

## Exploring the reactivity of L-tellurocystine, Te-protected tellurocysteine conjugates and diorganodiselenides towards hydrogen peroxide: Synthesis and molecular structure analysis

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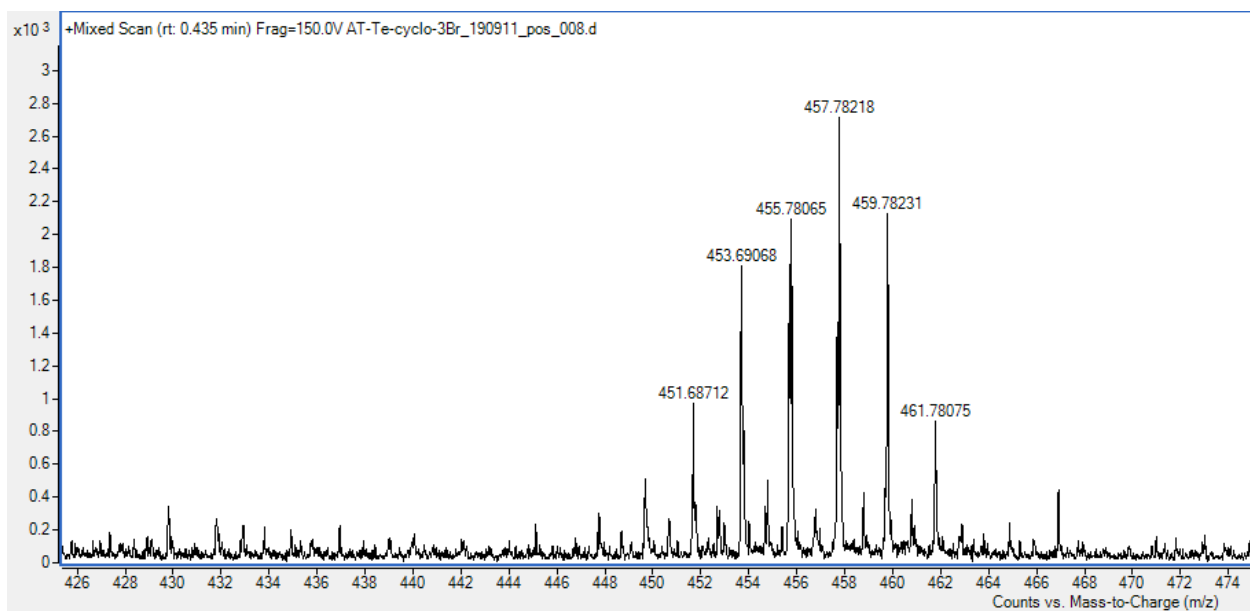
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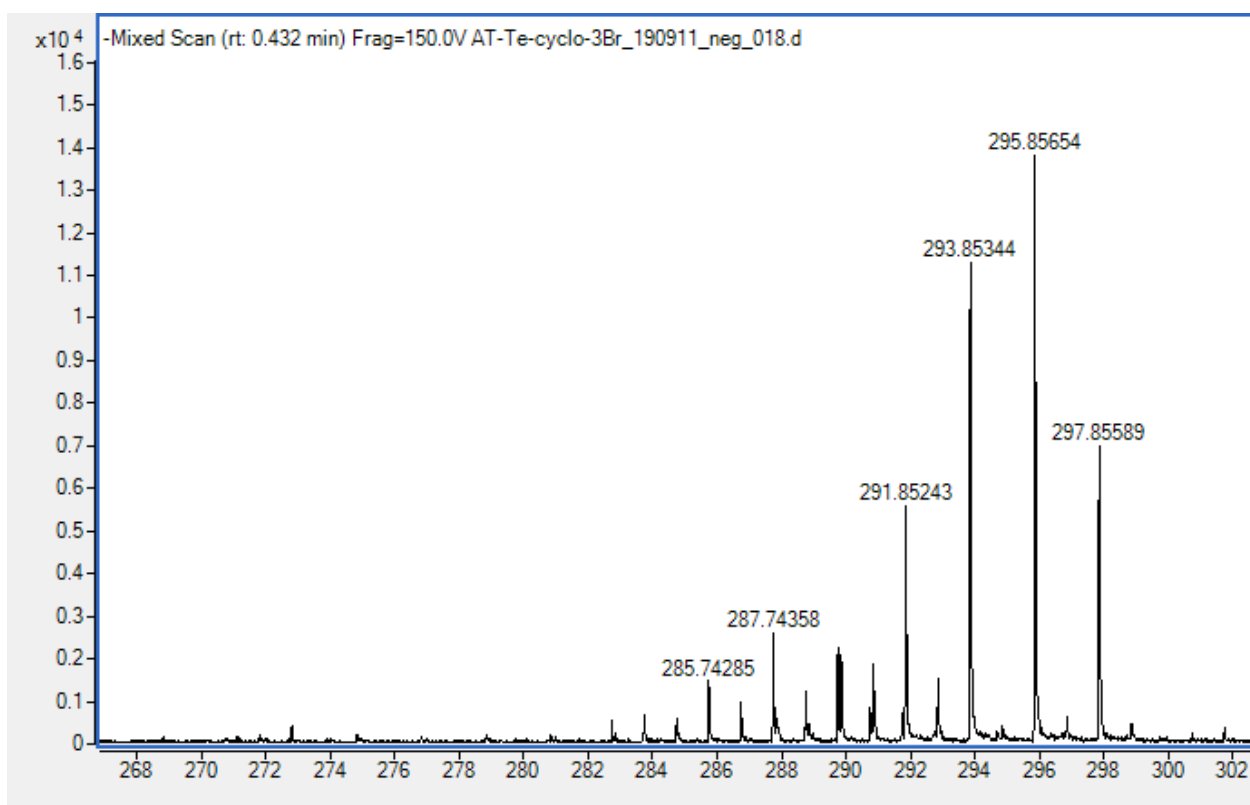
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<b>Contents</b>	<b>Page No.</b>
Spectral data	<b>S2-S21</b>
Mechanism for the synthesis of <b>9</b>	<b>S22</b>
Crystallographic data and structure refinement details of <b>5</b> , <b>8, 9, 14, 15, 16, and 17</b>	<b>S23</b>
Molecular structures of <b>15-17</b>	<b>S24</b>
The important geometric parameters of <b>5, 8, and 9</b>	<b>S24-S26</b>
Comparison of the geometrical parameters of <b>14-17</b>	<b>S26</b>
Packing diagrams of compounds <b>5, 8, 9, 14, 15, 16, and 17</b>	<b>S27-S31</b>



**Figure S1.** HR-MS spectrum of compound **5**



**Figure S2.** HR-MS spectrum of compound **5**

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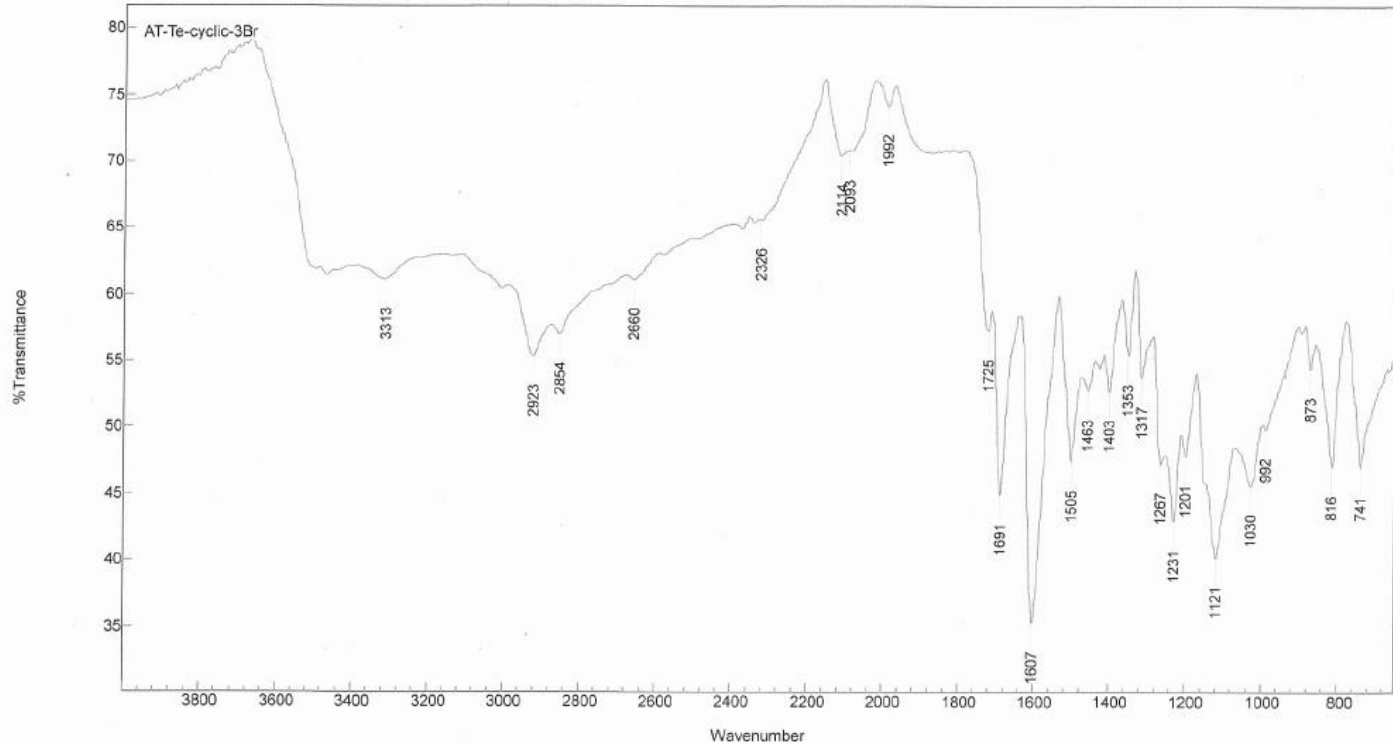


