

Supplement Information

Design Strategy for TATB-like Insensitive High Explosives: Rational Design and High-Throughput Screening Based on Fused-Ring Frameworks

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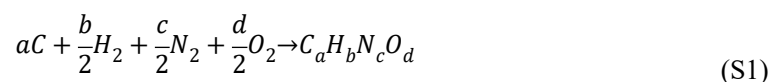
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Calculation of enthalpy of formation using the definition method

The enthalpy change of producing one mole of a compound from its simple substances in their standard states is defined as the standard molar enthalpy of formation of the compound. Taking the compound $C_aH_bN_cO_d$ as an example, the corresponding general equation for its formation reaction is as follows:



By definition, the enthalpy of formation is the reaction enthalpy of the above **Equation S1**. The enthalpy of reaction is determined by calculating the difference between the enthalpy of the products and the enthalpy of the reactants. To calculate the enthalpy of each species involved in the reaction, quantum chemistry computational programs such as Gaussian or ORCA can be used. Carbon is a solid at room temperature, but the enthalpy value obtained from quantum chemistry computational programs corresponds

to its formation in the gaseous state. Subtracting the sublimation enthalpy ($H_{sub}(C)$) from the enthalpy value ($H(C)$) obtained from quantum chemistry computational programs is necessary to determine the enthalpy of carbon in its stable phase (solid).

In summary, the formula for calculating the enthalpy of formation using the definition method is as follows:

$$\Delta_f H_m^\theta = \Delta_r H_m^\theta = H(C_a H_b N_c O_d) - a[H(C) - H_{sub}(C)] - \frac{b}{2}H(H_2) - \frac{c}{2}H(N_2) - \frac{d}{2}H(O_2) \quad (S2)$$

The enthalpy values above correspond to the stable phase at 298 K. As such, the calculated enthalpy of formation is also determined at this temperature.

Table S1 SYBA Score of classic explosives

Explosives	SMILES	SYBA
RDX	<chem>O=[N+](=[O-])N1CN([N+](=O)[O-])CN([N+](=O)[O-])C1</chem>	2.1
HMX	<chem>O=[N+](=[O-])N1CN([N+](=O)[O-])CN([N+](=O)[O-])CN([N+](=O)[O-])C1</chem>	2.1
FOX-7	<chem>NC(N)=C([N+](=O)[O-])[N+](=O)[O-]</chem>	5.7
CL-20	<chem>O=[N+](=[O-])N1C2C3N([N+](=O)[O-])C1C1N([N+](=O)[O-])C(C(N1[N+](=O)[O-])N3[N+](=O)[O-])N2[N+](=O)[O-]</chem>	1.3
PETN	<chem>O=[N+](=[O-])OCC(CO[N+](=O)[O-])(CO[N+](=O)[O-])CO[N+](=O)[O-]</chem>	15.0
HNS	<chem>O=[N+](=[O-])c1cc([N+](=O)[O-])c(C=Cc2c([N+](=O)[O-])cc([N+](=O)[O-])cc2[N+](=O)[O-])c([N+](=O)[O-])c1</chem>	22.9
TNT	<chem>Cc1c([N+](=O)[O-])cc([N+](=O)[O-])cc1[N+](=O)[O-]</chem>	34.5
DNAN	<chem>COc1ccc([N+](=O)[O-])cc1[N+](=O)[O-]</chem>	54.4
TATB	<chem>Nc1c([N+](=O)[O-])c(N)c([N+](=O)[O-])c(N)c1[N+](=O)[O-]</chem>	11.8
DATB	<chem>Nc1c([N+](=O)[O-])cc([N+](=O)[O-])c(N)c1[N+](=O)[O-]</chem>	19.5
LLM-105	<chem>Nc1c([N+](=O)[O-])nc([N+](=O)[O-])c(N)[n+]1[O-]</chem>	14.2
ANPZ	<chem>Nc1nc(N)c([N+](=O)[O-])nc1[N+](=O)[O-]</chem>	12.9
BITE-101	<chem>Nc1[n+](=[O-])nc2c([N+](=O)[O-])c([N+](=O)[O-])nn12</chem>	17.5
PTX	<chem>Nc1c([N+](=O)[O-])nnc2c([N+](=O)[O-])c([N+](=O)[O-])nn12</chem>	17.8
NAPTO	<chem>[N-]=[N+]=Nc1n[n+](=[O-])nc2c([N+](=O)[O-])n[nH]c12</chem>	16.5
ICM-103	<chem>[N-]=[N+]=Nc1n[n+](=[O-])nc2[nH]nc([N+](=O)[O-])c12</chem>	18.2
ICM-104	<chem>Nc1nc(N)n2nc([N+](=O)[O-])c([N+](=O)[O-])c2n1</chem>	20.3

Table S2 USPEX parameter settings

Parameter Category	Parameter Name	Parameter Value	Description / Explanation
Optimization Goal	optType	Enthalpy	Searching for the most stable structure with the lowest energy.
System Settings	numSpecies	4	Number of chemical species (Z).
Population Parameters	populationSize	20	Population size
	initialPopSize	20	Initial population size
	numGenerations	20	Maximum generations for the evolutionary algorithm.
Stopping Criterion	stopCrit	10	Calculation stops if no new, better structure is found for 10 consecutive generations.
Variation Operators	fracGene	0.20	Heredity (Crossover).
	fracRand	0.30	Random structure generation.
	fracAtomsMut	0.10	Atom displacement mutation.
	fracRotMut	0.10	Lattice rotation mutation.
	fracPerm	0.10	Permutation (atom swap).
	fracLatMut	0.10	Lattice mutation.
	fracTopRand	0.10	Topology randomization.
	mutationDegree	4.00	Degree/strength of mutation.
	DisplaceInLatmutation	4.00	Intra-lattice displacement mutation degree.
Geometric Constraints	symmetries	14, 2, 19, 15, 4, 61, 29, 33, 7, 9, 62	Allowed list of space group numbers.
Calculation Interface	abinitioCode	7	Corresponds to the CP2K software.
Calculation Conditions	ExternalPressure	0	Structural optimization is performed at zero external pressure.

Table S3 CP2K input file parameter settings

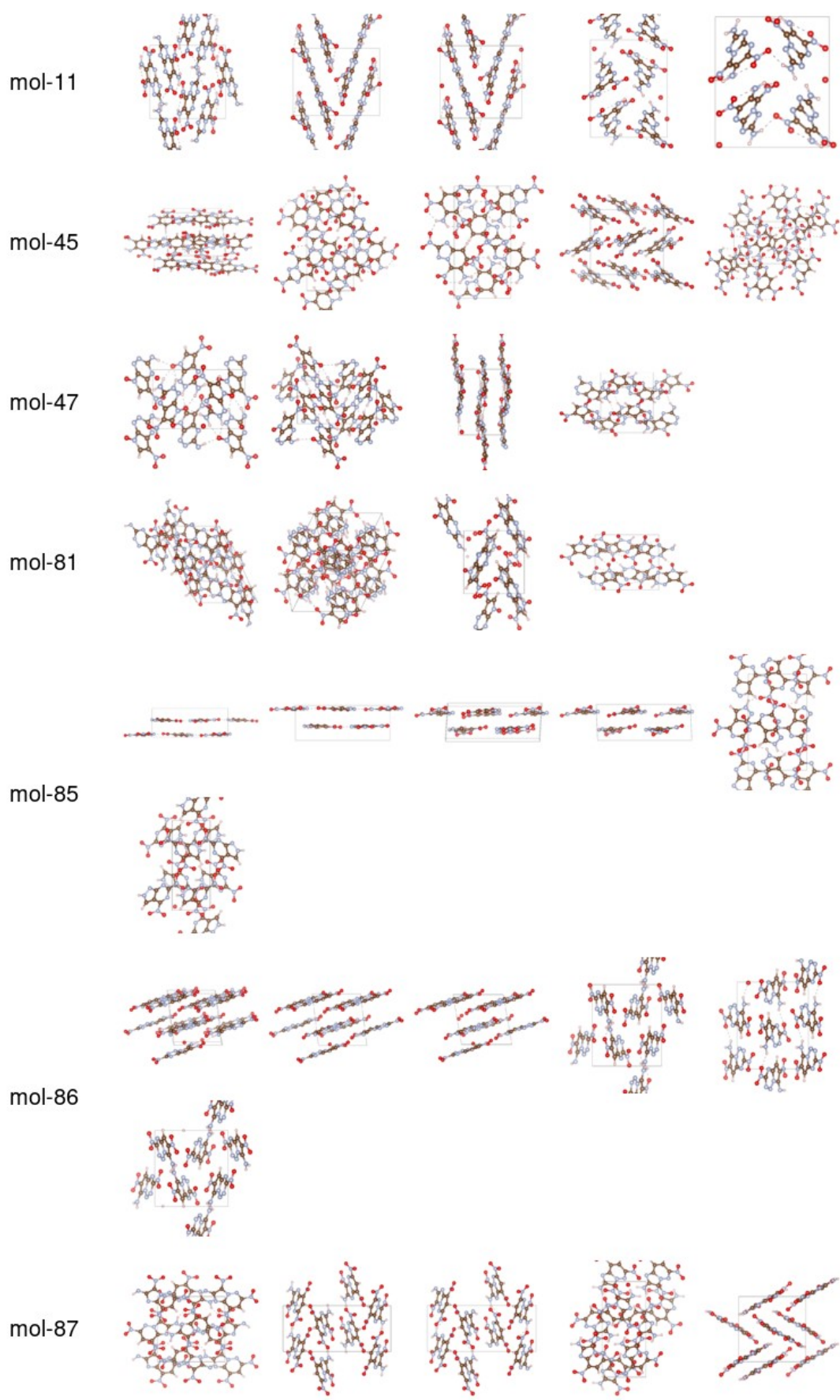
Parameter Category	Parameter Name	Parameter Value	Description
Calculation Type	RUN_TYPE	CELL_OPT	simultaneously optimizes atomic positions and the unit cell
Convergence Criteria	MAX_DR	1.0E-4	Convergence threshold for maximum atomic displacement
	MAX_FORCE	1.0E-3	Convergence threshold for maximum force on atoms
	RMS_DR	1.0E-4	Convergence threshold for root mean square (RMS) of atomic displacements
	RMS_FORCE	1.0E-3	Convergence threshold for RMS of forces on atoms
Optimization Control	MAX_ITER	500	Maximum number of geometry optimization iterations
	PRESSURE_TOLERANCE	100.0	Pressure convergence tolerance (unit:

