Electronic Supplementary Information

Understanding the amino ↔ imino tautomeric preference in (imidazole)imidazolidine-N-aryl(alkyl) systems: a case study of moxonidine drug and insights from Cambridge Structural Database (CSD).

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Table S1. Sorting of 180 structures from CSD into 107 amino tautomers and 72 imino tautomers.

107 structures represented as Amino Tautomer

ABPHAK10, ABUSUN, ADANAV, AFURBA, AHOXOL, ASOSUX, AYATEA, AZELIB, BEWLOF, BOCYOH,
BOCZIC, BOGFUZ, BOGREV, CAFNOO CIVRUV, COJXEE, DEMDAB, DIDWOE ECATOT, ECATUZ,
ECAVAH, ECAVEL, EDEFUP, EFECAT, EFECEX EPAJEL, EYAMIB, EYUJEO, FUBQEY, GOLFUI,
HACJUR, HEDVAP, HEXBAO, HORDEX, HORFID HORFOJ, HORFUP, IRITAF, JAZMON, JOQNUY,
KEQZUC, KUXJOC, LAHQES, LERTIL, LIGSUP MACPIM, MAFRIW, MAFROC, MAJRAS, MAVYUE,
MILGUK, MILHAR, MILHEV, MUJKAE, MUZBAL NEFRUM, NEHPAS, NEHPEW, NUQBAD, NUZJOH,
PERLAA, PIBPEX, PIDJOD, PIDJUJ, PIDKAQ, PIDKEU, PUYDET, QABDON, QEQXIT, REFREB
REJVEI, SACZAX, SAGQEW, SIZFIQ, SUKNAN, TASWEP, TORNAQ, UBIJOE, UBIJUK, UCUZID
ULIJIJ, UNUMEW, VAHXOR, VEHDUH, VERZEY, VEVPOD VIHJUR, VOBLAZ, WEFQAB, WEKKON,
WIBMIE WIPBAY, XASWUL, XENKAD, XIBPOO, XOZCUL, XUDNOA, XUDNUG, XUDPAO, XUQTOT,
YEDTUX YEYNEW, YUHBUY, YULGIW, ZENREP, ZIKPAK, ZIKPEO

73 structures represented as Imino Tautomer

ADAKUM, AKIWUM, ALALEF, BABBUB, BAFMUS, BAFNAZ, CIQNOG, CNHYDM COPZOX, EKELAH,
GEMMAN01, GENSUO, GIXYUI, GIXZIX, GOLNIE, HACJOL, HANFOS01, HIGGOU HODQOG, HODSUO,
IQAFEL, KABFID, KATVAC, KATXIO, KEPDUF, KEPFAN, KEPFER, KEQGET KIBRAO, LUVPOH,
MECVAT, MECVEX, MEYWOC, MITBOH, MOKKAZ, MUFBUK, MUZBIT, NATGUL PAQQED, PIBGOY,
QIBBOS, QIQDEB, QOGQOS, QOTVAW, RUGGIK, SEDZUW, SEFBAG, SIMGUR, SINNAE, SIZSAW
SUTWIO, TAKXAG, TAKXEK, TAKXIO, TIAMEN10, TORNEU, TURVOR, UBIJIY, VEHFAP, VIGRIN
VOVCUE, XAQNOU, XEBQOM, XERHOS, XUDPES, YAKSIN, YIQZAA, ZAYQOF, ZEKPEM, ZEKPIQ
ZEKPOW, ZEKPOW01, ZIFKEG

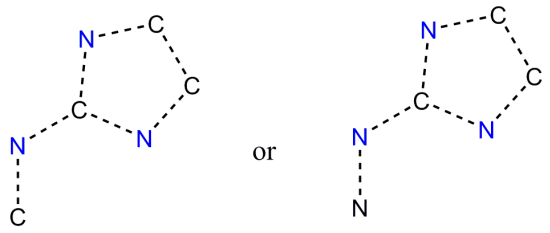


Figure S1. Two fragments are used for querying into Cambridge Structural Database, Conquest version 1.16, CSD version 5.35 (Nov 2013 release) + 2 updates (Nov 2013 + Feb 2014). Filters applied are 3D coordinates, No error, No polymeric, No powder and only organics to extract 827 hits. Ionic structures are excluded to leave 640 hits. Structures were manually analyzed for systems which can tautomerize. 180 hits are obtained.

