

## Supplementary Materials

### Synthesis and Antiparasitic Activity of New Trithiolato-Bridged Dinuclear Ruthenium(II)-Arene - Carbohydrate Conjugates

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## Experimental chemistry

### 1. General

Chemicals were purchased from Aldrich, Alfa Aesar, Acros Organics, ABCR, and TCI Chemicals and used without further purification. Reactions were performed under inert atmosphere (N<sub>2</sub>) using Schlenk techniques with dry solvents (Acros Organics) preserved over molecular sieves. <sup>1</sup>H (400.13 MHz) and <sup>13</sup>C (100.62 MHz) NMR spectra were recorded on a Bruker Avance II 400 spectrometer at 298 K. The chemical shifts are reported in parts per million (ppm) and referenced to residual solvent peaks [1] (CDCl<sub>3</sub>, <sup>1</sup>H δ 7.26, <sup>13</sup>C{<sup>1</sup>H} δ 77.16 ppm; DMSO-*d*<sub>6</sub>, <sup>1</sup>H δ 2.50, <sup>13</sup>C{<sup>1</sup>H} δ 39.52 ppm), and coupling constants (*J*) are reported in hertz (Hz). High resolution electrospray ionization mass spectra (ESI-MS) were carried out by the Mass Spectrometry and Protein Analyses Services at DCBP and were obtained on a LTQ Orbitrap XL ESI (Thermo) operated in positive ion mode. Thermal elemental analyses were carried out by the Mass Spectrometry and Protein Analyses Services at DCBP and were obtained on a Flash 2000 Organic Elemental Analyzer (Thermo Scientific). Reactions were monitored by TLC using Merck TLC silica gel coated aluminium sheets 60 F254 and visualized with UV at 254 nm, and KMnO<sub>4</sub> stain. Compounds were purified by column flash chromatography on silica gel using the elution systems indicated.

### Abbreviations

*BF<sub>3</sub>·Et<sub>2</sub>O* – Boron trifluoride diethyl etherate

*DMAP* – 4-(Dimethylamino)-pyridine

*DMF* – Dimethylformamide

*EDCI* – *N*-(3-Dimethylaminopropyl)-*N'*-ethylcarbodiimide hydrochloride

*EtOAc* – Ethyl acetate

*Hex* – *n*-Hexane

*TBAF* – Tetrabutylammonium fluoride

*THF* – Tetrahydrofuran

For the description of the NMR spectra: *Ar* – arene, *Tr* – triazole.

### 2. Synthesis of the trithiolato-bridged dinuclear ruthenium(II)-arene intermediates 2-9

The dithiolato intermediate **1** ([(*η*<sup>6</sup>-*p*-MeC<sub>6</sub>H<sub>4</sub>Pr<sup>*i*</sup>)<sub>2</sub>Ru<sub>2</sub>(μ<sub>2</sub>-SCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>-*p*-Bu<sup>*t*</sup>)<sub>2</sub>Cl<sub>2</sub>]) was prepared and purified by adapting a previously published protocol [2,3].

Compounds **2** ([(*η*<sup>6</sup>-*p*-MeC<sub>6</sub>H<sub>4</sub>Pr<sup>*i*</sup>)<sub>2</sub>Ru<sub>2</sub>(μ<sub>2</sub>-SCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>-*p*-Bu<sup>*t*</sup>)<sub>2</sub>(μ<sub>2</sub>-SC<sub>6</sub>H<sub>4</sub>-*p*-OH)]Cl), **3** ([(*η*<sup>6</sup>-*p*-MeC<sub>6</sub>H<sub>4</sub>Pr<sup>*i*</sup>)<sub>2</sub>Ru<sub>2</sub>(μ<sub>2</sub>-SCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>-*p*-Bu<sup>*t*</sup>)<sub>2</sub>(μ<sub>2</sub>-SC<sub>6</sub>H<sub>4</sub>-*p*-NH<sub>2</sub>)]Cl), **4** ([(*η*<sup>6</sup>-*p*-MeC<sub>6</sub>H<sub>4</sub>Pr<sup>*i*</sup>)<sub>2</sub>Ru<sub>2</sub>(μ<sub>2</sub>-SCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>-*p*-Bu<sup>*t*</sup>)<sub>2</sub>(μ<sub>2</sub>-SC<sub>6</sub>H<sub>4</sub>-*p*-CH<sub>2</sub>CO<sub>2</sub>H)]Cl), and **5** ([(*η*<sup>6</sup>-*p*-MeC<sub>6</sub>H<sub>4</sub>Pr<sup>*i*</sup>)<sub>2</sub>Ru<sub>2</sub>(μ<sub>2</sub>-SCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>-*p*-Bu<sup>*t*</sup>)<sub>2</sub>(μ<sub>2</sub>-SC<sub>6</sub>H<sub>4</sub>-*o*-CH<sub>2</sub>OH)]Cl) were synthesised and purified according to previously reported protocols [2-4].

The synthesis of compounds **7** ([(*η*<sup>6</sup>-*p*-MeC<sub>6</sub>H<sub>4</sub>Pr<sup>*i*</sup>)<sub>2</sub>Ru<sub>2</sub>(μ<sub>2</sub>-SCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>-*p*-Bu<sup>*t*</sup>)<sub>2</sub>(μ<sub>2</sub>-SC<sub>6</sub>H<sub>4</sub>-*p*-NH-R)]Cl, R = (C=O)-(CH<sub>2</sub>)<sub>3</sub>-C≡CH), **8** ([(*η*<sup>6</sup>-*p*-MeC<sub>6</sub>H<sub>4</sub>Pr<sup>*i*</sup>)<sub>2</sub>Ru<sub>2</sub>(μ<sub>2</sub>-SCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>-*p*-Bu<sup>*t*</sup>)<sub>2</sub>(μ<sub>2</sub>-SC<sub>6</sub>H<sub>4</sub>-*p*-CH<sub>2</sub>-

(C=O)-NH-R)]Cl, R = CH<sub>2</sub>-C≡CH) and **9** [(η<sup>6</sup>-*p*-MeC<sub>6</sub>H<sub>4</sub>Pr<sup>i</sup>)<sub>2</sub>Ru<sub>2</sub>(μ<sub>2</sub>-SCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>-*p*-Bu<sup>t</sup>)<sub>2</sub>(μ<sub>2</sub>-SC<sub>6</sub>H<sub>4</sub>-*o*-CH<sub>2</sub>-N<sub>3</sub>)]Cl), was described in detail in precedent reports [5,6].

### Synthesis of [(η<sup>6</sup>-*p*-MeC<sub>6</sub>H<sub>4</sub>Pr<sup>i</sup>)<sub>2</sub>Ru<sub>2</sub>(μ<sub>2</sub>-SCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>-*p*-Bu<sup>t</sup>)<sub>2</sub>(μ<sub>2</sub>-SC<sub>6</sub>H<sub>4</sub>-*p*-O-R)]Cl (R = (C=O)-(CH<sub>2</sub>)<sub>3</sub>-C≡CH) (**6**)

To a solution of 5-hexynoic acid (0.095 g, 0.847 mmol, 1.2 equiv.) in dry CH<sub>2</sub>Cl<sub>2</sub> (40 mL) at r.t. under inert atmosphere (N<sub>2</sub>) were successively added **2** (0.700 g, 0.706 mmol, 1 equiv.), EDCI (0.271 g, 1.412 mmol, 2 equiv.) and DMAP (0.043 g, 0.353 mmol, 0.5 equiv.). The reaction mixture was stirred at r.t. for 24 h and then concentrated to dryness under reduced pressure. Purification by column chromatography using CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>OH 10:1 (v/v) as eluent afforded **6** as an orange solid (0.360 g, 0.332 mmol, yield 47%).

**<sup>1</sup>H-NMR (CDCl<sub>3</sub>) δ<sub>H</sub>, ppm:** 7.79 (2H, d, 2xS-(Ar)C-CH-CH-C-O, <sup>3</sup>J<sub>H,H</sub> = 8.5 Hz), 7.39-7.50 (8H, m, 4xCH<sub>2</sub>-(Ar)C-CH-CH-C-C(CH<sub>3</sub>)<sub>3</sub>, 4xS-CH<sub>2</sub>-(Ar)C-CH-CH-CH-C-C(CH<sub>3</sub>)<sub>3</sub>), 7.06 (2H, d, 2xS-(Ar)C-CH-CH-CH-C-O, <sup>3</sup>J<sub>H,H</sub> = 8.5 Hz), 5.14 (2H, d, 2xCH<sub>3</sub>-(Ar)C-CH-CH-C, <sup>3</sup>J<sub>H,H</sub> = 5.7 Hz), 5.02 (2H, d, 2xCH<sub>3</sub>-(Ar)C-CH-CH-C, <sup>3</sup>J<sub>H,H</sub> = 5.8 Hz), 4.93 (2H, d, 2xCH<sub>3</sub>-(Ar)C-CH-CH-C, <sup>3</sup>J<sub>H,H</sub> = 5.7 Hz), 4.63 (2H, d, 2xCH<sub>3</sub>-(Ar)C-CH-CH-C, <sup>3</sup>J<sub>H,H</sub> = 5.8 Hz), 3.61 (2H, s, 2xS-CH<sub>2</sub>-(Ar)C-CH-CH-C-C(CH<sub>3</sub>)<sub>3</sub>), 3.44 (2H, s, 2xS-CH<sub>2</sub>-(Ar)C-CH-CH-C-C(CH<sub>3</sub>)<sub>3</sub>), 2.74 (2H, t, (C=O)-CH<sub>2</sub>-(CH<sub>2</sub>)<sub>2</sub>-C≡CH, <sup>3</sup>J<sub>H,H</sub> = 7.4 Hz), 2.36 (2H, td, (C=O)-(CH<sub>2</sub>)<sub>2</sub>-CH<sub>2</sub>-C≡CH, <sup>3</sup>J<sub>H,H</sub> = 6.8 Hz, <sup>4</sup>J<sub>H,H</sub> = 2.6 Hz), 2.03 (1H, t, (C=O)-(CH<sub>2</sub>)<sub>3</sub>-C≡CH, <sup>4</sup>J<sub>H,H</sub> = 2.6 Hz), 1.97 (2H, qvint, (C=O)-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-C≡CH, <sup>3</sup>J<sub>H,H</sub> = 7.2 Hz), 1.83-1.93 (2H, m, 2x(Ar)C-CH-CH-C-CH(CH<sub>3</sub>)<sub>2</sub>), 1.77 (6H, s, 2xCH<sub>3</sub>-(Ar)C-CH-CH-C), 1.36 (9H, s, S-CH<sub>2</sub>-(Ar)C-CH-CH-C-C(CH<sub>3</sub>)<sub>3</sub>), 1.33 (9H, s, S-CH<sub>2</sub>-(Ar)C-CH-CH-C-C(CH<sub>3</sub>)<sub>3</sub>), 0.94 (6H, d, (Ar)C-CH-CH-C-CH(CH<sub>3</sub>)<sub>2</sub>, <sup>3</sup>J<sub>H,H</sub> = 6.8 Hz), 0.89 (6H, d, (Ar)C-CH-CH-C-CH(CH<sub>3</sub>)<sub>2</sub>, <sup>3</sup>J<sub>H,H</sub> = 6.8 Hz).

**<sup>13</sup>C-NMR (CDCl<sub>3</sub>) δ<sub>C</sub>, ppm:** 171.4 (1C, (C=O)-(CH<sub>2</sub>)<sub>3</sub>-C≡CH), 151.9, 151.8 (2C, 2xS-CH<sub>2</sub>-(Ar)C-CH-CH-C-C(CH<sub>3</sub>)<sub>3</sub>), 151.1 (1C, S-(Ar)C-CH-CH-C-O), 136.8 (2C, 2xS-CH<sub>2</sub>-(Ar)C-CH-CH-C-C(CH<sub>3</sub>)<sub>3</sub>), 135.2 (1C, S-(Ar)C-CH-CH-C-O), 133.7 (2C, 2xS-(Ar)C-CH-CH-C-O), 129.4, 129.2 (4C, 4xS-CH<sub>2</sub>-(Ar)C-CH-CH-C-C(CH<sub>3</sub>)<sub>3</sub>), 125.7, 125.5 (4C, 4xS-CH<sub>2</sub>-(Ar)C-CH-CH-C-C(CH<sub>3</sub>)<sub>3</sub>), 122.4 (2C, 2xS-(Ar)C-CH-CH-C-O), 107.2 (2C, 2xCH<sub>3</sub>-(Ar)C-CH-CH-C), 100.7 (2C, 2xCH<sub>3</sub>-(Ar)C-CH-CH-C), 84.3 (2C, 2xCH<sub>3</sub>-(Ar)C-CH-CH-C), 83.8 (4C, 4xCH<sub>3</sub>-(Ar)C-CH-CH-C), 83.1 (1C, (C=O)-(CH<sub>2</sub>)<sub>3</sub>-C≡CH), 82.7 (2C, 2xCH<sub>3</sub>-(Ar)C-CH-CH-C), 69.6 (1C, (C=O)-(CH<sub>2</sub>)<sub>2</sub>-C≡CH), 40.1 (1C, S-CH<sub>2</sub>-(Ar)C-CH-CH-C-C(CH<sub>3</sub>)<sub>3</sub>), 39.7 (1C, S-CH<sub>2</sub>-(Ar)C-CH-CH-C-C(CH<sub>3</sub>)<sub>3</sub>), 34.91, 34.87 (2C, 2xS-CH<sub>2</sub>-(Ar)C-CH-CH-C-C(CH<sub>3</sub>)<sub>3</sub>), 33.0 (1C, (C=O)-CH<sub>2</sub>-(CH<sub>2</sub>)<sub>2</sub>-C≡CH), 31.55, 31.53 (6C, 2xS-CH<sub>2</sub>-(Ar)C-CH-CH-C-C(CH<sub>3</sub>)<sub>3</sub>), 31.0 (2C, 2x(Ar)CH-CH-C-CH(CH<sub>3</sub>)<sub>2</sub>), 23.5 (1C, (C=O)-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-C≡CH), 23.2 (2C, (Ar)CH-CH-C-CH(CH<sub>3</sub>)<sub>2</sub>), 22.7 (2C, (Ar)CH-CH-C-CH(CH<sub>3</sub>)<sub>2</sub>), 18.3 (2C, 2xCH<sub>3</sub>-(Ar)C-CH-CH), 17.9 (1C, (C=O)-(CH<sub>2</sub>)<sub>2</sub>-CH<sub>2</sub>-C≡CH).

R<sub>f</sub>(CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>OH 10:1 (v/v)) = 0.452.

**ESI-MS(+):** *m/z* found 1049.2544 [M-Cl]<sup>+</sup>, calcd. for C<sub>54</sub>H<sub>70</sub>O<sub>2</sub>Ru<sub>2</sub>S<sub>3</sub><sup>+</sup> 1049.2541.

**Elemental analysis (%):** calcd. for C<sub>54</sub>H<sub>69</sub>ClO<sub>2</sub>Ru<sub>2</sub>S<sub>3</sub> C 59.84, H 6.42; found C 59.49, H 6.46.

### 3. Synthesis of the azide and alkyne functionalized carbohydrate intermediates 10-18

The azide functionalized carbohydrate derivative **10** was prepared and purified by adapting the literature procedure [7,8].

#### Synthesis of (2*R*,3*R*,4*S*,5*R*,6*R*)-2-(acetoxymethyl)-6-azidotetrahydro-2*H*-pyran-3,4,5-triyl triacetate (**10**)

To a solution of (2*R*,3*R*,4*S*,5*R*,6*S*)-2-(acetoxymethyl)-6-bromotetrahydro-2*H*-pyran-3,4,5-triyl triacetate (0.500 g, 1.220 mmol, 1 equiv.) in THF (15 mL) were successively added at r.t. azidotrimethylsilane (0.190 g, 1.647 mmol, 1.35 equiv.) and TBAF (1.60 mL, 1.600 mmol, 1.3 equiv.). The reaction mixture was further stirred at r.t. for 4 h, then the mixture was filtered through a plug of silica gel, and the filtrate was concentrated under reduced pressure to dryness. The residue was crystallized from EtOH abs. to afford **10** as a white solid (0.229 mg, 0.616 mmol, yield 51%).

<sup>1</sup>H-NMR (CDCl<sub>3</sub>) δ<sub>H</sub>, ppm: 5.22 (1H, t, N<sub>3</sub>-CH-CH-CH<sub>2</sub>-OAc, <sup>3</sup>J<sub>H,H</sub> = 9.4 Hz), 5.10 (1H, t, N<sub>3</sub>-CH-CH-CH-CH<sub>2</sub>-OAc, <sup>3</sup>J<sub>H,H</sub> = 9.6 Hz), 4.95 (1H, t, N<sub>3</sub>-CH-CH-OAc, <sup>3</sup>J<sub>H,H</sub> = 9.5 Hz), 4.64 (1H, d, N<sub>3</sub>-CH-CH-OAc, <sup>3</sup>J<sub>H,H</sub> = 8.8 Hz), 4.27 (1H, dd, CH-CH<sub>2</sub>-OAc, <sup>2</sup>J<sub>H,H</sub> = 12.5 Hz, <sup>3</sup>J<sub>H,H</sub> = 4.8 Hz), 4.17 (1H, dd, CH-CH<sub>2</sub>-OAc, <sup>2</sup>J<sub>H,H</sub> = 12.4 Hz, <sup>3</sup>J<sub>H,H</sub> = 2.3 Hz), 3.79 (1H, ddd, CH-CH<sub>2</sub>-OAc, <sup>3</sup>J<sub>H,H</sub> = 10.0 Hz, <sup>3</sup>J<sub>H,H</sub> = 4.8 Hz, <sup>3</sup>J<sub>H,H</sub> = 2.3 Hz), 2.10 (3H, s, O-(C=O)-CH<sub>3</sub>), 2.07 (3H, s, O-(C=O)-CH<sub>3</sub>), 2.03 (3H, s, O-(C=O)-CH<sub>3</sub>), 2.01 (3H, s, O-(C=O)-CH<sub>3</sub>).

<sup>13</sup>C-NMR (CDCl<sub>3</sub>) δ<sub>C</sub>, ppm: 170.7 (1C, O-(C=O)-CH<sub>3</sub>), 170.3 (1C, O-(C=O)-CH<sub>3</sub>), 169.4 (1C, O-(C=O)-CH<sub>3</sub>), 169.3 (1C, O-(C=O)-CH<sub>3</sub>), 88.1 (1C, N<sub>3</sub>-CH-CH-OAc), 74.2 (1C, CH-CH<sub>2</sub>-OAc), 72.8 (N<sub>3</sub>-CH-CH-CH-OAc), 70.8 (1C, N<sub>3</sub>-CH-CH-OAc), 68.0 (1C, CH-CH-CH<sub>2</sub>-OAc), 61.8 (1C, CH-CH<sub>2</sub>-OAc), 20.8 (1C, O-(C=O)-CH<sub>3</sub>), 20.70 (1C, O-(C=O)-CH<sub>3</sub>), 20.68 (2C, 2xO-(C=O)-CH<sub>3</sub>).

R<sub>f</sub>(EtOAc/Hex 2:3 (v/v)) = 0.446.

ESI-MS(+): *m/z* found 391.1449 [M+H<sub>2</sub>O]<sup>+</sup>, 396.0998 [M+Na]<sup>+</sup>, 746.2064 [2M]<sup>+</sup>, 769.2112 [2M+Na]<sup>+</sup>; calcd. for C<sub>14</sub>H<sub>21</sub>N<sub>3</sub>O<sub>10</sub> 391.1227, C<sub>14</sub>H<sub>19</sub>N<sub>3</sub>NaO<sub>9</sub><sup>+</sup> 396.1014, C<sub>28</sub>H<sub>38</sub>N<sub>6</sub>O<sub>18</sub> 746.2243, C<sub>28</sub>H<sub>38</sub>N<sub>6</sub>NaO<sub>18</sub><sup>+</sup> 769.2135.

The bromo **11-13** [9,10] and azide **14-16** [7,8,10] functionalized carbohydrate derivatives were prepared and purified by adapting the literature procedures.

#### Synthesis of (2*R*,3*R*,4*S*,5*R*,6*R*)-2-(acetoxymethyl)-6-(2-bromoethoxy)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (**11**)

To a solution of 1,2,3,4,6-penta-O-acetyl-β-D-glucopyranose (1.000 g, 2.560 mmol, 1 equiv.) in dry CH<sub>2</sub>Cl<sub>2</sub> (40 mL) at 0°C under inert atmosphere (N<sub>2</sub>) were added 2-bromoethanol (0.625 g, 5.120 mmol, 2 equiv.) and BF<sub>3</sub>·Et<sub>2</sub>O (0.508 g, 7.680 mmol, 3 equiv.). The reaction mixture was stirred at r.t. for 24 h and the reaction evolution was verified by TLC. The reaction mixture was concentrated under reduced pressure, then the crude was solubilized in EtOAc (20 mL) and washed with H<sub>2</sub>O (20 mL), and the aqueous phase was further extracted with EtOAc (2x20 mL). The combined organic phases were washed with brine (10 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and

concentrated under reduced pressure. Purification by column chromatography using a mixture EtOAc/Hex 2:3 (v/v) as eluent afforded **11** as a white solid (0.359 g, 0.790 mmol, yield 32%).

