Supplemental Information for

Long Vibrational Lifetime R-selenocyanate Probes for Ultrafast Infrared Spectroscopy: Properties and Synthesis

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1. Synthesis

A. Preparation of 3-Indole Selenocyanate

The synthesis was performed in a manner modified from that previously reported by Kachanov *et. al.*[1] Selenium dioxide (3.33 g, 30 mmol) was first crushed into a fine powder and then added to a stirring solution of malononitrile (1.0g, 15 mmol) in 25 mL of dimethyl sulfoxide (DMSO) at room temperature. The solution turned dark, cloudy red and within minutes began bubbling vigorously. After the bubbling was complete and the solution turned transparent red, indole (1.75g, 15 mmol) was carefully added to the solution and the reaction allowed to stir at room temperature for four hours. The solution was then extracted using 2 x 50 mL of ethyl acetate and the organic layer washed with water (5 x 20 mL) and brine (1 x 20 mL). The crude product was further purified with column chromatography using a 1:1 ratio of ethyl acetate to hexane. The product was concentrated and crystallized from hexane to give a light brown solid (2.96g, 89% yield, mp 98-

100 °C). ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm): 8.63 (br s, 1H), 7.76 (m, 1H) 7.54 (d, *J*= 5.0 Hz, 1H) 7.45 (m, 1H) 7.32 (m, 2H). ^{13}C NMR (126 MHz, CDCl3): δ (ppm): 135.98, 131.86, 128.68, 123.74, 121.82, 119.52, 111.92, 102.06, 89.36.

B. Preparation of *p*-Aniline Selenocyanate

As described above, selenium dioxide (3.33 g, 30 mmol) was first crushed into a fine powder and then added to a stirring solution of malononitrile (1.0 g, 15 mmol) in 25 mL of DMSO at room temperature. The solution turned dark, cloudy red and within minutes began bubbling vigorously. After the bubbling was complete and the solution turned clear transparent red, aniline (2.8 mL, 30.6 mmol) was quickly added to the solution and the reaction allowed to stir at room temperature for four hours. When the reaction finished, it was poured into excess water and formed a green-yellow precipitate. The solid was filtered and washed with water. The compound was then re-dissolved and decolorized in methanol using activated carbon. The solution was filtered through celite, and water was added until a white powder was observed. The mixture was then heated until the powder disappeared and put into a freezer resulting in long needle-like white crystals (2.8 g, 94.7 % yield, mp 86-88 °C). ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm): 7.47-7.45 (dd, *J*=10.0 Hz, 2H), 6.66-6.64 (dd, *J*=10.0 Hz, 2H), 3.93(br s, 2H).^{13}C NMR (126 MHz, CDCl3): δ (ppm): 148.74, 136.49, 116.26, 107.27, 102.58. ^{1}H NMR (500 MHz, DMSO): δ (ppm): 7.36-7.34 (dd, *J*=10.0 Hz, 2H), 6.60-6.58 (dd, *J*= 10.0 Hz, 2H), 5.63 (s, 2H). ^{13}C NMR (126 MHz, DMSO): δ (ppm): 151.25, 136.92, 115.49, 105.89, 105.47.

C. Preparation of (Z)-3-(4-selenocyanatophenylcarbamoyl)acrylic acid

Following a method modified from the synthesis previously reported by Shaaban *et. al*.,[2] maleic anhydride (2.685 g, 27.4 mmol) was dissolved in 25 mL of anhydrous toluene. *p*-Aniline selenocyanate (3.6 g, 18.27 mmol) was dissolved in hot toluene and added dropwise to the solution. The reaction was stirred over-night and the resulting precipitate collected by filtration. The solid was washed with hot toluene, dried under reduced pressure, and collected as a white solid (5.01 g, 93 % yield, mp 161-166 °C) ^{1}H NMR (500 MHz, DMSO): δ 12.98 (br s, 1H), 10.54 (s, 1H), 7.68 (m, 4H), 6.48-6.46 (dd, *J*=10.0 Hz, 1H), 6.33-6.31 (dd, *J*=10.0Hz, 1H). ^{13}C NMR (126 MHz, DMSO): δ (ppm): 167.39, 164.04, 140.43, 135.26, 132.06, 130.74, 121.17, 117.58, 105.79.

D. Preparation of Norbornene dicarboximide-phenyl selenocyanate

A 200 mL two-neck round-bottom flask fitted with a Dean-Stark trap and a condenser was flame dried and purged with argon gas. The flask was charged with *cis*-5-Norbornene-endo-2,3-dicarboxylic anhydride (2.70 g, 16.45 mmol) and *p*-Aniline selenocyanate (3.24 g, 16.45 mmol). Anhydrous toluene (100 mL) was added to the flask via cannula transfer under argon gas. The solids dissolved and was further stirred at room temperature for 12 hrs to give the amide acid. The flask was cooled in an ice bath and trimethylamine (2.29 mL, 16.45 mmol) was added dropwise. The reaction mixture was refluxed in an oil bath at 120 °C for 12 hrs and formed an off-white precipitate. The flask was then cooled to room temperature resulting in more white solid precipitating out of solution. The white solid was filtered and washed with more toluene, water, methanol, and diethyl ether sequentially to give a pure imide product as a white solid (4.9 g, 87 % yield, mp 217-225 °C). ^{1}H NMR (500 MHz, DMSO): δ (ppm): 7.83 (d, *J*= 8.5 Hz, 2H), 7.37 (d, *J*= 8.5 Hz, 2H), 6.37 (s, 2H), 3.21 (s, 2H), 2.87 (s, 2H), 1.44 (d, *J*= 9.9 Hz, 2H). ^{13}C NMR (126

MHz, DMSO): δ (ppm): 177.06, 138.34, 134.41, 133.47, 128.93, 124.73, 105.73, 48.17, 45.51, 43.26. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm): 7.73 (d, *J*=8.6 Hz, 2H), 7.37 (d, J= 8.6 Hz, 2H), 6.36 (s, 2H), 3.41 (s, 2H), 2.87 (s, 2H), 1.64 (d, *J*= 10.0 Hz, 1H), 1.44 (d, *J*= 10.0 Hz, 1H). ^{13}C NMR (126 MHz, CDCl3): δ (ppm): 176.51, 138.06, 133.30, 133.17, 128.05, 122.02, 100.72, 48.17, 45.51, 43.26.

E. Preparation of *p*-Nitrophenyl Selenocyanate [5]:

Using a method modified from that previously reported by Schmid *et. al.*[3] 4-nitroaniline (1.38 g, 10 mmol) was added to a 250 mL 3 neck flask containing 40 mL of 20 % sulfuric acid. After complete dissolution, the solution was cooled to 0 °C using an ice-water bath. Sodium nitrite (0.85 g, 10 mmol) was dissolved in 5 mL of water, chilled, and added to the reaction mixture over a period of 15 minutes while stirring. Crushed ice was periodically added to the reaction mixture to prevent the temperature from going above 5 °C. After the sodium nitrite addition was complete, the reaction was stirred for an additional 10 minutes. Sodium acetate was then added to increase the pH of the reaction mixture to 6. Potassium selenocyanate (1.44 g, 10 mmol) was dissolved in 15 mL of water, chilled in an ice-water bath, and added to the reaction mixture slowly. The reaction was slowly brought to room temperature and allowed to stir for 48 hours. After completion, the reaction was filtered, extracted with ethyl acetate, and dried over magnesium sulfate. The solvent was removed by rotary evaporation to yield a brown solid. Further purification was done with column chromatography using a 5:1 ratio of hexane to ethyl acetate. The product was collected, and solvent removed to give a light-yellow solid. (0.850 g, 37.4 % yield, mp 139-141 °C). ^{1}H NMR (500 MHz, $CDCl_3$): *δ* (ppm): 8.27 (d, *J*= 5.0 Hz, 2H), 7.79 (d, *J*= 5.0 Hz, 2H). ^{13}C NMR (126 MHz, CDCl3): δ (ppm) 148.40, 131.60, 130.96, 125.17, 99.48. ^{1}H NMR (500 MHz, DMSO): *δ*

(ppm): 8.24 (d, *J*= 5.0 Hz, 2H), 7.78 (d, *J*= 5.0 Hz, 2H). ^{13}C NMR (126 MHz, DMSO): δ (ppm) 147.98, 134.36, 133.38, 125.02, 105.18.

2. Nuclear Magnetic Resonance (NMR) spectroscopy

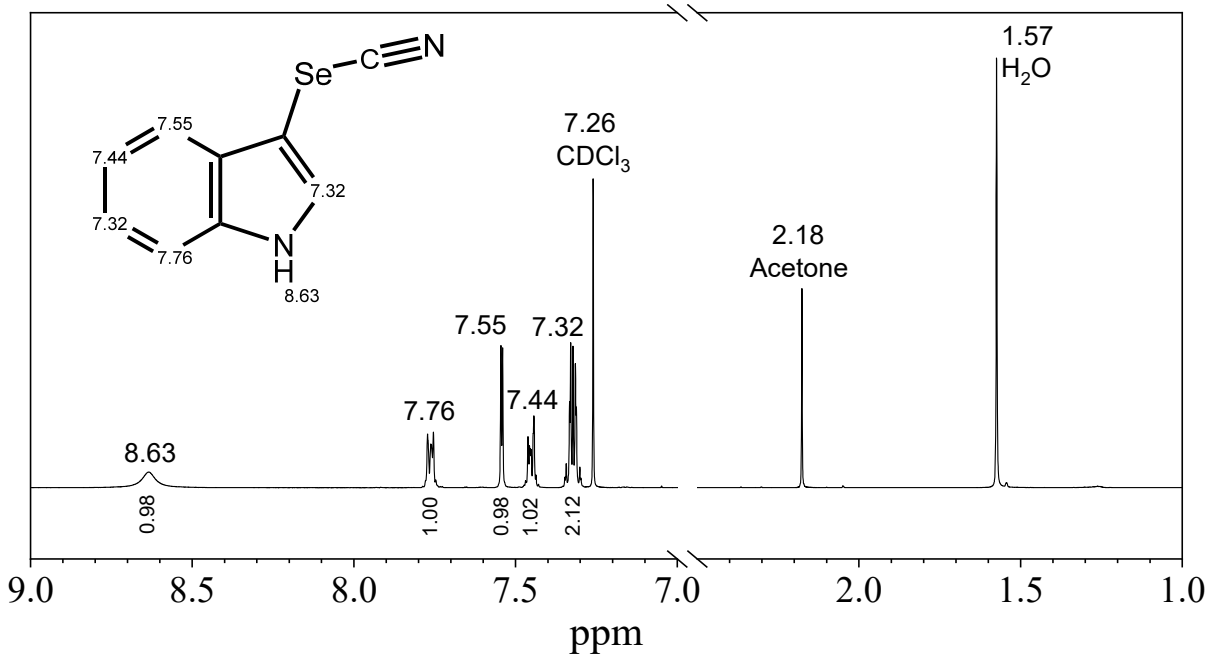

Figure S1. 3-Indole Selenocyanate: ^{1}H NMR (500 MHz, $CDCl_3$): *δ* (ppm): 8.63 (br s, 1H), 7.76 (m, 1H) 7.54 (d, *J*= 5.0 Hz, 1H) 7.45 (m, 1H) 7.32 (m, 2H).

