Electronic Supporting Information for

Aminofluoroalkoxide amido and boryloxo lead(II) complexes

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Experimental section

General procedures

All manipulations were performed under an inert atmosphere using standard Schlenk techniques or in a dry, solvent-free glovebox (Jacomex; $O_2 < 1$ ppm, $H_2O < 5$ ppm). $[Pb[N(SiMe_3)_2]_2]$[1] was prepared following literature protocol. Solvents (THF, Et_2O, pentane, and toluene) were purified and dried (water contents below 8 ppm) over columns of alumina (MBraun SPS). THF was further distilled under argon from sodium mirror/benzophenone ketyl. All deuterated solvents (Eurisotop, Saclay, France) were stored in sealed ampules over activated 3 Å molecular sieves and were thoroughly degassed by several freeze-thaw vacuum cycles.

NMR spectra were recorded on Bruker AM-400 or AM-500 spectrometers. All ^1H and $^{13}C\{^1H\}$ chemical shifts (reported in ppm) were determined using residual signals of the deuterated solvents and were calibrated vs $SiMe_4$. Assignment of the signals was carried out using 1D (^1H, $^{13}C\{^1H\}$) and 2D (COSY, HMBC, HSQC) NMR experiments. ^{207}Pb NMR spectra were referenced against a solution of $[Pb[N(SiMe_3)_2]_2]$ in benzene-d_6 ($\delta^{207}Pb = 4916$ ppm at 298 K). ^{29}Si NMR spectra were referenced against $SiMe_4$. ^{19}F chemical shifts were determined by external reference to an aqueous solution of $NaBF_4$. Melting points were measured in sealed glass capillaries loaded with ca. 3-5 mg of the complex.

Synthesis of 2-$Et_2NCH_2C(CF_3)_2OH$ ({RO^F}H)

Diethylamine (0.58 g, 7.93 mmol) and 2,2-bis(trifluoromethyl)oxirane (1.42 g, 7.88 mmol) were reacted in refluxing diethyl ether (20 mL) for 12 h. The volatiles were then removed under vacuum to afford {RO^F}H as an analytically pure colourless oil. Isolated yield 1.79 g (90%).

^{1}H NMR (benzene-d_6, 298 K, 300.13 MHz): δ = 6.67 (br s, 1H, OH), 2.52 (s, 2H, $CH_2C(CF_3)_2$), 2.11 (q, 4H, $^3J_{HH}$ = 7.2 Hz, NCH_2CH_3), 0.52 (t, 6H, $^3J_{HH}$ = 7.2 Hz, NCH_2CH_3) ppm.

^{13}C{^{1}H} NMR (benzene-d_6, 298 K, 75.48 MHz): δ = 124.41 (q, $^1J_{CF}$ = 289 Hz, CF_3), 71.84 (hept, $^2J_{CF}$ = 29 Hz, $C(CF_3)_2$), 51.26 ($CH_2C(CF_3)_2$), 47.51 (NCH_2CH_3), 11.21 (CH_3) ppm.

^{19}F{^{1}H} NMR (benzene-d_6, 298 K, 376.47 MHz): δ = –77.78 (s) ppm

Elemental analysis for $C_8H_{13}F_6NO$: theo, C, 37.95; H, 5.18; N, 5.53; found, C, 37.9; H, 5.2; N, 5.7.

ESI-MS: $[M+Na]^+$ $C_8H_{13}F_6NONa$, m/z theo 276.07395, found 276.0793 (0 ppm).

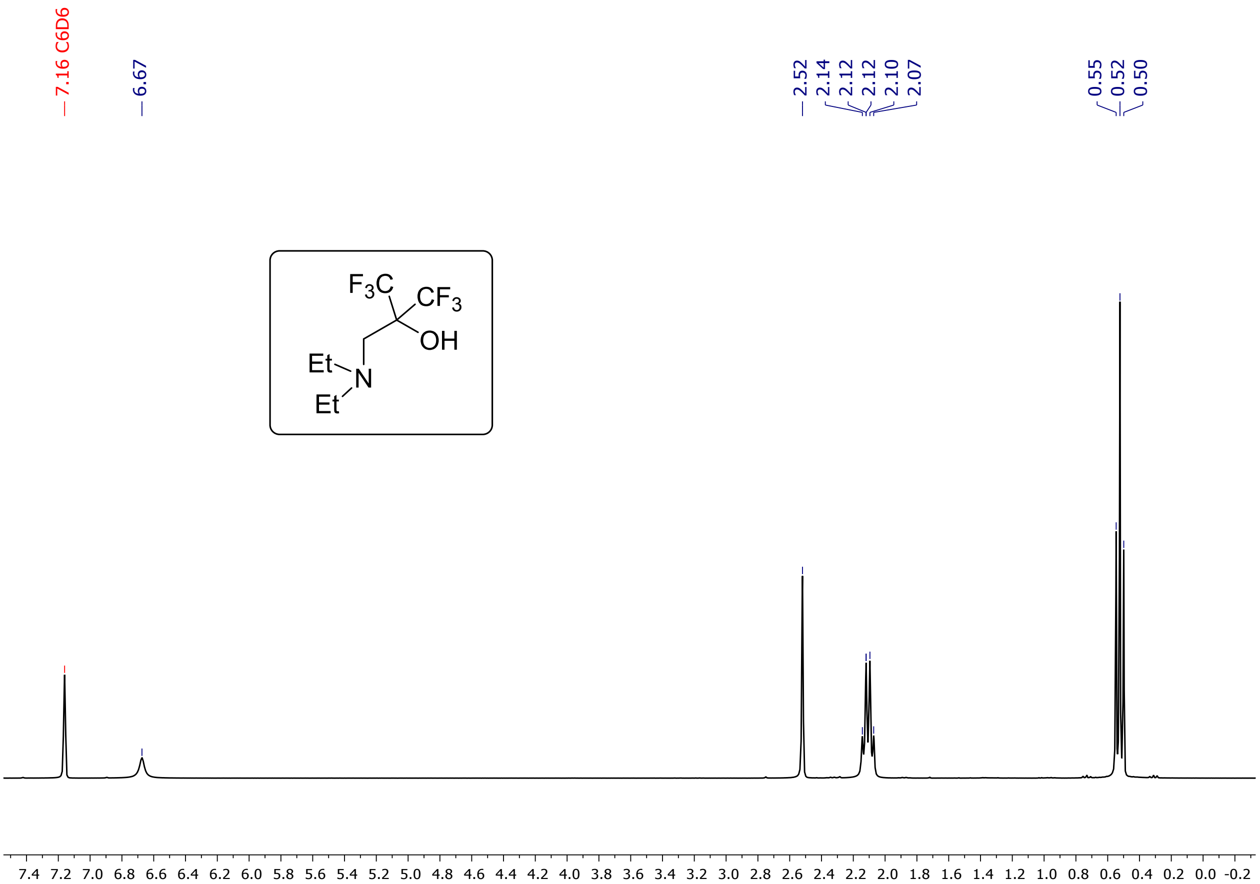

Figure S1. ^{1}H NMR spectrum (benzene-d_6, 298 K, 300.13 MHz) of {RO^F}H.

Synthesis of $[\{RO^F\}PbN(SiMe_3)_2]$ (1)

A solution of $\{RO^F\}H$ (0.70 g, 2.78 mmol) in Et_2O (15 mL) was added dropwise to a solution of $[Pb\{N(SiMe_3)_2\}_2]$ (1.47 g, 2.78 mmol) in Et_2O (18 mL). The reaction mixture was stirred at room temperature for 1 h and all the volatiles were then removed under vacuum. The title compound was obtained as a pale yellow solid (1.35 g, 78%) with good solubility in: diethyl ether, petroleum ether, benzene and toluene. Colourless monocrystals suitable for X-ray analysis were grown from a concentrated Et_2O solution stored at –43 °C.
M. p. = 83 °C.

^1H NMR (benzene-d_6, 400.13 MHz, 298 K): δ = 2.74 (s, 2H, $CH_2C(CF_3)_2$), 2.59 (m, 2H, NCH_2CH_3), 2.49 (m, 2H, CH_2CH_3), 0.53 (t, 6H, $^3J_{HH}$ = 7.2 Hz, CH_2CH_3), 0.32 (s, 18H, $SiCH_3$) ppm.

$^{13}C\{^1H\}$ NMR (benzene-d_6, 125.77 MHz, 300 K): δ = 128.00 (q, $^1J_{CF}$ = 292 Hz, CF_3), 83.98 (hept, $^2J_{CF}$ = 28 Hz, $C(CF_3)_2$), 51.88 ($CH_2C(CF_3)_2$), 48.16 (CH_2CH_3), 9.54 (CH_2CH_3), 5.89 ($SiCH_3$) ppm.

