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Supporting Information

Synthesis and Characterization of Stable Iron Pentacarbonyl Radical Cation Salts

*J. M. Rall, M. Schorpp, M. Keilwerth, M. Mayländer, C. Friedmann, M. Daub, S. Richert, K. Meyer, I. Krossing**

Electronic Supporting Information

to

Synthesis and Characterization of a Stable Iron Pentacarbonyl Radical Cation Salt

by

Jan M. Rall, Marcel Schorpp, Martin Keilwerth, Maximilian Mayländer, Christian Friedmann, Michael Daub, Sabine Richert, Karsten Meyer, Ingo Krossing*

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1 General Synthetic Methods and Characterization Techniques

General Synthetic Methods

Unless stated otherwise, all manipulations were performed under an inert argon atmosphere, using standard Schlenk line and glovebox techniques. All glassware was dried overnight in an oven set to 180 °C and flame-dried under vacuum prior to use. CH_2Cl_2 and *n*-pentane were collected using a solvent purification system and stored over activated 3.0 Å molecular sieves.[1] 1,2-difluorobenzene (*o*DFB) (Fluorochem) and 1,2,3,4-tetrafluorobenzene (4FB) (Fluorochem) were refluxed over CaH_2 and distilled and stored over activated 3.0 Å molecular sieves. Traces of less fluorinated benzenes were removed by stirring 4FB over $Ag[Al(OR^F)_4]$ for 24 h at room temperature. Due to this procedure, 4FB gets contaminated by traces of $HOC(CF_3)_3$ (<1%). $NO[Al(OR^F)_4]$[2] {R^F = $C(CF_3)_3$}, $Ag[Al(OR^F)_4]$[3], $NO[F\text{-}\{Al(OR^F)_3\}_2]$[4] and $LiN(C_6F_5)_2$[5] were synthesized according to their literature procedures.

Single Crystal X-ray Diffraction

Single crystal X-ray diffraction data was collected using a D8 Venture Photon III HPAD (Bruker) detector diffractometer. The crystals were selected under perfluoropolyether oil, mounted on 0.1 to 0.3 mm diameter CryoLoops and quench-cooled using an open flow N_2 cooling device (Oxford Cryosystems).[6] The data was collected at 100 K using monochromated Mo Kα radiation (λ = 0.71073 Å). Data processing was done with SHELXs/XL and refined by least squares on weighted F_2 values for all reflections. Disordering of fragments was done with the help of the implemented DSR tool.[7,8] Graphical representations have been prepared using Mercury 3.7 (crystal packing) and Olex2-1.3.

Powder Diffraction

Powder diffractograms were recorded with the sample sealed by perfluoropolyalkylether oil (AB128330, abcr GMBH & Co. KG) in a 0.3 mm thick capillary (Hilgenberg GmbH, wall thickness 0.01 mm) at 100 K in the 2θ range 2.0-40.0° with a STOE STADI P powder diffractometer using Mo Kα radiation (λ = 0.709300 Å), equipped with a Ge(111) monochromator and Mythen 1K detector. Data acquisition, processing and the calculation of powder diffractograms from single crystal data were performed using the STOE WinXPOW package. To ensure the crystalline phase purity of the sample, a Rietveld refinement was performed using the GSAS-II[9] software. The structural model

on which the refinement is based was taken from the single crystal study and was not further refined. Successively, background, profile and cell parameters were refined. The graphical representation was done using OriginPro (2020).

IR Spectroscopy

ATR FT-IR spectra of solid samples were recorded at ambient temperature on a ZnSe crystal on a FT-IR Bruker ALPHA with a QuickSnap Platinum ATR sampling module inside an inert atmosphere glovebox. The spectra were recorded in a range from 4000-400 cm^{-1}, with 64 scans and a resolution of 2 cm^{-1}. ATR FT-IR spectra of solutions were recorded in a range from 4000-400 cm^{-1}, with 16 scans and a resolution of 2 cm^{-1}. Data processing was carried out with the software package OPUS 7.5. All signal intensities were normalized and the relative band intensities described as followed: $\geq$ 0.8 = very strong (vs), $\geq$ 0.6 = strong (s), $\geq$ 0.5 medium (m), $\geq$ 0.3 = medium weak (mw), $\geq$ 0.2 = weak (w), $\geq$ 0.1 = very weak (vw). The graphical representation was done using OriginPro (2020).

EPR

The continuous wave (cw) EPR spectrum of solid $[Fe(CO)_5]^{\bullet+}$ was recorded at the X-band (9.75 GHz) on a Bruker EMXnano benchtop EPR spectrometer at 100 K. The modulation frequency was set to 100 kHz and the modulation amplitude to 0.2 mT at a microwave power of 4 mW (14 dB). For a better resolution of the **g**-tensor an additional cw EPR spectrum was measured at the Q-band (34 GHz) on a Bruker ELEXSYS E580 spectrometer with an EN5107D2 resonator at 100 K. The modulation frequency was set to 50 kHz and the modulation amplitude to 0.2 mT at a microwave power of 0.1 mW (20 dB). After data acquisition, the spectra were baseline-corrected, frequency-corrected to 9.75 GHz/34 GHz and field-corrected using a carbon fiber standard with g = 2.002644.[10] The global numerical simulation of the experimental spectra was done using EasySpin functions in MATLAB.[11]

Additional EPR spectra in solution were recorded on a JOEL continuous wave spectrometer JES-FA200, equipped with an X-band Gunn diode oscillator bridge, a cylindric mode cavity, and a helium cryostat. The samples were measured under nitrogen atmosphere in quartz glass EPR tubes at 95 K. The EPR spectra were recorded at the X-band (8.95 GHz). The modulation amplitude was set to 0.7 mT at a microwave power of 1.0 mW.

NMR

NMR samples were prepared under inert atmosphere in NMR tubes equipped with a gas-tight J. Young valve. ^{1}H-, ^{13}C-, ^{19}F-, ^{27}Al-NMR spectra were acquired either on a Bruker Biospin Avance II+ 400 MHz WB, a Bruker Avance 200 MHz or a Bruker Avance III HD 300 MHz spectrometer. NMR spectra were reported relative to TMS and calibrated to residual solvent resonances.[12] The data analysis and graphical representation was performed using the Bruker TOPSPIN 3.2 software.

Cyclovoltammetry

For the collection of cyclovoltammetry (CV) measurements a three-electrode setup was used, consisting of a Pt disk working electrode, a Pt net as counter electrode and a Pt wire in a separated Fc/Fc^{+}-solution, to a concentration of 10 mM of each compound, as reference electrode. Blank measurements were collected with a 100 mM solution of conducting salt $[NBu_4][Al(OR^F)_4]$ in 4FB. After that, the analyte was added to a concentration of 10 mM. For both measurements different scan rates of 20, 50 and 100 mVs^{-1} were used. The graphical representation was done using OriginPro (2020).

Mössbauer

Zero-field ^{57}Fe-Mössbauer spectra were recorded on a WissEl Mössbauer spectrometer (MRG-500) at a temperature of 77 K in constant acceleration mode. ^{57}Co/Rh was used as the γ-radiation source. WinNormos for Igor Pro software was used for the quantitative evaluation of the spectral parameters (least squares fitting to Lorentzian peaks). The minimum experimental line widths were 0.21 mms^{-1} (full width at half maximum, FWHM). The temperature of the sample was controlled by a MBBC-HE0106 MOESSBAUER He/N2 cryostat within an accuracy of +/- 0.3 K. Least-square fitting of the Lorentzian signals was carried out with the "Mfit" software, developed by Dr. Eckhard Bill (MPI CEC, Mülheim/Ruhr). The isomer shifts were reported relative to α-iron reference at 300 K.

SQUID

Magnetism data of microcrystalline and powdered samples (10.0-25.0 mg), loaded within polycarbonate gel capsules, were collected on a Quantum Design MPMS-3 SQUID magnetometer. The DC susceptibility was recorded in the temperature range of 2-300 K with an applied DC field of 1 T,

unless stated otherwise. Values of the magnetic susceptibility were corrected for the core diamagnetism of the sample using tabulated Pascal's constants.[13] For simulation and analysis of the data, the program "JUlX2" written by Dr. Eckhard Bill (MPI CEC, Mülheim/Ruhr) was used.

Evans NMR Method

NMR samples were prepared under inert atmosphere in NMR tubes equipped with a gas-tight J. Young valve. **1** was weighted into an NMR tube (4.2 mg, 8.5 mg, 16.1 mg and 31.7 mg) and a stock solution of TMS in 4FB (0.03 M) was added (706.3 mg, 719.8 mg, 711.3 mg, 701.2 mg). A sealed capillary of the stock solution was added to the NMR tube. The ^{1}H-NMR spectra were acquired on a Bruker Avance II Widebore 400 MHz spectrometer. Data analysis was performed using the Bruker TOPSPIN 3.2 software. Further data analysis and graphical representation was done using OriginPro (2020).

Computational Details

The quantum chemical calculations were carried out with the TURBOMOLE software[14,15] using BP86[16,17] or B3LYP[18–20] functionals with def2-TZVPP[21] basis sets, in combination with the D3BJ[22,23] dispersion correction. A fine integration grid (m4) and the default SCF convergence criteria (10^{-7} a.u) were used. All frequency calculations (if applicable via the module AOFORCE[24], otherwise via the module NUMFORCE) were simulated without scaling factor and a FWHM of 10 cm^{-1}. All calculated structures were checked for consistency in terms of geometric conversion, sensible electron occupations and the absence of imaginary vibrational frequencies.

Single point calculations were done at the B3LYP/EPR-II(CP(PPP for Fe)[25–27] level of theory of the cation $[Fe(CO)_5]^{\bullet+}$ based on a cutout from the obtained scXRD structure of $[Fe(CO)_5]^{\bullet+}[Al(OR^F)_4]^-$ (**1**) using ORCA[28,29] to obtain the g-tensor.

2 Experimental Procedures

2.1 Synthesis and Oxidation of Phenazine^{F}

Synthesis of Phenazine^{F}

A 250 mL Schlenk tube was charged with $LiN(C_6F_5)_2$ (7.1 g, 19.9 mmol) and under slow stirring and dynamic vacuum heated to 180 °C. The temperature was increased to 200 °C and the tap to the vacuum manifold was closed. After 10-60 min, the reaction proceeded instantaneous forming a white and black precipitate in the entire Schlenk tube. The residue was taken up in a mixture of Et_2O (100 mL) and THF (50 mL). The organic layer was washed with HCl (10%, 30 mL) and the aqueous layer was extracted with Et_2O (3 x 30 mL). The combined organic layers were washed with H_2O (30 mL) and brine (30 mL), then dried over $MgSO_4$. The solvent was removed under reduced pressure yielding a sticky dark brown residue. The residue was suspended in MeCN (2 pipettes) and washed with Et_2O (2 pipettes) yielding off-white phenazine^{F} (0.7 g, 9.99 mmol, 11%).

^{19}F-NMR: (282.45 MHz, $CDCl_3$, 298 K) δ = –141.5 (m, 4F), –150.4 (m, 4F), –154.3 (m, 2F), –160.3 (m, 4F), –161.2 (m, 4F) ppm.

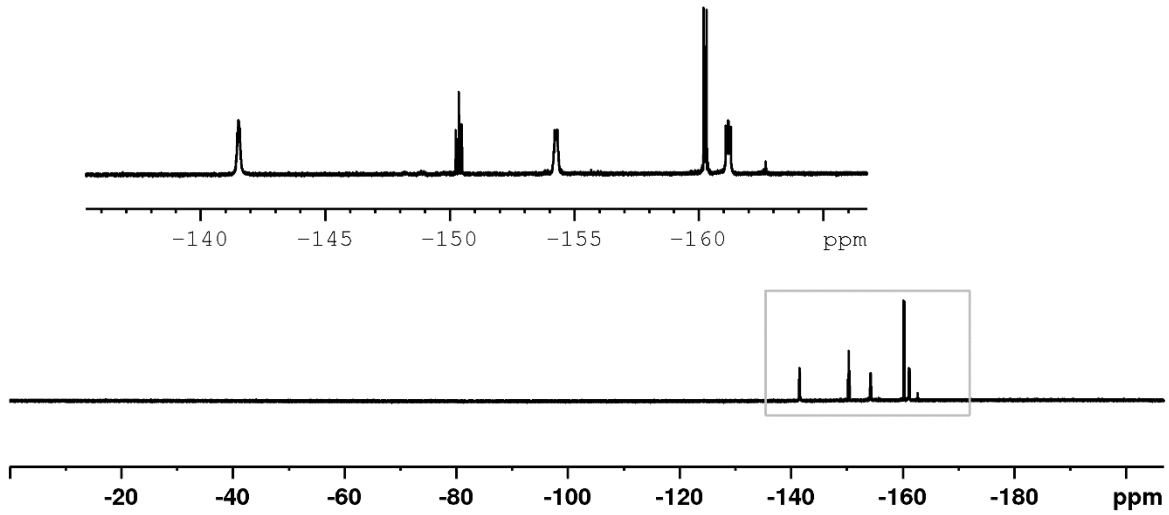

Figure S1: ^{19}F-NMR (188.31 MHz, $CDCl_3$, 298 K) spectrum of phenazine^{F}.

Synthesis of [Phenazine^{F}][Al(OR^{F})$_4$] using Ag[Al(OR^{F})$_4$]

Phenazine^{F} (900 mg, 1.37 mmol) and Ag[Al(OR^{F})$_4$] (1.47 g, 1.37 mmol, 1.00 eq.) were weighted into an H-cell equipped with a G4 frit. A mixture of SO_2/Br_2 was condensed onto the solids at –78 °C (ensuring an excess of Br_2). The purple reaction mixture was stirred at ambient temperature for 18 h. The SO_2/Br_2 mixture was condensed into the empty arm of the H-cell to allow for complete precipitation of AgBr and poured back onto the crude mixture. The suspension was filtered by the internal frit and extracted three times by back condensing the SO_2/Br_2 mixture. The SO_2/Br_2 mixture was removed and the product dried under reduced pressure yielding dark purple [Phenazine^{F}][Al(OR^{F})$_4$] (2.07 g, 1.27 mmol, 93%).

Synthesis of [Phenazine^{F}][Al(OR^{F})$_4$] using NO[Al(OR^{F})$_4$]

Phenazine^{F} (500 mg, 0.76 mmol) and NO[Al(OR^{F})$_4$] (758 mg, 0.76 mmol, 1.00 eq.) were weighted into a Schlenk tube. CH_2Cl_2 (20 mL) was added to the solids. The reaction mixture was stirred at ambient temperature for 18 h. Neutral NO gas was removed through three cycles by the freeze pump thaw method. The solvent was removed under reduced pressure yielding dark purple [Phenazine^{F}][Al(OR^{F})$_4$] (1150 mg, 0.71 mmol, 93%).

^{19}F-NMR: (188.31 MHz, 4FB, 298 K) δ = –76.5 (s, 36F, [Al{OC(C*F*$_3$)$_3$}$_4$]$^-$) ppm.

^{27}Al-NMR: (78.22 MHz, 4FB, 298 K): δ = 34.4 (s, 1Al, [*Al*(OR^{F})$_4$]$^-$) ppm.

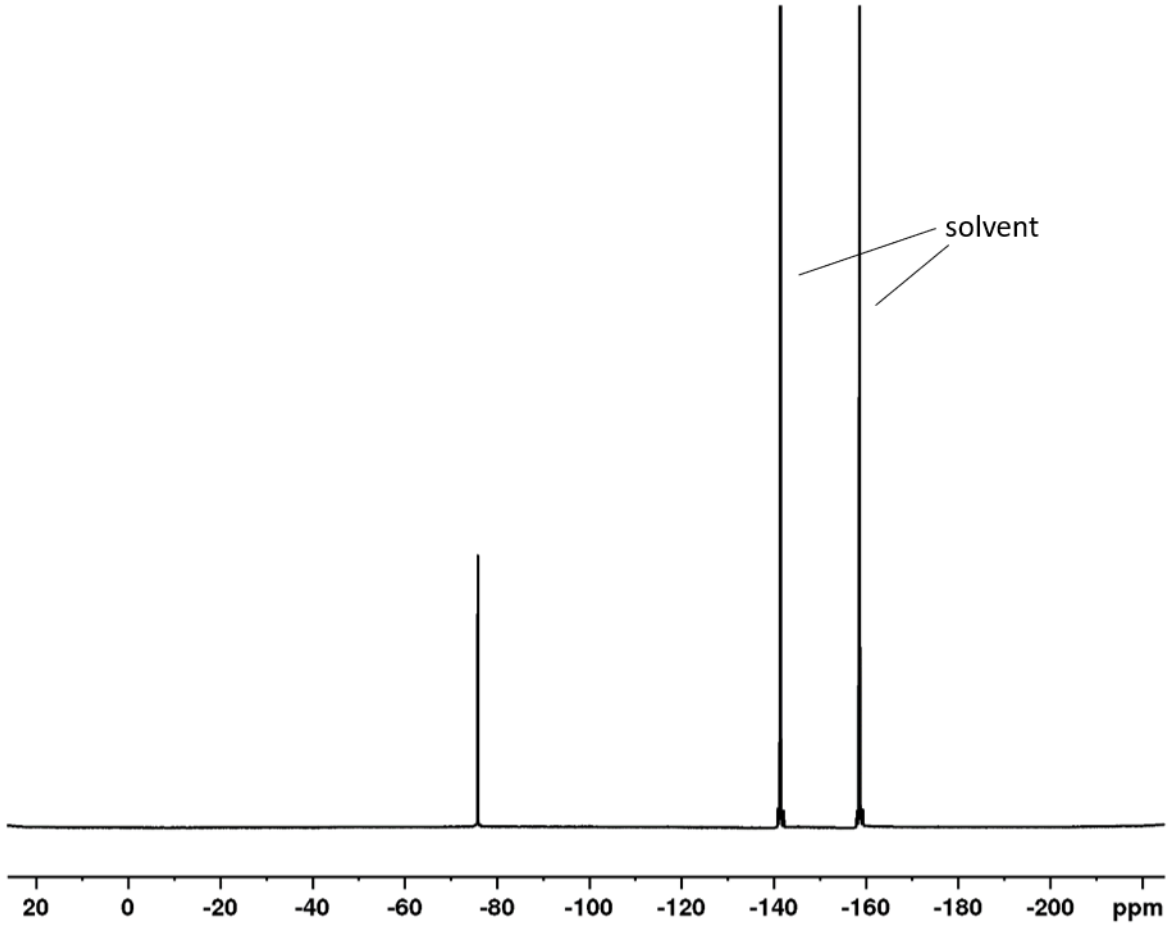

Figure S2: ^{19}F-NMR (188.31 MHz, 4FB, 298 K) spectrum of [phenazine^{F}][Al(OR^{F})$_4$] using [NO][Al(OR^{F})$_4$].

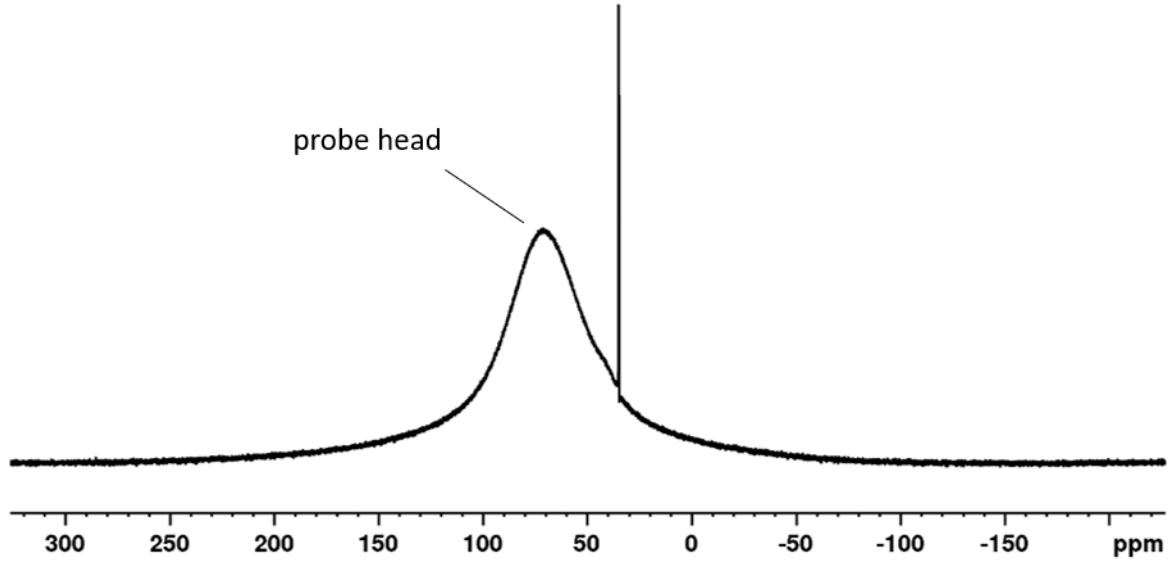

Figure S3: ^{27}Al-NMR (78.22 MHz, 4FB, 298 K) spectrum of [phenazine^{F}][Al(OR^{F})$_4$] using [NO][Al(OR^{F})$_4$].

Synthesis of [Phenazine^{F}][F-{Al(OR^{F})$_3$}$_2$] using NO[F-{Al(OR^{F})$_3$}$_2$]

Phenazine^{F} (150 mg, 0.23 mmol) and NO[F-{Al(OR^{F})^3}$_2$] (344 mg, 0.23 mmol, 1.00 eq.) were weighted into a Schlenk tube. CH_2Cl_2 (10 mL) was added to the solids. The reaction mixture was stirred at ambient temperature for 18 h. Neutral NO gas was removed through three cycles by the freeze pump thaw method. The solvent was removed under reduced pressure yielding dark purple [Phenazine^{F}][F-{Al(OR^{F})^3}$_2$] (396 mg, 0.18 mmol, 81%). Crystals suitable for scXRD analysis were grown by layering a solution of [Phenazine^{F}][F-{Al(OR^{F})$_3$}$_2$] in *o*DFB with *n*-pentane.

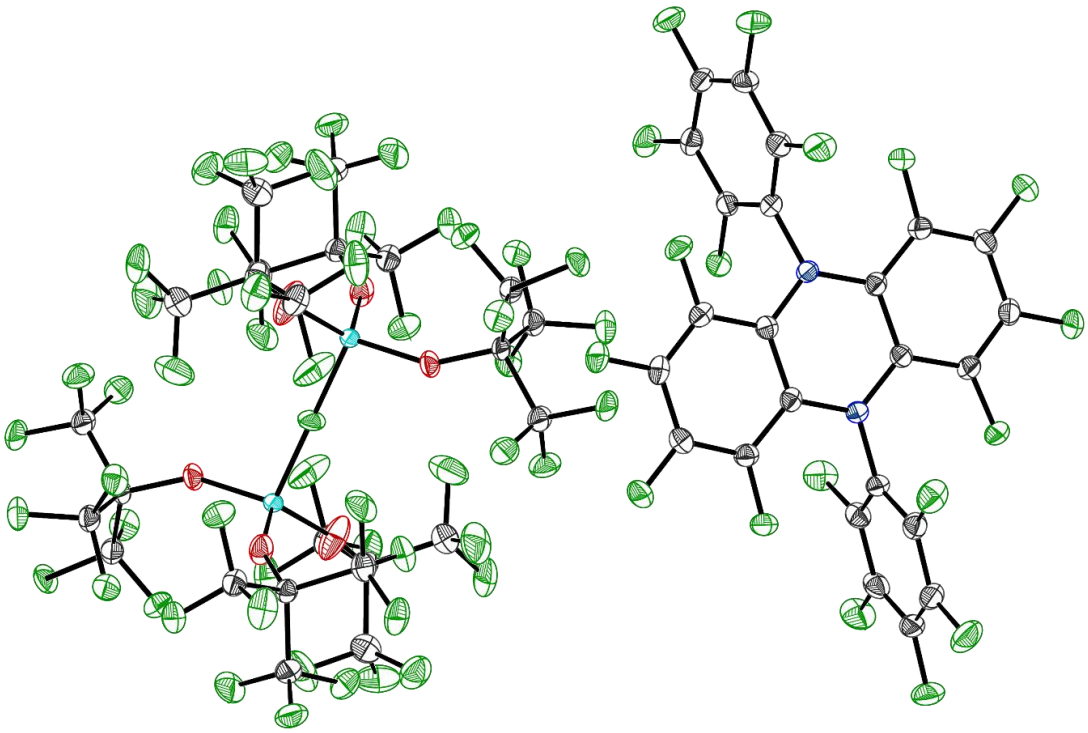

Figure S4: Molecular structure of [Phenazine^{F}][F-{Al(OR^{F})$_3$}$_2$]. Thermal displacement ellipsoids set at 50% probability.

2.2 Deelectronation of $Fe(CO)_5$

Synthesis of $[Fe(CO)_5oDFB][Al(OR^F)_4]$ in 1,2-Difluorobenzene using impure $[Phenazine^F][Al(OR^F)_4]$ from Ag^+/Br_2 Route

$[Phenazine^F][Al(OR^F)_4]$ (150 mg, 0.09 mmol) was weighted into a Schlenk tube. *o*DFB (2 mL) was added, resulting in a deep purple solution. A stock solution of $Fe(CO)_5$ in *o*DFB (2 mL, 0.09 mmol, 1.00 eq.) was added, which resulted in the reaction mixture turning instantaneously dark green. The reaction mixture was stirred at ambient temperature for 1.5 h. Green crystals of $[Fe(CO)_5oDFB][Al(OR^F)_4]$ and red crystals of minor by-product $[Fe_2(CO)_8Br][F\text{-}\{Al(OR^F)_3\}_2]$ were obtain by layering the reaction mixture with *n*-pentane (18.1 mg, 0.01 mmol, 15%). These crystals were suitable for scXRD.

ATR-FT-IR (ZnSe): 2128 (vw), 2116 (w), 2110 (w), 2083 (vw), 1506 (vw), 1352 (vw), 1297 (vw), 1263 (vw), 1239 (s), 1209 (vs), 1176 (w), 1153 (w), 968 (vs), 832 (vw), 759 (vw), 726 (s), 576 (vw), 560 (vw) cm^{-1}.

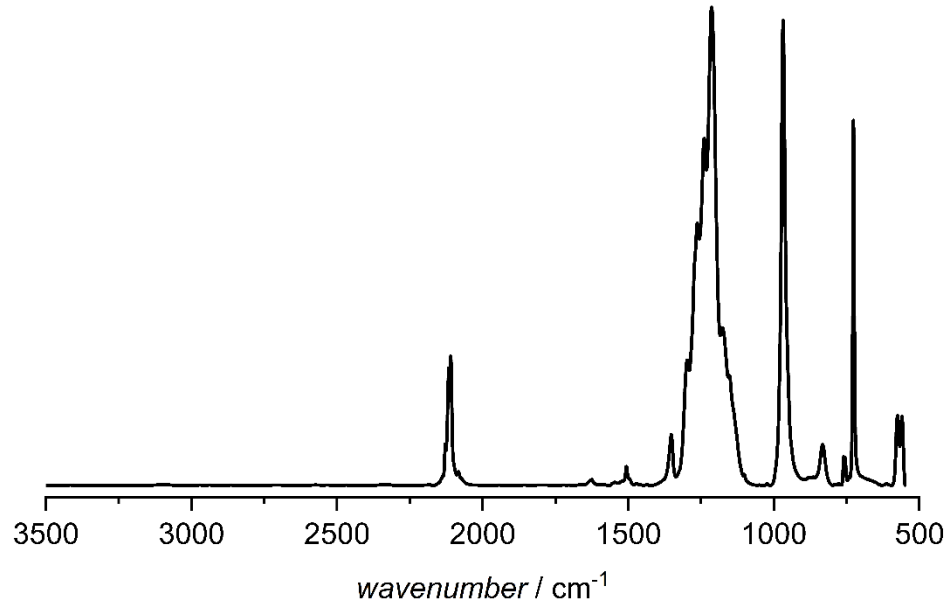

Figure S5: Full experimental ZnSe-ATR-FT-IR spectrum of solid $[Fe(CO)_5oDFB][Al(OR^F)_4]$.

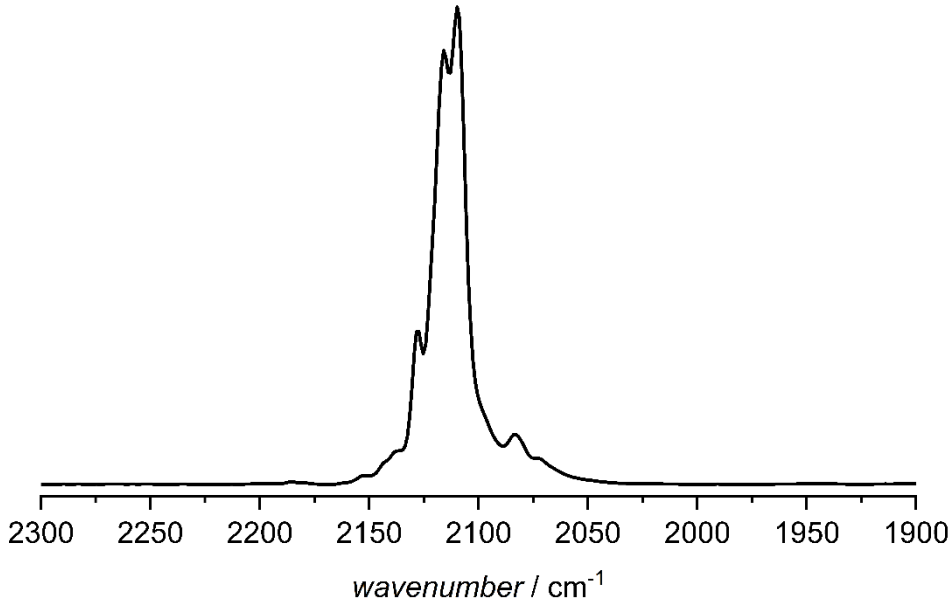

Figure S6: The carbonyl region of experimental ZnSe-ATR-FT-IR spectrum of solid $[Fe(CO)_5$*o*DFB$][Al(OR^F)_4]$.

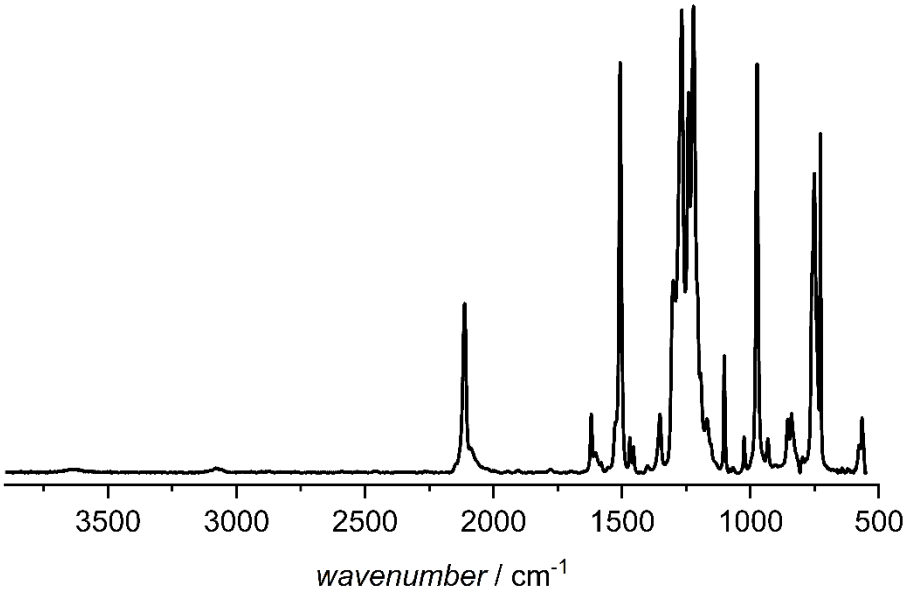

Figure S7: Full experimental ZnSe-ATR-FT-IR spectrum of $[Fe(CO)_5$*o*DFB$][Al(OR^F)_4]$ in *o*DFB.

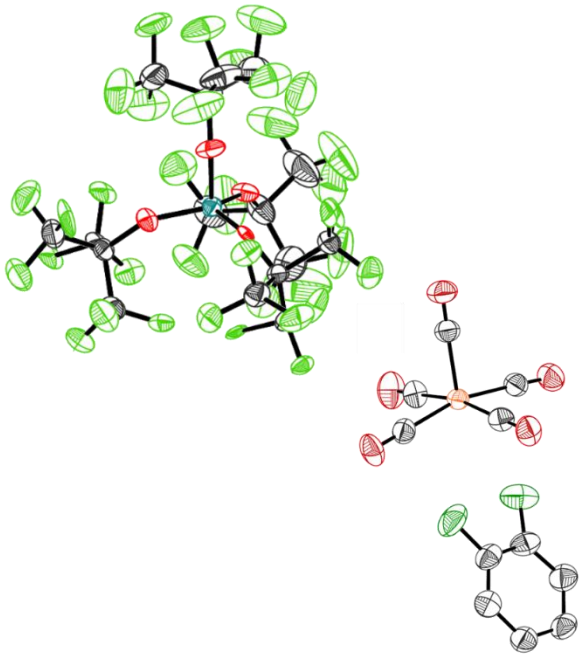

Figure S8: Molecular structure of $[Fe(CO)_5oDFB][Al(OR^F)_4]$. Protons omitted for clarity. Thermal displacement ellipsoids were set at 50% probability.