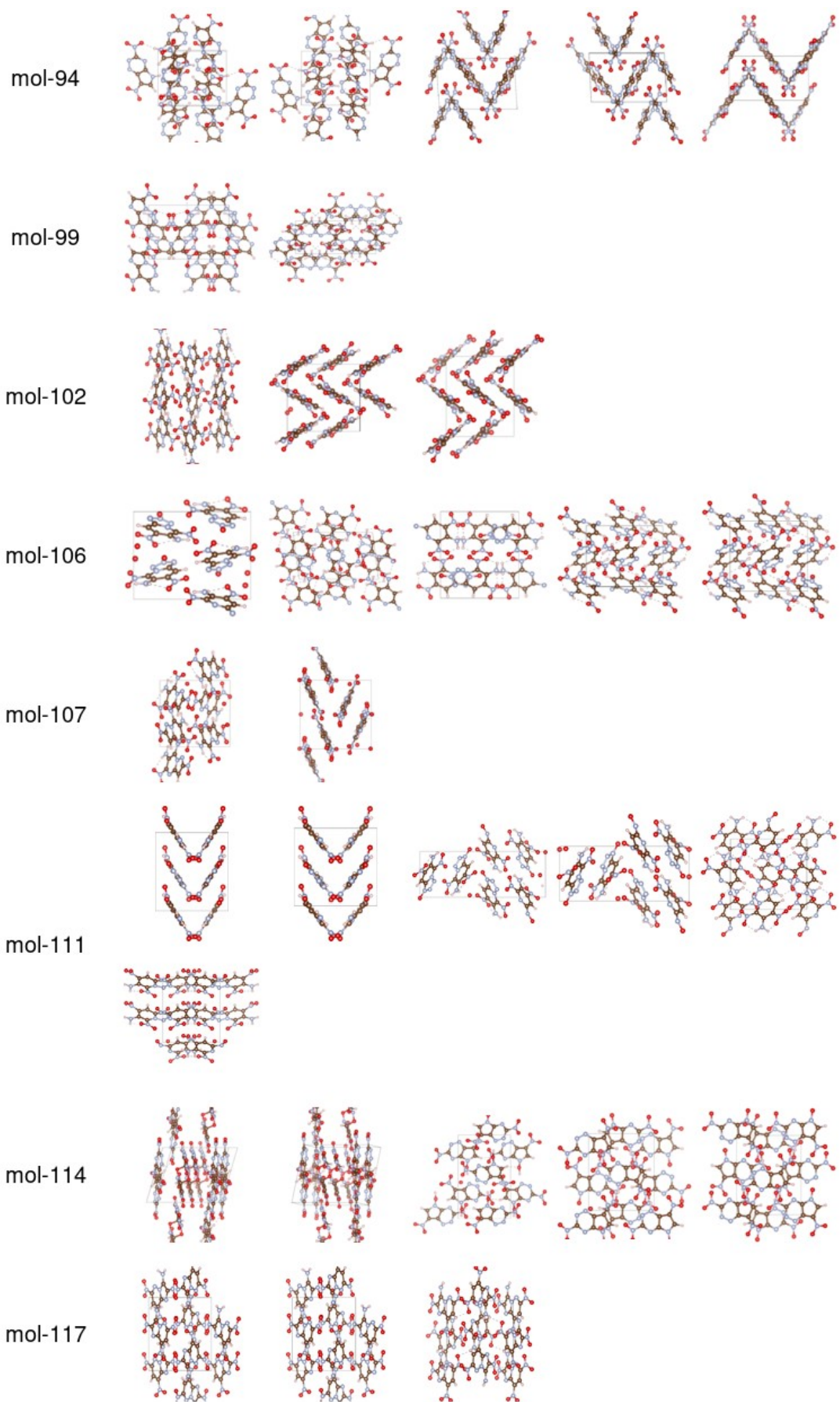
Parameter Category	Parameter Name	Parameter Value	Description
			bar)
Calculation Method	METHOD	Quickstep	CP2K's hybrid Gaussian and plane-wave method
	METHOD	xTB	Extended Tight-Binding Density Functional Theory
	DISPERSION_PARAMETER_FILE	dftd3.dat	Enables DFT-D3 dispersion correction
k-point Settings	KPOINTS SCHEME	3×3×3	k-point grid scheme and density
SCF Settings	EPS_SCF	1.0E-6	Self-Consistent Field (SCF) energy convergence criterion
	SCF_GUESS	ATOMIC	Initial electron density guess based on atomic orbitals
	MAX_SCF	250	Maximum number of iterations for a single SCF cycle
	MIXING METHOD	DIRECT_P_MIXING	Charge density mixing method
	MIXING ALPHA	0.3	Charge density mixing parameter

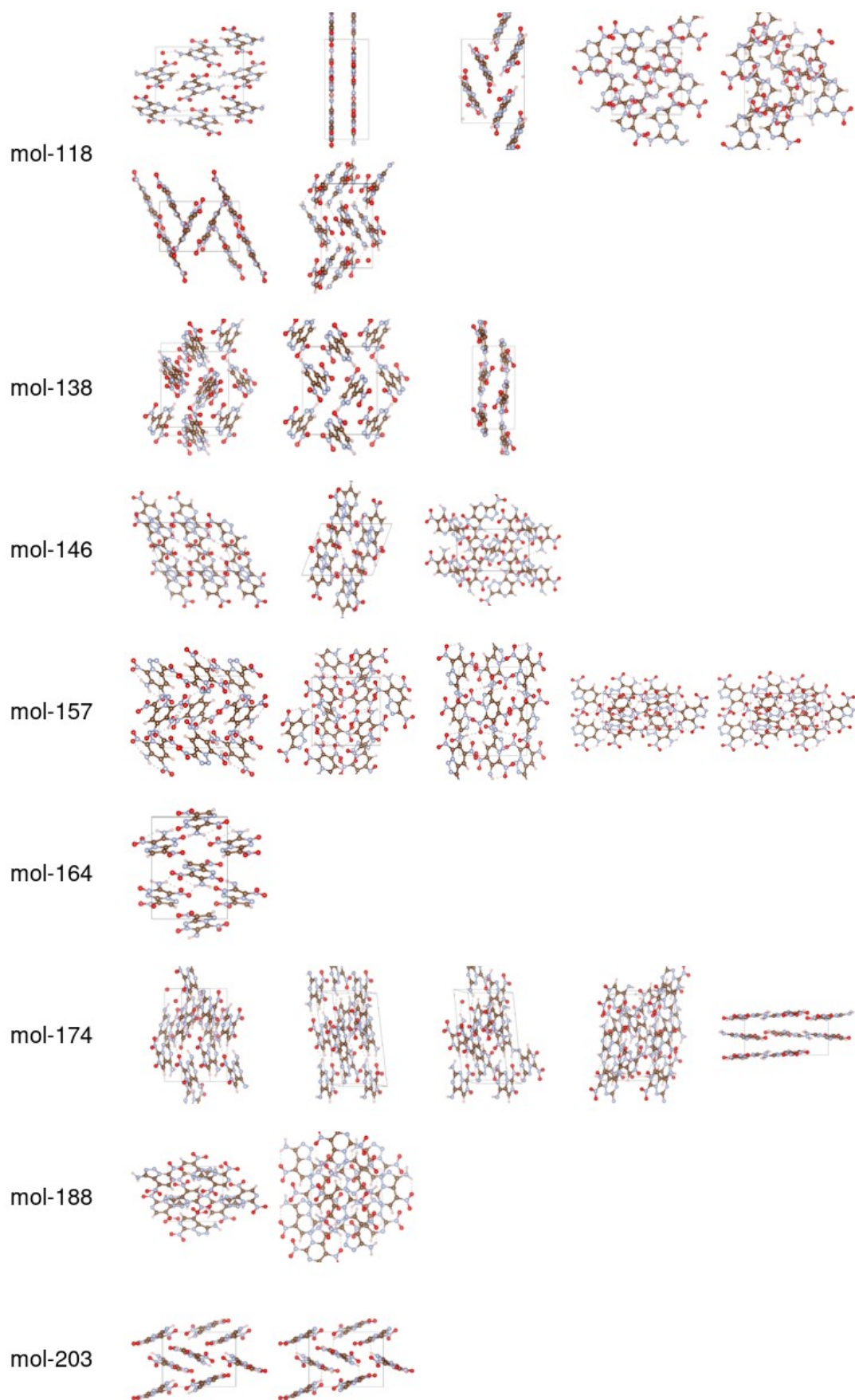
Table S4 The 100 molecules selected for crystal structure prediction.

