Synthesis of Lewis acid-base adducts between trimesityltriels and potassium cyanate and its heavier homologues

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1. NMR spectra

The signals marked with " * " are to be assigned to the respective solvents used.
The signals marked with " # " are to be assigned to silicon grease.

1.1 Compound $\mathbf{1_{NCO}}$

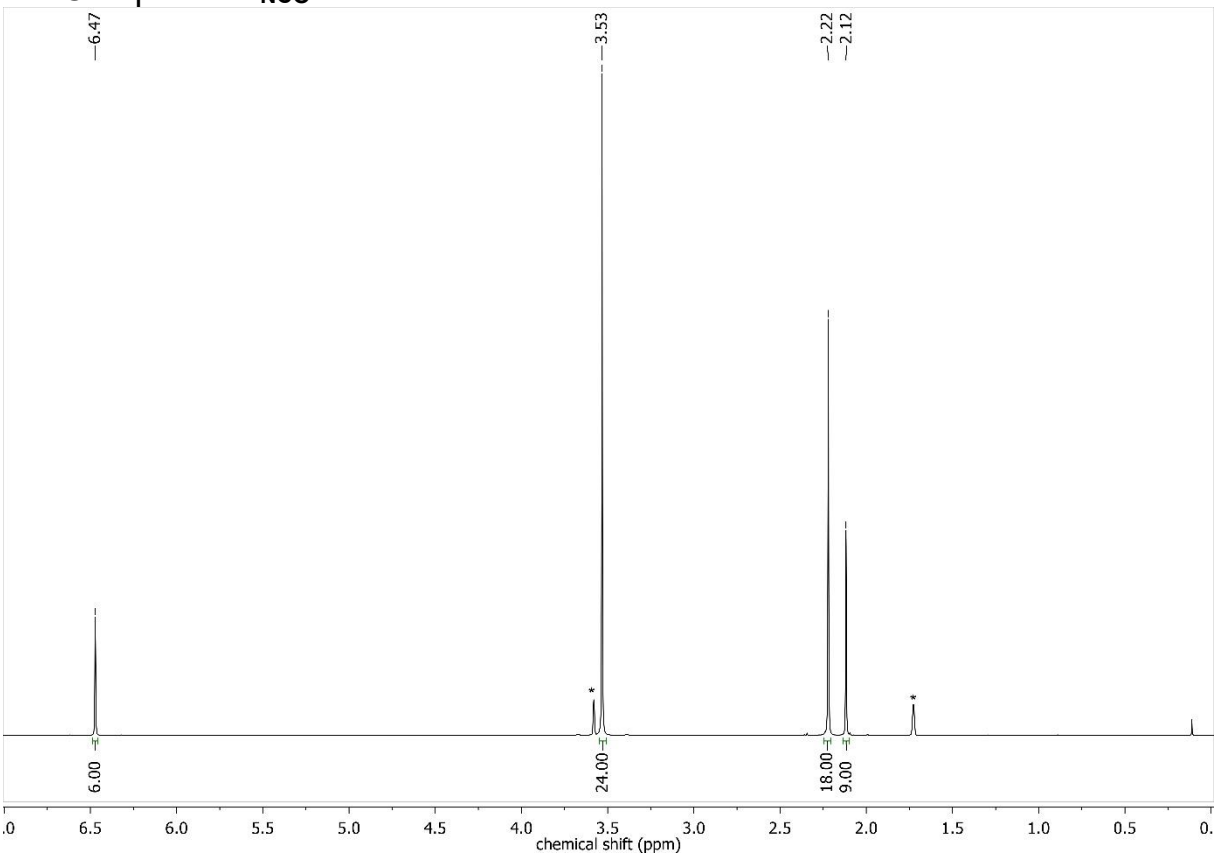

Figure S1: ^{1}H spectrum (300 MHz, 298K) of $\mathbf{1_{NCO}}$ in THF-d_8.

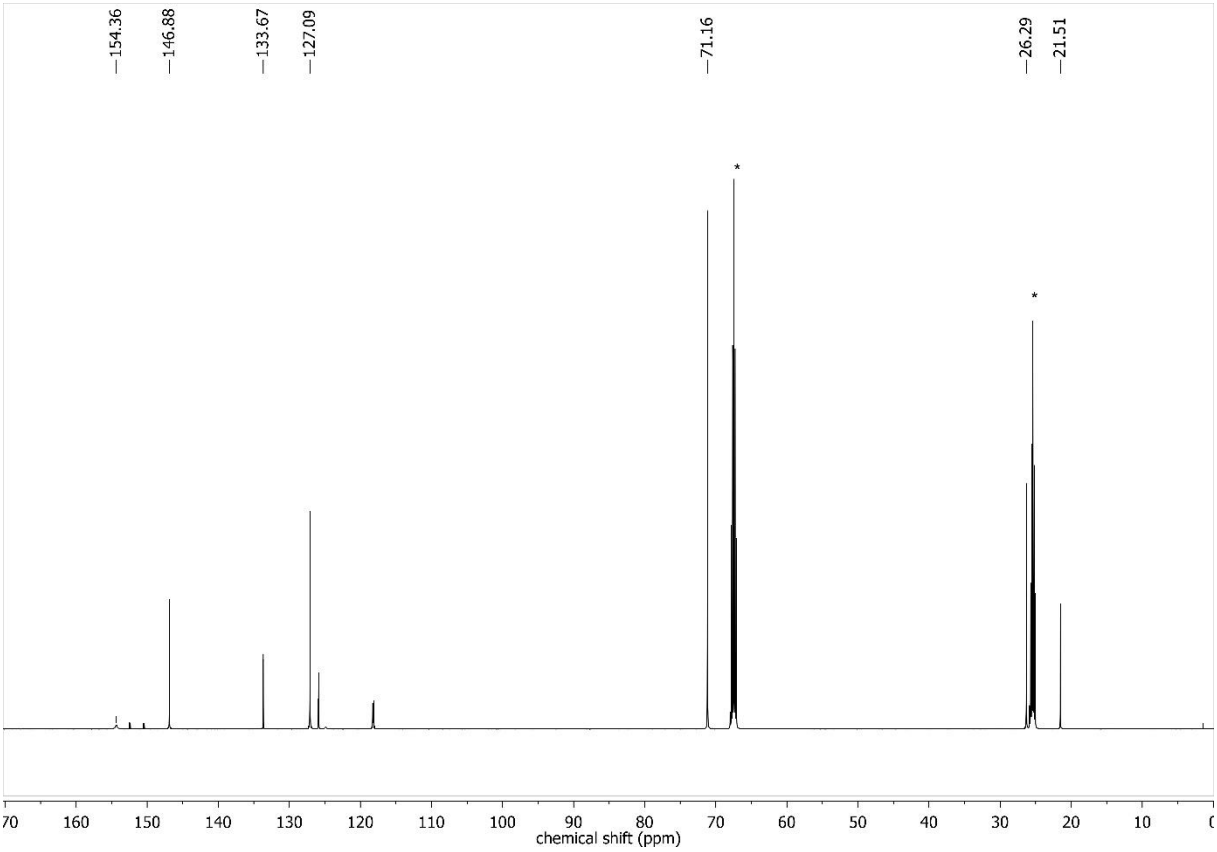

Figure S2: ^{13}C spectrum (75 MHz, 298K) of **1$_{NCO}$** in THF-d_8.

1.2 Compound $\mathbf{1_{NCS}}$

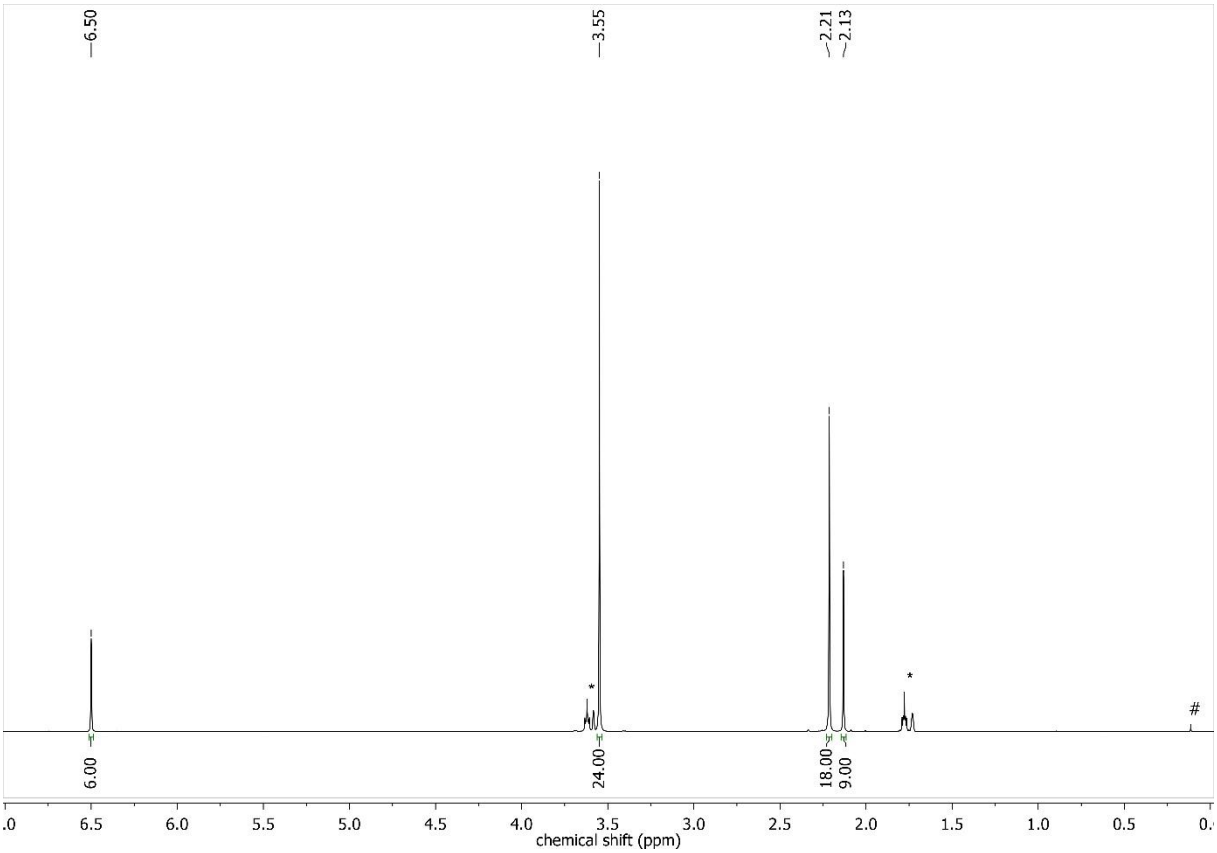

Figure S3: ^{1}H spectrum (300 MHz, 298K) of $\mathbf{1_{NCS}}$ in THF-d_8.

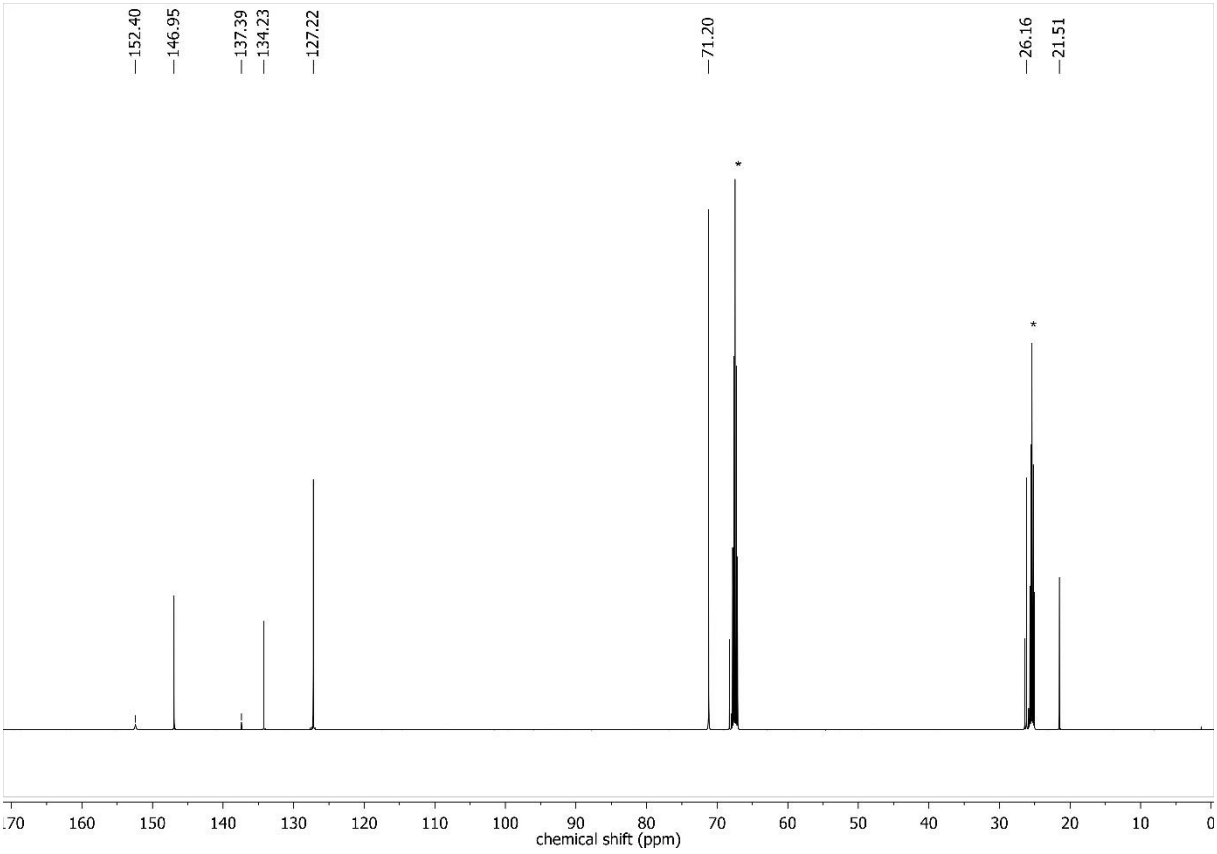

Figure S4: ^{13}C spectrum (75 MHz, 298K) of **1_{NCS}** in THF-d_8.