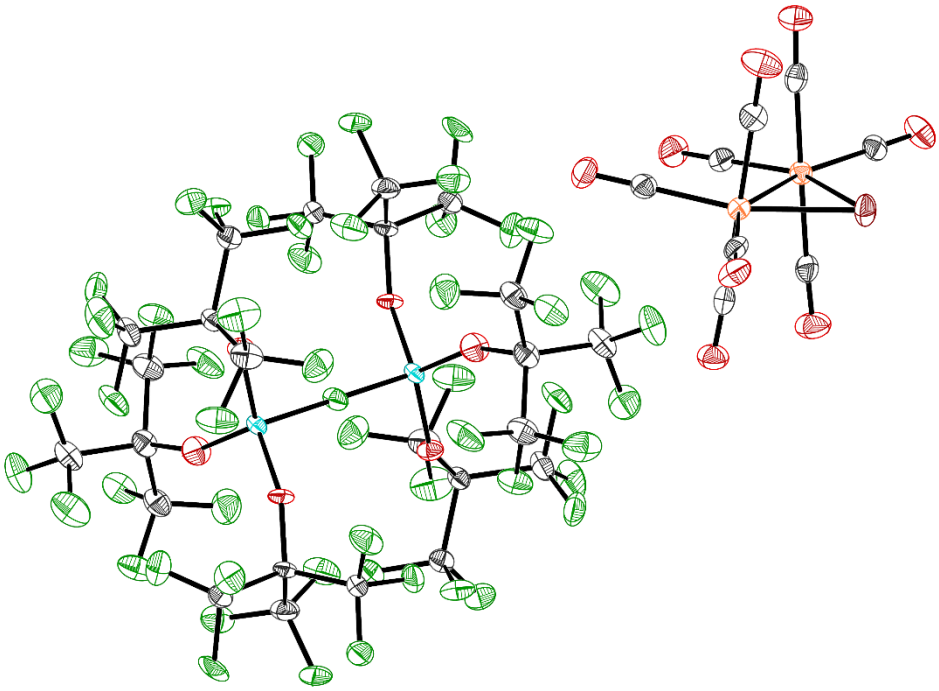

Figure S9: Molecular structure of minor by-product $[Fe_2(CO)_8Br][F\text{-}\{Al(OR^F)_3\}_2]$. Thermal displacement ellipsoids were set at 50% probability.

Synthesis of $[Fe(CO)_5][Al(OR^F)_4]$ in 1,2,3,4-Tetrafluorobenzene using pristine $[Phenazine^F][Al(OR^F)_4]$ from NO-Route

$[Phenazine^F][Al(OR^F)_4]$ (400 mg, 0.25 mmol) was weighted into a Schlenk tube. A stock solution of $Fe(CO)_5$ in 1,2,3,4-tetrafluorobenzene (2.46 mL, 0.25 mmol, 1.00 eq.) was added, after which the reaction mixture instantaneously turned dark green. The reaction mixture was stirred at ambient temperature for 1.5 h. The solution was layered with *n*-pentane and $[Fe(CO)_5][Al(OR^F)_4]$ (**1**) was obtained as dark green crystals suitable for scXRD (200 mg, 0.17 mmol, 70%).

^{13}C-NMR (75.48 MHz, 4FB, 298 K): δ = 120 (q, ^1J(C,F) = 291 Hz, 12C, $[Al\{OC(CF_3)_3\}_4]^-$) ppm.

^{19}F-NMR (282.45 MHz, 4FB, 298 K): δ = –75.3 (s, 36F, $[Al\{OC(CF_3)_3\}_4]^-$) ppm.

^{27}Al-NMR (78.22 MHz, 4FB, 298 K): δ = –34.7 (s, 1Al, $[Al\{OC(CF_3)_3\}_4]^-$) ppm.

ATR-FT-IR (ZnSe): 2128 (w), 2113 (s), 2082 (vw), 1352 (vw), 1301 (s), 1297 (w), 1265 (m), 1238 (s), 1217 (vs), 1175 (w), 970 (vs), 727 (s), 576 (vw), 574 (vw) cm^{-1}.

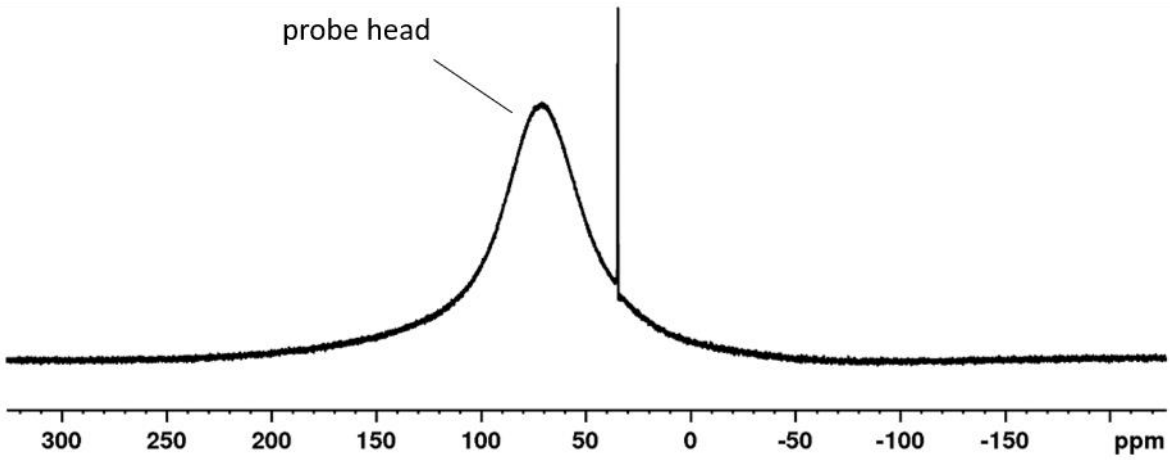

Figure S10: ^{27}Al-NMR (78.22 MHz, 4FB, 298 K) spectrum of pristine $[Fe(CO)_5][Al(OR^F)_4]$ (**1**). The broad peak centered at about 70 ppm results from the probe head.

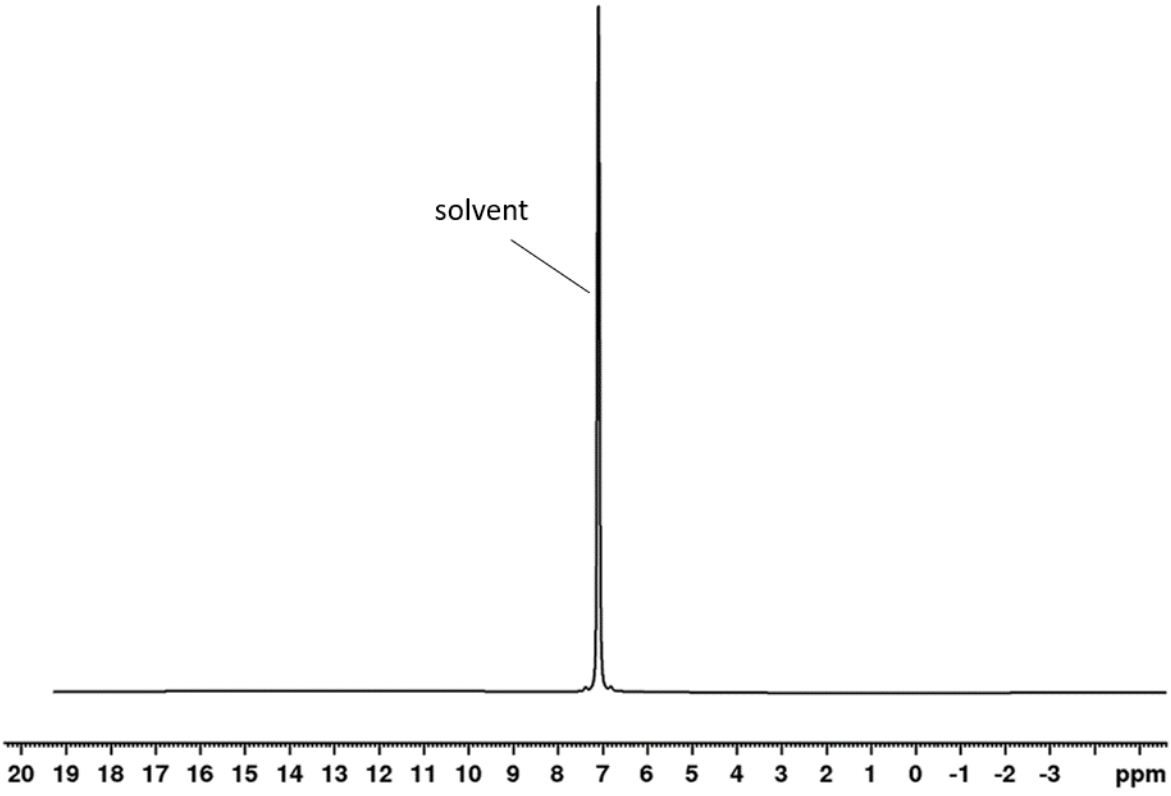

Figure S11: ^{1}H-NMR (300.18 MHz, 4FB, 298 K) spectrum of pristine $[Fe(CO)_5][Al(OR^F)_4]$ (**1**). Only solvent signal is evident.

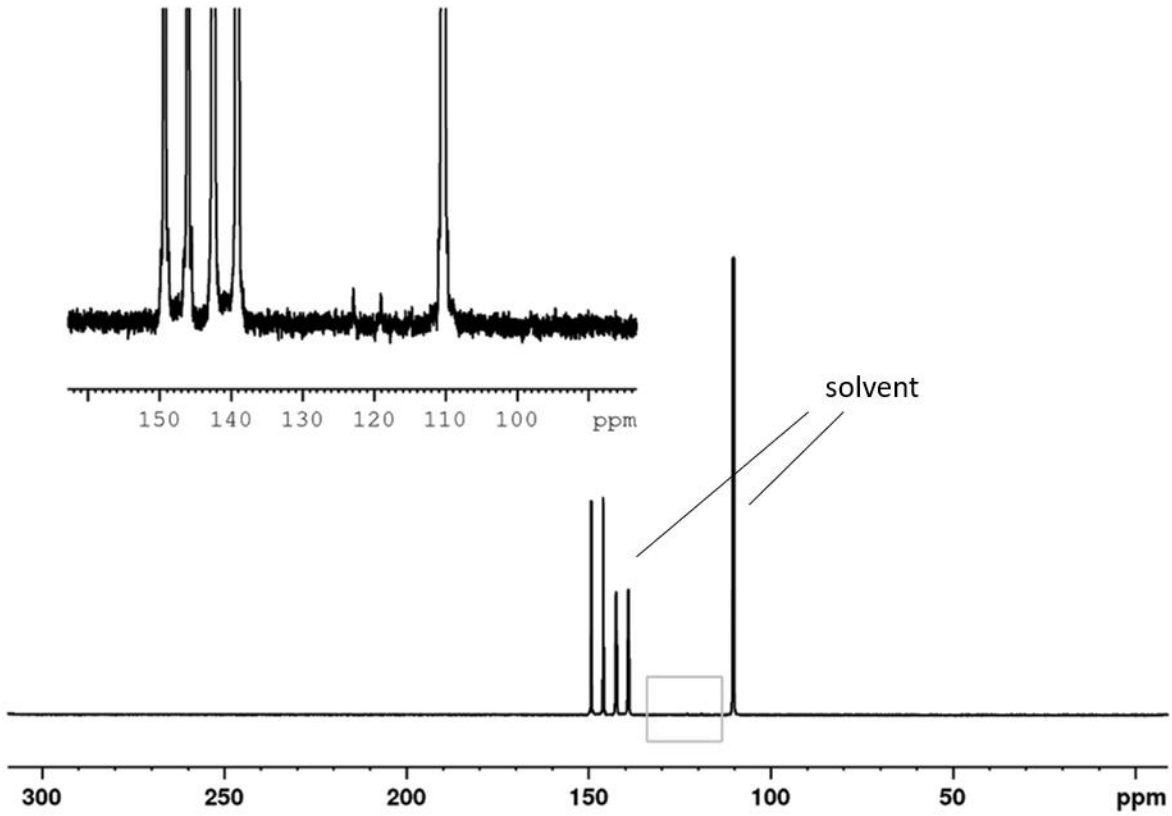

Figure S12: $^{13}C\{^{1}H\}$-NMR (75.48 MHz, 4FB, 298 K): spectrum of pristine $[Fe(CO)_5][Al(OR^F)_4]$ (**1**).

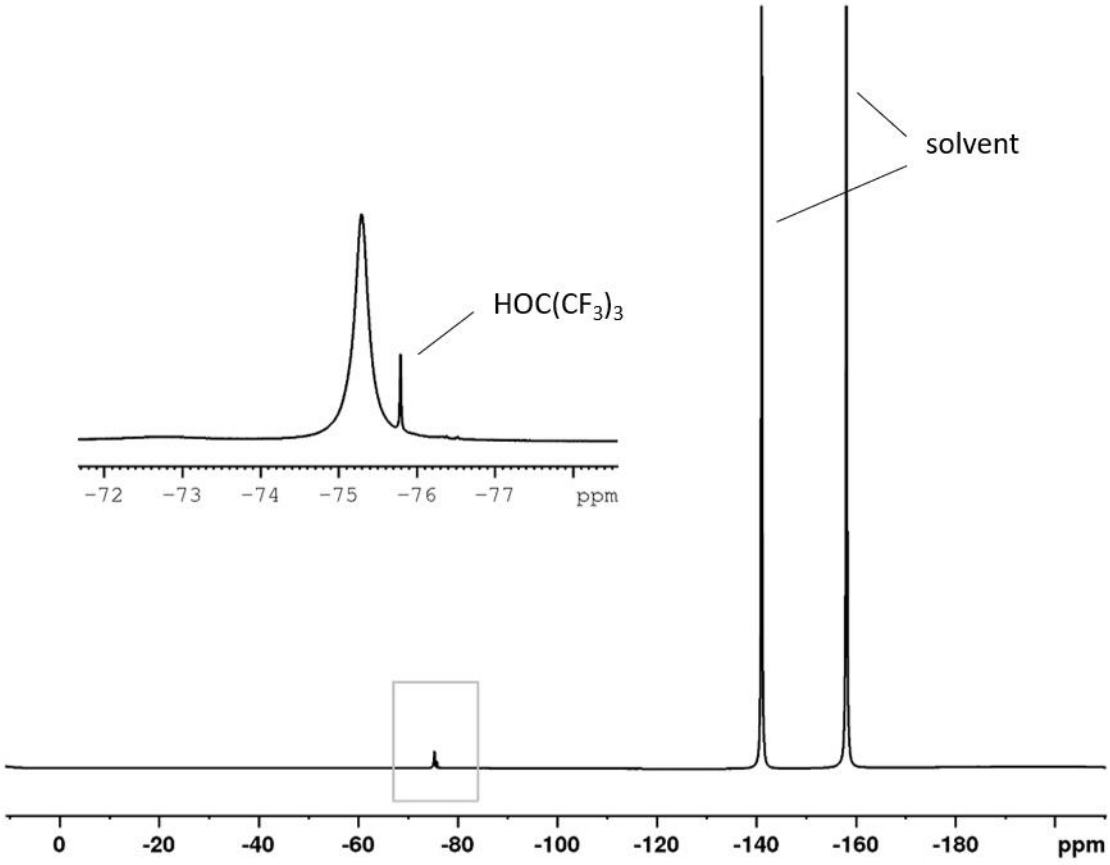

Figure S13: ^{19}F-NMR (282.45 MHz, 4FB, 298 K) spectrum of pristine $[Fe(CO)_5][Al(OR^F)_4]$ (**1**).

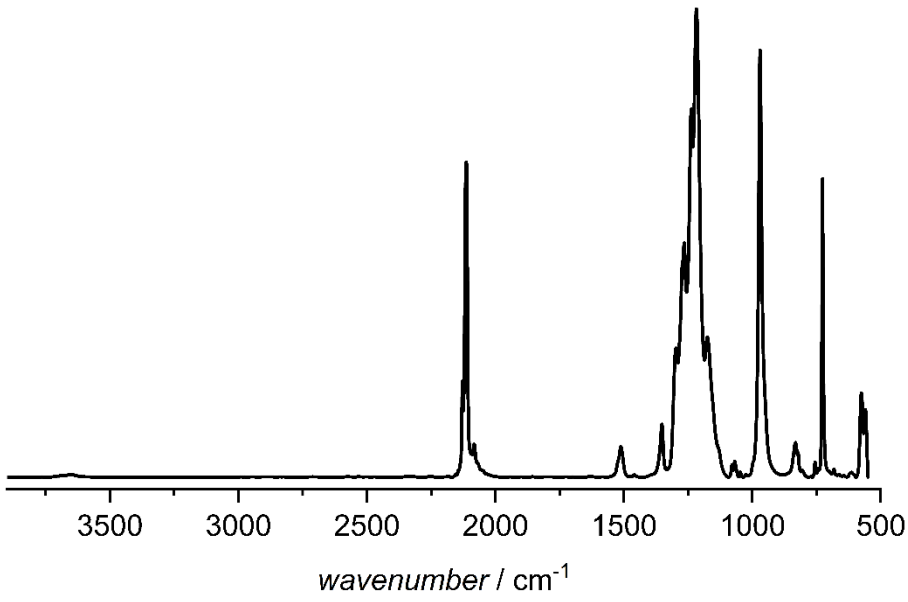

Figure S14: Full experimental ZnSe-ATR-FT-IR spectrum of solid $[Fe(CO)_5][Al(OR^F)_4]$ (**1**).

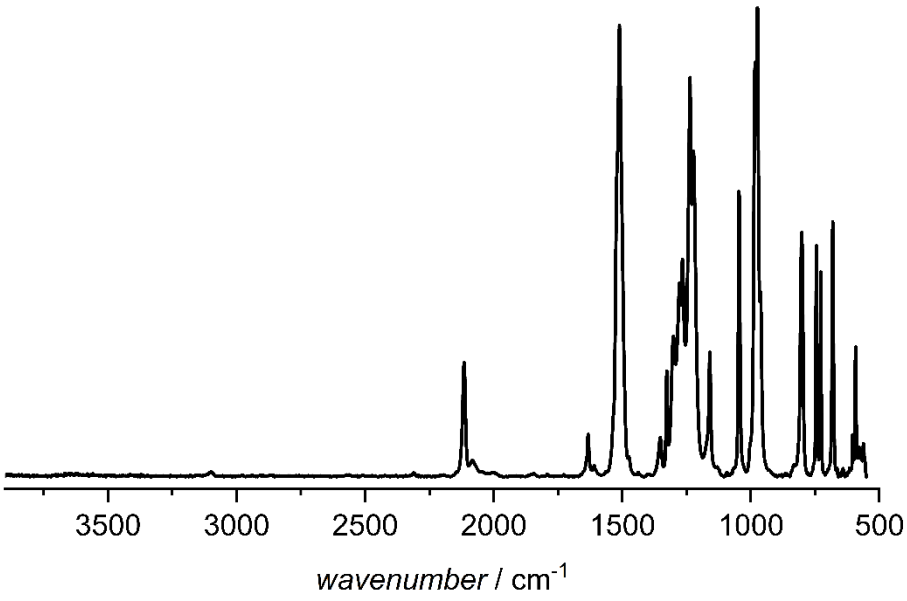

Figure S15: Full experimental ZnSe-ATR-FT-IR spectrum of $[Fe(CO)_5][Al(OR^F)_4]$ (**1**) in 4FB.

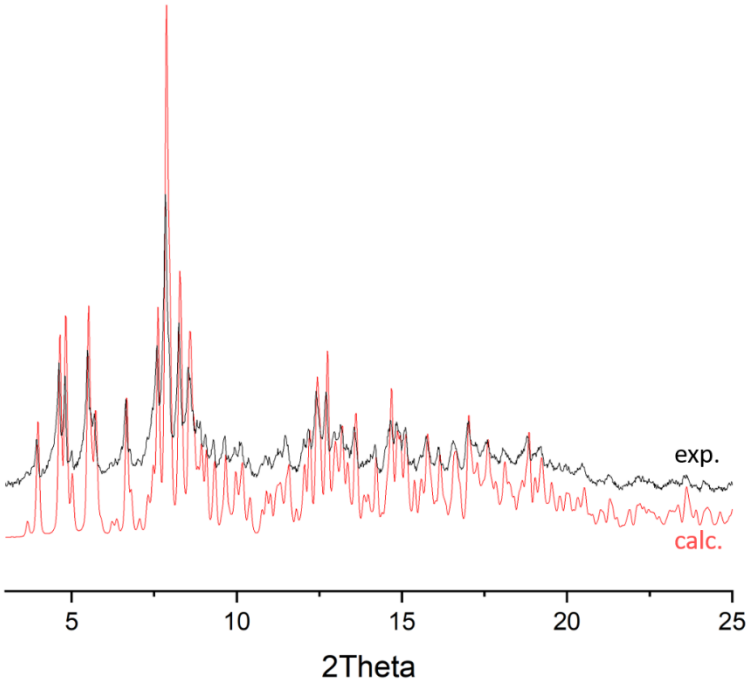

Figure S16: (Black) pXRD analysis of bulk material of $[Fe(CO)_5][Al(OR^F)_4]$ (**1**)**.** (Red) Simulated powder diffraction pattern from obtained crystalline $[Fe(CO)_5][Al(OR^F)_4]$ (**1**)**.** Experimental and simulated pattern are in accordance.

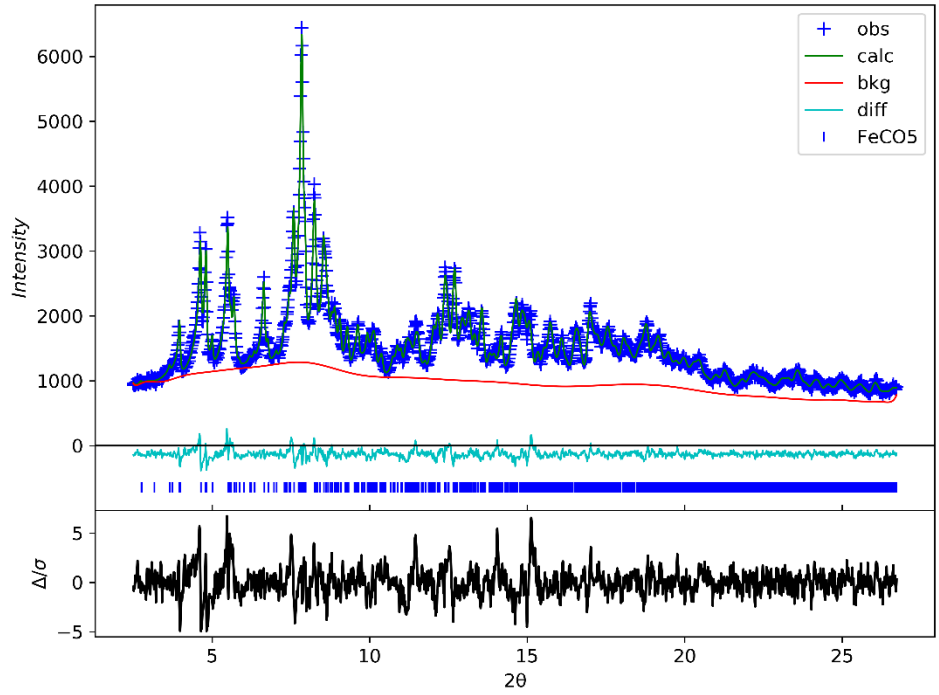

Figure S17: Results of the Rietveld refinement for the pXRD analysis of bulk material of $[Fe(CO)_5][Al(OR^F)_4]$ (**1**)**.** The structural model on which the refinement is based was taken from the single crystal study and was not further refined. A very good agreement with the measured powder diffraction pattern is observed (blue data points and green line). As can be seen from the difference plot (black and turquoise line), no further crystalline phases can be detected. Nevertheless, amorphous impurities cannot be excluded from the result.

Table S1:Crystallographic Data of $[Fe(CO)_5][Al(OR^F)_4]$ (**1**) from the Rietveld refinement.

Crystal system	Orthorhombic
Space-group	$P2_12_12_1$
Cell parameters / Å	a=14.2348(15), b= 16.8524(18), c= 29.514(3)
Cell volume / $Å^3$	7080.2(9)
Z	8
Temperature/K	100
ρ_{calc} g/cm^3	2.1820
Radiation	Mo-Kα_1 (λ = 0.70930)
2Θ range for data collection	2.50 to 26.72
Data / Parameter	1616 / 36
R_F/R_F^2 %	1.37 / 3.93
wR / %	3.53
GOF	1.49

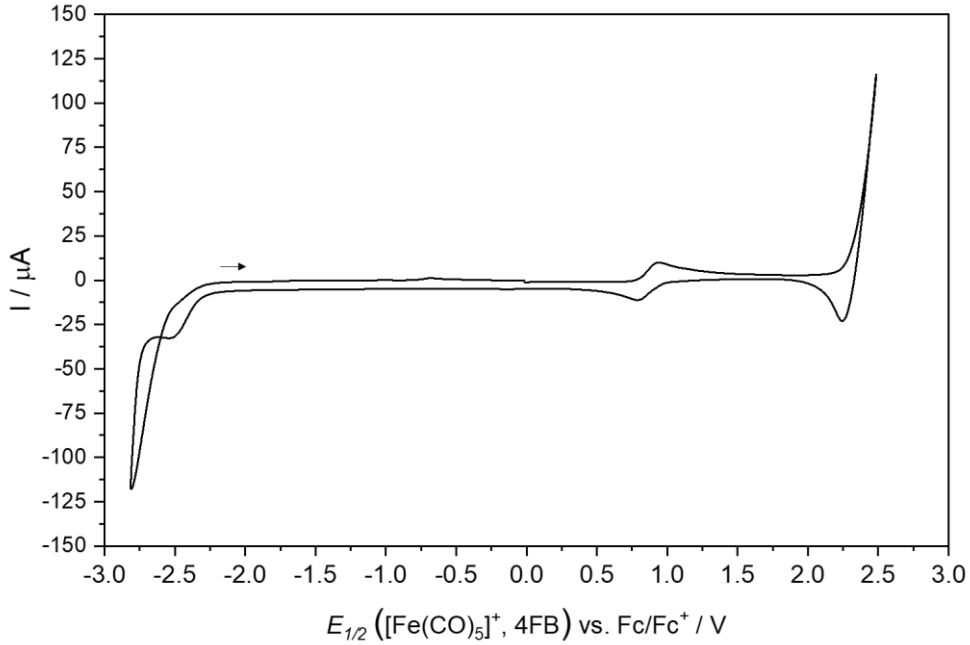

Figure S18: Exemplary full cyclic voltammogram of **1** (10 mM) in 4FB with $[NBu_4][Al(OR^F)_4]$ as conducting salt. The full solvent window is shown using a scan rate of 100 mVs^{-1}.

Synthesis of $[Fe(CO)_5][F\text{-}\{Al(OR^F)_3\}_2]$ (2) in 1,2,3,4-Tetrafluorobenzene

$[Phenazine^F][F\text{-}\{Al(OR^F)_3\}_2]$ (200 mg, 0.09 mmol) was weighted into a Schlenk tube. A stock solution of $Fe(CO)_5$ in 1,2,3,4-tetrafluorobenzene (0.93 mL, 0.09 mmol, 1.00 eq.) was added, turning the reaction mixture instantaneously to a dark green solution. The reaction mixture was stirred at ambient temperature for 1.5 h. The solution was layered with *n*-pentane and $[Fe(CO)_5][F\text{-}\{Al(OR^F)_3\}_2]$ (**2**) was obtained as dark green crystals suitable for scXRD (73 mg, 0.04 mmol, 48%).

^{13}C-NMR (50.32 MHz, 4FB, 298 K): only solvent signals

^{19}F-NMR (188.31 MHz, 4FB, 298 K): δ = –75.3 (s, 54F, $[F\text{-}\{Al(O\mathit{R}^F)_3\}_2]^-$), –184.6 (s, 1F, $[\mathit{F}\text{-}\{Al(OR^F)_3\}_2]^-$ ppm.

ATR-FT-IR (ZnSe): 2116 (s), 2084 (vw), 1354 (vw), 1301 (w), 1266 (s), 1245 (vs), 1216 (vs), 1180 (m), 974 (vs), 862(vw), 727 (s), 636 (vw), 574 (w) cm^{-1}.

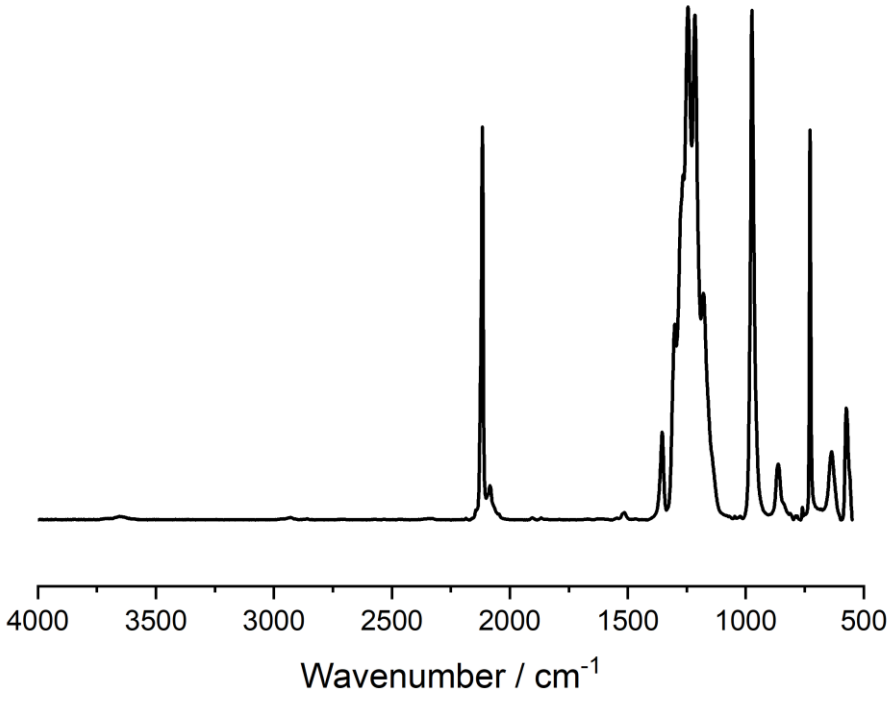

Figure S19: Full experimental ZnSe-ATR-FT-IR spectrum of solid $[Fe(CO)_5][F\text{-}\{Al(OR^F)_3\}_2]$ (**2**).

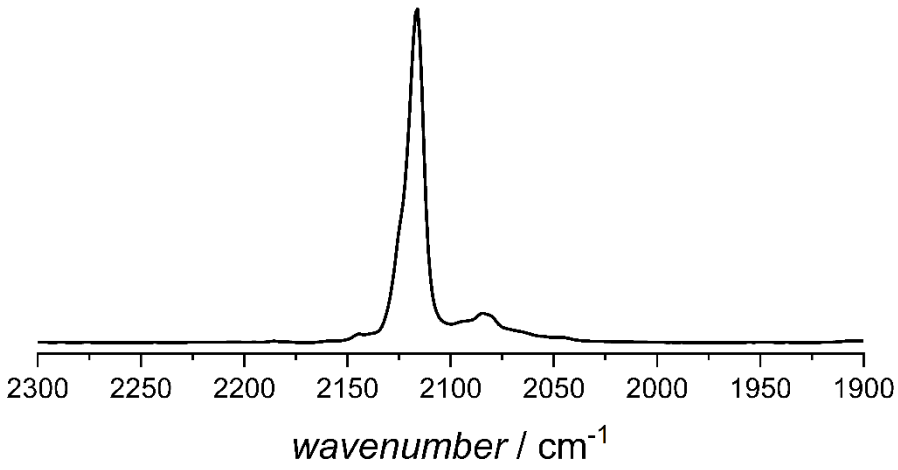

Figure S20: The carbonyl region of experimental ZnSe-ATR-FT-IR spectrum of solid $[Fe(CO)_5][F\text{-}\{Al(OR^F)_3\}_2]$ (**2**).

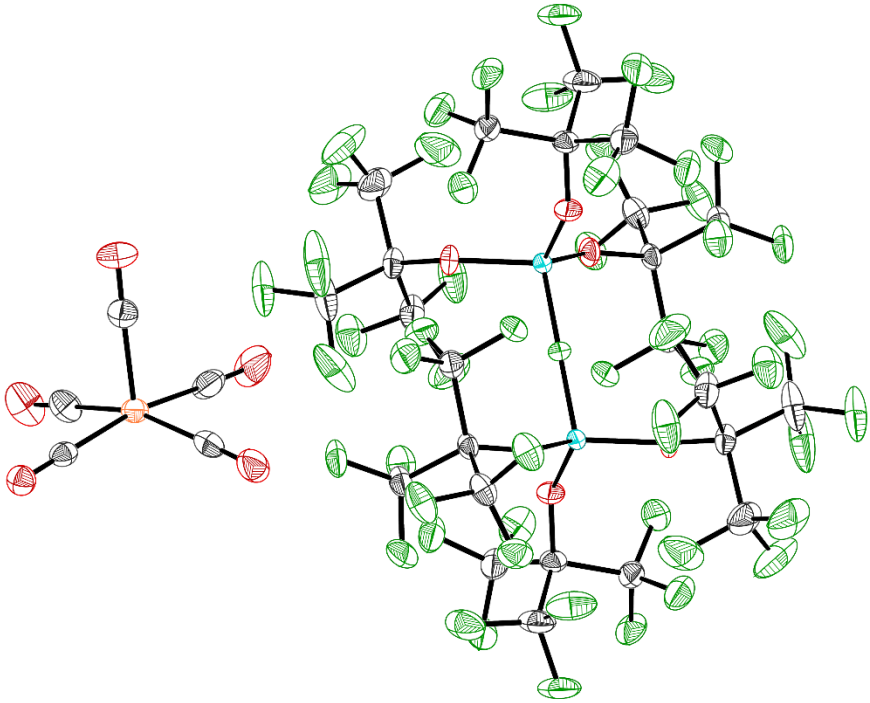

Figure S21: Molecular structure of $[Fe(CO)_5][F\text{-}\{Al(OR^F)_3\}_2]$ (**2**). Thermal displacement ellipsoids were set at 50% probability.

