

## Supporting Information

### Probing interactions through space using spin-spin coupling

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#### 1. Experimental Section

Additional  $^{13}\text{C}$  NMR and IR spectroscopy data for compounds **2-9**.

**5-(4-fluorophenyltelluro)-6-(phenylselenyl)acenaphthene [Acenap(TeFp)(SePh)] (2):** IR (KBr disk):  $\nu_{\text{max}}$   $\text{cm}^{-1}$  3057w, 2923w, 1872w, 1638w, 1575vs, 1479vs, 1436s, 1408w, 1328s, 1294w, 1249w, 1223vs, 1158s, 1101w, 1069w, 1019w, 841s, 814vs, 737vs, 688s, 666w, 616w, 602w, 572w, 504s, 473w, 413w, 324w;  $^{13}\text{C}$  NMR (75.5 MHz;  $\text{CDCl}_3$ ; 25°C;  $\text{Me}_4\text{Si}$ )  $\delta$  = 163.7(q,  $^1J(\text{C},\text{F}) = 248.6$  Hz), 150.3(q), 146.2(q), 143.5(q,  $^3J(\text{C},\text{F}) = 7.6$  Hz), 141.8(q), 141.6(s), 136.4(q), 136.1(q) 135.9(s), 130.1(s), 129.6(s), 126.9(s), 123.4(q), 121.7(s), 120.9(s), 117.6(d,  $^2J(\text{C},\text{F}) = 20.4$  Hz), 117.0(q, d,  $^4J(\text{C},\text{F}) = 3.8$  Hz), 113.5(q), 30.8 (s,  $\text{CH}_2$ ), 30.1(s,  $\text{CH}_2$ ).

**5-(4-methylphenyltelluro)-6-(phenylselenyl)acenaphthene [Acenap(TeTol)(SePh)] (3):** IR (KBr disk):  $\nu_{\text{max}}$   $\text{cm}^{-1}$  3029w, 2912s, 1872w, 1591w, 1574s, 1475s, 1434s, 1406s, 1328s, 1252w, 1231w, 1209w, 1180w, 1096w, 1058w, 1013s, 839vs, 797vs, 736vs, 689vs, 603w, 572w, 483s, 455s;  $^{13}\text{C}$  NMR (75.5 MHz;  $\text{CDCl}_3$ ; 25 °C;  $\text{Me}_4\text{Si}$ )  $\delta$  = 150.2(q), 146.0(q), 141.7(q), 141.5(s), 141.4(s), 138.9(q), 136.4(q), 136.2(q), 136.0(s), 131.1(s), 130.2(s), 129.6(s), 126.8(s), 123.6(q), 121.7(s), 120.7(s), 118.8(q), 113.6(s), 30.8(s,  $\text{CH}_2$ ), 30.8(s,  $\text{CH}_2$ ), 22.0(s,  $\text{CH}_3$ ).

**5-(4-methoxyphenyltelluro)-6-(phenylselenyl)acenaphthene [Acenap(TeAn-p)(SePh)] (4):** IR (KBr disk):  $\nu_{\text{max}}$   $\text{cm}^{-1}$  3056s, 3002s, 2935s, 2831s, 2528w, 2485w, 2422w, 2370w, 2274w, 2032w, 1936w, 1883s, 1792w, 1739w, 1627w, 1583vs, 1484vs, 1460vs, 1434vs, 1407vs, 1326vs, 1300s, 1282vs, 1243vs, 1176vs, 1100s, 1065s, 1027vs, 930w, 905w, 842vs, 814vs, 788s, 733vs, 684vs, 604s, 588s, 516s, 476s, 454s, 325w;  $^{13}\text{C}$  NMR (75.5 MHz;  $\text{CDCl}_3$ ; 25 °C;  $\text{Me}_4\text{Si}$ )  $\delta$  = 160.6(q), 150.2 (q), 146.0 (q), 143.1(s), 141.8(q), 141.6(s), 136.4(q), 136.2(q), 135.8(s), 130.2(s), 129.6(s), 126.8(s), 123.5(q), 121.7(s), 120.8(s), 116.1(s), 114.0(q), 112.4(q), 55.6(s,  $\text{CH}_3$ ), 30.9(s,  $\text{CH}_2$ ), 30.1 (s,  $\text{CH}_2$ ).