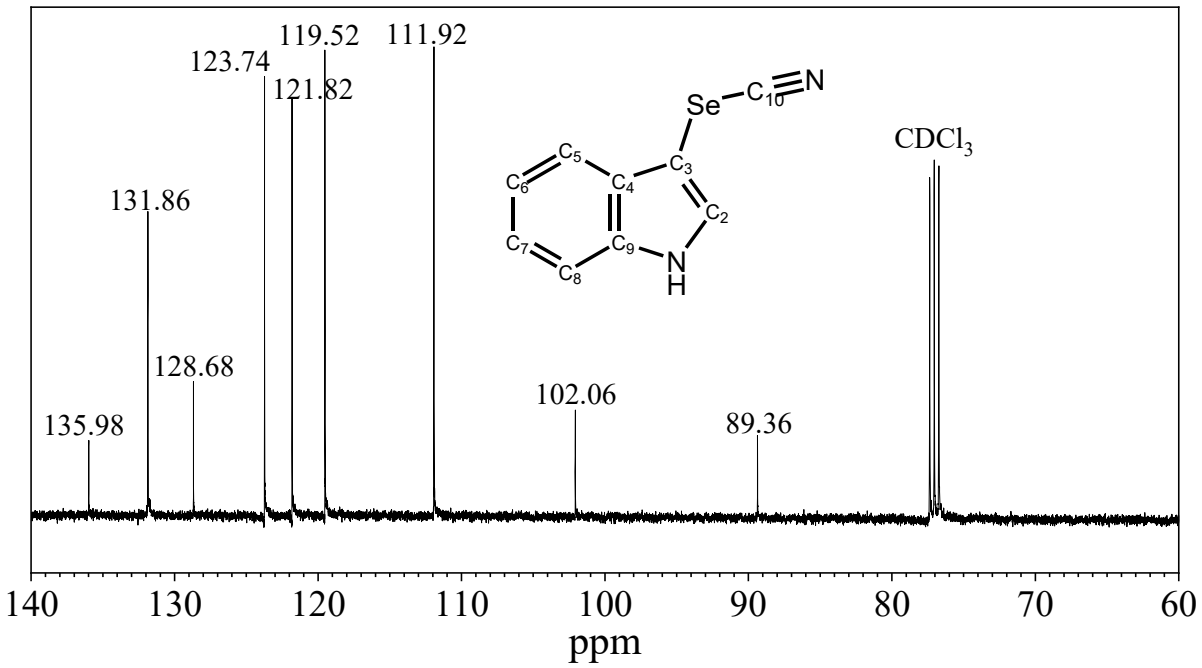

Figure S2. 3-Indole Selenocyanate: ^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm): 135.98 (C_9), 131.86 (C_4), 128.68 (C_2), 123.74 (C_7), 121.82 (C_5), 119.52 (C_6), 111.92 (C_8), 102.06 (C_{10}), 89.36 (C_3).

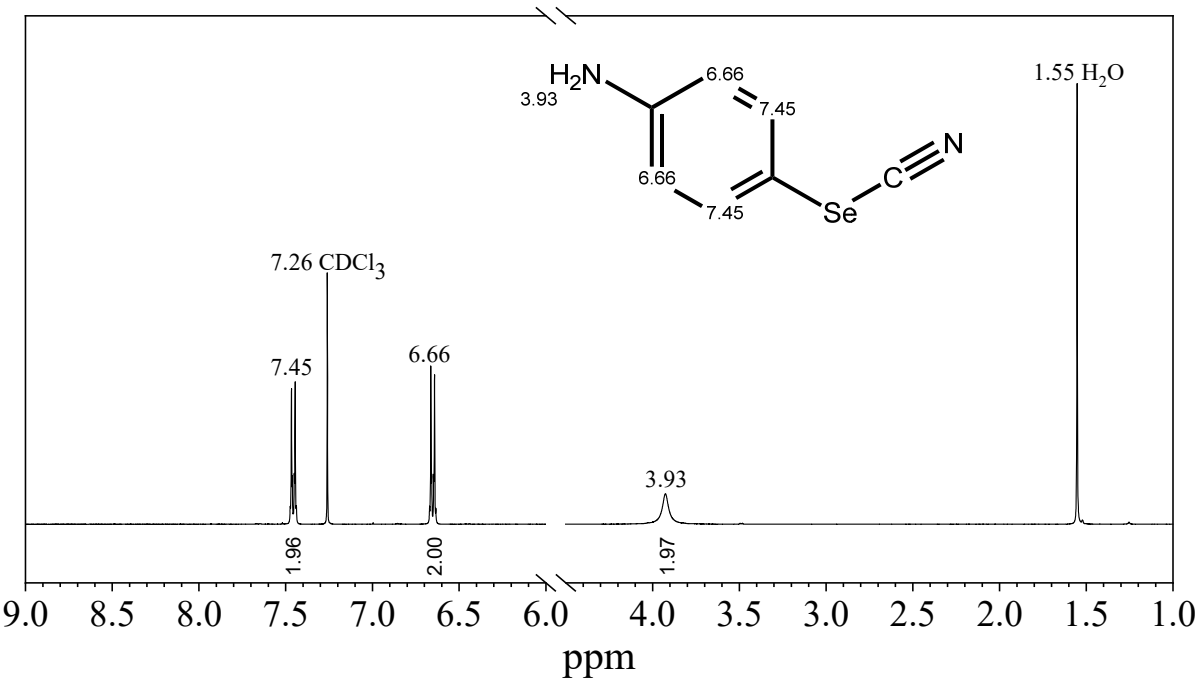

Figure S3: *p*-Aniline Selenocyanate: ^1H NMR (500 MHz, $CDCl_3$): δ (ppm): 7.47-7.45 (dd, *J*=10.0 Hz, 2H), 6.66-6.64 (dd, *J*=10.0 Hz, 2H), 3.93(br s, 2H).

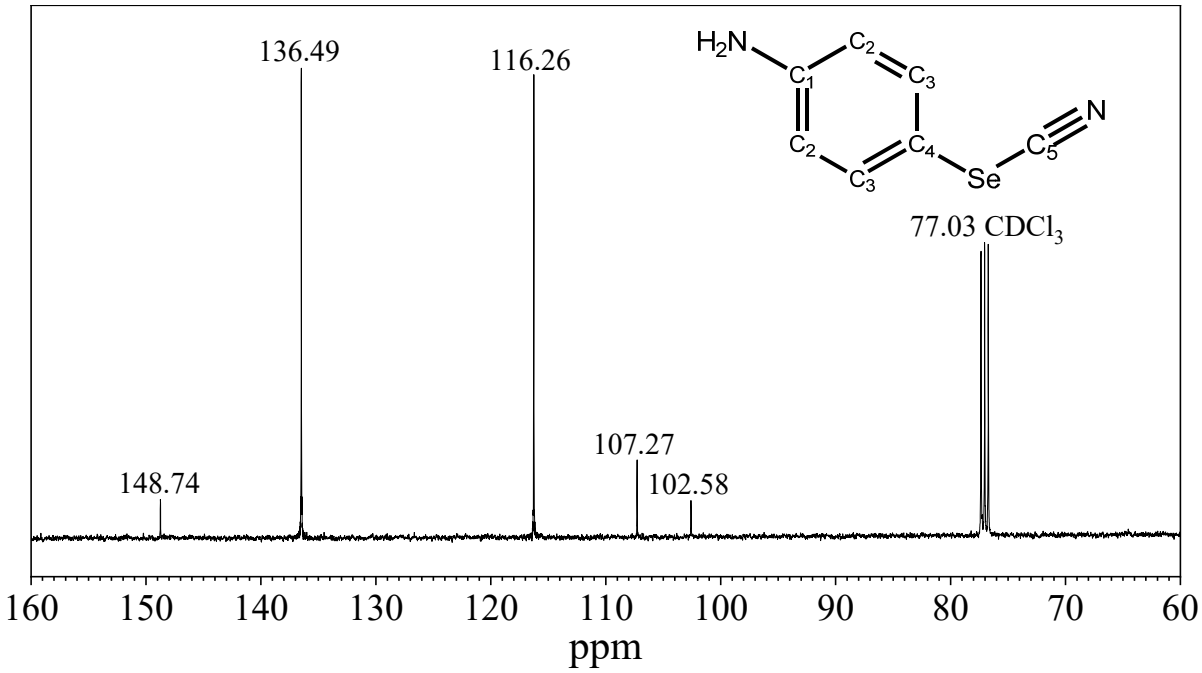

Figure S4: *p*-Aniline Selenocyanate: ^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm): 148.74 (C_1), 136.49 (C_3), 116.26 (C_2), 107.27 (C_4), 102.58 (C_5).

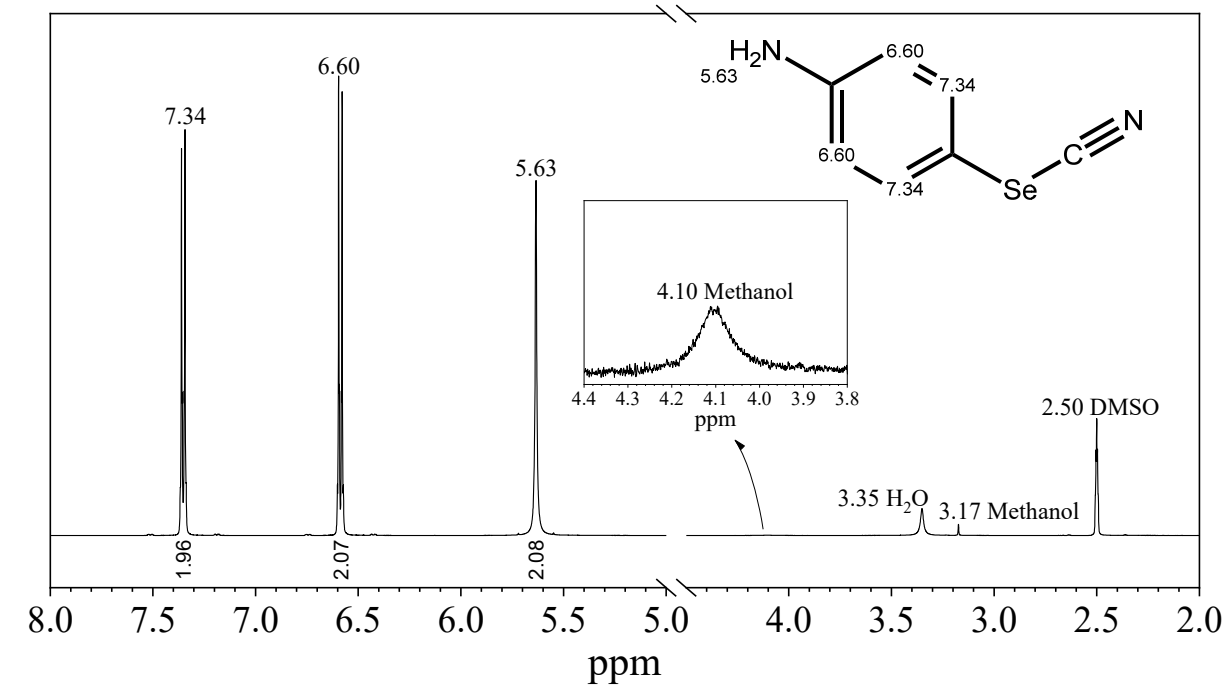

Figure S5: *p*-Aniline Selenocyanate: ^1H NMR (500 MHz, DMSO): δ (ppm): 7.36-7.34 (dd, *J*=10.0 Hz, 2H), 6.60-6.58 (dd, *J*= 10.0 Hz, 2H), 5.63 (s, 2H).