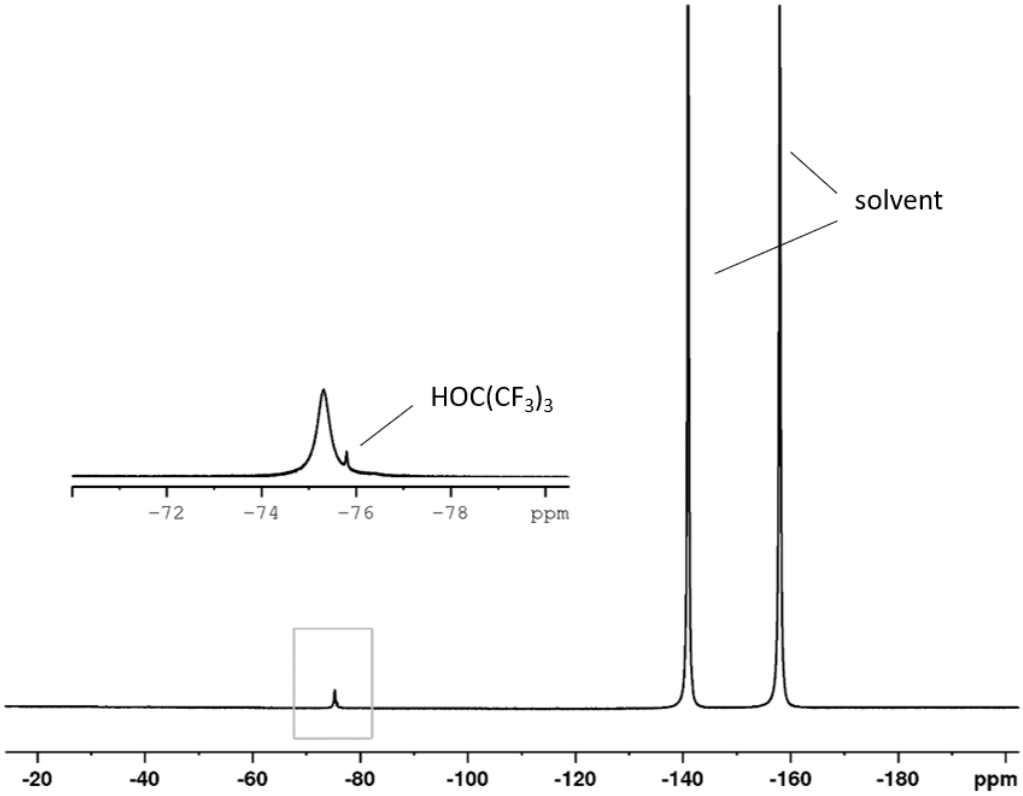

Figure S22: ^{19}F-NMR (188.31 MHz, 4FB, 298 K) spectrum of $[Fe(CO)_5][F\text{-}\{Al(OR^F)_3\}_2]$ (**2**).

3 EPR Spectra of $[Fe(CO)_5]^{\bullet+}[Al(OR^F)_4]^-$ (1) as a Solid and in Solution

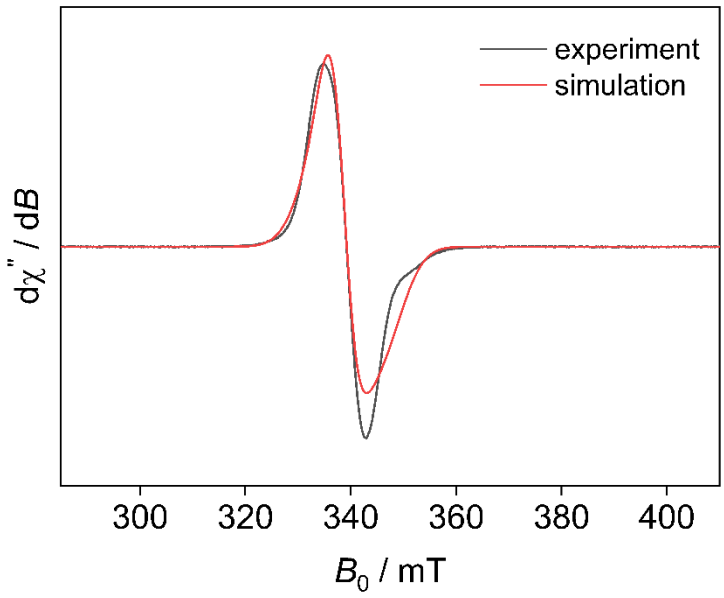

Figure S23: Continuous wave EPR spectrum of solid **1** at the X-band (9.75 GHz) at 100 K.

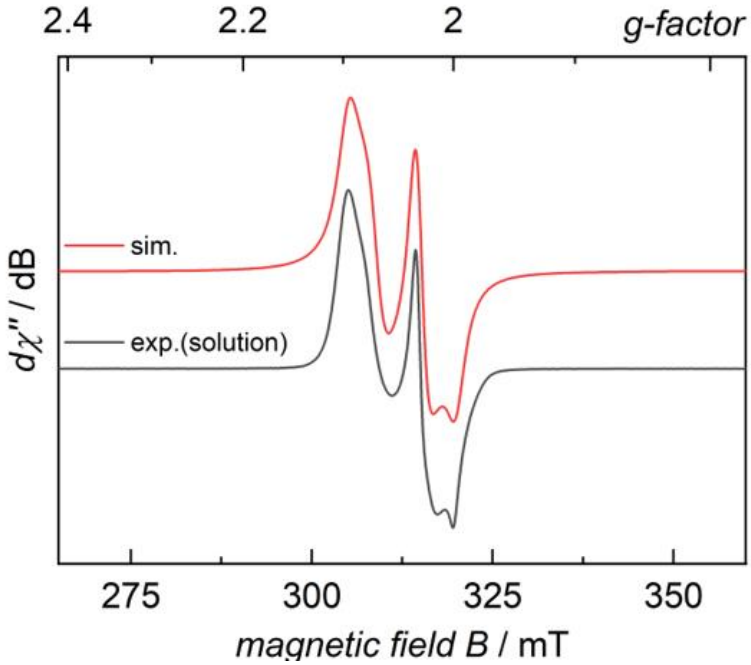

Figure S24: X-band EPR spectrum of **1** in a frozen solution of *o*DFB at 95 K.

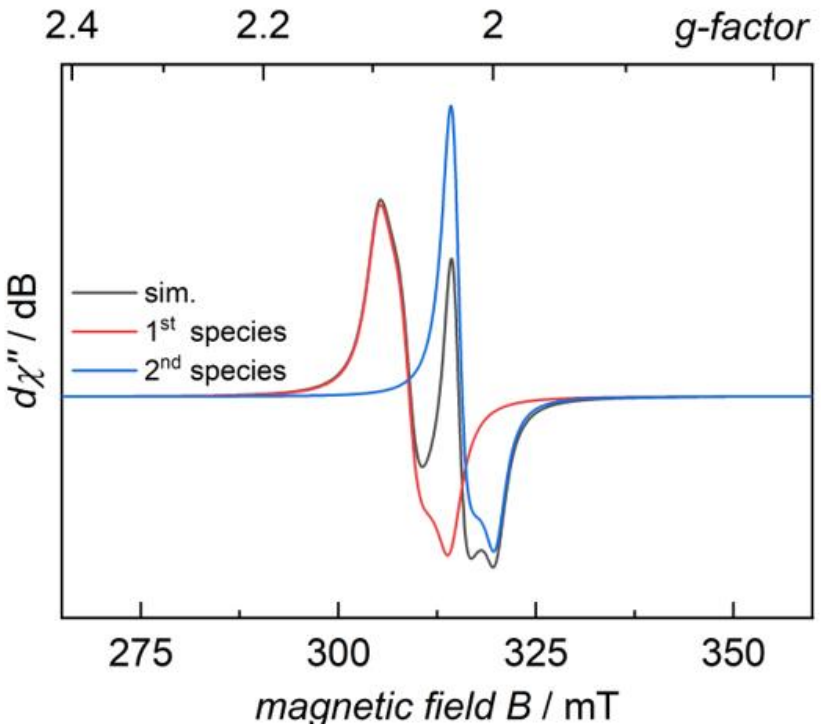

Figure S25: Simulated X-band EPR spectra. The 1st species refers to solid **1** (red), 2nd species refers to $[Fe(CO)_5oDFB]^{\bullet+}$ (blue). Sim is the combination of the 1st and 2nd species (gray).

4 Magnetic Measurement of $[Fe(CO)_5]^{\bullet+}[Al(OR^F)_4]^-$ (1) in Solution and as Solid

Evans NMR method was used to determine the effective magnetic moment μ_{eff} in solution.[30,31] For this, four solutions with different concentrations of **1** in 4FB were prepared. TMS was added as reference molecule. The mass susceptibilities χ_g are given by Eq. (1):[32,33]

$$\chi_g = \frac{3\Delta v}{4\pi v_0 m} + \chi_0 + \frac{\chi_0(\delta_0 - \delta_s)}{m} \quad (1)$$

Where Δv is the difference in frequency shift of the probe molecule, in reference to TMS in Hz, v_0 is the NMR spectrometer frequency in Hz, m is the mass of the probe per cm^3 of solution, χ_0 is the mass susceptibility of 4FB, δ_0 is the density of the pure solvent and δ_s is the density of 4FB.

For diluted solutions, Eq. (1) can be simplified to Eq. (2):[32,33]

$$\chi_g = \frac{3\Delta v}{4\pi v_0 m} \tag{2}$$

By multiplication of χ_g with the molecular mass of the solute M the molar susceptibilities χ_m of a solute can be calculated (Eq. 3):

$$\chi_m = \frac{3\Delta v}{4\pi v_0 m} M \tag{3}$$

Through linear regression according to Eq. (4) the molar susceptibilities χ_m of **1** in 4FB were calculated (Figure S22).

$$\Delta v = \frac{4\pi v_0 \chi_m}{3M} m \tag{4}$$

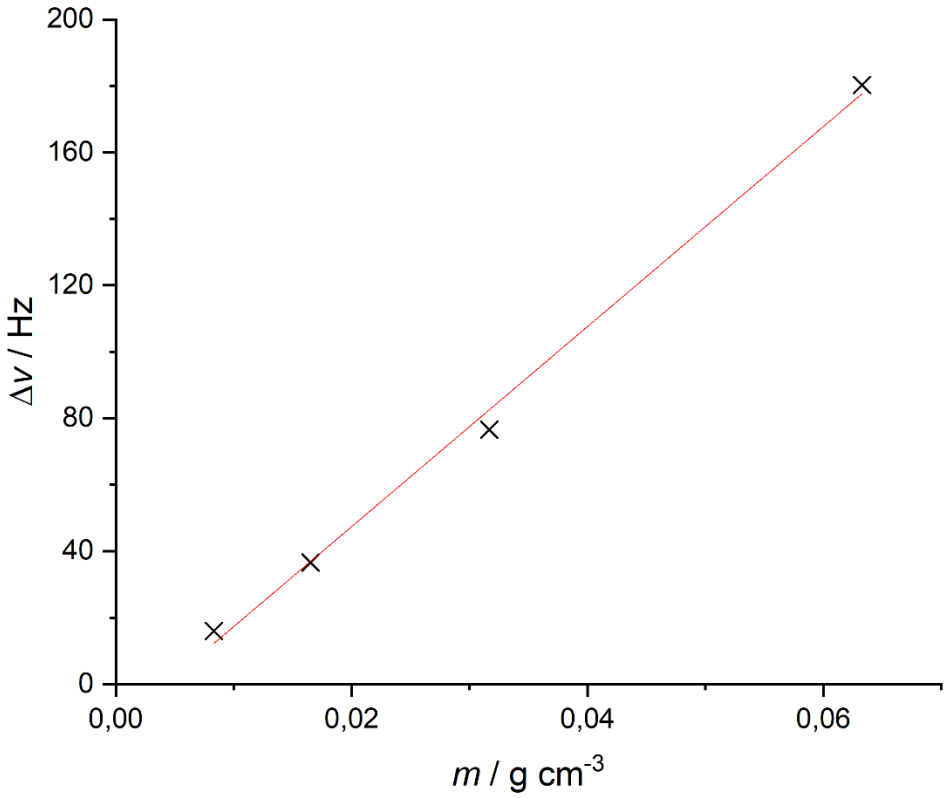

Figure S26: Plot of Δv against m for multiple solutions of **1** in 4FB.

The paramagnetic molar susceptibilities χ_p can be determined according to Eq. (5):[13]

$$\chi_p = \chi_m - \chi_D \tag{5}$$

The diamagnetic contribution χ_D was estimated by determining the molar susceptibility χ_m of diamagnetic $[Co(CO)_5][Al(OR^F)_4]$ in 4FB in analogy to **1**. Thus, the effective magnetic moment of **1** can be calculated by Eq. (7), where T is the temperature in Kelvin.[32]

$$\mu_{eff} = 2.828\sqrt{\chi_p T} \tag{6}$$

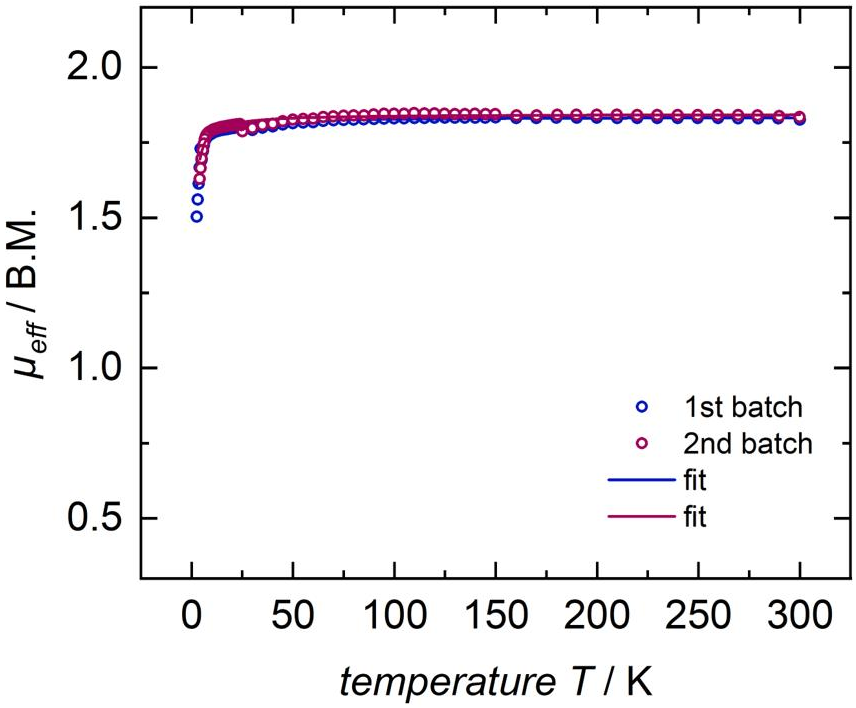

Figure S27: SQUID magnetization measurements of two independently synthesized, microcrystalline solid samples of $[Fe(CO)_5][Al(OR^F)_4]$ (**1**) in the temperature range 2-300 K with an applied magnetic field of 1 T. The solid lines represent the best global fit obtained for S = 1/2.

5 ^{57}Fe Mössbauer Measurements of $Fe(CO)_5$ and $Na_2[Fe(CO)_4]$

Mössbauer spectra of neutral $Fe(CO)_5$ and anionic $[Fe(CO_4)]^{2-}$ have been collected (Figure S28 and Figure S29). The isomer shifts and quadrupole splittings are presented in Table S2.

Table S2: Isomer shifts and quadrupole splittings.

	$[Fe(CO)_4]^{2-}$	$Fe(CO)_5$
$\boldsymbol{\delta}$ [mms^{-1}]	–0.16(1)	–0.08(1)
$\Delta \boldsymbol{E}_Q$ [mms^{-1}]	0.19(1)	2.55(1)

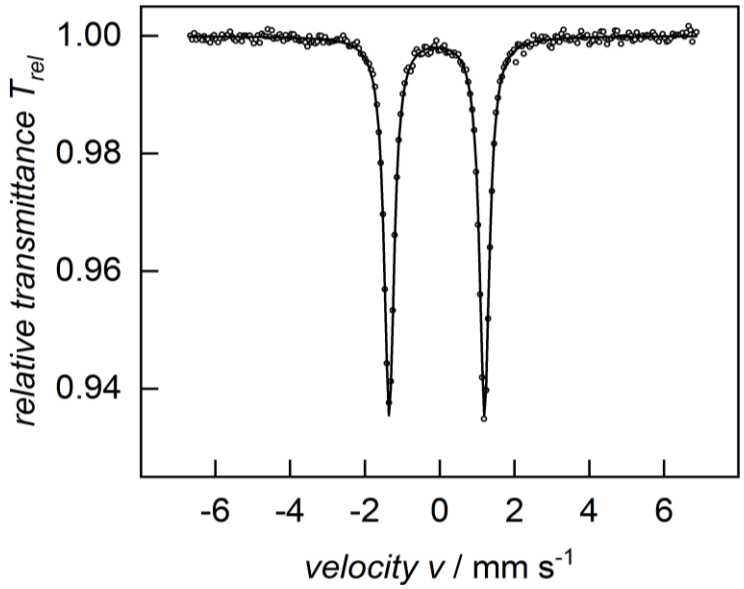

Figure S28: Zero-field ^{57}Fe Mössbauer spectrum of $Fe(CO)_5$ recorded at 77 K. The gray data points are experimental data together with a numerical fit (black line).

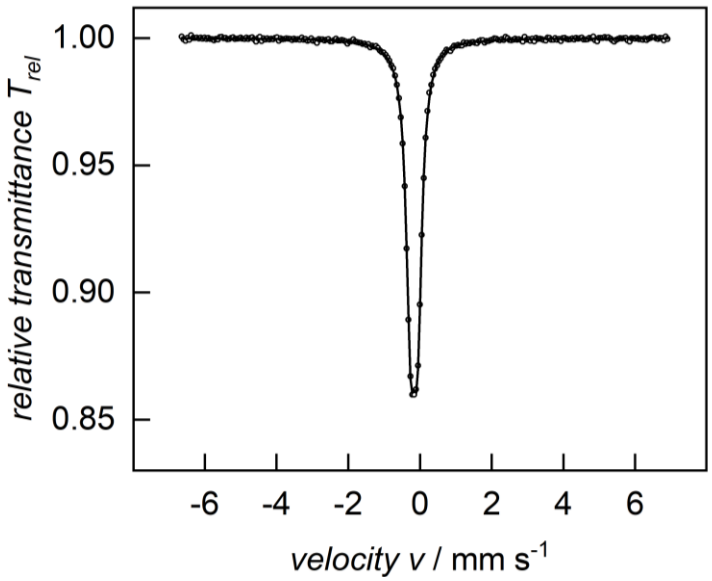

Figure S29: Zero-field ^{57}Fe Mössbauer spectrum of $[Fe(CO)_4]^{2-}$ recorded at 77 K. The gray data points are experimental data together with a numerical fit (black line).

6 Crystallographic Data

Table S3: Crystallographic data of [phenazine^F][F-{Al(OR^F)$_3$}$_2$], [Fe(CO)$_5$oDFB][Al(OR^F)$_4$] and [Fe$_2$(CO)$_8$Br][F-{Al(ORF)$_3$}$_2$].

Name	[phenazine^F][F-{Al(OR^F)$_3$}$_2$]	[Fe(CO)$_5$oDFB][Al(OR^F)$_4$]	[Fe$_2$(CO)$_8$Br][F-{Al(ORF)$_3$}$_2$]
Empirical formula	$C_{48}Al_2F_{73}N_2O_6$	$C_{54}H_8Al_2F_{76}Fe_2O_{18}$	$C_{32}Al_2BrF_{55}Fe_2O_{14}$
Formula weight	2141.46	2554.26	1898.89
Temperature [K]	100(2)	150(2)	100(2)
Crystal system	monoclinic	monoclinic	orthorhombic
Space group (number)	$P2_1/c$ (14)	$P2/c$ (13)	$P\mathrm{bcn}$ (60)
a [Å]	24.734(3)	21.666(6)	18.2753(14)
b [Å]	18.6697(18)	9.826(3)	13.8505(10)
c [Å]	14.1476(14)	19.222(5)	21.9188(16)
α [°]	90	90	90
β [°]	102.081(4)	89.993(9)	90
γ [°]	90	90	90
Volume [Å^3]	6388.3(11)	4092.1(19)	5548.1(7)
Z	4	4	4
ρ_{calc} [gcm^{-3}]	2.227	2.073	2.273
μ [mm^{-1}]	0.313	0.614	1.521
F(000)	4132	2476	3648
Crystal size [mm^3]	0.5×0.48×0.08	0.517×0.341×0.140	0.35×0.32×0.24
Crystal colour	purple	green	orange
Crystal shape	plate	block	block
Radiation	MoK_α (λ=0.71073 Å)	MoK_α (λ=0.71073 Å)	MoK_α (λ=0.71073 Å)
2Θ range [°]	2.76 to 54.46 (0.78 Å)	2.83 to 63.16 (0.68 Å)	3.69 to 52.80 (0.80 Å)
Index ranges	-31 ≤ h ≤ 31 -23 ≤ k ≤ 23 -18 ≤ l ≤ 18	-31 ≤ h ≤ 31 -13 ≤ k ≤ 14 -28 ≤ l ≤ 28	-22 ≤ h ≤ 22 -17 ≤ k ≤ 17 -27 ≤ l ≤ 27
Reflections collected	311254	281340	350530
Independent reflections	14181 R_{int} = 0.1013 R_{sigma} = 0.0361	13549 R_{int} = 0.0537 R_{sigma} = 0.0224	5697 R_{int} = 0.0458 R_{sigma} = 0.0074
Completeness to Θ = 25.242°	100.0 %	99.9 %	100.0 %
Data / Restraints / Parameters	14181/7893/1310	13549/14489/1627	5697/2922/607
Goodness-of-fit on F^2	1.036	1.066	1.351
Final *R* indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0398 wR_2 = 0.0945	R_1 = 0.0574 wR_2 = 0.1561	R_1 = 0.0664 wR_2 = 0.1499
Final *R* indexes [all data]	R_1 = 0.0565 wR_2 = 0.1051	R_1 = 0.0769 wR_2 = 0.1788	R_1 = 0.0672 wR_2 = 0.1501
Largest peak/hole [eÅ^{-3}]	0.46/-0.33	0.69/-0.42	0.92/-0.67
CCDC Nr.	2144643	2144645	2144641

Table S4: Crystallographic data of $[Fe(CO)_5][Al(OR^F)_4]$ (**1**) and $[Fe(CO)_5][F\text{-}\{Al(OR^F)_3\}_2]$ (**2**).

Name	$[Fe(CO)_5][Al(OR^F)_4]$	$[Fe(CO)_5][F\text{-}\{Al(OR^F)_3\}_2]$
Empirical formula	$C_{21}AlF_{36}FeO_9$	$C_{29}Al_2F_{55}FeO_{11}$
Formula weight	1163.04	1679.10
Temperature [K]	100(2)	100(2)
Crystal system	orthorhombic	triclinic
Space group (number)	$P2_12_12_1$ (19)	$P\bar{1}$ (2)
a [Å]	14.1960(8)	10.718(4)
b [Å]	16.8308(10)	11.572(5)
c [Å]	29.4979(19)	21.359(7)
α [°]	90	101.657(14)
β [°]	90	101.838(16)
γ [°]	90	97.805(14)
Volume [Å^3]	7047.9(7)	2495.6(16)
Z	8	2
ρ_{calc} [gcm^{-3}]	2.192	2.235
μ [mm^{-1}]	0.693	0.599
F(000)	4488	1618
Crystal size [mm^3]	0.28×0.15×0.07	0.222×0.182×0.058
Crystal colour	green	green
Crystal shape	block	plate
Radiation	MoK_α (λ=0.71073 Å)	MoK_α (λ=0.71073 Å)
2Θ range [°]	2.76 to 55.82 (0.76 Å)	3.66 to 54.56 (0.78 Å)
Index ranges	-18 ≤ h ≤ 18 -21 ≤ k ≤ 22 -38 ≤ l ≤ 38	-13 ≤ h ≤ 13 -14 ≤ k ≤ 14 -27 ≤ l ≤ 27
Reflections collected	147475	180046
Independent reflections	16846 R_{int} = 0.0626 R_{sigma} = 0.0391	11181 R_{int} = 0.0624 R_{sigma} = 0.0219
Completeness to Θ = 25.242°	100.0 %	99.9 %
Data / Restraints / Parameters	16846/12780/1347	11181/13308/1267
Goodness-of-fit on F^2	1.062	1.129
Final *R* indexes [I≥2σ(I)]	R_1 = 0.0383 wR_2 = 0.0819	R_1 = 0.0494 wR_2 = 0.1189
Final *R* indexes [all data]	R_1 = 0.0545 wR_2 = 0.0900	R_1 = 0.0587 wR_2 = 0.1234
Largest peak/hole [eÅ^{-3}]	0.69/-0.40	1.04/-0.40
Flack X parameter	0.029(14)	
CCDC Nr.	2144646	2144650

Atom coordinates, bond lengths and bond angles:

Table S5. Atomic coordinates and U_{eq} [Å^2] for [phenazine^F][F-{Al(OR^F)$_3$}$_2$].

Atom	*x*	*y*	*z*	U_{eq}
Al01	0.46284(2)	0.42699(3)	0.53217(4)	0.01499(11)
F1	0.13772(5)	0.36984(6)	0.95249(10)	0.0310(3)
Al02	0.03972(2)	0.57069(3)	0.46838(4)	0.01680(12)
F2	0.05078(5)	0.44851(7)	0.96106(10)	0.0337(3)
N2	0.25693(7)	0.57465(8)	1.03347(12)	0.0193(3)
C2	0.20488(8)	0.54297(10)	1.01836(13)	0.0191(4)
C3	0.15678(8)	0.58168(10)	1.02454(15)	0.0226(4)
C4	0.10580(8)	0.55053(11)	1.00376(15)	0.0228(4)
F5	0.36662(5)	0.63443(6)	1.06831(10)	0.0294(3)
C5	0.10015(8)	0.47869(11)	0.97838(15)	0.0239(4)
F6	0.45228(5)	0.55492(7)	1.05694(10)	0.0302(3)
C6	0.14614(8)	0.43899(10)	0.97376(15)	0.0224(4)
F7	0.44180(5)	0.41399(7)	1.01787(9)	0.0286(3)
C7	0.29826(8)	0.46170(10)	1.00385(13)	0.0182(4)
F8	0.34368(5)	0.35078(6)	0.98851(9)	0.0283(3)
F008	0.500000	0.500000	0.500000	0.0300(4)
C8	0.30394(8)	0.53542(10)	1.02860(13)	0.0187(4)
F9	0.27972(6)	0.63765(7)	1.21486(9)	0.0350(3)
C9	0.35729(8)	0.56560(10)	1.04607(14)	0.0210(4)
F10	0.29206(6)	0.78281(8)	1.23701(10)	0.0418(3)
F00G	0.000000	0.500000	0.500000	0.0332(4)
C10	0.40276(8)	0.52503(11)	1.04065(14)	0.0222(4)
F11	0.28072(6)	0.86681(7)	1.07966(12)	0.0429(4)
C11	0.39714(8)	0.45250(11)	1.01957(14)	0.0217(4)
F12	0.25536(6)	0.80982(7)	0.89947(11)	0.0407(3)
C12	0.34607(8)	0.42132(10)	1.00286(14)	0.0209(4)
F13	0.24647(6)	0.66470(7)	0.87912(9)	0.0339(3)
C13	0.23847(8)	0.36817(10)	0.91987(14)	0.0194(4)
F14	0.23306(6)	0.29493(7)	1.05172(9)	0.0341(3)
C14	0.23200(9)	0.30125(11)	0.95734(15)	0.0237(4)
F15	0.21593(6)	0.17802(6)	0.93382(10)	0.0366(3)
C15	0.22343(9)	0.24222(11)	0.89786(16)	0.0262(4)
F16	0.21574(6)	0.19298(7)	0.74358(10)	0.0343(3)
C16	0.22350(8)	0.24994(11)	0.80095(16)	0.0248(4)
F17	0.23504(6)	0.32289(7)	0.67079(9)	0.0331(3)
C17	0.23227(8)	0.31605(11)	0.76325(14)	0.0232(4)
F18	0.24690(5)	0.43981(6)	0.78800(8)	0.0244(2)
C18	0.23893(8)	0.37528(10)	0.82287(14)	0.0201(4)
C19	0.26184(8)	0.65127(10)	1.04659(15)	0.0209(4)
C20	0.27366(8)	0.68058(11)	1.13844(15)	0.0246(4)
C21	0.27996(9)	0.75361(12)	1.14926(17)	0.0288(5)
C22	0.27405(9)	0.79665(11)	1.06868(18)	0.0294(5)
C23	0.26134(8)	0.76792(11)	0.97693(17)	0.0276(5)
C24	0.25615(8)	0.69483(11)	0.96638(15)	0.0238(4)
N1	0.24567(7)	0.43141(8)	0.97979(11)	0.0182(3)
C1	0.19916(8)	0.46958(10)	0.99134(13)	0.0187(4)
F3	0.06106(5)	0.58817(6)	1.00844(10)	0.0302(3)
F4	0.15860(5)	0.65037(6)	1.05047(10)	0.0321(3)
O1_1	0.43999(6)	0.45886(8)	0.62994(10)	0.0226(3)
C1_1	0.39696(8)	0.46123(10)	0.67627(13)	0.0197(4)
C2_1	0.40677(9)	0.52642(11)	0.74638(14)	0.0245(4)

F1_1	0.39641(6)	0.58748(6)	0.69782(9)	0.0327(3)
F2_1	0.37391(6)	0.52414(7)	0.81111(9)	0.0318(3)
F3_1	0.45853(5)	0.52859(7)	0.79606(9)	0.0309(3)
C3_1	0.39656(8)	0.39121(11)	0.73554(15)	0.0237(4)
F4_1	0.40145(5)	0.33465(6)	0.68102(9)	0.0301(3)
F5_1	0.43827(5)	0.38995(7)	0.81192(9)	0.0306(3)
F6_1	0.34970(5)	0.38353(6)	0.76805(10)	0.0311(3)
C4_1	0.34076(8)	0.47019(11)	0.60382(15)	0.0236(4)
F7_1	0.32398(5)	0.40779(6)	0.56125(9)	0.0285(3)
F8_1	0.30089(5)	0.49334(7)	0.64716(9)	0.0294(3)
F9_1	0.34545(5)	0.51649(7)	0.53502(9)	0.0286(3)
O1_2	0.40984(6)	0.41378(8)	0.43593(10)	0.0284(3)
C1_2	0.38946(8)	0.38789(10)	0.34645(13)	0.0196(4)
C2_2	0.37504(9)	0.30729(11)	0.35219(16)	0.0271(4)
F1_2	0.42028(6)	0.26727(7)	0.36359(10)	0.0366(3)
F2_2	0.33993(6)	0.28489(7)	0.27281(11)	0.0394(3)
F3_2	0.35139(6)	0.29529(7)	0.42695(11)	0.0414(3)
C3_2	0.33611(8)	0.43045(11)	0.30370(14)	0.0237(4)
F4_2	0.34371(6)	0.50005(7)	0.31723(11)	0.0393(3)
F5_2	0.29505(5)	0.41099(7)	0.34494(9)	0.0288(3)
F6_2	0.31918(6)	0.41986(8)	0.20820(9)	0.0381(3)
C4_2	0.43228(9)	0.39685(11)	0.28113(15)	0.0262(4)
F7_2	0.43422(6)	0.46496(7)	0.25335(11)	0.0405(3)
F8_2	0.41973(6)	0.35694(8)	0.20128(9)	0.0362(3)
F9_2	0.48241(5)	0.37912(8)	0.32859(9)	0.0339(3)
O1_3	0.50959(8)	0.36071(9)	0.55251(12)	0.0445(5)
C1_3	0.54317(8)	0.30806(10)	0.59522(14)	0.0227(4)
C2_3	0.55660(9)	0.31737(12)	0.70696(16)	0.0294(5)
F1_3	0.51450(6)	0.29640(9)	0.74486(10)	0.0437(4)
F2_3	0.60075(5)	0.28024(8)	0.74963(9)	0.0369(3)
F3_3	0.56588(8)	0.38576(8)	0.73017(11)	0.0523(4)
C3_3	0.59741(9)	0.31095(12)	0.55731(17)	0.0330(5)
F4_3	0.58764(7)	0.32029(9)	0.46258(11)	0.0480(4)
F5_3	0.62935(7)	0.36487(9)	0.59774(13)	0.0576(5)
F6_3	0.62682(5)	0.25059(8)	0.57718(11)	0.0406(3)
C4_3	0.51488(9)	0.23463(12)	0.56872(17)	0.0318(5)
F7_3	0.51726(6)	0.21547(8)	0.47916(10)	0.0397(3)
F8_3	0.53777(7)	0.18329(7)	0.62833(11)	0.0482(4)
F9_3	0.46166(6)	0.23871(10)	0.57364(11)	0.0526(4)
O1_4	0.08853(6)	0.58887(10)	0.56811(11)	0.0374(4)
C1_4	0.10493(8)	0.60841(11)	0.66158(14)	0.0246(4)
C2_4	0.12268(10)	0.68835(13)	0.6657(2)	0.0429(6)
F1_4	0.07878(7)	0.73047(8)	0.64762(13)	0.0529(4)
F2_4	0.15309(8)	0.70591(8)	0.75157(15)	0.0742(6)
F3_4	0.15229(7)	0.70184(9)	0.59952(16)	0.0700(6)
C3_4	0.15513(9)	0.56120(11)	0.70806(15)	0.0248(4)
F4_4	0.14643(6)	0.49415(7)	0.68120(11)	0.0416(3)
F5_4	0.20127(5)	0.58241(7)	0.68311(10)	0.0352(3)
F6_4	0.16476(6)	0.56254(7)	0.80500(9)	0.0365(3)
C4_4	0.05808(10)	0.59746(14)	0.71723(16)	0.0356(5)
F7_4	0.05203(6)	0.52793(9)	0.73397(13)	0.0558(5)
F8_4	0.06781(7)	0.63134(11)	0.80154(11)	0.0635(5)
F9_4	0.01030(6)	0.62048(9)	0.66559(10)	0.0430(4)
O1_5	-0.00673(11)	0.63617(13)	0.43585(17)	0.0398(6)
C1_5	-0.03758(10)	0.69206(13)	0.39563(18)	0.0228(5)
C2_5	-0.04771(11)	0.68732(15)	0.28402(19)	0.0341(6)
F1_5	-0.00295(8)	0.70753(12)	0.25282(12)	0.0542(5)

