

Supporting Information

Low-valent Group 6 Metals/ $\text{Al}(\text{C}_6\text{F}_5)_3$ Donor-Acceptor Systems for CO_2 Activation and Cleavage.

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1 Experimental Section

1.1 General Considerations

All reactions were performed in flame- or oven-dried glassware with rigorous exclusion of air and moisture, using a nitrogen filled Jacomex glove box ($O_2 < 1.0$ ppm, $H_2O < 1$ ppm). Solvents used were pre-dried (*n*-pentane, toluene, and tetrahydrofuran by passing through a Puresolv MD 7 solvent purification machine; chlorobenzene by distillation over CaH_2 ; benzene by distillation over Na/benzophenone), degassed by freeze-pump-thaw cycles, dried over molecular sieves and stored in the glove box. C_6D_6 , C_6D_5Cl and (purchased from Eurisotop) were degassed by freeze-pump-thaw cycles, dried over molecular sieves and stored in the glove box. The M(depe)-dinitrogen (M = Mo, W) complexes,¹⁻⁷ $Al(C_6F_5)_3(tol)$ (**AICF·tol**),⁸ *trans*-[W(depe)₂(N₂)(μ-N₂)Al(C₆F₅)₃] (**1^W**), *trans*-[Mo(depe)₂(N₂)(μ-N₂)Al(C₆F₅)₃] (**1^{Mo}**), *cis*-[W(depe)₂{(μ-N₂-Al(C₆F₅)₃)₂}] and *cis*-[Mo(depe)₂{(μ-N₂-Al(C₆F₅)₃)₂}]⁹ were prepared according to reported procedures and stored in the glove box. ¹H, ¹³C, ¹⁹F and ³¹P NMR spectra were recorded using NMR tubes equipped with J. Young valves on a Bruker Avance III 400 spectrometer. Chemical shifts are reported in parts per million (ppm) downfield from tetramethylsilane and are referenced to the most upfield residual solvent resonance as the internal standard in ¹H NMR (C_6HD_5 : δ reported = 7.16 ppm, C_6HD_4Cl : δ reported = 6.96 ppm, THF-*d*₈: δ reported = 1.72 ppm). ¹¹B, ¹⁹F and ³¹P NMR spectra were calibrated according to the IUPAC recommendation using a unified chemical shift scale based on the proton resonance of tetramethylsilane as primary reference.^{10,11} ¹H and ¹³C NMR assignments were confirmed by ¹H-¹H COSY and ¹H-¹³C HSQC and HMBC experiment if required. Data are reported as follows: chemical shift, multiplicity (b = broad, s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, h = hextuplet, hept = heptuplet, m = multiplet), coupling constant (Hz), and integration. Infrared (IR) spectra were recorded in the glove box ($O_2 < 1.0$ ppm, $H_2O < 1$ ppm) on an Agilent Cary 630 FT-IR spectrophotometer equipped with ATR or transmission modules and are reported in wavenumbers (cm^{-1}) with (s), (m), (w) indicating strong, medium, and weak absorption respectively. Elemental analyses were performed on samples sealed in tin capsules under Ar or N₂ by the Analytical Service of the Laboratoire de Chimie de Coordination; results are the average of two independent measurements.

X-ray structural determinations. Experimental details regarding XRD measurements are provided in the dedicated section below. CCDC 2355268-2355270 contain the supplementary crystallographic data for this paper. These data are provided free of charge.

1.2 Procedure to perform a precise addition of a known number of moles of CO₂

In cases where a precise addition of the number of moles of carbon dioxide was required, as for the synthesis of **2**, we used the following procedure:

- i) The volume of the headspace of the glassware used (Schlenk flask or NMR tube) was first determined by subtracting the total volume of the system (Schlenk flask or tube) from the volume of the solution (solvent).
- ii) We performed freeze-pump-thaw cycles of the solution and finally put the system and Schlenk lines under dynamic vacuum.
- iii) We switched to static vacuum in the Schlenk lines and closed the system.
- iv) Immediately afterwards, we opened the CO₂ bottle and admitted a precise pressure of carbon dioxide into the vacuum lines (the key is closed to vacuum) using a digital manometer connected to the Schlenk lines. The digital manometer we used is a

Vacuubrand manometer capable of measuring pressures between 10^{-3} and 10^3 mbars within a 0.1 mbar precision.

- v) We opened the Schlenk flask or NMR tube (which had returned to room temperature) and carefully adjusted the desired pressure to obtain the desired number of moles in the system using the ideal gas law equation.
- vi) We closed the system.

1.3 Synthetic procedures

1.3.1 Synthesis of **2** – *cis*-[W(depe)₂(CO)(μ-O)Al(C₆F₅)₃]

A 3.5 mL colourless solution of Al(C₆F₅)₃(tol) (48 mg, 77 μmol, 1.0 eq.) was added dropwise into a 2.5 mL red toluene solution of [W(depe)₂(N₂)₂] (50 mg, 77 μmol, 1.0 eq.). The resulting purple solution (relating to *in situ* [W(depe)₂(N₂)(μ-N₂)Al(C₆F₅)₃], **1^w**) was sealed in a 41 mL Schlenk flask. Next, the gas phase was evacuated under vacuum (toluene solution frozen in N_{2(l)}). CO₂ gas (136 mbars, 195 μmol, 2.60 eq.) was added in the system at room temperature (ca. 293K). The resulting solution turned deep blue/greenish and was left over stirring at room temperature for 30 minutes. At the beginning of the reaction, some gas evolved (likely decoordination of the N₂ ligands into N₂ gas). The gas phase was evacuated and the Schlenk flask was brought in the N₂-filled glovebox. The solution was filtered (a small portion of brown solids - ca. 5 mg - were discarded). Afterwards, the filtrate was saturated with 3 mL of *n*-hexanes, and put at T = -40 °C for 3 days which induced the growing of compound **2** as green block-shaped single crystals suitable for an XRD study (50 mg, 56 % yield). Product **2** is only stable in solid-state at low temperature (T = -40 °C). In solution (in C₆D₆ or C₆D₅Cl), it degrades quickly (in one hour) precluding advanced NMR characterisations (¹³C{¹H} and 2D NMR acquisitions especially). ¹H NMR (400 MHz, C₆D₆, 298 K) δ 1.50 (b), 0.87 (b). ¹⁹F NMR (376.2 MHz, C₆D₆, 298 K) δ -119.9 (dd, ³J_{F-F}=31 Hz & 10 Hz, 6F, CF_{ortho}), -157.5 (t, ³J_{F-F}=21 Hz, 3F, CF_{para}), -163.2 (m, 6F, CF_{meta}). ³¹P{¹H} NMR (163.2 MHz, C₆D₆, 298 K) δ 38.6 (s, 4P). IR-ATR (298 K, cm⁻¹) σ 2968 (m, νC-H), 2938 (m, νC-H), 2916 (m, νC-H), 2881 (m, νC-H), 1750 (s, ν(C≡O)), 1636 (m), 1505 (s), 1432 (s). Elemental analysis calcd (%) for C₃₉H₄₈AlF₁₅O₂P₄W.0.8(C₆H₁₄)-0.6(C₇H₈): C 44.60, H 4.99. Found: C 44.41, H 5.02

1.3.2 Synthesis of **3** – *trans*-[Mo(depe)₂(η²-CO₂){(μ-η²(C,O):η¹(O))-CO₂-Al(C₆F₅)₃}]

A 5 mL colourless benzene solution of Al(C₆F₅)₃(tol) (46 mg, 74 μmol, 1.0 eq.) was added dropwise into a 5 mL orange benzene solution of *trans*-[Mo(depe)₂(N₂)₂] (42 mg, 74 μmol, 1.0 eq.). The resulting wine/purple solution (relating to *in situ trans*-[Mo(depe)₂(N₂)(μ-N₂-AICF)] adduct, **1^{Mo}**) was sealed in a 22 mL Rodaviss Shlenck flask. Next, the solution was reduced to a volume of ca. 8 mL and the gas phase was evacuated (C₆H₆ frozen in N_{2(l)}). Afterwards, dried CO₂ (about 1.2 atm, 0.59 mmol, 8.0 eq.) was added into the stirring benzene solution of **1^{Mo}**. Instantly, the solution turned first green (nitrogen evolution noticed) then light orange. The latter was stirred at room temperature for one hour. C₆H₆ volatiles were removed *in vacuo* yielding crude **3** as a light orange oily foam. A fine orange powder of product **3** was obtained by dissolving the crude foam in 4 mL of *n*-hexanes, then filtrating it in a new 5 mL vial, precipitating it at low temperature (vial put at T = -40 °C for one day), and drying it *in vacuo* for 2 hours (45 mg, 54% yield). Note that using a smaller excess of CO₂ (from 2 to 3 eq.) did not change the reactivity. ¹H NMR (400 MHz, C₆D₆, 298 K) δ 2.83 (b), 1.68 (b), 1.43 (b), 1.26 (b), 0.95 (b), 0.67 (b). ¹⁹F NMR (376.2 MHz, C₆D₆, 298K) δ -121.4 (dd, ³J_{F-F}=28 Hz & 17 Hz, 6F, CF_{ortho}), -154.7 (t, ³J_{F-F}=20 Hz, 3F, CF_{para}), -162.7 (m, 6F, CF_{meta}). ³¹P{¹H} NMR (163.2 MHz, C₆D₆, 298K) δ 49.4 (b, 2P), 40.6 & 39.7 (d & b, 2P). IR-ATR (298K, cm⁻¹) σ 2968 (m, νC-H), 2943 (m, νC-H), 2911 (m, νC-H), 2884 (m, νC-H), 1714 (w, ν_{sym}η²-CO₂), 1636 (m), 1583 (s, ν_{sym}μ-CO₂), 1505 (s), 1432 (s), 1225 (s, ν_{asym}μ-CO₂), 1194 (s, ν_{asym}η²-CO₂). Elemental analysis calcd (%) for C₄₀H₄₈AlF₁₅O₄P₄Mo: C 42.72, H 4.30 Found: 40.71, H 4.14.