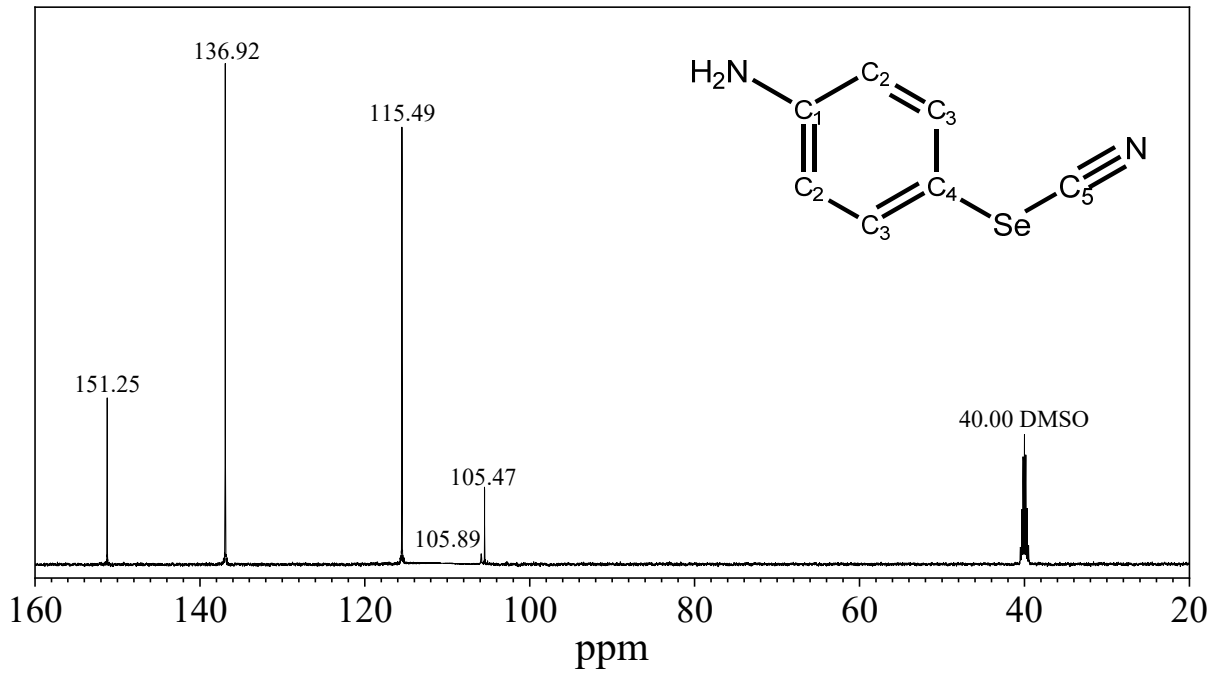

Figure S6: *p*-Aniline Selenocyanate: ^{13}C NMR (126 MHz, DMSO): δ (ppm): 151.25 (C_1), 136.92 (C_3), 115.49 (C_2), 105.89 (C_4), 105.47 (C_5).

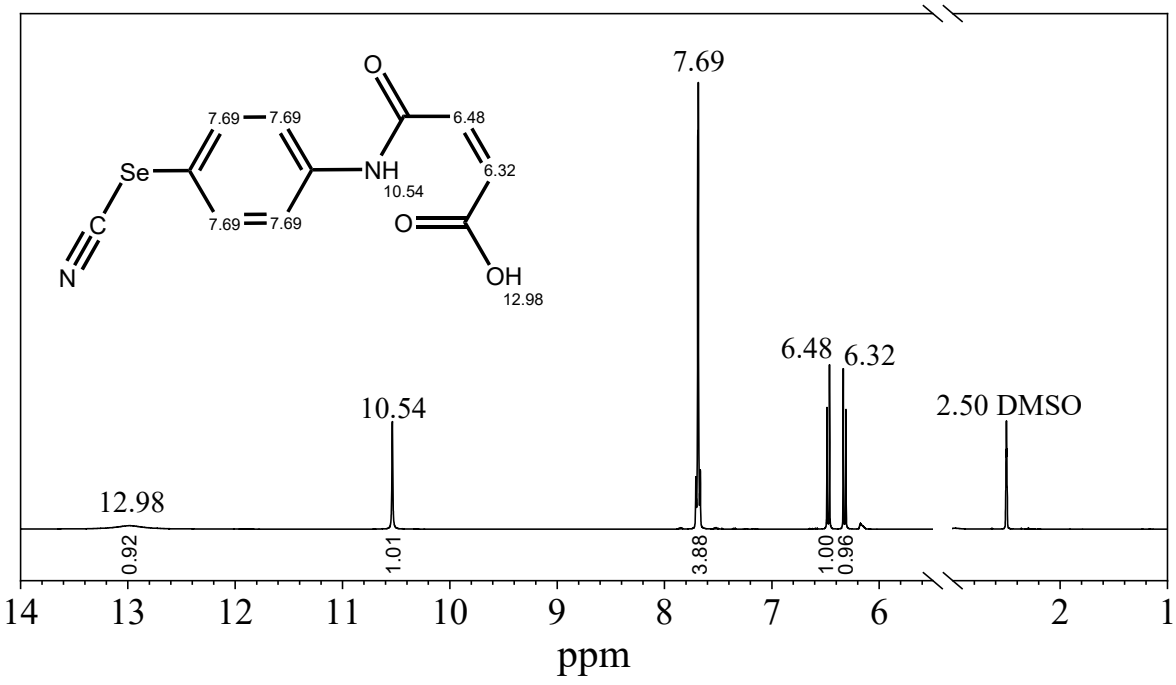

Figure S7: (Z)-3-(4-selenocyanatophenylcarbamoyl)acrylic acid: ^{1}H NMR (500 MHz, DMSO): δ 12.98 (br s, 1H), 10.54 (s, 1H), 7.68 (m, 4H), 6.48-6.46 (dd, J=10.0 Hz, 1H), 6.33-6.31 (dd, J=10.0Hz, 1H).

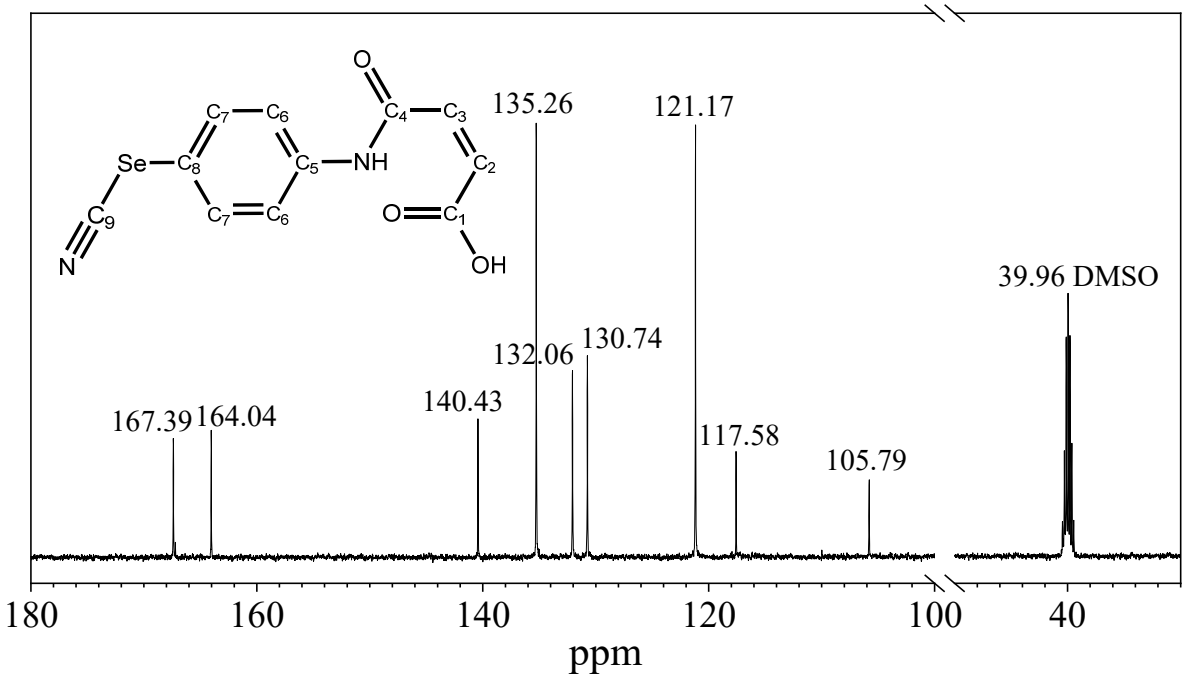

Figure S8: (Z)-3-(4-selenocyanatophenylcarbamoyl)acrylic acid: ^{13}C NMR (126 MHz, DMSO): δ (ppm): 167.39 (C_1), 164.04 (C_4), 140.43 (C_5), 135.26 (C_7), 132.06 (C_2), 130.74 (C_3), 121.17 (C_6), 117.58 (C_8), 105.79 (C_9).

