Supporting informations

Solid state structure and solution behaviour of organoselenium(II) compounds containing 2-{$E(CH_2CH_2)_2NCH_2$}C_6H_4 groups (E = O, NMe)

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Solid state structure - supramolecular architectures

$[2\text{-}\{MeN(CH_2CH_2)_2NCH_2\}C_6H_4]_2Se_2$ (2)

- the crystal contains a 1:1 mixture of 1:1 mixtures of (R_{N1},S_{N3}) and (S_{N1},R_{N3}) isomers
- the crystal contains parallel chains built from either (R_{N1},S_{N3}) or (S_{N1},R_{N3}) isomers

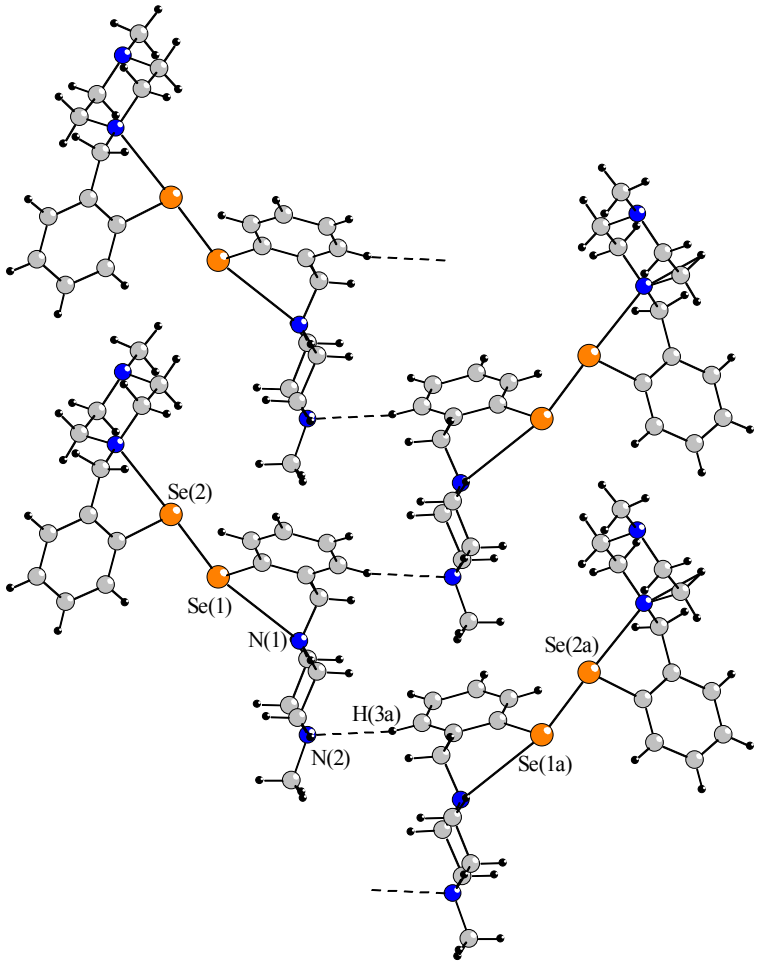


Figure S1. View along *c* axis of the chain polymer of (R_{N1},S_{N3})-**2** isomers based on intermolecular hydrogen contacts. Symmetry equivalent positions: H(3a) (2.5-x, -0.5+y, 0.5-z). Intermolecular contacts within a chain: N(2)···H(3a)$_{aryl}$ 2.67 Å (c.f. $\sum r_{vdW}$(N,H) 2.74 Å). No further inter-chain contacts.

[2-{O(CH$_2$CH$_2$)$_2$NCH$_2$}C$_6$H$_4$]SeCl (3)

- the crystal contains only the *S* isomer
- intramolecular distances Cl(1)···H(6) 2.67 Å $\sum r_{vdW}$(Cl,H) 3.01 Å

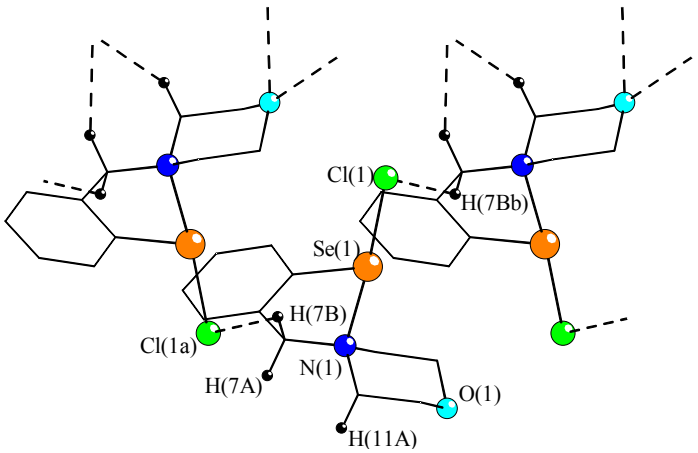


Figure S2. View of the chain polymer of *S*-**2** isomers based on intermolecular hydrogen contacts (only hydrogens involved in intermolecular interactions are shown). Symmetry equivalent positions: Cl(1a) (-0.5+x, 0.5-y, -z); H(7Bb) (0.5+x, 0.5-y, -z). Intermolecular contacts within a chain: Cl(1)···H(7Bb)$_{methylene}$ 2.89 Å.

