Supporting Information

Polydentate Chalcogen Bonding: Anion Trapping with a Water-stable Host Compound Carrying Se–CF_3 Functions

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Experimental procedures

General considerations

Reactions under inert conditions were performed using conventional Schlenk techniques with nitrogen as inert gas or in a glove box with argon as inert gas. Volatile compounds were handled using standard high-vacuum techniques. THF was dried over potassium, benzene was dried over Na/K alloy and dichloromethane and chloroform were dried over calcium hydride or molecular sieve. All solvents were distilled and degassed prior to use.

Chemicals were purchased from commercial sources and were dried prior to use, if necessary [2-bromopropane (99 %), tetraphenylphosphonium chloride (98 %), tetraphenylphosphonium bromide (97 %), tetraphenylphosphonium iodide (98 %), sulfuryl chloride (98.5 %)].

1,8-Bis[(trimethylstannyl)ethynyl]anthracene (**3**)[1] and the *syn*-photodimer of 1,8-bis[(trimethylstannyl)ethynyl]anthracene (**4**)[2], benzyl(trifluoromethyl) selenide (**6**)[3], the ethyl derivate of the Schwesinger base, P_4-*t*-Bu (**7**)[4] and its hydrochloride [**7**·H]Cl[4] were prepared according to the literature. Additionally, a modified protocol for the synthesis and purification of (trifluoromethyl)-selanylchloride (**5**)[5] is presented in the syntheses section.

NMR spectra were recorded on a Bruker Avance III 300 and Avance III 500 HD spectrometer at ambient temperature. Chemical shifts were referenced to the residual proton or carbon signal of the solvent (CD_2Cl_2: ^{1}H: 5.32 ppm, ^{13}C: 54.0 ppm; $CDCl_3$: ^{1}H: 7.26 ppm, ^{13}C: 77.2 ppm) or externally (^{19}F: $CFCl_3$, ^{77}Se: $SeMe_2$). Elemental analyses were carried out using an EURO EA Elemental Analyzer. SC-XRD was performed on a Rigaku Supernova diffractometer using Cu-Kα or Mo-Kα radiation.

Syntheses

1,8-Bis[(trifluoromethylselanly)ethynyl]anthracene (1): To a solution of 1,8-bis[(trimethylstannyl)ethynyl]anthracene (**3**, 800 mg, 1.45 mmol) in dichloromethane (10 mL) (trifluoromethyl)selanylchloride (**5**, 3.40 mmol, 2.3 eq.) was added by condensation using high vacuum techniques. The reaction mixture was stirred at 0 °C for 15 min and additional 30 min at ambient temperature. All volatile compounds were removed under reduced pressure and 1,8-bis[(trifluoromethylselanyl)-ethynyl]anthracene (**1**, 753 mg, 1.45 mmol, quant. yield) was obtained as a yellow solid. If the product is impure for some reason, we recommend recrystallization from carbon tetrachloride or washing with *n*-hexane using a glass frit. – ^{1}H NMR (500 MHz, $CDCl_3$): δ [ppm] = 9.07 (s, 1H, H9), 8.34 (s, 1H, H10), 7.97 (d, $^3J_{H,H}$ = 8.5 Hz, 2H, H4/H5), 7.74 (d, $^3J_{H,H}$ = 6.9 Hz, 2H, H2/H7), 7.42 (dd, $^3J_{H,H}$ = 8.5 Hz, 6.9 Hz, 2H, H3/H6). – ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ [ppm] = 132.4 (s, C2/C7), 131.5 (s, C^q), 131.4 (s, C^q), 130.4 (s, C4/C5), 127.9 (s, C10), 125.1 (s, C3/C6), 123.3 (s, C9), 121.0 (q, $^1J_{F,C}$ = 336.6 Hz, CF_3), 120.2 (s, C^q), 105.4 (s, **C**≡C–Se), 67.3 (s, C≡**C**–Se). – ^{19}F NMR (471 MHz, $CDCl_3$): δ [ppm] = −35.8 (s, CF_3). – ^{77}Se NMR (96 MHz, $CDCl_3$): δ [ppm] = 455.7 (s, $SeCF_3$). – Elemental analysis calcd (%) for $C_{20}H_8F_6Se_2$ (M_r = 520.22): C 46.18, H 1.55; found: C 46.10, H 1.51.

***Syn*-dimer of 1,8-bis[(trifluoromethylselanly)ethynyl]anthracene (2):** To a solution of the *syn*-dimer of 1,8-bis[(trimethyl-stannyl)ethynyl]anthracene (**4**, 815 mg, 738 µmol) in dichloromethane (10 mL) (trifluoromethyl)selanylchloride (**5**, 4.4 mmol, 6 eq.) was added by condensation using high vacuum techniques. The reaction mixture was stirred at 0 °C for 30 min and additional 3 h at ambient temperature. All volatile compounds were removed under reduced pressure and the *syn*-dimer of 1,8-bis[(trifluoromethylselanly)ethynyl]anthracene (**2**, 768 mg, 738 µmol, quant.) was obtained as a beige solid. If the product is impure for some reason, we recommend recrystallization from benzene. – ^{1}H NMR (500 MHz, $CDCl_3$): δ [ppm] = 7.07 (dd, $^3J_{H,H}$ = 7.7 Hz, $^4J_{H,H}$ = 1.3 Hz, 4H, H2/H7), 6.93 (dd, $^3J_{H,H}$ = 7.3 Hz, $^4J_{H,H}$ = 1.3 Hz, 4H, H4/H5), 6.84 (t, $^3J_{H,H}$ = 7.6 Hz, 4H, H3/H6), 5.74 (s, 2H, H9), 4.55 (s, 2H, H10). – ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ [ppm] = 144.4 (s, C^q), 143.4 (s, C^q), 130.5 (s, C2/C7), 128.2 (s, C4/C5), 126.2 (s, C3/C6), 120.9 (q, $^1J_{F,C}$ = 336.9 Hz, CF_3), 120.6 (s, C^q), 105.7 (s, **C**≡C–Se), 65.9 (s, C≡**C**–Se), 53.3 (s, C10), 47.7 (s, C9). – ^{19}F NMR (471 MHz, $CDCl_3$): δ [ppm] = −36.0 (s, CF_3). – ^{77}Se NMR (96 MHz, $CDCl_3$): δ [ppm] = 454.8 (s, $SeCF_3$). – Elemental analysis calcd (%) for $C_{40}H_{16}F_{12}Se_4$ (M_r = 1040.43): C 46.18, H 1.55; found: C 45.97, H 1.46.

(Trifluoromethyl)selanylchloride, $ClSeCF_3$ (5):

This is an alternative procedure to the original protocol by Wakeman[5] for the synthesis of $ClSeCF_3$, which uses a high vacuum line and isothermal distillation techniques. The method described here allowed the complete removal of SO_2, which was necessary for the *in situ* crystallization of $ClSeCF_3$ (**5**), but is not necessary for the tin-selenium exchange reactions described above.

Benzyl(trifluoromethyl) selenide (**6**, 6.30 g, 26.3 mmol) was placed in an ampoule, equipped with a magnetic stirring bar and cooled with liquid nitrogen. Sulfuryl chloride (3.55 g, 26.3 mmol) was added in one portion and the mixture was slowly allowed to reach ambient temperature. After 15 min at ambient temperature, all volatile compounds were transferred into another ampoule by condensation using a high vacuum line. This condensated mixture, mainly containing $ClSeCF_3$ (**5**), SO_2 (approx. 1:1) and minor amounts of volatile selenium compounds was purified by isothermal fractional distillation (column temperature: −40 °C). $ClSeCF_3$ (**5**, 3.00 g, 16.4 mmol, 62 %) was isolated after the SO_2 fraction as a deep red, volatile liquid. The NMR data were in total accordance with the literature.[5]

[{$(Et_2N)_3PN$}$_3PN(H)^tBu$]Br ([7·H]Br):

To a solution of **7** (4.11 g, 4.64 mmol) in *n*-pentane (100 mL), 2-bromopropane (0.6 mL, 6 mmol) was added with a syringe. After the reaction mixture has been stirred overnight at ambient temperature, the supernatant solution was removed. The precipitate was washed with *n*-pentane (3 x 30 mL). All volatile compounds were removed under reduced pressure and [**7**·H]Br (4.19 g, 4.33 mmol, 93%) was obtained as a colorless solid. – ^{1}H NMR (500 MHz, $CDCl_3$): δ [ppm] = 3.08 (dq, $^3J_{P,H}$ = 10.0 Hz, $^3J_{H,H}$ = 7.1 Hz, 36H, NC**H**$_2$CH$_3$), 1.98 (d, $^2J_{P,H}$ = 7.6 Hz, 1H, NH), 1.23 (s, 9H, C(CH$_3$)$_3$), 1.05 (t, $^3J_{H,H}$ = 7.1 Hz, 54H, NCH$_2$C**H**$_3$). – ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ [ppm] = 50.7 (d, $^2J_{P,C}$ = 3.7 Hz, **C**(CH$_3$)$_3$), 39.1 (d, $^2J_{P,C}$ = 5.5 Hz, N**C**H$_2$CH$_3$), 31.5 (d, $^3J_{P,C}$ = 4.8 Hz, C(**C**H$_3$)$_3$), 13.5 (d, $^3J_{P,C}$ = 3.2 Hz, NCH$_2$**C**H$_3$). – ^{31}P NMR (203 MHz, $CDCl_3$): δ [ppm] = 7.4 (d, tridec, $^2J_{P,P}$ = 70.4 Hz, $^3J_{P,H}$ = 10.0 Hz, NP(NEt$_2$)$_3$), −33.9 (qd, $^2J_{P,P}$ = 70.5 Hz, $^2J_{P,H}$ = 7.5 Hz, PN^{t}Bu). – Elemental analysis calcd (%) for $C_{40}H_{100}N_{13}P_4Br$ (M_r = 967.13): C 49.68, H 10.42, N 18.83, Br 8.26; found: C 49.75, H 10.37, N 18.91.

[{$(Et_2N)_3PN$}$_3PN(H)^tBu$]I ([7·H]I):

To a solution of [**7**·H]Cl (4.88 g, 5.29 mmol) in acetone (100 mL), sodium iodide (0.81 g, 5.4 mmol) was added. After the reaction mixture was stirred overnight at ambient temperature, the suspension was filtered with a glass frit. Crystallization of the filtrate yielded [**7**·H]I (4.57 g, 4.51 mmol, 85%) as a colorless solid. – ^{1}H NMR (500 MHz, $CDCl_3$): δ [ppm] = 3.09 (dq, $^3J_{P,H}$ = 10.0 Hz, $^3J_{H,H}$ = 7.1 Hz, 36H, NC**H**$_2$CH$_3$), 1.99 (d, $^2J_{P,H}$ = 7.6 Hz, 1H, NH), 1.24 (s, 9H, C(CH$_3$)$_3$), 1.06 (t, $^3J_{H,H}$ = 7.1 Hz, 54H, NCH$_2$C**H**$_3$). – ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ [ppm] = 50.7 (d, $^2J_{P,C}$ = 3.8 Hz, **C**(CH$_3$)$_3$), 39.1 (d, $^2J_{P,C}$ = 5.5 Hz, N**C**H$_2$CH$_3$), 31.5 (d, $^3J_{P,C}$ = 5.0 Hz, C(**C**H$_3$)$_3$), 13.6 (d, $^3J_{P,C}$ = 3.2 Hz, NCH$_2$**C**H$_3$). – ^{31}P NMR (203 MHz, $CDCl_3$): δ [ppm] = 7.4 (d, tridec, $^2J_{P,P}$ = 70.4 Hz, $^3J_{P,H}$ = 9.9 Hz, NP(NEt$_2$)$_3$), −33.9 (qd, $^2J_{P,P}$ = 70.4 Hz, $^2J_{P,H}$ = 7.6 Hz, PN^{t}Bu). – Elemental analysis calcd (%) for $C_{40}H_{100}N_{13}P_4I$ (M_r = 1014.13): C 47.37, H 9.94, N 17.96, I 12.51; found: C 47.25, H 9.94, N 17.91.

Crystallization of hosts 1 , host 2, the adduct [1·2 THF]$_2$, the salts [7·H]Br and [7·H]I and $ClSeCF_3$ (5):

Host system **1** was crystallized by concentrating a solution of the compound in a mixture of toluene and *n*-hexane or by cooling a hot saturated solution in carbon tetrachloride. The adduct [**1**·2 THF]$_2$ was crystallized by slowly evaporating solvent from a saturated solution of host system **1** in THF. Host system **2** was crystallized by cooling a hot saturated solution of the compound in benzene. Crystals of (trifluoromethyl)selanyl chloride (**5**) were grown by the *in situ* crystallization technique[6] in a sealed capillary in which a small amount of **5** was placed (for details see the Crystallographic data section). [**7**·H]Br was crystallized by cooling a solution of the compound in dichloromethane and [**7**·H]I was crystallized as a cocrystal with acetone by cooling a solution of the compound in acetone.

General procedure for the preparation and crystallization of the halide adducts of host 2:

The halide adducts [**2**·Cl][PPh$_4$], [**2**·Cl][**7**·H], [**2**·Br][**7**·H] and [**2**·I][**7**·H] were prepared in quantitative yield by adding one equivalent of the respective halide salt to a solution of host **2** in $CDCl_3$ in a Young NMR tube. After preparation, the adducts were analyzed by NMR spectroscopy. Single crystals of the adducts suitable for X-ray diffraction were obtained by suspending the host compound and 1.1 equivalents of halide salt in a mixture of benzene and dichloromethane (approx. 20 µmol in 0.6 mL benzene and 0.05 mL dichloromethane) in a sealed vessel. This suspension was heated until it is completely dissolved and then allowed to slowly reach ambient temperature, at which point partially crystalline material of the halide adduct precipitates. The substance for elemental analysis was prepared by washing this precipitate with *n*-hexane, followed by drying the substance *in vacuo*. The NMR spectroscopy data and elemental analyses for the compounds are provided below. Attempts to obtain single crystals of the adducts [**2**·Br][PPh$_4$] and [**2**·I][PPh$_4$] failed: in case of [**2**·Br][PPh$_4$], the crystal was not suitable for SC-XRD and in case of [**2**·I][PPh$_4$], the crystals obtained were found to be 'free' host **2** as well as PPh$_4$I.