1.3.3 Synthesis of 4 – *trans*-[Mo(depe)₂{(μ-η²(C,O):η¹(O))-CO₂-Al(C₆F₅)₃}]₂

From adduct 5 (medium-scale reaction). In a 25 mL Schlenk flask, a 3 mL colourless C₆H₆ solution of Al(C₆F₅)₃(tol) (44 mg, 71 μmol, 2.0 eq) was added dropwise into a 3 mL orange C₆H₆ (with 10 drops of C₆H₅Cl to solubilize all the starting materials) solution of *trans*-[Mo(depe)₂(N₂)₂] (0.02 g, 36 μmol, 1.0 eq.). The resulting solution turned first green (relating to *trans*-[Mo(depe)₂(μ-N₂-AICF)₂] adduct) then progressively brown/red after 1 hour (relating to the two-fold *cis* adduct **5** - *cis*-[Mo(depe)₂(μ-N₂-AICF)₂]). The Schlenk flask was connected to vacuum lines and the N₂ gas phase was evacuated by freeze-pump thaw (solvent frozen in liquid N₂ and use of dynamic vacuum in the flask). Next, dried CO_{2(g)} (1.2 atm, 0.99 mmol, 22 eq) was added to the stirring solution of **5** at room temperature which quickly triggered a colour change from brown to light orange after a few minutes. The resulting solution was left over stirring at room temperature for 17 hours. Solvent volatiles were removed *in vacuo* yielding a crude yellow oil. The latter was triturated with *n*-hexane (*ca.* 4 mL) forming an orange solid in a colourless supernatant. The liquid phase was removed by decantation and filtration and the orange solid was dried *in vacuo* for 1 hour yielding product **5** as a fine orange powder (41.4 mg, 70% yield).

From complex 3 (NMR-scales reaction). A 0.4 mL colourless C₆D₆ solution of Al(C₆F₅)₃(tol) (6.0 mg, 9.7 μmol, 1.0 eq.) was added dropwise into a 0.2 mL orange C₆D₆ solution of compound **3** (11 mg, 9.6 μmol, 1.0 eq.). The resulting orange solution was sealed in a J-Young NMR tube and analysed by NMR spectroscopy. The latter showed the clean formation of product **4**.

¹H NMR (400 MHz, C₆D₆, 298 K) δ 2.49 (m), 2.20 (m), 2.07 (m), 1.60 (m), 1.30 (m), 1.10 (m), 1.00 (m), 0.88 (m), 0.70 (m), 0.53 (m), 0.43 (m), 0.18 (m). ¹⁹F NMR (376.2 MHz, C₆D₆, 298 K) δ -121.61 (dd, ³J_{F-F} = 40.0 & 15.0 Hz, 6F, CF_{ortho}), -121.75 (dd, ³J_{F-F} = 40.0 & 15.0 Hz, 6F, CF_{ortho}), -153.16 (t, ³J_{F-F}=20 Hz, 3F, CF_{para}), -153.19 (t, ³J_{F-F}=20 Hz, 3F, CF_{para}), -161.80 (m, 12F, CF_{meta}). ³¹P{¹H} NMR (163.2 MHz, C₆D₆, 298K) δ 46.7 – 45.9 (m, 1P), 45.2 – 44.4 (m, 1P), 40.4 – 39.2 (m, 2P). IR-ATR (298K, cm⁻¹): 2973 (w, νC-H), 2945 (w, νC-H), 2911 (w, νC-H), 2882 (w, νC-H), 1850 (w), 1636 (m), 1575 (s, ν_{sym}μ-CO₂), 1508 (s), 1441 (s), 1227 (s, ν_{asym}μ-CO₂). **Elemental analysis** calcd (%) for C₅₈H₄₈Al₂F₃₀O₄P₄Mo: C 42.15, H 2.93, N 0.00. Found: C 41.85, H 2.78, N 0.06.

1.3.4 Synthesis of 6 - [Mo(depe)₂{(μ-η²(C,N):η¹(O))-PhNCO-Al(C₆F₅)₃}]

A 0.4 mL colourless C₆D₆ solution of phenyl isocyanate (*ca.* 12 μmol, 1.0 eq.) was added dropwise into a 0.4 mL burgundy C₆D₆ solution of **1**^{Mo} (12 mg, 11 μmol, 1.0 eq.). Instantly, the colour of the solution turned from purple to dark blue. The latter was sealed in a J-Young NMR tube for analysis. After 3 hours, the tube was brought back in the N₂-filled glovebox. The C₆D₆ solution of **6** (*ca.* 0.8 mL) was transferred in a 5 mL vial, saturated with 3.5 mL of *n*-pentane, and stored in the freezer (T = -40 °C) for 7 days yielding product **6** as blue single-platelets-like crystals that were recovered by filtration and dried *in vacuo* for 2 hours (10.0 mg, 81% yield). ¹H NMR (400 MHz, C₆D₆, 298 K) δ 6.82 (t, ³J_{H-H}=7.6 Hz, 2H, CH_{PhNCO}), 6.71 (m, 1H, CH_{PhNCO}), 6.68 (m, 2H, CH_{PhNCO}), 1.70 (m, 4H, CH₂), 1.31 (m, 4H, CH₂), 1.17 (b, 4H, CH₂), 1.07 (m, 8H, CH₂), 0.91 (m, 12H, CH₃), 0.84 (b, 4H, CH₂), 0.69 (t, ³J_{H-H}=7.4 Hz, 12H, CH₃). ¹⁹F NMR (376.2 MHz, C₆D₆, 298K) δ -121.6 (dd, ³J_{F-F}=28 Hz & 18 Hz, 6F, CF_{ortho}), -156.2 (t, ³J_{F-F}=19 Hz, 3F, CF_{para}), -163.2 (m, 6F, CF_{meta}). ³¹P{¹H} NMR (163.2 MHz, C₆D₆, 298 K) δ 75.3 (b). IR-ATR (298 K, cm⁻¹) σ 2960 (m, νC-H), 2938 (m, νC-H), 2913 (m, νC-H), 2877 (m, νC-H), 1637 (m), 1593 (m), 1535 (m), 1506 (s), 1441 (s), 1301 (s). **Elemental analysis** calcd (%) for C₄₅H₅₃AlF₁₅ONP₄Mo: C 46.77, H 4.62, N 1.21. Found: C 44.46, H 5.06, N 1.31

2 NMR spectroscopic data

Figure S1. ^1H NMR spectrum (400 MHz, C_6D_6 , 298 K) of compound **2**.

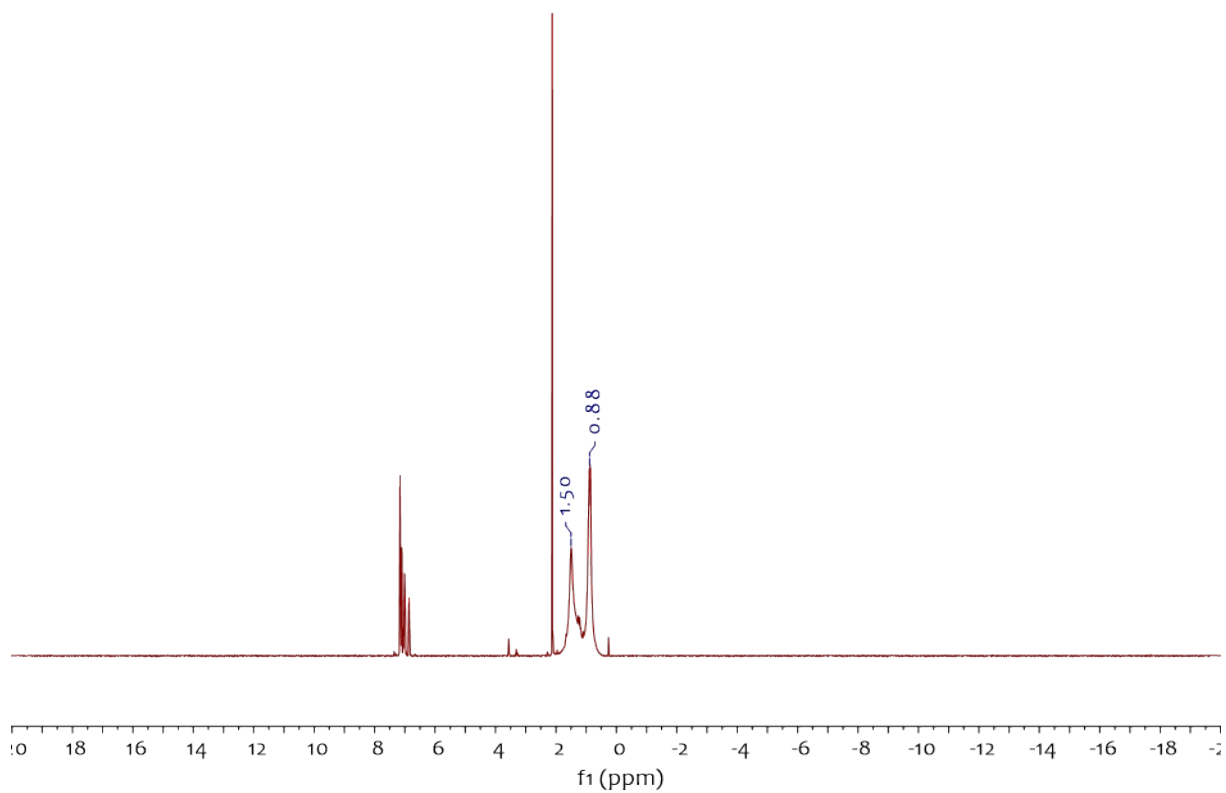


Figure S2. ^{19}F NMR spectrum (376.2 MHz, C_6D_6 , 298 K) of compound **2**.

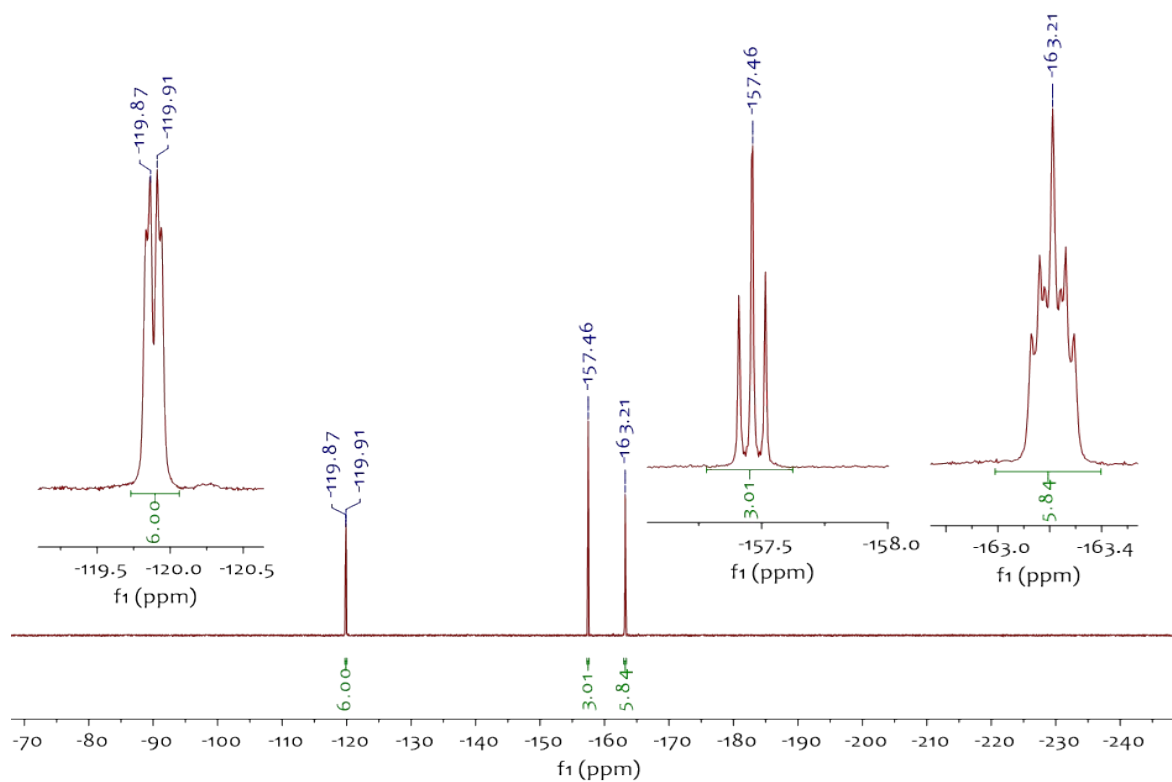


Figure S3. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (163.2 MHz, C_6D_6 , 298 K) of compound **2**.

