Supporting Information

$Al(OCAr^{F}_{3})_3$ – A Thermally Stable Lewis Superacid

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General Information

Reactions were carried out under inert atmosphere using standard Schlenk techniques. Moisture and air sensitive substances were stored in a conventional argon-flushed glovebox (BRAUN). Dry solvents were collected from a MB-SPS-800 (BRAUN) solvent system and kept on molecular sieves under an inert atmosphere. NMR spectra were recorded at the following spectrometers: BRUKER Avance DPX-200 and BRUKER Avance WB-360. ESI mass spectra were measured on a BRUKER Esquire LC. Elemental analyses were performed using a CHN(S) Vario Micro Cube (ELEMENTAR). IR spectra were recorded on an ATR-FT-IR spectrometer (BRUKER) in a nitrogen flushed glovebox. Thermogravimetric analyses (TGA) and differential scanning calorimetry (DSC) measurements were conducted using a Mettler Toledo TGA/DSC 3+ Star^e System. The sample was heated with a temperature gradient of 10 K·min^{-1}. The perfluorinated alcohol $(C_6F_5)_3COH$ was prepared according to a literature procedure.[1]

Synthetic Procedures

Synthesis of $Al(OCAr^F{}_3)_3$ (1)

A solution of $(C_6F_5)_3COH$ (4.77 g, 9.00 mmol, 3.0 eq.) in toluene (100 mL) was added dropwise to a solution of triethylaluminum (0.34 g, 3.00 mmol, 1.0 eq.) in toluene (50 mL) at -78 ºC. The colorless solution was allowed to reach room temperature after 1 h. After stirring the reaction mixture at room temperature for 1 h, it was heated to 90 ºC until the gas evolution had ceased after 1 h. A white precipitate formed after 30 min and the suspension was left overnight at -30 ºC. The solution was decanted from the white solid and the residue was washed with *n*-hexane (40 mL) twice. Drying *in vacuo* gave 3.21 g $Al(OCAr^F{}_3)_3$ (1.99 mmol, 66%) as a white powder. Colorless crystals suitable for XRD analysis were obtained from an analogous procedure in which the precipitation from the reaction mixture began after removing it from the refrigerator.

^{13}C NMR (50 MHz, THF-d_8, 20 °C, TMS) (THF-d_8 adduct): δ=145.7 (d, ^1J(C,F) = 248.1 Hz, CF), 141.9 (dt, ^1J(C,F) = 255.0 Hz, ^2J(C,F) = 13.5 Hz, *p*-CF), 138.5 (dt, ^1J(C,F) = 253.7 Hz, ^2J(C,F) = 15.1 Hz, CF), 119.6 (s, *ipso*-C), 76.0 ppm (s, *C*O);[2] ^{19}F NMR (188 MHz, THF-d_8, 20 °C, $CFCl_3$) (THF-d_8 adduct): δ=-142.0 (d, ^3J(F,F) = 19.4 Hz, 12F, *o*-F), -142.6 (d, ^3J(F,F) = 20.0 Hz, 6F, *o*-F), -156.7 (t, ^3J(F,F) = 20.9 Hz, 6F, *p*-F), -157.7 (t, ^3J(F,F) = 20.7 Hz, 3F, *p*-F), -165.3 (t, ^3J(F,F) = 19.5 Hz, 12F, *m*-F), -165.7 ppm (t, ^3J(F,F) = 19.9 Hz, 6F, *m*-F);[2] elemental analysis calcd (%) for $C_{57}AlF_{45}O_3$: C 42.40, H 0.00, N 0.00; found: C 42.88, H 0.27, N 0.00; IR: $\tilde{\nu}$=1652 (w), 1527 (m), 1486 (s), 1407 (w), 1307 (w), 1194 (w), 1134 (s), 1026 (m), 1015 (m), 985 (s), 960 (m), 896 (w), 795 (s), 754 (w), 725 (w), 704 (m), 695 (m), 637 (w), 622 (w), 580 (w), 488 (w), 463 cm^{-1} (w).

Synthesis of $Al(OCAr^F{}_3)_3$·MeCN·PhMe (2)

A solution of triethylaluminum in *n*-hexane (1M, 1.5 mL, 1.50 mmol, 1 eq.) was added in one portion to a solution of $(C_6F_5)_3COH$ (2.39 g, 4.50 mmol, 3.0 eq.) in toluene (75 mL) at -78 ºC. The reaction mixture was allowed to reach room temperature after 1 h and stirred for another 1 h. It was stirred at 90 ºC for 1 h. Acetonitrile was added (0.2 mL) to the hot reaction mixture leading to immediate crystallization of the product. The obtained crystals were suitable for XRD analysis. The reaction mixture was left for further crystallization over three days and the supernatant was removed by decantation. The colorless crystals were washed with toluene (25 mL) and *n*-hexane (25 mL) twice and dried *in vacuo* to yield 1.87 g $Al(OCAr^F{}_3)_3$·MeCN·PhMe (1.07 mmol, 71%) as a white solid.

^{1}H NMR (200 MHz, CD_2Cl_2, 20 °C, TMS): δ=7.27-7.15 (m, 5H, C_6H_5), 2.57 (s, 3H, *CH*$_3$CN), 2.33 ppm (s, 3H, Ph*CH*$_3$); ^{19}F NMR (188 MHz, CD_2Cl_2, 20 °C, $CFCl_3$): δ=-142.5 (d, ^3J(F,F) = 20.0 Hz, 18F, *o*-F), -156.1 (t, ^3J(F,F) = 20.9 Hz, 9F, *p*-F), -164.7 ppm (t, ^3J(F,F) = 19.6 Hz, 18F, *m*-F); elemental analysis calcd (%) for $C_{66}H_{11}AlF_{45}NO_3$: C 45.36, H 0.63, N 0.80; found: C 45.30, H 0.58, N 0.83; IR: $\tilde{\nu}$=2344

(w), 2314 (w), 1653 (w), 1527 (m), 1489 (s), 1402 (w), 1369 (w), 1302 (m), 1200 (m), 1129 (m), 1117 (m), 1025 (m), 1008 (m), 995 (m), 980 (m), 959 (m), 890 (w), 828 (w), 796 (m), 788 (m), 767 (w), 747 (w), 731 (w), 713 (w), 698 (m), 689 (m), 646 (w), 631 (w), 618 (w), 579 (w), 487 (w), 466 (w), 453 (w), 422 cm^{-1} (w).

The adduct with deuterated acetonitrile $Al(OCAr^{F}{}_3)_3 \cdot CD_3CN \cdot PhMe$ was prepared in an analogous procedure and revealed the following signals in the IR spectrum: IR: $\tilde{\nu}$=2338 (w), 1653 (w), 1527 (m), 1490 (s), 1402 (w), 1302 (w), 1200 (m), 1129 (m), 1117 (m), 1025 (m), 1008 (s), 995 (s), 980 (m), 960 (m), 889 (w), 872 (w), 796 (m), 788 (m), 767 (w), 747 (w), 731 (w), 713 (w), 698 (m), 689 (m), 646 (w), 632 (w), 618 (w), 579 (w), 487 (w), 466 (w), 453 (w), 421 cm^{-1} (w).

Synthesis of $Al(OCAr^{F}{}_3)_3 \cdot THF$ (3)

A solution of triethylaluminum in *n*-hexane (1M, 1.5 mL, 1.50 mmol, 1 eq.) was added in one portion to a solution of $(C_6F_5)_3COH$ (2.39 g, 4.50 mmol, 3.0 eq.) in toluene (75 mL) at -78 ºC. The reaction mixture was allowed to reach room temperature after 1 h and stirred for another 1 h. It was stirred at 90 ºC for 1 h. THF was added (0.2 mL) to the hot reaction mixture leading to crystallization of the product after 1 h. The obtained crystals were suitable for XRD analysis. The reaction mixture was left for further crystallization over three days and the supernatant was decanted from the colorless crystals. They were washed with *n*-hexane (25 mL) twice and dried *in vacuo* to yield 1.78 g $Al(OCAr^{F}{}_3)_3 \cdot THF$ (1.06 mmol, 70%) as a white solid.

^1H NMR (200 MHz, CD_2Cl_2, 20 °C, TMS): δ=3.91-3.84 (m, 4H, O*CH*$_2$), 1.99-1.92 ppm (m, 4H, OCH$_2$*CH*$_2$); ^{19}F NMR (188 MHz, CD_2Cl_2, 20 °C, $CFCl_3$): δ=-141.7 (d, ^3J(F,F) = 19.5 Hz, 18F, *o*-F), -155.4 (t, ^3J(F,F) = 20.9 Hz, 9F, *p*-F), -164.3 ppm (t, ^3J(F,F) = 20.0 Hz, 18F, *m*-F); elemental analysis calcd (%) for $C_{61}H_8AlF_{45}O_4$: C 43.44, H 0.48, N 0.00; found: C 43.15, H 0.51, N 0.00; IR: $\tilde{\nu}$=1651 (w), 1527 (m), 1486 (s), 1406 (w), 1306 (w), 1176 (m), 1130 (m), 1025 (m), 1009 (m), 998 (m), 980 (m), 855 (w), 860 (w), 796 (m), 787 (m), 769 (w), 749 (w), 735 (w), 711 (w), 699 (m), 674 (w), 648 (w), 631 (w), 581 (w), 488 (w), 444 (w), 411 cm^{-1} (w).

Synthesis of $Al(OCAr^{F}{}_3)_3 \cdot Et_2O$ (4)

A solution of $(C_6F_5)_3COH$ (2.39 g, 4.50 mmol, 3 eq.) in toluene (100 ml) was added dropwise to a solution of triethylaluminum in toluene (50 mL) at -78 °C. The yellow reaction mixture was stirred at -78 °C for 1 h and allowed to reach room temperature. It was stirred at that temperature for 1 h and another 1 h at 90 °C until the gas evolution had ceased. After cooling the solution to room temperature, diethyl ether (0.3 mL) was added and the reaction mixture was kept at -78 °C overnight. Colorless crystals suitable for XRD analysis formed after removing the flask from the fridge. They were separated from the supernatant by decantation, washed with toluene (15 mL) and twice with hexane (20 mL). After drying *in vacuo* at 50 °C, 762 mg $Al(OCAr^{F}{}_3)_3 \cdot Et_2O$ (0.45 mmol, 30%) were obtained as a white solid.

$Al(OCAr^{F}{}_3)_3 \cdot Et_2O$ reveals more complicated ^1H and ^{19}F NMR spectra compared to the other Lewis acid base adducts of $Al(OCAr^{F}{}_3)_3$ (for ^{19}F NMR spectrum see Figure S14); ^1H NMR (200 MHz, C_6D_6, 20 °C, TMS): δ=3.65 (quart, ^3J(H,H) = 6.9 Hz, O*CH*$_2$), 3.51 (quart, ^3J(H,H) = 7.0 Hz, O*CH*$_2$), 3.25 (quart, ^3J(H,H) = 7.0 Hz, O*CH*$_2$), 1.10 (t, ^3J(H,H) = 7.0 Hz, *CH*$_3$), 0.54 (t, ^3J(H,H) = 7.0 Hz, *CH*$_3$), 0.45 ppm (t, ^3J(H,H) = 7.0 Hz, *CH*$_3$) (the quartets are in a 0.89 : 0.70 : 1.00 ratio, the ratio of the triplets is 1.00 : 0.64 : 0.81 (different ratios due to signal overlap)); elemental analysis calcd (%) for $C_{61}H_{10}AlF_{45}O_4$: C 43.39, H 0.60, N 0.00; found: C 43.56, H 0.86, N 0.20; IR: $\tilde{\nu}$=1652 (w), 1528 (m), 1481 (s), 1403 (w), 1302 (w), 1130 (w), 1023 (m), 1009 (s), 993 (s), 981 (s), 981 (s), 881 (w), 796 (m), 789 (m), 767 (w), 749 (w), 700 (m), 676 (w), 644 (w), 630 (w), 580 (w), 555 (w), 488 (w), 455 (w), 445 (w), 417 cm^{-1} (w).

Synthesis of Al(OCAr$^{F}_{3}$)$_3$·Pyridine (5)

A solution of $(C_6F_5)_3COH$ (2.39 g, 4.50 mmol, 3 eq.) in toluene (100 ml) was added dropwise to a solution of triethylaluminum in toluene (50 mL) at -78 °C. The yellow reaction mixture was stirred at -78 °C for 1 h and allowed to reach room temperature. It was stirred at that temperature for 1 h and another 1 h at 90 °C until the gas evolution had ceased. Pyridine (0.3 mL) was added leading to the precipitation of a white solid. The reaction mixture was filtered through a syringe filter and left for crystallization at 4 °C overnight. It was separated from the supernatant by decantation and washed with toluene (20 mL) and twice with hexane (50 mL). Drying *in vacuo* yielded 797 mg Al(OCAr$^{F}_{3}$)$_3$·pyridine (0.47 mmol, 31%) as a white solid.

^{1}H NMR (200 MHz, CD_2Cl_2, 20 °C, TMS): δ=8.28 (d, ^3J(H,H) = 5.3 Hz, 2H, *o*-H), 8.13 (d, ^3J(H,H) = 7.7 Hz, 1H, *p*-H), 7.47 ppm (d, ^3J(H,H) = 7.1 Hz, 2H, *m*-H); ^{19}F NMR (188 MHz, CD_2Cl_2, 20 °C, $CFCl_3$): δ=-141.6 (d, ^3J(F,F) = 20.0 Hz, 18F, *o*-F), -155.8 (t, ^3J(F,F) = 21.2 Hz, 9F, *p*-F), -164.4 ppm (t, ^3J(F,F) = 19.6 Hz, 18F, *m*-F); elemental analysis calcd (%) for $C_{62}H_5AlF_{45}NO_3$: C 43.97, H 0.30, N 0.83; found: C 44.29, H 0.44, N 1.11; IR: $\tilde{\nu}$=1652 (w), 1621 (w), 1528 (m), 1491 (s), 1480 (s), 1455 (w), 1402 (w), 1303 (w), 1213 (w), 1176 (w), 1130 (m), 1076 (w), 1058 (w), 1026 (m), 1011 (s), 992 (s), 982 (m), 883 (w), 796 (m), 788 (m), 766 (w), 749 (w), 699 (m), 658 (w), 646 (w), 631 (w), 619 (w), 580 (w), 488 (w), 459 (w), 412 cm^{-1} (w).

Synthesis of Al(OCAr$^{F}_{3}$)$_3$·OPEt$_3$ (6)

A solution of triethylphosphine oxide (42 mg, 0.310 mmol, 1.0 eq.) in dichloromethane (7.5 mL) was added dropwise to a suspension of Al(OCAr$^{F}_{3}$)$_3$ (500 mg, 0.310 mmol, 1.0 eq.) in dichloromethane (7.5 mL). A clear solution formed. After stirring at room temperature overnight, the formation of a white precipitate was observed which was separated from the supernatant by decantation by a syringe. It was washed with hexane twice (15 mL) and dried *in vacuo* to yield 353 mg Al(OCAr$^{F}_{3}$)$_3$·OPEt$_3$ (0.202 mmol, 65%) as a white solid. Colorless crystals suitable for XRD analysis formed from the supernatant at 4 ºC.

^{1}H NMR (200 MHz, CD_2Cl_2, 20 °C, TMS): δ=2.01 (dquart, ^2J(P,H) = 14.1 Hz, ^3J(H,H) = 7.8 Hz, 6H, *CH$_2$*), 1.14-0.98 ppm (dt, ^3J(P,H) = 18.7 Hz, ^3J(H,H) = 7.6 Hz, 9H, *CH$_3$*); ^{19}F NMR (188 MHz, CD_2Cl_2, 20 °C, $CFCl_3$): δ=-141.7 (d, ^3J(F,F) = 20.8 Hz, 18F, *o*-F), -157.0 (t, ^3J(F,F) = 20.9 Hz, 9F, *p*-F), -165.3 ppm (t, ^3J(F,F) = 19.8 Hz, 18F, *m*-F); ^{31}P NMR (81 MHz, CD_2Cl_2, 20 °C, 85% H_3PO_4): δ=73.9 ppm; elemental analysis calcd (%) for $C_{63}H_{15}AlF_{45}O_4P$: C 43.27, H 0.86, N 0.00; found: C 43.34, H 0.73, N 0.12; IR: $\tilde{\nu}$=1652 (w), 1526 (m), 1489 (s), 1480 (s), 1402 (w), 1302 (w), 1176 (m), 1126 (m), 1022 (s), 1007 (s), 992 (s), 979 (s), 955 (s), 878 (m), 795 (w), 787 (m), 767 (m), 748 (w), 697 (m), 685 (w), 674 (w), 646 (w), 626 (m), 603 (w), 581 (w), 514 (w), 485 (w), 454 (w), 441 cm^{-1} (w).

Synthesis of [Cs(THF)][FAl(OCAr$^{F}_{3}$)$_3$] (7)

Acetonitrile (50 mL) was added to a mixture of Al(OCAr$^{F}_{3}$)$_3$ (1000 mg, 0.619 mmol, 1.0 eq.) and CsF (188 mg, 1.239 mmol, 2.0 eq.) and the suspension was stirred at room temperature for 1 h. The white solid dissolved after 30 min and the reaction mixture changed color to yellow and finally to pink. It was filtered through a syringe filter and the pink filtrate was evaporated to dryness *in vacuo*. The red residue was washed with diethyl ether (15 mL) three times. The remaining white solid was recrystallized from THF / *n*-hexane (10 mL / 20 mL) at -30 ºC overnight. The colorless prisms were separated by decantation and washed with *n*-hexane (20 mL) twice. After drying *in vacuo*, 665 mg [Cs(THF)][FAl(OCAr$^{F}_{3}$)$_3$] (0.362 mmol, 58%) were obtained as a white solid. Single crystals suitable for XRD measurements were obtained by layering a solution of [Cs(THF)][FAl(OCAr$^{F}_{3}$)$_3$] in THF with *n*-hexane (1:2) at 4 ºC.

^{1}H NMR (200 MHz, CD_3CN, 20 °C, TMS): δ=3.67-3.60 (m, 4H, O*CH$_2$*), 1.83-1.76 ppm (m, 4H, OCH$_2$*CH$_2$*); ^{13}C NMR (50 MHz, CD_3CN, 20 °C, TMS): δ=146.0 (d, ^1J(C,F) = 250.1 Hz, CF), 141.3 (dt,

^{1}J(C,F) = 248.4 Hz, ^{2}J(C,F) = 13.7 Hz, *p*-CF), 138.4 (dt, ^{1}J(C,F) = 248.0 Hz, ^{2}J(C,F) = 14.4 Hz, CF), 120.9 (s, *ipso*-C C_6F_5), 76.8 (s, *C*O), 68.3 (s, O*C*H$_2$), 26.3 ppm (s, OCH$_2$*C*H$_2$); ^{19}F NMR (188 MHz, CD_3CN, 20 °C, $CFCl_3$): δ=-135.5 (d, ^{3}J(F,F) = 17.1 Hz, 18F, *o*-F), -154.9 (t, ^{3}J(F,F) = 20.4 Hz, 9F, *p*-F), -162.4 (t, ^{3}J(F,F) = 17.9 Hz, 18F, *m*-F), -171.1 ppm (s, 1F, Al-F); (-)-ESI-MS (MeCN): m/z (%): 1633 (100) [*M*]$^-$; elemental analysis calcd (%) for $C_{57}AlCsF_{46}O_3$: C 39.85, H 0.44, N 0.00; found: C 39.41, H 0.56, N 0.24; IR: $\tilde{\nu}$=1651 (w), 1524 (m), 1491 (s), 1479 (s), 1402 (w), 1298 (w), 1245 (w), 1200 (w), 1125 (m), 1112 (m), 1022 (s), 1006 (s), 980 (s), 956 (m), 874 (w), 815 (w), 795 (m), 787 (m), 768 (w), 749 (w), 723 (m), 695 (m), 683 (w), 668 (w), 644 (w), 625 (m), 580 (w), 489 (w), 453 (w), 437 cm^{-1} (w).

Synthesis of [Ag(Et$_2$O)(MeCN)][FAl(OCAr$^{F}_3$)$_3$] (8)

Acetonitrile (40 mL) was added to a mixture of Al(OCAr$^{F}_3$)$_3$ (1000 mg, 0.619 mmol, 1.0 eq.) and AgF (157 mg, 1.239 mmol, 2.0 eq.). The suspension was stirred in the dark at room temperature for 3 h. The reaction mixture had changed color to brown and was filtered through a syringe filter. The slightly brown filtrate was evaporated to dryness *in vacuo* and the red residue was suspended in diethyl ether (25 mL). It was filtered through a syringe filter and the colorless filtrate was mixed with *n*-hexane (60 mL) and left at 4 ºC overnight for precipitation. The precipitated colorless needles were separated from the supernatant by decantation and washed with *n*-hexane (20 mL) twice. It was dried *in vacuo* to give 831 mg [Ag(Et$_2$O)(MeCN)][FAl(OCAr$^{F}_3$)$_3$] (0.448 mmol, 72%) as a white solid. Single crystals suitable for XRD analysis were obtained by slow evaporation of a solution of [Ag(Et$_2$O)(MeCN)][FAl(OCAr$^{F}_3$)$_3$] in a mixture of diethyl ether and *n*-hexane.

^{1}H NMR (200 MHz, CD_3CN, 20 °C, TMS): δ=3.42 (q, ^{3}J(H,H) = 7.0 Hz, 4H, CH_2), 1.96 (s, 3H, *C*H$_3$CN), 1.12 ppm (t, 6H, ^{3}J(H,H) = 7.0 Hz, CH$_2$*C*H$_3$); ^{13}C NMR (50 MHz, CD_3CN, 20 °C, TMS): δ=146.0 (d, ^{1}J(C,F) = 252.0 Hz, CF), 142.2 (dd, ^{1}J(C,F) = 248.6 Hz, ^{2}J(C,F) = 13.2 Hz, *p*-CF), 138.3 (d, ^{1}J(C,F) = 249.4 Hz, CF), 120.8 (s, *ipso*-C C_6F_5), 76.8 (s, *C*O), 66.3 (s, O*C*H$_2$CH$_3$), 15.6 ppm (s, OCH$_2$*C*H$_3$) (the signals of MeCN were not observed due to overlay with the signals of CD_3CN); ^{19}F NMR (188 MHz, CD_3CN, 20 °C, $CFCl_3$): δ=-135.4 (d, ^{3}J(F,F) = 16.4 Hz, 18F, *o*-F), -154.9 (t, ^{3}J(F,F) = 20.4 Hz, 9F, *p*-F), -162.4 (t, ^{3}J(F,F) = 18.0 Hz, 18F, *m*-F), -171.1 ppm (s, 1F, Al-F); (+)-ESI-MS (MeCN): m/z (%): 148 (100) [Ag(MeCN)]$^+$, 107 (65) [Ag]$^+$; (-)-ESI-MS (MeCN): m/z (%): 1633 (100) [*M*]$^-$; IR: $\tilde{\nu}$=1651 (w), 1524 (m), 1490 (s), 1399 (w), 1301 (w), 1154 (m), 1131 (m), 1111 (m), 1068 (w), 1023 (s), 1009 (s), 992 (s), 980 (m), 955 (w), 870 (w), 813 (m), 795 (m), 786 (w), 768 (w), 748 (w), 737 (m), 701 (m), 684 (w), 651 (w), 627 (w), 617 (w), 581 (w), 504 (w), 488 (w), 466 (w), 441 (w), 422 cm^{-1} (w).