**<sup>1</sup>H-NMR (CDCl<sub>3</sub>) δ<sub>H</sub>, ppm:** 5.21 (1H, t, Br-(CH<sub>2</sub>)<sub>2</sub>-O-CH-CH-CH-OAc, <sup>3</sup>J<sub>H,H</sub> = 9.5 Hz), 5.08 (1H, t, Br-(CH<sub>2</sub>)<sub>2</sub>-O-CH-CH-CH-OAc, <sup>3</sup>J<sub>H,H</sub> = 9.5 Hz), 5.01 (1H, dd, Br-(CH<sub>2</sub>)<sub>2</sub>-O-CH-CH-OAc, <sup>3</sup>J<sub>H,H</sub> = 9.6 Hz, <sup>3</sup>J<sub>H,H</sub> = 8.0 Hz), 4.57 (1H, d, Br-(CH<sub>2</sub>)<sub>2</sub>-O-CH-CH-OAc, <sup>3</sup>J<sub>H,H</sub> = 8.0 Hz), 4.26 (1H, dd, CH-CH<sub>2</sub>-OAc, <sup>2</sup>J<sub>H,H</sub> = 12.3 Hz, <sup>3</sup>J<sub>H,H</sub> = 4.8 Hz), 4.14 (1H, m, CH-CH<sub>2</sub>-OAc, <sup>2</sup>J<sub>H,H</sub> = 12.4 Hz), 4.11-4.19 (1H, m, Br-CH<sub>2</sub>-CH<sub>2</sub>-O), 3.78-3.87 (1H, m, Br-CH<sub>2</sub>-CH<sub>2</sub>-O), 3.70 (1H, ddd, CH-CH<sub>2</sub>-OAc, <sup>3</sup>J<sub>H,H</sub> = 10.0 Hz, <sup>3</sup>J<sub>H,H</sub> = 4.8 Hz, <sup>3</sup>J<sub>H,H</sub> = 2.4 Hz), 3.42-3.49 (2H, m, O-CH<sub>2</sub>-CH<sub>2</sub>-Br), 2.09 (3H, s, O-(C=O)-CH<sub>3</sub>), 2.07 (3H, s, O-(C=O)-CH<sub>3</sub>), 2.02 (3H, s, O-(C=O)-CH<sub>3</sub>), 2.00 (3H, s, O-(C=O)-CH<sub>3</sub>).

**<sup>13</sup>C-NMR (CDCl<sub>3</sub>) δ<sub>C</sub>, ppm:** 170.8 (1C, O-(C=O)-CH<sub>3</sub>), 170.4 (1C, O-(C=O)-CH<sub>3</sub>), 169.6 (2C, 2xO-(C=O)-CH<sub>3</sub>), 101.2 (1C, Br-(CH<sub>2</sub>)<sub>2</sub>-O-CH-CH-OAc), 72.8 (1C, Br-(CH<sub>2</sub>)<sub>2</sub>-O-CH-CH-CH-OAc), 72.1 (1C, CH-CH<sub>2</sub>-OAc), 71.2 (1C, Br-(CH<sub>2</sub>)<sub>2</sub>-O-CH-CH-OAc), 69.9 (1C, Br-CH<sub>2</sub>-CH<sub>2</sub>-O), 68.5 (1C, Br-(CH<sub>2</sub>)<sub>2</sub>-O-CH-CH-CH-CH-OAc), 62.0 (1C, CH-CH<sub>2</sub>-OAc), 30.0 (1C, Br-CH<sub>2</sub>-CH<sub>2</sub>-O), 20.9 (2C, 2xO-(C=O)-CH<sub>3</sub>), 20.8 (1C, O-(C=O)-CH<sub>3</sub>), 20.7 (1C, O-(C=O)-CH<sub>3</sub>).

**R<sub>f</sub>**(EtOAc/Hex 2:3 (v/v)) = 0.436.

**ESI-MS(+):** *m/z* found 472.0804 [M+H<sub>2</sub>O]<sup>+</sup>, 477.0353 [M+Na]<sup>+</sup>, 931.0834 [2M+Na]<sup>+</sup>, calcd. for C<sub>16</sub>H<sub>25</sub>BrO<sub>11</sub> 472.0580, C<sub>16</sub>H<sub>23</sub>BrNaO<sub>10</sub><sup>+</sup> 477.0367, C<sub>32</sub>H<sub>46</sub>Br<sub>2</sub>NaO<sub>20</sub><sup>+</sup> 931.0841.

### Synthesis of (2*R*,3*S*,4*S*,5*R*,6*R*)-2-(acetoxymethyl)-6-(2-bromoethoxy)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (**12**)

To a solution of 1,2,3,4,6-penta-O-acetyl-β-D-galactopyranose (1.000 g, 2.560 mmol, 1 equiv.) in dry CH<sub>2</sub>Cl<sub>2</sub> (40 mL) at 0 °C under inert atmosphere (N<sub>2</sub>) were added 2-bromoethanol (0.625 g, 5.120 mmol, 2 equiv.) and BF<sub>3</sub>·Et<sub>2</sub>O (0.508 g, 7.680 mmol, 3 equiv.). The mixture was stirred at r.t. for 24 h and the reaction evolution was verified by TLC. The reaction mixture was concentrated under reduced pressure, the crude was solubilized in EtOAc (20 mL) and washed with H<sub>2</sub>O (20 mL), and then the aqueous phase was further extracted with EtOAc (2x20 mL). The combined organic phases were washed with brine (10 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated under reduced pressure. Purification by column chromatography using a mixture EtOAc/Hex 2:3 (v/v) as eluent afforded **12** as a white solid (0.466 g, 1.027 mmol, yield 41%).

**<sup>1</sup>H-NMR (CDCl<sub>3</sub>) δ<sub>H</sub>, ppm:** 5.39 (1H, dd, Br-(CH<sub>2</sub>)<sub>2</sub>-O-CH-CH-CH-CH-OAc, <sup>3</sup>J<sub>H,H</sub> = 3.4 Hz, <sup>3</sup>J<sub>H,H</sub> = 0.9 Hz), 5.23 (1H, dd, Br-(CH<sub>2</sub>)<sub>2</sub>-O-CH-CH-OAc, <sup>3</sup>J<sub>H,H</sub> = 10.5 Hz, <sup>3</sup>J<sub>H,H</sub> = 8.0 Hz), 5.02 (1H, dd, Br-(CH<sub>2</sub>)<sub>2</sub>-O-CH-CH-CH-OAc, <sup>3</sup>J<sub>H,H</sub> = 10.5 Hz, <sup>3</sup>J<sub>H,H</sub> = 3.4 Hz), 4.53 (1H, d, Br-(CH<sub>2</sub>)<sub>2</sub>-O-CH-CH-OAc, <sup>3</sup>J<sub>H,H</sub> = 8.0 Hz), 4.09-4.21 (3H, m, CH-CH<sub>2</sub>-OAc, Br-CH<sub>2</sub>-CH<sub>2</sub>-O), 3.91 (1H, td, CH-CH<sub>2</sub>-OAc, <sup>3</sup>J<sub>H,H</sub> = 6.6 Hz, <sup>3</sup>J<sub>H,H</sub> = 1.0 Hz), 3.82 (1H, ddd, Br-CH<sub>2</sub>-CH<sub>2</sub>-O, <sup>2</sup>J<sub>H,H</sub> = 11.3 Hz, <sup>3</sup>J<sub>H,H</sub> = 7.4 Hz, <sup>3</sup>J<sub>H,H</sub> = 6.3 Hz), 3.48 (1H, d, O-CH<sub>2</sub>-CH<sub>2</sub>-Br, <sup>3</sup>J<sub>H,H</sub> = 6.0 Hz), 3.46 (1H, dd, O-CH<sub>2</sub>-CH<sub>2</sub>-Br, <sup>3</sup>J<sub>H,H</sub> = 5.8 Hz, <sup>3</sup>J<sub>H,H</sub> = 2.1 Hz), 2.15 (3H, s, O-(C=O)-CH<sub>3</sub>), 2.08 (3H, s, O-(C=O)-CH<sub>3</sub>), 2.05 (3H, s, O-(C=O)-CH<sub>3</sub>), 1.98 (3H, s, O-(C=O)-CH<sub>3</sub>).

**<sup>13</sup>C-NMR (CDCl<sub>3</sub>) δ<sub>C</sub>, ppm:** 170.5 (1C, O-(C=O)-CH<sub>3</sub>), 170.4 (1C, O-(C=O)-CH<sub>3</sub>), 170.3 (1C, O-(C=O)-CH<sub>3</sub>), 169.7 (1C, O-(C=O)-CH<sub>3</sub>), 101.7 (1C, Br-(CH<sub>2</sub>)<sub>2</sub>-O-CH-CH-OAc), 70.99 (1C, CH-CH<sub>2</sub>-OAc),

70.90 (1C, Br-(CH<sub>2</sub>)<sub>2</sub>-O-CH-CH-CH-OAc), 69.9 (1C, Br-CH<sub>2</sub>-CH<sub>2</sub>-O), 68.7 (1C, Br-(CH<sub>2</sub>)<sub>2</sub>-O-CH-CH-OAc), 67.1 (1C, Br-(CH<sub>2</sub>)<sub>2</sub>-O-CH-CH-CH-OAc), 61.4 (1C, CH-CH<sub>2</sub>-OAc), 30.1 (1C, Br-CH<sub>2</sub>-CH<sub>2</sub>-O), 21.0 (1C, O-(C=O)-CH<sub>3</sub>), 20.82 (1C, O-(C=O)-CH<sub>3</sub>), 20.80 (1C, O-(C=O)-CH<sub>3</sub>), 20.7 (1C, O-(C=O)-CH<sub>3</sub>).

$R_f(\text{EtOAc/Hex } 2:3 \text{ (v/v)}) = 0.436$ .

**ESI-MS(+):**  $m/z$  found 472.0804 [M+H<sub>2</sub>O]<sup>+</sup>, 477.0354 [M+Na]<sup>+</sup>, 931.0835 [2M+Na]<sup>+</sup>, calcd. for C<sub>16</sub>H<sub>25</sub>BrO<sub>11</sub> 472.0580, C<sub>16</sub>H<sub>23</sub>BrNaO<sub>10</sub><sup>+</sup> 477.0367, C<sub>32</sub>H<sub>46</sub>Br<sub>2</sub>NaO<sub>20</sub><sup>+</sup> 931.0841.

### Synthesis of (2R,3S,4S,5R,6R)-2-(acetoxymethyl)-6-(4-bromobutoxy)tetrahydro-2H-pyran-3,4,5-triyl triacetate (13)

To a solution of 1,2,3,4,6-penta-O-acetyl-β-D-galactopyranose (1.000 g, 2.560 mmol, 1 equiv.) in dry CH<sub>2</sub>Cl<sub>2</sub> (40 mL) at 0 °C under inert atmosphere (N<sub>2</sub>) were added 4-bromo-1-butanol (0.765 g, 5.120 mmol, 2 equiv.) and BF<sub>3</sub>·Et<sub>2</sub>O (0.508 g, 7.680 mmol, 3 equiv.). The mixture was stirred at r.t. for 24 h and the reaction evolution was verified by TLC. The reaction mixture was concentrated under reduced pressure, then the crude was solubilized in EtOAc (20 mL) and washed with H<sub>2</sub>O (20 mL), and the aqueous phase was further extracted with EtOAc (2x20 mL). The combined organic phases were washed with brine (10 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and then concentrated under reduced pressure. Purification by column chromatography using a mixture EtOAc/Hex 2:3 (v/v) as eluent afforded **13** as a white solid (0.565 g, 1.173 mmol, yield 47%).

**<sup>1</sup>H-NMR (CDCl<sub>3</sub>) δ<sub>H</sub>, ppm:** 5.43 (1H, dd, Br-(CH<sub>2</sub>)<sub>4</sub>-O-CH-CH-CH-CH-OAc, <sup>3</sup>J<sub>H,H</sub> = 3.3 Hz, <sup>3</sup>J<sub>H,H</sub> = 1.3 Hz), 5.28-5.34 (1H, m, Br-(CH<sub>2</sub>)<sub>4</sub>-O-CH-CH-OAc, <sup>3</sup>J<sub>H,H</sub> = 10.4 Hz, <sup>3</sup>J<sub>H,H</sub> = 2.0 Hz), 5.07-5.12 (2H, m, Br-(CH<sub>2</sub>)<sub>4</sub>-O-CH-CH-CH-OAc, Br-(CH<sub>2</sub>)<sub>4</sub>-O-CH-CH-OAc, <sup>3</sup>J<sub>H,H</sub> = 3.7 Hz), 4.16-4.20 (1H, m, CH-CH<sub>2</sub>-OAc, <sup>3</sup>J<sub>H,H</sub> = 6.1 Hz, <sup>3</sup>J<sub>H,H</sub> = 1.0 Hz), 4.10 (1H, dd, CH-CH<sub>2</sub>-OAc, <sup>2</sup>J<sub>H,H</sub> = 14.32 Hz, <sup>3</sup>J<sub>H,H</sub> = 7.2 Hz), 4.07 (1H, d, CH-CH<sub>2</sub>-OAc, <sup>3</sup>J<sub>H,H</sub> = 6.5 Hz), 3.73 (1H, dt, Br-(CH<sub>2</sub>)<sub>3</sub>-CH<sub>2</sub>-O, <sup>2</sup>J<sub>H,H</sub> = 10.0 Hz, <sup>3</sup>J<sub>H,H</sub> = 6.0 Hz), 3.40-3.47 (3H, m, Br-(CH<sub>2</sub>)<sub>3</sub>-CH<sub>2</sub>-O, Br-CH<sub>2</sub>-(CH<sub>2</sub>)<sub>3</sub>-O, <sup>3</sup>J<sub>H,H</sub> = 6.7 Hz, <sup>3</sup>J<sub>H,H</sub> = 1.5 Hz), 2.12 (3H, s, O-(C=O)-CH<sub>3</sub>), 2.06 (3H, s, O-(C=O)-CH<sub>3</sub>), 2.03 (3H, s, O-(C=O)-CH<sub>3</sub>), 1.97 (3H, s, O-(C=O)-CH<sub>3</sub>), 1.90-1.99 (2H, m, Br-CH<sub>2</sub>-CH<sub>2</sub>-(CH<sub>2</sub>)<sub>2</sub>-O, <sup>3</sup>J<sub>H,H</sub> = 6.8 Hz), 1.70-1.79 (2H, m, Br-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-O, <sup>3</sup>J<sub>H,H</sub> = 6.0 Hz).

$R_f(\text{EtOAc/Hex } 2:3 \text{ (v/v)}) = 0.464$ .

**ESI-MS(+):**  $m/z$  found 481.0285 [M-H]<sup>+</sup>, 500.1117 [M+H<sub>2</sub>O]<sup>+</sup>, 505.0671 [2M+Na]<sup>+</sup>, calcd. for C<sub>18</sub>H<sub>26</sub>BrO<sub>10</sub><sup>+</sup> 481.0704, C<sub>18</sub>H<sub>29</sub>BrO<sub>11</sub> 500.0893, C<sub>18</sub>H<sub>27</sub>NaO<sub>10</sub><sup>+</sup> 505.0680.

### Synthesis of (2R,3R,4S,5R,6R)-2-(acetoxymethyl)-6-(2-azidoethoxy)tetrahydro-2H-pyran-3,4,5-triyl triacetate (14)

To a solution of **11** (0.300 g, 0.658 mmol, 1 equiv.) in dry DMF (10 mL) at r.t. under inert atmosphere (N<sub>2</sub>) was added NaN<sub>3</sub> (0.214 g, 3.290 mmol, 5 equiv.). The reaction mixture was stirred at 70°C for 24 h, then was filtered and the filtrate was concentrated under reduced pressure. The residue was solubilized in EtOAc (20 mL) and washed with H<sub>2</sub>O (20 mL), and the aqueous phase

was further extracted with EtOAc (2x20 mL). The combined organic phases were washed with brine (20 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated under reduced pressure to afford **14** as a brown liquid (0.130 g, 0.312 mmol, yield 47%).

**<sup>1</sup>H-NMR (CDCl<sub>3</sub>) δ<sub>H</sub>, ppm:** 5.20 (1H, t, N<sub>3</sub>-(CH<sub>2</sub>)<sub>2</sub>-O-CH-CH-CH-OAc, <sup>3</sup>J<sub>H,H</sub> = 9.5 Hz), 5.08 (1H, t, N<sub>3</sub>-(CH<sub>2</sub>)<sub>2</sub>-O-CH-CH-CH-OAc, <sup>3</sup>J<sub>H,H</sub> = 9.7 Hz), 5.01 (1H, dd, N<sub>3</sub>-(CH<sub>2</sub>)<sub>2</sub>-O-CH-CH-OAc, <sup>3</sup>J<sub>H,H</sub> = 8.0 Hz, <sup>3</sup>J<sub>H,H</sub> = 9.6 Hz), 4.59 (1H, d, N<sub>3</sub>-(CH<sub>2</sub>)<sub>2</sub>-O-CH-CH-OAc, <sup>3</sup>J<sub>H,H</sub> = 8.0 Hz), 4.24 (1H, dd, CH-CH<sub>2</sub>-OAc, <sup>2</sup>J<sub>H,H</sub> = 12.3 Hz, <sup>3</sup>J<sub>H,H</sub> = 4.7 Hz), 4.15 (1H, dd, CH-CH<sub>2</sub>-OAc, <sup>2</sup>J<sub>H,H</sub> = 12.4 Hz, <sup>3</sup>J<sub>H,H</sub> = 2.4 Hz), 3.99-4.05 (1H, ddd, N<sub>3</sub>-CH<sub>2</sub>-CH<sub>2</sub>-O, <sup>2</sup>J<sub>H,H</sub> = 10.6 Hz, <sup>3</sup>J<sub>H,H</sub> = 4.8 Hz, <sup>3</sup>J<sub>H,H</sub> = 3.7 Hz), 3.65-3.74 (2H, m, CH-CH<sub>2</sub>-OAc, N<sub>3</sub>-CH<sub>2</sub>-CH<sub>2</sub>-O), 3.44-3.52 (1H, ddd, O-CH<sub>2</sub>-CH<sub>2</sub>-N<sub>3</sub>, <sup>2</sup>J<sub>H,H</sub> = 13.4 Hz, <sup>3</sup>J<sub>H,H</sub> = 8.3 Hz, <sup>3</sup>J<sub>H,H</sub> = 3.4 Hz), 3.24-3.31 (1H, ddd, O-CH<sub>2</sub>-CH<sub>2</sub>-N<sub>3</sub>, <sup>2</sup>J<sub>H,H</sub> = 13.4 Hz, <sup>3</sup>J<sub>H,H</sub> = 4.7 Hz, <sup>3</sup>J<sub>H,H</sub> = 3.4 Hz), 2.07 (3H, s, O-(C=O)-CH<sub>3</sub>), 2.04 (3H, s, O-(C=O)-CH<sub>3</sub>), 2.01 (3H, s, O-(C=O)-CH<sub>3</sub>), 1.99 (3H, s, O-(C=O)-CH<sub>3</sub>).

**R<sub>f</sub>**(EtOAc/Hex 2:3 (v/v)) = 0.418.

**ESI-MS(+):** *m/z* found 435.1713 [M+H<sub>2</sub>O]<sup>+</sup>, 440.1263 [M+Na]<sup>+</sup>, 852.3102 [2M+H<sub>2</sub>O]<sup>+</sup>, 857.2650 [2M+Na]<sup>+</sup>, calcd. for C<sub>16</sub>H<sub>25</sub>N<sub>3</sub>O<sub>11</sub> 435.1484, C<sub>16</sub>H<sub>23</sub>N<sub>3</sub>NaO<sub>10</sub><sup>+</sup> 440.1276, C<sub>32</sub>H<sub>48</sub>N<sub>6</sub>O<sub>20</sub> 852.2876, C<sub>32</sub>H<sub>46</sub>N<sub>6</sub>NaO<sub>20</sub><sup>+</sup> 857.2659.

### Synthesis of (2R,3S,4S,5R,6R)-2-(acetoxymethyl)-6-(2-azidoethoxy)tetrahydro-2H-pyran-3,4,5-triyl triacetate (**15**)

To a solution of **12** (0.300 g, 0.658 mmol, 1 equiv.) in dry DMF (10 mL) at r.t. under inert atmosphere (N<sub>2</sub>) was added NaN<sub>3</sub> (0.214 g, 3.290 mmol, 5 equiv.). The reaction mixture was stirred at 70°C for 24 h, then it was filtered, and the filtrate was concentrated under reduced pressure. The residue was solubilized in EtOAc (20 mL) and washed with H<sub>2</sub>O (20 mL), and the aqueous phase was further extracted with EtOAc (2x20 mL). The combined organic phases were washed with brine (10 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and then concentrated under reduced pressure to afford **15** as a brown liquid (0.202 g, 0.485 mmol, yield 74%).

**<sup>1</sup>H-NMR (CDCl<sub>3</sub>) δ<sub>H</sub>, ppm:** 5.39 (1H, dd, N<sub>3</sub>-(CH<sub>2</sub>)<sub>2</sub>-O-CH-CH-CH-CH-OAc, <sup>3</sup>J<sub>H,H</sub> = 3.4 Hz, <sup>3</sup>J<sub>H,H</sub> = 0.7 Hz), 5.24 (1H, dd, N<sub>3</sub>-(CH<sub>2</sub>)<sub>2</sub>-O-CH-CH-CH-OAc, <sup>3</sup>J<sub>H,H</sub> = 10.5 Hz, <sup>3</sup>J<sub>H,H</sub> = 8.0 Hz), 5.02 (1H, dd, N<sub>3</sub>-(CH<sub>2</sub>)<sub>2</sub>-O-CH-CH-CH-OAc, <sup>3</sup>J<sub>H,H</sub> = 10.5 Hz, <sup>3</sup>J<sub>H,H</sub> = 3.4 Hz), 4.56 (1H, d, N<sub>3</sub>-(CH<sub>2</sub>)<sub>2</sub>-O-CH-CH-CH-OAc, <sup>3</sup>J<sub>H,H</sub> = 8.0 Hz), 4.18 (1H, dd, CH-CH<sub>2</sub>-OAc, <sup>2</sup>J<sub>H,H</sub> = 11.3 Hz, <sup>3</sup>J<sub>H,H</sub> = 6.6 Hz), 4.12 (1H, dd, CH-CH<sub>2</sub>-OAc, <sup>2</sup>J<sub>H,H</sub> = 11.3 Hz, <sup>3</sup>J<sub>H,H</sub> = 6.7 Hz), 4.04 (1H, ddd, O-CH<sub>2</sub>-CH<sub>2</sub>-N<sub>3</sub>, <sup>2</sup>J<sub>H,H</sub> = 10.7 Hz, <sup>3</sup>J<sub>H,H</sub> = 4.7 Hz, <sup>3</sup>J<sub>H,H</sub> = 3.5 Hz), 3.92 (1H, td, CH-CH<sub>2</sub>-OAc, <sup>3</sup>J<sub>H,H</sub> = 6.6 Hz, <sup>3</sup>J<sub>H,H</sub> = 1.0 Hz), 3.69 (1H, ddd, O-CH<sub>2</sub>-CH<sub>2</sub>-N<sub>3</sub>, <sup>2</sup>J<sub>H,H</sub> = 10.9 Hz, <sup>3</sup>J<sub>H,H</sub> = 8.5 Hz, <sup>3</sup>J<sub>H,H</sub> = 3.4 Hz), 3.50 (1H, ddd, O-CH<sub>2</sub>-CH<sub>2</sub>-N<sub>3</sub>, <sup>2</sup>J<sub>H,H</sub> = 13.3 Hz, <sup>3</sup>J<sub>H,H</sub> = 8.6 Hz, <sup>3</sup>J<sub>H,H</sub> = 3.5 Hz), 3.30 (1H, ddd, O-CH<sub>2</sub>-CH<sub>2</sub>-N<sub>3</sub>, <sup>2</sup>J<sub>H,H</sub> = 13.4 Hz, <sup>3</sup>J<sub>H,H</sub> = 4.5 Hz, <sup>3</sup>J<sub>H,H</sub> = 3.5 Hz), 2.15 (3H, s, O-(C=O)-CH<sub>3</sub>), 2.08 (3H, s, O-(C=O)-CH<sub>3</sub>), 2.05 (3H, s, O-(C=O)-CH<sub>3</sub>), 1.98 (3H, s, O-(C=O)-CH<sub>3</sub>).