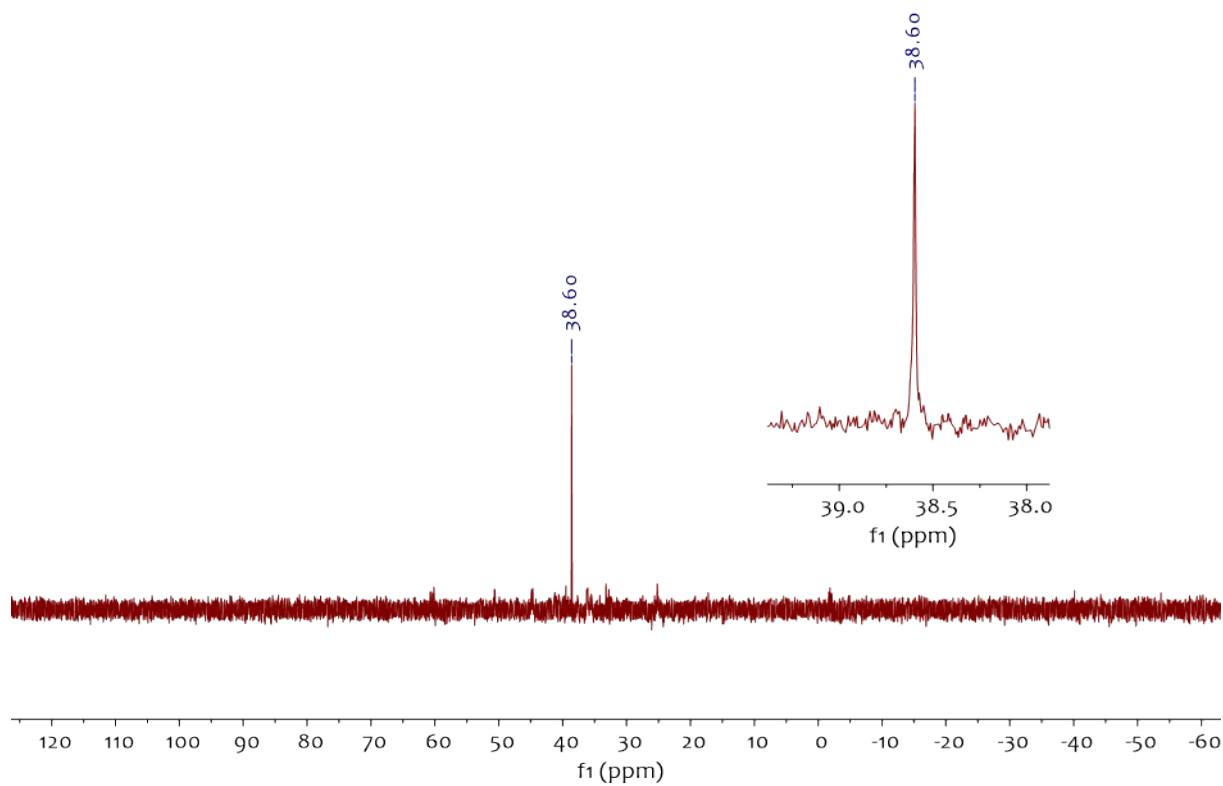


Figure S4. ^1H NMR spectrum (400 MHz, C_6D_6 , 298 K) of compound **3**.

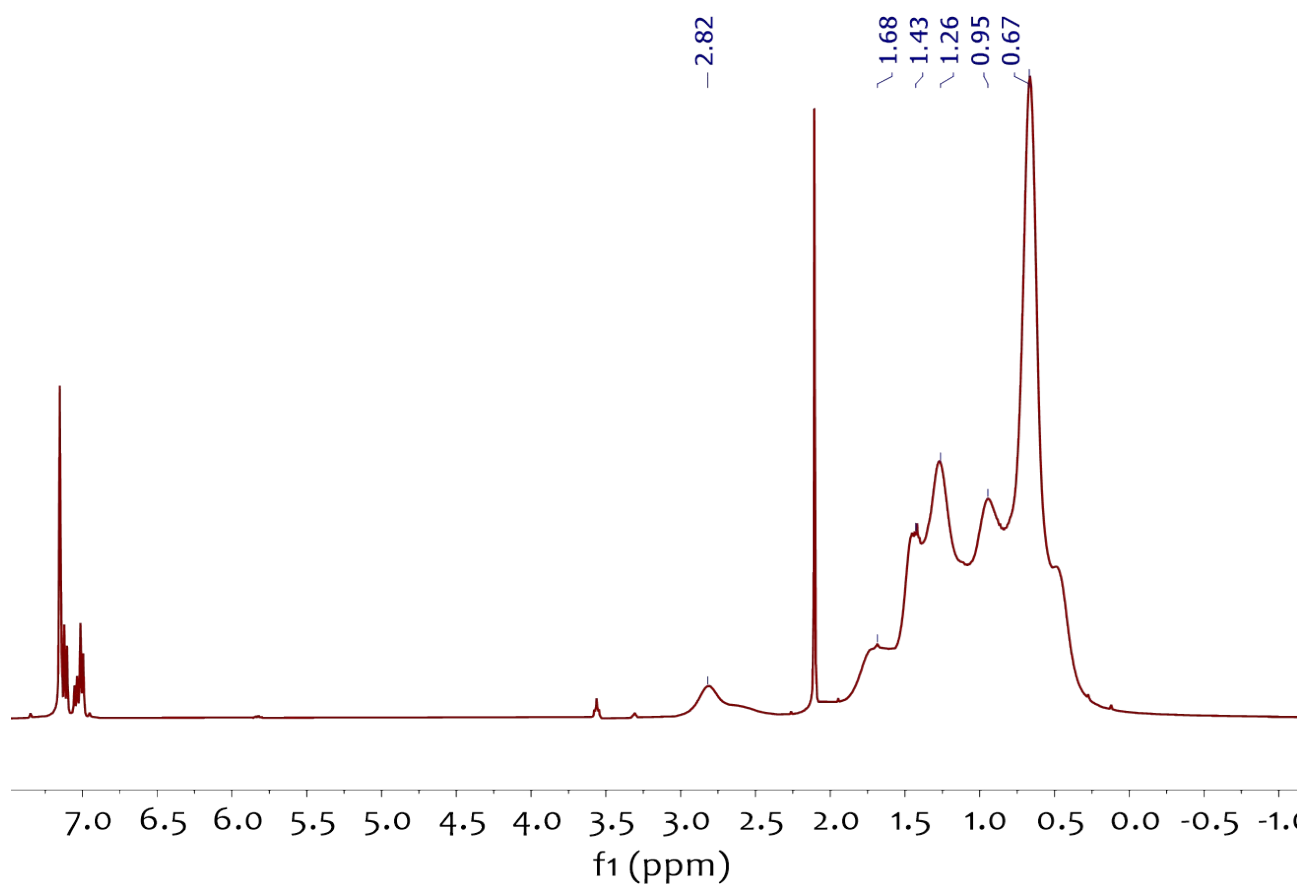


Figure S5. ^{19}F NMR spectrum (376.2 MHz, C_6D_6 , 298 K) of compound **3**.

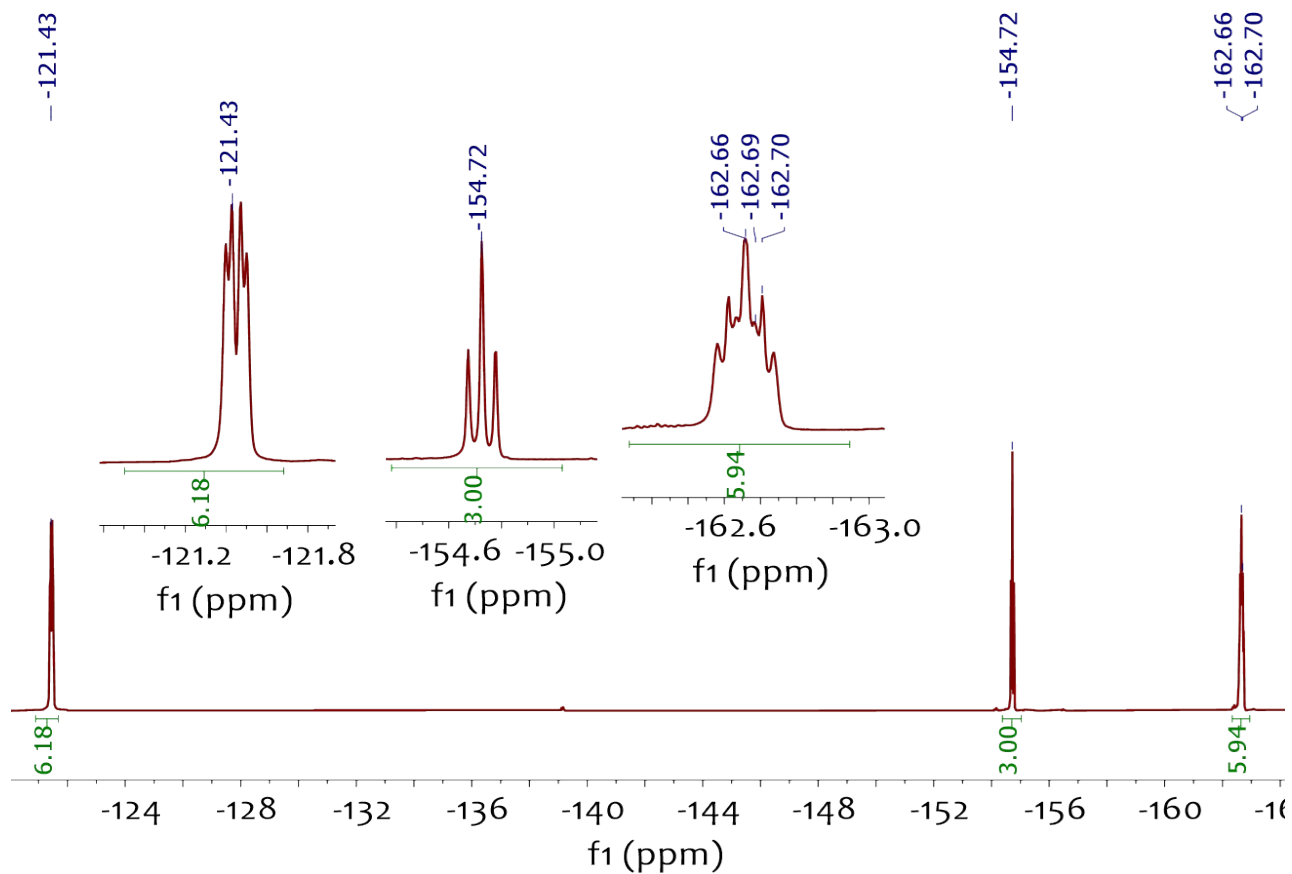


Figure S6. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (163.2 MHz, C_6D_6 , 298 K) of compound **3**.

