

Electronic Supporting Information for

Of perfluorinated aryllead(II) complexes

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Contents

<i>Contents</i>	<i>pages</i>
Experimental section	
General procedures	p. S3
Synthesis of $[\text{Mg}_3(\mu_2\text{-Br})_3(\mu_3\text{-Cl})_2(\text{OEt}_2)_6]^+[\text{Pb}(\text{C}_6\text{F}_5)_3]^-$ (1)	p. S4
Figure S1. ^1H NMR spectrum (THF- <i>d</i> ₈ , 500.13 MHz, 300 K) of 1	p. S5
Figure S2. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (THF- <i>d</i> ₈ , 125.77 MHz, 300 K) of 1	p. S6
Figure S3. ^{19}F NMR spectrum (THF- <i>d</i> ₈ , 470.52 MHz, 300 K) of 1	p. S7
Figure S4. $^{207}\text{Pb}\{^1\text{H}\}$ NMR spectrum (THF- <i>d</i> ₈ , 83.79 MHz, 300 K) of 1	p. S8
Figure S5. Stacked ^{19}F NMR spectra (THF- <i>d</i> ₈ , 376.47 MHz, 300 K) of the reaction between $\text{C}_6\text{F}_5\text{MgBr}$ and PbBr_2 (2:1 molar ratio) with the formation of $[\text{Mg}_3(\mu_2\text{-Br})_3(\mu_3\text{-Br})_2(\text{OEt}_2)_6]^+[\text{Pb}(\text{C}_6\text{F}_5)_3]^-$	p. S9
Figure S6. ^{19}F NMR spectrum (THF- <i>d</i> ₈ , 376.47 MHz, 300 K) of crystalline $[\text{Pb}(\text{C}_6\text{F}_5)_4]$	p. S10
Synthesis of $[\text{Pb}(\text{C}_6\text{F}_5)_2(\text{dx})]_\infty$ (2)	p. S11
Figure S7. ^1H NMR spectrum (THF- <i>d</i> ₈ , 500.13 MHz, 300 K) of 2	p. S12
Figure S8. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (THF- <i>d</i> ₈ , 125.77 MHz, 300 K) of 2	p. S13
Figure S9. ^{19}F NMR spectrum (THF- <i>d</i> ₈ , 470.52 MHz, 300 K) of 2	p. S14
Figure S10. $^{207}\text{Pb}\{^1\text{H}\}$ NMR spectrum (THF- <i>d</i> ₈ , 83.92 MHz, 300 K) of 2	p. S15
Synthesis of $[(\text{C}_5\text{F}_5)_3\text{SnSn}(\text{C}_6\text{F}_5)_3]$ (3)	p. S16
Figure S11. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (THF- <i>d</i> ₈ , 100.62 MHz, 300 K) of 3	p. S17
Figure S12. ^{19}F NMR spectrum (THF- <i>d</i> ₈ , 376.44 MHz, 300 K) of 3	p. S18
Figure S13. $^{119}\text{Sn}\{^1\text{H}\}$ NMR spectrum (THF- <i>d</i> ₈ , 149.14 MHz, 300 K) of 3	p. S19
Figure S14. ^{19}F NMR spectrum (CDCl_3 , 300 K, 376.47 MHz) of 3	p. S20
X-ray diffraction crystallography	pp. S21-S23
Table S1. Crystal data and structure refinement for 1 and 2	p. S24
Table S2. Crystal data and structure refinement for $[\text{Pb}(\text{C}_6\text{F}_5)_4]$, $[(\text{C}_5\text{F}_5)_3\text{SnSn}(\text{C}_6\text{F}_5)_3]\cdot(\text{dx})$ and $[\text{MgBr}_2(\text{DMAP})_2]$	p. S25
Table S3. Selected interatomic distances and bond angles of 1	p. S26
Figure S16. ORTEP representation of the new polymorph structure of $[\text{Pb}(\text{C}_6\text{F}_5)_4]$	p. S27
Figure S17. Intermolecular C–H···F contacts in the crystal of 2	p. S28
Figure S18. View along <i>b</i> axis of the polymer structure of 2	p. S29
Figure S19. ORTEP representation of the molecular structure of $[(\text{C}_5\text{F}_5)_3\text{SnSn}(\text{C}_6\text{F}_5)_3]\cdot(\text{dx})$	p. S30
Figure S20. ORTEP representation of the molecular structure of $[\text{MgBr}_2(\text{DMAP})_2]$	p. S31
References	p. S32

Experimental section

General procedures

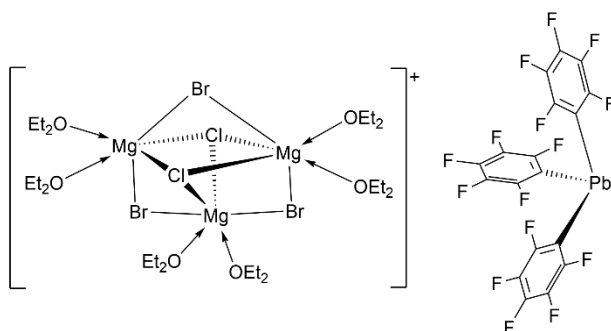
All manipulations were performed under an inert atmosphere using standard Schlenk techniques or in a dry, solvent-free glovebox (Jacomex; O₂ < 1 ppm, H₂O < 5 ppm) for catalyst loading. Solvents (THF, Et₂O, petroleum ether and toluene) were purified and dried (water contents below 8 ppm) over columns 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 ¹³C{¹H} chemical shifts (reported in ppm) were determined using residual signals of the deuterated solvents and were calibrated vs SiMe₄. Assignment of the signals was carried out using 1D (¹H, ¹³C{¹H}) and 2D (COSY, HMBC, HSQC) NMR experiments. ²⁰⁷Pb NMR spectra were referenced against a solution of Pb[N(SiMe₃)₂]₂^[1] in benzene-d₆ (δ²⁰⁷Pb = 4916 ppm at 298 K). ¹⁹F chemical shifts were determined by external reference to an aqueous solution of NaBF₄. ¹¹⁹Sn NMR spectra were referenced against a solution of Ph₃SnCl in CDCl₃ (δ¹¹⁹Sn = -44.7 ppm at 298 K)^[2].

Owing to the very sensitive nature of the new complexes **1** and **2**, we were unable to obtain reproducible and reliable elemental and mass spectrometry analysis for these two complexes.

Synthesis of $[\text{Mg}_3(\mu_2\text{-Br})_3(\mu_3\text{-Cl})_2(\text{OEt}_2)_6]^+[\text{Pb}(\text{C}_6\text{F}_5)_3]^-$ (**1**)

A dark-brown solution of $\text{C}_6\text{F}_5\text{MgBr}$ in Et_2O (2.978 g, 19.0 mL, 0.58 M, 10.98 mmol) was added dropwise, for 20 minutes, to a slurry of PbCl_2 (1.527 g, 5.49 mmol) in Et_2O (35 mL) at $-60\text{ }^\circ\text{C}$, avoiding light. After 4 h, the reaction mixture had reached room temperature and the orange-brown solution was separated from the precipitate by cannula filtration, concentrated to half of its initial volume and stored at $-35\text{ }^\circ\text{C}$. The title compound was isolated as a pale brown crystalline solid, 1.400 g (25%).



^1H NMR ($\text{THF-}d_8$, 500.13 MHz, 300 K): δ 3.36 (q, 24H, $^3J_{\text{H-H}} = 7.0$ Hz, OCH_2), 1.09 (t, 36H, $^3J_{\text{H-H}} = 7.0$ Hz, CH_3) ppm.

$^{13}\text{C}\{^1\text{H}\}$ NMR ($\text{THF-}d_8$, 125.77 MHz, 300 K): δ 148.21 (ddm, $^1J_{\text{F-C}} = 225$ Hz, $^2J_{\text{F-C}} = 27$ Hz, *ortho-C*), 139.52 (dm, $^1J_{\text{F-C}} = 243$ Hz, *para-C*), 137.64 (dm, $^1J_{\text{F-C}} = 256$ Hz, *meta-C*), 102.24 (td, $^2J_{\text{F-C}} = 24$ Hz, $^3J_{\text{F-C}} = 3$ Hz, *ipso-C*), 66.31 (s, CH_2), 15.69 (s, CH_3) ppm.

^{19}F NMR ($\text{THF-}d_8$, 470.52 MHz, 300 K): δ -113.44 (m, 6F, *ortho-C* $_6\text{F}_5$), -161.52 (t, 3F, $^3J_{\text{F-F}} = 19.9$ Hz, $^4J_{\text{F-Pb}} = 14.0$ Hz, *para-C* $_6\text{F}_5$), -163.73 (m, 6F, *meta-C* $_6\text{F}_5$) ppm.

$^{207}\text{Pb}\{^1\text{H}\}$ NMR ($\text{THF-}d_8$, 83.88 MHz, 299 K): δ 1090 (br) ppm.

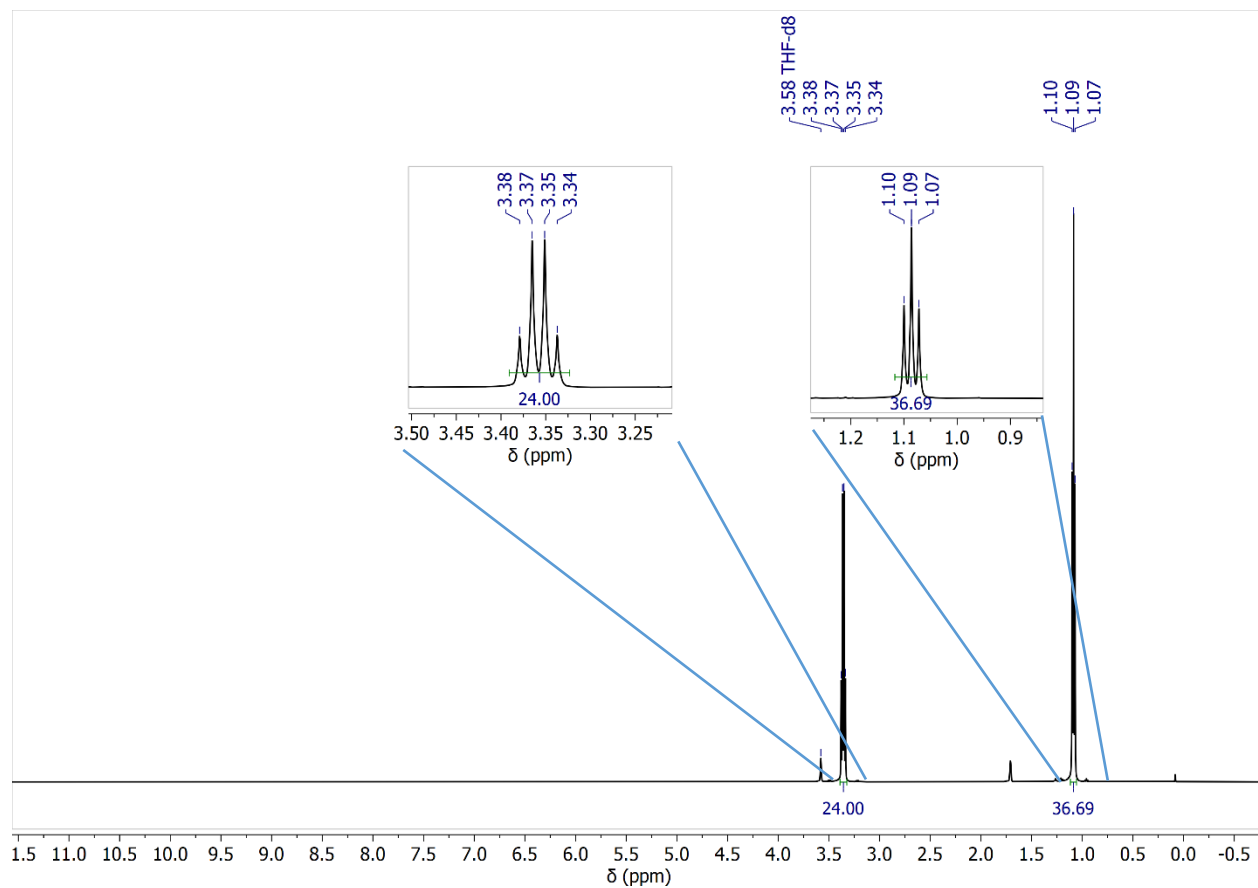


Figure S1. ^1H NMR spectrum (THF- d_8 , 500.13 MHz, 300 K) of $[\text{Mg}_3(\mu_2\text{-Br})_3(\mu_3\text{-Cl})_2(\text{OEt})_6]^+[\text{Pb}(\text{C}_6\text{F}_5)_3]^-$ (**1**).

