Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Novel Cationic 1,2,4-Selenadiazoles: Synthesis via Addition of 2-Pyridylselenyl Halides to Unactivated Nitriles, Structures and Four-center Se···N Contacts

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General remarks

All manipulations were carried out in air. All the reagents, used in this study, were obtained from the commercial sources (Aldrich, TCI-Europe, Strem, ABCR). Commercially available solvents were purified by conventional methods and distilled immediately prior to use. NMR spectra were recorded on a Bruker Avance III (^{1}H: 400 MHz); chemical shifts (δ) are given in ppm relative to TMS, coupling constants (J) in Hz. The solvent signals were used as references ($CDCl_3$: δ_C = 77.16 ppm; residual $CHCl_3$ in $CDCl_3$: δ_H = 7.26 ppm; CD_2Cl_2: δ_C = 53.84 ppm; residual $CHDCl_2$ in CD_2Cl_2: δ_H = 5.32 ppm); ^{1}H and ^{13}C assignments were established using NOESY, HSQC and HMBC experiments. C, H, and N elemental analyses were carried out on a Euro EA 3028HT CHNS/O analyzer. Mass-spectra were obtained on a Bruker micrOTOF spectrometer equipped with electrospray ionization (ESI) source; MeOH, CH_2Cl_2 or MeOH/CH_2Cl_2 mixture was used as a solvent. IR spectra were recorded with a Nicolet Magna IR-750 FTIR spectrometer for KBr pellets in the region 400–4000 cm^{-1}. 2-pyridinoselenyl bromide and di(2-pyridyl) diselenide were obtained by method reported by Toshimitsu *et al.*[1] 2-pyridinoselenyl chloride was obtained by method reported by Khrustalev *et al.*[2]

The single-crystal X-ray diffraction data were collected on a three-circle Bruker APEX-II CCD diffractometer (λ(MoK_α)-radiation, graphite monochromator, φ and ω scan mode) (for **3** and **4**) and a three-circle Bruker D8 QUEST PHOTON-III CCD (λ(MoK_α)-radiation, graphite monochromator, φ and ω scan mode) (for **5**). The data were indexed and integrated using the SAINT program (Bruker, *SAINT*, Bruker AXS Inc., Madison, WI, **2013**) and corrected for absorption using the SADABS program (Krause, L., Herbst-Irmer, R., Sheldrick G. M., Stalke D., *J. Appl. Cryst.*, **2015**, *48*, 3–10). For details, see Table 1. The structures were determined by direct methods and refined by full-matrix least square technique on F^2 in anisotropic approximation for non-hydrogen atoms. The hydrogen atoms were placed in calculated positions and refined within the riding model with fixed isotropic displacement parameters [U_{iso}(H) = 1.5U_{eq}(C) for the methyl groups and 1.2U_{eq}(C) for the other groups]. All calculations were carried out using the SHELXTL program suite (Sheldrick, G. M. *Acta Cryst.*, **2015**, *C71*, 3–8). Crystallographic data for **3-5** have been deposited with the Cambridge Crystallographic Data Center, CCDC 1014259 (**3**), 1014261 (**4**) and CCDC 2070444 (**5**). The supplementary crystallographic data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table S1. Values of the density of all electrons – $\rho(\mathbf{r})$, Laplacian of electron density – $\nabla^2\rho(\mathbf{r})$ and appropriate λ_2 eigenvalues, energy density – H_b, potential energy density – $V(\mathbf{r})$, and Lagrangian kinetic energy – $G(\mathbf{r})$ (a.u.) at the bond critical points (3, –1) corresponding for Se···N noncovalent interactions in **3**, **4**, and **5** and approximately estimated strengths of these contacts E_{int} (kcal/mol).

Contact*	$\rho(\mathbf{r})$	$\nabla^2\rho(\mathbf{r})$	λ_2	H_b	$V(\mathbf{r})$	$G(\mathbf{r})$	E_{int}**
3							
Se···N 2.986 Å	0.015	0.047	-0.015	0.001	-0.009	0.010	2.8
4							
Se···N 2.942 Å	0.016	0.050	-0.016	0.001	-0.010	0.011	3.1
5							
Se···N 3.008 Å	0.014	0.044	-0.014	0.001	-0.008	0.010	2.5

* The Bondi's (shortest) van der Waals (vdW) radii for Se and N atoms are 1.90 and 1.55 Å, respectively.[3]