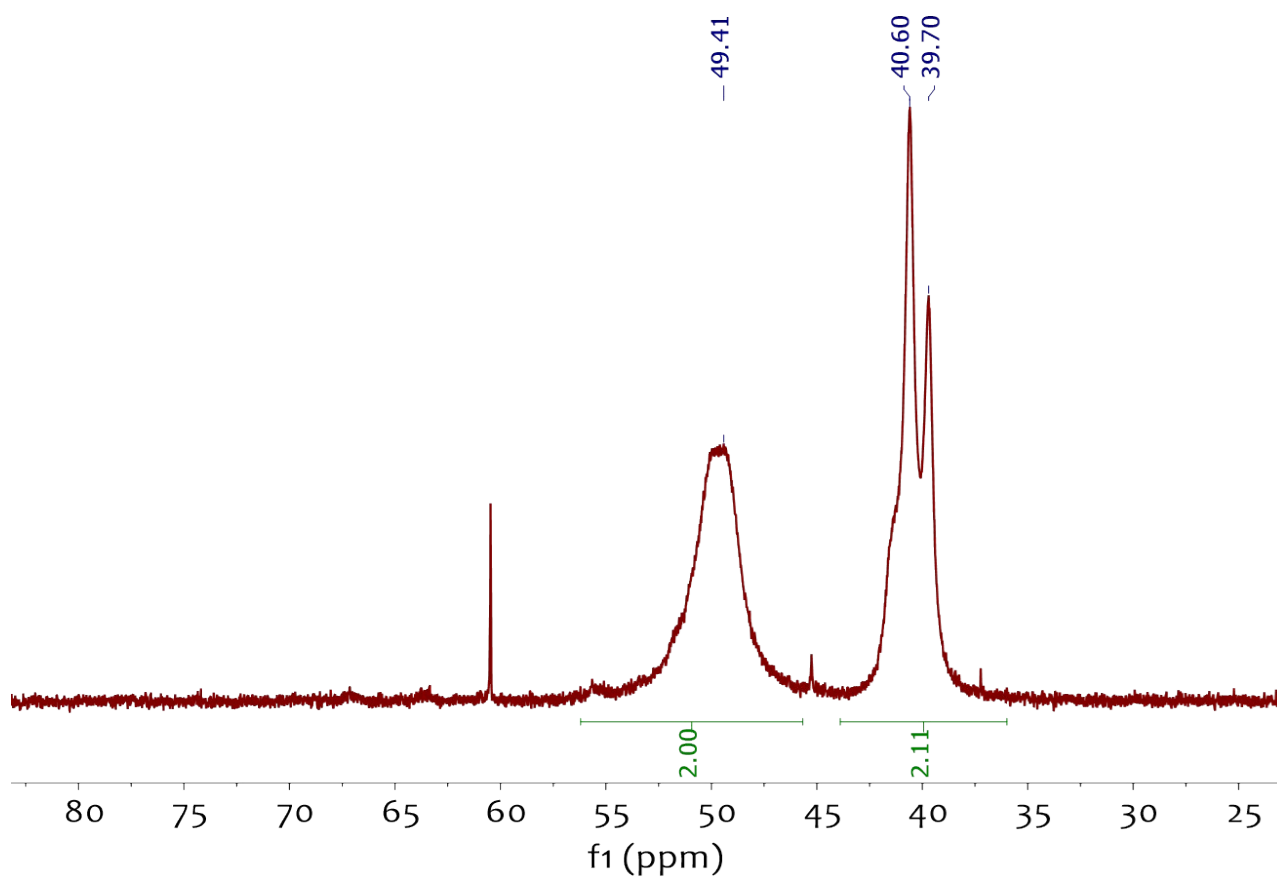


Figure S7. ^1H NMR spectrum (400 MHz, C_6D_6 , 298 K) of compound **4**.

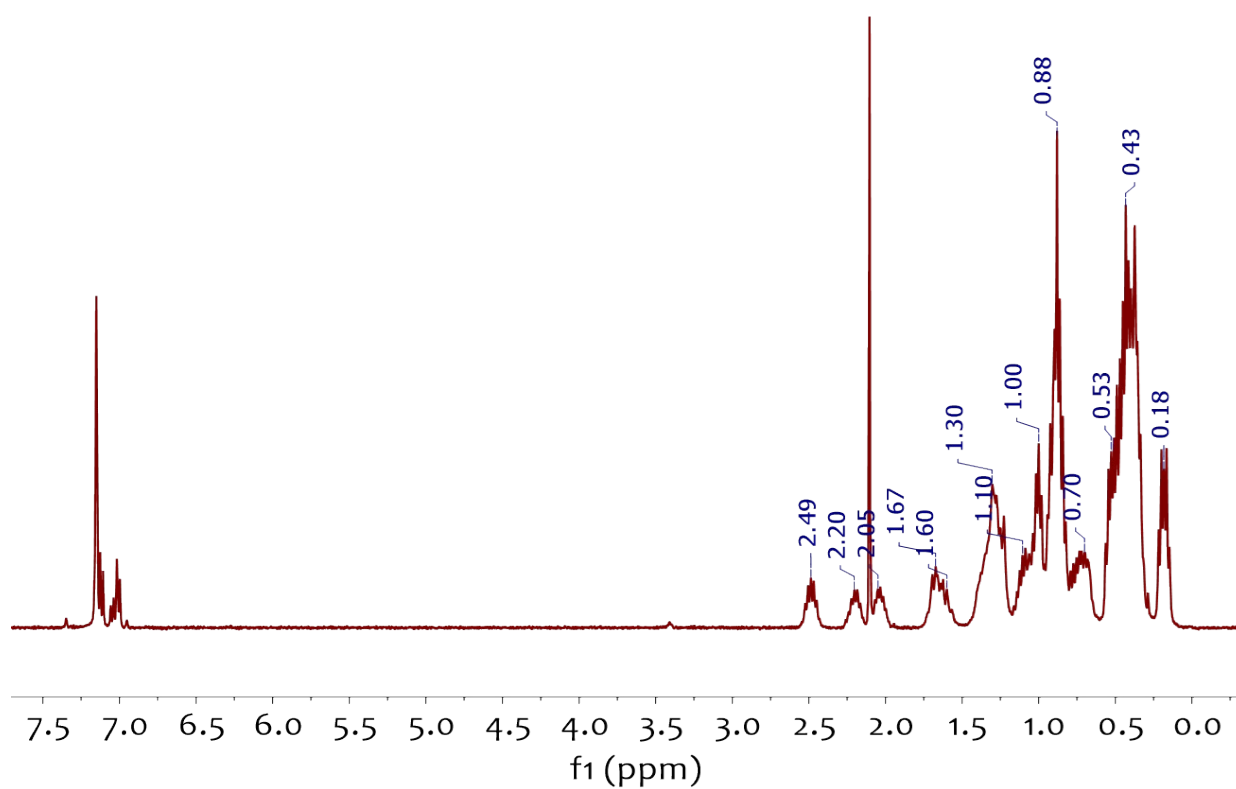


Figure S8. ^{19}F NMR spectrum (376.2 MHz, C_6D_6 , 298 K) of compound **4** (C=19 mmol/L)

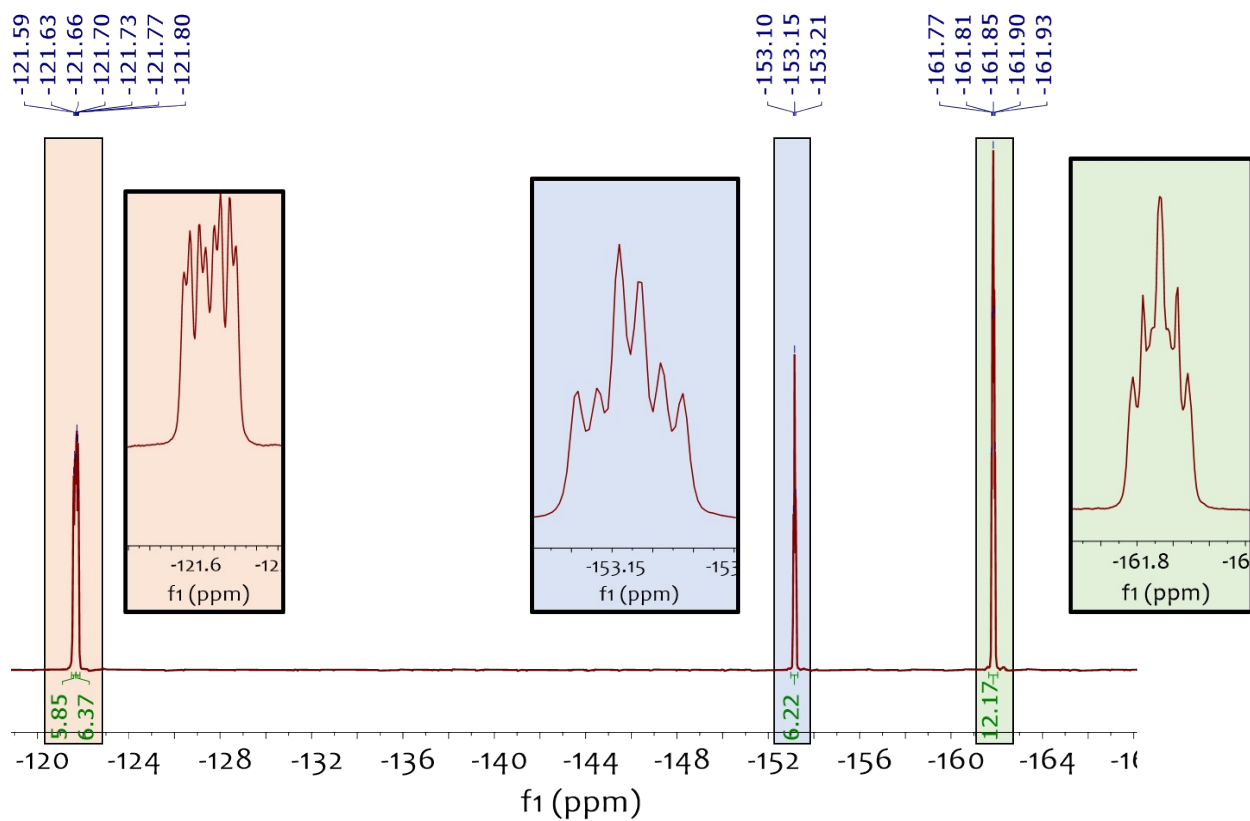


Figure S9. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (163.2 MHz, C_6D_6 , 298 K) of compound **4**.