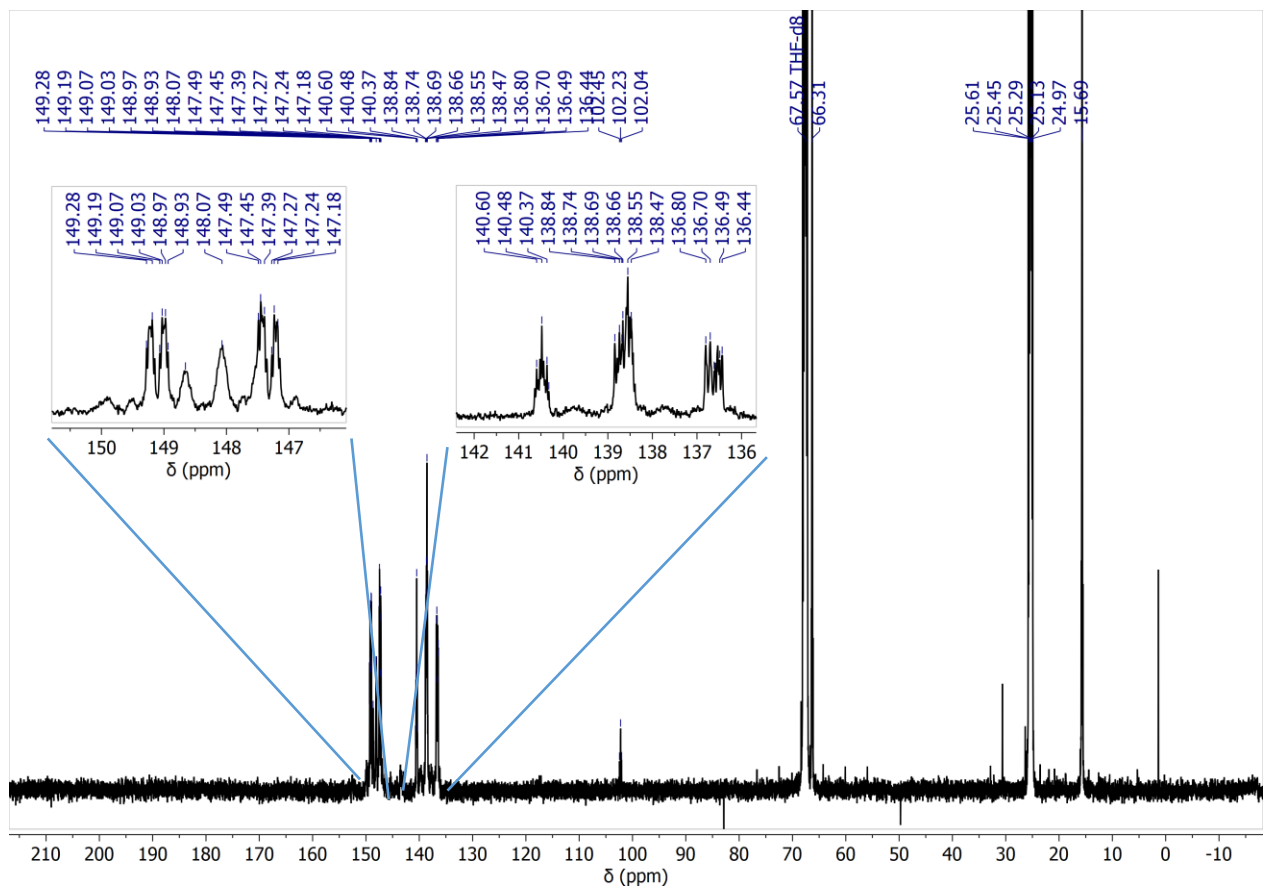


Figure S2. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum ($\text{THF-}d_8$, 125.77 MHz, 300 K) of $[\text{Mg}_3(\mu_2\text{-Br})_3(\mu_3\text{-Cl})_2(\text{OEt})_6]^+[\text{Pb}(\text{C}_6\text{F}_5)_3]^-$ (**1**).

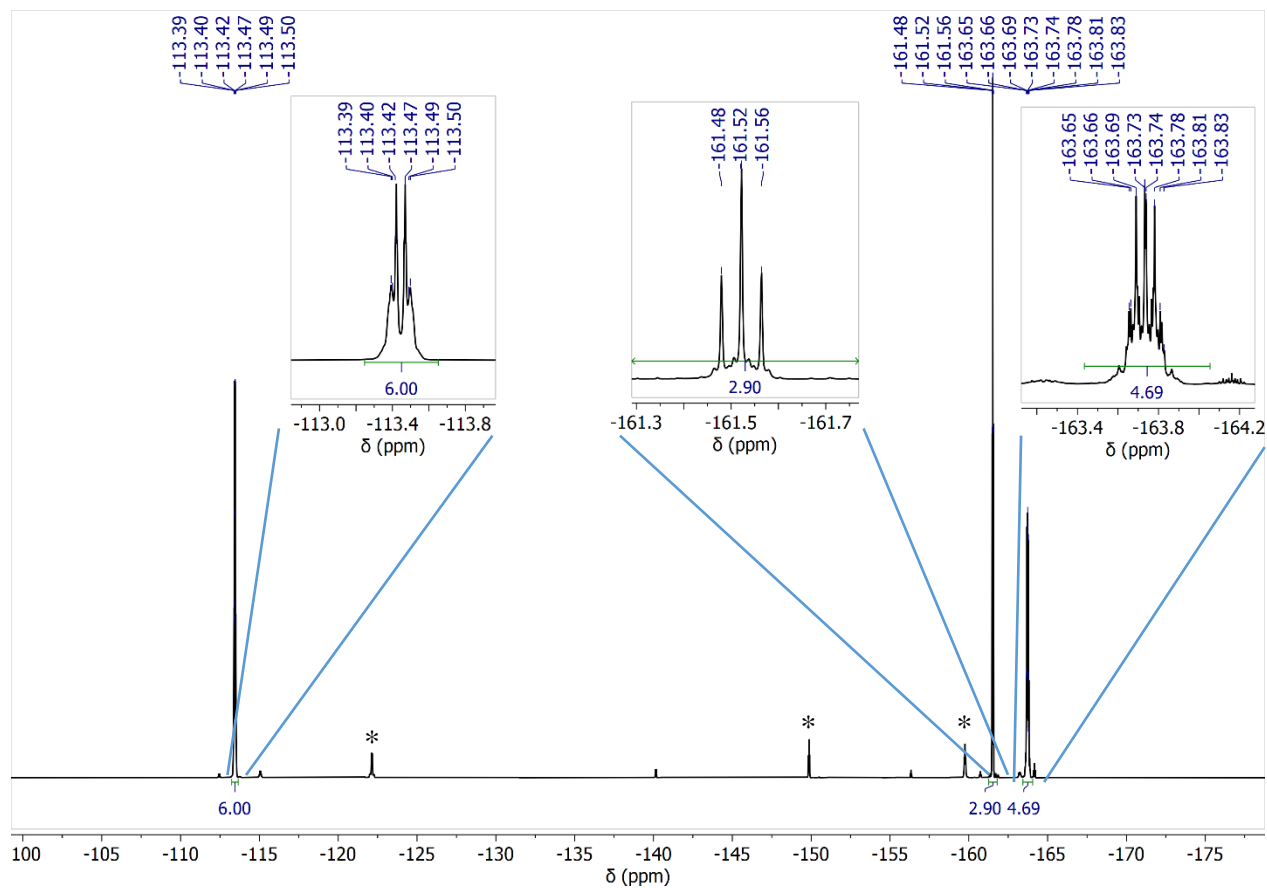


Figure S3. ^{19}F NMR spectrum ($\text{THF-}d_8$, 470.52 MHz, 300 K) of $[\text{Mg}_3(\mu_2\text{-Br})_3(\mu_3\text{-Cl})_2(\text{OEt}_2)_6]^+[\text{Pb}(\text{C}_6\text{F}_5)_3]^-$ (1). Resonances for residual $\text{Pb}(\text{C}_6\text{F}_5)_4$ indicated by *.

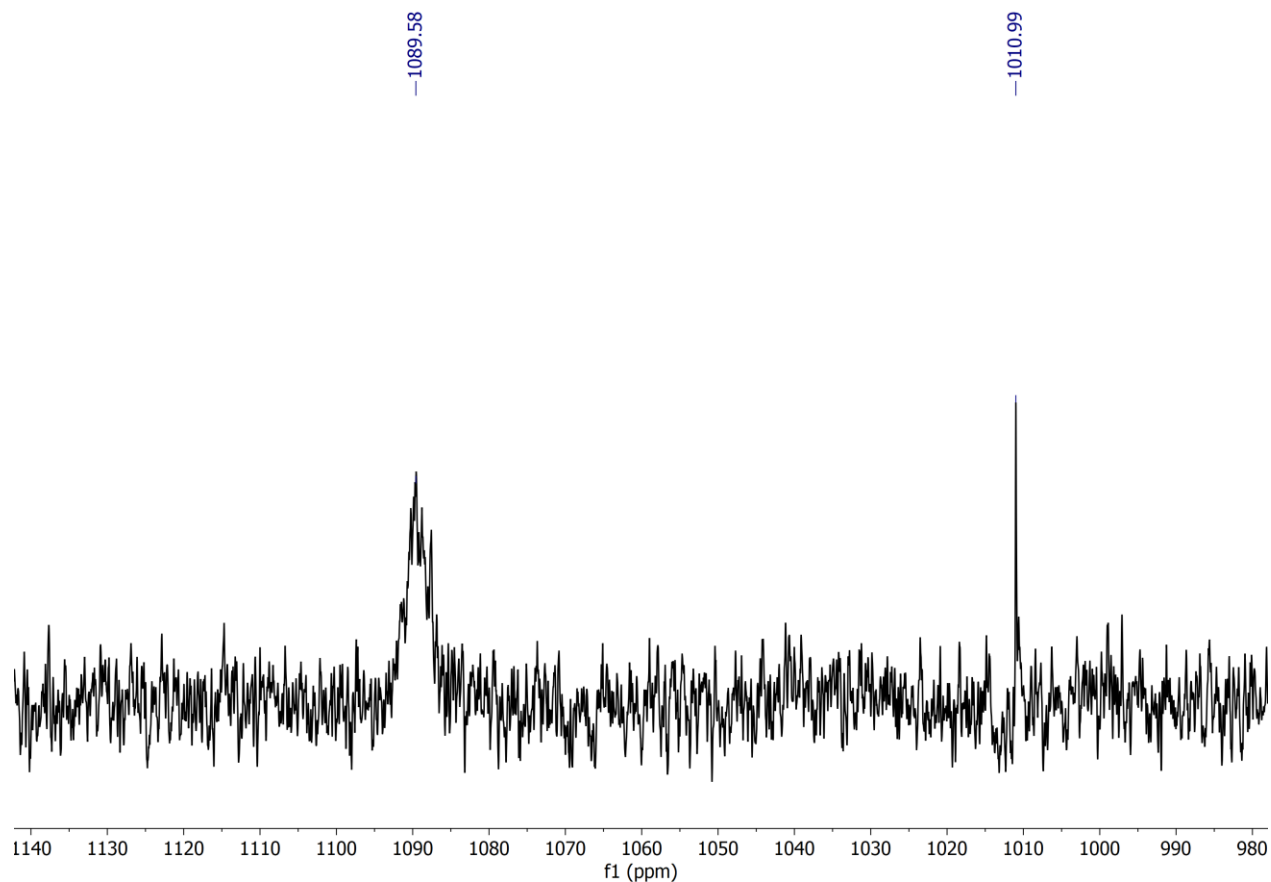


Figure S4. $^{207}\text{Pb}\{^1\text{H}\}$ NMR spectrum (THF- d_8 , 83.79 MHz, 300 K) of $[\text{Mg}_3(\mu_2\text{-Br})_3(\mu_3\text{-Cl})_2(\text{OEt}_2)_6]^+[\text{Pb}(\text{C}_6\text{F}_5)_3]^-$ (**1**). On the basis of the ^{19}F NMR data (Figures S3 and S6), the very minor resonance at 1011 ppm is assigned to $\text{Pb}(\text{C}_6\text{F}_5)_4$, although it does not match the value reported elsewhere (-391 ppm in CDCl_3).^[3]

