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Electronic Supporting Information

to

Facile and Systematic Access to the Least-coordinating WCA $[(R^FO)_3Al{-}F{-}Al(OR^F)_3]^-$ and Its Lewis Basic Brother $[F{-}Al(OR^F)_3]^-$ ($R^F = C(CF_3)_3$)

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Contents:

General Considerations

All reactions were carried out in an inert gas atmosphere of argon, using standard vacuum and Schlenk techniques or a glove box to exclude air and moisture. All solvents and reagents were dried using standard drying agents (CaH_2, P_4O_{10}) and were subsequently distilled into airtight vessels. Solution NMR spectra were recorded on a Bruker Avance II WB 400 MHz, Bruker Avance III HD 300 MHz and a Bruker Avance DPX 200 MHz NMR spectrometer using the software package Bruker Topspin 3.2 for analysis. Samples were prepared in 5 mm NMR tubes and then flame-sealed in vacuo. Resonances are given in ppm and referenced to $SiMe_4$ for the ^1H, ^{13}C and ^{29}Si NMR spectra, to $CFCl_3$ for the ^{19}F NMR spectra and to a 1.1 M solution of $Al(NO_3)_3$ in D_2O for the ^{27}Al NMR spectra. Raman spectra were measured on a Bruker Vertex 70 with a Bruker RAM II module in a range of 50 – 4000 cm^{-1} and analyzed with the OPUS software package. IR spectra were measured on a Bruker Alpha Fourier transform IR spectrometer in a range of 400 – 4000 cm^{-1} using a diamond ATR unit and analyzed with the OPUS software package.

[NMR 1] R. K. Harris, E. D. Becker, S. M. Cabral de Menezes, R. Goodfellow, P. Granger, *Pure Appl. Chem.* **2001**, *73*, 1795.

Single Crystal Diffraction: Obtained single crystals were coated with perfluoroether oil and mounted on 0.1 mm micromounts at the respective crystallization temperature. The crystal structure data were collected from the shock-cooled crystals at 100 K, on a Bruker SMART APEXII QUAZAR CCD area detector diffractometer using Mo-K_α radiation. Data reduction was done with SAINT[1] and scaling of the data and absorption correction was performed by SADABS[2]. The structures were solved by intrinsic phasing using SHELXT[3] and were refined by full matrix least squares minimization on F^2 using all reflections with SHELXL[4] in the ShelXle[5] GUI. In addition, a riding model was used to attribute idealized positions to all hydrogen atoms. The disorder of the OR^F groups in the compounds was treated using DSR.[6] The graphical representations were prepared using the software Mercury 3.6.[7]

[1] *SAINT*, BRUKER-AXS, Madison, Wisconsin, USA, **2013**.
[2] L. Krause, R. Herbst-Irmer, G. M. Sheldrick, D. Stalke, *J. Appl. Cryst.* **2015**, *48*, 3–10.
[3] G. M. Sheldrick, *Acta Cryst. A* **2015**, *71*, 3–8.
[4] G. M. Sheldrick, *Acta Cryst. C* **2015**, *71*, 3–8.
[5] C. B. Hubschle, G. M. Sheldrick and B. Dittrich, *J. Appl. Cryst.* **2011**, *44*, 1281-1284.
[6] D. Kratzert, J. J. Holstein, I. Krossing, *J. Appl. Cryst.* **2015**, *48*, 933–938. *www.xs3.uni-freiburg.de/research/dsr*
[7] C. F. Macrae, P. R. Edgington, P. McCabe, E. Pidcock, G. P. Shields, R. Taylor, M. Towler, J. van de Streek, *J. Appl. Cryst.* **2006**, *39*, 453–457.

Experimental Details

Synthesis of Me_3SiF

A two-necked flask was equipped with a reflux condenser (−30°C), followed by a cooling trap (−78°C). $(NH_4)_2SiF_6$ (20.0 g, 0.11 mmol) was weighed into the flask and suspended in glyme (60 ml). After addition of Me_3SiCl (18.5 ml, 0.14 mmol, 1.3 eq.) the reaction mixture was refluxed for 1 h. Then the reflux condenser was allowed to reach 20°C and the Me_3SiF was distilled into the cooling trap. Then the Me_3SiF was distilled into an airtight vessel (8.1 g, 80 %). In order to remove residual SiF_4, the Me_3SiF was cooled to −40°C. The SiF_4 was then removed in vacuo.

^{1}H-NMR (400.17 MHz, 298 K, CD_2Cl_2): δ = 0.27 (d, $^3J_{H-F}$ = 7.4 Hz, (C**H$_3$**)$_3$SiF) ppm.
^{19}F-NMR (376.49 MHz, 298 K, CD_2Cl_2): δ = –158 (dec, Me_3SiF) ppm.
^{29}Si-NMR (79.50 MHz, 298 K, CD_2Cl_2): δ = 33.3 (d, $^1J_{Si-F}$ = 290 Hz, Me_3**Si**F) ppm.

Synthesis of $Me_3Si{-}F{-}Al(OR^F)_3$

$AlEt_3$ (15 ml, 109 mmol) was dissolved in heptane (120 ml) and cooled to −40°C. Under vigorous stirring with a large (!) stirring bar, HOR^F (30 ml, 215 mmol, 2.0 eq.) was added dropwise (!) to the reaction mixture, while keeping the cooling bath between −40 and −20°C. During the addition of HOR^F, gas evolution (C_2H_6) could be observed and the viscosity of the solution increased and also small amounts of precipitate formed. After complete addition of HOR^F, Me_3SiF (12.5 g, 136 mmol, 1.2 eq.) was condensed onto the reaction mixture at −40°C. The solution was stirred for 5 min. and then more HOR^F (20 ml, 108 mmol, 1.0 eq.) was added slowly. The cooling bath was removed and the reaction mixture was allowed to reach r.t., which led to the dissolving of the precipitate. After 30 min more HOR^F (5.0 ml, 36 mmol, 0.3 eq.) was added and the solution was stirred overnight. From the solution, a white powder crystallized and the solvent was removed in vacuo. The product was obtained as a white crystalline powder (85.4 g, 103 mmol, 94 %).

^{1}H-NMR (300.18 MHz, 298 K, CD_2Cl_2/*o*–DFB): δ = 0.78 (d, $^3J_{H-F}$ = 12.6 Hz, (C**H$_3$**)$_3$Si−F−Al(OR^F)$_3$) ppm.
^{19}F-NMR (282.45 MHz, 298 K, CD_2Cl_2/*o*–DFB): δ = –75.8 (s, 27 F, $Me_3Si{-}F{-}Al(O\mathbf{R^F})_3$), −156.2 (dec, $^3J_{H-F}$ = 12.6 Hz, 1 F, $Me_3Si{-}\mathbf{F}{-}Al(OR^F)_3$), ppm.
^{27}Al-NMR (78.22 MHz, 298 K, CD_2Cl_2/*o*–DFB): δ = 37 (s, br, $Me_3Si{-}F{-}Al(OR^F)_3$) ppm.
^{29}Si-NMR (59.64 MHz, 298 K, CD_2Cl_2/*o*–DFB): δ = 83.7 (d, $^1J_{Si-F}$ = 285 Hz,Me_3**Si**−F−Al(OR^F)$_3$) ppm.

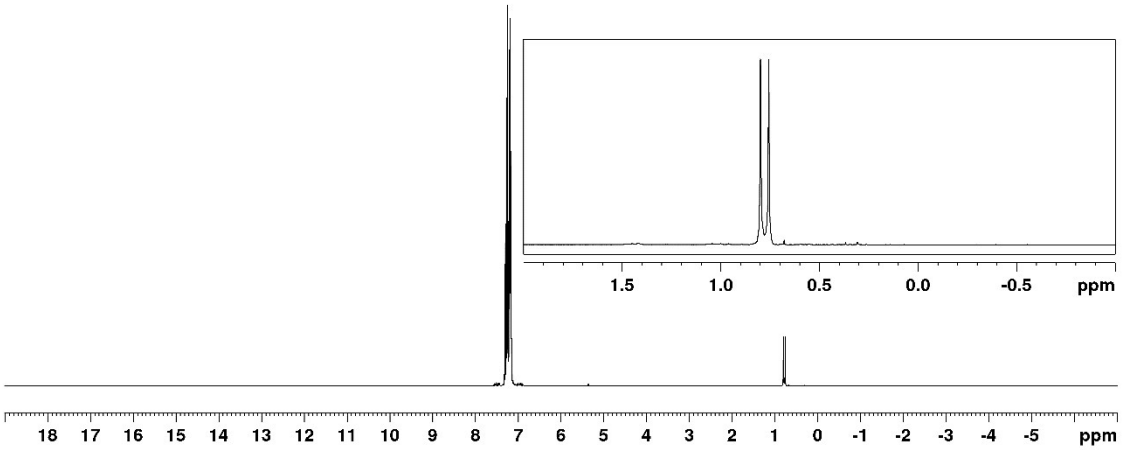

Figure S- 1: ^{1}H-NMR spectrum (300.18 MHz, 298 K, CD_2Cl_2/*o*–DFB) of $Me_3Si–F–Al(OR^F)_3$.

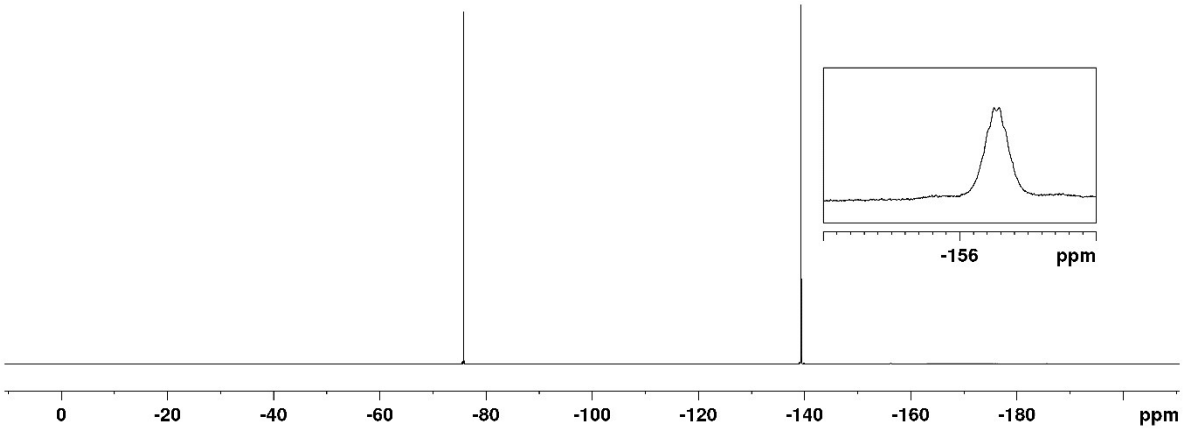

Figure S- 2: ^{19}F-NMR spectrum (282.45 MHz, 298 K, CD_2Cl_2/*o*–DFB) of $Me_3Si–F–Al(OR^F)_3$.

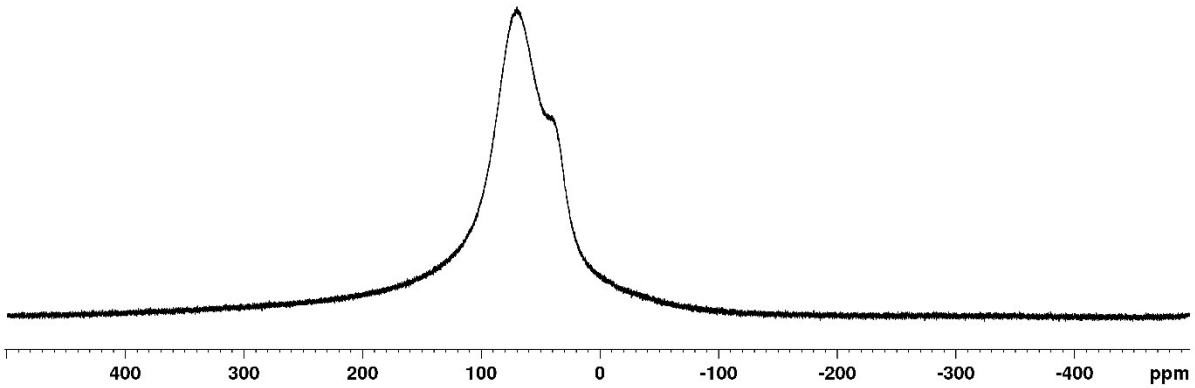

Figure S- 3: ^{27}Al-NMR spectrum (78.22 MHz, 298 K, CD_2Cl_2/*o*–DFB) of $Me_3Si–F–Al(OR^F)_3$.

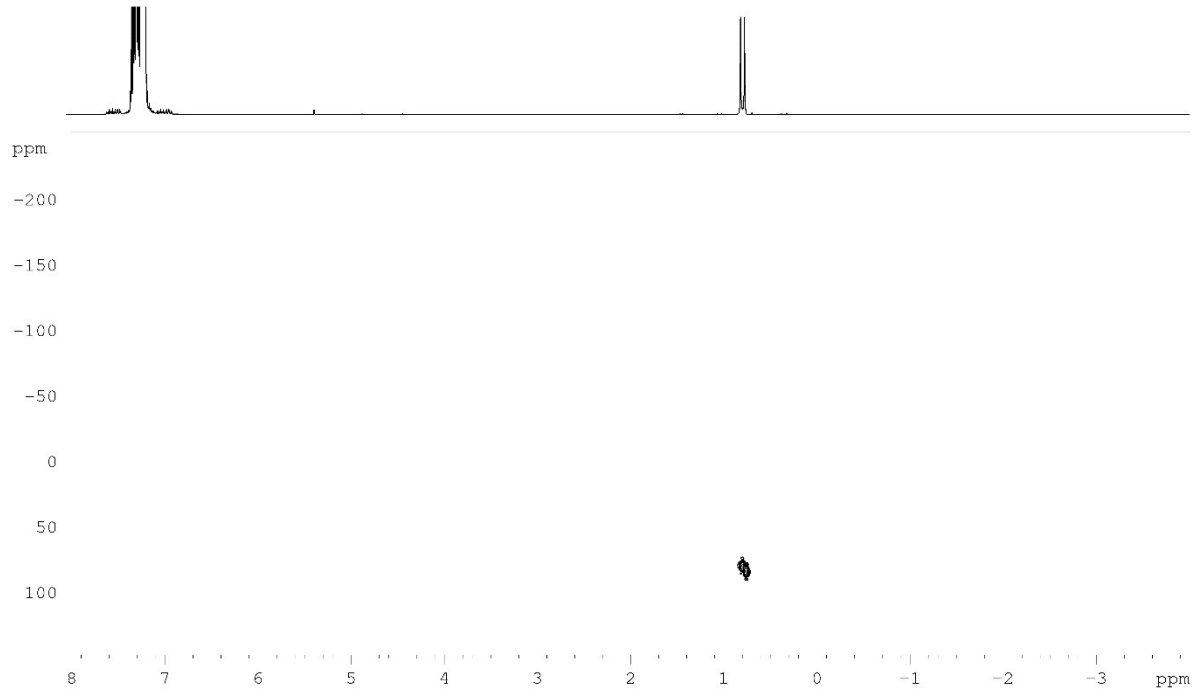

Figure S- 4: $^{1}H,^{29}Si$ HMBC NMR spectrum (300.18 MHz, 298 K, CD_2Cl_2/*o*–DFB) of $Me_3Si–F–Al(OR^F)_3$.

Synthesis of [Li(NCCCl$_3$)][*f–al*]

$Me_3Si–F–Al(OR^F)_3$ (998 mg, 1.21 mmol) and $LiPF_6$ (183 mg, 1.20 mmol, 1.00 eq.) were suspended in *o*–DFB (3 ml) and Cl_3CCN (1 ml) and heated to 60°C. The evolving gas was allowed to evaporate from the solution. After 4 h the solvent was removed in vacuo and the residue was dissolved in *o*–DFB (1 ml). The product was then precipitated by addition of CH_2Cl_2 (5 ml). After removal of the solvent in vacuo the product was obtained as colorless powder (912 mg, 1.01 mmol, 84 %).
In order to obtain single crystals of the product, the CH_2Cl_2 in the reaction solution was removed under reduced pressure until the product was dissolved again (~2 ml). The solution was stored at −40°C and yielded single crystals of [Li(NCCCl$_3$)][*f–al*].

^{7}Li-NMR (116.66 MHz, 298 K, CD_3CN/*o*–DFB): δ = −2.5 (s, Li^+) ppm.
^{19}F-NMR (282.45 MHz, 298 K, CD_3CN/*o*–DFB): δ = –76.1 (d, 27 F, $^{5}J_{F–F}$ = 2 Hz, $[F–Al(O\mathbf{R^F})_3]^-$), –186.2 (m, 1 F, $[\mathbf{F}–Al(OR^F)_3]^-$) ppm.
^{27}Al-NMR (78.22 MHz, 298 K, CD_3CN/*o*–DFB): δ = 41.1 (d, $^{1}J_{Al–F}$ = 30 Hz, $[F–\mathbf{Al}(OR^F)_3]^-$) ppm.
ATR-IR (diamond): ṽ = 1354 (w), 1298 (w), 1254 (vs), 1240 (vs), 1217 (vs), 1179 (s), 1033 (vw), 970 (vs), 871 (w), 843 (w), 795 (m), 758 (w), 725 (vs), 663 (w), 567 (w), 536 (w), 507 (w), 451 (w), 388 (m) cm^{-1}.
FT–Raman: ṽ = 2939 (17), 2923 (17), 2909 (17), 2758 (17), 2286 (100), 800 (50), 758 (33), 749 (33), 725 (0), 704 (0), 570 (33), 538 (33), 501 (67), 330 (50), 297 (17), 266 (83), 180 (83) cm^{-1}.

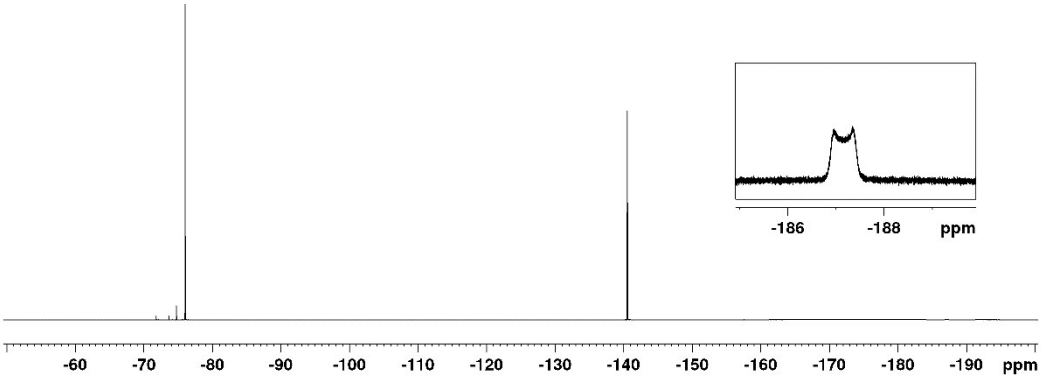

Figure S- 5: ^{19}F-NMR spectrum (282.45 MHz, 298 K, CD_3CN/*o*–DFB/Cl_3CCN) of [Li(NCCCl$_3$)][*f–al*].

The doublet at $\delta^{19}F = -73$ ppm results from small residues of $[PF_6]^-$.

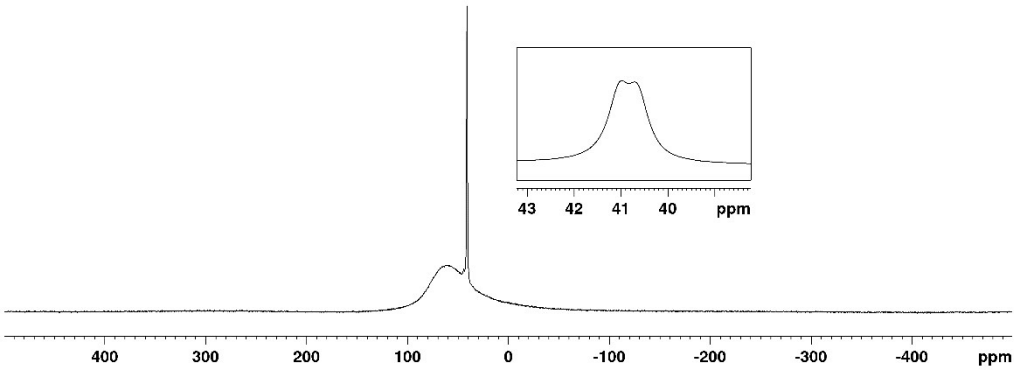

Figure S- 6: ^{27}Al-NMR spectrum (78.22 MHz, 298 K, CD_3CN/*o*–DFB/Cl_3CCN) of [Li(NCCCl$_3$)][*f–al*].

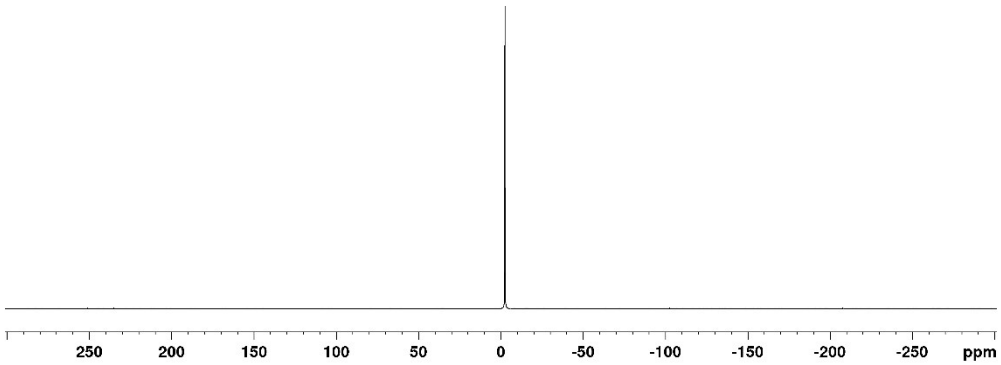

Figure S- 7: ^{7}Li-NMR spectrum (116.66 MHz, 298 K, CD_3CN/*o*–DFB/Cl_3CCN) of [Li(NCCCl$_3$)][*f–al*].

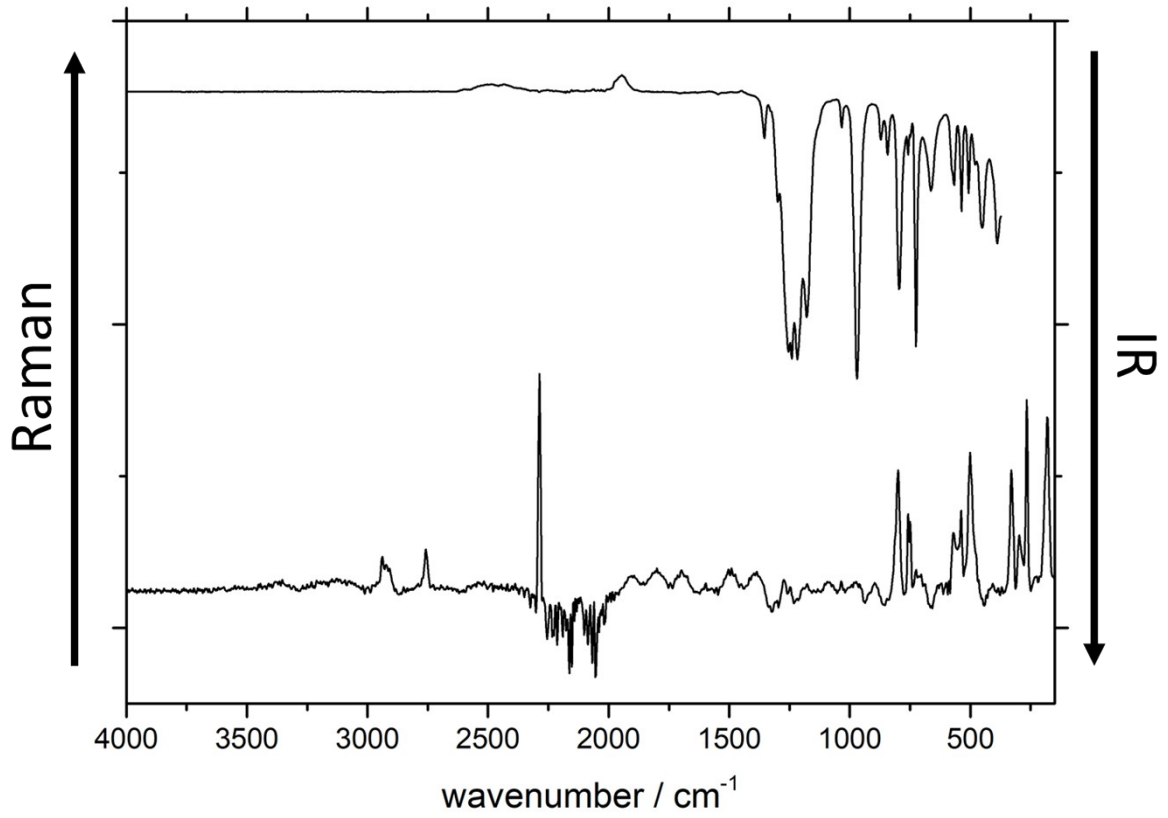

Figure S- 8: ATR-IR (top) and Raman (bottom) spectra of [Li(NCCCl$_3$][*f–al*]. The vibrational bands at ~3000 cm^{-1} are caused by fingerprints inside the Raman spectrometer.

Reaction of $Me_3Si–F–Al(OR^F)_3$ with DMC

$Me_3Si–F–Al(OR^F)_3$ was filled in an NMR tube and dissolved in dimethyl carbonate (DMC). Immediately, a slight gas evolution was visible. The sample was then analyzed in the NMR spectrometer.
In the ^{1}H and ^{13}C NMR spectra no signal of DMC–$Al(OR^F)_3$ is not visible due to dynamic exchange. The sample contained small amounts of $Me_3Si–O–SiMe_3$ impurities.

^{1}H-NMR (300.18 MHz, 298 K, DMC): δ = 3.79 (s, $(CH_3O)_2CO$), 0.25 (d, $^3J_{H–F}$ = 7.4 Hz, $(CH_3)_3SiF$) ppm.
^{13}C-NMR (75.48 MHz, 298 K, DMC): δ = 53.9 (s, $(CH_3O)_2CO$), 156.3 (s, $(CH_3O)_2CO$) ppm.
^{19}F-NMR (282.45 MHz, 298 K, DMC): δ = –76.5 (s, DMC–$Al(OR^F)_3$), −158.8 (dec, $^3J_{H–F}$ = 7.4 Hz, $(CH_3)_3SiF$) ppm.
^{27}Al-NMR (78.22 MHz, 298 K, DMC): δ = 37 (s, br, DMC–$Al(OR^F)_3$) ppm.

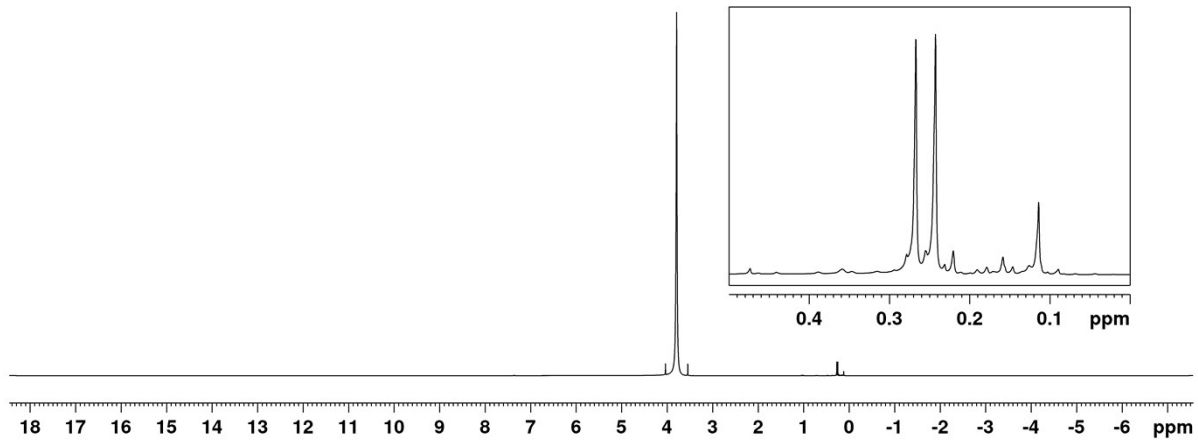

Figure S- 9: ^{1}H-NMR spectrum (300.18 MHz, 298 K, DMC) of the reaction of $Me_3Si{-}F{-}Al(OR^F)_3$ with DMC.

