

Chalcogen bonding interactions in a series of aromatic organic selenocyanates

Jan Alfuth,^{a,b} Olivier Jeannin,^a and Marc Fourmigué^{a,*}

^a Université de Rennes, CNRS, ISCR (Institut des Sciences Chimiques de Rennes) UMR 6226, 35000 Rennes, France

^b Department of Organic Chemistry, Gdańsk University of Technology, 80-233 Gdańsk, Poland

SUPPLEMENTARY INFORMATION

Fig S1, S2	page 2
Table S1	page 3
ESP calculations, Table S2	page 5
NMR spectra	page 6

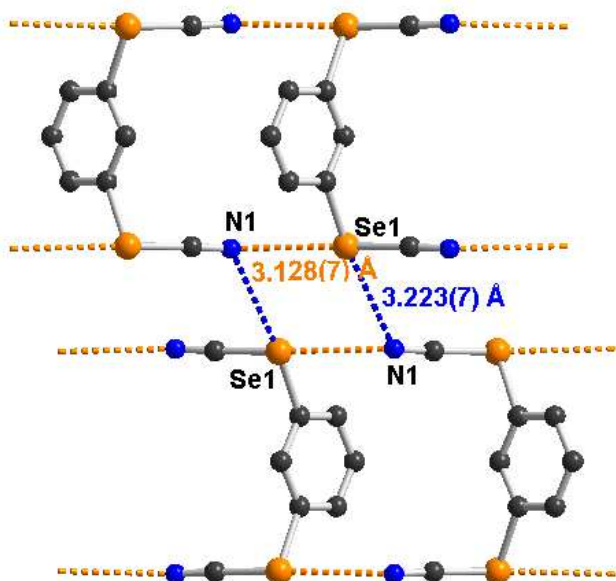


Fig S1 Detail of the solid-state organization for **2**. ChB interactions in the prolongation of the (NC)–Se bonds are in orange dotted lines, those in the prolongation of the C_{Ar}–Se bond in blue dotted lines.

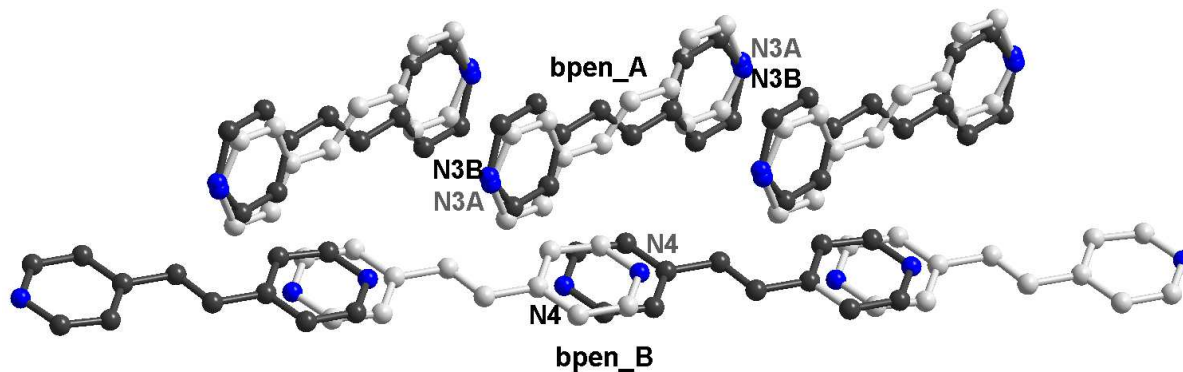


Fig S2 Detail of the disorder model of the two crystallographically independent bpen molecules in its adduct with

