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Supplementary material to

DFT calculations and electrochemical studies on azulene ligands for heavy metal ions detection using chemically modified electrodes

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Experimental and predicted chemical shifts.

Table 1. Comparative predicted and experimental $^1\text{H-NMR}$ shifts for **L1**.

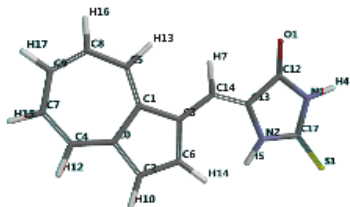
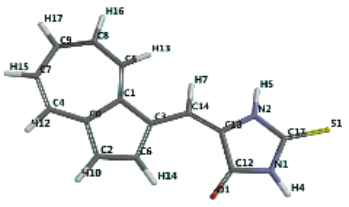
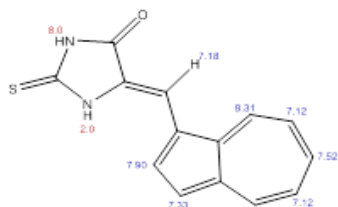
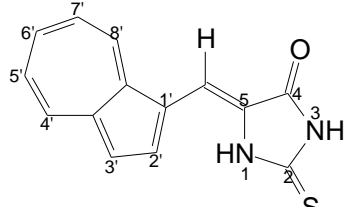
				
	L1 - Z isomer Calculated Data, $^1\text{H-NMR}$ DFT Method	L1 - E isomer Calculated Data, $^1\text{H-NMR}$, DFT Method	L1 - Z and E Calculated Data $^1\text{H-NMR}$ Chem Draw	Experimental data $^1\text{H-NMR}$ (DMSO-d ₆ , δ ppm, J Hz) [5]
H7	6.79	6.16	7.18	7.15 (1H s, CH=)
H15	7.20 $^3J = 9.7$ 9.8	7.20 $^3J = 9.7$ 9.7	7.12	7.39 (1H, t, $^3J_{\text{H,H}} = 9.8$, C(5')-H)
H16	7.28 $^3J = 9.9$ 10.1	7.19 $^3J = 9.9$ 10.3	7.12	7.43 (1H, t, $^3J_{\text{H,H}} = 9.8$, C(7')-H)
H10	7.30 $^3J = 4.2$	7.26 $^3J = 3.7$	7.33	7.54 (1H, d, $^3J_{\text{H,H}} = 4.2$, C(3')-H)
H17	7.77 $^3J = 9.8$ 9.9	7.69 $^3J = 9.7$ 9.9	7.52	7.81 (1H, t, $^3J_{\text{H,H}} = 9.8$, C(6')-H)
H12	8.10 $^3J = 9.7$	8.07 $^3J = 9.7$	8.31	8.42 (1H, d, $^3J_{\text{H,H}} = 9.4$ Hz, C(4')-H)
H14	7.77 $^3J = 4.2$	9.87 $^3J = 3.7$	7.90	8.72 (1H, d, $^3J_{\text{H,H}} = 4.5$, C(2')-H)
H13	8.35 $^3J = 10.1$	7.99 $^3J = 10.3$	8.31	8.74 (1H, d, $^3J_{\text{H,H}} = 9.9$ Hz, C(8')-H)
H4	6.32	6.44	8.0	12.03 (1H, s, NH)
H5	6.91	6.12	2.0	12.19 (1H, s, NH)

Table 2. Comparative predicted and experimental ^{13}C -NMR shifts for **L1**.

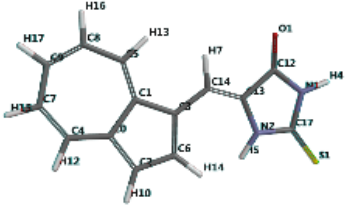
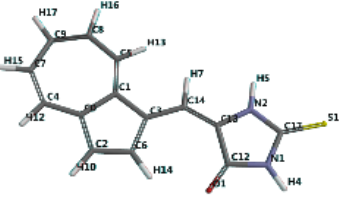
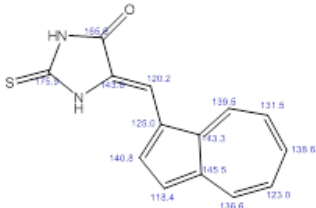
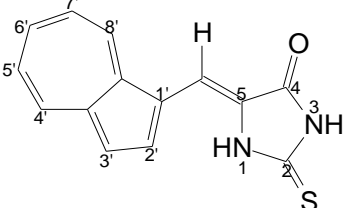
				
