Figure S1. Vibrational frequencies for model compounds **4**, **5**, and **6** (a, b, and c respectively). QM frequencies are represented as crosses and MM frequencies as x's.

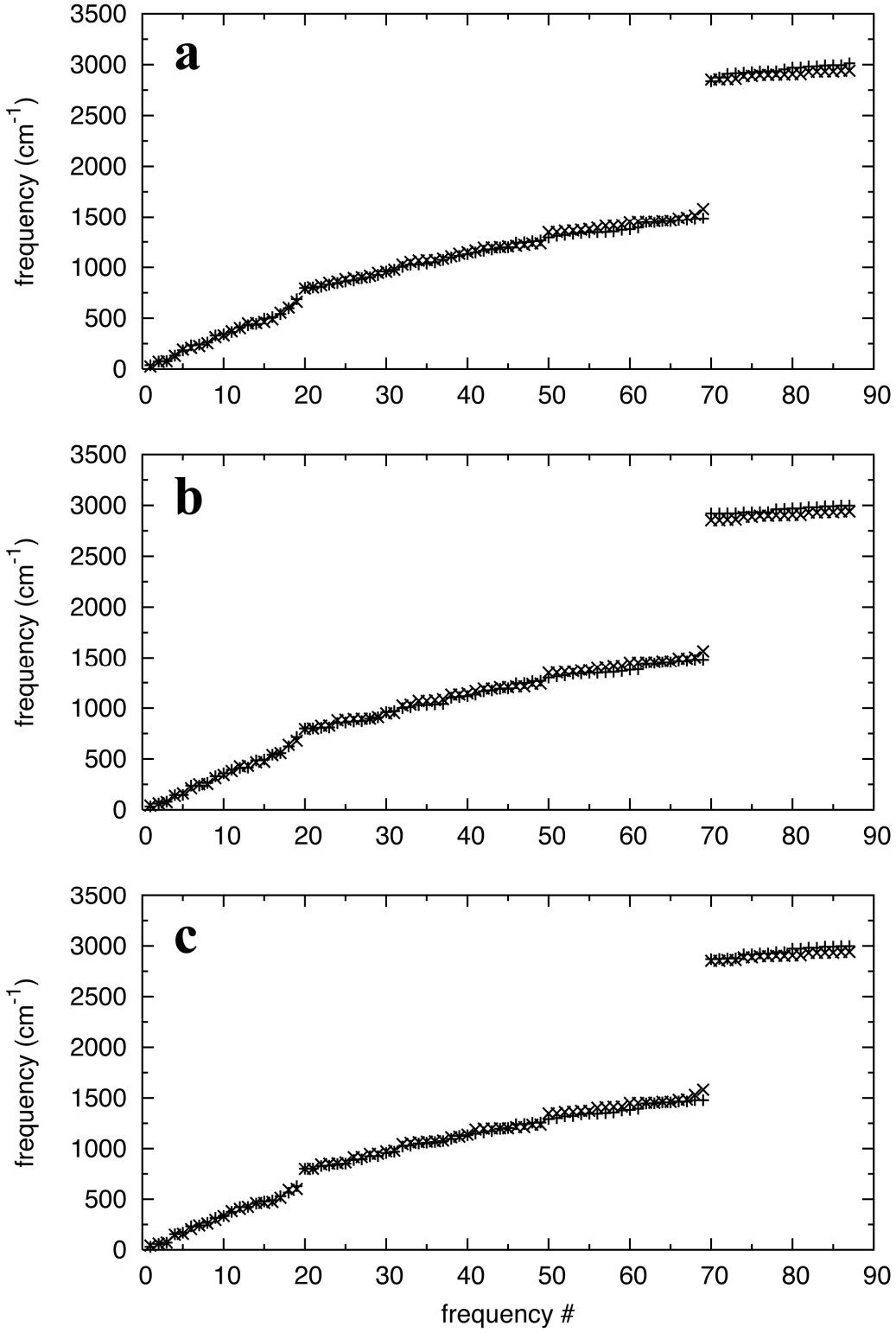


Figure S2. Vibrational frequencies for model compounds **7** and **8** (a and b, respectively). QM frequencies are represented as crosses and MM frequencies as x's.

