

Electronic Supplementary Information

**Removal of mercury and lead ions from water by bioinspired N₃Se₃
type small sized moieties**

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1. General information

Materials and Methods

All the chemicals were purchased from CDH, Avra & Merck and used without further purification. All the solvents used in preparation and purification of species were used after purification by standard methods.¹ The various diaryl diselenides were prepared by literature method.² All the synthetic manipulations were carried out under N₂ atmosphere.

Characterization

¹H and ¹³C[¹H] NMR spectra were recorded on a JEOL Resonance Inc (Model-ECZ-500R) multinuclear NMR spectrometer using CDCl₃ as the solvent and tetramethylsilane (TMS) as an internal reference. ⁷⁷Se NMR were recorded on Bruker Avance Neo 600 MHz NMR spectrometer using CDCl₃ or CD₃CN as the solvent and diphenyl diselenide as an external reference. High-resolution mass spectra (HRMS) were obtained on a SCIEX Model-X500R QTOF mass spectrometer operated in Q-TOF ESI mode. Absorption spectra were recorded on a JASCO V-730 double beam spectrophotometer. All ultraviolet–visible (UV–vis) spectra were recorded at 25°C. FT-IR were recorded on Perkin Elmer FT-IR spectrometer. The concentrations of heavy metals (Hg, Pb) in the solutions were quantified by ICP-MS using Agilent 7800 ICP-MS mainframe spectrometer with Ar⁺ ion plasma gas and an electron multiple detector for detection at ppb concentration levels.

2. Synthetic Procedures

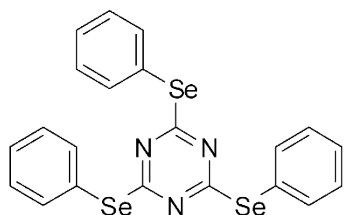
General procedure for synthesis of species 1-3

In a 100 mL Schlenk flask, aryldiselenide (1.5 eq.) was dissolved in 15 mL aq. THF (99:1) maintained under N₂ atmosphere. To this, NaBH₄ (3.3 eq) was added in small batches. The formation of sodium aryl selenolate was indicated by disappearance of yellow color. To this colorless solution, cyanuric chloride (1 eq.) was added in small batches over a period of 0.5 h. The completion of reaction was monitored by thin layer chromatography (TLC). Upon completion of the reaction, the product was extracted into chloroform (10 ml × 3). The combined organic extracts were washed with water, dried over anhydrous sodium sulfate and concentrated under reduced pressure to afford analytically pure solid products.

General procedure for synthesis of species 4-7

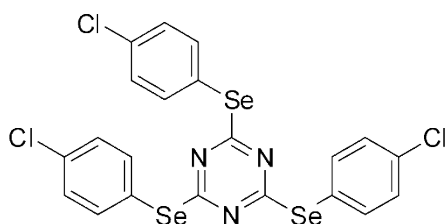
In a 100 mL Schlenk flask, the aryldiselenide (Ar₂Se₂; 1.5 eq.) was dissolved in 15 mL aq. THF (99:1) maintained under N₂ atmosphere. To this, NaBH₄ (3.3 eq) was added in small batches. The formation of sodium aryl selenolate (Na⁺ArSe⁻) was indicated by disappearance of yellow color. To this colorless solution, cyanuric chloride (1.5 eq.) was added in small batches over a period of 0.5 h. The reaction mixture was allowed to stir for 3h. Thereafter 1.5 equivalents of sodium arylselenolate (Na⁺Ar'Se⁻) of the was added dropwise using a pressure equilibrating funnel. The completion of reaction was monitored by thin layer chromatography (TLC). Upon completion of the reaction, the product was extracted into chloroform (10 ml × 3). The combined organic extracts were washed with water, dried over anhydrous sodium sulfate and concentrated under reduced pressure to afford crude products. It was purified by column chromatography [adsorbent: silica; eluent: hexane] affording analytically pure solid products.

3. Characterization data of species 1-7



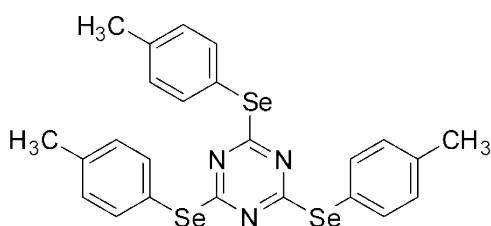
2,4,6-tris(phenylselanyl)-1,3,5-triazine (**1**): -

Pale yellow solid; **Yield** =71%; **Melting point** 100°C. **IR** (KBr pellets): ν (in cm^{-1}) 3056, 3017, 2574, 2411, 2207, 1915, 1635, 1576, 1445, 1224, 1176, 1020, 786, 732, 686, 472. **^1H NMR** (CDCl_3 , 500 MHz): δ (in ppm) 7.45(d, 6H, $J=10\text{Hz}$), 7.31(t, 6H, $J=10\text{Hz}$), 7.21(t, 3H, $J=10\text{Hz}$). **^{13}C [^1H] NMR** (CDCl_3 , 125 MHz): δ (in ppm) 180.5, 135.8, 129.2, 129.1 and 125.8. **^{77}Se NMR** (CDCl_3 , 114.45 MHz): δ (in ppm) 469.5. **HRMS** (m/z) calculated 549.8835 $[\text{M}+\text{H}]^+$, observed 549.8860.



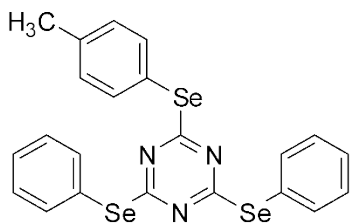
2,4,6-tris(*p*-chlorophenylselanyl)-1,3,5-triazine (**2**): -

Pale yellow solid; **Yield** =71%; **Melting point** 106°C. **IR** (KBr pellets): ν (in cm^{-1}) 2906, 2580, 2415, 2189, 1902, 1636, 1560, 1455, 1224, 1088, 1011, 814, 789, 730, 490. **^1H NMR** (CDCl_3 , 500MHz): δ (in ppm) 7.36 (d, 6H, $J=10\text{Hz}$), 7.21 (d, 6H, $J=10\text{Hz}$). **^{13}C [^1H] NMR** (CDCl_3 , 125 MHz): δ (in ppm) 180.4, 137.3, 135.8, 129.5, 123.6. **^{77}Se NMR** (CDCl_3 , 114.45 MHz): δ (in ppm) 467.1. **HRMS** (m/z) calculated 651.7665 $[\text{M}+\text{H}]^+$, observed 651.1572.



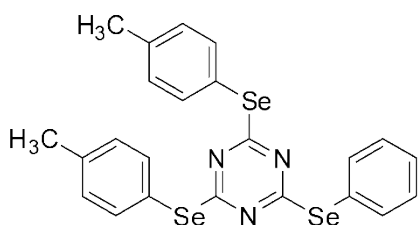
2,4,6-tris(*p*-tolylselanyl)-1,3,5-triazine (**3**): -

Pale yellow solid; **Yield** =52%; **Melting point** 115°C. **IR** (KBr pellets): ν (in cm^{-1}) 2925, 2856, 1456, 1247, 1221, 1015, 802, 489. **^1H NMR** (CDCl_3 , 500MHz): δ (in ppm) 7.34 (d, 6H, $J=5\text{Hz}$), 7.00 (d, 6H, $J=5\text{Hz}$), 2.36 (s, 9H). **^{13}C [^1H] NMR** (CDCl_3 ,125 MHz): δ (in ppm) 180.6, 138.8, 135.7, 129.9, 122.4, 21.5. **^{77}Se NMR** (CDCl_3 , 114.45 MHz): δ (in ppm) 491.5. **HRMS** (m/z) calculated 591.9304 $[\text{M}+\text{H}]^+$, observed 591.9356.



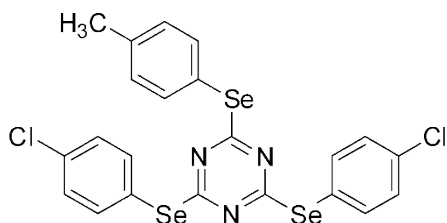
2,4-bis(phenylselanyl)-6-(*p*-tolylselanyl)-1,3,5-triazine (**4**): -

Pale yellow solid; **Yield** =38%; **Melting point** 115°C. **IR** (KBr pellets): ν (in cm^{-1}) 3055, 2924, 2577, 1578, 1465, 1228, 1017, 789, 735, 686, 471. **^1H NMR** (CDCl_3 , 500MHz): δ (in ppm) 7.46 (d, 4H, $J=10\text{Hz}$), 7.31 (m, 4H), 7.21 (d, 2H, $J=10\text{Hz}$), 7.2 (d, 2H, $J=10\text{Hz}$), 7.0 (t, 2H, $J=5\text{Hz}$), 2.36 (s, 3H). **^{13}C [^1H] NMR** (CDCl_3 , 125 MHz): δ (in ppm) 180.5, 139, 135.7, 130.1, 129.3, 129.2, 129, 128.8, 125.8, 21.5. **^{77}Se NMR** (CDCl_3 , 114.45 MHz): δ (in ppm) 501.4 (major), 500.6, 494.7 (major), 493.4. **HRMS** (m/z) calculated 563.8991 [$\text{M}+\text{H}$] $^+$, observed 563.9024.



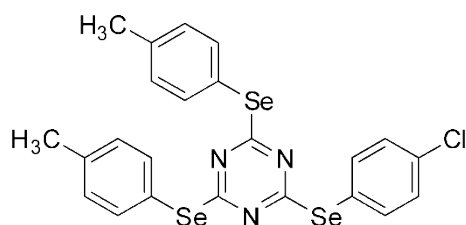
2-(phenylselanyl)-4,6-bis(*p*-tolylselanyl)-1,3,5-triazine (**5**): -

Pale yellow solid; **Yield** =44%; **Melting point** 98°C. **IR** (KBr pellets): ν (in cm^{-1}) 3057, 2922, 2581, 1907, 1592, 1498, 1245, 1016, 805, 787, 735, 688, 489. **^1H NMR** (CDCl_3 , 500MHz): δ (in ppm) 7.46 (t, 2H, $J=10\text{Hz}$), 7.34 (d, 2H, $J=5\text{Hz}$), 7.19 (m, 3H), 7.0 (d, 4H, $J=5\text{Hz}$), 2.36 (s, 6H). **^{13}C [^1H] NMR** (CDCl_3 , 125 MHz): δ (in ppm) 180.6, 138.9, 135.8, 135.7, 130, 129.9, 129.1, 122.4, 122.3, 21.5. **^{77}Se NMR** (CDCl_3 , 114.45 MHz): δ (in ppm) 500.6 (major), 500.1, 493.4 (major), 492.5. **HRMS** (m/z) calculated 577.9148 [$\text{M}+\text{H}$] $^+$, observed 577.9189.



2,4-bis(*p*-chlorophenylselanyl)-6-(*p*-tolylselanyl)-1,3,5-triazine (**6**): -

Pale yellow solid; **Yield** =21%; **Melting point** 82°C. **IR** (KBr pellets): ν (in cm^{-1}) 2923, 2582, 1906, 1568, 1464, 1387, 1252, 1227, 1174, 1086, 1010, 813, 790, 494. **^1H NMR** (CDCl_3 , 500MHz): δ (in ppm) 7.36 (d, $J=10\text{Hz}$, 4H), 7.21 (d, $J=10\text{Hz}$, 4H), 7.18 (d, 2H, $J=10\text{Hz}$), 7.05 (d, 2H, $J=10\text{Hz}$), 2.4 (s, 3H). **^{13}C [^1H] NMR** (CDCl_3 , 125 MHz): δ (in ppm) 180.4, 137.3, 137.2, 135.9, 135.8, 130, 129.5, 129.4, 123.6, 21.5. **^{77}Se NMR** (CDCl_3 , 114.45 MHz): δ (in ppm) 499 (major), 498.1, 496 (major), 496.2. **HRMS** (m/z) calculated 631.8212 [$\text{M}+\text{H}$] $^+$, observed 631.8261.



2-(*p*-chlorophenylselanyl)-4,6-bis(*p*-tolylselanyl)-1,3,5-triazine (**7**): -

Pale yellow solid; **Yield** =22%; **Melting point** 108°C. **IR** (KBr pellets): ν (in cm^{-1}) 2915, 2579, 1641, 1465, 1236, 1173, 1088, 1013, 801 789, 492. **^1H NMR** (CDCl_3 , 500MHz): δ (in ppm) 7.35 (d, 4H, $J=10\text{Hz}$), 7.1 (d, 2H, $J=10\text{Hz}$), 7.05 (d, 4H, $J=10\text{Hz}$), 7.01 (d, 2H, $J=5\text{Hz}$), 2.36 (s, 6H). **^{13}C [^1H] NMR** (CDCl_3 , 125 MHz): δ (in ppm) 180.6, 139.2, 137.2, 135.8, 135.7, 130, 129.9, 129.4, 129.3, 21.5. **^{77}Se NMR** (CDCl_3 , 114.45 MHz): δ (in ppm) 496 (major), 495.2, 493.6 (major), 492.6. **HRMS** (m/z) calculated 611.8758 [$\text{M}+\text{H}$] $^+$, observed 611.8795.

4. Copies of multinuclear NMR (^1H , $^{13}\text{C}\{^1\text{H}\}$, ^{77}Se) & HRMS

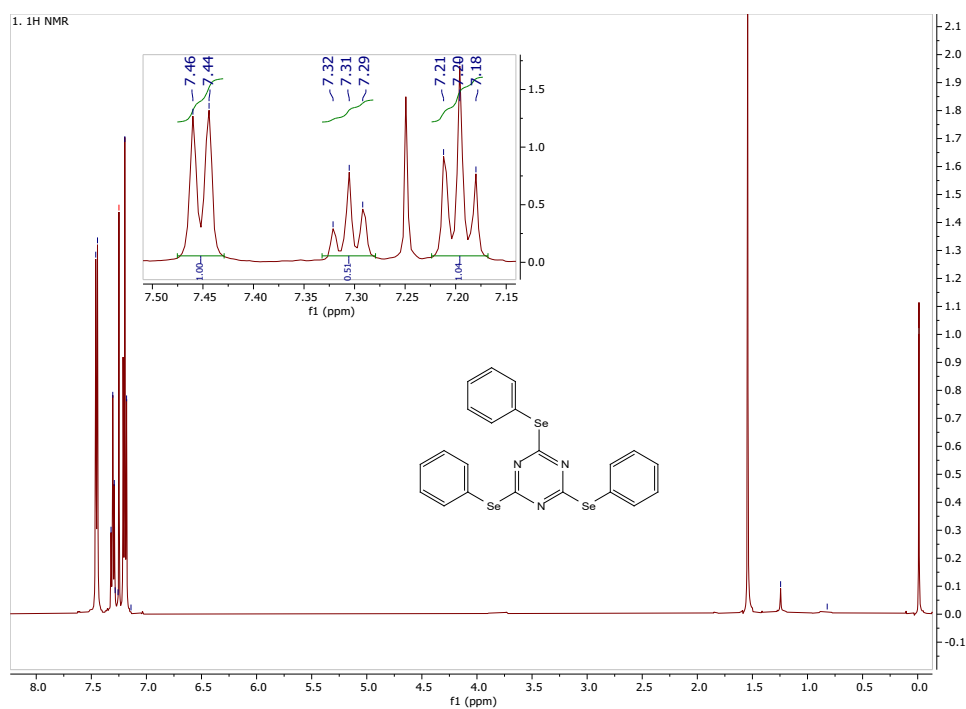


Fig. S1: ^1H NMR of species 1 in CDCl_3 .

