

Supporting Information

Oxidation and Lewis Acidity Dependent Deformation of Sb/P Frustrated Lewis Pair Adducts to Chalcogens

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Experimental Procedures

General Information

All operations involving air- and moisture-sensitive substances were performed under conventional Schlenk techniques or in a glove box with argon as inert gas. Volatile compounds were handled in a vacuum line. All solvents (*n*-hexane, toluene, benzene- d_6 dried over Na/K alloy; dichloromethane over calcium hydride; cyclopentane and dichloromethane- d_2 dried over molecular sieves) were distilled and degassed prior use. $(F_5C_2)_2SbCH_2P(tBu)_2$ was prepared according to literature.¹ The other chemicals (N_2O (food grade), S_8 ($\geq 99\%$, sublimed before use), Se (powder, 99+ %), Te (powder, 99.5 %), *o*-chloranil (97 %)) are commercially available and were used without further purification unless otherwise stated. NMR spectra were recorded using a Bruker Avance III 600 spectrometer at ambient conditions. NMR spectroscopic chemical shifts were referenced to the residual proton or carbon peaks of the solvent (CD_2Cl_2 : 1H : 5.32 ppm, ^{13}C : 54.0 ppm) or externally (^{19}F : $CFCl_3$, ^{31}P : 85% H_3PO_4 in H_2O). EI-MS was performed on a Shimadzu GCMS-QP2020 NX mass spectrometer in positive mode. Samples were introduced by a push rod in aluminium crucibles (direct inlet method). Elemental analyses were performed by staff at the University of Bielefeld using a HEKATECH EURO Element Analyser. SC-XRD was performed on a Rigaku Supernova diffractometer using Cu-K α or Mo-K α radiation.

Syntheses

$(F_5C_2)_2SbCH_2P(O)(tBu)_2$ (**2**):

N_2O (3 mmol) was condensed onto a degassed ($3 \times$ freeze-pump-thaw) solution of **1** (0.26 g, 0.50 mmol) in *n*-hexane (5 mL). The thawed solution was stirred overnight at room temperature. A colourless solid crystallised at $-78\text{ }^\circ C$, which was washed with *n*-hexane (3×1 mL) after removal of the mother liquor. The solid was dried under vacuum. The needle-shaped crystals of **2** (0.27 g, 0.50 mmol, quant.) were suitable for X-ray diffraction.

Analytical data:

1H NMR (600 MHz, CD_2Cl_2): δ [ppm] = 2.66 (d, $^2J_{P,H} = 6$ Hz, 2H, CH_2), 1.29 (d, $^3J_{P,H} = 14$ Hz, 18H, $C(CH_3)_3$).

$^{13}C\{^1H\}$ NMR (151 MHz, CD_2Cl_2): δ [ppm] = 122.9 (m, CF_2), 120.5 (qt, $^1J_{F,C} = 284$ Hz, $^2J_{F,C} = 28$ Hz, CF_3), 36.6 (d, $^1J_{P,C} = 59$ Hz, $C(CH_3)_3$), 26.9 (s, $C(CH_3)_3$), 16.3 (d, $^1J_{P,C} = 47$ Hz, CH_2).

^{19}F NMR (565 MHz, CD_2Cl_2): δ [ppm] = -82.3 (m, CF_3), $-109.4/-110.6$ (m, AB-spin system, CF_2 , broad).

$^{31}P\{^1H\}$ NMR (243 MHz, CD_2Cl_2): δ [ppm] = 63.7 (s).

Elemental analysis calcd (%) for $C_{13}H_{20}F_{10}OPSb$ ($M_r = 535.02$): C 29.18, H 3.77; found: C 29.69, H 3.68.

MS (EI, 70 eV): $m/z = 415.1$ [$M - C_2F_5$] $^+$, 359.0 [$M - C_2F_5 - C_4H_8$] $^+$, 296.1 [$M - 2C_2F_5$] $^+$, 239.9 [$MH - 2C_2F_5 - C_4H_9$] $^+$, 183.9 [$M - 2C_2F_5 - C_4H_7$] $^+$, 119.2 [C_2F_5] $^+$, 57.1 [C_4H_9] $^+$.

(F₅C₂)₂SbCH₂P(S)(tBu)₂ (3):

A solution of **1** (0.49 g, 0.95 mmol) in toluene (10 mL) was added to elemental sulphur (60 mg, 1.9 mmol) and was stirred for 20 h at room temperature. To remove residual sulphur, the suspension was filtered and the filtrate was concentrated and kept at 0 °C overnight. The supernatant liquid was removed and dried under vacuum. **3** (0.41 g, 0.75 mmol, 79 %) was received as beige crystalline solid, whose crystals were suitable for X-ray diffraction.

Analytical data:

¹H NMR (600 MHz, CD₂Cl₂): δ [ppm] = 2.79 (d, ²J_{P,H} = 8 Hz, 2H, CH₂), 1.38 (d, ³J_{P,H} = 16 Hz, 18H, C(CH₃)₃).

¹³C{¹H} NMR (151 MHz, CD₂Cl₂): δ [ppm] = 123.7 (m, CF₂), 120.7 (qt, ¹J_{F,C} = 284 Hz, ²J_{F,C} = 28 Hz, CF₃), 39.0 (d, ¹J_{P,C} = 39 Hz, C(CH₃)₃), 27.4 (m, C(CH₃)₃), 17.9 (d, ¹J_{P,C} = 37 Hz, CH₂).

¹⁹F NMR (565 MHz, CD₂Cl₂): δ [ppm] = -82.3 (s, CF₃), -108.2/-110.5 (m, AB-spin system CF₂, broad).

³¹P{¹H} NMR (243 MHz, CD₂Cl₂): δ [ppm] = 76.6 (s).

Elemental analysis calcd (%) for C₁₃H₂₀F₁₀PSSb (*M_r* = 551.08): C 28.33, H 3.66, S 5.82; found: C 28.05, H 3.61, S 6.15.

MS (EI, 70 EV): *m/z* = 431.1 [M - C₂F₅]⁺, 375.0 [M - C₂F₅ - C₄H₈]⁺, 312.1 [M - 2C₂F₅]⁺, 255.9 [MH - 2C₂F₅ - C₄H₉]⁺, 199.9 [M - 2C₂F₅ - C₄H₇]⁺, 57.1 [C₄H₉]⁺.

(F₅C₂)₂SbCH₂P(Se)(tBu)₂ (4):

A solution of **1** (0.50 g, 0.96 mmol) in toluene (10 mL) was added to elemental selenium (0.26 g, 3.3 mmol) and was stirred for 20 h at room temperature. The suspension was filtered to remove residual selenium. The solvent was removed from the filtrate under reduced pressure and the residue was dried under vacuum. **4** (0.38 g, 0.64 mmol, 66 %) was obtained as colourless solid. Single crystals suitable for X-ray diffraction were obtained from a saturated solution of **4** in cyclopentane at -20 °C.

Analytical data:

¹H NMR (600 MHz, CD₂Cl₂): δ [ppm] = 2.93 (d, ²J_{P,H} = 9 Hz, 2H, CH₂), 1.40 (d, ³J_{P,H} = 16 Hz, 18H, C(CH₃)₃).

¹³C{¹H} NMR (151 MHz, CD₂Cl₂): δ [ppm] = 124.2 (m, CF₂), 120.7 (qt, ¹J_{F,C} = 285 Hz, ²J_{F,C} = 28 Hz, CF₃), 38.7 (d, ¹J_{P,C} = 31 Hz, C(CH₃)₃), 27.7 (m, C(CH₃)₃), 17.5 (d, ¹J_{P,C} = 31 Hz, CH₂).

¹⁹F NMR (565 MHz, CD₂Cl₂): δ [ppm] = -82.2 (s, CF₃), -107.8/-110.5 (m, AB-spin system CF₂, broad).

³¹P{¹H} NMR (243 MHz, CD₂Cl₂): δ [ppm] = 73.0 (s).

Elemental analysis calcd (%) for C₁₃H₂₀F₁₀PSbSe (*M_r* = 597.99): C 26.11, H 3.37; found: C 26.44, H 3.38.

MS (EI, 70 EV): *m/z* = 479.0 [M - C₂F₅]⁺, 422.9 [M - C₂F₅ - C₄H₈]⁺, 360.0 [M - 2C₂F₅]⁺, 303.9 [MH - 2C₂F₅ - C₄H₉]⁺, 57.1 [C₄H₉]⁺.

(F₅C₂)₂SbCH₂P(Te)(tBu)₂ (5):

A solution of **1** (0.52 g, 0.99 mmol) in toluene (10 mL) was added to elemental tellurium (0.16 g, 1.3 mmol) and was stirred for 20 h at room temperature. The greenish suspension was filtered to remove residual tellurium. The solvent was removed from the filtrate under reduced pressure and the residue was dried under vacuum. **5** (0.51 g, 0.78 mmol, 79 %) was obtained as yellow crystalline solid. Single crystals suitable for X-ray diffraction were obtained from a saturated solution of **4** in cyclopentane at -20 °C.

Analytical data:

¹H NMR (600 MHz, CD₂Cl₂): δ [ppm] = 3.18 (d, ²J_{P,H} = 10 Hz, 2H, CH₂), 1.42 (d, ³J_{P,H} = 16 Hz, 18H, C(CH₃)₃).

¹³C{¹H} NMR (151 MHz, CD₂Cl₂): δ [ppm] = 124.0 (m, CF₂), 120.8 (qt, ¹J_{F,C} = 285 Hz, ²J_{F,C} = 29 Hz, CF₃), 38.1 (d, ¹J_{P,C} = 22 Hz, C(CH₃)₃), 28.1 (m, C(CH₃)₃), 17.7 (d, ¹J_{P,C} = 25 Hz, CH₂).

¹⁹F NMR (565 MHz, CD₂Cl₂): δ [ppm] = -82.2 (s, CF₃), -106.5/-110.4 (m, AB-spin system CF₂, broad).

³¹P{¹H} NMR (243 MHz, CD₂Cl₂): δ [ppm] = 45.4 (s).

Elemental analysis calcd (%) for C₁₃H₂₀F₁₀PSbTe (M_r = 646.62): C 24.15, H 3.12; found: C 24.46, H 3.11.

MS (EI, 70 EV): m/z = 529.0 [M - C₂F₅]⁺, 472.9 [M - C₂F₅ - C₄H₈]⁺, 57.1 [C₄H₉]⁺.

(F₅C₂)₂Sb(CH₂)(μ-O)P(tBu)₂Cat^{Cl} (6):

A red solution of *o*-chloranil (2.8 mg, 11 μmol) in *n*-hexane (3 mL) was added to a solution of **2** (5 mg, 9 μmol) in *n*-hexane (0.5 mL), whereby the added solution immediately decoloured. The mixture was stirred overnight at room temperature. The resulting solid was separated from the supernatant liquid, washed with *n*-hexane (1 mL) and dried under vacuum. **6** (6 mg, 8 μmol, 89 %) was obtained as colourless solid. Single crystals suitable for X-ray diffraction were obtained from a solution of **6** in C₆D₆.

Analytical data:

¹H NMR (600 MHz, CD₂Cl₂): δ [ppm] = 4.38 (d, ²J_{P,H} = 5 Hz, 2H, CH₂), 1.47 (d, ³J_{P,H} = 16 Hz, 18H, C(CH₃)₃).

¹³C{¹H} NMR (151 MHz, CD₂Cl₂): δ [ppm] = 144.3 (s, Cat^{Cl}), 124.8 (m, CF₂), 122.3 (s, Cat^{Cl}), 120.1 (qt, ¹J_{F,C} = 286 Hz, ²J_{F,C} = 28 Hz, CF₃), 117.7 (s, Cat^{Cl}), 51.2 (s, CH₂), 37.7 (d, ¹J_{P,C} = 48 Hz, C(CH₃)₃), 27.7 (s, C(CH₃)₃).

¹³C{¹⁹F} NMR (151 MHz, CD₂Cl₂): δ [ppm] = 144.3 (s, Cat^{Cl}), 124.9 (s, CF₂), 122.3 (s, Cat^{Cl}), 120.1 (s, CF₃), 117.7 (s, Cat^{Cl}), 51.2 (m, CH₂, broad), 37.7 (m, C(CH₃)₃), 27.6 (m, C(CH₃)₃).

¹⁹F NMR (565 MHz, CD₂Cl₂): δ [ppm] = -79.5 (s, CF₃), -108.8/-110.7 (m, AB-spin system, CF₂, broad).

³¹P{¹H} NMR (243 MHz, CD₂Cl₂): δ [ppm] = 88.4 (s).

Elemental analysis calcd (%) for C₁₉H₂₀Cl₄F₁₀O₃PSb (M_r = 780.88): C 29.22, H 2.58; found: C 29.21, H 2.52.

(F₃C₂)₂Sb(CH₂)(μ-S)P(tBu)₂·Cat^{Cl} (7**):**

A red solution of *o*-chloranil (12 mg, 47 μmol) in *n*-hexane (3 mL) was added to a solution of **3** (23 mg, 42 μmol) in *n*-hexane (0.5 mL) under immediate decolourisation leaving finally a yellowish mixture. The mixture was stirred overnight at room temperature. The resulting solid was separated from the supernatant liquid, washed with *n*-hexane (1 mL) and dried under vacuum. A mixture of **7** and **3** was obtained. After recrystallisation in *n*-hexane, yellow crystals of **7** (29 mg) were obtained, whose were suitable for X-ray diffraction. NMR data and elemental analysis indicate the presence of some minor undefined impurities, which were not removable.

Analytical data:

¹H NMR (600 MHz, CD₂Cl₂): δ [ppm] = 4.68 (s, 2H, CH₂, broad), 1.56 (d, ³J_{P,H} = 18 Hz, 18H, C(CH₃)₃).

¹³C{¹H} NMR (151 MHz, CD₂Cl₂): δ [ppm] = 144.3 (s, Cat^{Cl}, broad), 122.2 (s, Cat^{Cl}, broad), 120.2 (qt, ¹J_{F,C} = 286 Hz, ²J_{F,C} = 28 Hz, CF₃), 118.1 (s, Cat^{Cl}, broad), 55.8 (d, ¹J_{P,C} = 30 Hz, CH₂), 40.4 (d, ¹J_{P,C} = 29 Hz, C(CH₃)₃), 28.5 (s, C(CH₃)₃), CF₂ signal not observable, due to low intensity and strong broadening.

¹³C{¹⁹F} NMR (151 MHz, CD₂Cl₂): δ [ppm] = 144.2 (s, Cat^{Cl}, broad), 123.7 (s, CF₂, broad), 122.1 (s, Cat^{Cl}, broad), 120.2 (s, CF₃, broad), 118.1 (s, Cat^{Cl}, broad), 55.8 (m, CH₂), 40.4 (m, C(CH₃)₃), 28.5 (m, C(CH₃)₃).

¹⁹F NMR (565 MHz, CD₂Cl₂): δ [ppm] = -77.9 (s, CF₃), -81.2 (s, CF₃), -104.7/-106.9 (d, ²J_{F,F} = 294 Hz, AB-spin system, CF₂, broad), -113.5/-116.6 (d, ²J_{F,F} = 304 Hz, AB-spin system, CF₂, broad).

³¹P{¹H} NMR (243 MHz, CD₂Cl₂): δ [ppm] = 78.9 (s).

Elemental analysis calcd (%) for C₁₉H₂₀Cl₄F₁₀O₂PSSb (M_r = 796.94): C 28.64, H 2.53, S 4.02; found: C 30.40, H 2.33, S 3.82.

(F₃C₂)₂Sb(CH₂)(μ-Se)P(tBu)₂·Cat^{Cl} (8**):**

A red solution of *o*-chloranil (13 mg, 51 μmol) in *n*-hexane (3 mL) was added to a solution of **4** (26 mg, 43 μmol) in *n*-hexane (0.5 mL), under immediate decolourisation leaving finally an orange mixture. The mixture was stirred overnight at room temperature. The resulting solid was separated from the supernatant liquid, washed with *n*-hexane (1 mL) and dried under vacuum. A mixture of **8** and **4** was obtained. After recrystallisation in *n*-hexane, orange crystals of **8** (29 mg, 34 μmol, 79 %) were obtained, whose were suitable for X-ray diffraction.

Analytical data:

¹H NMR (600 MHz, CD₂Cl₂): δ [ppm] = 4.92 (m, 2H, CH₂), 1.58 (m, 18H, C(CH₃)₃).

¹³C{¹H} NMR (151 MHz, CD₂Cl₂): δ [ppm] = 144.5 (s, Cat^{Cl}), 144.0 (s, Cat^{Cl}), 122.4 (s, Cat^{Cl}), 121.8 (s, Cat^{Cl}), 118.4 (s, Cat^{Cl}), 118.1 (s, Cat^{Cl}), 56.8 (d, ¹J_{P,C} = 26 Hz, CH₂), 40.6 (d, ¹J_{P,C} = 23 Hz, C(CH₃)₃), 28.9 (s, C(CH₃)₃^A), 28.5 (s, C(CH₃)₃^B), CF₂ and CF₃ signals not observable, due to low intensity and strong broadening. – ¹³C{¹⁹F} NMR (151 MHz, CD₂Cl₂): δ [ppm] = 144.2 (s, Cat^{Cl}, broad), 125.4 (s, CF₂, broad), 122.1 (s, Cat^{Cl}, broad), 120.2 (s, CF₃, broad), 118.1 (s, Cat^{Cl}, broad), 55.8 (m, CH₂), 40.4 (m, C(CH₃)₃), 29.2 (m, C(CH₃)₃^A), 28.3 (m, C(CH₃)₃^B).

¹⁹F NMR (565 MHz, CD₂Cl₂): δ [ppm] = -77.8 (m, CF₃^A), -81.3 (m, CF₃^B), -105.2/-107.9 (m, AB-spin system, CF₂^A, broad), -113.5/-116.6 (m, AB-spin system, CF₂^B, broad).

³¹P{¹H} NMR (243 MHz, CD₂Cl₂): δ [ppm] = 73.2 (s).

Elemental analysis calcd (%) for $C_{19}H_{20}Cl_4F_{10}O_2PSbSe$ ($M_r = 843.86$): C 27.04, H 2.39; found: C 27.41, H 2.38.

$(F_3C_2)_2Sb(CH_2)(Cat^{Cl})P(tBu)_2 \cdot Cat^{Cl}$ (9**):**

A red solution of *o*-chloranil (0.55 g, 2.2 mmol) in dichloromethane (10 mL) was added to a solution of **1** (0.53 g, 1.0 mmol) in dichloromethane (20 mL) at room temperature under immediate decolourisation. The yellow solution was concentrated under reduced pressure. Colourless crystals were grown at -20 °C. After isolation and drying under vacuum, **9** (0.80 g, 0.79 mmol, 79 %) was obtained in the form of orange crystals. Single crystals suitable for X-ray diffraction were obtained from a solution of **9** in C_6D_6 .

A red solution of *o*-chloranil (13 mg, 53 μ mol) in dichloromethane (4 mL) was added to a solution of **10** (32 mg, 42 μ mol) in dichloromethane (6 mL) at room temperature under immediate decolourisation. The yellow solution was concentrated under reduced pressure. Colourless crystals grew at -20 °C. After isolation and drying them under vacuum, **9** was obtained in the form of orange crystals.

