Supporting Information

Targeted high resolution ion mobility separation coupled to ultra-high resolution mass spectrometry of endocrine disruptors in complex mixtures

Paolo Benigni[1]; Christopher J. Thompson[2]; Mark E. Ridgeway[2],

Melvin A. Park[2], and Francisco Fernandez-Lima[1,3*].

[1] *Department of Chemistry and Biochemistry, Florida International University, Miami, USA*

[2] *Bruker Daltonics Inc., Billerica, Massachusetts, USA*

[3] *Biomolecular Sciences Institute, Florida International University, Miami, FL 33199*

Table of Contents:

METHODS

Ion Mobility Spectrometry – Mass Spectrometry Separation

The reduced mobility, K_0, of an ion in a TIMS cell is described by:

$$K_0 = \frac{v_g}{E}\frac{n}{n_o} = \frac{A}{(V_{elution} - V_{base})} \quad (1)$$

where v_g , E, n_0, $V_{elution}$ and V_{base} are the velocity of the gas, applied electric field, standard gas density, elution and base voltages, respectively. The constant A can be determined using calibration standards of known reduced mobilities.

Reduced mobility values (K_0) were correlated with CCS (Ω) using the equation:

$$\Omega = \frac{(18\pi)^{1/2}}{16}\frac{ze}{(k_B T)^{1/2}}\left[\frac{1}{m_I} + \frac{1}{m_b}\right]^{1/2}\frac{1}{K_0}\frac{1}{N^*} \quad (3)$$

where z is the charge of the ion, k_B is the Boltzmann constant, N^* is the number density and m_I and m_b refer to the masses of the ion and bath gas, respectively. [1]

Theoretical Calculations

Candidate structures were proposed for each molecular ion observed in the IMS-FT-ICR MS experiments. The initial pool of candidate structures was obtained using serial molecular dynamics simulations of annealing and geometry optimization cycles in a NVT thermostat (equivalent to the approach described in ref [2]) using AMBER03 force field in YASARA software. In particular, the NVT thermostat was set to recreate the IMS cell experiment; the simulation box contained the molecular ion of interest with bath and dopant gas molecules. Final structures were optimized at the DFT/B3LYP/6-31G(d,p) level using Gaussian software.[3]

Vibrational frequencies were calculated to guarantee that the optimized structures correspond to a real minima in the energy space and zero-point energy corrections were applied to calculate the relative stability between the structures. Theoretical ion-neutral collision cross sections were calculated using MOBCAL [4,5] and IMoS (v 1.04b) [6-8] software for nitrogen as a bath gas at ca. 300K. In the IMoS calculations, 100 total rotations were performed using the diffuse hard sphere scattering method with a Maxwell distribution. Partial atomic charges were calculated using the Merz-Singh-Kollman scheme constrained to the molecular dipole moment. [9,10] All optimized geometries and partial atomic charges are provided in the supporting information.

Figure S1. Relative abundance of the oxygen containing series ($CxHyO_{1-15}$) identified in the SRFA sample.

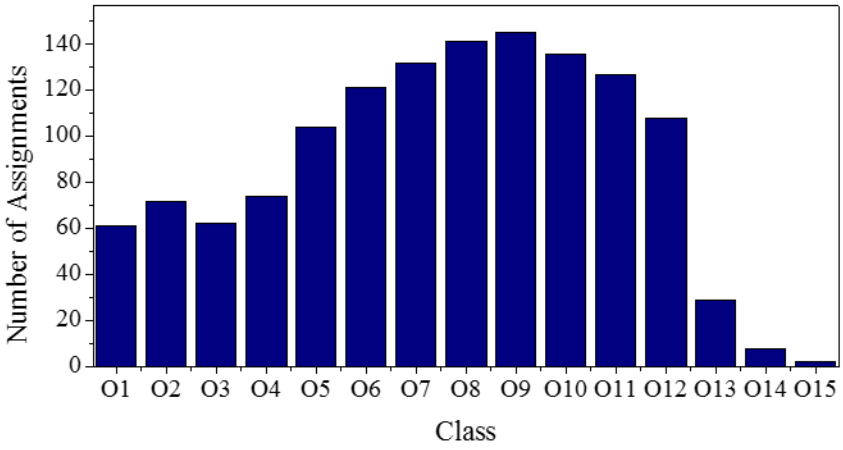


Figure S2. Double Bond Equivalents (DBE) as a function of the carbon number for the oxygen containing series ($C_xH_yO_{1-15}$) identified in the SRFA sample.