Table S1 Crystallographic data

Compound	1d	2	3
CCDC	2280515	2280516	2280517
Formula	C ₁₂ H ₁₂ N ₂ Se ₂	C ₈ H ₄ N ₂ Se ₂	C ₆ H ₂ N ₂ SSe ₂
FW (g·mol ⁻¹)	342.16	286.05	292.08
T (K)	150(2)	293(2)	150(2)
Crystal system	monoclinic	orthorhombic	orthorhombic
Space group	P2 ₁ /c	Pnma	Pnma
a (Å)	18.0460(12)	11.563(6)	11.2833(19)
b (Å)	8.3234(5)	17.139(8)	18.088(3)
c (Å)	18.3738(12)	4.8436(19)	4.0560(7)
α (deg)	90.00	90.00	90.00
β (deg)	118.457(3)	90.00	90.00
γ (deg)	90.00	90.00	90.00
V (Å ³)	2426.4(3)	959.9(8)	827.8(2)
Z	8	4	4
Cryst. dim. (mm)	0.34×0.12×0.10	0.15×0.06×0.02	0.15×0.05×0.04
D _{calc} (g·cm ⁻³)	1.873	1.979	2.344
Radiation source	Mo-Kα	Mo-Kα	Mo-Kα
μ (mm ⁻¹)	6.068	7.648	9.114
Total refls	16796	5309	6457
Abs. corr.	multi-scan	multi-scan	multi-scan
T _{min} , T _{max}	0.422, 0.545	0.582, 0.858	0.585, 0.695
Uniq refls (R _{int})	5489 (0.0467)	1132 (0.0792)	990 (0.0272)
Refl. (I > 2σ(I))	3820	672	935
GOF	0.977	1.056	1.095
R1, wR2 (I > 2σ(I))	0.0373, 0.0609	0.0688, 0.1798	0.0182, 0.0449
R1, wR2 (all data)	0.0694, 0.0669	0.1206, 0.2156	0.0194, 0.0453
Res. dens. (e/Å ³)	+0.623, -0.644	+1.056, -1.424	+0.614, -0.481

Table S1 (continued) Crystallographic data

Compound	4	(2) ₂ (bpen_A)(bpen_B) _{0.5}	(4) (bpen)
CCDC	2280518	2280519	2280520
Formula	C ₈ H ₄ N ₂ Se ₂	C ₃₄ H ₂₃ N ₇ Se ₄	C ₂₀ H ₁₄ N ₄ Se ₂
FW (g·mol ⁻¹)	286.05	845.43	468.27
T (K)	150(2)	150(2)	150(2)
Crystal system	monoclinic	triclinic	monoclinic
Space group	P2 ₁ /c	P $\bar{1}$	P2 ₁ /c
a (Å)	9.1170(12)	7.4494(15)	8.8342(15)
b (Å)	4.0552(5)	9.201(2)	14.079(3)
c (Å)	11.8113(13)	12.306(3)	7.6447(14)
α (deg)	90.00	74.580(8)	90.00
β (deg)	95.910(5)	89.306(7)	110.592(7)
γ (deg)	90.00	88.669(7)	90.00
V (Å ³)	434.36(9)	812.9(3)	890.1(3)
Z	2	1	2
Cryst. dim. (mm)	0.11×0.05×0.03	0.13×0.08×0.03	0.09×0.08×0.06
D _{calc} (g·cm ⁻³)	2.187	1.727	1.747
Radiation source	Mo-K α	Mo-K α	Mo-K α
μ (mm ⁻¹)	8.451	4.55	4.165
Total refls	4064	16229	8351
Abs. corr.	multi-scan	multi-scan	multi-scan
T _{min} , T _{max}	0.608, 0.776	0.652, 0.872	0.694, 0.779
Uniq refls (R _{int})	958 (0.025)	3325 (0.0448)	2014 (0.0299)
Refl. (I > 2 σ (I))	850	2964	1906
GOF	1.114	1.136	1.095
R1, wR2 (I > 2 σ (I))	0.0184, 0.0422	0.0320, 0.0759	0.0194, 0.0498
R1, wR2 (all data)	0.0214, 0.0435	0.0361, 0.0783	0.021, 0.0507
Res. dens. (e/Å ³)	+0.305, -0.514	+0.637, -0.58	+0.382, -0.52