$^{19}F\{^1H\}$ NMR (benzene-d_6, 376.47 MHz, 298K): δ = –76.65 (s, $^4J_{PbF}$ = 161 Hz) ppm.

$^{29}Si\{^1H\}$ NMR (C_6D_6, 79.49 MHz, 298K): δ = –3.64 (s) ppm.

$^{207}Pb\{^1H\}$ NMR (benzene-d_6, 83.93 MHz, 298 K): δ = 2619 ppm.

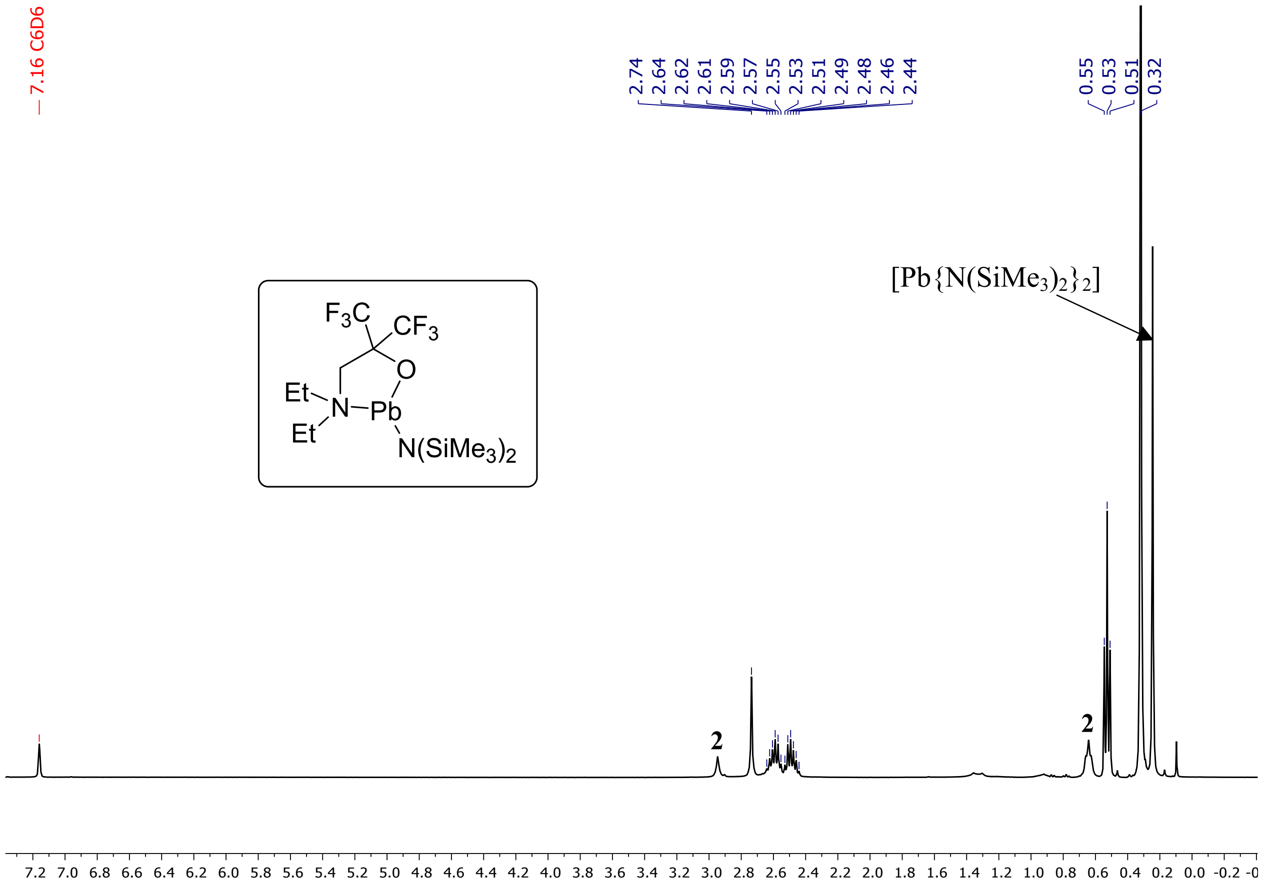

Figure S2. ^{1}H NMR spectrum (benzene-d_6, 298 K, 300.13 MHz) of [{RO^F}PbN(SiMe$_3$)$_2$] (**1**). Resonances at 2.95 and 0.64 ppm ([Pb{RO^F}$_2$], aka **2**) and 0.24 ppm ([Pb{N(SiMe$_3$)$_2$}$_2$]) indicate limited ligand redistribution in solution.

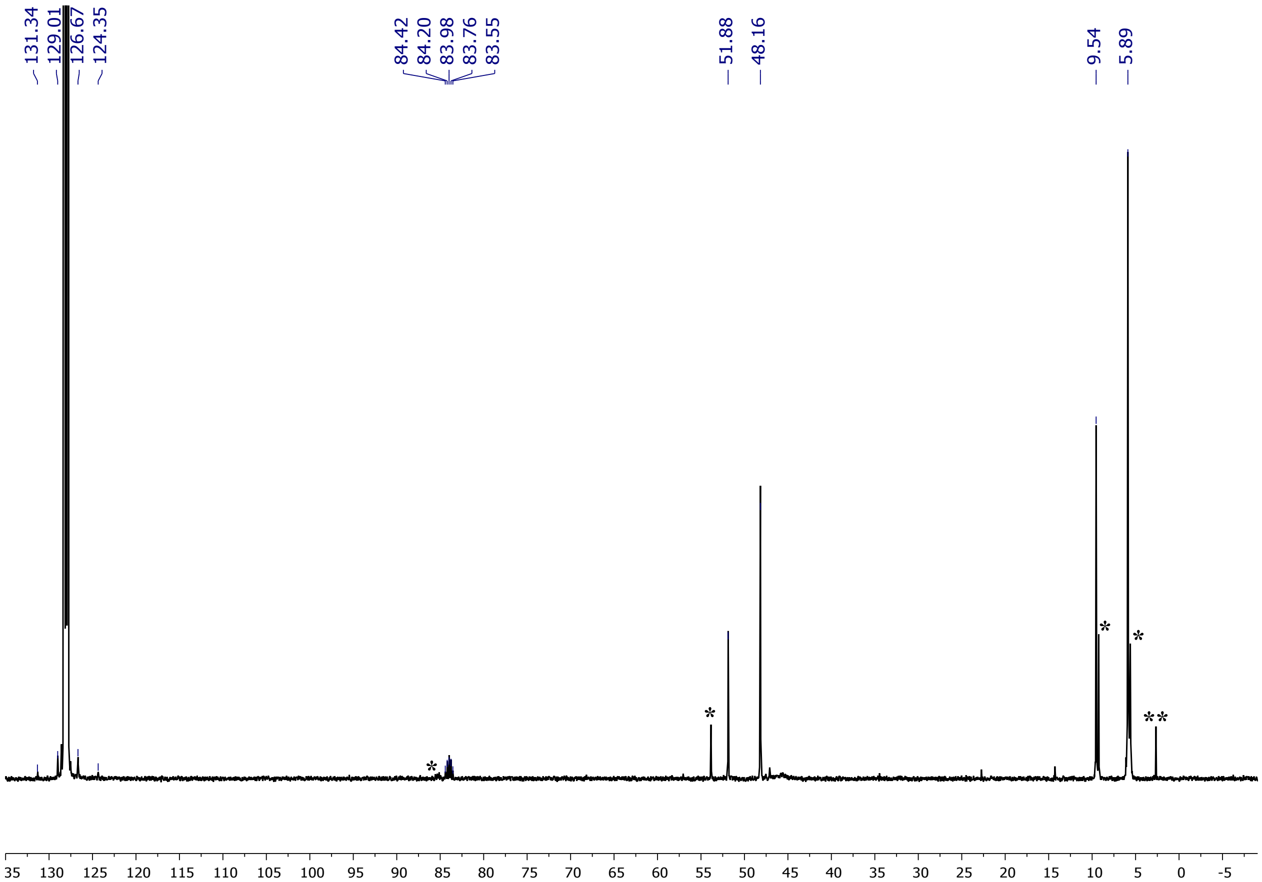

Figure S3. $^{13}C\{^1H\}$ NMR spectrum (benzene-d_6, 298 K, 125.77 MHz) of $[\{RO^F\}PbN(SiMe_3)_2]$ (**1**). Resonances for $[Pb\{RO^F\}_2]$ (**2**) and $[Pb\{N(SiMe_3)_2\}_2]$ indicated by * and **, respectively.

