STRUCTURAL CHEMISTRY

Volume 78 (2022)

Supporting information for article:

3,4-Bis-*O*-propargyl-1,2:5,6-di-*O*-isopropylidene-d-mannitol: a study of multiple weak hydrogen bonds in the solid state

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S1. Experimental

S1.1. Synthesis

The synthesis of 3,4-bis-*O*-propargyl-1,2:5,6-di-*O*-isopropylidene-D-mannitol **1** (IUPAC systematic name: (1*R*,2*R*)-1,2-bis((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)-1,2-bis(prop-2-yn-1-yloxy)ethane has been reported (Mohammed, 2012) and the X-ray diffraction sample crystallized from EtOAc/*n*-hexane as colourless prisms, m.p. 50-52 °C.

S1.2. Refinement

A colourless block like crystal of **1** with dimensions of 0.19 X 0.21 X 0.24 mm^3, selected under the polarizing microscope (Leica M165Z), was picked up on a MicroMount (MiTeGen, USA) consisting of a thin polymer tip with a wicking aperture. The X-ray diffraction measurements were carried out on a Bruker kappa-II CCD diffractometer at 150 K using IμS Incoatec Microfocus Source with Mo-Kα radiation (λ = 0.710723 Å). The single crystal, mounted on the goniometer using a cryo loop for intensity measurements, was coated with immersion oil type NVH and then quickly transferred to the cold nitrogen stream generated by an Oxford Cryostream 700 series. Symmetry related absorption corrections using the program SADABS (Bruker, 2016) were applied and the data were corrected for Lorentz and polarisation effects using Bruker APEX3 software (Bruker, 2016). The structure was solved by program SHELXT (Sheldrick, 2015*a*) (with intrinsic phasing) and the full-matrix least-square refinements were carried out using SHELXL (Sheldrick, 2015*b*) through the OLEX2 (Dolomanov, 2009) suite of software. Details of the experimental crystallographic data collected for compound **1** are summarized in Table 1. The non-hydrogen atoms were refined anisotropically but the hydrogen atoms were not located in the difference Fourier map. Instead, hydrogen atoms were geometrically placed and constrained according to their environment using different AFIX commands available in SHELXL (Sheldrick, 2015*b*) operating via the OLEX2 (Dolomanov, 2009) platform. The CCDC submission number is 2055328.

The geometric characteristics of hydrogen bonds are summarized in Table S1.

Table S1 Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C7A—H7AA···O1B^{i}	0.99	2.55	3.393 (3)	142.5
C9A—H9A···O6C^{ii}	0.95	2.58	3.375 (3)	140.8

C13A—H13A···O6A^{iii}	0.95	2.34	3.246 (3)	158.2
C18A—H18B···O5C^{iv}	0.98	2.62	3.581 (3)	168.1
C5B—H5BA···O3A^{v}	0.98	2.59	3.525 (3)	160.0
C9B—H9B···O3C	0.95	2.19	3.121 (3)	167.1
C13B—H13B···O6B^{iii}	0.95	2.21	3.138 (3)	164.7
C16B—H16B···O1C	1.00	2.69	3.584 (2)	149.1
C4C—H4CB···O2A^{vi}	0.98	2.57	3.536 (3)	169.1
C6C—H6C···O5A^{vi}	1.00	2.67	3.458 (2)	135.7
C9C—H9C···O2A^{vii}	0.95	2.71	3.542 (3)	146.6
C11C—H11E···O2B^{viii}	0.99	2.38	3.372 (3)	176.9
C13C—H13C···O6C^{ix}	0.95	2.34	3.278 (3)	167.8

Symmetry codes: (i) *x*−1, *y*−1, *z*; (ii) *x*, *y*−1, *z*−1; (iii) *x*+1, *y*, *z*; (iv) *x*, *y*, *z*−1; (v) *x*+1, *y*+1, *z*; (vi) *x*, *y*, *z*+1; (vii) *x*, *y*+1, *z*+1; (viii) *x*−1, *y*, *z*; (ix) *x*, *y*−1, *z*.

