Table S1. Frequency of structural classes amongst the 197 structures retained for analysis

P 21/c, Z = 4 (1)	84
P n m a, Z = 4 (m)	18
P 21/c, Z = 6 (1, –1)	16
P c a 21, Z = 4 (1)	12
P n a 21, Z = 4 (1)	11
P 21 21 21, Z = 4 (1)	11
P b c a, Z = 8 (1)	7
P –1, Z = 3 (1, –1)	7
C c, Z = 8 (1, 1)	4
P 21, Z = 2 (1)	2
P –3, Z = 3 (3, –3)	2
P 21, Z = 4 (1, 1)	2
P –1, Z = 4 (1, 1)	2
P b c n, Z = 8 (1)	1
P 41 21 2, Z = 8 (1)	1
C 2/c, Z = 16 (1, 1)	1
C m c m, Z = 4 (m m 2)	1
P 3 1 c, Z = 6 (1)	1
R –3, Z = 54 (1, 1, 1)	1
I 41 c d, Z = 8 (2)	1
P 41, Z = 4 (1)	1
P c, Z = 4 (1, 1)	1
C 2/c, Z = 4 (2)	1
P 4/n n c, Z = 4 (4)	1
P 21/c, Z = 8 (1, –1, –1)	1
P b c m, Z = 4 (m)	1
C 2/m, Z = 6 (2/m, m)	1
P 21 21 21, Z = 8 (1, 1)	1
C c, Z = 4 (1)	1
P 42 b c, Z = 8 (1)	1

Table S2. Full list of identified structures containing only centrosymmetric molecules (rms < 0.1 Å), with at least one having non-centrosymmetric crystallographic site symmetry

(1) Triclinic (20 structures, 11 with established missed symmetry)

Refcode	Structural Class	Unconstrained overlay (rms Å, rotation type)		Constrained overlay (rms Å, rotation type)		
AWAZIH	P 1, Z = 1 (1)					**Missed symmetry**: P –1, Z = 1 (–1)
BOPFER	P –1, Z = 3 (1, –1)	0.0194	either	0.0194	either	
BUNDIX	P –1, Z = 3 (1, –1)	0.1092	either	0.1092	either	
CERLOA	P –1, Z = 4 (1, –1, –1)					**Missed symmetry:** P –1, Z = 2 (–1, –1) Cell: 10.416, 10.224, 11.501, 89.80, 84.41, 60.43
ECOBUT	P –1, Z = 2 (1)					**Missed symmetry:** P –1, Z = 1 (–1) Cell: 8.1835, 9.8676, 11.6664, 81.031, 81.754, 66.919
FESVEF	P 1, Z = 1 (1)					**Missed symmetry**: P –1, Z = 1 (–1)
FIFXEX	P –1, Z = 3 (1, –1)	0.0580	either	0.0580	either	
GEKMAK	P –1, Z = 3 (1, –1)	0.0942	either	0.0942	either	
MIDREW	P –1, Z = 3 (1, –1)					**Missed symmetry:** P –1, Z = 1 (–1) Cell: 10.005, 12.8100 10.3566, 88.44, 89.21, 77.10
MUHXOC	P 1, Z = 2 (1, 1)					**Missed symmetry**: P –1, Z = 2 (–1, –1)
NAVNAA	P 1, Z = 1 (1)					**Missed symmetry**: P –1, Z = 1 (–1)
PAYZEU	P 1, Z = 2 (1, 1)					**Missed symmetry**: P –1, Z = 2 (–1, –1)
QIBDEL	P –1, Z = 5 (1, 1, –1)					**Missed symmetry:** P –1, Z = 1 (–1) Cell: 9.274, 10.817, 13.441, 87.85, 76.20, 65.38
RARBAO	P 1, Z = 1 (1)					**Missed symmetry**: P –1, Z = 1 (–1)
RAVREM	P –1, Z = 4 (1, 1)	0.0751	improper	0.0751	improper	
SOMXOH01	P –1, Z = 4 (1, 1)	0.0254	proper	0.0254	proper	
VARFAV	P –1, Z = 3 (1, –1)	0.0455	either	0.0455	either	
WEHFIY	P –1, Z = 3 (1, –1)	0.0643	either	0.5121	either	Difference between shape and type match due to exchange of N3 and C22 in the molecule on the inversion centre
XINJOT	P –1, Z = 3 (1, –1)	0.0592	either	0.0592	either	
YEDQUU	P 1, Z = 1 (1)					**Missed symmetry**: P –1, Z = 1 (–1)