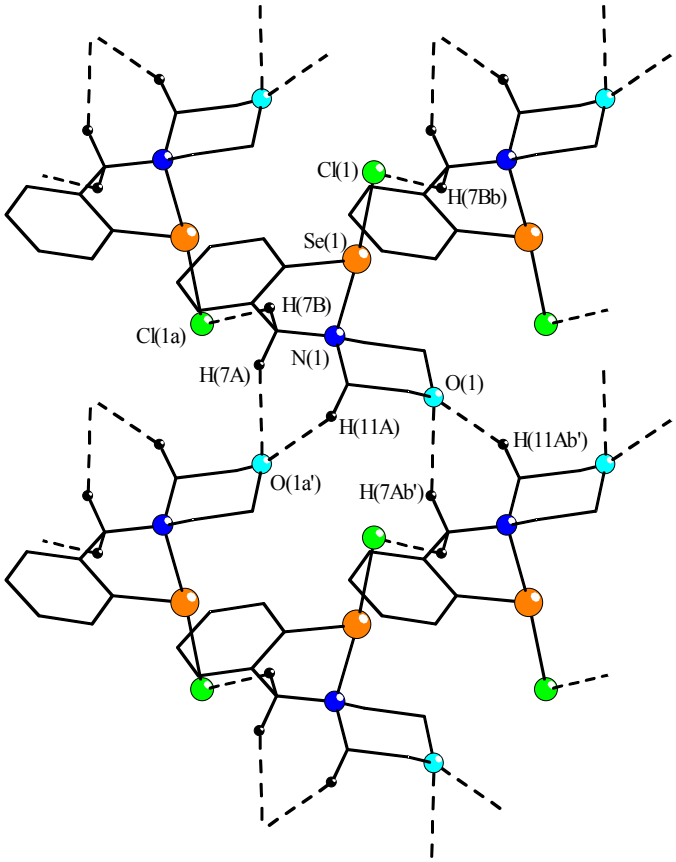


Figure S3. View of a layer network built from parallel chains of *S*-**2** isomers, connected through inter-chain hydrogen contacts (only hydrogens involved in intermolecular interactions are shown). Symmetry equivalent positions: O(1a') (-0.5+x, -0.5-y, -z); H(7Ab'), H(11Ab') (0.5+x, -0.5-y, -z). Intermolecular contacts between chains: O(1)···H(7Ab')$_{methylene}$ 2.50 Å, O(1)···H(11Ab')$_{N\text{-}methylene\text{-}ring}$ 2.56 Å (c.f. $\sum r_{vdW}$(O,H) 2.60 Å). No further inter-layer contacts.

[2-{O(CH$_2$CH$_2$)$_2$NCH$_2$}C$_6$H$_4$]SeBr·HBr (4·HBr)

- intramolecular distances Br(2)···H(2) 2.555(7) Å $\sum r_{vdW}$(Br,H) 3.15 Å

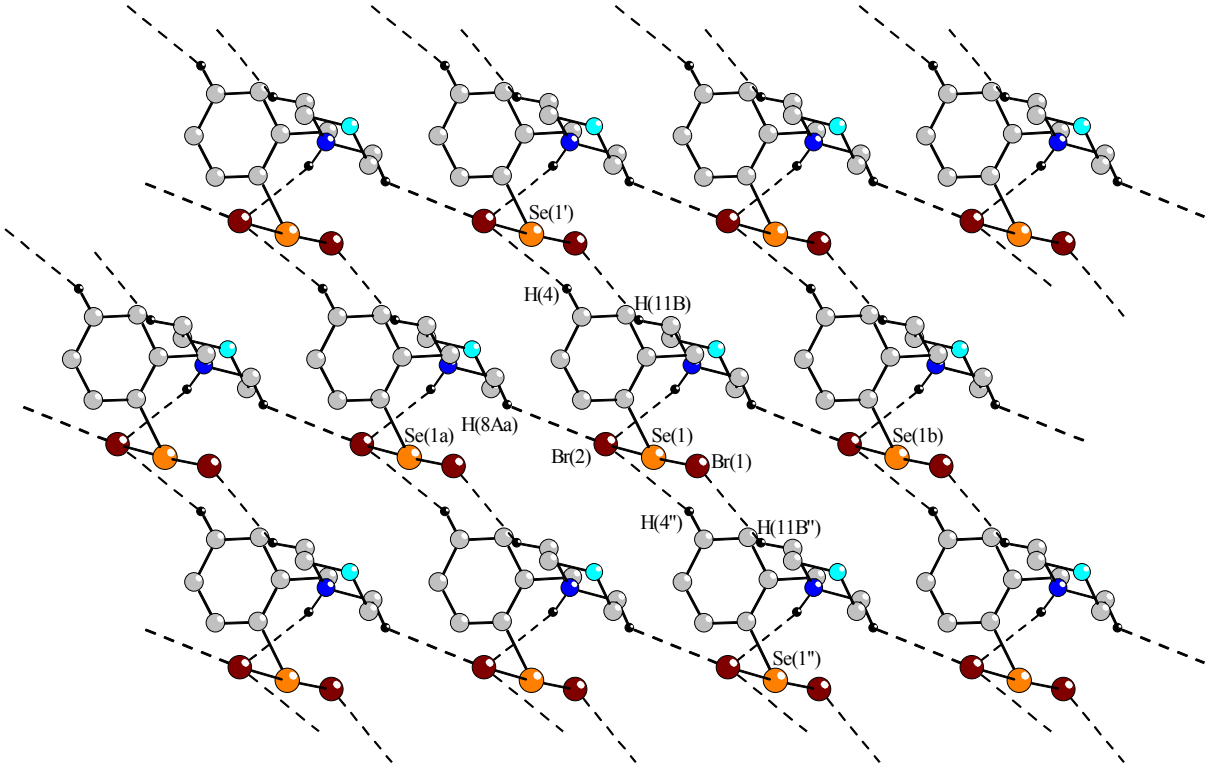


Figure S4. View along *a* axis of the layer network built from **4**·HBr units through intermolecular hydrogen contacts (only hydrogens involved in hydrogen contacts are shown). Symmetry equivalent positions: Se(1a) (x, y, 1+z); Se(1b) (x, y, -1+z); Se(1') (1.5-x, 0.5+y, 0.5+z); Se(1'') (1.5-x, -0.5+y, -0.5+z). Intermolecular contacts within a layer: Br(1)···H(11B'')$_{\text{N-methylene-ring}}$ 3.02 Å, Br(2)···H(8Aa)$_{\text{N-methylene-ring}}$ 3.05 Å, Br(2)···H(4'')$_{\text{aryl}}$ 3.06 Å.

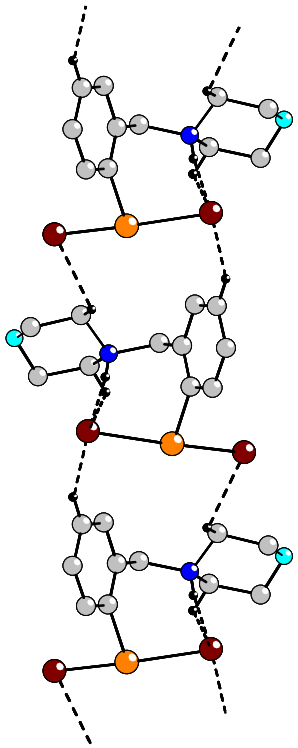


Figure S5. View along *c* axis of the layer network in the crystal of **4**·HBr.