** $E_{int} \approx -V(\mathbf{r})/2$[4]

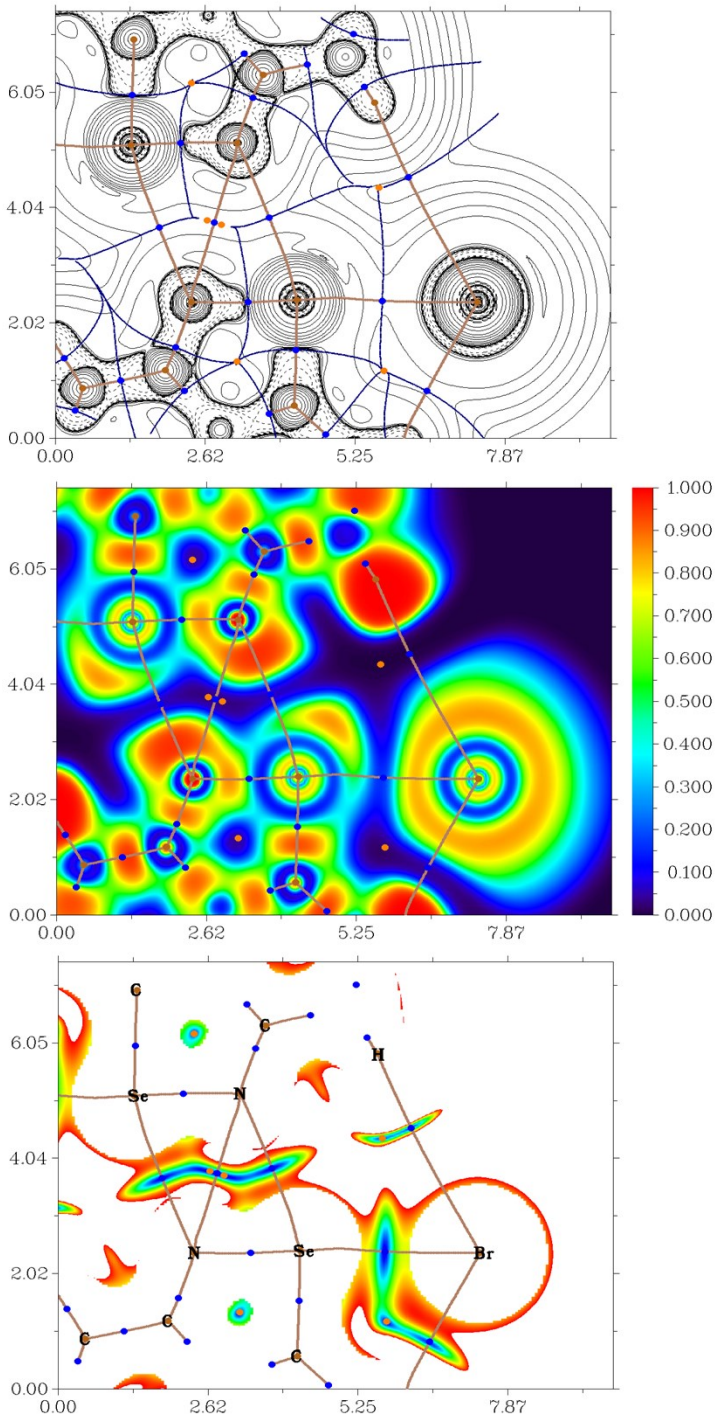


Figure S1. Contour line diagram of the Laplacian of electron density distribution $\nabla^2\rho(\mathbf{r})$, bond paths, and selected zero-flux surfaces (top panel), visualization of electron localization function (ELF, center panel) and reduced density gradient (RDG, bottom panel) analyses for Se···N noncovalent interactions in **4**. Bond critical points (3, –1) are shown in blue, nuclear critical points (3, –3) – in pale brown, ring critical points (3, +1) – in orange, bond paths are shown as pale brown lines, length units – Å, and the color scale for the ELF and RDG maps are presented in a.u.