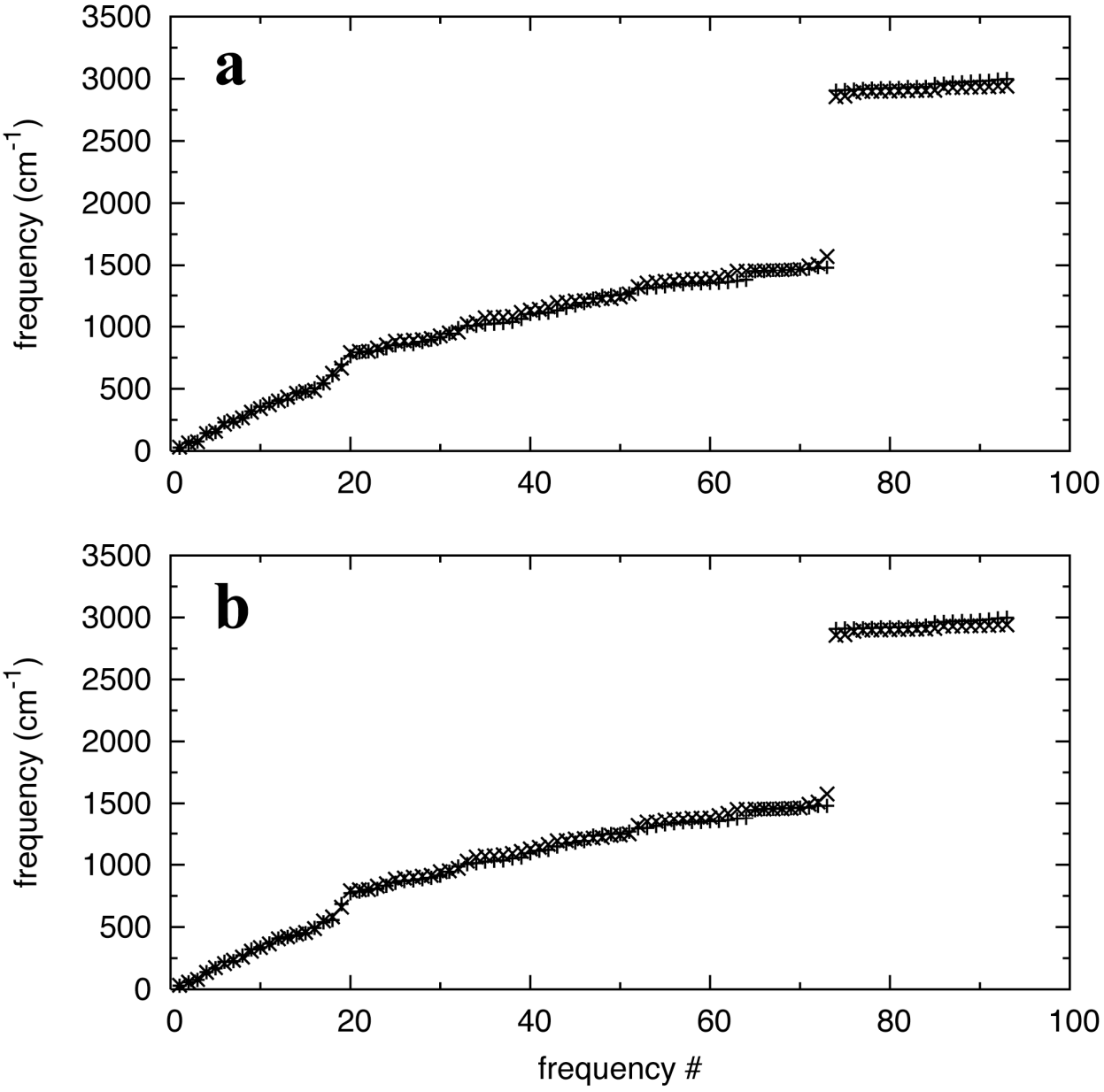
