

Electronic Supporting Information for:

Bis(imino)carbazolate lead(II) fluoride and related halides

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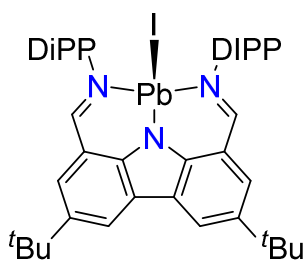
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Experimental Procedures

General Considerations:

All manipulations were performed under an inert atmosphere by using standard Schlenk techniques or in a dry, solvent-free glovebox (Jacomex; $O_2 < 1$ ppm, $H_2O < 2$ ppm). THF was distilled under argon from Na/benzophenone prior to use. Hexanes, toluene, and Et_2O were collected from MBraun SPS-800 purification alumina columns and thoroughly degassed with argon before being stored on 4 Å molecular sieves. Deuterated solvents (Eurisotop, Saclay, France) were stored in sealed ampoules over activated 4 Å molecular sieves and degassed by a minimum of three freeze–thaw cycles. NMR spectra were recorded with Bruker AM-300, AM-400 or AM-500 spectrometers at 25 °C unless otherwise noted. All chemical shifts (δ) [ppm] were determined relative to the residual signal of the deuterated solvent or to an external standard in $[D_6]$ benzene or $[D_8]$ toluene. Assignment of the signals was assisted by 1D (1H , ^{13}C) and 2D (COSY, HMBC, and HMQC) NMR experiments. $\{Carb^{DiPP}\}H$,¹ $\{[Carb^{DiPP}]K.(thf)\}$,¹ $[Li\{CH(SiMe_3)_2\}]$ ² and $[Me_3SnF]$ ³ were prepared per the literature procedures. All other chemicals were provided by commercial suppliers and used as received. Combustion analysis of the complexes could not be carried out reliably and reproducibly due to their air- and moisture-sensitivity.

$\{[Carb^{DiPP}]Pb(I)\}$ (1)



To a Schlenk flask in a glovebox was added PbI_2 (580 mg, 1.26 mmol) and $[K\{Carb^{DiPP}\}.(thf)_2]$ (700 mg, 0.84 mmol). The Schlenk vessel was sealed and removed from the glovebox and attached to a Schlenk line. Degassed thf (30 mL) was added and the reaction mixture was left to stir for 16 h. The solvent was removed under reduced pressure and the yellow residue was extracted with toluene (20 mL) and filtered to give a bright yellow solution. Removal of the solvent under reduced pressure gave the complex as a bright yellow powder. Crystals suitable for an X-ray diffraction study were grown from a supersaturated toluene solution at 60 °C. Yield: 620 mg (75%).

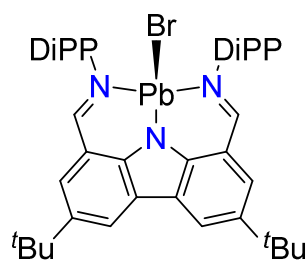
1H NMR (500.13 MHz, $[D_8]$ toluene, 300 K): δ 8.59 (d, $^4J_{HH} = 1.9$ Hz, 2H, CH -Carb); 8.42 (s, 2H, $CH=N$); 7.63 (d, $^4J_{HH} = 2.0$ Hz, 2H, CH -Carb); 7.21 (m, 2H, Ar-**H**); 7.15-7.05 (m, 4H Ar-**H**); 3.82 (hept, $^3J_{HH} = 6.5$ Hz, 2H, $CH(CH_3)_2$); 3.07 (hept, $^3J_{HH} = 6.8$ Hz, 2H, $CH(CH_3)_2$); 1.39 (d, $^3J_{HH} = 7.4$ Hz, 6H, $CH(CH_3)_2$); 1.38 (s, 18H, $C(CH_3)_3$); 1.18 (d, $^3J_{HH} = 6.8$ Hz, 6H, $CH(CH_3)_2$); 1.10 (d, $^3J_{HH} = 7.4$ Hz, 6H, $CH(CH_3)_2$); 0.95 (d, $^3J_{HH} = 6.9$ Hz, 6H, $CH(CH_3)_2$) ppm.

1H NMR (400.13 MHz, $[D_6]$ benzene, 298 K): δ 8.62 (d, $^4J_{HH} = 2.0$ Hz, 2H, CH -Carb); 8.37 (s, 2H, $CH=N$); 7.62 (d, $^4J_{HH} = 1.9$ Hz, 2H, CH -Carb); 7.24 (m, 2H Ar-**H**); 7.13-7.04 (m, 4H, Ar-**H**); 3.88 (hept, $^3J_{HH} = 6.7$ Hz, 2H, $CH(CH_3)_2$); 3.05 (hept, $^3J_{HH} = 6.7$ Hz, 2H, $CH(CH_3)_2$); 1.44 (d, $^3J_{HH} = 6.7$ Hz, 6H, $CH(CH_3)_2$); 1.36 (s, 18H, $C(CH_3)_3$); 1.17 (d, $^3J_{HH} = 6.8$ Hz, 6H, $CH(CH_3)_2$); 1.10 (d, $^3J_{HH} = 7.1$ Hz, 6H, $CH(CH_3)_2$); 0.94 (d, $^3J_{HH} = 6.7$ Hz, 6H, $CH(CH_3)_2$) ppm.

$^{13}C\{^1H\}$ NMR (125.77 MHz, $[D_8]$ toluene, 300 K): δ 168.77 ($CH=N$); 146.65 (Ar-C); 145.19 (Ar-C); 142.42 (Ar-C); 141.43 (Ar-C); 140.80 (Ar-C); 132.92 (Ar-C); 129.68 (Ar-C); 128.64 (Ar-C); 127.33 (Ar-C); 123.88 (Ar-C); 123.81 (Ar-C); 122.93 (Ar-C); 34.81 ($C(CH_3)_3$); 32.26 ($C(CH_3)_3$); 29.32 ($CH(CH_3)_2$); 28.60 ($CH(CH_3)_2$); 26.44 ($CH(CH_3)_2$); 25.57 ($CH(CH_3)_2$); 25.49 ($CH(CH_3)_2$); 24.2 ($CH(CH_3)_2$) ppm.

^{207}Pb NMR (104.79 MHz, $[D_6]$ benzene, 292 K): δ 1542 ppm.

[{Carb^{DiPP}}Pb(Br)] (2)



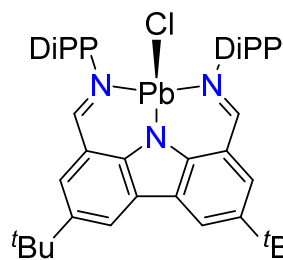
A Schlenk flask in a glovebox was loaded with PbBr₂ (262 mg, 0.71 mmol) and [K{Carb^{DiPP}}.(thf)₂] (500 mg, 0.60 mmol). The Schlenk flask was sealed and removed from the glovebox and attached to a Schlenk line. Thf (30 mL) was added and the reaction mixture was left to stir for 16 h. The solvent was removed under reduced pressure and the yellow residue was extracted with toluene (30 mL) and filtered to give a bright yellow solution. Removal of the solvent under reduced pressure gave the complex as a bright yellow powder. Crystals suitable for an X-ray diffraction study were grown from a saturated toluene solution at room temperature. Yield: 444 mg (79%).

¹H NMR (500.13 MHz, [D₆]benzene, 300 K): δ 8.66 (d, ⁴J_{HH} = 2.1 Hz, 2H, CH-Carb); 8.44 (s, 2H, CH=N); 7.63 (d, ⁴J_{HH} = 2.1 Hz, 2H, CH-Carb); 7.26 (m, 2H, Ar-H); 7.21-7.11 (m, 4H, Ar-H); 3.84 (hept, ³J_{HH} = 6.9 Hz, 2H, CH(CH₃)₂); 3.03 (hept, ³J_{HH} = 6.8 Hz, 2H, CH(CH₃)₂); 1.47 (d, ³J_{HH} = 6.7 Hz, 6H, CH(CH₃)₂); 1.39 (s, 18H, C(CH₃)₃); 1.12 (d, ³J_{HH} = 6.8 Hz, 6H, CH(CH₃)₂); 1.08 (d, ³J_{HH} = 6.9 Hz, 6H, CH(CH₃)₂); 0.95 (d, ³J_{HH} = 6.8 Hz, 6H, CH(CH₃)₂) ppm.

¹³C{¹H} NMR (125.77 MHz, [D₆]benzene, 300 K): δ 167.91 (CH=N); 146.27 (Ar-C); 144.56 (Ar-C); 142.31 (Ar-C); 140.99 (Ar-C); 140.32 (Ar-C); 132.74 (Ar-C); 129.34 (Ar-C); 128.57 (Ar-C); 126.96 (Ar-C); 125.70 (Ar-C); 123.54 (Ar-C); 123.47 (Ar-C); 122.25 (Ar-C); 34.42 (C(CH₃)₃); 31.94 (C(CH₃)₃); 28.95 (CH(CH₃)₂); 28.22 (CH(CH₃)₂); 26.32 (CH(CH₃)₂); 25.26 (CH(CH₃)₂); 24.86 (CH(CH₃)₂); 23.73 (CH(CH₃)₂) ppm.

²⁰⁷Pb NMR (104.74 MHz, [D₆]benzene, 292 K): δ 1054 ppm.

[{Carb^{DiPP}}PbCl] (3)



To a Schlenk flask in a glovebox was added PbCl₂ (600 mg, 2.16 mmol) and [Li{Carb^{DiPP}}.(thf)₂] (1.68 g, 2.10 mmol). The Schlenk vessel was sealed and removed from the glovebox and attached to a Schlenk line. Degassed thf (30 mL) was added and the reaction mixture was left to stir for 16 h. The solvent was removed under reduced pressure and the yellow residue was extracted in toluene (30 mL) and filtered to give a bright yellow solution. Removal of the solvent under reduced pressure gave the complex as a bright yellow powder. Crystals suitable for an X-ray diffraction study were grown from cooling a saturated toluene solution from 60 °C to room temperature. Yield: 1.62 g (82%).

¹H NMR (500.13 MHz, [D₈]toluene, 300 K): δ 8.69 (d, ⁴J_{HH} = 2.1 Hz, 2H, CH-Carb); 8.45 (s, 2H, CH=N); 7.63 (d, ⁴J_{HH} = 2.1 Hz, 2H, CH-Carb); 7.27 (m, 2H, Ar-H); 7.18-7.12 (m, 4H, Ar-H); 3.79 (hept, ³J_{HH} = 6.8 Hz, 2H, CH(CH₃)₂); 3.00 (hept, ³J_{HH} = 6.8 Hz, 2H, CH(CH₃)₂); 1.47 (d, ³J_{HH} = 6.6 Hz, 6H, CH(CH₃)₂); 1.41 (s, 18H, C(CH₃)₃); 1.07 (d, ³J_{HH} = 6.6 Hz, 6H, CH(CH₃)₂); 1.06 (d, ³J_{HH} = 6.8 Hz, 6H, CH(CH₃)₂); 0.96 (d, ³J_{HH} = 6.8 Hz, 6H, CH(CH₃)₂) ppm.

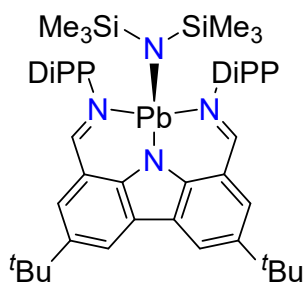
¹H NMR (500.13 MHz, [D₆]benzene, 300 K): δ 8.69 (d, ⁴J_{HH} = 2.1 Hz, 2H, CH-Carb); 8.45 (s, 2H, CH=N); 7.63 (d, ⁴J_{HH} = 2.1 Hz, 2H, CH-Carb); 7.27 (dd, J_{HH} = 7.8, 1.5 Hz, 2H, Ar-H); 7.19-7.11 (m, 4H, Ar-H); 3.79 (hept, ³J_{HH} = 6.9 Hz, 2H, CH(CH₃)₂); 3.01 (hept, ³J_{HH} = 6.7 Hz, 2H, CH(CH₃)₂); 1.46 (d, ³J_{HH} = 6.7 Hz, 6H, CH(CH₃)₂); 1.41 (s, 18H, C(CH₃)₃); 1.07 (d, ³J_{HH} = 6.7 Hz, 6H, CH(CH₃)₂); 1.06 (d, ³J_{HH} = 6.7 Hz, 6H, CH(CH₃)₂); 0.96 (d, ³J_{HH} = 6.7 Hz, 6H, CH(CH₃)₂) ppm.

¹³C{¹H} NMR (125.77 MHz, [D₈]toluene, 300 K): δ 167.92 (CH=N); 146.42 (Ar-C); 144.93 (Ar-C); 142.78 (Ar-C); 141.17 (Ar-C); 140.55 (Ar-C); 133.02 (Ar-C); 129.68 (Ar-C); 128.86 (Ar-C); 127.33 (Ar-C); 126.02 (Ar-C); 125.62 (Ar-C); 123.8; 123.78; 123.72 (Ar-C); 122.54; 34.81 (C(CH₃)₃); 32.32 (C(CH₃)₃); 29.35 (CH(CH₃)₂); 28.55 (CH(CH₃)₂); 26.73 (CH(CH₃)₂); 25.59 (CH(CH₃)₂); 24.89 (CH(CH₃)₂); 24.13 (CH(CH₃)₂) ppm.

¹³C{¹H} NMR (125.77 MHz, [D₆]benzene, 300 K): δ 167.61 (CH=N); 146.20 (Ar-C); 144.54 (Ar-C); 142.46 (Ar-C); 140.89 (Ar-C); 140.23 (Ar-C); 132.78 (Ar-C); 129.34 (Ar-C); 128.57 (Ar-C); 126.96 (Ar-C); 125.70 (Ar-C); 125.30 (Ar-C); 123.47 (Ar-C); 122.19 (Ar-C); 34.43 (C(CH₃)₃); 31.97 (C(CH₃)₃); 28.93 (CH(CH₃)₂); 28.17 (CH(CH₃)₂); 26.32 (CH(CH₃)₂); 25.30 (CH(CH₃)₂); 24.57 (CH(CH₃)₂); 23.78 (CH(CH₃)₂) ppm.

²⁰⁷Pb NMR (104.71 MHz, [D₆]benzene, 292 K): δ 791 ppm.

[{Carb^{DiPP}}PbN(SiMe₃)₂] (4)



In a glovebox a Schlenk flask was loaded with [Pb{N(SiMe₃)₂}₂] (1.00 g, 1.89 mmol) and {Carb^{DiPP}}-H (1.11 g, 1.70 mmol) along with a stir bar. The flask was removed from the glovebox, attached to a Schlenk manifold and the contents were dissolved in toluene (40 mL). The flask was equipped with a reflux condenser, the reaction was heated to reflux and left to stir for 48 h. After that time the volatiles were removed under pressure and the yellow residue was washed with hexanes (20 mL), filtered and dried to give the title compound as an intense yellow powder. Crystallisation of the washings also yielded a small amount of **4**. Combined yield

(powder + crystallised washings): 1.43 g (81%)

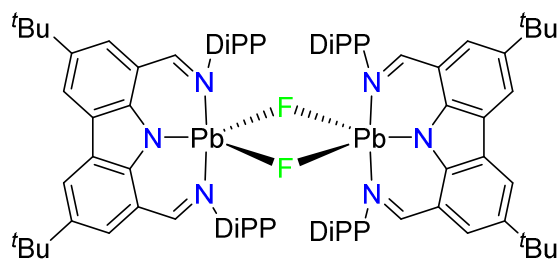
¹H NMR (500.13 MHz, [D₈]toluene, 350 K): δ 8.58 (d, ⁴J_{HH} = 2.1 Hz, 2H, CH-Carb); 8.50 (s, 2H, CH=N); 7.63 (d, ⁴J_{HH} = 2.1 Hz, 2H, CH-Carb); 7.17-7.04 (m, 6H, Ar-H); 3.42 (hept, ³J_{HH} = 6.8 Hz, 4H, CH(CH₃)₂); 1.47 (d, ³J_{HH} = 6.6 Hz, 6H, CH(CH₃)₂); 1.41 (s, 18H, C(CH₃)₃); 1.30 (d, ³J_{HH} = 6.6 Hz, 12H, CH(CH₃)₂); 1.17 (br, 12H, CH(CH₃)₂); -0.26 (s, 18H, Si(CH₃)₃) ppm.

¹H NMR (500.13 MHz, [D₆]benzene, 298 K): δ 8.69 (d, ⁴J_{HH} = 2.1 Hz, 2H, CH-Carb); 8.52 (s, 2H, CH=N); 7.66 (d, ⁴J_{HH} = 2.1 Hz, 2H, CH-Carb); 7.27-7.11 (m, 6H, Ar-H); 3.47 (hept, ³J_{HH} = 6.9 Hz, 2H, CH(CH₃)₂); 1.40 (s, 18H, C(CH₃)₃); 1.33 (br, 18H, CH(CH₃)₂); 0.96 (br, 6H, CH(CH₃)₂); -0.13 (s, 12H, Si(CH₃)₃) ppm.

¹³C{¹H} NMR (125.77 MHz, [D₈]toluene, 350 K): δ 169.75 (CH=N); 148.91 (Ar-C); 145.61 (Ar-C); 141.12 (Ar-C); 141.06 (Ar-C); 132.93 (Ar-C); 129.50 (Ar-C); 128.81 (Ar-C); 126.91 (Ar-C); 124.64 (br, Ar-C); 122.97 (Ar-C); 122.62 (Ar-C); 34.80 (C(CH₃)₃); 32.31 (C(CH₃)₃); 29.01 (CH(CH₃)₂); 25.61 (br, CH(CH₃)₂); 25.35 (CH(CH₃)₂); 6.63 (Si(CH₃)₃) ppm.

²⁰⁷Pb NMR (104.77 MHz, [D₆]benzene, 291 K): δ 1347 (br) ppm.

[{Carb^{DiPP}}Pb(μ -F)] (5)



In a glovebox a Schlenk flask was loaded with [{Carb^{DiPP}}PbN(SiMe₃)₂] (**4**) (500 mg, 0.48 mmol) and freshly sublimed [Me₃SnF] (89 mg, 0.49 mmol) along with a stir bar. The flask was removed from the glovebox, attached to a Schlenk manifold, and toluene (50 mL) was added. The reaction was heated to 85 °C and left to stir for 7 days. After that time the volatiles were removed under reduced pressure and hexanes (40 mL) was added to give a yellow suspension. The suspension was filtered via filter cannula, and the solution was left to crystallise at room temperature over several days. The remaining solid was dried under reduced pressure (50 °C, 1×10^{-3} mbar) for 1 h. The crystals were isolated by decantation and dried under reduced pressure. Yield: 340 mg (81%)

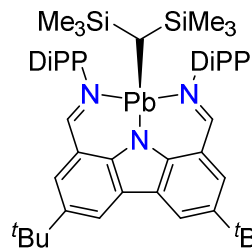
¹H NMR (500.13 MHz, [D₆]benzene, 300 K): δ 8.71 (d, $^4J_{\text{HH}} = 1.8$ Hz, 2H, CH-Carb); 8.37 (s, 2H, CH=N); 7.61 (d, $^4J_{\text{HH}} = 2.0$ Hz, 2H, CH-Carb); 7.28 (br, 2H *para*-C₆H₃); 7.26-7.09 (m, 4H, Ar-H); 3.78 (br, 2H, CH(CH₃)₂); 2.94 (br, 2H, CH(CH₃)₂); 1.47 (br, 6H, CH(CH₃)₂); 1.42 (s, 18H, C(CH₃)₃); 1.04 (br, 6H, CH(CH₃)₂); 1.03 (d, 12H, $^3J_{\text{HH}} = 6.9$ Hz, CH(CH₃)₂) ppm.