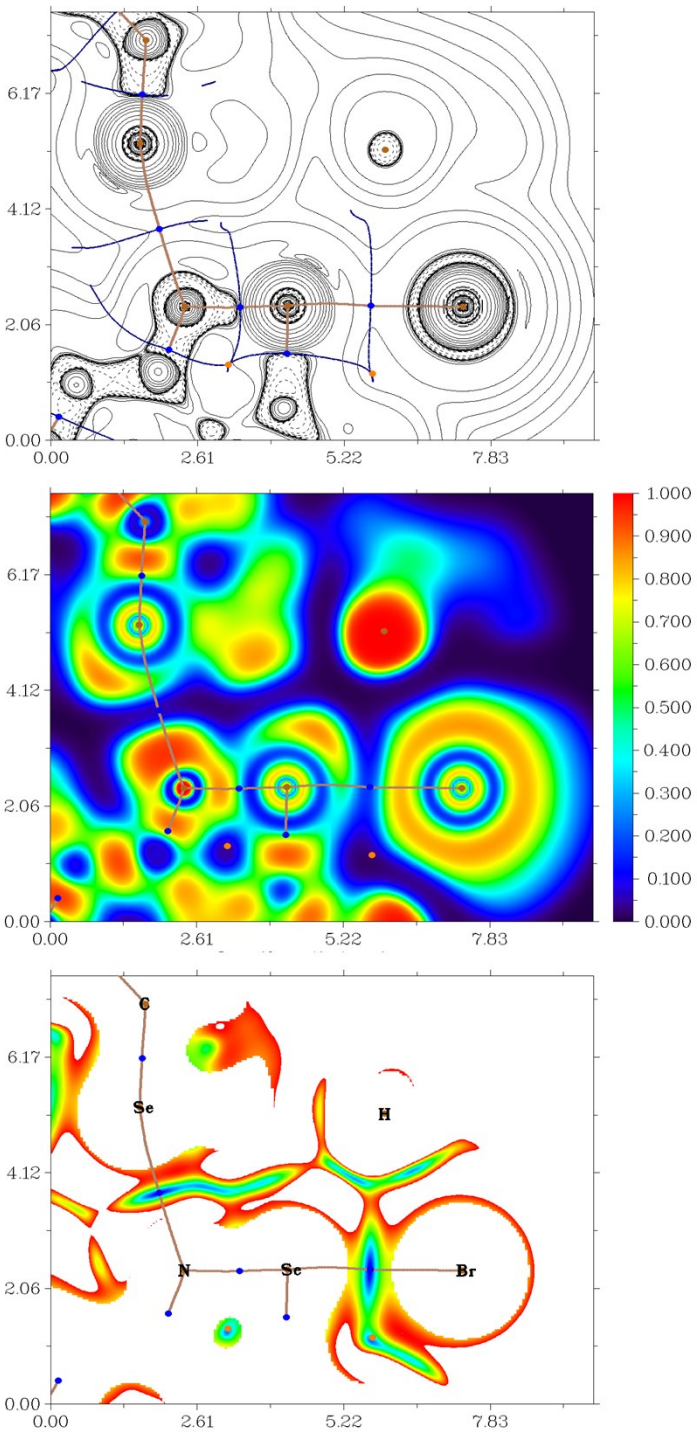


Figure S2. Contour line diagram of the Laplacian of electron density distribution $\nabla^2\rho(\mathbf{r})$, bond paths, and selected zero-flux surfaces (top panel), visualization of electron localization function (ELF, center panel) and reduced density gradient (RDG, bottom panel) analyses for Se···N noncovalent interactions in **5**. Bond critical points (3, –1) are shown in blue, nuclear critical points (3, –3) – in pale brown, ring critical points (3, +1) – in orange, bond paths are shown as pale brown lines, length units – Å, and the color scale for the ELF and RDG maps are presented in a.u.