Analytical data of [**2**·Cl][PPh$_4$]:

^{1}H NMR (500 MHz, CDCl$_3$): δ [ppm] = 7.90 (m, 4H, H^p), 7.79 (m, 8H, H^o), 7.61 (m, 8H, H^m), 7.04 (dd, $^3J_{\mathrm{H,H}}$ = 7.8 Hz, $^4J_{\mathrm{H,H}}$ = 1.2 Hz, 4H, H2/H7), 6.92 (dd, $^3J_{\mathrm{H,H}}$ = 7.4 Hz, $^4J_{\mathrm{H,H}}$ = 1.3 Hz, 4H, H4/H5), 6.82 (t, $^3J_{\mathrm{H,H}}$ = 7.6 Hz, 4H, H3/H6), 5.71 (s, 2H, H9), 4.55 (s, 2H, H10). – ^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$): δ [ppm] = 144.4 (s, C^q), 143.4 (s, C^q), 136.0 (d, $^4J_{\mathrm{P,C}}$ = 3.0 Hz, C^p), 134.5 (d, $^3J_{\mathrm{P,C}}$ = 10.3 Hz, C^m), 131.0 (d, $^2J_{\mathrm{P,C}}$ = 12.9 Hz, C^o), 130.4 (s, C2/C7), 128.2 (s, C4/C5), 126.2 (s, C3/C6), 120.8 (q, $^1J_{\mathrm{F,C}}$ = 336.9 Hz, CF$_3$), 120.5 (s, C^q), 117.5 (d, $^1J_{\mathrm{P,C}}$ = 89.5 Hz, C^i), 105.7 (s, **C**≡C–Se), 65.8 (s, C≡**C**–Se), 53.2 (s, C10), 47.7 (s, C9). – ^{19}F NMR (471 MHz, CDCl$_3$): δ [ppm] = −36.1 (s, CF$_3$). – ^{31}P NMR (203 MHz, CDCl$_3$): δ [ppm] = 23.2 (m, PPh$_4$). – ^{77}Se NMR (96 MHz, CDCl$_3$): δ [ppm] = 454.8 (s, SeCF$_3$). – Elemental analysis calcd (%) for C$_{64}$H$_{36}$ClF$_{12}$PSe$_4$· 2 C$_6$H$_6$ (M_r = 1571.51): C 58.09, H 3.08; found: C 58.15, H 2.87.

Analytical data of [**2**·Cl][**7**·H]:

^{1}H NMR (500 MHz, CDCl$_3$): δ [ppm] = 7.04 (dd, $^3J_{\mathrm{H,H}}$ = 7.8 Hz, $^4J_{\mathrm{H,H}}$ = 1.3 Hz, 4H, H2/H7), 6.93 (dd, $^3J_{\mathrm{H,H}}$ = 7.5 Hz, $^4J_{\mathrm{H,H}}$ = 1.3 Hz, 4H, H4/H5), 6.82 (t, $^3J_{\mathrm{H,H}}$ = 7.6 Hz, 4H, H3/H6), 5.70 (s, 2H, H9), 4.56 (s, 2H, H10), 3.10 (dq, $^3J_{\mathrm{P,H}}$ = 10.0 Hz, $^3J_{\mathrm{H,H}}$ = 7.1 Hz, 36H, NC**H**$_2$CH$_3$), 2.00 (d, $^2J_{\mathrm{P,H}}$ = 7.7 Hz, 1H, NH), 1.25 (s, 9H, C(CH$_3$)$_3$), 1.07 (t, $^3J_{\mathrm{H,H}}$ = 7.1 Hz, 54H, NCH$_2$C**H**$_3$). – ^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$): δ [ppm] = 144.4 (s, C^q), 143.4 (s, C^q), 130.4 (s, C2/C7), 128.3 (s, C4/C5), 126.2 (s, C3/C6), 120.8 (q, $^1J_{\mathrm{F,C}}$ = 336.9 Hz, CF$_3$), 120.4 (s, C^q), 105.7 (s, **C**≡C–Se), 65.7 (s, C≡**C**–Se), 53.2 (s, C10), 50.8 (d, $^2J_{\mathrm{P,C}}$ = 3.8 Hz, **C**(CH$_3$)$_3$), 47.7 (s, C9), 39.1 (d, $^2J_{\mathrm{P,C}}$ = 5.5 Hz, N**C**H$_2$CH$_3$), 31.6 (d, $^3J_{\mathrm{P,C}}$ = 4.7 Hz, C(**C**H$_3$)$_3$), 13.6 (d, $^3J_{\mathrm{P,C}}$ = 2.9 Hz, NCH$_2$**C**H$_3$). – ^{19}F NMR (471 MHz, CDCl$_3$): δ [ppm] = −36.1 (s, CF$_3$). – ^{31}P NMR (203 MHz, CDCl$_3$): δ [ppm] = 7.4 (d, tridec, $^2J_{\mathrm{P,P}}$ = 70.3 Hz, $^3J_{\mathrm{P,H}}$ = 10.0 Hz, NP(NEt$_2$)$_3$), −33.9 (qd, $^2J_{\mathrm{P,P}}$ = 70.5 Hz, $^2J_{\mathrm{P,H}}$ = 7.5 Hz, PN^{t}Bu). – ^{77}Se NMR (96 MHz, CDCl$_3$): δ [ppm] = 454.6 (s, SeCF$_3$). – Elemental analysis calcd (%) for C$_{80}$H$_{116}$ClF$_{12}$N$_{13}$P$_4$Se$_4$ (M_r = 1963.11): C 48.95, H 5.96, N 9.28; found: C 48.99, H 6.02, N 9.11.

Analytical data of [**2**·Br][**7**·H]:

^{1}H NMR (500 MHz, CDCl$_3$): δ [ppm] = 7.03 (dd, $^3J_{\mathrm{H,H}}$ = 7.8 Hz, $^4J_{\mathrm{H,H}}$ = 1.3 Hz, 4H, H2/H7), 6.95 (dd, $^3J_{\mathrm{H,H}}$ = 7.5 Hz, $^4J_{\mathrm{H,H}}$ = 1.3 Hz, 4H, H4/H5), 6.81 (t, $^3J_{\mathrm{H,H}}$ = 7.6 Hz, 4H, H3/H6), 5.70 (s, 2H, H9), 4.60 (s, 2H, H10), 3.09 (dq, $^3J_{\mathrm{P,H}}$ = 10.0 Hz, $^3J_{\mathrm{H,H}}$ = 7.1 Hz, 36H, NC**H**$_2$CH$_3$), 1.99 (d, $^2J_{\mathrm{P,H}}$ = 7.6 Hz, 1H, NH), 1.24 (s, 9H, C(CH$_3$)$_3$), 1.06 (t, $^3J_{\mathrm{H,H}}$ = 7.1 Hz, 54H, NCH$_2$C**H**$_3$). – ^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$): δ [ppm] = 144.4 (s, C^q), 143.5 (s, C^q), 130.3 (s, C2/C7), 128.3 (s, C4/C5), 126.1 (s, C3/C6), 120.8 (q, $^1J_{\mathrm{F,C}}$ = 336.8 Hz, CF$_3$), 120.4 (s, C^q), 105.7 (s, **C**≡C–Se), 65.6 (s, C≡**C**–Se), 53.1 (s, C10), 50.8 (d, $^2J_{\mathrm{P,C}}$ = 3.7 Hz, **C**(CH$_3$)$_3$), 47.7 (s, C9), 39.1 (d, $^2J_{\mathrm{P,C}}$ = 5.6 Hz, N**C**H$_2$CH$_3$), 31.5 (d, $^3J_{\mathrm{P,C}}$ = 5.2 Hz, C(**C**H$_3$)$_3$), 13.6 (d, $^3J_{\mathrm{P,C}}$ = 3.0 Hz, NCH$_2$**C**H$_3$). – ^{19}F NMR (471 MHz, CDCl$_3$): δ [ppm] = −36.1 (s, CF$_3$). – ^{31}P NMR (203 MHz, CDCl$_3$): δ [ppm] = 7.4 (d, tridec, $^2J_{\mathrm{P,P}}$ = 70.4 Hz, $^3J_{\mathrm{P,H}}$ = 10.0 Hz, NP(NEt$_2$)$_3$), −33.9 (qd, $^2J_{\mathrm{P,P}}$ = 70.4 Hz, $^2J_{\mathrm{P,H}}$ = 7.7 Hz, PN^{t}Bu). – ^{77}Se NMR (96 MHz, CDCl$_3$): δ [ppm] = 454.7 (s, SeCF$_3$). – Elemental analysis calcd (%) for C$_{80}$H$_{116}$BrF$_{12}$N$_{13}$P$_4$Se$_4$ (M_r = 2007.56): C 47.86, H 5.82, N 9.07; found: C 47.74, H 5.81, N 8.91.

Analytical data of [**2**·I][**7**·H]:

^{1}H NMR (500 MHz, CDCl$_3$): δ [ppm] = 7.03 (dd, $^3J_{\mathrm{H,H}}$ = 7.7 Hz, $^4J_{\mathrm{H,H}}$ = 1.3 Hz, 4H, H2/H7), 6.96 (dd, $^3J_{\mathrm{H,H}}$ = 7.4 Hz, $^4J_{\mathrm{H,H}}$ = 1.3 Hz, 4H, H4/H5), 6.82 (t, $^3J_{\mathrm{H,H}}$ = 7.6 Hz, 4H, H3/H6), 5.70 (s, 2H, H9), 4.61 (s, 2H, H10), 3.10 (dq, $^3J_{\mathrm{P,H}}$ = 10.0 Hz, $^3J_{\mathrm{H,H}}$ = 7.1 Hz, 36H, NC**H**$_2$CH$_3$), 2.00 (d, $^2J_{\mathrm{P,H}}$ = 7.6 Hz, 1H, NH), 1.25 (s, 9H, C(CH$_3$)$_3$), 1.07 (t, $^3J_{\mathrm{H,H}}$ = 7.1 Hz, 54H, NCH$_2$C**H**$_3$). – ^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$): δ [ppm] = 144.4 (s, C^q), 143.5 (s, C^q), 130.3 (s, C2/C7), 128.3 (s, C4/C5), 126.1 (s, C3/C6), 120.8 (q,

$^1J_{F,C}$ = 336.8 Hz, CF_3), 120.4 (s, C^q), 105.7 (s, **C**≡C–Se), 65.6 (s, C≡**C**–Se), 53.1 (s, C10), 50.8 (d, $^2J_{P,C}$ = 3.8 Hz, **C**$(CH_3)_3$), 47.7 (s, C9), 39.1 (d, $^2J_{P,C}$ = 5.5 Hz, N**C**H_2CH_3), 31.5 (d, $^3J_{P,C}$ = 5.0 Hz, C(**C**$H_3)_3$), 13.6 (d, $^3J_{P,C}$ = 3.1 Hz, NCH_2**C**H_3). – ^{19}F NMR (471 MHz, $CDCl_3$): δ [ppm] = −36.1 (s, CF_3). – ^{31}P NMR (203 MHz, $CDCl_3$): δ [ppm] = 7.4 (d, tridec, $^2J_{P,P}$ = 70.4 Hz, $^3J_{P,H}$ = 10.0 Hz, $NP(NEt_2)_3$), −33.9 (qd, $^2J_{P,P}$ = 70.2 Hz, $^2J_{P,H}$ = 7.5 Hz, PN^tBu). – ^{77}Se NMR (96 MHz, $CDCl_3$): δ [ppm] = 454.7 (s, $SeCF_3$). – Elemental analysis calcd (%) for $C_{80}H_{116}IF_{12}N_{13}P_4Se_4$ (M_r = 2054.56): C 46.77, H 5.69, N 8.86; found: C 46.97, H 5.64, N 8.74.

NMR spectroscopic data

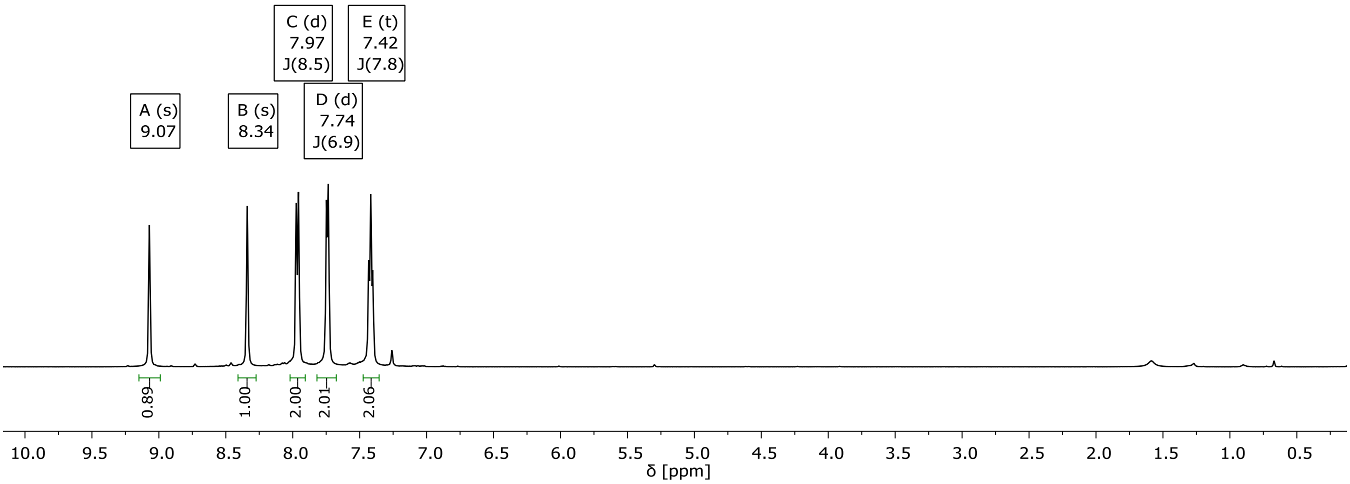

Figure S1. ^{1}H NMR spectrum of **1** in $CDCl_3$ (500 MHz)

