Density functional theory study of crown ether–magnesium complexes: from a solvated ion to an ion trap

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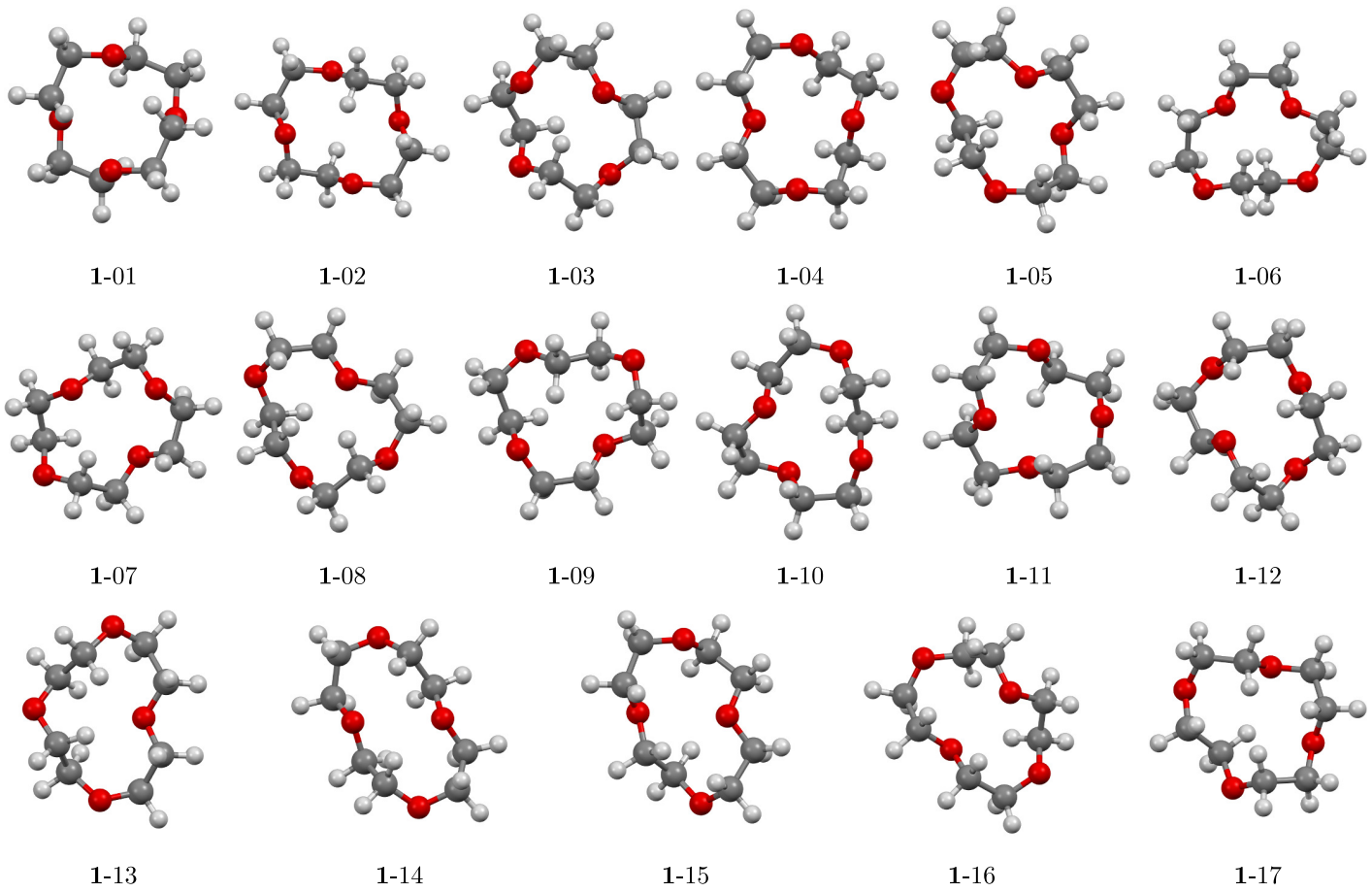


Figure S1: Crown **1** conformers optimized at M06-2X/6-31+G(d,p) level.

Table S1: Relative energy E (in kcal/mol) of crown **1** conformers computed at the M06-2X/6-31+G(d,p) level.

Conformer	E	Conformer	E	Conformer	E	Conformer	E	Conformer	E	Conformer	E
1-01	0.0	**1**-02	2.3	**1**-03	2.5	**1**-04	2.8	**1**-05	2.8	**1**-06	3.1
1-07	3.2	**1**-08	3.5	**1**-09	3.6	**1**-10	3.9	**1**-11	4.0	**1**-12	4.1
1-13	4.3	**1**-14	4.6	**1**-15	5.4	**1**-16	5.6	**1**-17	5.7		

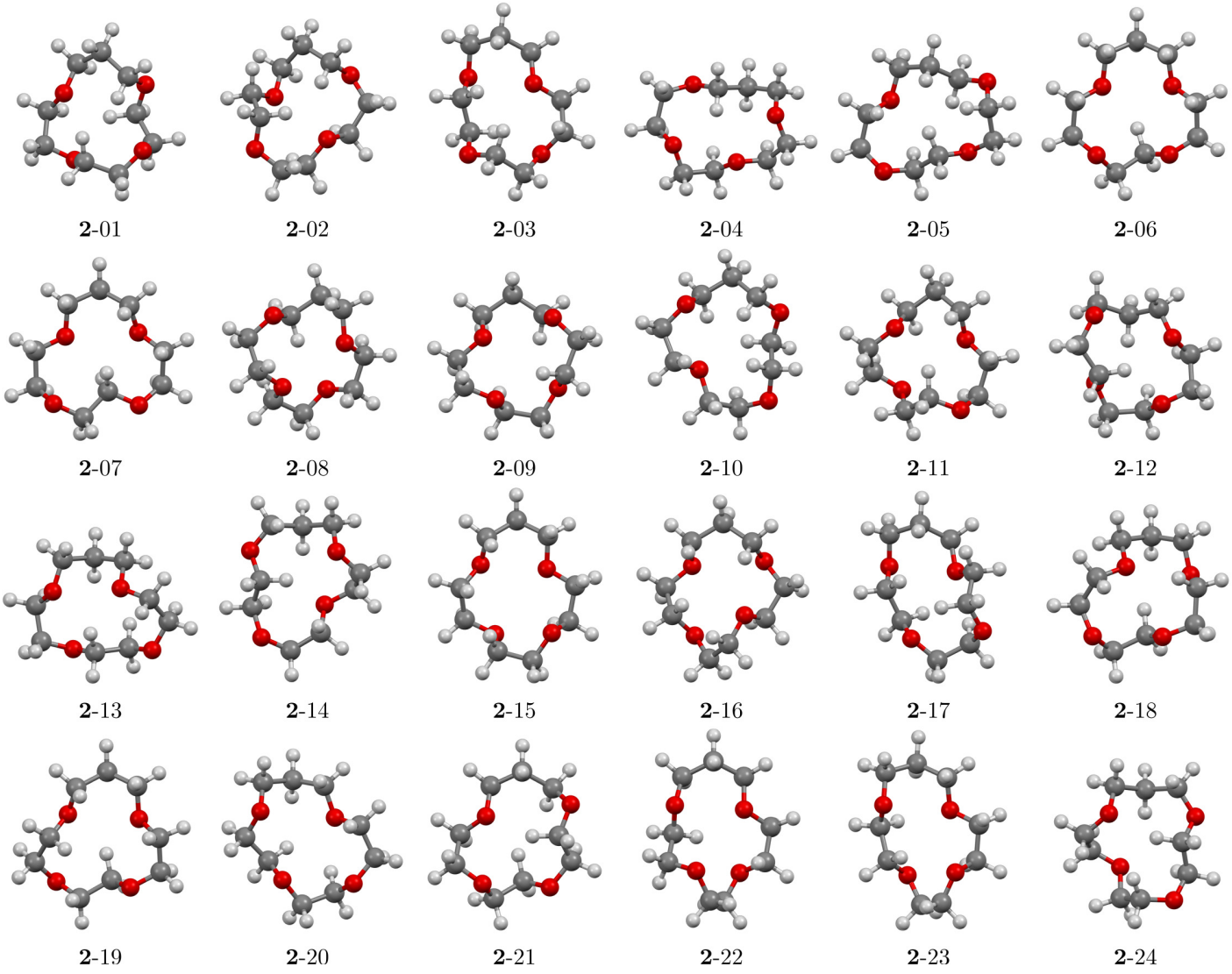


Figure S2: Crown **2** conformers optimized at M06-2X/6-31+G(d,p) level.

Table S2: Relative energy *E* (in kcal/mol) of crown **2** conformers computed at the M06-2X/6-31+G(d,p) level.

Conformer	*E*	Conformer	*E*	Conformer	*E*	Conformer	*E*	Conformer	*E*	Conformer	*E*
2-01	0.0	**2**-02	1.1	**2**-03	1.9	**2**-04	2.1	**2**-05	2.3	**2**-06	2.3
2-07	2.6	**2**-08	2.8	**2**-09	2.9	**2**-10	3.2	**2**-11	3.3	**2**-12	3.6
2-13	3.8	**2**-14	4.1	**2**-15	4.2	**2**-16	4.3	**2**-17	4.7	**2**-18	4.7
2-19	4.7	**2**-20	4.9	**2**-21	5.4	**2**-22	5.6	**2**-23	5.7	**2**-24	7.0

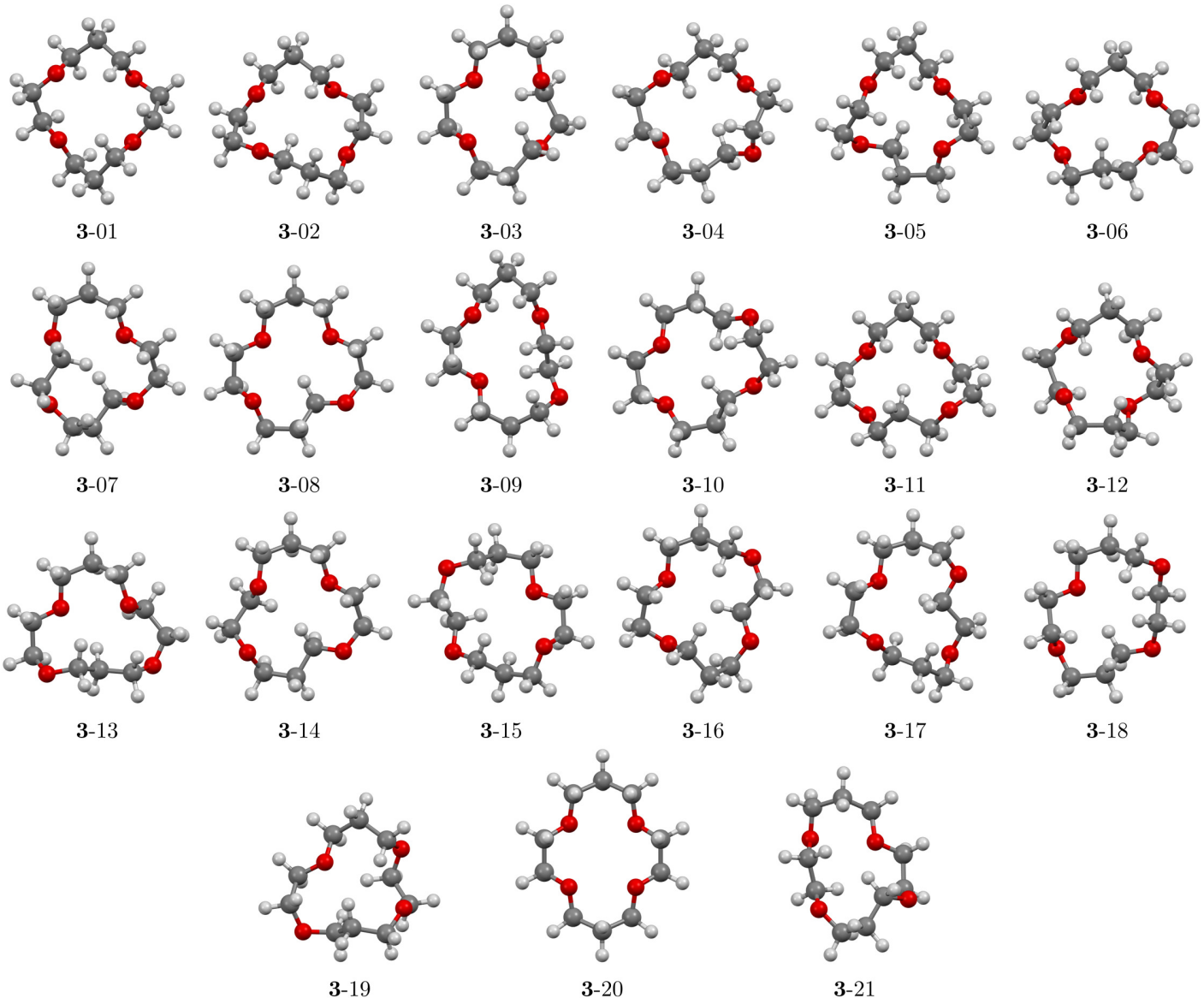


Figure S3: Crown **3** conformers optimized at M06-2X/6-31+G(d,p) level.

Table S3: Relative energy E (in kcal/mol) of crown **3** conformers computed at the M06-2X/6-31+G(d,p) level.

Conformer	E	Conformer	E	Conformer	E	Conformer	E	Conformer	E	Conformer	E
3-01	0.0	**3**-02	0.8	**3**-03	0.9	**3**-04	1.5	**3**-05	2.0	**3**-06	2.8
3-07	3.0	**3**-08	3.2	**3**-09	3.6	**3**-10	3.7	**3**-11	4.0	**3**-12	4.0
3-13	4.4	**3**-14	4.5	**3**-15	4.6	**3**-16	4.8	**3**-17	5.1	**3**-18	5.2
3-19	5.5	**3**-20	6.4	**3**-21	6.5						

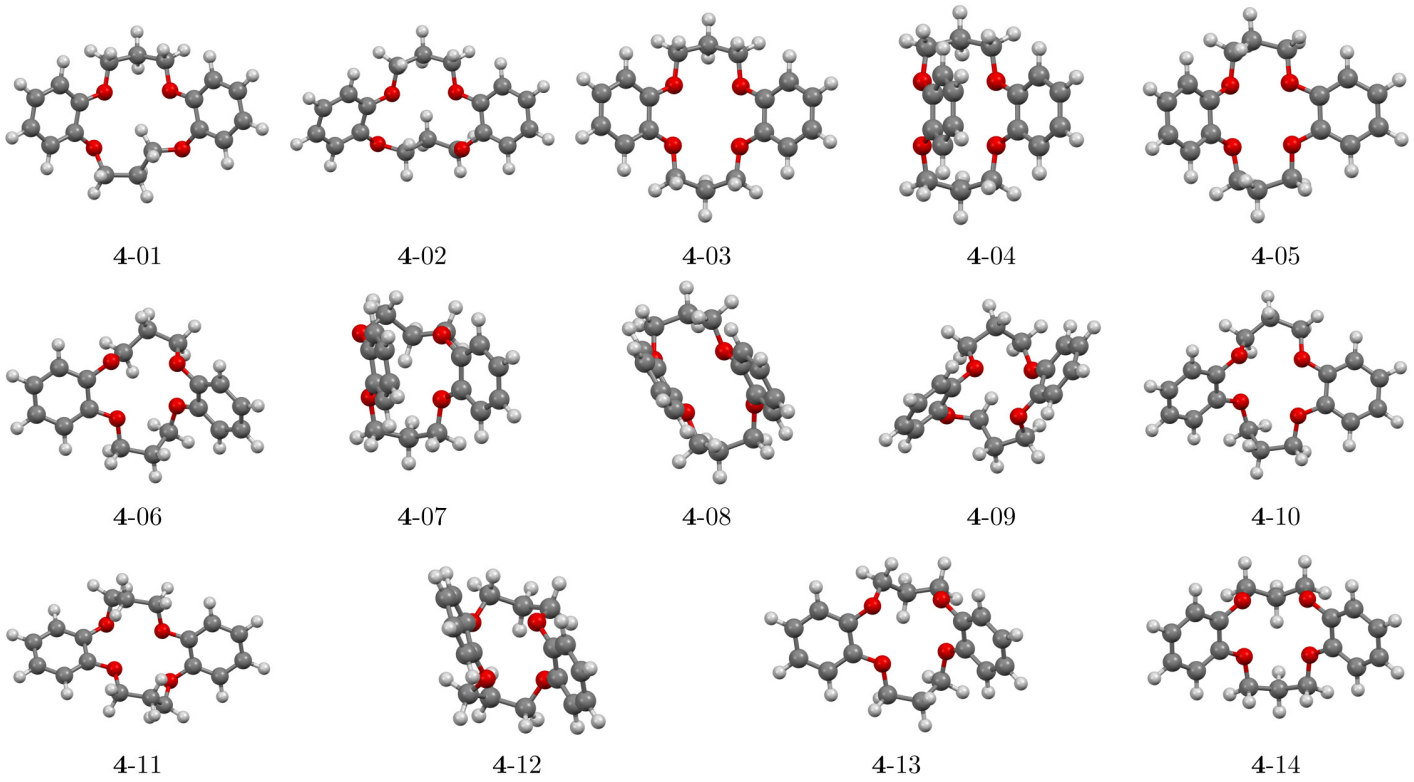


Figure S4: Crown **4** conformers optimized at M06-2X/6-31+G(d,p) level.

Table S4: Relative energy E (in kcal/mol) of crown **4** conformers computed at the M06-2X/6-31+G(d,p) level.