1.3 Compound $\mathbf{1_{NCSe}}$

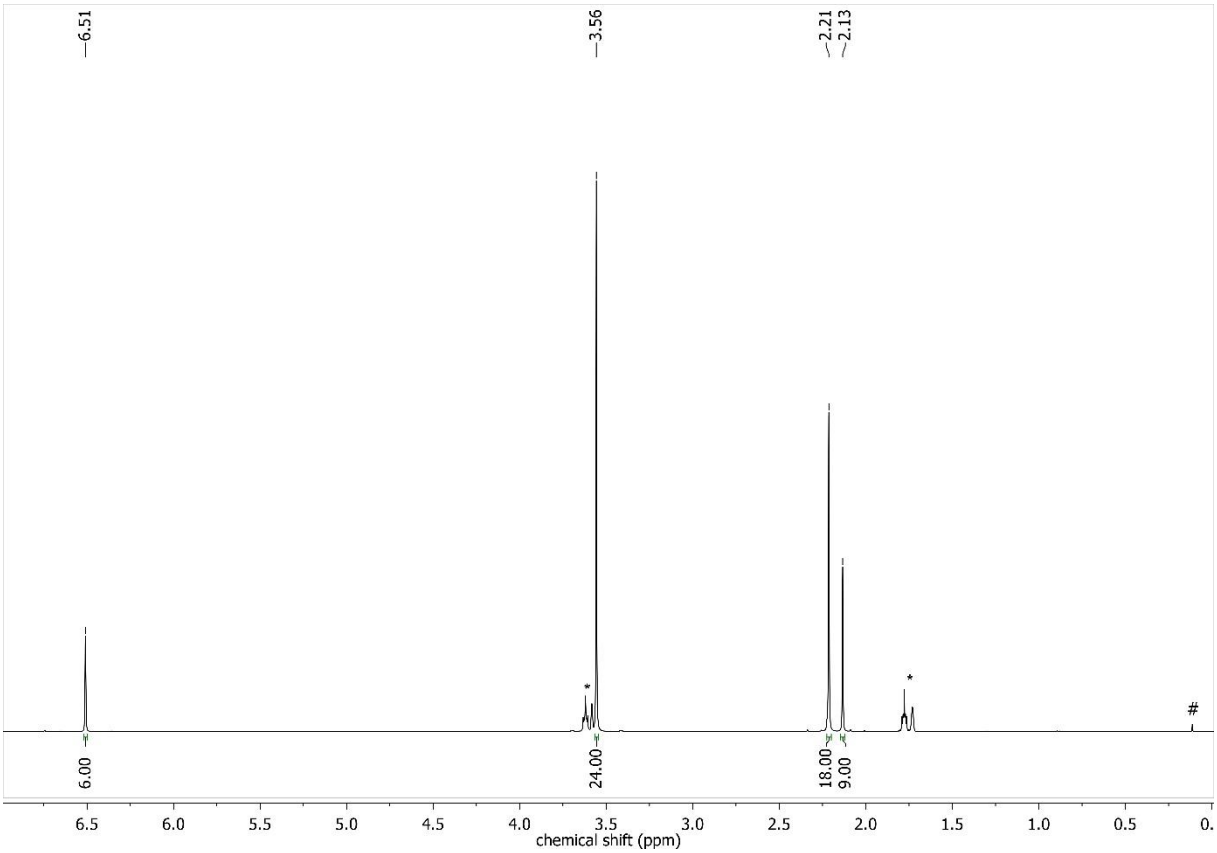

Figure S5: ^{1}H spectrum (300 MHz, 298K) of $\mathbf{1_{NCSe}}$ in THF-d_8.

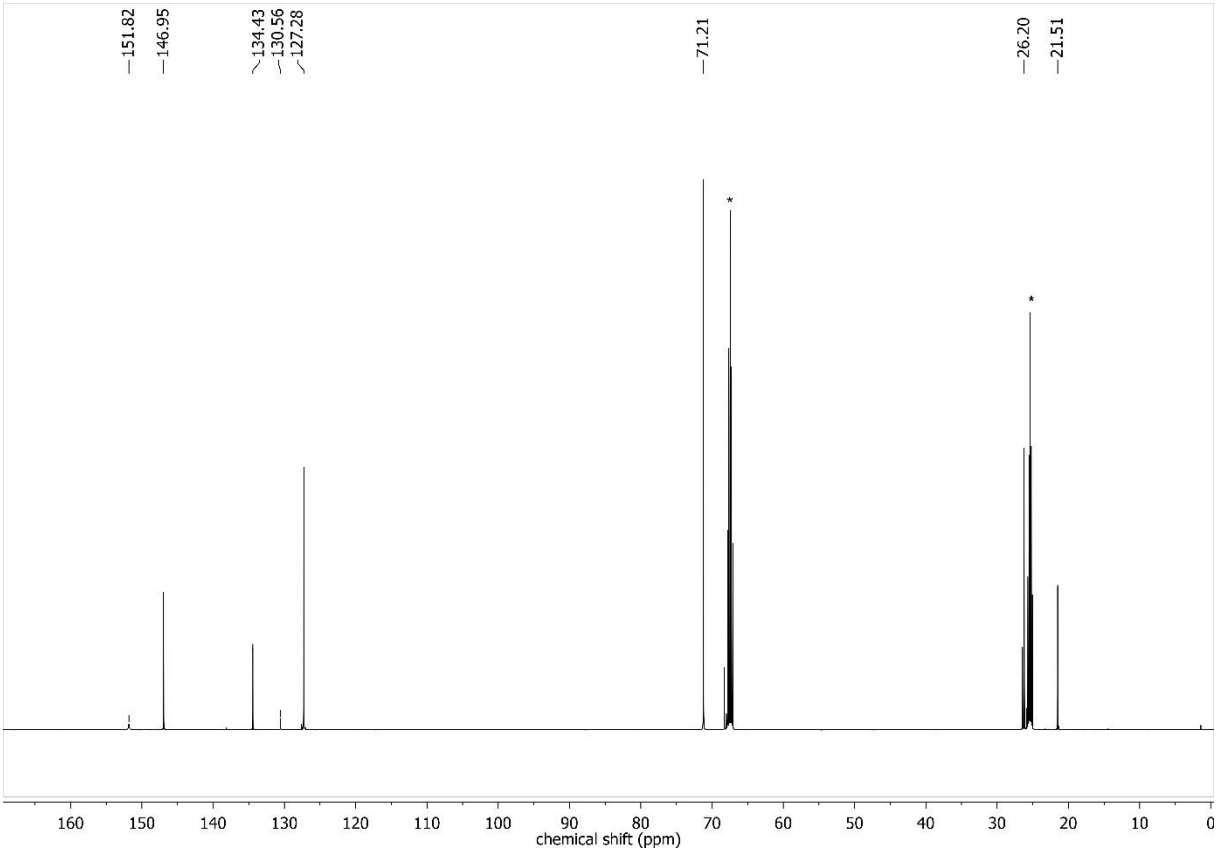

Figure S6: ^{13}C spectrum (75 MHz, 298K) of $\mathbf{1_{NCSe}}$ in THF-d_8.

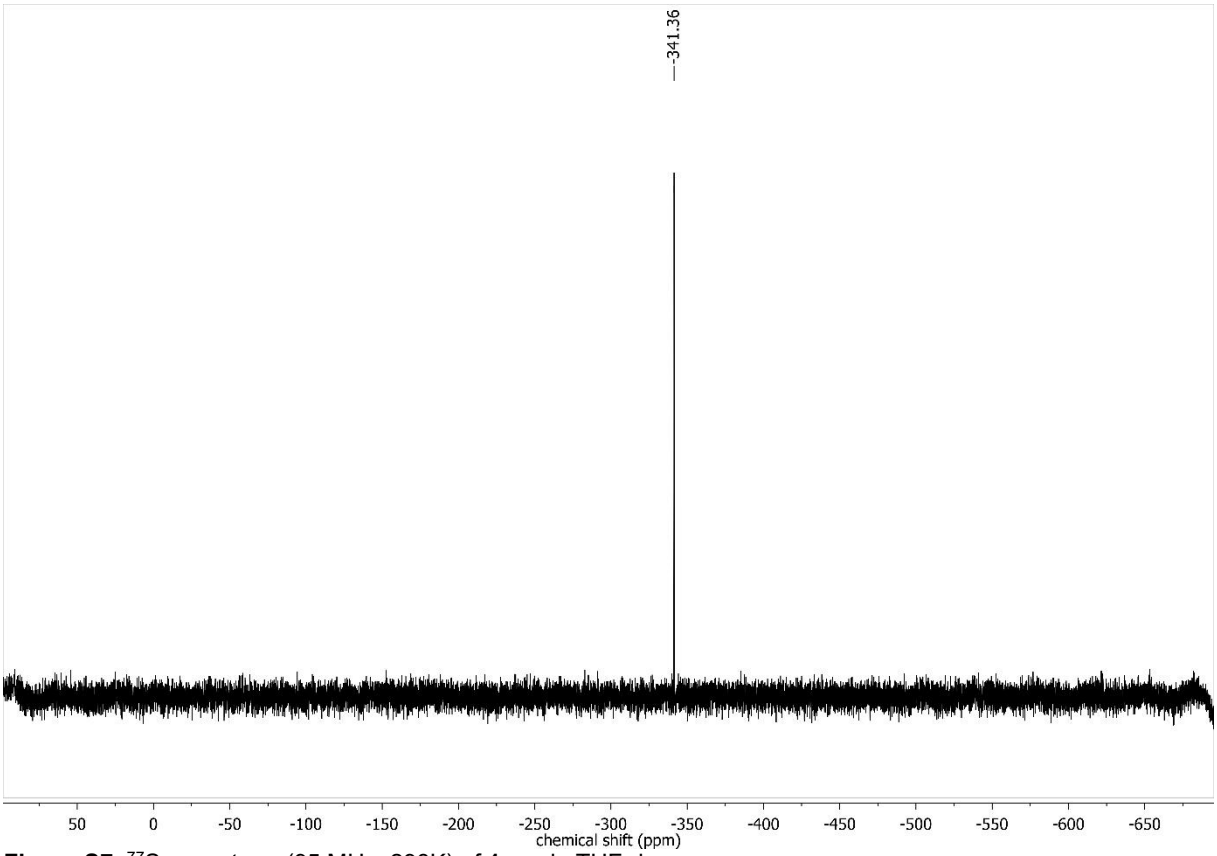

Figure S7: ^{77}Se spectrum (95 MHz, 298K) of **1$_{NCSe}$** in THF-d_8.

1.4 Compound $\mathbf{2_{NCO}}$

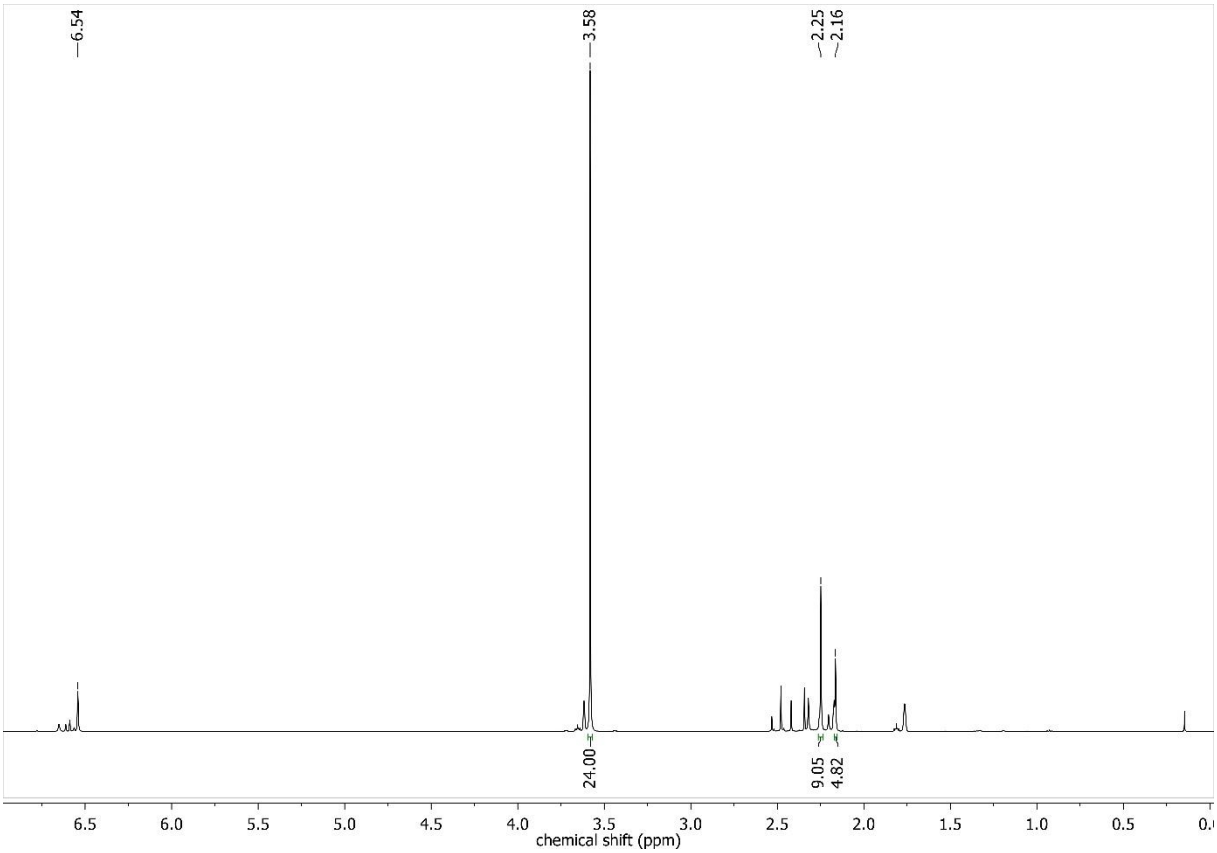

Figure S8: ^{1}H spectrum (300 MHz, 298K) of $\mathbf{2_{NCO}}$ in THF-d_8.