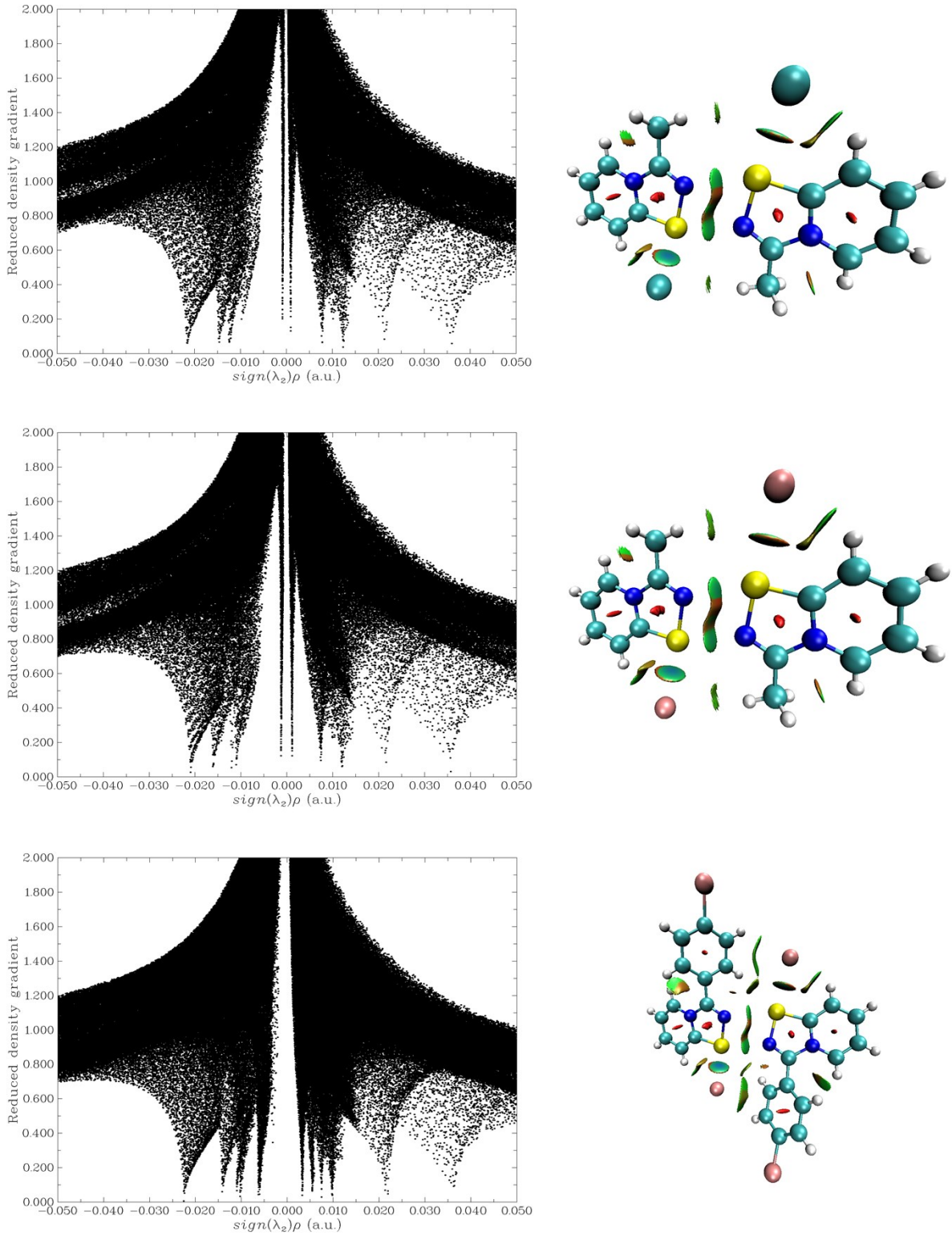


Figure S3. NCI plots for model associates **3** (top), **4** (middle), and **5** (bottom) and visualization of intermolecular contacts in 3D using NCI analysis technique.

Computational details. The single point calculations based on the experimental X-ray geometries of **3**, **4**, and **5** have been carried out at the DFT level of theory using the dispersion-corrected hybrid functional ωB97XD[5] with the help of Gaussian-09 [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, M. J. A.;, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, 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, C. J.;, D. J. Fox, in Gaussian 09, Revision C.01, Gaussian, Inc., Wallingford, CT, 2010.] program package. The 6-31+G* basis sets were used for all atoms. The topological analysis of the electron density distribution with the help of the atoms in molecules (QTAIM) method, electron localization function (ELF) and reduced density gradient (RDG) analyses have been performed by using the Multiwfn program (version 3.7).[6] The VMD program[7] was used for visualization of noncovalent interactions (NCI). The Cartesian atomic coordinates for model associates are presented in **Table S2**.

Table S2. Cartesian atomic coordinates for model associates.

Atom	X	Y	Z
3			
Se	0.641315	4.155704	5.152904
N	-0.167629	5.722133	5.698478
C	0.554734	6.751535	5.450027
N	1.809178	6.520046	4.827593
C	2.060629	5.206216	4.554159
C	3.262282	4.839200	3.938810
H	3.445418	3.928302	3.742310
C	4.178874	5.823708	3.621005
H	5.002306	5.595024	3.205386
C	3.884249	7.164100	3.916438
H	4.512679	7.841639	3.696324
C	2.708047	7.507172	4.514387
H	2.514158	8.415919	4.711756
C	0.141089	8.146457	5.781503
H	-0.758562	8.137197	6.169654

H	0.138465	8.689030	4.965304
H	0.771250	8.529092	6.426930
Cl	2.213788	1.690199	4.331684
Se	-2.648330	5.197396	7.275891
N	-1.839387	3.630967	6.730317
C	-2.561749	2.601565	6.978769
N	-3.816193	2.833054	7.601203
C	-4.067645	4.146884	7.874636
C	-5.269297	4.513900	8.489986
H	-5.452433	5.424798	8.686485
C	-6.185889	3.529392	8.807790
H	-7.009321	3.758076	9.223409
C	-5.891265	2.189000	8.512358
H	-6.519694	1.511461	8.732472
C	-4.715062	1.845928	7.914408
H	-4.521173	0.937181	7.717039
C	-2.148105	1.206643	6.647293
H	-1.248453	1.215903	6.259141
H	-2.145480	0.664070	7.463492
H	-2.778265	0.824008	6.001865
Cl	-4.220803	7.662901	8.097112
4			
Se	0.730778	5.285678	5.291790
N	-0.113993	3.723737	5.817468
C	0.579154	2.682443	5.528707
N	1.834116	2.895918	4.895763
C	2.113078	4.216372	4.647495
C	3.313085	4.559284	4.021384
H	3.524563	5.469209	3.848027
C	4.193154	3.547934	3.656954
H	5.014038	3.761409	3.229255
C	3.865718	2.218787	3.921419
H	4.466960	1.529099	3.664547
C	2.697118	1.894228	4.541456
H	2.484019	0.987201	4.726202
C	0.128101	1.301135	5.823288
H	-0.759351	1.329147	6.239599
H	0.762433	0.874185	6.436999
H	0.081796	0.787249	4.990667
Br	2.321583	7.890556	4.478061
Se	-2.531458	4.373822	7.362031
N	-1.686687	5.935763	6.836353
C	-2.379834	6.977057	7.125113
N	-3.634796	6.763582	7.758058
C	-3.913758	5.443128	8.006326
C	-5.113765	5.100216	8.632437
H	-5.325243	4.190291	8.805794
C	-5.993834	6.111566	8.996867