¹³C{¹H} NMR (125.77 MHz, [D₆]benzene, 300 K): δ 166.58 (CH=N); 146.37 (Ar-C); 146.74 (Ar-C); 142.95 (br, *ipso*-C₆H₃); 140.68 (Ar-C); 139.94 (br, C₆H₃); 132.36 (Ar-C); 126.31 (Ar-C); 125.31 (br, C₆H₃); 123.48 (br, C₆H₃); 123.10 (Ar-C); 122.00 (Ar-C); 34.36 (C(CH₃)₃); 32.01 (C(CH₃)₃); 28.63 (br, CH(CH₃)₂); 28.12 (br, CH(CH₃)₂); 26.06 (br, CH(CH₃)₂); 25.16 (br, CH(CH₃)₂); 24.03 (br, CH(CH₃)₂) ppm.

¹⁹F{¹H} NMR (470.54 MHz, [D₆]benzene, 300 K): δ -109.68 ($^1J_{\text{FPb}} = 3350$ Hz) (br, Pb-F) ppm.

²⁰⁷Pb NMR (104.66 MHz, [D₆]benzene, 292 K): δ 332 ($^1J_{\text{PbF}} = 3350$ Hz) ppm.

[{Carb^{DiPP}}PbCH(SiMe₃)₂] (6)



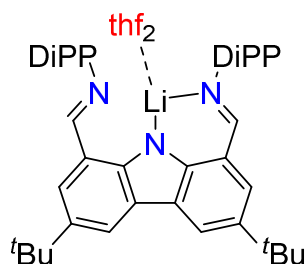
A solution of [Li{CH(SiMe₃)₂}] (74 mg, 0.45 mmol) in toluene (10 mL) was added dropwise to a solution of [{Carb^{DiPP}}PbCl] (**3**) (400 mg, 0.45 mmol) in toluene (20 mL) at –78 °C. The solution was warmed up to room temperature and stirred for 2 h, generating an orange solution. The solvent was removed under reduced pressure, and the residue was extracted with a solution of petroleum ether (30 mL) spiked with toluene (1 mL), filtered via a cannula filtration and concentrated to 5 mL. The Schlenk flask was transferred to a fridge and left to crystallise. Orange crystals of the complex [{Carb^{DiPP}}PbCH(SiMe₃)₂] (**6**) formed as orange prisms after 72 h at 4 °C. The crystals were isolated by filtration and dried under reduced pressure for 1 h. Further concentration of the mother liquor to 1 mL yielded a second crop of crystals. Combined yield: 65 mg + 121 mg = 186 mg (44%).

¹H NMR (400.13 MHz, [D₆]benzene, 300 K): δ 8.65 (d, ⁴J_{HH} = 1.7 Hz, 2H, CH-Carb); 8.47 (s, 2H, CH=N); 7.62 (d, ⁴J_{HH} = 2.1 Hz, 2H, CH-Carb); 7.17–7.10 (m, 6H, Ar-H); 3.58 (br, 4H, CH(CH₃)₂); 1.39 (s, 18H, C(CH₃)₃); 1.34 (br, 12H, CH(CH₃)₂); 1.18 (br, 12H, CH(CH₃)₂); –0.21 (s, 18H, Si(CH₃)₃); –0.97 (s, 1H, PbCH) ppm.

¹³C{¹H} NMR (100.62 MHz, [D₆]benzene, 300 K): δ 169.84 (CH=N); 148.03 (Ar-C); 144.97 (Ar-C); 140.83 (br, *ipso*-C₆H₃); 140.01 (Ar-C); 132.88 (Ar-C); 128.51 (Ar-C); 126.62 (Ar-C); 124.48 (br, C₆H₃); 123.01 (Ar-C); 121.89 (Ar-C); 75.55 (PbCH); 34.38 (C(CH₃)₃); 31.93 (C(CH₃)₃); 28.74 (br, CH(CH₃)₂); 24.87 (br, CH(CH₃)₂); 5.07 (Si(CH₃)₃) ppm.

²⁰⁷Pb NMR (83.80 MHz, [D₆]benzene, 302 K): δ 2950 ppm.

[Li{Carb^{DiPP}}.(thf)₂] (24-thf)



A 100 mL Schlenk flask was loaded with {Carb^{DiPP}}-H (200 mg, 0.31 mmol), dissolved in hexanes (30 mL) and cooled to 0 °C with an ice/water bath. A solution on *n*-BuLi in hexanes (2.37M, 0.14 mL) was added dropwise and the solution left to stir for 1 h at room temperature generating a suspension. After 5 min thf (1 mL) was added resulting in a pale-yellow solution. The solution was concentrated to 1 mL and left at room temperature. After 4 d small crystals of the title compound had grown. After 24 h at –30 °C, pale yellow crystals of the title compound had formed. Drying under reduced pressure (40 °C, 1 ×10^{–3} mbar) results in partial desolvation to [Li{Carb^{DiPP}}.thf_{1.5}]. Yield: 171 mg (72%)

¹H NMR (500.13 MHz, [D₆]benzene, 300 K): δ 8.74 (d, ⁴J_{HH} = 1.8 Hz, 2H, CH-Carb); 8.39 (s, 2H, CH=N); 7.70 (d, ⁴J_{HH} = 1.9 Hz, 2H, CH-Carb); 7.06 (m, 6H, (C₆H₃)); 3.56 (m, 6H, 2,5-CH₂ thf); 3.04 (hept, ³J_{HH} = 6.8 Hz 4H, CH(CH₃)₂); 1.51 (s, 18H, C(CH₃)₃); 1.41 (m, 6H, 3,4-CH₂ thf); 1.06 (br, 12H, CH(CH₃)₂); 0.97 (br, 12H, CH(CH₃)₂) ppm.

¹³C{¹H} NMR (125.77 MHz, [D₆]benzene, 300 K) δ 170.11 (CH=N); 150.23 (Ar-C); 150.09 (Ar-C); 139.55 (Ar-C); 138.56 (Ar-C); 128.86 (C4-H Carb); 127.19 (Ar-C); 125.56 (Ar-C); 123.93 (C₆H₃); 123.09 (C₆H₃); 119.19 (Ar-C); 67.83 (2,5-CH₂ thf); 34.86 (C(CH₃)₃); 32.48 (C(CH₃)₃); 28.59 (CH(CH₃)₂); 25.82 (3,4-CH₂ thf); 24.26 (br, CH(CH₃)₂); 23.82 (br, CH(CH₃)₂) ppm.

⁷Li NMR (155.51 MHz, [D₆]benzene, 300 K) δ 3.50 ppm.

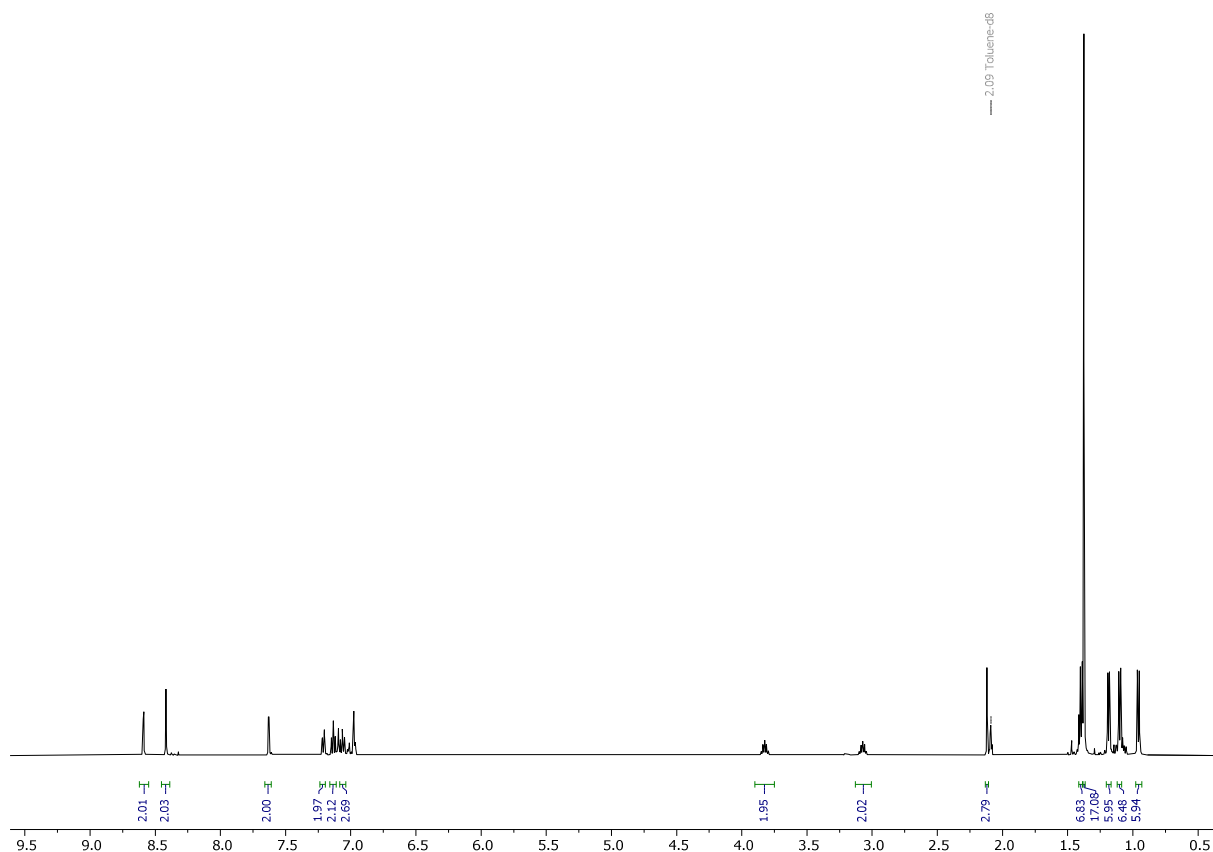


Figure S1. ^1H NMR spectrum (500.13 MHz, $[\text{D}_8]\text{toluene}$, 300 K) of $[\{\text{Carb}^{\text{DiPP}}\}\text{PbI}]$ (**1**).

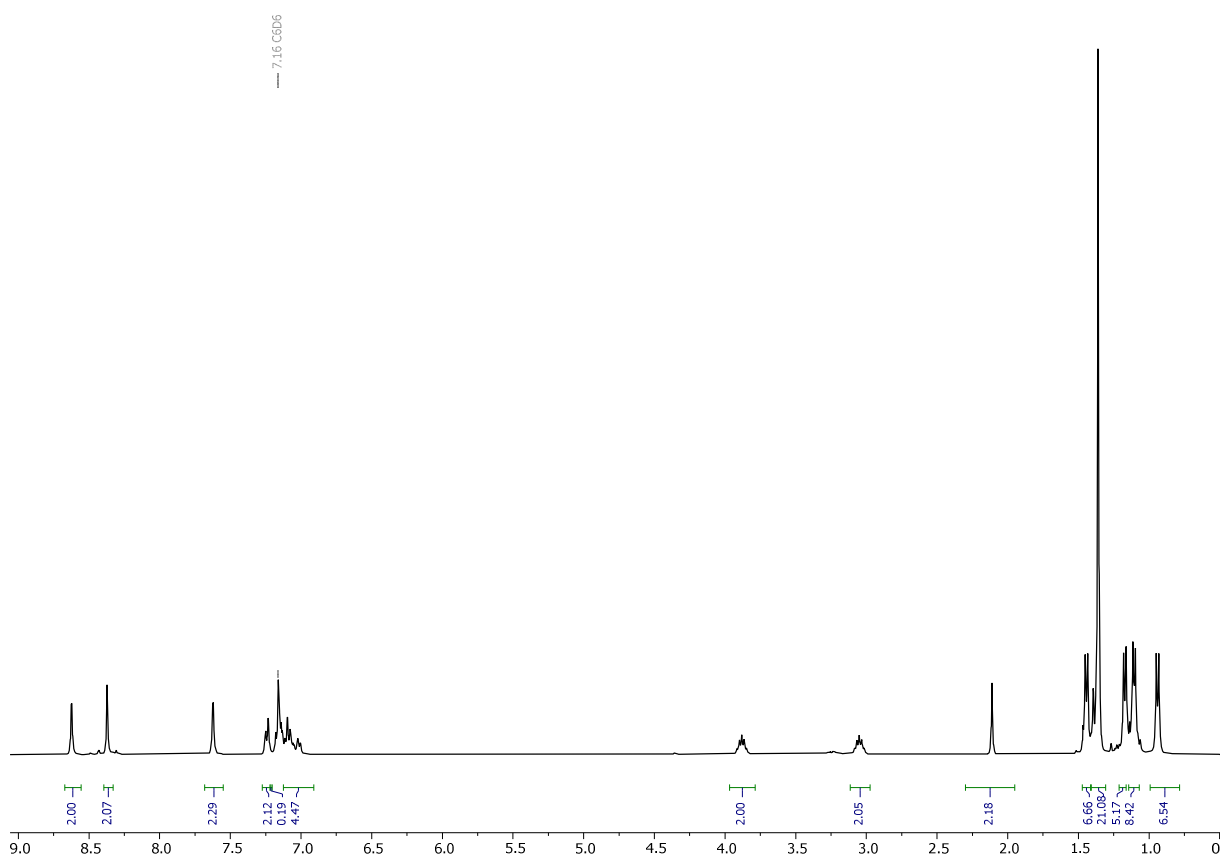


Figure S2. ^1H NMR spectrum (400.13 MHz, $[\text{D}_6]\text{benzene}$, 299 K) of $[\{\text{Carb}^{\text{DiPP}}\}\text{PbI}]$ (**1**).

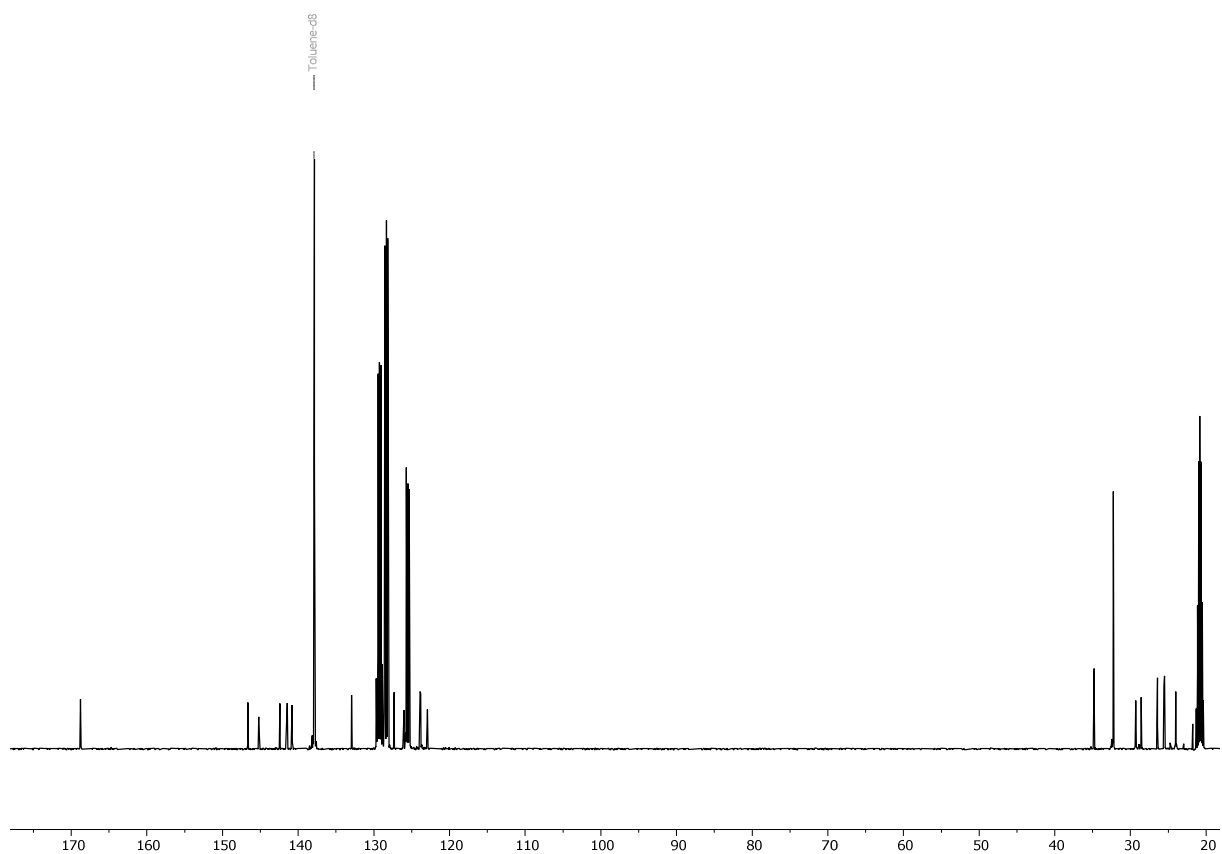


Figure S3. ¹³C{¹H} NMR spectrum (125.77 MHz, [D₈]toluene, 300 K) of [{Carb^{DiPP}}PbI] (1).

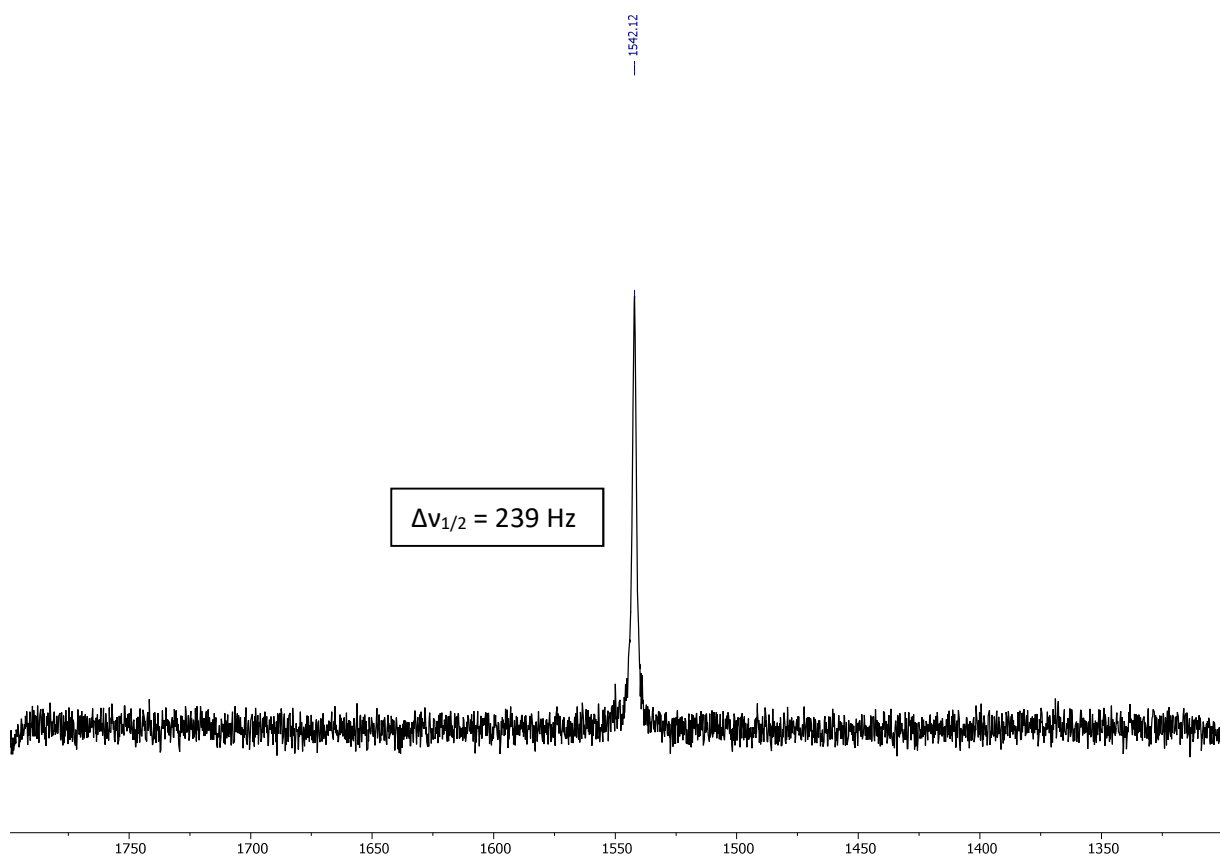


Figure S4. ²⁰⁷Pb NMR spectrum (104.79 MHz, [D₆]benzene, 292 K) of [{Carb^{DiPP}}PbI] (1).

