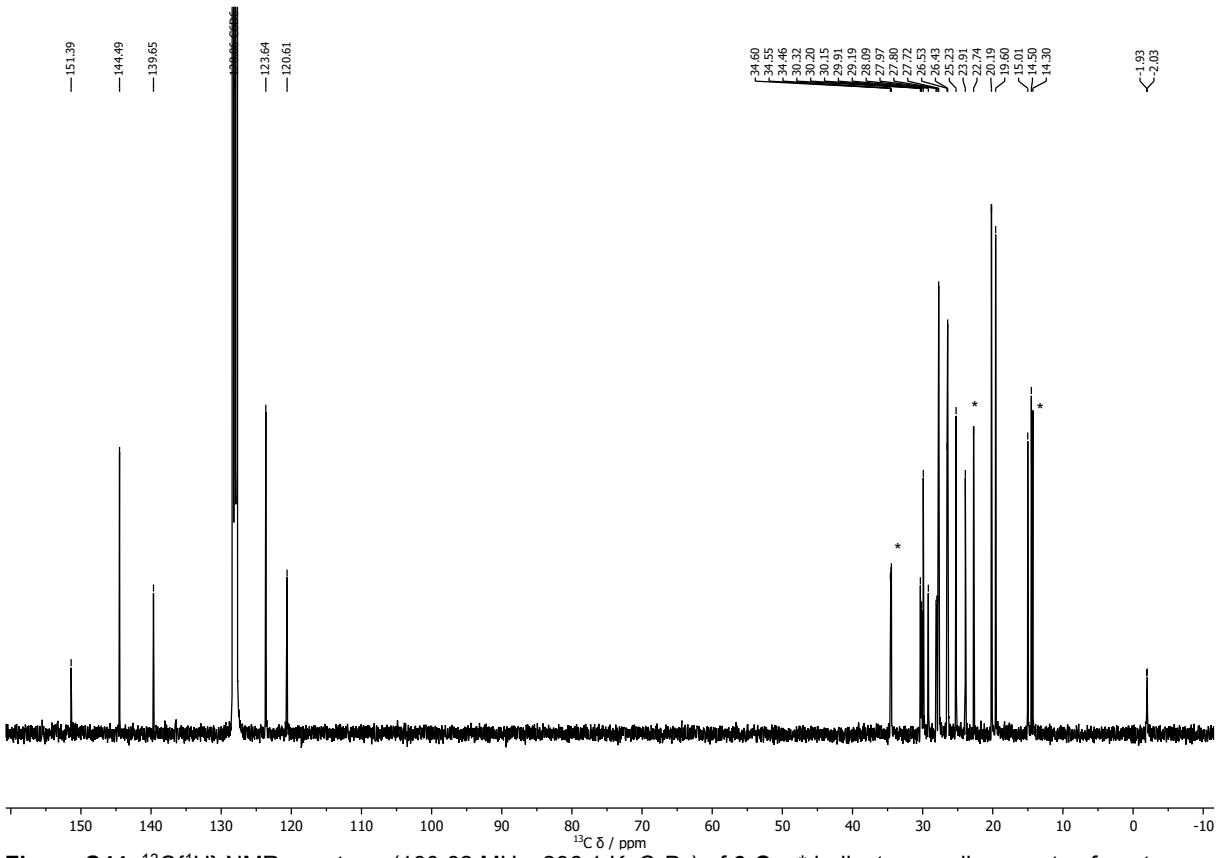


Figure S44. $^{13}C\{^{1}H\}$ NMR spectrum (100.62 MHz, 296.1 K, C_6D_6) of **6-Cy**; * indicates small amounts of pentane.

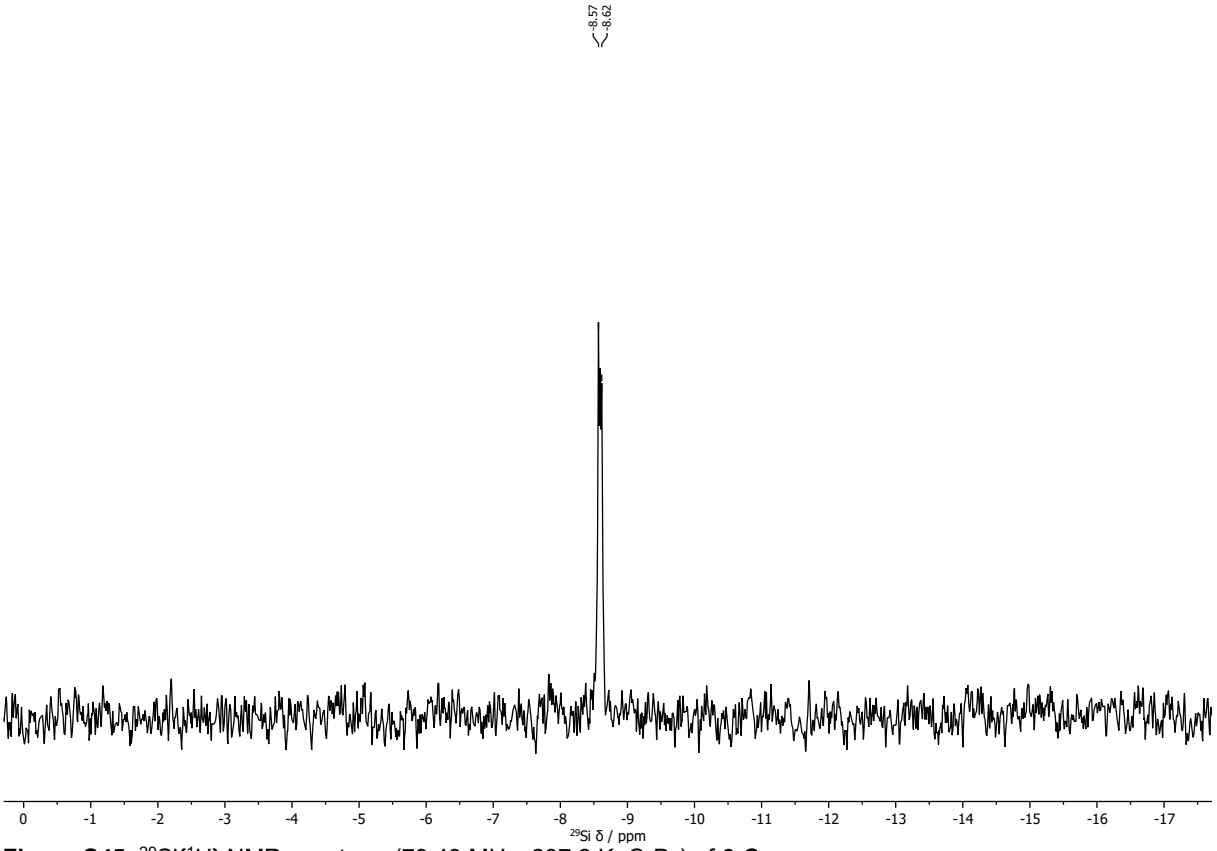


Figure S45. $^{29}Si\{^{1}H\}$ NMR spectrum (79.49 MHz, 297.2 K, C_6D_6) of **6-Cy**.

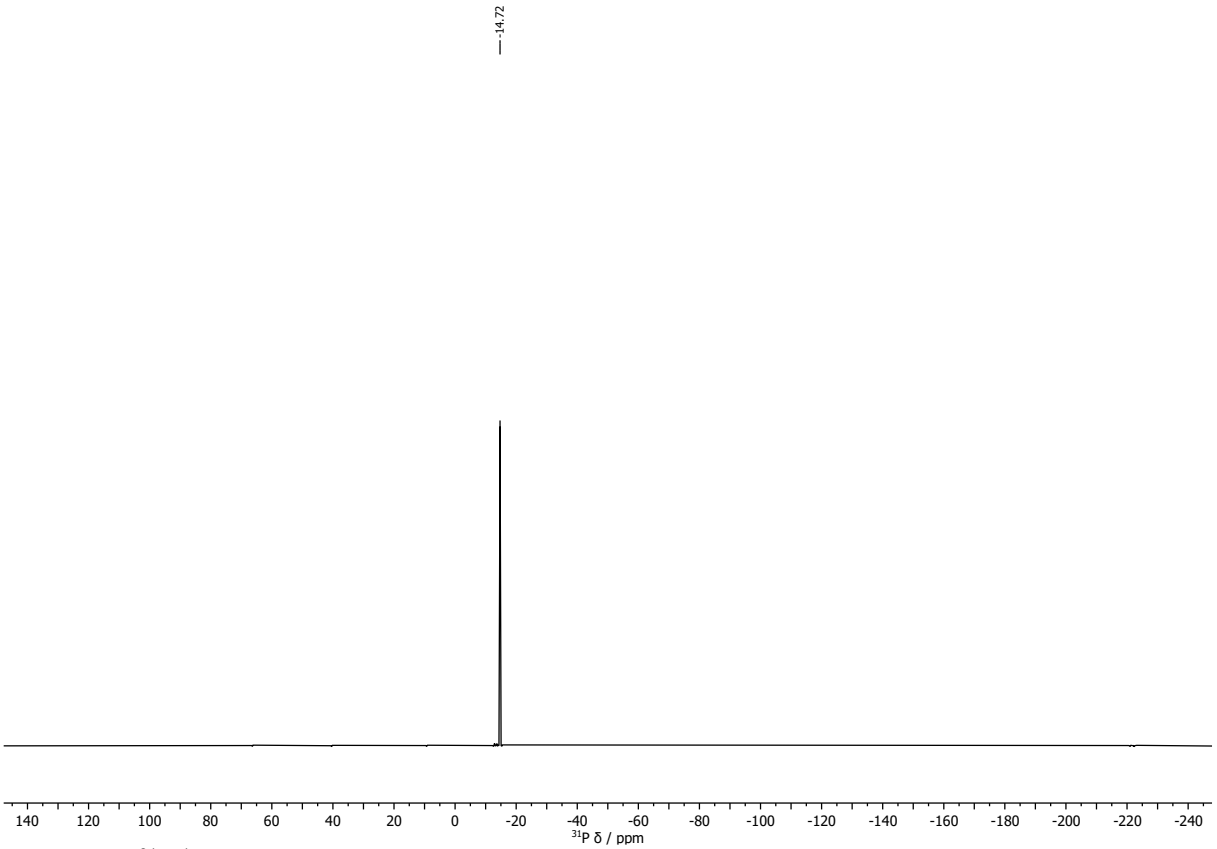


Figure S46. $^{31}P\{^{1}H\}$ NMR spectrum (161.97 MHz, 296.0 K, C_6D_6) of **6-Cy**.

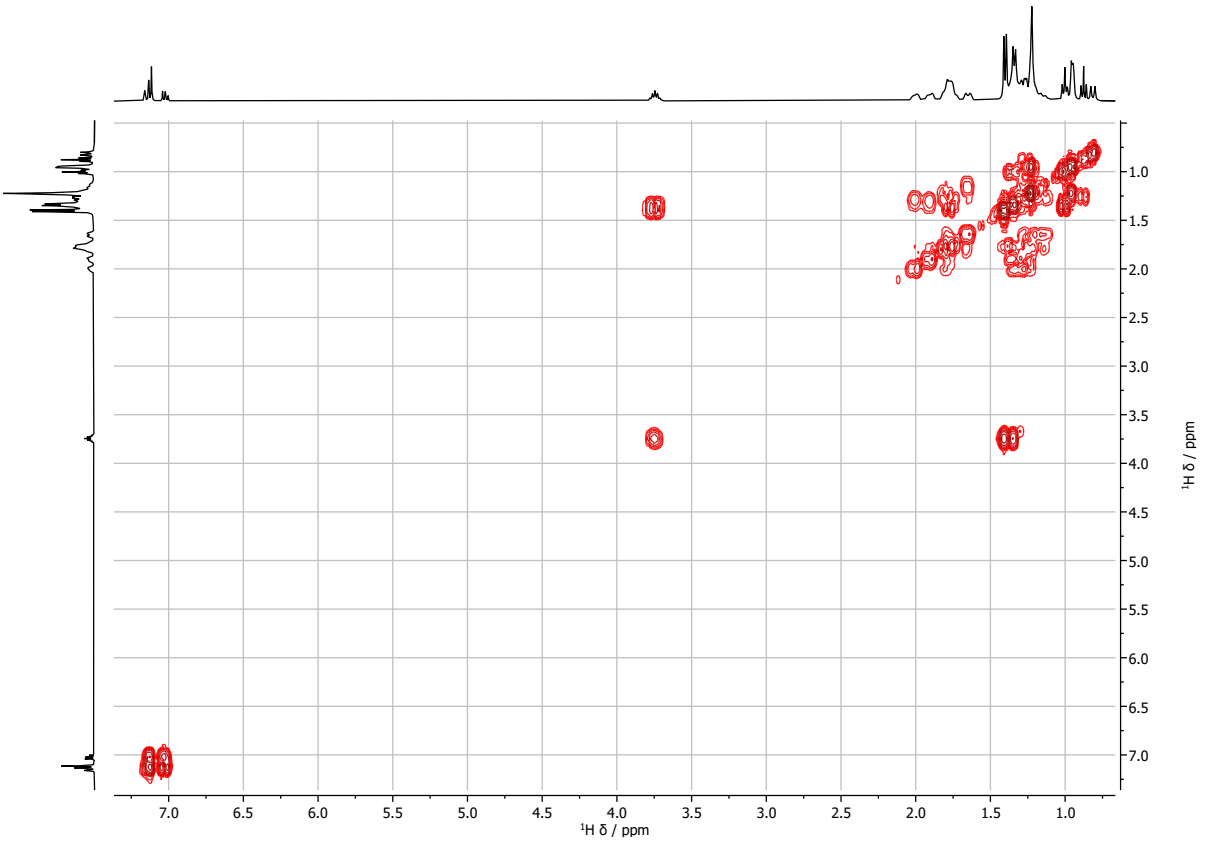


Figure S47. COSY NMR spectrum (400.13 / 400.13 MHz, 295.5 K, C_6D_6) of **6-Cy**.

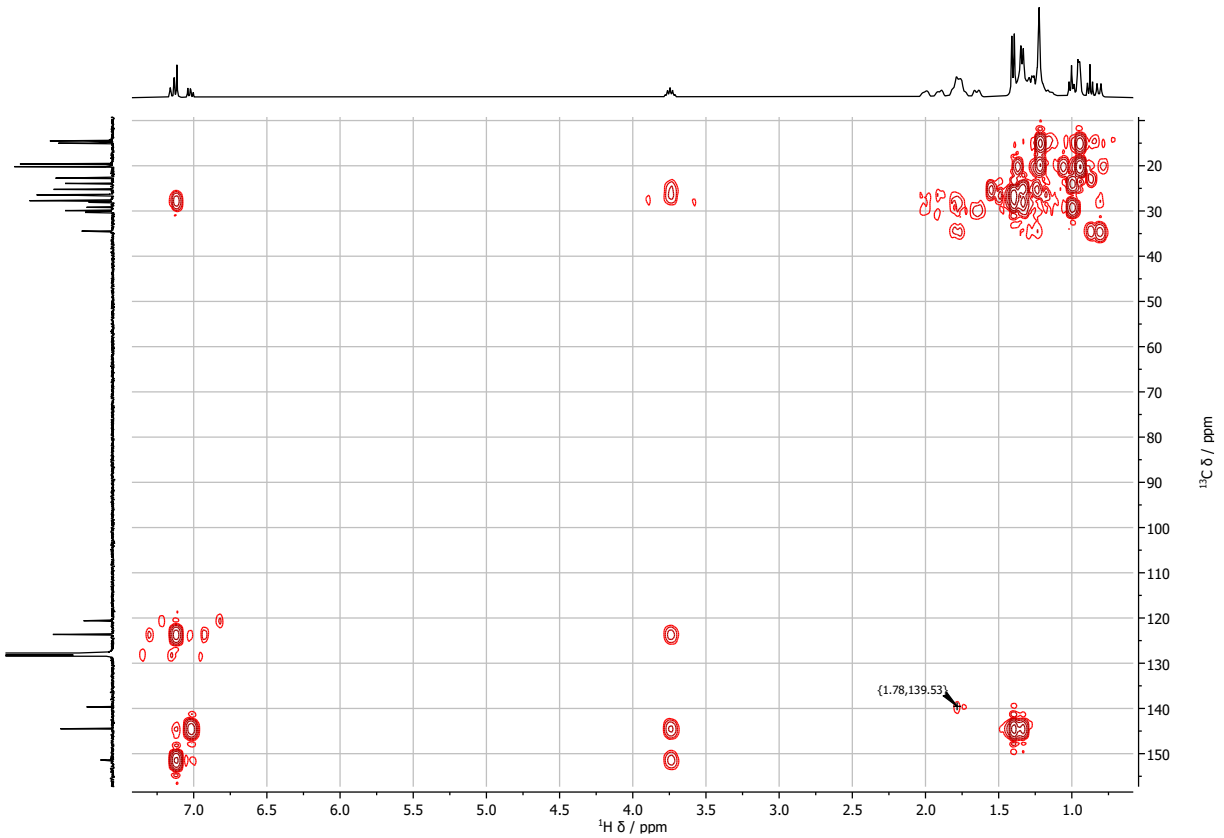


Figure S48. HMBC NMR spectrum (400.13 / 100.62 MHz, 295.4 K, C_6D_6) of **6-Cy**.

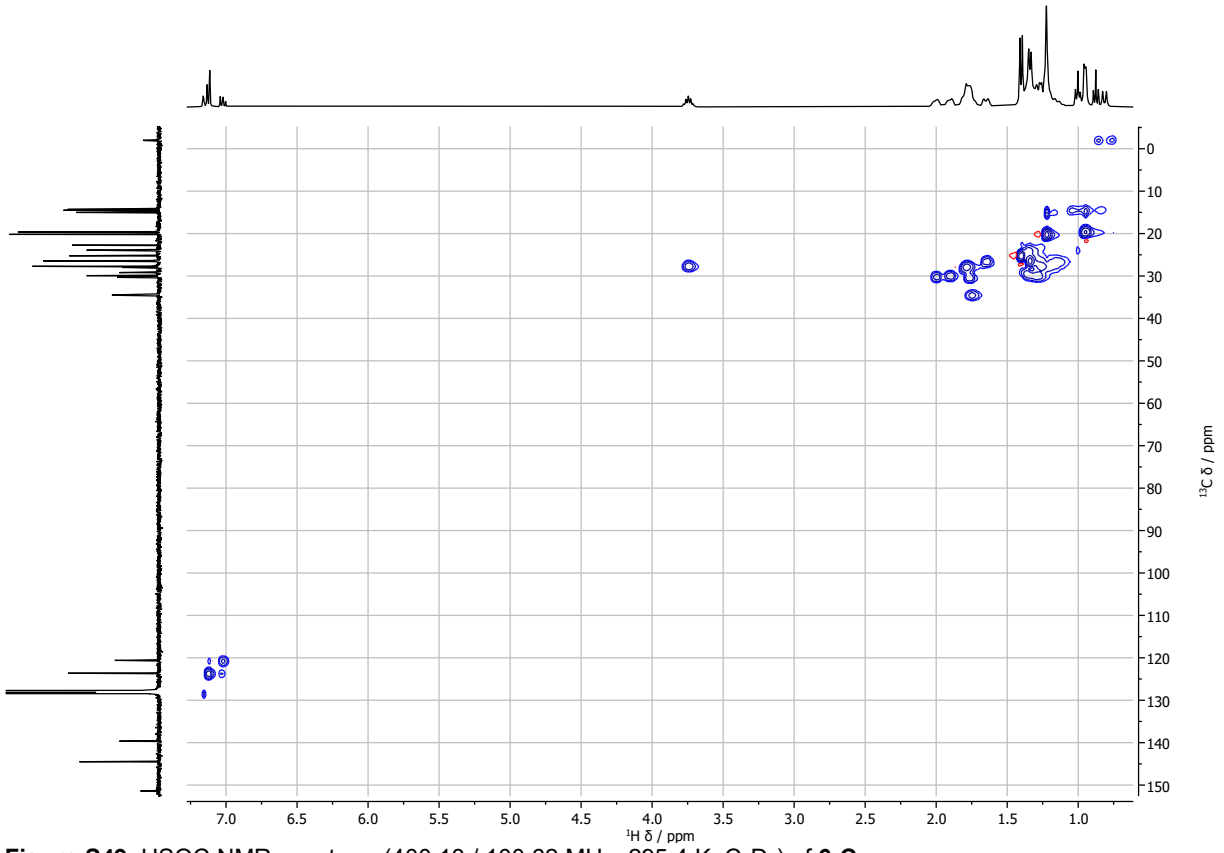
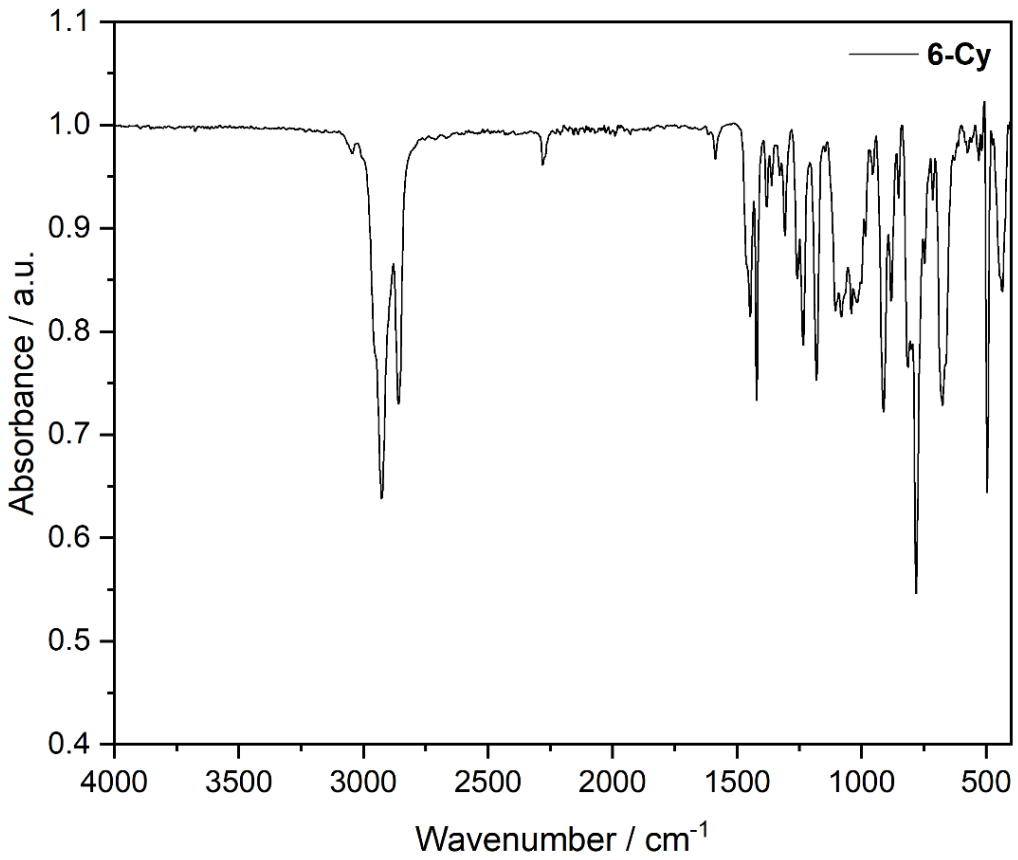


Figure S49. HSQC NMR spectrum (400.13 / 100.62 MHz, 295.4 K, C_6D_6) of **6-Cy**.



FigureS50. ATR-IR spectrum of **6-Cy**.