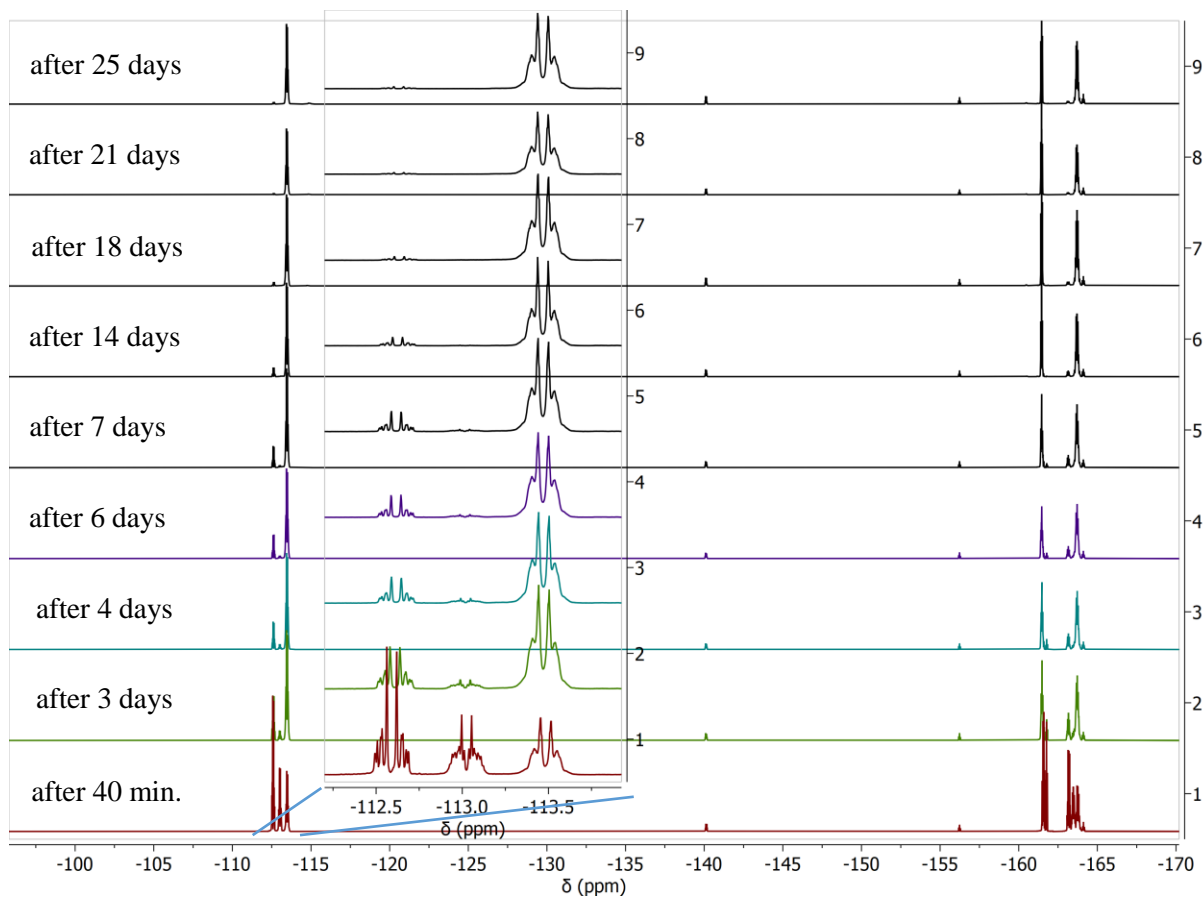


Figure S5. Stacked ^{19}F NMR spectra (THF- d_8 , 376.47 MHz, 300 K) of the reaction between $\text{C}_6\text{F}_5\text{MgBr}$ and PbBr_2 (2:1 molar ratio) with the formation of $[\text{Mg}_3(\mu_2\text{-Br})_3(\mu_3\text{-Br})_2(\text{OEt})_6]^+[\text{Pb}(\text{C}_6\text{F}_5)_3]^-$. It shows slow formation of the title compound within 18-21 days.

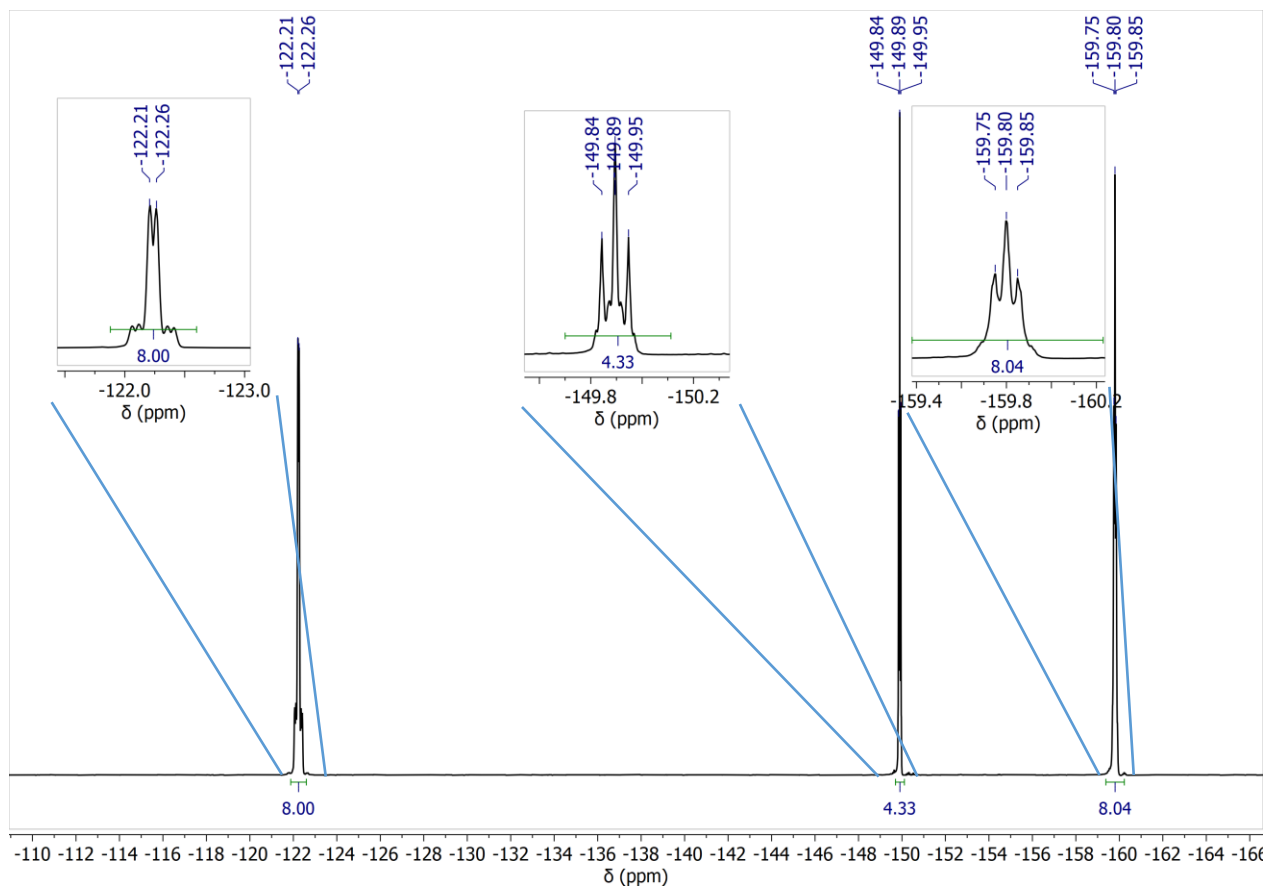
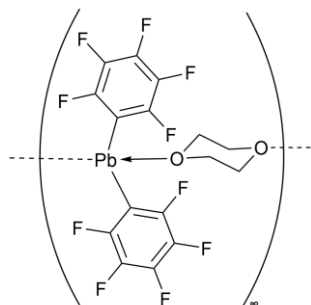


Figure S6. ^{19}F NMR spectrum ($\text{THF-}d_8$, 376.47 MHz, 300 K) of crystalline $[\text{Pb}(\text{C}_6\text{F}_5)_4]$ (crystals identity was also confirmed by XRD).

Synthesis of $[\text{Pb}(\text{C}_6\text{F}_5)_2(\text{dx})]_\infty$ (2)



A dark-brown solution of $\text{C}_6\text{F}_5\text{MgBr}$ in Et_2O (1.098 g, 7.7 mL, 0.53 M, 4.05 mmol) was added dropwise for 15 minutes, to a slurry of PbBr_2 (0.743 g, 2.02 mmol) in Et_2O (35 mL) at -78°C , avoiding light. After 4 h, the reaction mixture reached room temperature and 1 mL of dioxane was added at once, resulting immediately in the formation of a big amount of white precipitate. The reaction mixture was stirred overnight, after which the pale yellow solution was isolated from the white precipitate by cannula filtration, concentrated to incipient crystallization and stored at -35°C . Colorless crystals of the title compound were isolated after one day, 0.770 g (60%).

^1H NMR ($\text{THF-}d_8$, 500.13 MHz, 300 K): δ 3.56 (s, 8H, CH_2) ppm.

$^{13}\text{C}\{^1\text{H}\}$ NMR ($\text{THF-}d_8$, 125.77 MHz, 300 K): δ 180.60 (tm, $^1J_{\text{F-C}} = 66$ Hz, *ortho-C*), 147.38 (ddm, $^1J_{\text{F-C}} = 227$ Hz, $^2J_{\text{F-C}} = 25$ Hz, *para-C*), 140.55 (ddm, $^1J_{\text{F-C}} = 258$ Hz, *meta-C*), 102.30 (td, $^2J_{\text{F-C}} = 23$ Hz, $^3J_{\text{F-C}} = 3$ Hz, *ipso-C*) 67.98 (s, CH_2) ppm.

^{19}F NMR ($\text{THF-}d_8$, 470.52 MHz, 300 K): δ -116.77 (m, 4F, *orto-C* $_6\text{F}_5$), -157.89 (t, 2F, $^3J_{\text{F-F}} = 19.8$ Hz, *para-C* $_6\text{F}_5$), -161.54 (m, 4F, *meta-C* $_6\text{F}_5$) ppm.

$^{207}\text{Pb}\{^1\text{H}\}$ NMR ($\text{THF-}d_8$, 83.96 MHz, 300 K): δ 2541 (s) ppm.

