

Supplementary information

^{77}Se and ^{13}C NMR Characterization of Selenium Cyanides

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General Information

NMR were recorded at 400 MHz on a Bruker Avance III HD spectrometer. Chemical shifts (δ) are reported in ppm. NMR data are reported as follows: chemical shift (δ), multiplicity, coupling constant (J) in Hertz and integrated intensity. ^{77}Se NMR spectra were recorded at 76.0 MHz and referenced to the diphenyl diselenide ($\text{C}_6\text{H}_5\text{SeSeC}_6\text{H}_5$; 463.0 ppm) using the substitution method (IUPAC). ^{13}C NMR spectra were recorded at 100 MHz and referenced to deuterated solvent (CDCl_3 ; 77.2 ppm or $\text{DMSO-}d_6$; 39.51 ppm or D_3CCN 1.39 ppm). Spectra were recorded in deuterated solvents at 25°C. Mass spectra (MS) were obtained on a gas chromatograph coupled to a Shimadzu GCMS-QP2010 mass spectrometer. Fragments are described by its mass/charge ratio (m/z) with the relative abundance (%) in parentheses. Melting point were determined using a PDF III Marte with 0.1 °C precision. Infrared (FT-IR) analyses were recorded on a Shimadzu IR Affinity Spectrometer operating in a range of 4000-400 cm^{-1} , with a resolution of 4 cm^{-1} and 64 scans. The samples were ground with spectroscopic grade KBr, then pressed into disks before FT-IR analysis. The NMR and FT-IR experiments were carried out at the Central Analítica – Centro de Ciências Química, Farmacêuticas e de Alimentos – Universidade Federal de Pelotas – UFPel – Pelotas – Brazil.

All solvents and reagents are commercially available (Sigma Aldrich[®]) and were used without any previous treatment. Temperatures above room temperature were maintained by use of a mineral oil bath with an electrically heated coil connected to an adjustable controller.

Experimental Procedure Se(CN)₂

Se(CN)₂ was prepared according to the Woollins and co-workers.¹ Sulfuryl chloride (0.417 g, 3.090 mmol) was added to selenium powder (0.244 g, 3.090 mmol), and the mixture was stirred for 10 min. Then tetrahydrofuran (5 mL) was added, and the solution was stirred for 1 h to give a clear brown solution of selenium dichloride. Silver cyanide (0.827 g, 6.180 mmol) was added with tetrahydrofuran (20 mL), and the solution was stirred for 1 h. The solvent was then removed in vacuo, and dichloromethane (30 mL) was added. The solution was filtered through a Celite pad and washed with dichloromethane (20 mL), and the solvent was removed in vacuo to yield the product as a white solid. ¹³C{¹H} NMR (DMSO-*d*₆, 25 °C): δ 103.7 ppm; ⁷⁷Se{¹H} NMR (DMSO-*d*₆, 25 °C): δ 440.5 ppm.

Experimental Procedure Se₂(CN)₂

Se₂(CN)₂ was prepared according to the Woollins and co-workers.¹ A mixture of silver selenocyanate (2.028 g, 9.526 mmol) and iodine (1.209 g, 4.763 mmol) was stirred for 2 h below -20 °C. The mixture was filtered to remove precipitated silver iodide, leaving the yellow solution of Se₂(CN)₂ in THF solvent (10 mL). This solution was analyzed in NMR study due the higher instability of Se₂(CN)₂. ¹³C{¹H} NMR (DMSO-*d*₆, 25 °C): δ 101.7 ppm; ⁷⁷Se{¹H} NMR (DMSO-*d*₆, 25 °C): δ 259.84 ppm.

Experimental Procedures for the synthesis of Se₃(CN)₂ (TSD)²

Experimental Procedure 1 – Without Purification

To a round-bottled flask selenium dioxide (0.67 g, 6 mmol) was added with stirring to solution of malononitrile (0.2 g, 3 mmol) in DMSO (2 mL). The mixture became reddish after 10-12 minutes (exothermic reaction). The mixture was diluted with water (6 mL) and after cooling, a yellow precipitate was formed within 10 minutes. The precipitate was filtered, dried under vacuum and the TSD was obtained in 45% yield (Yellow solid).

¹ C. J. Burchell, P. Kilian, A. M. Z. Slawin, J. D. Woollins, *Inorg. Chem.* **2006**, *45*, 710-716.

² The procedures were performed according to the following reference: A. V. Kachanov, O. Y. Slabko, O. V. Baranova, E. V. Shilova, V. A. Kaminskii, *Tetrahedron Lett.* **2004**, *45*, 4461-4463.

Experimental Procedure 2 – Washed with Water

To a round-bottled flask selenium dioxide (0.67 g, 6 mmol) was added with stirring to solution of malononitrile (0.2 g, 3 mmol) in DMSO (2 mL). The mixture became reddish after 10-12 minutes (exothermic reaction). The mixture was diluted with water (6 mL) and after cooling, a yellow precipitate was formed within 10 minutes. The precipitate formed was filtered and washed with 20 mL of H₂O and then dried under vacuum where the TSD was obtained in 41 % yield (Yellow solid).

