

Supplementary Material

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Background

According to the quantum chemistry code, the keywords used must be the most appropriate to address the numerical precision of the calculation. The keywords used according to ORCA recommendations were:

- (a) The functionals employed were B3LYP and PBE0. B3LYP is a hybrid functional in which the non-localized Hartree-Fock approach is mixed with the energy functional from the generalized gradient approximation (20% Hartree-Fock exchange). The Perdew-Wang gradient-corrected correlation energy (used in Becke's work), is exchanged for the Lee-Yang-Parr correlation energy [24]. The PBE0 is a hybrid version of the PBE functional with one parameter: a predefined exact exchange amount [27].
- (b) Energies and geometries generally converge at the DFT level when using a balanced polarized triple-zeta basis set. With ORCA 5.0, the DHF-TZVP base was used, derived from the Def2-TZVP bases with minor modifications for elements 5s, 6s, 4d and 5d and iodine [27].
- (c) The auxiliary basis used was Def2/J, as it is a universal Coulomb adjustment basis and is suitable for all basis sets of the def2 type [27].
- (d) The RIJCOSX keyword was used to speed up DFT optimizations. The RI-J keyword is used for Coulomb integrals and COSX numerical integration is used for HF switching [49].
- (e) The DFT Integration Grid was DefGrid3, to control the overall accuracy of the DFT grid. The number 3 (maximum) used makes it the highest quality grid and is close to the limit if we consider a huge grid as a reference [27,49]. The NOFINALGRIDX keyword was also used, turning off the final grid in COSX (the algorithm of chain of spheres to handle quantum mechanical exchange) [27].
- (f) For geometry optimizations, we use standard SCF (Self Consistent Field) convergence like TightSCF to reduce noise in gradients [27].
- (g) To obtain a fully optimized geometry (gradient even closer to zero than the standards) the TightOPT keyword was used [27].
- (h) Since DFTs do not include dispersion forces, the B3DJ correction (Atom-pairwise dispersion correction to the DFT energy with Becke-Johnson damping) was employed to account for most of this contribution to the energy [27].
- (i) The keyword used for the vibrational frequencies to be generated was FREQ [49].

Table S1. 2C-H: crystal conformation, xyz coordinates and conformers.