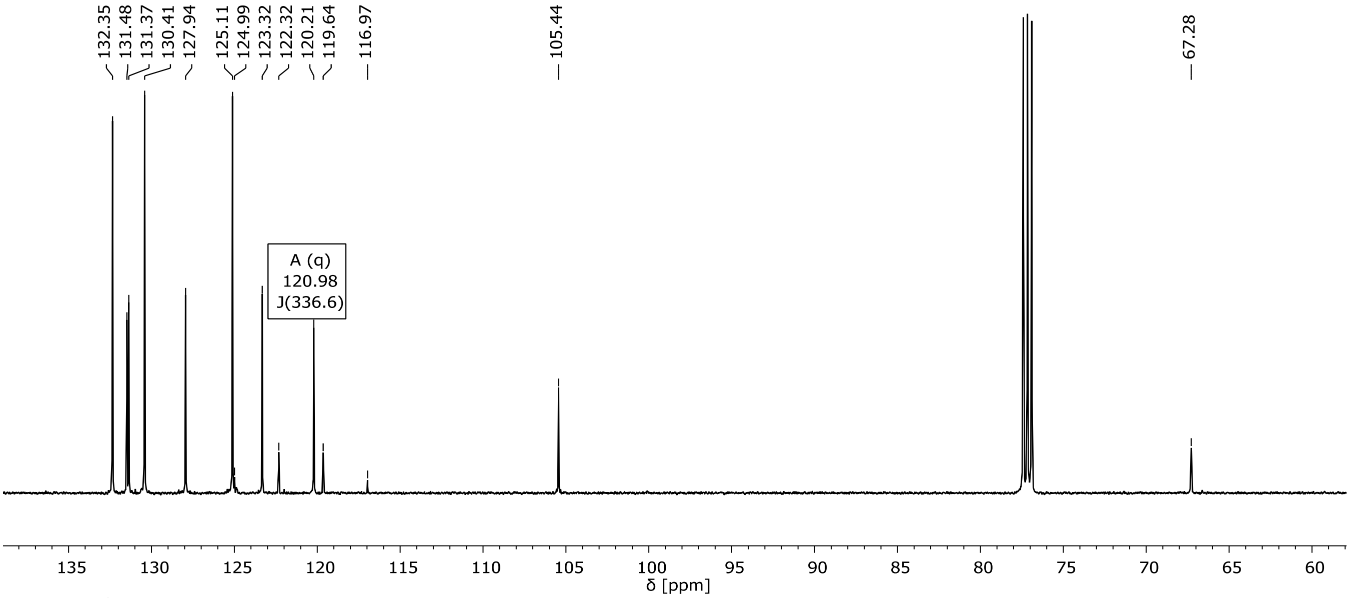

Figure S2. $^{13}C\{^1H\}$ NMR spectrum of **1** in $CDCl_3$ (126 MHz)

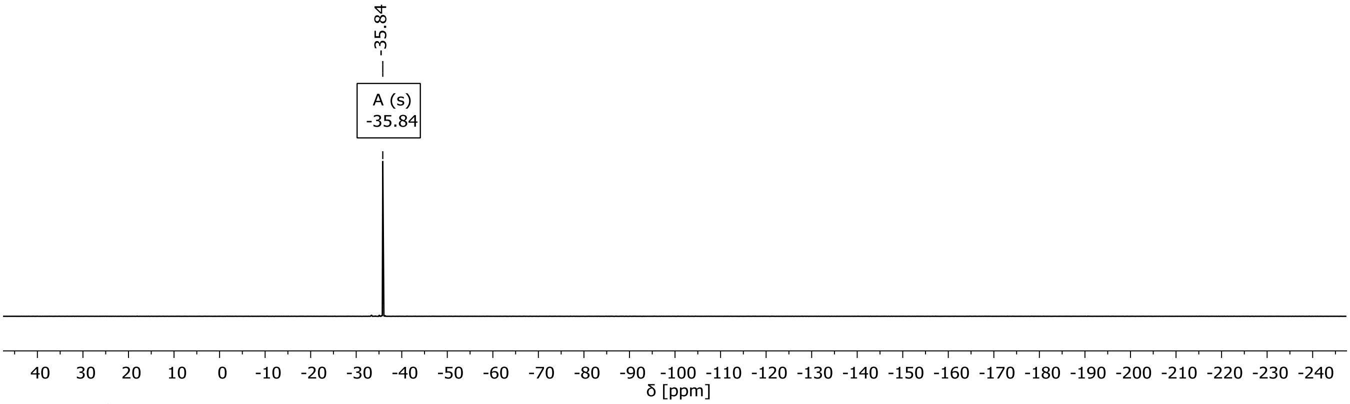

Figure S3. ^{19}F NMR spectrum of **1** in $CDCl_3$ (471 MHz)

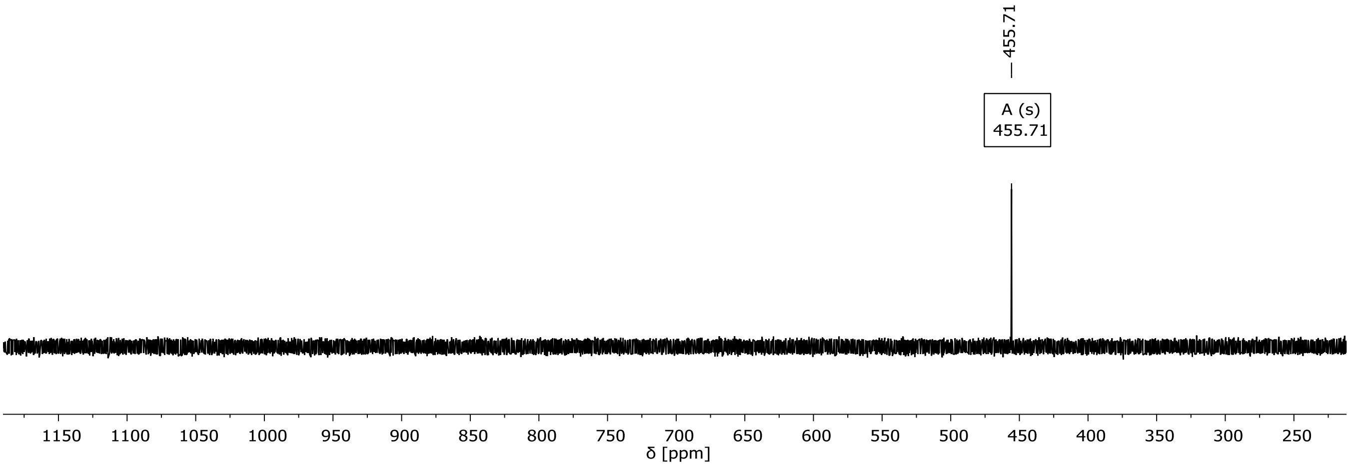

Figure S4. ^{77}Se NMR spectrum of **1** in $CDCl_3$ (96 MHz)

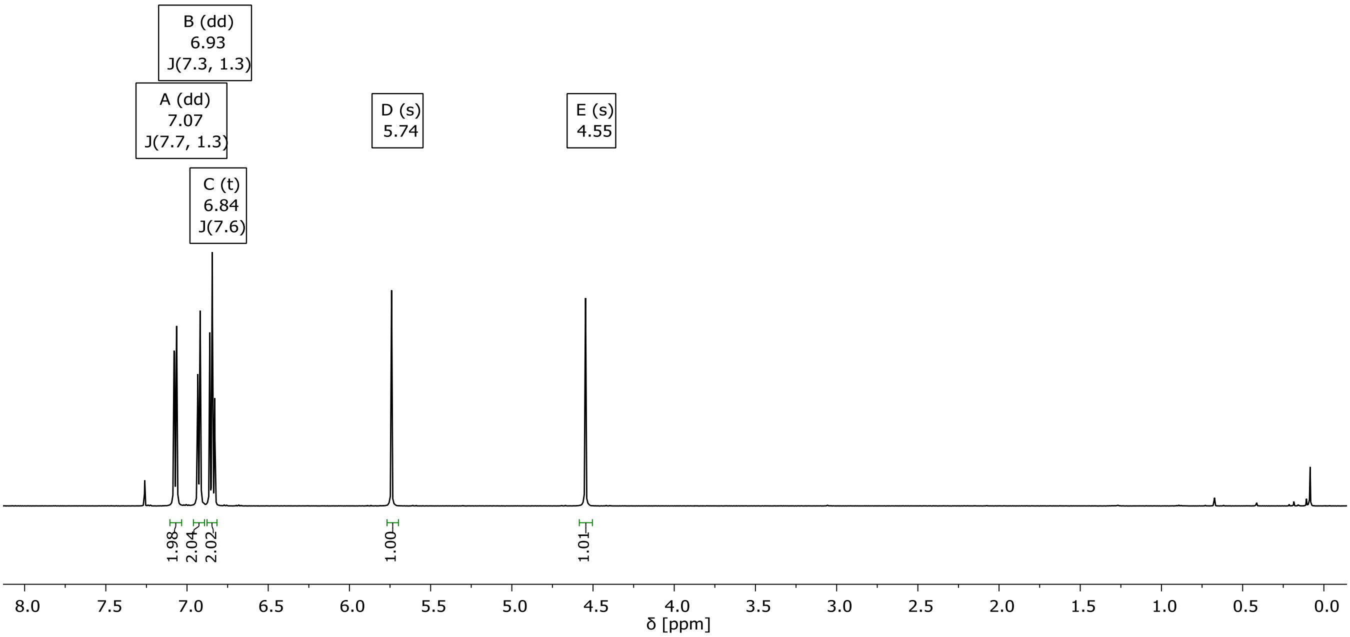

Figure S5. ^{1}H NMR spectrum of **2** in $CDCl_3$ (500 MHz)

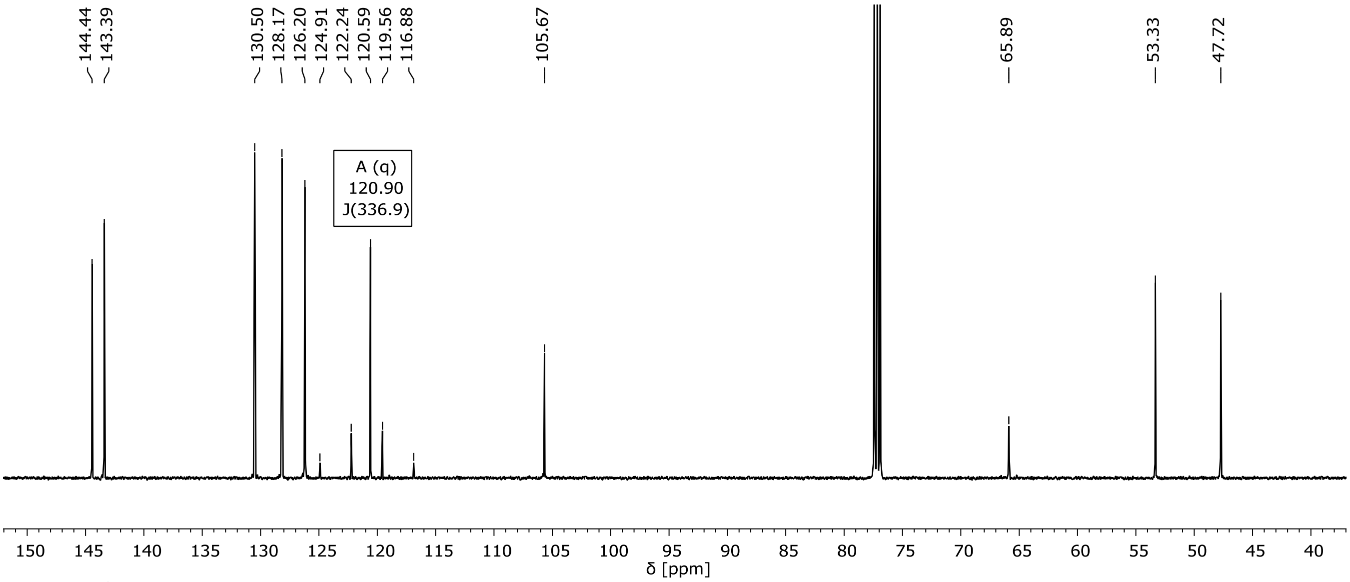

Figure S6. $^{13}C\{^{1}H\}$ NMR spectrum of **2** in $CDCl_3$ (126 MHz)

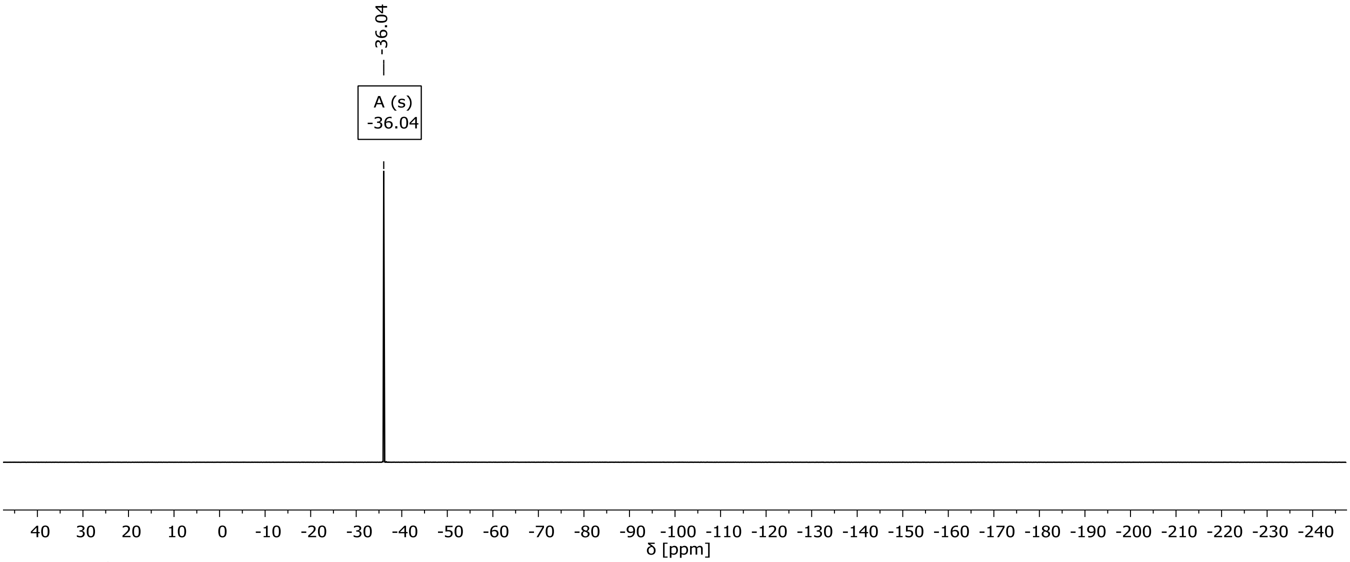

Figure S7. ^{19}F NMR spectrum of **2** in $CDCl_3$ (471 MHz)