S1.3. Analyses of the Cambridge Structural Database (CSD)

S1.3.1. Searches of the CSD based on MERCURY Crystal Packing Features (PFF)

A total of thirty-three individual searches of the Cambridge Structural Database (CSD) for Crystal Packing Features (referred to here as PFFs) illustrated in Figure S1 were carried out on eleven unique sets of Donor ***D*** (A1, A2, B, C, D) and Acceptor ***A*** (E, F, G, H, I, J) propargylic contacts that were recognised within the crystal structure of compound **1** (Fig. S2). Search criteria specified consideration of Cyclicity and were given a Low setting tolerance Level of Geometric Similarity. Where bifurcation was evident, individual PFF searches were performed for each partner pair and then for the two interactions together. The output of each search was recorded with a Positive result (a numerical and itemized list of known structures, with structure codes, that fell within the Low Level of Geometric Similarity), and a Negative result (included a corresponding numerical and itemized list of known structures containing the components of the search query, but where the geometric tolerances were not met). The reference codes of structures regarded as Positive and

Negative hits under each PFF search result, and their total numbers and percentages, were compiled into Microsoft Excel spreadsheets. A spreadsheet of the results with matching Positive and Negative structure codes aligned (with the exception of search B1.2) was constructed (Table S2), and the numerical data summarized in graphical form (Fig. 9, see Section 3.4.2).