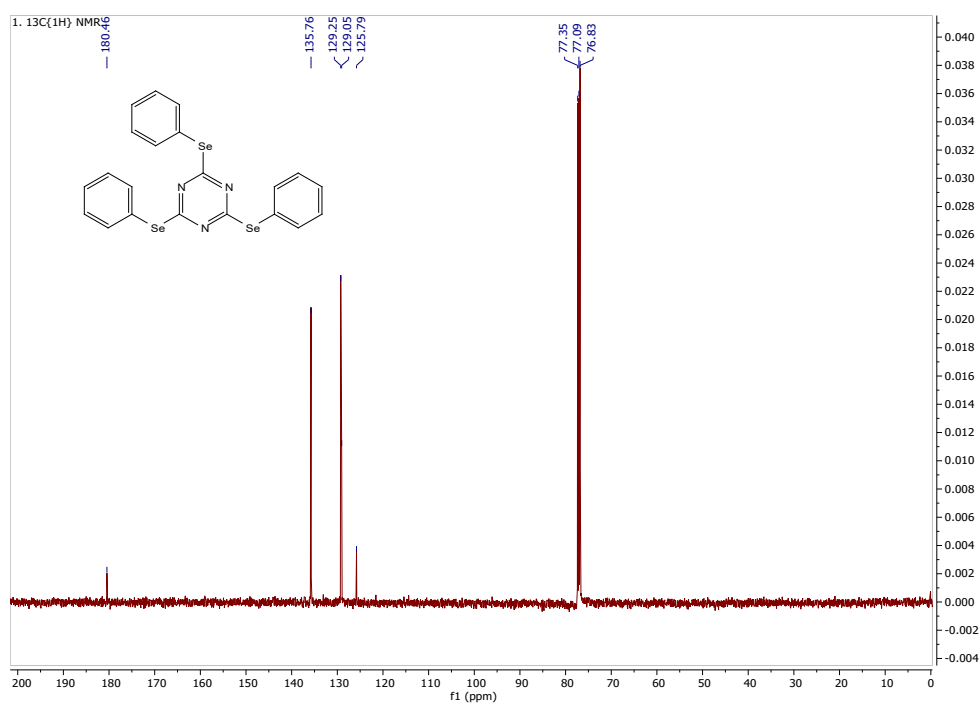


Fig. S2: $^{13}\text{C}\{^1\text{H}\}$ NMR of species 1 in CDCl_3 .

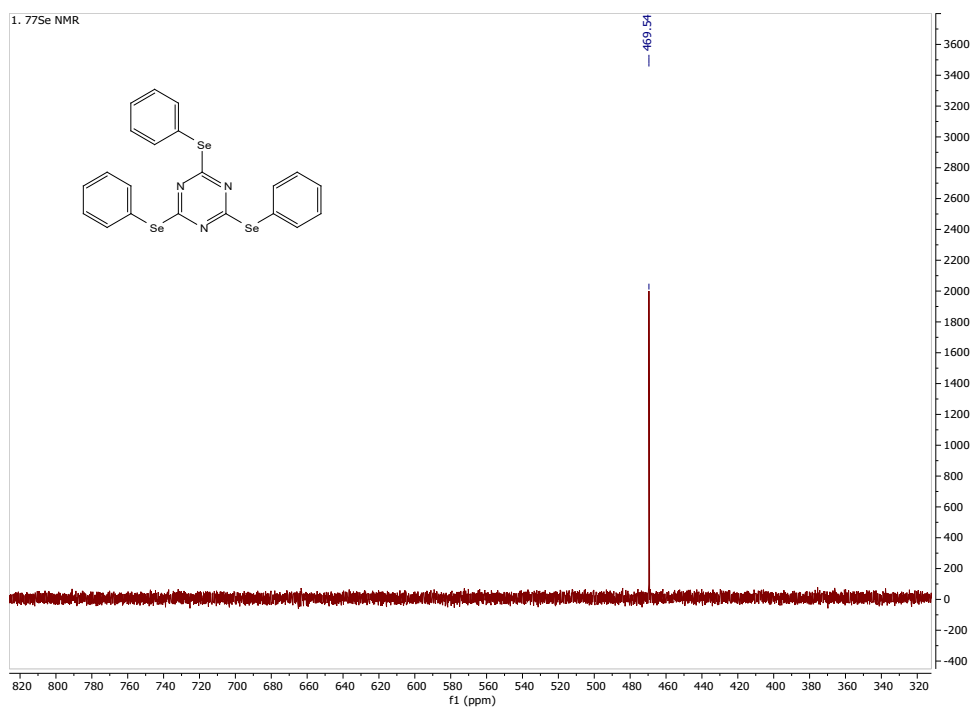


Fig. S3: ⁷⁷Se NMR of species 1 in CDCl₃.

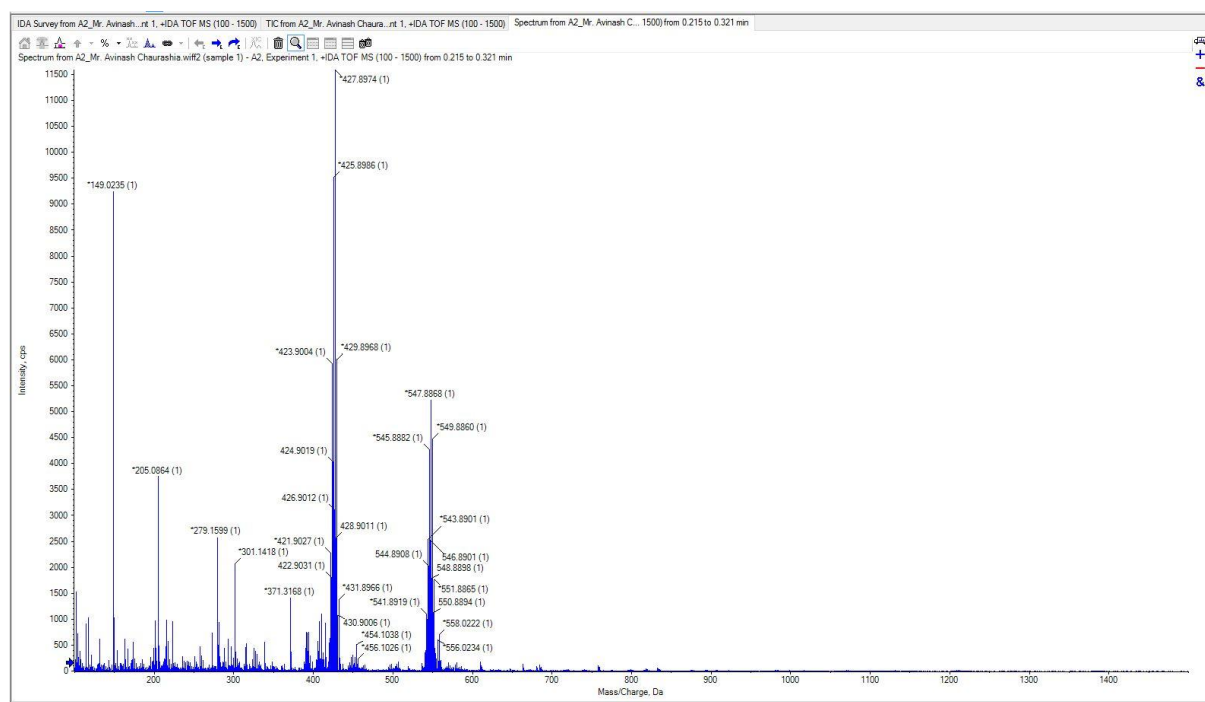


Fig. S4: HRMS data of species 1.

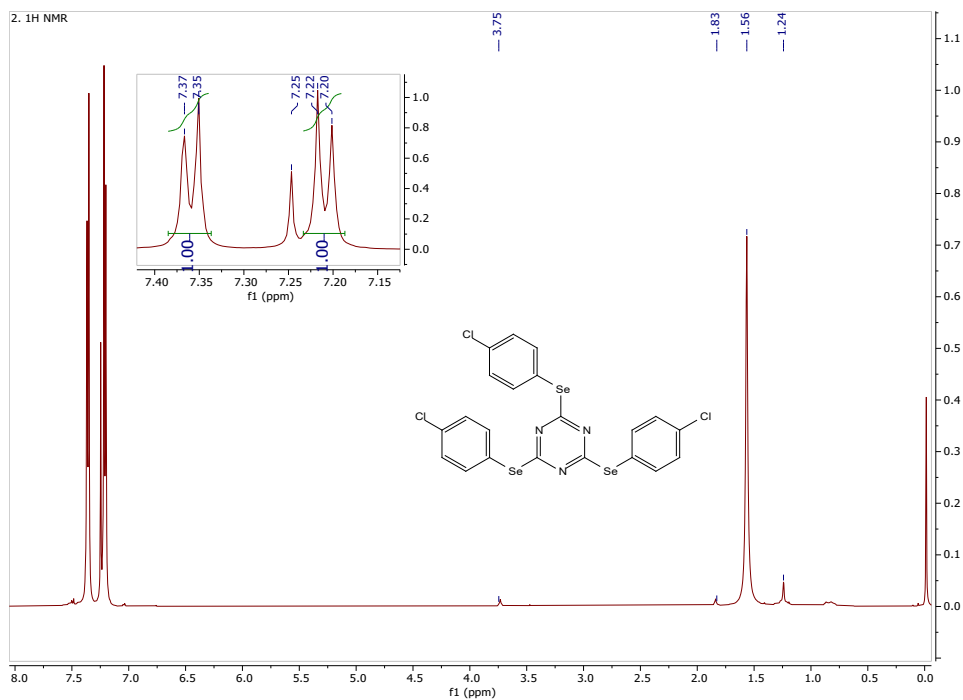


Fig. S5: ^1H NMR of species **2** in CDCl_3 .

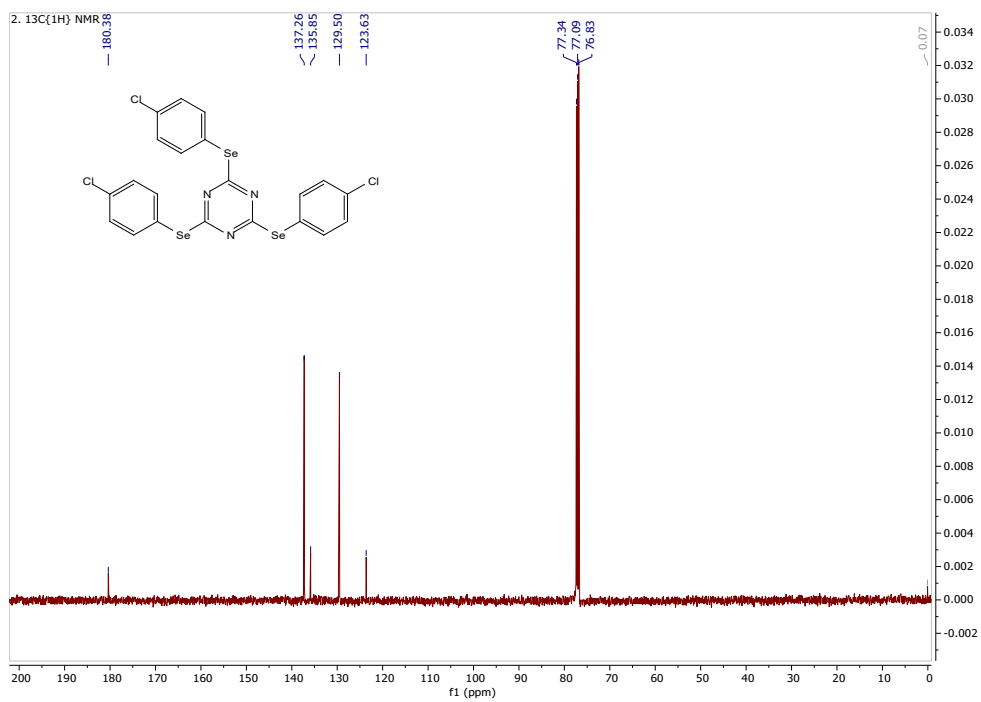


Fig. S6: $^{13}\text{C}\{^1\text{H}\}$ NMR of species **2** in CDCl_3 .

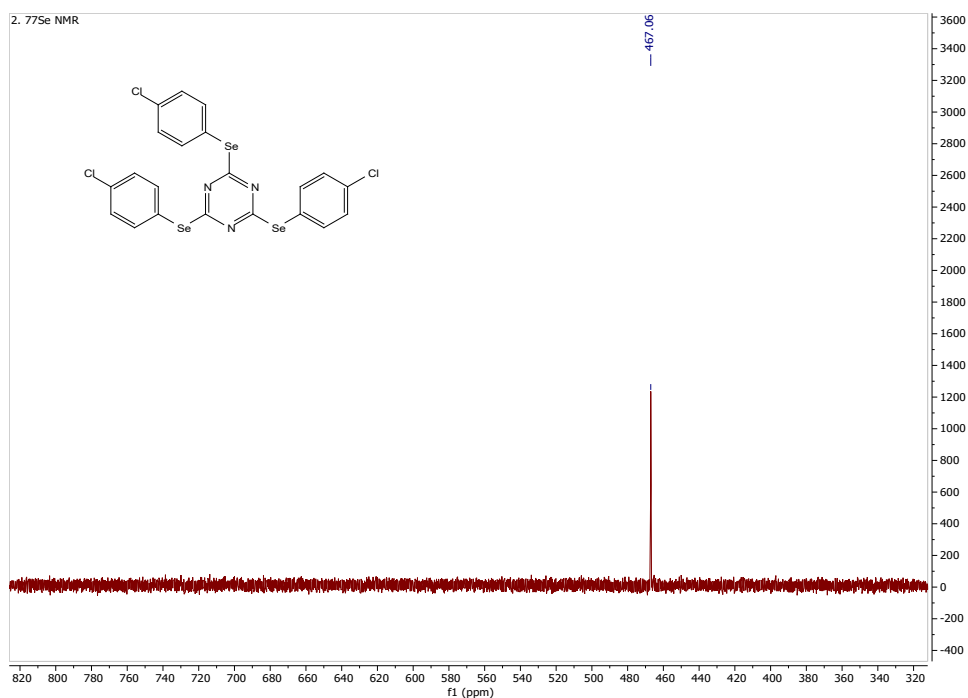


Fig. S7: ⁷⁷Se NMR of species 2 in CDCl₃.

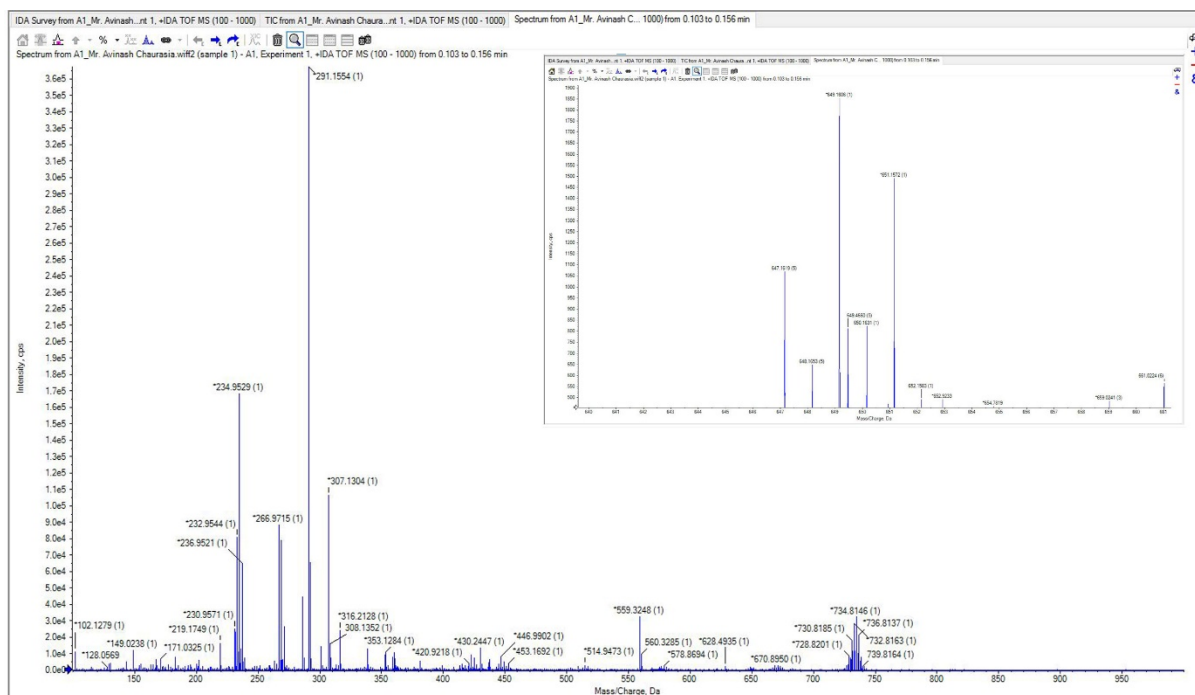


Fig. S8: HRMS data of species 2.