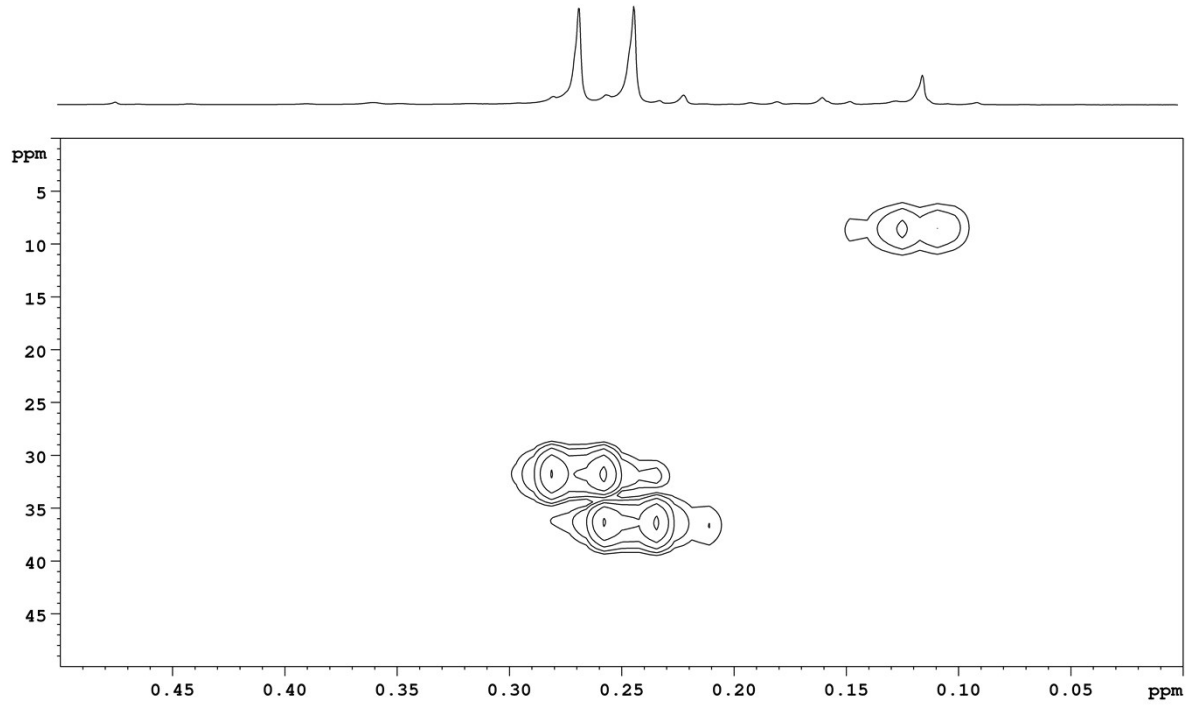

Figure S- 10: ^{1}H,^{29}Si HMBC NMR spectrum (298 K, DMC) of the reaction of $Me_3Si{-}F{-}Al(OR^F)_3$ with DMC.

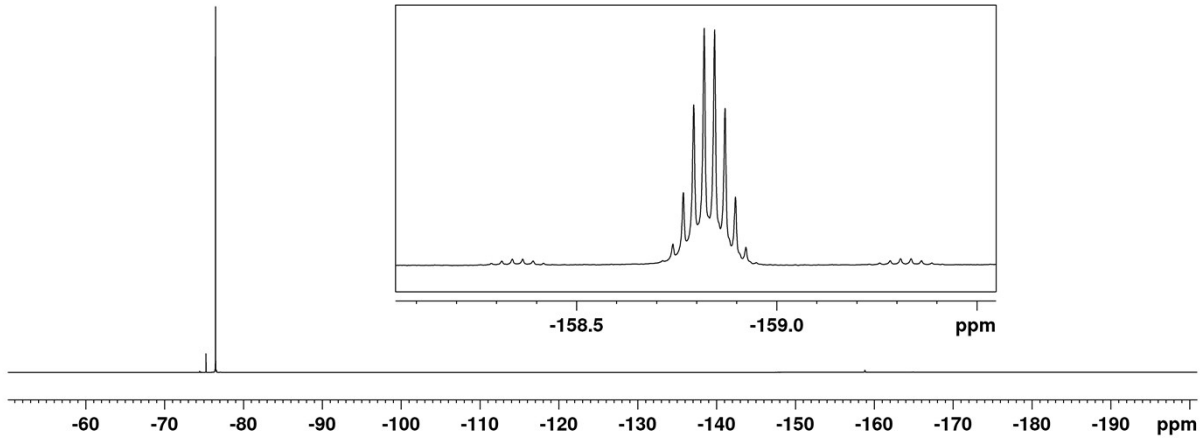

Figure S- 11: ^{19}F-NMR spectrum (282.45 MHz, 298 K, DMC) of the reaction of $Me_3Si{-}F{-}Al(OR^F)_3$ with DMC.

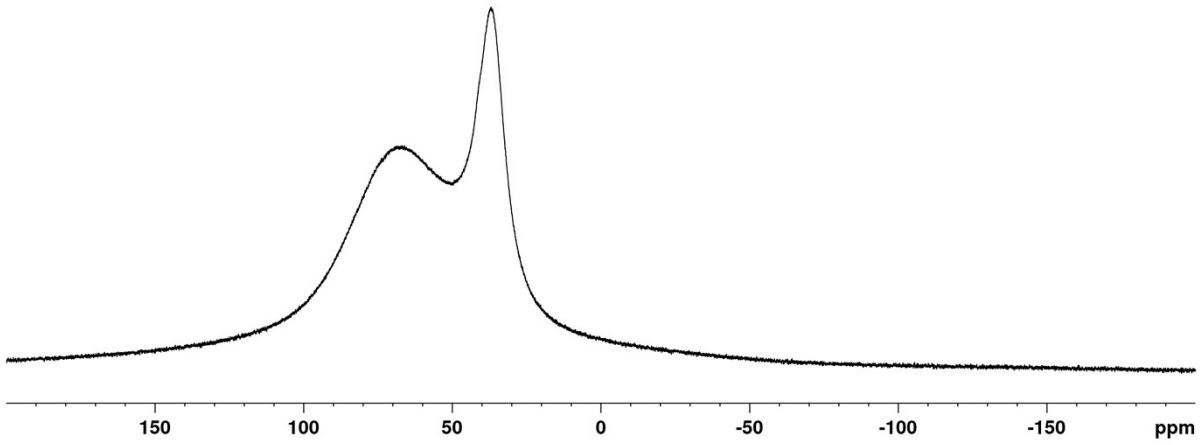

Figure S- 12: ^{27}Al-NMR spectrum (78.22 MHz, 298 K, DMC) of the reaction of $Me_3Si–F–Al(OR^F)_3$ with DMC.

Large scale synthesis of DMC–Al(OR^F)$_3$

In order to prevent loss of the synthesized Me_3SiF, a large scale synthesis of DMC–Al(OR^F)$_3$ starting from $AlEt_3$ and HOR^F was established. This allows for the synthesis of larger amounts of [Li(DMC)$_2$][*f–al*].

$AlEt_3$ (5.0 ml, 36 mmol) was dissolved in hexane (50 ml) and cooled to −40°C. Under vigorous stirring, HOR^F (10 ml, 72 mmol, 2.0 eq.) was added within 10 min to the reaction mixture, while keeping the cooling bath between −40 and −20°C. During the addition of HOR^F, gas evolution (C_2H_6) could be observed and the viscosity of the solution increased and also small amounts of precipitate formed. After complete addition of HOR^F, $(MeO)_2CO$ (DMC, 5.0 ml, 59 mmol, 1.6 eq.) was added to the reaction mixture at −40°C. The solution was allowed to reach r.t. for 5 min, then cooled to −20°C. Then HOR^F (8.0 ml, 43 mmol, 1.2 eq.) was added slowly. The cooling bath was removed and the reaction mixture was allowed to reach r.t., which led to the dissolving of the precipitate. When no more gas evolution was visible, the solvent was removed in vacuo. The product was obtained as colorless powder (27.4 g, 33 mmol, 93 %). Single crystals of DMC–Al(OR^F)$_3$ could be obtained by storing the reaction mixture at 2°C.

^{1}H-NMR (300.18 MHz, 298 K, CD_2Cl_2): δ = 4.21 (s, (C**H$_3$**O)$_2$CO–Al(OR^F)$_3$) ppm.
^{13}C-NMR (75.48 MHz, 298 K, CD_2Cl_2): δ = 60.8 (s, (**C**H$_3$O)$_2$CO–Al(OR^F)$_3$), 160.0 (s, (CH$_3$O)$_2$**C**O–Al(OR^F)$_3$) ppm.
^{19}F-NMR (282.45 MHz, 298 K, CD_2Cl_2): δ = –76.0 (s, DMC–Al(O**R^F**)$_3$) ppm.
^{27}Al-NMR (78.22 MHz, 298 K, CD_2Cl_2): δ = 37 (s, br, DMC–**Al**(OR^F)$_3$) ppm.
ATR-IR (diamond): ṽ = 1641 (s), 1534 (s), 1458 (vs), 1436 (vs), 1383 (s), 1356 (vs), 1299 (s), 1240 (w), 1213 (w), 1175 (m), 1118 (vs), 968 (w), 889 (s), 862 (s), 813 (vs), 795 (vs), 725 (w), 669 (vs), 592 (s), 568 (vs), 536 (s), 482 (s), 446 (m).

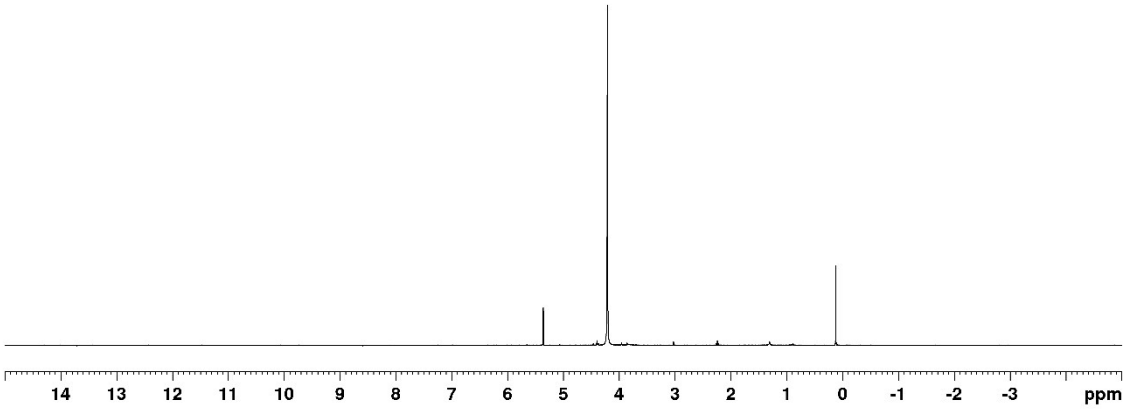

Figure S- 13: ^{1}H-NMR spectrum (300.18 MHz, 298 K, CD_2Cl_2) of DMC−Al(OR^F)$_3$.

The signal at δ^1H = 0.10 ppm results from small amounts of grease in the sample.

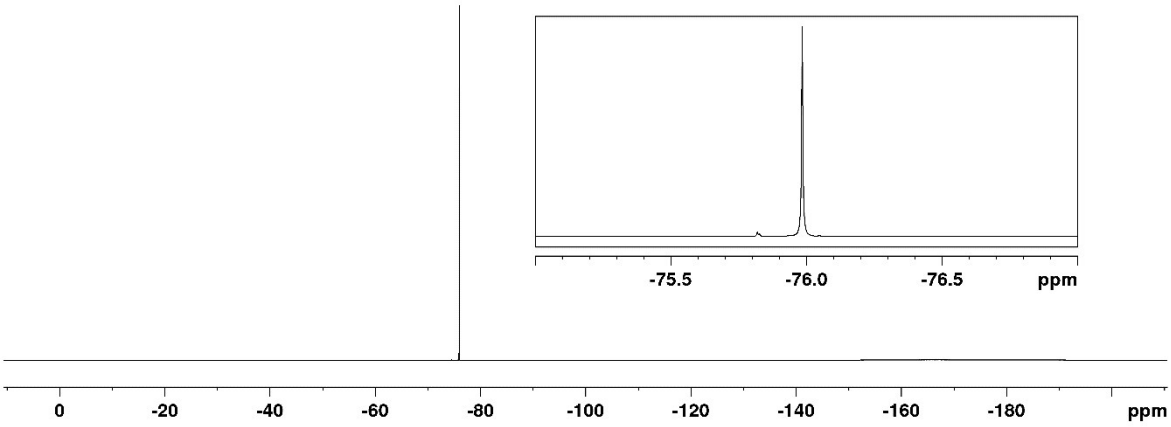

Figure S- 14: ^{19}F-NMR spectrum (282.45 MHz, 298 K, CD_2Cl_2) of DMC−Al(OR^F)$_3$.

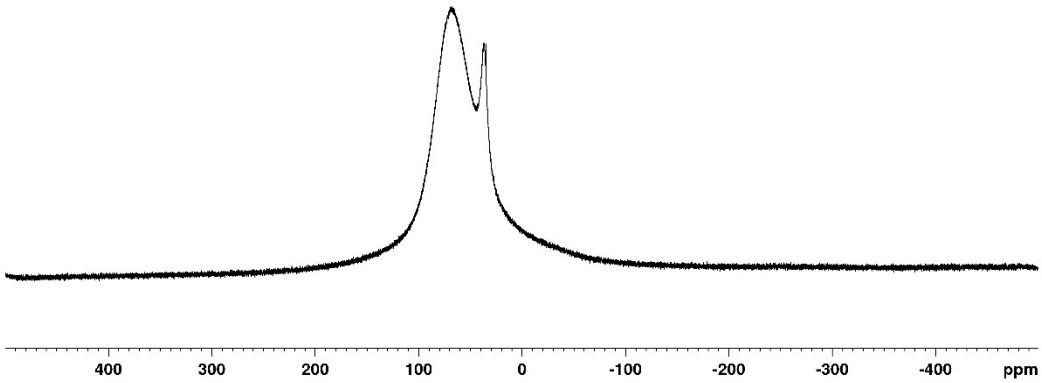

Figure S- 15: ^{27}Al-NMR spectrum (78.22 MHz, 298 K, CD_2Cl_2) of DMC−Al(OR^F)$_3$.

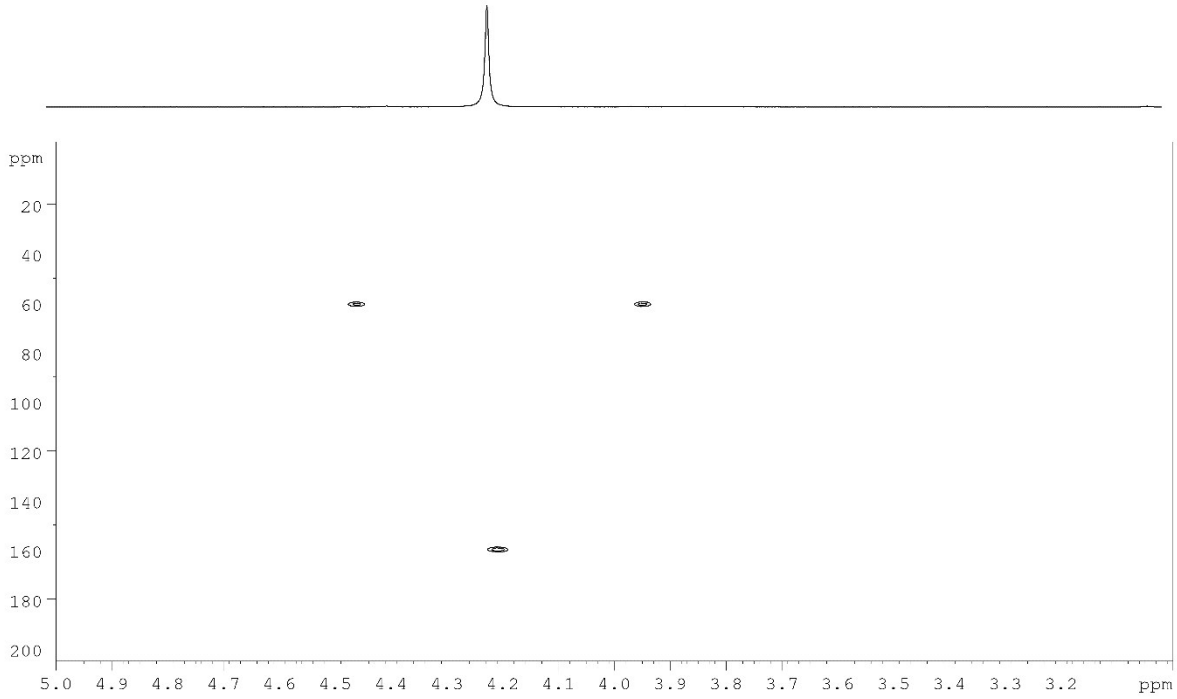

Figure S- 16: $^{1}H,^{13}C$ HMBC NMR spectrum (300.18 MHz, 298 K, CD_2Cl_2) of DMC−Al(OR^F)$_3$.

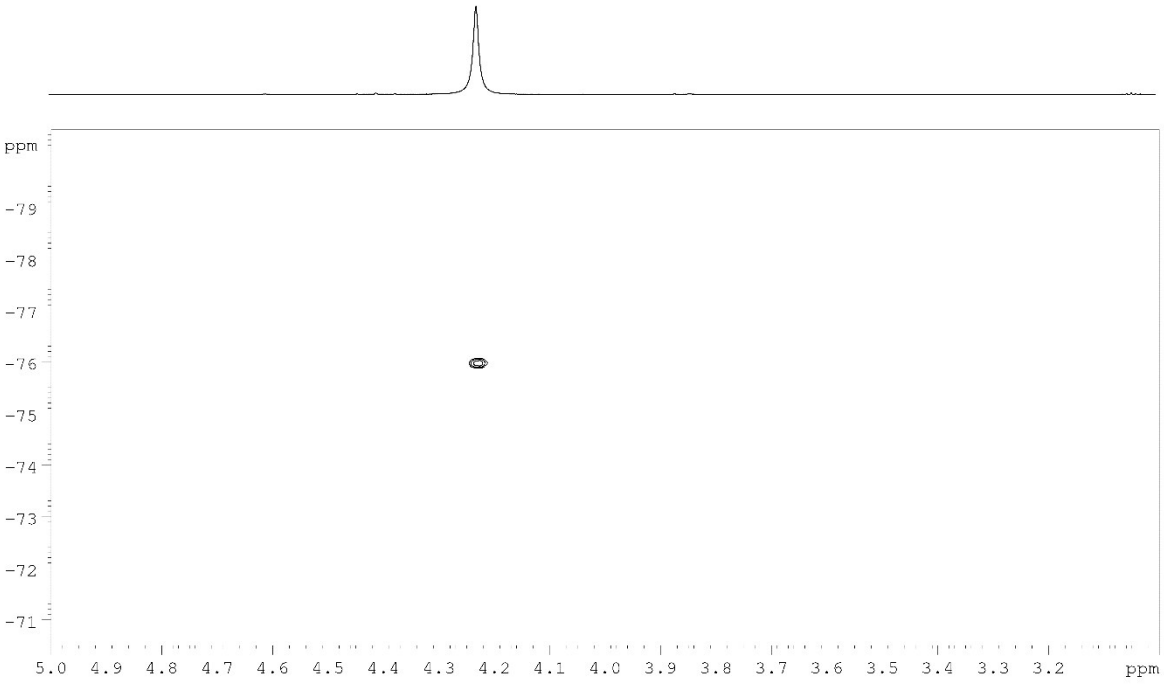

Figure S- 17: $^{1}H,^{19}F$ HOESY NMR spectrum (300.18 MHz, 298 K, CD_2Cl_2) of DMC−Al(OR^F)$_3$.

Synthesis of [Li(DMC)$_2$][*f*−*al*]

Me_3Si−F−Al(OR^F)$_3$ (985 mg, 1.20 mmol) and $LiPF_6$ (178 mg, 1.17 mmol, 1.0 eq.) were dissolved in DMC (2 ml) and heated to 60°C. After 6 h the solvent was slowly removed in vacuo at 60°C. The product was obtained as colorless powder (951 mg, 1.01 mmol, 86 %). The composition of the cation was determined by addition of *o*−DFB to the NMR as internal

standard for integration. Single crystals of $[Li(DMC)_3][f\text{–}al]$ could be obtained by addition of CH_2Cl_2 to the reaction solution, followed by storage at −30°C.

^{1}H-NMR (300.18 MHz, 298 K, CD_3CN/*o*–DFB): δ = 3.75 (s, $[Li(\mathbf{DMC})_2]^+$ ppm.
^{7}Li-NMR (116.66 MHz, 298 K, CD_3CN/*o*–DFB): δ = −2.6 (s, Li^+) ppm.
^{19}F-NMR (282.45 MHz, 298 K, CD_3CN/*o*–DFB): δ = –76.1 (d, 27 F, $^{5}J_{F-F}$ = 2 Hz, $[F–Al(O\mathbf{R^F})_3]^-$), –186.2 (m, 1 F, $[\mathbf{F}–Al(OR^F)_3]^-$) ppm.
^{27}Al-NMR (78.22 MHz, 298 K, CD_3CN/*o*–DFB): δ = 41.1 (d, $^{1}J_{Al-F}$ = 32 Hz, $[F–\mathbf{Al}(OR^F)_3]^-$) ppm.

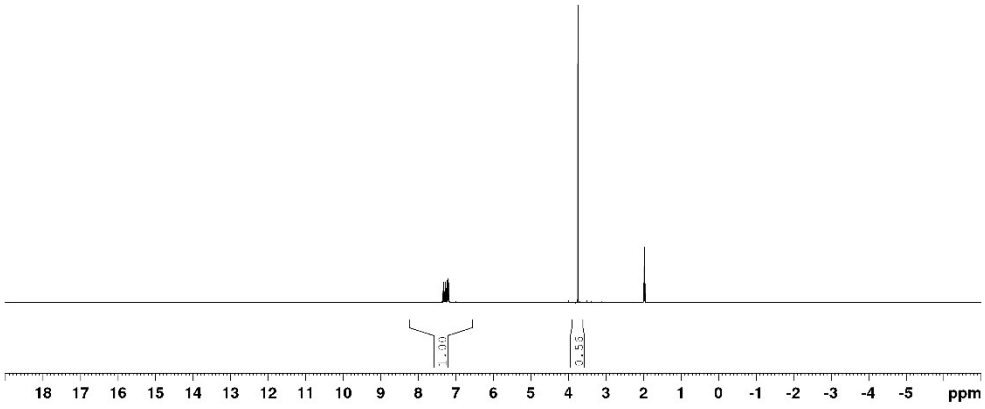

Figure S- 18: ^{1}H-NMR spectrum (300.18 MHz, 298 K, CD_3CN/*o*–DFB) of $[Li(DMC)_2][f\text{–}al]$.

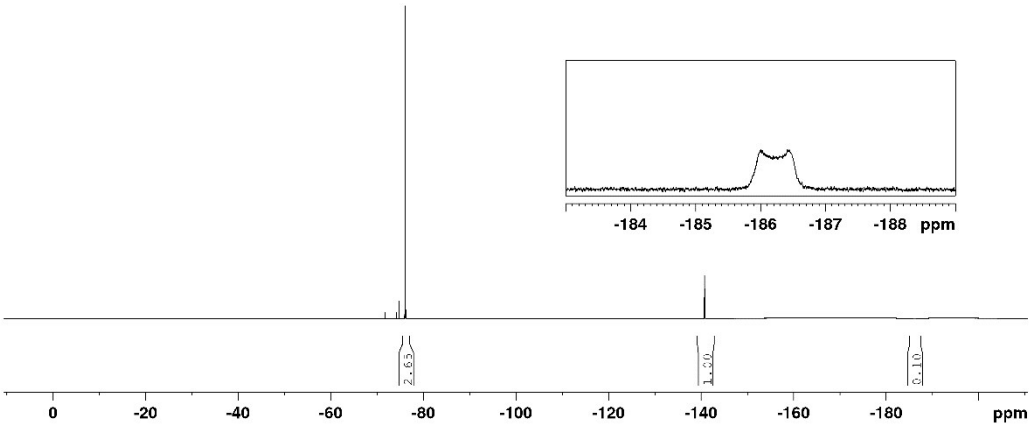

Figure S- 19: ^{19}F-NMR spectrum (282.45 MHz, 298 K, CD_3CN/*o*–DFB) of $[Li(DMC)_2][f\text{–}al]$.

The doublet at $\delta^{19}F$ = −73 ppm results from small residues of $[PF_6]^-$.

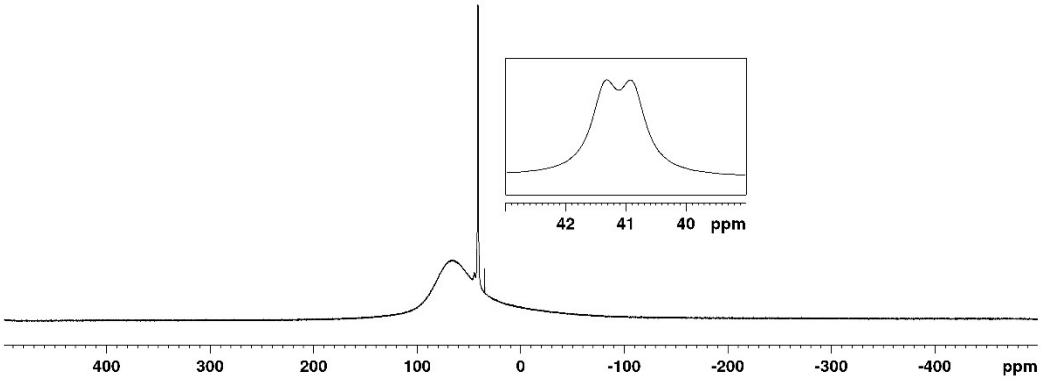

Figure S- 20: ^{27}Al-NMR spectrum (78.22 MHz, 298 K, CD_3CN/*o*–DFB) of $[Li(DMC)_2][f\text{–}al]$.

The signal at δ^{27}Al = 34.2 ppm results from an unidentified impurity.

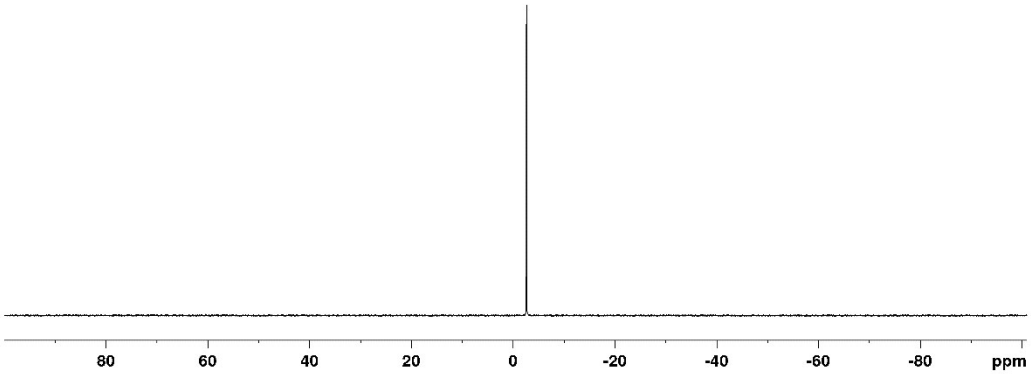

Figure S- 21: ^{7}Li-NMR spectrum (116.66 MHz, 298 K, CD_3CN/*o*–DFB) of [Li(DMC)$_2$][*f–al*].

Synthesis of K[*f–al*]

$Me_3Si–F–Al(OR^F)_3$ (995 mg, 1.21 mmol) and KPF_6 (462 mg, 2.51 mmol, 2.1 eq.) were weighed into a Schlenk vessel equipped with a bubbler and dissolved in *o*–DFB (5 ml). The mixture was heated to 60°C, which led to gas evolution. After 9 h solvent was slowly removed in vacuo at 60°C. The remaining colorless powder (779 mg raw yield) contained residual KPF_6. Further purification was achieved by extraction of the solid with *o*–DFB (4 x 2 ml). After removal of the solvent the product was obtained as a colorless powder (223 mg, 0.28 mmol, 23% raw yield). The K[*f–al*] obtained this way had a purity of about 80 % and was suitable for IR- and Raman spectroscopy.

NMR spectra were taken in Et_2O/CD_2Cl_2 in order to dissolve all solids. The basicity of Et_2O led to dissociation of [*al–f–al*]$^-$ into $Et_2O–Al(OR^F)_3$ and [*f–al*]$^-$. The ratios of the compounds in solution was calculated accordingly.

^{19}F-NMR (282.45 MHz, 298 K, CD_2Cl_2/Et_2O): δ = –74.9 (s, $KOC(C\mathbf{F}_3)_3$, 6%), −75.9 (s, $Et_2O–Al(O\mathbf{R}^F)_3$, 4%), −76.0 (s, unknown impurity), –76.2 (d, $^5J_{F–F}$ = 1.8 Hz, $[F–Al(O\mathbf{R}^F)_3]^-$, 78%), −76.4 (t, $^5J_{F–F}$ = 1.0 Hz, $[F_2Al(O\mathbf{R}^F)_2]^-$, 12%) –184.5 (sext, $^1J_{Al–F}$ = 48 Hz, $[\mathbf{F}–Al(OR^F)_3]^-$) ppm.
^{27}Al-NMR (78.22 MHz, 298 K, CD_2Cl_2/Et_2O): δ = 40 (d, $^1J_{Al–F}$ = 48 Hz, $[F–\mathbf{Al}(OR^F)_3]^-$) ppm.
ATR-IR (diamond): ṽ = 1357 (vs), 1298 (s), 1243 (w), 1194 (w), 1009 (vs), 967 (w), 817 (vs), 771 (vs), 756 (vs), 725 (w), 563 (vs), 536 (s), 443 (s), 391 (s).
FT–Raman: ṽ = 2937 (13), 2909 (13), 2757 (13), 1338 (13), 1311 (13), 1273 (25), 1251 (25), 1230 (13), 817 (38), 771 (100), 753 (50), 735 (38), 572 (25), 539 (63), 429 (13), 367 (25), 327 (100), 298 (25), 258 (13), 227 (13).