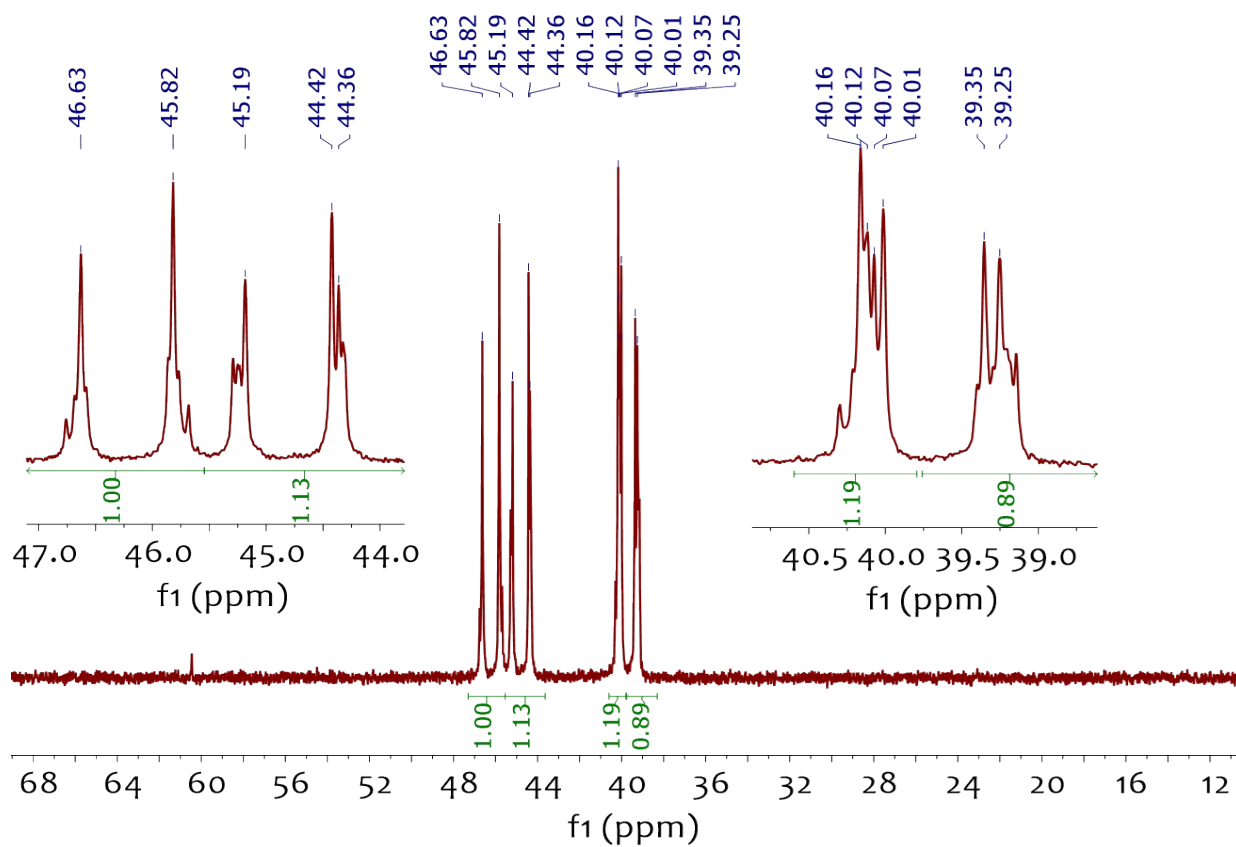


Figure S10. VT- ^1H NMR spectra (400 MHz, C_6D_6) of compound **4** showing a total coalescence from $T=348\text{K}$ (three symmetrical depe signals)

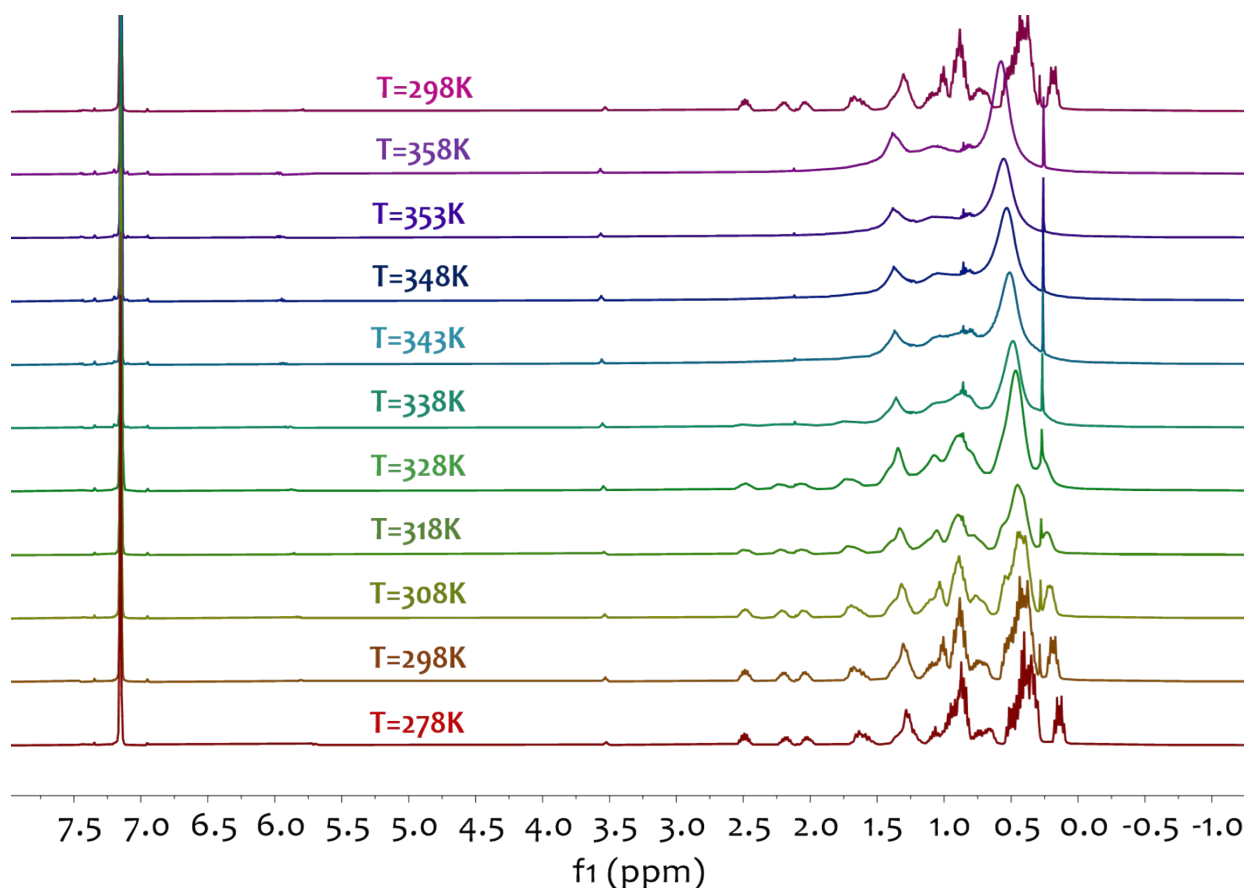


Figure S11. VT- $^{31}\text{P}\{^1\text{H}\}$ - NMR spectra (400 MHz, C_6D_6) of compound **4** that displays a coalescence (from six signals into two broad signals) at T=358K.

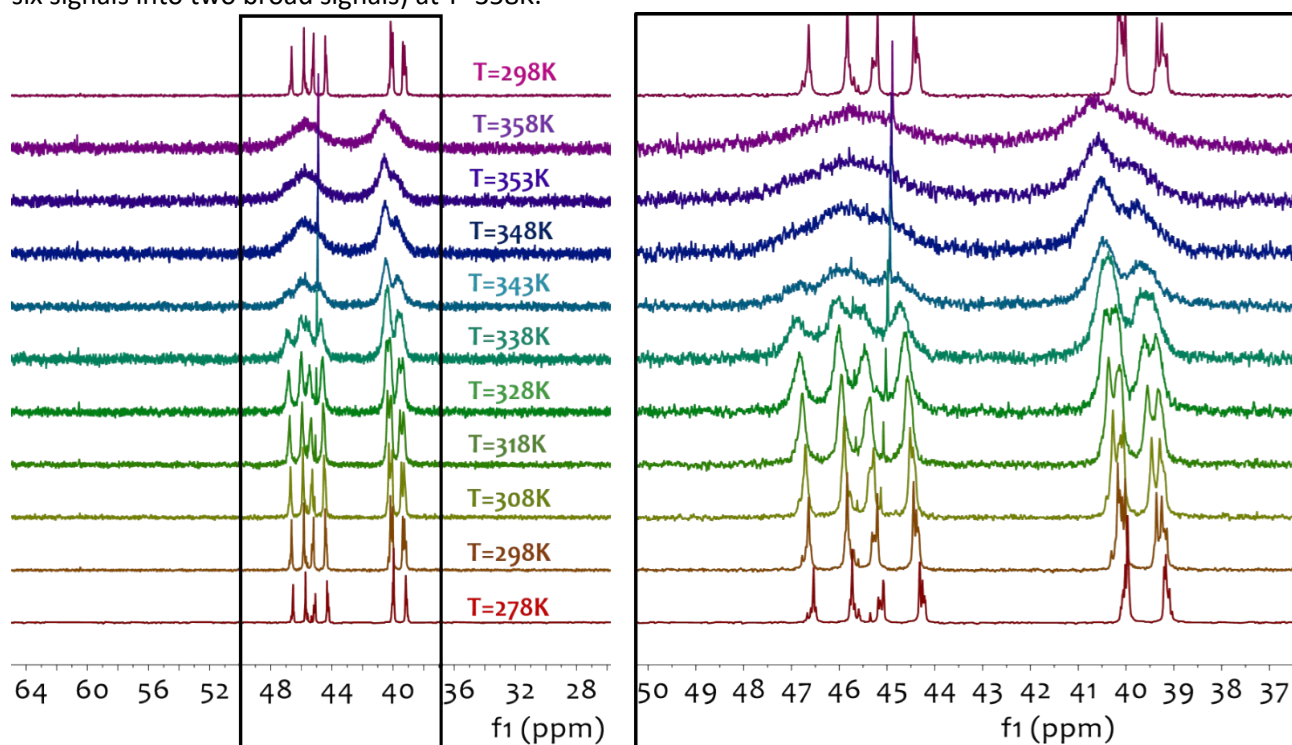


Figure S12. VT- ^{19}F - NMR spectra (400 MHz, C_6D_6) of compound **4** showing no notable effects of the temperature. The first two spectra (bottom) represent the same compound at two different concentrations (19 mM vs 14 mM) at T=298K. When the concentration increases, we observed a

decoalescence of the *ortho* and *para* signals into two resonances. This phenomenon is attributed to an intermolecular π -stacking of the AICF perfluoroaryl rings.