**5-(2-methoxyphenyltelluro)-6-(phenylselenyl)acenaphthene [Acenap(TeAn-o)(SePh)] (5):** IR (KBr disk):  $\nu_{\text{max}}$   $\text{cm}^{-1}$  3045w, 0.22w, 3007w, 2954w, 2919s, 2826w, 2035w, 1888w, 1855w, 1653w, 1591w, 1575vs, 1459vs, 1436vs, 1426s, 1409s, 1329s, 1293s, 1269s, 1243vs, 1174s, 1168s, 1116s, 1101s, 1054s, 1020vs, 999s, 928w, 839s, 812s, 791s, 749vs, 139vs, 714s, 690vs, 669s, 645w, 614w, 602s, 566w, 536w, 493w, 478s, 455w, 440w, 416w;  $^{13}\text{C}$  NMR (75.5 MHz;  $\text{CDCl}_3$ ; 25 °C;  $\text{Me}_4\text{Si}$ )  $\delta$  = 161.4(q), 149.8(q), 146.3(q), 141.9(s), 141.7(q), 140.7(s), 137.4(s), 136.8(q), 129.6(q), 131.1(s), 130.9(s), 129.6(s) 127.0(s), 124.3(q), 122.(s), 121.7(s), 120.7(s), 113.5(q), 112.3(q), 110.6(s), 56.5(s,  $\text{CH}_3$ ), 30.8(s,  $\text{CH}_2$ ), 30.2(s,  $\text{CH}_2$ ).

**5-(4-tertbutylphenyltelluro)-6-(phenylselenyl)acenaphthene [Acenap(TeTp)(SePh)] (6):** IR (KBr disk):  $\nu_{\text{max}}$   $\text{cm}^{-1}$  3450w,

3052w, 2954s, 1657w, 1577s, 1475s, 1437s, 1406s, 1384s, 1332s, 1253s, 1230s, 1110s, 1060s, 843s, 820vs, 737s, 687s, 666s, 605w, 551s, 460w, 277s;  $^{13}\text{C}$  NMR (75.5 MHz;  $\text{CDCl}_3$ ; 25 °C;  $\text{Me}_4\text{Si}$ )  $\delta$  = 152.1(q), 150.2(q), 146.0(q), 141.7(q), 141.5(s), 141.0(s), 138.2(q), 136.4(q), 136.2(s), 130.3(s), 129.6(s), 127.3(s), 126.8(s), 123.7(q), 121.7(s), 120.7(s), 119.0(q), 113.6(q), 35.2(s,  $\text{C}(\text{CH}_3)_3$ ), 31.8(s, 3 x  $\text{CH}_3$ ), 30.8(s,  $\text{CH}_2$ ), 30.1(s,  $\text{CH}_2$ ).

**5-(2,4,6-trimethylphenyltelluro)-6-(phenylselenyl)acenaphthene [Acenap(TeMes)(SePh)] (7):** IR (KBr disk):  $\nu_{\text{max}}$   $\text{cm}^{-1}$  3019w, 2915s, 1657w, 1577s, 1476s, 1436vs, 1375w, 1324s, 1290w, 1250w, 1232w, 1156w, 1099w, 1069w, 1020s, 891w, 842vs, 814s, 728vs, 686s, 603w, 542w, 487w, 455w, 330w;  $^{13}\text{C}$  NMR (75.5 MHz;  $\text{CDCl}_3$ ; 25 °C;  $\text{Me}_4\text{Si}$ )  $\delta$  = 150.2(q), 146.1(q), 145.7(q), 141.8(q), 141.5(s), 139.5(q), 136.6(q), 136.5(q), 134.4(s), 130.4(s), 129.5(s), 127.9(s), 126.7(s), 126.2(q), 123.7(q), 121.9(s), 120.7(s), 30.8(s,  $\text{CH}_2$ ), 30.1(s,  $\text{CH}_2$ ), 29.2(s, 2 x  $\text{CH}_3$ ), 21.6(s,  $\text{CH}_3$ ).