(2) Monoclinic (129 structures, 14 with established missed symmetry)

Refcode	Structural Class	Unconstrained overlay (rms Å, rotation type)		Constrained overlay (rms Å, rotation type)		
ADIPAC05	P 21/c, Z = 6 (1, –1)	0.0728	either	0.0728	either	
AJUQOL01	P 21, Z = 2 (1)					**Missed symmetry**: P 21/c, Z = 2 (–1)
ASALPD11	P 21/c, Z = 4 (1)	—	—	—	—	
AZPHEN10	P 21/c, Z = 4 (1)	—	—	—	—	
BAJVIR	P 21/c, Z = 6 (1, –1)	0.1157	either	0.1157	either	
BATQIX	C c, Z = 4 (1)					**Missed symmetry**: C 2/c, Z = 4 (–1)
BCODYN02	P 21/c, Z = 4 (1)	—	—	—	—	
BEJNOT	P 21/c, Z = 4 (1)	—	—	—	—	
BEQWEA	C 2/c, Z = 8 (1)	—	—	—	—	
BIGLIM	P 21, Z = 2 (1)					**Missed symmetry**: P 21/c, Z = 2 (–1)
BIPHNE01	P 21/c, Z = 6 (1, –1)	0.0194	either	0.0194	either	
BIWYOV	P 21/c, Z = 4 (1)	—	—	—	—	
BONFIT	P 21/c, Z = 4 (1)	—	—	—	—	
BUCFEC	P 21/c, Z = 4 (1)	—	—	—	—	
BZOBPH	P 21/c, Z = 4 (1)	—	—	—	—	
CACDOA	P 21/c, Z = 4 (1)	—	—	—	—	
CALZAR	P 21/c, Z = 4 (1)	—	—	—	—	
CUSZEV	P 21/c, Z = 4 (1)	—	—	—	—	
DAWVEC	P 21/c, Z = 4 (1)	—	—	—	—	
DAWVIG	P 21/c, Z = 4 (1)	—	—	—	—	
DCLANT10	P 21/c, Z = 4 (1)	—	—	—	—	
DEBCES	P 21/c, Z = 4 (1)	—	—	—	—	
DEPQAQ	C c, Z = 8 (1, 1)	0.4542	proper	0.4542	proper	
DEXBEN	P 21, Z = 2 (1)					**Missed symmetry**: P 21/c, Z = 2 (–1)
DIHDON	P 21/c, Z = 4 (1)	—	—	—	—	
DIMNAP01	P 21/c, Z = 4 (1)	—	—	—	—	
DOTXAL	P 21/c, Z = 4 (1)	—	—	—	—	
DPYBDL	P 21/c, Z = 4 (1)	—	—	—	—	
EGUWUY	P 21/c, Z = 4 (1)	—	—	—	—	