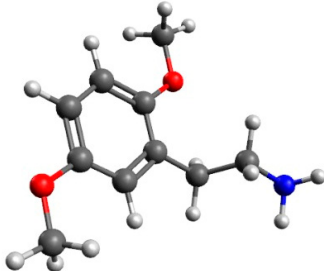
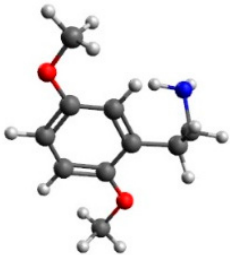
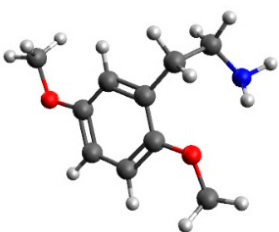
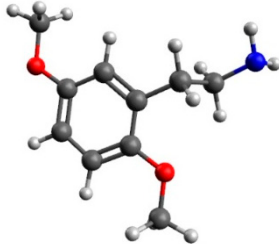
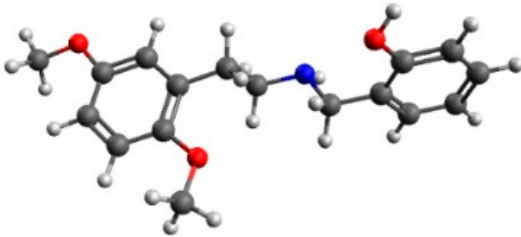
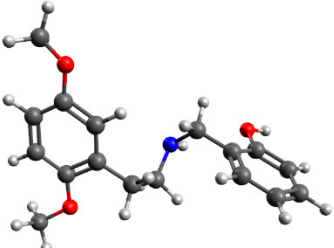
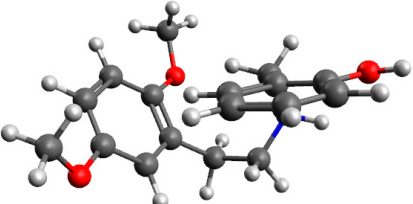
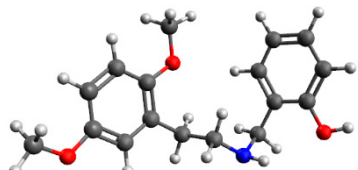
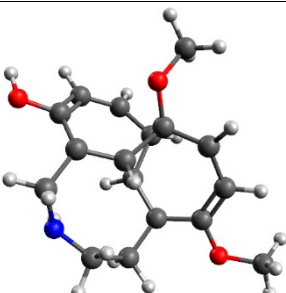
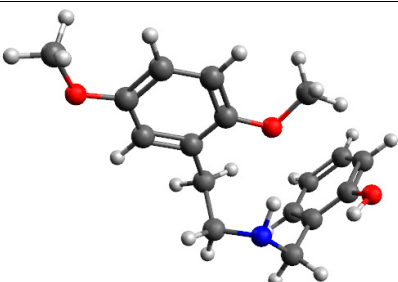
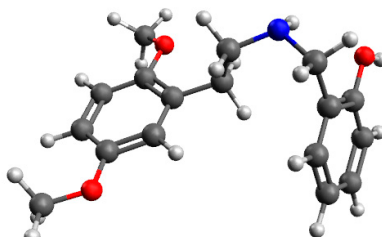
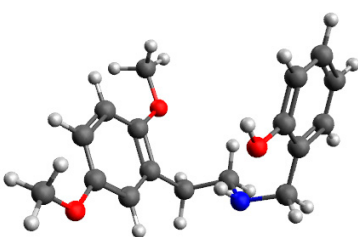
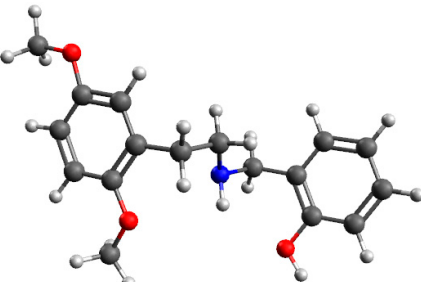
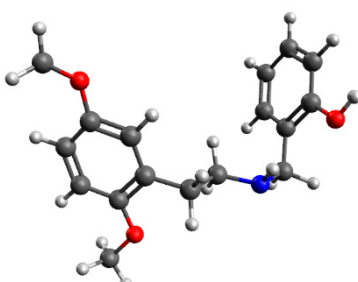
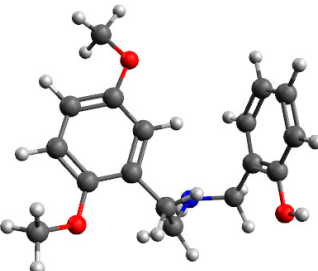
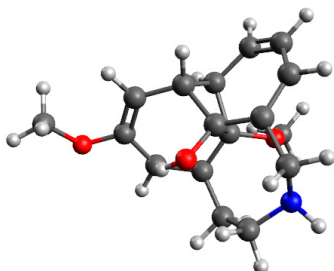
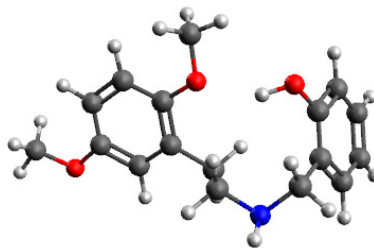
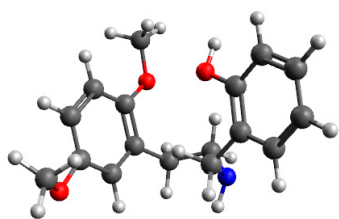
2C-H				
				