Conformer	E	Conformer	E	Conformer	E	Conformer	E	Conformer	E	Conformer	E
4-01	0.0	**4**-02	0.7	**4**-03	0.7	**4**-04	1.0	**4**-05	1.4	**4**-06	2.5
4-07	2.8	**4**-08	3.4	**4**-09	3.5	**4**-10	4.4	**4**-11	4.5	**4**-12	4.7
4-13	4.9	**4**-14	5.2								

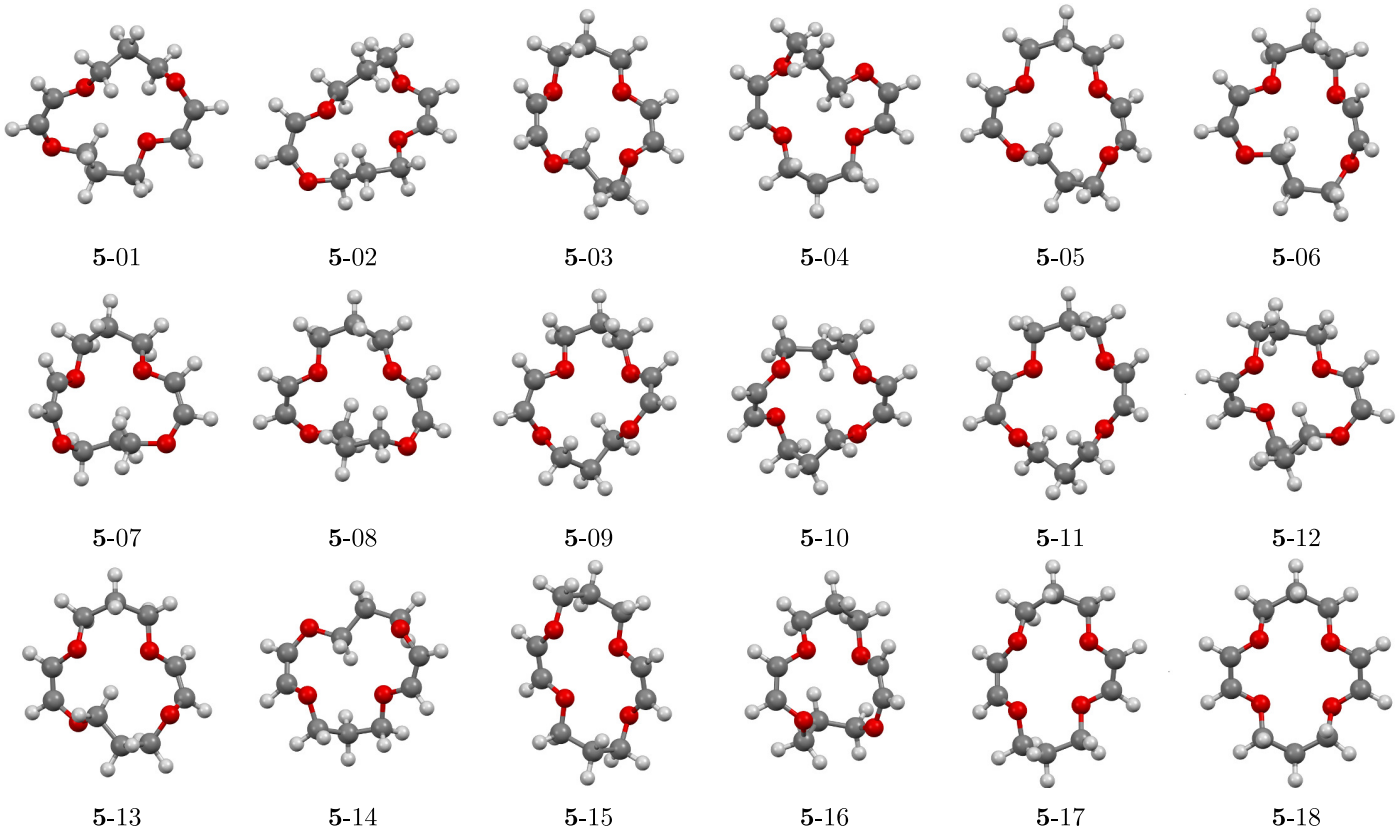


Figure S5: Crown **5** conformers optimized at M06-2X/6-31+G(d,p) level.

Table S5: Relative energy E (in kcal/mol) of crown **5** conformers computed at the M06-2X/6-31+G(d,p) level.

Conformer	E	Conformer	E	Conformer	E	Conformer	E	Conformer	E	Conformer	E
5-01	0.0	**5**-02	1.0	**5**-03	1.3	**5**-04	1.9	**5**-05	2.2	**5**-06	2.3
5-07	2.3	**5**-08	2.4	**5**-09	2.4	**5**-10	2.4	**5**-11	2.7	**5**-12	2.8
5-13	3.0	**5**-14	3.3	**5**-15	4.1	**5**-16	5.1	**5**-17	6.8	**5**-18	8.3

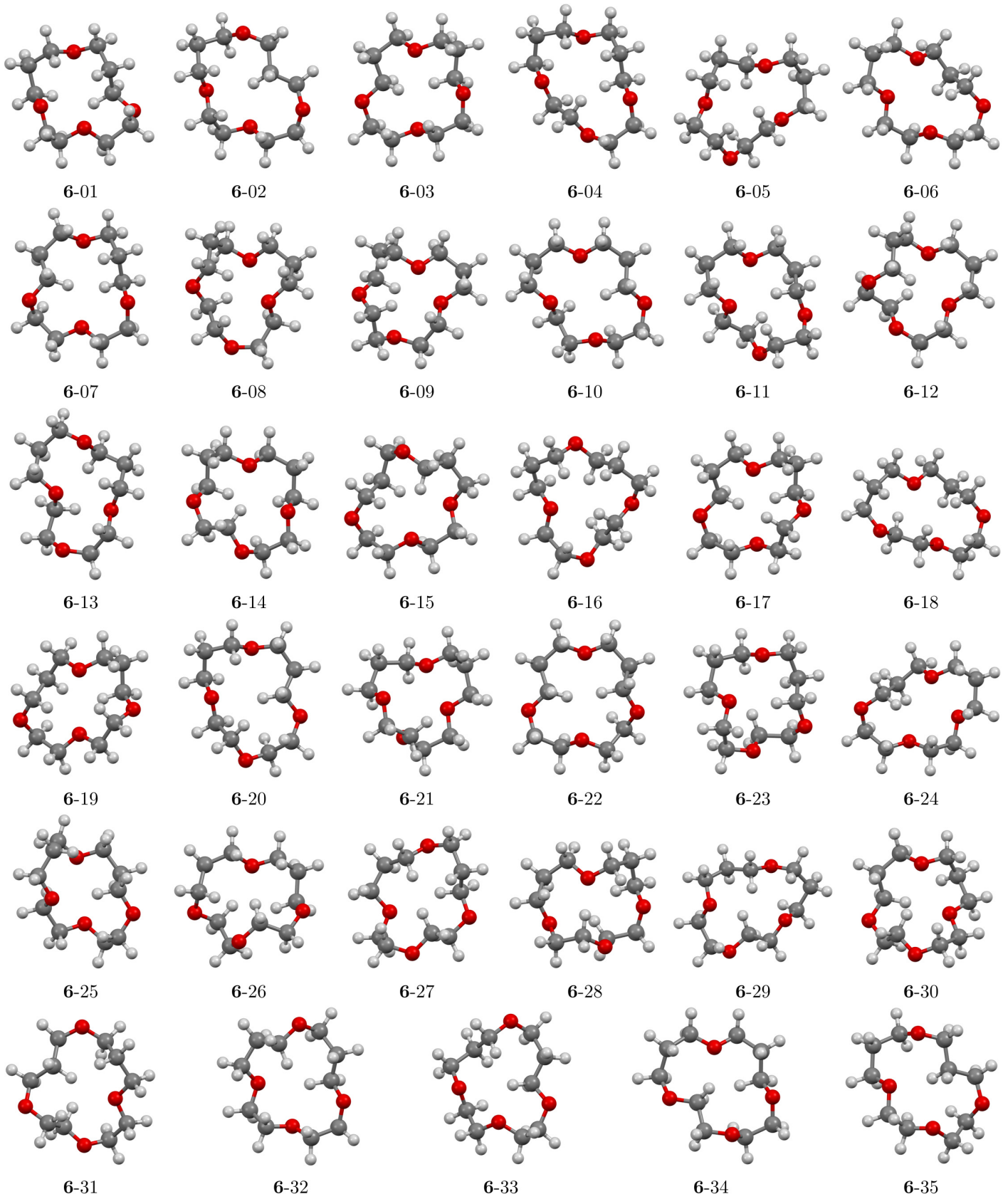


Figure S6: Crown **6** conformers optimized at M06-2X/6-31+G(d,p) level.

Table S6: Relative energy E (in kcal/mol) of crown **6** conformers computed at the M06-2X/6-31+G(d,p) level.

Conformer	E	Conformer	E	Conformer	E	Conformer	E	Conformer	E	Conformer	E
6-01	0.0	**6**-02	1.1	**6**-03	1.5	**6**-04	1.7	**6**-05	1.7	**6**-06	1.8
6-07	1.9	**6**-08	1.9	**6**-09	2.6	**6**-10	2.8	**6**-11	2.9	**6**-12	3.2
6-13	3.3	**6**-14	3.4	**6**-15	3.6	**6**-16	3.7	**6**-17	3.7	**6**-18	3.8
6-19	3.8	**6**-20	3.9	**6**-21	4.2	**6**-22	4.2	**6**-23	4.3	**6**-24	4.3
6-25	4.4	**6**-26	4.6	**6**-27	5.1	**6**-28	5.1	**6**-29	5.1	**6**-30	5.2
6-31	5.7	**6**-32	5.8	**6**-33	6.3	**6**-34	6.5	**6**-35	7.7		

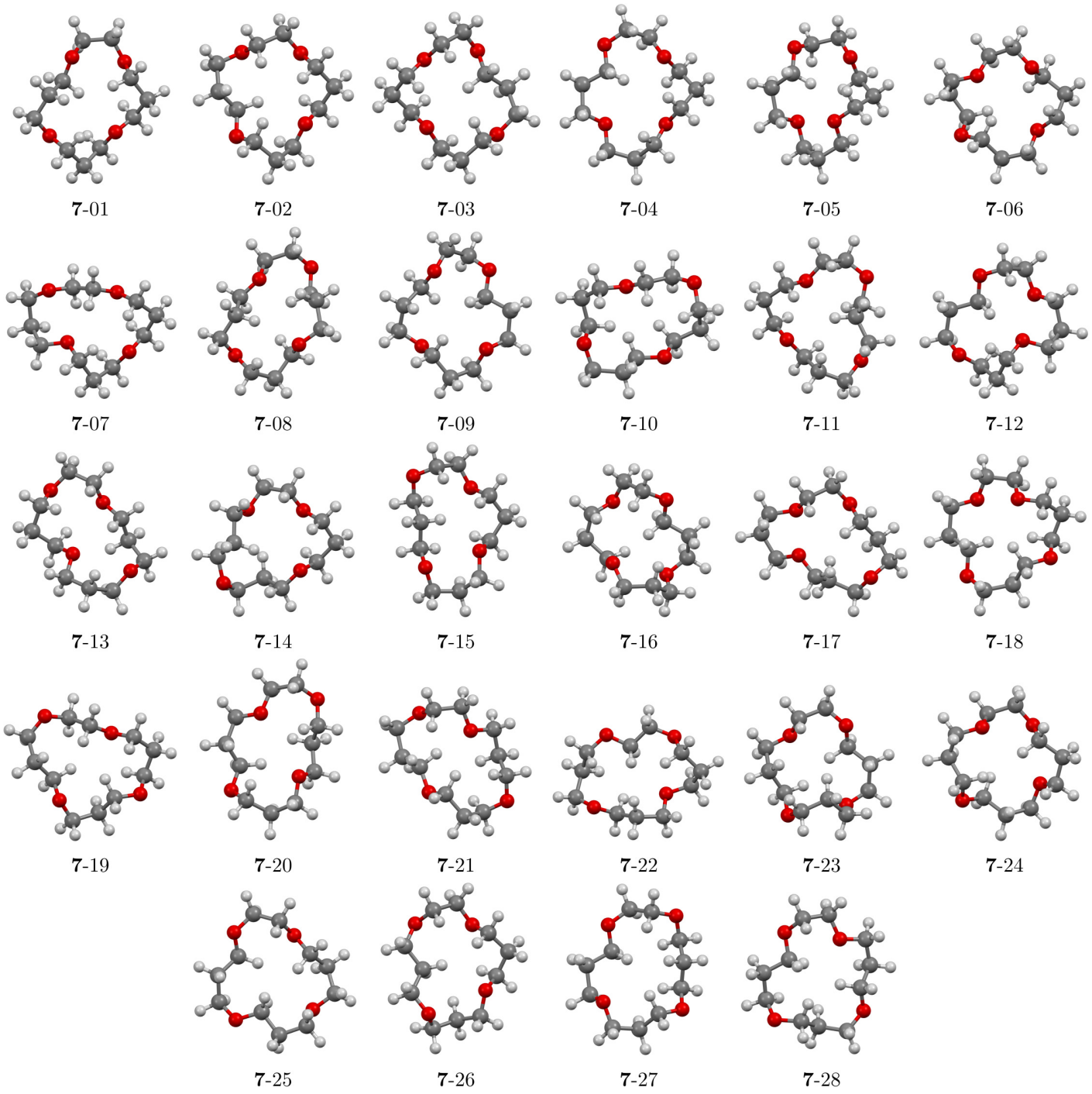


Figure S7: Crown **7** conformers optimized at M06-2X/6-31+G(d,p) level.

Table S7: Relative energy E (in kcal/mol) of crown **7** conformers computed at the M06-2X/6-31+G(d,p) level.

Conformer	E	Conformer	E	Conformer	E	Conformer	E	Conformer	E	Conformer	E
7-01	0.0	7-02	1.4	7-03	1.7	7-04	2.9	7-05	3.2	7-06	3.4
7-07	4.0	7-08	4.4	7-09	4.4	7-10	4.9	7-11	4.9	7-12	5.5
7-13	5.7	7-14	5.7	7-15	5.7	7-16	5.8	7-17	5.8	7-18	5.9
7-19	6.1	7-20	6.1	7-21	6.4	7-22	6.7	7-23	7.4	7-24	7.7
7-25	8.3	7-26	8.7	7-27	9.1	7-28	10.3				

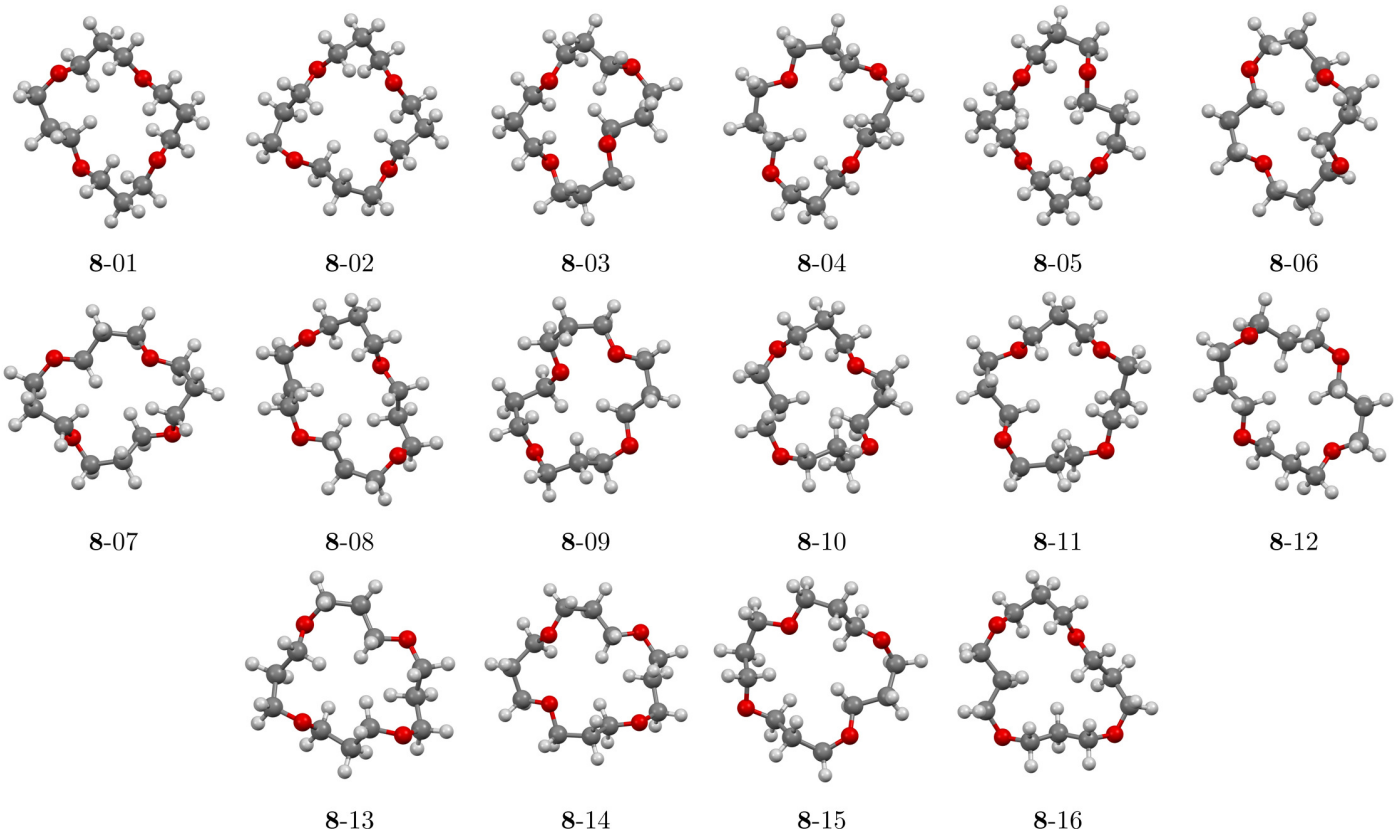


Figure S8: Crown **8** conformers optimized at M06-2X/6-31+G(d,p) level.

Table S8: Relative energy E (in kcal/mol) of crown **8** conformers computed at the M06-2X/6-31+G(d,p) level.

Conformer	E	Conformer	E	Conformer	E	Conformer	E	Conformer	E	Conformer	E
8-01	0.0	**8**-02	2.6	**8**-03	3.0	**8**-04	3.7	**8**-05	4.6	**8**-06	4.7
8-07	4.7	**8**-08	5.9	**8**-09	6.7	**8**-10	7.5	**8**-11	8.1	**8**-12	8.8
8-13	9.7	**8**-14	9.7	**8**-15	10.2	**8**-16	10.7				

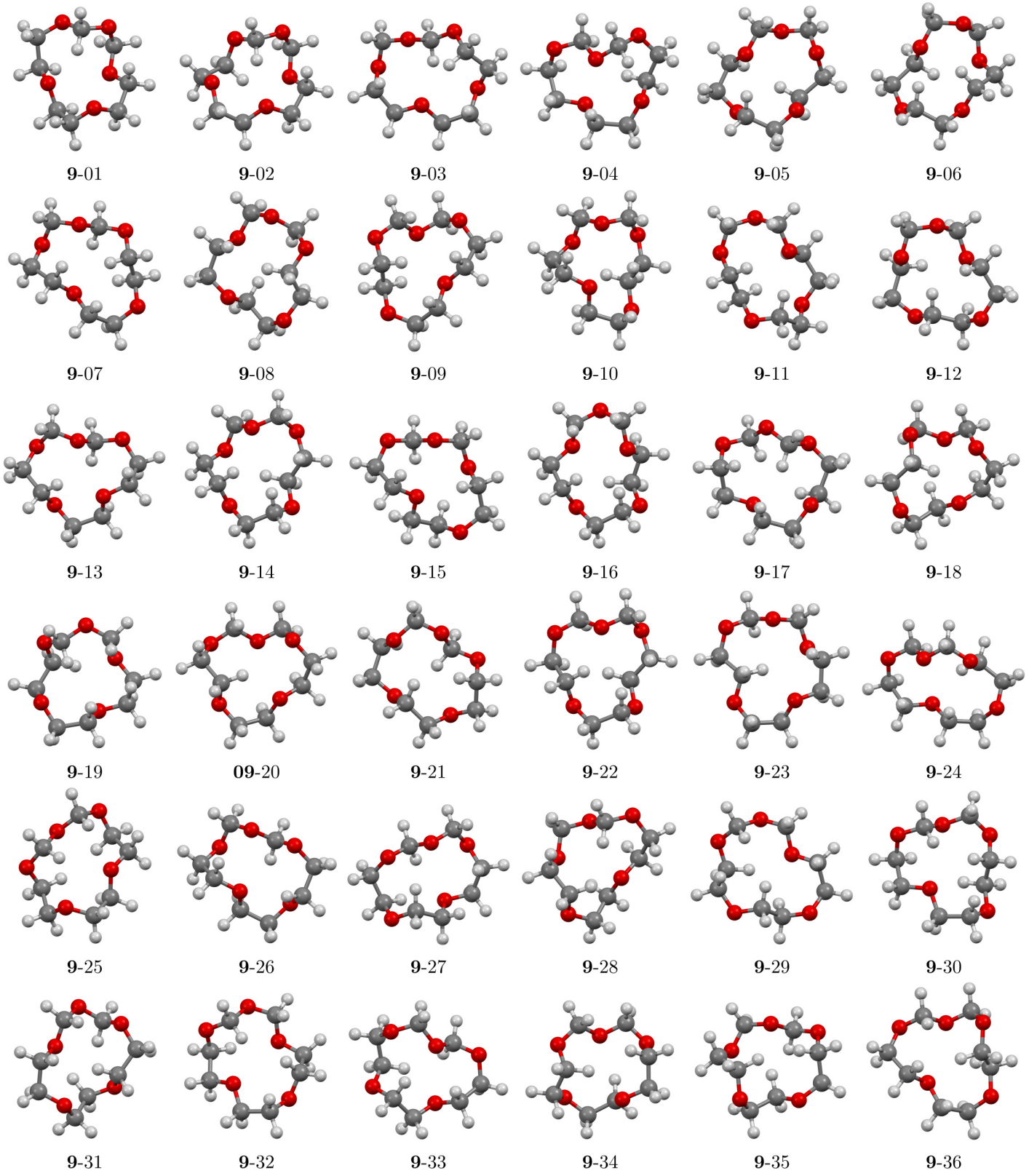


Figure S9: Crown **9** conformers optimized at M06-2X/6-31+G(d,p) level.

