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Sulfur–selenium displacement in polyfluoroindene-fused 1,2,6-selenadiazine

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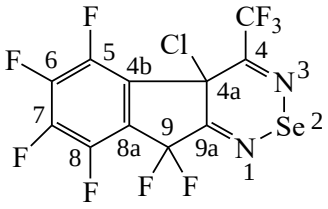
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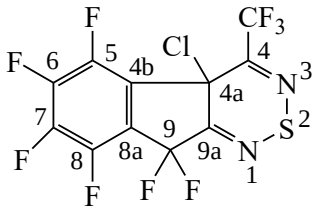
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Scheme S1 4*a*-Chloro-5,6,7,8,9,9-hexafluoro-4-(trifluoromethyl)-4*a*,9-dihydroindeno[2,1-*c*][1,2,6]selenadiazine **1** and 4*a*-chloro-5,6,7,8,9,9-hexafluoro-4-(trifluoromethyl)-4*a*,9-dihydroindeno[2,1-*c*][1,2,6]thiadiazine **3**, together with atom numbering.

Synthesis of 4*a*-chloro-5,6,7,8,9,9-hexafluoro-4-(trifluoromethyl)-4*a*,9-dihydroindeno[2,1-*c*][1,2,6]thiadiazine 3 from 4*a*-chloro-5,6,7,8,9,9-hexafluoro-4-(trifluoromethyl)-4*a*,9-dihydroindeno[2,1-*c*][1,2,6]selenadiazine 1

At ambient temperature, a solution of 0.32 g (0.96 mmol) 3-(1-amino-2,2,2-trifluoroethyliden)-1,1,4,5,6,7-hexafluoro-2-iminoindan[S1] and 0.36 g (3.53 mmol) NEt_3 in 2 ml of THF was added over a period of 0.5 h to a stirred solution of 0.23 g (1.06 mmol) $SeCl_4$ in 2 ml THF. The reaction mixture was stirred for additional 2.5 h and centrifuged. The solution obtained contained ~1:1 mixture of 4*a*-chloro-5,6,7,8,9,9-hexafluoro-4-(trifluoromethyl)-4*a*,9-dihydroindeno[2,1-

c][1,2,6]selenadiazine **1** and 4*a*-hydroxy-5,6,7,8,9,9-hexafluoro-4-(trifluoromethyl)-4*a*,9-dihydroindeno[2,1-*c*][1,2,6]selenadiazine **2** (^{19}F NMR, the spectra corresponded to ref.[S2]). To a portion (0.5 ml) of the solution containing ~0.12 mmol of **1** + **2**, 0.03 g (0.20 mmol) of $SOCl_2$ was added and the mixture was heated at 45°C for 1 h, after which only compound **1** was observed (^{13}C and ^{9}F NMR; both spectra corresponded to ref.[S2]). On one-month storage of the solution at room temperature, 4*a*-chloro-5,6,7,8,9,9-hexafluoro-4-(trifluoromethyl)-4*a*,9-dihydroindeno[2,1-*c*][1,2,6]thiadiazine **3** was detected (^{19}F NMR; the spectrum corresponded to ref.[S3]). To the solution, 0.05 g (0.41 mmol) of $SOCl_2$ was added and the mixture was heated at 48°C for 5 h to give ~1:1 mixture of compounds **1** and **3** (^{19}F NMR). The mixture was kept at room temperature for another two months, after which it exhibited only 4*a*-chloro-5,6,7,8,9,9-hexafluoro-4-(trifluoromethyl)-4*a*,9-dihydroindeno[2,1-*c*][1,2,6]thiadiazine **3** in quantitative yield (^{13}C and ^{19}F NMR, both spectra corresponded to ref.[S3]; for graphical view, see section S2). MS (direct injection of the reaction solution), m/z, measured / calculated for $[\mathbf{3}–Cl]^+$: 362.96413 / 362.96384.