name	SMILES	name	SMILES
out11	<chem>n12nc(N)nc1nc(N(=O)=O)c(N)c2N(=O)=O</chem>	out396	<chem>n12[n+][([O-])c(N(=O)=O)nc1ncc(N(=O)=O)c2N</chem>
out45	<chem>n12nc(N(=O)=O)nc1cc(N(=O)=O)c(N)c2N(=O)=O</chem>	out397	<chem>n12nc(N(=O)=O)cc1[n+][([O-])nc(N)c2N(=O)=O</chem>
out47	<chem>c12c(N(=O)=O)c[n+][([O-])c1n[nH]c(N)n2</chem>	out401	<chem>n12c(N(=O)=O)c(N)nc1c(N(=O)=O)c[n+][([O-])n2</chem>
out81	<chem>c12[n+][([O-])cc(N(=O)=O)c1n[nH]c(N)n2</chem>	out402	<chem>n12cnc(N(=O)=O)c1n[n+][([O-])c(N)c2N(=O)=O</chem>
out85	<chem>c12n[nH]cc1c(N(=O)=O)nc(N(=O)=O)n2</chem>	out406	<chem>n12c(N(=O)=O)c(N)nc1c(N(=O)=O)nc(N(=O)=O)c2</chem>
out86	<chem>n12c(N)c(N(=O)=O)cc1nc(N(=O)=O)mn2</chem>	out417	<chem>n12cnc(N(=O)=O)c1n[n+][([O-])c(N)c2N</chem>
out87	<chem>n12c(N(=O)=O)c(N)nc1c(N(=O)=O)cc(N(=O)=O)n2</chem>	out432	<chem>n12ncc(N(=O)=O)c1n[n+][([O-])c(N(=O)=O)c2N</chem>
out94	<chem>c12[nH]cc(N(=O)=O)c1nnc(N(=O)=O)n2</chem>	out435	<chem>n12c(N(=O)=O)cnc1c(N(=O)=O)nncc2N</chem>
out99	<chem>n12c(N(=O)=O)cnc1c(N(=O)=O)c(N)mn2</chem>	out444	<chem>n12c(N(=O)=O)cnc1c(N(=O)=O)c(N)[n+][([O-])n2</chem>
out102	<chem>n12ncc(N(=O)=O)c1nc(N(=O)=O)c(N)c2N(=O)=O</chem>	out448	<chem>c12[nH]nc(N(=O)=O)c1[n+][([O-])cc(N(=O)=O)n2</chem>
out106	<chem>n12n[n+][([O-])nc1cc(N(=O)=O)c(N)c2N(=O)=O</chem>	out449	<chem>n12c(N(=O)=O)enc1c(N(=O)=O)n[n+][([O-])c2N</chem>
out107	<chem>n12nc(N(=O)=O)cc1nc(N(=O)=O)c(N)c2N(=O)=O</chem>	out458	<chem>n12[n+][([O-])nc(N(=O)=O)c1cc(N(=O)=O)c(N)c2N</chem>
out111	<chem>n12nn[n+][([O-])c1cc(N(=O)=O)c(N)c2N(=O)=O</chem>	out459	<chem>n12c(N(=O)=O)cnc1c(N(=O)=O)c(N)c(N(=O)=O)n2</chem>
out114	<chem>c12[n+][([O-])cc(N(=O)=O)c1[nH]nc(N(=O)=O)n2</chem>	out481	<chem>n12nnc(N(=O)=O)c1c(N)c(N(=O)=O)cc2N(=O)=O</chem>
out117	<chem>n12c(N)c(N(=O)=O)nc1c(N(=O)=O)cc(N(=O)=O)n2</chem>	out494	<chem>n12c(N(=O)=O)cc(N(=O)=O)c1[n+][([O-])nc(N)n2</chem>
out118	<chem>n12cnc(N(=O)=O)c1nc(N)nc2N(=O)=O</chem>	out497	<chem>n12c(N)[n+][([O-])nc1c(N(=O)=O)cc(N(=O)=O)n2</chem>
out138	<chem>c12nnc(N(=O)=O)c1n[nH]cc2N(=O)=O</chem>	out507	<chem>n12c(N(=O)=O)c(N)nc1c(N)[n+][([O-])[n+][([O-])c2</chem>
out146	<chem>n12nnc(N(=O)=O)c1ncc(N(=O)=O)c2N</chem>	out508	<chem>n12ncc(N(=O)=O)c1nc(N(=O)=O)c(N)n2</chem>
out157	<chem>n12nnc(N(=O)=O)c1cc(N(=O)=O)c(N)c2N(=O)=O</chem>	out514	<chem>n12c[n+][([O-])c(N)c1n[n+][([O-])c(N)c2N(=O)=O</chem>
out164	<chem>n12ncc(N(=O)=O)c1n[n+][([O-])c(N)c2N(=O)=O</chem>	out520	<chem>c12[n+][([O-])c(N(=O)=O)cc1n[nH]c(N)n2</chem>
out174	<chem>n12c(N(=O)=O)[n+][([O-])cc1c(N)nc(N)n2</chem>	out523	<chem>n12c[n+][([O-])c(N(=O)=O)c1nc(N(=O)=O)c(N)n2</chem>
out188	<chem>n12nnc(N)c1c(N(=O)=O)cnc2N(=O)=O</chem>	out525	<chem>n12c(N(=O)=O)cnc1c(N)c(N(=O)=O)mn2</chem>
out203	<chem>n12c[n+][([O-])c(N(=O)=O)c1nc(N)nc2N(=O)=O</chem>	out529	<chem>n12c(N(=O)=O)c(N)c(N(=O)=O)c1nn[n+][([O-])c2</chem>
out214	<chem>c12c(N(=O)=O)[n+][([O-])cc1n[nH]c(N)n2</chem>	out531	<chem>c12n[n+][([O-])c(N)c1n[nH]cc2N(=O)=O</chem>
out230	<chem>n12nnc1cc(N(=O)=O)c(N)c2N(=O)=O</chem>	out534	<chem>n12c(N)c(N(=O)=O)cc1nc(N(=O)=O)n[n+][2[O-]</chem>
out238	<chem>n12nc(N(=O)=O)cc1n[n+][([O-])c(N)c2N(=O)=O</chem>	out541	<chem>c12c[n+][([O-])c(N(=O)=O)c1n[nH]c(N)n2</chem>
out242	<chem>n12nc(N(=O)=O)c(N)c1cc(N(=O)=O)c(N)c2N(=O)=O</chem>	out569	<chem>c12[nH]cc(N(=O)=O)c1[n+][([O-])nc(N(=O)=O)n2</chem>

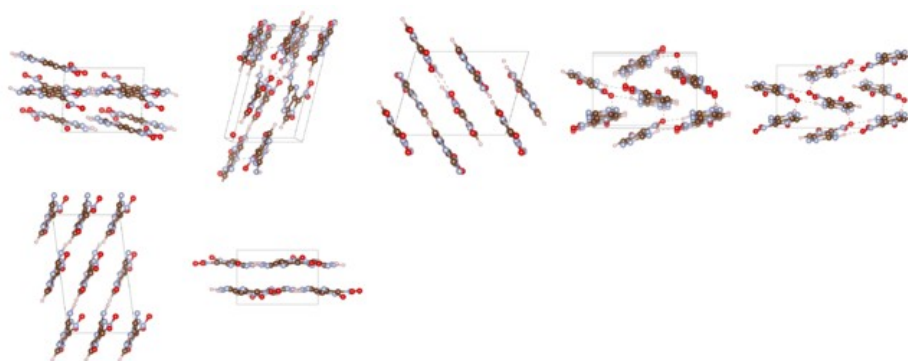
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out245	n12[n+][[O-]]nc(N(=O)=O)c1ncc(N(=O)=O)c2N	out571	n12[n+][[O-]]c(N(=O)=O)nc1cc(N(=O)=O)c(N)c2N
out247	n12n[n+][[O-]]nc1c(N)c(N(=O)=O)cc2N(=O)=O	out578	n12[n+][[O-]][n+][[O-]]c(N)c1ncc(N(=O)=O)c2N
out254	c12nc(N(=O)=O)nc1n[nH]cc2N(=O)=O	out582	n12nc(N)nc1c(N(=O)=O)cc(N(=O)=O)[n+][2][O-]
out255	n12nnc1c(N(=O)=O)c(N)c(N(=O)=O)c2	out583	n12c(N(=O)=O)nc(N(=O)=O)c1nc(N)c(N(=O)=O)c2
out264	n12c(N(=O)=O)c(N)nc1cc(N(=O)=O)nn2	out586	n12c[n+][[O-]]nc1c(N(=O)=O)c(N)nc2N(=O)=O
out271	n12c(N(=O)=O)nc(N(=O)=O)c1ncc(N(=O)=O)c2N	out587	n12cc(N(=O)=O)nc1nc(N(=O)=O)c(N)c2N(=O)=O
out274	n12c(N(=O)=O)cc(N(=O)=O)c1nc(N)nn2	out594	n12nnc(N)c1c(N(=O)=O)nc2N(=O)=O
out276	c12n[n+][[O-]]c(N(=O)=O)c1n[nH]cc2N(=O)=O	out597	n12nc(N(=O)=O)cc1c(N(=O)=O)nc(N)c2N(=O)=O
out279	n12c(N(=O)=O)c(N)cc1nc(N(=O)=O)nn2	out601	n12cnc(N(=O)=O)c1nc(N(=O)=O)c(N)c2N(=O)=O
out281	n12cc(N(=O)=O)nc1n[n+][[O-]]c(N)c2N(=O)=O	out603	n12n[n+][[O-]]c(N)c1c(N)c(N(=O)=O)cc2N(=O)=O
out287	n12ncc(N(=O)=O)c1nnc(N(=O)=O)c2N	out624	n12cc(N(=O)=O)nc1c(N(=O)=O)nc(N)c2N(=O)=O
out296	n12c(N)cc(N(=O)=O)c1nc(N(=O)=O)nn2	out625	n12c(N(=O)=O)cc(N(=O)=O)c1nc(N(=O)=O)nc2N
out305	c12c(N(=O)=O)cnc1[nH]nc(N(=O)=O)n2	out629	n12nc(N(=O)=O)nc1c[n+][[O-]]c(N)c2N(=O)=O
out318	n12c(N(=O)=O)cc(N(=O)=O)c1nc(N)c(N(=O)=O)n2	out634	n12cc(N(=O)=O)nc1nnc(N(=O)=O)c2N
out330	n12c[n+][[O-]]c(N(=O)=O)c1nc(N)c(N(=O)=O)c2N	out655	n12nnc(N(=O)=O)c1c[n+][[O-]]c(N)c2N(=O)=O
out353	n12c(N)c(N(=O)=O)nc1c(N(=O)=O)cc(N)[n+][2][O-]	out669	c12cc(N(=O)=O)[n+][[O-]]c1n[nH]c(N)n2
out360	n12n[n+][[O-]]c(N)c1cc(N(=O)=O)c(N)c2N(=O)=O	out670	n12nc(N(=O)=O)nc1c(N)c(N(=O)=O)cc2N(=O)=O
out373	n12c(N(=O)=O)c(N)nc1c(N(=O)=O)n[n+][[O-]]c2	out673	n12c[n+][[O-]]c(N)c1nc(N(=O)=O)nc2N(=O)=O
out374	n12cnc(N(=O)=O)c1nc(N(=O)=O)c(N)n2	out674	c12nc(N(=O)=O)[n+][[O-]]c1n[nH]cc2N(=O)=O
out386	n12c(N(=O)=O)[n+][[O-]]cc1c(N(=O)=O)nc(N)n2	out685	n12ncc(N(=O)=O)c1nnc(N)c2N(=O)=O
out390	n12c(N(=O)=O)cc(N(=O)=O)c1nc(N(=O)=O)c(N)n2	out688	n12c(N(=O)=O)[n+][[O-]]c(N(=O)=O)c1nc(N)nc2
out392	n12n[n+][[O-]]c(N(=O)=O)c1ncc(N(=O)=O)c2N	out693	n12cc(N(=O)=O)nc1c(N(=O)=O)nnc2N



