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Supplementary Information

Phosphido complexes derived from 1,1'-ferrocenediyl-bridged secondary diphosphines

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Table S1 Crystal data and structure refinement details

	rac-H_2**1a**	*meso*-H_2**1b**	*meso*-H_2**1e**	[Li_2(μ-**1a**)(TMEDA)$_2$]	[Li_2(μ-**1b**)(TMEDA)$_2$]	[Li_2(μ-**1d**)(TMEDA)]$_2$	[{Zr(NMe$_2$)$_3$}$_2$(μ-**1a**)]
Chemical formula	$C_{22}H_{20}FeP_2$	$C_{18}H_{28}FeP_2$	$C_{26}H_{16}F_{12}FeP_2$	$C_{34}H_{50}FeLi_2N_4P_2$	$C_{30}H_{58}FeLi_2N_4P_2$	$C_{52}H_{92}Fe_2Li_4N_4P_4$	$C_{34}H_{54}FeN_6P_2Zr_2$
Formula mass	402.17	362.19	674.18	646.45	606.47	1036.63	847.06
Crystal system	monoclinic	triclinic	monoclinic	triclinic	orthorhombic	triclinic	monoclinic
Space group	$P2_1/n$	P-1	$P2_1/c$	P-1	$Pca2_1$	P-1	$P2_1/c$
a/Å	5.9967(14)	5.9610(8)	8.9360(7)	10.8879(8)	21.7734(5)	10.5717(9)	13.4517(4)
b/Å	26.083(7)	8.9856(11)	8.1613(5)	12.9242(8)	13.2129(4)	10.9440(9)	16.4468(4)
c/Å	11.900(4)	9.7083(12)	18.0145(16)	14.9695(10)	24.9840(7)	13.6502(10)	35.2138(13)
α/°	90	65.070(9)	90	101.557(5)	90	70.253(6)	90
β/°	101.87(2)	80.485(10)	94.549(7)	91.535(6)	90	80.074(6)	98.545(3)
γ/°	90	78.753(10)	90	111.792(5)	90	89.001(7)	90
Unit cell volume/Å^3	1821.6(8)	460.48(11)	1309.65(18)	1904.4(2)	7187.6(3)	1462.7(2)	7704.1(4)
T/K	200(2)	100(2)	173(2)	173(2)	173(2)	173(2)	100(2)
Z	4	1	2	2	8	1	8
μ/mm^{-1}	1.005	0.985	0.800	0.506	0.531	0.640	1.017
No. of refl. measured	8393	3222	9409	13776	39434	10283	50852
Independent	3184	1601	2310	6666	12455	5103	14256
reflections [R_{int}]	[0.0417]	[0.0219]	[0.0276]		[0.0376]	[0.0427]	[0.0418]
Final R_1 (wR_2)	0.0379	0.0385	0.0364	0.0635	0.0468	0.0494	0.0388
[$I > 2\sigma(I)$]	(0.0929)	(0.1411)	(0.0887)	(0.1713)	(0.1350)	(0.1228)	(0.0931)
Final R_1 (wR_2)	0.0537	0.0397	0.0537	0.0776	0.0644	0.0701	0.0500
[all data]	(0.1006)	(0.1425)	(0.0953)	(0.1870)	(0.1548)	(0.1372)	(0.1001)
Goodness of fit on F^2	1.025	1.299	1.029	1.095	0.841	1.054	1.031
CCDC number	1536257	1536258	1536259	1536260	1536261	1536262	15362603

Table S1 (continued) Crystal data and structure refinement details

	[{Zr(NMe$_2$)$_3$}$_2$(μ-**1e**)]	[(NiCp)$_2$(μ-**1a**)]·C_6H_6	[Ni(μ$_2$-OH){NiCp(μ$_2$-**1b**)}]$_2$ [(NiCp)$_2$(μ-**1b**)]·3C_6H_6	[NiCp(H**1b**)]	[{Ni[NiCp(μ$_2$-**1b**)]}$_2${μ$_2$-η^5:η^5-(C_5H_4)$_2$}]·2THF	[Ni{[NiCp(μ-**1a**)]}$_2$]	[Ni(H**1b**)$_2$]
Chemical formula	$C_{38}H_{50}F_{12}FeN_6P_2Zr_2$	$C_{38}H_{34}FeNi_2P_2$	$C_{92}H_{118}Fe_3Ni_6O_2P_6$	$C_{23}H_{32}FeNiP_2$	$C_{64}H_{86}Fe_2Ni_4O_2P_4$	$C_{54}H_{46}Fe_2Ni_3P_4$	$C_{36}H_{54}Fe_2NiP_4$
Formula mass	1119.07	725.86	1961.49	484.98	1357.74	1106.62	781.08
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	triclinic	triclinic
Space group	*C*2/*c*	*P*2$_1$/*c*	*C*2/*c*	*Cc*	*P*2$_1$/*c*	*P*-1	*P*-1
a/Å	41.181(3)	12.0027(4)	10.1479(4)	20.4381(14)	14.0188(8)	10.126(3)	10.5735(6)
b/Å	12.8318(13)	9.7307(4)	18.7714(6)	6.4522(3)	10.6198(5)	11.395(3)	12.3319(7)
c/Å	18.5900(15)	27.0982(8)	45.164(2)	18.5152(12)	20.1658(12)	12.124(3)	14.3840(8)
α/°	90	90	90	90	90	103.44(2)	87.958(5)
β/°	108.288(6)	90.452(2)	96.353(3)	116.319(5)	96.178(5)	106.87(2)	74.515(4)
γ/°	90	90	90	90	90	115.18(2)	87.467(5)
Unit cell volume/Å^3	9327.4(15)	3164.8(2)	8550.5(6)	2188.5(2)	2984.8(3)	1104.5(5)	1805.2(2)
T/K	100(2)	173(2)	173(2)	173(2)	173(2)	173(2)	153(2)
Z	8	4	4	4	2	1	2
μ/mm^{-1}	0.897	1.758	1.944	1.675	1.860	2.080	1.511
No. of refl. measured	18502	31471	56233	5786	13143	7162	12583
Independent	8501	5582	7535	3458	5250	3832	6327
reflections [R_{int}]	[0.1011]	[0.0144]	[0.0220]	[0.0259]	[0.1261]	[0.1557]	[0.0189]
Final R_1 (wR_2)	0.0899	0.0294	0.0254	0.0629	0.0812	0.1439	0.0282
[$I > 2\sigma(I)$]	(0.2209)	(0.0739)	(0.0629)	(0.1524)	(0.1681)	(0.3669)	(0.0741)
Final R_1 (wR_2)	0.1300	0.0325	0.0298	0.0633	0.1654	0.1853	0.0315
[all data]	(0.2589)	(0.0756)	(0.0653)	(0.1533)	(0.2120)	(0.4285)	(0.0799)
Goodness of fit on F^2	0.997	1.058	1.035	1.059	1.068	1.398	1.088
CCDC number	1536264	1536265	1536267	1536266	1536268	1536269	1536270

Table S2 Selected bond lengths (Å) and angles (°) for the nickel complexes of this study which were obtained by serendipity

	Average Ni–P	Ni–P–Ni	P–Ni–P	C–P–C
[Ni(μ_2-OH){NiCp(μ_2-**1b**)}]$_2$[a,b]	2.17 (Ni2)	96.06(3)	74.94(3)	101.4(1)
	2.18 (Ni3)	96.16(3)	74.60(3)	101.3(1)
[{Ni[NiCp(μ_2-**1b**)]}$_2${μ_2-η^5:η^5-(C_5H_4)$_2$}][c]	2.17	96.7(1)	75.1(1)	100.9(5)
		96.6(1)	74.8(1)	101.8(5)
[Ni{[NiCp(μ_2-**1a**)]}$_2$][c]	2.19	89.1(2)	77.41(15) (Ni1)[d]	100.8(8)
		88.1(2)	102.59(15) (Ni1)	102.5(8)
			78.9(2) (Ni2)[d]	
[Ni(H**1b**)$_2$][e]	2.17		105.70(3)[d]	99.7(1)
			111.32(2)	99.2(1)
			112.31(3)	
			111.40(2)	
			111.60(2)	
			104.66(2)[d]	

[a] Molecular C_{2h} symmetry. [b] O–Ni–O 79.0(1), Ni–O–Ni 101.0(1), average P–Ni–O 103.1 and 175.9. [c] Molecular C_i symmetry. [d] Chelate bite angle. [e] Approximate D_2 symmetry, because the phosphino and phosphido P atom could not be distinguished from one another experimentally.

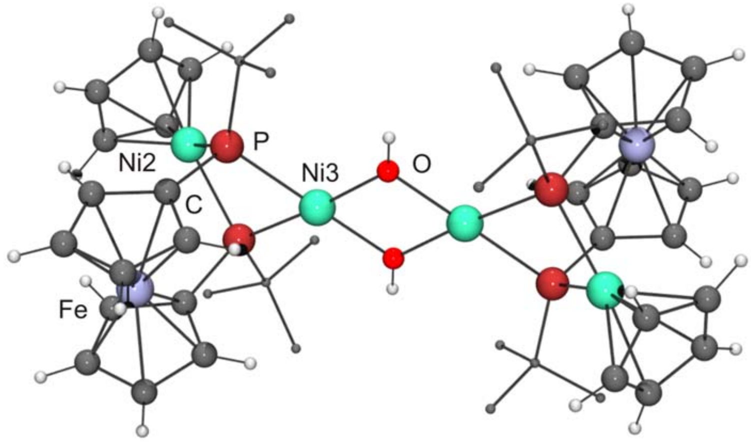


Fig. S1 Molecular structure of [Ni(μ_2-OH){NiCp(μ_2-**1b**)}]$_2$ in the co-crystal with [(NiCp)$_2$(μ-**1b**)]. *tert*-Butyl carbon atoms are shown as smaller circles without hydrogen atoms for clarity.

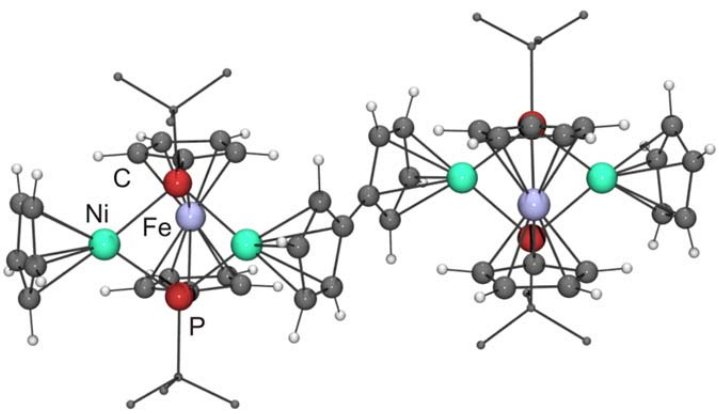


Fig. S2 Molecular structure of [{Ni[NiCp(μ_2-**1b**)]}$_2${μ_2-η^5:η^5-(C_5H_4)$_2$}] in the crystal. *tert*-Butyl carbon atoms are shown as smaller circles without hydrogen atoms for clarity.

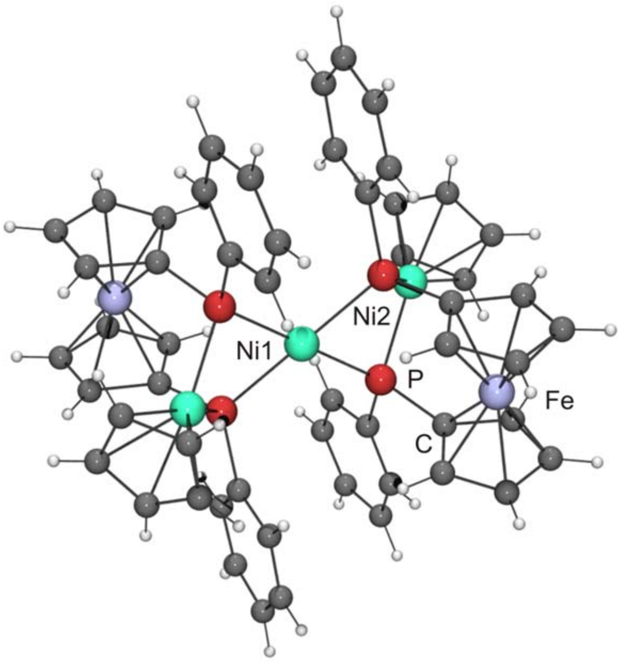


Fig. S3 Molecular structure of [Ni{[NiCp(μ-**1a**)]}$_2$] in the crystal.

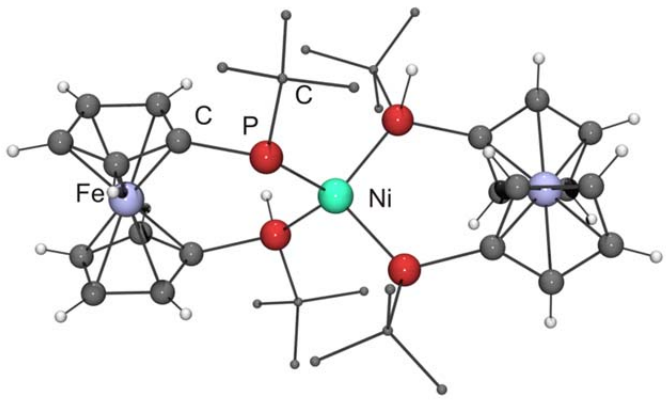


Fig. S4 Molecular structure of [Ni(H**1b**)$_2$] in the crystal. *tert*-Butyl carbon atoms are shown as smaller circles without hydrogen atoms for clarity.

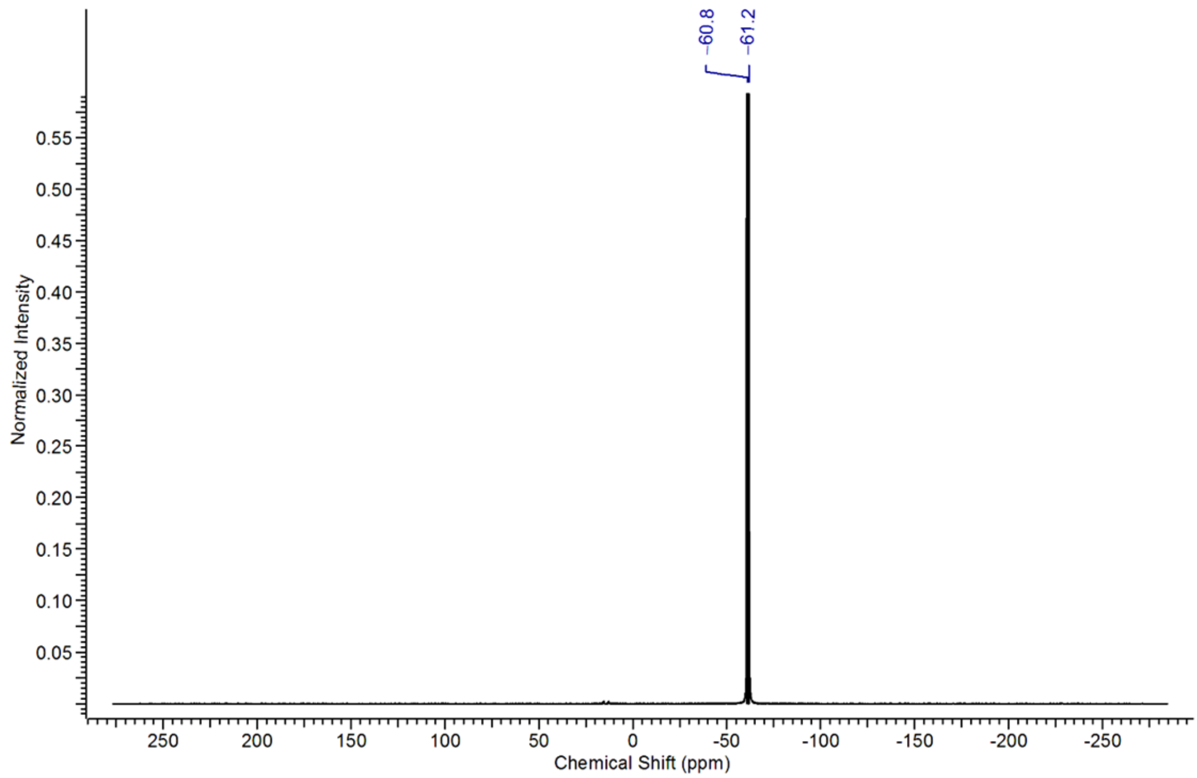


Fig. S5 ^{31}P NMR spectrum of H_2**1a** (C_6D_6, 202.3 MHz).

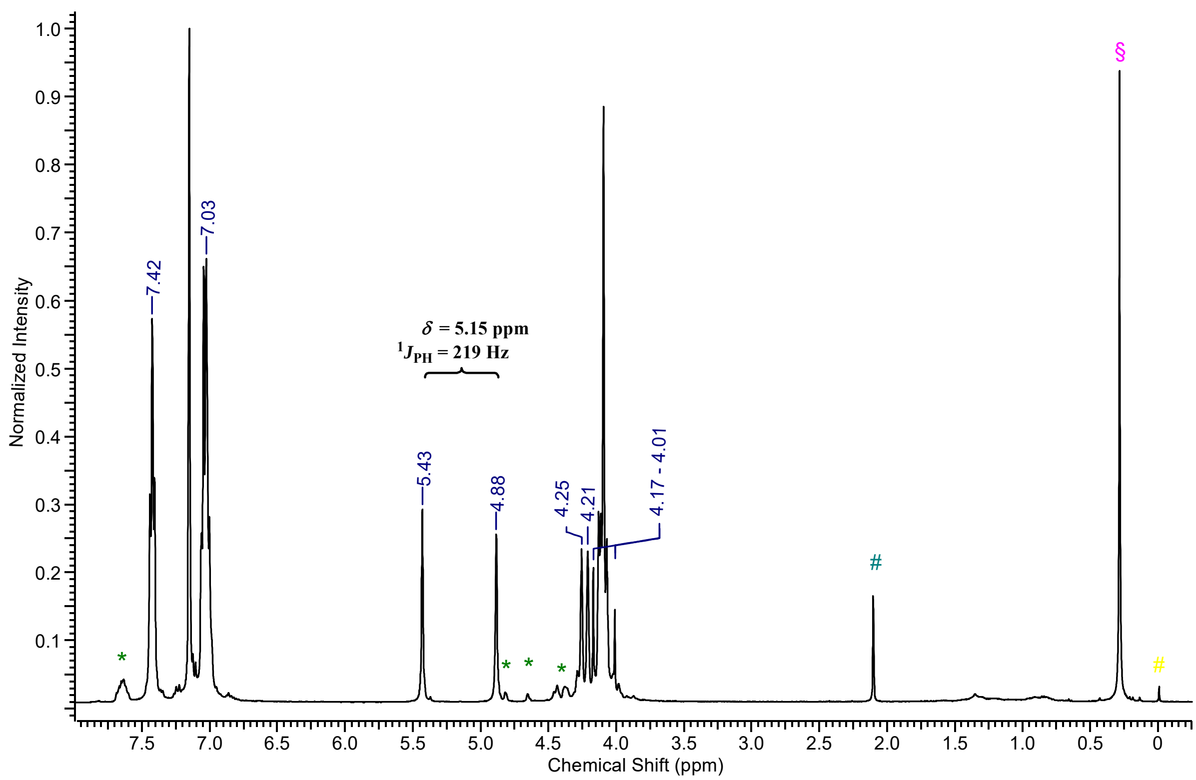


Fig. S6 ^{1}H NMR spectrum of H_2**1a** (C_6D_6, 399.9 MHz). Signals marked belongs to trace amounts of unidentified impurities (*) and TMS (#) as well as small amounts of toluene (#) and to silicon grease (§).

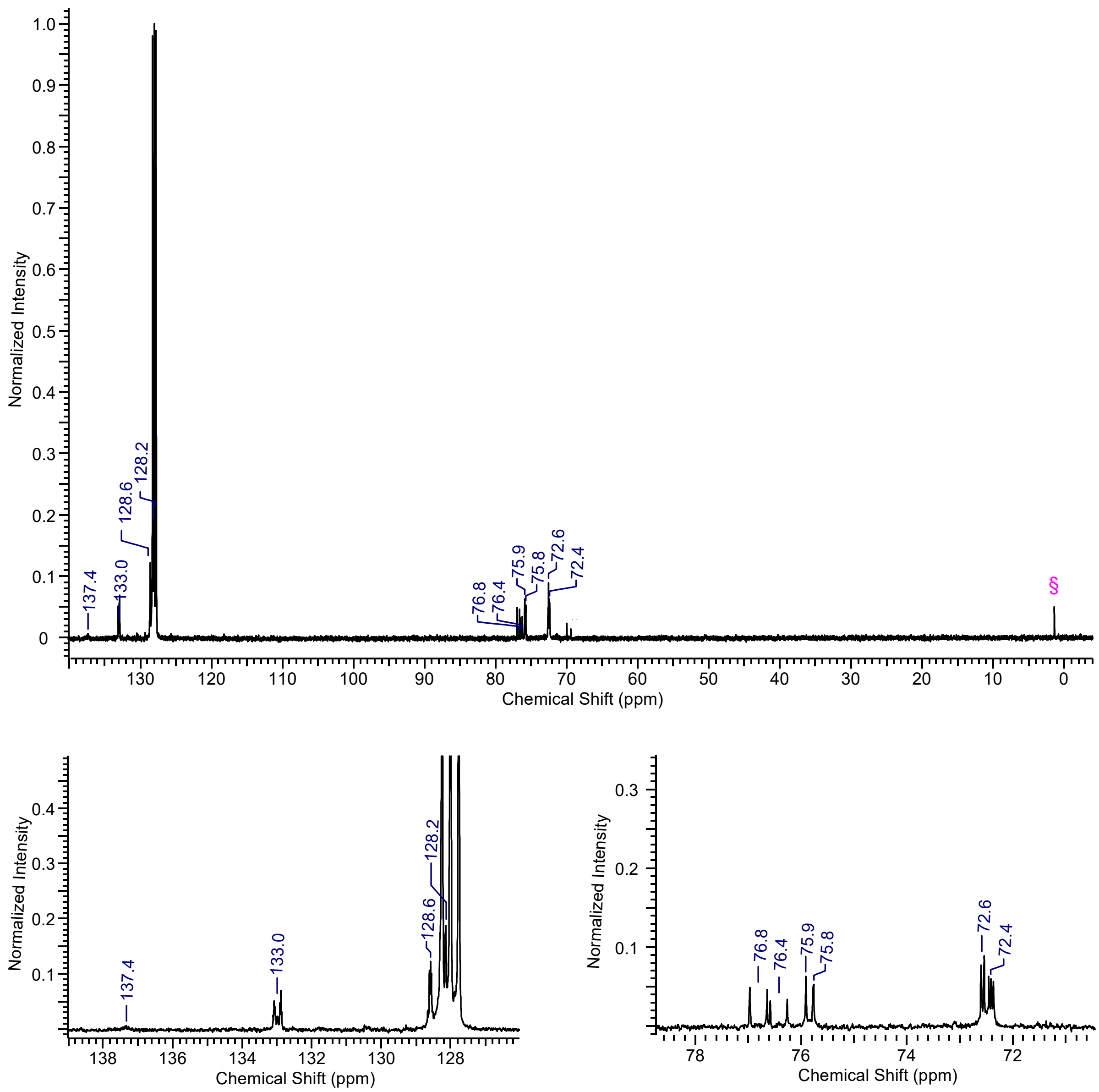


Fig. S7 ^{13}C NMR spectrum of H_2**1a** (C_6D_6, 100.5 MHz). The signal marked belongs to silicon grease (§).