A red solution of *o*-chloranil (10 mg, 39 μ mol) in *n*-hexane (3 mL) was added to a solution of **5** (21 mg, 33 μ mol) in *n*-hexane (0.5 mL) under immediate decolourisation leaving finally a yellowish mixture. The mixture was stirred overnight at room temperature, whereby a black solid precipitated. The solid was collected on a filter and the filtrate was dried under vacuum. **9** (23 mg, 23 μ mol, 70 %) was obtained as a yellow solid.

Analytical data:

1H NMR (600 MHz, CD_2Cl_2): δ [ppm] = 3.09 (dd, $^2J_{H,H} = 14$ Hz, $^2J_{P,H} = 6$ Hz, 1H, CH_2^A), 2.89 (dd, $^2J_{H,H} = 14$ Hz, $^2J_{P,H} = 5$ Hz, 1H, CH_2^B), 1.77 (d, $^3J_{P,H} = 17$ Hz, 9H, $C(CH_3)_3^A$), 1.43 (d, $^3J_{P,H} = 17$ Hz, 9H, $C(CH_3)_3^B$).

$^{13}C\{^1H\}$ NMR (151 MHz, CD_2Cl_2): δ [ppm] = 145.9 (s, Cat^{Cl}), 145.2 (s, Cat^{Cl}), 144.8 (s, Cat^{Cl}), 141.9 (m, Cat^{Cl}), 129.7 (s, Cat^{Cl}), 127.0 (s, Cat^{Cl}), 124.5 (s, Cat^{Cl}), 123.6 (m, Cat^{Cl}), 122.2 (s, Cat^{Cl}), 121.5 (s, Cat^{Cl}), 120.0 (m, CF_3), 118.7 (s, Cat^{Cl}), 116.0 (s, Cat^{Cl}), 40.9 (d, $^1J_{P,C} = 56$ Hz, $C(CH_3)_3^A$), 40.1 (d, $^1J_{P,C} = 40$ Hz, $C(CH_3)_3^B$), 27.2 (s, $C(CH_3)_3^A$), 26.8 (s, $C(CH_3)_3^B$), 19.5 (d, $^1J_{P,C} = 44$ Hz, CH_2), CF_2 signal not observable, due to low intensity and strong broadening.

^{19}F NMR (565 MHz, CD_2Cl_2): δ [ppm] = -80.2 (m, CF_3^A), -82.1 (m, CF_3^B), $-110.9/-113.6$ (m, AB-spin system, CF_2^A , broad), $-114.7/-117.3$ (m, AB-spin system, CF_2^B , broad).

$^{31}P\{^1H\}$ NMR (243 MHz, CD_2Cl_2): δ [ppm] = 110.0 (s).

Elemental analysis calcd (%) for $C_{25}H_{20}Cl_8F_{10}O_4PSb$ ($M_r = 1010.75$): C 29.71, H 1.99; found: C 30.05, H 1.81.

$(F_3C_2)_2Sb(CH_2)(Cat^{Cl})P(tBu)_2$ (10**):**

At -60 °C a red solution of *o*-chloranil (0.23 mg, 0.94 mmol) in dichloromethane (10 mL) was added to a solution of **1** (0.52 mg, 1.0 mmol) in dichloromethane (20 mL) over 30 min, the added drops decolourising immediately. The yellowish solution was concentrated under reduced pressure at room temperature. Colourless crystals grew at -20 °C. After isolation and drying under vacuum, **10** (0.61 g, 0.80 mmol, 85 %) was obtained as colourless crystals. Single crystals suitable for X-ray diffraction were obtained from a solution of **10** in C_6D_6 .

Analytical data:

1H NMR (600 MHz, CD_2Cl_2): δ [ppm] = 2.90 (m, 2H, CH_2), 1.51 (d, $^3J_{P,H} = 16$ Hz, 18H, $C(CH_3)_3$).

¹³C{¹H} NMR (151 MHz, CD₂Cl₂): δ [ppm] = 152.1 (s, Cat^{Cl}), 142.1 (m, Cat^{Cl}), 130.0 (s, Cat^{Cl}), 126.0 (s, Cat^{Cl}), 122.2 (m, Cat^{Cl}), 121.0 (m, CF₃), 116.9 (s, Cat^{Cl}), 39.6 (d, ¹J_{P,C} = 48 Hz, C(CH₃)₃), 27.2 (s, C(CH₃)₃), 10.8 (d, ¹J_{P,C} = 50 Hz, CH₂), CF₂ signal not observable, due to low intensity and strong broadening.

¹⁹F NMR (565 MHz, CD₂Cl₂): δ [ppm] = -81.3 (m, CF₃), -112.5 (m, CF₂, broad).

³¹P{¹H} NMR (243 MHz, CD₂Cl₂): δ [ppm] = 111.4 (s).

Elemental analysis calcd (%) for C₁₉H₂₀Cl₄F₁₀O₂PSb (*M_r* = 764.88): C 29.84, H 2.64; found: C 30.01, H 2.57.

NMR spectroscopic data

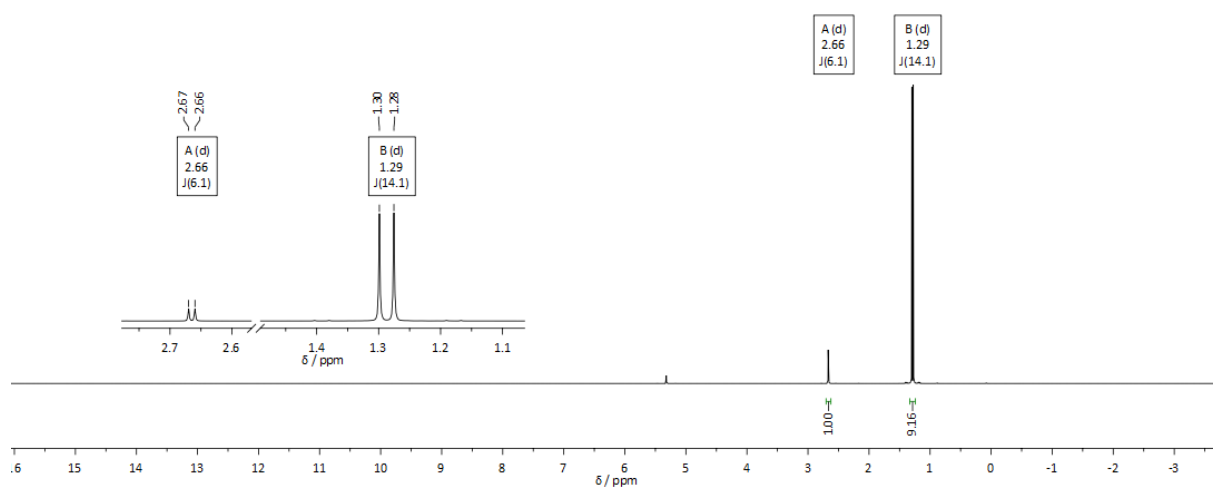


Figure S1 ^1H NMR spectrum of **2** in CD_2Cl_2 .

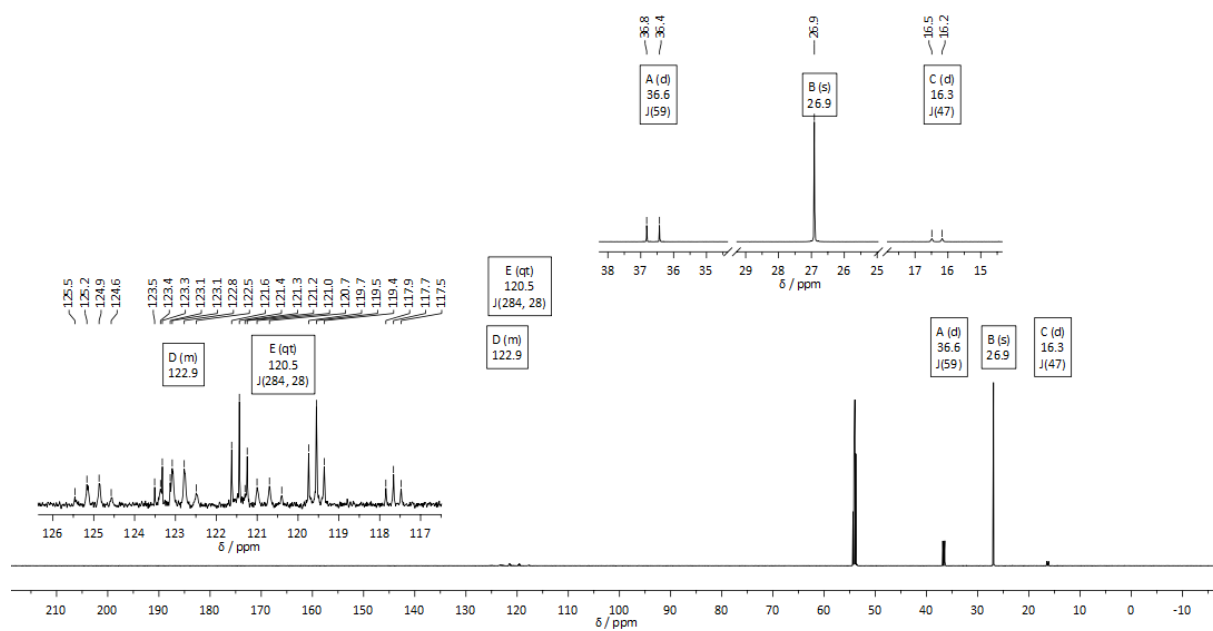


Figure S2 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **2** in CD_2Cl_2 .

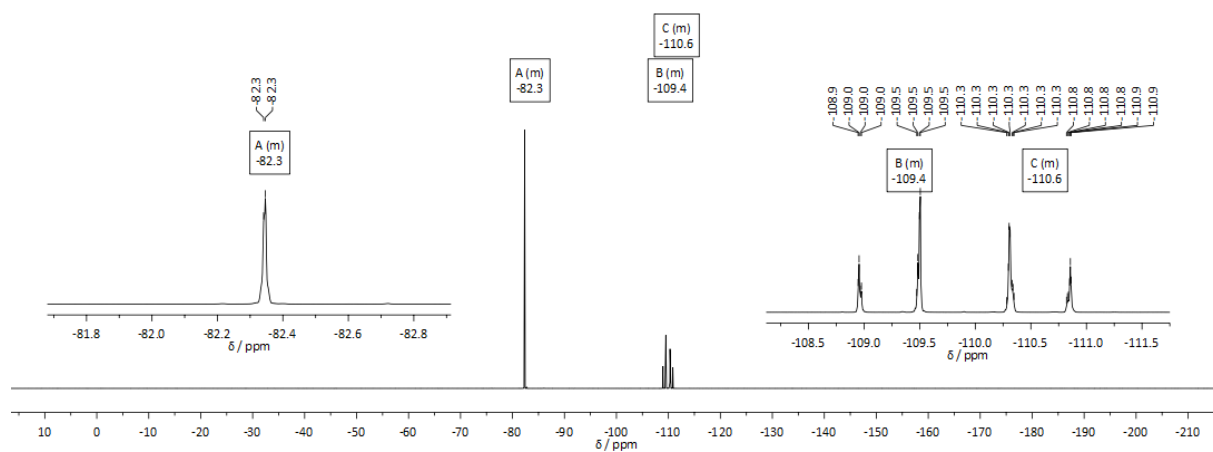


Figure S3 ^{19}F NMR spectrum of **2** in CD_2Cl_2 .

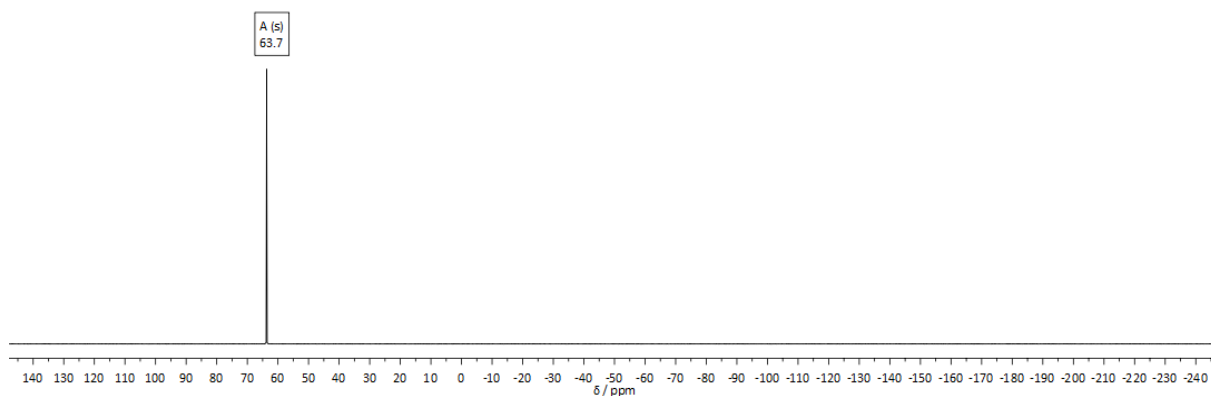


Figure S4 $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **2** in CD_2Cl_2 .

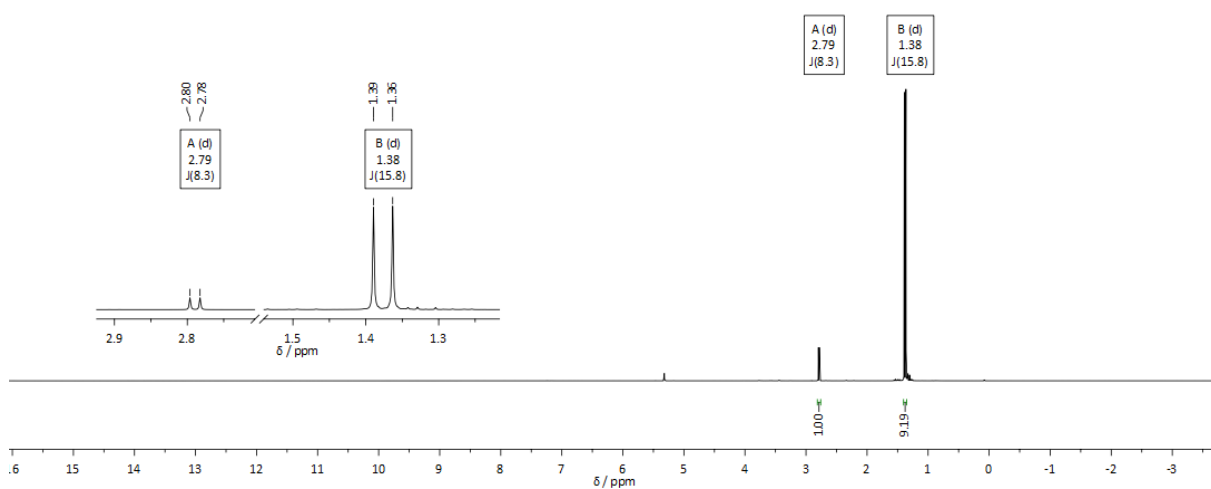


Figure S5 ^1H NMR spectrum of **3** in CD_2Cl_2 .

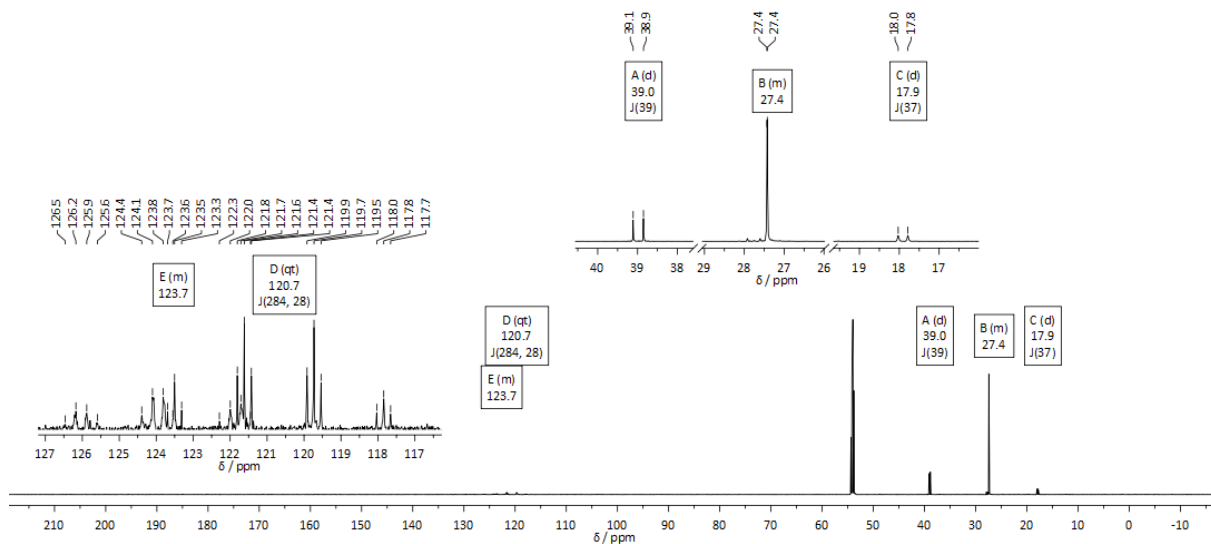


Figure S6 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **3** in CD_2Cl_2 .

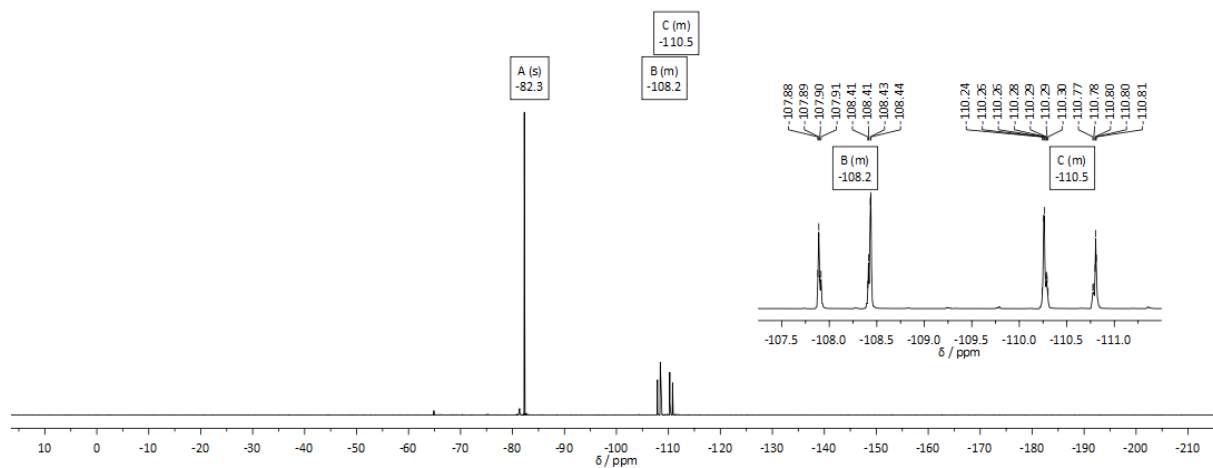


Figure S7 ^{19}F NMR spectrum of **3** in CD_2Cl_2 .