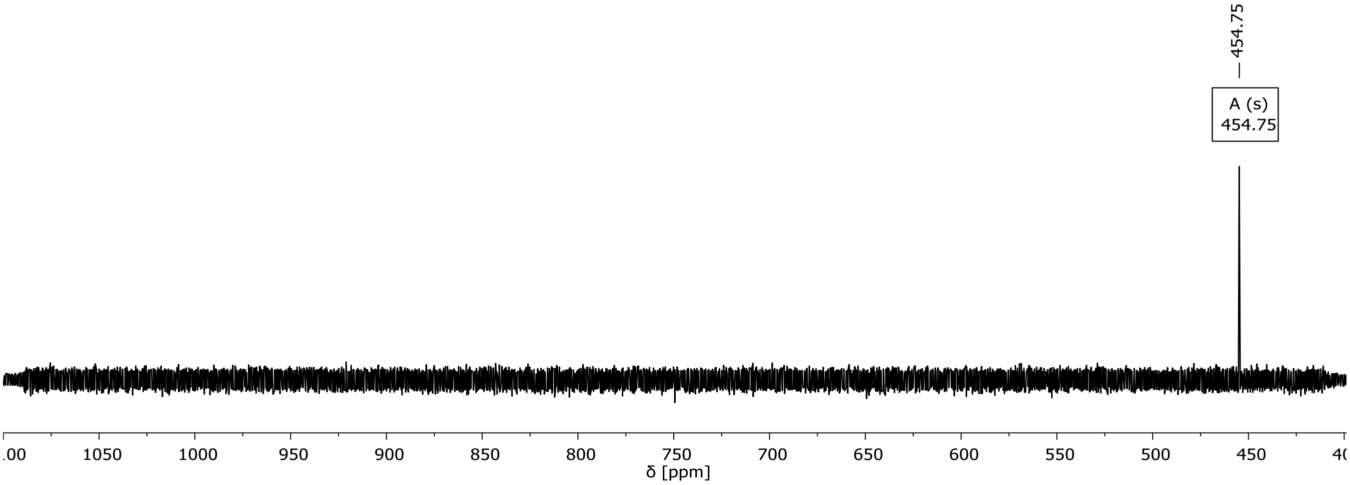

Figure S8. ^{77}Se NMR spectrum of **2** in $CDCl_3$ (96 MHz)

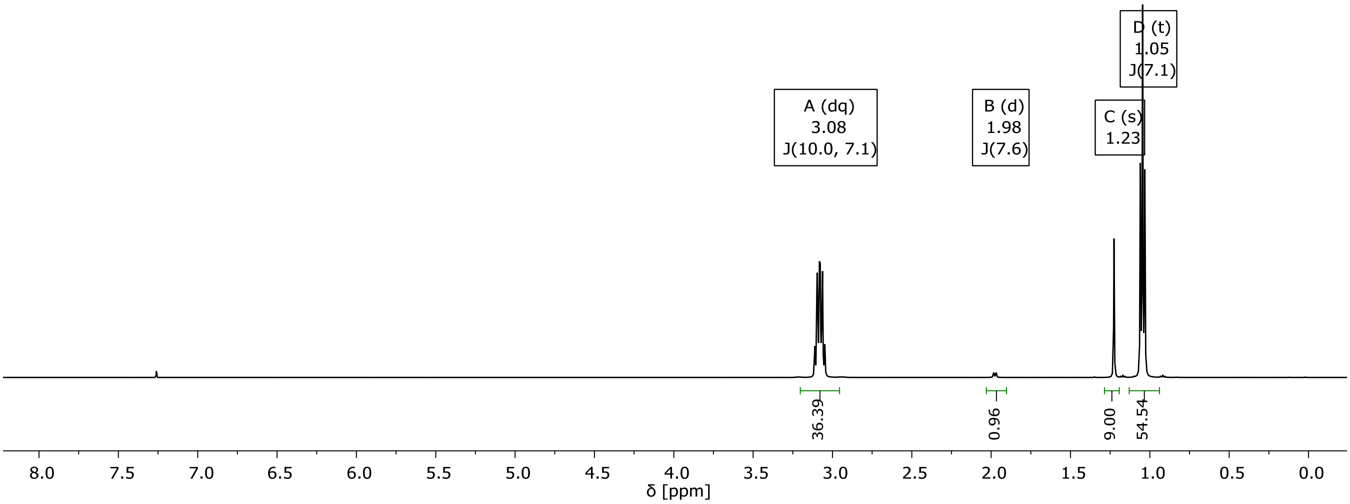

Figure S9. ^{1}H NMR spectrum of [**7**·H]Br in $CDCl_3$ (500 MHz)

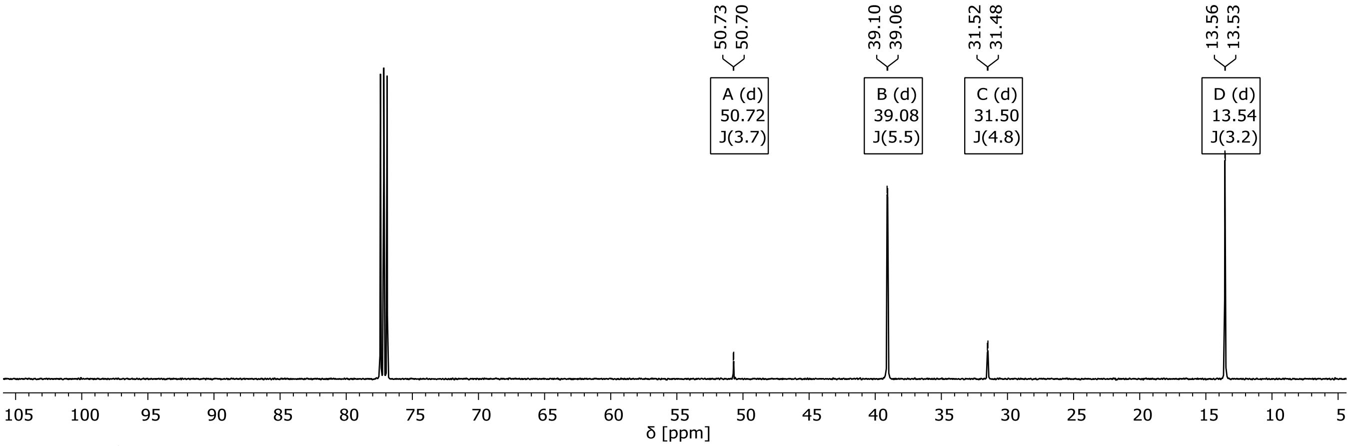

Figure S10. ^{13}C{^{1}H} NMR spectrum of [**7**·H]Br in CDCl$_3$ (126 MHz)

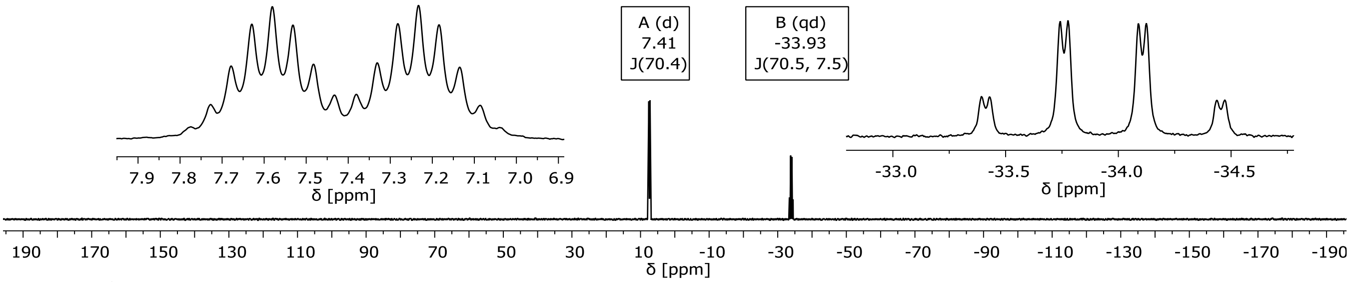

Figure S11. ^{31}P NMR spectrum of [**7**·H]Br in CDCl$_3$ (203 MHz)

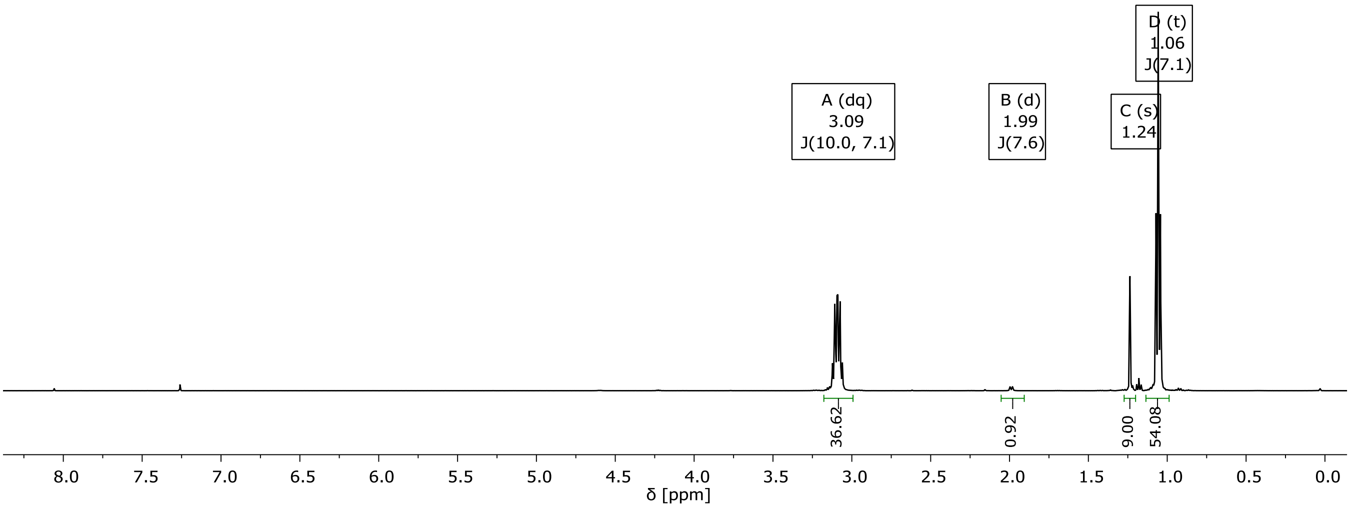

Figure S12. ^{1}H NMR spectrum of [**7**·H]I in CDCl$_3$ (500 MHz)

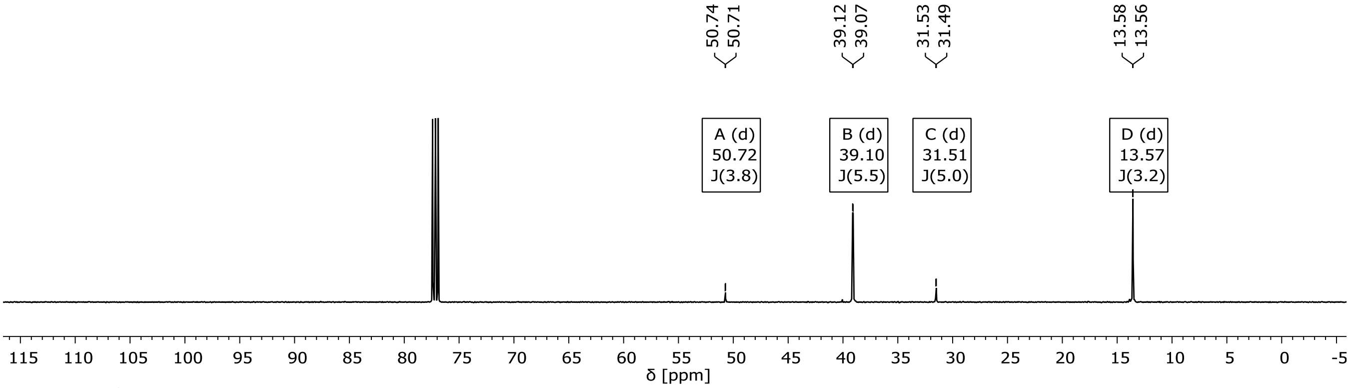

Figure S13. ^{13}C{^{1}H} NMR spectrum of [**7**·H]I in CDCl$_3$ (126 MHz)

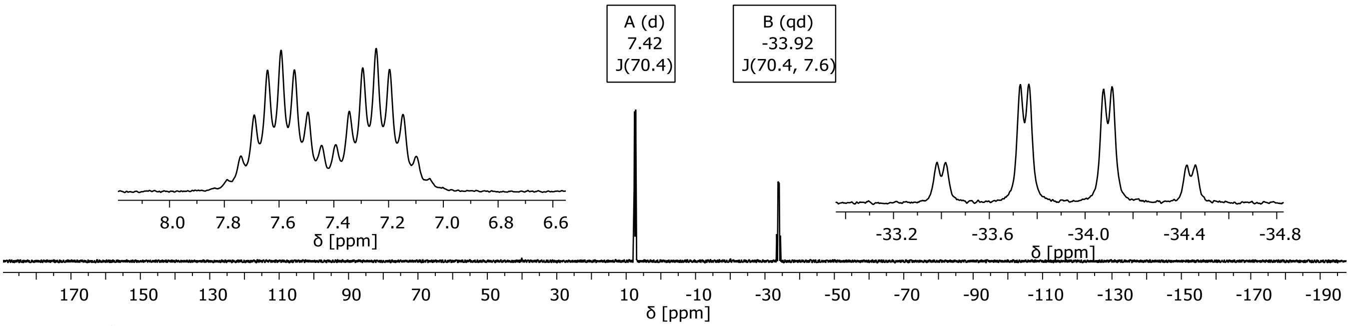

Figure S14. ^{31}P NMR spectrum of [**7**·H]I in CDCl$_3$ (203 MHz)