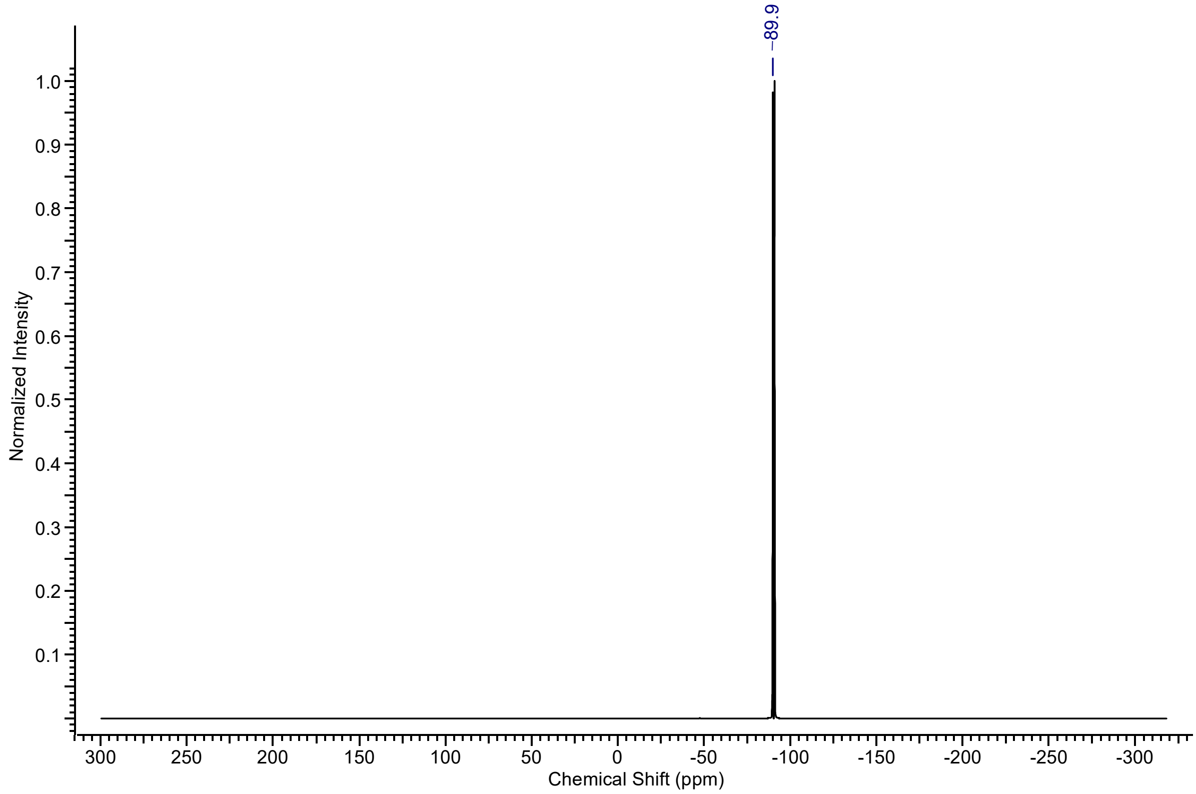


Fig. S8 ^{31}P NMR spectrum of H_2**1c** (C_6D_6, 202.3 MHz).

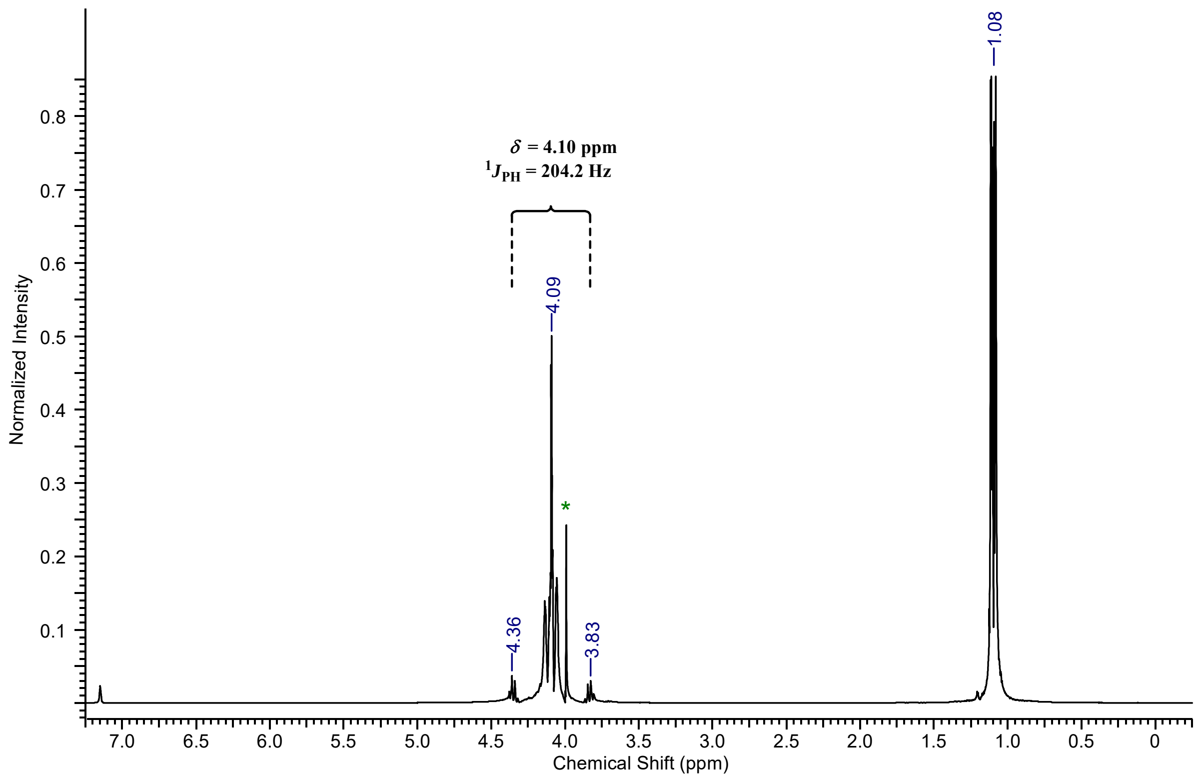


Fig. S9 ^{1}H NMR spectrum of H_2**1c** (C_6D_6, 399.9 MHz). The signal marked belongs to trace amounts of [FeCp{η^5-C_5H_4(PHMe)}] (*).

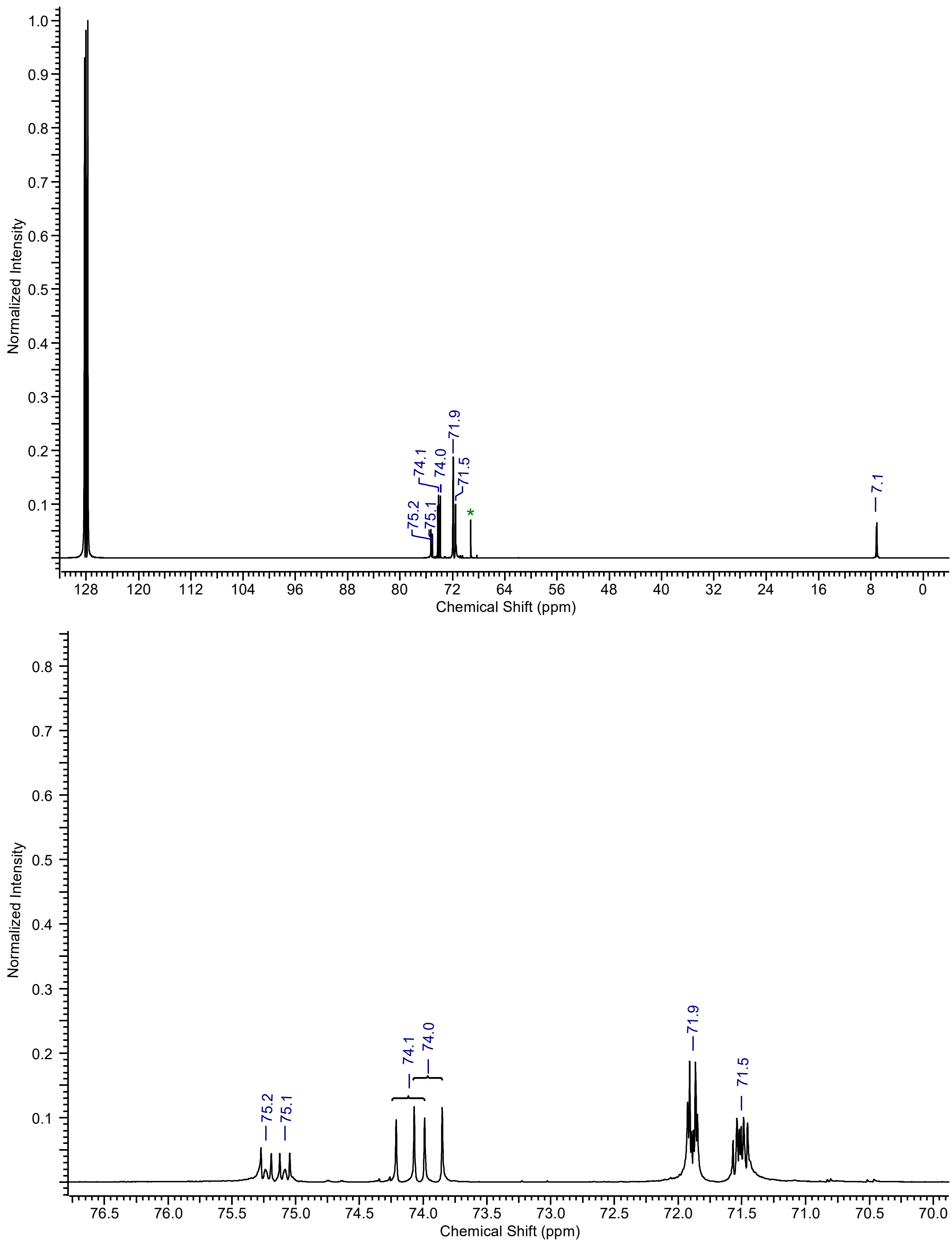


Fig. S10 ^{13}C NMR spectrum of H_2**1c** (C_6D_6, 100.5 MHz). The signal marked belongs to trace amounts of [FeCp{η^5-C_5H_4(PHMe)}] (*).

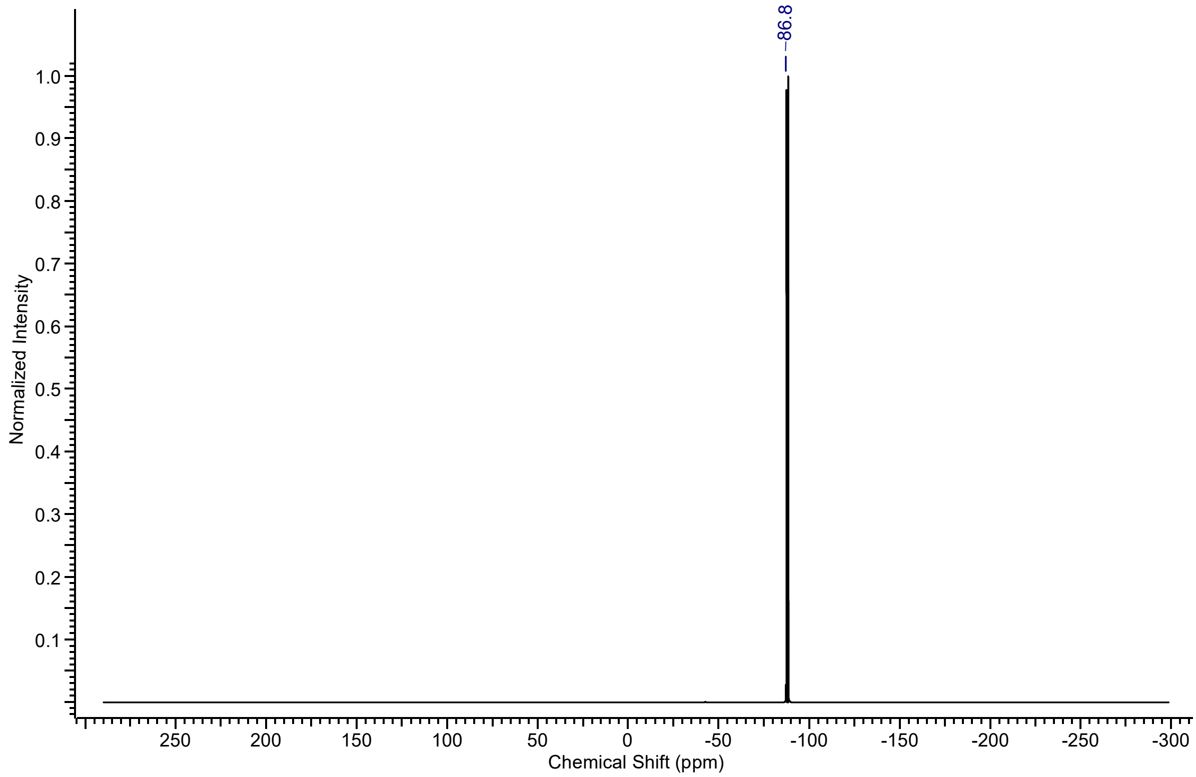


Fig. S11 ^{31}P NMR spectrum of H_2**1d** (C_6D_6, 202.3 MHz).

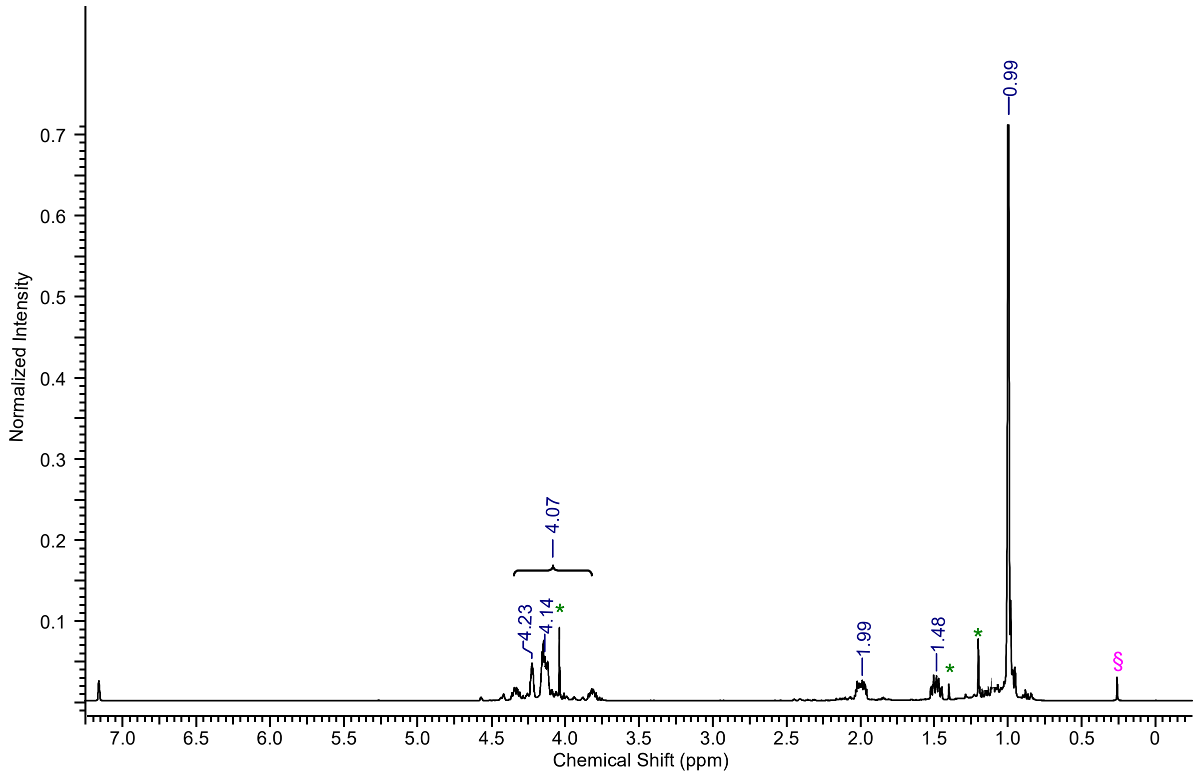


Fig. S12 ^{1}H NMR spectrum of H_2**1d** (C_6D_6, 399.9 MHz). Signals marked belong to trace amounts of [FeCp{η^5-C_5H_4(PHNp)}] (*) and silicon grease (§).

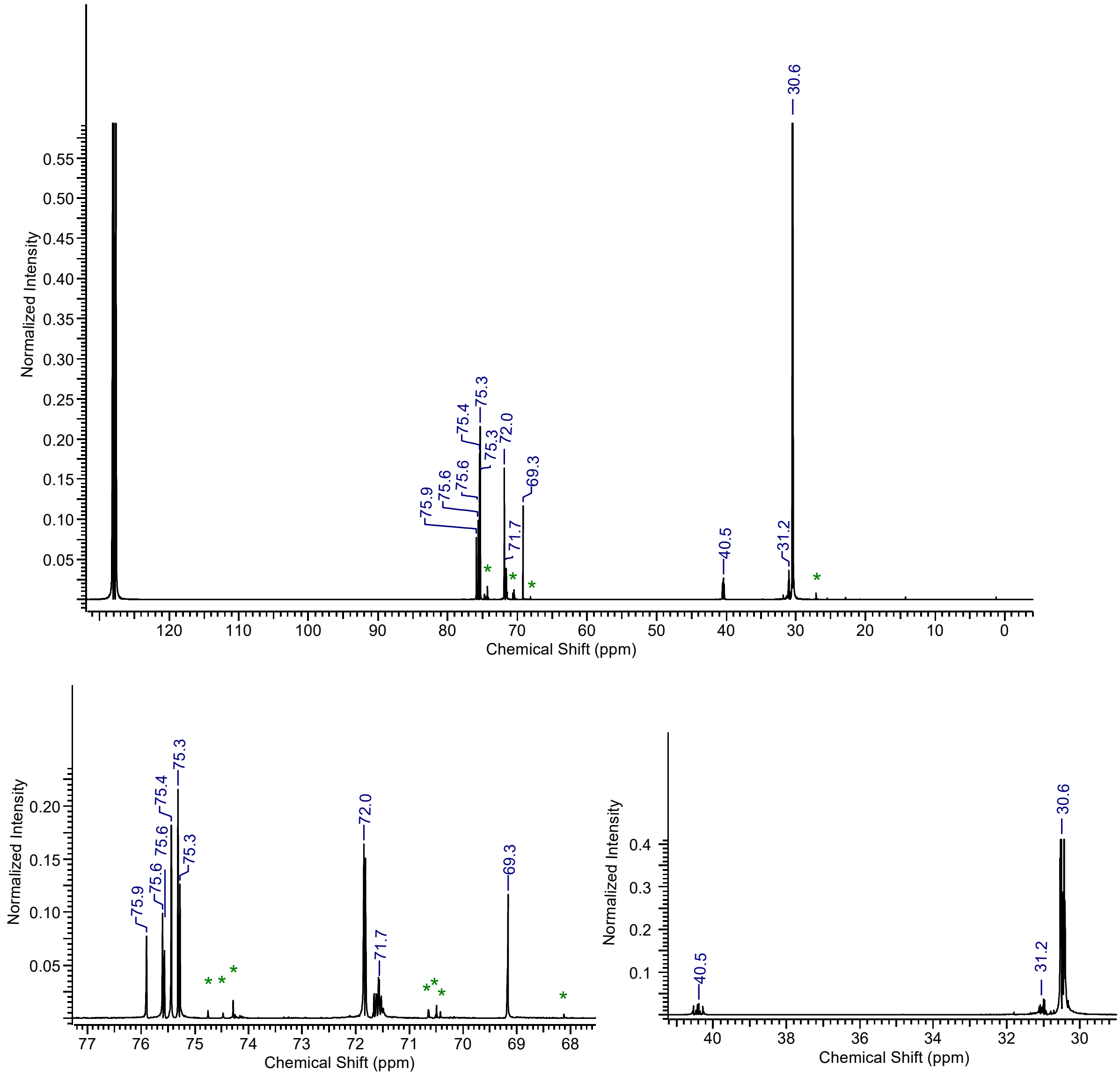


Fig. S13 ^{13}C NMR spectrum of H_2**1d** (C_6D_6, 100.5 MHz). Signals marked belong to trace amounts of [FeCp{η^5-C_5H_4(PHNp)}] (*).

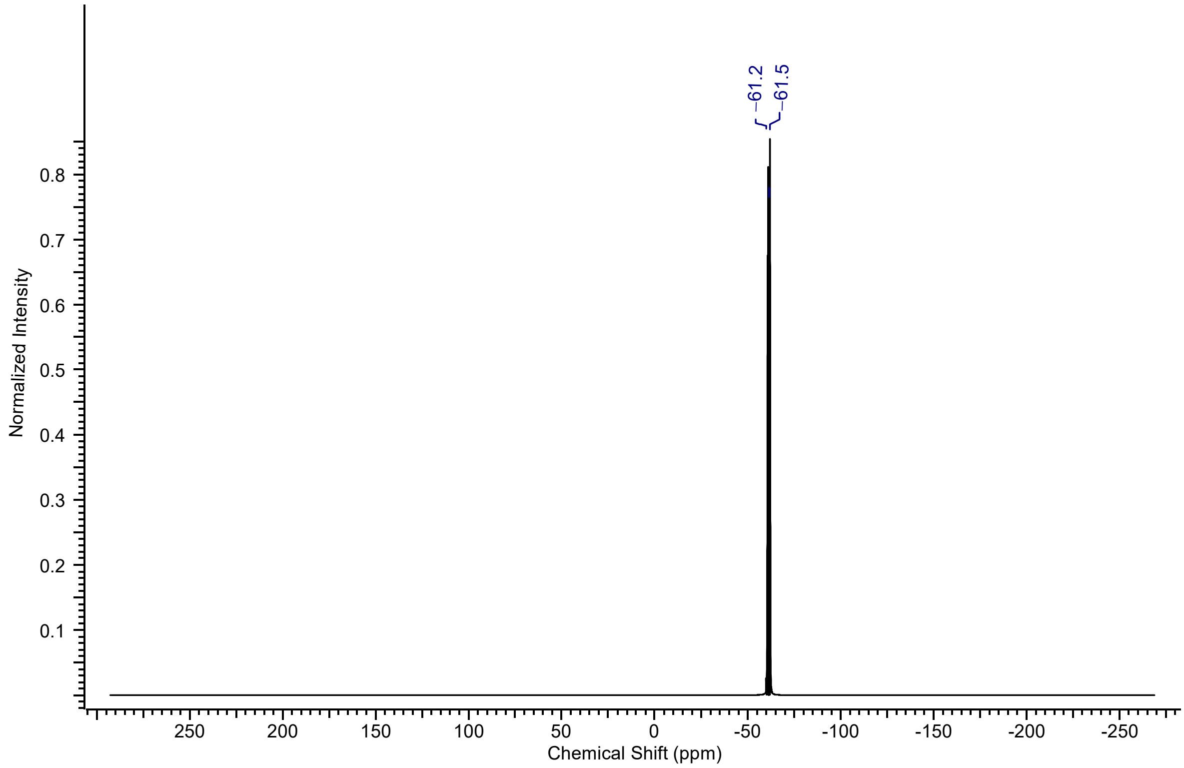


Fig. S14 ^{31}P NMR spectrum of H_2**1e** (C_6D_6, 202.3 MHz).