F2_5	-0.08944(17)	0.72793(17)	0.2401(3)	0.0502(7)
F3_5	-0.05877(9)	0.62020(10)	0.25459(14)	0.0552(5)
C3_5	-0.09363(11)	0.68922(15)	0.4281(2)	0.0320(6)
F4_5	-0.08658(8)	0.67656(11)	0.52141(13)	0.0490(5)
F5_5	-0.12535(7)	0.63746(9)	0.38083(15)	0.0465(5)
F6_5	-0.12156(13)	0.75054(18)	0.4098(3)	0.0453(6)
C4_5	-0.00776(10)	0.76333(13)	0.43053(19)	0.0310(5)
F7_5	-0.01273(6)	0.77916(9)	0.51979(11)	0.0407(4)
F8_5	-0.02862(17)	0.81806(14)	0.3745(3)	0.0465(6)
F9_5	0.04583(12)	0.7587(2)	0.43026(18)	0.0475(7)
O1_6	0.06777(6)	0.53357(9)	0.37949(11)	0.0316(3)
C1_6	0.11338(9)	0.52926(11)	0.34012(15)	0.0258(4)
C2_6	0.12157(11)	0.60107(12)	0.29017(17)	0.0362(5)
F1_6	0.08368(7)	0.60941(8)	0.20938(11)	0.0515(4)
F2_6	0.17113(7)	0.60566(8)	0.26708(12)	0.0520(4)
F3_6	0.11669(7)	0.65572(7)	0.34823(11)	0.0474(4)
C3_6	0.16575(10)	0.51213(13)	0.41831(17)	0.0354(5)
F4_6	0.15434(7)	0.46276(8)	0.47873(11)	0.0485(4)
F5_6	0.18335(6)	0.57007(8)	0.47057(11)	0.0425(3)
F6_6	0.20685(7)	0.48791(10)	0.37995(12)	0.0580(5)
C4_6	0.10351(10)	0.46827(12)	0.26404(16)	0.0325(5)
F7_6	0.10732(7)	0.40463(7)	0.30639(11)	0.0449(4)
F8_6	0.14061(6)	0.46989(8)	0.20670(10)	0.0417(3)
F9_6	0.05400(6)	0.47296(8)	0.20674(10)	0.0431(3)
O1_7	-0.0046(8)	0.6251(10)	0.3975(13)	0.020(4)
C1_7	-0.0358(7)	0.6843(10)	0.3707(11)	0.028(4)
C2_7	0.0038(7)	0.7487(9)	0.3727(14)	0.039(4)
F1_7	0.0435(13)	0.748(2)	0.4518(17)	0.047(5)
F2_7	-0.0231(18)	0.8103(14)	0.366(4)	0.049(5)
F3_7	0.0282(8)	0.7448(12)	0.2975(14)	0.060(5)
C3_7	-0.0704(7)	0.6716(10)	0.2677(12)	0.038(4)
F4_7	-0.1120(6)	0.6283(9)	0.2714(13)	0.050(5)
F5_7	-0.0402(8)	0.6415(12)	0.2125(13)	0.056(4)
F6_7	-0.0905(18)	0.7328(15)	0.227(3)	0.048(5)
C4_7	-0.0749(7)	0.6971(10)	0.4408(13)	0.033(4)
F7_7	-0.0982(8)	0.6363(9)	0.461(2)	0.065(7)
F8_7	-0.1162(13)	0.7411(19)	0.402(3)	0.046(5)
F9_7	-0.0497(8)	0.7262(12)	0.5243(13)	0.068(6)

U_{eq} is defined as 1/3 of the trace of the orthogonalized U_{ij} tensor.

Table S6: Bond lengths and angles for [phenazine^{F}][F-{Al(OR^{F})$_3$}$_2$].

Atom–Atom	**Length [Å]**
Al01–O1_3	1.6770(16)
Al01–O1_2	1.6989(15)
Al01–O1_1	1.7070(14)
Al01–F008	1.7564(5)
F1–C6	1.332(2)
Al02–O1_7	1.668(18)
Al02–O1_5	1.675(2)
Al02–O1_4	1.6884(16)
Al02–O1_6	1.7053(15)
Al02–F00G	1.7581(6)
F2–C5	1.320(2)
N2–C8	1.388(2)
N2–C2	1.392(2)
N2–C19	1.444(2)
C2–C3	1.410(3)
C2–C1	1.422(3)
C3–F4	1.332(2)
C3–C4	1.364(3)
C4–F3	1.324(2)
C4–C5	1.388(3)
F5–C9	1.331(2)
C5–C6	1.371(3)
F6–C10	1.322(2)
C6–C1	1.404(3)
F7–C11	1.322(2)
C7–N1	1.394(2)
C7–C12	1.405(3)

C7–C8	1.420(3)	C1_3–C3_3	1.546(3)
F8–C12	1.332(2)	C1_3–C4_3	1.549(3)
C8–C9	1.409(3)	C1_3–C2_3	1.556(3)
F9–C20	1.329(2)	C2_3–F1_3	1.326(3)
C9–C10	1.371(3)	C2_3–F3_3	1.326(3)
F10–C21	1.331(3)	C2_3–F2_3	1.327(2)
C10–C11	1.387(3)	C3_3–F4_3	1.323(3)
F11–C22	1.325(2)	C3_3–F5_3	1.332(3)
C11–C12	1.366(3)	C3_3–F6_3	1.339(3)
F12–C23	1.329(2)	C4_3–F8_3	1.323(3)
F13–C24	1.332(2)	C4_3–F7_3	1.330(3)
C13–C14	1.380(3)	C4_3–F9_3	1.335(3)
C13–C18	1.381(3)	O1_4–C1_4	1.350(2)
C13–N1	1.443(2)	C1_4–C4_4	1.545(3)
F14–C14	1.335(2)	C1_4–C3_4	1.552(3)
C14–C15	1.376(3)	C1_4–C2_4	1.553(3)
F15–C15	1.330(2)	C2_4–F1_4	1.322(3)
C15–C16	1.379(3)	C2_4–F3_4	1.328(3)
F16–C16	1.327(2)	C2_4–F2_4	1.329(3)
C16–C17	1.380(3)	C3_4–F4_4	1.313(2)
F17–C17	1.330(2)	C3_4–F5_4	1.324(2)
C17–C18	1.380(3)	C3_4–F6_4	1.342(2)
F18–C18	1.332(2)	C4_4–F9_4	1.324(3)
C19–C24	1.379(3)	C4_4–F8_4	1.327(3)
C19–C20	1.384(3)	C4_4–F7_4	1.333(3)
C20–C21	1.377(3)	O1_5–C1_5	1.347(3)
C21–C22	1.377(3)	C1_5–C2_5	1.549(3)
C22–C23	1.379(3)	C1_5–C3_5	1.550(3)
C23–C24	1.376(3)	C1_5–C4_5	1.551(3)
N1–C1	1.392(2)	C2_5–F2_5	1.326(4)
O1_1–C1_1	1.362(2)	C2_5–F1_5	1.329(3)
C1_1–C4_1	1.554(3)	C2_5–F3_5	1.331(3)
C1_1–C3_1	1.554(3)	C3_5–F4_5	1.316(3)
C1_1–C2_1	1.557(3)	C3_5–F5_5	1.333(3)
C2_1–F3_1	1.326(2)	C3_5–F6_5	1.334(3)
C2_1–F1_1	1.328(2)	C4_5–F7_5	1.327(3)
C2_1–F2_1	1.346(2)	C4_5–F9_5	1.329(4)
C3_1–F4_1	1.328(2)	C4_5–F8_5	1.329(4)
C3_1–F5_1	1.329(2)	O1_6–C1_6	1.361(2)
C3_1–F6_1	1.341(2)	C1_6–C2_6	1.548(3)
C4_1–F9_1	1.325(2)	C1_6–C3_6	1.550(3)
C4_1–F7_1	1.337(2)	C1_6–C4_6	1.551(3)
C4_1–F8_1	1.337(2)	C2_6–F1_6	1.327(3)
O1_2–C1_2	1.350(2)	C2_6–F3_6	1.331(3)
C1_2–C3_2	1.551(3)	C2_6–F2_6	1.336(3)
C1_2–C2_2	1.553(3)	C3_6–F4_6	1.327(3)
C1_2–C4_2	1.553(3)	C3_6–F6_6	1.328(3)
C2_2–F1_2	1.327(2)	C3_6–F5_6	1.331(3)
C2_2–F3_2	1.330(3)	C4_6–F9_6	1.322(3)
C2_2–F2_2	1.335(3)	C4_6–F7_6	1.325(3)
C3_2–F4_2	1.321(2)	C4_6–F8_6	1.346(2)
C3_2–F5_2	1.323(2)	O1_7–C1_7	1.356(14)
C3_2–F6_2	1.343(2)	C1_7–C4_7	1.541(12)
C4_2–F9_2	1.323(2)	C1_7–C3_7	1.546(12)
C4_2–F8_2	1.335(2)	C1_7–C2_7	1.548(12)
C4_2–F7_2	1.335(2)	C2_7–F2_7	1.323(13)
O1_3–C1_3	1.346(2)	C2_7–F1_7	1.325(13)

C2_7–F3_7	1.329(13)
C3_7–F5_7	1.315(13)
C3_7–F4_7	1.318(13)
C3_7–F6_7	1.327(13)
C4_7–F7_7	1.329(13)
C4_7–F9_7	1.332(13)
C4_7–F8_7	1.334(13)

Atom–Atom–Atom	Angle [°]
O1_3–Al01–O1_2	114.78(9)
O1_3–Al01–O1_1	116.85(8)
O1_2–Al01–O1_1	111.67(7)
O1_3–Al01–F008	103.75(8)
O1_2–Al01–F008	105.24(6)
O1_1–Al01–F008	102.68(5)
O1_7–Al02–O1_4	130.2(6)
O1_5–Al02–O1_4	114.34(12)
O1_7–Al02–O1_6	97.0(6)
O1_5–Al02–O1_6	117.10(10)
O1_4–Al02–O1_6	111.59(8)
O1_7–Al02–F00G	106.2(7)
O1_5–Al02–F00G	103.31(10)
O1_4–Al02–F00G	106.15(7)
O1_6–Al02–F00G	102.59(6)
C8–N2–C2	121.70(16)
C8–N2–C19	118.70(16)
C2–N2–C19	119.40(16)
N2–C2–C3	122.54(17)
N2–C2–C1	119.19(17)
C3–C2–C1	118.21(17)
F4–C3–C4	116.51(17)
F4–C3–C2	122.01(18)
C4–C3–C2	121.48(18)
F3–C4–C3	120.51(18)
F3–C4–C5	119.07(18)
C3–C4–C5	120.42(18)
F2–C5–C6	120.31(18)
F2–C5–C4	119.97(18)
C6–C5–C4	119.69(18)
F1–C6–C5	116.29(18)
F1–C6–C1	122.03(18)
C5–C6–C1	121.68(18)
N1–C7–C12	121.62(17)
N1–C7–C8	119.51(17)
C12–C7–C8	118.86(17)
Al01–F008–Al01	180.0
N2–C8–C9	122.95(17)
N2–C8–C7	118.90(17)
C9–C8–C7	118.15(17)
F5–C9–C10	116.28(17)
F5–C9–C8	122.49(17)
C10–C9–C8	121.23(18)
Al02–F00G–Al02	180.0
F6–C10–C9	119.86(18)
F6–C10–C11	119.80(18)
C9–C10–C11	120.32(18)
F7–C11–C12	120.73(18)
F7–C11–C10	119.22(18)
C12–C11–C10	120.03(18)
F8–C12–C11	117.24(17)
F8–C12–C7	121.43(17)
C11–C12–C7	121.30(18)
C14–C13–C18	119.64(18)
C14–C13–N1	121.69(17)
C18–C13–N1	118.67(17)
F14–C14–C15	120.61(18)
F14–C14–C13	118.99(18)
C15–C14–C13	120.39(19)
F15–C15–C14	120.25(19)
F15–C15–C16	120.25(19)
C14–C15–C16	119.49(19)
F16–C16–C15	119.62(19)
F16–C16–C17	119.65(19)
C15–C16–C17	120.73(18)
F17–C17–C18	120.01(18)
F17–C17–C16	120.70(18)
C18–C17–C16	119.27(18)
F18–C18–C17	120.43(17)
F18–C18–C13	119.17(17)
C17–C18–C13	120.39(18)
C24–C19–C20	120.31(18)
C24–C19–N2	119.13(18)
C20–C19–N2	120.53(18)
F9–C20–C21	121.1(2)
F9–C20–C19	119.42(18)
C21–C20–C19	119.5(2)
F10–C21–C22	119.8(2)
F10–C21–C20	120.5(2)
C22–C21–C20	119.7(2)
F11–C22–C21	119.4(2)
F11–C22–C23	119.5(2)
C21–C22–C23	121.07(19)
F12–C23–C24	120.2(2)
F12–C23–C22	120.76(19)
C24–C23–C22	119.1(2)
F13–C24–C23	120.93(19)
F13–C24–C19	118.77(18)
C23–C24–C19	120.3(2)
C1–N1–C7	121.04(16)
C1–N1–C13	119.00(16)
C7–N1–C13	118.01(15)
N1–C1–C6	122.36(17)
N1–C1–C2	119.14(17)
C6–C1–C2	118.46(17)
C1_1–O1_1–Al01	145.64(13)
O1_1–C1_1–C4_1	111.54(15)
O1_1–C1_1–C3_1	109.04(15)
C4_1–C1_1–C3_1	109.91(15)
O1_1–C1_1–C2_1	107.37(15)
C4_1–C1_1–C2_1	109.55(16)
C3_1–C1_1–C2_1	109.36(15)
F3_1–C2_1–F1_1	107.97(16)
F3_1–C2_1–F2_1	107.09(16)
F1_1–C2_1–F2_1	107.49(16)

F3_1–C2_1–C1_1	111.47(16)	F5_3–C3_3–C1_3	110.91(19)
F1_1–C2_1–C1_1	110.73(16)	F6_3–C3_3–C1_3	111.74(18)
F2_1–C2_1–C1_1	111.90(16)	F8_3–C4_3–F7_3	108.31(19)
F4_1–C3_1–F5_1	107.98(16)	F8_3–C4_3–F9_3	107.65(19)
F4_1–C3_1–F6_1	107.72(16)	F7_3–C4_3–F9_3	107.81(18)
F5_1–C3_1–F6_1	107.38(16)	F8_3–C4_3–C1_3	112.05(18)
F4_1–C3_1–C1_1	110.10(16)	F7_3–C4_3–C1_3	111.16(18)
F5_1–C3_1–C1_1	111.23(16)	F9_3–C4_3–C1_3	109.71(19)
F6_1–C3_1–C1_1	112.25(16)	C1_4–O1_4–Al02	152.74(15)
F9_1–C4_1–F7_1	107.71(16)	O1_4–C1_4–C4_4	111.09(17)
F9_1–C4_1–F8_1	108.19(16)	O1_4–C1_4–C3_4	108.15(17)
F7_1–C4_1–F8_1	107.39(16)	C4_4–C1_4–C3_4	109.13(17)
F9_1–C4_1–C1_1	110.56(16)	O1_4–C1_4–C2_4	108.73(19)
F7_1–C4_1–C1_1	110.73(16)	C4_4–C1_4–C2_4	110.13(19)
F8_1–C4_1–C1_1	112.09(16)	C3_4–C1_4–C2_4	109.58(17)
C1_2–O1_2–Al01	151.33(13)	F1_4–C2_4–F3_4	107.6(2)
O1_2–C1_2–C3_2	107.61(15)	F1_4–C2_4–F2_4	108.4(2)
O1_2–C1_2–C2_2	110.04(16)	F3_4–C2_4–F2_4	107.9(2)
C3_2–C1_2–C2_2	109.33(16)	F1_4–C2_4–C1_4	110.5(2)
O1_2–C1_2–C4_2	110.61(16)	F3_4–C2_4–C1_4	110.4(2)
C3_2–C1_2–C4_2	110.08(16)	F2_4–C2_4–C1_4	111.9(2)
C2_2–C1_2–C4_2	109.15(16)	F4_4–C3_4–F5_4	107.84(17)
F1_2–C2_2–F3_2	107.96(17)	F4_4–C3_4–F6_4	107.28(17)
F1_2–C2_2–F2_2	108.03(17)	F5_4–C3_4–F6_4	106.76(17)
F3_2–C2_2–F2_2	107.41(17)	F4_4–C3_4–C1_4	110.53(17)
F1_2–C2_2–C1_2	110.80(17)	F5_4–C3_4–C1_4	112.01(17)
F3_2–C2_2–C1_2	110.42(17)	F6_4–C3_4–C1_4	112.17(16)
F2_2–C2_2–C1_2	112.07(17)	F9_4–C4_4–F8_4	108.32(19)
F4_2–C3_2–F5_2	107.76(16)	F9_4–C4_4–F7_4	107.1(2)
F4_2–C3_2–F6_2	107.19(17)	F8_4–C4_4–F7_4	108.1(2)
F5_2–C3_2–F6_2	107.26(17)	F9_4–C4_4–C1_4	110.72(18)
F4_2–C3_2–C1_2	111.34(17)	F8_4–C4_4–C1_4	112.4(2)
F5_2–C3_2–C1_2	110.87(16)	F7_4–C4_4–C1_4	110.08(18)
F6_2–C3_2–C1_2	112.19(16)	C1_5–O1_5–Al02	167.8(2)
F9_2–C4_2–F8_2	108.49(17)	O1_5–C1_5–C2_5	110.1(2)
F9_2–C4_2–F7_2	107.46(17)	O1_5–C1_5–C3_5	108.1(2)
F8_2–C4_2–F7_2	107.40(17)	C2_5–C1_5–C3_5	109.7(2)
F9_2–C4_2–C1_2	110.76(16)	O1_5–C1_5–C4_5	109.9(2)
F8_2–C4_2–C1_2	112.14(17)	C2_5–C1_5–C4_5	109.8(2)
F7_2–C4_2–C1_2	110.41(16)	C3_5–C1_5–C4_5	109.3(2)
C1_3–O1_3–Al01	162.67(15)	F2_5–C2_5–F1_5	107.6(3)
O1_3–C1_3–C3_3	108.51(18)	F2_5–C2_5–F3_5	107.6(3)
O1_3–C1_3–C4_3	109.43(18)	F1_5–C2_5–F3_5	107.1(2)
C3_3–C1_3–C4_3	109.12(17)	F2_5–C2_5–C1_5	112.9(3)
O1_3–C1_3–C2_3	110.81(16)	F1_5–C2_5–C1_5	110.7(2)
C3_3–C1_3–C2_3	109.41(17)	F3_5–C2_5–C1_5	110.6(2)
C4_3–C1_3–C2_3	109.53(17)	F4_5–C3_5–F5_5	108.3(2)
F1_3–C2_3–F3_3	107.08(18)	F4_5–C3_5–F6_5	107.7(3)
F1_3–C2_3–F2_3	107.63(18)	F5_5–C3_5–F6_5	107.3(3)
F3_3–C2_3–F2_3	107.88(19)	F4_5–C3_5–C1_5	111.4(2)
F1_3–C2_3–C1_3	111.05(18)	F5_5–C3_5–C1_5	110.2(2)
F3_3–C2_3–C1_3	110.37(18)	F6_5–C3_5–C1_5	111.8(3)
F2_3–C2_3–C1_3	112.60(17)	F7_5–C4_5–F9_5	108.0(2)
F4_3–C3_3–F5_3	107.55(19)	F7_5–C4_5–F8_5	107.1(3)
F4_3–C3_3–F6_3	107.44(19)	F9_5–C4_5–F8_5	108.1(3)
F5_3–C3_3–F6_3	107.36(19)	F7_5–C4_5–C1_5	111.2(2)
F4_3–C3_3–C1_3	111.61(19)	F9_5–C4_5–C1_5	110.6(3)

F8_5–C4_5–C1_5	111.7(3)
C1_6–O1_6–Al02	145.67(14)
O1_6–C1_6–C2_6	109.53(17)
O1_6–C1_6–C3_6	111.13(17)
C2_6–C1_6–C3_6	109.55(19)
O1_6–C1_6–C4_6	107.69(17)
C2_6–C1_6–C4_6	109.61(17)
C3_6–C1_6–C4_6	109.29(18)
F1_6–C2_6–F3_6	107.6(2)
F1_6–C2_6–F2_6	107.50(19)
F3_6–C2_6–F2_6	108.0(2)
F1_6–C2_6–C1_6	111.0(2)
F3_6–C2_6–C1_6	110.16(18)
F2_6–C2_6–C1_6	112.43(19)
F4_6–C3_6–F6_6	108.1(2)
F4_6–C3_6–F5_6	107.19(19)
F6_6–C3_6–F5_6	108.3(2)
F4_6–C3_6–C1_6	110.14(19)
F6_6–C3_6–C1_6	112.05(19)
F5_6–C3_6–C1_6	110.85(19)
F9_6–C4_6–F7_6	107.79(19)
F9_6–C4_6–F8_6	106.83(18)
F7_6–C4_6–F8_6	107.43(18)
F9_6–C4_6–C1_6	111.60(18)
F7_6–C4_6–C1_6	111.02(18)
F8_6–C4_6–C1_6	111.94(18)
C1_7–O1_7–Al02	158.3(14)
O1_7–C1_7–C4_7	110.1(13)
O1_7–C1_7–C3_7	107.9(13)
C4_7–C1_7–C3_7	109.4(12)
O1_7–C1_7–C2_7	107.9(13)
C4_7–C1_7–C2_7	110.4(12)
C3_7–C1_7–C2_7	111.1(12)
F2_7–C2_7–F1_7	110(2)
F2_7–C2_7–F3_7	107.5(19)
F1_7–C2_7–F3_7	107.2(17)
F2_7–C2_7–C1_7	111.4(19)
F1_7–C2_7–C1_7	111.3(16)
F3_7–C2_7–C1_7	109.6(13)
F5_7–C3_7–F4_7	108.0(16)
F5_7–C3_7–F6_7	109(2)
F4_7–C3_7–F6_7	109(2)
F5_7–C3_7–C1_7	110.7(13)
F4_7–C3_7–C1_7	109.8(13)
F6_7–C3_7–C1_7	110.9(19)
F7_7–C4_7–F9_7	107.7(17)
F7_7–C4_7–F8_7	106.5(19)
F9_7–C4_7–F8_7	106.7(19)
F7_7–C4_7–C1_7	111.3(13)
F9_7–C4_7–C1_7	113.1(14)
F8_7–C4_7–C1_7	111.2(18)

Symmetry transformations used to generate equivalent atoms:
#1: 1-X, 1-Y, 1-Z; #2: -X, 1-Y, 1-Z;

Table S7: Atomic coordinates and U_{eq} [Å^2] for[Fe(CO)$_5$*o*DFB][Al(OR^F)$_4$].

Atom	*x*	*y*	*z*	U_{eq}
Fe1	0.24996(3)	0.91845(3)	0.39989(2)	0.03278(9)
Al1	0.000000	0.30072(15)	0.250000	0.0268(3)
Al2	0.500000	0.30089(15)	0.250000	0.0263(3)
O1	0.11404(15)	0.9370(4)	0.4179(3)	0.0582(11)
O2	0.2501(2)	0.6585(3)	0.48027(14)	0.0673(6)
O3	0.38802(16)	0.9374(4)	0.4197(2)	0.0557(10)
O4	0.2498(2)	1.2062(2)	0.34909(13)	0.0548(5)
O5	0.2506(2)	0.7965(2)	0.25615(11)	0.0592(6)
C1	0.1646(2)	0.9298(4)	0.4115(3)	0.0428(11)
C2	0.2486(3)	0.7556(3)	0.45050(14)	0.0442(5)
C3	0.3362(2)	0.9296(4)	0.4111(3)	0.0404(10)
C4	0.2485(2)	1.0984(3)	0.36807(14)	0.0399(5)
C5	0.2502(3)	0.8388(3)	0.30941(13)	0.0420(5)
C1_1	0.2030(8)	1.2341(19)	0.5387(10)	0.047(3)
C2_1	0.2642(8)	1.2229(17)	0.5490(9)	0.051(3)
C3_1	0.2952(9)	1.315(2)	0.5891(11)	0.057(3)
H3_1	0.338145	1.305844	0.597701	0.068
C4_1	0.2605(10)	1.425(2)	0.6175(12)	0.052(3)
H4_1	0.280800	1.499160	0.639355	0.062
C5_1	0.1999(10)	1.422(2)	0.6130(12)	0.051(3)
H5_1	0.176276	1.481403	0.641537	0.061
C6_1	0.1697(8)	1.3353(18)	0.5683(10)	0.046(3)
H6_1	0.127021	1.346101	0.558406	0.056
F1_1	0.1750(10)	1.141(2)	0.4955(11)	0.0775(14)
F2_1	0.2902(9)	1.1134(17)	0.5189(8)	0.0698(14)
O1_2	0.0677(6)	0.2363(13)	0.2025(7)	0.0336(19)
C1_2	0.0897(6)	0.1277(17)	0.1693(9)	0.0333(14)
C2_2	0.0440(5)	0.0626(12)	0.1197(6)	0.0461(16)
F1_2	-0.0101(4)	0.0283(10)	0.1559(5)	0.047(2)
F2_2	0.0610(5)	-0.0528(14)	0.0919(7)	0.051(2)
F3_2	0.0226(6)	0.1453(15)	0.0717(7)	0.070(3)
C3_2	0.1450(5)	0.1794(11)	0.1282(7)	0.0573(18)
F4_2	0.1907(6)	0.2284(13)	0.1643(7)	0.070(2)
F5_2	0.1420(5)	0.2998(10)	0.1006(7)	0.077(2)
F6_2	0.1745(5)	0.0793(10)	0.0929(7)	0.068(3)
C4_2	0.1220(5)	0.0119(12)	0.2074(6)	0.0438(17)
F7_2	0.1573(6)	0.0529(13)	0.2588(5)	0.046(2)
F8_2	0.1619(7)	-0.0458(14)	0.1603(7)	0.072(3)
F9_2	0.0910(5)	-0.0891(11)	0.2310(6)	0.056(2)
O1_3	0.0278(3)	0.4095(9)	0.3151(5)	0.0392(19)
C1_3	0.0754(3)	0.4675(7)	0.3474(4)	0.0316(17)
C2_3	0.1275(4)	0.5173(8)	0.2988(4)	0.0491(19)
F1_3	0.1638(2)	0.4063(6)	0.2809(3)	0.0412(12)
F2_3	0.1643(5)	0.6096(8)	0.3294(5)	0.101(4)
F3_3	0.1100(5)	0.5853(9)	0.2433(4)	0.078(3)
C3_3	0.0517(4)	0.5977(7)	0.3863(4)	0.051(2)
F4_3	-0.0032(3)	0.5707(6)	0.4151(4)	0.062(2)
F5_3	0.0447(5)	0.6984(7)	0.3425(5)	0.103(3)
F6_3	0.0891(3)	0.6334(6)	0.4390(3)	0.0540(15)
C4_3	0.1031(3)	0.3712(7)	0.4017(3)	0.0352(14)
F7_3	0.0660(3)	0.3565(8)	0.4560(3)	0.0631(18)
F8_3	0.1602(3)	0.4036(8)	0.4256(4)	0.067(2)
F9_3	0.1124(2)	0.2473(5)	0.3710(3)	0.0430(11)
O1_4	0.4390(6)	0.2026(8)	0.2183(5)	0.042(2)

C1_4	0.4131(4)	0.1308(9)	0.1661(5)	0.0358(14)
C2_4	0.3459(4)	0.0981(9)	0.1839(5)	0.0700(19)
F1_4	0.3377(4)	0.0624(9)	0.2512(4)	0.090(2)
F2_4	0.3221(3)	-0.0076(9)	0.1504(5)	0.081(2)
F3_4	0.3089(3)	0.2002(9)	0.1787(6)	0.098(2)
C3_4	0.4102(5)	0.2206(11)	0.0981(6)	0.070(2)
F4_4	0.4618(5)	0.2096(10)	0.0620(5)	0.086(3)
F5_4	0.3849(8)	0.3412(11)	0.1138(8)	0.139(6)
F6_4	0.3669(6)	0.1617(14)	0.0565(6)	0.123(4)
C4_4	0.4518(4)	0.0036(10)	0.1530(6)	0.072(2)
F7_4	0.5129(3)	0.0561(12)	0.1484(7)	0.112(4)
F8_4	0.4421(5)	-0.0520(10)	0.0891(6)	0.099(4)
F9_4	0.4420(7)	-0.0769(12)	0.2081(8)	0.133(5)
O1_5	0.4654(5)	0.4310(10)	0.3011(5)	0.0322(15)
C1_5	0.4217(5)	0.4717(10)	0.3477(5)	0.0306(13)
C2_5	0.4506(5)	0.5932(9)	0.3877(5)	0.0390(16)
F1_5	0.5047(5)	0.5639(12)	0.4159(7)	0.052(2)
F2_5	0.4103(7)	0.6360(12)	0.4375(8)	0.055(3)
F3_5	0.4592(6)	0.7016(9)	0.3490(5)	0.062(2)
C3_5	0.3666(4)	0.5134(10)	0.3005(6)	0.0382(15)
F4_5	0.3321(7)	0.4079(13)	0.2769(7)	0.042(2)
F5_5	0.3821(5)	0.5815(12)	0.2430(6)	0.062(2)
F6_5	0.3276(5)	0.5996(9)	0.3340(5)	0.0556(19)
C4_5	0.3977(4)	0.3635(8)	0.4005(4)	0.0280(13)
F7_5	0.3963(5)	0.2415(8)	0.3711(6)	0.045(2)
F8_5	0.3440(4)	0.4038(10)	0.4275(4)	0.0475(18)
F9_5	0.4314(5)	0.3437(11)	0.4589(5)	0.048(2)
O1_11	0.5278(4)	0.3918(8)	0.1814(3)	0.0352(13)
C1_11	0.5716(4)	0.4775(10)	0.1579(5)	0.0519(17)
C2_11	0.5488(6)	0.5262(13)	0.0877(5)	0.098(3)
F1_11	0.5538(6)	0.4149(11)	0.0421(5)	0.113(4)
F2_11	0.5817(8)	0.6282(15)	0.0595(9)	0.125(5)
F3_11	0.4909(6)	0.5665(18)	0.0863(9)	0.134(5)
C3_11	0.5769(5)	0.6049(9)	0.2060(5)	0.082(2)
F4_11	0.5879(4)	0.5770(11)	0.2703(5)	0.066(2)
F5_11	0.5319(7)	0.6894(10)	0.1863(10)	0.168(6)
F6_11	0.6283(7)	0.6772(16)	0.1882(7)	0.165(6)
C4_11	0.6337(4)	0.3975(9)	0.1516(4)	0.0636(17)
F7_11	0.6592(6)	0.4087(15)	0.2161(6)	0.073(3)
F8_11	0.6696(4)	0.4516(12)	0.1029(6)	0.124(4)
F9_11	0.6216(5)	0.2669(10)	0.1265(7)	0.082(3)
O1_9	0.5649(7)	0.2283(15)	0.2925(8)	0.0296(12)
C1_9	0.5846(5)	0.1267(12)	0.3340(6)	0.0322(11)
C2_9	0.6122(6)	0.0069(11)	0.2961(6)	0.0480(15)
F1_9	0.5733(7)	-0.0989(13)	0.2848(10)	0.064(2)
F2_9	0.6480(7)	-0.0753(11)	0.3322(7)	0.068(2)
F3_9	0.6285(7)	0.0378(13)	0.2345(6)	0.063(2)
C3_9	0.6320(5)	0.2036(11)	0.3799(6)	0.0423(14)
F4_9	0.6007(7)	0.3221(13)	0.4008(10)	0.065(3)
F5_9	0.6748(4)	0.2601(10)	0.3513(6)	0.0538(18)
F6_9	0.6602(5)	0.1166(13)	0.4264(6)	0.063(2)
C4_9	0.5351(5)	0.0651(12)	0.3826(6)	0.0504(15)
F7_9	0.5004(7)	0.1454(11)	0.4110(8)	0.080(3)
F8_9	0.5645(8)	-0.0168(16)	0.4284(7)	0.060(3)
F9_9	0.4986(7)	-0.0086(16)	0.3349(9)	0.070(3)
O1_7	-0.0454(5)	0.3859(10)	0.1949(6)	0.059(2)
C1_7	-0.0692(4)	0.4913(10)	0.1605(5)	0.0470(17)