H	-6.814718	5.898091	9.424566
C	-5.666398	7.440713	8.732402
H	-6.267640	8.130401	8.989274
C	-4.497798	7.765272	8.112365
H	-4.284699	8.672299	7.927619
C	-1.928781	8.358365	6.830532
H	-1.041329	8.330353	6.414222
H	-2.563113	8.785315	6.216822
H	-1.882476	8.872251	7.663154
Br	-4.122263	1.768944	8.175760
5			
Br	16.333245	3.598517	13.842437
Se	11.278378	1.984460	7.064190
N	12.045624	2.309666	8.698919
C	13.326448	2.321785	8.644499
N	13.920140	2.068007	7.363263
C	13.002576	1.874822	6.374239
C	13.432346	1.628885	5.071708
H	12.802743	1.532649	4.367797
C	14.771318	1.526946	4.818536
H	15.075921	1.363701	3.933620
C	15.699588	1.664528	5.865530
H	16.629604	1.572569	5.692805
C	15.265681	1.928286	7.124288
H	15.889885	2.015255	7.835297
C	14.153219	2.571286	9.854753
C	15.241904	3.438124	9.855936
H	15.522706	3.851583	9.047917
C	15.917408	3.696179	11.044894
H	16.679244	4.266467	11.050810
C	15.470453	3.115198	12.213741
C	14.386567	2.263331	12.237402
H	14.092159	1.877673	13.053702
C	13.732060	1.980325	11.041345
H	12.995273	1.380810	11.036613
Br	10.033665	1.350585	4.278122
Br	4.752580	3.598517	3.903216
Se	9.807448	1.984460	10.681463
N	9.040201	2.309666	9.046734
C	7.759377	2.321785	9.101154
N	7.165685	2.068007	10.382390
C	8.083249	1.874822	11.371414
C	7.653480	1.628885	12.673945
H	8.283082	1.532649	13.377856
C	6.314507	1.526946	12.927117
H	6.009904	1.363701	13.812033
C	5.386238	1.664528	11.880123
H	4.456221	1.572569	12.052847

C	5.820144	1.928286	10.621365
H	5.195940	2.015255	9.910356
C	6.932606	2.571286	7.890900
C	5.843921	3.438124	7.889717
H	5.563120	3.851583	8.697736
C	5.168417	3.696179	6.700759
H	4.406581	4.266467	6.694843
C	5.615372	3.115198	5.531912
C	6.699259	2.263331	5.508251
H	6.993666	1.877673	4.691951
C	7.353766	1.980325	6.704308
H	8.090553	1.380810	6.709040
Br	11.052160	1.350585	13.467531

Table S3. Crystal data and structure refinement.

Compound	**3**	**4**	**5**
Empirical formula	$C_7H_7ClN_2Se$	$C_7H_7BrN_2Se$	$C_{12}H_8Br_2N_2Se$
Formula weight	233.56	278.02	418.96
Temperature, K	120(2)	120(2)	100(2)
Crystal size, mm	0.05×0.20×0.25	0.15×0.15×0.25	0.02×0.20×0.24
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$	$C2/c$
a, Å	7.0750(4)	7.1030(5)	29.431(2)
b, Å	9.3531(5)	9.6595(7)	7.1286(5)
c, Å	12.5898(7)	12.7813(9)	13.0733(9)
α, deg.	90	90	90
β, deg.	99.1730(10)	98.099(2)	115.186(2)
γ, deg.	90	90	90
V, Å^3	822.45(8)	868.20(11)	2482.1(3)
Z	4	4	8
D_{calc}, g·cm^{-3}	1.886	2.127	2.242
Absorption coefficient, μ	4.821	8.862	9.441
F(000)	456	528	1584
Theta range for data collection	2.72-32.60	2.65-32.60	3.06-32.61
Index ranges	-10 < h < 10 -14 < k < 14 -19 < l < 19	-10 < h < 10 -14 < k < 14 -19 < l < 19	-44 < h < 44 -10 < k < 10 -19 < l < 19
Reflections collected	12580	13339	27223
Independent reflections, R_{int}	3005, 0.034	3178, 0.048	4533, 0.119
Reflections observed with $I > 2\sigma(I)$	2688	2587	3039
Data / restraints/ parameters	3005 / 0 / 101	3178 / 0 / 101	4533 / 0 / 154
R_1 [$I > 2\sigma(I)$]	0.023	0.030	0.045
wR_2 [all data]	0.059	0.076	0.096
Goodness-of-fit on F^2	1.074	1.028	1.032
T_{min} / T_{max}	0.315 / 0.722	0.128 / 0.242	0.112 / 0.743
$\Delta\rho_{max}$ / $\Delta\rho_{min}$, e·Å^{-3}	0.502 / -0.748	0.863 / -0.520	0.873 / -1.227

Table S4. Selected geometrical parameters (Å and °) for **3**, **4** and **5**.