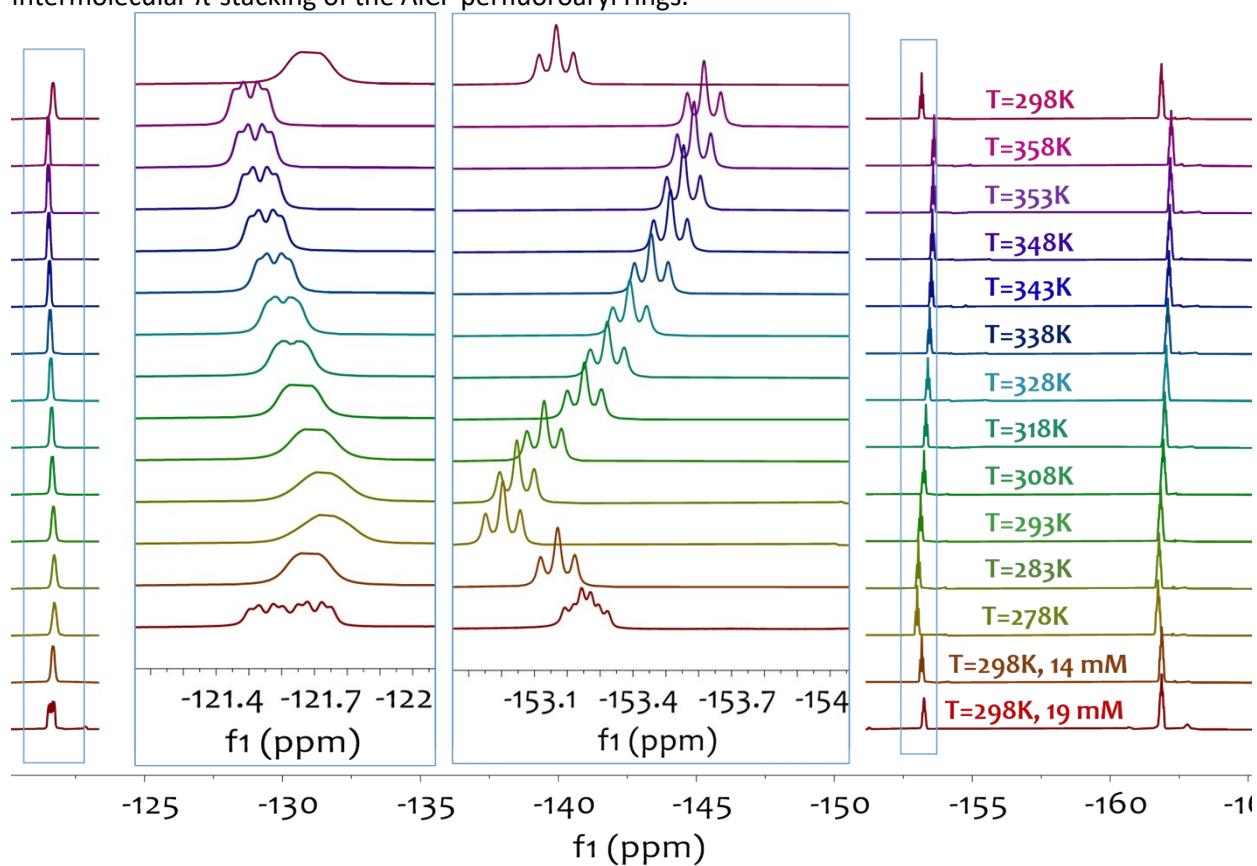


Figure S13. ^1H NMR spectrum (400 MHz, C_6D_6 , 298 K) of compound **6**.

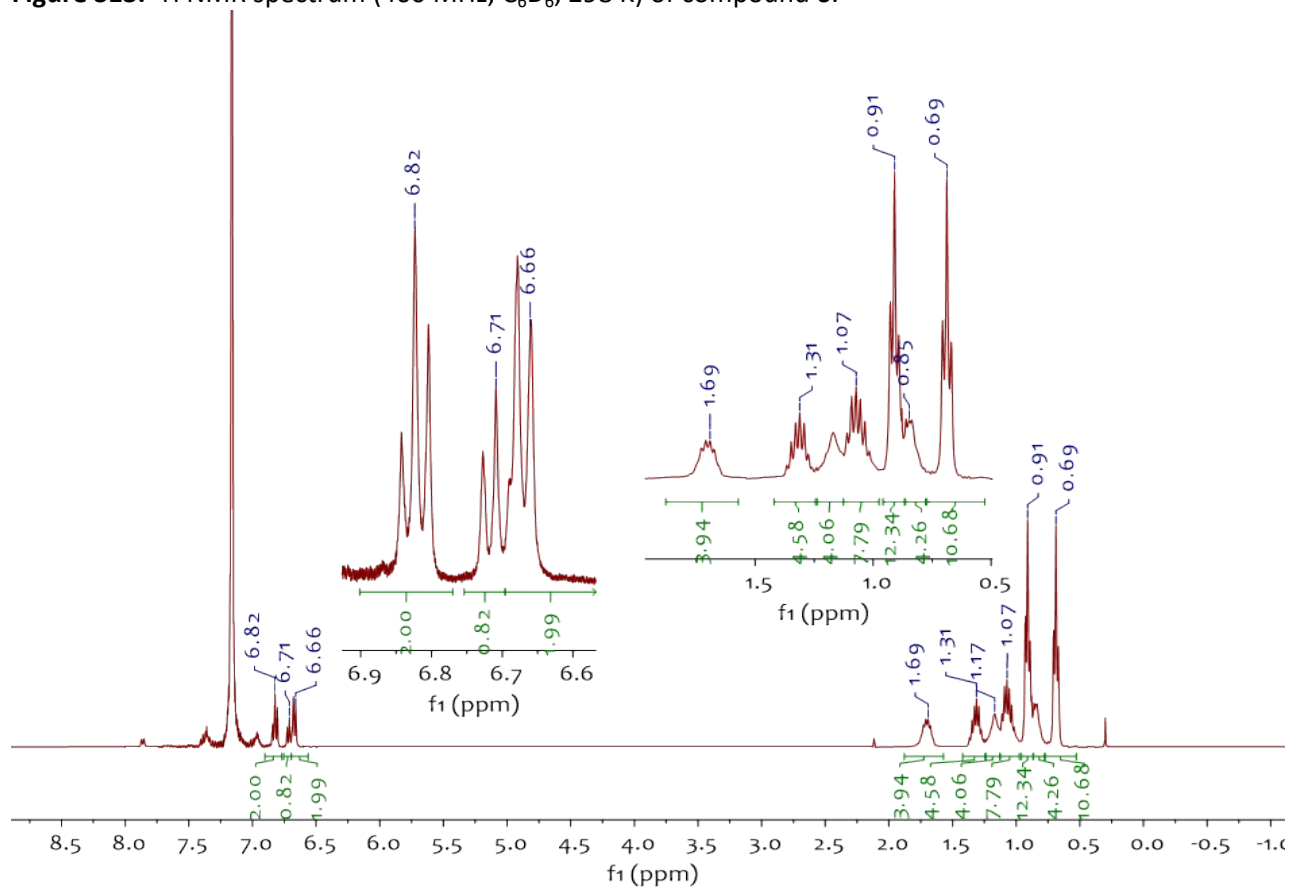


Figure S14. ^{19}F NMR spectrum (376.2 MHz, C_6D_6 , 298 K) of compound **6**.