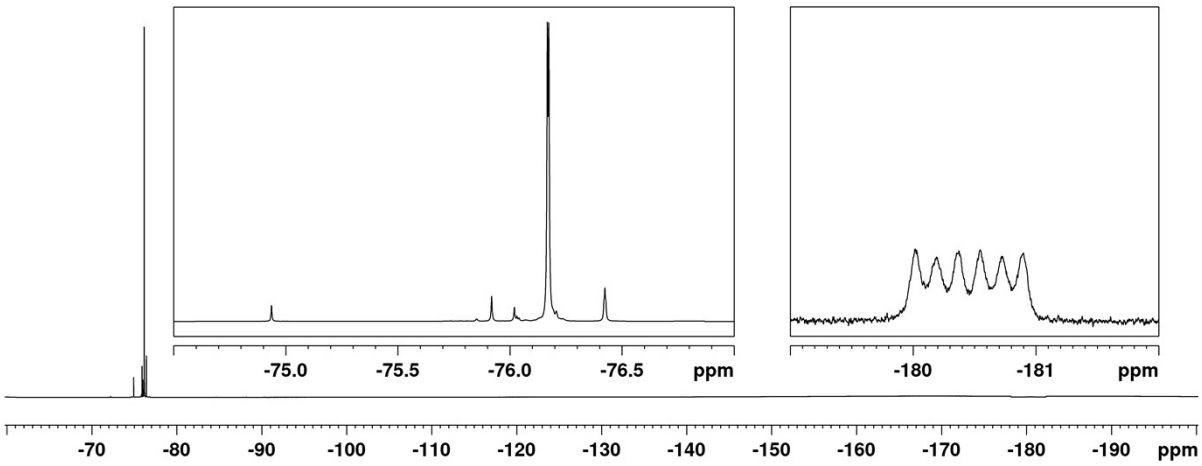

Figure S- 22: ^{19}F-NMR spectrum (282.45 MHz, 298 K, CD_2Cl_2/Et_2O) of K[*f*–*al*].

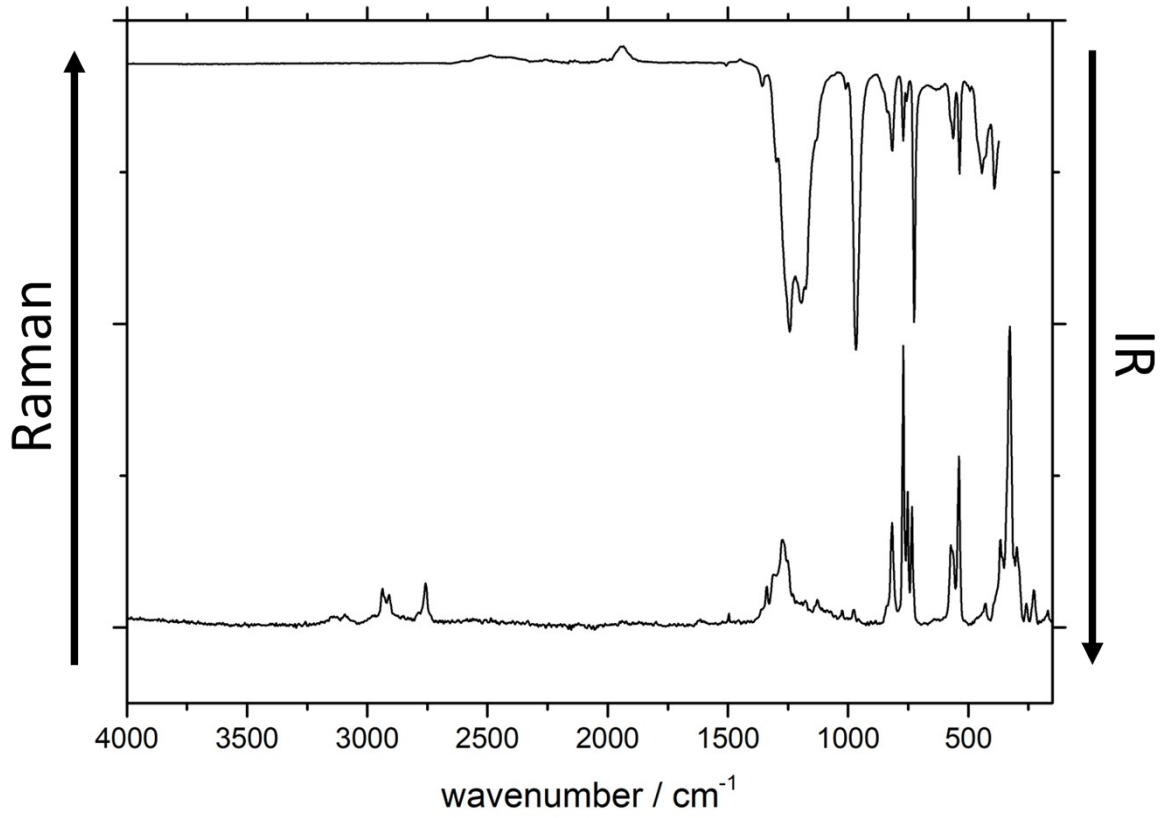

Figure S- 23: ATR-IR (top) and Raman (bottom) spectra of K[*f*–*al*]. The vibrational bands at ~3000 cm^{-1} are caused by fingerprints inside the Raman spectrometer.

Synthesis of K[*al*–*f*–*al*]

$Me_3Si–F–Al(OR^F)_3$ (2.17 g, 2.6 mmol) and KPF_6 (241 mg, 1.3 mmol, 0.5 eq.) were weighed into a Schlenk vessel equipped with a bubbler and dissolved in *o*–DFB (5 ml). The mixture was heated to 60°C, which led to gas evolution. After 3 h the gas evolution had stopped and the solvent was slowly removed in vacuo at 60°C. The product was obtained as a colorless powder (1.78 g, 1.2 mmol, 90 %).

^{19}F-NMR (376.54 MHz, 298 K, CD_2Cl_2/*o*–DFB): δ = –75.5 (d, 54 F, [F{Al(O**R^F**)$_3$}$_2$]$^-$), –184.5 (s, 1 F, [**F**{Al(OR^F)$_3$}$_2$]$^-$) ppm.
^{27}Al-NMR (104.27 MHz, 298 K, CD_2Cl_2/*o*–DFB): δ = 35 (s, br, [F{**Al**(OR^F)$_3$}$_2$]$^-$) ppm.

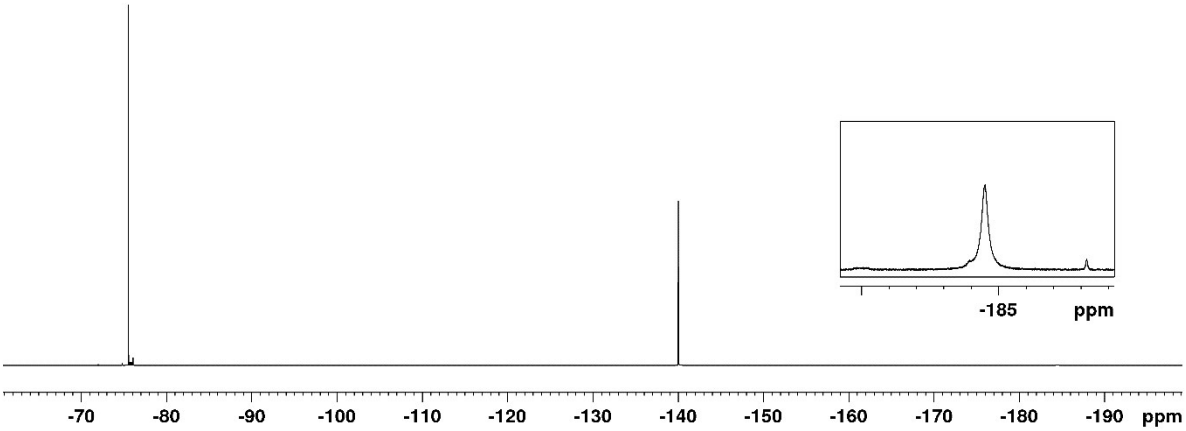

Figure S- 24: ^{19}F-NMR spectrum (376.54 MHz, 298 K, CD_2Cl_2/*o*–DFB) of K[*al*–*f*–*al*].

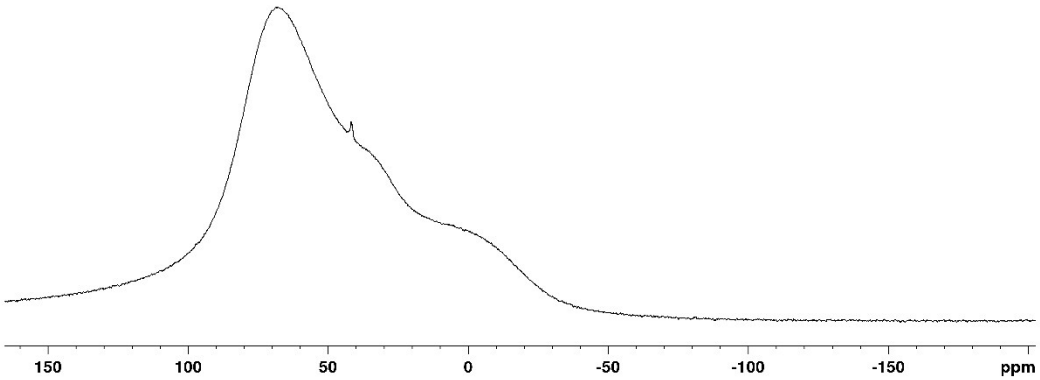

Figure S- 25: ^{27}Al-NMR spectrum (104.27 MHz, 298 K, CD_2Cl_2/*o*–DFB) of K[*al*–*f*–*al*].

The sharp signal at δ^{27}Al = 42 ppm was generated by small amounts of [*f*–*al*]$^-$.

Synthesis of Ag[*f*–*al*]

a) in CH_2Cl_2

In a double bulb vessel connected by a G4 frit plate, $AgPF_6$ (320 mg, 1.27 mmol) and Me_3Si–F–Al(OR^F)$_3$ (1.04 g, 1.27 mmol, 1.0 eq.) were weighed in one bulb of the vessel and CH_2Cl_2 was condensed onto the solids at 77 K. Then the vessel was equipped with a bubbler in order to allow for evaporation of the evolving PF_5 .The reaction mixture was thawed under stirring, which led to evolution of gaseous PF_5. After stirring for 1 h at room temperature the mixture was allowed to sediment for 5 h during which little dark precipitate formed. The colorless solution was filtered and the solvent was removed in vacuo. The product was obtained as an off-white powder (1.06 g, 1.24 mmol, 98 %). By integration of NMR spectra taken in *o*–DFB, the cation was identified as [Ag(CH_2Cl_2)]$^+$.

^{19}F-NMR (282.45 MHz, CD_2Cl_2, 298 K): δ = –75.8 (s, 27 F, [F–Al(O**R^F**)$_3$]$^-$), –189.9 (m, 1 F, [**F**–Al(OR^F)$_3$}) ppm.

^{27}Al-NMR (104.27 MHz, CD_2Cl_2, 298 K): δ = 39.8 (d, $^1J_{F-Al}$ = 43 Hz, 1 Al, [F−**Al**$(OR^F)_3$]$^-$) ppm.

b) in o−DFB

Ag[PF_6] (298 mg, 1.2 mmol) and Me_3Si-F-Al$(OR^F)_3$ (990 mg, 1.2 mmol, 1.0 eq.) were dissolved in $C_6H_4F_2$ (ca. 5 mL) and cooled to −20°C. The mixture was allowed to warm up to r.t. while stirring, concomitant by an evolution of gas (PF_5 and Me_3SiF). After a few minutes, a slightly yellow solution was obtained. All volatiles were removed in vacuo to afford a colorless powder (798 mg, 1.0 mmol, 84 %, x = 0.2). The composition of this compound is [Ag(*o*−DFB)$_x$][*f*−*al*] with x = 0 – 2, depending on the drying time.

^{1}H-NMR (200.13 MHz, CD_2Cl_2, 298 K): δ = 7.27-7.07 (m, 4 H, [Ag(*o*−C_6**H_4**F_2)$_x$]$^+$) ppm
^{19}F-NMR (188.31 MHz, CD_2Cl_2, 298 K): δ = −75.8 (d, 27 F, $^5J_{F,F}$ = 2 Hz, [FAl(O**R^F**)$_3$]$^-$), −139.4 (m, 2 F, [Ag(*o*−C_6**H_4**F_2)$_x$]$^+$), −199.0 (m, 1 F, [**F**Al$(OR^F)_3$]$^-$) ppm
^{27}Al-NMR (78.22 MHz, CD_2Cl_2, 298 K): δ = 39.7 (d, $^1J_{Al-F}$ = 45 Hz, [F**Al**$(OR^F)_3$]$^-$).

c) in SO_2

Me_3Si−F−Al$(OR^F)_3$ (863 mg, 1.05 mmol) and $AgPF_6$ (270 mg, 1.07 mmol, 1.02 eq.) were weighed into a Schlenk vessel. Then SO_2 (~2 ml) was condensed onto this mixture at −78°C. The Schlenk vessel was equipped with a bubbler in order to remove the evolving PF_5 and the reaction solution was stirred at −20°C. The reaction solution was allowed to reach −5°C within 1.5 h, then the solvent was removed in vacuo. The product was obtained as colorless powder (888 mg, 1.03 mmol, 98 %).

^{19}F-NMR (282.45 MHz, CD_2Cl_2, 298 K): δ = –75.8 (s, 27 F, [F−Al(O**R^F**)$_3$]$^-$), –189.9 (m, 1 F, [**F**−Al$(OR^F)_3$}) ppm.
^{27}Al-NMR (104.27 MHz, CD_2Cl_2, 298 K): δ = 39.8 (d, $^1J_{F-Al}$ = 43 Hz, 1 Al, [F−**Al**$(OR^F)_3$]$^-$) ppm.
ATR-IR (diamond): $\tilde{\nu}$ = 1359 (vs), 1300 (vs), 1244 (w), 1209 (m), 1173 (m), 1133 (vs), 1074 (vs), 973 (w), 968 (w), 857 (vs), 807 (vs), 761 (s), 726 (w), 577 (vs), 565 (vs), 556 (vs), 537 (s), 473 (vs), 434 (vs), 415 (vs), 394 (s).
FT–Raman: $\tilde{\nu}$ = 1331 (20), 1267 (40), 812 (40), 762 (100), 723 (20), 573 (20), 540 (60), 367 (20), 328 (80), 300 (20), 231 (20).

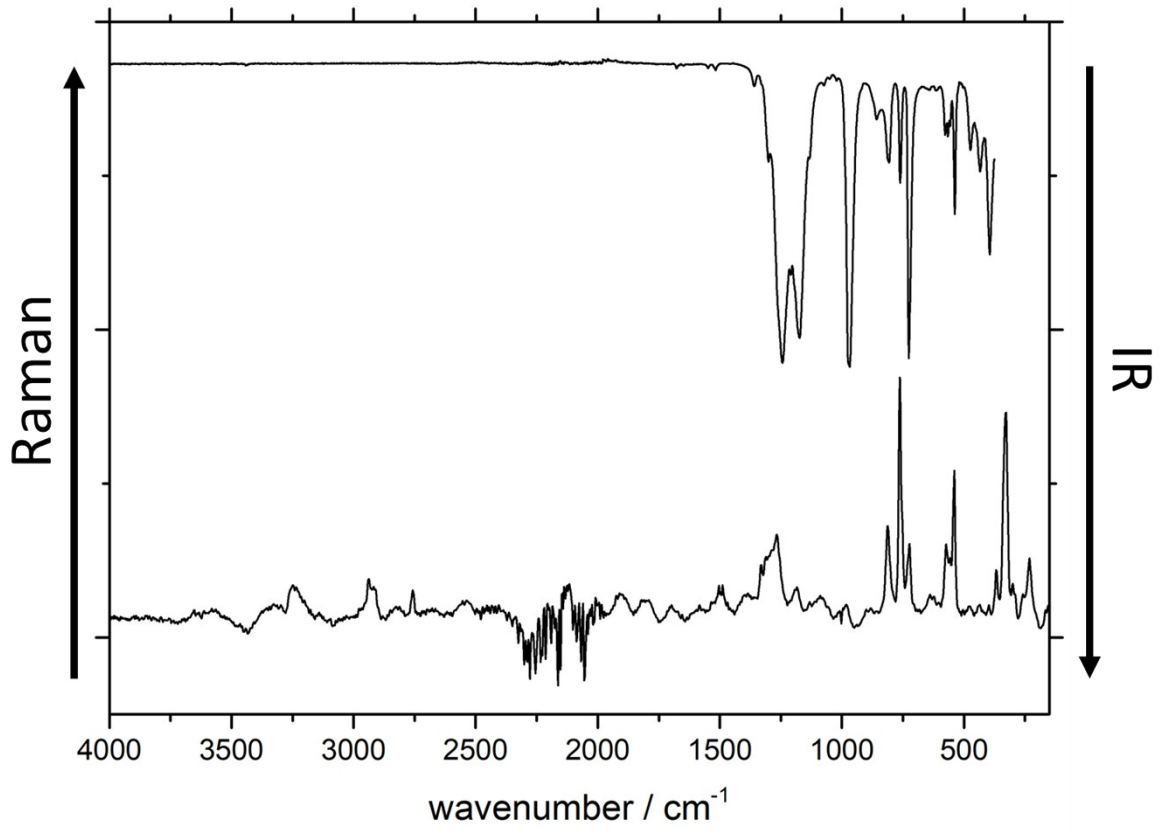

Figure S- 26: ATR-IR (top) and Raman (bottom) spectra of Ag[*f–al*]. The vibrational bands at ~3000 cm^{-1} are caused by fingerprints inside the Raman spectrometer.

Synthesis of Ag[*al–f–al*]

a) in CH_2Cl_2

In a double bulb vessel connected by a G4 frit plate, $AgPF_6$ (318 mg. 1.26 mmol) and $Me_3Si{-}F{-}Al(OR^F)_3$ (2.07 g, 2.51 mmol, 2.0 eq.) were weighed in one bulb of the vessel and CH_2Cl_2 was condensed onto the solids at 77 K. Then the vessel was equipped with a bubbler in order to allow for evaporation of the evolving PF_5 .The reaction mixture was thawed under stirring, which led to evolution of gaseous PF_5. After stirring for 1 h at room temperature the mixture was allowed to sediment for 5 h during which little dark precipitate formed. The colorless solution was filtered and the solvent was removed in vacuo. The product was obtained as a fine white powder (1.95 g, 1.22 mmol, 97 %). By integration of NMR spectra taken in *o*−DFB, the cation was identified as $[Ag(CH_2Cl_2)_3]^+$.

^{19}F-NMR (282.45 MHz, CD_2Cl_2, 298 K): δ = –75.8 (s, 54 F, $[F\{Al(O\mathbf{R^F})_3\}_2]^-$), –184.8 (s, br, 1 F, $[\mathbf{F}\{Al(OR^F)_3\}_2]^-$) ppm.
^{27}Al-NMR (104.27 MHz, CD_2Cl_2, 298 K): δ = ca. 37.1 (s, br, 2 Al, $[F\{\mathbf{Al}(OR^F)_3\}_2]^-$) ppm.

b) in o−DFB

$Ag[PF_6]$ (637 mg, 2.5 mmol) and Me_3Si-F-$Al(OR^F)_3$ (4.33 g, 5.2 mmol, 2.1 eq.) were dissolved in $C_6H_4F_2$ (ca. 5 mL) and cooled to −20°C. The mixture was allowed to warm up to r.t. while stirring, concomitant by an evolution of gas (PF_5 and Me_3SiF). After a few minutes, a colorless solution was obtained. All volatiles were removed in vacuo to afford a colorless powder ($[Ag(o\text{−}DFB)_2][al\text{−}f\text{−}al]$, 4.32 g, 2.4 mmol, 96 %). Alternatively, the concentrated solution can be crystallized from layering with *n*-pentane to give colorless crystals of $[Ag(o\text{−}DFB)_3][al\text{−}f\text{−}al]$.

^{1}H-NMR (300.18 MHz, CD_2Cl_2, 298 K): δ = 7.26-7.08 (m, 8 H, $[Ag(o\text{−}C_6\mathbf{H_4}F_2)_2]^+$) ppm
^{19}F-NMR (282.45 MHz, CD_2Cl_2, 298 K): δ = –75.8 (s, 54 F, $[F\{Al(O\mathbf{R^F})_3\}_2]^-$), –139.4 (m, 4 F, $[Ag(o\text{−}C_6H_4\mathbf{F_2})_2]^+$), –184.9 (s, br, 1 F, $[\mathbf{F}\{Al(OR^F)_3\}_2]^-$) ppm.
^{27}Al-NMR (104.27 MHz, CD_2Cl_2, 298 K): δ = ca. 37.1 (s, br, 2 Al, $[F\{\mathbf{Al}(OR^F)_3\}_2]^-$) ppm.

c) in SO_2

In a double bulb vessel connected by a G4 frit plate and equipped with a bubbler, $AgPF_6$ (231 mg, 0.91 mmol) and Me_3Si−F−$Al(OR^F)_3$ (1.51 g, 1.83 mmol, 2.0 eq.) were weighed in one bulb of the vessel. SO_2 was condensed onto the solids at −78°C. The turbid solution was then stirred for 2 h at −20°C, then for 10 min at 0°C. During this time, the evolution of PF_5 was observed. The solution was filtered and the residue was extracted two more times with SO_2. After removal of the solvent in vacuo the product was obtained as a solvent-free colorless powder (1.37 g, 0.86 mmol, 95 %).

^{19}F-NMR (376.54 MHz, 298 K, CD_2Cl_2): δ = −75.8 (s, 54 F, $[F\{Al(O\mathbf{R^F})_3\}_2]^-$), −184.9 (s, 1F, $[\mathbf{F}\{Al(OR^F)_3\}_2]^-$) ppm.
^{27}Al-NMR (104.27 MHz, 298 K, CD_2Cl_2): δ = 35.0 (s, br, $[F\{\mathbf{Al}(OR^F)_3\}_2]^-$) ppm.
ATR-IR (diamond): $\tilde{\nu}$ = 1353 (vs), 1300 (vs), 1243 (m), 1211 (m), 1176 (s), 970 (m), 862 (vs), 760 (vs), 726 (m), 695 (vs), 638 (vs), 569 (vs), 537 (s), 473 (vs), 450 (s), 382 (vs).
FT–Raman: $\tilde{\nu}$ = 1305 (5), 1279 (10), 816 (30), 753 (100), 696 (25), 572 (20), 539 (30), 367 (15), 325 (45), 307 (40), 292 (15), 233 (10).

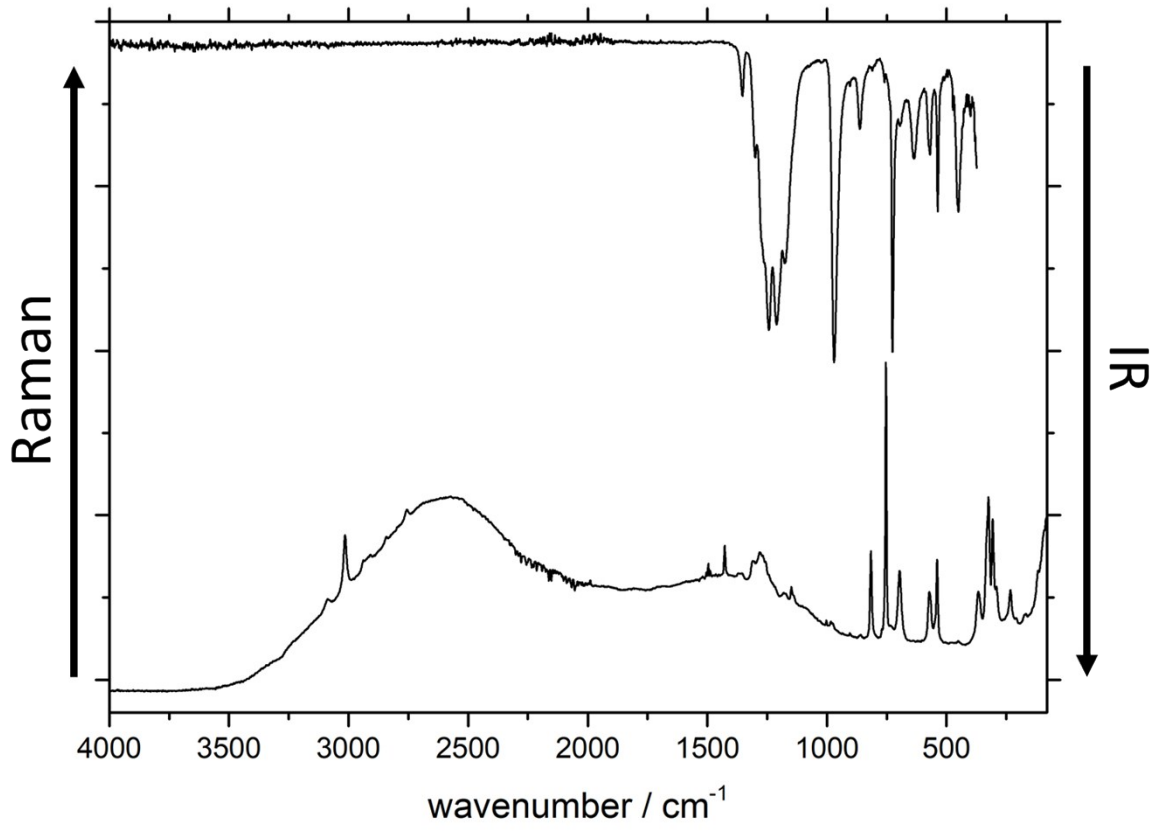

Figure S- 27: ATR-IR (top) and Raman (bottom) spectra of Ag[*al–f–al*] containing small amounts of *o*DFB. The vibrational bands at ~3000 cm^{-1} are caused by fingerprints inside the Raman spectrometer.

Synthesis of [NO][*f–al*]

[NO][PF_6] (106 mg, 0.61 mmol) and $Me_3Si–F–Al(OR^F)_3$ (500 mg, 0.61 mmol, 1.0 eq.) were weighed in a Schlenk vessel and SO_2 was condensed onto the solids at −78°C. The Schlenk vessel was equipped with a bubbler in order to remove the evolving PF_5 and the reaction solution was stirred at −20°C. The reaction solution was allowed to reach −5°C within 1 h, then the solvent was removed in vacuo. The product was obtained as colorless powder (447 mg, 0.57 mmol, 94 %).

^{19}F-NMR (376.54 MHz, SO_2, 298 K): δ = –75.8 (s, 27 F, [F–Al(O**R^F**)$_3$]$^-$), –142.0 (sext, 1 F, [**F**–Al(OR^F)$_3$]$^-$) ppm.
^{27}Al-NMR (104.27 MHz, SO_2, 298 K): δ = 41.1 (d, $^1J_{F–Al}$ = 44 Hz, 1 Al, [F–**Al**(OR^F)$_3$]$^-$) ppm.
ATR-IR (diamond): $\tilde{\nu}$ = 1355 (vs), 1300 (s), 1243 (w), 1205 (w), 1183 (w), 968 (w), 821 (vs), 766 (vs), 725 (w), 646 (vs), 573 (vs), 561 (vs), 536 (s), 445 (s), 387 (s).
FT–Raman: $\tilde{\nu}$ = 2313 (86), 1313 (14), 1266 (29), 816 (29), 768 (71), 753 (57), 731 (29), 573 (29), 539 (57), 446 (14), 367 (29), 326 (100), 298 (14), 231 (14), 169 (14).

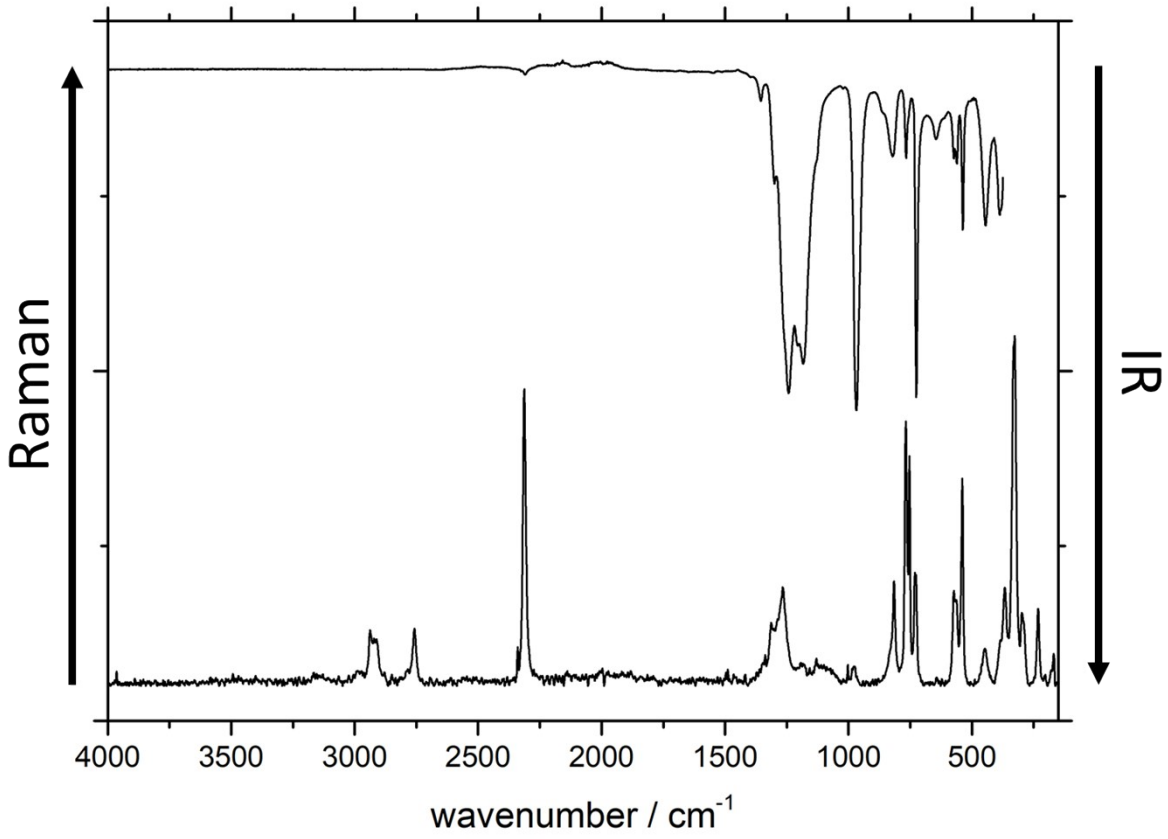

Figure S- 28: ATR-IR (top) and Raman (bottom) spectra of [NO][*f–al*]. The vibrational bands at ~3000 cm^{-1} are caused by fingerprints inside the Raman spectrometer.