**5-(2,4,6-triisopropylphenyltelluro)-6-(phenylselenyl)acenaphthene [Acenap(TeTip)(SePh)] (8):** IR (KBr disk):  $\nu_{\text{max}}$   $\text{cm}^{-1}$  3057w, 2954vs, 1867w, 1600w, 1589s, 1577vs, 1553s, 1476vs, 1456s, 1436s, 1407s, 1378s, 1359s, 1328s, 1309s, 1293w, 1251s, 1233s, 1176w, 1162w, 1149w, 1113w, 1100s, 1068s, 1020s, 998s, 933s, 876s, 838vs, 813s, 747s, 731vs, 689s, 667s, 647w, 618w, 605w, 489w, 455.7s;  $^{13}\text{C}$  NMR (75.5 MHz;  $\text{CDCl}_3$ ; 25 °C;  $\text{Me}_4\text{Si}$ )  $\delta$  = 155.7(q), 150.9(q), 150.3(q), 145.7(q), 141.9(q), 141.5(s), 136.7(q), 136.3(q), 135.8(s), 130.5(s), 129.5(s), 127.7(q), 126.7(s), 123.7(q), 121.9(s), 121.7(s), 120.7(s), 114.9(q), 39.8(s, 2 x  $\text{CHMe}_2$ ), 34.7(s, 1 x  $\text{CHMe}_2$ ), 30.83(s,  $\text{CH}_2$ ), 30.1(s,  $\text{CH}_2$ ), 25.3(s, 4 x  $\text{CH}_3$ ), 24.5(s, 2 x  $\text{CH}_3$ ).

**5-(naphthyltelluro)-6-(phenylselenyl)acenaphthene [Acenap(TeNap)(SePh)] (9):** IR (KBr disk):  $\nu_{\text{max}}$   $\text{cm}^{-1}$  3051s, 2914w, 2824w, 1939w, 1868w, 1599w, 1574s, 1552w, 1494w, 1475s, 1435s, 1407s, 1324s, 1251s, 1230w, 1193w, 1098s, 1064w, 1018s, 946w, 909w, 839s, 791s, 768s, 731s, 686s, 665w, 602w, 524w, 455w, 408w;  $^{13}\text{C}$  NMR (75.5 MHz;  $\text{CDCl}_3$ ; 25°C;  $\text{Me}_4\text{Si}$ )  $\delta$  = 150.4(q), 146.0(q), 142.0(s), 141.8(q), 141.6(s), 138.7(q), 137.0(q), 136.3(s), 134.0(q), 133.8(s), 132.7(q), 130.9(s), 130.2(s), 129.6(s), 129.2(s), 127.5(s), 127.2(s), 126.9(s), 126.7(s), 125.8(q), 123.5(q), 121.8(s), 120.8(s), 113.0(q), 30.8(s,  $\text{CH}_2$ ), 30.0(s,  $\text{CH}_2$ ).

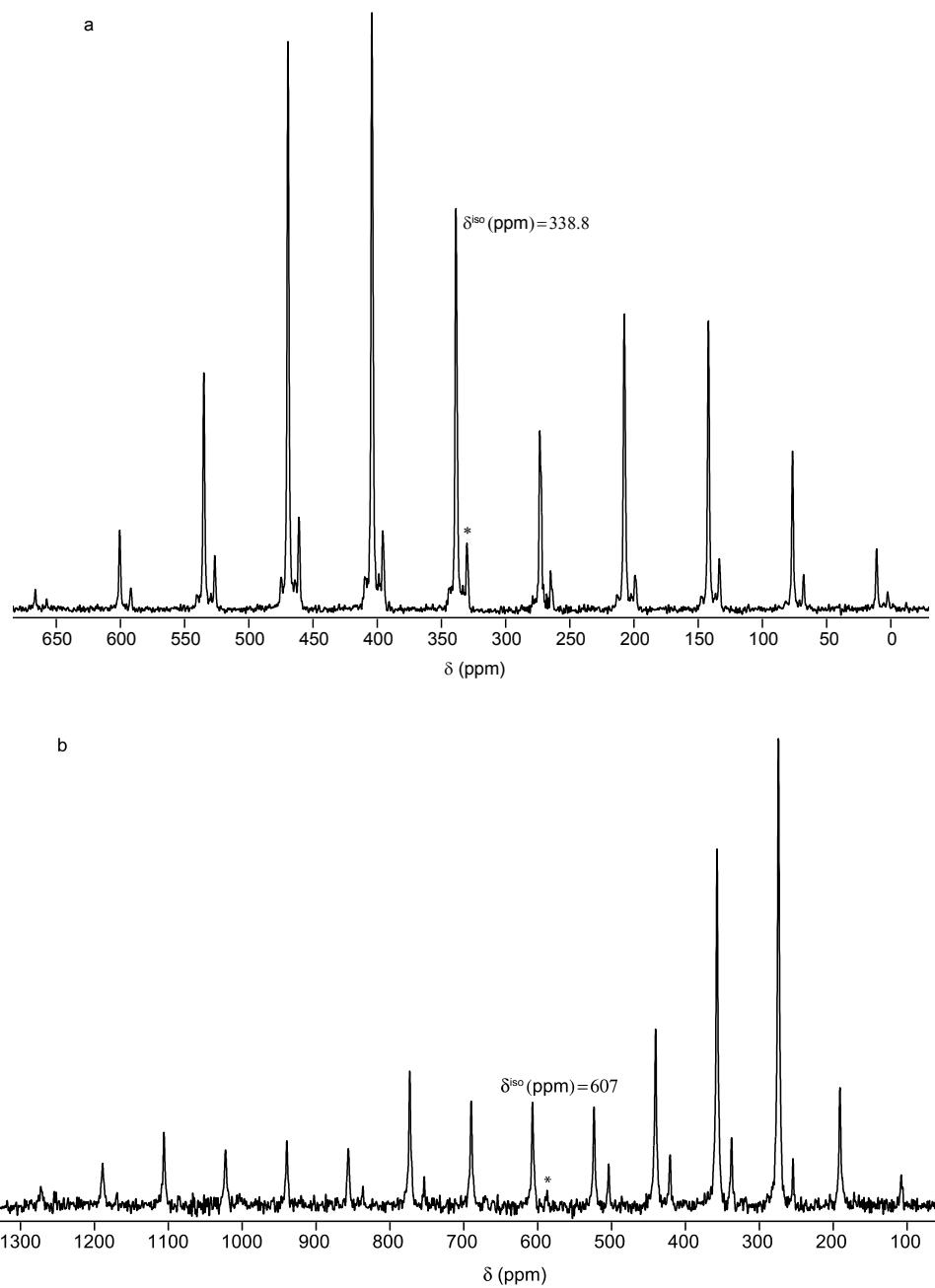
## 2. Solid-State NMR Experimental Details