1.5 Compound $\mathbf{2_{NCS}}$

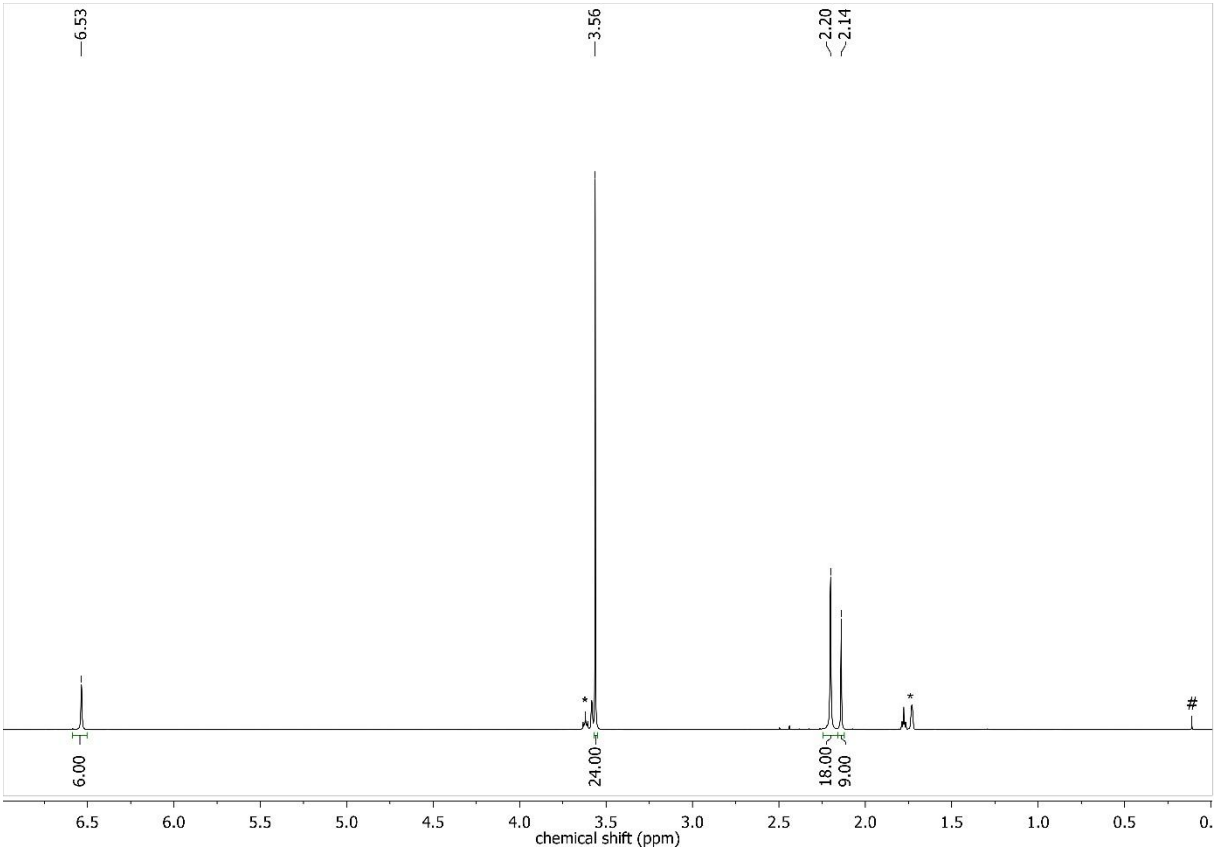

Figure S9: ^{1}H spectrum (300 MHz, 298K) of $\mathbf{2_{NCS}}$ in THF-d_8.

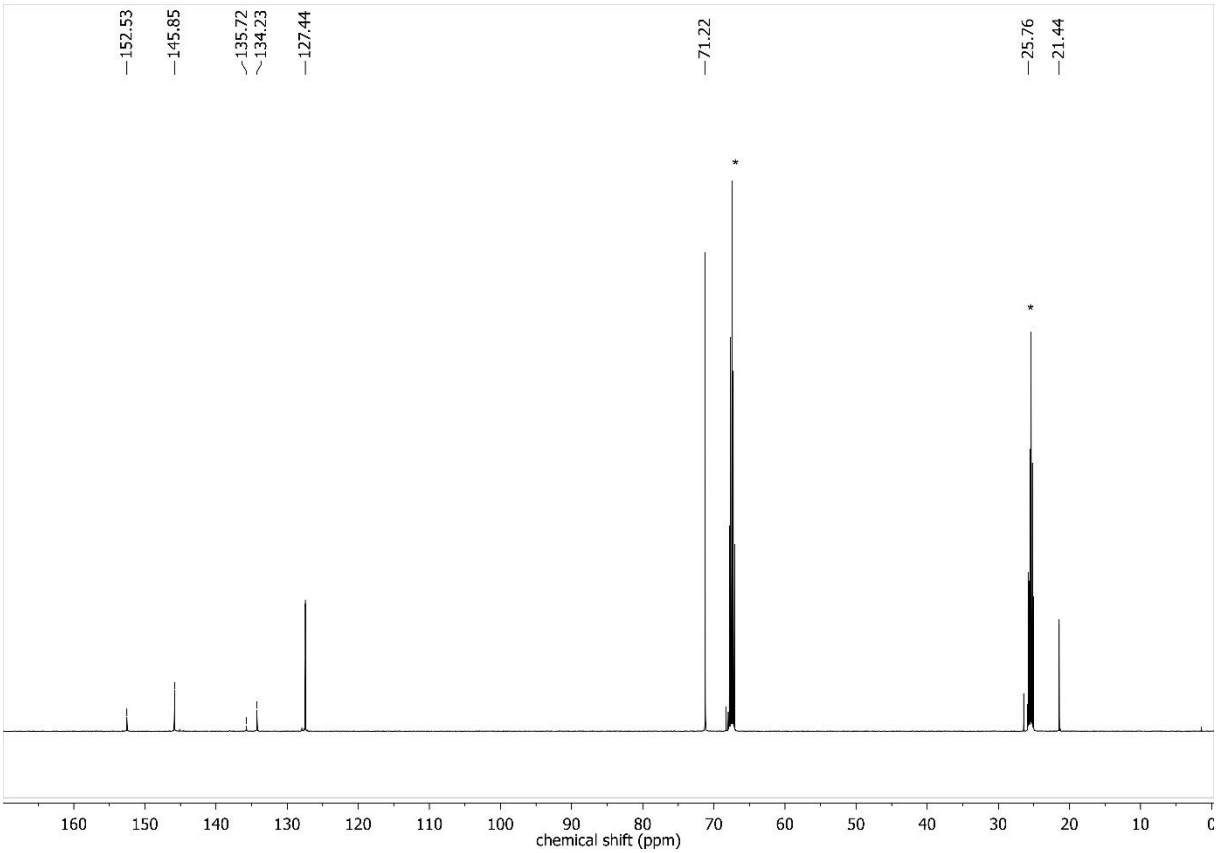

Figure S10: ^{13}C spectrum (75 MHz, 298K) of **2_{NCS}** in THF-d_8.

1.6 Compound $\mathbf{2_{NCSe}}$

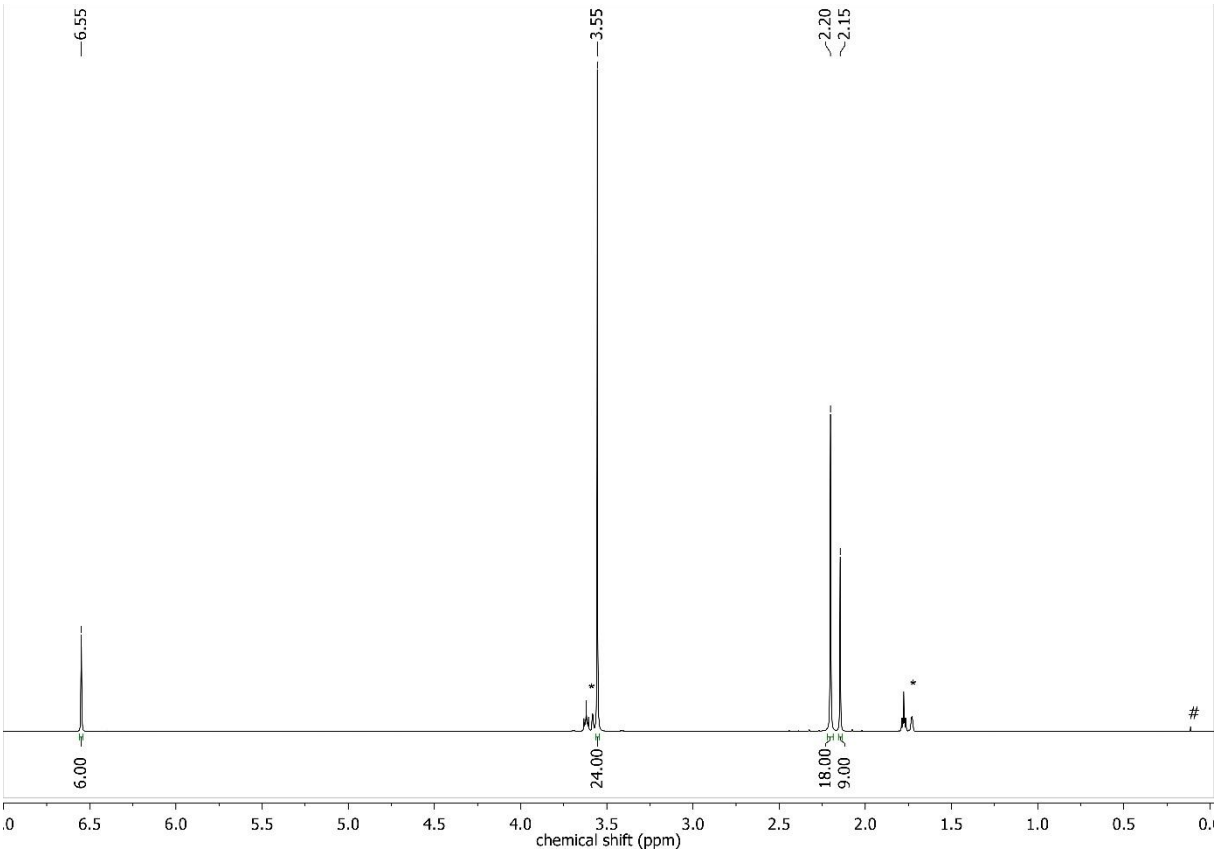

Figure S11: ^{1}H spectrum (300 MHz, 298K) of $\mathbf{2_{NCSe}}$ in THF-d_8.

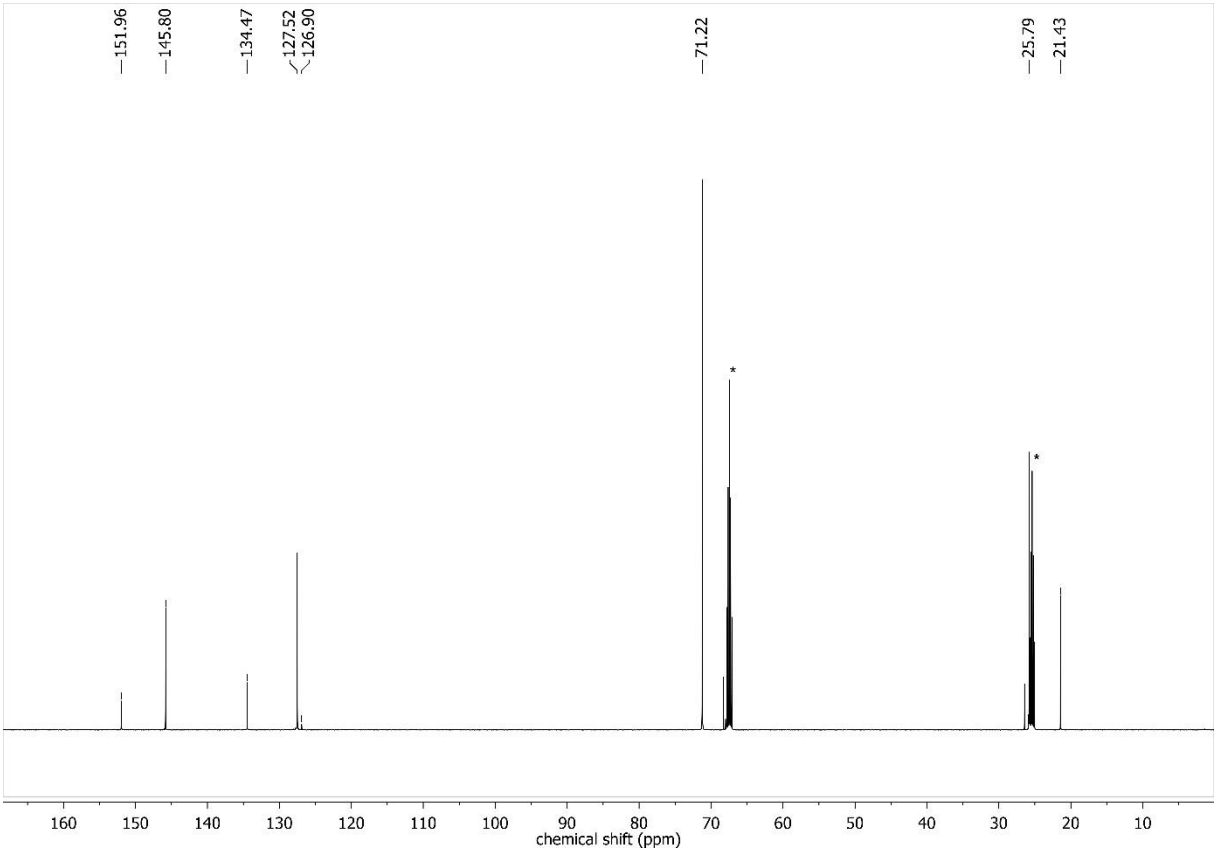

Figure S12: ^{13}C spectrum (75 MHz, 298K) of $\mathbf{2_{NCSe}}$ in THF-d_8.