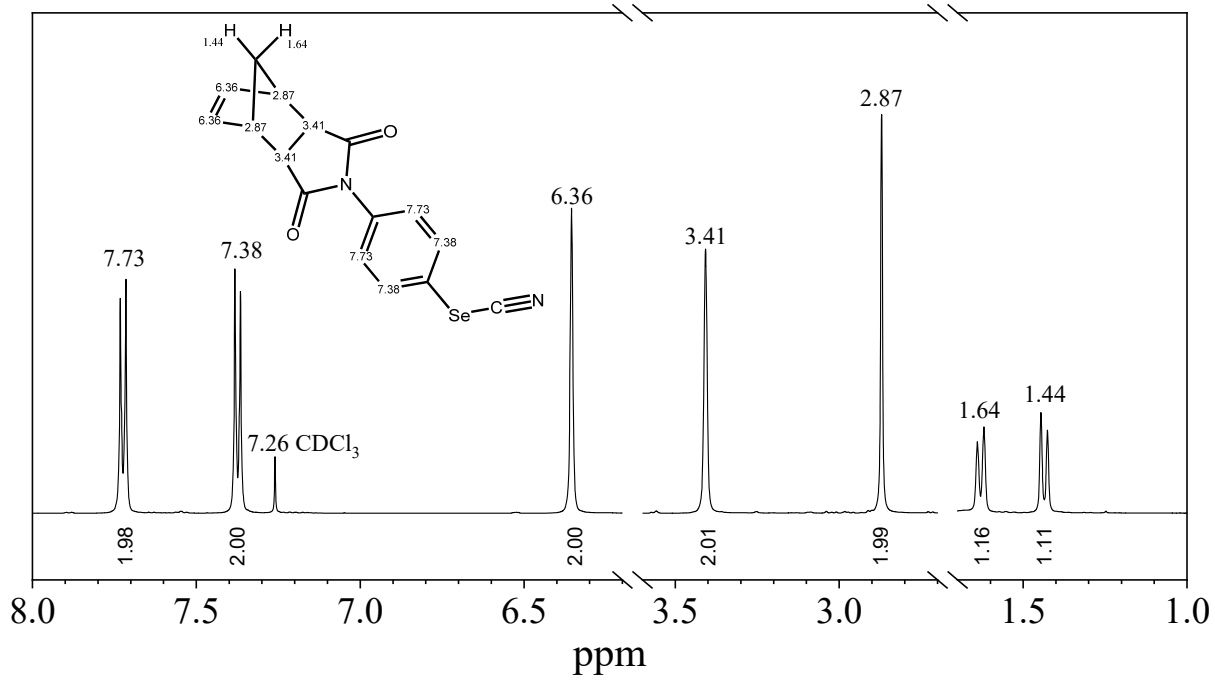

Figure S9: Norbornene dicaboximide-phenyl selenocyanate: ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm): 7.73 (d, *J*=8.6 Hz, 2H), 7.37 (d, J= 8.6 Hz, 2H), 6.36 (s, 2H), 3.41 (s, 2H), 2.87 (s, 2H), 1.64 (d, *J*= 10.0 Hz, 1H), 1.44 (d, *J*= 10.0 Hz, 1H).

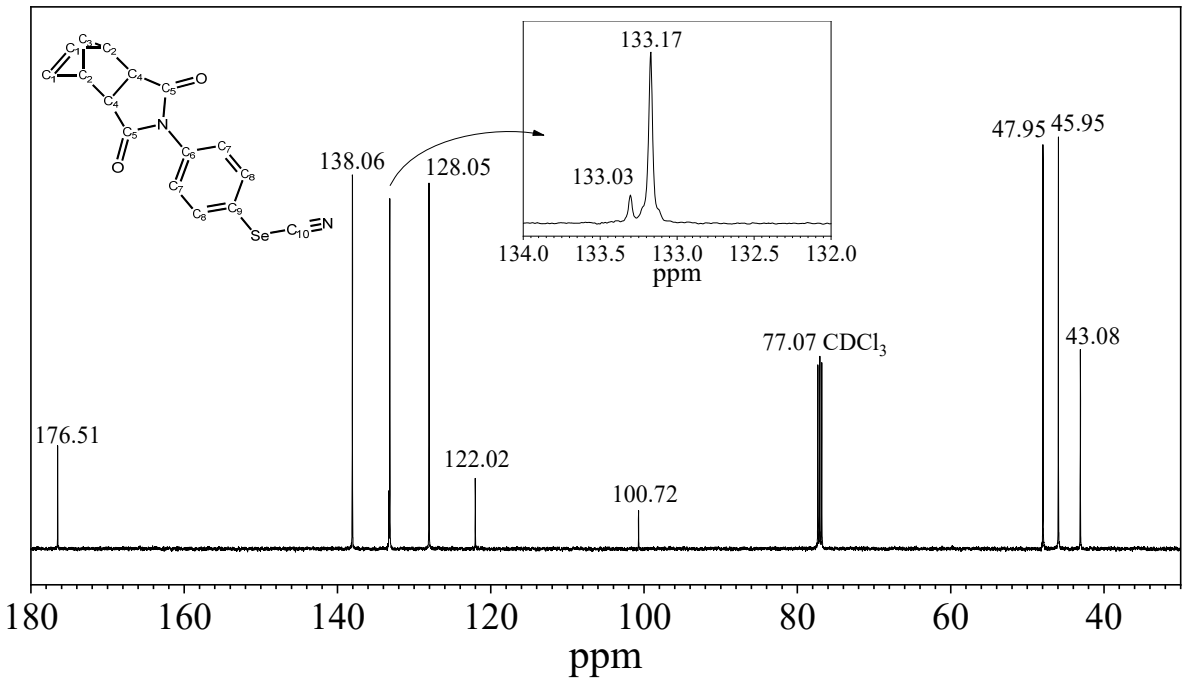

Figure S10: Norbornene dicaboximide-phenyl selenocyanate: ^{13}C NMR (126 MHz, CDCl3): δ (ppm): 176.51 (C_5), 138.06 (C_8), 133.30 (C_1), 133.17 (C_6), 128.05 (C_7), 122.02 (C_9), 100.72 (C_{10}), 47.95 (C_3), 45.95 (C_4), 43.08 (C_2).

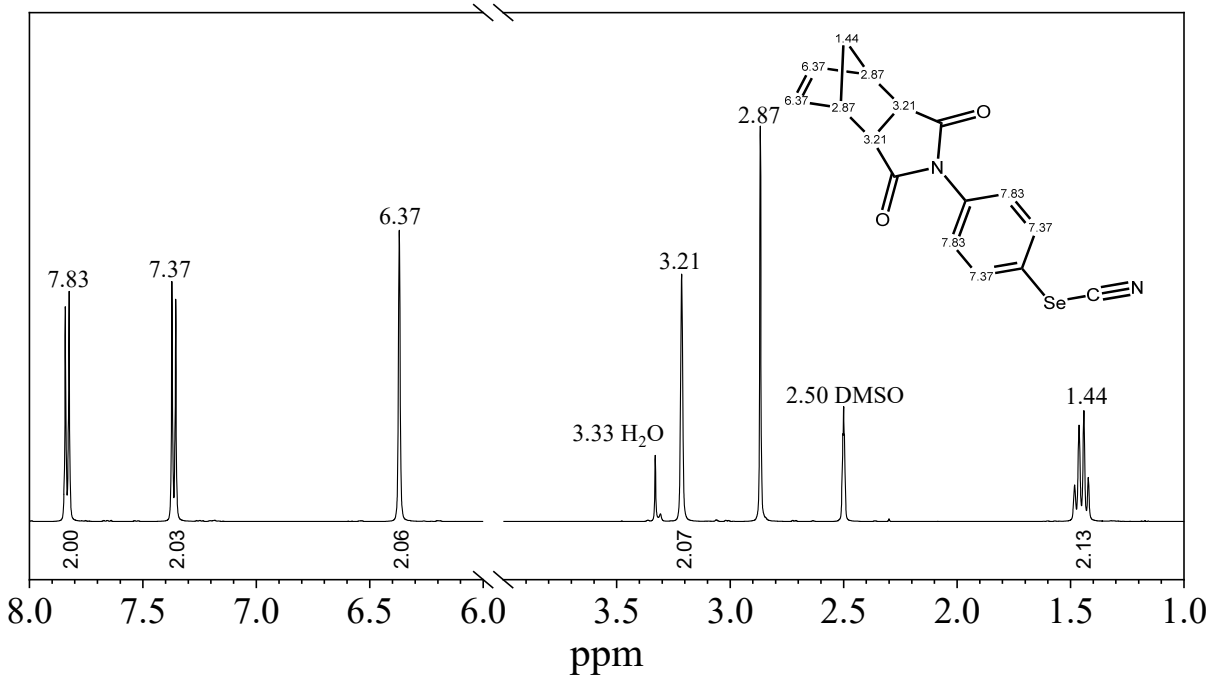

Figure S11: Norbornene dicaboximide-phenyl selenocyanate: ^{1}H NMR (500 MHz, DMSO): δ (ppm): 7.83 (d, *J*= 8.5 Hz, 2H), 7.37 (d, *J*= 8.5 Hz, 2H), 6.37 (s, 2H), 3.21 (s, 2H), 2.87 (s, 2H), 1.44 (m, 2H).

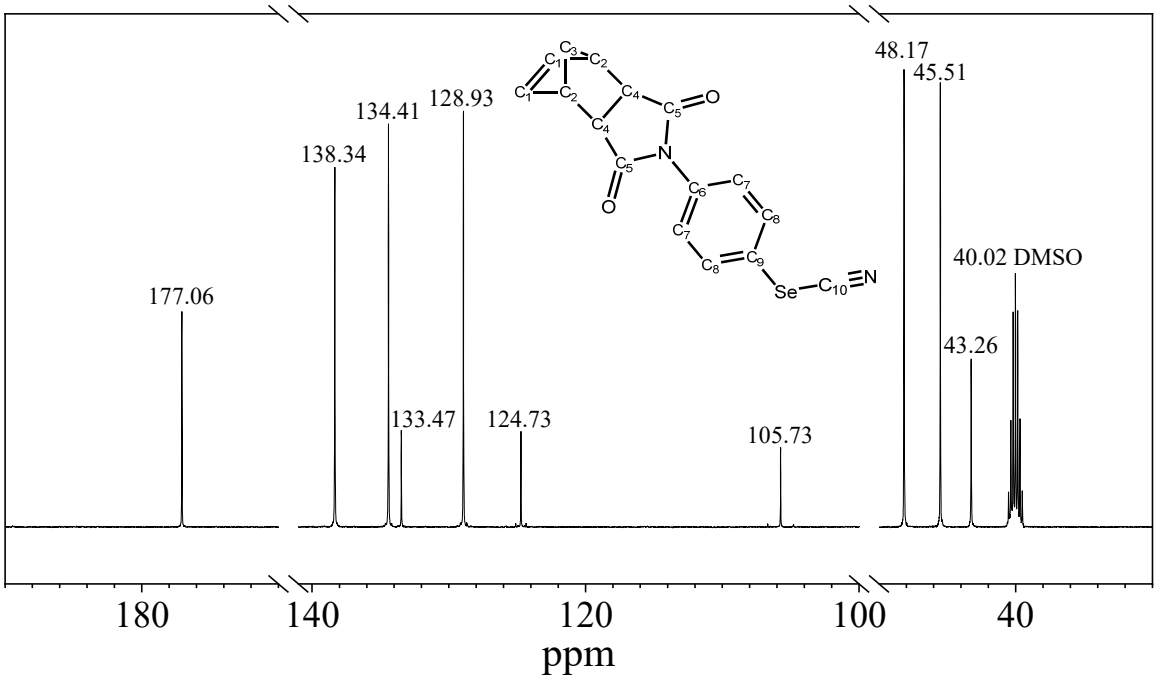

Figure S12: Norbornene dicaboximide-phenyl selenocyanate: ^{13}C NMR (126 MHz,DMSO): δ (ppm): 177.06 (C_7), 138.34 (C_8), 134.41 (C_1), 133.47 (C_6), 128.93 (C_7), 124.73 (C_9), 105.73 (C_{10}), 48.17 (C_3), 45.51 (C_4), 43.26 (C_2).