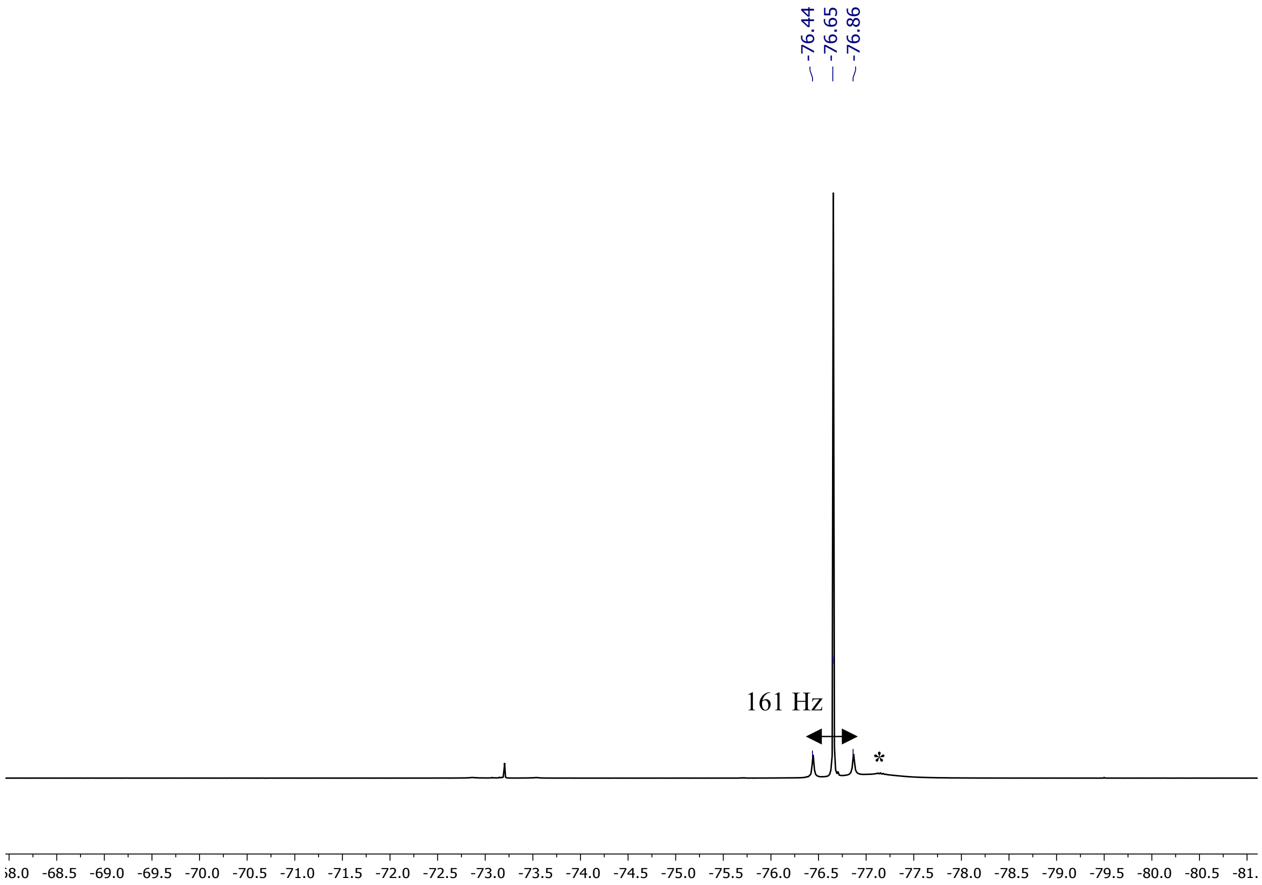

Figure S4. $^{19}F\{^1H\}$ NMR spectrum (benzene-d_6, 298 K, 376.47 MHz) of [{RO^F}PbN(SiMe$_3$)$_2$] (**1**). Resonances for [Pb{RO^F}$_2$] (**2**) indicated by *.

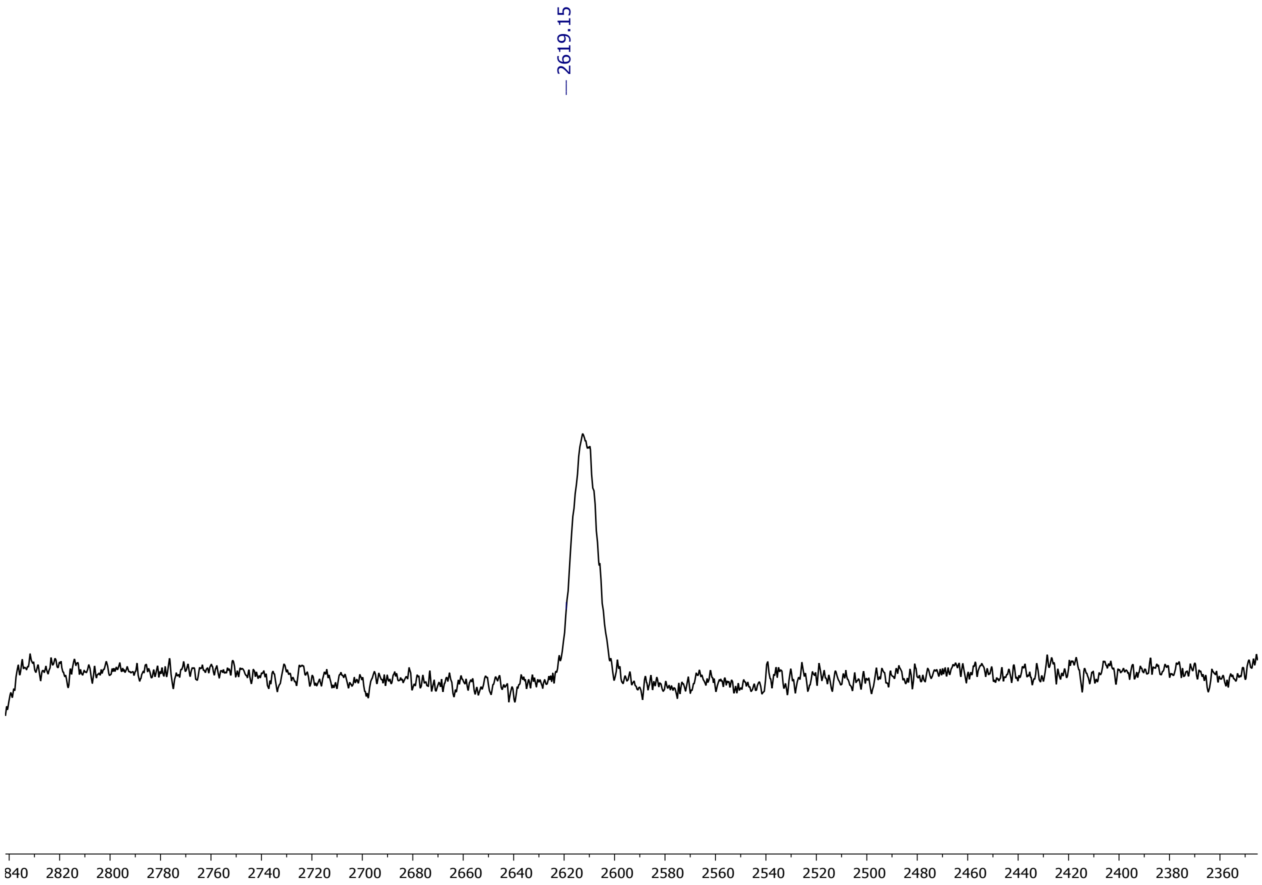

Figure S5. ^{207}Pb{^{1}H} NMR spectrum (benzene-d_6, 298 K, 83.93 MHz) of [{RO^F}PbN(SiMe$_3$)$_2$] (**1**).

Synthesis of [Pb{RO^F}$_2$] (2)

A solution of {RO^F}H (0.36 g, 1.43 mmol) in Et$_2$O (10 mL) was added dropwise to a solution of [Pb{N(SiMe$_3$)$_2$}$_2$] (0.38 g, 0.72 mmol) in Et$_2$O (10 mL). The reaction mixture was stirred at room temperature for 2 h and all the volatiles were then removed under vacuum. The title compound was obtained as a white solid with good solubility in: diethyl ether, petroleum ether, benzene and toluene (0.49 g, 97%). Colourless monocrystals suitable for XRD analysis were grown from a concentrated petroleum ether solution stored at –43 °C.

^{1}H NMR (benzene-d_6, 400.16 MHz, 298 K): δ = 2.95 (s, 4H, CH_2C(CF$_3$)$_2$), 2.62 (br s, 8H, CH_2CH$_3$), 0.65 (t, 12H, $^3J_{HH}$ = 6.7 Hz, NCH$_2$CH_3) ppm.