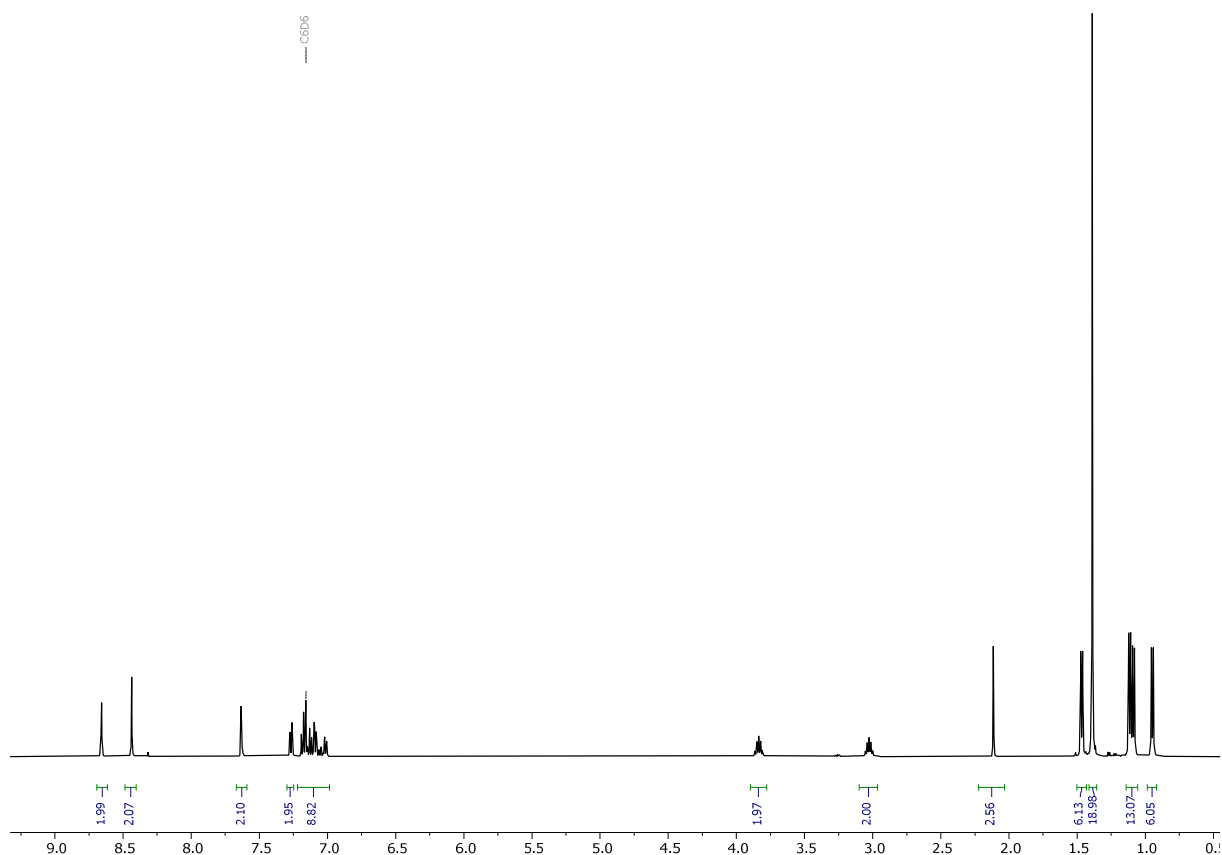


Figure S5. ¹H NMR spectrum (500.13 MHz, [D₆]benzene, 300 K) of [{Carb^{DiPP}}PbBr] (2).

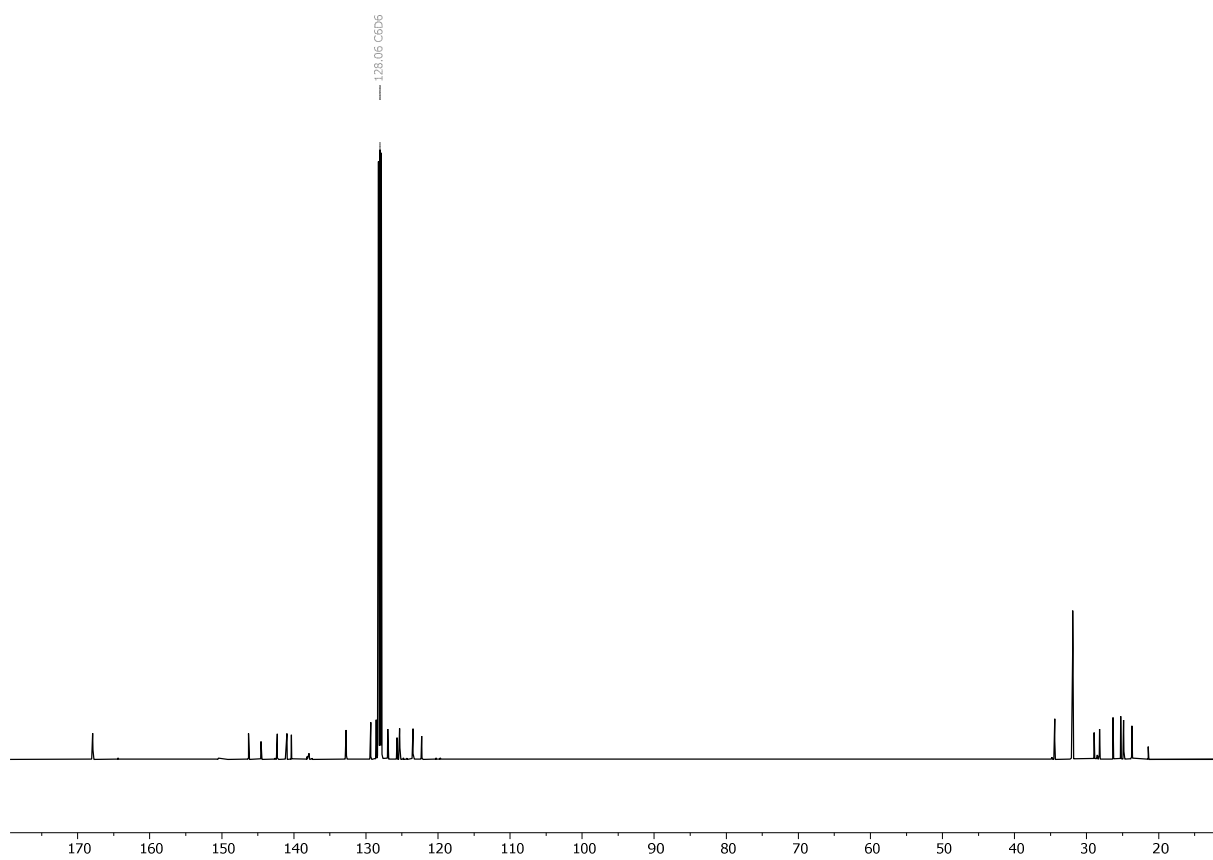


Figure S6. ¹³C{¹H} NMR spectrum (125.77 MHz, [D₆]benzene, 300 K) of [{Carb^{DiPP}}PbBr] (2).

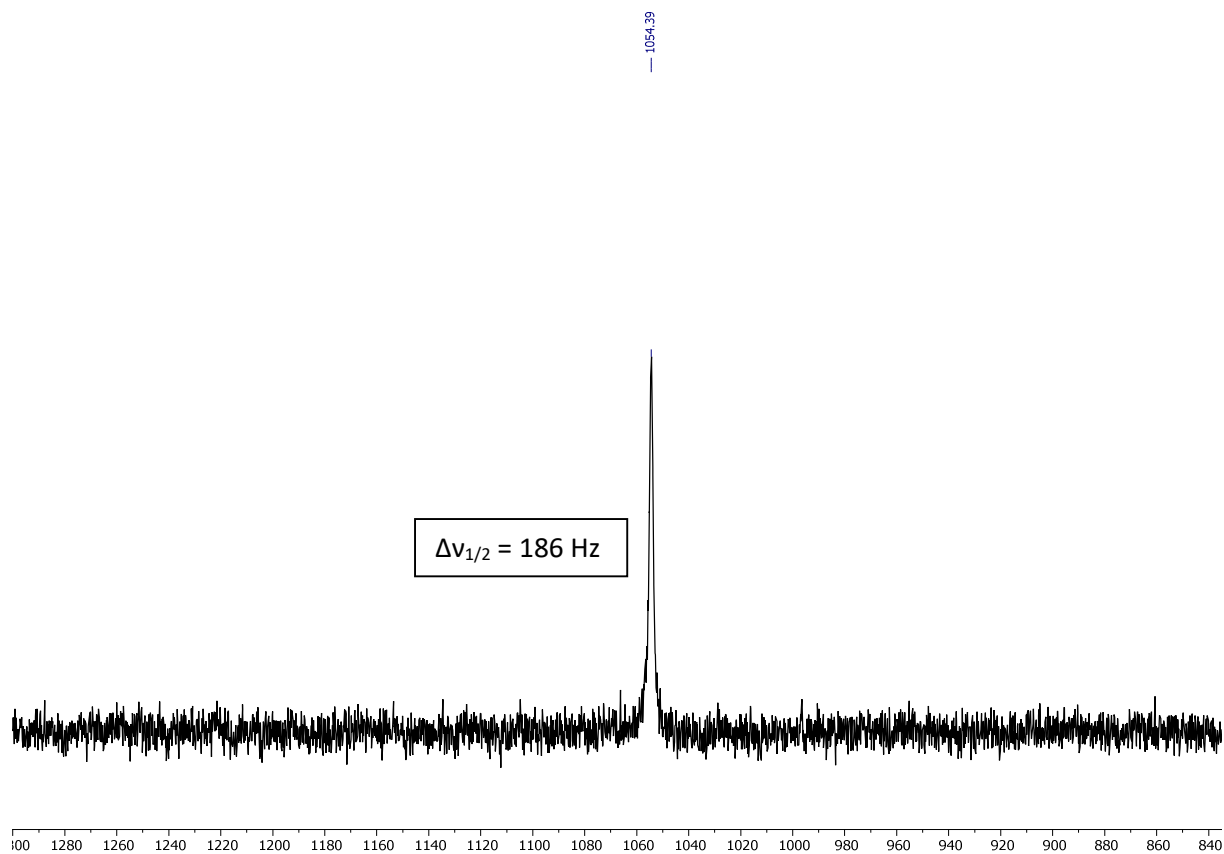


Figure S7. ^{207}Pb NMR spectrum (104.74 MHz, $[\text{D}_6]\text{benzene}$, 292 K) of $[\{\text{Carb}^{\text{DiPP}}\}\text{PbBr}]$ (**2**).

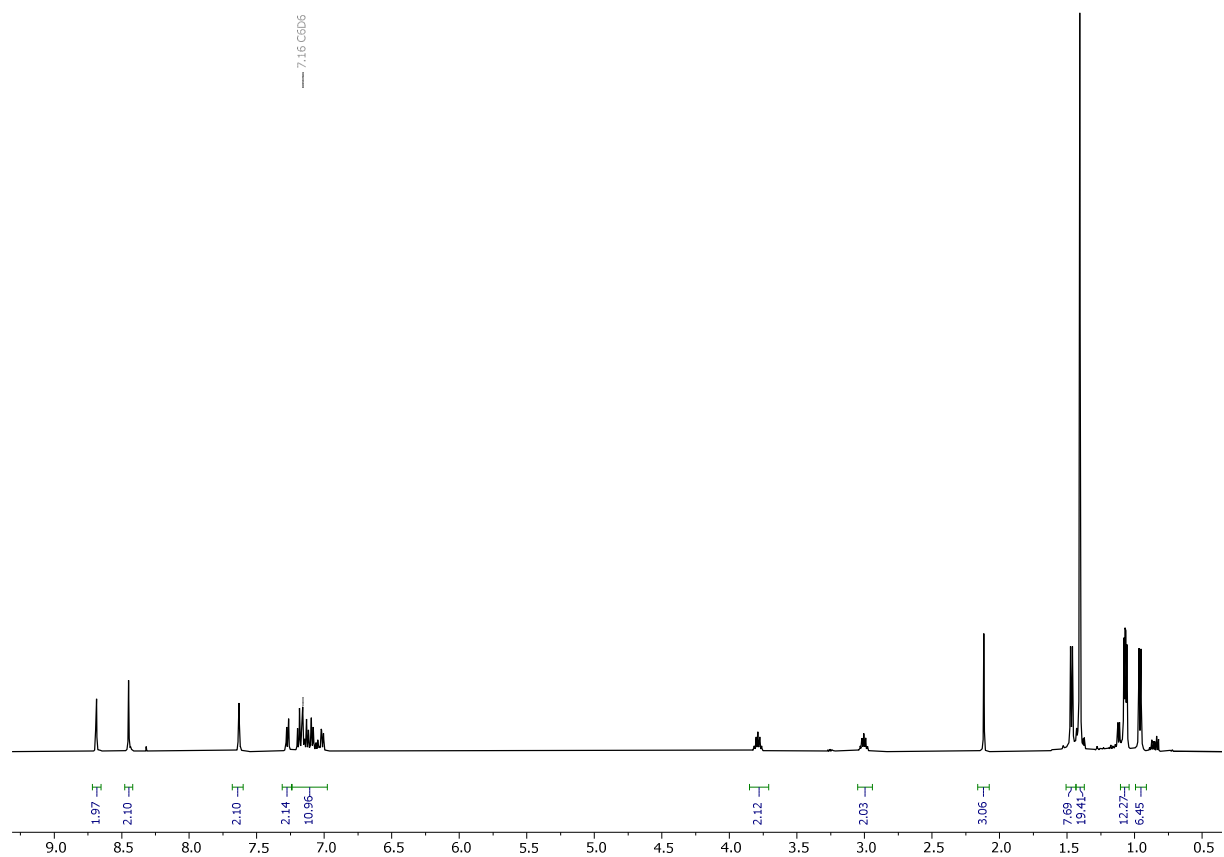


Figure S8. ^1H NMR spectrum (500.13 MHz, $[\text{D}_6]\text{benzene}$, 300 K) of $[\{\text{Carb}^{\text{DiPP}}\}\text{PbCl}]$ (**3**).

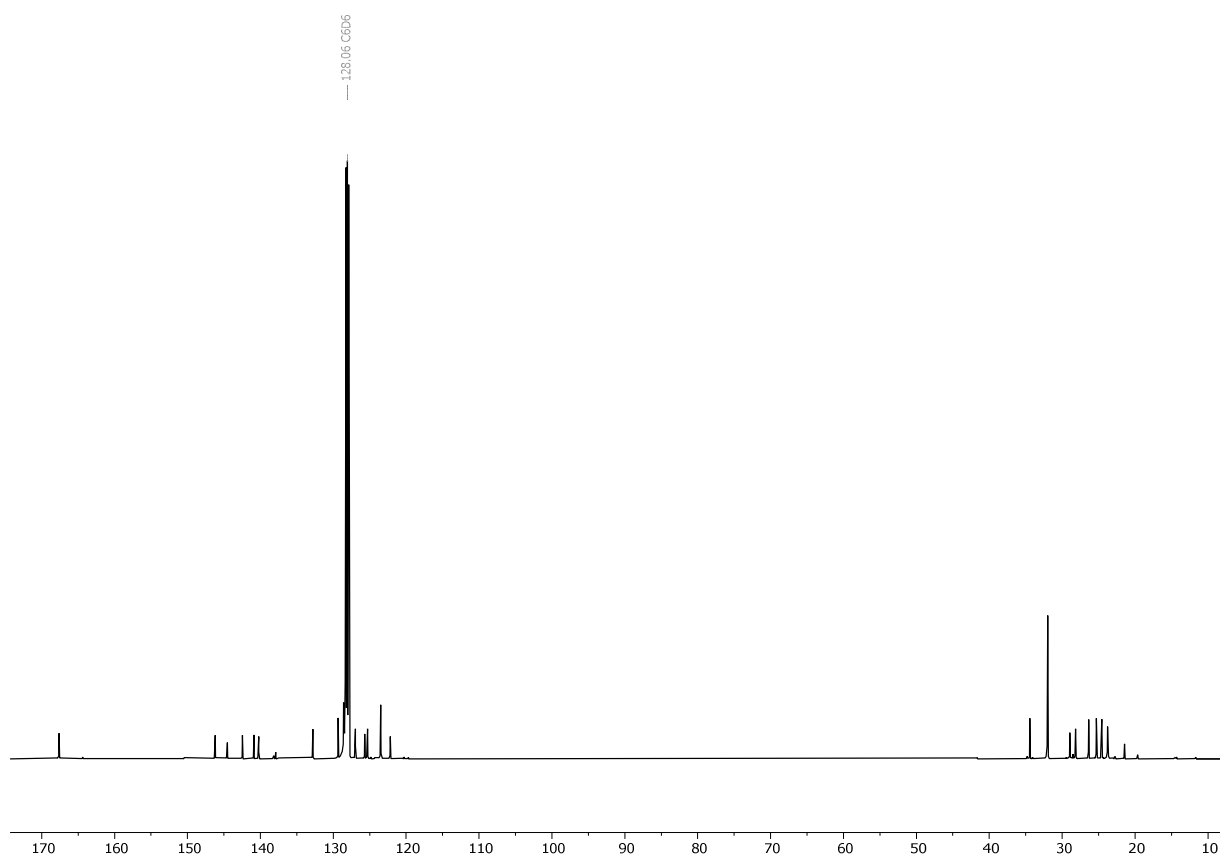


Figure S9. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (125.77 MHz, $[\text{D}_6]\text{benzene}$, 300 K) of $[\{\text{Carb}^{\text{DiPP}}\}\text{PbCl}]$ (**3**).

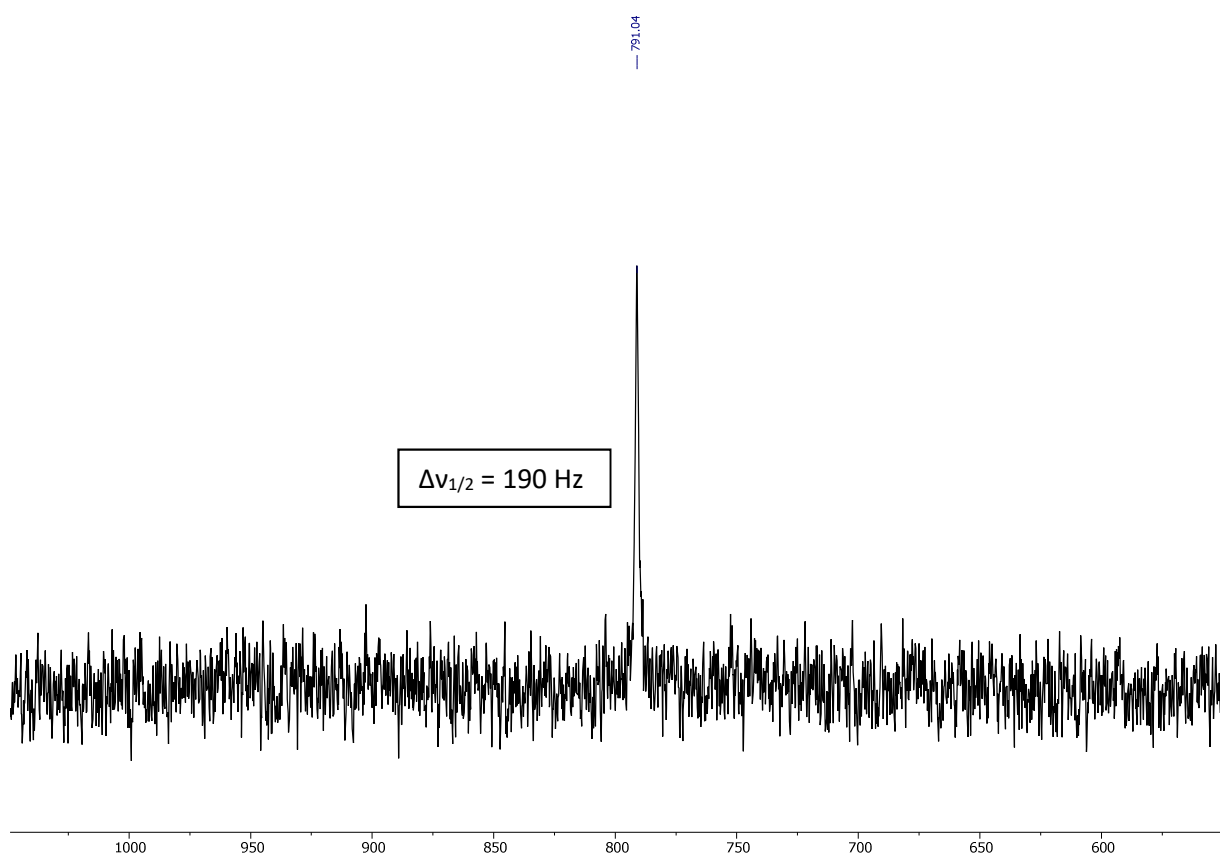


Figure S10. ^{207}Pb NMR spectrum (104.71 MHz, $[\text{D}_6]\text{benzene}$, 292 K) of $[\{\text{Carb}^{\text{DiPP}}\}\text{PbCl}]$ (**3**).