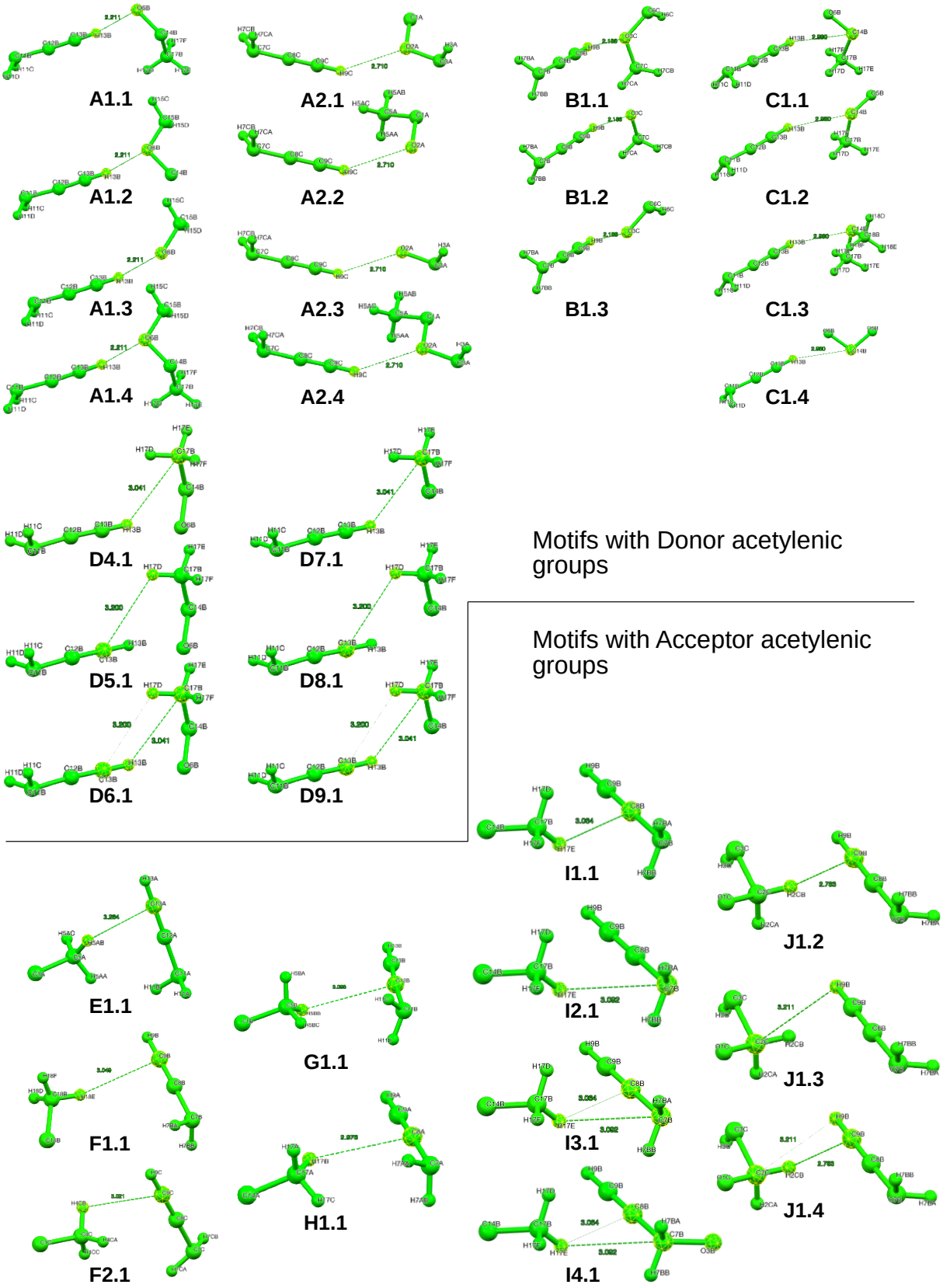