Figure S3. FT-IR spectrum of compound 5

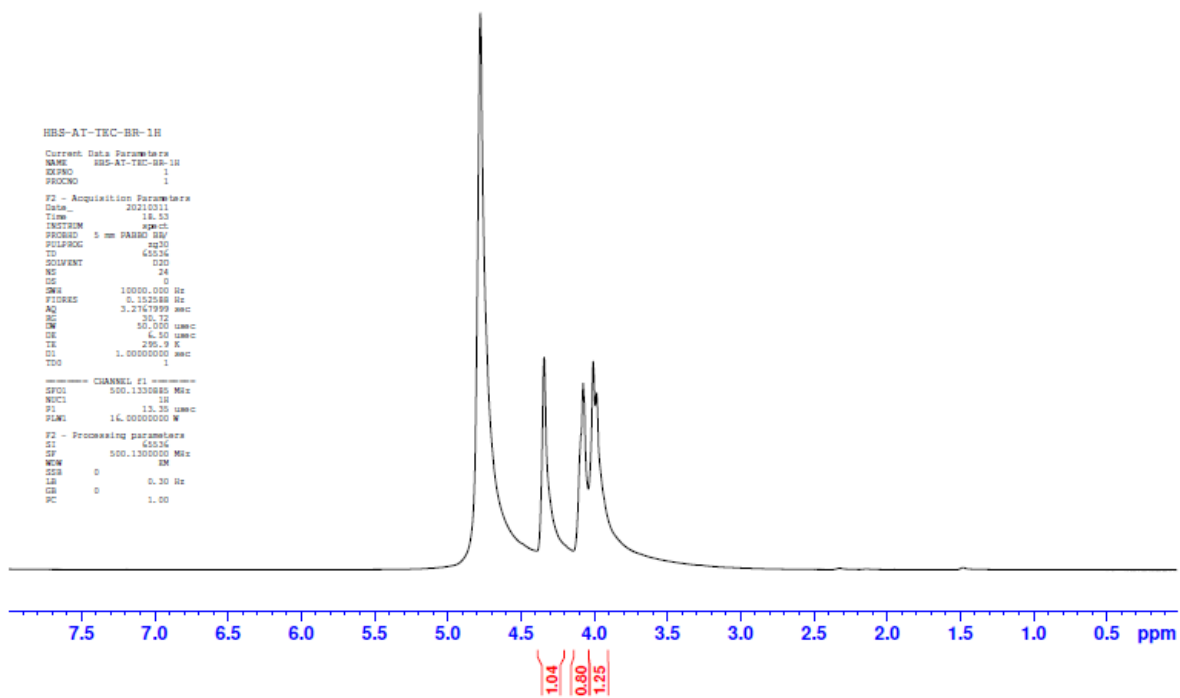


Figure S4. <sup>1</sup>H NMR spectrum of compound 5

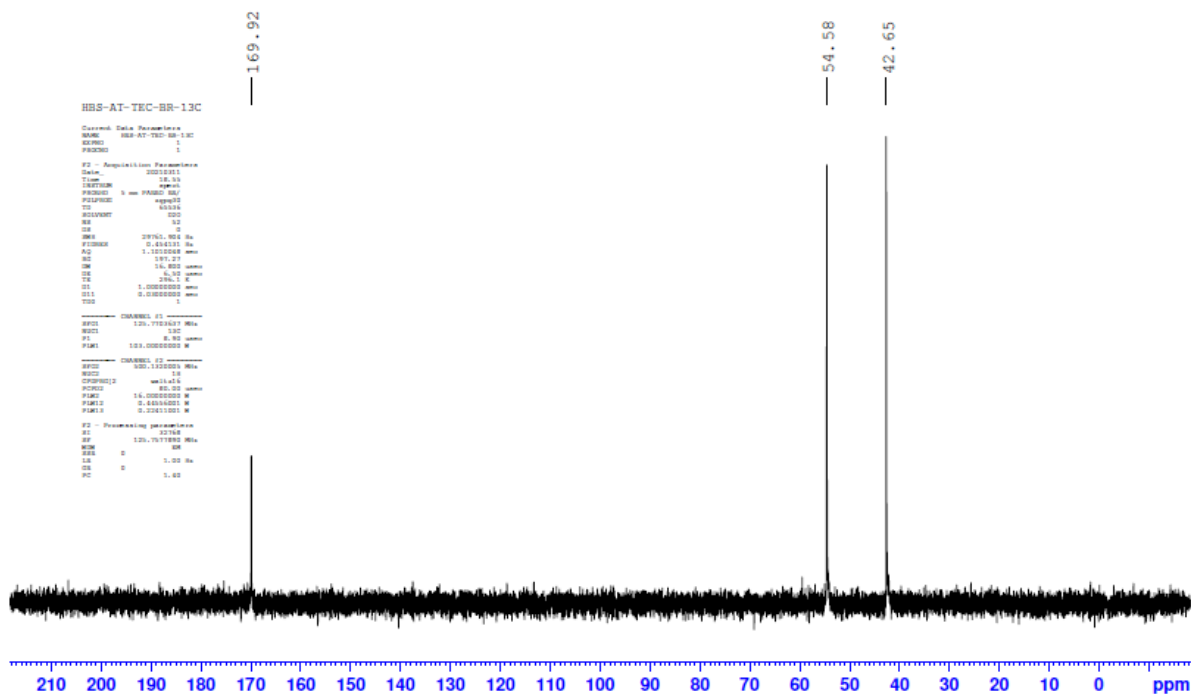


Figure S5.  $^{13}\text{C}$  NMR spectrum of compound 5

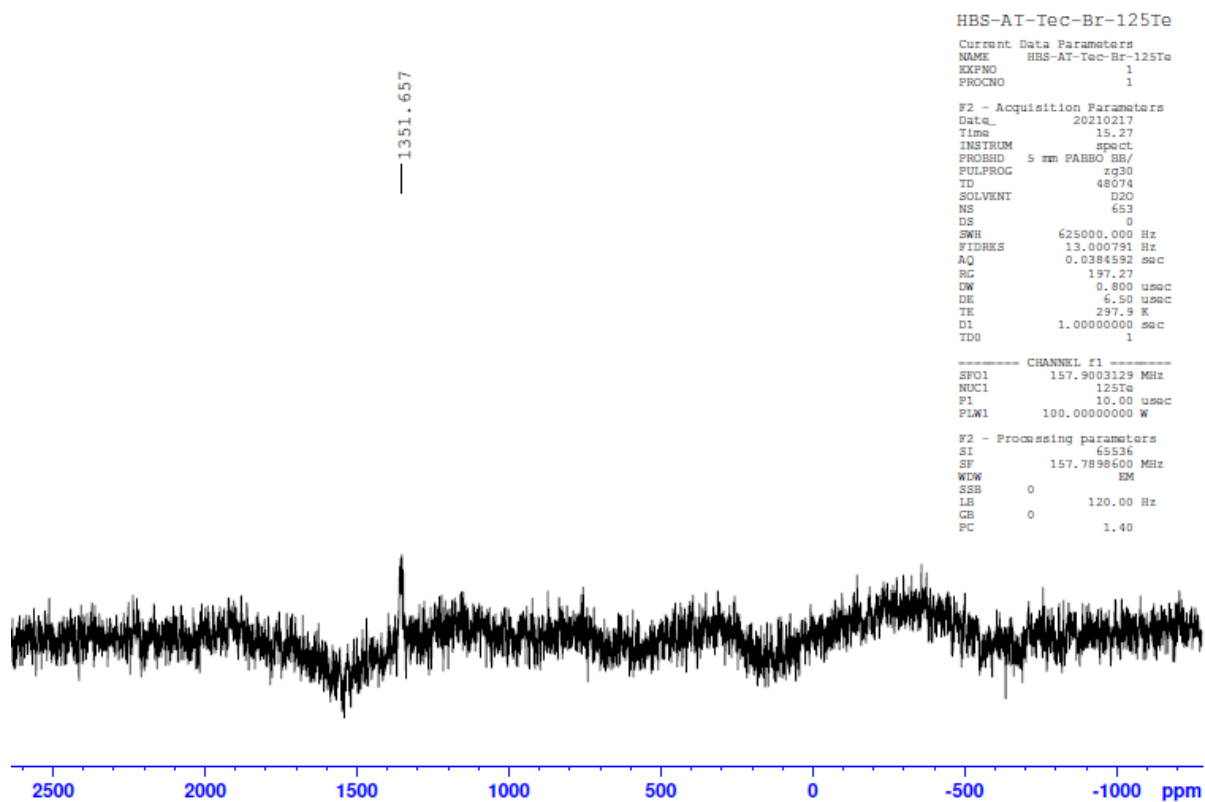
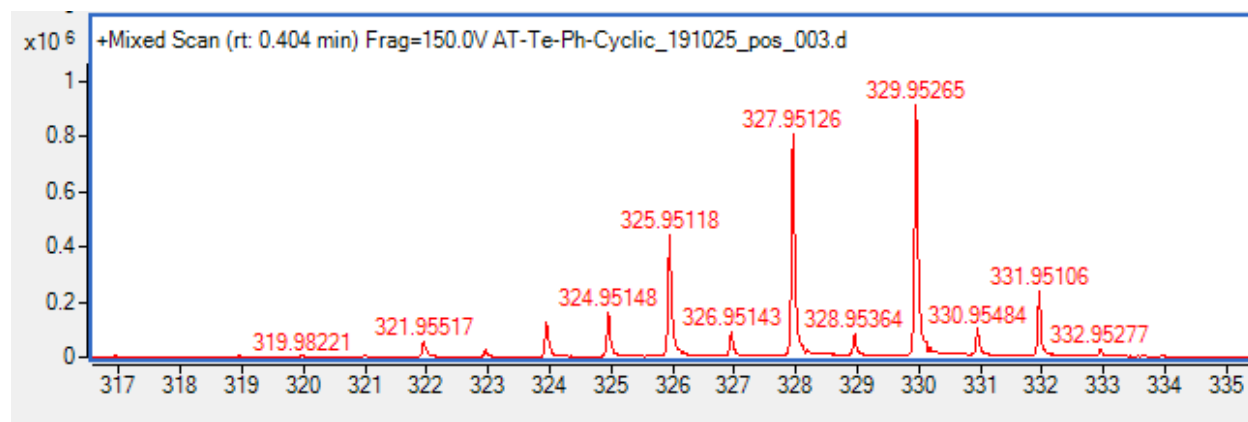
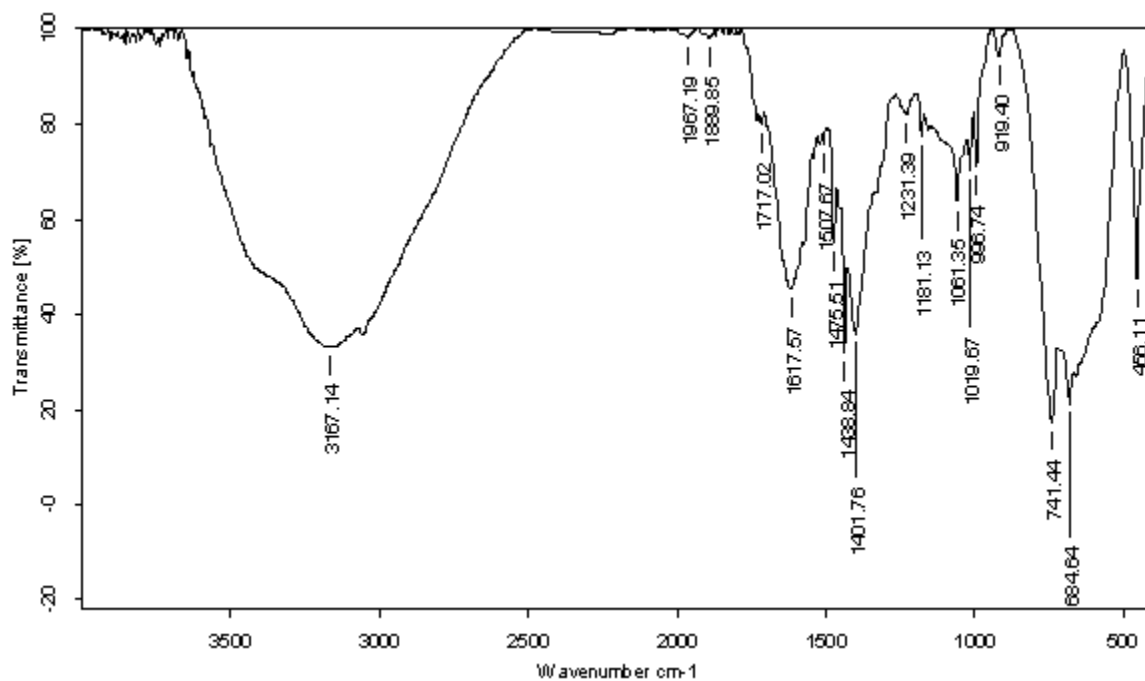


Figure S6.  $^{125}\text{Te}$  NMR spectrum of compound 5



**Figure S7.** HR-MS spectrum of compound **8**



**Figure S8.** FT-IR spectrum of compound **8**

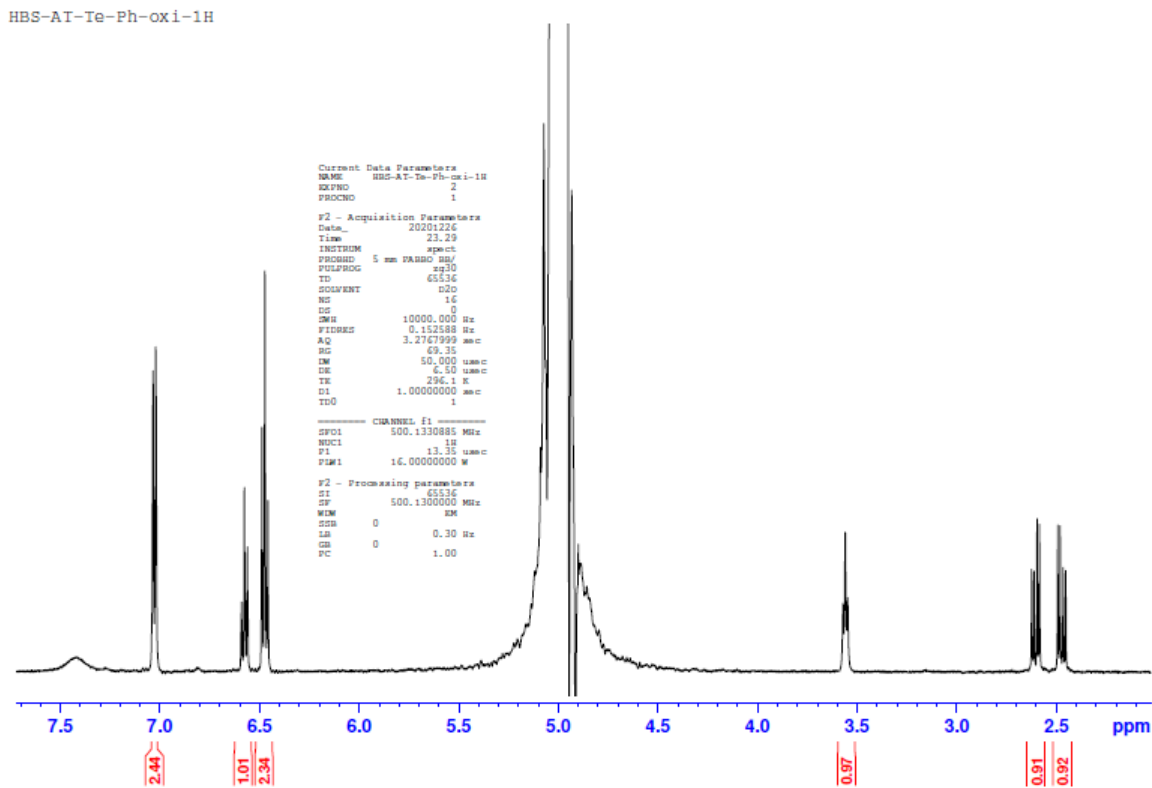


Figure S9. <sup>1</sup>H NMR spectrum of compound **8**

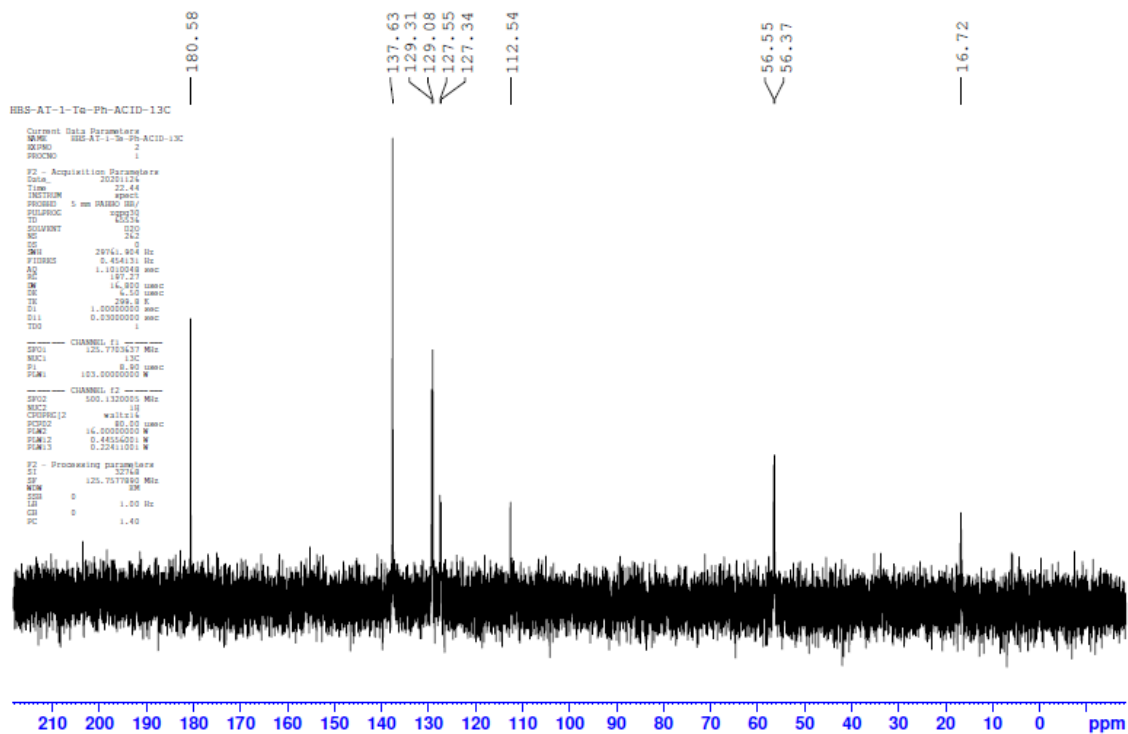
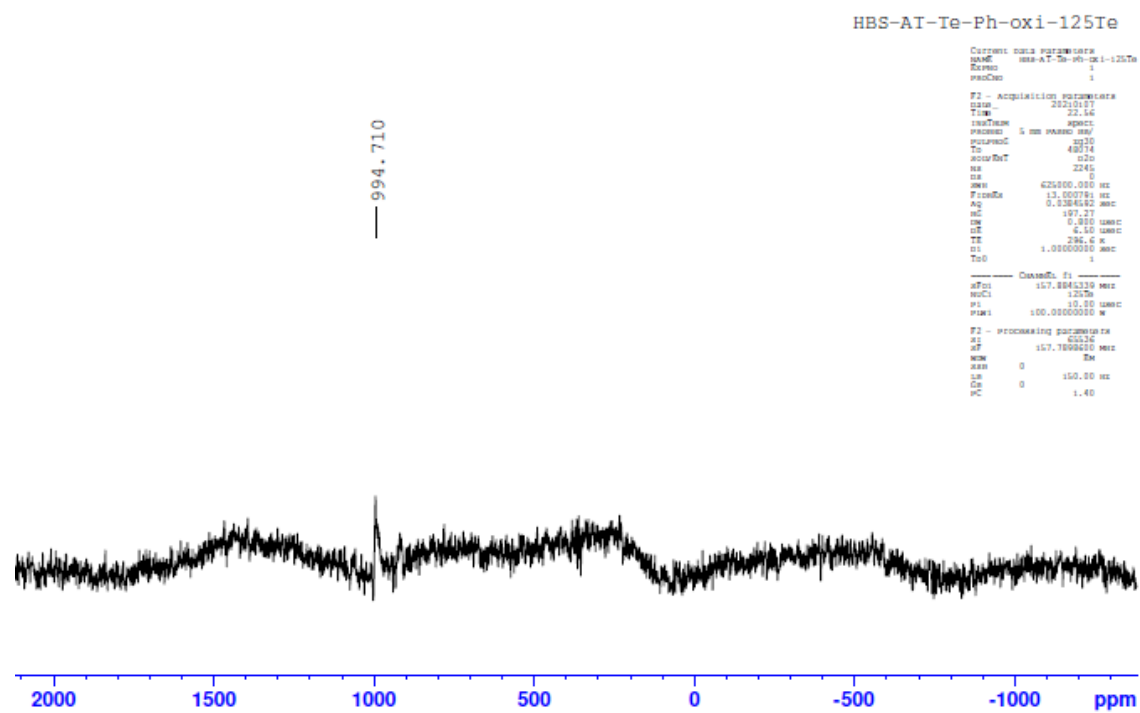
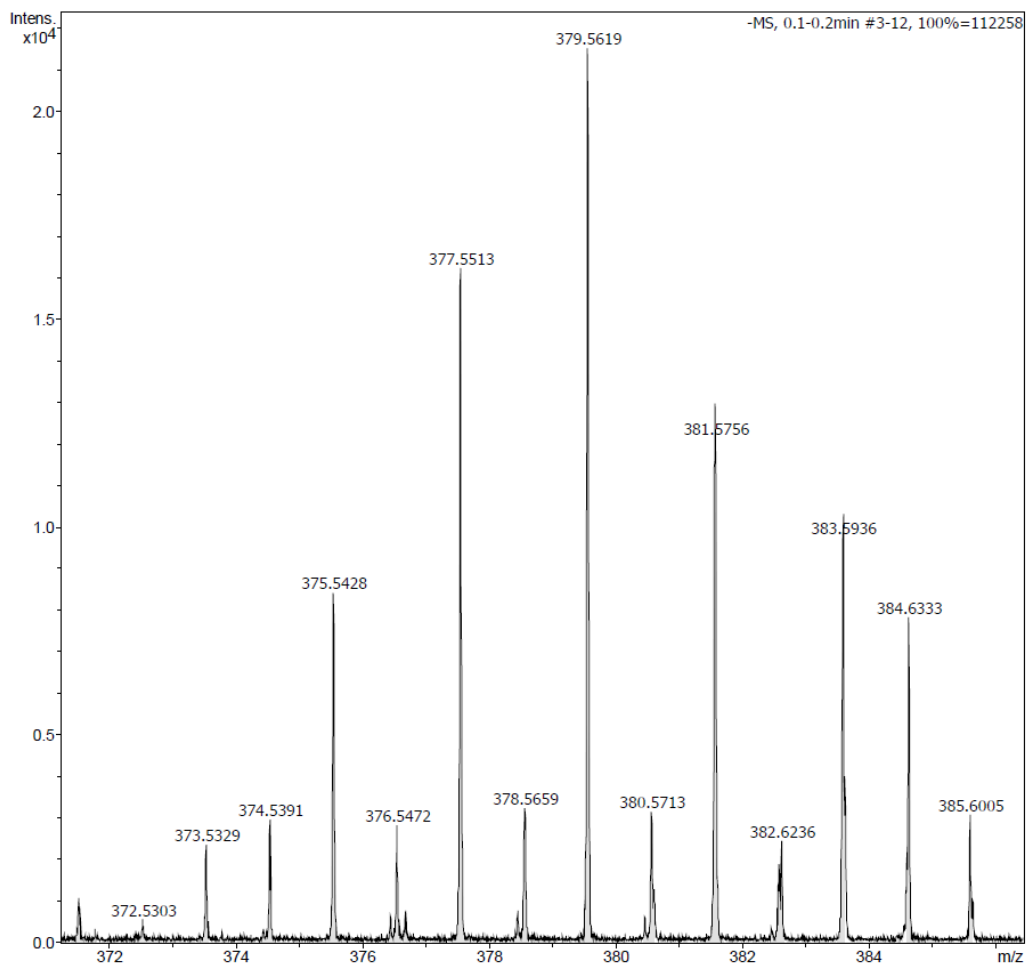