C2_7	-0.0743(4)	0.6199(8)	0.2103(5)	0.0646(18)
F1_7	-0.0207(4)	0.6809(7)	0.2158(5)	0.092(2)
F2_7	-0.1154(5)	0.7055(9)	0.1860(6)	0.111(3)
F3_7	-0.0859(4)	0.5690(11)	0.2708(5)	0.065(2)
C3_7	-0.1345(5)	0.4674(12)	0.1344(6)	0.095(2)
F4_7	-0.1333(6)	0.3414(12)	0.1058(8)	0.129(4)
F5_7	-0.1747(4)	0.4886(19)	0.1886(7)	0.152(4)
F6_7	-0.1479(6)	0.5613(13)	0.0842(6)	0.157(4)
C4_7	-0.0271(6)	0.5333(11)	0.1002(6)	0.100(3)
F7_7	-0.0440(7)	0.4311(10)	0.0471(4)	0.131(4)
F8_7	-0.0397(8)	0.6539(9)	0.0777(5)	0.148(5)
F9_7	0.0326(4)	0.5228(10)	0.1182(6)	0.128(3)
O1_8	-0.0607(3)	0.2031(7)	0.2802(4)	0.0326(13)
C1_8	-0.0849(4)	0.1294(11)	0.3322(6)	0.0354(13)
C2_8	-0.1526(4)	0.1062(11)	0.3011(6)	0.078(2)
F1_8	-0.1874(4)	0.1985(12)	0.3159(7)	0.117(3)
F2_8	-0.1811(3)	0.0144(10)	0.3349(6)	0.110(3)
F3_8	-0.1406(6)	0.0792(12)	0.2353(5)	0.111(3)
C3_8	-0.0579(4)	-0.0134(10)	0.3457(6)	0.0713(19)
F4_8	-0.0029(4)	-0.0258(11)	0.3683(8)	0.135(4)
F5_8	-0.0667(5)	-0.0943(8)	0.2948(6)	0.099(3)
F6_8	-0.0903(6)	-0.0695(10)	0.3998(7)	0.141(4)
C4_8	-0.0892(4)	0.2132(8)	0.3998(4)	0.0523(15)
F7_8	-0.0385(4)	0.2079(11)	0.4384(5)	0.078(2)
F8_8	-0.1368(3)	0.1673(9)	0.4411(4)	0.0658(18)
F9_8	-0.0961(6)	0.3409(8)	0.3910(4)	0.068(2)
O1_6	0.5299(4)	0.1715(12)	0.2956(6)	0.0296(12)
C1_6	0.5809(5)	0.1252(13)	0.3306(6)	0.0336(12)
C2_6	0.5720(6)	-0.0226(13)	0.3559(7)	0.0510(16)
F1_6	0.5959(9)	-0.1066(14)	0.3086(9)	0.075(3)
F2_6	0.6019(6)	-0.0499(14)	0.4162(7)	0.066(2)
F3_6	0.5115(4)	-0.0456(11)	0.3715(7)	0.060(2)
C3_6	0.5894(7)	0.2078(15)	0.3985(7)	0.0452(16)
F4_6	0.5847(7)	0.3403(13)	0.3840(8)	0.046(2)
F5_6	0.5491(7)	0.1642(18)	0.4471(8)	0.062(3)
F6_6	0.6483(6)	0.1966(18)	0.4221(8)	0.056(3)
C4_6	0.6370(4)	0.1406(11)	0.2825(5)	0.0347(13)
F7_6	0.6597(4)	0.2657(10)	0.2787(5)	0.0469(18)
F8_6	0.6865(3)	0.0726(10)	0.2999(5)	0.0449(17)
F9_6	0.6241(4)	0.1016(13)	0.2183(5)	0.045(2)
O1_12	0.4479(5)	0.3750(13)	0.3014(7)	0.0149(19)
C1_12	0.4319(6)	0.4813(14)	0.3441(7)	0.0300(16)
C2_12	0.4030(6)	0.4269(14)	0.4121(7)	0.0418(19)
F1_12	0.4478(8)	0.361(2)	0.4465(11)	0.049(3)
F2_12	0.3672(7)	0.5240(15)	0.4414(8)	0.059(3)
F3_12	0.3618(6)	0.3333(15)	0.3958(7)	0.043(2)
C3_12	0.3786(6)	0.5441(16)	0.3023(8)	0.038(2)
F4_12	0.4007(9)	0.548(3)	0.2385(8)	0.045(3)
F5_12	0.3247(5)	0.4790(13)	0.3038(8)	0.041(2)
F6_12	0.3559(9)	0.6580(18)	0.3297(12)	0.060(3)
C4_12	0.4849(5)	0.5805(12)	0.3605(7)	0.0351(18)
F7_12	0.5017(8)	0.6539(13)	0.3033(8)	0.057(3)
F8_12	0.4759(5)	0.6569(12)	0.4169(6)	0.035(2)
F9_12	0.5355(4)	0.5029(11)	0.3760(6)	0.032(2)
O1_10	0.0305(5)	0.1743(9)	0.2033(5)	0.0236(13)
C1_10	0.0813(6)	0.1245(12)	0.1676(6)	0.0312(14)
C2_10	0.1294(6)	0.2264(14)	0.1427(7)	0.0590(19)

F1_10	0.1610(5)	0.2685(12)	0.2040(7)	0.066(2)
F2_10	0.1546(7)	0.1942(19)	0.0821(8)	0.078(3)
F3_10	0.0979(10)	0.3476(16)	0.1279(11)	0.077(3)
C3_10	0.0445(5)	0.1103(11)	0.0984(5)	0.0355(16)
F4_10	-0.0140(4)	0.1177(12)	0.1197(6)	0.054(2)
F5_10	0.0642(7)	0.2032(14)	0.0534(6)	0.064(3)
F6_10	0.0492(6)	-0.0115(12)	0.0690(7)	0.052(2)
C4_10	0.0842(5)	-0.0111(11)	0.2051(5)	0.0430(16)
F7_10	0.0246(5)	-0.0584(10)	0.2099(6)	0.058(2)
F8_10	0.1233(6)	-0.1042(11)	0.1773(6)	0.058(3)
F9_10	0.0943(6)	0.0000(11)	0.2727(4)	0.062(2)
C1_13	0.2837(3)	1.2464(6)	0.5469(3)	0.0480(12)
C2_13	0.2205(3)	1.2446(6)	0.5486(3)	0.0487(12)
C3_13	0.1888(3)	1.3387(7)	0.5868(4)	0.0578(15)
H3_13	0.144985	1.340462	0.586853	0.069
C4_13	0.2230(4)	1.4331(7)	0.6263(4)	0.0607(17)
H4_13	0.202305	1.495884	0.655705	0.073
C5_13	0.2842(4)	1.4343(6)	0.6224(4)	0.0559(15)
H5_13	0.306366	1.503171	0.646507	0.067
C6_13	0.3161(4)	1.3408(8)	0.5853(4)	0.0617(17)
H6_13	0.359927	1.340282	0.585669	0.074
F1_13	0.3149(3)	1.1568(5)	0.5064(3)	0.0698(14)
F2_13	0.1916(3)	1.1485(6)	0.5106(3)	0.0775(14)

U_{eq} is defined as 1/3 of the trace of the orthogonalized U_{ij} tensor.

Table 8: Bond lengths and angles for $[Fe(CO)_5oDFB][Al(OR^F)_4]$.

Atom–Atom	**Length [Å]**
Fe1–C1	1.867(5)
Fe1–C4	1.872(3)
Fe1–C2	1.873(3)
Fe1–C3	1.885(5)
Fe1–C5	1.907(3)
Fe1–F2_1	3.109(16)
Fe1–F1_1	3.29(2)
Fe1–F2_13	3.351(6)
Fe1–F1_13	3.415(6)
Al1–O1_10	1.669(8)
Al1–O1_7	1.671(8)
Al1–O1_8	1.727(7)
Al1–O1_3	1.753(7)
Al1–O1_2	1.840(12)
Al2–O1_12	1.667(11)
Al2–O1_6	1.674(11)
Al2–O1_11	1.702(6)
Al2–O1_4	1.747(9)
Al2–O1_9	1.776(13)
Al2–O1_5	1.779(8)
O1–C1	1.104(6)
O2–C2	1.113(4)
O3–C3	1.136(6)
O4–C4	1.120(3)
O5–C5	1.105(3)
C1_1–C2_1	1.343(15)
C1_1–C6_1	1.354(13)
C1_1–F1_1	1.376(12)
C2_1–F2_1	1.346(12)
C2_1–C3_1	1.364(13)
C3_1–C4_1	1.426(14)
C3_1–H3_1	0.9500
C4_1–C5_1	1.316(16)
C4_1–H4_1	0.9500
C5_1–C6_1	1.376(14)
C5_1–H5_1	0.9500
C6_1–H6_1	0.9500
O1_2–C1_2	1.33(2)
C1_2–C2_2	1.518(15)
C1_2–C3_2	1.522(16)
C1_2–C4_2	1.524(15)
C2_2–F2_2	1.307(12)
C2_2–F3_2	1.314(12)
C2_2–F1_2	1.405(12)
C3_2–F5_2	1.298(12)
C3_2–F4_2	1.301(13)
C3_2–F6_2	1.354(10)
F4_2–F5_2	1.76(2)
C4_2–F9_2	1.282(12)
C4_2–F7_2	1.312(12)
C4_2–F8_2	1.374(12)
O1_3–C1_3	1.333(9)
C1_3–C4_3	1.531(9)
C1_3–C2_3	1.545(9)
C1_3–C3_3	1.568(8)
C2_3–F3_3	1.316(9)
C2_3–F2_3	1.343(9)
C2_3–F1_3	1.388(9)
C3_3–F5_3	1.308(9)

C3_3–F4_3	1.339(9)	O1_7–C1_7	1.332(10)
C3_3–F6_3	1.345(9)	C1_7–C3_7	1.520(11)
C4_3–F7_3	1.324(7)	C1_7–C4_7	1.532(11)
C4_3–F8_3	1.357(8)	C1_7–C2_7	1.589(10)
C4_3–F9_3	1.368(8)	C2_7–F3_7	1.292(10)
O1_4–C1_4	1.349(9)	C2_7–F1_7	1.311(10)
C1_4–C4_4	1.525(10)	C2_7–F2_7	1.311(9)
C1_4–C2_4	1.529(10)	C3_7–F4_7	1.354(11)
C1_4–C3_4	1.579(11)	C3_7–F6_7	1.366(11)
C2_4–F3_4	1.289(10)	C3_7–F5_7	1.373(11)
C2_4–F2_4	1.327(8)	C4_7–F8_7	1.291(11)
C2_4–F1_4	1.352(10)	C4_7–F9_7	1.343(11)
C3_4–F4_4	1.320(10)	C4_7–F7_7	1.477(11)
C3_4–F5_4	1.339(11)	O1_8–C1_8	1.343(15)
C3_4–F6_4	1.362(11)	C1_8–C4_8	1.540(11)
C4_4–F9_4	1.339(11)	C1_8–C3_8	1.542(12)
C4_4–F8_4	1.362(10)	C1_8–C2_8	1.601(11)
C4_4–F7_4	1.424(10)	C2_8–F1_8	1.213(11)
O1_5–C1_5	1.362(11)	C2_8–F2_8	1.271(11)
C1_5–C2_5	1.551(10)	C2_8–F3_8	1.319(11)
C1_5–C3_5	1.556(10)	C3_8–F4_8	1.274(10)
C1_5–C4_5	1.559(10)	C3_8–F5_8	1.275(11)
C2_5–F3_5	1.313(11)	C3_8–F6_8	1.370(11)
C2_5–F1_5	1.323(11)	C4_8–F9_8	1.276(10)
C2_5–F2_5	1.362(10)	C4_8–F7_8	1.326(10)
C3_5–F5_5	1.335(10)	C4_8–F8_8	1.378(8)
C3_5–F4_5	1.356(11)	O1_6–C1_6	1.371(12)
C3_5–F6_5	1.357(10)	C1_6–C4_6	1.534(11)
C4_5–F7_5	1.325(9)	C1_6–C2_6	1.544(12)
C4_5–F8_5	1.335(9)	C1_6–C3_6	1.548(12)
C4_5–F9_5	1.353(10)	C2_6–F1_6	1.333(12)
O1_11–C1_11	1.348(9)	C2_6–F2_6	1.353(12)
C1_11–C2_11	1.514(10)	C2_6–F3_6	1.363(12)
C1_11–C3_11	1.560(11)	C3_6–F4_6	1.335(13)
C1_11–C4_11	1.563(10)	C3_6–F5_6	1.350(12)
C2_11–F3_11	1.316(12)	C3_6–F6_6	1.359(12)
C2_11–F2_11	1.344(11)	C4_6–F8_6	1.309(9)
C2_11–F1_11	1.406(12)	C4_6–F9_6	1.322(10)
C3_11–F4_11	1.287(11)	C4_6–F7_6	1.325(11)
C3_11–F5_11	1.337(11)	O1_12–C1_12	1.373(13)
C3_11–F6_11	1.363(10)	C1_12–C3_12	1.537(12)
C4_11–F8_11	1.328(9)	C1_12–C4_12	1.538(12)
C4_11–F7_11	1.361(11)	C1_12–C2_12	1.546(12)
C4_11–F9_11	1.396(10)	C2_12–F3_12	1.318(13)
O1_9–C1_9	1.347(12)	C2_12–F1_12	1.343(13)
C1_9–C2_9	1.507(11)	C2_12–F2_12	1.352(12)
C1_9–C4_9	1.547(11)	C3_12–F4_12	1.318(13)
C1_9–C3_9	1.549(11)	C3_12–F5_12	1.332(12)
C2_9–F3_9	1.272(11)	C3_12–F6_12	1.332(13)
C2_9–F2_9	1.317(11)	C4_12–F8_12	1.334(11)
C2_9–F1_9	1.356(12)	C4_12–F7_12	1.363(12)
C3_9–F5_9	1.213(11)	C4_12–F9_12	1.368(11)
C3_9–F6_9	1.380(11)	O1_10–C1_10	1.386(13)
C3_9–F4_9	1.406(12)	C1_10–C4_10	1.516(11)
C4_9–F7_9	1.219(11)	C1_10–C2_10	1.522(11)
C4_9–F8_9	1.352(12)	C1_10–C3_10	1.557(11)
C4_9–F9_9	1.412(12)	C2_10–F2_10	1.325(12)

C2_10–F3_10	1.403(13)
C2_10–F1_10	1.423(12)
C3_10–F6_10	1.328(10)
C3_10–F5_10	1.329(11)
C3_10–F4_10	1.334(11)
C4_10–F9_10	1.323(11)
C4_10–F8_10	1.356(10)
C4_10–F7_10	1.377(12)
C1_13–F1_13	1.356(6)
C1_13–C2_13	1.369(7)
C1_13–C6_13	1.379(7)
C2_13–F2_13	1.347(6)
C2_13–C3_13	1.367(8)
C3_13–C4_13	1.408(8)
C3_13–H3_13	0.9500
C4_13–C5_13	1.328(9)
C4_13–H4_13	0.9500
C5_13–C6_13	1.352(8)
C5_13–H5_13	0.9500
C6_13–H6_13	0.9500

Atom–Atom–Atom	**Angle [°]**
C1–Fe1–C4	88.0(2)
C1–Fe1–C2	88.5(2)
C4–Fe1–C2	167.64(13)
C1–Fe1–C3	164.98(11)
C4–Fe1–C3	90.0(2)
C2–Fe1–C3	90.3(2)
C1–Fe1–C5	97.8(3)
C4–Fe1–C5	95.14(11)
C2–Fe1–C5	97.09(12)
C3–Fe1–C5	97.2(2)
C1–Fe1–F2_1	98.8(4)
C4–Fe1–F2_1	70.3(3)
C2–Fe1–F2_1	98.5(3)
C3–Fe1–F2_1	66.5(4)
C5–Fe1–F2_1	157.4(4)
C1–Fe1–F1_1	53.4(3)
C4–Fe1–F1_1	62.9(4)
C2–Fe1–F1_1	105.7(5)
C3–Fe1–F1_1	112.8(3)
C5–Fe1–F1_1	141.7(4)
F2_1–Fe1–F1_1	46.9(3)
C1–Fe1–F2_13	60.69(19)
C4–Fe1–F2_13	64.13(15)
C2–Fe1–F2_13	103.93(16)
C3–Fe1–F2_13	105.19(18)
C5–Fe1–F2_13	148.96(19)
C1–Fe1–F1_13	107.24(18)
C4–Fe1–F1_13	63.58(14)
C2–Fe1–F1_13	106.30(15)
C3–Fe1–F1_13	58.84(17)
C5–Fe1–F1_13	145.78(18)
F2_13–Fe1–F1_13	46.54(8)
O1_7–Al1–O1_8	92.4(4)
O1_7–Al1–O1_3	110.5(4)
O1_8–Al1–O1_3	111.1(4)
O1_7–Al1–O1_2	109.1(6)
O1_8–Al1–O1_2	125.6(5)
O1_3–Al1–O1_2	106.9(5)
O1_12–Al2–O1_6	106.5(6)
O1_11–Al2–O1_4	106.7(4)
O1_11–Al2–O1_9	106.7(6)
O1_4–Al2–O1_9	122.5(5)
O1_11–Al2–O1_5	101.5(4)
O1_4–Al2–O1_5	105.7(5)
O1_9–Al2–O1_5	111.6(6)
O1–C1–Fe1	179.5(6)
O2–C2–Fe1	177.5(6)
O3–C3–Fe1	178.1(5)
O4–C4–Fe1	177.6(5)
O5–C5–Fe1	177.9(3)
C2_1–C1_1–C6_1	121.6(9)
C2_1–C1_1–F1_1	118.1(12)
C6_1–C1_1–F1_1	120.3(12)
C1_1–C2_1–F2_1	114.6(12)
C1_1–C2_1–C3_1	121.0(9)
F2_1–C2_1–C3_1	124.4(12)
C2_1–C3_1–C4_1	117.3(11)
C2_1–C3_1–H3_1	121.3
C4_1–C3_1–H3_1	121.3
C5_1–C4_1–C3_1	118.9(10)
C5_1–C4_1–H4_1	120.5
C3_1–C4_1–H4_1	120.5
C4_1–C5_1–C6_1	121.9(10)
C4_1–C5_1–H5_1	119.1
C6_1–C5_1–H5_1	119.1
C1_1–C6_1–C5_1	117.6(11)
C1_1–C6_1–H6_1	121.2
C5_1–C6_1–H6_1	121.2
C1_1–F1_1–Fe1	124.1(11)
C2_1–F2_1–Fe1	133.7(11)
C1_2–O1_2–Al1	143.0(10)
O1_2–C1_2–C2_2	113.9(12)
O1_2–C1_2–C3_2	105.3(10)
C2_2–C1_2–C3_2	109.2(12)
O1_2–C1_2–C4_2	122.2(13)
C2_2–C1_2–C4_2	106.7(11)
C3_2–C1_2–C4_2	97.9(11)
F2_2–C2_2–F3_2	110.4(12)
F2_2–C2_2–F1_2	103.3(10)
F3_2–C2_2–F1_2	101.7(11)
F2_2–C2_2–C1_2	116.0(11)
F3_2–C2_2–C1_2	114.3(10)
F1_2–C2_2–C1_2	109.6(10)
F5_2–C3_2–F4_2	85.4(11)
F5_2–C3_2–F6_2	118.8(11)
F4_2–C3_2–F6_2	100.2(11)
F5_2–C3_2–C1_2	118.4(11)
F4_2–C3_2–C1_2	116.4(11)
F6_2–C3_2–C1_2	112.9(11)
C3_2–F4_2–F5_2	47.2(7)
C3_2–F5_2–F4_2	47.4(7)
F9_2–C4_2–F7_2	106.1(11)

F9_2–C4_2–F8_2	104.1(11)	O1_5–C1_5–C3_5	103.1(8)
F7_2–C4_2–F8_2	104.9(10)	C2_5–C1_5–C3_5	113.3(8)
F9_2–C4_2–C1_2	120.5(10)	O1_5–C1_5–C4_5	117.3(8)
F7_2–C4_2–C1_2	113.6(10)	C2_5–C1_5–C4_5	109.7(7)
F8_2–C4_2–C1_2	106.2(11)	C3_5–C1_5–C4_5	107.6(7)
C1_3–O1_3–Al1	149.3(6)	F3_5–C2_5–F1_5	106.4(10)
O1_3–C1_3–C4_3	110.9(7)	F3_5–C2_5–F2_5	103.8(9)
O1_3–C1_3–C2_3	114.8(7)	F1_5–C2_5–F2_5	110.3(11)
C4_3–C1_3–C2_3	108.8(6)	F3_5–C2_5–C1_5	113.7(9)
O1_3–C1_3–C3_3	108.4(6)	F1_5–C2_5–C1_5	113.1(9)
C4_3–C1_3–C3_3	108.0(6)	F2_5–C2_5–C1_5	109.1(9)
C2_3–C1_3–C3_3	105.6(6)	F5_5–C3_5–F4_5	104.2(10)
F3_3–C2_3–F2_3	100.6(8)	F5_5–C3_5–F6_5	103.7(9)
F3_3–C2_3–F1_3	111.2(7)	F4_5–C3_5–F6_5	107.0(10)
F2_3–C2_3–F1_3	107.6(7)	F5_5–C3_5–C1_5	114.9(9)
F3_3–C2_3–C1_3	116.1(8)	F4_5–C3_5–C1_5	114.7(9)
F2_3–C2_3–C1_3	112.5(6)	F6_5–C3_5–C1_5	111.5(9)
F1_3–C2_3–C1_3	108.4(6)	F7_5–C4_5–F8_5	114.5(9)
F5_3–C3_3–F4_3	108.3(9)	F7_5–C4_5–F9_5	103.7(8)
F5_3–C3_3–F6_3	111.0(8)	F8_5–C4_5–F9_5	100.9(8)
F4_3–C3_3–F6_3	105.9(7)	F7_5–C4_5–C1_5	110.3(8)
F5_3–C3_3–C1_3	110.4(6)	F8_5–C4_5–C1_5	110.0(7)
F4_3–C3_3–C1_3	109.1(6)	F9_5–C4_5–C1_5	117.2(8)
F6_3–C3_3–C1_3	112.0(7)	C1_11–O1_11–Al2	146.8(6)
F7_3–C4_3–F8_3	108.2(7)	O1_11–C1_11–C2_11	105.4(8)
F7_3–C4_3–F9_3	109.4(6)	O1_11–C1_11–C3_11	110.8(8)
F8_3–C4_3–F9_3	102.7(6)	C2_11–C1_11–C3_11	107.4(8)
F7_3–C4_3–C1_3	111.5(6)	O1_11–C1_11–C4_11	108.6(8)
F8_3–C4_3–C1_3	116.2(6)	C2_11–C1_11–C4_11	111.8(8)
F9_3–C4_3–C1_3	108.3(6)	C3_11–C1_11–C4_11	112.7(8)
C1_4–O1_4–Al2	149.7(9)	F3_11–C2_11–F2_11	105.8(12)
O1_4–C1_4–C4_4	108.8(8)	F3_11–C2_11–F1_11	107.1(12)
O1_4–C1_4–C2_4	109.9(8)	F2_11–C2_11–F1_11	106.7(11)
C4_4–C1_4–C2_4	112.8(7)	F3_11–C2_11–C1_11	115.1(11)
O1_4–C1_4–C3_4	109.9(8)	F2_11–C2_11–C1_11	114.9(11)
C4_4–C1_4–C3_4	110.1(7)	F1_11–C2_11–C1_11	106.6(9)
C2_4–C1_4–C3_4	105.3(7)	F4_11–C3_11–F5_11	122.6(12)
F3_4–C2_4–F2_4	109.2(8)	F4_11–C3_11–F6_11	101.6(10)
F3_4–C2_4–F1_4	101.2(8)	F5_11–C3_11–F6_11	101.6(11)
F2_4–C2_4–F1_4	102.1(8)	F4_11–C3_11–C1_11	114.3(8)
F3_4–C2_4–C1_4	114.4(8)	F5_11–C3_11–C1_11	106.1(9)
F2_4–C2_4–C1_4	115.2(6)	F6_11–C3_11–C1_11	109.2(10)
F1_4–C2_4–C1_4	113.2(8)	F8_11–C4_11–F7_11	111.9(10)
F4_4–C3_4–F5_4	122.5(11)	F8_11–C4_11–F9_11	103.5(9)
F4_4–C3_4–F6_4	103.8(10)	F7_11–C4_11–F9_11	117.8(10)
F5_4–C3_4–F6_4	103.1(12)	F8_11–C4_11–C1_11	110.9(8)
F4_4–C3_4–C1_4	110.9(9)	F7_11–C4_11–C1_11	103.8(8)
F5_4–C3_4–C1_4	108.9(10)	F9_11–C4_11–C1_11	109.1(7)
F6_4–C3_4–C1_4	106.0(9)	C1_9–O1_9–Al2	145.2(12)
F9_4–C4_4–F8_4	116.9(11)	O1_9–C1_9–C2_9	114.8(11)
F9_4–C4_4–F7_4	114.3(11)	O1_9–C1_9–C4_9	115.3(11)
F8_4–C4_4–F7_4	103.4(9)	C2_9–C1_9–C4_9	105.1(9)
F9_4–C4_4–C1_4	105.5(9)	O1_9–C1_9–C3_9	100.7(10)
F8_4–C4_4–C1_4	113.1(8)	C2_9–C1_9–C3_9	113.2(10)
F7_4–C4_4–C1_4	103.0(8)	C4_9–C1_9–C3_9	107.8(9)
C1_5–O1_5–Al2	150.1(9)	F3_9–C2_9–F2_9	118.2(12)
O1_5–C1_5–C2_5	105.8(8)	F3_9–C2_9–F1_9	101.9(12)

F2_9–C2_9–F1_9	88.9(11)	F4_8–C3_8–C1_8	120.0(9)
F3_9–C2_9–C1_9	111.9(10)	F5_8–C3_8–C1_8	112.4(8)
F2_9–C2_9–C1_9	117.3(10)	F6_8–C3_8–C1_8	107.4(9)
F1_9–C2_9–C1_9	115.4(10)	F9_8–C4_8–F7_8	102.2(9)
F5_9–C3_9–F6_9	103.7(9)	F9_8–C4_8–F8_8	108.0(8)
F5_9–C3_9–F4_9	96.9(10)	F7_8–C4_8–F8_8	106.5(8)
F6_9–C3_9–F4_9	122.7(12)	F9_8–C4_8–C1_8	114.9(8)
F5_9–C3_9–C1_9	118.2(10)	F7_8–C4_8–C1_8	113.6(7)
F6_9–C3_9–C1_9	111.1(9)	F8_8–C4_8–C1_8	110.9(7)
F4_9–C3_9–C1_9	104.4(10)	C1_6–O1_6–Al2	145.2(10)
F7_9–C4_9–F8_9	112.6(13)	O1_6–C1_6–C4_6	108.1(9)
F7_9–C4_9–F9_9	106.1(13)	O1_6–C1_6–C2_6	111.6(10)
F8_9–C4_9–F9_9	112.5(12)	C4_6–C1_6–C2_6	112.4(9)
F7_9–C4_9–C1_9	116.4(10)	O1_6–C1_6–C3_6	109.6(10)
F8_9–C4_9–C1_9	107.4(10)	C4_6–C1_6–C3_6	111.1(9)
F9_9–C4_9–C1_9	101.3(10)	C2_6–C1_6–C3_6	104.0(10)
C1_7–O1_7–Al1	158.7(10)	F1_6–C2_6–F2_6	106.0(13)
O1_7–C1_7–C3_7	113.8(9)	F1_6–C2_6–F3_6	114.9(13)
O1_7–C1_7–C4_7	110.8(9)	F2_6–C2_6–F3_6	103.9(11)
C3_7–C1_7–C4_7	110.3(9)	F1_6–C2_6–C1_6	108.5(11)
O1_7–C1_7–C2_7	110.3(9)	F2_6–C2_6–C1_6	113.4(11)
C3_7–C1_7–C2_7	104.9(7)	F3_6–C2_6–C1_6	110.1(9)
C4_7–C1_7–C2_7	106.4(8)	F4_6–C3_6–F5_6	113.8(13)
F3_7–C2_7–F1_7	106.1(9)	F4_6–C3_6–F6_6	102.8(12)
F3_7–C2_7–F2_7	115.9(9)	F5_6–C3_6–F6_6	110.5(13)
F1_7–C2_7–F2_7	109.7(9)	F4_6–C3_6–C1_6	109.1(11)
F3_7–C2_7–C1_7	104.4(8)	F5_6–C3_6–C1_6	109.9(12)
F1_7–C2_7–C1_7	110.6(7)	F6_6–C3_6–C1_6	110.6(12)
F2_7–C2_7–C1_7	110.1(8)	F8_6–C4_6–F9_6	105.2(9)
F4_7–C3_7–F6_7	109.6(11)	F8_6–C4_6–F7_6	100.5(9)
F4_7–C3_7–F5_7	117.3(12)	F9_6–C4_6–F7_6	107.2(10)
F6_7–C3_7–F5_7	107.4(11)	F8_6–C4_6–C1_6	116.5(10)
F4_7–C3_7–C1_7	104.9(8)	F9_6–C4_6–C1_6	111.5(8)
F6_7–C3_7–C1_7	109.1(9)	F7_6–C4_6–C1_6	114.7(9)
F5_7–C3_7–C1_7	108.4(9)	C1_12–O1_12–Al2	148.9(10)
F8_7–C4_7–F9_7	111.1(12)	O1_12–C1_12–C3_12	100.5(10)
F8_7–C4_7–F7_7	109.8(10)	O1_12–C1_12–C4_12	114.7(10)
F9_7–C4_7–F7_7	111.4(11)	C3_12–C1_12–C4_12	114.4(10)
F8_7–C4_7–C1_7	112.0(10)	O1_12–C1_12–C2_12	110.2(11)
F9_7–C4_7–C1_7	111.0(9)	C3_12–C1_12–C2_12	106.0(10)
F7_7–C4_7–C1_7	101.0(8)	C4_12–C1_12–C2_12	110.4(10)
C1_8–O1_8–Al1	147.9(7)	F3_12–C2_12–F1_12	105.6(14)
O1_8–C1_8–C4_8	111.3(8)	F3_12–C2_12–F2_12	101.8(12)
O1_8–C1_8–C3_8	117.9(8)	F1_12–C2_12–F2_12	123.4(15)
C4_8–C1_8–C3_8	111.6(8)	F3_12–C2_12–C1_12	108.3(11)
O1_8–C1_8–C2_8	99.0(8)	F1_12–C2_12–C1_12	106.9(12)
C4_8–C1_8–C2_8	109.6(7)	F2_12–C2_12–C1_12	109.9(12)
C3_8–C1_8–C2_8	106.4(7)	F4_12–C3_12–F5_12	110.7(15)
F1_8–C2_8–F2_8	96.3(10)	F4_12–C3_12–F6_12	118.5(17)
F1_8–C2_8–F3_8	119.8(12)	F5_12–C3_12–F6_12	94.1(13)
F2_8–C2_8–F3_8	116.3(10)	F4_12–C3_12–C1_12	103.0(11)
F1_8–C2_8–C1_8	112.1(9)	F5_12–C3_12–C1_12	117.1(12)
F2_8–C2_8–C1_8	110.8(9)	F6_12–C3_12–C1_12	114.1(14)
F3_8–C2_8–C1_8	101.9(8)	F8_12–C4_12–F7_12	113.4(11)
F4_8–C3_8–F5_8	110.0(10)	F8_12–C4_12–F9_12	104.7(10)
F4_8–C3_8–F6_8	100.5(11)	F7_12–C4_12–F9_12	104.9(11)
F5_8–C3_8–F6_8	104.7(10)	F8_12–C4_12–C1_12	114.5(10)

F7_12–C4_12–C1_12	111.7(11)
F9_12–C4_12–C1_12	106.8(10)
C1_10–O1_10–Al1	147.5(9)
O1_10–C1_10–C4_10	96.2(8)
O1_10–C1_10–C2_10	117.9(11)
C4_10–C1_10–C2_10	134.3(11)
O1_10–C1_10–C3_10	92.7(8)
C4_10–C1_10–C3_10	110.3(9)
C2_10–C1_10–C3_10	98.1(8)
F2_10–C2_10–F3_10	103.0(13)
F2_10–C2_10–F1_10	126.9(12)
F3_10–C2_10–F1_10	98.9(12)
F2_10–C2_10–C1_10	113.7(11)
F3_10–C2_10–C1_10	106.7(12)
F1_10–C2_10–C1_10	105.1(9)
F6_10–C3_10–F5_10	108.5(11)
F6_10–C3_10–F4_10	104.7(10)
F5_10–C3_10–F4_10	117.9(11)
F6_10–C3_10–C1_10	114.0(10)
F5_10–C3_10–C1_10	109.2(10)
F4_10–C3_10–C1_10	102.7(8)
F9_10–C4_10–F8_10	109.8(9)
F9_10–C4_10–F7_10	96.7(10)
F8_10–C4_10–F7_10	112.7(11)
F9_10–C4_10–C1_10	113.6(10)
F8_10–C4_10–C1_10	115.6(10)
F7_10–C4_10–C1_10	106.9(9)
F1_13–C1_13–C2_13	120.3(6)
F1_13–C1_13–C6_13	119.3(6)
C2_13–C1_13–C6_13	120.4(6)
F2_13–C2_13–C3_13	122.2(6)
F2_13–C2_13–C1_13	117.4(7)
C3_13–C2_13–C1_13	120.4(5)
C2_13–C3_13–C4_13	118.1(5)
C2_13–C3_13–H3_13	120.9
C4_13–C3_13–H3_13	120.9
C5_13–C4_13–C3_13	120.1(6)
C5_13–C4_13–H4_13	120.0
C3_13–C4_13–H4_13	120.0
C4_13–C5_13–C6_13	122.2(6)
C4_13–C5_13–H5_13	118.9
C6_13–C5_13–H5_13	118.9
C5_13–C6_13–C1_13	118.7(6)
C5_13–C6_13–H6_13	120.7
C1_13–C6_13–H6_13	120.7
C1_13–F1_13–Fe1	125.7(4)
C2_13–F2_13–Fe1	129.9(4)

Table S9: Atomic coordinates and U_{eq} [Å^2] for $[Fe_2(CO)_8Br][F\text{-}\{Al(OR^F)_3\}_2]$.