Synthesis of [NO][*al–f–al*]

A double-Schlenk flask was equipped inside the glove box with Me_3Si-F-Al(OR^F)$_3$ (504 mg, 0.61 mmol, 2.0 eq.) and [NO][PF_6] (56 mg, 0.32 mmol, 1.0 eq.). SO_2 (ca. 3 mL) was then condensed onto the reaction mixture at –196°C and the flask was equipped with a bubbler. The vessel was then carefully vented with Ar and the bubbler was opened towards the fume hood while the reaction mixture was stirred at –35°C for 60 min (evolution of PF_5!). Then, the volatiles were removed at 0°C and a white solid was obtained which was further dried in vacuo (440 mg, 0.29 mmol, 88 %).

^{19}F-NMR (376.54 MHz, $C_6H_2F_4$, 298 K): δ = –75.8 (s, 54 F, [F{Al(O**R^F**)$_3$}$_2$]$^-$), –184.4 (s, 1 F, [**F**{Al(OR^F)$_3$}$_2$]$^-$) ppm.
^{27}Al-NMR (104.27 MHz, $C_6H_2F_4$, 298 K): δ = 36 (s, br, 2 Al, [F{**Al**(OR^F)$_3$}$_2$]$^-$) ppm.
ATR-IR (diamond): $\tilde{\nu}$ = 1354 (vw), 1301 (w), 1247 (vs), 1212 (vs), 1074 (vw), 968 (vs), 862 (vw), 760 (vw), 751 (vw), 726 (vs), 640 (w), 569 (w).
FT–Raman: $\tilde{\nu}$ = 2340 (17), 1319 (11), 1271 (11), 1253 (13), 979 (4), 815 (36), 753 (100), 571 (26), 539 (34), 365 (23), 326 (57), 293 (17), 235 (13).

Synthesis of $[Ph_3C][f\text{–}al]$

In a Schlenk vessel equipped with a bubbler, $[Ph_3C][PF_6]$ (451 mg, 1.16 mmol) and $Me_3Si{-}F{-}Al(OR^F)_3$ (1.00 g, 1.21 mmol, 1.04 eq.) were weighed in one bulb of the vessel and CH_2Cl_2 (5 ml) was added onto the solids. Immediately the evolution of a gas (PF_5 and Me_3SiF) was observed. The reaction mixture was stirred for 1 h at rt. After removal of the solvent in vacuo the product was obtained as a yellow powder (1.10 g, 1.10 mmol, 95 %).

^{1}H-NMR (300.18 MHz, CD_2Cl_2, 298 K): δ = 8.33 (m, 3 H, $[\mathbf{Ph}_3C]^+$), 7.94 (m, 6 H, $[\mathbf{Ph}_3C]^+$), 7.72 (m, 6 H, $[\mathbf{Ph}_3C]^+$) ppm
^{13}C-NMR (75.48 MHz, 298 K, CD_2Cl_2): δ = 130.9 ($[\mathbf{Ph}_3C]^+$), 140.0 ($[\mathbf{Ph}_3C]^+$), 142.9 ($[\mathbf{Ph}_3C]^+$), 143.7 ($[\mathbf{Ph}_3C]^+$), 210.7 ($[Ph_3\mathbf{C}]^+$) ppm.
^{19}F-NMR (282.45 MHz, CD_2Cl_2, 298 K): δ = –75.8 (d, $^5J_{F-F}$ = 1.7 Hz,27 F, $[F{-}Al(O\mathbf{R^F})_3]^-$), –186.1 (m, br, 1 F, $[\mathbf{F}{-}Al(OR^F)_3]^-$) ppm.
^{27}Al-NMR (104.27 MHz, CD_2Cl_2, 298 K): δ = 41.1 (s, 1 Al, $[F{-}\mathbf{Al}(OR^F)_3]^-$) ppm.
ATR-IR (diamond): $\tilde{\nu}$ = 1585 (m), 1485 (s), 1452 (s), 1357 (m), 1295 (m), 1265 (w), 1238 (vw), 1210 (vw), 1187 (w), 1167 (w), 1030 (vs), 997 (s), 967 (vw), 841 (s), 825 (m), 806 (s), 766 (m), 725 (w), 699 (w), 661 (vs), 623 (s), 609 (s), 559 (s), 536 (m), 495 (vs), 446 (m), 402 (m).

Synthesis of $[Ph_3C][al\text{–}f\text{–}al]$

$[Ph_3C][PF_6]$ (1.52 g, 3.91 mmol) and $Me_3Si{-}F{-}Al(OR^F)_3$ (6.70 g, 8.13 mmol, 2.1 eq.) were weighed into a Schlenk vessel equipped with a bubbler. After addition of *o*–DFB (10 ml), immediately a fierce evolution of PF_5 was observed, which was finished after several seconds. After stirring for 1 h at room temperature, the solvent was slowly removed in vacuo. The product was obtained as a fine yellow powder (5.94 g, 3.44 mmol, 88 %).

^{1}H-NMR (300.18 MHz, 298 K, CD_2Cl_2): δ = 7.71 (m, 2 H, $[Ph_3C]^+$), 7.94 (m, 2 H, $[Ph_3C]^+$), 8.33 (m, 1 H, $[Ph_3C]^+$) ppm.
^{13}C-NMR (75.48 MHz, 298 K, CD_2Cl_2): δ = 130.9 ($[\mathbf{Ph}_3C]^+$), 140.0 ($[\mathbf{Ph}_3C]^+$), 142.8 ($[\mathbf{Ph}_3C]^+$), 143.9 ($[\mathbf{Ph}_3C]^+$), 210.8 ($[Ph_3\mathbf{C}]^+$) ppm.
^{19}F-NMR (282.45 MHz, 298 K, CD_2Cl_2): δ = –75.8 (d, 54 F, $^5J_{F-F}$ = 0.5 Hz, $[F\{Al(O\mathbf{R^F})_3\}_2]^-$), –184.9 (s, 1 F, $[\mathbf{F}\{Al(OR^F)_3\}_2]^-$) ppm.
^{27}Al-NMR (78.22 MHz, 298 K, CD_2Cl_2): δ = 37 (s, br, $[F\{\mathbf{Al}(OR^F)_3\}_2]^-$) ppm.

Investigations on the $Al(OR^F)_3$ exchange reactions of $[al\text{–}f\text{–}al]^-$ and $[f\text{–}al]^-$

Non-stoichiometric amounts of Ag[*f*–*al*] and Ag[*al*–*f*–*al*] were filled into an NMR tube and dissolved in *o*–DFB and CD_2Cl_2 (1:1). For both anions the $^1J_{Al-F}$ couplings are resolved in the NMR spectra, proving the absence of an exchange of $Al(OR^F)_3$ between these anions. Al decoupling of the ^{19}F NMR spectrum leads to sharp signals of the Al-F atom for both anions.

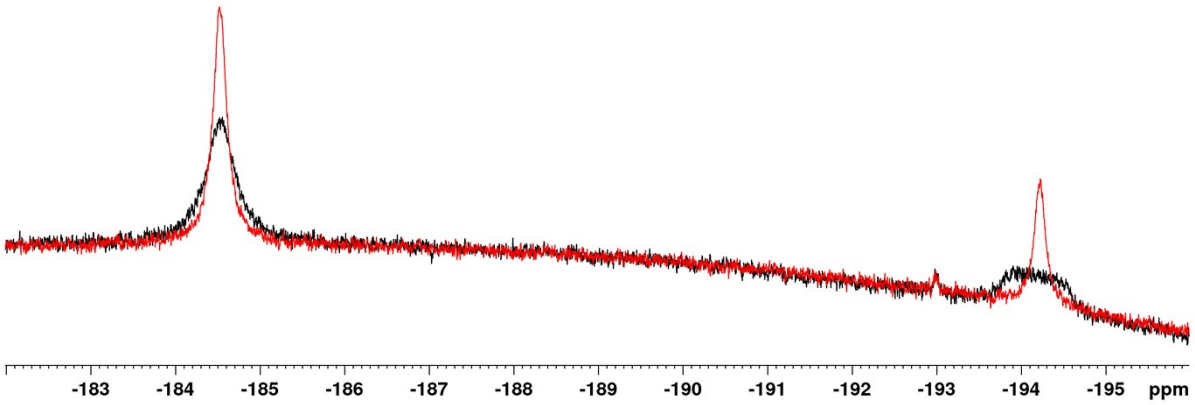

Figure S- 29: ^{19}F-NMR spectrum (282.45 MHz, 298 K, *o*–DFB/CD_2Cl_2) in the (Al-)F region of the mixture of Ag[*f*–*al*] and Ag[*al*–*f*–*al*]; black) ^{19}F NMR spectrum; red) ^{19}F{^{27}Al} NMR spectrum.

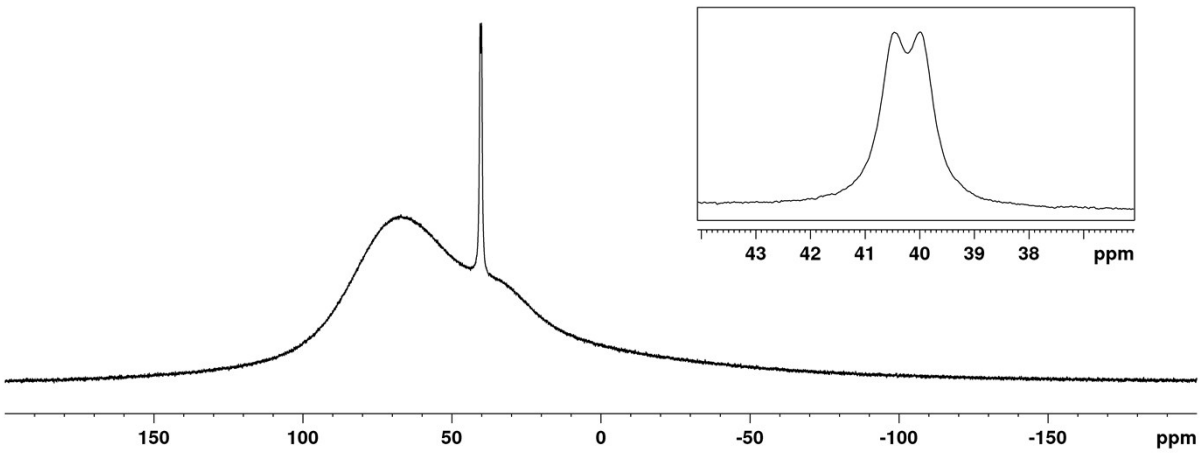

Figure S- 30: ^{27}Al-NMR spectrum (78.22 MHz, 298 K, *o*–DFB/CD_2Cl_2) of the mixture of Ag[*f*–*al*] and Ag[*al*–*f*–*al*.

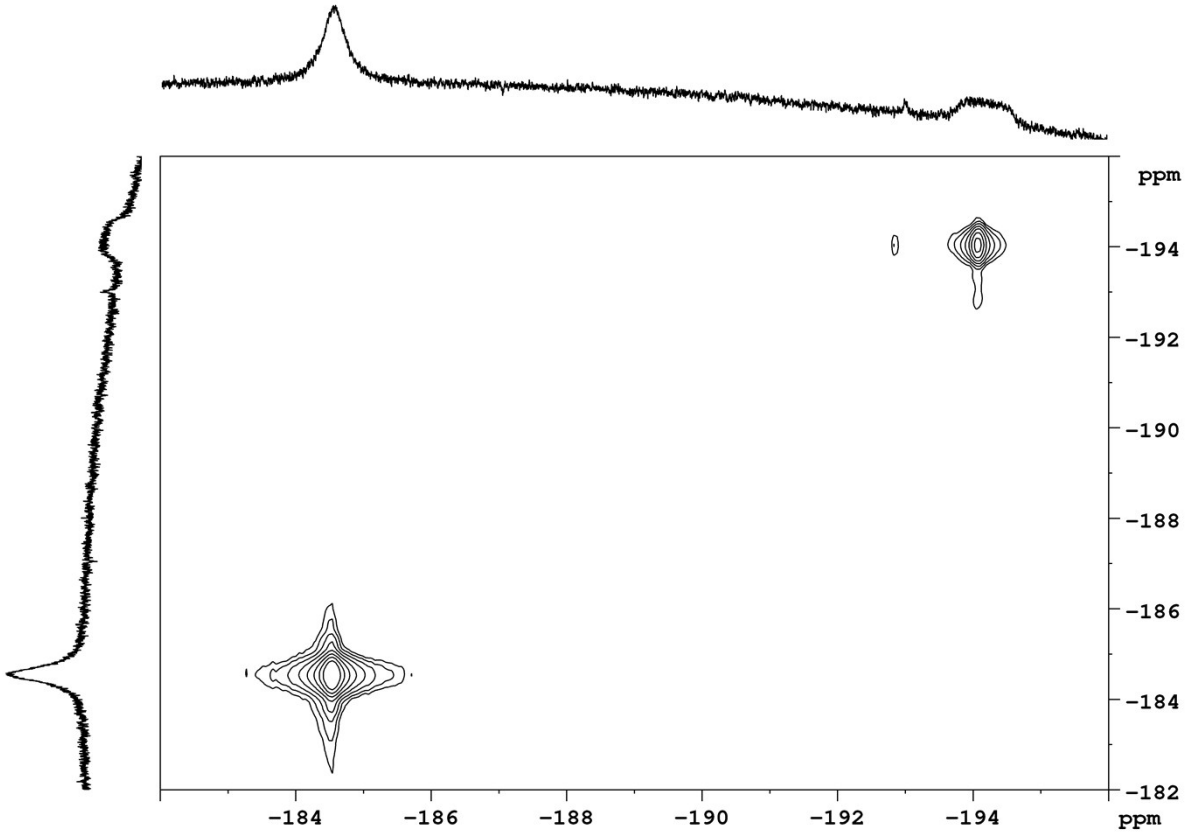

Figure S- 31: $^{19}F,^{19}F$ EXSY NMR spectrum (282.45 MHz, 298 K, *o*–DFB/CD_2Cl_2 mixing time: 1.6 s) of the mixture of Ag[*f–al*] and Ag[*al–f–al*].

Reactions of $Me_3Si–F–Al(OR^F)_3$ with [Cat][BF_4]

a) $[Cat]^+ = K^+$

$Me_3Si–F–Al(OR^F)_3$ (2.17 g, 2.6 mmol) and KBF_4 (165 mg, 1.3 mmol, 0.5 eq.) were weighed into a Schlenk vessel equipped with a bubbler and dissolved in *o*–DFB (10 ml). The solution was heated to 80°C for 2 h, which led to formation of a colorless precipitate.

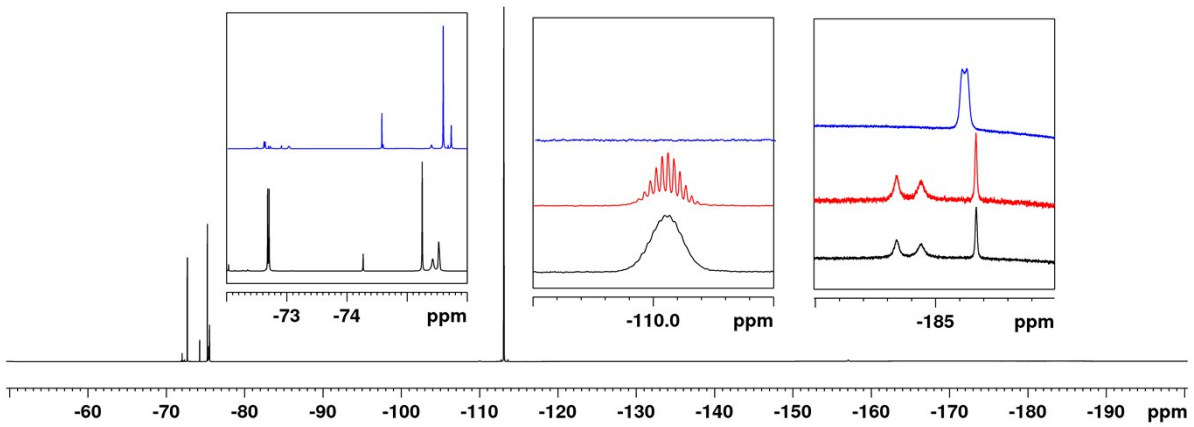

Figure S- 32: ^{19}F-NMR spectrum (282.45 MHz, 298 K) of the reaction of $Me_3Si–F–Al(OR^F)_3$ with KBF_4; black) in $C_6H_5F/CDCl_3$; red) $^{19}F\{^{11}B\}$ NMR spectrum in $C_6H_5F/CDCl_3$; blue) in C_6H_5F/Acetone-d6.

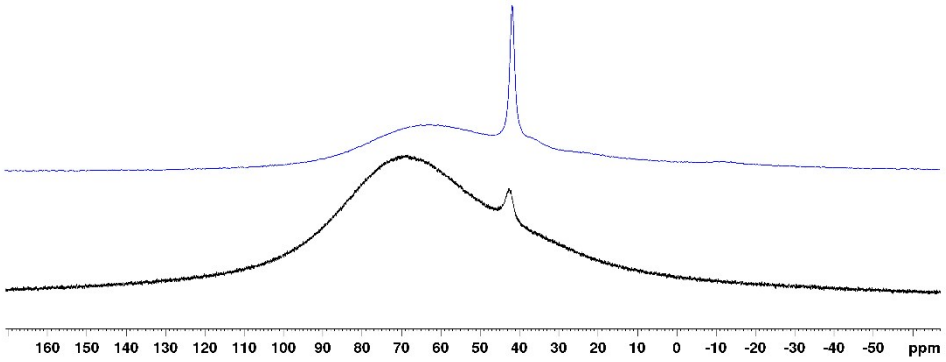

Figure S- 33: ^{27}Al-NMR spectrum (78.22 MHz, 298 K) of the reaction of $Me_3Si–F–Al(OR^F)_3$ with KBF_4; black) in $C_6H_5F/CDCl_3$; blue) in C_6H_5F/Acetone-d6..

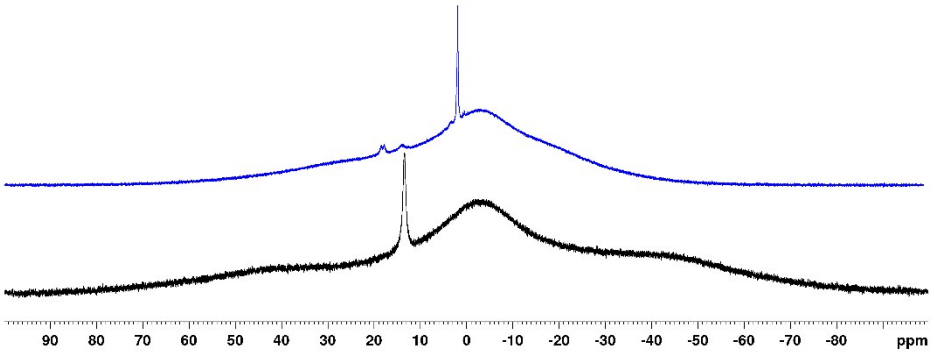

Figure S- 34: ^{11}B-NMR spectrum (96.31 MHz, 298 K) of the reaction of $Me_3Si–F–Al(OR^F)_3$ with KBF_4; black) in $C_6H_5F/CDCl_3$; blue) in C_6H_5F/Acetone-d6..

b) $[Cat]^+ = Ag^+$

$Me_3Si–F–Al(OR^F)_3$ (2.17 g, 2.6 mmol) and $AgBF_4$ (255 mg, 1.3 mmol, 0.5 eq.) were weighed into a Schlenk vessel equipped with a bubbler and dissolved in PhF (5 ml). The solution was stirred for 2 days and then stored at −30°C. From the reaction solution single crystals of $[Ag(PhF)_2][F_2B(OR^F)_2]$ could be obtained.

Reaction of Ag[*al–f–al*] with R_3SiX

a) Ph_3SiCl

Ag[*al–f–al*] (151 mg, 0.09 mmol) and Ph_3SiCl (29 mg, 0.10 mmol, 1.0 eq.) were weighed into a Schlenk vessel and were dissolved in *o*–DFB (2 ml). The solution was stirred overnight, which led to formation of small amounts of a black precipitate. NMR spectra mainly showed signals of the starting materials. The ^{29}Si NMR Signal of Ph_3SiCl is shifted by 0.5 ppm compared to pure Ph_3SiCl (δ^{29}Si = 1.2 ppm), probably due to adduct formation.

^{1}H-NMR (400.17 MHz, 298 K, *o*–DFB/Toluene-d8): δ = 7.60-7.64 (m, 15H, **Ph_3**SiCl) ppm.
^{19}F-NMR (282.45 MHz, 298 K, *o*–DFB/Toluene-d8): δ = −75.2 (s, 54F, $[(OR^F)_3Al–F–Al(OR^F)_3]^-$), −169.2 (s, 1F, Ph_3Si**F**), −184.3 (s, 1F, [al–**f**–al]$^-$) ppm.
^{29}Si-NMR (79.5 MHz, 298 K, *o*–DFB/Toluene-d8): δ = 1.7 (s, Ph_3**Si**Cl), −3.9 (s, Ph_3**Si**F) ppm.

b) tBu_3SiBr

Ag[*al–f–al*] (151 mg, 0.09 mmol) and $t\text{Bu}_3\text{SiBr}$ (56 mg, 0.2 mmol, 2.0 Äq.) were weighed into a Schlenk vessel and cooled with liquid N_2. After addition of CH_2Cl_2 the reaction solution was warmed to −40°C and stirred overnight, which led to formation of small amounts of a black precipitate. NMR spectra of the reaction solution mainly showed signals of the starting materials. The ^{29}Si NMR Signal of $t\text{Bu}_3\text{SiBr}$ is shifted by 2.0 ppm compared to the literature (δ^{29}Si = 41.3 ppm), probably due to adduct formation.
Storage of the reaction solution at −40°C yielded needle-shaped crystals of $[\text{Ag}(t\text{Bu}_3\text{SiBr})_2(\text{CH}_2\text{Cl}_2)_2][al–f–al]$.

^{1}H-NMR (300.18 MHz, 298 K, CD_2Cl_2): δ = 1.25 (s, 27H, ***t*Bu**$_3$SiBr) ppm.
^{13}C-NMR (75.48 MHz, 298 K, CD_2Cl_2): δ = 24.5 (s, 3C, Me_3**C**SiBr), 29.9 (s, 9C, **Me**$_3$CSiBr) ppm.
^{19}F-NMR (282.45 MHz, 298 K, CD_2Cl_2): δ = −184.9 (s, 1F, [al−**f**−al]$^-$), −75.8 (s, 54F, [(**R^F**O)$_3$Al−F−Al(O**R^F**)$_3$]$^-$) ppm.
^{29}Si-NMR (59.64 MHz, 298 K, CD_2Cl_2): δ = 43.3 (s, $t\text{Bu}_3$**Si**Br) ppm.

c) Me_3SiI

Ag[*al–f–al*] (235 mg, 0.148 mmol) was dissolved in 1,2,3-$C_6H_3F_3$ (2 ml) and toluene (0.2 ml). After addition of Me_3SiI (0.02 ml, 29 mg, 0.145 mmol) a colorless precipitate (AgI) formed. The orange solution was stirred for another 30 min and then analyzed by NMR spectroscopy.

^{1}H-NMR (400.17 MHz, 298 K, $C_6H_3F_3$/toluene): δ = 0.14 (dec, $^6J_{H-F}$ = 0.4 Hz, **Me**$_3$SiOC(CF$_3$)$_3$), 0.55 (d, $^3J_{H-F}$ = 12.8 Hz, **Me**$_3$Si−F−Al(OR^F)$_3$), 0.59 (s, br, unknown side product), 0.67 (s, unknown side product) ppm.
^{19}F-NMR (376.54 MHz, 298 K, $C_6H_3F_3$/toluene): δ = −184.8 (s, [*al–**f**–al*]$^-$), −156.6 (s, br, Me$_3$Si−**F**−Al(OR^F)$_3$), −76.4 (s, Me$_3$Si−F−Al(O**R^F**)$_3$), −76.0 (s, [*al–f–al*]$^-$), −74.8 (s, Me$_3$SiOC(C**F$_3$**)$_3$) ppm.
^{27}Al-NMR (104.27 MHz, 298 K, $C_6H_3F_3$/toluene): δ = 40 (s, br, Me$_3$Si−F−Al(OR^F)$_3$ / [***al***–*f*–***al***]$^-$) ppm.
^{29}Si-NMR (79.50 MHz, 298 K, $C_6H_3F_3$/toluene): δ = 28.1 (s, Me$_3$**Si**OC(CF$_3$)$_3$), 61.3 (s, unknown side product), 84.6 (d, $^1J_{Si-F}$ = 260 Hz, Me$_3$**Si**−F−Al(OR^F)$_3$) ppm.

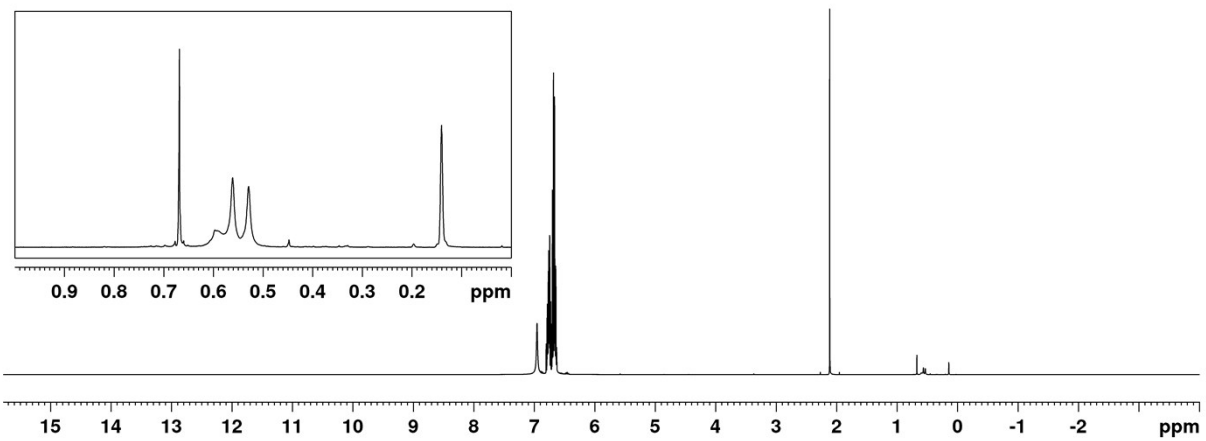

Figure S- 35: ^{1}H-NMR spectrum (400.17 MHz, 298 K, $C_6H_3F_3$/toluene) of the reaction of Ag[*al–f–al*] with Me_3SiI.

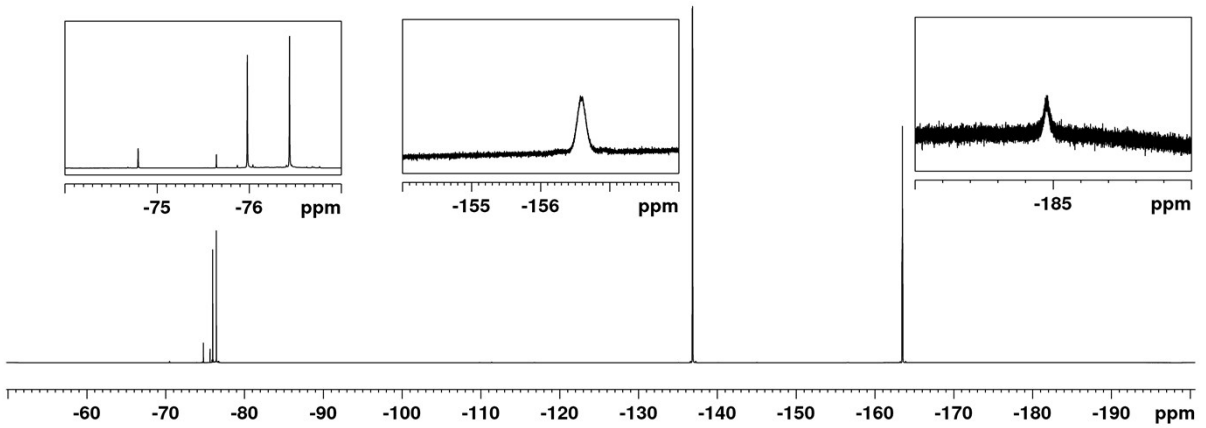

Figure S- 36: ^{19}F-NMR spectrum (376.54 MHz, 298 K, $C_6H_3F_3$/toluene) of the reaction of Ag[*al–f–al*] with Me_3SiI. The ratio between $Me_3Si–F–Al(OR^F)_3$ and $[al–f–al]^-$ is 2.4 : 1.

