Electronic Supplementary Information for Dalton Transactions


# 18-membered Cyclic Esters Derived from Glycolide and Lactide: Preparations, Structures and Coordination to Sodium Ions

Supporting Information

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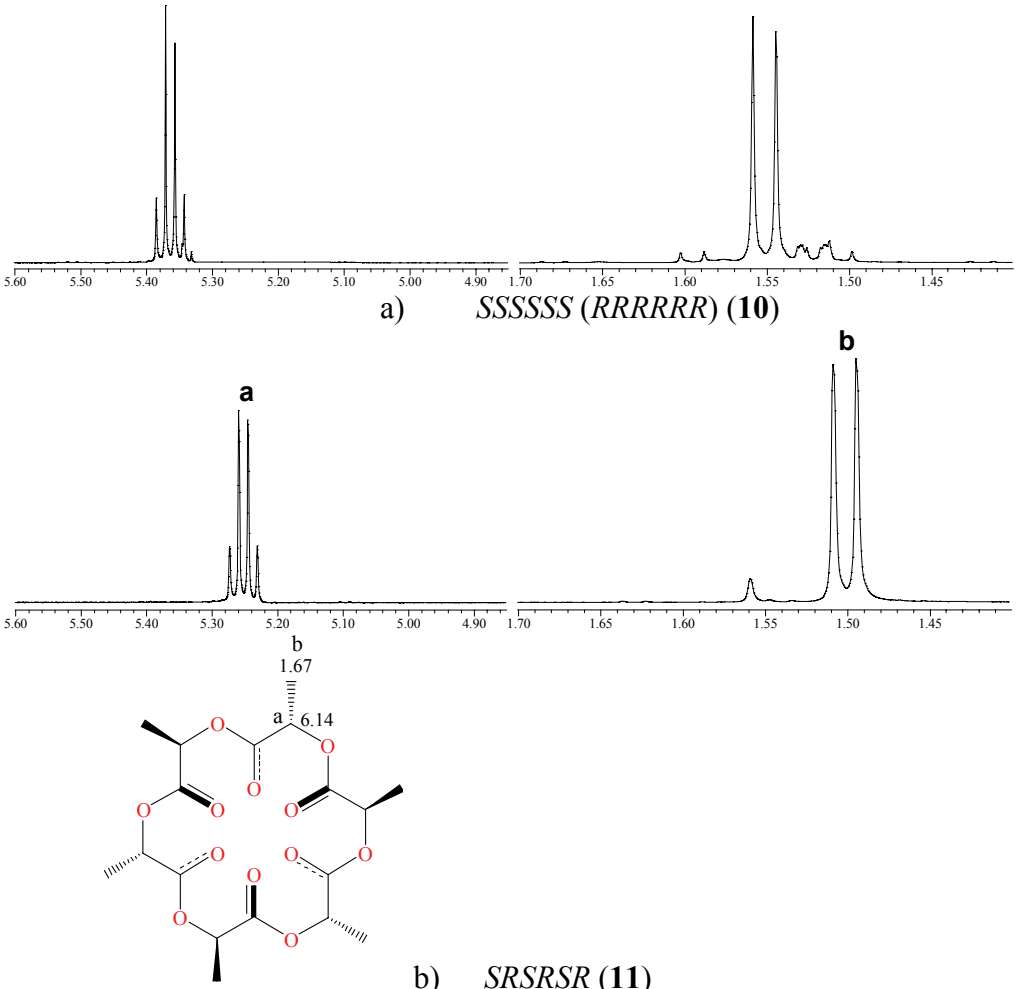
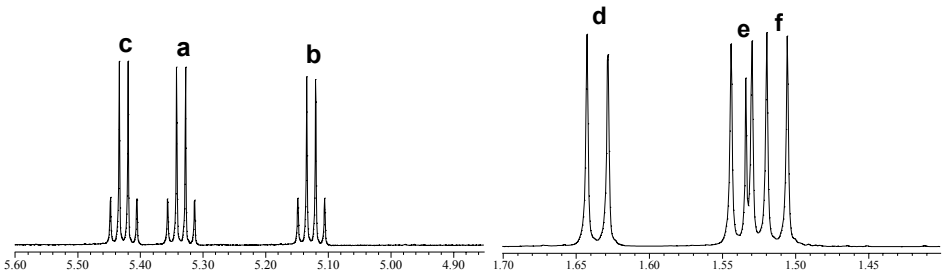
## $^1$H NMR and calculations for $A_6$ molecules