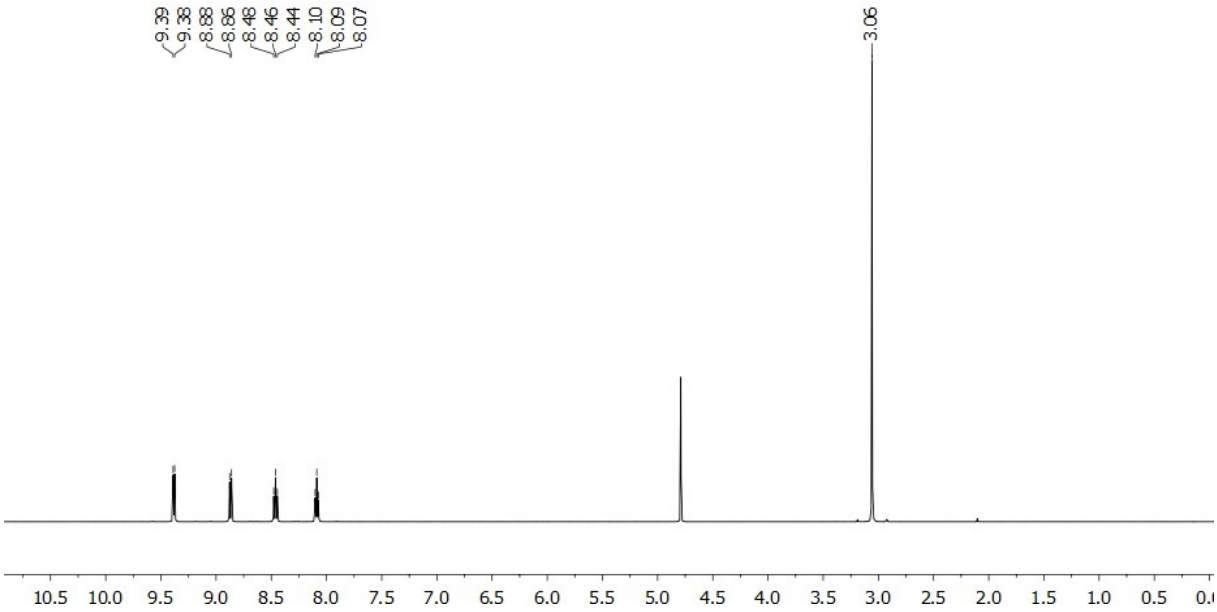
Parameter/Compound	**3**	**4**	**5**
Se1─N2	1.8455(13)	1.852(2)	1.905(4)
Se1─C5	1.8646(14)	1.862(2)	1.860(4)
N2─C3	1.2820(19)	1.284(3)	1.282(6)
C3─N4	1.4192(18)	1.422(3)	1.435(5)
N4─C5	1.3654(18)	1.372(3)	1.363(5)
Se1...N2A	2.9862(13)	2.941(2)	3.008(4)
Se1...Hal1 (3, 4), Se1...Hal2 (5)	3.0374(4)	3.1588(4)	3.1166(6)
N2─Se1─C5	87.16(6)	87.29(10)	87.31(17)
Se1─N2─C3	112.16(10)	111.94(17)	112.5(3)
N2─C3─N4	116.88(13)	117.1(2)	116.7(4)
C3─N4─C5	114.05(12)	113.9(2)	113.2(4)
Se1─C5─N4	109.73(10)	109.82(17)	110.3(3)
N2─Se1**…**Hal1 (3, 4), N2─Se1**…**Hal2 (5)	174.78(4)	176.72(7)	178.1(1)
C5─Se1**…**Hal1(3, 4), C5─Se1**…**Hal2 (5)	88.65(4)	90.60(8)	91.5(1)
N2─Se1**…**N2A	68.21(5)	70.26(9)	72.8(1)
C5─Se1**…**N2A	154.29(5)	156.70(9)	160.1(1)
Hal1**…**Se1**…**N2A	115.48(3)	111.53(4)	108.30(8)
C5─Se1─N2─C3	-0.4(1)	0.2(2)	0.3(3)
Se1─N2─C3─N4	-0.3(2)	0.8(3)	-0.9(4)
N2─C3─N4─C5	1.2(2)	0.8(3)	1.2(5)
N2─C3─N4─C9	-178.9(1)	179.1(2)	-174.2(4)
C9─N4─C5─Se1	178.7(1)	-179.0(2)	174.7(3)
C3─N4─C5─Se1	-1.4(1)	1.7(3)	-0.9(4)
N2─Se1─C5─N4	1.0(1)	-1.1(2)	0.4(3)
N2─Se1─C5─C6	179.5(1)	-179.6(3)	179.9(4)

