# Supporting Information

# for

# Self-assembly of $Ru_4$ and $Ru_8$ assemblies by coordination using organometallic $Ru(II)_2$ precursors: Synthesis, characterization and properties

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**Infrared and NMR spectra of the macrocycles 2a, 2b and 2c and solid-state packing diagram of macrocycle 2a.**

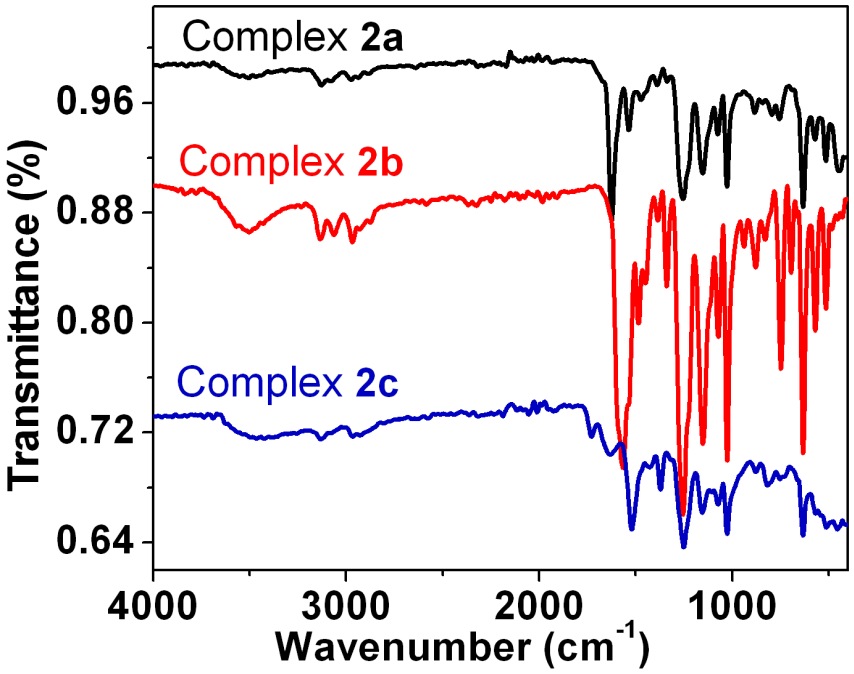


**Figure S1:** Infrared spectrum of the macrocycles **2a**–**2c**.

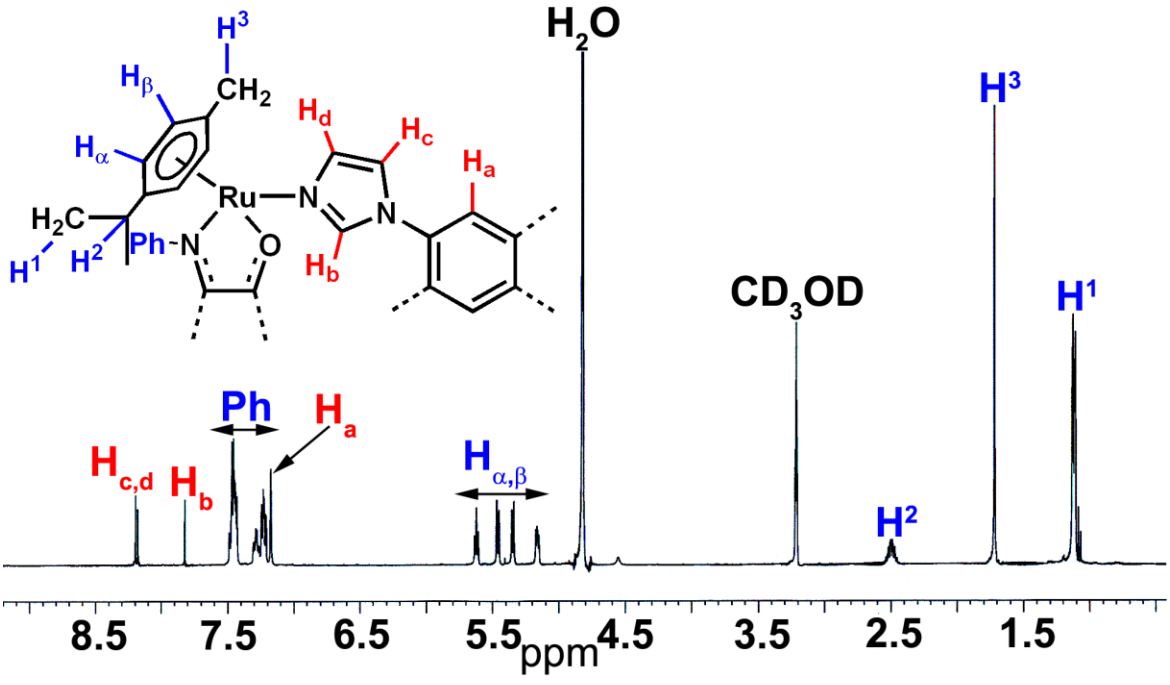