Atom	*x*	*y*	*z*	U_{eq}
Fe1	0.57591(5)	0.41631(6)	0.75670(4)	0.01843(19)
O1	0.5543(3)	0.4394(4)	0.8899(2)	0.0304(10)
C1	0.5592(3)	0.4305(4)	0.8390(3)	0.0225(13)
Br2	0.500000	0.27681(6)	0.750000	0.0267(2)
O2	0.6139(3)	0.6224(3)	0.7462(2)	0.0355(11)
Al03	0.57839(9)	0.93444(12)	0.52138(7)	0.0140(3)
O3	0.7216(2)	0.3324(4)	0.7853(2)	0.0321(11)
C3	0.5950(3)	0.4014(5)	0.6738(3)	0.0247(13)
F004	0.500000	1.000000	0.500000	0.0223(10)
O4	0.6095(3)	0.3908(4)	0.6244(2)	0.0389(13)
C4	0.6668(3)	0.3645(4)	0.7741(3)	0.0219(12)
C2	0.5983(3)	0.5438(4)	0.7502(3)	0.0237(13)
O1_1	0.5474(3)	0.8360(3)	0.5589(2)	0.0313(11)
C1_1	0.5199(3)	0.7461(4)	0.5666(2)	0.0226(12)
C2_1	0.4684(3)	0.7468(4)	0.6234(3)	0.0270(13)
F1_1	0.5077(2)	0.7494(3)	0.67486(16)	0.0349(9)
F2_1	0.4267(2)	0.6678(3)	0.62509(17)	0.0315(9)
F3_1	0.4256(3)	0.8227(3)	0.6226(2)	0.0434(11)
C3_1	0.4762(3)	0.7142(5)	0.5095(3)	0.0284(13)
F4_1	0.5132(2)	0.7365(3)	0.45913(16)	0.0331(9)
F5_1	0.4127(2)	0.7609(4)	0.50727(19)	0.0426(11)
F6_1	0.4630(2)	0.6199(3)	0.50893(19)	0.0407(10)
C4_1	0.5840(3)	0.6746(4)	0.5781(3)	0.0272(13)
F7_1	0.6161(2)	0.6498(3)	0.52615(19)	0.0388(10)
F8_1	0.5609(2)	0.5934(3)	0.6055(2)	0.0392(10)
F9_1	0.6342(2)	0.7139(3)	0.6142(2)	0.0424(11)
O1_2	0.6187(2)	0.9199(3)	0.45201(17)	0.0189(8)
C1_2	0.6830(3)	0.9092(4)	0.4218(2)	0.0176(11)
C2_2	0.7192(3)	0.8121(4)	0.4398(3)	0.0265(13)
F1_2	0.6820(2)	0.7380(3)	0.41588(19)	0.0345(9)
F2_2	0.7880(2)	0.8055(3)	0.4202(2)	0.0449(12)
F3_2	0.7189(2)	0.8025(3)	0.50013(17)	0.0352(9)
C3_2	0.7367(3)	0.9940(5)	0.4364(3)	0.0276(13)
F4_2	0.7000(2)	1.0772(3)	0.43895(19)	0.0369(9)
F5_2	0.7698(2)	0.9808(3)	0.48972(17)	0.0379(10)
F6_2	0.7885(2)	1.0038(3)	0.39358(19)	0.0417(11)
C4_2	0.6655(3)	0.9101(4)	0.3525(2)	0.0218(11)
F7_2	0.6477(2)	0.9985(3)	0.33409(16)	0.0310(9)
F8_2	0.7220(2)	0.8795(3)	0.31877(17)	0.0326(9)
F9_2	0.6092(2)	0.8518(3)	0.34065(16)	0.0295(8)
O1_3	0.6290(12)	1.0091(16)	0.5682(6)	0.018(4)
C1_3	0.6457(5)	1.0365(7)	0.6261(5)	0.018(2)
C2_3	0.6562(5)	1.1480(6)	0.6254(4)	0.025(2)
F1_3	0.5910(5)	1.1907(6)	0.6212(3)	0.038(2)
F2_3	0.6885(8)	1.1813(10)	0.6758(6)	0.039(3)
F3_3	0.6966(10)	1.1746(15)	0.5779(8)	0.035(4)
C3_3	0.7179(5)	0.9882(6)	0.6464(4)	0.0224(19)
F4_3	0.7177(11)	0.8945(10)	0.6334(10)	0.034(4)
F5_3	0.7755(4)	1.0291(6)	0.6190(5)	0.032(2)
F6_3	0.7292(7)	0.9969(11)	0.7066(4)	0.033(3)
C4_3	0.5839(5)	1.0099(7)	0.6711(4)	0.025(2)
F7_3	0.5896(5)	0.9185(5)	0.6893(3)	0.0323(18)
F8_3	0.5829(14)	1.0647(13)	0.7211(5)	0.033(4)
F9_3	0.5191(8)	1.0208(14)	0.6437(12)	0.036(4)

O1_4	0.6322(18)	1.003(2)	0.5659(9)	0.017(5)
C1_4	0.6454(7)	1.0299(9)	0.6244(7)	0.018(3)
C2_4	0.7047(6)	1.1109(9)	0.6230(6)	0.024(3)
F1_4	0.6903(15)	1.174(2)	0.5786(11)	0.030(6)
F2_4	0.7088(11)	1.1596(15)	0.6753(8)	0.034(4)
F3_4	0.7702(6)	1.0713(10)	0.6128(7)	0.035(3)
C3_4	0.6748(6)	0.9433(8)	0.6617(6)	0.021(3)
F4_4	0.6211(6)	0.8880(8)	0.6823(5)	0.026(2)
F5_4	0.7201(15)	0.8903(15)	0.6280(14)	0.028(6)
F6_4	0.7117(11)	0.9736(16)	0.7111(7)	0.028(4)
C4_4	0.5744(7)	1.0684(9)	0.6545(6)	0.022(3)
F7_4	0.5180(11)	1.0105(19)	0.6432(18)	0.029(6)
F8_4	0.582(2)	1.077(2)	0.7147(7)	0.033(6)
F9_4	0.5581(6)	1.1563(7)	0.6328(5)	0.029(2)

U_{eq} is defined as 1/3 of the trace of the orthogonalized U_{ij} tensor.

Table S10: Bond lengths and angles for $[Fe_2(CO)_8Br][F\text{-}\{Al(OR^F)_3\}_2]$.

Atom–Atom	**Length [Å]**
Fe1–C2	1.818(6)
Fe1–C1	1.840(6)
Fe1–C4	1.849(6)
Fe1–C3	1.862(7)
Fe1–Br2	2.3832(11)
Fe1–Fe1$^{\#1}$	2.7901(17)
O1–C1	1.126(8)
O2–C2	1.129(7)
Al03–O1_4	1.68(2)
Al03–O1_1	1.691(4)
Al03–O1_2	1.702(4)
Al03–O1_3	1.725(16)
Al03–F004	1.7598(16)
O3–C4	1.123(8)
C3–O4	1.124(8)
O1_1–C1_1	1.353(7)
C1_1–C3_1	1.550(7)
C1_1–C4_1	1.555(7)
C1_1–C2_1	1.559(7)
C2_1–F3_1	1.311(7)
C2_1–F2_1	1.335(7)
C2_1–F1_1	1.337(6)
C3_1–F6_1	1.328(7)
C3_1–F5_1	1.330(7)
C3_1–F4_1	1.331(7)
C4_1–F7_1	1.326(7)
C4_1–F9_1	1.327(7)
C4_1–F8_1	1.343(7)
O1_2–C1_2	1.357(6)
C1_2–C2_2	1.549(7)
C1_2–C4_2	1.552(7)
C1_2–C3_2	1.563(7)
C2_2–F3_2	1.330(6)
C2_2–F2_2	1.333(6)
C2_2–F1_2	1.337(7)
C3_2–F5_2	1.328(6)
C3_2–F4_2	1.335(7)
C3_2–F6_2	1.341(6)
C4_2–F7_2	1.329(6)
C4_2–F9_2	1.335(6)
C4_2–F8_2	1.338(6)
O1_3–C1_3	1.360(10)
C1_3–C3_3	1.544(10)
C1_3–C4_3	1.544(10)
C1_3–C2_3	1.557(10)
C2_3–F3_3	1.328(12)
C2_3–F1_3	1.334(10)
C2_3–F2_3	1.335(10)
C3_3–F4_3	1.330(12)
C3_3–F5_3	1.339(10)
C3_3–F6_3	1.340(10)
C4_3–F7_3	1.333(10)
C4_3–F8_3	1.333(11)
C4_3–F9_3	1.336(12)
O1_4–C1_4	1.357(13)
C1_4–C3_4	1.549(12)
C1_4–C4_4	1.551(12)
C1_4–C2_4	1.560(12)
C2_4–F1_4	1.329(13)
C2_4–F2_4	1.332(12)
C2_4–F3_4	1.337(12)
C3_4–F4_4	1.325(11)
C3_4–F5_4	1.330(13)
C3_4–F6_4	1.341(12)
C4_4–F7_4	1.329(13)
C4_4–F8_4	1.332(12)
C4_4–F9_4	1.341(11)

Atom–Atom–Atom	**Angle [°]**
C2–Fe1–C1	90.6(3)
C2–Fe1–C4	101.0(3)
C1–Fe1–C4	89.3(3)
C2–Fe1–C3	89.4(3)
C1–Fe1–C3	178.7(3)
C4–Fe1–C3	89.5(3)

C2–Fe1–Br2	156.0(2)	F3_2–C2_2–F1_2	108.1(5)
C1–Fe1–Br2	92.87(19)	F2_2–C2_2–F1_2	107.5(5)
C4–Fe1–Br2	102.76(19)	F3_2–C2_2–C1_2	109.8(5)
C3–Fe1–Br2	87.6(2)	F2_2–C2_2–C1_2	112.4(5)
C2–Fe1–Fe1	102.4(2)	F1_2–C2_2–C1_2	110.5(5)
C1–Fe1–Fe1	86.5(2)	F5_2–C3_2–F4_2	108.2(5)
C4–Fe1–Fe1	156.19(19)	F5_2–C3_2–F6_2	107.9(5)
C3–Fe1–Fe1	94.8(2)	F4_2–C3_2–F6_2	107.2(5)
Br2–Fe1–Fe1	54.17(2)	F5_2–C3_2–C1_2	111.3(5)
O1–C1–Fe1	175.1(6)	F4_2–C3_2–C1_2	110.0(5)
Fe1–Br2–Fe1	71.66(5)	F6_2–C3_2–C1_2	112.0(5)
O1_4–Al03–O1_1	111.8(11)	F7_2–C4_2–F9_2	108.1(5)
O1_4–Al03–O1_2	109.4(10)	F7_2–C4_2–F8_2	108.2(5)
O1_1–Al03–O1_2	119.0(2)	F9_2–C4_2–F8_2	107.2(5)
O1_1–Al03–O1_3	112.0(7)	F7_2–C4_2–C1_2	110.8(4)
O1_2–Al03–O1_3	111.7(7)	F9_2–C4_2–C1_2	110.1(4)
O1_4–Al03–F004	109.8(12)	F8_2–C4_2–C1_2	112.3(4)
O1_1–Al03–F004	105.82(19)	C1_3–O1_3–Al03	147.4(16)
O1_2–Al03–F004	100.14(15)	O1_3–C1_3–C3_3	109.9(11)
O1_3–Al03–F004	106.6(8)	O1_3–C1_3–C4_3	111.4(11)
O4–C3–Fe1	176.8(6)	C3_3–C1_3–C4_3	109.8(7)
Al03–F004–Al03	180.0	O1_3–C1_3–C2_3	107.1(11)
O3–C4–Fe1	179.1(6)	C3_3–C1_3–C2_3	109.1(7)
O2–C2–Fe1	178.3(6)	C4_3–C1_3–C2_3	109.5(8)
C1_1–O1_1–Al03	158.1(4)	F3_3–C2_3–F1_3	108.7(10)
O1_1–C1_1–C3_1	110.6(5)	F3_3–C2_3–F2_3	107.9(12)
O1_1–C1_1–C4_1	109.1(5)	F1_3–C2_3–F2_3	107.4(9)
C3_1–C1_1–C4_1	109.7(5)	F3_3–C2_3–C1_3	110.6(11)
O1_1–C1_1–C2_1	108.5(5)	F1_3–C2_3–C1_3	109.3(8)
C3_1–C1_1–C2_1	109.6(4)	F2_3–C2_3–C1_3	112.9(9)
C4_1–C1_1–C2_1	109.3(4)	F4_3–C3_3–F5_3	108.5(10)
F3_1–C2_1–F2_1	108.5(5)	F4_3–C3_3–F6_3	107.4(12)
F3_1–C2_1–F1_1	108.1(5)	F5_3–C3_3–F6_3	106.4(9)
F2_1–C2_1–F1_1	107.7(5)	F4_3–C3_3–C1_3	111.0(11)
F3_1–C2_1–C1_1	110.8(5)	F5_3–C3_3–C1_3	111.1(7)
F2_1–C2_1–C1_1	111.2(5)	F6_3–C3_3–C1_3	112.2(9)
F1_1–C2_1–C1_1	110.5(5)	F7_3–C4_3–F8_3	107.2(10)
F6_1–C3_1–F5_1	108.6(5)	F7_3–C4_3–F9_3	108.1(11)
F6_1–C3_1–F4_1	108.3(5)	F8_3–C4_3–F9_3	107.1(13)
F5_1–C3_1–F4_1	107.5(5)	F7_3–C4_3–C1_3	111.2(8)
F6_1–C3_1–C1_1	112.4(5)	F8_3–C4_3–C1_3	113.5(11)
F5_1–C3_1–C1_1	109.9(5)	F9_3–C4_3–C1_3	109.6(11)
F4_1–C3_1–C1_1	110.0(5)	C1_4–O1_4–Al03	144(2)
F7_1–C4_1–F9_1	108.2(5)	O1_4–C1_4–C3_4	110.4(16)
F7_1–C4_1–F8_1	107.9(5)	O1_4–C1_4–C4_4	110.3(16)
F9_1–C4_1–F8_1	107.1(5)	C3_4–C1_4–C4_4	109.4(10)
F7_1–C4_1–C1_1	111.1(5)	O1_4–C1_4–C2_4	107.6(16)
F9_1–C4_1–C1_1	110.8(5)	C3_4–C1_4–C2_4	109.1(9)
F8_1–C4_1–C1_1	111.6(5)	C4_4–C1_4–C2_4	110.0(10)
C1_2–O1_2–Al03	145.5(4)	F1_4–C2_4–F2_4	108.1(16)
O1_2–C1_2–C2_2	109.8(4)	F1_4–C2_4–F3_4	108.9(14)
O1_2–C1_2–C4_2	107.4(4)	F2_4–C2_4–F3_4	107.5(13)
C2_2–C1_2–C4_2	110.1(4)	F1_4–C2_4–C1_4	110.3(15)
O1_2–C1_2–C3_2	111.2(4)	F2_4–C2_4–C1_4	112.7(13)
C2_2–C1_2–C3_2	109.4(4)	F3_4–C2_4–C1_4	109.3(10)
C4_2–C1_2–C3_2	108.9(4)	F4_4–C3_4–F5_4	109.4(14)
F3_2–C2_2–F2_2	108.4(5)	F4_4–C3_4–F6_4	106.2(11)

F5_4–C3_4–F6_4	108.0(16)
F4_4–C3_4–C1_4	111.7(10)
F5_4–C3_4–C1_4	110.5(15)
F6_4–C3_4–C1_4	111.0(12)
F7_4–C4_4–F8_4	108.7(17)
F7_4–C4_4–F9_4	108.1(14)
F8_4–C4_4–F9_4	107.2(14)
F7_4–C4_4–C1_4	111.3(16)
F8_4–C4_4–C1_4	111.2(15)
F9_4–C4_4–C1_4	110.3(10)

Symmetry transformations used to generate equivalent atoms:
#1: 1-X, +Y, 1.5-Z; #2: 1-X, 2-Y, 1-Z;

Table S11: Atomic coordinates and U_{eq} [Å^2] for $[FeCO_5][Al(OR^F)_4]$ (**1**).

Atom	*x*	*y*	*z*	U_{eq}
Fe1	0.63923(4)	0.75232(4)	0.12815(2)	0.02271(13)
C1	0.7117(3)	0.6927(3)	0.16886(16)	0.0296(10)
C2	0.6966(3)	0.6981(3)	0.08045(16)	0.0274(10)
Al1	-0.05482(8)	0.32476(7)	0.38576(4)	0.0176(2)
O3	0.7551(3)	0.6564(2)	0.19296(12)	0.0400(9)
C3	0.5937(3)	0.8267(3)	0.08620(17)	0.0292(10)
Al2	0.54476(8)	0.26769(6)	0.13205(4)	0.0178(2)
O4	0.7305(2)	0.6648(2)	0.05147(11)	0.0335(8)
C4	0.6009(3)	0.8201(3)	0.17518(17)	0.0296(10)
C5	0.5313(3)	0.6847(2)	0.13056(15)	0.0236(8)
O5	0.5686(3)	0.8722(2)	0.06090(13)	0.0383(8)
Fe1A	1.03314(4)	0.16953(3)	0.13320(2)	0.02301(13)
O1A	1.1705(2)	0.14028(19)	0.20860(12)	0.0307(7)
C1A	1.1207(3)	0.1534(2)	0.17995(16)	0.0250(9)
O7	0.4692(2)	0.64428(18)	0.13227(11)	0.0306(7)
O6	0.5776(3)	0.8622(2)	0.20267(12)	0.0372(8)
C2A	0.9387(3)	0.1661(3)	0.17716(18)	0.0296(10)
O2A	0.8827(3)	0.1629(2)	0.20397(13)	0.0400(8)
C3A	0.9408(3)	0.1514(3)	0.08883(18)	0.0306(10)
O3A	0.8854(3)	0.1404(2)	0.06289(13)	0.0372(8)
C4A	1.1281(4)	0.1539(2)	0.08963(16)	0.0276(10)
O4A	1.1849(3)	0.1460(2)	0.06353(12)	0.0346(8)
C5A	1.0368(3)	0.2828(2)	0.12896(15)	0.0250(9)
O5A	1.0383(2)	0.34893(17)	0.12549(11)	0.0300(7)
O1_1	-0.15650(19)	0.37992(16)	0.37743(9)	0.0203(6)
C1_1	-0.2507(3)	0.3813(2)	0.38360(13)	0.0196(8)
C2_1	-0.2748(3)	0.3828(3)	0.43472(16)	0.0311(10)
F1_1	-0.2580(2)	0.45537(19)	0.45214(10)	0.0429(8)
F2_1	-0.3647(2)	0.3650(2)	0.44335(10)	0.0432(7)
F3_1	-0.2210(2)	0.3312(2)	0.45698(9)	0.0405(7)
C3_1	-0.2983(3)	0.3074(2)	0.36178(16)	0.0287(10)
F4_1	-0.2581(2)	0.28958(17)	0.32262(10)	0.0387(7)
F5_1	-0.2916(2)	0.24337(15)	0.38893(11)	0.0420(7)
F6_1	-0.39094(18)	0.31890(17)	0.35396(10)	0.0362(7)
C4_1	-0.2912(3)	0.4563(3)	0.36035(15)	0.0264(9)
F7_1	-0.2942(2)	0.44731(18)	0.31540(9)	0.0374(7)
F8_1	-0.37830(18)	0.47301(15)	0.37445(10)	0.0331(6)
F9_1	-0.23741(19)	0.51945(14)	0.36886(11)	0.0363(6)
O1_2	0.0254(2)	0.35714(16)	0.34540(9)	0.0212(6)
C1_2	0.0376(3)	0.3824(2)	0.30214(13)	0.0216(8)
C2_2	-0.0309(3)	0.4511(3)	0.29022(16)	0.0319(10)
F1_2	-0.1162(2)	0.4245(2)	0.28012(10)	0.0440(8)
F2_2	-0.0003(3)	0.4952(2)	0.25549(12)	0.0555(9)
F3_2	-0.0396(2)	0.49957(15)	0.32589(11)	0.0424(7)
C3_2	0.1400(3)	0.4127(3)	0.29741(15)	0.0313(10)
F4_2	0.2000(2)	0.3630(2)	0.31717(11)	0.0505(9)
F5_2	0.1494(2)	0.48296(18)	0.31795(10)	0.0443(8)
F6_2	0.1666(2)	0.4213(2)	0.25439(10)	0.0431(8)
C4_2	0.0208(4)	0.3128(3)	0.26878(16)	0.0397(12)
F7_2	0.0914(3)	0.26065(19)	0.27080(12)	0.0582(10)
F8_2	0.0146(3)	0.3373(2)	0.22571(10)	0.0553(9)
F9_2	-0.0581(2)	0.27423(19)	0.27886(10)	0.0483(8)
O1_3	-0.0009(2)	0.33925(16)	0.43792(10)	0.0219(6)
C1_3	0.0498(3)	0.3868(2)	0.46564(13)	0.0207(8)

C2_3	0.0755(3)	0.3383(3)	0.50886(15)	0.0322(10)
F1_3	0.0017(2)	0.29689(17)	0.52370(9)	0.0390(7)
F2_3	0.1042(2)	0.38512(19)	0.54273(9)	0.0430(8)
F3_3	0.1441(2)	0.28668(17)	0.50008(11)	0.0455(8)
C3_3	0.1430(3)	0.4142(3)	0.44249(15)	0.0281(9)
F4_3	0.1256(2)	0.47160(15)	0.41215(9)	0.0332(6)
F5_3	0.1830(2)	0.35418(17)	0.42022(10)	0.0373(7)
F6_3	0.2056(2)	0.4425(2)	0.47202(10)	0.0421(7)
C4_3	-0.0088(3)	0.4604(3)	0.47954(15)	0.0262(9)
F7_3	-0.0495(2)	0.49298(15)	0.44310(9)	0.0333(6)
F8_3	0.0429(2)	0.51719(15)	0.49939(9)	0.0356(7)
F9_3	-0.0774(2)	0.44013(17)	0.50831(9)	0.0364(7)
O1_4	-0.0817(5)	0.2255(3)	0.3816(2)	0.0216(9)
C1_4	-0.0577(4)	0.1486(3)	0.39020(19)	0.0252(11)
C2_4	-0.1264(4)	0.1136(3)	0.4255(2)	0.0372(14)
F1_4	-0.2099(2)	0.0980(2)	0.40711(17)	0.0484(11)
F2_4	-0.0929(8)	0.0459(4)	0.4437(3)	0.0575(14)
F3_4	-0.1404(4)	0.1645(5)	0.45983(18)	0.0467(14)
C3_4	0.0437(4)	0.1429(3)	0.40860(19)	0.0315(12)
F4_4	0.1008(5)	0.1941(4)	0.3868(3)	0.0365(12)
F5_4	0.0485(3)	0.1615(2)	0.45270(12)	0.0401(9)
F6_4	0.0819(3)	0.0705(2)	0.40395(16)	0.0439(11)
C4_4	-0.0649(4)	0.1018(3)	0.3453(2)	0.0355(13)
F7_4	0.0090(3)	0.1180(3)	0.31852(14)	0.0466(12)
F8_4	-0.0652(4)	0.0227(2)	0.3519(2)	0.0517(13)
F9_4	-0.1420(5)	0.1204(4)	0.32246(17)	0.0483(12)
O1_5	0.44040(19)	0.31833(16)	0.12269(9)	0.0201(6)
C1_5	0.3645(3)	0.3523(2)	0.14228(13)	0.0203(8)
C2_5	0.3093(3)	0.2912(2)	0.17144(14)	0.0226(9)
F1_5	0.34866(18)	0.27959(15)	0.21183(8)	0.0290(6)
F2_5	0.21985(17)	0.31279(15)	0.17912(9)	0.0279(6)
F3_5	0.30660(19)	0.22052(14)	0.15079(9)	0.0297(6)
C3_5	0.2976(3)	0.3828(3)	0.10432(16)	0.0308(10)
F4_5	0.3471(2)	0.41842(19)	0.07165(10)	0.0467(8)
F5_5	0.2524(2)	0.32190(19)	0.08519(10)	0.0412(7)
F6_5	0.2339(2)	0.43334(17)	0.11956(11)	0.0424(8)
C4_5	0.3943(3)	0.4225(3)	0.17323(16)	0.0293(10)
F7_5	0.4173(2)	0.48593(15)	0.14849(11)	0.0426(8)
F8_5	0.3258(2)	0.44442(17)	0.20188(11)	0.0414(7)
F9_5	0.4693(2)	0.40220(17)	0.19780(9)	0.0350(6)
O1_6	0.5256(2)	0.20358(17)	0.17685(10)	0.0233(6)
C1_6	0.5625(3)	0.1545(2)	0.20828(14)	0.0222(8)
C2_6	0.4797(3)	0.1107(3)	0.23197(15)	0.0295(10)
F1_6	0.43793(19)	0.15793(17)	0.26294(9)	0.0340(6)
F2_6	0.5072(2)	0.04547(17)	0.25406(11)	0.0433(8)
F3_6	0.4141(2)	0.09027(16)	0.20262(10)	0.0378(7)
C3_6	0.6284(4)	0.0919(3)	0.18598(16)	0.0313(10)
F4_6	0.6856(2)	0.12675(18)	0.15600(10)	0.0387(7)
F5_6	0.5784(2)	0.03740(16)	0.16362(11)	0.0465(8)
F6_6	0.6820(2)	0.05419(18)	0.21610(10)	0.0431(8)
C4_6	0.6189(3)	0.2015(3)	0.24413(15)	0.0266(9)
F7_6	0.70324(19)	0.22310(17)	0.22852(9)	0.0343(6)
F8_6	0.6331(2)	0.15960(18)	0.28235(9)	0.0378(7)
F9_6	0.5735(2)	0.26767(16)	0.25581(10)	0.0367(7)
O1_7	0.5735(2)	0.21798(17)	0.08310(10)	0.0249(6)
C1_7	0.5431(3)	0.1812(2)	0.04471(14)	0.0256(9)
C2_7	0.6309(4)	0.1499(3)	0.01987(17)	0.0401(12)

F1_7	0.6795(3)	0.20998(19)	0.00146(12)	0.0557(10)
F2_7	0.6097(3)	0.09934(18)	-0.01370(11)	0.0499(9)
F3_7	0.6889(2)	0.11250(19)	0.04852(12)	0.0484(8)
C3_7	0.4766(3)	0.1107(3)	0.05618(16)	0.0323(10)
F4_7	0.4153(2)	0.13159(17)	0.08822(10)	0.0371(7)
F5_7	0.5256(2)	0.04860(16)	0.07156(11)	0.0427(7)
F6_7	0.4272(2)	0.08653(19)	0.02012(11)	0.0474(8)
C4_7	0.4893(4)	0.2404(3)	0.01384(15)	0.0376(11)
F7_7	0.4012(2)	0.2507(2)	0.02752(10)	0.0456(8)
F8_7	0.4863(3)	0.2152(2)	-0.02959(10)	0.0581(10)
F9_7	0.5322(3)	0.31089(17)	0.01365(11)	0.0521(9)
O1_8	0.6378(2)	0.32927(17)	0.14615(10)	0.0231(6)
C1_8	0.7033(3)	0.3830(2)	0.13379(15)	0.0236(8)
C2_8	0.7672(4)	0.3501(3)	0.09601(19)	0.0407(12)
F1_8	0.7233(3)	0.3518(2)	0.05606(11)	0.0561(10)
F2_8	0.8475(2)	0.39153(19)	0.09132(12)	0.0492(8)
F3_8	0.7912(2)	0.27507(18)	0.10443(14)	0.0586(10)
C3_8	0.7642(4)	0.4024(3)	0.17603(18)	0.0396(12)
F4_8	0.7119(3)	0.4114(2)	0.21258(11)	0.0555(9)
F5_8	0.8246(2)	0.3435(2)	0.18429(13)	0.0569(9)
F6_8	0.8151(2)	0.46911(19)	0.17060(12)	0.0532(9)
C4_8	0.6557(3)	0.4611(3)	0.1170(2)	0.0396(12)
F7_8	0.6228(2)	0.50375(17)	0.15193(14)	0.0557(10)
F8_8	0.7156(2)	0.50779(19)	0.09429(14)	0.0563(10)
F9_8	0.5840(2)	0.44435(19)	0.08979(12)	0.0486(8)
O1_9	-0.084(4)	0.226(2)	0.375(2)	0.0216(9)
C1_9	-0.0627(18)	0.1474(19)	0.3816(9)	0.024(5)
C2_9	0.0397(17)	0.1320(17)	0.3661(10)	0.031(5)
F1_9	0.097(4)	0.191(3)	0.380(2)	0.033(6)
F2_9	0.076(3)	0.064(2)	0.3819(13)	0.045(6)
F3_9	0.047(3)	0.129(3)	0.3209(10)	0.045(6)
C3_9	-0.1306(18)	0.0976(18)	0.3517(11)	0.039(5)
F4_9	-0.2156(17)	0.0921(16)	0.3706(16)	0.059(9)
F5_9	-0.142(4)	0.130(4)	0.3111(13)	0.048(6)
F6_9	-0.099(3)	0.023(2)	0.346(2)	0.052(7)
C4_9	-0.078(2)	0.127(2)	0.4320(9)	0.032(6)
F7_9	-0.153(3)	0.165(5)	0.4495(17)	0.044(7)
F8_9	-0.093(6)	0.049(3)	0.438(2)	0.053(6)
F9_9	-0.005(2)	0.148(2)	0.4576(10)	0.046(6)

U_{eq} is defined as 1/3 of the trace of the orthogonalized U_{ij} tensor.

Table S12: Bond lengths and angles for $[FeCO_5][Al(OR^F)_4]$ (**1**).

