Supporting Information for:

Interaction of Anti-Thyroid Drugs with Iodine: The Isolation and Characterization of Two Unusual Ionic Deselenides Derived from Se-Methimazole

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Figure S1 FT-IR Spectrum of compound **6**.

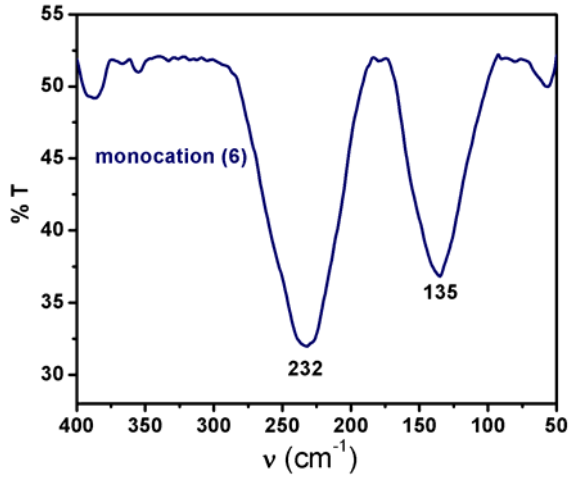


Figure S2 FT-IR Spectra of compounds **5** and **7**.

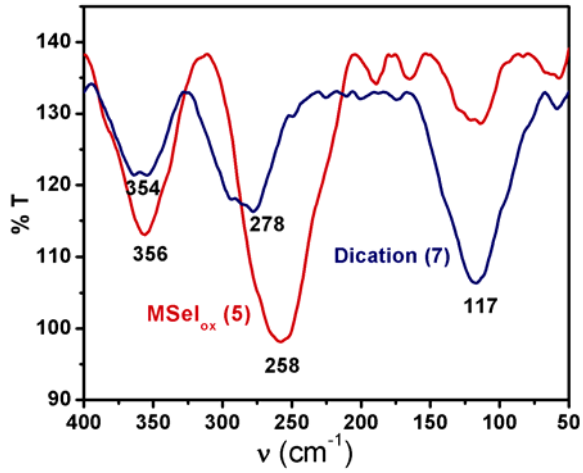


Figure S3. Molecular structures of monocation 6 showing the hydrogen bonding between two monocations.

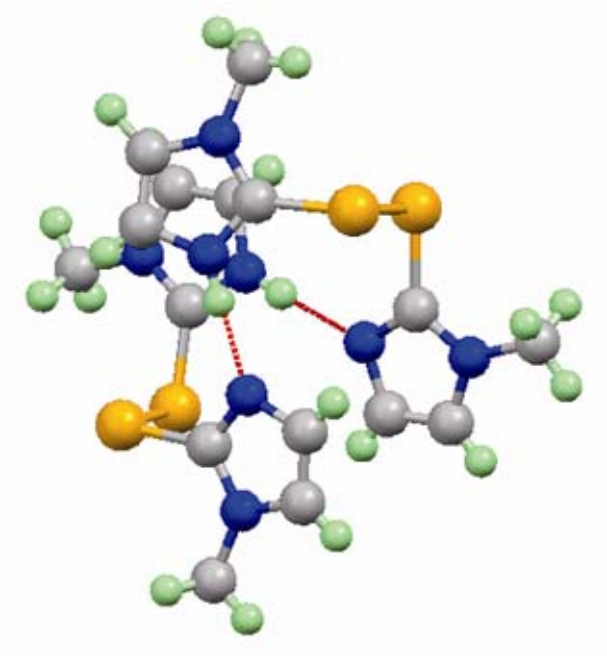
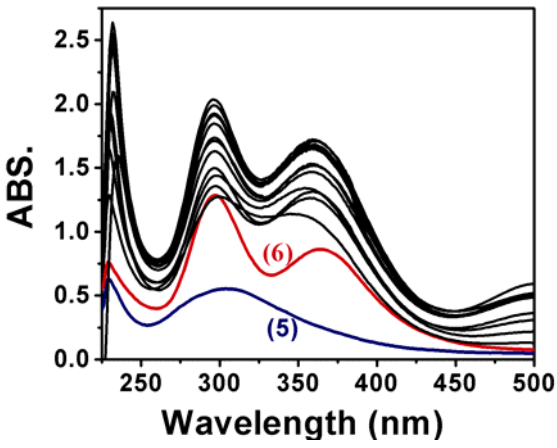


Figure S4. UV-Vis spectra of compound **5** (5 x 10^{-5} M) and compound **6** (5x10^{-5} M), in dichloromethane. UV-Vis spectra of solutions with constant concentrations (10^{-4} M) of **5** and increasing quantities of iodine in dichloromethane ([I_2]/ [**5**]): 1:1, 2:1, 3:1, 4:1, 4.55:1, 4.76:1, 5.0:1, 5.17:1, 5.22:1, 5.33:1, 5.42:1.