4*a*-Chloro-5,6,7,8,9,9-hexafluoro-4-(trifluoromethyl)-4*a*,9-dihydroindeno[2,1-*c*][1,2,6]selenadiazine **1**, white crystals, m. p. 130ºC, CCDC deposition number 1179905.[S2]

4*a*-Chloro-5,6,7,8,9,9-hexafluoro-4-(trifluoromethyl)-4*a*,9-dihydroindeno[2,1-*c*][1,2,6]thiadiazine **3**, quantitative yield (^{13}C and ^{19}F NMR); colorless liquid, b. p. 70ºC / 2 Torr.[S3] ^{13}C and ^{19}F NMR spectra (for graphical view, see section S2), and high-resolution MS spectrum (see above) agree with previously reported.[S3]

S2. NMR spectra

^{13}C and ^{19}F NMR spectra of compounds **1** and **3** (Figures S1-S5) measured with Bruker WP-200 SY and Bruker DRX-500 instruments correspond to previously reported.[S2,S3] Chemical shifts δ, ppm, are referenced to TMS (^{13}C) and C_6F_6 (^{19}F; $\delta^{19}F = –162.9$ with respect to $CFCl_3$). Spin-spin coupling constants J are given in Hz. For atom numbering in signal assignment, see Scheme S1. Due to a magnetic storage failure, in Figures S1-S5 printed copies of the spectra are presented.

4*a*-Chloro-5,6,7,8,9,9-hexafluoro-4-(trifluoromethyl)-4*a*,9-dihydroindeno[2,1-*c*][1,2,6]selenadiazine **1**

^{13}C NMR (Figure S1): 149.2 (t, $^2J_{C–F}$ = 24; C9*a*); 146.2 and 145.8 (dd, dd, $^1J_{C–F}$ = 258, $^2J_{C–F}$ = 12; C-5, C-8); 145.6 and 144.2 (dt, dt, $^1J_{C–F}$ = 260, $^2J_{C–F}$ = 14; C-6 and C-7); 142.8 (q, $^2J_{C–F}$ = 38; C-4); 123.2 (d, $^2J_{C–F}$ = 11; C-4*b*); 118.3 (td, $^2J_{C–F}$ = 26, $^2J_{C–F}$ = 15; C-8a); 119.6 (q, $^1J_{C–F}$ = 279; CF_3), 115.9 (t, $^1J_{C–F}$ = 250; C-9); 51.3 (s, C-4*a*).

^{19}F NMR (Figure S2): 97.3 (d, $^{6}J_{CF3–F-5)}$ = 24; CF_3); 76.8 (quasi-dm, $^{2}J_{F–F}$ = 285; F-9), 71.4 (quasi-dd, $^{2}J_{F–F}$ = 285, $^{4}J_{F-8–F-9}$ = 5; F-9); 32.4 (qddd, $^{6}J_{CF3–F-5)}$ = 24, $^{3}J_{F-5–F-6}$ = 19, $^{5}J_{F-5–F-8}$ = 16, $^{4}J_{F-5–F-7}$ = 8; F-5); 21.9 (dddt, $^{3}J_{F-7–F-8}$ = 21, $^{5}J_{F-5–F-8)}$ = 16, $^{4}J_{F-6–F-8}$ = 7, $^{4}J_{F-8–F-9}$ = 5; F-8); 17.6 (td, $^{3}J_{F-5–F-6}$ = $^{3}J_{F-6–F-7}$ = 19, $^{4}J_{F-6–F-8)}$ = 7; F6); 15.9 (ddd, $^{3}J_{F-7–F-8}$ = 21, $^{3}J_{F-6–F-7}$ = 19, $^{4}J_{(F-5–F-7}$ = 8; F-7).

4*a*-Chloro-5,6,7,8,9,9-hexafluoro-4-(trifluoromethyl)-4*a*,9-dihydroindeno[2,1-*c*][1,2,6]thiadiazine **3**

^{13}C NMR: (Figure S3): 145.1 (dd, $^{1}J_{C–F}$ = 263, $^{2}J_{C–F}$ = 13) and 144.4 (dd, $^{1}J_{C–F}$ = 263, $^{2}J_{C–F}$ = 12; C-5, C-8); 144.9 (dt, $^{1}J_{C–F}$ = 264, $^{2}J_{C–F}$ = 14) and 143.3 (dt, $^{1}J_{C–F}$ = 264, $^{2}J_{C–F}$ = 14; C-6, C-7); 142.7 (dd, $^{2}J_{C–F}$; CF_3); 117.2 (td, $^{2}J_{C–F}$ = 26, $^{2}J_{C–F}$ = 15; C-8*a*); 115.3 (t, $^{1}J_{C–F}$ = 251; C-9); 47.7 (s; C-4*a*).