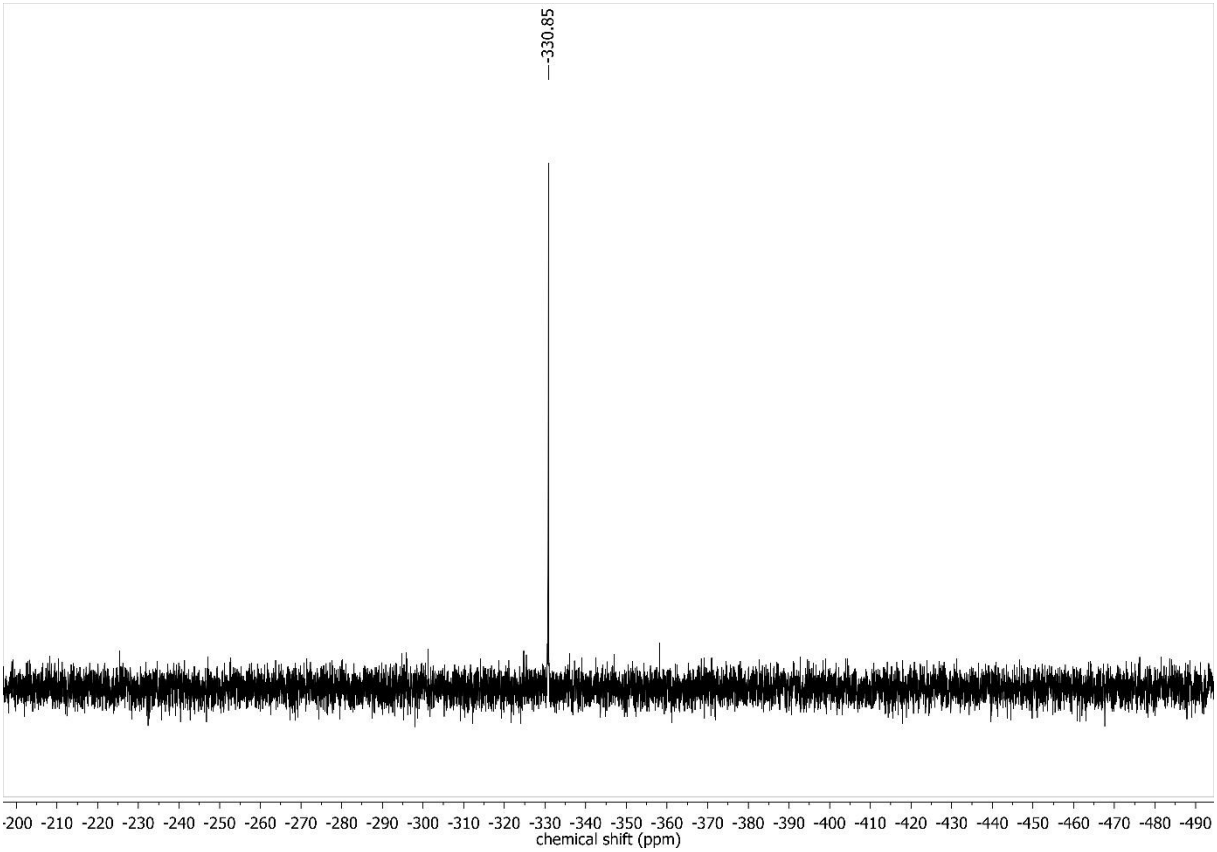

Figure S13: ^{77}Se spectrum (95 MHz, 298K) of **2$_{NCSe}$** in THF-d_8.

1.7 Compound $\mathbf{3_{NCO}}$

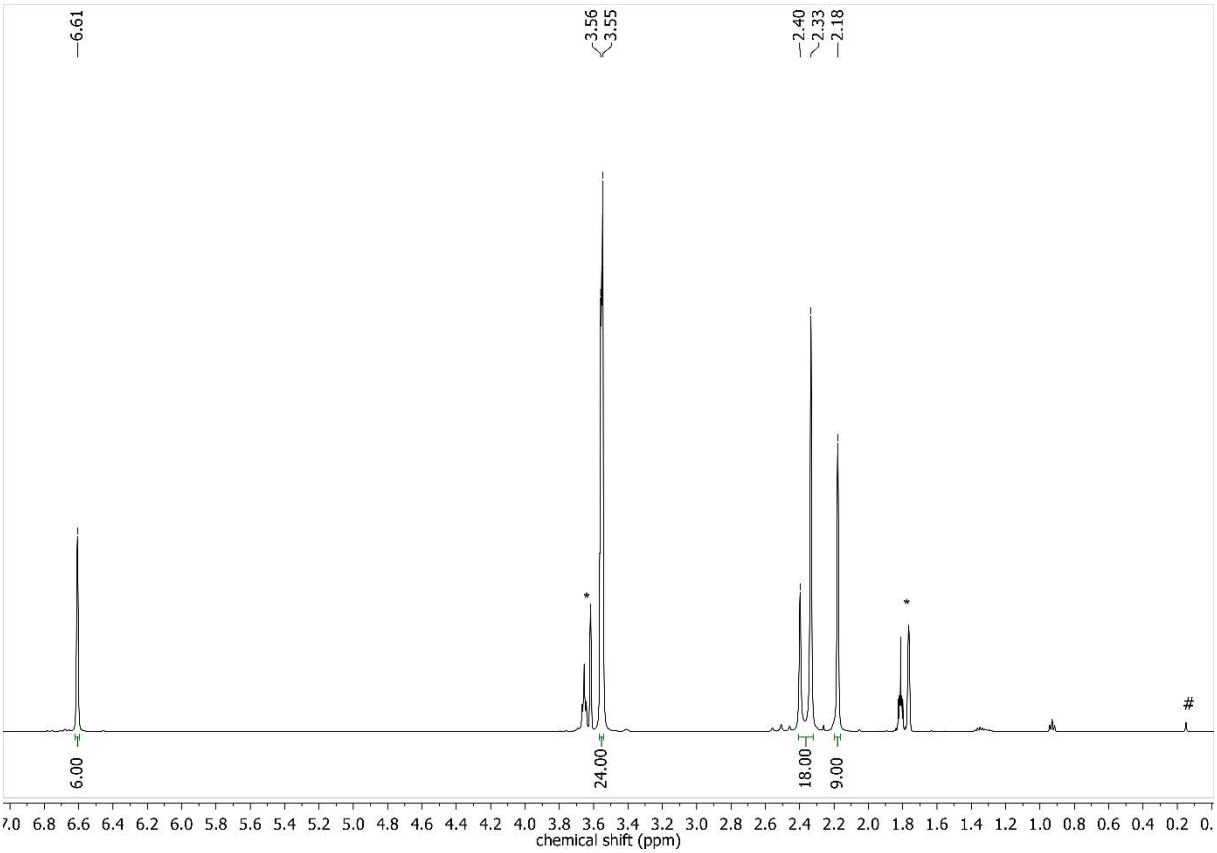

Figure S14: ^{1}H spectrum (300 MHz, 298K) of $\mathbf{3_{NCO}}$ in THF-d_8.

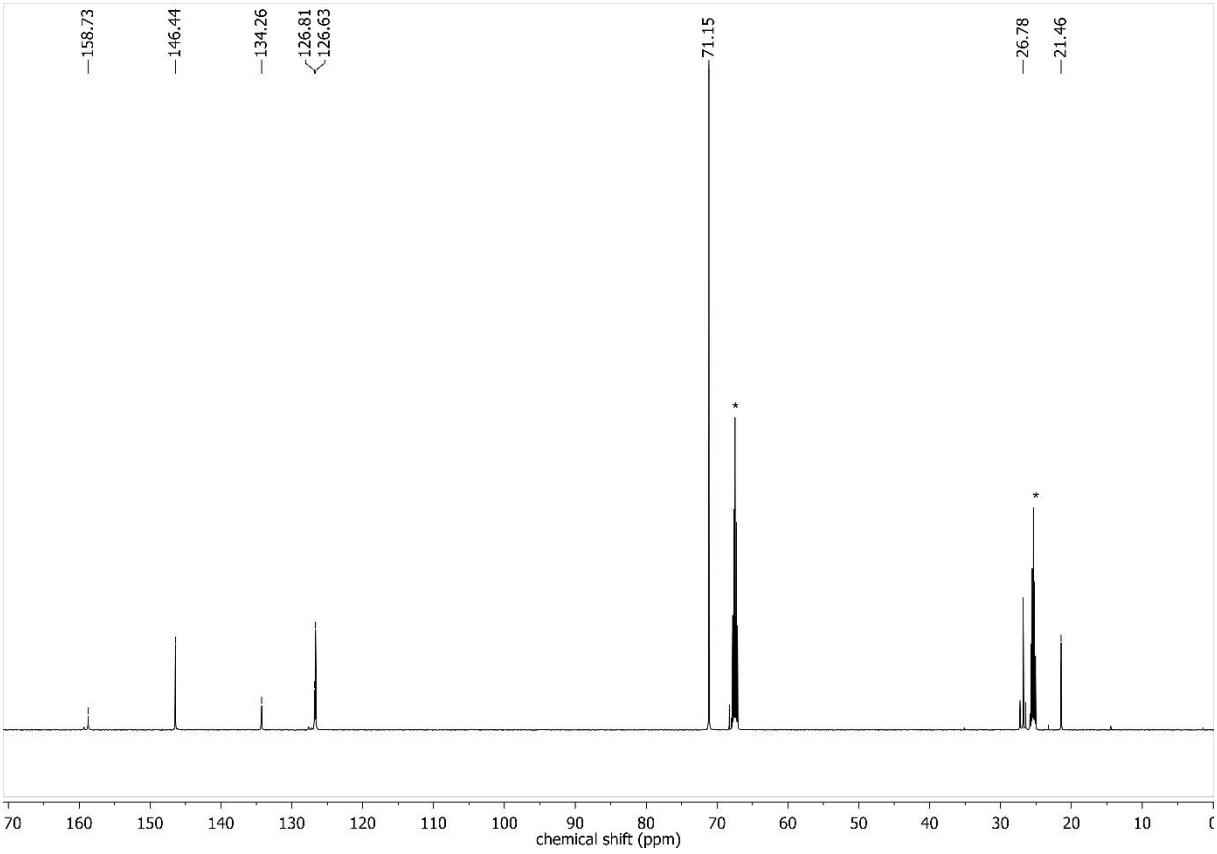

Figure S15: ^{13}C spectrum (75 MHz, 298K) of **3_{NCO}** in THF-d_8.

1.8 Compound $\mathbf{3_{NCS}}$

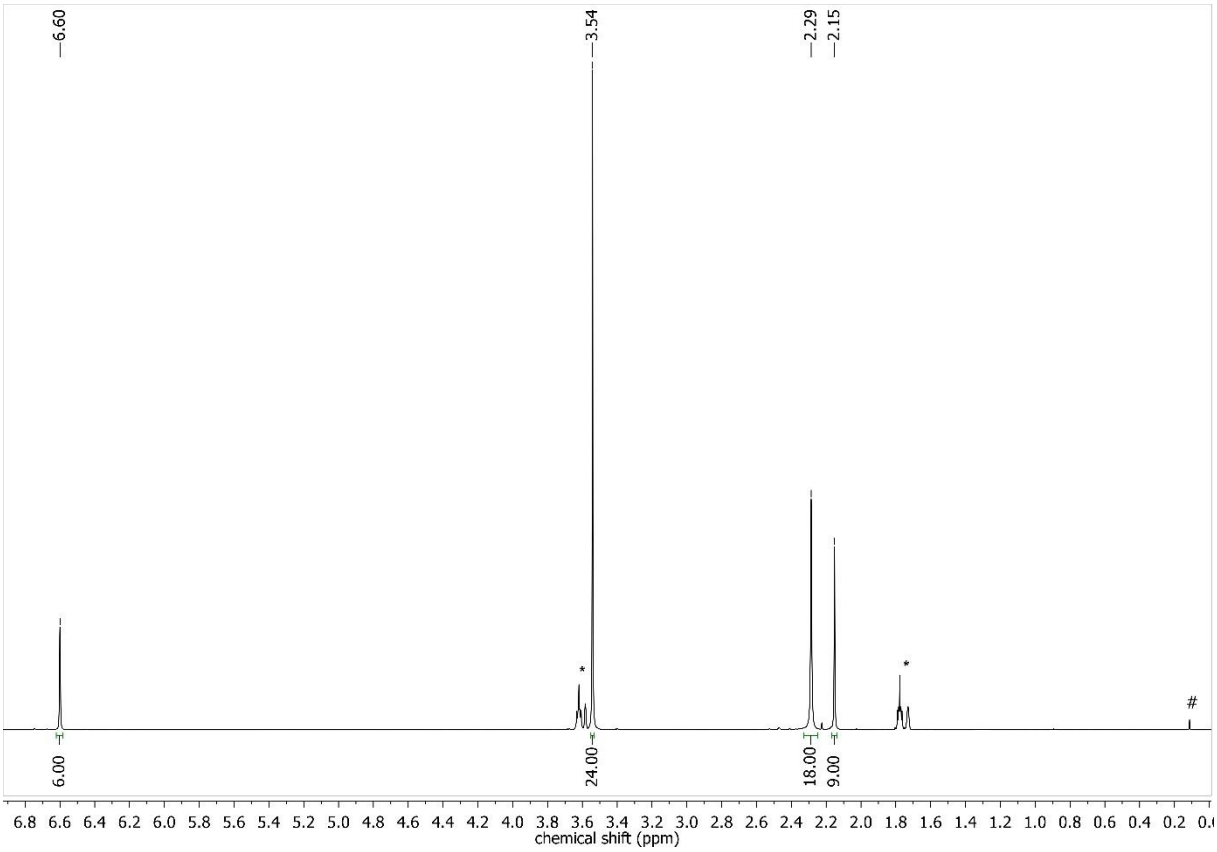

Figure S16: ^{1}H spectrum (300 MHz, 298K) of $\mathbf{3_{NCS}}$ in THF-d_8.