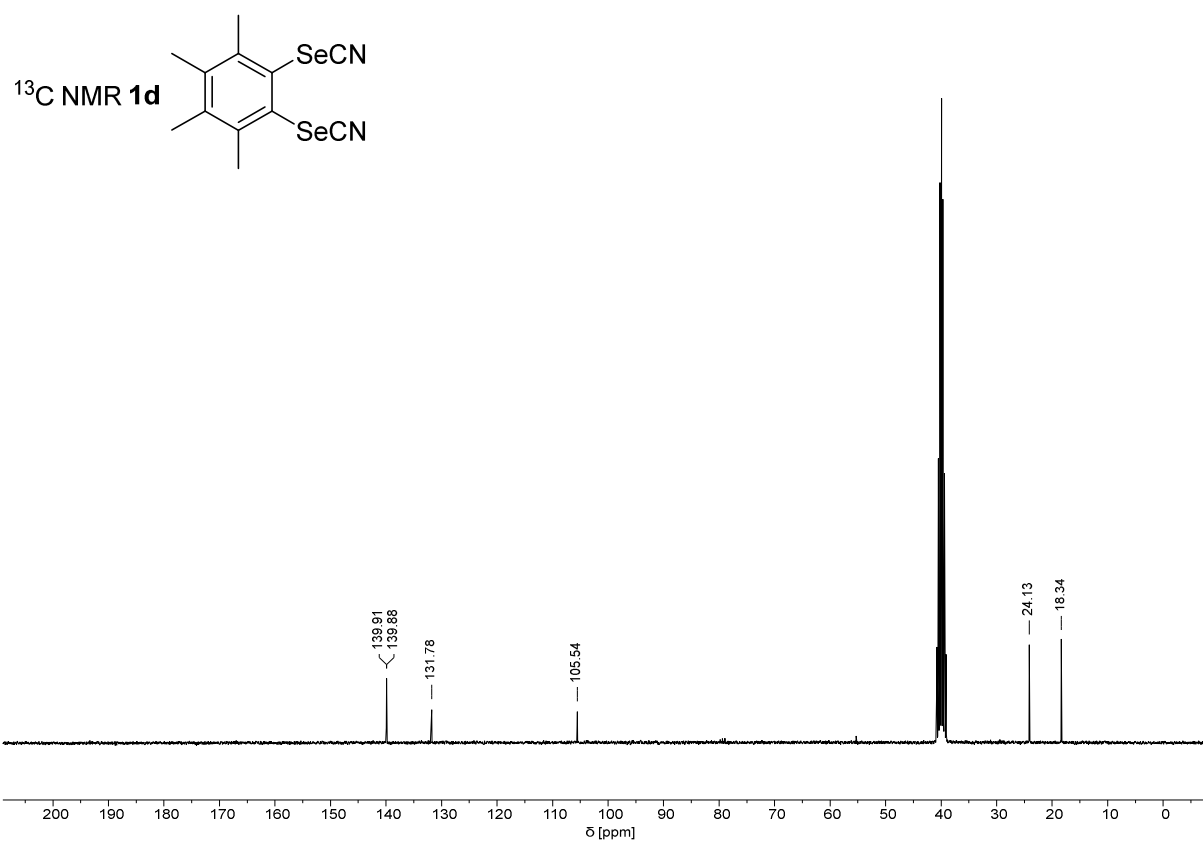
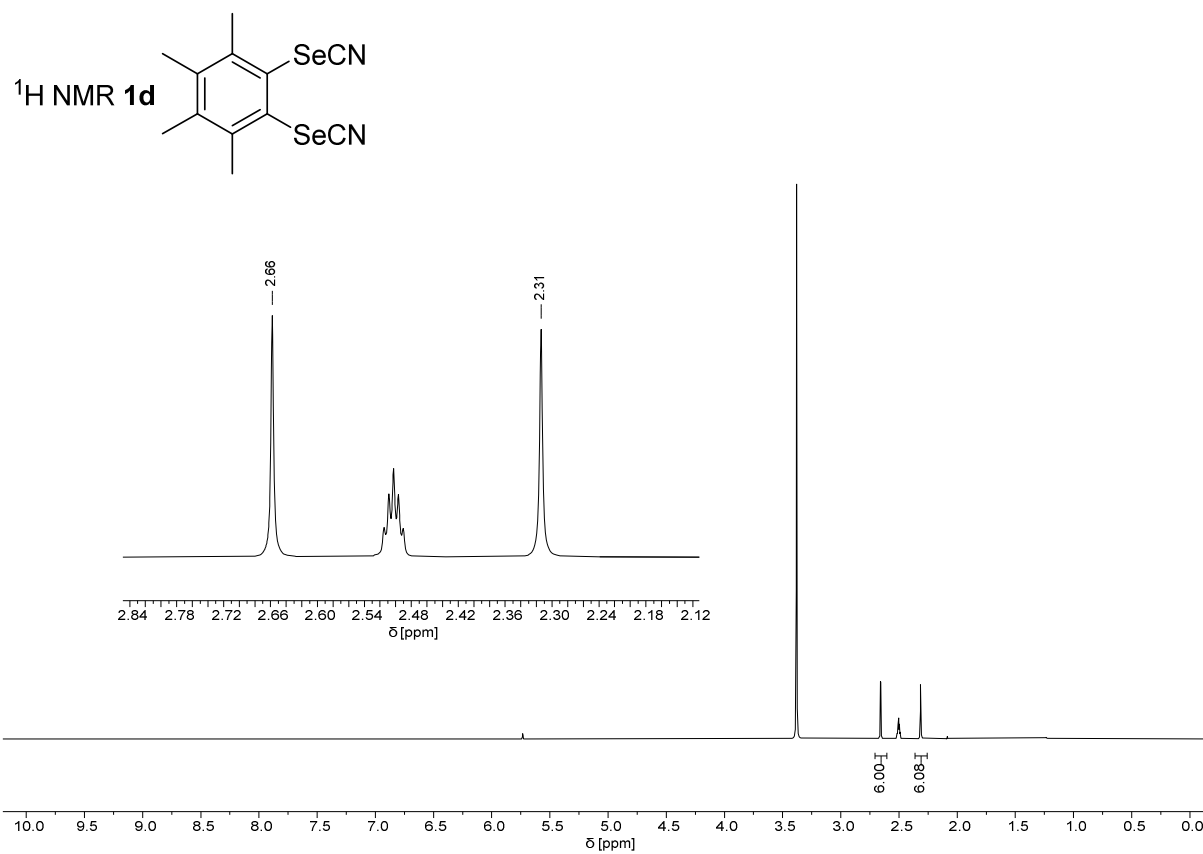
ESP calculations