**Table S1.** Experimental details, the number of coadded transients, recycle intervals and cross-polarisation contact times (where appropriate) used for recording the  $^{77}\text{Se}$  solid-state NMR spectra.

Sample	Experiment	Magnetic field (T)	Number of transients	Recycle interval / s	Contact time / ms
<b>6</b>	CP MAS	9.4	17248	3	8
<b>8</b>	CP MAS	9.4	1656	3	8

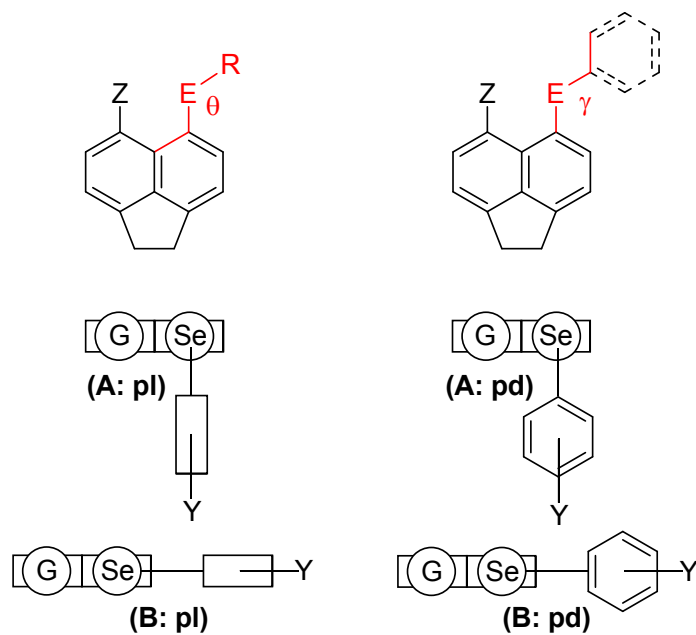
**Table S2.** Experimental details, the number of coadded transients, recycle intervals and cross-polarisation contact times (where appropriate) used for recording the  $^{125}\text{Te}$  solid-state NMR spectra.

