Electronic Supporting Information

To

Guilty and charged. A stable solution of the hexamethylbenzene radical cation as ligand forming oxidising agent.

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S-1 Experimental Details and Characterisation Techniques

All reactions and manipulations were carried out under an inert argon atmosphere, using standard Schlenk-line and glovebox (Box atmosphere kept below 1 ppm H_2O/O_2) techniques. Glassware has been stored over-night in an oven set to 180°C and flame dried under vacuum prior to use. C_6Me_6 (Alfa Aesar, >99 %) was sublimed under dynamic vacuum prior to use. In (ABCR, 99.99 %) and Ga (Alfa Aesar, 99.99 %) were used as received. I_2 was sublimed under static vacuum. CH_2Cl_2 and pentane were collected from a solvent purification system (SPS) and oxygen removed by purging with Argon. PhF, *o*-DFB, CD_2Cl_2, hexane and heptane were stirred over CaH_2 and distilled. All solvents were stored over activated 3 Å molecular sieves in gas tight ampoules.

Powder Diffraction. Powder diffractograms were recorded with the sample sealed with perfluoropolyalkylether oil (AB128330, abcr GmbH & Co. KG) in a 0.3 mm thick capillary (Hilgenberg GmbH, wall thickness 0.01 mm) at 100(10) K in the 2θ range 2.0-40.0° with a STOE STADI P powder diffractometer with Mo-$K_{\alpha1}$ radiation (λ = 0.709300 Å) equipped with a Ge-(111) monochromator and Mythen 1K detector. Data acquiring, processing and the calculation of powder diffractograms from single-crystal data were performed using STOE WinXPOW® package. All powder diffractograms were background corrected.

ATR-IR and Raman Spectroscopy. ATR FT-IR spectra were recorded at ambient temperature on a Diamond crystal on a FTIR Bruker ALPHA with a QuickSnap Platinum ATR sampling module inside an inert atmosphere glovebox. Spectra were recorded in a range from 4000-500 cm^{-1}. The spectra were recorded with 64 scans and a resolution of 2 cm^{-1}. The Raman spectra were recorded at ambient temperature on a Vertex 70 IR-spectrometer with installed RAM II Raman module. Data processing was carried out with the software package OPUS 7.5. For all spectra, signal intensity was normalised to and the relative band intensities were described as follows: ≥ 0.8 = very very strong (vvs), ≥ 0.7 = very strong (vs), ≥ 0.6 = strong (s), ≥ 0.5 = medium strong (ms), ≥ 0.4 = medium (m), ≥ 0.3 = medium weak (mw), ≥ 0.2 = weak (w), ≥ 0.1 = very weak (vw), < 0.1 = very very weak (vvw).

Single crystal X-ray diffraction. Single crystal X-ray diffraction data were collected using a Bruker SMART APEX2 Quazar CCD area detector diffractometer. Crystals were selected under perfluoropolyether oil, mounted on 0.1 to 0.3 mm diameter CryoLoops and quench-cooled using an Oxford Cryosystems open flow N_2 cooling device.[1] Data were collected at 100 K using monochromated Cu Kα radiation 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.[2] Graphical representations have been prepared using Olex2-1.2.

NMR spectroscopy. NMR samples were prepared inside an inert atmosphere glovebox in either flame sealable NMR tubes or NMR tubes equipped with a gas-tight J.Young valve. ^{1}H, ^{13}C, ^{19}F, ^{27}Al, ^{31}P, ^{71}Ga, ^{115}In-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. ^{1}H and ^{13}C NMR spectra are reported relative to TMS and were calibrated to residual solvent resonances.[3] Data analysis was performed using Bruker TOPSPIN 3.5 software. The broad resonance at $\delta = 70$ ppm observed in ^{27}Al-NMR spectra corresponds to a background from Al-nuclei in the probe head.

EPR spectroscopy. Continuous-wave electron paramagnetic resonance spectroscopy was performed on a Bruker EMX spectrometer with a Bruker ER 041 MR microwave bridge. The spectra were recorded at room temperature, using a Bruker 4122-SHQ-E resonator in the X band. The microwave frequency was controlled with a Systron Donner 6520 microwave frequency counter.

Electron spray ionisation (ESI). Electron spray ionisation mass spectra were recorded on an Advion Express CMS$_L$ by the use of an ESI-ion source with a ESI-voltage 3500 V. Capillary temperature was set to 180 °C with capillary voltage of 100 V, the source gas temperature was set to 80 °C. Source voltage was varied between 15, 20, 30, 50 V to check for fragmentation of detected species. Data analysis was performed with Advion Data Express software; graphical representations were done with group internal software.

Quantum Chemical Calculations. All quantum chemical calculations were carried out with the TURBOMOLE program package using BP86 functionals with def-SV(P) basis sets and D3(BJ) dispersion correction.[4] Vibrational frequencies were calculated using the AOFORCE-module.[5] All calculated structures were checked for consistency in terms of geometric conversion, sensible electron occupations and the absence of imaginary vibrational frequencies. Thermal contributions to the enthalpy and free energy of the systems were calculated with the FREEH application based on the analysis of the vibrations obtained by BP86/def2-def-SV(P)/D3(BJ) calculations.

S-1.1 Synthesis of $[C_6Me_6][Al(OR^F)_4]$ **1**

S-1.1.1 Synthesis of **1** in SO_2

C_6Me_6 (0.033 g, 0.205 mmol) and $Ag[Al(OR^F)_4]$ (0.220 g, 0.205 mmol, 1 eq.) were weighed into one arm of a H-cell equipped with a G4 frit. Iodine (0.026 g, 0.102 mmol, 0.5 eq.) was added under a positive stream of Argon to the empty arm and sublimed to the other arm under reduced pressure. At -78°C SO_2 (7 ml) was vacuum transferred onto the reaction mixture. The reaction mixture was then stirred at ambient temperature for 12 h. The supernatant solution was separated from the formed AgI by filtration over the internal frit and the precipitate extracted three times with SO_2 by recondensation

and filtration. The solvent was removed under reduced pressure to yield the title compound as dark red oily solid.

Additional data on gathered EPR spectra. Comparison of different ratios of magnetically equivalent protons (9:9, 6:12, 12:6):

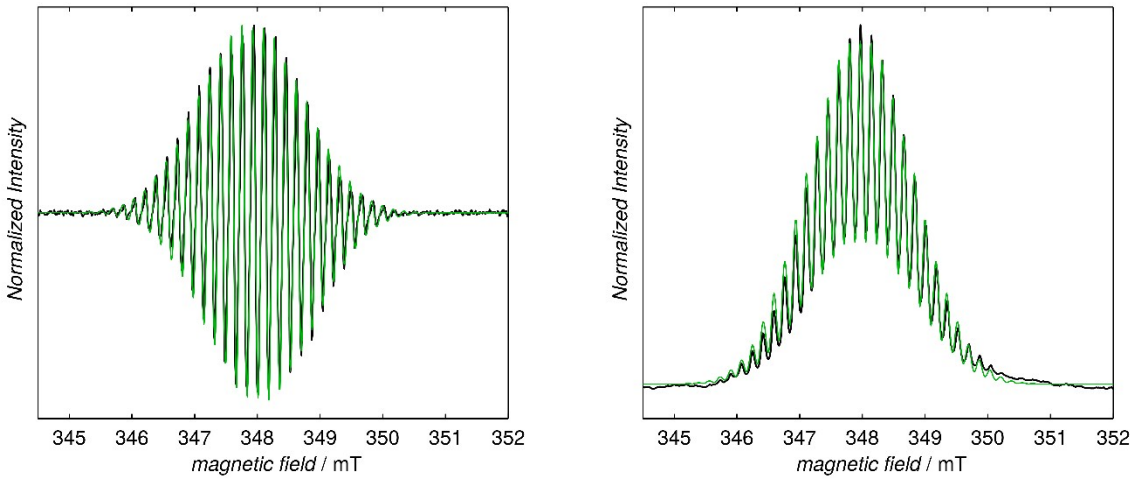


Figure S 1 ***Ratio: 9:9*** *Field modulated liquid state cw-EPR spectrum (left, black) and integrated spectrum (right, black). The corresponding fit is shown in green.*

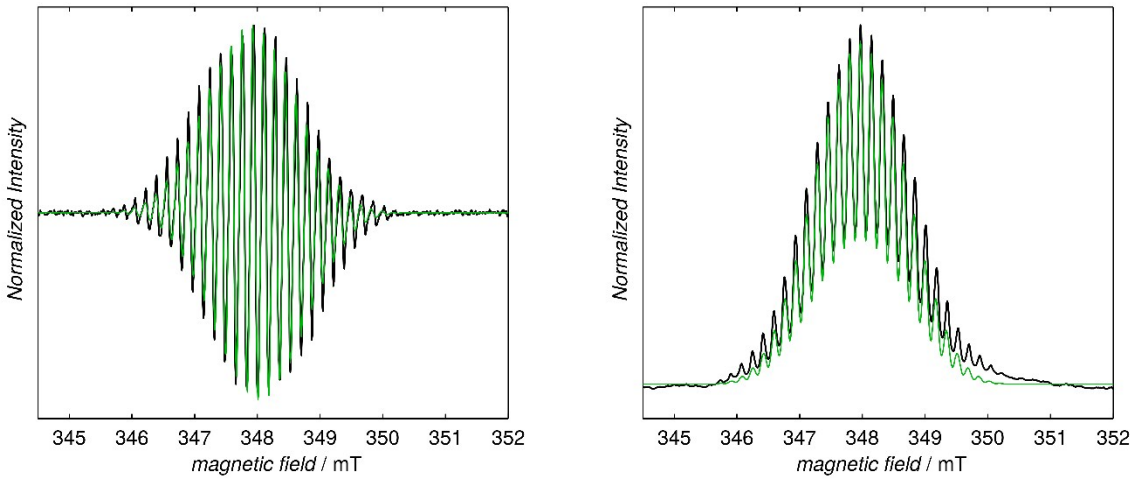


Figure S 2 ***Ratio: 12:6*** *Field modulated liquid state cw-EPR spectrum (left, black) and integrated spectrum (right, black). The corresponding fit is shown in green.*

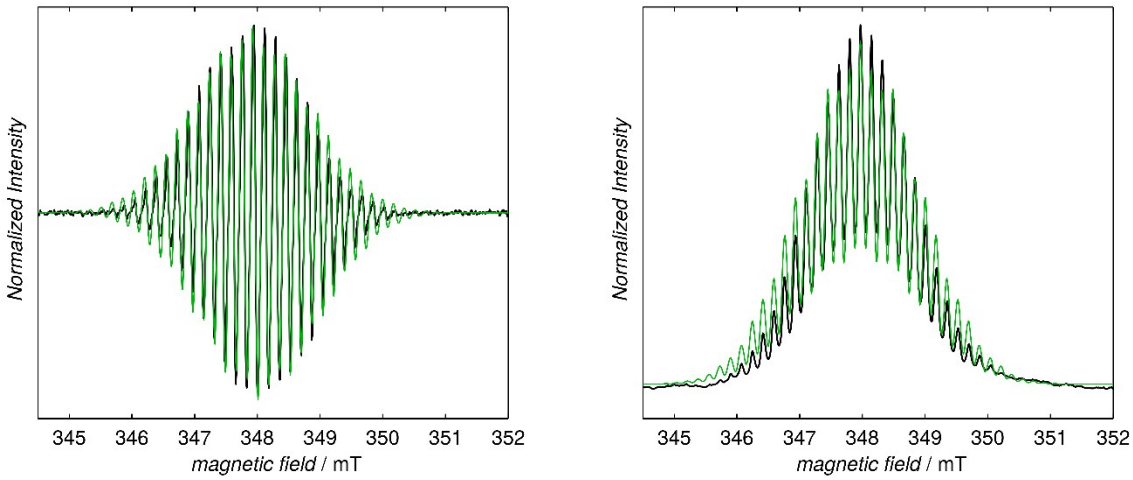
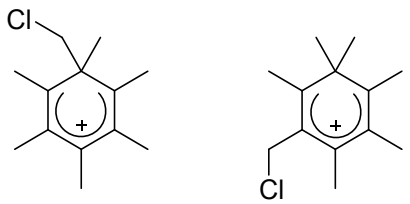


Figure S 3 ***Ratio 6:12*** *Field modulated liquid state cw-EPR spectrum (left, black) and integrated spectrum (right, black). The corresponding fit is shown in green.*

S-1.1.2 Synthesis of **1** in CH_2Cl_2; Isolation of $[C_6Me_6CH_2Cl][Al(OR^F)_4]$ **1a**

$Ag[Al(OR^F)_4]$ (300 mg, 0.279 mmol) and C_6Me_6 (45 mg, 0.279 mmol, 1.00 eq.) were weighed into the reaction vessel and dissolved in CH_2Cl_2 (8 ml). Iodine (35 mg, 0.140 mmol, 0.50 eq.) was added under argon flow to the stirred reaction mixture. Within ten minutes the solution developed a dark intensive violet-red colour, accompanied by formation of a yellow precipitate. The reaction mixture was filtered and concentrated to half volume. Half of the obtained solution was further concentrated to yield blood red poorly diffracting crystals at −25 °C. The other half of the obtained solution was layered with pentane (10 ml). On the solvent interface the dark red colour was slowly changing for bright yellow. Citron yellow crystals suitable for scXRD were obtained from the layered sample.

Due to high disorder in both cation and anion part the received molecular structure was not satisfactorily refined. While $[Al(OR^F)_4]^-$ was clearly assignable the remaining electron density suggested presence of six membered planar ring with five in plane residues and two residues above and underneath the ring plane. The isolated crystals were used in further NMR experiments.



1a **1a'**

^{1}H-NMR (400.16 MHz, CD_2Cl_2, 298 K) comp. **1a** δ = 4.16 (s, 2H, –CH_2Cl), 2.88 (s, 3H, *p*–CH_3), 2.67 (s, 6H, *o*–CH_3), 2.38 (s, 6H, *m*–CH_3), 1.51 (s, 3H, *ipso*–CH_3) ppm. comp. **1a'** δ = 4.63 (s, 2H, –CH_2Cl), 2.97 (s, 3H, *p*–CH_3), 2.77 (s, 3H, *o*–CH_3), 2.68 (s, 3H, *o*–CH_3), 2.38 (s, 3H, *m*–CH_3), 1.60 (s, 6H, *ipso*–CH_3) ppm. C_6Me_6 δ = 2.25 (s, 18H, –CH_3) ppm. ^{13}C-NMR (100.62 MHz, CD_2Cl_2, 298 K) comp. **1a** δ = 194.3 (*p*–CCH_3), 141.8 (*m*–CCH_3), 61.1 (*ipso*–C(CH_3)CH_2Cl), 46.5 (–CH_2Cl), 25.5 (*p*–CH_3), 23.8 (*ipso*–CH_3), 21.8 (*o*–CH_3), 16.0 (*m*–

CH_3) ppm. comp **1a'** δ = 202.6 (o–CCH_3), 198.8 (*o*–CCH_3), 190.4 (*p*–CCH_3), 138.3 (–CCH_2Cl), 57.6 (*ipso*–$C(CH_3)_2$), 37.7 (–CH_2Cl), 24.8 (*ipso*–CH_3), 24.1 (*p*–CH_3), 23.7 (*o*–CH_3), 21.6 (*o*–CH_3), 16.1 (*m*–CH_3) ppm. C_6Me_6 δ = 132.2 (–CCH_3), 16.8 (–CH_3) ppm. ^{19}F-NMR (376.54 MHz, CD_2Cl_2, 298 K) δ = −74.6 (s, 9F, $HOC(CF_3)_3$), −75.8 (s, 36F, $[Al\{OC(CF_3)\}_4]^-$). ^{27}Al-NMR (104.27 MHz, CD_2Cl_2, 298 K) δ = 34.6 (s, 1Al, $[Al\{OC(CF_3)\}_4]^-$).

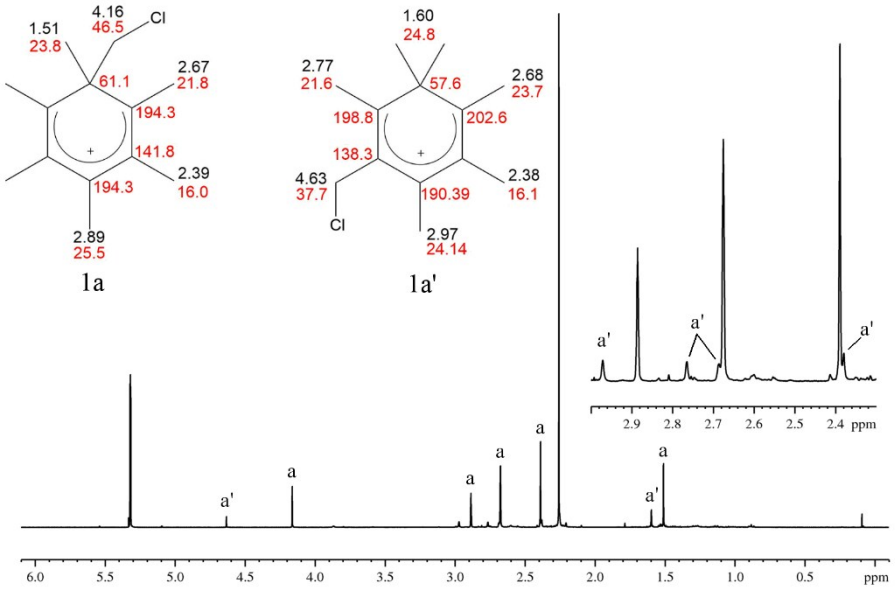


Figure S 4 ^{1}H-NMR (400.17 MHz, CD_2Cl_2, 298 K) spectrum of isolated crystals from reaction of $Ag[Al(OR^F)_4]$/0.5 I_2 with C_6Me_6 in CH_2Cl_2. (^{1}H chemical shift in black, ^{13}C chemical shift in red determined from ^{1}H-^{13}C hmbc and hsqc experiments). Inset shows magnified region.

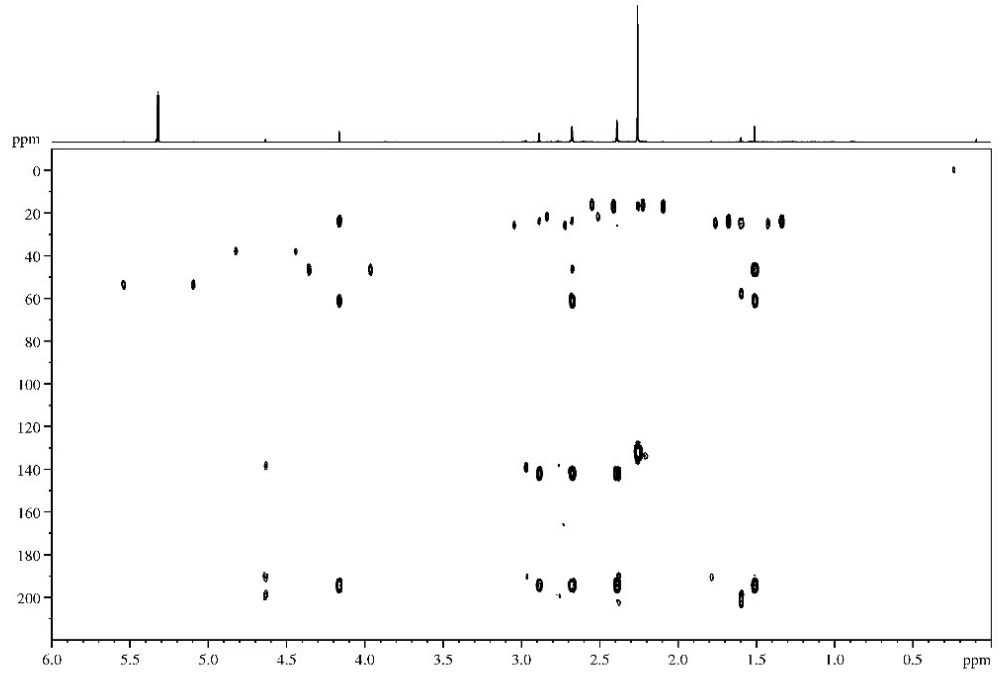


Figure S 5 $^{1}H,^{13}C$-HMBC-NMR spectrum of isolated crystals from the reaction between $Ag[Al(OR^F)_4]$ and C_6Me_6 in CH_2Cl_2.

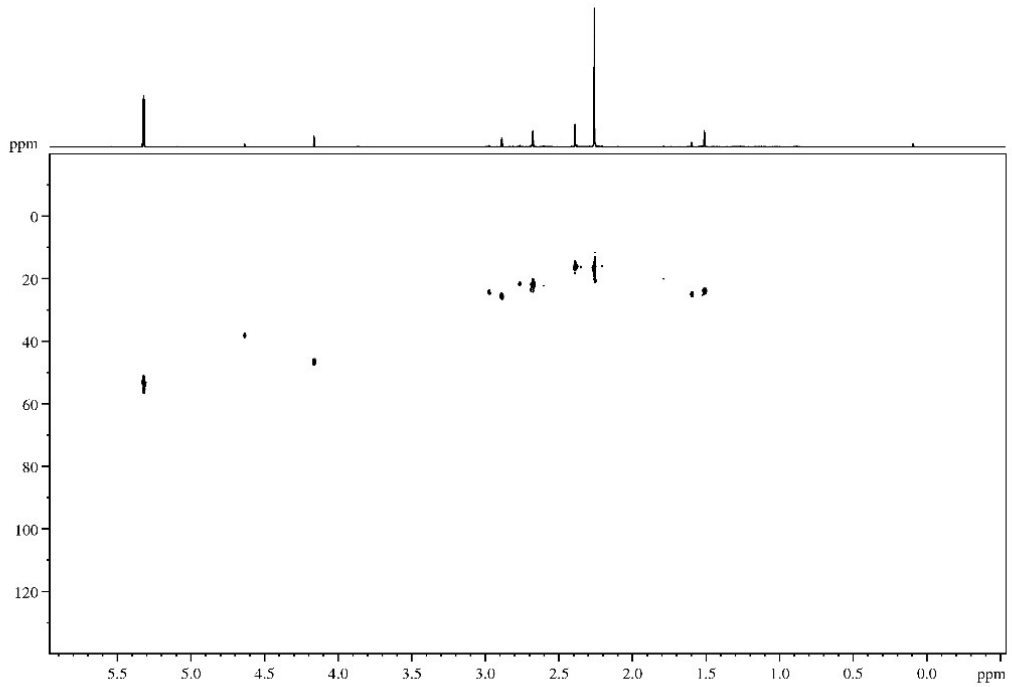


Figure S 6 $^{1}H,^{13}C$-HSQC-NMR spectrum of isolated crystals from the reaction between $Ag[Al(OR^F)_4]$ and C_6Me_6 in CH_2Cl_2.