Synthesis of [Tl(MeCN)][FAl(OCAr$^{F}_3$)$_3$] (9)

Acetonitrile (50 mL) was added to a mixture of Al(OCAr$^{F}_3$)$_3$ (1000 mg, 0.619 mmol, 1.0 eq.) and TlF (138 mg, 0.619 mmol, 1.0 eq.) and the white suspension was stirred for 20 h at 60 °C. It was filtered through a syringe filter and the filtrate was evaporated to dryness *in vacuo*. The remaining greasy residue was recrystallized from dichloromethane / *n*-hexane (10 mL / 20 mL) at -30 °C. The resulting colorless crystals was washed twice with *n*-hexane (20 mL) and dried *in vacuo* to give 948 mg [Tl(MeCN)][FAl(OCAr$^{F}_3$)$_3$] (0.504 mmol, 82%) as a white solid. Single crystals suitable for XRD analysis were obtained by layering a solution of [Tl(MeCN)][FAl(OCAr$^{F}_3$)$_3$] in THF with *n*-hexane resulting in the crystallization of [Tl(THF)][FAl(OCAr$^{F}_3$)$_3$].

^{1}H NMR (200 MHz, CD_2Cl_2, 20 °C, TMS): δ=1.99 ppm (s, 3H, *C*H$_3$CN); ^{13}C NMR (50 MHz, CD_3CN, 20 °C, TMS): δ=146.0 (d, ^{1}J(C,F) = 251.7 Hz, CF), 141.3 (dd, ^{1}J(C,F) = 248.6 Hz, ^{2}J(C,F) = 13.4 Hz, *p*-CF), 138.3 (dt, ^{1}J(C,F) = 248.9 Hz, ^{2}J(C,F) = 14.6 Hz, CF), 120.9 (s, *ipso*-C C_6F_5), 76.8 ppm (s, *C*O) (the signals of MeCN were not observed due to overlay with the signals of CD_3CN); ^{19}F NMR (188 MHz, CD_3CN, 20 °C, $CFCl_3$): δ=-141.2 (d, ^{3}J(F,F) = 16.5 Hz, 18F, *o*-F), -160.8 (t, ^{3}J(F,F) = 20.4 Hz, 9F, *p*-

F), -168.3 (t, ^{3}J(F,F) = 18.1 Hz, 18F, *m*-F), -176.9 ppm (s, 1F, Al-F); (+)-ESI-MS (MeCN): m/z (%): 205 (100) $[Tl]^+$; (-)-ESI-MS (MeCN): m/z (%): 1633 (100) $[M]^-$; elemental analysis calcd (%) for $C_{59}H_3AlF_{46}NO_3Tl$: C 37.71, H 0.16, N 0.75; found: C 37.85, H 0.08, N 0.88; IR: $\tilde{\nu}$=1651 (w), 1524 (w), 1478 (s), 1402 (s), 1335 (w), 1298 (w), 1240 (w), 1183 (w), 1125 (w), 1022 (m), 1006 (s), 989 (s), 977 (s), 957 (w), 875 (w), 822 (w), 795 (m), 788 (m), 767 (w), 749 (w), 734 (w), 698 (m), 686 (m), 662 (w), 644 (w), 627 (m), 580 (w), 552 (w), 488 (w), 455 (w), 439 cm^{-1} (w).

Synthesis of $[S(NMe_2)_3][FAl(OC(C_6F_5)_3)_3]$ (10)

A suspension of $[(Me_2N)_3S][F_2Si(CH_3)_3]$ (34 mg, 0.124 mmol, 1.0 eq.) in THF (5 mL) was added dropwise to a solution of $Al(OCAr^{F}_3)_3$ (200 mg, 0.124 mmol, 1.0 eq.) in THF (5 mL). The reaction mixture was stirred overnight and evaporated to dryness *in vacuo*. The white residue was washed twice with diethyl ether (15 mL) and dried *in vacuo* to give 125 mg of $[S(NMe_2)_3][AlF(OC(C_6F_5)_3)_3]$ (0.070 mmol, 56%) as a white solid.

^{1}H NMR (360 MHz, CD_2Cl_2, 20 °C, TMS): δ=2.93 ppm (s, 18H); ^{13}C NMR (91 MHz, CD_2Cl_2, 20 °C, TMS): δ=146.6 (d, ^{1}J(C,F) = 254.3 Hz, CF), 140.7 (dt, ^{1}J(C,F) = 253.1 Hz, ^{2}J(C,F) = 13.2 Hz, *p*-CF), 137.7 (dt, ^{1}J(C,F) = 249.3 Hz, ^{2}J(C,F) = 15.1 Hz, CF), 120.6 (s, *ipso*-C), 76.2 (s, *C*O), 38.9 ppm (s, CH_3); ^{19}F NMR (188 MHz, CD_2Cl_2, 20 °C, $CFCl_3$): δ=-140.6 (d, ^{3}J(F,F) = 18.2 Hz, 18F, *o*-F), -159.6 (t, ^{3}J(F,F) = 21.1 Hz, 9F, *p*-F), -167.0 (t, ^{3}J(F,F) = 19.1 Hz, 18F, *m*-F), -178.4 ppm (s, 1F, Al-F); (+)-ESI-MS (MeCN): m/z (%): 164 (100) $[M]^+$, 120 (30) $[M\text{-}NMe_2]^+$; (-)-ESI-MS (MeCN): m/z (%): 1633 (100) $[M]^-$; IR: $\tilde{\nu}$=1650 (w), 1522 (m), 1493 (s), 1401 (w), 1295 (w), 1185 (w), 1153 (m), 1132 (m), 1115 (m), 1023 (s), 1013 (s), 992 (m), 979 (m), 959 (m), 946 (m), 908 (w), 870 (w), 813 (w), 794 (m), 783 (m), 770 (w), 748 (w), 734 (w), 699 (s), 686 (m), 650 (w), 630 (w), 617 (w), 581 (w), 507 (w), 488 (w), 469 (w), 440 cm^{-1} (w).

Synthesis of $[Ph_3C][FAl(OCAr^{F}_3)_3]$ (11)

A solution of triphenylmethyl fluoride (162 mg, 0.619 mmol, 1.0 eq.) in toluene (15 mL) was added to a suspension of $Al(OCAr^{F}_3)_3$ (1000 mg, 0.619 mmol, 1.0 eq.) in toluene (5 mL). The reaction mixture changed color to red and was stirred at room temperature for 10 min and another 30 min at 90 ºC. It was stirred at room temperature overnight leading to precipitation of an orange solid. All volatiles were removed *in vacuo* and the orange residue was recrystallized twice from dichloromethane / *n*-hexane (15 mL / 30 mL) at 4 ºC. The orange crystals were washed with *n*-hexane (30 mL) and dried *in vacuo* to give 747 mg (0.398 mmol, 64%) of $[Ph_3C][FAl(OCAr^{F}_3)_3]$. Single crystals suitable for XRD analysis were obtained by layering a solution of $[Ph_3C][FAl(OCAr^{F}_3)_3]$ in dichloromethane with *n*-hexane at 4 ºC.

^{1}H NMR (360 MHz, CD_2Cl_2, 20 °C, TMS): δ=8.29 (t, ^{3}J(H,H) = 7.5 Hz, 3H, *p*-H), 7.91 (t, ^{3}J(H,H) = 7.9 Hz, 6H, *m*-H), 7.69 ppm (d, ^{3}J(H,H) = 7.3 Hz, 6H, *o*-H); ^{13}C NMR (91 MHz, CD_2Cl_2, 20 °C, TMS): δ=211.3 (s, $[Ph_3C]^+$), 145.6 (d, ^{1}J(C,F) = 249.5 Hz, CF), 144.1 (s, *p*-C $[Ph_3C]^+$), 143.1 (s, *o*-C $[Ph_3C]^+$), 140.7 (dt, ^{1}J(C,F) = 253.1 Hz, ^{2}J(C,F) = 13.4 Hz, *p*-CF), 140.4 (s, *ipso*-C $[Ph_3C]^+$), 138.4 (dt, ^{1}J(C,F) = 249.4 Hz, ^{2}J(C,F) = 14.8 Hz, CF), 131.1 (s, *m*-C $[Ph_3C]^+$), 120.6 (s, *ipso*-C C_6F_5), 76.2 ppm (s, *C*O); ^{19}F NMR (188 MHz, CD_2Cl_2, 20 °C, $CFCl_3$): δ=-140.9 (d, ^{3}J(F,F) = 17.8 Hz, 18F, *o*-F), -159.9 (t, ^{3}J(F,F) = 21.1 Hz, 9F, *p*-F), -167.2 (t, ^{3}J(F,F) = 19.1 Hz, 18F, *m*-F), -178.6 ppm (s, 1F, Al-F); (+)-ESI-MS (MeCN): m/z (%): 243 (100) $[Ph_3C]^+$, (-)-ESI-MS (MeCN): m/z (%): 1633 (100) $[M]^-$; elemental analysis calcd (%) for $C_{76}H_{15}AlF_{46}O_3$: C 48.64, H 0.81, N 0.00; found: C 48.49, H 1.20, N 0.24; IR: $\tilde{\nu}$=1650 (w), 1584 (w), 1522 (m), 1483 (s), 1450 (m), 1403 (w), 1357 (m), 1296 (m), 1172 (m), 1127 (m), 1104 (m), 1022 (m), 1005 (m), 990 (s), 979 (s), 955 (m), 872 (w), 842 (w), 813 (w), 794 (m), 787 (m), 766 (m), 748 (m), 700 (s), 691 (s), 645 (w), 625 (m), 609 (w), 579 (w), 488 (w), 469 (w), 440 cm^{-1} (m) .

Synthesis of $[Ph_3C][ClAl(OCAr^F{}_3)_3]$ (12)

Triphenylmethyl chloride (173 mg, 0.619 mmol, 1.0 eq.) was added to a suspension of $Al(OC(C_6F_5)_3)_3$ (1000 mg, 0.619 mmol, 1.0 eq.) in toluene (25 mL). The reaction mixture changed color to red and was stirred at room temperature for 10 min and another 30 min at 90 ºC. It was stirred at room temperature overnight leading to precipitation of a yellow solid. All volatiles were removed *in vacuo* and the yellow residue was recrystallized twice from dichloromethane / hexane (15 mL / 30 mL) at 4 ºC. The yellow crystals were washed with hexane (30 mL) and dried *in vacuo* to give 920 mg of $[Ph_3C][ClAl(OCAr^F{}_3)_3]$ (0.486 mmol, 79%). Single crystals suitable for XRD analysis were obtained by layering a solution of $[Ph_3C][ClAl(OCAr^F{}_3)_3]$ in dichloromethane with hexane at 4 ºC.

^{1}H NMR (200 MHz, CD_2Cl_2, 20 °C, TMS): δ=8.28 (t, ^3J(H,H) = 7.2 Hz, 3H, *p*-H), 7.89 (t, ^3J(H,H) = 7.9 Hz, 6H, *m*-H), 7.68 ppm (d, ^3J(H,H) = 7.7 Hz, 6H, *o*-H); ^{13}C NMR (50 MHz, CD_2Cl_2, 20 °C, TMS): δ=211.3 (s, [*C*Ph$_3$]$^+$), 145.5 (d, ^1J(C,F) = 251.8 Hz, CF), 144.1 (s, *p*-C [CPh$_3$]$^+$), 143.1 (s, *o*-C [CPh$_3$]$^+$), 140.6 (dt, ^1J(C,F) = 246.1 Hz, ^2J(C,F) = 13.7 Hz, *p*-CF), 137.8 (dt, ^1J(C,F) = 251.7 Hz, ^2J(C,F) = 15.0 Hz, CF), 131.1 (s, *m*-C [CPh$_3$]$^+$), 120.3 (s, *ipso*-C C_6F_5), 75.9 ppm (s, *C*O), *ipso*-C [CPh$_3$]$^+$ was not observed due to signal overlay; ^{19}F NMR (188 MHz, CD_2Cl_2, 20 °C, $CFCl_3$): δ=-140.8 (d, ^3J(F,F) = 18.1 Hz, 18F, *o*-F), -160.2 (t, ^3J(F,F) = 21.0 Hz, 9F, *p*-F), -167.5 ppm (t, ^3J(F,F) = 17.9 Hz, 18F, *m*-F); (+)-ESI-MS (MeCN): m/z (%): 243 (100) [CPh$_3$]$^+$, (-)-ESI-MS (MeCN): m/z (%): 1649 (100) [*M*]$^-$; elemental analysis calcd (%) for $C_{76}H_{15}AlClF_{45}O_3$: C 48.21, H 0.80, N 0.00; found: C 47.88, H 0.85, N 0.17; IR: $\tilde{\nu}$=1650 (w), 1586 (m), 1523 (m), 1482 (s), 1451 (m), 1402 (w), 1359 (m), 1297 (m), 1189 (w), 1164 (w), 1126 (m), 1109 (m), 1021 (m), 1007 (m), 991 (m), 978 (m), 953 (w), 875 (w), 794 (m), 786 (m), 766 (m), 747 (w), 694 (m), 682 (w), 647 (w), 635 (w), 623 (m), 609 (w), 579 (w), 489 (w), 457 (m), 438 cm^{-1} (w).

Synthesis of $[Li(THF)_2][FAl(OCAr^F{}_3)_3]$ (13)

A solution of LiBr (12 mg, 0.138 mmol, 1.0 eq.) in THF (0.1 mL) was added dropwise to a solution of $[Ag(Et_2O)(MeCN)][AlF(OC(C_6F_5)_3)_3]$ (266 mg, 0.138 mmol, 1.0 eq.) in diethyl ether (15 mL). A beige precipitate formed immediately and the suspension was stirred for 1 h at room temperature. It was filtered through a syringe filter and the colorless filtrate was evaporated to dryness *in vacuo*. The white residue was washed twice with hexane (15 mL) and dried *in vacuo* to give 196 mg of $[Li(THF)_2][FAl(OCAr^F{}_3)_3]$ (0.110 mmol, 80%) as a white powder. Singe crystals suitable for XRD analysis were obtained from cooling a concentrated solution of $[Li(THF)_2][FAl(OCAr^F{}_3)_3]$ in diethyl ether to -30 ºC revealing $[Li(Et_2O)_2][FAl(OCAr^F{}_3)_3]\cdot 0.5Et_2O$.

^{1}H NMR (200 MHz, [D$_3$]MeCN, 20 °C, TMS): δ=3.67-3.61 (m, 8H, O*CH$_2$*), 1.83-1.77 ppm (m, 8H, OCH$_2$*CH$_2$*); ^{13}C NMR (50 MHz, [D$_3$]MeCN, 20 °C, TMS): δ=145.9 (d, ^1J(C,F) = 251.1 Hz, CF), 141.1 (dd, ^1J(C,F) = 236.7 Hz, ^2J(C,F) = 13.5 Hz, *p*-CF), 138.2 (dt, ^1J(C,F) = 248.9 Hz, ^2J(C,F) = 14.5 Hz, CF), 120.8 (s, *ipso*-C C_6F_5), 76.7 (s, *C*O), 68.3 (O*CH$_2$*), 26.2 ppm (OCH$_2$*CH$_2$*); ^{19}F NMR (188 MHz, [D$_3$]MeCN, 20 °C, $CFCl_3$): δ=-141.2 (d, ^3J(F,F) = 16.4 Hz, 18F, *o*-F), -160.6 (t, ^3J(F,F) = 20.5 Hz, 9F, *p*-F), -168.2 (t, ^3J(F,F) = 18.2 Hz, 18F, *m*-F), -177.3 ppm (s, 1F, Al-F); (-)-ESI-MS (MeCN): m/z (%): 1633 (100) [*M*]$^-$; IR: $\tilde{\nu}$=2891 (w), 1651 (w), 1621 (w), 1524 (m), 1481 (s), 1404 (w), 1335 (w), 1301 (w), 1244 (w), 1183 (w), 1128 (m), 1022 (s), 1007 (s), 992 (s), 979 (s), 956 (w), 917 (w), 879 (w), 822 (w), 795 (m), 787 (m), 768 (w), 749 (w), 733 (w), 697 (m), 669 (w), 647 (w), 628 (m), 581 (w), 553 (w), 488 (w), 454 (w), 444 cm^{-1} (m).

Synthesis of $[NBu_4][FAl(OCAr^{F}_3)_3]$ (14)

NBu_4Br (35 mg, 0.108 mmol, 1.0 eq.) was added to a solution of $[Ag(Et_2O)(MeCN)][FAl(OC(C_6F_5)_3)_3]$ (200 mg, 0.108 mmol, 1.0 eq.) in dichloromethane (10 mL) leading to immediate precipitation of AgBr. The white suspension was stirred for 1 h at room temperature, filtered through a syringe filter and reduced to about half of its volume *in vacuo*. It was layered with hexane (12 mL) and left for crystallization at 4 ºC for 2 h. The white crystals were separated from the colorless supernatant by decantation with a syringe, washed with hexane (15 mL) and dried *in vacuo* to give 79 mg of $[NBu_4][FAl(OCAr^{F}_3)_3]$ (0.042 mmol, 39%) as a white solid.

^{1}H NMR (200 MHz, [D$_3$]MeCN, 20 °C, TMS): δ=3.11-3.03 (m, 8H, N*CH$_2$*), 1.68-1.52 (m, 8H, NCH$_2$*CH$_2$*), 1.35 (sext, ^3J(H,H) = 7.3 Hz, 8H, *CH$_2$*CH$_3$), 0,96 ppm (t, ^3J(H,H) = 7.2 Hz, 12H, CH$_3$); ^{13}C NMR (50 MHz, CD$_3$CN, 20 °C, TMS): δ=146.1 (d, ^1J(C,F) = 251.4 Hz, CF), 141.2 (dd, ^1J(C,F) = 249.7 Hz, ^2J(C,F) = 13.7 Hz, *p*-CF), 138.3 (dt, ^1J(C,F) = 247.1 Hz, ^2J(C,F) = 14.3 Hz, CF), 120.8 (s, *ipso*-C C$_6$F$_5$), 76.8 (s, *C*O), 59.4 (N*C*H$_2$), 24.3 (NCH$_2$*C*H$_2$), 20.3 (*C*H$_2$CH$_3$), 13.7 ppm (*C*H$_3$); ^{19}F NMR (188 MHz, [D$_3$]MeCN, 20 °C, CFCl$_3$): δ=-141.2 (d, ^3J(F,F) = 16.2 Hz, 18F, *o*-F), -160.6 (t, ^3J(F,F) = 20.4 Hz, 9F, *p*-F), -168.2 (t, ^3J(F,F) = 18.2 Hz, 18F, *m*-F), -176.8 ppm (s, 1F, Al-F); (+)-ESI-MS (MeCN): m/z (%): 242 (100) $[C_{16}H_{36}N]^+$; (-)-ESI-MS (MeCN): m/z (%): 1633 (100) [*M*]$^-$; elemental analysis calcd (%) for $C_{73}H_{36}AlF_{46}NO_3$: C 46.74, H 1.93, N 0.75; found: C 46.56, H 1.93, N 1.10; IR: $\tilde{\nu}$=2963 (w), 2081 (w), 1651 (w), 1523 (m), 1491 (s), 1400 (w), 1299 (w), 1209 (w), 1155 (w), 1130 (m), 1108 (m), 1023 (m), 1009 (s), 991 (s), 979 (s), 954 (s), 869 (m), 813 (w), 795 (w), 786 (m), 768 (s), 747 (w), 734 (m), 701 (m), 683 (m), 649 (w), 627 (w), 616 (w), 581 (w), 489 (w), 467 (w), 443 cm^{-1} (w).

Synthesis of $[FeCp_2][FAl(OCAr^{F}_3)_3]$ (15)

A solution of $[Ag(Et_2O)(MeCN)][FAl(OC(C_6F_5)_3)_3]$ (200 mg, 0.108 mmol, 1.0 eq.) in dichloromethane (6 mL) was added dropwise to a solution of ferrocene (29 mg, 0.156 mmol, 1.5 eq.) in dichloromethane (6 mL) at 0 ºC leading to an immediate color change to dark blue. The reaction mixture was stirred for 30 min at 0 ºC and another 30 min at room temperature. It was filtered through a syringe filter to remove elemental silver, reduced to about half of its volume *in vacuo* and layered with hexane (12 mL). Leaving the reaction mixture for crystallization at 4 ºC for 2 h resulted in the formation a dark blue precipitate. The yellow supernatant was removed by decantation and the blue solid was washed twice with hexane (15 mL). Drying *in vacuo* yielded 138 mg $[FeCp_2][FAl(OCAr^{F}_3)_3]$ (0.076 mmol, 70%) as a blue solid. Dark blue needles suitable for XRD analysis were obtained by layering a concentrated solution of $[FeCp_2][FAl(OCAr^{F}_3)_3]$ in dichloromethane with hexane.