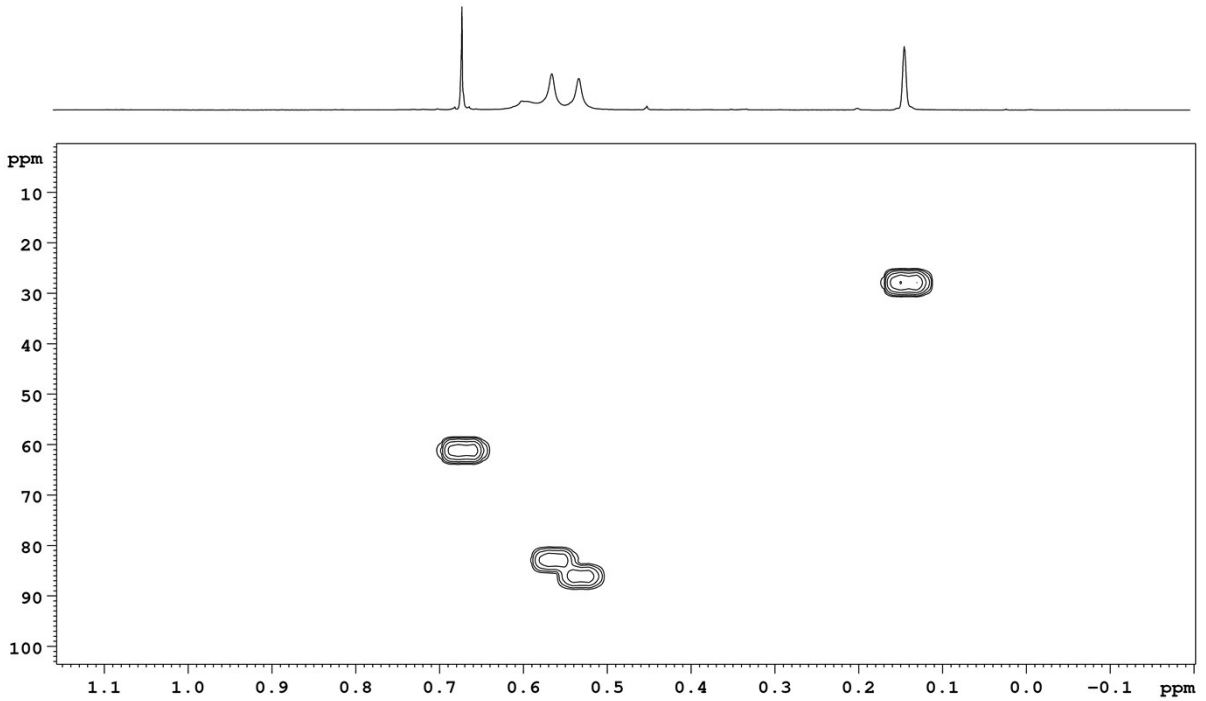

Figure S- 37: ^{1}H,^{29}Si HMBC NMR spectrum (400.17 MHz, 79.50 MHz 298 K, $C_6H_3F_3$/toluene) of the reaction of Ag[*al–f–al*] with Me_3SiI.

Reaction of Ag[*f*–*al*] with PCl_3

Ag[*f*–*al*] (195 mg, 0.23 mmol) was weighed into a Schlenk vessel and dissolved in *o*–DFB (1 ml). Then PCl_3 (0.02 ml, 0.23 mmol, 1.0 eq.) was added and the solution became turbid after few seconds. The reaction mixture was stirred overnight. The reaction solution was analyzed by NMR spectroscopy.

^{19}F-NMR (376.54 MHz, 298 K, *o*–DFB/CD_2Cl_2): δ = −33.4 (d, $^1J_{P-F}$ = 1400 Hz, P**F_3**), −37.8 (d, $^1J_{P-F}$ = 1375 Hz, P**F_2**Cl), −58.0 (d, $^1J_{P-F}$ = 1320 Hz, P**F**Cl_2), –75.6 (s, 54 F, $[F\{Al(OR^F)_3\}_2]^-$), –184.6 (s, 1 F, $[\mathbf{F}\{Al(OR^F)_3\}_2]^-$) ppm.
^{27}Al-NMR (104.27 MHz, 298 K, *o*–DFB/CD_2Cl_2): δ = 37 (s, br, $[F\{\mathbf{Al}(OR^F)_3\}_2]^-$) ppm.
^{31}P-NMR (161.99 MHz, 298 K, *o*–DFB/CD_2Cl_2): δ = 219.2 (s, **P**Cl_3), 218.1 (d, $^1J_{P-F}$ = 1320 Hz, **P**FCl_2), 104.6 (q, $^1J_{P-F}$ = 1400 Hz, **P**F_3) ppm.

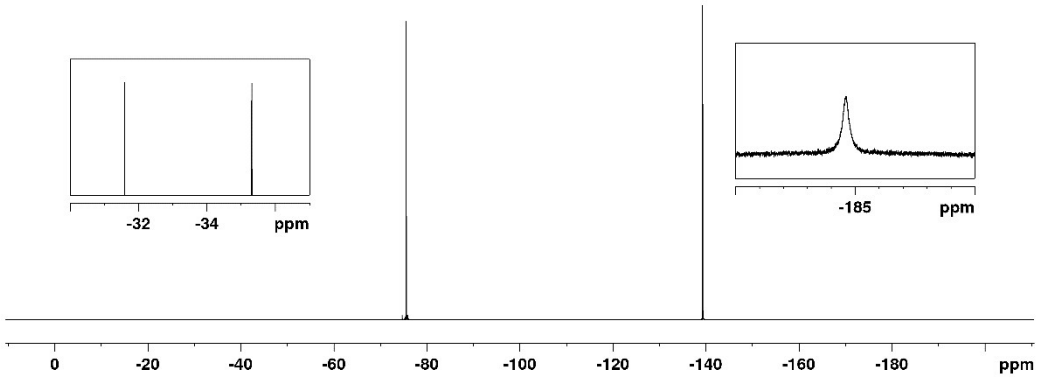

Figure S- 38: ^{19}F-NMR spectrum (376.54 MHz, 298 K, *o*–DFB/CD_2Cl_2) of the reaction of Ag[*f*–*al*] with PCl_3.

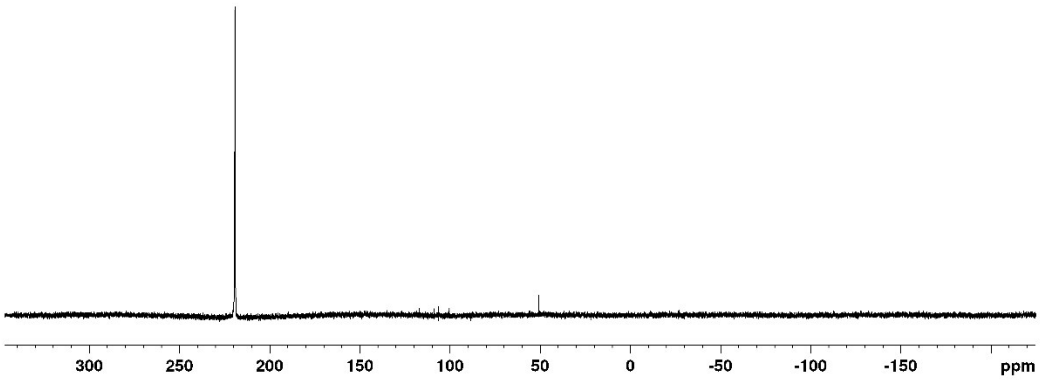

Figure S- 39: ^{31}P-NMR spectrum (166.99 MHz, 298 K, *o*–DFB/CD_2Cl_2) of the reaction of Ag[*f*–*al*] with PCl_3.

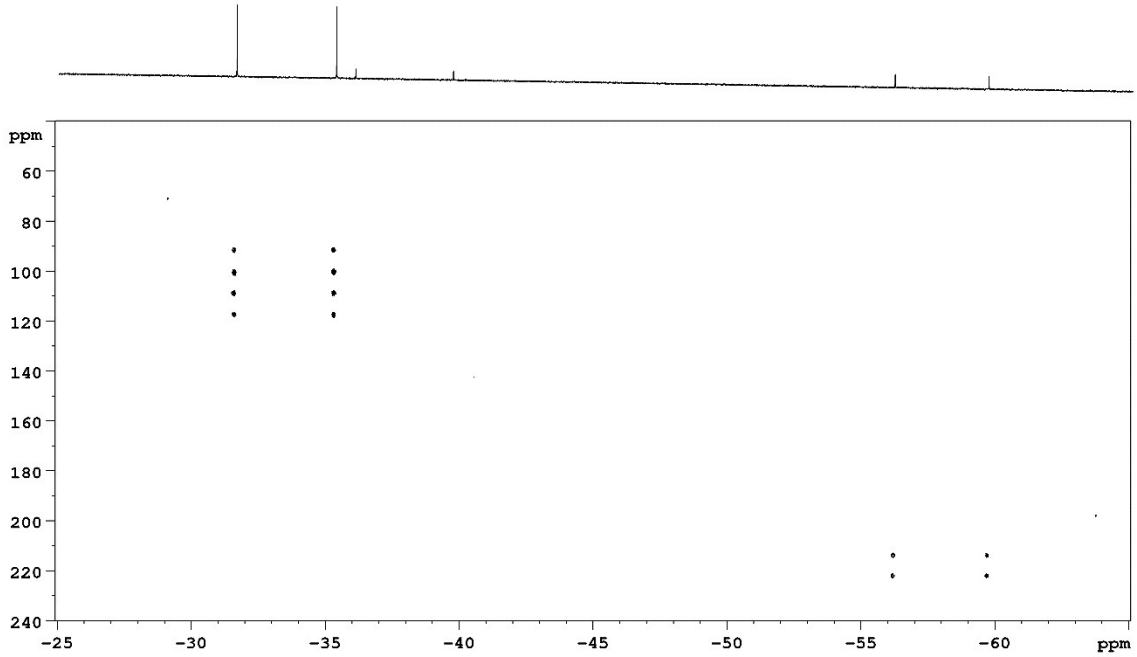

Figure S- 40: $^{19}F,^{31}P$ COSY-NMR spectrum (376.54 MHz, 298 K, *o*–DFB/CD_2Cl_2) of the reaction of Ag[*f*–*al*] with PCl_3.

Crystal Structure Data

Crystal Structures of $[SeCl_3][WCA]$

Since the original data of these crystal structures will be published separate (see Ref. 33), only the asymmetric units of the different $[SeCl_3][WCA]$ salts will be shown here (Figure S-41). It should be noted, that in case of $[SeCl_3][al–f–al]$ the anion is located at an inversion center, which is commonly observed in structures containing $[al–f–al]^-$ as anion. Therefore the asymmetric unit formally shows two $[f–al]^-$ anions. In reality each of these $[f–al]^-$ anions is one half of $[al–f–al]^-$ with the (Al–)F atom being only 50% occupied.

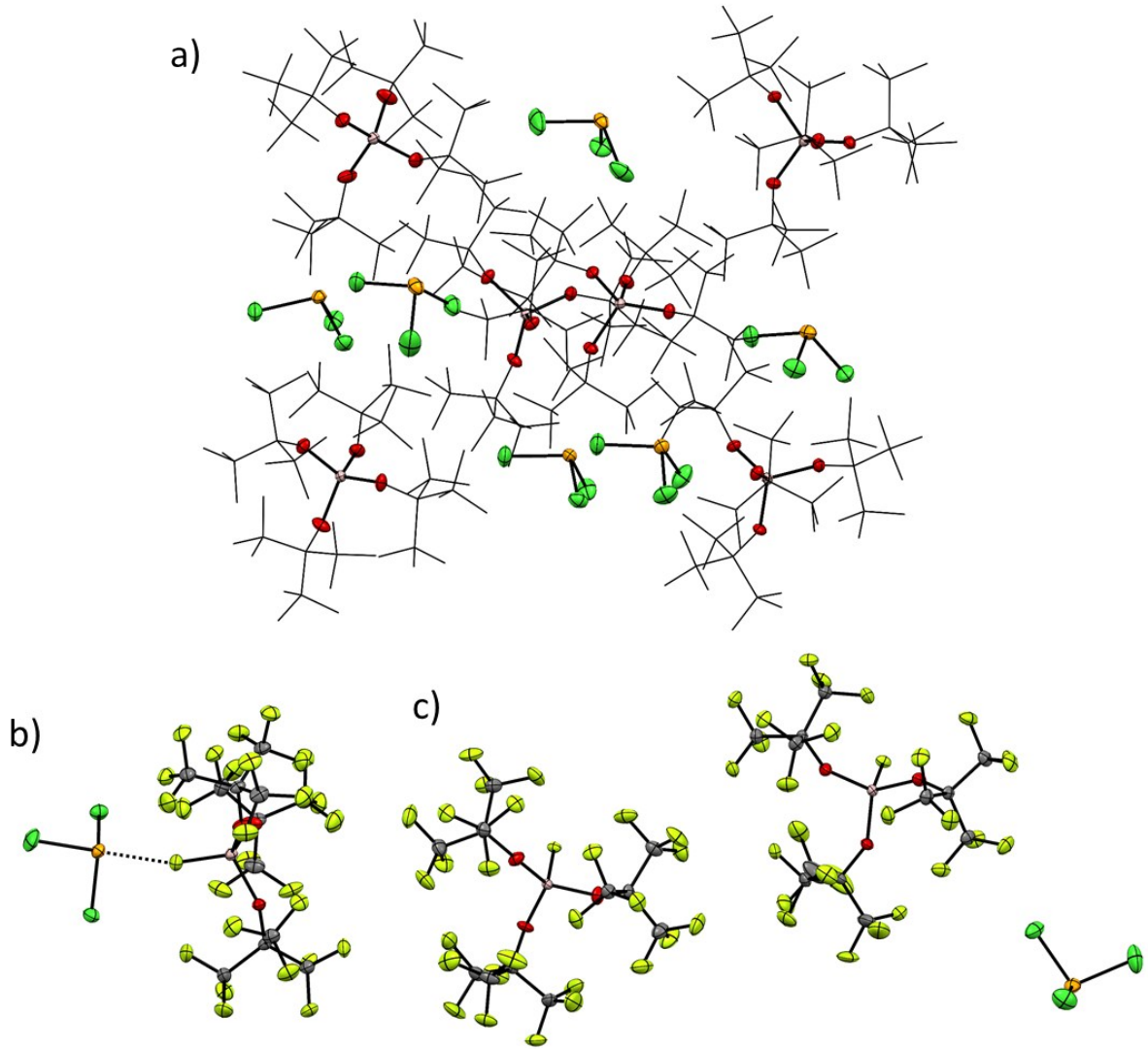

Figure S- 41: Asymmetric unit of $[SeCl_3]^+[WCA]^-$ at 100 K with thermal ellipsoids at 50% probability level. Disorder was omitted for clarity. a) $[SeCl_3]^+[Al(OR^F)_4]^-$. The $C(CF_3)_3$ moieties are shown in wireframe; b) $[SeCl_3]^+[f–al]^-$; c) $[SeCl_3]^+[al–f–al]^-$. The anion is located at an inversion center and therefore the asymmetric unit contains two half anions. Scheme: Se (orange), Cl (green), Al (pink), O (red), F (light green), C (grey).

Crystal Structure of [Li(NCCCl$_3$)][*f*–*al*]

[Li(NCCCl$_3$)][*f*–*al*] was synthesized as described above and crystals suited for SC-XRD could be obtained from the reaction solution at −40°C. Equivalent C–C and C–F bond distances and thermal ellipsoids were equalized by using SADI, SIMU and RIGU commands.

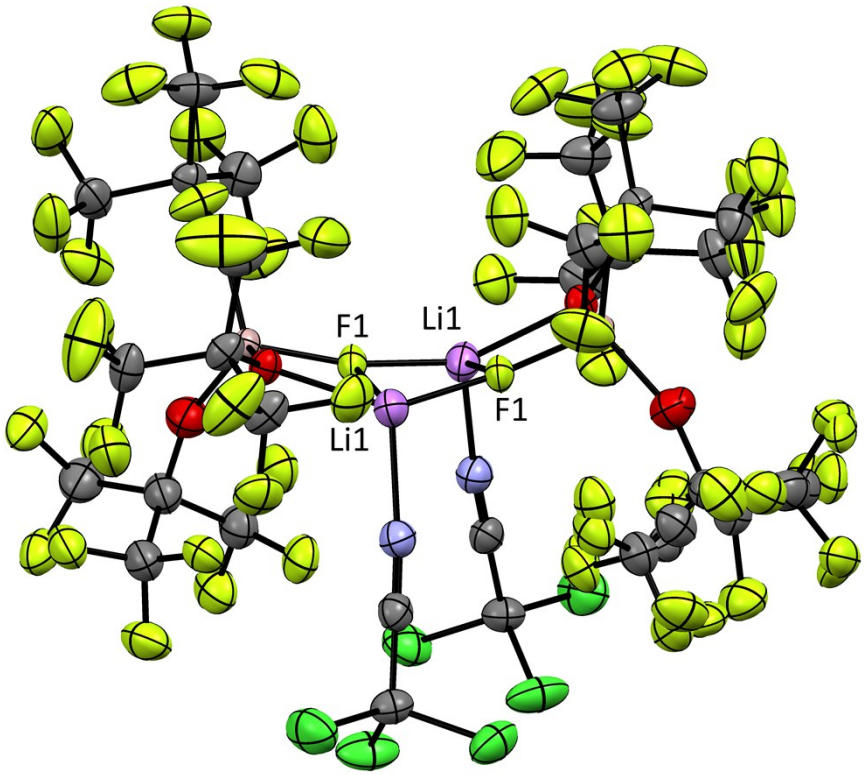

Figure S- 42: Molecular structure of [Li(NCCCl$_3$)][*f*–*al*] with thermal ellipsoids at 50% probability level. Some of the OR^F groups were disordered over two positions. Only the most occupied moiety is shown. Scheme: Li (violet), Al (pink), O (red), F (light green), Cl (green), C (grey), N (blue) H (white).

Table S-1. Crystal data and structure refinement for [Li(NCCCl$_3$)][*f*–*al*].

CCDC number	CCDC 1845808	
Empirical formula	C28 Al2 Cl6 F56 Li2 N2 O6	
Formula weight	1804.84	
Temperature	373(2) K	
Wavelength	71.073 pm	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 3041.36(13) pm	a= 90°.
	b = 1173.18(5) pm	b= 129.575(9)°.
	c = 2062.58(15) pm	g = 90°.
Volume	5.6726(8) nm^3	
Z	4	
Density (calculated)	2.113 Mg/m^3	
Absorption coefficient	0.562 mm^{-1}	

F(000)	3472
Crystal size	0.200 x 0.200 x 0.200 mm^3
Theta range for data collection	3.132 to 27.480°.
Index ranges	-39<=h<=39, -15<=k<=15, -26<=l<=26
Reflections collected	79101
Independent reflections	6479 [R(int) = 0.0677]
Completeness to theta = 25.242°	99.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.000 and 0.795
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6479 / 2844 / 587
Goodness-of-fit on F^2	1.092
Final R indices [I>2sigma(I)]	R1 = 0.0651, wR2 = 0.1807
R indices (all data)	R1 = 0.0841, wR2 = 0.1964
Extinction coefficient	n/a
Largest diff. peak and hole	1.555 and -0.554 e.$Å^{-3}$

Crystal Structure of DMC−Al(OR^F)$_3$

DMC−Al(OR^F)$_3$ was synthesized as described above. Crystals suited for SC-XRD could be obtained from the reaction solution by addition of CH_2Cl_2, followed by storage at −30°C. Equivalent C−C, C−O and C−F bond distances and thermal ellipsoids in the disordered $OC(CF_3)_3$ and DMC groups were equalized by using SADI, SIMU and RIGU commands.

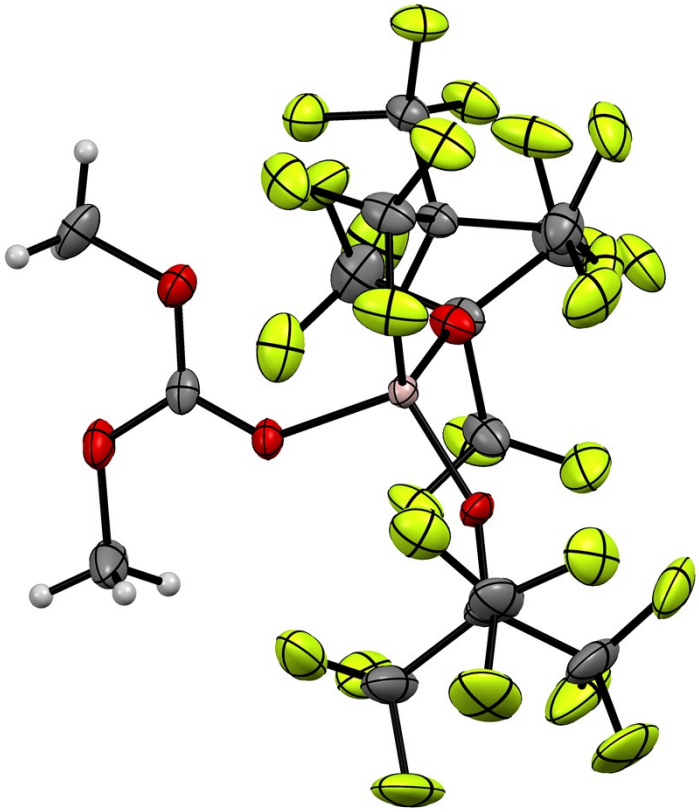

Figure S-43: Molecular structure of DMC–Al(OR^F)$_3$ with thermal ellipsoids at 50% probability level. H atoms are shown as spheres of arbitrary radius. Some of the OR^F groups and the DMC group were disordered over two positions. Only the most occupied moiety is shown. Scheme: Al (pink), O (red), F (light green), C (grey), H (white).

Table S-2. Crystal data and structure refinement for DMC–Al(OR^F)$_3$.

CCDC number	CCDC 1845809	
Empirical formula	C15 H6 Al F27 O6	
Formula weight	822.18	
Temperature	100(2) K	
Wavelength	71.073 pm	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 1080.66(3) pm	a= 90°.
	b = 1395.80(4) pm	b= 90.190(2)°.
	c = 1729.77(5) pm	g = 90°.
Volume	2.60915(13) nm^3	
Z	4	
Density (calculated)	2.093 Mg/m^3	
Absorption coefficient	0.305 mm^{-1}	
F(000)	1600	
Crystal size	0.15 x 0.15 x 0.01 mm^3	
Theta range for data collection	1.875 to 30.588°.	
Index ranges	-14<=h<=15, -19<=k<=19, -24<=l<=24	

Reflections collected	82953
Independent reflections	7987 [R(int) = 0.0404]
Completeness to theta = 25.242°	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7461 and 0.7064
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	7987 / 5038 / 719
Goodness-of-fit on F^2	0.931
Final R indices [I>2sigma(I)]	R1 = 0.0429, wR2 = 0.0991
R indices (all data)	R1 = 0.0721, wR2 = 0.1161
Extinction coefficient	n/a
Largest diff. peak and hole	0.390 and -0.291 e.$Å^{-3}$

Crystal Structure of $[Li(DMC)_3][f\text{–}al]$

$[Li(DMC)_3][f\text{–}al]$ was synthesized as described above and crystals suited for SC-XRD could be obtained from the reaction solution by addition of CH_2Cl_2, followed by storage at −30°C. Equivalent C–C, C–O and C–F bond distances and thermal ellipsoids in the disordered $OC(CF_3)_3$ and DMC groups were equalized by using SADI, SIMU and RIGU commands.

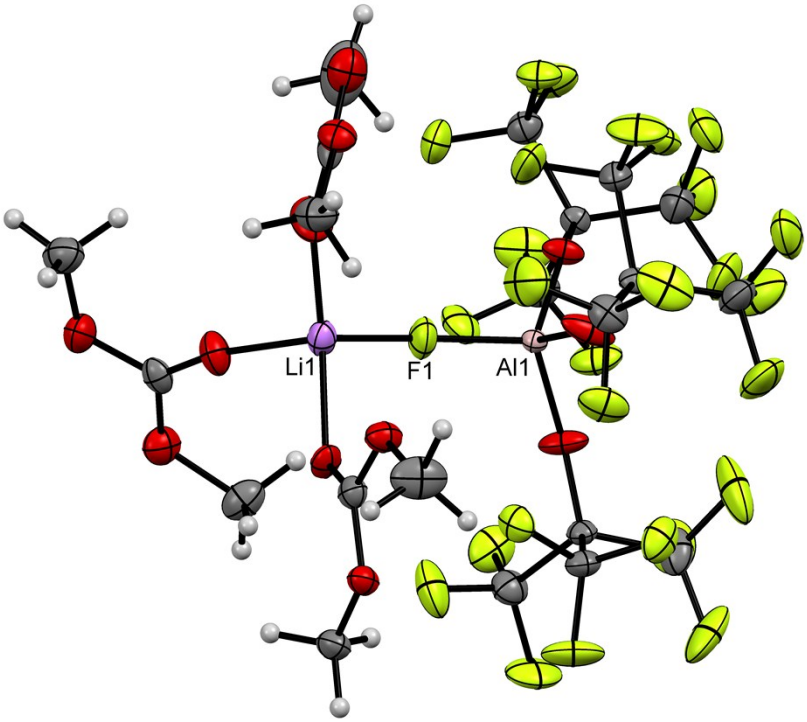

Figure S- 44: Molecular structure of $[Li(DMC)_3][f\text{–}al]$ with thermal ellipsoids at 50% probability level. For clarity, only one of two independent molecules of the asymmetric unit is shown and H atoms are shown as spheres of arbitrary radius. Some of the OR^F groups and the DMC groups were disordered over two positions. Only the most occupied moiety is shown. Scheme: Li (violet), Al (pink), O (red), F (light green), Cl (green), C (grey), H (white).

Table S-3. Crystal data and structure refinement for $[Li(DMC)_3][f\text{–}al]$.

CCDC number	CCDC 1845810	
Empirical formula	C21 H18 Al F28 Li O12	
Formula weight	1028.27	
Temperature	100(2) K	
Wavelength	71.073 pm	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 3592.21(16) pm	a= 90°.
	b = 1074.68(5) pm	b= 102.381(2)°.
	c = 1939.85(9) pm	g = 90°.
Volume	7.3146(6) nm^3	
Z	8	
Density (calculated)	1.867 Mg/m^3	
Absorption coefficient	0.253 mm^{-1}	
F(000)	4064	
Crystal size	0.140 x 0.080 x 0.040 mm^3	
Theta range for data collection	1.161 to 25.408°.	
Index ranges	-43<=h<=43, -12<=k<=12, -23<=l<=23	
Reflections collected	256191	
Independent reflections	13451 [R(int) = 0.0588]	
Completeness to theta = 25.242°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7454 and 0.6989	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	13451 / 11779 / 1458	
Goodness-of-fit on F^2	1.037	
Final R indices [I>2sigma(I)]	R1 = 0.0449, wR2 = 0.1036	
R indices (all data)	R1 = 0.0618, wR2 = 0.1132	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.644 and -0.489 $e.Å^{-3}$	

Crystal Structure of $[Ag(o\text{–}DFB)_3][f\text{–}al]$

$[Ag(o\text{–}DFB)_3][f\text{–}al]$ was synthesized as described above and crystals suited for SC-XRD could be obtained from the reaction solution by layering with pentane at rt. Equivalent C–C and C–F bond distances and thermal ellipsoids in the disordered *o*–DFB groups were equalized by using SADI, SIMU and RIGU commands.

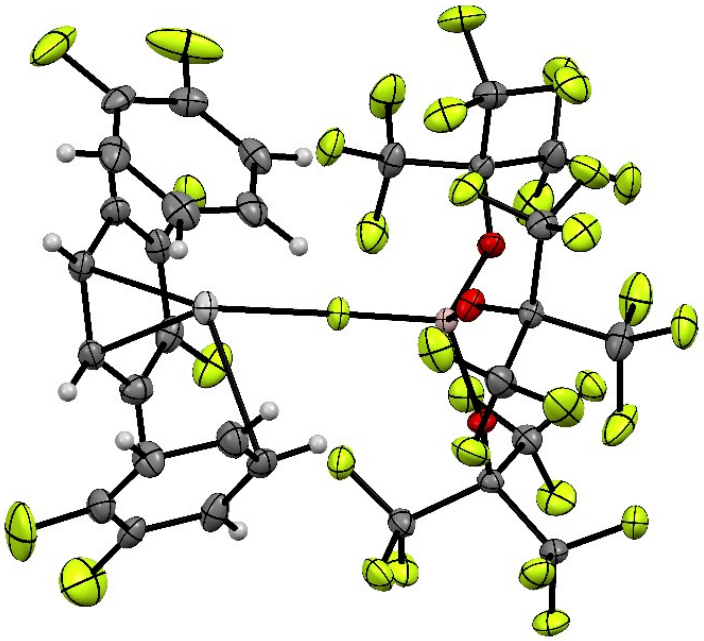

Figure S- 45: Molecular structure of [Ag(*o*–DFB)$_3$][*f*–*al*] with thermal ellipsoids at 50% probability level. H atoms are shown as spheres of arbitrary radius. Some of the *o*–DFB groups were disordered over two or three positions. Only the most occupied moiety is shown. Scheme: Ag (light grey), Al (pink), O (red), F (light green), C (grey), H (white).