Figure S10. <sup>13</sup>C NMR spectrum of compound **8**



**Figure S11.**  $^{125}\text{Te}$  NMR spectrum of compound **8**



**Figure S12.** HR-MS spectrum of compound **9**



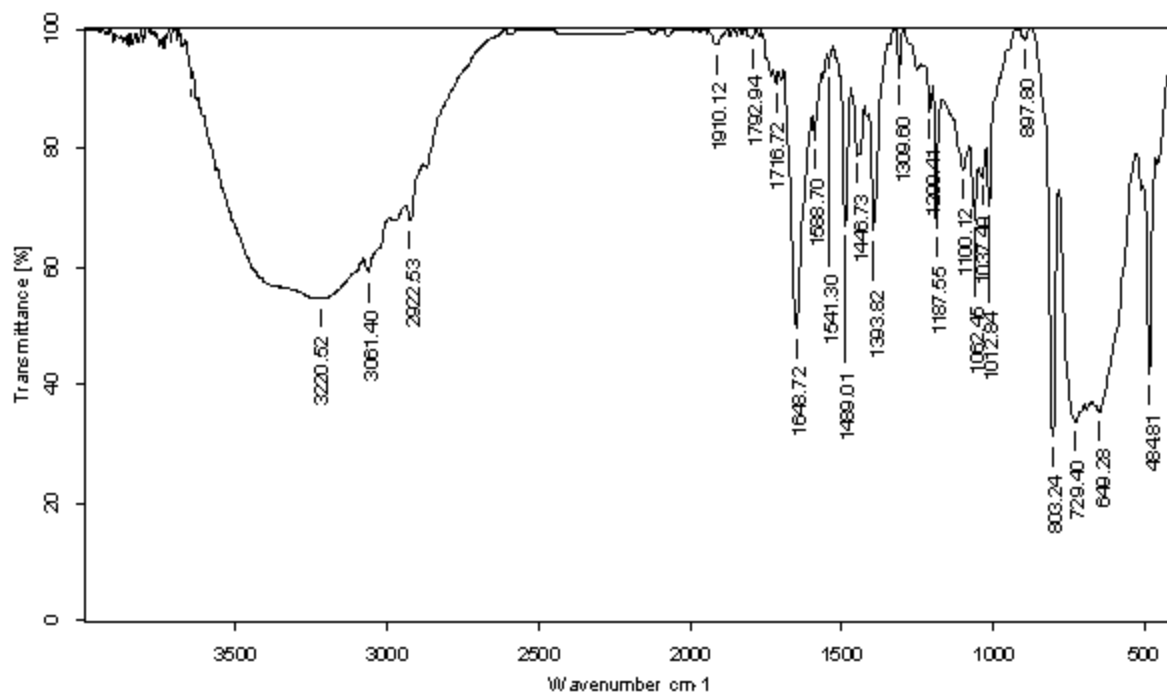


Figure S13. FT-IR spectrum of compound 9

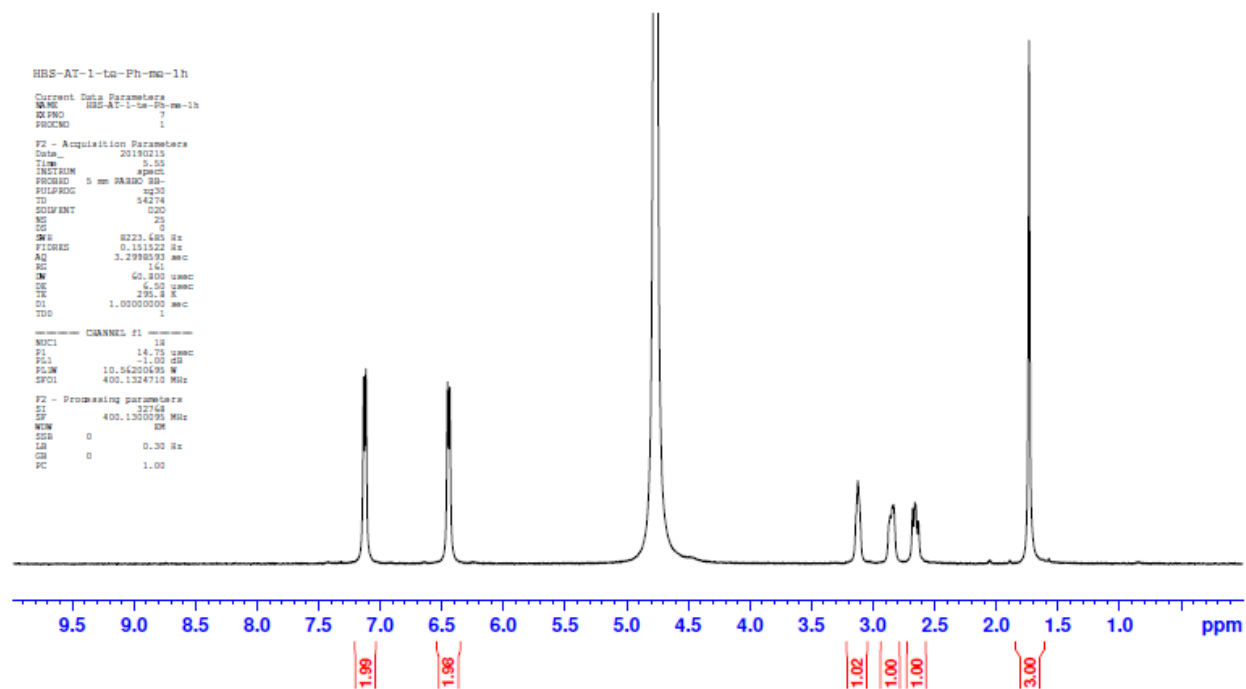


Figure S14. <sup>1</sup>H NMR spectrum of compound 9

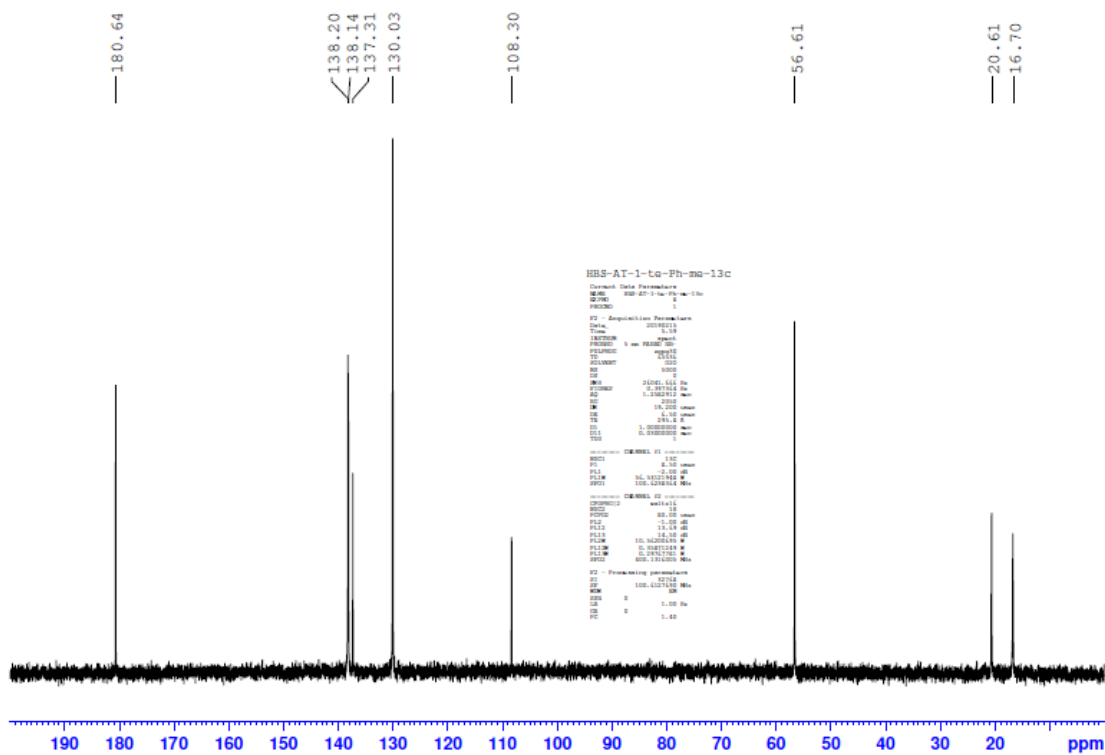


Figure S15.  $^{13}\text{C}$  NMR spectrum of compound **9**

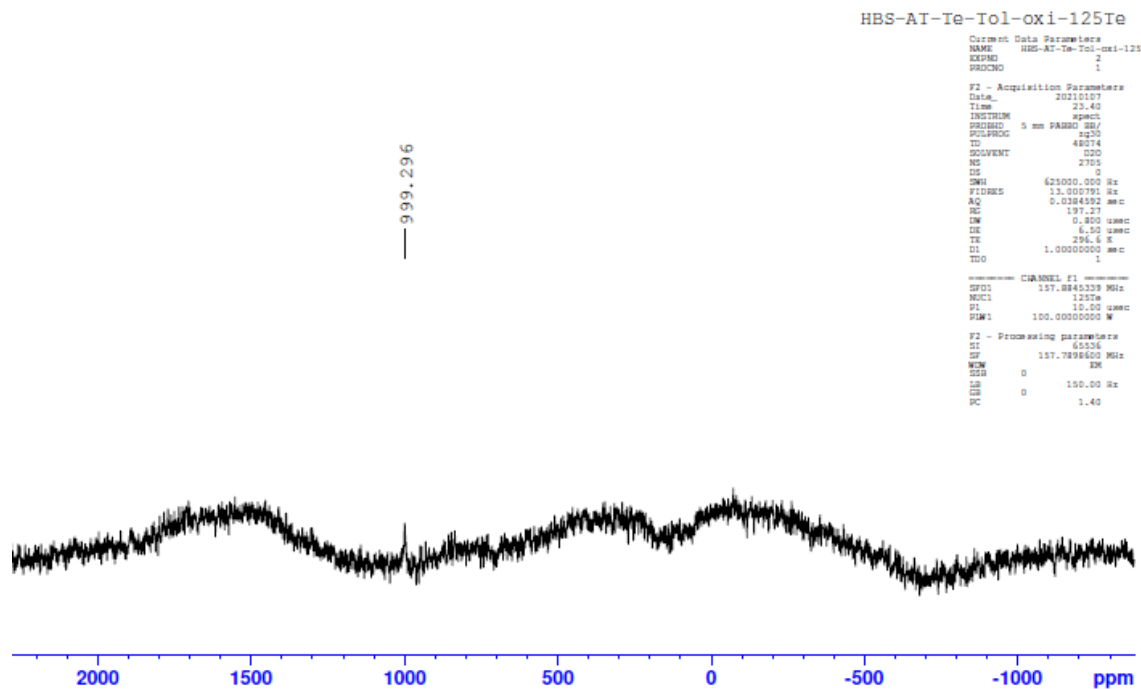
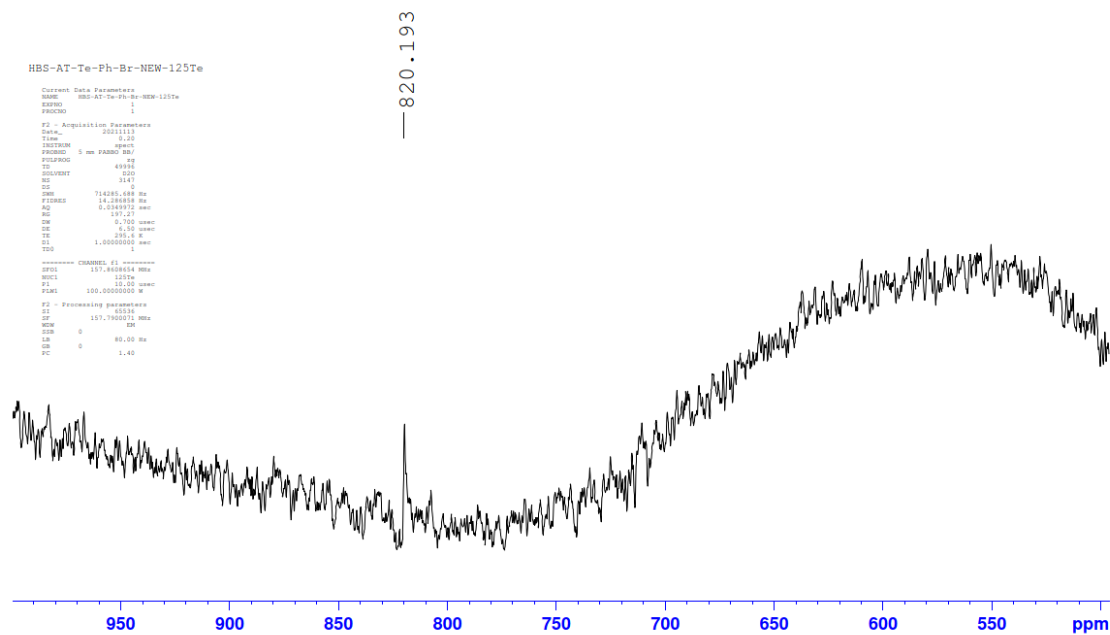
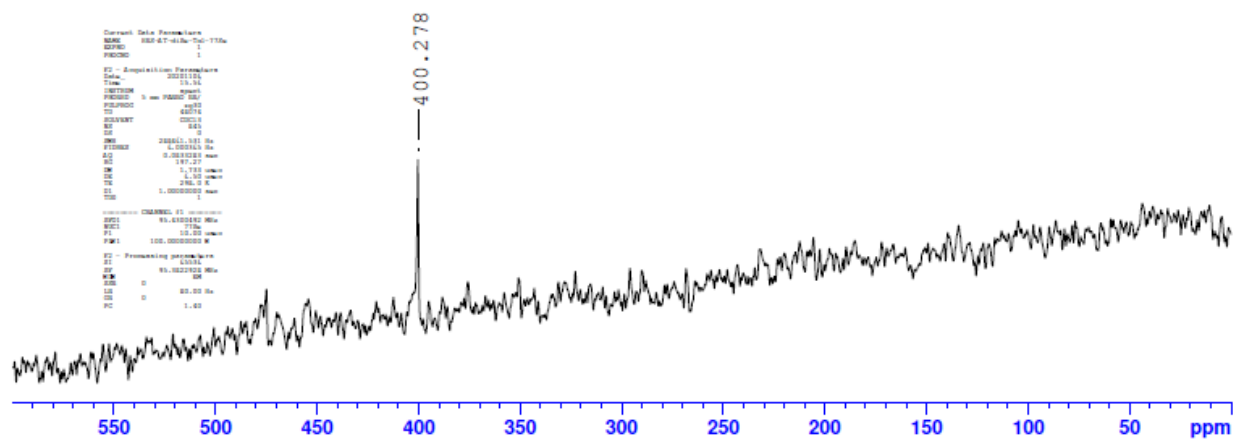