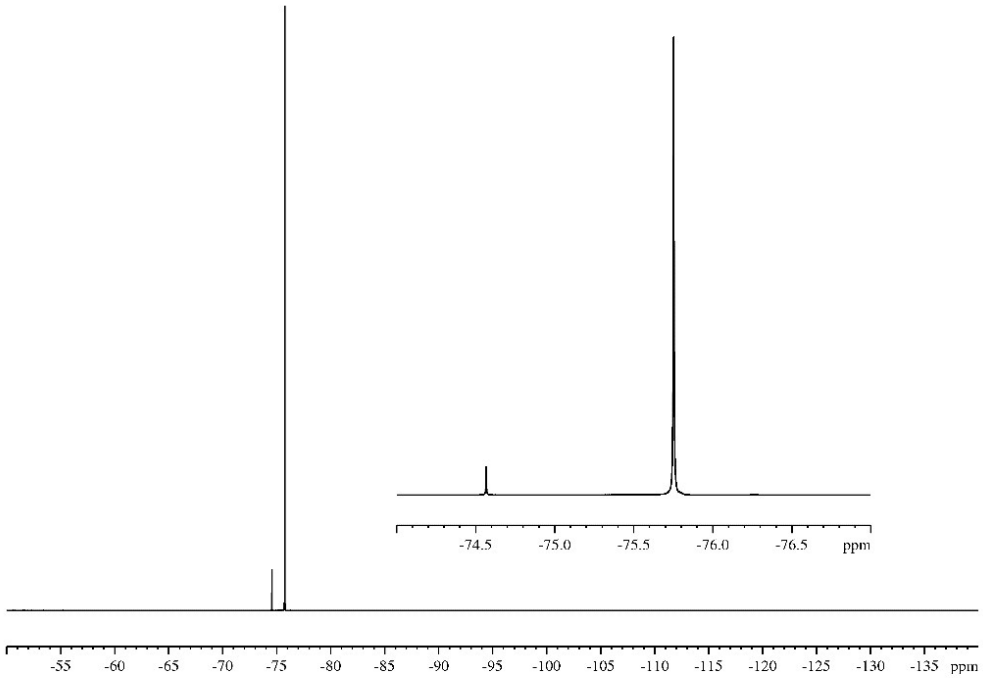


Figure S 7 ^{19}F-NMR (376.54 MHz, CD_2Cl_2, 298 K) spectrum of isolated crystals from the reaction between $Ag[Al(OR^F)_4]$ and C_6Me_6 in CH_2Cl_2.

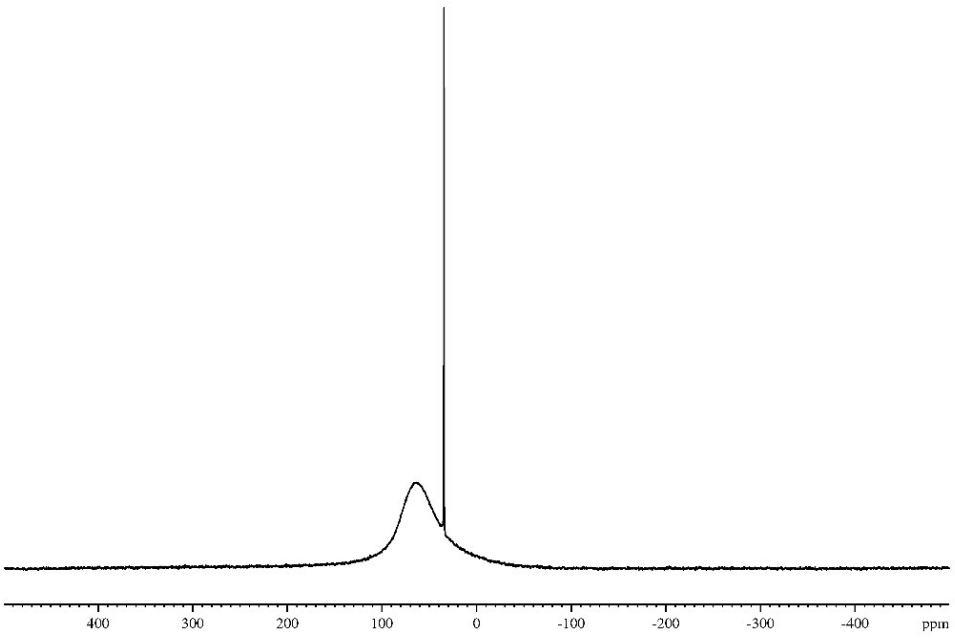
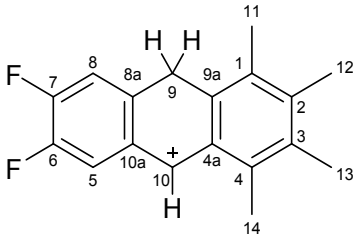


Figure S 8 ^{27}Al-NMR (104.27 MHz, CD_2Cl_2, 298 K) spectrum of isolated crystals from the reaction between $Ag[Al(OR^F)_4]$ and C_6Me_6 in CH_2Cl_2. The broad resonance at δ = 70 ppm observed in ^{27}Al-NMR spectra corresponds to background from Al-nuclei in the probe head.

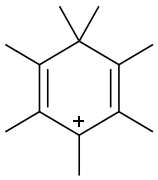
S-1.1.3 Synthesis of **1** in oDFB; and Isolation of 6,7-difluoro-1,2,3,4-tetramethylanthracenyl tetrafluorotertbutoxyaluminate **1a**

$Ag[Al(OR^F)_4]$ (0.136 g, 0.126 mmol) and C_6Me_6 (0.019 g, 0.36 mmol, 1 eq.) were dissolved in *o*-DFB (1 ml). Iodine (0.016 g, 0.063 mmol, 0.5 eq.) was added under positive argon flow to the stirred reaction mixture. Within five minutes the solution developed a dark intensive brown-red colour, accompanied by formation of a yellow precipitate. The reaction mixture was stirred for 2 h at ambient temperature, and the supernatant filtered away from formed AgI and used in further NMR experiments. Dark red needle type crystals suitable for scXRD were grown by layering of the rest of this solution with *n*-pentane (10 ml).

Due to high disorder in the anionic part as well as an underlying superstructure, the received molecular structure was not satisfactorily refineable. Both the cationic and anionic moiety are assignable. The molecular structure shows a structure motif for the cationic part, which was assigned as $\mathbf{1b}^{+\cdot}$ due to the dark red colour of the crystals.



1b-H^+



$[C_6Me_7]^+$

^{1}H-NMR (400.17 MHz, 1,2-$C_6H_4F_2$, 298 K) δ = 2.18 (br. s, $\omega_{1/2}$ = 118 Hz) ppm. comp. **1b**-H^+ δ = 9.55 (s, 1H, 10-C*H*), 7.92 (m, 1H, 5-C*H*), 7.64 (m, 1H, 8-C*H*), 4.45 (s, 2H, 9-CH_2), 2.70 (s, 3H, 14-CH_3), 2.45 (s, 3H, 12-CH_3), 2.35 (s, 3H, 11-CH_3), 2.27 (s, 3H, 13-CH_3) ppm. comp. $[C_6Me_7]^+$ δ = 2.60 (s, 3H, *p*–CH_3), 2.47 (s, 6H, *o*–CH_3), 2.12 (s, 6H, *m*–CH_3), 1,41 (s, 6H, *ipso*–CH_3) ppm. unknown arene δ = 3.68 (s, –CH_2), 2.10 (br s, –CH_3) ppm. ^{13}C-NMR (100.62 MHz, $C_6H_4F_2$-1,2, 298 K) comp. **1b**-H^+ δ = 169.8 (10-*C*H), 165.1 (2-*C*CH_3), 160.9 (6/7-*C*F), 158.1 (6/7-*C*F), 149.2 (9a-*C*), 148.7 (4-*C*CH_3), 147.9 (8a-*C*), 140.5 (3-*C*CH_3), 136.9 (1-*C*CH_3), 131.4 (4a-*C*), 128.3 (10a-*C*), 124.6 (5-*C*H), 118.3 (8-*C*H), 19.5 (12-*C*H_3), 15.6 (13-*C*H_3), 15.0 (14-*C*H_3), 14.2 (11-*C*H_3). comp. $[C_6Me_7]^+$ δ = 202.0 (*o*–*C*CH_3), 190.1 (*p*–*C*CH_3), 139.3 (*m*–*C*CH_3), 56.9 (*ipso*–*C*$(CH_3)_2$), 25.8 (*p*–*C*H_3), 24.7 (*ipso*–*C*H_3), 21.0 (*o*–*C*H_3), 14.3 (*m*–*C*H_3) ppm. ^{19}F-NMR (376.54 MHz, 1,2-$C_6F_2H_4$, 298 K) δ = −69.9 (m, epoxide, OC_4F_8), −75.1 (br. s, F–[$Al(OR^F)_3$]), −75.3 (s, 36 F, [Al{$OC(CF_3)_3$}$_4$]$^-$), −75.5 (s, [$(R^FO)_3Al$–F–$Al(OR^F)_3$]) ppm. ^{27}Al-NMR (104.27 MHz, 1,2-$C_6F_2H_4$, 298 K) δ = 35.0 ppm (s, $[Al(OR^F)_4]^-$). ESI-MS (1,2-$C_6F_2H_4$) positive ion mode: 161.1 m/z ($C_{12}H_{17}$), 163.1 m/z ($C_{12}H_{19}$), 270.1 m/z ($C_{18}H_{16}F_2$, $\mathbf{1b}^{+\cdot}$), 271.1 m/z ($C_{18}H_{17}F_2$, **1b-H**$^+$), negative ion mode: 966.7 m/z ($AlO_4C_{16}F_{36}$).

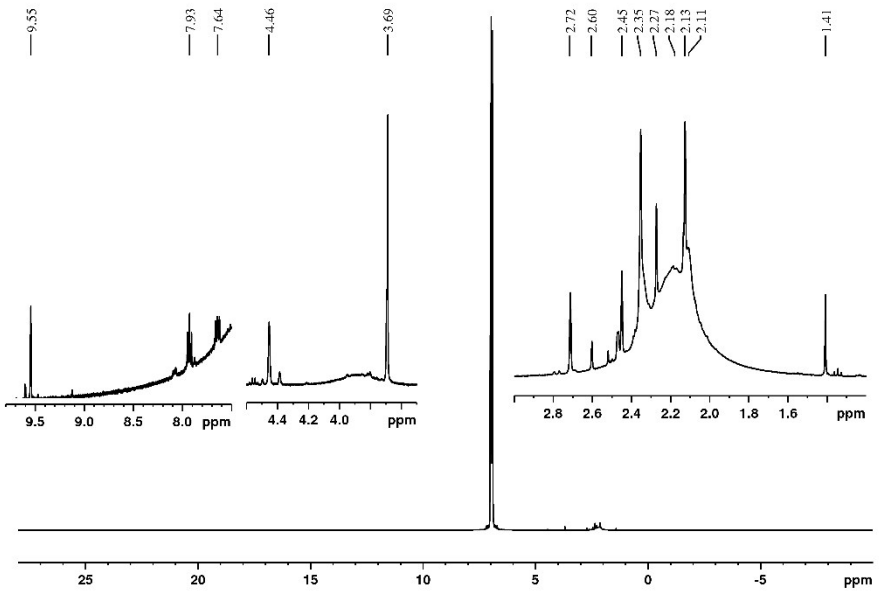


Figure S 9 ^{1}H-NMR (400.17 MHz, 1,2-$C_6H_4F_2$, 298 K) of a reaction between C_6Me_6, [Ag(OR^F)$_4$] and I_2.

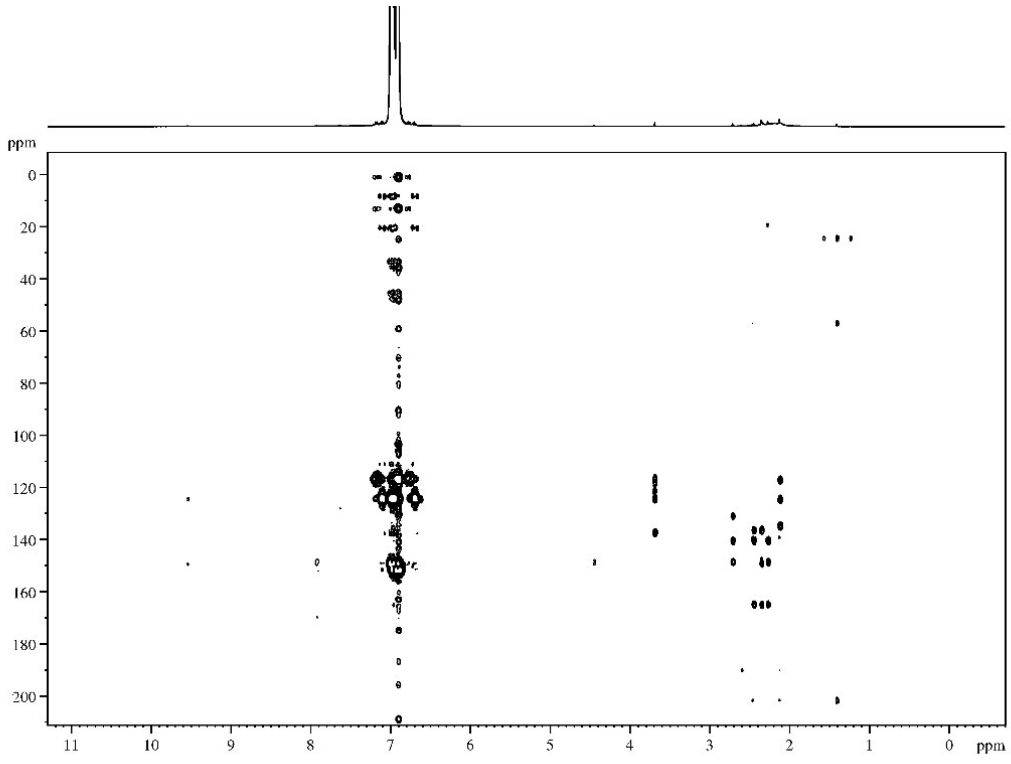


Figure S 10. ^{1}H-^{13}C(hmbc) NMR spectrum of a reaction between C_6Me_6, [Ag(OR^F)$_4$] and I_2.

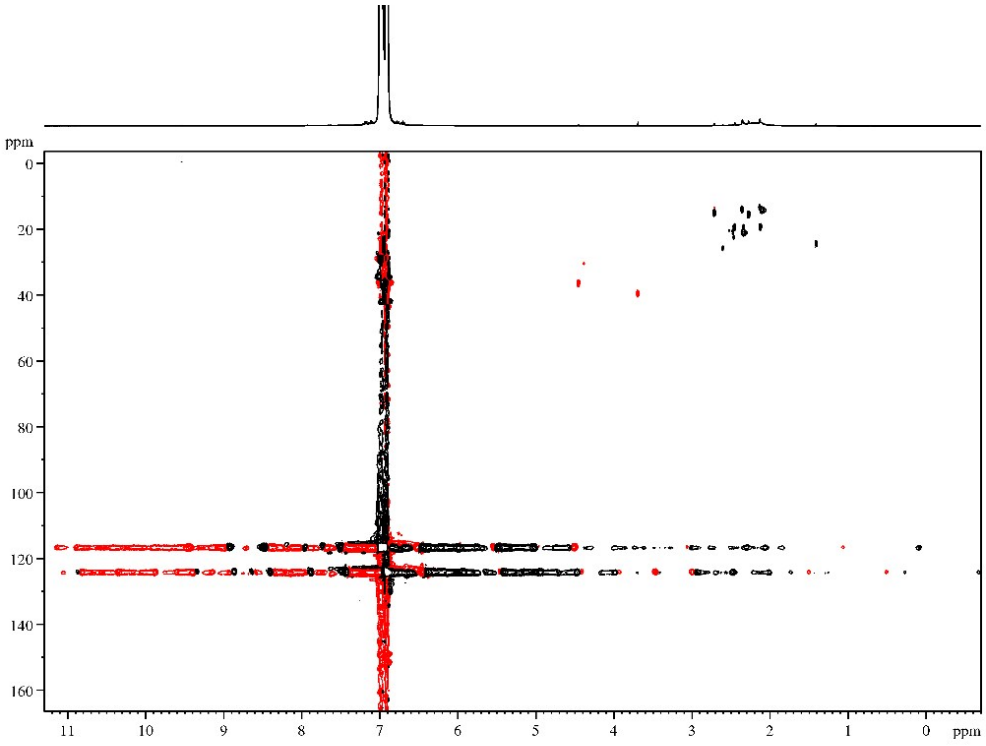


Figure S 11 ^{1}H-^{13}C(edited hsqc) NMR spectrum of a reaction between C_6Me_6, $[Ag(OR^F)_4]$ and I_2.

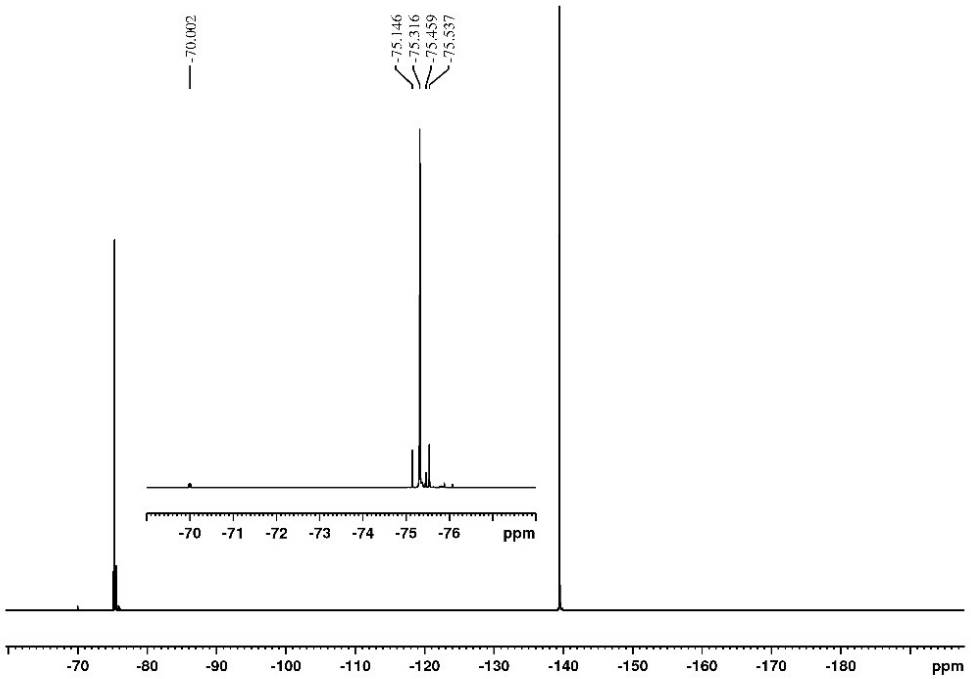


Figure S 12 ^{19}F-NMR (376.54 MHz, 1,2-$C_6F_2H_4$, 298 K) of a reaction between C_6Me_6, $[Ag(OR^F)_4]$ and I_2.

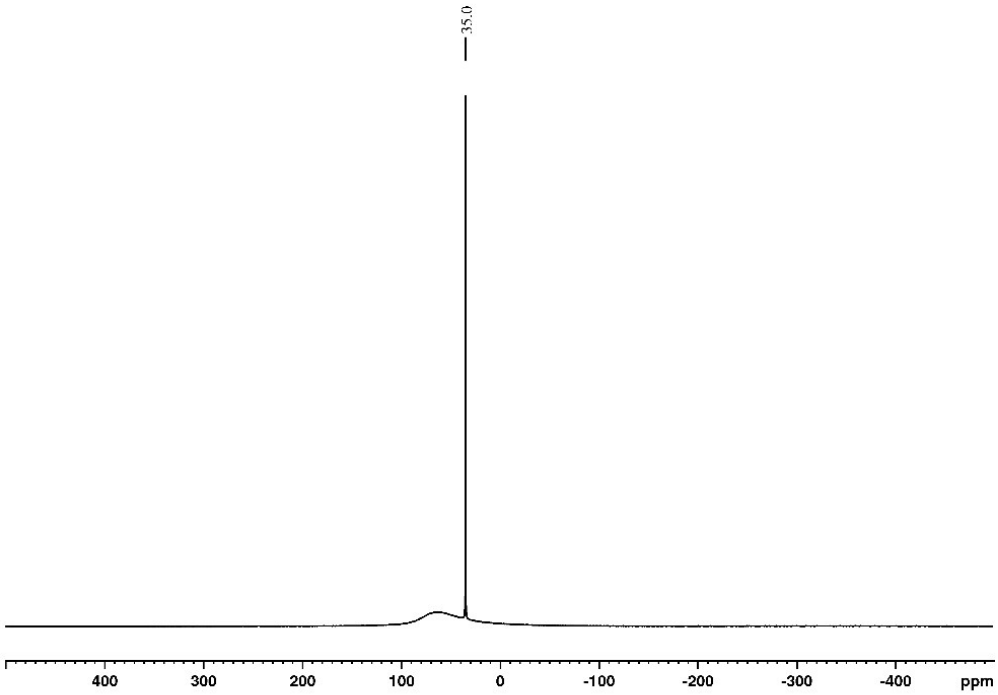


Figure S 13 ^{27}Al-NMR (104.27 MHz, 1,2-$C_6F_2H_4$, 298 K) of reaction between C_6Me_6, [Ag(OR^F)$_4$] and I_2. The broad resonance at δ = 70 ppm observed in ^{27}Al-NMR spectra corresponds to background from Al-nuclei in the probe head.