**R<sub>f</sub>**(EtOAc/Hex 2:3 (v/v)) = 0.400.

**ESI-MS(+):** *m/z* found 435.1719 [M+H<sub>2</sub>O]<sup>+</sup>, 440.1266 [M+Na]<sup>+</sup>, 857.2654 [2M+Na]<sup>+</sup>, calcd. for C<sub>16</sub>H<sub>25</sub>N<sub>3</sub>O<sub>11</sub> 435.1489, C<sub>14</sub>H<sub>19</sub>O<sub>9</sub><sup>+</sup> C<sub>16</sub>H<sub>23</sub>N<sub>3</sub>NaO<sub>10</sub><sup>+</sup> 440.1276, C<sub>32</sub>H<sub>46</sub>N<sub>6</sub>NaO<sub>20</sub><sup>+</sup> 857.2659.

### Synthesis of (2R,3S,4S,5R,6R)-2-(acetoxymethyl)-6-(4-azidobutoxy)tetrahydro-2H-pyran-3,4,5-triyl triacetate (16)

To a solution of **13** (0.240 g, 0.496 mmol, 1 equiv.) in dry DMF (10 mL) at r.t. under inert atmosphere (N<sub>2</sub>) was added NaN<sub>3</sub> (0.161 g, 1.480 mmol, 5 equiv.). The reaction mixture was stirred at 70 °C for 24 h, then it was filtered and the filtrate was concentrated under reduced pressure. The residue was solubilized in EtOAc (20 mL), washed with H<sub>2</sub>O (20 mL), and the aqueous phase was further extracted with EtOAc (2×20 mL). The organic phases were combined, washed with brine (10 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated under reduced pressure to afford **16** as a brown liquid (0.253 g, 0.567 mmol, quant. yield).

**<sup>1</sup>H-NMR (CDCl<sub>3</sub>) δ<sub>H</sub>, ppm:** 5.42 (1H, dd, N<sub>3</sub>-(CH<sub>2</sub>)<sub>4</sub>-O-CH-CH-CH-CH-OAc, <sup>3</sup>J<sub>H,H</sub> = 3.4 Hz, <sup>3</sup>J<sub>H,H</sub> = 1.2 Hz), 5.28-5.34 (1H, m, N<sub>3</sub>-(CH<sub>2</sub>)<sub>4</sub>-O-CH-CH-OAc), 5.06-5.12 (2H, m, N<sub>3</sub>-(CH<sub>2</sub>)<sub>4</sub>-O-CH-CH-CH-OAc, N<sub>3</sub>-(CH<sub>2</sub>)<sub>4</sub>-O-CH-CH-OAc, <sup>3</sup>J<sub>H,H</sub> = 3.7 Hz), 4.15-4.20 (1H, m, CH-CH<sub>2</sub>-OAc, <sup>3</sup>J<sub>H,H</sub> = 6.2 Hz, <sup>3</sup>J<sub>H,H</sub> = 0.9 Hz), 4.07 (2H, d, CH-CH<sub>2</sub>-OAc, <sup>3</sup>J<sub>H,H</sub> = 6.6 Hz), 3.68-3.75 (1H, m, N<sub>3</sub>-(CH<sub>2</sub>)<sub>3</sub>-CH<sub>2</sub>-O), 3.38-3.46 (1H, m, N<sub>3</sub>-(CH<sub>2</sub>)<sub>3</sub>-CH<sub>2</sub>-O), 3.28-3.33 (2H, m, N<sub>3</sub>-CH<sub>2</sub>-(CH<sub>2</sub>)<sub>3</sub>-O), 2.12 (3H, s, O-(C=O)-CH<sub>3</sub>), 2.05 (3H, s, O-(C=O)-CH<sub>3</sub>), 2.02 (3H, s, O-(C=O)-CH<sub>3</sub>), 1.96 (3H, s, O-(C=O)-CH<sub>3</sub>), 1.64-1.69 (4H, m, N<sub>3</sub>-CH<sub>2</sub>-CH<sub>2</sub>-(CH<sub>2</sub>)<sub>2</sub>-O, N<sub>3</sub>-(CH<sub>2</sub>)<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-O, <sup>3</sup>J<sub>H,H</sub> = 3.3 Hz).

**<sup>13</sup>C-NMR (CDCl<sub>3</sub>) δ<sub>C</sub>, ppm:** 170.49 (1C, O-(C=O)-CH<sub>3</sub>), 170.46 (1C, O-(C=O)-CH<sub>3</sub>), 170.3 (1C, O-(C=O)-CH<sub>3</sub>), 170.1 (1C, O-(C=O)-CH<sub>3</sub>), 96.3 (1C, N<sub>3</sub>-(CH<sub>2</sub>)<sub>4</sub>-O-CH-CH-OAc), 68.3 (1C, N<sub>3</sub>-(CH<sub>2</sub>)<sub>4</sub>-O-CH-CH-CH-OAc), 68.2 (1C, N<sub>3</sub>-(CH<sub>2</sub>)<sub>4</sub>-O-CH-CH-CH-CH-OAc), 68.0 (1C, N<sub>3</sub>-(CH<sub>2</sub>)<sub>3</sub>-CH<sub>2</sub>-O), 67.7 (1C, N<sub>3</sub>-(CH<sub>2</sub>)<sub>4</sub>-O-CH-CH-OAc), 66.4 (1C, CH-CH<sub>2</sub>-OAc), 61.9 (1C, CH-CH<sub>2</sub>-OAc), 51.2 (1C, N<sub>3</sub>-CH<sub>2</sub>-(CH<sub>2</sub>)<sub>3</sub>-O), 26.6 (1C, N<sub>3</sub>-(CH<sub>2</sub>)<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-O), 25.8 (1C, N<sub>3</sub>-CH<sub>2</sub>-CH<sub>2</sub>-(CH<sub>2</sub>)<sub>2</sub>-O), 20.83 (1C, O-(C=O)-CH<sub>3</sub>), 20.76 (1C, O-(C=O)-CH<sub>3</sub>), 20.74 (1C, O-(C=O)-CH<sub>3</sub>), 20.71 (1C, O-(C=O)-CH<sub>3</sub>).

**R<sub>f</sub>**(EtOAc/Hex 2:3 (v/v)) = 0.491.

**ESI-MS(+):** *m/z* found 463.2036 [M+H<sub>2</sub>O]<sup>+</sup>, 468.1586 [M+Na]<sup>+</sup>, 913.3295 [2M+Na]<sup>+</sup>, calcd. for C<sub>18</sub>H<sub>29</sub>N<sub>3</sub>O<sub>11</sub> 463.1802, C<sub>18</sub>H<sub>27</sub>N<sub>3</sub>NaO<sub>10</sub><sup>+</sup> 468.1589, C<sub>36</sub>H<sub>54</sub>N<sub>6</sub>NaO<sub>20</sub><sup>+</sup> 913.3285.

The alkyne functionalized carbohydrate derivatives **17** and **18** were prepared and purified by adapting a literature procedure [11].

### Synthesis of (2R,3R,4S,5R,6R)-2-(acetoxymethyl)-6-(pent-4-yn-1-yloxy)tetrahydro-2H-pyran-3,4,5-triyl triacetate (17)

To a solution of 1,2,3,4,6-penta-O-acetyl-β-D-glucopyranose (1.000 g, 2.560 mmol, 1 equiv.) in dry CH<sub>2</sub>Cl<sub>2</sub> (20 mL) at 0 °C under inert atmosphere (N<sub>2</sub>) were added 4-pentyn-1-ol (0.253 g, 3.070 mmol, 1.2 equiv.) and BF<sub>3</sub>·Et<sub>2</sub>O (0.727 g, 5.120 mmol, 2 equiv.). The reaction mixture was stirred at r.t. for 2 h. Then anhydrous K<sub>2</sub>CO<sub>3</sub> (0.48 g) was added and the reaction mixture was further stirred at r.t. for 1 h. The suspension was filtered, and the filtrate was washed with H<sub>2</sub>O (2×20 mL). The unified aqueous phases were extracted with CH<sub>2</sub>Cl<sub>2</sub> (2×20 mL). The organic phases were combined, washed with brine (10 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated under reduced



pressure. Washing of the crude using a CH<sub>2</sub>Cl<sub>2</sub>/Hex mixture afforded **17** as a brown liquid (0.686 g, 1.643 mmol, yield 64%).

**<sup>1</sup>H-NMR (CDCl<sub>3</sub>) δ<sub>H</sub>, ppm:** 5.19 (1H, t, HC≡C-(CH<sub>2</sub>)<sub>3</sub>-O-CH-CH-CH-OAc, <sup>3</sup>J<sub>H,H</sub> = 9.5 Hz), 5.06 (1H, t, HC≡C-(CH<sub>2</sub>)<sub>3</sub>-O-CH-CH-CH-OAc, <sup>3</sup>J<sub>H,H</sub> = 9.5 Hz), 4.97 (1H, dd, HC≡C-(CH<sub>2</sub>)<sub>3</sub>-O-CH-CH-OAc, <sup>3</sup>J<sub>H,H</sub> = 8.0 Hz, <sup>3</sup>J<sub>H,H</sub> = 9.5 Hz), 4.49 (1H, d, HC≡C-(CH<sub>2</sub>)<sub>3</sub>-O-CH-CH-OAc, <sup>3</sup>J<sub>H,H</sub> = 8.0 Hz), 4.25 (1H, dd, CH-CH<sub>2</sub>-OAc, <sup>2</sup>J<sub>H,H</sub> = 12.1 Hz, <sup>3</sup>J<sub>H,H</sub> = 4.7 Hz), 4.12 (1H, dd, CH-CH<sub>2</sub>-OAc, <sup>2</sup>J<sub>H,H</sub> = 12.2 Hz, <sup>3</sup>J<sub>H,H</sub> = 2.5 Hz), 3.94 (1H, dt, HC≡C-(CH<sub>2</sub>)<sub>2</sub>-CH<sub>2</sub>-O, <sup>2</sup>J<sub>H,H</sub> = 9.7 Hz, <sup>3</sup>J<sub>H,H</sub> = 5.5 Hz), 3.68 (1H, ddd, CH-CH<sub>2</sub>-OAc, <sup>2</sup>J<sub>H,H</sub> = 9.9 Hz, <sup>3</sup>J<sub>H,H</sub> = 5.0 Hz, <sup>3</sup>J<sub>H,H</sub> = 2.5 Hz), 3.57-3.65 (1H, m, HC≡C-(CH<sub>2</sub>)<sub>2</sub>-CH<sub>2</sub>-O, <sup>3</sup>J<sub>H,H</sub> = 5.2 Hz), 2.20-2.28 (2H, m, HC≡C-CH<sub>2</sub>-(CH<sub>2</sub>)<sub>2</sub>-O, <sup>3</sup>J<sub>H,H</sub> = 6.6 Hz, <sup>3</sup>J<sub>H,H</sub> = 2.7 Hz), 2.04 (3H, s, O-(C=O)-CH<sub>3</sub>), 2.02 (3H, s, O-(C=O)-CH<sub>3</sub>), 2.01 (3H, s, O-(C=O)-CH<sub>3</sub>), 1.99 (3H, s, O-(C=O)-CH<sub>3</sub>), 1.93 (1H, t, HC≡C-(CH<sub>2</sub>)<sub>3</sub>-O, <sup>3</sup>J<sub>H,H</sub> = 2.7 Hz), 1.69-1.89 (2H, m, HC≡C-CH<sub>2</sub>-CH<sub>2</sub>-O, <sup>3</sup>J<sub>H,H</sub> = 7.3 Hz).

**R<sub>f</sub>**(EtOAc/Hex 2:3 (v/v)) = 0.393.

**ESI-MS(+):** *m/z* found 437.1410 [M+Na]<sup>+</sup>, 851.2944 [2M+Na]<sup>+</sup>, calcd. for C<sub>19</sub>H<sub>26</sub>NaO<sub>10</sub><sup>+</sup> 437.1418, C<sub>38</sub>H<sub>52</sub>NaO<sub>20</sub><sup>+</sup> 851.2944.

### Synthesis of (2R,3S,4S,5R,6R)-2-(acetoxymethyl)-6-(pent-4-yn-1-yloxy)tetrahydro-2H-pyran-3,4,5-triyl triacetate (**18**)

To a solution of 1,2,3,4,6-penta-O-acetyl-β-D-galactopyranose (1.000 g, 2.560 mmol, 1 equiv.) in dry CH<sub>2</sub>Cl<sub>2</sub> (20 mL) at 0°C under inert atmosphere (N<sub>2</sub>) were added 4-pentyn-1-ol (0.253 g, 3.070 mmol, 1.2 equiv.) and BF<sub>3</sub>·Et<sub>2</sub>O (0.727 g, 5.120 mmol, 2 equiv.). The reaction mixture was stirred at r.t. for 2 h, then anhydrous K<sub>2</sub>CO<sub>3</sub> (0.48 g) was added and the reaction mixture was further stirred at r.t. for 1 h. The suspension was filtered, and the filtrate was washed with H<sub>2</sub>O (2 × 20 mL). The unified aqueous phases were extracted with CH<sub>2</sub>Cl<sub>2</sub> (2 × 10 mL). The organic phases were combined, washed with brine (10 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated under reduced pressure. Washing of the crude using a CH<sub>2</sub>Cl<sub>2</sub>/Hex mixture afforded **18** as a brown liquid (0.495 g, 1.185 mmol, yield 46%).

**<sup>1</sup>H-NMR (CDCl<sub>3</sub>) δ<sub>H</sub>, ppm:** 5.31-5.36 (1H, m, HC≡C-(CH<sub>2</sub>)<sub>3</sub>-O-CH-CH-CH-CH-OAc), 5.10-5.17 (1H, m, HC≡C-(CH<sub>2</sub>)<sub>3</sub>-O-CH-CH-CH-OAc, <sup>3</sup>J<sub>H,H</sub> = 10.4 Hz), 4.94-5.00 (1H, m, HC≡C-(CH<sub>2</sub>)<sub>3</sub>-O-CH-CH-CH-OAc, <sup>3</sup>J<sub>H,H</sub> = 10.5 Hz), 4.42 (1H, d, HC≡C-(CH<sub>2</sub>)<sub>3</sub>-O-CH-CH-OAc, <sup>3</sup>J<sub>H,H</sub> = 7.9 Hz), 4.06-4.16 (2H, m, CH-CH<sub>2</sub>-OAc), 4.00-4.06 (1H, m, HC≡C-(CH<sub>2</sub>)<sub>3</sub>-O), 3.89-3.96 (1H, m, HC≡C-(CH<sub>2</sub>)<sub>2</sub>-CH<sub>2</sub>-O), 3.87 (1H, t, CH-CH<sub>2</sub>-OAc, <sup>3</sup>J<sub>H,H</sub> = 6.7 Hz), 3.54-3.63 (1H, m, HC≡C-(CH<sub>2</sub>)<sub>2</sub>-CH<sub>2</sub>-O), 2.17-2.24 (2H, m, HC≡C-CH<sub>2</sub>-(CH<sub>2</sub>)<sub>2</sub>-O, <sup>3</sup>J<sub>H,H</sub> = 6.5 Hz), 2.09 (3H, s, O-(C=O)-CH<sub>3</sub>), 2.01 (1H, s, O-(C=O)-CH<sub>3</sub>), 1.99 (1H, s, O-(C=O)-CH<sub>3</sub>), 1.92 (1H, s, O-(C=O)-CH<sub>3</sub>), 1.74-1.85 (1H, m, HC≡C-CH<sub>2</sub>-CH<sub>2</sub>-O, <sup>3</sup>J<sub>H,H</sub> = 6.4 Hz), 1.64-1.74 (1H, m, HC≡C-CH<sub>2</sub>-CH<sub>2</sub>-O, <sup>3</sup>J<sub>H,H</sub> = 6.2 Hz).

**R<sub>f</sub>**(EtOAc/Hex 2:3 (v/v)) = 0.393.

**ESI-MS(+):** *m/z* found 432.1851 [M+H<sub>2</sub>O]<sup>+</sup>, 437.1401 [M+Na]<sup>+</sup>, 851.2927 [2M+Na]<sup>+</sup> calcd. for C<sub>19</sub>H<sub>28</sub>O<sub>11</sub> 432.1632, C<sub>19</sub>H<sub>26</sub>NaO<sub>10</sub><sup>+</sup> 437.1418, C<sub>38</sub>H<sub>52</sub>NaO<sub>20</sub><sup>+</sup> 851.2944.

#### 4. Synthesis of the carbohydrate functionalized trithiolato-bridged dinuclear ruthenium(II)-arene complexes 19-26

The carbohydrate functionalized trithiolato Ru(II)-arene complexes were prepared and purified by adapting a literature procedure [6,12].

##### Synthesis of $[(\eta^6\text{-}p\text{-MeC}_6\text{H}_4\text{Pr}^i)_2\text{Ru}_2(\mu_2\text{-SCH}_2\text{C}_6\text{H}_4\text{-}p\text{-Bu}^t)_2(\mu_2\text{-SC}_6\text{H}_4\text{-}p\text{-R})]\text{Cl}$ ( $\text{R} = [2\text{-}((4\text{-}((2R,3R,4S,5R,6R)\text{-}3,4,5\text{-triacetoxy-6-(acetoxymethyl)tetrahydro-2H-pyran-2-yl)-1H-1,2,3-triazol-4-yl)butanoyl)oxy)]$ ) (**19**)

To a solution of **6** (0.200 g, 0.184 mmol, 1 equiv.) in dry DMF (10 mL) at r.t. under inert atmosphere ( $\text{N}_2$ ) were successively added **10** (0.082 g, 0.221 mmol, 1.2 equiv.),  $\text{CuSO}_4\cdot 5\text{H}_2\text{O}$  (0.045 g, 0.184 mmol, 1 equiv.) and sodium ascorbate (0.073 g, 0.368 mmol, 2 equiv.). The reaction mixture was stirred at r.t. for 24 h, then it was diluted with EtOAc (100 mL), washed with  $\text{H}_2\text{O}$  (2x100 mL), and the aqueous phase was further extracted with EtOAc (2x100 mL). The organic phases were combined, washed with brine (100 mL), dried over anhydrous  $\text{Na}_2\text{SO}_4$ , filtered, and concentrated under reduced pressure. Purification by column chromatography using  $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$  10:1 (v/v) as eluent afforded **19** as an orange solid (0.076 g, 0.052 mmol, yield 28%).