Theoretical Calculations

All calculations were performed using Gaussian98 suite of quantum chemical programs. The hybrid Becke 3-Lee-Yang-Parr (B3LYP) exchange correlation functional was applied for DFT calculations. Geometries were fully optimized at B3LYP level of theory using the 6-31G(d) basis sets. All stationary points were characterized as minima by corresponding Hessian indices. The HOMO calculations were done at B3LYP/6-31G(d) level. The solvent effect was included in the calculations at the same level using Tomasi's polarizable continuum model (PCM) in the water solution. All structures are characterized as potential energy minimums at the B3LYP level by verifying that all vibrational frequencies are real.

Table S1

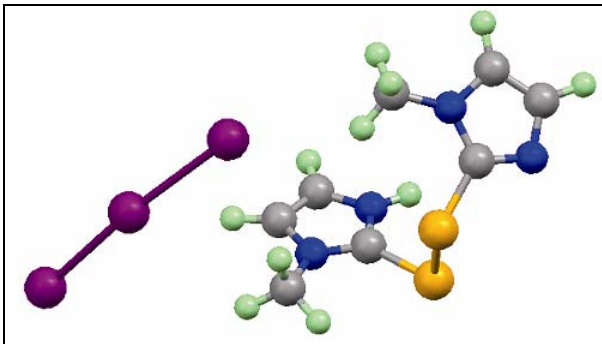
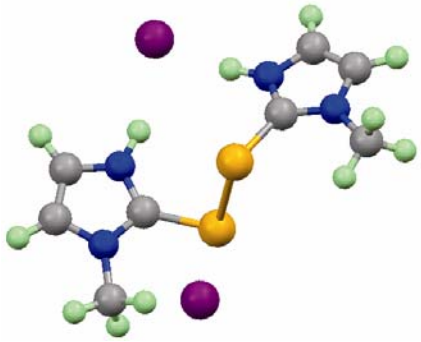
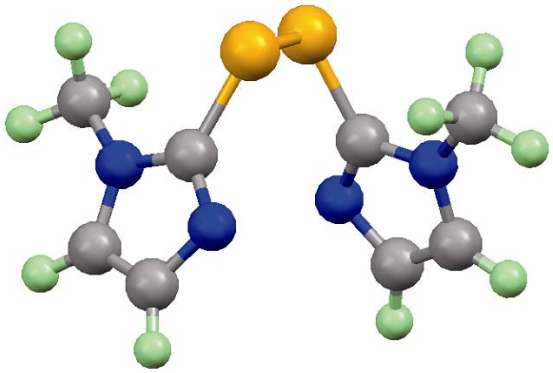
 Compound **6**	 Compound **7**
53 1.766941 2.001418 -2.000614	53 1.040885 -3.532466 -.155020
53 2.008726 5.065789 -2.120669	53 .870834 2.758894 -2.456025
53 1.243051 -1.179281 -1.637736	34 -1.438473 .246976 2.078796
34 -.743909 -2.943393 2.976146	34 -.281604 1.442689 -.170714
34 -2.068162 -.957082 3.383782	7 -2.034068 -2.139578 .552668
7 -3.055433 -.030132 .853952	1 -1.037681 -2.445355 .449481
7 -3.026353 -4.648063 2.789618	7 -3.827165 -1.027952 1.046138
6 -1.992656 -4.095639 2.166029	7 1.977762 -.287621 .412700
7 -1.928781 -4.477591 .838209	1 1.516810 -1.182166 .109808
6 -2.005076 -.091379 1.703520	7 2.372565 1.770265 .967371
7 -1.000320 .594392 1.120946	6 -2.469331 -1.030780 1.179047
6 -2.978339 -5.331946 .641764	6 -3.087875 -2.839854 .019951
1 -3.145923 -5.810851 -.312216	1 -2.931883 -3.753982 -.531045
6 -2.718145 .687401 -.270806	6 -4.219856 -2.150911 .333881
1 -3.406290 .858535 -1.082959	1 -5.257508 -2.350651 .117509
6 -3.646995 -5.411823 1.850427	6 -4.738087 -.025909 1.589326
1 -4.535522 -5.983635 2.082550	1 -5.520006 .181424 .855153
6 -1.415880 1.064710 -.108248	1 -4.169103 .881481 1.794678
1 -.739390 1.601586 -.760641	1 -5.191479 -.385022 2.518212
6 -.897263 -4.164593 -.150893	6 1.441566 .940762 .432511
1 -.472325 -3.178128 .036904	6 3.245872 -.259231 .928635
1 -1.347388 -4.163806 -1.145295	1 3.834588 -1.159458 1.011361
1 -.094387 -4.907385 -.119769	6 3.505852 1.037461 1.267158
6 .370199 .722301 1.633499	1 4.383593 1.500008 1.690031
1 .348857 .620208 2.718398	6 2.238832 3.219090 1.114457
1 .757572 1.699689 1.345235	1 3.011763 3.567554 1.800753
1 .981471 -.057627 1.168709	1 1.251172 3.450098 1.516116
1 -3.947148 -.466930 1.048712	1 2.345691 3.697238 .136608