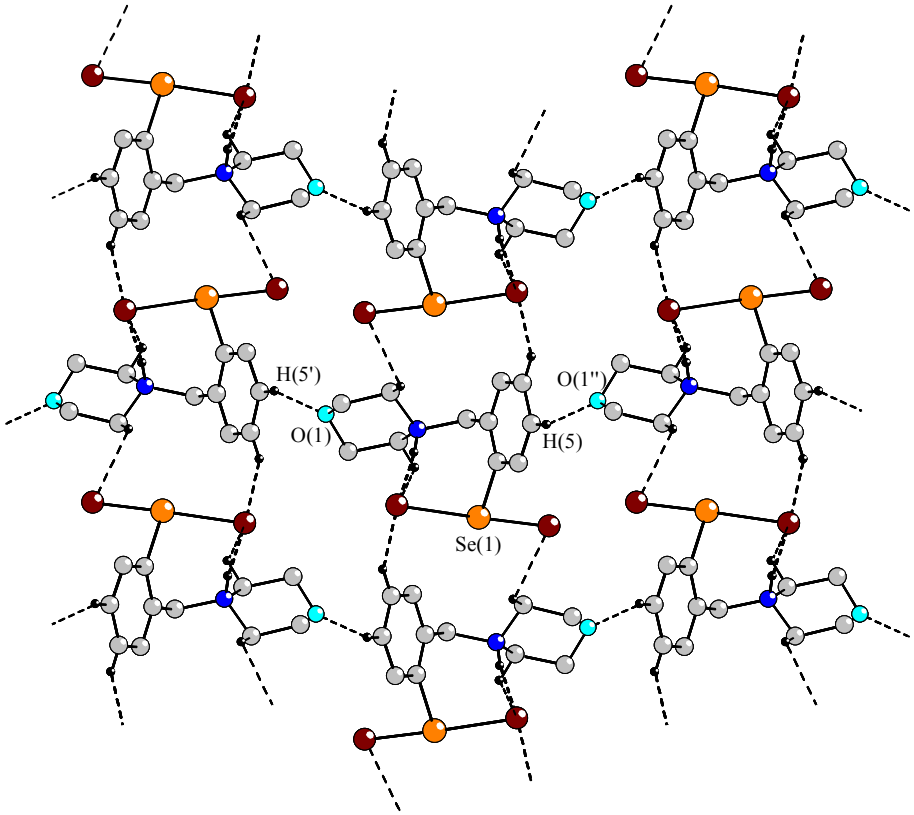


Figure S6. View along *c* axis of the tridimensional network in the crystal of **4**·HBr built through inter-layer hydrogen contacts (only hydrogens involved in hydrogen contacts are shown). Symmetry equivalent positions: H(5') (-0.5+x, 0.5-y, -1+z); O(1'') (0.5+x, 0.5-y, 1+z). Intermolecular contacts between layers: O(1)···H(5')$_{aryl}$ 2.37 Å (c.f. $\sum r_{vdW}$(O,H) 2.60 Å).

[2-{O(CH$_2$CH$_2$)$_2$NCH$_2$}C$_6$H$_4$]SeI (5)

- the crystal contains a 1:1 mixture of *R* and *S* isomers
- intramolecular distances I(1)···H(6) 2.96 Å $\sum r_{vdW}$(I,H) 3.35 Å

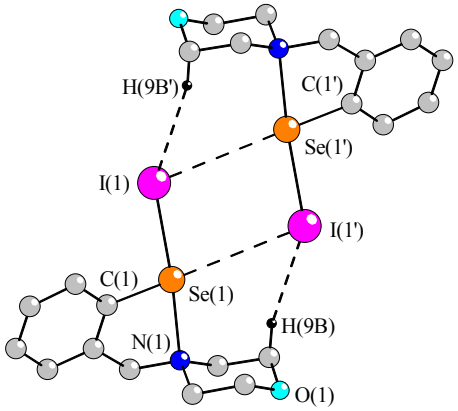


Figure S7. View of the dimer association of *R* and *S* isomers in the crystal of **5** (only hydrogens involved in hydrogen contacts are shown). Symmetry equivalent positions: Se(1') (2-x, -y, 1-z). Intermolecular contacts within the dimer unit: Se(1)···I(1') 3.96 Å; I(1)···H(9B')$_{O\text{-methylene-ring}}$ 3.28 Å (c.f. $\sum r_{vdW}$(Se,I) 4.15 Å).

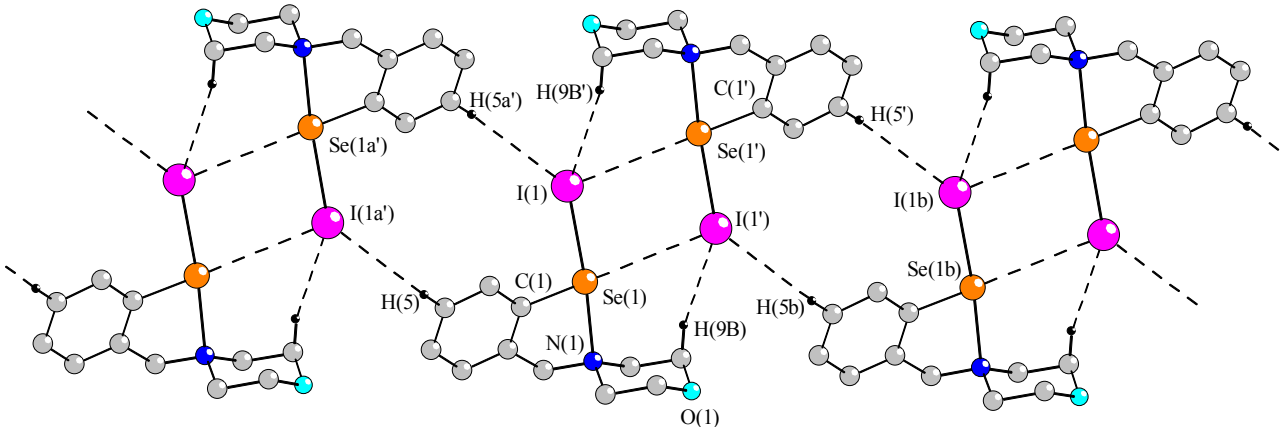


Figure S8. View of the columnar chain polymer in the crystal of **5** based on hydrogen contacts between dimer units (only hydrogens involved in hydrogen contacts are shown). Symmetry equivalent positions: Se(1a') (2-x, -y, 2-z); Se(1b) (x, y, -1+z). Inter-dimer contacts within a chain: I(1)···H(5a')$_{aryl}$ 3.29 Å.