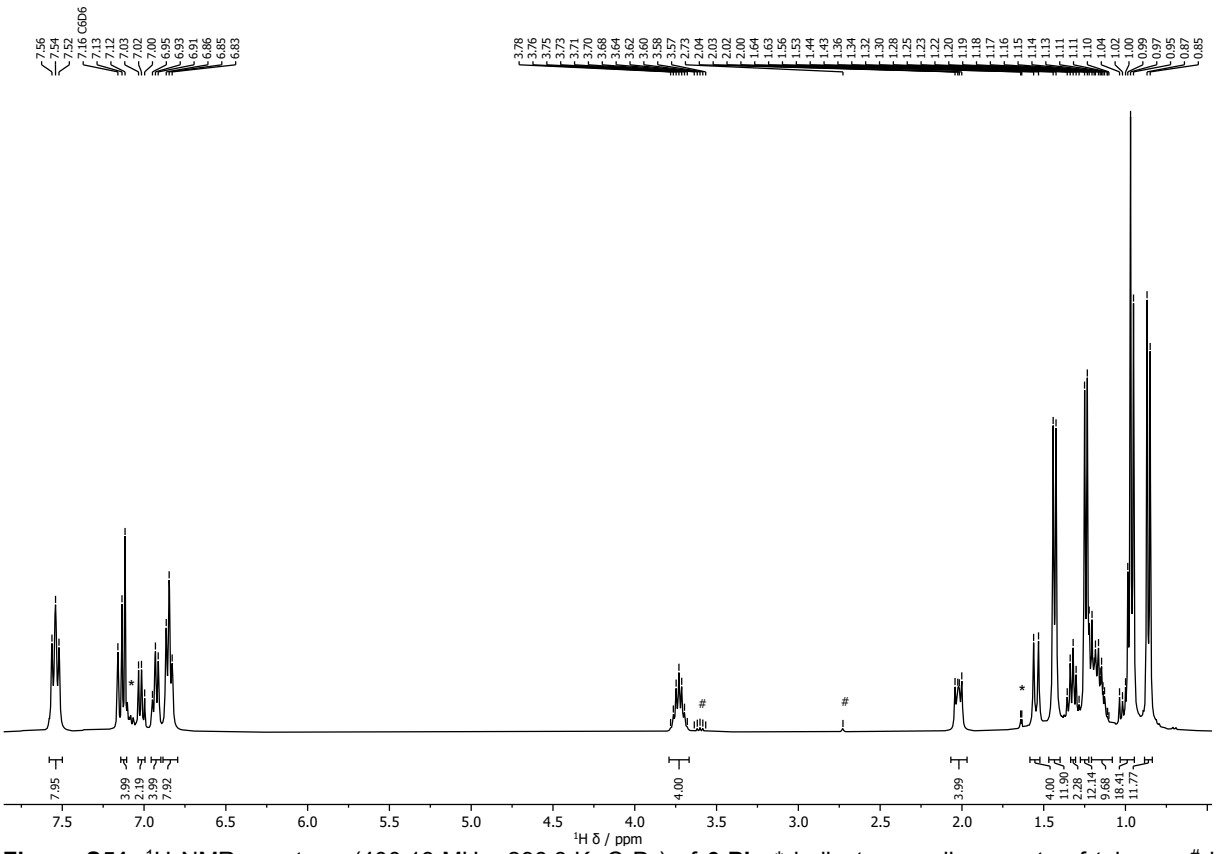


Figure S51. ^{1}H NMR spectrum (400.13 MHz, 296.3 K, C_6D_6) of **6-Ph**; * indicates small amounts of toluene, # indicates protonated ligand.

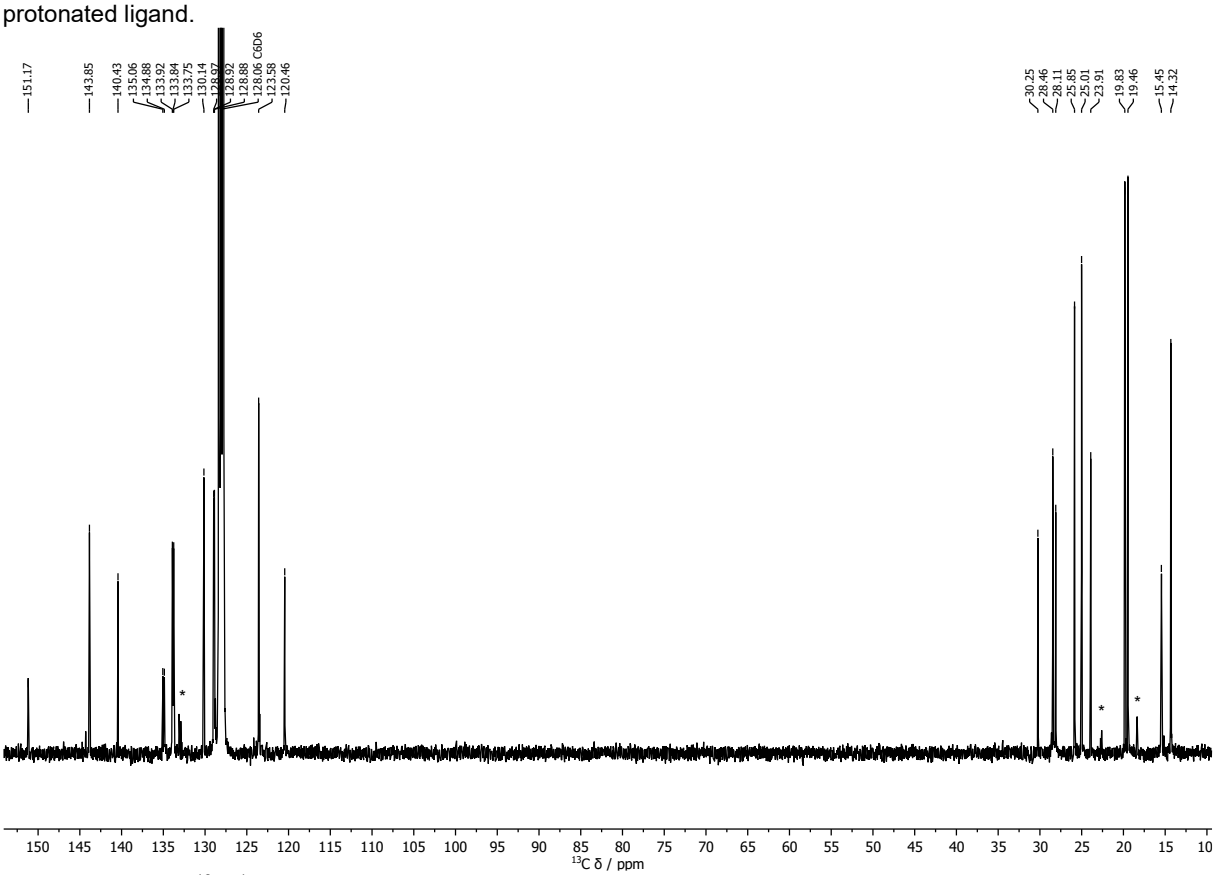


Figure S52. $^{13}C\{^{1}H\}$ NMR spectrum (100.62 MHz, 296.8 K, C_6D_6) of **6-Ph**; * indicates protonated ligand.

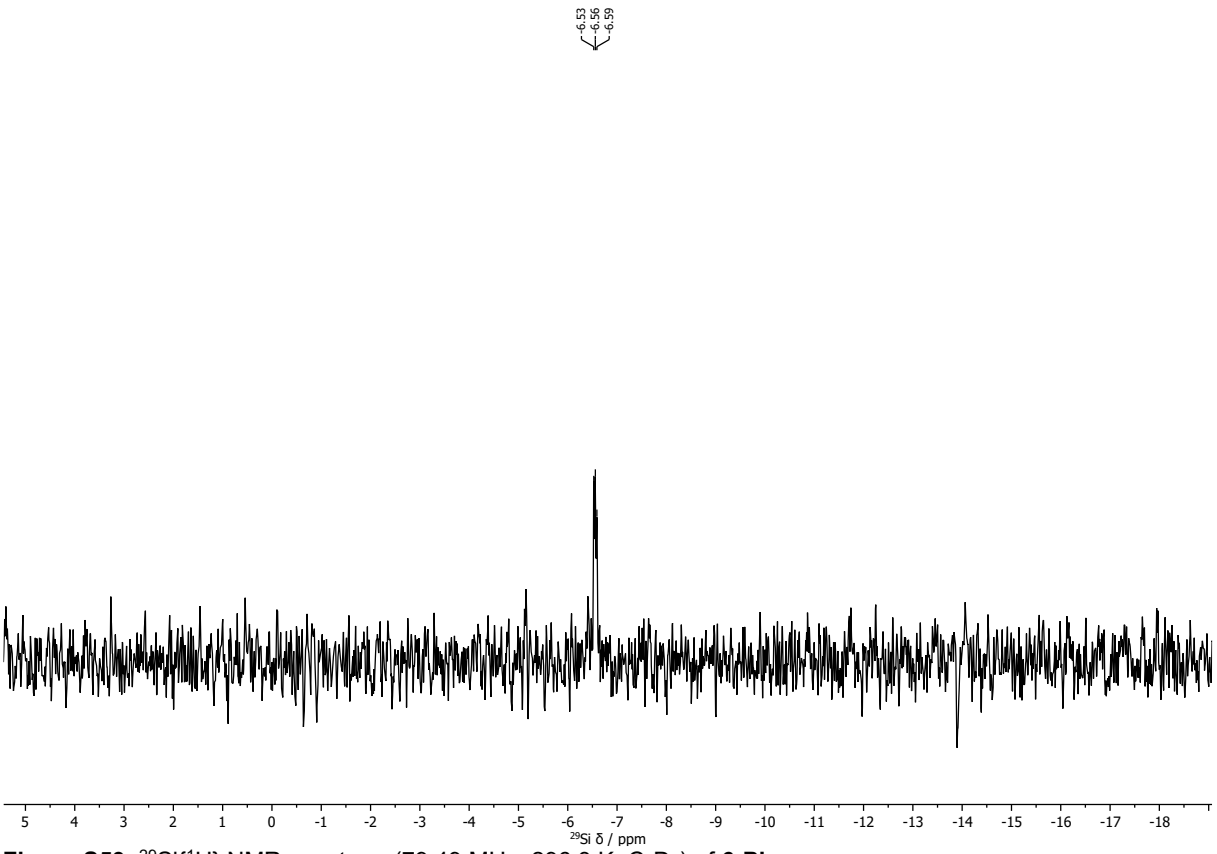


Figure S53. $^{29}Si\{^{1}H\}$ NMR spectrum (79.49 MHz, 296.3 K, C_6D_6) of **6-Ph**.

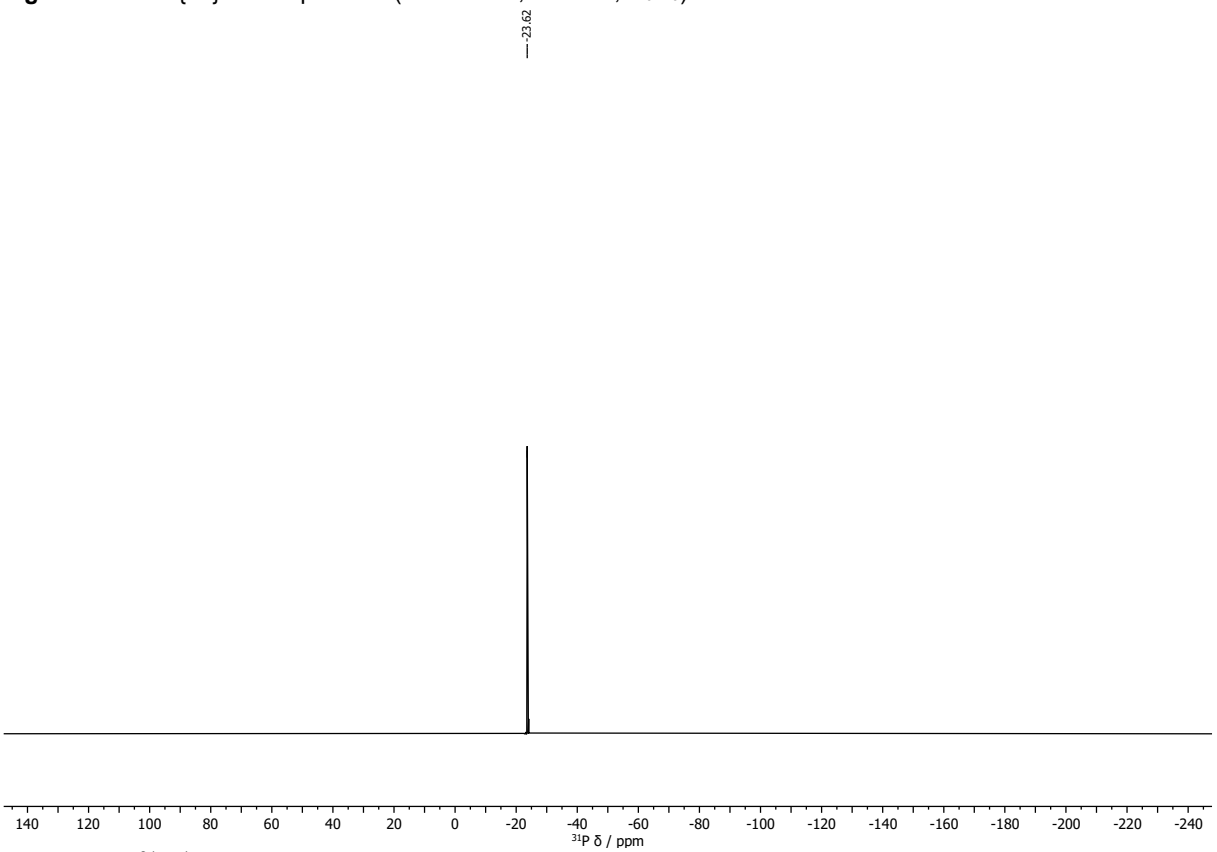


Figure S54. $^{31}P\{^{1}H\}$ NMR spectrum (161.97 MHz, 296.7 K, C_6D_6) of **6-Ph**.

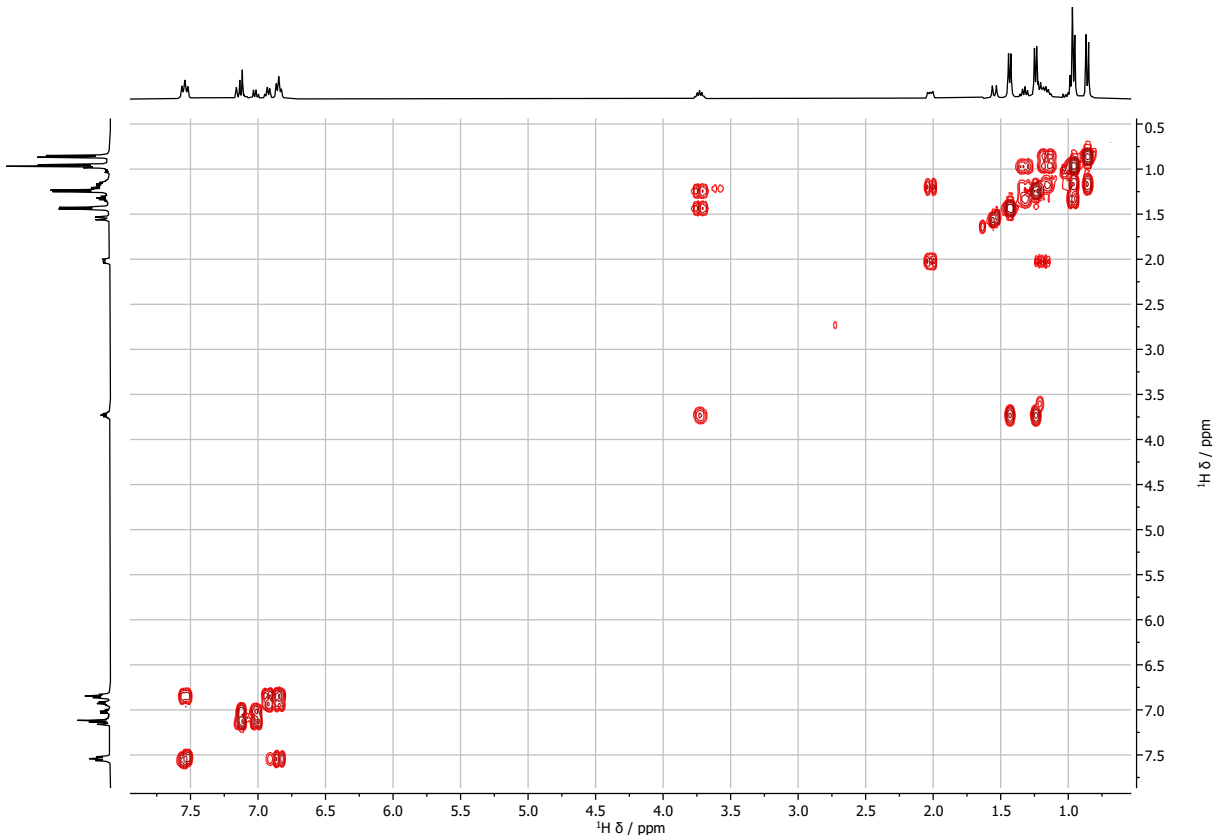


Figure S55. COSY NMR spectrum (400.13 / 400.13 MHz, 296.2 K, C_6D_6) of **6-Ph**.

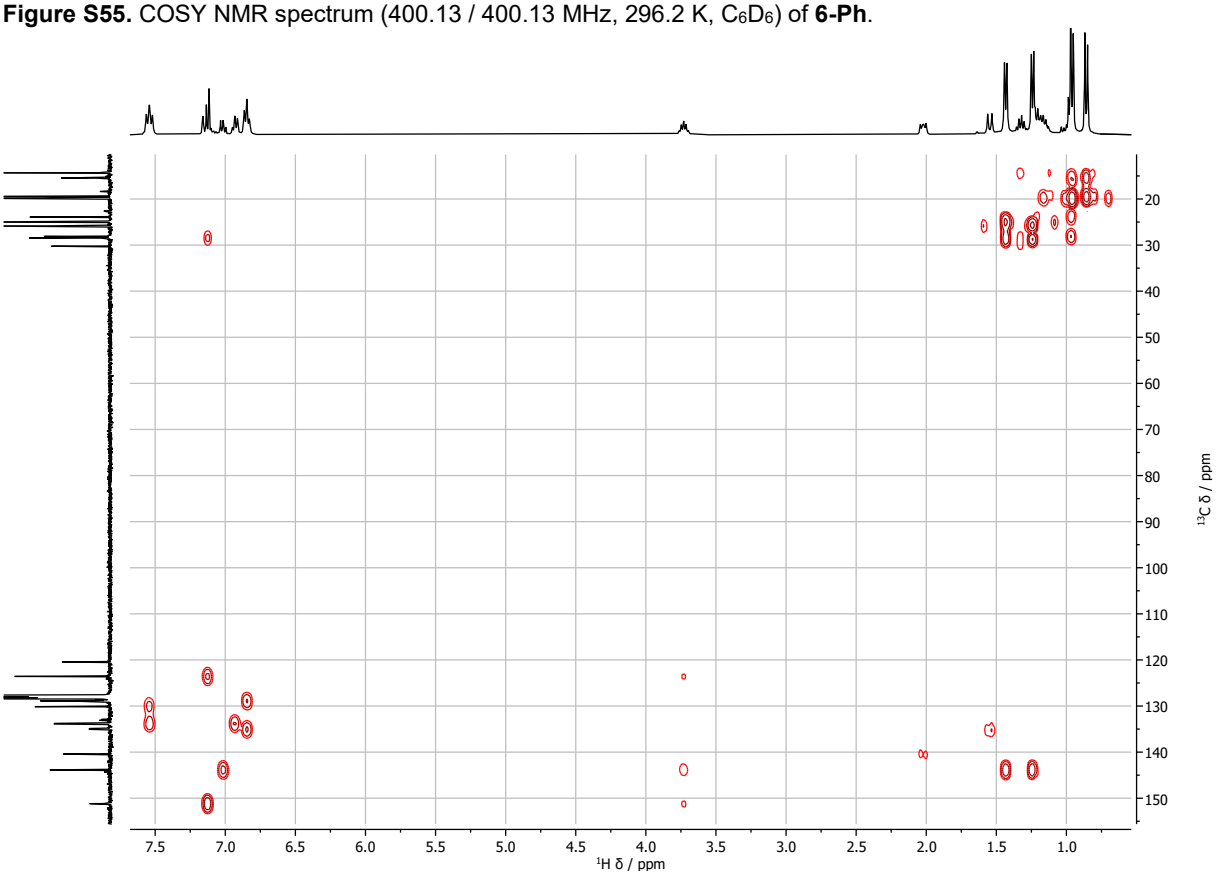


Figure S56. HMBC NMR spectrum (400.13 / 100.62 MHz, 296.1 K, C_6D_6) of **6-Ph**.

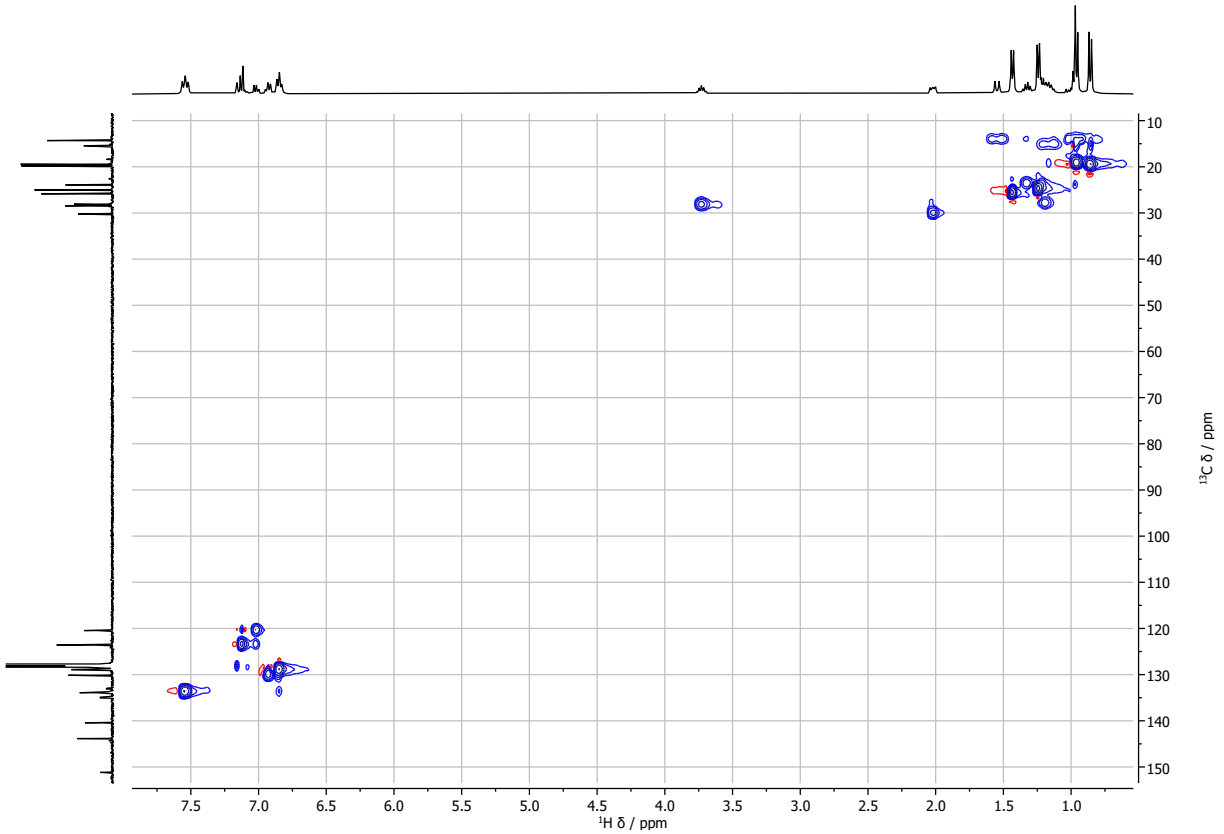


Figure S57. HSQC NMR spectrum (400.13 / 100.62 MHz, 296.2 K, C_6D_6) of **6-Ph**.