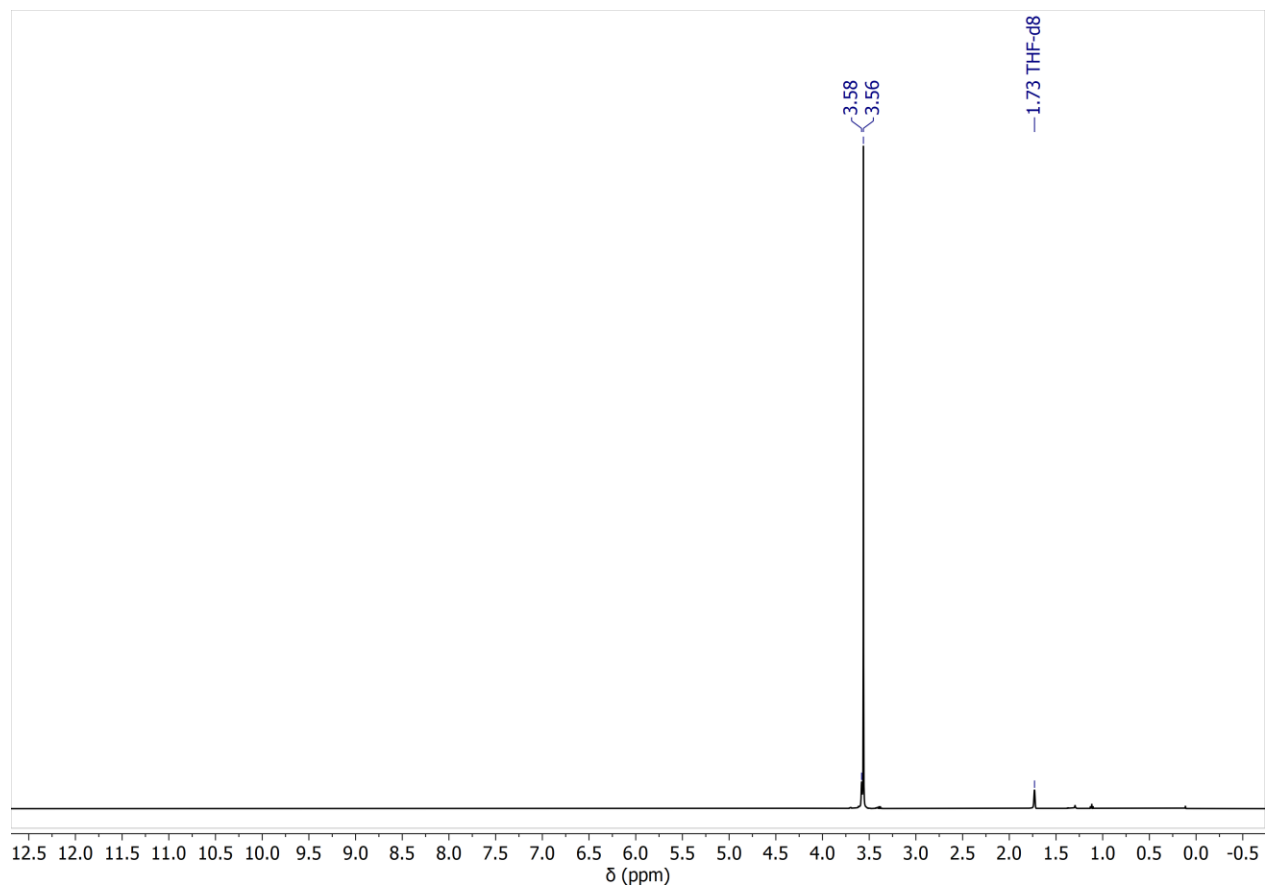


Figure S7. ¹H NMR spectrum (THF-*d*₈, 500.13 MHz, 300 K) of [Pb(C₆F₅)₂(dx)]_∞ (**2**).

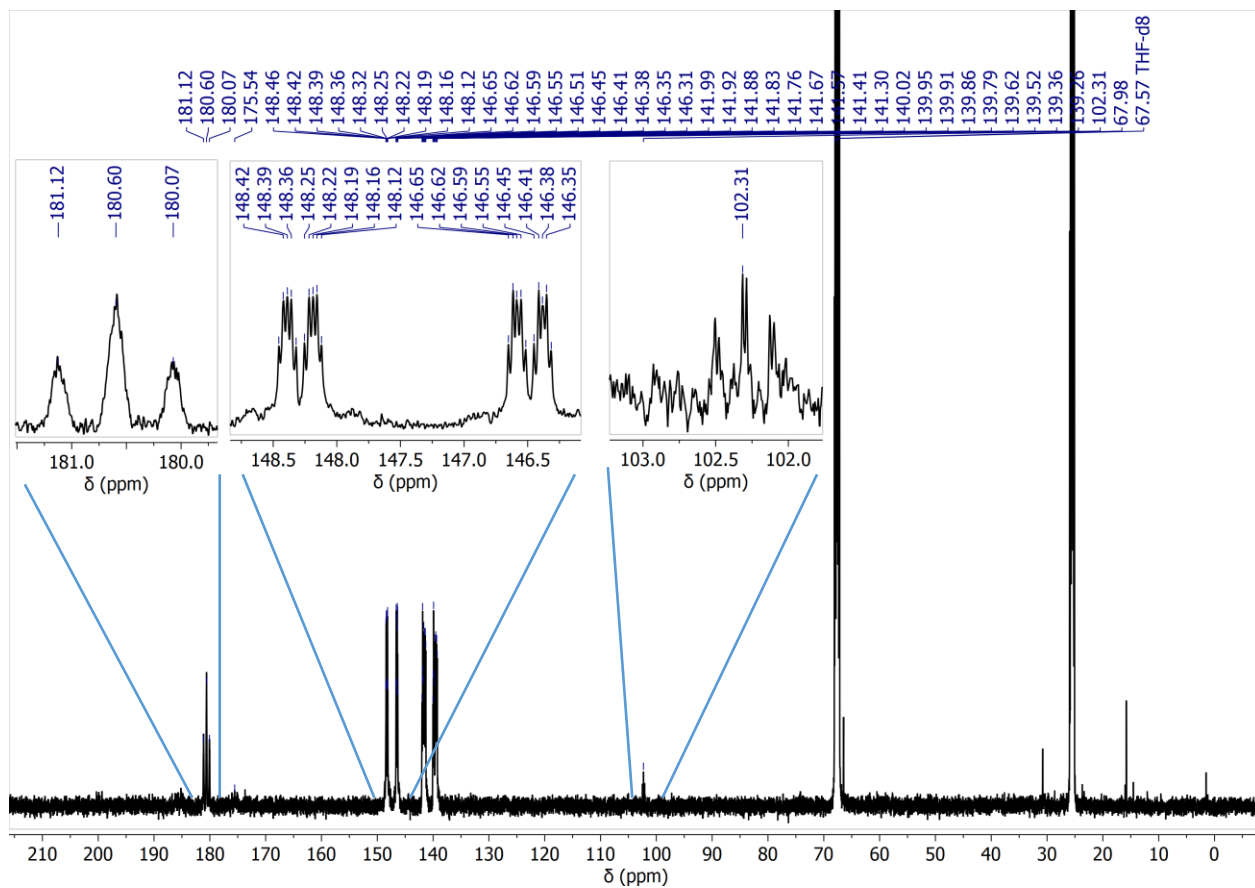


Figure S8. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (THF- d_8 , 125.77 MHz, 300 K) of $[\text{Pb}(\text{C}_6\text{F}_5)_2(\text{dx})]_\infty$ (**2**).

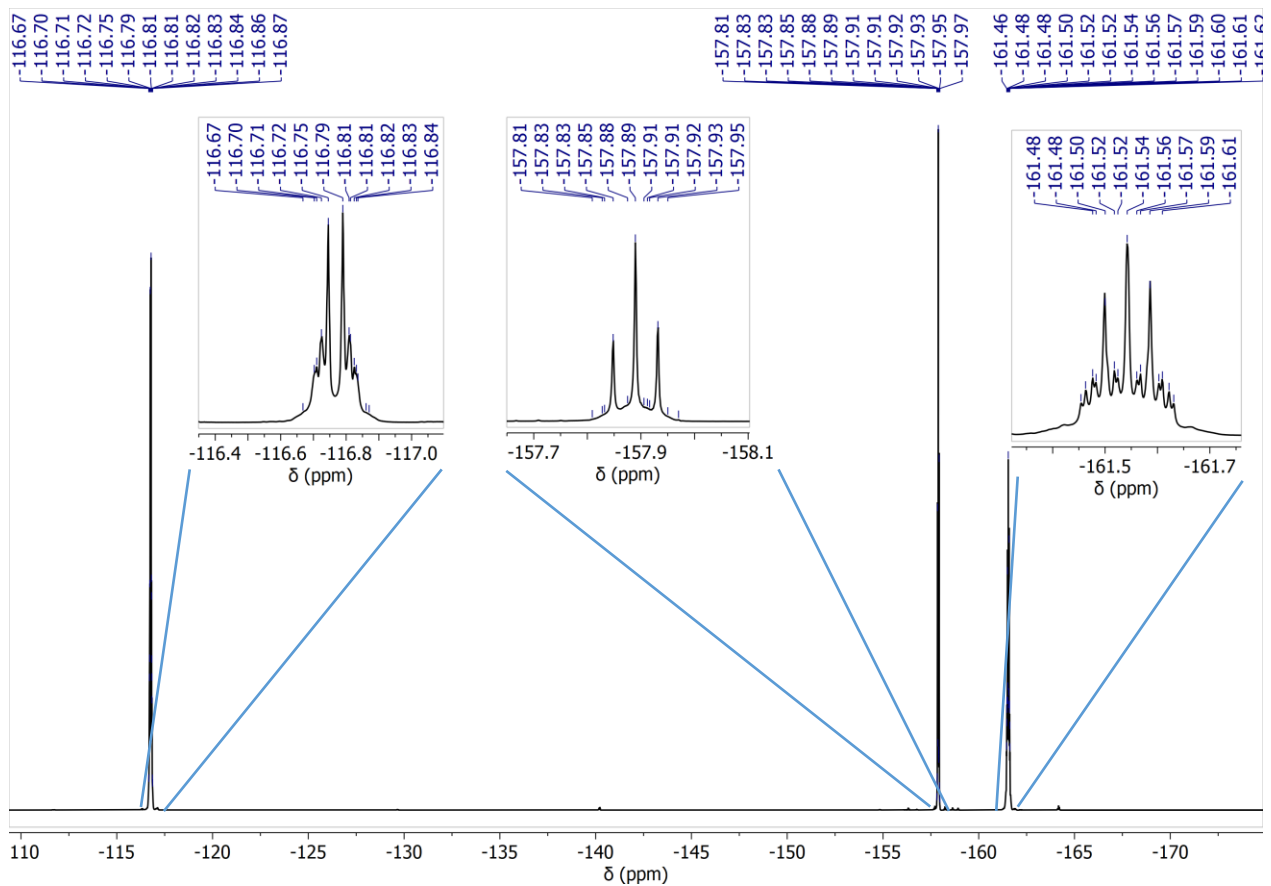


Figure S9. ^{19}F NMR spectrum ($\text{THF-}d_8$, 470.52 MHz, 300 K) of $[\text{Pb}(\text{C}_6\text{F}_5)_2(\text{dx})]_\infty$ (2).

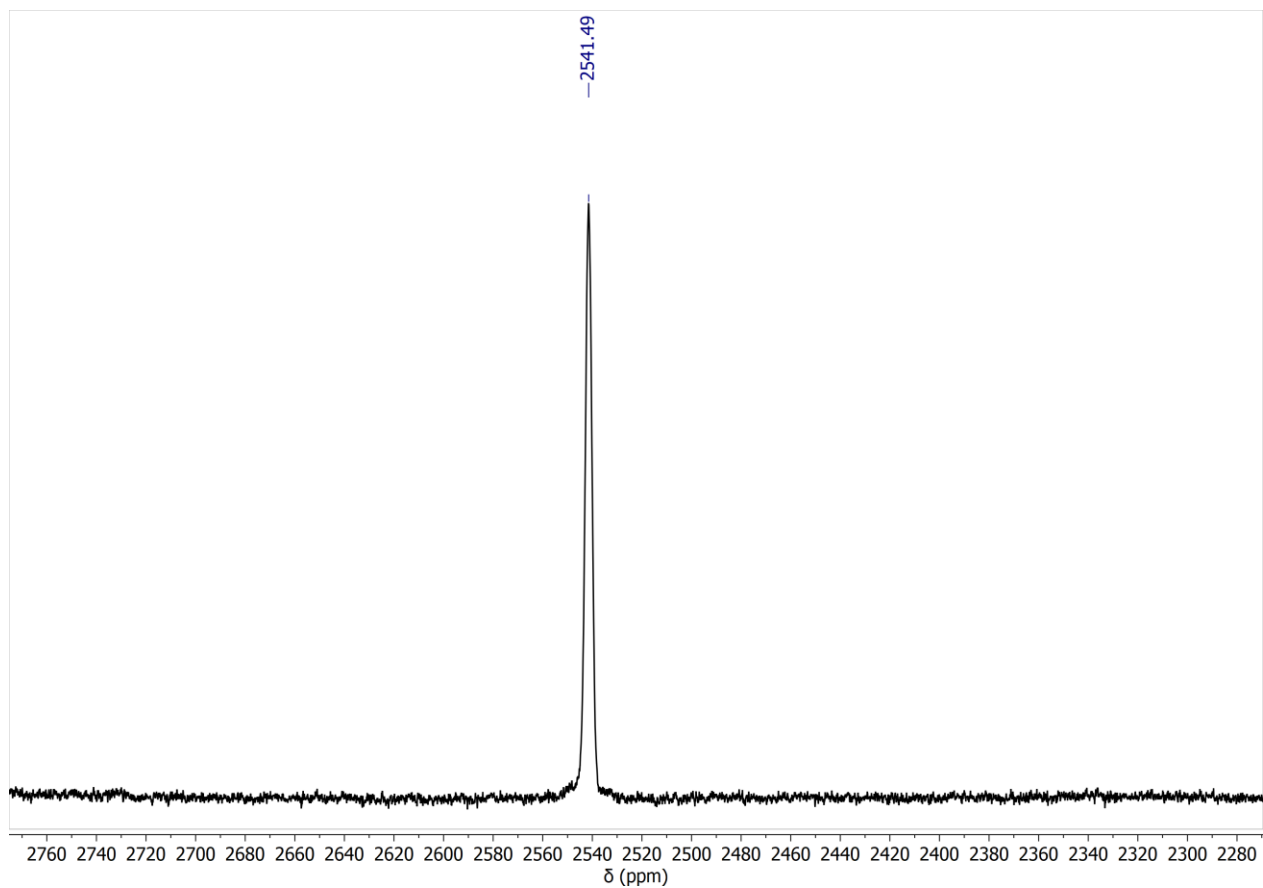
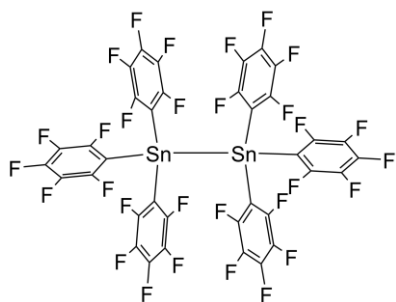


Figure S10. ^{207}Pb NMR spectrum (THF- d_8 , 83.92 MHz, 300 K) of $[\text{Pb}(\text{C}_6\text{F}_5)_2(\text{dx})]_\infty$ (**2**).