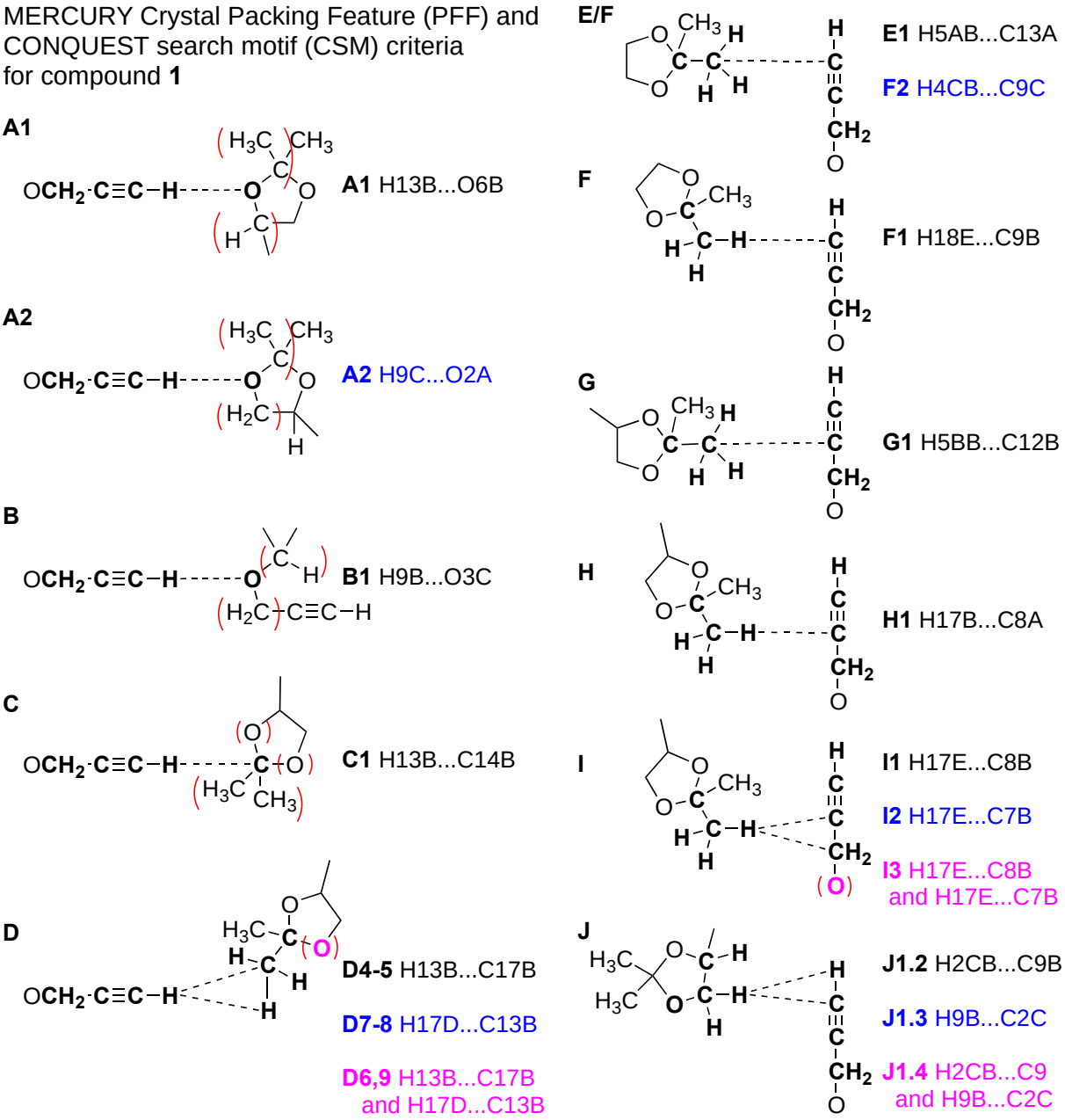