ESALIM	P 21/c, Z = 4 (1)	—	—	—	—	
EWOSUE	P 21/c, Z = 4 (1)	—	—	—	—	
EZAGOB	P 21/c, Z = 4 (1)	—	—	—	—	
FAGLUU	P 21/c, Z = 4 (1)	—	—	—	—	
FAHWIU	P 21/c, Z = 6 (1, –1)	0.0835	either	0.0835	either	
FECCOF01	P 21/c, Z = 4 (1)	—	—	—	—	
FEDGOK	P 21/c, Z = 4 (1)	—	—	—	—	
FEFBIB	C 2/c, Z = 16 (1, 1)	0.0535	improper	0.0535	improper	
FEQTIF	P 21/c, Z = 4 (1)	—	—	—	—	
FIGWEY	C c, Z = 4 (1)					**Missed symmetry**: C 2/c, Z = 4 (–1)
FIPDAJ	P 21/c, Z = 4 (1)	—	—	—	—	
FISDAM	P 21, Z = 2 (1)					**Missed symmetry**: P 21/c, Z = 2 (–1)
FIXPUX	P 21/c, Z = 4 (1)	—	—	—	—	
FOJVAC	P 21, Z = 2 (1)	—	—	—	—	
FONJUN	P 21/c, Z = 4 (1)	—	—	—	—	
FUMAAC	P 21/c, Z = 6 (1, –1)	0.0163	either	0.0163	either	
GAGVAL	P 21/c, Z = 4 (1)	—	—	—	—	
GALTES	P 21/c, Z = 6 (1, –1)	0.0151	either	0.0151	either	
GEHTET	C 2, Z = 4 (1)					**Missed symmetry**: C 2/c, Z = 4 (–1)
GEHYAT	P 21/c, Z = 4 (1)	—	—	—	—	
GICPOX	P 21/c, Z = 6 (1, –1)	0.0267	either	0.0267	either	
HIHTUN	P 21/c, Z = 4 (1)	—	—	—	—	
HOMQEF	P 21/c, Z = 4 (1)	—	—	—	—	
ICAVEN	P c, Z = 2 (1)					**Missed symmetry**: P 21/c, Z = 2 (–1)
JAQJAN	P 21/c, Z = 4 (1)	—	—	—	—	
JAZSEJ	P 21/c, Z = 4 (1)	—	—	—	—	
JIBPUF	P 21/c, Z = 4 (1)	—	—	—	—	
KASNEY	P 21/c, Z = 4 (1)	—	—	—	—	
KATKOF	P 21/c, Z = 6 (1, –1)	0.0645	either	0.0645	either	
KETYOX	P 21, Z = 2 (1)					**Missed symmetry**: P 21/c, Z = 2 (–1)
KEVRUZ	P c, Z = 4 (1, 1)	0.0770	proper	0.0770	proper	
LAYKUS	P 21/c, Z = 4 (1)	—	—	—	—	
LIYCOL	P 21/c, Z = 4 (1)	—	—	—	—	

MEACCU01	C 2/c, Z = 4 (2)	—	—	—	—	
METJAW	P 21/c, Z = 4 (1)	—	—	—	—	
MHPYFE	P 21/c, Z = 4 (1)	—	—	—	—	
MOFORM01	P 21/c, Z = 6 (1, –1)	0.0202	either	0.0202	either	
MPTZTE10	P 21/c, Z = 4 (1)	—	—	—	—	
NAFWOG	P 21/c, Z = 4 (1)	—	—	—	—	
NICLAN	P 21, Z = 2 (1)					**Missed symmetry**: P 21/c, Z = 2 (–1)
NIDTHC11	P 21/c, Z = 4 (1)	—	—	—	—	
NIMAPS01	P 21/c, Z = 4 (1)	—	—	—	—	
NIWLAG	P 21/c, Z = 4 (1)	—	—	—	—	
OCIZOQ	P 21/c, Z = 4 (1)	—	—	—	—	
OFNAPH05	P 21/c, Z = 6 (1, –1)	0.0178	either	0.0178	either	
PATNUT	C c, Z = 8 (1, 1)	0.0471	improper	0.0471	improper	
PDTHBA10	P 21/c, Z = 6 (1, –1)	0.0594	either	0.0594	either	
PENDAM	P 21/c, Z = 8 (1, –1, –1)	0.0187	either	0.0187	either	
		0.0161	either	0.0161	either	
		0.0168	either	0.0168	either	
PERLEN05	P 21/c, Z = 4 (1)	—	—	—	—	
PEWXAQ01	P 21/c, Z = 4 (1)	—	—	—	—	
PHENAZ11	P 21/c, Z = 4 (1)	—	—	—	—	
PIBXON	P 21, Z = 2 (1)					**Missed symmetry**: P 21/c, Z = 2 (–1)
PIDFEN	P 21/c, Z = 4 (1)	—	—	—	—	
PIKZEO	P 21, Z = 2 (1)					**Missed symmetry**: P 21/c, Z = 2 (–1)
PIPFEZ	P 21/c, Z = 4 (1)	—	—	—	—	
PIZDOR	P 21/c, Z = 4 (1)					**Missed symmetry:** P 21/c, Z = 2 (–1) Cell: 3.3812, 11.5180, 8.3834, 90, 110.2, 90
PORPIN02	P 21/c, Z = 4 (1)	—	—	—	—	
POVSEY	P 21/c, Z = 6 (1, –1)	0.7041	either	0.7041	either	
PYRENE02	P 21/c, Z = 4 (1)	—	—	—	—	
PYRENE06	P 21/c, Z = 4 (1)	—	—	—	—	
QACSOD	P 21/c, Z = 4 (1)	—	—	—	—	
QATTIO	P 21/c, Z = 4 (1)	—	—	—	—	
QEMHIA	P 21, Z = 4 (1, 1)	0.0492	proper	0.0492	proper	