^{19}F NMR (Figure S4): 95.9 (3F, CF_3), 73.5 (1F_A, F-9), 70.5 (1F_B, $J_{A–B}$ = 288, F-9), 32.3 (1F; F-5); 23.2 (1F; F-8); 18.8 (1F; F-6); 16.6 (1F, F-7); $J_{CF3–F-5}$ = 25; $J_{F-5–F-6}$ = 20, $J_{F-5–F-7}$ = 9; $J_{F-5–F-8}$ = 16; $J_{F-6–F-7}$ = 20, $J_{F-6–F-8}$ = 7, $J_{F-7–F-8}$ = 21; $J_{F-8–F-9}$ = 5.

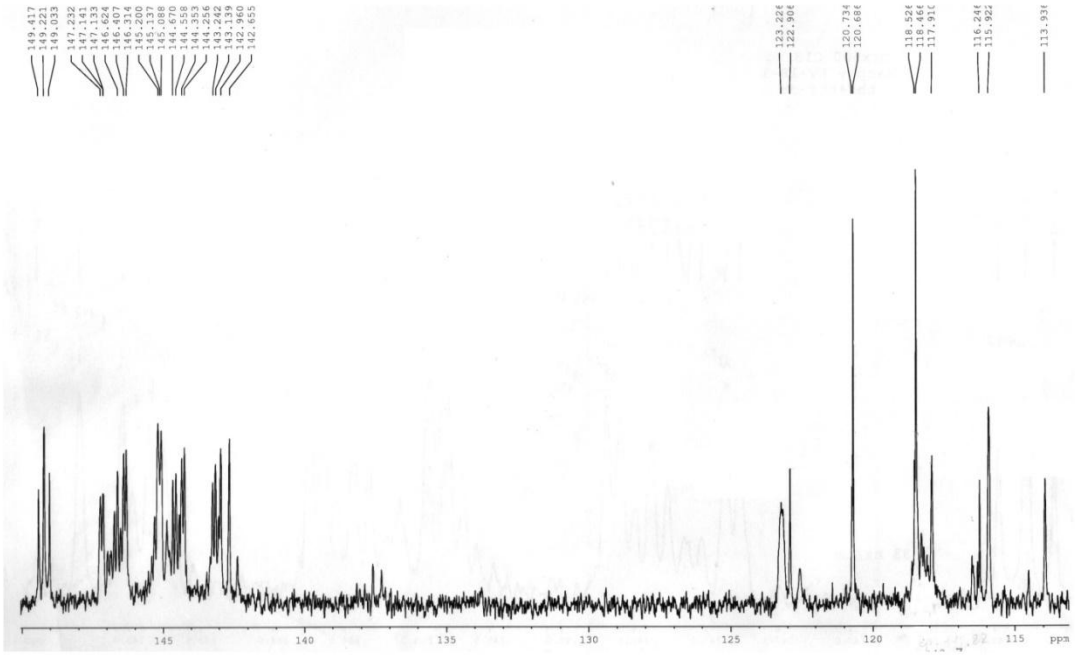


Figure S1 ^{13}C NMR spectrum of compound **1**.