Table S-4. Crystal data and structure refinement for [Ag(*o*–DFB)$_3$][*f*–*al*].

CCDC number	CCDC 1845811	
Empirical formula	C30 H12 Ag Al F34 O3	
Formula weight	1201.25	
Temperature	100(2) K	
Wavelength	71.073 pm	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 1026.59(2) pm	a= 90°.
	b = 1746.05(4) pm	b= 99.0980(10)°.
	c = 2099.05(5) pm	g = 90°.
Volume	3.71516(14) nm^3	
Z	4	
Density (calculated)	2.148 Mg/m^3	
Absorption coefficient	0.774 mm^{-1}	
F(000)	2328	
Crystal size	0.6 x 0.2 x 0.05 mm^3	
Theta range for data collection	1.525 to 33.453°.	
Index ranges	-15<=h<=15, -23<=k<=26, -27<=l<=30	
Reflections collected	138683	
Independent reflections	12900 [R(int) = 0.0231]	
Completeness to theta = 25.242°	100.0 %	

Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7466 and 0.6267
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	12900 / 2245 / 813
Goodness-of-fit on F^2	1.022
Final R indices [I>2sigma(I)]	R1 = 0.0276, wR2 = 0.0674
R indices (all data)	R1 = 0.0324, wR2 = 0.0704
Extinction coefficient	n/a
Largest diff. peak and hole	0.858 and -0.639 e.$Å^{-3}$

Crystal Structure of [Ag(*o*–DFB)$_3$][*al–f–al*]

[Ag(*o*–DFB)$_3$][*al–f–al*] was synthesized as described above and crystals suited for SC-XRD could be obtained from the reaction solution by storage at −30°C. Equivalent C–C and C–F bond distances and thermal ellipsoids in the disordered *o*–DFB groups were equalized by using SADI, SIMU and RIGU commands.

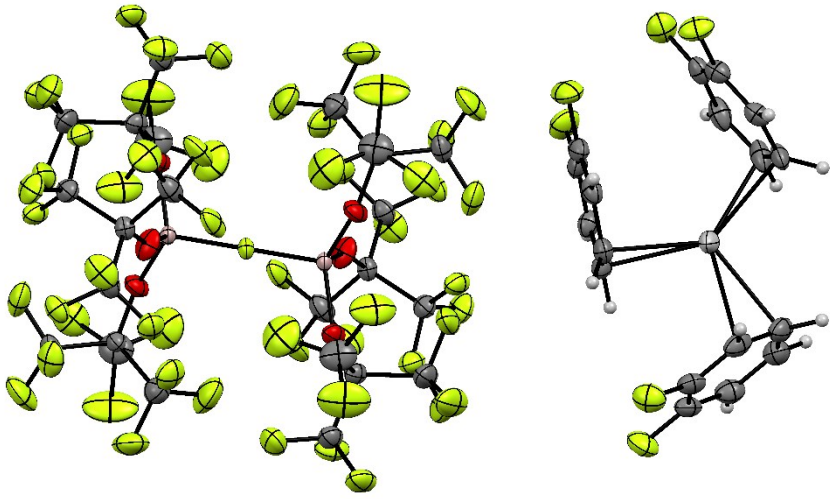

Figure S- 46: Molecular structure of [Ag(*o*–DFB)$_3$][*al–f–al*] with thermal ellipsoids at 50% probability level. For clarity, only one of two independent molecules of the asymmetric unit is shown and H atoms are shown as spheres of arbitrary radius. Some of the OR^F groups were disordered over two positions. Only the most occupied moiety is shown. Scheme: Ag (light grey), Al (pink), O (red), F (light green), C (grey), H (white).

Table S-5. Crystal data and structure refinement for [Ag(*o*–DFB)$_3$][*al–f–al*].

CCDC number	CCDC 1845817
Empirical formula	C42 H12 Ag Al2 F61 O6
Formula weight	1933.35
Temperature	100(2) K
Wavelength	71.073 pm
Crystal system	Triclinic
Space group	P-1

Unit cell dimensions	a = 1548.56(4) pm	a= 76.0930(10)°.
	b = 1768.66(5) pm	b= 84.0230(10)°.
	c = 2256.79(6) pm	g = 81.6170(10)°.
Volume	5.9204(3) nm^3	
Z	4	
Density (calculated)	2.169 Mg/m^3	
Absorption coefficient	0.611 mm^{-1}	
F(000)	3736	
Crystal size	0.220 x 0.210 x 0.200 mm^3	
Theta range for data collection	0.932 to 26.855°.	
Index ranges	-19<=h<=17, -21<=k<=22, -28<=l<=28	
Reflections collected	130364	
Independent reflections	25254 [R(int) = 0.0276]	
Completeness to theta = 25.242°	99.8 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	25254 / 40740 / 2528	
Goodness-of-fit on F^2	1.047	
Final R indices [I>2sigma(I)]	R1 = 0.0555, wR2 = 0.1448	
R indices (all data)	R1 = 0.0771, wR2 = 0.1604	
Extinction coefficient	n/a	
Largest diff. peak and hole	2.616 and -0.478 e.$Å^{-3}$	

Crystal Structure of [Ag(*o*–DFB)$_2$][*al–f–al*]

[Ag(*o*–DFB)$_2$][*al–f–al*] was synthesized as described above and crystals suited for SC-XRD could be obtained from the reaction solution by layering with pentane. Equivalent C–C and C–F bond distances and thermal ellipsoids in the disordered *o*–DFB groups were equalized by using SADI, SIMU and RIGU commands. The Ag atoms in the cation were disordered over eight positions.

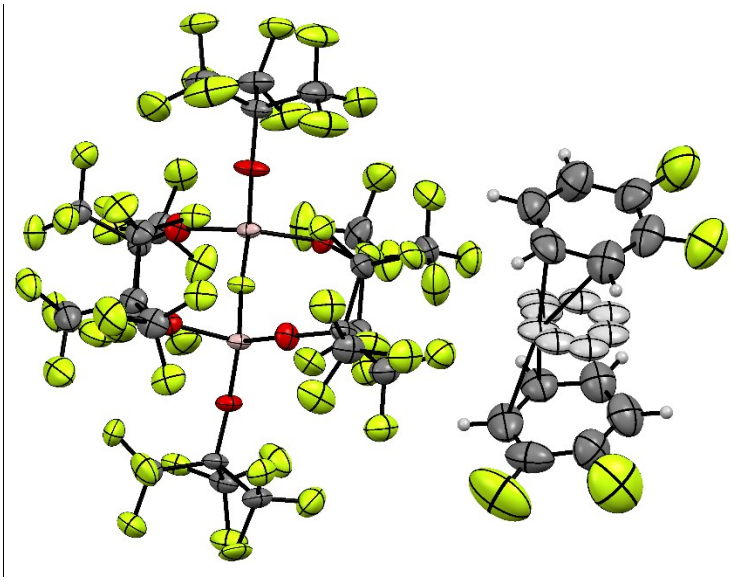

Figure S- 47: Molecular structure of [Ag(*o*–DFB)$_2$][*al–f–al*] with thermal ellipsoids at 50% probability level. For clarity, H atoms are shown as spheres of arbitrary radius. Some of the OR^F groups were disordered over two positions. Only the most occupied moiety is shown. Scheme: Ag (light grey), Al (pink), O (red), F (light green), C (grey), H (white).

Table S-6. Crystal data and structure refinement for [Ag(*o*–DFB)$_2$][*al–f–al*].

CCDC number	CCDC 1845812	
Empirical formula	C36 H8 Ag Al2 F59 O6	
Formula weight	1819.46	
Temperature	100(2) K	
Wavelength	71.073 pm	
Crystal system	Monoclinic	
Space group	Cc	
Unit cell dimensions	a = 1310.28(12) pm	a= 90°.
	b = 2939.0(3) pm	b= 99.674(4)°.
	c = 1412.90(12) pm	g = 90°.
Volume	5.3636(8) nm^3	
Z	4	
Density (calculated)	2.253 Mg/m^3	
Absorption coefficient	0.662 mm^{-1}	
F(000)	3504	
Crystal size	0.23 x 0.15 x 0.10 mm^3	
Theta range for data collection	1.722 to 29.599°.	
Index ranges	-18<=h<=17, -40<=k<=39, -19<=l<=19	
Reflections collected	60147	
Independent reflections	14011 [R(int) = 0.0275]	
Completeness to theta = 25.242°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7459 and 0.7057	

Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	14011 / 19238 / 1510
Goodness-of-fit on F^2	0.994
Final R indices [I>2sigma(I)]	R1 = 0.0633, wR2 = 0.1652
R indices (all data)	R1 = 0.0782, wR2 = 0.1793
Absolute structure parameter	0.47(4)
Extinction coefficient	n/a
Largest diff. peak and hole	0.942 and -0.501 e.$Å^{-3}$

Crystal Structure of $[Ag(o\text{–}DFB)_2][Al(OR^F)_4]$

$[Ag(o\text{–}DFB)_2][Al(OR^F)_4]$ was synthesized as described in the literature in *o*–DFB and crystals suited for SC-XRD could be obtained from the reaction solution by layering with pentane. Equivalent C–C and C–F bond distances and thermal ellipsoids in the disordered *o*–DFB groups were equalized by using SADI, SIMU and RIGU commands. The Ag atoms in the cation are disordered over an inversion center.

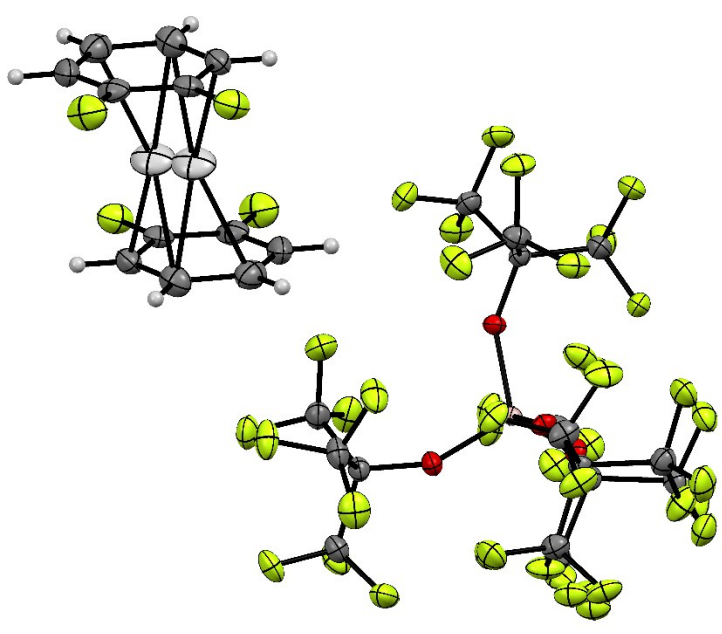

Figure S- 48: Molecular structure of $[Ag(o\text{–}DFB)_2][Al(OR^F)_4]$ with thermal ellipsoids at 50% probability level. For clarity, H atoms are shown as spheres of arbitrary radius. Some of the OR^F groups were disordered over two positions. Only the most occupied moiety is shown. Scheme: Ag (light grey), Al (pink), O (red), F (light green), C (grey), H (white).

Table S-7. Crystal data and structure refinement for $[Ag(o\text{–}DFB)_2][Al(OR^F)_4]$.

CCDC number	CCDC 1845813
Empirical formula	C28 H8 Ag Al F40 O4
Formula weight	1303.19
Temperature	100(2) K
Wavelength	71.073 pm

Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 1415.65(5) pm	a= 90°.
	b = 1845.64(6) pm	b= 91.200(2)°.
	c = 1465.10(5) pm	g = 90°.
Volume	3.8271(2) nm^3	
Z	4	
Density (calculated)	2.262 Mg/m^3	
Absorption coefficient	0.785 mm^{-1}	
F(000)	2512	
Crystal size	0.200 x 0.200 x 0.050 mm^3	
Theta range for data collection	1.775 to 27.100°.	
Index ranges	-18<=h<=18, 0<=k<=23, 0<=l<=18	
Reflections collected	9266	
Independent reflections	9266 [R(int) = ?]	
Completeness to theta = 25.242°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.746333 and 0.683262	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	9266 / 3079 / 697	
Goodness-of-fit on F^2	1.029	
Final R indices [I>2sigma(I)]	R1 = 0.0446, wR2 = 0.1066	
R indices (all data)	R1 = 0.0685, wR2 = 0.1172	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.687 and -0.425 e.$Å^{-3}$	

Crystal Structure of [NO][*al*−*f*−*al*]

[NO][*al*−*f*−*al*] was synthesized as described above and crystals suited for SC-XRD could be obtained from the reaction solution by storage at −30°C. Equivalent C−C and C−F bond distances and thermal ellipsoids in the disordered OR^F groups were equalized by using SADI, SIMU and RIGU commands.

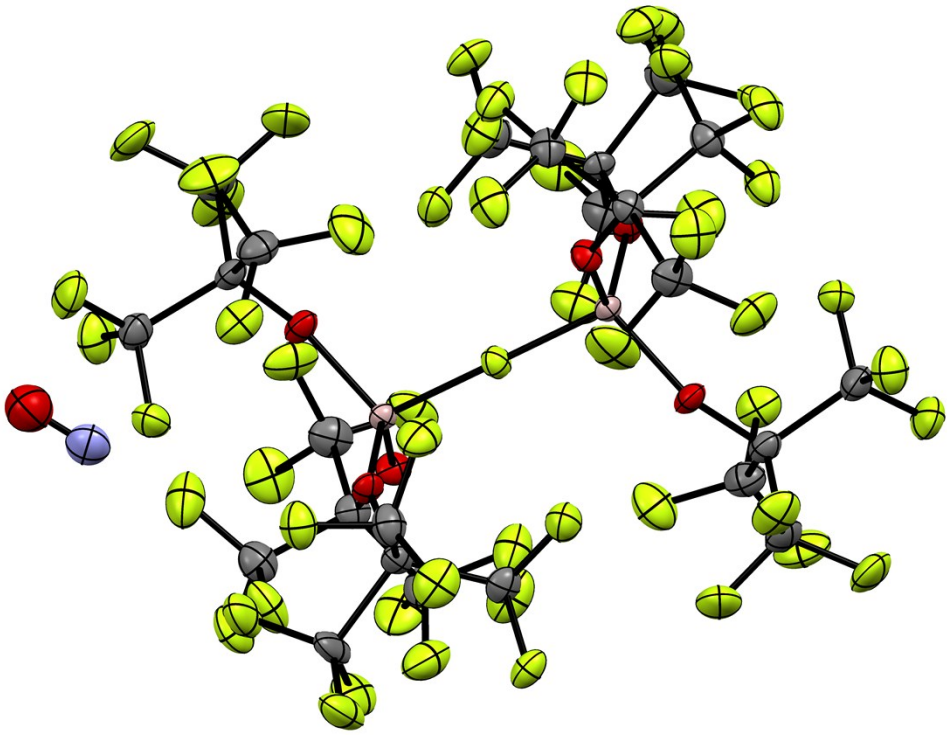

Figure S- 49: Molecular structure of [NO][*al–f–al*] with thermal ellipsoids at 50% probability level. Some of the OR^F groups were disordered over two positions. Only the most occupied moiety is shown. Scheme: N (blue), Al (pink), O (red), F (light green), C (grey), H (white).

Table S-8. Crystal data and structure refinement for [NO][*al–f–al*].

CCDC number	CCDC 18458114	
Empirical formula	C24 Al2 F55 N O7	
Formula weight	1513.21	
Temperature	100(2) K	
Wavelength	71.073 pm	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 1068.41(2) pm	a= 90°.
	b = 1829.66(3) pm	b= 94.8220(10)°.
	c = 2237.98(3) pm	g = 90°.
Volume	4.35938(12) nm^3	
Z	4	
Density (calculated)	2.306 Mg/m^3	
Absorption coefficient	0.350 mm^{-1}	
F(000)	2912	
Crystal size	0.160 x 0.100 x 0.070 mm^3	
Theta range for data collection	1.440 to 27.102°.	
Index ranges	-13<=h<=13, -23<=k<=23, -28<=l<=28	
Reflections collected	70133	

Independent reflections	9618 [R(int) = 0.0415]
Completeness to theta = 25.242°	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7457 and 0.7115
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	9618 / 12483 / 1073
Goodness-of-fit on F^2	1.039
Final R indices [I>2sigma(I)]	R1 = 0.0489, wR2 = 0.1079
R indices (all data)	R1 = 0.0726, wR2 = 0.1202
Extinction coefficient	n/a
Largest diff. peak and hole	0.449 and -0.372 e.$Å^{-3}$

Crystal Structure of $[Ag(PhF)_2][F_2B(OR^F)_2]$

The reaction of $Me_3Si{-}F{-}Al(OR^F)_3$ with $AgBF_4$ yielded crystals of $[Ag(PhF)_2][F_2B(OR^F)_2]$ suited for SC-XRD from the reaction solution by storage at −30°C. Equivalent C−C and C−F bond distances and thermal ellipsoids in the disordered OR^F groups were equalized by using SADI, SIMU and RIGU commands.

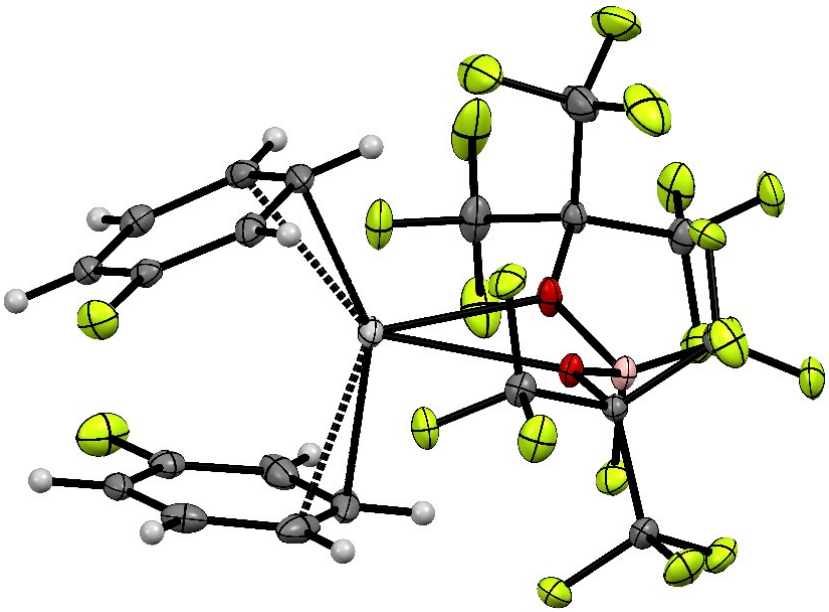

Figure S- 50: Molecular structure of $[Ag(PhF)_2][F_2B(OR^F)_2]$ with thermal ellipsoids at 50% probability level. For clarity, only one of two independent molecules of the asymmetric unit is shown and H atoms are shown as spheres of arbitrary radius. Some of the OR^F groups were disordered over two positions. Only the most occupied moiety is shown. Scheme: Ag (light grey), B (pink), O (red), F (light green), C (grey), H (white).

Table S-9. Crystal data and structure refinement for $[Ag(PhF)_2][F_2B(OR^F)_2]$.

CCDC number	CCDC 1845815
Empirical formula	C20 H10 Ag B F22 O2
Formula weight	818.96

Temperature	100(2) K	
Wavelength	71.073 pm	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 3437.12(10) pm	a= 90°.
	b = 1064.65(3) pm	b= 100.4520(10)°.
	c = 1378.45(4) pm	g = 90°.
Volume	4.9605(2) nm^3	
Z	8	
Density (calculated)	2.193 Mg/m^3	
Absorption coefficient	1.000 mm^{-1}	
F(000)	3168	
Crystal size	0.400 x 0.250 x 0.200 mm^3	
Theta range for data collection	1.205 to 32.351°.	
Index ranges	-48<=h<=49, -14<=k<=15, -19<=l<=20	
Reflections collected	123649	
Independent reflections	15178 [R(int) = 0.0187]	
Completeness to theta = 25.242°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7464 and 0.6502	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	15178 / 3333 / 893	
Goodness-of-fit on F^2	1.141	
Final R indices [I>2sigma(I)]	R1 = 0.0265, wR2 = 0.0568	
R indices (all data)	R1 = 0.0306, wR2 = 0.0581	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.608 and -1.121 e.$Å^{-3}$	

Crystal Structure of $[Ag(tBu_3SiBr)_2(CH_2Cl_2)_2][al–f–al]$

The reaction of Ag[*al–f–al*] with Me_3SiBr in CH_2Cl_2 yielded crystals of $[Ag(tBu_3SiBr)_2(CH_2Cl_2)_2][al–f–al]$ suited for SC-XRD from the reaction solution by storage at −40°C. Equivalent C−C and C−F bond distances and thermal ellipsoids in the disordered OR^F groups were equalized by using SADI, SIMU and RIGU commands.

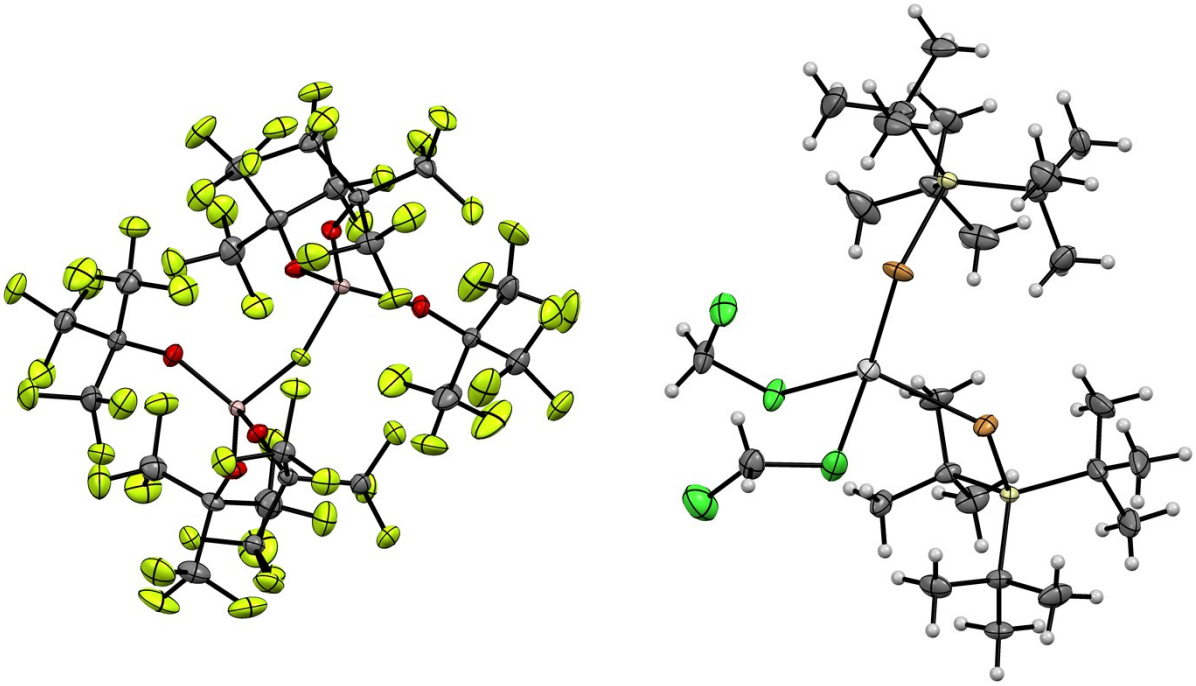

Figure S- 51: Molecular structure of [Ag(tBu$_3$SiBr)$_2$(CH$_2$Cl$_2$)$_2$][*al–f–al*] with thermal ellipsoids at 50% probability level. H atoms are shown as spheres of arbitrary radius. Scheme: Ag (light grey), Al (pink), O (red), F (light green), Cl (green), Br (brown), C (grey), H (white).

Table S-10. Crystal data and structure refinement for [Ag(tBu$_3$SiBr)$_2$(CH$_2$Cl$_2$)$_2$][*al–f–al*].

CCDC number	CCDC 1845816	
Empirical formula	C50 H58 Ag Al2 Br2 Cl4 F55 O6 Si2	
Formula weight	2319.57	
Temperature	100(2) K	
Wavelength	71.073 pm	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 1547.60(18) pm	a= 89.488(4)°.
	b = 1661.5(2) pm	b= 67.742(4)°.
	c = 1829.67(19) pm	g = 70.537(4)°.
Volume	4.0680(8) nm^3	
Z	2	
Density (calculated)	1.894 Mg/m^3	
Absorption coefficient	1.582 mm^{-1}	
F(000)	2280.0	
Crystal size	0.39 x 0.39 x 0.27 mm^3	
Theta range for data collection	1.214 to 26.099°.	
Index ranges	-19<=h<=19, -20<=k<=20, -18<=l<=22	
Reflections collected	85154	
Independent reflections	16093 [R(int) = 0.0181]	

Completeness to theta = 25.242°	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7453 and 0.6110
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	16093 / 5916 / 1117
Goodness-of-fit on F^2	1.029
Final R indices [I>2sigma(I)]	R1 = 0.0272, wR2 = 0.0665
R indices (all data)	R1 = 0.0327, wR2 = 0.0693
Extinction coefficient	n/a
Largest diff. peak and hole	0.753 and -0.621 e.$Å^{-3}$

Quantum Chemical Calculations

DFT optimizations were carried out with TURBOMOLE[QC 1,2] using the BP86[QC 3,4] density functional (RI approximation[QC 5a]) in combination with the def-SV(P) basis set[QC 5b,c] and D3 dispersion correction with Becke-Johnson damping.[QC 5d,e] Vibrational frequencies were calculated analytically with the AOFORCE[QC 6,7] module and all structures represented true minima without imaginary frequencies on the respective hypersurface. Thermodynamic terms were calculated with inclusion of zero-point energy and thermal contributions to the enthalpy/entropy (FREEH tool; unscaled BP86 vibrational frequencies). Solvation effects were calculated using the COSMO[QC 8] module combined with a geometry optimization. Default options and standard optimized COSMO radii included in the module were used. For Al a radius of 1.404 Å was used. For the calculation of the reaction energies in solution FREEH enthalpy/entropy of the gas phase calculation were used for the COSMO calculations.

[QC 1] O. Treutler, R. Ahlrichs, *J. Chem. Phys.* **1995**, *102*, 346.
[QC 2] R. Ahlrichs, M. Baer, M. Haeser, H. Horn, C. Koelmel, *Chem. Phys. Lett.* **1989**, *162*, 165.
[QC 3] J. P. Perdew, *Phys. Rev. B* **1986**, *34*.
[QC 4] A. D. Becke, *Phys. Rev. A: Gen. Phys.* **1988**, *38*, 3098.
[QC 5] a) K. Eichkorn, O. Treutler, H. Oehm, M. Haeser, R. Ahlrichs, *Chem. Phys. Lett.* **1995**, *242*, 652; b) A. Schäfer, H. Horn, R. Ahlrichs, *J. Chem. Phys.* **1992**, *97*, 2571-2577; c) A. Schäfer, C. Huber, R. Ahlrichs, *The Journal of Chemical Physics* **1994**, *100*, 5829; d) S. Grimme, J. Antony, S. Ehrlich, H. Krieg, *The Journal of Chemical Physics* **2010**, *132*, 154104; e) S. Grimme, S. Ehrlich, L. Goerigk, *Journal of Computational chemistry* **2011**, *32*, 1456.
[QC 6] P. Deglmann, F. Furche, R. Ahlrichs, *Chem. Phys. Lett.* **2002**, *362*, 511.
[QC 7] P. Deglmann, F. Furche, *J. Chem. Phys.* **2002**, *117*, 9535.
[QC 8] A. Klamt, G. Schueuermann, *J. Chem. Soc., Perkin Trans. 2* **1993**, 799.
[QC 9] A. Schäfer, A. Klamt, D. Sattel, J. C. W. Lohrenz, F. Eckert, *Phys. Chem. Chem. Phys.* **2000**, *2*, 2187.

Calculations of the FIA
The fluoride ion affinity (FIA)[FIA 1] for [*al–f–al*]$^-$ was calculated by the following reaction (BP86−D3(BJ)/def-SV(P)):

$$[al\text{-}f\text{-}al]^- + [COF_3]^- \xrightarrow{\Delta_r H^\circ_{(g)}} 2\,[f\text{-}al]^- + COF_2$$

After substracting the FIA of COF_2 (FIA = 209 kJ·mol^{-1} [FIA 2]) from Δ*H* the FIAs for [*al–f–al*]$^-$ were obtained.

[FIA 1] T. E. Mallouk, G. L. Rosenthal, G. Mueller, R. Brusasco, N. Bartlett, *Inorg. Chem.* **1984**, *23*, 3167.
[FIA 2] K. O. Christe, D. A. Dixon, D. McLemore, W. W. Wilson, J. A. Sheehy, J. A. Boatz, *J. Fluorine Chem.* **2000**, *101*, 151.