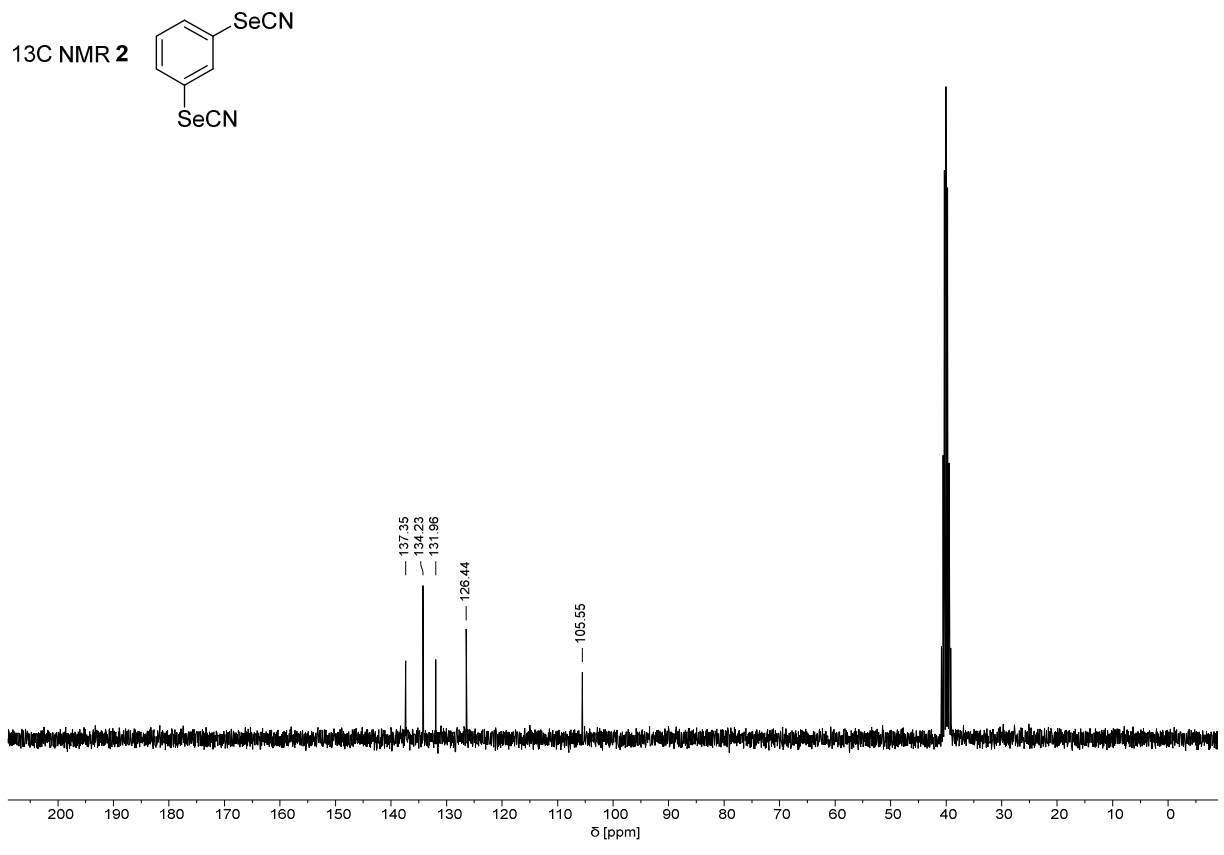
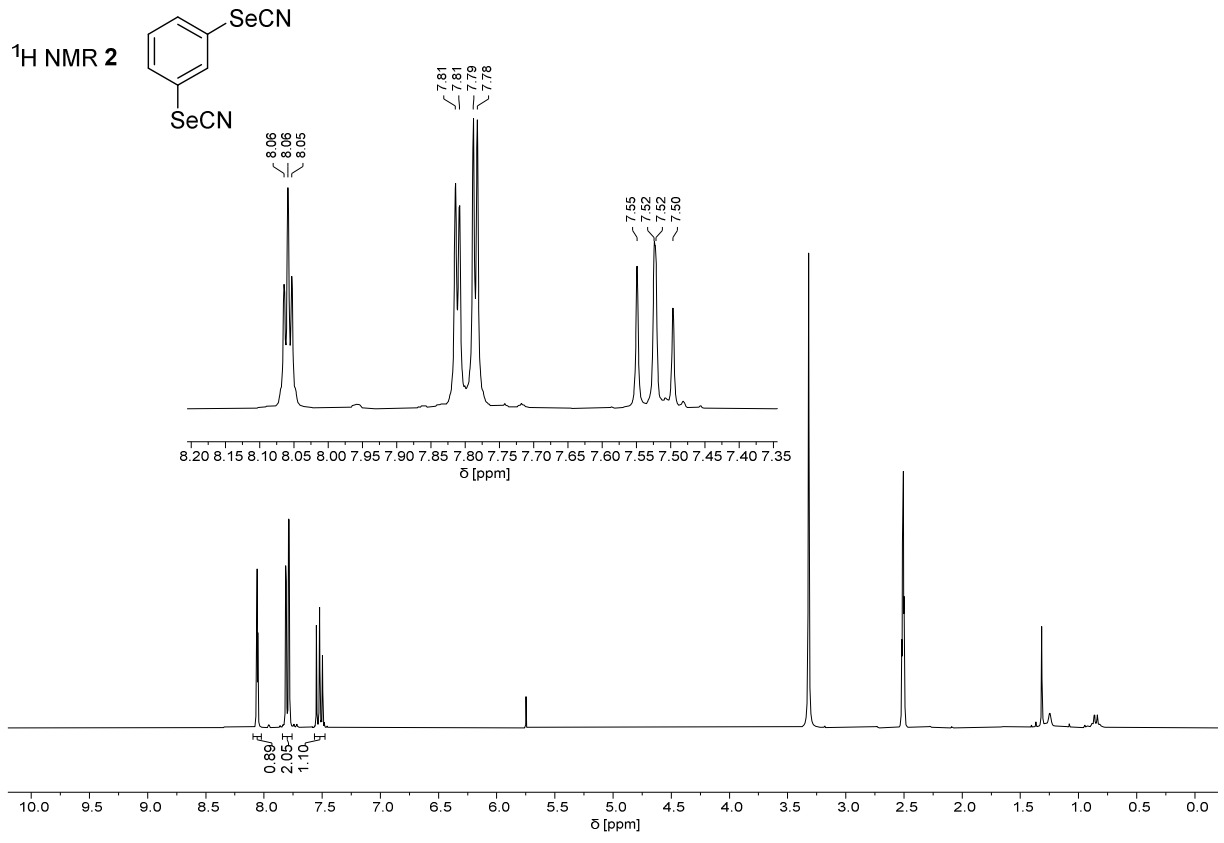
Molecular structures of the four compounds have been optimized in gas phase (vacuum) with Gaussian09 software¹ using Density Functional Theory. B3LYP functional was used, completed with D3 dispersion Grimme dispersion correction.² The Def2TZVPP basis set was employed for all atoms.³ Frequency calculations were performed in order to check that true energy minima were obtained. Isosurfaces of electron density ($\rho = 0.002$ a.u.) mapped with the corresponding total electrostatic potential were calculated and drawn with AIMAll software.⁴ Values of $V_{S,max}$ of all σ -holes on Se atoms and $V_{S,min}$ of N atoms are reported in Table S2.