Atom–Atom	**Length [Å]**
Fe1–C2	1.865(5)
Fe1–C1	1.872(5)
Fe1–C3	1.876(5)
Fe1–C4	1.876(5)
Fe1–C5	1.910(4)
C1–O3	1.122(6)
C2–O4	1.130(6)
Al1–O1_4	1.718(5)
Al1–O1_1	1.734(3)
Al1–O1_2	1.735(3)
Al1–O1_3	1.736(3)
Al1–O1_9	1.74(4)
C3–O5	1.126(6)
Al2–O1_7	1.718(3)
Al2–O1_6	1.728(3)
Al2–O1_8	1.730(3)
Al2–O1_5	1.731(3)
C4–O6	1.127(6)
C5–O7	1.115(5)
Fe1A–C2A	1.866(5)
Fe1A–C1A	1.876(5)
Fe1A–C3A	1.877(5)
Fe1A–C4A	1.881(5)
Fe1A–C5A	1.911(4)
O1A–C1A	1.123(6)

C2A–O2A	1.123(6)	C1_5–C4_5	1.552(6)
C3A–O3A	1.113(6)	C1_5–C2_5	1.553(5)
C4A–O4A	1.123(6)	C1_5–C3_5	1.555(6)
C5A–O5A	1.118(5)	C2_5–F1_5	1.330(5)
O1_1–C1_1	1.350(5)	C2_5–F3_5	1.337(5)
C1_1–C2_1	1.547(6)	C2_5–F2_5	1.341(5)
C1_1–C4_1	1.547(6)	C3_5–F6_5	1.321(5)
C1_1–C3_1	1.555(5)	C3_5–F5_5	1.335(6)
C2_1–F3_1	1.330(5)	C3_5–F4_5	1.335(5)
C2_1–F2_1	1.335(5)	C4_5–F9_5	1.333(5)
C2_1–F1_1	1.347(6)	C4_5–F7_5	1.333(5)
C3_1–F4_1	1.323(5)	C4_5–F8_5	1.340(5)
C3_1–F5_1	1.346(5)	O1_6–C1_6	1.347(5)
C3_1–F6_1	1.349(5)	C1_6–C4_6	1.545(6)
C4_1–F9_1	1.333(5)	C1_6–C2_6	1.553(6)
C4_1–F8_1	1.334(5)	C1_6–C3_6	1.555(6)
C4_1–F7_1	1.335(5)	C2_6–F3_6	1.318(5)
O1_2–C1_2	1.356(5)	C2_6–F2_6	1.335(5)
C1_2–C3_2	1.547(6)	C2_6–F1_6	1.349(5)
C1_2–C4_2	1.547(6)	C3_6–F6_6	1.331(5)
C1_2–C2_2	1.552(6)	C3_6–F5_6	1.335(5)
C2_2–F1_2	1.325(6)	C3_6–F4_6	1.336(5)
C2_2–F3_2	1.337(6)	C4_6–F9_6	1.332(5)
C2_2–F2_2	1.337(5)	C4_6–F7_6	1.333(5)
C3_2–F4_2	1.328(5)	C4_6–F8_6	1.345(5)
C3_2–F6_2	1.332(5)	O1_7–C1_7	1.361(5)
C3_2–F5_2	1.336(6)	C1_7–C2_7	1.539(6)
C4_2–F9_2	1.329(6)	C1_7–C4_7	1.551(6)
C4_2–F7_2	1.334(6)	C1_7–C3_7	1.553(6)
C4_2–F8_2	1.338(6)	C2_7–F3_7	1.338(6)
O1_3–C1_3	1.351(5)	C2_7–F1_7	1.338(6)
C1_3–C4_3	1.548(6)	C2_7–F2_7	1.340(5)
C1_3–C2_3	1.557(6)	C3_7–F4_7	1.332(5)
C1_3–C3_3	1.559(6)	C3_7–F5_7	1.335(6)
C2_3–F3_3	1.331(6)	C3_7–F6_7	1.337(5)
C2_3–F1_3	1.332(5)	C4_7–F7_7	1.325(6)
C2_3–F2_3	1.336(5)	C4_7–F9_7	1.333(6)
C3_3–F5_3	1.332(5)	C4_7–F8_7	1.350(5)
C3_3–F6_3	1.333(5)	O1_8–C1_8	1.347(5)
C3_3–F4_3	1.340(5)	C1_8–C2_8	1.540(6)
C4_3–F9_3	1.337(5)	C1_8–C3_8	1.552(6)
C4_3–F7_3	1.338(5)	C1_8–C4_8	1.559(6)
C4_3–F8_3	1.339(5)	C2_8–F3_8	1.332(6)
O1_4–C1_4	1.362(5)	C2_8–F1_8	1.334(6)
C1_4–C3_4	1.541(7)	C2_8–F2_8	1.343(6)
C1_4–C2_4	1.543(7)	C3_8–F4_8	1.318(6)
C1_4–C4_4	1.546(7)	C3_8–F5_8	1.334(6)
C2_4–F1_4	1.331(7)	C3_8–F6_8	1.344(5)
C2_4–F3_4	1.341(8)	C4_8–F9_8	1.326(6)
C2_4–F2_4	1.346(8)	C4_8–F8_8	1.338(5)
C3_4–F5_4	1.340(6)	C4_8–F7_8	1.341(6)
C3_4–F6_4	1.341(6)	O1_9–C1_9	1.36(2)
C3_4–F4_4	1.347(8)	C1_9–C4_9	1.542(17)
C4_4–F9_4	1.322(8)	C1_9–C2_9	1.545(17)
C4_4–F7_4	1.340(7)	C1_9–C3_9	1.551(18)
C4_4–F8_4	1.345(6)	C2_9–F2_9	1.333(18)
O1_5–C1_5	1.350(5)	C2_9–F3_9	1.339(18)

C2_9–F1_9	1.341(19)
C3_9–F5_9	1.325(19)
C3_9–F4_9	1.332(19)
C3_9–F6_9	1.338(19)
C4_9–F9_9	1.332(19)
C4_9–F8_9	1.334(19)
C4_9–F7_9	1.346(19)

Atom–Atom–Atom	Angle [°]
C2–Fe1–C1	88.9(2)
C2–Fe1–C3	88.8(2)
C1–Fe1–C3	166.0(2)
C2–Fe1–C4	169.14(19)
C1–Fe1–C4	90.6(2)
C3–Fe1–C4	89.0(2)
C2–Fe1–C5	94.98(19)
C1–Fe1–C5	95.62(19)
C3–Fe1–C5	98.38(19)
C4–Fe1–C5	95.86(19)
O3–C1–Fe1	179.3(5)
O4–C2–Fe1	179.3(4)
O1_4–Al1–O1_1	109.0(3)
O1_4–Al1–O1_2	113.7(3)
O1_1–Al1–O1_2	106.31(14)
O1_4–Al1–O1_3	107.3(2)
O1_1–Al1–O1_3	114.68(15)
O1_2–Al1–O1_3	105.93(15)
O1_1–Al1–O1_9	106.9(19)
O1_2–Al1–O1_9	110(2)
O1_3–Al1–O1_9	113.2(19)
O5–C3–Fe1	178.2(4)
O1_7–Al2–O1_6	112.10(15)
O1_7–Al2–O1_8	108.21(15)
O1_6–Al2–O1_8	108.10(15)
O1_7–Al2–O1_5	108.01(15)
O1_6–Al2–O1_5	107.12(15)
O1_8–Al2–O1_5	113.38(15)
O6–C4–Fe1	178.3(4)
O7–C5–Fe1	178.8(4)
C2A–Fe1A–C1A	87.77(19)
C2A–Fe1A–C3A	88.7(2)
C1A–Fe1A–C3A	162.09(19)
C2A–Fe1A–C4A	170.22(19)
C1A–Fe1A–C4A	90.41(19)
C3A–Fe1A–C4A	90.1(2)
C2A–Fe1A–C5A	95.49(19)
C1A–Fe1A–C5A	100.01(19)
C3A–Fe1A–C5A	97.81(19)
C4A–Fe1A–C5A	94.29(19)
O1A–C1A–Fe1A	176.2(4)
O2A–C2A–Fe1A	178.7(5)
O3A–C3A–Fe1A	179.2(5)
O4A–C4A–Fe1A	178.8(4)
O5A–C5A–Fe1A	178.4(4)
C1_1–O1_1–Al1	144.6(3)
O1_1–C1_1–C2_1	110.6(3)
O1_1–C1_1–C4_1	108.8(3)
C2_1–C1_1–C4_1	109.7(3)
O1_1–C1_1–C3_1	111.1(3)
C2_1–C1_1–C3_1	108.7(3)
C4_1–C1_1–C3_1	107.9(3)
F3_1–C2_1–F2_1	107.9(4)
F3_1–C2_1–F1_1	107.6(4)
F2_1–C2_1–F1_1	107.5(4)
F3_1–C2_1–C1_1	110.1(4)
F2_1–C2_1–C1_1	113.2(4)
F1_1–C2_1–C1_1	110.3(4)
F4_1–C3_1–F5_1	107.9(4)
F4_1–C3_1–F6_1	107.7(4)
F5_1–C3_1–F6_1	106.6(4)
F4_1–C3_1–C1_1	110.8(4)
F5_1–C3_1–C1_1	111.3(4)
F6_1–C3_1–C1_1	112.3(3)
F9_1–C4_1–F8_1	107.7(3)
F9_1–C4_1–F7_1	107.2(4)
F8_1–C4_1–F7_1	107.7(3)
F9_1–C4_1–C1_1	110.7(3)
F8_1–C4_1–C1_1	112.3(3)
F7_1–C4_1–C1_1	111.1(3)
C1_2–O1_2–Al1	145.9(3)
O1_2–C1_2–C3_2	107.9(3)
O1_2–C1_2–C4_2	110.0(3)
C3_2–C1_2–C4_2	109.6(4)
O1_2–C1_2–C2_2	111.5(3)
C3_2–C1_2–C2_2	108.8(4)
C4_2–C1_2–C2_2	108.9(4)
F1_2–C2_2–F3_2	107.4(4)
F1_2–C2_2–F2_2	108.2(4)
F3_2–C2_2–F2_2	107.2(4)
F1_2–C2_2–C1_2	111.8(4)
F3_2–C2_2–C1_2	109.5(4)
F2_2–C2_2–C1_2	112.6(4)
F4_2–C3_2–F6_2	107.7(4)
F4_2–C3_2–F5_2	107.1(4)
F6_2–C3_2–F5_2	107.9(4)
F4_2–C3_2–C1_2	110.8(4)
F6_2–C3_2–C1_2	112.9(4)
F5_2–C3_2–C1_2	110.2(4)
F9_2–C4_2–F7_2	107.6(4)
F9_2–C4_2–F8_2	107.9(4)
F7_2–C4_2–F8_2	107.1(4)
F9_2–C4_2–C1_2	110.9(4)
F7_2–C4_2–C1_2	110.7(4)
F8_2–C4_2–C1_2	112.4(4)
C1_3–O1_3–Al1	148.7(3)
O1_3–C1_3–C4_3	110.4(3)
O1_3–C1_3–C2_3	108.0(3)
C4_3–C1_3–C2_3	109.2(3)
O1_3–C1_3–C3_3	111.2(3)
C4_3–C1_3–C3_3	109.5(3)
C2_3–C1_3–C3_3	108.4(3)
F3_3–C2_3–F1_3	107.4(4)
F3_3–C2_3–F2_3	107.9(4)
F1_3–C2_3–F2_3	107.6(4)

F3_3–C2_3–C1_3	110.8(4)	F5_5–C3_5–C1_5	110.2(3)
F1_3–C2_3–C1_3	111.0(4)	F4_5–C3_5–C1_5	110.3(4)
F2_3–C2_3–C1_3	112.0(4)	F9_5–C4_5–F7_5	107.9(4)
F5_3–C3_3–F6_3	108.0(4)	F9_5–C4_5–F8_5	107.9(4)
F5_3–C3_3–F4_3	107.2(4)	F7_5–C4_5–F8_5	107.6(4)
F6_3–C3_3–F4_3	107.6(4)	F9_5–C4_5–C1_5	110.0(3)
F5_3–C3_3–C1_3	110.7(3)	F7_5–C4_5–C1_5	110.7(4)
F6_3–C3_3–C1_3	112.7(4)	F8_5–C4_5–C1_5	112.5(4)
F4_3–C3_3–C1_3	110.5(4)	C1_6–O1_6–Al2	148.0(3)
F9_3–C4_3–F7_3	107.4(4)	O1_6–C1_6–C4_6	111.0(3)
F9_3–C4_3–F8_3	107.7(4)	O1_6–C1_6–C2_6	107.9(3)
F7_3–C4_3–F8_3	107.2(3)	C4_6–C1_6–C2_6	109.1(3)
F9_3–C4_3–C1_3	110.8(4)	O1_6–C1_6–C3_6	111.0(3)
F7_3–C4_3–C1_3	110.3(3)	C4_6–C1_6–C3_6	108.9(4)
F8_3–C4_3–C1_3	113.2(4)	C2_6–C1_6–C3_6	108.9(3)
C1_4–O1_4–Al1	148.8(5)	F3_6–C2_6–F2_6	108.3(4)
O1_4–C1_4–C3_4	111.0(5)	F3_6–C2_6–F1_6	106.7(4)
O1_4–C1_4–C2_4	109.3(5)	F2_6–C2_6–F1_6	106.4(4)
C3_4–C1_4–C2_4	109.2(5)	F3_6–C2_6–C1_6	111.3(4)
O1_4–C1_4–C4_4	108.0(5)	F2_6–C2_6–C1_6	112.9(4)
C3_4–C1_4–C4_4	109.4(4)	F1_6–C2_6–C1_6	110.9(3)
C2_4–C1_4–C4_4	110.0(5)	F6_6–C3_6–F5_6	107.8(4)
F1_4–C2_4–F3_4	107.5(5)	F6_6–C3_6–F4_6	107.7(4)
F1_4–C2_4–F2_4	108.0(6)	F5_6–C3_6–F4_6	107.3(4)
F3_4–C2_4–F2_4	107.0(6)	F6_6–C3_6–C1_6	112.7(4)
F1_4–C2_4–C1_4	111.3(5)	F5_6–C3_6–C1_6	110.8(4)
F3_4–C2_4–C1_4	111.1(5)	F4_6–C3_6–C1_6	110.4(3)
F2_4–C2_4–C1_4	111.7(6)	F9_6–C4_6–F7_6	107.2(4)
F5_4–C3_4–F6_4	106.9(4)	F9_6–C4_6–F8_6	107.1(4)
F5_4–C3_4–F4_4	106.4(5)	F7_6–C4_6–F8_6	107.3(4)
F6_4–C3_4–F4_4	106.9(5)	F9_6–C4_6–C1_6	110.8(3)
F5_4–C3_4–C1_4	112.0(4)	F7_6–C4_6–C1_6	111.7(4)
F6_4–C3_4–C1_4	113.5(4)	F8_6–C4_6–C1_6	112.5(4)
F4_4–C3_4–C1_4	110.7(5)	C1_7–O1_7–Al2	147.7(3)
F9_4–C4_4–F7_4	107.4(5)	O1_7–C1_7–C2_7	107.1(4)
F9_4–C4_4–F8_4	107.8(5)	O1_7–C1_7–C4_7	110.6(3)
F7_4–C4_4–F8_4	106.8(5)	C2_7–C1_7–C4_7	109.8(4)
F9_4–C4_4–C1_4	111.7(5)	O1_7–C1_7–C3_7	111.0(3)
F7_4–C4_4–C1_4	110.5(4)	C2_7–C1_7–C3_7	109.6(4)
F8_4–C4_4–C1_4	112.3(5)	C4_7–C1_7–C3_7	108.6(4)
C1_5–O1_5–Al2	145.4(3)	F3_7–C2_7–F1_7	107.2(5)
O1_5–C1_5–C4_5	110.9(3)	F3_7–C2_7–F2_7	107.8(4)
O1_5–C1_5–C2_5	111.0(3)	F1_7–C2_7–F2_7	107.2(4)
C4_5–C1_5–C2_5	108.4(3)	F3_7–C2_7–C1_7	111.0(4)
O1_5–C1_5–C3_5	108.6(3)	F1_7–C2_7–C1_7	110.6(4)
C4_5–C1_5–C3_5	109.8(3)	F2_7–C2_7–C1_7	112.8(4)
C2_5–C1_5–C3_5	108.0(3)	F4_7–C3_7–F5_7	107.8(4)
F1_5–C2_5–F3_5	106.8(3)	F4_7–C3_7–F6_7	107.6(4)
F1_5–C2_5–F2_5	106.6(3)	F5_7–C3_7–F6_7	107.8(4)
F3_5–C2_5–F2_5	106.9(3)	F4_7–C3_7–C1_7	110.5(4)
F1_5–C2_5–C1_5	112.4(3)	F5_7–C3_7–C1_7	110.8(4)
F3_5–C2_5–C1_5	110.6(3)	F6_7–C3_7–C1_7	112.2(4)
F2_5–C2_5–C1_5	113.1(3)	F7_7–C4_7–F9_7	108.5(4)
F6_5–C3_5–F5_5	108.0(4)	F7_7–C4_7–F8_7	107.5(4)
F6_5–C3_5–F4_5	108.5(4)	F9_7–C4_7–F8_7	106.9(4)
F5_5–C3_5–F4_5	107.0(4)	F7_7–C4_7–C1_7	111.7(4)
F6_5–C3_5–C1_5	112.7(4)	F9_7–C4_7–C1_7	110.4(4)

F8_7–C4_7–C1_7	111.7(4)
C1_8–O1_8–Al2	149.8(3)
O1_8–C1_8–C2_8	111.2(3)
O1_8–C1_8–C3_8	108.0(4)
C2_8–C1_8–C3_8	109.1(4)
O1_8–C1_8–C4_8	110.7(3)
C2_8–C1_8–C4_8	109.1(4)
C3_8–C1_8–C4_8	108.6(4)
F3_8–C2_8–F1_8	107.7(4)
F3_8–C2_8–F2_8	107.1(4)
F1_8–C2_8–F2_8	107.1(4)
F3_8–C2_8–C1_8	110.9(4)
F1_8–C2_8–C1_8	110.8(4)
F2_8–C2_8–C1_8	112.9(4)
F4_8–C3_8–F5_8	107.3(4)
F4_8–C3_8–F6_8	107.8(4)
F5_8–C3_8–F6_8	107.3(4)
F4_8–C3_8–C1_8	111.5(4)
F5_8–C3_8–C1_8	110.4(4)
F6_8–C3_8–C1_8	112.3(4)
F9_8–C4_8–F8_8	108.1(4)
F9_8–C4_8–F7_8	108.2(4)
F8_8–C4_8–F7_8	106.9(4)
F9_8–C4_8–C1_8	110.3(4)
F8_8–C4_8–C1_8	112.3(4)
F7_8–C4_8–C1_8	110.9(4)
C1_9–O1_9–Al1	148(4)
O1_9–C1_9–C4_9	108(3)
O1_9–C1_9–C2_9	109(3)
C4_9–C1_9–C2_9	112.3(19)
O1_9–C1_9–C3_9	108(3)
C4_9–C1_9–C3_9	109.9(19)
C2_9–C1_9–C3_9	109.0(17)
F2_9–C2_9–F3_9	106(2)
F2_9–C2_9–F1_9	107(3)
F3_9–C2_9–F1_9	106(3)
F2_9–C2_9–C1_9	114(2)
F3_9–C2_9–C1_9	112(2)
F1_9–C2_9–C1_9	111(3)
F5_9–C3_9–F4_9	107(3)
F5_9–C3_9–F6_9	108(3)
F4_9–C3_9–F6_9	106(2)
F5_9–C3_9–C1_9	112(3)
F4_9–C3_9–C1_9	111(2)
F6_9–C3_9–C1_9	111(2)
F9_9–C4_9–F8_9	108(3)
F9_9–C4_9–F7_9	105(3)
F8_9–C4_9–F7_9	107(3)
F9_9–C4_9–C1_9	112(2)
F8_9–C4_9–C1_9	112(3)
F7_9–C4_9–C1_9	112(2)

Table S13: Atomic coordinates and U_{eq} [Å^2] for [Fe(CO)$_5$][F-{Al(OR^F)$_3$}$_2$] (**2**).

Atom	*x*	*y*	*z*	U_{eq}
Al1	0.61602(8)	1.11426(8)	0.55902(4)	0.01544(18)
F1	0.500000	1.000000	0.500000	0.0197(5)
Fe1	0.03780(5)	0.66341(4)	0.74227(2)	0.02417(11)
C1	-0.0186(3)	0.7812(3)	0.79862(16)	0.0244(7)
Al2	0.47579(8)	0.34563(8)	-0.00130(4)	0.01541(18)
F2	0.500000	0.500000	0.000000	0.0190(5)
O2	0.2419(3)	0.8542(3)	0.72789(15)	0.0516(8)
C2	0.1646(4)	0.7831(4)	0.73224(18)	0.0357(9)
O1	-0.0516(2)	0.8516(2)	0.83230(12)	0.0295(5)
O3	0.1624(3)	0.4799(3)	0.67147(19)	0.0625(10)
C3	0.1174(4)	0.5489(4)	0.6990(2)	0.0390(9)
O4	-0.0966(4)	0.4732(3)	0.79388(16)	0.0515(8)
C4	-0.0477(4)	0.5452(3)	0.77430(19)	0.0337(8)
O5	-0.1705(3)	0.6467(3)	0.62011(14)	0.0403(7)
C5	-0.0942(4)	0.6550(3)	0.66595(18)	0.0293(7)
O1_1	0.6536(2)	1.0388(2)	0.61931(11)	0.0240(5)
C1_1	0.7391(3)	1.0372(3)	0.67550(15)	0.0235(6)
C2_1	0.8647(3)	0.9980(3)	0.65868(16)	0.0263(7)
F1_1	0.8356(2)	0.9103(2)	0.60526(11)	0.0410(5)
F2_1	0.9338(2)	0.9582(2)	0.70732(11)	0.0347(5)
F3_1	0.9410(2)	1.0887(2)	0.64851(12)	0.0398(5)
C3_1	0.7760(4)	1.1630(4)	0.72382(17)	0.0372(9)
F4_1	0.6815(3)	1.1842(3)	0.75340(12)	0.0565(8)
F5_1	0.7942(3)	1.2474(2)	0.69075(13)	0.0500(7)
F6_1	0.8846(2)	1.1746(2)	0.76978(11)	0.0470(6)
C4_1	0.6741(3)	0.9444(4)	0.70784(18)	0.0343(8)
F7_1	0.5526(2)	0.9559(3)	0.70706(12)	0.0456(6)
F8_1	0.7383(2)	0.9580(3)	0.77027(11)	0.0487(7)
F9_1	0.6716(2)	0.8325(2)	0.67556(13)	0.0443(6)
O1_2	0.5527(4)	1.2395(4)	0.5780(2)	0.0230(9)
C1_2	0.4584(4)	1.2987(3)	0.59446(18)	0.0201(7)
C2_2	0.3410(4)	1.2709(4)	0.53423(19)	0.0297(8)
F1_2	0.3818(4)	1.2740(5)	0.47963(16)	0.0390(10)
F2_2	0.2608(4)	1.3487(5)	0.5399(2)	0.0444(11)
F3_2	0.2740(3)	1.1613(3)	0.52663(15)	0.0427(8)
C3_2	0.4143(4)	1.2600(3)	0.65347(18)	0.0261(7)
F4_2	0.4973(5)	1.3141(5)	0.7096(2)	0.0387(11)
F5_2	0.4070(3)	1.1429(3)	0.64720(16)	0.0348(8)
F6_2	0.2978(3)	1.2855(3)	0.65788(15)	0.0370(7)
C4_2	0.5161(4)	1.4353(3)	0.61498(19)	0.0289(8)
F7_2	0.6332(3)	1.4575(3)	0.65435(19)	0.0378(8)
F8_2	0.4418(3)	1.4979(2)	0.64592(15)	0.0424(7)
F9_2	0.5261(3)	1.4777(2)	0.56240(13)	0.0365(7)
O1_3	0.7419(5)	1.1423(5)	0.5229(3)	0.0220(8)
C1_3	0.8052(4)	1.2157(4)	0.4925(2)	0.0245(8)
C2_3	0.7135(4)	1.2829(4)	0.4538(2)	0.0331(9)
F1_3	0.6017(4)	1.2113(6)	0.4246(3)	0.0585(13)
F2_3	0.7636(5)	1.3236(4)	0.4077(2)	0.0459(12)
F3_3	0.6921(4)	1.3786(3)	0.4934(2)	0.0517(10)
C3_3	0.9152(4)	1.3067(4)	0.5449(2)	0.0443(10)
F4_3	1.0098(3)	1.2555(4)	0.5692(2)	0.0704(13)
F5_3	0.8661(8)	1.3577(7)	0.5952(2)	0.0666(15)
F6_3	0.9655(4)	1.3955(4)	0.5212(2)	0.0630(11)
C4_3	0.8649(5)	1.1353(5)	0.4435(3)	0.0447(10)

F7_3	0.9243(6)	1.0602(4)	0.4733(3)	0.0737(16)
F8_3	0.9511(4)	1.1985(4)	0.4207(2)	0.0571(12)
F9_3	0.7743(5)	1.0727(3)	0.39152(16)	0.0667(11)
O1_4	0.4132(2)	0.3326(2)	0.06499(11)	0.0215(5)
C1_4	0.4361(3)	0.3134(3)	0.12659(15)	0.0217(6)
C2_4	0.5734(4)	0.3788(4)	0.16764(18)	0.0377(9)
F1_4	0.6638(2)	0.3141(3)	0.15365(11)	0.0458(6)
F2_4	0.5835(2)	0.3959(3)	0.23236(11)	0.0584(8)
F3_4	0.6045(2)	0.4836(2)	0.15412(13)	0.0495(6)
C3_4	0.3335(3)	0.3656(3)	0.16069(17)	0.0286(7)
F4_4	0.21690(19)	0.33537(19)	0.11982(10)	0.0309(4)
F5_4	0.3640(2)	0.48434(19)	0.17943(12)	0.0418(6)
F6_4	0.3248(2)	0.3233(2)	0.21434(10)	0.0360(5)
C4_4	0.4226(3)	0.1782(3)	0.12350(17)	0.0301(7)
F7_4	0.2963(2)	0.12495(19)	0.10500(11)	0.0361(5)
F8_4	0.4736(2)	0.1559(2)	0.18119(11)	0.0436(6)
F9_4	0.4819(2)	0.1261(2)	0.07963(11)	0.0383(5)
O1_5	0.3625(2)	0.29349(19)	-0.07470(11)	0.0209(4)
C1_5	0.2740(3)	0.1969(3)	-0.11258(15)	0.0203(6)
C2_5	0.2353(3)	0.2189(3)	-0.18302(17)	0.0307(7)
F1_5	0.1603(2)	0.3013(2)	-0.18470(12)	0.0405(5)
F2_5	0.1717(2)	0.1187(2)	-0.22706(10)	0.0431(6)
F3_5	0.3414(2)	0.2582(2)	-0.20170(10)	0.0374(5)
C3_5	0.3313(3)	0.0806(3)	-0.11591(17)	0.0264(7)
F4_5	0.4022(2)	0.08228(18)	-0.05690(11)	0.0329(5)
F5_5	0.4076(2)	0.0717(2)	-0.15785(11)	0.0377(5)
F6_5	0.2391(2)	-0.01952(18)	-0.13519(11)	0.0348(5)
C4_5	0.1511(3)	0.1833(3)	-0.08399(17)	0.0279(7)
F7_5	0.1754(2)	0.1374(2)	-0.03149(11)	0.0355(5)
F8_5	0.04925(19)	0.1105(2)	-0.12757(11)	0.0369(5)
F9_5	0.1185(2)	0.2888(2)	-0.06570(13)	0.0414(6)
O1_6	0.6284(10)	0.3091(16)	0.0094(8)	0.022(3)
C1_6	0.7399(7)	0.3028(6)	-0.0109(3)	0.0193(15)
C2_6	0.7485(5)	0.1694(4)	-0.0356(3)	0.0261(11)
F1_6	0.7096(11)	0.1053(9)	0.0044(6)	0.042(3)
F2_6	0.8685(4)	0.1547(5)	-0.0378(3)	0.0387(11)
F3_6	0.6725(8)	0.1245(5)	-0.0967(3)	0.0344(14)
C3_6	0.7435(4)	0.3685(4)	-0.0673(2)	0.0233(10)
F4_6	0.7676(8)	0.4863(5)	-0.0430(3)	0.0313(12)
F5_6	0.6295(11)	0.3391(11)	-0.1105(7)	0.0316(19)
F6_6	0.8354(7)	0.3418(5)	-0.0986(5)	0.0307(13)
C4_6	0.8554(4)	0.3629(5)	0.0489(2)	0.0249(11)
F7_6	0.8308(16)	0.4639(11)	0.0825(5)	0.037(2)
F8_6	0.9658(5)	0.3872(6)	0.0316(4)	0.0382(14)
F9_6	0.8730(7)	0.2914(5)	0.0905(3)	0.0360(14)
O1_7	0.6170(19)	0.298(3)	0.0037(16)	0.016(4)
C1_7	0.7346(13)	0.2977(9)	-0.0111(5)	0.018(3)
C2_7	0.8001(8)	0.2042(8)	0.0200(4)	0.0241(19)
F1_7	0.8477(14)	0.2468(10)	0.0845(5)	0.035(3)
F2_7	0.9002(8)	0.1790(9)	-0.0052(5)	0.035(2)
F3_7	0.7147(15)	0.1031(14)	0.0079(11)	0.026(4)
C3_7	0.7167(8)	0.2645(8)	-0.0869(4)	0.0250(19)
F4_7	0.625(2)	0.316(2)	-0.1156(14)	0.035(4)
F5_7	0.6817(18)	0.1469(10)	-0.1113(6)	0.041(3)
F6_7	0.8258(14)	0.2984(11)	-0.1045(9)	0.035(3)
C4_7	0.8192(8)	0.4249(7)	0.0182(4)	0.0241(19)
F7_7	0.7823(14)	0.5004(10)	-0.0180(5)	0.032(2)

F8_7	0.9447(9)	0.4225(11)	0.0206(7)	0.034(2)
F9_7	0.810(3)	0.4690(18)	0.0794(8)	0.034(4)
O1_8	0.732(4)	1.153(3)	0.5241(19)	0.033(4)
C1_8	0.7893(17)	1.2237(16)	0.4899(9)	0.035(3)
C2_8	0.8219(18)	1.3559(15)	0.5311(9)	0.046(3)
F1_8	0.7141(19)	1.4014(19)	0.5279(12)	0.053(4)
F2_8	0.901(2)	1.4245(18)	0.5070(12)	0.056(5)
F3_8	0.877(4)	1.365(4)	0.5940(11)	0.059(6)
C3_8	0.9147(17)	1.1794(17)	0.4783(10)	0.048(3)
F4_8	0.895(3)	1.0613(17)	0.4531(13)	0.049(5)
F5_8	1.001(2)	1.204(2)	0.5366(10)	0.061(5)
F6_8	0.977(3)	1.2417(19)	0.4443(11)	0.046(5)
C4_8	0.6908(18)	1.2114(16)	0.4234(8)	0.036(3)
F7_8	0.686(2)	1.1066(14)	0.3830(8)	0.049(4)
F8_8	0.726(3)	1.297(2)	0.3939(14)	0.040(5)
F9_8	0.574(2)	1.219(4)	0.4317(15)	0.046(5)
O1_9	0.529(3)	1.223(3)	0.5722(18)	0.026(4)
C1_9	0.4388(18)	1.2801(15)	0.5959(8)	0.028(3)
C2_9	0.5041(17)	1.3688(16)	0.6628(9)	0.036(3)
F1_9	0.517(4)	1.316(3)	0.7129(13)	0.034(5)
F2_9	0.434(2)	1.4527(19)	0.6762(11)	0.050(5)
F3_9	0.623(2)	1.424(2)	0.6638(15)	0.043(5)
C3_9	0.3784(19)	1.3474(18)	0.5447(9)	0.035(3)
F4_9	0.349(3)	1.277(3)	0.4840(11)	0.039(5)
F5_9	0.458(2)	1.4458(18)	0.5457(13)	0.052(5)
F6_9	0.269(2)	1.379(3)	0.5567(15)	0.034(5)
C4_9	0.3299(17)	1.1838(15)	0.6035(8)	0.033(3)
F7_9	0.257(2)	1.127(2)	0.5438(9)	0.044(5)
F8_9	0.254(2)	1.229(2)	0.6400(11)	0.046(5)
F9_9	0.380(2)	1.1020(19)	0.6304(13)	0.042(5)

U_{eq} is defined as 1/3 of the trace of the orthogonalized U_{ij} tensor.

Table S14: Bond lengths and angles for $[Fe(CO)_5][F\text{-}\{Al(OR^F)_3\}_2]$.