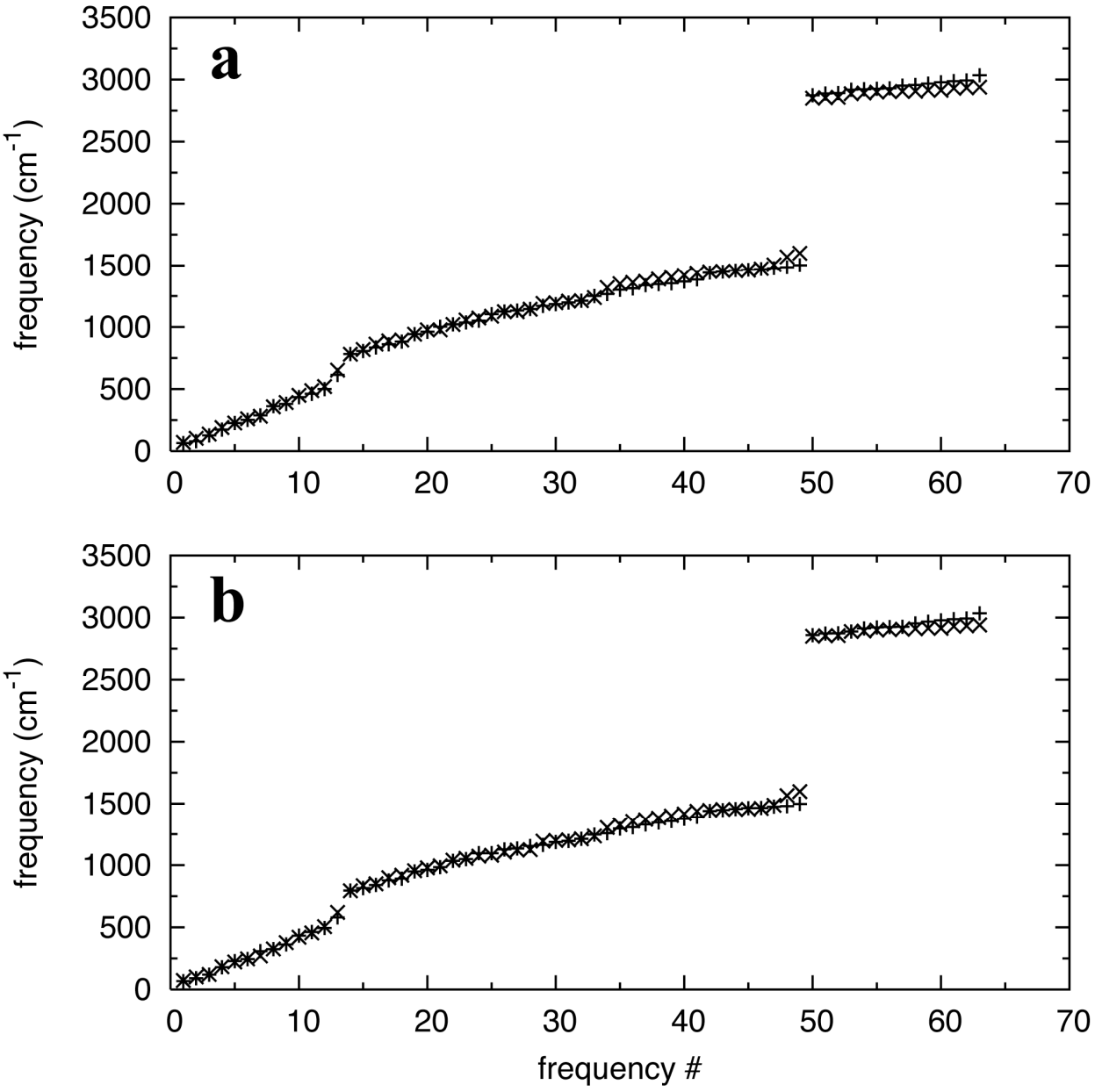