Synthesis of $[(C_6F_5)_3SnSn(C_6F_5)_3]$ (3)



A dark-brown solution of C_6F_5MgBr in Et_2O (2.861 g, 19 mL, 0.55 M, 10.55 mmol) was added dropwise for 20 minutes, to a slurry of $SnCl_2$ (1.000 g, 5.27 mmol) in Et_2O (20 mL) at $-78\text{ }^\circ\text{C}$. After 2 h, the cold bath was removed and the reaction mixture was left under stirring to reach room temperature overnight. The crude was filtered to give a clear brown solution which was concentrated to half of its volume and stored

at $-35\text{ }^\circ\text{C}$. pale brown crystals of $[(C_6F_5)_3SnSn(C_6F_5)_3]$ were isolated after one day, 0.770 g (35%).

$^{13}\text{C}\{^1\text{H}\}$ NMR ($\text{THF-}d_8$, 100.62 MHz, 300 K): δ 148.01 (dm, $^1J_{\text{F-C}} = 245\text{ Hz}$, *ortho-C*), 142.62 (dm, $^1J_{\text{F-C}} = 249\text{ Hz}$, *para-C*), 137.88 (dm, $^1J_{\text{F-C}} = 247\text{ Hz}$, *meta-C*), 121.86 (tm, $^2J_{\text{F-C}} = 38\text{ Hz}$, *ipso-C*) ppm.

^{19}F NMR ($\text{THF-}d_8$, 376.44 MHz, 300 K): δ -123.28 (dd, 12F, $^3J_{\text{F-F}} = 21.2\text{ Hz}$, $^4J_{\text{F-F}} = 5.0\text{ Hz}$, $^3J_{\text{F-Sn}} = 111\text{ Hz}$, *ortho-}C_6F_5*), -157.11 (t, 6F, $^3J_{\text{F-F}} = 19.7\text{ Hz}$, *para-}C_6F_5*), -163.65 (m, 12F, *meta-}C_6F_5*) ppm.

$^{119}\text{Sn}\{^1\text{H}\}$ NMR ($\text{THF-}d_8$, 149.14 MHz, 300 K): δ 478 (br) ppm.

^{19}F NMR (CDCl_3 , 376.47 MHz, 300 K): δ -121.50 (d, 12F, $^3J_{\text{F-F}} = 18.0\text{ Hz}$, *ortho-}C_6F_5*), -144.91 (t, 6F, $^3J_{\text{F-F}} = 20.0\text{ Hz}$, *para-}C_6F_5*), -157.02 (m, 12F, *meta-}C_6F_5*) ppm.

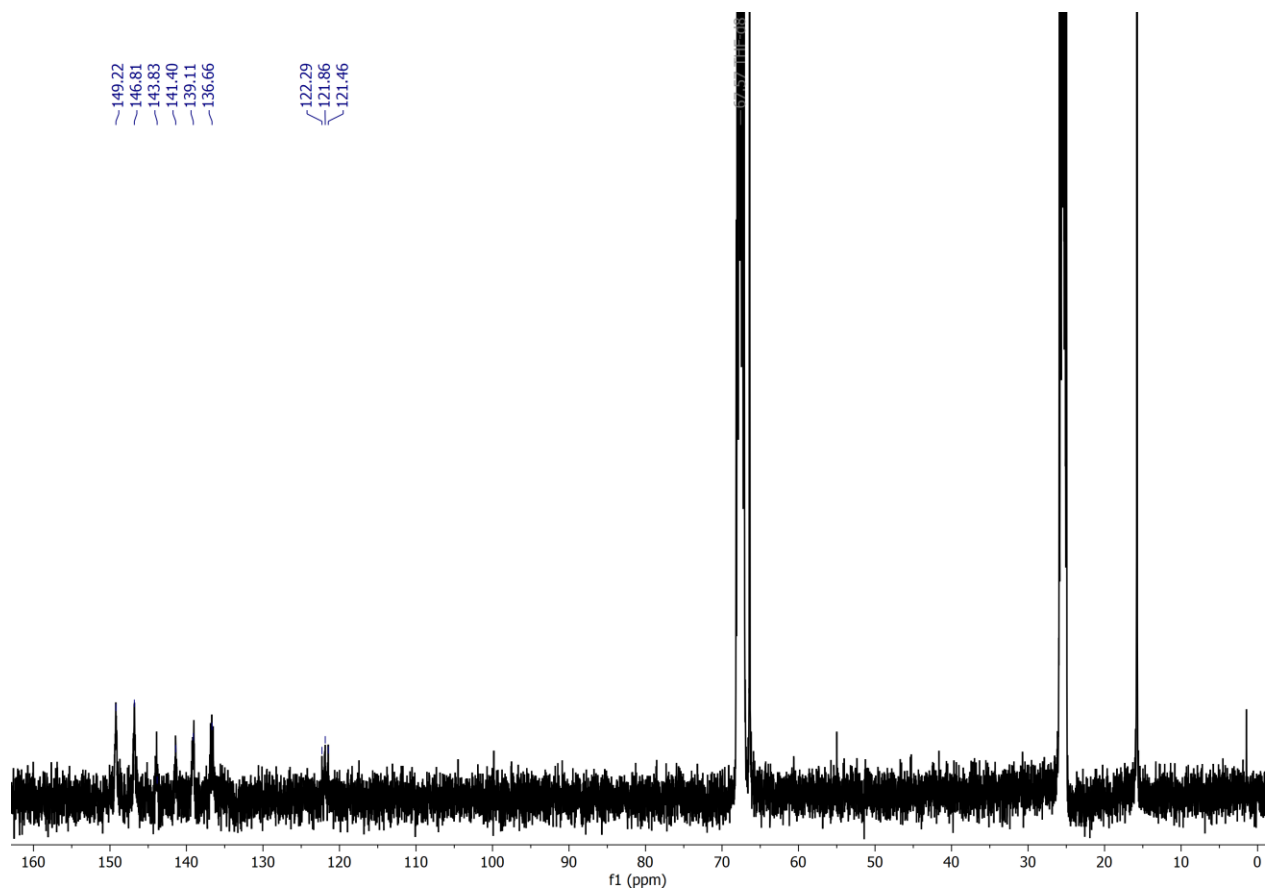


Figure S11. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum ($\text{THF-}d_8$, 300 K, 100.62 MHz) of $[(\text{C}_6\text{F}_5)_3\text{SnSn}(\text{C}_6\text{F}_5)_3]$ (**3**)

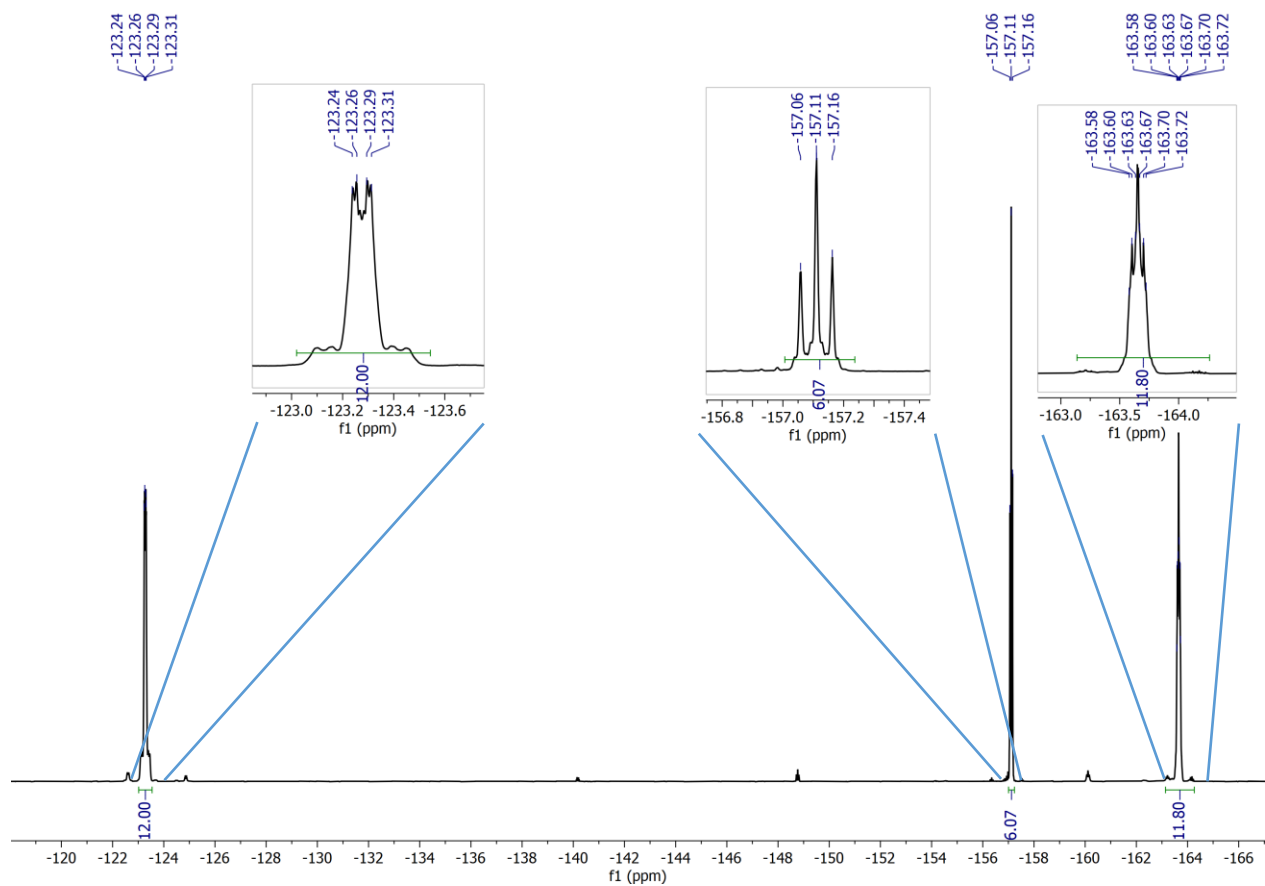


Figure S12. ^{19}F NMR spectrum ($\text{THF-}d_8$, 300 K, 376.44 MHz) of $[(\text{C}_6\text{F}_5)_3\text{SnSn}(\text{C}_6\text{F}_5)_3]$ (**3**).