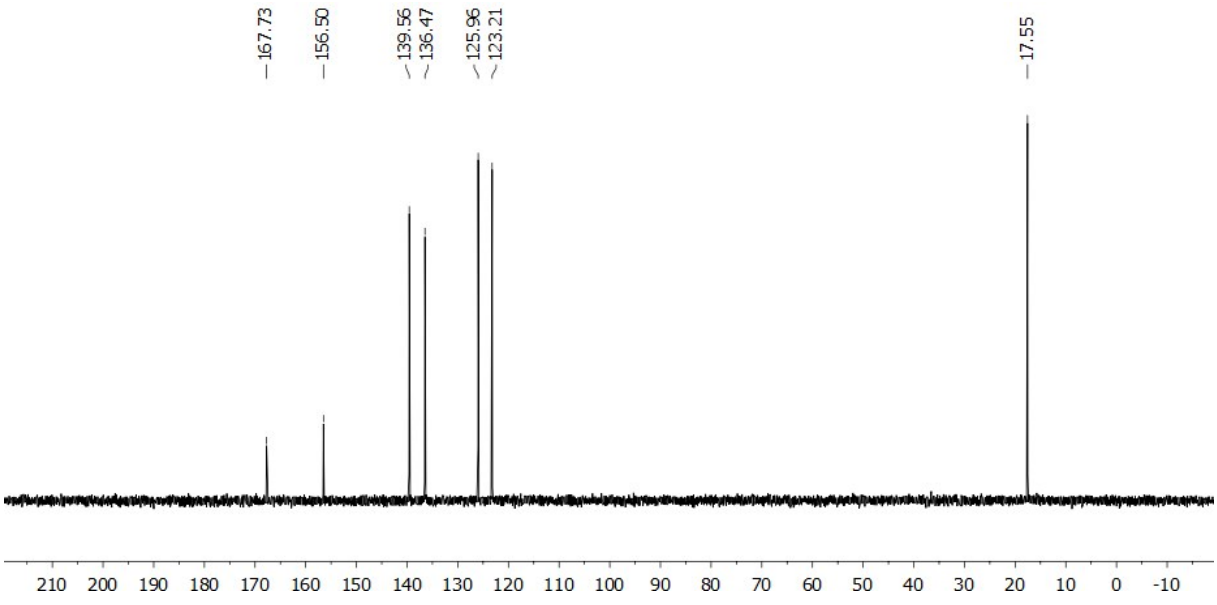
Synthesis of compounds 3−5.

3. 2-Pyridylselenyl chloride (2.6 mmol, 500 mg) was stirred in MeCN (10 mL) at room temperature for 3 h. A colorless precipitate gradually formed, which was filtered, washed with MeCN (3×3 mL), and dried under vacuum. Yield: 580 mg (96%). m.p. 187–188°C. Anal. Calcd for C7H7ClN2Se: C, 36.01; H, 3.02; N, 12.00. Found: C, 35.93; H, 3.09; N, 11.92. ^{1}H NMR (400 MHz, D_2O) δ 9.38 (d, J = 6.8 Hz, 1H, H5), 8.87 (d, J = 8.7 Hz, 1H, H8), 8.46 (t, J = 8.4 Hz, 1H, H7), 8.09 (t, J = 7.4 Hz, 1H, H6), 3.06 (s, 3H, CH_3). ^{13}C{^{1}H} NMR δ 167.73 (C3), 156.50 (C9), 139.56 (C5), 136.47 (C8), 125.96 (C7), 123.21 (C6), 17.55 (Me). MS (ESI$^+$), found: 198.9763 [M – Cl]$^+$; calcd for $C_7H_7N_2Se$: 198.9769.