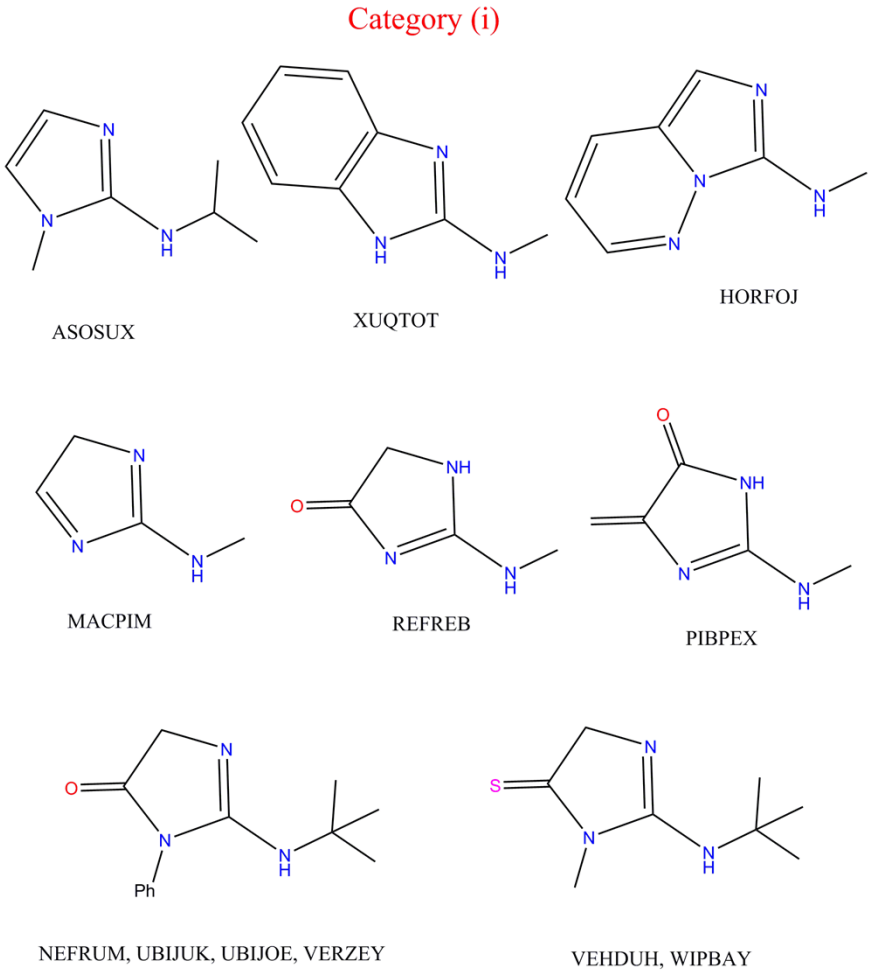


Figure S2. Various conjugated fragments observed in category (i) structures.

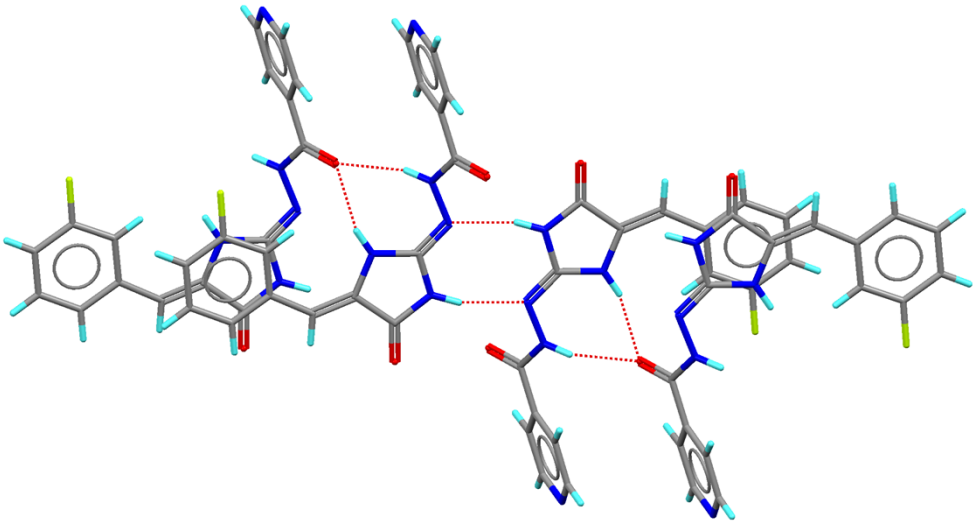


Figure S3. XUDPES structure crystallizes as imino tautomer and allows infinite chain of bifurcated N-H…O interactions and N-H…N dimers in the crystal