Sample	Experiment	Magnetic field (T)	Number of transients	Recycle interval / s	Contact time / ms
<b>6</b>	CP MAS	9.4	54264	3	8
<b>8</b>	CP MAS	9.4	46560	3	8

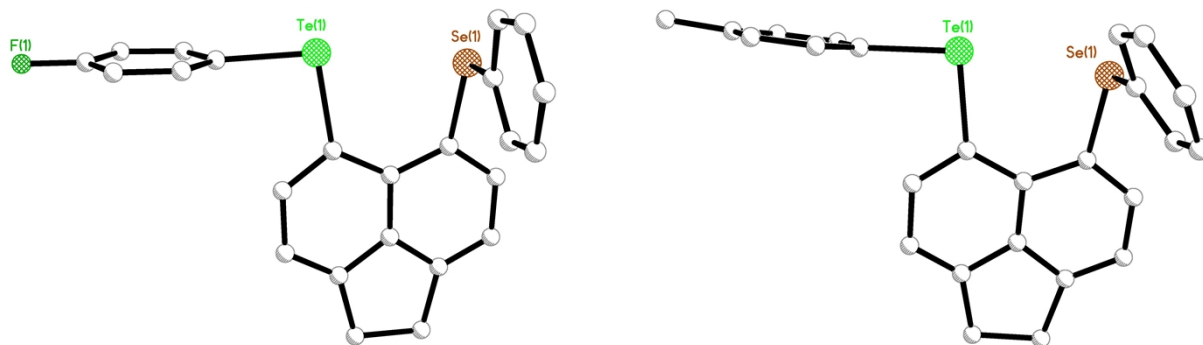


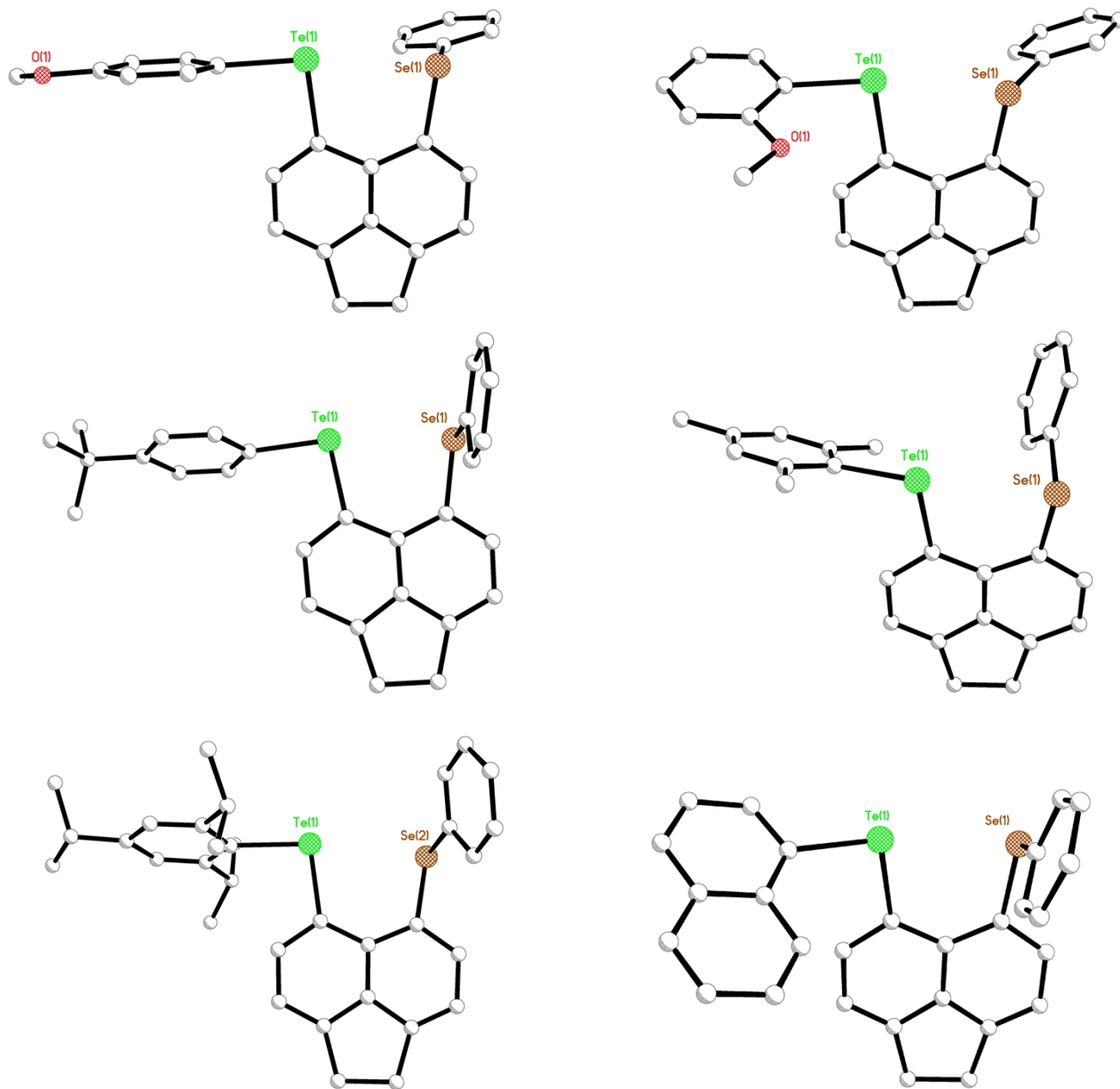
**Figure S1.**  $^{77}\text{Se}$  (a) and  $^{125}\text{Te}$  (b) solid-state NMR spectra of compound **6**, recorded using MAS rates of 5 kHz and 10.5 kHz, respectively. The values quoted correspond to the isotropic chemical shift. The presence of an as yet unidentified impurity is observed in both spectra (indicated by \*).