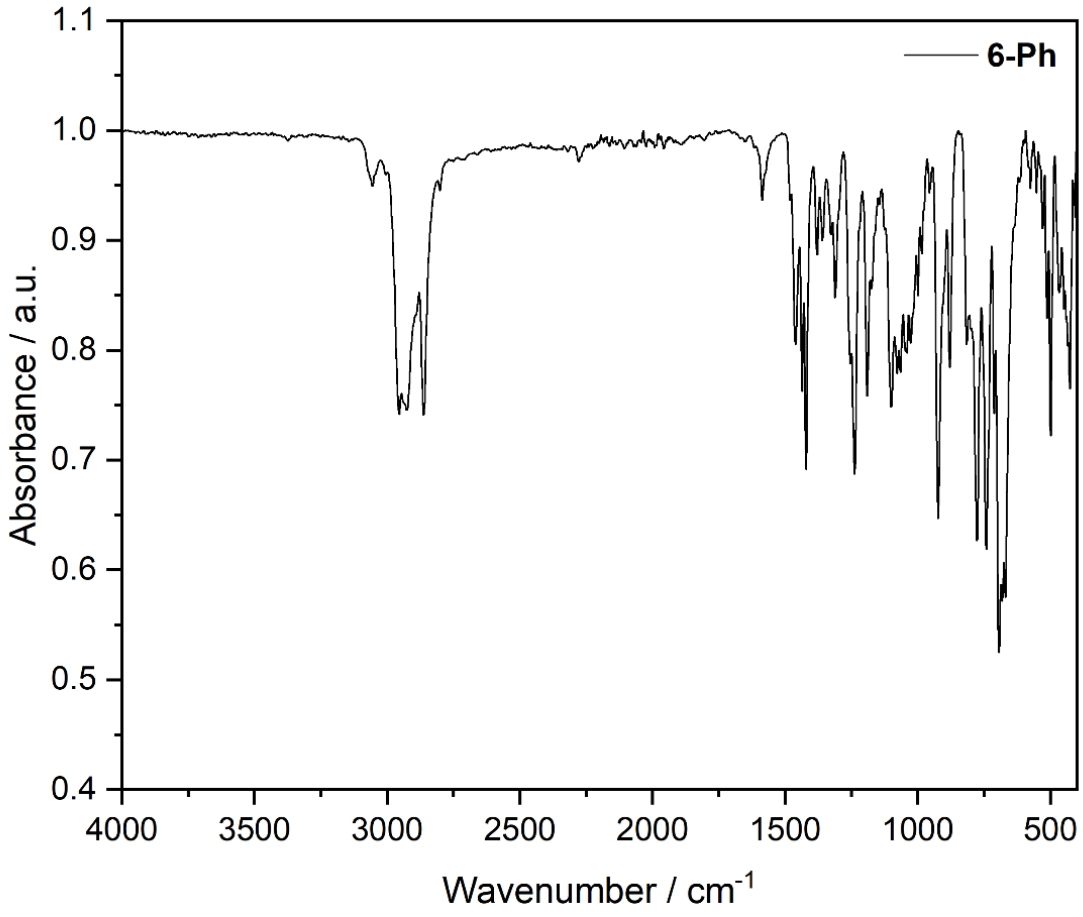


Figure S58. ATR-IR spectrum of **6-Ph**.

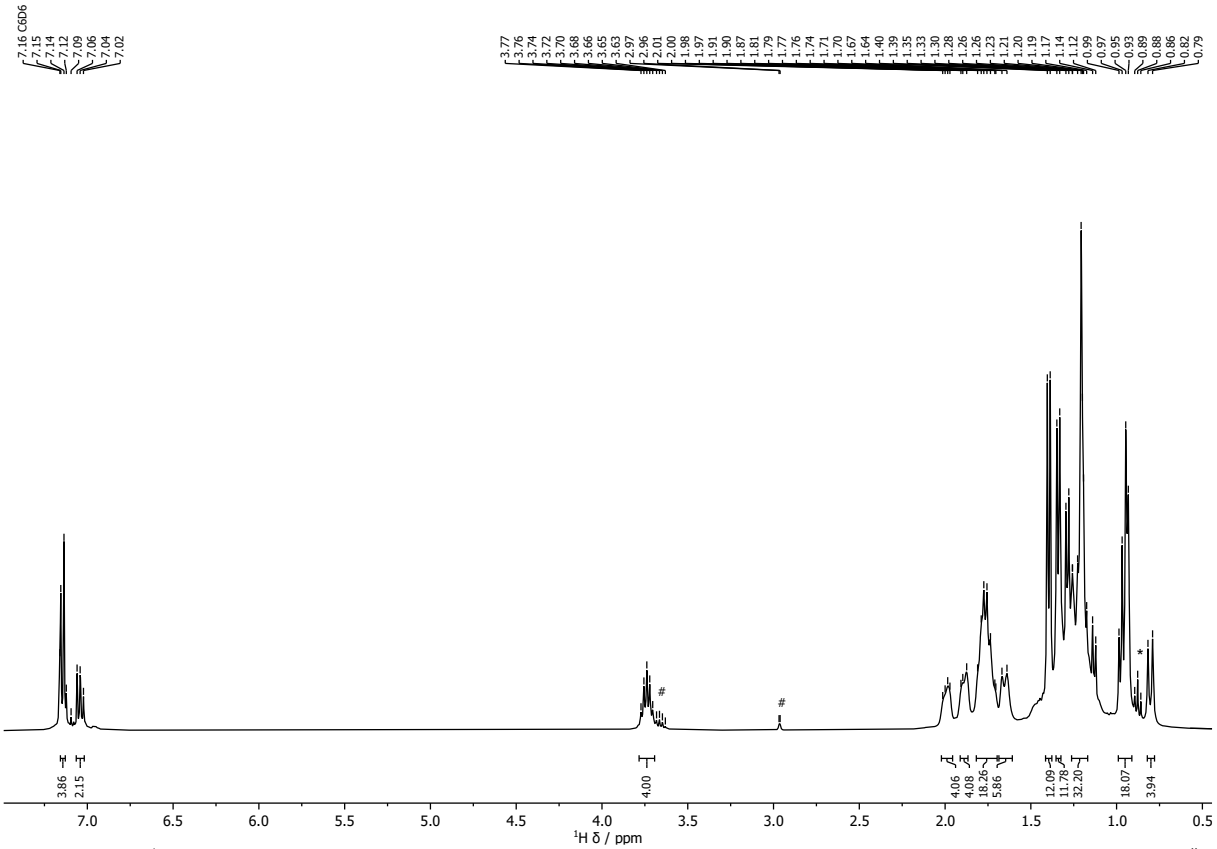


Figure S59. ^{1}H NMR spectrum (400.13 MHz, 294.8 K, C_6D_6) of **7**; * indicates small amounts of pentane, # indicates protonated ligand.

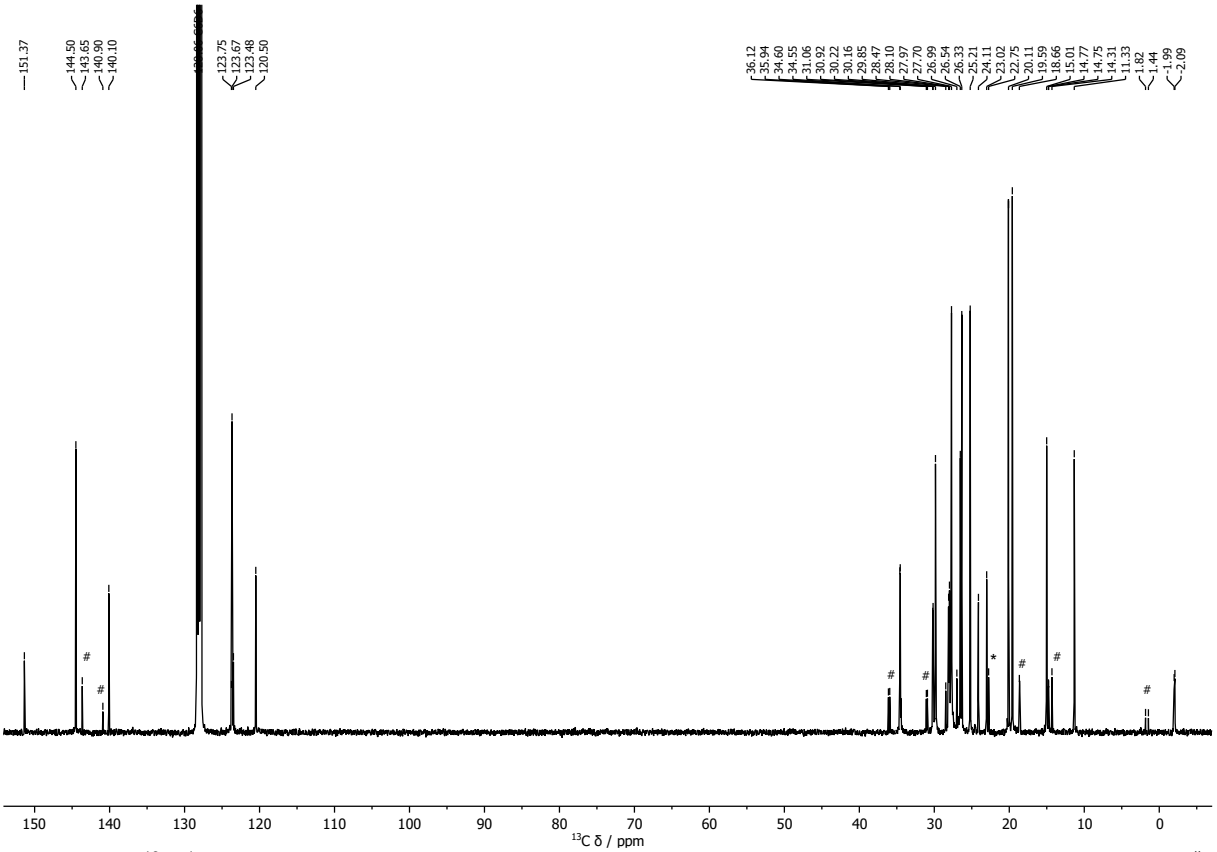


Figure S60. $^{13}C\{^{1}H\}$ NMR spectrum (100.62 MHz, 295.9 K, C_6D_6) of **7**; * indicates small amounts of pentane, # indicates protonated ligand.

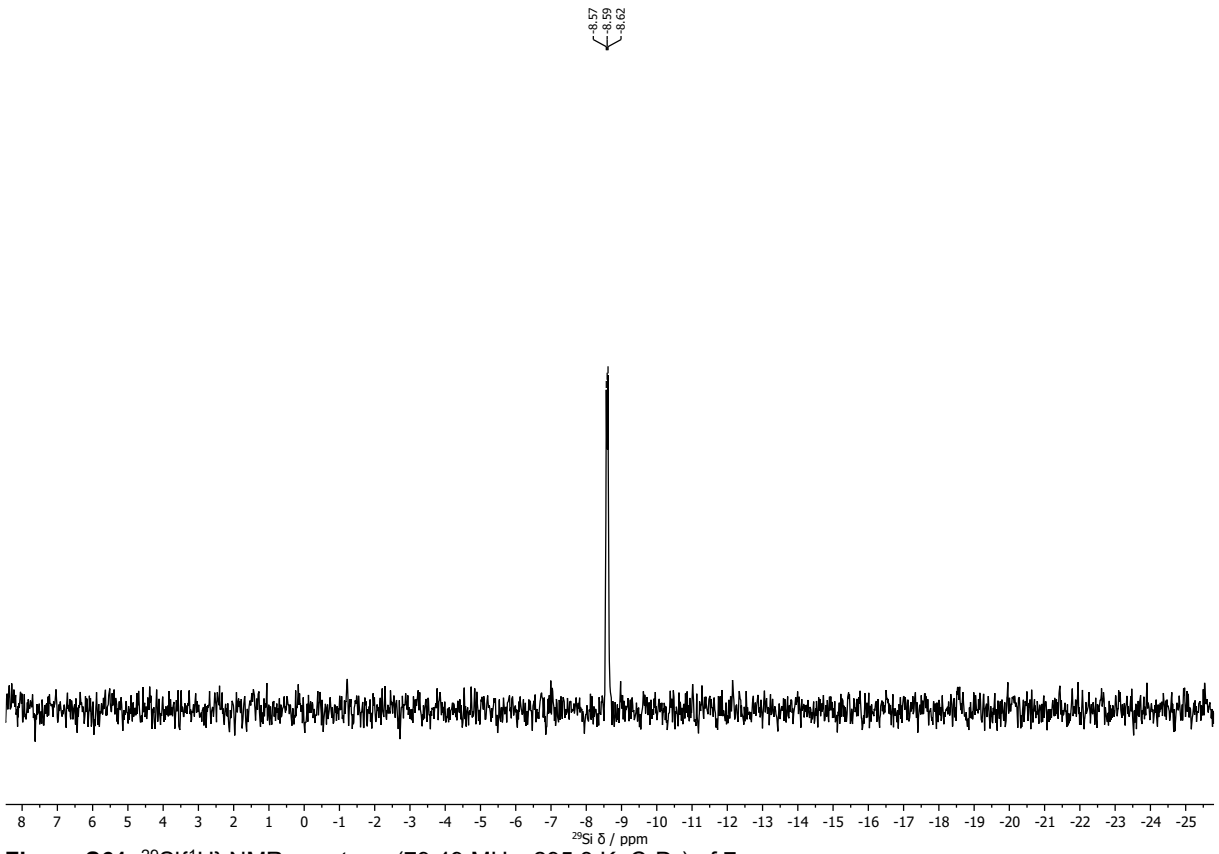


Figure S61. $^{29}Si\{^{1}H\}$ NMR spectrum (79.49 MHz, 295.3 K, C_6D_6) of **7**.

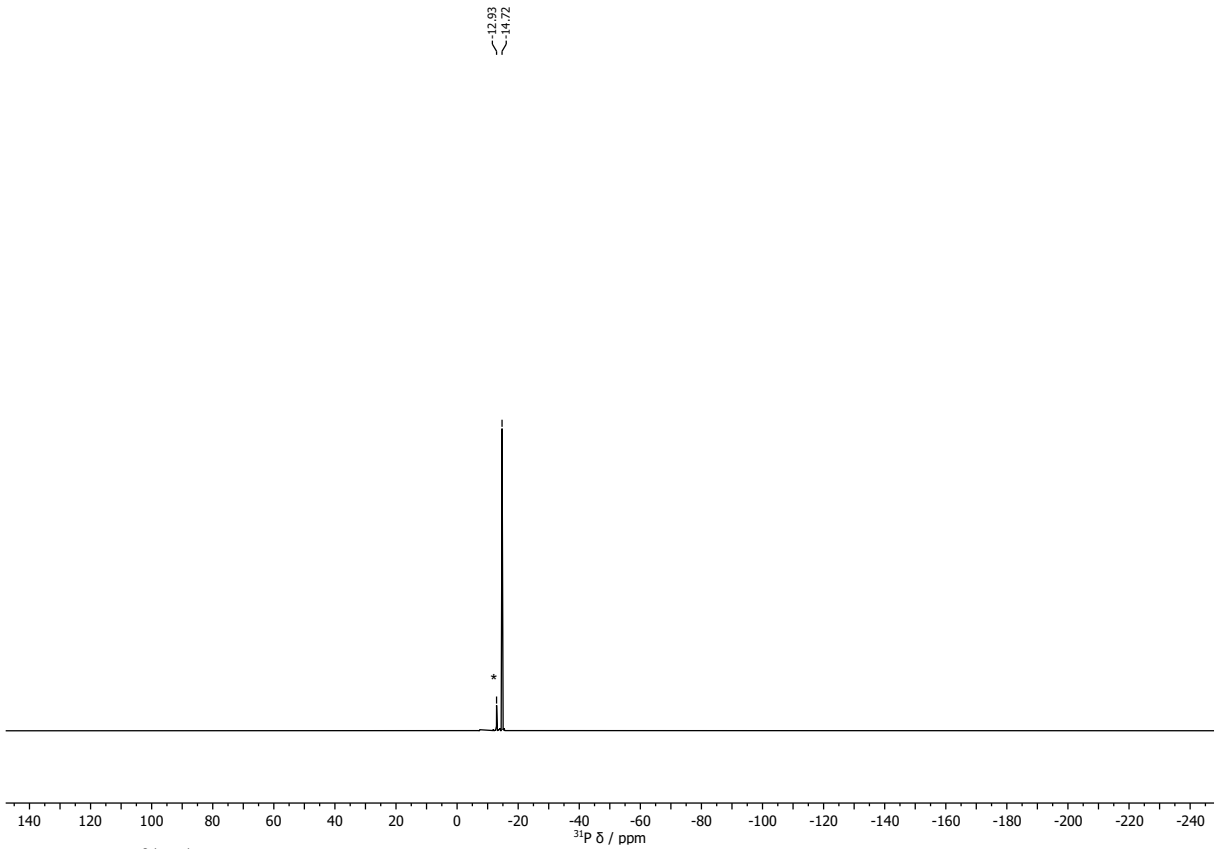


Figure S62. $^{31}P\{^{1}H\}$ NMR spectrum (161.97 MHz, 295.6 K, C_6D_6) of **7**; * indicates protonated ligand.

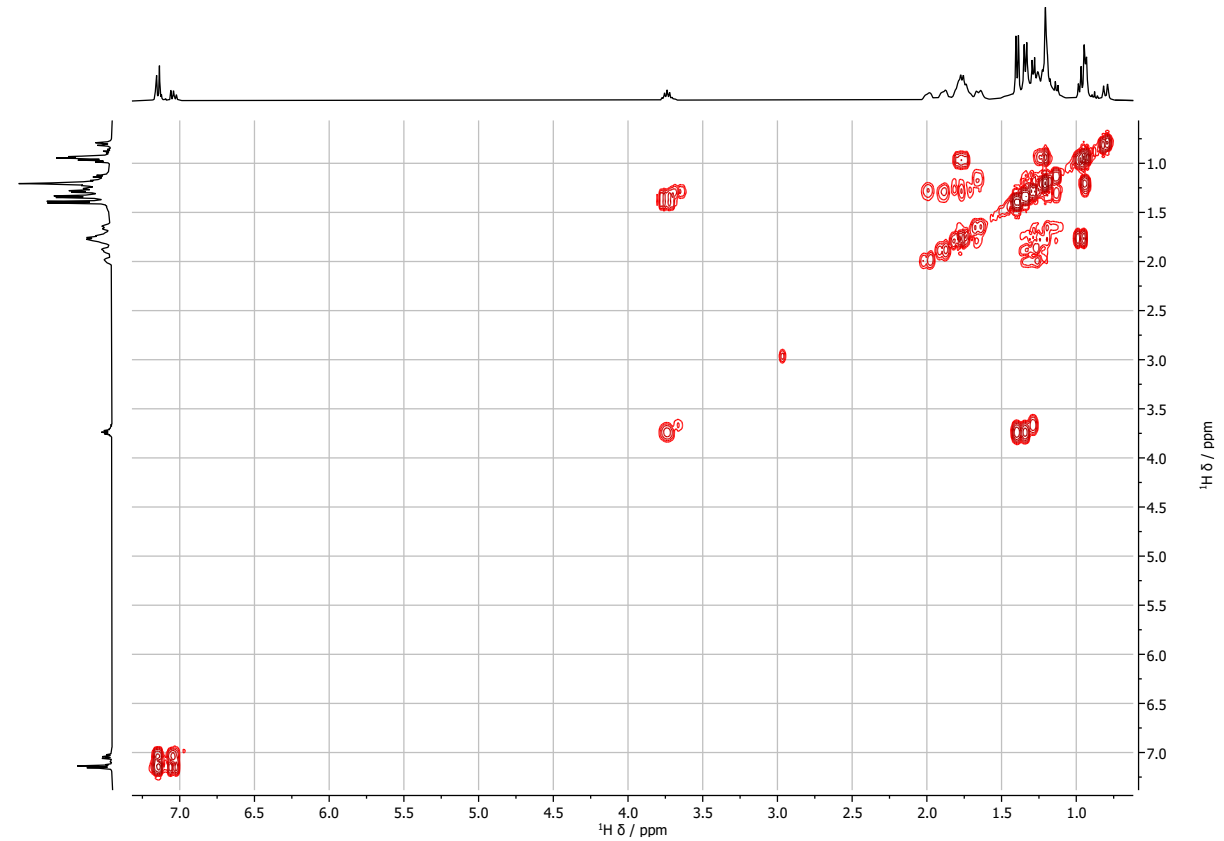


Figure S63. COSY NMR spectrum (400.13 / 400.13 MHz, 295.2 K, C_6D_6) of **7**.

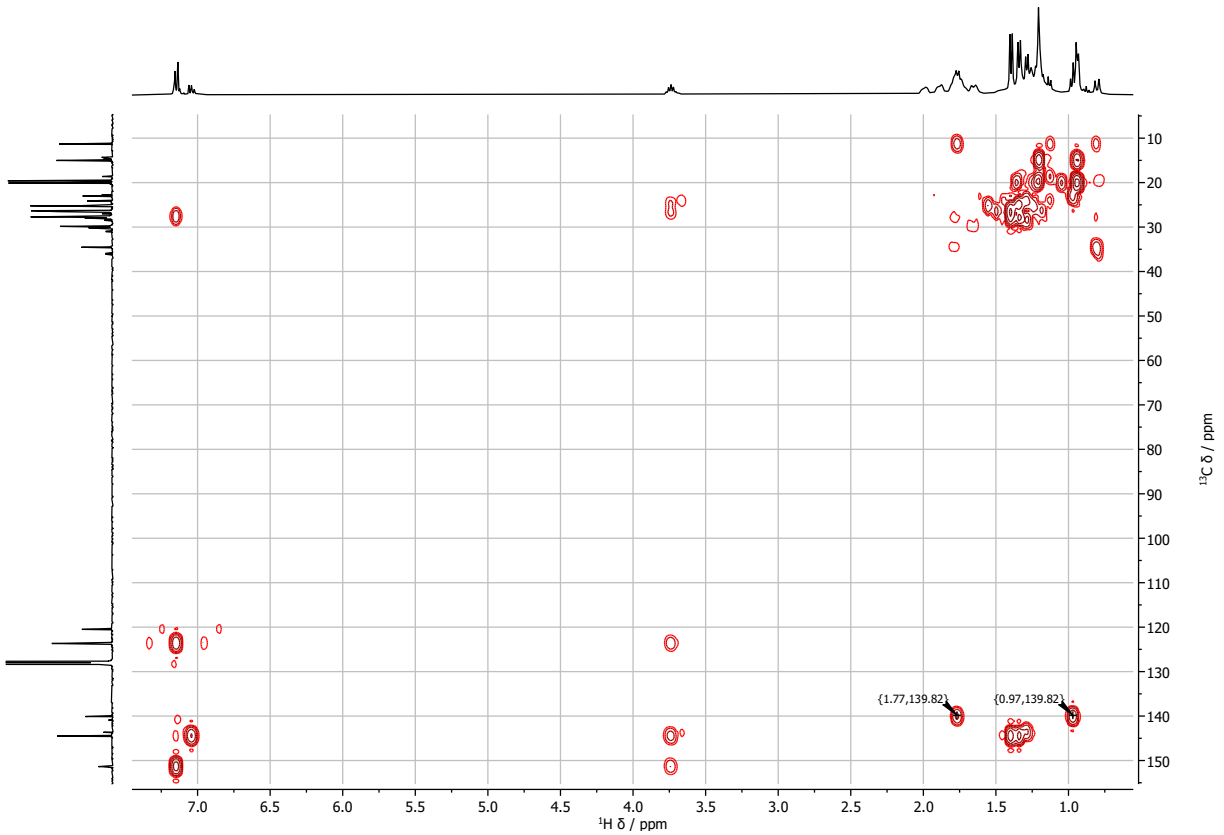


Figure S64. HMBC NMR spectrum (400.13 / 100.62 MHz, 295.1 K, C_6D_6) of **7**.