	L1 - Z isomer Calculated Data, ^{13}C -NMR DFT Method	L1 - E isomer Calculated Data ^{13}C -NMR DFT Method	L1 - Z and E Calculated Data ^{13}C -NMR Chem Draw	Experimental data ^{13}C -NMR 75 MHz, CDCl_3 , 25 °C [5]
C14	105.08	110.63	120.2	102.2 (CH=)
C2	120.43	120.39	118.4	120.8 (C3')
C13	124.64	124.70	143.6	121.1 (C5)
C3	123.65	123.68	125.0	124.5 (C1')
C8	125.40	124.99	131.5	126.0 (C7')
C7	126.11	126.48	123.0	126.7 (C5')
C5	135.65	131.86	139.5	134.8 (C8')
C6	135.21	144.47	140.8	137.1 (C2')
C4	138.62	137.31	136.6	138.2 (C4')
C1	139.70	139.89	143.3	139.6 (C8a')
C9	140.06	138.49	138.6	140.1 (C6')
C0	142.14	144.44	145.5	143.2 (C3a')
C12	164.05	162.71	175.9	166.0 (C4)
C17	178.15	177.01	165.6	177.1 (C2)

Table 3. Comparative predicted and experimental $^1\text{H-NMR}$ shifts for L2.

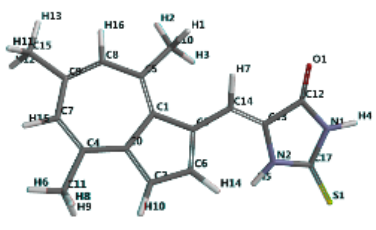
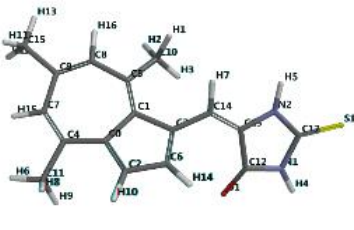
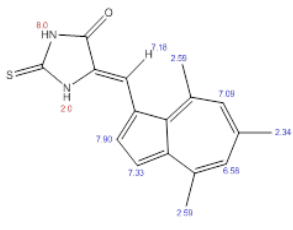
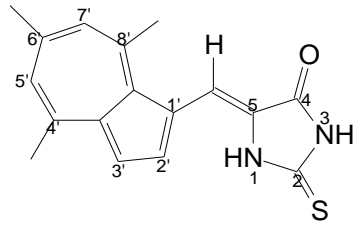
				
	L2 - Z isomer Calculated data, $^1\text{H-NMR}$ DFT Method	L2 - E isomer Calculated Data $^1\text{H-NMR}$ DFT Method	L2 - Z and E Calculated Data Chem Draw $^1\text{H-NMR}$	Experimental data $^1\text{H-NMR}$ (DMSO-d ₆ , δ ppm, J Hz [5])
H11,H12,H13	2.50	2.48	2.34	2.58 [3H, s, Me ₆]
H6, H8, H9	2.66	2.67	2.59	2.80 [3H, s, Me ₄]
H1, H2, H3	2.88	2.76	2.59	3.02 [3H, s, Me ₈]
H15	6.97	7.00	6.58	7.22 (1H, s, (C5')- H)
H16	6.96	6.92	7.09	7.24 (1H, s, (C7')- H)
H7	7.04	6.51	7.18	7.35 (1H, s, CH=)
H10	7.18 $^3J = 4.2$	7.13 $^3J = 4.0$	7.33	7.39 (1H, d, $^3J_{\text{H,H}} = 4.6$, (C3')-H)
H14	7.57 $^3J = 4.2$	9.69 $^3J = 4.0$	7.90	8.06 (1H, d, $^3J_{\text{H,H}} = 4.6$, (C2')-H)
H4	6.28	6.39	8.0	12.03 (1H, s, NH)
H5	6.88	5.99	2.0	12.19 (1H, s, NH)

Table 4. Comparative predicted and experimental ^{13}C -NMR shifts for L2.

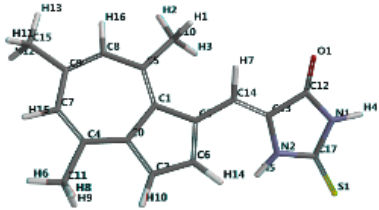
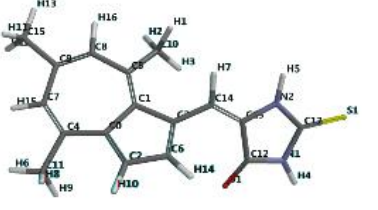
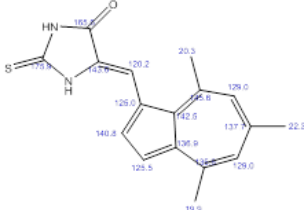
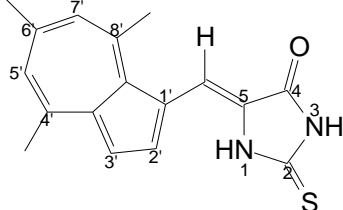
				