**Figure S2:** $^{1}$H NMR spectrum of the macrocycle **2b** recorded in $CD_3OD$ with the peak assignments.

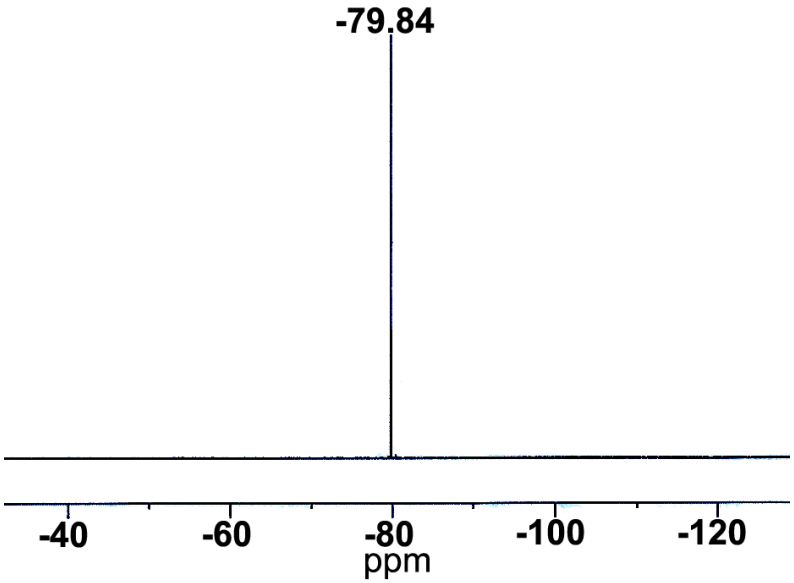


**Figure S3:** $^{19}F$ NMR spectrum of the macrocycle **2b** recorded in $CD_3OD$ with the peak assignment.

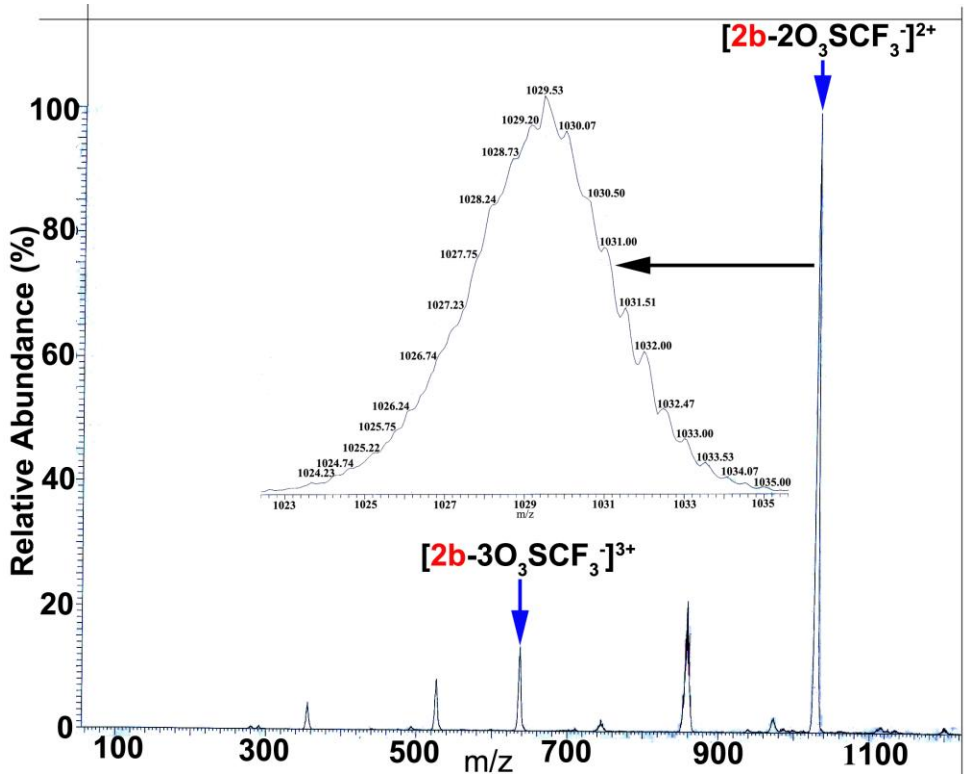


**Figure S4:** ESIMS spectrum of the macrocycle **2b** recorded in acetonitrile. Inset: experimentally observed isotopic distribution for the [**2b** – $2O_3SCF_3^-$]$^{2+}$ fragment.