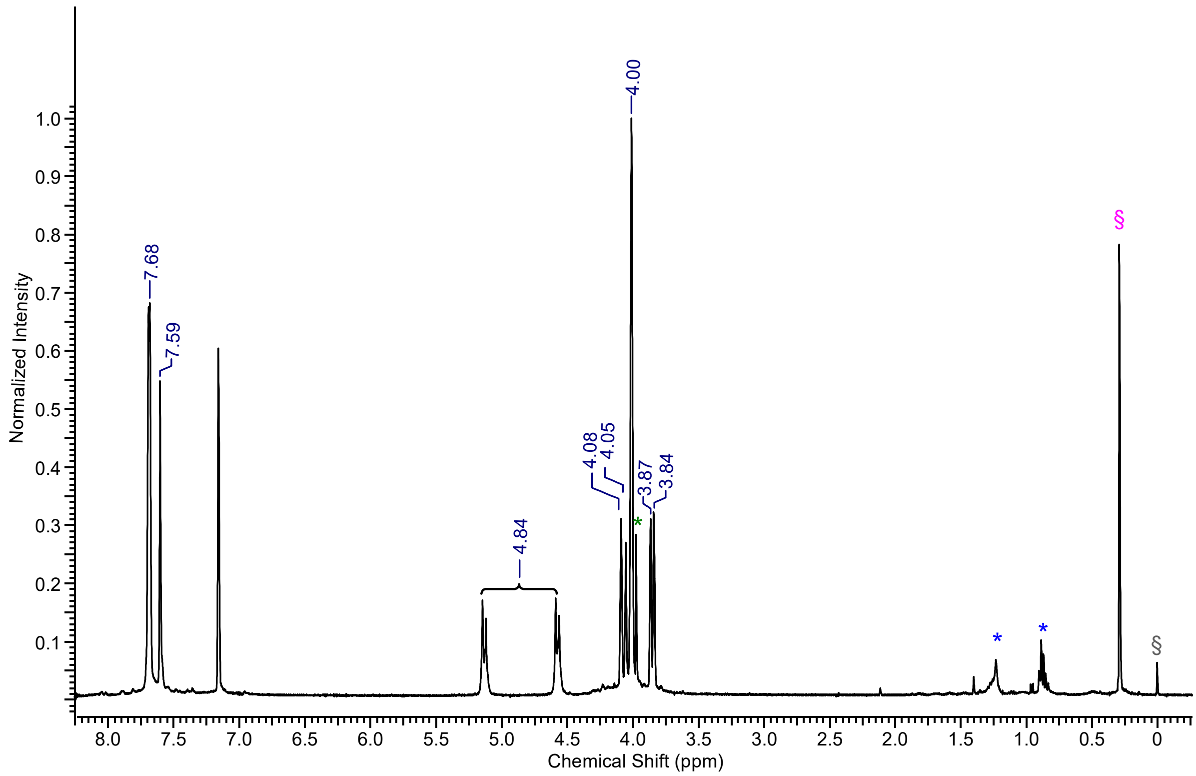


Fig. S15 ^{1}H NMR spectrum of H_2**1e** (C_6D_6, 399.9 MHz). Signals marked belong to trace amounts of [FeCp{η^5-C_5H_4(PHXyF)}] (*), *n*-hexane (*), silicon grease (§) and TMS (§).

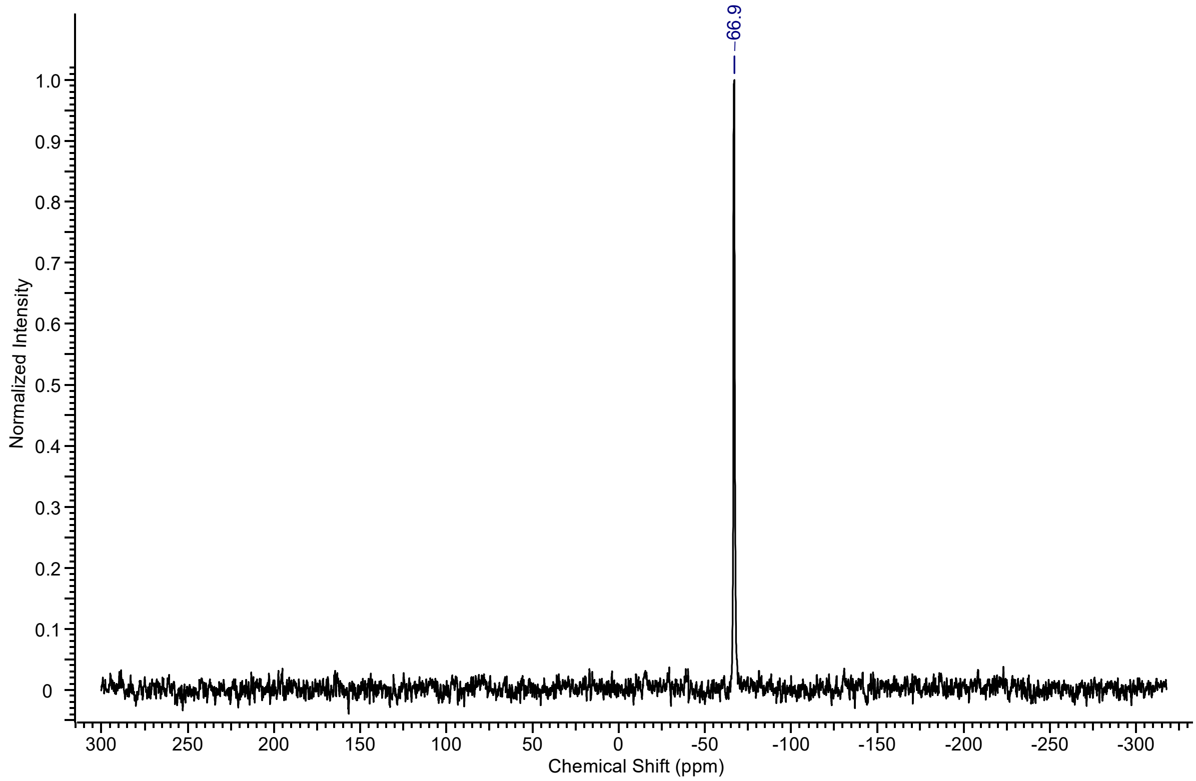


Fig. S16 ^{31}P NMR spectrum of [Li_2(μ-**1a**)($TMEDA)_2$] (C_6D_6, 202.3 MHz).

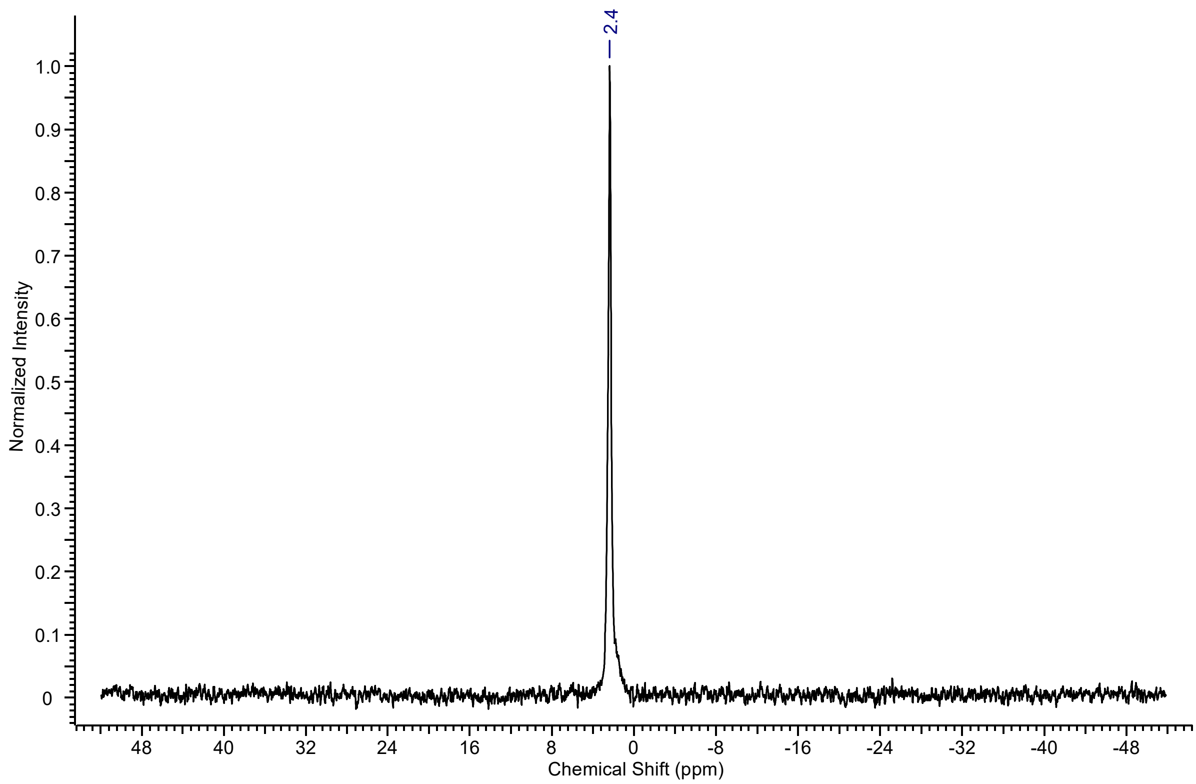


Fig. S17 ^{7}Li NMR spectrum of [Li_2(μ-**1a**)($TMEDA)_2$] (C_6D_6, 194.2 MHz).

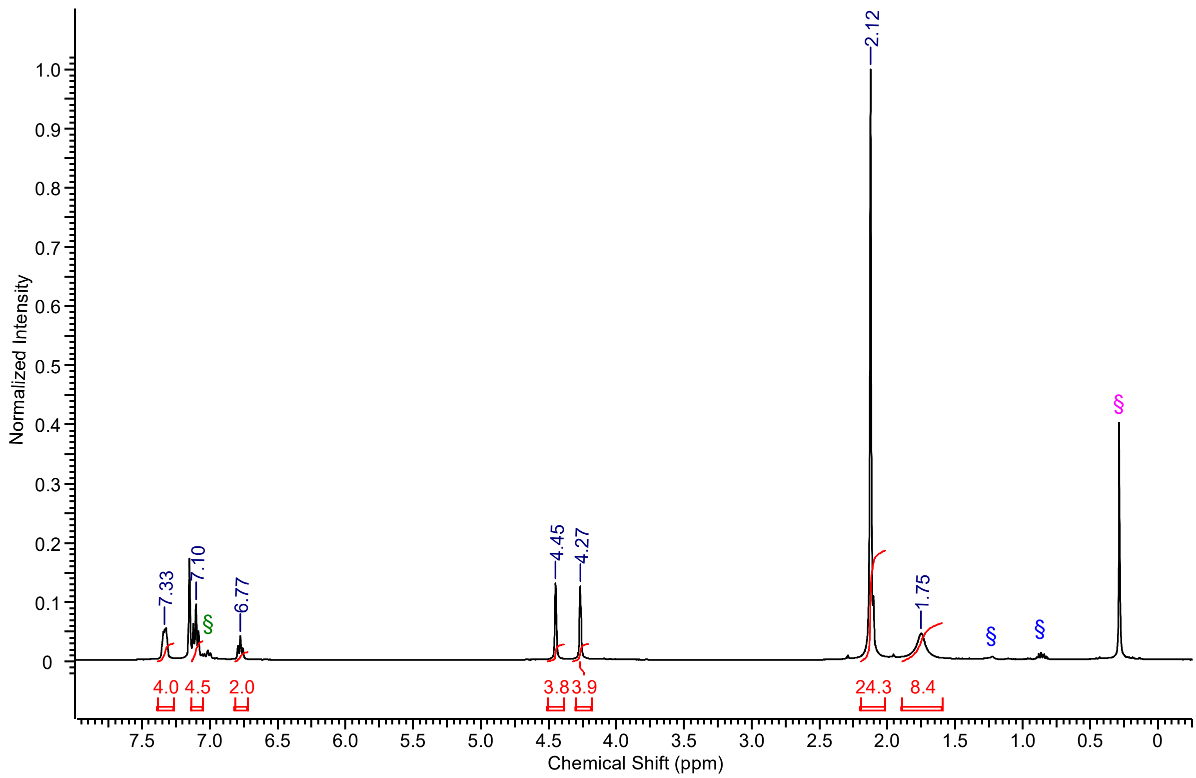


Figure S18 ^{1}H NMR spectrum of [Li_2(μ-**1a**)(TMEDA)$_2$] (C_6D_6, 399.9 MHz). Signals marked belong to trace amounts of toluene (§) and *n*-hexane (§) and to silicon grease (§).

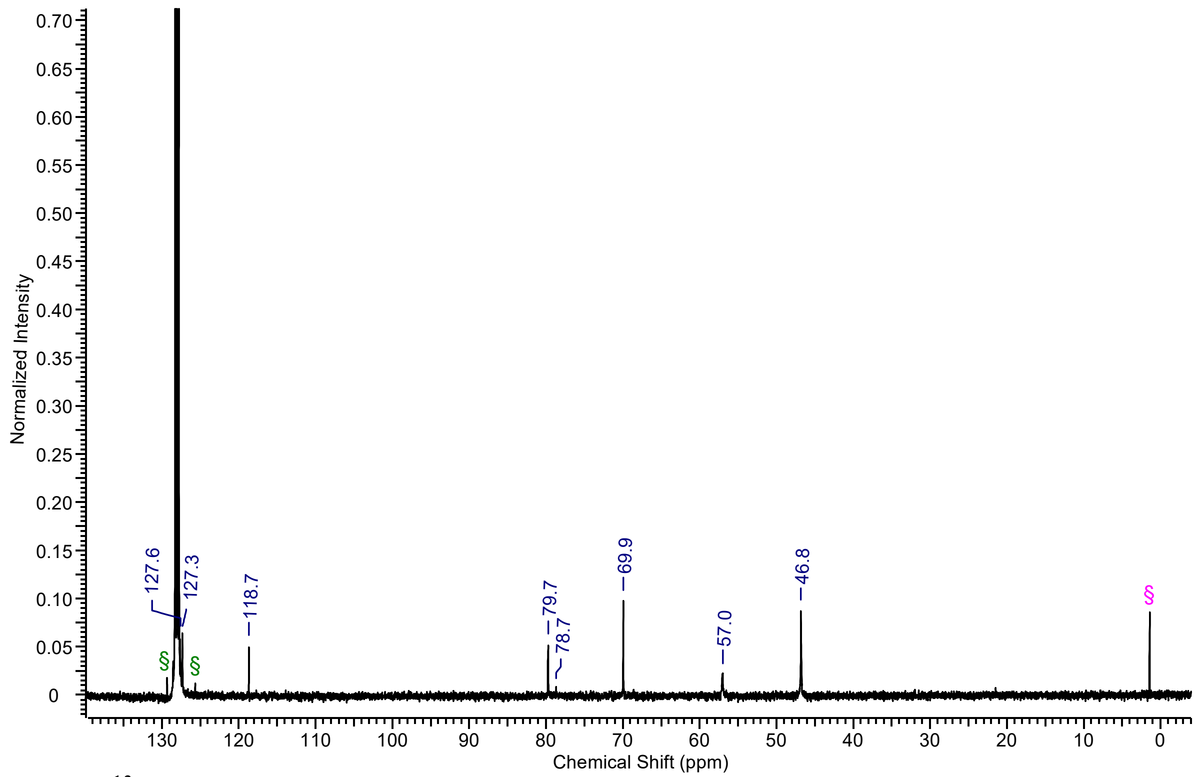


Fig. S19 ^{13}C NMR spectrum of [Li_2(μ-**1a**)(TMEDA)$_2$] (C_6D_6, 100.5 MHz). Signals marked belong to trace amounts of toluene (§) and to silicon grease (§).

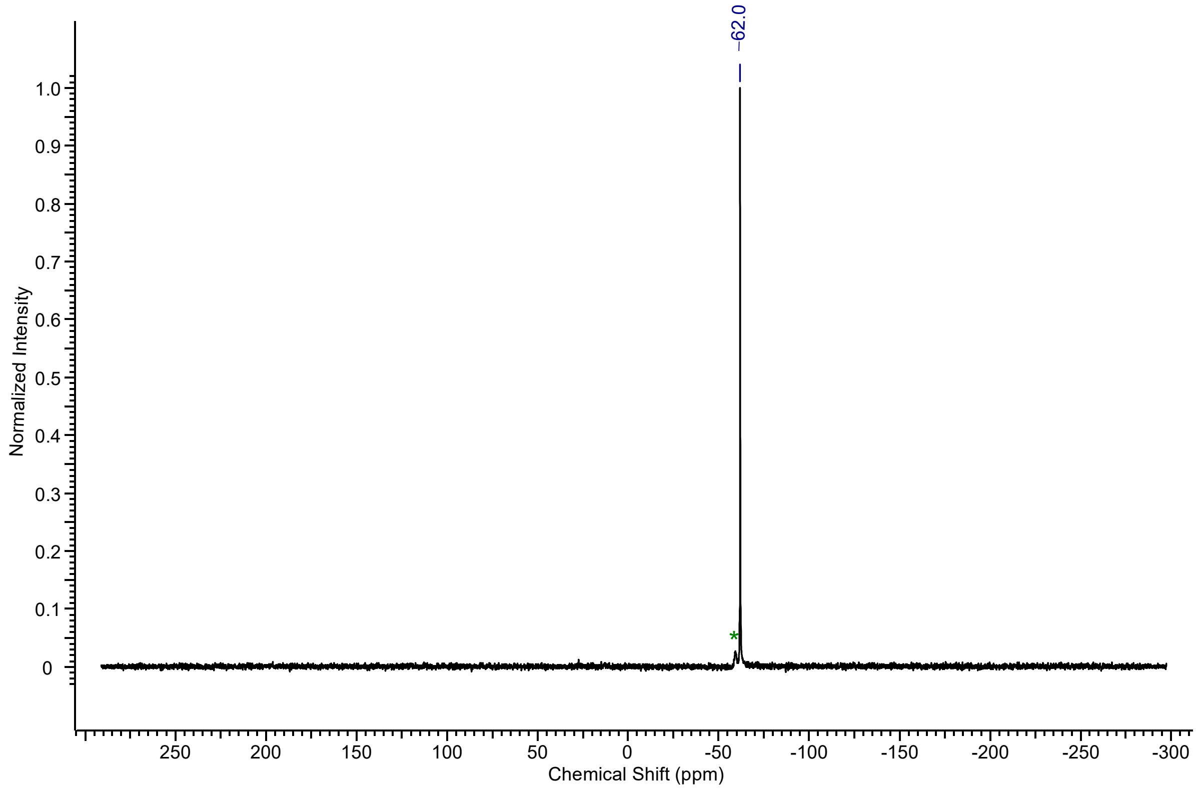


Fig. S20 ^{31}P NMR spectrum of [Li_2(μ-**1a**)$(TMEDA)_2$] (THF-d_8, 202.3 MHz). The signal marked belongs to trace amounts of an unidentified species (*).

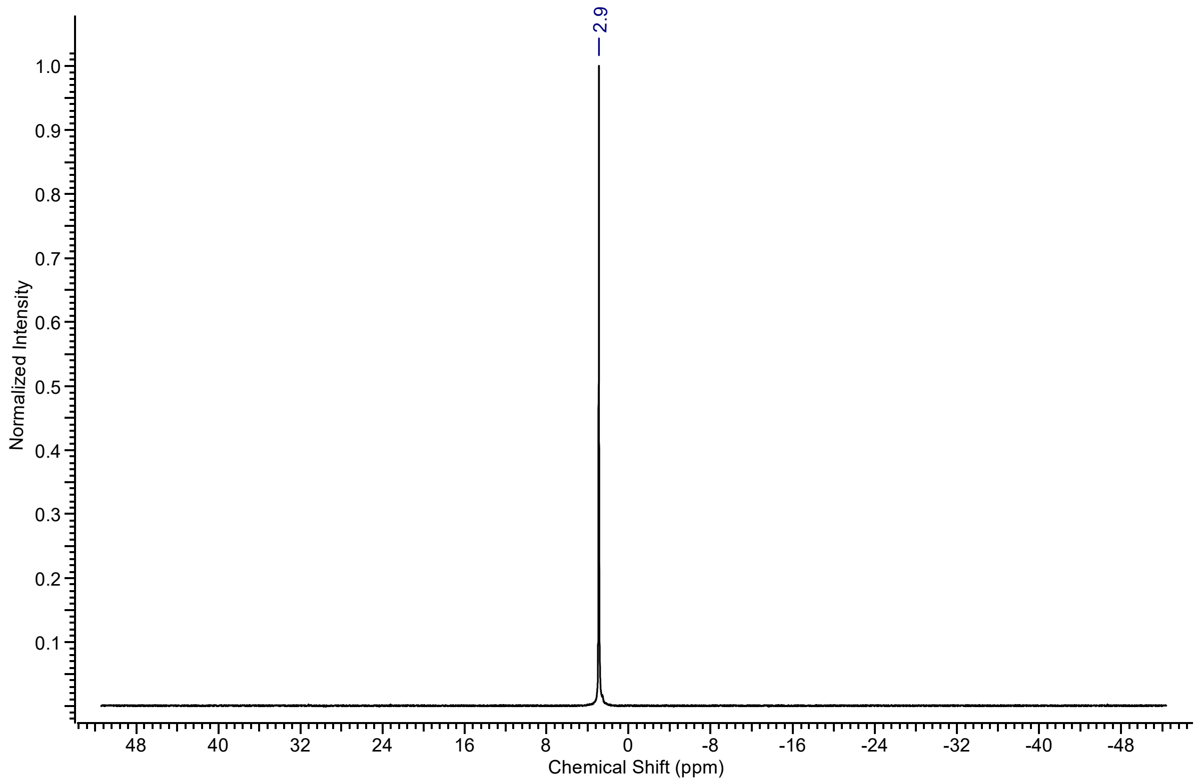


Fig. S21 ^{7}Li NMR spectrum of [Li_2(μ-**1a**)$(TMEDA)_2$] (THF-d_8, 194.2 MHz).