### 3. Crystal structure analyses

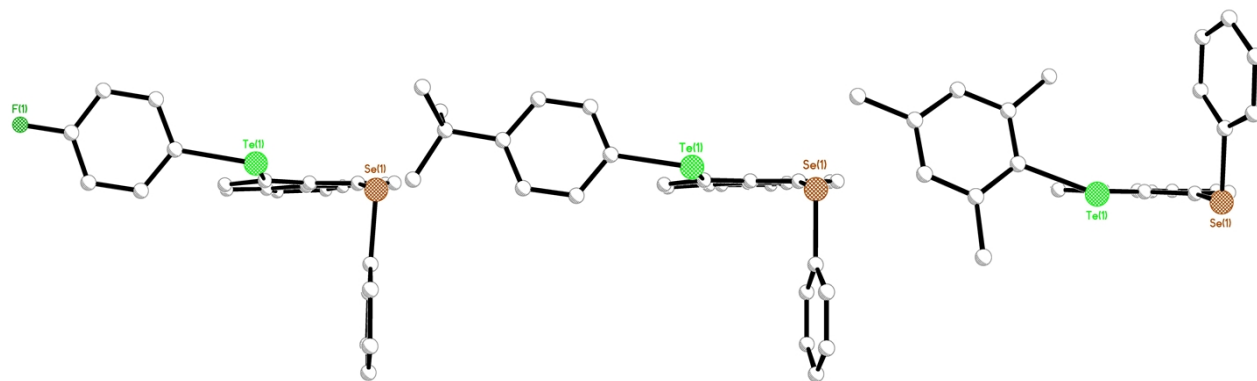


**Figure S2.** The absolute conformation of aromatic rings is calculated from torsion angles  $\theta$  (defining rotation around the E- $C_{\text{Acenap}}$  bond) and  $\gamma$  (defining rotation around the E- $C_{\text{Ar}}$  bond) and classified by types A (axial, perpendicular), B (equatorial, planar) or C (twist) and **pd** (perpendicular), **pl** (planar) or **np** (not planar or perpendicular).<sup>1,2</sup>





**Figure S3.** Molecular structures of compounds 2-9.



**Figure S4.** Compounds **2** Te(Fp), **6** Te(Tp) and **7** Te(Mes) adopt similar (**B:pd**; **A:pl**) type conformations to **8** Te(Tip).