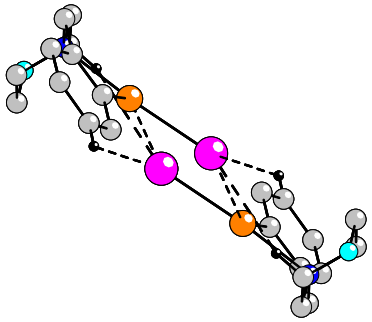


Figure S9. View along *c* axis of the columnar chain polymer in the crystal of **5**.

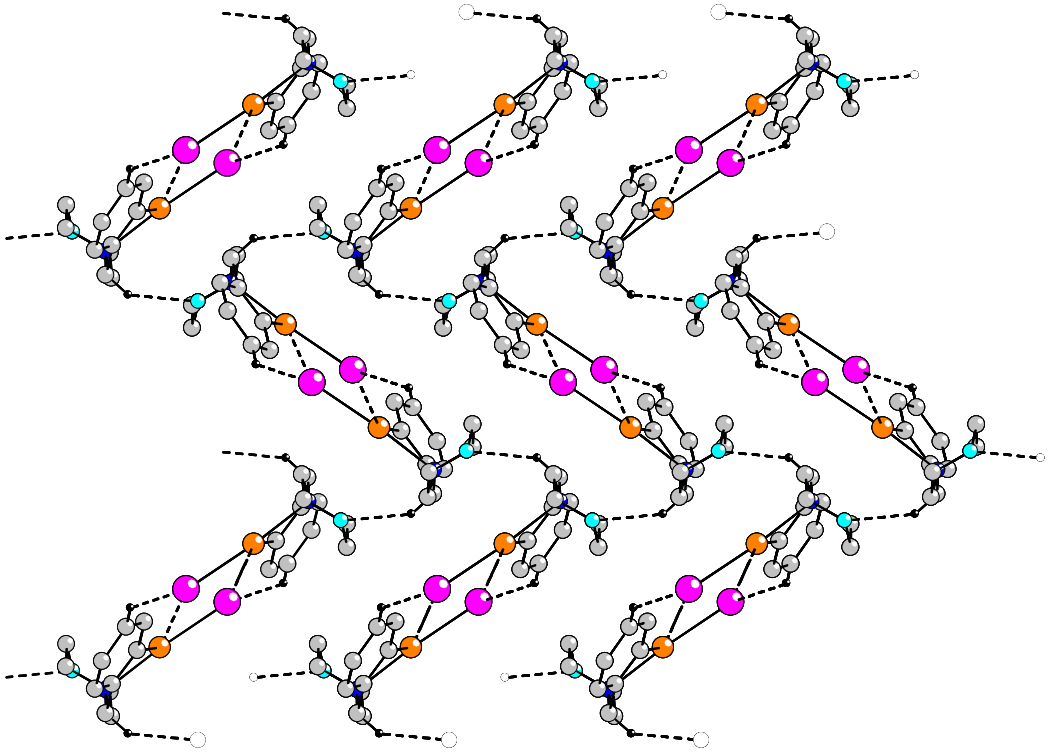


Figure S10. View along *c* axis of the tridimesional network built from columnar chain polymers in the crystal of **5**, through oxygen-hydrogen inter-chain contacts (only hydrogens involved in hydrogen contacts are shown). Inter-chain contacts: O(1)···H(7B)$_{methylene}$ 2.51 Å (c.f. $\sum r_{vdW}$(O,H) 2.60 Å).

[2-{MeN(CH$_2$CH$_2$)$_2$NCH$_2$}C$_6$H$_4$]SeI (6)

- the crystal contains a 1:1 mixture of *R* and *S* isomers
- intramolecular distances I(1)···H(6) 2.87 Å $\sum r_{vdW}$(I,H) 3.35 Å

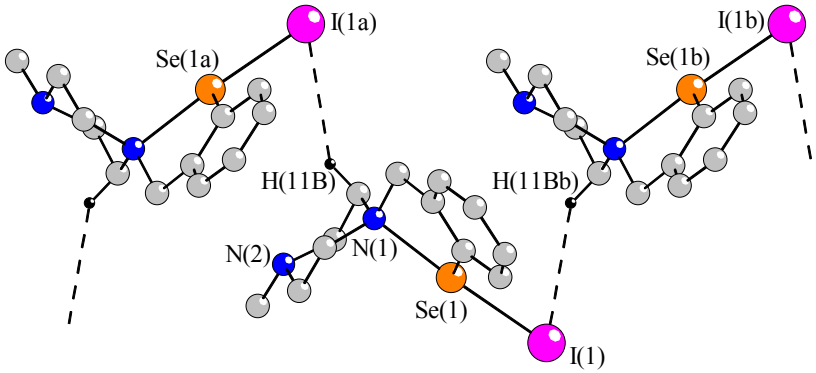


Figure S11. View along *a* axis of the chain polymer of alternating *S* and *R* isomers in the crystal of **6** (only hydrogens involved in intermolecular interactions are shown). Symmetry equivalent positions: Se(1a) (x, 1.5-y, 0.5+z); Se(1b) (x, 1.5-y, -0.5+z). Intermolecular contacts within a chain: I(1)···H11Bb)$_{N\text{-methylene-ring}}$ 3.31 Å. No further inter-chain contacts.