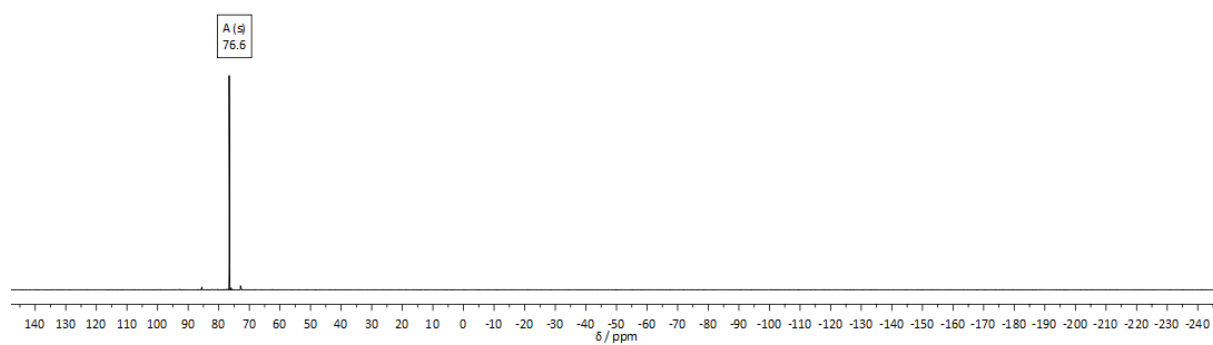


Figure S8 $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **3** in CD_2Cl_2 .

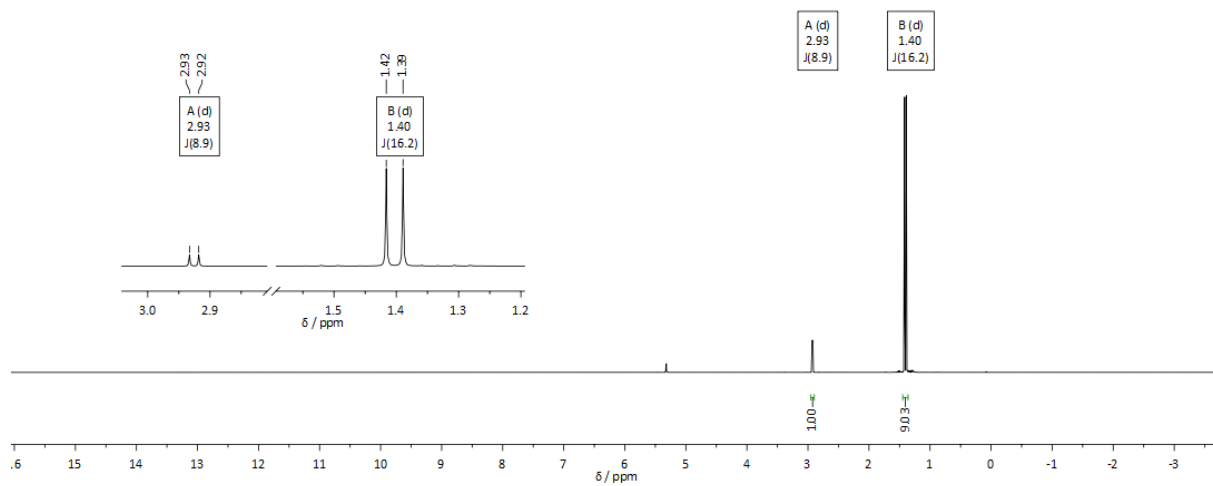


Figure S9 ^1H NMR spectrum of **4** in CD_2Cl_2 .

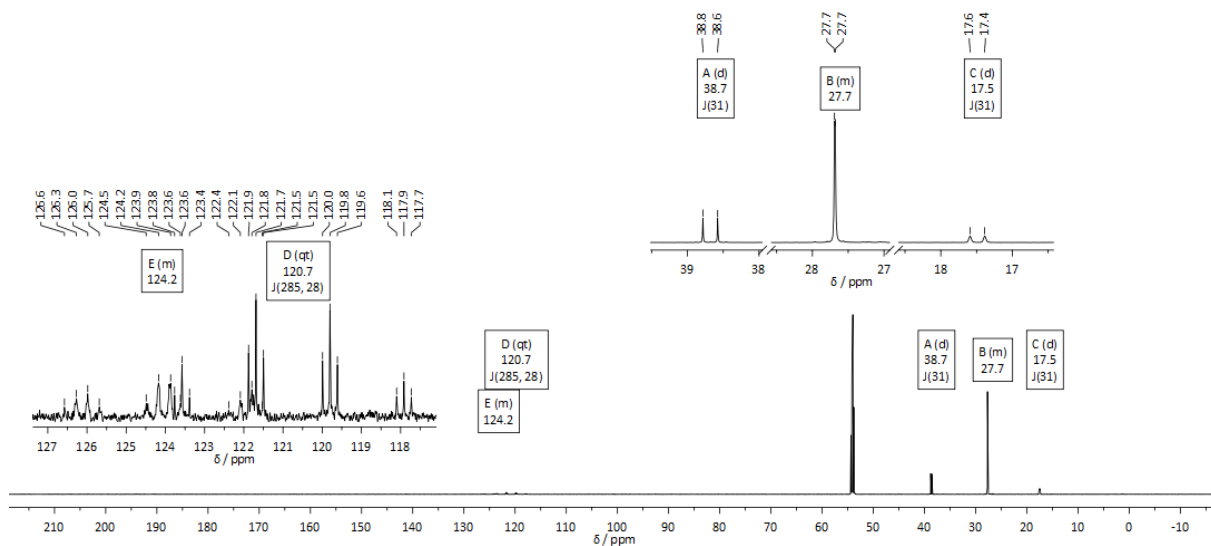


Figure S10 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **4** in CD_2Cl_2 .

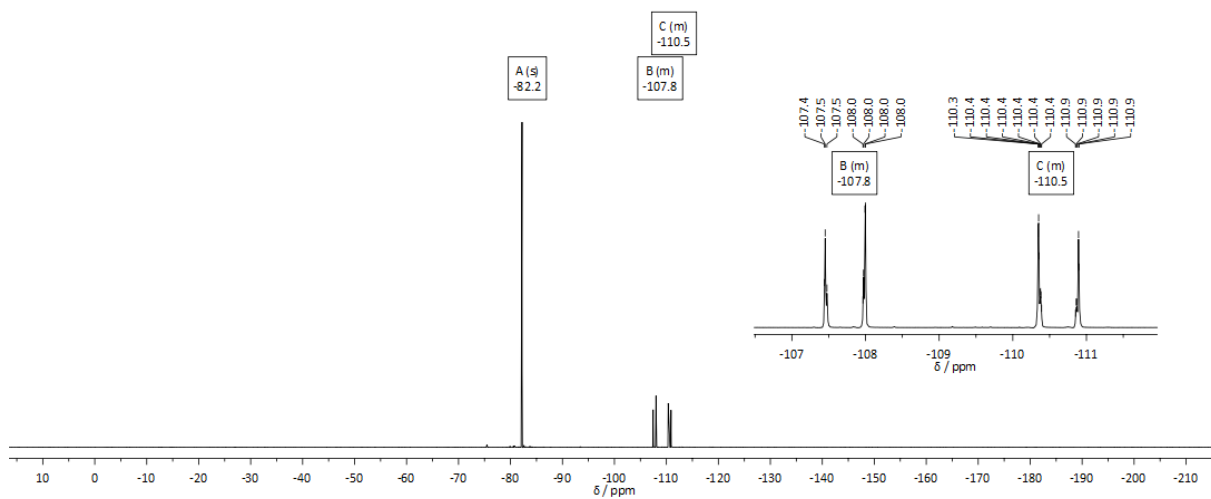


Figure S11 ^{19}F NMR spectrum of **4** in CD_2Cl_2 .

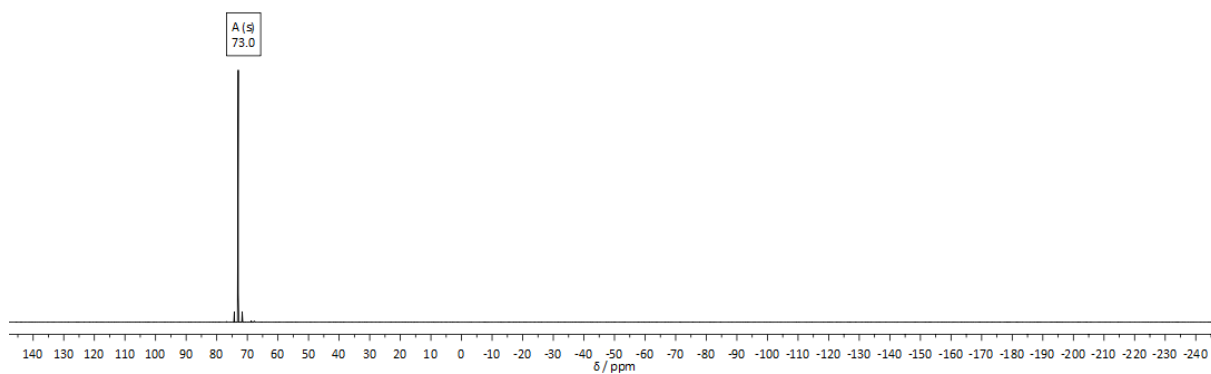


Figure S12 $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **4** in CD_2Cl_2 .

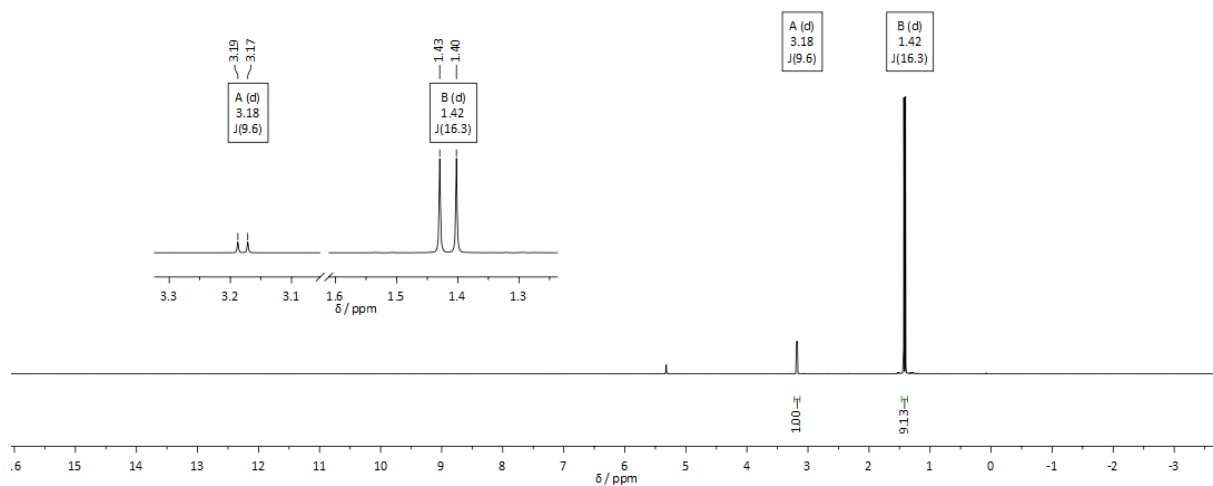


Figure S13 ^1H NMR spectrum of **5** in CD_2Cl_2 .

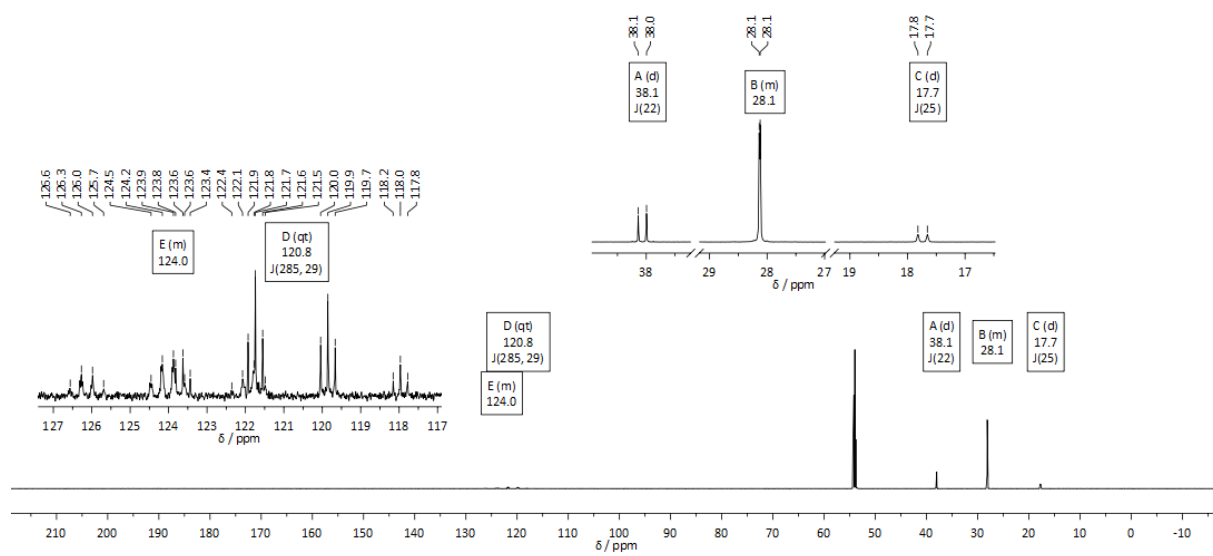


Figure S14 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **5** in CD_2Cl_2 .

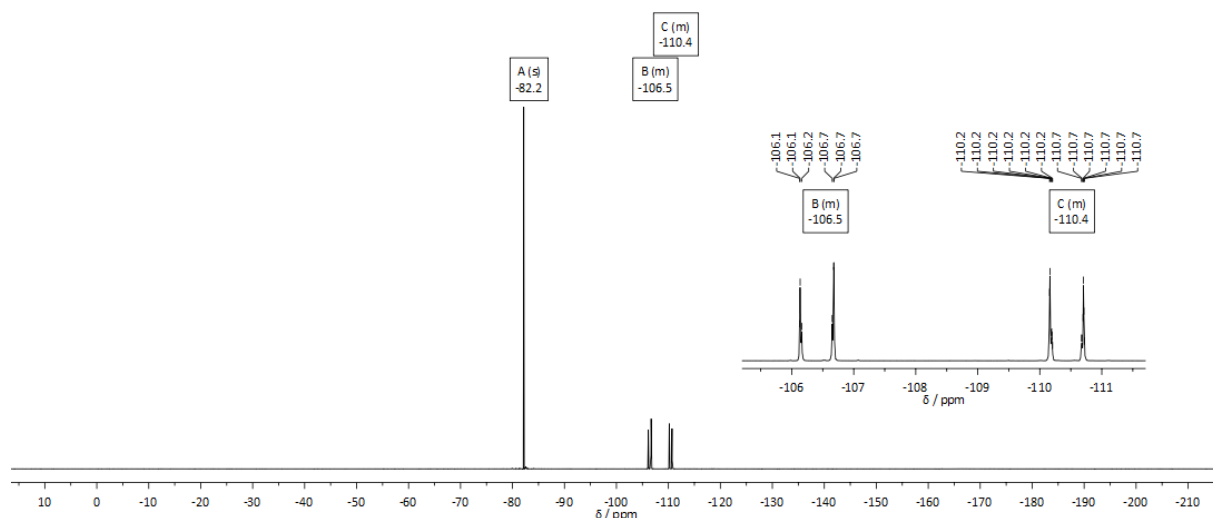


Figure S15 ^{19}F NMR spectrum of **5** in CD_2Cl_2 .

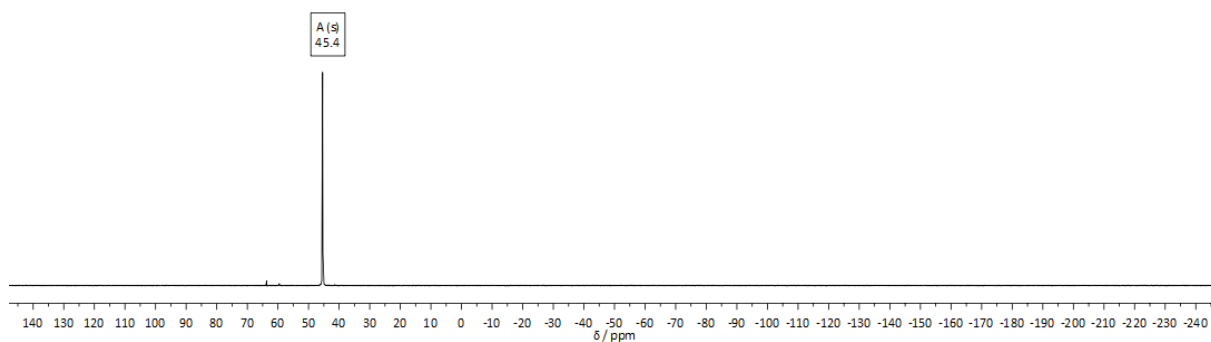


Figure S16 $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **5** in CD_2Cl_2 .

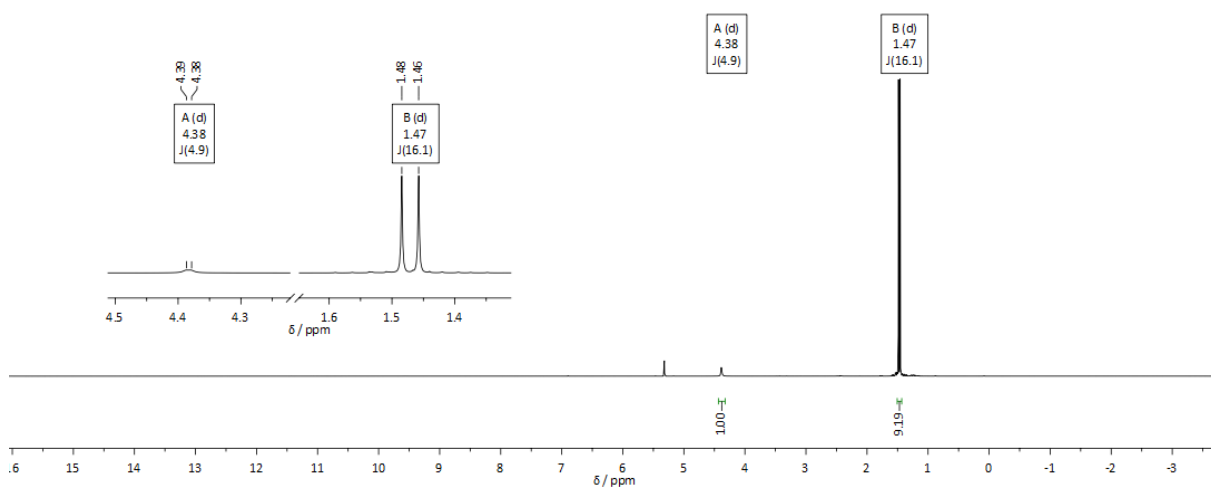


Figure S17 ^1H NMR spectrum of **6** in CD_2Cl_2 .