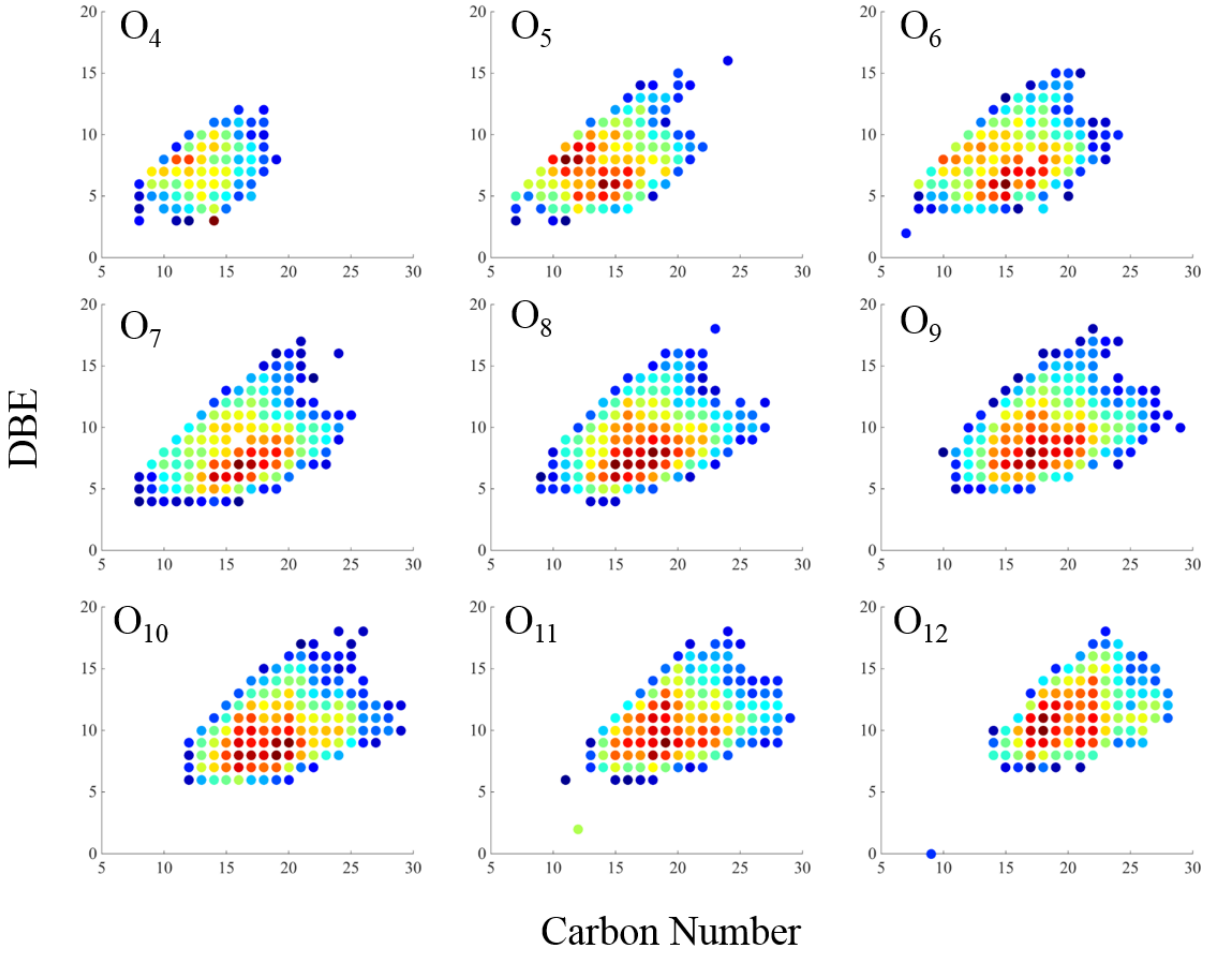
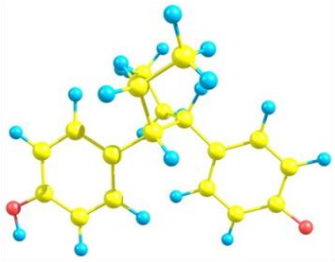