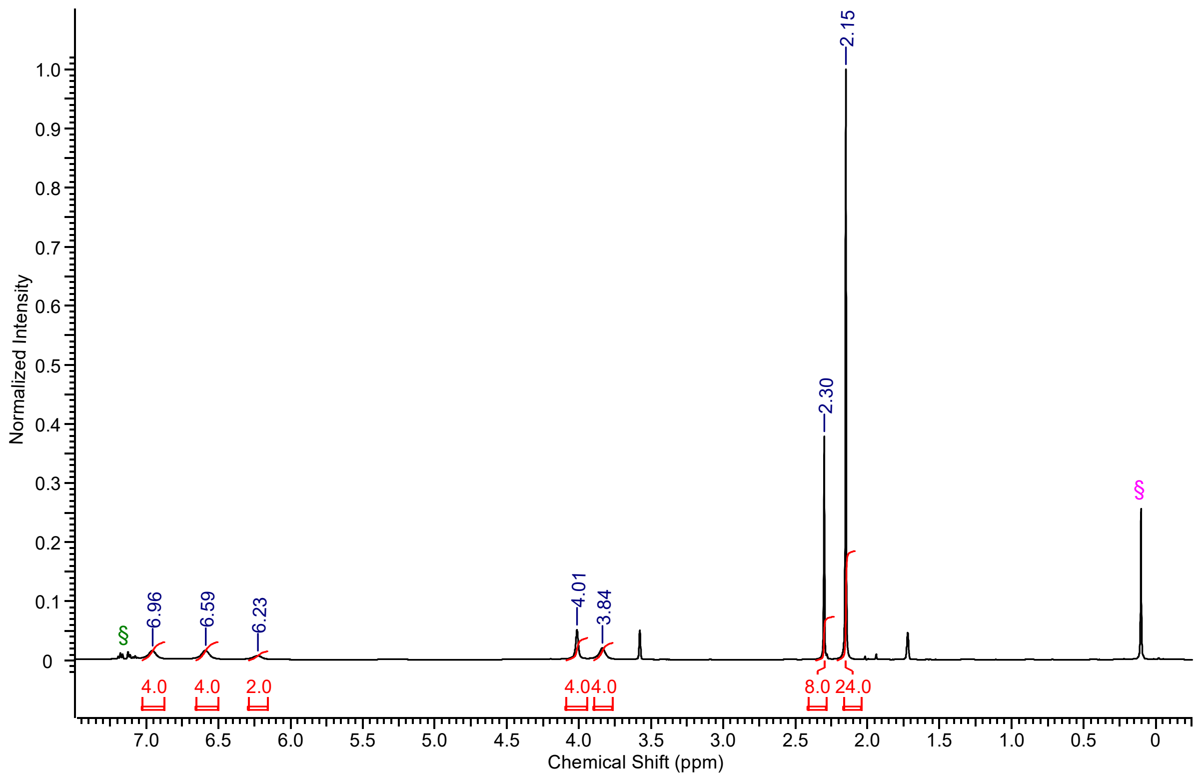


Fig. S22 [1]H NMR spectrum of [Li_2(μ-**1a**)(TMEDA)$_2$] (THF-d_8, 399.9 MHz). Signals marked belong to trace amounts of toluene (§) and to silicon grease (§).

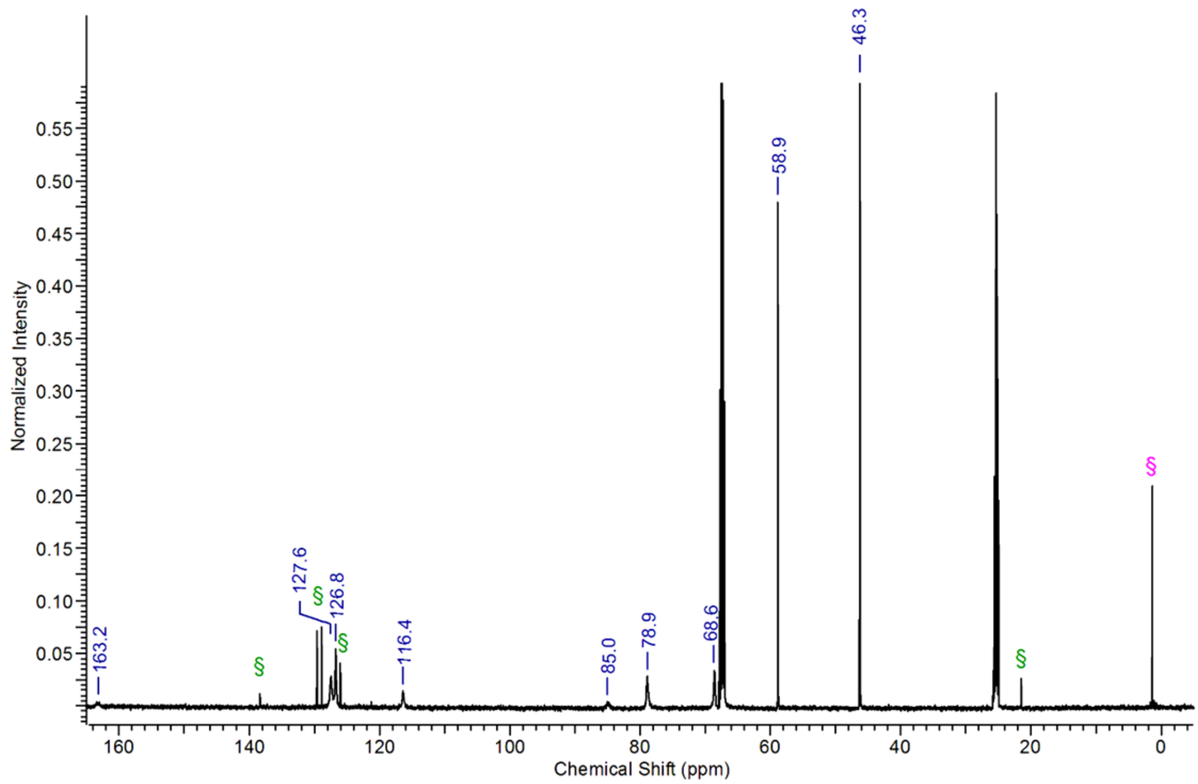
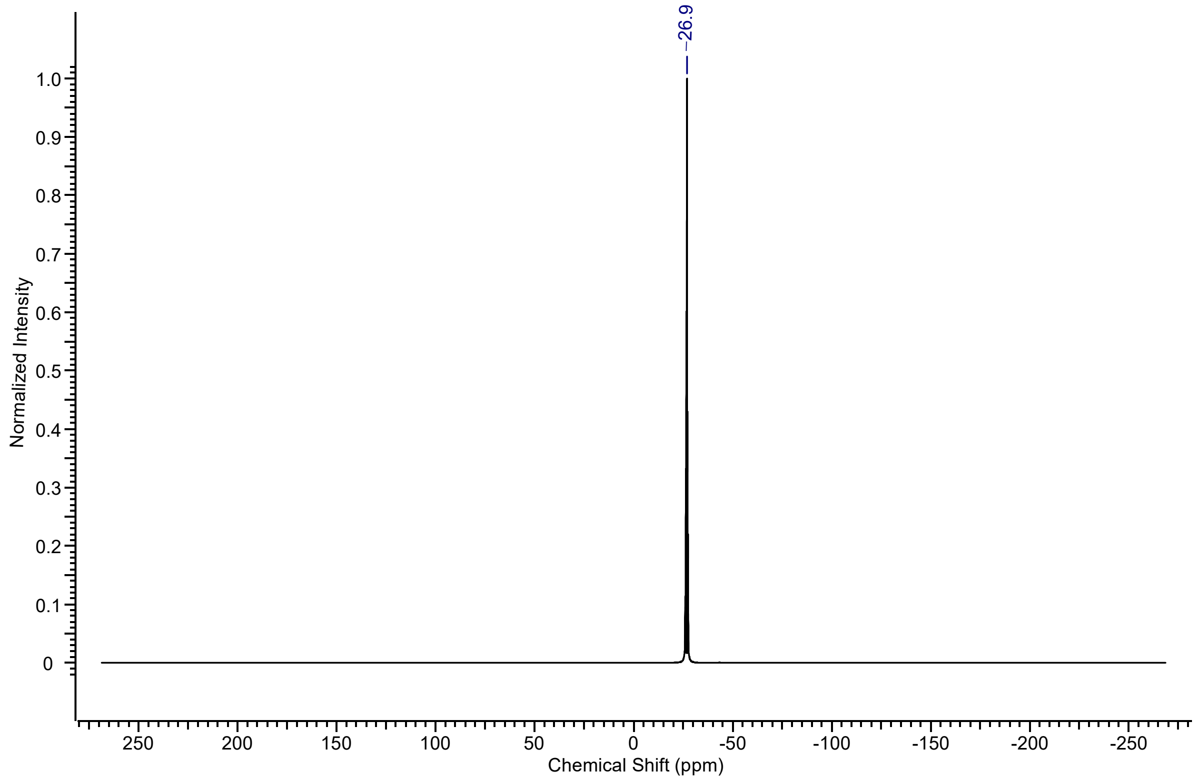


Fig. S23 [13]C NMR spectrum of [Li_2(μ-**1a**)(TMEDA)$_2$] (THF-d_8, 100.6 MHz). Signals marked belong to trace amounts of toluene (§) and to silicon grease (§).



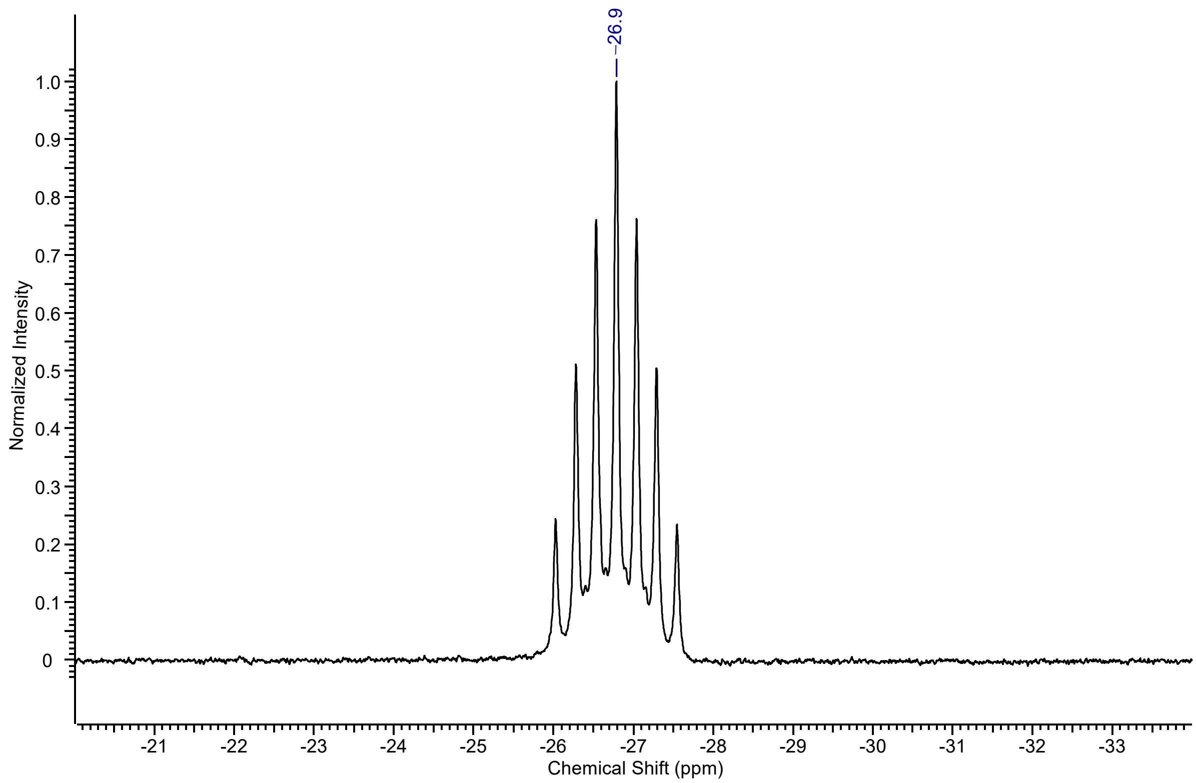


Fig. S24 ^{31}P NMR spectrum of [Li_2(μ-**1b**)(TMEDA)$_2$] (C_6D_6, 202.3 MHz).

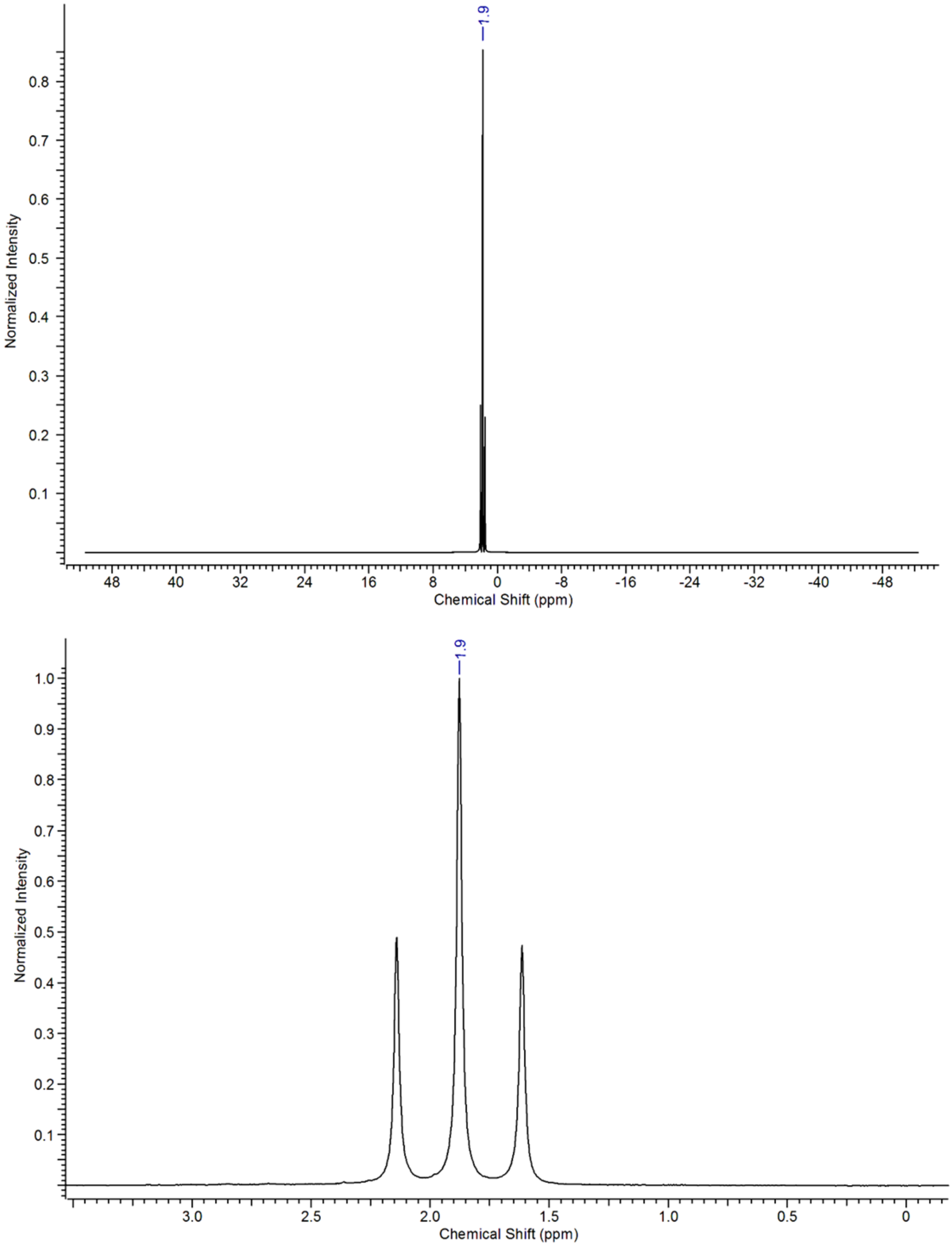


Fig. S25 ^{7}Li NMR spectrum of $[Li_2(\mu$-**1b**$)(TMEDA)_2]$ (C_6D_6, 194.2 MHz).

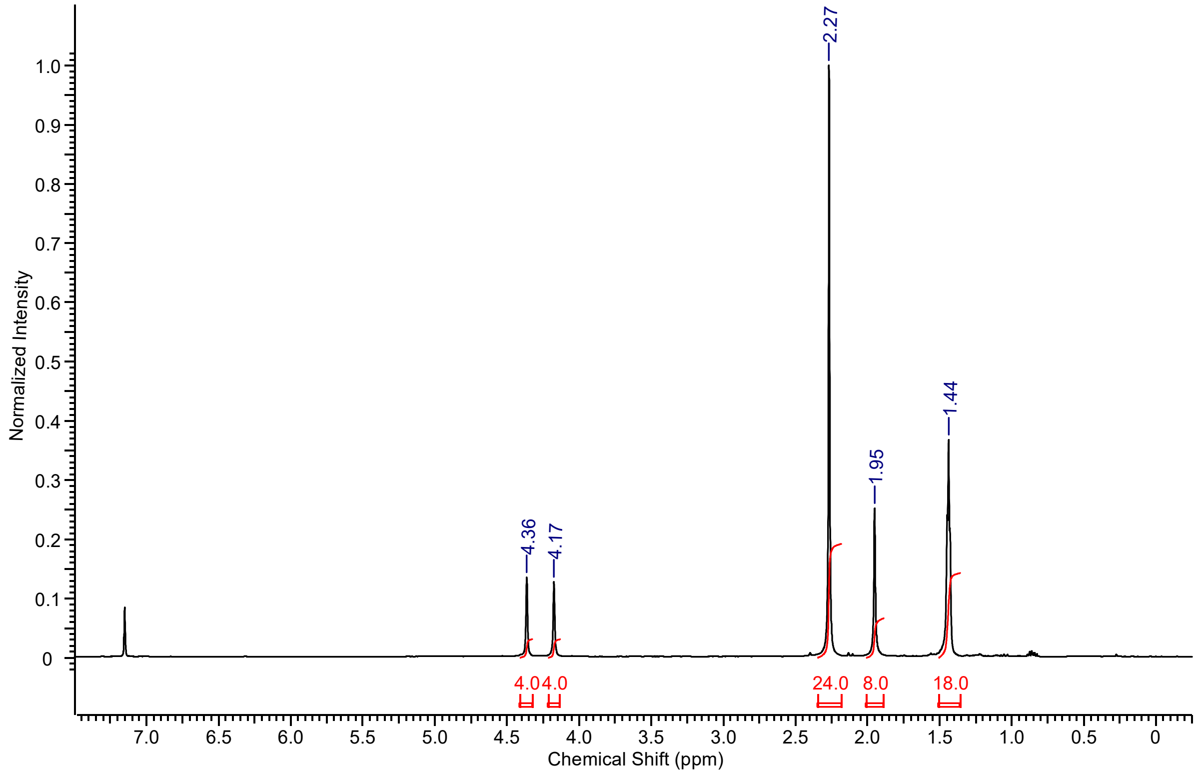


Fig. S26 ^{1}H NMR spectrum of [Li_2(μ-**1b**)(TMEDA)$_2$] (C_6D_6, 399.9 MHz).

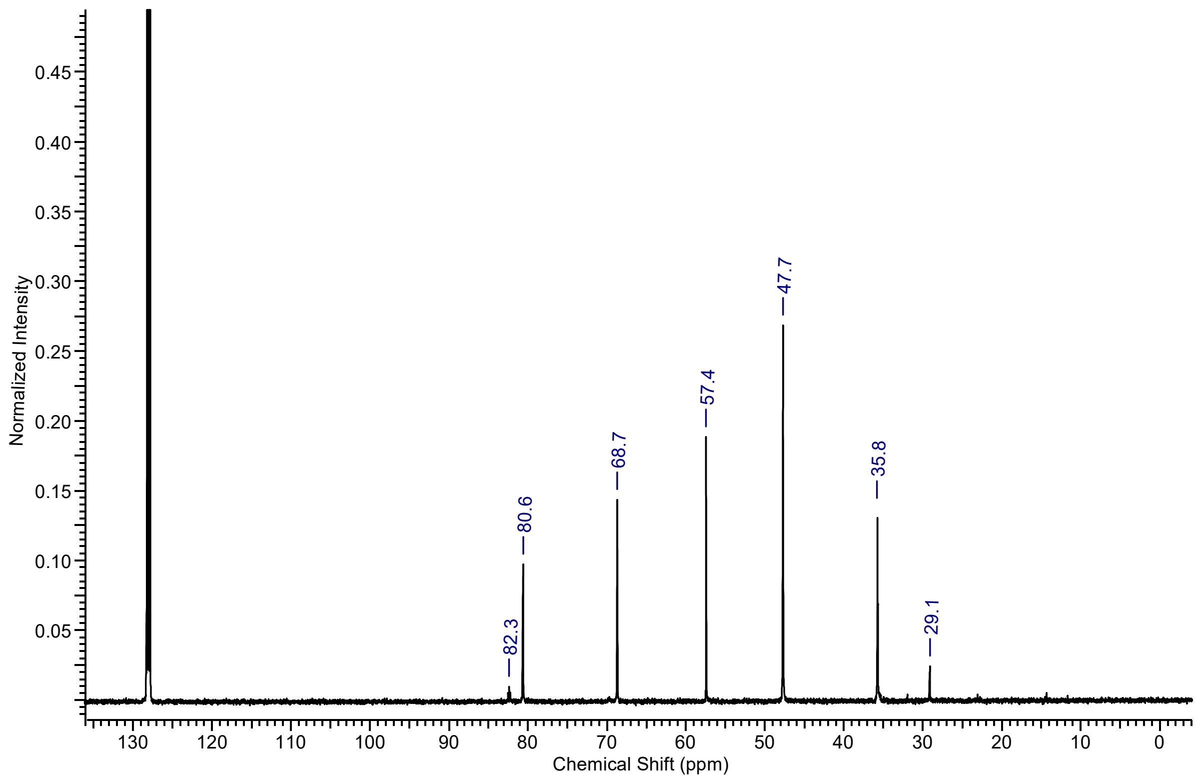


Fig. S27 ^{13}C NMR spectrum of [Li_2(μ-**1b**)(TMEDA)$_2$] (C_6D_6, 100.6 MHz).

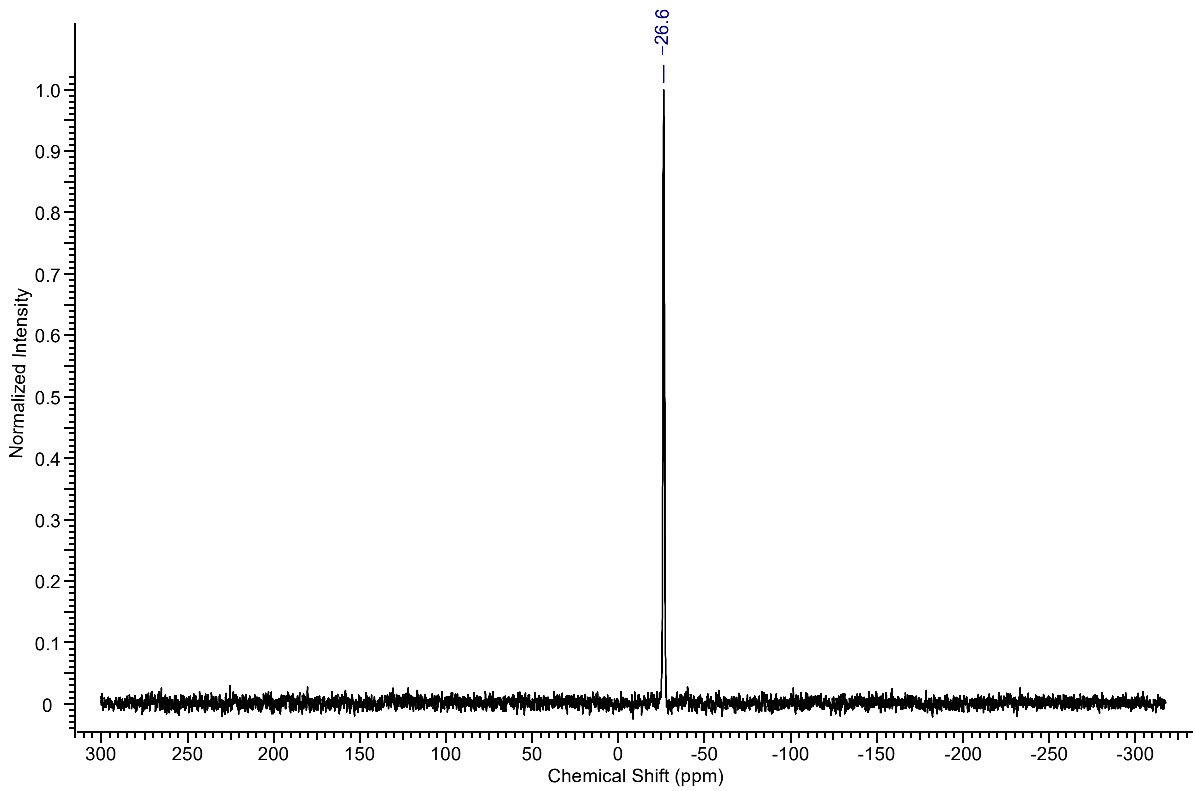


Fig. S28 ^{31}P NMR spectrum of [Li_2(μ-**1b**)(TMEDA)$_2$] (THF-d_8, 202.3 MHz).