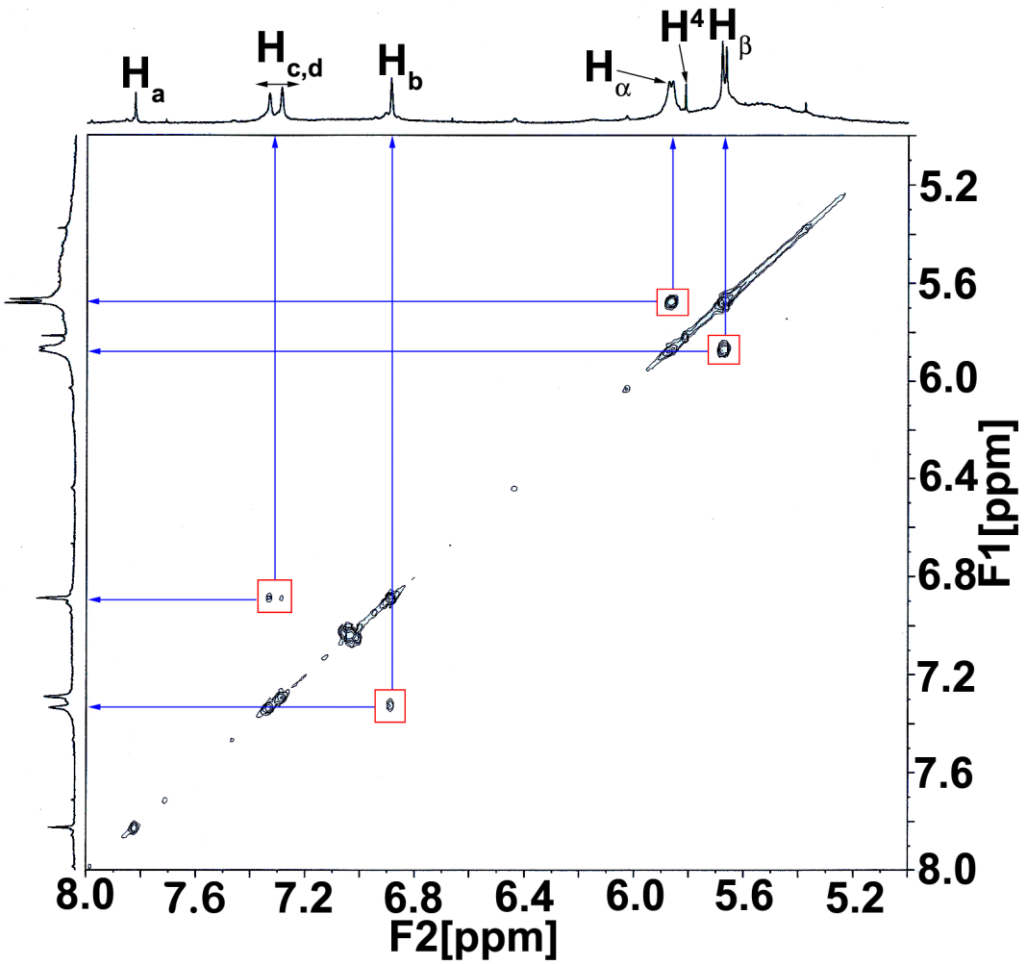


**Figure S5:** $^{1}H–^{1}H$ NMR spectrum of the macrocyclic cage **2c** recorded in $CD_3CN$.

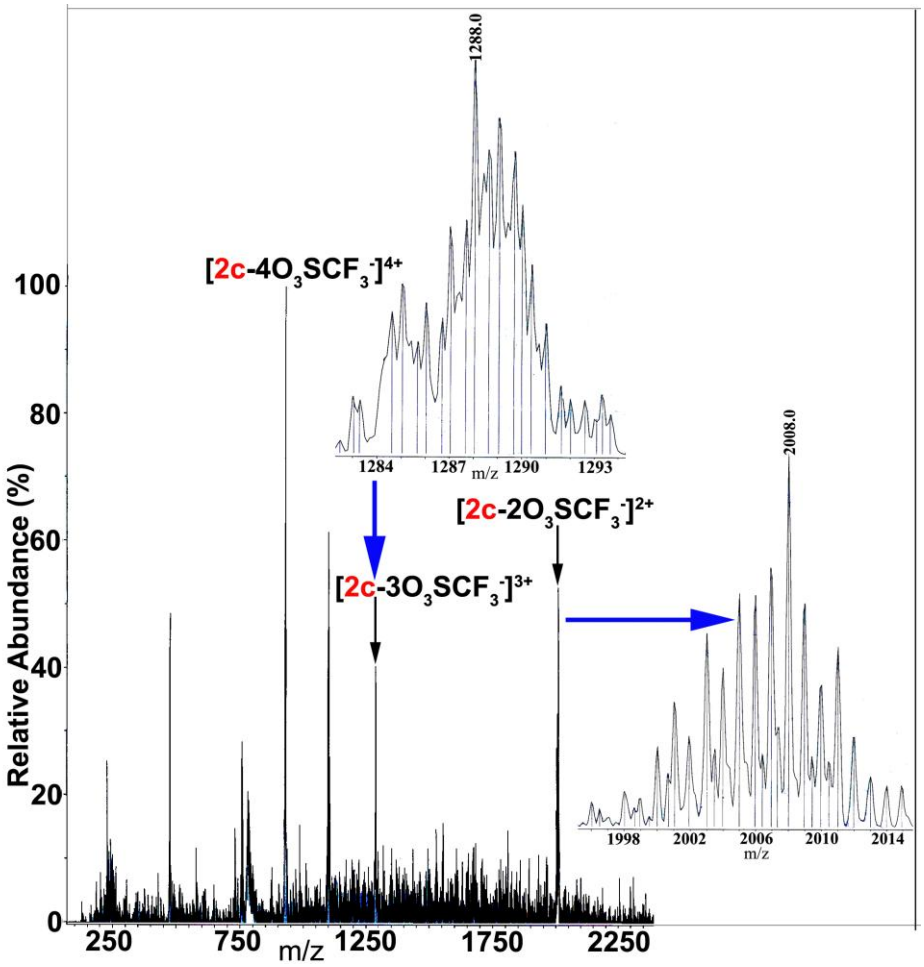


**Figure S6:** ESIMS spectrum of the macrocyclic cage **2c** recorded in acetonitrile. Inset: experimentally observed isotopic distribution for the [**2c** – $2O_3SCF_3^-$]$^{2+}$ and [**2c** – $3O_3SCF_3^-$]$^{3+}$ fragments.