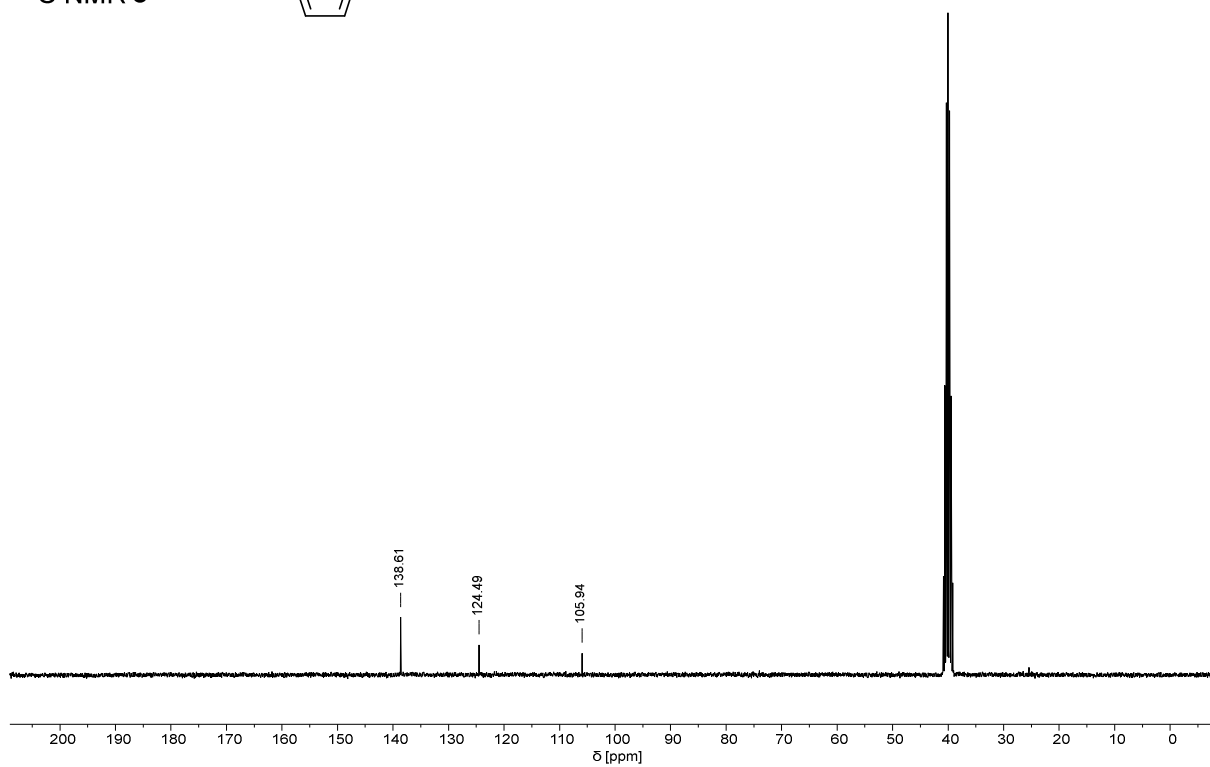
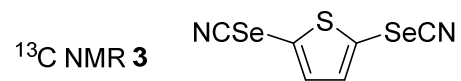
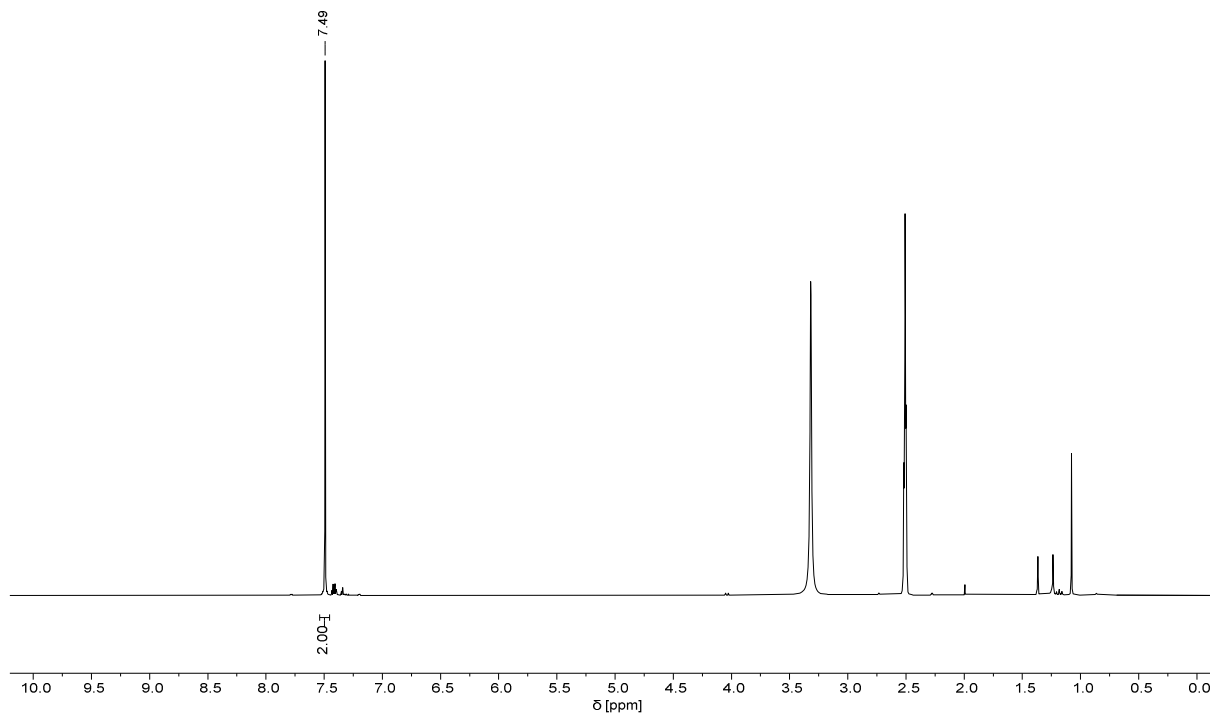
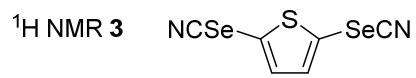
Table S2 $V_{S,max}$ values calculated for the different ChB donors