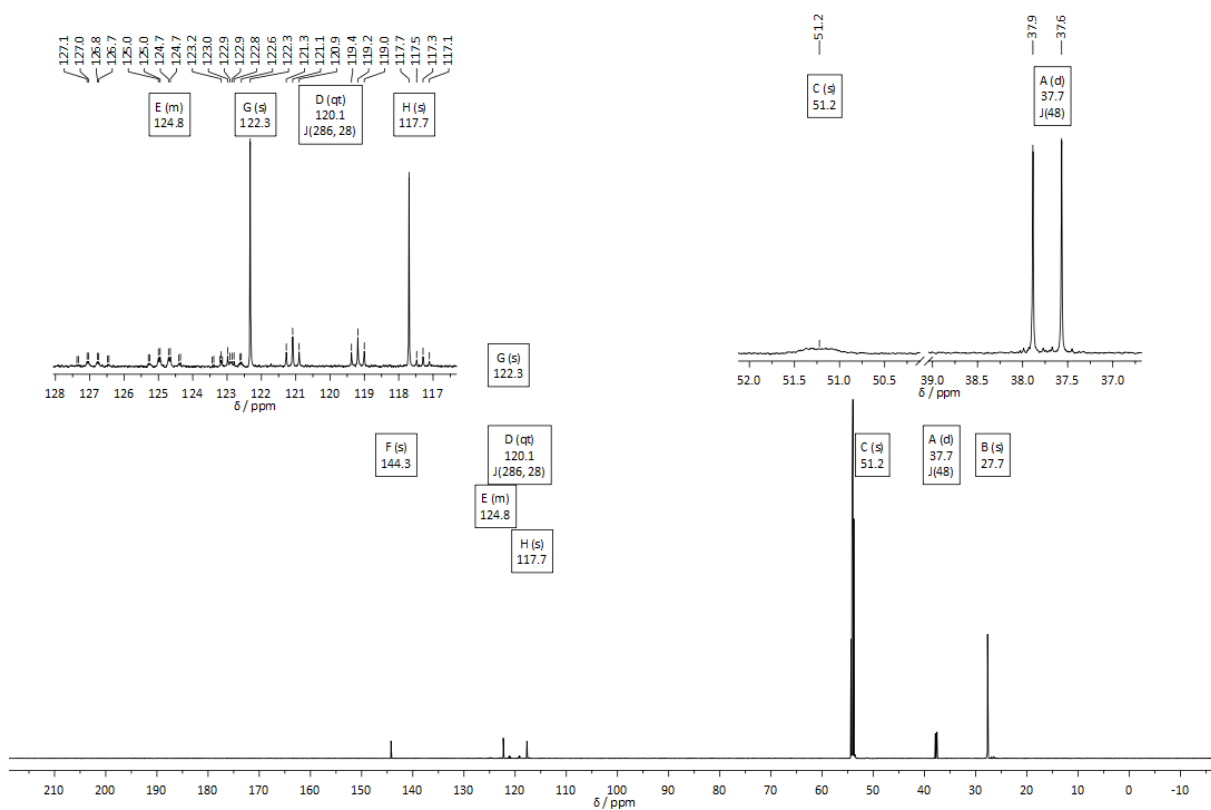


Figure S18 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **6** in CD_2Cl_2 .

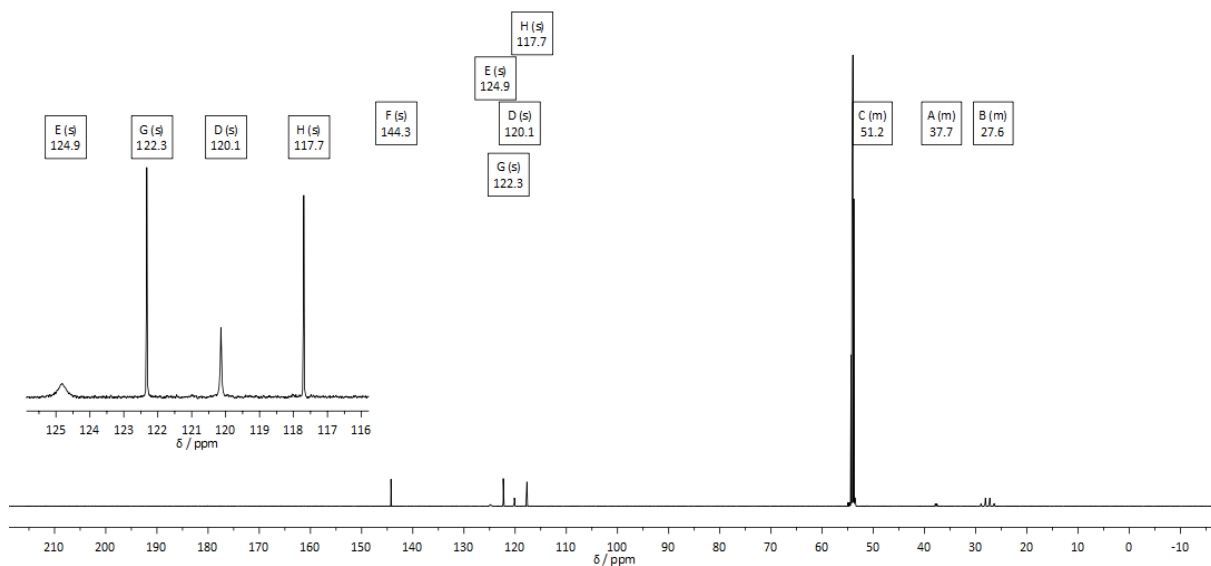


Figure S19 $^{13}\text{C}\{^{19}\text{F}\}$ NMR spectrum of **6** in CD_2Cl_2 .

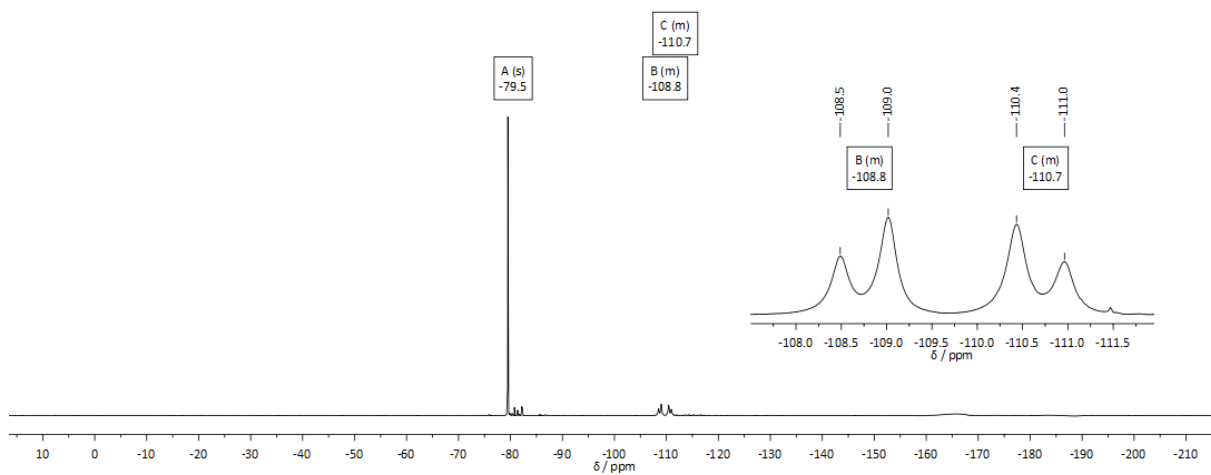


Figure S20 ^{19}F NMR spectrum of **6** in CD_2Cl_2 .

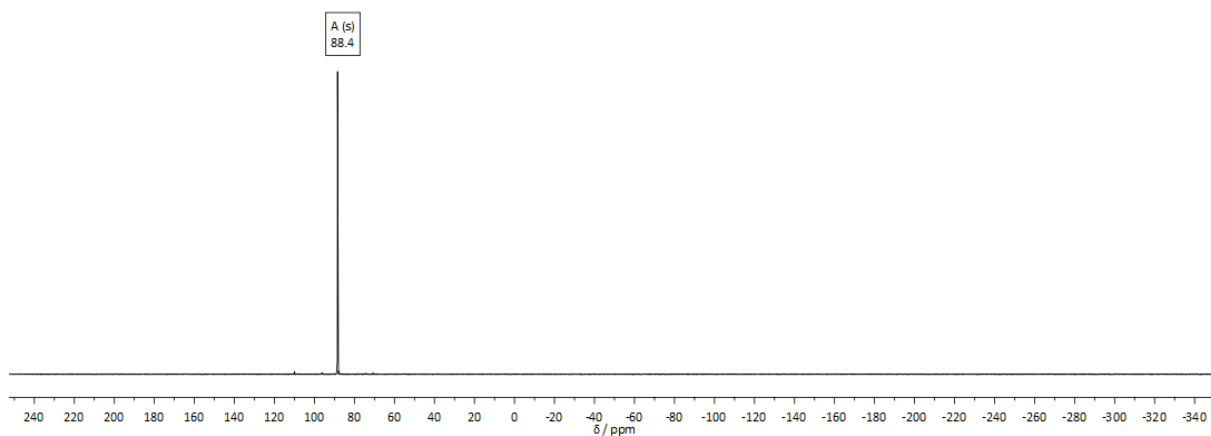


Figure S21 $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **6** in CD_2Cl_2 .

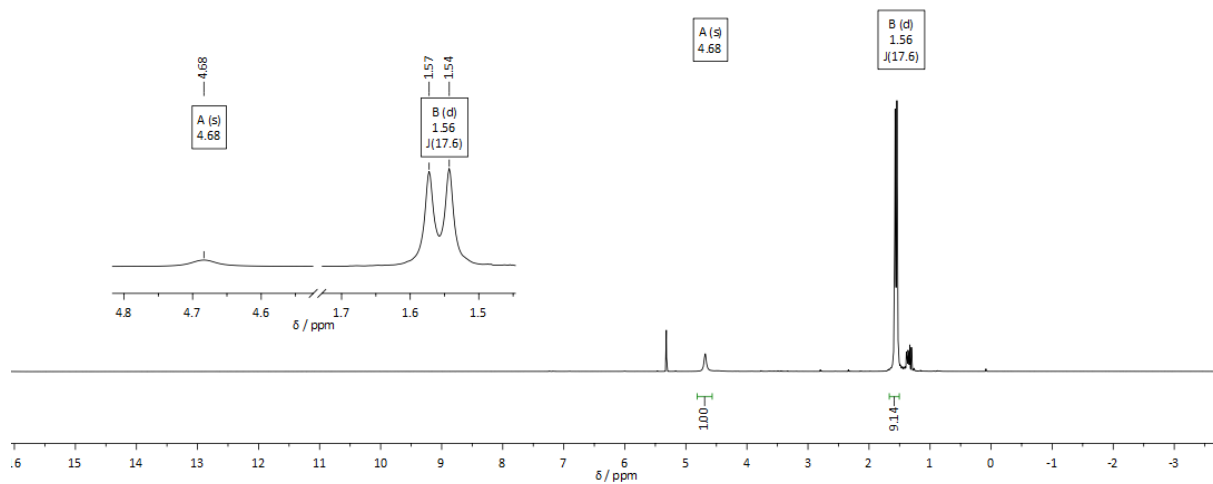


Figure S22 ^1H NMR spectrum of **7** in CD_2Cl_2 .

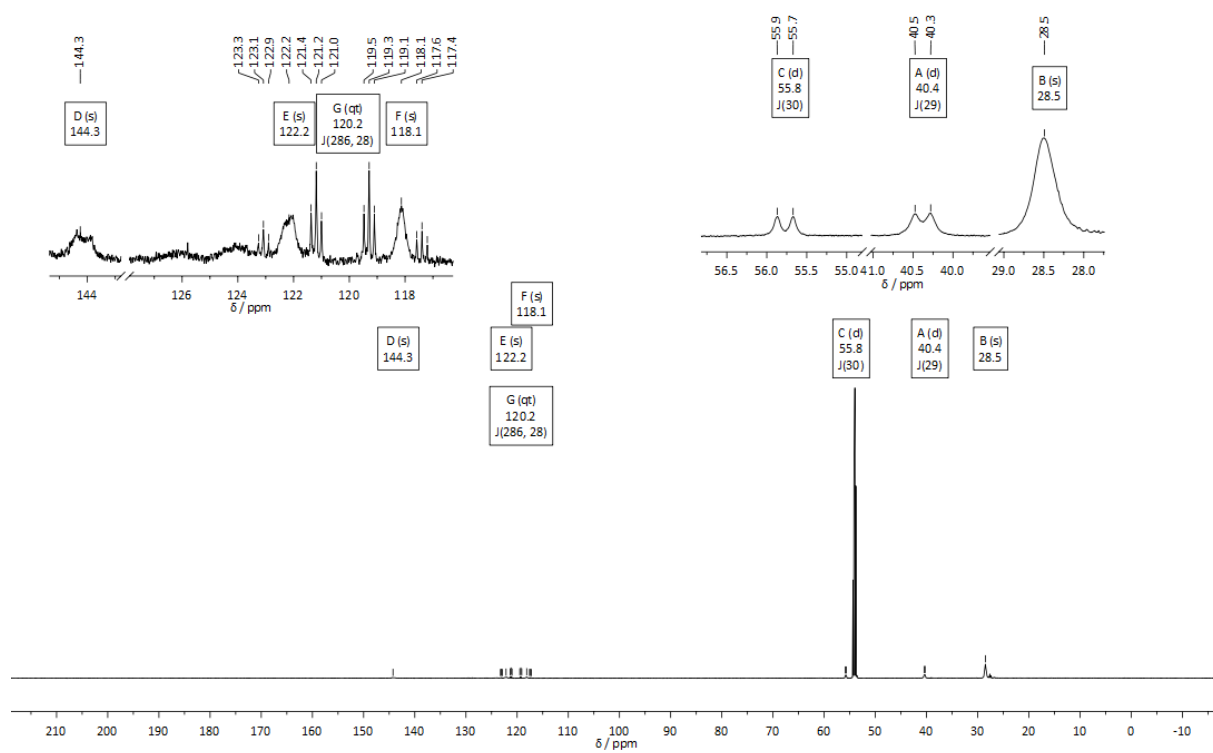


Figure S23 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **7** in CD_2Cl_2 .

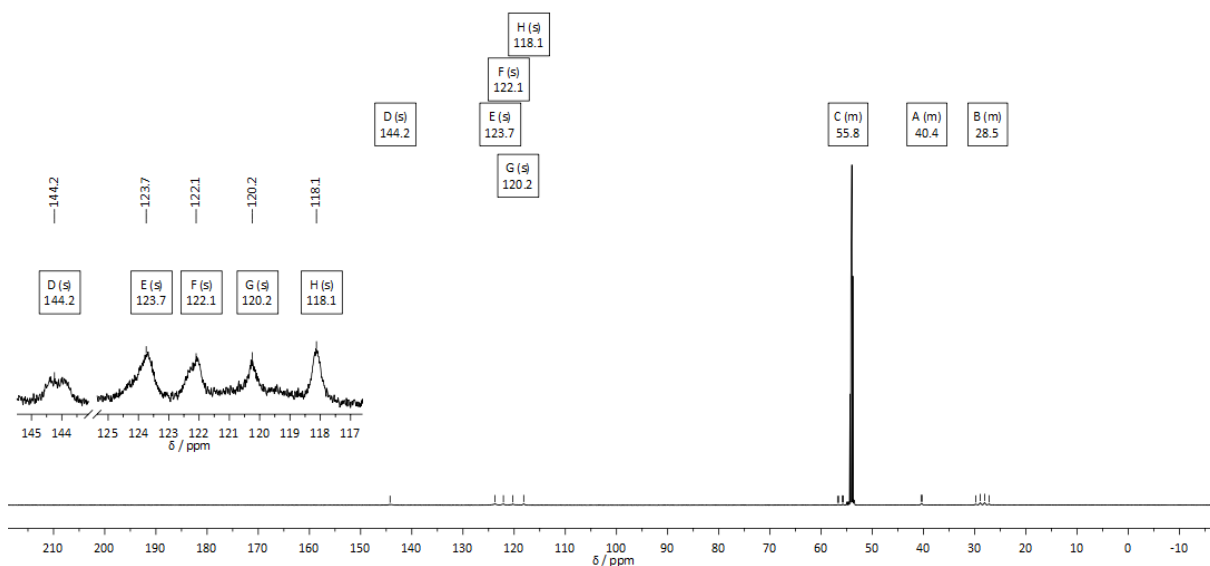


Figure S24 $^{13}\text{C}\{^{19}\text{F}\}$ NMR spectrum of **7** in CD_2Cl_2 .

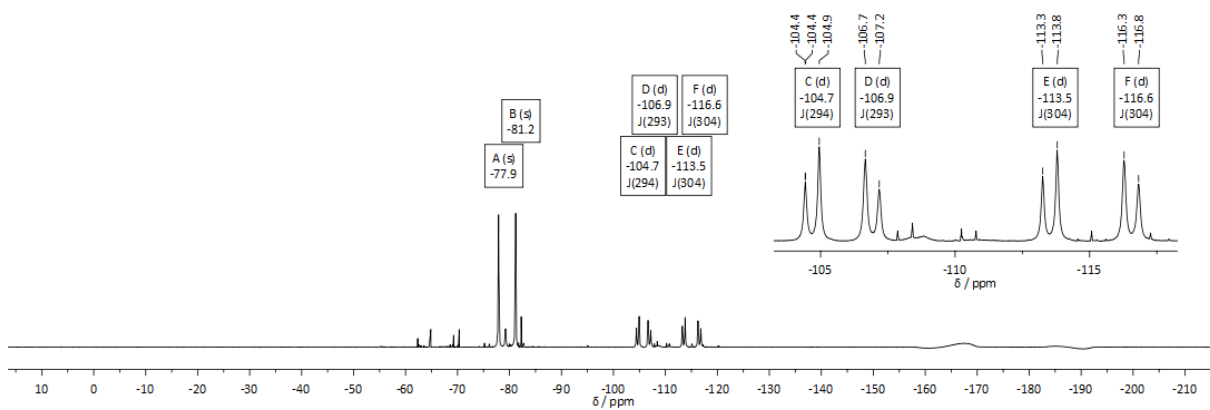


Figure S25 ^{19}F NMR spectrum of **7** in CD_2Cl_2 .