Experimental Procedure 3 – Recrystallized in Benzene

To a round-bottled flask selenium dioxide (0.67 g, 6 mmol) was added with stirring to solution of malononitrile (0.2 g, 3 mmol) in DMSO (2 mL). The mixture became reddish after 10-12 minutes (exothermic reaction). The mixture was diluted with water (6 mL) and after cooling, a yellow precipitate was formed within 10 minutes. The precipitate formed was filtered, dried under vacuum, and crystallized using benzene as solvent. TSD was obtained in 37 % yield (Yellow solid).

Experimental Procedure 4 – Washed with Ethanol

To a round-bottled flask selenium dioxide (0.67 g, 6 mmol) was added with stirring to solution of malononitrile (0.2 g, 3 mmol) in DMSO (2 mL). The mixture became reddish after 10-12 minutes (exothermic reaction). The mixture was diluted with water (6 mL) and after cooling, a yellow precipitate was formed within 10 minutes. The precipitate formed was filtered and washed with 20 mL of ethanol then dried under vacuum the TSD was obtained in 40 % yield (Red solid). This distinct color is result of a degradation derived from the ethanol solvent.

Experimental Procedure 5 – Washed with DCM

To a round-bottled flask selenium dioxide (0.67 g, 6 mmol) was added with stirring to solution of malononitrile (0.2 g, 3 mmol) in DMSO (2 mL). The mixture became reddish after 10-12 minutes (exothermic reaction). The mixture was diluted with water (6 mL) and after cooling, a yellow precipitate was formed within 10 minutes. The precipitate formed was filtered and washed with 20 mL of dichloromethane and then dried under vacuum and the TSD was obtained in 40 % yield (Yellow solid).

Melting Point Results

The samples of $\text{Se}_3(\text{CN})_2$ were obtained from the experimental procedures previously described.

Table S1: Melting points results.^a

Entry	Procedure	Melting Point (°C)
1	1	134-136
2	2	134-136
3	3	133-134
4	4	132-135
5	5	130-131

^a The melting point experiments were performed in triplicate.

NMR samples

To prepare the NMR experiments, 5 mg of the TSD was added in 750 μL of the deuterated solvent. The solubility was evaluated along with the purity of the TSD samples. The TSD was not soluble in CDCl_3 , D_2O , $\text{Py}-d_5$ and $\text{Benzene}-d_6$ solvents.

NMR sample of procedure 1 was centrifuged to eliminate the presence of elemental selenium (Figure S1).



Figure S1: NMR sample of TSD in $\text{DMSO}-d_6$ after centrifuged.

When the TSD was solubilized in MeOD- d_4 , the color solution changed for red color, as can be seen in the Figure S2. The $^{77}\text{Se}\{-^1\text{H}\}$ NMR experiment of this solution did not show signals, possibly due the degradation.



Figure S2: NMR sample of TSD in MeOD- d_4 .