Figure S3. Vibrational frequencies for model compounds **11** and **12** (a and b, respectively). QM frequencies are represented as crosses and MM frequencies as x's.



S4-S8. CHARMM-compatible patches for 1→1, 1→2, 1→3, 1→4, and 1→6 linkages between hexopyranoses. Patches are compatible with the CHARMM hexopyranose monosaccharide force field described in: Guvench, O.; Greene, S. N.; Kamath, G.; Brady, J. W.; Venable, R. M.; Pastor, R. W.; Mackerell, A. D. *J. Comput. Chem.* **2008**, *29*, 2543-2564. Complete CHARMM carbohydrate force field files, which also include hexopyranose monosaccharides, acyclic polyalcohols, acyclic carbohydrates, and inositol, can be downloaded from http://mackerell.umaryland.edu.

S4. 1→1

```
PRES 11            0.22
dele atom 1HO1
dele atom 2HO1
dele atom 2O1
ATOM 1C1  CC3162   0.29
ATOM 1O1  OC302   -0.36
ATOM 2C1  CC3162   0.29
BOND 1O1  2C1
```

S5. 1→2

```
PRES 12             0.02
dele atom 1HO2
dele atom 2HO1
dele atom 2O1
ATOM 1C2  CC3161    0.09
ATOM 1O2  OC301    -0.36
ATOM 2C1  CC3162    0.29
BOND 1O2  2C1
```

S6. 1→3

```
PRES 13             0.02
dele atom 1HO3
dele atom 2HO1
dele atom 2O1
ATOM 1C3  CC3161    0.09
ATOM 1O3  OC301    -0.36
ATOM 2C1  CC3162    0.29
BOND 1O3  2C
```

S7. 1→4

```
PRES 14             0.02
```

```
dele atom 1HO4
dele atom 2HO1
dele atom 2O1
ATOM 1C4  CC3161    0.09
ATOM 1O4  OC301    -0.36
ATOM 2C1  CC3162    0.29
BOND 1O4  2C1
```

S8. 1→6

```
PRES 16            -0.07
dele atom 1HO6
dele atom 2HO1
dele atom 2O1
ATOM 1C6   CC321    0.00
ATOM 1O6   OC301   -0.36
ATOM 2C1   CC3162   0.29
BOND 1O6 2C1
```