Table S2



Compound **5**

34	-.826571	1.369227	.758382
7	-.962393	-1.170191	2.029444
7	-2.334036	-1.037146	.264970
6	-1.393237	-.403716	1.040430
6	-2.492052	-2.290540	.802463
1	-3.161693	-3.015203	.362572
6	-1.652933	-2.343964	1.894191
1	-1.508050	-3.165681	2.582599
6	-2.921589	-.5	961271
1	-3.346496	.47	70237
1	-3.707774	-1.195065	-1.297134
1	-2.146632	-.425186	-1.727918
34	.340372	1.127922	-1.321008
7	1.477480	-1.475352	-1.433380
7	2.563815	-.143028	.000936
6	1.524459	-.270264	-.888572
6	3.202468	-1.358198	.019622
1	4.049224	-1.543217	.664470
6	2.528882	-2.154935	-.880568
1	2.743489	-3.179553	-1.152990
6	2.825612	1.010038	.850205
1	2.882574	1.910940	.233330
1	3.772464	.862696	1.372047
1	2.009953	1.127121	1.569747

Table S3

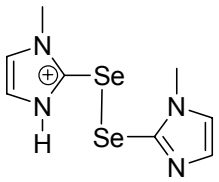
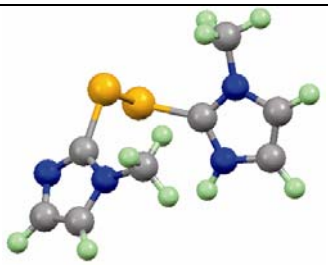
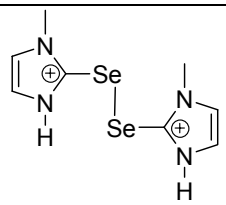
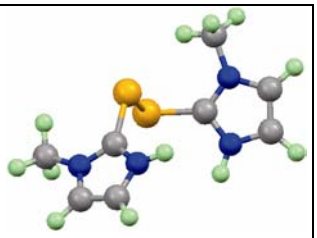
 Compound **8**	 Compound **8**	 Compound **9**	 Compound **9**
34 -1.066358 .206305 1.185613		34 -.780842 .247328 1.196220	
34 -.566753 1.446664 -.799557		34 .135523 1.214265 -.780631	
7 1.926060 .421466 -1.842556		7 -1.274256 -2.562595 .672973	
7 -2.507777 -1.754815 -.258621		1 -.428756 -2.841042 1.160223	
6 -1.430071 -1.481092 .461665		7 -2.867721 -1.312874 -.102983	
7 -.602955 -2.581961 .592947		7 2.526399 -.271569 -1.479929	
6 1.292718 1.154376 -.902879		1 2.036340 -.797301 -2.196355	
7 2.250361 1.646123 -.089213		7 2.920024 1.193747 .069570	
6 -1.228391 -3.602415 -.069385		6 -1.667427 -1.278884 .516792	
1 -.817982 -4.601909 -.092384		6 -2.218641 -3.415500 .159429	
6 3.288274 .447170 -1.635465		1 -2.118085 -4.490287 .194854	
1 3.986186 -.061519 -2.282032		6 -3.217943 -2.623511 -.340482	
6 -2.391754 -3.067085 -.595726		1 -4.141883 -2.889437 -.832944	
1 -3.143663 -3.567401 -1.190511		6 -3.668858 -.137176 -.490715	
6 3.489221 1.209587 -.521895		1 -3.386166 .183436 -1.496508	
1 4.400269 1.480454 -.010944		1 -3.486085 .661991 .227919	
6 .614314 -2.693561 1.387808		1 -4.723297 -.412922 -.471921	
1 .989292 -1.687774 1.582530		6 1.941287 .658873 -.693284	
1 1.364060 -3.266795 .837035		6 3.873573 -.330820 -1.225659	
1 .411876 -3.189678 2.341803		1 4.540947 -.994121 -1.755919	
6 1.981990 2.470339 1.096152		6 4.117322 .586865 -.238632	
1 1.245442 3.231519 .833340		1 5.039750 .855751 .255051	
1 2.911465 2.941265 1.414729		6 2.738210 2.241915 1.090698	
1 1.582658 1.837823 1.892867		1 2.513869 1.779182 2.054997	
1 1.438545 -.056531 -2.591886		1 1.919202 2.891784 .781779	
		1 3.658752 2.821265 1.162528	