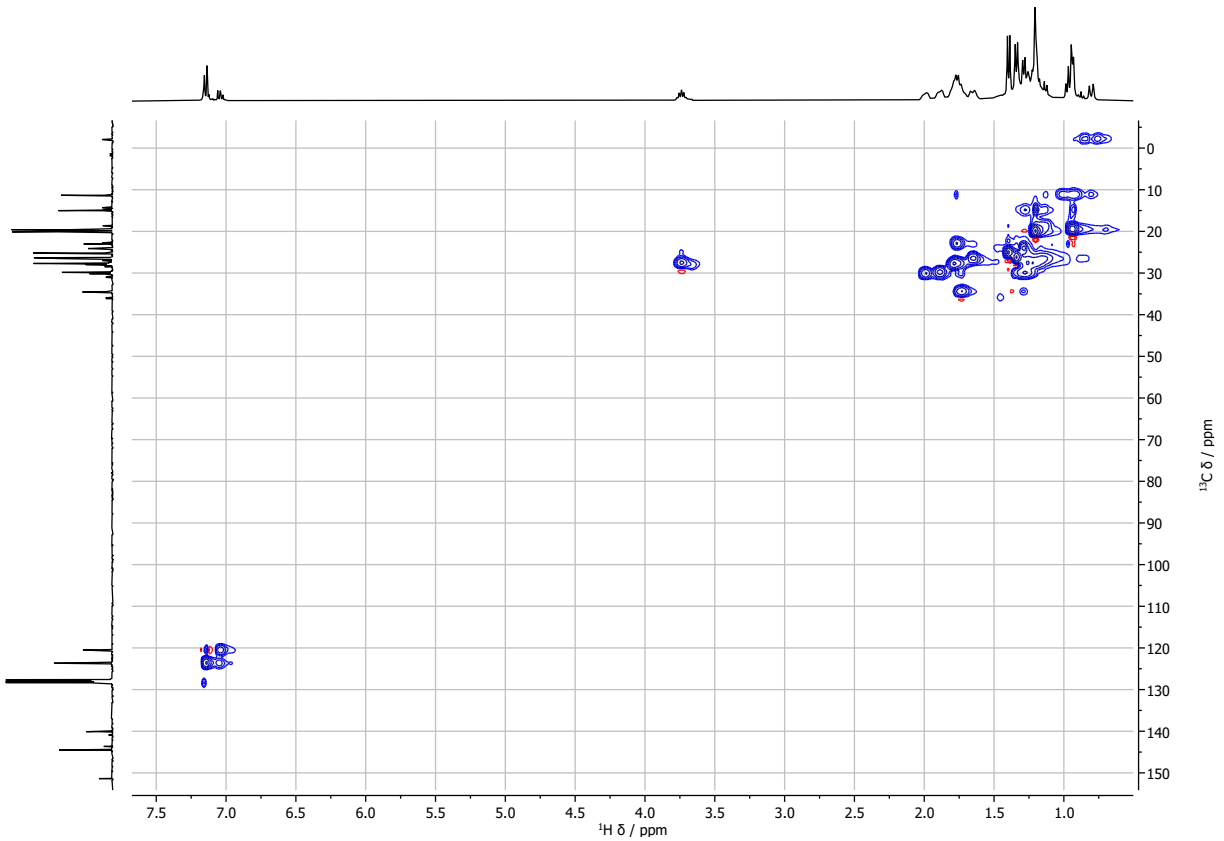


Figure S65. HSQC NMR spectrum (400.13 / 100.62 MHz, 295.2 K, C_6D_6) of **7**.

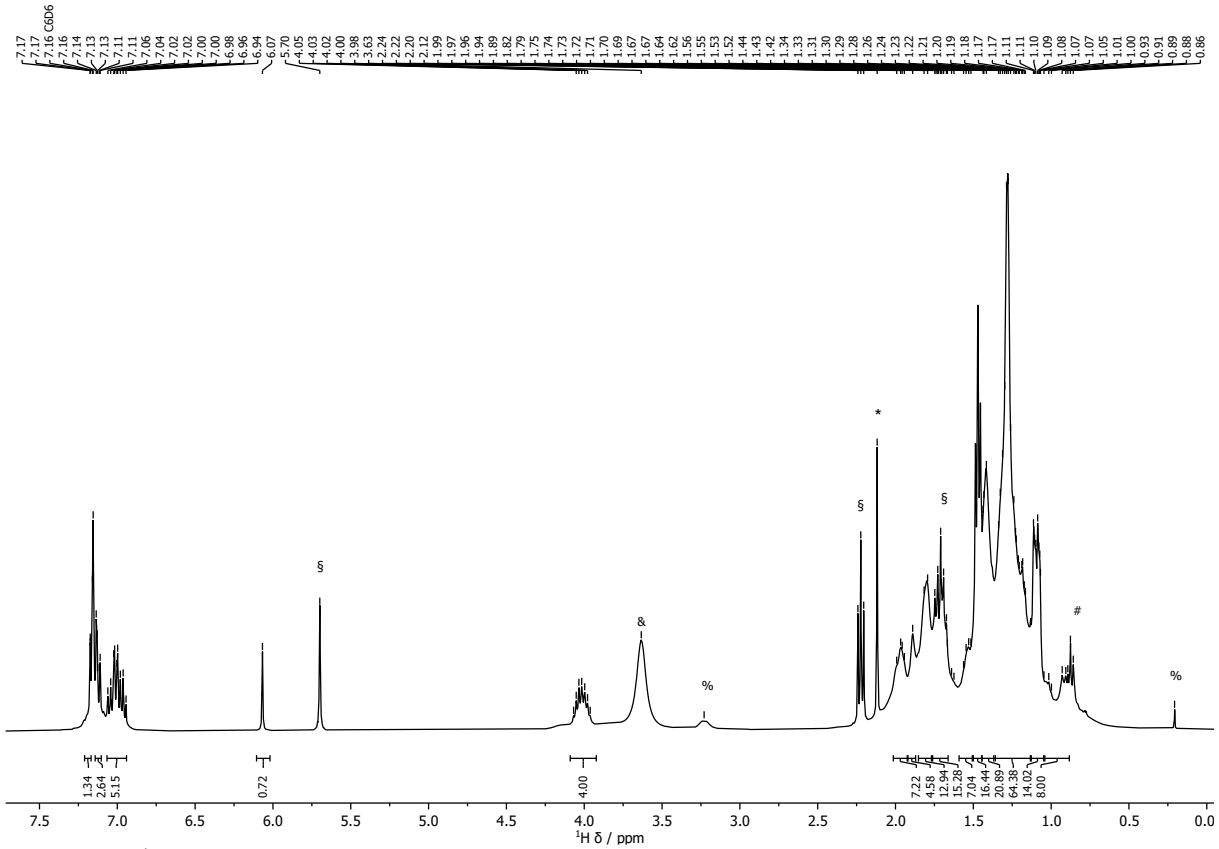


Figure S66. ^{1}H NMR spectrum (400.13 MHz, 294.9 K, C_6D_6) of **8** before removing all volatiles; * indicates small amounts of toluene, # indicates small amounts of pentane, & indicates small amounts of THF, § marks free c-C_5H_8, % marks unknown impurities.

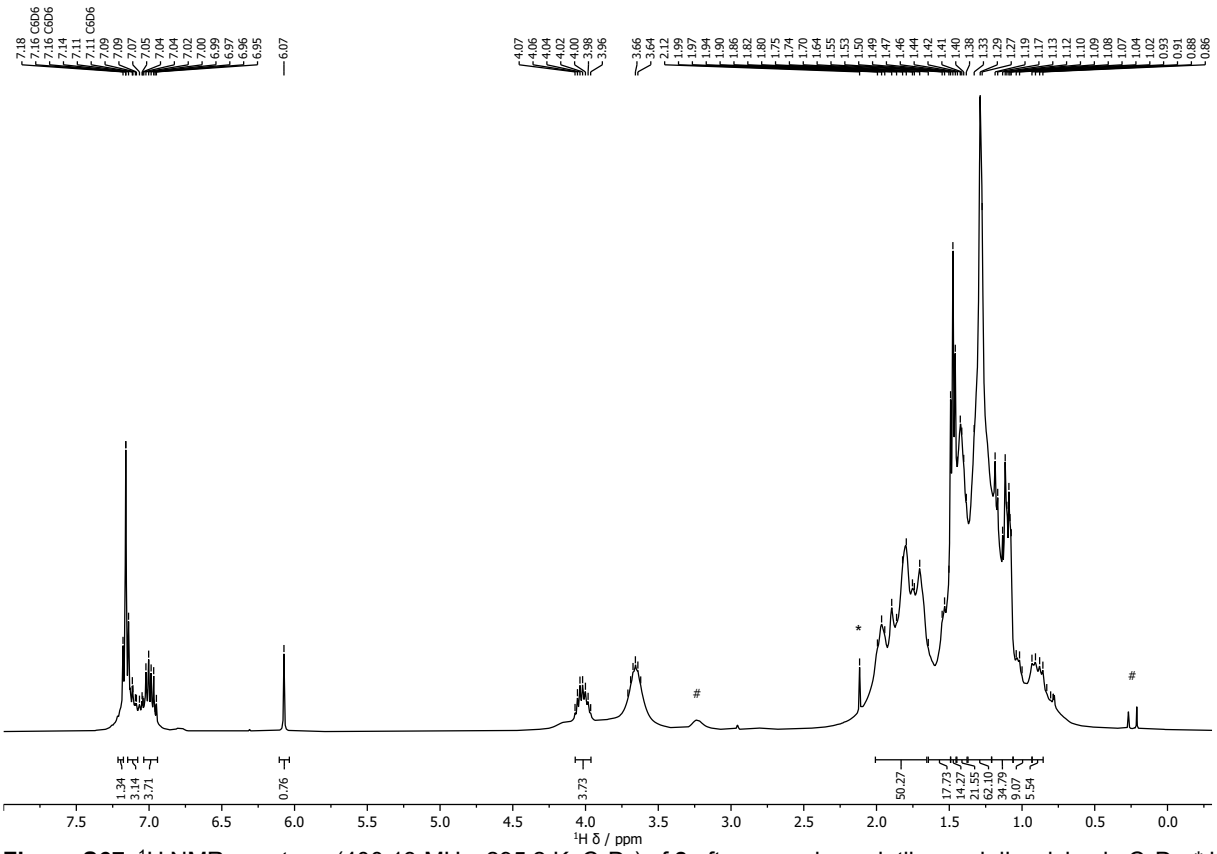


Figure S67. ^{1}H NMR spectrum (400.13 MHz, 295.2 K, C_6D_6) of **8** after removing volatiles and dissolving in C_6D_6; * indicates small amounts of toluene, # marks unknown impurities.

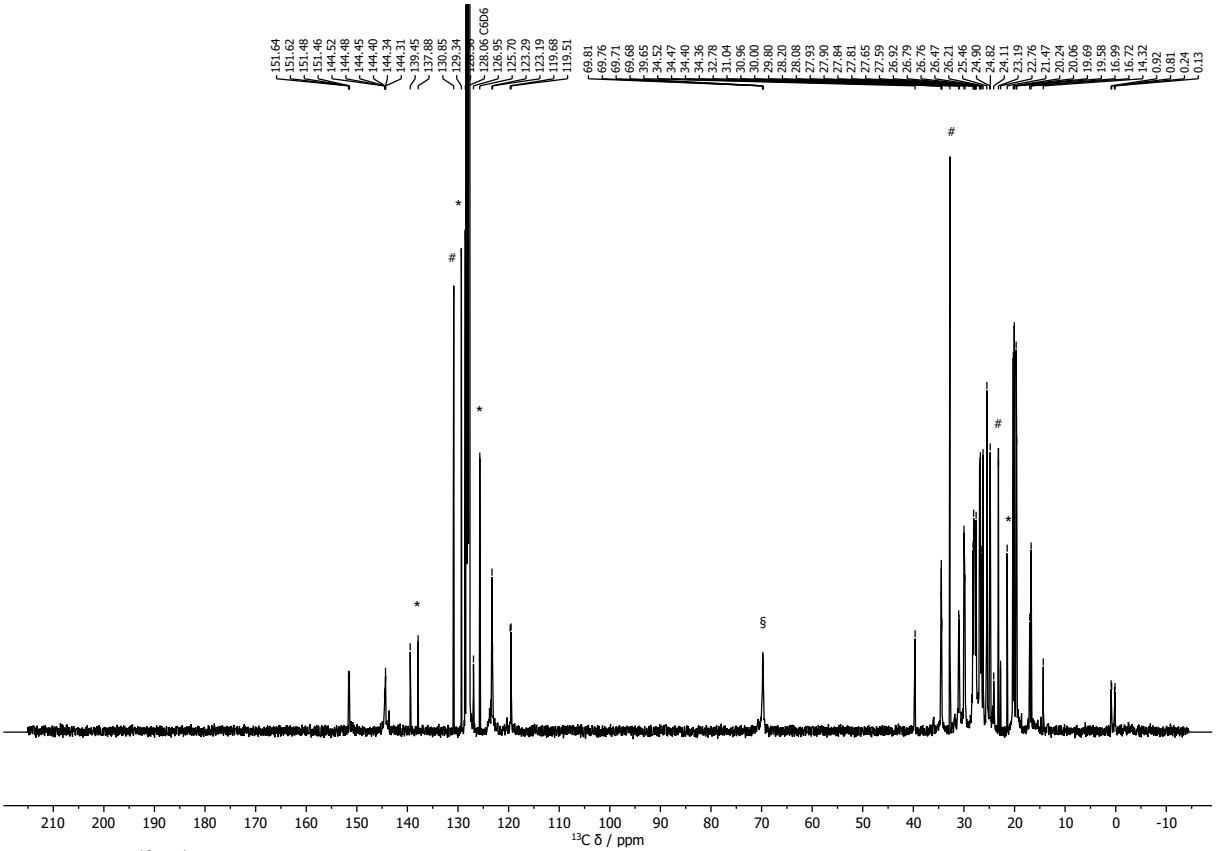


Figure S68. $^{13}C\{^{1}H\}$ NMR spectrum (100.62 MHz, 295.5 K, C_6D_6) of **8** before removing all volatiles; *indicates small amounts of toluene, #indicates free c-C_5H_8, §marks THF.

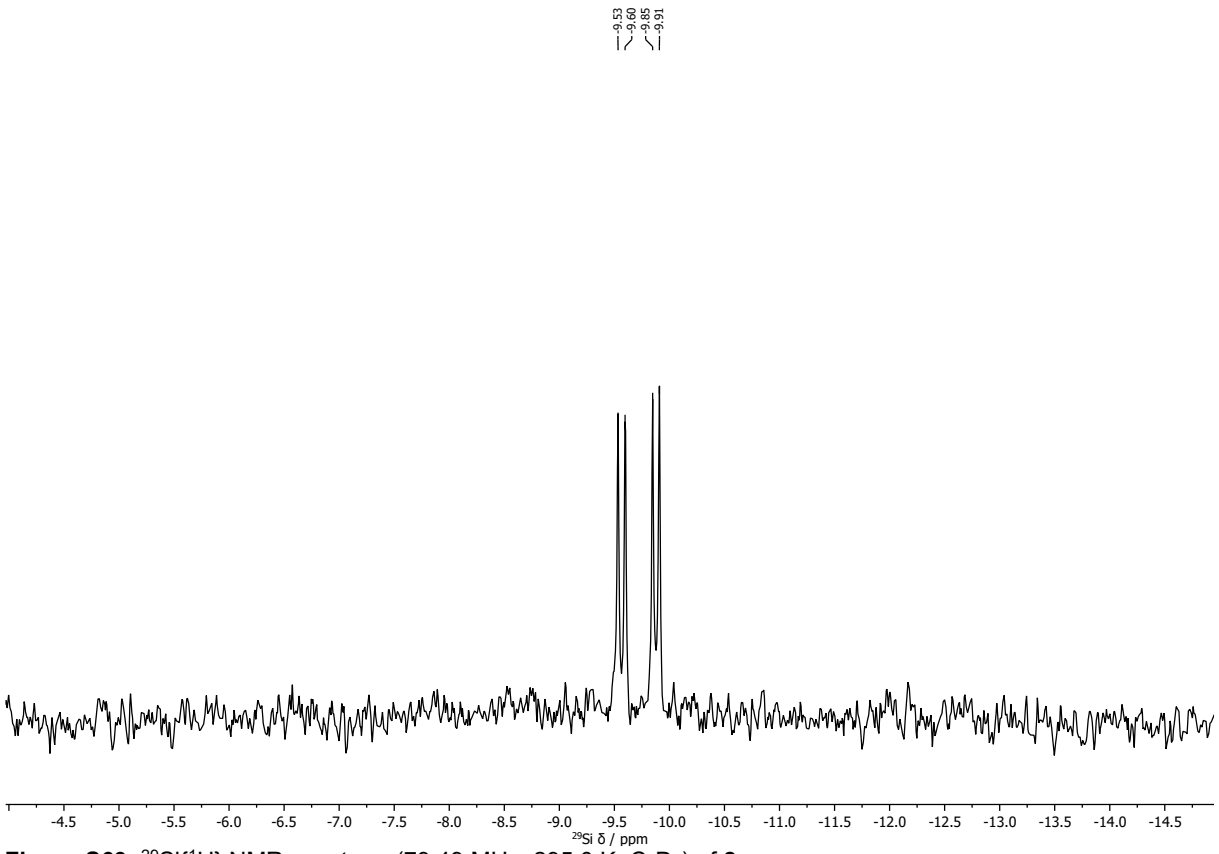


Figure S69. $^{29}Si\{^{1}H\}$ NMR spectrum (79.49 MHz, 295.0 K, C_6D_6) of **8**.

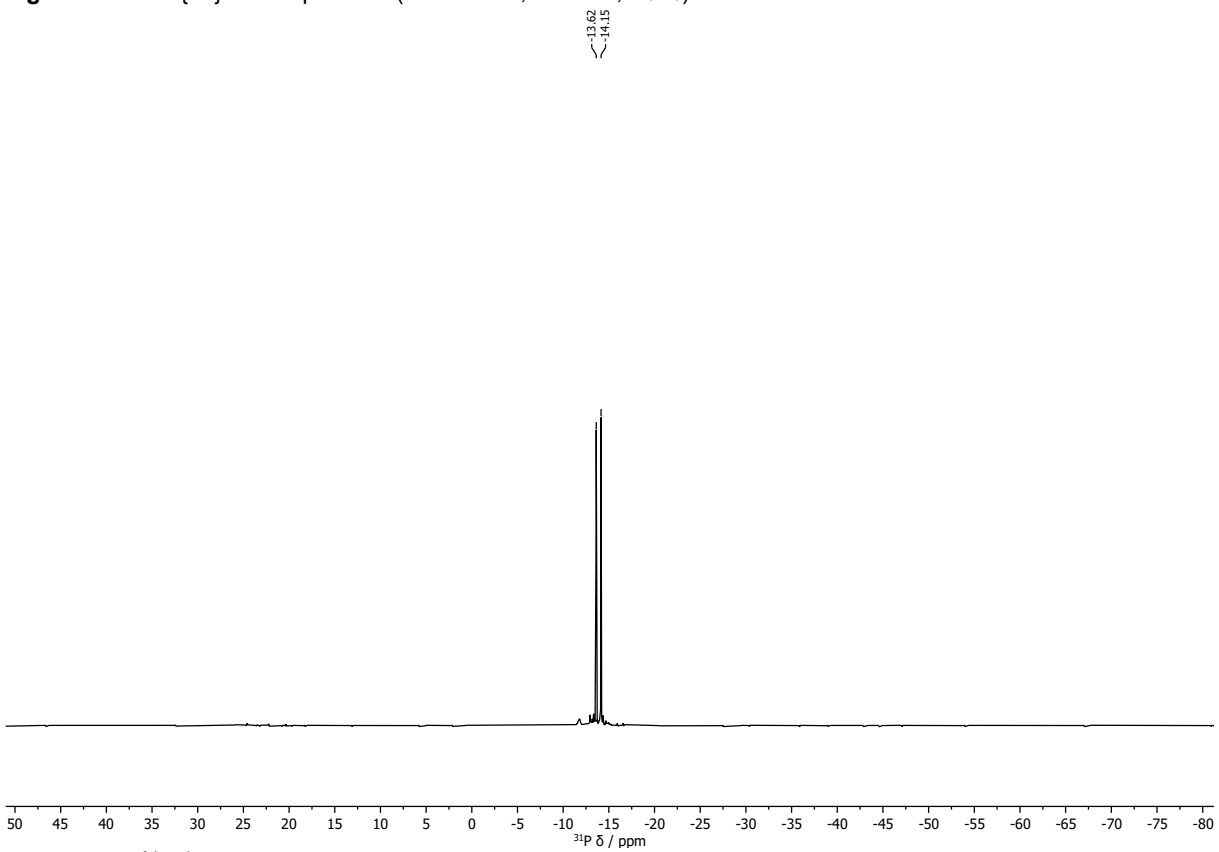


Figure S70. $^{31}P\{^{1}H\}$ NMR spectrum (161.97 MHz, 295.2 K, C_6D_6) of **8**.

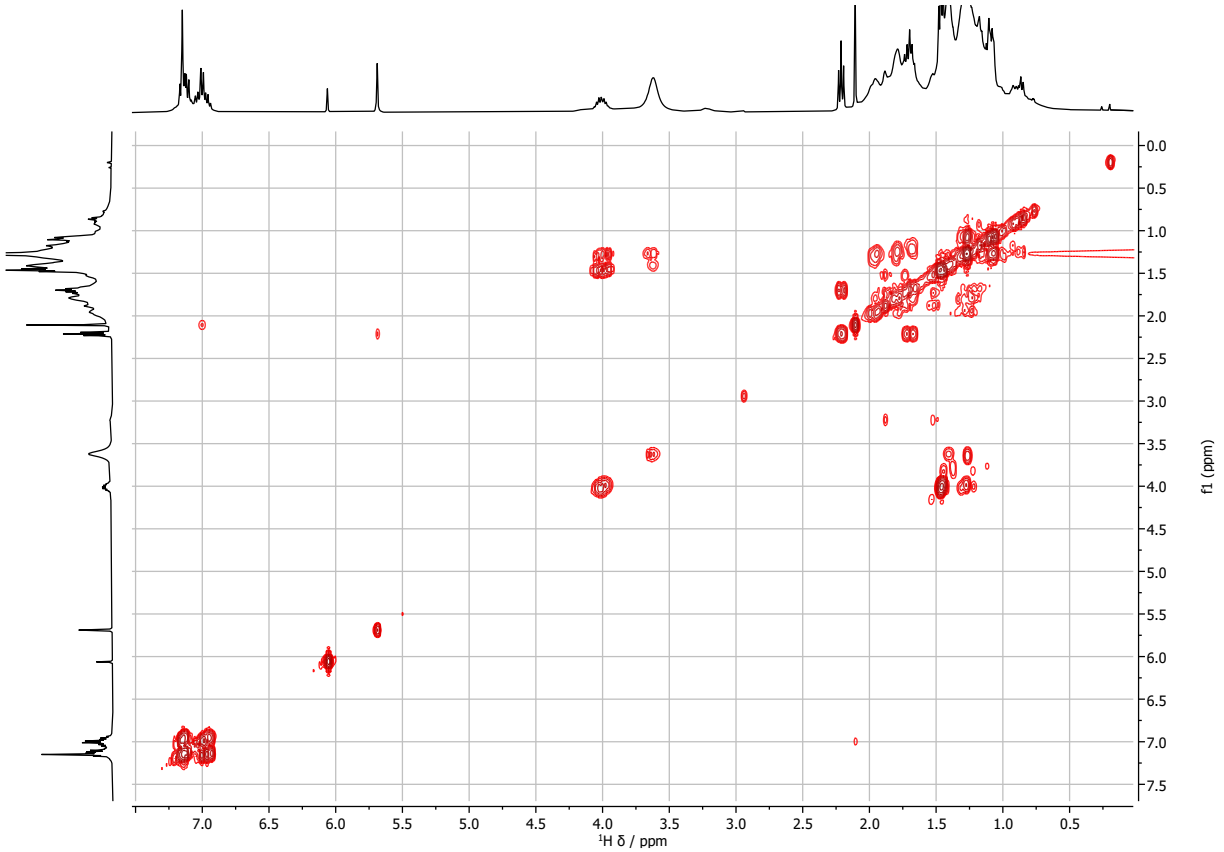


Figure S71. COSY NMR spectrum (400.13 / 400.13 MHz, 294.9 K, C_6D_6) of **8** before removing all volatiles.