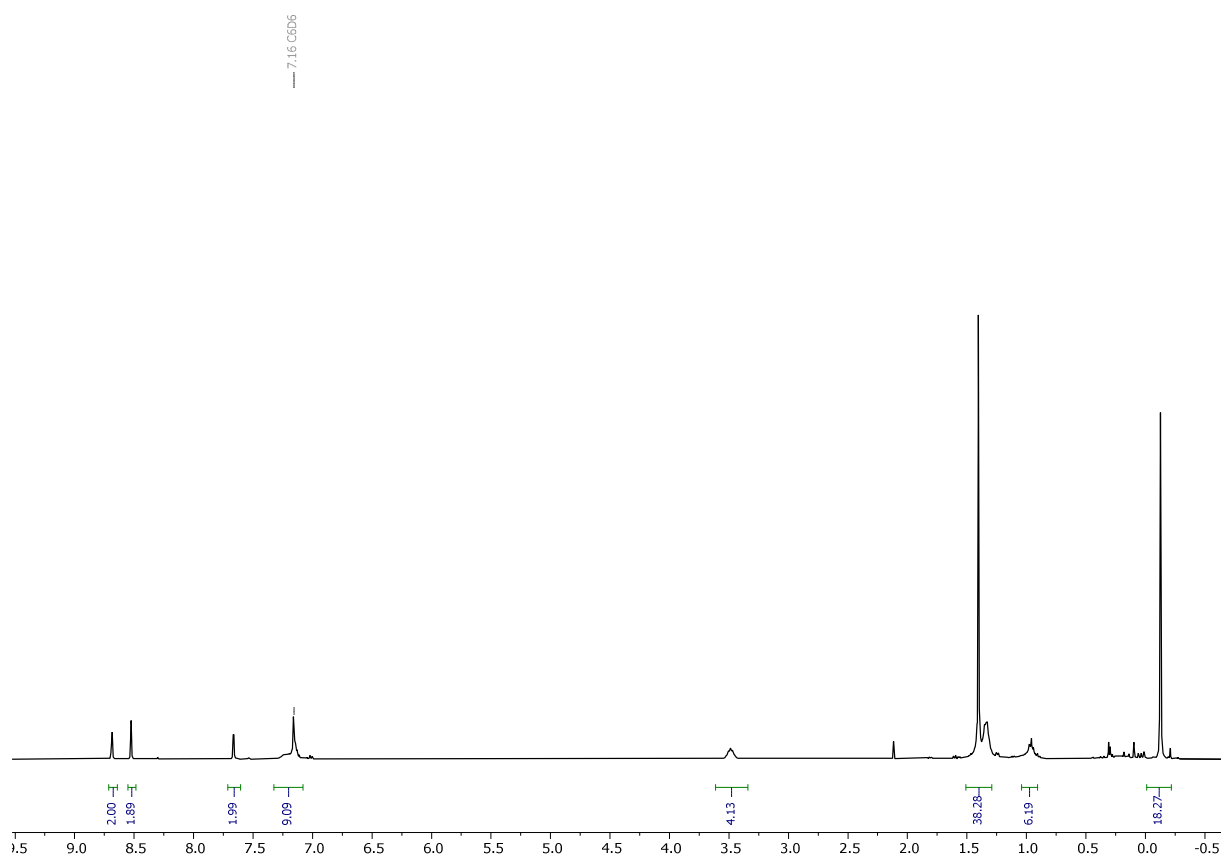


Figure S11. ¹H NMR spectrum (400.16 MHz, [D₆]benzene, 298 K) of [{Carb^{DiPP}}PbN(SiMe₃)₂] (**4**).

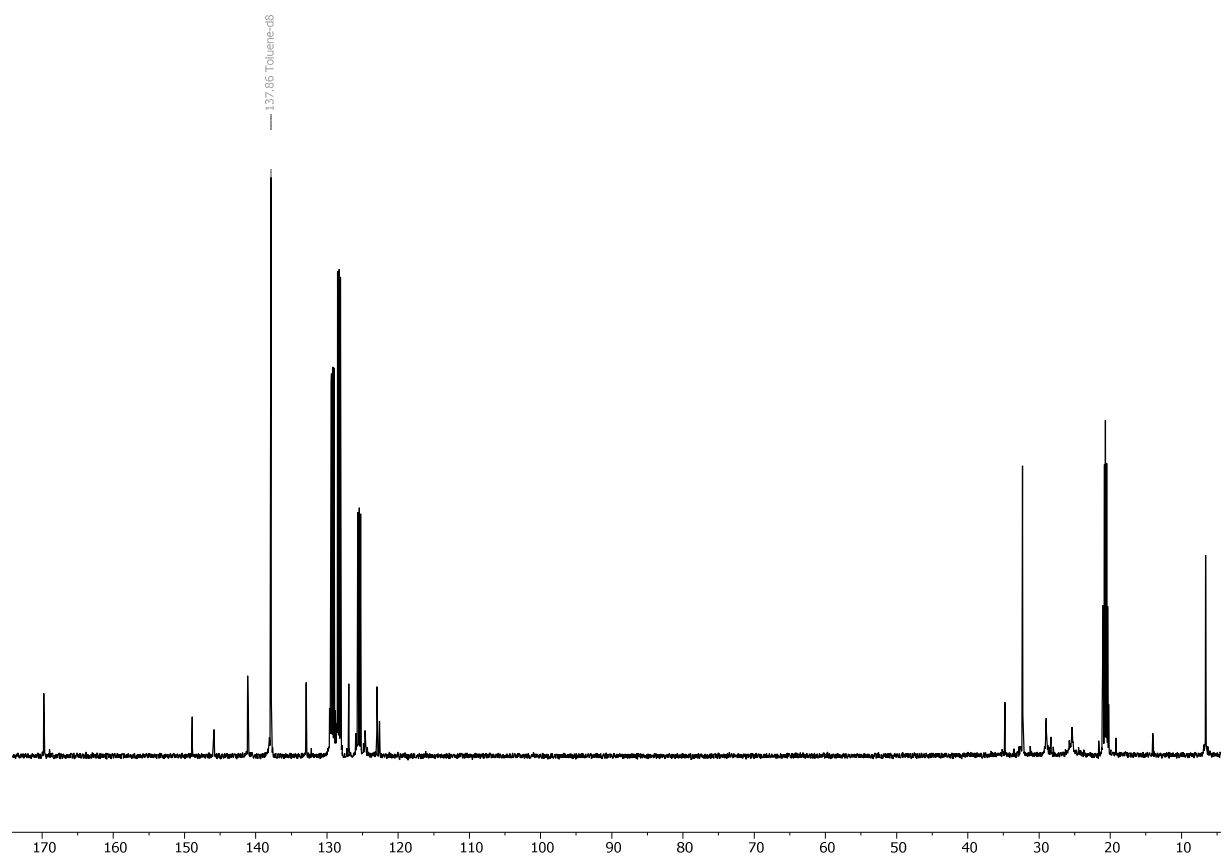


Figure S12. ¹³C{¹H} NMR spectrum (125.77 MHz, [D₈]toluene, 350 K) of [{Carb^{DiPP}}PbN(SiMe₃)₂] (**4**).

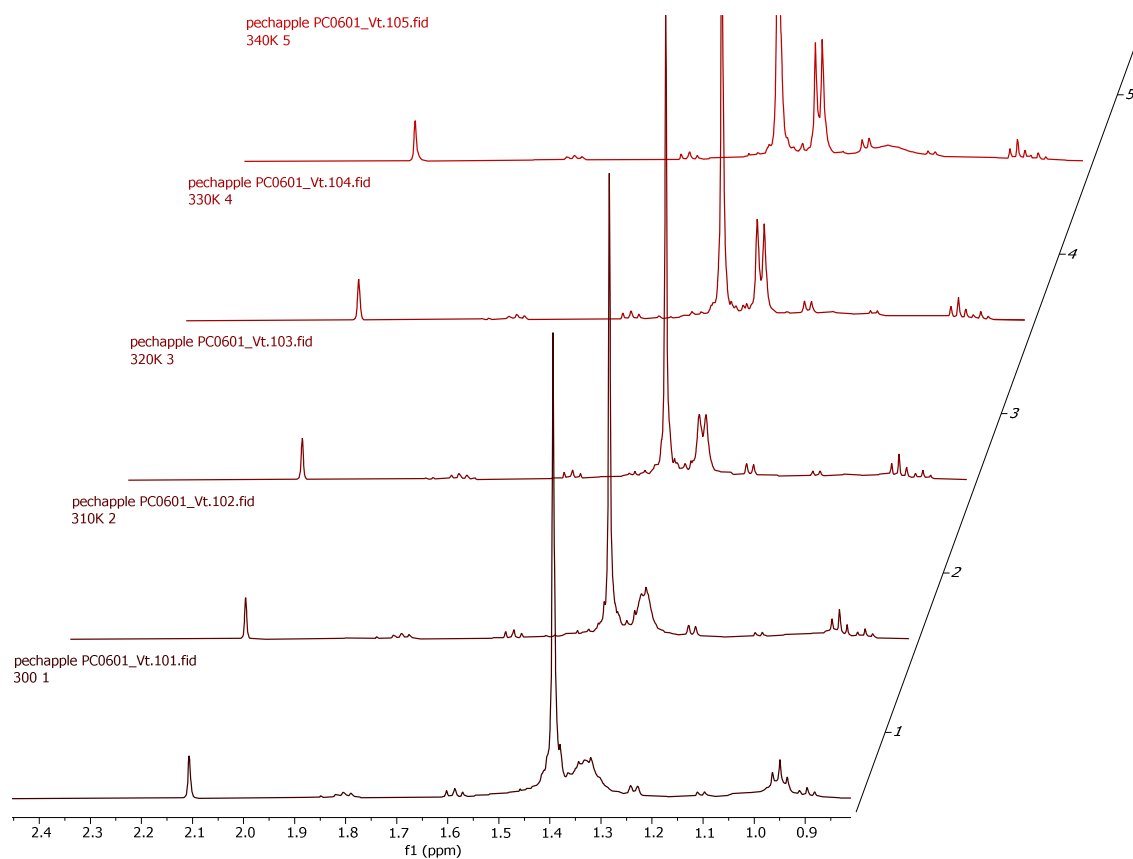


Figure S13. ^1H NMR spectrum (500.13 MHz, $[\text{D}_6]\text{benzene}$, 300 K (bottom) to 350 K (top) in 10 K increments of $[\{\text{Carb}^{\text{DiPP}}\}\text{PbN}(\text{SiMe}_3)_2]$ (**4**) showing sharpening of one *i*Pr resonance (δ_{H} 1.33 ppm). The other *i*Pr resonances (300 K, δ_{H} 1.33, 0.96 ppm) coalesce to a broad peak at δ_{H} 1.19 ppm at 350 K.

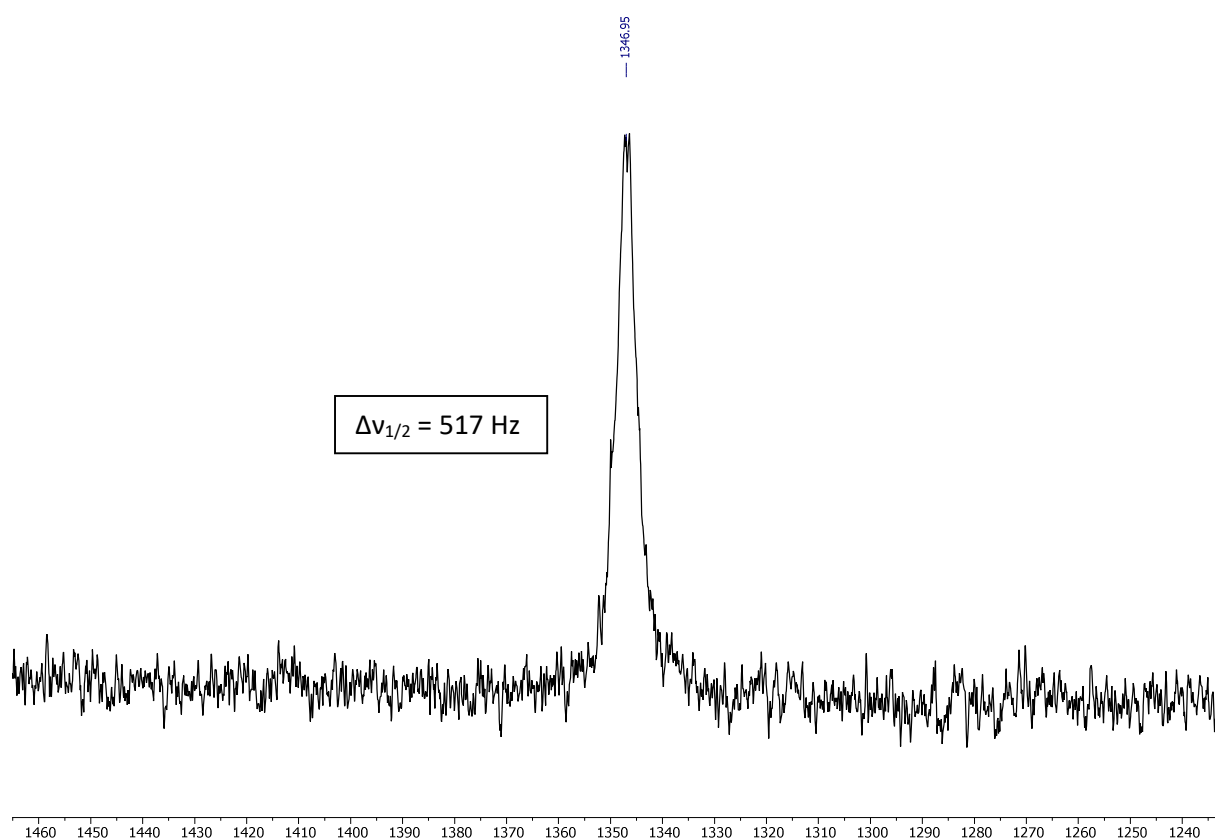


Figure S14. ^{207}Pb NMR spectrum (104.77 MHz, $[\text{D}_6]\text{benzene}$, 291 K) of $[\{\text{Carb}^{\text{DiPP}}\}\text{PbN}(\text{SiMe}_3)_2]$ (**4**).

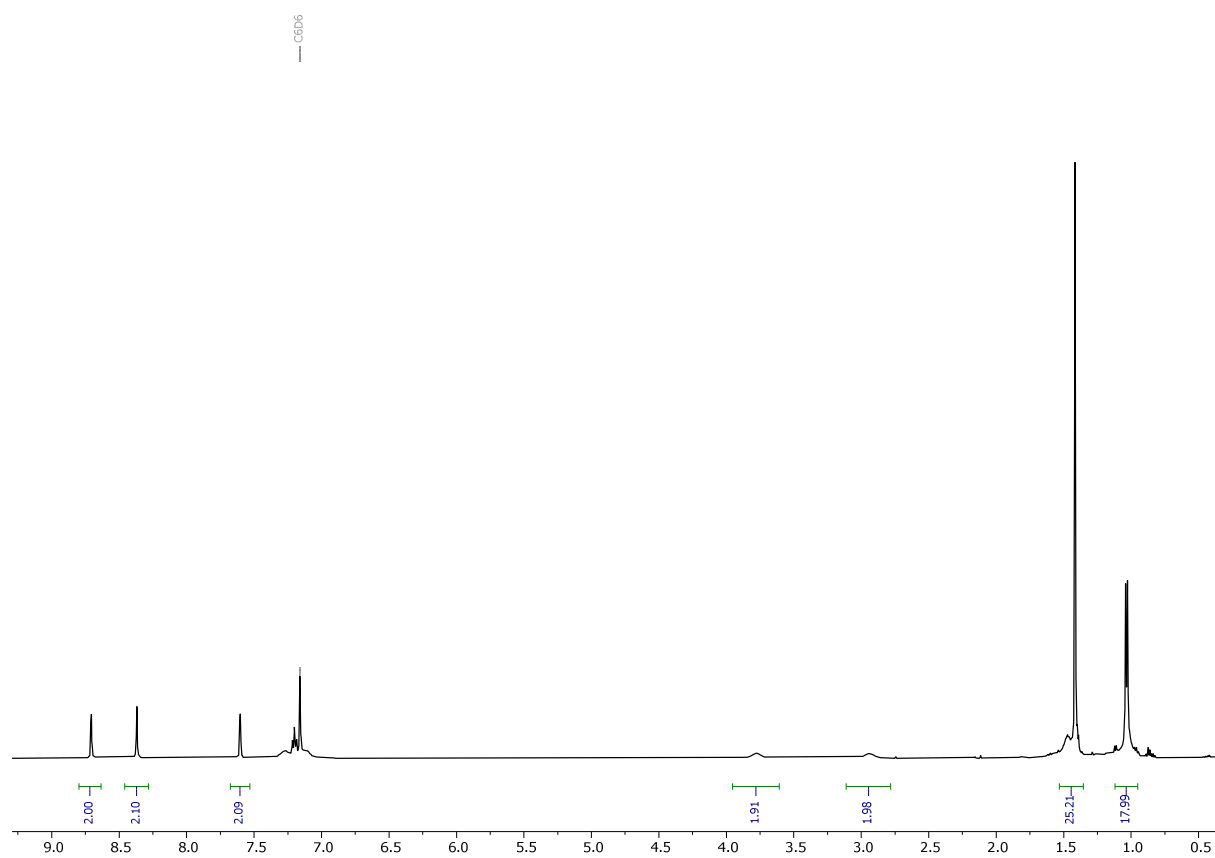


Figure S15. ^1H NMR spectrum (500.13 MHz, $[\text{D}_6]\text{benzene}$, 300 K) of $[\{\text{Carb}^{\text{DiPP}}\}\text{PbF}]$ (**5**).