^{19}F NMR (188 MHz, [D$_3$]MeCN, 20 °C, CFCl$_3$): δ=-141.2 (d, ^3J(F,F) = 16.0 Hz, 18F, *o*-F), -160.6 (t, ^3J(F,F) = 20.4 Hz, 9F, *p*-F), -168.2 (t, ^3J(F,F) = 18.1 Hz, 18F, *m*-F), -176.8 ppm (s, 1F, Al-F); (+)-ESI-MS (MeCN): m/z (%): 186 (100) $[C_{10}H_{10}Fe]^+$; (+)-ESI-HRMS (MeCN): m/z calcd for $C_{10}H_{10}Fe^+$: 186.0126 [*M*]$^+$; found: 186.0126; (-)-ESI-MS (MeCN): m/z (%): 1633 (100) [*M*]$^-$; (-)-ESI-HRMS (MeCN): m/z calcd for $C_{57}AlF_{46}O_3^-$: 1632.8934 [*M*]$^-$; found: 1632.8947; elemental analysis calcd (%) for $C_{67}H_{10}AlF_{46}FeO_3$: C 44.23, H 0.55, N 0.00; found: C 43.85, H 0.64, N 0.51; IR: $\tilde{\nu}$=3114 (w), 1651 (w), 1522 (m), 1494 (s), 1401 (w), 1295 (w), 1152 (m), 1133 (m), 1116 (m), 1024 (s), 1014 (s), 980 (m), 960 (w), 870 (w), 854 (w), 813 (w), 795 (m), 783 (m), 770 (w), 748 (w), 734 (w), 700 (m), 651 (w), 630 (w), 617 (w), 581 (w), 507 (w), 440 cm^{-1} (w).

Competition Experiments between $Al(OCAr^{F}{}_3)_3$ and SbF_6 Salts

Toluene (0.5 mL) is added to a mixture of $Al(OCAr^{F}{}_3)_3$ (10.1 mg, 6.3 µmol, 1 eq.) and NBu_4SbF_6 (3.0 mg, 6.3 µmol, 1 eq.) and the suspension is treated with ultrasonic for 1 h. The previously white solid turned grey and the ^{19}F NMR spectrum of the supernatant reveals the formation of $[FAl(OCAr^{F}{}_3)_3]^-$ and the free alcohol $Ar^{F}{}_3COH$. The formation of $Ar^{F}{}_3COH$ can be referred to the decomposition of $Al(OCAr^{F}{}_3)_3$ by HF which is formed from the reaction of SbF_5 with toluene.[3] A similar ^{19}F NMR spectrum was observed when the experiment is repeated in dichloromethane resulting in the formation of a beige reaction mixture. Suspending equimolar mixtures of $Al(OCAr^{F}{}_3)_3$ and $AgSb_6$ in 1,2-difluorobenzene or dichloromethane led to a color change to dark blue (in $C_6H_4F_2$) or beige (in CH_2Cl_2). $[FAl(OCAr^{F}{}_3)_3]^-$ could not be detected in the ^{19}F NMR spectra which revealed very unselective reactions due to the formation of SbF_5.

Thermogravimetric Analysis and Differential Scanning Calorimetry

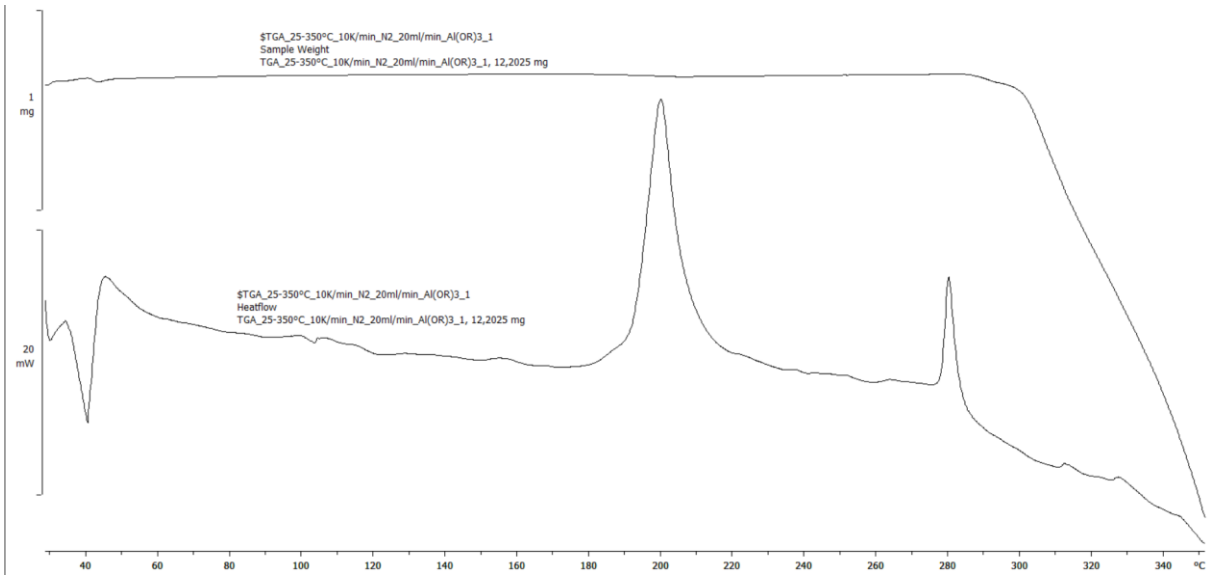

Figure S1. Thermogravimetric analysis (top curve) and differential scanning calorimetry (bottom curve) of $Al(OCAr^{F}{}_3)_3$.

Crystallographic Data

Intensity data were collected using a Bruker Venture D8 diffractometer at 100 K with graphite-monochromated Mo-Kα (0.7107 Å) radiation. All the structures were solved by direct methods and refined based on F^2 by use of the SHELX program package implemented in WinGX.[4] Mercury (version 3.8)[5] and Platon[6] were used for evaluation during refinement. All non-hydrogen atoms were refined by using anisotropic displacement parameters. Hydrogen atoms were refined at idealized positions and fixed thermal parameters. Molecular structures were illustrated with Diamond 3[7] using thermal ellipsoids at the 50% probability level and balls with an arbitrarily fixed radius. Hydrogen atoms are omitted for clarity. Crystal structures were deposited at the Cambridge Crystallographic Data Centre (CCDC, https://www.ccdc.cam.ac.uk/) with the numbers 1818681-1818687, 1863847-1863852 and 1866467.

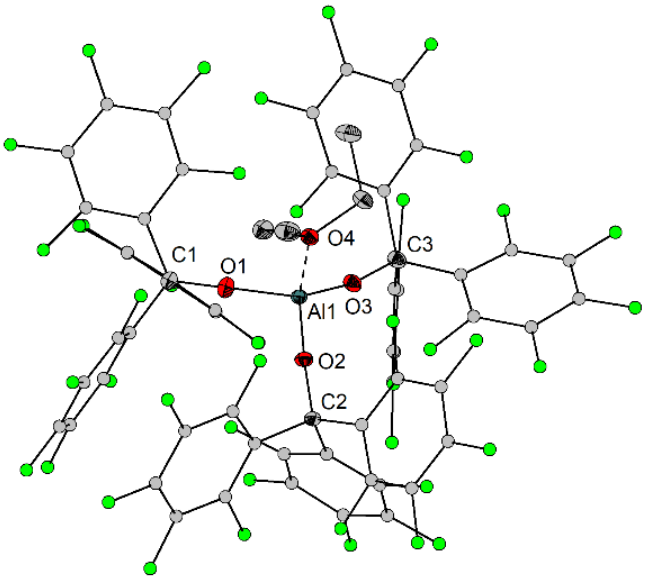

Figure S2. Molecular structure of $Al(OCAr^{F}{}_{3})_3 \cdot Et_2O$ (ellipsoids with 50% probability, balls with a arbitrarily fixed radius; hydrogen atoms are omitted for clarity, the unit cell contains residual electron density representing a severely disordered molecule of diethyl ether and toluene which has been treated as a diffuse contribution to the overall scattering without specific atom positions by Squeeze/OLEX). Selected bond lengths /Å: Al1-O1 1.696(1), Al1-O2 1.707(1), Al1-O3 1.705(1), Al1-O4 1.877(1).

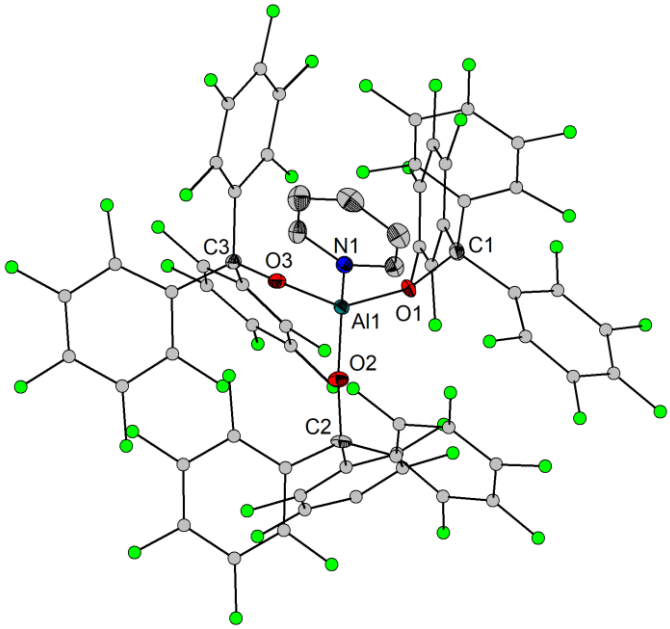

Figure S3. Molecular structure of $Al(OCAr^{F}{}_{3})_3 \cdot$pyridine (ellipsoids with 50% probability, balls with a arbitrarily fixed radius; hydrogen atoms are omitted for clarity, only one out of five molecules in the asymmetric unit is displayed). Selected bond lengths /Å: Al1-O1 1.711(3), Al1-O2 1.699(3), Al1-O3 1.704(3), Al1-N1 1.974(3), Al2-N2 1.971(3), Al3-N3 1.956(3), Al4-N4 1.964(3), Al5-N5 1.965(3).

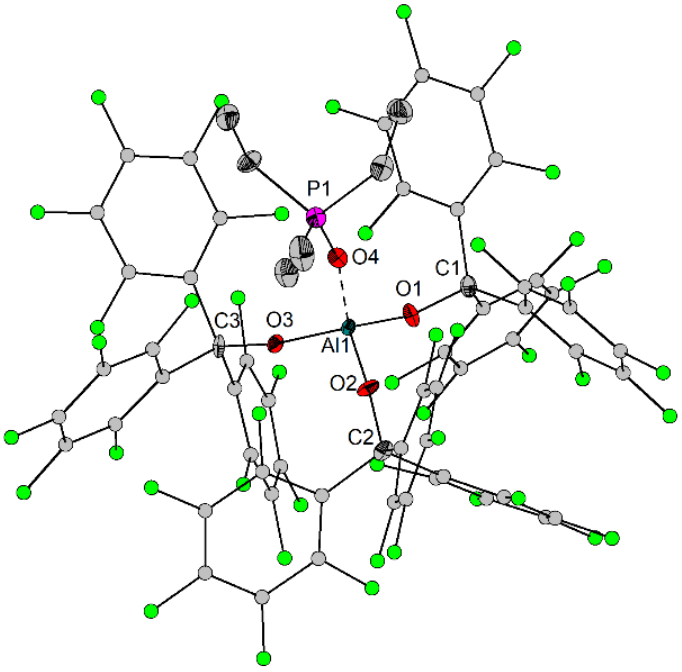

Figure S4. Molecular structure of $Al(OCAr^{F}{}_{3})_3 \cdot OPEt_3$ (ellipsoids with 50% probability, balls with a arbitrarily fixed radius; hydrogen atoms are omitted for clarity, only one out of two molecules in the asymmetric unit is displayed). Bond parameters are not discussed due to the low quality of the crystal structure.

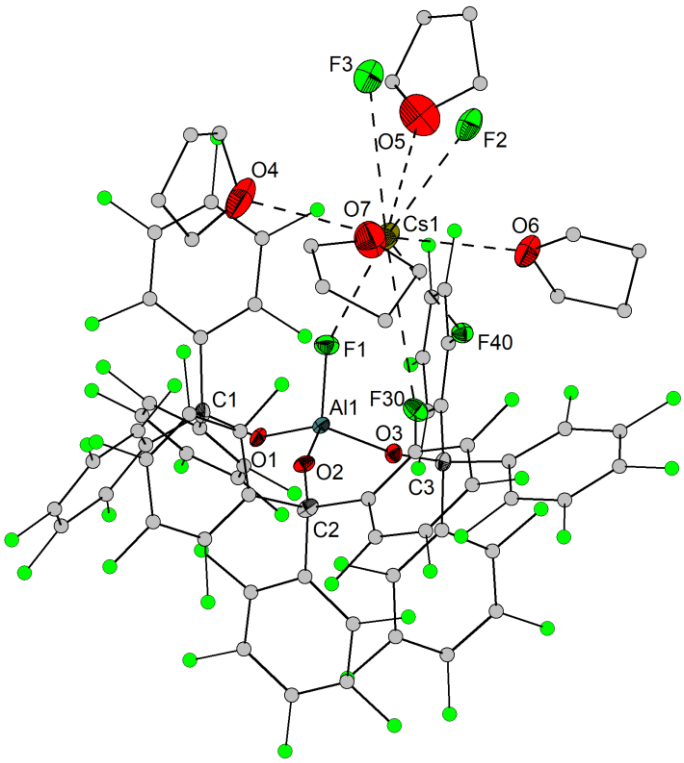

Figure S5. Molecular structure of $[Cs(THF)_4][FAl(OCAr^{F}{}_{3})_3]$ (ellipsoids with 50% probability, balls with a arbitrarily fixed radius; hydrogen atoms omitted for clarity, only one out of two molecules in the asymmetric unit is displayed). Selected bond lengths /Å and angles /°: Al1-O1 1.739(2), Al1-O2 1.724(2), Al1-O3 1.718(2), Al1-F1 1.695(2), Cs1···F1 2.886(2), Cs1-O4 3.108(3), Cs1-O5 3.035(4), Cs1-O6 3.074(3), Cs1-O7 3.075(4), Al2-O8 1.723(2), Al2-O9 1.717(2), Al2-O10 1.734(3), Al2-F100 1.696(2), Cs2···F100 2.869(2), Cs2-O11 3.037(4), Cs2-O12 3.174(4), Cs2-O13 3.024(4), Cs2-O14 3.077(3), Al1-F1-Cs1 151.5(1), Al2-F100-Cs2 153.6(1).

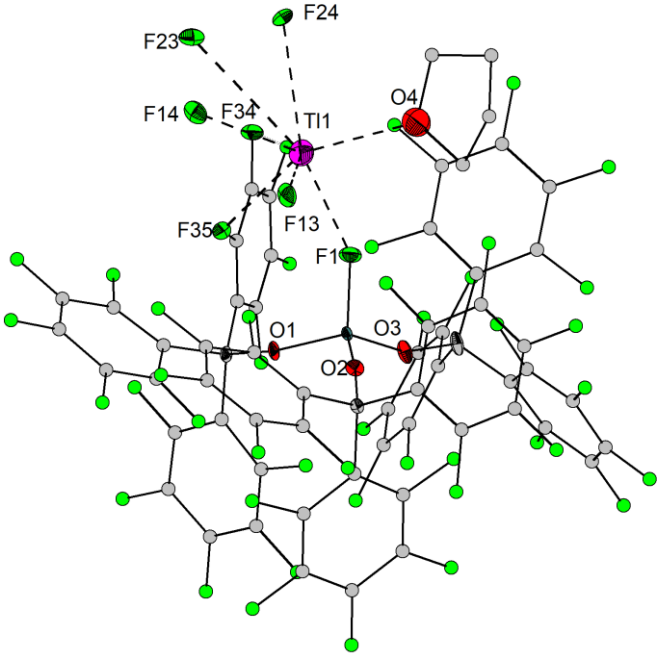

Figure S6. Molecular structure of [Tl(THF)][FAl(OCAr$^{F}_{3}$)$_3$] (ellipsoids with 50% probability, balls with a arbitrarily fixed radius; hydrogen atoms omitted for clarity). Selected bond lengths /Å and angles /°: Al1-O1 1.716(2), Al1-O2 1.699(2), Al1-O3 1.720(2), Al1-F1 1.716(2), F1-Tl1 2.506(2), Tl1-O4 2.556(4), Al1-F1-Tl1 152.3(1).

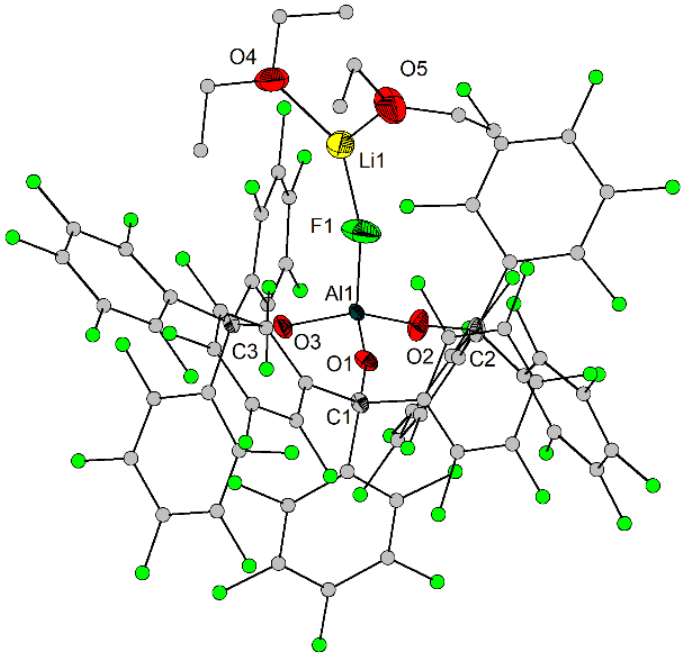

Figure S7. Molecular structure of [Li(Et$_2$O)$_2$][FAl(OCAr$^{F}_{3}$)$_3$]·0.5Et$_2$O (ellipsoids with 50% probability, balls with a arbitrarily fixed radius; hydrogen and a non-coordinating ether molecule are omitted for clarity). Selected bond lengths /Å and angles /°: Al1-O1 1.727(2), Al1-O2 1.708(2), Al1-O3 1.708 (2), Al1-F1 1.759(2), Li1···F1 1.828(6), Li1···O4 1.941(6), Li1···O5 1.980(6), Al1-F1-Li1 159.9(2).

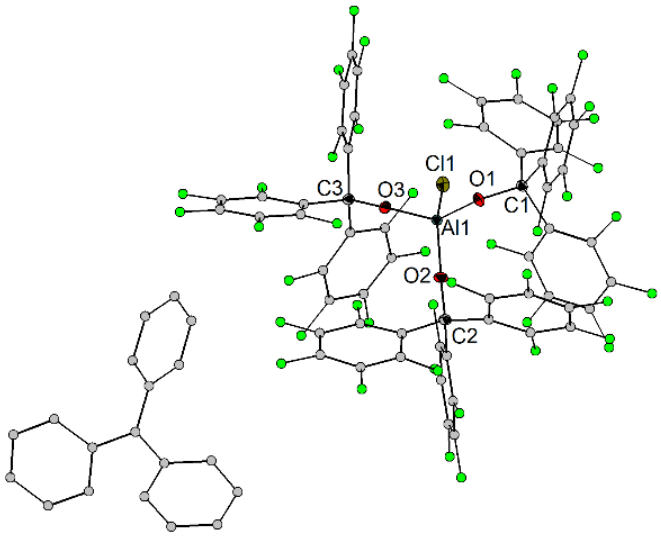

Figure S8. Molecular structure of $[Ph_3C][ClAl(OCAr^{F}_3)_3]$ (ellipsoids with 50% probability, balls with a arbitrarily fixed radius; hydrogen atoms omitted for clarity). Selected bond lengths /Å and angles /°: Al1-Cl1 2.1748(6), Al1-O1 1.729(1), Al1-O2 1.722(1), Al1-O3 1.711(1).

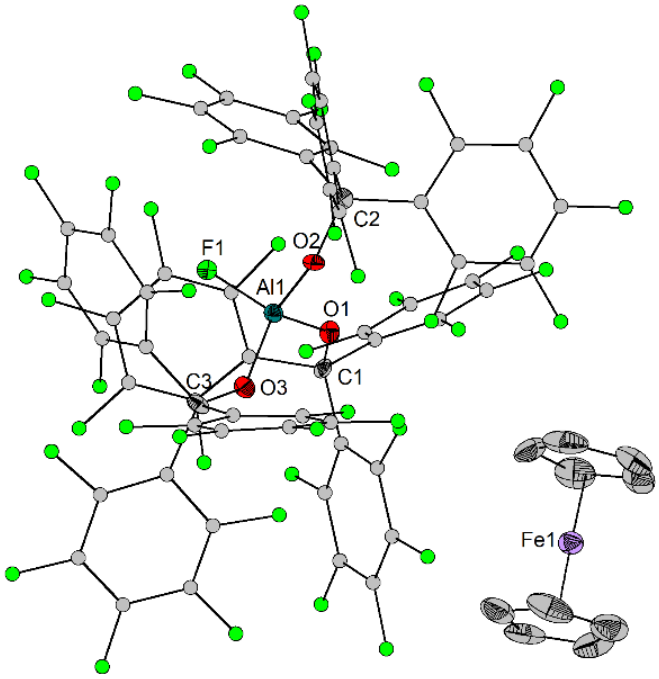

Figure S9. Molecular structure of $[FeCp_2][FAl(OCAr^{F}_3)_3]$ (ellipsoids with 50% probability, balls with a arbitrarily fixed radius; hydrogen atoms omitted for clarity). Selected bond lengths /Å and angles /°: Al1-F1 1.681(4), Al1-O1 1.743(5), Al1-O2 1.732(4), Al1-O3 1.739(5). Distances between Fe1 and the centroids of the Cp rings: 1.705(1) and 1.708(1) Å.

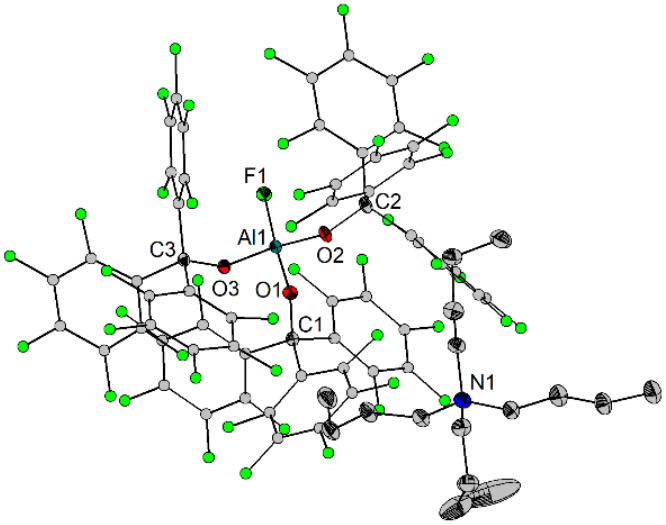

Figure S10. Molecular structure of $[NBu_4][FAl(OCAr^{F}{}_3)_3]$ (ellipsoids with 50% probability, balls with a arbitrarily fixed radius; hydrogen atoms omitted for clarity). Selected bond lengths /Å and angles /°: Al1-F1 1.678(1), Al1-O1 1.724(1), Al1-O2 1.744(1), Al1-O3 1.723(1).