^{13}C{^{1}H} NMR (benzene-d_6, 100.63 MHz, 300 K): δ = 128.02 (q, $^1J_{CF}$ = 290 Hz, CF$_3$), 85.35 (hept, $^2J_{F\text{-}C}$ = 27 Hz, C(CF$_3$)$_2$), 53.85 (CH$_2$C(CF$_3$)$_2$), 45.70 (br, CH$_2$CH$_3$), 9.23 (CH$_2$$CH_3$) ppm.

^{19}F{^{1}H} NMR (benzene-d_6, 376.47 MHz, 298K): δ = –77.09 (br s) ppm.

^{207}Pb{^{1}H} NMR (benzene-d_6, 83.81 MHz, 298 K): δ = 1187 ppm.

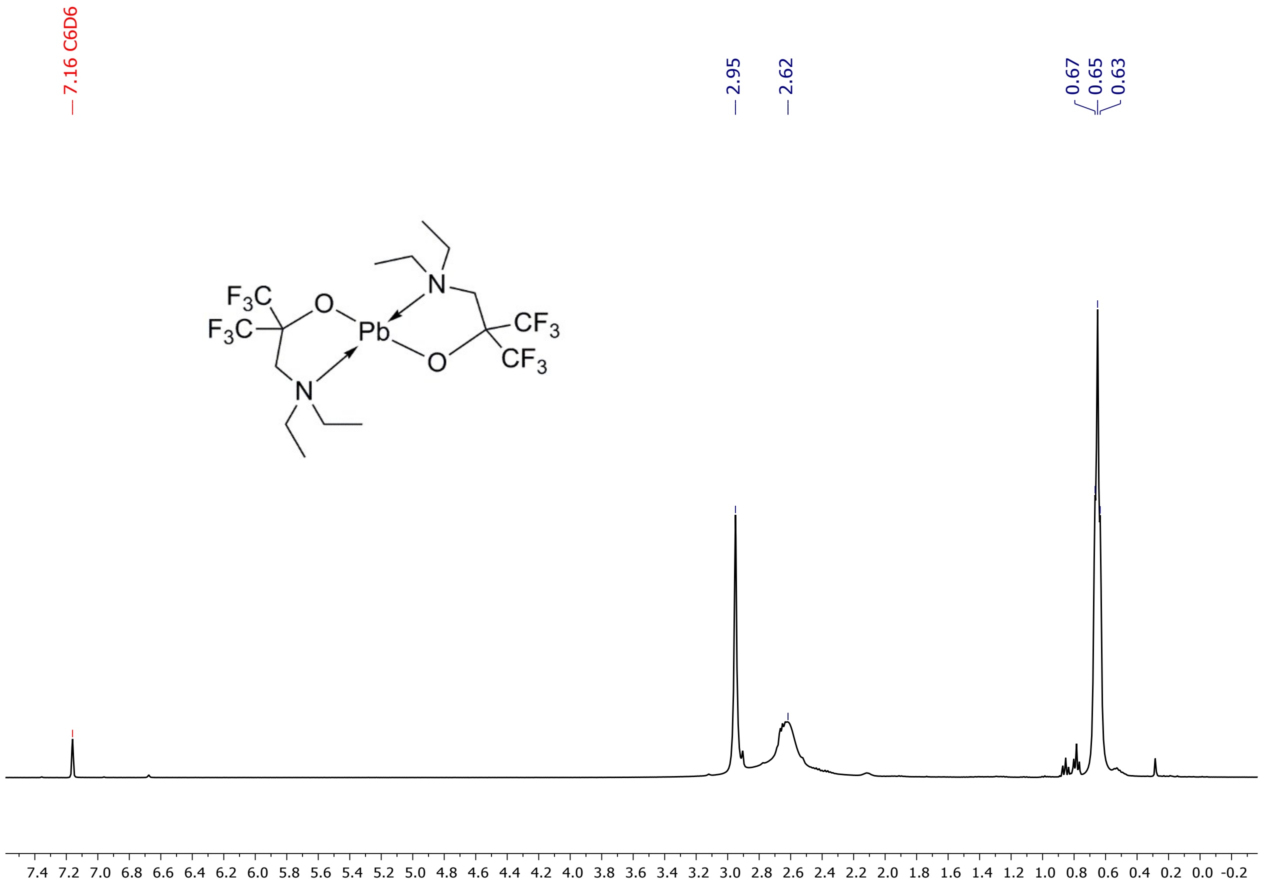

Figure S6. ^{1}H NMR spectrum (benzene-d_6, 298 K, 400.16 MHz) of [Pb{RO^F}$_2$] (**2**).

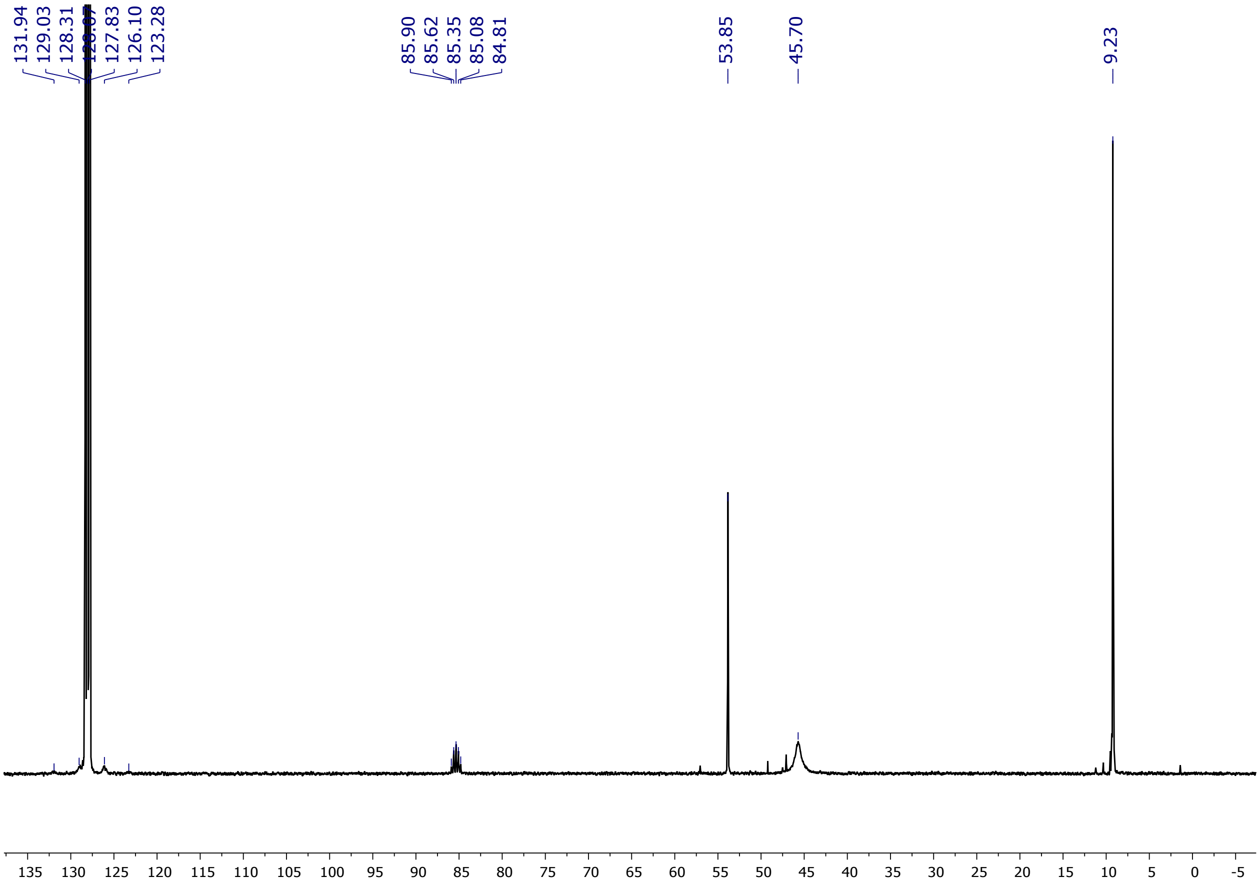

Figure S7. $^{13}C\{^1H\}$ NMR spectrum (benzene-d_6, 298 K, 100.63 MHz) of $[Pb\{RO^F\}_2]$ (**2**).