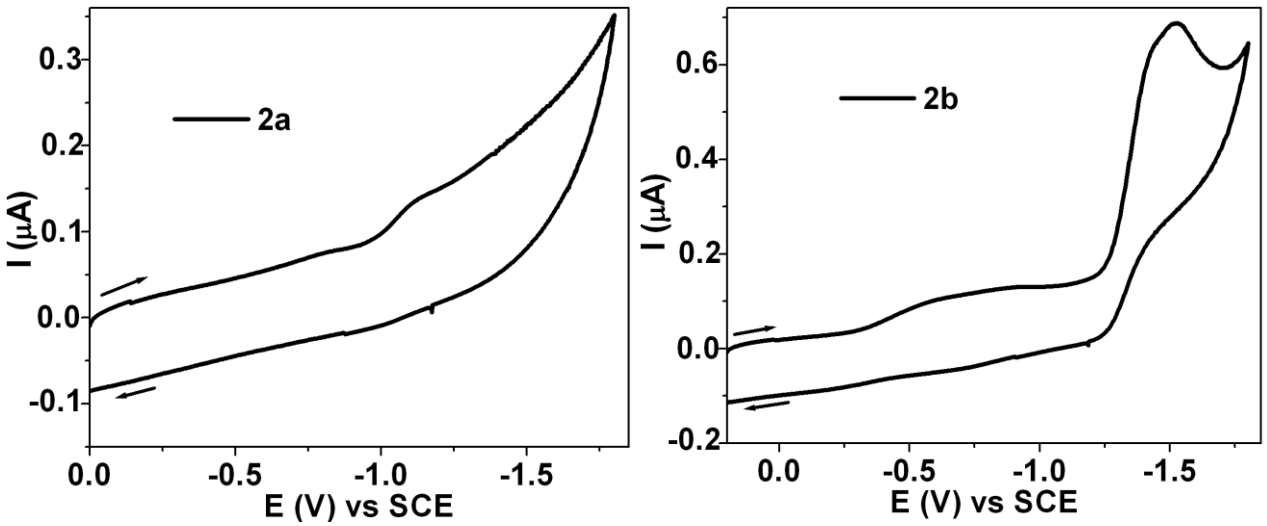


**Figure S7:** Cyclic voltammogram of macrocycle **2a** (left) and **2b** (right) performed in $CH_2Cl_2$/0.1M $(n\text{-}Bu)_4NPF_6$ with a scan rate of 100 mV $s^{-1}$ versus SCE at 298 K.