Table S9: Relative energy E (in kcal/mol) of crown **9** conformers computed at the M06-2X/6-31+G(d,p) level.

Conformer	E	Conformer	E	Conformer	E	Conformer	E	Conformer	E	Conformer	E
9-01	0.0	**9**-02	1.0	**9**-03	1.3	**9**-04	1.5	**9**-05	1.6	**9**-06	1.7
9-07	1.8	**9**-08	2.2	**9**-09	2.5	**9**-10	3.1	**9**-11	3.3	**9**-12	3.3
9-13	3.3	**9**-14	3.6	**9**-15	3.8	**9**-16	4.2	**9**-17	4.3	**9**-18	4.5
9-19	4.8	**9**-20	5.0	**9**-21	5.2	**9**-22	5.4	**9**-23	5.4	**9**-24	5.5
9-25	5.6	**9**-26	5.6	**9**-27	6.2	**9**-28	6.2	**9**-29	6.3	**9**-30	6.6
9-31	6.6	**9**-32	6.7	**9**-33	6.7	**9**-34	6.9	**9**-35	9.3	**9**-36	9.7

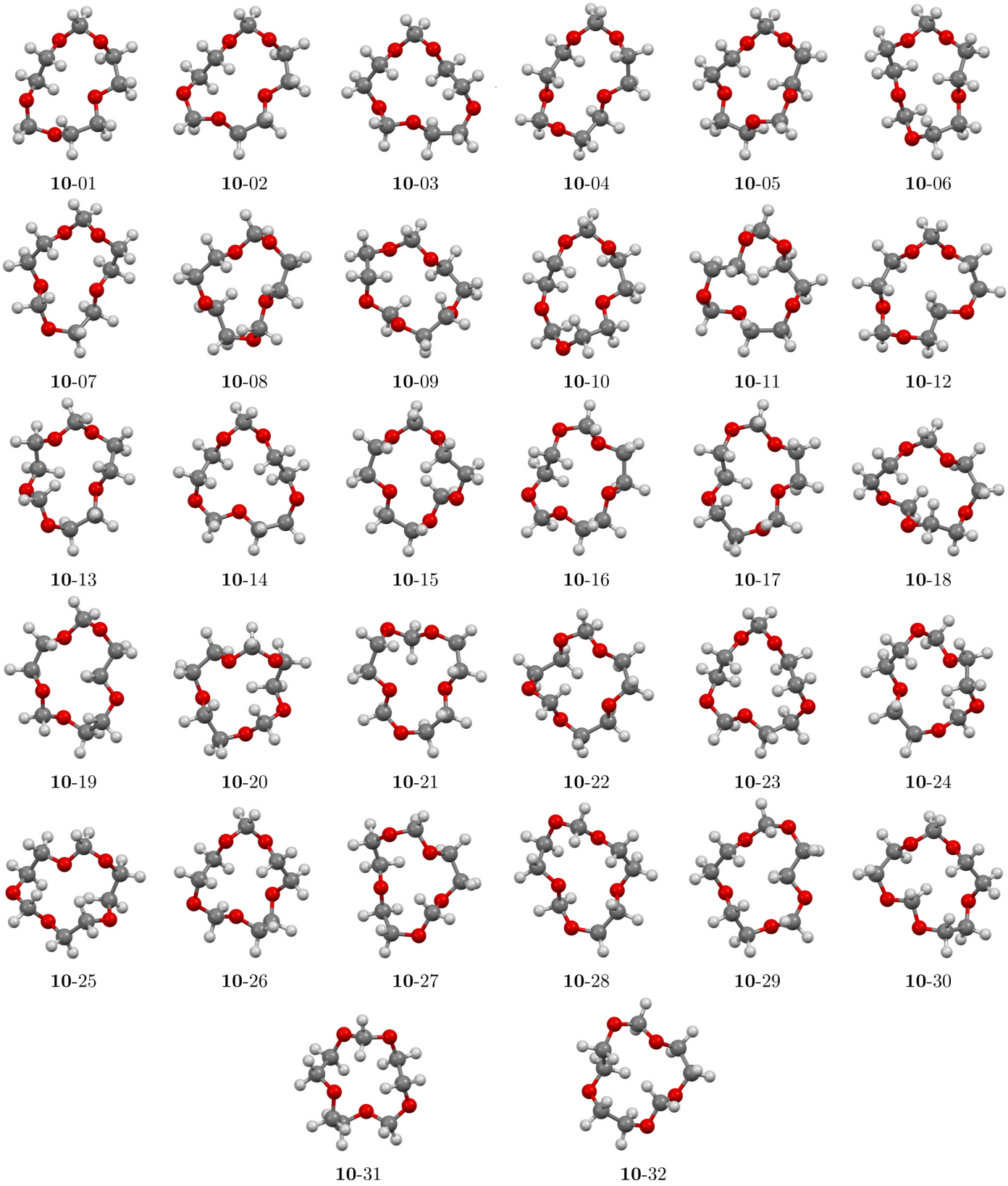


Figure S10: Crown **10** conformers optimized at M06-2X/6-31+G(d,p) level.

Table S10: Relative energy E (in kcal/mol) of crown **10** conformers computed at the M06-2X/6-31+G(d,p) level.

Conformer	E	Conformer	E	Conformer	E	Conformer	E	Conformer	E	Conformer	E
10-01	0.0	**10**-02	2.2	**10**-03	2.3	**10**-04	2.9	**10**-05	3.2	**10**-06	3.2
10-07	3.3	**10**-08	4.2	**10**-09	4.4	**10**-10	4.5	**10**-11	4.5	**10**-12	4.8
10-13	5.1	**10**-14	5.3	**10**-15	5.6	**10**-16	6.0	**10**-17	6.3	**10**-18	6.4
10-19	6.6	**10**-20	6.7	**10**-21	6.8	**10**-22	6.8	**10**-23	7.0	**10**-24	7.6
10-25	7.6	**10**-26	7.8	**10**-27	8.1	**10**-28	8.3	**10**-29	9.3	**10**-30	9.6
10-31	9.9	**10**-32	10.5								

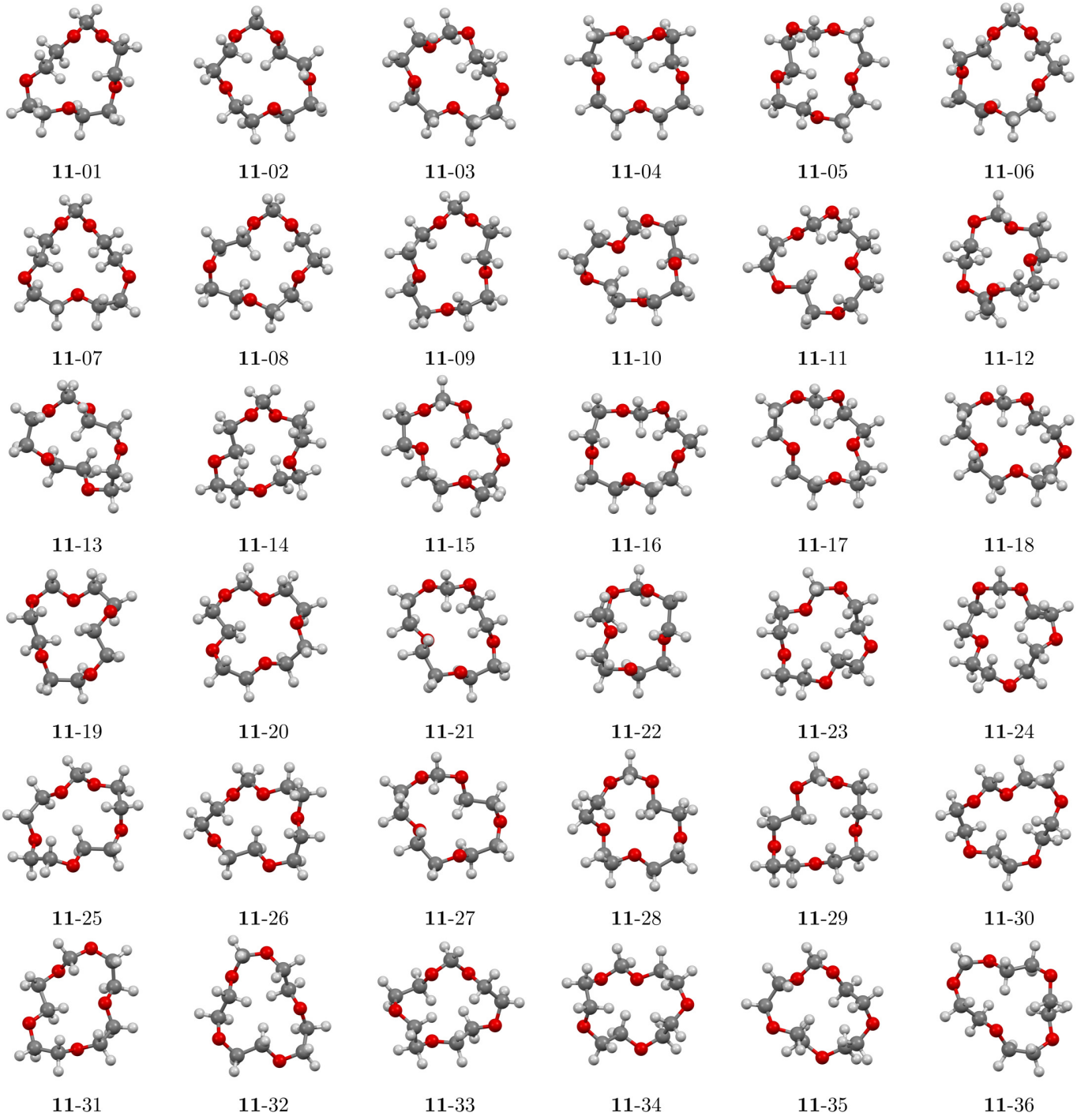


Figure S11: Crown **11** conformers optimized at M06-2X/6-31+G(d,p) level.

Table S11: Relative energy E (in kcal/mol) of crown **11** conformers computed at the M06-2X/6-31+G(d,p) level.

Conformer	E	Conformer	E	Conformer	E	Conformer	E	Conformer	E	Conformer	E
11-01	0.0	**11**-02	0.7	**11**-03	1.7	**11**-04	2.5	**11**-05	2.8	**11**-06	2.9
11-07	3.1	**11**-08	3.3	**11**-09	3.5	**11**-10	4.3	**11**-11	4.6	**11**-12	4.8
11-13	5.1	**11**-14	5.1	**11**-15	5.1	**11**-16	5.2	**11**-17	5.6	**11**-18	5.8
11-19	5.8	**11**-20	5.9	**11**-21	5.9	**11**-22	6.1	**11**-23	6.6	**11**-24	6.7
11-25	6.7	**11**-26	6.9	**11**-27	7.0	**11**-28	7.0	**11**-29	7.0	**11**-30	7.2
11-31	7.5	**11**-32	7.8	**11**-33	8.3	**11**-34	8.6	**11**-35	9.1	**11**-36	9.3

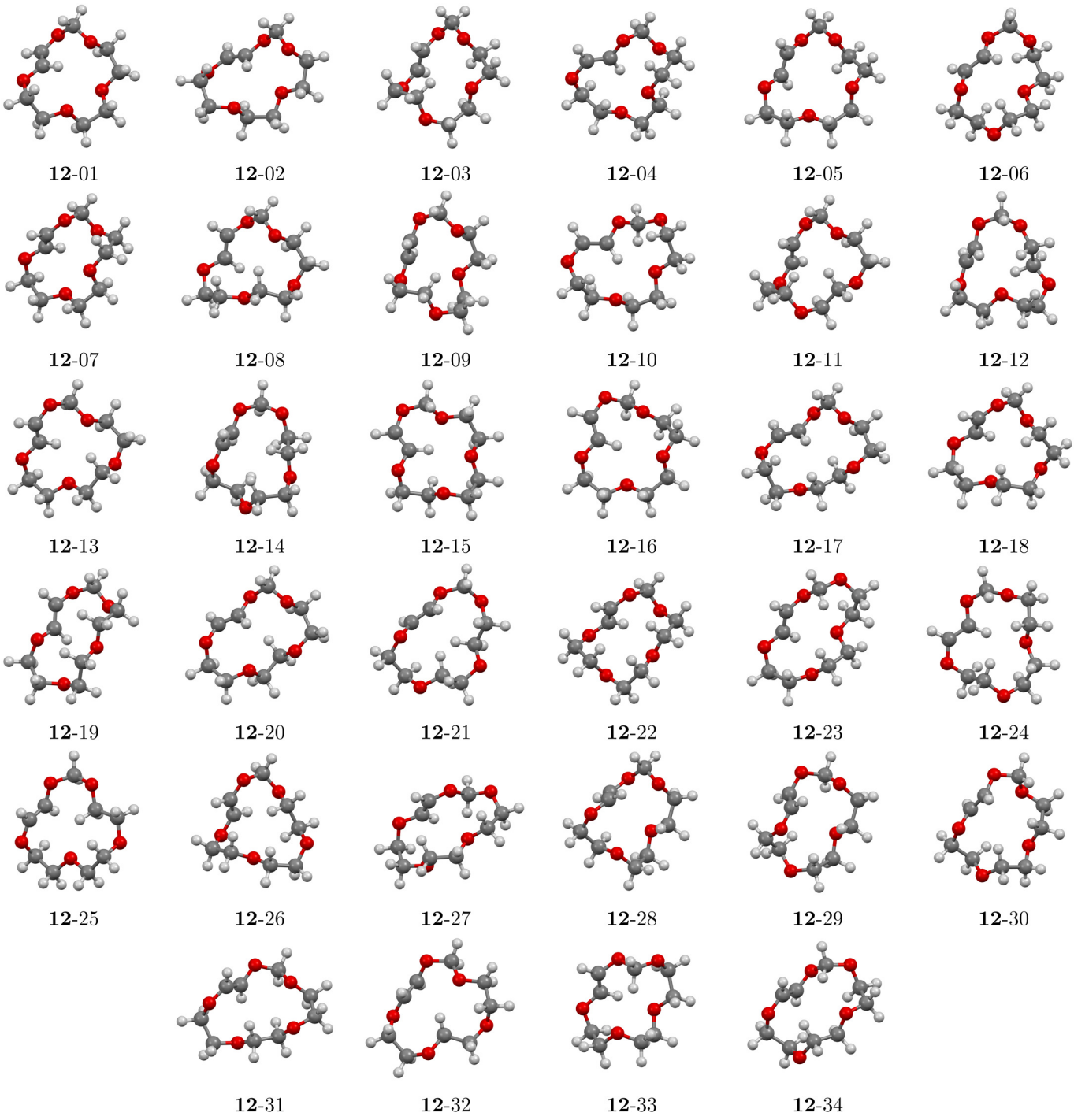


Figure S12: Crown **12** conformers optimized at M06-2X/6-31+G(d,p) level.

Table S12: Relative energy E (in kcal/mol) of crown **12** conformers computed at the M06-2X/6-31+G(d,p) level.

Conformer	E	Conformer	E	Conformer	E	Conformer	E	Conformer	E	Conformer	E
12-01	0.0	**12**-02	0.7	**12**-03	1.0	**12**-04	1.2	**12**-05	1.5	**12**-06	1.5
12-07	1.5	**12**-08	1.9	**12**-09	2.2	**12**-10	2.6	**12**-11	2.7	**12**-12	2.8
12-13	3.1	**12**-14	3.2	**12**-15	3.4	**12**-16	3.4	**12**-17	3.5	**12**-18	3.7
12-19	4.4	**12**-20	4.5	**12**-21	4.5	**12**-22	4.6	**12**-23	4.8	**12**-24	5.2
12-25	5.2	**12**-26	5.3	**12**-27	5.4	**12**-28	5.5	**12**-29	5.5	**12**-30	5.7
12-31	6.3	**12**-32	6.3	**12**-33	8.2	**12**-34	8.4				

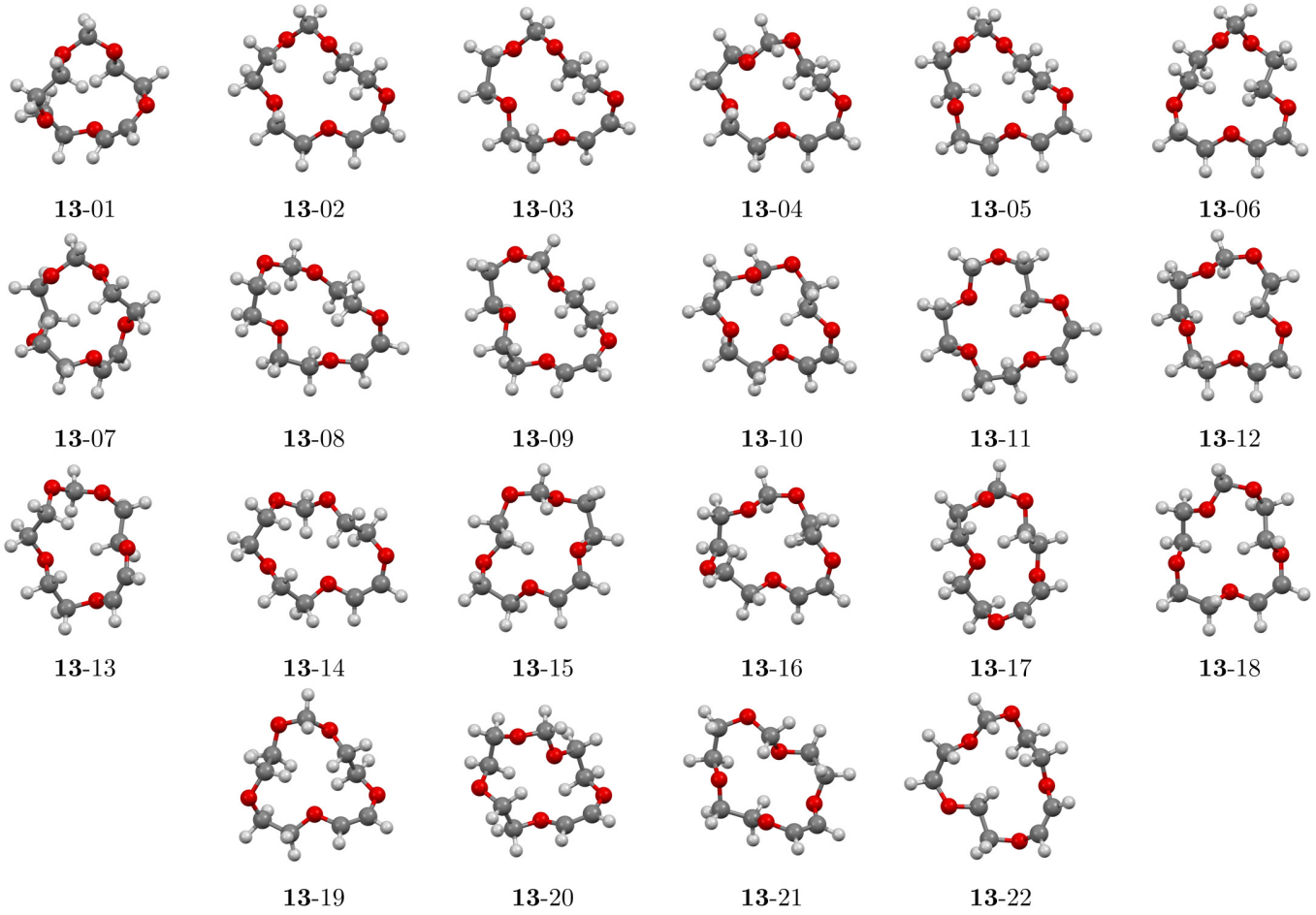


Figure S13: Crown **13** conformers optimized at M06-2X/6-31+G(d,p) level.