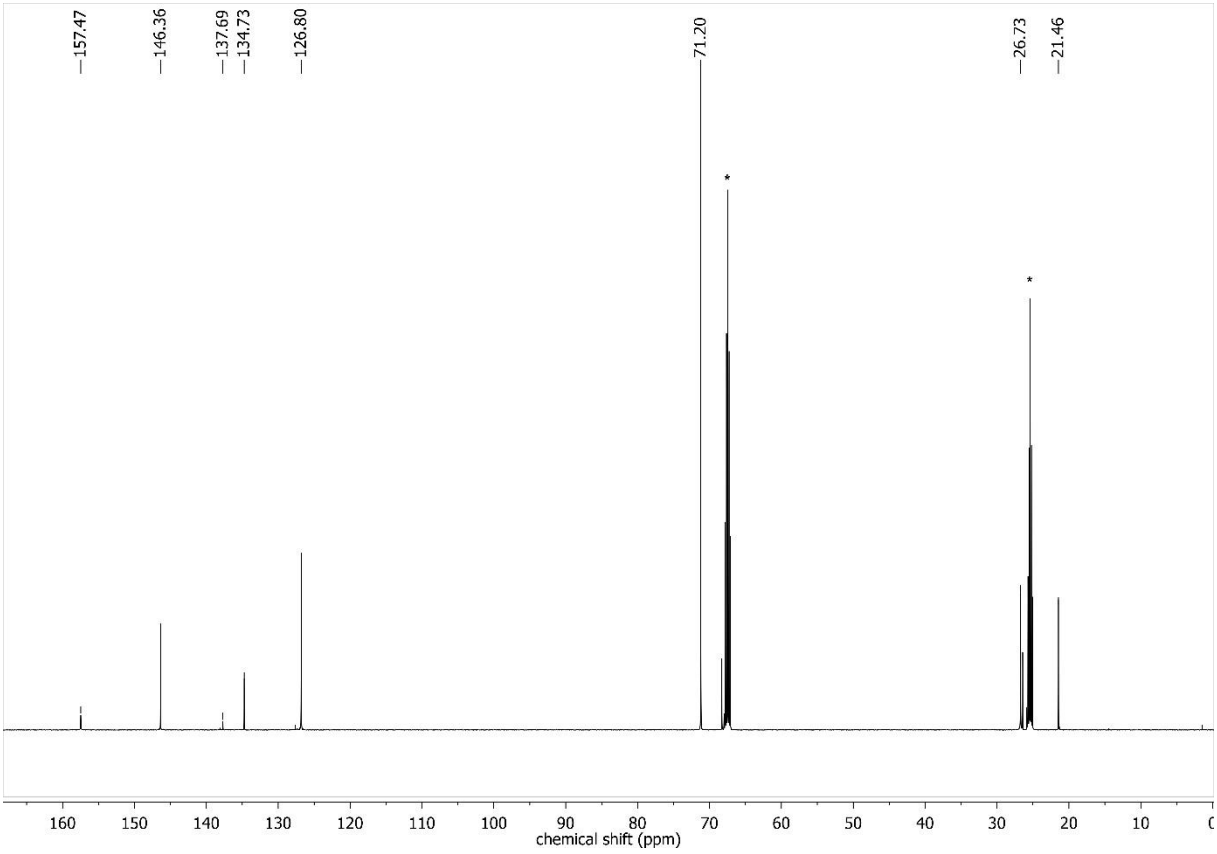

Figure S17: ^{13}C spectrum (75 MHz, 298K) of $\mathbf{3_{NCO}}$ in THF-d_8.

1.9 Compound $\mathbf{3_{NCSe}}$

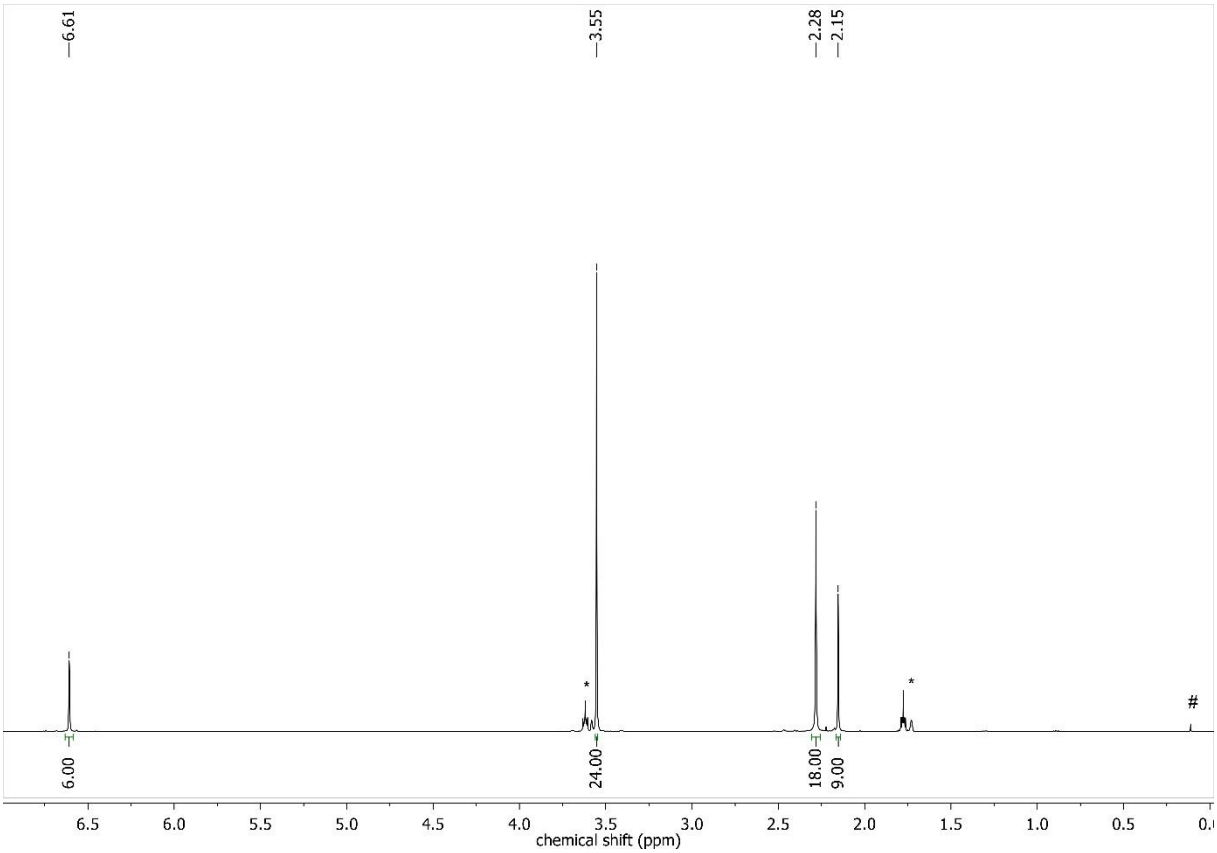

Figure S18: ^{1}H spectrum (300 MHz, 298K) of $\mathbf{3_{NCSe}}$ in THF-d_8.

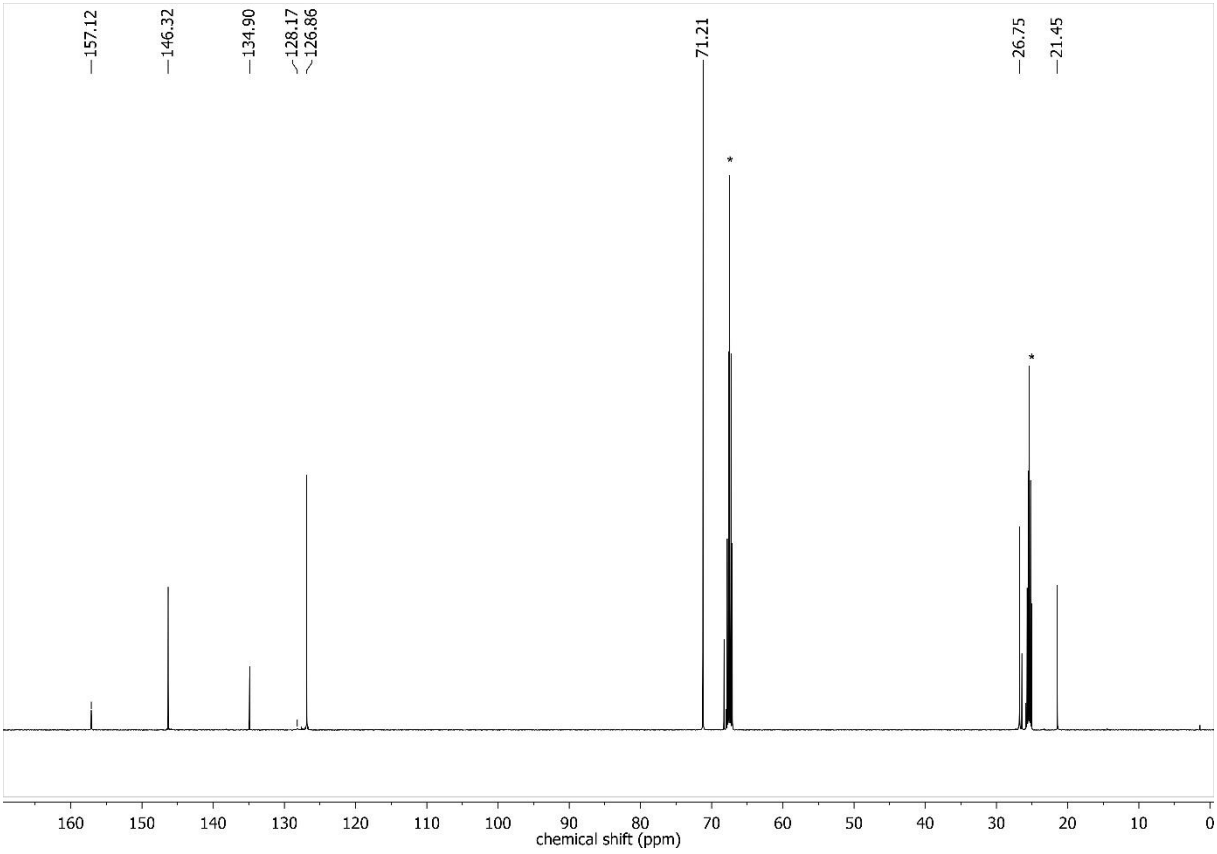

Figure S19: ^{13}C spectrum (75 MHz, 298K) of $\mathbf{3_{NCSe}}$ in THF-d_8.

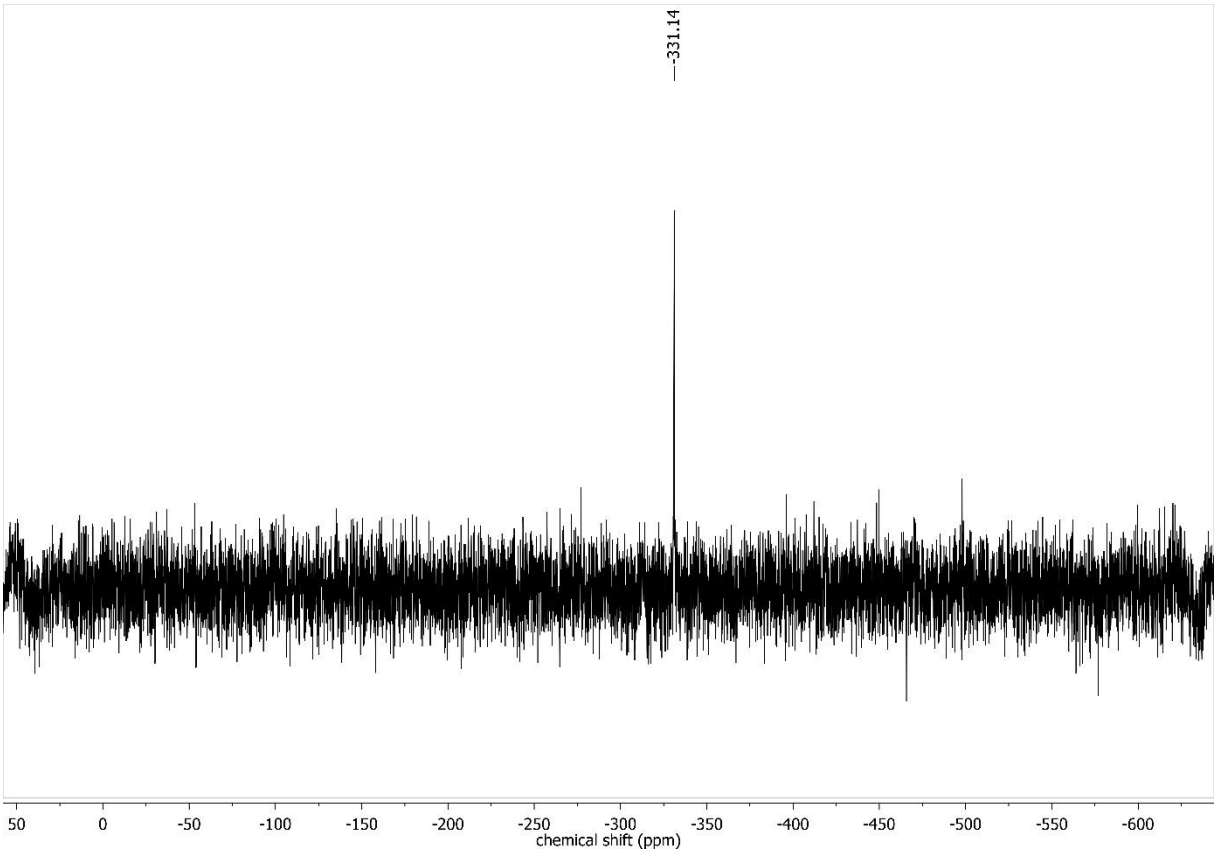

Figure S20: ^{77}Se spectrum (95 MHz, 298K) of **3$_{NCSe}$** in THF-d_8.