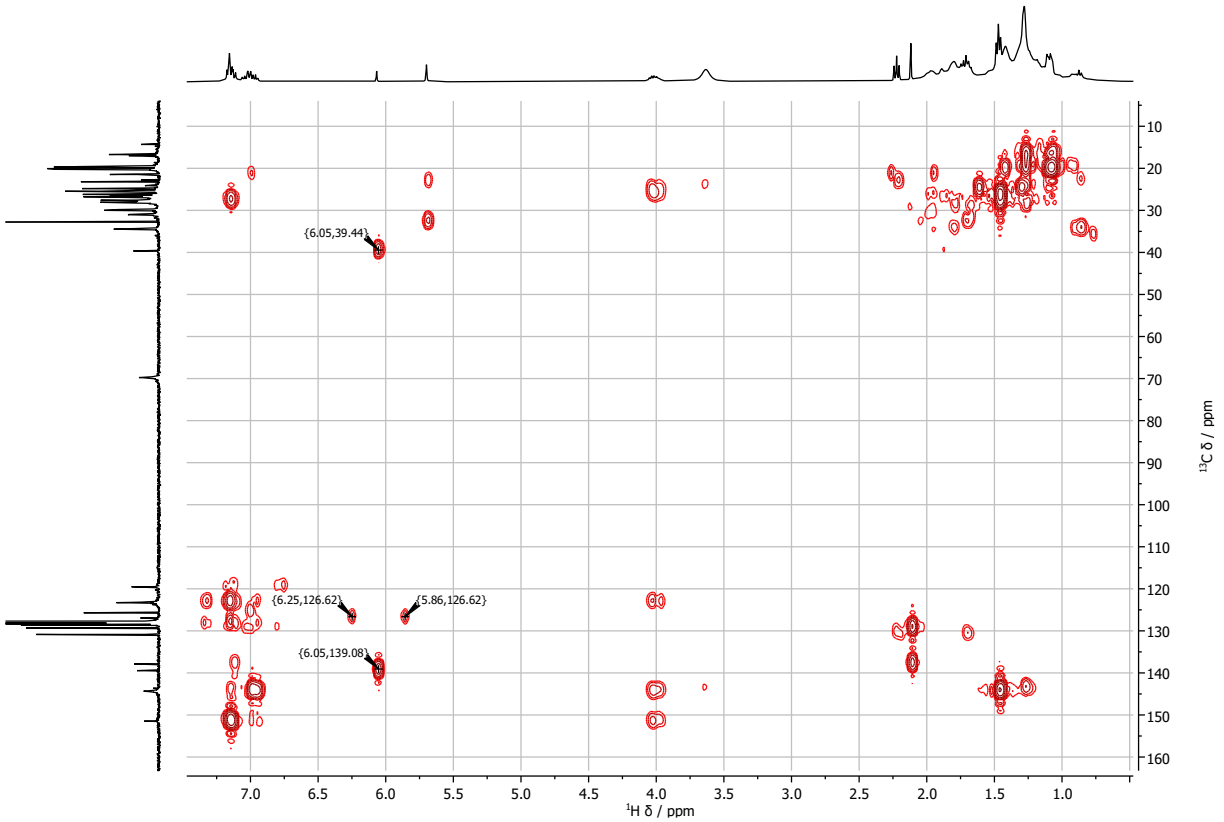


Figure S72. HMBC NMR spectrum (400.13 / 100.62 MHz, 294.8 K, C_6D_6) of **8** before removing all volatiles.

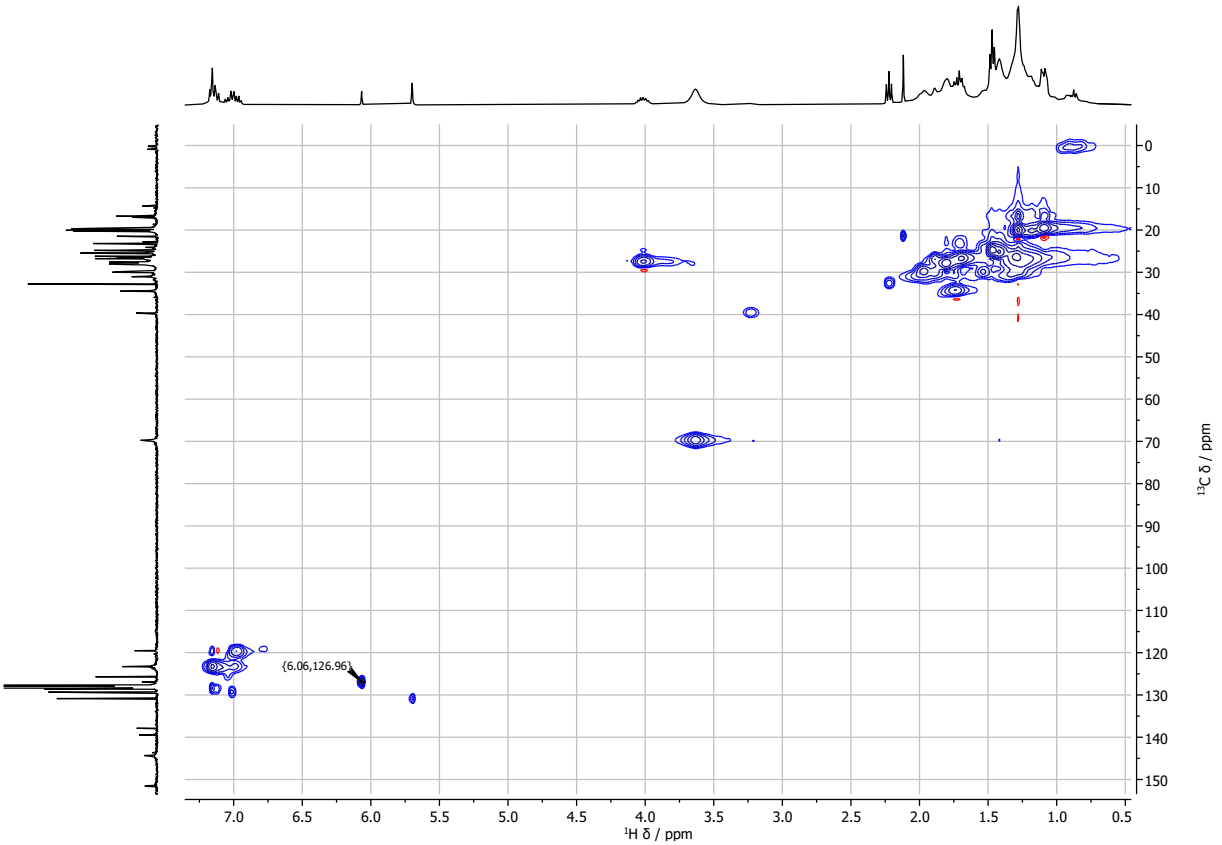


Figure S73. HSQC NMR spectrum (400.13 / 100.62 MHz, 294.9 K, C_6D_6) of **8** before removing all volatiles.

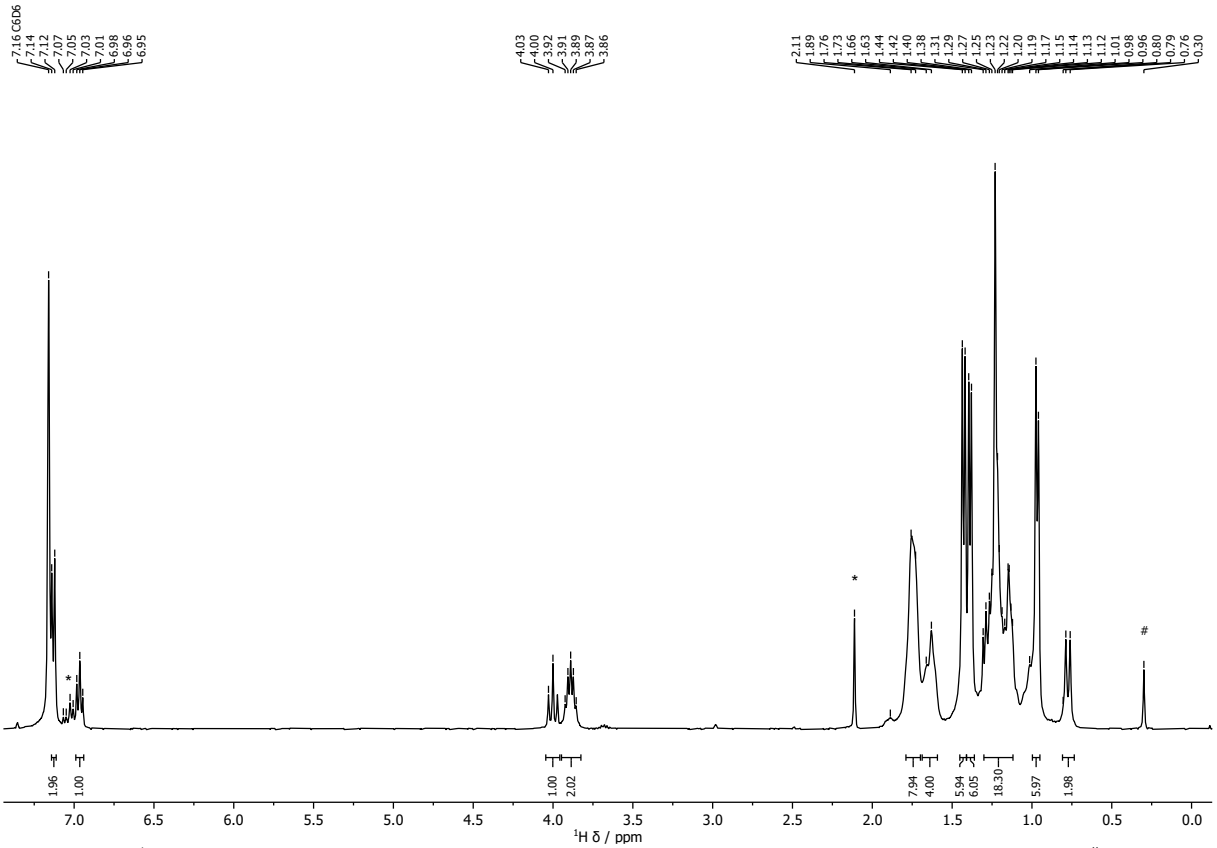


Figure S74. ^{1}H NMR spectrum (400.13 MHz, 294.8 K, C_6D_6) of **9**; * indicates small amounts of toluene, # marks an unknown impurity.

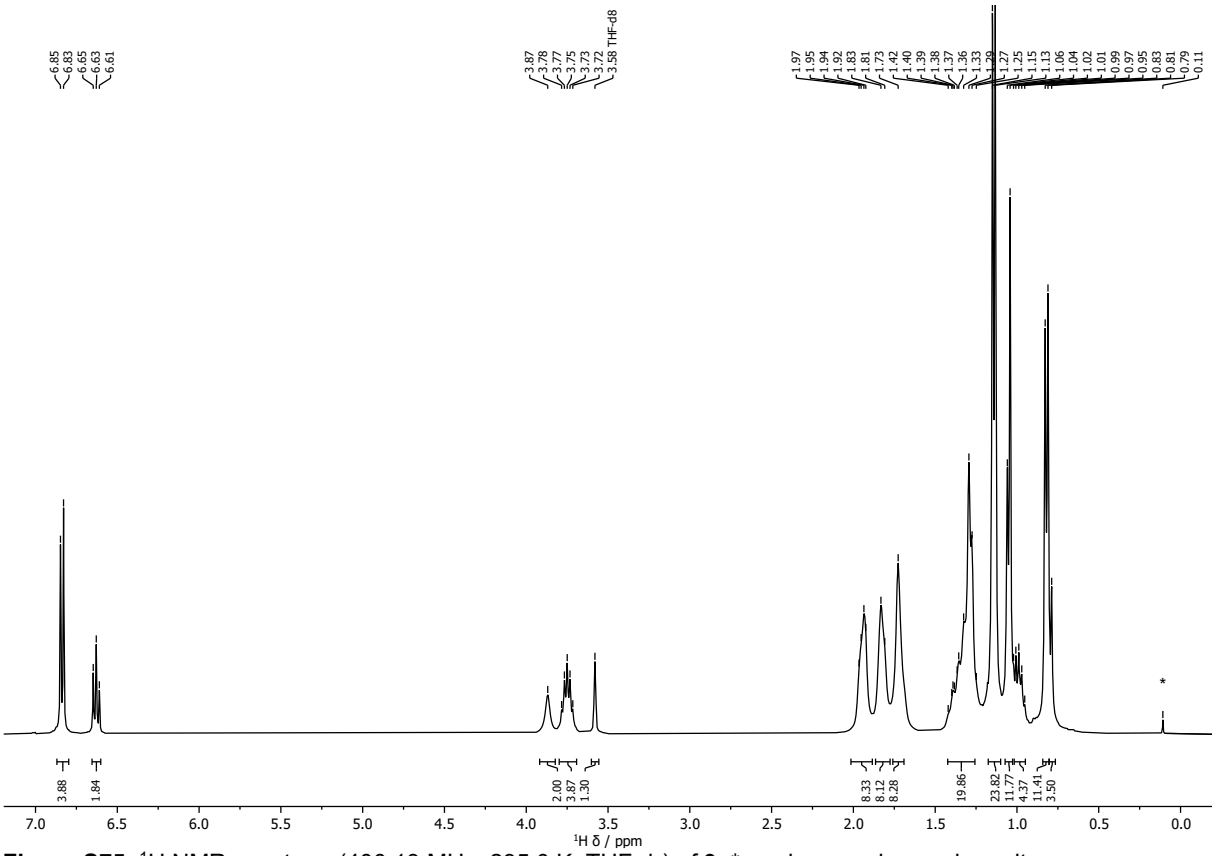


Figure S75. ^{1}H NMR spectrum (400.13 MHz, 295.0 K, THF-d_8) of **9**; * marks an unknown impurity.

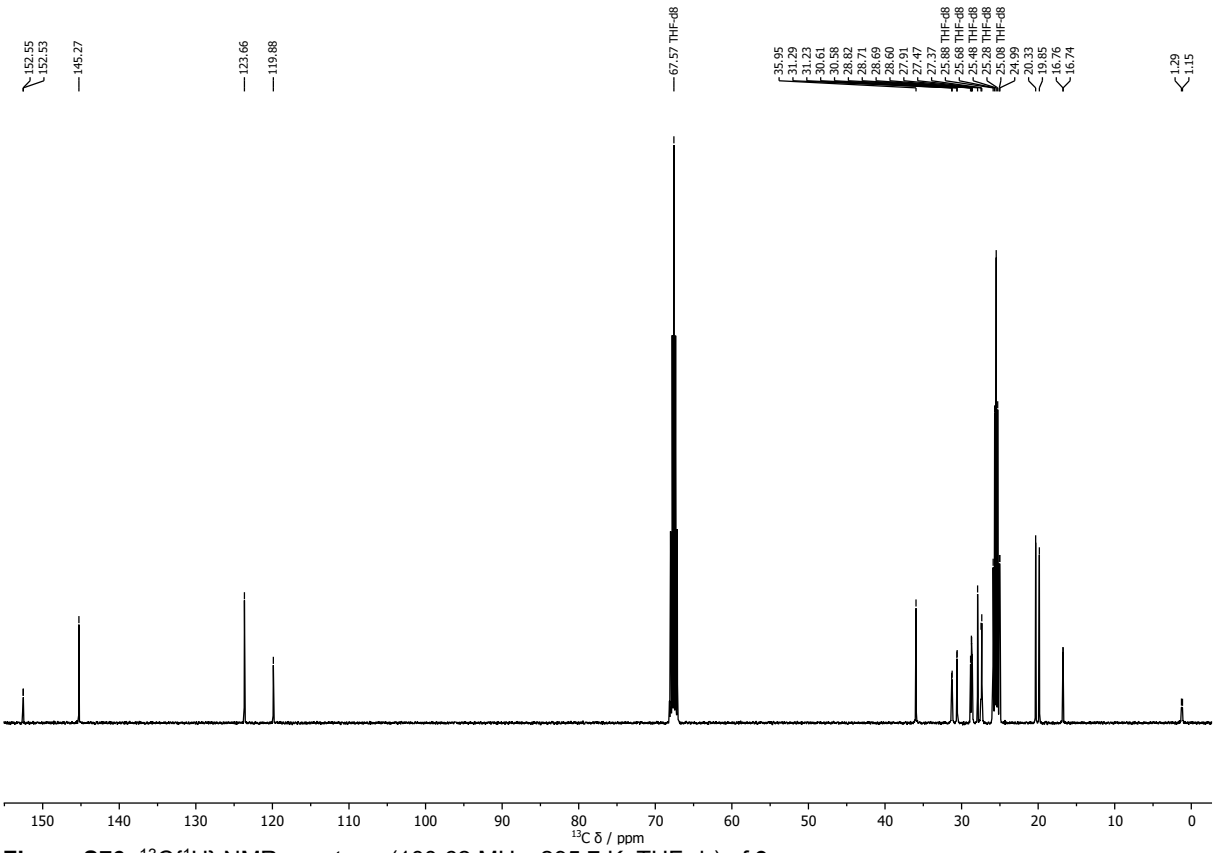


Figure S76. ^{13}C{^{1}H} NMR spectrum (100.62 MHz, 295.7 K, THF-d_8) of **9**.

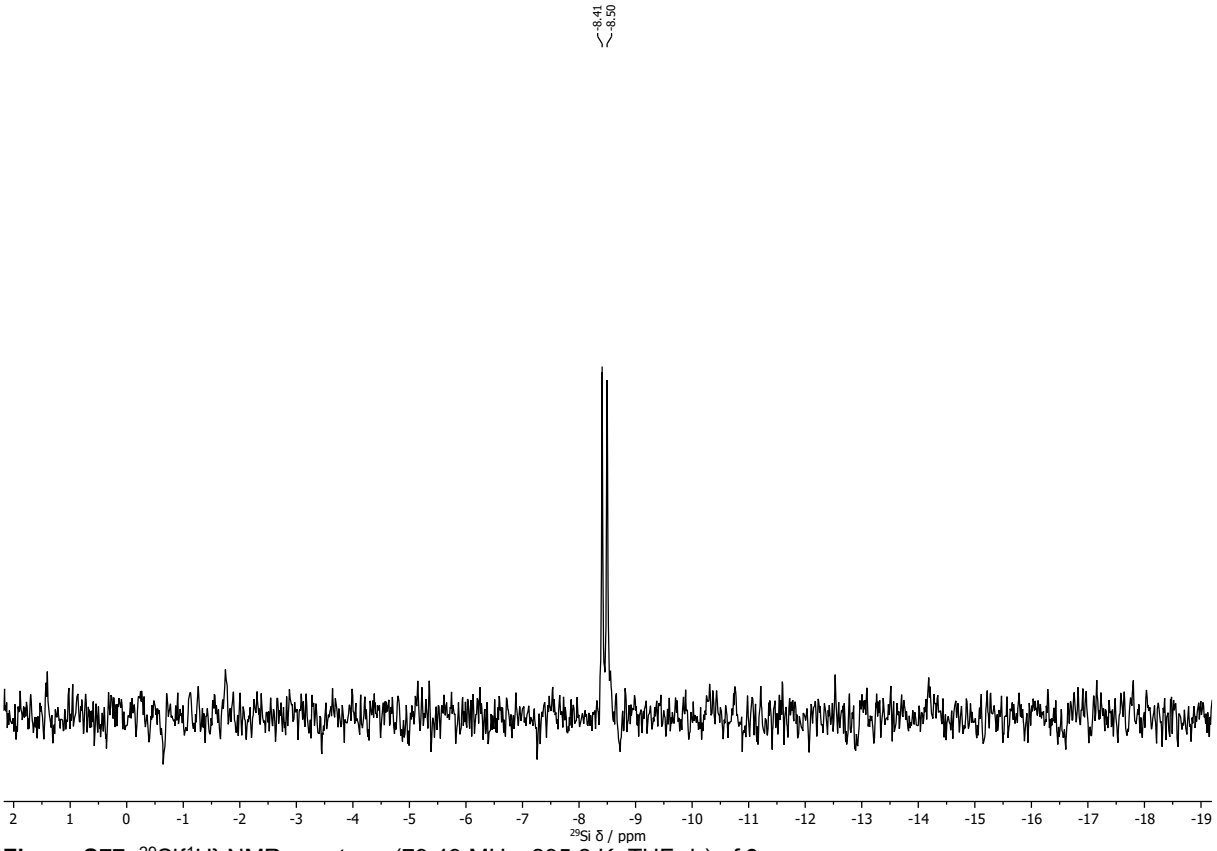


Figure S77. $^{29}Si\{^{1}H\}$ NMR spectrum (79.49 MHz, 295.2 K, THF-d_8) of **9**.

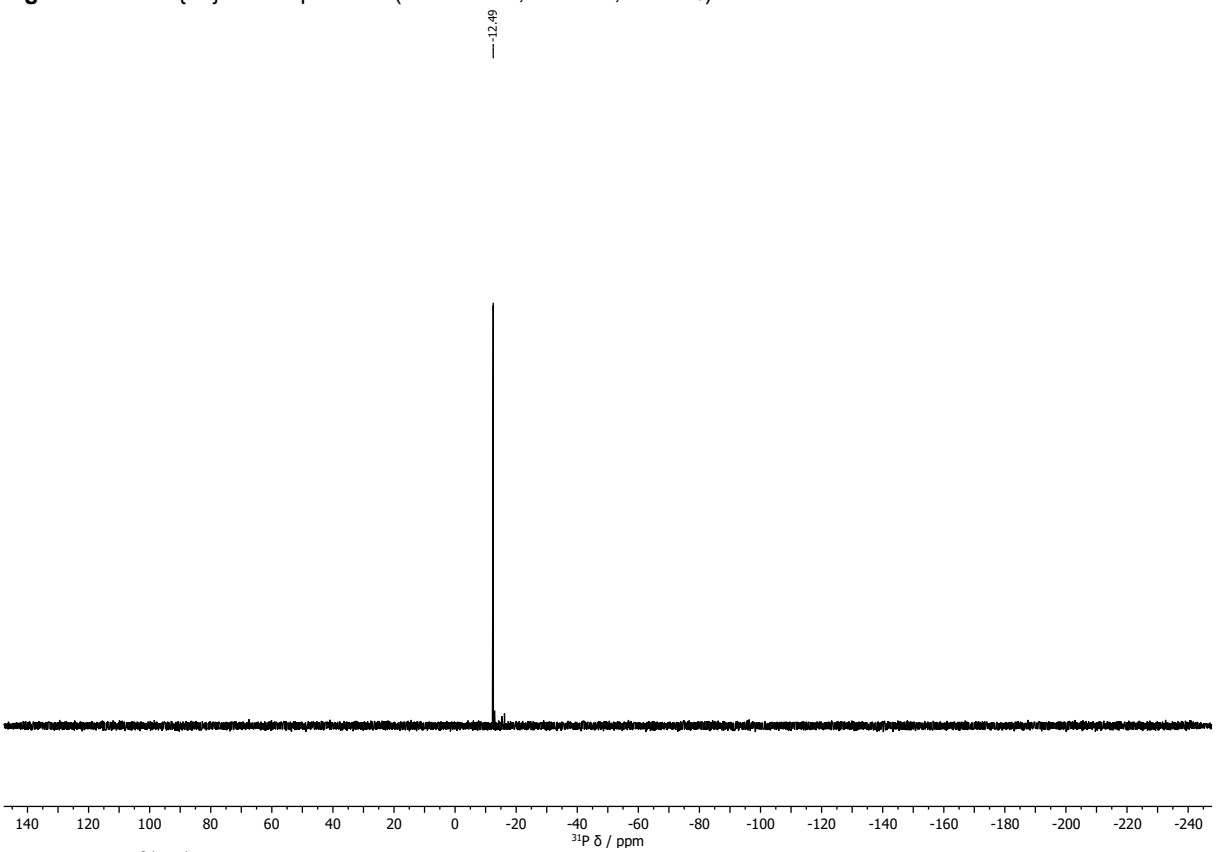


Figure S78. $^{31}P\{^{1}H\}$ NMR spectrum (161.97 MHz, 294.7 K, C_6D_6) of **9**.