Table S13: Relative energy E (in kcal/mol) of crown **13** conformers computed at the M06-2X/6-31+G(d,p) level.

Conformer	E	Conformer	E	Conformer	E	Conformer	E	Conformer	E	Conformer	E
13-01	0.0	**13**-02	0.2	**13**-03	1.0	**13**-04	1.2	**13**-05	1.2	**13**-06	1.4
13-07	2.0	**13**-08	2.3	**13**-09	3.0	**13**-10	3.3	**13**-11	4.0	**13**-12	4.1
13-13	4.1	**13**-14	4.2	**13**-15	4.3	**13**-16	4.8	**13**-17	4.8	**13**-18	4.9
13-19	5.2	**13**-20	5.9	**13**-21	7.1	**13**-22	7.2				

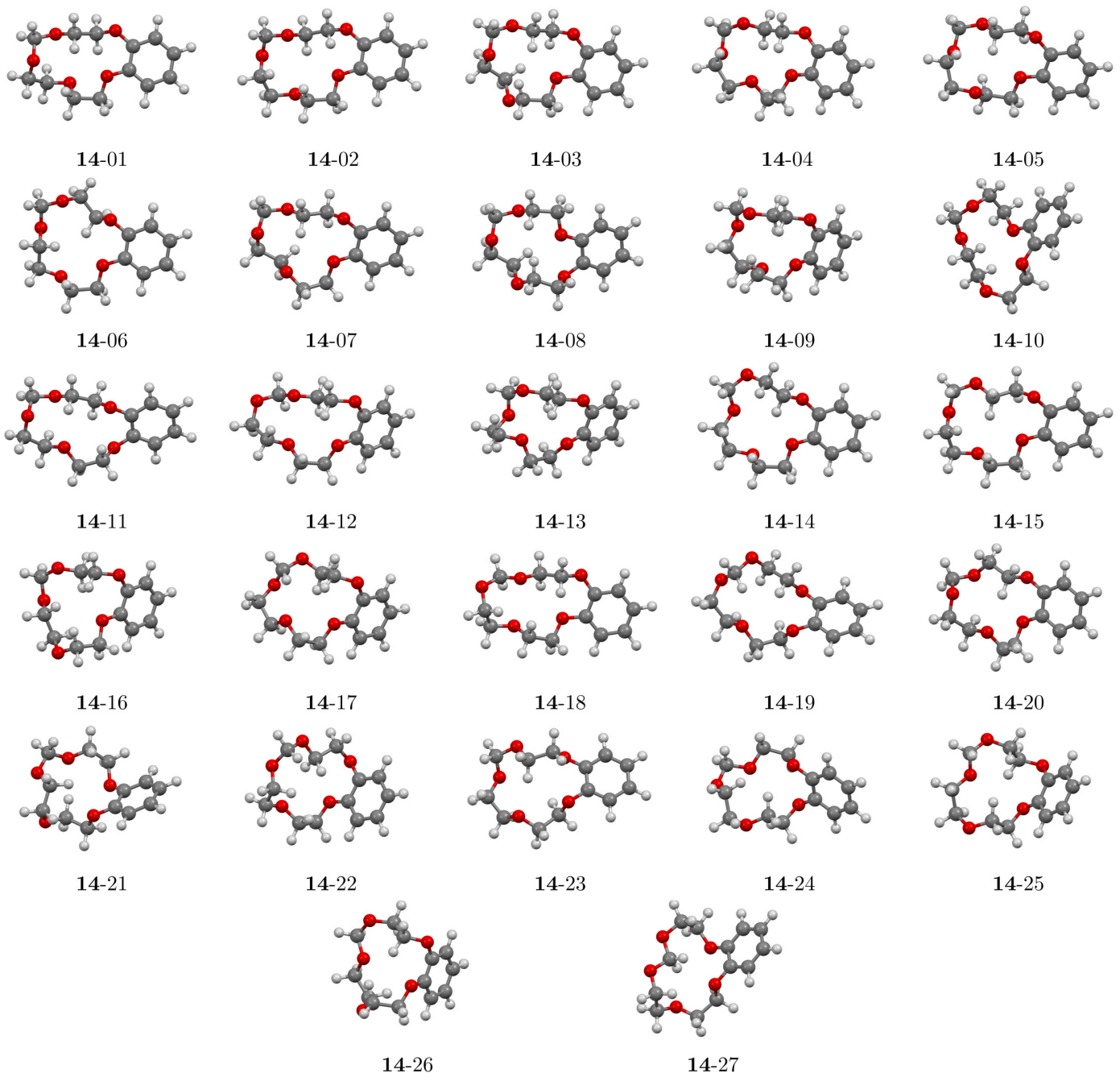


Figure S14: Crown **14** conformers optimized at M06-2X/6-31+G(d,p) level.

Table S14: Relative energy E (in kcal/mol) of crown **14** conformers computed at the M06-2X/6-31+G(d,p) level.

Conformer	E	Conformer	E	Conformer	E	Conformer	E	Conformer	E	Conformer	E
14-01	0.0	**14**-02	0.5	**14**-03	0.8	**14**-04	1.6	**14**-05	1.6	**14**-06	1.9
14-07	2.0	**14**-08	2.4	**14**-09	2.5	**14**-10	2.6	**14**-11	2.8	**14**-12	3.2
14-13	3.3	**14**-14	3.9	**14**-15	4.1	**14**-16	4.2	**14**-17	4.2	**14**-18	4.4
14-19	4.5	**14**-20	4.8	**14**-21	5.5	**14**-22	5.6	**14**-23	6.2	**14**-24	6.7
14-25	6.9	**14**-26	8.1	**14**-27	8.1						

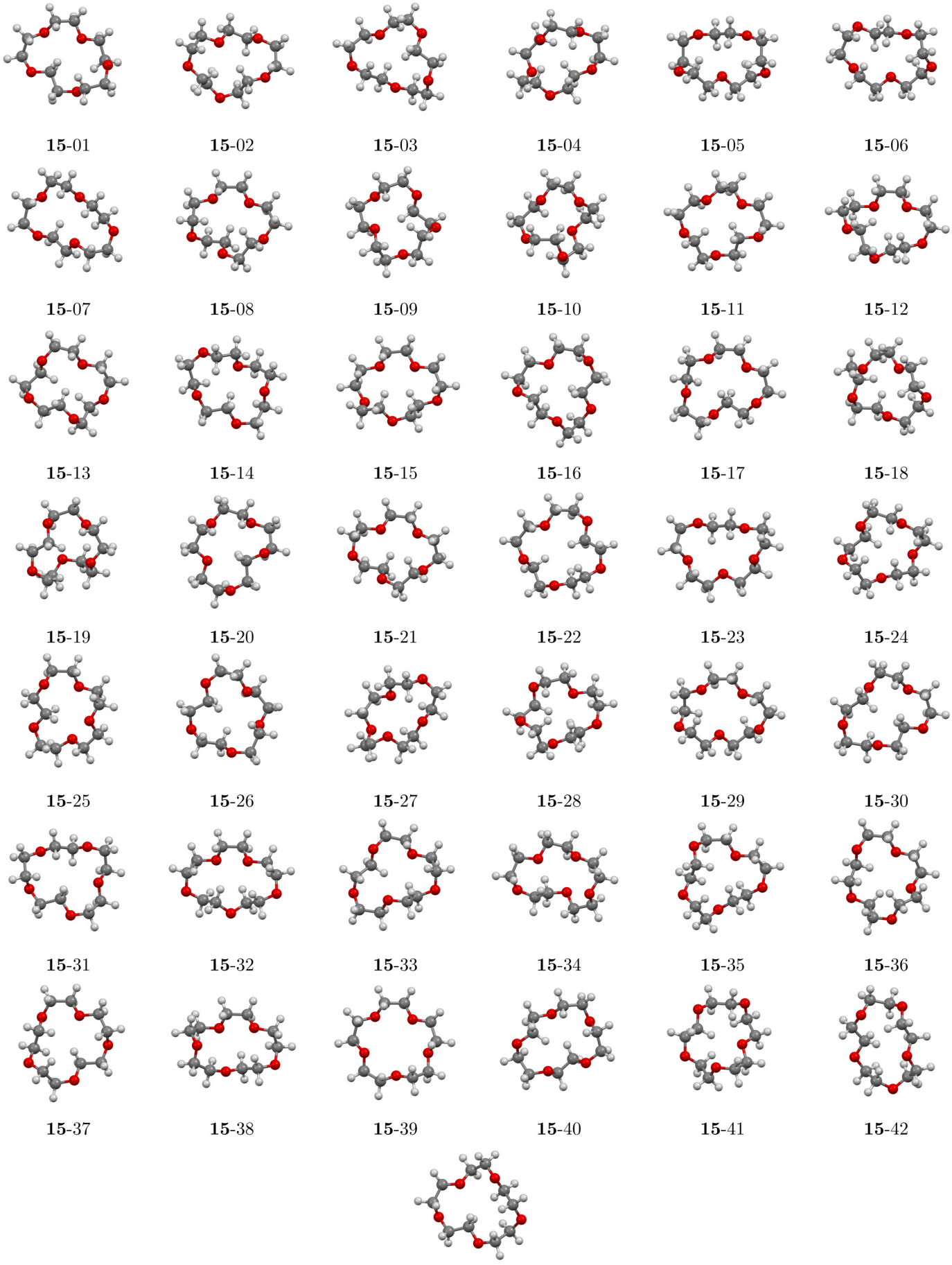


Figure S15: Crown **15** conformers optimized at M06-2X/6-31+G(d,p) level.

Table S15: Relative energy E (in kcal/mol) of crown **15** conformers computed at the M06-2X/6-31+G(d,p) level.

Conformer	E	Conformer	E	Conformer	E	Conformer	E	Conformer	E	Conformer	E
15-01	0.0	**15**-02	0.3	**15**-03	0.7	**15**-04	0.7	**15**-05	0.8	**15**-06	1.1
15-07	1.2	**15**-08	1.3	**15**-09	1.3	**15**-10	1.6	**15**-11	1.6	**15**-12	1.8
15-13	2.2	**15**-14	2.3	**15**-15	2.3	**15**-16	2.4	**15**-17	2.4	**15**-18	2.4
15-19	2.6	**15**-20	2.8	**15**-21	2.9	**15**-22	2.9	**15**-23	2.9	**15**-24	3.0
15-25	3.1	**15**-26	3.1	**15**-27	3.2	**15**-28	3.2	**15**-29	3.5	**15**-30	3.6
15-31	3.7	**15**-32	3.7	**15**-33	3.8	**15**-34	3.8	**15**-35	4.1	**15**-36	4.2
15-37	4.6	**15**-38	4.7	**15**-39	4.7	**15**-40	5.0	**15**-41	5.5	**15**-42	7.2
15-43	8.0										

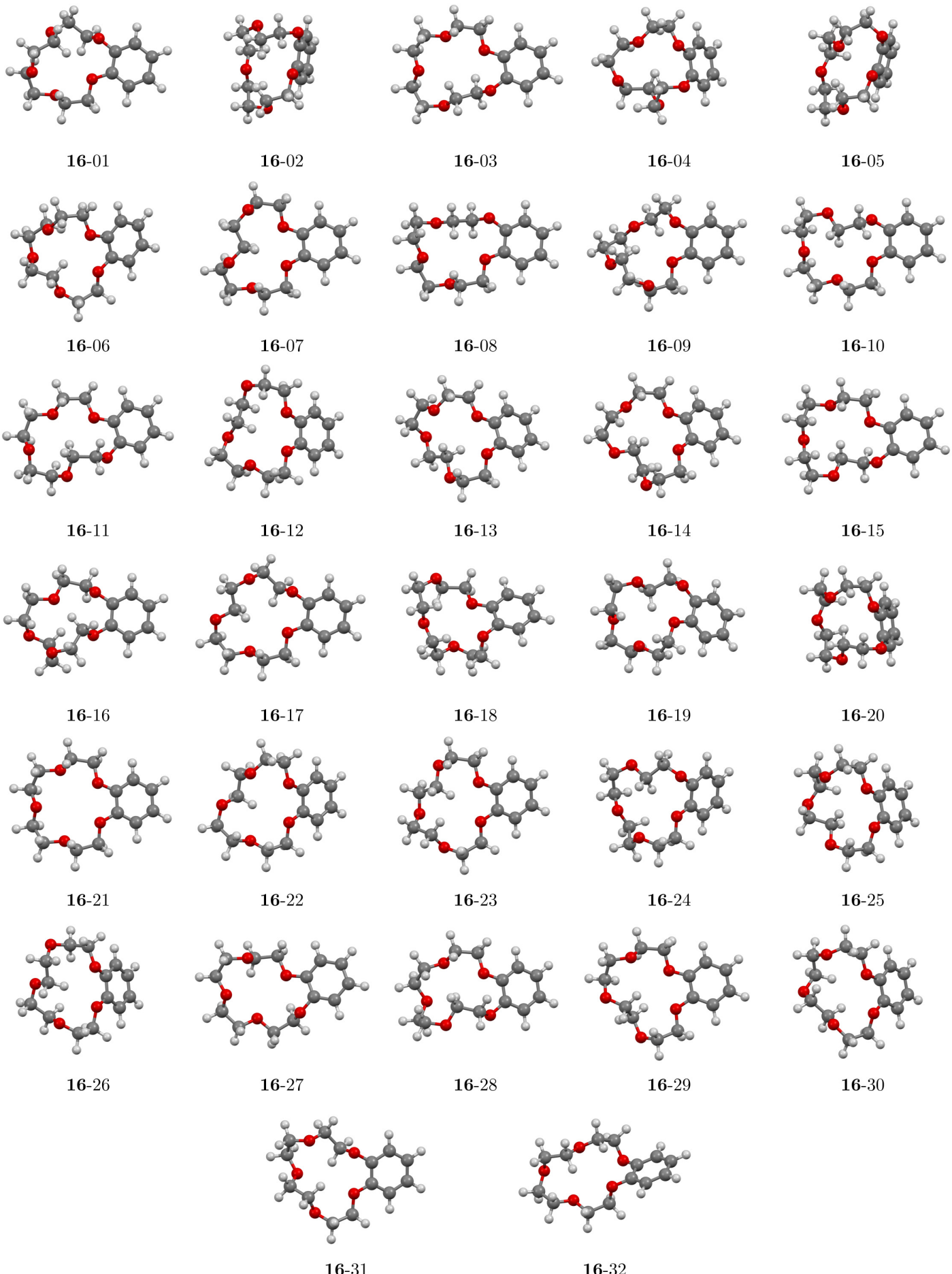


Figure S16: Crown **16** conformers optimized at M06-2X/6-31+G(d,p) level.

Table S16: Relative energy E (in kcal/mol) of crown **16** conformers computed at the M06-2X/6-31+G(d,p) level.

Conformer	E	Conformer	E	Conformer	E	Conformer	E	Conformer	E	Conformer	E
16-01	0.0	**16**-02	1.2	**16**-03	2.1	**16**-04	2.1	**16**-05	2.2	**16**-06	2.3
16-07	2.4	**16**-08	2.5	**16**-09	2.6	**16**-10	2.8	**16**-11	3.1	**16**-12	3.2
16-13	3.2	**16**-14	3.7	**16**-15	3.9	**16**-16	4.1	**16**-17	4.2	**16**-18	4.3
16-19	4.6	**16**-20	4.7	**16**-21	4.8	**16**-22	4.9	**16**-23	4.9	**16**-24	5.2
16-25	5.2	**16**-26	5.6	**16**-27	5.8	**16**-28	6.0	**16**-29	6.6	**16**-30	6.6
16-31	7.4	**16**-32	7.6								

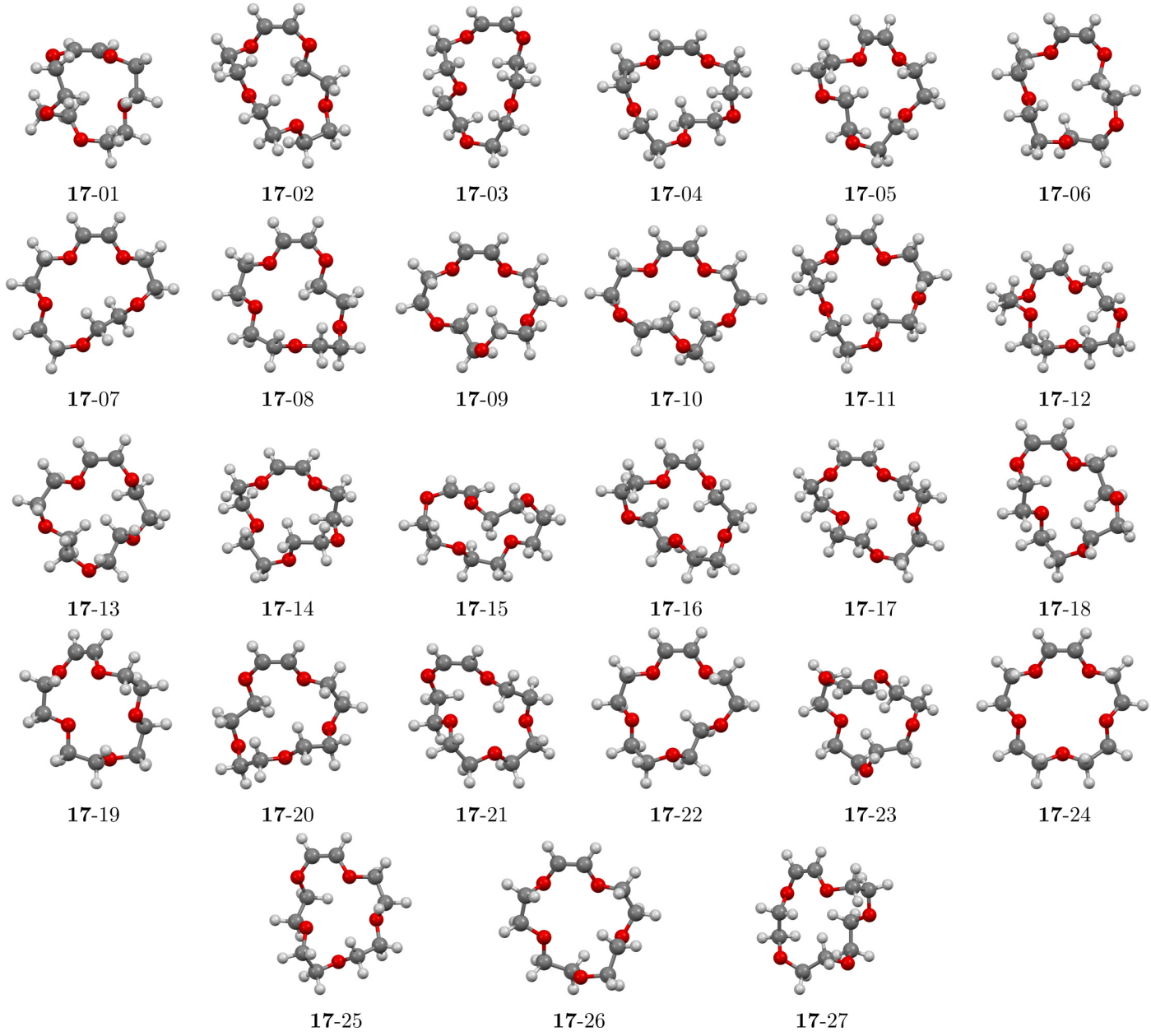


Figure S17: Crown **17** conformers optimized at M06-2X/6-31+G(d,p) level.