	L2 - Z isomer Calculated data ^{13}C -NMR DFT Method	L2 - E isomer Calculated Data ^{13}C -NMR DFT Method	L2 - Z and E Calculated Data Chem Draw ^{13}C -NMR	Experimental data ^{13}C -NMR 75 MHz, DMSO, 25°C [5]
C11	27.20	27.35	19.9	25.2 (Me ₄)
C10	31.55	31.57	20.3	27.8 (Me ₈)
C15	29.43	29.06	22.3	28.8 (Me ₆)
C14	112.89	116.86	120.2	111.6 (CH=)
C2	117.50	118.24	125.5	117.8 (C3')
C13	124.05	122.67	143.6	122.3 (C5)
C3	125.17	125.27	125.0	124.2 (C1')
C6	133.22	142.74	140.8	136.4 (C2')
C8	133.13	133.49	129.0	129.9 (C7')
C7	130.21	130.99	129.0	131.5 (C5')
C0	139.08	141.90	136.9	135.2 (C3a')
C1	137.32	138.88	142.5	139.5 (C8a')
C4	147.27	145.79	135.0	146.7 (C4')
C5	151.47	147.47	145.6	147.9 (C8')
C9	148.78	146.76	137.7	148.2 (C6')
C12	163.62	162.43	165.6	165.7 (C4)
C17	180.80	176.36	175.9	177.2 (C2)

Table 5. Comparative predicted and experimental $^1\text{H-NMR}$ shifts for **L3**.

	L3 – Z isomer Calculated data $^1\text{H-NMR}$ DFT Method	L3 - E isomer Calculated Data $^1\text{H-NMR}$ DFT Method	L3 - Z and E Calculated Data $^1\text{H-NMR}$ Chem Draw	Experimental data $^1\text{H-NMR}$ (DMSO-d ₆ , δ ppm, J Hz [5])
H10, H15, H18, H11, H19, H20	1.39, $^3J = 6.4$	1.39 $^3J = 6.4$	1.20	1.30 (6 H, d, $^3J_{\text{H,H}} = 6.9$, (Me ₂ CH)
H6, H8, H9	2.89	2.77	2.59	3.00 (3H, s, Me ₈)
H1, H3, H2	2.48	2.44	2.59	2.57 (3H, s, Me ₃)
H13	2.90 $^3J = 6.4(x6)$	2.92 $^3J = 6.4(x6)$	2.87	3.11 (6 H, d, $^3J_{\text{H,H}} = 6.9$, (CH ₃) ₂ CH)
H16	7.05 $^3J = 11.6$	7.03 $^3J = 11.7$	7.12	7.19 91H, d, $^3J_{\text{H,H}} = 9.8$, C(7')-H)
H7	7.06	6.54	7.18	7.38 (1H s, CH=)
H17	7.56 $^3J = 11.6$	7.52 $^3J = 11.7$	7.52	7.54 (1H, dd, $^3J_{\text{H,H}} = 11$, $^4J_{\text{H,H}} = 1.6$ C(6')-H)
H12	7.94	7.92	8.31	8.13 (1H, t=d, $^4J_{\text{H,H}} = 1.6$ Hz, C(4')-H)
H14	7.53	9.74	7.90	8.17 (1H, s, C(2')-H)
H4	6.28	6.40	8.0	12.18 (H, s, NH)
H5	6.88	5.99	2.0	12.18 (H, s, NH)

Table 6. Comparative predicted and experimental ^{13}C -NMR shifts for **L3**.

	L3 - Z isomer Calculated data ^{13}C -NMR DFT Method	L3 - E isomer Calculated Data ^{13}C -NMR DFT Method	L3 - Z and E Calculated Data ^{13}C -NMR Chem Draw	Experimental data ^{13}C -NMR 75 MHz, DMSO, 25°C [5]
C10	13.87	13.86	12.8	12.79 (Me ₃)
C16, C18	25.18	25.24	19.1	24.16 ((CH ₃) ₂ C)
C11	30.73	30.60	28.2	27.98 (Me ₈)
C15	40.85	40.80	38.1	37.11 ((CH ₃) ₂ C)
C14	111.76	115.98	120.2	110.6 (C=)
C2	128.04	128.88	130.5	127.3 (C3')
C13	123.82	123.07	146.6	123.8 (C5)
C3	122.37	123.39	125.0	119.6 (C1')
C8	131.32	132.17	135.5	130.7 (C7')
C6	136.89	146.13	139.3	134.5 (C2')
C4	139.03	137.54	133.9	136.5 (C4')
C7	143.50	144.49	139.5	144.1 (C5')
C9	136.38	134.77	134.8	138.7 (C6')
C1	138.31	139.37	142.5	136.7 (C8a')
C0	141.38	144.67	147.2	140.8 (C3a')
C5	150.87	146.63	152.7	146.9 (C8')
C12	163.68	162.28	165.6	165.7 (C4)
C17	180.56	176.10	175.9	176.8 (C2)