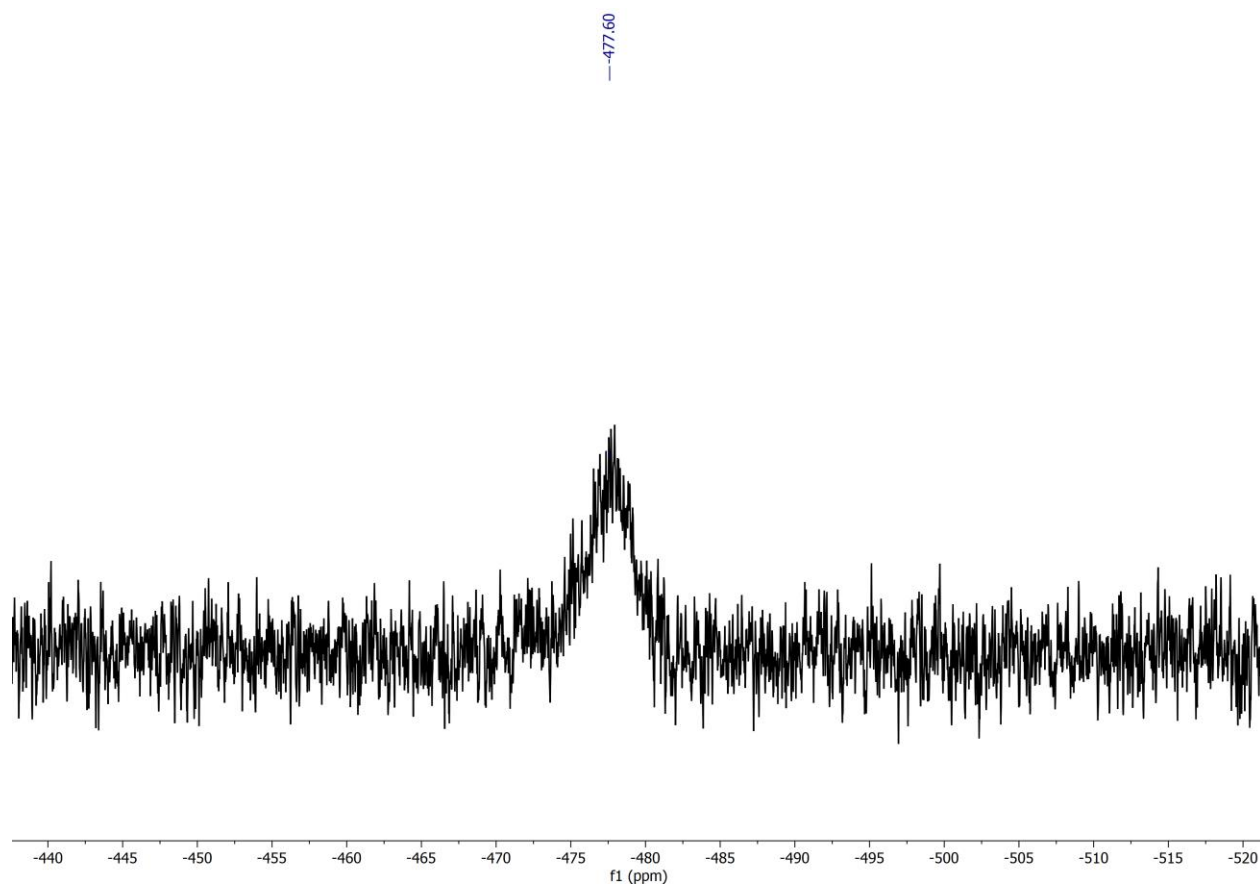


Figure S13. $^{119}\text{Sn}\{^1\text{H}\}$ NMR spectrum (THF- d_8 , 149.14 MHz, 300 K) of $[(\text{C}_6\text{F}_5)_3\text{SnSn}(\text{C}_6\text{F}_5)_3]$ (**3**).

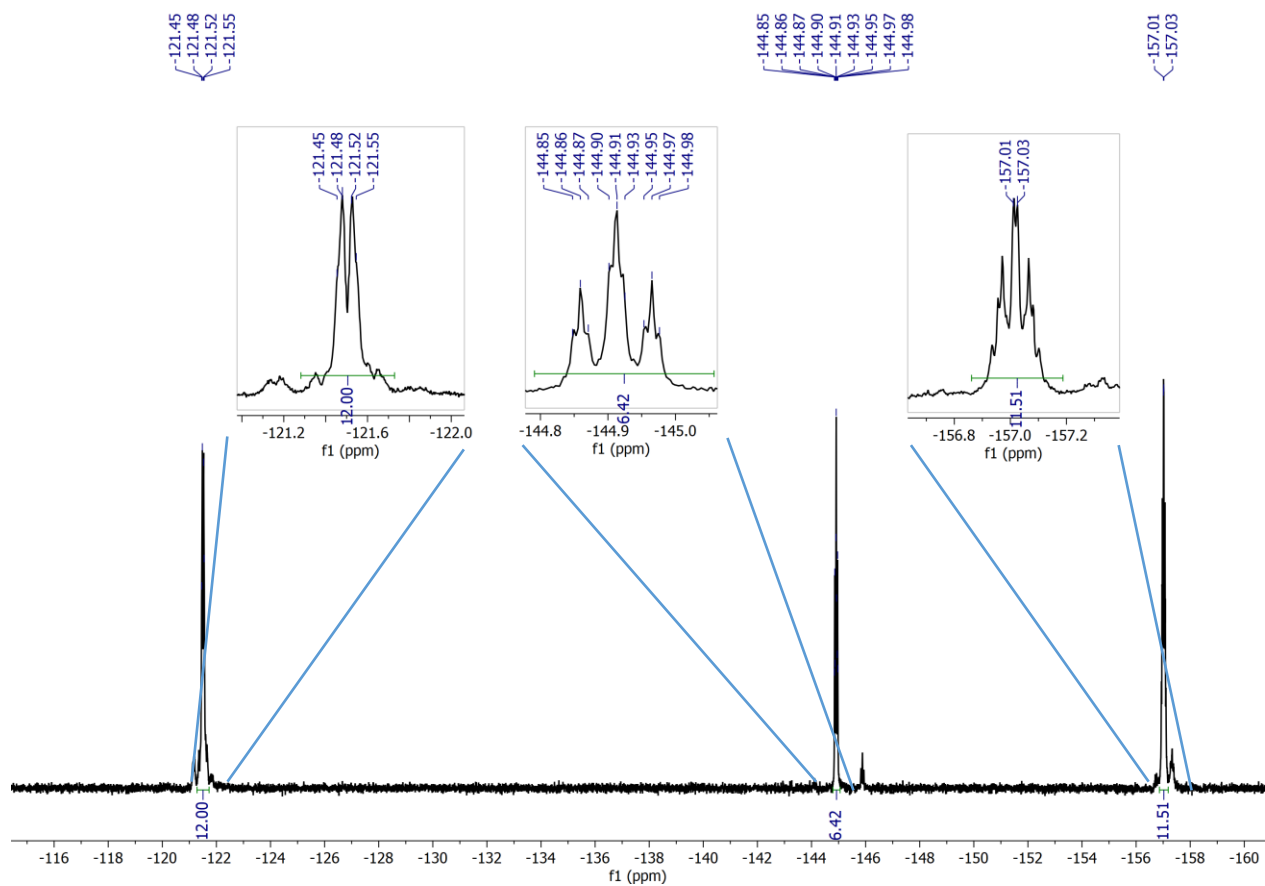


Figure S14. ^{19}F NMR spectrum (CDCl_3 , 300 K, 376.47 MHz) of $[(\text{C}_6\text{F}_5)_3\text{SnSn}(\text{C}_6\text{F}_5)_3]$ (**3**).

Observation. The ^{19}F (CDCl_3) chemical shifts found for $[(\text{C}_6\text{F}_5)_3\text{SnSn}(\text{C}_6\text{F}_5)_3]$ were different that those reported by López-de-Luzuriaga.^[4]

X-ray diffraction crystallography

[Mg₃(μ₂-Br)₃(μ₃-Cl)₂(OEt₂)₆]⁺[Pb(C₆F₅)₃]⁻ (**1**): (C₁₈F₁₅Pb · C₂₄H₆₀Br_{3.44}Cl_{1.56}); M = 1554.19. A suitable crystal for X-ray diffraction single crystal experiment (colourless block, dimensions = 0.380 x 0.320 x 0.180 mm) was selected and mounted with a cryoloop on the goniometer head of a D8 Venture (Bruker-AXS) diffractometer equipped with a CMOS-PHOTON70 detector, using Mo-Kα radiation (λ = 0.71073 Å, multilayer monochromator) at T = 168(2) K. Crystal structure has been described in triclinic symmetry and *P* 1 (I.T.#2) centric space group (*R*_{int} = 0.0635). Cell parameters have been refined as follows: a = 13.228(3), b = 13.887(3), c = 17.570(4) Å, α = 69.038(8), β = 85.126(6), γ = 85.016(7)°, V = 2997.8(12) Å³. Number of formula unit Z is equal to 2 and calculated density d and absorption coefficient μ values are 1.722 g.cm⁻³ and 5.293 mm⁻¹ respectively. Crystal structure was solved by dual-space algorithm using *SHELXT* program,^[5] and then refined with full-matrix least-squares methods based on F² (*SHELXL* program^[6]). The contribution of the disordered solvents to the calculated structure factors was estimated following the BYPASS algorithm,^[7] implemented as the SQUEEZE option in PLATON.^[8] 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 F² with 13776 unique intensities and 640 parameters converged at ωR(F²) = 0.1394 (R_F = 0.0564) for 9556 observed reflections with I > 2σ. CCDC number: 2400987.

[Pb(C₆F₅)₂(dx)]_∞ (**2**): (C₁₆H₈F₁₀O₂Pb); M = 629.41. A suitable crystal for X-ray diffraction single crystal experiment (colourless block, dimensions = 0.190 x 0.120 x 0.080 mm) was selected and mounted with a cryoloop on the goniometer head of a D8 Venture (Bruker-AXS) diffractometer equipped with a CMOS-PHOTON70 detector, using Mo- Kα 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 (*R*_{int} = 0.0322). Cell parameters have been refined as follows: a = 7.8568(8), b = 7.9859(8), c = 15.6528(15) Å, α = 95.693(3), β = 91.114(4), γ = 115.308(3)°, V = 881.38(15) Å³. Number of formula unit Z is equal to 2 and calculated density d and absorption coefficient μ values are 2.372 g.cm⁻³ and 9.682 mm⁻¹ respectively. Crystal structure was solved by dual-space algorithm using *SHELXT* program,^[5] and then refined with full-matrix least-squares methods based on F² (*SHELXL* program^[6]). 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 F² with 3994 unique intensities and 263 parameters converged at ωR(F²) = 0.0572 (R_F = 0.0238) for 3859 observed reflections with I > 2σ. In the CHECKCIF procedure, no A-type and B-type meaningful alerts has remained. CCDC number: 2400988.

[Pb(C₆F₅)₄]: (C₂₄F₂₀Pb); M = 875.43. A suitable crystal for X-ray diffraction single crystal experiment (colourless block, dimensions = 0.270 x 0.220 x 0.090 mm) was selected and mounted with a cryoloop on the goniometer head of a D8 Venture (Bruker-AXS) diffractometer equipped with a CMOS-PHOTON70 detector, using Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$, multilayer monochromator) at T = 150(2) K. Crystal structure has been described in orthorhombic symmetry and P b c a (I.T.#61) centric space group ($R_{\text{int}} = 0.0288$). Cell parameters have been refined as follows: a = 7.9565(4), b = 17.7225(9), c = 34.0045(17) \AA , V = 4794.9(4) \AA^3 . Number of formula unit Z is equal to 8 and calculated density d and absorption coefficient μ values are 2.425 g.cm⁻³ and 7.209 mm⁻¹ respectively. Crystal structure was solved by dual-space algorithm using SHELXT program,^[5] and then refined with full-matrix least-squares methods based on F² (SHELXL program^[6]). All atoms were refined with anisotropic atomic displacement parameters. A final refinement on F² with 5831 unique intensities and 407 parameters converged at $\omega R(F^2) = 0.1084$ ($R_F = 0.0326$) for 5067 observed reflections with $I > 2\sigma$. In the CHECKCIF procedure, no A-type and B-type meaningful alerts has remained. CCDC number: 2400989.