Table S17: Relative energy E (in kcal/mol) of crown **17** conformers computed at the M06-2X/6-31+G(d,p) level.

Conformer	E	Conformer	E	Conformer	E	Conformer	E	Conformer	E	Conformer	E
17-01	0.0	**17**-02	0.2	**17**-03	0.8	**17**-04	1.6	**17**-05	1.7	**17**-06	2.0
17-07	2.3	**17**-08	2.5	**17**-09	3.1	**17**-10	3.1	**17**-11	3.2	**17**-12	3.4
17-13	3.5	**17**-14	3.9	**17**-15	4.0	**17**-16	4.4	**17**-17	4.5	**17**-18	4.8
17-19	4.8	**17**-20	4.8	**17**-21	4.8	**17**-22	4.9	**17**-23	5.3	**17**-24	5.8
17-25	5.8	**17**-26	5.9	**17**-27	7.7						

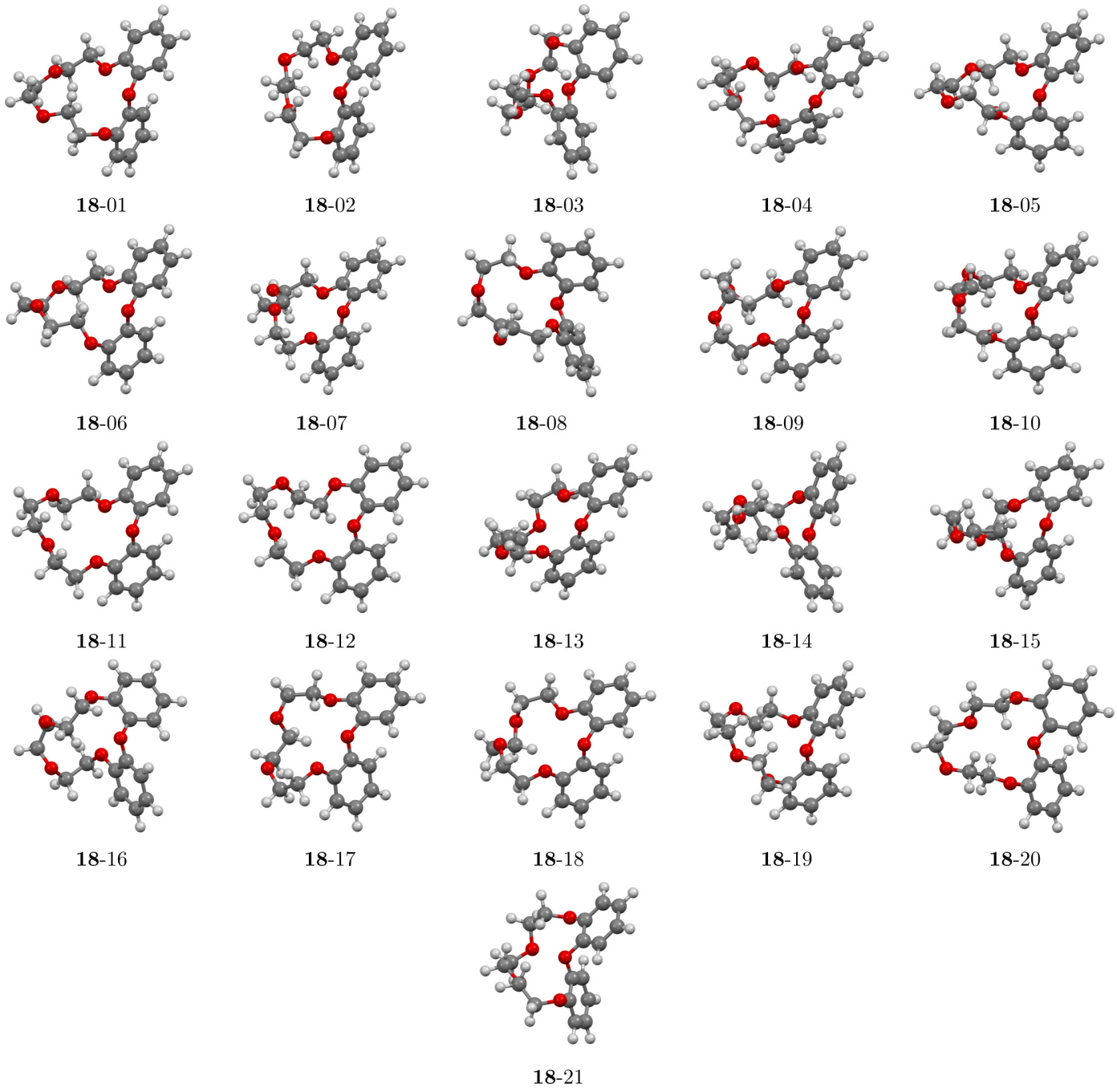


Figure S18: Crown **18** conformers optimized at M06-2X/6-31+G(d,p) level.

Table S18: Relative energy E (in kcal/mol) of crown **18** conformers computed at the M06-2X/6-31+G(d,p) level.

Conformer	E	Conformer	E	Conformer	E	Conformer	E	Conformer	E	Conformer	E
18-01	0.0	**18**-02	0.4	**18**-03	0.6	**18**-04	0.6	**18**-05	0.7	**18**-06	0.7
18-07	0.8	**18**-08	1.5	**18**-09	1.6	**18**-10	1.7	**18**-11	1.8	**18**-12	1.9
18-13	2.7	**18**-14	2.7	**18**-15	3.2	**18**-16	3.2	**18**-17	3.7	**18**-18	4.0
18-19	4.2	**18**-20	4.3	**18**-21	4.6						

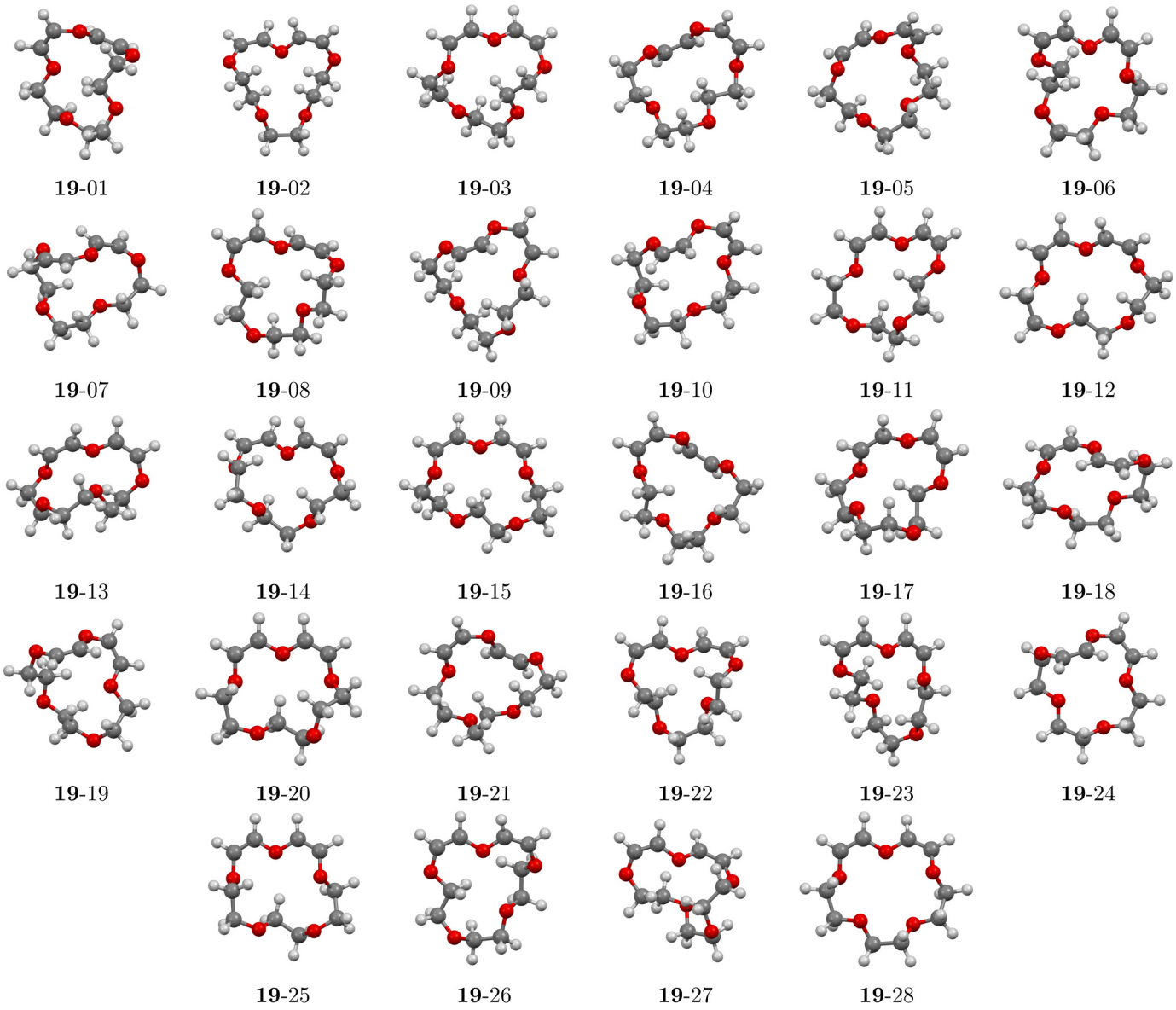


Figure S19: Crown **19** conformers optimized at M06-2X/6-31+G(d,p) level.

Table S19: Relative energy E (in kcal/mol) of crown **19** conformers computed at the M06-2X/6-31+G(d,p) level.

Conformer	E	Conformer	E	Conformer	E	Conformer	E	Conformer	E	Conformer	E
19-01	0.0	**19**-02	0.3	**19**-03	0.6	**19**-04	0.8	**19**-05	1.3	**19**-06	1.4
19-07	1.4	**19**-08	1.6	**19**-09	1.6	**19**-10	1.9	**19**-11	2.1	**19**-12	2.3
19-13	2.4	**19**-14	2.4	**19**-15	2.4	**19**-16	2.7	**19**-17	2.7	**19**-18	2.8
19-19	2.8	**19**-20	3.0	**19**-21	3.1	**19**-22	3.4	**19**-23	3.8	**19**-24	4.2
19-25	4.5	**19**-26	4.5	**19**-27	4.7	**19**-28	6.2				

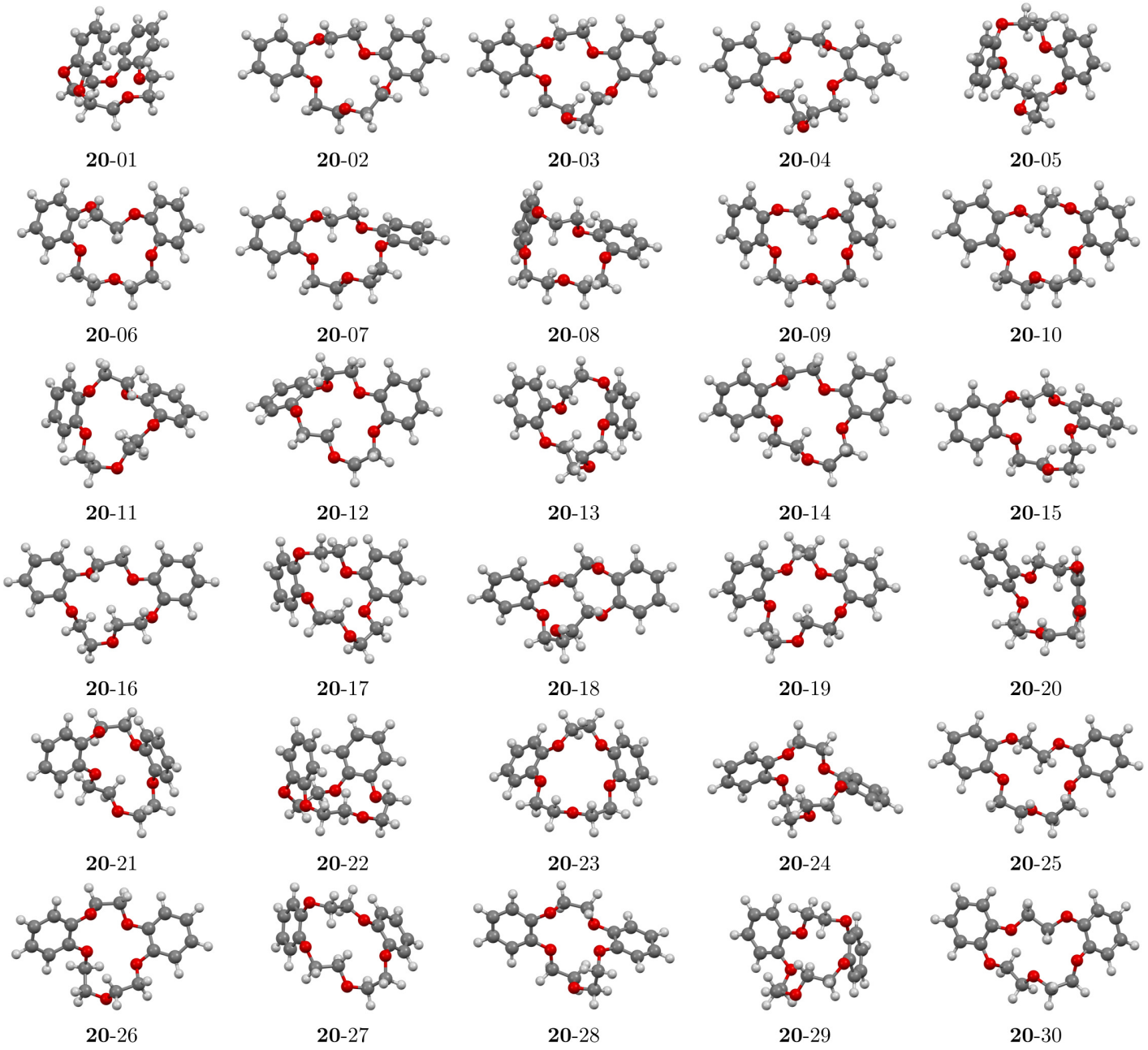


Figure S20: Crown **20** conformers optimized at M06-2X/6-31+G(d,p) level.

Table S20: Relative energy E (in kcal/mol) of crown **20** conformers computed at the M06-2X/6-31+G(d,p) level.

Conformer	E	Conformer	E	Conformer	E	Conformer	E	Conformer	E	Conformer	E
20-01	0.0	**20**-02	0.8	**20**-03	1.2	**20**-04	1.5	**20**-05	1.9	**20**-06	2.0
20-07	2.0	**20**-08	2.2	**20**-09	2.2	**20**-10	2.3	**20**-11	2.5	**20**-12	2.7
20-13	2.8	**20**-14	2.8	**20**-15	3.1	**20**-16	3.2	**20**-17	3.3	**20**-18	3.4
20-19	3.6	**20**-20	3.8	**20**-21	3.8	**20**-22	3.8	**20**-23	3.9	**20**-24	3.9
20-25	4.3	**20**-26	4.4	**20**-27	4.6	**20**-28	5.1	**20**-29	5.7	**20**-30	6.9

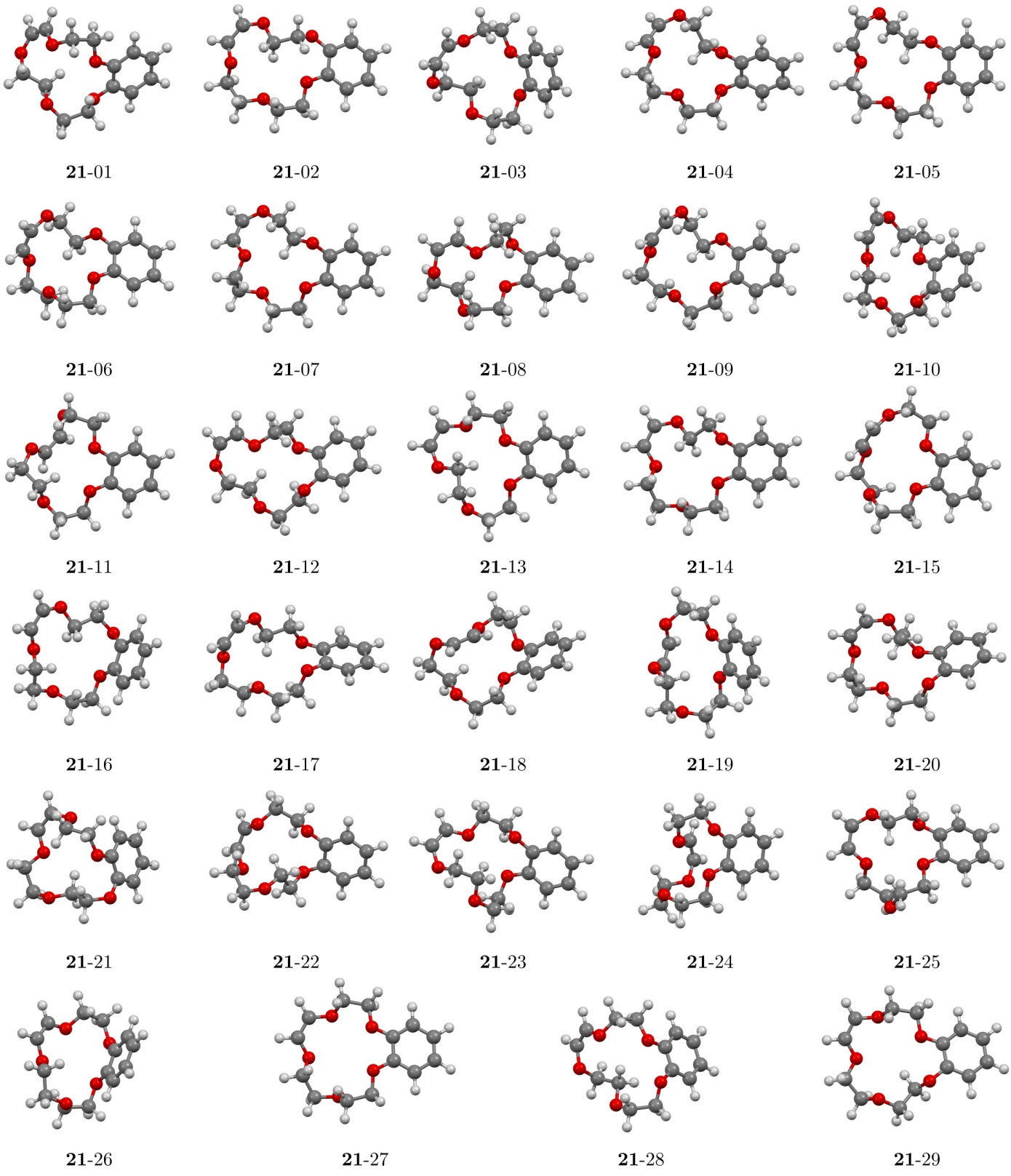


Figure S21: Crown **21** conformers optimized at M06-2X/6-31+G(d,p) level.