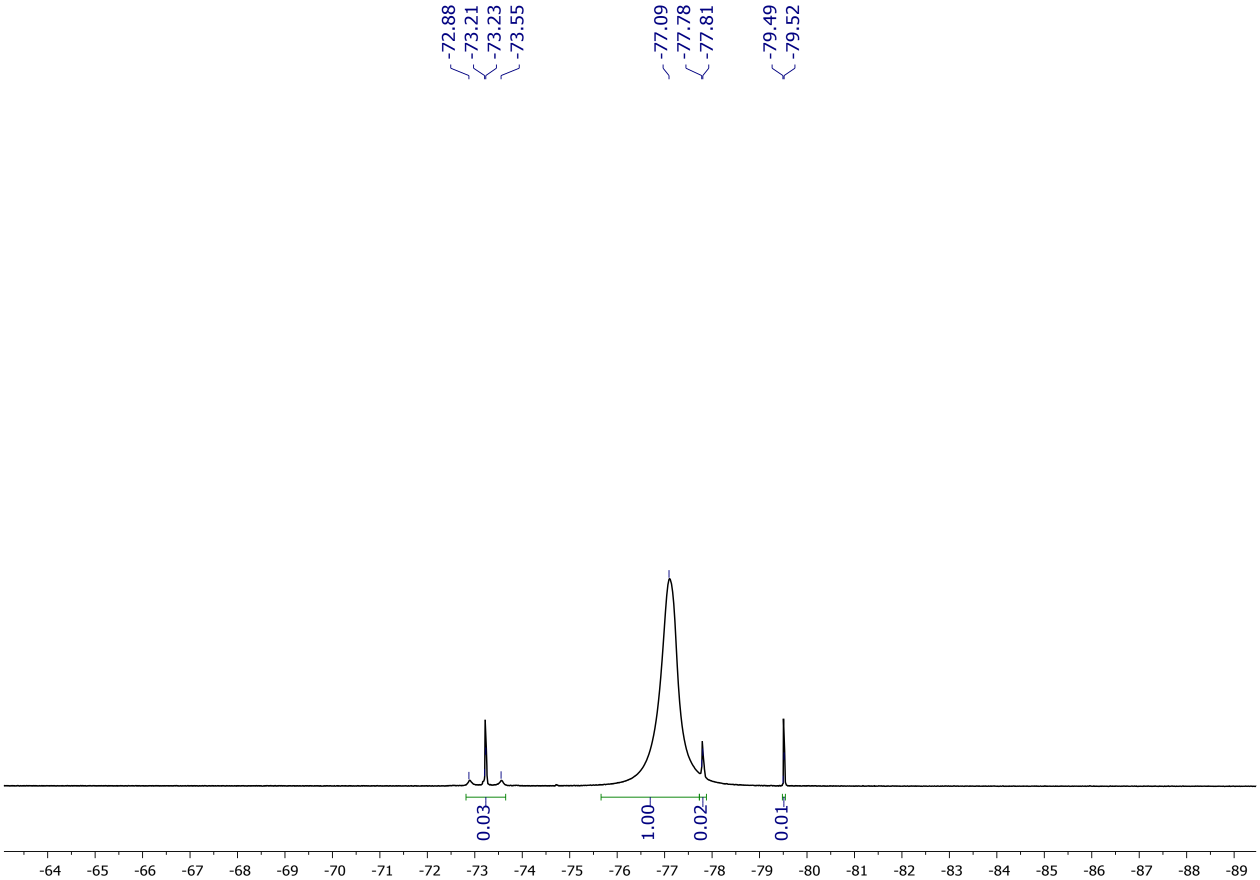

Figure S8. $^{19}F\{^{1}H\}$ NMR spectrum (benzene-d_6, 298 K, 376.47 MHz) of of [Pb{RO^F}$_2$] (**2**). The resonance at –77.8 ppm corresponds to residual {RO^F}H. Those at –73.22 and –79.50 ppm belong to minute amounts (1-3%) of unidentified species.

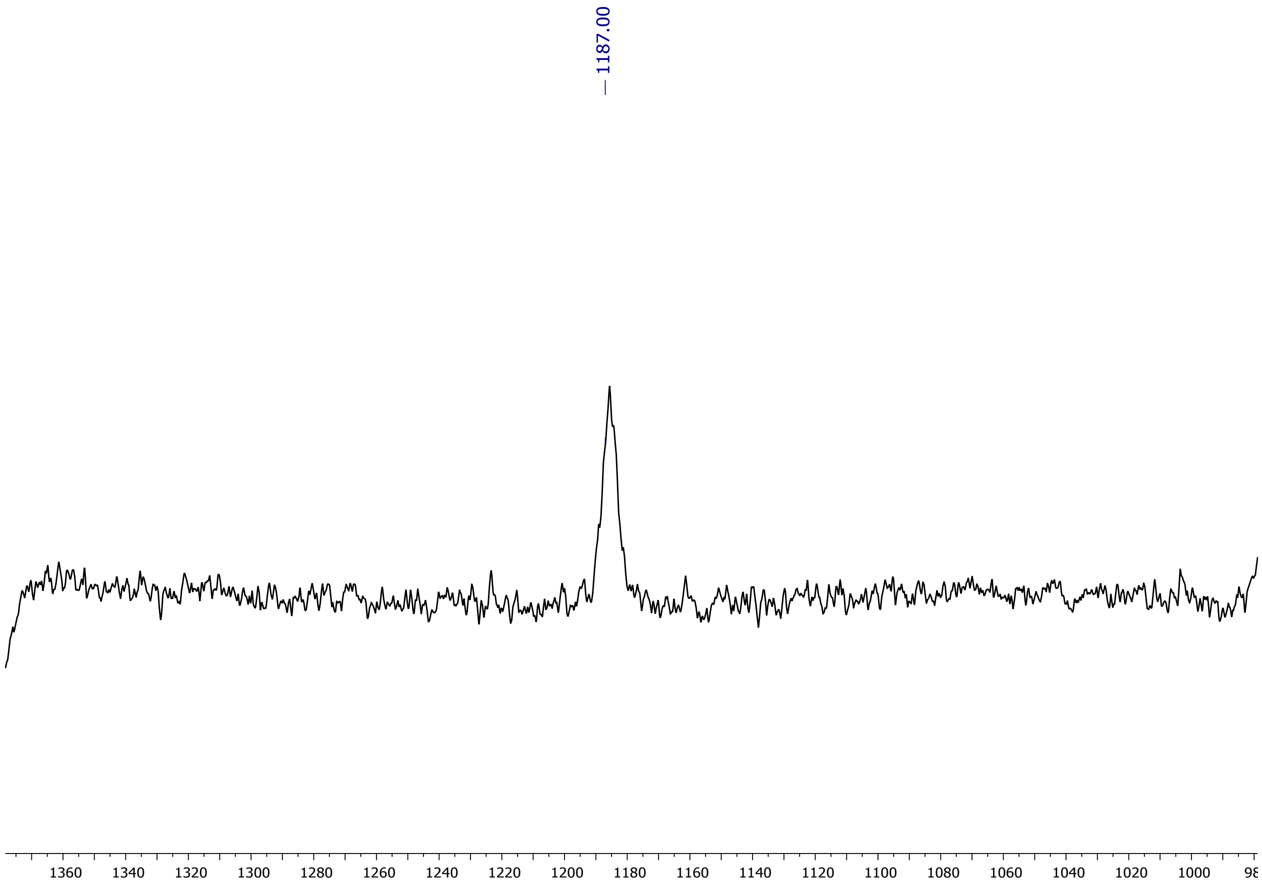

Figure S9. ^{207}Pb{^{1}H} NMR spectrum (benzene-d_6, 298 K, 83.81 MHz) of [Pb{RO^{F}}$_2$] (**2**).

Synthesis of [$\{RO^F\}PbOB\{CH(SiMe_3)_2\}_2$] (3)

A solution of $\{(Me_3Si)_2CH\}_2BOH$ (170 mg, 0.490 mmol) in Et_2O (8 mL) was added dropwise to a solution of **1** (304 mg, 0.490 mmol) in Et_2O (6 mL). The reaction mixture was stirred at room temperature for 1 h and all the volatiles were then removed under vacuum. The title compound was obtained as an off-white crystalline solid (375 mg, 95%) showing good solubility in: diethyl ether, petroleum ether and benzene. Colourless monocrystals suitable for XRD analysis were grown from a concentrated petroleum ether solution stored at –43 °C.

M. p. = 128 °C.

^{1}H NMR (benzene-d_6, 400.13 MHz, 298 K): δ = 2.90 (s, 2H, $CH_2C(CF_3)_2$), 2.85 (m, 2H, CH_2CH_3), 2.53 (m, 2H, CH_2CH_3), 0.60 (m, 6H, CH_2CH_3) 0.50 (s, 2H, BC*H*), 0.27 (s, 36H, SiCH_3) ppm.

^{13}C NMR (benzene-d_6, 125.77 MHz, 300 K): δ = 127.53 (q, $^1J_{CF}$ = 289 Hz, *C*F$_3$), 85.52 (hept, $^2J_{CF}$ = 28 Hz, *C*(CF$_3$)$_2$), 53.62 (s, *C*H$_2$(CF$_3$)$_2$), 46.61 (s, $^2J_{PbC}$ = 25.4 Hz, *C*H$_2$CH$_3$), 25.88 (s, B*C*H), 9.10 (br s, CH$_2$*C*H$_3$), 3.46 (s,$^1J_{SiC}$ = 50.3 Hz, $^5J_{PbC}$ = 18.7 Hz, Si*C*H$_3$) ppm.