		σ -hole on Se (stronger, opposite to CN)			σ -hole on Se (weaker, opposite to Ph)			ESP on N			
		Ha	kJ/mol	kcal/mol	Ha	kJ/mol	kcal/mol	Ha	kJ/mol	kcal/mol	
		ISOVALUE = 0.001									
	PhSeCN	0.0508	133.4	31.9	0.0340	89.3	21.3	-0.0571	-149.9	-35.8	
	2	0.0661	173.5	41.5	0.0447	117.4	28.0	-0.0504	-132.3	-31.6	
	3	0.0571	149.9	35.8	0.0472	123.9	29.6	-0.0566	-148.6	-35.5	
	4	0.0609	159.9	38.2	0.0434	113.9	27.2	-0.0503	-132.1	-31.6	
	1d		0.0506	132.9	31.8	0.0354	92.9	22.2	-0.0614	-161.2	-38.5
			0.0417	109.5	26.2	0.0302	79.3	19.0	-0.0601	-157.8	-37.7
ISOVALUE = 0.002											
	PhSeCN	0.0671	176.2	42.1	0.0486	127.6	30.5	-0.0641	-168.3	-40.2	
	2	0.0831	218.2	52.1	0.0601	157.8	37.7	-0.0570	-149.7	-35.8	
	3	0.0731	191.9	45.9	0.0633	166.2	39.7	-0.0632	-165.9	-39.7	
	4	0.0782	205.3	49.1	0.0587	154.1	36.8	-0.0569	-149.4	-35.7	
	1d		0.0654	171.7	41.0	0.0497	130.5	31.2	-0.0683	-179.3	-42.9
			0.0565	148.3	35.5	0.0447	117.4	28.0	-0.0673	-176.7	-42.2