Figure S1 MERCURY Crystal Packing Features (PFF) used for searches of the CSD.

MERCURY Crystal Packing Feature (PFF) and CONQUEST search motif (CSM) criteria for compound **1**



NOTES: (1) ***D***...***A*** elements are as indicated after the search code; (2) **Fixed** search elements are indicated in bold; (3) Individually **varied** search elements are marked in parentheses.

Figure S2 Structural features of **1** used to define PFF and CSM contact search motifs.

Table S2 Structure codes of positive and negative hits derived from MERCURY PFF searches (Table contains two parts).

Search	A1.1	A1.2	A1.3	A1.4	A2.1	A2.2	A2.3	A2.4	B1.1	B1.2	B1.3	C1.1	C1.2	C1.3	C1.4	D4	D5	D6	D7	D8	D9	E1	F1	F2	G1	H1	I1	I2	I3	I4	J1.2	J1.3	J1.4
Positive hits	1	1	1	0	5	7	4	2	2	6	5	9	4	5	6	8	8	8	10	10	10	0	4	3	1	3	2	2	2	0	0	0	0
Negative hits	-9	-9	-34	-5	-20	-21	-61	-10	-5	-330	-17	-19	-24	-29	-15	-20	-20	-20	-66	-66	-66	-71	-72	-73	-75	-73	-74	-74	-74	-27	-11	-11	-11
Total hits	10	10	35	5	25	28	65	12	7	336	22	28	28	34	21	28	28	28	76	76	76	71	76	76	76	76	76	76	76	27	11	11	11
%Positive	10	10	2.9	0	20	25	6.2	16.7	28.6	1.8	22.7	32.1	14.3	14.7	28.6	28.6	28.6	28.6	13.2	13.2	13.2	0	5.3	3.9	1.3	3.9	2.6	2.6	2.6	0	0	0	0
%Negative	90	90	97.1	100	80	75	93.8	83.3	71.4	98.2	77.3	67.9	85.7	85.3	71.4	71.4	71.4	71.4	86.8	86.8	86.8	100	94.7	96.1	98.7	96.1	97.4	97.4	97.4	100	100	100	100
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	JEWQIM	JEWQIM	JEWQIM												JEWQIM																		
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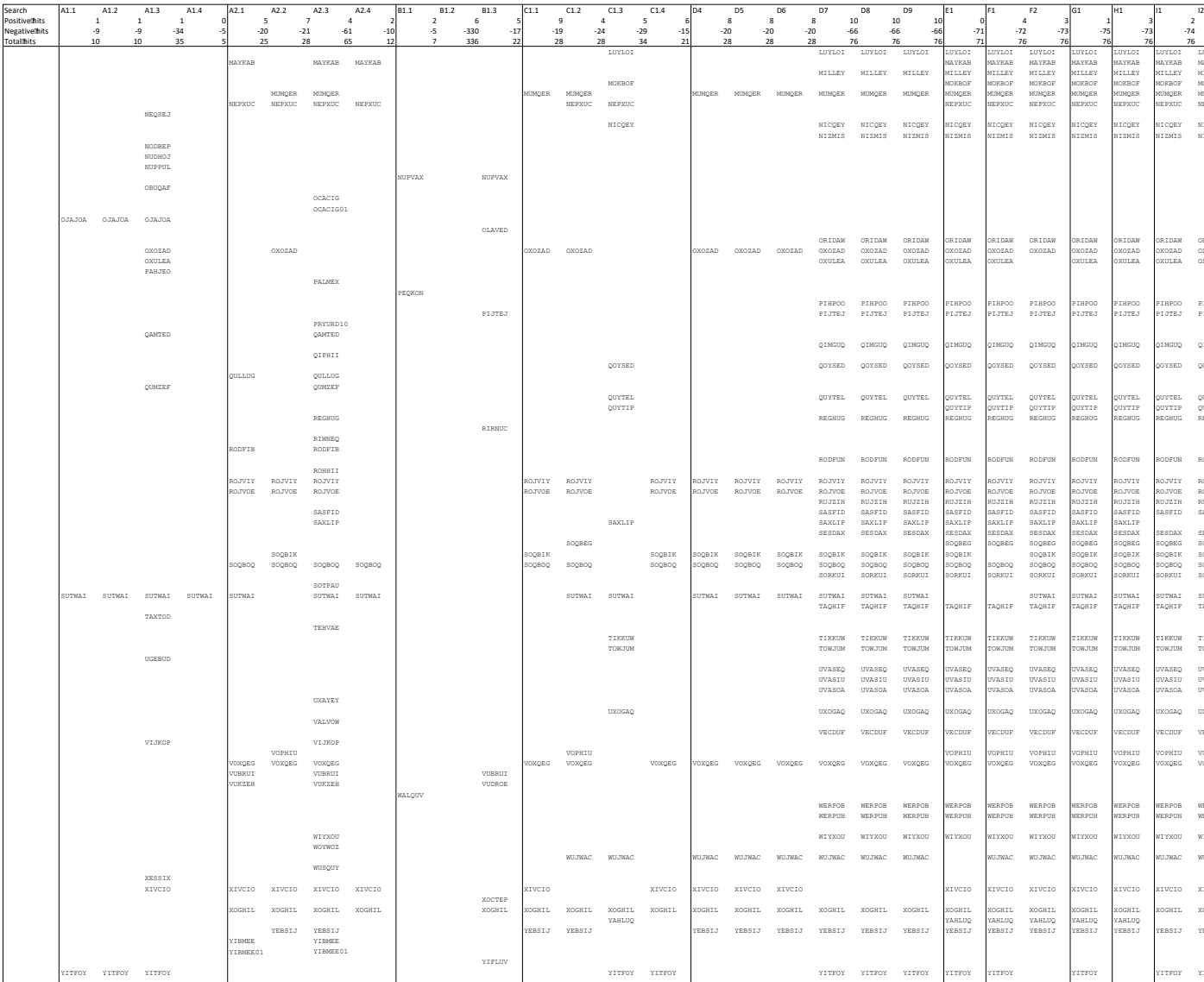