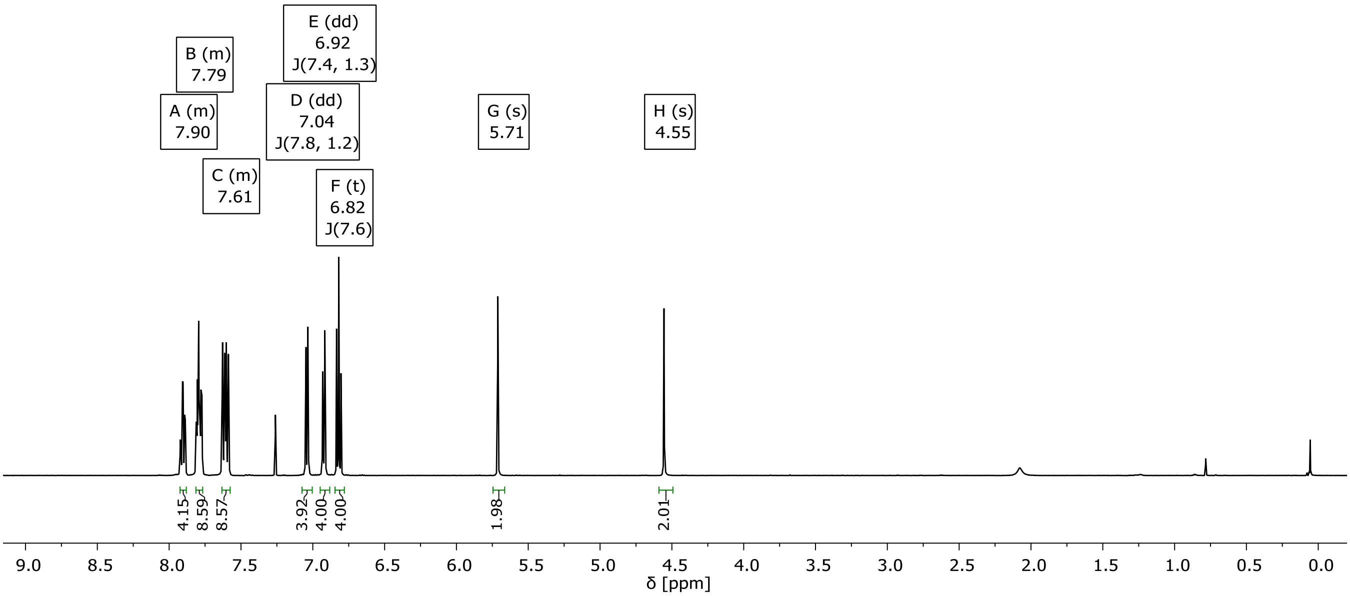

Figure S15. ^{1}H NMR spectrum of [**2**·Cl][PPh$_4$] in CDCl$_3$ (500 MHz)

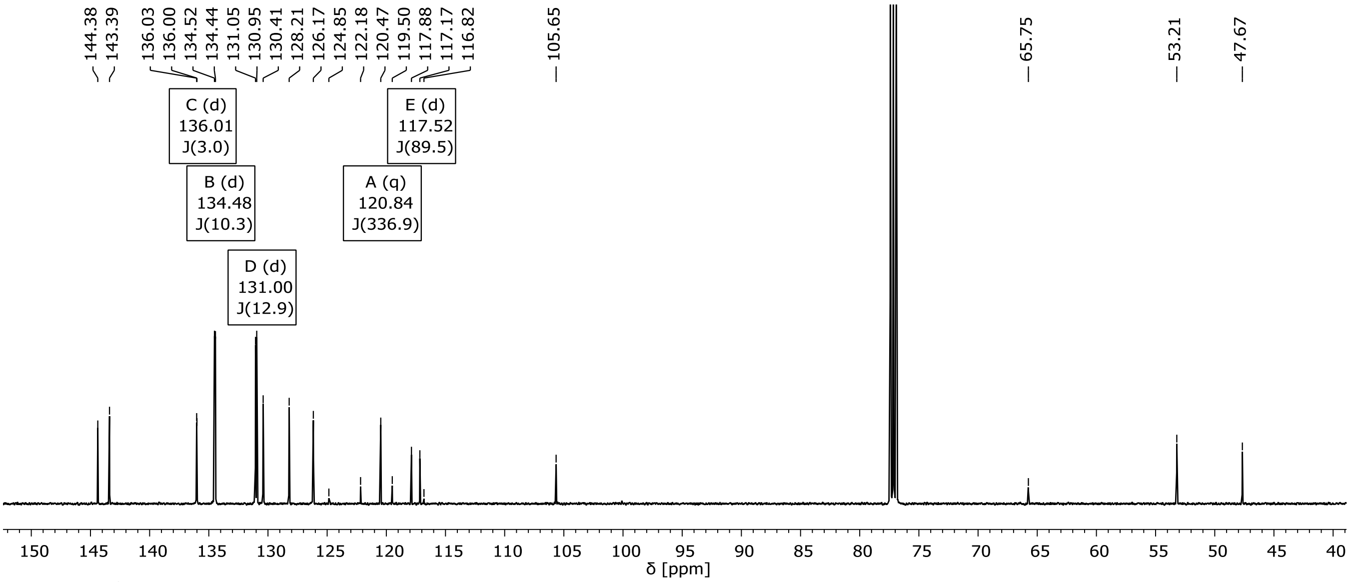

Figure S16. ^{13}C{^{1}H} NMR spectrum of [**2**·Cl][PPh$_4$] in CDCl$_3$ (126 MHz)

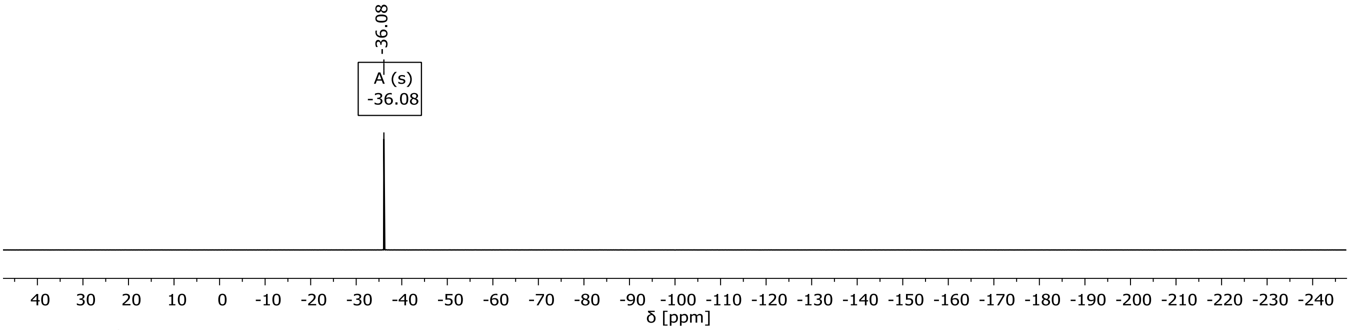

Figure S17. ^{19}F NMR spectrum of [**2**·Cl][PPh$_4$] in CDCl$_3$ (471 MHz)

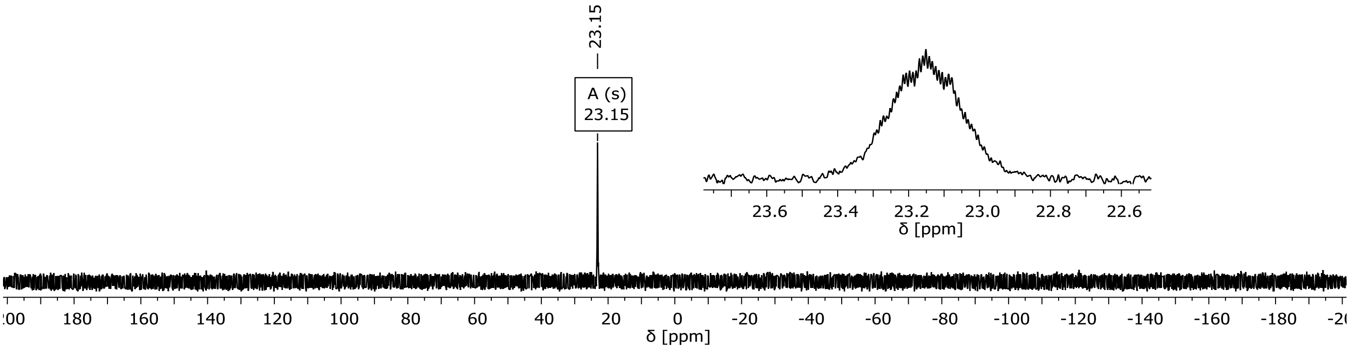

Figure S18. ^{31}P NMR spectrum of [**2**·Cl][PPh$_4$] in CDCl$_3$ (203 MHz)

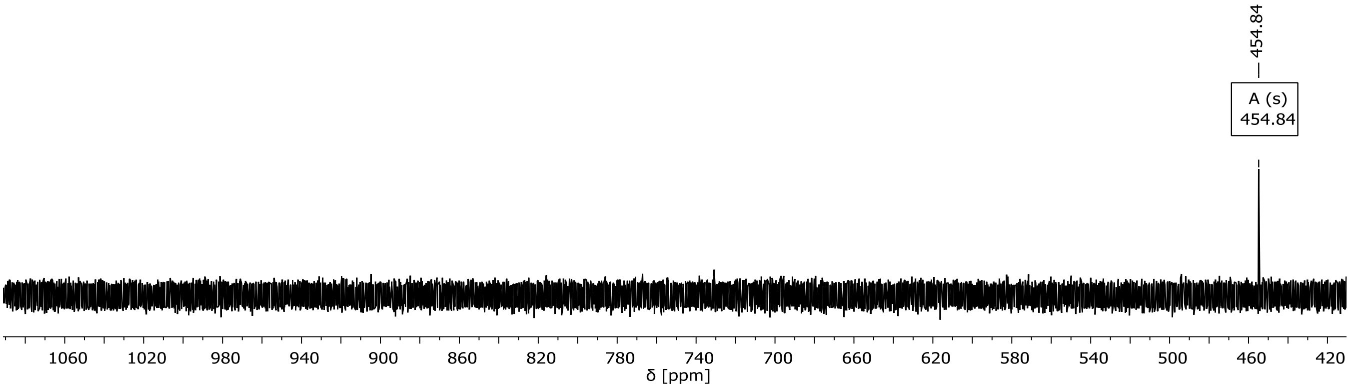

Figure S19. ^{77}Se NMR spectrum of [**2**·Cl][PPh$_4$] in CDCl$_3$ (96 MHz)

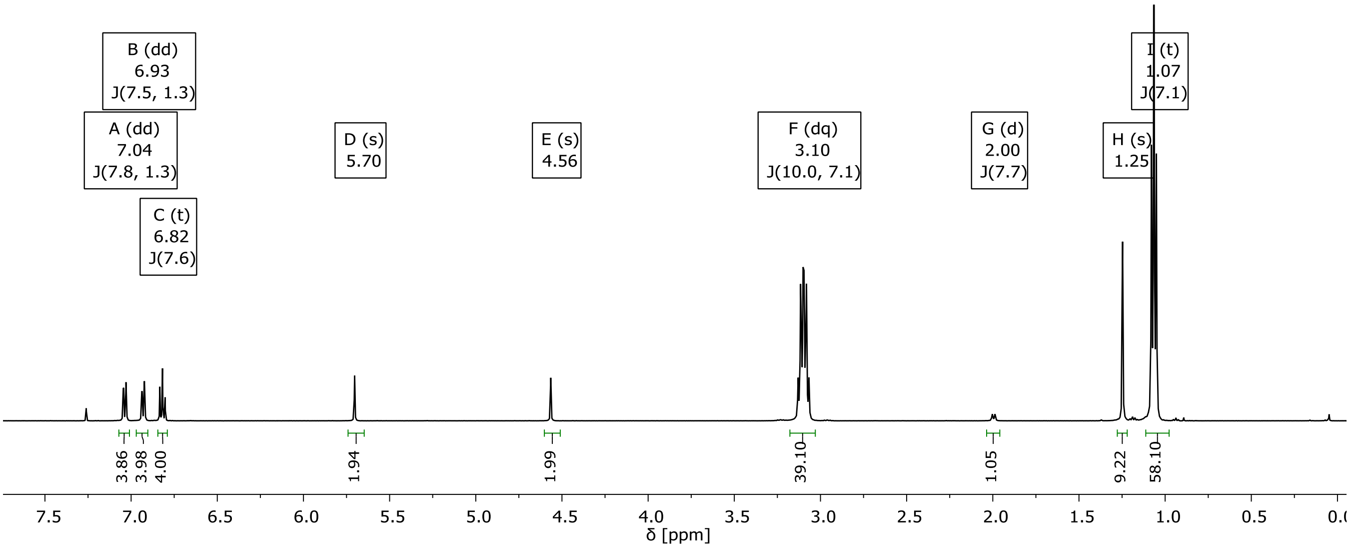

Figure S20. ^{1}H NMR spectrum of [**2**·Cl][**7**·H] in CDCl$_3$ (500 MHz)

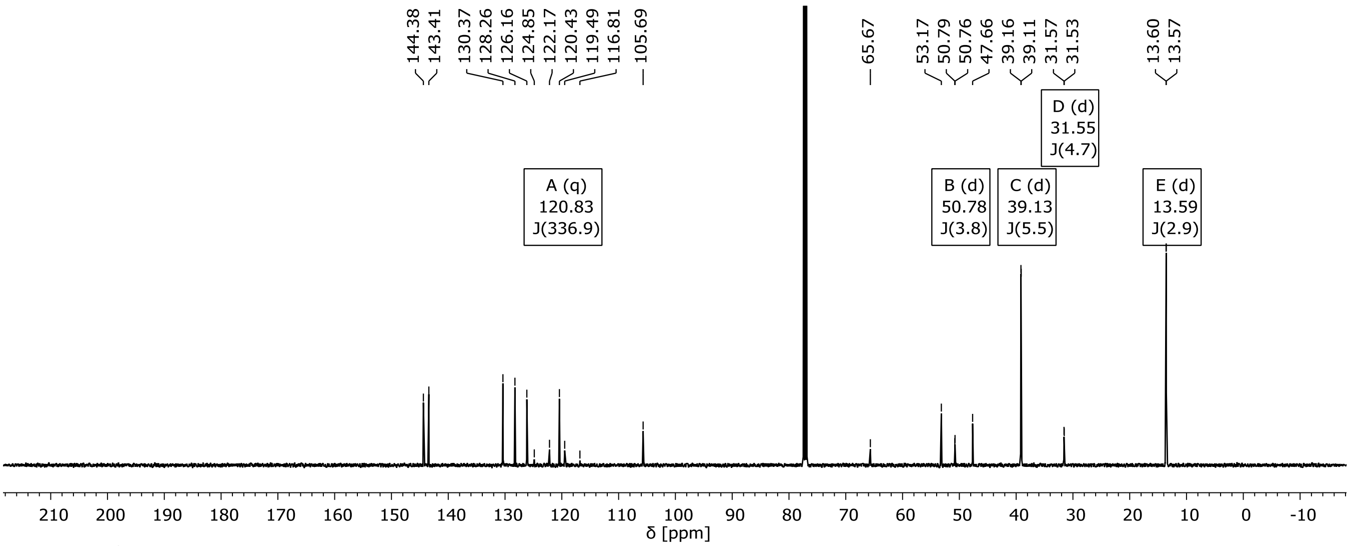

Figure S21. $^{13}C\{^1H\}$ NMR spectrum of [**2**·Cl][**7**·H] in $CDCl_3$ (126 MHz)