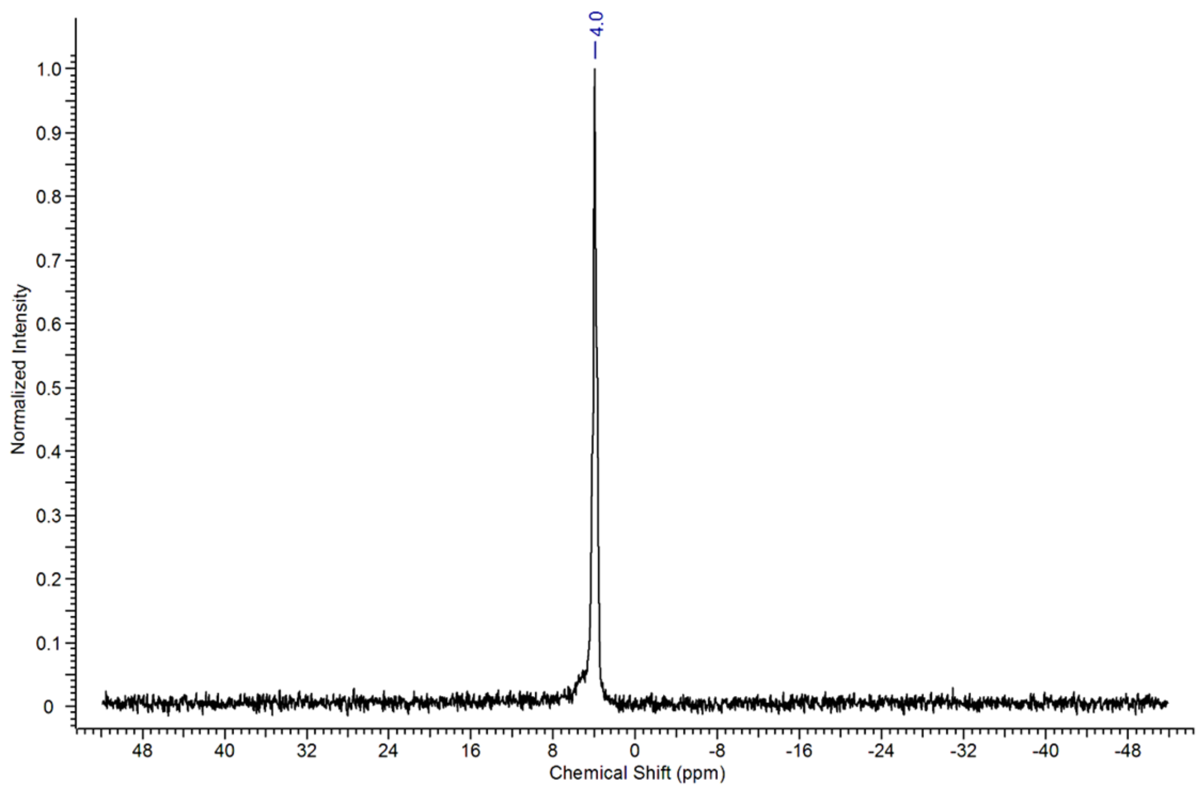


Fig. S29 ^{7}Li NMR spectrum of [Li_2(μ-**1b**)(TMEDA)$_2$] (THF-d_8, 194.2 MHz).

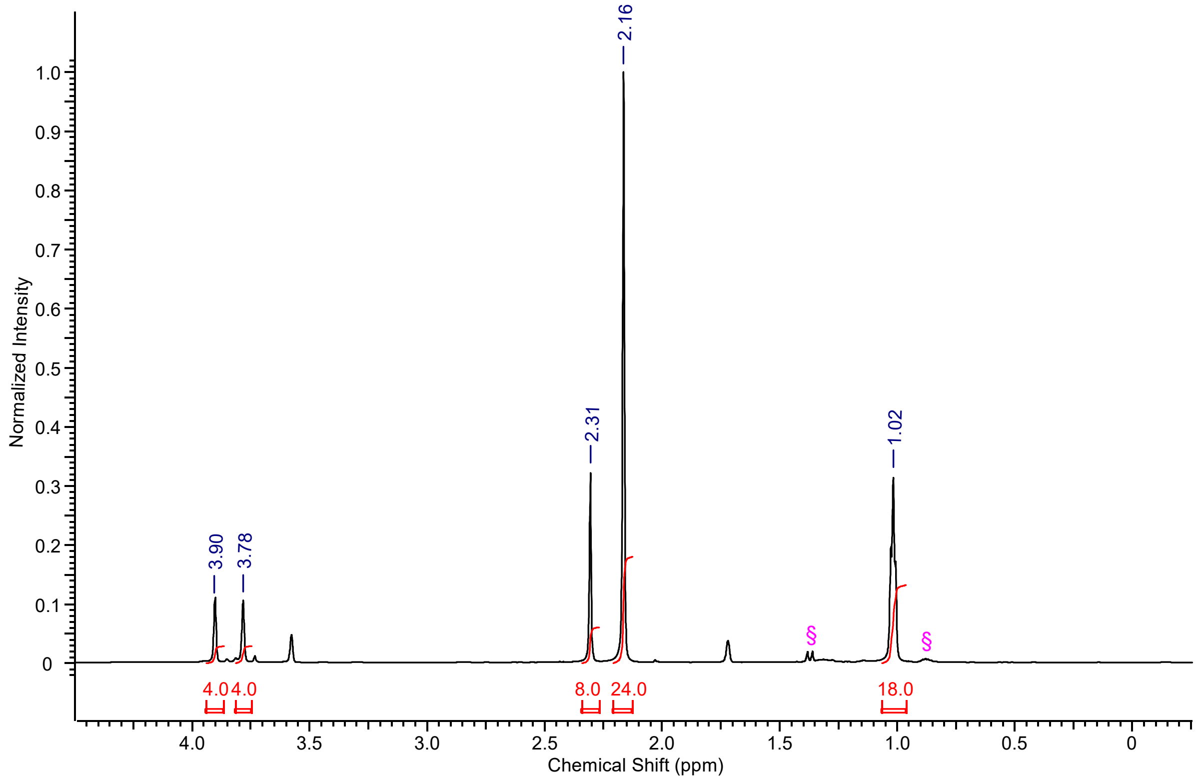


Fig. S30 [1]H NMR spectrum of [Li_2(μ-**1b**)(TMEDA)$_2$] (THF-d_8, 399.9 MHz). Signals marked belong to trace amounts of *n*-hexane (§).

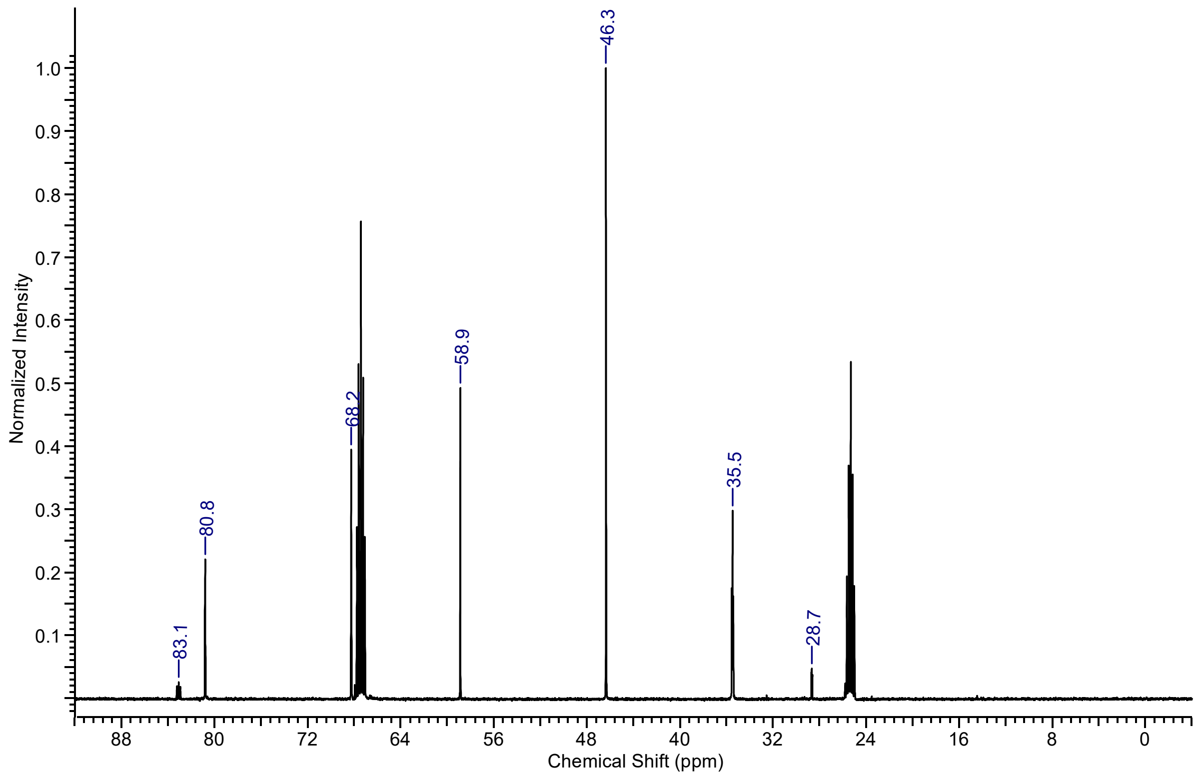


Fig. S31 [13]C NMR spectrum of [Li_2(μ-**1b**)(TMEDA)$_2$] (THF-d_8, 100.6 MHz).

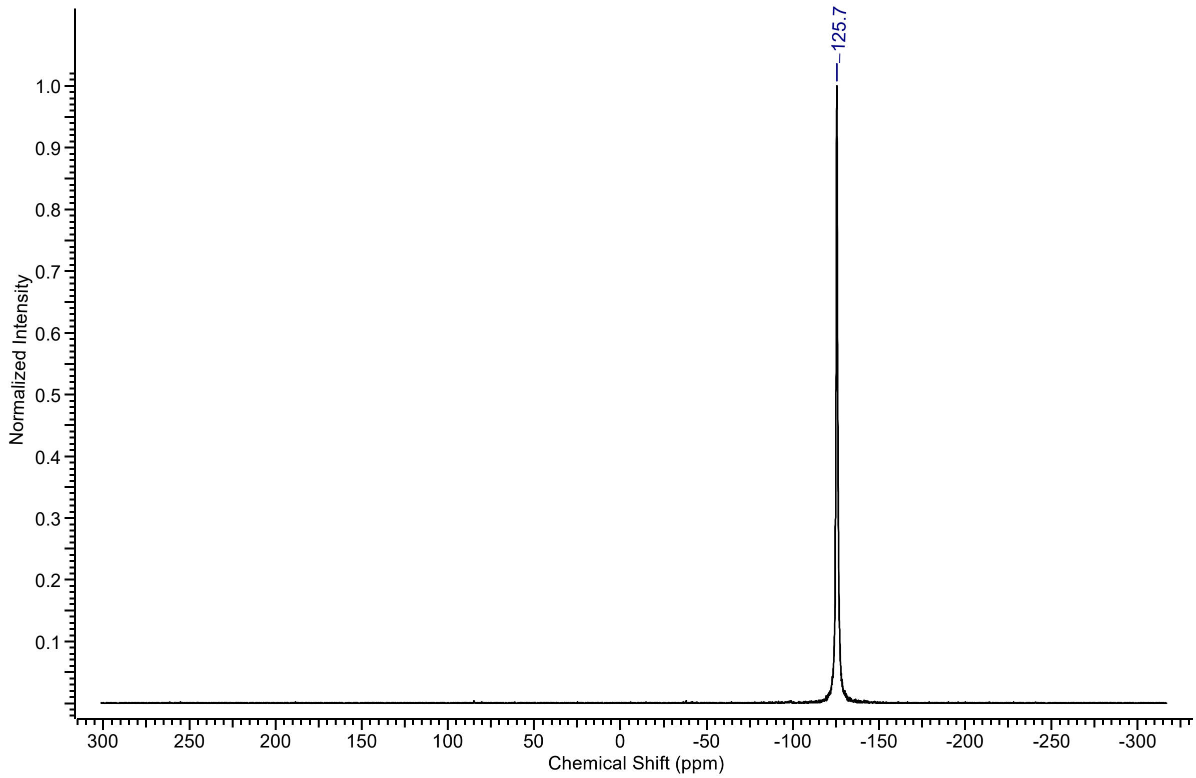


Fig. S32 ^{31}P NMR spectrum of [Li_4(μ-**1c**)$_2$(TMEDA)$_3$] (THF-d_8, 202.3 MHz).

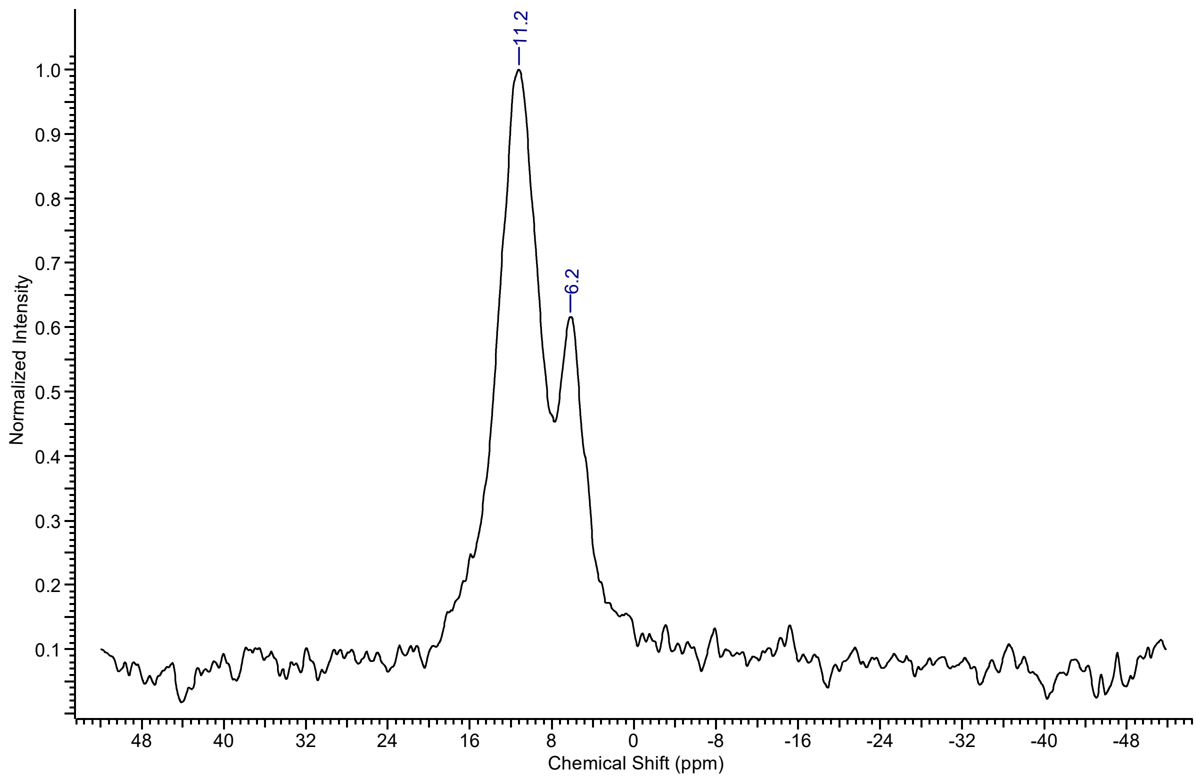


Fig. S33 ^{7}Li NMR spectrum of[Li_4(μ-**1c**)$_2$(TMEDA)$_3$] (THF-d_8, 194.2 MHz).

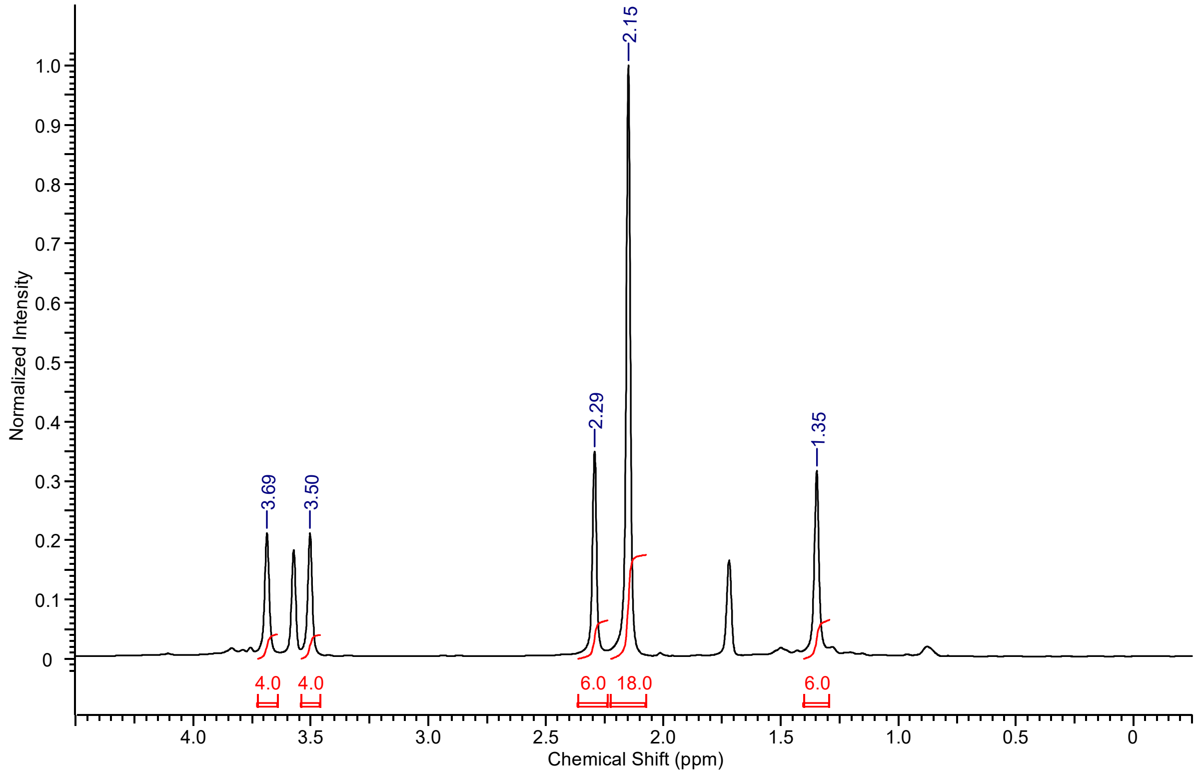


Fig. S34 ^{1}H NMR spectrum of [Li_4(μ-**1c**)$_2$(TMEDA)$_3$] (THF-d_8, 399.9 MHz).

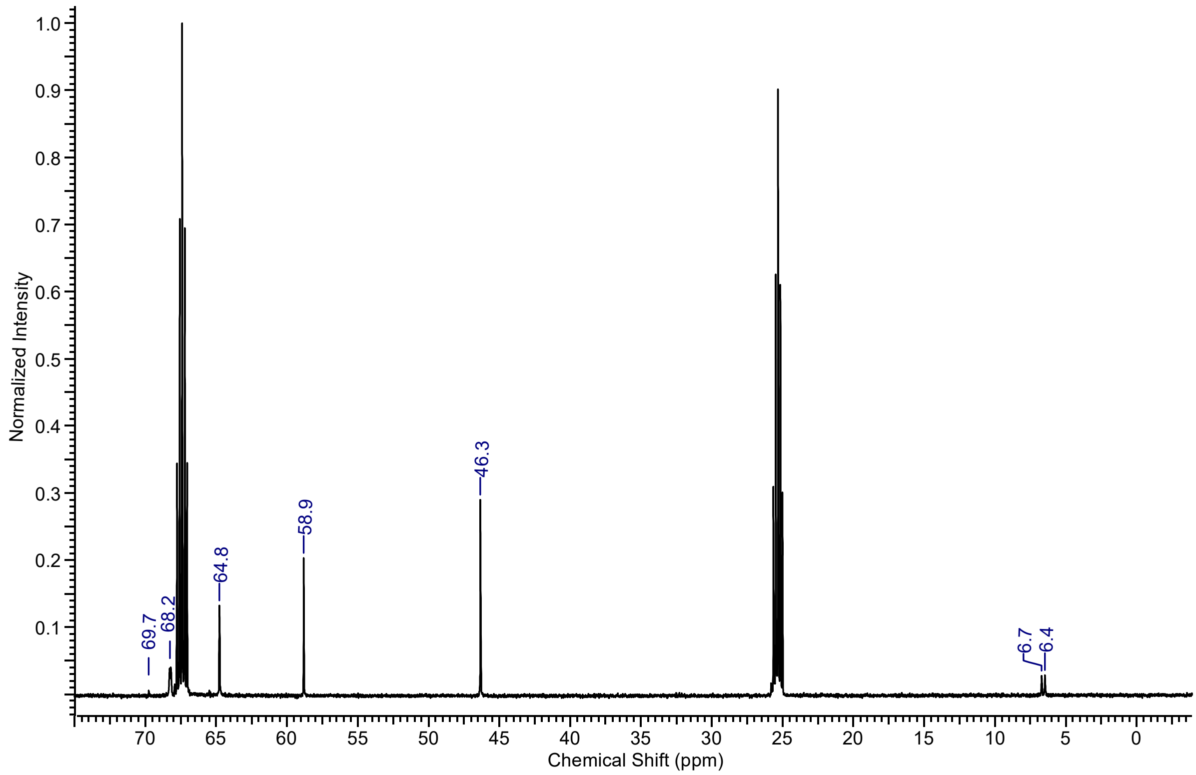


Fig. S35 ^{13}C NMR spectrum of [Li_4(μ-**1c**)$_2$(TMEDA)$_3$] (THF-d_8, 100.6 MHz).