Solution behaviour

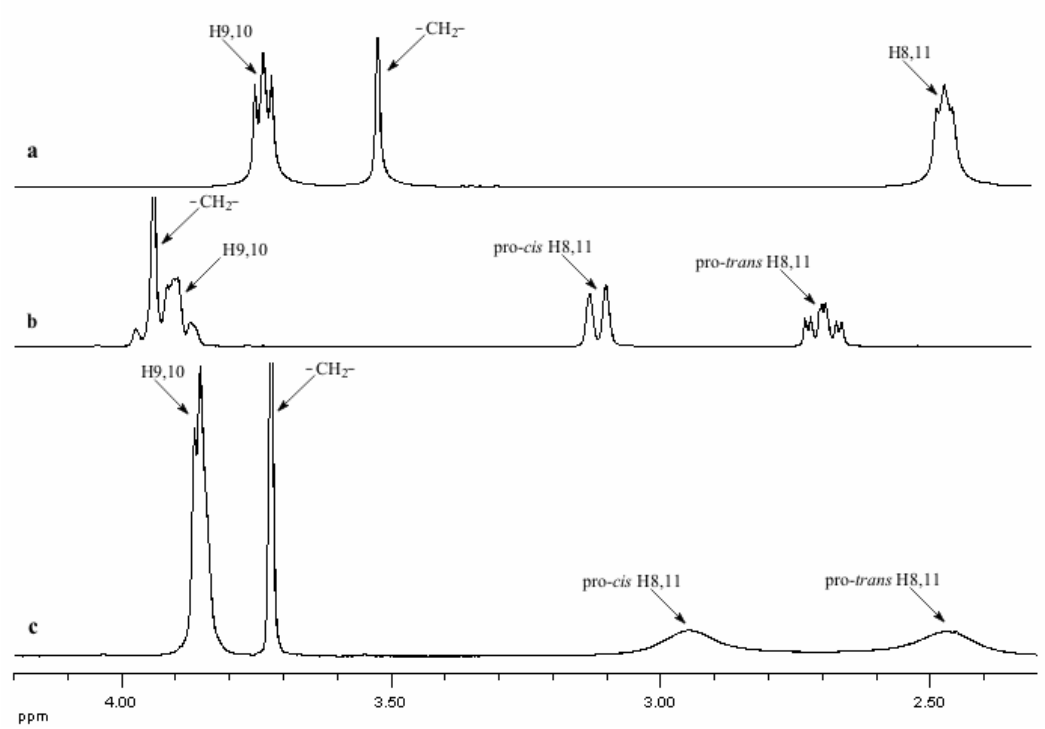


Figure S12. The aliphatic region of the ^{1}H NMR spectrum ($CDCl_3$, 400 MHz, 26ºC) of (a) [2-O(CH_2CH_2)$_2$NCH_2]C_6H_5; (b) [2-{O(CH_2CH_2)$_2$NCH_2}C_6H_4]SeCl (**3**); (c) [2-{O(CH_2CH_2)$_2$NCH_2}C_6H_4]SeI (**5**).

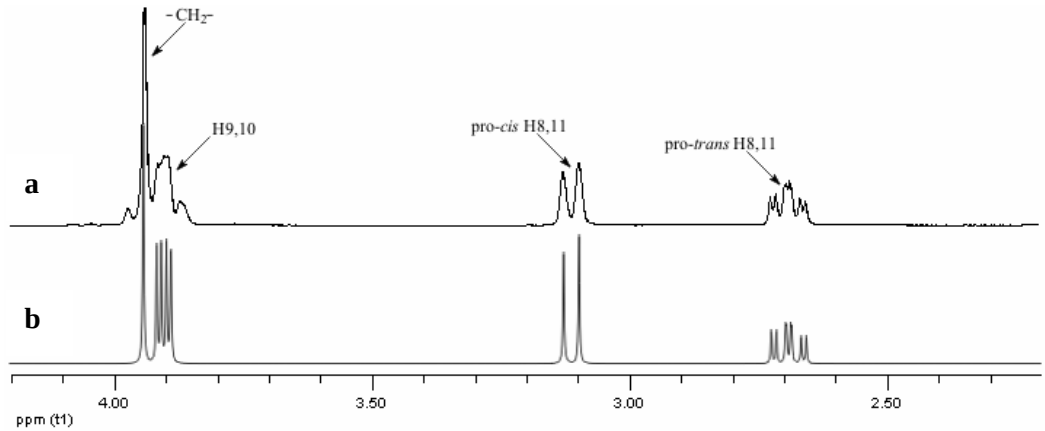


Figure S13. (a) The aliphatic region of the ^{1}H NMR spectrum of [2-{O(CH_2CH_2)$_2$NCH_2}C_6H_4]SeCl (**3**) ($CDCl_3$, 400 MHz, 26ºC), and (b) simulation of the ^{1}H aliphatic region for **3** on the basis of the following parameters:

δ 2.690 ppm [ddd, N-C*H*$_2$-CH_2, pro-*trans*-$H_{8,11}$, $^{2}J_{HH}$ 12.0, $^{3}J_{HH}$ 11.1, $^{3}J_{HH}$ 4.0 Hz];
δ 3.110 ppm [d, N-C*H*$_2$-CH_2, pro-*cis*-$H_{8,11}$, $^{2}J_{HH}$ 12.0];
δ 3.900 ppm [m, -CH_2-C*H*$_2$-O, $H_{9,10}$, $^{3}J_{HH}$ 11.1, $^{3}J_{HH}$ 4.0 Hz (with pro-*trans*-$H_{8,11}$)];
δ 3.940 ppm [s, C_6H_4-C*H*$_2$-N, H_7].