Table S21: Relative energy E (in kcal/mol) of crown **21** conformers computed at the M06-2X/6-31+G(d,p) level.

Conformer	E	Conformer	E	Conformer	E	Conformer	E	Conformer	E	Conformer	E
21-01	0.0	**21**-02	0.8	**21**-03	0.8	**21**-04	1.2	**21**-05	1.3	**21**-06	1.3
21-07	1.5	**21**-08	1.5	**21**-09	1.9	**21**-10	1.9	**21**-11	2.0	**21**-12	2.2
21-13	2.4	**21**-14	2.7	**21**-15	2.7	**21**-16	2.8	**21**-17	2.9	**21**-18	3.1
21-19	3.3	**21**-20	3.4	**21**-21	3.6	**21**-22	3.7	**21**-23	3.8	**21**-24	3.9
21-25	4.0	**21**-26	4.7	**21**-27	4.8	**21**-28	5.0	**21**-29	5.6		

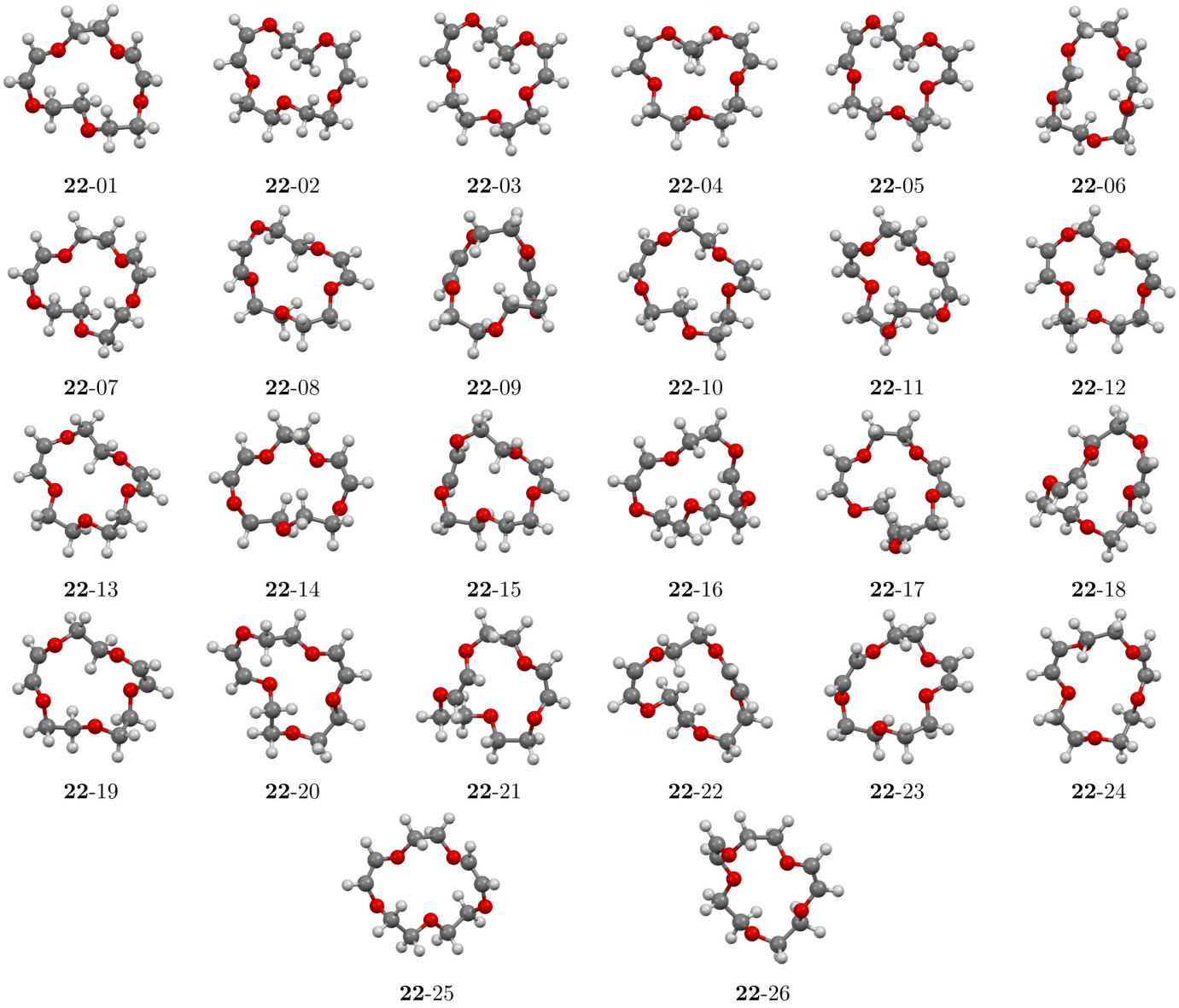


Figure S22: Crown **22** conformers optimized at M06-2X/6-31+G(d,p) level.

Table S22: Relative energy E (in kcal/mol) of crown **22** conformers computed at the M06-2X/6-31+G(d,p) level.

Conformer	E	Conformer	E	Conformer	E	Conformer	E	Conformer	E	Conformer	E
22-01	0.0	**22**-02	0.3	**22**-03	0.7	**22**-04	1.1	**22**-05	1.3	**22**-06	1.5
22-07	1.8	**22**-08	1.9	**22**-09	2.5	**22**-10	2.8	**22**-11	2.9	**22**-12	2.9
22-13	3.1	**22**-14	3.6	**22**-15	4.0	**22**-16	4.3	**22**-17	4.6	**22**-18	4.7
22-19	5.2	**22**-20	5.4	**22**-21	5.5	**22**-22	5.6	**22**-23	6.2	**22**-24	6.9
22-25	7.1	**22**-26	8.2								

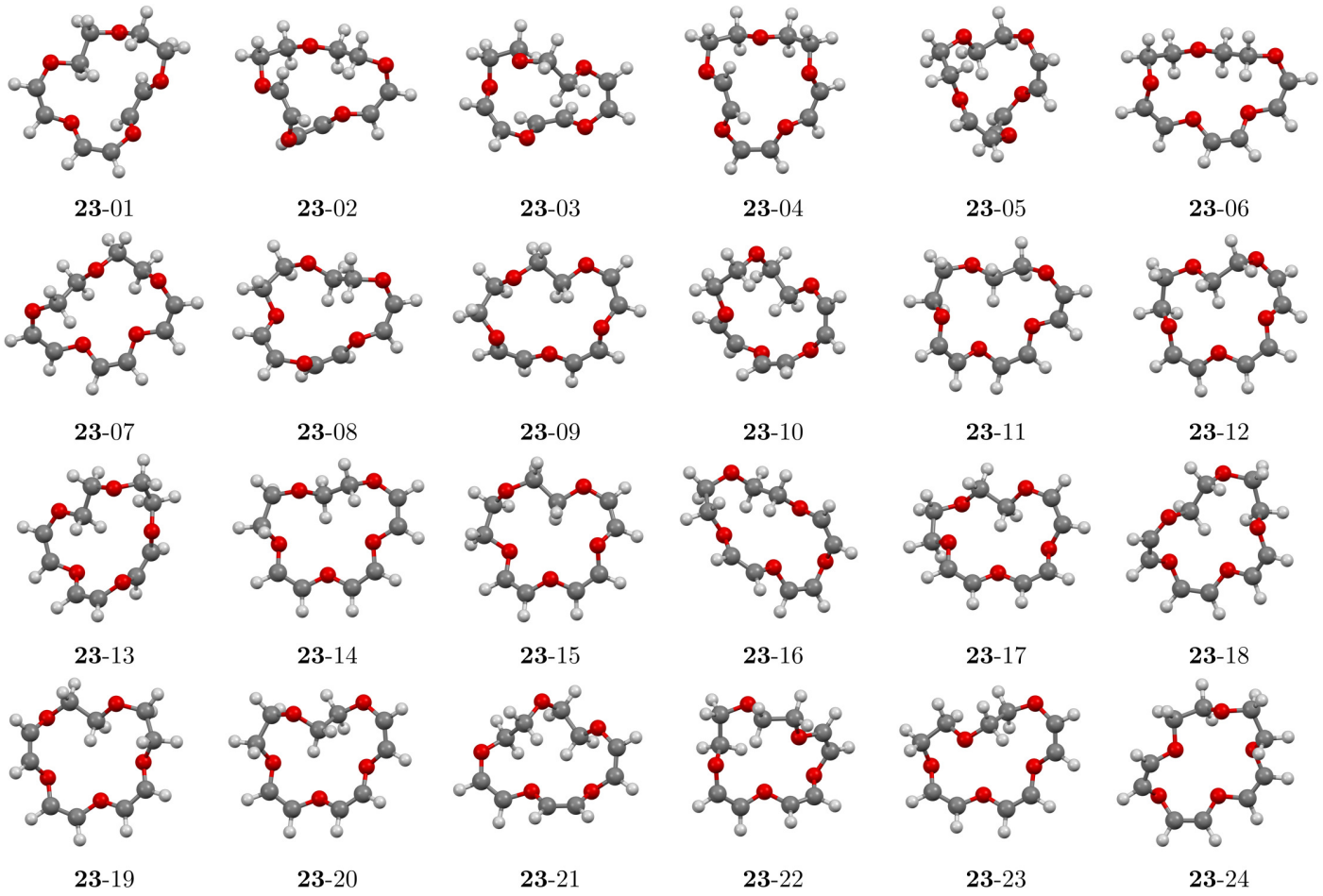


Figure S23: Crown **23** conformers optimized at M06-2X/6-31+G(d,p) level.

Table S23: Relative energy E (in kcal/mol) of crown **23** conformers computed at the M06-2X/6-31+G(d,p) level.

Conformer	E	Conformer	E	Conformer	E	Conformer	E	Conformer	E	Conformer	E
23-01	0.0	**23**-02	0.2	**23**-03	1.1	**23**-04	1.2	**23**-05	1.2	**23**-06	1.2
23-07	1.7	**23**-08	1.9	**23**-09	2.0	**23**-10	2.1	**23**-11	2.1	**23**-12	2.2
23-13	2.4	**23**-14	2.4	**23**-15	2.6	**23**-16	2.8	**23**-17	2.9	**23**-18	3.1
23-19	3.1	**23**-20	3.7	**23**-21	4.0	**23**-22	4.3	**23**-23	4.5	**23**-24	5.9

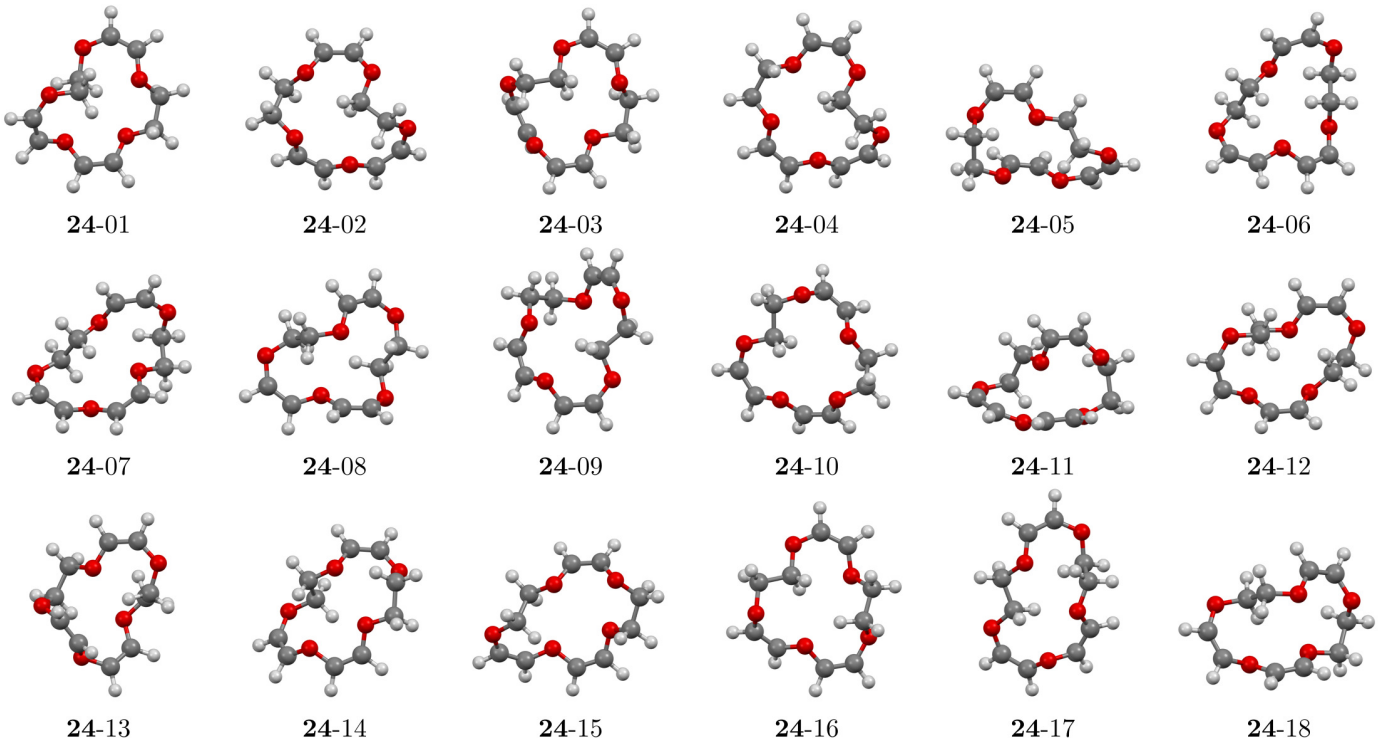


Figure S24: Crown **24** conformers optimized at M06-2X/6-31+G(d,p) level.

Table S24: Relative energy E (in kcal/mol) of crown **24** conformers computed at the M06-2X/6-31+G(d,p) level.

Conformer	E	Conformer	E	Conformer	E	Conformer	E	Conformer	E	Conformer	E
24-01	0.0	**24**-02	0.2	**24**-03	1.3	**24**-04	1.3	**24**-05	1.4	**24**-06	1.5
24-07	1.6	**24**-08	2.5	**24**-09	2.6	**24**-10	2.6	**24**-11	3.0	**24**-12	3.0
24-13	3.6	**24**-14	3.6	**24**-15	4.0	**24**-16	4.7	**24**-17	5.2	**24**-18	5.2

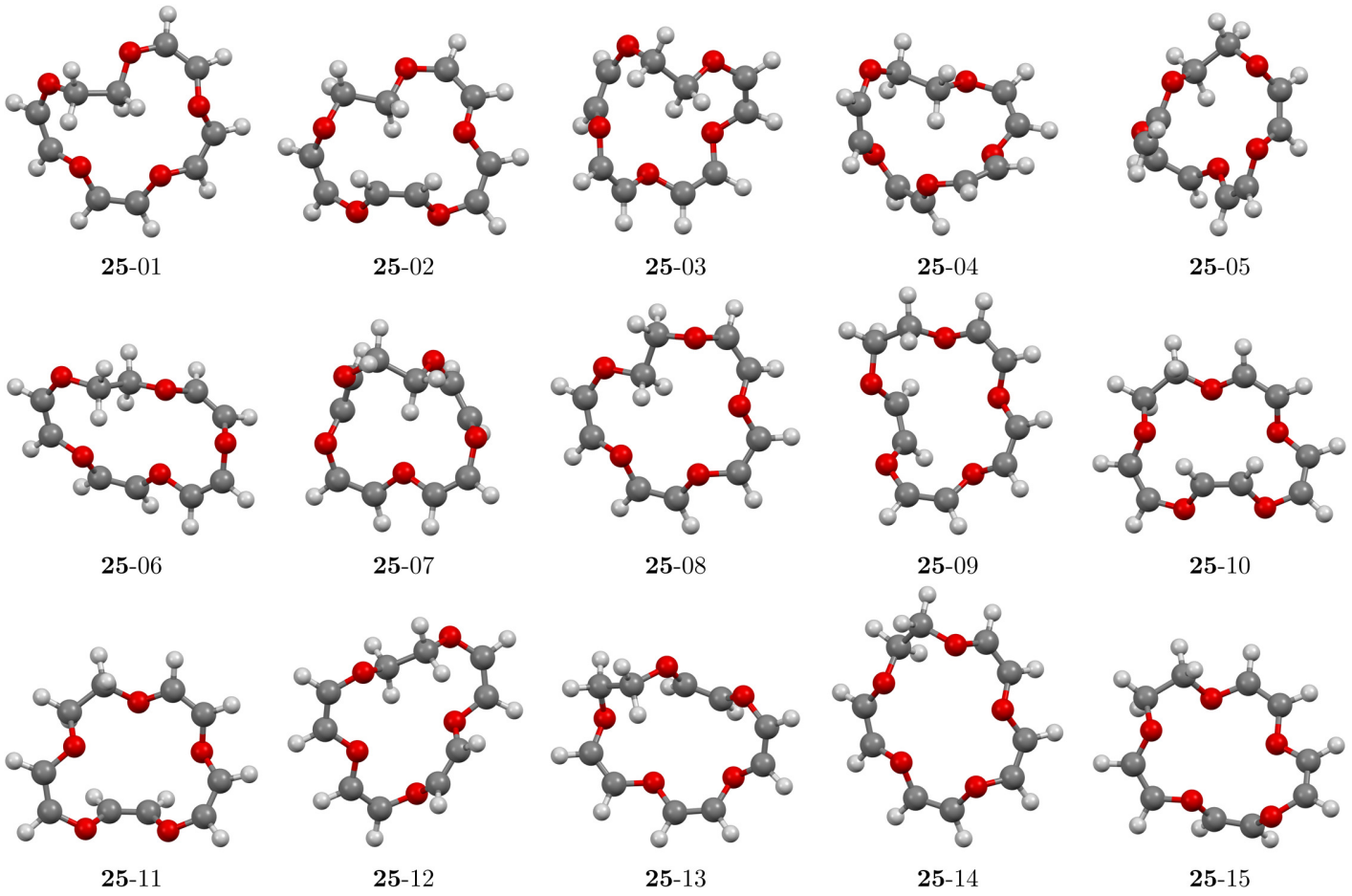
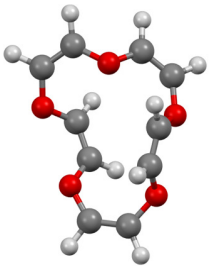


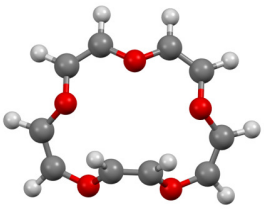
Figure S25: Crown **25** conformers optimized at M06-2X/6-31+G(d,p) level.