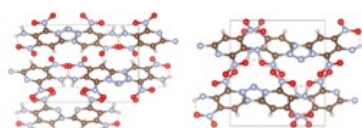




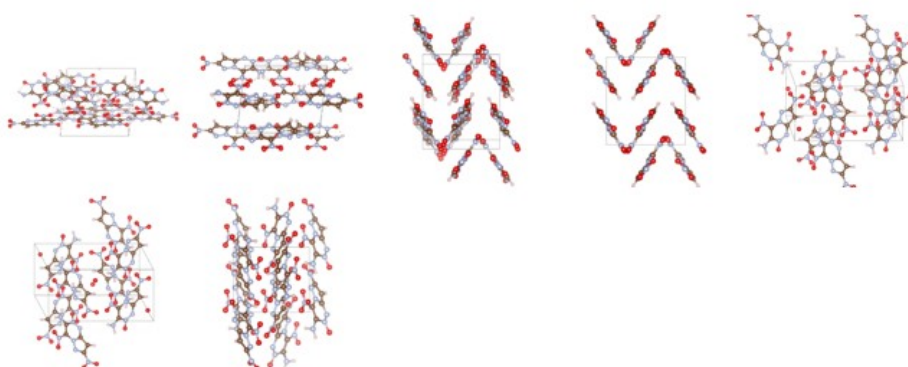
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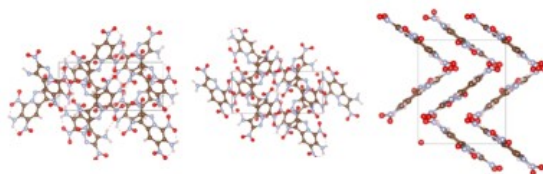
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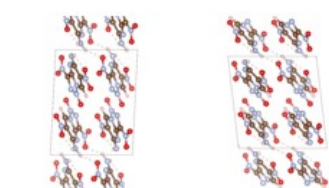
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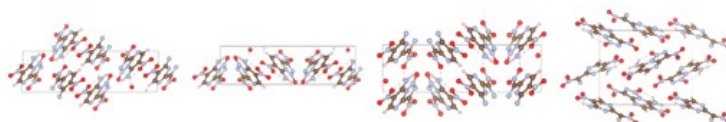
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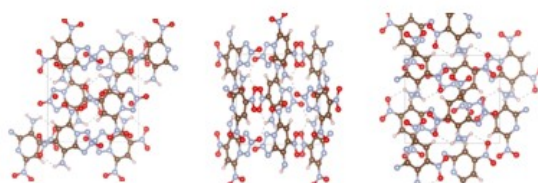
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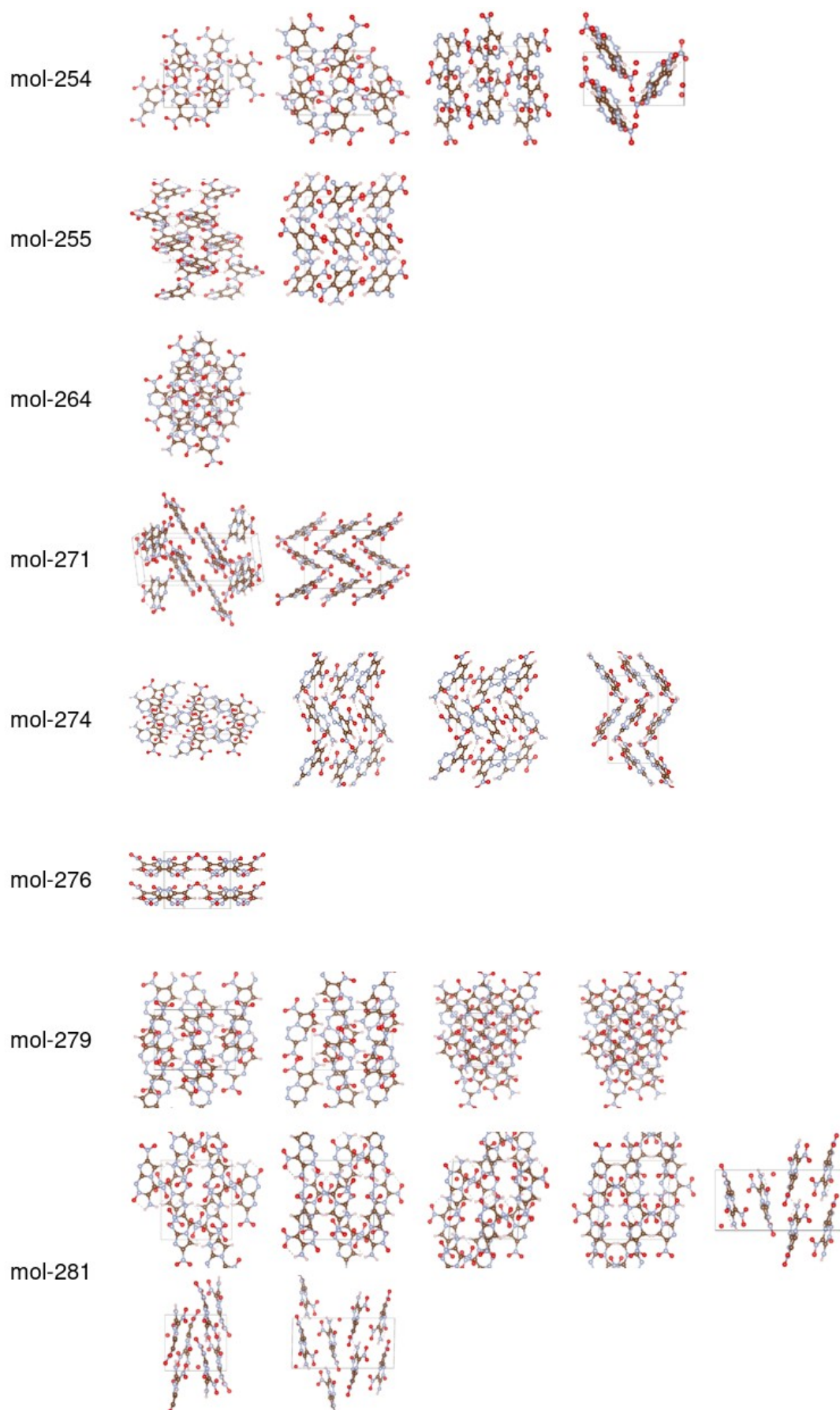