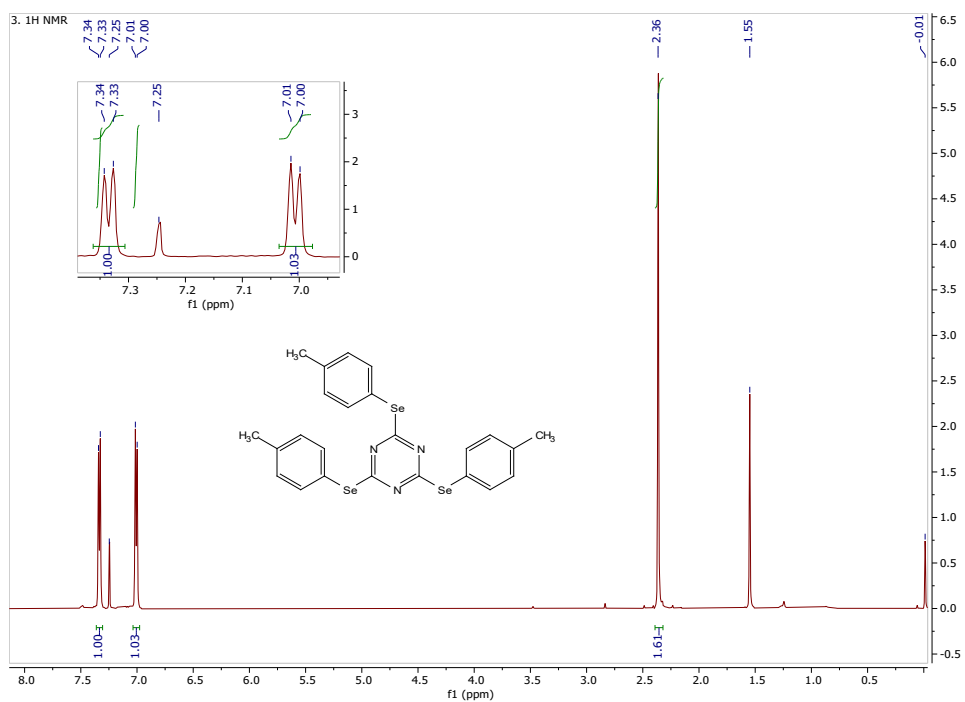


Fig. S9: ^1H NMR of species **3** in CDCl_3 .

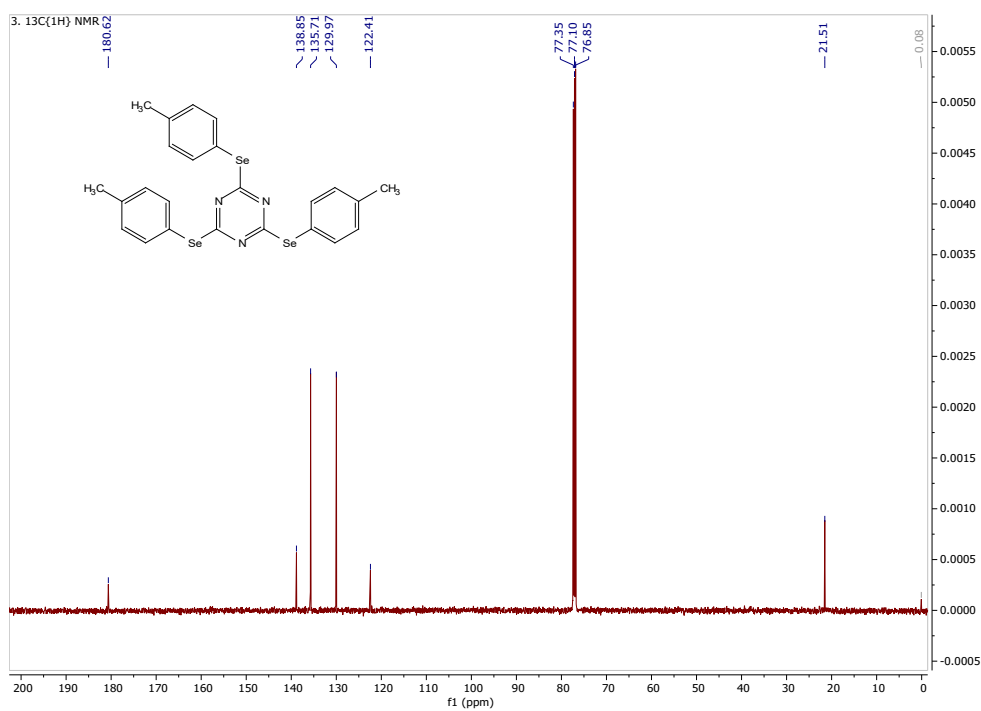


Fig. S10: $^{13}\text{C}\{^1\text{H}\}$ NMR of species **3** in CDCl_3 .

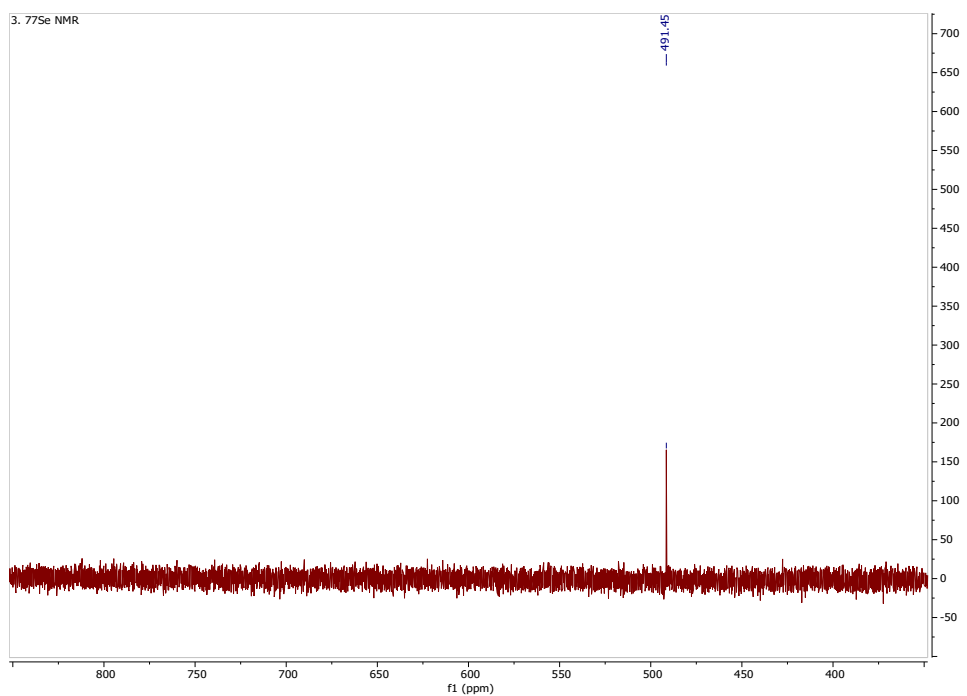


Fig. S11: ^{77}Se NMR of species **3** in CDCl_3 .

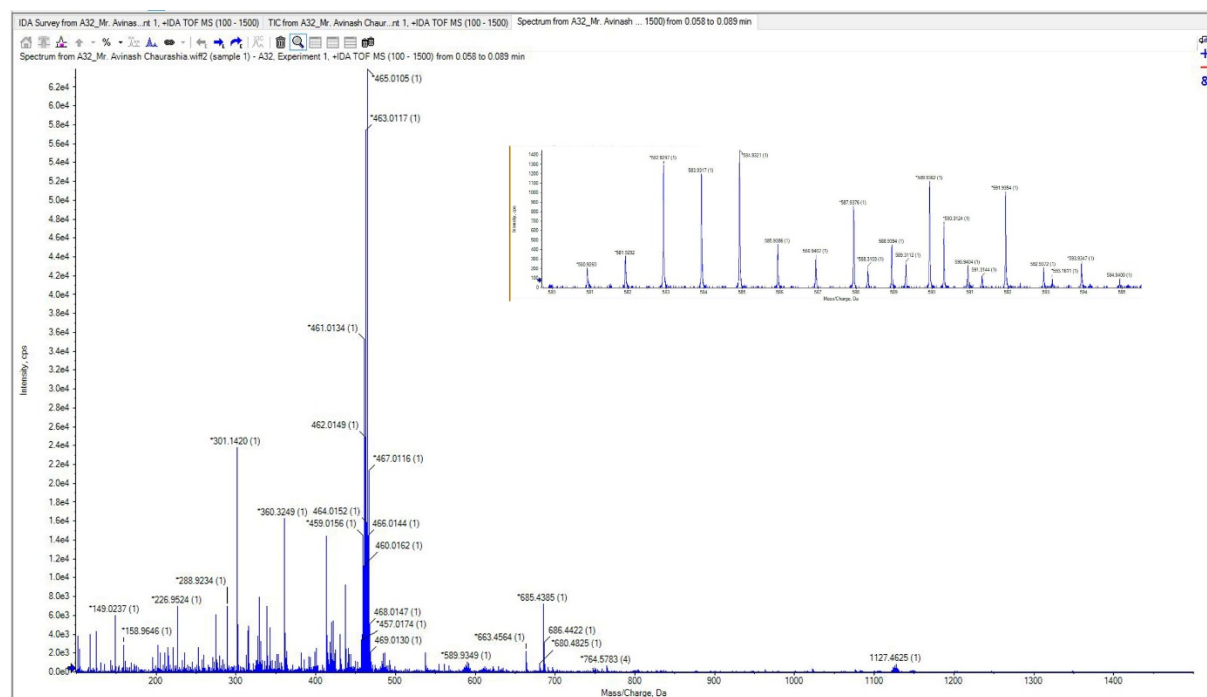


Fig. S12: HRMS data of species **3**.

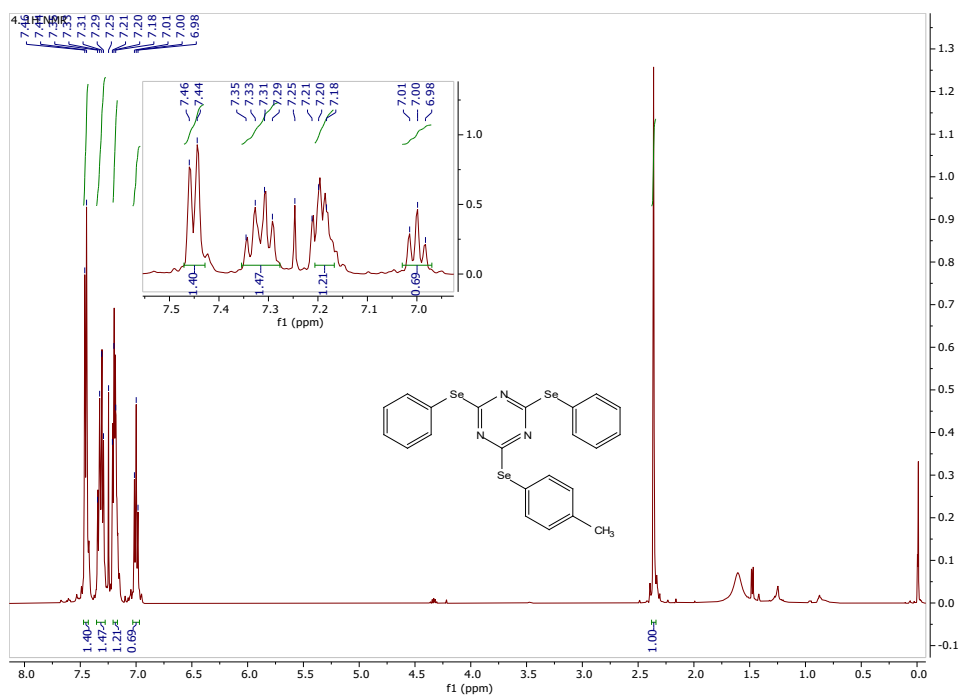


Fig. S13: ^1H NMR of species 4 in CDCl_3 .

^{13}C NMR

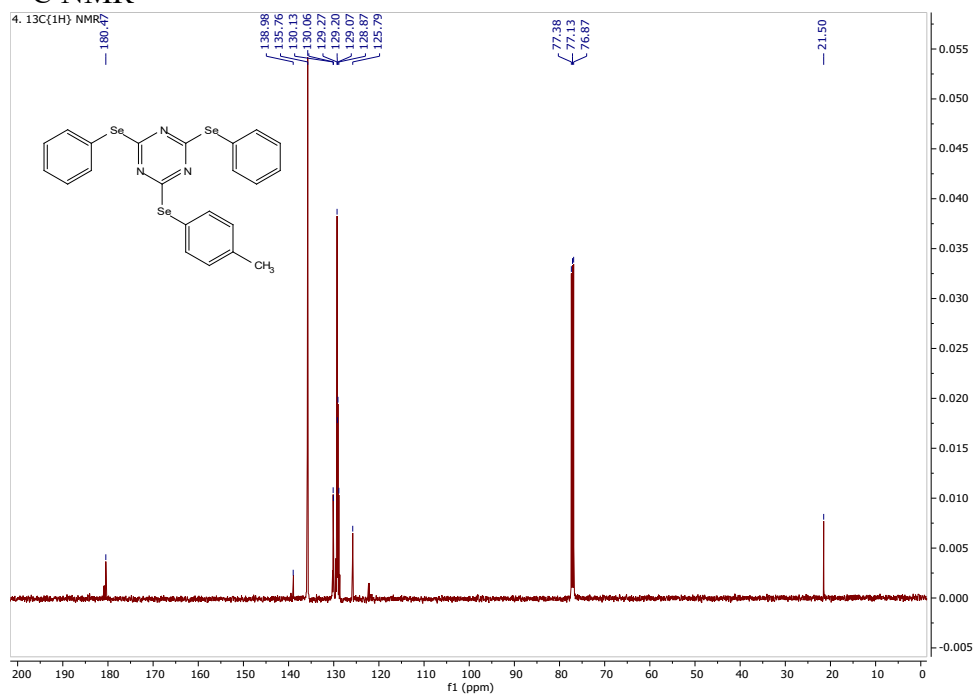


Fig. S14: $^{13}\text{C}\{^1\text{H}\}$ NMR of species 4 in CDCl_3 .

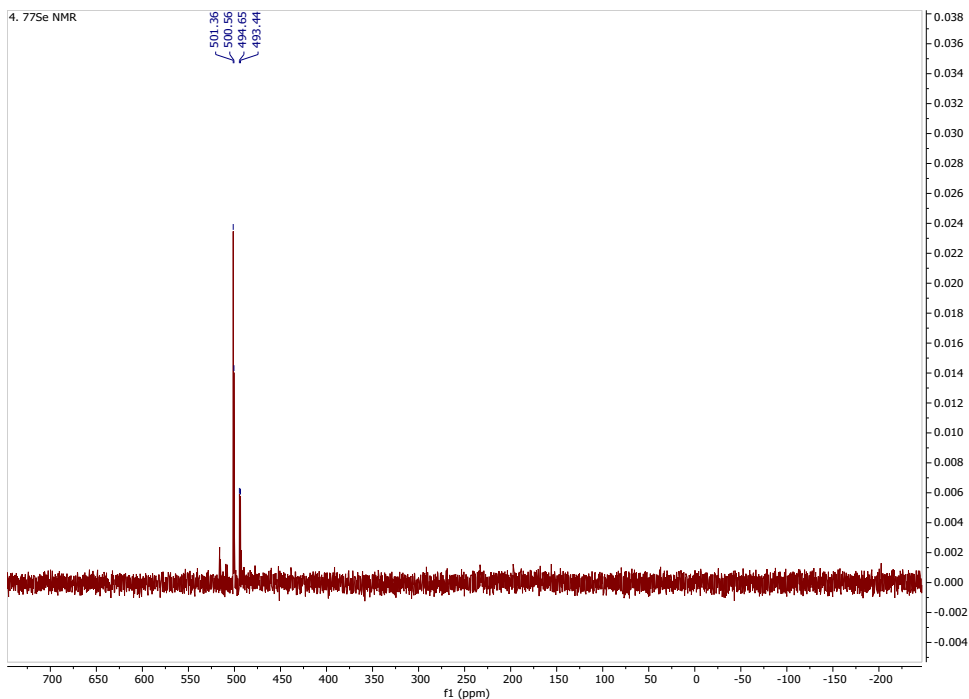


Fig. S15 : ^{77}Se NMR of species **4** in CDCl_3 .