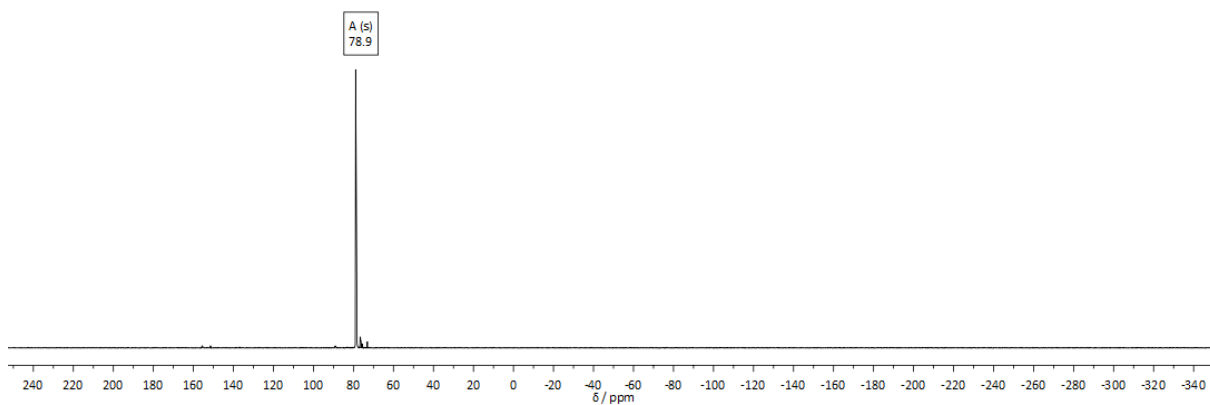


Figure S26 $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **7** in CD_2Cl_2 .

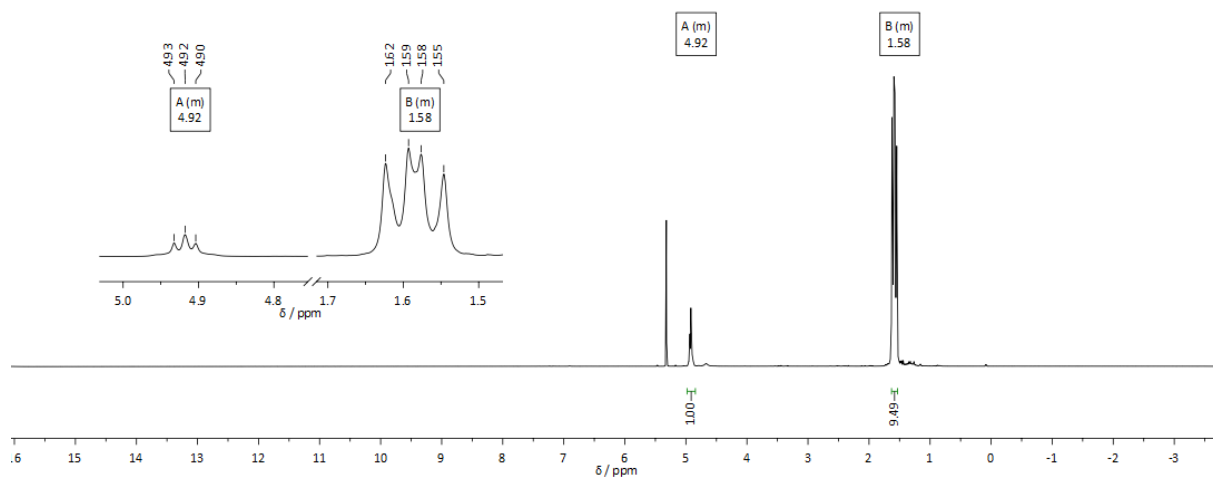


Figure S27 ^1H NMR spectrum of **8** in CD_2Cl_2 .

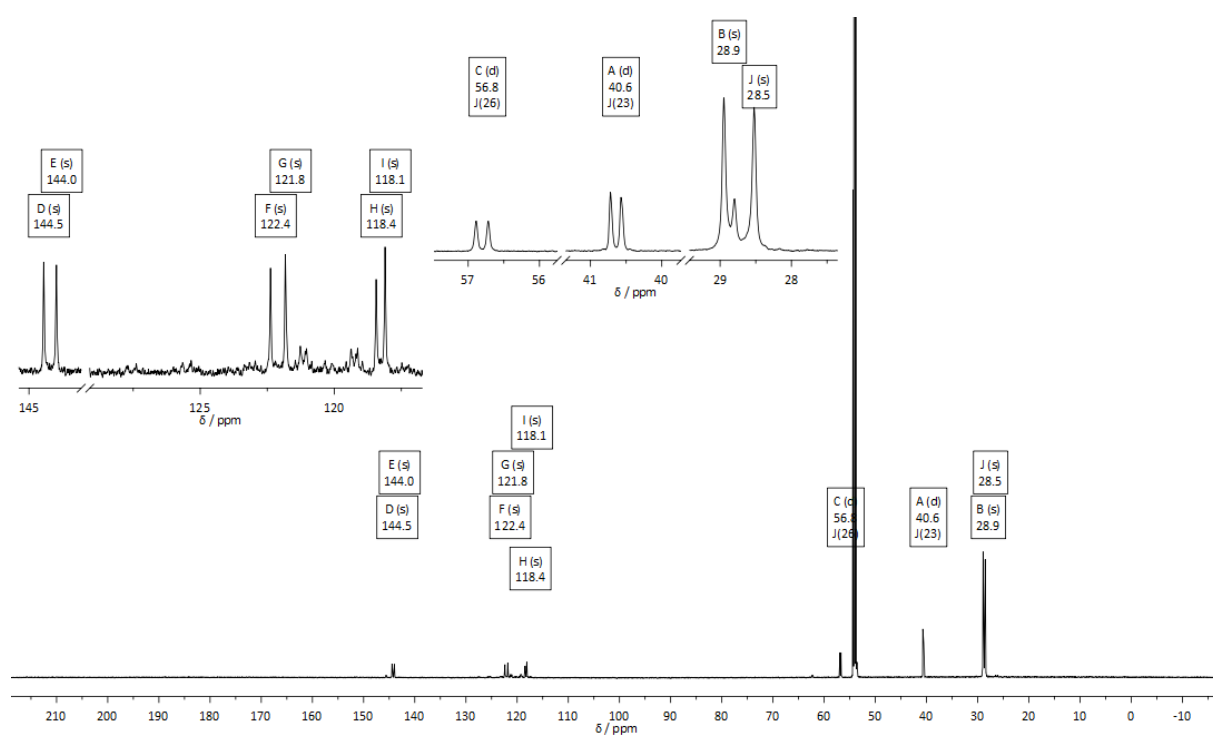


Figure S28 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **8** in CD_2Cl_2 .

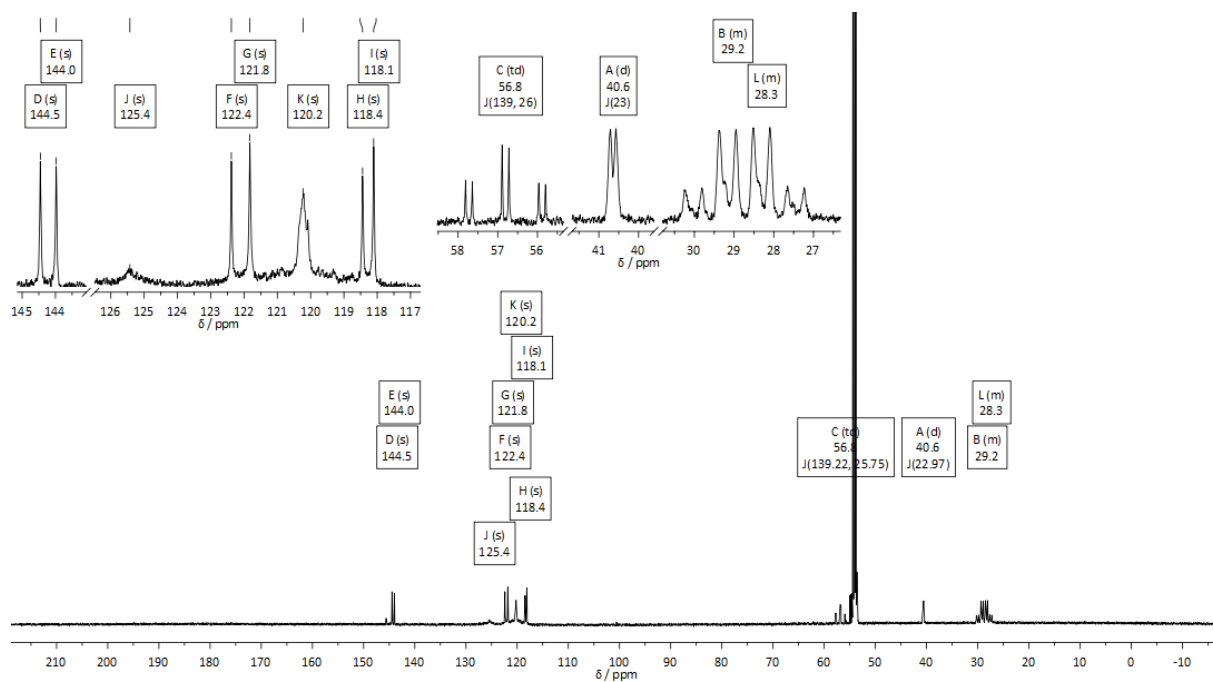


Figure S29 $^{13}\text{C}\{^{19}\text{F}\}$ NMR spectrum of **8** in CD_2Cl_2 .

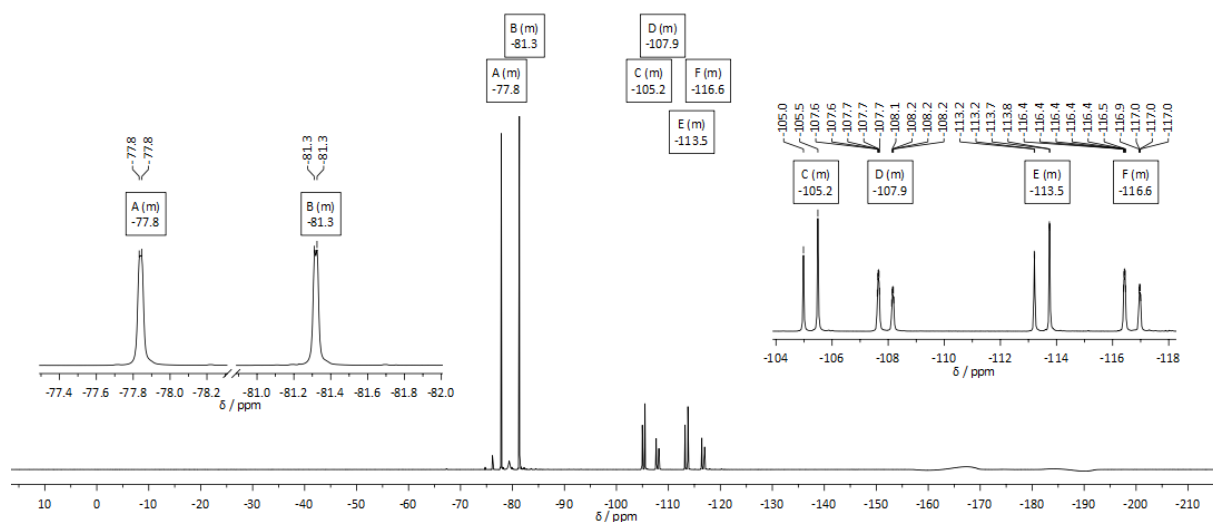


Figure S30 ^{19}F NMR spectrum of **8** in CD_2Cl_2 .

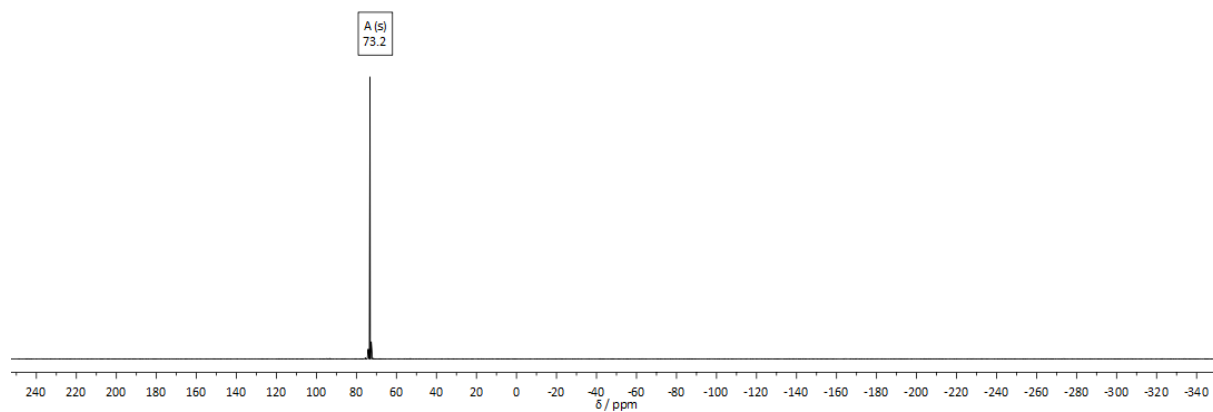


Figure S31 $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **8** in CD_2Cl_2 .

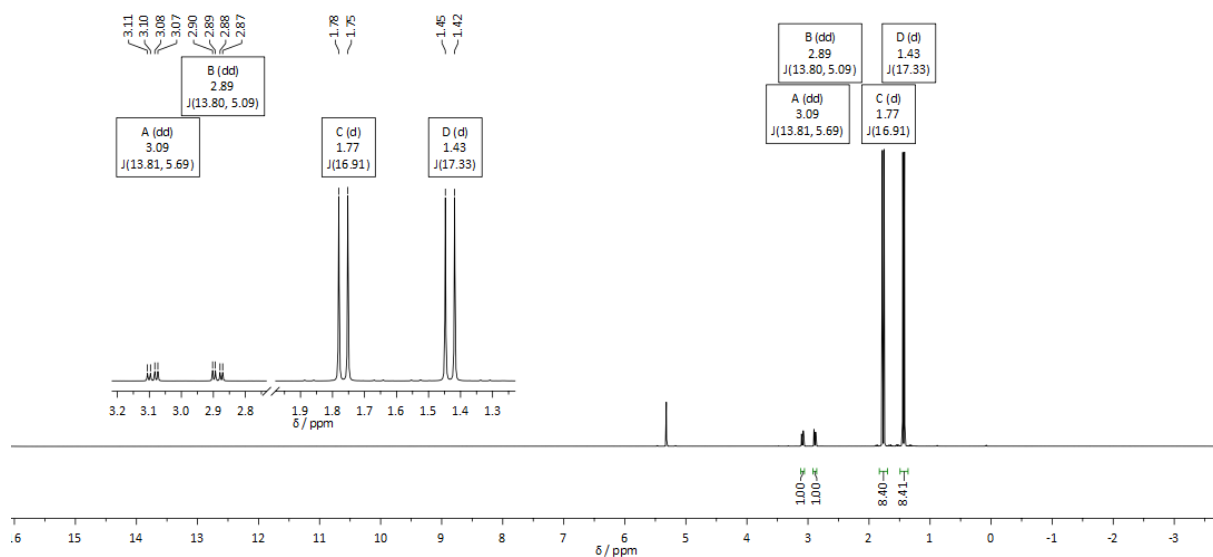


Figure S32 ^1H NMR spectrum of **9** in CD_2Cl_2 .

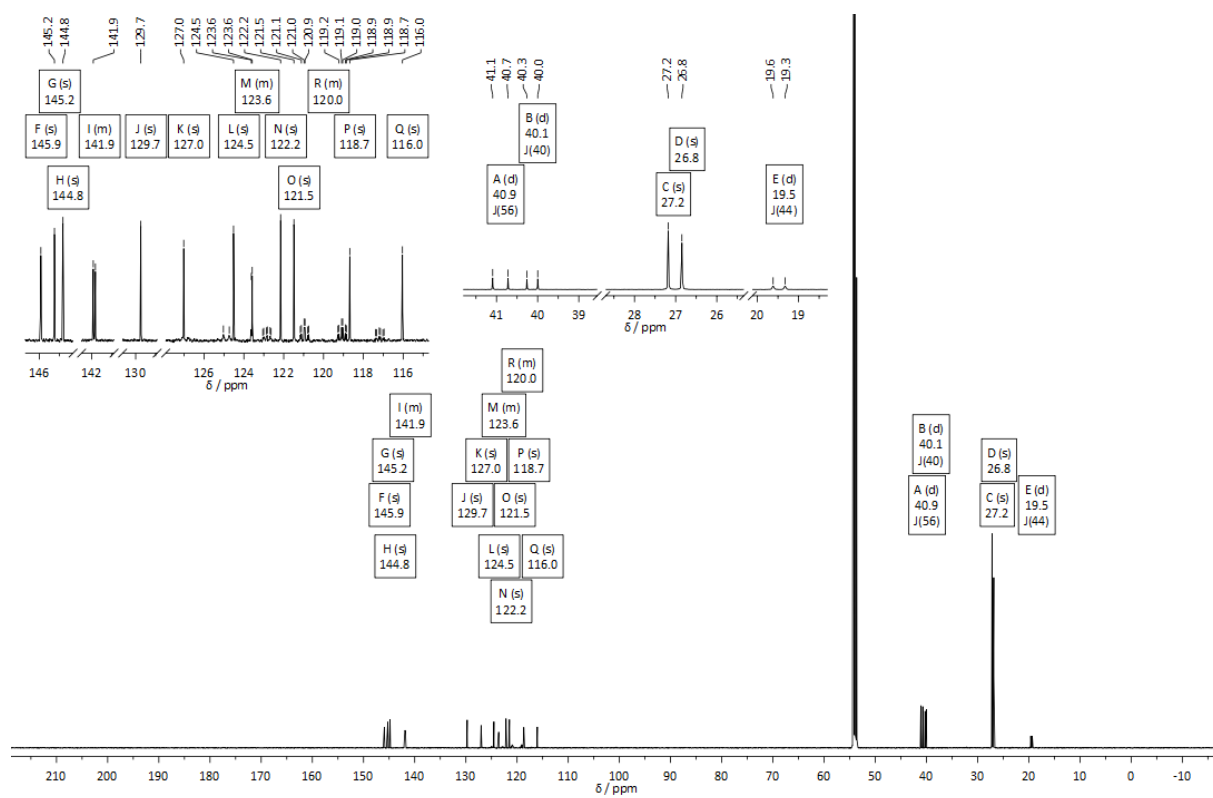


Figure S33 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **9** in CD_2Cl_2 .

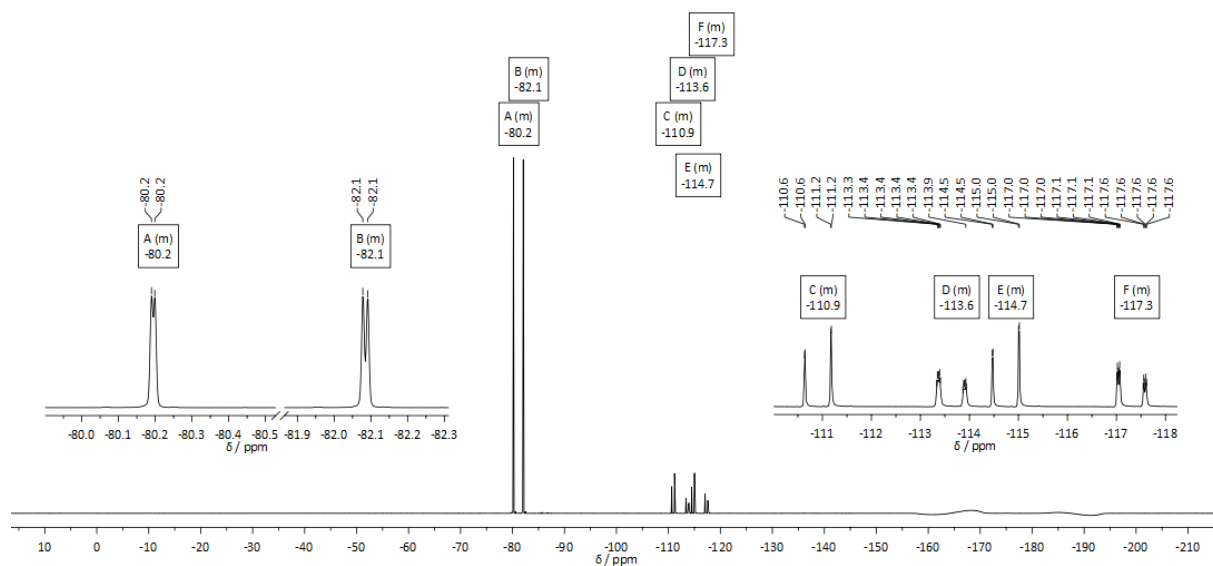


Figure S34 ^{19}F NMR spectrum of **9** in CD_2Cl_2 .