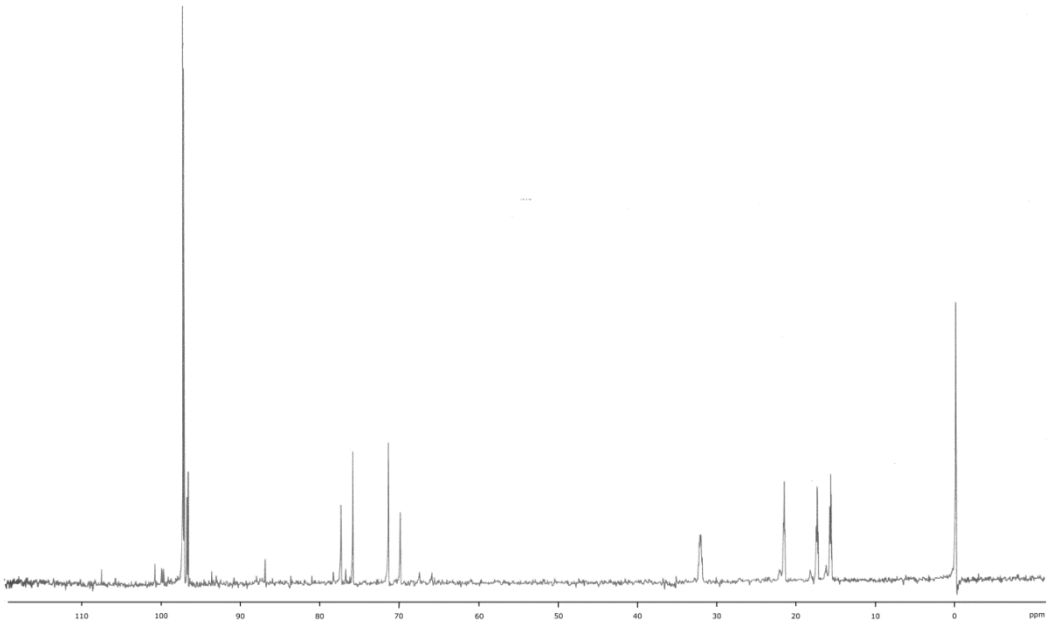


Figure S2 ^{19}F NMR spectrum of compound **1**.

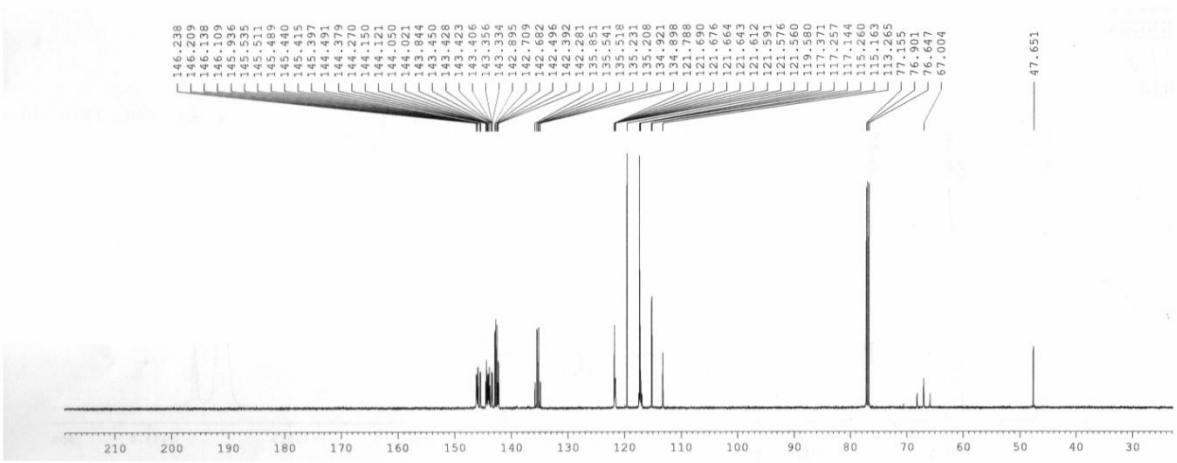


Figure S3 ^{13}C NMR spectrum of compound **3**.