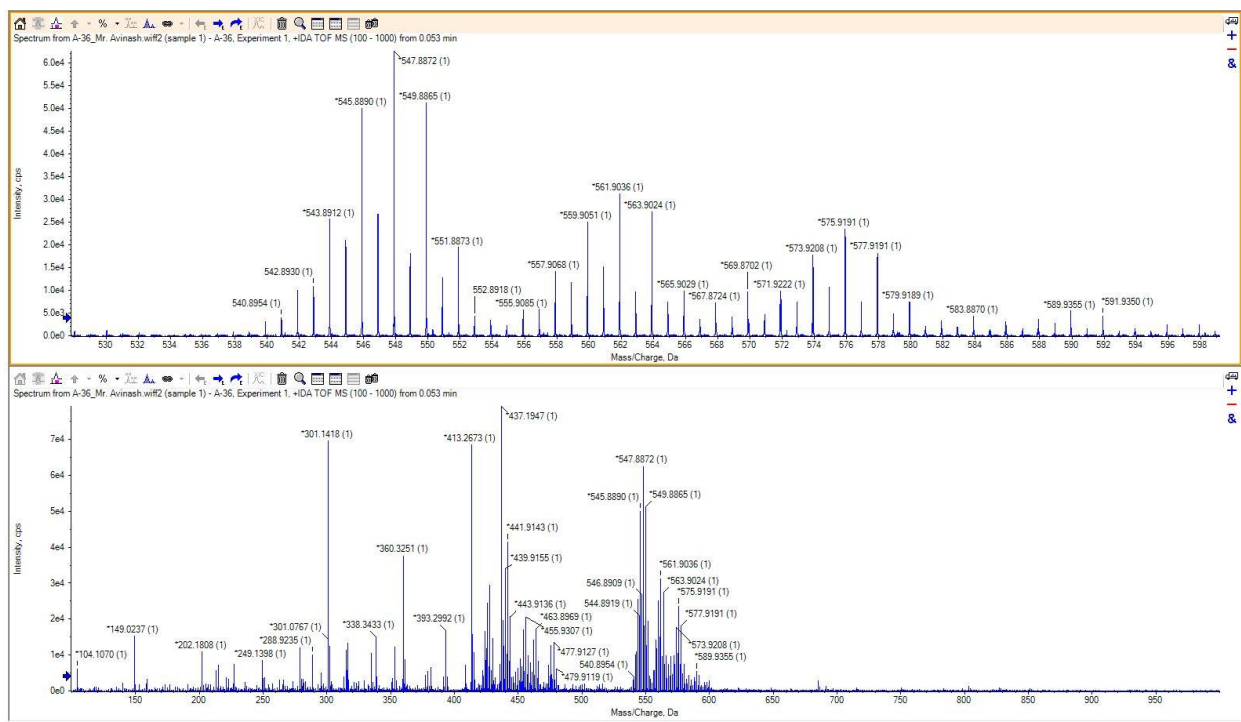


Fig. S16: HRMS data of species **4**.

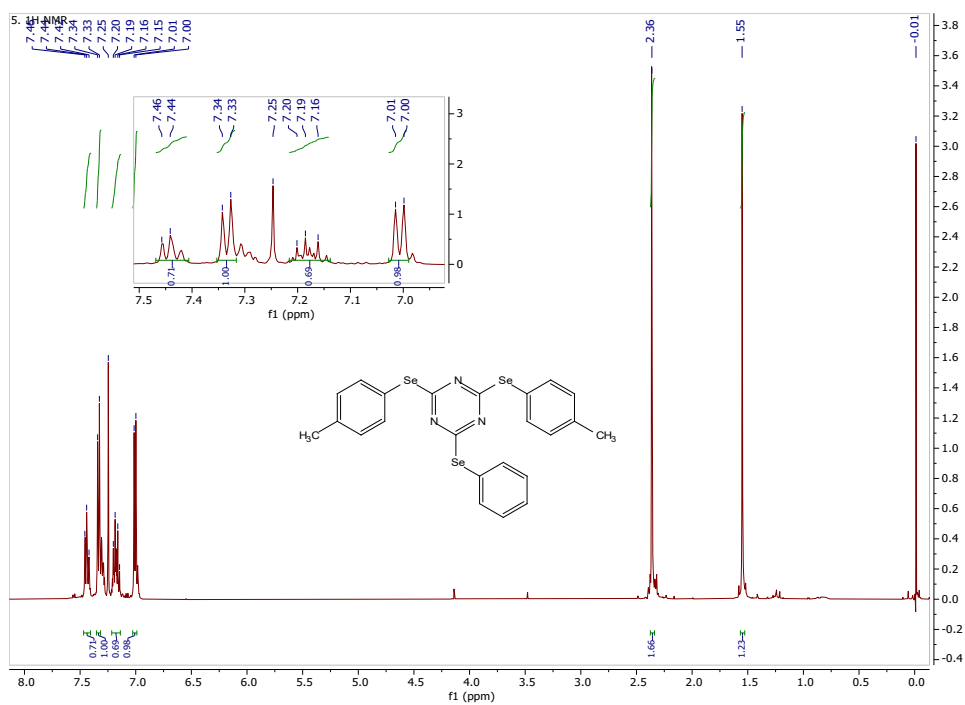


Fig. S17: ^1H NMR of species **5** in CDCl_3 .

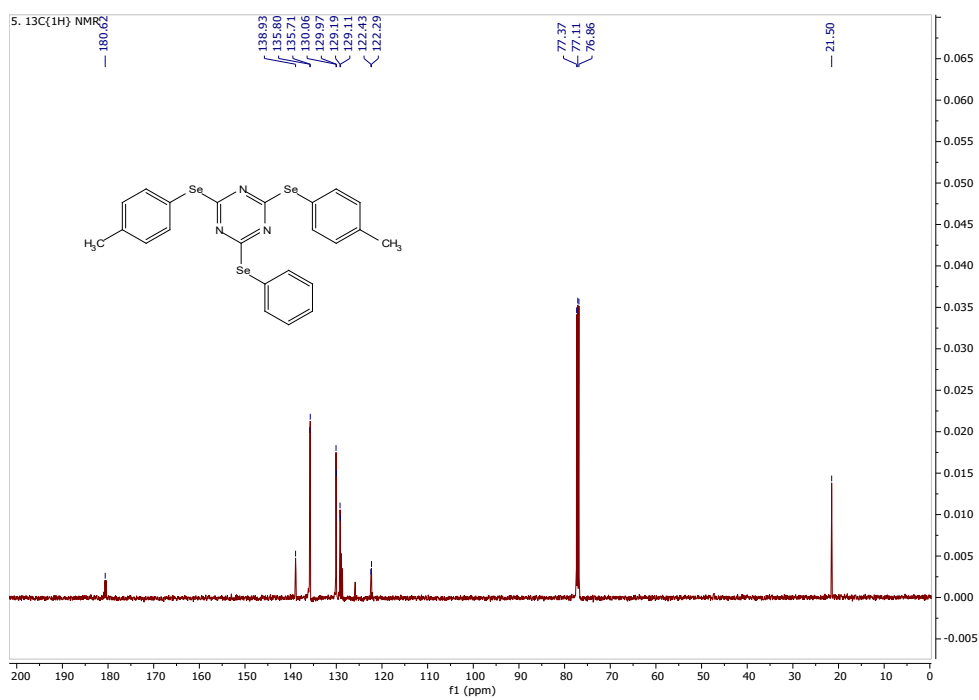


Fig. S18: $^{13}\text{C}\{^1\text{H}\}$ NMR of species **5** in CDCl_3 .

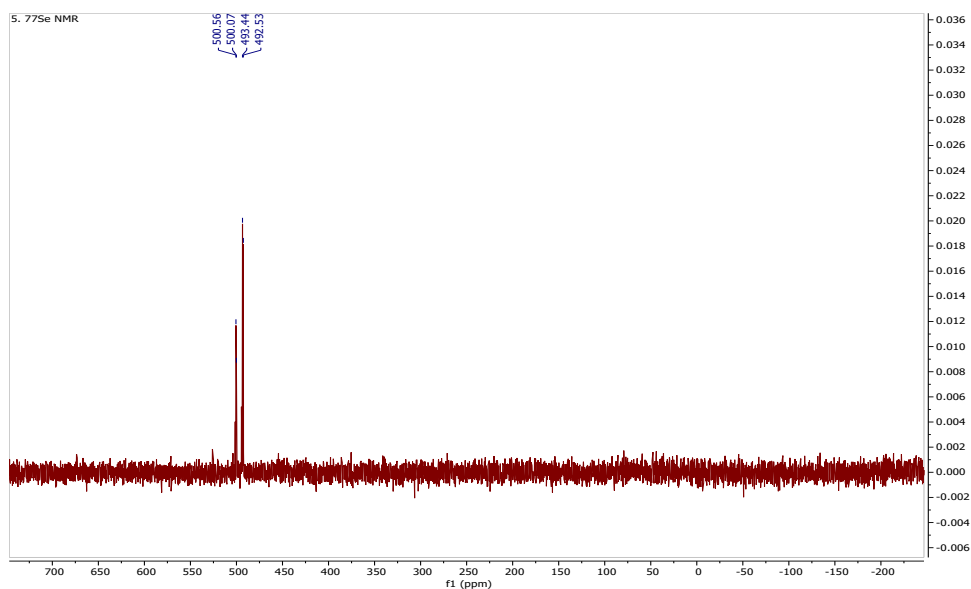


Fig. S19: ^{77}Se NMR of species **5** in CDCl_3 .

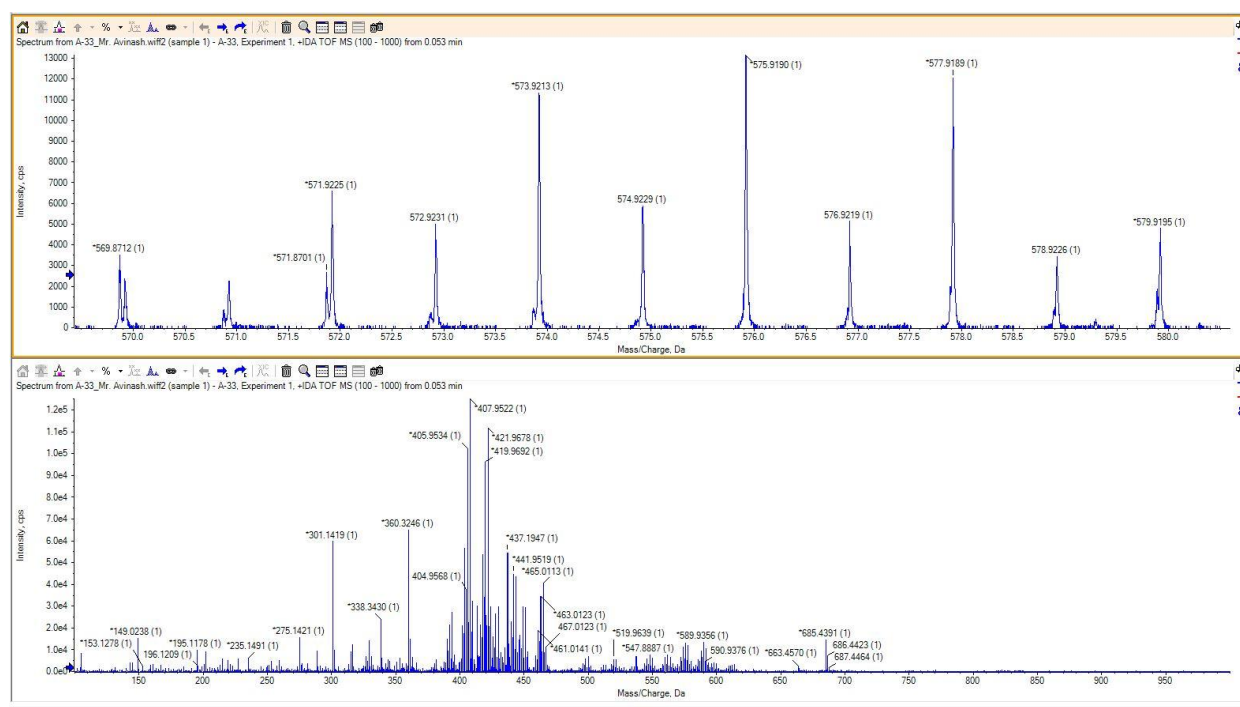


Fig. S20: HRMS data of species **5**.

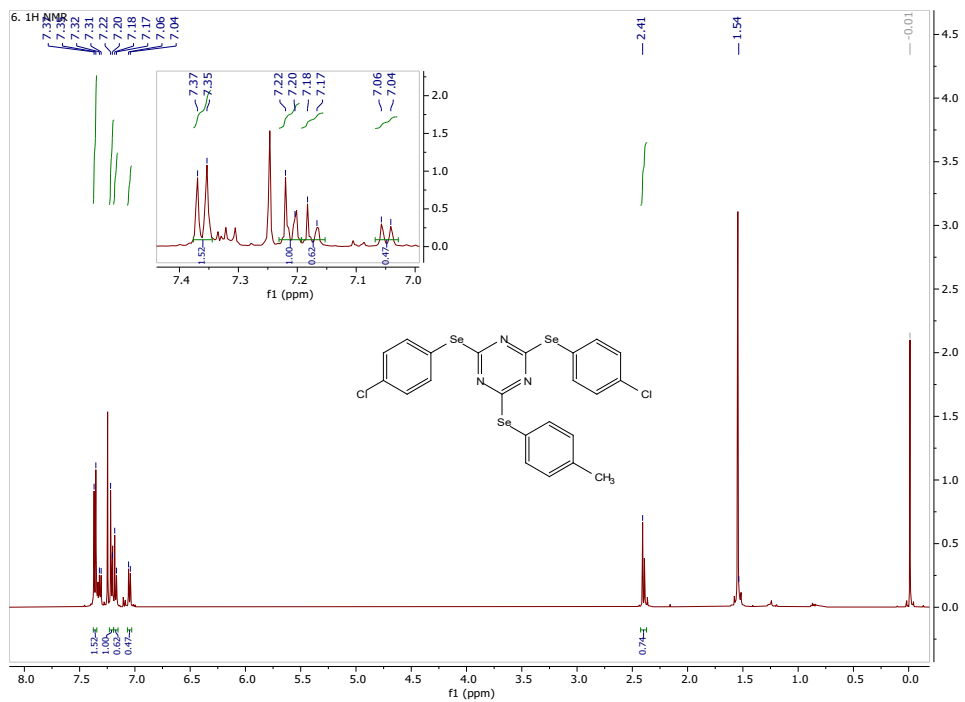


Fig. S21: ^1H NMR of species **6** in CDCl_3 .

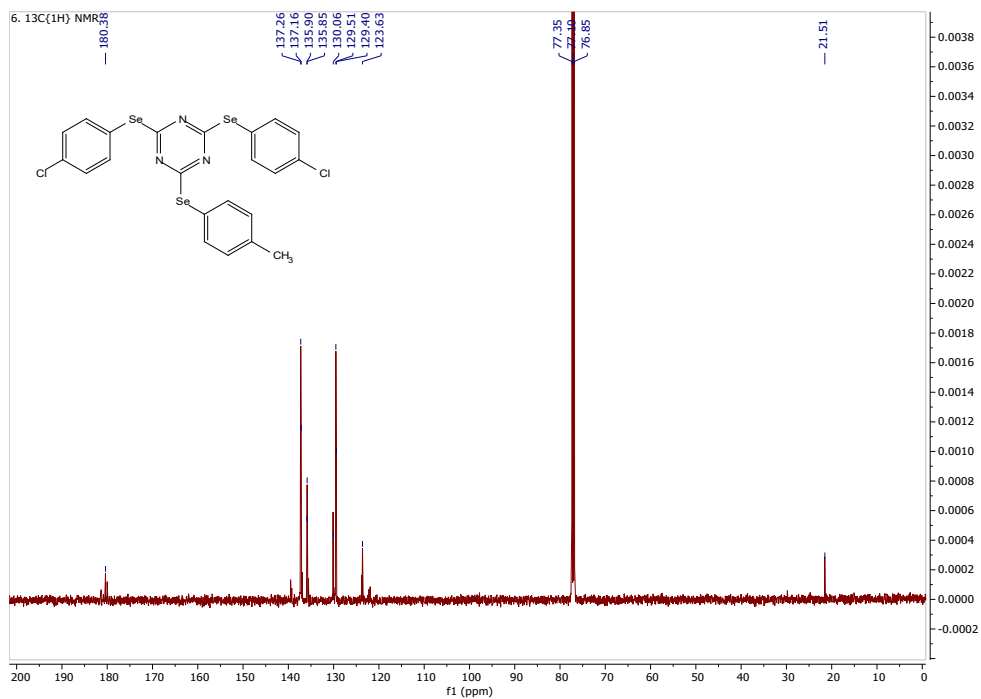


Fig. S22: $^{13}\text{C}\{^1\text{H}\}$ NMR of species **6** in CDCl_3 .