3. IR spectra

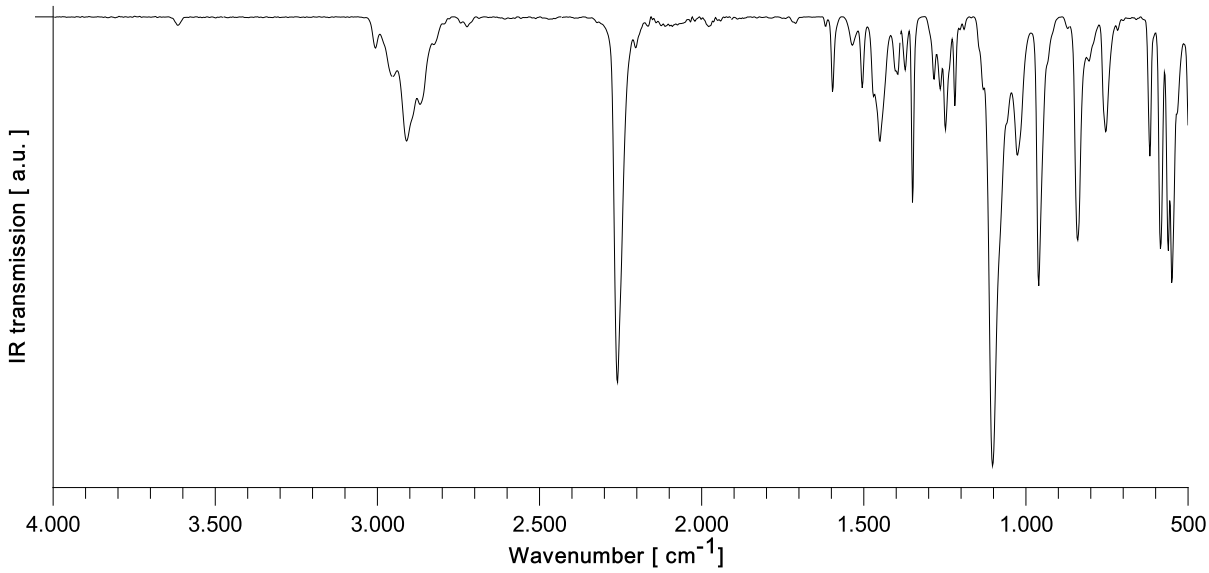

Figure S21: IR spectrum of $\mathbf{1}_{NCO}$ measured at room temperature.

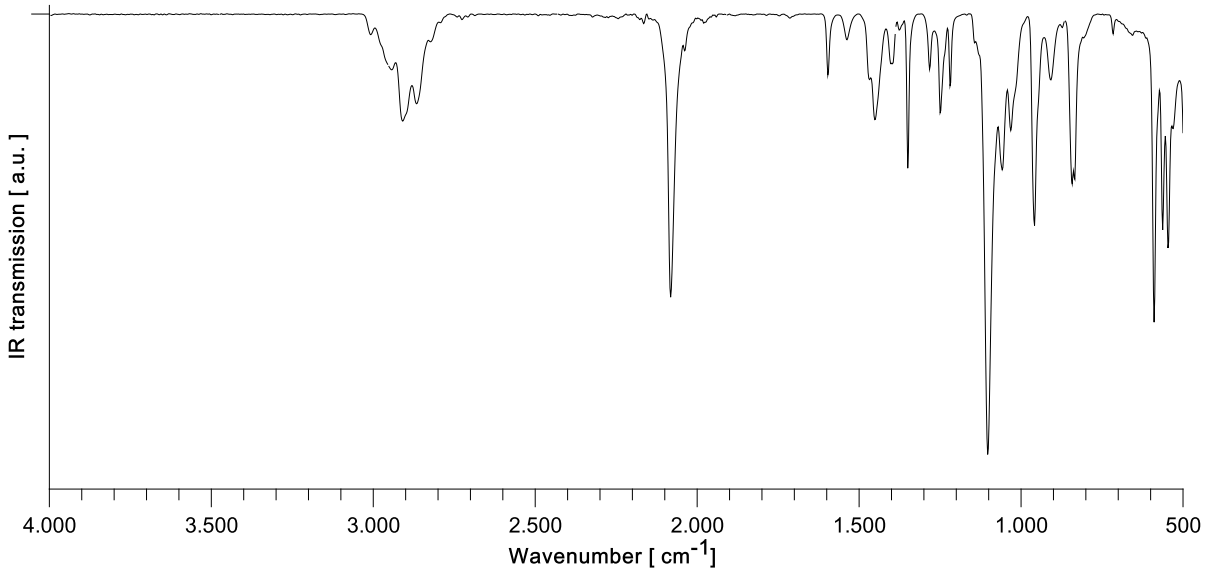

Figure S22: IR spectrum of $\mathbf{1}_{NCS}$ measured at room temperature.

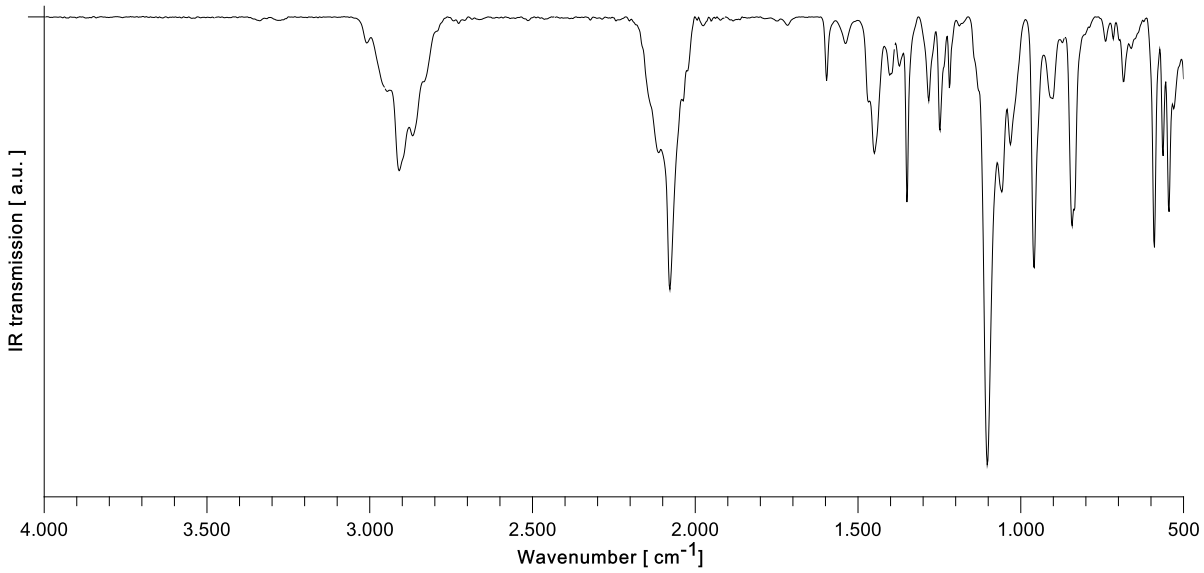

Figure S23: IR spectrum of $\mathbf{1}_{\mathbf{NCSe}}$ measured at room temperature.

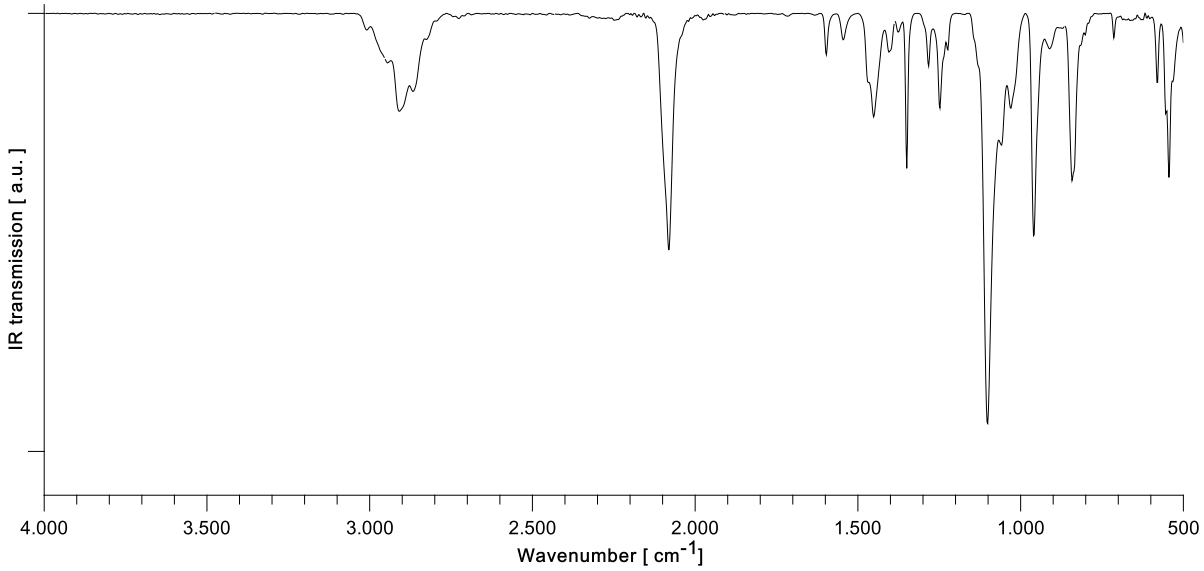

Figure S24: IR spectrum of $\mathbf{2}_{\mathbf{NCS}}$ measured at room temperature.

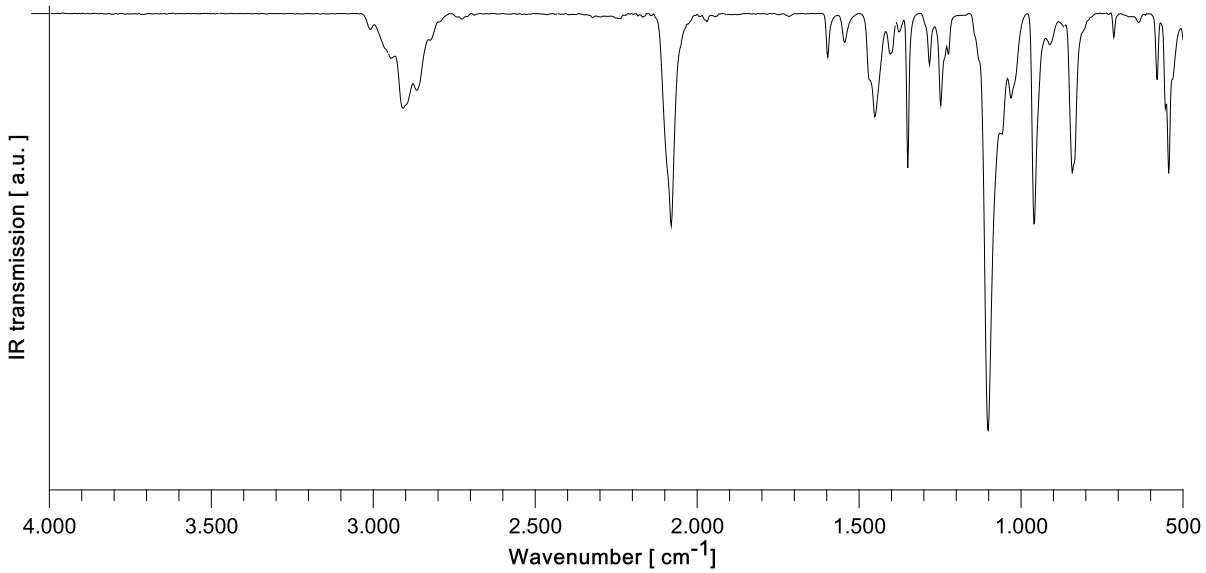

Figure S25: IR spectrum of $\mathbf{2_{NCSe}}$ measured at room temperature.

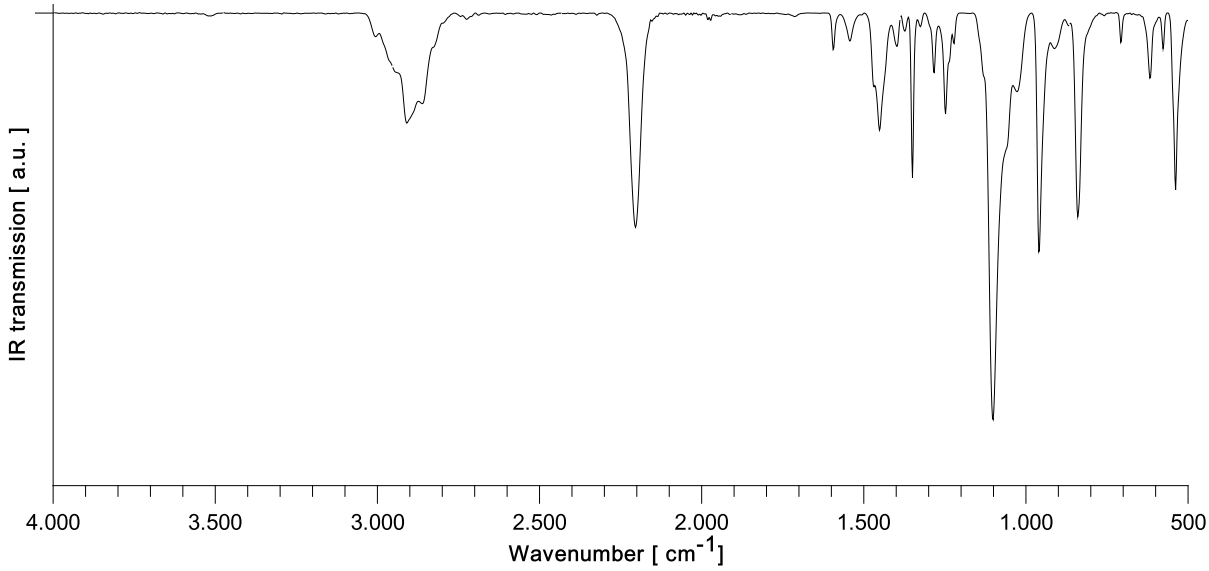

Figure S26: IR spectrum of $\mathbf{3_{NCO}}$ measured at room temperature.