[(C₆F₅)₃SnSn(C₆F₅)₃](dx): (C₃₆F₃₀Sn₂ · C₄H₈O₂); M = 1327.84. A suitable crystal for X-ray diffraction single crystal experiment (colourless block, dimensions = 0.170 x 0.070 x 0.040 mm) was selected and mounted with a cryoloop on the goniometer head of a D8 Venture (Bruker-AXS) diffractometer equipped with a CMOS-PHOTON70 detector, using Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$, multilayer monochromator) at T = 150(2) K. Crystal structure has been described in triclinic symmetry and P 1 (I.T.#2) centric space group ($R_{\text{int}} = 0.0298$). Cell parameters have been refined as follows: a = 9.9952(10), b = 10.1428(11), c = 10.8362(12) \AA , $\alpha = 95.488(4)$, $\beta = 95.241(4)$, $\gamma = 112.298(4)^\circ$, V = 1002.00(19) \AA^3 . Number of formula unit Z is equal to 1 and calculated density d and absorption coefficient μ values are 2.201 g.cm⁻³ and 1.427 mm⁻¹ respectively. Crystal structure was solved by dual-space algorithm using SHELXT program,^[5] and then refined with full-matrix least-squares methods based on F² (SHELXL program^[6]). 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 F² with 4532 unique intensities and 334 parameters converged at $\omega R(F^2) = 0.0983$ ($R_F = 0.0421$) for 3911 observed reflections with $I > 2\sigma$. In the CHECKCIF procedure, no A-type and B-type meaningful alerts has remained. CCDC number: 2400990.

[Mg₂Br₂(DMAP)₂]: (C₁₄H₂₀Br₂MgN₄); M = 428.47. A suitable crystal for X-ray diffraction single crystal experiment (colourless prism, dimensions = 0.070 x 0.040 x 0.030 mm) was selected and mounted with a cryoloop on the goniometer head of a D8 Venture (Bruker-AXS) diffractometer equipped with a CMOS-PHOTON70 detector, using Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$, multilayer monochromator) at T = 150(2) K. Crystal structure has been described in orthorhombic symmetry and P c c n (I.T.#56) centric space group ($R_{\text{int}} = 0.1237$). Cell parameters have been refined as follows: a = 14.220(4), b = 14.478(4), c = 17.924(4) \AA , V = 3690.2(17) \AA^3 . Number of formula unit Z is equal to 8 and calculated density d and absorption coefficient μ values are 1.542 g.cm⁻³ and 4.426 mm⁻¹ respectively. Crystal structure was solved by dual-space algorithm using SHELXT program,^[5] and then refined with full-matrix least-squares methods based on F² (SHELXL program^[6]). 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 F² with 4193 unique intensities and 195 parameters converged at $\omega R(F^2) = 0.1116$ ($R_F = 0.0586$) for 1938 observed reflections with $I > 2\sigma$. In the CHECKCIF procedure, no A-type and B-type meaningful alerts has remained. CCDC number: 2400991.

Table S1. Crystal data and structure refinement for **1** and **2**.

	[Mg ₃ (μ ₂ -Br) ₃ (μ ₃ -Cl) ₂ (OEt ₂) ₆] ⁺ [Pb(C ₆ F ₅) ₃] ⁻ (1)	[Pb(C ₆ F ₅) ₂ (dx)] _∞ (2)
CCDC number	2400987	2400988
Formula	C ₄₂ H ₅₈ Br _{3.44} Cl _{1.56} F ₁₅ Mg ₃ O ₆ Pb	C ₁₆ H ₈ F ₁₀ O ₂ Pb
Mol. wt [g/mol]	1554.19	629.41
Crystal system	triclinic	triclinic
Space group	<i>P</i> -1	<i>P</i> -1
a [Å]	13.228(3)	7.8568(8)
b [Å]	13.887(3)	7.9859(8)
c [Å]	17.570(4)	15.6258(15)
α [°]	69.038(8)	95.693(3)
β [°]	85.126(6)	91.114(4)
γ [°]	85.016(7)	115.308(3)
V [Å ³]	2997.8(12)	881.38(15)
Z	2	2
Density (g cm ⁻³)	1.722	2.372
Abs. coeff., (mm ⁻¹)	5.293	9.682
F(000)	1516	584
Crystal size, mm	0.380 × 0.320 × 0.180	0.190 × 0.120 × 0.080
θ range [°]	2.041 to 27.6183	2.622 to 27.501
Limiting indices	-17 < h < 17 -18 < k < 17 -22 < l < 22	-10 < h < 10 -10 < k < 10 -20 < l < 18
R(int)	0.0635	0.0322
Reflections collected	44671 / 13776	10064 / 3994
Refl. Unique [I > 2σ (I)]	9556	3859
Completeness to θ	0.989	0.985
Data/ restraints/ param.	13776 / 0 / 640	3994 / 0 / 263
Goodness-of-fit	1.032	1.036
R ₁ [I > 2σ (I)] (all data)	0.0564 (0.0957)	0.0238 (0.0252)
wR ₂ [I > 2σ (I)] (all data)	0.1394 (0.1594)	0.0572 (0.0578)
Largest diff. [e Å ⁻³]	1.753 and -2.203	1.806 and -1.857

Table S2. Crystal data and structure refinement for [Pb(C₆F₅)₄], [(C₆F₅)₃SnSn(C₆F₅)₃]·(dx) · (dx) and [MgBr₂(DMAP)₂].

	[Pb(C ₆ F ₅) ₄]	[(C ₆ F ₅) ₃ SnSn(C ₆ F ₅) ₃]·(dx)	[MgBr ₂ (DMAP) ₂]
CCDC number	2400989	2400990	2400991
Formula	C ₂₄ F ₂₀ Pb	C ₄₀ H ₈ F ₃₀ O ₂ Sn ₂	C ₁₄ H ₂₀ Br ₂ MgN ₄
Mol. wt [g/mol]	875.43	1327.84	428.47
Crystal system	orthorhombic	triclinic	orthorhombic
Space group	<i>P b c a</i>	<i>P</i> -1	<i>P c c n</i>
a [Å]	7.9565(4)	9.9952(10)	14.220(4)
b [Å]	17.7225(9)	10.1428(11)	14.478(4)
c [Å]	34.0045(17)	10.8362(12)	17.924(4)
α [°]	90	95.488(4)	90
β [°]	90	95.241(4)	90
γ [°]	90	112.298(4)	90
V [Å ³]	4794.9(4)	1002.00(19)	3690.2(17)
Z	8	1	8
Density (g cm ⁻³)	2.425	2.201	1.542
Abs. coeff., (mm ⁻¹)	7.209	1.427	4.426
F(000)	3248	634	1712
Crystal size, mm	0.270 × 0.220 ×	0.170 × 0.070 × 0.040	0.070 × 0.040 ×
θ range [°]	2.133 to 27.503	2.436 to 27.513	2.007 to 27.479
Limiting indices	-7 < h < 10 -23 < k < 23 -44 < l < 44	-12 < h < 11 -13 < k < 13 -14 < l < 14	-18 < h < 15 -18 < k < 18 -22 < l < 20
R(int)	0.0288	0.0298	0.1237
Reflections collected	38223 / 5831	10571 / 4532	13800 / 4193
Refl. Unique [I > 2σ (I)]	5067	3911	1938
Completeness to θ	0.999	0.984	0.988
Data/ restraints/ param.	5831 / 0 / 407	4532 / 0 / 334	4193 / 0 / 195
Goodness-of-fit	1.440	1.043	0.978
R ₁ [I > 2σ (I)] (all data)	0.0326 (0.0386)	0.0421 (0.0532)	0.0586 (0.1598)
wR ₂ [I > 2σ (I)] (all data)	0.1084 (0.1116)	0.0983 (0.1095)	0.1116 (0.1422)
Largest diff. [e Å ⁻³]	3.860 and -5.818	2.298 and -1.676	0.629 to -0.520

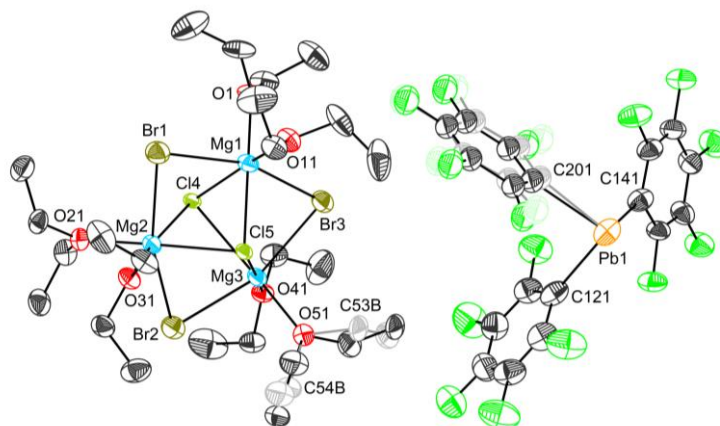


Figure S15. ORTEP representation of the molecular solid-state structure of **1**. Ellipsoids at the 50% probability level. H atoms omitted for clarity.

Table S3. Selected interatomic distances and bond angles of **1**.

Interatomic distances (Å)				Bond angles (°)	
Mg1–O1	2.038(5)	Pb1–C201	2.291(18)	C201–Pb1–C121	89.2(6)
Mg1–O11	2.059(5)	Pb1–C121	2.341(9)	C201–Pb1–C141	95.6(7)
Mg1–Cl5	2.524(3)	Pb1–C141	2.370(8)	C121–Pb1–C141	97.3(3)
Mg1–Br1	2.657(2)	Pb1–C101	2.415(9)	C121–Pb1–C101	86.0(5)
Mg1–Br3	2.663(2)			C141–Pb1–C101	100.0(6)
Mg1–Cl4	2.683(2)				
Mg1–Mg2	3.326(3)				
Mg1–Mg3	3.388(3)				
Mg2–O31	2.049(5)				
Mg2–O21	2.054(5)				
Mg2–Cl5	2.589(3)				
Mg2–Br2	2.610(2)				
Mg2–Cl4	2.620(3)				
Mg2–Br1	2.639(2)				
Mg2–Mg3	3.332(3)				
Mg3–O41	2.040(5)				
Mg3–O51	2.056(5)				
Mg3–Cl5	2.579(3)				
Mg3–Br2	2.608(2)				
Mg3–Br3	2.649(2)				
Mg3–Cl4	2.697(2)				

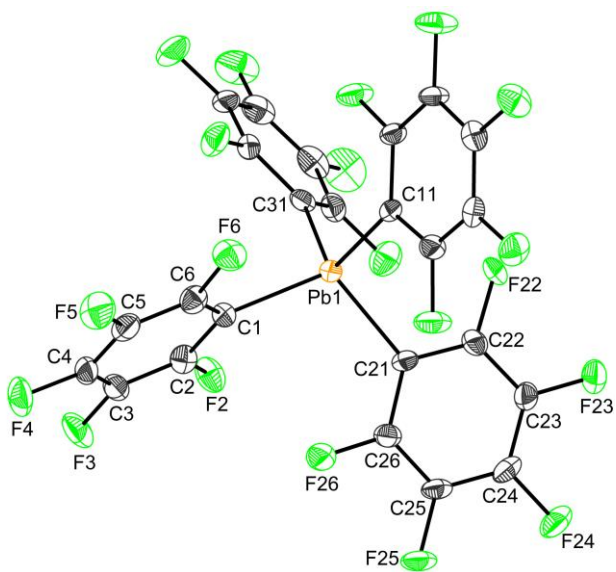
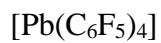


Figure S16. ORTEP representation of the new polymorph structure of [Pb(C₆F₅)₄]. Ellipsoids at the 50% probability level. Selected interatomic distances (Å): Pb1–C21 = 2.187(4), Pb1–C1 = 2.193(4), Pb1–C31 = 2.193(4), Pb1–C11 = 2.200(4); and bond angles (°): C21–Pb1–C1 = 110.80(16), C21–Pb1–C31 = 111.50(15), C1–Pb1–C31 = 104.08(16), C21–Pb1–C11 = 104.86(15), C1–Pb1–C11 = 113.51(15), C31–Pb1–C11 = 112.26(15).