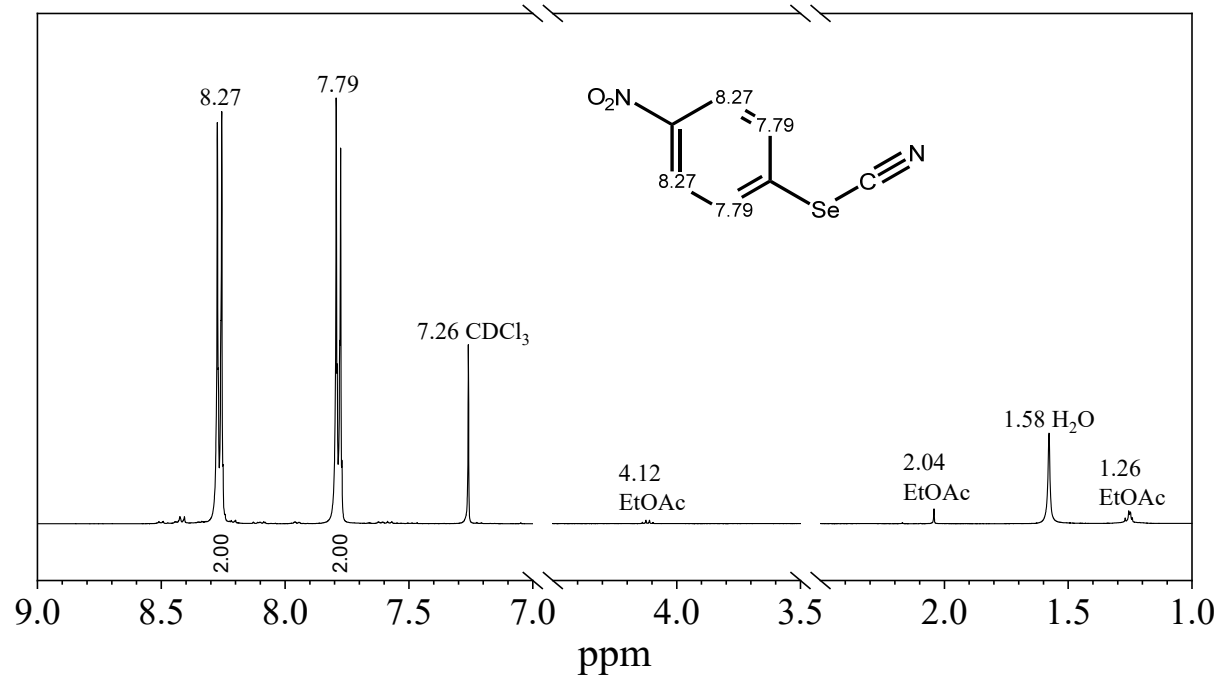

Figure S13: *p*-Nitrophenyl Selenocyanate: ^1H NMR (500 MHz, $CDCl_3$): δ (ppm): 8.27 (d, J= 5.0 Hz, 2H), 7.79 (d, J= 5.0 Hz, 2H).

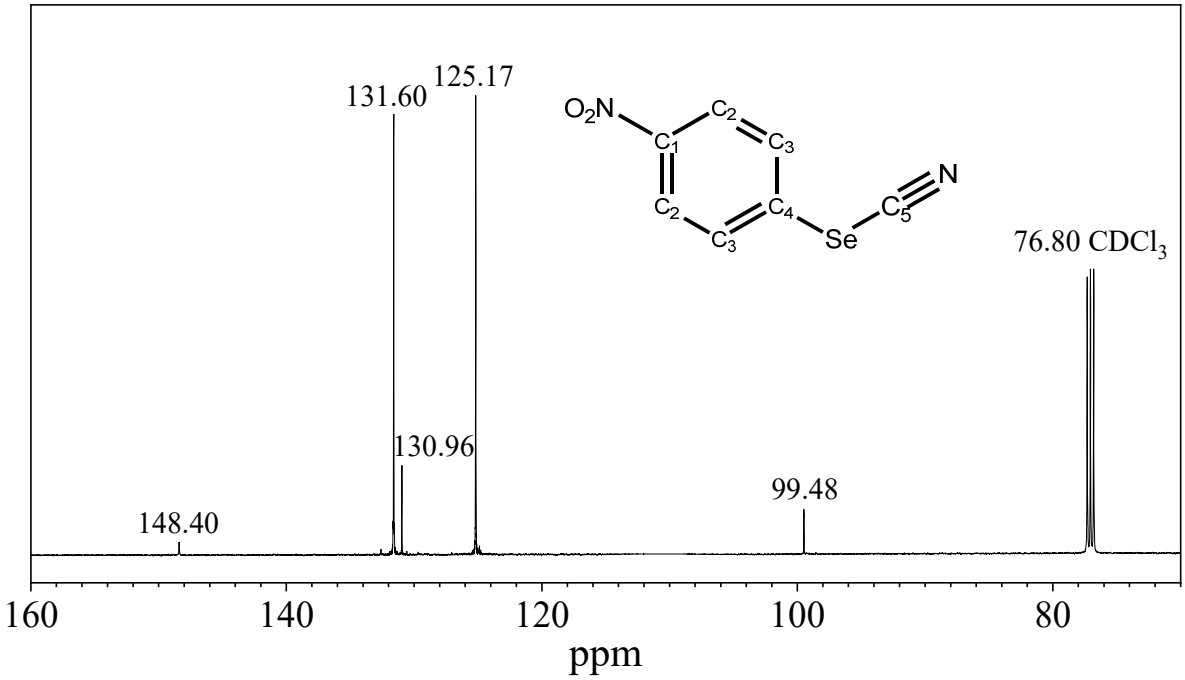

Figure S14: *p*-Nitrophenyl Selenocyanate: ^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) 148.40 (C_1), 131.60 (C_2), 130.96 (C_4), 125.17 (C_3), 99.48 (C_5).

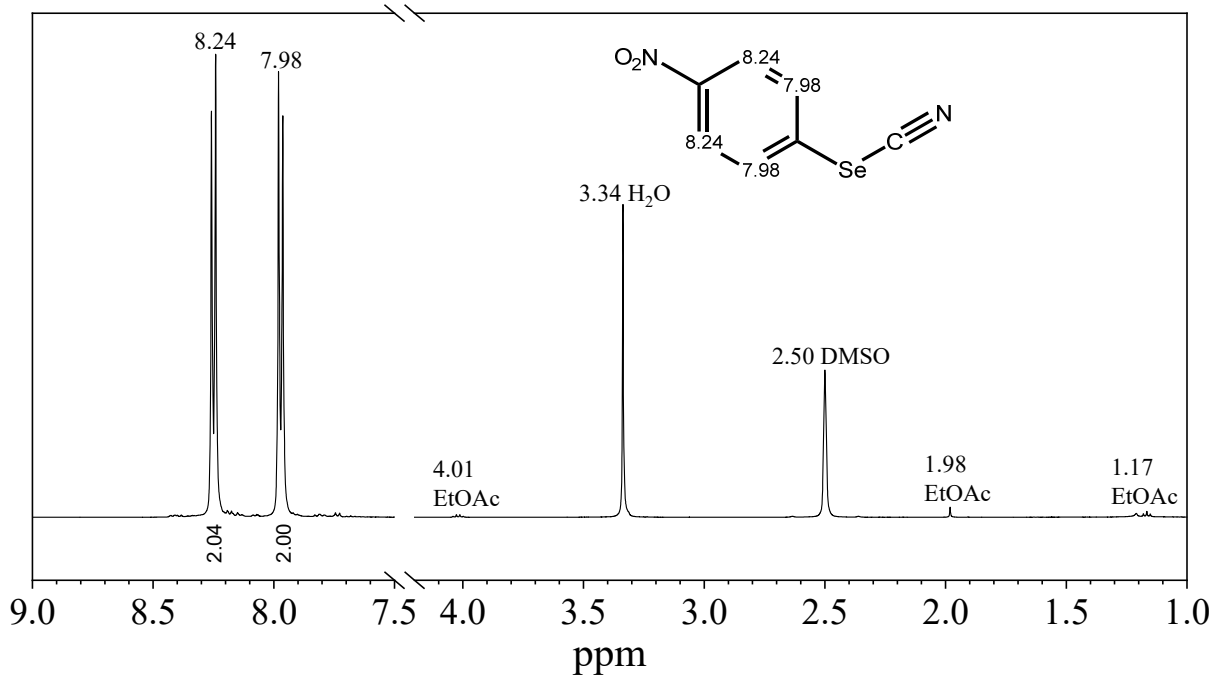

Figure S15: *p*-Nitrophenyl Selenocyanate: ^{1}H NMR (500 MHz, DMSO): δ (ppm): 8.24 (d, *J*= 5.0 Hz, 2H), 7.78 (d, *J*= 5.0 Hz, 2H).

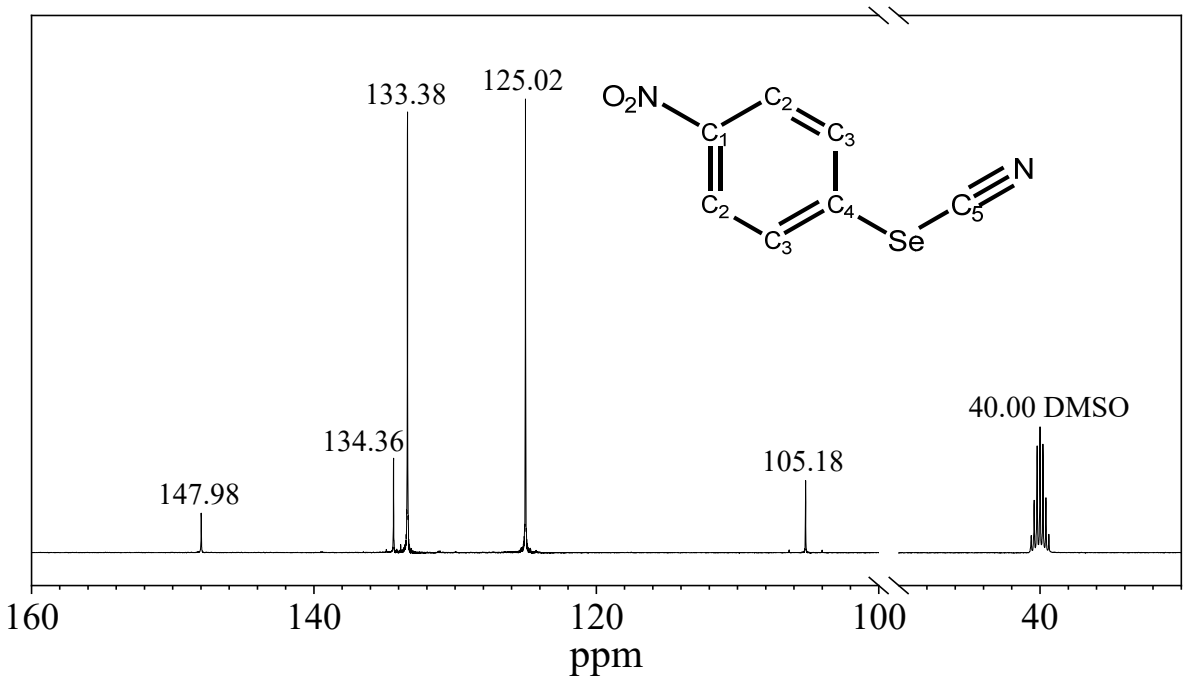

Figure S16: *p*-Nitrophenyl Selenocyanate: ^{13}C NMR (126 MHz, DMSO): δ (ppm) 147.98 (C_1), 134.36 (C_4), 133.38 (C_2), 125.02 (C_3), 105.18 (C_5).