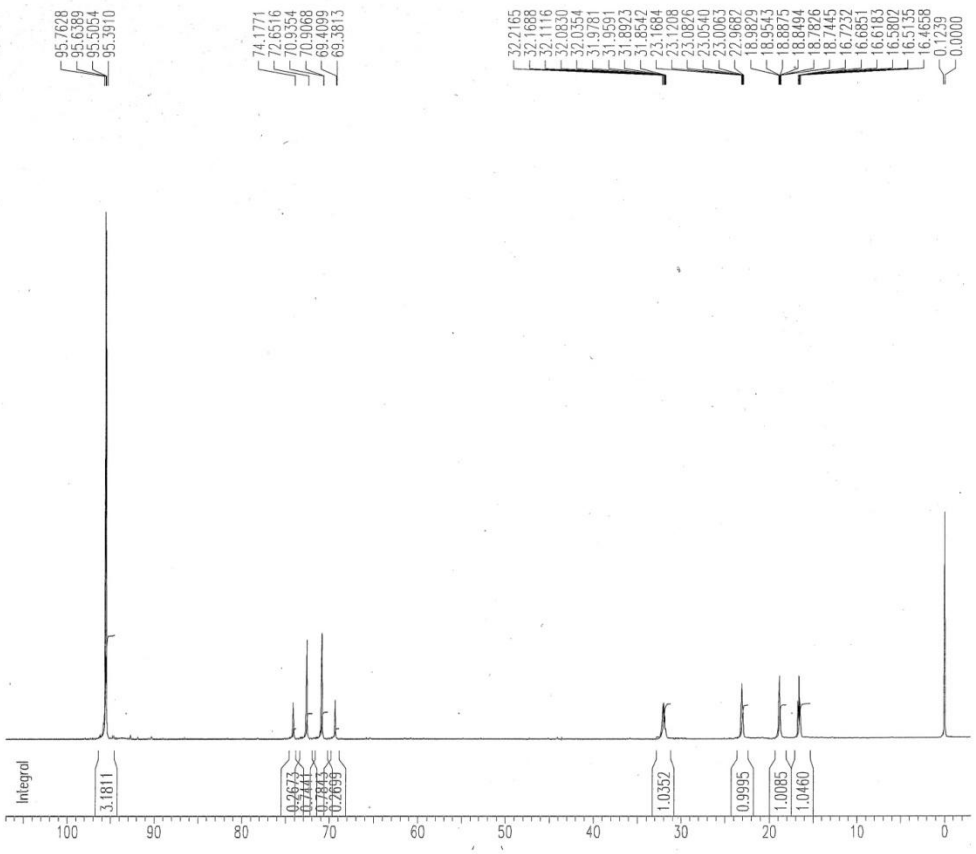


Figure S4 ^{19}F NMR spectrum of compound **3**.