Table S1. Crystal data and structure refinement.

	$Al(OCAr^{F}_{3})_3$	**$Al(OCAr^{F}_{3})_3$ ·MeCN·PhMe**	**$Al(OCAr^{F}_{3})_3$ ·THF·PhMe**
empirical formula	$C_{57}AlF_{45}O_3$	$C_{59}H_3AlF_{45}NO_3$, C_7H_8	$C_{61}H_8AlF_{45}O_4$, C_7H_8
mol. weight [g mol^{-1}]	1614.55	1747.74	1778.79
crystal habit	colorless block	colorless block	colorless block
crystal size [mm^3]	0.30 · 0.25 · 0.15	0.14 · 0.14 · 0.08	0.23 · 0.14 · 0.14
crystal system	triclinic	triclinic	triclinic
space group	P -1	P -1	P -1
a [Å]	13.5287(3)	13.2289(3)	12.9745(6)
b [Å]	14.9354(3)	14.1466(3)	14.9114(7)
c [Å]	15.4422(3)	17.4224(4)	32.7214(15)
α [°]	87.6480(10)	86.2990(10)	84.388(2)
β [°]	65.2530(10)	85.7940(10)	88.756(2)
γ [°]	71.9140(10)	67.5030(10)	88.372(2)
volume [$Å^3$]	2679.32(10)	3001.90(12)	6296.5(5)
Z	2	2	4
density [g cm^{-3}]	2.001	1.934	1.876
T [K]	100	100	100
absorption coeff. [mm^{-1}]	0.246	0.228	0.220
Θ range [°]	2.51 to 30.10	2.23 to 30.09	2.32 to 30.25
index ranges	-18 <= h <= 18, -20 <= k <= 20, -20 <= l <= 20	-18 <= h <= 18, -19 <= k <= 19, -24 <= l <= 24	-18 <= h <= 18, -21 <= k <= 21, -46 <= l <= 46
reflns collected	245897	341249	351222
independent reflns	15751 [R(int) = 0.1021]	17626 [R(int) = 0.0643]	36947 [R(int) = 0.0947]
absorption correction	multi-scan	multi-scan	multi-scan
max. and min. transmission	0.7460 and 0.7162	0.7460 and 0.7046	0.7460 and 0.6971
transmissiondata/restraints/ parameters	15751 / 0 / 955	17626 / 0 / 1047	36947 / 0 / 2127
goodness-of-fit on F^2	1.016	1.037	1.046
final R indices [I>2s(I)]	R1 = 0.0437	R1 = 0.0345	R1 = 0.0700
R indices (all data)	wR2 = 0.0924	wR2 = 0.0864	wR2 = 0.1762
larg. diff. peak/hole [e $Å^{-3}$]	0.402 / -0.308	0.487 / -0.304	1.045 / -0.499
treatment of H atoms	none	constr	constr
CCDC-number	1818681	1818682	1818684

Table S1 (continued).

	$Al(OCAr^{F}_3)_3 \cdot Et_2O$	**$Al(OCAr^{F}_3)_3$ ·Pyridine**	**$Al(OCAr^{F}_3)_3 \cdot OPEt_3$**
empirical formula	$C_{61}H_{10}AlF_{45}O_4$, C_7H_8	$C_{62}H_5AlF_{45}NO_3$	$C_{63}H_{15}AlF_{45}O_4P$
mol. weight [g mol^{-1}]	1780.80	1693.65	1748.70
crystal habit	colorless block	colorless block	colorless block
crystal size [mm^3]	0.3 · 0.2 · 0.1	0.24 · 0.14 · 0.08	0.25 · 0.20 · 0.15
crystal system	triclinic	triclinic	monoclinic
space group	P -1	P -1	P 21/c
a [Å]	12.4730(5)	22.4236(10)	24.8884(12)
b [Å]	12.4862(5)	24.0454(11)	23.4948(12)
c [Å]	24.3363(9)	29.5270(14)	22.4273(10)
α [°]	92.2640(10)	91.684(2)	90
β [°]	102.0690(10)	111.560(2)	105.820(2)
γ [°]	109.5180(10)	98.389(2)	90
volume [$Å^3$]	3468.7(2)	14588.4(12)	12617.6(11)
Z	2	10	8
density [g cm^{-3}]	1.705	1.928	1.841
T [K]	100	100	100
absorption coeff. [mm^{-1}]	0.200	0.232	0.242
Θ range [°]	2.16 to 25.03	2.22 to 25.00	2.17 to 26.00
index ranges	-14 <= h <= 14, -14 <= k <= 14, -28 <= l <= 28	-26 <= h <= 26, -28 <= k <= 28, -34 <= l <= 35	-30 <= h <= 30, -28 <= k <= 28, -27 <= l <= 26
reflns collected	121416	553523	411726
independent reflns	12246 [R(int) = 0.0435]	51367 [R(int) = 0.0852]	24752 [R(int) = 0.1120]
absorption correction	multi-scan	multi-scan	multi-scan
max. and min. transmission	0.7455 and 0.6814	0.746 and 0.689	0.7456 and 0.6137
transmissiondata/restraints/ parameters	12246 / 0 /1067	51367 / 18 / 5041	24752 / 0 / 2060
goodness-of-fit on F^2	1.043	1.099	1.128
final R indices [I>2s(I)]	R1 = 0.0310	R1 = 0.0614	R1 = 0.0975
R indices (all data)	wR2 = 0.0842	wR2 = 0.1449	wR2 = 0.2412
larg. diff. peak/hole [e $Å^{-3}$]	0.435 and -0.291	0.907 / -0.692	1.076 / -0.721
treatment of H atoms	constr	constr	constr
CCDC-number	1863847	1866467	1863848

Table S1 (continued).

	[Cs(THF)$_4$] [FAl(OCAr$^F_3$)$_3$]	**[Ag(MeCN)(Et$_2$O)] [FAl(OCAr$^F_3$)$_3$]**	**[Tl(THF)] [FAl(OCAr$^F_3$)$_3$]**
empirical formula	$C_{73}H_{32}AlCsF_{46}O_7$	$C_{63}H_{13}AgAlF_{46}NO_4$	$C_{61}H_8AlF_{46}O_4Tl$
mol. weight [g mol^{-1}]	2054.87	1856.59	1910.02
crystal habit	colorless block	colorless block	colorless block
crystal size [mm^3]	0.30 · 0.30 · 0.20	0.20 · 0.20 · 0.15	0.07 · 0.07 · 0.05
crystal system	triclinic	monoclinic	triclinic
space group	P -1	P 1 21/c 1	P -1
a [Å]	13.4499(5)	11.7732(3)	12.8874(3)
b [Å]	13.5054(5)	24.2075(7)	13.3620(4)
c [Å]	44.2327(16)	21.9598(6)	19.1533(5)
α [°]	98.1980(10)	90	81.2440(10)
β [°]	92.5750(10)	90.5680(10)	86.3460(10)
γ [°]	90.2870(10)	90	65.3350(10)
volume [Å^3]	7944.0(5)	6258.2(3)	2962.38(14)
Z	4	4	2
density [g cm^{-3}]	1.718	1.970	2.141
T [K]	100	100	100
absorption coeff. [mm^{-1}]	0.638	0.527	2.939
Θ range [°]	2.21 to 26.00	2.41 to 27.50	2.15 to 30.05
index ranges	-16 <= h <= 16, -16 <= k <= 16, -54 <= l <= 54	-15 <= h <= 15, -31 <= k <= 31, -28 <= l <= 28	-18 <= h <= 18, -18 <= k <= 18, -26 <= l <= 26
reflns collected	535842	356555	214376
independent reflns	31254 [R(int) = 0.0912]	14369 [R(int) = 0.0425]	17307 [R(int) = 0.0565]
absorption correction	multi-scan	multi-scan	multi-scan
max. and min. transmission	0.7462 and 0.6808	0.7461 and 0.7014	0.7460 and 0.6591
transmissiondata/restraints/ parameters	31254 / 0 / 2306	14369 / 0 / 1056	17307 / 0 / 1018
goodness-of-fit on F^2	1.080	1.100	1.035
final R indices [I>2s(I)]	R1 = 0.0550	R1 = 0.0297	R1 = 0.0449
R indices (all data)	wR2 = 0.1140	wR2 = 0.0709	wR2 = 0.1121
larg. diff. peak/hole [e Å^{-3}]	1.338 / -1.736	0.702 / -0.599	4.010 / -3.358
treatment of H atoms	constr	constr	constr
CCDC-number	1818683	1818687	1818685

Table S1 (continued).

	$[Ph_3C][FAl(OCAr^{F}_3)_3]\cdot CH_2Cl_2$	**$[Ph_3C][ClAl(OCAr^{F}_3)_3]$**	**$[Li(Et_2O)_2][FAl(OCAr^{F}_3)_3]\cdot 0.5Et_2O$**
empirical formula	$C_{76}H_{15}AlF_{46}O_3$, CH_2Cl_2	$C_{76}H_{15}AlClF_{45}O_3$	$C_{65}H_{20}AlF_{46}LiO_5$, $(C_4H_{10}O)_{0.5}$
mol. weight [g mol^{-1}]	1961.79	1893.31	1825.79
crystal habit	yellow block	yellow block	colorless block
crystal size [mm^3]	0.20 · 0.20 · 0.15	0.43 · 0.35 · 0.28	0.06 · 0.06 · 0.05
crystal system	triclinic	triclinic	monoclinic
space group	P -1	P -1	P 2(1)/n
a [Å]	11.8720(2)	13.8546(4)	13.5375(3)
b [Å]	13.5786(3)	14.2421(4)	24.2062(5)
c [Å]	22.6501(4)	20.1247(6)	20.9262(4)
α [°]	83.4410(10)	94.5130(10)	90
β [°]	84.2750(10)	96.0290(10)	104.0200(10)
γ [°]	85.1470(10)	119.0260(10)	90
volume [Å^3]	3599.41(12)	3414.42(17)	6653.1(2)
Z	2	2	4
density [g cm^{-3}]	1.810	1.842	1.823
T [K]	100	100	100
absorption coeff. [mm^{-1}]	0.275	0.246	0.214
Θ range [°]	2.21 to 28.58	2.44 to 28.36	2.18 to 30.07
index ranges	-15 <= h <= 15, -18 <= k <= 18, -30 <= l <= 30	-18 <= h <= 18, -19 <= k <= 19, -26 <= l <= 26	-19 <= h <= 19, -34 <= k <= 34, -29 <= l <= 29
reflns collected	244883	154736	753649
independent reflns	18346 [R(int) = 0.0613]	17021 [R(int) = 0.0545]	19478 [R(int) = 0.0878]
absorption correction	multi-scan	multi-scan	multi-scan
max. and min. transmission	0.7457 and 0.7159	0.7457 and 0.6940	0.7460 and 0.7112
transmissiondata/restraints/ parameters	18346 / 0 / 1162	17021 / 0 / 1135	19478 / 0 / 1106
goodness-of-fit on F^2	1.096	1.014	1.061
final R indices [I>2s(I)]	R1 = 0.0439	R1 = 0.0388	R1 = 0.0617
R indices (all data)	wR2 = 0.0916	wR2 = 0.0836	wR2 = 0.1675
larg. diff. peak/hole [e Å^{-3}]	0.370 / -0.542	0.349 / -0.331	1.883 / -1.253
treatment of H atoms	constr	constr	constr
CCDC-number	1818686	1863850	1863849

Table S1 (continued).

	[$FeCp_2$] [$Al(OCAr^{F}_3)_3$]	**[NBu_4] [$Al(OCAr^{F}_3)_3$]**
empirical formula	$C_{67}H_{10}AlF_{46}FeO_3$	$C_{57}AlF_{46}O_3$, $C_{16}H_{36}N$
mol. weight [g mol^{-1}]	1819.58	1876.01
crystal habit	blue block	colorless block
crystal size [mm^3]	0.15 · 0.15 · 0.10	0.30 · 0.30 · 0.10
crystal system	triclinic	triclinic
space group	P 1	P -1
a [Å]	11.6429(4)	13.3297(5)
b [Å]	11.6834(4)	14.3059(4)
c [Å]	12.0655(4)	22.5568(8)
α [°]	97.981(2)	71.8670(10)
β [°]	101.382(2)	75.4450(10)
γ [°]	98.800(2)	63.6220(10)
volume [$Å^3$]	1565.64(9)	3629.8(2)
Z	1	2
density [g cm^{-3}]	1.930	1.716
T [K]	100	100
absorption coeff. [mm^{-1}]	0.445	0.197
Θ range [°]	2.22 to 28.47	2.34 to 28.38
index ranges	-15 <= h <= 15, -15 <= k <= 15, -16 <= l <= 16	-17 <= h <= 17, -18 <= k <= 19, -30 <= l <= 30
reflns collected	36831	195049
independent reflns	15488 [R(int) = 0.0716]	18093 [R(int) = 0.0415]
absorption correction	multi-scan	multi-scan
max. and min. transmission	0.7457 and 0.6743	0.7456 and 0.6681
transmissiondata/restraints/ parameters	15488 / 0 / 1063	18093 / 0 / 1121
goodness-of-fit on F^2	1.023	1.054
final R indices [I>2s(I)]	R1 = 0.0539	R1 = 0.0389
R indices (all data)	wR2 = 0.1377	wR2 = 0.0906
larg. diff. peak/hole [e $Å^{-3}$]	0.653 / -0.505	0.491 / -0.369
treatment of H atoms	constr	constr.
CCDC-number	1863852	1863851

^{19}F NMR Spectra

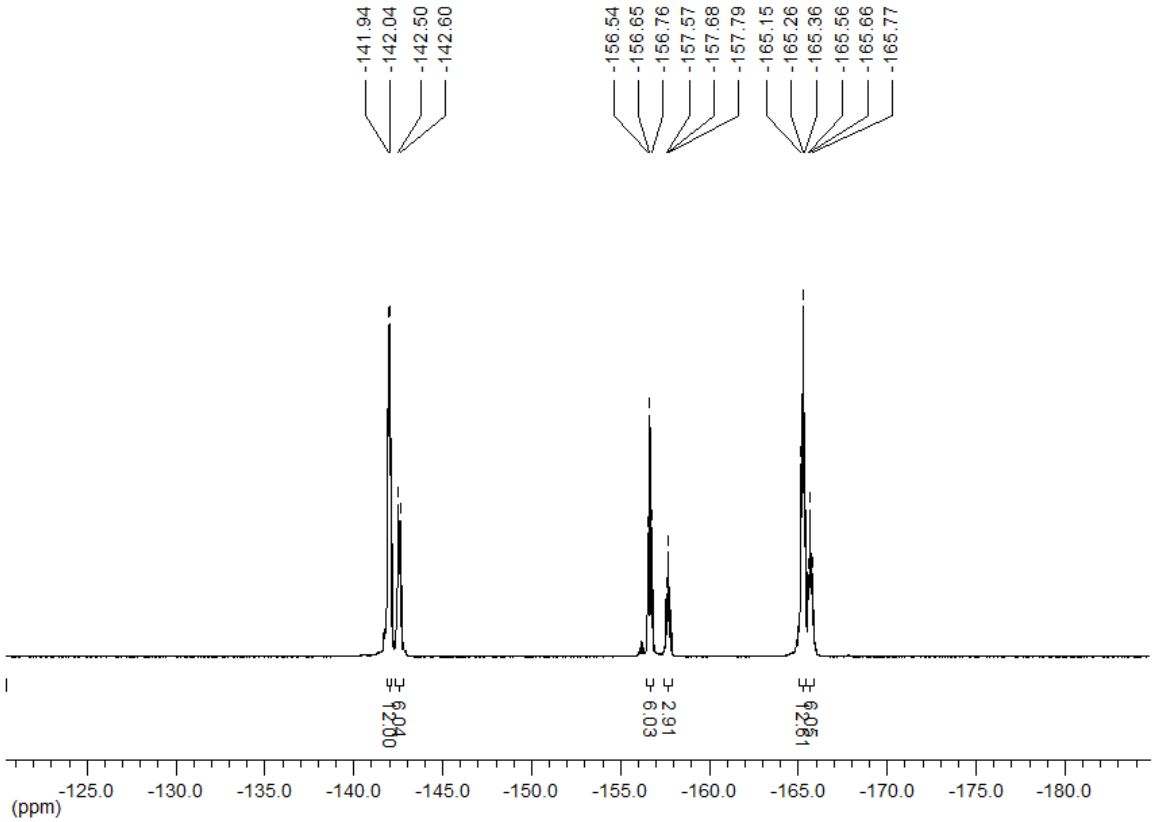

Figure S11. ^{19}F NMR spectrum of Al(OCAr$^{F}_{3}$)$_3$·THFd$_8$ (188 MHz, THF-d$_8$, 20 °C).

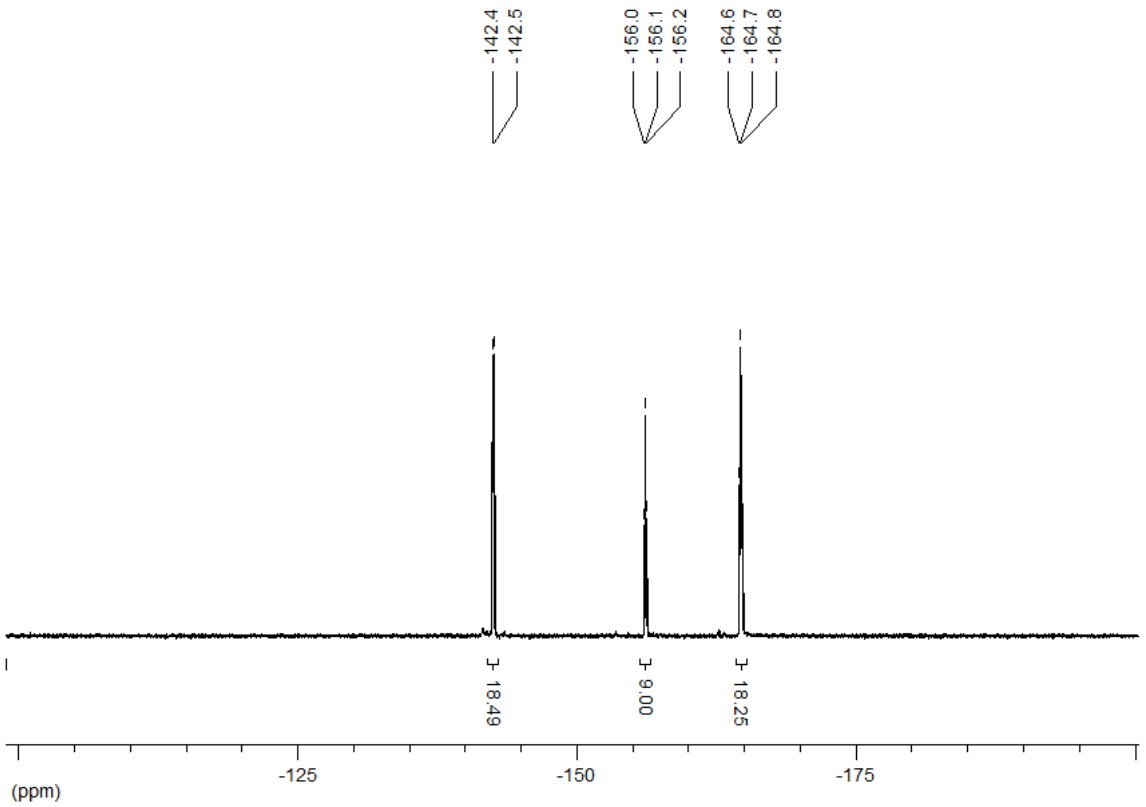

Figure S12. ^{19}F NMR spectrum of Al(OCAr$^{F}_{3}$)$_3$·MeCN·PhMe (188 MHz, CD_2Cl_2, 20 °C).

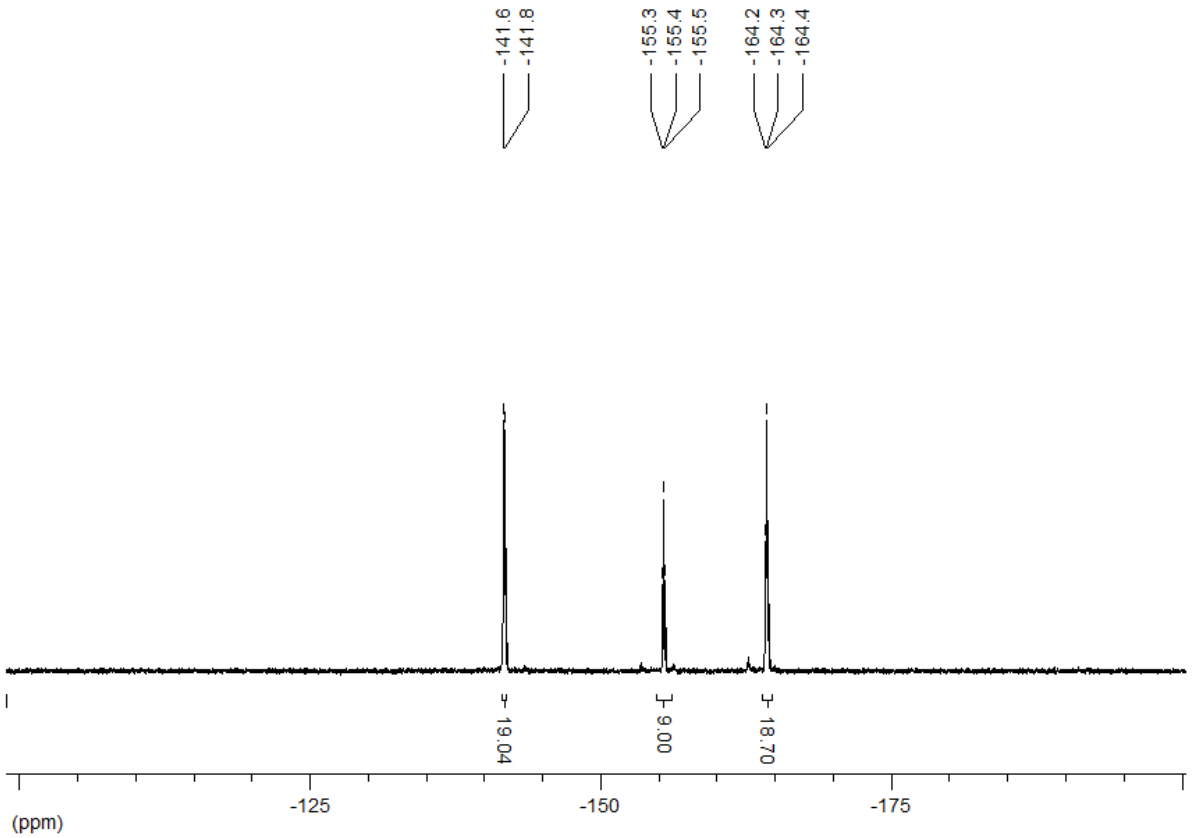

Figure S13. ^{19}F NMR spectrum of $Al(OCAr^{F}{}_{3})_3 \cdot THF$ (188 MHz, CD_2Cl_2, 20 °C).