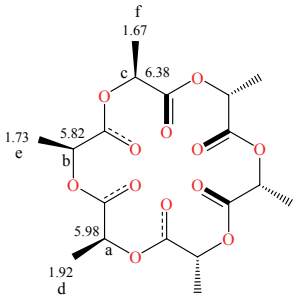



a) *SSSSSS* (*RRRRRR*) (**10**)

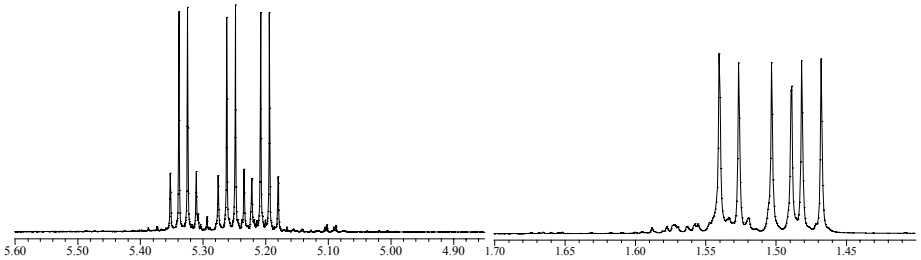
b) *SRSRSR* (**11**)

**Figure S1** $^1$H NMR spectra ($CDCl_3$, 500 MHz) of isomer **10** and **11**, and calculated chemical shifts for **11**.



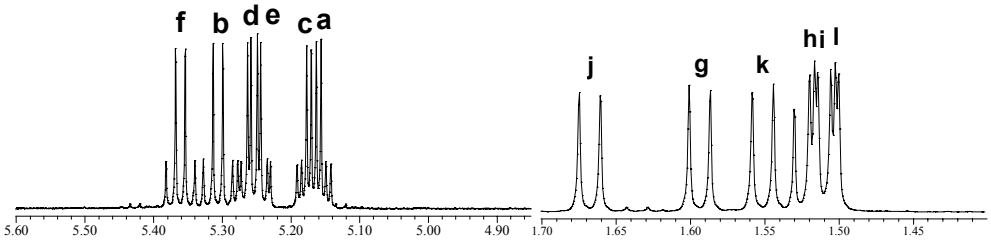




a) *SSSRRR* (**4**)




b) *SRRSRR* (*RSSRSS*) (**7**)

**Figure S2** $^{1}$H NMR spectra ($CDCl_3$, 500 MHz) of isomer **4**, and **7** and calculated chemical shifts for **4**.