Table S25: Relative energy E (in kcal/mol) of crown **25** conformers computed at the M06-2X/6-31+G(d,p) level.

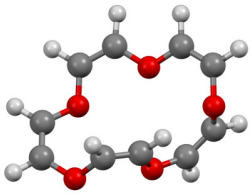
Conformer	E	Conformer	E	Conformer	E	Conformer	E	Conformer	E	Conformer	E
25-01	0.0	**25**-02	0.2	**25**-03	0.8	**25**-04	1.2	**25**-05	1.5	**25**-06	1.6
25-07	1.8	**25**-08	1.9	**25**-09	2.0	**25**-10	2.6	**25**-11	2.6	**25**-12	2.8
25-13	3.6	**25**-14	5.5	**25**-15	5.9						



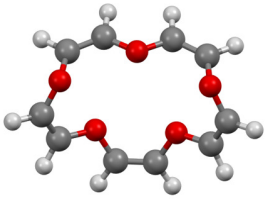
26-01



26-02



26-03



26-04

Figure S26: Crown **26** conformers optimized at M06-2X/6-31+G(d,p) level.

Table S26: Relative energy E (in kcal/mol) of crown **26** conformers computed at the M06-2X/6-31+G(d,p) level.

Conformer	E	Conformer	E	Conformer	E	Conformer	E
26-01	0.0	**26**-02	2.7	**26**-03	3.7	**26**-04	6.0

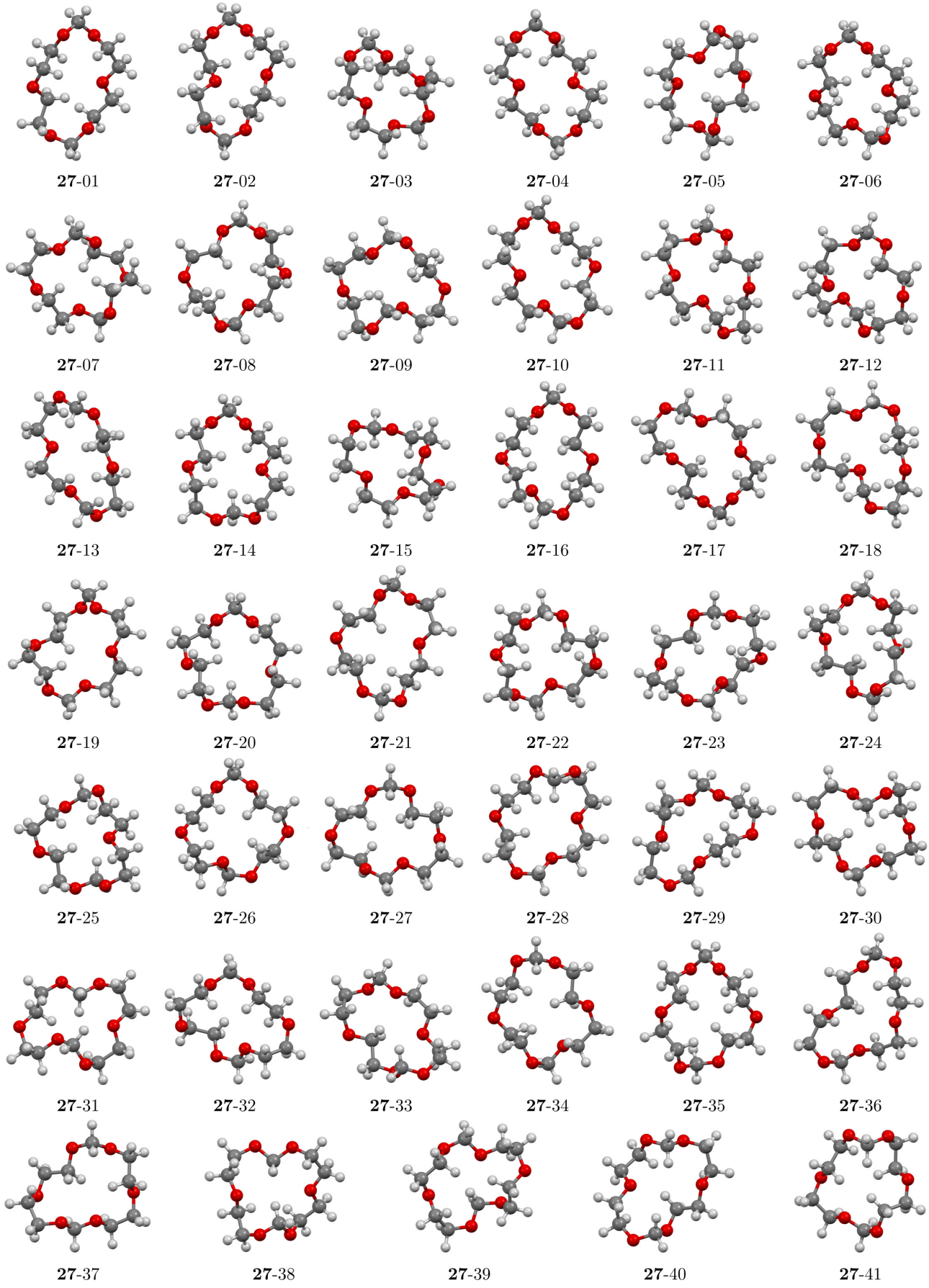


Figure S27: Crown **27** conformers optimized at M06-2X/6-31+G(d,p) level.

Table S27: Relative energy E (in kcal/mol) of crown **27** conformers computed at the M06-2X/6-31+G(d,p) level.

Conformer	E	Conformer	E	Conformer	E	Conformer	E	Conformer	E	Conformer	E
27-01	0.0	**27**-02	0.1	**27**-03	0.3	**27**-04	0.4	**27**-05	1.3	**27**-06	2.4
27-07	2.8	**27**-08	3.5	**27**-09	3.8	**27**-10	3.9	**27**-11	4.2	**27**-12	4.4
27-13	4.5	**27**-14	4.8	**27**-15	4.8	**27**-16	5.1	**27**-17	5.1	**27**-18	5.2
27-19	5.5	**27**-20	6.1	**27**-21	6.6	**27**-22	6.6	**27**-23	6.6	**27**-24	6.7
27-25	6.7	**27**-26	6.8	**27**-27	6.9	**27**-28	7.4	**27**-29	7.5	**27**-30	7.6
27-31	7.9	**27**-32	8.0	**27**-33	8.2	**27**-34	8.4	**27**-35	8.9	**27**-36	9.3
27-37	9.5	**27**-38	9.7	**27**-39	10.1	**27**-40	10.3	**27**-41	11.0		

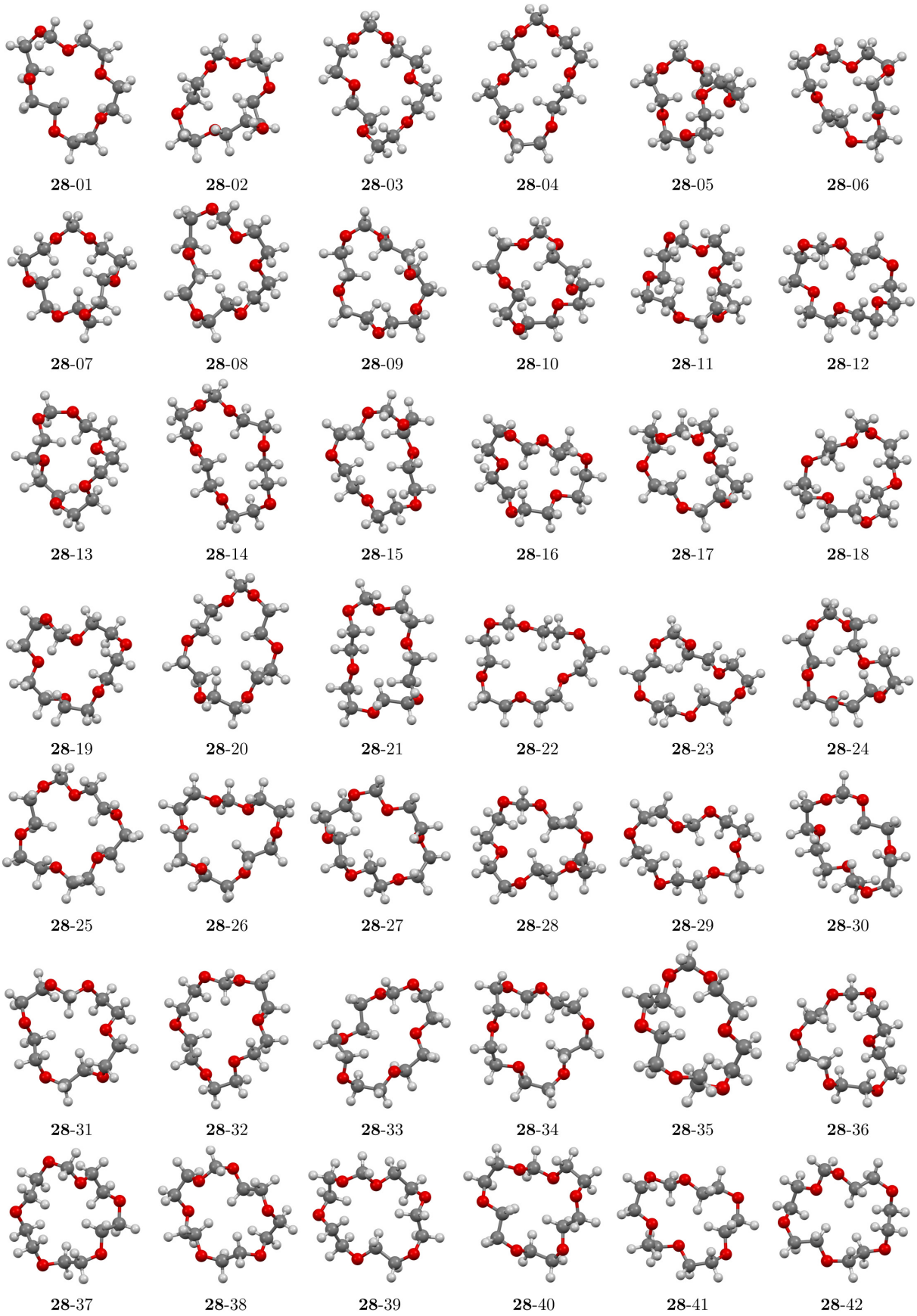


Figure S28: Crown **28** conformers optimized at M06-2X/6-31+G(d,p) level.

Table S28: Relative energy E (in kcal/mol) of crown **28** conformers computed at the M06-2X/6-31+G(d,p) level.

Conformer	E	Conformer	E	Conformer	E	Conformer	E	Conformer	E	Conformer	E
28-01	0.0	**28**-02	0.0	**28**-03	0.1	**28**-04	0.3	**28**-05	0.5	**28**-06	0.8
28-07	1.1	**28**-08	1.5	**28**-09	1.8	**28**-10	2.2	**28**-11	2.2	**28**-12	2.4
28-13	2.6	**28**-14	2.7	**28**-15	2.7	**28**-16	2.8	**28**-17	2.8	**28**-18	2.9
28-19	3.1	**28**-20	3.2	**28**-21	3.4	**28**-22	3.9	**28**-23	4.0	**28**-24	4.0
28-25	4.1	**28**-26	4.2	**28**-27	4.3	**28**-28	4.7	**28**-29	4.9	**28**-30	5.1
28-31	5.1	**28**-32	5.4	**28**-33	5.5	**28**-34	5.5	**28**-35	6.0	**28**-36	6.5
28-37	6.9	**28**-38	6.9	**28**-39	7.4	**28**-40	7.7	**28**-41	7.9	**28**-42	9.3

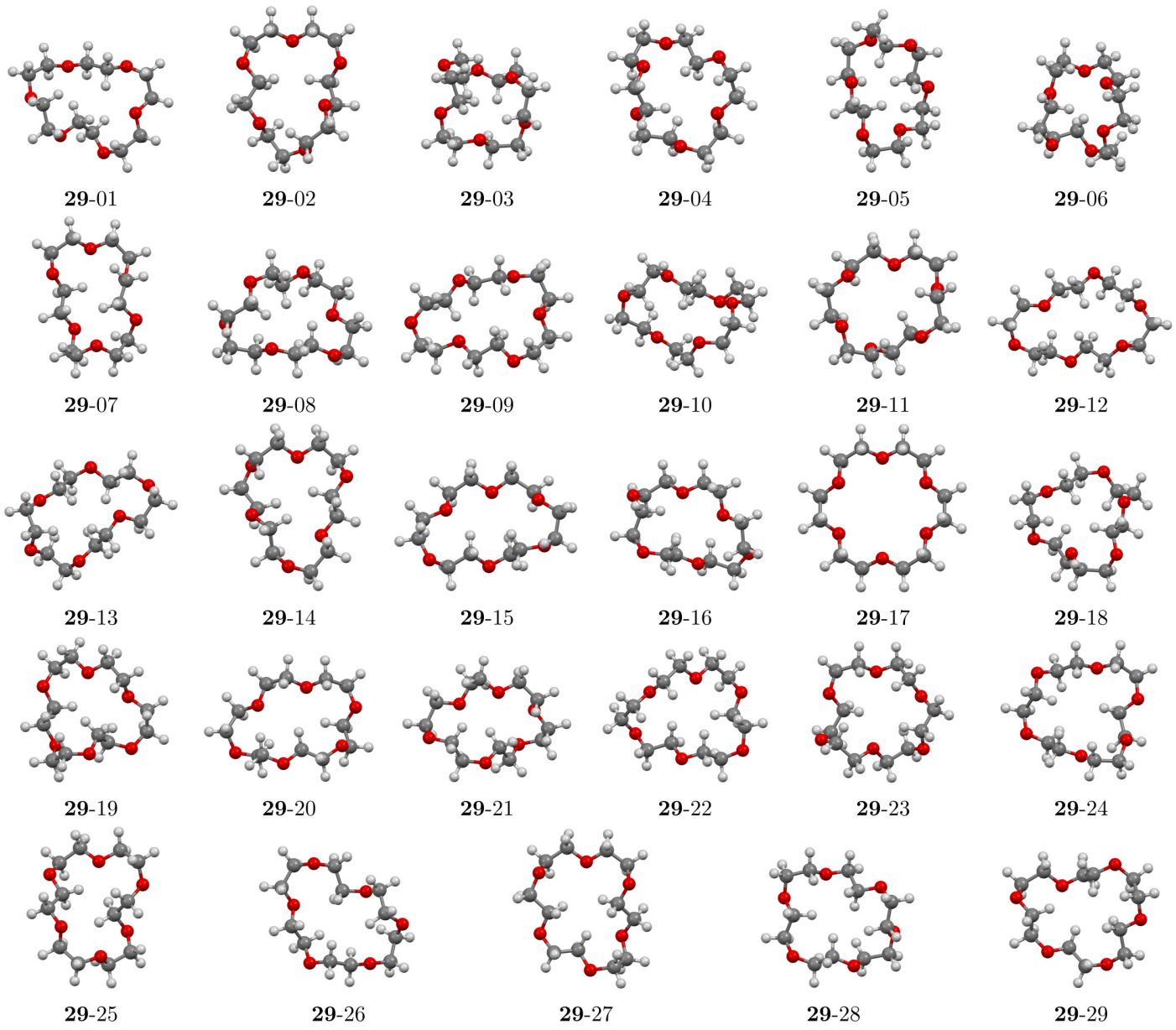


Figure S29: Crown **29** conformers optimized at M06-2X/6-31+G(d,p) level.

Table S29: Relative energy E (in kcal/mol) of crown **29** conformers computed at the M06-2X/6-31+G(d,p) level.

Conformer	E	Conformer	E	Conformer	E	Conformer	E	Conformer	E	Conformer	E
29-01	0.0	**29**-02	0.1	**29**-03	0.8	**29**-04	0.8	**29**-05	1.1	**29**-06	1.2
29-07	1.5	**29**-08	1.7	**29**-09	1.7	**29**-10	1.9	**29**-11	2.2	**29**-12	2.3
29-13	2.5	**29**-14	2.6	**29**-15	2.9	**29**-16	3.4	**29**-17	3.6	**29**-18	3.9
29-19	4.1	**29**-20	4.3	**29**-21	4.5	**29**-22	4.5	**29**-23	4.6	**29**-24	4.8
29-25	5.0	**29**-26	5.5	**29**-27	5.5	**29**-28	6.1	**29**-29	7.7		

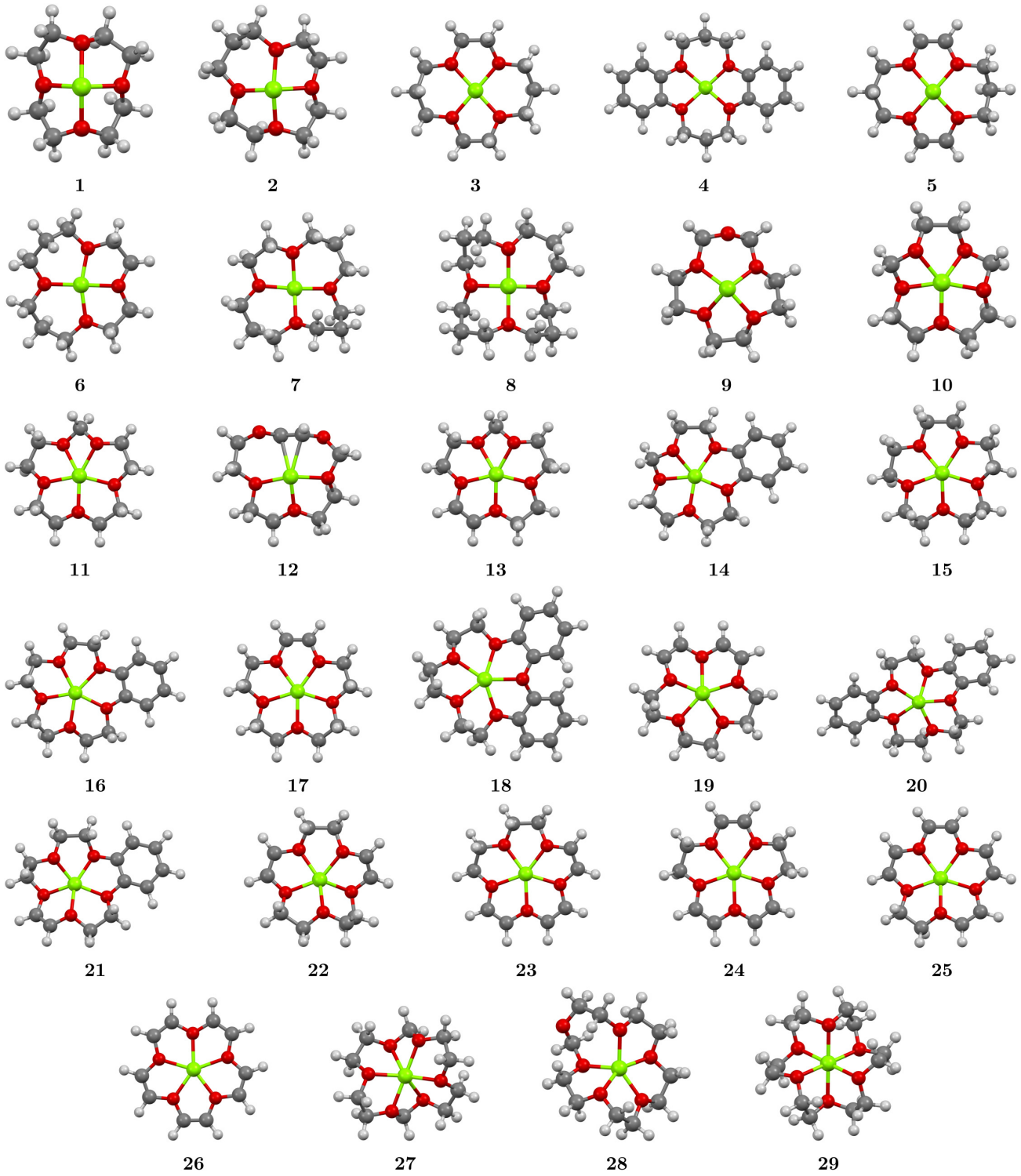


Figure S30: Structures of crown–magnesium complexes optimized at 6-311+G(d,p) level.