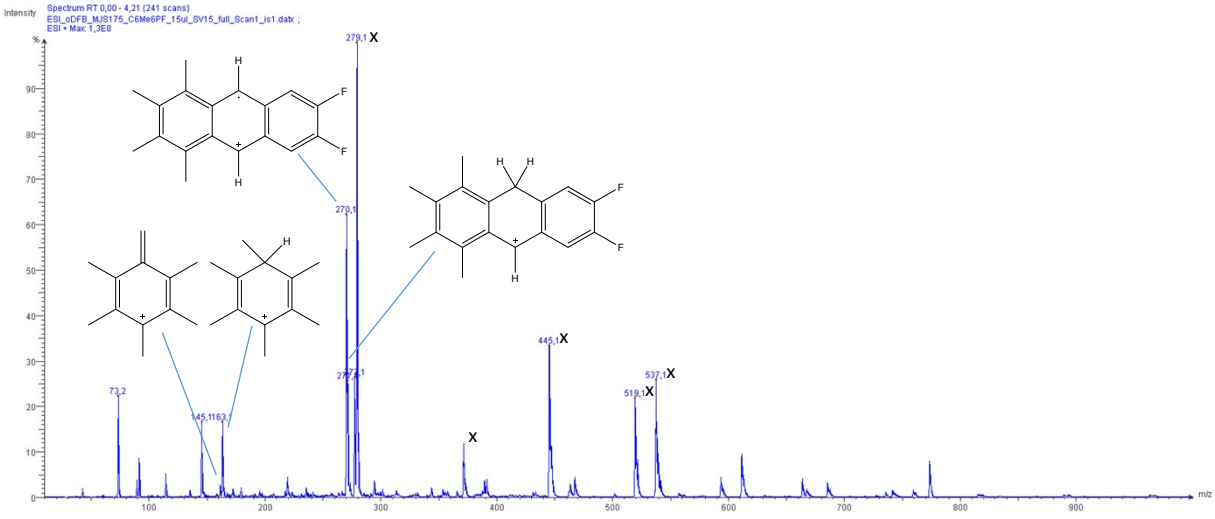


*Figure S 14 positive ion mode ESI-Mass Spectrum of dilute solution of [C_6Me_6][Al(OR^F)$_4$] **1** in 1,2-$C_6H_4F_2$. Source voltage 15V. Mass envelopes marked with x could not be assigned and have been observed in several unrelated measurements. See also Figure S 21.*

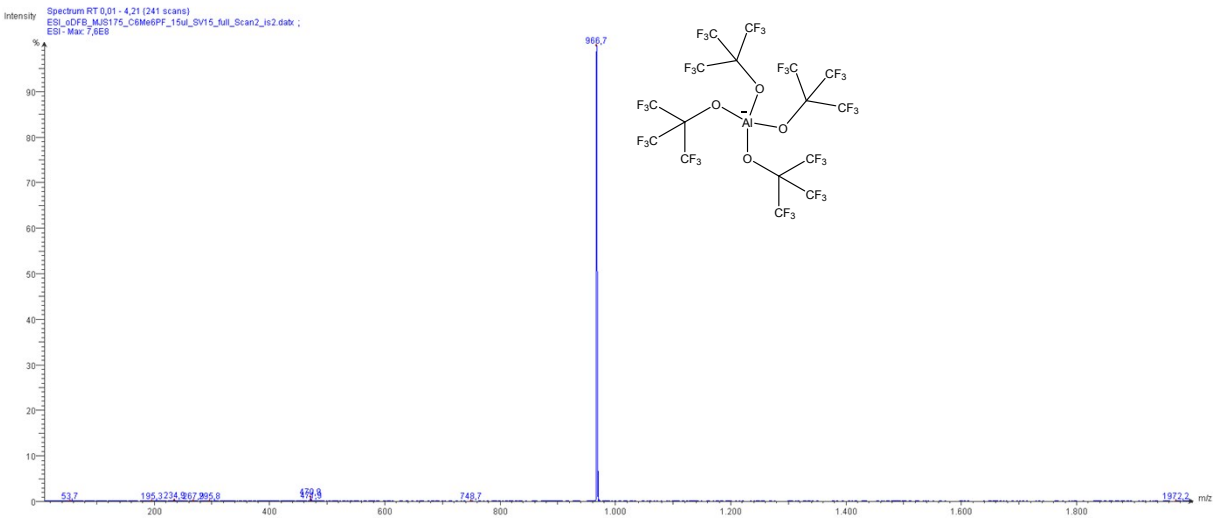


*Figure S 15 negative ion mode ESI-Mass Spectrum of dilute solution of $[C_6Me_6][Al(OR^F)_4]$ **1** in 1,2-$C_6H_4F_2$. Source voltage 15V.*

S-1.2 Synthesis of $[Ga(C_6Me_6)][Al(OR^F)_4]$ **2**

C_6Me_6 (0.038 g, 0.236 mmol) and $Ag[Al(OR^F)_4]$ (0.254 g, 0.236 mmol, 1 eq.) were dissolved in 1,2-difluorobenzene (3 ml). Iodine (0.030 g, 0.118 mmol, 0.5 eq.) was added under a positive stream of Argon to the stirred solution. The reaction mixture was stirred at ambient temperature for 2 h. The supernatant dark red solution was separated from the formed AgI by filtration into a separate Schlenk flask equipped with a droplet of Ga (0.066 g, 0.946 mmol, 4 eq.). The reaction mixture was stirred at room temperature for 5 d until complete decolourisation of the supernatant solution. The supernatant was filtered and layered with pentane (7 ml) to yield the title compound as colourless crystals (0.160 g, 0.133 mmol, crystalline yield 56 %). ^{1}H-NMR (300.18 MHz, 1,2-$C_6F_2H_4$, 298 K) δ = 2.27 ppm (s, 18 H,$[Ga(C_6(CH_3)_6)]^+$). ^{13}C-NMR (75.48 MHz, 1,2-$C_6F_2H_4$, 298 K) δ = 15.5 (s, $[Ga(C_6(CH_3)_6)]^+$), 139.9 ppm (s, $[Ga(C_6(CH_3)_6)]^+$). ^{19}F-NMR (282.45 MHz, 1,2-$C_6F_2H_4$, 298 K) δ = −75.3 (s, 36 F, $[Al\{OC(CF_3)_3\}_4]^-$) ppm. ^{27}Al-NMR (78.22 MHz, 1,2-$C_6F_2H_4$, 298 K) δ = 35.0 ppm (s, $[Al(OR^F)_4]^-$). ^{71}Ga-NMR (91.55 MHz, 1,2-$C_6F_2H_4$, 298 K) δ = −710.9 ppm (s, $[Ga(C_6Me_6)]$). ESI-MS (1,2-$C_6F_2H_4$) positive ion mode: 231.0 m/z ($GaC_{12}H_{18}$), negative ion mode: 966.6 m/z ($AlO_4C_{16}F_{36}$). IR (64 scans, Diamond ATR, corrected): $\tilde{\nu}$/cm^{-1} (intensity) = 2932 (vw), 2861 (vw), 1470 (vw), 1352 (w), 1298 (m), 1266 (s), 1240 (vs), 1218 (vs), 1169 (w), 1067 (vw), 973 (vs), 832 (vw), 756 (vw), 728 (s), 561 (vw), 537 (vw), 447 (vw). FT Raman (8 x 1000 scans, 25 mW): $\tilde{\nu}$/cm^{-1} (intensity) = 2936 (m), 2756 (vw), 1554 (vw), 1398 (w), 1294 (m), 1239 (vw), 798 (m), 746 (m), 554 (vs), 539 (w), 449 (m), 367 (vw), 322 (m), 288 (vw), 233 (vw), 136 (w)

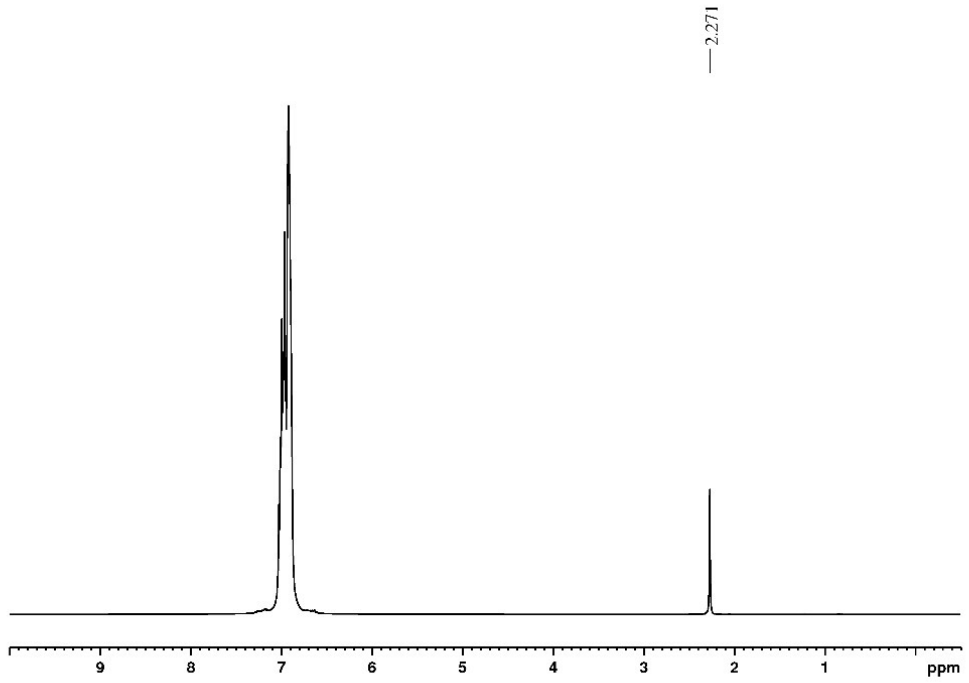


*Figure S 16: ^{1}H-NMR (300.18 MHz, 1,2-$C_6F_2H_4$, 298 K) spectrum of [Ga(C_6Me_6)][Al(OR^F)$_4$] **2**.*

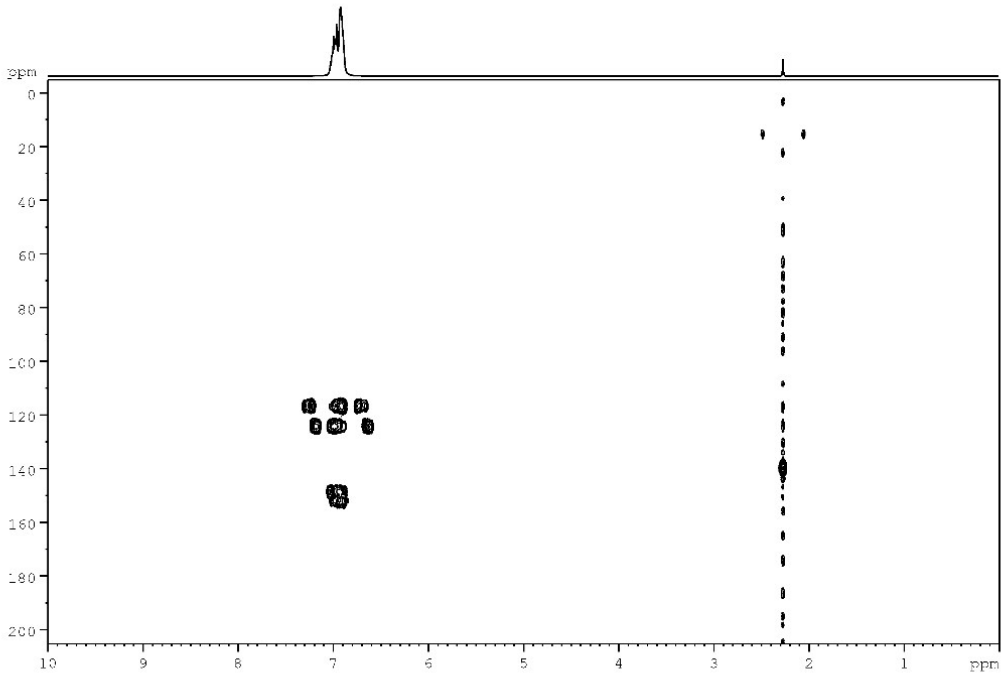


*Figure S 17 ^{1}H-^{13}C (hmbc)-NMR (75.48 MHz, 1,2-$C_6F_2H_4$, 298 K) spectrum of [Ga(C_6Me_6)][Al(OR^F)$_4$] **2**.*

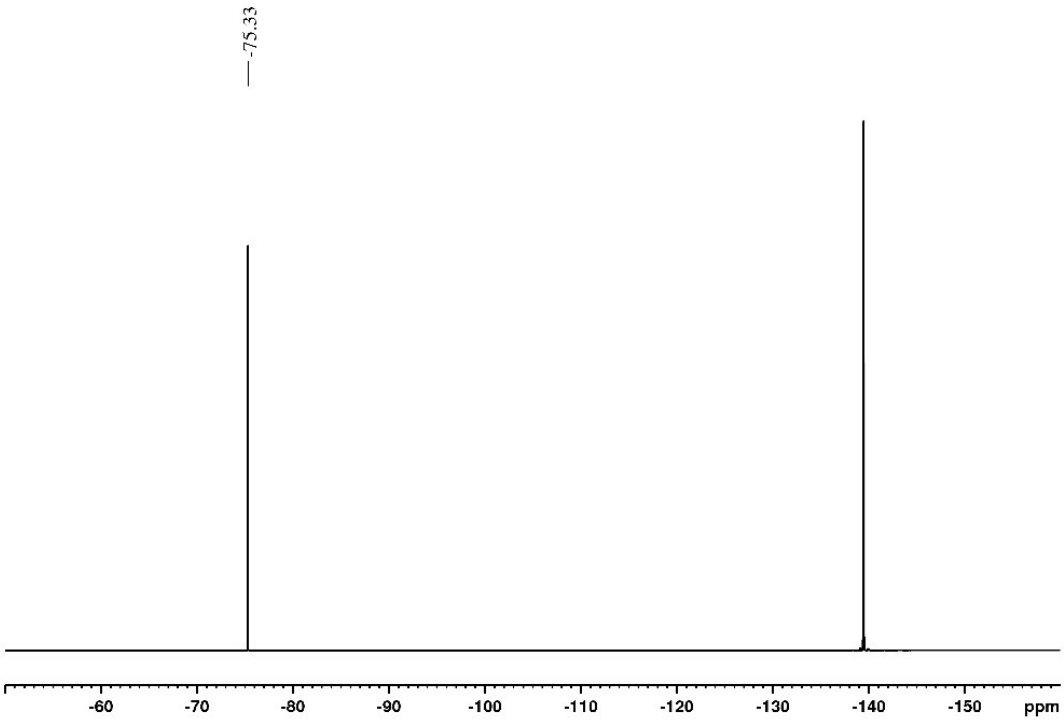


*Figure S 18 ^{19}F-NMR (282.45 MHz, 1,2-$C_6F_2H_4$, 298 K) spectrum of [Ga(C_6Me_6)][Al(OR^F)$_4$] **2**.*

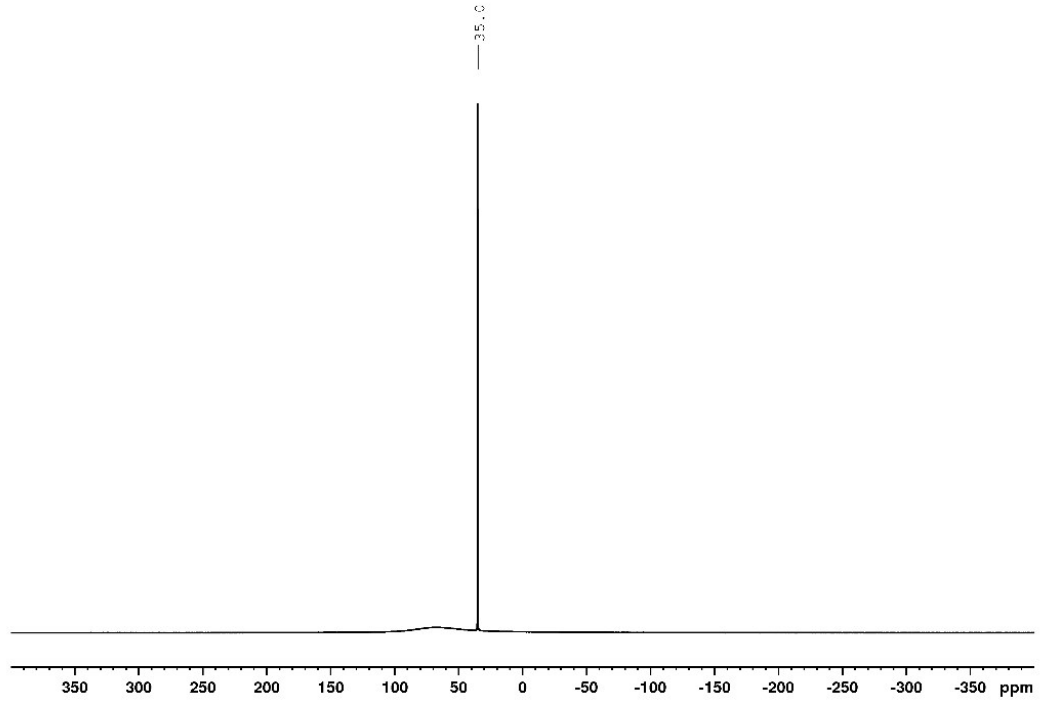


*Figure S 19 ^{27}Al-NMR (78.22 MHz, 1,2-$C_6F_2H_4$, 298 K) spectrum of [Ga(C_6Me_6)][Al(OR^F)$_4$] **2**. The broad resonance at δ = 70 ppm observed in ^{27}Al-NMR spectra corresponds to background from Al-nuclei in the probe head.*

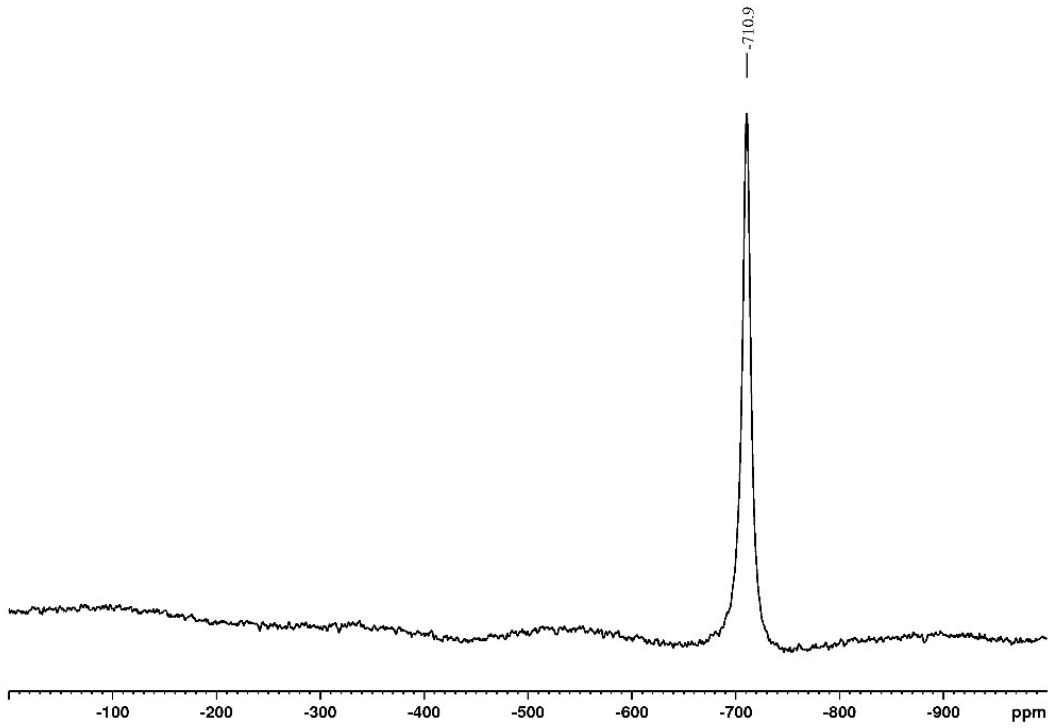


*Figure S 20 ^{71}Ga-NMR (91.55 MHz, 1,2-$C_6F_2H_4$, 298 K) spectrum of [Ga(C_6Me_6)][Al(OR^F)$_4$] **2**.*

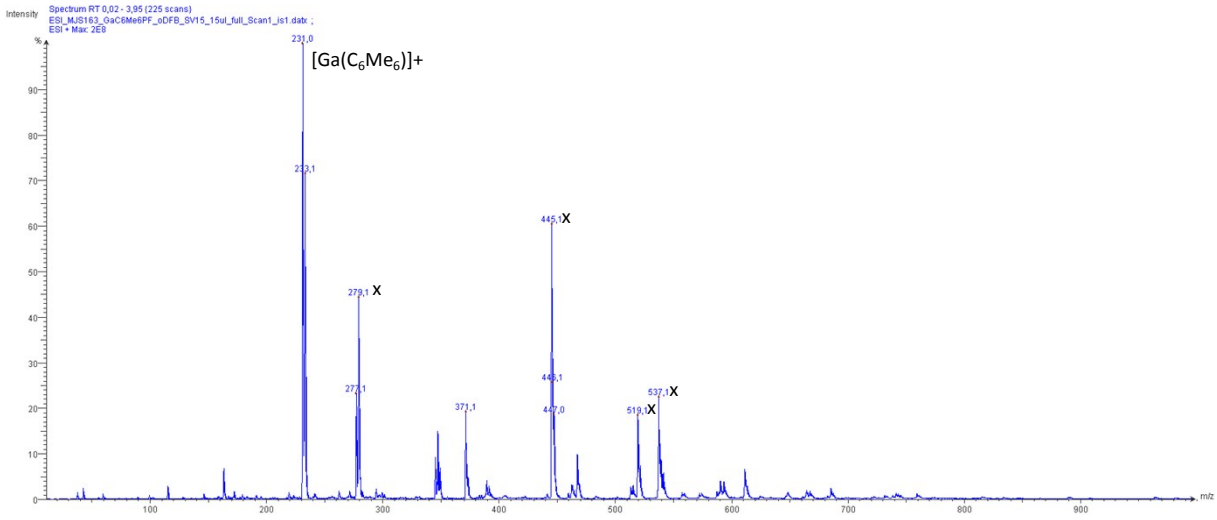


*Figure S 21 positive ion mode ESI-Mass Spectrum of dilute solution of [Ga(C_6Me_6)][Al(OR^F)$_4$] **2** in 1,2-$C_6H_4F_2$. Source voltage 15V. Mass envelopes marked with x could not be assigned and have been observed in several unrelated measurements. See also Figure S 14.*