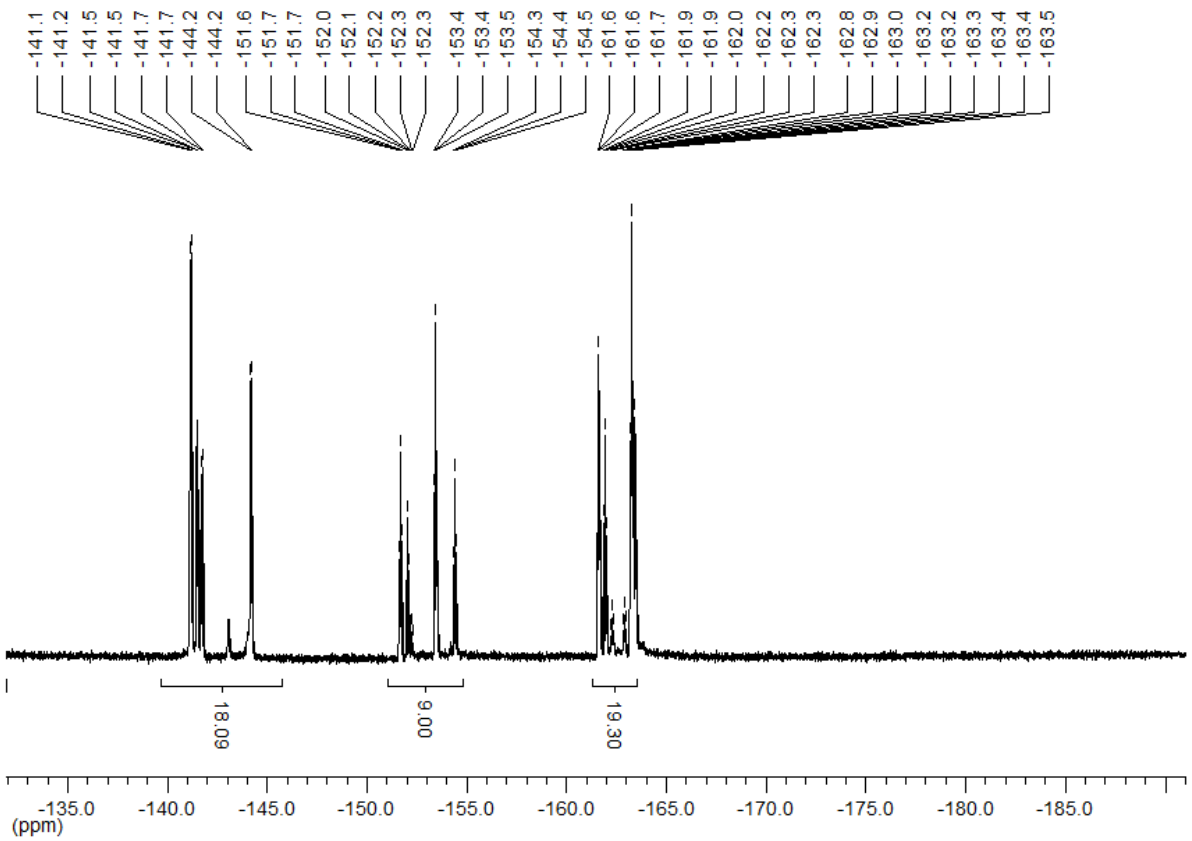

Figure S14. ^{19}F NMR spectrum of $Al(OCAr^{F}{}_{3})_3 \cdot Et_2O$ (188 MHz, C_6D_6, 20 °C).

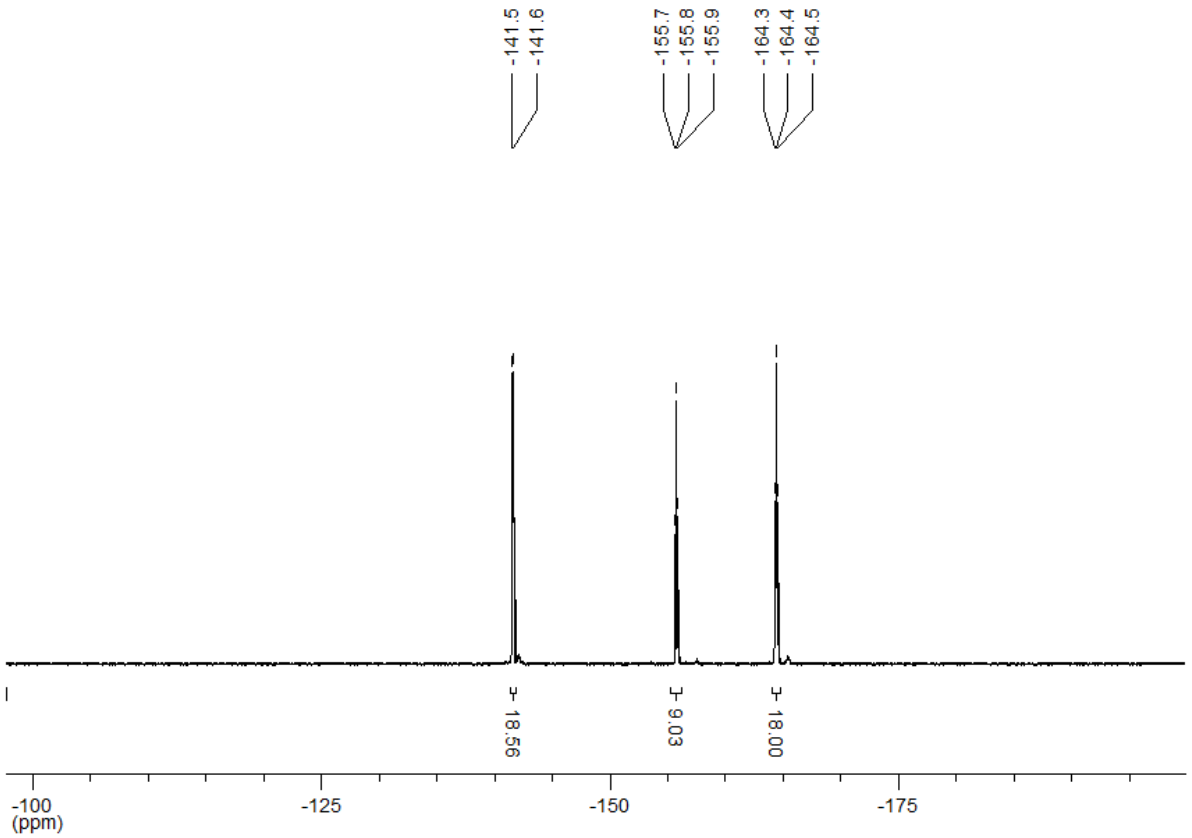

Figure S15. ^{19}F NMR spectrum of $Al(OCAr^{F}{}_{3})_3$·pyridine (188 MHz, CD_2Cl_2, 20 °C).

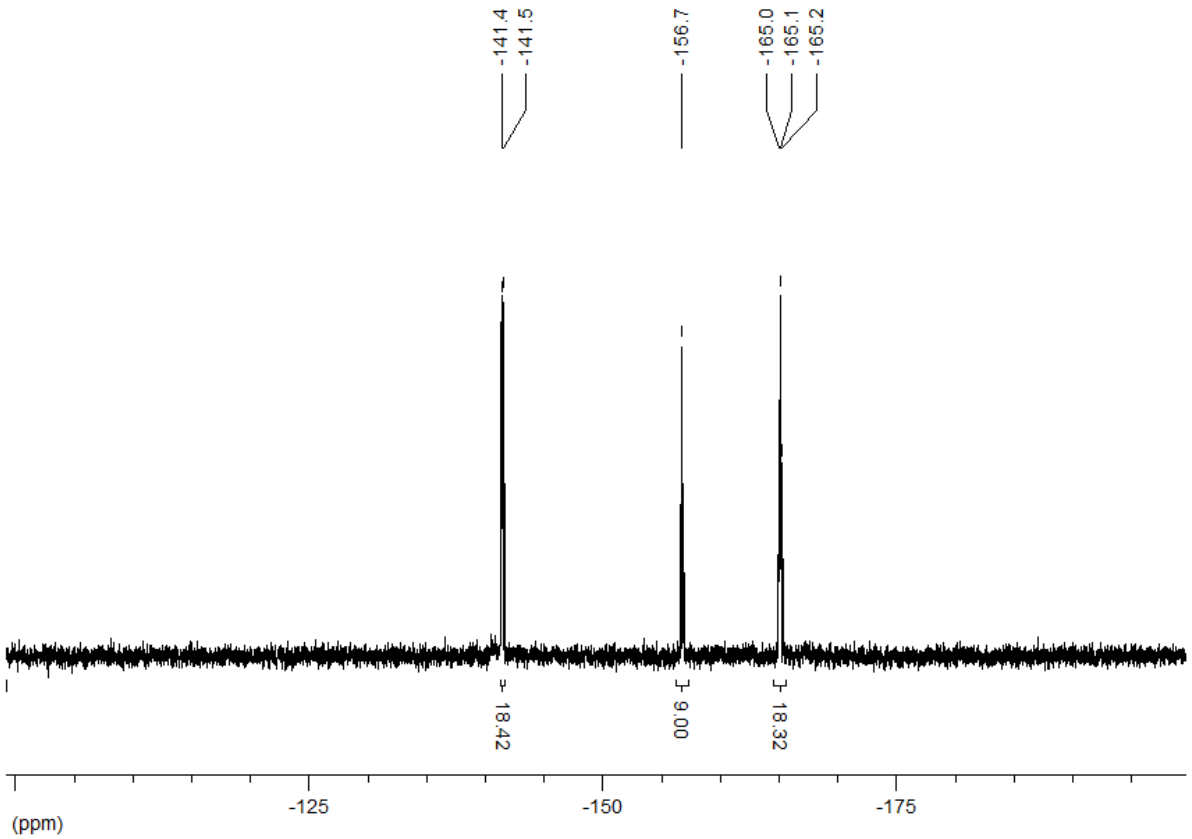

Figure S16. ^{19}F NMR spectrum of $Al(OCAr^{F}{}_{3})_3$·$OPEt_3$ (188 MHz, CD_2Cl_2, 20 °C).

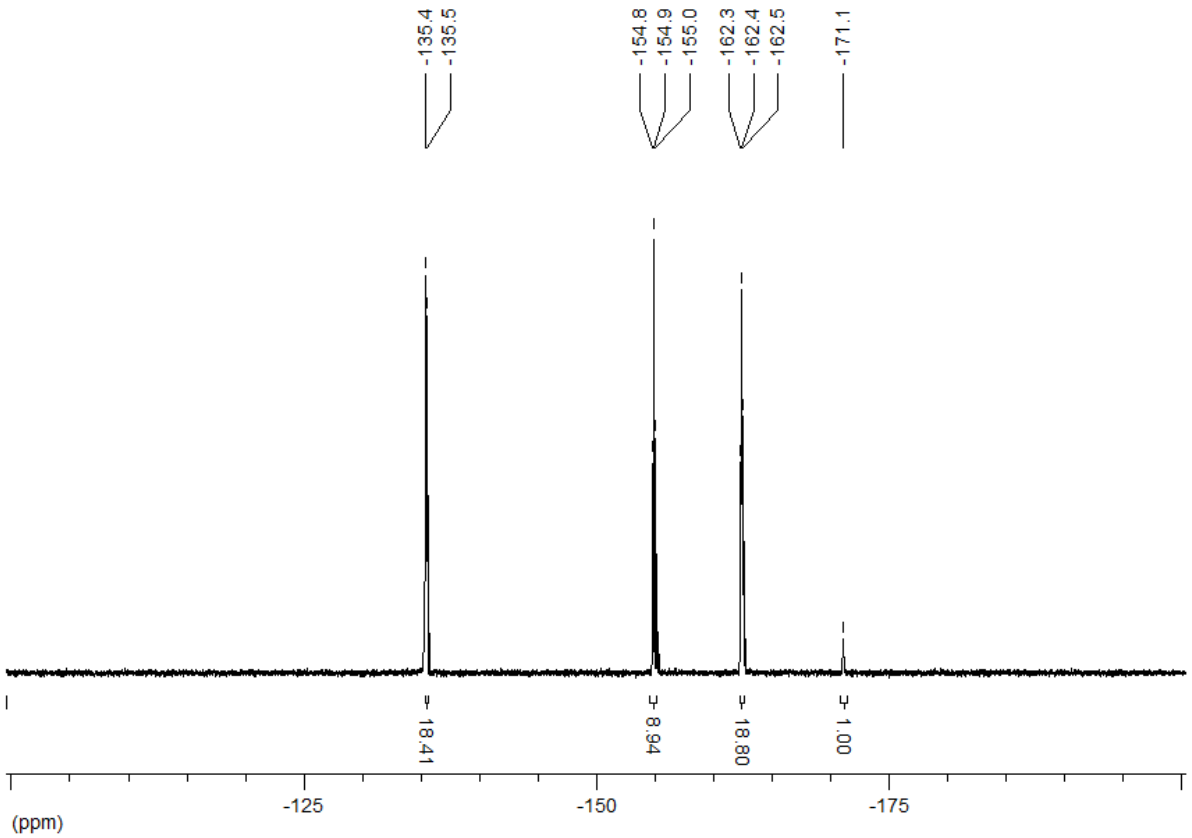

Figure S17. ^{19}F NMR spectrum of [Cs(THF)][FAl(OCAr$^{F}_{3}$)$_3$] (188 MHz, [D$_3$]MeCN, 20 °C).

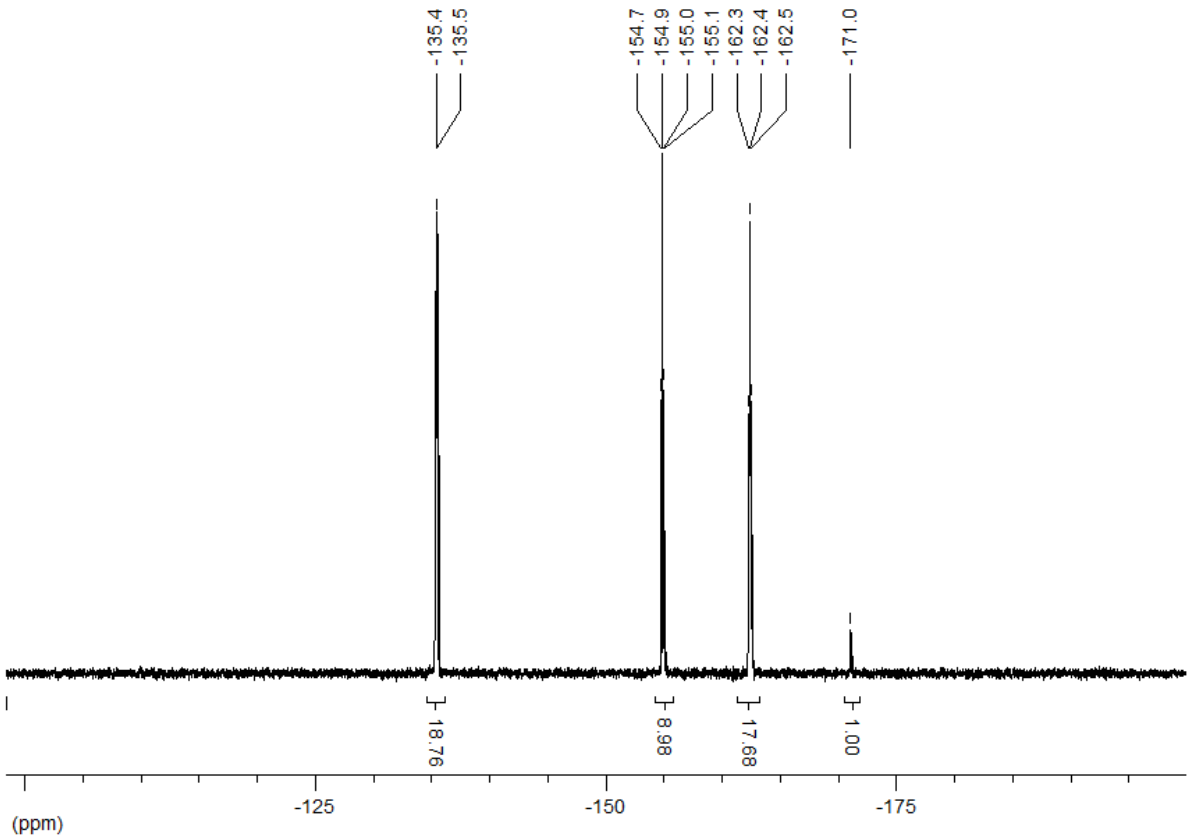

Figure S18. ^{19}F NMR spectrum of [Ag(Et$_2$O)(MeCN)][FAl(OCAr$^{F}_{3}$)$_3$] (188 MHz, [D$_3$]MeCN, 20 °C).

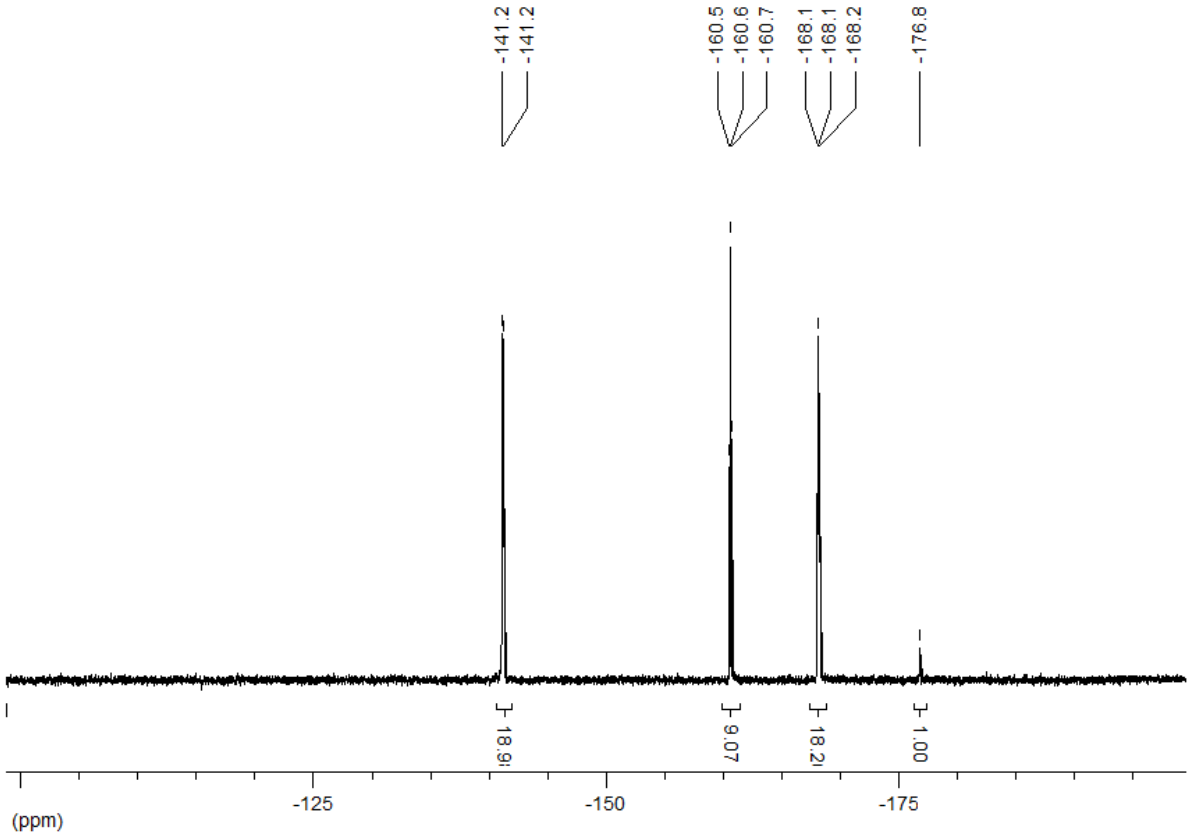

Figure S19. ^{19}F NMR spectrum of [Tl(MeCN)][FAl(OCAr$^{F}_{3}$)$_3$] (188 MHz, [D$_3$]MeCN, 20 °C).