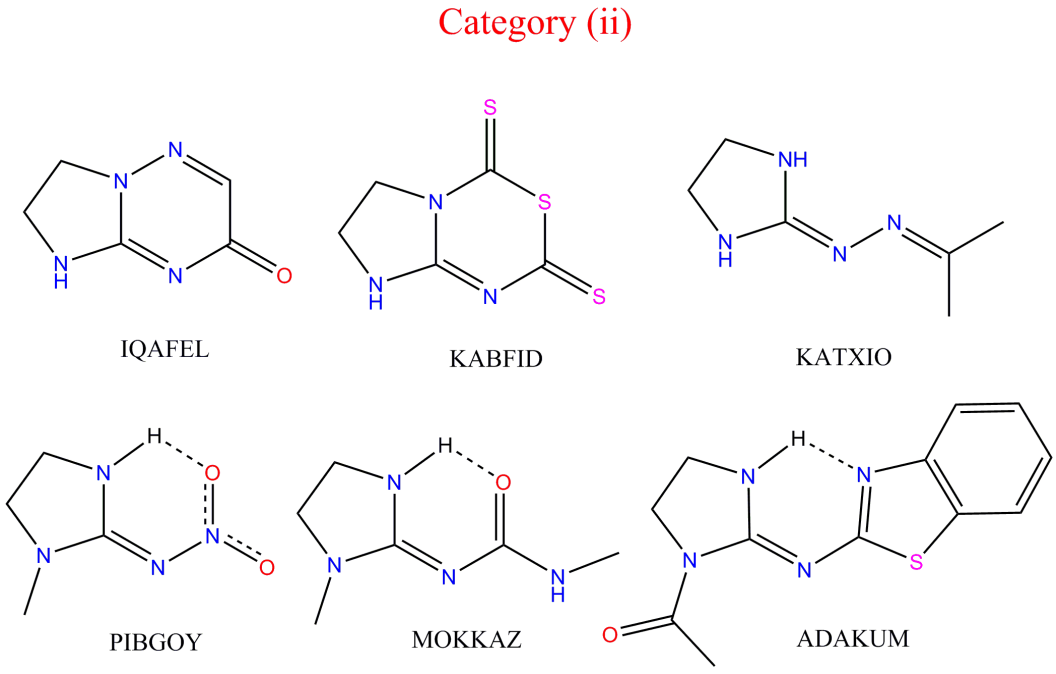


Figure S4. Various conjugated fragments noticed in category (ii) structures.