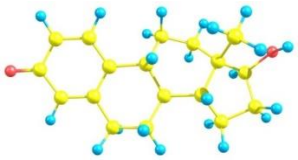
Table S1. Candidate structures geometry and atomic charges for the EDC targeted compounds.

hexestrol



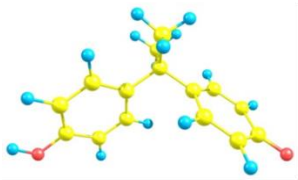
Atom	Coordinates			Partial Charges
C	0.8034	2.15838	2.24896	-0.108
C	-0.21698	3.37566	-1.59239	-0.19335
O	4.8143	-2.37175	0.16052	-0.58302
C	1.53285	0.11356	-0.51033	0.1909
C	2.74572	0.63684	-0.04164	-0.25453
C	1.41577	-1.24955	-0.77242	-0.25405
C	3.82829	-0.21481	0.15241	-0.19728
C	2.4834	-2.10793	-0.55404	-0.24588
C	3.70626	-1.58804	-0.10714	0.33254
C	0.37166	1.02882	-0.7567	-0.11688
C	-0.6334	1.14454	0.43539	0.0906
O	-5.18129	-2.17482	-0.21793	-0.85452
C	-4.03312	-1.4351	-0.06098	0.50131
C	-4.19282	-0.03789	-0.06441	-0.18143
C	-2.76328	-2.00894	0.10471	-0.21694
C	-3.07505	0.76602	0.0895	-0.3696
C	-1.65919	-1.18418	0.27951	-0.39997
C	-1.79769	0.20792	0.24294	0.15352
C	0.87728	2.43308	-1.15482	0.25519
C	-0.00855	0.95028	1.82994	0.00863
H	-0.17632	0.60017	-1.63563	0.02301
H	-1.04883	2.19181	0.39931	0.0272
H	1.3658	1.98634	3.17437	0.00238
H	1.54628	2.38337	1.4554	0.02363
H	0.18808	3.05168	2.39506	0.00295
H	-0.79084	2.98863	-2.43923	0.0401
H	-0.93574	3.52604	-0.76616	0.02962
H	0.17098	4.36532	-1.86486	0.01117
H	4.5845	-3.26623	-0.06084	0.38571
H	2.79821	1.71399	0.20467	0.13639
H	0.4566	-1.64321	-1.14255	0.16813
H	4.75423	0.19555	0.56934	0.13926
H	2.37686	-3.16523	-0.81444	0.1224
H	-5.1733	0.40376	-0.28478	0.09234
H	-2.63893	-3.09578	0.15073	0.08216
H	-3.15793	1.85975	0.01296	0.10605
H	-0.64955	-1.62231	0.35621	0.17303
H	1.63604	2.33815	-1.9592	-0.0789
H	1.43387	2.86084	-0.28286	-0.06256
H	0.66424	0.0692	1.79637	0.02509
H	-0.77556	0.69885	2.58441	-0.00641