**Table S3.** Crystallographic data for compounds **2-4**.

	<b>2</b>	<b>3</b>	<b>4</b>
Empirical Formula	C <sub>24</sub> H <sub>17</sub> FSeTe	C <sub>25</sub> H <sub>20</sub> SeTe	C <sub>25</sub> H <sub>20</sub> OSeTe
Formula Weight	530.96	526.99	542.99
Temperature (°C)	-148(1)	-100	-148(1)
Crystal Colour, Habit	colorless, block	colorless, prism	colorless, chunk
Crystal Dimensions (mm <sup>3</sup> )	0.120 X 0.090 X 0.060	0.120 X 0.090 X 0.020	0.150 X 0.120 X 0.030
Crystal System	monoclinic	triclinic	monoclinic
Lattice Parameters	a = 9.8746(9) Å	a = 10.854(2) Å	a = 8.212(5) Å
	b = 22.045(2) Å	b = 12.244(2) Å	b = 11.442(2) Å
	c = 9.7763(8) Å	c = 17.599(2) Å	c = 22.113(3) Å
	-	α = 106.370(8)°	-
	β = 116.385(8)°	β = 92.585(7)°	β = 99.96(4)°
	-	γ = 114.888(8)°	-
Volume (Å <sup>3</sup> )	1906.4(4)	1999.4(5)	2046(2)
Space Group	P2 <sub>1</sub> /c	P-1	P2 <sub>1</sub> /n
Z Value	4	4	4
Dcalc (g/cm <sup>3</sup> )	1.850	1.751	1.762
F000	1024	1024	1056
μ(MoKα) (cm <sup>-1</sup> )	34.852	33.155	32.457
No. of Reflections Measured	14559	11859	15073
Rint	0.0296	0.0309	0.0961
Min and Max Transmissions	0.670 - 0.811	0.530 - 0.936	0.486 - 0.907
Independ. Reflection (No. Variables)	3359(244)	6653(489)	3606(253)
Reflection/Parameter Ratio	13.77	13.61	14.25
Residuals: R1 (I>2.00σ(I))	0.0178	0.0343	0.0667
Residuals: R (All Reflections)	0.0216	0.0525	0.1079
Residuals: wR <sub>2</sub> (All Reflections)	0.0652	0.0597	0.1918
Goodness of Fit Indicator	1.261	1.033	1.065
Maximum peak in Final Diff. Map	0.51 e <sup>-</sup> /Å <sup>3</sup>	0.46 e <sup>-</sup> /Å <sup>3</sup>	1.00 e <sup>-</sup> /Å <sup>3</sup>
Minimum peak in Final Diff. Map	-0.53 e <sup>-</sup> /Å <sup>3</sup>	-0.55 e <sup>-</sup> /Å <sup>3</sup>	-2.12 e <sup>-</sup> /Å <sup>3</sup>

**Table S4.** Crystallographic data for compounds **5-7**.

	<b>5</b>	<b>6</b>	<b>7</b>
Empirical Formula	C <sub>25</sub> H <sub>20</sub> OSeTe	C <sub>28</sub> H <sub>26</sub> SeTe	C <sub>27</sub> H <sub>24</sub> SeTe
Formula Weight	542.99	569.07	555.05
Temperature (°C)	-148(1)	-148	-100
Crystal Colour, Habit	colorless, chunk	colorless, chunk	colorless, block
Crystal Dimensions (mm <sup>3</sup> )	0.120 X 0.090 X 0.030	0.120 X 0.090 X 0.060	0.120 X 0.060 X 0.050
Crystal System	triclinic	triclinic	monoclinic
Lattice Parameters	a = 8.645(4) Å	a = 9.656(1) Å	a = 9.7619(7) Å
	b = 14.625(7) Å	b = 10.492(2) Å	b = 30.047(2) Å
	c = 17.253(9) Å	c = 12.795(2) Å	c = 8.084(2) Å
	α = 109.466(12)°	α = 79.476(6)°	-

	$\beta = 97.975(10)^\circ$	$\beta = 73.922(6)^\circ$	$\beta = 113.571(8)^\circ$
	$\gamma = 93.276(6)^\circ$	$\gamma = 70.177(5)^\circ$	-
Volume ( $\text{\AA}^3$ )	2024(2)	1166.2(3)	2173.2(5)
Space Group	P-1	P-1	P2 <sub>1</sub> /c
Z Value	4	2	4
Dcalc (g/cm <sup>3</sup> )	1.782	1.621	1.696
F000	1056	560	1088
$\mu(\text{MoK}\alpha)$ (cm <sup>-1</sup> )	32.812	28.488	30.550
No. of Reflections Measured	15382	8975	14054
Rint	0.0524	0.0232	0.0238
Min and Max Transmissions	0.607 - 0.906	0.703 - 0.843	0.685 - 0.858
Independ. Reflection (No. Variables)	7076(505)	4100(271)	3762(265)
Reflection/Parameter Ratio	14.01	15.13	14.20
Residuals: R1 (I>2.00 $\sigma$ (I))	0.0655	0.0234	0.0213
Residuals: R (All Reflections)	0.0884	0.0298	0.0258
Residuals: $wR_2$ (All Reflections)	0.2857	0.0737	0.0567
Goodness of Fit Indicator	1.226	1.168	1.149
Maximum peak in Final Diff. Map	2.42 e <sup>-</sup> / $\text{\AA}^3$	0.42 e <sup>-</sup> / $\text{\AA}^3$	0.35 e <sup>-</sup> / $\text{\AA}^3$
Minimum peak in Final Diff. Map	-2.33 e <sup>-</sup> / $\text{\AA}^3$	-0.43 e <sup>-</sup> / $\text{\AA}^3$	-0.36 e <sup>-</sup> / $\text{\AA}^3$