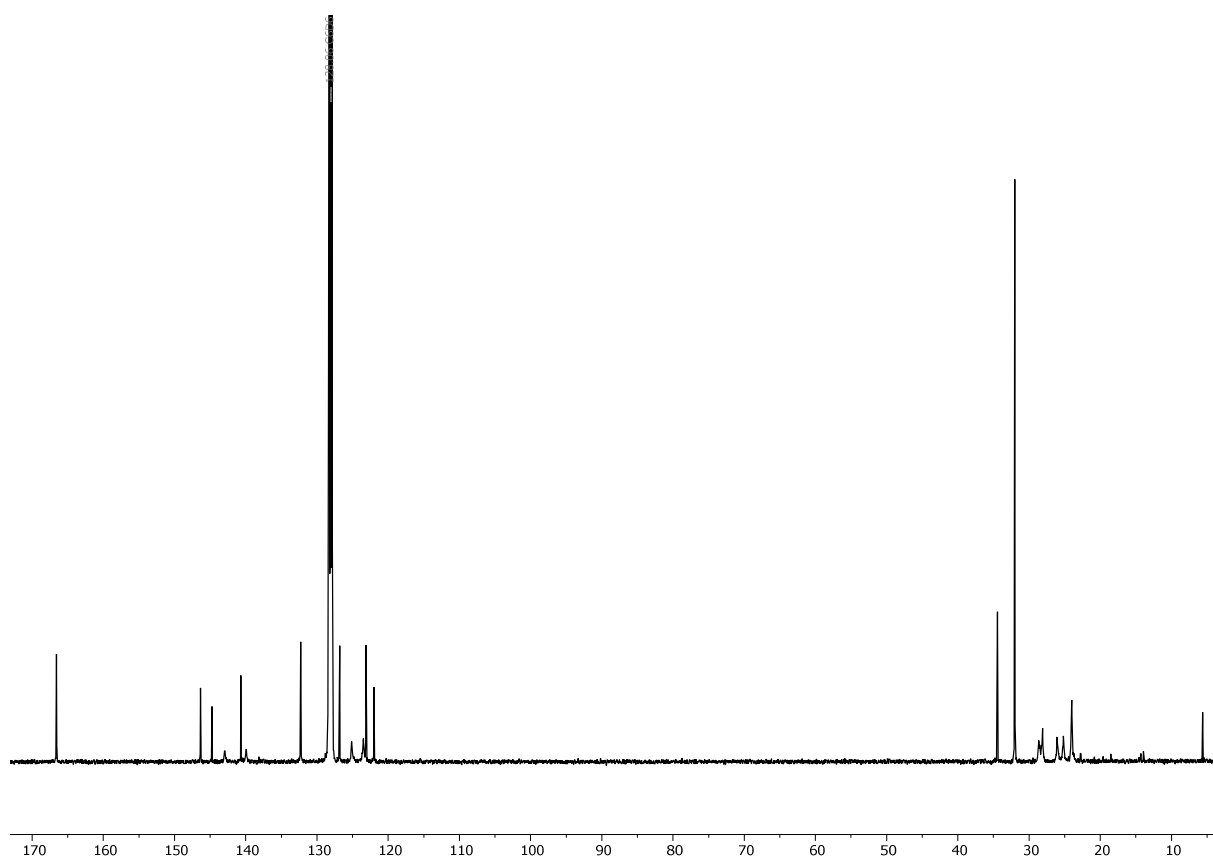


Figure S16. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (125.77 MHz, $[\text{D}_6]\text{benzene}$, 300 K) of $[\{\text{Carb}^{\text{DiPP}}\}\text{PbF}]$ (**5**).

— 347.77
— 315.69

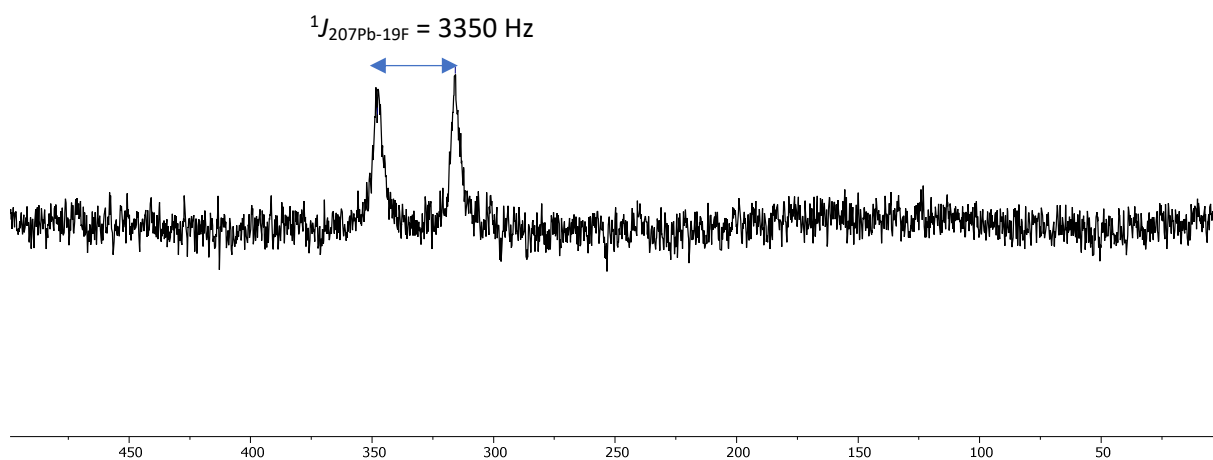


Figure S17. ^{207}Pb NMR spectrum (104.66 MHz, $[\text{D}_6]\text{benzene}$, 292 K) of $[\{\text{Carb}^{\text{DiPP}}\}\text{PbF}]$ (**5**).

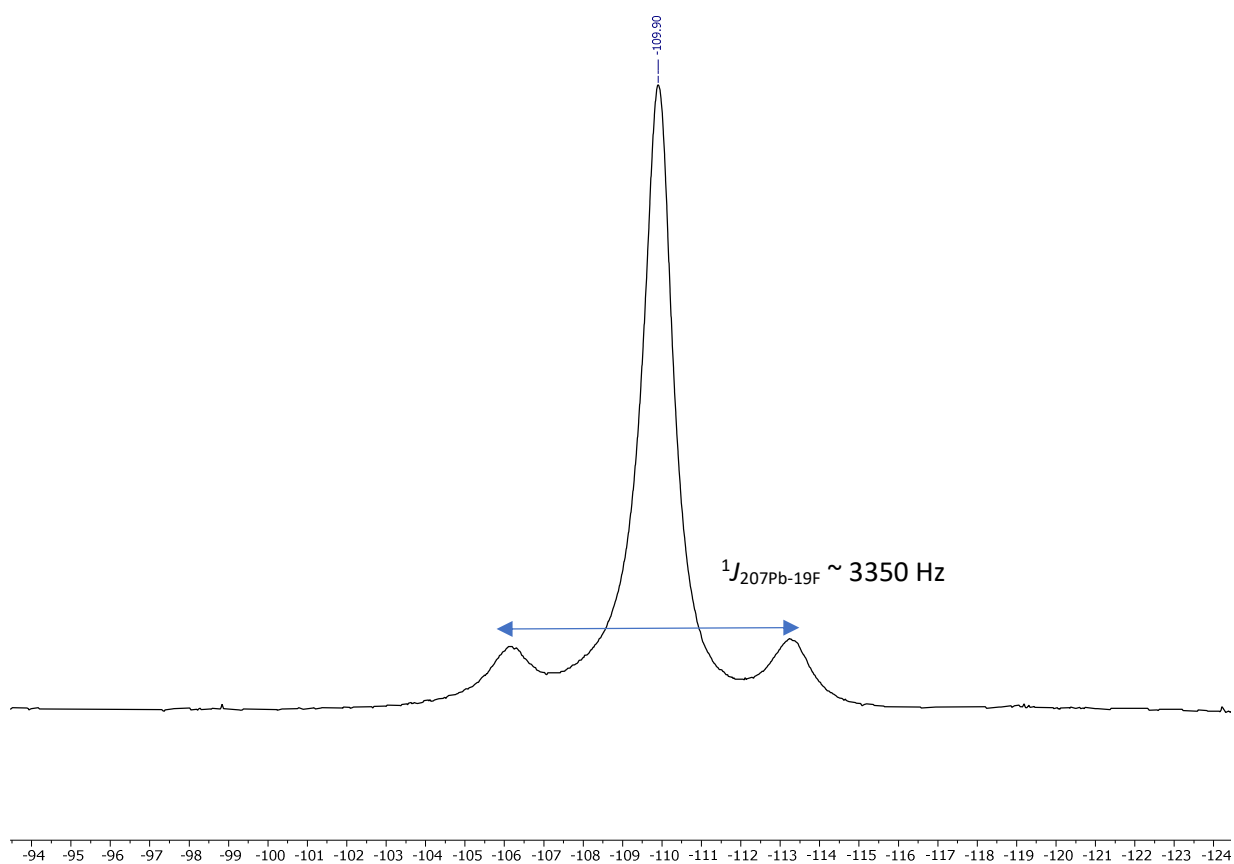


Figure S18. ^{19}F NMR spectrum (470.54 MHz, $[\text{D}_6]$ benzene, 292 K) of $[\{\text{Carb}^{\text{DiPP}}\}\text{PbF}]$ (**5**).

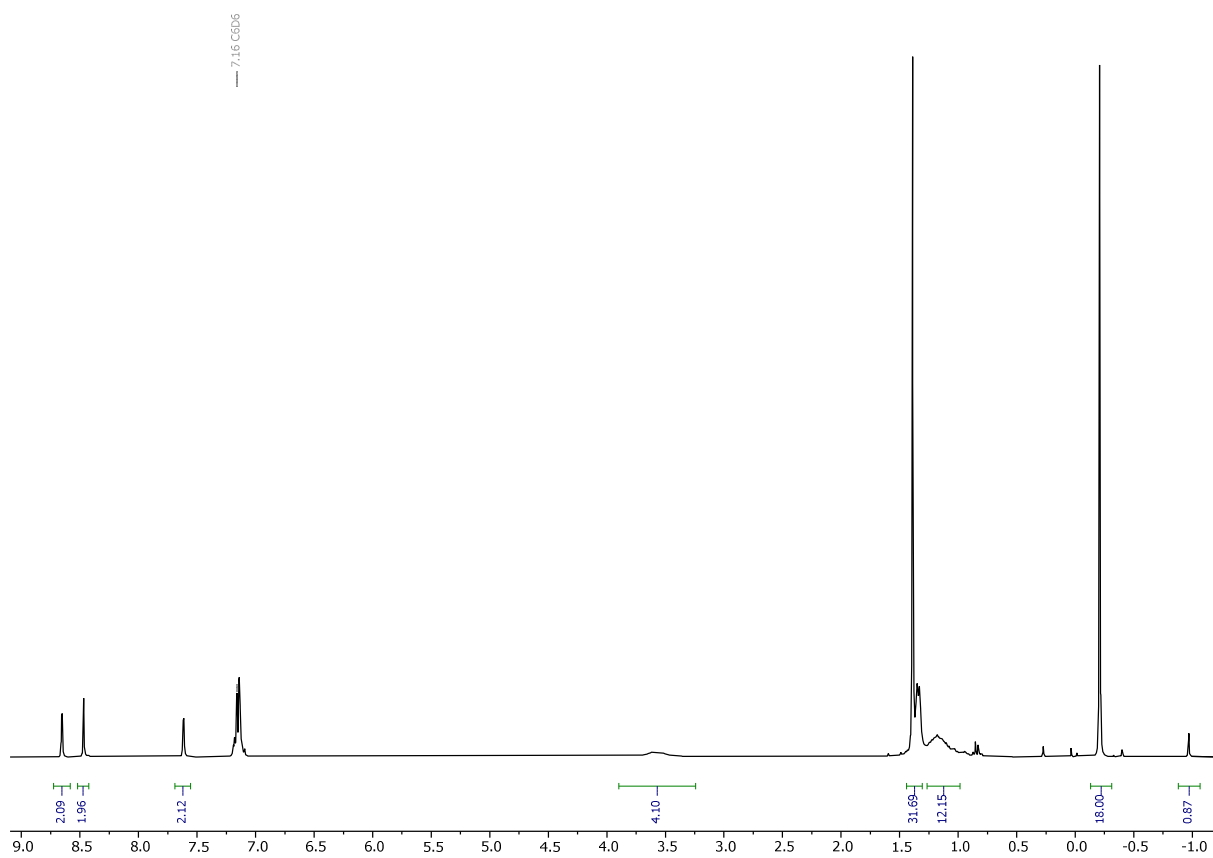


Figure S19. ^1H NMR spectrum (300.13 MHz, $[\text{D}_6]$ benzene, 300 K) of $[\{\text{Carb}^{\text{DiPP}}\}\text{PbCH}(\text{SiMe}_3)_2]$ (**6**).

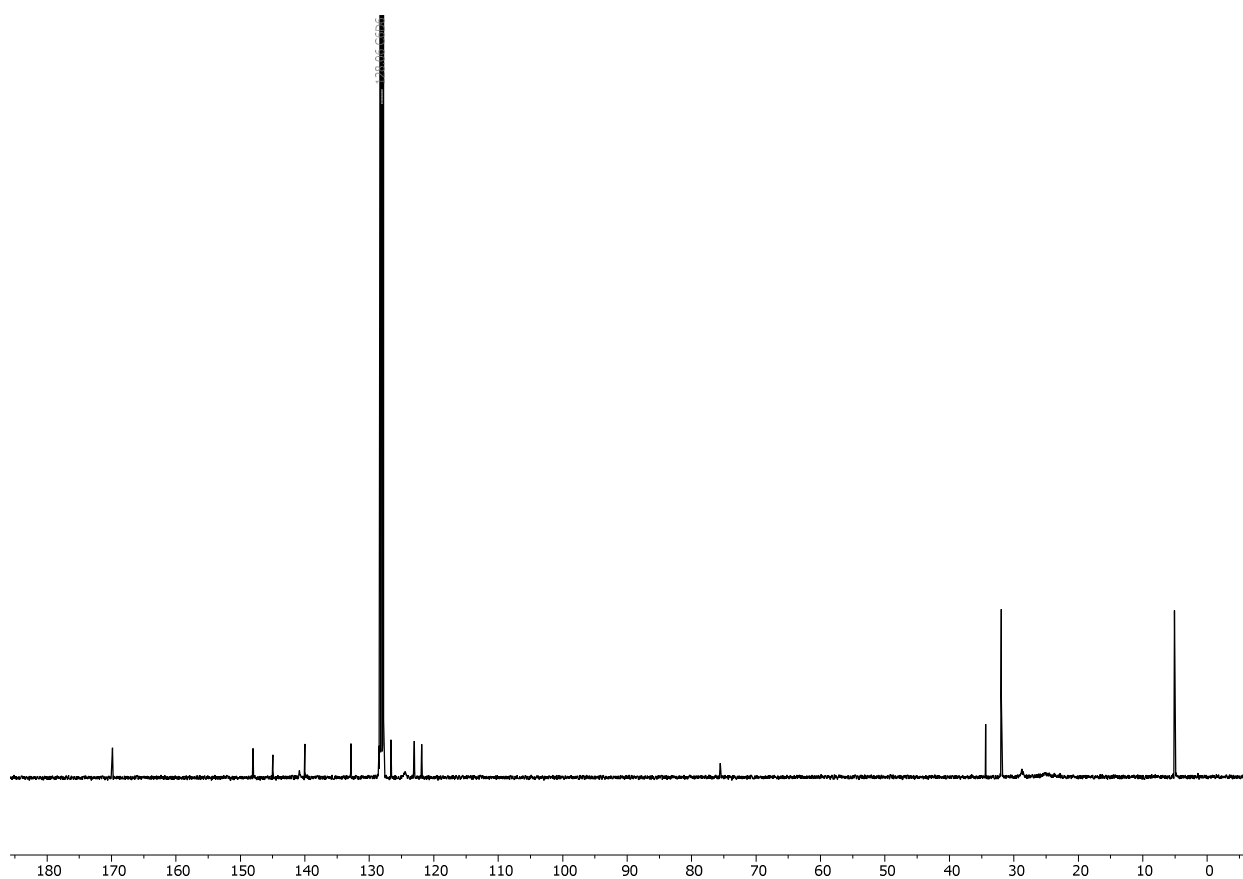


Figure S20. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (125.77 MHz, $[\text{D}_6]\text{benzene}$, 300 K) of $[\{\text{Carb}^{\text{DiPP}}\}\text{PbCH}(\text{SiMe}_3)_2]$ (**6**).

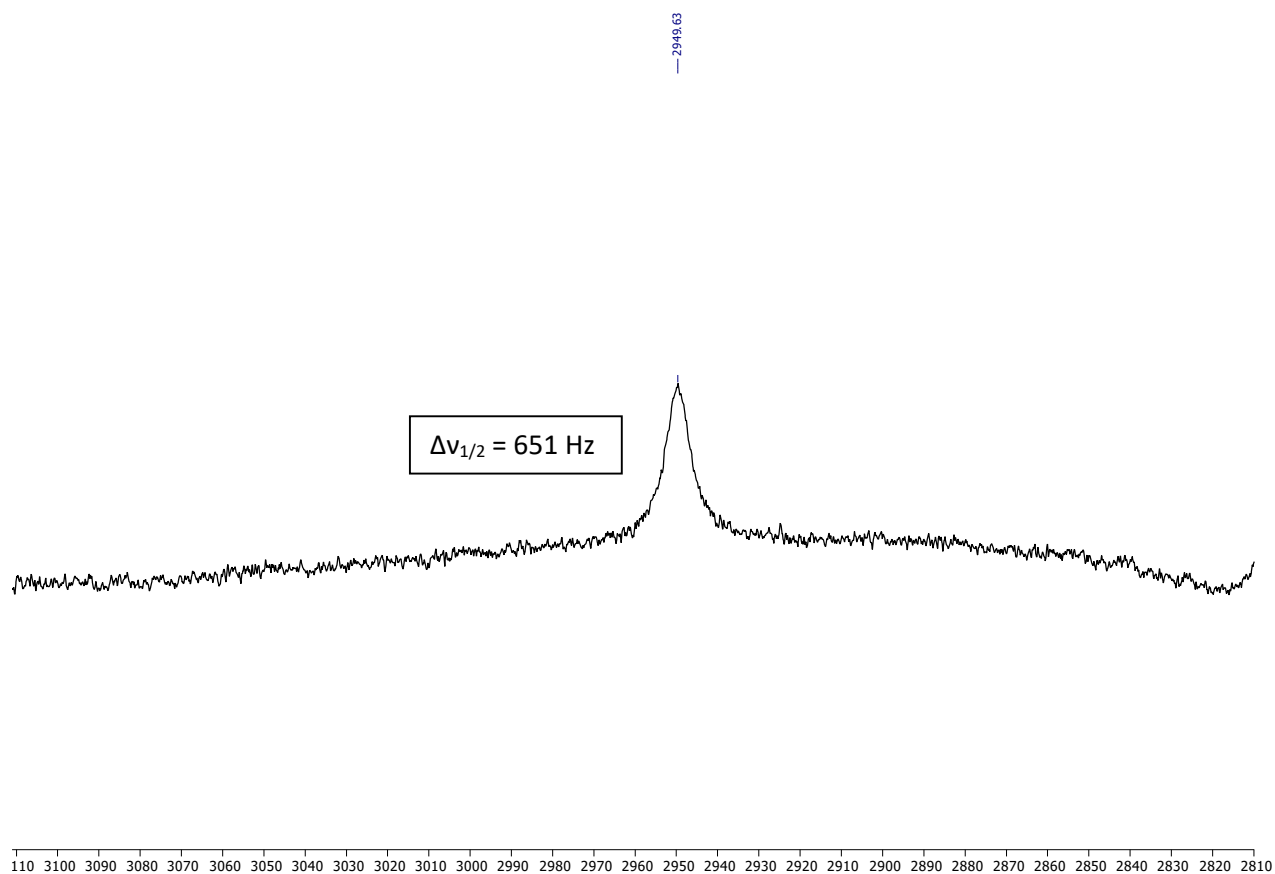


Figure S21. ^{207}Pb NMR spectrum (83.99 MHz, $[\text{D}_6]$ benzene, 300 K) of $[\{\text{Carb}^{\text{DiPP}}\}\text{PbCH}(\text{SiMe}_3)_2]$ (**6**).