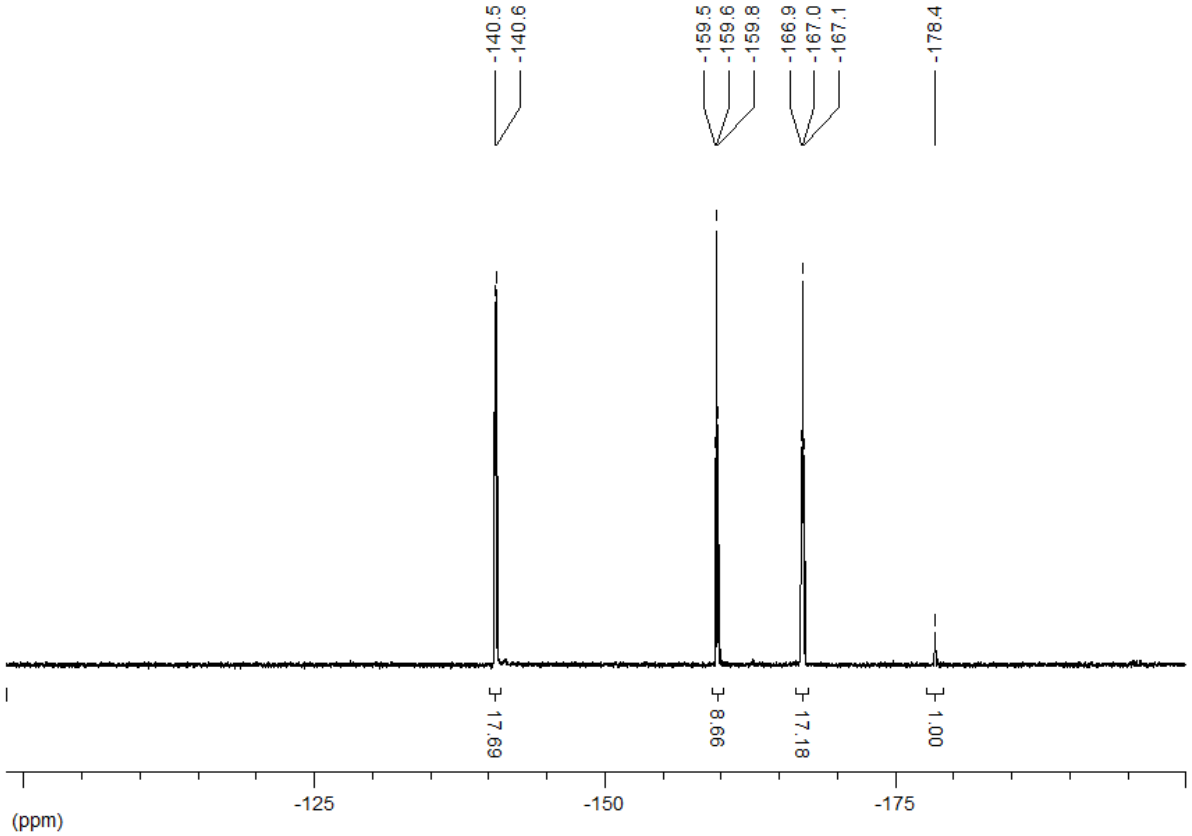

Figure S20. ^{19}F NMR spectrum of [S(NMe$_2$)$_3$][FAl(OC(C$_6$F$_5$)$_3$)$_3$] (188 MHz, CD$_2$Cl$_2$, 20 °C).

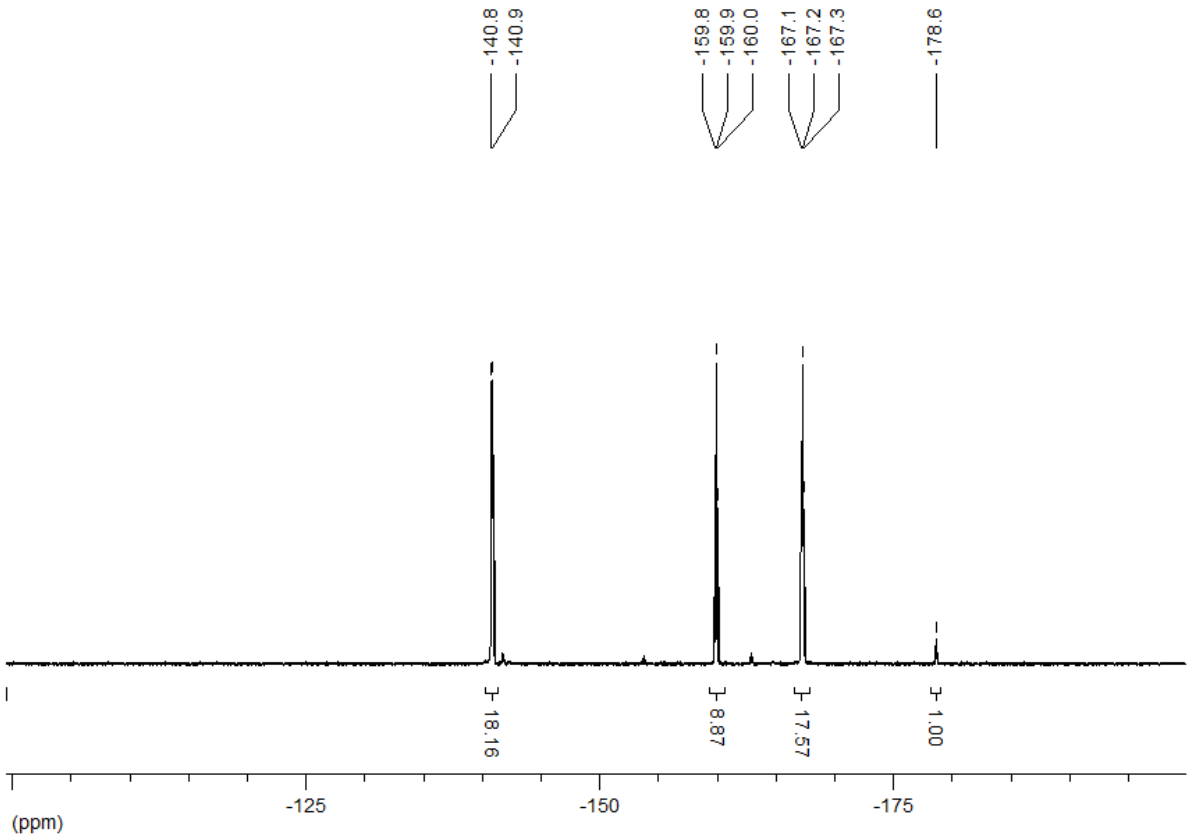

Figure S21. ^{19}F NMR spectrum of $[Ph_3C][FAl(OCAr^{F}_3)_3]$ (188 MHz, CD_2Cl_2, 20 °C).

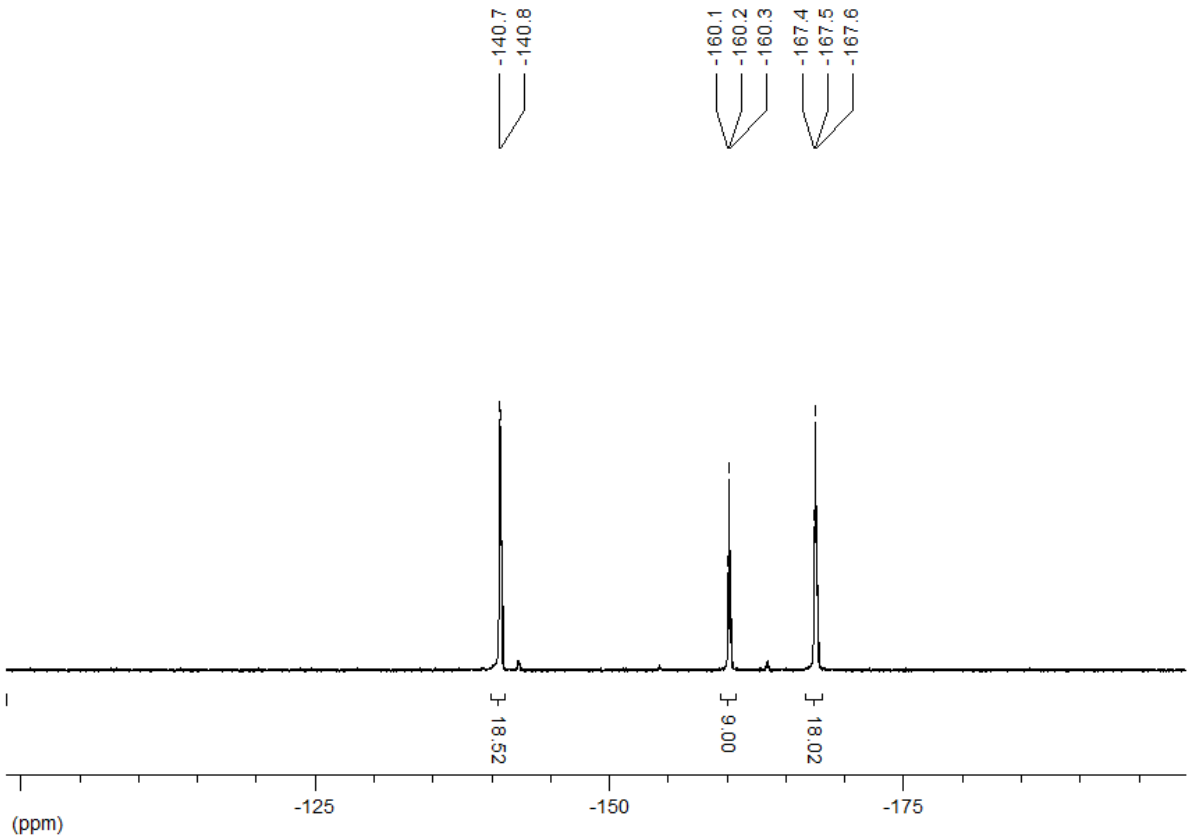

Figure S22. ^{19}F NMR spectrum of $[Ph_3C][ClAl(OCAr^{F}_3)_3]$ (188 MHz, CD_2Cl_2, 20 °C).

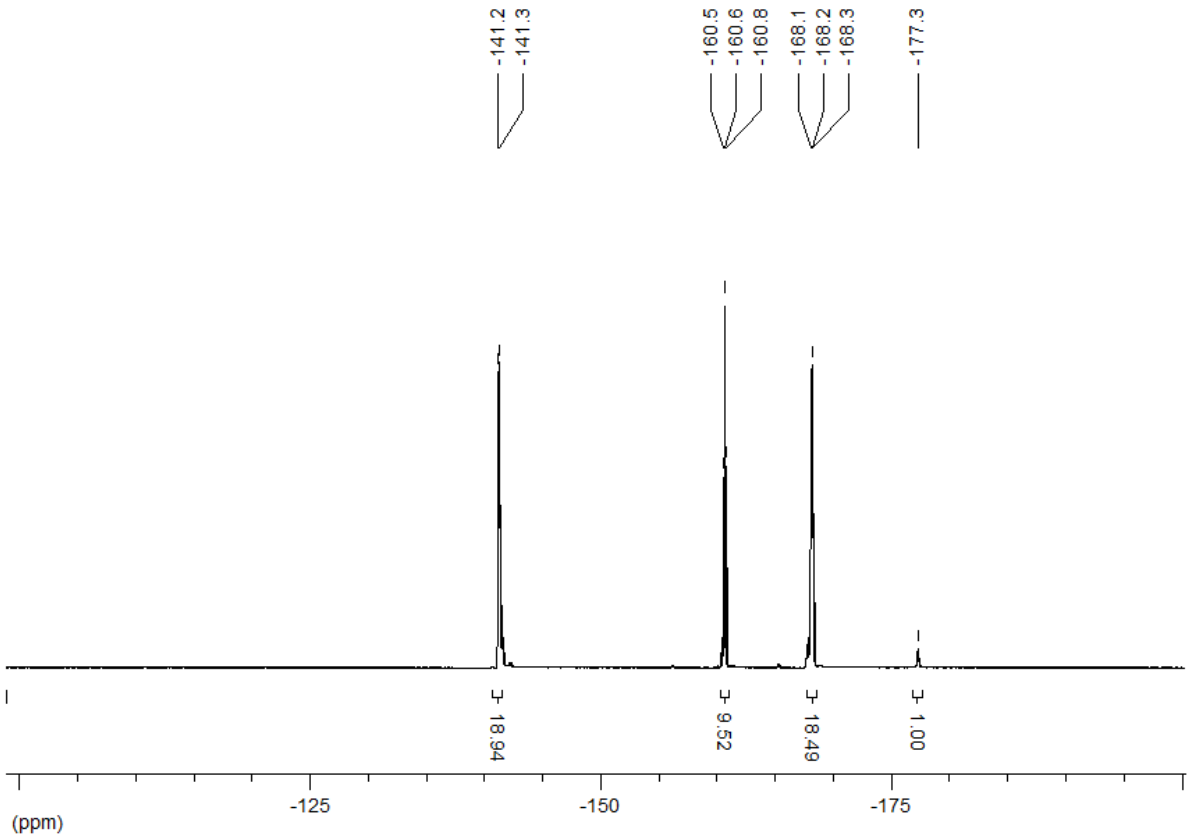

Figure S23. ^{19}F NMR spectrum of $[Li(THF)_2][FAl(OCAr^F{}_3)_3]$ (188 MHz, $[D_3]MeCN$, 20 °C).

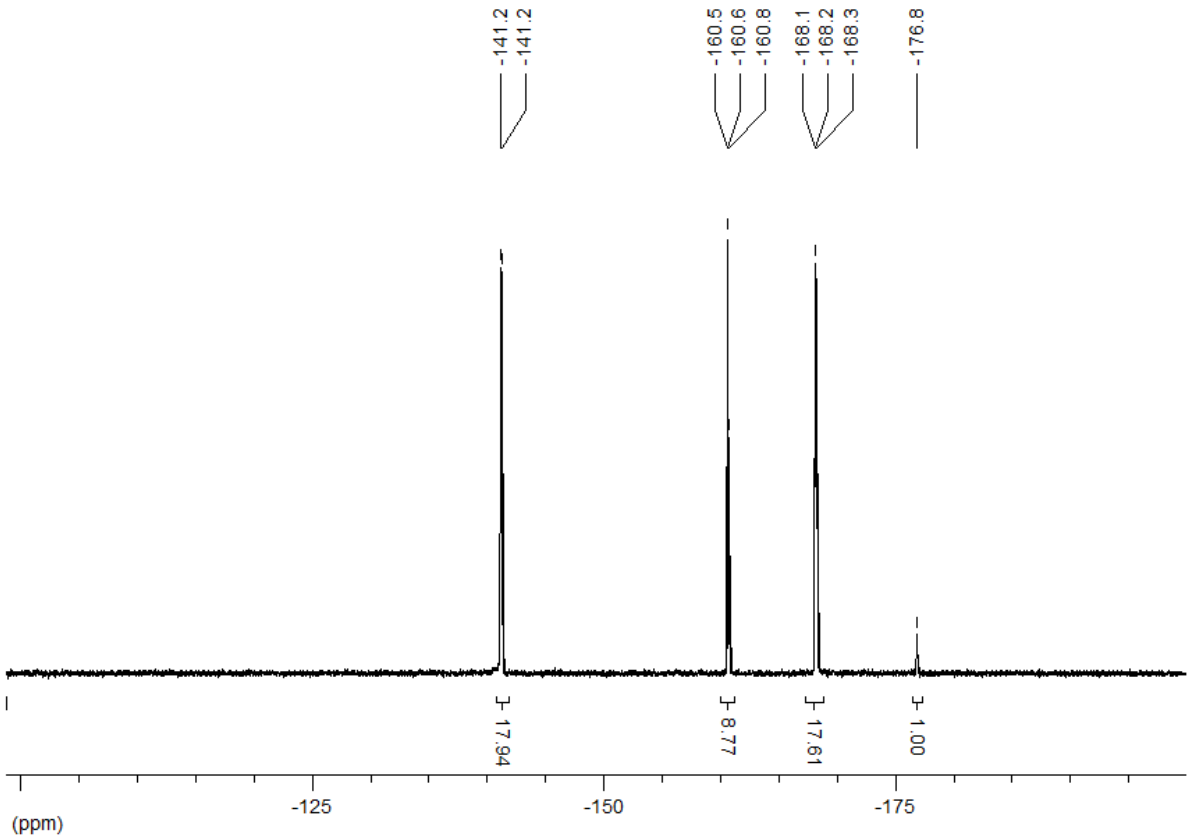

Figure S24. ^{19}F NMR spectrum of $[FeCp_2][FAl(OCAr^F{}_3)_3]$ (188 MHz, $[D_3]MeCN$, 20 °C).

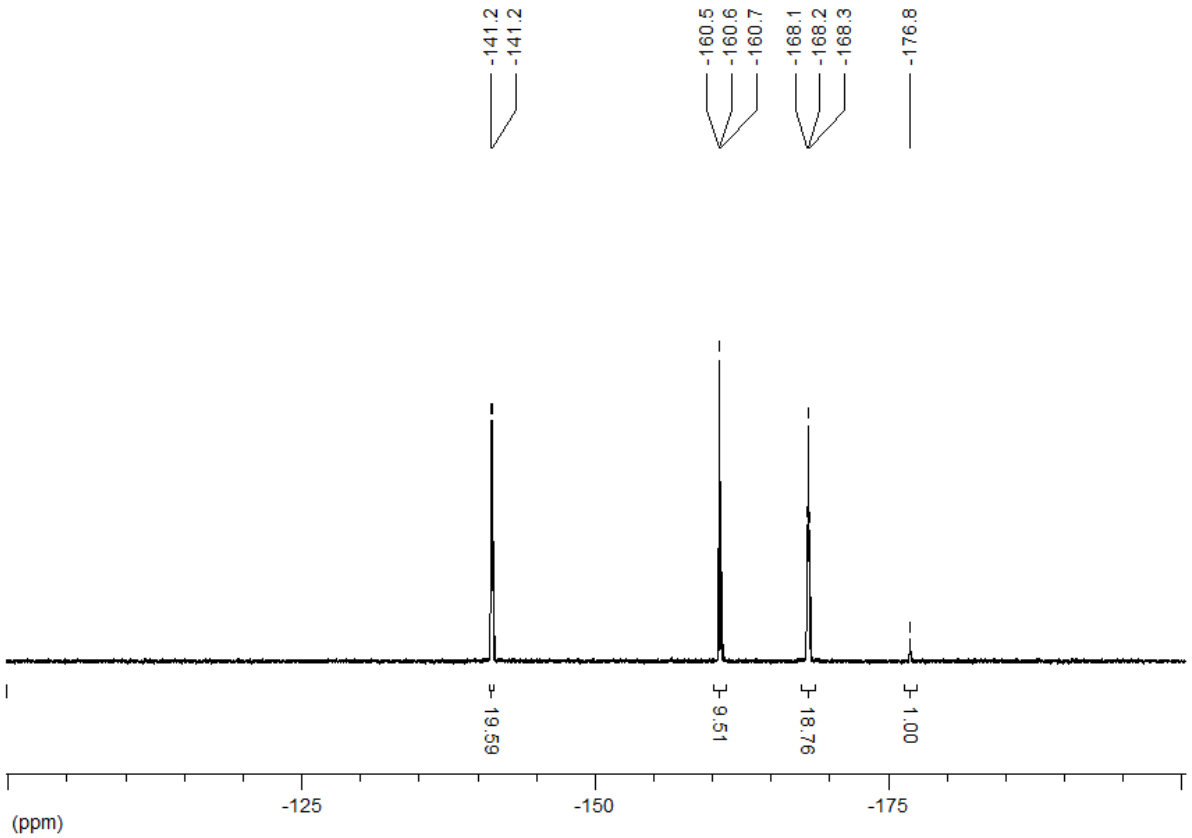

Figure S25. ^{19}F NMR spectrum of $[NBu_4][FAl(OCAr^F{}_3)_3]$ (188 MHz, $[D_3]MeCN$, 20 °C).

Computational Details

The geometries of the compounds have been fully optimized with gradient-corrected density functional theory (DFT) in the form of Becke's three-parameter hybrid B3LYP[8] functional with 6-311++G(2d,2p) all electron basis set[9] using the Gaussian 09 program package.[10] Basis set superposition error (BSSE) was evaluated using the counterpoise method[11] and amounts 12-17 kJ mol^{-1} for the FIA. Since the counterpoise method overestimates BSSE, the computed FIA lies in between BSSE corrected and BSSE uncorrected values.[12] All stationary points of the potential energy surface (PES) were characterized by analytic evaluation of second derivatives, with the exception of highly demanding $Al(OCAr^F{}_3)_3$ and its anion. In all other cases optimized structures correspond to minima on their respective potential energy surfaces.

Table S2. Fluoride ion affinities (FIA) for the studied Lewis acids, kJ·mol^{-1}. BSSE-corrected values in *italics*.

Compound	FIA	Level of theory	Reference
$AlCl_3$	484, *472*	B3LYP/6-311++G(2d,2p)	present work
	503	MP2/6-311++G(2d,2p)// B3LYP/6-311++G(2d,2p)	present work
	498	BP86/SV(P)	[13]
	457	BP86/SV(P)	[14]
	502	CCSD(T)(FC)[a]	[13]
	479	MP2/PDZ	[15]
SbF_5	478, *466*	B3LYP/6-311++G(2d,2p)	present work
	501	MP2/6-311++G(2d,2p)// B3LYP/6-311++G(2d,2p)	present work
	495	CCSD(T)FC [a]	[13]
	493	BP86/SV(P)	[13]
	489	RI-BP86/SV(P)	[16]
	503	MP2/PDZ	[15]
$B(C_6F_5)_3$	413, *398*	B3LYP/6-311++G(2d,2p)	present work
	451	MP2/6-311++G(2d,2p)// B3LYP/6-311++G(2d,2p)	present work
	444	BP86/SV(P)	[14,16]
	452	BP86/SV(P)	[13]
$C_6H_5F{\cdot}Al(OC(CF_3)_3)_3$	495, *492* [b]	B3LYP/6-311++G(2d,2p)	present work
	505	BP86/SV(P)	[14]
	465	MP2/6-311++G(2d,2p)// B3LYP/6-311++G(2d,2p)	present work
$Al(OCAr^F{}_3)_3$	536, *520*	B3LYP/6-311++G(2d,2p)	present work
	555	MP2/6-311++G(2d,2p)// B3LYP/6-311++G(2d,2p)	present work
$Al(OC(CF_3)_3)_3$	541, *525*	B3LYP/6-311++G(2d,2p)	present work
	547	MP2/6-311++G(2d,2p)// B3LYP/6-311++G(2d,2p)	present work
	543	BP86/SV(P)	[13]
	537	BP86/SV(P)	[14,16]
$Al(N(C_6F_5)_2)_3$	555	BP86-D3/def-TZVP	[17]

[a] $\Delta E = \Delta E(CCSD(T)/AVDZ) - \Delta E(MP2/AVDZ) + \Delta E(MP2/AVQZ)$.

[b] Values for the process $C_6H_5F{\cdot}Al(OC(CF_3)_3)_3) + F^- = [FAl(OC(CF_3)_3)_3]^- + C_6H_5F$

Table S3. FIA, kJ mol^{-1}, of selected Lewis acids, computed at different computational levels and using different computational schemes.