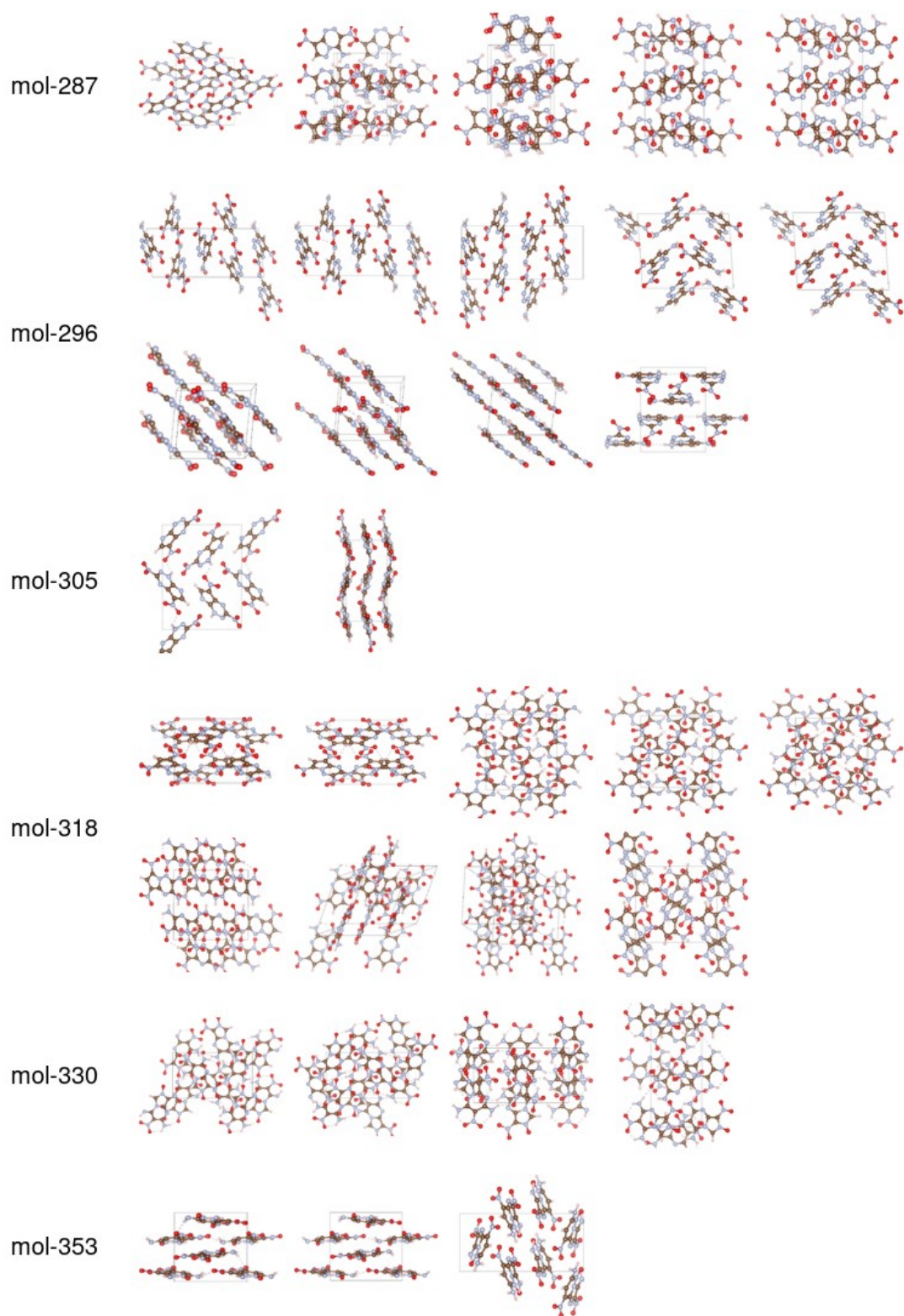
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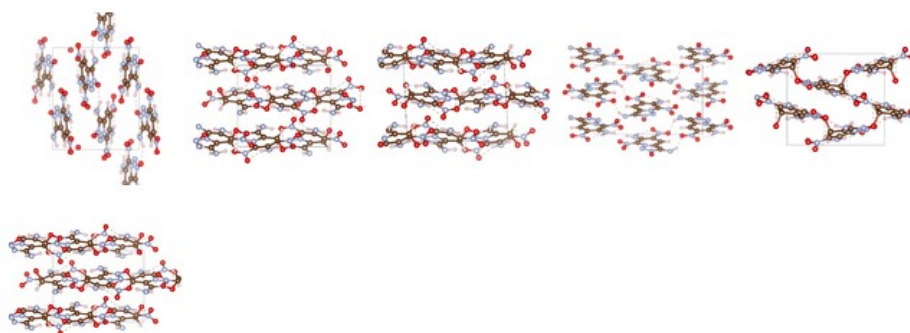
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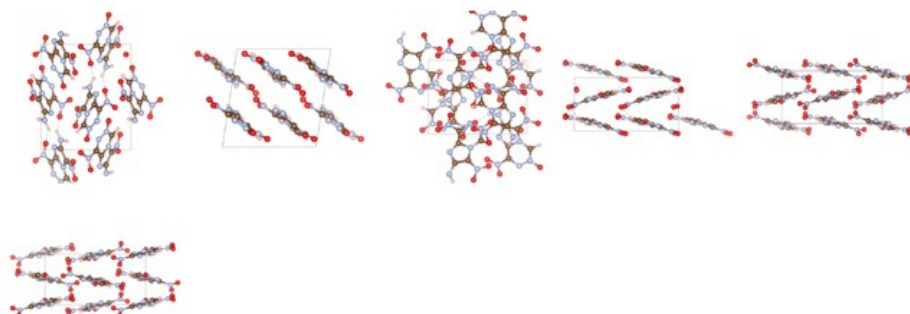




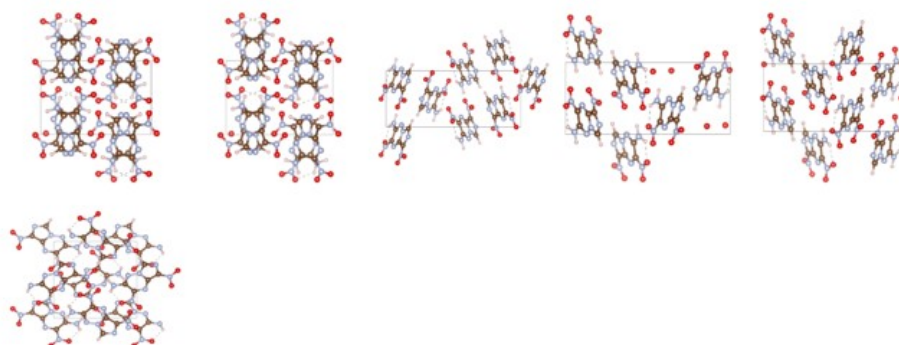
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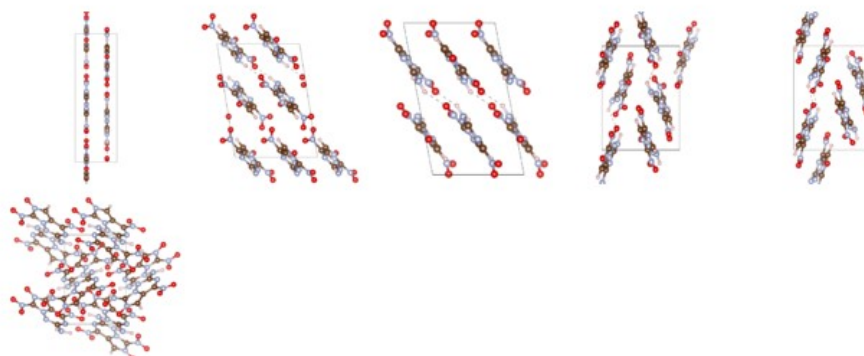
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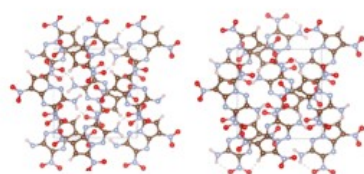
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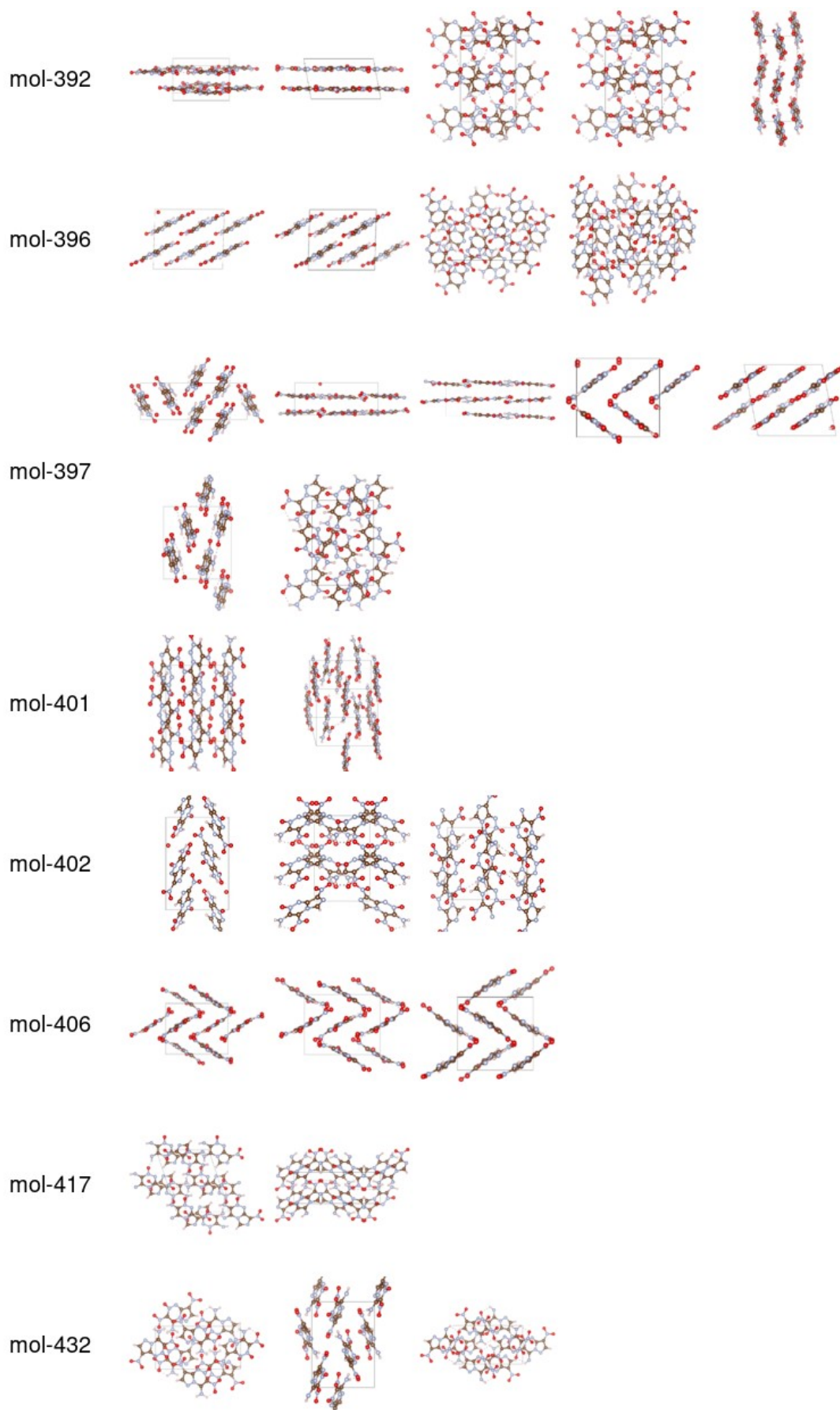