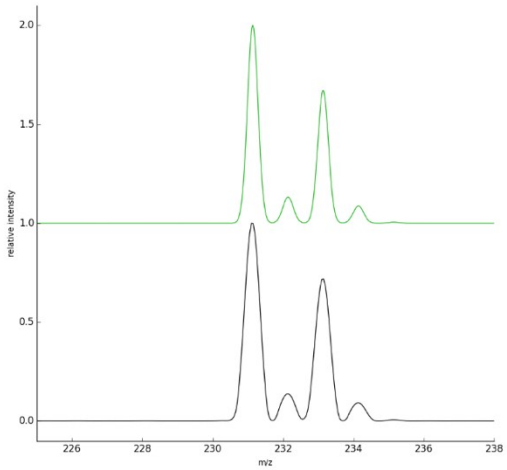


*Figure S 22 (black) magnified section of positive ion mode ESI-Mass Spectrum of dilute solution of [Ga(C_6Me_6)][Al(OR^F)$_4$] **2** in 1,2-$C_6H_4F_2$. Source voltage 15V. (green) simulated isotopic distribution pattern for 231.0 m/z ($GaC_{12}H_{18}$).*

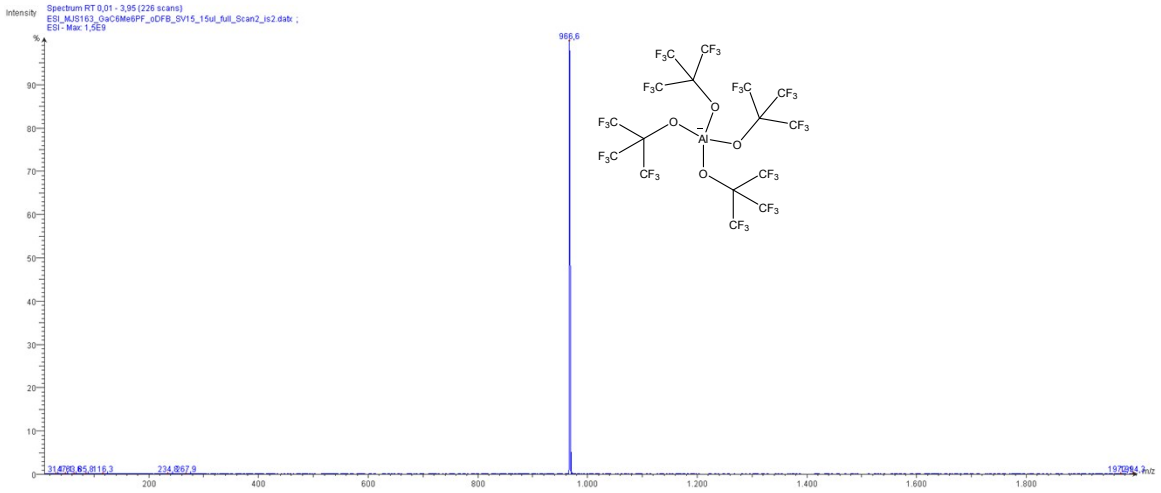


*Figure S 23 negative ion mode ESI-Mass Spectrum of dilute solution of [Ga(C_6Me_6)][Al(OR^F)$_4$] **2** in 1,2-$C_6H_4F_2$. Source voltage 15V.*

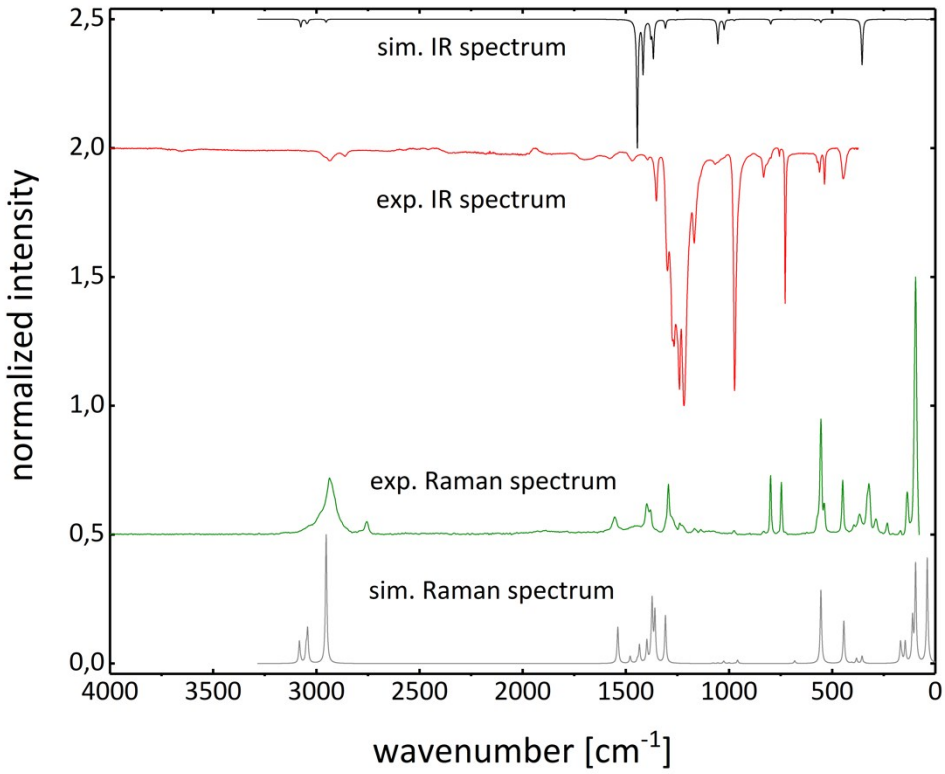


*Figure S 24: Experimental Raman and IR data on [Ga(C_6Me_6)][Al(OR^F)$_4$]**2**. Simulated Raman and IR data on [Ga(C_6Me_6)]$^+$ (BP86/def2-def-SV(P)/D3(BJ)). IR (diamond ATR-corrected, 64 scans); Raman (25 mw, 8 x 1000 scans median).*

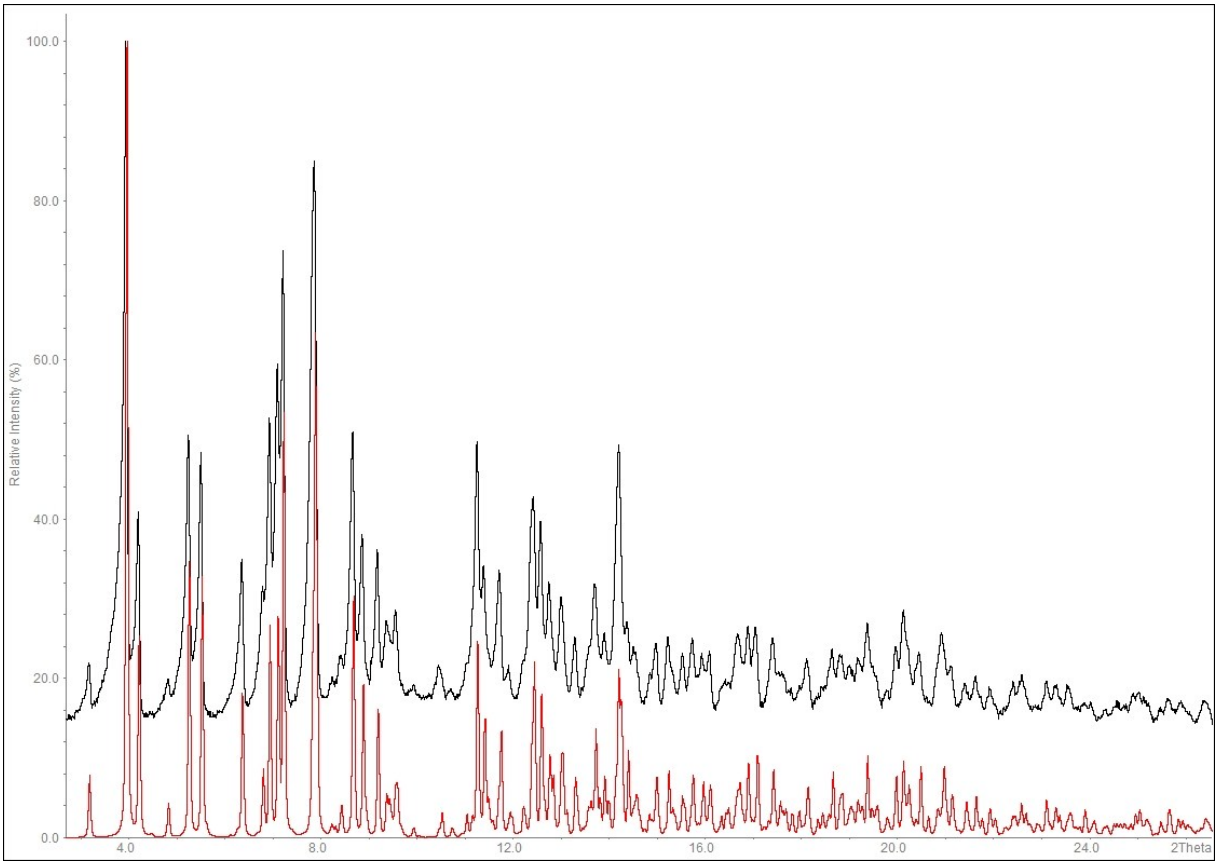


*Figure S 25 (black) Powder diffractogram of [Ga(C_6Me_6)][Al(OR^F)$_4$] **2** at 100(10) K. (red) simulated diffractogram of the single-crystal X-ray analysis, measured at 100(2) K.*

S-1.3 Synthesis of $[In(C_6Me_6)][Al(OR^F)_4]$ **3**

C_6Me_6 (0.063 g, 0.386 mmol) and $Ag[Al(OR^F)_4]$ (0.415 g, 0.386 mmol, 1 eq.) were dissolved in 1,2-difluorobenzene (3 ml). Iodine (0.049 g, 0.190 mmol, 0.5 eq.) was added under a positive stream of Argon to the stirred solution. The reaction mixture was stirred at ambient temperature for 2 h. The supernatant dark red solution was separated from the formed AgI (dried in vacuo, 0.079 mg , 0.336 mmol, 87 %) by filtration into a separate Schlenk flask equipped with thinly sheeted Indium (0.058 g, 0.502 mmol, 1.3 eq.). The reaction mixture was stirred at room temperature for 5 d until complete decolourisation of the supernatant solution. The supernatant was filtered and layered with pentane (7 ml) to yield the title compound as colourless crystals (0.248 g, 0.386 mmol, crystalline yield 51.6 %). ^{1}H-NMR (300.18 MHz, 1,2-$C_6F_2H_4$, 298 K) δ = 2.24 ppm (s, 18 H,$[In(C_6(CH_3)_6)]^+$). ^{13}C-NMR (75.48 MHz, 1,2-$C_6F_2H_4$, 298 K) δ = 15.5 (s, $[In(C_6(CH_3)_6)]^+$), 139.9 ppm (s, $[In(C_6(CH_3)_6)]^+$). ^{19}F-NMR (282.45 MHz, 1,2-$C_6F_2H_4$, 298 K) δ = −75.3 (s, 36 F, $[Al\{OC(CF_3)_3\}_4]^-$) ppm. ^{27}Al-NMR (78.22 MHz, 1,2-$C_6F_2H_4$, 298 K) δ = 35.0 ppm (s, $[Al(OR^F)_4]^-$). ^{115}In-NMR (65.77 MHz, 1,2-$C_6F_2H_4$, 298 K) δ = −1301.0 ppm (s, $[In(C_6Me_6)]$). ESI-MS (1,2-$C_6F_2H_4$) positive ion mode: 277.0 m/z ($InC_{12}H_{18}$), 390.9 m/z ($InC_{18}H_{22}F_2$), negative ion mode: 966.3 m/z ($AlO_4C_{16}F_{36}$). IR (64 scans, Diamond ATR, corrected): $\tilde{\nu}$/cm^{-1} (intensity) = 1351 (vw), 1297 (w), 1265 (m), 1237 (s), 1209 (vs), 1168 (m), 968 (vs), 831 (vw), 727 (vs), 561 (vw), 537 (w), 442 (w). FT Raman (8 x 1000 scans, 25 mW): $\tilde{\nu}$/cm^{-1} (intensity) = 2936 (m), 1399 (w), 1382 (w), 1292 (m), 798 (m), 746 (m), 554 (vs), 539 (w), 450 (w), 2756 (vw), 1168 (vw), 1083 (vw), 978 (vw), 322 (m), 233 (w), 116 (w).

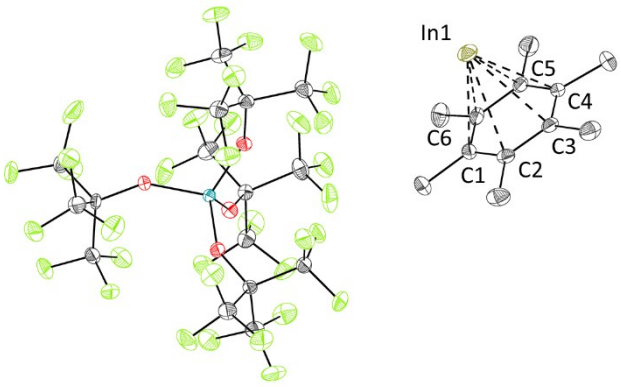


*Figure S 26 Molecular structure of **3**. Thermal displacement ellipsoids drawn at 50 % probability. Hydrogen atoms were omitted for clarity. Selected bond distances (given in Å): In1–C1 2.888(1), In1–C2 2.887(1), In1–C3 2.876(1), In1–C4 2.877(1), In1–C5 2.853(1), In1–C6 2.893(1), C1–C2 1.412 (2), C2–C3 1.408(2), C3–C4 1.411(2), C5–C6 1.412(2), C6–C1 1.410(2).*

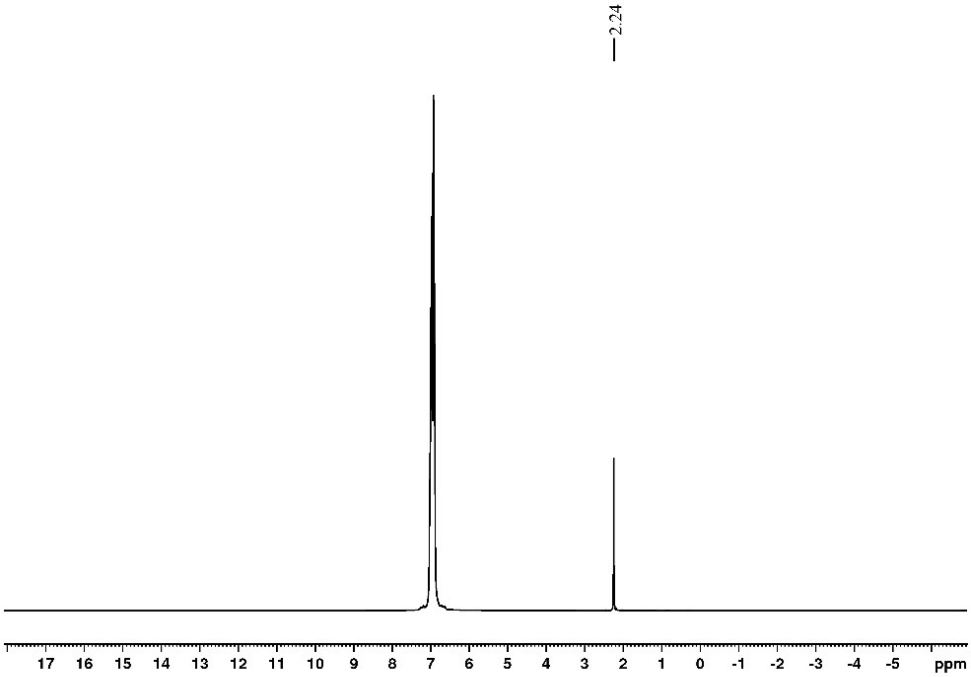


*Figure S 27 ^{1}H-NMR (300.18 MHz, 1,2-$C_6F_2H_4$, 298 K) of [In(C_6Me_6][Al(OR^F)$_4$] **3**.*

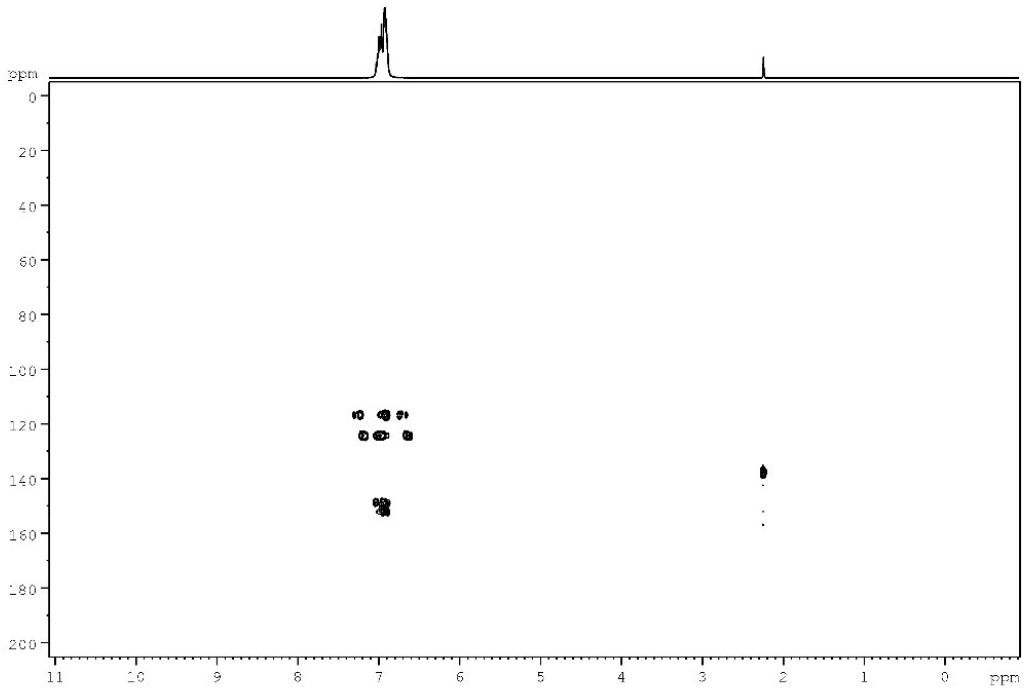


*Figure S 28 ^{1}H-^{13}C (hmbc)-NMR (75.48 MHz, 1,2-$C_6F_2H_4$, 298 K) of [In(C_6Me_6][Al(OR^F)$_4$] **3**.*

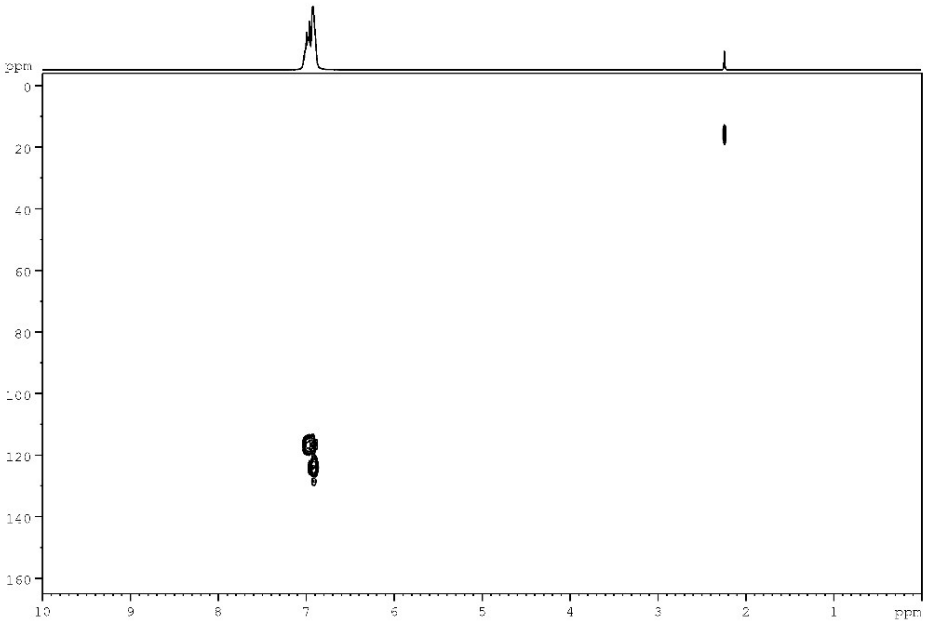


*Figure S 29 ^{1}H-^{13}C (hsqc)-NMR (75.48 MHz, 1,2-$C_6F_2H_4$, 298 K) of [In(C_6Me_6][Al(OR^F)$_4$] **3**.*