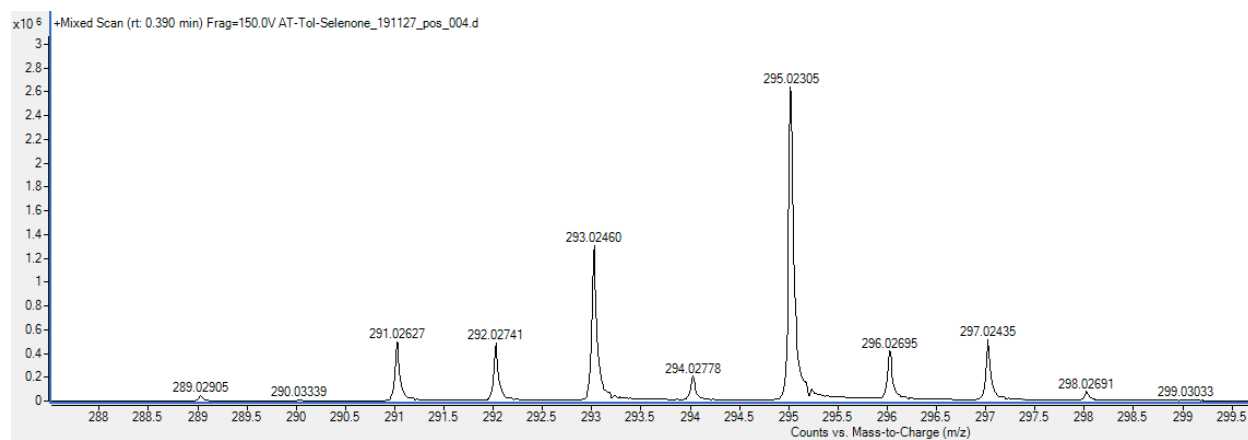
Figure S16.  $^{125}\text{Te}$  NMR spectrum of compound **9**



**Figure S17.**  $^{125}\text{Te}$  NMR spectrum of the reaction aliquot of **6** with  $\text{H}_2\text{O}_2/\text{HBr}$ .

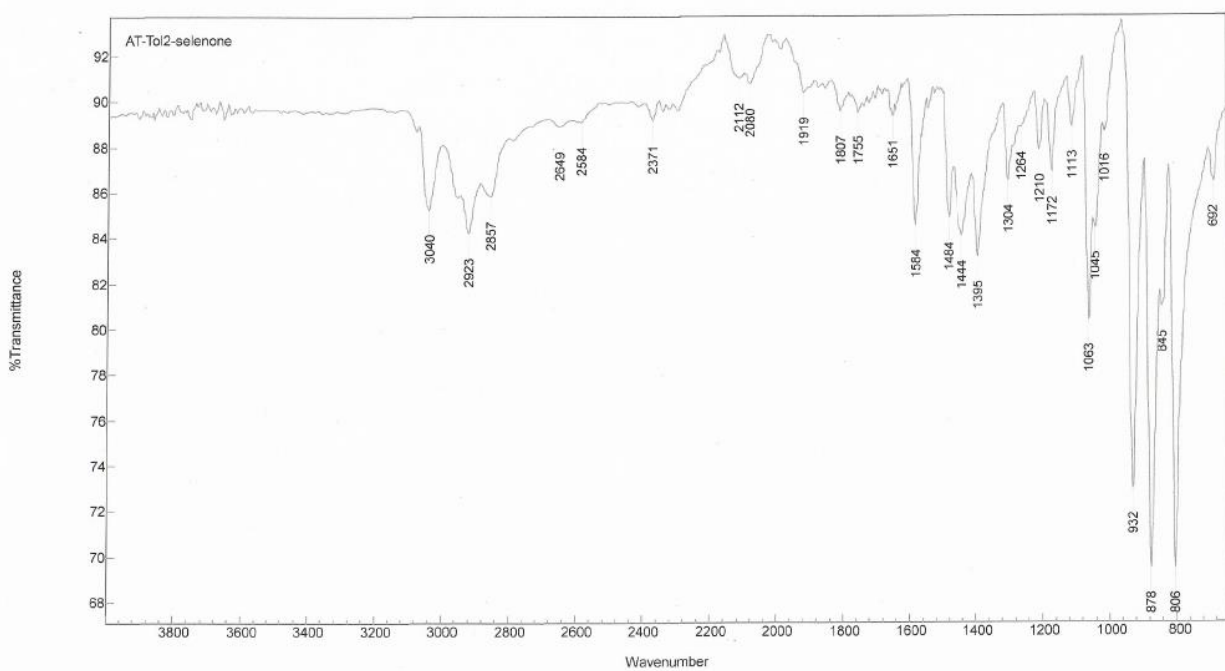


**Figure S18.**  $^{77}\text{Se}$  NMR spectrum of compound **12**



**Figure S19.** HR-MS spectrum of compound **14**

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**Figure S20.** FT-IR spectrum of compound **14**