Selected NMR Spectra

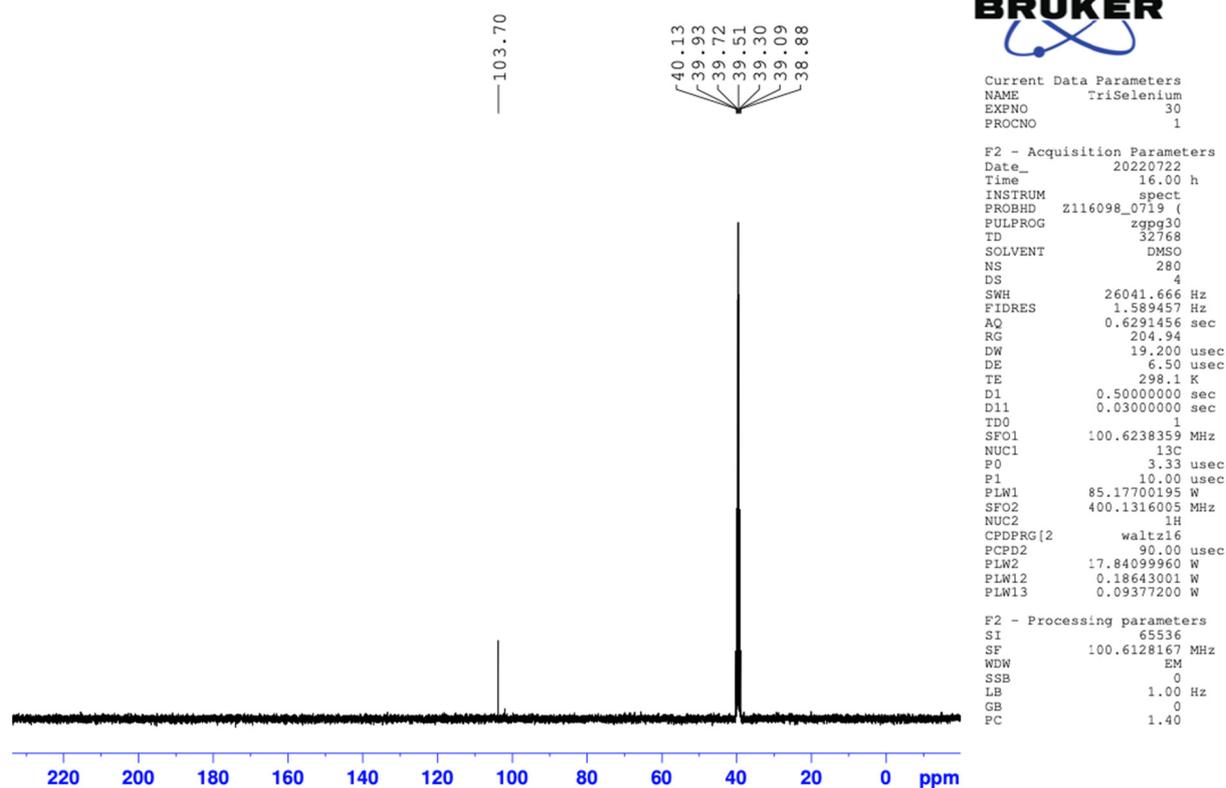


Figure S3: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $\text{Se}(\text{CN})_2$ in $\text{DMSO-}d_6$.

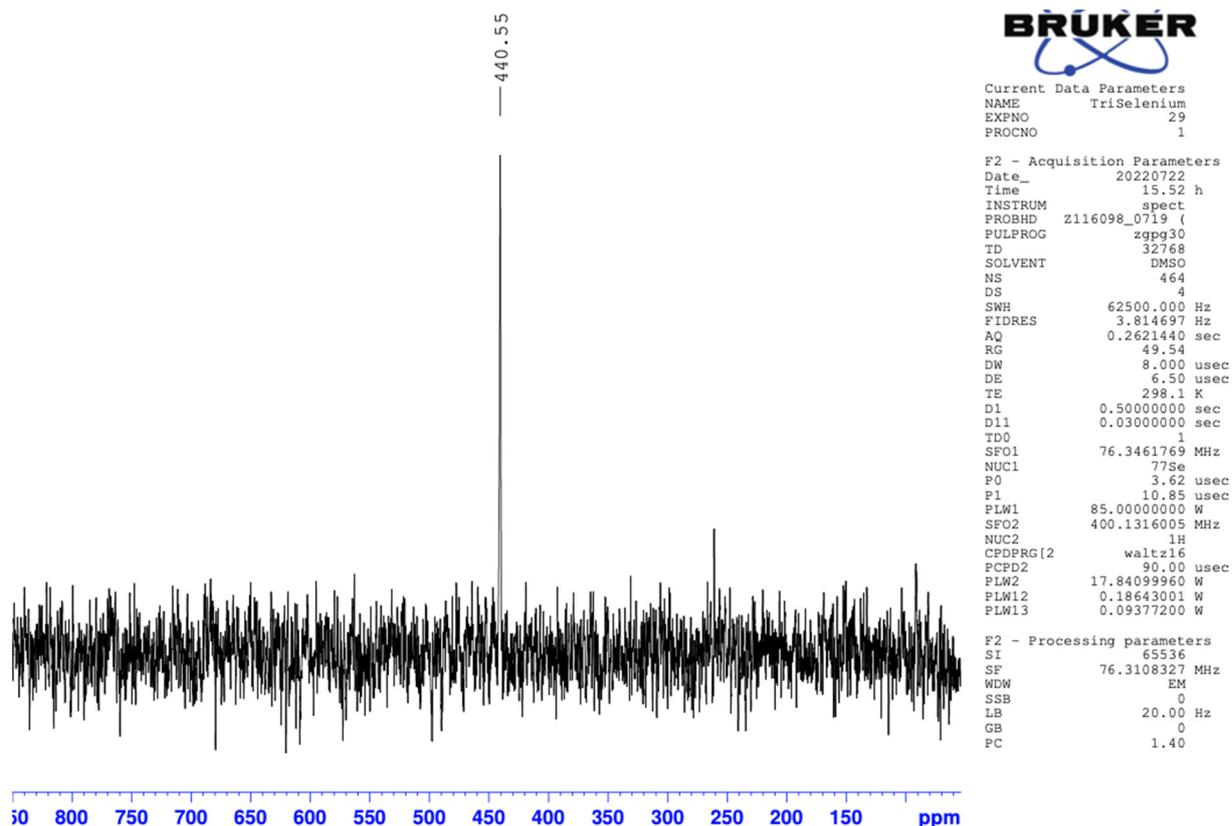


Figure S4: $^{77}\text{Se}\{^1\text{H}\}$ NMR spectrum of $\text{Se}(\text{CN})_2$ in $\text{DMSO-}d_6$.