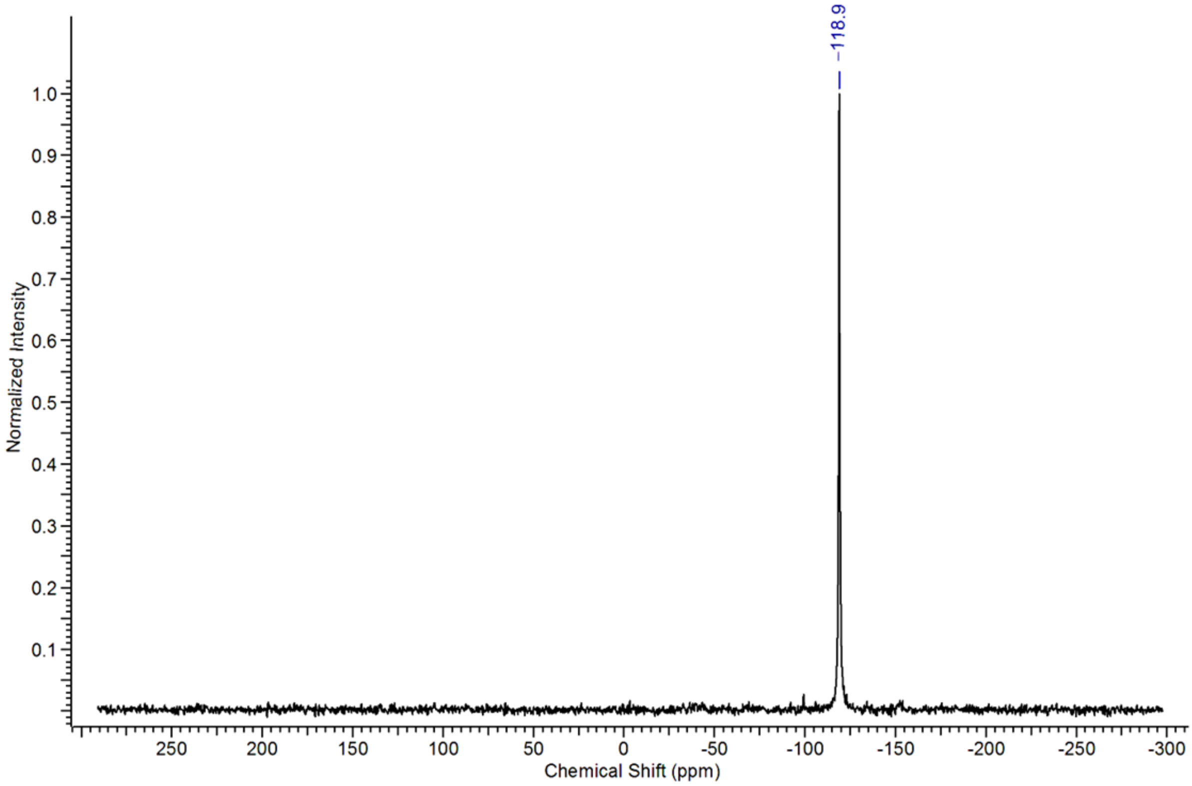


Fig. S36 ^{31}P NMR spectrum of [Li_2(μ-**1d**)(TMEDA)]$_2$ (THF-d_8, 202.3 MHz).

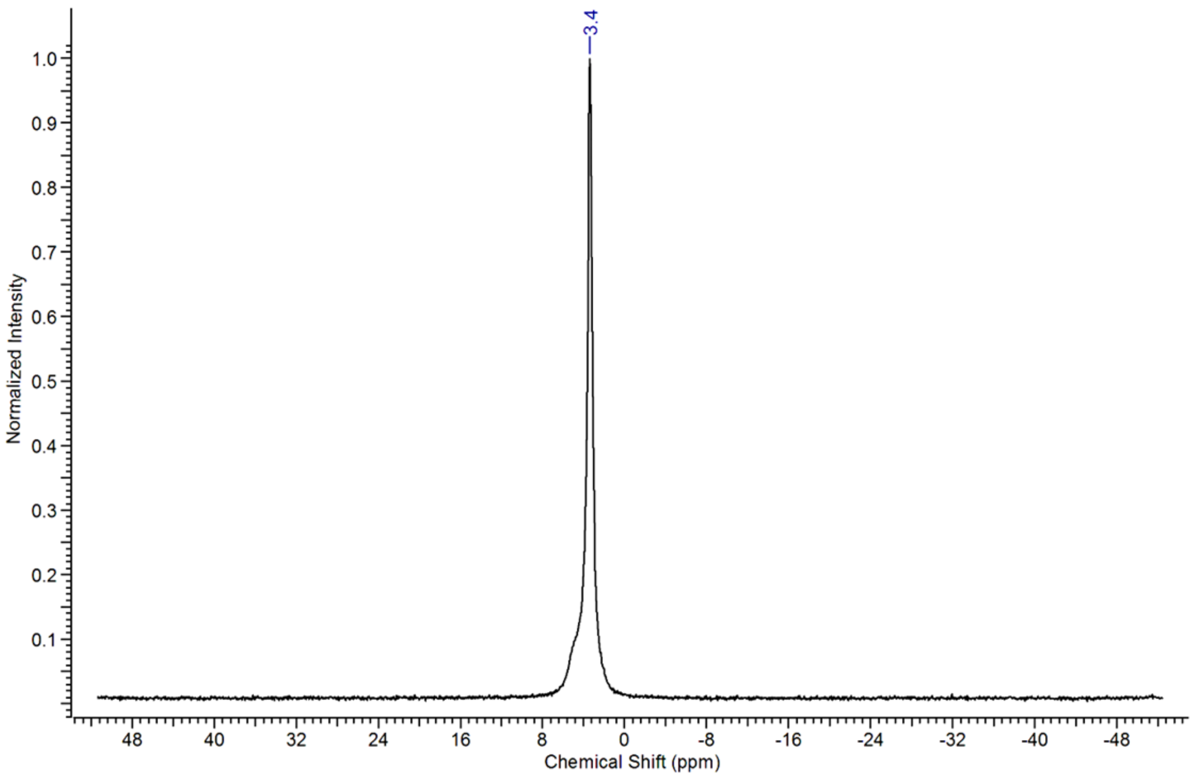


Fig. S37 ^{7}Li NMR spectrum of [Li_2(μ-**1d**)(TMEDA)]$_2$ (THF-d_8, 194.2 MHz).

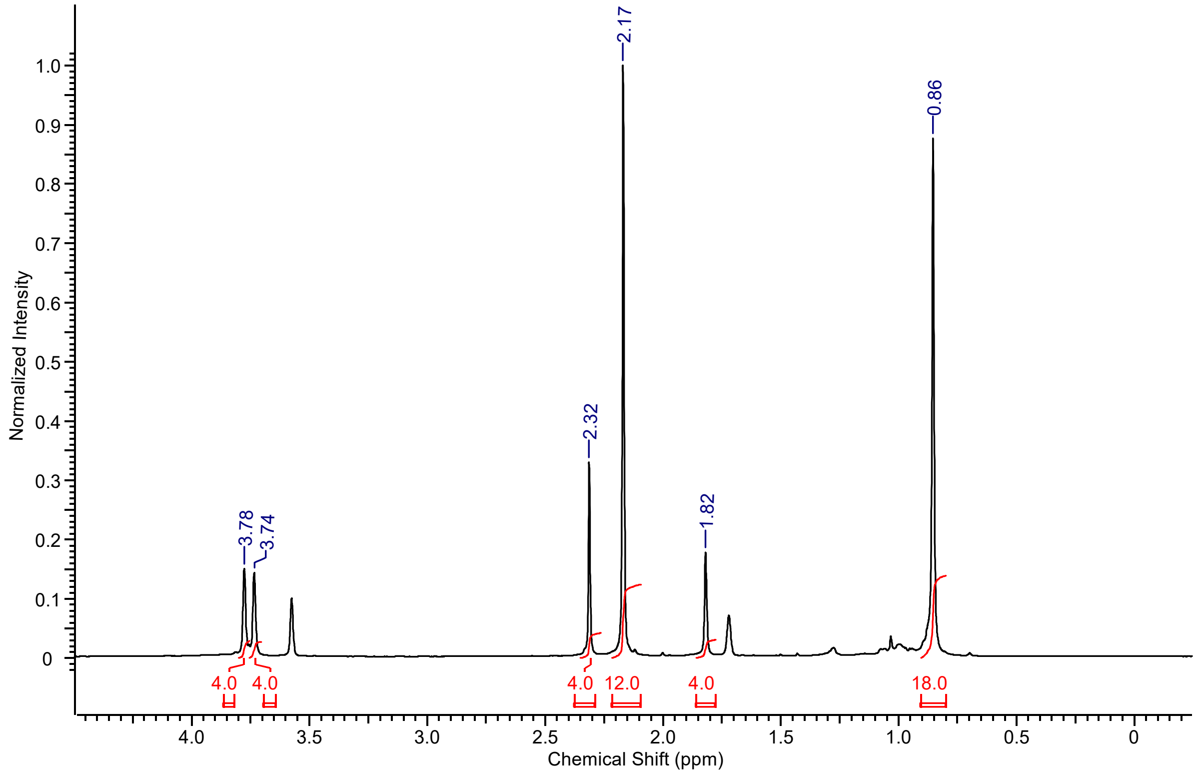


Fig. S38 ^{1}H NMR spectrum of $[Li_2(\mu\text{-}\mathbf{1d})(TMEDA)]_2$ (THF-d_8, 399.9 MHz).

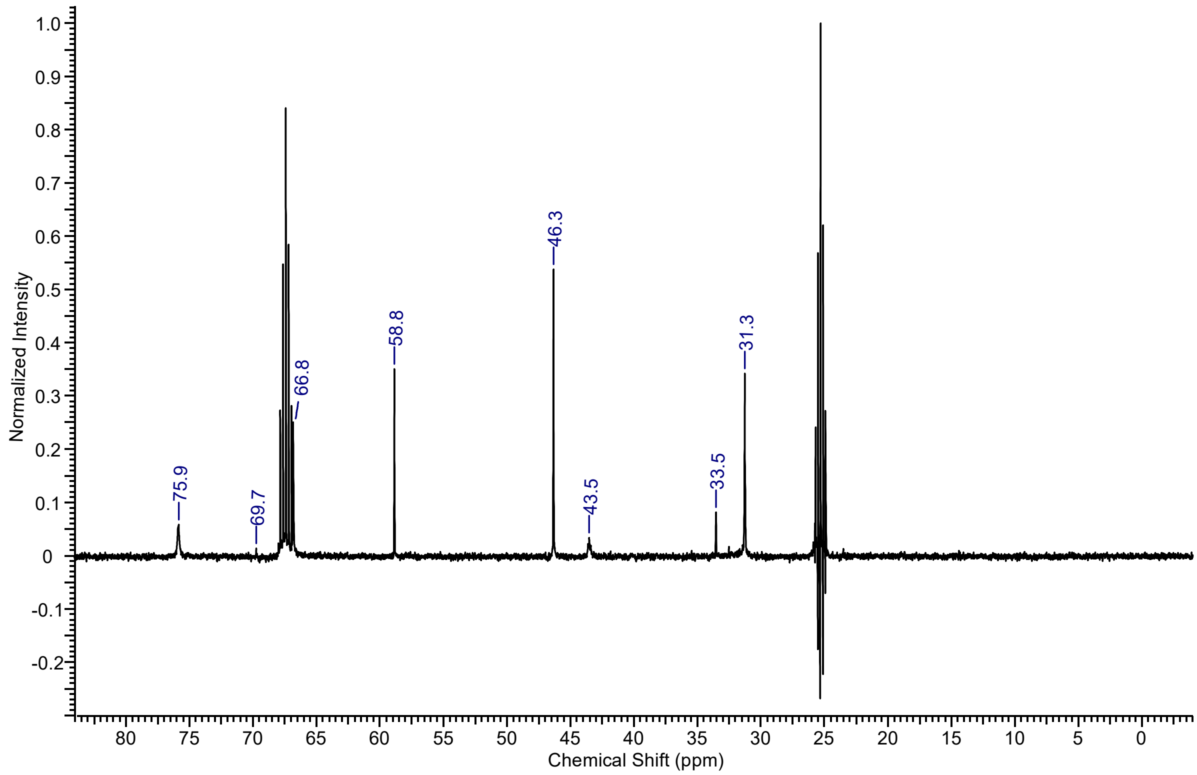


Fig. S39 ^{13}C NMR spectrum of $[Li_2(\mu\text{-}\mathbf{1d})(TMEDA)]_2$ (THF-d_8, 100.6 MHz).

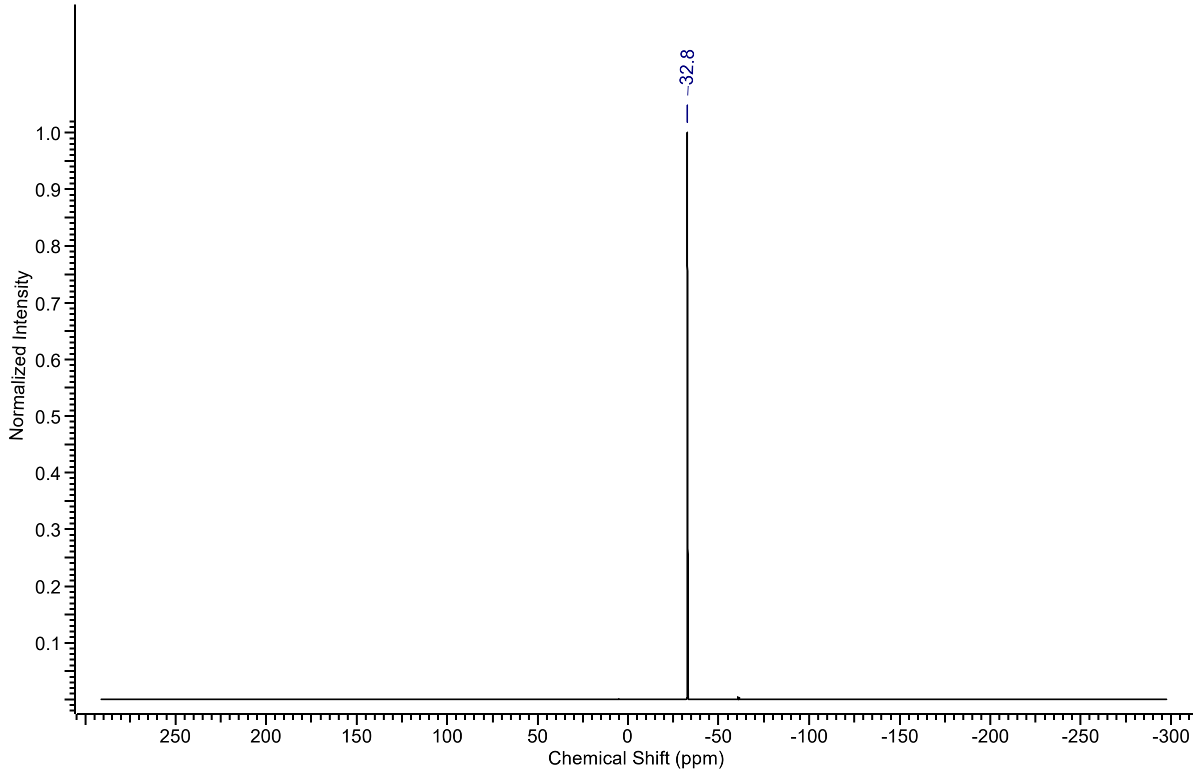


Fig. S40 ^{31}P NMR spectrum of [{Zr(NMe$_2$)$_3$}$_2$(μ-**1a**)] (C_6D_6, 202.3 MHz).

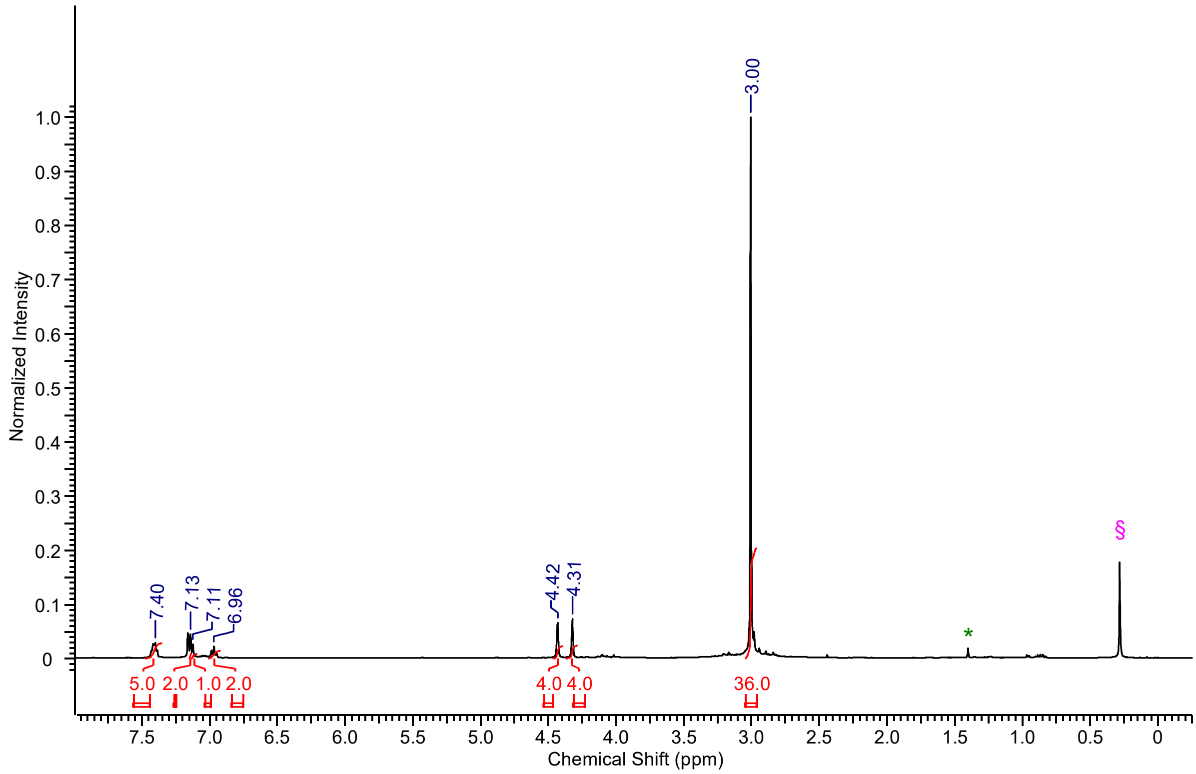


Fig. S41 ^{1}H NMR spectrum of [{Zr(NMe$_2$)$_3$}$_2$(μ-**1a**)] (C_6D_6, 399.9 MHz). Signals marked belong to trace amounts of THF (*) and silicon grease (§).

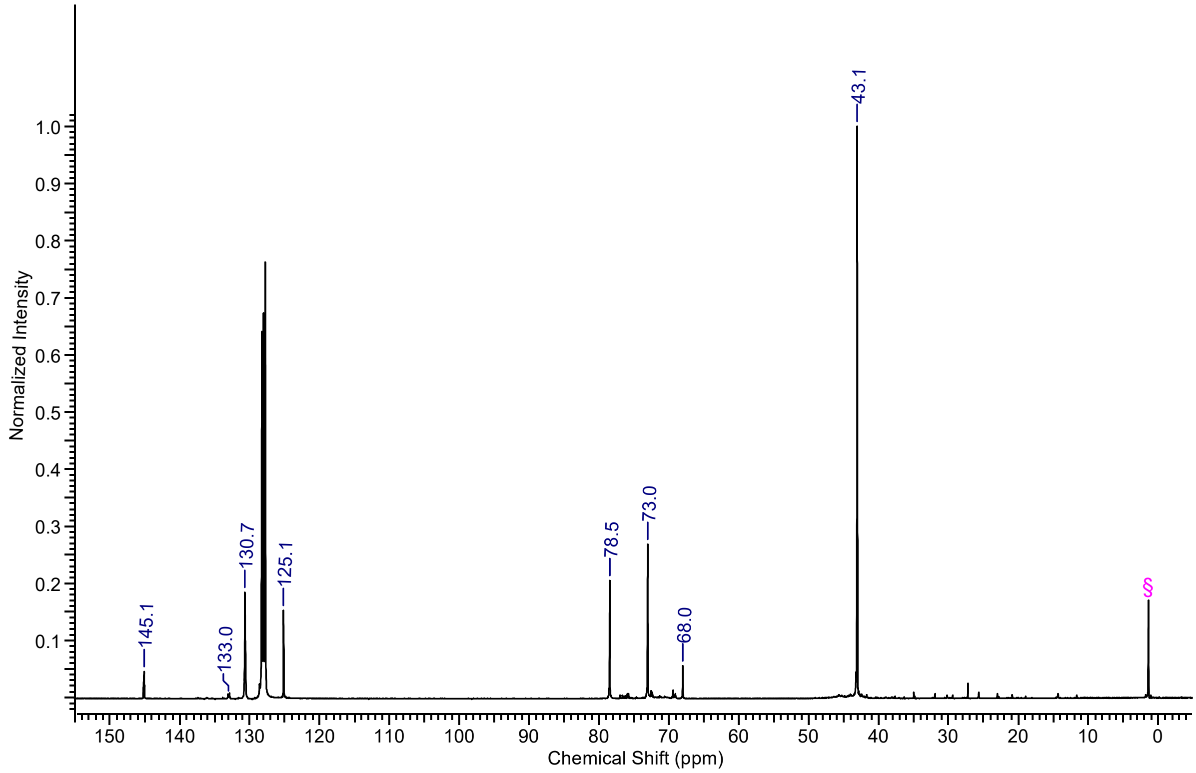


Fig. S42 ^{13}C NMR spectrum of [{Zr(NMe$_2$)$_3$}$_2$(μ-**1a**)] (C_6D_6, 100.6 MHz). The signal marked belongs to small amounts of silicon grease (§).