	Exp. (high level)	BP86/SVP [143]	B3LYP/6-311++G(2d,2p)			B3LYP-D3/6-311++G(2d,2p)// B3LYP/6-311++G(2d,2p)		M06/6-311++G(2d,2p)// B3LYP/6-311++G(2d,2p)		MP2/6-311++G(2d,2p)// B3LYP/6-311++G(2d,2p)	
Compound			direct	direct (BSSE)	isodesmic	direct	isodesmic	direct	isodesmic	direct	isodesmic
COF_2	209	-	205	194	-	207	-	211	-	205	
BF_3	346 [14]	342	330	319	334	333	335	337	336	343	347
SbF_5	495 [14]	493	478	466	482	482	484	505	503	501	505
$AlCl_3$	502 [14]	498	484	472	488	488	490	502	500	503	507
$B(C_6F_5)_3$	-	452	413	398	417	422	424	431	429	451	454
$Al\{OC(CF_3)_3\}_3$	-	543	541	525	545	547	549	552	551	547	551
$Al\{OC(CF_3)_3\}_3 \cdot C_6H_5F$	-	-	495	492	499	470	472	487	486	465	468
$Al\{OC(C_6F_5)_3\}_3$	-	-	536	519	540	545	547	549	547	555	559

direct: Computed form the reaction LA + F^- =LAF^-.
direct. (BSSE): the same corrected to the basis set superposition energy (BSSE) error.
isodesmic: Computed form the reaction LA + COF_3^- =LAF^- + COF_2 coupled with the experimental value of FIA of COF_2 (209 kJ mol^{-1}).

Computation of FIA

In addition to the FIA computed using the reaction via direct F^- addition to LA, these values were also computed using the isodesmic reaction LA + COF_3^- → LAF^- + COF_2 and experimental gas phase FIA value of COF_2 (209 kJ mol^{-1}). This approach has been used by Christie et al.[16], and more recently by Stephan and coworkers.[18] Values are given in Table S1. At the each employed level of theory, the differences between FIA values obtained from F^- addition and the isodesmic reaction approach is less than 4 kJ mol^{-1}, indicating that the chosen basis set is large enough to compute the absolute electron affinities. However, the values of FIA at B3LYP/6-311++G(2d,2p) method for reference compounds, such as BF_3, SbF_5, and $AlCl_3$ are underestimated by 15 kJ mol^{-1}. BSSE corrected values are by circa 12 kJ mol^{-1} lower. The inclusion of dispersion correction via single point energy computation at B3LYP/6-311++G(2d,2p) optimized geometries using D3 Grimme approach increases the FIA values by 5-7 kJ mol^{-1}, and using M06 Truhlar functional by 11-20 kJ mol^{-1}. However, in both cases the FIA of $B(C_6F_5)_3$ is underestimated compared to values obtained using isodesmic reactions at BP86/SVP level,[143] calibrated against the high level ab initio methods.[143] The most consistent set of FIA data was obtained using *ab inito* MP2/6-311++G(2d,2p) single point energies at B3LYP/6-311++G(2d,2p) optimized geometries.

Table S4. Total energies E^{o}_{0}, BSSE corrected energies $E^{o}_{0(BSSE)}$, sum of electronic and thermal enthalpies H^{o}_{298} (Hartree) and standard entropies S^{o}_{298} (cal $mol^{-1}K^{-1}$). B3LYP/6-311++(2d,2p) level of theory.

Compound	E^{o}_{0}	$E^{o}_{0(BSSE)}$	H^{o}_{298}	S^{o}_{298}
C_6H_5F	-331.5917371		-331.493652	72.147
F^-	-99.8886932		-99.886333	34.767
COF_2	-313.1241625		-313.106046	61.914
COF_3^-	-413.090954	-413.0866821	-413.07081	66.337
BF_3	-324.6790842		-324.662383	60.888
BF_4^-	-424.693655	-424.6894409	-424.67446	64.574
SbF_5	-739.8084345		-739.78908	86.136
SbF_6^-	-839.879183	-839.8746121	-839.856753	83.493
$AlCl_3$	-1623.352313		-1623.341275	74.989
$AlCl_3F^-$	-1723.425462	-1723.420596	-1723.411014	83.089
$B(C_6F_5)_3$	-2208.990018		-2208.806451	192.195
$[B(C_6F_5)_3F]^-$	-2309.036136	-2309.030437	-2308.85032	196.628
$Al(OC(CF_3)_3)_3$	-3622.461268		-3622.253432	251.024
$[FAl(OC(CF_3)_3)_3]^-$	-3722.555944	-3722.549985	-3722.3453	265.125
$Al(OC(CF_3)_3)_3 \cdot C_6H_5F$	-3954.070266	-3954.065487	-3953.762323	295.193
$Al(OCAr^F_3)_3$	-7134.928079			
$[FAl(OCAr^F_3)_3]^-$	-7135.643522	-7135.640927		

Table S5. Reaction energies $\Delta E°_0$, standard enthalpies $\Delta H°_{298}$, Gibbs energies $\Delta G°_{298}$ (kJ mol^{-1}) and standard entropies $\Delta S°_{298}$ (J mol^{-1} K^{-1}) for the considered gas phase processes. B3LYP/6-311++(2d,2p) level of theory.

Process	$\Delta E°_0$	$\Delta E°_{0(BSSE)}$	$\Delta H°_{298}$	$\Delta S°_{298}$	$\Delta G°_{298}$
$COF_2 + F^- = COF_3^-$	-205.0	-193.8	-205.9	-127.0	-168.1
$SbF_5 + F^- = SbF_6^-$	-478.0	-466.0	-476.1	-156.5	-429.4
$AlCl_3 + F^- = AlCl_3F^-$	-484.3	-471.5	-481.5	-111.6	-448.3
$B(C_6F_5)_3 + F^- = [B(C_6F_5)_3F]^-$	-413.3	-398.4	-413.6	-126.9	-375.8
$Al(OC(CF_3)_3)_3 + F^- = [FAl(OC(CF_3)_3)_3]^-$	-540.8	-525.2	-539.6	-86.5	-513.9
$Al(OC(CF_3)_3)_3 \cdot C_6H_5F + F^- = [FAl(OC(CF_3)_3)_3]^- + C_6H_5F$	-495.5	-492.4	-499.6	30.6	-508.7
$Al(OCAr^F_3)_3 + F^- = [FAl(OCAr^F_3)_3]^-$	-536.3	-519.5			

Table S6. Total energies E^{o}_{0} (Hartree) at different levels of theory computed at B3LYP/6-311++(2d,2p) optimized geometries.

Compound\Level of theory	**MP2**/6-311++(2d,2p)	**B3LYP-D3**/6-311++(2d,2p)	**M06**/6-311++(2d,2p)
C_6H_5F	-330.7390689	-331.5974632	-331.3643923
F^-	-99.703831	-99.88869321	-99.8506077
COF_2	-312.5122944	-313.1247139	-313.0023095
COF_3^-	-412.2943458	-413.0922309	-412.9331019
BF_3	-324.0654386	-324.6797683	-324.566859
BF_4^-	-423.8999748	-424.695125	-424.5460104
SbF_5	-738.1934101	-739.8111628	-739.6389605
SbF_6^-	-838.0882096	-839.8835084	-839.6818793
$AlCl_3$	-1621.203425	-1623.355184	-1623.218258
$AlCl_3F^-$	-1721.098976	-1723.429893	-1723.260036
$B(C_6F_5)_3$	-2204.363648	-2209.029893	-2208.002474
$[B(C_6F_5)_3F]^-$	-2304.239165	-2309.07918	-2308.01706
$Al(OC(CF_3)_3)_3$	-3615.582687	-3622.527738	-3621.225153
$[FAl(OC(CF_3)_3)_3]^-$	-3715.494955	-3722.624824	-3721.286044
$Al(OC(CF_3)_3)_3 \cdot C_6H_5F$	-3946.353157	-3954.154501	-3952.614313
$Al(OCAr^F{}_3)_3$	-7120.231972	-7135.124771	-7131.879806
$[FAl(OCAr^F{}_3)_3]^-$	-7220.147278	-7235.221196	-7231.939365

Electrostatic Potentials

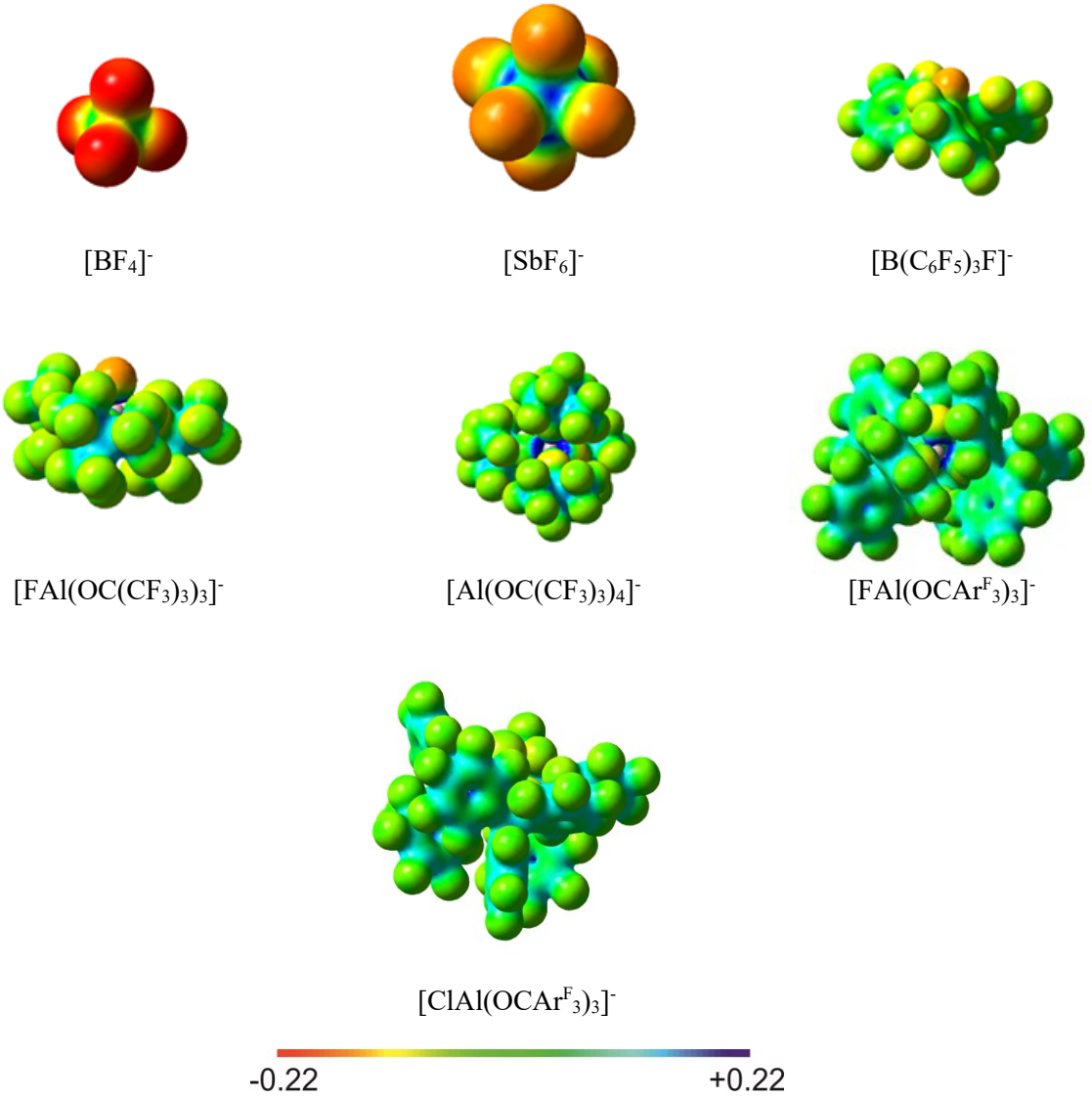

Figure S26. Projection of the calculated electrostatic potential onto a 0.025 e^{-} $Bohr^{-3}$ isodensity surface for studied WCA. B3LYP/6-311++G(2d,2p) level of theory. For $[ClAl(OCAr^{F}_{3})_{3}]^{-}$ electrostatic potential was computed using experimental geometry in compound $[CPh_{3}]^{+}[ClAl(OCAr^{F}_{3})_{3}]^{-}$.

Global Electrophilicity Index

The base-independent Lewis acidity criterion, global electrophilicity index GEI,[19,20] denoted as ω, was recently used as a simple quantitative assessment of Lewis acidity of 20 fluorophenylboranes by Stephan.[18]

$\omega = \frac{\chi^2}{2\eta}$, where $\eta = E_{LUMO} - E_{HOMO}$, $\chi = ½(E_{LUMO} + E_{HOMO})$.[18]

We have also explored a performance GEI for studied Lewis acids (Table S7). Our results indicate that GEI cannot be used for judging the Lewis acidity towards F^- for Lewis acids of different types (Figure S2). The R^2 value for the linear correlation is close to zero, indicating the absence of the correlation.

Table S7. Energies of HOMO E_{HOMO}, LUMO E_{LUMO}, the Mulliken electronegativity χ, chemical hardness η and Global Electrophilicity Index ω, in eV, and FIA in kJ mol^{-1} for studied Lewis acids.

Lewis acid	E_{HOMO}	E_{LUMO}	χ	η	ω	FIA
COF_2	-15.302	1.790	6.756	17.092	1.335	205
SbF_5	-17.863	-0.362	9.113	17.502	2.372	501
$AlCl_3$	-12.681	0.762	5.959	13.443	1.321	503
$B(C_6F_5)_3$	-10.526	-0.236	5.381	10.290	1.407	451
BF_3	-18.096	1.446	8.325	19.541	1.773	343
$Al\{OC(CF_3)_3\}_3$	-14.112	1.586	6.263	15.698	1.249	547
$Al\{OC(C_6F_5)_3\}_3$	-10.416	0.912	4.752	11.328	0.997	555

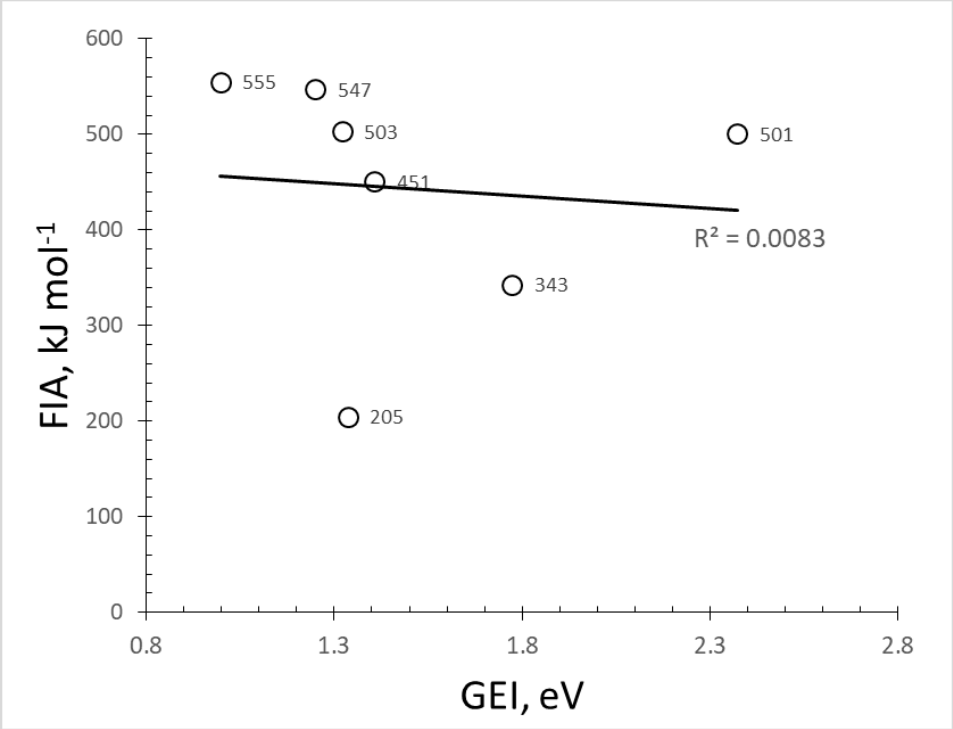

Figure S27. The GEI-FIA relationship for the studied Lewis acids.

Table S8. Optimized geometries of theoretically studied compounds. xyz coordinates in angstroms. B3LYP/6-311++(2d,2p) level of theory.

	COF_2		
8	0.000000000	0.000000000	1.316226000
6	0.000000000	0.000000000	0.145728000
9	0.000000000	-1.066025000	-0.633565000
9	0.000000000	1.066025000	-0.633565000
	COF_3^-		
8	0.000000000	0.000000000	1.410573000
9	0.000000000	1.279482000	-0.461961000
9	1.108064000	-0.639741000	-0.461961000
6	0.000000000	0.000000000	0.198058000
9	-1.108064000	-0.639741000	-0.461961000
	BF_3		
5	0.000000000	0.000000000	0.000000000
9	0.000000000	1.313903000	0.000000000
9	1.137874000	-0.656952000	0.000000000
9	-1.137874000	-0.656952000	0.000000000
	BF_4^-		
9	0.814433000	0.814433000	0.814433000
5	0.000000000	0.000000000	0.000000000
9	-0.814433000	-0.814433000	0.814433000
9	-0.814433000	0.814433000	-0.814433000
9	0.814433000	-0.814433000	-0.814433000
	$AlCl_3$		
13	0.000000000	0.000000000	0.000000000
17	0.000000000	2.081028000	0.000000000
17	1.802223000	-1.040514000	0.000000000
17	-1.802223000	-1.040514000	0.000000000
	$AlCl_3F^-$		
13	0.000000000	0.000000000	0.294330000
9	0.000000000	0.000000000	1.980513000
17	0.000000000	2.052352000	-0.424527000
17	1.777389000	-1.026176000	-0.424527000
17	-1.777389000	-1.026176000	-0.424527000
	C_6H_5F		
6	0.000000000	0.000000000	0.924363000
6	0.000000000	1.213504000	0.259260000
6	0.000000000	-1.213504000	0.259260000
6	0.000000000	1.204520000	-1.132386000
6	0.000000000	-1.204520000	-1.132386000
6	0.000000000	0.000000000	-1.829860000
1	0.000000000	2.134294000	0.823970000
1	0.000000000	-2.134294000	0.823970000
1	0.000000000	2.142698000	-1.669715000
1	0.000000000	-2.142698000	-1.669715000
1	0.000000000	0.000000000	-2.910601000
9	0.000000000	0.000000000	2.279176000
	SbF_5		
9	0.000000000	-0.003437000	1.866622000
51	0.000000000	-0.000072000	-0.000793000
9	0.000000000	1.622621000	-0.925264000
9	0.000000000	-1.619813000	-0.930830000
9	1.876331000	0.000517000	-0.003017000
9	-1.876332000	0.000517000	-0.003017000
	SbF_6^-		
9	0.000000000	0.000000000	1.912776000
9	0.000000000	1.912776000	0.000000000

9	0.000000000	-1.912776000	0.000000000
9	1.912776000	0.000000000	0.000000000
9	-1.912776000	0.000000000	0.000000000
51	0.000000000	0.000000000	0.000000000
9	0.000000000	0.000000000	-1.912776000

$B(C_6F_5)_3$

6	-0.000878000	1.563932000	0.006594000
6	1.356171000	-0.784249000	0.003353000
6	-1.358736000	-0.785425000	-0.005712000
6	0.004436000	4.389609000	0.011834000
6	0.886354000	2.306168000	0.790909000
6	-0.885548000	2.312322000	-0.774663000
6	-0.889030000	3.696788000	-0.794206000
6	0.895137000	3.690518000	0.815504000
9	1.760597000	1.680070000	1.593600000
9	-1.762169000	1.692472000	-1.579645000
9	-1.737196000	4.368741000	-1.573787000
9	1.746079000	4.356457000	1.597271000
9	0.006958000	5.717752000	0.014144000
6	-3.808276000	-2.195087000	-0.021482000
6	-2.458700000	-0.378010000	0.754870000
6	-1.551710000	-1.937144000	-0.774285000
6	-2.748237000	-2.633152000	-0.804010000
6	-3.661884000	-1.062957000	0.768895000
9	-2.368609000	0.702595000	1.544929000
9	-0.564104000	-2.397991000	-1.556831000
9	-2.892956000	-3.714527000	-1.570952000
9	-4.676892000	-0.649085000	1.528510000
9	-4.959433000	-2.857227000	-0.028827000
6	3.807350000	-2.190875000	0.006194000
6	1.553328000	-1.937417000	0.768355000
6	2.452690000	-0.373471000	-0.760247000
6	3.656731000	-1.056834000	-0.780623000
6	2.750741000	-2.632149000	0.791587000
9	0.569247000	-2.400849000	1.553844000
9	2.357890000	0.709220000	-1.547092000
9	4.668366000	-0.639529000	-1.542869000
9	2.899750000	-3.715263000	1.555277000
9	4.959228000	-2.851859000	0.007657000
5	-0.001747000	-0.002970000	0.001905000

$[B(C_6F_5)_3F]^-$

6	0.000000000	1.592458000	0.291493000
6	1.379109000	-0.796229000	0.291493000
6	-1.379109000	-0.796229000	0.291493000
6	0.021093000	4.371968000	-0.313184000
6	0.822942000	2.502809000	0.951931000
6	-0.789657000	2.152756000	-0.704194000
6	-0.799779000	3.506950000	-1.013384000
6	0.844408000	3.862397000	0.676519000
9	1.687864000	2.085355000	1.895905000
9	-1.603360000	1.383682000	-1.462499000
9	-1.595616000	3.988429000	-1.986567000
9	1.661923000	4.693395000	1.349624000
9	0.026118000	5.686056000	-0.594372000
6	-3.796782000	-2.167717000	-0.313184000
6	-2.578967000	-0.538716000	0.951931000
6	-1.469513000	-1.760241000	-0.704194000
6	-2.637218000	-2.446104000	-1.013384000
6	-3.767138000	-1.199920000	0.676519000
9	-2.649902000	0.419056000	1.895905000
9	-0.396623000	-2.080391000	-1.462499000