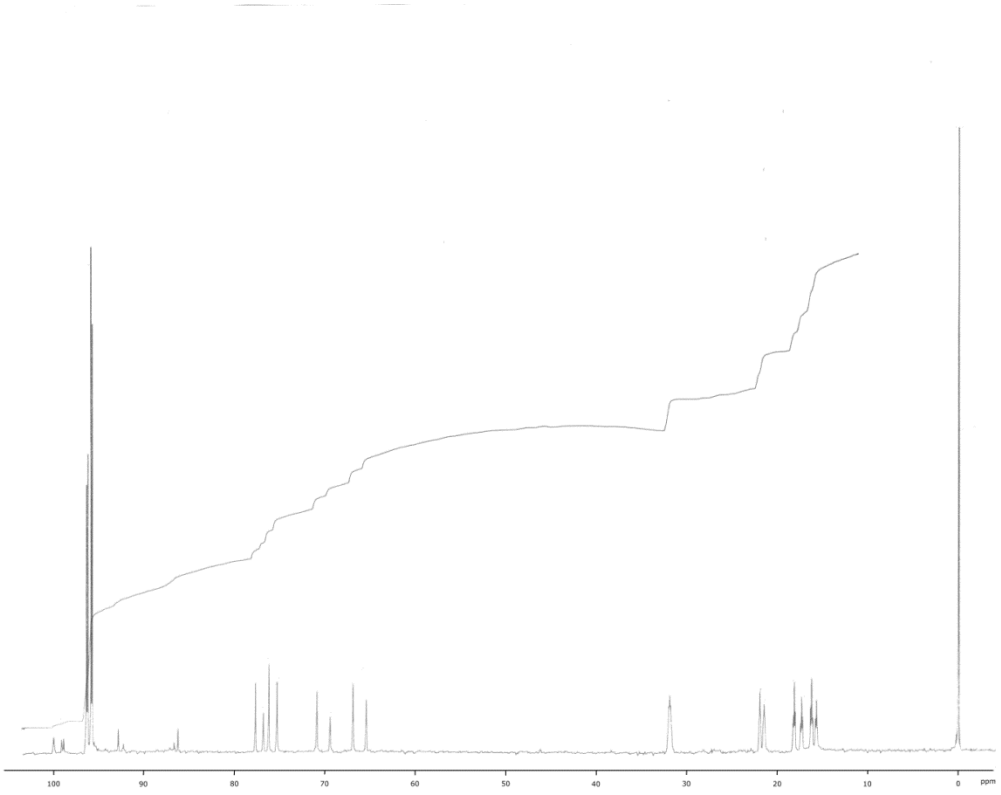


Figure S5 ^{19}F NMR spectrum of the **1** + $SOCl_2$ reaction mixture exhibiting the simultaneous presence of compounds **1** and **3**.

S3. Computational results

DFT calculations have been performed at the B3LYP/6-31G(d) level of theory with the *GAMESS* program.[S4] Solvation was taken into account by the polarizable continuum model[S5-S7] using the built-in parameters for THF. Calculated total free energies (E, a. u.) in THF solvent and XYZ coordinates (Å) of compounds are given in Tables S1-S7.

Table S1 Reagent $SOCl_2$, E = –1393.5445259622

Atom	Atomic coordinates		
	X	Y	Z
Cl	0.2672909508	1.6335294910	0.8924495710
Cl	0.2672867651	–1.6335354911	0.8924443131
O	0.0439813962	0.0000038624	–1.5542560670
S	–0.5785591122	0.0000021378	–0.2316378171

Table S2 Starting compound **1**, E = –4287.8137932263

Atom	Atomic coordinates		
	X	Y	Z
C	2.8900922238	–1.3242945764	0.3149551820
C	3.2676556164	–0.2705805158	0.0775486548
C	3.2676556164	0.9656149088	–0.3337065862
C	1.896612791	1.1660443264	–0.4871893736
C	1.0100593355	0.1316274124	–0.2092145950
C	1.5286371730	–1.1177521084	0.1654173811
C	–0.4924581948	0.0816085793	–0.3696148270
C	0.4486686050	–2.1441157263	0.3024440088
C	–0.8264342312	–1.3589699195	–0.0060014355
C	–1.4442223867	1.0167179572	1.0167179572
C	–0.9952188148	2.3706885671	0.9159852703
Cl	–0.8778584124	0.3080015777	–2.2151245826
F	5.0826437050	–0.4367098060	0.2185843693
F	4.1165653124	1.9646971344	–0.5766730373

F	1.4787071021	2.3601026441	–0.9158755531
F	3.3747467488	–2.5178611549	0.6725363617
F	0.390601400	–2.6926337383	1.5515194886
F	0.6111211090	–3.1907705223	–0.5614747529
F	–0.8488425093	3.2674362505	–0.0785166143
F	–1.8963454802	2.8579821222	1.7761982773
F	0.1827727283	2.2739128546	1.5669345212
N	–1.9687169634	–1.9147959022	0.0809262502
N	–2.7014778294	0.7944903277	0.4748004066
Se	–3.4413479217	–0.8098695874	0.0180249782

Table S3 Intermediate **A**

Atom	Atomic coordinates		
	X	Y	Z
C	0.3328324891	0.5579211190	–0.4434592414
C	1.7983269797	0.186892329	–0.3878481376
C	1.9683367072	–1.0931126029	0.1624223932
C	0.6469345998	–1.7281133525	0.4706728779
C	–0.3568879453	–0.7131960728	–0.0807693524
C	3.2237477699	–1.6617125642	0.3223486145
C	4.3464571019	–0.9396249486	–0.0941490474
C	4.1847114265	0.3218595904	–0.6753338480
C	2.9118026069	0.8908231555	–0.8343125955
C	–0.2535634804	1.5909581104	0.5530259678
C	0.6895868286	2.501079798	1.3564080472
Cl	–3.6837332613	2.9051020315	–0.5124840893
Cl	–0.1138870766	1.1141815721	–2.1554959043
Cl	–2.6103785375	–2.6103785375	–1.1547264333
F	2.8313354248	2.0814851752	–1.4263109228
F	3.3841262535	–2.8791597133	0.8467122777
F	5.5699107001	–1.4509780609	0.0449910872
F	5.2610314359	0.9912898771	–1.0870712062
F	0.4485784556	–1.9283629103	1.8204658035
F	0.4999134329	–2.960391912	–0.1190614628