O	0.00946	0.86438	14.17955	
N	0.93359	3.29309	20.77385	
H	1.50936	4.09881	21.01397	
H	-0.01647	3.64114	20.65732	
C	3.96311	-0.95116	18.82499	
H	4.37325	-1.00315	19.83816	
H	3.70285	-1.96942	18.51822	
H	4.73575	-0.52587	18.17603	
O	2.81119	-0.11987	18.86606	
C	2.14442	0.09768	17.68995	
C	1.00806	0.92483	17.77159	
C	0.27055	1.21124	16.60492	
H	-0.59926	1.85492	16.68905	
C	0.64497	0.67168	15.37464	
C	-1.12406	1.72233	14.18256	
H	-1.51320	1.76488	13.16061	
H	-1.91869	1.32755	14.82411	
H	-0.84600	2.73988	14.47619	
C	1.40966	2.72278	19.51195	
H	1.37589	3.49665	18.73621	
H	2.45903	2.43399	19.63346	
C	0.56105	1.51682	19.09377	
H	-0.49311	1.81580	19.01970	
H	0.58945	0.73833	19.86720	
C	2.51423	-0.43881	16.45528	
H	3.37750	-1.08608	16.34521	
C	1.76616	-0.15419	15.30953	
H	2.06252	-0.58259	14.35502	
Identified conformers:				
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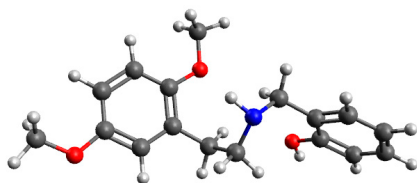
Table S2. 25H-NBOH: crystal conformation, xyz coordinates and conformers.

25H-NBOH				
				
O	17.67503	3.67325	12.26497	
O	20.65958	7.52022	8.90835	
H	21.14324	7.73222	8.09462	
N	20.98553	6.49625	12.24808	
H	21.35615	7.11035	12.97063	
C	20.64204	8.62789	9.70874	
C	18.04025	1.51024	13.35766	
H	16.98625	1.33727	13.54829	
C	20.23112	8.50143	11.04087	
C	18.94995	0.54270	13.80320	
H	18.55462	-0.33502	14.30293	
C	20.76640	1.86168	12.94147	
H	21.83532	1.99513	12.78583	
C	20.58716	10.89331	11.32653	
H	20.56402	11.77661	11.95945	
C	18.48743	2.66189	12.70552	
C	19.83598	7.16699	11.62792	
H	19.04967	7.33468	12.37612	
H	19.38200	6.54912	10.84616	
C	16.27535	3.42673	12.25166	
H	15.79092	4.28119	11.76910	
H	16.03303	2.53321	11.66660	
H	15.88127	3.35306	13.27020	
C	21.01861	9.86529	9.18501	
H	21.32891	9.96362	8.14965	
C	20.40152	4.09271	11.82811	
H	21.35680	3.87055	11.33446	
H	19.72138	4.38672	11.02099	
C	19.86559	2.84167	12.49203	
O	21.30388	-0.14222	13.99808	
C	20.59536	5.21903	12.85478	
H	19.70482	5.35124	13.48198	
H	21.39951	4.91943	13.53933	
C	20.98810	10.99908	9.99631	
H	21.27635	11.96526	9.59102	
C	20.31726	0.71806	13.60333	
C	20.91715	-1.20632	14.85824	
H	21.82353	-1.74331	15.15392	
H	20.44289	-0.82710	15.76989	
H	20.26450	-1.91491	14.33828	