^{19}F{^{1}H} NMR (benzene-d_6, 376.47 MHz, 298K): δ = –77.09 (s, $^4J_{PbF}$ = 125 Hz) ppm.

^{11}B{^{1}H} NMR (benzene-d_6, 128.4 MHz, 298K): δ = 49.5 (br) ppm.

^{29}Si{^{1}H} NMR (benzene-d_6, 376.47 MHz, 298K): δ = –3.49 (s) ppm.

^{207}Pb{^{1}H} NMR (benzene-d_6, 83.83 MHz, 299 K): δ = 1425 (m, $^4J_{PbF} \approx$ 125 Hz) ppm.

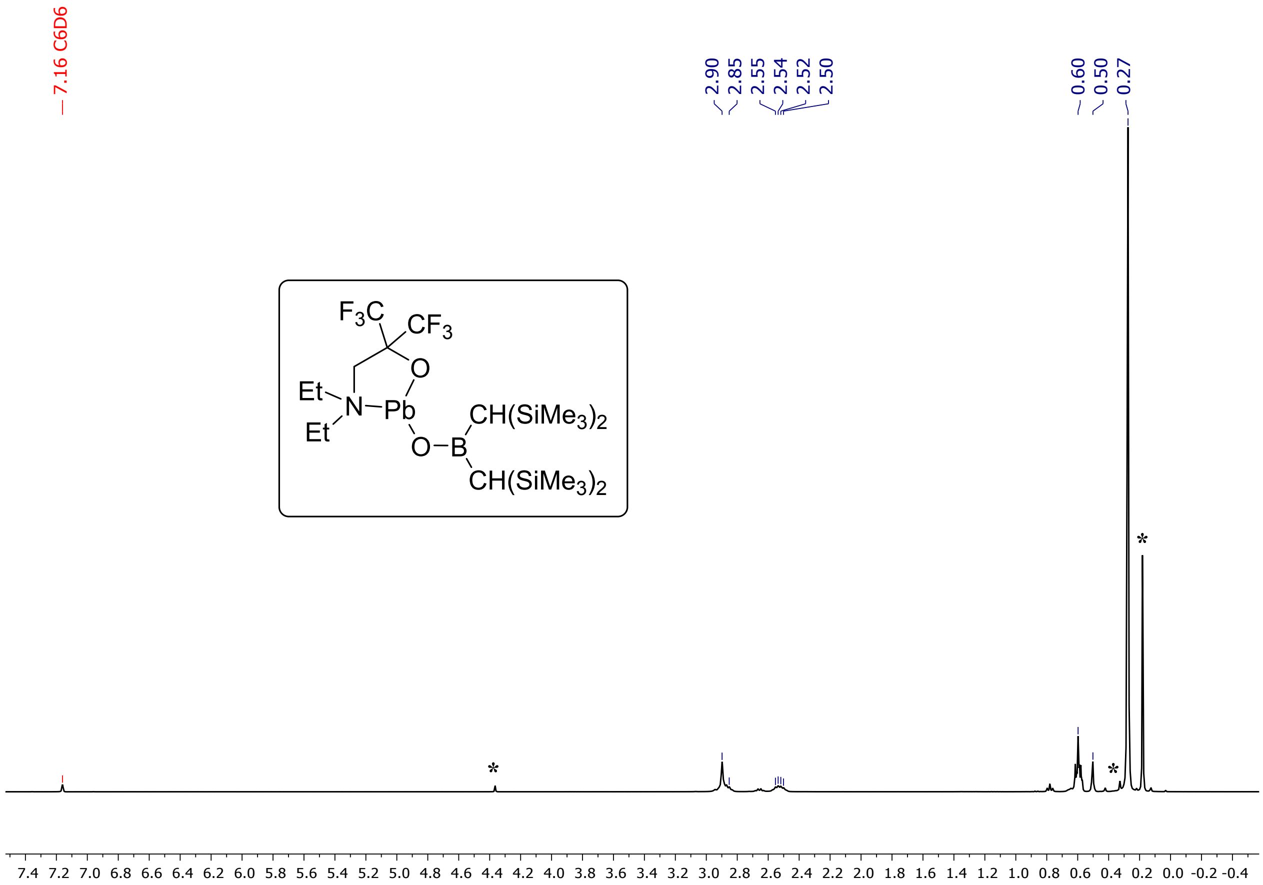

Figure S10. ^{1}H NMR spectrum (benzene-d_6, 298 K, 400.16 MHz) of [{RO^F}PbOB{CH(SiMe$_3$)$_2$}$_2$] (**3**). Resonances labelled with an asterisk correspond to free borinic acid {(Me$_3$Si)$_2$CH}$_2$BOH.

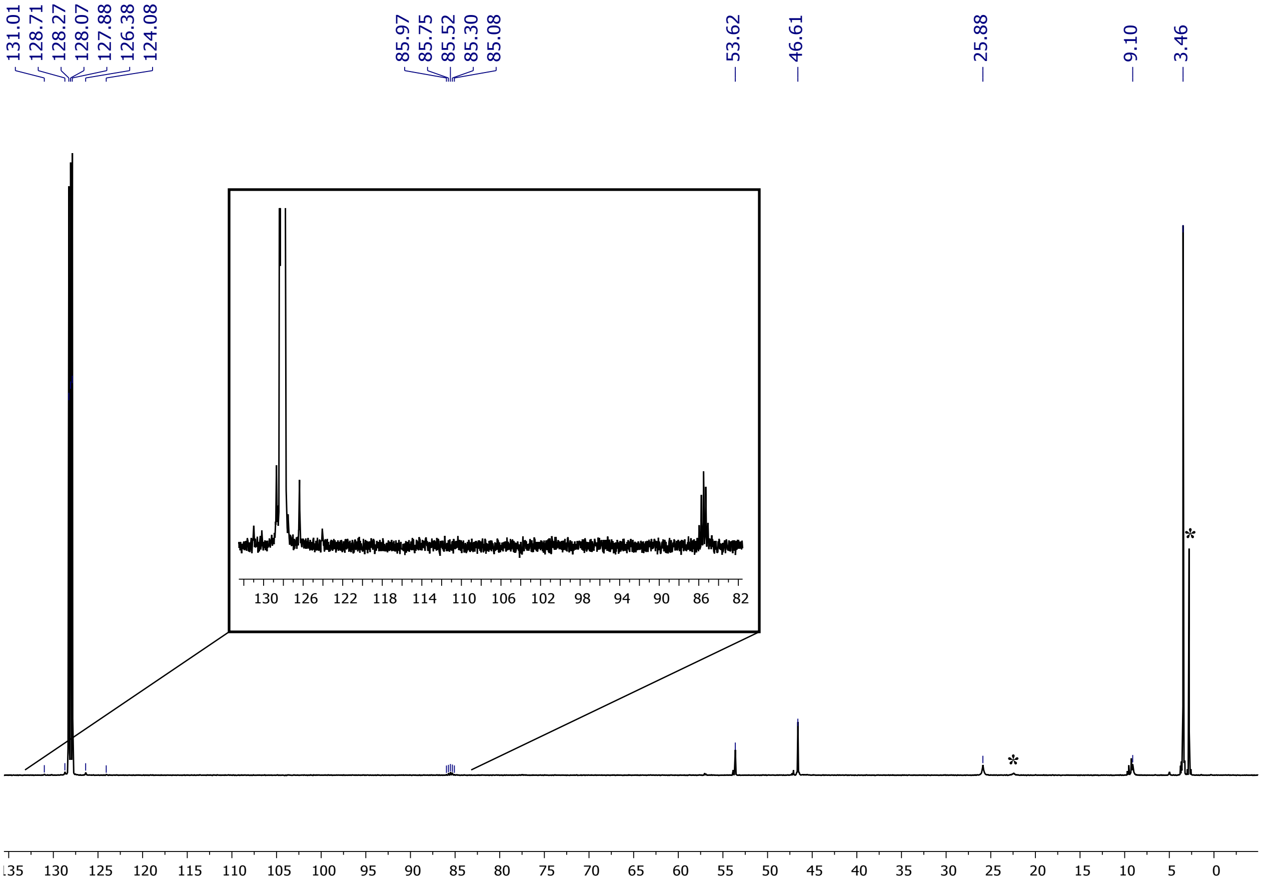

Figure S11. $^{13}C\{^1H\}$ NMR spectrum (benzene-d_6, 298 K, 125.77 MHz) of $[\{RO^F\}PbOB\{CH(SiMe_3)_2\}_2]$ (**3**). Resonances labelled with an asterisk correspond to free borinic acid $\{(Me_3Si)_2CH\}_2BOH$.