F	1.4101331533	3.3063269070	0.5423824066
F	1.5651907028	1.7488325243	2.0764312821
F	0.0056902302	3.2727947009	2.2092032208
N	–1.5029602551	1.6816237590	0.7456483806
N	–1.6545218598	–0.8579255710	–0.1031633300
O	–3.6661887068	–2.2128019731	1.2186159034
S	–2.3646356978	–2.5828402153	0.6493576187
Se	–2.8764860139	0.6636029872	–0.1626872727

Table S4 Intermediate **B**, E = –5681.3543158333

Atom	Atomic coordinates		
	X	Y	Z
C	0.3189410264	0.4550799534	–0.4932096516
C	1.7951089299	0.1256710147	–0.3801903853
C	2.007438554	–1.0978588011	0.2724747985
C	0.7176127391	–1.76647381	0.6051075462
C	–0.3380942201	–0.8502067872	–0.0504197504
C	3.2826826370	–1.6050978481	0.4668072498
C	4.3761501737	–0.8880442130	–0.0124972529
C	4.1743705727	0.3168394041	–0.6862720608
C	2.8880001713	0.824193298	–0.8793810608
C	–0.2563067859	1.5836186719	0.3964194788
C	0.7119746394	2.4086014106	1.2508023398
Cl	–4.2697919610	2.9716723621	0.3287745930
Cl	–0.1175533087	0.8373455898	–2.2382730413
Cl	–2.6562540008	–3.3377666711	–1.5538055592
F	2.7549512683	1.9620092924	–1.5617316934
F	3.4791609994	–2.7729642960	1.0823031475
F	5.6125591229	–1.3536328376	0.1503426779
F	5.2243667129	0.9820522035	–1.1617310306
F	0.4704805554	–1.8777898192	1.9433224599
F	0.6303766393	–3.0306935344	0.0942941533
F	1.5982412691	3.0786907882	0.4868410511
F	0.0716326203	3.2969376658	2.0102418238

F	1.4161693904	1.5896991204	2.0672233123
N	–1.5854654140	–1.0501097806	–0.1982173973
N	–1.4817623249	1.9005690152	0.5288704114
O	–3.5552936680	–2.1450494568	1.0363648494
S	–2.2855071838	–2.5761004112	0.4390173924
Se	–2.9887856906	1.1775087924	–0.1616653640

Table S5 Intermediate **C**

Atom	Atomic coordinates		
	X	Y	Z
C	–0.8598999035	–0.2875765297	–0.5996321213
C	–2.3660204002	–0.4094692616	–0.5277136186
C	–2.9139726494	0.6259868465	0.2453921774
C	–1.8501914099	1.5713598650	0.7133528311
C	–0.5934996921	1.0429958477	1.0429958477
C	–4.2797961706	0.7339593865	0.4640409558
C	–5.1304080582	–0.2101820327	–0.1194086722
C	–4.5968746052	–1.2251464515	–0.9197023439
C	–3.2142996645	–1.3281799521	–1.1368688117
C	0.0451216421	–1.2544149476	0.2066977780
C	–0.5454480328	–2.5473596601	0.7921874763
Cl	–0.3048808358	–0.3439914700	–2.3684805564
Cl	0.6011071073	4.6809207673	–0.4087792147
Cl	3.0722430284	2.4560948004	–1.4532815578
Cl	2.5752296901	–3.6506464792	0.7474793857
Cl	5.2795616588	–1.2746093508	–1.5908319416
F	–2.7803649811	–2.3004950781	–1.9374417431
F	–4.7996879062	1.7190361470	1.2003781267
F	–6.4485049960	–0.1416452478	0.0692811822
F	–5.4197923357	–2.1066793958	–1.4870077294
F	–1.6904865426	1.5655673728	2.0829683938
F	–2.1109223853	2.8758603372	0.3695358134
F	–0.9982163141	–3.3687019067	–0.1828230125
F	0.3667847035	–3.2133726033	1.5096665707