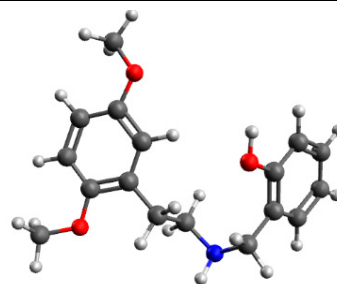
	C	20.21552	9.65216	11.84737
	H	19.90832	9.58428	12.88851
Identified conformers				
				
Conf #1				
				
Conf #2				
				
Conf #3				
				
Conf #4				
				
Conf #5				
				
Conf #6				
				
Conf #7				
				
Conf #8				
				
Conf #9				
				
Conf #10				
				
Conf #11				
				
Conf #12				



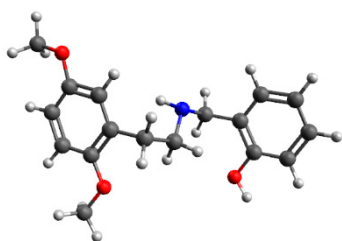
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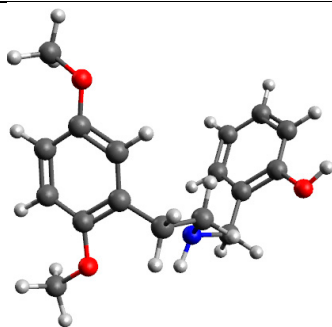
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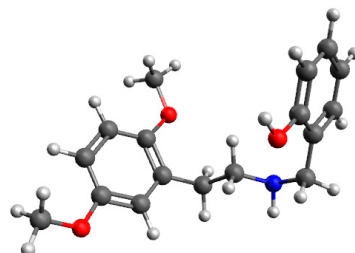
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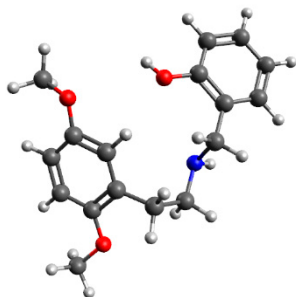
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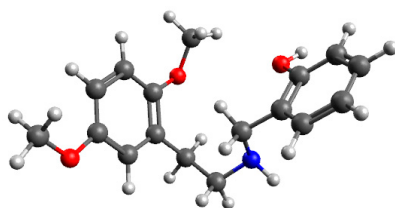
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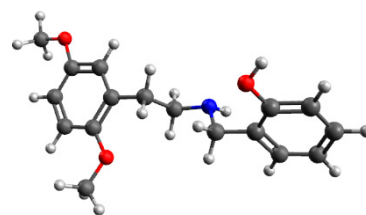
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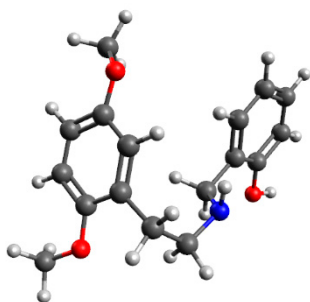
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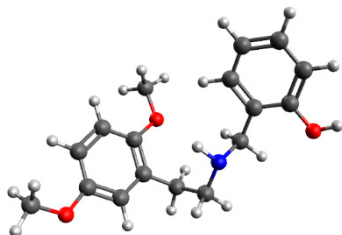
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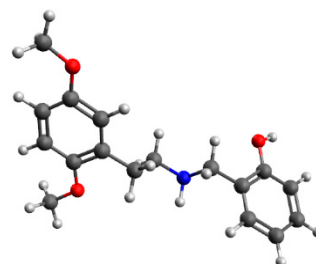
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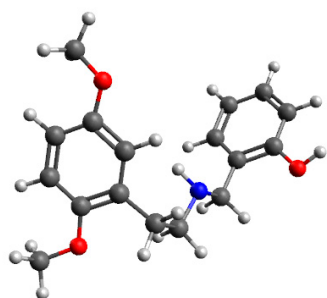
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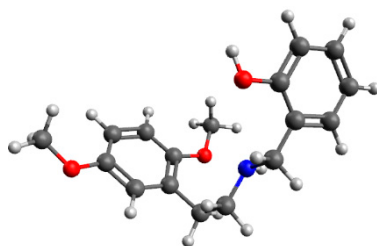
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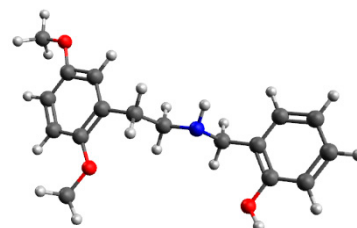
Conf #24