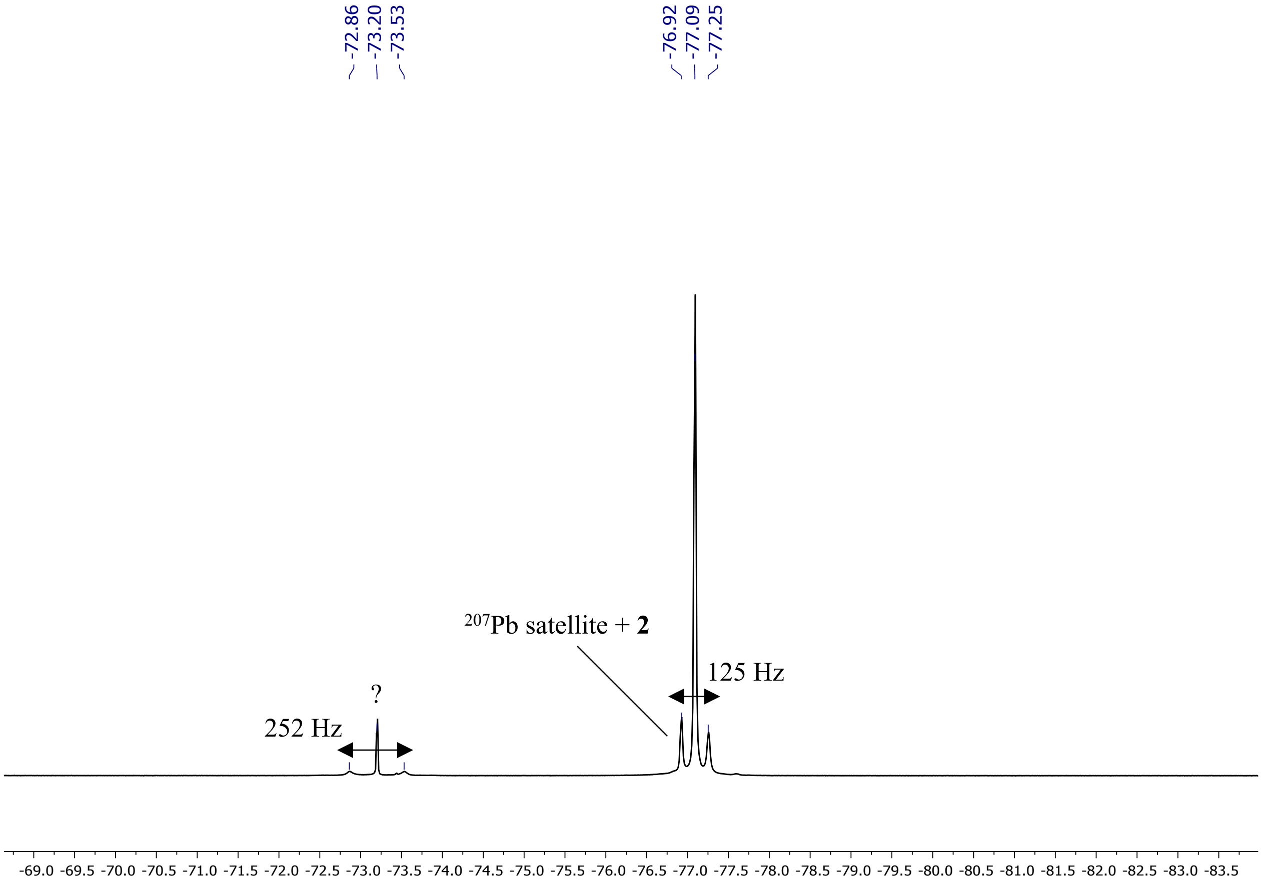

Figure S12. ^{19}F{^{1}H} NMR spectrum (benzene-*d*$_6$, 298 K, 376.47 MHz) of [{RO^F}PbOB{CH(SiMe$_3$)$_2$}$_2$] (**3**). Resonance at –73.2 ppm, between 3-15% depending on the conditions of NMR analysis, not identified (see main text). The resonance for residual [Pb{RO^F}$_2$] (**2**) overlaps with the left satellite at –76.9 ppm.

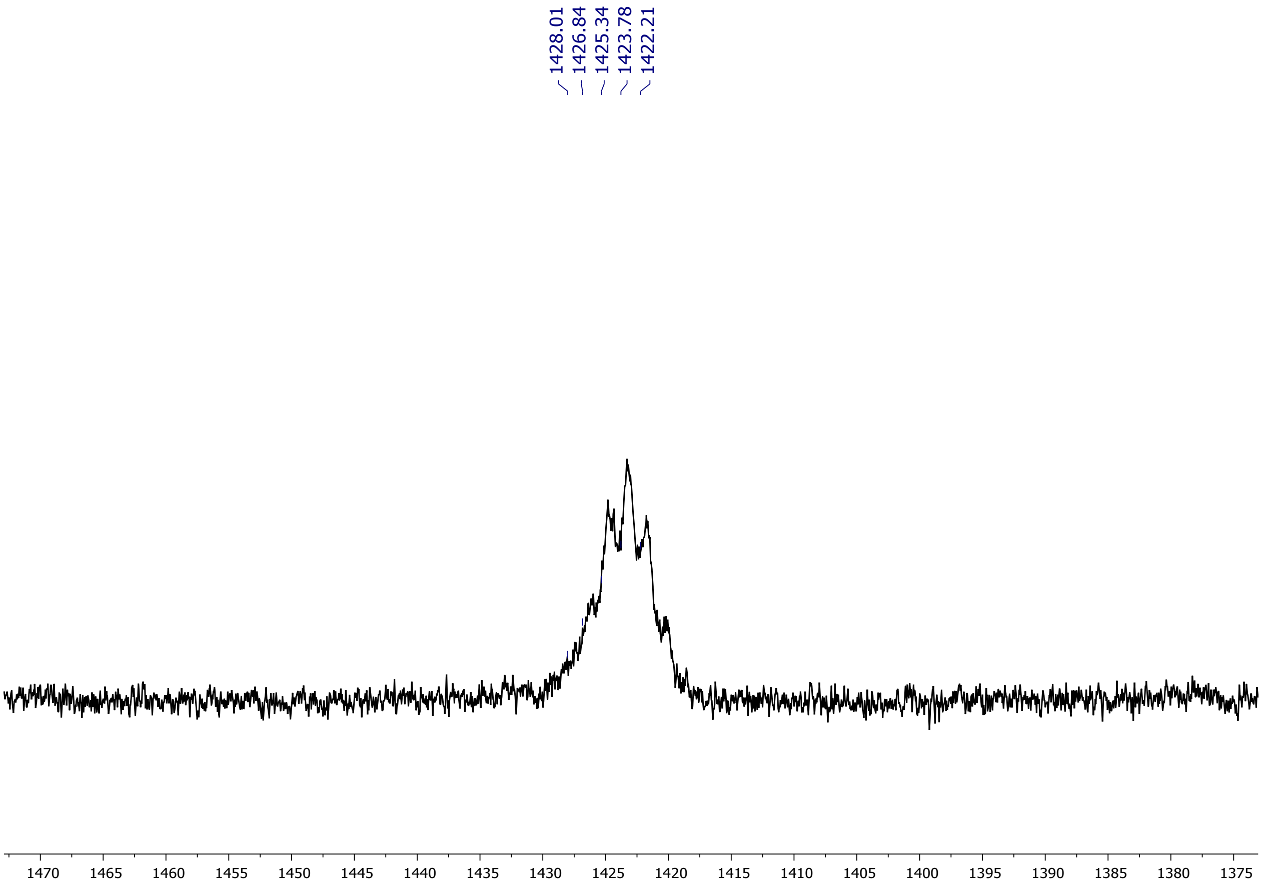

Figure S13. ^{207}Pb{^{1}H} NMR spectrum (benzene-d_6, 298 K, 83.83 MHz) of [{RO^{F}}PbOB{CH(SiMe$_3$)$_2$}$_2$] (**3**).

Synthesis of [$Pb_4(\mu_3\text{-}O)_2\{\mu_2\text{-}OB(2,4,6\text{-}i\mathrm{Pr}_3\text{-}C_6H_2)_2\}_4$] (4)

A solution of $\{2,4,6\text{-}i\mathrm{Pr}_3\text{-}C_6H_2\}_2BOH$ (0.26 g, 0.60 mmol) in Et_2O (8 mL) was added dropwise to a solution of [$Pb\{N(SiMe_3)_2\}_2$] (0.16 g, 0.30 mmol) in Et_2O (8 mL). The reaction mixture was stirred at room temperature for 1.5 h, then filtered and all the volatiles were then removed under vacuum from the clear solution. Toluene was added over the remaining solid and suitable crystals for X-ray analysis were obtained after 1 week at –43 °C.