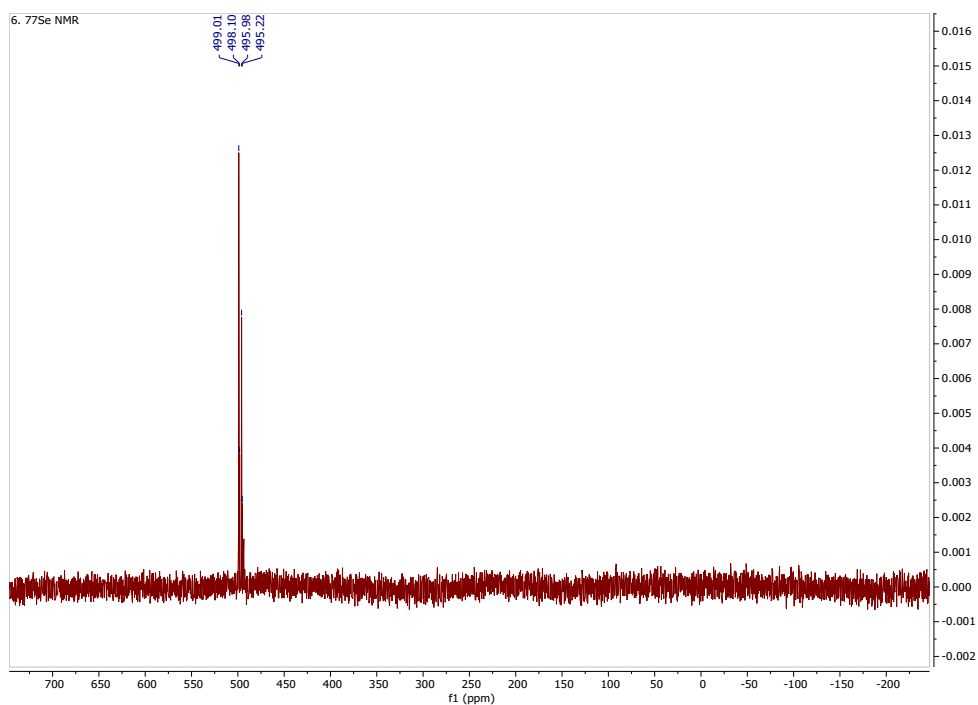


Fig. S23: ^{77}Se NMR data of species **6** in CDCl_3 .

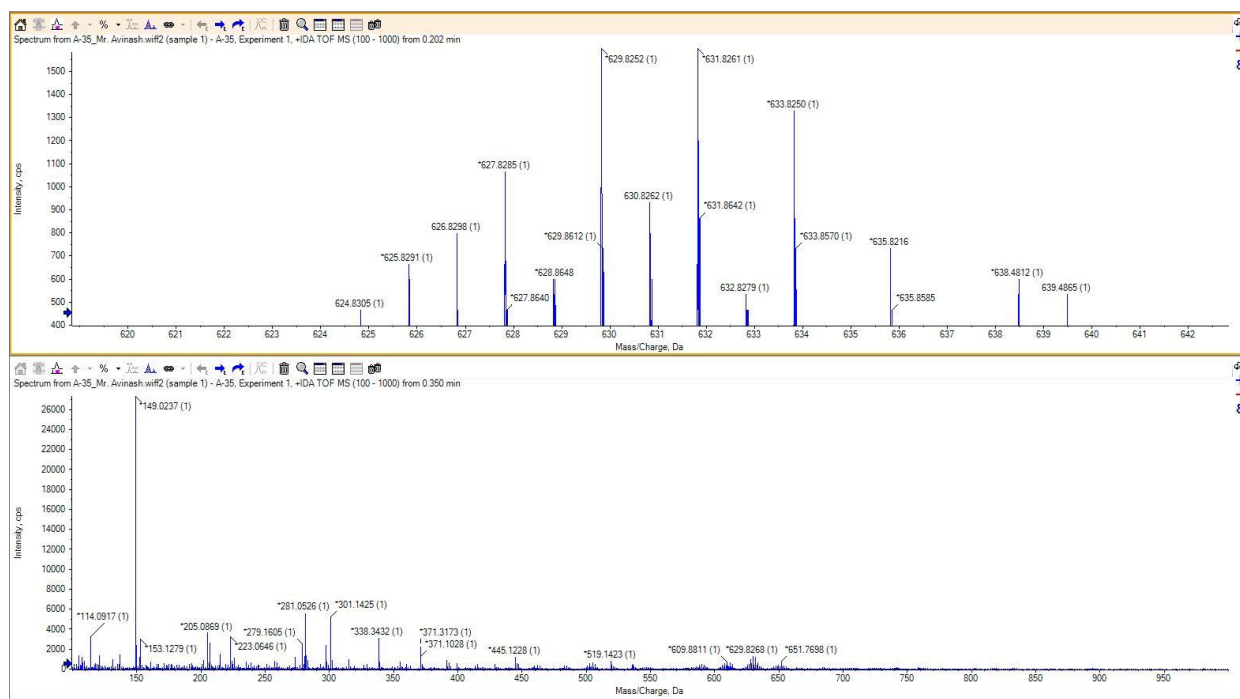


Fig. S24: HRMS data of species **6**.

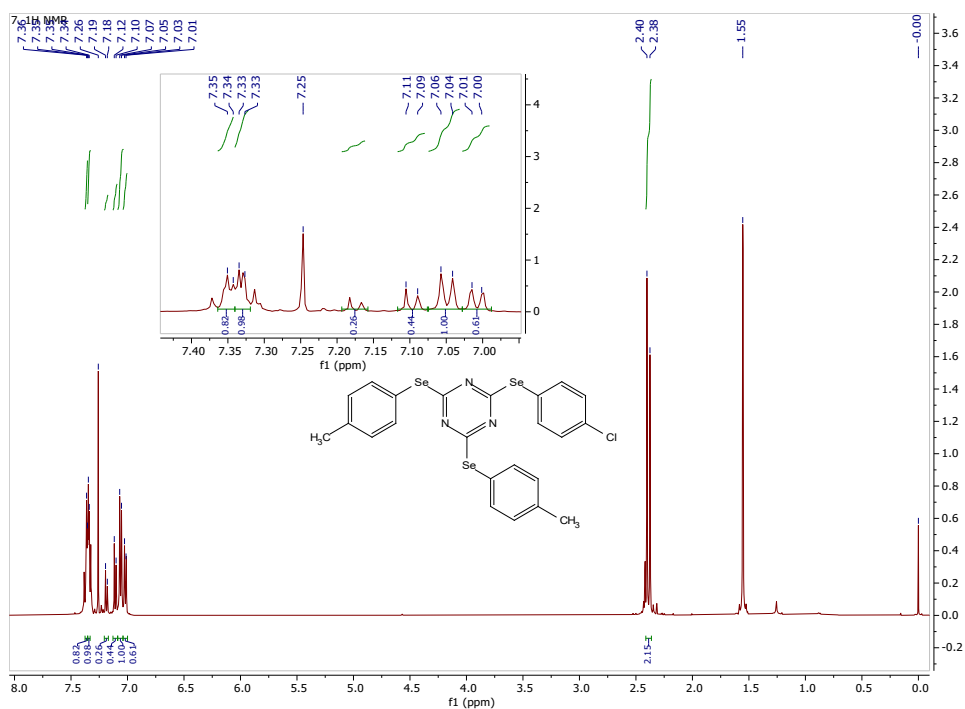


Fig. S25: ^1H NMR of species **7** in CDCl_3 .

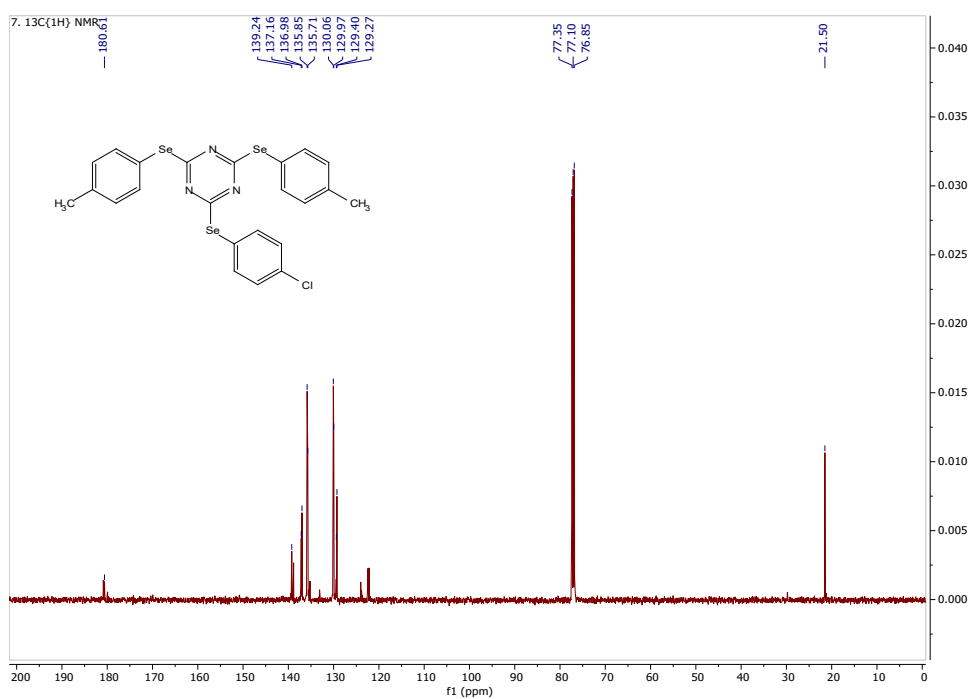


Fig. S26: $^{13}\text{C}\{^1\text{H}\}$ NMR of species **7** in CDCl_3 .

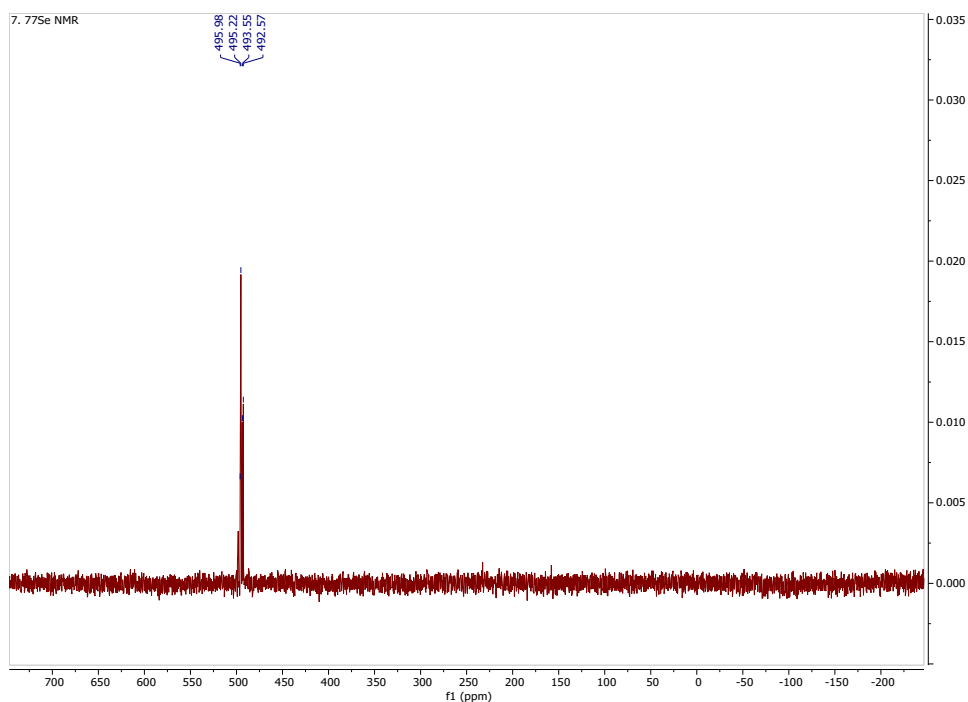


Fig. S27: ⁷⁷Se NMR of species **7** in CDCl₃.

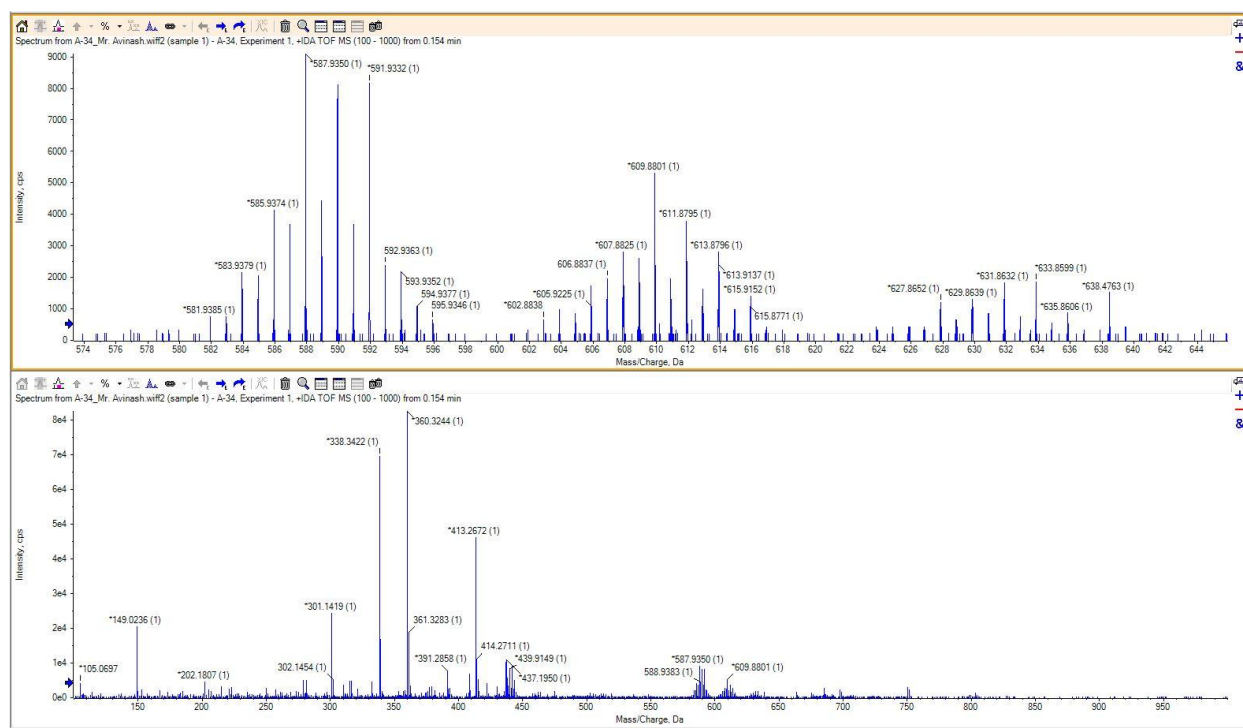


Fig. S28: HRMS data of species **7**.

5. Crystallographic data

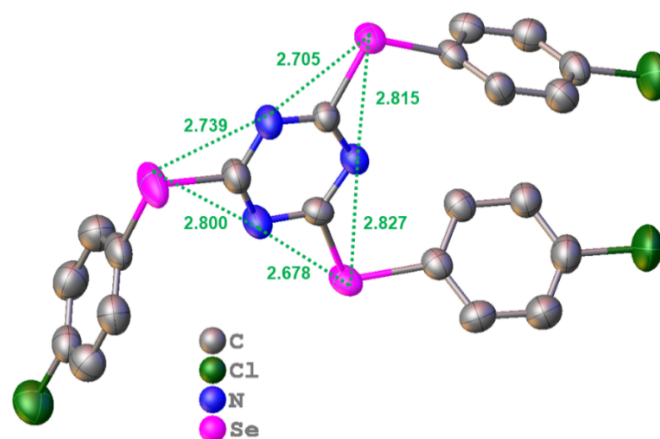


Fig. S29: Molecular structure of species **2** showing the Se-N distances.