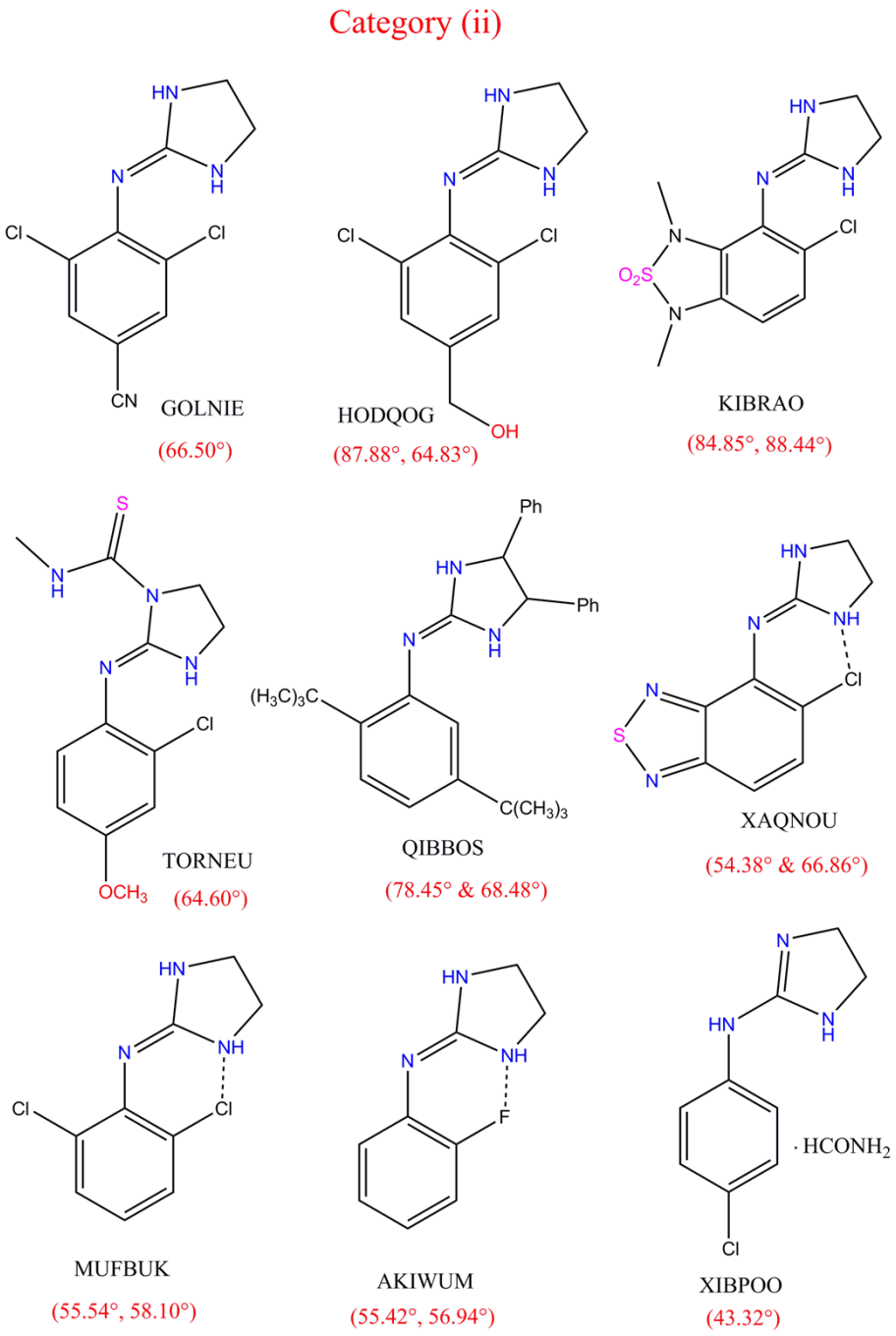
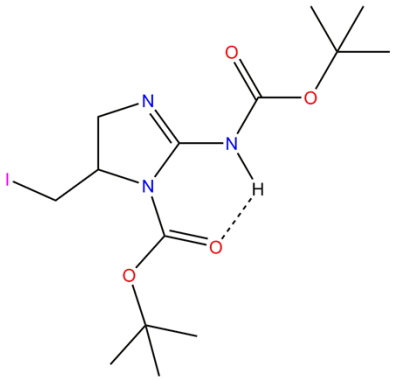
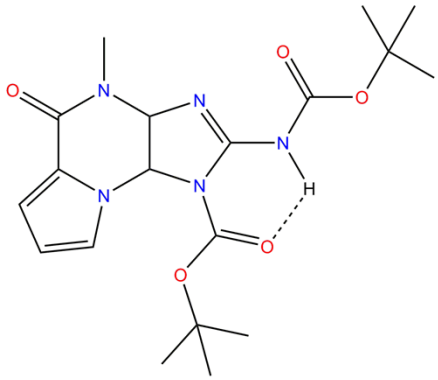


Figure S5. Nine structures in category (ii) which have close resemblances to moxonidine and all of them crystallize as imino tautomer except XIBPOO. Dihedral angles between planes of aromatic and imidazolidine ring are provided. Two values are provided for structures with two molecules in the asymmetric unit.

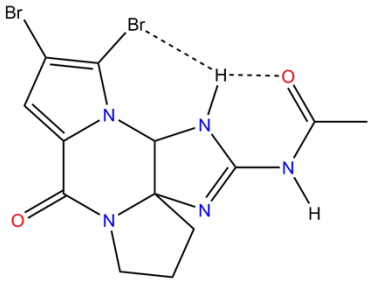
Category (ii)



HACJUR, Amino tautomer



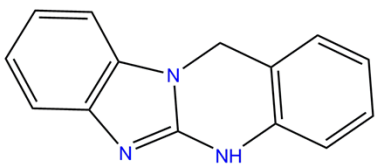
AHOXOL, Amino tautomer



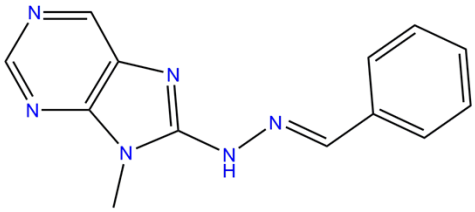
ABPHAK10, Amino tautomer

Figure S6. Molecular diagrams of three exceptional structures in category (ii). Intramolecular N-H…O hydrogen bonds stabilizing the amino tautomers are shown.