$^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta_{\text{H}}$ , ppm: 7.79 (2H, d,  $2x\text{S-(Ar)C-CH-CH-C-O-(C=O)}$ ,  $^3J_{\text{H,H}} = 8.6$  Hz), 7.74 (1H, O-(C=O)-(CH<sub>2</sub>)<sub>3</sub>-(Tr)C-CH-N), 7.38-7.50 (8H, m,  $4x\text{S-CH}_2\text{-(Ar)C-CH-CH-C-C(CH}_3)_3$ ,  $4x\text{S-CH}_2\text{-(Ar)C-CH-CH-C-C(CH}_3)_3$ ), 7.06 (2H, d,  $2x\text{S-(Ar)C-CH-CH-C-O-(C=O)}$ ,  $^3J_{\text{H,H}} = 8.6$  Hz), 5.96 (1H, d, (Tr)N-CH-CH-OAc,  $^3J_{\text{H,H}} = 9.3$  Hz), 5.51 (1H, t, (Tr)N-CH-CH-OAc,  $^3J_{\text{H,H}} = 9.5$  Hz), 5.43 (1H, t, (Tr)N-CH-CH-CH-OAc,  $^3J_{\text{H,H}} = 9.3$  Hz), 5.25 (1H, t, (Tr)N-CH-CH-CH-CH-OAc,  $^3J_{\text{H,H}} = 9.4$  Hz), 5.12 (2H, d,  $2x\text{CH}_3\text{-(Ar)C-CH-CH-C}$ ,  $^3J_{\text{H,H}} = 5.7$  Hz), 5.00 (2H, d,  $2x\text{CH}_3\text{-(Ar)C-CH-CH-C}$ ,  $^3J_{\text{H,H}} = 5.8$  Hz), 4.91 (2H, d,  $2x\text{CH}_3\text{-(Ar)C-CH-CH-C}$ ,  $^3J_{\text{H,H}} = 5.8$  Hz), 4.62 (2H, d,  $2x\text{CH}_3\text{-(Ar)C-CH-CH-C}$ ,  $^3J_{\text{H,H}} = 5.8$  Hz), 4.31 (1H, dd, CH-CH<sub>2</sub>-OAc,  $^2J_{\text{H,H}} = 12.6$  Hz,  $^3J_{\text{H,H}} = 4.8$  Hz), 4.15 (1H, dd, CH-CH<sub>2</sub>-OAc,  $^2J_{\text{H,H}} = 12.6$  Hz,  $^3J_{\text{H,H}} = 2.0$  Hz), 4.07 (1H, ddd, CH-CH<sub>2</sub>-OAc,  $^3J_{\text{H,H}} = 10.1$  Hz,  $^3J_{\text{H,H}} = 4.8$  Hz,  $^3J_{\text{H,H}} = 2.1$  Hz), 3.61 (2H, s, S-CH<sub>2</sub>-(Ar)C-CH-CH-C-(CH<sub>3</sub>)<sub>3</sub>), 3.42 (2H, s, S-CH<sub>2</sub>-(Ar)C-CH-CH-C-(CH<sub>3</sub>)<sub>3</sub>), 2.87 (2H, t, O-(C=O)-CH<sub>2</sub>-(CH<sub>2</sub>)<sub>2</sub>-(Tr)C,  $^3J_{\text{H,H}} = 6.7$  Hz), 2.64 (2H, t, O-(C=O)-(CH<sub>2</sub>)<sub>2</sub>-CH<sub>2</sub>-(Tr)C,  $^3J_{\text{H,H}} = 7.4$  Hz), 2.15 (2H, qvint, O-(C=O)-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-(Tr)C,  $^3J_{\text{H,H}} = 7.4$  Hz), 2.08 (3H, s, O-(C=O)-CH<sub>3</sub>), 2.06 (3H, s, O-(C=O)-CH<sub>3</sub>), 2.02 (3H, s, O-(C=O)-CH<sub>3</sub>), 1.89 (2H, sept,  $2x\text{(Ar)C-CH-CH-C-CH(CH}_3)_2$ ,  $^3J_{\text{H,H}} = 6.9$  Hz), 1.87 (3H, s, O-(C=O)-CH<sub>3</sub>), 1.76 (6H, s,  $2x\text{CH}_3\text{-(Ar)C-CH-CH-C}$ ), 1.36 (9H, s, S-CH<sub>2</sub>-(Ar)C-CH-CH-C-C(CH<sub>3</sub>)<sub>3</sub>), 1.32 (9H, s, S-CH<sub>2</sub>-(Ar)C-CH-CH-C-C(CH<sub>3</sub>)<sub>3</sub>), 0.94 (6H, d, (Ar)C-CH-CH-C-CH(CH<sub>3</sub>)<sub>2</sub>,  $^3J_{\text{H,H}} = 6.9$  Hz), 0.89 (6H, d, (Ar)C-CH-CH-C-CH(CH<sub>3</sub>)<sub>2</sub>,  $^3J_{\text{H,H}} = 6.9$  Hz).

$^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ )  $\delta_{\text{C}}$ , ppm: 171.5 (1C, O-(C=O)-(CH<sub>2</sub>)<sub>3</sub>-(Tr)C), 170.7 (1C, O-(C=O)-CH<sub>3</sub>), 170.0 (1C, O-(C=O)-CH<sub>3</sub>), 169.5 (1C, O-(C=O)-CH<sub>3</sub>), 169.1 (1C, O-(C=O)-CH<sub>3</sub>), 151.9, 151.8 (2C,  $2x\text{S-CH}_2\text{-(Ar)C-CH-CH-C-C(CH}_3)_3$ ), 151.1 (1C, S-(Ar)C-CH-CH-C-O), 147.7 (1C, O-(C=O)-(CH<sub>2</sub>)<sub>3</sub>-(Tr)C-CH-N), 136.7 (2C,  $2x\text{S-CH}_2\text{-(Ar)C-CH-CH-C-C(CH}_3)_3$ ), 135.1 (1C, S-(Ar)C-CH-CH-C-O), 133.7 (2C,  $2x\text{S-(Ar)C-CH-CH-C-O}$ ), 129.4, 129.2 (4C,  $4x\text{S-CH}_2\text{-(Ar)C-CH-CH-C-C(CH}_3)_3$ ), 125.7, 125.5 (4C,  $4x\text{S-CH}_2\text{-(Ar)C-CH-CH-C-C(CH}_3)_3$ ), 122.5 (2C,  $2x\text{S-(Ar)C-CH-CH-C-O}$ ), 120.3 (1C, O-(C=O)-(CH<sub>2</sub>)<sub>3</sub>-(Tr)C-CH-N), 107.2

(2C, 2xCH<sub>3</sub>-(Ar)C-CH-CH-C), 100.7 (2C, 2xCH<sub>3</sub>-(Ar)C-CH-CH-C), 85.6 (1C, (Tr)N-CH-CH-OAc), 84.3 (2C, 2xCH<sub>3</sub>-(Ar)C-CH-CH-C), 83.8 (4C, 4xCH<sub>3</sub>-(Ar)C-CH-CH-C), 82.6 (2C, 2xCH<sub>3</sub>-(Ar)C-CH-CH-C), 75.1 (1C, CH-CH<sub>2</sub>-OAc), 73.0 (1C, (Tr)N-CH-CH-CH-OAc), 70.4 (1C, (Tr)N-CH-CH-OAc), 67.9 (1C, (Tr)N-CH-CH-CH-CH-OAc), 61.7 (1C, CH-CH<sub>2</sub>-OAc), 40.1 (1C, S-CH<sub>2</sub>-(Ar)C-CH-CH-C-C(CH<sub>3</sub>)<sub>3</sub>), 39.7 (1C, S-CH<sub>2</sub>-(Ar)C-CH-CH-C-C(CH<sub>3</sub>)<sub>3</sub>), 34.91 (1C, S-CH<sub>2</sub>-(Ar)C-CH-CH-C-C(CH<sub>3</sub>)<sub>3</sub>), 34.87 (1C, S-CH<sub>2</sub>-(Ar)C-CH-CH-C-C(CH<sub>3</sub>)<sub>3</sub>), 33.5 (1C, O-(C=O)-(CH<sub>2</sub>)<sub>2</sub>-CH<sub>2</sub>-(Tr)C), 31.55 (3C, S-CH<sub>2</sub>-(Ar)C-CH-CH-C-C(CH<sub>3</sub>)<sub>3</sub>), 31.52 (3C, S-CH<sub>2</sub>-(Ar)C-CH-CH-C-C(CH<sub>3</sub>)<sub>3</sub>), 31.0 (2C, 2xCH<sub>3</sub>-(Ar)C-CH-CH-C-CH(CH<sub>3</sub>)<sub>2</sub>), 24.9 (1C, O-(C=O)-CH<sub>2</sub>-(CH<sub>2</sub>)<sub>2</sub>-(Tr)C), 24.4 (1C, O-(C=O)-(CH<sub>2</sub>)<sub>2</sub>-CH<sub>2</sub>-(Tr)C), 23.2 (2C, (Ar)CH-CH-C-CH-(CH<sub>3</sub>)<sub>2</sub>), 22.7 (2C, (Ar)CH-CH-C-CH-(CH<sub>3</sub>)<sub>2</sub>), 20.9 (1C, O-(C=O)-CH<sub>3</sub>), 20.7 (2C, 2xO-(C=O)-CH<sub>3</sub>), 20.4 (1C, O-(C=O)-CH<sub>3</sub>), 18.3 (2C, 2xCH<sub>3</sub>-(Ar)C-CH-CH).

$R_f(\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH } 10:1 \text{ (v/v)}) = 0.526$ .

**ESI-MS(+):**  $m/z$  found 1422.3648  $[\text{M}-\text{Cl}]^+$ , calcd. for  $\text{C}_{68}\text{H}_{88}\text{N}_3\text{O}_{11}\text{Ru}_2\text{S}_3^+$  1422.3662.

**Elemental analysis (%)**: calcd. for  $\text{C}_{68}\text{H}_{88}\text{ClN}_3\text{O}_{11}\text{Ru}_2\text{S}_3 \cdot 0.46\text{CH}_2\text{Cl}_2$  C 54.95, H 5.99, N 2.81; found C 54.93, H 6.16, N 2.85.

**Synthesis of  $[(\eta^6\text{-}p\text{-MeC}_6\text{H}_4\text{Pr}^i)_2\text{Ru}_2(\mu_2\text{-SCH}_2\text{C}_6\text{H}_4\text{-}p\text{-Bu}^t)_2(\mu_2\text{-SC}_6\text{H}_4\text{-}p\text{-R})]\text{Cl}$  ( $\text{R} = [2\text{-}(4\text{-}((2R,3R,4S,5R,6R)\text{-}3,4,5\text{-triacetoxy-6-(acetoxymethyl)tetrahydro-2H-pyran-2-yl)-1H-1,2,3\text{-triazol-4-yl})\text{butanamido}]]$  (**20**))**

To a solution of **7** (0.220 g, 0.203 mmol, 1 equiv.) in dry DMF (10 mL) at r.t. under inert atmosphere ( $\text{N}_2$ ) were successively added **10** (0.090 g, 0.242 mmol, 1.2 equiv.),  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  (0.051 g, 0.203 mmol, 1 equiv.) and sodium ascorbate (0.080 g, 0.406 mmol, 2 equiv.). The reaction mixture was stirred at r.t. for 24 h. Then the mixture was diluted with EtOAc (100 mL), washed with  $\text{H}_2\text{O}$  (2x100 mL), and the aqueous phase was further extracted with EtOAc (2x100 mL). The organic phases were combined, washed with brine (100 mL), dried over anhydrous  $\text{Na}_2\text{SO}_4$ , filtered, and concentrated under reduced pressure. Purification by column chromatography using  $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH } 10:1 \text{ (v/v)}$  as eluent afforded **20** as an orange solid (0.206g, 0.146 mmol, yield 72%).

**$^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta_{\text{H}}$ , ppm:** 11.17 (1H,  $\text{NH-(C=O)-(CH}_2)_3$ ), 8.12 (2H, d,  $2x\text{S-(Ar)C-CH-CH-C-NH-(C=O)}$ ,  $^3J_{\text{H,H}} = 8.2 \text{ Hz}$ ), 8.04 (1H,  $\text{NH-(C=O)-(CH}_2)_3\text{-(Tr)C-CH-N}$ ), 7.58 (2H, d,  $2x\text{S-(Ar)C-CH-CH-C-NH-(C=O)}$ ,  $^3J_{\text{H,H}} = 8.2 \text{ Hz}$ ), 7.35-7.52 (8H, m,  $4x\text{S-CH}_2\text{-(Ar)C-CH-CH-C-C(CH}_3)_3$ ,  $4x\text{S-CH}_2\text{-(Ar)C-CH-CH-C-C(CH}_3)_3$ ), 5.90 (1H, d,  $(\text{Tr})\text{N-CH-CH-OAc}$ ,  $^3J_{\text{H,H}} = 9.4 \text{ Hz}$ ), 5.61 (1H, t,  $(\text{Tr})\text{N-CH-CH-OAc}$ ,  $^3J_{\text{H,H}} = 9.4 \text{ Hz}$ ), 5.40 (1H, t,  $(\text{Tr})\text{N-CH-CH-CH-OAc}$ ,  $^3J_{\text{H,H}} = 9.4 \text{ Hz}$ ), 5.27 (1H, t,  $(\text{Tr})\text{N-CH-CH-CH-CH-OAc}$ ,  $^3J_{\text{H,H}} = 9.3 \text{ Hz}$ ), 4.98 (2H, d,  $2x\text{CH}_3\text{-(Ar)C-CH-CH-C}$ ,  $^3J_{\text{H,H}} = 5.4 \text{ Hz}$ ), 4.88 (2H, d,  $2x\text{CH}_3\text{-(Ar)C-CH-CH-C}$ ,  $^3J_{\text{H,H}} = 5.6 \text{ Hz}$ ), 4.69 (2H, d,  $2x\text{CH}_3\text{-(Ar)C-CH-CH-C}$ ,  $^3J_{\text{H,H}} = 5.5 \text{ Hz}$ ), 4.61 (2H, d,  $2x\text{CH}_3\text{-(Ar)C-CH-CH-C}$ ,  $^3J_{\text{H,H}} = 5.5 \text{ Hz}$ ), 4.29 (1H, dd,  $\text{CH-CH}_2\text{-OAc}$ ,  $^2J_{\text{H,H}} = 12.5 \text{ Hz}$ ,  $^3J_{\text{H,H}} = 4.6 \text{ Hz}$ ), 4.16 (1H, dd,  $\text{CH-CH}_2\text{-OAc}$ ,  $^2J_{\text{H,H}} = 12.4 \text{ Hz}$ ,  $^3J_{\text{H,H}} = 1.2 \text{ Hz}$ ), 4.01 (1H, ddd,  $\text{CH-CH}_2\text{-OAc}$ ,  $^3J_{\text{H,H}} = 10.0 \text{ Hz}$ ,  $^3J_{\text{H,H}} = 4.8 \text{ Hz}$ ,  $^3J_{\text{H,H}} = 2.0 \text{ Hz}$ ), 3.55 (2H, s,  $\text{S-CH}_2\text{-(Ar)C-CH-CH-C-(CH}_3)_3$ ), 3.36 (2H, s,  $\text{S-CH}_2\text{-(Ar)C-CH-CH-C-(CH}_3)_3$ ), 2.89 (2H, t,  $\text{NH-(C=O)-(CH}_2)_2\text{-CH}_2\text{-(Tr)C}$ ,  $^3J_{\text{H,H}} = 7.4 \text{ Hz}$ ), 2.77 (2H, t,  $\text{NH-(C=O)-CH}_2\text{-(CH}_2)_2\text{-(Tr)C}$ ,  $^3J_{\text{H,H}} = 7.3 \text{ Hz}$ ), 2.15 (2H, qvint,  $\text{NH-(C=O)-CH}_2\text{-CH}_2\text{-CH}_2\text{-(Tr)C}$ ,  $^3J_{\text{H,H}} = 7.2 \text{ Hz}$ ), 2.09 (3H, s, O-

(C=O)-CH<sub>3</sub>), 2.05 (3H, s, O-(C=O)-CH<sub>3</sub>), 2.02 (3H, s, O-(C=O)-CH<sub>3</sub>), 1.95-2.06 (2H, m, 2x(Ar)C-CH-CH-C-CH(CH<sub>3</sub>)<sub>2</sub>), 1.86 (3H, s, O-(C=O)-CH<sub>3</sub>), 1.66 (6H, s, 2xCH<sub>3</sub>-(Ar)C-CH-CH-C), 1.37 (9H, s, S-CH<sub>2</sub>-(Ar)C-CH-CH-C-C(CH<sub>3</sub>)<sub>3</sub>), 1.34 (9H, s, S-CH<sub>2</sub>-(Ar)C-CH-CH-C-C(CH<sub>3</sub>)<sub>3</sub>), 0.99 (6H, d, (Ar)C-CH-CH-C-CH(CH<sub>3</sub>)<sub>2</sub>, <sup>3</sup>J<sub>H,H</sub> = 6.8 Hz), 0.93 (6H, d, (Ar)C-CH-CH-C-CH(CH<sub>3</sub>)<sub>2</sub>, <sup>3</sup>J<sub>H,H</sub> = 6.8 Hz).

**<sup>13</sup>C-NMR (CDCl<sub>3</sub>) δ<sub>c</sub>, ppm:** 173.3 (1C, NH-(C=O)-(CH<sub>2</sub>)<sub>3</sub>-(Tr)C), 170.9 (1C, O-(C=O)-CH<sub>3</sub>), 170.2 (1C, O-(C=O)-CH<sub>3</sub>), 169.5 (1C, O-(C=O)-CH<sub>3</sub>), 168.9 (1C, O-(C=O)-CH<sub>3</sub>), 152.02, 151.99 (2C, 2xS-CH<sub>2</sub>-(Ar)C-CH-CH-C-C(CH<sub>3</sub>)<sub>3</sub>), 148.5 (1C, NH-(C=O)-(CH<sub>2</sub>)<sub>3</sub>-(Tr)C-CH-N), 141.5 (1C, S-(Ar)C-CH-CH-C-NH), 136.8, 136.5 (2C, 2xS-CH<sub>2</sub>-(Ar)C-CH-CH-C-C(CH<sub>3</sub>)<sub>3</sub>), 132.7 (2C, 2xS-(Ar)C-CH-CH-C-NH), 129.34 (1C, S-(Ar)C-CH-CH-C-NH), 129.31, 129.1 (4C, 4xS-CH<sub>2</sub>-(Ar)C-CH-CH-C-C(CH<sub>3</sub>)<sub>3</sub>), 125.71, 125.65 (4C, 4xS-CH<sub>2</sub>-(Ar)C-CH-CH-C-C(CH<sub>3</sub>)<sub>3</sub>), 121.1 (1C, NH-(C=O)-(CH<sub>2</sub>)<sub>3</sub>-(Tr)C-CH-N), 120.5 (2C, 2xS-(Ar)C-CH-CH-C-NH), 107.8 (2C, 2xCH<sub>3</sub>-(Ar)C-CH-CH-C), 100.1 (2C, 2xCH<sub>3</sub>-(Ar)C-CH-CH-C), 85.6 (1C, (Tr)N-CH-CH-OAc), 84.3 (2C, 2xCH<sub>3</sub>-(Ar)C-CH-CH-C), 83.9 (2C, 2xCH<sub>3</sub>-(Ar)C-CH-CH-C), 83.2 (2C, 2xCH<sub>3</sub>-(Ar)C-CH-CH-C), 82.2 (2C, 2xCH<sub>3</sub>-(Ar)C-CH-CH-C), 75.0 (1C, CH-CH<sub>2</sub>-OAc), 73.3 (1C, (Tr)N-CH-CH-CH-OAc), 70.3 (1C, (Tr)N-CH-CH-CH-OAc), 68.0 (1C, (Tr)N-CH-CH-CH-CH-OAc), 61.8 (1C, CH-CH<sub>2</sub>-OAc), 39.9 (1C, S-CH<sub>2</sub>-(Ar)C-CH-CH-C-C(CH<sub>3</sub>)<sub>3</sub>), 39.2 (1C, S-CH<sub>2</sub>-(Ar)C-CH-CH-C-C(CH<sub>3</sub>)<sub>3</sub>), 36.8 (1C, NH-(C=O)-CH<sub>2</sub>-(CH<sub>2</sub>)<sub>2</sub>-(Tr)C), 34.93 (1C, S-CH<sub>2</sub>-(Ar)C-CH-CH-C-C(CH<sub>3</sub>)<sub>3</sub>), 34.91 (1C, S-CH<sub>2</sub>-(Ar)C-CH-CH-C-C(CH<sub>3</sub>)<sub>3</sub>), 31.6 (6C, 2xS-CH<sub>2</sub>-(Ar)C-CH-CH-C-C(CH<sub>3</sub>)<sub>3</sub>), 31.1 (2C, 2x(Ar)CH-CH-C-CH(CH<sub>3</sub>)<sub>2</sub>), 25.4 (1C, NH-(C=O)-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-(Tr)C), 25.3 (1C, NH-(C=O)-CH<sub>2</sub>-CH<sub>2</sub>-(Tr)C), 23.1 (2C, (Ar)CH-CH-C-CH(CH<sub>3</sub>)<sub>2</sub>), 23.0 (2C, (Ar)CH-CH-C-CH(CH<sub>3</sub>)<sub>2</sub>), 20.9 (1C, O-(C=O)-CH<sub>3</sub>), 20.7 (2C, 2xO-(C=O)-CH<sub>3</sub>), 20.4 (1C, O-(C=O)-CH<sub>3</sub>), 18.1 (2C, 2xCH<sub>3</sub>-(Ar)C-CH-CH).

**R<sub>f</sub>**(CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>OH 10:1 (v/v)) = 0.404.

**ESI-MS(+):** *m/z* found 1421.3807 [M-Cl]<sup>+</sup>, calcd. for C<sub>68</sub>H<sub>89</sub>N<sub>4</sub>O<sub>10</sub>Ru<sub>2</sub>S<sub>3</sub><sup>+</sup> 1421.3822.

**Elemental analysis (%):** calcd. for C<sub>68</sub>H<sub>89</sub>ClN<sub>4</sub>O<sub>10</sub>Ru<sub>2</sub>S<sub>3</sub>·0.35CH<sub>2</sub>Cl<sub>2</sub> C 55.25, H 6.08, N 3.87; found C 55.25, H 6.19, N 3.80.

**Synthesis of [(η<sup>6</sup>-*p*-MeC<sub>6</sub>H<sub>4</sub>Pr<sup>i</sup>)<sub>2</sub>Ru<sub>2</sub>(μ<sub>2</sub>-SCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>-*p*-Bu<sup>t</sup>)<sub>2</sub>(μ<sub>2</sub>-SC<sub>6</sub>H<sub>4</sub>-*p*-R)]Cl (R = [2-(4-(1-(2-(((2*R*,3*R*,4*S*,5*R*,6*R*)-3,4,5-triacetoxy-6-(acetoxymethyl)tetrahydro-2*H*-pyran-2-yl)oxy)ethyl)-1*H*-1,2,3-triazol-4-yl)butanamido]) (21)**

To a solution of **7** (0.162 g, 0.155 mmol, 1 equiv.) in dry DMF (10 mL) at r.t. under inert atmosphere (N<sub>2</sub>) were successively added **14** (0.130 g, 0.311 mmol, 2 equiv.), CuSO<sub>4</sub>·5H<sub>2</sub>O (0.040 g, 0.155 mmol, 1 equiv.) and sodium ascorbate (0.061 g, 0.311 mmol, 2 equiv.). The reaction mixture was stirred at r.t. for 24 h, then it was solubilized with EtOAc (100 mL), washed with H<sub>2</sub>O (2x100 mL), and the aqueous phase was further extracted with EtOAc (2x100 mL). The organic phases were combined, washed with brine (100 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated to dryness under reduced pressure. Purification by column chromatography using CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>OH 10:1 (v/v) mixture as eluent afforded **21** as an orange solid (0.155 g, 0.103 mmol, yield 66%).