Table 1: Crystallographic data of species **2**.

Empirical formula	C ₂₁ H ₁₂ Cl ₃ N ₃ Se ₃
Formula weight	650.7592
Temperature/K	293
Crystal system	monoclinic
Space group	P21/c
a/Å	24.4179(6)
b/Å	8.94957(18)
c/Å	10.6055(3)
α/°	90
β/°	97.759(2)
γ/°	90
Volume/Å ³	2296.39(9)
Z	4
ρ _{calc} g/cm ³	1.879
μ /mm ⁻¹	5.168
F(000)	1248.0
Radiation Mo Kα	0.71073
2θ range for data collection/°	2.426 to 27.079
Goodness-of-fit on F	1.123
Final R indexes [I>=2σ (I)]	0.0551(3723)
Final R indexes [all data]	0.1023(4930)
Completeness	0.973
CCDC deposit number	2364346

6. Solution State Studies and binding constant

UV-Visible spectra were recorded at 25°C using JASCO V-730 UV-Visible Spectrophotometer. A stock solution of the 1.0 mM of species **1-7** was prepared in acetonitrile. The stock solution of nitrate salts of Hg^{2+} & Pb^{2+} having strength of 1.0 mM in acetonitrile were also prepared. For UV-titration experiments, 30 μl from stock solution of each species was diluted to 3 ml with acetonitrile in a quartz cuvette. The appropriate aliquot from the stock solution of metal ions (Hg^{2+} & Pb^{2+}) were added to these solutions. The UV-visible spectra were then recorded in each case.

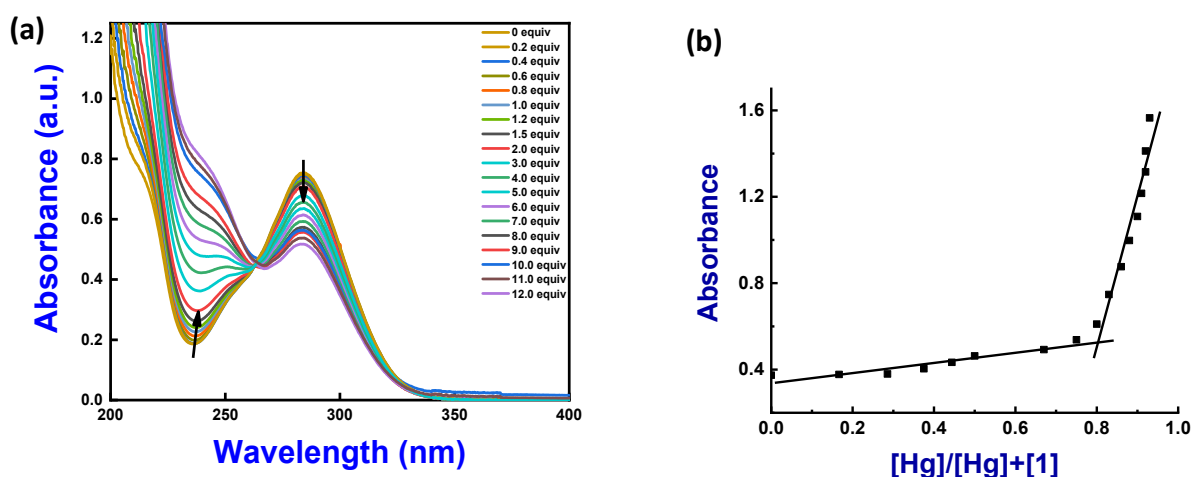


Fig. S30: (a) Absorption spectrum of **1** and the changes observed upon gradual addition of $\text{Hg}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ in acetonitrile. (b) Job's plot based on the changes in absorption at 235 nm.

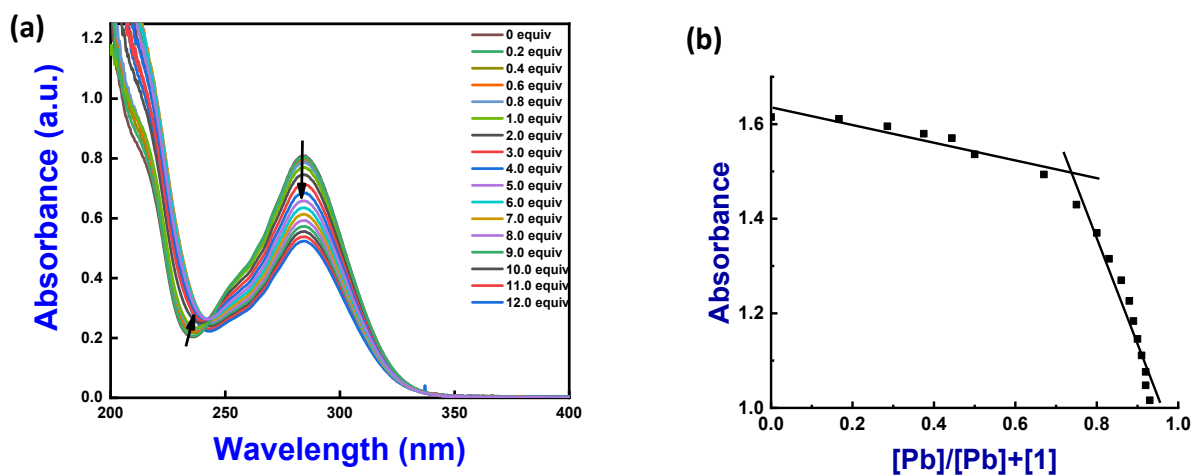


Fig. S31: (a) Absorption spectrum of **1** and the changes observed upon gradual addition of $\text{Pb}(\text{NO}_3)_2$ in acetonitrile. (b) Job's plot based on the changes in absorption at 284 nm.

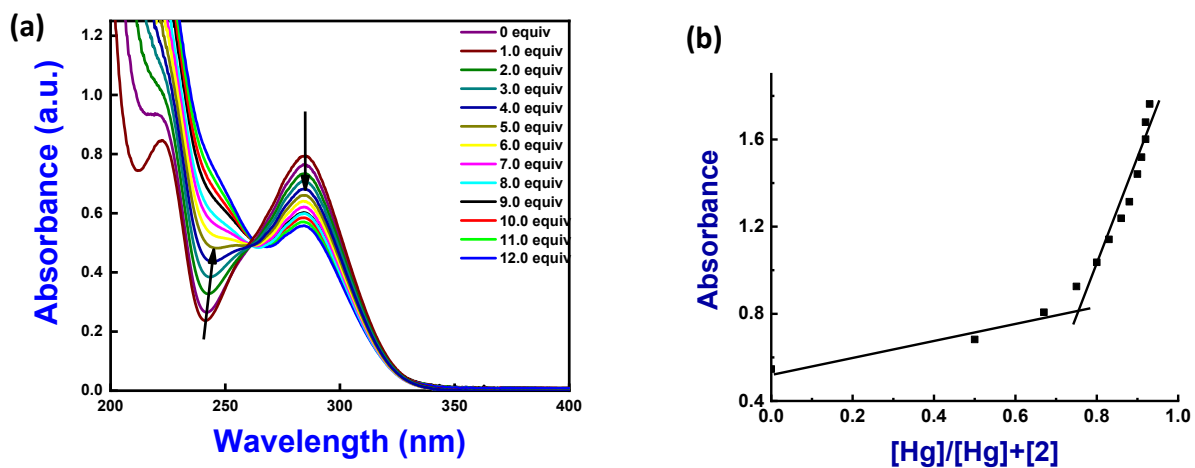


Fig. S32: (a) Absorption spectrum of **2** and the changes observed upon gradual addition of $\text{Hg}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ in acetonitrile. (b) Job's plot based on the changes in absorption at 240 nm.

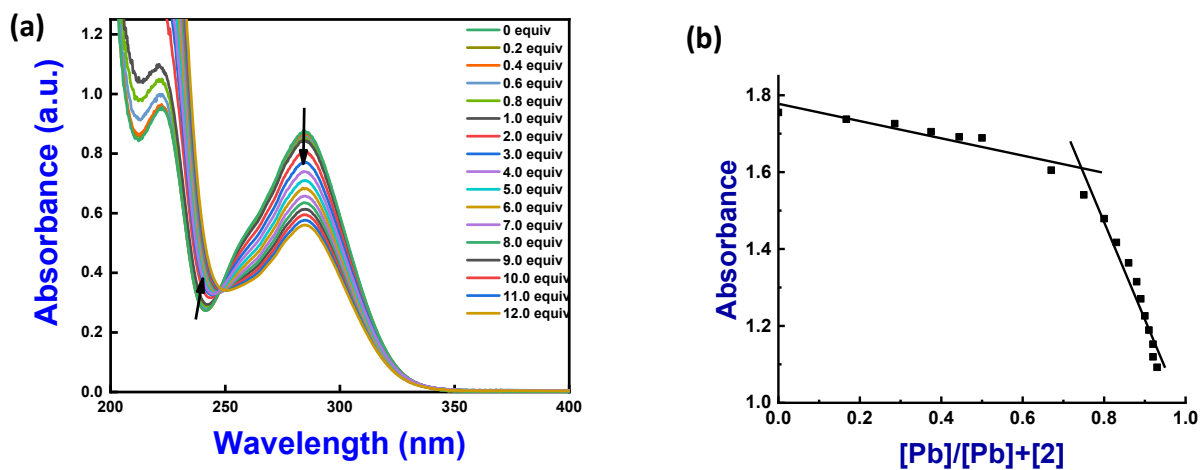


Fig. S33: (a) Absorption spectrum of **2** and the changes observed upon gradual addition of $\text{Pb}(\text{NO}_3)_2$ in acetonitrile. (b) Job's plot based on the changes in absorption at 284 nm.

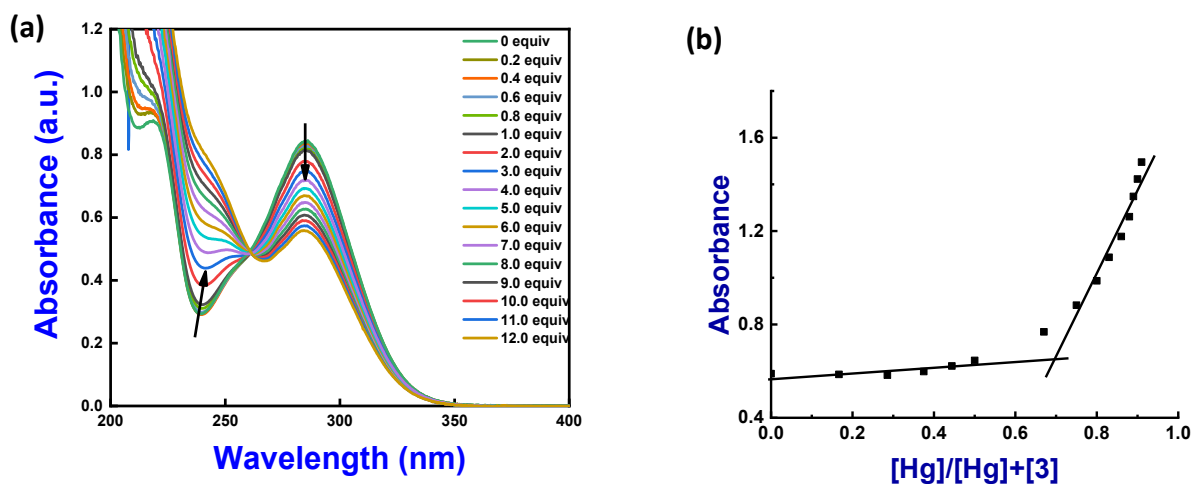


Fig. S34: (a) Absorption spectrum of **3** and the changes observed upon gradual addition of $\text{Hg}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ in acetonitrile. (b) Job's plot based on the changes in absorption at 240 nm.

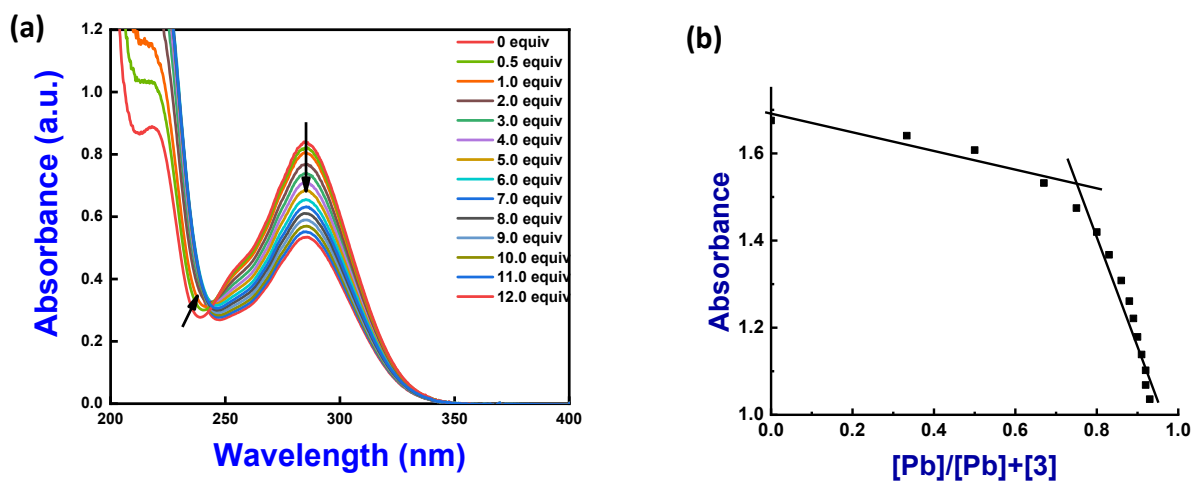


Fig. S35: (a) Absorption spectrum of **3** and the changes observed upon gradual addition of $\text{Pb}(\text{NO}_3)_2$ in acetonitrile. (b) Job's plot based on the changes in absorption at 285 nm.

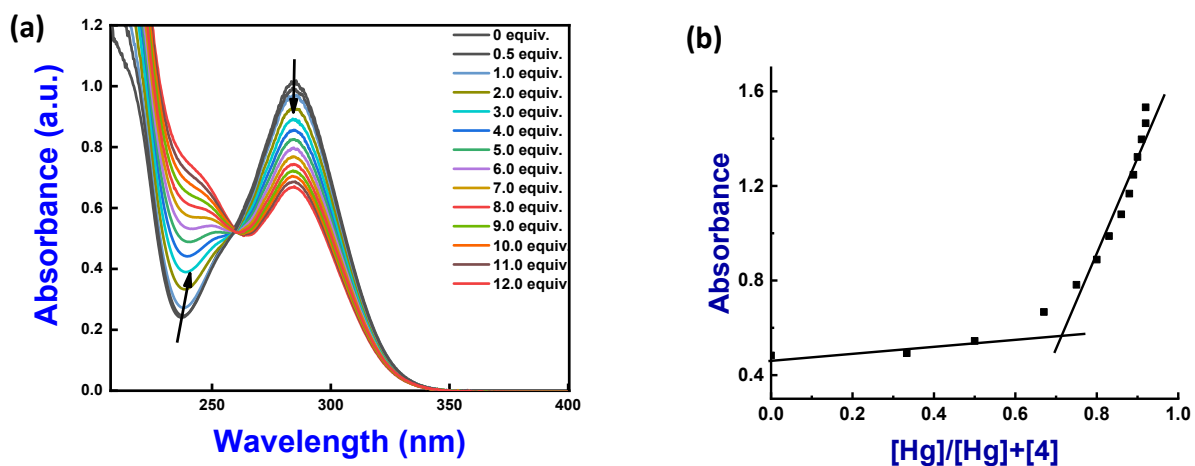


Fig. S36: (a) Absorption spectrum of **4** and the changes observed upon gradual addition of $\text{Hg}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ in acetonitrile. (b) Job's plot based on the changes in absorption at 238 nm.