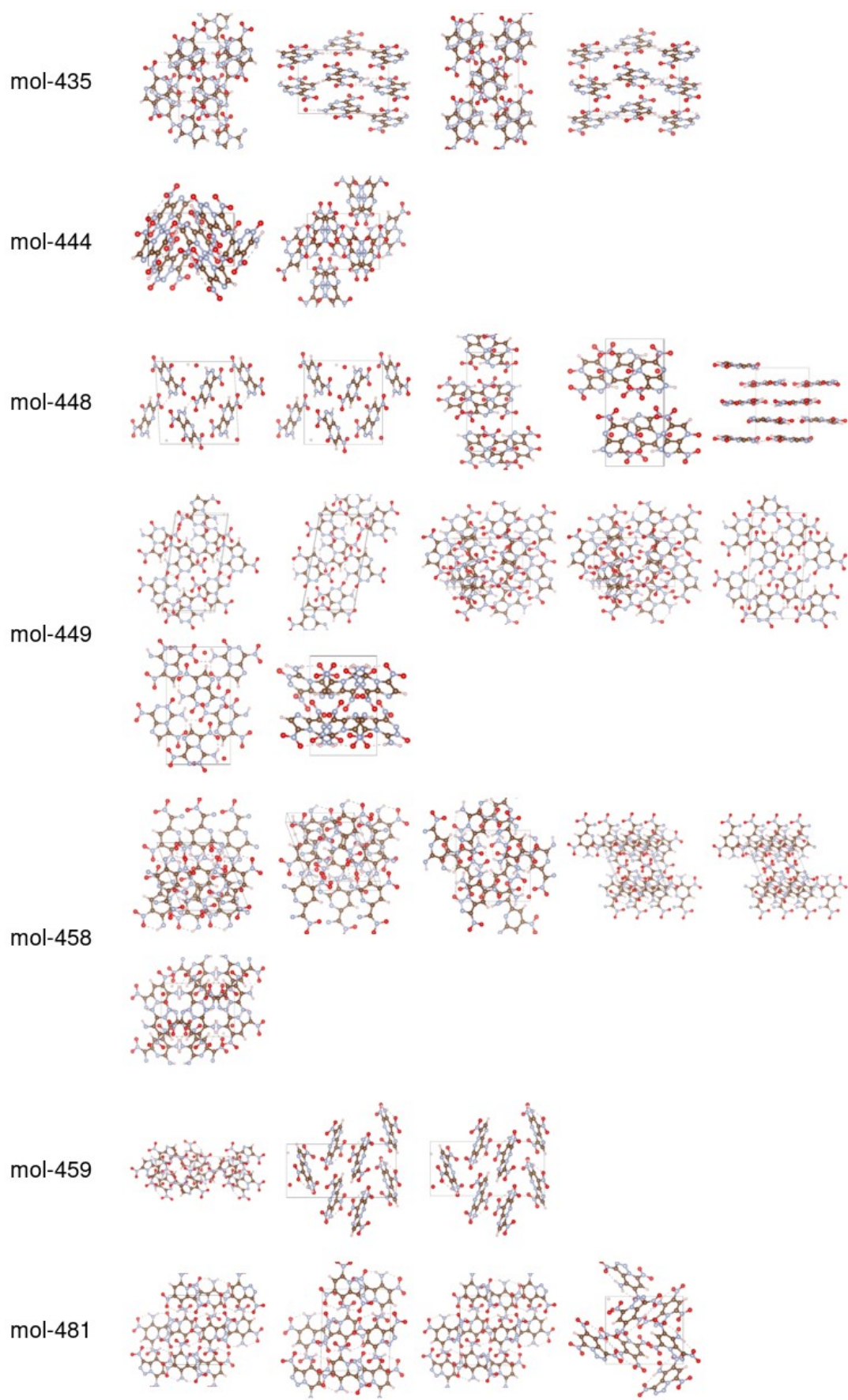
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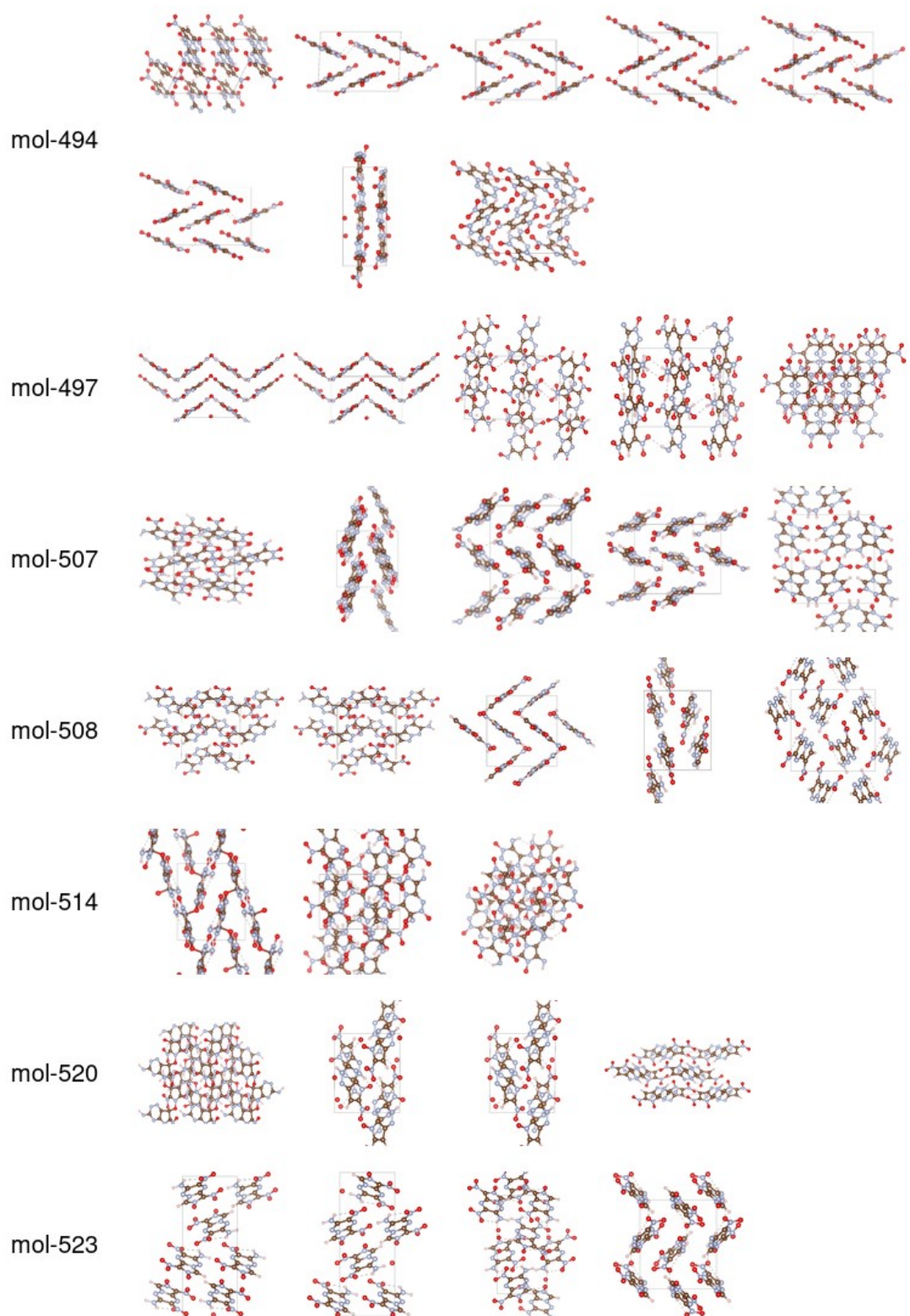