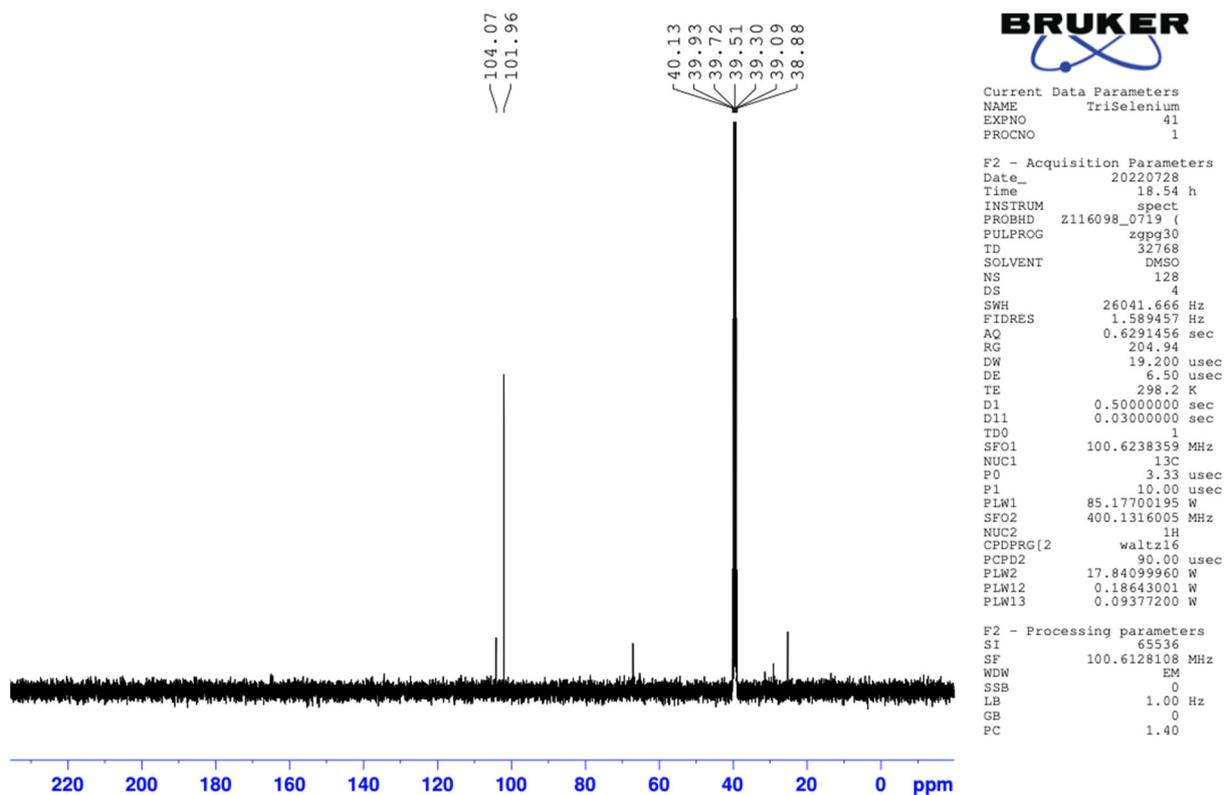


Figure S5: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $\text{Se}_2(\text{CN})_2$ in $\text{DMSO-}d_6$.