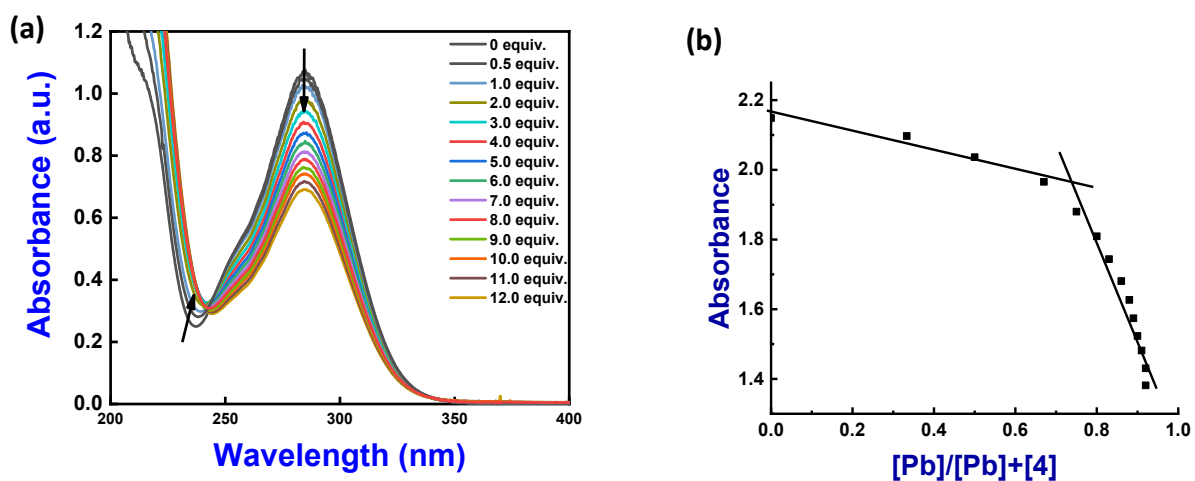


Fig. S37: (a) Absorption spectrum of **4** and the changes observed upon gradual addition of $\text{Pb}(\text{NO}_3)_2$ in acetonitrile. (b) Job's plot based on the changes in absorption at 285 nm.

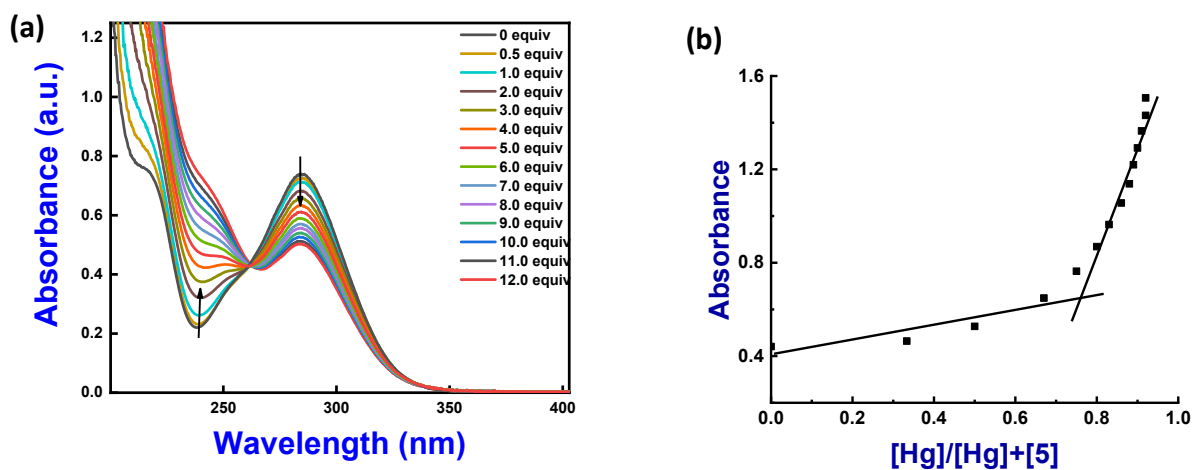


Fig. S38: (a) Absorption spectrum of **5** and the changes observed upon gradual addition of $\text{Hg}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ in acetonitrile. (b) Job's plot based on the changes in absorption at 240 nm.

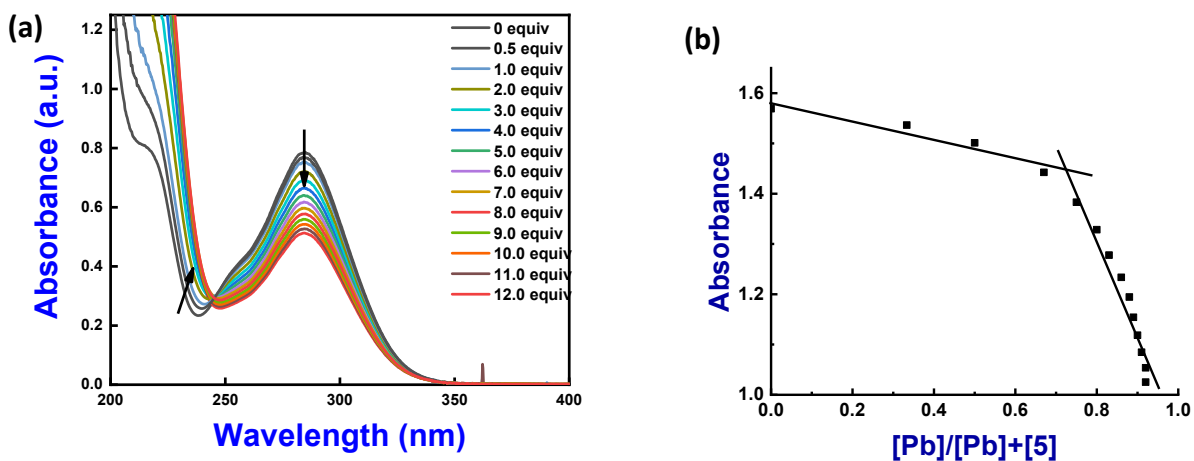


Fig. S39: (a) Absorption spectrum of **5** and the changes observed upon gradual addition of $\text{Pb}(\text{NO}_3)_2$ in acetonitrile. (b) Job's plot based on the changes in absorption at 285 nm.

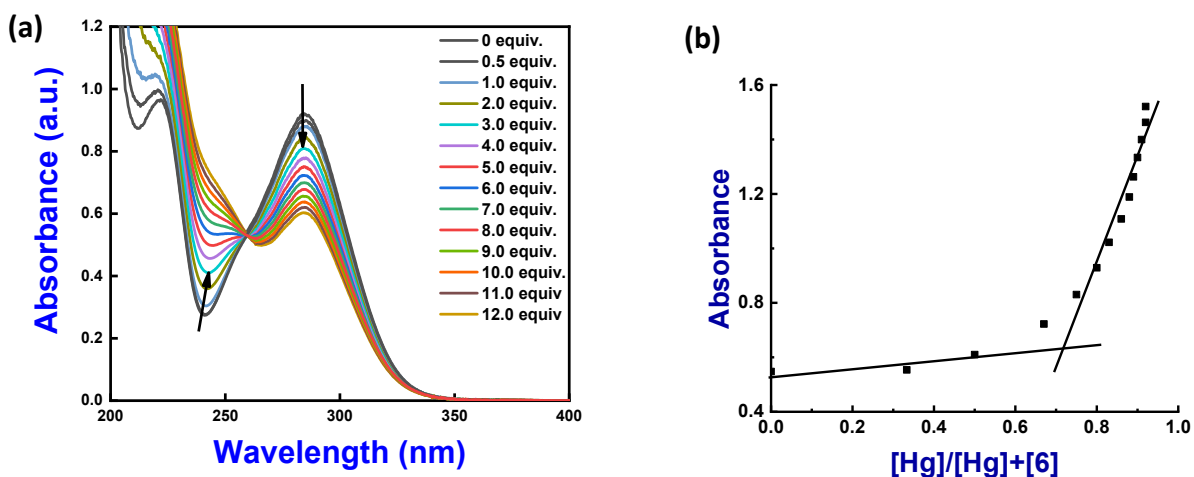


Fig. S40: (a) Absorption spectrum of **6** and the changes observed upon gradual addition of $\text{Hg}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ in acetonitrile. (b) Job's plot based on the changes in absorption at 241 nm.

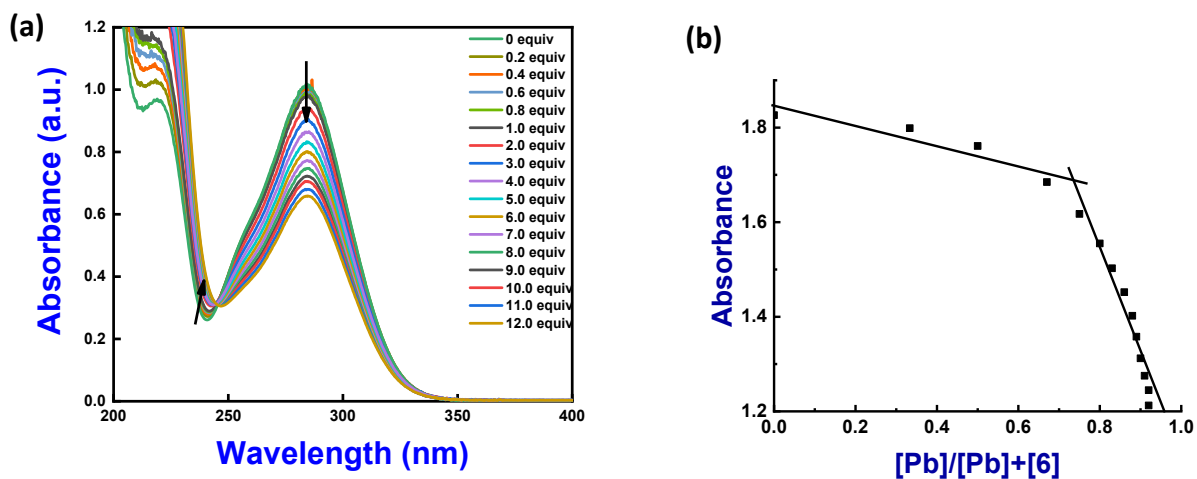


Fig. S41: (a) Absorption spectrum of **6** and the changes observed upon gradual addition of $\text{Pb}(\text{NO}_3)_2$ in acetonitrile. (b) Job's plot based on the changes in absorption at 285 nm.

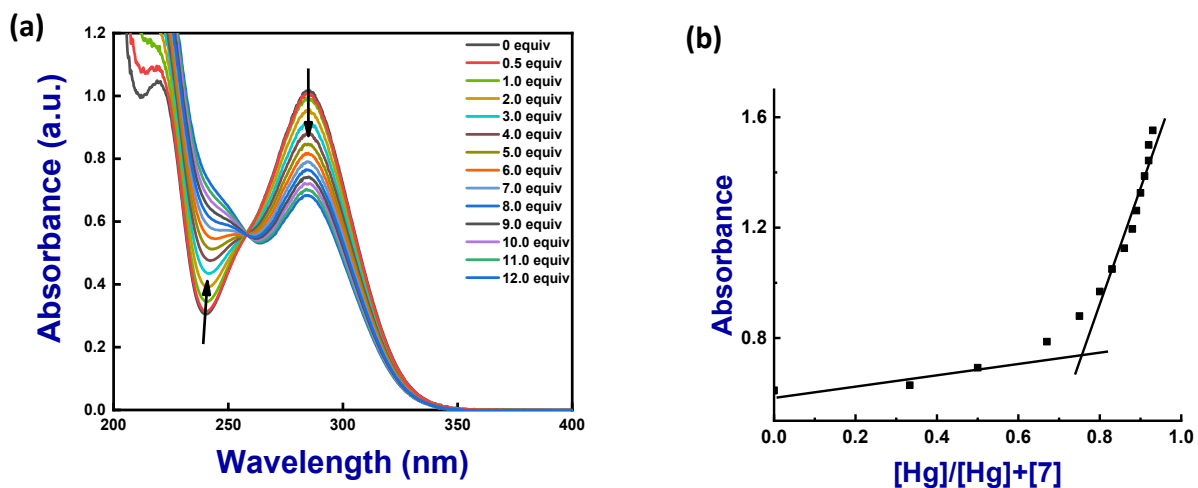


Fig. S42: (a) Absorption spectrum of **7** and the changes observed upon gradual addition of $\text{Hg}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ in acetonitrile. (b) Job's plot based on the changes in absorption at 238 nm.

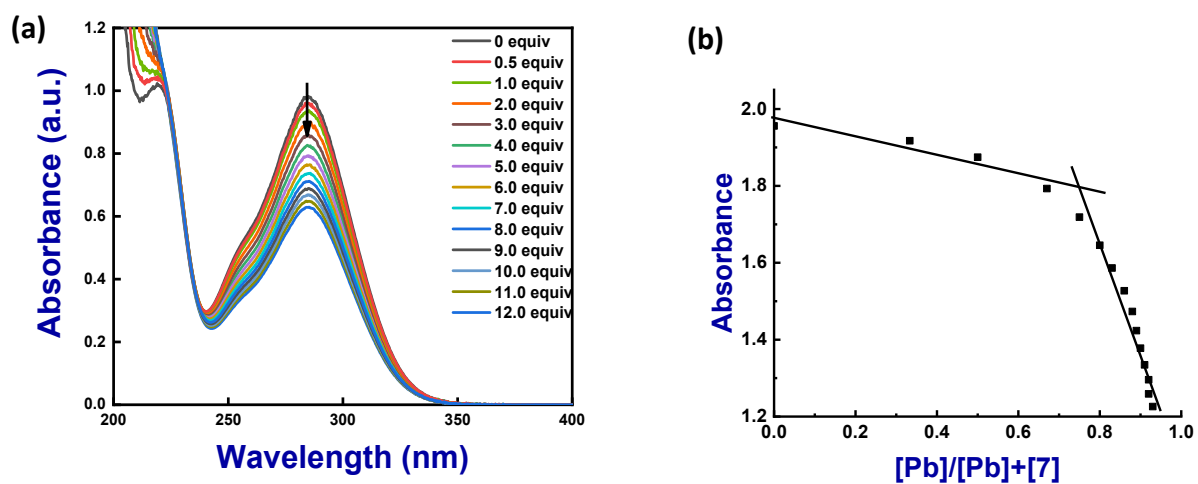


Fig. S43: (a) Absorption spectrum of **7** and the changes observed upon gradual addition of $\text{Pb}(\text{NO}_3)_2$ in acetonitrile. (b) Job's plot based on the changes in absorption at 284 nm.

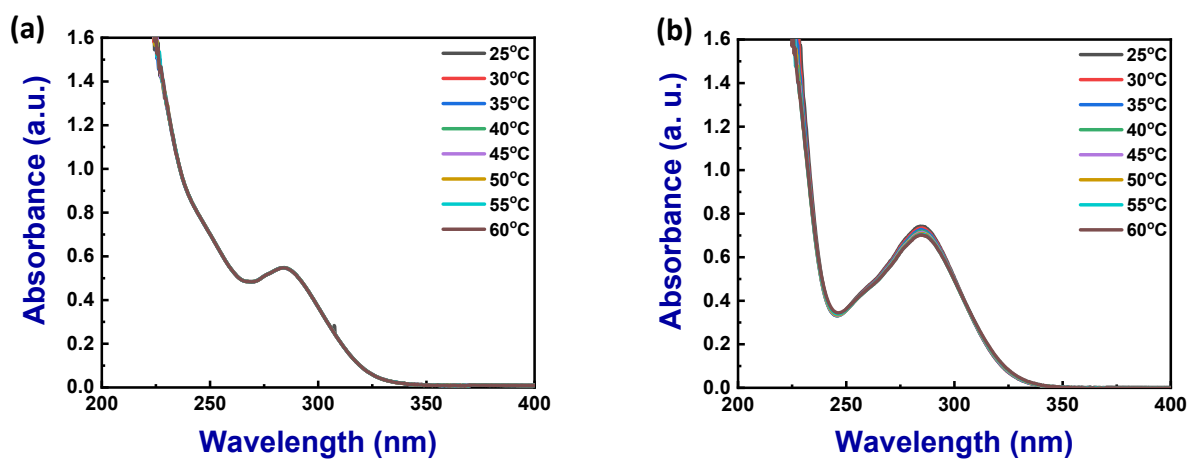


Fig. S44: Temperature dependent absorption spectrum of species **3** with (a) $\text{Hg}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$, (b) $\text{Pb}(\text{NO}_3)_2$ recorded in acetonitrile.

Table 2: Binding constants (K_a) for the species **1-7** with $\text{Hg}(\text{II})$ and $\text{Pb}(\text{II})$ determined by UV-Visible data.