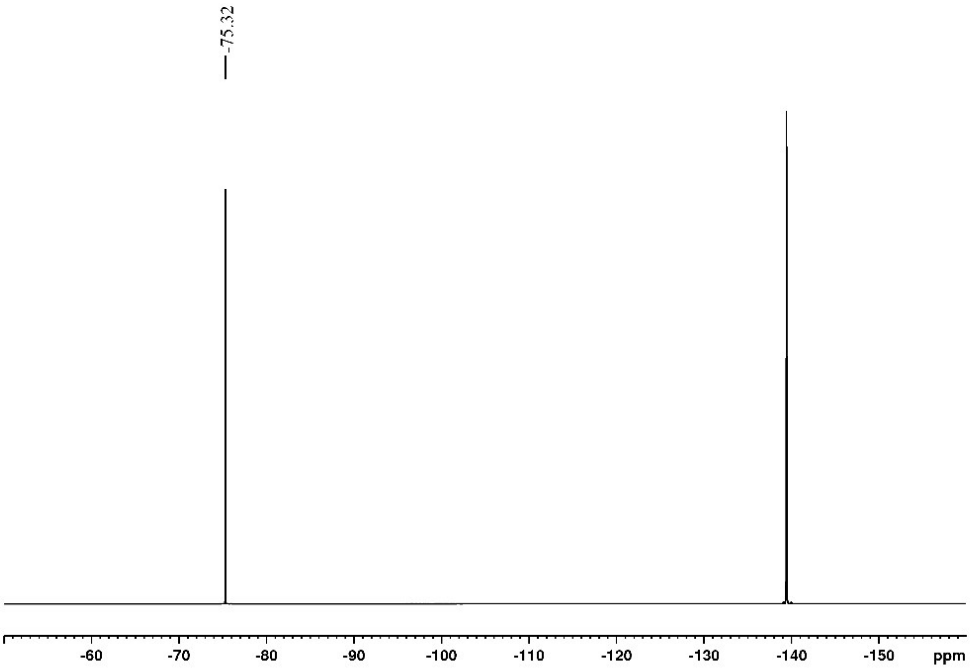


*Figure S 30 ^{19}F-NMR (282.45 MHz, 1,2-$C_6F_2H_4$, 298 K) of [In(C_6Me_6][Al(OR^F)$_4$] **3**.*

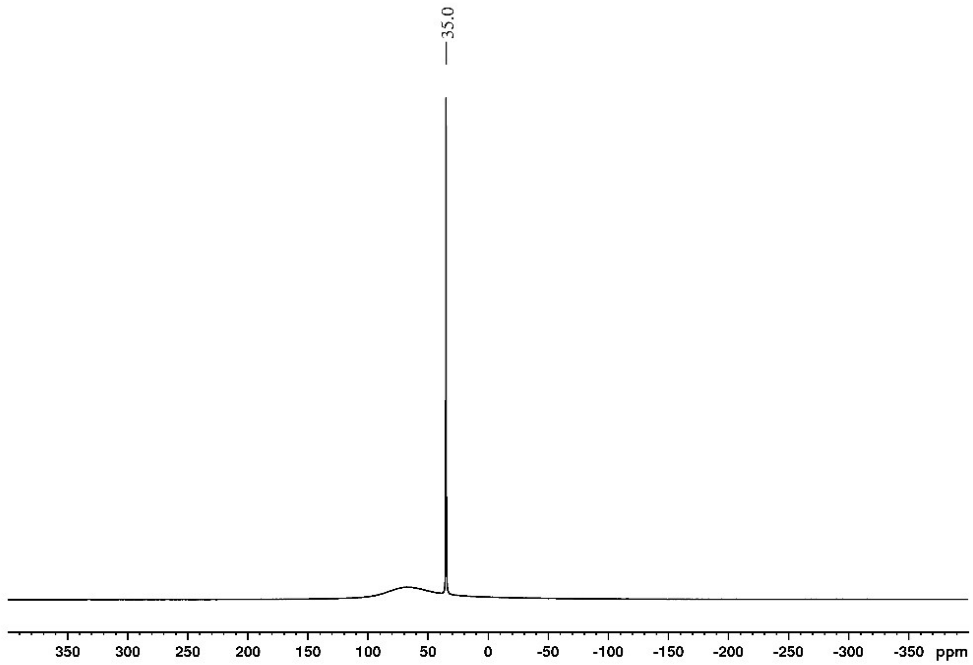


*Figure S 31 ^{27}Al-NMR (78.22 MHz, 1,2-$C_6F_2H_4$, 298 K) of [In(C_6Me_6][Al(OR^F)$_4$] **3**. The broad resonance at δ = 70 ppm observed in ^{27}Al-NMR spectra corresponds to background from Al-nuclei in the probe head.*

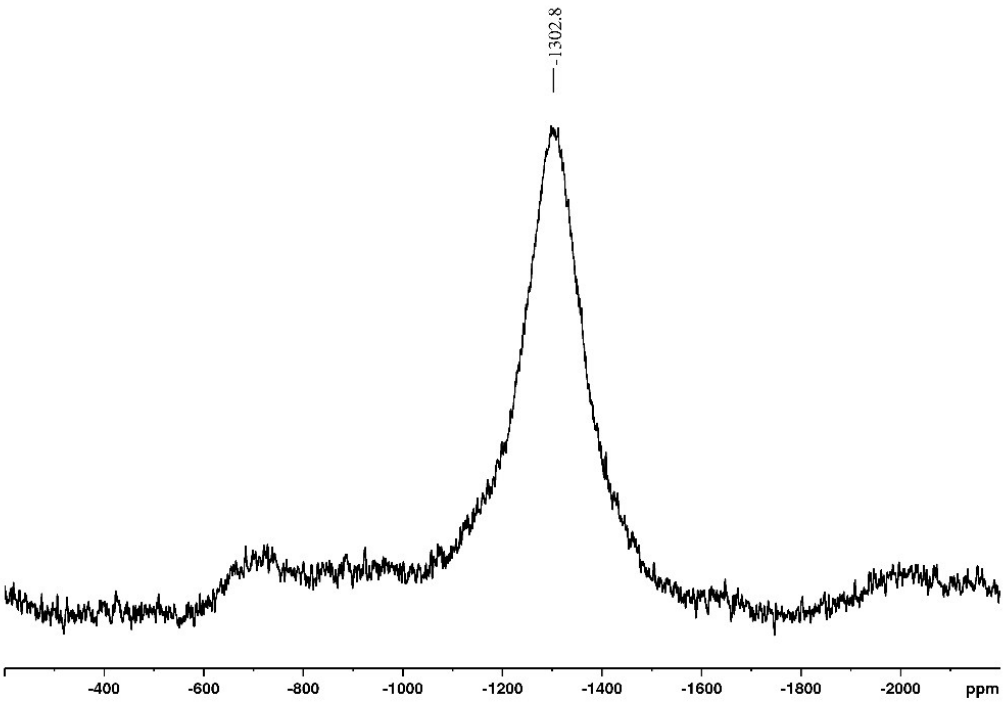


*Figure S 32 ^{115}In-NMR (65.77 MHz, 1,2-$C_6F_2H_4$, 298 K) of [In(C_6Me_6][Al(OR^F)$_4$] **3**.*

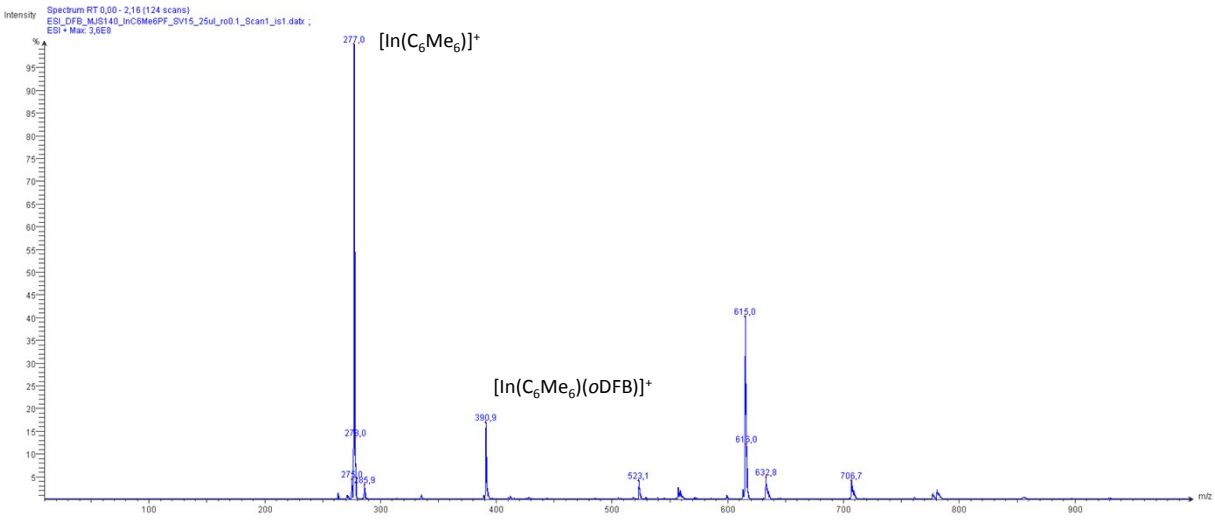


*Figure S 33 positive ion mode ESI-Mass Spectrum of dilute solution of [In(C$_6$Me$_6$)][Al(OR^F)$_4$] **3** in 1,2-C$_6$H$_4$F$_2$. Source voltage 15V.*

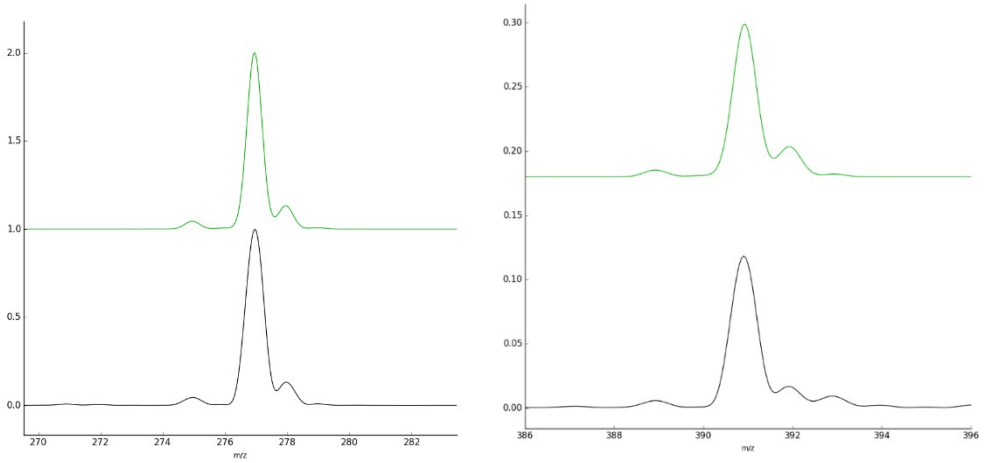


*Figure S 34 (black) magnified section of positive ion mode ESI-Mass Spectrum of dilute solution of [In(C$_6$Me$_6$)][Al(OR^F)$_4$] **3** in 1,2-C$_6$H$_4$F$_2$. Source voltage 15V. (green) simulated isotopic distribution pattern for 277.0 m/z (InC$_{12}$H$_{18}$) = In(C$_6$Me$_6$)$^+$, 390.9 m/z (InC$_{18}$H$_{22}$F$_2$)$^+$ = In(C$_6$Me$_6$)(oDFB)$^+$.*

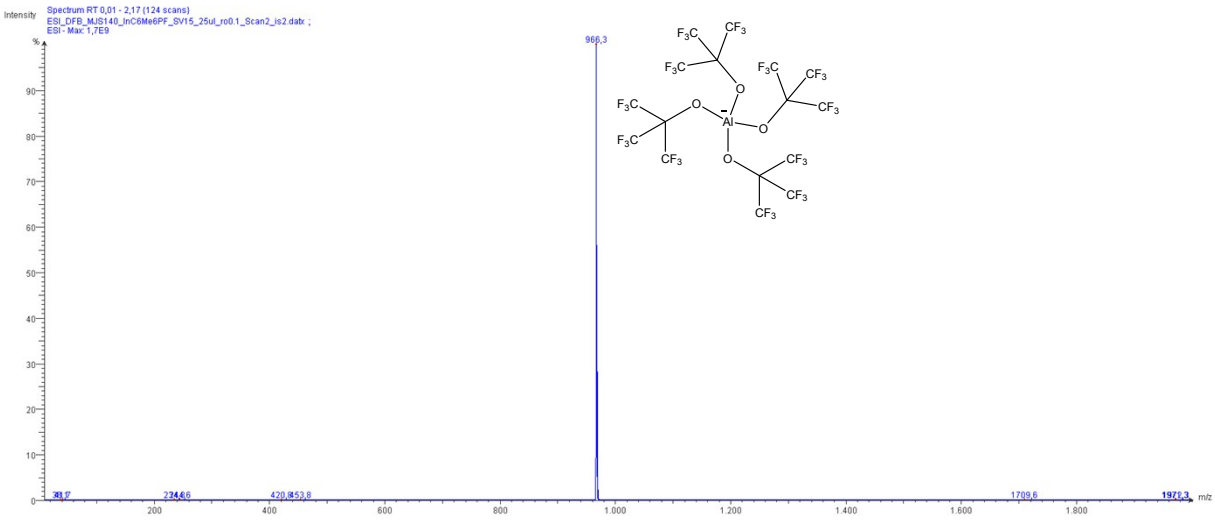


*Figure S 35 negative ion mode ESI-Mass Spectrum of dilute solution of [In(C$_6$Me$_6$)][Al(OR^F)$_4$] **3** in 1,2-C$_6$H$_4$F$_2$. Source voltage 15V.*

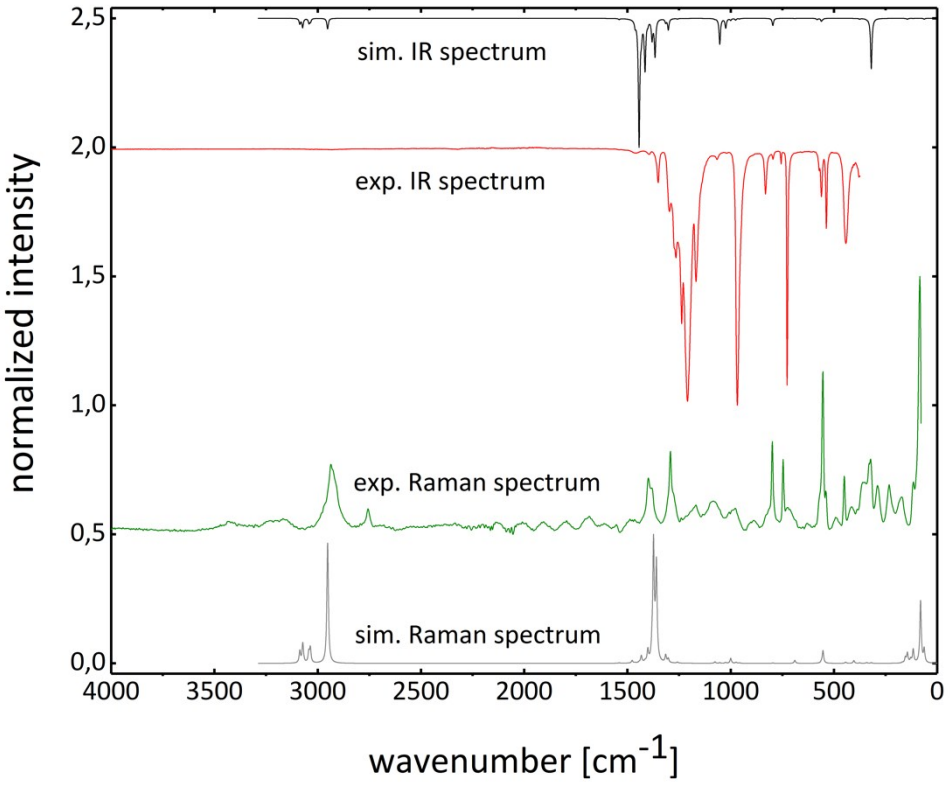


*Figure S 36 Experimental Raman and IR data on [In(C$_6$Me$_6$)][Al(OR^F)$_4$] **3**. Simulated Raman and IR data on [In(C$_6$Me$_6$)]$^+$ (BP86/def2-def-SV(P)/D3(BJ)) IR (diamond ATR-corrected, 64 scans); Raman (25 mw, 8 x 1000 scans median).*

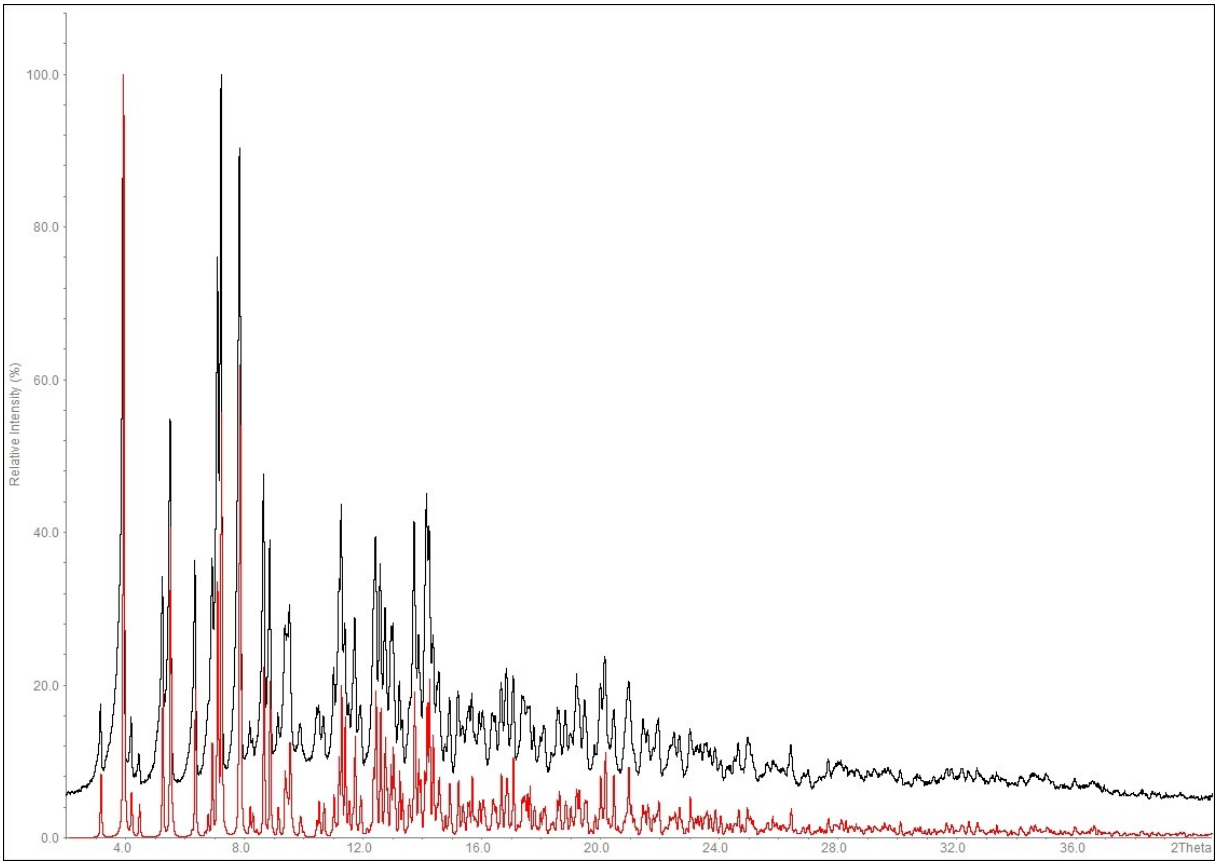


*Figure S 37 (black) Powder diffractogram of [In(C$_6$Me$_6$)][Al(OR^F)$_4$] **3** at 100(10) K. (red) simulated diffractogram of the single-crystal X-ray analysis, measured at 100(2) K.*

S-1.4 Synthesis of [In(Mes)][Al(OR^F)$_4$] **4**

Ag[Al(OR^F)$_4$] (0.250 g, 0.232 mmol) was dissolved in 1,2-difluorobenzene (3 ml). Mesitylene (0.032 ml, 0.232 mmol, 1 eq.) was added to the stirred Solution. After stirring for 10 min the reaction mixture was cooled to −20 °C and Iodine (0.029 g, 0.116 mmol, 0.5 eq.) was added under a positive stream of Argon to the reaction mixture. The reaction mixture was stirred for 2 h at −20°C until complete dissolution of Iodine and precipitation of AgI. The supernatant pale red solution was separated from the precipitate by filtration into a separate Schlenk flask equipped with thinly sheeted Indium (0.040 g, 0.349 mmol, 1.5 eq.). The reaction mixture was stirred at room temperature for 1 d until complete decolourisation of the supernatant solution. The supernatant was filtered and layered with *n*-pentane (8 ml) to yield the title compound as colourless crystals (0.080 g, 0.067 mmol, crystalline yield 28.6 %).

S-1.5 Crystal structure of [Ag(C$_6$Me$_6$)$_2$][Al(OR^F)$_4$]

During work on this topic, crystals of [Ag(C$_6$Me$_6$)$_2$][Al(OR^F)$_4$] **4** suitable for scXRD were grown from a concentrated *o*DFB solution at −25 °C. They were only characterized by their crystal structure.

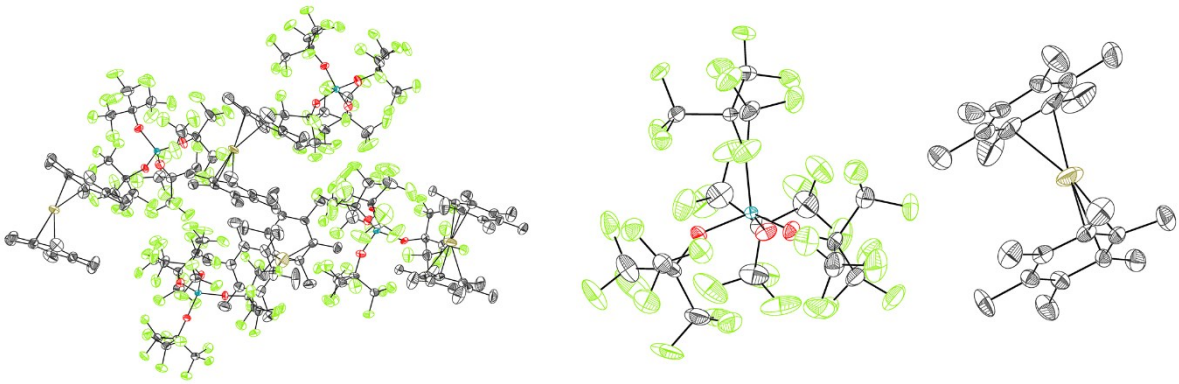


Figure S 38 Molecular structure of [Ag(C$_6$Me$_6$)$_2$][Al(OR^F)$_4$]. Thermal displacement ellipsoids drawn at 50 % probability. Hydrogen atoms were omitted for clarity. Left contents of asymmetric unit. 4 crystallographically unequal cations. Molecular structure of one cation anion pair.