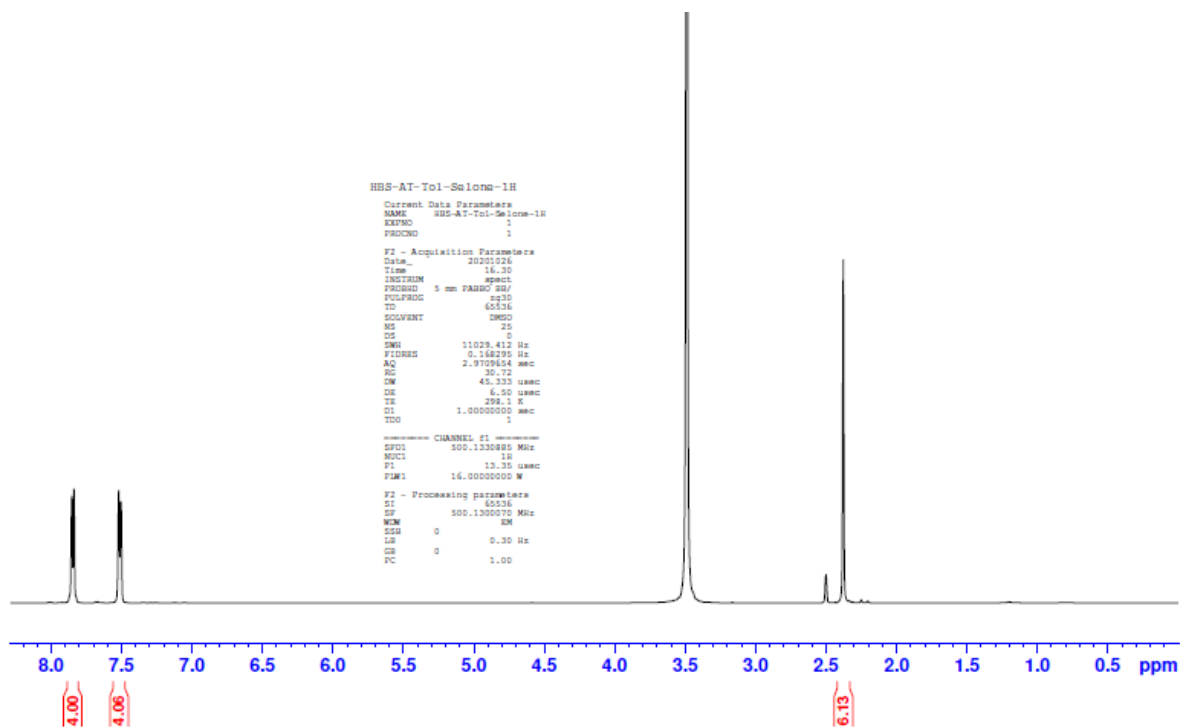


Figure S21. <sup>1</sup>H NMR spectrum of compound 14

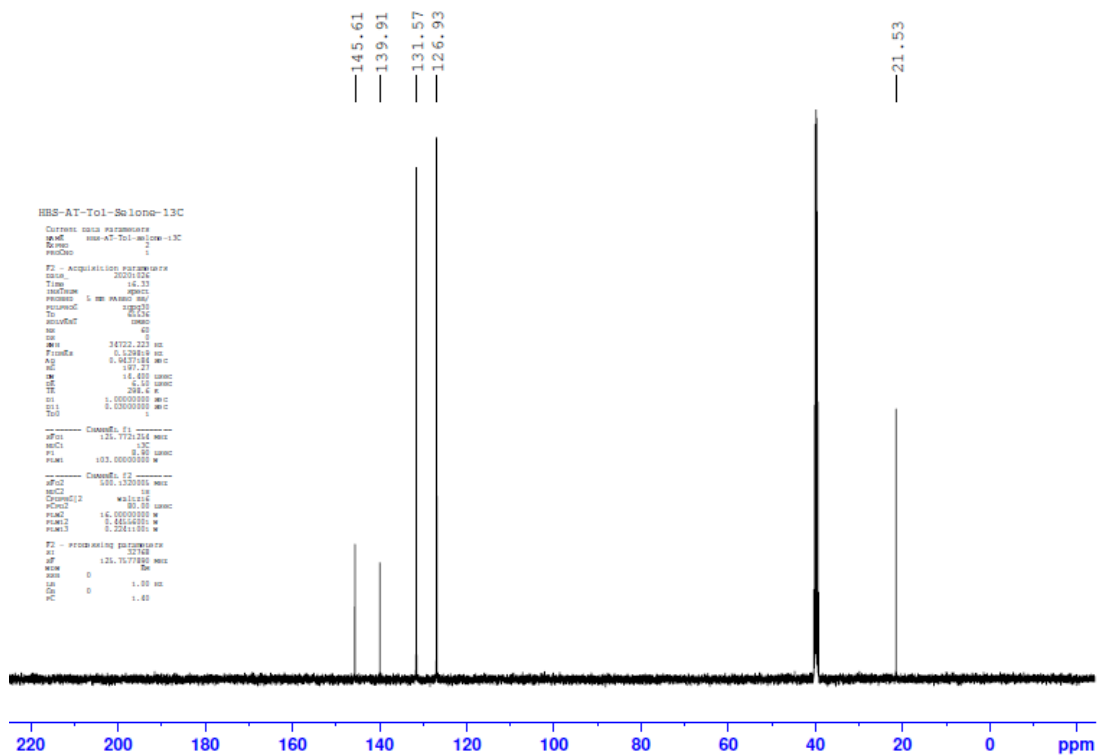


Figure S22. <sup>13</sup>C NMR spectrum of compound 14

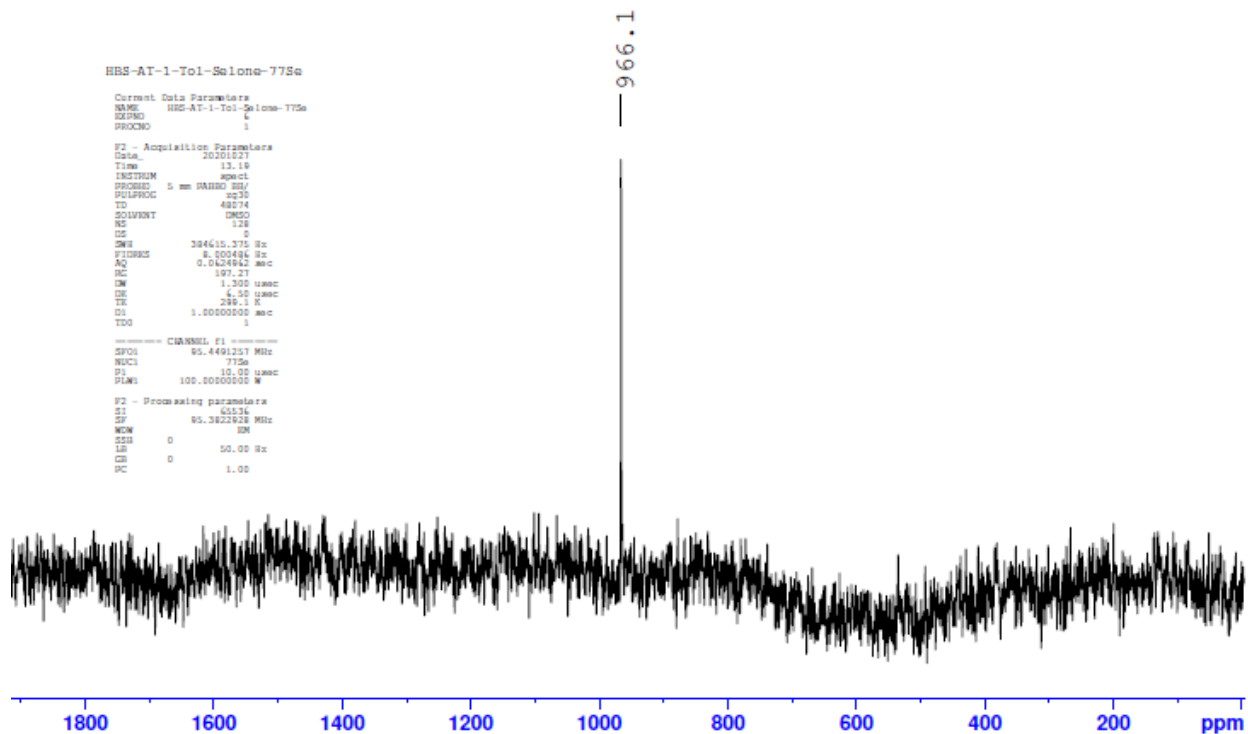


Figure S23.  $^{77}\text{Se}$  NMR spectrum of compound 14

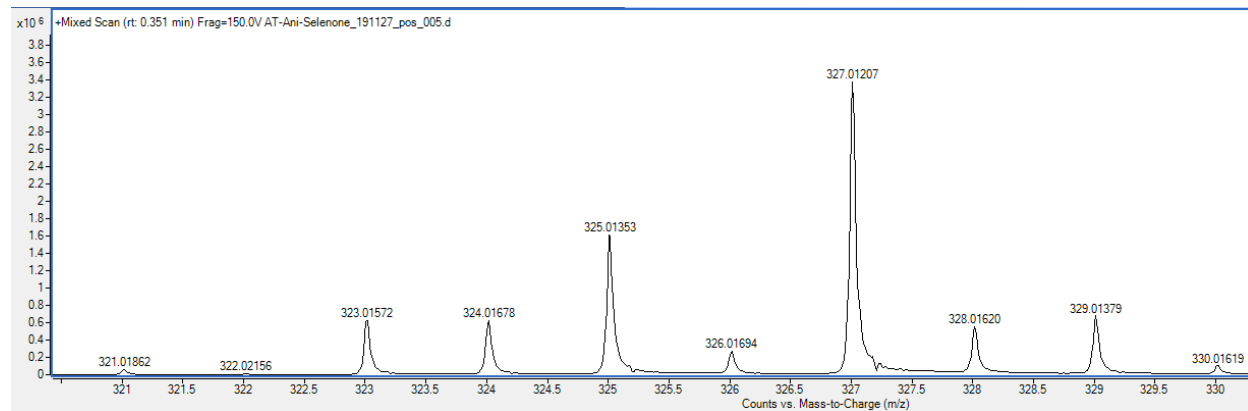


Figure S24. HR-MS spectrum of compound 15

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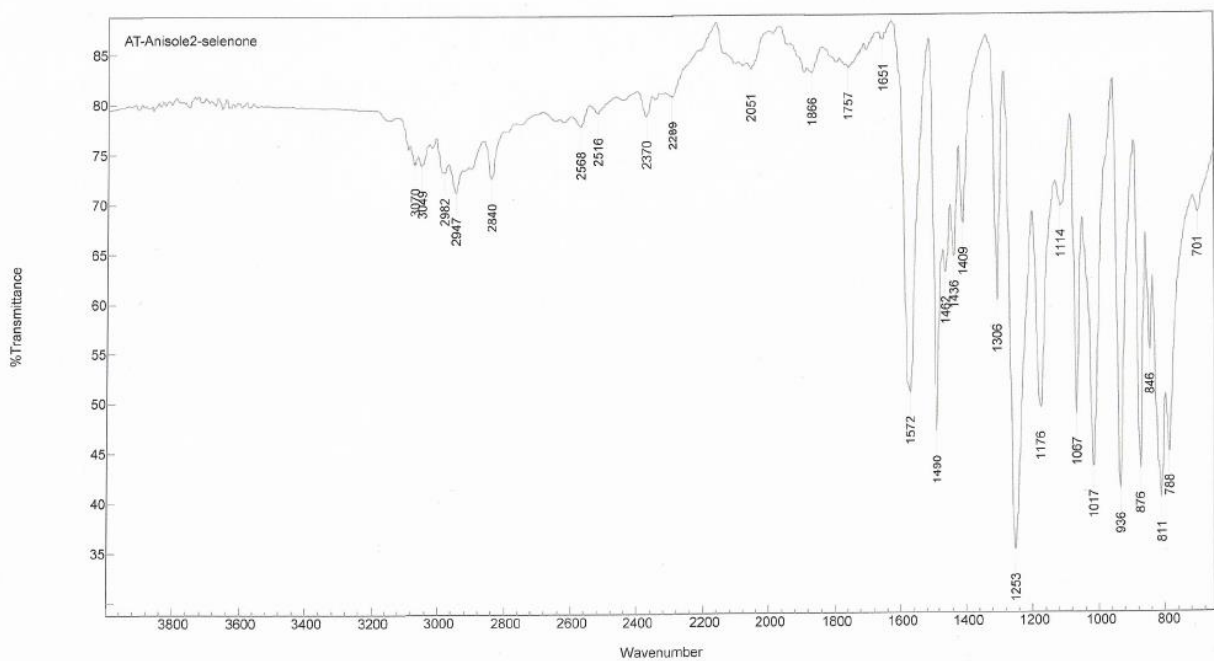


Figure S25. FT-IR spectrum of compound 15

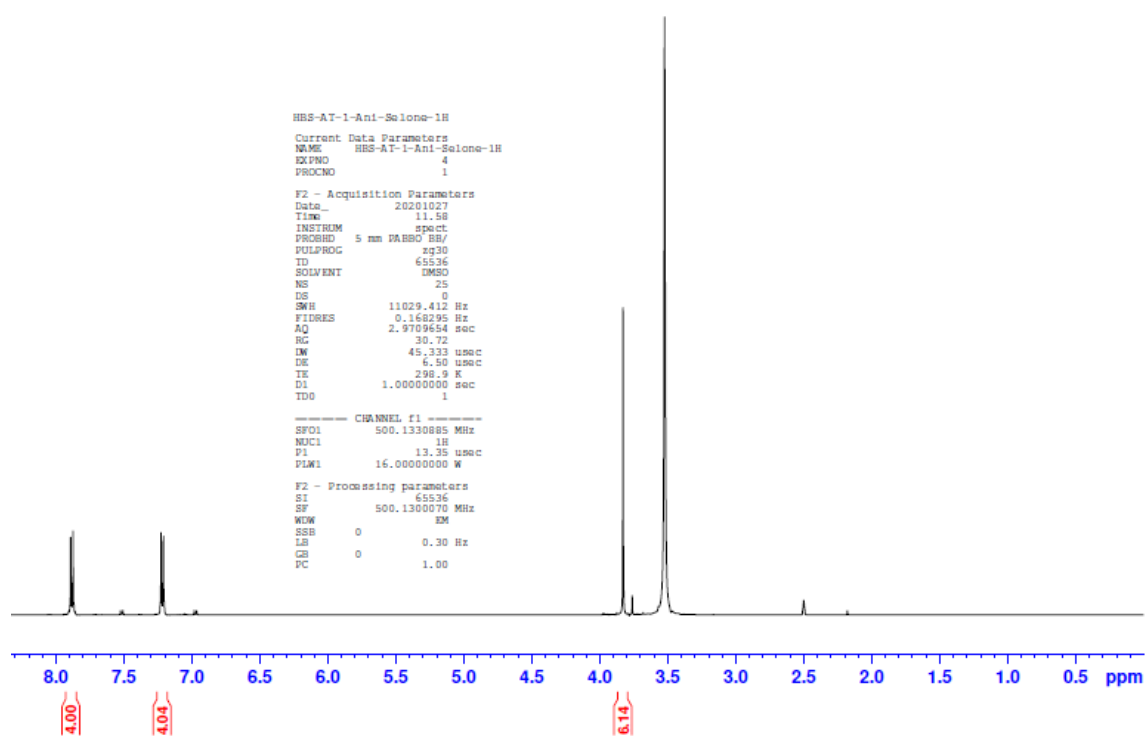


Figure S26. <sup>1</sup>H NMR spectrum of compound 15

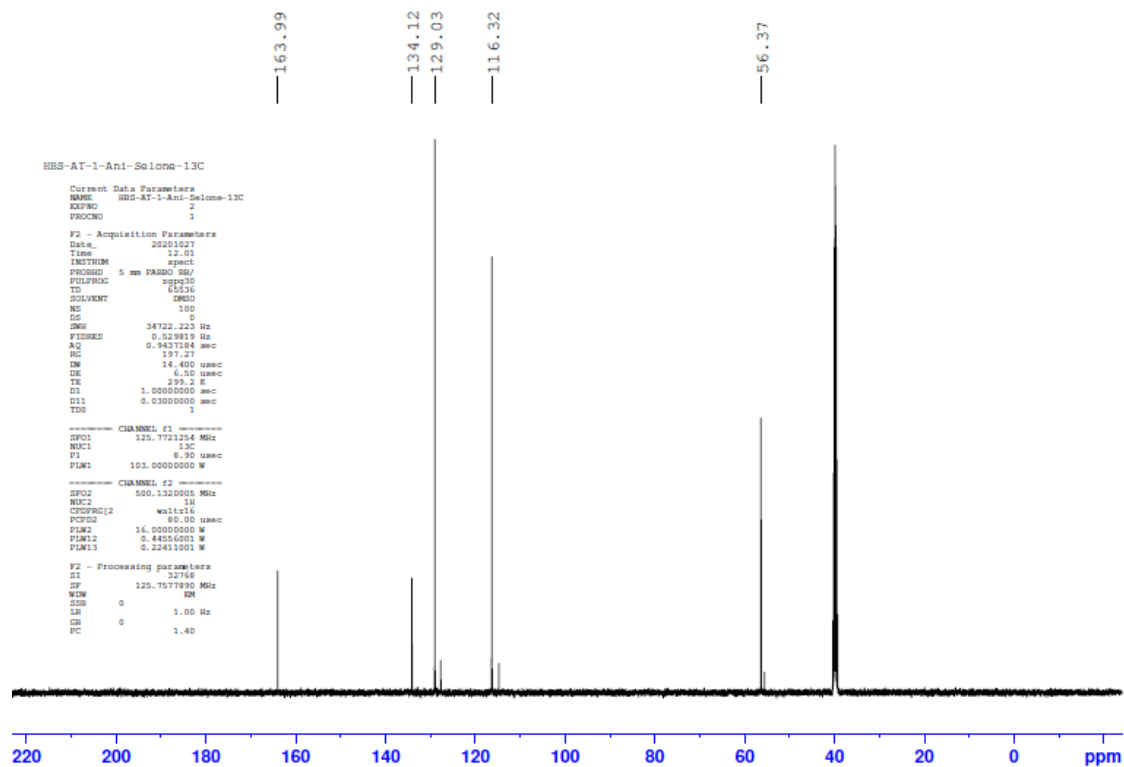


Figure S27.  $^{13}\text{C}$  NMR spectrum of compound 15

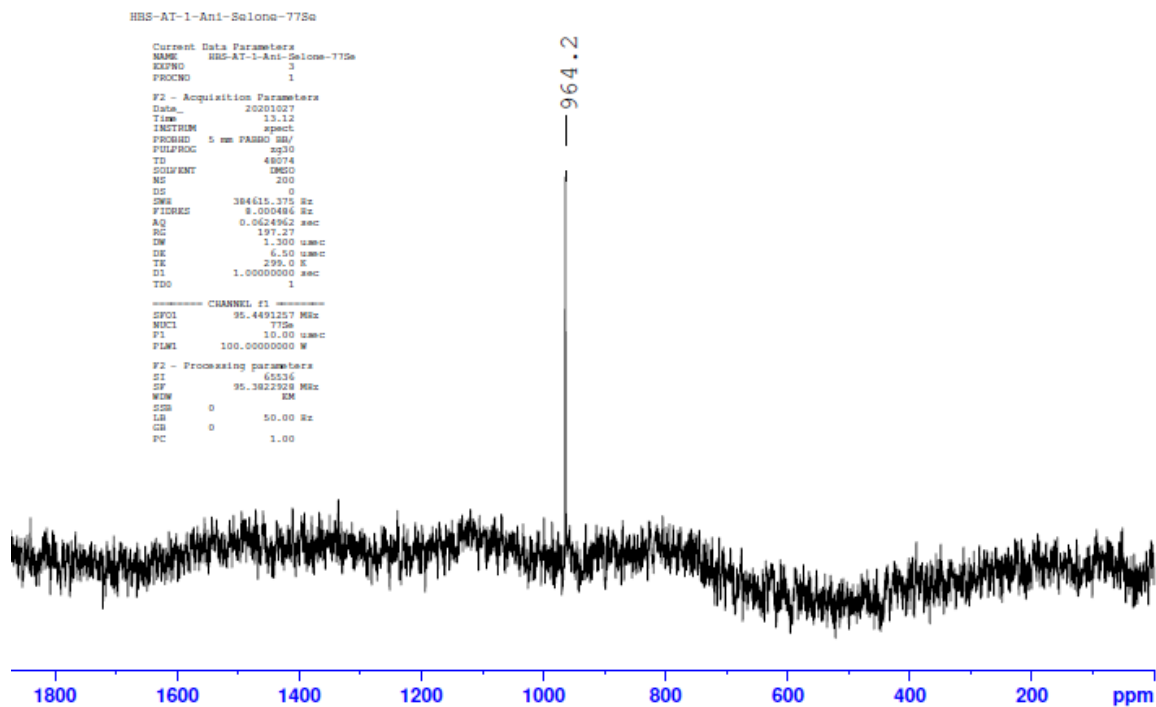
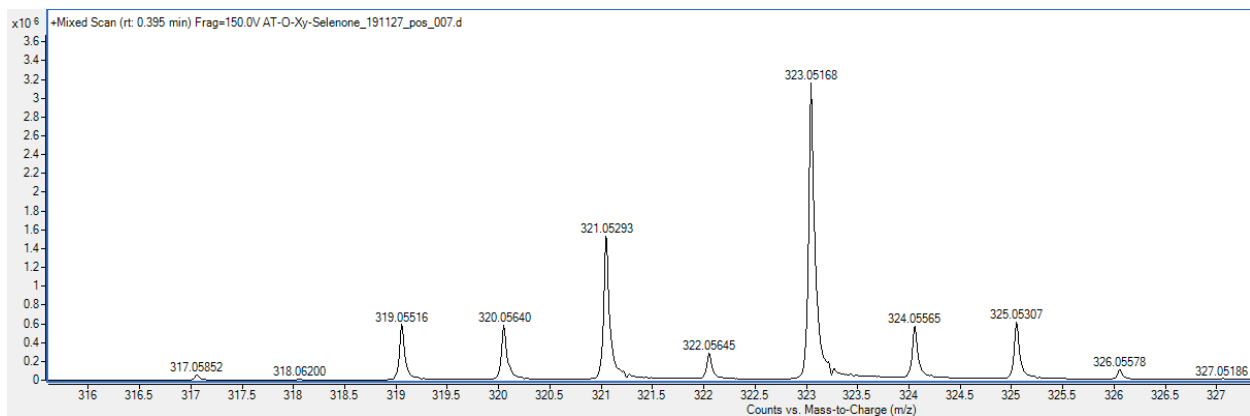


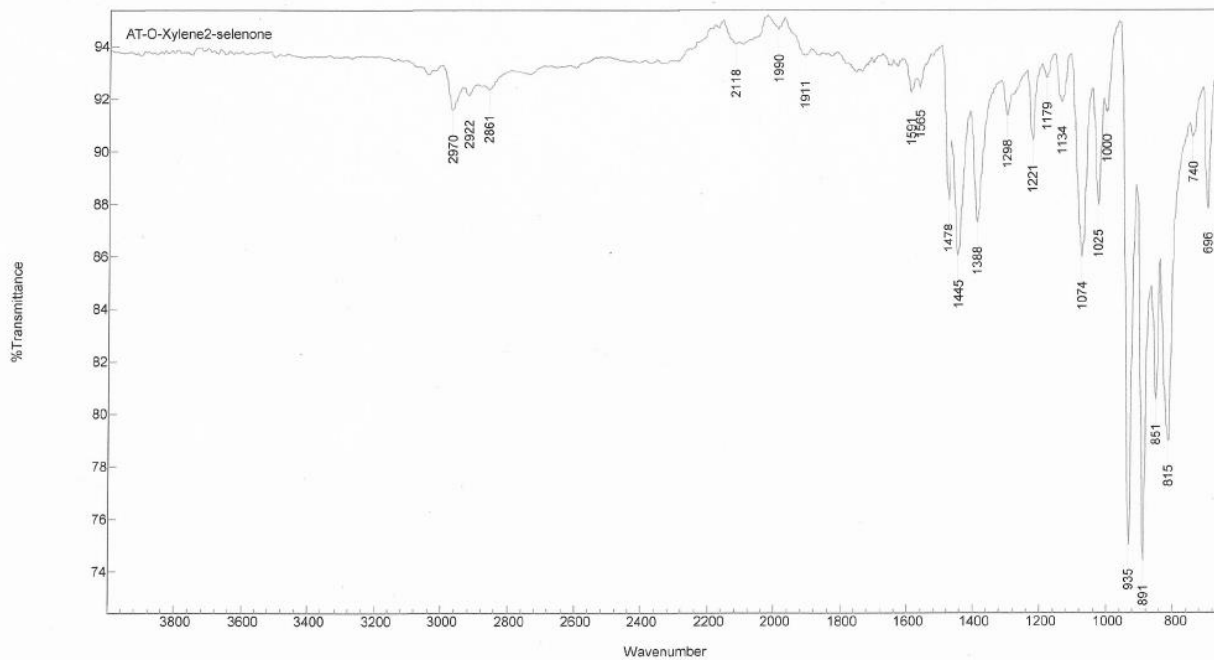
Figure S28.  $^{77}\text{Se}$  NMR spectrum of compound 15