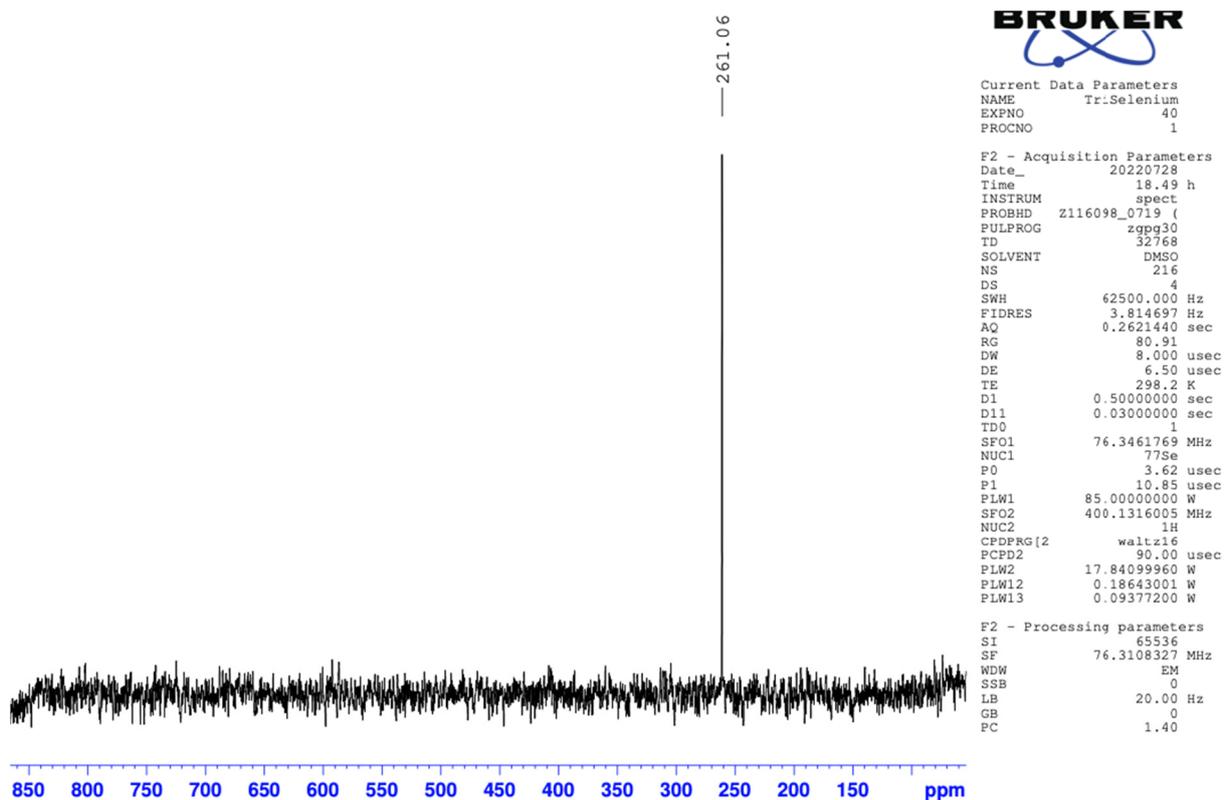


Figure S6: $^{77}\text{Se}\{^1\text{H}\}$ NMR spectrum of $\text{Se}_2(\text{CN})_2$ in $\text{DMSO-}d_6$.

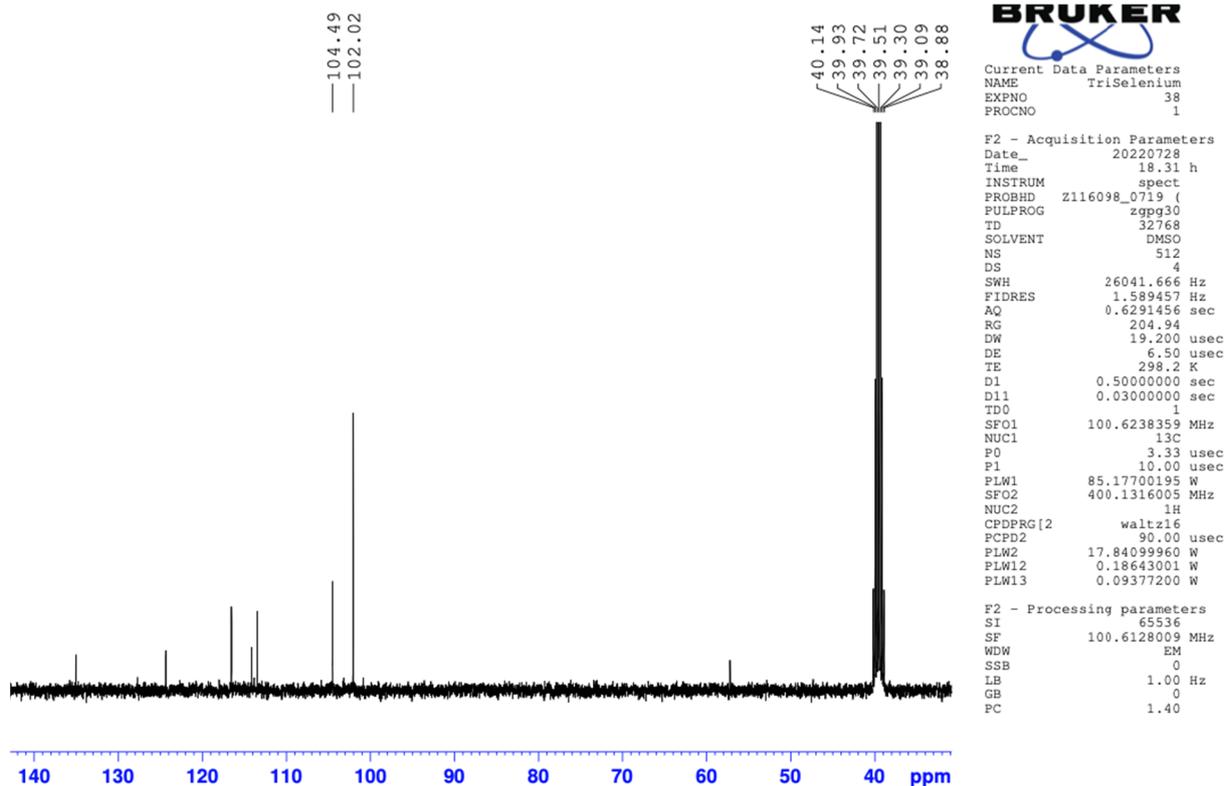


Figure S7: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of TSD in $\text{DMSO-}d_6$ prepared *in situ*.