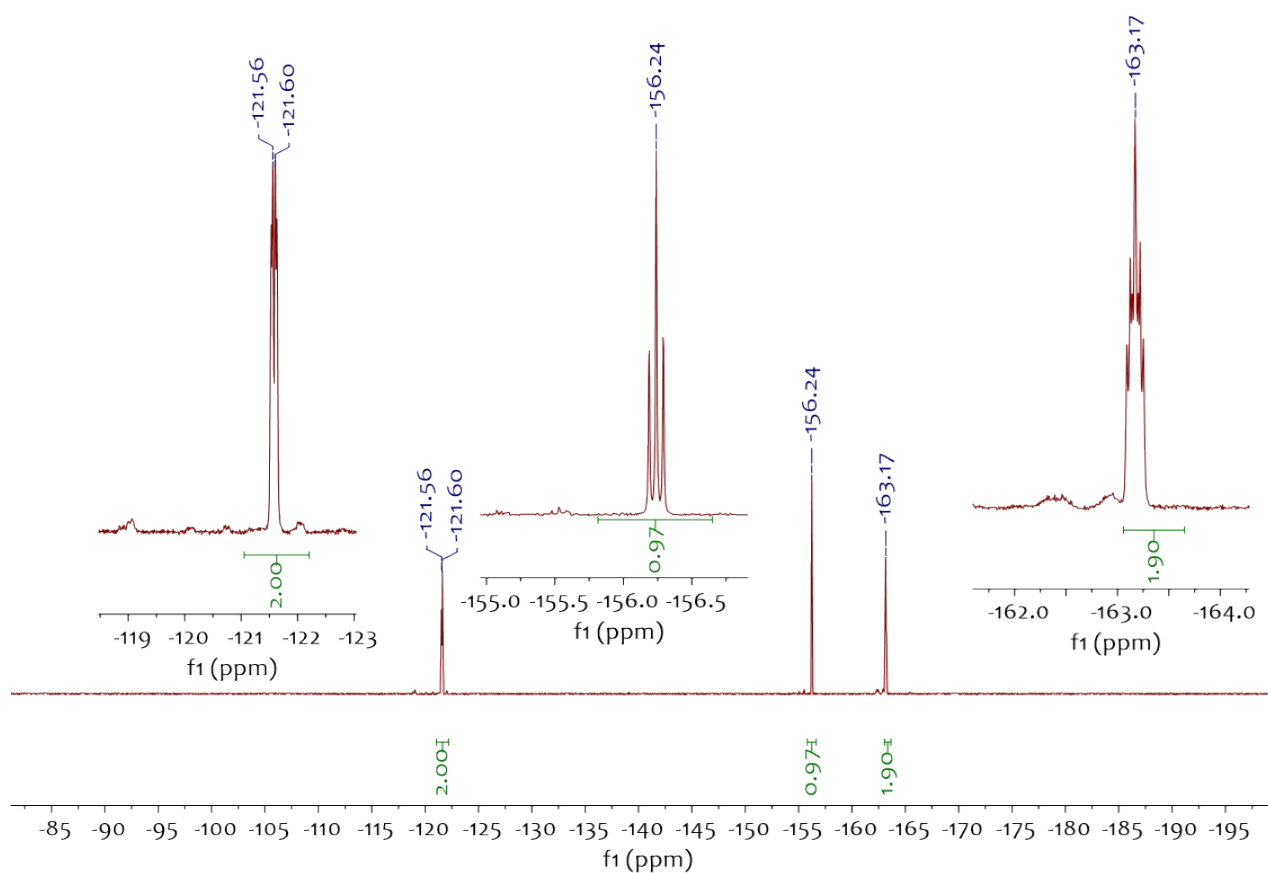
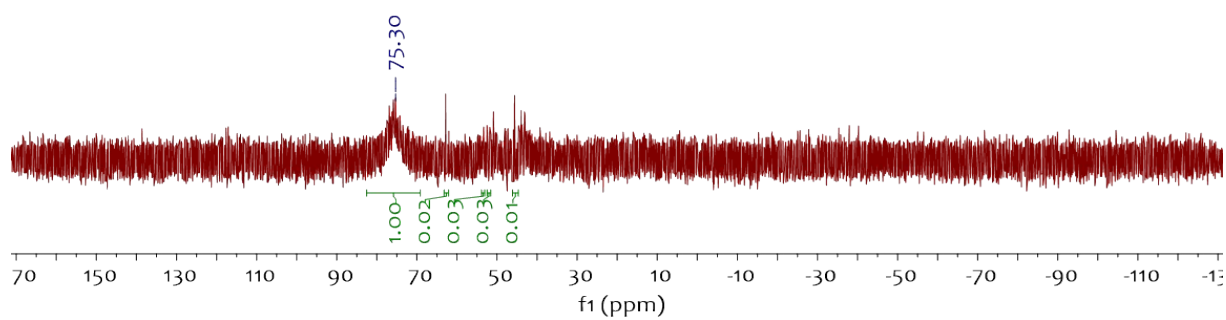


Figure S15. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (163.2 MHz, C_6D_6 , 298 K) of compound **6**.



3 IR spectroscopic data

Figure S16. ATR spectrum (298 K, under nitrogen) of compound 2.

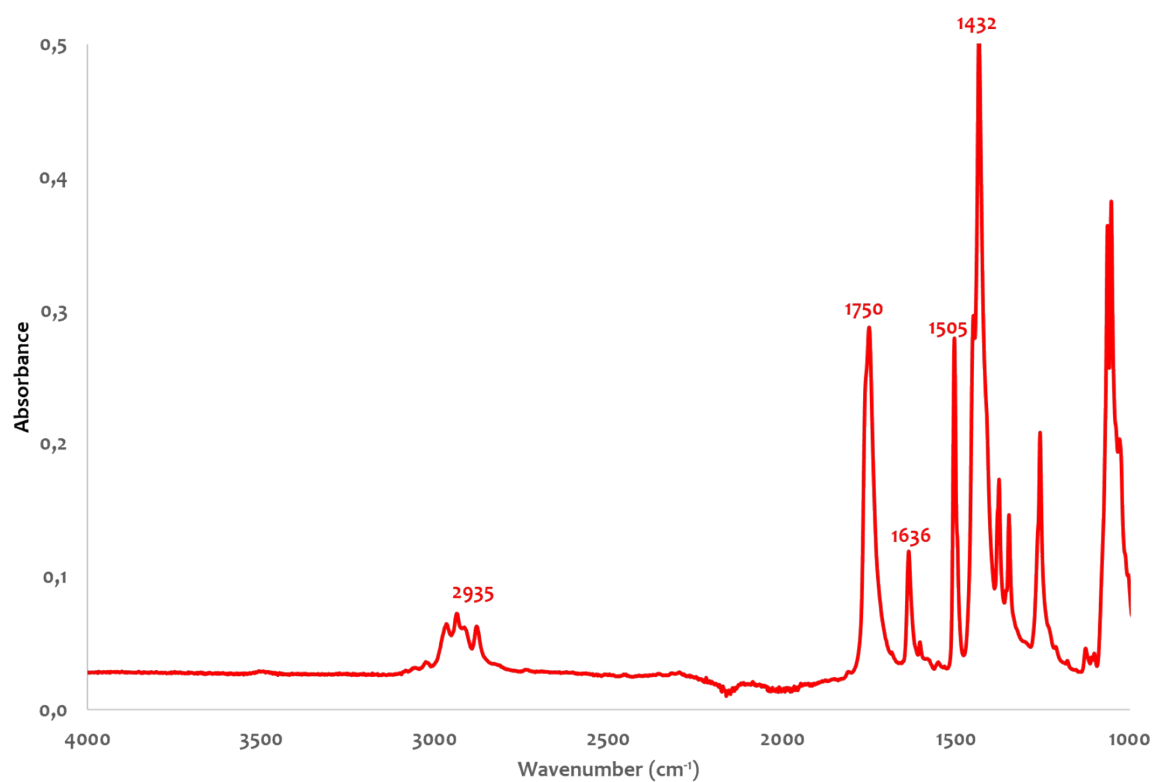


Figure S17. ATR spectrum (298 K, under nitrogen) of compound 3.

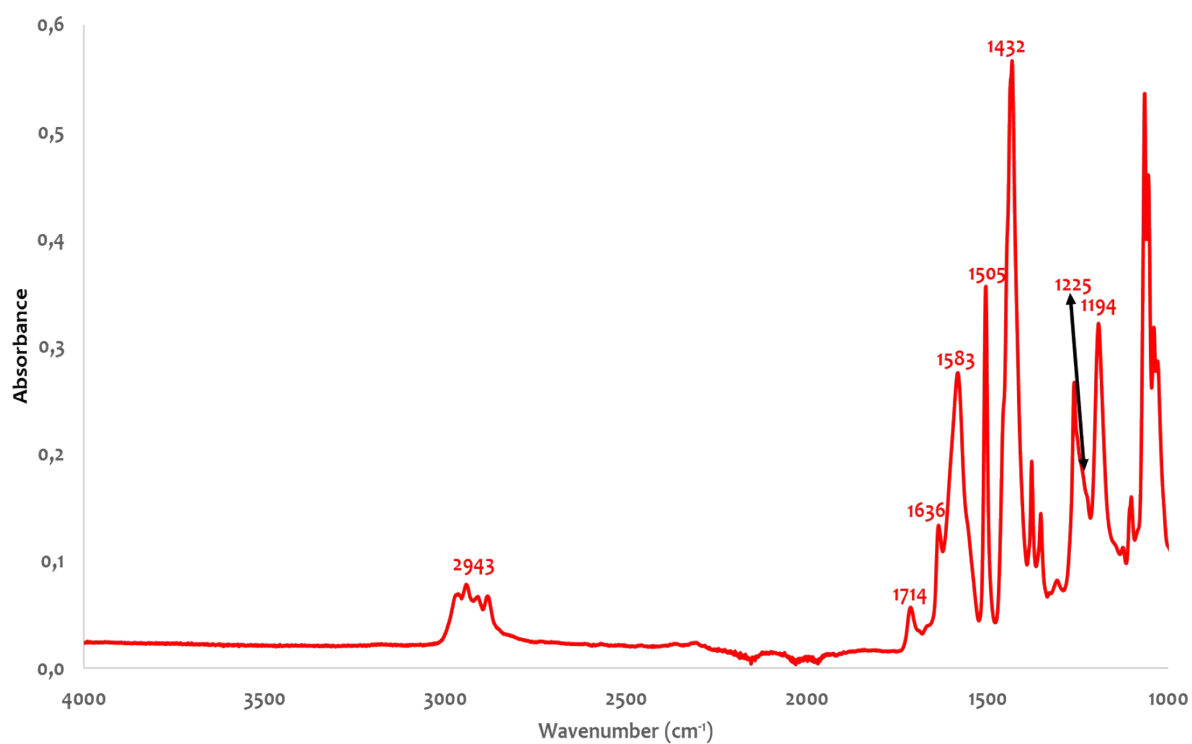


Figure S18. ATR spectrum (298 K, under nitrogen) of compound **4**.