3. Hammett Correlation

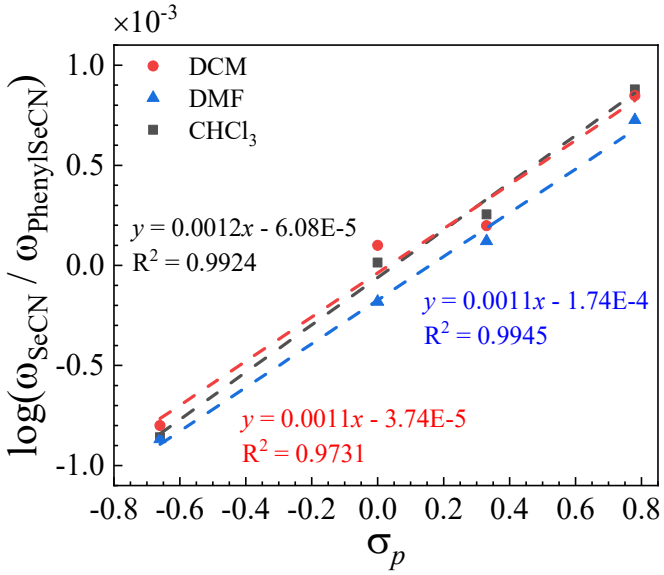

Figure S17 - Hammett correlation of the σ_p constant with vibrational frequency of selenocyanate probes in dichloromethane (DCM), dimethyl sulfoxide (DMSO), and chloroform ($CHCl_3$). The correlation is shown to be solvent-independent.

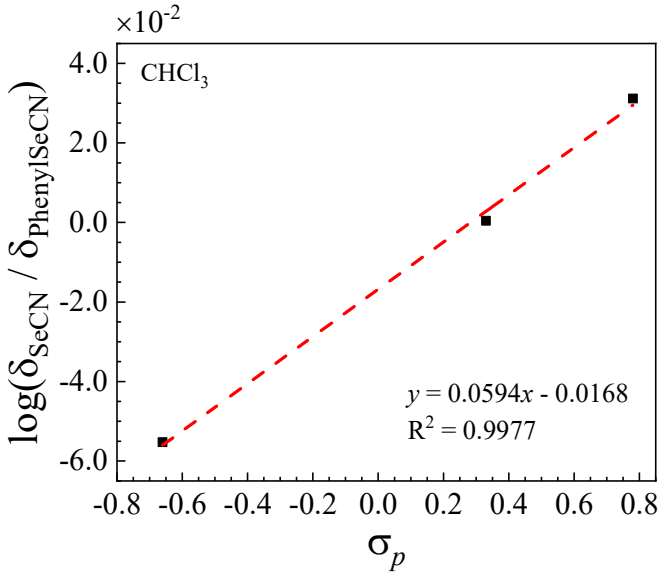

Figure S18 – Hammett correlation of the σ_p constant with ipso carbon ^{13}C peak shift of the selenocyanate probes in chloroform ($CHCl_3$). By comparison to the correlation in Fig. 3(B), this correlation demonstrates that the trend is solvent-independent.

4. Vibrational anharmonicity of CN stretch

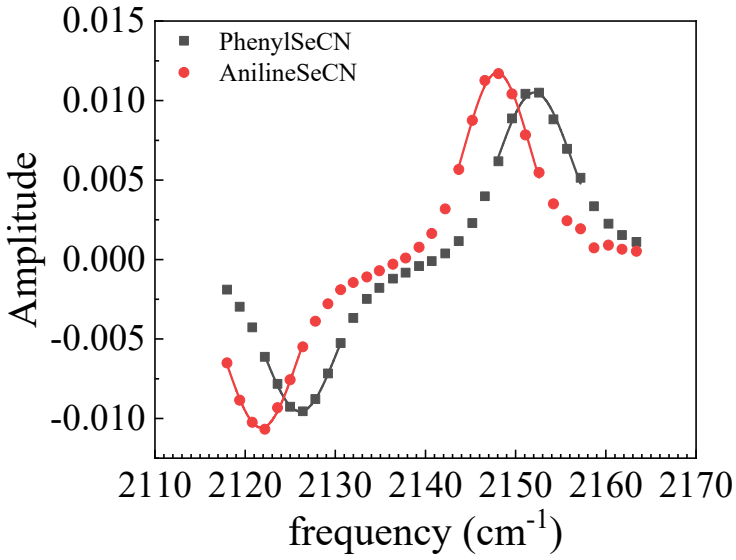

Figure S19. Nonlinear signal of PhenylSeCN and AnilineSeCN. The traces were fit using Gaussian functions around the peak of the 0-1 and 1-2 vibrational transitions to capture their center frequencies. The frequency difference between the two transitions determines the anharmonicity of the CN stretch mode.

Table S1. Anharmonicity of the CN stretch vibration in PhenylSeCN and AnilineSeCN

Probe	0-1 frequency (cm^{-1})	1-2 frequency (cm^{-1})	Anharmonicity (cm^{-1})	Percent anharmonicity
PhenylSeCN	2152 ± 0.1	2126 ± 0.1	26 ± 0.1	1.2 %
AnilineSeCN	2148 ± 0.1	2122 ± 0.1	26 ± 0.1	1.2 %

5. DFT calculation

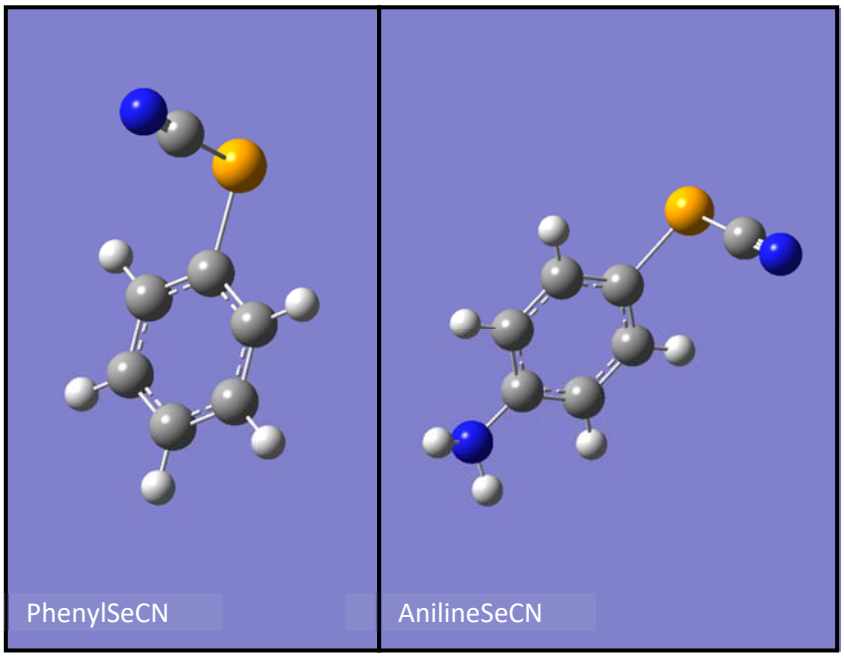

Figure S20. Optimized structure of PhenylSeCN and AnilineSeCN using a DFT calculation in Gaussian 6.0.16. The calculation was performed using a B3LYP and the 6-31G(d,p) basis set. The structure was optimized and the vibrational frequencies of all intramolecular modes calculated. The vibrational mode of interest for the discussion presented in the main text is the Se-CN stretch. The DFT calculation calculated a frequency of 534 cm^{-1} in PhenylSeCN and 520 cm^{-1} in AnilineSeCN.

6. Transition dipole strength calculations

A. Benzonitrile standard

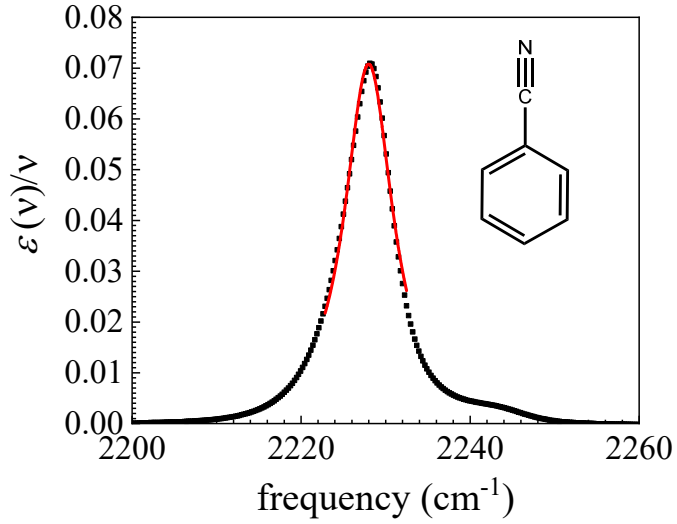

Figure S21. Molar absorptivity as a function of vibrational frequency of Benzonitrile in DMF. The spectrum was calculated following Eq. 4 and Eq. 5. The concentration of benzonitrile was 242.5 ± 0.8 mM and the pathlength 0.0250 ± 0.0001 cm.

The Voigt fit of the spectrum shown in Fig. S21 yielded the following parameterization of the absorption spectrum of PhenylSeCN in DMF given in Table S2.

Table S2. Full parameterization of PhenylSeCN absorption spectrum in DMF, where ω is the center frequency.

Parameter	Value
ω (cm^{-1})	2228.0 ± 0.03
Area	0.76 ± 0.02
FWHM (cm^{-1})	6.9 ± 0.09

It can be seen that the Voigt profile fits the experimental data well. The area of the spectrum corresponds to the integral of Eq. 4 by:

$$\int \frac{\varepsilon(\nu)}{\nu} d\nu = 0.76 \pm 0.02 \frac{L}{cm \times mol}$$

Using this value in Eq.4, we obtained $|\mu_{01}|^2 = 0.0070 \pm 0.0002$ D^2 for benzonitrile. This value was comparable to the literature transition dipole strength of 0.0086 D^2.[4] We thus confirmed that using Eq. 4 and 5, we can calculate the transition dipole strength of a molecule.