S-2 Crystallographic data

	$[Ga(C_6Me_6)][Al(OR^F)_4]$ **2**	$[In(C_6Me_6)][Al(OR^F)_4]$ **3**	$[In(Mes)][Al(OR^F)_4]$ **4**	$[Ag(C_6Me_6)_2][Al(OR^F)_4]$
Empirical formula	$C_{28}O_4F_{36}AlGaH_{18}$	$C_{28}O_4F_{36}AlInH_{18}$	$C_{25}O_4F_{36}AlInH_{12}$	$C_{40}O_4F_{36}AlAgH_{36}$
Formula weight	1199.12	1244.22	1202.15	1399.54
Temperature/K	100.0	100.00	100.01	99.97
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1$	$P2_1$
a/Å	10.5553(3)	10.57120(10)	10.6026(6)	22.3404(15)
b/Å	14.7194(5)	14.7281(2)	17.5964(11)	20.5472(10)
c/Å	25.9642(8)	26.0049(4)	11.1567(6)	23.5734(15)
α/°	90	90	90	90
β/°	100.032(2)	100.3630(10)	113.373(3)	109.7860(10)
γ/°	90	90	90	90
Volume/Å^3	3973.3(2)	3982.75(9)	1910.7(2)	10182.1(11)
Z	4	4	2	8
ρ_{calc}g/cm^3	2.005	2.075	2.090	1.826
μ/mm^{-1}	0.921	0.821	0.852	0.586
F(000)	2344.0	2416.0	1160.0	5536.0
Crystal size/mm^3	0.3 × 0.2 × 0.15	0.3 × 0.2 × 0.2	0.25 × 0.15 × 0.08	0.35 × 0.3 × 0.27
Radiation	Mo Kα (λ = 0.71073)	Mo Kα (λ = 0.71073)	Mo Kα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range /°	3.186 to 65.184	3.184 to 71.406	3.978 to 54.668	1.836 to 55.794
Index ranges	-15 ≤ h ≤ 15, -22 ≤ k ≤ 20, -39 ≤ l ≤ 37	-17 ≤ h ≤ 17, -20 ≤ k ≤ 23, -39 ≤ l ≤ 41	-13 ≤ h ≤ 13, -22 ≤ k ≤ 22, -14 ≤ l ≤ 13	-28 ≤ h ≤ 29, -27 ≤ k ≤ 27, -30 ≤ l ≤ 30
Reflections collected	88397	77243	32910	199622
Independent reflections	14357 [R_{int} = 0.0256, R_{sigma} = 0.0195]	16521 [R_{int} = 0.0252, R_{sigma} = 0.0250]	8220 [R_{int} = 0.0407, R_{sigma} = 0.0403]	48425 [R_{int} = 0.0318, R_{sigma} = 0.0316]
Data/restraints/parameters	14357/4412/764	16521/4418/764	8220/2911/607	48425/77182/3741
Goodness-of-fit on F^2	1.022	1.073	1.050	1.023
Final R indexes [I>=2σ (I)]	R_1 = 0.0310, wR_2 = 0.0807	R_1 = 0.0333, wR_2 = 0.0749	R_1 = 0.0414, wR_2 = 0.0991	R_1 = 0.0690, wR_2 = 0.1846
Final R indexes [all data]	R_1 = 0.0426, wR_2 = 0.0854	R_1 = 0.0492, wR_2 = 0.0803	R_1 = 0.0456, wR_2 = 0.1008	R_1 = 0.0839, wR_2 = 0.1996
Largest diff. peak/hole / e Å^{-3}	0.79/-0.33	0.92/-0.42	1.30/-0.57	4.27/-2.18
CCDC ref.	1846095	1846096	1846097	1846770

*Table S 1 Fractional Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Parameters (Å²×10³) for [Ga(C_6Me_6)][Al(OR^F)$_4$] **2**. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.*

Atom	*x*	*y*	*z*	U(eq)
Ga1	8399.4(2)	2595.6(2)	6483.3(2)	28.57(4)
Al1	3356.5(3)	2572.0(2)	3776.8(2)	11.88(6)
C1	10070.7(10)	1524.1(8)	6133.3(5)	18.5(2)
C2	10835.7(10)	2182.8(9)	6436.9(4)	18.6(2)
C3	10699.5(11)	3111.2(8)	6305.0(4)	19.1(2)
C4	9826.8(11)	3375.1(8)	5852.8(5)	19.6(2)
C5	9084.2(10)	2713.3(9)	5542.0(5)	20.8(2)
C6	9222.8(10)	1787.6(9)	5675.4(5)	20.2(2)
C7	10198.5(13)	539.0(9)	6288.2(6)	30.8(3)
C8	11868.5(13)	1900.9(12)	6886.8(5)	33.5(3)
C9	11510.9(14)	3811.9(10)	6634.4(5)	30.0(3)
C10	9723.1(14)	4355.4(9)	5677.4(6)	29.6(3)
C11	8169.5(13)	3006.2(12)	5057.5(5)	32.6(3)
C12	8523.9(14)	1070.7(11)	5316.6(6)	33.0(3)
O1_5	1707(12)	2450(20)	3632(9)	16(3)
C1_5	664(11)	2590(7)	3259(4)	17(2)
C2_5	681(6)	1969(5)	2779(2)	28.3(14)
F1_5	1835(9)	1986(7)	2646(4)	26.4(16)
F2_5	-175(5)	2227(5)	2361.6(19)	42.9(15)
F3_5	377(16)	1117(8)	2857(7)	35(2)
C3_5	-547(5)	2372(4)	3506(2)	25.1(12)
F4_5	-780(8)	3025(5)	3824(3)	35.6(15)
F5_5	-364(11)	1624(7)	3794(3)	34.5(18)
F6_5	-1586(4)	2267(4)	3141(2)	32.9(11)
C4_5	583(6)	3603(4)	3082(3)	27.4(13)
F7_5	930(20)	4172(10)	3483(6)	27(2)
F8_5	-621(9)	3804(14)	2872(6)	46(3)
F9_5	1344(8)	3771(6)	2735(3)	35.7(17)
O1_4	4243.5(7)	1793.6(6)	3490.1(3)	16.38(14)
C1_4	4701.1(10)	938.4(8)	3490.6(4)	16.22(19)
C2_4	5210.5(12)	796.5(9)	2969.3(5)	23.5(2)
F1_4	4381.0(9)	1099.1(7)	2565.1(3)	36.9(2)

Atom	*x*	*y*	*z*	U(eq)
F2_4	5433.8(9)	-77.6(6)	2880.2(4)	37.4(2)
F3_4	6311.9(8)	1237.9(7)	2982.3(4)	38.3(2)
C3_4	5824.7(12)	792.8(10)	3958.9(5)	26.9(3)
F4_4	5369.7(9)	662.5(7)	4402.4(3)	39.0(2)
F5_4	6583.7(8)	1509.2(7)	4024.0(4)	42.3(2)
F6_4	6550.7(8)	71.5(6)	3893.5(3)	36.2(2)
C4_4	3624.0(12)	228.8(9)	3525.6(5)	25.2(2)
F7_4	2932.8(8)	488.2(6)	3885.9(4)	34.43(19)
F8_4	4073.8(10)	-601.4(6)	3649.7(4)	40.8(2)
F9_4	2808.5(8)	165.4(7)	3075.4(4)	36.2(2)
O1_3	3740.3(7)	3645.7(6)	3580.2(3)	16.73(15)
C1_3	4691.4(10)	4233.2(8)	3527.4(4)	15.57(18)
C2_3	4093.8(12)	5200.3(8)	3457.8(5)	22.9(2)
F1_3	3377.2(8)	5291.9(6)	2985.7(3)	33.86(19)
F2_3	4989.3(8)	5853.2(5)	3514.6(4)	32.76(18)
F3_3	3333.6(8)	5355.8(6)	3807.1(4)	31.77(18)
C3_3	5769.7(11)	4218.3(9)	4019.8(5)	22.0(2)
F4_3	6039.0(7)	3364.0(6)	4164.4(3)	30.16(18)
F5_3	5400.5(8)	4644.8(6)	4420.7(3)	32.66(18)
F6_3	6861.9(7)	4607.0(6)	3936.8(3)	32.56(19)
C4_3	5295.2(12)	3989.3(9)	3038.9(5)	23.0(2)
F7_3	6084.9(8)	3281.7(6)	3138.7(4)	32.89(18)
F8_3	5960.6(8)	4673.8(6)	2879.2(3)	32.76(18)
F9_3	4384.2(8)	3758.4(7)	2637.6(3)	34.20(19)
O1_2	1719(3)	2459(5)	3563(2)	16.5(7)
C1_2	697(3)	2640.0(19)	3182.6(12)	15.2(5)
C2_2	-18.3(14)	3493.9(11)	3328.9(6)	23.3(3)
F1_2	-613.0(19)	3331.9(13)	3733.0(7)	34.5(4)
F2_2	-906(2)	3799(3)	2931.1(13)	33.6(4)
F3_2	802(6)	4161(3)	3470.0(17)	41.5(10)
C3_2	1105.3(13)	2787.0(11)	2639.8(6)	20.5(3)
F4_2	2019(2)	2200.3(19)	2572.4(11)	31.9(5)
F5_2	1589.9(18)	3611.0(14)	2604.1(7)	28.6(3)
F6_2	133.5(11)	2690.8(10)	2240.1(4)	32.7(3)

Atom	*x*	*y*	*z*	U(eq)
C4_2	-222.9(14)	1806.5(11)	3144.9(6)	24.8(3)
F7_2	270(4)	1113.5(18)	2927.0(18)	38.2(8)
F8_2	-1389.0(11)	1989.3(10)	2870.4(6)	42.3(4)
F9_2	-382(3)	1537.9(16)	3617.5(7)	30.7(4)
O1_1	3710.1(8)	2422.6(6)	4447.2(3)	16.44(15)
C1_1	3327.6(11)	2477.6(8)	4915.8(4)	16.63(19)
C2_1	2502.9(12)	3343.7(9)	4956.3(5)	23.1(2)
F1_1	2961.6(8)	4044.5(6)	4726.7(4)	32.29(18)
F2_1	2468.4(8)	3578.3(6)	5451.3(3)	31.50(18)
F3_1	1285.0(7)	3221.4(6)	4718.4(3)	32.63(18)
C3_1	2543.2(12)	1618.6(9)	5007.2(5)	24.3(2)
F4_1	3301.2(9)	890.7(6)	5077.2(3)	32.02(18)
F5_1	1625.7(8)	1452.5(6)	4597.2(3)	31.36(18)
F6_1	1976.7(9)	1698.6(7)	5428.6(3)	36.8(2)
C4_1	4554.5(12)	2529.4(9)	5346.7(5)	23.9(2)
F7_1	5421.0(7)	1919.5(6)	5260.8(3)	30.76(18)
F8_1	4306.7(9)	2378.2(7)	5827.9(3)	36.7(2)
F9_1	5103.7(8)	3345.5(6)	5346.8(3)	32.28(18)

*Table S 2 Fractional Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Parameters (Å²×10³) for [In(C₆Me₆)][Al(OR^F)₄] **3**. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor*

Atom	*x*	*y*	*z*	U(eq)
In1	1771.0(2)	7445.8(2)	3496.5(2)	25.95(3)
Al1	6645.0(3)	7425.2(2)	6218.3(2)	11.55(6)
C1	868.9(12)	7298.4(10)	4477.4(5)	19.9(2)
C2	139.4(12)	6646.2(9)	4153.1(5)	19.5(2)
C5	-98.7(12)	8504.4(9)	3893.9(5)	18.2(2)
C4	-846.6(12)	7855.6(9)	3577.2(5)	18.6(2)
C3	-713.1(12)	6923.8(9)	3700.5(5)	19.0(2)
C9	-1521.5(16)	6232.5(11)	3359.5(6)	30.7(3)
C12	1415.0(15)	8932.8(12)	4726.6(6)	32.4(3)
C11	-231.1(15)	9497.9(10)	3754.3(7)	31.8(3)
C10	-1873.1(15)	8154.3(13)	3125.6(6)	33.3(3)
C8	231.6(16)	5662.6(10)	4319.9(6)	30.6(3)

Atom	*x*	*y*	*z*	U(eq)
C7	1757.9(15)	6991.0(13)	4964.9(6)	32.4(3)
C6	737.0(12)	8229.5(9)	4353.4(5)	19.1(2)
O1_5	8299(11)	7551(16)	6359(7)	12.5(16)
C1_5	9333(10)	7403(6)	6732(4)	16.7(17)
C2_5	9435(4)	6406(3)	6923.8(18)	25.0(10)
F1_5	8681(6)	6256(4)	7274(2)	32.5(11)
F2_5	10651(8)	6197(9)	7145(4)	38.6(18)
F3_5	9140(20)	5839(14)	6519(7)	39(4)
C3_5	10548(4)	7614(3)	6481.1(18)	22.1(9)
F4_5	10391(15)	8465(7)	6349(4)	27.5(15)
F5_5	10781(5)	6944(3)	6178(2)	31.6(10)
F6_5	11605(3)	7735(3)	6841.8(16)	30.5(8)
C4_5	9351(4)	8044(3)	7207.1(17)	24.8(10)
F7_5	9635(17)	8892(7)	7109(7)	36.7(18)
F8_5	10214(4)	7802(3)	7625.6(14)	38.5(10)
F9_5	8199(10)	8037(7)	7348(4)	28.6(15)
O1_4	5794.1(8)	8214.9(6)	6511.2(3)	16.71(16)
C1_4	5327.9(11)	9067.7(8)	6506.3(4)	15.4(2)
C2_4	4836.4(13)	9214.0(10)	7029.0(5)	22.4(3)
F1_4	3743.3(9)	8768.7(7)	7023.0(4)	36.8(2)
F2_4	4610.1(10)	10089.3(7)	7112.4(4)	37.6(2)
F3_4	5680.3(9)	8923.9(7)	7432.4(3)	35.2(2)
C3_4	6394.2(14)	9779.0(10)	6463.7(6)	25.0(3)
F4_4	7072.9(9)	9514.3(7)	6102.2(4)	34.2(2)
F5_4	7222.4(9)	9855.8(7)	6909.4(4)	36.1(2)
F6_4	5934.3(10)	10604.1(6)	6333.9(4)	40.9(2)
C4_4	4189.7(13)	9201.7(10)	6041.9(5)	24.4(3)
F7_4	4622.9(10)	9318.2(7)	5595.4(3)	36.0(2)
F8_4	3464.2(9)	9922.2(7)	6103.4(4)	33.6(2)
F9_4	3433.9(9)	8480.5(7)	5986.5(4)	39.2(2)
O1_3	6248.6(9)	7559.1(6)	5549.4(3)	16.10(16)
C1_3	6601.9(12)	7500.0(8)	5077.0(5)	16.0(2)
C2_3	7434.9(13)	6639.1(9)	5034.1(5)	21.6(2)
F1_3	8654.7(8)	6772.6(7)	5267.5(4)	31.04(19)

Atom	*x*	*y*	*z*	U(eq)
F2_3	7450.4(9)	6403.8(6)	4540.5(3)	30.17(19)
F3_3	6997.1(9)	5938.7(6)	5270.3(4)	31.5(2)
C3_3	5355.0(14)	7435.5(10)	4655.4(5)	22.8(3)
F4_3	4485.0(8)	8038.8(7)	4744.9(3)	30.13(19)
F5_3	4820.7(9)	6615.2(7)	4663.1(3)	31.37(19)
F6_3	5565.4(10)	7581.6(7)	4169.6(3)	34.7(2)
C4_3	7360.6(14)	8362.0(10)	4974.7(5)	23.6(3)
F7_3	6592.5(9)	9084.3(6)	4907.5(4)	31.9(2)
F8_3	7897.5(9)	8281.9(7)	4547.8(4)	35.1(2)
F9_3	8296.9(9)	8539.7(6)	5375.7(4)	31.43(19)
O1_2	6262.8(8)	6360.1(6)	6426.8(3)	16.92(16)
C1_2	5316.8(11)	5774.9(8)	6485.3(4)	15.4(2)
C2_2	5917.2(13)	4809.6(9)	6551.8(5)	22.8(3)
F1_2	6659.2(9)	4652.7(6)	6198.3(4)	31.44(19)
F2_2	5025.9(9)	4153.0(6)	6497.7(4)	32.9(2)
F3_2	6654.9(9)	4714.8(6)	7020.6(4)	33.9(2)
C3_2	4746.6(13)	6016.0(10)	6979.9(5)	23.1(3)
F4_2	3957.0(9)	6726.5(6)	6884.7(4)	33.8(2)
F5_2	5674.9(10)	6244.1(7)	7375.6(3)	34.8(2)
F6_2	4091.3(9)	5332.3(7)	7141.8(4)	33.9(2)
C4_2	4219.7(12)	5786.4(9)	5999.9(5)	21.1(2)
F7_2	3939.6(8)	6641.4(6)	5856.8(4)	29.55(19)
F8_2	3139.1(8)	5397.0(6)	6090.0(4)	31.5(2)
F9_2	4568.1(9)	5364.3(7)	5596.4(3)	31.9(2)
O1_1	8288(5)	7520(7)	6427(3)	16.0(9)
C1_1	9331(4)	7344(3)	6797.8(18)	14.4(7)
C2_1	8945.4(18)	7226.7(14)	7345.1(7)	19.8(4)
F1_1	8060(4)	7836(3)	7412(2)	31.6(7)
F2_1	9938.3(14)	7321.0(12)	7737.3(5)	31.2(3)
F3_1	8433(2)	6415.2(18)	7393.9(9)	27.0(4)
C3_1	10005.6(18)	6466.2(13)	6658.0(8)	21.9(4)
F4_1	10580(2)	6602.0(14)	6248.2(8)	32.0(4)
F5_1	9125(8)	5805(6)	6533(3)	34.8(15)
F6_1	10889(3)	6163(4)	7051.7(16)	31.9(6)

Atom	*x*	*y*	*z*	U(eq)
C4_1	10273.0(18)	8157.1(14)	6818.0(8)	24.8(4)
F7_1	10392(6)	8361(4)	6278(2)	42.6(11)
F8_1	11440.4(15)	7960.2(13)	7084.2(8)	40.9(5)
F9_1	9811(7)	8868(3)	7036(3)	38.2(9)

*Table S 3 Fractional Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Parameters (Å²×10³) for [In(Mes)][Al(OR^F)$_4$] **4**. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor*

Atom	*x*	*y*	*z*	U(eq)
In1	-3473.6(4)	6994.3(3)	2803.6(4)	33.05(12)
C1	-1894(6)	6165(4)	1571(6)	28.3(13)
C6	-3153(7)	5781(4)	1166(7)	31.4(14)
Al1	7146.2(17)	4300.8(10)	6369.5(18)	20.7(4)
C2	-1881(6)	6911(5)	1139(6)	32.2(15)
C3	-3093(7)	7268(4)	310(7)	34.0(16)
C4	-4321(6)	6869(4)	-74(6)	32.3(16)
C5	-4370(7)	6117(4)	337(7)	31.8(15)
C7	-555(7)	5792(4)	2439(7)	35.4(16)
C9	-5715(7)	5687(5)	-113(9)	44.0(19)
C8	-3046(9)	8058(5)	-185(9)	47(2)
O1_4	7470(5)	3830(3)	5155(4)	26.7(10)
C1_4	8218(6)	3286(4)	4906(6)	28.1(13)
C2_4	9778(7)	3425(4)	5677(7)	35.1(14)
F1_4	10207(5)	4000(3)	5155(5)	49.7(11)
F2_4	10547(4)	2825(3)	5708(5)	47.2(11)
F3_4	10041(4)	3614(3)	6904(4)	46.0(11)
C3_4	7848(7)	2485(4)	5254(7)	34.8(14)
F4_4	6506(4)	2428(3)	4940(5)	47.3(11)
F5_4	8454(5)	2353(2)	6531(4)	45.0(11)
F6_4	8218(4)	1929(3)	4648(4)	43.2(9)
C4_4	7898(7)	3315(4)	3424(6)	35.6(15)
F7_4	6656(5)	3016(3)	2730(4)	47.1(11)
F8_4	8809(5)	2928(3)	3112(4)	44.9(11)
F9_4	7881(5)	4025(2)	3027(4)	42.7(10)
O1_3	8299(4)	5013(3)	7130(4)	27.2(9)