Conf #25

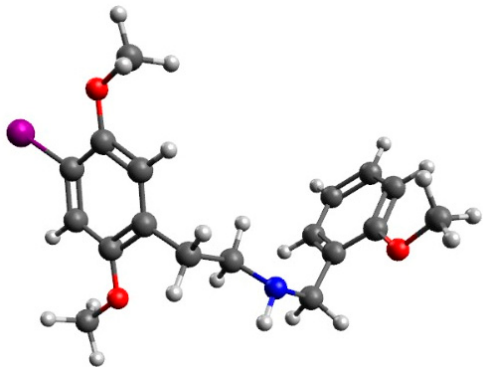


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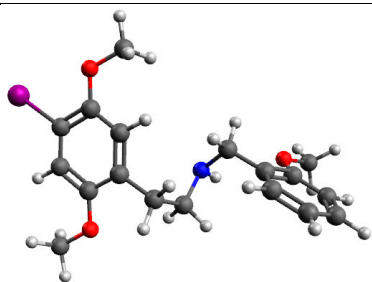
Conf #27

Table S3. 25I-NBOMe: crystal conformation, xyz coordinates and conformers.

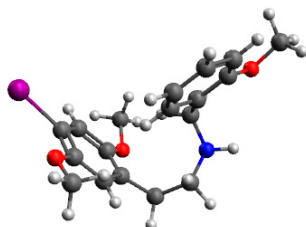
25I-NBOMe				
				
I	13.89360	3.10027	1.64997	
O	8.53452	2.44965	2.46301	
O	12.99217	5.67512	3.30566	
N	6.67026	4.39774	5.91045	
H	5.91509	4.26693	5.23957	
O	6.12445	5.72845	8.90341	
C	7.18981	4.89669	9.13039	
C	7.31725	3.79874	8.25879	
C	10.60153	5.24030	3.58967	
H	10.43811	6.14529	4.16774	
C	6.36657	3.58793	7.09925	
H	5.34802	3.82449	7.43089	
H	6.33186	2.52402	6.82932	
C	9.49472	4.40027	3.35694	
C	12.02328	3.71582	2.39438	
C	11.87252	4.91132	3.11108	
C	8.15526	4.76791	3.96517	
H	7.34957	4.54956	3.25290	
H	8.11297	5.85153	4.13720	
C	9.66261	3.20849	2.63096	
C	10.92953	2.87235	2.15254	
H	11.09048	1.95490	1.59722	
C	8.11065	5.06041	10.17223	
H	8.03742	5.88592	10.87197	
C	7.93935	4.01539	5.28550	
H	7.95628	2.93430	5.10152	
H	8.77320	4.25184	5.95667	
C	8.37274	2.88732	8.45389	
H	8.49076	2.03861	7.78360	
C	9.15607	4.15003	10.34789	
H	9.86639	4.29016	11.15842	
C	9.28727	3.06354	9.49008	
H	10.10104	2.35604	9.62468	
C	8.65948	1.23441	1.73595	
H	8.99898	1.41803	0.71142	
H	7.66712	0.77661	1.67958	
H	9.32085	0.53312	2.25502	
C	12.84329	6.90610	4.00081	