F	–1.5939856948	–2.2553803199	1.6084646354
N	0.5927439194	1.5866199171	0.0691085365
N	1.3921981763	–0.9574084494	0.4458040859
O	2.1122730645	3.2268244007	1.6909452544
O	3.9241692166	–1.6891271514	1.6093380992
S	0.7463779841	3.2727773116	1.1549951726
S	2.5324535697	–2.2370570816	1.4957664252
Se	2.2274233160	0.5618503708	–0.2299889305

Table S6 Intermediate **D** + $SeCl_2$, E = –7074.8921041373

Atom	Atomic coordinates		
	X	Y	Z
C	–0.8751755728	–0.3367170826	–0.3777849672
C	–2.3894141387	–0.4257887012	–0.3795092420
C	–2.9736541614	0.5917634076	0.3895977695
C	–1.9410564431	1.5026568033	0.9564164527
C	–0.6366359734	1.0500860851	0.2719927473
C	–4.3492390797	0.7164904783	0.5101549133
C	–5.1705877004	–0.1922445899	–0.1517097372
C	–4.6006143046	–1.1936296516	–0.9407651593
C	–3.2154632420	–1.3149965650	–1.0579508456
C	–0.8171824474	–2.6723142792	0.9351432532
C	–0.0747678551	–1.4156653046	0.4292765938
Cl	3.8239604791	2.1972972399	–2.4546829103
Cl	–0.2187462482	–0.3621177543	–2.0751614160
Cl	0.5878784127	4.3779381812	–0.7313946036
Cl	2.6084297905	–3.6417592925	–0.0952781305
Cl	5.8194266209	–0.1682590548	–1.0677869995
F	–2.7334046894	–2.2811936579	–1.8426668820
F	–4.8937795842	1.6962775263	1.2335173248
F	–6.4947483358	–0.0994170484	–0.0633011734
F	–5.3937287955	–2.0397985360	–1.5930066282
F	–1.8007921020	1.3939557090	2.3138099425
F	–2.1883319579	–2.1883319579	0.6995681243

F	–1.1113796706	–3.4574453959	–0.1096020708
F	–0.0470727002	–3.3689765900	1.7859536812
F	–1.9521726287	–2.3548268995	1.5700718393
N	0.4716121505	1.6560190549	0.1929648057
N	1.1665158834	1.191415667	0.5381041568
O	2.0469290088	3.0946494425	1.5616247048
O	3.5167710643	–1.2092933541	1.3925454631
S	0.6599886094	3.1902490833	1.0857167909
S	2.3607485566	–2.1211143686	1.4413087612
Se	3.7861215537	0.6795422958	–0.8356139965

Table S7 Final product **3**, E = –2284.7858407268

Atom	Atomic coordinates		
	X	Y	Z
C	2.6797991383	–1.0309167484	0.2907239383
C	3.3858450855	0.1533707646	0.0958843746
C	2.6999198622	1.3168713960	–0.2528612480
C	1.3137904557	1.3132425527	–0.4040171542
C	0.5982437628	0.1434111559	–0.1766525843
C	1.3018377588	–1.0276065315	0.1504725399
C	–0.8724139926	–0.1400100334	–0.3715743055
C	0.3910471769	–2.2148710464	0.2310811220
C	–0.9843129062	–1.6109795172	–0.0316038328
C	–1.9862788896	0.6000768173	0.3328742916
C	–1.8401611862	2.0347918467	0.8309958970
Cl	–1.2478596522	0.0441881310	–2.2337893705
F	4.7111593997	0.1849480118	0.2310121264
F	3.3850362517	2.4428789188	–0.4531102561
F	0.7197489153	2.4443834863	–0.7917633508
F	3.3444072198	–2.1500355145	0.5948841984
F	0.4232075895	–2.8367475752	1.4447905795
F	0.7054554028	–3.1708952923	–0.6940812212
F	–1.7974401940	2.8921056059	–0.2066647621
F	–2.8678859096	2.3849746454	1.6111817307

F	–0.7056095652	2.1841352054	1.5460372663
N	–2.0554560025	–2.2989593170	0.0742880752
N	–3.1684001551	0.1037445538	0.4428614090
S	–3.5224907244	–1.4791160409	0.0876332396

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