Atom–Atom	**Length [Å]**
Al1–O1_8	1.63(3)
Al1–O1_9	1.68(2)
Al1–O1_2	1.693(4)
Al1–O1_1	1.709(2)
Al1–O1_3	1.712(4)
Al1–F1	1.7664(10)
Fe1–C3	1.864(4)
Fe1–C4	1.864(4)
Fe1–C1	1.880(4)
Fe1–C2	1.881(4)
Fe1–C5	1.903(4)
C1–O1	1.119(4)
Al2–O1_7	1.67(2)
Al2–O1_4	1.711(2)
Al2–O1_5	1.713(2)
Al2–O1_6	1.726(11)
Al2–F2	1.7636(11)
O2–C2	1.118(5)
O3–C3	1.116(5)
O4–C4	1.120(5)
O5–C5	1.118(4)
O1_1–C1_1	1.358(4)
C1_1–C3_1	1.552(5)
C1_1–C4_1	1.553(5)
C1_1–C2_1	1.563(4)
C2_1–F1_1	1.315(4)
C2_1–F3_1	1.323(4)
C2_1–F2_1	1.346(4)
C3_1–F4_1	1.324(5)
C3_1–F6_1	1.331(4)
C3_1–F5_1	1.332(5)
C4_1–F7_1	1.325(4)
C4_1–F9_1	1.332(5)
C4_1–F8_1	1.336(4)
O1_2–C1_2	1.361(4)
C1_2–C2_2	1.549(5)
C1_2–C4_2	1.554(5)
C1_2–C3_2	1.558(5)
C2_2–F3_2	1.331(5)
C2_2–F2_2	1.331(5)
C2_2–F1_2	1.332(5)
C3_2–F4_2	1.315(6)
C3_2–F5_2	1.324(5)

C3_2–F6_2	1.338(4)
C4_2–F7_2	1.320(5)
C4_2–F9_2	1.331(4)
C4_2–F8_2	1.332(4)
O1_3–C1_3	1.359(4)
C1_3–C2_3	1.546(5)
C1_3–C3_3	1.548(6)
C1_3–C4_3	1.554(6)
C2_3–F1_3	1.313(6)
C2_3–F3_3	1.328(5)
C2_3–F2_3	1.348(5)
C3_3–F4_3	1.311(6)
C3_3–F6_3	1.331(5)
C3_3–F5_3	1.355(8)
C4_3–F9_3	1.320(7)
C4_3–F8_3	1.330(5)
C4_3–F7_3	1.332(6)
O1_4–C1_4	1.357(4)
C1_4–C4_4	1.538(5)
C1_4–C2_4	1.551(5)
C1_4–C3_4	1.560(4)
C2_4–F3_4	1.317(5)
C2_4–F2_4	1.336(4)
C2_4–F1_4	1.348(5)
C3_4–F4_4	1.326(4)
C3_4–F5_4	1.326(4)
C3_4–F6_4	1.349(4)
C4_4–F9_4	1.329(4)
C4_4–F8_4	1.332(4)
C4_4–F7_4	1.351(4)
O1_5–C1_5	1.355(4)
C1_5–C3_5	1.549(4)
C1_5–C2_5	1.558(4)
C1_5–C4_5	1.564(4)
C2_5–F1_5	1.329(4)
C2_5–F2_5	1.332(4)
C2_5–F3_5	1.333(4)
C3_5–F4_5	1.326(4)
C3_5–F5_5	1.330(4)
C3_5–F6_5	1.348(4)
C4_5–F9_5	1.321(4)
C4_5–F7_5	1.329(4)
C4_5–F8_5	1.336(4)
O1_6–C1_6	1.357(7)
C1_6–C2_6	1.549(7)
C1_6–C4_6	1.551(8)
C1_6–C3_6	1.555(7)
C2_6–F2_6	1.329(6)
C2_6–F1_6	1.330(10)
C2_6–F3_6	1.347(8)
C3_6–F5_6	1.326(9)
C3_6–F4_6	1.326(7)
C3_6–F6_6	1.334(7)
C4_6–F8_6	1.323(6)
C4_6–F7_6	1.331(10)
C4_6–F9_6	1.335(7)
O1_7–C1_7	1.360(12)
C1_7–C3_7	1.552(11)
C1_7–C2_7	1.552(11)
C1_7–C4_7	1.554(11)
C2_7–F3_7	1.328(12)
C2_7–F1_7	1.332(11)
C2_7–F2_7	1.336(9)
C3_7–F5_7	1.326(11)
C3_7–F4_7	1.329(12)
C3_7–F6_7	1.332(11)
C4_7–F7_7	1.325(11)
C4_7–F9_7	1.333(12)
C4_7–F8_7	1.340(10)
O1_8–C1_8	1.368(14)
C1_8–C3_8	1.551(13)
C1_8–C4_8	1.553(13)
C1_8–C2_8	1.556(13)
C2_8–F3_8	1.328(13)
C2_8–F1_8	1.328(13)
C2_8–F2_8	1.330(13)
C3_8–F6_8	1.330(13)
C3_8–F4_8	1.333(13)
C3_8–F5_8	1.342(14)
C4_8–F9_8	1.311(13)
C4_8–F7_8	1.327(13)
C4_8–F8_8	1.336(13)
O1_9–C1_9	1.365(14)
C1_9–C2_9	1.544(13)
C1_9–C3_9	1.554(13)
C1_9–C4_9	1.558(13)
C2_9–F2_9	1.327(13)
C2_9–F1_9	1.328(13)
C2_9–F3_9	1.334(13)
C3_9–F5_9	1.320(13)
C3_9–F6_9	1.332(13)
C3_9–F4_9	1.333(13)
C4_9–F8_9	1.319(13)
C4_9–F9_9	1.323(13)
C4_9–F7_9	1.336(13)

Atom–Atom–Atom	**Angle [°]**
O1_8–Al1–O1_9	111.8(18)
O1_2–Al1–O1_1	117.5(2)
O1_2–Al1–O1_3	110.5(2)
O1_1–Al1–O1_3	112.2(2)
O1_8–Al1–F1	107.1(15)
O1_9–Al1–F1	101.4(12)
O1_2–Al1–F1	110.65(16)
O1_1–Al1–F1	99.35(9)
O1_3–Al1–F1	105.5(2)
Al1–F1–Al1	180.0
C3–Fe1–C4	89.58(18)
C3–Fe1–C1	170.05(16)
C4–Fe1–C1	89.60(15)
C3–Fe1–C2	88.32(18)
C4–Fe1–C2	162.47(18)
C1–Fe1–C2	89.49(16)
C3–Fe1–C5	94.06(17)

C4–Fe1–C5	98.20(17)	F4_2–C3_2–C1_2	111.1(4)
C1–Fe1–C5	95.87(15)	F5_2–C3_2–C1_2	110.5(3)
C2–Fe1–C5	99.31(17)	F6_2–C3_2–C1_2	112.1(3)
O1–C1–Fe1	179.7(4)	F7_2–C4_2–F9_2	107.4(4)
O1_4–Al2–O1_5	112.72(12)	F7_2–C4_2–F8_2	108.0(3)
O1_4–Al2–O1_6	110.5(5)	F9_2–C4_2–F8_2	107.4(3)
O1_5–Al2–O1_6	121.5(6)	F7_2–C4_2–C1_2	111.4(3)
O1_7–Al2–F2	109.7(10)	F9_2–C4_2–C1_2	110.8(3)
O1_4–Al2–F2	105.72(9)	F8_2–C4_2–C1_2	111.7(3)
O1_5–Al2–F2	98.78(9)	C1_3–O1_3–Al1	147.7(4)
O1_6–Al2–F2	105.4(6)	O1_3–C1_3–C2_3	112.4(4)
Al2–F2–Al2	180.0	O1_3–C1_3–C3_3	109.0(4)
O2–C2–Fe1	178.1(4)	C2_3–C1_3–C3_3	110.1(4)
O3–C3–Fe1	178.0(4)	O1_3–C1_3–C4_3	107.1(4)
O4–C4–Fe1	178.5(4)	C2_3–C1_3–C4_3	108.7(4)
O5–C5–Fe1	177.7(3)	C3_3–C1_3–C4_3	109.4(4)
C1_1–O1_1–Al1	145.7(2)	F1_3–C2_3–F3_3	108.6(4)
O1_1–C1_1–C3_1	110.9(3)	F1_3–C2_3–F2_3	108.5(4)
O1_1–C1_1–C4_1	107.9(3)	F3_3–C2_3–F2_3	106.3(4)
C3_1–C1_1–C4_1	109.9(3)	F1_3–C2_3–C1_3	110.0(4)
O1_1–C1_1–C2_1	109.7(3)	F3_3–C2_3–C1_3	111.2(4)
C3_1–C1_1–C2_1	109.1(3)	F2_3–C2_3–C1_3	112.1(4)
C4_1–C1_1–C2_1	109.3(3)	F4_3–C3_3–F6_3	108.1(4)
F1_1–C2_1–F3_1	108.1(3)	F4_3–C3_3–F5_3	108.0(5)
F1_1–C2_1–F2_1	107.1(3)	F6_3–C3_3–F5_3	107.0(5)
F3_1–C2_1–F2_1	107.7(3)	F4_3–C3_3–C1_3	112.2(4)
F1_1–C2_1–C1_1	110.8(3)	F6_3–C3_3–C1_3	112.3(4)
F3_1–C2_1–C1_1	110.9(3)	F5_3–C3_3–C1_3	109.0(5)
F2_1–C2_1–C1_1	112.1(3)	F9_3–C4_3–F8_3	106.3(4)
F4_1–C3_1–F6_1	108.5(3)	F9_3–C4_3–F7_3	109.2(5)
F4_1–C3_1–F5_1	107.7(3)	F8_3–C4_3–F7_3	108.0(5)
F6_1–C3_1–F5_1	107.7(3)	F9_3–C4_3–C1_3	110.9(4)
F4_1–C3_1–C1_1	110.6(3)	F8_3–C4_3–C1_3	112.8(4)
F6_1–C3_1–C1_1	112.4(3)	F7_3–C4_3–C1_3	109.6(4)
F5_1–C3_1–C1_1	109.8(3)	C1_4–O1_4–Al2	146.2(2)
F7_1–C4_1–F9_1	107.3(3)	O1_4–C1_4–C4_4	110.4(3)
F7_1–C4_1–F8_1	108.4(3)	O1_4–C1_4–C2_4	111.2(3)
F9_1–C4_1–F8_1	107.8(3)	C4_4–C1_4–C2_4	109.4(3)
F7_1–C4_1–C1_1	110.9(3)	O1_4–C1_4–C3_4	107.4(3)
F9_1–C4_1–C1_1	111.0(3)	C4_4–C1_4–C3_4	109.7(3)
F8_1–C4_1–C1_1	111.2(3)	C2_4–C1_4–C3_4	108.6(3)
C1_2–O1_2–Al1	153.2(4)	F3_4–C2_4–F2_4	108.7(3)
O1_2–C1_2–C2_2	109.3(3)	F3_4–C2_4–F1_4	106.9(3)
O1_2–C1_2–C4_2	107.7(3)	F2_4–C2_4–F1_4	106.7(3)
C2_2–C1_2–C4_2	110.4(3)	F3_4–C2_4–C1_4	111.1(3)
O1_2–C1_2–C3_2	110.7(3)	F2_4–C2_4–C1_4	112.3(3)
C2_2–C1_2–C3_2	109.7(3)	F1_4–C2_4–C1_4	110.8(3)
C4_2–C1_2–C3_2	109.0(3)	F4_4–C3_4–F5_4	108.5(3)
F3_2–C2_2–F2_2	108.2(4)	F4_4–C3_4–F6_4	107.2(3)
F3_2–C2_2–F1_2	108.0(4)	F5_4–C3_4–F6_4	108.0(3)
F2_2–C2_2–F1_2	107.7(4)	F4_4–C3_4–C1_4	110.5(3)
F3_2–C2_2–C1_2	109.9(3)	F5_4–C3_4–C1_4	110.7(3)
F2_2–C2_2–C1_2	112.7(4)	F6_4–C3_4–C1_4	111.8(3)
F1_2–C2_2–C1_2	110.2(3)	F9_4–C4_4–F8_4	107.7(3)
F4_2–C3_2–F5_2	107.4(4)	F9_4–C4_4–F7_4	107.8(3)
F4_2–C3_2–F6_2	107.7(4)	F8_4–C4_4–F7_4	107.8(3)
F5_2–C3_2–F6_2	107.7(3)	F9_4–C4_4–C1_4	110.4(3)

F8_4–C4_4–C1_4	112.5(3)	C3_7–C1_7–C4_7	109.6(8)
F7_4–C4_4–C1_4	110.4(3)	C2_7–C1_7–C4_7	109.9(8)
C1_5–O1_5–Al2	143.8(2)	F3_7–C2_7–F1_7	110.4(12)
O1_5–C1_5–C3_5	111.0(2)	F3_7–C2_7–F2_7	108.2(11)
O1_5–C1_5–C2_5	107.5(3)	F1_7–C2_7–F2_7	106.5(9)
C3_5–C1_5–C2_5	109.6(3)	F3_7–C2_7–C1_7	109.6(10)
O1_5–C1_5–C4_5	110.0(2)	F1_7–C2_7–C1_7	110.8(9)
C3_5–C1_5–C4_5	109.3(3)	F2_7–C2_7–C1_7	111.2(8)
C2_5–C1_5–C4_5	109.4(3)	F5_7–C3_7–F4_7	107.8(14)
F1_5–C2_5–F2_5	108.1(3)	F5_7–C3_7–F6_7	106.7(10)
F1_5–C2_5–F3_5	107.8(3)	F4_7–C3_7–F6_7	108.5(15)
F2_5–C2_5–F3_5	108.0(3)	F5_7–C3_7–C1_7	111.4(8)
F1_5–C2_5–C1_5	111.3(3)	F4_7–C3_7–C1_7	110.2(14)
F2_5–C2_5–C1_5	111.7(3)	F6_7–C3_7–C1_7	112.1(10)
F3_5–C2_5–C1_5	109.9(3)	F7_7–C4_7–F9_7	108.1(12)
F4_5–C3_5–F5_5	108.0(3)	F7_7–C4_7–F8_7	108.2(10)
F4_5–C3_5–F6_5	108.1(3)	F9_7–C4_7–F8_7	107.2(14)
F5_5–C3_5–F6_5	107.4(3)	F7_7–C4_7–C1_7	110.7(8)
F4_5–C3_5–C1_5	109.4(3)	F9_7–C4_7–C1_7	111.3(12)
F5_5–C3_5–C1_5	111.1(3)	F8_7–C4_7–C1_7	111.2(9)
F6_5–C3_5–C1_5	112.7(3)	C1_8–O1_8–Al1	152(3)
F9_5–C4_5–F7_5	108.1(3)	O1_8–C1_8–C3_8	108.6(17)
F9_5–C4_5–F8_5	108.2(3)	O1_8–C1_8–C4_8	107.4(18)
F7_5–C4_5–F8_5	107.6(3)	C3_8–C1_8–C4_8	110.9(12)
F9_5–C4_5–C1_5	110.7(3)	O1_8–C1_8–C2_8	108.7(18)
F7_5–C4_5–C1_5	109.9(3)	C3_8–C1_8–C2_8	110.5(12)
F8_5–C4_5–C1_5	112.2(3)	C4_8–C1_8–C2_8	110.7(12)
C1_6–O1_6–Al2	149.9(13)	F3_8–C2_8–F1_8	108.5(19)
O1_6–C1_6–C2_6	109.4(9)	F3_8–C2_8–F2_8	109(2)
O1_6–C1_6–C4_6	108.0(8)	F1_8–C2_8–F2_8	106.5(16)
C2_6–C1_6–C4_6	109.5(5)	F3_8–C2_8–C1_8	112.3(19)
O1_6–C1_6–C3_6	110.4(9)	F1_8–C2_8–C1_8	109.7(14)
C2_6–C1_6–C3_6	109.5(5)	F2_8–C2_8–C1_8	111.1(14)
C4_6–C1_6–C3_6	110.0(5)	F6_8–C3_8–F4_8	112.4(17)
F2_6–C2_6–F1_6	107.8(7)	F6_8–C3_8–F5_8	102.0(16)
F2_6–C2_6–F3_6	107.5(5)	F4_8–C3_8–F5_8	108.0(17)
F1_6–C2_6–F3_6	108.8(7)	F6_8–C3_8–C1_8	113.2(15)
F2_6–C2_6–C1_6	112.4(5)	F4_8–C3_8–C1_8	112.6(16)
F1_6–C2_6–C1_6	109.9(7)	F5_8–C3_8–C1_8	108.0(14)
F3_6–C2_6–C1_6	110.4(5)	F9_8–C4_8–F7_8	108.9(18)
F5_6–C3_6–F4_6	108.3(7)	F9_8–C4_8–F8_8	107.7(18)
F5_6–C3_6–F6_6	108.9(8)	F7_8–C4_8–F8_8	107.5(17)
F4_6–C3_6–F6_6	107.8(5)	F9_8–C4_8–C1_8	111.7(16)
F5_6–C3_6–C1_6	109.8(7)	F7_8–C4_8–C1_8	110.0(14)
F4_6–C3_6–C1_6	109.8(5)	F8_8–C4_8–C1_8	111.0(15)
F6_6–C3_6–C1_6	112.2(5)	C1_9–O1_9–Al1	157(3)
F8_6–C4_6–F7_6	109.0(8)	O1_9–C1_9–C2_9	109.8(17)
F8_6–C4_6–F9_6	107.4(5)	O1_9–C1_9–C3_9	108.2(17)
F7_6–C4_6–F9_6	106.6(7)	C2_9–C1_9–C3_9	110.8(12)
F8_6–C4_6–C1_6	112.7(5)	O1_9–C1_9–C4_9	108.5(16)
F7_6–C4_6–C1_6	110.3(7)	C2_9–C1_9–C4_9	110.8(12)
F9_6–C4_6–C1_6	110.6(5)	C3_9–C1_9–C4_9	108.7(12)
C1_7–O1_7–Al2	152(2)	F2_9–C2_9–F1_9	106.2(19)
O1_7–C1_7–C3_7	109.9(15)	F2_9–C2_9–F3_9	107.9(17)
O1_7–C1_7–C2_7	108.3(15)	F1_9–C2_9–F3_9	106.5(18)
C3_7–C1_7–C2_7	110.1(8)	F2_9–C2_9–C1_9	111.0(14)
O1_7–C1_7–C4_7	108.9(15)	F1_9–C2_9–C1_9	112.9(16)

F3_9–C2_9–C1_9	112.0(16)
F5_9–C3_9–F6_9	108.0(18)
F5_9–C3_9–F4_9	108.2(18)
F6_9–C3_9–F4_9	107.4(17)
F5_9–C3_9–C1_9	111.9(14)
F6_9–C3_9–C1_9	110.5(16)
F4_9–C3_9–C1_9	110.7(17)
F8_9–C4_9–F9_9	107.5(17)
F8_9–C4_9–F7_9	108.9(16)
F9_9–C4_9–F7_9	106.9(17)
F8_9–C4_9–C1_9	113.7(15)
F9_9–C4_9–C1_9	110.7(15)
F7_9–C4_9–C1_9	108.9(14)

Symmetry transformations used to generate equivalent atoms:
#1: 1-X, 2-Y, 1-Z; #2: 1-X, 1-Y, -Z;

7 Quantum Chemical Calculations

Table S15: SCF Energy, FreeH energy and FreeH entropy of presented compounds.

Compound	SCF/ Hartree	FreeH energy [kJ/mol]	FreeH entropy [kJ/mol]
$[Fe(CO)_5]^{\bullet+}$ in C_{4v}	–1830.743371438	139.87	0.45513
$[Fe(CO)_5]^{\bullet+}$ in C_{2v}	–1830.101932301	138.04	0.46378
$[Fe(CO)_5]^{\bullet+}$ in C_{4v} with ^{13}C axial isotope	–1830.743371446	139.47	0.45575
$[Fe(CO)_5]^{\bullet+}$ in C_{4v} with one ^{13}C equatorial isotope	–1830.743364605	139.44	0.46732
$[Fe(CO)_5]^{\bullet+}$ in presence of –0.3e point charges	–1831.238180570	139.91	0.46572

Graphic of $[Fe(CO)_5]^{\bullet+}$:

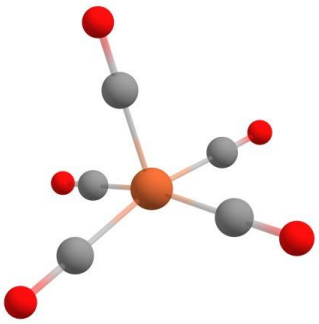

Table S16: Atom coordinates of $[Fe(CO)_5]^{\bullet+}$ in C_{4v}.

0.00000000000000	0.00000000000000	0.47188976815579	fe
0.00000000000000	3.48329789506462	0.85796673993665	c
-0.00000000000000	5.62170246988202	1.07446652659246	o
0.00000000000000	-3.48329789506462	0.85796673993665	c
0.00000000000000	-5.62170246988202	1.07446652659246	o
3.48329789506462	-0.00000000000000	0.85796673993665	c
5.62170246988202	0.00000000000000	1.07446652659246	o
-3.48329789506462	-0.00000000000000	0.85796673993665	c
-5.62170246988202	-0.00000000000000	1.07446652659246	o
0.00000000000000	0.00000000000000	-3.03926623750873	c
0.00000000000000	0.00000000000000	-5.19051882009860	o

Table S17: Vibrational spectrum of $[Fe(CO)_5]^{\bullet+}$ in C_{4v}.

# mode	symmetry	wave number cm**(-1)	IR intensity km/mol	selection rules IR	RAMAN
1		-0.00	0.00000	-	-
2		-0.00	0.00000	-	-
3		-0.00	0.00000	-	-
4		-0.00	0.00000	-	-
5		0.00	0.00000	-	-
6		0.00	0.00000	-	-
7	b1	45.93	0.00000	NO	YES
8	e	79.83	0.03520	YES	YES
9	e	79.83	0.03520	YES	YES
10	b2	95.73	0.00000	NO	YES
11	e	99.87	1.27405	YES	YES
12	e	99.87	1.27405	YES	YES
13	a1	103.88	0.73251	YES	YES
14	e	336.28	0.01071	YES	YES
15	e	336.28	0.01071	YES	YES
16	a2	354.81	0.00000	NO	NO
17	b1	375.92	0.00000	NO	YES
18	a1	388.25	0.01765	YES	YES
19	a1	421.81	5.95980	YES	YES
20	e	423.65	14.44500	YES	YES
21	e	423.65	14.44500	YES	YES
22	b1	429.07	0.00000	NO	YES
23	e	489.67	1.66730	YES	YES
24	e	489.67	1.66730	YES	YES
25	b2	530.86	0.00000	NO	YES
26	a1	604.83	70.84663	YES	YES
27	e	607.67	88.40870	YES	YES
28	e	607.67	88.40870	YES	YES
29	e	2101.94	855.45298	YES	YES
30	e	2101.94	855.45298	YES	YES
31	a1	2106.00	410.53214	YES	YES
32	b1	2119.61	0.00000	NO	YES
33	a1	2171.11	4.23665	YES	YES

Graphic of the transition state of $[Fe(CO)_5]^{\bullet+}$ in C_{2v}:

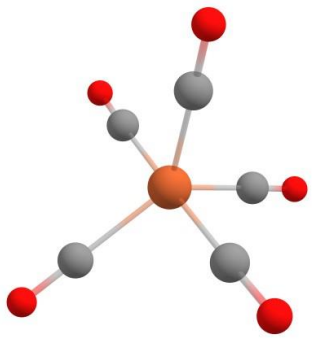

Table S18: Atom coordinates of the transition state of $[Fe(CO)_5]^{\bullet+}$ in C_{2v}.

0.05231087658940	0.12251200946792	-0.16682081776768	fe
0.97415348825330	0.49090210185250	3.27583325720406	c
1.54434488285331	0.74384803595184	5.30728551089112	o
0.96933404390281	2.25957329584900	-3.10011195324520	c
1.48838400698667	3.46906270890595	-4.75714179453257	o
-2.84114180153247	2.09988934172146	0.42106792249854	c
-4.57954962800985	3.25563816802423	0.80578611597697	o
2.92491732305575	-1.90159243678696	-0.69176205238501	c
4.63023197158039	-3.13396001285121	-0.97265145406391	o
-1.97700675303327	-2.82913533308322	-0.06924606400843	c
-3.18597822167361	-4.57673787905108	-0.05223867056793	o

Table S19: Vibrational spectrum of the transition state of $[Fe(CO)_5]^{\bullet+}$ in C_{2v}.

# mode	symmetry	wave number cm**(-1)	IR intensity km/mol	selection rules IR	RAMAN
1	a	-244.40	0.00000	YES	YES
2		-0.00	0.00000	-	-
3		0.00	0.00000	-	-
4		0.00	0.00000	-	-
5		0.00	0.00000	-	-
6		0.00	0.00000	-	-
7		0.00	0.00000	-	-
8	a	69.69	0.07723	YES	YES
9	a	79.56	0.78377	YES	YES
10	a	84.45	0.19928	YES	YES
11	a	89.66	0.00001	YES	YES
12	a	100.02	1.12369	YES	YES
13	a	104.79	0.89611	YES	YES
14	a	138.53	0.33492	YES	YES
15	a	302.53	2.07287	YES	YES
16	a	305.39	0.01038	YES	YES
17	a	321.57	0.43423	YES	YES
18	a	337.81	0.00007	YES	YES
19	a	361.49	14.71332	YES	YES
20	a	370.65	0.05269	YES	YES
21	a	387.04	6.28696	YES	YES
22	a	393.72	12.59000	YES	YES
23	a	454.83	0.69606	YES	YES
24	a	504.05	22.36541	YES	YES
25	a	522.57	0.00029	YES	YES
26	a	548.22	56.98917	YES	YES
27	a	555.65	30.99505	YES	YES
28	a	594.17	61.05792	YES	YES
29	a	2190.55	677.30629	YES	YES
30	a	2204.57	886.90214	YES	YES
31	a	2206.90	254.15155	YES	YES
32	a	2232.58	339.90705	YES	YES
33	a	2262.52	23.95940	YES	YES

Table S20: Atom coordinates of $[Fe(CO)_5]^{\bullet+}$ with ^{13}C axial isotope.

-0.00073226887344	0.41233824047360	-0.18569431561772	fe
0.02290423652537	2.41488460560895	2.69076364389802	c
0.03777241270421	3.62457880055027	4.46730707927908	o
-0.02564377248878	-0.91836759044348	-3.42774001408301	c
-0.04081128128581	-1.75496767632156	-5.40753199797469	o
-3.48473396504020	0.75671210291658	-0.34658389714616	c
-5.62353128454110	0.94968432075949	-0.43595698244683	o
3.48143374733552	0.74789653054349	-0.39624438793009	c
5.61920154404351	0.93585549394940	-0.51583494985986	o
0.00707211105018	-2.67036631805007	1.49319997889826	c
0.01175995464845	-4.55971619857217	2.52189941812211	o

Table S21: Vibrational spectrum of $[Fe(CO)_5]^{\bullet+}$ with ^{13}C axial isotope.

# mode	symmetry	wave number	IR intensity	selection rules	
#		cm**(-1)	km/mol	IR	RAMAN
1		-0.00	0.00000	-	-
2		0.00	0.00000	-	-
3		0.00	0.00000	-	-
4		0.00	0.00000	-	-
5		0.00	0.00000	-	-
6		0.00	0.00000	-	-
7	b1	45.94	0.00000	NO	YES
8	e	79.70	0.03851	YES	YES
9	e	79.70	0.03851	YES	YES
10	b2	95.74	0.00000	NO	YES
11	e	99.87	1.27531	YES	YES
12	e	99.87	1.27531	YES	YES
13	a1	103.61	0.71299	YES	YES
14	e	331.57	0.00434	YES	YES
15	e	331.57	0.00434	YES	YES
16	a2	354.81	0.00000	NO	NO
17	b1	375.89	0.00000	NO	YES
18	a1	385.82	0.07945	YES	YES
19	a1	419.65	5.84798	YES	YES
20	e	422.28	13.74194	YES	YES
21	e	422.28	13.74194	YES	YES
22	b1	429.08	0.00000	NO	YES
23	e	482.61	2.53204	YES	YES
24	e	482.61	2.53204	YES	YES
25	b2	530.86	0.00000	NO	YES
26	a1	604.78	70.74019	YES	YES
27	e	606.97	87.97904	YES	YES
28	e	606.97	87.97904	YES	YES
29	a1	2061.25	370.76160	YES	YES
30	e	2101.94	855.42801	YES	YES
31	e	2101.94	855.42801	YES	YES
32	b1	2119.61	0.00000	NO	YES
33	a1	2168.25	23.87063	YES	YES

Table S22: Atom coordinates of $[Fe(CO)_5]^{\bullet+}$ with one ^{13}C equatorial isotope

-0.00073226887344	0.41233824047360	-0.18569431561772	fe
0.02290423652537	2.41488460560895	2.69076364389802	c
0.03777241270421	3.62457880055027	4.46730707927908	o
-0.02564377248878	-0.91836759044348	-3.42774001408301	c
-0.04081128128581	-1.75496767632156	-5.40753199797469	o
-3.48473396504020	0.75671210291658	-0.34658389714616	c
-5.62353128454110	0.94968432075949	-0.43595698244683	o
3.48143374733552	0.74789653054349	-0.39624438793009	c
5.61920154404351	0.93585549394940	-0.51583494985986	o
0.00707211105018	-2.67036631805007	1.49319997889826	c
0.01175995464845	-4.55971619857217	2.52189941812211	o

Table S23: Vibrational spectrum of $[Fe(CO)_5]^{\bullet+}$ with one ^{13}C equatorial isotope.

# mode	symmetry	wave number cm**(-1)	IR intensity km/mol	selection rules IR	RAMAN
1		-0.00	0.00000	-	-
2		0.00	0.00000	-	-
3		0.00	0.00000	-	-
4		0.00	0.00000	-	-
5		0.00	0.00000	-	-
6		0.00	0.00000	-	-
7	a	45.85	0.00012	YES	YES
8	a	79.71	0.03240	YES	YES
9	a	79.75	0.03031	YES	YES
10	a	95.44	0.00058	YES	YES
11	a	99.53	1.25946	YES	YES
12	a	99.71	1.28306	YES	YES
13	a	103.84	0.73251	YES	YES
14	a	333.14	0.01217	YES	YES
15	a	336.13	0.01037	YES	YES
16	a	351.52	0.00208	YES	YES
17	a	373.57	0.01595	YES	YES
18	a	387.53	0.02000	YES	YES
19	a	420.18	7.01571	YES	YES
20	a	421.79	13.76880	YES	YES
21	a	422.02	12.62439	YES	YES
22	a	426.44	0.44547	YES	YES
23	a	486.64	1.88226	YES	YES
24	a	488.38	0.93034	YES	YES
25	a	525.88	0.51108	YES	YES
26	a	601.30	70.06879	YES	YES
27	a	602.33	88.31752	YES	YES
28	a	607.21	87.92519	YES	YES
29	a	2065.25	624.86173	YES	YES
30	a	2101.89	855.58079	YES	YES
31	a	2105.79	432.22349	YES	YES
32	a	2115.06	162.41488	YES	YES
33	a	2164.25	23.13827	YES	YES

Graphic of $[Fe(CO)_5]^{\bullet+}$ in presence of –0.3*e* point charges:

The position of the fluorine atoms and cation was obtained from the scXRD structure of $[Fe(CO)_5][Al(OR^F)_4]$ (**1**), representing the nearest contact point between the cation and the anion. A charge of –0.3e was chosen, due to calculations revealing this to be the partial negative charge typically residing in -CF_3 groups of the aluminate anion (cf. related work[34]).

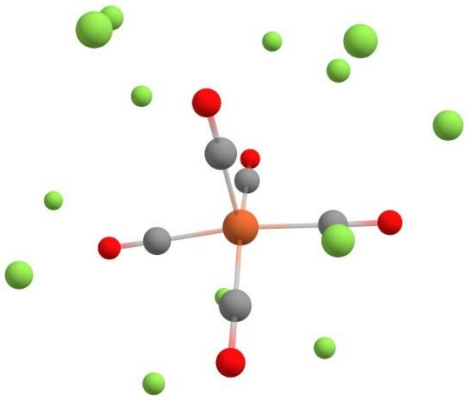

Table S24: Atom coordinates of $[Fe(CO)_5]^{\bullet+}$ in presence of –0.3e point charges (coordinates obtained from scXRD).

```
$coord
   17.14833672545167      23.92798997975182       7.14345954836085      fe
   19.09245672684867      22.03174052054385       9.41275417265283       c
   18.68737692450002      22.20349016910658       4.48452040470616       c
   20.25673022031348      20.87719722689473      10.75616047464929       o
   15.92692358315655      26.29369087201771       4.80504252188231       c
   19.59679628361942      21.14436481666820       2.86908991679595       o
   16.12007438008068      26.08377442491591       9.76505014488844       c
   14.25294749017931      21.77729645676748       7.27780017856050       c
   15.25357826015603      27.74084691770837       3.39474558425248       o
   12.58701785104072      20.49171388445844       7.37311985401275       o
   15.49501722874271      27.42279089312486      11.29742339016910       o
   13.36767127202812      22.36283754511340       1.32110753372588       f
   19.34194403900014      21.27158684855638      -2.39806245215010       f
   10.61794968534641      19.55662826511438       2.38189584515393       f
   10.48757181083011      26.04560762637684       8.14070014966999       f
    9.78364316022863      27.51184612647397       3.15783817891264       f
   21.46124165214995      27.44823416566682      10.19148385244537       f
   21.91729303725813      27.16770999164450       4.44717185757906       f
   24.12243523907132      22.07626813721840       6.31010166575764       f
   19.19708141373858      16.15056700082764       5.25600298481076       f
   11.19472055474794      15.45529707532920       8.27727065669669       f
   15.07840064840322      20.92585956432997      13.21442393195160       f
    9.84266119682682      20.97897598624095      12.13245368039261       f
   11.44152445580244      24.41620639322727      13.61187113048289       f
```

Table S25: Vibrational spectrum of $[Fe(CO)_5]^{\bullet+}$ in presence of –0.3e point charges (coordinates obtained from scXRD).

```
$vibrational spectrum
#  mode     symmetry     wave number   IR intensity    selection rules
#                         cm**(-1)      km/mol          IR      RAMAN
     1                      -0.00        0.00000         -        -
     2                      -0.00        0.00000         -        -
     3                       0.00        0.00000         -        -
     4                       0.00        0.00000         -        -
     5                       0.00        0.00000         -        -
     6                       0.00        0.00000         -        -
     7        a             37.91        0.17338       YES      YES
     8        a             80.73        0.39488       YES      YES
     9        a             83.54        0.42936       YES      YES
    10        a             98.04        0.19804       YES      YES
    11        a            104.02        0.77028       YES      YES
    12        a            105.95        0.28101       YES      YES
    13        a            110.72        2.24313       YES      YES
    14        a            330.75        0.01999       YES      YES
    15        a            334.93        0.03587       YES      YES
    16        a            362.03        0.02235       YES      YES
    17        a            375.22        0.87776       YES      YES
    18        a            380.93        0.74871       YES      YES
    19        a            423.35        6.22450       YES      YES
    20        a            429.47        4.39964       YES      YES
    21        a            433.79        3.55038       YES      YES
    22        a            445.64        0.21677       YES      YES
    23        a            482.25        6.93588       YES      YES
    24        a            486.54        6.36382       YES      YES
    25        a            539.03        0.78560       YES      YES
    26        a            614.57       77.92819       YES      YES
    27        a            619.96       93.08094       YES      YES
    28        a            623.93       89.94672       YES      YES
    29        a           2062.92     1140.46706       YES      YES
    30        a           2075.77      862.53320       YES      YES
    31        a           2099.42      248.31165       YES      YES
    32        a           2141.97      295.82794       YES      YES
    33        a           2179.14       71.14947       YES      YES
```

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