α-estradiol



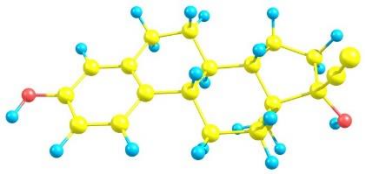
Atom	Coordinates			Partial Charges
O	0.04883	0.0121	-0.01332	-0.70981
C	0.02021	-0.0005	1.41582	0.43585
C	1.39989	-0.00471	2.07929	-0.37502
C	1.06723	0.28389	3.54576	0.12247
C	-0.04325	1.3621	3.48955	-0.02663
C	-0.77078	1.16527	2.10186	0.2388
C	-0.6833	2.45003	1.26056	-0.35231
C	-2.24258	0.77119	2.32073	-0.02242
C	-3.02893	1.74555	3.21893	-0.04844
C	-2.19706	2.29923	4.41389	0.23056
C	-3.03682	2.59354	5.65075	-0.34997
C	-4.28218	3.24527	5.53244	-0.0108
C	-5.05333	3.60151	6.62658	-0.51027
C	-0.99825	1.37092	4.69583	0.04208
C	-0.30212	1.77913	5.99718	-0.07501
C	-1.25462	1.62917	7.18442	0.02157
C	-2.58575	2.32847	6.96122	0.17201
C	-3.35124	2.68446	8.06997	-0.53202
C	-4.63464	3.33601	7.98515	0.75933
O	-5.32805	3.65268	9.00102	-0.82494
H	0.46141	0.83509	-0.29709	0.37772
H	-0.48326	-0.9425	1.65551	0.01289
H	1.93682	-0.9433	1.91609	0.07261
H	2.01365	0.80336	1.65842	0.06573
H	0.68279	-0.62535	4.0246	-0.04193
H	1.93498	0.60562	4.12584	-0.00845
H	0.44734	2.34433	3.46794	-0.01749
H	-1.20288	2.3395	0.30335	0.06274
H	-1.13929	3.28702	1.79337	0.07455
H	0.35801	2.73313	1.06033	0.0474
H	-2.73919	0.65812	1.34911	-0.02005
H	-2.25963	-0.22349	2.78074	-0.04855
H	-3.41475	2.57823	2.62264	0.00963
H	-3.90827	1.22642	3.61086	0.00233
H	-1.74775	3.24987	4.07204	-0.04135
H	-4.65788	3.48835	4.53877	0.05393
H	-6.009	4.10159	6.48661	0.12489
H	-1.38048	0.34858	4.84231	0.00823
H	0.60021	1.17566	6.15889	-0.0223
H	0.02498	2.82511	5.91218	0.00443
H	-1.42348	0.55669	7.36411	-0.01613
H	-0.78717	2.01686	8.09633	0.00054
H	-2.97814	2.46654	9.06965	0.11362

bisphenol A



Atom	Coordinates			Partial Charges
C	0.06363	0.01932	0.04499	-0.32861
C	0.02513	-0.00237	1.59253	0.44587
C	1.49503	0.02355	2.07974	-0.28817
C	-0.66097	-1.26344	2.13768	0.0274
C	-0.85368	-1.42056	3.52668	-0.17188
C	-1.43697	-2.54946	4.07914	-0.43208
C	-1.89724	-3.66433	3.27861	0.70566
C	-1.69266	-3.47224	1.86297	-0.39056
C	-1.10419	-2.32845	1.333	-0.2722
O	-2.42975	-4.70344	3.77598	-0.81462
C	-0.73907	1.26477	2.03276	0.05477
C	-2.14195	1.29103	1.9498	-0.20249
C	-2.88173	2.42279	2.27544	-0.23879
C	-2.22727	3.57516	2.71443	0.42191
C	-0.84037	3.57804	2.8187	-0.40027
C	-0.11125	2.43273	2.47586	-0.15015
O	-2.99964	4.67533	3.03757	-0.60259
H	0.54567	0.93865	-0.30321	0.04047
H	0.63089	-0.83177	-0.34303	0.06067
H	-0.94079	-0.01724	-0.38336	0.0446
H	1.55347	0.0863	3.16889	0.02942
H	1.9827	-0.9059	1.77643	0.04747
H	2.06454	0.85816	1.65156	0.02636
H	-0.54491	-0.61924	4.19796	0.09518
H	-1.5691	-2.62429	5.15613	0.11752
H	-2.02111	-4.26996	1.20057	0.10107
H	-0.99117	-2.27596	0.25304	0.12381
H	-2.66078	0.38801	1.647	0.13939
H	-3.96454	2.41908	2.21062	0.15299
H	-0.32117	4.46737	3.17079	0.14619
H	0.96736	2.47124	2.5709	0.12542
H	-2.41675	5.37531	3.34904	0.38623