QEWROA	P 21/c, Z = 4 (1)	—	—	—	—	
QUATER10	P 21/c, Z = 4 (1)	—	—	—	—	
RASVIR	C c, Z = 8 (1, 1)	0.0751	improper	0.0751	improper	
REWCUS	C c, Z = 8 (1, 1)	0.0598	proper	0.0598	proper	
RILNAB	P c, Z = 2 (1)					**Missed symmetry**: P 21/c, Z = 2 (–1)
SAMRUU	P 21, Z = 2 (1)	—	—	—	—	
SEMVEL	P 21/c, Z = 4 (1)	—	—	—	—	
SIZYUV	P 21/c, Z = 4 (1)	—	—	—	—	
SUSWUY	P 21/c, Z = 6 (1, –1)	0.2326	either	0.2326	either	
TAMXIO	P 21, Z = 4 (1, 1)	0.0304	improper	0.0304	improper	
TCYNBZ01	P 21/c, Z = 4 (1)	—	—	—	—	
TCYQME02	C c, Z = 4 (1)					**Missed symmetry**: C 2/c, Z = 4 (–1)
TEMKOL	P 21/c, Z = 4 (1)	—	—	—	—	
TERFUR	P 21/c, Z = 4 (1)	—	—	—	—	
TETRAZ01	P 21/c, Z = 6 (1, –1)	0.0388	either	0.0388	either	
TIFFAP	P 21/c, Z = 4 (1)	—	—	—	—	
TISZUQ	P 21/c, Z = 4 (1)	—	—	—	—	
TMDPDS01	C 2/m, Z = 6 (2/m, m)	0.0612	either	0.0612	either	
TURDUF	P 21/c, Z = 4 (1)	—	—	—	—	
TUWYIT	P 21/c, Z = 6 (1, –1)	0.0640	either	0.0640	either	
VINJOR	P 21/c, Z = 4 (1)	—	—	—	—	
VIPKIO03	P 21/c, Z = 4 (1)	—	—	—	—	
WAGZUA	P 21/c, Z = 4 (1)	—	—	—	—	
WATHUU	P 21/c, Z = 4 (1)	—	—	—	—	
WIDGEV	P 21/c, Z = 4 (1)	—	—	—	—	
WIMFUT	P 21/c, Z = 4 (1)	—	—	—	—	
WOWSEG	P 21/c, Z = 4 (1)	—	—	—	—	
WUWMAC	P 21/c, Z = 4 (1)	—	—	—	—	
XEXLIV	P 21/c, Z = 4 (1)	—	—	—	—	
XUJCEK	P 21/c, Z = 4 (1)	—	—	—	—	
YATYOH	P 21/c, Z = 4 (1)	—	—	—	—	
YECTEF	P 21/c, Z = 4 (1)	—	—	—	—	
YUCYOK	P 21/c, Z = 4 (1)	—	—	—	—	

ZABGOY	P 21/c, Z = 4 (1)	—	—	—	—	
ZAQZUM	P 21/c, Z = 4 (1)	—	—	—	—	
ZAXDEH	C c, Z = 4 (1)	—	—	—	—	
ZZZKNU01	P 21/c, Z = 6 (1, –1)	0.0336	either	0.0336	either	

(3) Orthorhombic (72 structures, 8 with established missed symmetry)