Table S4. Data obtained from geometry optimization of all the compounds using B3LYP level.

No.	Compounds	Basis set	Phase	Energy (kcal/mol)
1	**5**	6-31G(d)	Gas	3343728.80
2	**5**	3-21G(d)	Gas	3330671.13
3	**5**	3-21G(d)	Water	3330667.57
4	**6**	6-31G(d) for Se, C, N, and H. 3-21G(d) for I.	Gas	16314001.87
5	**7**	6-31G(d) for Se, C, N, and H. 3-21G(d) for I.	Gas	11990911.96
6	**8**	6-31G(d)	Gas	3343971.29
7	**8**	3-21G(d)	Gas	3330922.53
8	**8**	3-21G(d)	Water	3330921.41
9	**9**	6-31G(d)	Gas	3344149.26
10	**9**	3-21G(d)	Gas	3331110.11
11	**9**	3-21G(d)	Water	3331106.59
12	$\mathbf{I_3^-}$	3-21G(d)	Gas	12971714.92
13	$\mathbf{I_3^-}$	3-21G(d)	Water	12971714.86
14	$\mathbf{I^-}$	3-21G(d)	Gas	4323916.86
15	$\mathbf{I^-}$	3-21G(d)	Water	4323916.86

Calculation of Free energy of the reactions:: To determine the relative possibilities for a number of biologically relevant oxidation and reduction reactions, the sum of the thermal and electronic free energies (zero point energy corrected) were taken as the ΔG° for each compound. All calculations were carried out B3LYP level using 3-21G(d) basis set.

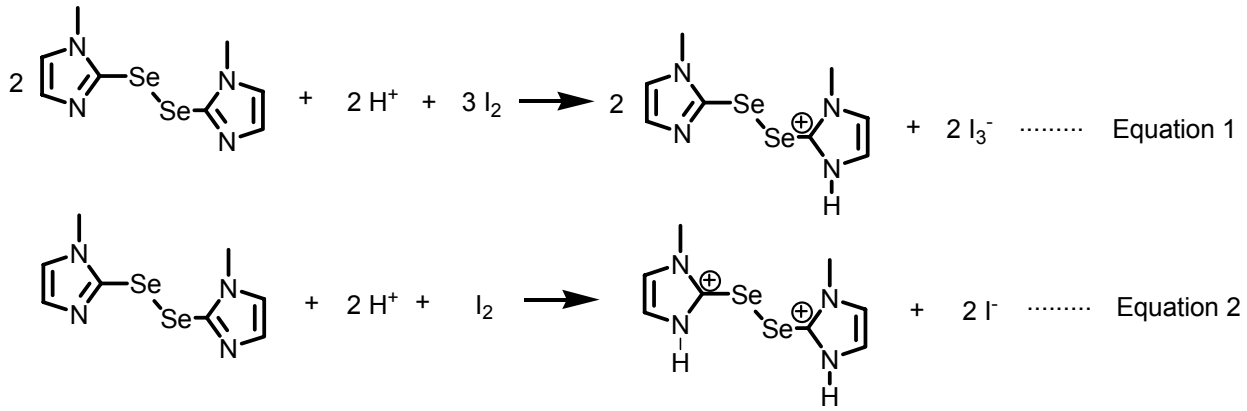


Table S5.