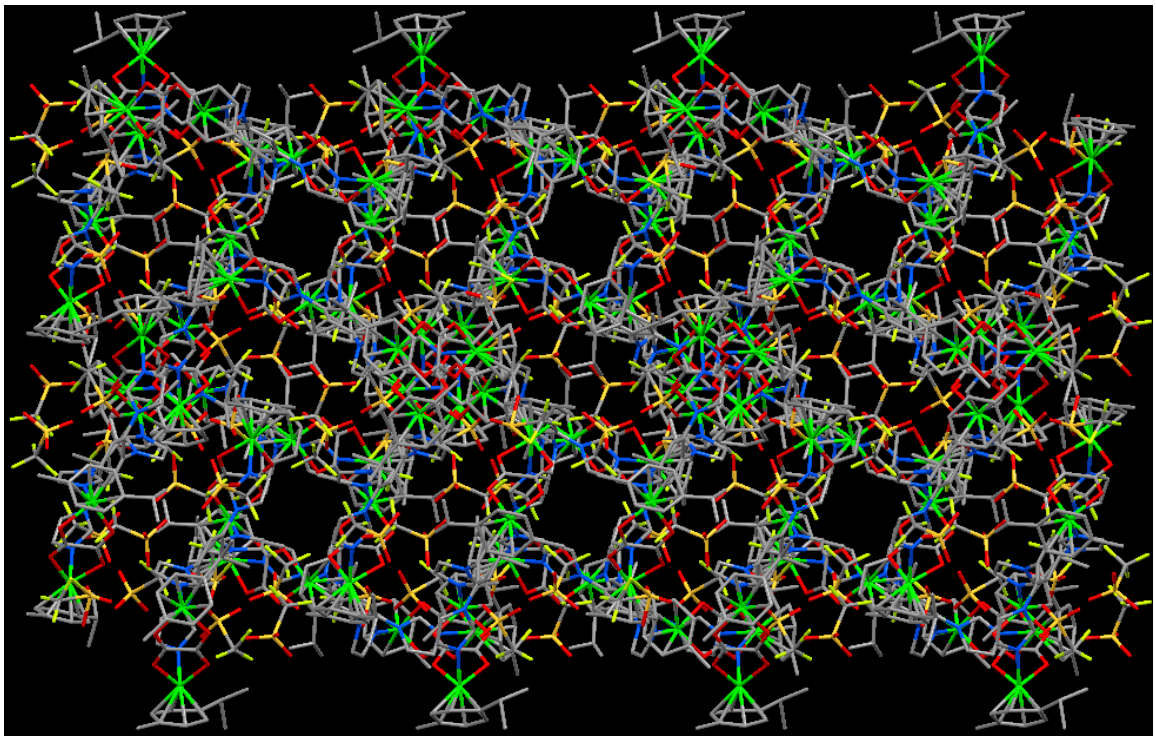

**Figure S8:** Solid-state packing diagram along crystallographic *c*-axis of macrocycle **2a**.

**Table S1:** Selected bond distances (Å) and angles (deg) for **2a**.

| **2a** | | | | | |
|---|---|---|---|---|---|
| Ru(3)-O(5) | 2.117(14) | Ru(3)-N(6) | 2.135(13) | Ru(3)-O(6) | 2.139(11) |
| Ru(3)-C(25) | 2.15(2) | Ru(3)-C(21) | 2.16(3) | Ru(3)-C(23) | 2.16(3) |
| Ru(3)-C(24) | 2.14(4) | Ru(3)-C(22) | 2.17(2) | Ru(3)-C(26) | 2.17(3) |
| Ru(4)-C(36) | 2.12(2) | Ru(4)-O(8) | 2.143(10) | Ru(4)-C(35) | 2.15(2) |
| Ru(4)-C(32) | 2.161(17) | Ru(4)-N(8) | 2.159(11) | Ru(4)-O(7) | 2.164(13) |
| Ru(4)-C(33) | 2.185(16) | Ru(4)-C(31) | 2.22(3) | Ru(4)-C(34) | 2.224(17) |
| O(5)-Ru(3)-N(6) | 83.4(5) | O(5)-Ru(3)-O(6) | 78.9(5) | | |
| N(6)-Ru(3)-O(6) | 84.7(5) | O(5)-Ru(3)-C(25) | 109.0(13) | | |
| N(6)-Ru(3)-C(25) | 167.3(12) | O(6)-Ru(3)-C(25) | 100.1(11) | | |
| O(5)-Ru(3)-C(21) | 170.9(10) | N(6)-Ru(3)-C(21) | 98.1(10) | | |
| O(6)-Ru(3)-C(21) | 110.2(10) | C(25)-Ru(3)-C(21) | 69.2(12) | | |
| O(5)-Ru(3)-C(23) | 99.2(14) | N(6)-Ru(3)-C(23) | 107.7(10) | | |
| O(6)-Ru(3)-C(23) | 167.2(10) | C(25)-Ru(3)-C(23) | 68.4(14) | | |
| C(21)-Ru(3)-C(23) | 71.8(14) | O(5)-Ru(3)-C(24) | 90.4(13) | | |
| N(6)-Ru(3)-C(24) | 144.4(12) | O(6)-Ru(3)-C(24) | 128.5(11) | | |
| C(25)-Ru(3)-C(24) | 36.8(12) | C(21)-Ru(3)-C(24) | 83.2(14) | | |
| C(23)-Ru(3)-C(24) | 38.8(11) | O(5)-Ru(3)-C(22) | 130.5(13) | | |
| N(6)-Ru(3)-C(22) | 92.5(9) | O(6)-Ru(3)-C(22) | 150.1(14) | | |
| C(25)-Ru(3)-C(22) | 77.4(10) | C(21)-Ru(3)-C(22) | 40.7(11) | | |
| C(23)-Ru(3)-C(22) | 35.6(13) | C(24)-Ru(3)-C(22) | 65.4(13) | | |