Atom	*x*	*y*	*z*	U(eq)
C1_3	8700(6)	5733(4)	7079(6)	31.1(13)
C2_3	10033(9)	5875(5)	8296(8)	53(2)
F1_3	9801(7)	5989(3)	9356(5)	77.8(19)
F2_3	10738(6)	6479(3)	8147(5)	66.8(16)
F3_3	10869(5)	5277(3)	8513(6)	69.2(17)
C3_3	8987(7)	5854(4)	5834(7)	36.0(15)
F4_3	7975(5)	5545(3)	4792(4)	43.3(10)
F5_3	10147(5)	5533(3)	5936(5)	51.7(12)
F6_3	9061(5)	6586(2)	5556(5)	44.7(11)
C4_3	7597(8)	6319(4)	7090(8)	46.8(18)
F7_3	6595(5)	6371(3)	5905(6)	55.8(13)
F8_3	8113(6)	7005(4)	7454(6)	71.7(15)
F9_3	7029(6)	6086(3)	7887(6)	66.4(16)
O1_2	5541(4)	4703(3)	5650(4)	27.6(9)
C1_2	4219(6)	4657(4)	4784(6)	32.9(14)
C2_2	4047(7)	5140(5)	3571(7)	48.6(19)
F1_2	4043(6)	5884(3)	3823(6)	70.8(16)
F2_2	2880(5)	4992(4)	2543(5)	65.2(16)
F3_2	5066(5)	5019(4)	3197(5)	63.7(15)
C3_2	3785(7)	3832(4)	4353(7)	42.3(17)
F4_2	4293(5)	3356(3)	5375(5)	50.2(11)
F5_2	4258(5)	3598(3)	3484(5)	56.7(13)
F6_2	2419(4)	3738(3)	3823(5)	55.1(13)
C4_2	3287(7)	4983(5)	5438(8)	45.4(17)
F7_2	3163(4)	4488(3)	6291(5)	52.3(12)
F8_2	2041(5)	5156(3)	4576(5)	57.3(14)
F9_2	3852(5)	5607(3)	6134(5)	56.4(13)
O1_1	7303(4)	3638(3)	7571(4)	26.1(10)
C1_1	7476(6)	3538(3)	8820(6)	26.1(12)
C2_1	6239(6)	3871(4)	9051(6)	28.5(13)
F1_1	5951(4)	4570(2)	8549(4)	34.3(9)
F2_1	6433(4)	3917(2)	10301(4)	37.4(9)
F3_1	5101(4)	3455(2)	8448(4)	32.2(8)
C3_1	7544(6)	2660(4)	9083(7)	32.4(14)

Atom	*x*	*y*	*z*	U(eq)
F4_1	8774(4)	2390(3)	9236(4)	40.7(10)
F5_1	6612(4)	2288(2)	8099(4)	34.9(9)
F6_1	7330(4)	2495(2)	10163(4)	37.4(9)
C4_1	8818(6)	3907(4)	9791(6)	33.9(15)
F7_1	9822(4)	3809(3)	9377(4)	41.1(10)
F8_1	9224(5)	3625(3)	10984(4)	46.8(12)
F9_1	8648(4)	4658(2)	9887(4)	41.8(10)

Table S 4 Fractional Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Parameters (Å²×10³) for [Ag(C₆Me₆)₂][Al(OR^F)₄]. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{ij} tensor

Atom	*x*	*y*	*z*	U(eq)
Ag1	3913.7(3)	2287.5(6)	2074.6(3)	67.3(3)
Ag2	1415.0(5)	2304.7(7)	7116.1(5)	90.8(4)
Ag3	8979.8(3)	1986.8(5)	2171.7(4)	58.5(2)
Ag4	3552.3(4)	7309.1(5)	2807.5(4)	65.5(2)
Al1	6946.9(8)	4467.5(8)	4658.7(7)	13.9(3)
Al2	-423.6(8)	5030.6(8)	-343.2(7)	13.3(3)
Al3	4599.7(8)	4999.8(8)	-349.7(7)	14.6(3)
Al4	1950.7(8)	4474.0(9)	4670.3(7)	16.5(3)
C1_28	2930(18)	1330(12)	2384(12)	22(6)
C2_28	2662(18)	1940(12)	2394(14)	26(6)
C3_28	2678(19)	2413(12)	1969(15)	31(6)
C4_28	2860(20)	2226(14)	1476(14)	26.4(18)
C5_28	3100(20)	1594(14)	1447(14)	25(6)
C6_28	3110(20)	1140(12)	1890(14)	22(6)
C7_28	2970(20)	830(16)	2869(15)	45(10)
C8_28	2380(20)	2100(20)	2884(18)	57(12)
C9_28	2410(20)	3083(14)	2007(19)	51(11)
C10_28	2670(30)	2630(30)	909(19)	72(15)
C11_28	3190(30)	1400(30)	862(18)	69(14)
C12_28	3340(20)	456(13)	1853(18)	43(9)
O1_31	6810(20)	3656(14)	4590(20)	25(8)
C1_31	7016(9)	3041(13)	4585(8)	28(5)

Atom	*x*	*y*	*z*	U(eq)
C2_31	7689(9)	3037(11)	4532(10)	45(5)
F1_31	7730(11)	3509(12)	4156(12)	56(6)
F2_31	7830(20)	2480(16)	4310(20)	56(9)
F3_31	8119(8)	3099(9)	5076(9)	61(6)
C3_31	7027(11)	2673(12)	5164(9)	52(6)
F4_31	6437(11)	2516(10)	5128(12)	79(7)
F5_31	7273(15)	3040(12)	5649(9)	69(7)
F6_31	7390(20)	2135(15)	5260(20)	77(12)
C4_31	6546(9)	2706(9)	4020(8)	34(4)
F7_31	5944(9)	2840(14)	3970(13)	52(6)
F8_31	6610(30)	2060(11)	4010(20)	50(8)
F9_31	6635(11)	2937(9)	3522(7)	55(5)
O1_30	1610(30)	4780(30)	3995(15)	41(12)
C1_30	1618(13)	4811(13)	3430(13)	46(8)
C2_30	1241(17)	5412(15)	3095(12)	60(10)
F1_30	668(19)	5460(30)	3152(17)	81(13)
F2_30	1090(20)	5350(20)	2492(11)	66(13)
F3_30	1560(30)	5966(18)	3290(30)	120(20)
C3_30	2314(14)	4837(19)	3434(19)	76(11)
F4_30	2648(16)	4330(20)	3730(20)	55(10)
F5_30	2610(20)	5380(20)	3700(30)	150(20)
F6_30	2310(20)	4830(40)	2870(20)	91(18)
C4_30	1318(16)	4175(14)	3089(14)	52(7)
F7_30	1720(20)	3668(16)	3243(13)	53(8)
F8_30	1150(30)	4250(20)	2495(13)	77(14)
F9_30	800(20)	4010(30)	3220(30)	55.0(18)
C1_1	7956(3)	1115(3)	2208(3)	28.9(13)
C2_1	8137(3)	1215(3)	1694(3)	24.6(12)
C3_1	8031(3)	1825(3)	1398(3)	27.0(13)
C4_1	7748(3)	2335(3)	1631(3)	25.4(12)
C5_1	7544(3)	2216(3)	2117(3)	25.6(12)
C6_1	7652(3)	1613(3)	2416(3)	27.0(13)
C7_1	8069(4)	454(4)	2509(4)	45(2)
C8_1	8393(4)	648(4)	1436(5)	45(2)

Atom	*x*	*y*	*z*	U(eq)
C9_1	8130(4)	1891(5)	793(3)	42.7(19)
C10_1	7653(5)	2992(4)	1333(4)	46(2)
C11_1	7177(4)	2744(4)	2311(4)	45(2)
C12_1	7435(5)	1511(5)	2947(4)	46(2)
C1_2	9367(3)	2581(4)	3410(3)	32.7(14)
C2_2	9734(3)	2091(3)	3247(3)	29.1(13)
C3_2	9998(3)	2221(3)	2790(3)	25.2(12)
C4_2	9881(3)	2830(3)	2491(3)	29.7(14)
C5_2	9501(3)	3300(3)	2639(3)	31.2(14)
C6_2	9255(3)	3173(4)	3099(3)	33.6(15)
C7_2	9119(6)	2452(7)	3924(5)	69(3)
C8_2	9860(5)	1457(5)	3589(5)	53(2)
C9_2	10479(4)	1755(4)	2692(4)	46(2)
C10_2	10199(5)	2972(5)	2027(4)	48(2)
C11_2	9375(5)	3951(4)	2319(5)	57(3)
C12_2	8847(5)	3686(6)	3253(6)	61(3)
C1_3	591(3)	1347(3)	7377(3)	29.9(14)
C2_3	877(3)	1236(3)	6941(3)	32.7(14)
C3_3	706(3)	1633(3)	6414(3)	30.3(14)
C4_3	238(3)	2121(3)	6332(3)	31.1(14)
C5_3	-58(3)	2211(4)	6770(3)	32.5(14)
C6_3	112(3)	1822(4)	7286(3)	30.8(14)
C7_3	780(5)	928(5)	7938(4)	48(2)
C8_3	1324(6)	666(5)	6991(6)	66(3)
C9_3	977(5)	1479(5)	5912(4)	51(2)
C10_3	25(5)	2541(5)	5766(4)	49(2)
C11_3	-567(5)	2724(5)	6672(5)	56(3)
C12_3	-223(5)	1897(5)	7735(4)	44.9(19)
C1_4	2335(4)	2334(4)	8511(3)	37.0(15)
C2_4	2675(3)	2269(4)	8113(3)	34.6(15)
C3_4	2543(3)	2689(3)	7609(3)	25.3(12)
C4_4	2074(3)	3172(3)	7516(3)	27.9(13)
C5_4	1712(3)	3215(3)	7907(3)	30.8(14)
C6_4	1850(3)	2795(3)	8404(3)	30.5(14)

Atom	*x*	*y*	*z*	U(eq)
C7_4	2506(7)	1896(7)	9056(5)	75(4)
C8_4	3191(6)	1766(7)	8213(5)	73(4)
C9_4	2938(4)	2644(5)	7197(4)	40.8(18)
C10_4	2006(7)	3682(5)	7033(5)	69(4)
C11_4	1204(5)	3730(5)	7807(5)	58(3)
C12_4	1498(5)	2867(6)	8852(5)	56(3)
C1_5	4065(4)	6261(4)	3005(4)	42.3(17)
C2_5	4366(4)	6379(4)	2575(4)	37.2(16)
C3_5	4854(3)	6845(4)	2689(3)	33.0(14)
C4_5	5051(4)	7187(4)	3234(3)	34.5(15)
C5_5	4730(4)	7092(3)	3653(3)	34.3(15)
C6_5	4252(4)	6627(3)	3543(3)	37.4(16)
C7_5	3604(6)	5701(5)	2918(8)	85(5)
C8_5	4176(6)	5994(6)	2000(5)	65(3)
C9_5	5179(5)	6961(6)	2228(4)	56(2)
C10_5	5596(5)	7664(6)	3367(5)	60(3)
C11_5	4942(6)	7478(5)	4238(4)	59(3)
C12_5	3955(6)	6477(7)	4024(6)	82(5)
C1_6	3103(3)	7812(3)	1550(3)	30.1(14)
C2_6	2585(3)	7382(4)	1432(3)	29.7(13)
C3_6	2234(3)	7354(4)	1828(3)	29.2(13)
C4_6	2401(3)	7759(3)	2344(3)	26.6(13)
C5_6	2904(3)	8204(3)	2455(3)	27.0(13)
C6_6	3265(3)	8233(3)	2055(3)	29.5(13)
C7_6	3459(5)	7840(5)	1108(5)	52(2)
C8_6	2395(5)	6954(5)	881(4)	53(2)
C9_6	1664(4)	6909(5)	1688(4)	50(2)
C10_6	2014(4)	7716(5)	2768(4)	40.4(18)
C11_6	3015(5)	8705(5)	2950(4)	51(2)
C12_6	3786(5)	8725(5)	2132(6)	60(3)
C1_8	4968(3)	2317(4)	2758(3)	28.4(13)
C2_8	4729(3)	2082(4)	3206(3)	33.9(15)
C3_8	4385(3)	2507(4)	3457(3)	35.1(15)
C4_8	4250(3)	3150(4)	3233(3)	33.1(15)

Atom	*x*	*y*	*z*	U(eq)
C5_8	4472(3)	3377(4)	2780(3)	33.3(14)
C6_8	4841(3)	2960(4)	2547(3)	31.4(14)
C7_8	5442(4)	1907(4)	2575(4)	43.5(19)
C8_8	4857(5)	1384(4)	3424(4)	51(2)
C9_8	4170(5)	2271(7)	3969(4)	62(3)
C10_8	3850(4)	3590(6)	3477(5)	56(3)
C11_8	4335(4)	4085(4)	2587(4)	44.2(19)
C12_8	5162(4)	3227(5)	2119(4)	40.6(18)
C1_7	2995(5)	1147(4)	2199(5)	31(2)
C2_7	2701(5)	1646(5)	2407(4)	29(2)
C3_7	2584(4)	2254(4)	2103(4)	23.9(19)
C4_7	2751(5)	2350(5)	1586(4)	26.4(18)
C5_7	3030(6)	1826(6)	1365(4)	30(2)
C6_7	3169(6)	1237(5)	1689(5)	32(2)
C7_7	3091(7)	484(7)	2508(8)	69(5)
C8_7	2482(7)	1555(9)	2949(5)	63(4)
C9_7	2275(6)	2803(7)	2326(6)	55(4)
C10_7	2552(7)	2959(7)	1214(8)	67(5)
C11_7	3109(7)	1861(10)	749(5)	67(5)
C12_7	3476(7)	681(7)	1475(9)	76(6)
O1_13	6309(12)	4865(15)	4770(14)	23(6)
C1_13	5857(7)	4855(6)	5034(6)	25(3)
C2_13	5394(6)	5423(6)	4773(5)	38(3)
F1_13	5722(12)	5957(10)	4712(11)	67(6)
F2_13	5051(7)	5595(12)	5121(6)	45(4)
F3_13	4979(6)	5278(9)	4231(5)	69(5)
C3_13	5485(6)	4204(6)	4907(6)	46(3)
F4_13	5823(6)	3726(5)	5273(7)	57(3)
F5_13	5371(16)	4021(12)	4336(9)	57(7)
F6_13	4925(9)	4230(13)	4994(13)	57(6)
C4_13	6164(5)	4949(7)	5724(5)	37(3)
F7_13	6686(8)	4569(11)	5927(10)	54(6)
F8_13	5774(15)	4787(13)	6033(14)	54(5)
F9_13	6332(6)	5566(6)	5871(6)	56(3)

Atom	*x*	*y*	*z*	U(eq)
O1_27	1413(9)	4625(13)	5035(12)	65(7)
C1_27	883(8)	4935(8)	5032(6)	53(4)
C2_27	313(7)	4510(8)	4671(7)	53(4)
F1_27	363(16)	4349(11)	4138(9)	59(6)
F2_27	-249(10)	4827(17)	4531(15)	63(7)
F3_27	276(9)	3982(7)	4965(10)	104(7)
C3_27	917(7)	5013(10)	5696(7)	66(5)
F4_27	1284(6)	5530(10)	5968(6)	100(7)
F5_27	1165(12)	4481(12)	6001(9)	114(9)
F6_27	328(9)	5043(14)	5738(11)	93(9)
C4_27	799(7)	5639(8)	4768(7)	62(4)
F7_27	1348(10)	5953(13)	4933(13)	119(9)
F8_27	408(11)	5967(13)	4999(12)	105(9)
F9_27	571(6)	5621(7)	4180(6)	61(3)
O1_25	1944(13)	3670(9)	4550(12)	60(7)
C1_25	1966(7)	3042(8)	4712(7)	36(4)
C2_25	2593(7)	2759(7)	4681(7)	47(4)
F1_25	2697(8)	2939(8)	4181(7)	59(4)
F2_25	2593(13)	2109(8)	4679(14)	64(5)
F3_25	3086(6)	2955(6)	5144(7)	70(4)
C3_25	1954(8)	2975(6)	5375(7)	53(4)
F4_25	1364(8)	3027(7)	5377(8)	81(5)
F5_25	2297(9)	3456(6)	5704(7)	66(5)
F6_25	2168(10)	2413(5)	5626(9)	54(4)
C4_25	1417(8)	2637(9)	4282(8)	65(5)
F7_25	863(6)	2956(7)	4141(11)	90(7)
F8_25	1383(17)	2057(9)	4531(15)	133(11)
F9_25	1480(9)	2511(8)	3757(6)	109(6)
O1_24	1840(9)	3667(9)	4488(8)	24(3)
C1_24	1935(7)	3040(9)	4653(6)	31(4)
C2_24	1260(8)	2731(9)	4461(8)	55(5)
F1_24	948(7)	2909(7)	4828(8)	74(5)
F2_24	1271(14)	2073(9)	4488(10)	71(5)
F3_24	950(13)	2924(15)	3888(8)	125(11)

Atom	*x*	*y*	*z*	U(eq)
C3_24	2368(9)	2715(9)	4352(8)	67(5)
F4_24	2899(11)	3065(12)	4452(13)	110(9)
F5_24	2044(13)	2644(13)	3775(7)	137(9)
F6_24	2560(20)	2117(11)	4553(18)	101(11)
C4_24	2248(8)	2963(10)	5348(7)	59(5)
F7_24	2876(7)	3082(8)	5537(9)	85(6)
F8_24	2152(18)	2379(12)	5539(14)	117(10)
F9_24	1983(13)	3386(14)	5623(9)	118(10)
O1_20	5296.7(19)	4745(2)	190.6(19)	22.3(9)
C1_20	5932(3)	4658(3)	353(3)	23.7(12)
C2_20	6094(3)	4130(3)	-47(3)	27.3(13)
F1_20	5685(2)	3638(2)	-151(2)	42.4(11)
F2_20	6687(2)	3898(2)	206(2)	35.5(10)
F3_20	6050(2)	4369(2)	-587.2(19)	37.8(10)
C3_20	6250(3)	5300(3)	274(4)	37.7(16)
F4_20	6265(3)	5719(3)	715(3)	61.3(16)
F5_20	5929(2)	5594(2)	-243(3)	49.3(13)
F6_20	6854(2)	5233(3)	296(3)	53.5(14)
C4_20	6182(3)	4437(4)	1019(3)	40.4(17)
F7_20	5914(3)	4776(3)	1346(2)	59.1(16)
F8_20	6819(2)	4511(3)	1269(2)	51.7(14)
F9_20	6052(3)	3806(3)	1070(2)	50.3(13)
O1_15	-643(2)	4948(2)	-1116.5(19)	25.4(9)
C1_15	-591(3)	4599(3)	-1582(2)	24.1(12)
C2_15	-545(4)	3857(3)	-1455(3)	35.0(15)
F1_15	-161(2)	3733(2)	-897.5(19)	40.9(11)
F2_15	-321(3)	3528(2)	-1830(2)	46.4(12)
F3_15	-1121(3)	3615(2)	-1516(2)	45.7(11)
C3_15	-1178(3)	4751(4)	-2144(3)	35.1(15)
F4_15	-1143(2)	5345(2)	-2363(2)	42.1(11)
F5_15	-1707(2)	4737(3)	-2006(2)	46.6(12)
F6_15	-1246(3)	4314(3)	-2587(2)	48.0(12)
C4_15	15(3)	4823(3)	-1716(3)	31.2(14)
F7_15	84(2)	5466(2)	-1671(2)	39.9(10)

Atom	*x*	*y*	*z*	U(eq)
F8_15	8(3)	4649(3)	-2269(2)	44.5(11)
F9_15	539(2)	4563(2)	-1320(2)	38.4(10)
O1_12	6317(17)	4860(20)	4782(19)	22(9)
C1_12	5861(8)	4856(8)	5038(7)	24(4)
C2_12	5240(6)	4540(8)	4608(6)	30(3)
F1_12	4927(8)	4948(8)	4170(7)	47(4)
F2_12	4843(11)	4379(16)	4901(14)	39(5)
F3_12	5370(20)	3996(14)	4362(13)	43(8)
C3_12	6083(7)	4482(8)	5648(6)	32(3)
F4_12	6690(10)	4641(11)	5970(15)	35(6)
F5_12	6035(8)	3838(6)	5551(7)	43(3)
F6_12	5734(19)	4619(17)	5998(18)	50(7)
C4_12	5709(7)	5568(7)	5162(7)	34(3)
F7_12	6181(7)	5806(8)	5632(7)	47(4)
F8_12	5177(8)	5603(15)	5301(9)	36(4)
F9_12	5626(15)	5948(13)	4683(10)	42(5)
O1_11	6790(10)	3646(7)	4666(10)	22(3)
C1_11	6977(5)	3029(6)	4616(4)	24(2)
C2_11	6369(5)	2636(5)	4256(5)	38(2)
F1_11	6010(3)	2500(4)	4593(4)	47.5(19)
F2_11	6506(11)	2063(6)	4058(9)	54(4)
F3_11	6006(6)	2973(6)	3780(5)	51(3)
C3_11	7464(6)	2998(5)	4280(5)	38(2)
F4_11	7900(5)	3469(5)	4469(5)	50(2)
F5_11	7175(5)	3087(4)	3687(3)	58(2)
F6_11	7766(11)	2414(7)	4356(9)	54(4)
C4_11	7273(5)	2725(6)	5254(4)	32(2)
F7_11	7872(3)	2946(3)	5511(4)	47(2)
F8_11	7290(7)	2068(6)	5233(6)	42(3)
F9_11	6950(5)	2890(5)	5608(4)	44(2)
O1_21	3972(2)	4718(2)	-152(2)	28.8(10)
C1_21	3742(3)	4237(3)	103(3)	32.4(14)
C2_21	3048(4)	4101(5)	-304(4)	49(2)
F1_21	2736(2)	4639(4)	-503(3)	76(2)