**<sup>1</sup>H-NMR (CDCl<sub>3</sub>) δ<sub>H</sub>, ppm:** 11.13 (1H, s br, (Ar)C-NH-(C=O)), 8.11 (2H, d, 2xS-(Ar)C-CH-CH-C-NH-(C=O), <sup>3</sup>J<sub>H,H</sub> = 8.6 Hz), 8.02 (1H, s, O-(CH<sub>2</sub>)<sub>2</sub>-(Tr)N-CH-CH-C), 7.58 (2H, d, 2xS-(Ar)C-CH-CH-C-NH-(C=O), <sup>3</sup>J<sub>H,H</sub> = 8.5 Hz), 7.36-7.53 (8H, m, 4xS-CH<sub>2</sub>-(Ar)C-CH-CH-C-C(CH<sub>3</sub>)<sub>3</sub>, 4xS-CH<sub>2</sub>-(Ar)C-CH-CH-C-C(CH<sub>3</sub>)<sub>3</sub>), 5.18 (1H, t, (Tr)N-(CH<sub>2</sub>)<sub>2</sub>-O-CH-CH-CH-OAc, <sup>3</sup>J<sub>H,H</sub> = 9.5 Hz), 5.07 (1H, t, (Tr)N-(CH<sub>2</sub>)<sub>2</sub>-O-CH-CH-CH-CH-OAc, <sup>3</sup>J<sub>H,H</sub> = 9.8 Hz), 4.95-5.02 (1H, m, (Tr)N-(CH<sub>2</sub>)<sub>2</sub>-O-CH-CH-OAc), 4.98 (2H, d, 2xCH<sub>3</sub>-(Ar)C-CH-CH-C, <sup>3</sup>J<sub>H,H</sub> = 5.3 Hz), 4.88 (2H, d, 2xCH<sub>3</sub>-(Ar)C-CH-CH-C, <sup>3</sup>J<sub>H,H</sub> = 5.8 Hz), 4.69 (2H, d, 2xCH<sub>3</sub>-(Ar)C-CH-CH-C, <sup>3</sup>J<sub>H,H</sub> = 5.7 Hz), 4.65 (1H, d, (Tr)N-(CH<sub>2</sub>)<sub>2</sub>-O-CH-CH-OAc, <sup>3</sup>J<sub>H,H</sub> = 8.0 Hz), 4.61 (2H, d, 2xCH<sub>3</sub>-(Ar)C-CH-CH-C, <sup>3</sup>J<sub>H,H</sub> = 5.8 Hz), 4.54-4.60 (2H, m, (Tr)N-CH<sub>2</sub>-CH<sub>2</sub>-O-CH-OAc, <sup>3</sup>J<sub>H,H</sub> = 4.9 Hz), 4.28 (1H, dd, CH-CH<sub>2</sub>-OAc, <sup>2</sup>J<sub>H,H</sub> = 12.0 Hz, <sup>3</sup>J<sub>H,H</sub> = 4.6 Hz), 4.24-4.31 (1H, m, (Tr)N-CH<sub>2</sub>-CH<sub>2</sub>-O-CH-OAc), 4.15 (1H, dd, CH-CH<sub>2</sub>-OAc, <sup>2</sup>J<sub>H,H</sub> = 12.2 Hz, <sup>3</sup>J<sub>H,H</sub> = 1.9 Hz), 4.11-4.19 (1H, m, (Tr)N-CH<sub>2</sub>-CH<sub>2</sub>-O-CH-CH-OAc), 3.80 (1H, ddd, CH-CH<sub>2</sub>-OAc, <sup>3</sup>J<sub>H,H</sub> = 10.0 Hz, <sup>3</sup>J<sub>H,H</sub> = 4.3 Hz, <sup>3</sup>J<sub>H,H</sub> = 2.1 Hz), 3.55 (2H, s, S-CH<sub>2</sub>-(Ar)C-CH-CH-C-(CH<sub>3</sub>)<sub>3</sub>), 3.35 (2H, s, S-CH<sub>2</sub>-(Ar)C-CH-CH-C-(CH<sub>3</sub>)<sub>3</sub>), 2.82-2.92 (2H, m, NH-(C=O)-(CH<sub>2</sub>)<sub>2</sub>-CH<sub>2</sub>-(Tr)C), 2.69-2.79 (2H, m, NH-(C=O)-CH<sub>2</sub>-(CH<sub>2</sub>)<sub>2</sub>-(Tr)C), 2.10-2.19 (2H, m, NH-(C=O)-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-(Tr)C), 2.09 (3H, s, O-(C=O)-CH<sub>3</sub>), 2.00 (3H, s, O-(C=O)-CH<sub>3</sub>), 1.97 (3H, s, O-(C=O)-CH<sub>3</sub>), 1.96 (3H, s, O-(C=O)-CH<sub>3</sub>), 1.95-2.04 (2H, m, 2x(Ar)C-CH-CH-C-CH(CH<sub>3</sub>)<sub>2</sub>), 1.66 (6H, s, 2xCH<sub>3</sub>-(Ar)C-CH-CH-C), 1.37 (9H, s, S-CH<sub>2</sub>-(Ar)C-CH-CH-C-C(CH<sub>3</sub>)<sub>3</sub>), 1.34 (9H, s, S-CH<sub>2</sub>-(Ar)C-CH-CH-C-C(CH<sub>3</sub>)<sub>3</sub>), 0.99 (6H, d, (Ar)C-CH-CH-C-CH(CH<sub>3</sub>)<sub>2</sub>, <sup>3</sup>J<sub>H,H</sub> = 6.8 Hz), 0.94 (6H, d, (Ar)C-CH-CH-C-CH(CH<sub>3</sub>)<sub>2</sub>, <sup>3</sup>J<sub>H,H</sub> = 6.9 Hz).

**<sup>13</sup>C-NMR (CDCl<sub>3</sub>) δ<sub>C</sub>, ppm:** 173.4 (1C, NH-(C=O)-(CH<sub>2</sub>)<sub>3</sub>-(Tr)C), 170.9 (1C, O-(C=O)-CH<sub>3</sub>), 170.3 (1C, O-(C=O)-CH<sub>3</sub>), 169.63 (1C, O-(C=O)-CH<sub>3</sub>), 169.59 (1C, O-(C=O)-CH<sub>3</sub>), 152.02, 152.00 (2C, 2xS-CH<sub>2</sub>-(Ar)C-CH-CH-C-C(CH<sub>3</sub>)<sub>3</sub>), 147.7 (NH-(C=O)-(CH<sub>2</sub>)<sub>3</sub>-(Tr)C-CH-N), 141.5 (1C, S-(Ar)C-CH-CH-C-NH), 136.8, 136.5 (2C, 2xS-CH<sub>2</sub>-(Ar)C-CH-CH-C-C(CH<sub>3</sub>)<sub>3</sub>), 132.7 (3C, 2xS-(Ar)C-CH-CH-C-NH, S-(Ar)C-CH-CH-C-NH), 129.3, 129.0 (4C, 4xS-CH<sub>2</sub>-(Ar)C-CH-CH-C-C(CH<sub>3</sub>)<sub>3</sub>), 125.70, 125.65 (4C, 4xS-CH<sub>2</sub>-(Ar)C-CH-CH-C-C(CH<sub>3</sub>)<sub>3</sub>), 123.0 (NH-(C=O)-(CH<sub>2</sub>)<sub>3</sub>-(Tr)C-CH-N), 120.4 (2C, 2xS-(Ar)C-CH-CH-C-NH), 107.8 (2C, 2xCH<sub>3</sub>-(Ar)C-CH-CH-C), 100.8 (1C, (Tr)N-(CH<sub>2</sub>)<sub>2</sub>-O-CH-CH-OAc), 100.1 (2C, 2xCH<sub>3</sub>-(Ar)C-CH-CH-C), 84.3 (2C, 2xCH<sub>3</sub>-(Ar)C-CH-CH-C), 83.9 (2C, 2xCH<sub>3</sub>-(Ar)C-CH-CH-C), 83.2 (2C, 2xCH<sub>3</sub>-(Ar)C-CH-CH-C), 82.2 (2C, 2xCH<sub>3</sub>-(Ar)C-CH-CH-C), 73.0 (1C, (Tr)N-(CH<sub>2</sub>)<sub>2</sub>-O-CH-CH-CH-OAc), 71.9 (1C, CH-CH<sub>2</sub>-OAc), 71.1 (1C, (Tr)N-(CH<sub>2</sub>)<sub>2</sub>-O-CH-CH-OAc), 68.5 (1C, (Tr)N-(CH<sub>2</sub>)<sub>2</sub>-O-CH-CH-CH-CH-OAc), 68.1 (1C, (Tr)N-CH<sub>2</sub>-CH<sub>2</sub>-O-CH-CH-OAc), 61.9 (1C, CH-CH<sub>2</sub>-OAc), 49.7 (1C, (Tr)N-CH<sub>2</sub>-CH<sub>2</sub>-O-CH-CH-OAc), 39.9 (1C, S-CH<sub>2</sub>-(Ar)C-CH-CH-C-C(CH<sub>3</sub>)<sub>3</sub>), 39.2 (1C, S-CH<sub>2</sub>-(Ar)C-CH-CH-C-C(CH<sub>3</sub>)<sub>3</sub>), 36.6 (1C, NH-(C=O)-(CH<sub>2</sub>)<sub>2</sub>-CH<sub>2</sub>-(Tr)C), 34.93 (1C, S-CH<sub>2</sub>-(Ar)C-CH-CH-C-C(CH<sub>3</sub>)<sub>3</sub>), 34.90 (1C, S-CH<sub>2</sub>-(Ar)C-CH-CH-C-C(CH<sub>3</sub>)<sub>3</sub>), 31.54 (3C, S-CH<sub>2</sub>-(Ar)C-CH-CH-C-C(CH<sub>3</sub>)<sub>3</sub>), 31.53 (3C, S-CH<sub>2</sub>-(Ar)C-CH-CH-C-C(CH<sub>3</sub>)<sub>3</sub>), 31.1 (2C, 2x(Ar)CH-CH-C-CH(CH<sub>3</sub>)<sub>2</sub>), 25.3 (2C, NH-(C=O)-CH<sub>2</sub>-(CH<sub>2</sub>)<sub>2</sub>-(Tr)C, NH-(C=O)-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-(Tr)C), 23.1 (2C, (Ar)CH-CH-C-CH(CH<sub>3</sub>)<sub>2</sub>), 23.0 (2C, (Ar)CH-CH-C-CH(CH<sub>3</sub>)<sub>2</sub>), 20.9 (1C, O-(C=O)-CH<sub>3</sub>), 20.8 (1C, O-(C=O)-CH<sub>3</sub>), 20.7 (2C, 2xO-(C=O)-CH<sub>3</sub>), 18.1 (2C, 2xCH<sub>3</sub>-(Ar)C-CH-CH).

**R<sub>f</sub>**(CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>OH 10:1 (v/v)) = 0.509.

**ESI-MS(+):** *m/z* found 1465.4104 [M-Cl]<sup>+</sup>, calcd. for C<sub>70</sub>H<sub>93</sub>N<sub>4</sub>O<sub>11</sub>Ru<sub>2</sub>S<sub>3</sub><sup>+</sup> 1465.4084.

**Elemental analysis (%)**: calcd. for  $C_{70}H_{93}ClN_4O_{11}Ru_2S_3 \cdot 0.9CH_2Cl_2$  C 55.48 H, 6.71, N 3.37; found C 55.46, H 6.50, N 3.52.

**Synthesis of  $[(\eta^6\text{-}p\text{-MeC}_6\text{H}_4\text{Pr}^i)_2\text{Ru}_2(\mu_2\text{-SCH}_2\text{C}_6\text{H}_4\text{-}p\text{-Bu}^t)_2(\mu_2\text{-SC}_6\text{H}_4\text{-}p\text{-R})]\text{Cl}$  ( $R = [2\text{-(4-(1-(2-(((2R,3R,4S,5S,6R)\text{-}3,4,5\text{-triacetoxy-6-(acetoxymethyl)tetrahydro-2H-pyran-2-yl)oxy)ethyl)-1H-1,2,3-triazol-4-yl)butanamido})]$  (**22**)**

To a solution of **7** (0.162 g, 0.155 mmol, 1 equiv.) in dry DMF (10 mL) at r.t. under inert atmosphere ( $N_2$ ) were successively added **15** (0.130 g, 0.311 mmol, 2 equiv.),  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  (0.040 g, 0.155 mmol, 1 equiv.) and sodium ascorbate (0.061 g, 0.311 mmol, 2 equiv.). The reaction mixture was stirred at r.t. for 24 h, then it was solubilized in EtOAc (100 mL), washed with  $\text{H}_2\text{O}$  (2x100 mL), and the aqueous phase was further extracted with EtOAc (2x100 mL). The organic phases were combined, washed with brine (100 mL), dried over anhydrous  $\text{Na}_2\text{SO}_4$ , filtered, and concentrated to dryness under reduced pressure. Purification by column chromatography using  $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$  10:1 (v/v) mixture as eluent afforded **22** as an orange solid (0.151 g, 0.100 mmol, yield 65%).

**$^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta_{\text{H}}$ , ppm**: 11.12 (1H, s br,  $(Ar)\text{C-NH-C(=O)}$ ), 8.10 (2H, d,  $2 \times \text{S-(Ar)C-CH-CH-C-NH-C(=O)}$ ,  $^3J_{\text{H,H}} = 8.5$  Hz), 8.02 (1H, s br,  $\text{O-(CH}_2)_2\text{-(Tr)N-CH-C}$ ), 7.57 (2H, d,  $2 \times \text{S-(Ar)C-CH-CH-C-NH-C(=O)}$ ,  $^3J_{\text{H,H}} = 8.3$  Hz), 7.36-7.51 (8H, m,  $4 \times \text{S-CH}_2\text{-(Ar)C-CH-CH-C-C(CH}_3)_3$ ,  $4 \times \text{S-CH}_2\text{-(Ar)C-CH-CH-C-C(CH}_3)_3$ ), 5.38 (1H, d,  $(\text{Tr})\text{N-(CH}_2)_2\text{-O-CH-CH-CH-CH-OAc}$ ,  $^3J_{\text{H,H}} = 3.0$  Hz), 5.18 (1H, dd,  $(\text{Tr})\text{N-(CH}_2)_2\text{-O-CH-CH-OAc}$ ,  $^3J_{\text{H,H}} = 10.4$  Hz,  $^3J_{\text{H,H}} = 8.0$  Hz), 4.96-5.02 (1H, m,  $(\text{Tr})\text{N-(CH}_2)_2\text{-O-CH-CH-CH-OAc}$ ,  $^3J_{\text{H,H}} = 3.4$  Hz), 4.98 (2H, d,  $2 \times \text{CH}_3\text{-(Ar)C-CH-CH-C}$ ,  $^3J_{\text{H,H}} = 5.5$  Hz), 4.87 (2H, d,  $2 \times \text{CH}_3\text{-(Ar)C-CH-CH-C}$ ,  $^3J_{\text{H,H}} = 5.8$  Hz), 4.69 (2H, d,  $2 \times \text{CH}_3\text{-(Ar)C-CH-CH-C}$ ,  $^3J_{\text{H,H}} = 5.7$  Hz), 4.63 (1H, d,  $(\text{Tr})\text{N-(CH}_2)_2\text{-O-CH-CH-OAc}$ ,  $^3J_{\text{H,H}} = 8.0$  Hz), 4.60 (2H, d,  $2 \times \text{CH}_3\text{-(Ar)C-CH-CH-C}$ ,  $^3J_{\text{H,H}} = 5.9$  Hz), 4.54-4.59 (2H, m,  $(\text{Tr})\text{N-CH}_2\text{-CH}_2\text{-O}$ ), 4.28 (1H, dt,  $(\text{Tr})\text{N-CH}_2\text{-CH}_2\text{-O}$ ,  $^2J_{\text{H,H}} = 10.9$  Hz,  $^3J_{\text{H,H}} = 4.4$  Hz), 4.13-4.18 (2H, m,  $\text{CH-CH}_2\text{-OAc}$ ,  $^3J_{\text{H,H}} = 7.5$  Hz,  $^3J_{\text{H,H}} = 1.7$  Hz), 4.09-4.18 (1H, m,  $(\text{Tr})\text{N-CH}_2\text{-CH}_2\text{-O}$ ), 4.00 (1H, t,  $\text{CH-CH}_2\text{-OAc}$ ,  $^3J_{\text{H,H}} = 6.9$  Hz), 3.54 (2H, s,  $\text{S-CH}_2\text{-(Ar)C-CH-CH-C-(CH}_3)_3$ ), 3.35 (2H, s,  $\text{S-CH}_2\text{-(Ar)C-CH-CH-C-(CH}_3)_3$ ), 2.81-2.91 (2H, m,  $\text{NH-C(=O)-(CH}_2)_2\text{-CH}_2\text{-(Tr)C}$ ), 2.71-2.78 (2H, m,  $\text{NH-C(=O)-CH}_2\text{-(CH}_2)_2\text{-(Tr)C}$ ), 2.09-2.23 (2H, m,  $\text{NH-C(=O)-CH}_2\text{-CH}_2\text{-CH}_2\text{-(Tr)C}$ ), 2.13 (3H, s,  $\text{O-C(=O)-CH}_3$ ), 2.04 (3H, s,  $\text{O-C(=O)-CH}_3$ ), 1.97 (3H, s,  $\text{O-C(=O)-CH}_3$ ), 1.94 (3H, s,  $\text{O-C(=O)-CH}_3$ ), 1.92-2.02 (2H, m,  $2 \times (\text{Ar})\text{C-CH-CH-C-CH(CH}_3)_2$ ), 1.66 (6H, s,  $2 \times \text{CH}_3\text{-(Ar)C-CH-CH-C}$ ), 1.36 (9H, s,  $\text{S-CH}_2\text{-(Ar)C-CH-CH-C-C(CH}_3)_3$ ), 1.34 (9H, s,  $\text{S-CH}_2\text{-(Ar)C-CH-CH-C-C(CH}_3)_3$ ), 0.98 (6H, d,  $(\text{Ar})\text{C-CH-CH-C-CH(CH}_3)_2$ ,  $^3J_{\text{H,H}} = 6.8$  Hz), 0.94 (6H, d,  $(\text{Ar})\text{C-CH-CH-C-CH(CH}_3)_2$ ,  $^3J_{\text{H,H}} = 6.9$  Hz).

**$^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ )  $\delta_{\text{C}}$ , ppm**: 173.4 (1C,  $(\text{Ar})\text{C-NH-C(=O)}$ ), 170.6 (1C,  $\text{O-C(=O)-CH}_3$ ), 170.4 (1C,  $\text{O-C(=O)-CH}_3$ ), 170.1 (1C,  $\text{O-C(=O)-CH}_3$ ), 169.7 (1C,  $\text{O-C(=O)-CH}_3$ ), 152.01, 151.98 (2C,  $2 \times \text{S-CH}_2\text{-(Ar)C-CH-CH-C-C(CH}_3)_3$ ), 147.4 (1C,  $\text{O-(CH}_2)_2\text{-(Tr)N-CH-C}$ ), 141.5 (1C,  $\text{S-(Ar)C-CH-CH-C-NH}$ ), 136.8, 136.5 (2C,  $2 \times \text{S-CH}_2\text{-(Ar)C-CH-CH-C-C(CH}_3)_3$ ), 132.7 (2C,  $2 \times \text{S-(Ar)C-CH-CH-C-NH}$ ), 129.4 (1C,  $\text{S-(Ar)C-CH-CH-C-NH}$ ), 129.3, 129.0 (4C,  $4 \times \text{S-CH}_2\text{-(Ar)C-CH-CH-C-C(CH}_3)_3$ ), 125.7, 125.6 (4C,  $4 \times \text{S-CH}_2\text{-(Ar)C-CH-CH-C-C(CH}_3)_3$ ), 123.2 (1C,  $\text{O-(CH}_2)_2\text{-(Tr)N-CH-C}$ ), 120.4 (2C,  $2 \times \text{S-(Ar)C-CH-CH-C-NH}$ ), 107.8 (2C,  $2 \times \text{CH}_3\text{-(Ar)C-CH-CH-C}$ ), 101.1 (1C,  $(\text{Tr})\text{N-(CH}_2)_2\text{-O-CH-CH-OAc}$ ), 100.1 (2C,

2xCH<sub>3</sub>-(Ar)C-CH-CH-C), 84.3 (2C, 2xCH<sub>3</sub>-(Ar)C-CH-CH-C), 83.8 (2C, 2xCH<sub>3</sub>-(Ar)C-CH-CH-C), 83.2 (2C, 2xCH<sub>3</sub>-(Ar)C-CH-CH-C), 82.2 (2C, 2xCH<sub>3</sub>-(Ar)C-CH-CH-C), 71.0 (1C, (Tr)N-(CH<sub>2</sub>)<sub>2</sub>-O-CH-CH-CH-OAc), 70.8 (1C, CH-CH<sub>2</sub>-OAc), 68.6 (1C, (Tr)N-(CH<sub>2</sub>)<sub>2</sub>-O-CH-CH-OAc), 67.9 (1C, (Tr)N-CH<sub>2</sub>-CH<sub>2</sub>-O), 67.3 (1C, (Tr)N-(CH<sub>2</sub>)<sub>2</sub>-O-CH-CH-CH-CH-OAc), 61.5 (1C, CH-CH<sub>2</sub>-OAc), 49.8 (1C, (Tr)N-CH<sub>2</sub>-CH<sub>2</sub>-O-CH), 39.9 (1C, S-CH<sub>2</sub>-(Ar)C-CH-CH-C-C(CH<sub>3</sub>)<sub>3</sub>), 39.2 (1C, S-CH<sub>2</sub>-(Ar)C-CH-CH-C-C(CH<sub>3</sub>)<sub>3</sub>), 36.7 (1C, NH-(C=O)-CH<sub>2</sub>-(CH<sub>2</sub>)<sub>2</sub>-(Tr)C), 34.92 (1C, S-CH<sub>2</sub>-(Ar)C-CH-CH-C-C(CH<sub>3</sub>)<sub>3</sub>), 34.89 (1C, S-CH<sub>2</sub>-(Ar)C-CH-CH-C-C(CH<sub>3</sub>)<sub>3</sub>), 31.53 (3C, S-CH<sub>2</sub>-(Ar)C-CH-CH-C-C(CH<sub>3</sub>)<sub>3</sub>), 31.52 (3C, S-CH<sub>2</sub>-(Ar)C-CH-CH-C-C(CH<sub>3</sub>)<sub>3</sub>), 31.1 (2C, 2xCH<sub>3</sub>-(Ar)C-CH-CH-C-CH(CH<sub>3</sub>)<sub>2</sub>), 25.3 (1C, NH-(C=O)-(CH<sub>2</sub>)<sub>2</sub>-CH<sub>2</sub>-(Tr)C), 25.2 (1C, NH-(C=O)-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-(Tr)C), 23.1 (2C, (Ar)CH-CH-C-CH-(CH<sub>3</sub>)<sub>2</sub>), 23.0 (2C, (Ar)CH-CH-C-CH-(CH<sub>3</sub>)<sub>2</sub>), 20.88 (1C, O-(C=O)-CH<sub>3</sub>), 20.85 (1C, O-(C=O)-CH<sub>3</sub>), 20.81 (1C, O-(C=O)-CH<sub>3</sub>), 20.7 (1C, O-(C=O)-CH<sub>3</sub>), 18.1 (2C, 2xCH<sub>3</sub>-(Ar)C-CH-CH).