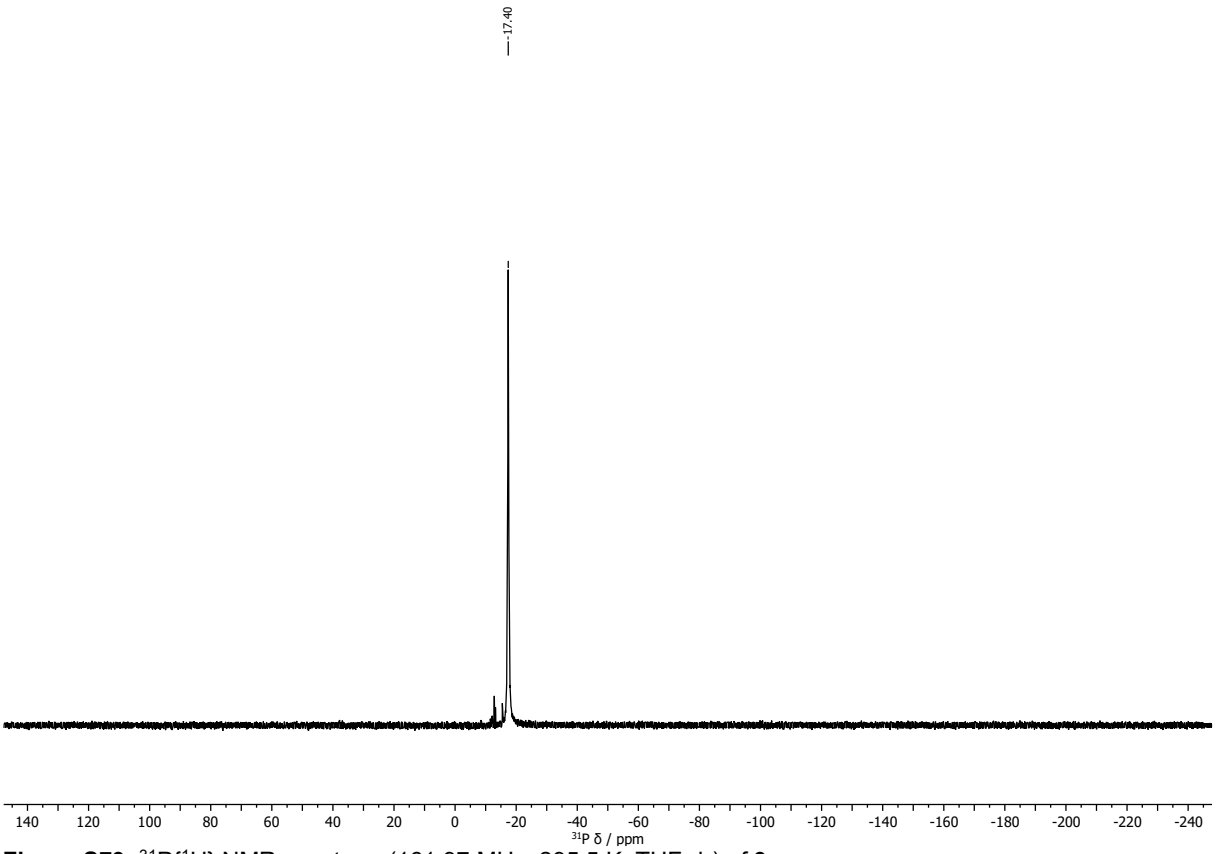


Figure S79. $^{31}P\{^{1}H\}$ NMR spectrum (161.97 MHz, 295.5 K, THF-d_8) of **9**.

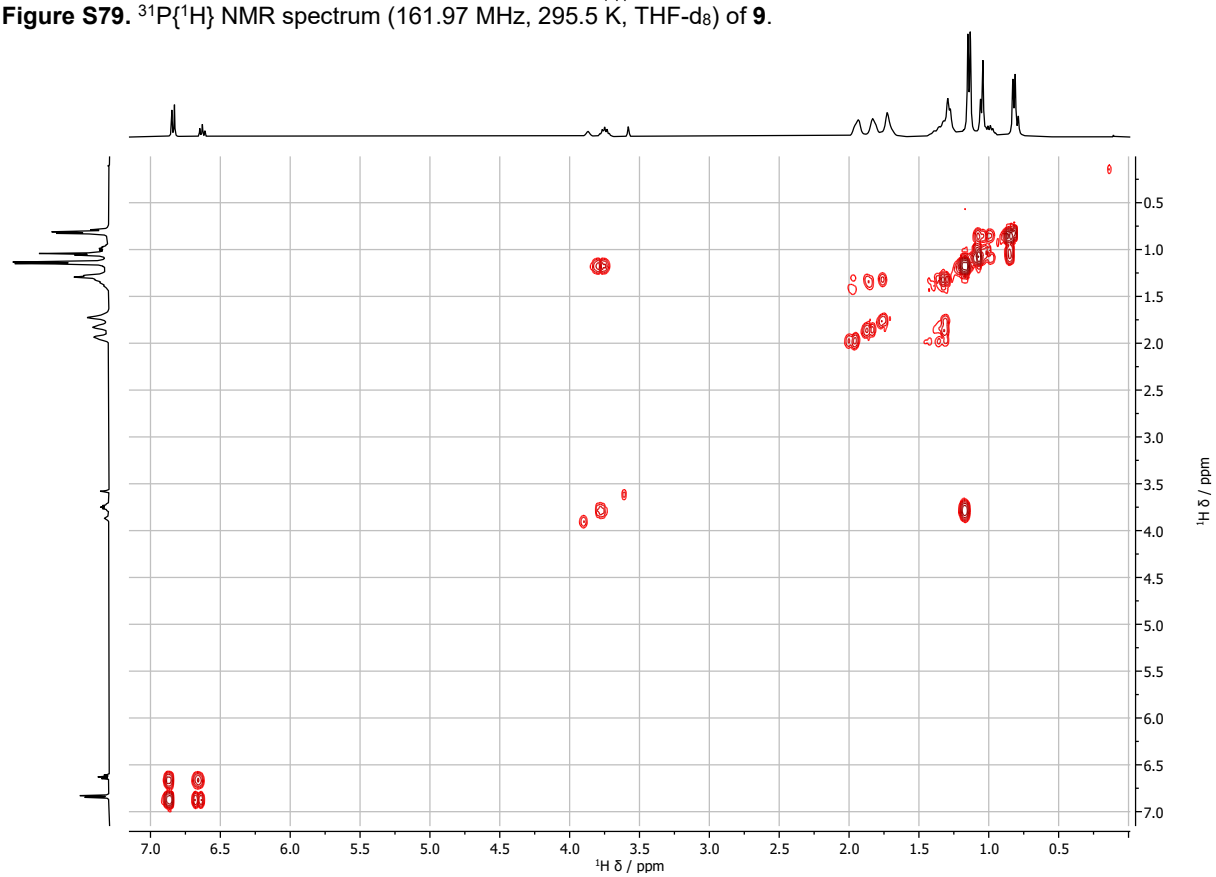


Figure S80. COSY NMR spectrum (400.13 / 400.13 MHz, 295.1 K, THF-d_8) of **9**.

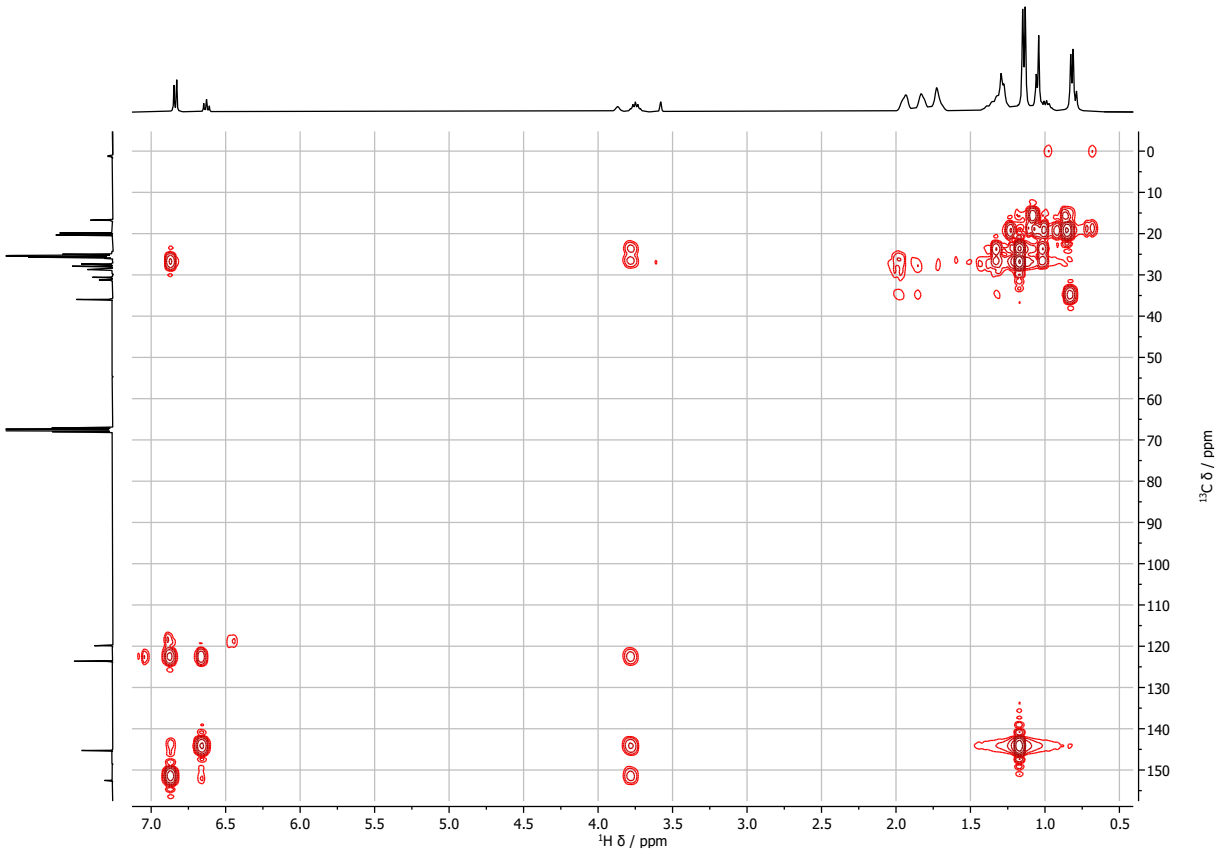


Figure S81. HMBC NMR spectrum (400.13 / 100.62 MHz, 295.0 K, THF-d_8) of **9**.

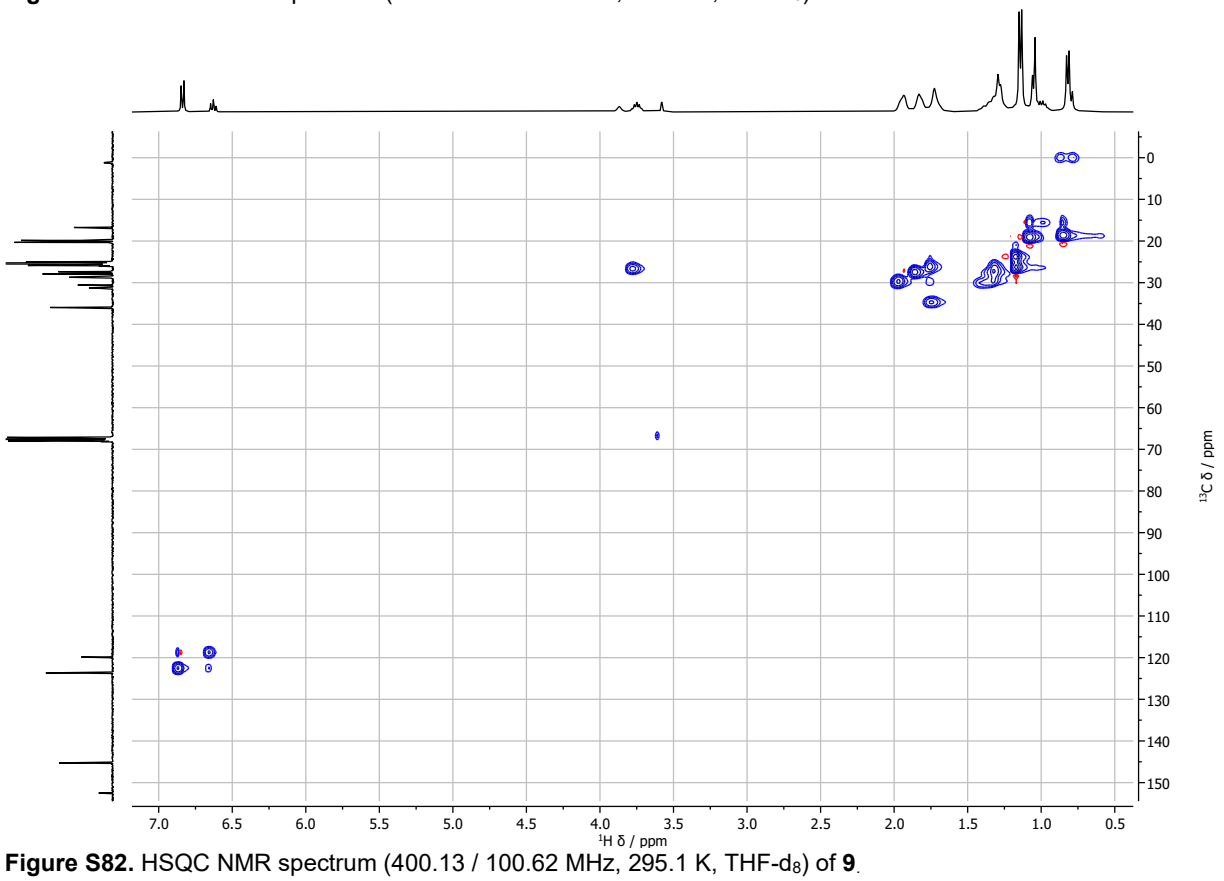


Figure S82. HSQC NMR spectrum (400.13 / 100.62 MHz, 295.1 K, THF-d_8) of **9**.

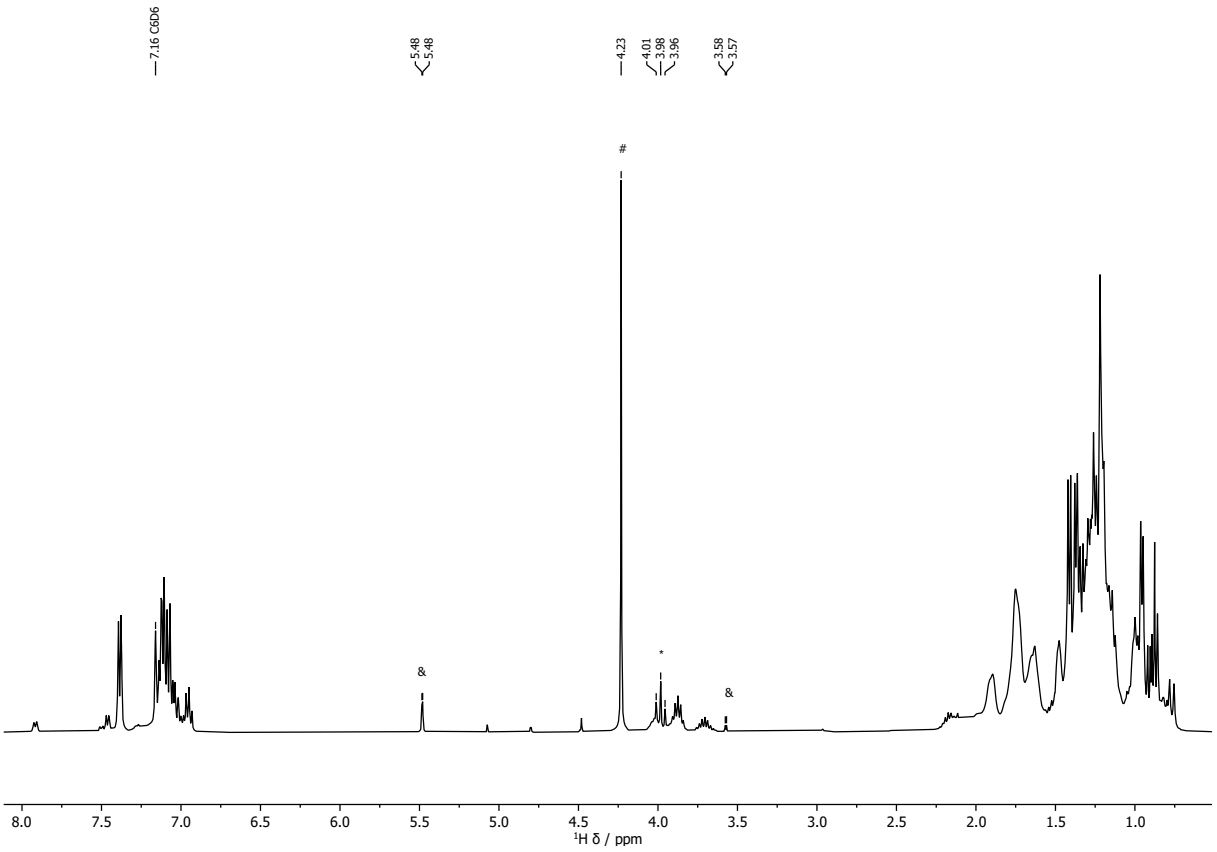


Figure S83. ^{1}H NMR spectrum (400.13 MHz, 294.8 K, C_6D_6) of reaction of 6-Cy with $PhSiH_3$ after 6 days at 60 °C; * indicates the Mg-H (t, $^{2}J_{HP}$ = 11.2 Hz), # indicates PhSiH3 and & marks unidentified Si-H species.

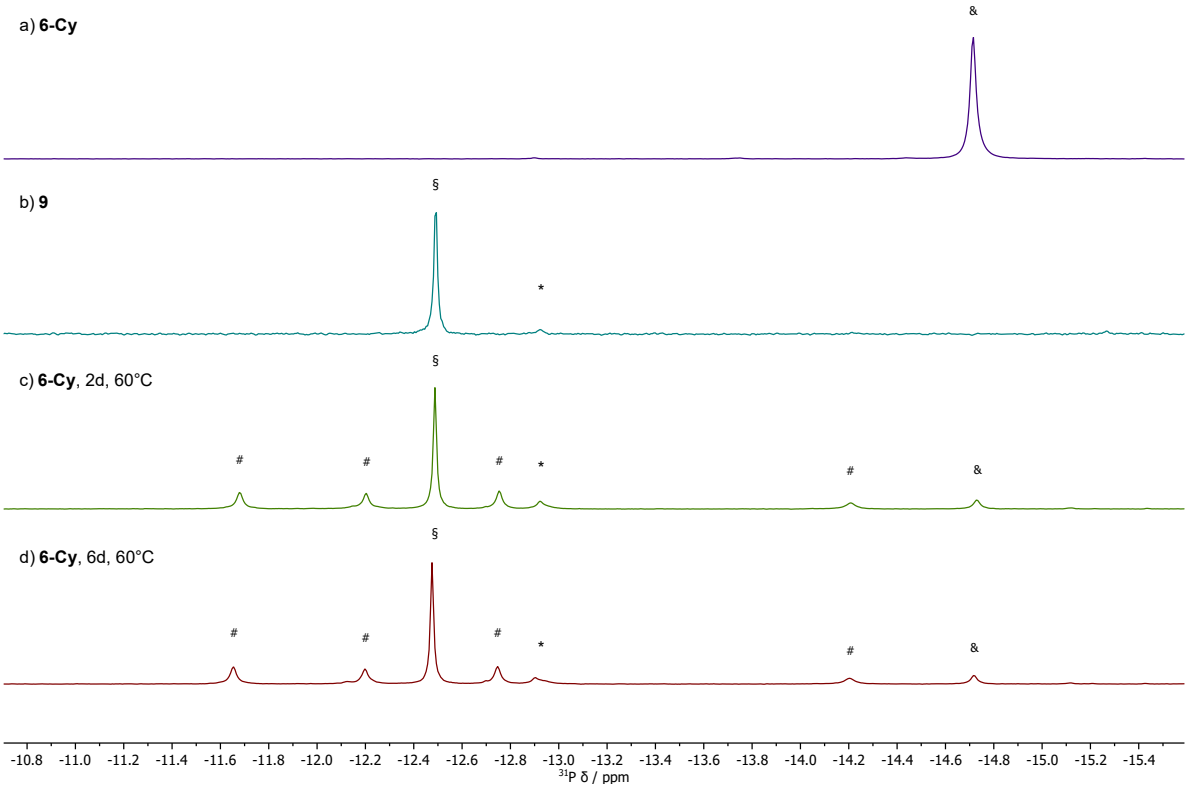


Figure S84. $^{31}P\{^{1}H\}$ NMR spectrum (161.97 MHz, C_6D_6) of a) **6-Cy**, b) **9**, reaction of **6-Cy** with $PhSiH_3$ at 60 °C after c) 2 days and d) 6 days.

2 X-ray crystallographic details

Single crystals of **1-Cy**, **1-Ph**, **2**, **3**, **4**, **5**, **6-Cy**, **6-Ph**, and **9** suitable for X-ray structural analysis were mounted in perfluoroalkyl ether oil on a nylon loop and positioned in a 150 K cold N_2 gas stream. Data collection was performed with a STOE StadiVari diffractometer (MoKα radiation) equipped with a DECTRIS PILATUS 300K detector. Structures were solved by Direct Methods (SHELXS-97),[4] or using SHELXT-16,[5] and refined by full-matrix least-squares calculations against F^2 (SHELXL-2018).[6] The positions of the hydrogen atoms were calculated and refined using a riding model, aside from hydride ligands in **9**, and those associated with the CH_3 groups in **2**, which were located in the electron difference map and freely refined. All non-hydrogen atoms were treated with anisotropic displacement parameters. Crystal data, details of data collections, and refinements for all structures can be found in their CIF files, which are available free of charge via www.ccdc.cam.ac.uk/data_request/cif, and are summarized in Table S1-S3.

Table S1. Summary of X-ray crystallographic data for **1-Cy**, **1-Ph**, **2**, and **3**.