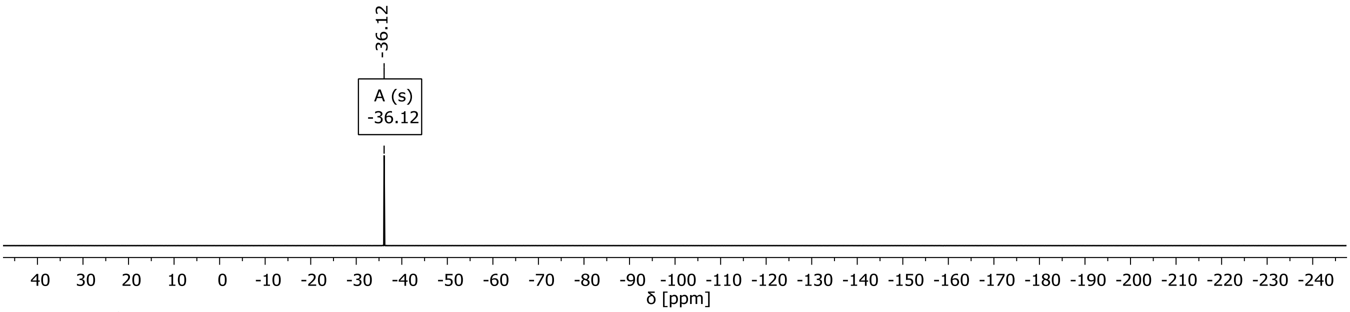

Figure S22. ^{19}F NMR spectrum of [**2**·Cl][**7**·H] in $CDCl_3$ (471 MHz)

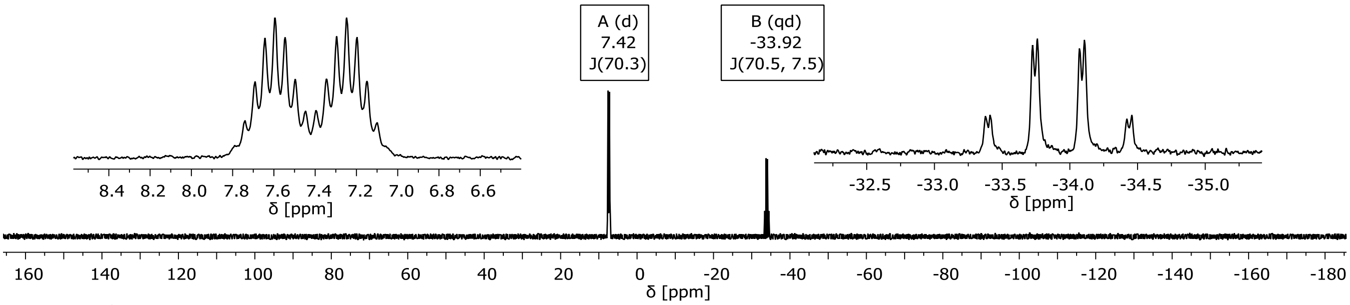

Figure S23. ^{31}P NMR spectrum of [**2**·Cl][**7**·H] in $CDCl_3$ (203 MHz)

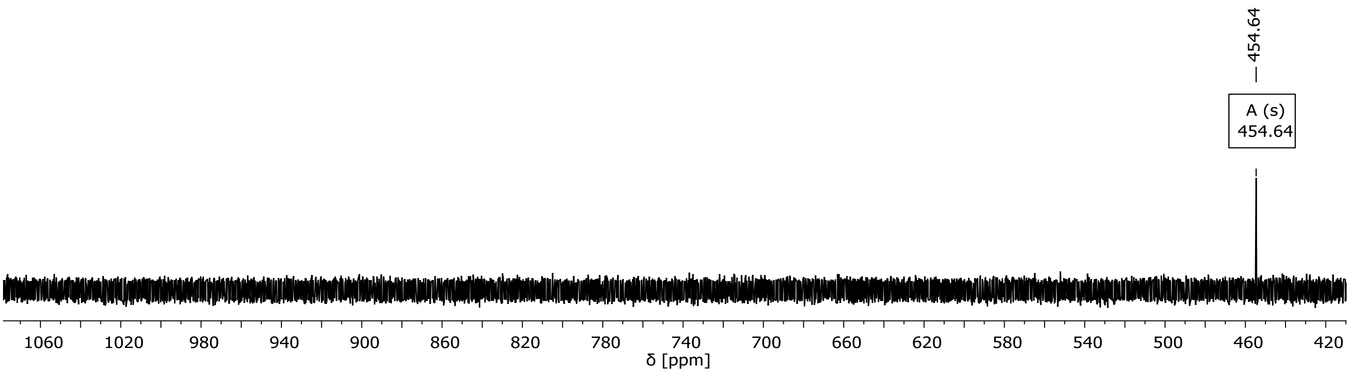

Figure S24. ^{77}Se NMR spectrum of [**2**·Cl][**7**·H] in $CDCl_3$ (96 MHz)

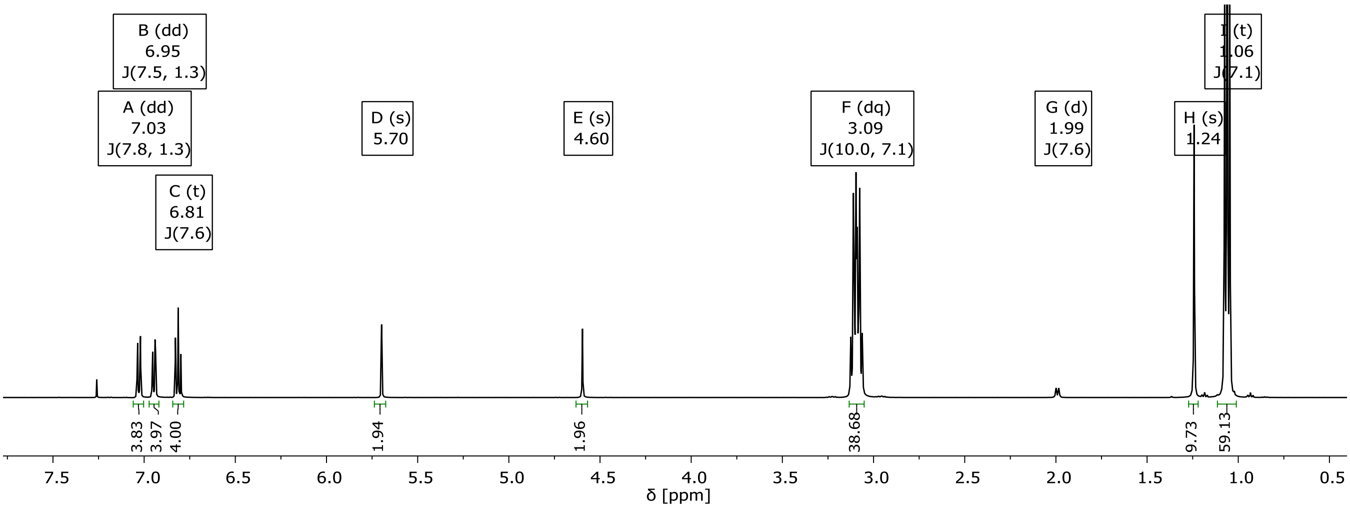

Figure S25. ^{1}H NMR spectrum of [**2**·Br][**7**·H] in CDCl$_3$ (500 MHz)

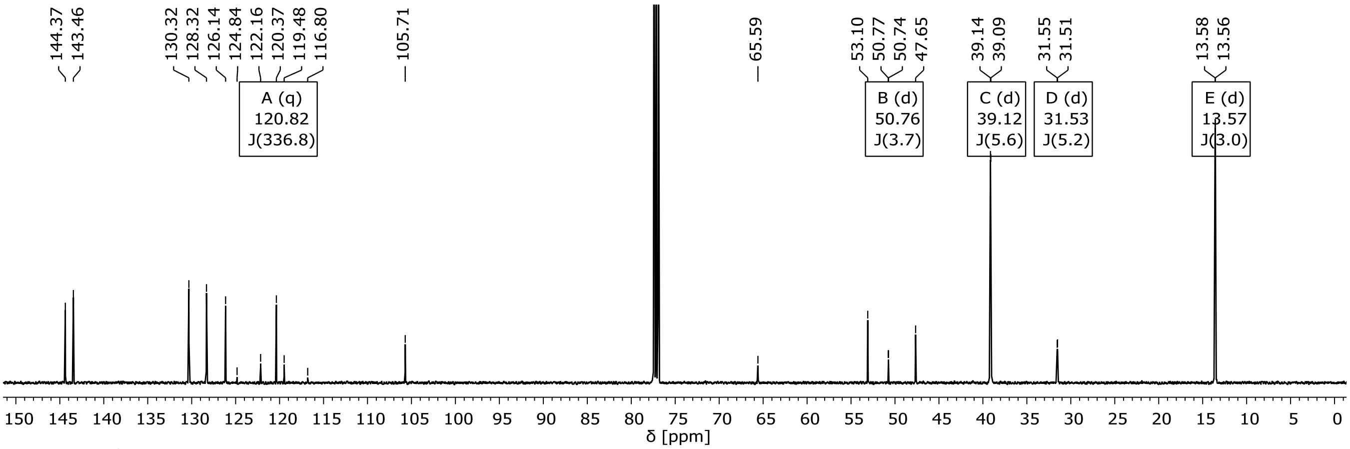

Figure S26. ^{13}C{^{1}H} NMR spectrum of [**2**·Br][**7**·H] in CDCl$_3$ (126 MHz)

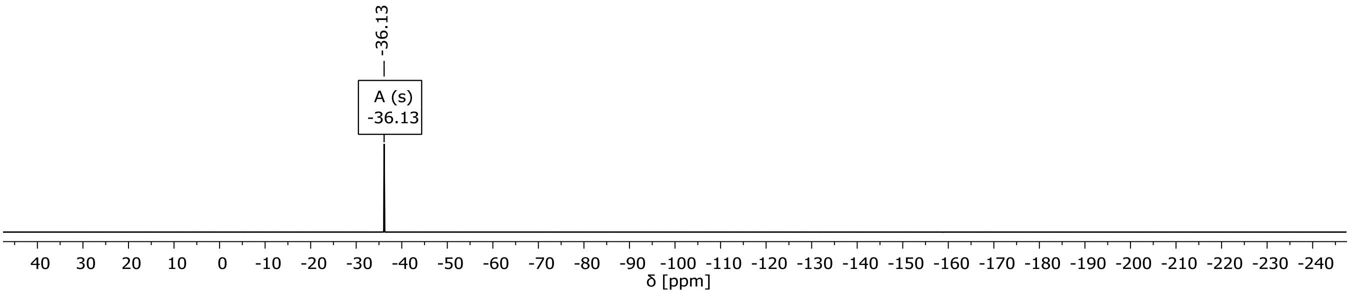

Figure S27. ^{19}F NMR spectrum of [**2**·Br][**7**·H] in CDCl$_3$ (471 MHz)

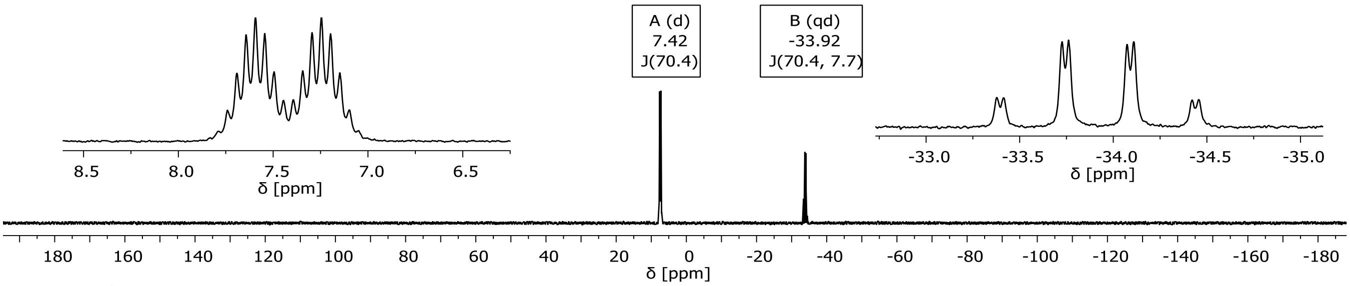

Figure S28. ^{31}P NMR spectrum of [**2**·Br][**7**·H] in CDCl$_3$ (203 MHz)

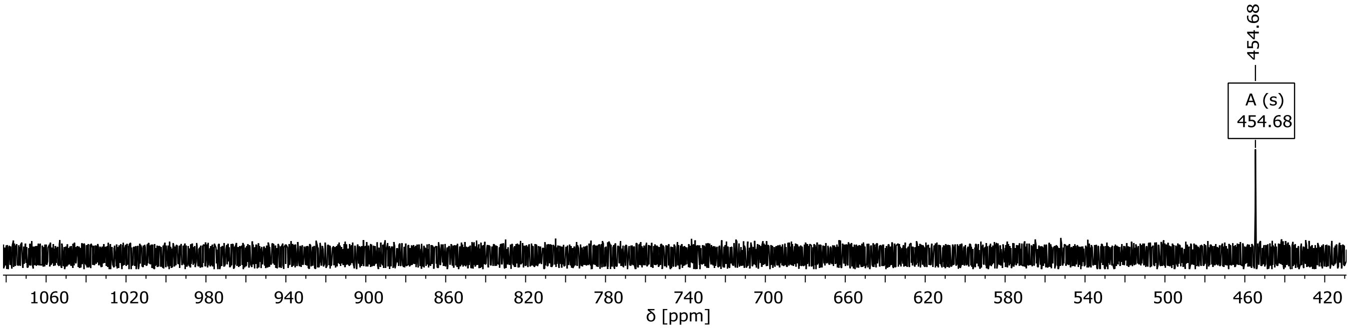

Figure S29. ^{77}Se NMR spectrum of [**2**·Br][**7**·H] in $CDCl_3$ (96 MHz)