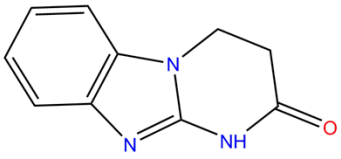
Category (iii)



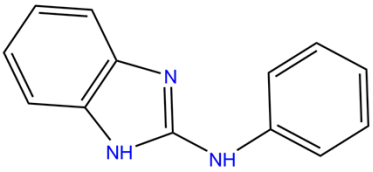
LIGSUP



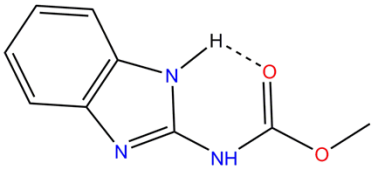
HEXBAO



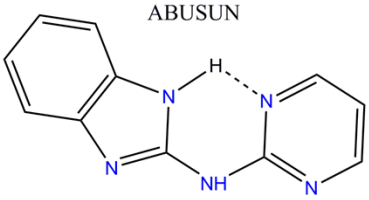
BOGREV



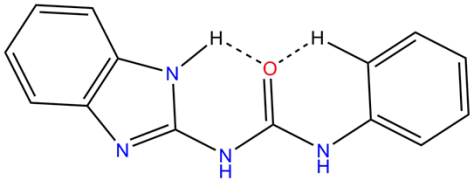
ABUSUN



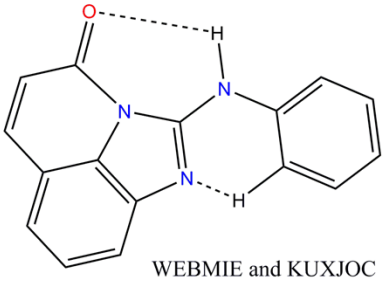
PIDJOD



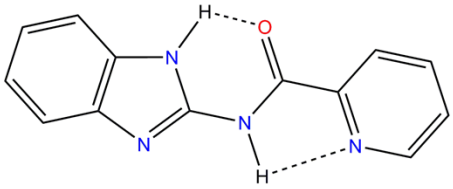
ULIJIJ