$R_f$ (CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>OH 10:1 (v/v)) = 0.561.

**ESI-MS(+):**  $m/z$  found 1465.4096 [M-Cl]<sup>+</sup>, calcd. for C<sub>70</sub>H<sub>93</sub>N<sub>4</sub>O<sub>11</sub>Ru<sub>2</sub>S<sub>3</sub><sup>+</sup> 1465.4084.

**Elemental analysis (%)**: calcd. for C<sub>70</sub>H<sub>93</sub>ClN<sub>4</sub>O<sub>11</sub>Ru<sub>2</sub>S<sub>3</sub>·CH<sub>2</sub>Cl<sub>2</sub> C 55.58, H 6.72, N 3.37; found C 55.57, H 6.45, N 3.57.

**Synthesis of [(η<sup>6</sup>-*p*-MeC<sub>6</sub>H<sub>4</sub>Pr)<sub>2</sub>Ru<sub>2</sub>(μ<sub>2</sub>-SCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>-*p*-Bu<sup>t</sup>)<sub>2</sub>(μ<sub>2</sub>-SC<sub>6</sub>H<sub>4</sub>-*p*-R)]Cl (R = [2-(4-(1-(4-(((2*R*,3*R*,4*S*,5*S*,6*R*)-3,4,5-triacetoxy-6-(acetoxymethyl)tetrahydro-2*H*-pyran-2-yl)oxy)butyl)-1*H*-1,2,3-triazol-4-yl)butanamido)] (23)**

To a solution of **7** (0.212 g, 0.202 mmol, 1 equiv.) in dry DMF (10 mL) at r.t., under inert atmosphere (N<sub>2</sub>) were successively added **16** (0.180 g, 0.404 mmol, 2 equiv.), CuSO<sub>4</sub>·5H<sub>2</sub>O (0.050 g, 0.202 mmol, 1 equiv.) and sodium ascorbate (0.080 g, 0.404 mmol, 2 equiv.). The reaction mixture was stirred at r.t. for 24 h, then it was solubilized with EtOAc (100 mL), washed with H<sub>2</sub>O (2x100 mL), the aqueous phase was further extracted with EtOAc (2x100 mL). The organic phases were combined, washed with brine (100 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated under reduced pressure. Purification by column chromatography using CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>OH (10:1 (v/v)) as eluent afforded **23** as an orange solid (0.228 g, 0.149 mmol, yield 74%).

**<sup>1</sup>H-NMR (CDCl<sub>3</sub>) δ<sub>H</sub>, ppm**: 11.13 (1H, s br, (Ar)C-NH-(C=O)), 8.10 (2H, d, 2xS-(Ar)C-CH-CH-C-NH-(C=O), <sup>3</sup>J<sub>H,H</sub> = 8.5 Hz), 8.06 (1H, s br, O-(CH<sub>2</sub>)<sub>4</sub>-(Tr)N-CH-C), 7.56 (2H, d, 2xS-(Ar)C-CH-CH-C-NH-(C=O), <sup>3</sup>J<sub>H,H</sub> = 8.3 Hz), 7.36-7.50 (8H, m, 4xS-CH<sub>2</sub>-(Ar)C-CH-CH-C-C(CH<sub>3</sub>)<sub>3</sub>, 4xS-CH<sub>2</sub>-(Ar)C-CH-CH-C-C(CH<sub>3</sub>)<sub>3</sub>), 5.44 (1H, dd, (Tr)N-(CH<sub>2</sub>)<sub>4</sub>-O-CH-CH-CH-CH-OAc, <sup>3</sup>J<sub>H,H</sub> = 3.5 Hz, <sup>3</sup>J<sub>H,H</sub> = 1.0 Hz), 5.32 (1H, dd, (Tr)N-(CH<sub>2</sub>)<sub>4</sub>-O-CH-CH-CH-OAc, <sup>3</sup>J<sub>H,H</sub> = 10.8 Hz, <sup>3</sup>J<sub>H,H</sub> = 3.4 Hz), 5.12 (1H, dd, (Tr)N-(CH<sub>2</sub>)<sub>4</sub>-O-CH-CH-OAc, <sup>3</sup>J<sub>H,H</sub> = 10.8 Hz, <sup>3</sup>J<sub>H,H</sub> = 3.6 Hz), 5.07 (1H, d, (Tr)N-(CH<sub>2</sub>)<sub>4</sub>-O-CH-CH-OAc, <sup>3</sup>J<sub>H,H</sub> = 3.7 Hz), 4.97 (2H, d, 2xCH<sub>3</sub>-(Ar)C-CH-CH-C, <sup>3</sup>J<sub>H,H</sub> = 5.7 Hz), 4.87 (2H, d, 2xCH<sub>3</sub>-(Ar)C-CH-CH-C, <sup>3</sup>J<sub>H,H</sub> = 5.8 Hz), 4.69 (2H, d, 2xCH<sub>3</sub>-(Ar)C-CH-CH-C, <sup>3</sup>J<sub>H,H</sub> = 5.7 Hz), 4.60 (2H, d, 2xCH<sub>3</sub>-(Ar)C-CH-CH-C, <sup>3</sup>J<sub>H,H</sub> = 5.8 Hz), 4.41 (2H, t, (Tr)N-CH<sub>2</sub>-(CH<sub>2</sub>)<sub>3</sub>-O, <sup>3</sup>J<sub>H,H</sub> = 6.9 Hz), 4.20 (1H, t, CH-CH<sub>2</sub>-OAc, <sup>3</sup>J<sub>H,H</sub> = 6.7 Hz), 4.08 (1H, m, CH-CH<sub>2</sub>-OAc, <sup>3</sup>J<sub>H,H</sub> = 2.0 Hz), 4.07 (1H, m, CH-CH<sub>2</sub>-OAc, <sup>3</sup>J<sub>H,H</sub> = 3.1 Hz), 3.75 (1H, dt, (Tr)N-(CH<sub>2</sub>)<sub>3</sub>-CH<sub>2</sub>-O, <sup>3</sup>J<sub>H,H</sub> = 9.9 Hz, <sup>3</sup>J<sub>H,H</sub> = 6.0 Hz), 3.54 (2H, s, S-CH<sub>2</sub>-(Ar)C-CH-CH-C-(CH<sub>3</sub>)<sub>3</sub>), 3.44

(1H, dt, (Tr)N-(CH<sub>2</sub>)<sub>3</sub>-CH<sub>2</sub>-O, <sup>3</sup>J<sub>H,H</sub> = 9.9 Hz, <sup>3</sup>J<sub>H,H</sub> = 6.4 Hz), 3.35 (2H, s, S-CH<sub>2</sub>-(Ar)C-CH-CH-C-(CH<sub>3</sub>)<sub>3</sub>), 2.82-2.91 (2H, m br, NH-(C=O)-(CH<sub>2</sub>)<sub>2</sub>-CH<sub>2</sub>-(Tr)C), 2.70-2.78 (2H, m br, NH-(C=O)-CH<sub>2</sub>-(CH<sub>2</sub>)<sub>2</sub>-(Tr)C), 2.09-2.20 (2H, m br, NH-(C=O)-CH<sub>2</sub>-CH<sub>2</sub>-(Tr)C), 2.11 (3H, s, O-(C=O)-CH<sub>3</sub>), 2.06 (3H, s, O-(C=O)-CH<sub>3</sub>), 2.04 (3H, s, O-(C=O)-CH<sub>3</sub>), 1.96 (3H, s, O-(C=O)-CH<sub>3</sub>), 1.93-2.03 (2H, m, 2x(Ar)C-CH-CH-C-CH(CH<sub>3</sub>)<sub>2</sub>, <sup>3</sup>J<sub>H,H</sub> = 7.0 Hz), 1.66 (6H, s, 2xCH<sub>3</sub>-(Ar)C-CH-CH-C), 1.36 (9H, s, S-CH<sub>2</sub>-(Ar)C-CH-CH-C-C(CH<sub>3</sub>)<sub>3</sub>), 1.34 (9H, s, S-CH<sub>2</sub>-(Ar)C-CH-CH-C-C(CH<sub>3</sub>)<sub>3</sub>), 0.98 (6H, d, (Ar)C-CH-CH-C-CH(CH<sub>3</sub>)<sub>2</sub>, <sup>3</sup>J<sub>H,H</sub> = 6.8 Hz), 0.93 (6H, d, (Ar)C-CH-CH-C-CH(CH<sub>3</sub>)<sub>2</sub>, <sup>3</sup>J<sub>H,H</sub> = 6.9 Hz).

<sup>13</sup>C-NMR (CDCl<sub>3</sub>) δ<sub>c</sub>, ppm: 173.5 (1C, (Ar)C-NH-(C=O)), 170.63 (1C, O-(C=O)-CH<sub>3</sub>), 170.61 (1C, O-(C=O)-CH<sub>3</sub>), 170.4 (1C, O-(C=O)-CH<sub>3</sub>), 170.0 (1C, O-(C=O)-CH<sub>3</sub>), 152.0, 151.97 (2C, 2xS-CH<sub>2</sub>-(Ar)C-CH-CH-C-C(CH<sub>3</sub>)<sub>3</sub>), 143.6 (1C, O-(CH<sub>2</sub>)<sub>4</sub>-(Tr)N-CH-C), 141.5 (1C, S-(Ar)C-CH-CH-C-NH), 136.8, 136.5 (2C, 2xS-CH<sub>2</sub>-(Ar)C-CH-CH-C-C(CH<sub>3</sub>)<sub>3</sub>), 132.7 (2C, 2xS-(Ar)C-CH-CH-C-NH), 129.4 (1C, S-(Ar)C-CH-CH-C-NH), 129.3, 129.0 (4C, 4xS-CH<sub>2</sub>-(Ar)C-CH-CH-C-C(CH<sub>3</sub>)<sub>3</sub>), 125.7, 125.6 (4C, 4xS-CH<sub>2</sub>-(Ar)C-CH-CH-C-C(CH<sub>3</sub>)<sub>3</sub>), 122.7 (1C, O-(CH<sub>2</sub>)<sub>4</sub>-(Tr)N-CH-C), 120.4 (2C, 2xS-(Ar)C-CH-CH-C-NH), 107.8 (2C, 2xCH<sub>3</sub>-(Ar)C-CH-CH-C), 100.1 (2C, 2xCH<sub>3</sub>-(Ar)C-CH-CH-C), 96.4 (1C, (Tr)N-(CH<sub>2</sub>)<sub>4</sub>-O-CH-CH-OAc), 84.3 (2C, 2xCH<sub>3</sub>-(Ar)C-CH-CH-C), 83.8 (2C, 2xCH<sub>3</sub>-(Ar)C-CH-CH-C), 83.2 (2C, 2xCH<sub>3</sub>-(Ar)C-CH-CH-C), 82.2 (2C, 2xCH<sub>3</sub>-(Ar)C-CH-CH-C), 68.3 (1C, (Tr)N-(CH<sub>2</sub>)<sub>4</sub>-O-CH-CH-CH-CH-OAc), 68.12 (1C, (Tr)N-(CH<sub>2</sub>)<sub>4</sub>-O-CH-CH-OAc), 68.05 (1C, (Tr)N-(CH<sub>2</sub>)<sub>3</sub>-CH<sub>2</sub>-O), 67.9 (1C, (Tr)N-(CH<sub>2</sub>)<sub>4</sub>-O-CH-CH-CH-CH-OAc), 66.4 (1C, CH-CH<sub>2</sub>-OAc), 62.0 (1C, CH-CH<sub>2</sub>-OAc), 49.9 (1C, (Tr)N-CH<sub>2</sub>-(CH<sub>2</sub>)<sub>3</sub>-O), 39.9 (1C, S-CH<sub>2</sub>-(Ar)C-CH-CH-C-C(CH<sub>3</sub>)<sub>3</sub>), 39.2 (1C, S-CH<sub>2</sub>-(Ar)C-CH-CH-C-C(CH<sub>3</sub>)<sub>3</sub>), 36.8 (1C, NH-(C=O)-CH<sub>2</sub>-(CH<sub>2</sub>)<sub>2</sub>-(Tr)C), 34.91 (1C, S-CH<sub>2</sub>-(Ar)C-CH-CH-C-C(CH<sub>3</sub>)<sub>3</sub>), 34.88 (1C, S-CH<sub>2</sub>-(Ar)C-CH-CH-C-C(CH<sub>3</sub>)<sub>3</sub>), 31.53 (3C, S-CH<sub>2</sub>-(Ar)C-CH-CH-C-C(CH<sub>3</sub>)<sub>3</sub>), 31.51 (3C, S-CH<sub>2</sub>-(Ar)C-CH-CH-C-C(CH<sub>3</sub>)<sub>3</sub>), 31.1 (2C, 2xCH<sub>3</sub>-(Ar)C-CH-CH-C-CH(CH<sub>3</sub>)<sub>2</sub>), 27.2 (1C, (Tr)N-(CH<sub>2</sub>)<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-O), 26.5 (1C, (Tr)N-CH<sub>2</sub>-CH<sub>2</sub>-(CH<sub>2</sub>)<sub>2</sub>-O), 25.4 (2C, NH-(C=O)-(CH<sub>2</sub>)<sub>2</sub>-CH<sub>2</sub>-(Tr)C, NH-(C=O)-CH<sub>2</sub>-CH<sub>2</sub>-(Tr)C), 23.1 (2C, (Ar)CH-CH-C-CH(CH<sub>3</sub>)<sub>2</sub>), 23.0 (2C, (Ar)CH-CH-C-CH(CH<sub>3</sub>)<sub>2</sub>), 21.0 (1C, O-(C=O)-CH<sub>3</sub>), 20.9 (1C, O-(C=O)-CH<sub>3</sub>), 20.8 (2C, 2xO-(C=O)-CH<sub>3</sub>), 18.1 (2C, 2xCH<sub>3</sub>-(Ar)C-CH-CH).

R<sub>f</sub>(CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>OH 10:1 (v/v)) = 0.534.

ESI-MS(+): *m/z* found 1493.4407 [M-Cl]<sup>+</sup>, calcd. for C<sub>72</sub>H<sub>97</sub>N<sub>4</sub>O<sub>11</sub>Ru<sub>2</sub>S<sub>3</sub><sup>+</sup> 1493.4403.

Elemental analysis (%): calcd. for C<sub>72</sub>H<sub>97</sub>ClN<sub>4</sub>O<sub>11</sub>Ru<sub>2</sub>S<sub>3</sub>·1.5CH<sub>3</sub>OH·0.3H<sub>2</sub>O C 55.81, H 6.60, N 3.54; found: C 55.84, H 6.60, N 3.54.

**Synthesis of [(η<sup>6</sup>-*p*-MeC<sub>6</sub>H<sub>4</sub>Pr<sup>i</sup>)<sub>2</sub>Ru<sub>2</sub>(μ<sub>2</sub>-SCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>-*p*-Bu<sup>t</sup>)<sub>2</sub>(μ<sub>2</sub>-SC<sub>6</sub>H<sub>4</sub>-*p*-CH<sub>2</sub>-(C=O)-R)]Cl (R = (((1-(2-(((2*R*,3*R*,4*S*,5*R*,6*R*)-3,4,5-triacetoxy-6-(acetoxymethyl)tetrahydro-2*H*-pyran-2-yl)oxy)ethyl)-1*H*-1,2,3-triazol-4-yl)methyl)amino)) (24)**

To a solution of **8** (0.173 g, 0.415 mmol, 1.2 equiv.) in dry DMF (10 mL) at r.t. under inert atmosphere (N<sub>2</sub>) were successively added CuSO<sub>4</sub>·5H<sub>2</sub>O (0.086 g, 0.3444 mmol, 1 equiv.) and sodium ascorbate (0.137 g, 0.694 mmol, 2 equiv.). After 10 min, **14** (0.3698 g, 0.0346 mmol, 1 equiv.) was also added and the reaction mixture was stirred overnight at r.t.. The mixture solubilized in EtOAc (100 mL), and the organic phase was washed with water (2x100 mL), brine (100 mL), dried over Na<sub>2</sub>SO<sub>4</sub>,



filtered and concentrated under reduced pressure. Purification by column chromatography using a mixture CH<sub>2</sub>Cl<sub>2</sub>/MeOH (10:1, v/v) as eluent afforded **24** as an orange solid (0.3945 g, 0.2654 mmol, 76%).

**<sup>1</sup>H-NMR (CDCl<sub>3</sub>) δ<sub>H</sub>, ppm:** 9.07 (1H, t br, S-(Ar)C-CH-CH-C-CH<sub>2</sub>-(C=O)-NH, <sup>3</sup>J<sub>H,H</sub> = 4.5 Hz), 8.31 (1H, s, (C=O)-NH-CH<sub>2</sub>-(Tr)C-CH), 7.60 (2H, d, 2xS-(Ar)C-CH-CH-C-CH<sub>2</sub>-(C=O), <sup>3</sup>J<sub>H,H</sub> = 8.2 Hz), 7.54 (2H, d, 2xS-(Ar)C-CH-CH-C-CH<sub>2</sub>-(C=O), <sup>3</sup>J<sub>H,H</sub> = 7.9 Hz), 7.35-7.50 (8H, m, 4xS-CH<sub>2</sub>-(Ar)C-CH-CH-C-C(CH<sub>3</sub>)<sub>3</sub>, 4xS-CH<sub>2</sub>-(Ar)C-CH-CH-C-C(CH<sub>3</sub>)<sub>3</sub>, <sup>3</sup>J<sub>H,H</sub> = 8.3 Hz), 5.17 (1H, t, (Tr)N-(CH<sub>2</sub>)<sub>2</sub>-O-CH-CH-CH-OAc, <sup>3</sup>J<sub>H,H</sub> = 9.5 Hz), 5.04 (1H, t, (Tr)N-(CH<sub>2</sub>)<sub>2</sub>-O-CH-CH-CH-CH-OAc, <sup>3</sup>J<sub>H,H</sub> = 9.7 Hz), 5.00 (2H, d, 2xCH<sub>3</sub>-(Ar)C-CH-CH-C, <sup>3</sup>J<sub>H,H</sub> = 5.8 Hz), 4.95 (1H, t, (Tr)N-(CH<sub>2</sub>)<sub>2</sub>-O-CH-CH-OAc, <sup>3</sup>J<sub>H,H</sub> = 8.2 Hz), 4.88 (2H, d, 2xCH<sub>3</sub>-(Ar)C-CH-CH-C, <sup>3</sup>J<sub>H,H</sub> = 5.8 Hz), 4.77 (2H, d, 2xCH<sub>3</sub>-(Ar)C-CH-CH-C, <sup>3</sup>J<sub>H,H</sub> = 5.8 Hz), 4.61 (1H, d, (Tr)N-(CH<sub>2</sub>)<sub>2</sub>-O-CH-CH-OAc, <sup>3</sup>J<sub>H,H</sub> = 8.0 Hz), 4.54-4.59 (4H, m, NH-CH<sub>2</sub>-(Tr)C-CH-N, 2xCH<sub>3</sub>-(Ar)C-CH-CH-C), 4.51 (2H, t, (Tr)N-CH<sub>2</sub>-CH<sub>2</sub>-O, <sup>3</sup>J<sub>H,H</sub> = 5.6 Hz), 4.26 (1H, dd, CH-CH<sub>2</sub>-OAc, <sup>2</sup>J<sub>H,H</sub> = 12.3 Hz, <sup>3</sup>J<sub>H,H</sub> = 4.3 Hz), 4.19-4.26 (1H, m, (Tr)N-CH<sub>2</sub>-CH<sub>2</sub>-O, <sup>3</sup>J<sub>H,H</sub> = 5.2 Hz), 4.11 (1H, dd, CH-CH<sub>2</sub>-OAc, <sup>2</sup>J<sub>H,H</sub> = 12.5 Hz, <sup>3</sup>J<sub>H,H</sub> = 1.7 Hz), 4.05 (1H, dt, (Tr)N-CH<sub>2</sub>-CH<sub>2</sub>-O, <sup>3</sup>J<sub>H,H</sub> = 10.5 Hz, <sup>3</sup>J<sub>H,H</sub> = 6.6 Hz), 3.83 (2H, s, S-(Ar)C-CH-CH-C-CH<sub>2</sub>-(C=O)-NH), 3.77 (1H, ddd, CH-CH<sub>2</sub>-OAc, <sup>3</sup>J<sub>H,H</sub> = 10.0 Hz, <sup>3</sup>J<sub>H,H</sub> = 4.7 Hz, <sup>3</sup>J<sub>H,H</sub> = 2.3 Hz), 3.56 (2H, s, S-CH<sub>2</sub>-(Ar)C-CH-CH-C-C(CH<sub>3</sub>)<sub>3</sub>), 3.35 (2H, s, S-CH<sub>2</sub>-(Ar)C-CH-CH-C-C(CH<sub>3</sub>)<sub>3</sub>), 2.08 (3H, s, O-(C=O)-CH<sub>3</sub>), 1.99 (3H, s, O-(C=O)-CH<sub>3</sub>), 1.97 (3H, s, O-(C=O)-CH<sub>3</sub>), 1.95 (3H, s, O-(C=O)-CH<sub>3</sub>), 1.90 (2H, sept, 2x(Ar)C-CH-CH-C-CH(CH<sub>3</sub>)<sub>2</sub>, <sup>3</sup>J<sub>H,H</sub> = 6.8 Hz), 1.68 (6H, s, 2xCH<sub>3</sub>-(Ar)C-CH-CH-C), 1.35 (9H, s, S-CH<sub>2</sub>-(Ar)C-CH-CH-C-C(CH<sub>3</sub>)<sub>3</sub>), 1.33 (9H, s, S-CH<sub>2</sub>-(Ar)C-CH-CH-C-C(CH<sub>3</sub>)<sub>3</sub>), 0.93 (6H, d, (Ar)C-CH-CH-C-CH(CH<sub>3</sub>)<sub>2</sub>, <sup>3</sup>J<sub>H,H</sub> = 6.8 Hz), 0.88 (6H, d, (Ar)C-CH-CH-C-CH(CH<sub>3</sub>)<sub>2</sub>, <sup>3</sup>J<sub>H,H</sub> = 6.8 Hz).