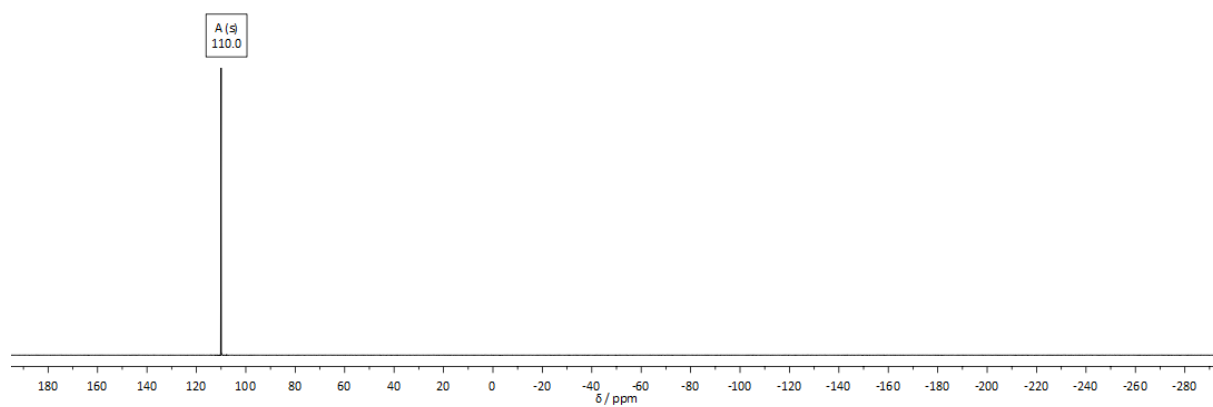


Figure S35 $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **9** in CD_2Cl_2 .

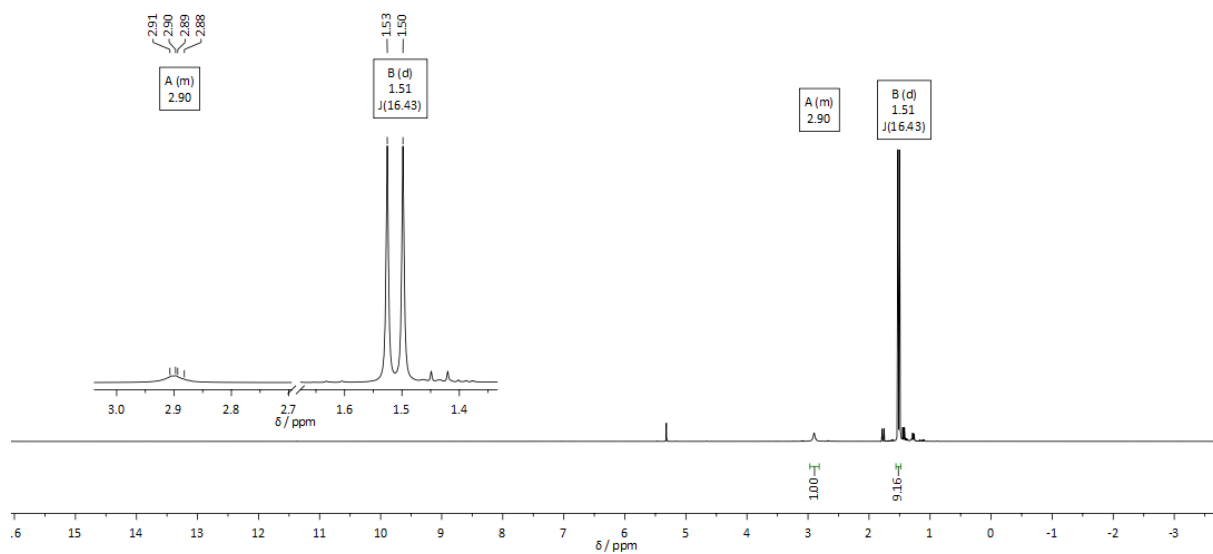


Figure S36 ^1H NMR spectrum of **10** in CD_2Cl_2 .

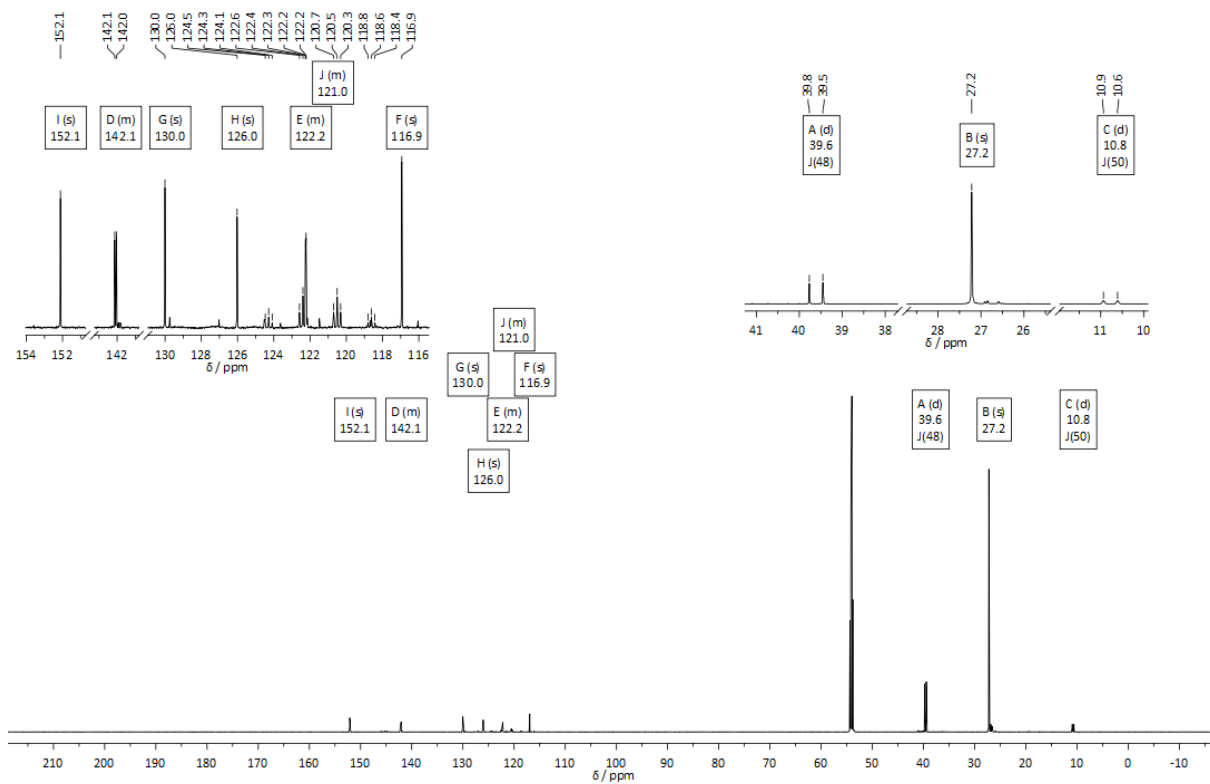


Figure S37 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **10** in CD_2Cl_2 .

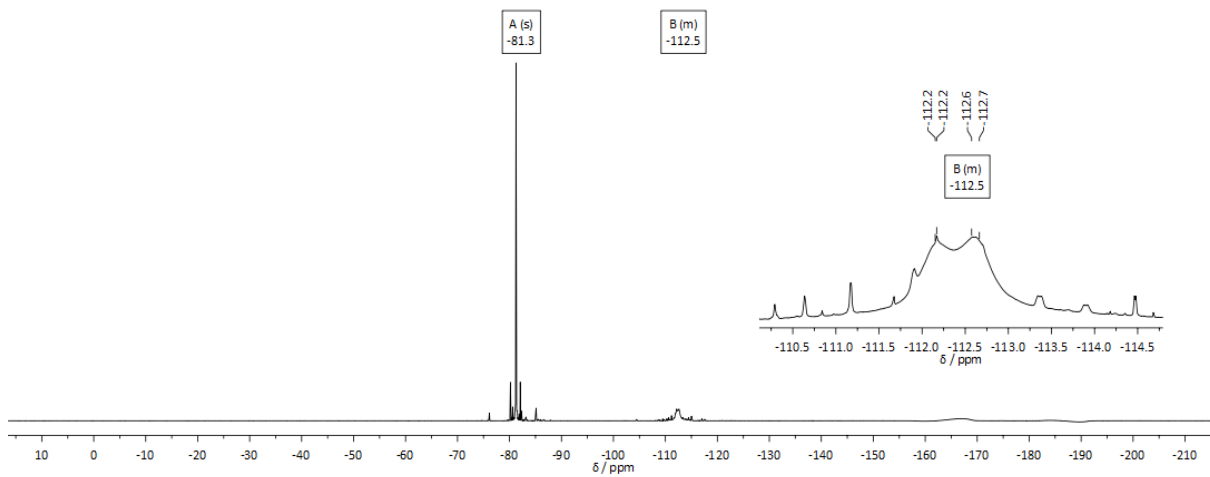


Figure S38 ^{19}F NMR spectrum of **10** in CD_2Cl_2 .

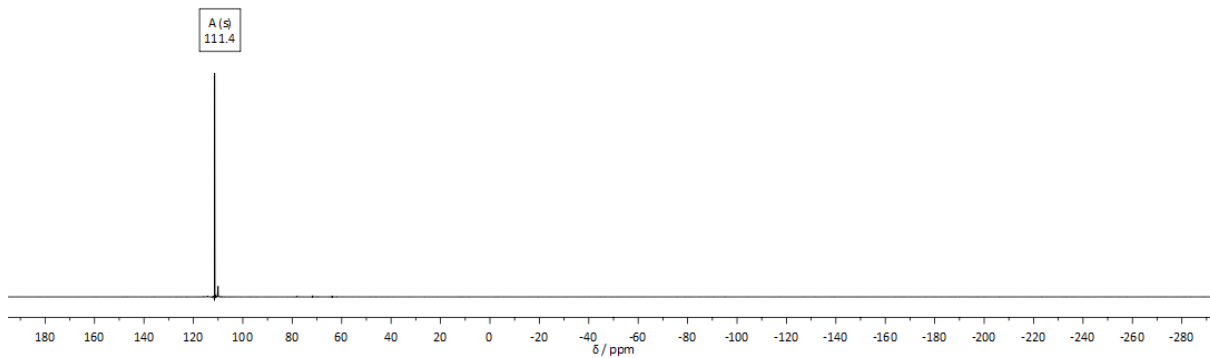


Figure S39 $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **10** in CD_2Cl_2 .

Crystallographic data

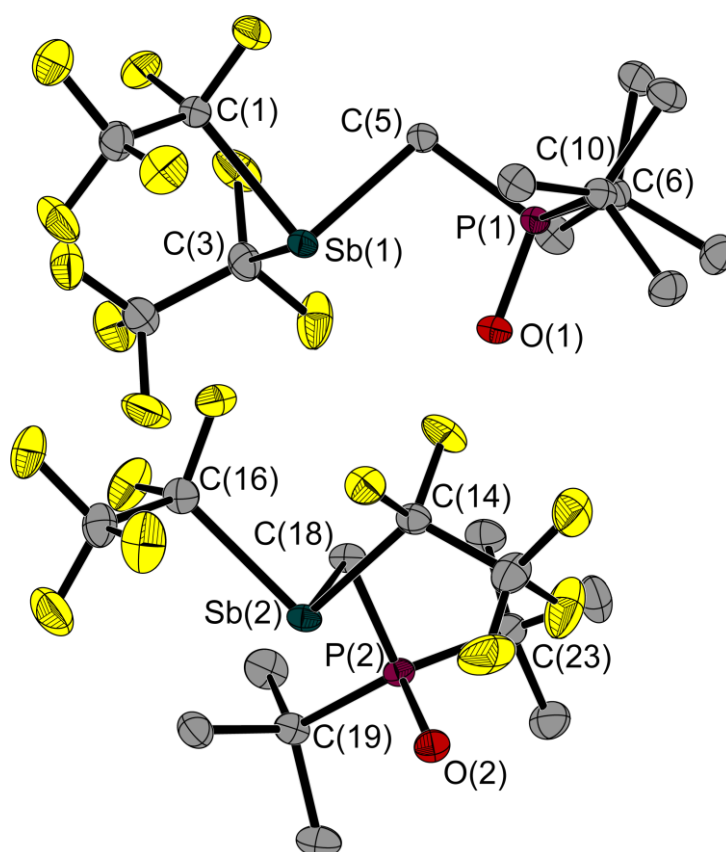


Figure S40 Molecular structure of compound **2** in the solid state. Ellipsoids are set at 50 % probability; hydrogen atoms are omitted for clarity. Selected bond lengths, atom distances [Å] and angles [°]: Sb(1)–C(1) 2.260(3), Sb(1)–C(3) 2.236(4), Sb(1)–C(5) 2.174(3), P(1)–C(5) 1.812(3), P(1)–C(6) 1.844(4), P(1)–C(10) 1.858(3), P(1)–O(1) 1.509(3), P(2)–O(2) 1.504(3), Sb(1)···O(1) 2.784(3), Sb(2)···O(2) 2.888(3); C(1)–Sb(1)–C(3) 94.8(1), C(1)–Sb(1)–C(5) 91.6(2), C(1)–Sb(1)–O(1) 153.9(1), C(5)–Sb(1)–C(3) 91.2(2), C(5)–P(1)–C(6) 107.7(2), C(5)–P(1)–C(10) 107.3(2), C(6)–P(1)–C(10) 114.4(2), O(1)–P(1)–C(5) 106.0(2), O(1)–P(1)–C(6) 111.6(2), O(1)–P(1)–C(10) 109.3(2), P(1)–C(5)–Sb(1) 100.7(2), P(2)–C(18)–Sb(2) 102.2(2).

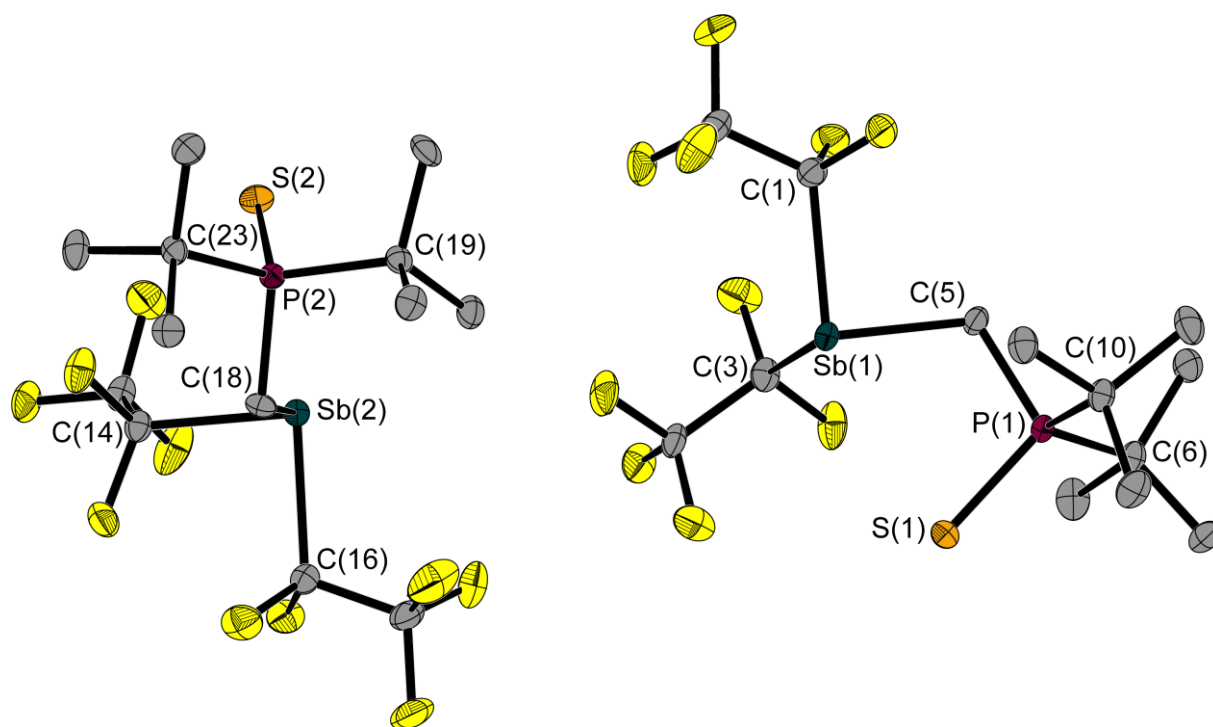


Figure S41 Molecular structure of compound **3** in the solid state. Ellipsoids are set at 50 % probability; hydrogen atoms are omitted for clarity. Selected bond lengths, atom distances [Å] and angles [°]: Sb(1)–C(1) 2.269(6), Sb(1)–C(3) 2.260(5), Sb(1)–C(5) 2.176(5), P(1)–C(5) 1.813(5), P(1)–C(6) 1.871(5), P(1)–C(10) 1.873(5), P(1)–S(1) 1.982(2), P(2)–S(2) 1.976(2), Sb(1)⋯S(1) 3.145(1), Sb(2)⋯S(2) 3.108(1); C(1)–Sb(1)–C(3) 93.7(2), C(1)–Sb(1)–C(5) 86.4(2), C(1)–Sb(1)–S(1) 153.4(2), C(5)–Sb(1)–C(3) 94.0(2), C(5)–P(1)–C(6) 106.3(2), C(5)–P(1)–C(10) 106.7(2), C(6)–P(1)–C(10) 113.5(2), S(1)–P(1)–C(5) 106.9(2), S(1)–P(1)–C(6) 112.4(2), S(1)–P(1)–C(10) 110.5(2), P(1)–C(5)–Sb(1) 106.8(2), P(2)–C(18)–Sb(2) 106.0(2).