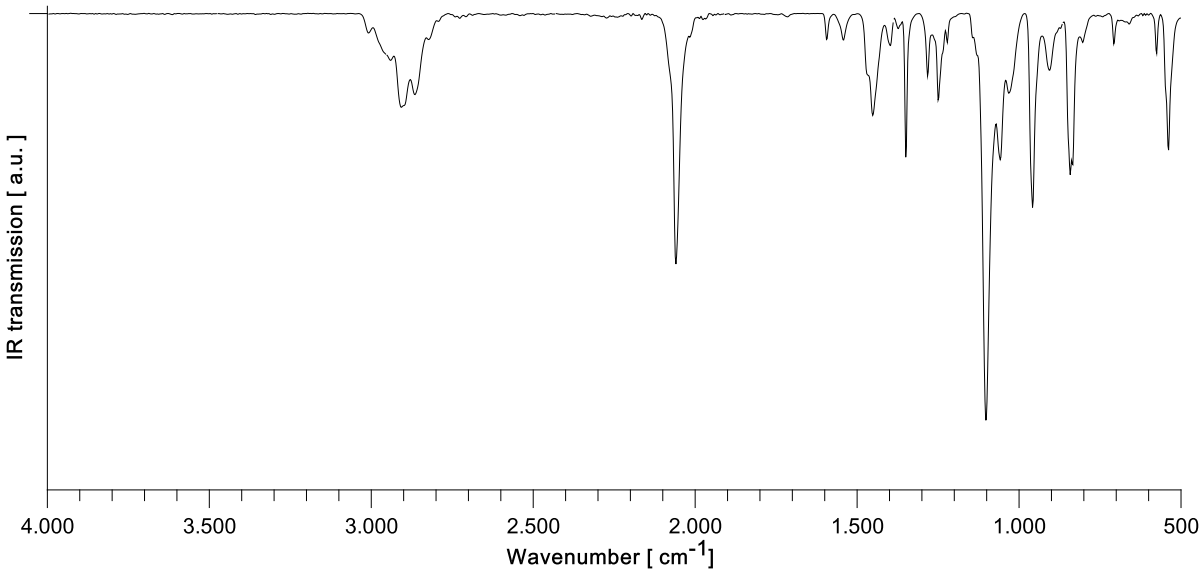

Figure S27: IR spectrum of $\mathbf{3_{NCS}}$ measured at room temperature.

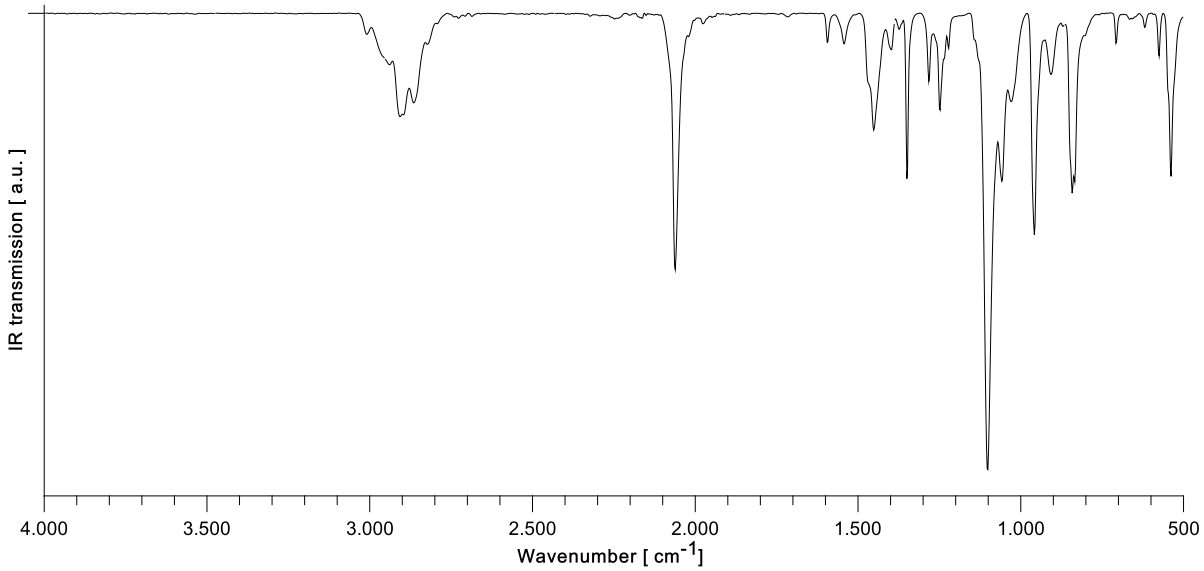

Figure S28: IR spectrum of $\mathbf{3_{NCSe}}$ measured at room temperature.

3. Additional experimental details

3.1 Synthesis of $\mathbf{2_{NCO}}$

For the synthesis of $\mathbf{2_{NCO}}$, KNCO (100 mg, 1.23 mmol, 1.00 eq), 18c6 (324 mg, 1.23 mmol, 1.00 eq) and $GaMes_3$ (525 mg, 1.23 mmol, 1.00 eq) were reacted. In the course of our investigations, the reaction conditions were varied considerably, as none of the experiments investigated yielded the target product in satisfactory purity. Reactions in 1,2-difluorobenzene, Et_2O, THF, toluene, *n*-pentane, and reaction temperatures ranging from −78 °C to 25 °C were investigated. In addition, various purification methods were investigated. These included crystallization experiments in the above-mentioned solvents and mixtures thereof at different temperatures (5 °C, −32 °C, and −72 °C) as well as overlay experiments. As mentioned above, the target product could be obtained from all reaction attempts. However, it was not possible to isolate the product cleanly.

3.2 Synthesis of $\mathbf{3_{NCO}}$

For the synthesis of $\mathbf{3_{NCO}}$, KNCO (91 mg, 1.13 mmol, 1.00 eq),18c6 (294 mg, 1.13 mmol, 1.00 eq) and $InMes_3$ (617 mg, 1.13 mmol, 1.00 eq) were reacted. In the course of our investigations, the reaction conditions were varied considerably, as none of the experiments investigated yielded the target product in satisfactory purity. Reactions in 1,2-difluorobenzene, Et_2O, THF, toluene, *n*-pentane, and reaction temperatures ranging from −78 °C to 25 °C were investigated. In addition, various purification methods were investigated. These included crystallization experiments in the above-mentioned solvents and mixtures thereof at different temperatures (5 °C, −32 °C, and −72 °C) as well as overlay experiments. As mentioned above, the target product could be obtained from all reaction attempts. However, it was not possible to isolate the product cleanly.

3.2 Solubility studies

To investigate the solubility of the various compounds used and synthesised, a defined quantity of the substances was dissolved by slowly adding solvent until the solid had completely dissolved. The quantity of solvent added was then weighed and the solubility of the respective compound was calculated from this. All work steps were carried out in the Glovebox under inert conditions. All solvents examined were freshly purified according to standard methods prior to use.

4. Crystallographic data

Table S 1: Selected single crystal X-ray data collection and refinement parameters for **1**$_{NCO}$, **1**$_{NCS}$, **1**$_{NCSe}$, **2**$_{NCS}$, **2**$_{NCSe}$, **3**$_{NCO}$, **3**$_{NCS}$ and **3**$_{NCSe}$.

	1$_{NCO}$	**1**$_{NCS}$	**1**$_{NCSe}$	**2**$_{NCS}$	**2**$_{NCSe}$	**3**$_{NCO}$	**3**$_{NCS}$	**3**$_{NCSe}$
Formula	$C_{52}H_{65}AlF_4KNO_7$	$C_{46}H_{69}AlKNO_{7.5}S$	$C_{46}H_{69}AlKNO_{7.5}Se$	$C_{46}H_{69}GaKNO_{7.5}S$	$C_{46}H_{69}GaKNO_{7.5}Se$	$C_{47.71}H_{73}Cl_{0.29}InKN_{0.71}O_{8.71}$	$C_{46}H_{69}InKNO_{7.5}S$	$C_{46}H_{69}InKNO_{7.5}Se$
CCDC	2545163	2545162	2545158	2545159	2545161	2545160	2545156	2545157
F. w. / g mol^{-1}	958.13	854.16	900.55	896.90	943.40	960.11	942.00	988.90
Crystal system	orthorhombic	triclinic	triclinic	triclinic	triclinic	monoclinic	triclinic	triclinic
Space group	*Pbca*	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
a / Å	14.3321(2)	11.7458(5)	11.8073(4)	11.7795(7)	11.7902(5)	17.8221(11)	11.8816(6)	11.9452(6)
b / Å	24.4640(5)	12.4943(6)	12.5652(4)	12.5231(6)	12.5649(5)	15.0924(9)	12.6343(6)	12.7173(6)
c / Å	29.1550(6)	16.5881(8)	16.6158(5)	16.5158(9)	16.5272(6)	20.1132(12)	16.4570(8)	16.3620(7)
α / °	90	105.777(2)	74.0990(10)	106.005(2)	106.116(2)	90	73.966(2)	106.256(2)
β / °	90	90.224(2)	89.7520(10)	90.182(2)	90.093(2)	93.332(2)	89.996(2)	90.148(2)
γ / °	90	95.378(2)	84.4790(10)	95.081(2)	95.076(2)	90	85.199(2)	94.401(2)
V / Å^3	10222.3(3)	2331.27(19)	2359.19(13)	2331.7(2)	2342.06(16)	1498.61(5)	2365.3(2)	2378.40(19)
Z	8	2	2	2	2	4	2	2
Radiation, λ / Å	1.54186 (Cu K$_\alpha$)	0.71073 (Mo K$_\alpha$)	0.71073 (Mo K$_\alpha$)	0.71073 (Mo K$_\alpha$)	0.71073 (Mo K$_\alpha$)	0.71073 (Mo K$_\alpha$)	0.71073 (Mo K$_\alpha$)	0.71073 (Mo K$_\alpha$)
Temp / K	100	100	100	100	100	100	100	100
ρ_{calc} / g cm^{-3}	1.245	1.217	1.268	1.277	1.338	1.181	1.323	1.381
μ / mm^{-1}	1.615	0.227	0.952	0.773	1.502	0.575	0.680	1.398
Reflections collected	163614	85712	73746	87053	89227	117357	58372	78370
Ind. Reflns.	8987	9154	11835	12065	11629	13383	11794	13661
Parameters	677	550	550	550	551	560	532	532
R_{int} / $R_{(\sigma)}$ / %	11.93/ 4.77	8.59 / 5.64	7.70 / 6.31	5.26 / 4.37	3.72 / 2.57	8.40 / 5.69	7.98 / 7.00	5.33 / 4.60
*R*1/*wR*2,[a] $I \geq 2\sigma I$ / %	8.06/ 20.85	4.52 / 11.09	5.35 / 13.57	4.11 / 10.18	3.05 / 8.23	6.14 / 14.23	5.69 / 13.79	4.48 / 12.38
*R*1/*wR*2,[a] all data / %	10.33/ 22.42	6.19 / 11.63	8.36 / 14.65	6.29 / 10.76	3.91 / 8.43	9.00 / 15.50	7.88 / 14.66	6.11 / 1298
GOF	0.987	1.107	1.041	1.046	1.095	1.030	1.052	1.077
Twin Law	–	–	–	–	–	–	–	–
BASF	–	–	–	–	–	–	–	–

[a] $R1 = [\Sigma||F_o| - |F_c||]/\Sigma|F_o|$; $wR2 = \{[\Sigma w[(F_o)^2 - (F_c)^2]^2]/[\Sigma w(F_o^2)^2\}^{1/2}$; $w = [\sigma^2(F_o)^2 + (AP)^2 + BP]^{-1}$, where $P = [(F_o)^2 + 2(F_c)^2]/3$ and the A and B values are 0.149900 and 0 for **1**$_{NCO}$, 0.052900 and 0.511900 for **1**$_{NCS}$, 0.068300 and 1.695200 for **1**$_{NCSe}$, 0.053100 and 0.847200 for **2**$_{NCS}$, 0.045800 and 0.574900 for **2**$_{NCSe}$, 0.061700 and 13.607901 for **3**$_{NCO}$, 0.065400 and 3.991800 for **3**$_{NCS}$, 0.071200 and 1.110800 for **3**$_{NCSe}$.

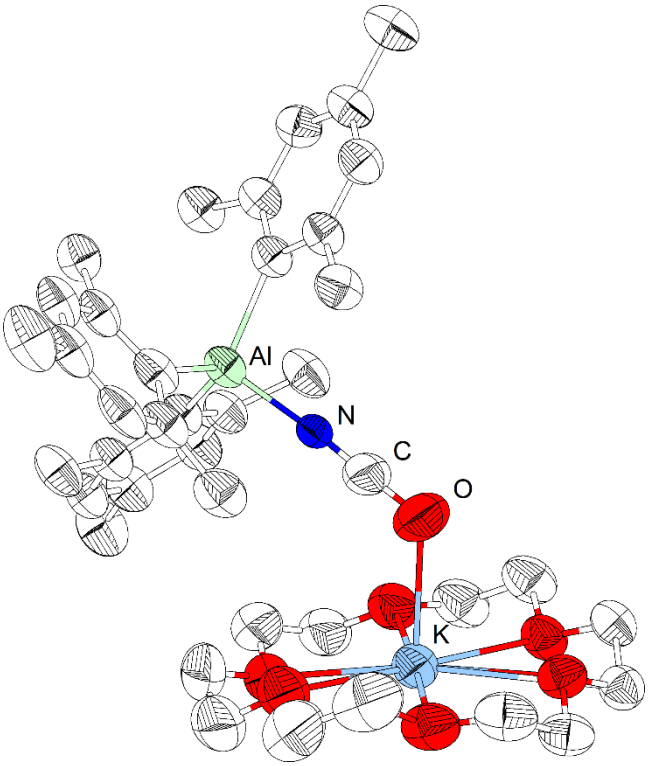

Figure S29: Molecular structure of $\mathbf{1}_{NCO}$. Hydrogen atoms are omitted for clarity. Ellipsoids drawn with 50% probability level.