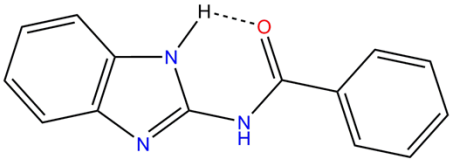
ECATOT



WEBMIE and KUXJOC



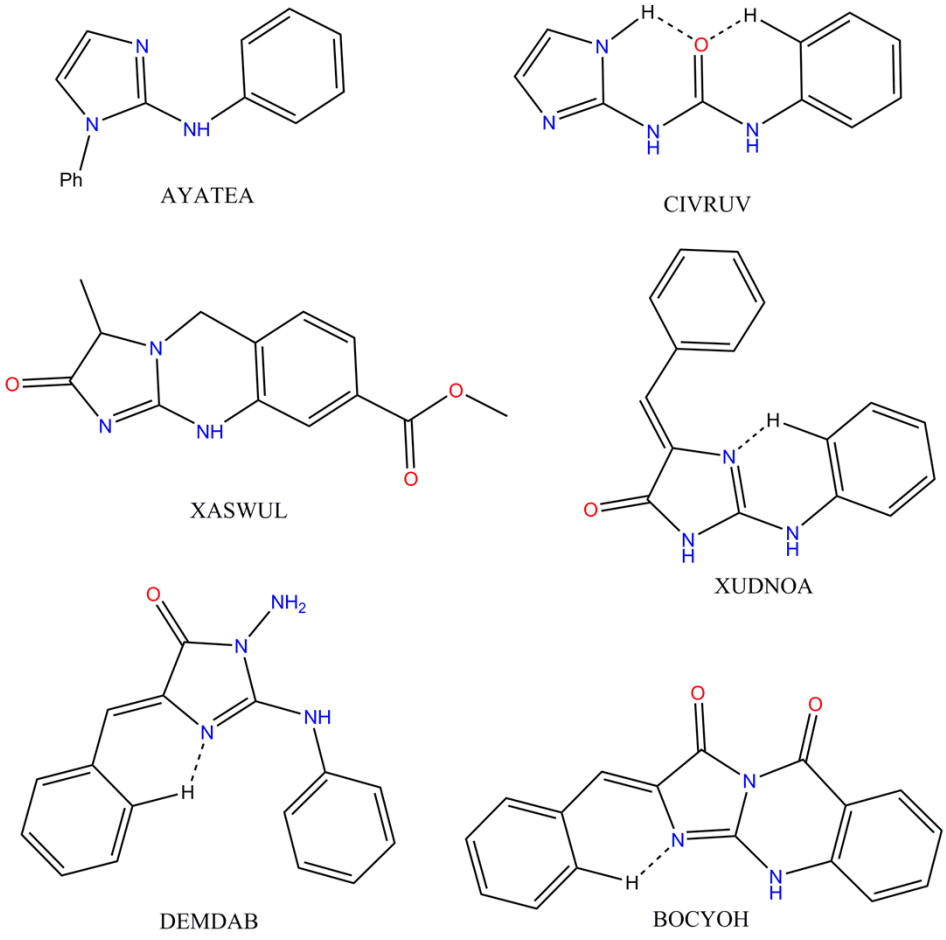
MILHAR



XENKAD

(a)

Category (iii)



(b)

Figure S7. Category (iii) structures which crystallized as amino tautomers are shown in (a) and (b).

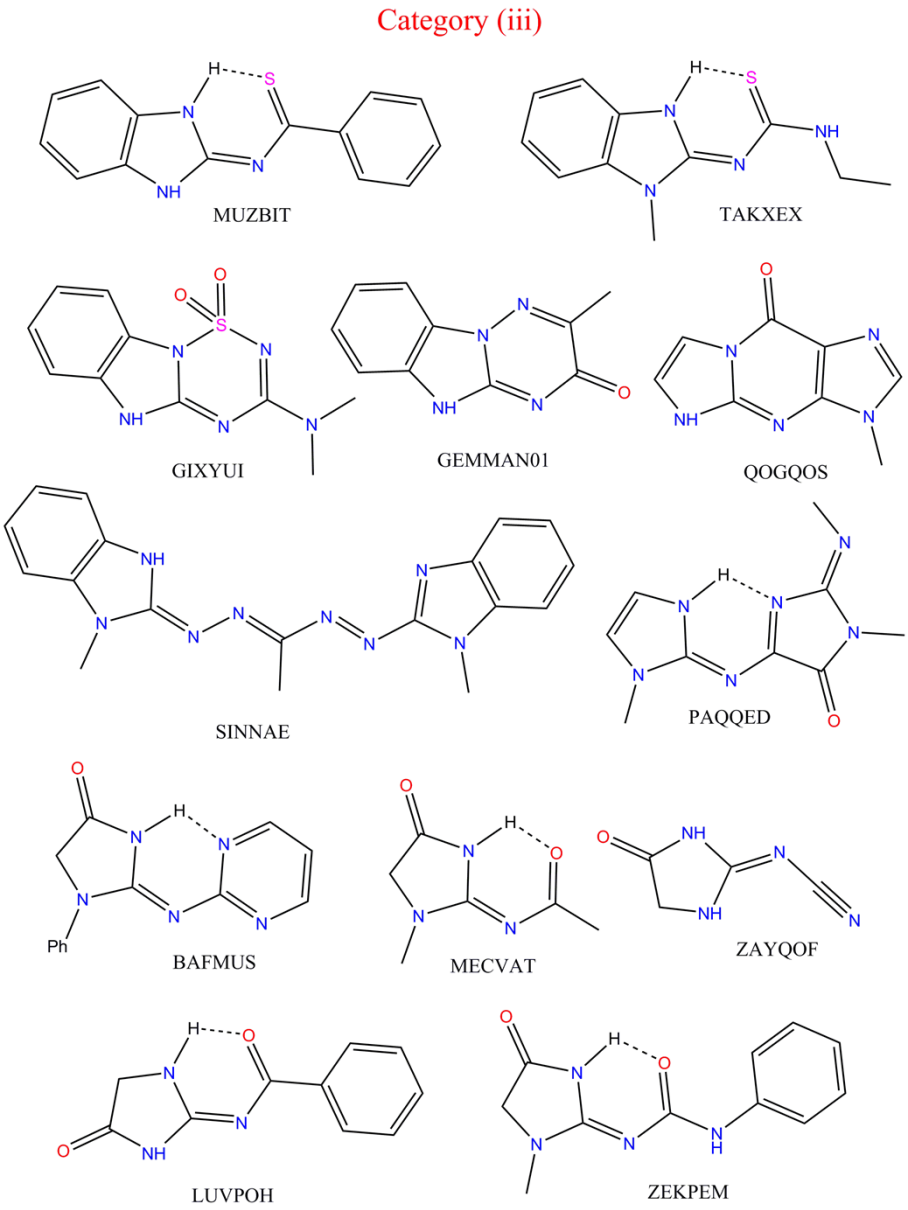


Figure S8. Category (iii) structures which crystallized as imino tautomers.