Equations	Phase	ΔG^0 (kcal/mol)
Eq. **1**	Gas	-907.83
Eq. **2**	Gas	-493.27
Eq. **1**	Water[a]	-637.36
Eq. **2**	Water	-501.94

[a]In water phase H^+ was omitted for both reaction.

Lactoperoxidase-catalyzed iodination of L-tyrosine:

(a) Inhibition of LPO-catalyzed iodination of L-tyrosine by different concentration of MSeI (**4**) was carried out by a HPLC method. The incubation mixtures for the HPLC analysis contained KI (1×10^{-3} M), L-tyrosine (1×10^{-3} M), hydrogen peroxide (1×10^{-3} M) and LPO enzyme (1 µg) in 0.05 M phosphate buffer, pH 7.4. The mixture was incubated at room temperature and aliquots (10 µl) injected onto the HPLC column and eluted with gradient solvent system (0.1% TFA in water-MeCN). The decrease in the amount of tyrosine (µg) was calculated from the calibration plot. The chromatograms were extracted at 277 nm.

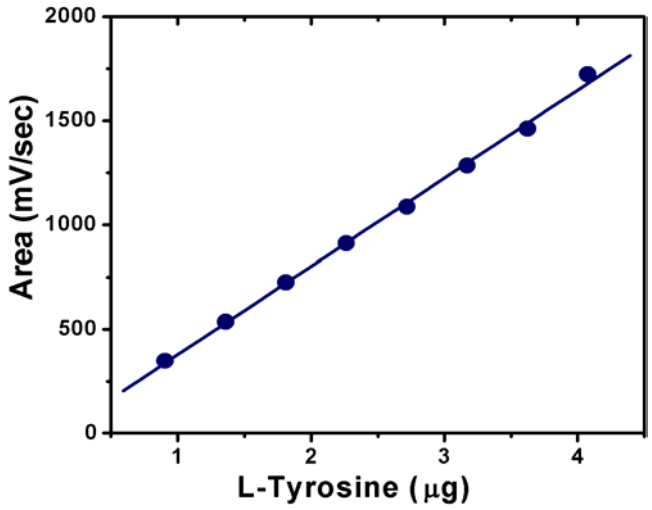


Figure S5: Calibration plot obtained by plotting the peak area versus quantity of L-tyrosine.

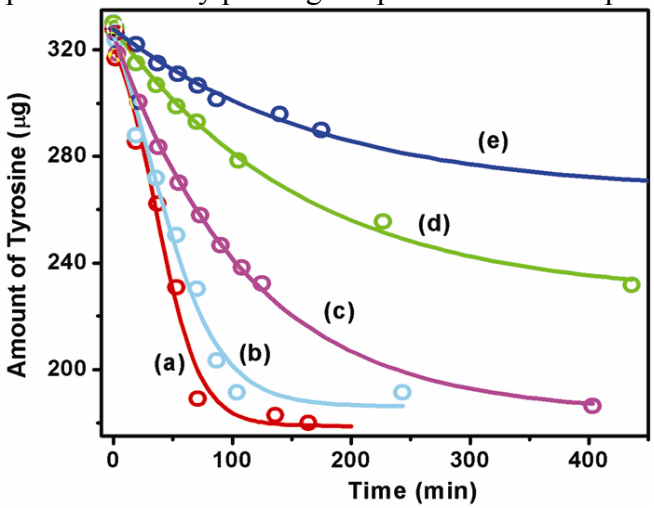


Figure S6: Decrease in the amount of tyrosine with time. (a) control; (b) 6 µM of **4**; (c) 9 µM of **4**; (d) 12 µM of **4**; (d) 15 µM of **4** and (e) 20 µM of **4**.

(b) The effect of hydrogen peroxide concentration on the Inhibition (Figure 1 in the manuscript**)**: In this HPLC assay, the incubation mixtures contained KI (1×10^{-4} M), L-tyrosine (9×10^{-4} M) and LPO enzyme (1.5 µg) in 0.05 M phosphate buffer, pH 7.4. The mixtures were incubated at room temperature and aliquots (10 µl) were injected onto the HPLC column and eluted with gradient solvent system (0.1% TFA in water-MeCN). The formation of the monoiodo tyrosine was followed at 295 nm.