Species	Metal ion	Binding constant (K_a/ M^{-1})
1	$\text{Hg}(\text{II})$	3.07×10^2
	$\text{Pb}(\text{II})$	3.12×10^2
2	$\text{Hg}(\text{II})$	6.42×10^2
	$\text{Pb}(\text{II})$	7.29×10^2
3	$\text{Hg}(\text{II})$	4.34×10^3
	$\text{Pb}(\text{II})$	2.26×10^3
4	$\text{Hg}(\text{II})$	2.39×10^3
	$\text{Pb}(\text{II})$	1.44×10^3
5	$\text{Hg}(\text{II})$	1.49×10^2
	$\text{Pb}(\text{II})$	8.13×10^2
6	$\text{Hg}(\text{II})$	1.44×10^3
	$\text{Pb}(\text{II})$	2.04×10^2
7	$\text{Hg}(\text{II})$	9.48×10^2
	$\text{Pb}(\text{II})$	2.21×10^2

7. Copies of HRMS and ⁷⁷Se NMR of species 3 with Hg(NO₃)₂ and Pb(NO₃)₂

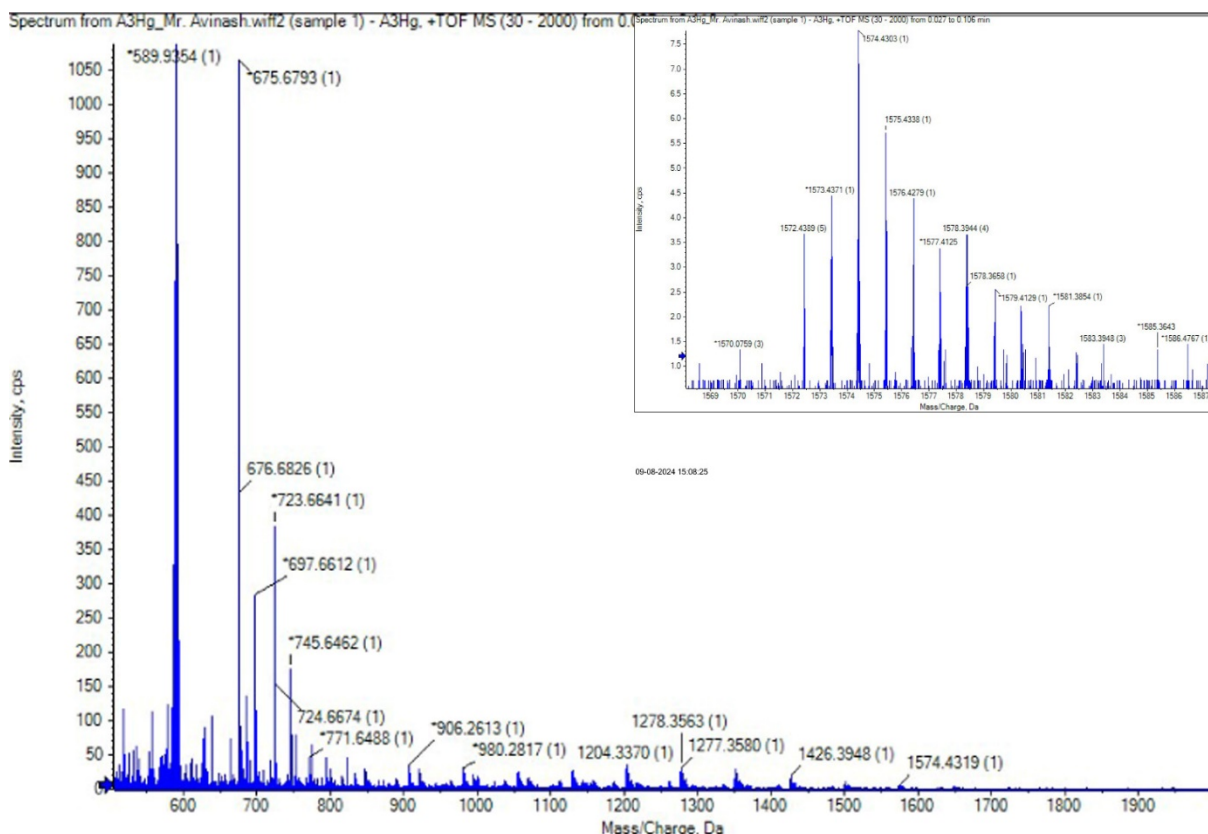


Fig. S45: HRMS of species 3 with Hg(NO₃)₂. Inset showing the expanded portion for the molecular ion peak.

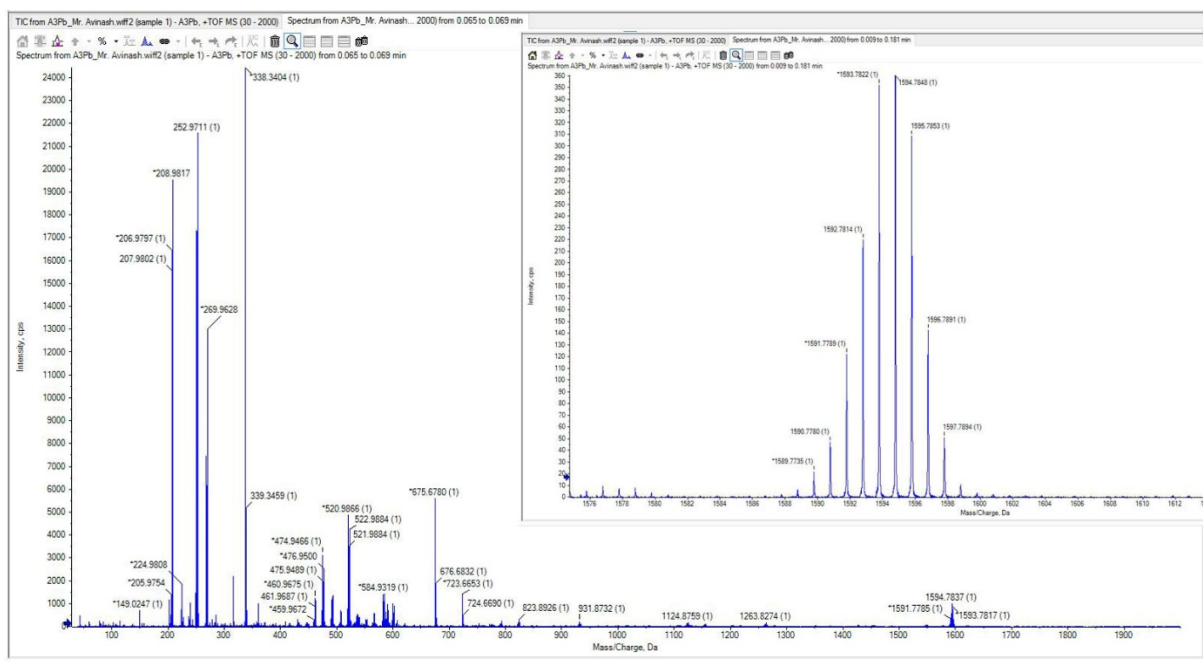


Fig. S46: HRMS of species 3 with Pb(NO₃)₂. Inset showing the expanded portion for the molecular ion peak.

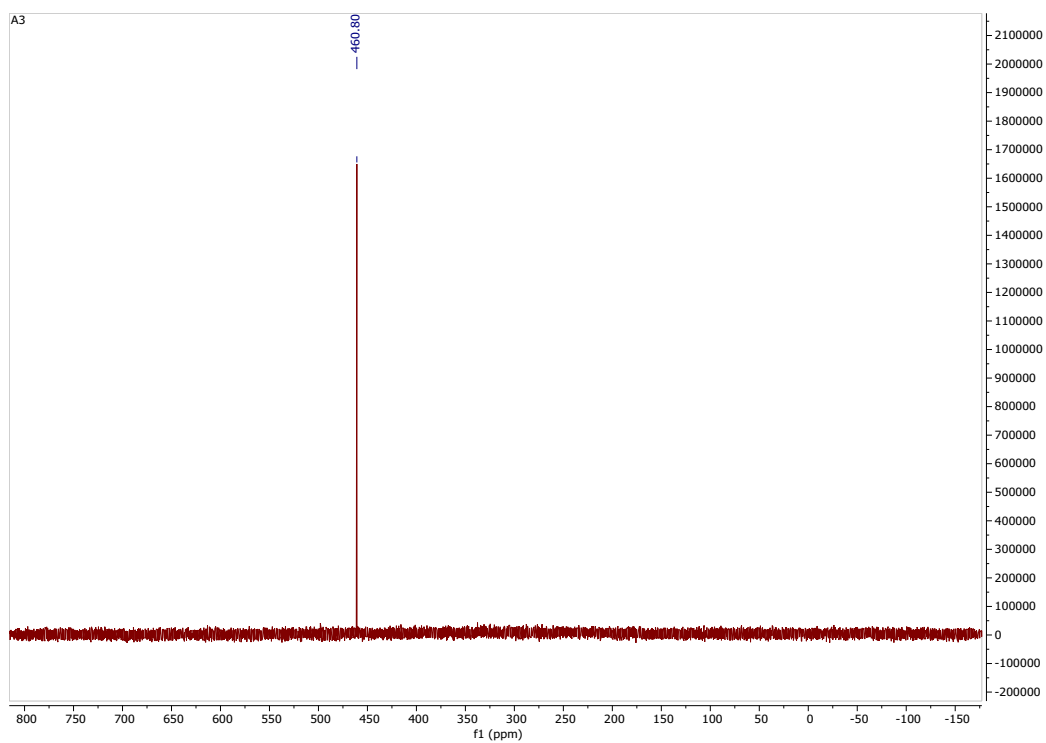


Fig. S47: ^{77}Se NMR of species **3** in CD_3CN .

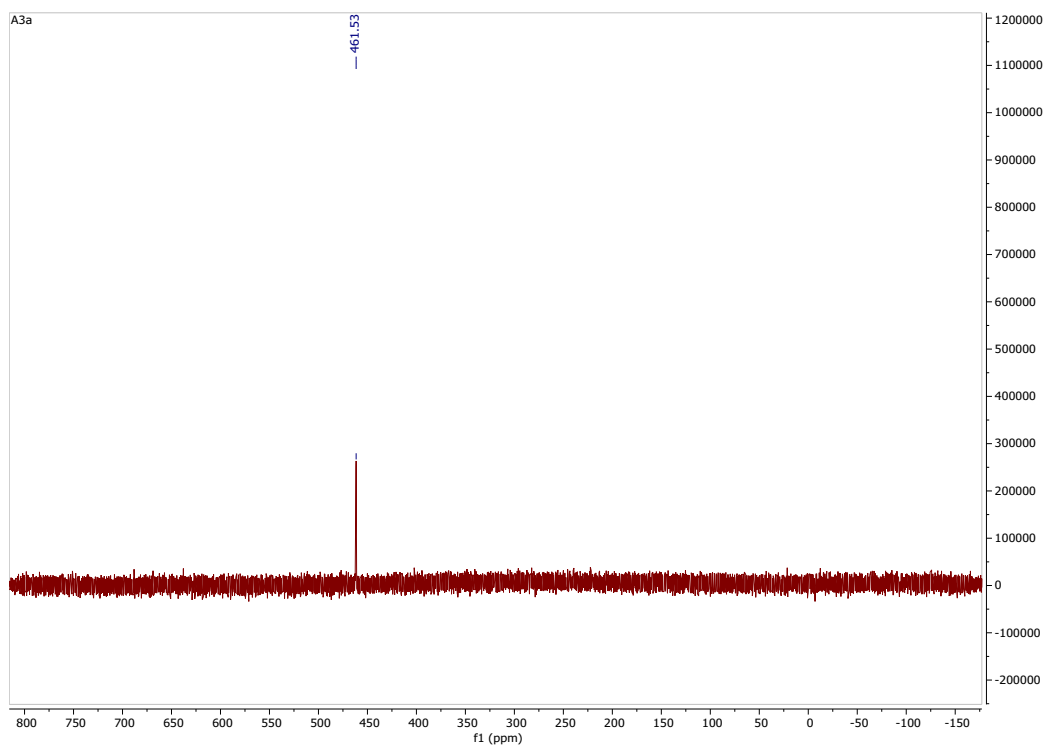


Fig. S48: ^{77}Se NMR of species **3** with 3 equivalents of $\text{Hg}(\text{NO}_3)_2$ in CD_3CN .

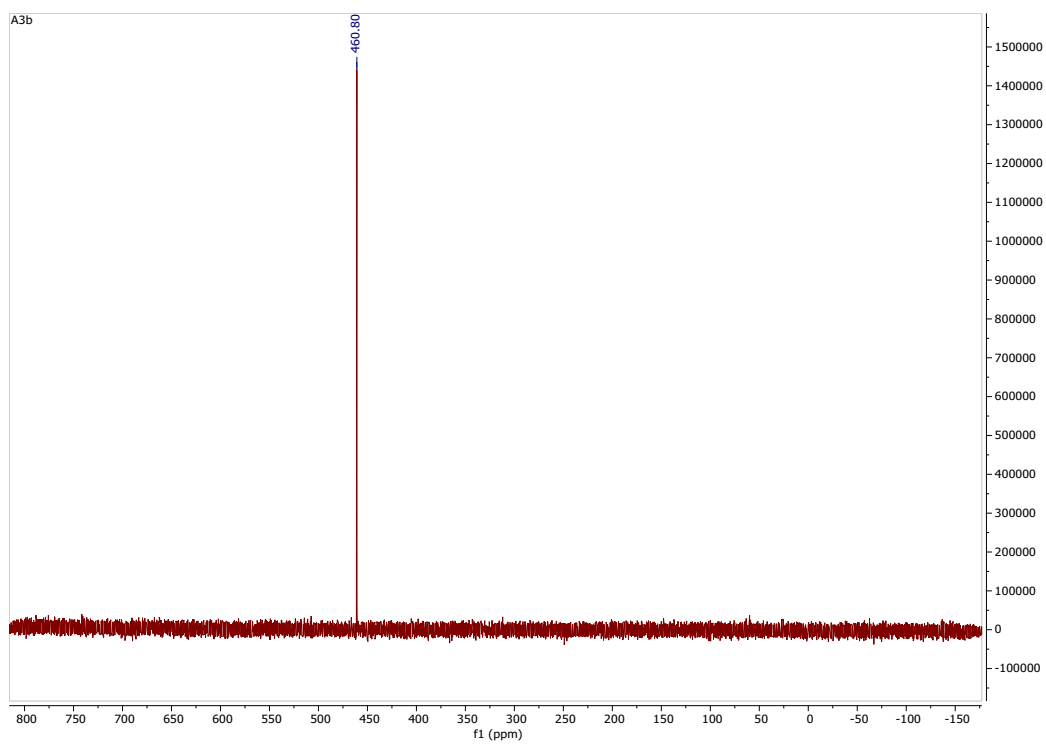


Fig. S49: ^{77}Se NMR of species **3** with 3 equivalents of $\text{Pb}(\text{NO}_3)_2$ in CD_3CN .

8. ICP-MS studies

For each experiment weighed amount of species were suspended in a 100 ml round bottom flask containing 50 ml aqueous solution of $\text{Hg}(\text{NO}_3)_2$ or $\text{Pb}(\text{NO}_3)_2$ with a strength 200 ppm at neutral pH unless mentioned otherwise. The reaction mixture was allowed to stir at room temperature for 12 hours to ensure maximum uptake of the metal ions by the species. Thereafter the mixture was filtered through a $0.2\mu\text{m}$ syringe filter. The resultant solution was diluted 100 times and the filtrate thus collected was analyzed by using ICP-MS to determine the mercury and lead content.

The absorption capacity and removal efficiency were calculated using the following formulae.³

Absorption capacity

$$q_e = \frac{(C_o - C_e)V}{m}$$

Removal efficiency

$$q_e = \frac{(C_o - C_e)100}{C_o}$$

where C_o = Initial concentration of $\text{Hg}(\text{II})/\text{Pb}(\text{II})$

C_e = Final concentration of $\text{Hg}(\text{II})/\text{Pb}(\text{II})$

V = Volume

m = Mass of adsorbent.

10. References

1. W. L. F. Armarego,; D. D. Perrin, *Purification of Laboratory Chemicals*; Butterworth-Heinemann: Oxford, **2002**.
2. C. Paulmier. *Selenium Reagents & Intermediates in Organic Synthesis*; Elsevier, **2013**.
3. N. Huang, L. Zhai, H. Xu and D. Jiang, *J. Am. Chem. Soc.*, 2017, **139**, 2428–2434.