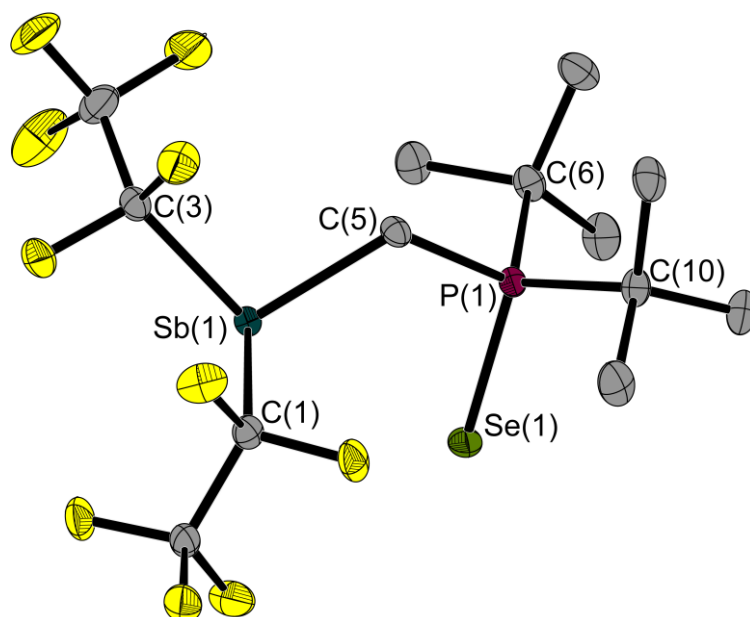


Figure S42 Molecular structure of compound **4** in the solid state. Ellipsoids are set at 50 % probability; hydrogen atoms are omitted for clarity. Selected bond lengths, atom distances [Å] and angles [°]: Sb(1)–C(1) 2.257(2), Sb(1)–C(3) 2.272(2), Sb(1)–C(5) 2.178(2), P(1)–C(5) 1.820(2), P(1)–C(6) 1.874(2), P(1)–C(10) 1.873(2), P(1)–Se(1) 2.131(2), Sb(1)⋯Se(1) 3.171(1); C(1)–Sb(1)–C(3) 87.6(1), C(1)–Sb(1)–C(5) 93.1(1), C(3)–Sb(1)–Se(1) 161.0(1), C(5)–Sb(1)–C(3) 91.6(1), C(5)–P(1)–C(6) 106.9(1), C(5)–P(1)–C(10) 106.9(1), C(6)–P(1)–C(10) 113.7(1), Se(1)–P(1)–C(5) 106.1(1), Se(1)–P(1)–C(6) 110.4(1), Se(1)–P(1)–C(10) 112.4(1), P(1)–C(5)–Sb(1) 107.6(1).

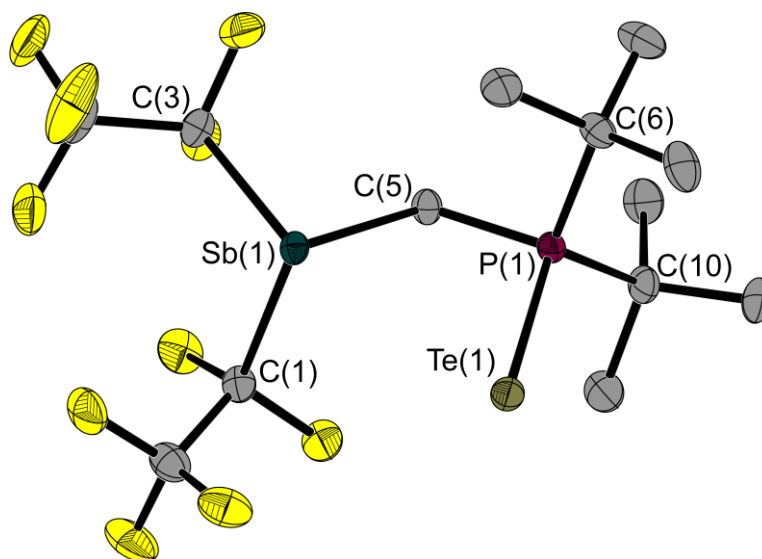


Figure S43 Molecular structure of compound **5** in the solid state. Ellipsoids are set at 50 % probability; hydrogen atoms are omitted for clarity. Selected bond lengths, atom distances [Å] and angles [°]: Sb(1)–C(1) 2.259(2), Sb(1)–C(3) 2.282(2), Sb(1)–C(5) 2.176(2), P(1)–C(5) 1.824(2), P(1)–C(6) 1.878(2), P(1)–C(10) 1.876(2), P(1)–Te(1) 2.382(2), Sb(1)⋯Te(1) 3.362(1); C(1)–Sb(1)–C(3) 91.7(1), C(1)–Sb(1)–C(5) 94.0(1), C(3)–Sb(1)–Te(1) 157.8(1), C(5)–Sb(1)–C(3) 86.3(1), C(5)–P(1)–C(6) 106.6(1), C(5)–P(1)–C(10) 105.9(1), C(6)–P(1)–C(10) 114.2(1), Te(1)–P(1)–C(5) 105.9(1), Te(1)–P(1)–C(6) 110.6(1), Te(1)–P(1)–C(10) 113.0(1), P(1)–C(5)–Sb(1) 109.1(1).

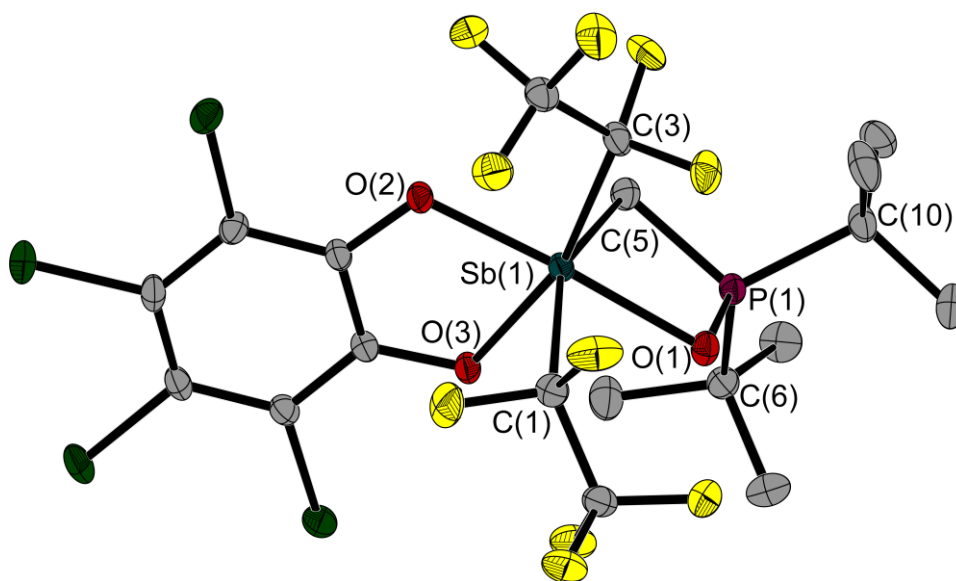


Figure S44 Molecular structure of compound **6** in the solid state. Ellipsoids are set at 50 % probability; hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Sb(1)–C(1) 2.240(2), Sb(1)–C(3) 2.279(2), Sb(1)–C(5) 2.194(2), Sb(1)–O(1) 2.158(1), Sb(1)–O(2) 2.009(1), Sb(1)–O(3) 2.044(1), P(1)–C(5) 1.809(2), P(1)–C(6) 1.853(2), P(1)–C(10) 1.844(2), P(1)–O(1) 1.567(1); C(1)–Sb(1)–C(3) 93.2(1), C(1)–Sb(1)–C(5) 154.8(1), C(5)–Sb(1)–C(3) 96.3(1), O(1)–Sb(1)–C(1) 83.8(1), O(1)–Sb(1)–C(3) 103.5(1), O(1)–Sb(1)–C(5) 71.2(1), O(1)–Sb(1)–O(2) 173.3(1), O(1)–Sb(1)–O(3) 93.1(1), O(2)–Sb(1)–C(1) 98.6(1), O(2)–Sb(1)–C(3) 82.6(1), O(2)–Sb(1)–C(5) 105.7(1), O(2)–Sb(1)–O(3) 80.9(1), O(3)–Sb(1)–C(1) 85.3(1), O(3)–Sb(1)–C(3) 163.0(1), O(3)–Sb(1)–C(5) 92.1(1), C(5)–P(1)–C(6) 113.6(1), C(5)–P(1)–C(10) 111.3(1), C(6)–P(1)–C(10) 114.2(1), O(1)–P(1)–C(5) 97.0(1), O(1)–P(1)–C(6) 109.5(1), O(1)–P(1)–C(10) 109.9(1), P(1)–C(5)–Sb(1) 91.5(1), P(1)–O(1)–Sb(1) 100.0(1).

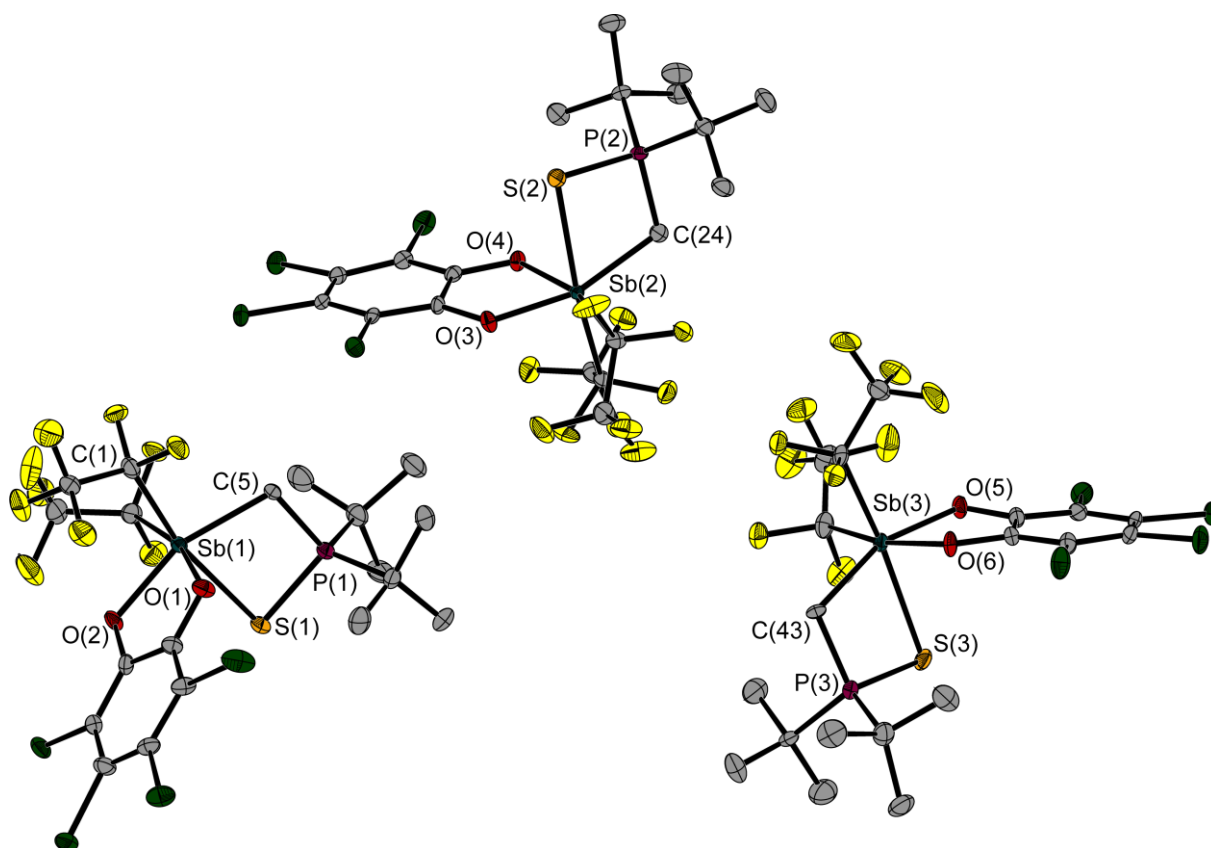


Figure S45 Molecular structure of compound **7** in the solid state. Ellipsoids are set at 50 % probability; hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Sb(1)–C(1) 2.231(7), Sb(1)–C(4) 2.259(6), Sb(1)–C(5) 2.178(6), Sb(1)–S(1) 2.633(2), Sb(2)–S(2) 2.619(2), Sb(3)–S(3) 2.621(2), Sb(1)–O(1) 2.052(4), Sb(1)–O(2) 2.027(4), P(1)–C(5) 1.811(6), P(1)–C(6) 1.880(8), P(1)–C(10) 1.866(7), P(1)–S(1) 2.036(2), P(2)–S(2) 2.036(2), P(3)–S(3) 2.031(2); C(1)–Sb(1)–C(4) 96.4(3), C(1)–Sb(1)–C(5) 92.6(2), C(5)–Sb(1)–C(4) 103.1(2), S(1)–Sb(1)–C(1) 167.2(2), S(1)–Sb(1)–C(4) 91.5(2), S(1)–Sb(1)–C(5) 75.8(2), S(1)–Sb(1)–O(1) 89.9(2), S(1)–Sb(1)–O(2) 86.5(2), O(1)–Sb(1)–C(1) 84.8(2), O(1)–Sb(1)–C(4) 166.3(2), O(1)–Sb(1)–C(5) 90.4(2), O(1)–Sb(1)–O(2) 80.6(2), O(2)–Sb(1)–C(1) 104.1(2), O(2)–Sb(1)–C(4) 86.0(2), O(2)–Sb(1)–C(5) 160.1(2), C(5)–P(1)–C(6) 110.3(3), C(5)–P(1)–C(10) 109.4(3), C(6)–P(1)–C(10) 114.0(4), S(1)–P(1)–C(5) 101.2(2), S(1)–P(1)–C(6) 109.4(2), S(1)–P(1)–C(10) 111.8(2), P(1)–C(5)–Sb(1) 101.2(3), P(2)–C(24)–Sb(2) 101.4(3), P(3)–C(43)–Sb(3) 100.9(3), P(1)–S(1)–Sb(1) 81.8(1), P(2)–S(2)–Sb(2) 81.9(1), P(3)–S(3)–Sb(3) 82.1(1).

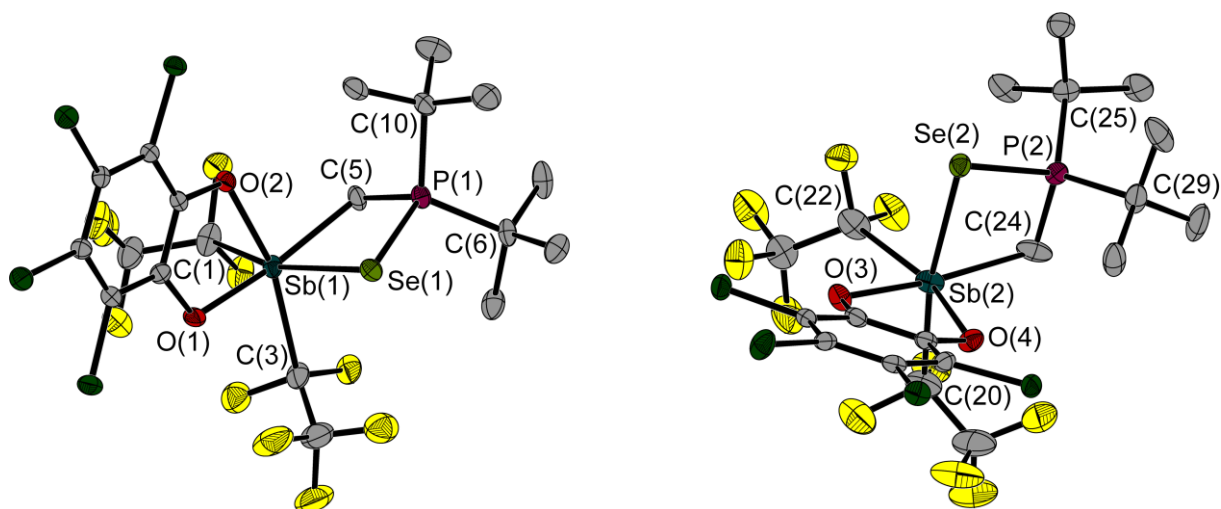


Figure S46 Molecular structure of compound **8** in the solid state. Ellipsoids are set at 30 % probability; hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Sb(1)–C(1) 2.264(7), Sb(1)–C(3) 2.250(7), Sb(1)–C(5) 2.193(7), Sb(1)–Se(1) 2.748(1), Sb(2)–Se(2) 2.703(1), Sb(1)–O(1) 2.024(5), Sb(1)–O(2) 2.035(4), P(1)–C(5) 1.833(7), P(1)–C(6) 1.864(7), P(1)–C(10) 1.869(7), P(1)–Se(1) 2.194(2), P(2)–Se(2) 2.187(2); C(1)–Sb(1)–C(3) 91.4(3), C(1)–Sb(1)–C(5) 87.6(3), C(5)–Sb(1)–C(3) 104.7(3), Se(1)–Sb(1)–C(1) 164.9(2), Se(1)–Sb(1)–C(3) 95.7(2), Se(1)–Sb(1)–C(5) 77.7(2), Se(1)–Sb(1)–O(1) 96.3(2), Se(1)–Sb(1)–O(2) 89.4(2), O(1)–Sb(1)–C(1) 97.6(3), O(1)–Sb(1)–C(3) 84.7(3), O(1)–Sb(1)–C(5) 169.2(2), O(1)–Sb(1)–O(2) 80.4(2), O(2)–Sb(1)–C(1) 87.1(2), O(2)–Sb(1)–C(3) 164.8(3), O(2)–Sb(1)–C(5) 90.4(2), C(5)–P(1)–C(6) 108.9(3), C(5)–P(1)–C(10) 108.4(3), C(6)–P(1)–C(10) 114.9(3), Se(1)–P(1)–C(5) 101.5(2), Se(1)–P(1)–C(6) 110.8(3), Se(1)–P(1)–C(10) 111.5(2), P(1)–C(5)–Sb(1) 102.5(3), P(2)–C(24)–Sb(2) 102.5(3), P(1)–Se(1)–Sb(1) 78.2(1), P(2)–Se(2)–Sb(2) 79.4(1).