17-α- Ethynylestradiol



Atom	Coordinates			Partial Charges
O	-6.31537	-0.18184	-0.16129	-0.59389
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C	-4.19663	0.88466	-0.05573	-0.35196
C	-2.80173	0.85445	0.06373	0.15109
C	-2.12829	-0.3771	0.20345	-0.10616
C	-2.90867	-1.54159	0.22159	-0.05672
C	-4.29678	-1.51284	0.10194	-0.43044
C	-0.61003	-0.43838	0.38229	0.02366
C	0.04981	-1.70492	-0.20717	0.03103
C	1.57611	-1.7413	0.00901	-0.27009
C	2.26078	-0.46364	-0.48605	0.91017
C	1.576	0.7526	0.17922	0.01049
C	2.50637	1.94114	-0.13682	-0.22884
C	3.92548	1.31021	-0.21393	0.07504
C	3.75045	-0.23694	0.01525	-0.21566
C	3.91077	-0.58534	1.42084	0.49672
C	3.9238	-0.79025	2.65084	-1.09294
O	4.7174	-0.9886	-0.77094	-0.71367
C	0.08243	0.85051	-0.12667	0.07903
C	-0.6018	2.06817	0.50009	0.04711
C	-2.0504	2.17318	0.02108	-0.1237
C	2.21129	-0.41162	-2.02854	-0.64517
H	-0.41767	-0.46814	1.46607	0.01222
H	1.67255	0.56862	1.25637	0.00821
H	-0.06806	0.91783	-1.21589	-0.04855
H	-6.69499	-1.06558	-0.11813	0.38978
H	-4.71419	1.83358	-0.16028	0.16244
H	-2.42669	-2.5048	0.33658	0.10935
H	-4.86732	-2.4386	0.12138	0.15244
H	-0.37825	-2.59809	0.25859	0.00509
H	-0.20035	-1.77122	-1.27447	-0.04177
H	1.80489	-1.84865	1.07407	0.04333
H	1.99513	-2.62131	-0.49305	0.00619
H	2.23513	2.41593	-1.08804	0.01384
H	2.44595	2.71542	0.632	0.03501
H	4.37796	1.49493	-1.19665	-0.03201
H	4.60538	1.70863	0.53731	-0.00291
H	4.70365	-0.63194	-1.66631	0.40495
H	-0.56812	1.97709	1.59322	-0.01649
H	-0.06473	2.98724	0.24549	-0.01475
H	-2.058	2.53974	-1.01476	0.03362
H	-2.6008	2.91919	0.60571	0.02818
H	2.73125	-1.27978	-2.44488	0.0985
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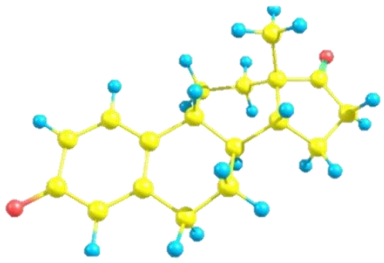
estrone