**Figure S29.** HR-MS spectrum of compound **16**

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**Figure S30.** FT-IR spectrum of compound **16**

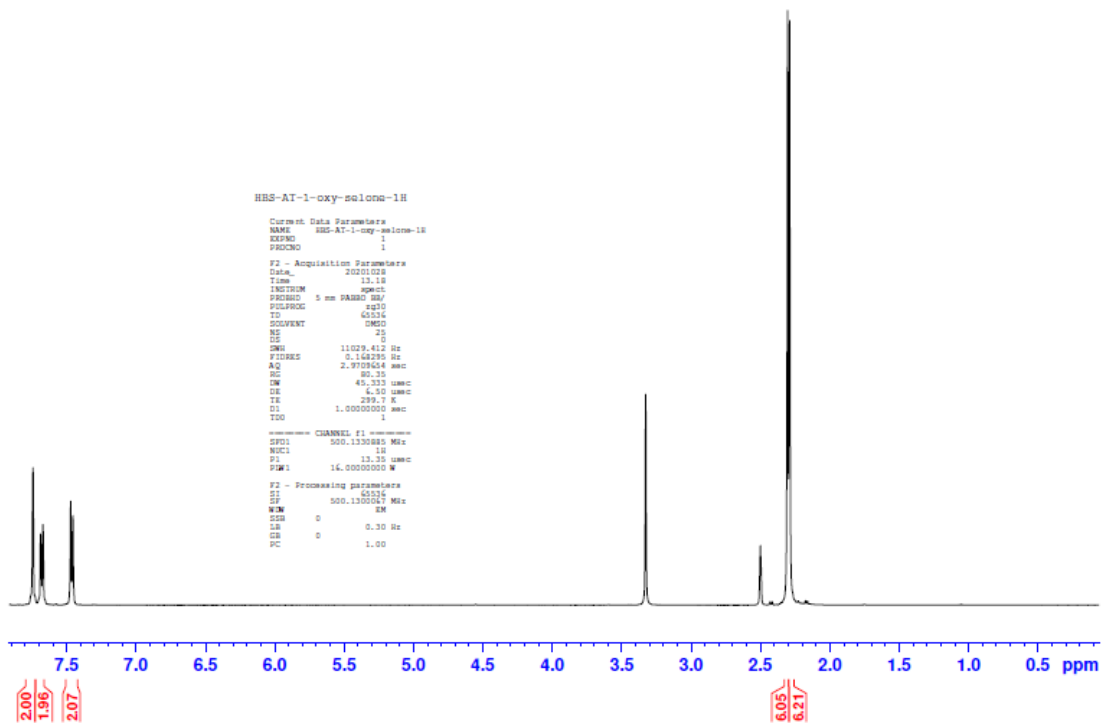


Figure S31.  $^1\text{H}$  NMR spectrum of compound **16**

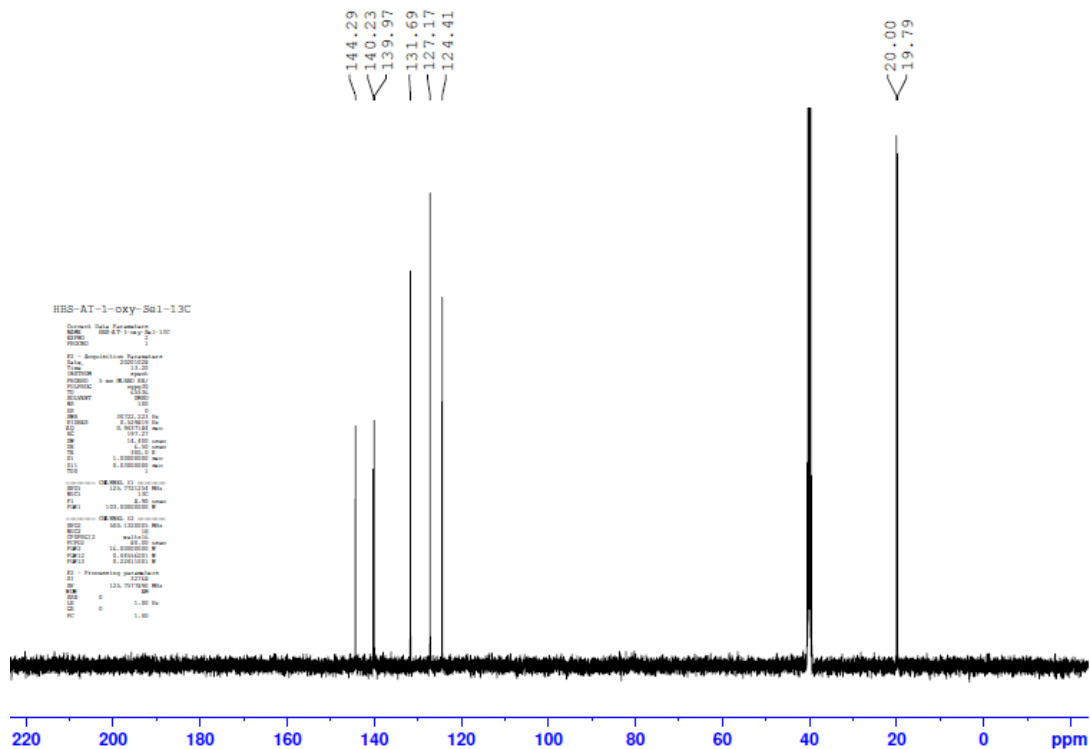


Figure S32.  $^{13}\text{C}$  NMR spectrum of compound **16**

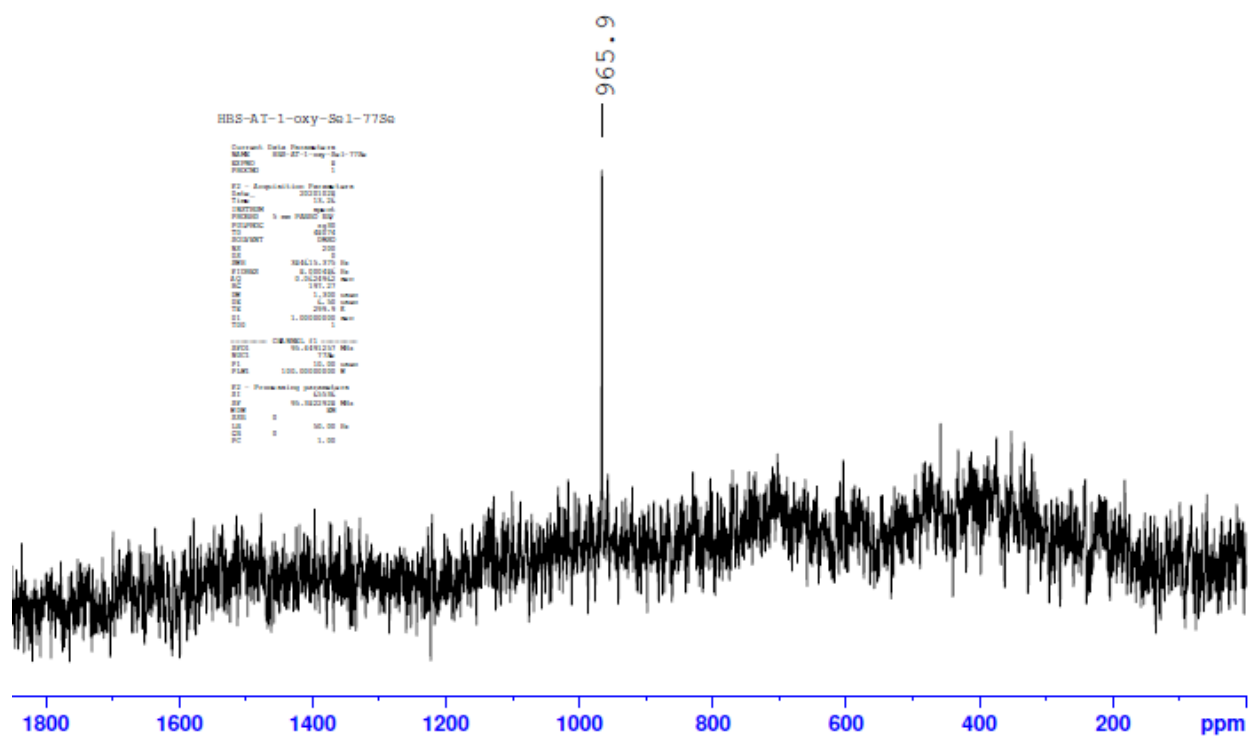


Figure S33.  $^{77}\text{Se}$  NMR spectrum of compound **16**

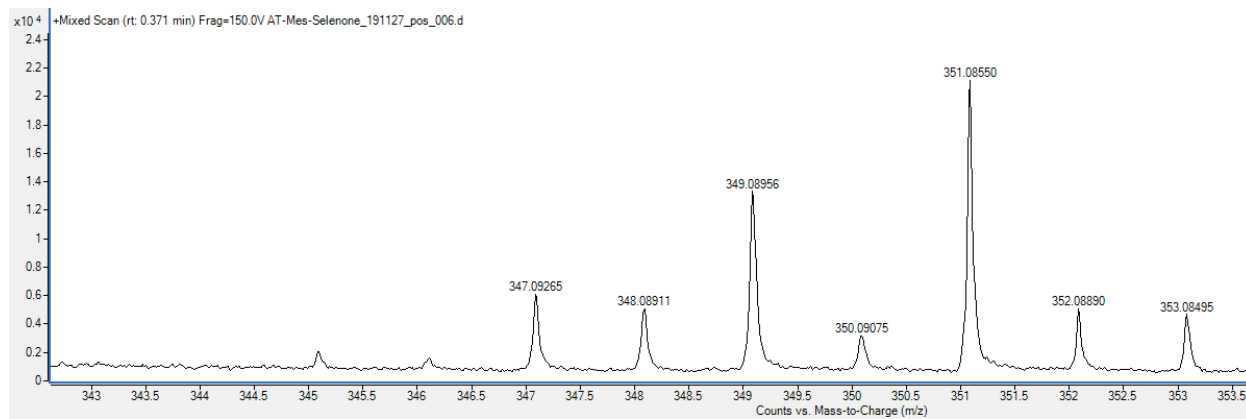


Figure S34. HR-MS spectrum of compound **17**

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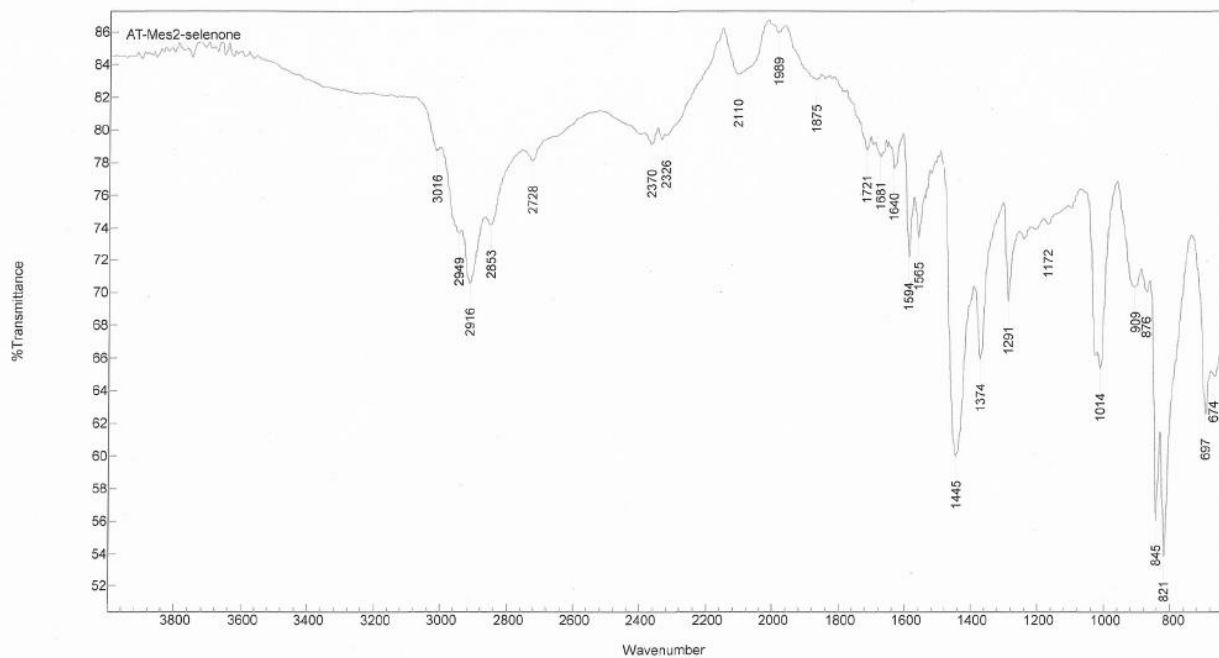