Optimized coordinates and energies of the calculated compounds:

Atomic coordinates are given in Å, SCF energies are given in Hartree, the FREEH energy is given in kJ mol^{-1}, and the FREEH entropy is given in kJ mol^{-1} K^{-1}. $H^0_{(g)}$, $G^0_{(g)}$ and $G^0_{(solv)}$ are calculated by the following equations:

$H^0_{(g)}$ = SCF energy + FREEH energy + R·T

$G^0_{(g)}$ = SCF energy + FREEH energy + R·T – T·FREEH entropy

$G^0_{solv} = G^0_{(g)} + \Delta_{solv}G^0$ with $\Delta_{solv}G^0$ = COSMO energy - SCF energy + 7.96 kJ mol^{-1}

BP86/def-SV(P)

COF_2

C	0.00000	0.00000	0.09545
O	0.00000	0.00000	1.28032
F	1.07294	0.00000	-0.68794
F	-1.07294	0.00000	-0.68794

SCF energy = -312.8029859210
FREEH energy = 44.84
FREEH entropy = 0.25983

$[COF_3]^-$

C	-0.00000	0.00000	0.15221
O	0.00000	0.00000	1.37582
F	0.64255	1.11292	-0.50932
F	0.64255	-1.11292	-0.50932
F	-1.28509	0.00000	-0.50932

SCF energy = -412.6373271036
FREEH energy = 51.64
FREEH entropy = 0.27750

$[F–Al(OR^F)_3]^-$ ([*f–al*]$^-$)

F	-1.17384	-0.56180	2.06645
Al	-0.37466	-0.19700	0.62257
O	1.34539	0.16068	0.88528
C	2.22788	1.01979	1.43362
C	3.58122	0.24022	1.67007
F	3.34554	-0.95781	2.22511
F	4.22474	0.03104	0.50069
F	4.43321	0.91281	2.48602
C	2.49781	2.23142	0.45234
F	1.49218	3.12971	0.50444
F	3.64706	2.89319	0.74832
F	2.59105	1.79482	-0.81278
C	1.71556	1.58266	2.81632
F	0.43076	1.96553	2.71691
F	1.78676	0.63781	3.77811
F	2.43304	2.65241	3.24216
O	-1.07359	1.20505	-0.21565
C	-2.20914	1.75431	-0.69256
C	-2.97702	2.52008	0.45915
F	-3.63510	1.65360	1.25912
F	-3.89136	3.40189	-0.02215
F	-2.11278	3.20379	1.22462
C	-1.81139	2.78641	-1.81989
F	-1.28624	3.90868	-1.28059
F	-0.88854	2.25872	-2.63759
F	-2.87275	3.16172	-2.57889
C	-3.17167	0.66615	-1.31127
F	-3.25964	-0.39523	-0.49066
F	-4.42861	1.13614	-1.51264
F	-2.70713	0.23004	-2.50023
O	-0.42666	-1.53942	-0.54014
C	0.01125	-2.78195	-0.82391
C	-0.05411	-3.72336	0.44095
F	-1.33207	-4.04818	0.73322
F	0.63063	-4.88154	0.26597
F	0.46215	-3.10065	1.51453
C	1.50014	-2.74228	-1.35980
F	1.67211	-1.69589	-2.18087
F	2.37885	-2.61949	-0.34308
F	1.83381	-3.86716	-2.04585
C	-0.92139	-3.37406	-1.95318
F	-2.21192	-3.13650	-1.67439
F	-0.64925	-2.80130	-3.14651
F	-0.77227	-4.71504	-2.10334

SCF energy = -3718.877857464
FREEH energy = 548.64
FREEH entropy = 1.14241

$[(R^FO)_3Al–F–Al(OR^F)_3]^-$ ([*al–f–al*]$^-$)

Al	-1.1769512	0.0308906	-1.3973779
O	-0.8456166	-1.5135007	-2.1443676
O	-2.8022558	0.0654694	-0.7670515

O	-0.8165503	1.4722058	-2.3005314
C	-0.0001128	2.2963848	-3.0038569
C	0.9158968	1.4726984	-3.9897976
F	1.3793645	0.3737025	-3.3677301
F	1.9756585	2.1856656	-4.4277871
F	0.2162077	1.0693251	-5.0698737
C	-0.8934728	3.2930619	-3.8394615
F	-1.4246146	4.2455122	-3.0463697
C	0.9060847	3.1148610	-2.0066874
F	1.8791987	2.3187567	-1.5126155
F	0.1754654	3.5595512	-0.9755685
F	1.4962994	4.1769121	-2.5977608
F	-1.9041653	2.6381764	-4.4292240
F	-0.1765391	3.9174390	-4.8042440
C	-3.8749571	0.7938390	-0.3636183
C	-1.2804879	-2.4718806	-3.0046733
C	-0.1232209	-2.7897532	-4.0320991
F	-0.0447081	-1.8216788	-4.9712247
F	-0.3224987	-3.9654927	-4.6736393
F	1.0578406	-2.8519686	-3.4059847
C	-1.6281599	-3.7839969	-2.1989740
F	-0.5052801	-4.4140560	-1.8017827
F	-2.3471729	-4.6571942	-2.9449565
F	-2.3451016	-3.4850368	-1.1051634
C	-2.5622872	-2.0068175	-3.8004038
F	-2.4348845	-0.7098890	-4.1458416
F	-3.6717466	-2.1191393	-3.0441170
F	-2.7592908	-2.7218948	-4.9290497
C	-3.4906616	1.6945785	0.8730349
F	-3.3928663	0.9527921	1.9925113
F	-4.3932061	2.6734429	1.1010505
F	-2.2933025	2.2703539	0.6553912
C	-5.0114697	-0.2173822	0.0562022
F	-4.5068553	-1.2172113	0.7899843
F	-5.5924483	-0.7598758	-1.0355670
F	-5.9825887	0.3883460	0.7799767
C	-4.4094679	1.7150296	-1.5300262
F	-3.6369840	2.8125950	-1.6663649
F	-5.6777392	2.1326491	-1.3094927
F	-4.3876989	1.0505306	-2.6960578
Al	1.1566533	-0.0278995	1.4096989
O	0.8411298	-1.4464032	2.3638941
O	0.8255421	1.5235800	2.1392498
O	2.7310456	-0.0883369	0.6653033
C	3.8412537	-0.8034377	0.3469761
C	3.4789081	-2.2921437	-0.0403668
F	3.2907213	-3.0454979	1.0630382
F	4.4466037	-2.8813339	-0.7768669
F	2.3387546	-2.3133159	-0.7497796
C	4.5317635	-0.1017120	-0.8865742
F	4.5560399	1.2274934	-0.7184974
C	4.8462618	-0.8174880	1.5639355
F	4.1872847	-1.0582576	2.7095948
F	5.4682428	0.3726734	1.6919523
F	5.8019543	-1.7651204	1.4218414
F	3.8524299	-0.3644859	-2.0209716
F	5.8065557	-0.5252234	-1.0604124
C	1.2560960	2.5022868	2.9776766
C	0.0423618	-2.3103053	3.0388762
C	-0.8479420	-3.1148883	2.0168127
F	-1.8378625	-2.3246737	1.5485794
F	-1.4130587	-4.2095486	2.5701105
F	-0.1053548	-3.5077154	0.9716699
C	0.9579162	-3.3127820	3.8426900
F	1.5072606	-4.2302061	3.0213268
F	0.2551402	-3.9804770	4.7889012
F	1.9558211	-2.6552051	4.4499560
C	-0.8913563	-1.5386959	4.0509056
F	-1.3688281	-0.4239341	3.4716630
F	-0.2036614	-1.1666176	5.1511225
F	-1.9407688	-2.2857934	4.4561852
C	1.6263140	1.9084861	4.3928212
F	0.5179711	1.6312605	5.1077490
F	2.3873923	2.7501598	5.1258455
F	2.3102762	0.7576156	4.2379679
C	0.0859150	3.5470990	3.1462307
F	-1.0807527	2.9190886	3.3481198
F	-0.0369406	4.3089350	2.0419670
F	0.3026467	4.3753675	4.1967715
C	2.5247281	3.2318552	2.3828198
F	3.6264948	2.4675361	2.5440027
F	2.7589965	4.4212310	2.9841460
F	2.3672794	3.4533807	1.0713599
F	-0.0438820	-0.0145512	0.0328987

SCF energy = -7337.852033461
FREEH energy = 1097.70
FREEH entropy = 2.02172

BP86-D3(BJ)/def-SV(P)

COF_2

C	0.00000	0.00000	0.09548
O	0.00000	0.00000	1.28034
F	-1.07291	0.00000	-0.68791

F	1.07291	0.00000	-0.68791

SCF energy = -312.8049642616
FREEH energy = 44.85
FREEH entropy = 0.25983

$[COF_3]^-$

C	-0.00000	0.00000	0.15219
O	0.00000	0.00000	1.37577
F	0.64252	1.11288	-0.50932
F	0.64252	-1.11288	-0.50932
F	-1.28504	0.00000	-0.50932

SCF energy GEOOPT = -412.6401543431
FREEH energy = 51.64
FREEH entropy = 0.27749

$[F–Al(OR^F)_3]^-$ ([*f–al*]$^-$)

F	-1.2738272	-0.6714239	2.2510177
Al	-0.4718268	-0.2744813	0.8172892
O	1.2620204	-0.0179498	1.0788598
C	2.1458432	0.9215402	1.4683591
C	3.5255737	0.2022785	1.7138275
F	3.3472567	-0.9406692	2.3922319
F	4.1204570	-0.1054052	0.5407688
F	4.3938250	0.9713118	2.4197374
C	2.3324118	2.0209381	0.3489329
F	1.3329373	2.9252657	0.3803841
F	3.4986997	2.7051562	0.4895264
F	2.3339825	1.4499231	-0.8640742
C	1.6845771	1.6205254	2.8013419
F	0.3810553	1.9431310	2.7273052
F	1.8391666	0.7925913	3.8571385
F	2.3786939	2.7543926	3.0662864
O	-1.0905694	1.2042932	0.0677088
C	-2.1350716	1.7312665	-0.5994829
C	-2.9648798	2.6468952	0.3794516
F	-3.7167885	1.8938344	1.2122042
F	-3.8024047	3.4909053	-0.2760115
F	-2.1435188	3.3900840	1.1359503
C	-1.5748322	2.6064060	-1.7834252
F	-1.0555565	3.7652021	-1.3223843
F	-0.6000405	1.9508151	-2.4290237
F	-2.5344784	2.9265567	-2.6893291
C	-3.0847104	0.6199578	-1.1909132
F	-3.2889942	-0.3451835	-0.2767409
F	-4.2976488	1.1108400	-1.5492701
F	-2.5405617	0.0478163	-2.2827830
O	-0.6043950	-1.5506558	-0.4047313
C	-0.0367129	-2.6961743	-0.8275246
C	0.0737515	-3.7386217	0.3461934
F	-1.1407937	-4.2397725	0.6602270
F	0.8808039	-4.7852141	0.0430702
F	0.5639379	-3.1446837	1.4485203
C	1.4053327	-2.4373821	-1.4222633
F	1.4213963	-1.2880255	-2.1115962
F	2.3308597	-2.3517075	-0.4458716
F	1.7998105	-3.4322977	-2.2608453
C	-0.9578384	-3.2861144	-1.9610578
F	-2.2490448	-3.2162343	-1.6039331
F	-0.8115824	-2.5852608	-3.1065222
F	-0.6763159	-4.5846690	-2.2385488

SCF energy = -3718.966567137
FREEH energy = 549.69
FREEH entropy = 1.12307

$[(R^FO)_3Al–F–Al(OR^F)_3]^-$ ([*al–f–al*]$^-$)

Al	-1.18955	-0.09642	-1.36439
O	-0.86225	-1.68221	-2.01450
O	-2.81669	-0.05962	-0.74571
O	-0.88280	1.31839	-2.32615
C	0.04456	2.09689	-2.93609
C	1.01895	1.21544	-3.80323
F	1.35061	0.10500	-3.11627
F	2.15536	1.86352	-4.13026
F	0.42025	0.82509	-4.94636
C	-0.70993	3.11338	-3.86899
F	-1.27631	4.10150	-3.14735
C	0.86847	2.88511	-1.85255
F	1.73638	2.04529	-1.24564
F	0.05000	3.37663	-0.91387
F	1.57522	3.90653	-2.38139
F	-1.68315	2.49236	-4.55021
F	0.13096	3.68865	-4.76179
C	-3.79283	0.77727	-0.31031
C	-1.36217	-2.59332	-2.88913
C	-0.22187	-2.97585	-3.90612
F	-0.05597	-1.99182	-4.81662
F	-0.50088	-4.11654	-4.58015
F	0.94106	-3.14423	-3.26582
C	-1.81348	-3.88048	-2.10306
F	-0.74681	-4.59899	-1.70241

F	-2.58802	-4.68762	-2.86784
F	-2.51806	-3.53975	-1.01317
C	-2.59888	-2.02461	-3.68537
F	-2.37778	-0.72759	-3.98578
F	-3.72433	-2.08343	-2.94848
F	-2.82476	-2.68820	-4.83862
C	-3.27836	1.62075	0.91439
F	-3.21964	0.86287	2.02467
F	-4.06294	2.68698	1.17638
F	-2.03339	2.06650	0.65510
C	-5.00759	-0.11702	0.13507
F	-4.58280	-1.16461	0.85268
F	-5.66377	-0.59552	-0.94408
F	-5.89685	0.57577	0.88507
C	-4.25787	1.75377	-1.45783
F	-3.39392	2.77931	-1.59818
F	-5.48037	2.28092	-1.21157
F	-4.31412	1.09965	-2.62819
Al	1.16065	0.08085	1.37715
O	0.96096	-1.35999	2.32687
O	0.70186	1.61933	2.05777
O	2.74710	0.14376	0.67343
C	3.83315	-0.58344	0.31149
C	3.41501	-1.98269	-0.28450
F	3.13738	-2.86290	0.69915
F	4.38302	-2.52165	-1.05687
F	2.30665	-1.84322	-1.03076
C	4.61014	0.23790	-0.78444
F	4.67696	1.53126	-0.44142
C	4.76681	-0.80512	1.55858
F	4.03923	-1.17172	2.62564
F	5.41711	0.33288	1.87923
F	5.69703	-1.76165	1.33317
F	3.97863	0.15588	-1.97294
F	5.87412	-0.21721	-0.95588
C	1.13558	2.55689	2.93950
C	0.10471	-2.25317	2.88107
C	-0.81162	-2.87798	1.76575
F	-1.75417	-1.98348	1.39338
F	-1.43730	-4.00045	2.17473
F	-0.07375	-3.17118	0.68522
C	0.95883	-3.38511	3.56081
F	1.47566	-4.21887	2.63629
F	0.21320	-4.12846	4.41315
F	1.97800	-2.85391	4.25065
C	-0.79219	-1.55013	3.96695
F	-1.20612	-0.35624	3.50729
F	-0.09219	-1.33160	5.09962
F	-1.88153	-2.27974	4.28872
C	1.52628	1.89395	4.31420
F	0.43157	1.56789	5.02739
F	2.29360	2.69687	5.08109
F	2.21502	0.75610	4.08318
C	-0.04084	3.57515	3.16649
F	-1.19544	2.92352	3.36628
F	-0.19326	4.37344	2.09291
F	0.18441	4.36631	4.24339
C	2.39185	3.31945	2.36695
F	3.49438	2.54701	2.46631
F	2.63501	4.47280	3.03195
F	2.21246	3.61711	1.07372
F	-0.03161	-0.03819	0.02147

SCF energy = -7338.054736403
FREEH energy = 1100.04
FREEH entropy = 1.97596

$[PF_6]^-$

P	0.00000	0.00000	-0.00000
F	0.00000	-1.65285	0.00000
F	-0.00000	1.65285	-0.00000
F	-0.00000	0.00000	1.65285
F	-0.00000	-0.00000	-1.65285
F	-1.65285	-0.00000	0.00000
F	1.65285	0.00000	-0.00000

SCF energy = -940.1613250131
FREEH energy = 66.14
FREEH entropy = 0.30326

PF_5

P	-0.00000	0.00000	-0.00000
F	-0.79557	1.37797	0.00000
F	0.00000	0.00000	1.61284
F	-0.79557	-1.37797	0.00000
F	1.59115	0.00000	0.00000
F	0.00000	0.00000	-1.61284

SCF energy = -840.2548119432
FREEH energy = 57.04
FREEH entropy = 0.30760

$Me_3Si{-}F{-}Al(OR^F)_3$

Si	-0.57827	0.07487	-2.91554
C	0.81813	1.29983	-3.06793
C	-2.29430	0.79924	-2.82863

C	-0.38563	-1.45969	-3.96324
F	-0.36361	-0.61550	-1.30225
Al	0.08347	0.00316	0.39215
O	-0.63045	-1.18916	1.41006
C	-1.61332	-2.11331	1.58616
C	-2.21821	-1.91230	3.02730
F	-3.04503	-0.84525	3.03935
F	-1.23745	-1.68406	3.90962
F	-2.92002	-2.98950	3.43282
C	-0.98827	-3.55263	1.46600
F	-1.94077	-4.50082	1.34322
F	-0.18956	-3.61626	0.38560
F	-0.24471	-3.83830	2.54856
C	-2.75671	-1.95002	0.51377
F	-2.39387	-2.49080	-0.67441
F	-3.90787	-2.52513	0.89328
F	-2.98797	-0.63747	0.29009
O	-0.62477	1.58542	0.09598
C	-0.79217	2.69423	0.87860
C	-0.52353	3.96505	-0.00010
F	-0.41964	5.07700	0.75112
F	0.61761	3.81884	-0.69999
F	-1.52334	4.14451	-0.88913
C	-2.26955	2.71823	1.42194
F	-2.60897	3.91935	1.92688
F	-2.41294	1.79282	2.39216
F	-3.12987	2.41542	0.43528
C	0.21472	2.66600	2.08927
F	-0.18941	3.38884	3.13852
F	0.33333	1.36107	2.49549
F	1.43908	3.07531	1.72994
O	1.80718	0.08521	0.27764
C	2.98802	-0.58577	0.34625
C	4.13663	0.48627	0.25607
F	4.24530	1.15548	1.41932
F	3.85813	1.38064	-0.70753
F	5.32917	-0.07847	-0.02156
C	3.10487	-1.37786	1.70358
F	4.37641	-1.72361	1.98012
F	2.36507	-2.50618	1.65271
F	2.63603	-0.62688	2.71260
C	3.10521	-1.59217	-0.85761
F	4.09632	-2.48236	-0.69433
F	1.94618	-2.26646	-1.01013
F	3.32633	-0.92919	-2.01980
H	0.66103	2.17134	-2.40011
H	0.89166	1.66696	-4.11658
H	1.78663	0.82866	-2.79720
H	-3.04517	0.01856	-2.58152
H	-2.57554	1.26192	-3.80111
H	-2.33111	1.58088	-2.04063
H	-0.49026	-1.21648	-5.04424
H	-1.15318	-2.22057	-3.70311
H	0.61894	-1.90890	-3.80479

SCF energy = -4128.001104893

FREEH energy = 861.70

FREEH entropy = 1.26227

SO_2–Al(OR^F)$_3$

S	-1.48829	0.74877	-2.94386
O	-0.39203	-0.14423	-2.35327
Al	-0.00568	-0.07092	-0.45503
O	-0.62638	-1.55149	0.16327
C	-1.73669	-2.24642	0.53339
C	-2.36861	-1.60977	1.82863
F	-3.06044	-0.49283	1.51031
F	-1.39700	-1.25815	2.68275
F	-3.20832	-2.45753	2.44909
C	-1.28789	-3.72809	0.82597
F	-2.34775	-4.56083	0.88704
F	-0.46545	-4.15717	-0.14057
F	-0.62980	-3.79144	1.99699
C	-2.79073	-2.23698	-0.63271
F	-2.37776	-2.99328	-1.66302
F	-4.00270	-2.65181	-0.24797
F	-2.92272	-0.96142	-1.11344
O	-0.97202	1.36730	-0.23068
C	-0.93382	2.63907	0.27036
C	-0.75773	3.63102	-0.93504
F	-0.39479	4.86069	-0.55431
F	0.17968	3.14691	-1.78789
F	-1.90735	3.72192	-1.64412
C	-2.30292	2.91070	0.99619
F	-2.50807	4.22824	1.19161
F	-2.32578	2.29279	2.19109
F	-3.31587	2.42801	0.25900
C	0.25426	2.81940	1.28920
F	0.05363	3.85760	2.11774
F	0.37742	1.69692	2.02586
F	1.41645	3.01824	0.64025
O	1.68869	0.20200	-0.34683
C	2.88822	-0.45395	-0.33939
C	4.01612	0.64058	-0.32776
F	4.11012	1.20478	0.89126
F	3.72904	1.60860	-1.21079
F	5.21632	0.11445	-0.64507

C	3.00334	-1.35857	0.94523
F	4.27697	-1.70657	1.20277
F	2.28092	-2.48850	0.79032
F	2.51155	-0.70390	2.00949
C	3.01211	-1.34177	-1.63013
F	3.99628	-2.24939	-1.53976
F	1.84450	-1.99788	-1.83258
F	3.23214	-0.57764	-2.71690
O	-1.56117	0.65256	-4.40668

SCF energy = -4167.460872852
FREEH energy = 574.79
FREEH entropy = 1.19123

Me_3SiF

Si	0.00000	0.00000	0.43615
C	0.89923	-1.55750	-0.12092
C	0.89923	1.55750	-0.12092
C	-1.79845	0.00000	-0.12092
F	0.00000	0.00000	2.09156
H	0.38884	-2.47196	0.25515
H	1.94636	-1.57273	0.25515
H	0.93580	-1.62086	-1.23196
H	0.38884	2.47196	0.25515
H	1.94636	1.57273	0.25515
H	0.93580	1.62086	-1.23196
H	-2.33520	0.89923	0.25515
H	-2.33520	-0.89923	0.25515
H	-1.87161	0.00000	-1.23196

SCF energy = -508.9439675558
FREEH energy = 310.97
FREEH entropy = 0.35436

Me_3SiCl

Si	-0.00000	0.00000	0.41132
C	-0.89960	1.55815	-0.15263
C	-0.89960	-1.55815	-0.15263
C	1.79920	0.00000	-0.15263
Cl	-0.00000	0.00000	2.52137
H	-0.38813	2.47112	0.22369
H	-1.94598	1.57169	0.22369
H	-0.93051	1.61169	-1.26476
H	-0.38813	-2.47112	0.22369
H	-1.94598	-1.57169	0.22369
H	-0.93051	-1.61169	-1.26476
H	2.33412	-0.89942	0.22369
H	2.33412	0.89942	0.22369
H	1.86102	0.00000	-1.26476

SCF energy = -869.2788899828
FREEH energy = 309.53
FREEH entropy = 0.36300

$[Me_3Si]^+$

Si	0.00006	-0.00003	-0.00021
C	0.51998	1.76879	-0.06424
C	-1.78926	-0.43927	-0.09310
C	1.26932	-1.32952	0.15720
H	1.61855	1.90570	0.01829
H	0.16397	2.22836	-1.01858
H	0.01433	2.34010	0.75170
H	-2.45252	0.44499	-0.19619
H	-1.96271	-1.13237	-0.95189
H	-2.08150	-1.01280	0.82026
H	1.99773	-1.25584	-0.68664
H	1.86807	-1.16754	1.08657
H	0.83396	-2.35057	0.17684

SCF energy = -408.8229126821
FREEH energy = 297.91
FREEH entropy = 0.36826

CH_2Cl_2

C	0.00000	0.00000	0.14122
Cl	0.00000	-1.49815	-0.83682
Cl	0.00000	1.49815	-0.83682
H	-0.91218	0.00000	0.76598
H	0.91218	0.00000	0.76598

SCF energy = -959.4867692078
FREEH energy = 84.01
FREEH entropy = 0.27150

$[CH_2Cl]^+$

C	-0.09138	0.09457	0.00000
Cl	1.02705	-1.06324	0.00000
H	-0.46784	0.48434	-0.97252
H	-0.46784	0.48434	0.97252

SCF energy = -498.9955862583
FREEH energy = 71.72
FREEH entropy = 0.23827

BF_3

B	0.00000	0.00000	0.00000
F	-0.66177	1.14622	0.00000
F	-0.66177	-1.14622	0.00000
F	1.32354	0.00000	0.00000

SCF energy = -324.3194833005
FREEH energy = 41.39
FREEH entropy = 0.25544

$[F_3B–OR^F]^-$

B	0.08923	2.17847	0.81498
F	-0.85419	3.20223	0.69892
F	1.37270	2.63815	0.48582
F	0.07469	1.61115	2.09872
O	-0.33509	1.13354	-0.21684
C	-0.09374	-0.19385	-0.22843
C	-0.82893	-0.98140	0.94506
F	-1.15364	-2.25779	0.57198
F	-1.97129	-0.36382	1.27357
F	-0.07460	-1.10074	2.05468
C	-0.70180	-0.68988	-1.59982
F	-0.33166	-1.95112	-1.94265
F	-0.32809	0.11651	-2.60738
F	-2.05455	-0.66982	-1.54836
C	1.43799	-0.57035	-0.19678
F	1.62200	-1.92262	-0.12281
F	2.07695	-0.02848	0.84468
F	2.05401	-0.15018	-1.32533

SCF energy = -1449.918370528
FREEH energy = 217.62
FREEH entropy = 0.54990

$[F_5P–OR^F]^-$

P	-1.40048	-1.38388	1.18265
F	-2.04680	0.13102	1.07000
F	-0.69410	-2.85798	1.26236
F	-2.76500	-1.94005	1.90484
O	0.10187	-0.84120	0.40918
C	0.46263	0.26323	-0.29813
F	-0.75800	-0.99462	2.64326
F	-2.01985	-1.75766	-0.29874
C	0.38722	1.62922	0.51806
F	0.53754	1.39990	1.82552
F	-0.76507	2.30042	0.32805
F	1.38303	2.48560	0.13727
C	1.98919	-0.03115	-0.60716
F	2.53818	0.80265	-1.52489
F	2.14838	-1.28140	-1.06800
F	2.71687	0.08092	0.52672
C	-0.29589	0.44901	-1.67019
F	-1.61683	0.58239	-1.54165
F	-0.05793	-0.60270	-2.48308
F	0.15502	1.56627	-2.31606

SCF energy = -1965.866108003
FREEH energy = 234.88
FREEH entropy = 0.58119

$[OR^F]^-$

O	0.53850	1.75682	0.06111
C	0.16059	0.52370	0.01830
C	0.73622	-0.25205	-1.26404
F	0.67450	-1.62401	-1.22546
F	2.03555	0.06481	-1.46356
F	0.07320	0.12075	-2.39654
C	0.64118	-0.31178	1.30225
F	0.01521	-1.51592	1.51611
F	0.46555	0.41376	2.42972
F	1.97466	-0.59086	1.23073
C	-1.43641	0.37108	-0.04490
F	-1.96288	1.27168	-0.90518
F	-1.99902	0.62928	1.17085
F	-1.91684	-0.85726	-0.42938

SCF energy = -1125.516828966
FREEH energy = 166.13
FREEH entropy = 0.47186

$C_4F_8O–Al(OR^F)_3$

Al	0.11112	-0.01004	-0.22246
O	1.12873	-1.28000	0.30554
C	2.13981	-2.18590	0.30653
C	3.10720	-1.86112	1.50730
F	2.39150	-1.54131	2.60112
F	3.89973	-2.90591	1.81038
F	3.89005	-0.80693	1.20951
C	1.51051	-3.61590	0.49449
F	0.44269	-3.75364	-0.31021
F	2.38853	-4.59588	0.21248
F	1.08786	-3.77853	1.76528
C	2.94569	-2.13012	-1.04350
F	3.14865	-0.84786	-1.40039
F	4.13934	-2.74007	-0.94463

F	2.25061	-2.72335	-2.03663
O	-0.80299	0.12197	1.60104
C	-2.11334	-0.14358	2.19962
C	-0.83587	-0.32174	2.94320
F	-0.39801	0.53193	3.84402
F	-0.36044	-1.52988	3.17297
C	-2.98159	1.12607	2.33715
F	-3.31445	1.57467	1.12163
F	-4.09687	0.81091	3.02208
F	-2.33346	2.09842	2.98952
C	-2.86410	-1.41978	1.73255
F	-3.42856	-1.97228	2.82597
F	-2.01970	-2.30068	1.18913
F	-3.82946	-1.12737	0.85495
O	-1.48278	-0.33891	-0.89425
C	-1.82886	-0.36554	-2.22106
C	-3.02710	-1.36142	-2.41696
F	-2.81617	-2.48378	-1.71531
F	-4.17865	-0.81093	-1.99276
F	-3.16991	-1.68906	-3.71923
C	-2.24324	1.07834	-2.69451
F	-1.14387	1.85234	-2.82278
F	-2.88156	1.05489	-3.88007
F	-3.04403	1.64569	-1.78395
C	-0.59767	-0.86651	-3.06015
F	0.54154	-0.34713	-2.43078
F	-0.57081	-0.45143	-4.32181
F	-0.46558	-2.19275	-3.02645
O	0.62878	1.61811	-0.37911
C	1.33158	2.69220	0.06689
C	1.50993	2.62563	1.62797
F	1.80512	1.35416	1.99468
F	0.36113	2.95626	2.25484
F	2.48344	3.42929	2.07764
C	2.74392	2.71280	-0.62731
F	2.62020	2.41694	-1.92915
F	3.34427	3.91273	-0.51302
F	3.54679	1.78313	-0.06707
C	0.52098	3.98640	-0.31488
F	0.62646	4.24016	-1.63140
F	-0.78058	3.81029	-0.03033
F	0.96349	5.06598	0.36167