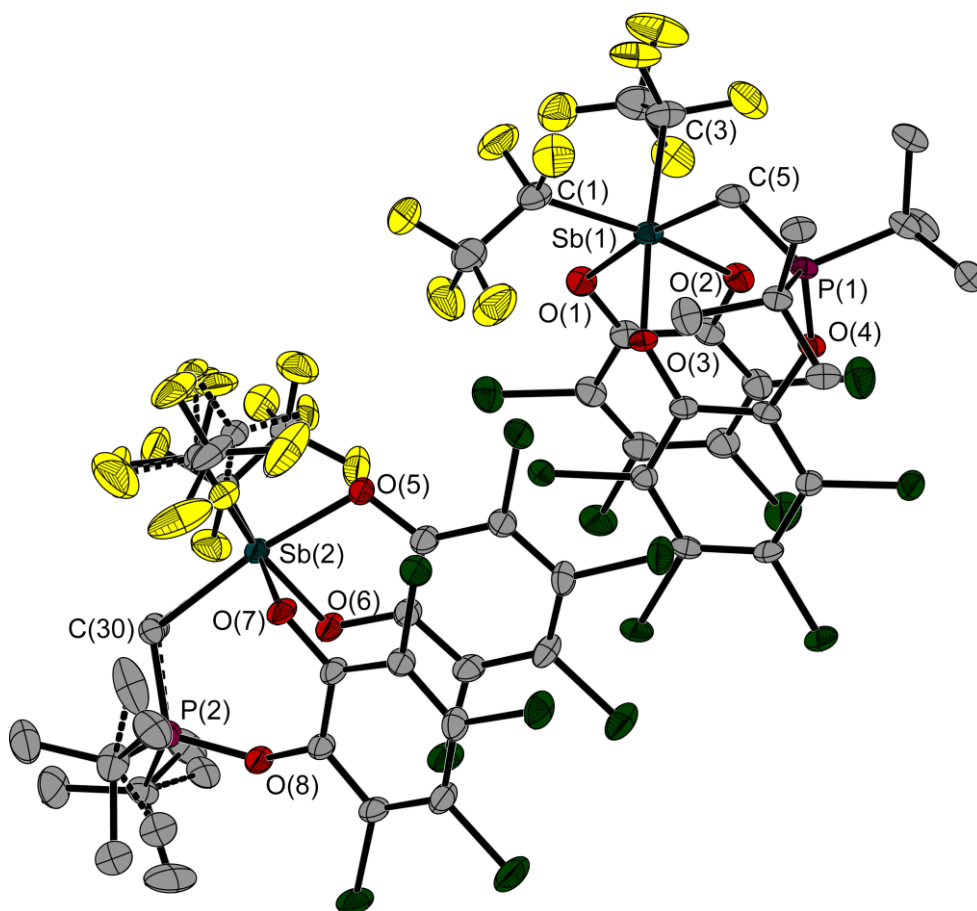


Figure S47 Molecular structure of compound **9** in the solid state. Ellipsoids are set at 50 % probability; hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°] for the non-disordered molecule: Sb(1)–C(1) 2.233(4), Sb(1)–C(3) 2.247(4), Sb(1)–C(5) 2.181(3), Sb(1)–O(1) 2.023(2), Sb(1)–O(2) 2.027(3), Sb(1)–O(3) 2.044(2), P(1)–C(5) 1.794(4), P(1)–C(6) 1.846(4), P(1)–C(10) 1.833(3), P(1)–O(4) 1.587(2); C(1)–Sb(1)–C(3) 93.7(2), C(1)–Sb(1)–C(5) 98.7(2), C(5)–Sb(1)–C(3) 89.7(2), O(1)–Sb(1)–C(1) 88.0(1), O(1)–Sb(1)–C(3) 94.5(2), O(1)–Sb(1)–C(5) 171.9(2), O(1)–Sb(1)–O(2) 81.2(1), O(1)–Sb(1)–O(3) 89.4(1), O(2)–Sb(1)–C(1) 169.1(1), O(2)–Sb(1)–C(3) 88.4(2), O(2)–Sb(1)–C(5) 92.0(2), O(2)–Sb(1)–O(3) 89.6(1), O(3)–Sb(1)–C(1) 89.1(1), O(3)–Sb(1)–C(3) 175.2(1), O(3)–Sb(1)–C(5) 86.1(1), C(5)–P(1)–C(6) 107.5(2), C(5)–P(1)–C(10) 110.6(2), C(6)–P(1)–C(10) 116.5(2), O(4)–P(1)–C(5) 113.8(2), O(4)–P(1)–C(6) 99.2(2), O(4)–P(1)–C(10) 109.0(2), P(1)–C(5)–Sb(1) 118.4(2).

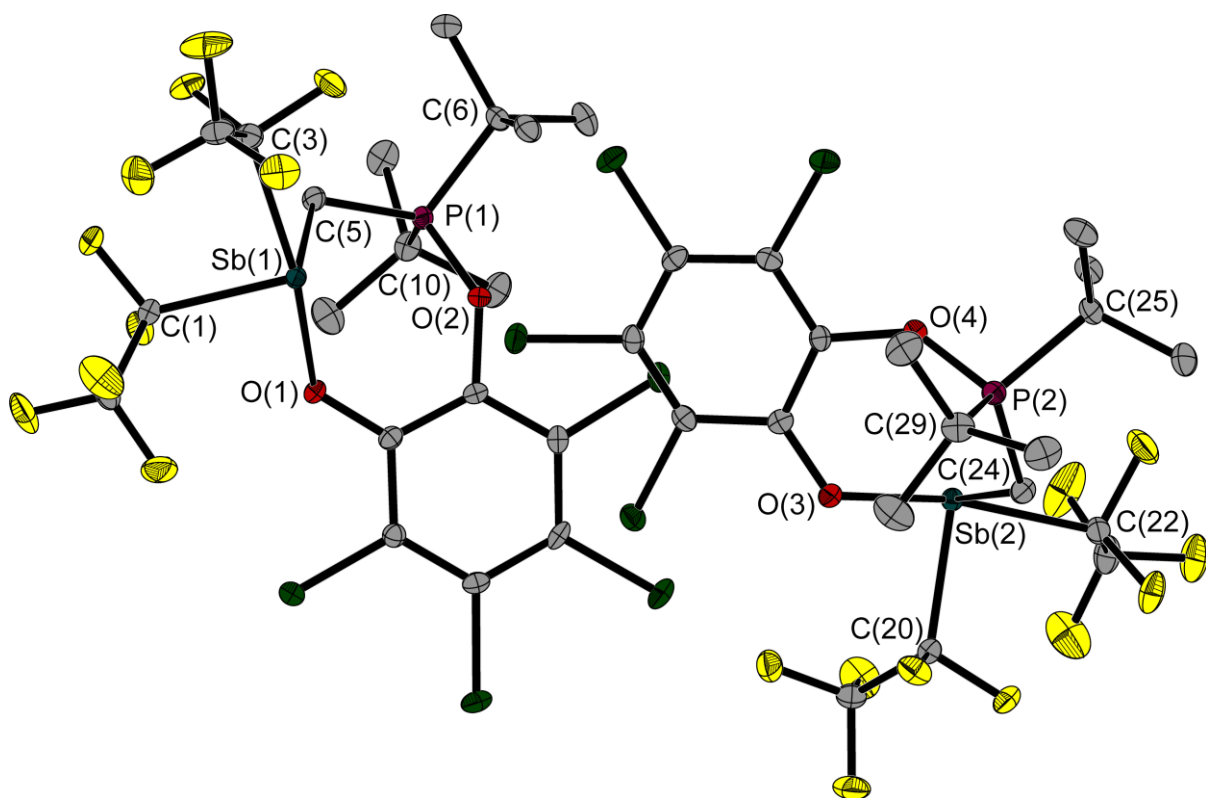


Figure S48 Molecular structure of compound **10** in the solid state. Ellipsoids are set at 50 % probability; hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°] for one of the two molecules in the asymmetric unit: Sb(1)–C(1) 2.242(2), Sb(1)–C(3) 2.316(2), Sb(1)–C(5) 2.186(2), Sb(1)–O(1) 2.316(1), P(1)–C(5) 1.782(2), P(1)–C(6) 1.847(2), P(1)–C(10) 1.848(2), P(1)–O(2) 1.593(1); C(1)–Sb(1)–C(3) 90.2(1), C(1)–Sb(1)–C(5) 92.4(1), C(5)–Sb(1)–C(3) 83.5(1), O(1)–Sb(1)–C(1) 78.4(1), O(1)–Sb(1)–C(3) 156.8(1), O(1)–Sb(1)–C(5) 77.0(1), C(5)–P(1)–C(6) 108.2(1), C(5)–P(1)–C(10) 111.0(1), C(6)–P(1)–C(10) 116.3(1), O(2)–P(1)–C(5) 111.4(1), O(2)–P(1)–C(6) 99.2(1), O(2)–P(1)–C(10) 110.2(1), P(1)–C(5)–Sb(1) 113.6(1).

X-Ray Diffraction Studies

Single crystals were examined on a Rigaku Supernova diffractometer. Using Olex2,² the structure was solved with the ShelXT³ structure solution program using Intrinsic Phasing and refined with the ShelXL⁴ refinement package using Least Squares minimisation.

The structure of **4** was solved with the ShelXS⁵ structure solution program using Direct Methods and also refined with ShelXL⁴ refinement package using Least Square minimisation.

A solution of **2** in *n*-hexane was cooled to -78 °C, whereupon colourless needle-shaped crystals suitable for diffraction experiments formed.

Beige crystals of **3** precipitated from a solution in toluene at 0 °C. Pseudo merohedral twin 1 0 0 0 -1 0 0 0 -1 2, BASF 0.14

Single crystals of **4** (colourless) and **5** (yellow) were received from saturated solutions in cyclopentane at -20 °C.

Single crystals of **6** (colourless), **9** (orange) and **10** (colourless) were received from saturated solutions in C₆D₆.

Recrystallisation of **7** and **8** in *n*-hexane led to single crystals (**7**: yellow, **8**: orange) suitable for diffraction experiments.

CCDC 2350426-2350434 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>

	2 ^[a]	3 ^[b]	4
Empirical formula	C ₁₃ H ₂₀ OF ₁₀ PSb	C ₁₃ H ₂₀ F ₁₀ PSSb	C ₁₃ H ₂₀ F ₁₀ PSbSe
<i>M_r</i>	535.01	551.07	597.97
λ [Å]	0.71073	0.71073	0.71073
<i>T</i> [K]	100.0(1)	100.0(1)	100.0(1)
<i>F</i> (000) [<i>e</i>]	1048	1080	1152
Crystal system	triclinic	monoclinic	orthorhombic
Space group	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁	<i>P</i> 2 ₁ 2 ₁ 2 ₁
<i>a</i> [Å]	10.6777(2)	6.5700(1)	6.71696(7)
<i>b</i> [Å]	11.9730(3)	24.8020(4)	11.89385(1)
<i>c</i> [Å]	15.3503(3)	11.8819(2)	24.6205(2)
α [°]	87.221(2)	90	90
β [°]	89.312(2)	90.318(2)	90
γ [°]	77.017(2)	90	90
<i>V</i> [Å ³]	1910.03(7)	1936.12(5)	1966.94(3)
<i>Z</i>	4	4	4
$\rho_{\text{calcd.}}$ [g cm ⁻³]	1.861	1.891	2.019
μ [mm ⁻¹]	1.621	1.702	3.420
2 θ range [°]	3.494–64.092	3.284–63.894	3.804–64.422
Index ranges <i>h</i>	–15 ≤ <i>h</i> ≤ 15	–9 ≤ <i>h</i> ≤ 9	–10 ≤ <i>h</i> ≤ 9
Index ranges <i>k</i>	–17 ≤ <i>k</i> ≤ 17	–36 ≤ <i>k</i> ≤ 35	–17 ≤ <i>k</i> ≤ 17
Index ranges <i>l</i>	–22 ≤ <i>l</i> ≤ 22	–17 ≤ <i>l</i> ≤ 17	–36 ≤ <i>l</i> ≤ 36
Reflexes collected	116799	38299	120071
Independent reflexes	20644	12310	6704
<i>R</i> _{int}	0.0270	0.0249	0.0363
Observed reflexes, <i>I</i> > 2 σ (<i>I</i>)	17695	12238	6490
Data/restraints/ parameters	20644/0/482	12310/1/482	6704/0/241
<i>R</i> ₁ / <i>wR</i> ₂ [<i>I</i> > 2 σ (<i>I</i>)]	0.0376/0.0926	0.0261/0.0650	0.0156/0.0304
<i>R</i> ₁ / <i>wR</i> ₂ (all data)	0.0452/0.0947	0.0265/0.0659	0.0175/0.0308
<i>GoF</i> on <i>F</i> ²	1.053	1.079	1.072
$\rho_{\text{max}}/\rho_{\text{min}}$ [<i>e</i> Å ⁻³]	2.15/–1.08	1.01/–1.04	0.54/–0.31
Flack parameter		–0.008(5)	0.0308(19)
CCDC number	2350426	2350427	2350428

[a] Twinned crystal, component 2 rotated by –179.9° around [0.01 0.03 1.00] (reciprocal) or [–0.00 –0.01 1.00] (direct), BASF 0.2505(5). [b] Pseudo merohedral twin, Matrix 1 0 0 0 –1 0 0 0 0 –1, ratio 86:14

	5	6	7
Empirical formula	C ₁₃ H ₂₀ F ₁₀ PSbTe	C ₁₉ H ₂₀ Cl ₄ F ₁₀ O ₃ PSb	C ₁₉ H ₂₀ Cl ₄ F ₁₀ O ₂ PSSb
<i>M_r</i>	646.61	780.87	796.93
λ [Å]	0.71073	0.71073	0.71073
<i>T</i> [K]	100.0(1)	100.0(1)	99.9(3)
<i>F</i> (000) [<i>e</i>]	612	764	4680
Crystal system	triclinic	triclinic	monoclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> [Å]	8.5637(2)	10.4459(2)	8.83394(11)
<i>b</i> [Å]	11.6657(3)	11.2266(2)	19.19795(19)
<i>c</i> [Å]	11.7952(3)	12.8446(3)	49.5311(5)
α [°]	93.533(2)	87.019(2)	90
β [°]	106.833(2)	72.235(2)	91.4434(10)
γ [°]	110.076(2)	68.647(2)	90
<i>V</i> [Å ³]	1042.20(5)	1333.05(5)	8397.50(16)
<i>Z</i>	2	2	12
$\rho_{\text{calcd.}}$ [g cm ⁻³]	2.060	1.945	1.891
μ [mm ⁻¹]	2.853	1.588	1.584
2 θ range [°]	3.666–64.26	3.336–64.7	5.078–60.068
Index ranges <i>h</i>	-12 ≤ <i>h</i> ≤ 12	-15 ≤ <i>h</i> ≤ 15	-12 ≤ <i>h</i> ≤ 12
Index ranges <i>k</i>	-17 ≤ <i>k</i> ≤ 17	-16 ≤ <i>k</i> ≤ 16	-27 ≤ <i>k</i> ≤ 27
Index ranges <i>l</i>	-17 ≤ <i>l</i> ≤ 17	-19 ≤ <i>l</i> ≤ 19	-69 ≤ <i>l</i> ≤ 69
Reflexes collected	31255	83450	162456
Independent reflexes	6853	8894	24488
<i>R</i> _{int}	0.0344	0.0466	0.0700
Observed reflexes, <i>I</i> > 2 σ (<i>I</i>)	6075	8214	22879
Data/restraints/ parameters	6853/0/241	8894/0/349	24488/13/1039
<i>R</i> ₁ / <i>wR</i> ₂ [<i>I</i> > 2 σ (<i>I</i>)]	0.0223/0.0455	0.0271/0.0673	0.0895/0.1561
<i>R</i> ₁ / <i>wR</i> ₂ (all data)	0.0271/0.0479	0.0309/0.0694	0.0956/0.1584
<i>GoF</i> on <i>F</i> ²	1.036	1.097	1.343
$\rho_{\text{max}}/\rho_{\text{min}}$ [<i>e</i> Å ⁻³]	0.73/-0.90	1.40/-0.63	1.41/-2.55
CCDC number	2350429	2350430	2350431

	8^[c]	9^[d]	10^[e]
Empirical formula	C ₁₉ H ₂₀ Cl ₄ F ₁₀ O ₂ PSbSe	C ₂₅ H ₂₀ Cl ₈ F ₁₀ O ₄ PSb	C ₁₉ H ₂₀ Cl ₄ F ₁₀ O ₂ PSb
<i>M_r</i>	843.83	1010.73	764.87
λ [Å]	1.54184	0.71073	0.71073
<i>T</i> [K]	100.0(1)	100.0(1)	100.0(1)
<i>F</i> (000) [<i>e</i>]	3264	3952	1496
Crystal system	monoclinic	monoclinic	triclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> $\bar{1}$
<i>a</i> [Å]	15.5087(4)	11.25738(7)	11.9408(3)
<i>b</i> [Å]	17.1296(4)	38.60501(18)	14.7066(4)
<i>c</i> [Å]	21.3832(7)	16.16983(12)	17.0446(4)
α [°]	90	90	77.029(2)
β [°]	94.395(3)	99.9478(7)	70.351(2)
γ [°]	90	90	69.951(2)
<i>V</i> [Å ³]	5663.9(3)	6921.62(8)	2627.82(13)
<i>Z</i>	8	8	4
$\rho_{\text{calcd.}}$ [g cm ⁻³]	1.979	1.940	1.933
μ [mm ⁻¹]	14.004	1.549	1.606
2 θ range [°]	5.716–136.496	3.316–60.066	2.97–64.456
Index ranges <i>h</i>	-12 ≤ <i>h</i> ≤ 18	-15 ≤ <i>h</i> ≤ 15	-17 ≤ <i>h</i> ≤ 17
Index ranges <i>k</i>	-20 ≤ <i>k</i> ≤ 20	-54 ≤ <i>k</i> ≤ 54	-21 ≤ <i>k</i> ≤ 21
Index ranges <i>l</i>	-25 ≤ <i>l</i> ≤ 25	-22 ≤ <i>l</i> ≤ 22	-25 ≤ <i>l</i> ≤ 25
Reflexes collected	46220	279858	94844
Independent reflexes	10305	20241	20292
<i>R</i> _{int}	0.0790	0.0455	0.0326
Observed reflexes, <i>I</i> > 2 σ (<i>I</i>)	8829	18660	17011
Data/restraints/ parameters	10305/0/698	20241/10/977	20292/0/680
<i>R</i> ₁ / <i>wR</i> ₂ [<i>I</i> > 2 σ (<i>I</i>)]	0.0580/0.1514	0.0526/0.1179	0.0220/0.0469
<i>R</i> ₁ / <i>wR</i> ₂ (all data)	0.0665/0.1602	0.0571/0.1199	0.0291/0.0479
<i>GoF</i> on <i>F</i> ²	1.058	1.217	0.897
$\rho_{\text{max}}/\rho_{\text{min}}$ [<i>e</i> Å ⁻³]	1.61/-1.98	1.74/-0.91	0.92/-0.47
CCDC number	2350432	2350433	2350434

[c] Small crystal and weak diffraction with Mo radiation, therefore, Cu radiation was used. [d] Disorder of C(29), F(17) to F(20), C(30), C(32), C(34) and C(36) over two sides (72:28). Suitable restraints and constraints were applied for disordered atoms. [e] Twinned crystal, component 2 rotated by -180.0° around [-0.32 0.01 0.95] (reciprocal) or [-0.71 0.00 0.71] (direct), ratio 60:40.

References

- 1 J. Kriefft, P. C. Trapp, Y. V. Vishnevskiy, B. Neumann, H.-G. Stammer and N. W. Mitzel, *Chem. Sci.* 2024, *in press*.
- 2 O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Crystallogr.*, 2009, **42**, 339–341.
- 3 G. M. Sheldrick, *Acta Crystallogr., Sect. A*, 2015, **71**, 3–8.
- 4 G. M. Sheldrick, *Acta Crystallogr., Sect. C*, 2015, **71**, 3–8.
- 5 G. M. Sheldrick, *Acta Crystallogr., Sect. A*, 2008, **64**, 112–122.