**Table S5.** Crystallographic data for compounds **8** and **9**.

	<b>8</b>	<b>9</b>
Empirical Formula	C <sub>33</sub> H <sub>36</sub> SeTe	C <sub>28</sub> H <sub>20</sub> SeTe
Formula Weight	639.21	563.03
Temperature (°C)	-148	-148(1)
Crystal Colour, Habit	colorless, chunk	colorless, chunk
Crystal Dimensions (mm <sup>3</sup> )	0.120 X 0.090 X 0.030	0.150 X 0.060 X 0.030
Crystal System	monoclinic	monoclinic
Lattice Parameters	a = 14.697(2) $\text{\AA}$	a = 29.375(3) $\text{\AA}$
	b = 14.367(2) $\text{\AA}$	b = 7.6824(8) $\text{\AA}$
	c = 14.835(2) $\text{\AA}$	c = 19.044(2) $\text{\AA}$
	-	-

	$\beta = 119.048(9)^\circ$	$\beta = 95.737(7)^\circ$
	-	-
Volume ( $\text{\AA}^3$ )	2738.6(5)	4276.1(8)
Space Group	P2 <sub>1</sub> /n	C2/c
Z Value	4	8
Dcalc (g/cm <sup>3</sup> )	1.550	1.749
F000	1280	2192
$\mu(\text{MoK}\alpha)$ (cm <sup>-1</sup> )	24.355	31.070
No. of Reflections Measured	20535	15814
Rint	0.0414	0.0351
Min and Max Transmissions	0.748 - 0.930	0.727 - 0.911
Independ. Reflection (No. Variables)	4827(316)	3763(271)
Reflection/Parameter Ratio	15.28	13.89
Residuals: R1 (I>2.00 $\sigma$ (I))	0.0284	0.0248
Residuals: R (All Reflections)	0.0382	0.0303
Residuals: wR <sub>2</sub> (All Reflections)	0.1078	0.0539
Goodness of Fit Indicator	1.288	1.097
Maximum peak in Final Diff. Map	0.75 e <sup>-</sup> / $\text{\AA}^3$	0.74 e <sup>-</sup> / $\text{\AA}^3$
Minimum peak in Final Diff. Map	-0.88 e <sup>-</sup> / $\text{\AA}^3$	-0.39 e <sup>-</sup> / $\text{\AA}^3$

#### 4. Computational Analyses

Starting from the coordinates from X-ray crystallography, geometries were fully optimized in the gas phase at the B3LYP level<sup>3</sup> using the Stuttgart-Dresden (SDD) effective core potential along with its double zeta valence basis sets for Te<sup>4</sup> (augmented with a set of d-polarization functions with exponent 0.237),<sup>5</sup> Curtis and Binning's 962(d) basis<sup>6</sup> on Se and 6-31G(d) basis elsewhere. Wiberg bond indices<sup>7</sup> were obtained in a natural bond orbital analysis<sup>8</sup> at the same level. This or similar levels have been useful for interpreting experimental findings for *peri*-naphthalene telluride derivatives.<sup>9</sup> Compound **1** was reoptimised using the PBE0 hybrid functional.<sup>10</sup> A fine integration grid (75 radial shells with 302 angular points per shell) was used throughout. These computations were performed using the Gaussian 09 program.<sup>11</sup>

Indirect spin-spin coupling constants (SSCCs) were computed<sup>12</sup> at the BP86<sup>13</sup> level for the B3LYP minima (for **1**, also at the PBE0<sup>10</sup> level using the PBE0 structure<sup>14</sup>) with the relativistic zeroth-order regular approximation including spin-orbit coupling (ZORA-SO),<sup>15,16</sup> together with a TZ2P basis of Slater-type orbitals and a fine integration grid (Integration 6). These calculations were performed with the ADF program.<sup>17,18</sup>

#### 5. References

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