B. Phenyl selenocyanate standard

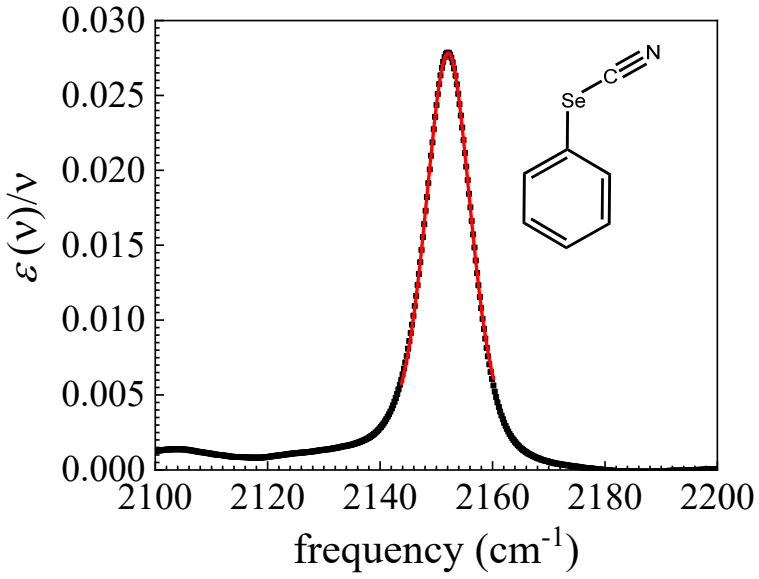

Figure S22. Molar absorptivity as a function of vibrational frequency of Phenyl Selenocyanate in DMF. The spectrum was calculated following Eq. 4 and Eq. 5. The concentration of Phenyl Selenocyanate was 244.5 ± 0.7 mM and the path length 0.0250 ± 0.0001 cm.

The same procedure outlined for benzonitrile was followed to calculate the transition dipole strength of PhenylSeCN.

Table S3. Parameterization of PhenylSeCN absorption spectrum in DMF using a Voigt function.

Parameter	Value
ω (cm^{-1})	2152.1 ± 0.01
Area	0.37 ± 0.02
FWHM (cm^{-1})	9.9 ± 0.02

$$\int \frac{\varepsilon(\nu)}{\nu} d\nu = 0.37 \pm 0.02 \frac{L}{cm \times mol}$$

This value was used in Eq. 4 to obtain $|\mu_{01}|^2 = 0.0034 \pm 0.0002$ D^2 for PhenylSeCN.

C. New selenocyanate probes

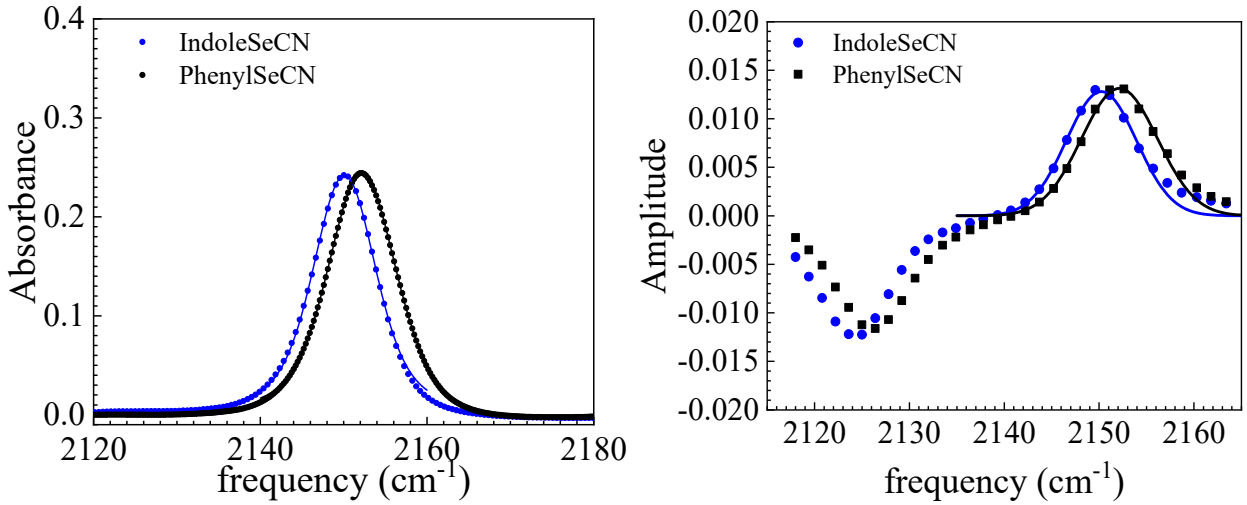

Figure S23. Baselined absorption spectrum (left) and pump-probe signal (right) 3-Indole Selenocyanate. The spectra for phenyl selenocyanate are shown for reference. The pump-probe signal was obtained from a time delay between pump and probe beams of 3 ps. The positive going feature is from the 0-1 transition, and the negative going feature is from the 1-2 transition.

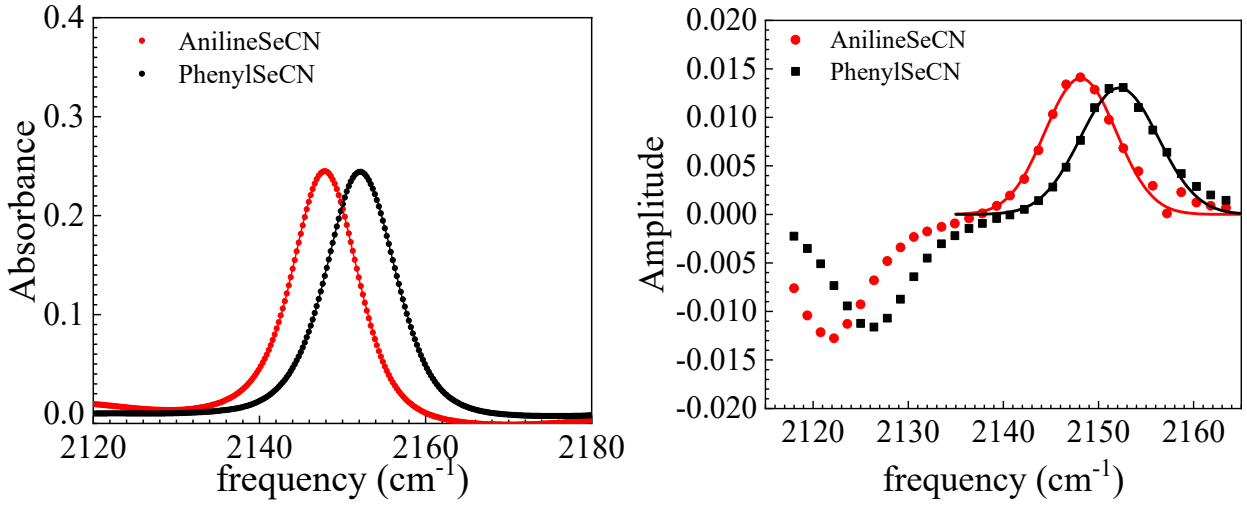

Figure S24. Baselined absorption spectrum (left) and pump-probe signal (right) *p*-Aniline Selenocyanate. The spectra for phenyl selenocyanate are shown for reference. The pump-probe signal was obtained from a time delay between pump and probe beams of 3 ps. The positive going feature is from the 0-1 transition, and the negative going feature is from the 1-2 transition.

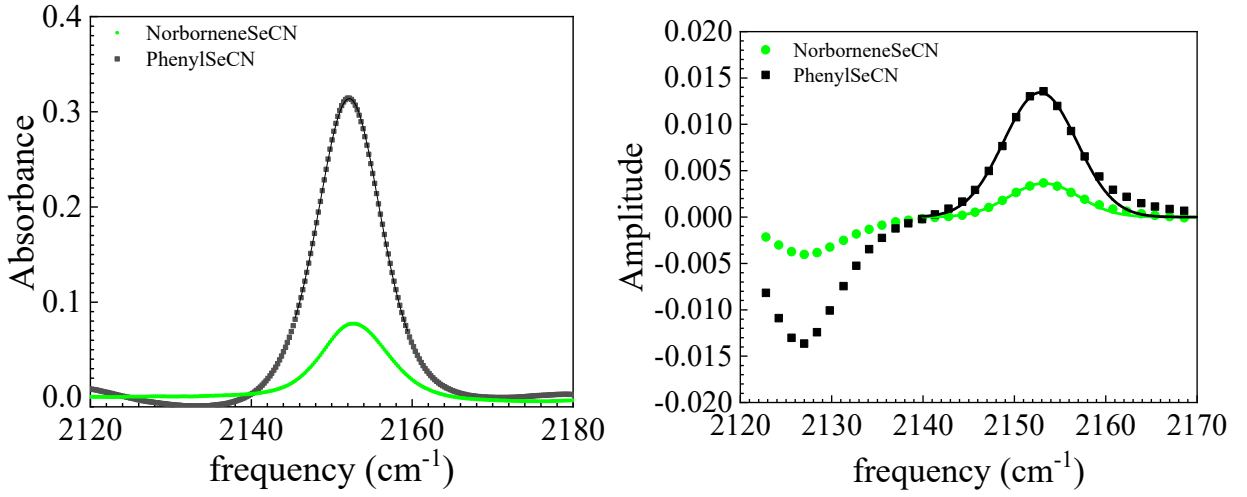

Figure S25. Baselined absorption spectrum (left) and pump-probe signal (right) Norbornene dicaboximide-phenyl selenocyanate. The spectra for phenyl selenocyanate are shown for reference. The pump-probe signal was obtained from a time delay between pump and probe beams of 3 ps. The positive going feature is from the 0-1 transition, and the negative going feature is from the 1-2 transition.

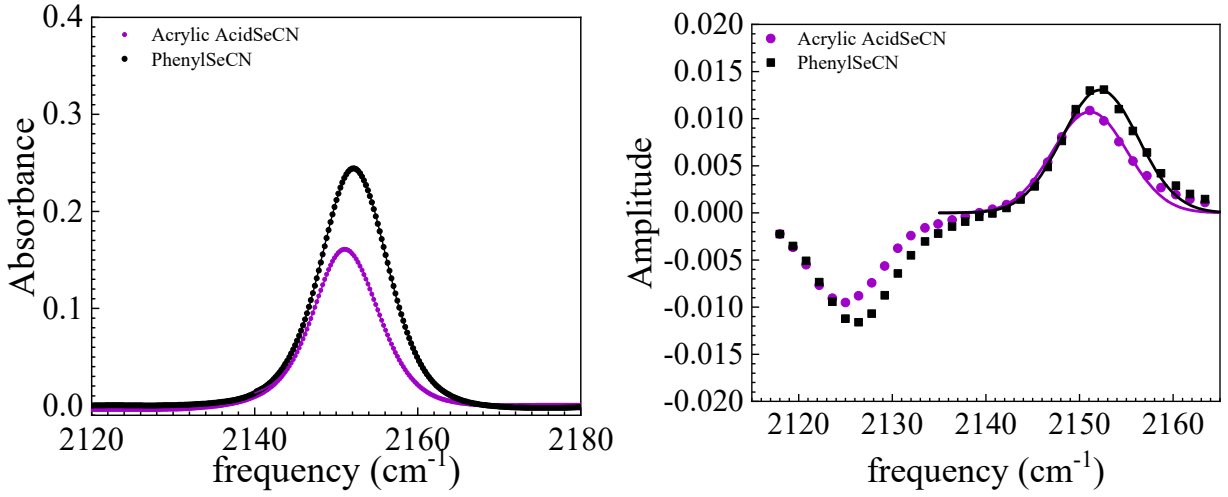

Figure S26. Baselined absorption spectrum (left) and pump-probe signal (right) (Z)-3-(4-selenocyanatophenylcarbamoyl)acrylic acid. The spectra for phenyl selenocyanate are shown for reference. The pump-probe signal was obtained from a time delay between pump and probe beams of 3 ps. The positive going feature is from the 0-1 transition, and the negative going feature is from the 1-2 transition.