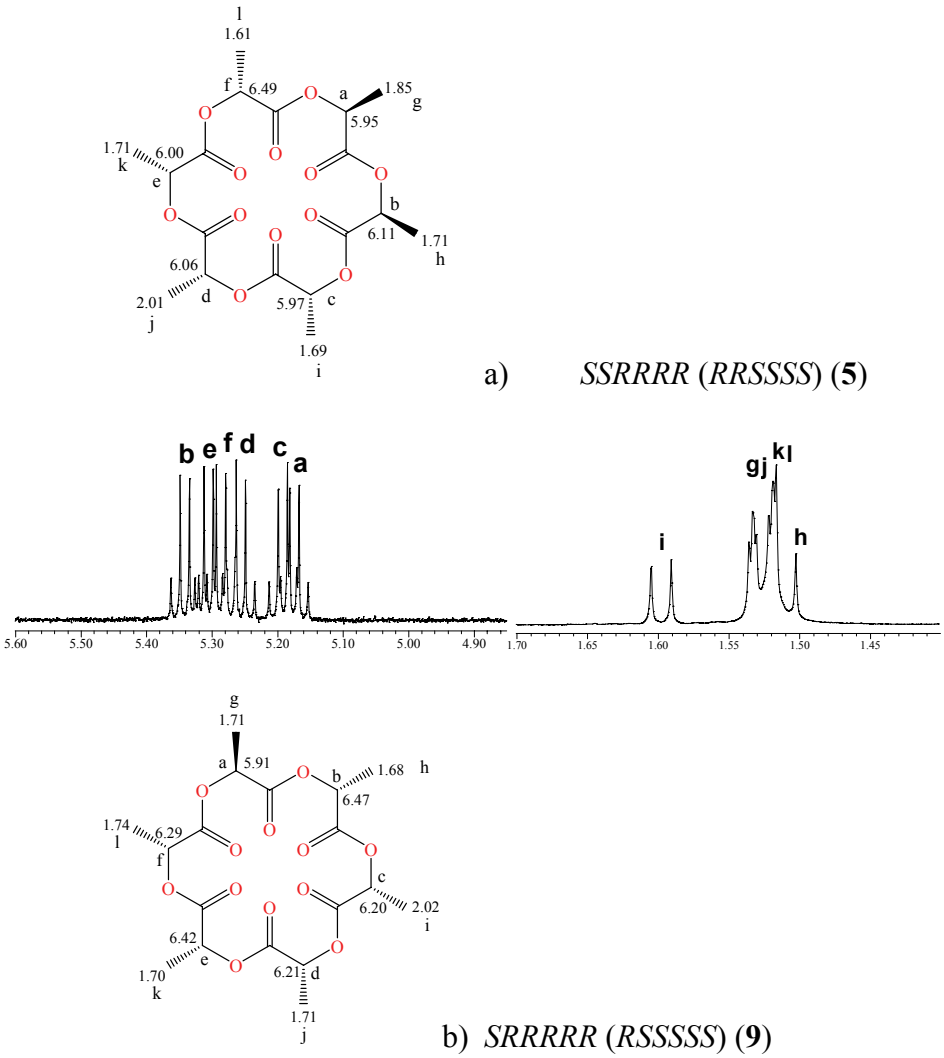
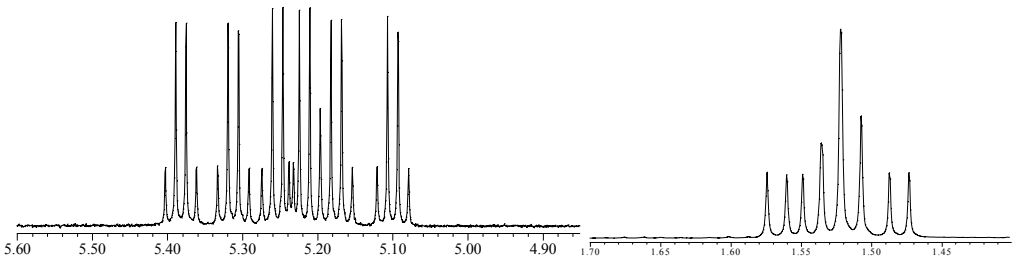
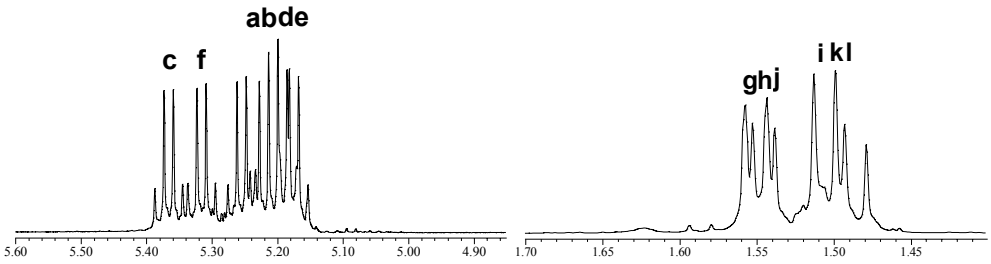
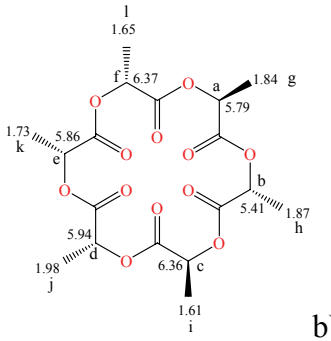



**Figure S3** $^{1}$H NMR spectra ($CDCl_3$, 500 MHz) and calculated chemical shifts of isomer **5** and **9**.




a) *SSRSRR* (*RRSRSS*) (**6**)




b) *SRSRRR* (*RSRSSS*) (**8**)

**Figure S4** $^{1}$H NMR spectra ($CDCl_3$, 500 MHz) of isomer **6** and **8** and calculated chemical shifts for **8**.