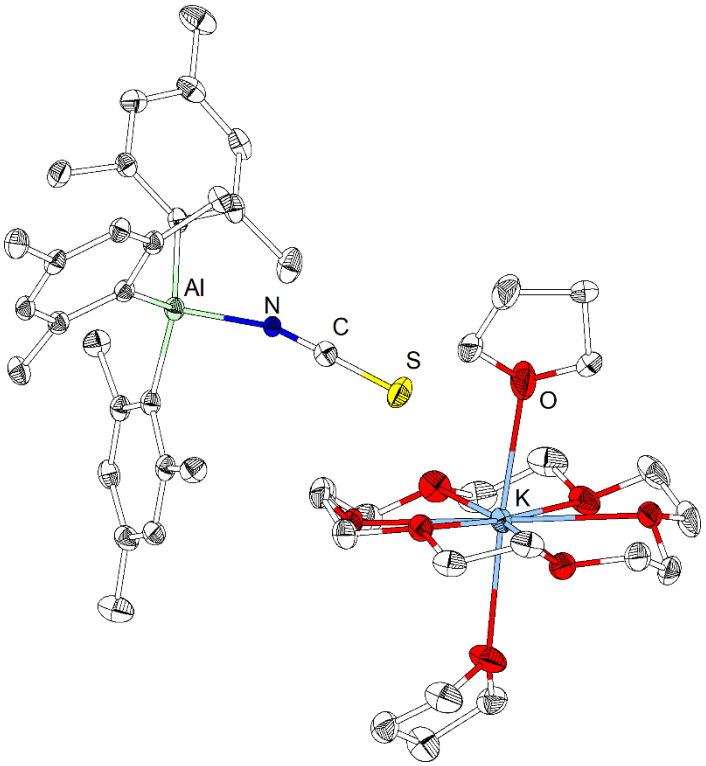

Figure S30: Molecular structure of $\mathbf{1}_{NCS}$. All hydrogen atoms bound to carbon are omitted for clarity. Ellipsoids drawn with 50% probability level.

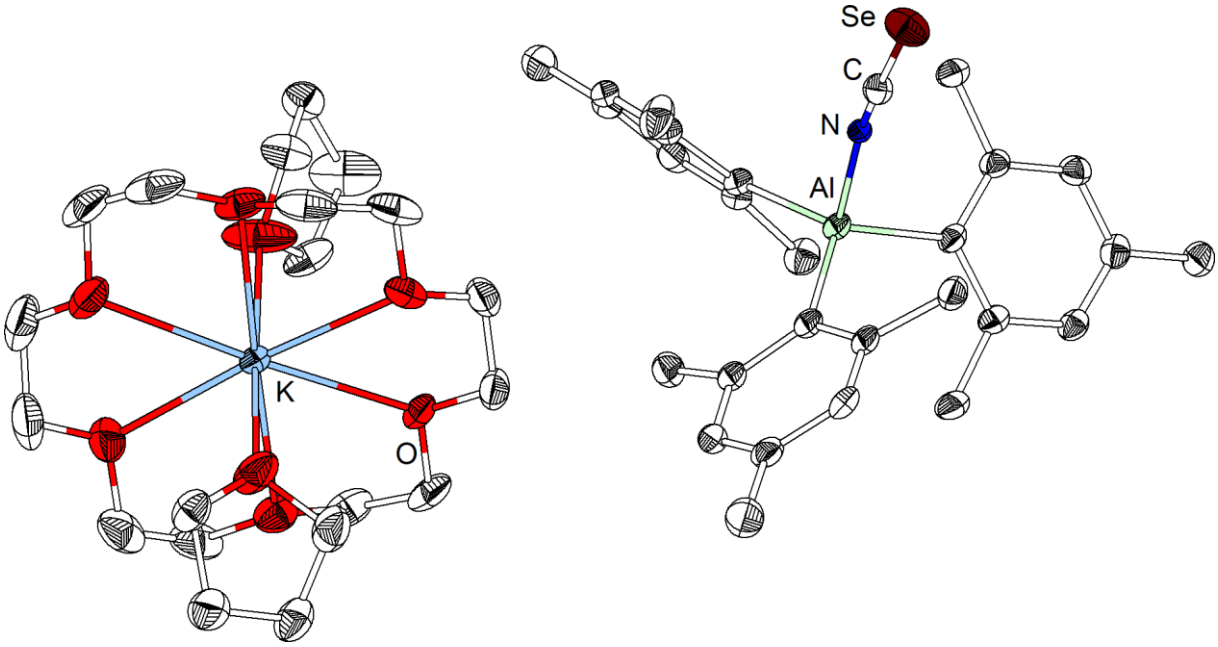

Figure S31: Molecular structure of $\mathbf{1}_{NCSe}$. All hydrogen atoms bound to carbon are omitted for clarity. Ellipsoids drawn with 50% probability level.

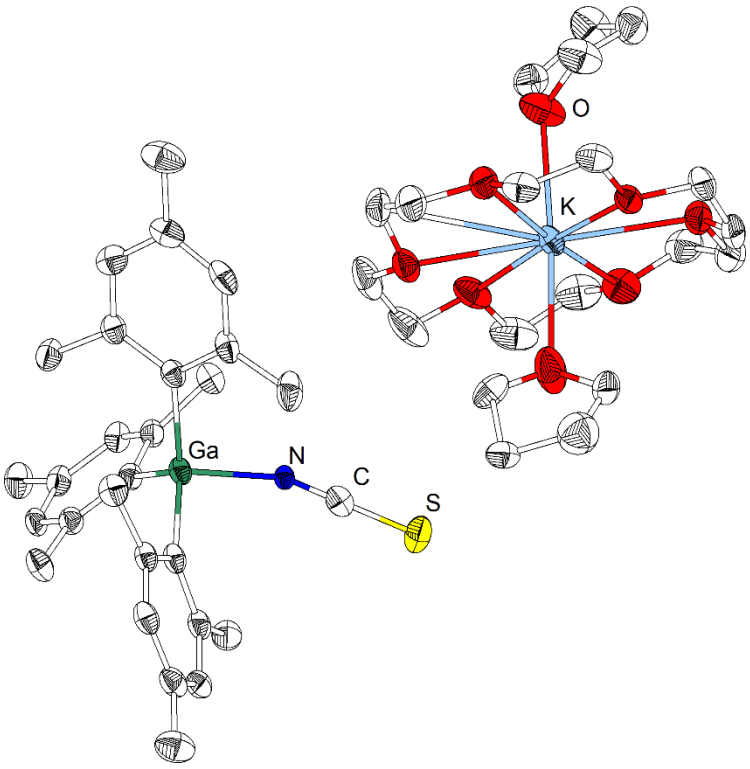

Figure S32: Molecular structure of $\mathbf{2}_{NCS}$. All hydrogen atoms bound to carbon are omitted for clarity. Ellipsoids drawn with 50% probability level.

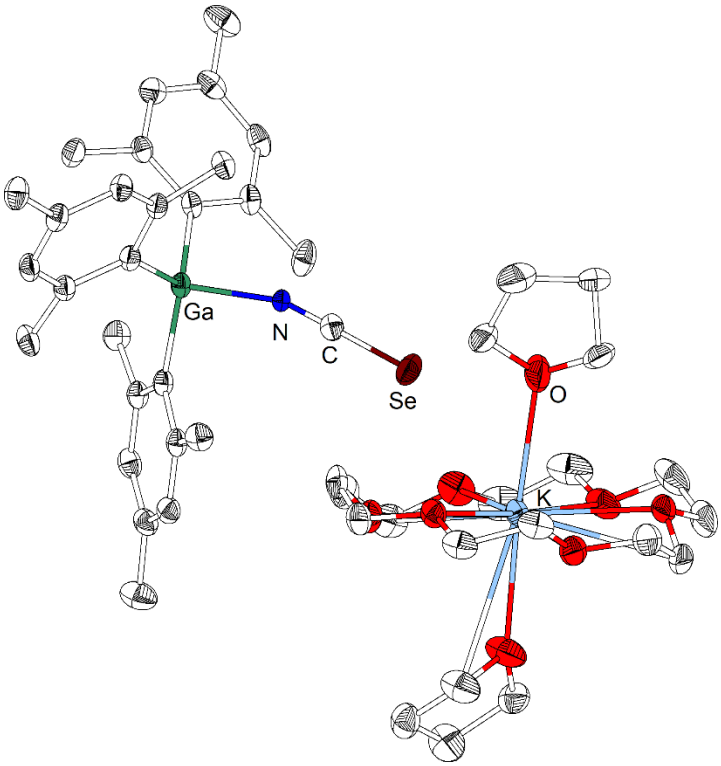

Figure S33: Molecular structure of **2**$_{NCSe}$. All hydrogen atoms bound to carbon are omitted for clarity. Ellipsoids drawn with 50% probability level.

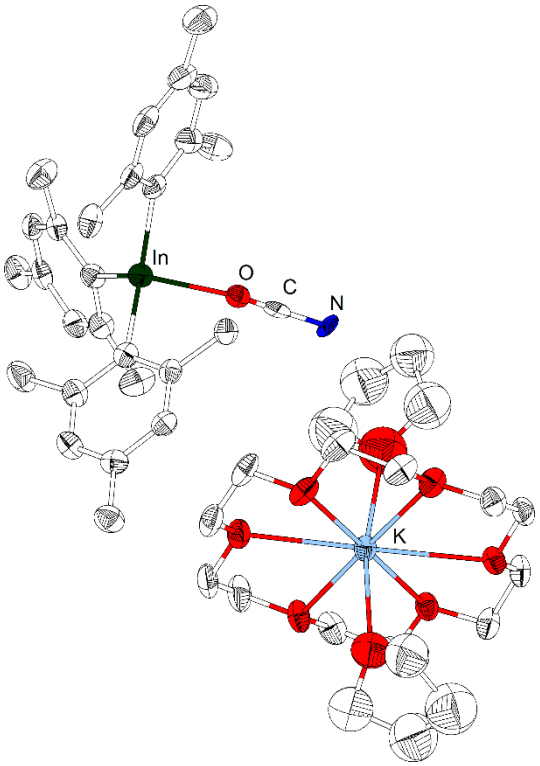

Figure S34: Molecular structure of **3**$_{NCO}$. All hydrogen atoms bound to carbon are omitted for clarity. Ellipsoids drawn with 50% probability level.

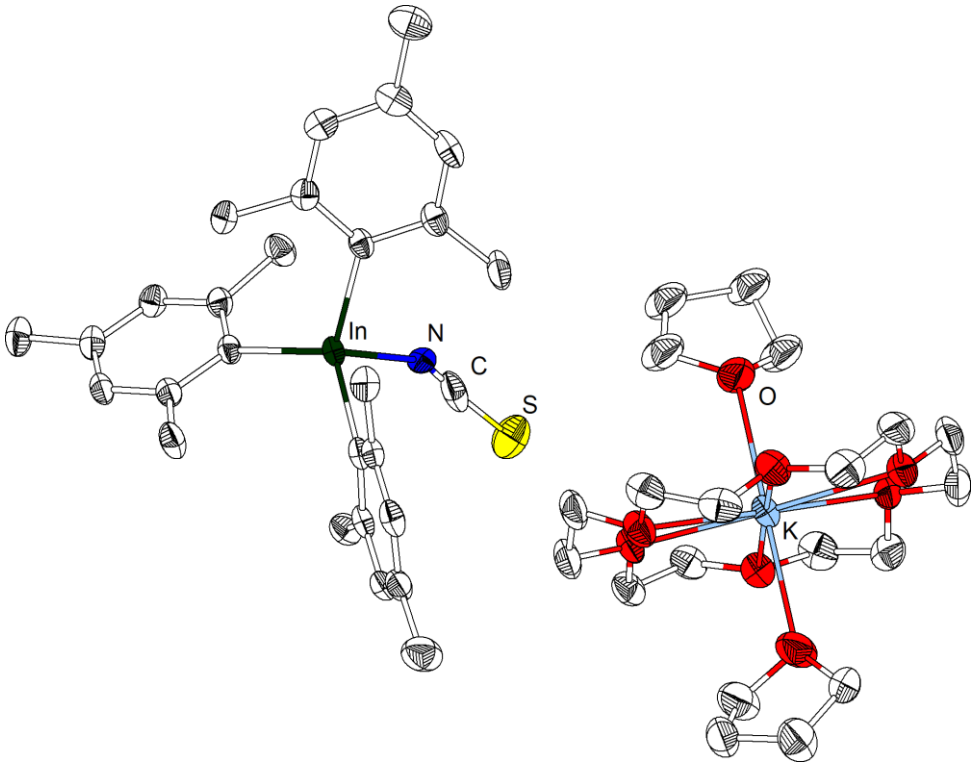

Figure S35: Molecular structure of $\mathbf{3}_{\mathbf{NCS}}$. All hydrogen atoms bound to carbon are omitted for clarity. Ellipsoids drawn with 50% probability level.

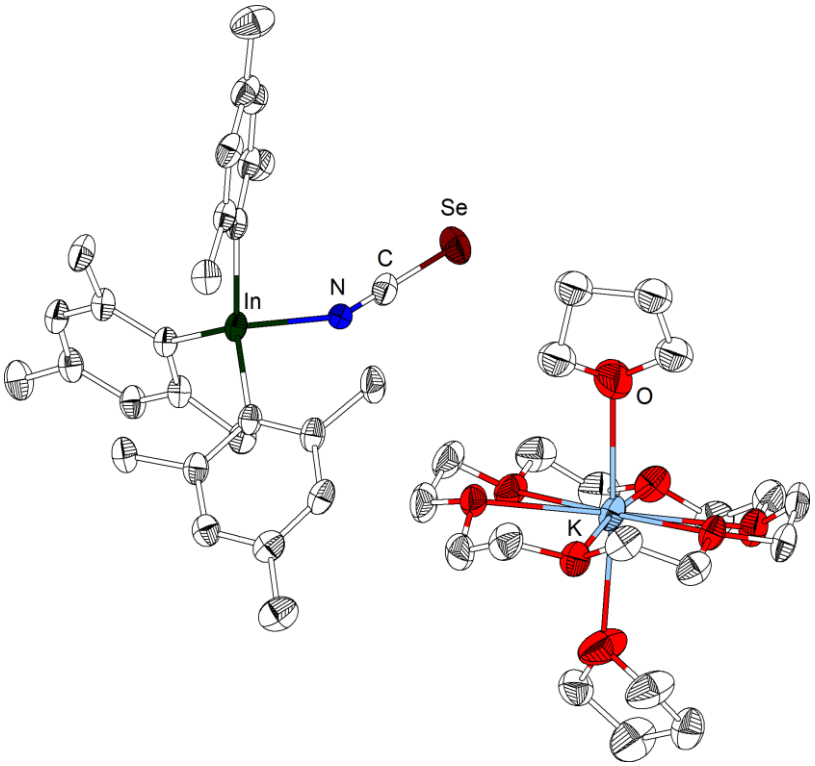

Figure S36: Molecular structure of $\mathbf{3}_{\mathbf{NCSe}}$. All hydrogen atoms bound to carbon are omitted for clarity. Ellipsoids drawn with 50% probability level.