	1-Cy	**1-Ph**	**2**	**3**
empirical form.	$C_{39}H_{72}MgNOPSi$	$C_{39}H_{60}MgNOPSi$	$C_{64}H_{116}Mg_2N_2P_2Si_2$	$C_{37}H_{68}MgNOPSi$
formula wt	654.34	642.25	1080.32	627.43
crystal syst.	triclinic	monoclinic	triclinic	monoclinic
space group	P−1	P21/n	P−1	P21/c
a (Å)	10.130(2)	15.960(3)	10.350(2)	20.032(4)
b (Å)	20.640(4)	14.180(3)	13.040(3)	19.501(4)
c (Å)	21.160(4)	17.720(4)	14.350(3)	19.921(4)
α (deg.)	112.90(3)	90	65.30(3)	90
β ($\delta\varepsilon\gamma$)	98.20(3)	105.90(3)	74.30(3)	95.54(3)
γ (deg.)	90.40(3)	90	71.30(3)	90
vol ($Å^3$)	4024.4(16)	3856.8(14)	1645.5(8)	7746(3)
Z	4	4	1	8
ρ(calc) ($g.cm^{-3}$)	1.080	1.106	1.090	1.076
μ (mm^{-1})	0.142	0.148	0.159	0.168
F(000)	1448	1400	596	2771
T (K)	150(2)	150(2)	150(2)	150(2)
Completeness to θ_{max} (%)	99.8	99.9	99.9	99.9
reflns collect.	18476	7568	6463	101284
unique reflns	8111	6681	5507	12934
R_{int}	0.0939	0.0160	0.0192	0.0240
R1 [$I>2\sigma(I)$]	0.0777	0.0372	0.0337	0.0425
*w*R2 (all data)	0.2460	0.1061	0.0963	0.1175
CCDC No.	2528198	2528199	2528200	2528201

Table S2. Summary of X-ray crystallographic data for **4**, **5**, and **6-Cy**.

	4	**5**	**6-Cy**
empirical form.	$C_{40}H_{72}MgNOPSi$, $0.5(C_8H_{10})$	$C_{74}H_{120}Mg_2N_2P_2Si_2$, C_6H_6	$C_{72}H_{128}Mg_2N_2O_2P_2Si_2$, $2(C_6H_6)$
formula wt	719.43	1282.56	1376.71
crystal syst.	triclinic	monoclinic	monoclinic
space group	P−1	P21/n	P21/c
a (Å)	10.630(2)	17.980(4)	15.8577(11)
b (Å)	11.190(2)	11.290(2)	19.8810(13)
c (Å)	19.260(4)	19.380(4)	26.5216(19)
α (deg.)	82.00(3)	90	90.00
β ($\delta\varepsilon\gamma$)	86.50(3)	102.80(3)	90.826(6)
γ (deg.)	73.50(3)	90	90.00
vol (Å^3)	2174.7(8)	3836.3(14)	8360.5(10)
Z	2	2	4
ρ(calc) (g.cm^{-3})	1.099	1.110	1.094
μ (mm^{-1})	0.137	0.146	0.140
F(000)	794	1404	3024
T (K)	150(2)	150(2)	150(2)
Completeness to θ_{max} (%)	99.8	100.0	99.7
reflns collect.	8524	7530	49582
unique reflns	7786	3040	13263
R_{int}	0.0121	0.1314	0.0226
R1 [$I>2\sigma(I)$]	0.0427	0.0592	0.0436
*w*R2 (all data)	0.1263	0.1212	0.1198
CCDC No.	2528202	2528203	2528204

Table S3. Summary of X-ray crystallographic data for **6-Ph**, **9**, and ^{Cy}**LMgEt(μ-MgEt$_2$)EtMg^{Cy}L**.

	6-Ph	**9**	**^{Cy}LMgEt(μ-MgEt$_2$)EtMg^{Cy}L**
empirical form.	$C_{72}H_{104}Mg_2N_2O_2P_2Si_2$	$C_{62}H_{112}Mg_2N_2P_2Si_2$	$C_{74}H_{140}Mg_4N_2P_2Si_2$
formula wt	1196.31	1052.27	1273.23
crystal syst.	monoclinic	monoclinic	monoclinic
space group	P21/c	P21/c	P21/n
a (Å)	15.420(3)	13.433(3)	19.190(4)
b (Å)	15.390(3)	12.450(3)	10.330(2)
c (Å)	30.350(6)	20.428(4)	22.220(4)
α (deg.)	90	90	90
β ($\delta\varepsilon\gamma$)	103.20(3)	106.70(3)	115.10(3)
γ (deg.)	90	90	90
vol (Å^3)	7012(3)	3272.3(12)	3988.8(16)
Z	4	2	2
ρ(calc) (g.cm^{-3})	1.133	1.068	1.060
μ (mm^{-1})	0.158	0.158	0.154
F(000)	2592	1160	1408
T (K)	150(2)	150(2)	150(2)
Completeness to θ_{max} (%)	99.7	100.0	100.0
reflns collect.	13725	29681	7842
unique reflns	7867	5249	4912
R_{int}	0.0593	0.0321	0.0559
R1 [$I>2\sigma(I)$]	0.0489	0.0673	0.0413
*w*R2 (all data)	0.1100	0.1889	0.1071
CCDC No.	2528205	2528206	2528207

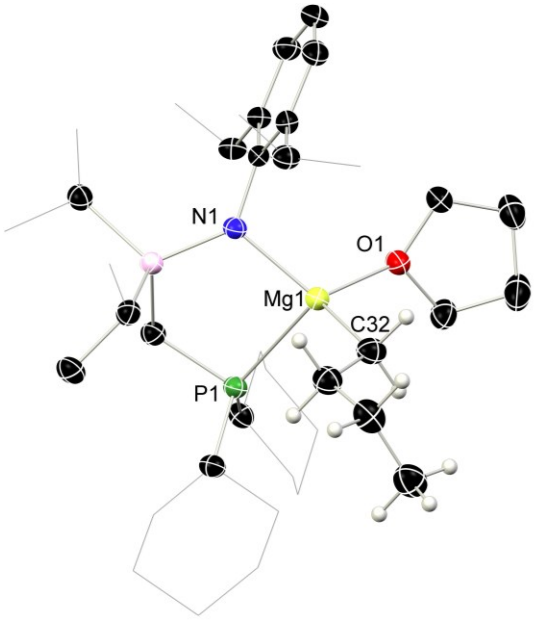


Figure S85. Molecular structure of **1-Cy**, with thermal ellipsoids at 30% probability and hydrogen atoms removed for clarity aside from those of the Mg-alkyl groups.

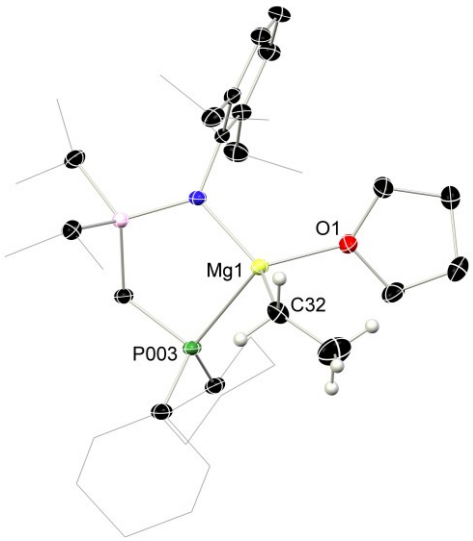


Figure S86. Molecular structure of **3**, with thermal ellipsoids at 30% probability and hydrogen atoms removed for clarity aside from those of the Mg-alkyl groups.

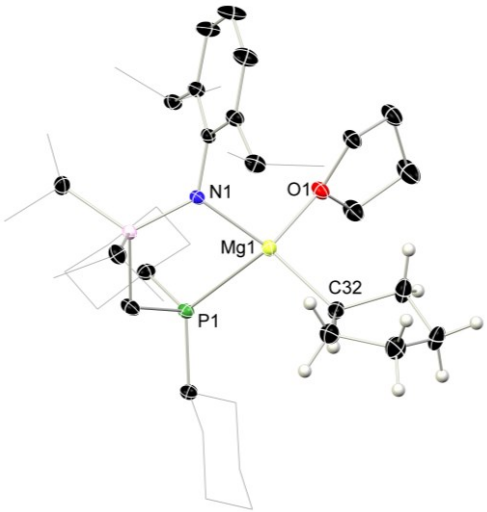


Figure S87. Molecular structure of **4**, with thermal ellipsoids at 30% probability and hydrogen atoms removed for clarity aside from those of the Mg-alkyl groups.

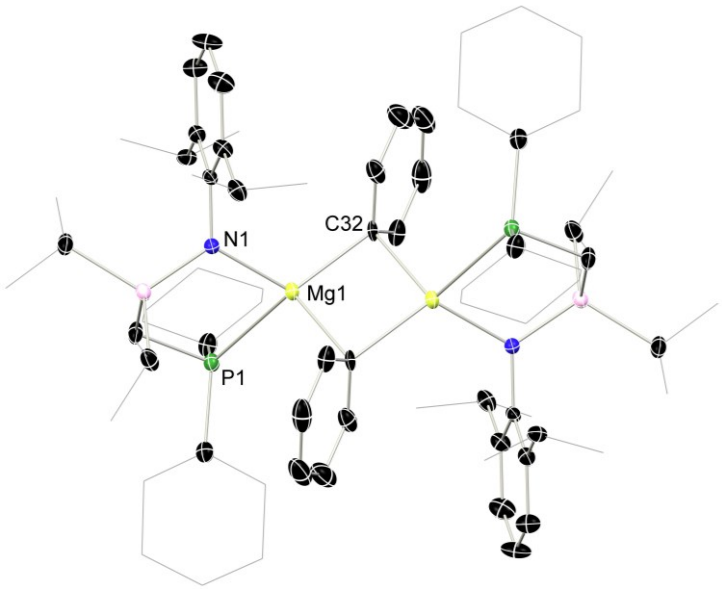


Figure S88. Molecular structure of **5**, with thermal ellipsoids at 30% probability and hydrogen atoms removed for clarity.

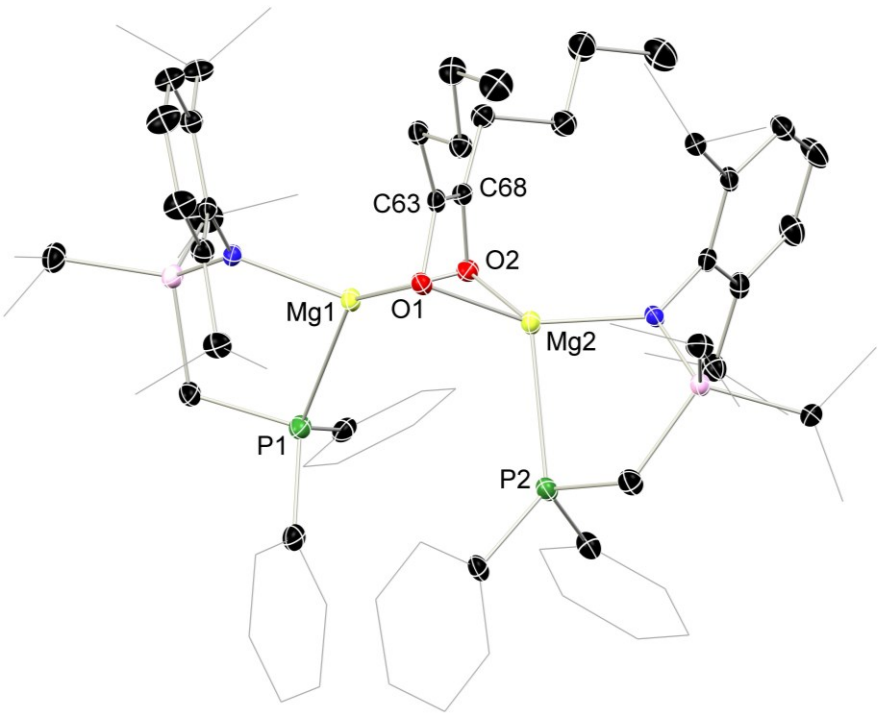


Figure S89. Molecular structure of **6-Ph**, with thermal ellipsoids at 30% probability and hydrogen atoms removed for clarity.

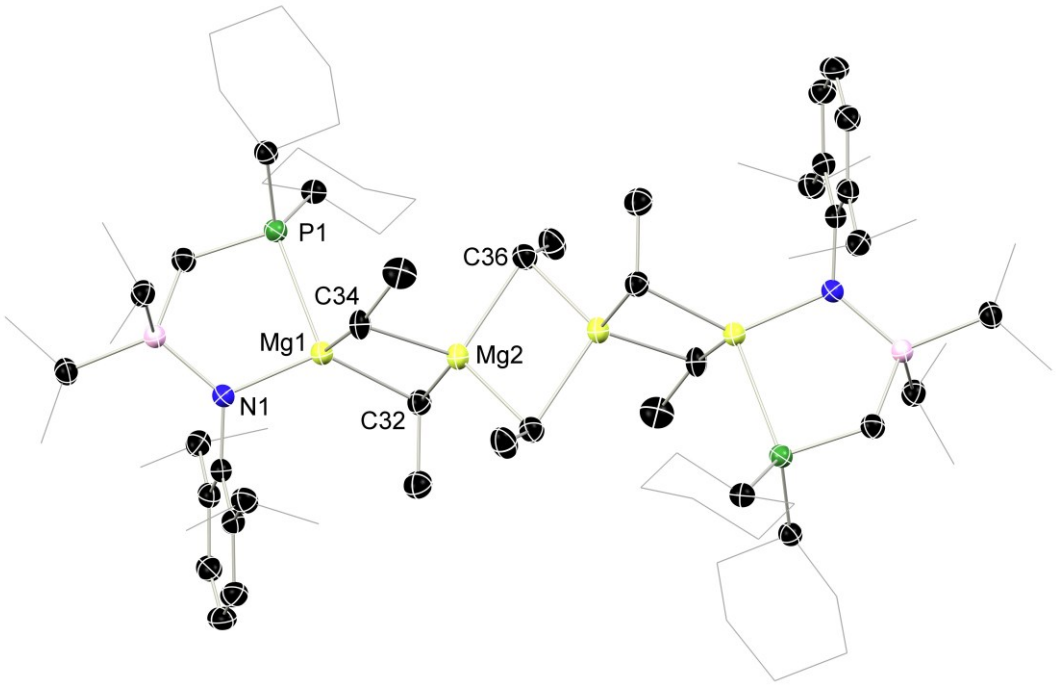


Figure S90. Molecular structure of ^{Cy}LMgEt(μ-MgEt$_2$)EtMg^{Cy}L, with thermal ellipsoids at 30% probability and hydrogen atoms removed for clarity.

3 Computational methods and details

All the geometry optimizations and frequency calculations reported in this paper were obtained with the ORCA 6.0.1 program.[7] Electron correlation was partially taken into account using the BP86[8,9] functional in conjunction with the D3(BJ) dispersion correction suggested by Grimme et al.,[10,11] the resolution-of-identity (RI) approach,[12] and the double-ζ quality plus polarization functions def2-SVP [13] basis set for all atoms, and the conductor-like polarizable continuum model (CPCM)[14] to include solvent effects. All species were characterized by frequency calculations: reactants and adducts exhibited positive definite Hessian matrices, while transition states showed a single negative eigenvalue in their diagonalized force constant matrices. Single-point energy refinements were carried out at the same DFT level using the much larger def2-TZVPP basis-set including solvent effects. This level is denoted (CPCM)-RI-BP86-D3BJ/def2-TZVPP//(CPCM)-RI-BP86-D3BJ/def2-SVP.

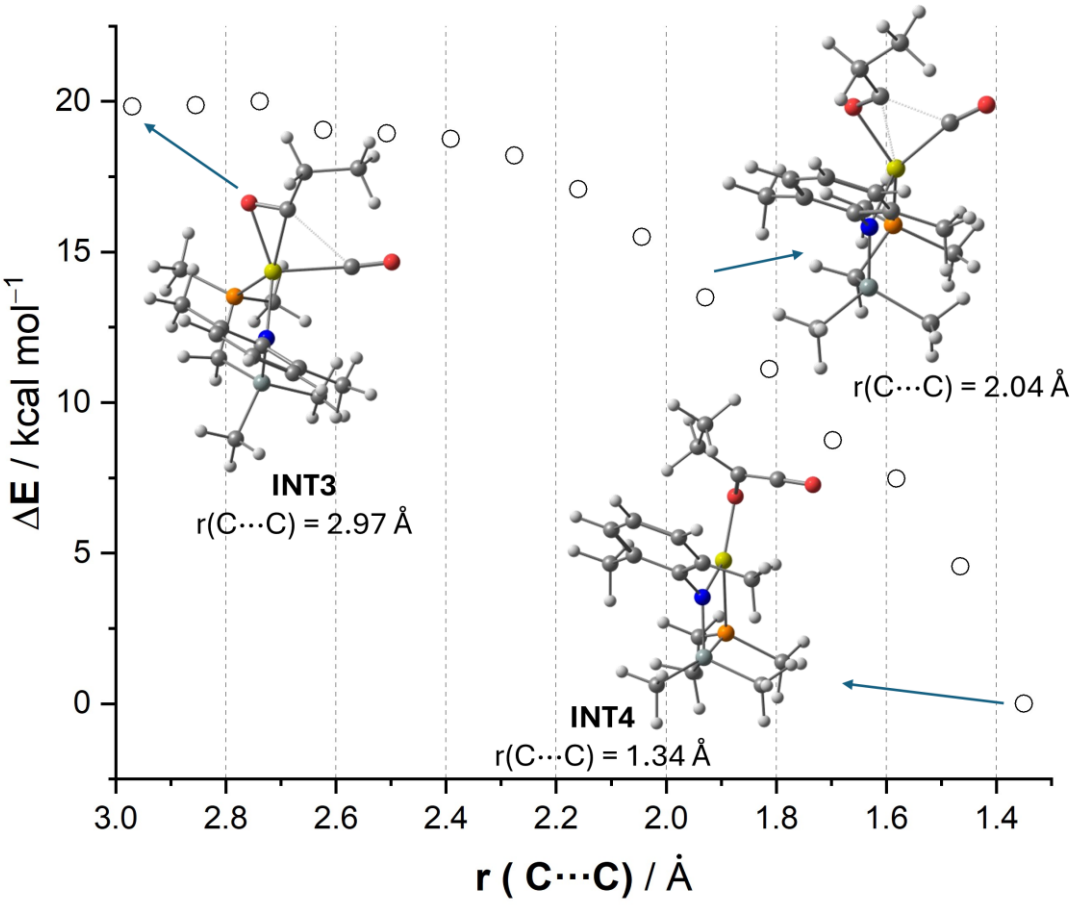


Figure S91. Relaxed-scan calculations for the transformation of **INT3** into **INT4**. All data have been calculated at the (CPCM)-RI-BP86-D3BJ/def2-SVP level.

Cartesian coordinates (in Å) and free energies (in a.u., at 298 K) of all the stationary points discussed in the text. All calculations have been performed at the (CPCM)-RI-BP86-D3BJ/def2-TZVPP//(CPCM)-RI-BP86-D3BJ/def2-SVP level.

1M: E= -1474.361911

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C	2.942638000	-0.158274000	-0.873315000
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C	-1.589396000	-1.677755000	1.069090000
H	-2.132699000	-2.635521000	1.221614000
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H	3.594595000	2.221498000	2.178372000
C	4.488752000	1.151530000	0.509445000
H	5.510301000	1.501742000	0.723228000
C	-1.441670000	3.193678000	-1.232024000
H	-0.718745000	3.954516000	-0.856271000
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H	-2.921924000	3.485004000	0.388538000
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H	-3.229481000	4.535465000	-1.018130000
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H	-3.323248000	-1.742940000	-1.530395000
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H	2.493316000	-2.093526000	-1.783123000
H	1.807927000	-0.699357000	-2.639230000
H	3.575927000	-1.051214000	-2.747560000
C	0.962683000	1.551538000	1.947756000
H	1.329304000	2.112743000	2.829122000

H	0.251793000	2.234893000	1.422919000
H	0.364228000	0.684931000	2.298334000

INT1: G = -1587.734100

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N	0.307614000	-0.365673000	-0.546997000
C	1.665543000	-0.446229000	-0.245330000
C	2.608610000	0.312622000	-1.018527000
C	2.143555000	-1.161195000	0.906038000
C	3.967028000	0.323704000	-0.653321000
H	4.677469000	0.909830000	-1.259382000
C	-2.154983000	-1.785969000	0.241713000
H	-3.055637000	-2.347154000	-0.087703000
H	-1.690641000	-2.346397000	1.080030000
C	3.513128000	-1.129004000	1.232363000
H	3.861352000	-1.676832000	2.123705000
C	4.428413000	-0.394039000	0.463050000
H	5.494587000	-0.373093000	0.736249000
C	-0.853967000	3.388167000	-0.324867000
H	-1.281832000	3.956319000	0.534402000
H	0.096015000	3.912532000	-0.578281000
C	-1.819776000	3.442722000	-1.525280000
H	-2.795528000	2.957007000	-1.297961000
H	-1.410652000	2.907113000	-2.411232000
H	-2.062602000	4.476219000	-1.873500000
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H	-2.285045000	-0.735354000	3.237316000
H	-3.546295000	0.536906000	3.073580000
H	-3.948721000	-1.187221000	2.693668000
C	-4.212278000	0.268537000	0.036656000
H	-4.972962000	-0.516102000	0.227016000
H	-4.593100000	1.247285000	0.389488000
H	-4.026021000	0.339577000	-1.052411000
C	-0.020544000	-3.222959000	-1.548505000
H	0.750720000	-3.086391000	-2.335046000
H	0.471058000	-3.691015000	-0.671939000
H	-0.783099000	-3.930344000	-1.936044000
C	-1.711921000	-0.873894000	-2.640253000
H	-2.571842000	-1.506600000	-2.946225000
H	-2.093221000	0.149616000	-2.435238000
H	-1.014859000	-0.792567000	-3.500305000
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H	1.560346000	0.436819000	-2.914690000
H	1.401919000	1.889482000	-1.916567000
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C	1.161266000	-1.880968000	1.792150000
H	1.644822000	-2.245233000	2.719339000
H	0.318895000	-1.209153000	2.068592000
H	0.697931000	-2.753731000	1.286438000
O	2.299125000	2.118777000	2.149460000

TS1: G = -1587.716214 (i = -313 cm-1)

P	2.438996000	-1.090782000	0.046475000
Si	-0.512005000	-2.063023000	-0.249243000
Mg	0.908200000	0.845428000	-0.604310000
C	1.809557000	2.526101000	-1.432130000
N	-0.658343000	-0.323996000	-0.218921000
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C	-2.252291000	0.639590000	1.407044000
C	-2.764507000	0.708345000	-1.002114000
C	-3.485533000	1.271192000	1.664879000
H	-3.752056000	1.512063000	2.707212000
C	1.350142000	-2.437354000	-0.573380000
H	1.636898000	-3.421571000	-0.143494000
H	1.508353000	-2.492205000	-1.672523000
C	-3.987770000	1.340340000	-0.701994000
H	-4.652227000	1.634052000	-1.531279000
C	-4.362821000	1.608689000	0.623161000
H	-5.324011000	2.099195000	0.841376000
C	4.155629000	-1.529817000	-0.462215000
H	4.223485000	-1.509312000	-1.567554000
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H	2.745795000	-2.341075000	2.157391000
H	3.168785000	-0.588530000	2.325375000
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H	-2.054450000	-2.648399000	1.646001000
C	-1.291162000	0.365550000	2.537526000
H	-1.123538000	-0.717176000	2.697804000
H	-0.290811000	0.798227000	2.319585000
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H	-2.216545000	-0.576023000	-2.680965000
O	2.454701000	3.428024000	-1.856951000
C	1.774439000	2.686830000	0.594733000
H	1.255953000	3.667268000	0.619249000
H	1.197203000	2.017586000	1.290103000
C	3.233706000	2.774203000	1.011222000
H	3.711196000	1.769961000	1.042315000
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H	3.390490000	3.243760000	2.007985000