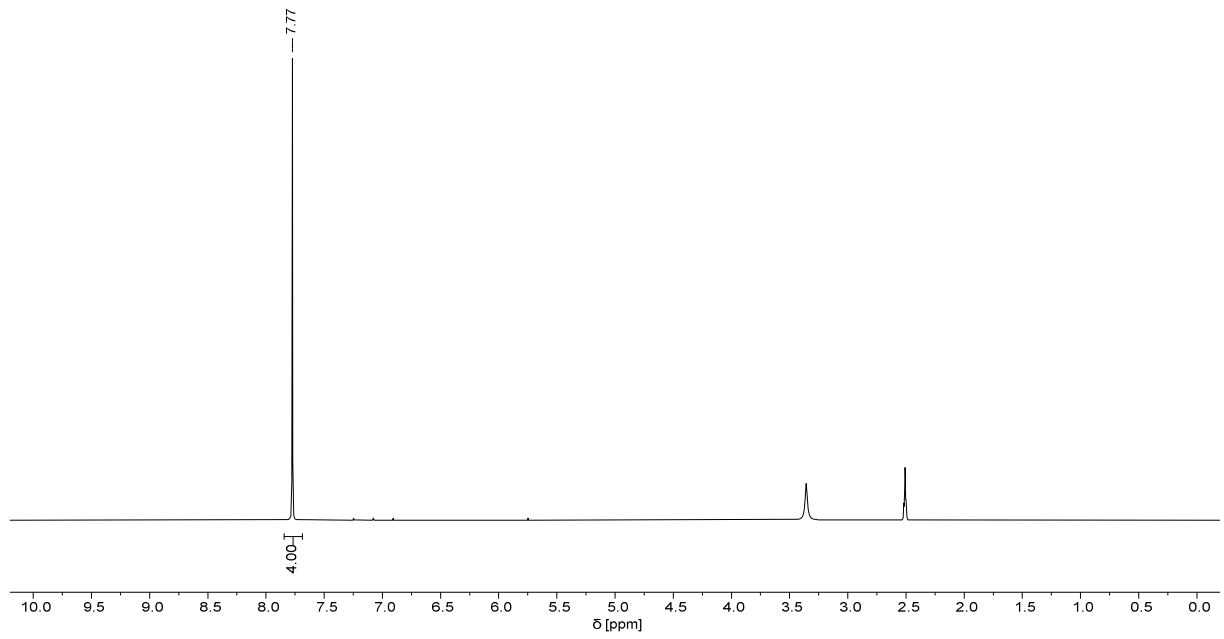
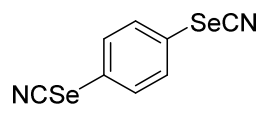
NMR spectra