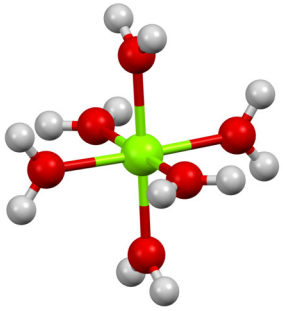


Figure S31: Structure of the magnesium ion coordinated with six water molecules optimized at 6-311+G(d,p) level.

Table S30: Changes in average Mg-O distances induced by the solvent, $\Delta\bar{r}_{\mathrm{r}}$(Mg-O); changes in Mg distances from the plane defined by crown's oxygen atoms, $\Delta r^{n_{\mathrm{O}}}_{\mathrm{plane}}$. All distances are presented in Å. $\Delta E^{\mathrm{CMg}}_{\mathrm{cl}}$, $\Delta E^{\mathrm{CMg}}_{\mathrm{xc}}$, and $\Delta E^{\mathrm{CMg}}_{\mathrm{int}}$ stand for the changes in classical, non-classical, and the overall crown–magnesium interaction energy caused by the presence of explicit solvent molecules. All energy components are presented in kcal/mol. Thin horizontal lines are used to emphasize that crowns **1**-**8**, **9**-**26**, and **27**-**29** contain 4, 5, and 6 oxygen atoms, respectively.

C	hydration induced changes				
	$\Delta\bar{r}_{\mathrm{r}}$(Mg-O)	$\Delta r^{n_{\mathrm{O}}}_{\mathrm{plane}}$	$\Delta E^{\mathrm{CMg}}_{\mathrm{cl}}$	$\Delta E^{\mathrm{CMg}}_{\mathrm{xc}}$	$\Delta E^{\mathrm{CMg}}_{\mathrm{int}}$
1	+0.034	+0.078			
2	+0.007	-0.430	42.4	8.8	51.2
3	+0.053	0.000	46.1	18.6	64.7
4	+0.043	-0.191	49.4	16.6	66.0
5	+0.038	-0.187	43.7	15.6	59.3
6	+0.047	-0.013	42.7	18.7	61.5
7	+0.073	-0.243	40.7	22.5	63.2
8	+0.107	-0.171	32.6	30.2	62.8
9	+0.015	-0.017			
10	+0.036	-0.210	35.9	17.8	53.7
11	+0.055	-0.057	45.0	19.0	64.0
12	-0.018	-0.353			
13	+0.046	+0.003	41.2	18.5	59.7
14	+0.046	-0.028	43.3	18.5	61.8
15	+0.081	-0.041	49.4	22.1	71.5
16	+0.063	-0.010			
17	+0.055	-0.005			
18	+0.073	-0.023			
19	+0.086	-0.066			
20	+0.109	-0.120			
21	+0.102	-0.004			
22	+0.099	-0.026			
23	+0.056	+0.008			
24	+0.049	-0.005			
25	+0.052	+0.035			
26	+0.047	+0.070			
27	+0.235	+0.110			
28	+0.142	-0.101			
29	+0.170	+0.252			

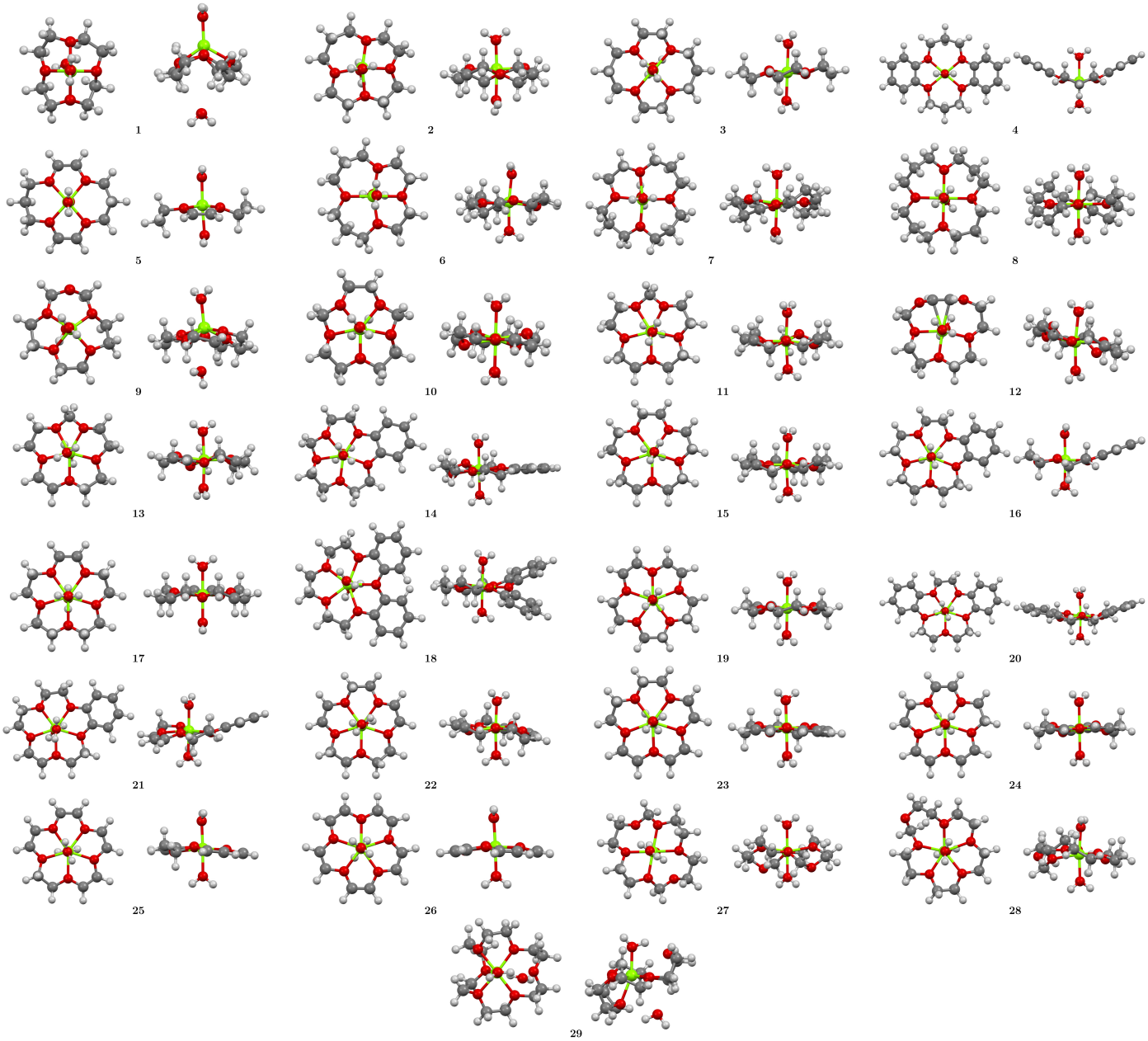


Figure S32: Structures of magnesium–crown complexes with the magnesium ion coordinated with two water molecules optimized at M06-2X/6-311+G(d,p) level.

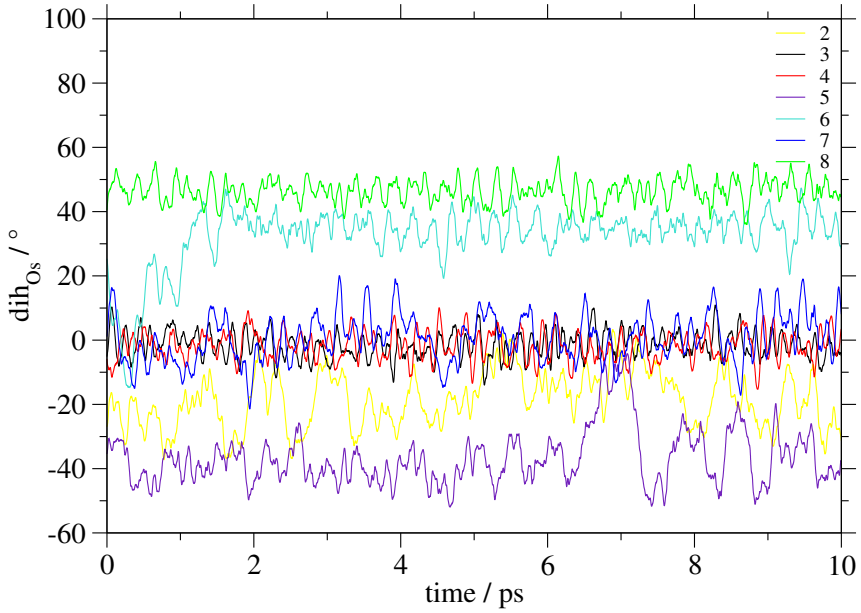


Figure S33: Time evolution of the dihedral angle d_{Os} formed by the four oxygen atoms in complexes of Mg^{2+} with crowns **2**-**8**.

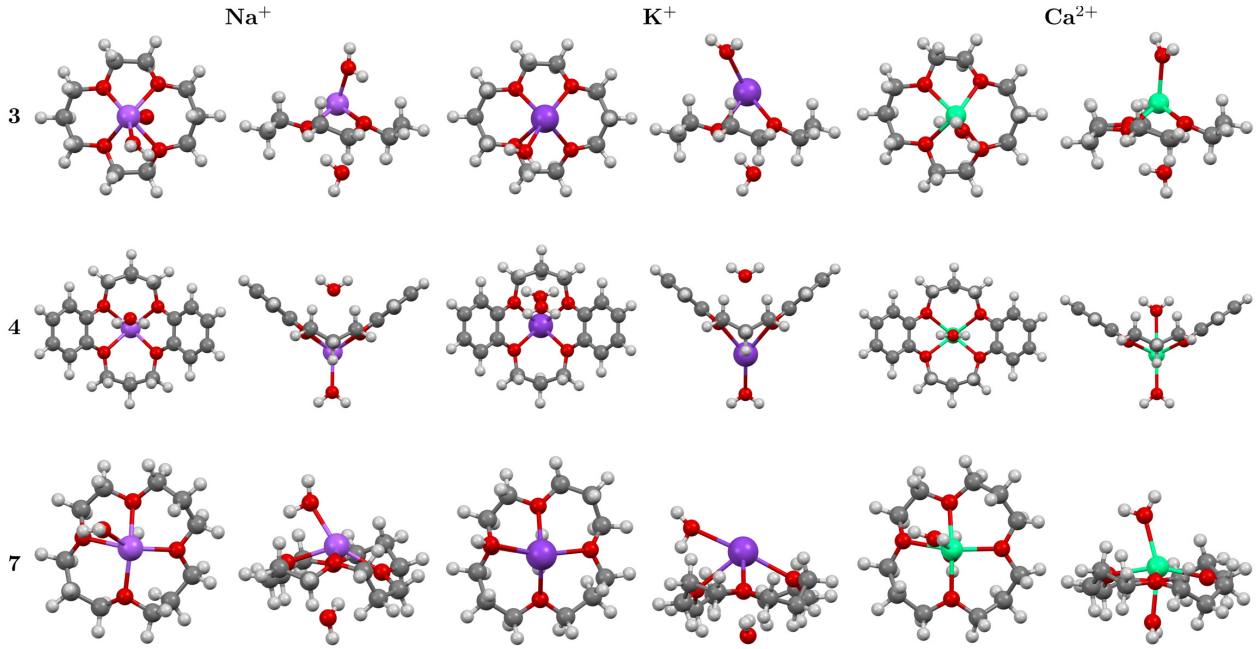


Figure S34: Structures of dihydrated complexes of Na^+ (the first and the second column), K^+ (the third and the fourth column), and Ca^{2+} (the fifth and the sixth column) with crowns **3**, **4**, and **7** optimized at M06-2X/6-311+G(d,p) level.

Table S31: Average IQA energy components (in kcal/mol) for Mg–solvent (MgS) and crown–solvent (CS) interaction: solvent deformation energy $\overline{E}^{S}_{def}$, solvent promotion energy $\overline{E}^{S}_{pro}$, as well as classical $\overline{E}^{MgS}_{cl}/\overline{E}^{CS}_{cl}$, non-classical $\overline{E}^{MgS}_{xc}/\overline{E}^{CS}_{xc}$, and overall $\overline{E}^{MgS}_{int}/\overline{E}^{CS}_{int}$ ion–solvent/crown–solvent interaction energy, abolute value of the difference in solvents' promotion energies ΔE^{S}_{pro}, abolute value of the difference in classical $\Delta E^{MgS}_{cl}/\Delta E^{CS}_{cl}$, non-classical $\Delta E^{MgS}_{xc}/\Delta E^{CS}_{xc}$, and overall $\Delta E^{MgS}_{int}/\Delta E^{CS}_{int}$ ion–solvent/crown–solvent interaction energy.

C	$\overline{E}^{S}_{def}$	$\overline{E}^{S}_{pro}$	$\overline{E}^{MgS}_{cl}/\overline{E}^{CS}_{cl}$	$\overline{E}^{MgS}_{xc}/\overline{E}^{CS}_{xc}$	$\overline{E}^{MgS}_{int}/\overline{E}^{CS}_{int}$	ΔE^{S}_{pro}	$\Delta E^{MgS}_{cl}/\Delta E^{CS}_{cl}$	$\Delta E^{MgS}_{xc}/\Delta E^{CS}_{xc}$	$\Delta E^{MgS}_{int}/\Delta E^{CS}_{int}$
2	0.1	32.3	-53.2 / 16.4	-11.6 / -38.8	-64.8 / -22.3	6.0	5.8 / 1.1	6.4 / 20.1	12.1 / 21.2
3	0.1	30.3	-54.1 / 18.2	-12.5 / -35.1	-66.6 / -16.9	0.0	0.0 / 0.0	0.0 / 0.0	0.0 / 0.0
4	0.1	30.8	-56.8 / 18.0	-12.8 / -34.8	-69.8 / -16.8	6.3	1.3 / 0.1	4.7 / 17.0	6.1 / 17.1
5	0.1	31.1	-56.3 / 17.6	-12.8 / -34.4	-69.1 / -16.8	9.0	1.0 / 0.3	6.0 / 26.1	7.0 / 25.7
6	0.1	30.6	-55.2 / 18.8	-12.4 / -35.8	-67.6 / -17.0	0.8	0.3 / 0.6	0.4 / 1.6	0.1 / 1.1
7	0.1	30.5	-56.2 / 20.2	-12.7 / -36.0	-69.0 / -15.8	0.2	0.5 / 0.2	0.4 / 0.3	0.9 / 0.4
8	0.1	32.0	-57.0 / 20.8	-13.0 / -38.1	-70.0 / -17.4	0.9	1.3 / 0.3	1.2 / 3.0	2.5 / 2.7
10	0.1	32.8	-54.0 / 16.6	-11.7 / -38.8	-65.6 / -22.3	0.2	0.1 / 0.0	0.0 / 0.1	0.1 / 0.2
11	0.2	31.0	-55.8 / 18.5	-13.4 / -35.3	-69.2 / -16.8	0.1	0.1 / 0.4	0.5 / 1.2	0.6 / 0.7
13	0.1	31.2	-55.4 / 17.8	-13.4 / -34.5	-68.7 / -16.6	0.5	0.3 / 0.2	0.1 / 1.4	0.4 / 1.5
14	0.1	30.8	-55.0 / 17.9	-13.4 / -34.4	-68.4 / -16.4	0.2	0.7 / 0.6	0.2 / 0.3	0.5 / 1.0
15	0.2	29.3	-57.3 / 20.4	-14.6 / -31.4	-71.9 / -11.0	0.0	0.0 / 0.0	0.0 / 0.0	0.0 / 0.0

Table S32: Distance of the metal ion from the center of mass defined by crown's oxygen atoms r(M–COM) (M = Mg, Na, K, Ca) in the optimized hydrated complexes $[CM(H_2O)_2]^{n+}$ (n = 2 for Mg and Ca; n = 1 for Na, K); average ion–oxygen distances $\overline{r}$(ion–O_i) (i = 1, 2, 3, 4) and the overall average ion–oxygen distance $\overline{r}$(ion–O); the number of solvent molecules n_S that coordinate the cation in the DFT-MD simulations. All distances are presented in Å.

crown	ion	r(M–COM)	$\overline{r}$(ion–O_1)	$\overline{r}$(ion–O_2)	$\overline{r}$(ion–O_3)	$\overline{r}$(ion–O_4)	$\overline{r}$(ion–O)	n_S
2	Mg	0.238	2.906	3.108	4.470	4.264	3.687	3.0
3	Mg	0.002	2.045	2.050	2.061	2.052	2.052	2.0
4	Mg	0.158	2.071	2.072	2.073	2.069	2.071	2.0
5	Mg	0.195	2.365	3.670	2.172	2.197	2.601	3.0
6	Mg	0.168	2.134	2.182	2.116	2.071	2.126	1.7
7	Mg	0.115	2.126	2.088	2.070	2.083	2.092	2.0
8	Mg	0.032	2.172	2.150	2.142	2.123	2.147	1.9
3	Na	1.075	2.128	2.098	2.069	2.174	2.117	1.2
3	K	1.739	2.927	3.093	3.271	3.055	3.086	3.3
3	Ca	1.059	2.637	2.615	2.575	2.635	2.616	3.9

Table S33: Selected geometric parameters in dihydrated complexes of Na^+, K^+, and Ca^{2+} with crowns **3**, **4**, and **7** optimized at M06-2X/6-31+G(d,p) level: difference in the two ion-S bond lengths, Δr(Mg–S); ion distances from the plane defined by crown's oxygen atoms/crown's and solvent's oxygen atoms, r^{O}_{plane} / $r^{O/S}_{plane}$.

crown	ion	Δr(Mg–S)	r^{O}_{plane}	$r^{O/S}_{plane}$
3	Na	1.089	1.062	0.491
3	K	1.273	1.724	0.827
3	Ca	0.912	1.048	0.029
4	Na	1.302	1.077	0.032
4	K	1.774	1.742	0.287
4	Ca	0.283	0.815	0.000
7	Na	0.902	0.842	0.576
7	K	1.150	1.609	1.400
7	Ca	0.100	0.526	0.109