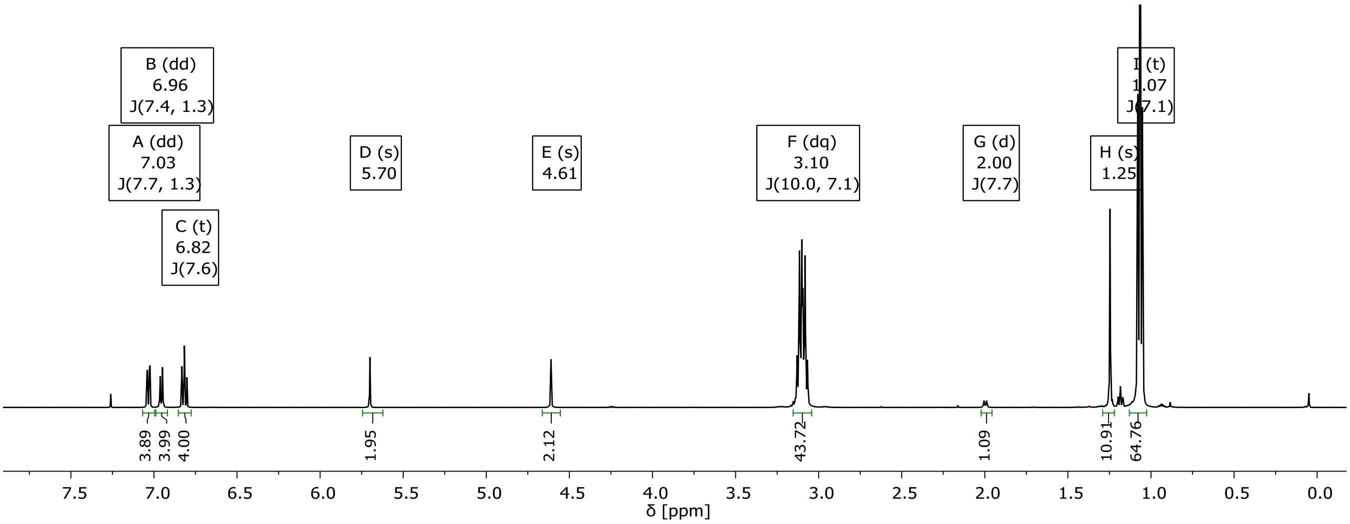

Figure S30. ^{1}H NMR spectrum of [**2**·I][**7**·H] in $CDCl_3$ (500 MHz)

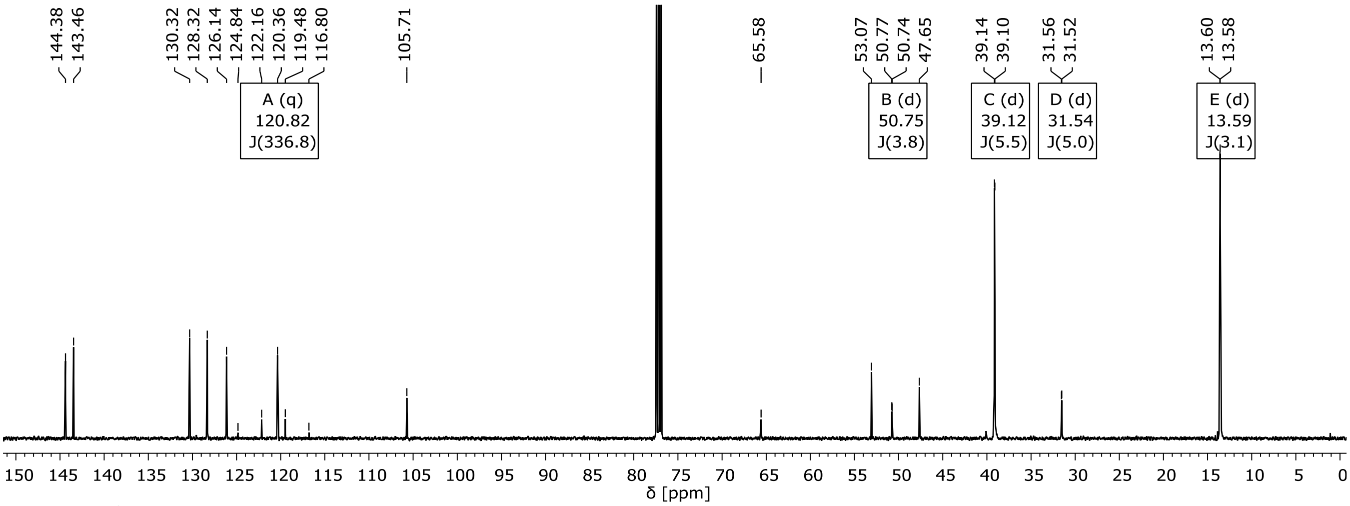

Figure S31. $^{13}C\{^{1}H\}$ NMR spectrum of [**2**·I][**7**·H] in $CDCl_3$ (126 MHz)

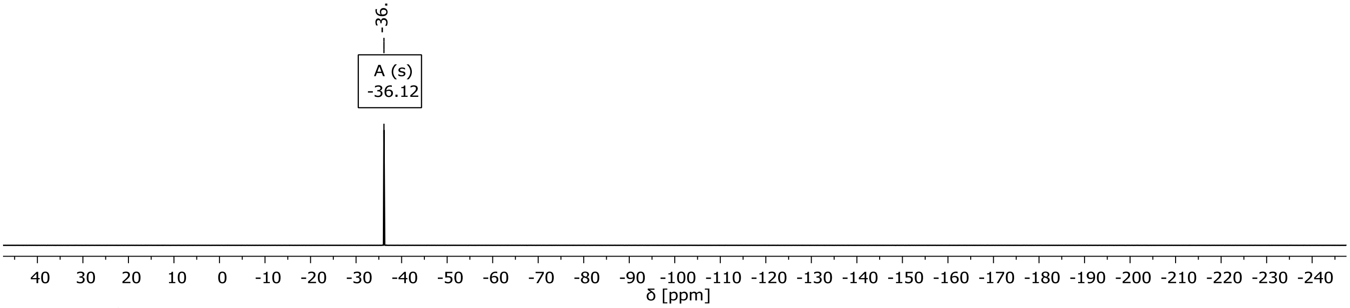

Figure S32. ^{19}F NMR spectrum of [**2**·I][**7**·H] in $CDCl_3$ (471 MHz)

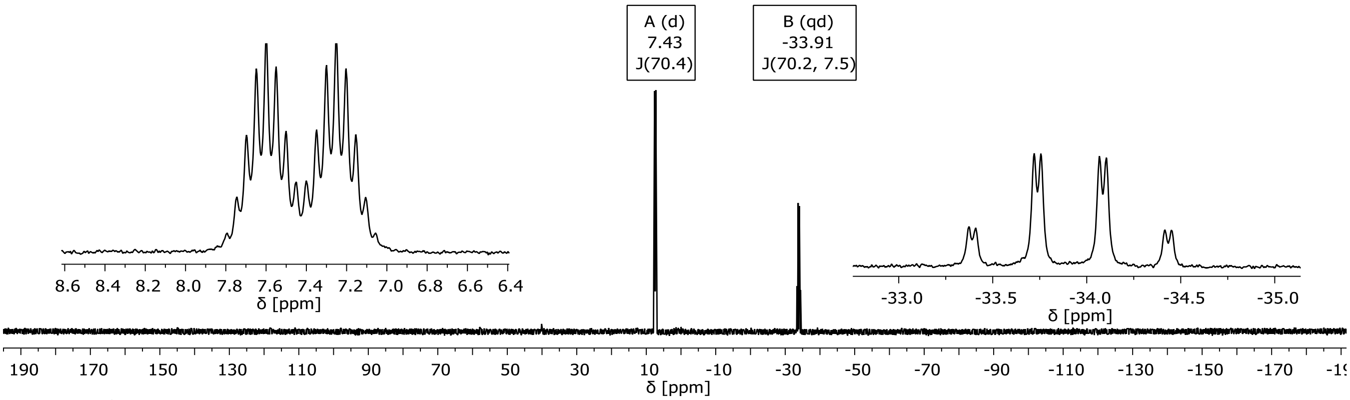

Figure S33. ^{31}P NMR spectrum of [**2**·I][**7**·H] in CDCl$_3$ (203 MHz)

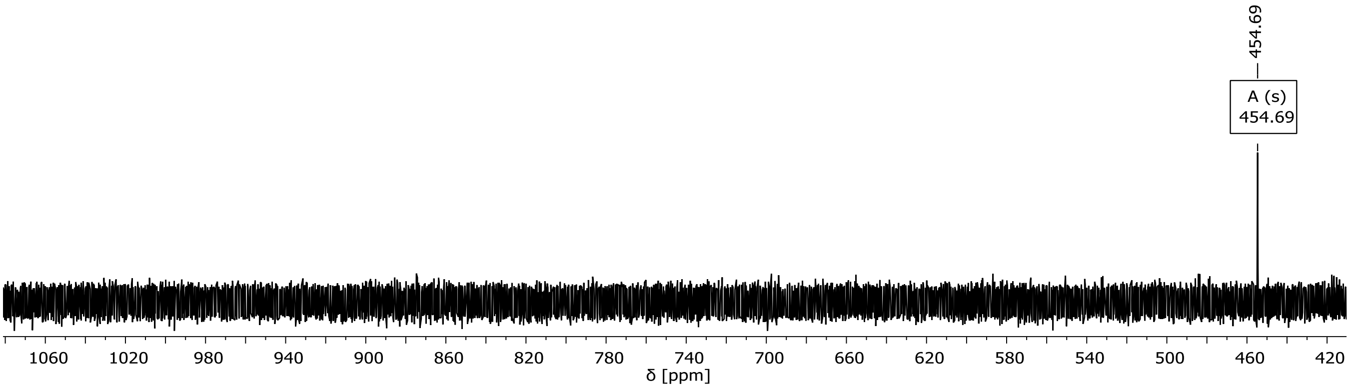

Figure S34. ^{77}Se NMR spectrum of [**2**·I][**7**·H] in CDCl$_3$ (96 MHz)

Crystallographic data

Single crystals were examined on a Rigaku Supernova diffractometer. The crystals were kept at 100.0(1) K during data collection. Using Olex2[7], the structures were solved with the ShelXT[8] structure solution program using Intrinsic Phasing and refined with the ShelXL[9] or olex2.refine[10] refinement package using Least Squares minimization.

2 x1.5C_6H_6 shows a disorder of two $SeCF_3$ groups in ratio 62:38. For the refinement non-spherical atom-form factors were applied using NoSpherA2.[11]

Crystals of **5** were in-situ grown by generating a seed manually at 173.5 K in a capillary filled with the liquid, afterwards the capillary was cooled with 1 K/h to 170 K and with 20 K/h to 100 K. For the refinement, non-spherical atom-form factors were applied using NoSpherA2.[11]

[**7**xH]IxMe$_2$CO shows a disorder of I1 over two sites with ratio 64:36, of C33/C34 with ratio 84:16, and of the actone solvent molecule with ratio 75:25. The hydrogen atom H(1) bonded at N(1) was refined isotropically.

[**7**xH]Br: The hydrogen atom H(1) bonded at N(1) was refined isotropically.

[**2**xCl][**7**xH] was a twinned crystal, component 2 rotated by 180.0° around [0.00 -0.00 1.00] (reciprocal) or [0.34 0.01 0.94] (direct), ratio 58:42. Additionally, a disorder of C(65)/C(66) over two sites in ratio 58:42 and disorder of C(68) over two sites in ratio 52:48 was obtained. H(1) was located as an electron density peak but was refined with restrained distance and a riding isotropic displacement parameter.

[**2**xBr][**7**xH] was a twinned crystal, component 2 rotated by 179.8° around [0.00 0.00 1.00] (reciprocal) or [0.35 0.02 0.94] (direct), ratio 61:39. A positional disorder of C(77) – C(80) was modelled. Bromide (78%) and hydroxide (22%) were mixed in the anion position. H(1) was located as an electron density peak but was refined with a riding isotropic displacement parameter.

[**2**xI][**7**xH] was a twinned crystal, component 2 rotated by 180.0°. around [0.00 0.00 1.00] (reciprocal) or [-0.40 0.00 0.92] (direct), ratio 55:45. Iodide (75%) and hydroxide (25%) were mixed in the anion position, the thermal motion of I(1) and O(1) were constrained to be same. H(1) was located as an electron density peak but was refined with a restrained distance.

[**2**xCl][PPh_4]x2C_6H_6: The crystal contained one disordered solvent benzene molecule, which could be refined at two positions with ratio of 76:24. An additional benzene molecule could not been refined reasonably, therefore, a solvent mask was calculated and 154 electrons were found in a volume of 706 Å^3 in one void per unit cell. This is consistent with the presence of one benzene molecule per asymmetric unit which account for 168 electrons per unit cell.

Details of the X-ray diffraction experiments are given in Tables S1 and S2. CCDC 2337865 – 2337874 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/conts/retrieving.html.

Table S1. Crystallographic data for compounds **1**, **2**, **5**, the THF adduct [**1**·2 THF]$_2$, [**7**·H]Br and [**7**·H]I.

Compound	**1**	**2**·1.5 C_6H_6	$ClSeCF_3$ (**5**)	[**1**·2 THF]$_2$	[**7**·H]Br	[**7**·H]I·Me_2CO
Empirical formula	$C_{20}H_8F_6Se_2$	$C_{49}H_{25}F_{12}Se_4$	CF_3ClSe	$C_{28}H_{24}F_6O_2Se_2$	$C_{40}H_{100}BrN_{13}P_4$	$C_{43}H_{106}IN_{13}OP_4$
M_r	520.18	1157.56	183.42	664.39	967.11	1072.18
T [K]	100.0(1)	100.0(1)	100.0(1)	100.0(1)	100.0(1)	100.0(1)
Radiation	Mo Kα	Mo Kα	Mo Kα	Mo Kα	Mo Kα	Mo Kα
Crystal system	monoclinic	triclinic	monoclinic	triclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P\bar{1}$	$P2_1/c$	$P\bar{1}$	Cc	$P2_1/n$
a [Å]	10.3541(3)	11.3597(3)	11.6701(4)	10.9375(6)	12.6557(3)	11.2326(2)
b [Å]	35.1101(8)	13.1741(3)	8.6917(3)	11.1688(6)	23.7019(5)	26.7724(4)
c [Å]	5.1523(1)	14.8239(4)	9.1211(3)	11.4551(7)	17.6543(4)	19.2696(3)
α [°]	90	84.490(2)	90	96.766(5)	90	90
β [°]	102.864(3)	88.860(2)	106.049(4)	98.009(5)	98.985(2)	99.9320(10)
γ [°]	90	79.798(2)	90	103.066(5)	90	90
Volume [Å^3]	1826.02(8)	2173.3(1)	889.12(6)	1333.55(14)	5230.7(2)	5707.98(16)
Z	4	2	8	2	4	4
ρ_{calc} [g cm^{-3}]	1.892	1.769	2.740	1.655	1.228	1.248
μ [mm^{-1}]	4.110	3.464	8.956	2.839	0.950	0.716
F(000) [e]	1000	1126.748	673.490	660	2104	2304
2Θ range [°]	4.036 – 64.416	5.02 – 65.68	6.6 – 82.16	3.634 – 64.434	5.536 – 65.88	3.724 – 68.882
Index ranges	$-15 \le h \le 15$	$-17 \le h \le 17$	$-21 \le h \le 21$	$-16 \le h \le 15$	$-19 \le h \le 18$	$-17 \le h \le 17$
	$-50 \le k \le 51$	$-19 \le k \le 20$	$-16 \le k \le 15$	$-16 \le k \le 16$	$-35 \le k \le 35$	$-41 \le k \le 42$
	$-7 \le l \le 7$	$-22 \le l \le 22$	$-16 \le l \le 16$	$-16 \le l \le 8$	$-26 \le l \le 26$	$-30 \le l \le 30$
Refl. collected	22039	135687	42856	15538	59330	243682
Independent refl.	6014	15436	5811	8435	17628	23174
R_{int}	0.0438	0.0394	0.0761	0.0361	0.0298	0.0581
Refl. with $I > 2\sigma(I)$	4627	12914	4838	6196	16556	18704
Data / restraints / parameters	6014 / 0 / 253	15436 / 0 / 726	5811 / 0 / 110	8435 / 0 / 343	17628 / 2 / 548	23174 / 0 / 647
Goodness-of-Fit on F^2	1.092	1.071	1.055	1.041	1.031	1.038
R_1/wR_2 [$I > 2\sigma(I)$]	0.0463 / 0.0968	0.0269 / 0.0549	0.0352 / 0.0820	0.0420 / 0.0790	0.0275 / 0.0611	0.0349 / 0.0767
R_1/wR_2 (all data)	0.0685 / 0.1048	0.0385 / 0.0591	0.0441 / 0.0888	0.0685 / 0.0895	0.0317 / 0.0632	0.0496 / 0.0825
ρ_{fin} (max/min) [e Å^{-3}]	0.96 / −0.54	0.66 / −0.87	1.72 / −1.38	0.89 / −0.49	0.48 / −0.33	0.58 / −0.68
CCDC	2337865	2337866	2337867	2337868	2337869	2337870

Table S2. Crystallographic data for the halide adducts [**2**·Cl][**7**·H], [**2**·Br][**7**·H], [**2**·I][**7**·H] and [**2**·Cl][PPh_4].