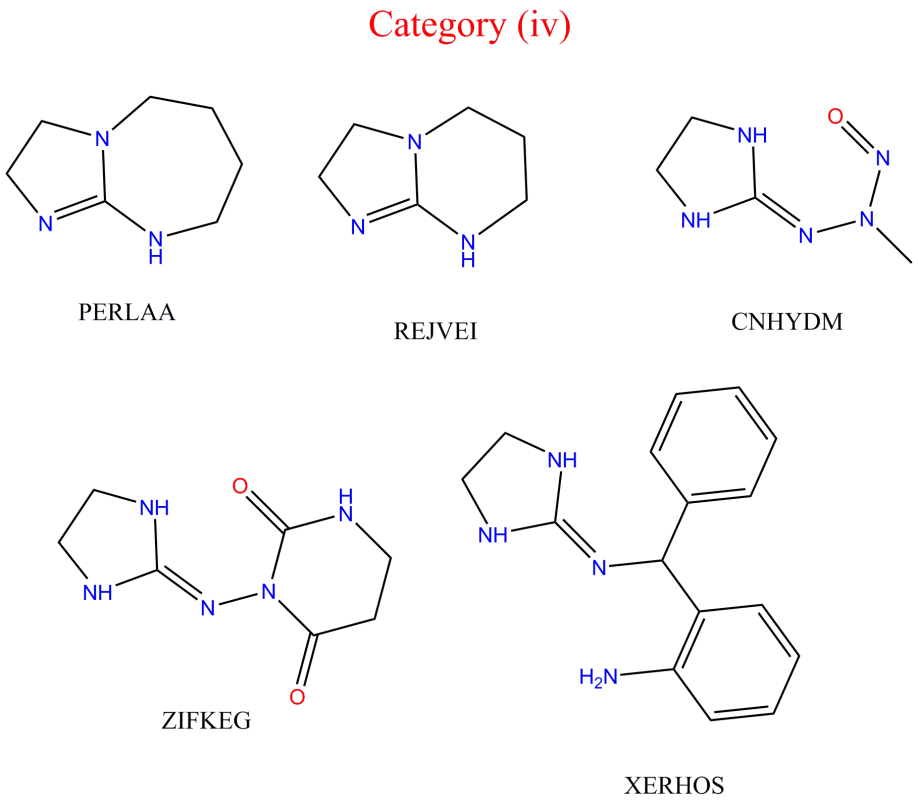
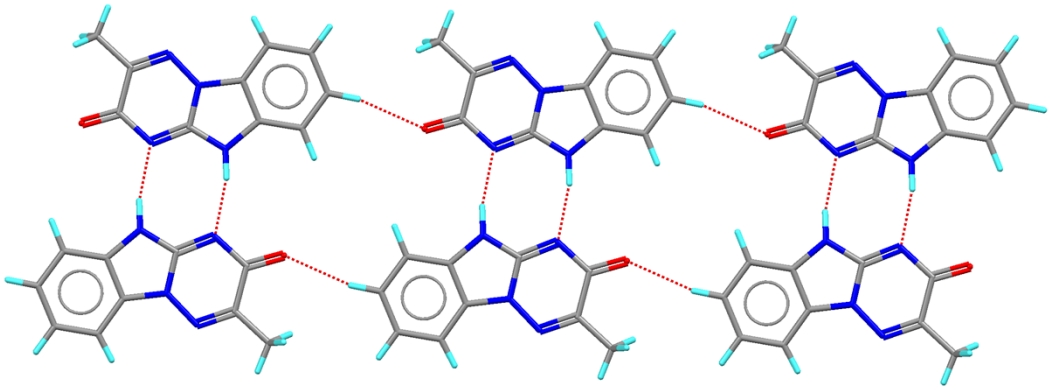
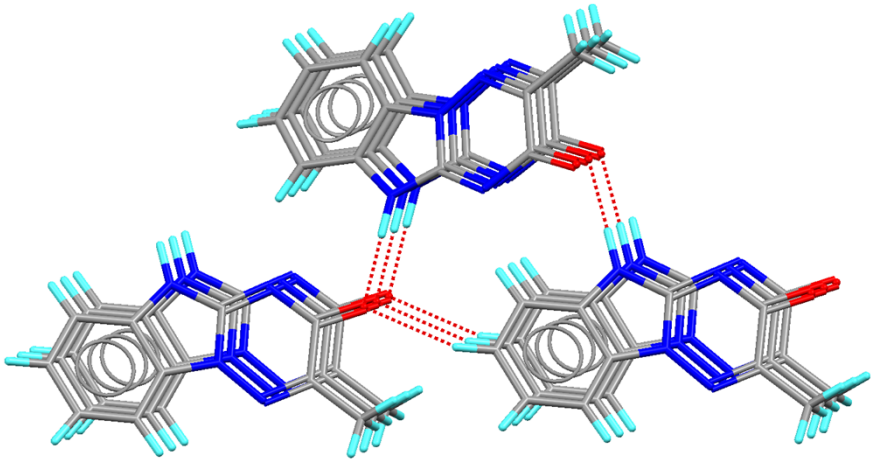