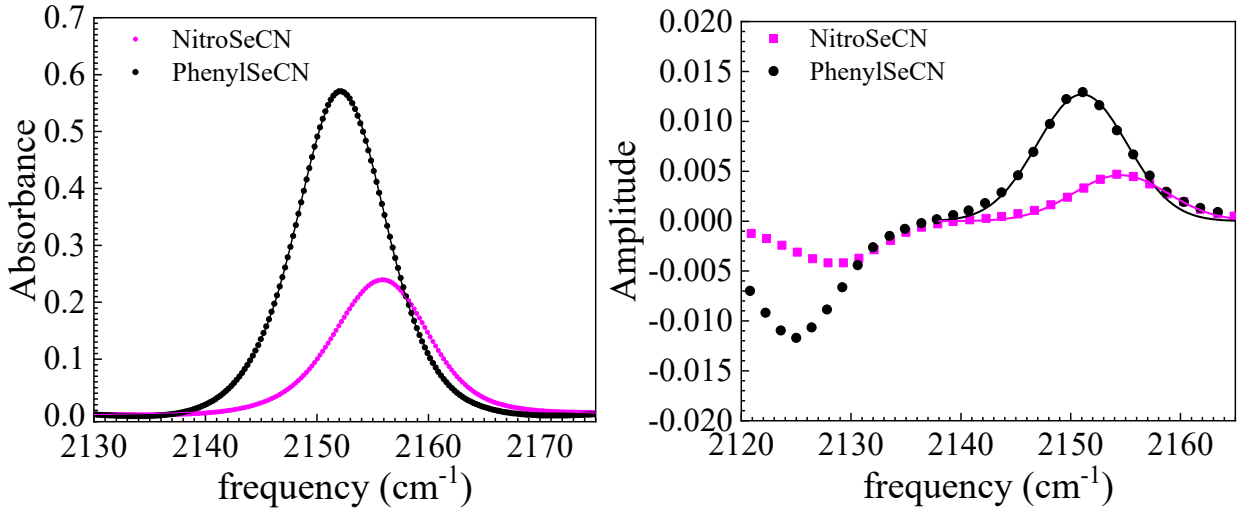

Figure S27. Baselined absorption spectrum (left) and pump-probe signal (right) NitroSeCN. The spectra for PhenylSeCN are shown for reference. The pump-probe signal was obtained from a time delay between pump and probe beams of 3 ps. The positive going feature is from the 0-1 transition, and the negative going feature is from the 1-2 transition.

The linear, $\chi^{(1)}$, and non-linear, $\chi^{(3)}$, signal amplitudes were extracted from the spectra presented in Figs. S23 – S27. For the non-linear signal, the amplitude of the 0-1 transition was used (higher frequency peak). The results are presented in Table S3. The signal amplitudes of the PhenylSeCN probe in DMF are included as the standard. The PhenylSeCN standards used for NorborneneSeCN and NitroSeCN were different from the one used for the other probes.

Table S4. Linear, $\chi^{(1)}$, and non-linear, $\chi^{(3)}$, signal amplitudes for all selenocyanate probes.

Probe	$\chi^{(1)}$ [a]	$\chi^{(3)}$ [b]	$\chi^{(3)} / \chi^{(1)}$	$\lvert\mu_{01}\rvert^2 / \lvert\mu_{01}\rvert^2_{Ph}$	$\lvert\mu_{01}\rvert^2$ **(D^2)**
PhenylSeCN	0.24 ± 1.15E-4	0.013 ± 0.001	0.054 ± 0.004	1	
IndoleSeCN	0.24 ± 1.15E-4	0.013 ± 0.001	0.054 ± 0.004	1.0 ± 0.1	0.0034 ± 0.0003
AnilineSeCN	0.24 ± 1.15E-4	0.014 ± 0.001	0.058 ± 0.004	1.1 ± 0.1	0.0037 ± 0.0003
Acrylic AcidSeCN	0.16 ± 1.15E-4	0.010 ± 0.001	0.063 ± 0.006	1.2 ± 0.1	0.0039 ± 0.0003
PhenylSeCN	0.31 ± 1.15E-4	0.014 ± 0.001	0.045 ± 0.003	1	
NorborneneSeCN	0.08 ± 1.15E-4	0.004 ± 0.001	0.050 ± 0.013	1.1 ± 0.3	0.0037 ± 0.001
PhenylSeCN	0.57 ± 1.15E-4	0.013 ± 0.001	0.023 ± 0.002	1	
NitroSeCN	0.24 ± 1.15E-4	0.005 ± 0.001	0.019 ± 0.004	0.9 ± 0.2	0.0029 ± 0.0007

[a] *The error bar was determined by measuring the root mean square noise on the FTIR detector. We obtained this by simulating an absorbance of 0.35 (typical for the raw spectra obtained for these calculations) and collecting a blank spectrum.*

[b] *Base-level noise of mercury cadmium telluride (MCT) array detector, 1 mV.*

7. Solvatochromism

Below we present the parametrization of the absorption spectra of all selenocyanate vibrational probes characterized in this study in solvents of varying static dielectric constant. All fits were done with a Voigt profile and the baseline offset was fixed to 0.

Table S5. Parameterization of the FTIR spectra of phenyl selenocyanate in solvents of varying static dielectric constant.

Solvent	ω (cm^{-1})	FWHM (cm^{-1})
Dimethyl sulfoxide	2150.2 ± 0.01	11.3 ± 0.05
Dimethylformamide	2152.1 ± 0.01	9.8 ± 0.02
Acetone	2155.3 ± 0.03	7.5 ± 0.12
Dichloromethane	2156.8 ± 0.05	7.9 ± 1.61
Tetrahydrofuran	2154.9 ± 0.02	7.8 ± 0.07
Methyl Acetate	2156.7 ± 0.04	7.5 ± 0.16
Chloroform	2157.6 ± 0.04	9.5 ± 0.13
Carbon tetrachloride	2158.8 ± 0.06	7.3 ± 1.20
Cyclohexane	2159.3 ± 0.10	6.3 ± 0.48
Hexane	2159.8 ± 0.08	6.7 ± 0.41

Table S6. Parameterization of the FTIR spectra of (Z)-3-(4-selenocyanatophenylcarbamoyl) acrylic acid in solvents of varying static dielectric constant.

Solvent	ω (cm^{-1})	FWHM (cm^{-1})
Dimethyl sulfoxide	2149.3 ± 0.02	11.1 ± 0.08
Dimethylformamide	2151.2 ± 0.01	9.6 ± 0.03
Chloroform	2157.7 ± 0.02	9.4 ± 0.08
Dichloromethane	2157.4 ± 0.02	7.7 ± 0.07

Table S7. Parameterization of the FTIR spectra of Norbornene dicarboximide-phenyl selenocyanate in solvents of varying static dielectric constant.

Solvent	ω (cm^{-1})	FWHM (cm^{-1})
Dimethyl sulfoxide	2150.2 ± 0.04	11.1 ± 0.18
Dimethylformamide	2152.7 ± 0.01	9.8 ± 0.03
Dichloromethane	2157.9 ± 0.03	8.1 ± 1.11
Chloroform	2159.0 ± 0.02	9.5 ± 0.11

Table S8. Parameterization of the FTIR spectra of 3-Indole Selenocyanate in solvents of varying static dielectric constant.

Solvent	ω (cm^{-1})	FWHM (cm^{-1})
Dimethyl sulfoxide	2148.3 ± 0.01	10.8 ± 0.02
Dimethylformamide	2150.1 ± 0.01	9.1 ± 0.04
Acetone	2153.2 ± 0.02	7.6 ± 0.09
Dichloromethane	2154.8 ± 0.01	9.8 ± 0.04
Tetrahydrofuran	2152.7 ± 0.02	7.6 ± 0.09
Methyl Acetate	2154.5 ± 0.03	7.2 ± 0.11
Chloroform	2155.4 ± 0.004	11.6 ± 0.01

Table S9. Parameterization of the FTIR spectra of *p*-Aniline Selenocyanate in solvents of varying static dielectric constant.

Solvent	ω (cm^{-1})	FWHM (cm^{-1})
Dimethyl sulfoxide	2145.9 ± 0.01	10.7 ± 0.04
Dimethylformamide	2147.8 ± 0.01	9.6 ± 0.04
Acetone	2151.2 ± 0.02	7.8 ± 0.07
Dichloromethane	2153.0 ± 0.01	7.9 ± 0.03
Tetrahydrofuran	2150.8 ± 0.02	7.6 ± 0.07
Methyl Acetate	2152.6 ± 0.04	7.1 ± 0.14
Chloroform	2153.4 ± 0.02	10.5 ± 0.05

Table S10. Parameterization of the FTIR spectra of *p*-Nitro Selenocyanate in solvents of varying static dielectric constant.

Solvent	ω (cm^{-1})	FWHM (cm^{-1})
Dimethyl sulfoxide	2154.2 ± 0.02	11.5 ± 0.07
Dimethylformamide	2155.9 ± 0.02	10.0 ± 0.07
Acetone	2158.8 ± 0.03	8.1 ± 0.10
Dichloromethane	2161.0 ± 0.03	7.3 ± 1.17
Tetrahydrofuran	2158.2 ± 0.03	8.1 ± 0.10
Methyl Acetate	2160.0 ± 0.03	7.8 ± 0.11
Chloroform	2162.0 ± 0.03	8.6 ± 0.11
Carbon tetrachloride	2161.7 ± 0.03	7.5 ± 0.09

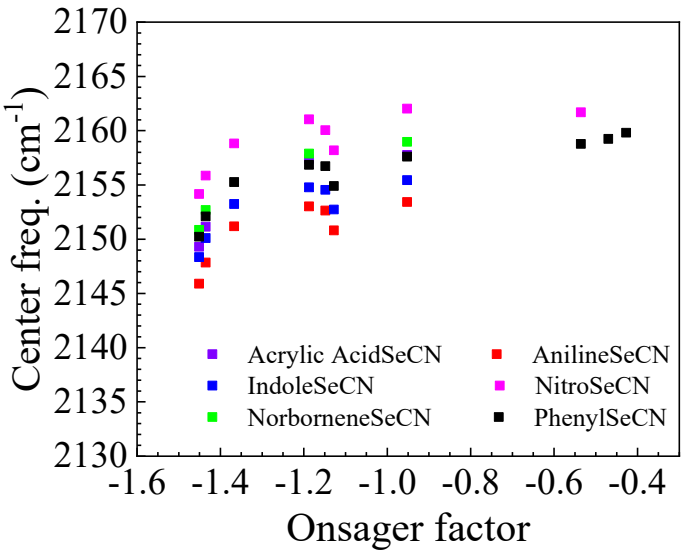

Figure S28. Onsager plot of all selenocyanate probes. This plot shows the raw data before being shifted to allow for comparison with PhenylSeCN data. It can be seen that all data sets display the same extent of local environment sensitivity.

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