**<sup>13</sup>C-NMR (CDCl<sub>3</sub>) δ<sub>C</sub>, ppm:** 171.4 (1C, S-(Ar)C-CH<sub>2</sub>-(C=O)-NH), 170.9 (1C, O-(C=O)-CH<sub>3</sub>), 170.2 (1C, O-(C=O)-CH<sub>3</sub>), 169.7 (1C, O-(C=O)-CH<sub>3</sub>), 169.6 (1C, O-(C=O)-CH<sub>3</sub>), 152.01, 151.98 (2C, 2xS-CH<sub>2</sub>-(Ar)C-CH-CH-C-C(CH<sub>3</sub>)<sub>3</sub>), 145.7 (1C, (C=O)-NH-CH<sub>2</sub>-(Tr)C-CH-N), 138.4 (1C, S-(Ar)C-CH-CH-CH<sub>2</sub>-(C=O)-NH), 136.7, 136.5 (2C, 2xS-CH<sub>2</sub>-(Ar)C-CH-CH-C-C(CH<sub>3</sub>)<sub>3</sub>), 134.8 (1C, S-(Ar)C-CH-CH-C-CH<sub>2</sub>-(C=O)-NH), 132.2 (2C, 2xS-(Ar)C-CH-CH-C-CH<sub>2</sub>-(C=O)-NH), 130.7 (2C, 2xS-(Ar)C-CH-CH-C-CH<sub>2</sub>-(C=O)-NH), 129.3, 129.1 (4C, 4xS-CH<sub>2</sub>-(Ar)C-CH-CH-C), 125.7, 125.6 (4C, 4xS-CH<sub>2</sub>-(Ar)C-CH-CH-C), 123.8 (1C, O-(CH<sub>2</sub>)<sub>2</sub>-(Tr)N-CH-C), 107.5 (2C, 2xCH<sub>3</sub>-(Ar)C-CH-CH-C), 100.8 (1C, (Tr)N-(CH<sub>2</sub>)<sub>2</sub>-O-CH-CH-OAc), 100.5 (2C, 2xCH<sub>3</sub>-(Ar)C-CH-CH-C), 83.8 (4C, 2xCH<sub>3</sub>-(Ar)C-CH-CH-C, 2xCH<sub>3</sub>-(Ar)C-CH-CH-C), 83.6 (2C, 2xCH<sub>3</sub>-(Ar)C-CH-CH-C), 82.4 (2C, 2xCH<sub>3</sub>-(Ar)C-CH-CH-C), 72.9 (1C, (Tr)N-(CH<sub>2</sub>)<sub>2</sub>-O-CH-CH-CH-OAc), 71.9 (1C, CH-CH<sub>2</sub>-OAc), 71.0 (1C, (Tr)N-(CH<sub>2</sub>)<sub>2</sub>-O-CH-CH-OAc), 68.5 (1C, (Tr)N-(CH<sub>2</sub>)<sub>2</sub>-O-CH-CH-CH-CH-OAc), 67.9 (1C, (Tr)N-CH<sub>2</sub>-CH<sub>2</sub>-O), 61.9 (1C, CH-CH<sub>2</sub>-OAc), 49.7 (1C, (Tr)N-CH<sub>2</sub>-CH<sub>2</sub>-O), 42.8 (1C, S-(Ar)C-CH-CH-C-CH<sub>2</sub>-(C=O)-NH), 39.9 (1C, S-CH<sub>2</sub>-(Ar)C-CH-CH-C-C(CH<sub>3</sub>)<sub>3</sub>), 39.3 (1C, S-CH<sub>2</sub>-(Ar)C-CH-CH-C-C(CH<sub>3</sub>)<sub>3</sub>), 36.0 (1C, NH-CH<sub>2</sub>-(Tr)C-CH-N), 34.91 (1C, S-CH<sub>2</sub>-(Ar)C-CH-CH-C-C(CH<sub>3</sub>)<sub>3</sub>), 34.88 (1C, S-CH<sub>2</sub>-(Ar)C-CH-CH-C-C(CH<sub>3</sub>)<sub>3</sub>), 31.52 (3C, S-CH<sub>2</sub>-(Ar)C-CH-CH-C-C(CH<sub>3</sub>)<sub>3</sub>), 31.50 (3C, S-CH<sub>2</sub>-(Ar)C-CH-CH-C-C(CH<sub>3</sub>)<sub>3</sub>), 31.0 (2C, 2x(Ar)CH-CH-C-CH(CH<sub>3</sub>)<sub>2</sub>), 23.1 (2C, (Ar)CH-CH-C-CH(CH<sub>3</sub>)<sub>2</sub>), 22.8 (2C, (Ar)CH-CH-C-CH(CH<sub>3</sub>)<sub>2</sub>),

20.91 (1C, O-(C=O)-CH<sub>3</sub>), 20.85 (1C, O-(C=O)-CH<sub>3</sub>), 20.7 (2C, 2xO-(C=O)-CH<sub>3</sub>), 18.1 (2C, 2xCH<sub>3</sub>-(Ar)C-CH-CH-C).

**ESI-MS(+):** *m/z* found 1451.3876 [M-Cl]<sup>+</sup>, calcd. for C<sub>69</sub>H<sub>91</sub>N<sub>4</sub>O<sub>11</sub>Ru<sub>2</sub>S<sub>3</sub><sup>+</sup> 1451.3928.

**Elemental analysis (%)**: calcd. for C<sub>69</sub>H<sub>91</sub>ClN<sub>4</sub>O<sub>11</sub>Ru<sub>2</sub>S<sub>3</sub> C 55.76, H 6.17, N 3.77; found C 54.90, H 6.27, N 3.51.

**Synthesis of [(η<sup>6</sup>-*p*-MeC<sub>6</sub>H<sub>4</sub>Pr<sup>*i*</sup>)<sub>2</sub>Ru<sub>2</sub>(μ<sub>2</sub>-SCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>-*p*-Bu<sup>*t*</sup>)<sub>2</sub>(μ<sub>2</sub>-SC<sub>6</sub>H<sub>4</sub>-*o*-CH<sub>2</sub>-R)]Cl (R = 2-(4-(3-(((2*R*,3*R*,4*S*,5*R*,6*R*)-3,4,5-triacetoxy-6-(acetoxymethyl)tetrahydro-2*H*-pyran-2-yl)oxy)propyl)-1*H*-1,2,3-triazol-1-yl)) (25)**

To a solution of **9** (0.250 g, 0.242 mmol, 1 equiv.) in dry DMF (10 mL) at r.t. under inert atmosphere (N<sub>2</sub>) were successively added **17** (0.200 g, 0.484 mmol, 2 equiv.), CuSO<sub>4</sub>·5H<sub>2</sub>O (0.060 g, 0.242 mmol, 1 equiv.) and sodium ascorbate (0.096 g, 0.484 mmol, 2 equiv.). The reaction mixture was further stirred at r.t. for 24 h, then it was diluted with EtOAc (100 mL), washed with H<sub>2</sub>O (2x100 mL), and the aqueous phase was further extracted with EtOAc (2x100 mL). The organic phases were combined, washed with brine (100 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated under reduced pressure. Purification by column chromatography using CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>OH 10:1 (v/v) afforded **25** as an orange solid (0.179 g, 0.125 mmol, yield 51%).

**<sup>1</sup>H-NMR (CDCl<sub>3</sub>) δ<sub>H</sub>, ppm**: 8.63 (1H, s br, O-(CH<sub>2</sub>)<sub>3</sub>-(Tr)C-CH<sub>2</sub>-N), 7.74 (1H, dd, S-(Ar)C-CH<sub>2</sub>-CH-CH-CH-C-CH<sub>2</sub>-N(Tr), <sup>3</sup>J<sub>H,H</sub> = 7.9 Hz, <sup>4</sup>J<sub>H,H</sub> = 1.1 Hz), 7.57 (2H, d, 2xS-CH<sub>2</sub>-(Ar)C-CH-CH<sub>2</sub>-C-C(CH<sub>3</sub>)<sub>3</sub>, <sup>3</sup>J<sub>H,H</sub> = 8.1 Hz), 7.48 (2H, d, 2xS-CH<sub>2</sub>-(Ar)C-CH<sub>2</sub>-CH-C-C(CH<sub>3</sub>)<sub>3</sub>, <sup>3</sup>J<sub>H,H</sub> = 8.2 Hz), 7.39-7.46 (4H, m, 2xS-CH<sub>2</sub>-(Ar)C-CH<sub>2</sub>-CH-C-C(CH<sub>3</sub>)<sub>3</sub>, 2xS-CH<sub>2</sub>-(Ar)C-CH-CH<sub>2</sub>-C-C(CH<sub>3</sub>)<sub>3</sub>, <sup>3</sup>J<sub>H,H</sub> = 8.7 Hz), 7.29 (1H, td, S-(Ar)C-CH-CH-CH<sub>2</sub>-CH-C-CH<sub>2</sub>-N(Tr)), <sup>3</sup>J<sub>H,H</sub> = 7.4 Hz, <sup>4</sup>J<sub>H,H</sub> = 0.8 Hz), 7.18-7.25 (2H, m, S-(Ar)C-CH-CH-CH-CH<sub>2</sub>-CH-C-CH<sub>2</sub>-N(Tr), S-(Ar)C-CH-CH<sub>2</sub>-CH-CH-C-CH<sub>2</sub>-N(Tr), <sup>3</sup>J<sub>H,H</sub> = 7.5 Hz, <sup>4</sup>J<sub>H,H</sub> = 1.4 Hz), 6.45 (1H, d, S-(Ar)C-C-CH<sub>2</sub>-N(Tr), <sup>2</sup>J<sub>H,H</sub> = 15.1 Hz), 6.39 (1H, d, S-(Ar)C-C-CH<sub>2</sub>-N(Tr), <sup>2</sup>J<sub>H,H</sub> = 15.4 Hz), 5.20 (1H, t, (Tr)C-(CH<sub>2</sub>)<sub>3</sub>-O-CH-CH-CH<sub>2</sub>-OAc, <sup>3</sup>J<sub>H,H</sub> = 9.5 Hz), 5.03-5.15 (5H, m, 2xCH<sub>3</sub>-(Ar)C-CH<sub>2</sub>-CH-C, 2xCH<sub>3</sub>-(Ar)C-CH-CH<sub>2</sub>-C, (Tr)C-(CH<sub>2</sub>)<sub>3</sub>-O-CH-CH-CH<sub>2</sub>-OAc), 4.97 (1H, dd, (Tr)C-(CH<sub>2</sub>)<sub>3</sub>-O-CH-CH<sub>2</sub>-OAc, <sup>3</sup>J<sub>H,H</sub> = 8.0 Hz, <sup>3</sup>J<sub>H,H</sub> = 9.5 Hz), 4.94 (1H, d, CH<sub>3</sub>-(Ar)C-CH-CH<sub>2</sub>-C, <sup>3</sup>J<sub>H,H</sub> = 6.2 Hz), 4.91 (1H, d, CH<sub>3</sub>-(Ar)C-CH-CH<sub>2</sub>-C, <sup>3</sup>J<sub>H,H</sub> = 5.8 Hz), 4.64 (1H, d, CH<sub>3</sub>-(Ar)C-CH<sub>2</sub>-CH-C, <sup>3</sup>J<sub>H,H</sub> = 6.2 Hz), 4.62 (1H, d, CH<sub>3</sub>-(Ar)C-CH<sub>2</sub>-CH-C, <sup>3</sup>J<sub>H,H</sub> = 6.1 Hz), 4.57 (1H, d, (Tr)C-(CH<sub>2</sub>)<sub>3</sub>-O-CH<sub>2</sub>-CH-OAc, <sup>3</sup>J<sub>H,H</sub> = 8.0 Hz), 4.26 (1H, dd, CH-CH<sub>2</sub>-OAc <sup>2</sup>J<sub>H,H</sub> = 12.3 Hz, <sup>3</sup>J<sub>H,H</sub> = 4.7 Hz), 4.10 (1H, dd, CH-CH<sub>2</sub>-OAc, <sup>2</sup>J<sub>H,H</sub> = 12.3 Hz, <sup>3</sup>J<sub>H,H</sub> = 2.1 Hz), 3.94 (1H, dt, O-CH<sub>2</sub>-(CH<sub>2</sub>)<sub>2</sub>-(Tr)C, <sup>2</sup>J<sub>H,H</sub> = 9.8 Hz, <sup>3</sup>J<sub>H,H</sub> = 6.2 Hz), 3.73 (1H, ddd, CH<sub>2</sub>-CH<sub>2</sub>-OAc, <sup>3</sup>J<sub>H,H</sub> = 10.0 Hz, <sup>3</sup>J<sub>H,H</sub> = 4.5 Hz, <sup>3</sup>J<sub>H,H</sub> = 2.2 Hz), 3.64 (2H, s, S-CH<sub>2</sub>-(Ar)C-CH-CH-C-(CH<sub>3</sub>)<sub>3</sub>), 3.57-3.68 (1H, m, O-CH<sub>2</sub>-(CH<sub>2</sub>)<sub>2</sub>-(Tr)C, <sup>3</sup>J<sub>H,H</sub> = 6.7 Hz), 3.37 (2H, s, S-CH<sub>2</sub>-(Ar)C-CH-CH-C-(CH<sub>3</sub>)<sub>3</sub>), 2.82 (2H, t, O-(CH<sub>2</sub>)<sub>2</sub>-CH<sub>2</sub>-(Tr)C, <sup>3</sup>J<sub>H,H</sub> = 7.4 Hz), 1.99-2.03 (2H, m, O-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-(Tr)C), 2.06 (3H, s, O-(C=O)-CH<sub>3</sub>), 2.02 (3H, s, O-(C=O)-CH<sub>3</sub>), 2.00 (3H, s, O-(C=O)-CH<sub>3</sub>), 1.97 (3H, s, O-(C=O)-CH<sub>3</sub>), 1.89 (2H, sept, 2x(Ar)C-CH-CH-C-CH(CH<sub>3</sub>)<sub>2</sub>, <sup>3</sup>J<sub>H,H</sub> = 6.9 Hz), 1.63 (3H, s, CH<sub>3</sub>-(Ar)C-CH-CH-C), 1.62 (3H, s, CH<sub>3</sub>-(Ar)C-CH-CH-C), 1.35 (9H, s, S-CH<sub>2</sub>-(Ar)C-CH-CH-C-C(CH<sub>3</sub>)<sub>3</sub>), 1.34 (9H, s, S-CH<sub>2</sub>-(Ar)C-CH-CH-C-C(CH<sub>3</sub>)<sub>3</sub>),

0.93 (6H, d, (Ar)C-CH-CH-C-CH(CH<sub>3</sub>)<sub>2</sub>, <sup>3</sup>J<sub>H,H</sub> = 6.8 Hz), 0.89 (6H, d, (Ar)C-CH-CH-C-CH(CH<sub>3</sub>)<sub>2</sub>, <sup>3</sup>J<sub>H,H</sub> = 6.9 Hz).

<sup>13</sup>C-NMR (CDCl<sub>3</sub>) δ<sub>c</sub>, ppm: 170.9 (1C, O-(C=O)-CH<sub>3</sub>), 170.3 (1C, O-(C=O)-CH<sub>3</sub>), 169.6 (2C, 2xO-(C=O)-CH<sub>3</sub>), 151.8, 151.6 (2C, 2xS-CH<sub>2</sub>-(Ar)C-CH-CH-C-CH<sub>3</sub>), 146.6 (1C, O-(CH<sub>2</sub>)<sub>3</sub>-(Tr)C-CH-N), 139.9 (1C, S-(Ar)C-C-CH<sub>2</sub>-(Tr)N), 137.9 (1C, S-(Ar)C-C-CH<sub>2</sub>-(Tr)N), 136.9, 136.6 (2C, 2xS-CH<sub>2</sub>-(Ar)C-CH-CH-C-CH<sub>3</sub>), 133.8 (1C, S-(Ar)C-CH-CH-CH-CH-C-CH<sub>2</sub>-(Tr)N), 130.2 (1C, S-(Ar)C-CH-CH-CH-CH-C-CH<sub>2</sub>-(Tr)N), 129.9 (2C, 2xS-CH<sub>2</sub>-(Ar)C-CH-CH-C-CH<sub>3</sub>), 129.1 (3C, 2xS-CH<sub>2</sub>-(Ar)C-CH-CH-C-CH<sub>3</sub>), S-(Ar)C-CH-CH-CH-CH-C-CH<sub>2</sub>-(Tr)N), 128.7 (1C, S-(Ar)C-CH-CH-CH-CH-C-CH<sub>2</sub>-(Tr)N), 125.7, 125.5 (4C, 4xS-CH<sub>2</sub>-(Ar)C-CH-CH-C-CH<sub>3</sub>), 124.6 (1C, (1C, S-(Ar)C-C-CH<sub>2</sub>-(Tr)N-CH-C)), 106.8 (2C, 2xCH<sub>3</sub>-(Ar)C-CH-CH-C), 101.2 (1C, (Tr)C-(CH<sub>2</sub>)<sub>3</sub>-O-CH-CH-OAc), 100.9 (2C, 2xCH<sub>3</sub>-(Ar)C-CH-CH-C), 83.7 (2C, 2xCH<sub>3</sub>-(Ar)C-CH-CH-C), 83.6 (4C, 2xCH<sub>3</sub>-(Ar)C-CH-CH-C, 2xCH<sub>3</sub>-(Ar)C-CH-CH-C), 82.7 (2C, 2xCH<sub>3</sub>-(Ar)C-CH-CH-C), 73.1 (1C, (Tr)C-(CH<sub>2</sub>)<sub>3</sub>-O-CH-CH-CH-OAc), 71.8 (1C, CH-CH<sub>2</sub>-OAc), 71.5 (1C, (Tr)C-(CH<sub>2</sub>)<sub>3</sub>-O-CH-CH-CH-OAc), 69.5 (1C, (Tr)N-(CH<sub>2</sub>)<sub>2</sub>-CH<sub>2</sub>-O), 68.6 (1C, (Tr)C-(CH<sub>2</sub>)<sub>3</sub>-O-CH-CH-CH-CH-OAc), 62.1 (1C, CH-CH<sub>2</sub>-OAc), 52.8 (1C, S-(Ar)C-C-CH<sub>2</sub>-N(Tr)), 40.4 (1C, S-CH<sub>2</sub>-(Ar)C-CH-CH-C-CH<sub>3</sub>), 39.1 (1C, S-CH<sub>2</sub>-(Ar)C-CH-CH-C-CH<sub>3</sub>), 34.9 (2C, 2xS-CH<sub>2</sub>-(Ar)C-CH-CH-C-CH<sub>3</sub>), 31.6, 31.5 (6C, S-CH<sub>2</sub>-(Ar)C-CH-CH-C-CH<sub>3</sub>), 30.9 (2C, 2xCH<sub>3</sub>-(Ar)C-CH-CH-C-CH<sub>3</sub>), 29.4 (1C, (Tr)C-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-O), 23.1 (2C, (Ar)CH-CH-C-CH-CH<sub>3</sub>), 22.7 (2C, (Ar)CH-CH-C-CH-CH<sub>3</sub>), 22.2 (1C, (Tr)C-CH<sub>2</sub>-(CH<sub>2</sub>)<sub>2</sub>-O), 20.90 (1C, O-(C=O)-CH<sub>3</sub>), 20.88 (1C, O-(C=O)-CH<sub>3</sub>), 20.7 (2C, 2xO-(C=O)-CH<sub>3</sub>), 18.2 (2C, 2xCH<sub>3</sub>-(Ar)C-CH-CH).

R<sub>f</sub>(CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>OH 10:1 (v/v)) = 0.500.

ESI-MS(+): *m/z* found 1408.3882 [M-Cl]<sup>+</sup>, calcd. for C<sub>68</sub>H<sub>90</sub>N<sub>3</sub>O<sub>10</sub>Ru<sub>2</sub>S<sub>3</sub><sup>+</sup> 1408.3870.

Elemental analysis (%): calcd. for C<sub>68</sub>H<sub>90</sub>ClN<sub>3</sub>O<sub>10</sub>Ru<sub>2</sub>S<sub>3</sub>·0.29CH<sub>2</sub>Cl<sub>2</sub> C 55.88, H 6.22, N 2.86; found C 55.89, H 6.43, N 2.81.