Figure S35. FT-IR spectrum of compound 17

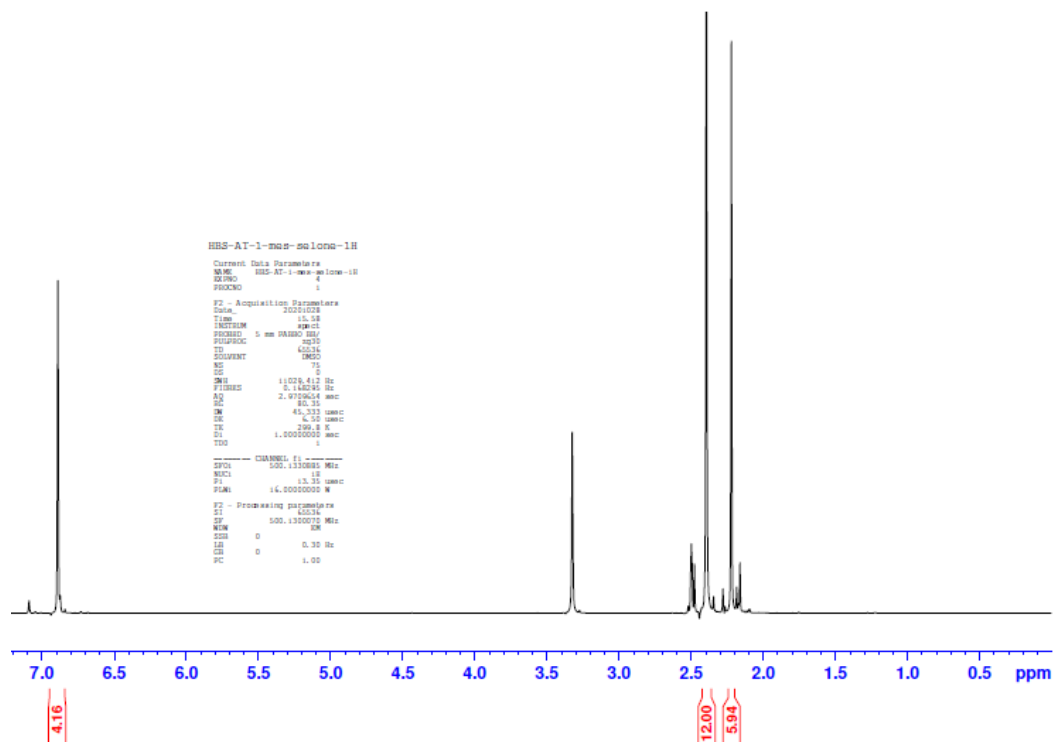


Figure S36. <sup>1</sup>H NMR spectrum of compound 17

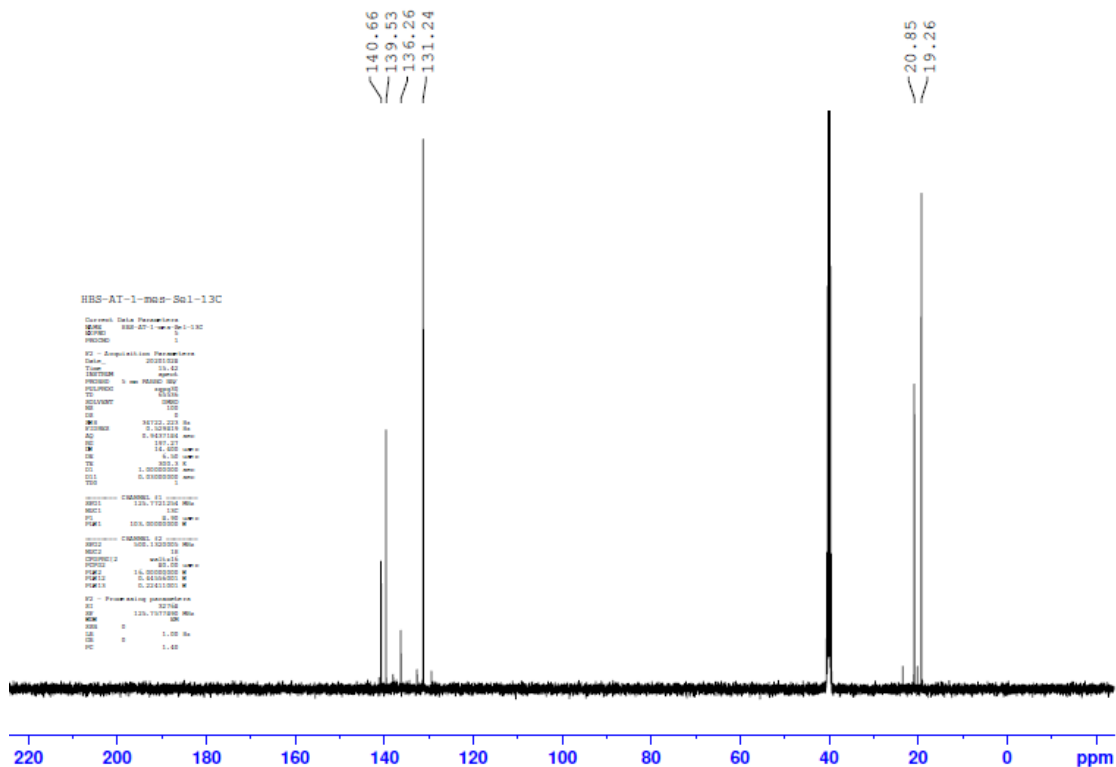


Figure S37. <sup>13</sup>C NMR spectrum of compound 17

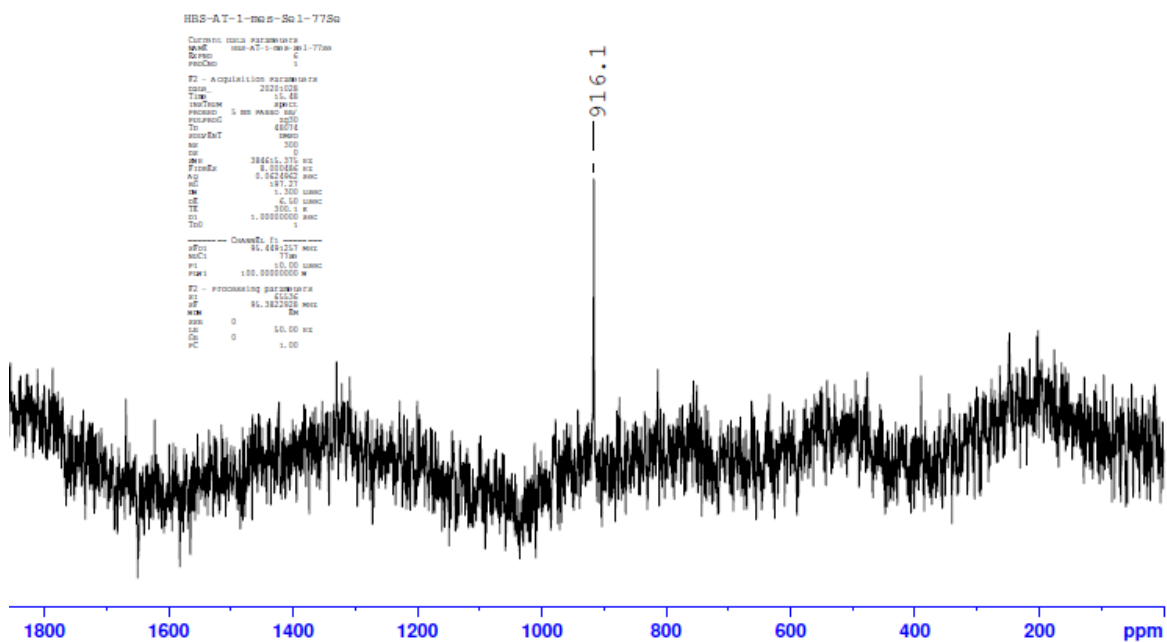
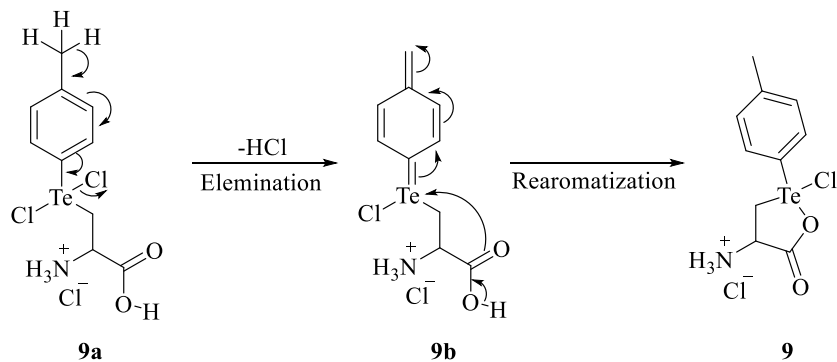


Figure S38. <sup>77</sup>Se NMR spectrum of compound 17

## Mechanism for the synthesis of **9**

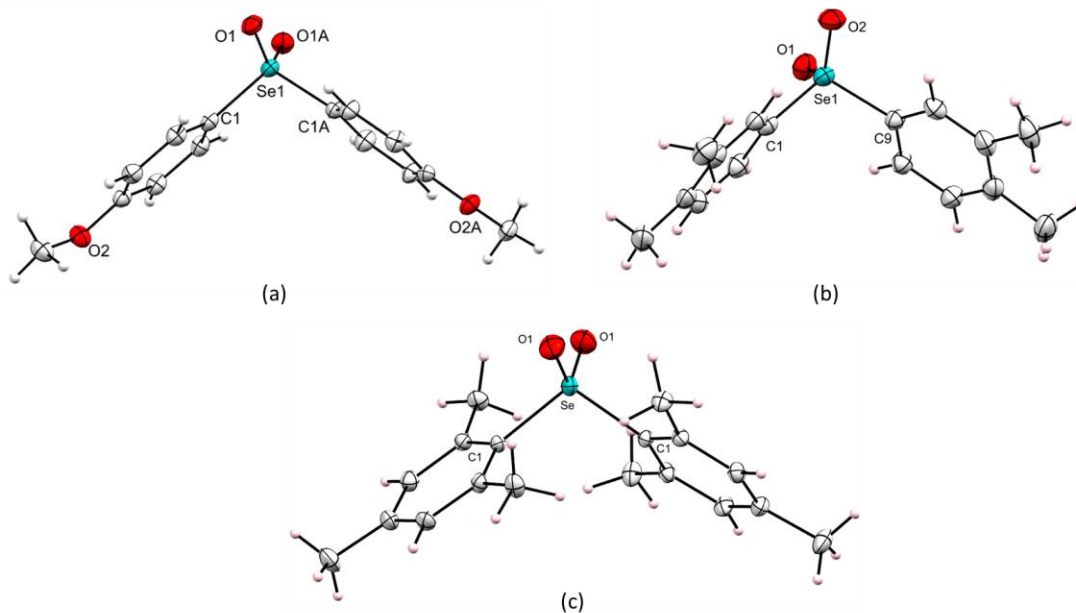
The mechanism for the formation of **9** involves the initial formation of dichlorotellurane species **9a**. Due to a possible hyperconjugation effect a facile HCl elimination took place to result in intermediate **9b**. In the subsequent step, a nucleophilic attack of the carboxylate group to the Te center followed by re-aromatization afforded the cyclic compound **9**.



**Scheme S1.** Plausible mechanism for the formation of compound **9**.

**Table S1.** Crystallographic data and refinement details for compounds **5**, **8**, **9**, **14**, **15**, **16**, and **17**

Compound	<b>5</b>	<b>8</b>	<b>9</b>	<b>14</b>	<b>15</b>	<b>16</b>	<b>17</b>
<b>Formula</b>	C <sub>3</sub> H <sub>10</sub> Br <sub>3</sub> NO <sub>4</sub> Te	C <sub>18.89</sub> H <sub>32</sub> Cl <sub>6</sub> N <sub>2</sub> O <sub>7.11</sub> Te <sub>2</sub>	C <sub>10</sub> H <sub>15</sub> Cl <sub>2</sub> NO <sub>3</sub> Te	C <sub>14</sub> H <sub>14</sub> O <sub>2</sub> Se	C <sub>14</sub> H <sub>14</sub> O <sub>4</sub> Se	C <sub>16</sub> H <sub>18</sub> O <sub>2</sub> Se	C <sub>18</sub> H <sub>22</sub> O <sub>2</sub> Se
<b>Crystal System</b>	Orthorhombic	monoclinic	monoclinic	monoclinic	monoclinic	triclinic	monoclinic
<b>Space group</b>	<i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>	<i>C</i> 2	<i>C</i> 2	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> -1	<i>C</i> 2/ <i>c</i>
<b>T/K</b>	123.00(10)	100(2)	100(2)	123.00(10)	123.00(10)	122.99(10)	100(2)
<b>a [Å]</b>	5.85996(15)	13.6819(2)	32.2340(6)	8.9483(4)	7.41562(5)	7.8964(16)	13.1440(3)
<b>b [Å]</b>	9.5789(3)	9.2677(10)	5.6150(11)	14.4494(5)	8.19270(5)	8.4010(17)	9.1631(18)
<b>c [Å]</b>	20.0889(5)	24.7845(4)	7.6100(15)	9.9106(4)	21.78490(14)	11.5880(2)	13.2700(3)
<b>α [°]</b>	90	90	90	90	90	92.16(3)	90
<b>β [°]</b>	90	100.1830(10)	100.28(3)	106.30(4)	93.5017(6)	96.22(3)	102.61(3)
<b>γ [°]</b>	90	90	90	90	90	106.84(3)	90
<b>V [Å<sup>3</sup>]</b>	1127.62(5)	3093.17(8)	1355.20(5)	1229.90(9)	1321.05(15)	729.50(3)	1559.8(6)
<b>Z</b>	4	4	4	4	4	2	4
<b>ρ<sub>calc</sub>/cm<sup>3</sup></b>	2.895	1.866	1.939	1.584	1.635	1.463	1.487
<b>μ/mm<sup>-1</sup></b>	13.249	20.001	2.585	3.039	3.931	2.569	2.410
<b>GOF</b>	1.004	1.081	1.112	1.006	1.107	1.086	1.025
<b>2θ range (deg)</b>	7.244 to 63.704	7.248 to 155.306	2.568 to 52.032	7.080 to 64.196	8.132 to 154.908	3.540 to 53.470	5.950 to 53.480
<b>Refs collected</b>	10892	6551	8390	13287	23988	22156	12872
<b>Unique/observed</b>	3186	6551	2559	3493	2814	3081	1655
<b>Parameters</b>	123	375	163	156	175	244	99
<b>R<sub>int</sub></b>	0.0359	0.0793	0.0624	0.0481	0.0455	0.1405	0.0432
<b>R<sub>1</sub>, wR2[I &gt; 2σ(I)]</b>	0.0222, 0.0429	0.0635, 0.1668	0.0281, 0.0664	0.0353, 0.0814	0.0259, 0.0679	0.0440, 0.1197	0.0359, 0.0943
<b>R<sub>1</sub>, wR2[All data]</b>	0.0245, 0.0433	0.0636, 0.1669	0.0282, 0.0664	0.0560, 0.0880	0.0264, 0.0683	0.0444, 0.1203	0.0360, 0.0943



**Figure S39.** Molecular structures of **15-17**; thermal ellipsoids are set at the 50 % probability level

**Table S2.** The important geometrical parameters of compound **5**

Bond length(Å)/ Bond Angle (°)	<b>5</b>
Te(1) – Br(1) Å	2.704(6)
Te(1) – Br(2) Å	2.665(6)
Te(1) – Br(3) Å	2.655(6)
Te(1) – C(1) Å	2.150(5)
Te(1) – O(1) Å	2.141(3)
C(3) – O(1) Å	1.295(6)
C(3) – O(2) Å	1.219(6)
Br(1) – Te(1) – Br(2) °	89.39(2)
Br(3) – Te(1) – Br(2) °	89.59(2)
Br(1) – Te(1) – Br(3) °	174.94(2)
O(1) – Te(1) – C(1) °	80.10(1)



**Table S3.** The important geometrical parameters of compound **8**

Bond length(Å)/ Bond Angle (°)	<b>8</b>
Te(1) – Cl(1A) Å	2.544(4)
Te(1) – Cl(2A) Å	2.482(4)
Te(2) – Cl(1B) Å	2.531(4)
Te(2) – Cl(2B) Å	2.485(4)
Te(1) – C(1A) Å	2.120(2)
Te(1) – C(7A) Å	2.132(1)
Te(2) – C(1B) Å	2.106(2)
Te(2) – C(7B) Å	2.153(2)
C(9A) – O(1A) Å	1.319(2)
C(9A) – O(2A) Å	1.220(2)
C(9B) – O(1B) Å	1.339(2)
C(9B) – O(2B) Å	1.209(2)
Cl(1A) – Te(1) – Cl(2A) °	171.22(1)
Cl(1B) – Te(2) – Cl(2B) °	172.38(1)
C(1A) – Te(1) – C(7A) °	99.56(6)
C(1B) – Te(2) – C(7B) °	96.56(6)

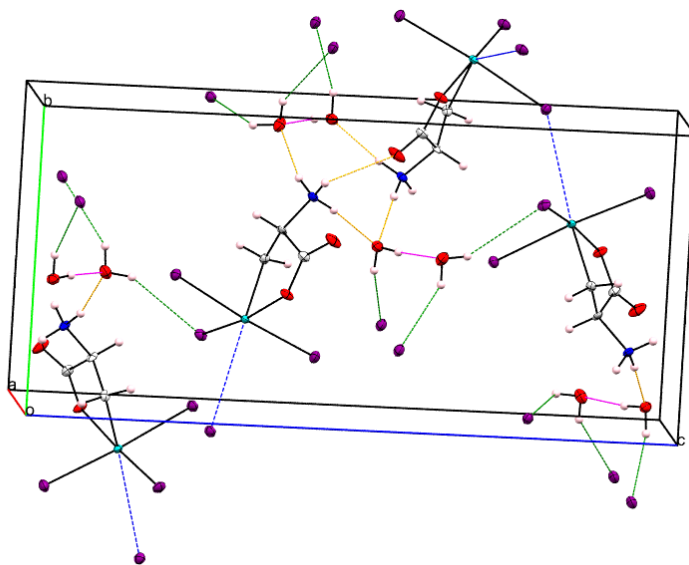
**Table S4.** The important geometrical parameters of compound **9**