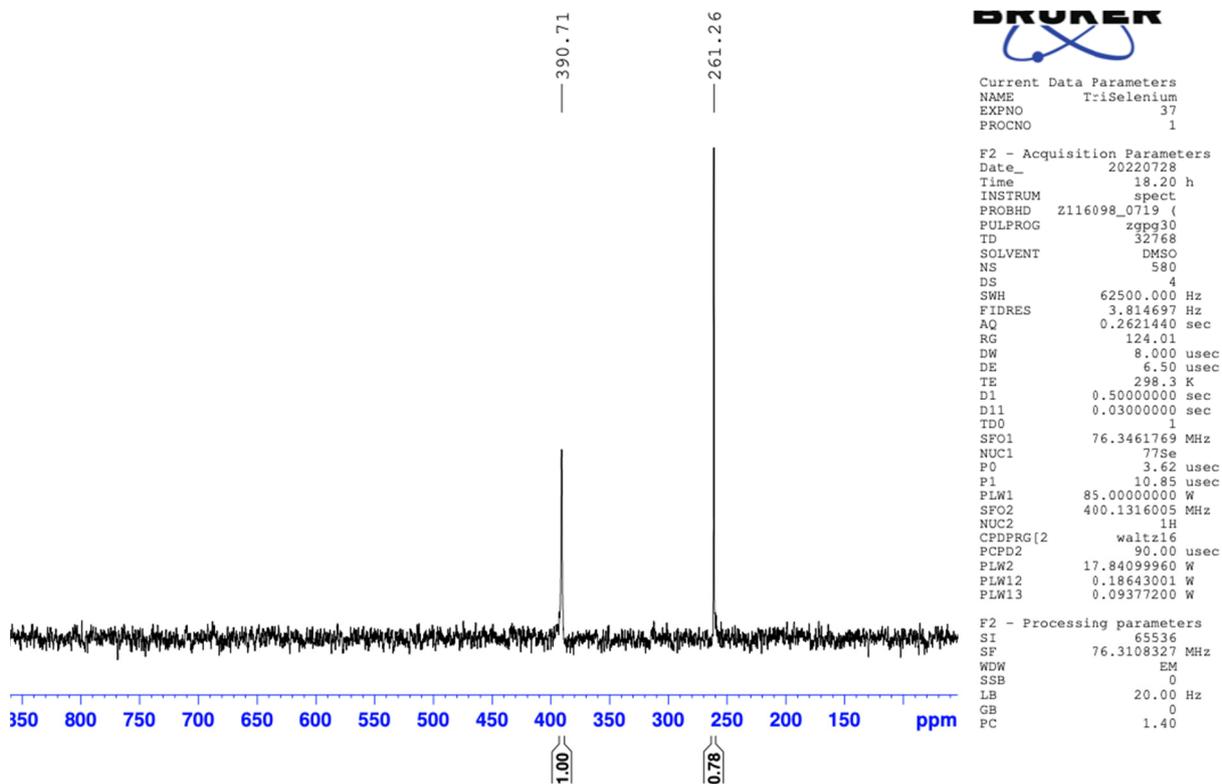


Figure S8: $^{77}\text{Se}\{^1\text{H}\}$ NMR spectrum of TSD in $\text{DMSO-}d_6$ prepared *in situ*.