### Synthesis of [(η<sup>6</sup>-*p*-MeC<sub>6</sub>H<sub>4</sub>Pr<sup>*i*</sup>)<sub>2</sub>Ru<sub>2</sub>(μ<sub>2</sub>-SCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>-*p*-Bu<sup>*t*</sup>)<sub>2</sub>(μ<sub>2</sub>-SC<sub>6</sub>H<sub>4</sub>-*o*-CH<sub>2</sub>-R)]Cl (R = 2-(4-(3-(((2*R*,3*R*,4*S*,5*S*,6*R*)-3,4,5-triacetoxy-6-(acetoxymethyl)tetrahydro-2*H*-pyran-2-yl)oxy)propyl)-1*H*-1,2,3-triazol-1-yl)) (26)

To a solution of **9** (0.250 g, 0.242 mmol, 1 equiv.) in dry DMF (10 mL) at r.t. under inert atmosphere (N<sub>2</sub>) were successively added **18** (0.200 g, 0.484 mmol, 2 equiv.), CuSO<sub>4</sub>·5H<sub>2</sub>O (0.060 g, 0.242 mmol, 1 equiv.) and sodium ascorbate (0.096 g, 0.484 mmol, 2 equiv.). The reaction mixture was further stirred at r.t. for 24 h, then it was diluted with EtOAc (100 mL), washed with H<sub>2</sub>O (2x100 mL), and the aqueous phase was further extracted with EtOAc (2x100 mL). The organic phases were combined, washed with brine (100 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated under reduced pressure. Purification by column chromatography using CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>OH mixture as eluent afforded **26** as an orange solid (0.223 g, 0.152 mmol, yield 63%).

<sup>1</sup>H-NMR (CDCl<sub>3</sub>) δ<sub>H</sub>, ppm: 8.66 (1H, s br, S-(Ar)C-C-CH<sub>2</sub>-(Tr)N-CH-C), 7.74 (1H, dd, S-(Ar)C-CH-CH-CH-CH-C-CH<sub>2</sub>-N(Tr), <sup>3</sup>J<sub>H,H</sub> = 7.8 Hz, <sup>4</sup>J<sub>H,H</sub> = 1.1 Hz), 7.57 (2H, d, 2xS-CH<sub>2</sub>-(Ar)C-CH-CH-C-CH<sub>3</sub>, <sup>3</sup>J<sub>H,H</sub> = 8.2 Hz), 7.48 (2H, d, 2xS-CH<sub>2</sub>-(Ar)C-CH-CH-C-CH<sub>3</sub>, <sup>3</sup>J<sub>H,H</sub> = 8.3 Hz), 7.39-7.45 (4H,

m, 2xS-CH<sub>2</sub>-(Ar)C-CH-CH-C-C(CH<sub>3</sub>)<sub>3</sub>, 2xS-CH<sub>2</sub>-(Ar)C-CH-CH-C-C(CH<sub>3</sub>)<sub>3</sub>, <sup>3</sup>J<sub>H,H</sub> = 8.7 Hz), 7.29 (1H, td, S-(Ar)C-CH-CH-CH-CH-C-CH<sub>2</sub>-N(Tr)), <sup>3</sup>J<sub>H,H</sub> = 7.6 Hz, <sup>4</sup>J<sub>H,H</sub> = 1.2 Hz), 7.22 (1H, dd, S-(Ar)C-CH-CH-CH-CH-CH-C-CH<sub>2</sub>-N(Tr)), <sup>3</sup>J<sub>H,H</sub> = 7.6 Hz, <sup>4</sup>J<sub>H,H</sub> = 1.5 Hz), 7.20 (1H, td, S-(Ar)C-CH-CH-CH-CH-C-CH<sub>2</sub>-N(Tr)), <sup>3</sup>J<sub>H,H</sub> = 7.3 Hz, <sup>4</sup>J<sub>H,H</sub> = 1.0 Hz), 6.47 (1H, d, S-(Ar)C-CH-CH-CH-CH-C-CH<sub>2</sub>-N(Tr)), <sup>2</sup>J<sub>H,H</sub> = 15.3 Hz), 6.41 (1H, d, S-(Ar)C-CH-CH-CH-CH-C-CH<sub>2</sub>-N(Tr)), <sup>2</sup>J<sub>H,H</sub> = 15.6 Hz), 5.37 (1H, dd, (Tr)C-(CH<sub>2</sub>)<sub>3</sub>-O-CH-CH-CH-CH-OAc, <sup>3</sup>J<sub>H,H</sub> = 3.3 Hz, <sup>3</sup>J<sub>H,H</sub> = 0.6 Hz), 5.19 (1H, dd, (Tr)C-(CH<sub>2</sub>)<sub>3</sub>-O-CH-CH-OAc, <sup>3</sup>J<sub>H,H</sub> = 10.5 Hz, <sup>3</sup>J<sub>H,H</sub> = 7.9 Hz), 5.06-5.13 (4H, m, 2xCH<sub>3</sub>-(Ar)C-CH-CH-C, 2xCH<sub>3</sub>-(Ar)C-CH-CH-C), 5.02 (1H, dd, (Tr)C-(CH<sub>2</sub>)<sub>3</sub>-O-CH-CH-CH-OAc, <sup>3</sup>J<sub>H,H</sub> = 10.5 Hz, <sup>3</sup>J<sub>H,H</sub> = 3.4 Hz), 4.95 (1H, d, CH<sub>3</sub>-(Ar)C-CH-CH-C, <sup>3</sup>J<sub>H,H</sub> = 5.8 Hz), 4.91 (1H, d, CH<sub>3</sub>-(Ar)C-CH-CH-C, <sup>3</sup>J<sub>H,H</sub> = 5.8 Hz), 4.64 (1H, d, CH<sub>3</sub>-(Ar)C-CH-CH-C, <sup>3</sup>J<sub>H,H</sub> = 6.1 Hz), 4.62 (1H, d, CH<sub>3</sub>-(Ar)C-CH-CH-C, <sup>3</sup>J<sub>H,H</sub> = 6.2 Hz), 4.55 (1H, d, (Tr)C-(CH<sub>2</sub>)<sub>3</sub>-O-CH-CH-OAc, <sup>3</sup>J<sub>H,H</sub> = 8.0 Hz), 4.13 (2H, d, CH-CH<sub>2</sub>-OAc, <sup>3</sup>J<sub>H,H</sub> = 6.7 Hz), 3.93-3.99 (1H, m, (Tr)C-(CH<sub>2</sub>)<sub>2</sub>-CH<sub>2</sub>-O, <sup>3</sup>J<sub>H,H</sub> = 6.1 Hz), 3.93 (1H, t, CH-CH<sub>2</sub>-OAc, <sup>3</sup>J<sub>H,H</sub> = 6.5 Hz), 3.64 (2H, s, S-CH<sub>2</sub>-(Ar)C-CH-CH-C-(CH<sub>3</sub>)<sub>3</sub>), 3.57-3.68 (1H, m, (Tr)C-(CH<sub>2</sub>)<sub>2</sub>-CH<sub>2</sub>-O, <sup>3</sup>J<sub>H,H</sub> = 6.9 Hz), 3.37 (2H, s, S-CH<sub>2</sub>-(Ar)C-CH-CH-C-(CH<sub>3</sub>)<sub>3</sub>), 2.82 (2H, t, (Tr)C-CH<sub>2</sub>-(CH<sub>2</sub>)<sub>2</sub>-O, <sup>3</sup>J<sub>H,H</sub> = 7.5 Hz), 2.12 (3H, s, O-(C=O)-CH<sub>3</sub>), 1.98-2.06 (2H, m, (Tr)C-CH<sub>2</sub>-CH<sub>2</sub>-O), 2.03 (3H, s, O-(C=O)-CH<sub>3</sub>), 2.02 (3H, s, O-(C=O)-CH<sub>3</sub>), 1.96 (3H, s, O-(C=O)-CH<sub>3</sub>), 1.89 (2H, sept, 2x(Ar)C-CH-CH-C-CH(CH<sub>3</sub>)<sub>2</sub>, <sup>3</sup>J<sub>H,H</sub> = 6.9 Hz), 1.63 (3H, s, CH<sub>3</sub>-(Ar)C-CH-CH-C), 1.62 (3H, s, CH<sub>3</sub>-(Ar)C-CH-CH-C), 1.35 (9H, s, S-CH<sub>2</sub>-(Ar)C-CH-CH-C-C(CH<sub>3</sub>)<sub>3</sub>), 1.34 (9H, s, S-CH<sub>2</sub>-(Ar)C-CH-CH-C-C(CH<sub>3</sub>)<sub>3</sub>), 0.93 (6H, d, (Ar)C-CH-CH-C-CH(CH<sub>3</sub>)<sub>2</sub>, <sup>3</sup>J<sub>H,H</sub> = 6.9 Hz), 0.89 (6H, d, (Ar)C-CH-CH-C-CH(CH<sub>3</sub>)<sub>2</sub>, <sup>3</sup>J<sub>H,H</sub> = 6.9 Hz).

<sup>13</sup>C-NMR (CDCl<sub>3</sub>) δ<sub>c</sub>, ppm: 170.6 (1C, O-(C=O)-CH<sub>3</sub>), 170.4 (1C, O-(C=O)-CH<sub>3</sub>), 170.2 (1C, O-(C=O)-CH<sub>3</sub>), 169.7 (1C, O-(C=O)-CH<sub>3</sub>), 151.8, 151.6 (2C, 2xS-CH<sub>2</sub>-(Ar)C-CH-CH-C(CH<sub>3</sub>)<sub>3</sub>), 146.6 (1C, S-(Ar)C-C-CH<sub>2</sub>-(Tr)N-CH-C), 140.0 (1C, S-(Ar)C-C-CH<sub>2</sub>-(Tr)N-CH-C), 137.8 (1C, S-(Ar)C-C-CH<sub>2</sub>-(Tr)N-CH-C), 136.9, 136.6 (2C, 2xS-CH<sub>2</sub>-(Ar)C-CH-CH-C-C(CH<sub>3</sub>)<sub>3</sub>), 133.7 (1C, S-(Ar)C-CH-CH-CH-CH-C-CH<sub>2</sub>-N(Tr)), 130.2 (1C, S-(Ar)C-CH-CH-CH-CH-C-CH<sub>2</sub>-N(Tr)), 129.9 (2C, 2xS-CH<sub>2</sub>-(Ar)C-CH-CH-C-C(CH<sub>3</sub>)<sub>3</sub>), 129.1 (3C, 2xS-CH<sub>2</sub>-(Ar)C-CH-CH-C-C(CH<sub>3</sub>)<sub>3</sub>, S-(Ar)C-CH-CH-CH-CH-C-CH<sub>2</sub>-N(Tr)), 128.7 (1C, S-(Ar)C-CH-CH-CH-CH-C-CH<sub>2</sub>-N(Tr)), 125.7, 125.5 (4C, 4xS-CH<sub>2</sub>-(Ar)C-CH-CH-C-C(CH<sub>3</sub>)<sub>3</sub>), 124.6 (1C, S-(Ar)C-C-CH<sub>2</sub>-(Tr)N-CH-C), 106.8 (2C, 2xCH<sub>3</sub>-(Ar)C-CH-CH-C), 101.4 (2C, 2xCH<sub>3</sub>-(Ar)C-CH-CH-C), 101.2 (1C, (Tr)C-(CH<sub>2</sub>)<sub>3</sub>-O-CH-CH-OAc), 83.8, 83.7 (2C, 2xCH<sub>3</sub>-(Ar)C-CH-CH-C), 83.6, 83.5 (4C, 4xCH<sub>3</sub>-(Ar)C-CH-CH-C), 82.7 (2C, 2xCH<sub>3</sub>-(Ar)C-CH-CH-C), 71.2 (1C, (Tr)C-(CH<sub>2</sub>)<sub>3</sub>-O-CH-CH-CH-OAc), 70.7 (1C, CH-CH<sub>2</sub>-OAc), 69.5 (1C, (Tr)C-(CH<sub>2</sub>)<sub>2</sub>-CH<sub>2</sub>-O), 69.1 (1C, (Tr)C-(CH<sub>2</sub>)<sub>3</sub>-O-CH-CH-OAc), 67.3 (1C, (Tr)C-(CH<sub>2</sub>)<sub>3</sub>-O-CH-CH-CH-CH-OAc), 61.4 (1C, CH-CH<sub>2</sub>-OAc), 52.8 (1C, S-(Ar)C-C-CH<sub>2</sub>-(Tr)N), 40.4 (1C, S-CH<sub>2</sub>-(Ar)C-CH-CH-C-C(CH<sub>3</sub>)<sub>3</sub>), 39.1 (1C, S-CH<sub>2</sub>-(Ar)C-CH-CH-C-C(CH<sub>3</sub>)<sub>3</sub>), 34.9 (2C, 2xS-CH<sub>2</sub>-(Ar)C-CH-CH-C-C(CH<sub>3</sub>)<sub>3</sub>), 31.6 (3C, S-CH<sub>2</sub>-(Ar)C-CH-CH-C-C(CH<sub>3</sub>)<sub>3</sub>), 31.5 (3C, S-CH<sub>2</sub>-(Ar)C-CH-CH-C-C(CH<sub>3</sub>)<sub>3</sub>), 30.9 (2C, 2xCH<sub>3</sub>-(Ar)C-CH-CH-C-CH(CH<sub>3</sub>)<sub>2</sub>), 29.5 (1C, (Tr)C-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-O), 23.1 (2C, (Ar)CH-CH-C-CH-(CH<sub>3</sub>)<sub>2</sub>), 22.8 (2C, (Ar)CH-CH-C-CH-(CH<sub>3</sub>)<sub>2</sub>), 22.2 (1C, (Tr)C-CH<sub>2</sub>-(CH<sub>2</sub>)<sub>2</sub>-O), 21.0 (1C, O-(C=O)-CH<sub>3</sub>), 20.83 (1C, O-(C=O)-CH<sub>3</sub>), 20.81 (1C, O-(C=O)-CH<sub>3</sub>), 20.7 (1C, O-(C=O)-CH<sub>3</sub>), 18.2 (2C, 2xCH<sub>3</sub>-(Ar)C-CH-CH).

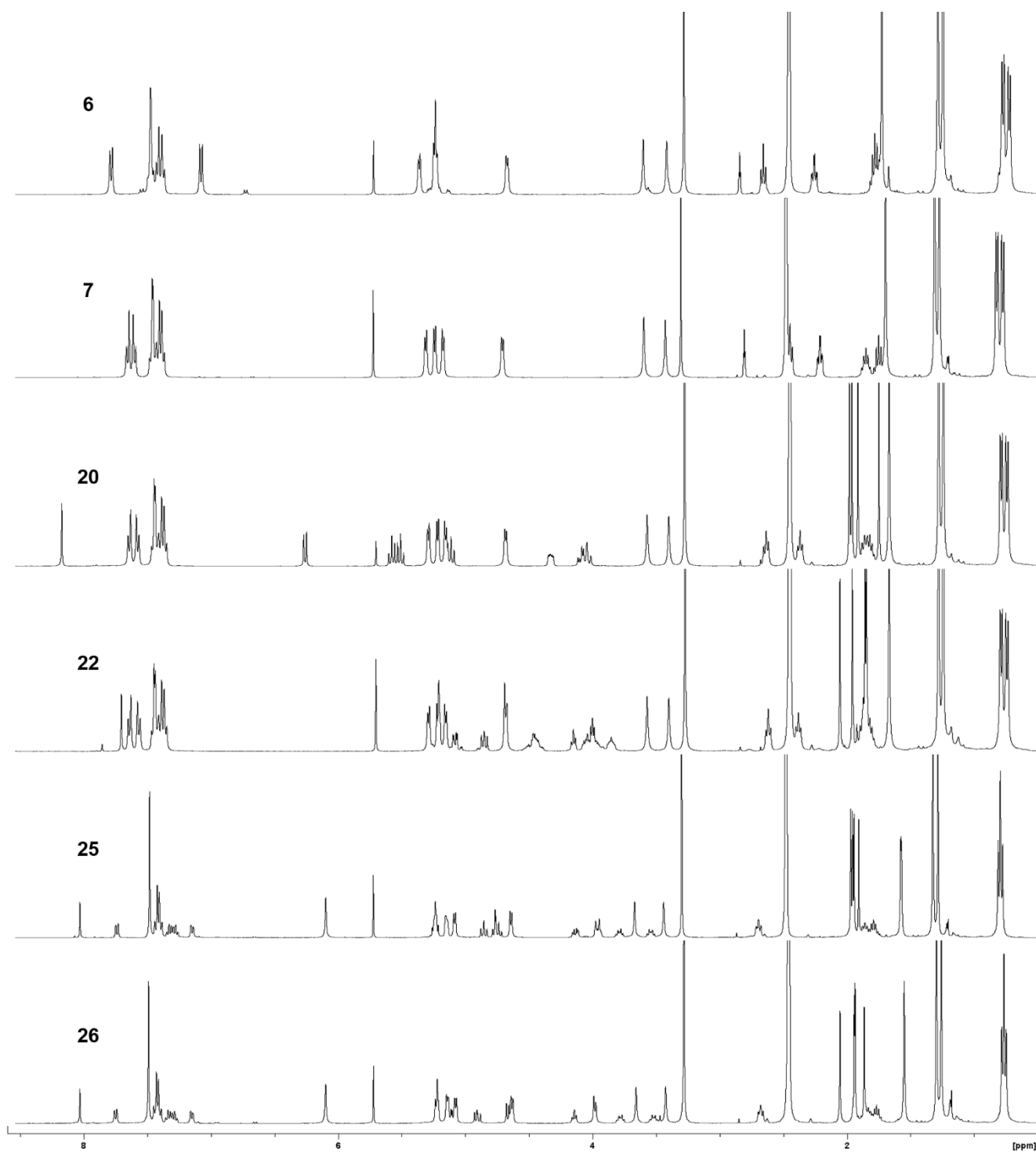
R<sub>f</sub>(CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>OH 10:1 (v/v)) = 0.468.

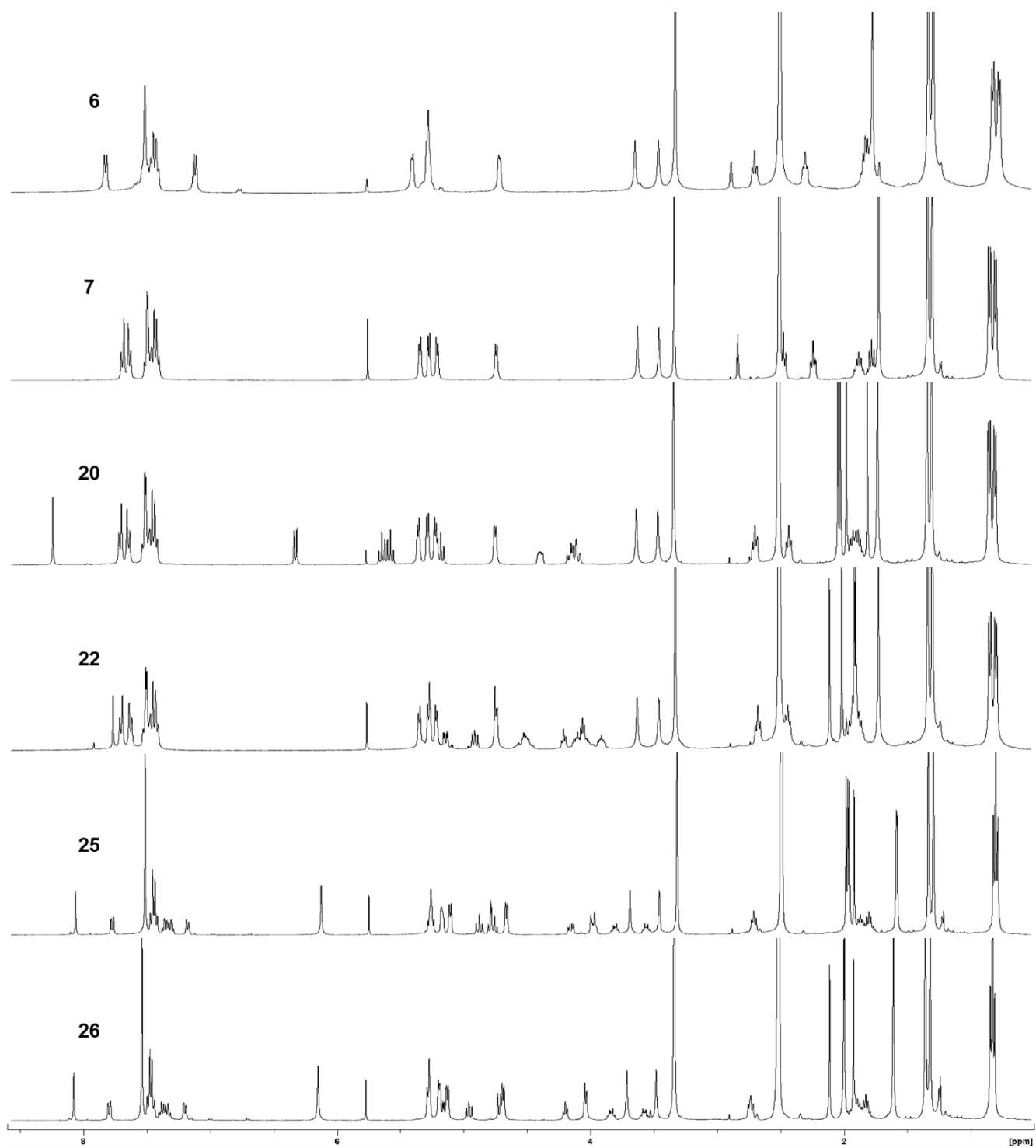
**ESI-MS(+):**  $m/z$  found 1408.3868  $[M-Cl]^+$ , calcd. for  $C_{68}H_{90}N_3O_{10}Ru_2S_3^+$  1408.3870.

**Elemental analysis (%):** calcd. for  $C_{68}H_{90}ClN_3O_{10}Ru_2S_3 \cdot 0.1CH_2Cl_2 \cdot 2.2H_2O$  C 54.85, H 6.39, N 2.82; found C 54.86, H 6.40, N 2.79.

### Stability in DMSO- $d_6$

**A**



**B**

**Figure S1.** <sup>1</sup>H NMR Spectra of **6**, **7**, **20**, **22**, **25** and **26** recorded in DMSO-d<sub>6</sub> at 25°C; (A) recorded 5 min after sample preparation, and (B) sample after > 30 days storage at 0–5°C in the dark.

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