Refcode	Structural Class	Unconstrained overlay (rms Å, rotation type)		Constrained overlay (rms Å, rotation type)		
AZOVIU	P 21 21 2, Z = 4 (1)	—	—	—	—	
BEWYUY01	P b c n, Z = 8 (1)	—	—	—	—	
BIGRIT	P b c a, Z = 8 (1)	—	—	—	—	
BOLCUA11	P b c a, Z = 8 (1)	—	—	—	—	
BUTMEI	P n m a, Z = 4 (m)	—	—	—	—	
CADCEP	P 21 21 21, Z = 4 (1)	—	—	—	—	
CAFVAG	P c a 21, Z = 4 (1)	—	—	—	—	
CAVREW	P n m a, Z = 4 (m)	—	—	—	—	
CEHMAE	P n a 21, Z = 4 (1)	—	—	—	—	
CEPDAC01	P n m a, Z = 4 (m)	—	—	—	—	
CLMSBC	P n m a, Z = 4 (m)	—	—	—	—	
CMSIGB	P n m a, Z = 4 (m)	—	—	—	—	
COANUL	P c a 21, Z = 4 (1)	—	—	—	—	
CYANAM01	P b c a, Z = 8 (1)					**Not centrosymmetric when H atoms are considered**
DAVFIQ	P n n 2, Z = 2 (2)					**Missed symmetry**: P n n m, Z = 2 (2/m)
DHBACN	P 21 21 21, Z = 4 (1)					**Missed symmetry**: P b c a, Z = 4 (–1)
DOGWOL	P c a 21, Z = 4 (1)	—	—	—	—	
DPHACT09	P b c a, Z = 8 (1)	—	—	—	—	
EABVUY	P c a 21, Z = 4 (1)	—	—	—	—	
EPNPHD10	P c a 21, Z = 4 (1)	—	—	—	—	
FDMUPD10	P 21 21 21, Z = 4 (1)	—	—	—	—	
FEGJOR	P n a 21, Z = 4 (1)	—	—	—	—	
FITXIP	C m c m, Z = 4 (m m 2)	—	—	—	—	
FOHCOU01	P n m a, Z = 4 (m)	—	—	—	—	

FONGUK	P n m a, Z = 4 (m)	—	—	—	—	
FUBYIK01	P n m a, Z = 4 (m)	—	—	—	—	
GEFJIK	P c a 21, Z = 4 (1)	—	—	—	—	
HEXBME11	P n m a, Z = 4 (m)	—	—	—	—	
HEXCET03	P n m a, Z = 4 (m)	—	—	—	—	
HONNIH	P n m a, Z = 4 (m)	—	—	—	—	
IBAYEQ	P 21 21 21, Z = 4 (1)					**Missed symmetry**: P b c a, Z = 4 (–1)
IBAYIU	P 21 21 21, Z = 4 (1)					**Missed symmetry**: P b c a, Z = 4 (–1)
JAJSIW	P c a 21, Z = 4 (1)	—	—	—	—	
JIXWIW	P n m a, Z = 4 (m)	—	—	—	—	
JOCQUN01	P 21 21 21, Z = 4 (1)	—	—	—	—	
KATTOO	P n a 21, Z = 4 (1)	—	—	—	—	
KIJDIQ	P n m a, Z = 4 (m)	—	—	—	—	
KOVSOD01	P n m a, Z = 4 (m)	—	—	—	—	
KULHEE	P c a 21, Z = 4 (1)	—	—	—	—	
LEDFUW	P c a 21, Z = 4 (1)	—	—	—	—	
LEFTEW	P n m a, Z = 4 (m)	—	—	—	—	
LEGFOS	P n m a, Z = 4 (m)	—	—	—	—	
LELSEA	P n a 21, Z = 4 (1)	—	—	—	—	
MOFORM	P 21 21 21, Z = 4 (1)	—	—	—	—	
MSLDNI05	I b a 2, Z = 4 (2)					**Missed symmetry**: I b a m, Z = 4 (2/m)
MUKSOA	P c a 21, Z = 4 (1)	—	—	—	—	
NIFHAM	P 21 21 21, Z = 4 (1)	—	—	—	—	
OXAZOL	I b a 2, Z = 4 (2)					**Missed symmetry**: I b a m, Z = 4 (2/m)
PIBWIN	P c a 21, Z = 4 (1)	—	—	—	—	
PIGNEY	P 21 21 21, Z = 4 (1)	—	—	—	—	
PIRGOM	P n a 21, Z = 4 (1)	—	—	—	—	
PIYKAJ	P b c m, Z = 4 (m)	—	—	—	—	
QEYWIA	P 21 21 21, Z = 4 (1)	—	—	—	—	
RALREC	P 21 21 21, Z = 4 (1)	—	—	—	—	
REMMUS	P b c a, Z = 8 (1)	—	—	—	—	
REPREK	P n a 21, Z = 4 (1)	—	—	—	—	
RERWEQ03	P 21 21 21, Z = 4 (1)					**Missed symmetry**: P b c a, Z = 4 (–1)