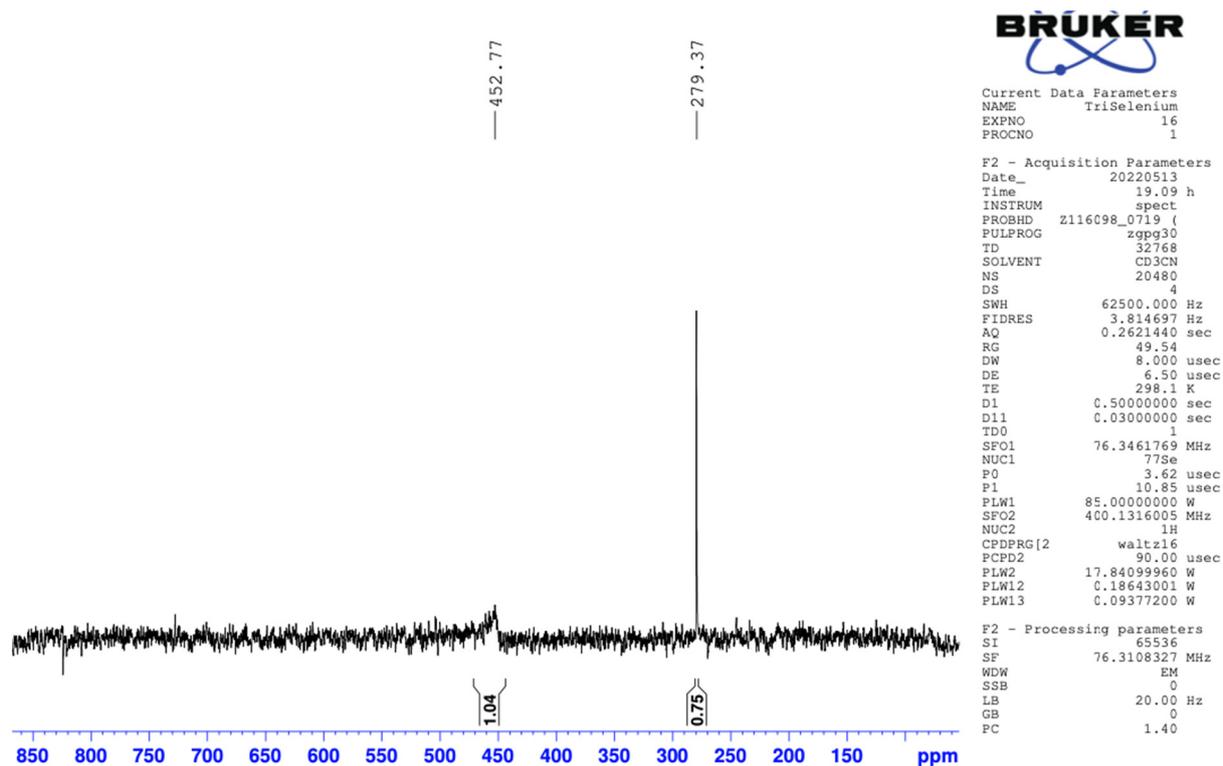


Figure S9: $^{77}\text{Se}\{^1\text{H}\}$ NMR spectrum of TSD in $\text{MeCN-}d_4$ from Procedure 1.
(Integrals are only to compare with spectrum of Figure S8 demonstrating that ratio of signals has maintained unchanged)

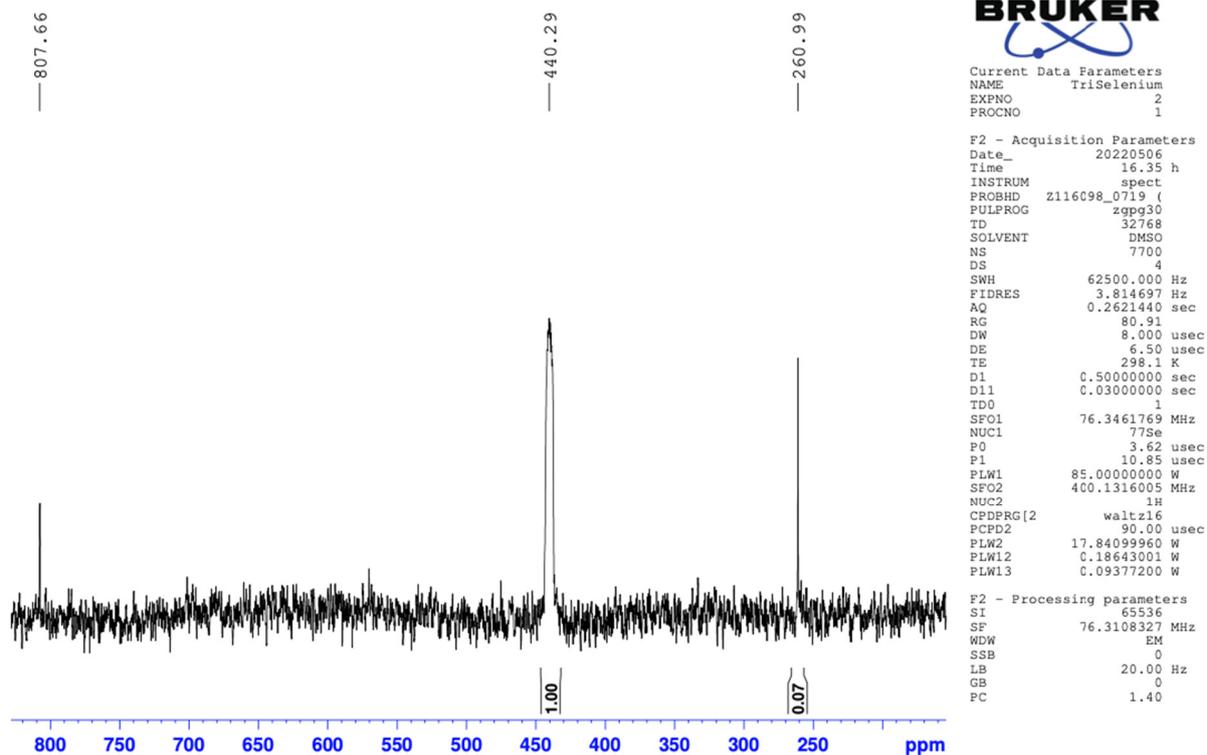


Figure S10: $^{77}\text{Se}\{^1\text{H}\}$ NMR spectrum of TSD in $\text{DMSO-}d_6$ from Procedure 2.