Figure S9. Category (iv) structures which crystallized as both amino and imino tautomer.

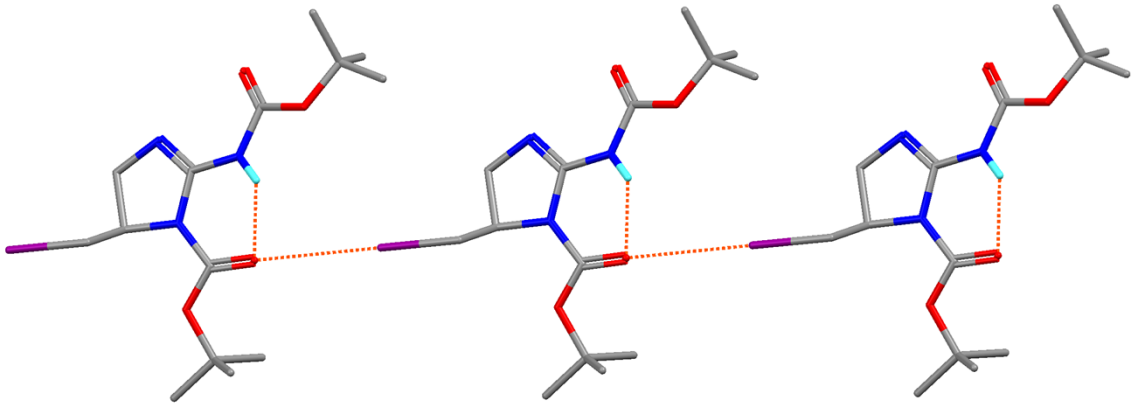


(a)

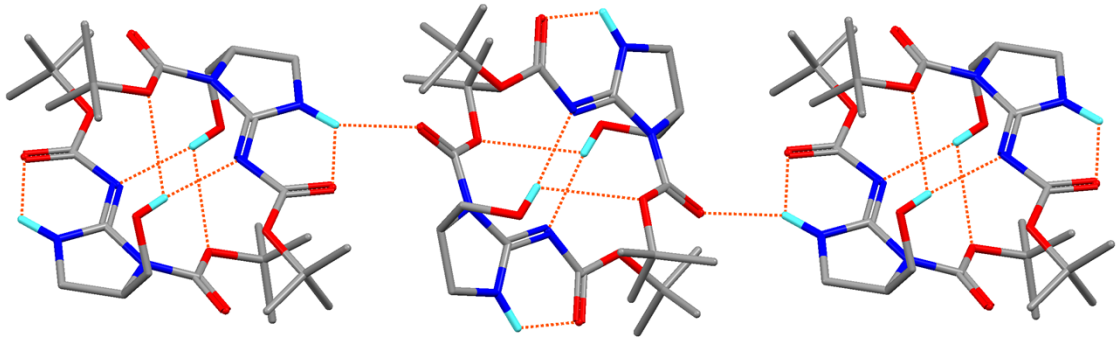


(b)

Figure S10. (a) Hydrogen bonding features leading to planar structure in GEMMAN. (b) Hydrogen bonding features leading to helical architecture in GEMMAN01 (polymorph). Both structures contain the less stable imino tautomer.



(a)



(b)

Figure S11. (a) Propagation of molecules in HACJUR crystal structure through short I…O contacts. (b) Interaction of hydroxyl groups with imino tautomer of HACJOL by O-H…N hydrogen bonds and propagation of molecules in the crystal through N-H…O hydrogen bonds.