S1.3.2. Searches based on liberally defined structural motifs using the CONQUEST search tool

Loosely constrained structural motifs derived from those shown in Figure S2 were established in the CONQUEST^{TM} search tool for propargylic Donor interactions: CSM_A1, CSM_A2, CSM1_R1, CSM1-R2, CSM1_R3, CSM1_R4, and Acceptor interactions: CSM1_R5 and CSM1_R6 (Fig. S3). Relevant distance parameters, D1 (**H**…***A***, Å) and D2 (***D***…***A***, Å), were liberally defined as within the sum of van der Waals radii + 1.0 Å, and the angular measurements, ANG (*D*–H…*A*, deg), limited to within 60—180 degrees. Where multiple contacts were recorded for a single compound, sometimes within the same category,

these were included for completeness. The values for D1, D2, and ANG for all matching contacts found in the CSD were recorded and the results displayed as scatter plots against Identity Number in Figure S3 and discussed more fully in Section 3.4.3.

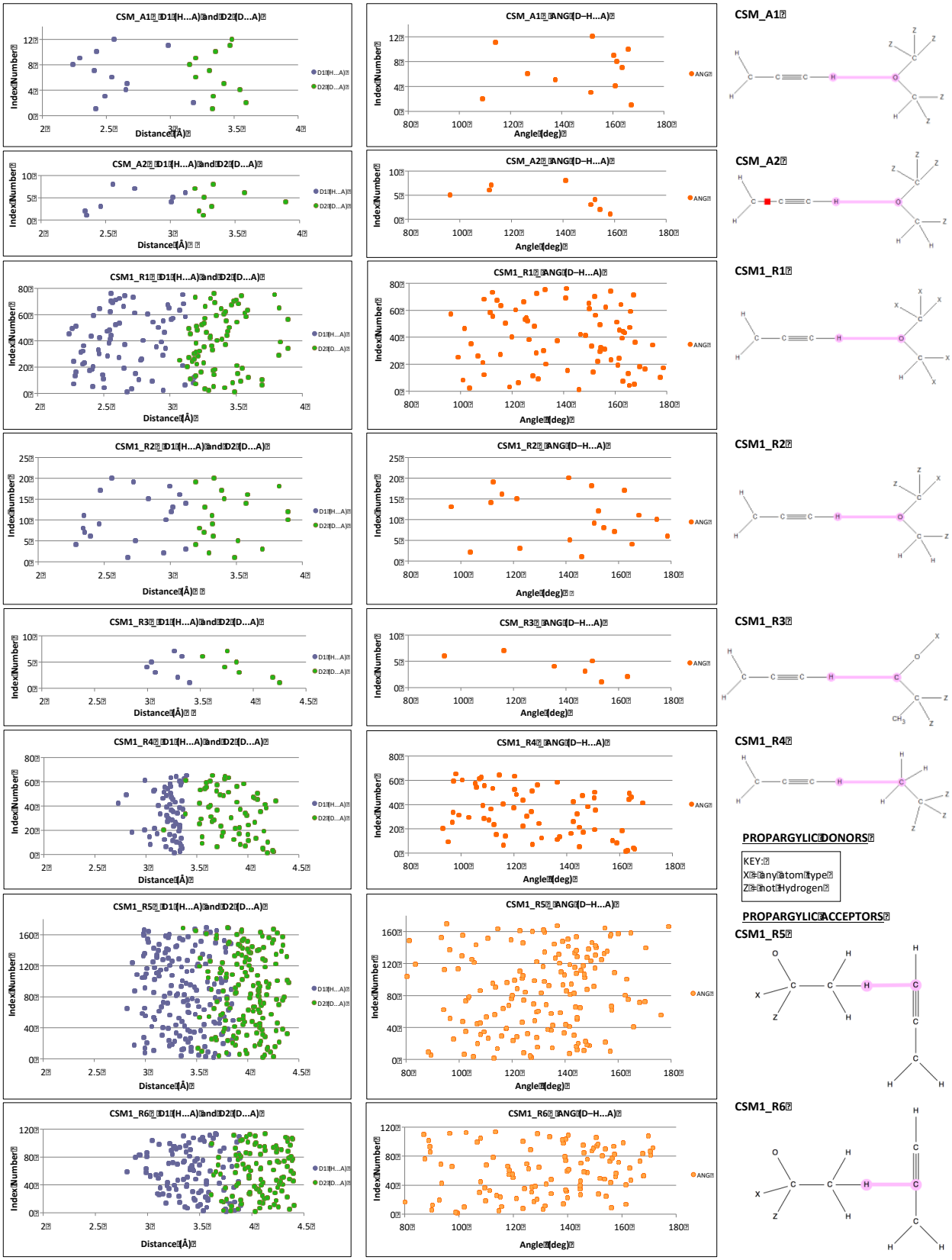
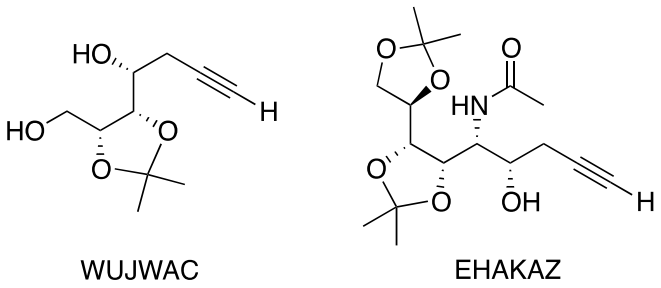


Figure S3 CONQUEST search motifs (right) and CSD search results showing scatter plots of Index Number versus D1 (blue) and D2 (green) (Å) (left) and ANG (orange) (deg) (middle) values.



WUJWAC EHAKAZ

Figure S4 Molecular structures of compounds with outlier contacts in Figure 10(*c*).

S2. References

Bruker (2016). APEX3, SAINT and SADABS. Bruker AXS Inc., Madison, WI, USA.

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