H	12.16352	7.58065	3.46986
H	13.82498	7.38794	4.04023
H	12.51364	6.73968	5.03158
C	6.11513	6.97414	9.58606
H	5.28190	7.56413	9.19228
H	7.03648	7.53774	9.40458
H	5.94272	6.83037	10.65745

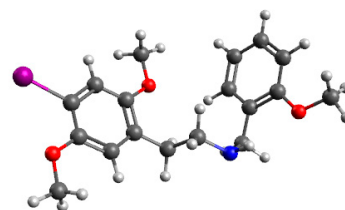
Identified conformers



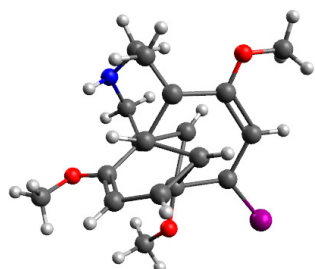
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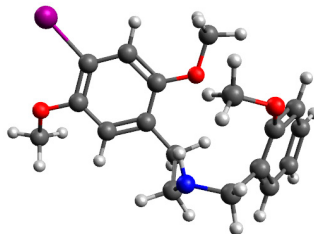
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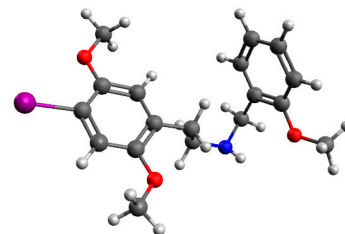
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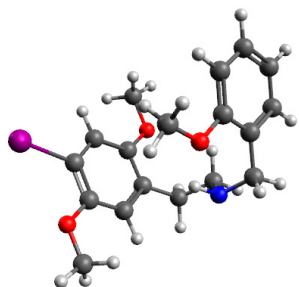
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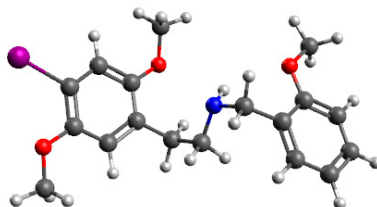
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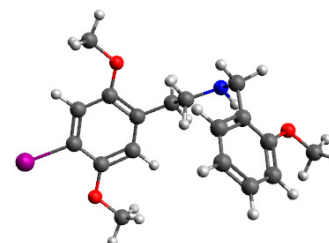
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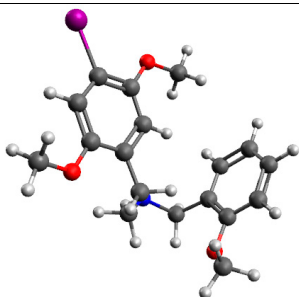
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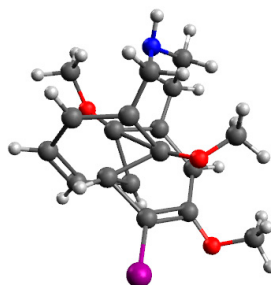
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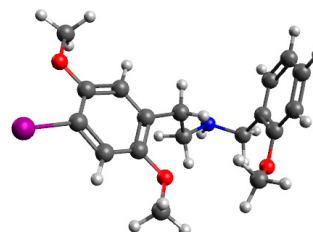
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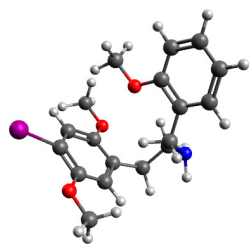
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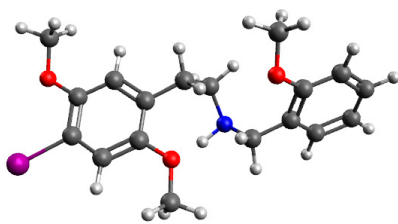