INT2: G = -1587.744169

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Mg	0.979993000	0.780616000	0.054077000
C	1.900120000	2.655853000	0.260276000
N	-0.723958000	-0.267591000	0.188835000
C	-1.959569000	0.332510000	-0.124226000
C	-2.961346000	0.548157000	0.872735000
C	-2.215343000	0.767823000	-1.463572000
C	-4.172620000	1.175884000	0.520675000
H	-4.933431000	1.340760000	1.301735000
C	0.887041000	-2.547369000	-0.691745000
H	1.214648000	-3.598772000	-0.541525000
H	0.504427000	-2.448419000	-1.730542000
C	-3.437766000	1.392784000	-1.776587000
H	-3.621580000	1.716621000	-2.814417000
C	-4.419882000	1.598787000	-0.794632000
H	-5.371484000	2.088738000	-1.052773000
C	3.263398000	-1.516433000	-2.109501000
H	2.643342000	-1.132237000	-2.943079000
H	4.179878000	-0.897025000	-2.039316000
H	3.542839000	-2.570369000	-2.312574000
C	3.418322000	-2.159715000	0.707428000
H	3.712898000	-3.180026000	0.387236000
H	4.325155000	-1.535897000	0.832654000
H	2.894960000	-2.220287000	1.680803000
C	-2.112764000	-2.928200000	-0.021563000
H	-2.969040000	-2.634853000	0.619639000
H	-2.389850000	-2.704976000	-1.072413000
H	-1.965923000	-4.023647000	0.078016000
C	-0.019749000	-2.421194000	2.229552000
H	0.317231000	-3.476973000	2.303454000
H	0.817009000	-1.769697000	2.560127000
H	-0.850875000	-2.273329000	2.948258000
C	-2.706264000	0.116985000	2.294667000
H	-2.761634000	-0.987304000	2.409087000
H	-1.685451000	0.406148000	2.620635000
H	-3.448443000	0.557431000	2.989031000
C	-1.176236000	0.536454000	-2.533840000
H	-1.549985000	0.844539000	-3.529815000
H	-0.241991000	1.112210000	-2.345222000
H	-0.876941000	-0.531404000	-2.582701000
O	1.636497000	2.508943000	-0.977920000
C	2.545246000	3.943115000	0.705401000
H	2.946610000	4.492328000	-0.177811000
H	1.699675000	4.553017000	1.105475000
C	3.596513000	3.744948000	1.804361000
H	3.168341000	3.195241000	2.667746000
H	4.460493000	3.158285000	1.429064000
H	3.982332000	4.716866000	2.171502000

INT3: G = -1701.117700

P	2.233249000	-1.895021000	-0.801912000
Si	-0.567659000	-2.149405000	0.494322000
Mg	1.186161000	0.428862000	-0.241901000
C	1.541026000	2.532056000	-0.523032000
N	-0.591137000	-0.455769000	0.101504000
C	-1.756644000	0.301281000	-0.102050000
C	-2.602509000	0.692841000	0.982912000
C	-2.090405000	0.735659000	-1.425738000
C	-3.739286000	1.485752000	0.731225000
H	-4.376896000	1.785963000	1.579455000
C	0.704916000	-2.926096000	-0.730224000
H	0.950818000	-3.990747000	-0.526706000
H	0.235589000	-2.867091000	-1.736096000
C	-3.235560000	1.526913000	-1.637042000
H	-3.482706000	1.845124000	-2.663468000
C	-4.064249000	1.904958000	-0.568434000
H	-4.956787000	2.524306000	-0.747315000
C	3.028253000	-2.276698000	-2.423513000
H	2.377424000	-1.901241000	-3.237493000
H	4.004836000	-1.756537000	-2.487957000
H	3.180181000	-3.368322000	-2.547222000
C	3.371375000	-2.677307000	0.422776000
H	3.527988000	-3.750758000	0.191724000
H	4.346124000	-2.150825000	0.407598000
H	2.937450000	-2.583070000	1.436680000
C	-2.249763000	-2.960289000	0.209517000
H	-3.014592000	-2.524751000	0.884927000
H	-2.586799000	-2.787257000	-0.833216000
H	-2.211512000	-4.054441000	0.390437000
C	0.070436000	-2.541099000	2.240138000
H	0.311780000	-3.619265000	2.354166000
H	0.990825000	-1.958828000	2.457063000
H	-0.676322000	-2.272044000	3.013978000
C	-2.253583000	0.275413000	2.388279000
H	-2.429048000	-0.809210000	2.554767000
H	-1.176365000	0.445480000	2.594972000
H	-2.857340000	0.826533000	3.135620000
C	-1.215680000	0.326008000	-2.585902000
H	-1.678472000	0.597381000	-3.554817000
H	-0.218170000	0.820419000	-2.557785000
H	-1.019232000	-0.765998000	-2.575499000
O	1.983957000	1.907754000	-1.536196000
C	1.599291000	4.036001000	-0.507220000
H	2.348357000	4.397827000	-1.249809000
H	0.597312000	4.343556000	-0.893647000
C	1.812564000	4.624664000	0.891800000
H	1.039671000	4.256521000	1.596507000
H	2.803065000	4.336639000	1.299758000
H	1.762976000	5.731540000	0.872792000
C	1.965334000	0.836710000	1.878438000
O	2.104232000	1.362481000	2.892838000

INT4: G = -1701.138364

P	2.261747000	-1.873221000	0.715560000
Si	-0.713349000	-2.632270000	1.248264000
Mg	0.817813000	0.154319000	1.367758000
C	2.999986000	1.975496000	1.291530000
N	-0.885810000	-0.889625000	1.287866000
C	-2.065383000	-0.225504000	0.903525000
C	-3.286619000	-0.355334000	1.638630000
C	-2.043345000	0.645722000	-0.234935000
C	-4.439655000	0.324241000	1.199507000
H	-5.371249000	0.214817000	1.779153000
C	0.884494000	-2.990552000	0.220787000
H	1.195828000	-4.057617000	0.241596000
H	0.630723000	-2.728779000	-0.829894000
C	-3.216148000	1.309466000	-0.640595000
H	-3.180846000	1.963093000	-1.527722000
C	-4.420230000	1.145537000	0.061491000
H	-5.332735000	1.666100000	-0.267100000
C	3.470738000	-1.837829000	-0.673707000
H	3.010280000	-1.340087000	-1.549114000
H	4.351277000	-1.251420000	-0.343760000
H	3.784481000	-2.864416000	-0.951909000
C	3.168048000	-2.771197000	2.044365000
H	3.524403000	-3.756076000	1.679692000
H	4.033160000	-2.155813000	2.358687000
H	2.500287000	-2.922345000	2.913645000
C	-2.131236000	-3.476975000	0.328743000
H	-3.093524000	-3.390131000	0.871207000
H	-2.264717000	-3.014920000	-0.671163000
H	-1.912749000	-4.555967000	0.187128000
C	-0.438270000	-3.403926000	2.958004000
H	-0.063450000	-4.445999000	2.876940000
H	0.306502000	-2.815728000	3.534338000
H	-1.373749000	-3.419356000	3.552292000
C	-3.322062000	-1.167310000	2.909165000
H	-3.340922000	-2.261336000	2.717865000
H	-2.416927000	-0.975524000	3.521672000
H	-4.221079000	-0.928311000	3.510209000
C	-0.753206000	0.855493000	-0.992764000
H	-0.924024000	1.388357000	-1.947959000
H	-0.029209000	1.502754000	-0.433564000
H	-0.242056000	-0.105555000	-1.217404000
O	1.764834000	1.731681000	1.830595000
C	3.213418000	3.263354000	0.525991000
H	2.472488000	3.291127000	-0.307414000
H	2.932174000	4.102355000	1.203622000
C	4.630405000	3.469791000	-0.018527000
H	5.381071000	3.478984000	0.798879000
H	4.914155000	2.663570000	-0.727074000
H	4.711569000	4.433565000	-0.558912000
C	3.998107000	1.088705000	1.438344000
O	4.868429000	0.282785000	1.613497000

INT5: G = -3175.504817

P	-5.193006000	0.802160000	1.436189000
Si	3.026486000	-2.026093000	1.124557000
P	0.752942000	-0.107015000	2.061519000
Si	-4.977106000	-1.185984000	-0.967629000
Mg	-2.996168000	1.104877000	0.194860000
Mg	2.444727000	1.212748000	0.544878000
O	-1.899985000	2.631589000	0.076806000
O	1.082178000	1.376976000	-1.170379000
N	-3.337493000	-0.655682000	-0.692642000
N	3.497597000	-0.524401000	0.407711000
C	-2.209963000	-1.261960000	-1.300112000
C	0.169360000	2.143717000	-0.955741000
C	1.167547000	-1.820107000	1.556259000
H	0.611391000	-1.998602000	0.610612000
H	0.822106000	-2.564801000	2.305547000
C	-1.625073000	-2.457220000	-0.773877000
C	4.729946000	-0.296935000	-0.242273000
C	-6.081573000	0.061435000	0.007546000
H	-6.349764000	0.901979000	-0.669199000
H	-7.028846000	-0.418379000	0.335783000
C	-0.717344000	3.008743000	-0.439705000
C	4.843912000	-0.472421000	-1.659379000
C	5.852865000	0.226638000	0.476532000
C	-0.437833000	4.487331000	-0.632119000
H	0.603882000	4.627187000	-0.990691000
H	-0.484540000	4.951087000	0.379586000
C	-1.579058000	-0.621374000	-2.417592000
C	-1.438679000	5.164972000	-1.577599000
H	-2.478217000	5.005645000	-1.227596000
H	-1.356122000	4.749314000	-2.602774000
C	6.062815000	-0.182624000	-2.303874000
H	6.134247000	-0.326029000	-3.395025000
C	-0.469483000	-2.991448000	-1.382942000
H	-0.029625000	-3.913215000	-0.968543000
H	-1.258475000	6.257922000	-1.631336000
C	-0.417700000	-1.179447000	-2.982589000
H	0.059675000	-0.668221000	-3.833661000
C	7.171841000	0.294866000	-1.588430000
H	8.116511000	0.518919000	-2.107973000
C	7.053382000	0.505679000	-0.205929000
H	7.907518000	0.908164000	0.363733000
C	0.137512000	-2.365846000	-2.479184000
H	1.045002000	-2.791283000	-2.932704000
C	5.729695000	0.522718000	1.950154000
H	4.841316000	1.160272000	2.148953000
H	5.586060000	-0.397328000	2.551227000
H	6.628405000	1.047504000	2.329384000
C	3.650964000	-0.932383000	-2.459801000
H	3.365628000	-1.974932000	-2.214635000
H	2.753090000	-0.318597000	-2.240640000
H	3.857310000	-0.881936000	-3.547256000
C	3.946904000	-2.503106000	2.722664000
H	3.876996000	-1.713251000	3.497906000

H	3.533823000	-3.442582000	3.149138000
H	5.023481000	-2.676019000	2.512507000
C	3.181874000	-3.536637000	-0.015616000
H	2.947073000	-4.476070000	0.528127000
H	2.496999000	-3.454903000	-0.882773000
H	4.219425000	-3.618744000	-0.402837000
C	1.210937000	-0.019343000	3.848761000
H	0.871928000	0.948133000	4.269265000
H	0.762071000	-0.854058000	4.425094000
H	2.314006000	-0.068140000	3.935009000
C	-1.102120000	-0.087809000	2.121993000
H	-1.452480000	-0.443264000	1.129837000
H	-1.502773000	-0.786054000	2.883972000
H	-1.457850000	0.940665000	2.341722000
C	-2.194334000	-3.141373000	0.445040000
H	-2.873445000	-3.976415000	0.175478000
H	-1.384786000	-3.568215000	1.070104000
H	-2.785694000	-2.432509000	1.055453000
C	-2.155985000	0.652717000	-2.986634000
H	-2.120836000	1.498088000	-2.261919000
H	-1.586150000	0.979834000	-3.877150000
H	-3.219738000	0.529448000	-3.271999000
C	-5.429003000	-2.920757000	-0.349344000
H	-4.867592000	-3.701305000	-0.902191000
H	-5.226208000	-3.052033000	0.731796000
H	-6.511706000	-3.099498000	-0.522527000
C	-5.477809000	-1.113836000	-2.793356000
H	-5.438045000	-0.075906000	-3.182835000
H	-4.783296000	-1.731559000	-3.401124000
H	-6.505022000	-1.504933000	-2.950753000
C	-5.091358000	-0.548888000	2.685284000
H	-4.433490000	-1.346931000	2.289934000
H	-4.646958000	-0.154570000	3.620034000
H	-6.094972000	-0.968661000	2.899575000
C	-6.339298000	2.031293000	2.190726000
H	-7.300965000	1.554557000	2.469477000
H	-5.870307000	2.471467000	3.093113000
H	-6.529636000	2.842305000	1.460846000
C	3.121046000	3.231152000	0.717603000
H	2.267019000	3.945798000	0.795526000
H	3.714210000	3.395393000	1.648007000
C	3.987922000	3.590720000	-0.508201000
H	3.423455000	3.480379000	-1.462005000
H	4.869396000	2.917726000	-0.599394000
H	4.388982000	4.634394000	-0.506368000

TS2: G = -3175.496729 (i = -155 cm-1)

P	-5.239014000	0.884508000	1.142297000
Si	2.953245000	-1.849139000	1.169772000
P	0.615876000	0.034423000	1.920863000
Si	-4.881464000	-1.222764000	-1.129762000
Mg	-2.937536000	1.091135000	0.058854000
Mg	2.118307000	1.222209000	0.148776000

O	-1.924909000	2.666974000	0.145228000
O	0.631814000	1.575585000	-1.445178000
N	-3.253087000	-0.707298000	-0.757019000
N	3.343708000	-0.383156000	0.324055000
C	-2.129741000	-1.396060000	-1.279619000
C	0.218708000	2.453454000	-0.688636000
C	1.093050000	-1.707435000	1.614353000
H	0.525447000	-2.020828000	0.711651000
H	0.807375000	-2.374309000	2.456153000
C	-1.630173000	-2.590398000	-0.670646000
C	4.586924000	-0.215557000	-0.326576000
C	-6.038232000	0.081322000	-0.305370000
H	-6.239419000	0.888366000	-1.043288000
H	-7.015198000	-0.369661000	-0.027009000
C	-0.674839000	3.177070000	0.018537000
C	4.697034000	-0.484472000	-1.728835000
C	5.718716000	0.325226000	0.361229000
C	-0.390558000	4.484594000	0.708644000
H	0.678154000	4.744639000	0.588706000
H	-0.564874000	4.337104000	1.800040000
C	-1.431615000	-0.853128000	-2.408164000
C	-1.287678000	5.622869000	0.198226000
H	-2.358880000	5.354653000	0.296257000
H	-1.087876000	5.834353000	-0.872571000
C	5.925474000	-0.282339000	-2.386311000
H	5.995039000	-0.500314000	-3.465013000
C	-0.502124000	-3.232491000	-1.225639000
H	-0.130191000	-4.154817000	-0.750105000
H	-1.113855000	6.555848000	0.772223000
C	-0.301365000	-1.516757000	-2.918483000
H	0.224499000	-1.085144000	-3.784778000
C	7.046412000	0.207714000	-1.697531000
H	8.000041000	0.364953000	-2.225085000
C	6.928600000	0.521377000	-0.335088000
H	7.791016000	0.943898000	0.206963000
C	0.159844000	-2.712120000	-2.344694000
H	1.036502000	-3.228578000	-2.763462000
C	5.602458000	0.738537000	1.807424000
H	4.630533000	1.241163000	1.993708000
H	5.636211000	-0.129331000	2.497375000
H	6.423219000	1.426054000	2.092180000
C	3.476239000	-0.913254000	-2.501992000
H	3.008757000	-1.822195000	-2.077932000
H	2.684841000	-0.132448000	-2.465627000
H	3.718584000	-1.100848000	-3.566408000
C	3.909647000	-2.161944000	2.785733000
H	3.836541000	-1.314872000	3.497036000
H	3.517151000	-3.071386000	3.289581000
H	4.985441000	-2.336431000	2.574074000
C	3.201238000	-3.418008000	0.131139000
H	3.064143000	-4.333775000	0.743953000
H	2.489759000	-3.457652000	-0.717447000
H	4.231199000	-3.437274000	-0.283818000
C	1.218752000	0.397935000	3.628520000

H	0.854715000	1.396899000	3.940744000
H	0.873386000	-0.367107000	4.353662000
H	2.325861000	0.418317000	3.618434000
C	-1.222006000	-0.011990000	2.161288000
H	-1.670637000	-0.516574000	1.278633000
H	-1.507014000	-0.608290000	3.051757000
H	-1.606105000	1.022780000	2.283388000
C	-2.256004000	-3.160199000	0.580026000
H	-2.852946000	-4.072212000	0.371348000
H	-1.475018000	-3.445521000	1.314192000
H	-2.935823000	-2.424718000	1.049087000
C	-1.910864000	0.426001000	-3.048813000
H	-1.882394000	1.286655000	-2.343542000
H	-1.270213000	0.705699000	-3.906559000
H	-2.958424000	0.341493000	-3.400177000
C	-5.395328000	-2.925883000	-0.473239000
H	-4.781135000	-3.728413000	-0.930129000
H	-5.302922000	-3.007236000	0.627744000
H	-6.454968000	-3.117200000	-0.746478000
C	-5.230041000	-1.239640000	-2.991536000
H	-5.164396000	-0.221760000	-3.427404000
H	-4.481362000	-1.878325000	-3.506383000
H	-6.237215000	-1.649639000	-3.215502000
C	-5.272977000	-0.392861000	2.471522000
H	-4.605403000	-1.228027000	2.183861000
H	-4.897626000	0.049811000	3.415014000
H	-6.300708000	-0.778996000	2.627029000
C	-6.412370000	2.173993000	1.739900000
H	-7.402313000	1.730625000	1.970726000
H	-6.001417000	2.653282000	2.650668000
H	-6.529904000	2.948624000	0.957003000
C	2.932760000	3.232329000	-0.089285000
H	2.339454000	4.168102000	-0.092217000
H	3.625984000	3.317743000	0.781159000
C	3.708981000	3.092918000	-1.408987000
H	3.031174000	2.883723000	-2.267866000
H	4.441926000	2.258721000	-1.379804000
H	4.285421000	4.007095000	-1.690726000

2M: G = -3175.624950

P	-3.806246000	2.117390000	-0.640948000
Si	3.565166000	-1.983114000	0.760641000
P	0.798925000	-1.657478000	2.183757000
Si	-4.453731000	-0.855580000	-1.107507000
Mg	-2.127154000	0.572636000	0.585281000
Mg	0.808754000	-0.555914000	-0.121504000
O	-1.319316000	1.193106000	2.259472000
O	-0.357088000	1.000870000	-0.276285000
N	-2.873030000	-1.041052000	-0.422503000
N	2.808491000	-0.648815000	-0.075858000
C	-1.913829000	-2.014882000	-0.671062000
C	0.025800000	2.100620000	0.511490000
C	2.246042000	-2.770370000	1.927101000

H	1.855110000	-3.696988000	1.456463000
H	2.709791000	-3.055682000	2.896489000
C	-1.861548000	-3.208617000	0.121766000
C	3.584988000	0.337145000	-0.728106000
C	-4.511987000	0.916762000	-1.862609000
H	-3.828587000	0.913394000	-2.738684000
H	-5.515038000	1.241717000	-2.213554000
C	-0.473788000	2.152205000	1.795710000
C	3.864728000	0.243621000	-2.128001000
C	4.035099000	1.497130000	-0.019662000
C	-0.207687000	3.307919000	2.730615000
H	0.639324000	3.922580000	2.362449000
H	0.107578000	2.890945000	3.714293000
C	-0.907779000	-1.826789000	-1.691069000
C	-1.453159000	4.188496000	2.935349000
H	-2.299920000	3.575433000	3.305642000
H	-1.769678000	4.652347000	1.977140000
C	4.626285000	1.244875000	-2.763016000
H	4.835891000	1.149740000	-3.841370000
C	-0.784856000	-4.103525000	-0.020277000
H	-0.752764000	-5.006135000	0.611859000
H	-1.272312000	5.003154000	3.667192000
C	0.168227000	-2.747342000	-1.787956000
H	0.932745000	-2.597614000	-2.566118000
C	5.103520000	2.356217000	-2.052822000
H	5.697753000	3.130942000	-2.561452000
C	4.790750000	2.478585000	-0.690603000
H	5.125141000	3.365891000	-0.128045000
C	0.247329000	-3.867386000	-0.942262000
H	1.091042000	-4.567445000	-1.029377000
C	3.631678000	1.711003000	1.415383000
H	2.526971000	1.641276000	1.518529000
H	4.061065000	0.946202000	2.091681000
H	3.955660000	2.706432000	1.777090000
C	3.275353000	-0.880650000	-2.940671000
H	3.423241000	-1.866869000	-2.462620000
H	2.174748000	-0.748662000	-3.043509000
H	3.700567000	-0.906836000	-3.962922000
C	5.063564000	-1.474639000	1.808695000
H	4.762963000	-0.943871000	2.734715000
H	5.647295000	-2.371532000	2.104917000
H	5.735646000	-0.805746000	1.231570000
C	4.166988000	-3.369698000	-0.391671000
H	4.560494000	-4.229700000	0.191400000
H	3.339061000	-3.736308000	-1.032184000
H	4.981132000	-3.009518000	-1.055029000
C	1.383818000	-0.404116000	3.396876000
H	0.540670000	0.292021000	3.577940000
H	1.707587000	-0.885617000	4.341952000
H	2.224557000	0.156991000	2.953349000
C	-0.397700000	-2.621174000	3.203360000
H	-0.699002000	-3.535935000	2.663679000
H	0.065938000	-2.897529000	4.172105000
H	-1.294959000	-1.999145000	3.389367000

C	-2.981491000	-3.474407000	1.090572000
H	-3.942684000	-3.612775000	0.551032000
H	-2.793746000	-4.381411000	1.697154000
H	-3.140197000	-2.607930000	1.765015000
C	-1.070112000	-0.718412000	-2.708492000
H	-1.221774000	0.265380000	-2.224494000
H	-0.184992000	-0.653985000	-3.371190000
H	-1.959527000	-0.911960000	-3.344163000
C	-5.803113000	-0.914492000	0.224519000
H	-5.896079000	-1.932935000	0.654641000
H	-5.550829000	-0.227307000	1.060392000
H	-6.794760000	-0.615214000	-0.176222000
C	-4.804062000	-2.136150000	-2.452491000
H	-4.067298000	-2.057895000	-3.278113000
H	-4.738822000	-3.163166000	-2.036554000
H	-5.819136000	-2.004303000	-2.881156000
C	-5.279589000	2.902333000	0.142592000
H	-5.863976000	2.126927000	0.674521000
H	-4.941402000	3.655526000	0.881189000
H	-5.924334000	3.391024000	-0.616141000
C	-3.062708000	3.478235000	-1.640633000
H	-3.796757000	3.915331000	-2.347693000
H	-2.682809000	4.265595000	-0.959520000
H	-2.202302000	3.066393000	-2.203708000
C	0.794887000	3.203451000	-0.202066000
H	0.195366000	4.143289000	-0.196430000
H	1.726261000	3.452553000	0.352490000
C	1.160454000	2.868413000	-1.651581000
H	0.258376000	2.648489000	-2.257018000
H	1.829355000	1.987362000	-1.712524000
H	1.696845000	3.716433000	-2.122468000

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