| | | | |
|---|---|---|---|
| O(5)-Ru(3)-C(26) | 144.2(10) | N(6)-Ru(3)-C(26) | 130.5(12) |
| O(6)-Ru(3)-C(26) | 91.7(8) | C(25)-Ru(3)-C(26) | 38.3(12) |
| C(21)-Ru(3)-C(26) | 37.8(9) | C(23)-Ru(3)-C(26) | 82.5(14) |
| C(24)-Ru(3)-C(26) | 68.6(15) | C(22)-Ru(3)-C(26) | 67.7(11) |
| C(36)-Ru(4)-O(8) | 151.6(9) | C(36)-Ru(4)-C(35) | 37.1(7) |
| O(8)-Ru(4)-C(35) | 163.1(9) | C(36)-Ru(4)-C(32) | 68.5(8) |
| O(8)-Ru(4)-C(32) | 91.7(6) | C(35)-Ru(4)-C(32) | 81.2(8) |
| C(36)-Ru(4)-N(8) | 92.5(7) | O(8)-Ru(4)-N(8) | 84.5(4) |
| C(35)-Ru(4)-N(8) | 111.9(8) | C(32)-Ru(4)-N(8) | 129.1(8) |
| C(36)-Ru(4)-O(7) | 129.5(9) | O(8)-Ru(4)-O(7) | 78.1(4) |
| C(35)-Ru(4)-O(7) | 99.4(10) | C(32)-Ru(4)-O(7) | 146.4(7) |
| N(8)-Ru(4)-O(7) | 82.1(4) | C(36)-Ru(4)-C(33) | 79.6(8) |
| O(8)-Ru(4)-C(33) | 97.5(6) | C(35)-Ru(4)-C(33) | 67.6(8) |
| C(32)-Ru(4)-C(33) | 38.1(6) | N(8)-Ru(4)-C(33) | 167.0(8) |
| O(7)-Ru(4)-C(33) | 110.9(8) | C(36)-Ru(4)-C(31) | 39.0(7) |
| O(8)-Ru(4)-C(31) | 113.4(8) | C(35)-Ru(4)-C(31) | 69.9(9) |
| C(32)-Ru(4)-C(31) | 38.7(7) | N(8)-Ru(4)-C(31) | 97.8(6) |
| O(7)-Ru(4)-C(31) | 168.5(8) | C(33)-Ru(4)-C(31) | 69.5(8) |
| C(36)-Ru(4)-C(34) | 67.5(8) | O(8)-Ru(4)-C(34) | 124.5(7) |
| C(35)-Ru(4)-C(34) | 38.6(7) | C(32)-Ru(4)-C(34) | 67.1(8) |
| N(8)-Ru(4)-C(34) | 148.8(8) | O(7)-Ru(4)-C(34) | 92.4(7) |