X-ray diffraction crystallography

[{RO^F}PbN(SiMe$_3$)$_2$] (**1**): ($C_{14}H_{30}F_6N_2OPbSi_2$); $M = 619.77$. D8 VENTURE Bruker AXS diffractometer, Mo-Kα radiation ($\lambda = 0.71073$ Å), $T = 150(2)$ K; monoclinic $P2_1/n$ (I.T.#14), a = 8.7972(8), b = 18.9590(14), c = 13.4726(11) Å, β = 97.627(4)°, $V = 2227.2(3)$ Å^3, $Z = 4$, $d = 1.848$ g.cm^{-3}, μ = 7.737 mm^{-1}. The structure was solved by dual-space algorithm using the *SHELXT* program,[2] and then refined with full-matrix least-squares methods based on F^2 (*SHELXL*).[3] 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 5021 unique intensities and 243 parameters converged at $\omega R(F^2) = 0.1410$ ($R(F) = 0.0604$) for 3474 observed reflections with $I > 2\sigma(I)$. CCDC number 1916553.

[Pb{RO^F}$_2$] (**2**): ($C_{16}H_{24}F_{12}N_2O_2Pb$); $M = 711.56$. D8 VENTURE Bruker AXS diffractometer equipped with a (CMOS) PHOTON 100 detector, Mo-Kα radiation ($\lambda = 0.71073$ Å, multilayer monochromator), $T = 150$ K; monoclinic $P2_1/c$ (I.T.#14), a = 17.312(2), b = 10.3487(10), c = 12.5829(15) Å, β = 95.768(5)°, $V = 2243.0(4)$ Å^3, $Z = 4$, $d = 2.107$ g.cm^{-3}, μ = 7.637 mm^{-1}. The structure was solved by dual-space algorithm using the *SHELXT* program,[2] and then refined with full-matrix least-squares methods based on F^2 (*SHELXL*).[3] 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 5119 unique intensities and 308 parameters converged at $\omega R_F{}^2 = 0.0642$ ($R_F = 0.0329$) for 4296 observed reflections with $I > 2\sigma(I)$. CCDC number 1916554.

[{RO^F}PbOB{CH(SiMe$_3$)$_2$}$_2$] (**3**): ($C_{22}H_{50}BF_6NO_2PbSi_4$); $M = 804.99$. D8 VENTURE Bruker AXS diffractometer equipped with a (CMOS) PHOTON 100 detector, [*], Mo-*Kα* radiation ($\lambda = 0.71073$ Å, multilayer monochromator), $T = 150$ K; monoclinic $P\,2_1/n$ (I.T.#14), $a = 13.0870(13)$, $b = 9.0118(8)$, $c = 29.884(3)$ Å, $\beta = 100.753(4)$ °, $V = 3462.6(6)$ Å^3. $Z = 4$, $d = 1.544$ g.cm^{-3}, $\mu = 5.063$ mm^{-1}. The structure was solved by dual-space algorithm using the *SHELXT* program,[2] and then refined with full-matrix least-squares methods based on F^2 (*SHELXL*).[3] 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 7951 unique intensities and 380 parameters converged at $\omega R_F{}^2 = 0.0722$ ($R_F = 0.0346$) for 6763 observed reflections with $I > 2\sigma(I)$. CCDC number 1916555.

[Pb$_4$(μ$_3$-O)$_2${μ$_2$-OB(2,4,6-*i*Pr$_3$-C$_6$H$_2$)$_2$}$_4$] (**4**): ($C_{120}H_{184}B_4O_6Pb_4$); $M = 2594.66$. D8 VENTURE Bruker AXS diffractometer equipped with a (CMOS) PHOTON 100 detector, Mo-Kα radiation ($\lambda = 0.71073$ Å, multilayer monochromator), $T = 150$ K; monoclinic $P2_1/n$ (I.T.#14), a = 13.4703(4), b = 17.3016(7), c =

25.8438(8) Å, β = 92.021(2) °, V = 6019.4(4) Å^3, Z = 2, d = 1.432 g.cm^{-3}, μ = 5.626 mm^{-1}. The structure was solved by dual-space algorithm using the *SHELXT* program,[2] and then refined with full-matrix least-squares methods based on F^2 (*SHELXL*).[3] 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 13672 unique intensities and 625 parameters converged at $\omega R_F^2 = 0.1156$ ($R_F = 0.0537$) for 9479 observed reflections with $I > 2\sigma(I)$. CCDC number 1916556.

Table S14. Crystal data and structure refinement for **1** and **2**.

	$[\{RO^F\}PbN(SiMe_3)_2]$ (**1**)	$[Pb\{RO^F\}_2]$ (**2**)
CCDC number	1916553	1916554
Formula	C14 H30 F6 N2 O Pb Si2	C16 H24 F12 N2 O2 Pb
Mol. wt [g/mol]	619.77	711.56
Crystal system	monoclinic	monoclinic
Space group	$P\ 2_1/n$	$P\ 2_1/c$
a [Å]	8.7972(8)	17.312(2)
b [Å]	18.9590(14)	10.3487(10)
c [Å]	13.4726(11)	12.5829(15)
α [°]	90	90
β [°]	97.627(4)	95.768(5)
γ [°]	90	90
V [Å^3]	2227.2(3)	2243.0(4)
Z	4	4
Density (g cm^{-3})	1.848	2.107
Abs. coeff., (mm^{-1})	7.737	7.637
F(000)	1200	1360
Crystal size, mm	0.510 × 0.430 × 0.170	0.180 × 0.090 × 0.060
θ range [°]	2.955 to 27.483	3.077 to 27.483
Limiting indices	$11 < h < 11$	$22 < h < 22$
	$24 < k < 24$	$13 < k < 9$
	$16 < l < 17$	$16 < l < 16$
R(int)	0.1248	0.0606
Reflections collected	16400 / 5021	31556 / 5119
Refl. Unique [I > 2σ (I)]	3474	4296
Completeness to θ	0.982	0.995
Data/ restraints/ param.	5021 / 0 / 243	5119 / 0 / 308
Goodness-of-fit	0.993	1.143
R_1 [I > 2σ (I)] (all data)	0.0604 (0.0996)	0.0329 (0.0457)
wR_2 [I > 2σ (I)] (all data)	0.1410 (0.1597)	0.0642 (0.0682)
Largest diff. [e A^{-3}]	3.694 and -4.555	1.520 and -1.857

Table S15. Crystal data and structure refinement for **3** and **4**.

	$[\{RO^F\}PbOB\{CH(SiMe_3)_2\}_2]$ (**3**)	$[Pb_4(\mu_3\text{-}O)_2\{\mu_2\text{-}OB(2,4,6\text{-}i Pr_3\text{-}C_6H_2)_2\}_4]$ (**4**)
CCDC number	1916555	1916556
Formula	C22 H50 B F6 N O2 Pb Si4	C120 H184 B4 O6 Pb4
Mol. wt [g/mol]	804.99	2594.66
Crystal system	monoclinic	monoclinic
Space group	*P* 2_1/*n*	*P* 2_1/*n*
a [Å]	13.0870(13)	13.4703(4)
b [Å]	9.0118(8)	17.3016(7)
c [Å]	29.884(3)	25.8438(8)
α [°]	90	90
β [°]	100.753(4)	92.021(2)
γ [°]	90	90
V [$Å^3$]	3462.6(6)	6019.4(4)
Z	4	2
Density (g cm^{-3})	1.544	1.432
Abs. coeff., (mm^{-1})	5.063	5.626
F(000)	1608	2600
Crystal size, mm	0.290 × 0.170 × 0.100	0.120 × 0.050 × 0.030
θ range [°]	2.364 to 27.559	2.354 to 27.519
Limiting indices	16 < h < 17	17 < h < 17
	11 < k < 11	22 < k < 22
	38 < l < 38	33 < l < 33
R(int)	0.0427	0.1135
Reflections collected	35241 / 7952	54935 / 13672
Refl. Unique [I > 2σ (I)]	6763	9479
Completeness to θ	0.995	0.985
Data/ restraints/ param.	7951 / 30 / 380	13672 / 552 / 625
Goodness-of-fit	1.250	1.011
R_1 [I > 2σ (I)] (all data)	0.0346 (0.0440)	0.0537 (0.1156)
wR_2 [I > 2σ (I)] (all	0.0722 (0.0750)	0.0939 (0.1312)
Largest diff. [e A^{-3}]	0.899 and -1.156	2.442 and -2.976

References

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3 G. M. Sheldrick, *Acta Cryst. Sect. C*, 2015, **71**, 3.