Bond length(Å)/ Bond Angle (°)	<b>9</b>
Te(1) – Cl(1) Å	2.466(2)
Te(1) – C(3) Å	2.124(6)
Te(1) – C(4) Å	2.117(5)
Te(1) – O(1) Å	2.160(4)
C(1) – O(1) Å	1.314(7)
C(1) – O(2) Å	1.206(7)
C(3) – Te(1) – Cl(1) °	89.20(1)
C(4) – Te(1) – Cl(1) °	89.50(1)
C(3) – Te(1) – C(4) °	98.10(2)
O(1) – Te(1) – Cl(1) °	168.00(1)
O(1) – Te(1) – C(3) °	79.72(2)

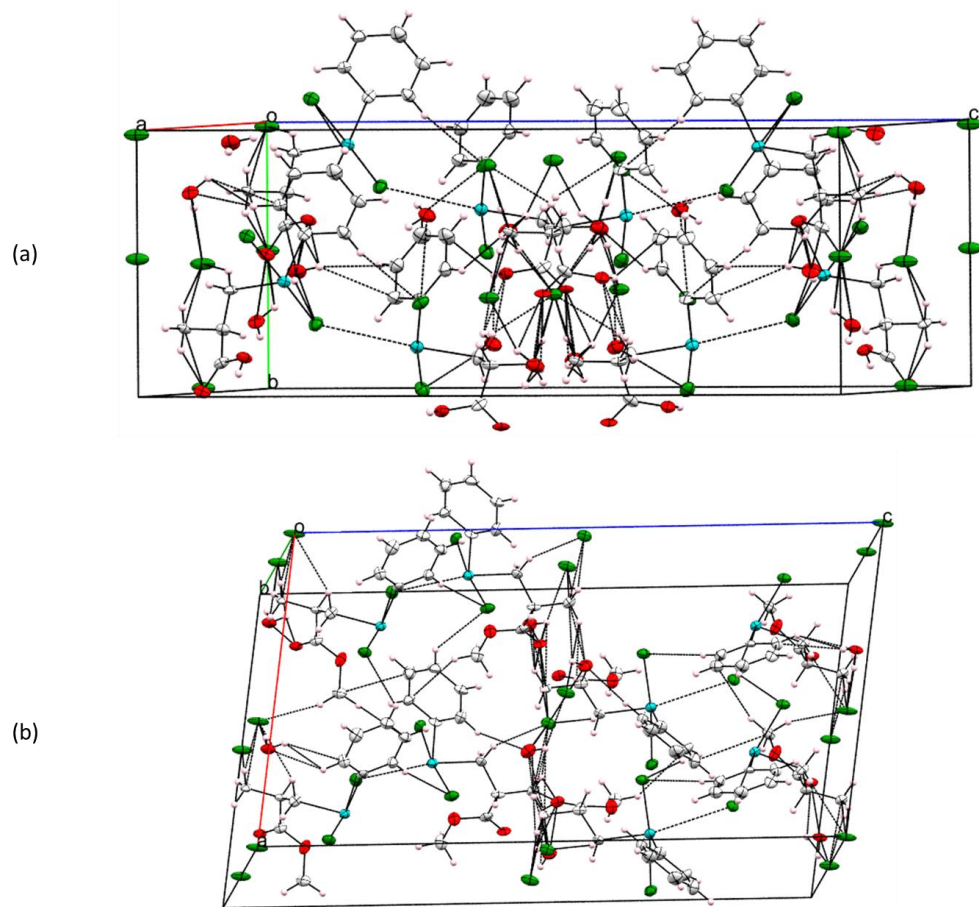
**Table S5.** Comparison of the important geometrical parameters of compounds **14-17**

Bond length(Å)/ Bond Angle (°)	<b>14</b>	<b>15</b>	<b>16</b>	<b>17</b>
Se(1) – O(1) Å	1.627(2)	1.620(1)	1.620(2)	1.609(2)
Se(1) – O(1A) Å	1.620(2)	1.619(1)	1.620(2)	1.609(2)
Se(1) – C(1) Å	1.904(3)	1.908(2)	1.903(3)	1.952
Se(1) – C(1A) Å	1.914(3)	1.903(2)	1.912(3)	1.952
O(1) – Se(1) – O(1A) °	117.87(9)	119.36(7)	118.37(1)	114.49(1)*
C(1) – Se(1) – O(1) °	108.07(1)	107.17(7)	107.30(1)	106.17
C(1) – Se(1) – O(1A) °	108.24(1)	106.46(7)	108.19(1)	111.38
C(1A) – Se(1) – O(1) °	108.51(1)	107.46(7)	108.19(1)	111.38
C(1A) – Se(1) – O(1A) °	108.11(1)	108.89(7)	108.35(1)	106.17
C(1) – Se(1) – C(1A) °	105.34(1)	106.87(7)	105.76(1)	107.10

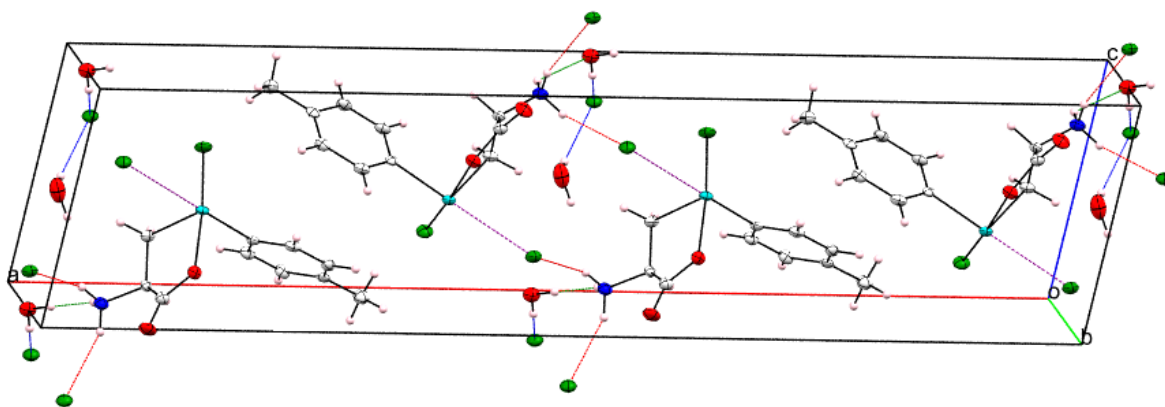
\*For **17**, bond angle is O(1)<sup>1</sup> – Se(1) – O(1)



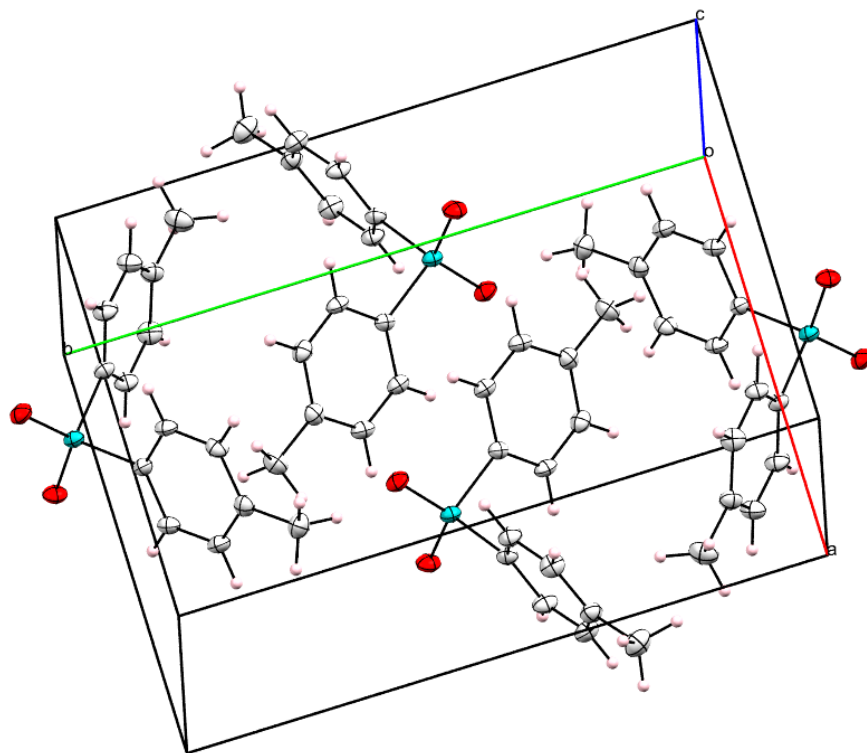
**Figure S40.** Packing diagram of compound **5**



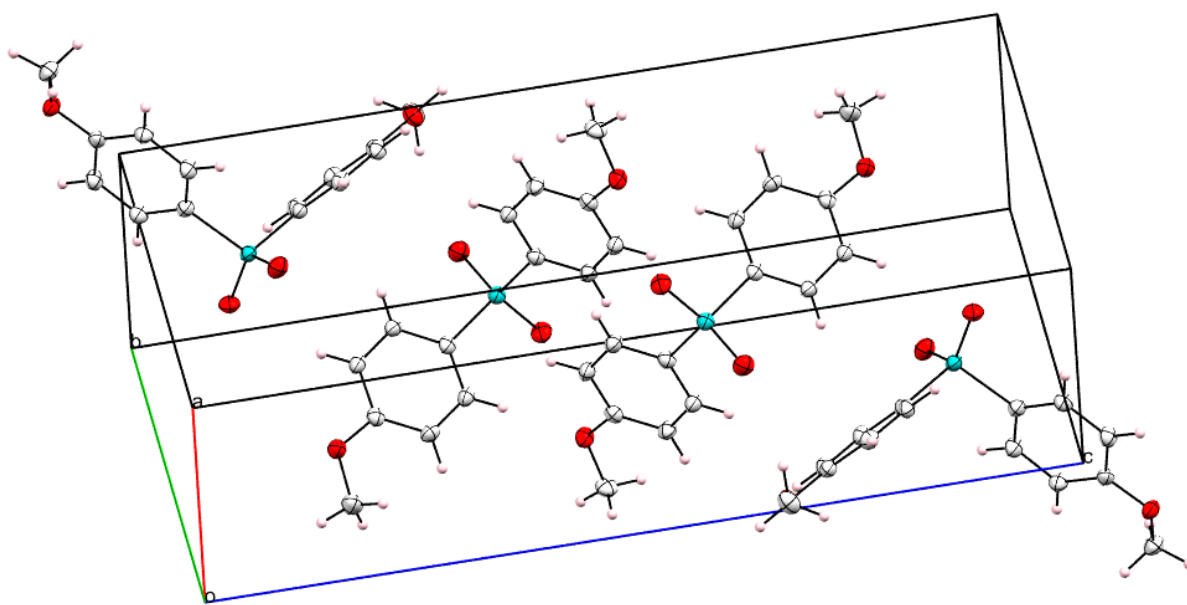
**Figure S41.** Packing diagram of compound **8** (a) and its methyl ester derivative (b)



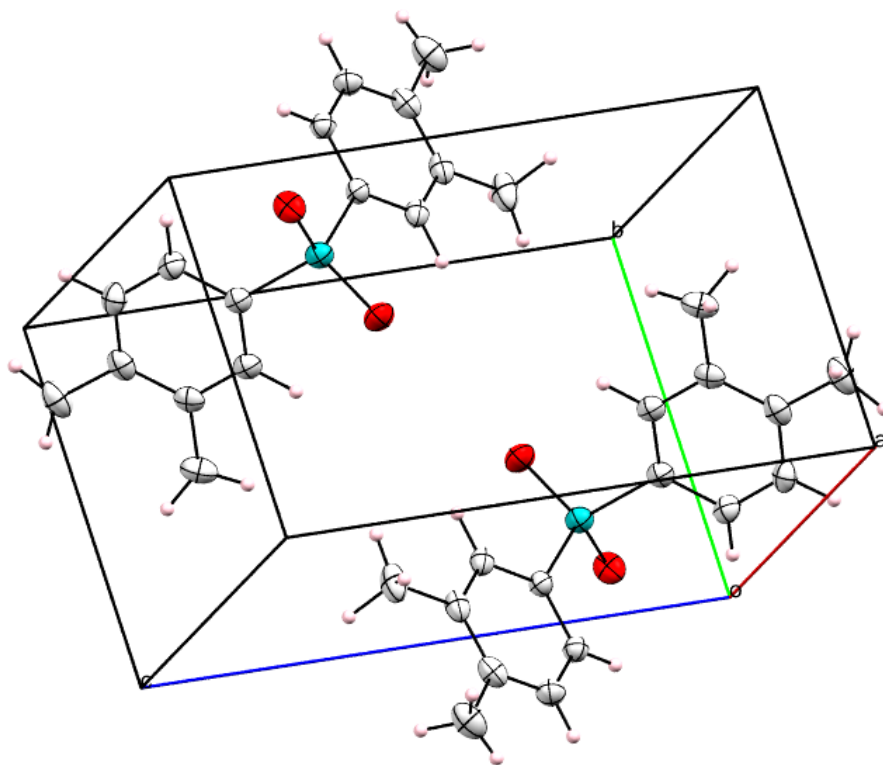
**Figure S42.** Packing diagram of compound **9**



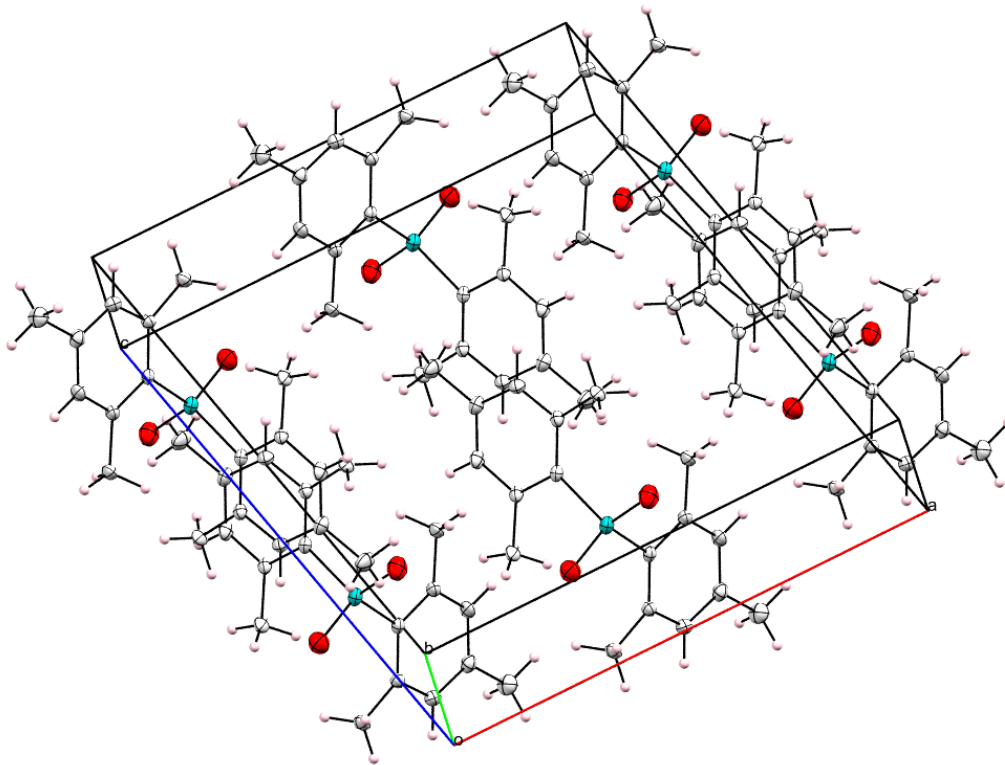
**Figure S43.** Packing diagram of compound **14**



**Figure S44.** Packing diagram of compound **15**



**Figure S45.** Packing diagram of compound **16**



**Figure S46.** Packing diagram of compound **17**