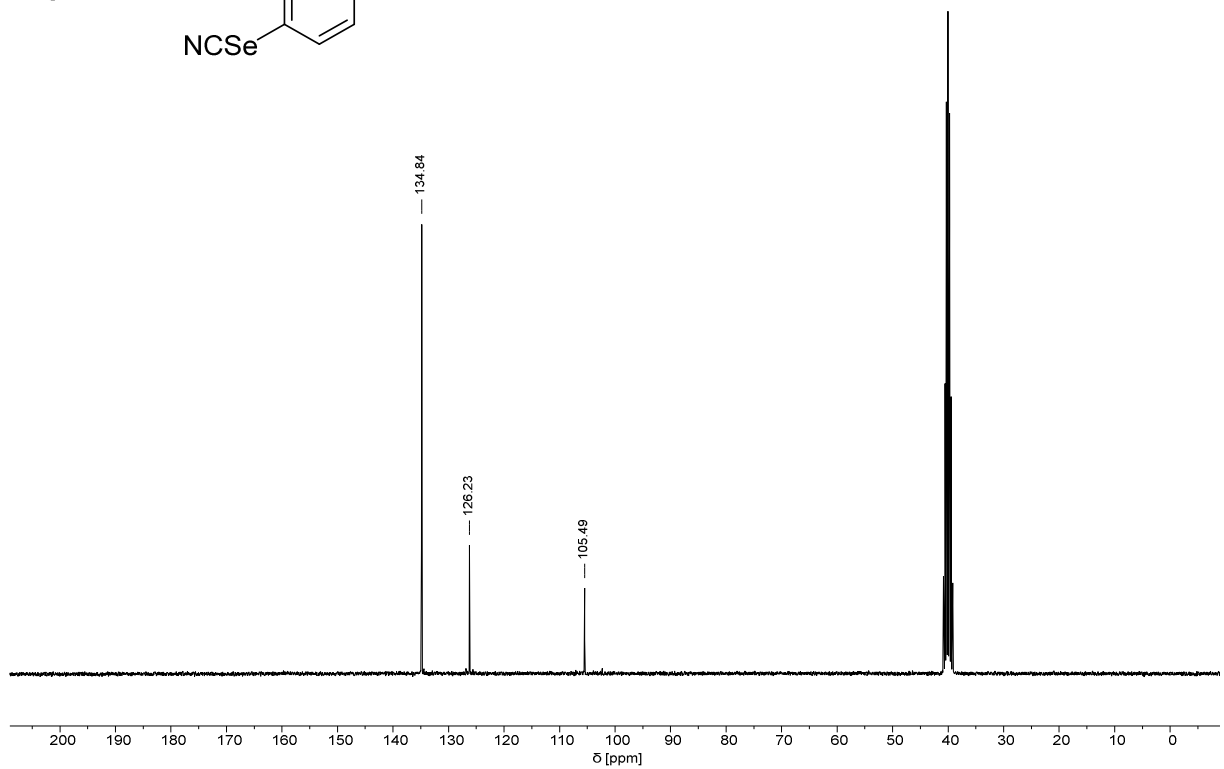
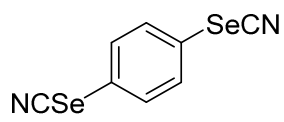




¹H NMR 4



¹³C NMR 4



References

- ¹ M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian 09 (Gaussian, Inc., Wallingford CT, 2009).
- ² S. Grimme, J. Antony, S. Ehrlich and H. Krieg, *J. Chem. Phys.*, 2010, **132**, 154104.
- ³ B. P. Pritchard, D. Altarawy, B. Didier, T. D. Gibson and T. L. Windus. *J. Chem. Inf. Model.* 2019, **59**, 4814–4820.
- ⁴ AIMAll (Version 19.10.12), T. A. Keith, TK Gristmill Software, Overland Park KS, USA, 2019 (aim.tkgristmill.com).