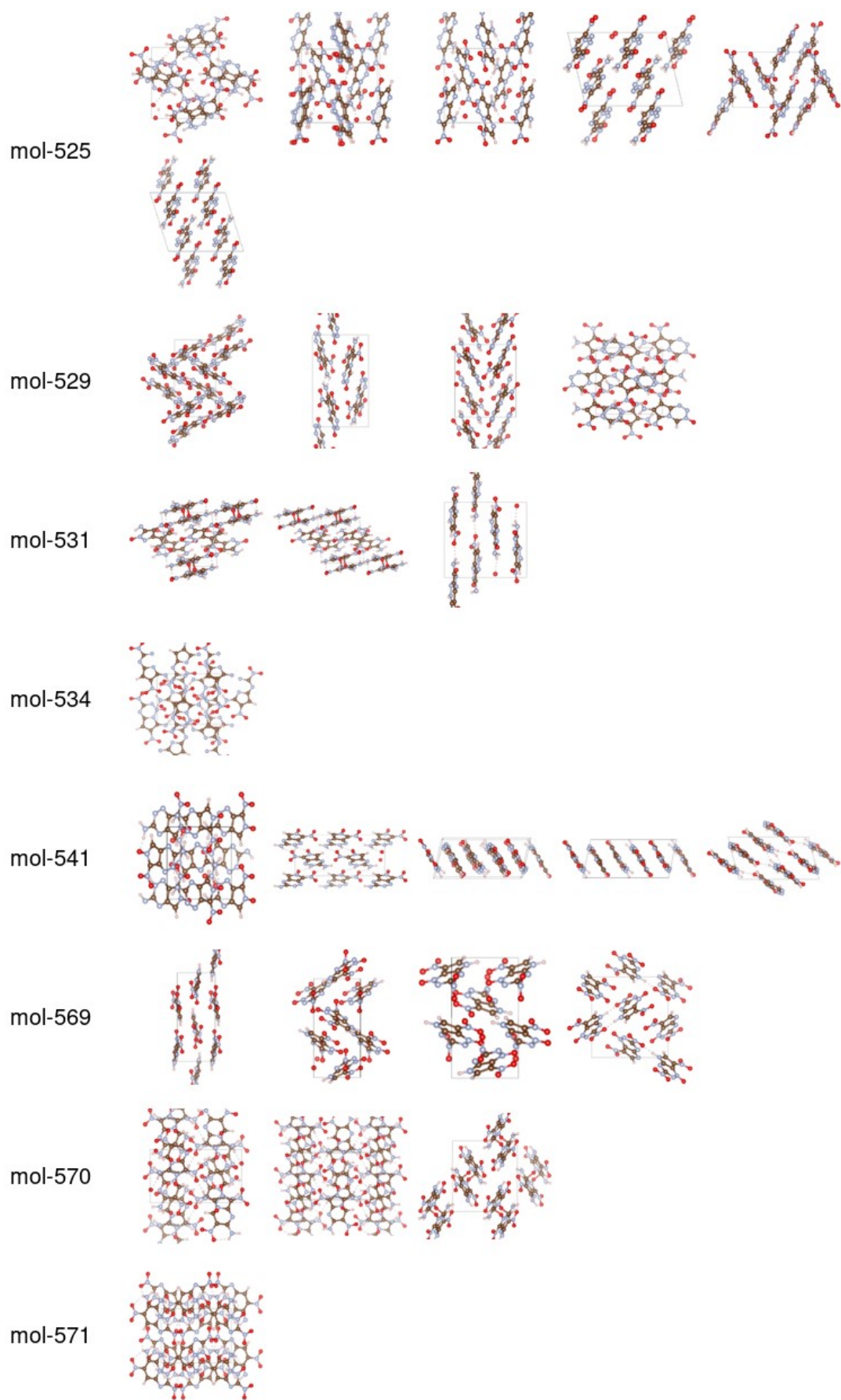
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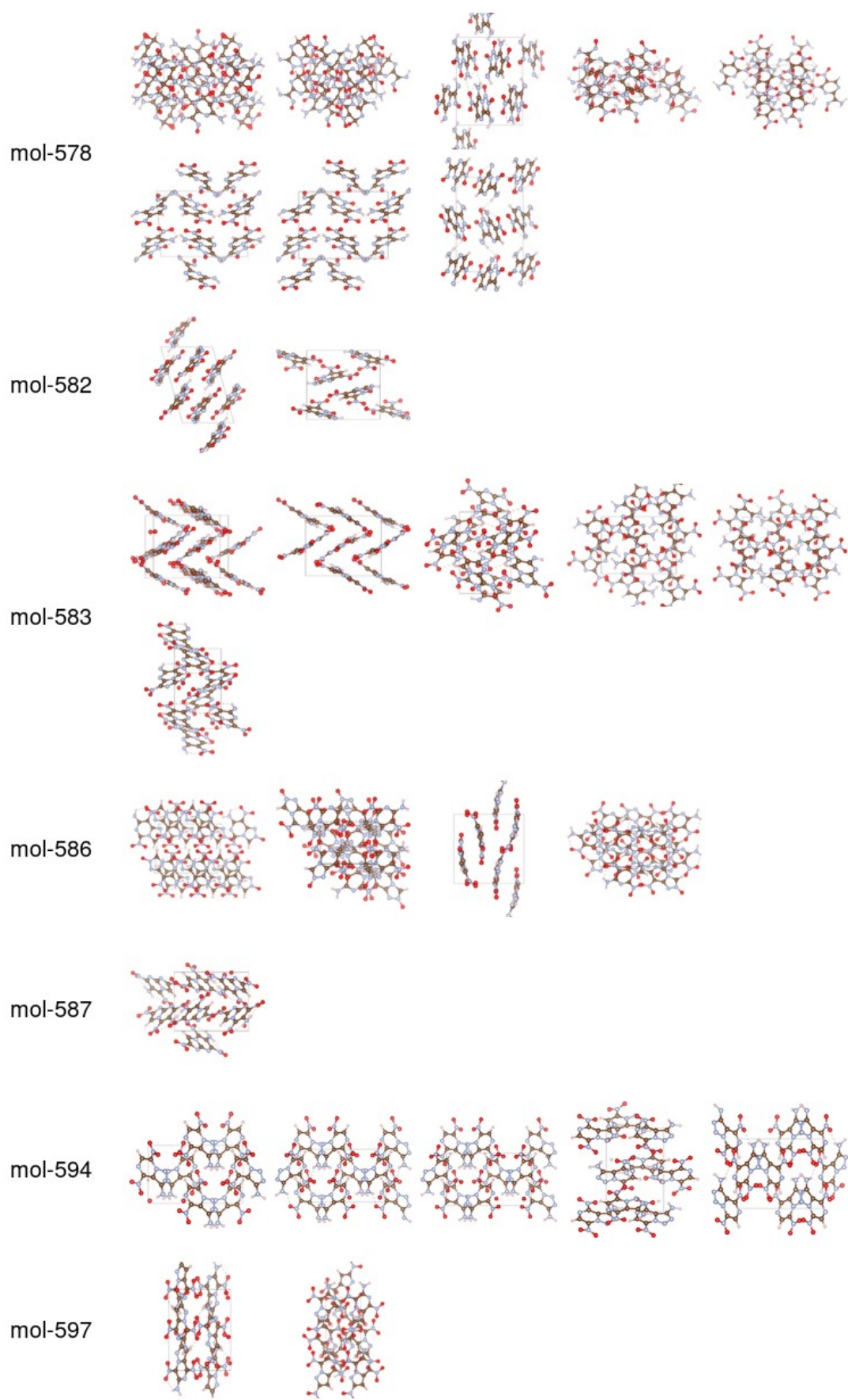