S9. CHARMM-compatible parameters for 1→1, 1→2, 1→3, 1→4, and 1→6 linkages between hexopyranoses. Parameters are compatible with the CHARMM hexopyranose monosaccharide force field described in: Guvench, O.; Greene, S. N.; Kamath, G.; Brady, J. W.; Venable, R. M.; Pastor, R. W.; Mackerell, A. D. *J. Comput. Chem.* **2008**, *29*, 2543-2564. Complete CHARMM carbohydrate force field files, which also include hexopyranose monosaccharides, acyclic polyalcohols, acyclic carbohydrates, and inositol, can be downloaded from http://mackerell.umaryland.edu.

```
BONDS
! atom types     Kb      b0
CC3162  OC301    360.00  1.395
CC3162  OC302    360.00  1.415
CC3161  OC301    360.00  1.415
CC321   OC301    360.00  1.415

ANGLES
! atom types             Ktheta  theta0
OC301   CC3162  CC3161   45.00   105.00
OC302   CC3162  CC3161   45.00   105.00
OC301   CC3161  CC3162   45.00   109.00
OC311   CC301   OC301    45.00   116.50
OC301   CC3162  OC3C61   90.00   112.00
OC302   CC3162  OC3C61   90.00   112.00
CC3162  OC301   CC331    95.00   109.70
CC3162  OC301   CC321    95.00   109.70
CC3162  OC302   CC3162   50.00   111.50
CC3161  OC301   CC3162   50.00   109.20
HCA1    CC3162  OC301    60.00   109.50
HCA1    CC3162  OC302    60.00   109.50
```

```
DIHEDRALS
! atom types                      Kchi  n  delta
CC3161  CC3161  CC3162  OC301    0.20  3    0.0
CC3161  CC3161  CC3162  OC302    0.20  3    0.0
CC3162  CC3161  CC3161  OC301    0.20  3    0.0
CC3161  CC3162  OC301   CC331    0.22  1    0.0
CC3161  CC3162  OC301   CC331    0.28  2  180.0
CC3161  CC3162  OC301   CC331    0.89  3    0.0
CC3161  CC3162  OC301   CC321    0.22  1    0.0
CC3161  CC3162  OC301   CC321    0.28  2  180.0
CC3161  CC3162  OC301   CC321    0.89  3    0.0
CC3161  CC3162  OC302   CC3162   0.73  1    0.0
CC3161  CC3162  OC302   CC3162   0.61  2  180.0
CC3161  CC3162  OC302   CC3162   0.00  3  180.0
CC3161  CC3162  OC301   CC3161   0.41  1  180.0
CC3161  CC3162  OC301   CC3161   0.66  2  180.0
CC3161  CC3162  OC301   CC3161   1.60  3    0.0
CC3162  CC3161  OC301   CC3162   0.13  1  180.0
CC3162  CC3161  OC301   CC3162   0.25  2  180.0
CC3162  CC3161  OC301   CC3162   0.06  3  180.0
CC3161  CC3161  OC301   CC3162   0.13  1  180.0
CC3161  CC3161  OC301   CC3162   0.25  2  180.0
CC3161  CC3161  OC301   CC3162   0.06  3  180.0
CC3163  CC3161  OC301   CC3162   0.13  1  180.0
CC3163  CC3161  OC301   CC3162   0.25  2  180.0
CC3163  CC3161  OC301   CC3162   0.06  3  180.0
CC3163  CC321   OC301   CC3162   0.64  1  180.0
CC3163  CC321   OC301   CC3162   0.03  2  180.0
CC3163  CC321   OC301   CC3162   0.61  3    0.0
OC301   CC3162  CC3161  OC311    2.65  1  180.0
OC301   CC3162  CC3161  OC311    0.00  2    0.0
OC301   CC3162  CC3161  OC311    0.13  3  180.0
OC302   CC3162  CC3161  OC311    2.65  1  180.0
OC302   CC3162  CC3161  OC311    0.00  2    0.0
OC302   CC3162  CC3161  OC311    0.13  3  180.0
OC301   CC3161  CC3162  OC311    2.65  1  180.0
OC301   CC3161  CC3162  OC311    0.00  2    0.0
OC301   CC3161  CC3162  OC311    0.13  3  180.0
OC301   CC3161  CC3162  OC301    0.59  1  180.0
OC301   CC3161  CC3162  OC301    1.16  2    0.0
OC301   CC3161  CC3162  OC3C61   2.75  1  180.0
OC301   CC3161  CC3162  OC3C61   0.26  2  180.0
OC301   CC3161  CC3162  OC3C61   0.10  3    0.0
HCA1    CC3161  CC3162  OC301    0.20  3    0.0
HCA1    CC3161  CC3162  OC302    0.20  3    0.0
OC301   CC3161  CC3162  HCA1     0.20  3    0.0
CC331   OC301   CC3162  HCA1     0.284 3    0.0
CC321   OC301   CC3162  HCA1     0.284 3    0.0
CC3161  OC301   CC3162  HCA1     0.284 3    0.0
CC3162  OC302   CC3162  HCA1     0.284 3    0.0
CC3162  OC301   CC3161  HCA1     0.284 3    0.0
CC3162  OC301   CC331   HCA3     0.284 3    0.0
CC3162  OC301   CC321   HCA2     0.284 3    0.0
CC3163  OC3C61  CC3162  OC301    0.41  1  180.0
```

```
CC3163  OC3C61  CC3162  OC301    0.89  2    0.0
CC3163  OC3C61  CC3162  OC301    0.05  3    0.0
CC3163  OC3C61  CC3162  OC302    0.41  1  180.0
CC3163  OC3C61  CC3162  OC302    0.89  2    0.0
CC3163  OC3C61  CC3162  OC302    0.05  3    0.0
CC331   OC301   CC3162  OC3C61   0.14  1    0.0
CC331   OC301   CC3162  OC3C61   0.97  2    0.0
CC331   OC301   CC3162  OC3C61   0.11  3  180.0
CC321   OC301   CC3162  OC3C61   0.14  1    0.0
CC321   OC301   CC3162  OC3C61   0.97  2    0.0
CC321   OC301   CC3162  OC3C61   0.11  3  180.0
CC3162  OC302   CC3162  OC3C61   0.53  1    0.0
CC3162  OC302   CC3162  OC3C61   0.74  2    0.0
CC3162  OC302   CC3162  OC3C61   0.16  3    0.0
CC3161  OC301   CC3162  OC3C61   0.05  1  180.0
CC3161  OC301   CC3162  OC3C61   0.91  2    0.0
CC3161  OC301   CC3162  OC3C61   1.27  3  180.0

NONBONDED
! atom type    epsilon   Rmin/2.0
OC301     0.0  -0.1000   1.6500
OC302     0.0  -0.1000   1.6500
```