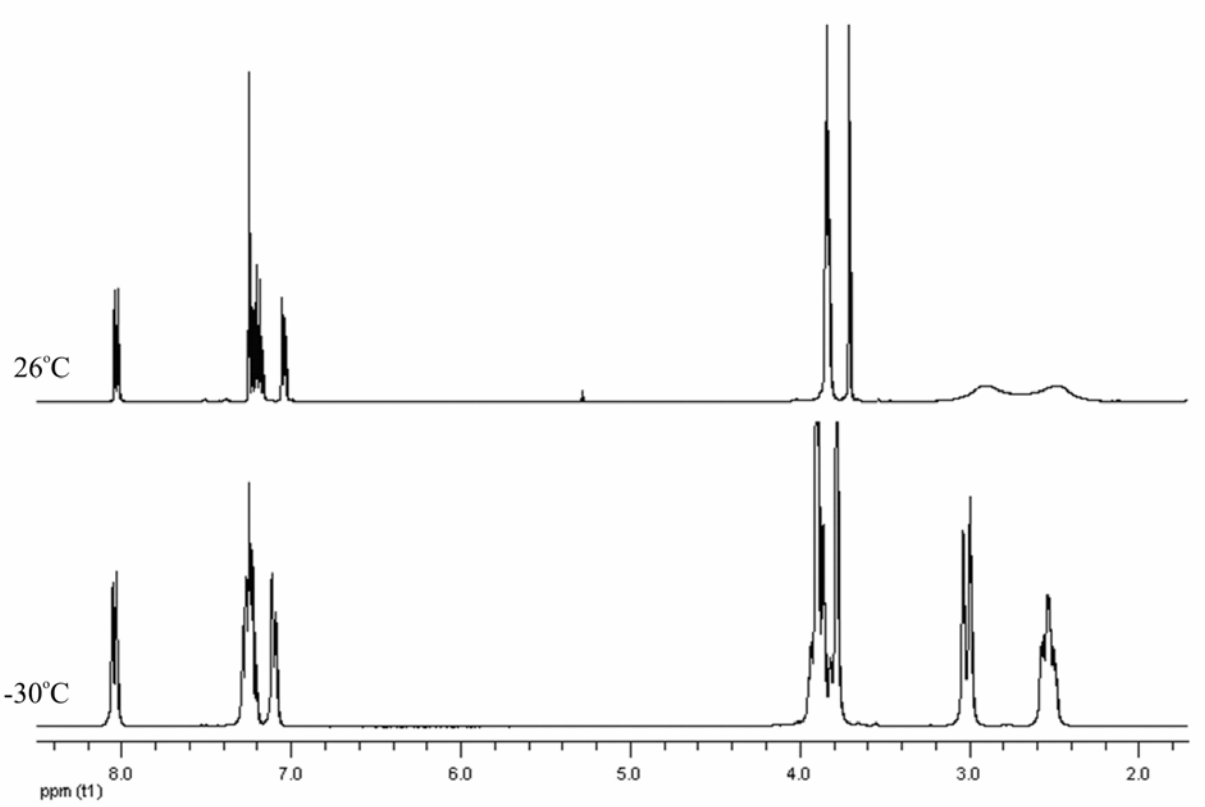
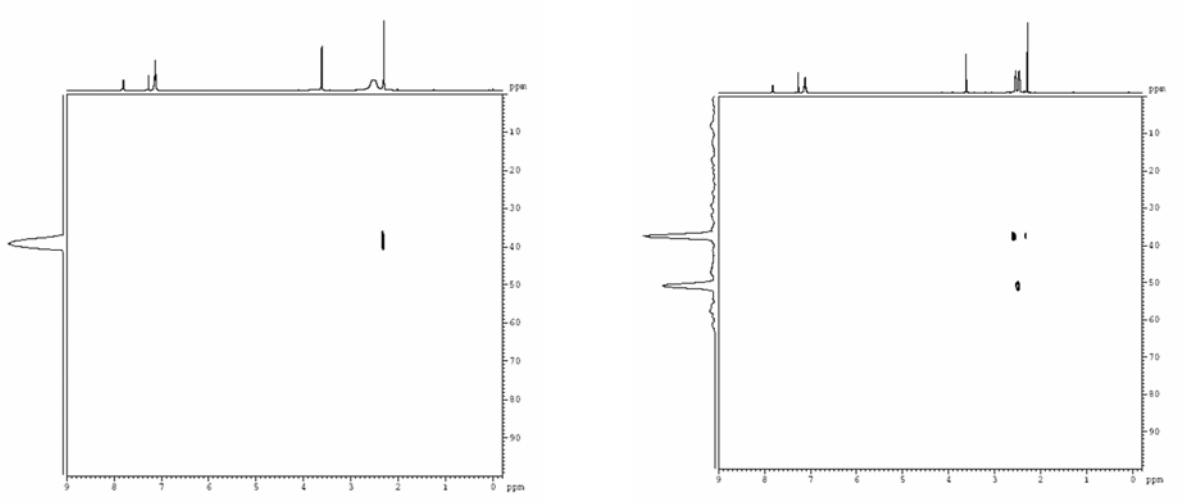


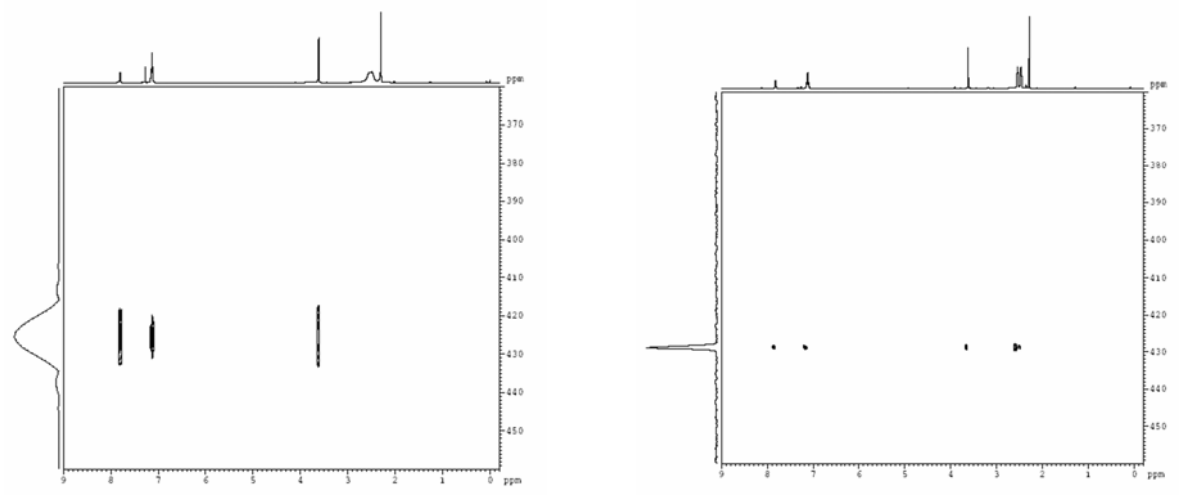
Figure S14. ^{1}H NMR spectra ($CDCl_3$) for [2-{$O(CH_2CH_2)_2NCH_2$}C_6H_4]SeI (**5**) at (a) 26 ºC (400 MHz), and (b) -30 ºC (300 MHz).

[2-{MeN(CH_2CH_2)$_2$NCH_2}C_6H_4]$_2$$Se_2$ (2)



(a) (b)

Figure S15. The 2D indirectly detected H,N-HMBC spectra (400 MHz, $CDCl_3$) for **2**: (a) 26 ºC; (b) 60 ºC.



(a) (b)

Figure S16. The 2D indirectly detected H,Se-HMBC spectra (400 MHz, $CDCl_3$) for **2**: (a) 26 ºC; (b) 60 ºC.