Atom	*x*	*y*	*z*	U(eq)
F2_21	2719(3)	3764(3)	-20(3)	64.0(17)
F3_21	3049(4)	3758(4)	-794(3)	81(2)
C3_21	4142(4)	3603(4)	163(4)	53(2)
F4_21	4669(3)	3632(3)	648(3)	65.0(17)
F5_21	4301(3)	3512(3)	-328(3)	61.3(15)
F6_21	3811(3)	3079(3)	235(4)	76(2)
C4_21	3759(4)	4452(5)	739(4)	53(2)
F7_21	4309(3)	4726(3)	1043(2)	61.2(16)
F8_21	3666(3)	3952(4)	1063(3)	72.1(19)
F9_21	3294(3)	4890(4)	689(4)	77(2)
O1_19	4597(2)	4681(2)	-1031.3(19)	26.7(10)
C1_19	4343(3)	4645(3)	-1629(3)	30.9(14)
C2_19	3679(4)	4984(6)	-1876(3)	60(2)
F1_19	3345(3)	4832(5)	-1528(3)	87(3)
F2_19	3353(3)	4778(5)	-2437(2)	76(2)
F3_19	3743(3)	5638(4)	-1869(3)	78(2)
C3_19	4789(4)	5003(4)	-1918(3)	38.3(16)
F4_19	5310(2)	4653(3)	-1845(2)	48.1(12)
F5_19	4989(3)	5568(2)	-1634(2)	50.1(12)
F6_19	4517(3)	5138(3)	-2504(2)	54.3(13)
C4_19	4294(5)	3933(4)	-1814(4)	53(2)
F7_19	4825(4)	3598(3)	-1511(2)	62.3(16)
F8_19	4204(4)	3850(3)	-2412(2)	69.5(19)
F9_19	3797(4)	3649(4)	-1712(3)	87(3)
O1_26	1487(7)	4794(8)	5066(11)	24(3)
C1_26	918(7)	5037(7)	5056(6)	30(3)
C2_26	774(8)	4755(7)	5604(7)	40(4)
F1_26	609(8)	4137(6)	5533(9)	72(5)
F2_26	347(8)	5128(7)	5754(10)	39(4)
F3_26	1290(8)	4758(8)	6095(7)	46(3)
C3_26	987(7)	5789(6)	5124(6)	37(3)
F4_26	1296(9)	6019(8)	4773(8)	51(4)
F5_26	1351(5)	5956(6)	5677(5)	48(3)
F6_26	424(9)	6096(9)	4992(9)	45(4)

Atom	*x*	*y*	*z*	U(eq)
C4_26	360(6)	4865(8)	4472(6)	43(4)
F7_26	340(7)	5277(9)	4031(5)	68(4)
F8_26	-208(9)	4906(18)	4548(16)	53(6)
F9_26	436(15)	4262(10)	4306(11)	65(7)
O1_23	1750(4)	4910(5)	4003(3)	31.0(19)
C1_23	1701(4)	4960(4)	3418(3)	26.3(16)
C2_23	2227(4)	4568(4)	3282(4)	38(2)
F1_23	2783(3)	4640(4)	3715(3)	49.7(17)
F2_23	2305(5)	4740(5)	2764(3)	57(2)
F3_23	2098(4)	3928(3)	3242(3)	55.3(18)
C3_23	1034(4)	4693(5)	3016(4)	47(2)
F4_23	576(3)	5108(5)	2990(3)	60(2)
F5_23	912(4)	4141(4)	3259(4)	55.0(18)
F6_23	1011(4)	4536(5)	2458(3)	61(2)
C4_23	1747(5)	5680(5)	3253(5)	50(2)
F7_23	1402(4)	6053(4)	3488(4)	55.7(19)
F8_23	1516(4)	5764(4)	2648(3)	64(2)
F9_23	2341(3)	5894(3)	3443(3)	57.4(18)
O1_22	2729(2)	4589(3)	5125(2)	35.0(11)
C1_22	3208(3)	4948(3)	5497(3)	26.4(13)
C2_22	3009(3)	5347(4)	5960(3)	32.2(14)
F1_22	2640(2)	5845(2)	5694(2)	41.5(11)
F2_22	3511(2)	5600(3)	6398(2)	43.5(11)
F3_22	2687(2)	4965(3)	6222(2)	47.8(12)
C3_22	3778(4)	4489(4)	5829(3)	41.7(17)
F4_22	3866(3)	4045(3)	5456(3)	51.5(13)
F5_22	3671(3)	4185(3)	6284(2)	56.4(15)
F6_22	4323(2)	4817(3)	6056(3)	60.0(15)
C4_22	3446(4)	5433(4)	5100(3)	37.9(16)
F7_22	3737(2)	5105(3)	4783(2)	49.0(12)
F8_22	3814(3)	5896(2)	5400(2)	48.2(12)
F9_22	2934(2)	5729(2)	4703(2)	44.1(11)
O1_14	366.8(19)	4834(2)	-12.3(19)	20.6(8)
C1_14	850(3)	4635(3)	474(2)	20.4(11)

Atom	*x*	*y*	*z*	U(eq)
C2_14	1404(3)	4406(4)	268(3)	32.8(14)
F1_14	1276(2)	3812(2)	13(2)	46.7(12)
F2_14	1960(2)	4373(3)	733(2)	48.7(13)
F3_14	1496(2)	4810(3)	-135(2)	39.7(10)
C3_14	1093(4)	5219(4)	921(3)	37.7(16)
F4_14	600(2)	5532(2)	998(2)	42.0(11)
F5_14	1406(3)	5647(2)	691(2)	48.7(12)
F6_14	1464(3)	5033(3)	1468(2)	51.7(13)
C4_14	641(3)	4067(3)	805(3)	30.3(13)
F7_14	292(2)	4304(3)	1128(2)	43.3(11)
F8_14	1144(2)	3760(2)	1193(2)	45.8(12)
F9_14	298(2)	3642(2)	418(2)	38.8(10)
O1_16	-864(2)	4524(2)	-60(2)	27.5(10)
C1_16	-1429(3)	4369(3)	0(3)	25.2(12)
C2_16	-1513(4)	4752(4)	537(3)	37.5(15)
F1_16	-965(2)	4782(3)	997(2)	47.2(12)
F2_16	-1944(2)	4480(3)	743(2)	45.8(12)
F3_16	-1697(3)	5364(3)	373(3)	50.9(13)
C3_16	-1996(3)	4512(4)	-585(3)	32.9(15)
F4_16	-2036(2)	4077(3)	-1014(2)	43.9(11)
F5_16	-1923(2)	5101(2)	-806(2)	40.6(11)
F6_16	-2555(2)	4518(3)	-497(2)	47.8(13)
C4_16	-1417(3)	3625(3)	133(3)	34.2(15)
F7_16	-1179(3)	3297(2)	-226(2)	43.1(11)
F8_16	-2003(2)	3390(3)	46(2)	43.6(11)
F9_16	-1059(2)	3498(2)	702(2)	40.7(11)
O1_10	7670(2)	4586(2)	5218.0(19)	20.5(8)
C1_10	8189(3)	4943(3)	5512(2)	18.6(11)
C2_10	8721(3)	4475(3)	5907(3)	29.9(13)
F1_10	8482(2)	4046(2)	6188.3(19)	36.2(10)
F2_10	9182(2)	4799(3)	6324(2)	42.2(11)
F3_10	8983(2)	4149(3)	5565(2)	44.4(11)
C3_10	8438(3)	5314(3)	5057(3)	28.2(13)
F4_10	8061(2)	5816(2)	4815(2)	39.0(10)

Atom	*x*	*y*	*z*	U(eq)
F5_10	8452(2)	4921(3)	4613.1(19)	40.2(11)
F6_10	9027.3(19)	5546(3)	5322(2)	38.4(10)
C4_10	8018(3)	5447(3)	5926(3)	25.6(12)
F7_10	7474(2)	5745(2)	5629(2)	34.7(9)
F8_10	8460(2)	5903(2)	6138(2)	43.6(11)
F9_10	7935(2)	5144(2)	6398.1(17)	34.5(9)
O1_9	6998(2)	4759(2)	3989.9(19)	25.0(9)
C1_9	6710(3)	5041(3)	3450(3)	24.6(12)
C2_9	5986(3)	4891(4)	3193(3)	33.5(15)
F1_9	5882(2)	4278(2)	3315(2)	42.1(11)
F2_9	5742(2)	4973(3)	2595.3(19)	45.7(12)
F3_9	5658(2)	5280(3)	3443(2)	43.0(11)
C3_9	6801(4)	5790(3)	3510(3)	35.1(15)
F4_9	7397(2)	5965(2)	3552(2)	40.7(10)
F5_9	6699(2)	6011(2)	4002(2)	41.2(10)
F6_9	6396(2)	6112(2)	3044(2)	45.4(11)
C4_9	7030(3)	4785(4)	3004(3)	32.4(14)
F7_9	7656(2)	4727(3)	3270.9(19)	37.9(10)
F8_9	6929(3)	5170(3)	2522.8(19)	43.8(11)
F9_9	6807(3)	4190(2)	2809(2)	47.1(12)
O1_18	4539(2)	5830(2)	-436(2)	29.0(10)
C1_18	4385(3)	6422(3)	-283(3)	29.9(13)
C2_18	4837(4)	6628(4)	345(4)	45.3(18)
F1_18	4943(3)	6123(3)	727(2)	55.4(14)
F2_18	4599(3)	7114(3)	586(3)	63.2(17)
F3_18	5406(3)	6812(3)	318(3)	58.4(15)
C3_18	4432(4)	6924(4)	-756(4)	44.1(17)
F4_18	3940(3)	6863(3)	-1273(3)	65.3(16)
F5_18	4969(3)	6826(3)	-880(3)	56.2(14)
F6_18	4443(4)	7536(2)	-569(3)	68.2(18)
C4_18	3688(4)	6427(4)	-277(4)	48.2(19)
F7_18	3304(2)	6099(3)	-746(3)	55.2(14)
F8_18	3450(3)	7033(3)	-306(3)	63.7(16)
F9_18	3658(3)	6145(3)	228(3)	64.2(16)

Atom	*x*	*y*	*z*	U(eq)
O1_17	-573(2)	5829(2)	-203(2)	23.0(9)
C1_17	-558(3)	6470(3)	-324(3)	22.6(12)
C2_17	-1027(3)	6610(3)	-972(3)	32.7(14)
F1_17	-783(3)	6428(2)	-1394(2)	48.0(12)
F2_17	-1163(2)	7245(2)	-1062(2)	42.2(11)
F3_17	-1570(2)	6295(3)	-1078(3)	55.3(15)
C3_17	-773(5)	6859(4)	135(4)	46.3(19)
F4_17	-489(4)	6628(3)	688(2)	63.7(17)
F5_17	-1407(3)	6800(3)	11(3)	64.8(17)
F6_17	-644(3)	7491(2)	141(3)	59.2(16)
C4_17	117(3)	6684(3)	-297(3)	36.1(15)
F7_17	492(3)	6748(3)	278(3)	59.9(16)
F8_17	117(2)	7261(2)	-567(2)	46.6(12)
F9_17	380(2)	6237(2)	-545(3)	50.0(13)

S-3 Quantum chemical calculations

Table S 5 SCF energy, FreeH energy and FreeH entropy of presented compounds. (*BP86/def2-def-SV(P)/D3(BJ)*)

Compound	SCF /*Hartree*	FreeH energy [kJ/mol]	FreeH entropy [kJ/mol K]
$[Ga(C_6Me_6)]^+$ **2**	−2392.531049311	726.50	0.54900
$[In(C_6Me_6)]^+$ **3**	−-469.5634913586	726.14	0.53824

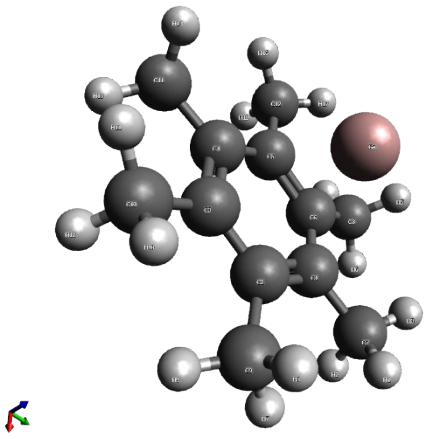


Figure S 39 Geometry optimised structure of $[Ga(C_6Me_6)]^+$.

Table S 6 Atomic coordinates of geometry optimised structure of $[Ga(C_6Me_6)]^+$.

Atom	*x*	*y*	*z*
C	0,716	1,24015	-0,02963
C	1,43181	0	-0,063
C	0,716	-1,24015	-0,02963
C	-0,71591	-1,23999	-0,063
C	-1,432	0	-0,02963
C	-0,71591	1,23999	-0,063
C	1,47211	2,54976	0,01886
C	-1,47081	2,54751	-0,16699
C	2,94161	0	-0,16699

Atom	*x*	*y*	*z*
C	1,47211	-2,54976	0,01886
C	-1,47081	-2,54751	-0,16699
C	-2,94421	0	0,01886
Ga	0	0	2,29196
H	2,44365	2,44819	0,54107
H	1,68841	2,9244	-1,00852
H	0,89836	3,34036	0,54107
H	-2,42528	2,41964	-0,71397
H	-1,71848	2,9765	0,83117
H	-0,88283	3,31018	-0,71397
H	3,30811	0,89054	-0,71397
H	3,43696	0	0,83117
H	3,30811	-0,89054	-0,71397
H	2,44365	-2,44819	0,54107
H	0,89836	-3,34036	0,54107
H	1,68841	-2,9244	-1,00852
H	-0,88283	-3,31018	-0,71397
H	-1,71848	-2,9765	0,83117
H	-2,42528	-2,41964	-0,71397
H	-3,34202	-0,89217	0,54107
H	-3,34202	0,89217	0,54107
H	-3,37681	0	-1,00852

Table S 7 Vibrational bands of $[Ga(C_6Me_6)]^+$.

	Symm.	*v* / cm^{-1}	IR	Raman
1		0	-	-
2		0	-	-
3		0	-	-
4		0	-	-
5		0	-	-
6		0	-	-
7	e	16,85	YES	YES
8	e	39,18	YES	YES
9	a2	39,18	YES	NO
10	e	95,69	YES	YES
11	e	95,69	YES	YES
12	a1	110,48	NO	YES
13	a2	110,48	YES	NO
14	e	133,44	YES	YES
15	e	145,91	YES	YES
16	a1	145,91	NO	YES
17	e	162,14	YES	YES
18	e	168,65	YES	YES
19	e	342,61	YES	YES
20	e	342,61	YES	YES
21	a1	355,09	NO	YES
22	a2	381,98	YES	NO
23	e	381,98	YES	YES
24	e	405,36	YES	YES
25	a2	405,36	YES	NO
26	e	443,47	YES	YES
27	e	443,47	YES	YES
28	a2	445,44	YES	NO
29	e	554,54	YES	YES
30	e	554,73	YES	YES
31	e	554,73	YES	YES
32	e	573,5	YES	YES
33	a2	582,41	YES	NO
34	a1	681,59	NO	YES
35	e	797,64	YES	YES
36	e	797,64	YES	YES
37	a2	958,64	YES	NO
38	e	958,64	YES	YES
39	e	974,41	YES	YES
40	a1	975,95	NO	YES
41	e	999,65	YES	YES
42	e	999,65	YES	YES
43	a2	1023,6	YES	NO
44	e	1023,6	YES	YES

	Symm.	ν / cm^{-1}	IR	Raman
45	e	1025,73	YES	YES
46	a1	1054,11	NO	YES
47	e	1054,11	YES	YES
48	e	1076,05	YES	YES
49	e	1076,91	YES	YES
50	e	1076,91	YES	YES
51	a1	1259,21	NO	YES
52	e	1308,18	YES	YES
53	e	1317,67	YES	YES
54	a2	1359,06	YES	NO
55	a1 1	1359,06	NO	YES
56	e1	1366,04	YES	YES
57	e1	1366,57	YES	YES
58	a2 1	1366,57	YES	NO
59	e1	1372,67	YES	YES
60	e1	1378,73	YES	YES
61	e 1	1378,73	YES	YES
62	e 1	1398,03	YES	YES
63	a2 1	1398,03	YES	NO
64	e 1	1416,5	YES	YES
65	e 1	1417,77	YES	YES
66	a1 1	1428,29	NO	YES
67	a1 1	1434,07	NO	YES
68	e 1	1434,07	YES	YES
69	e 1	1444,2	YES	YES
70	a2 1	1444,2	YES	NO
71	e 1	1464	YES	YES
72	e 1	1464	YES	YES
73	a2 1	1479,01	YES	NO
74	e 1	1538,82	YES	YES
75	e 1	1538,82	YES	YES
76	a2 1	2952,15	YES	NO
77	e 1	2952,48	YES	YES
78	e 1	2952,48	YES	YES
79	e 1	2953,96	YES	YES
80	e 1	2953,96	YES	YES
81	a1 1	2954,74	NO	YES
82	a2 1	3040,82	YES	NO
83	e 1	3042,38	YES	YES
84	e 1	3042,38	YES	YES
85	e 1	3047,28	YES	YES
86	e 1	3047,28	YES	YES
87	a1 1	3049,79	NO	YES
88	e 3	3071,96	YES	YES
89	e 3	3075,31	YES	YES
90	a1 3	3075,31	NO	YES
91	a2 3	3082,19	YES	NO
92	e 3	3082,19	YES	YES
93	e 3	3084,03	YES	YES

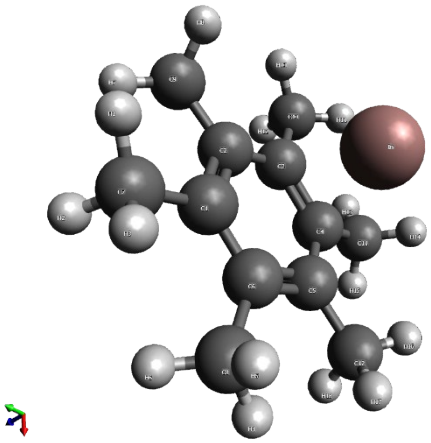


Figure S 40 Geometry optimised structure of $[In(C_6Me_6)]^+$.

Table S 8 Atomic coordinates of geometry optimised structure of $[In(C_6Me_6)]^+$.

Atom	*x*	*y*	*z*
C	0,36648	1,3838	0,02227
C	-1,01391	1,01016	0,0509
C	-1,38164	-0,37452	0,02227
C	-0,36787	-1,38315	0,0509
C	1,01517	-1,00928	0,02227

Atom	*x*	*y*	*z*
C	1,38178	0,37299	0,0509
C	0,76754	2,84361	-0,00229
C	2,83462	0,78478	0,1685
C	-2,09695	2,06246	0,1685
C	-2,84641	-0,7571	-0,00229
C	-0,73767	-2,84725	0,1685
C	2,07887	-2,08652	-0,00229
In	0	0	-2,57031
H	0,02869	3,47089	-0,53895
H	0,85557	3,25227	1,03118
H	1,74799	2,99618	-0,49464
H	3,47108	-0,03797	0,54444
H	3,26494	1,12032	-0,80278
H	2,94621	1,6302	0,87814
H	-1,70265	3,02503	0,54444
H	-2,6027	2,26736	-0,80278
H	-2,8849	1,7364	0,87814
H	-3,46876	0,01571	-0,49464
H	-3,02022	-1,7106	-0,53895
H	-3,24434	-0,88519	1,03118
H	-1,76843	-2,98706	0,54444
H	-0,66224	-3,38768	-0,80278
H	-0,06131	-3,3666	0,87814
H	1,72078	-3,01189	-0,49464
H	2,99153	-1,76029	-0,53895
H	2,38876	-2,36708	1,03118

Table S 9 Vibrational bands of $[In(C_6Me_6)]^+$.

	Symm.	ν / cm^{-1}	IR	Raman
1	0	0	-	YES
2	0	0	-	YES
3	0	0	-	YES
4	0	0	-	YES
5	0	0	-	YES
6	0	0	-	YES
7	a	62,5	YES	YES
8	e	63,14	YES	YES
9	e	63,14	YES	YES
10	e	80,57	YES	YES
11	e	80,57	YES	YES
12	e	116,1	YES	YES
13	e	116,1	YES	YES
14	a	128,46	YES	YES
15	e	144,28	YES	YES
16	e	144,28	YES	YES
17	a	154,05	YES	YES
18	a	168,51	YES	YES
19	a	319,18	YES	YES
20	e	341,2	YES	YES
21	e	341,2	YES	YES
22	e	375,38	YES	YES
23	e	375,38	YES	YES
24	e	403,56	YES	YES
25	e	403,56	YES	YES
26	a	442,27	YES	YES
27	e	443,61	YES	YES
28	e	443,61	YES	YES
29	a	553,12	YES	YES
30	e	560,71	YES	YES
31	e	560,71	YES	YES
32	a	570,68	YES	YES
33	a	581,75	YES	YES
34	a	689,48	YES	YES
35	e	795,93	YES	YES
36	e	795,93	YES	YES
37	e	957,51	YES	YES
38	e	957,51	YES	YES
39	a	973,31	YES	YES
40	a	976,04	YES	YES

	Symm.	ν / cm^{-1}	IR	Raman
41	e	999,9	YES	YES
42	e	999,9	YES	YES
43	e	1024,11	YES	YES
44	e	1024,11	YES	YES
45	a	1024,99	YES	YES
46	e	1052,9	YES	YES
47	e	1052,9	YES	YES
48	e	1076,17	YES	YES
49	e	1076,17	YES	YES
50	a	1076,33	YES	YES
51	a	1257,8	YES	YES
52	a	1302,11	YES	YES
53	a	1314,86	YES	YES
54	e	1359,69	YES	YES
55	e	1359,69	YES	YES
56	e	1366,24	YES	YES
57	e	1366,24	YES	YES
58	a	1367,02	YES	YES
59	a	1373,86	YES	YES
60	e	1380,82	YES	YES
61	e	1380,82	YES	YES
62	e	1401,33	YES	YES
63	e	1401,33	YES	YES
64	a	1414,69	YES	YES
65	a	1418,28	YES	YES
66	a	1432,48	YES	YES
67	e	1433,08	YES	YES
68	e	1433,08	YES	YES
69	e	1443,6	YES	YES
70	e	1443,6	YES	YES
71	e	1462,67	YES	YES
72	e	1462,67	YES	YES
73	a	1477,27	YES	YES
74	e	1540,13	YES	YES
75	e	1540,13	YES	YES
76	a	2951,16	YES	YES
77	e	2951,26	YES	YES
78	e	2951,26	YES	YES
79	e	2953,18	YES	YES
80	e	2953,18	YES	YES
81	a	2953,73	YES	YES
82	a	3034,67	YES	YES
83	e	3035,69	YES	YES
84	e	3035,69	YES	YES
85	e	3041,98	YES	YES
86	e	3041,98	YES	YES
87	a	3043,52	YES	YES
88	a	3071,23	YES	YES
89	e	3072,98	YES	YES
90	e	3072,98	YES	YES
91	e	3086,59	YES	YES
92	e	3086,59	YES	YES
93	a	3087,28	YES	YES

S-4 References

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