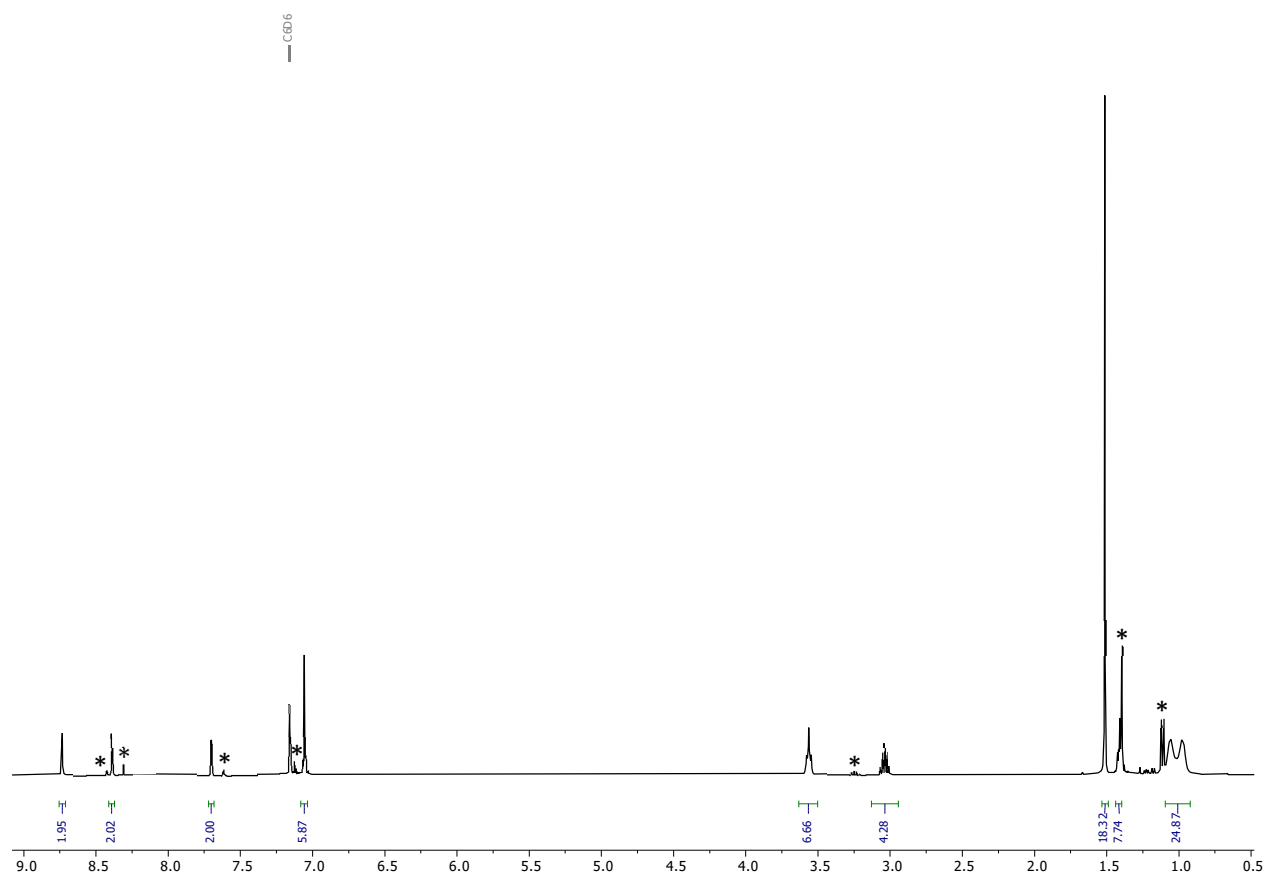


Figure S22. ^1H NMR spectrum (400.13 MHz, $[\text{D}_6]$ benzene, 302 K) of $[\{\text{Carb}^{\text{DiPP}}\}\text{Li}(\text{thf})_2]$. A small amount of the free proligand $\{\text{Carb}^{\text{DiPP}}\}\text{H}$, likely from partial hydrolysis during NMR preparation, is visible (*).

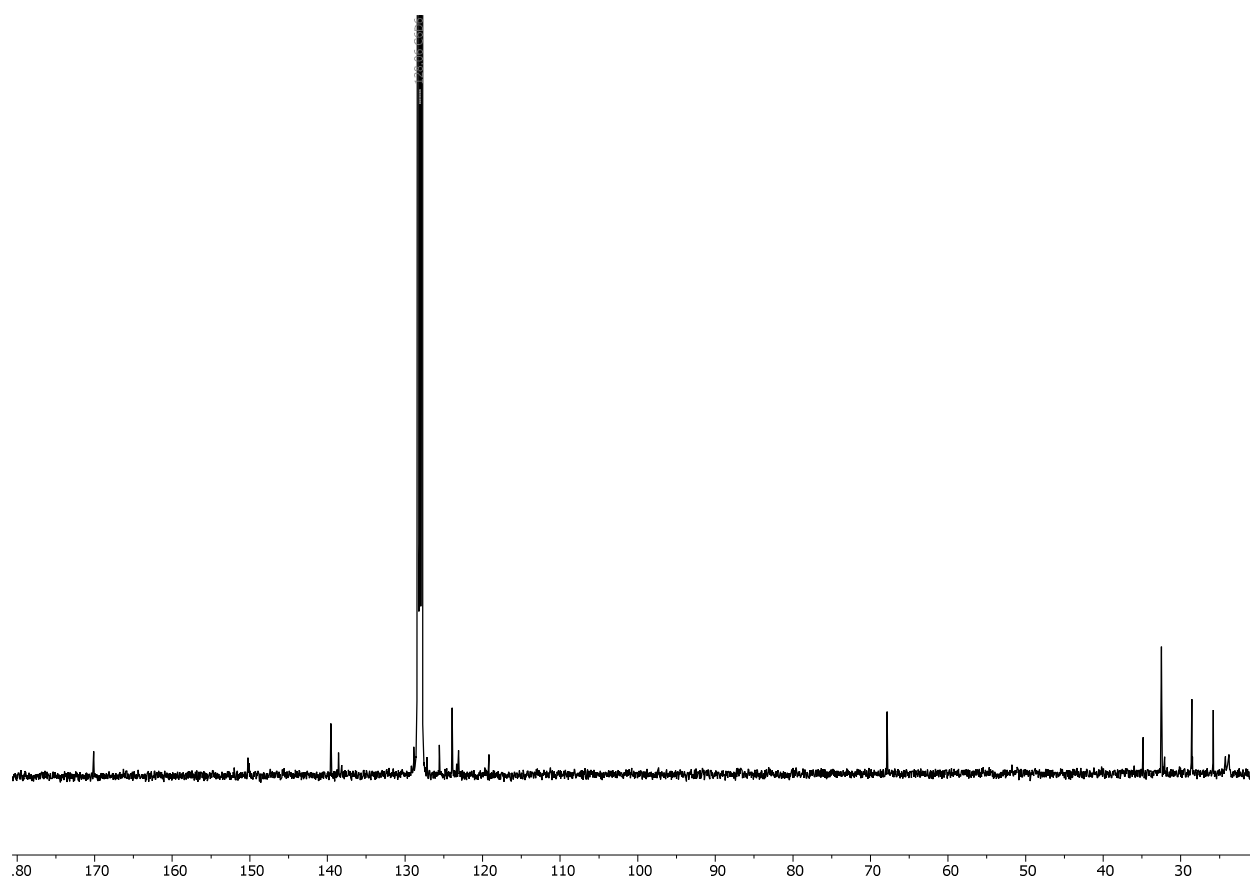


Figure S23. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (100.62 MHz, $[\text{D}_6]\text{benzene}$, 302 K) of $[\{\text{Carb}^{\text{DiPP}}\}\text{Li}(\text{thf})_2]$.

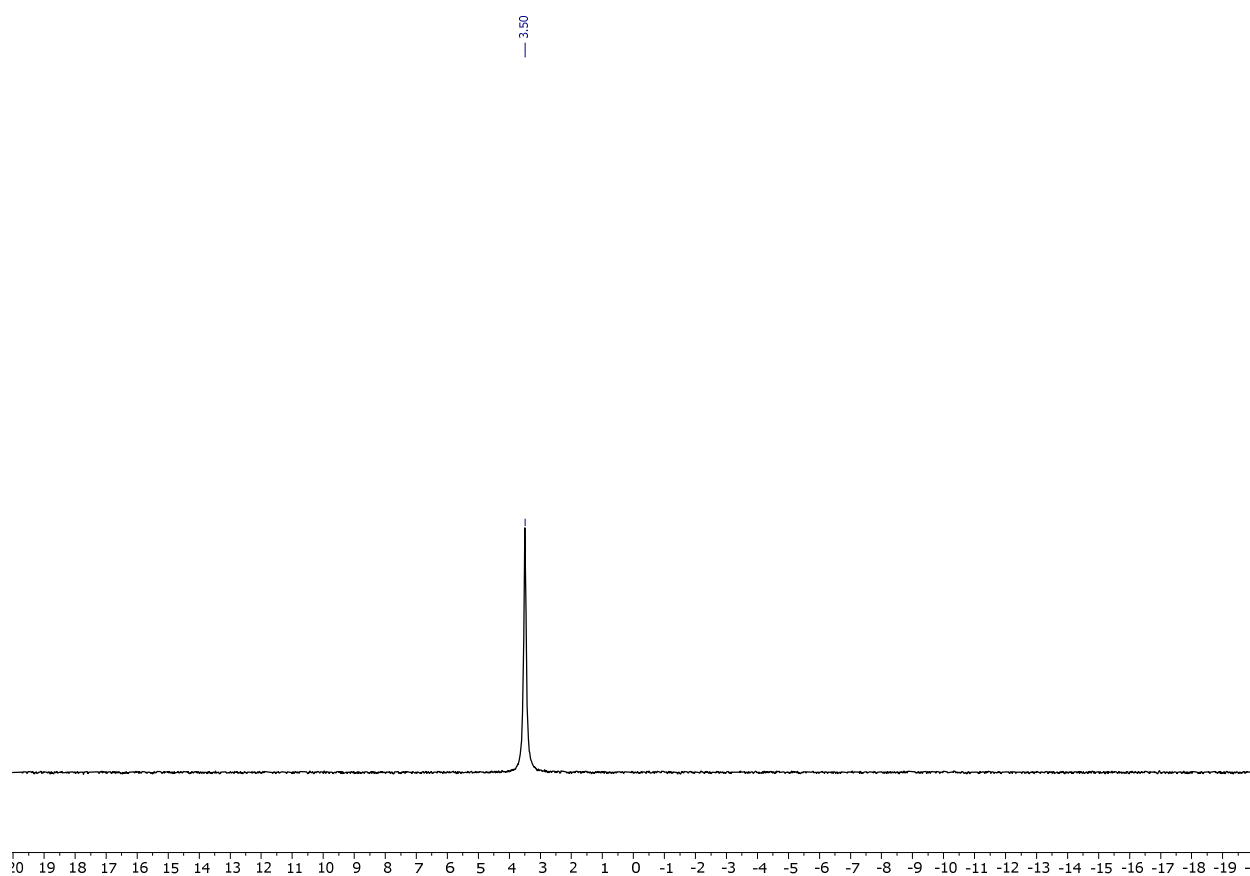


Figure S24. ^7Li NMR spectrum (155.51 MHz, $[\text{D}_6]\text{benzene}$, 302 K) of $[\{\text{Carb}^{\text{DiPP}}\}\text{Li}(\text{thf})_2]$.

Diffusion-ordered spectroscopy (DOSY) NMR measurements on complexes 1-5

All experiments were performed on a 500 MHz Bruker Avance III spectrometer using a 5 mm BBO probe at a nominal temperature of 292 K. Sample spinning was deactivated. All DOSY experiments were performed using a double stimulated echo sequence with bipolar gradient pulses with convection compensation. The following parameters were used unless otherwise stated: diffusion time = 330 ms, delay for gradient recovery = 0.2 ms, eddy current delay = 5 ms. For each DOSY-NMR experiment, a series of 16 spectra of 39 998 data points were collected over a total experiment time of 70 min. The gradient amplitude was increased in increments from 6.5 to 45.5 G cm⁻¹ for the maximum gradient strength in a linear ramp. The diffusion coefficients were measured in benzene-*d*₆. Non-deuterated toluene was employed as an internal reference. Results were analysed using External Calibration Curves (ECCs) calculated with toluene as described by Stalke and co-workers.⁴

DOSY Data processing: Data from DOSY experiments were processed using the Dynamics Center software (Bruker, Billerica, U.S.A., <https://bruker-labscape.store/collections/mr-software-1/products/dynamics-center>).

Estimation of molecular weights: The diffusion coefficients D_x measured for all the sample were converted into estimates of molecular weights $M_{W_{est}}$, using the empirical relationships derived by Stalke and co-workers.⁴

$$\log(D_{x,norm}) = \log(D_x) - \log(D_{ref}) + \log(D_{ref,fix}) \quad (1)$$

and

$$M_{W_{est}} = 10^{\frac{\log(D_{x,norm}) - \log(k)}{\alpha}} \quad (2)$$

where D_{ref} is the diffusion coefficient of an internal reference, chosen here to be the toluene, $\log(D_{ref,fix})$ is a tabulated value of the diffusion coefficient of the reference, and $\log(k)$ and α are empirical parameters determined by Stalke and co-workers by fitting a large set of diffusion data to eqn (2).⁴ Merged calibration curves were used since the molecular shape of all complexes was unknown. The samples usually had an identifiable resonance of the free ligand: {Carb^{DiPP}}H in solution.¹ This was used as an internal reference (ICC) to further access the quality of the data.⁵

Comparison between the calculated and the estimated molecular weights. The estimated molecular weights were obtained from a normalised diffusion coefficient measured in [D₆]benzene using toluene as an internal reference.⁴

	D_{toluene} (10 ¹⁰ m ² /s)	D_{complex} (10 ¹⁰ m ² /s)	calculated MW _{calc} (g/mol)	estimated MW _{det} (g/mol)	MW _{diff}
[{Carb ^{DiPP} }PbF]	14.60	4.395	879	866	2%
[{Carb ^{DiPP} }PbI]	16.20	4.550	987	1055	-6%
[{Carb ^{DiPP} }PbCl]	14.50	4.317	896	887	1%
[{Carb ^{DiPP} }PbBr]	14.37	4.330	940	901	4%
[{Carb ^{DiPP} }Pb N(SiMe ₃) ₂]	15.40	4.380	1021	1020	0%
[{Carb ^{DiPP} }PbH]	14.50	4.610	654	647	1%

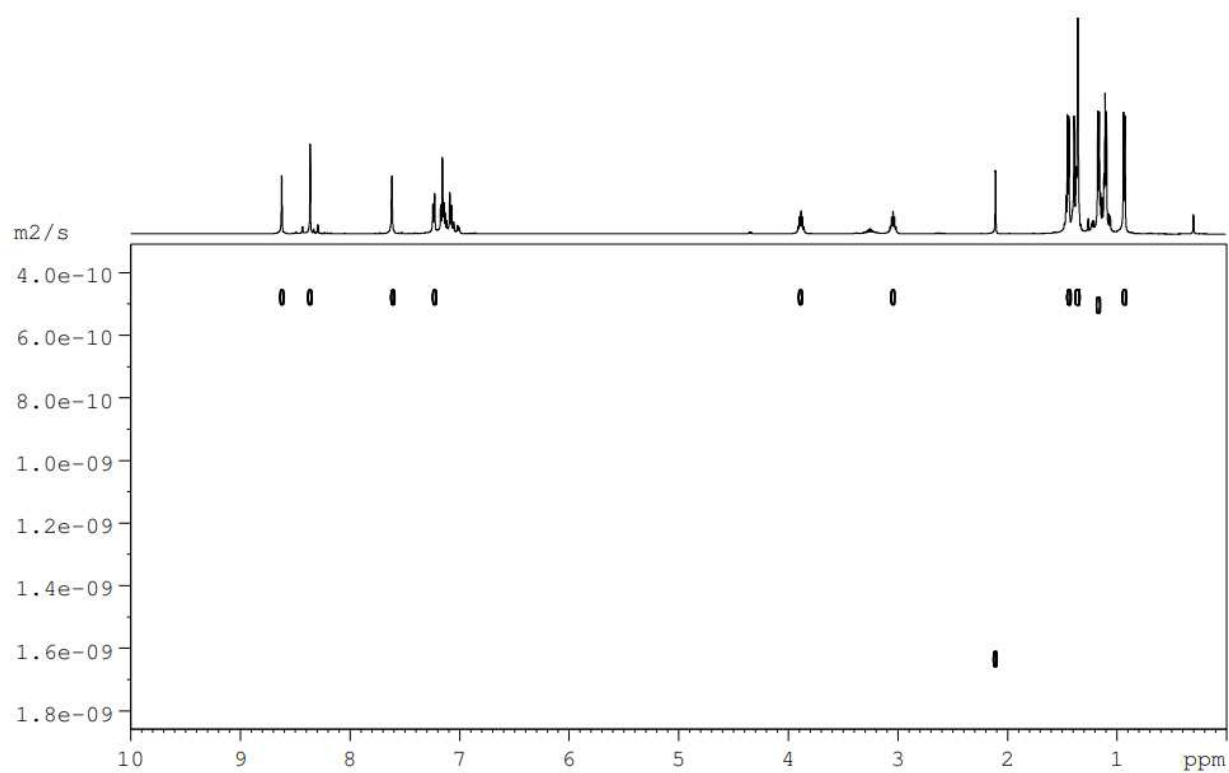


Figure S25. DOSY NMR spectrum (155.51 MHz, [D₆]benzene, 302 K) of [{Carb^{DiPP}}PbI] (**1**).

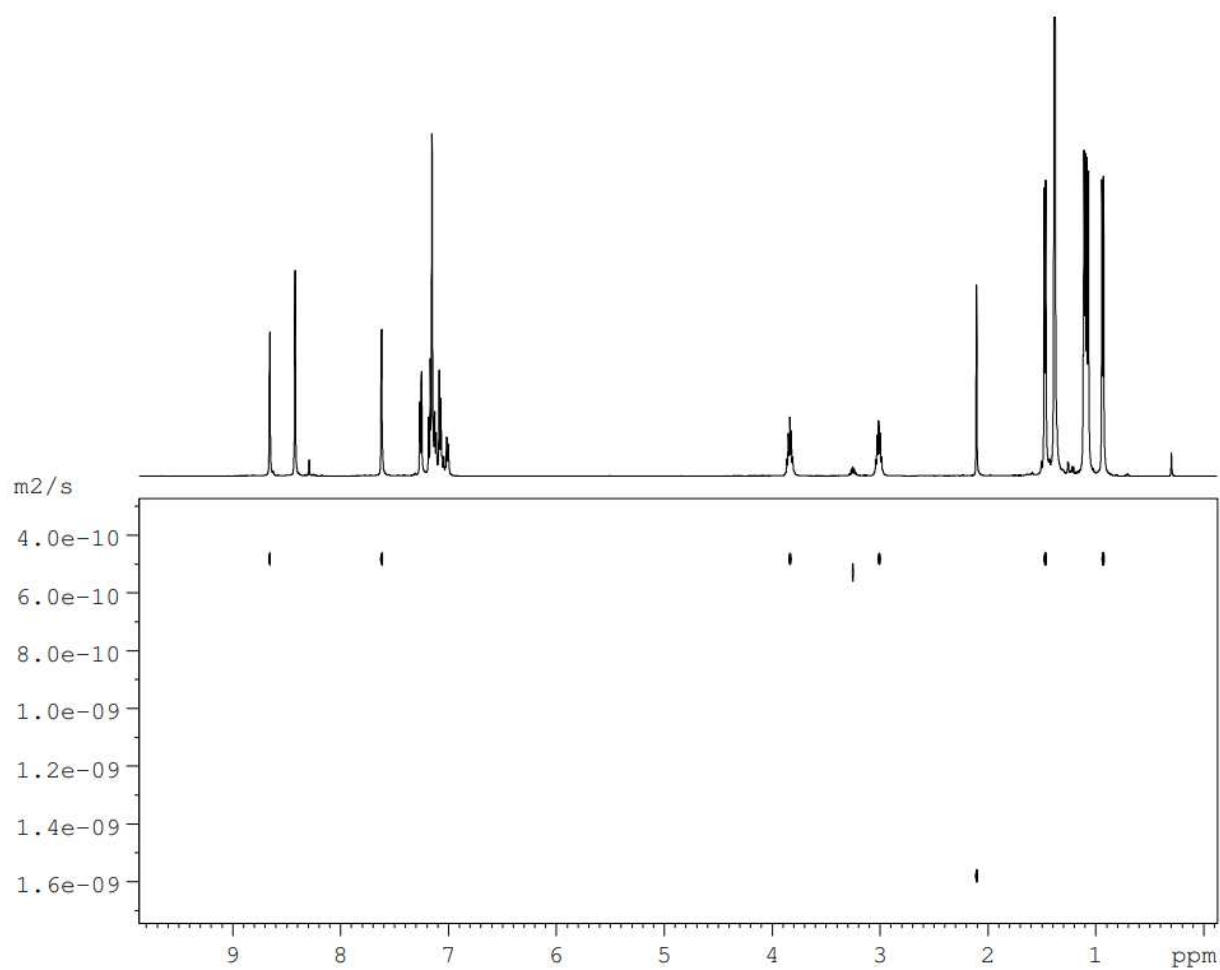


Figure S26. DOSY NMR spectrum (155.51 MHz, [D₆]benzene, 302 K) of [{Carb^{DiPP}}PbBr] (**2**).