[2-{O(CH$_2$CH$_2$)$_2$NCH$_2$}C$_6$H$_4$]SeCl (3)

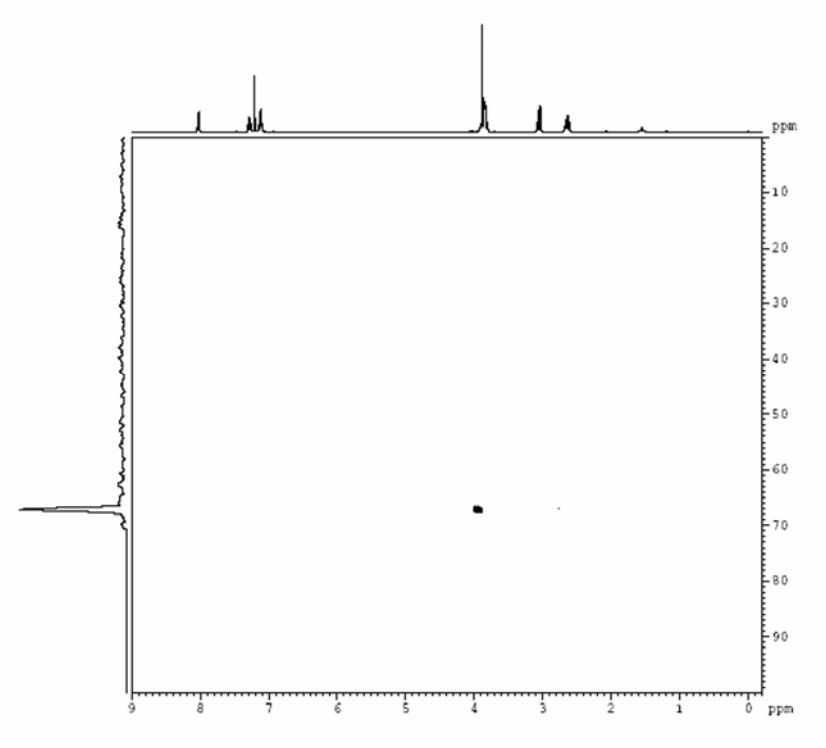


Figure S17. The 2D indirectly detected H,N-HMBC spectra (400 MHz, $CDCl_3$) for **3**, at 26 ºC.

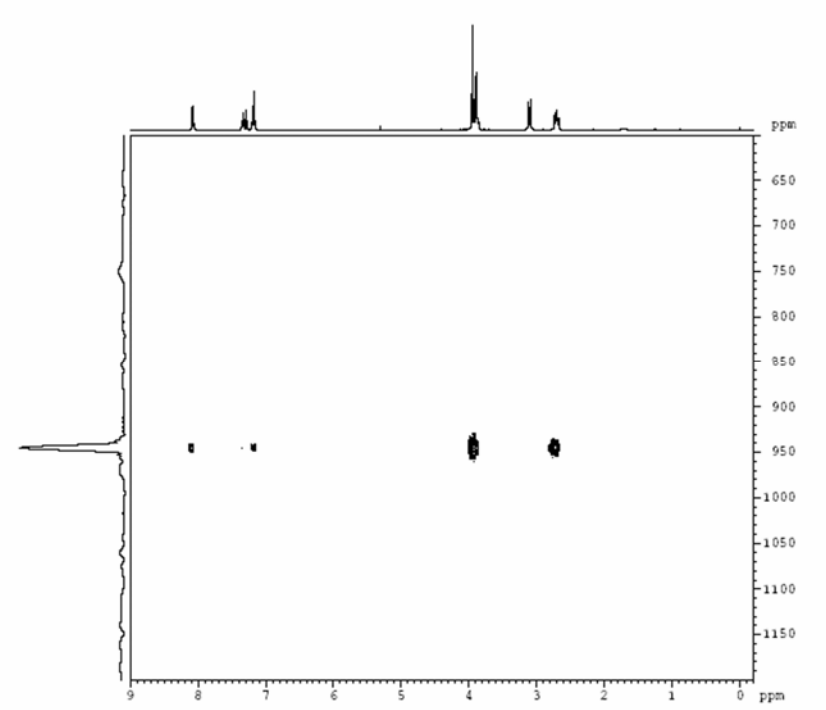


Figure S18. The 2D indirectly detected H,Se-HMBC spectra (400 MHz, $CDCl_3$) for **3**, at 26 ºC.

[2-{O(CH$_2$CH$_2$)$_2$NCH$_2$}C$_6$H$_4$]SeI (5)

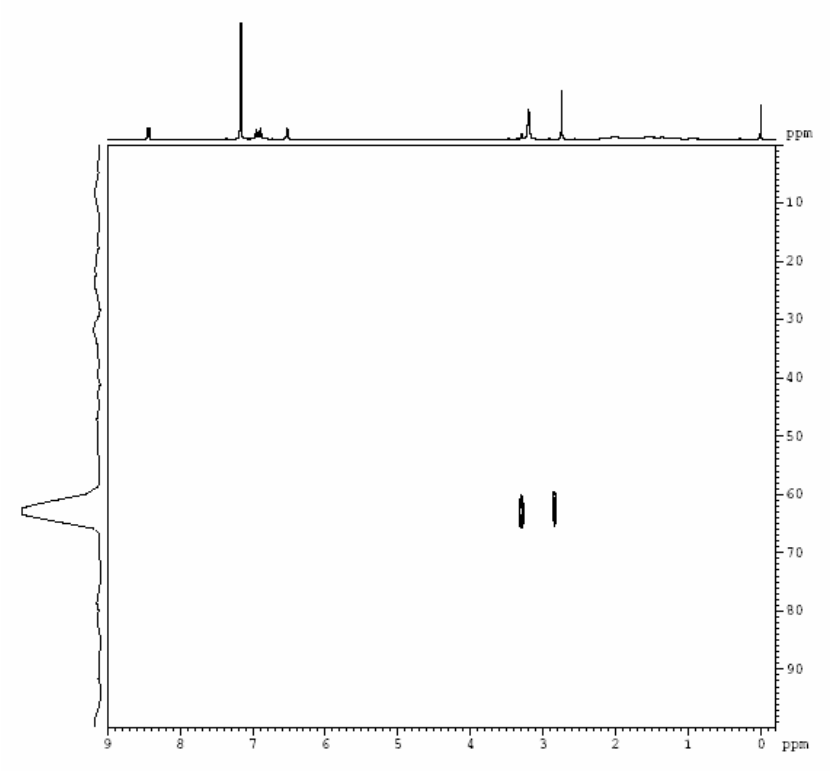


Figure S19. The 2D indirectly detected H,N-HMBC spectra (400 MHz, C_6D_6) for **5**, at 26 ºC.