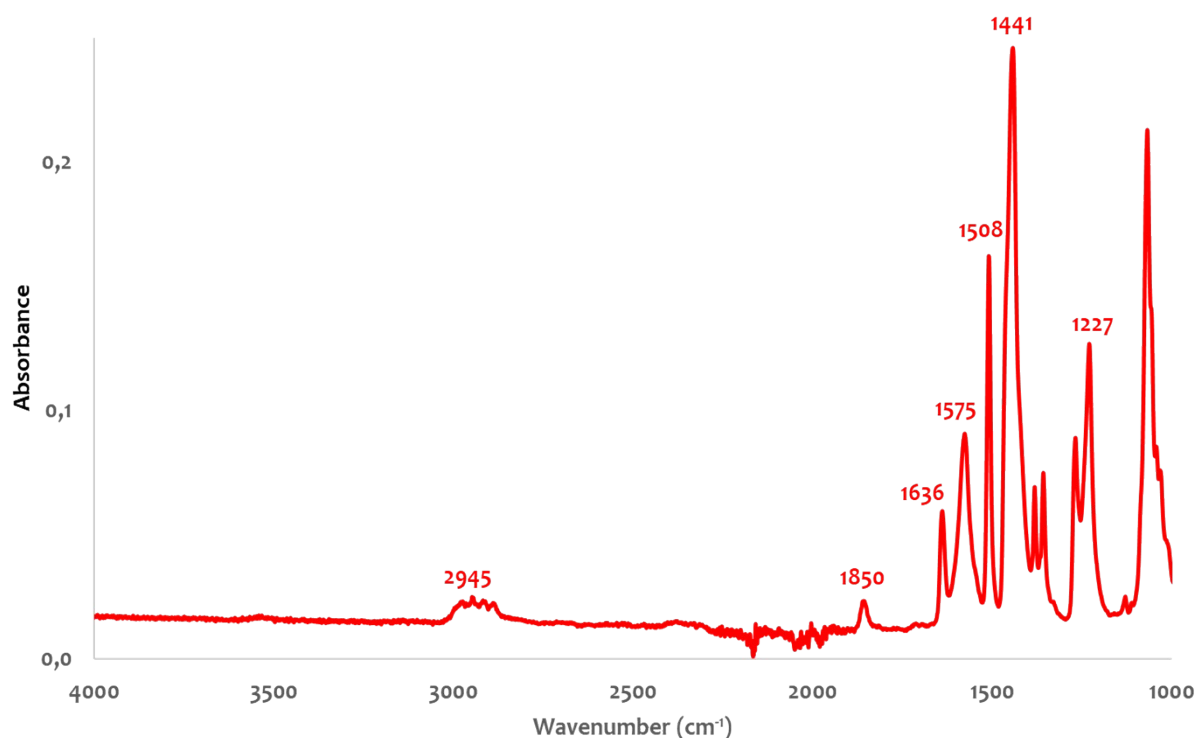


Figure S19. Stacked ATR spectra (298 K, under nitrogen) of compound **4** (top) vs **3** (middle) vs **1^{Mo}** (bottom) in the [2000-1000 cm^{-1}] window. The symmetric and asymmetric $\eta^2\text{-CO}_2$ stretches of **3** (1714 and 1194 cm^{-1} respectively) were assigned using literature data on similar $\eta^2\text{-CO}_2\text{-Mo}$ complexes and *via* its superimposition with the starting precursor **1^{Mo}**.¹²⁻¹⁴ Similarly, the symmetric and asymmetric $\mu\text{-}\eta^2(\text{C,O}):\eta^1(\text{O})\text{-CO}_2$ (bridging CO_2 between Mo and **AICF**) stretches of **3** and **4** (1575 and 1227 cm^{-1} respectively) were assigned using IR literature data on a similar Mo- $\mu\text{-CO}_2\text{-LA}$ (LA = Lewis Acid) complex and *via* its superimposition with the starting precursor **1^{Mo}**.¹³

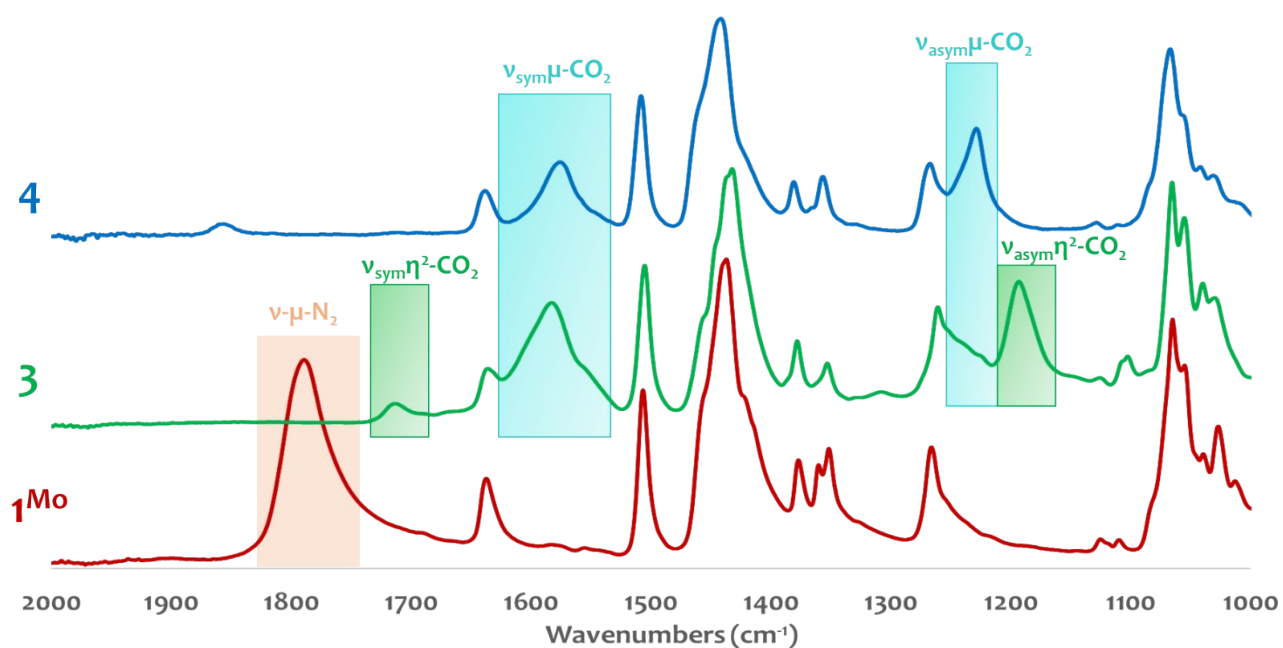
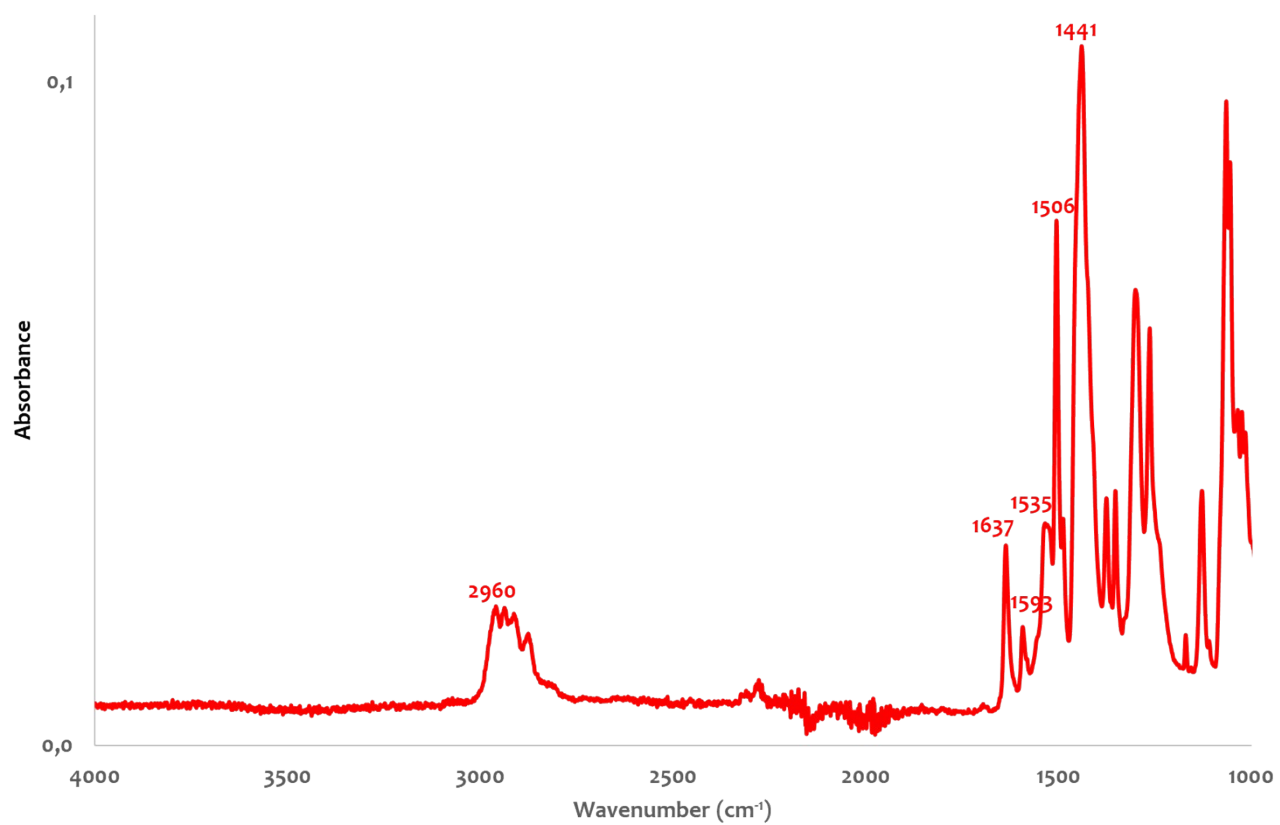


Figure S20. ATR spectrum (298 K, under nitrogen) of compound **6**.



4 Crystallographic data

4.1 Data collection and refinement

Data for compounds **2**, **4**, and **6** were collected at low temperature (100 K) on a XtaLAB Synergy, Dualflex, HyPix diffractometer using a Mo-K α radiation ($\lambda = 0.71073\text{\AA}$) micro-source and equipped with an Oxford Cryosystems Cryostream Cooler Device. The structures have been solved by Direct Methods and refined by means of least-squares procedures using the SHELXS97¹⁵ program included in the softwares package WinGX version 1.63¹⁶ or with the aid of the software package Crystal¹⁷. The Atomic Scattering Factors were taken from International tables for X-Ray Crystallography¹⁸. Hydrogen atoms were placed geometrically and refined using a riding model. All non-hydrogens atoms were anisotropically refined. Drawing of molecules in the following figures were performed with the program Mercury¹⁹ with 30% probability displacement ellipsoids for non-hydrogen atoms. The crystal structures have been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition numbers CCDC 2355268–2355270.

4.2 XRD data

Table S1. XRD data for compounds **2**, **4**, and **6**.

Compound	2	4	6
Formula	C ₃₉ H ₄₈ AlF ₁₅ O ₂ P ₄ W·2(C ₇ H ₈)	C ₅₈ H ₄₈ Al ₂ F ₃₀ MoO ₄ P ₄	C ₅₄ H ₆₂ AlF ₁₅ MoNOP ₄
cryst syst	Monoclinic	Monoclinic	Monoclinic
space group	P2 ₁ /n	P2 ₁ /n	I2/a
volume (Å ³)	5581.0(3)	4097.5(2)	12783.9(4)
a (Å)	13.8441(4)	13.8498(4)	24.8425(4)
b (Å)	11.8025(3)	14.1073(5)	20.3105(4)
c (Å)	34.6152(8)	21.9884(8)	27.5805(4)
α (deg)	90	90	90
β (deg)	99.341(2)	107.491(3)	113.272 (2)°
γ (deg)	90	90	90
Z	4	2	8
Formula weight (g/mol)	1352.75	1652.76	1272.88
density (g cm ⁻³)	1.610	1.340	1.323
Absorption Coeff. (mm ⁻¹)	5.87	3.22	3.45
F(000)	2720	1652	5207
θ_{\max} (°)	65.1	65.1	65.1
no. refined reflections	9502	6966	10899
no. refined restraints	0	0	4
no. refined parameters	702	438	703
wR(F ²)	0.094	0.229	0.082
R[F ² > 2 σ (F ²)]	0.039	0.083	0.030

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