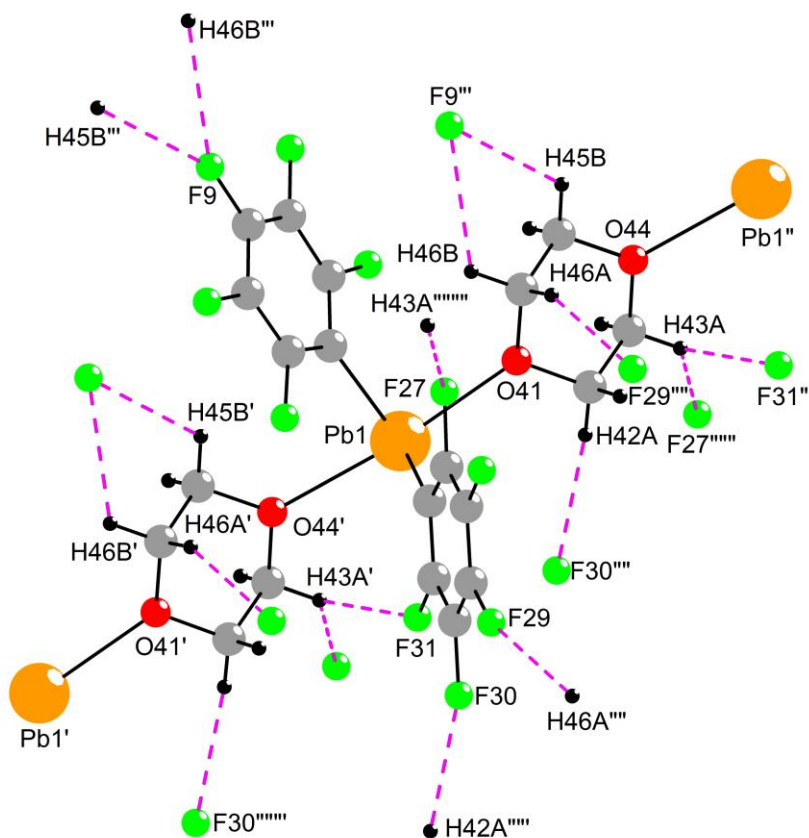
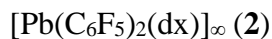


Figure S17. Intermolecular C–H···F contacts in the crystal of **2**. [symmetry equivalent atoms ($-I+x, y, z$), ($I+x, y, z$), ($I-x, I-y, -z$), ($I-x, I-y, I-z$), ($-x, -y, I-z$), ($x, -I+y, z$), ($-I-x, -y, I-z$), and ($x, I+y, z$) are given by ', ", "'", '"', ''', '''', ''''', '''''' and '''''''' respectively].

$$\sum r_{\text{vdW}}(\text{F,H}) = 2.66 \text{ \AA}^{[8]}$$

Intermolecular distances:	F9···H45B'''	2.50 Å
	F9···H46B'''	2.65 Å
	F27···H43''''''''	2.63 Å
	F29···H46''''	2.50 Å
	F30···H42A''''	2.51 Å
	F31···H43A'	2.58 Å

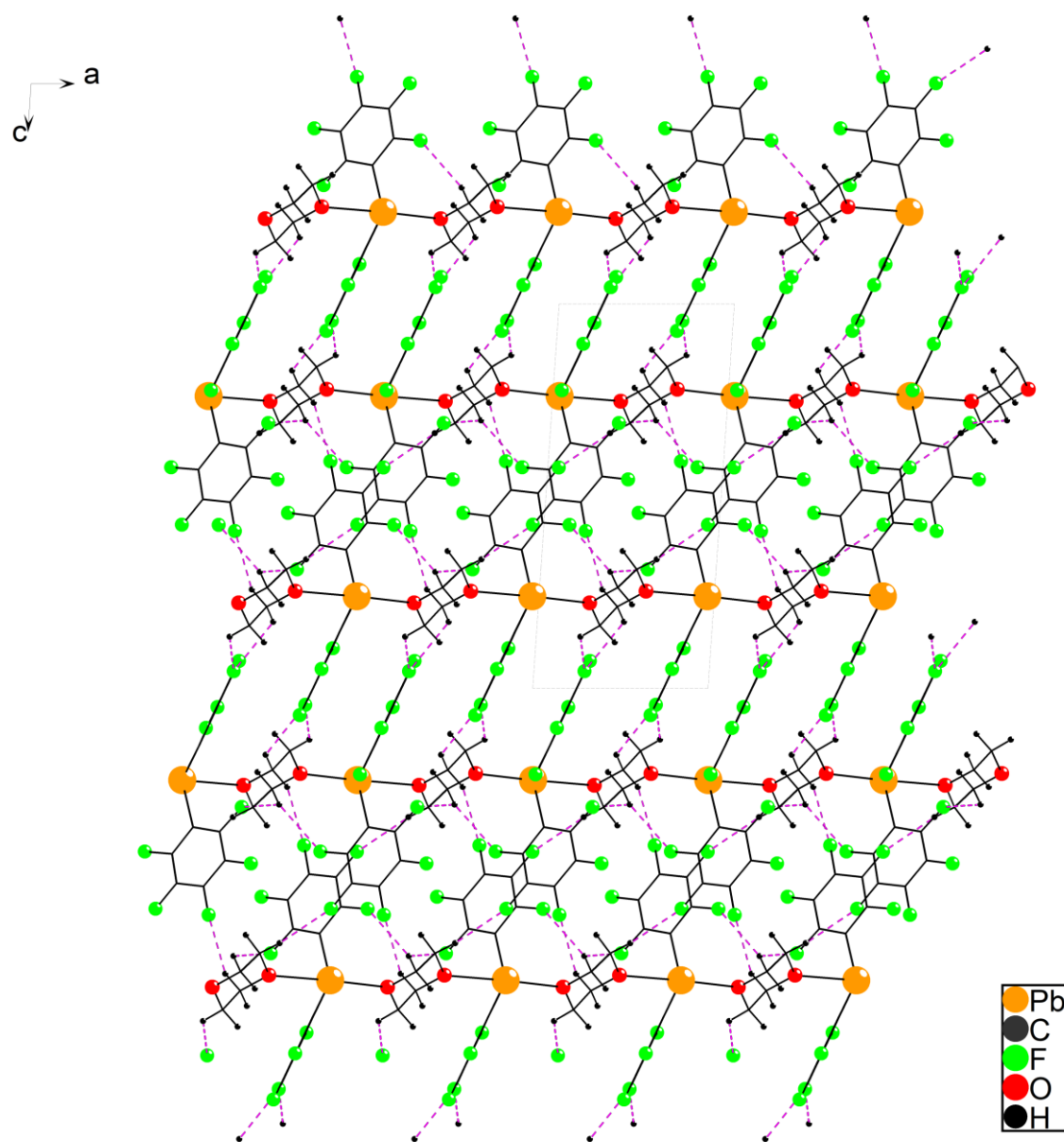


Figure S18. View along *b* axis of the polymer structure of **2**, showing parallel chain-like polymers connected via multiple C-H...F interactions.

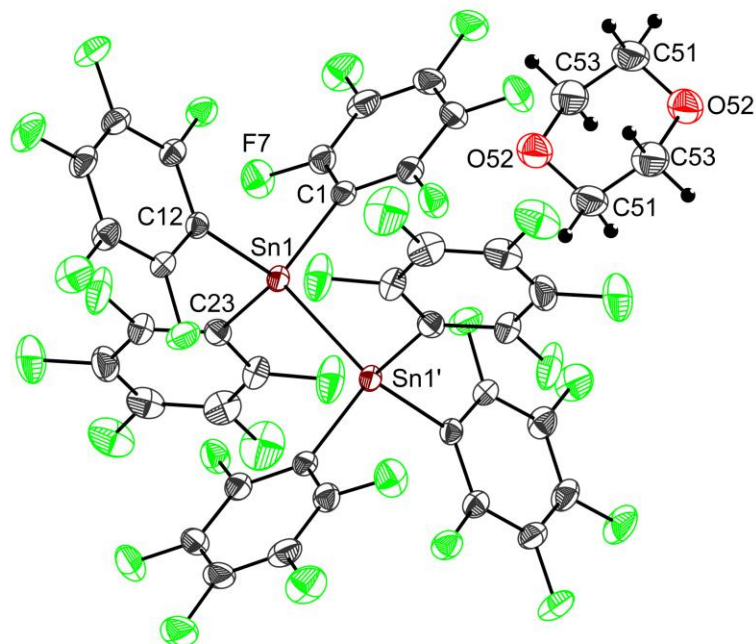
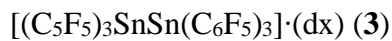


Figure S19. ORTEP representation of the molecular solid-state structure of $[(C_5F_5)_3SnSn(C_6F_5)_3] \cdot (dx)$ (**3**). Ellipsoids at the 50% probability level. Selected interatomic distances (Å): Sn1–C1 = 2.147(4), Sn1–C23 = 2.132(4), Sn1–C12 = 2.152(4), Sn1–Sn1' = 2.7855(6); and bond angles (°): C1–Sn1–C12 = 108.51(16), C1–Sn1–C23 = 105.82(17), C1–Sn1–Sn1' = 110.27(11), C12–Sn1–C23 = 106.89(16), C12–Sn1–Sn1' = 113.38(11), C23–Sn1–Sn1' = 111.62(12).

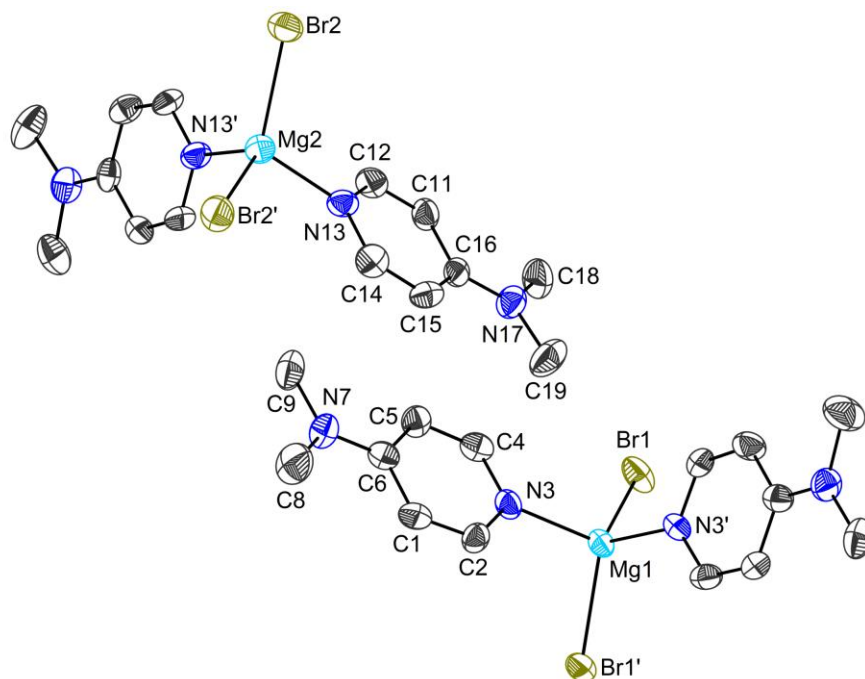
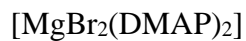


Figure S20. ORTEP representation of the molecular solid-state structure of [MgBr₂(DMAP)₂]. Ellipsoids at the 50% probability level. Hydrogen atoms omitted for clarity.

Table S4. Selected interatomic distances (Å) and bond angles (°) of [MgBr₂(DMAP)₂]

Mg1–Br1	2.4490(16)	Mg2–Br2	2.4363(18)
Mg1–N3	2.087(5)	Mg2–N13	2.068(6)
N3–Mg1–Br1	109.56(15)	N13–Mg2–Br2	112.93(15)
N3–Mg1–Br1'	104.69(15)	N13–Mg2–Br2'	106.97(15)
N3–Mg1–N3'	108.3(3)	N13–Mg2–N13'	98.2(3)
Br1–Mg1–Br1'	119.70(12)	Br2–Mg2–Br2'	117.26(13)

References

- 1 T. Heidemann, S. Mathur, *Eur. J. Inorg. Chem.*, 2014, 506.
- 2 B. Wrakmeyer, *Annu. Rep. NMR Spectrosc.*, 1985, **16**, 73.
- 3 T. M. Klapötke, B. Krumm, M. Niemitz, K. Polborn and C. M. Rienäcker, *J. Fluor. Chem.*, 2000, **104**, 129.
- 4 R. V. Bojan, J. M. López-de-Luzuriaga, M. Monge and M. E. Olmos, *J. Organomet. Chem.*, 2010, **695**, 2385.
- 5 G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Adv.*, 2015, **71**, 3.
- 6 G. M. Sheldrick, *Acta Crystallogr., Sect. C: Struct. Chem.*, 2015, **71**, 3.
- 7 P. van der Sluis and A. L. Spek, *Acta Crystallogr., Sect. A: Found. Adv.*, 1990, **46**, 194.
- 8 A. L. Spek, *J. Appl. Cryst.*, 2003, **36**, 7.
- 9 S. Alvarez, *Dalton Trans.*, 2013, **42**, 8617.