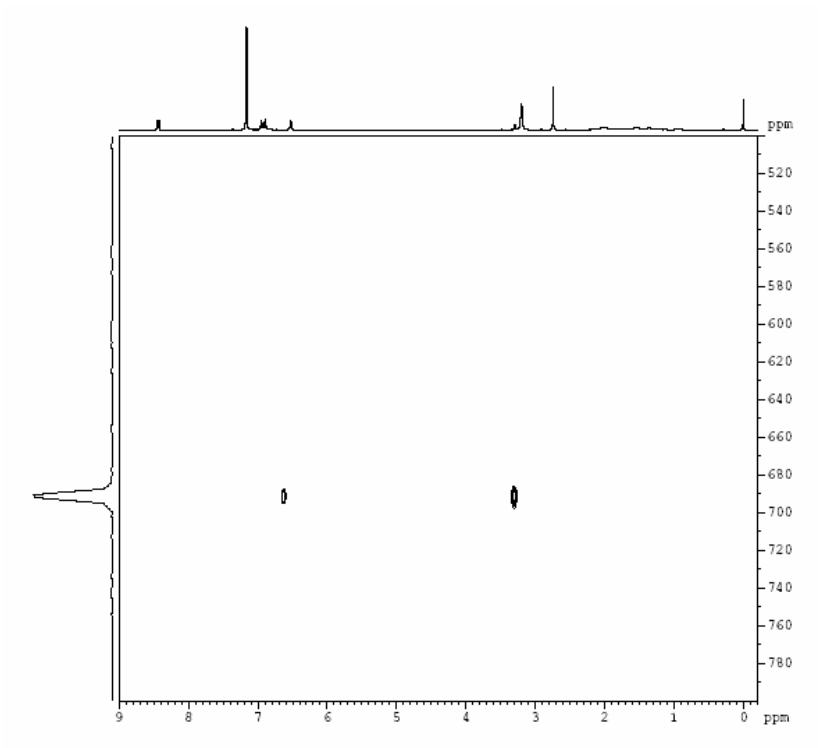
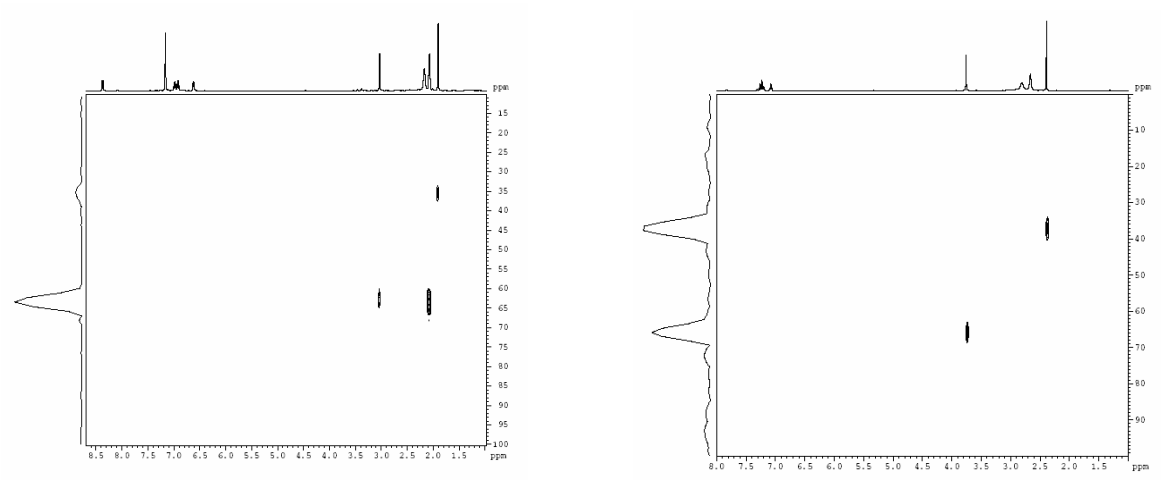


Figure S20. The 2D indirectly detected H,Se-HMBC spectra (400 MHz, C_6D_6) for **5**, at 26 ºC.

[2-{MeN(CH_2CH_2)$_2$NCH_2}C_6H_4]SeI (6)



(a) (b)

Figure S21. The 2D indirectly detected H,N-HMBC spectra (400 MHz) for **6**: (a) 65 ºC (C_6D_6); (b) 60 ºC ($CDCl_3$).

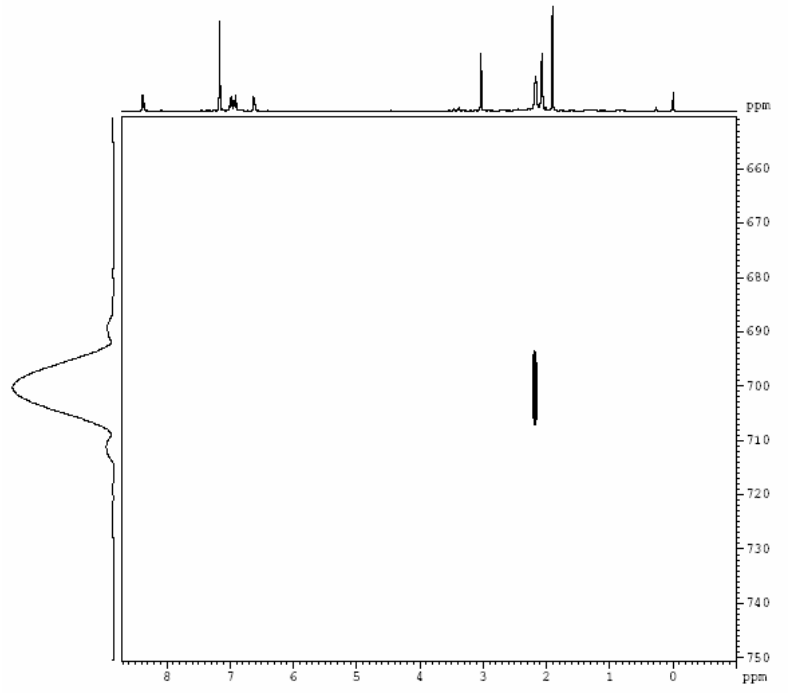


Figure S22. The 2D indirectly detected H,Se-HMBC spectra (400 MHz, C_6D_6) for **6**, at 65 ºC.