Atom	Coordinates			Partial Charges
O	-0.02394	-0.08503	-0.00103	-0.54838
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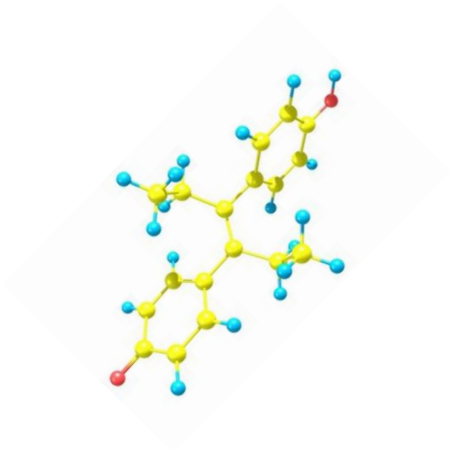
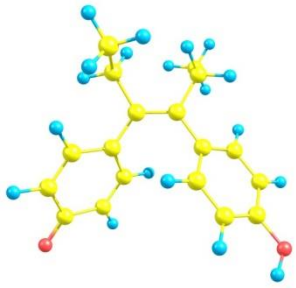
C	1.25924	-0.01154	2.08071	0.39826
C	2.13211	1.20697	1.70867	-0.12628
C	3.35511	1.36362	2.63859	0.04215
C	3.08468	0.94533	4.11289	0.09068
C	3.97426	1.66656	5.11795	-0.2525
C	5.35398	1.8247	4.86946	-0.06731
C	6.22051	2.41155	5.77646	-0.48002
C	5.77523	2.90492	7.06118	0.76769
O	6.55306	3.44841	7.90457	-0.82778
C	4.36469	2.71222	7.28912	-0.55554
C	3.50181	2.12363	6.36682	0.1763
C	2.02916	1.99699	6.72313	-0.00753
C	1.31895	0.90924	5.91655	-0.09923
C	1.58375	1.09493	4.42005	-0.01619
C	0.73755	0.14396	3.54777	0.10156
C	-0.74269	0.59471	3.41994	-0.03949
C	-1.24414	0.0001	2.10113	-0.29271
C	2.01312	-1.33166	1.82442	-0.34293
H	2.43996	1.12583	0.66181	-0.00129
H	1.51217	2.10909	1.77141	-0.00398
H	4.19594	0.78724	2.24227	-0.00338
H	3.67363	2.4099	2.62399	-0.01412
H	3.29523	-0.13649	4.18392	-0.01351
H	5.76492	1.46634	3.92591	0.06935
H	7.27713	2.51435	5.54042	0.11656
H	3.9721	3.05576	8.24503	0.12084
H	1.92909	1.79934	7.79603	0.01217
H	1.51948	2.95553	6.54385	-0.00496
H	1.68666	-0.0807	6.22081	0.02165
H	0.24081	0.92563	6.12375	-0.00678
H	1.29792	2.12826	4.16857	0.02054
H	0.75385	-0.84864	4.01801	-0.0599
H	-1.34276	0.29076	4.27982	0.02333
H	-0.78741	1.68838	3.36962	0.00463
H	-2.06338	0.53665	1.61823	0.0876
H	-1.56969	-1.04075	2.23342	0.07626
H	2.27349	-1.41618	0.76587	0.06878
H	2.92859	-1.38397	2.41581	0.06163
H	1.39516	-2.1956	2.09224	0.04378