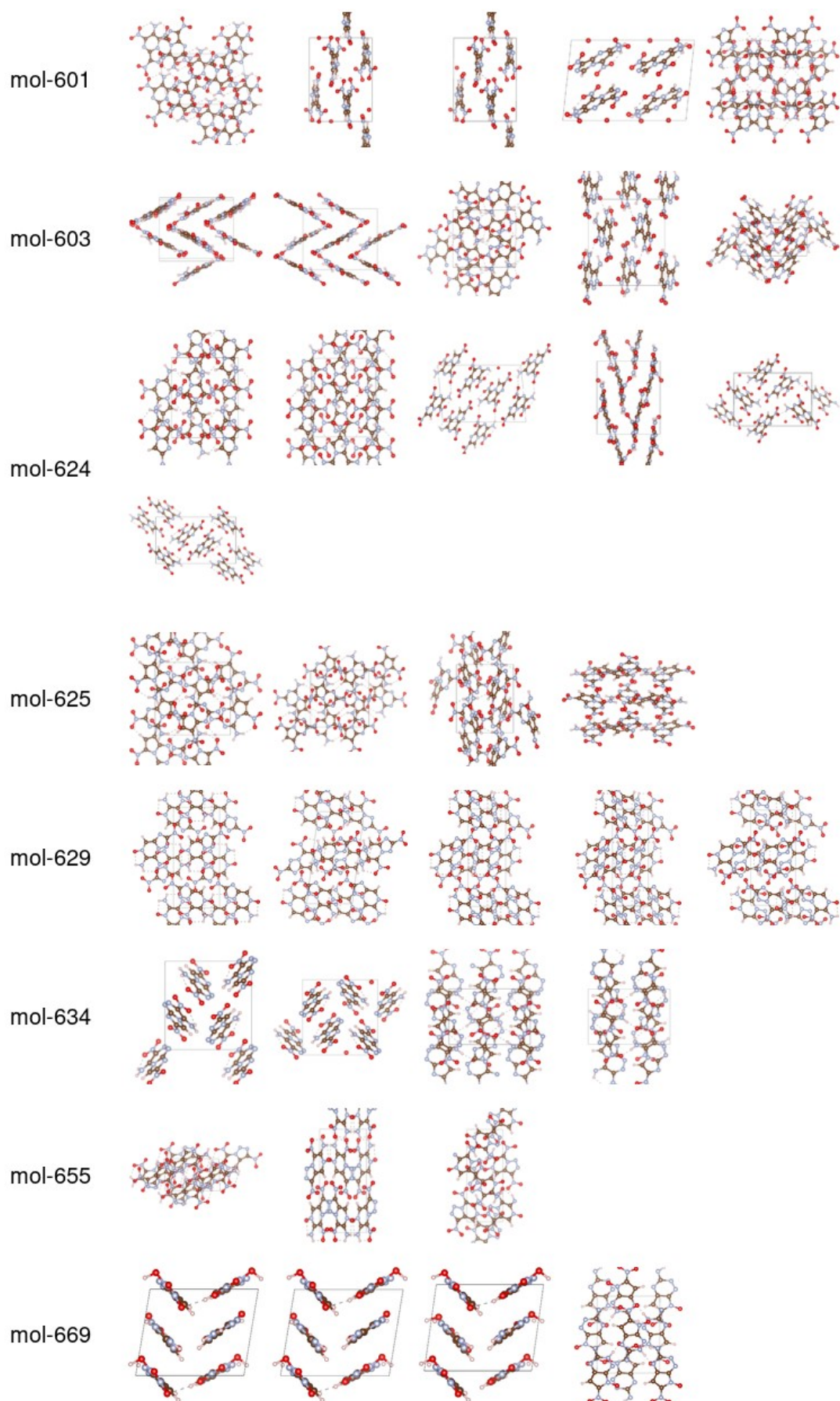












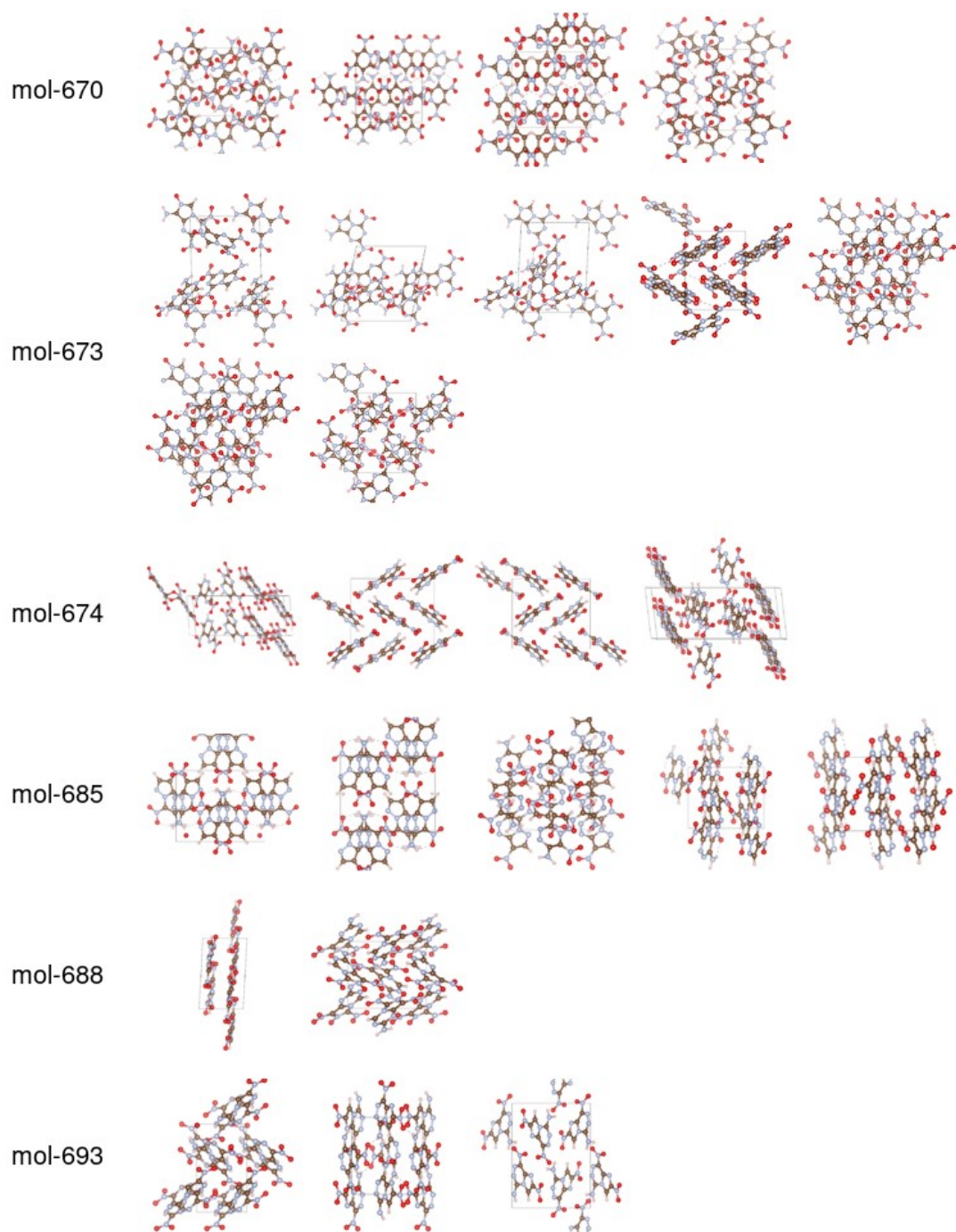


Figure S1 Predicted crystal structures of the 100 designed molecules from USPEX + xTB.

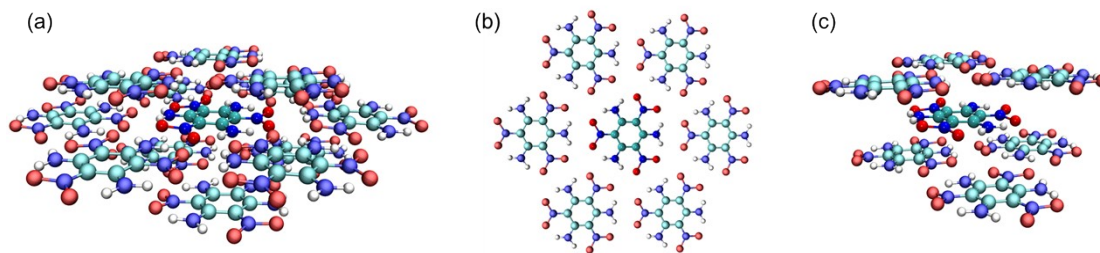


Figure S2 Fragment partitioning schemes for energy decomposition analysis: (a) overall; (b) intralayer; (c) interlayer.

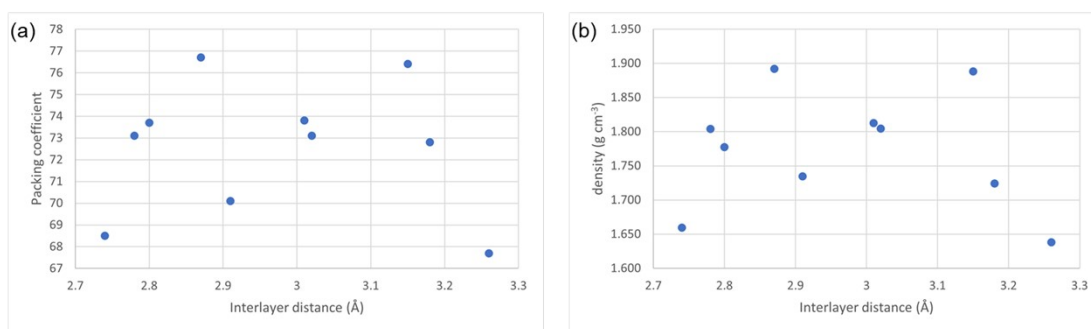


Figure S3 Scatter plots of interlayer spacing versus packing coefficient (a) and density (b).

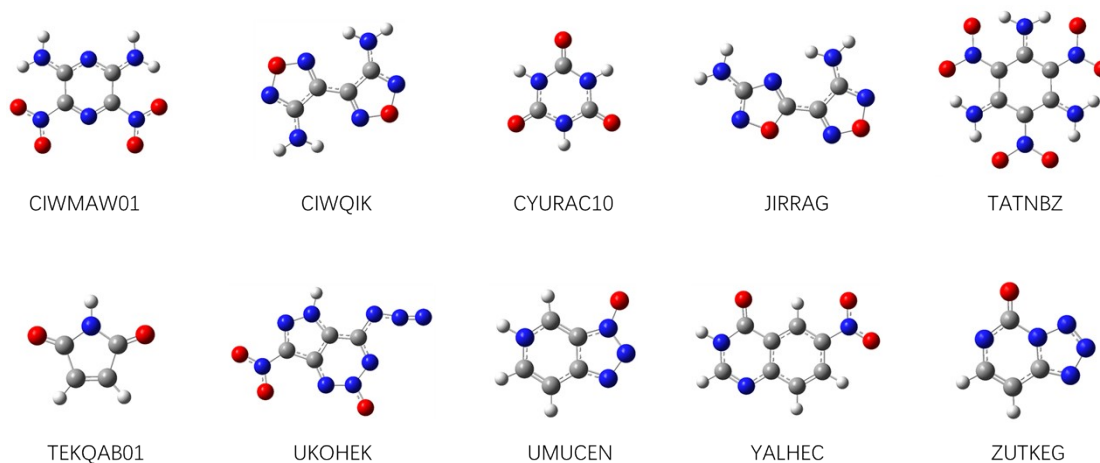


Figure S4 Energy decomposition analysis of intermolecular interactions for ten reported planar layered stacking molecules.

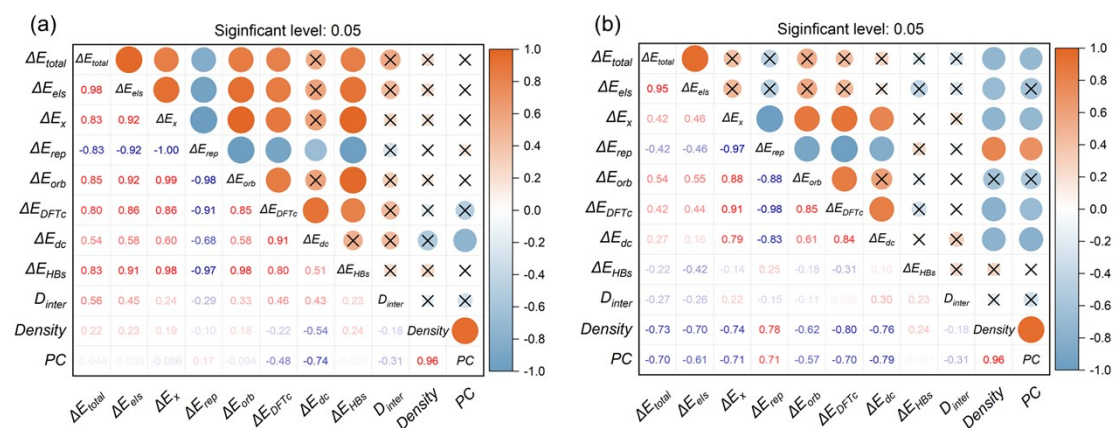


Figure S5 Correlation heat maps between density and intermolecular interaction energy decomposition terms for the Set-pl10: (a) intralayer intermolecular weak interactions; (b) interlayer weak interactions.

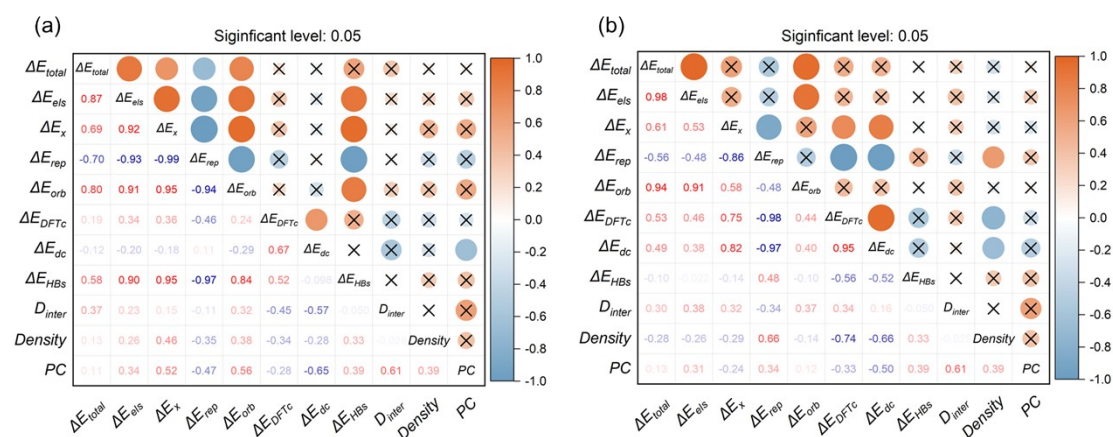


Figure S6 Correlation heat maps between density and intermolecular interaction energy decomposition terms for the ten reported molecules: (a) intralayer intermolecular weak interactions; (b) interlayer weak interactions.