9	-2.656273000	-3.376058000	-1.986567000
9	-4.895561000	-0.907430000	1.349624000
9	-4.937328000	-2.820409000	-0.594372000
6	3.775689000	-2.204251000	-0.313184000
6	1.756025000	-1.964093000	0.951931000
6	2.259170000	-0.392515000	-0.704194000
6	3.436997000	-1.060846000	-1.013384000
6	2.922730000	-2.662477000	0.676519000
9	0.962038000	-2.504411000	1.895905000
9	1.999984000	0.696710000	-1.462499000
9	4.251888000	-0.612370000	-1.986567000
9	3.233638000	-3.785965000	1.349624000
9	4.911210000	-2.865647000	-0.594372000
5	0.000000000	0.000000000	0.768230000
9	0.000000000	0.000000000	2.188569000

$Al(OC(CF_3)_3)_3$

13	0.129918000	-0.015124000	-0.138108000
9	4.062961000	-0.345317000	-0.438424000
9	3.976004000	-2.078372000	-1.724421000
9	4.521765000	-2.309108000	0.364769000
9	1.605284000	-3.363249000	-1.835564000
9	2.572390000	-4.218187000	-0.094329000
9	0.529072000	-3.489556000	0.035297000
9	2.823493000	-0.682646000	1.928831000
9	2.107071000	-2.699464000	2.168560000
9	0.717285000	-1.112472000	1.590682000
9	-2.307126000	-3.065117000	-0.923189000
9	-2.264887000	-2.843554000	1.225796000
9	-4.159304000	-2.793517000	0.165386000
9	-1.981233000	-0.285456000	2.135567000
9	-4.101034000	-0.691417000	1.913147000
9	-3.252776000	1.140115000	1.127654000
9	-4.939974000	-0.289210000	-0.749677000
9	-3.302949000	0.878240000	-1.562558000
9	-3.627712000	-1.141122000	-2.252685000
9	-1.101296000	3.519982000	1.481204000
9	-1.646102000	3.067333000	-0.561670000
9	-0.487882000	4.851404000	-0.114528000
9	0.217286000	1.323494000	-1.846991000
9	0.478615000	3.447910000	-2.283191000
9	2.183406000	2.245587000	-1.745805000
9	2.249854000	4.476344000	-0.032435000
9	2.872990000	2.584726000	0.831075000
9	1.534386000	3.876968000	1.928003000
8	1.476781000	-0.896945000	-0.791184000
8	-1.424349000	-0.615947000	-0.438305000
8	0.441197000	1.496972000	0.651986000
6	2.220775000	-1.824968000	-0.120025000
6	3.732110000	-1.636437000	-0.488894000
6	1.734398000	-3.263826000	-0.516216000
6	2.032932000	-1.614809000	1.428230000
6	-2.705749000	-0.874872000	-0.057178000
6	-2.873764000	-2.429127000	0.101641000
6	-3.035187000	-0.167585000	1.306437000
6	-3.672097000	-0.346534000	-1.176494000
6	0.624597000	2.710180000	0.048656000
6	-0.676805000	3.569772000	0.222133000
6	0.911030000	2.494224000	-1.484363000
6	1.848718000	3.431471000	0.709554000

$[Al(OC(CF_3)_3)_3F]^-$			
13	0.019480000	0.008607000	-0.950472000
9	0.249413000	0.256764000	-2.589599000
9	0.346584000	-4.143024000	-0.890313000
9	-1.537891000	-4.050059000	-1.940419000
9	-1.429494000	-4.984959000	0.015257000
9	-3.034073000	-1.779704000	-1.487670000
9	-3.575286000	-3.308967000	-0.050911000
9	-3.187141000	-1.283760000	0.610223000
9	0.252901000	-3.234578000	1.664028000
9	-1.856122000	-3.276516000	2.165638000
9	-0.819727000	-1.383184000	1.958109000
9	-3.758976000	1.615259000	-0.882288000
9	-3.590526000	1.706130000	1.269765000
9	-3.726010000	3.535786000	0.114531000
9	-1.051839000	1.752898000	2.259435000
9	-1.667207000	3.800559000	1.912575000
9	0.269335000	3.112686000	1.224383000
9	-1.334609000	4.595069000	-0.727817000
9	0.060678000	3.115999000	-1.472874000
9	-1.966135000	3.153840000	-2.220263000
9	2.474783000	-0.141990000	2.374473000
9	3.220149000	1.791539000	1.766933000
9	4.536877000	0.068299000	1.749795000
9	2.921195000	2.400975000	-0.873655000
9	4.824941000	1.395820000	-0.637552000
9	3.462487000	0.795686000	-2.213267000
9	4.588909000	-1.363712000	-0.613368000
9	2.622472000	-1.674873000	-1.467713000
9	2.978748000	-2.143631000	0.611302000
8	-0.490165000	-1.651642000	-0.708238000
8	-1.244898000	1.038868000	-0.298244000
8	1.481489000	0.318113000	-0.022663000
6	-1.257015000	-2.553524000	-0.081582000
6	-0.964965000	-3.959645000	-0.727770000
6	-2.791525000	-2.228550000	-0.253931000
6	-0.919774000	-2.615201000	1.454660000
6	-1.633521000	2.289705000	-0.001151000
6	-3.203598000	2.291730000	0.125208000
6	-1.012768000	2.749704000	1.373525000
6	-1.212086000	3.310875000	-1.121073000
6	2.817238000	0.182631000	0.025227000
6	3.274518000	0.475721000	1.503322000
6	3.521682000	1.211445000	-0.939917000
6	3.266052000	-1.273189000	-0.368077000

$Al(OC(CF_3)_3)_3 \cdot C_6H_5F$			
13	0.031531000	0.021550000	0.190890000
9	-0.147236000	-0.215708000	2.089045000
9	1.280121000	3.908072000	0.625800000
9	-0.770864000	4.396626000	1.089582000
9	0.130053000	5.129206000	-0.746020000
9	-2.641203000	2.645746000	0.196648000
9	-2.308565000	4.060544000	-1.410925000
9	-2.308138000	1.929202000	-1.814318000
9	1.668708000	2.903603000	-1.841785000
9	-0.122875000	3.359556000	-2.969049000
9	0.301472000	1.314749000	-2.369565000
9	-3.936553000	-0.858531000	-0.625258000
9	-3.161360000	-0.968818000	-2.639164000
9	-3.997888000	-2.737857000	-1.700649000
9	-0.492528000	-1.523006000	-2.825591000

9	-1.590967000	-3.392423000	-2.856694000
9	0.135526000	-3.162651000	-1.566703000
9	-2.180125000	-4.288230000	-0.270989000
9	-0.854210000	-3.087134000	0.955676000
9	-2.987086000	-2.766309000	1.045786000
9	3.266800000	-0.221984000	-2.022789000
9	3.454615000	-2.316100000	-1.529319000
9	4.989302000	-0.916955000	-0.903834000
9	2.308243000	-3.083193000	0.785603000
9	4.312193000	-2.454093000	1.314577000
9	2.604050000	-1.738639000	2.448662000
9	4.576793000	0.260976000	1.591766000
9	2.525351000	0.909617000	1.858529000
9	3.603376000	1.455813000	0.068254000
8	-0.151267000	1.731739000	0.201831000
8	-1.326966000	-0.833613000	-0.387617000
8	1.557422000	-0.685081000	-0.061455000
6	-0.405167000	2.778160000	-0.635143000
6	0.072925000	4.084960000	0.088047000
6	-1.948263000	2.866218000	-0.927064000
6	0.374782000	2.605826000	-1.987021000
6	-1.844071000	-1.976819000	-0.912089000
6	-3.268616000	-1.634064000	-1.482414000
6	-0.935196000	-2.532202000	-2.069488000
6	-1.975662000	-3.061443000	0.213944000
6	2.872565000	-0.822250000	0.252957000
6	3.669286000	-1.074389000	-1.078022000
6	3.039990000	-2.054263000	1.213986000
6	3.421582000	0.471870000	0.955244000
6	-1.182623000	0.067761000	3.046879000
6	-1.708796000	-1.017180000	3.701497000
6	-1.522522000	1.381769000	3.245602000
6	-2.689153000	-0.746290000	4.653314000
6	-2.506720000	1.621162000	4.203267000
6	-3.084707000	0.565100000	4.900992000
1	-1.376137000	-2.018707000	3.478698000
1	-1.056485000	2.174284000	2.682769000
1	-3.139165000	-1.565091000	5.195599000
1	-2.815510000	2.638173000	4.396531000
1	-3.846960000	0.764549000	5.640346000

$[Al(OC(CF_3)_3)_4]^-$

8	1.390838000	0.471468000	0.946478000
13	0.000000000	0.000000000	0.000000000
8	-1.390838000	-0.471468000	0.946478000
8	0.471468000	-1.390838000	-0.946478000
8	-0.471468000	1.390838000	-0.946478000
6	2.423863000	0.166265000	1.750039000
6	0.166265000	-2.423863000	-1.750039000
6	-2.423863000	-0.166265000	1.750039000
6	-0.166265000	2.423863000	-1.750039000
6	2.418786000	-1.347632000	2.184791000
6	2.337655000	1.066936000	3.039786000
6	3.774225000	0.472371000	1.001114000
6	0.472371000	-3.774225000	-1.001114000
6	1.066936000	-2.337655000	-3.039786000
6	-1.347632000	-2.418786000	-2.184791000
6	-2.337655000	-1.066936000	3.039786000
6	-3.774225000	-0.472371000	1.001114000
6	-2.418786000	1.347632000	2.184791000
6	-0.472371000	3.774225000	-1.001114000
6	-1.066936000	2.337655000	-3.039786000

6	1.347632000	2.418786000	-2.184791000
9	4.840616000	-0.077582000	1.617259000
9	3.992611000	1.795022000	0.928479000
9	3.735991000	0.000000000	-0.245464000
9	1.171118000	-1.746968000	2.446679000
9	3.161555000	-1.572790000	3.285716000
9	2.899454000	-2.132631000	1.210097000
9	1.392759000	0.606966000	3.874798000
9	2.015932000	2.320696000	2.717151000
9	3.498533000	1.107560000	3.724449000
9	2.320696000	-2.015932000	-2.717151000
9	0.606966000	-1.392759000	-3.874798000
9	1.107560000	-3.498533000	-3.724449000
9	0.000000000	-3.735991000	0.245464000
9	1.795022000	-3.992611000	-0.928479000
9	-0.077582000	-4.840616000	-1.617259000
9	-2.132631000	-2.899454000	-1.210097000
9	-1.572790000	-3.161555000	-3.285716000
9	-1.746968000	-1.171118000	-2.446679000
9	-3.498533000	-1.107560000	3.724449000
9	-1.392759000	-0.606966000	3.874798000
9	-2.015932000	-2.320696000	2.717151000
9	-4.840616000	0.077582000	1.617259000
9	-3.992611000	-1.795022000	0.928479000
9	-3.735991000	0.000000000	-0.245464000
9	-3.161555000	1.572790000	3.285716000
9	-2.899454000	2.132631000	1.210097000
9	-1.171118000	1.746968000	2.446679000
9	-2.320696000	2.015932000	-2.717151000
9	-0.606966000	1.392759000	-3.874798000
9	-1.107560000	3.498533000	-3.724449000
9	2.132631000	2.899454000	-1.210097000
9	1.572790000	3.161555000	-3.285716000
9	1.746968000	1.171118000	-2.446679000
9	-1.795022000	3.992611000	-0.928479000
9	0.077582000	4.840616000	-1.617259000
9	0.000000000	3.735991000	0.245464000

$Al(OCAr^{F}{}_{3})_{3}$

13	-0.122957000	-0.027929000	-0.035400000
9	-0.587785000	0.409189000	2.041389000
9	-0.714362000	0.707672000	4.627855000
9	-2.735870000	2.102156000	5.815761000
9	-4.691361000	3.196662000	4.263610000
9	-4.643417000	2.898946000	1.620498000
9	-0.650480000	3.611674000	0.692659000
9	-0.718990000	6.144339000	-0.085090000
9	-2.815567000	7.090278000	-1.549542000
9	-4.867535000	5.412938000	-2.181728000
9	-4.859578000	2.905253000	-1.407794000
9	-2.752028000	1.171057000	-2.647417000
9	-4.431777000	-0.482567000	-3.872112000
9	-6.320218000	-1.838895000	-2.451331000
9	-6.430682000	-1.538526000	0.254631000
9	-4.721219000	-0.005631000	1.523895000
9	-0.262062000	-0.766411000	-2.029118000
9	-0.920843000	-1.099683000	-4.533419000
9	-1.504057000	-3.564863000	-5.547082000
9	-1.376625000	-5.740658000	-3.913497000
9	-0.680924000	-5.483902000	-1.366291000
9	0.868372000	-2.492034000	2.562767000
9	3.391028000	-2.814810000	3.305338000

9	5.237909000	-3.795632000	1.557276000
9	4.477095000	-4.421498000	-0.983222000
9	1.993599000	-4.103216000	-1.773933000
9	-2.987197000	-2.585121000	-0.020398000
9	-4.764941000	-3.937120000	1.408467000
9	-3.984461000	-6.038488000	2.965264000
9	-1.355906000	-6.748592000	3.028668000
9	0.440809000	-5.441664000	1.624400000
9	3.529763000	3.866404000	1.078809000
9	2.998957000	6.176236000	-0.049692000
9	1.581834000	6.318649000	-2.372848000
9	0.683914000	4.023270000	-3.534468000
9	1.216319000	1.664557000	-2.453691000
9	1.358619000	2.477208000	2.080856000
9	2.027370000	2.321405000	4.643695000
9	4.190109000	0.850699000	5.424552000
9	5.651331000	-0.472751000	3.542295000
9	5.003798000	-0.378285000	1.001738000
9	2.418585000	-1.138915000	-2.004770000
9	4.233821000	-1.762819000	-3.774338000
9	6.586892000	-0.398889000	-3.941279000
9	7.056270000	1.666939000	-2.218012000
9	5.239066000	2.338555000	-0.396266000
8	-1.324587000	1.154995000	-0.326393000
8	-0.486846000	-1.652482000	0.391811000
8	1.519228000	0.398013000	-0.094247000
6	-2.560922000	1.613722000	0.116110000
6	-2.614367000	1.681340000	1.670461000
6	-1.651359000	1.136361000	2.509258000
6	-1.672616000	1.263252000	3.890502000
6	-2.697146000	1.969213000	4.495460000
6	-3.686741000	2.529357000	3.701211000
6	-3.633224000	2.375354000	2.327286000
6	-2.706709000	3.091615000	-0.379559000
6	-1.692316000	3.996499000	-0.055899000
6	-1.714749000	5.327637000	-0.438363000
6	-2.781885000	5.816065000	-1.174078000
6	-3.818929000	4.959199000	-1.494851000
6	-3.778857000	3.630605000	-1.090535000
6	-3.638307000	0.679287000	-0.498448000
6	-3.616382000	0.489908000	-1.885725000
6	-4.497532000	-0.346520000	-2.546014000
6	-5.467107000	-1.030877000	-1.827981000
6	-5.523010000	-0.871767000	-0.457346000
6	-4.611670000	-0.042039000	0.186334000
6	-0.191790000	-2.953323000	-0.009456000
6	-0.499926000	-3.124400000	-1.525266000
6	-0.558461000	-2.054412000	-2.409935000
6	-0.889672000	-2.173157000	-3.750355000
6	-1.182664000	-3.424069000	-4.267290000
6	-1.122150000	-4.527280000	-3.430301000
6	-0.778907000	-4.366192000	-2.097645000
6	1.293645000	-3.237061000	0.343371000
6	1.730873000	-2.931377000	1.637099000
6	3.037384000	-3.112302000	2.052670000
6	3.979537000	-3.619027000	1.170762000
6	3.586844000	-3.938080000	-0.115308000
6	2.267118000	-3.750644000	-0.509708000
6	-1.164867000	-3.875308000	0.791624000
6	-2.527716000	-3.575350000	0.760022000
6	-3.478086000	-4.279765000	1.480135000
6	-3.086446000	-5.351115000	2.266447000

6	-1.749325000	-5.704314000	2.299127000
6	-0.817120000	-4.982303000	1.564578000
6	2.662244000	1.183116000	-0.076537000
6	2.351379000	2.628370000	-0.594700000
6	2.804279000	3.828585000	-0.045588000
6	2.548220000	5.063160000	-0.628031000
6	1.829059000	5.141627000	-1.806516000
6	1.370547000	3.972361000	-2.390915000
6	1.641071000	2.752756000	-1.793362000
6	3.176094000	1.120636000	1.389433000
6	2.437363000	1.745507000	2.396689000
6	2.762806000	1.674249000	3.738498000
6	3.863047000	0.932122000	4.138991000
6	4.604795000	0.268240000	3.180141000
6	4.249190000	0.353289000	1.838503000
6	3.722112000	0.663254000	-1.102472000
6	3.529434000	-0.390865000	-1.992812000
6	4.481408000	-0.748970000	-2.943066000
6	5.675511000	-0.059553000	-3.034694000
6	5.907772000	0.992418000	-2.162107000
6	4.943873000	1.329438000	-1.230343000

$[FAl(OCAr^{F}{}_{3})_{3}]^{-}$

13	0.000000000	0.000000000	0.343885000
9	0.000000000	0.000000000	2.043162000
9	-2.579777000	-1.374415000	2.543478000
9	0.389563000	-1.544881000	-2.637936000
9	1.296789000	-2.188682000	4.827374000
9	0.099610000	2.921359000	2.543478000
9	-0.793930000	3.278896000	-1.945328000
9	2.480166000	-1.546945000	2.543478000
9	-5.201879000	-1.164498000	1.762221000
9	1.592455000	5.087208000	1.762221000
9	4.029006000	1.592279000	0.210857000
9	-0.635549000	-4.285361000	0.210857000
9	-6.335314000	-3.530026000	1.621502000
9	1.143124000	1.109812000	-2.637936000
9	-2.442642000	-2.327012000	-1.945328000
9	1.247060000	2.217393000	4.827374000
9	-1.532687000	0.435069000	-2.637936000
9	-1.860696000	7.493190000	-0.246797000
9	-2.279849000	5.460172000	-2.017050000
9	5.125893000	0.905537000	2.499664000
9	3.236572000	-0.951884000	-1.945328000
9	3.781200000	1.204634000	4.853933000
9	0.110565000	7.251556000	1.621502000
9	-0.847356000	-3.876932000	4.853933000
9	0.719497000	-5.754201000	-4.601851000
9	6.224750000	-3.721530000	1.621502000
9	2.265174000	-5.183666000	-0.219145000
9	4.623536000	3.500203000	-4.601851000
9	3.356599000	4.553532000	-0.219145000
9	-2.712341000	1.565971000	-4.685807000
9	-1.778728000	-4.891923000	2.499664000
9	0.000000000	-3.131941000	-4.685807000
9	-2.543849000	-0.028711000	4.827374000
9	3.609424000	-3.922710000	1.762221000
9	-3.588724000	-4.704493000	-2.017050000
9	1.865002000	-6.759397000	-2.333158000
9	2.712341000	1.565971000	-4.685807000
9	5.868572000	-0.755679000	-2.017050000
9	-5.558945000	-5.358005000	-0.246797000

9	-5.621774000	0.630135000	-0.219145000
9	-3.393457000	2.693082000	0.210857000
9	4.921309000	4.994838000	-2.333158000
9	7.419641000	-2.135185000	-0.246797000
9	-2.933844000	2.672298000	4.853933000
9	-5.343032000	2.253998000	-4.601851000
9	-6.786311000	1.764560000	-2.333158000
9	-3.347165000	3.986385000	2.499664000
8	-1.575052000	-0.537938000	-0.215674000
8	0.321658000	1.633004000	-0.215674000
8	1.253394000	-1.095066000	-0.215674000
6	-0.562690000	4.195951000	-1.001693000
6	-4.732686000	-1.991826000	0.816994000
6	1.040537000	-2.929305000	1.256524000
6	2.016584000	2.365784000	1.256524000
6	1.355074000	2.457696000	2.484014000
6	0.435169000	4.010540000	-0.036626000
6	-2.910472000	-0.259734000	-0.056076000
6	3.293958000	1.811169000	1.315736000
6	1.349814000	-3.283534000	-1.300108000
6	-0.245145000	-3.570083000	3.703727000
6	-1.337179000	5.344052000	-1.074837000
6	0.770697000	-2.805090000	-2.477058000
6	-3.518531000	0.472794000	-1.300108000
6	1.929938000	2.089672000	3.686108000
6	1.230300000	2.650409000	-0.056076000
6	0.844740000	-2.716211000	3.686108000
6	-3.959496000	-3.830058000	-1.074837000
6	-0.708994000	-4.085822000	2.509114000
6	-0.121542000	6.254133000	0.759173000
6	-0.078461000	-3.758236000	1.315736000
6	2.043931000	2.069988000	-2.477058000
6	-3.352455000	-2.585279000	-1.001693000
6	0.641371000	5.094540000	0.816994000
6	1.450890000	-2.402377000	2.484014000
6	-1.122781000	6.381829000	-0.184865000
6	3.255645000	-2.382138000	-0.036626000
6	2.866629000	2.299498000	-3.579154000
6	-3.690814000	-1.628403000	-0.036626000
6	-2.805964000	-0.055319000	2.484014000
6	-4.965436000	-4.163271000	-0.184865000
6	-5.355467000	-3.232325000	0.759173000
6	3.892923000	1.428905000	2.509114000
6	3.156786000	3.796678000	-1.313369000
6	4.091315000	-3.102713000	0.816994000
6	3.982844000	4.040575000	-2.393979000
6	3.214355000	1.572740000	3.703727000
6	1.680172000	-2.390676000	-0.056076000
6	6.088217000	-2.218558000	-0.184865000
6	3.915145000	-1.610672000	-1.001693000
6	-4.866413000	0.835518000	-1.313369000
6	5.296675000	-1.513995000	-1.074837000
6	1.507818000	-5.469532000	-2.393979000
6	-2.814628000	0.735102000	-2.477058000
6	0.923161000	-4.963938000	-3.543937000
6	-2.774678000	0.626539000	3.686108000
6	-4.760477000	1.682488000	-3.543937000
6	-3.424738000	1.332825000	-3.579154000
6	-5.490663000	1.428957000	-2.393979000
6	-3.215497000	1.947067000	1.315736000
6	-2.969210000	1.997343000	3.703727000
6	-3.057121000	0.563521000	1.256524000

6	0.558109000	-3.632323000	-3.579154000
6	1.709626000	-4.632196000	-1.313369000
6	2.168717000	2.810740000	-1.300108000
6	-3.183929000	2.656918000	2.509114000
6	3.837316000	3.281450000	-3.543937000
6	5.477009000	-3.021808000	0.759173000

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