SCF energy GEOOPT = -4644.686989998
FREEH energy = 710.67
FREEH entropy = 1.33007

$C_4F_8O-Al(OR^F)_2-F-Al(OR^F)_3$

Al	-1.16382	-0.00322	-1.33356
O	-0.83232	-1.49694	-2.13079
O	-2.41018	0.00506	-0.12339
O	-1.01567	1.50524	-2.15680
C	-0.18185	2.43278	-2.69483
C	0.75043	1.76403	-3.76876
F	1.20768	0.58563	-3.28137
F	1.81618	2.52728	-4.07547
F	0.07591	1.49933	-4.89784
C	-1.06495	3.54404	-3.37291
F	-1.61834	4.34068	-2.43813
C	0.69365	3.07248	-1.55465
F	1.68016	2.20666	-1.19197
F	-0.05885	3.29424	-0.46775
F	1.27433	4.22420	-1.92531
F	-2.05325	2.98151	-4.07944
F	-0.32991	4.31716	-4.20080
C	-3.65783	0.50322	0.11617
C	-1.19661	-2.42691	-3.05680
C	0.03355	-2.69589	-4.00198
F	0.19341	-1.67410	-4.86660
F	-0.11442	-3.83013	-4.71360
F	1.16210	-2.79947	-3.27932
C	-1.59420	-3.74964	-2.30479
F	-0.49801	-4.33863	-1.78135
F	-2.19635	-4.63390	-3.12368
F	-2.43125	-3.47236	-1.29178
C	-2.41198	-1.92565	-3.92248
F	-2.23569	-0.62447	-4.23020
F	-3.56350	-2.02501	-3.22961
F	-2.54703	-2.61959	-5.06554
C	-3.59144	1.46621	1.35896
F	-3.50430	0.76371	2.51111
F	-4.67739	2.25655	1.44320
F	-2.49848	2.24515	1.27440
C	-4.61353	-0.70863	0.41996
F	-4.00455	-1.58497	1.23475
F	-4.91995	-1.35469	-0.72241
F	-5.76169	-0.31201	1.00484
C	-4.20756	1.30712	-1.12334
F	-3.68761	2.54730	-1.16583
F	-5.54650	1.41158	-1.11624
F	-3.83771	0.67102	-2.25826
Al	1.05535	0.02655	1.42027
O	1.23843	-1.48521	2.28128
O	1.30756	1.62903	1.94813

O	2.88561	-0.17837	0.57995
C	3.66972	-1.12793	-0.23849
C	3.16022	-2.59240	-0.23509
F	3.28626	-3.16899	0.96258
F	3.88071	-3.29565	-1.12409
F	1.87070	-2.59431	-0.59618
C	4.07697	-0.57225	-1.63140
F	4.04948	0.76236	-1.63220
C	4.22550	-0.47921	0.97521
F	5.07320	0.52371	0.88332
F	4.36970	-1.11741	2.11402
F	3.26040	-1.03121	-2.58293
F	5.33142	-0.99059	-1.88313
C	1.70661	2.52832	2.89473
C	0.23837	-2.15472	2.95156
C	-0.35387	-3.26410	2.00724
F	-0.98318	-2.65270	0.97871
F	-1.23033	-4.05569	2.64442
F	0.62333	-4.02531	1.50347
C	0.84358	-2.78469	4.25354
F	1.63361	-3.82725	3.95340
F	-0.13900	-3.21262	5.07304
F	1.58243	-1.87261	4.90240
C	-0.90530	-1.13931	3.33697
F	-0.85504	-0.12927	2.32991
F	-0.68684	-0.50614	4.48244
F	-2.12688	-1.63188	3.32671
C	2.35432	1.78385	4.12076
F	1.40720	1.22368	4.89558
F	3.10772	2.58721	4.88086
F	3.13801	0.77424	3.66311
C	0.45284	3.35099	3.37423
F	-0.57379	2.51549	3.60827
F	0.07171	4.22711	2.43248
F	0.72025	4.02902	4.50754
C	2.77131	3.48712	2.24563
F	3.93149	2.81229	2.05801
F	3.02398	4.55260	3.02403
F	2.35578	3.91858	1.05044
F	0.28980	-0.03830	-0.15651

SCF energy GEOOPT = -7238.040425367
FREEH energy = 1089.98
FREEH entropy = 1.92241

COSMO (ε = 8.93)/BP86-D3(BJ)/def-SV(P)

F^-

COSMO energy = -99.8190863141

$[Me_3Si]^+$

Si	0.00010	-0.00009	-0.00101
C	0.51839	1.76602	-0.06393
C	-1.78604	-0.43940	-0.09393
C	1.26775	-1.32672	0.15676
H	1.61766	1.89210	0.01577
H	0.15604	2.21226	-1.02007
H	0.01279	2.32083	0.76105
H	-2.44008	0.45018	-0.20146
H	-1.94444	-1.13226	-0.95348
H	-2.06467	-1.00256	0.82798
H	1.98590	-1.24257	-0.69256
H	1.85330	-1.15478	1.09061
H	0.82331	-2.34300	0.17428

COSMO energy = -408.8998450633

Me_3SiF

Si	0.00000	0.00000	0.42133
C	0.90046	-1.55964	-0.11975
C	0.90046	1.55964	-0.11975
C	-1.80092	0.00000	-0.11975
F	-0.00000	0.00000	2.08826
H	0.38610	-2.47183	0.25712
H	1.94762	-1.57029	0.25712
H	0.93618	-1.62151	-1.23101
H	0.38610	2.47183	0.25712
H	1.94762	1.57029	0.25712
H	0.93618	1.62151	-1.23101
H	-2.33372	0.90155	0.25712
H	-2.33372	-0.90155	0.25712
H	-1.87236	0.00000	-1.23101

COSMO energy = -508.9476474420

Me_3SiCl

Si	-0.00000	0.00000	0.39459
C	-0.90094	1.56048	-0.15104
C	-0.90094	-1.56048	-0.15104
C	1.80189	0.00000	-0.15104
Cl	0.00000	0.00000	2.52457
H	-0.38555	2.47169	0.22456
H	-1.94777	1.56974	0.22456
H	-0.92961	1.61014	-1.26358
H	-0.38555	-2.47169	0.22456

H	-1.94777	-1.56974	0.22456
H	-0.92961	-1.61014	-1.26358
H	2.33332	-0.90195	0.22456
H	2.33332	0.90195	0.22456
H	1.85922	0.00000	-1.26358

COSMO energy = -869.2823401519

F^-

SCF energy = -99.68993876116

COF_2

C	0.00000	0.00000	0.09151
O	0.00000	0.00000	1.27899
F	-1.07277	0.00000	-0.68525
F	1.07277	0.00000	-0.68525

COSMO energy = -312.8080448842

$[COF_3]^-$

C	0.00000	0.00000	0.14323
O	-0.00000	0.00000	1.37210
F	0.63918	1.10710	-0.50511
F	0.63918	-1.10710	-0.50511
F	-1.27837	0.00000	-0.50511

COSMO energy = -412.7275330459

CH_2Cl_2

C	0.00000	0.00000	0.14834
Cl	0.00000	-1.49598	-0.84216
Cl	0.00000	1.49598	-0.84216
H	-0.91440	0.00000	0.76776
H	0.91440	0.00000	0.76776

COSMO energy = -959.4907195418

$[CH_2Cl]^+$

C	-0.09353	0.09693	0.00000
Cl	1.02335	-1.05944	0.00000
H	-0.46491	0.48125	-0.97264
H	-0.46491	0.48125	0.97264

COSMO energy = -499.0904465385

$[Al(OR^F)_4]^-$

Al	-0.00338	-0.00786	0.01423
O	0.64002	-1.61222	-0.32103
C	1.72166	-2.40885	-0.18736
C	2.74712	-1.86040	0.87979
F	2.08016	-1.33760	1.92451
F	3.56774	-2.82885	1.35150
F	3.52451	-0.88964	0.36063
C	1.22095	-3.83052	0.27175
F	0.12408	-4.18564	-0.41313
F	2.15600	-4.79370	0.08970
F	0.89810	-3.81545	1.58397
C	2.45414	-2.53777	-1.57543
F	2.57456	-1.33331	-2.15383
F	3.69441	-3.07106	-1.45269
F	1.75397	-3.32989	-2.41584
O	-0.56246	0.25105	1.66347
C	-1.55959	-0.01972	2.53187
C	-1.16440	0.61490	3.91842
F	-1.34040	1.95388	3.89729
F	-1.90505	0.12104	4.93966
F	0.12676	0.37741	4.19176
C	-2.92589	0.60765	2.05142
F	-3.50242	-0.15699	1.10135
F	-3.81643	0.72956	3.06733
F	-2.72030	1.82694	1.53312
C	-1.73947	-1.57328	2.70618
F	-2.89553	-1.89774	3.33050
F	-0.72380	-2.09444	3.42429
F	-1.73761	-2.17413	1.50160
O	-1.39099	0.23593	-1.03796
C	-1.91228	0.04944	-2.26784
C	-2.92478	-1.15768	-2.23653
F	-2.40175	-2.18725	-1.55418
F	-4.07721	-0.80451	-1.62755
F	-3.23994	-1.59377	-3.48064
C	-2.68086	1.36302	-2.67424
F	-1.80778	2.32874	-3.03604
F	-3.52753	1.16546	-3.71316
F	-3.39625	1.82730	-1.63972
C	-0.79875	-0.24678	-3.34417
F	0.27480	0.53013	-3.11744
F	-1.22365	-0.01508	-4.60798
F	-0.39432	-1.53264	-3.28016
O	1.33632	1.10547	-0.24309
C	1.75299	2.37620	-0.06421
C	1.94038	2.70226	1.46813
F	2.49138	1.65694	2.10196
F	0.75355	2.96410	2.05508
F	2.73788	3.78079	1.66813

C	3.14048	2.52590	-0.79487
F	3.10184	1.93799	-1.99944
F	3.48997	3.82275	-0.97373
F	4.12234	1.93379	-0.08095
C	0.72918	3.39714	-0.68669
F	0.79640	3.38179	-2.03346
F	-0.52617	3.06052	-0.33682
F	0.94732	4.66869	-0.27744

COSMO energy = -4744.7142036950

C_4F_8O–Al$(OR^F)_3$

Al	0.08930	-0.00698	-0.18735
O	1.16560	-1.24316	0.30101
C	2.15061	-2.17365	0.30066
C	3.12078	-1.87574	1.50615
F	2.41022	-1.54831	2.59927
F	3.89285	-2.93856	1.80448
F	3.92688	-0.83594	1.21571
C	1.49225	-3.59225	0.47948
F	0.42147	-3.70264	-0.32540
F	2.35086	-4.58832	0.18802
F	1.06887	-3.75753	1.74887
C	2.96208	-2.12973	-1.04742
F	3.19278	-0.85233	-1.40066
F	4.14458	-2.76415	-0.94447
F	2.26056	-2.70887	-2.04345
O	-0.80645	0.10359	1.61284
C	-2.11272	-0.13998	2.23539
C	-0.83140	-0.35054	2.96197
F	-0.35741	0.49129	3.84980
F	-0.37239	-1.56698	3.16797
C	-2.94856	1.15263	2.37700
F	-3.18603	1.64918	1.15357
F	-4.11310	0.85747	2.97490
F	-2.30942	2.08129	3.09648
C	-2.89532	-1.39052	1.75072
F	-3.49646	-1.93459	2.82278
F	-2.06516	-2.29039	1.21088
F	-3.82979	-1.05803	0.85207
O	-1.47271	-0.36625	-0.90518
C	-1.81474	-0.38669	-2.23201
C	-2.99905	-1.39819	-2.43478
F	-2.77259	-2.52195	-1.74109
F	-4.15858	-0.86646	-2.00665
F	-3.13902	-1.71843	-3.73959
C	-2.25233	1.05422	-2.69292
F	-1.16613	1.84745	-2.81898
F	-2.89476	1.03103	-3.87690
F	-3.05922	1.60316	-1.77580
C	-0.57618	-0.86084	-3.07721
F	0.55271	-0.33014	-2.45606
F	-0.57178	-0.43891	-4.33838
F	-0.42815	-2.18728	-3.05320
O	0.58949	1.62826	-0.36920
C	1.30577	2.69538	0.07004
C	1.48812	2.63656	1.63133
F	1.78571	1.36797	2.00214
F	0.34251	2.97254	2.25800
F	2.46517	3.44328	2.07186
C	2.71686	2.69859	-0.62700
F	2.58867	2.39697	-1.92754
F	3.33021	3.89394	-0.52197
F	3.51381	1.76526	-0.06425
C	0.50958	3.99678	-0.31764
F	0.61495	4.23999	-1.63763
F	-0.79222	3.84046	-0.02881
F	0.96844	5.07708	0.34818

COSMO energy = -4644.6914991082

[*al*–*f*–*al*]$^-$

Al	-1.18822	-0.09873	-1.36316
O	-0.85949	-1.68507	-2.00946
O	-2.81444	-0.06095	-0.74257
O	-0.88242	1.31652	-2.32455
C	0.04584	2.09571	-2.93201
C	1.02136	1.21576	-3.79919
F	1.35170	0.10378	-3.11308
F	2.15822	1.86421	-4.12239
F	0.42409	0.82716	-4.94328
C	-0.70730	3.11418	-3.86396
F	-1.27637	4.09860	-3.13878
C	0.86864	2.88166	-1.84648
F	1.73686	2.04181	-1.24049
F	0.04899	3.37072	-0.90661
F	1.57510	3.90522	-2.37149
F	-1.67918	2.49279	-4.54717
F	0.13436	3.69162	-4.75227
C	-3.78947	0.77760	-0.30827
C	-1.35994	-2.59514	-2.88519
C	-0.22098	-2.97401	-3.90486
F	-0.05721	-1.98599	-4.81152
F	-0.49904	-4.11237	-4.58025
F	0.94321	-3.14144	-3.26481

C	-1.80785	-3.88401	-2.10053
F	-0.73862	-4.59906	-1.69991
F	-2.58037	-4.69141	-2.86468
F	-2.51247	-3.54476	-1.00912
C	-2.59890	-2.02679	-3.67819
F	-2.37894	-0.72783	-3.97473
F	-3.72236	-2.08755	-2.93780
F	-2.82527	-2.68748	-4.83109
C	-3.27380	1.62290	0.91421
F	-3.21428	0.86683	2.02624
F	-4.05762	2.68980	1.17552
F	-2.02897	2.06797	0.65371
C	-5.00444	-0.11525	0.13922
F	-4.57750	-1.16122	0.85958
F	-5.65791	-0.59744	-0.93953
F	-5.89266	0.57878	0.88699
C	-4.25482	1.75286	-1.45677
F	-3.38958	2.77812	-1.59809
F	-5.47609	2.27988	-1.21098
F	-4.30955	1.09706	-2.62636
Al	1.16033	0.08321	1.37759
O	0.96178	-1.35831	2.32608
O	0.69891	1.62314	2.05144
O	2.74529	0.14469	0.67081
C	3.82992	-0.58469	0.30964
C	3.40945	-1.98185	-0.28892
F	3.12770	-2.86317	0.69297
F	4.37692	-2.52205	-1.06079
F	2.30236	-1.83919	-1.03687
C	4.60993	0.23611	-0.78449
F	4.67827	1.52907	-0.43881
C	4.76180	-0.81015	1.55742
F	4.03043	-1.17776	2.62242
F	5.41118	0.32716	1.88093
F	5.68960	-1.76722	1.33098
F	3.97693	0.15809	-1.97320
F	5.87145	-0.22160	-0.95625
C	1.13239	2.55962	2.93502
C	0.10437	-2.25192	2.87784
C	-0.80870	-2.87612	1.76008
F	-1.75191	-1.98241	1.38626
F	-1.43491	-3.99971	2.16569
F	-0.06854	-3.16765	0.68057
C	0.95713	-3.38435	3.55866
F	1.47711	-4.21505	2.63260
F	0.21011	-4.12803	4.40696
F	1.97473	-2.85167	4.25018
C	-0.79556	-1.54991	3.96183
F	-1.20771	-0.35519	3.50066
F	-0.09873	-1.33215	5.09571
F	-1.88594	-2.27963	4.27792
C	1.52311	1.89474	4.30877
F	0.42808	1.56540	5.01956
F	2.28968	2.69556	5.07582
F	2.21223	0.75666	4.07349
C	-0.04431	3.57714	3.16271
F	-1.19837	2.92344	3.36314
F	-0.19868	4.37262	2.08659
F	0.18126	4.36872	4.23708
C	2.38863	3.32304	2.36384
F	3.49007	2.54783	2.45846
F	2.63316	4.47301	3.03124
F	2.20776	3.62394	1.07067
F	-0.03102	-0.03849	0.02185

COSMO energy = -7338.0904129776

C_4F_8O–Al(OR^F)$_2$–F–Al(OR^F)$_3$

Al	-1.14109	-0.00752	-1.31119
O	-0.82094	-1.49250	-2.13037
O	-2.42375	-0.00916	-0.14081
O	-1.01887	1.50259	-2.14143
C	-0.19414	2.42830	-2.69613
C	0.72411	1.75732	-3.78152
F	1.19060	0.58388	-3.29934
F	1.78027	2.52487	-4.10940
F	0.02993	1.48867	-4.90041
C	-1.08860	3.53408	-3.36698
F	-1.63252	4.33536	-2.42975
C	0.69661	3.07560	-1.57186
F	1.68434	2.21392	-1.21541
F	-0.04442	3.31032	-0.47942
F	1.27211	4.22588	-1.96116
F	-2.08657	2.96671	-4.05777
F	-0.36855	4.30599	-4.20962
C	-3.66082	0.50517	0.10724
C	-1.19677	-2.41996	-3.05179
C	0.03504	-2.71726	-3.98701
F	0.21569	-1.70440	-4.85960
F	-0.13147	-3.85399	-4.69374
F	1.15506	-2.83599	-3.25860
C	-1.62540	-3.73272	-2.29813
F	-0.54656	-4.34552	-1.77064
F	-2.24513	-4.60500	-3.12004
F	-2.46239	-3.43509	-1.29088
C	-2.39704	-1.90172	-3.92898

F	-2.19938	-0.60507	-4.24069
F	-3.55649	-1.98095	-3.24541
F	-2.53532	-2.59798	-5.07149
C	-3.57830	1.46348	1.35364
F	-3.49576	0.75841	2.50217
F	-4.65734	2.26619	1.44294
F	-2.47921	2.23238	1.26461
C	-4.62975	-0.69603	0.41274
F	-4.02938	-1.58237	1.22044
F	-4.95183	-1.33399	-0.73143
F	-5.77157	-0.28682	1.00401
C	-4.21137	1.32054	-1.12504
F	-3.67631	2.55530	-1.16685
F	-5.55032	1.44506	-1.10043
F	-3.86678	0.68730	-2.26686
Al	1.10870	0.01178	1.42279
O	1.25447	-1.49792	2.28898
O	1.28393	1.62862	1.94761
O	2.91080	-0.17227	0.59274
C	3.70821	-1.12047	-0.21782
C	3.20026	-2.58532	-0.21164
F	3.32219	-3.16199	0.98356
F	3.90523	-3.28954	-1.10747
F	1.90361	-2.57671	-0.56801
C	4.09471	-0.56523	-1.61727
F	4.07451	0.77042	-1.61355
C	4.26840	-0.46989	0.99087
F	5.09864	0.54073	0.89517
F	4.40196	-1.10019	2.13049
F	3.24101	-1.01232	-2.54655
F	5.33175	-0.99401	-1.90539
C	1.69335	2.52496	2.89308
C	0.24952	-2.16865	2.94952
C	-0.33248	-3.27668	1.99818
F	-0.95487	-2.66357	0.96361
F	-1.21592	-4.06967	2.62411
F	0.64774	-4.03628	1.49994
C	0.84542	-2.80181	4.25489
F	1.64077	-3.84073	3.95647
F	-0.14352	-3.23550	5.06313
F	1.57555	-1.88941	4.91227
C	-0.89815	-1.15478	3.32667
F	-0.84723	-0.14934	2.32253
F	-0.68684	-0.52292	4.47410
F	-2.11904	-1.65391	3.31068
C	2.33149	1.77755	4.12319
F	1.37730	1.24225	4.90608
F	3.10260	2.57379	4.87298
F	3.09265	0.75116	3.66730
C	0.44604	3.35918	3.36729
F	-0.58830	2.53563	3.60425
F	0.07272	4.23441	2.41880
F	0.71774	4.04349	4.49604
C	2.76824	3.47344	2.24518
F	3.92315	2.79190	2.06606
F	3.02217	4.54271	3.01930
F	2.35895	3.90281	1.04543
F	0.30293	-0.03900	-0.14319

COSMO energy + OC. Corr. = -7238.0476179385

COSMO (ε = 16.3)/BP86-D3(BJ)/def-SV(P)

[*al–f–al*]$^{-}$

Al	-1.18828	-0.09905	-1.36233
O	-0.86308	-1.68623	-2.00805
O	-2.81362	-0.05798	-0.73961
O	-0.88071	1.31518	-2.32464
C	0.04810	2.09182	-2.93449
C	1.02370	1.20856	-3.79826
F	1.35289	0.09853	-3.10835
F	2.16119	1.85524	-4.12264
F	0.42699	0.81668	-4.94147
C	-0.70418	3.10742	-3.87028
F	-1.27380	4.09411	-3.14858
C	0.87074	2.88102	-1.85127
F	1.73680	2.04243	-1.24057
F	0.05072	3.37548	-0.91446
F	1.57949	3.90132	-2.37960
F	-1.67564	2.48379	-4.55211
F	0.13820	3.68184	-4.75964
C	-3.78664	0.78321	-0.30584
C	-1.36538	-2.59563	-2.88343
C	-0.22601	-2.97974	-3.90063
F	-0.05717	-1.99339	-4.80816
F	-0.50675	-4.11795	-4.57487
F	0.93648	-3.15016	-3.25807
C	-1.81913	-3.88212	-2.09816
F	-0.75313	-4.60104	-1.69576
F	-2.59405	-4.68704	-2.86225
F	-2.52333	-3.53904	-1.00758
C	-2.60107	-2.02387	-3.67906
F	-2.37607	-0.72600	-3.97669
F	-3.72575	-2.07967	-2.94000
F	-2.82802	-2.68512	-4.83135

C	-3.26614	1.63446	0.91043
F	-3.20279	0.88388	2.02599
F	-4.04845	2.70303	1.16929
F	-2.02209	2.07764	0.64310
C	-5.00035	-0.10673	0.15076
F	-4.57094	-1.14918	0.87492
F	-5.65792	-0.59429	-0.92300
F	-5.88526	0.59155	0.89827
C	-4.25575	1.75278	-1.45759
F	-3.39006	2.77647	-1.60786
F	-5.47544	2.28212	-1.20971
F	-4.31557	1.09077	-2.62348
Al	1.16022	0.08231	1.37811
O	0.96330	-1.36002	2.32566
O	0.69546	1.62087	2.05247
O	2.74523	0.14719	0.67187
C	3.83188	-0.57922	0.31084
C	3.41517	-1.97570	-0.29176
F	3.13206	-2.85947	0.68758
F	4.38552	-2.51279	-1.06214
F	2.30985	-1.83336	-1.04244
C	4.61216	0.24566	-0.78005
F	4.67728	1.53793	-0.43111
C	4.76219	-0.80590	1.55960
F	4.02965	-1.17782	2.62237
F	5.40839	0.33203	1.88709
F	5.69225	-1.76040	1.33225
F	3.98118	0.16933	-1.97002
F	5.87470	-0.20920	-0.95080
C	1.12756	2.55727	2.93689
C	0.10679	-2.25632	2.87449
C	-0.80376	-2.87990	1.75436
F	-1.74871	-1.98744	1.38185
F	-1.42785	-4.00591	2.15655
F	-0.06202	-3.16713	0.67477
C	0.96083	-3.38852	3.55400
F	1.48430	-4.21553	2.62651
F	0.21412	-4.13590	4.39903
F	1.97612	-2.85514	4.24845
C	-0.79590	-1.55816	3.95867
F	-1.21045	-0.36366	3.49891
F	-0.10075	-1.34055	5.09351
F	-1.88484	-2.29105	4.27226
C	1.52057	1.89156	4.30952
F	0.42661	1.55788	5.01991
F	2.28506	2.69334	5.07736
F	2.21283	0.75567	4.07219
C	-0.05114	3.57204	3.16643
F	-1.20375	2.91546	3.36640
F	-0.20773	4.36835	2.09117
F	0.17310	4.36270	4.24152
C	2.38172	3.32405	2.36568
F	3.48499	2.55122	2.45865
F	2.62401	4.47383	3.03397
F	2.19915	3.62567	1.07283
F	-0.03003	-0.04036	0.02171

COSMO energy = -7338.0933859142

[*f–al*]$^-$

F	-1.28739	-0.67329	2.23954
Al	-0.47067	-0.27458	0.80467
O	1.25570	-0.03618	1.09543
C	2.14005	0.91060	1.47219
C	3.51667	0.19295	1.73605
F	3.32851	-0.93952	2.43085
F	4.11316	-0.13565	0.56989
F	4.37927	0.97088	2.43317
C	2.33326	1.99086	0.33650
F	1.33607	2.89904	0.35089
F	3.50002	2.67004	0.46872
F	2.33215	1.39835	-0.86727
C	1.66986	1.62885	2.79048
F	0.36365	1.94936	2.69824
F	1.80908	0.81183	3.85667
F	2.35950	2.76303	3.04523
O	-1.08732	1.20759	0.07380
C	-2.12976	1.73781	-0.59756
C	-2.95854	2.65041	0.38342
F	-3.69781	1.88904	1.22255
F	-3.80237	3.48618	-0.26584
F	-2.13444	3.39521	1.13655
C	-1.56448	2.61320	-1.77785
F	-1.04030	3.76674	-1.31191
F	-0.58961	1.95212	-2.42084
F	-2.52060	2.93559	-2.68240
C	-3.07752	0.62758	-1.19224
F	-3.28399	-0.33772	-0.27416
F	-4.28608	1.11624	-1.55428
F	-2.52641	0.05069	-2.27783
O	-0.62428	-1.56065	-0.39717
C	-0.03845	-2.69543	-0.83024
C	0.10306	-3.73286	0.34312
F	-1.10136	-4.24577	0.67581
F	0.92106	-4.76438	0.03574
F	0.59630	-3.12279	1.43912

C	1.39075	-2.41012	-1.44139
F	1.37721	-1.25454	-2.12311
F	2.32713	-2.31215	-0.47611
F	1.78880	-3.39188	-2.28887
C	-0.96331	-3.29905	-1.95277
F	-2.25064	-3.24939	-1.57627
F	-0.84377	-2.58937	-3.09575
F	-0.66219	-4.58888	-2.23477

COSMO energy = -3719.0169799090

SO_2–Al(OR^F)$_3$

S	-1.47391	0.70187	-3.07041
O	-0.40342	-0.15111	-2.37637
Al	-0.03093	-0.05480	-0.49776
O	-0.61243	-1.54752	0.14431
C	-1.72289	-2.23430	0.52813
C	-2.32828	-1.60066	1.83773
F	-3.02183	-0.48048	1.54174
F	-1.33884	-1.25817	2.67717
F	-3.15874	-2.44980	2.47229
C	-1.28079	-3.71901	0.80826
F	-2.34328	-4.54701	0.88856
F	-0.47764	-4.15369	-0.17279
F	-0.59997	-3.79192	1.96806
C	-2.79763	-2.21067	-0.61999
F	-2.41063	-2.97627	-1.65361
F	-4.00685	-2.61533	-0.20931
F	-2.92063	-0.93773	-1.09302
O	-0.99130	1.36483	-0.19065
C	-0.93725	2.64388	0.28250
C	-0.78996	3.61867	-0.94206
F	-0.40656	4.85227	-0.58216
F	0.12517	3.11854	-1.80715
F	-1.95515	3.71079	-1.61611
C	-2.28616	2.93095	1.03937
F	-2.48109	4.25281	1.22479
F	-2.27901	2.33044	2.24585
F	-3.32094	2.44326	0.34010
C	0.27457	2.84215	1.26932
F	0.10135	3.90452	2.07602
F	0.41218	1.74140	2.03446
F	1.42414	3.01772	0.58934
O	1.67045	0.19701	-0.37606
C	2.86618	-0.45779	-0.34149
C	3.99204	0.63635	-0.25466
F	4.03730	1.16498	0.98449
F	3.74030	1.63020	-1.11863
F	5.20736	0.12270	-0.53826
C	2.94215	-1.40048	0.91973
F	4.21155	-1.73465	1.22378
F	2.25143	-2.53953	0.70395
F	2.39549	-0.78710	1.98233
C	3.04549	-1.30931	-1.65065
F	4.04147	-2.20670	-1.54683
F	1.89873	-1.97553	-1.91227
F	3.29747	-0.51304	-2.70681
O	-1.55872	0.42727	-4.50523

COSMO energy = -4167.4690337173