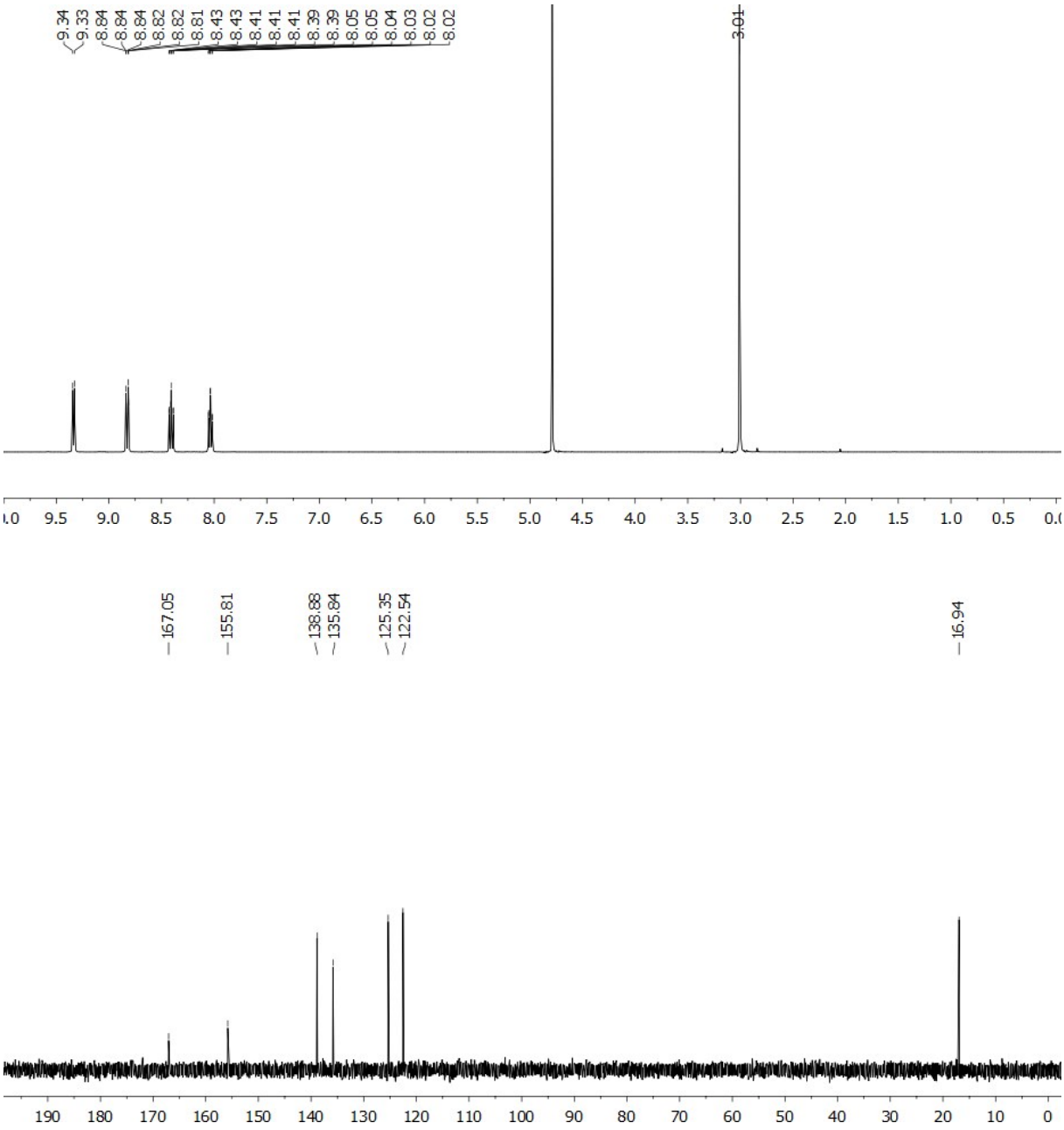
4. 2-Pyridylselenyl bromide (2.1 mmol, 500 mg) was stirred in MeCN (10 mL) at room temperature for 3 h. A colorless precipitate gradually formed, which was filtered, washed with MeCN (3×3 mL), and dried under vacuum. Yield: 545 mg (93%). m.p. 197–198 °C. Anal. Calcd for $C_7H_7BrN_2Se$: C, 30.25; H, 2.54; N, 10.08. Found: C, 30.19; H, 2.59; N, 10.02. ^{1}H NMR (400 MHz, D_2O) δ 9.34 (d, J = 7.1 Hz, 1H, H5), 8.83 (dt, J = 8.6 Hz, 1.0 Hz, 1H, H8), 8.41 (ddd, J = 8.6, 7.1, 1.1 Hz, 1H, H7), 8.03 (td, J = 7.1, 1.0 Hz, 1H, H6), 3.01 (s, 3H, CH_3). ^{13}C{^{1}H} NMR δ 167.05 (C3), 155.81 (C9), 138.88 (C5), 135.84 (C8), 125.35 (C7), 122.54 (C6), 16.94 (Me). MS (ESI$^+$), found: 198.9761 [M – Br]$^+$; calcd for $C_7H_7N_2Se$: 198.9769.

5. A solution of *p*-bromobenzonitrile (0.44 mmol, 80 mg) in CH_2Cl_2 (2 mL) was added to a solution of 2-pyridylselenyl bromide (0.42 mmol, 100 mg) in CH_2Cl_2 (10 mL), and the mixture was stirred at room temperature for 20 minutes. A colorless precipitate gradually formed, which was filtered, washed with CH_2Cl_2 (3×3 mL), and dried under vacuum. Yield: 162 mg (92%). m.p. 200–202 °C. Anal. Calcd for $C_{12}H_8Br_2N_2Se$: C, 34.40; H, 1.92; N, 6.69. Found: C, 34.52; H, 2.12; N, 6.81. ^{1}H and ^{13}C NMR spectra were not recorded due to insufficient solubility of **5** in common deuterated solvents and instability in DMSO-*d6*. MS (ESI$^+$), found: 338.9036 [M – Br]$^+$; calcd for $C_{12}H_8BrN_2Se$: 338.9036.





^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of **3** (D_2O).



^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of **4** (D_2O).

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