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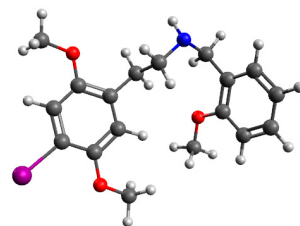
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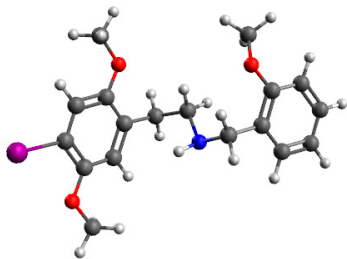
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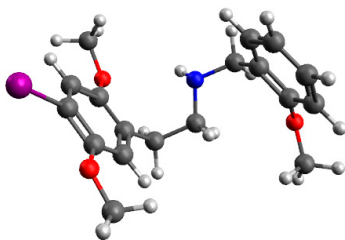
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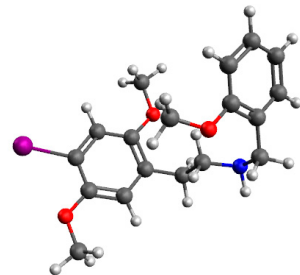
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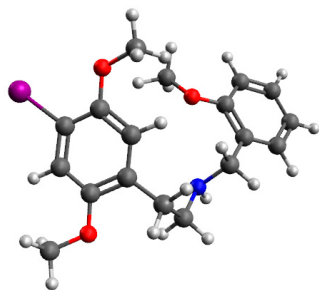
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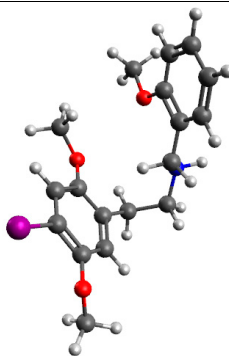
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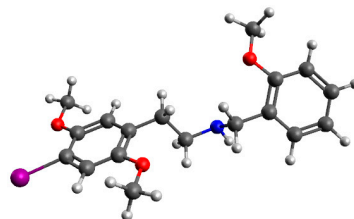
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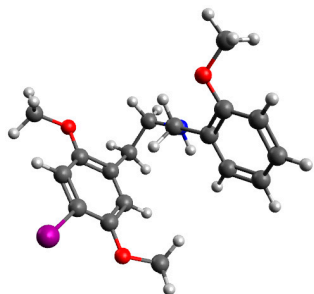
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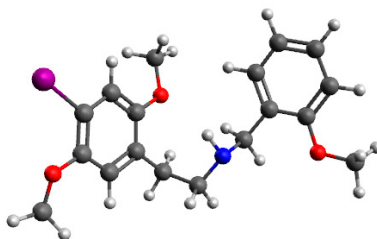
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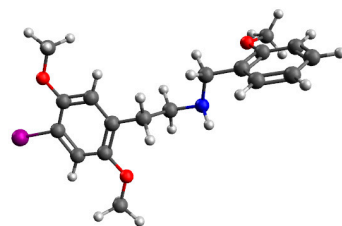
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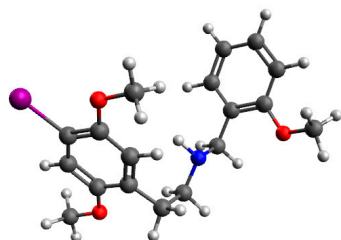
Conf #22



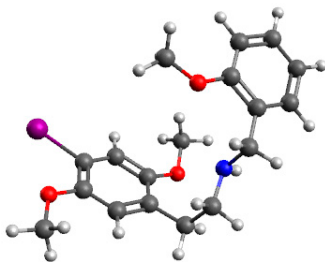
Conf #23



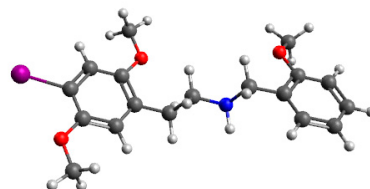
Conf #24



Conf #25



Conf #26



Conf #27