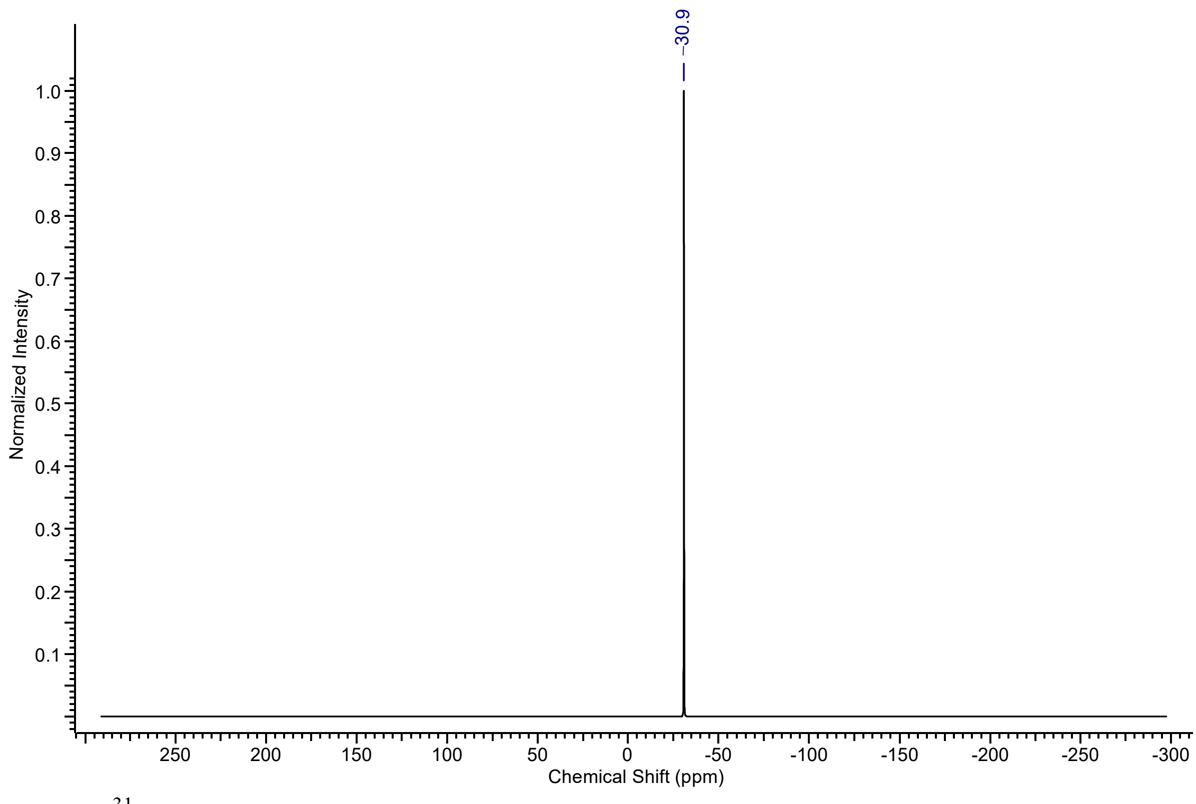


Fig. S43 ^{31}P NMR spectrum of [{Zr(NMe$_2$)$_3$}$_2$(μ-**1e**)] (C_6D_6, 202.3 MHz).

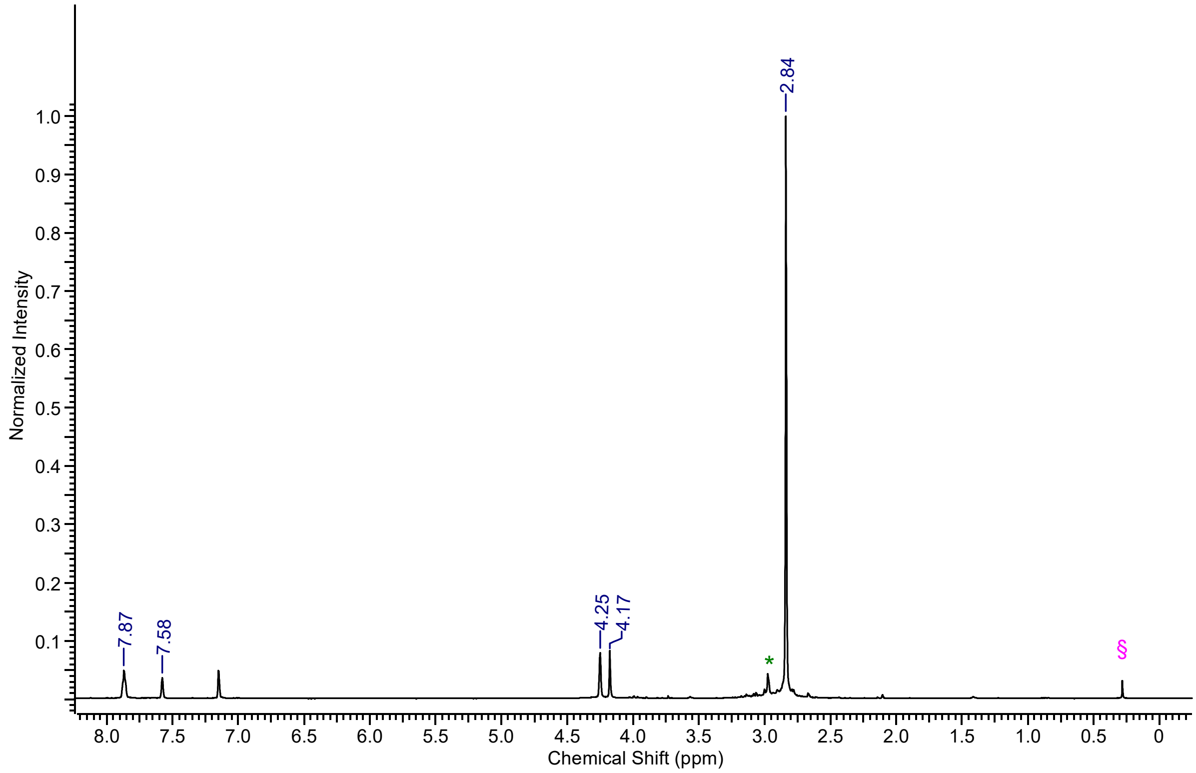


Fig. S44 ^{1}H NMR spectrum of [{Zr(NMe$_2$)$_3$}$_2$(μ-**1e**)] (C_6D_6, 399.9 MHz). Signals marked belong to trace amounts of unidentified impurities (*) and silicon grease (§).

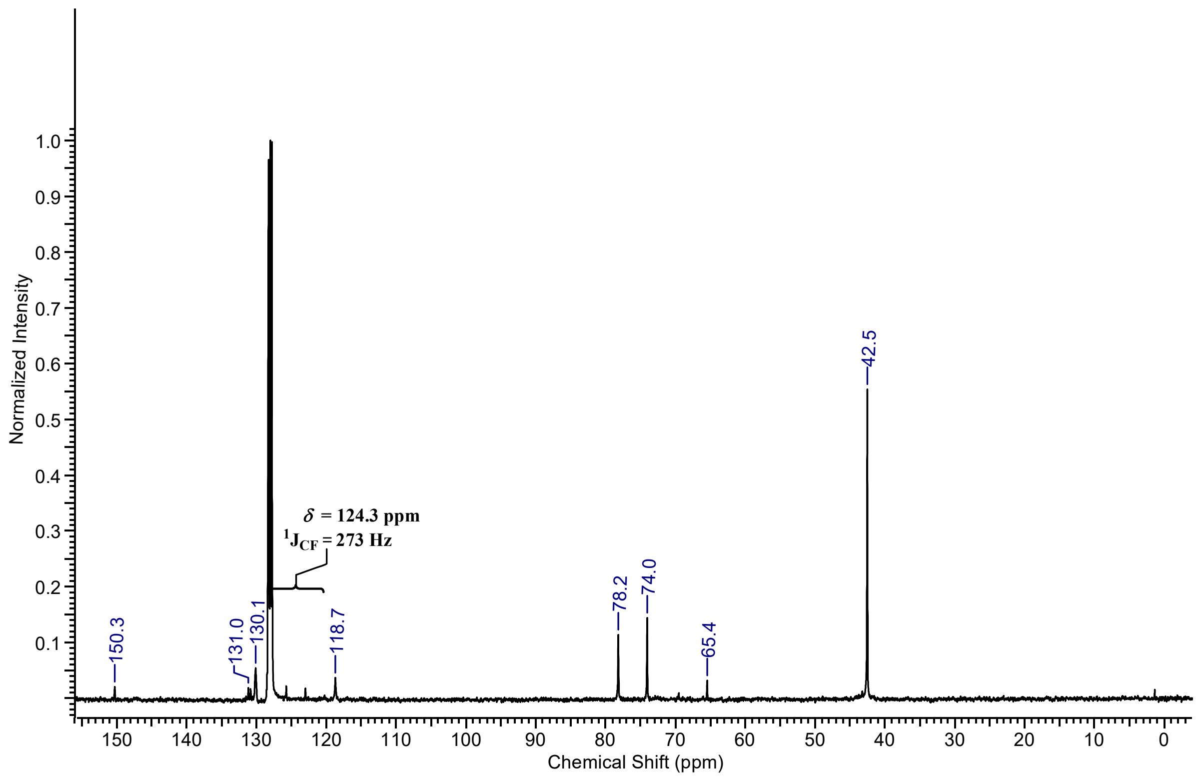


Fig. S45 ^{13}C NMR spectrum of [{Zr(NMe$_2$)$_3$}$_2$(μ-**1e**)] (C_6D_6, 100.6 MHz).

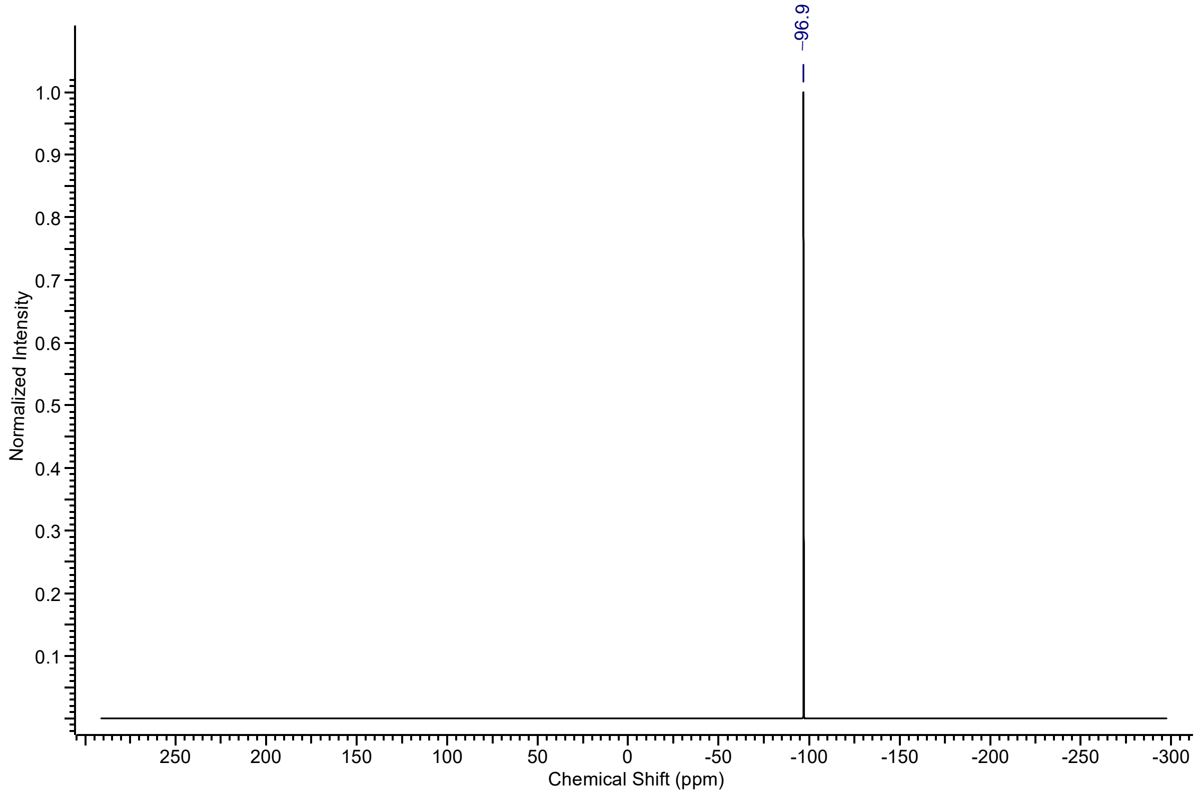


Fig. S46 ^{31}P NMR spectrum of [(NiCp)$_2$(μ-**1a**)] (C_6D_6, 202.3 MHz).

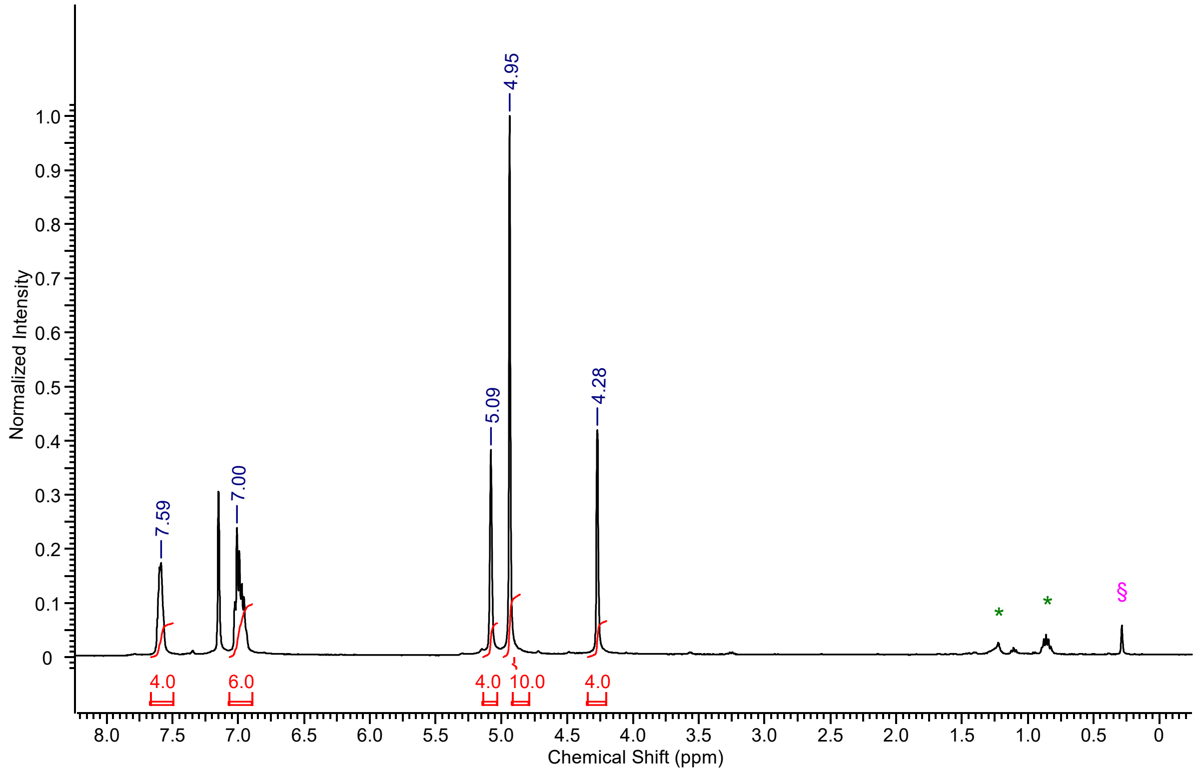


Fig. S47 ^{1}H NMR spectrum of [(NiCp)$_2$(μ-**1a**)] (C_6D_6, 399.9 MHz). Signals marked belong to trace amounts of *n*-hexane (*) and silicon grease (§).

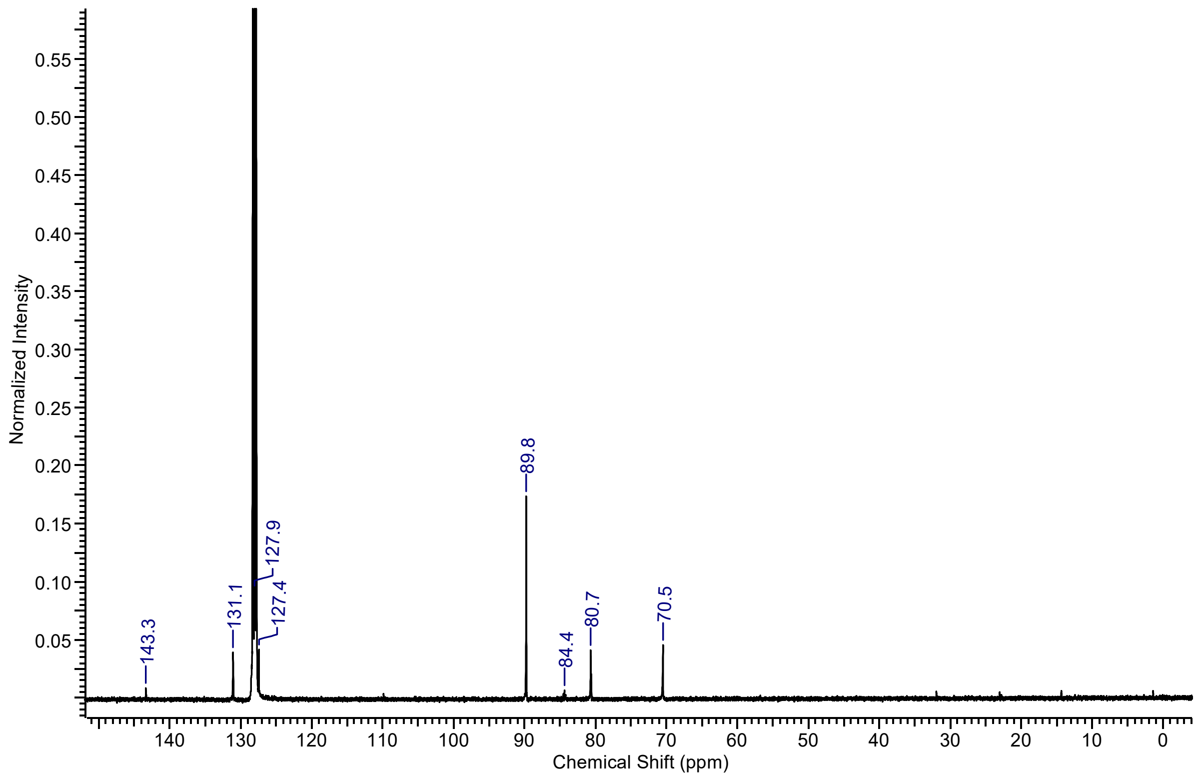


Fig. S48 ^{13}C NMR spectrum of [(NiCp)$_2$(μ-**1a**)] (C_6D_6, 100.6 MHz).

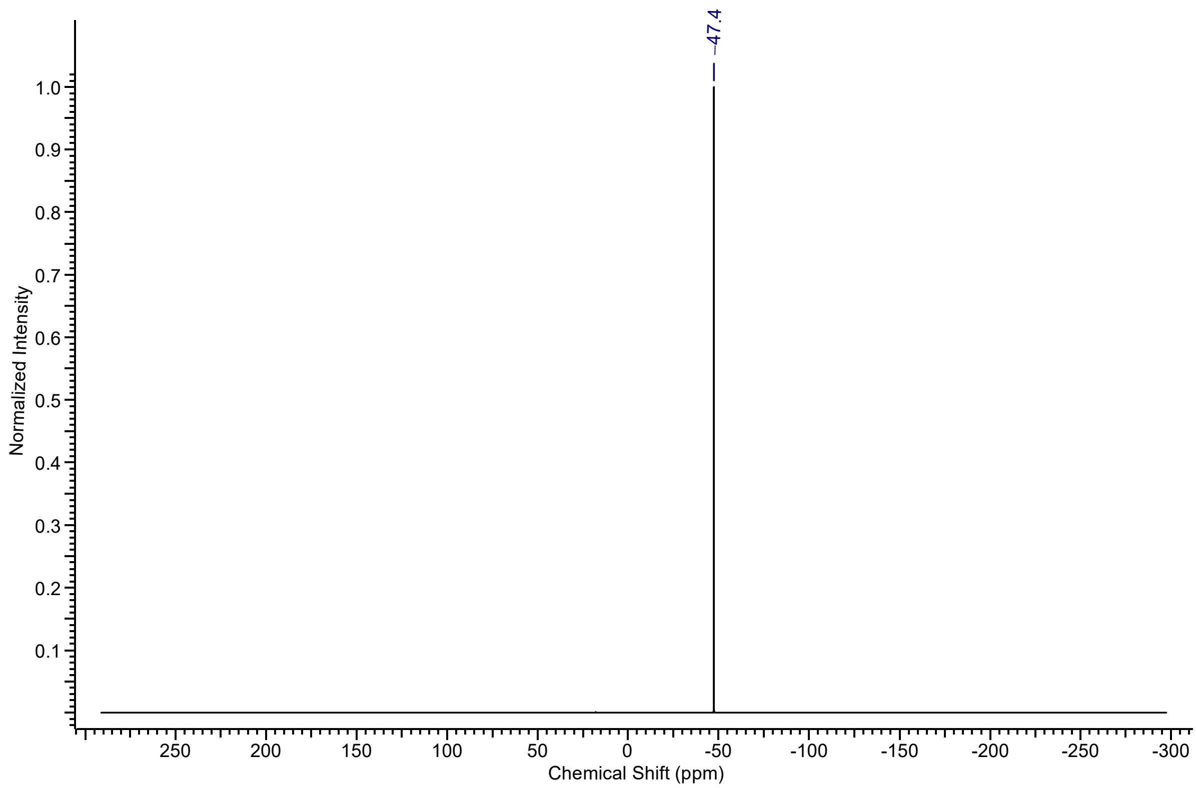


Fig. S49 ^{31}P NMR spectrum of [(NiCp)$_2$(μ-**1b**)] (C_6D_6, 202.3 MHz).

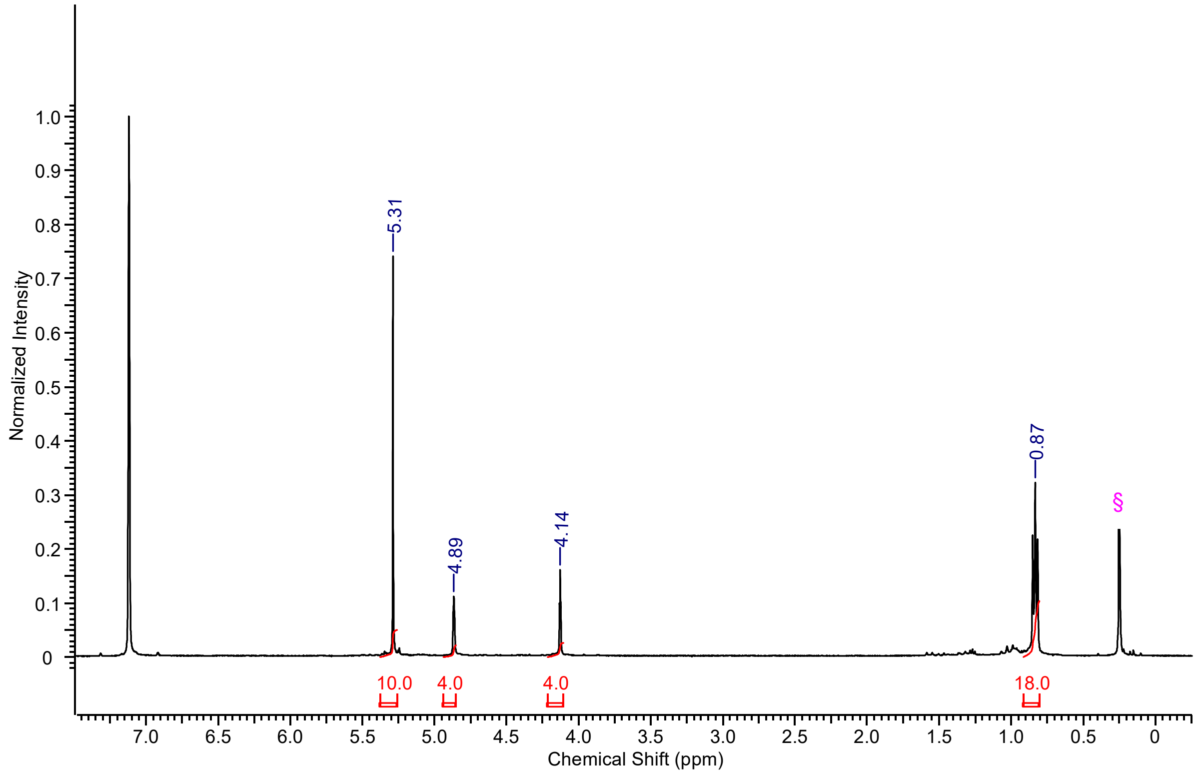


Fig. S50 [1]H NMR spectrum of [(NiCp)$_2$(μ-**1b**)] (C_6D_6, 399.9 MHz). The signal marked belongs to silicon grease (§).