| Compound | **1** | **2** | **3** |
|---|---|---|---|
| Formula | $C_{25}$ $H_{25}$ B $N_2$ | $C_{40}$ $H_{38}$ B $N_2$ Na $O_{12}$ | $C_{12}$ $H_{12}$ $O_{12}$ |
| Formula weight | 364.28 | 772.52 | 348.22 |
| Cryst system | orthorhombic | triclinic | monoclinic |
| Space group | Pbca | $P\bar{1}$ | $P\,2_1/c$ |
| a(Å) | 15.2297(11) | 12.920(1) | 7.668(1) |
| b(Å) | 11.7129(8) | 13.473(1) | 5.901(1) |
| c(Å) | 22.5154(18) | 13.977(2) | 16.004(3) |
| α(deg) | | 80.972(4) | |
| β(deg) | | 64.021(4) | 102.408(9) |
| γ(deg) | | 63.137(5) | |
| $V$(Å$^3$) | 4016.4(5) | 1948.6(3) | 707.3(2) |
| $Z$ | 8 | 2 | 2 |
| d(calcd)(g/cm$^3$) | 1.205 | 1.317 | 1.635 |
| absorp coeff(mm$^{-1}$) | 0.015 | 0.106 | 0.151 |
| Reflections collected | 48843 | 44653 | 17673 |
| Independent reflections | 3750 | 6794 | 1618 |
| R1(F)[a] (all data) | 0.0533 | 0.0805 | 0.0514 |
| wR2($F^2$)[a] (all data) | 0.1131 | 0.1388 | 0.1097 |

**Table S1** Crystallographic details for DMAP-$BPh_3$ (**1**), $(CH_2C(O)O)_6Na^+BPh_4^-$ $\cdot(CH_3CN)_2$ (**2**) and $CH_2C(O)O)_6$(**3**).

[a]$R1(F) = \Sigma||F_o|-|F_c||/\Sigma|F_o|$

$wR2(F^2) = [\Sigma[w(F_o^2-F_c^2)^2]/\Sigma w(F_o^2)^2]^{1/2}$

| Compounds | **5** | **9** | **12** |
|---|---|---|---|
| Formula | $C_{18}H_{24}O_{12}$ | $C_{18}H_{24}O_{12}$ | $C_{44}H_{47}O_{12}NBNa$ |
| Formula weight | 432.37 | 432.37 | 815.62 |
| Cryst system | monoclinic | orthorhombic | monoclinic |
| Space group | $P2_1/n$ | $P2_12_12_1$ | $P\ 2_1/n$ |
| a(Å) | 8.432(1) | 10.663(2) | 9.986(2) |
| b(Å) | 16.513(2) | 11.967(3) | 19.900(3) |
| c(Å) | 14.964(2) | 16.489(4) | 21.545(4) |
| α(deg) | | | |
| β(deg) | 93.048(5) | | 90.376(6) |
| γ(deg) | | | |
| $V$(Å$^3$) | 2080.7(4) | 2104.1(8) | 4281(1) |
| Z | 4 | 4 | 4 |
| d(calcd)(g/cm$^3$) | 1.380 | 1.365 | 1.265 |
| absorp coeff(mm$^{-1}$) | 0.118 | 0.116 | 0.100 |
| Reflections collected | 34054 | 16936 | 41693 |
| Independent reflections | 4751 | 2124 | 7541 |
| R1(F) (all data) | 0.0573 | 0.0387 | 0.0895 |
| wR2(F$^2$) (all data) | 0.0905 | 0.0881 | 0.0929 |

**Table S2** Crystallographic details for compounds (*S*,*S*,*R*,*R*,*R*,*R*)- $(CH_3CHC(O)O)_6$ (**5**), (*S*,*R*,*R*,*R*,*R*,*R*)- $(CH_3CHC(O)O)_6$ (**9**) and Na[(*S*,*R*,*S*,*R*,*S*,*R*)-$(CH_3CHC(O)O)_6$]$BPh_4$·$CH_3CN$ (**12**).
DMAP-$BPh_3$ (**1**)

| | | | |
|---|---|---|---|
| B-C(7) | 1.631(2) | B-C(13) | 1.636(2) |
| B-N(1) | 1.636(2) | B-C(1) | 1.637(2) |
| C(7)-B-C(13) | 112.03(12) | C(7)-B-N(1) | 108.65(11) |
| C(13)-B-N(1) | 104.74(11) | C(7)-B-C(1) | 110.77(12) |
| C(13)-B-C(1) | 111.89(12) | N(1)-B-C(1) | 108.47(11) |
| C(23)-N(1)-B | 125.17(12) | C(19)-N(1)-B | 119.06(12) |
| C(23)-N(1)-C(19) | 115.74(13) | | |