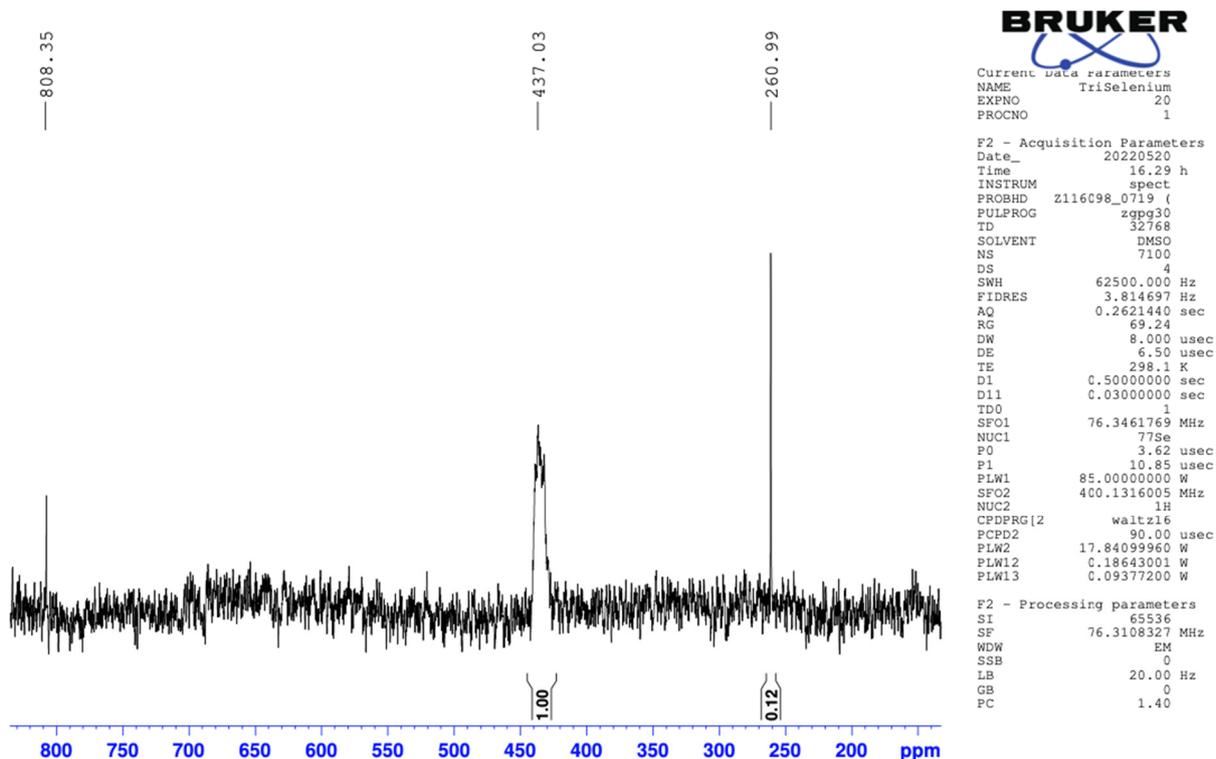


Figure S11: $^{77}\text{Se}\{^1\text{H}\}$ NMR spectrum of TSD in $\text{DMSO-}d_6$ from Procedure 3.

Selected IR Spectra

Figure S12: FTIR (KBr) of $\text{Se}_3(\text{CN})_2$ - $\bar{\nu}$: 3442, 2923, 1646, 1549, 1213, 674.

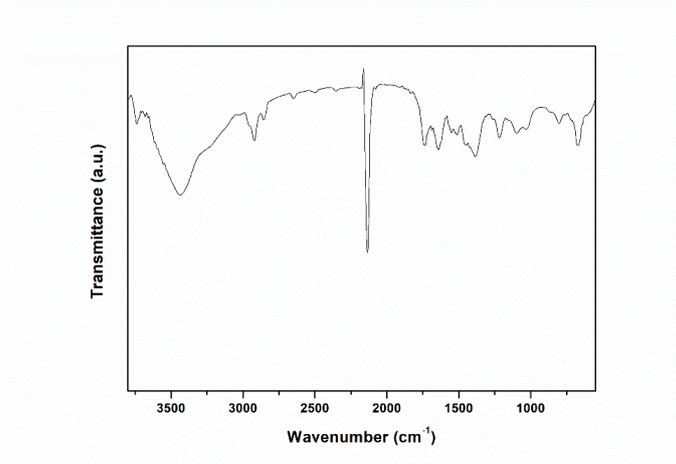


Figure S13: FTIR (KBr) of $\text{Se}_2(\text{CN})_2$ - $\bar{\nu}$: 3430, 2933, 2850, 2139, 1713, 1642, 1457, 1377, 1095, 804, 724, 671.

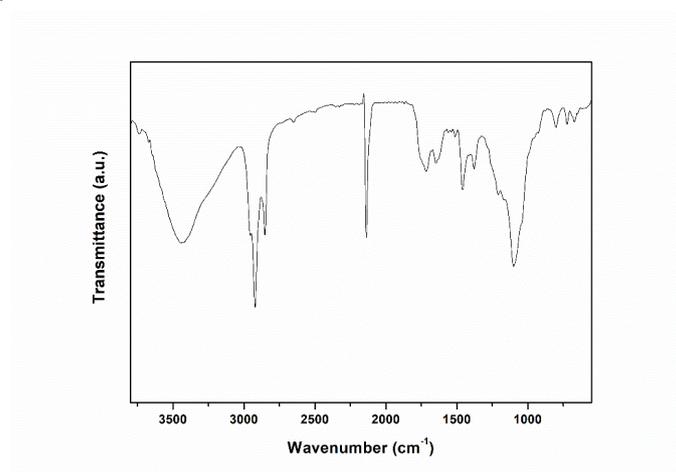


Figure S14: FTIR (KBr) of $\text{Se}(\text{CN})_2$ - $\bar{\nu}$: 3478, 2923, 2852, 2137, 1401, 1092, 801, 668.