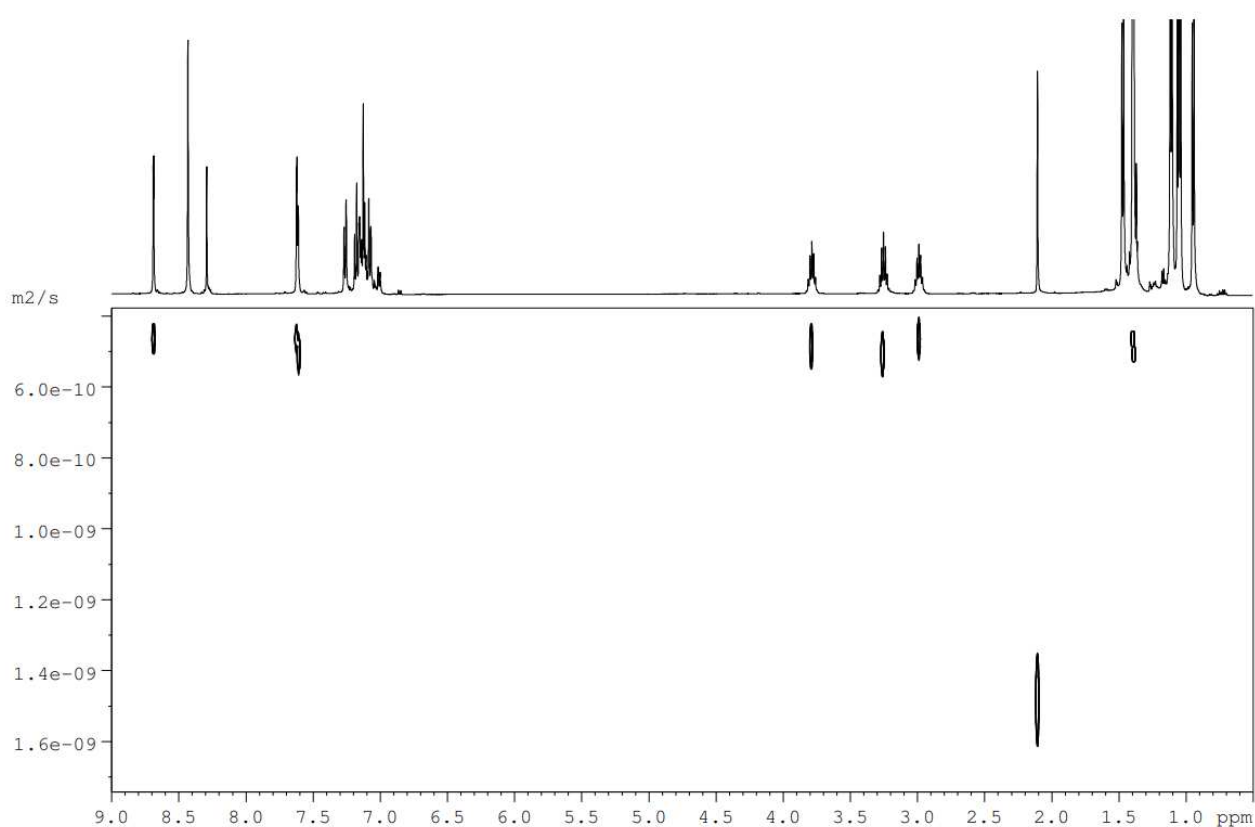


Figure S27. DOSY NMR spectrum (155.51 MHz, [D₆]benzene, 302 K) of [{Carb^{DiPP}}PbCl] (**3**).

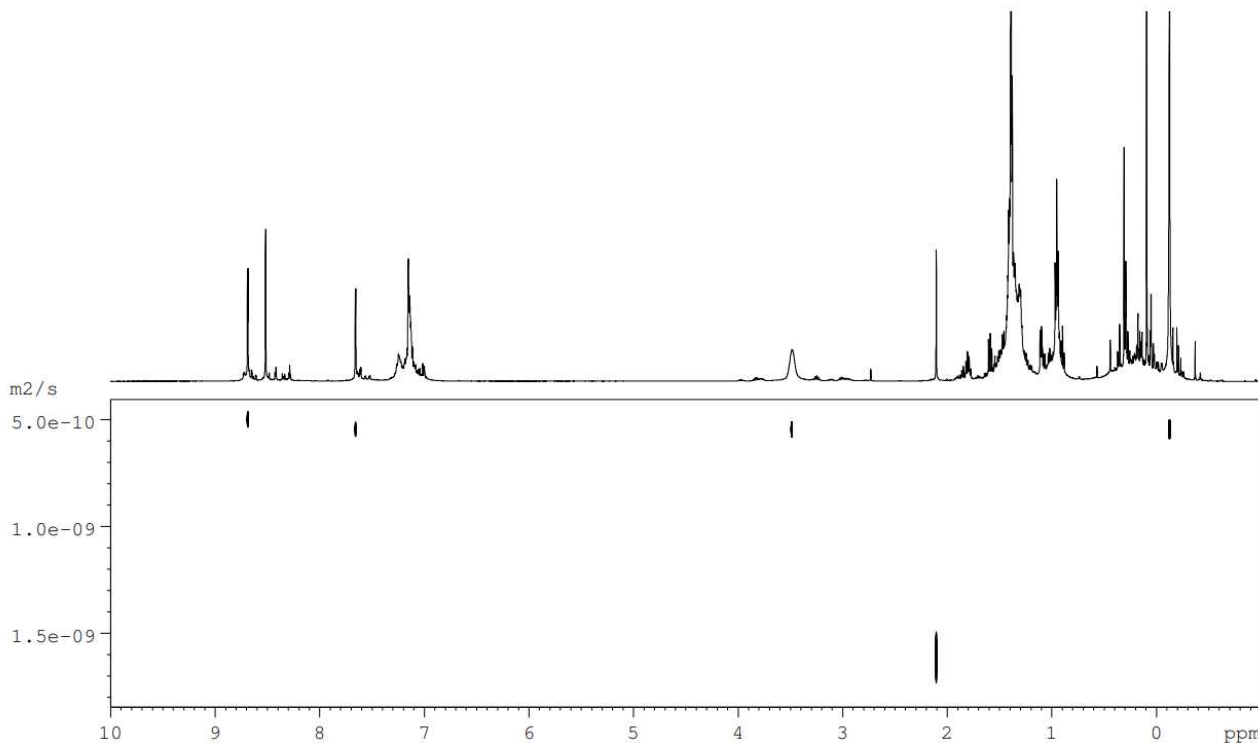


Figure S28. DOSY NMR spectrum (155.51 MHz, [D₆]benzene, 302 K) of an *in situ* generated samples of [{Carb^{DiPP}}PbN(SiMe₃)₂] (**4**). Free hexamethyldisilazane thus generated can also be observed in the spectrum.

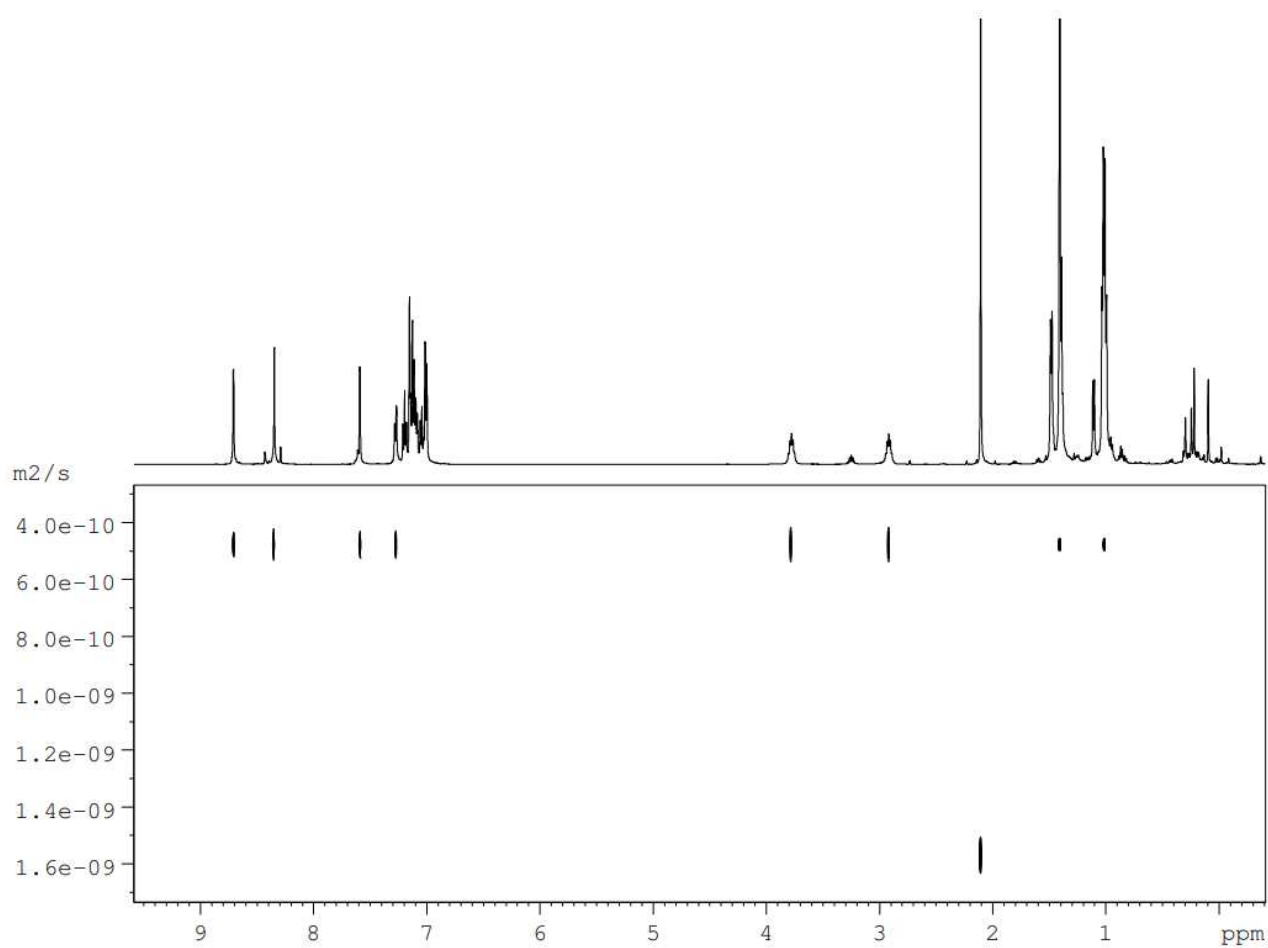


Figure S29. DOSY NMR spectrum (155.51 MHz, [D₆]benzene, 302 K) of [{Carb^{DiPP}}PbF] (**5**).

X-ray diffraction crystallography details

Compound	Complex Number	Experiment Number	CCDC Number
$[\{\text{Carb}^{\text{DiPP}}\}\text{PbI}]$	1	PC03095	2080122
$[\{\text{Carb}^{\text{DiPP}}\}\text{PbBr}]$	2	PC05026	2080123
$[\{\text{Carb}^{\text{DiPP}}\}\text{PbCl}]$	3	PC031052	2080124
$[\{\text{Carb}^{\text{DiPP}}\}\text{PbN}(\text{SiMe}_3)_2]$	4	PC0601	2080125
$[\{\text{Carb}^{\text{DiPP}}\}\text{Pb}(\mu\text{-F})_2]$	5	PC0604	2080126
$[\{\text{Carb}^{\text{DiPP}}\}\text{PbCH}(\text{SiMe}_3)_2]$	6	PC06051	2080127
$[\{\text{Carb}^{\text{DiPP}}\}\text{Li}(\text{thf})_2]$	-	PC05175	2080128

$[\{\text{Carb}^{\text{DiPP}}\}\text{PbI}]$ (1; CCDC 2080122, $\text{C}_{46}\text{H}_{58}\text{IN}_3\text{Pb}$); $M = 987.04$. D8 VENTURE Bruker AXS diffractometer equipped with a (CMOS) PHOTON 100 detector, Mo- $K\alpha$ radiation ($\lambda = 0.71073$ Å, multilayer monochromator), $T = 150$ K; monoclinic $P 2_1/c$ (I.T.#14), $a = 13.3032(15)$, $b = 14.2322(17)$, $c = 24.133(2)$ Å, $\beta = 92.876(4)^\circ$, $V = 4563.4(9)$ Å³. $Z = 4$, $d = 1.437$ g.cm⁻³, $\mu = 4.405$ mm⁻¹. The structure was solved by dual-space algorithm using the *SHELXT* program,⁶ and then refined with full-matrix least-squares methods based on F^2 (*SHELXL*).⁷ The contribution of the disordered solvents to the calculated structure factors was estimated following the *BYPASS* algorithm,⁸ implemented as the *SQUEEZE* option in *PLATON*.⁹ A new data set, free of solvent contribution, was then used in the final refinement. All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. H atoms were finally included in their calculated positions and treated as riding on their parent atom with constrained thermal parameters. A final refinement on F^2 with 10414 unique intensities and 462 parameters converged at $\omega R_F^2 = 0.0665$ ($R_F = 0.0292$) for 9244 observed reflections with $I > 2\sigma$.

$[\{\text{Carb}^{\text{DiPP}}\}\text{PbBr}]$ (2; CCDC 2080123, $\text{C}_{46}\text{H}_{58}\text{BrN}_3\text{Pb}\cdot\text{C}_7\text{H}_8$); $M = 1032.18$. A suitable crystal for X-ray diffraction single crystal experiment (yellow prism, dimensions = 0.080 x 0.070 x 0.040 mm) was selected and mounted with a cryoloop on the goniometer head of a D8 Venture diffractometer equipped with a (CMOS) PHOTON 100 detector, using Mo- $K\alpha$ radiation ($\lambda = 0.71073$ Å, multilayer monochromator) at $T = 150(2)$ K. Crystal structure has been described in monoclinic symmetry and $P 2_1/c$ (I.T.#14) centric space group. Cell parameters have been founded as follows: $a = 20.2426(19)$, $b = 10.3176(12)$, $c = 23.505(3)$ Å, $\beta = 90.646(4)^\circ$, $V = 4908.7(10)$ Å³. Number of formula unit Z is equal to 4 and calculated density d and absorption coefficient μ values are 1.397 g.cm⁻³ and 4.287 mm⁻¹ respectively. The structure was solved by dual-space algorithm using the *SHELXT* program,⁶ and then refined with full-matrix least-squares methods based on F^2 (*SHELXL* program).⁷ All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. H atoms were finally included in their calculated positions and treated as riding on their parent atom with constrained thermal parameters. A Final refinement on F^2 with 11326 unique intensities and 497 parameters converged at $\omega R_F^2 = 0.1176$ ($R_F = 0.0480$) for 9127 observed reflections with $I > 2\sigma$.

$[\{\text{Carb}^{\text{DiPP}}\}\text{PbCl}]$ (3; CCDC 2080124, $\text{C}_{46}\text{H}_{58}\text{ClN}_3\text{Pb}\cdot\text{C}_7\text{H}_8$); $M = 987.72$. A suitable crystal for X-ray diffraction single crystal experiment (yellow prism, dimensions = 0.150 x 0.060 x 0.030 mm) was selected and mounted with a cryoloop on the goniometer head of a D8 Venture diffractometer equipped with a (CMOS) PHOTON 100 detector, using Mo- $K\alpha$ radiation ($\lambda = 0.71073$ Å, multilayer monochromator) at $T = 150(2)$ K. Crystal structure has been described in monoclinic symmetry and $P 2_1/c$ (I.T.#14) centric space group. Cell parameters have been founded as follows: $a = 20.1691(19)$, $b = 10.2808(11)$, $c = 23.564(2)$ Å, $\beta = 90.349(3)^\circ$, $V = 4886.0(8)$ Å³. Number of formula unit Z is equal to 4 and calculated density d and absorption coefficient μ values are 1.343 g.cm⁻³ and 3.544 mm⁻¹ respectively. The structure was solved by dual-space algorithm using the *SHELXT* program,⁶ and then refined with full-matrix least-squares methods based on F^2 (*SHELXL* program).⁷ All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. H atoms were finally included in their calculated positions and treated as riding on their parent atom with constrained thermal parameters. A final refinement on F^2 with 11236 unique intensities and 497 parameters converged at $\omega R_F^2 = 0.1190$ ($R_F = 0.0405$) for 10142 observed reflections with $I > 2\sigma$.

[{Carb^{DIPP}}PbN(SiMe₃)₂] (4; CCDC 2080125, C₅₂H₇₆N₄PbSi₂); *M* = 1020.53. A suitable crystal for X-ray diffraction single crystal experiment (yellow plate, dimensions = 0.580 x 0.440 x 0.130 mm) was selected and mounted with a cryoloop on the goniometer head of a APEXII Kappa-CCD diffractometer equipped with a CCD plate detector, using Mo-*K*α radiation (λ = 0.71073 Å, graphite monochromator) at *T* = 150(2) K. Crystal structure has been described in triclinic symmetry and P-1 (I.T.#2) centric space group. Cell parameters have been refined as follows: *a* = 12.9223(7), *b* = 13.4651(7), *c* = 16.5207(10) Å, α = 69.747(2), β = 78.014(2), γ = 76.292(2)°, *V* = 2595.0(3) Å³. Number of formula unit *Z* is equal to 2 and calculated density *d* and absorption coefficient μ values are 1.306 g.cm⁻³ and 3.333 mm⁻¹ respectively. The structure was solved by dual-space algorithm using the SHELXT program,⁶ and then refined with full-matrix least-squares methods based on *F*² (SHELXL program).⁷ All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. H atoms were finally included in their calculated positions and treated as riding on their parent atom with constrained thermal parameters. A final refinement on *F*² with 11927 unique intensities and 552 parameters converged at $\omega R(F^2)$ = 0.0485 (*R*_F = 0.0233) for 10813 observed reflections with *I* > 2σ.

[{Carb^{DIPP}}Pb(μ-F)]₂ (5; CCDC 2080126, C₉₂H₁₁₆F₂N₆Pb₂); *M* = 1758.28. A suitable crystal for X-ray diffraction single crystal experiment (yellow board, dimensions = 0.120 x 0.030 x 0.010 mm) was selected and mounted with a cryoloop on the goniometer head of a D8 Venture diffractometer equipped with a (CMOS) PHOTON 100 detector, using Mo-*K*α radiation (λ = 0.71073 Å, multilayer monochromator) at *T* = 150(2) K. Crystal structure has been described in triclinic symmetry and P-1 (I.T.#2) centric space group. Cell parameters have been refined as follows: *a* = 13.0544(9), *b* = 13.2052(10), *c* = 13.3925(8) Å, α = 69.237(2), β = 75.073(2), γ = 75.456(3)°, *V* = 2053.0(2) Å³. Number of formula unit *Z* is equal to 1 and calculated density *d* and absorption coefficient μ values are 1.422 g.cm⁻³ and 4.148 mm⁻¹ respectively. The structure was solved by dual-space algorithm using the SHELXT program,⁶ and then refined with full-matrix least-squares methods based on *F*² (SHELXL program).⁷ All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. H atoms were finally included in their calculated positions and treated as riding on their parent atom with constrained thermal parameters. A final refinement on *F*² with 9392 unique intensities and 474 parameters converged at $\omega R(F^2)$ = 0.0524 (*R*_F = 0.0258) for 8578 observed reflections with *I* > 2σ.