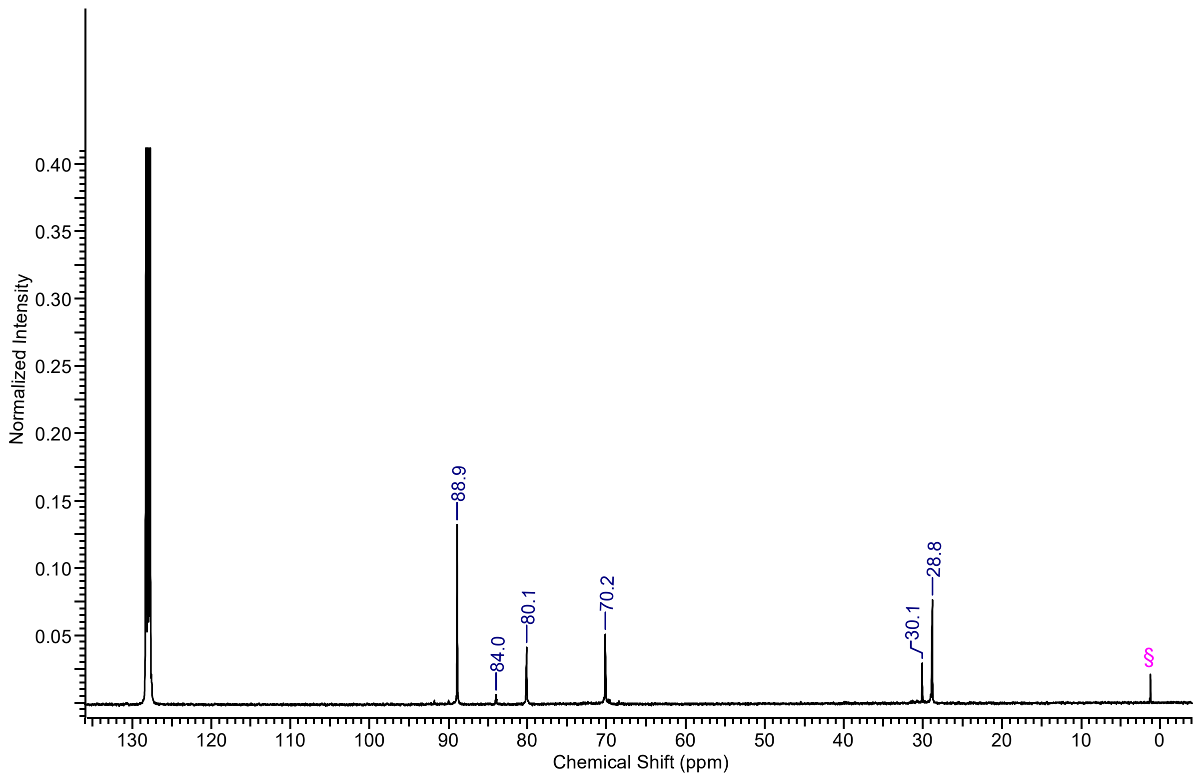


Fig. S51 [13]C NMR spectrum of [(NiCp)$_2$(μ-**1b**)] (C_6D_6, 100.6 MHz). The signal marked belongs to silicon grease (§).

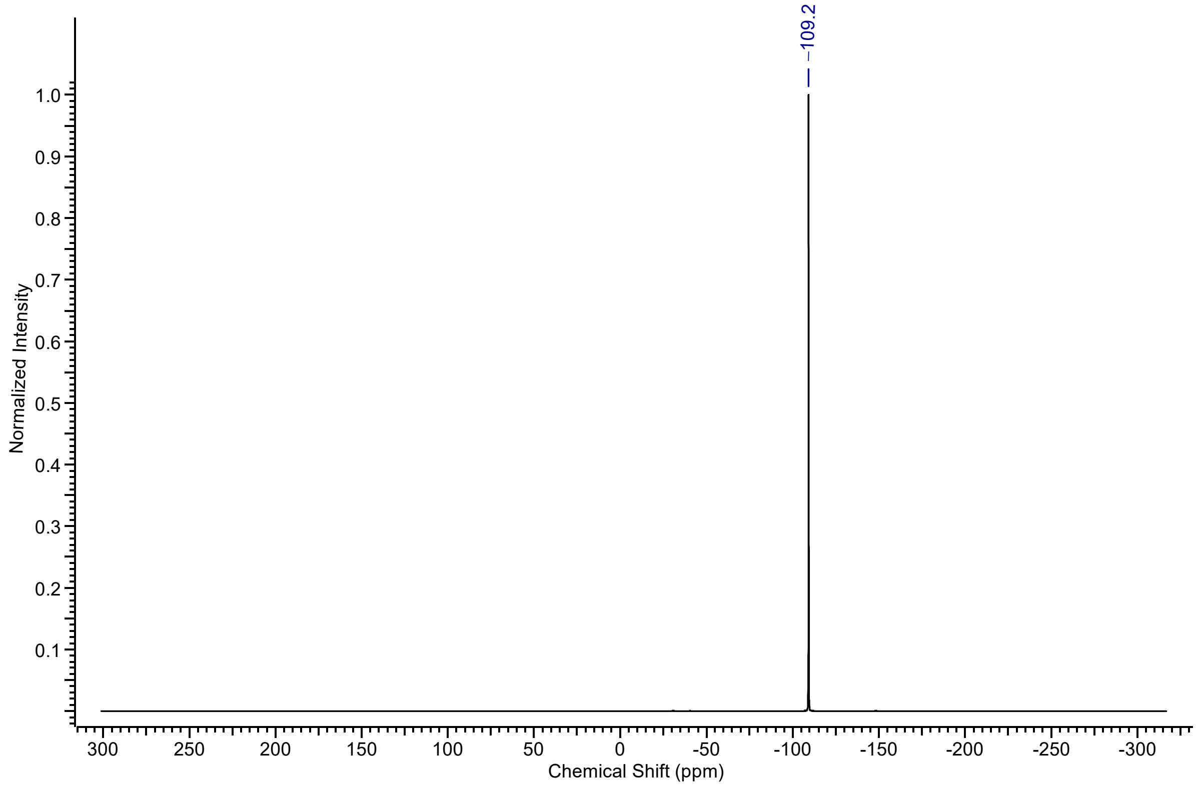


Fig. S52 ^{31}P NMR spectrum of [(NiCp)$_2$(μ-**1d**)] (C_6D_6, 202.3 MHz).

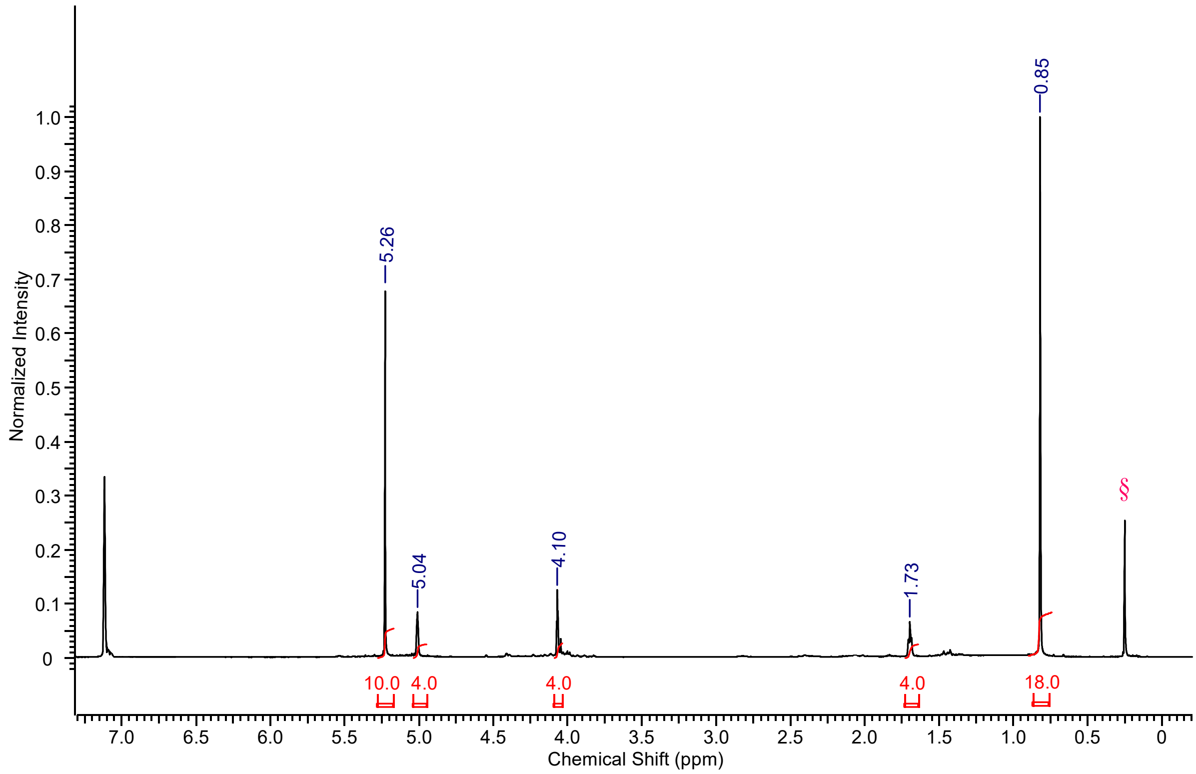


Fig. S53 ^{1}H NMR spectrum of [(NiCp)$_2$(μ-**1d**)] (C_6D_6, 399.9 MHz). The signal marked belongs to silicon grease (§).

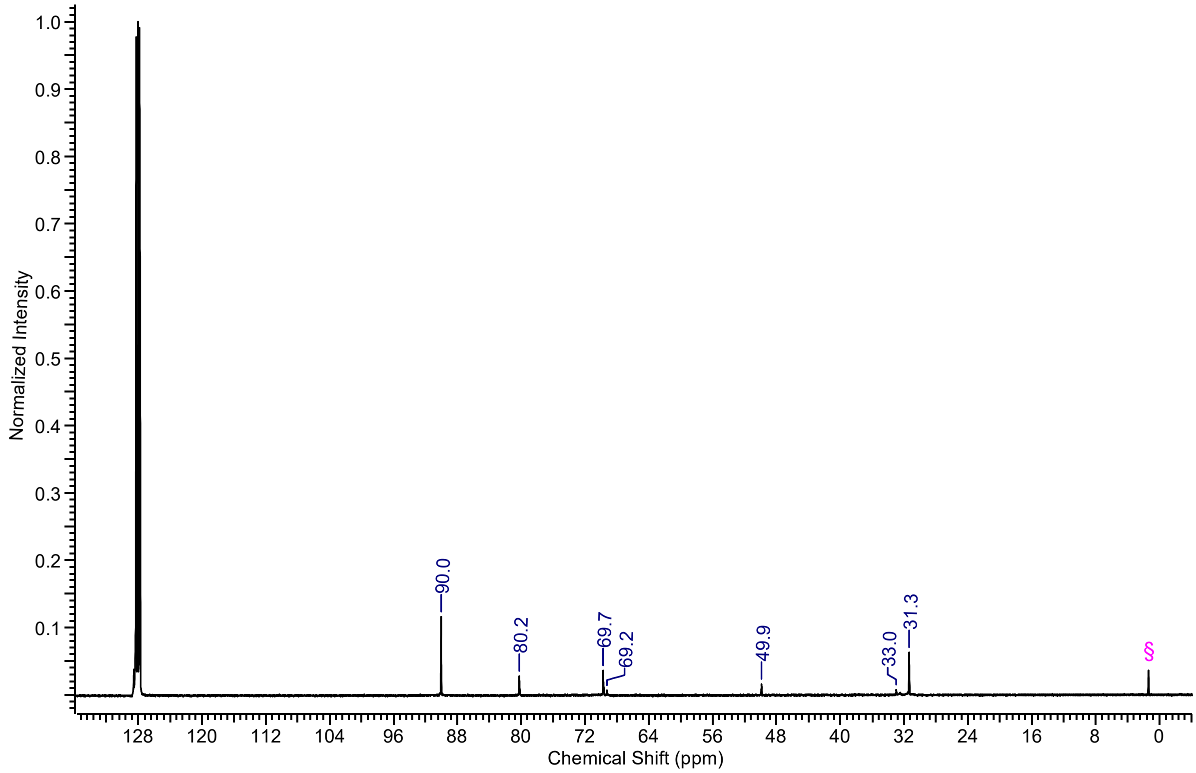


Fig. S54 ^{13}C NMR spectrum of [(NiCp)$_2$(μ-**1d**)] (C_6D_6, 100.6 MHz). The signal marked belongs to silicon grease (§).

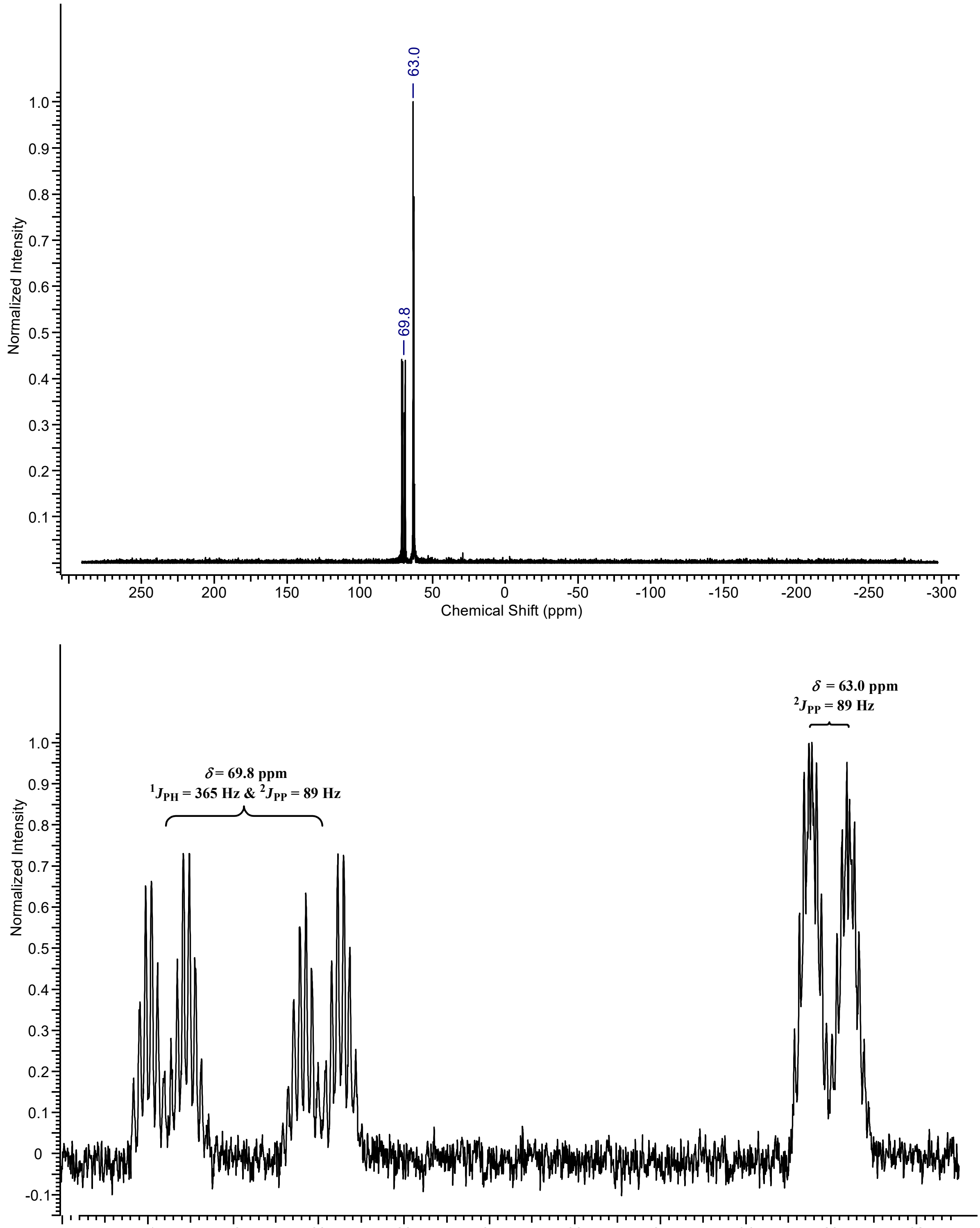


Fig. S55 ^{31}P NMR spectrum of [NiCp(H**1b**)] (C_6D_6, 202.3 MHz).

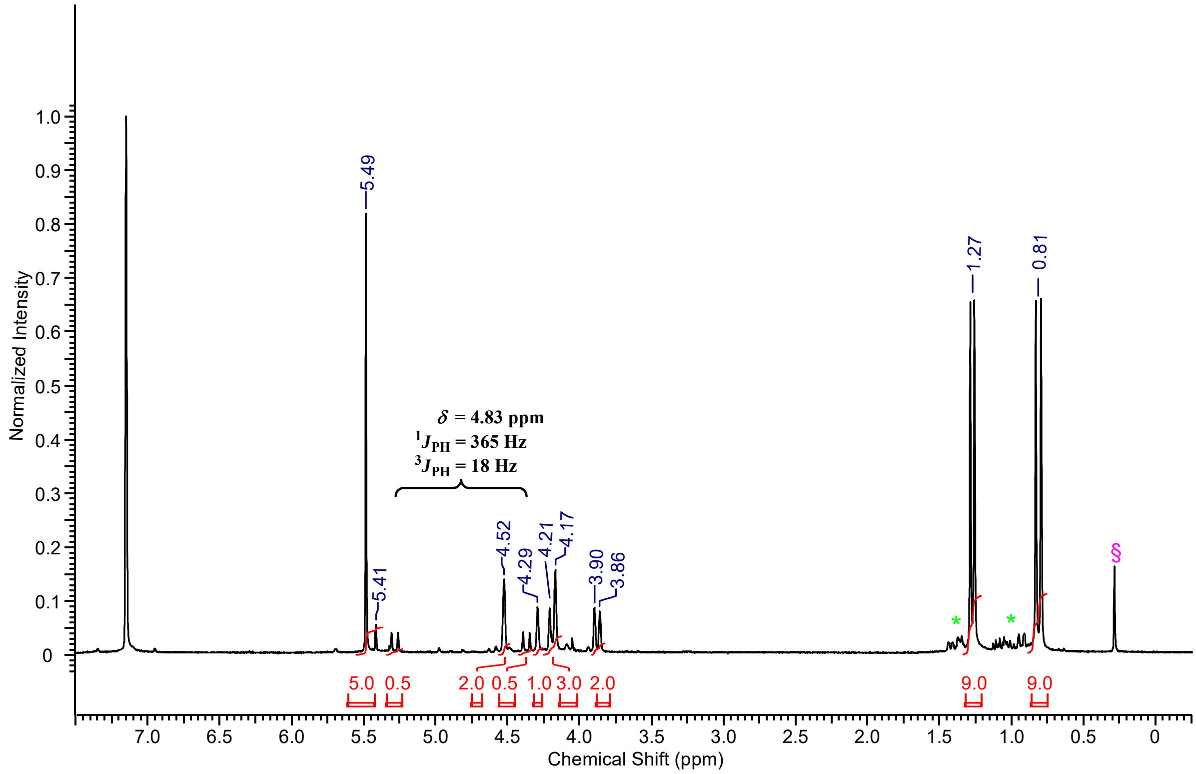


Fig. S56 ^{1}H NMR spectrum of [NiCp(H**1b**)] (C_6D_6, 399.9 MHz). Signals marked belong to trace amounts of unidentified impurities (*) and silicon grease (§).

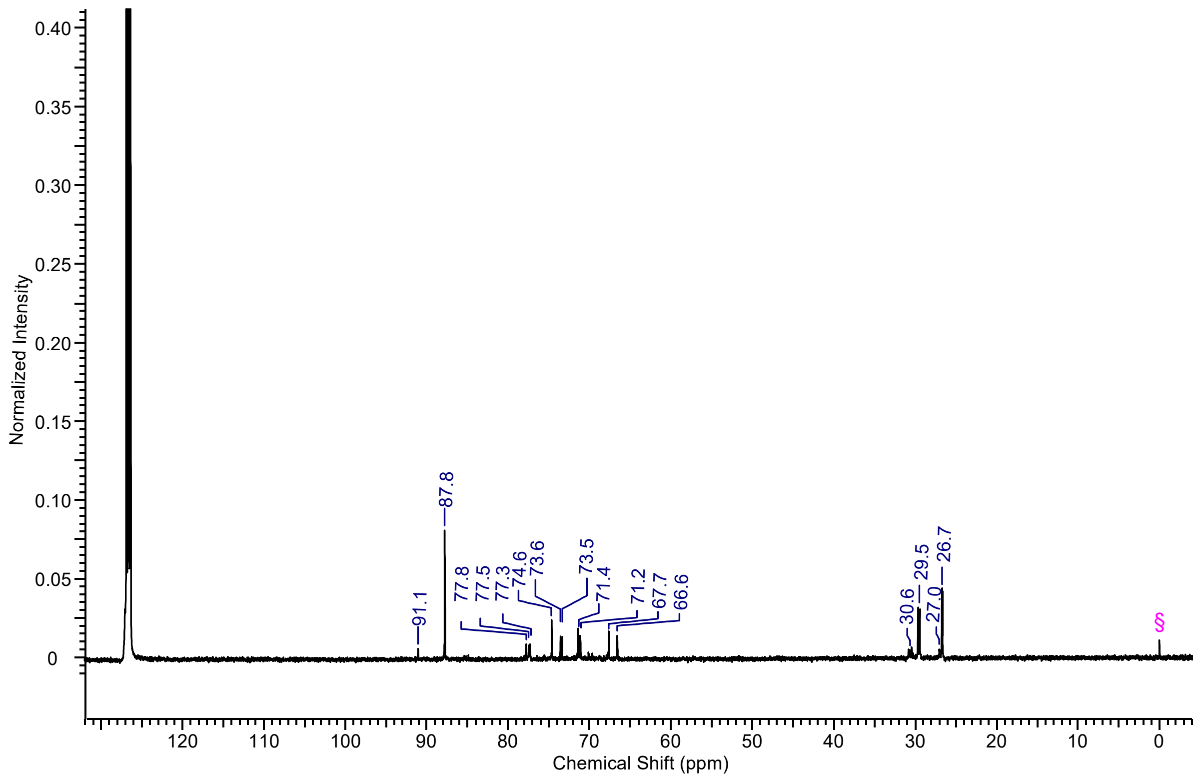


Fig. S57 ^{13}C NMR spectrum of [NiCp(H**1b**)] (C_6D_6, 100.6 MHz). The signal marked belongs to silicon grease (§).