$(CH_2C(O)O)_6Na^+BPh_4^-\cdot(CH_3CN)_2$ (**2**)

| | | | |
|---|---|---|---|
| Na-O(7) | 2.346(2) | Na-O(1) | 2.354(2) |
| Na-O(11) | 2.354(2) | Na-O(9) | 2.400(2) |
| Na-N(1) | 2.470(2) | Na-N(2) | 2.521(2) |
| O(1)-C(31) | 1.195(2) | O(2)-C(29) | 1.196(3) |
| O(3)-C(33) | 1.203(3) | O(7)-C(35) | 1.201(2) |
| O(9)-C(37) | 1.207(2) | O(11)-C(39) | 1.207(2) |
| O(7)-Na-O(1) | 87.98(6) | O(7)-Na-O(11) | 92.56(5) |
| O(1)-Na-O(11) | 171.03(6) | O(7)-Na-O(9) | 86.54(5) |
| O(1)-Na-O(9) | 95.53(6) | O(11)-Na-O(9) | 93.44(5) |
| O(7)-Na-N(1) | 170.91(7) | O(9)-Na-N(2) | 175.17(7) |
| N(1)-Na-N(2) | 98.73(7) | C(37)-O(9)-Na | 165.7(1) |

$(C_2H_2O_2)_6$ (**3**)

| | | | |
|---|---|---|---|
| O(1)-C(1) | 1.199(2) | O(2)-C(3) | 1.205(2) |
| O(3)-C(5) | 1.199(2) | O(4)-C(1) | 1.350(2) |
| O(4)-C(6)#1 | 1.438(2) | O(5)-C(3) | 1.338(2) |
| O(5)-C(2) | 1.432(2) | O(6)-C(5) | 1.343(2) |
| O(6)-C(4) | 1.437(2) | O(1)-C(1)-O(4) | 124.3(1) |
| O(1)-C(1)-C(2) | 126.0(1) | O(4)-C(1)-C(2) | 109.7(1) |
| O(5)-C(2)-C(1) | 109.8(1) | C(1)-O(4)-C(6)#1 | 114.1(1) |

#1 is the symmetry operation: -x, -y, -z

(*SSRRRR*)-$(CH_3CHC(O)O)_6$ (**5**)

| | | | |
|---|---|---|---|
| O(1)-C(1) | 1.200(1) | O(3)-C(4) | 1.195(1) |
| O(5)-C(7) | 1.202(1) | O(7)-C(10) | 1.195(2) |
| O(9)-C(13) | 1.202(2) | O(11)-C(16) | 1.204(1) |
| O(2)-C(1) | 1.354(1) | O(4)-C(4) | 1.338(2) |
| O(6)-C(7) | 1.339(1) | O(8)-C(10) | 1.353(1) |
| O(10)-C(13) | 1.333(2) | O(12)-C(16) | 1.336(2) |
| O(2)-C(2) | 1.445(1) | O(4)-C(5) | 1.453(1) |
| O(6)-C(8) | 1.442(1) | O(8)-C(11) | 1.446(2) |
| O(10)-C(14) | 1.458(2) | O(12)-C(17) | 1.442(1) |
| C(1)-O(2)-C(2) | 114.5 (1) | C(4)-O(4)-C(5) | 114.0 (1) |
| C(7)-O(6)-C(8) | 116.8(1) | C(10)-O(8)-C(11) | 116.3(1) |
| C(13)-O(10)-C(14) | 117.3(1) | C(16)-O(12)-C(17) | 116.7(1) |