(E)-diethylstilbestrol



Atom	Coordinates			Partial Charges
O	0.35169	0.11722	0.00505	-0.79451
C	0.32226	0.10512	1.26863	0.77529
C	1.06025	1.04425	2.08879	-0.47607
C	1.0055	1.0325	3.46875	-0.04206
C	0.23684	0.09375	4.20139	-0.09809
C	0.19769	0.07428	5.67122	-0.03201
C	0.11077	1.19439	6.45871	-0.33393
C	0.29771	1.14449	7.93657	0.20651
C	1.49658	0.6923	8.52076	-0.25161
C	1.69862	0.68211	9.89952	-0.2115
C	0.69519	1.14563	10.74921	0.42217
O	0.93416	1.12228	12.11084	-0.61866
C	-0.49814	1.62081	10.20655	-0.51349
C	-0.68534	1.61933	8.82379	0.05882
C	-0.27337	2.57724	5.92383	0.33861
C	-1.68138	2.64623	5.30687	-0.16906
C	0.18003	-1.31596	6.31485	0.11831
C	-1.20429	-1.74644	6.83327	-0.01346
C	-0.45436	-0.86677	3.41723	-0.0674
C	-0.43531	-0.86211	2.03571	-0.47209
H	1.69287	1.76166	1.57178	0.11777
H	1.62139	1.74198	4.01442	0.0818
H	2.29684	0.35496	7.87049	0.13305
H	2.63423	0.33314	10.32375	0.14521
H	0.15897	1.47146	12.56242	0.40582
H	-1.28618	1.98714	10.86167	0.16107
H	-1.62588	1.98701	8.42668	0.09097
H	-0.21295	3.29389	6.74966	-0.11902
H	0.44396	2.93117	5.18079	-0.03263
H	-1.90217	3.66098	4.95585	-0.00267
H	-1.76464	1.96763	4.4562	0.06269
H	-2.44812	2.36711	6.03789	0.00441
H	0.53189	-2.04383	5.58023	-0.04081
H	0.88375	-1.36139	7.14832	-0.00181
H	-1.16952	-2.76507	7.23759	-0.02402
H	-1.55025	-1.08088	7.62856	-0.02695
H	-1.95132	-1.7259	6.03506	-0.0091
H	-1.05118	-1.62765	3.91534	0.11356
H	-0.99735	-1.60633	1.47685	0.11491

(Z)-diethylstilbestrol



Atom	Coordinates			Partial Charges
O	-3.88502	-3.2652	-0.56398	-0.78584
C	-3.19784	-2.21287	-0.4369	0.74015
C	-1.97769	-1.96663	-1.1808	-0.38152
C	-1.22621	-0.82173	-1.02247	-0.11381
C	-1.59057	0.21965	-0.12925	-0.09566
C	-0.79002	1.43687	0.02821	0.04389
C	0.58264	1.50073	-0.05229	-0.47061
C	1.47904	0.32143	0.05923	0.41532
C	2.70728	0.24279	-0.62706	-0.31918
C	3.59325	-0.82466	-0.46256	-0.25034
C	3.27521	-1.85558	0.41394	0.41119
O	4.17016	-2.90178	0.55197	-0.6106
C	2.07373	-1.80183	1.12612	-0.33843
C	1.19927	-0.73701	0.94855	-0.2648
C	1.29835	2.83894	-0.22171	0.2861
C	1.34015	3.36324	-1.67135	-0.17192
C	-1.58421	2.72319	0.27353	0.12693
C	-1.58146	3.19444	1.74009	-0.11635
C	-2.8083	0.01967	0.57391	-0.13293
C	-3.56599	-1.12858	0.4505	-0.436
H	-1.67704	-2.72406	-1.90033	0.09828
H	-0.33121	-0.69787	-1.62484	0.12541
H	2.98332	1.02291	-1.32736	0.16927
H	4.52426	-0.86489	-1.01839	0.14418
H	3.77027	-3.56603	1.12278	0.38715
H	1.81739	-2.59806	1.82176	0.14722
H	0.27057	-0.72413	1.50462	0.19181
H	0.83598	3.60694	0.40463	-0.02513
H	2.3252	2.74571	0.14664	-0.06949
H	1.8718	4.3212	-1.73116	-0.00207
H	1.84256	2.65801	-2.33917	0.02394
H	0.33029	3.51108	-2.0642	0.03609
H	-1.205	3.53227	-0.35728	-0.00316
H	-2.6168	2.5629	-0.04347	-0.02995
H	-2.1707	4.11159	1.85857	0.00113
H	-2.00963	2.43301	2.3972	0.00981
H	-0.56717	3.39668	2.09598	0.0148
H	-3.15376	0.78356	1.26679	0.13667
H	-4.48129	-1.24729	1.02504	0.10846

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