RUNLAN	P n a 21, Z = 4 (1)	—	—	—	—	
SAFFUA	P b c a, Z = 8 (1)	—	—	—	—	
SEBJOY	P c a 21, Z = 4 (1)	—	—	—	—	
SENFUM	P n m a, Z = 4 (m)	—	—	—	—	
SIPJAC	P n a 21, Z = 4 (1)	—	—	—	—	
SIWDEH01	P n a 21, Z = 4 (1)	—	—	—	—	
TASPEJ	P n a 21, Z = 4 (1)	—	—	—	—	
TMPPDA	P 21 21 21, Z = 4 (1)	—	—	—	—	
UCEKIW	P 21 21 21, Z = 4 (1)	—	—	—	—	
WEVYAY	P n a 21, Z = 4 (1)					**Missed symmetry**: P b c n, Z = 4 (–1)
WIZFEQ01	P 21 21 21, Z = 8 (1, 1)	0.0083	improper	0.0083	improper	
XIFPAD	P 21 21 21, Z = 4 (1)	—	—	—	—	
YIMXAT	P n a 21, Z = 4 (1)	—	—	—	—	
YOYZIV	P b c a, Z = 8 (1)	—	—	—	—	
ZZZTLC01	P n m a, Z = 4 (m)	—	—	—	—	

(4) Tetragonal (8 structures, 3 with established missed symmetry)

Refcode	Structural Class	Unconstrained overlay (rms Å, rotation type)		Constrained overlay (rms Å, rotation type)		
DAZNAR	P 41 21 2, Z = 8 (1)	—	—	—	—	
IWAGUI	I 41 c d, Z = 8 (2)	—	—	—	—	
KARCOW	P 41, Z = 4 (1)	—	—	—	—	
NIPKEC	I –4, Z = 2 (–4)					**Missed symmetry**: I4/m, Z = 2 (4/m)
NUPREV	I –4, Z = 2 (–4)					**Missed symmetry**: I4/m, Z = 2 (4/m)
OMOSIL	P 4/n n c, Z = 4 (4)	—	—	—	—	
ZAVLIR	I –4, Z = 2 (–4)					**Missed symmetry**: I4/m, Z = 2 (4/m)
ZEWRAU	P 42 b c, Z = 8 (1)	—	—	—	—	

(5) Trigonal (5 structures, 1 with established missed symmetry)

Refcode	Structural Class	Unconstrained overlay (rms Å, rotation type)		Constrained overlay (rms Å, rotation type)		
HALPRN	P –3, Z = 3 (3, –3)	0.0693	either	0.0693	either	
HESKOF	P 3 1 c, Z = 6 (1)	—	—	—	—	

HYQUIN06	R –3, Z = 54 (1, 1, 1)	0.0197	improper	0.0197	improper	
		0.0135	proper	0.0135	proper	
		0.0212	improper	0.0212	improper	
XEWDUY	P –3, Z = 3 (3, –3)	0.0675	either	0.0675	either	
XUQMOL	R 3, Z = 3 (3)					**Missed symmetry**: R –3, Z = 3 (–3)

(6) Cubic (1 structure with established missed symmetry)

FOGRUO	I 2 3, Z = 2 (2 3)					**Missed symmetry**: I m –3, Z = 2 (m –3)