(*SRRRRR*)-$(CH_3CHC(O)O)_6$ (**9**)

| | | | |
|---|---|---|---|
| O(1)-C(1) | 1.194(3) | O(3)-C(4) | 1.202(3) |

| | | | |
|---|---|---|---|
| O(5)-C(7) | 1.198(3) | O(7)-C(10) | 1.198(3) |
| O(9)-C(13) | 1.201(3) | O(11)-C(16) | 1.203(3) |
| O(2)-C(2) | 1.444(3) | C(2)-C(3) | 1.511(4) |
| C(2)-C(4) | 1.518(4) | O(4)-C(5) | 1.457(3) |
| C(5)-C(6) | 1.513(4) | C(5)-C(7) | 1.517(4) |
| O(6)-C(8) | 1.444(3) | C(8)-C(9) | 1.513(4) |
| C(8)-C(10) | 1.519(4) | O(8)-C(11) | 1.450(3) |
| O(10)-C(14) | 1.441(3) | C(14)-C(15) | 1.521(4) |
| C(14)-C(16) | 1.517(4) | O(12)-C(17) | 1.438(3) |
| C(17)-C(18) | 1.512(4) | C(1)-C(17) | 1.519(4) |
| C(1)-O(2)-C(2) | 114.2(2) | C(4)-O(4)-C(5) | 117.2(2) |
| C(7)-O(6)-C(8) | 114.8 (2) | C(10)-O(8)-C(11) | 114.6 (2) |
| C(13)-O(10)-C(14) | 115.8(2) | C(16)-O(12)-C(17) | 116.4(2) |

(*SRSRSR*)- $(CH_3CHC(O)O)_6$ (**11**)

| | | | |
|---|---|---|---|
| O(1)-C(1) | 1.190(2) | O(2)-C(1) | 1.356(3) |
| O(2)-C(2) | 1.450(2) | C(1)-C(2)#1 | 1.526(2) |
| C(2)-C(3) | 1.515(3) | C(2)-C(1)#2 | 1.526(2) |
| C(1)-O(2)-C(2) | 114.4(2) | O(1)-C(1)-O(2) | 124.4(2) |
| O(1)-C(1)-C(2)#1 | 126.2(2) | O(2)-C(1)-C(2)#1 | 109.4(2) |
| O(2)-C(2)-C(3) | 107.2(2) | O(2)-C(2)-C(1)#2 | 107.2(1) |
| C(3)-C(2)-C(1)#2 | 110.9(2) | | |

#1 is the symmetry operation: x-y, x, -z
#2 is the symmetry operation: y, -x+y, -z

Na[(*S*,*R*,*S*,*R*,*S*,*R*)- $(CH_3CHC(O)O)_6]_2BPh_4 \cdot CH_3CN$ (**12**)

| | | | |
|---|---|---|---|
| Na-O(5A)#1 | 2.317(1) | Na-O(5B) | 2.322(1) |
| Na-O(3B)#2 | 2.339(1) | Na-O(1A)#1 | 2.342(1) |
| Na-O(1B) | 2.359(1) | Na-O(3A) | 2.368(1) |
| O(1A)-C(1A) | 1.204(2) | O(3A)-C(4A) | 1.208(2) |
| O(5A)-C(7A) | 1.202(2) | O(1B)-C(1B) | 1.205(2) |
| O(3B)-C(4B) | 1.203(2) | O(5B)-C(7B) | 1.204(2) |
| O(5A)#1-Na-O(5B) | 168.74(5) | O(5A)#1-Na-O(3B)#2 | 77.60(5) |
| O(5B)-Na-O(3B)#2 | 94.66(5) | O(5A)#1-Na-O(1A)#1 | 88.51(5) |
| O(5B)-Na-O(1A)#1 | 100.32(5) | O(3B)#2-Na-O(1A)#1 | 163.36(5) |
| O(5A)#1-Na-O(1B) | 97.30(5) | O(5B)-Na-O(1B) | 90.93(5) |
| O(3B)#2-Na-O(1B) | 90.92(5) | O(1A)#1-Na-O(1B) | 81.70(5) |
| O(5A)#1-Na-O(3A) | 91.82(5) | O(5B)-Na-O(3A) | 80.59(5) |
| O(3B)#2-Na-O(3A) | 94.91(5) | O(1A)#1-Na-O(3A) | 94.64(5) |
| O(1B)-Na-O(3A) | 170.05(5) | C(1A)-O(1A)-Na#1 | 161.1(1) |
| C(4A)-O(3A)-Na | 159.7(1) | C(7A)-O(5A)-Na#1 | 165.7(1) |

#1 is the symmetry operation: -x+2, -y, -z
#2 is the symmetry operation: -x+1, -y, -z

**Table S3.** Selected bond distances (Å) and angles (°) for complexes **1**, **2**, **3**, **5**, **9**, **11**, **12**.