[{Carb^{DIPP}}PbCH(SiMe₃)₂] (6; CCDC 2080127, C₅₃H₇₇N₃PbSi₂); *M* = 1019.54. A suitable crystal for X-ray diffraction single crystal experiment (orange prism, dimensions = 0.270 x 0.200 x 0.110 mm) was selected and mounted with a cryoloop on the goniometer head of a APEXII Kappa-CCD (Bruker-AXS) diffractometer equipped with a CCD plate detector, using Mo-*K*α radiation (λ = 0.71073 Å, graphite monochromator) at *T* = 150(2) K. Crystal structure has been described in triclinic symmetry and P-1 (I.T.#2) centric space group. Cell parameters have been refined as follows: *a* = 12.863(4), *b* = 13.581(5), *c* = 16.539(6) Å, α = 70.105(11), β = 79.200(12), γ = 76.778(9)°, *V* = 2625.9(15) Å³. Number of formula unit *Z* is equal to 2 and calculated density *d* and absorption coefficient μ values are 1.289 g.cm⁻³ and 3.293 mm⁻¹ respectively. The structure was solved by dual-space algorithm using the SHELXT program,⁶ and then refined with full-matrix least-squares methods based on *F*² (SHELXL program).⁷ All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. H atoms were finally included in their calculated positions and treated as riding on their parent atom with constrained thermal parameters. A final refinement on *F*² with 11957 unique intensities and 509 parameters converged at $\omega R(F^2)$ = 0.1012 (*R*_F = 0.0471) for 9780 observed reflections with *I* > 2σ.

[{Carb^{DIPP}}Li.(thf)]₂ (CCDC 2080128, C₅₄H₇₄LiN₃O₂); *M* = 804.10. A suitable crystal for X-ray diffraction single crystal experiment (yellow prism, dimensions = 0.400 x 0.330 x 0.220 mm) was selected and mounted with a cryoloop on the goniometer head of a APEXII Kappa-CCD diffractometer equipped with a CCD plate detector, using Mo-*K*α radiation (λ = 0.71073 Å, graphite monochromator) at *T* = 150(2) K. Crystal structure has been described in monoclinic symmetry and P 2₁/c (I.T.#14) centric space group. Cell parameters have been refined as follows: *a* = 29.934(4), *b* = 13.3039(13), *c* = 25.126(3) Å, β = 103.517(4)°, *V* = 9729.3(19) Å³. Number of formula unit *Z* is equal to 8 and calculated density *d* and absorption coefficient μ values are 1.098 g.cm⁻³ and 0.065 mm⁻¹ respectively. The structure was solved by dual-space algorithm using the SHELXT

program,⁶ and then refined with full-matrix least-squares methods based on F^2 (SHELXL program).⁷ All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. H atoms were finally included in their calculated positions and treated as riding on their parent atom with constrained thermal parameters. A final refinement on F^2 with 22154 unique intensities and 1104 parameters converged at $\omega R(F^2) = 0.1956$ ($R_F = 0.0803$) for 10579 observed reflections with $I > 2\sigma$.

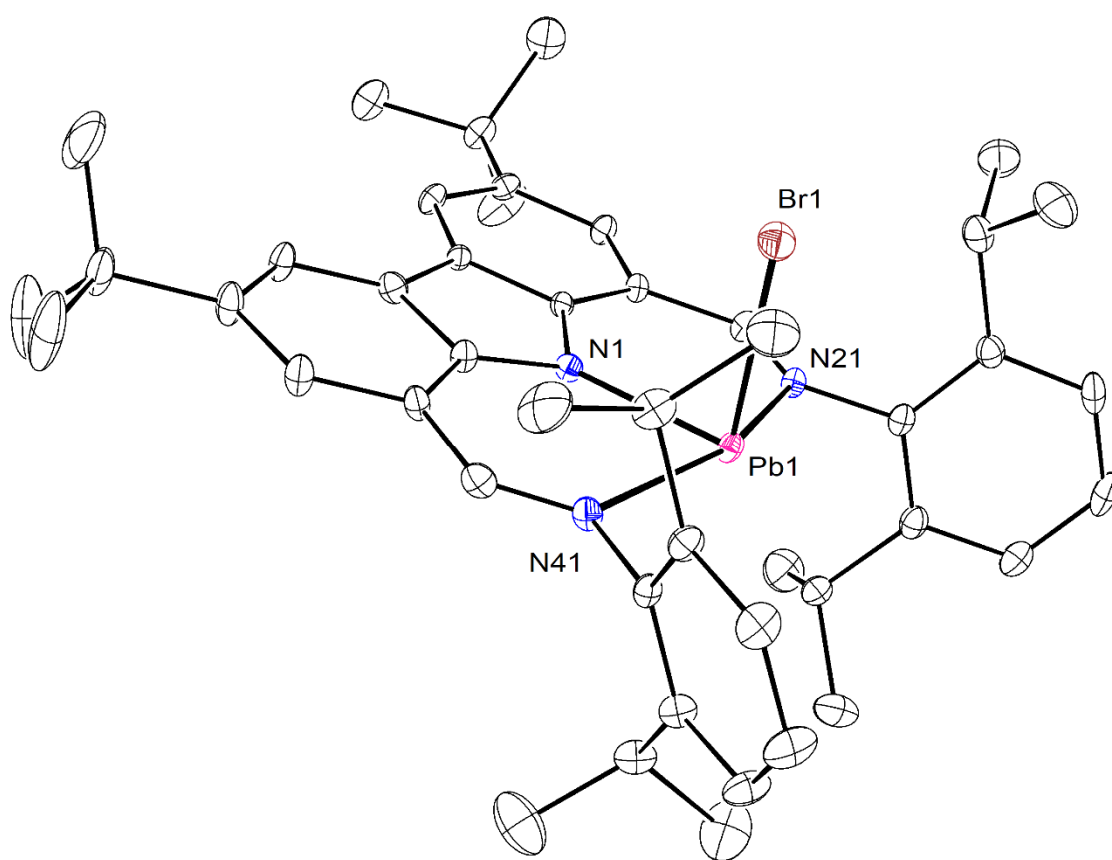


Figure S30: ORTEP representation of the molecular solid-state structure of $[\{\text{Carb}^{\text{DiPP}}\}\text{PbBr}]$ (**2**). Ellipsoids at the 30% probability level. Hydrogen atoms omitted for clarity. Non-coordinating toluene molecule present in the crystals lattice omitted for clarity. Selected bond lengths (Å) and angles (°): Pb1-Br1, 2.6925(7); Pb1-N1, 2.278(4); Pb1-N21, 2.535(5); Pb1-N41, 2.511(4); N1-Pb1-N21, 79.70(14); N1-Pb1-N41, 80.48(15); N21-Pb1-N41, 158.45(14); N1-Pb1-Br1, 87.71(11); Pb1-N1N41N21 plane, 0.227(4).

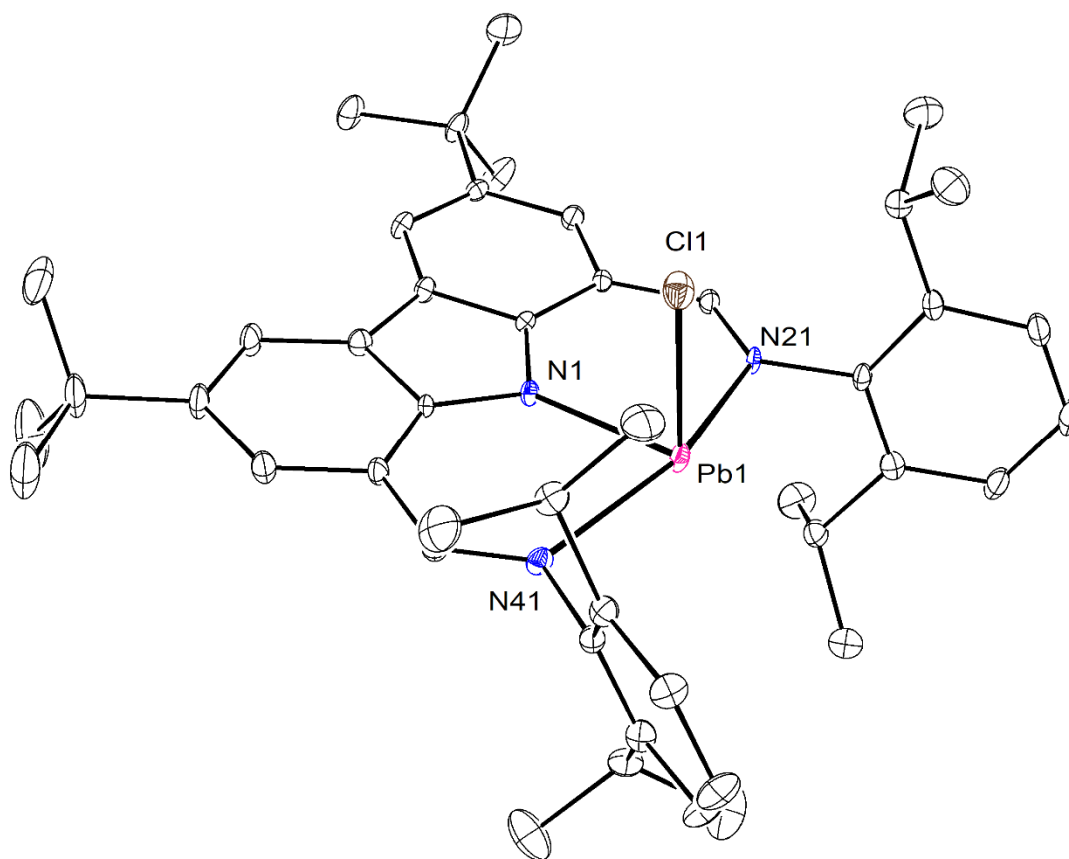


Figure S31: ORTEP representation of the molecular solid-state structure of $[\{\text{Carb}^{\text{DiPP}}\}\text{PbCl}]$ (**3**). Ellipsoids at the 30% probability level. Hydrogen atoms omitted for clarity. Non-coordinating toluene molecule present in the crystals lattice omitted for clarity. Selected bond lengths (Å) and angles (°): Pb1-Cl1, 2.5631(13); Pb1-N1, 2.292(3); Pb1-N21, 2.543(4); Pb1-N41, 2.510(4); N1-Pb1-N21, 79.29(12); N1-Pb1-N41, 80.81(12); N21-Pb1-N41, 158.18(12); N1-Pb1-Cl1, 88.05(10); Pb1-N1N41N21 plane, 0.240(4).

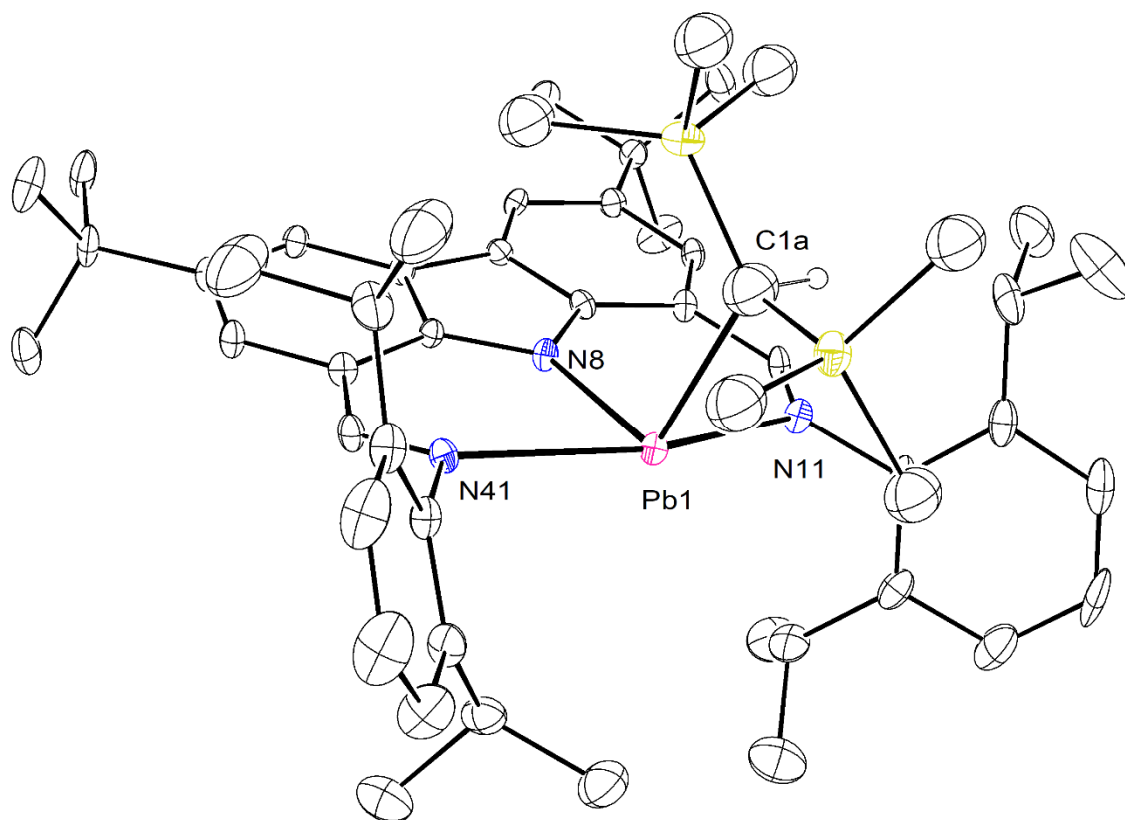


Figure S32: ORTEP representation of the molecular solid-state structure of $[\{\text{Carb}^{\text{DiPP}}\}\text{PbCH}(\text{SiMe}_3)_2]$ (**6**) (Ellipsoids at the 30% probability level. Hydrogen atoms omitted for clarity. The alkyl ligand was modeled over two positions, of which only the major component is shown. Selected bond lengths (Å) and angles (°): Pb1-C1a, 2.36(2); Pb1-N8, 2.344(4); Pb1-N11, 2.623(4); Pb1-N41, 2.652(4); N8-Pb1-C1a, 101.2(5); N8-Pb1-N11, 78.73(13); C1a-Pb1-N11, 84.9(5); N8-Pb1-N41, 80.22(13); N11-Pb1-N41, 158.63(13); Pb1-N8N41N11 plane, 0.105(5).

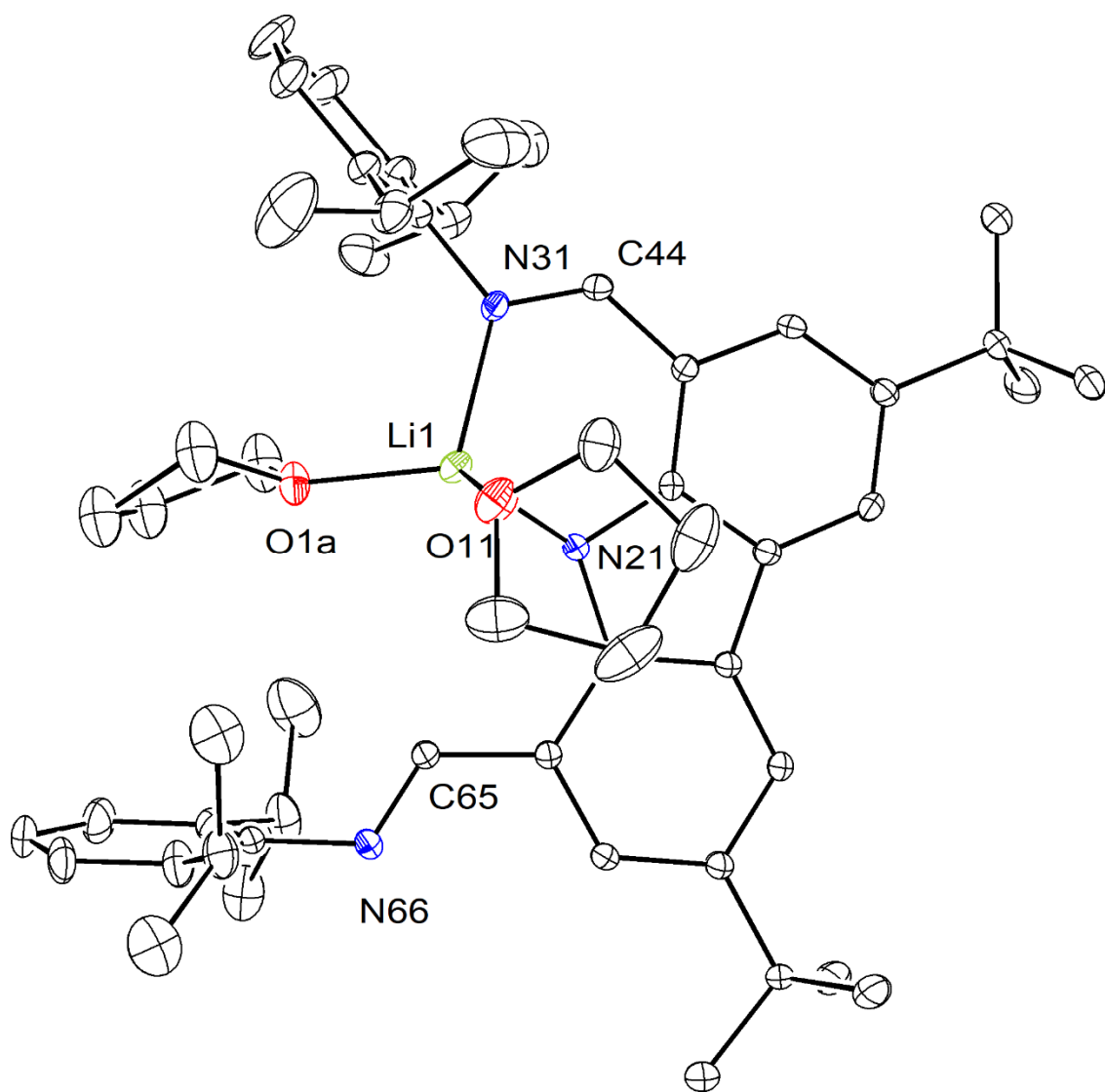


Figure S33: ORTEP representation of $[\{\text{Carb}^{\text{Dipp}}\}\text{Li}(\text{thf})_2]$. Only one molecule of the asymmetric unit cell shown. Hydrogen atoms and disorder on one *t*Bu group omitted for clarity. 30% probability ellipsoids. Selected bond lengths (Å) and angles (°): Li1-N21, 1.965(5); Li1-N31, 2.083(6); Li1-O1a, 1.946(6); Li1-O11, 2.036(6); N21-Li1-N31, 98.3(2); N21-Li1-O1a, 127.5(3); N21-Li1-O11, 100.2(3); O1a-Li1-O11, 110.0(3); N31-Li1-O11, 114.9(2).

Details for steric maps and buried volume (% V_{Bur}) calculations

Buried volume calculations were carried out on the complexes, **1**, **2** and **3**, as well as on their $\{\text{BDI}^{\text{Dipp}}\}$ -equivalents; $[\{\text{BDI}^{\text{Dipp}}\}\text{PbI}]$,¹⁰ $[\{\text{BDI}^{\text{Dipp}}\}\text{PbBr}]$ ¹⁰ and $[\{\text{BDI}^{\text{Dipp}}\}\text{PbCl}]$.¹⁰ using the SambVca 2.1 platform¹¹ from their respective crystal structure geometries. The required .cif files were downloaded from the CCDC¹² and converted to .xyz files. The following parameters were used for the calculations: $R = 3.5$ Å, scaled Bondi radii (1.17),¹³ mesh spacing (s) = 0.05 Å, calculations were run including hydrogen atoms. The topographic maps are a visual representation of the surface $S(x,y) = z_B$ of the filled voxels in the first coordination sphere, and have been described accurately in the literature by the programs authors.¹¹

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Author contributions

P. M. Chapple performed synthetic experimental work and data analysis, and assisted in writing of the draft. T. Roisnel performed the XRD analyses. J.-F. Carpentier participated to analysis of experimental data. H. Oulyadi and G. Hamdoun performed high-resolution and DOSY NMR analyses and carried out the analysis of the diffusion data and the determination of the molecular weights. Y. Sarazin was the lead investigator; he participated to the design of experiments, analysis of experimental data and writing of the draft.