Compound	[**2**·Cl][**7**·H]	[**2**·Br][**7**·H]	[**2**·I][**7**·H]	[**2**·Cl][PPh_4]·3 C_6H_6
Empirical formula	$C_{80}H_{116}ClF_{12}N_{13}P_4Se_4$	$C_{80}H_{116}Br_{0.76}F_{12}N_{13}O_{0.24}P_4Se_4$	$C_{80}H_{116}F_{12}I_{0.75}N_{13}O_{0.25}P_4Se_4$	$C_{82}H_{54}ClF_{12}PSe_4$
M_r	1963.02	1992.46	2027.30	1649.51
T [K]	100.0(1)	100.0(1)	100.0(1)	100.0(1)
Radiation	Cu Kα	Cu Kα	Mo Kα	Mo Kα
Crystal system	triclinic	triclinic	triclinic	monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P2_1/n$
a [Å]	10.7931(6)	10.76527(16)	10.7927(4)	17.1681(8)
b [Å]	19.8342(8)	19.8662(2)	20.0311(9)	21.1450(7)
c [Å]	21.4238(13)	21.4344(5)	21.5408(10)	21.2518(10)
α [°]	90.139(4)	90.3453(13)	89.415(4)	90
β [°]	100.496(5)	100.6199(16)	77.434(4)	111.640(5)
γ [°]	92.831(4)	92.8667(11)	87.161(3)	90
Volume [Å^3]	4503.7(4)	4499.36(13)	4539.8(3)	7171.1(6)
Z	2	2	2	4
ρ_{calc} [g cm^{-3}]	1.448	1.470	1.483	1.528
μ [mm^{-1}]	3.519	3.650	2.017	2.182
F(000) [e]	2016	2039	2066	3288
2Θ range [°]	6.09 – 153.204	6.072 – 152.73	6.318 – 56.982	6.466 – 60.066
Index ranges	$-13 \le h \le 13$	$-13 \le h \le 13$	$-14 \le h \le 14$	$-24 \le h \le 24$
	$-24 \le k \le 24$	$-24 \le k \le 24$	$-26 \le k \le 26$	$-29 \le k \le 29$
	$-26 \le l \le 26$	$-26 \le l \le 24$	$-28 \le l \le 28$	$-29 \le l \le 29$
Refl. collected	51472	65505	169663	173219
Independent refl.	26168	20805	24678	20941
R_{int}	0.0563	0.0372	0.1551	0.0474
Refl. with $I > 2\sigma(I)$	17752	19036	23694	17250
Data / restraints / parameters	26168 / 7 / 1083	20805 / 48 / 1079	24678 / 1 / 1057	20941 / 174 / 902
Goodness-of-Fit on F^2	1.006	1.060	1.328	1.018
R_1/wR_2 [$I > 2\sigma(I)$]	0.0642 / 0.1674	0.0554 / 0.1629	0.0645 / 0.1477	0.0317 / 0.0705
R_1/wR_2 (all data)	0.0917 / 0.1799	0.0592 / 0.1652	0.0705 / 0.1536	0.0441 / 0.0757
ρ_{fin} (max/min) [e Å^{-3}]	1.23 / −1.13	1.99 / −1.18	0.98 / −1.30	0.66 / −0.51
CCDC	2337871	2337872	2337873	2337874

Solid-state structures of [7·H]Br, [7·H]I and [2·Cl][7·H]

The solid state structures of [**7**·H]Br and [**7**·H]I are depicted in Figure S35. The hydrogen atoms H(1) bonded to N(1) were refined isotropically.

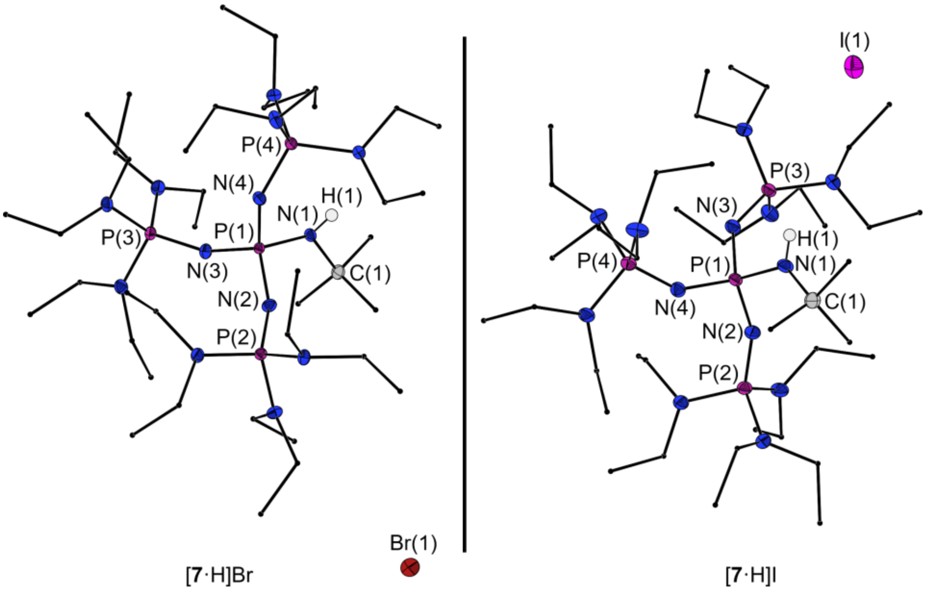
[**7**·H]Br [**7**·H]I

Figure S35 Molecular structures of [**7**·H]Br (left) and [**7**·H]I (right) in the solid state. Ellipsoids are set at 50% probability. Methyl and ethyl groups are depicted as sticks. In case of [**7**·H]I, two minor disordered ethyl groups, a disordered iodine atom and a disordered acetone molecule are omitted for clarity. Selected distances [Å] and angles [°] of [**7**·H]Br: P(1)–N(1) 1.671(2), P(1)–N(2) 1.587(2), P(1)–N(3) 1.582(2), P(1)–N(4) 1.606(2), N(2)–P(2) 1.543(2), N(1)–C(1) 1.479(2); N(1)–H(1) 0.80(2), P(1)–N(1)–C(1) 128.8(1), N(1)–P(1)–N(2) 109.1(1), P(1)–N(2)–P(2) 158.0(1); of [**7**·H]I: P(1)–N(1) 1.669(1), P(1)–N(2) 1.595(1), P(1)–N(3) 1.597(1), P(1)–N(4) 1.601(1), N(2)–P(2) 1.550(1), N(1)–C(1) 1.481(2), N(1)–H(1) 0.77(2); P(1)–N(1)–C(1) 131.6(1), N(1)–P(1)–N(2) 107.3(1), P(1)–N(2)–P(2) 156.0(1).

Since the structural characteristics of the relevant anion [**2**·Cl]$^{-}$ in the solid-state structures of [**2**·Cl][PPh_4] and [**2**·Cl][**7**·H] are comparable, only [**2**·Cl][PPh_4] is described in the main manuscript and the latter is described in Figure S36.

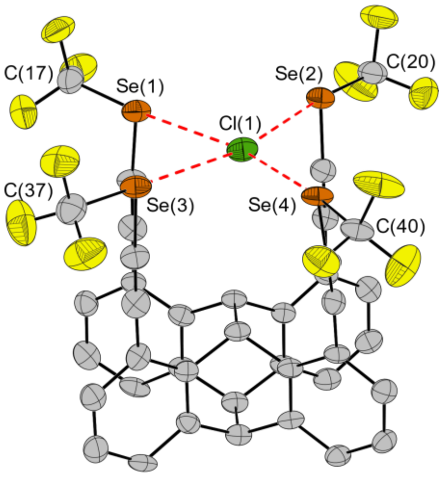

Figure S36. Molecular structure of [**2**·Cl][**7**·H] in the solid state. Hydrogen atoms and the cation are omitted for clarity. Ellipsoids are set at 50% probability. The red dotted lines mark Se···X distances below the sum of van der Waals radii. Selected distances [Å] and angles [°] of [**2**·Cl][**7**·H]: Se(1)···Cl(1) 3.104(2) Å, Se(2)···Cl(1) 3.199(2) Å, Se(3)···Cl(1) 3.203(2) Å, Se(4)···Cl(1) 3.104(2) Å, C(17)–Se(1) 1.945(8), C(20)–Se(2) 1.961(8), C(37)–Se(3) 1.957(8), C(40)–Se(4) 1.971(7); C(17)–Se(1)···Cl(1) 173.0(2), C(20)–Se(2)···Cl(1) 174.2(2), C(37)–Se(3)···Cl(1) 176.8(3), C(40)–Se(4)···Cl(1) 172.8(2).

Stability studies of host compounds 1 and 2

The compounds **1** and **2** were studied regarding their stability towards moisture, air, HCl and NaOH as well as their stability over time while storing them as solids and solutions.

To test their stability over time, the compounds were stored as solids (for 6 months exposed to air) and solutions in $CDCl_3$ (for 14 d exposed to air). Compound **1** was protected from sunlight, since it undergoes a slow photodimerization when exposed to sunlight. No decomposition was observed by NMR spectroscopic measurements.

To further test the stability towards air and hydrolysis, water was added to and air bubbled into solutions of compounds **1** and **2** in $CDCl_3$. After heating these samples (70 °C, 4 d), they were analyzed by NMR spectroscopy. No decomposition was observed. Next, concentrated aqueous hydrochloric acid (approx. 10 µL) or saturated NaOH solution (approx. 10 µL) were added to samples in $CDCl_3$. After heating these samples (70 °C, 4 d), they were analyzed by NMR spectroscopic measurements. Also, no decomposition could be observed (spectra are provided in Figure S37).

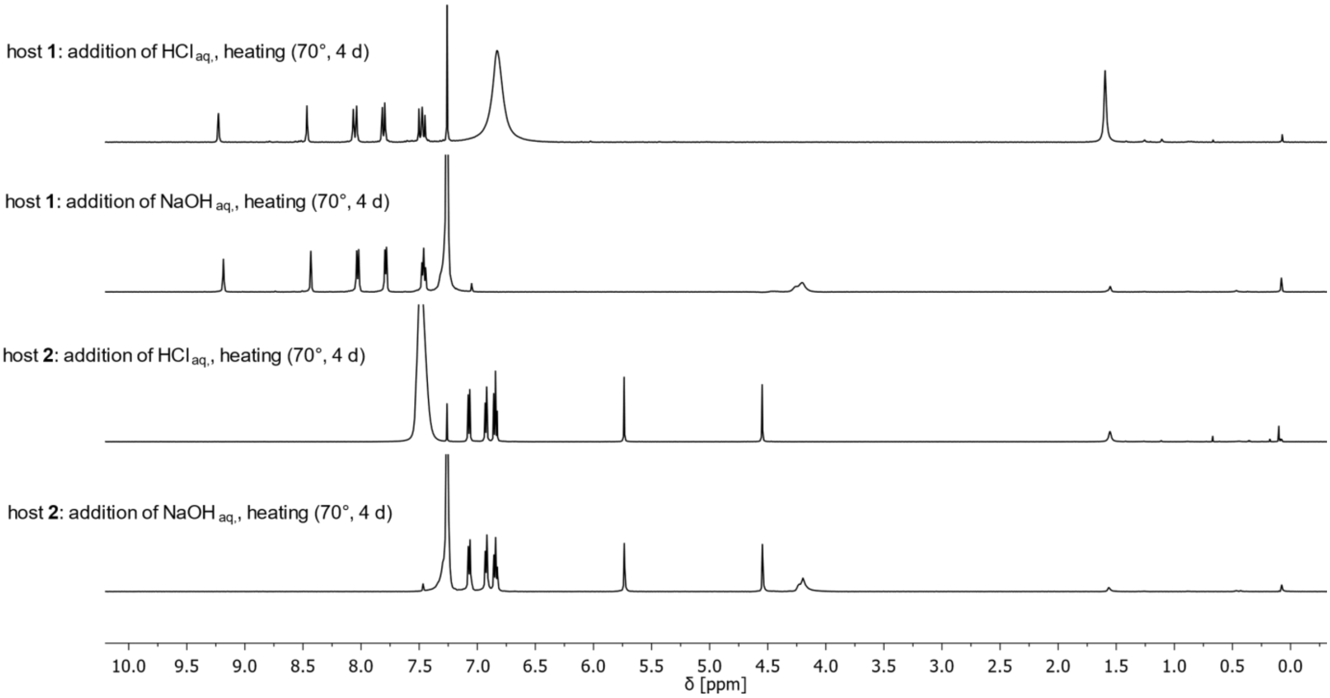

Figure S37. ^1H NMR spectra of compound **1** and **2** after treatment with hydrochloric acid or sodium hydroxide and heating in $CDCl_3$.

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