Synthesis and antiparasitic activity of new conjugates - organic drugs tethered to trithiolato-bridged dinuclear ruthenium(II)-arene complexes

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Supporting Information

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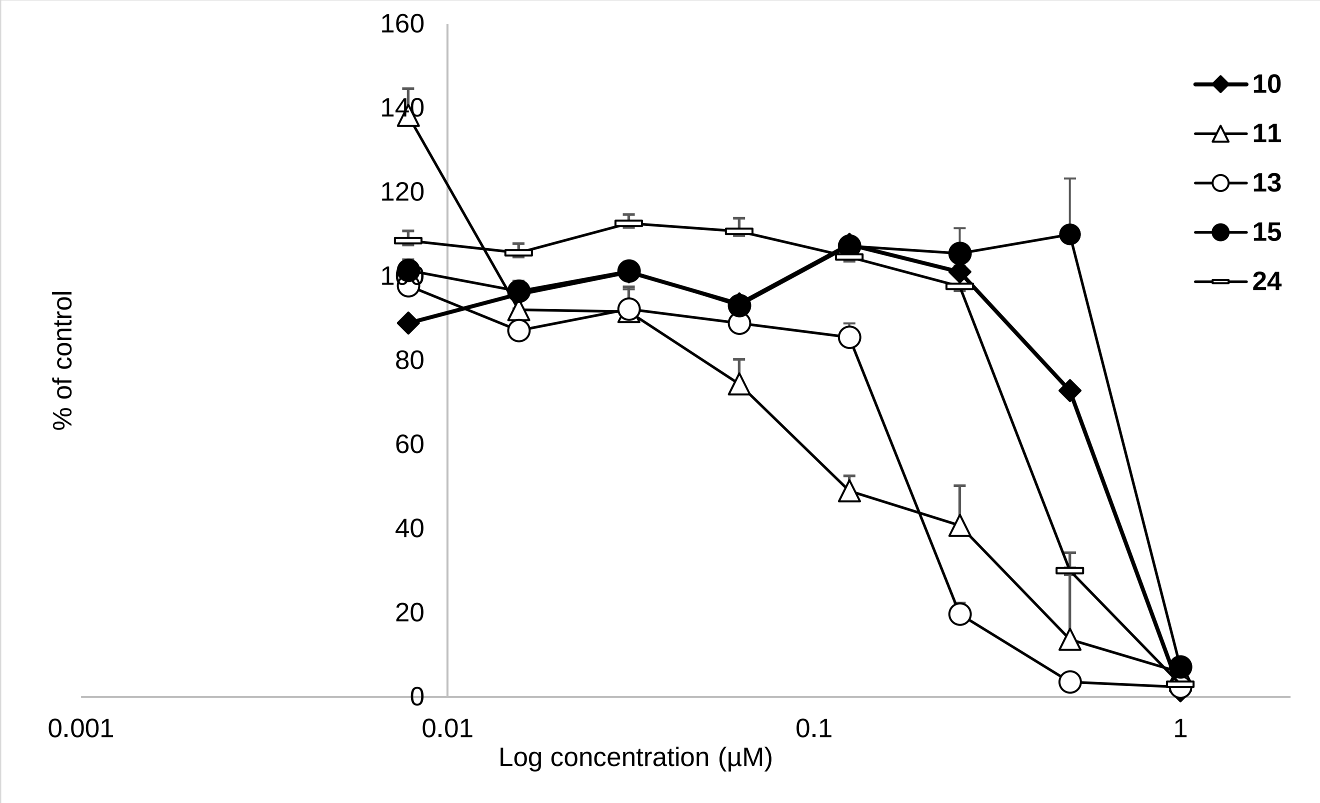

Figure S1. Dose response curves for compounds **10**, **11**, **13**, **15** and **24** as inhibitors of *T. gondii* β-gal tachyzoites proliferation. Vertical bars represent standard deviation for each tested concentration. Eight concentrations between 1 and 0.007 µM were used, each point being the average of six independent replicates.

EXPERIMENTAL PART CHEMISTRY

1. General

The 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_2) using Schlenk techniques with dry solvents (Acros Organics) preserved over molecular sieves. Reactions were monitored by TLC using Macherey-Nagel TLC silica gel coated aluminium sheets Alugram® Xtra SIL G/UV_{254} and visualised with UV at 254 nm and $KMnO_4$ stain. Compounds were purified by column flash chromatography on silica gel (Aldrich, 40-60 mesh) using the elution systems indicated. ^{1}H (300.13 and 400.13 MHz), ^{13}C (100.62 MHz) and ^{19}F (282.40 MHz) NMR spectra were recorded on a AVANCE III HD 300 and on a Bruker Avance II 400 spectrometers at 298 K. The chemical shifts are reported in parts per million (ppm) and referenced to residual solvent peaks ($CDCl_3$, ^{1}H δ 7.26, ^{13}C δ 77.16 ppm; MeOD-d_4, ^{1}H δ 3.31, ^{13}C δ 49.00 ppm; DMSO-d_6 ^{1}H δ 2.50 ^{13}C δ 39.52 ppm [1]), 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).

<u>Abbreviations:</u>

Ciprofloxacin - 1-Cyclopropyl-6-fluoro-4-oxo-7-(piperazin-1-yl)-1,4-dihydroquinoline-3-carboxylic acid

Dapsone - 4,4'-sulfonyldianiline
DIPEA - *N*,*N*-Diisopropylethylamine
DMAP - *N*,*N*-Dimethyl-4-aminopyridine
DMF – Dimethylformamide
HBTU – 2-(1 H -benzotriazol-1-yl)-1,1,3,3-tetramethyluronium hexafluorophosphate
HOBt·H_2O – 1-Hydroxybenzotriazole hydrate
EDCI – *N*-(3-Dimethylaminopropyl)-*N′*-ethylcarbodiimide hydrochloride
Menadione - 2-methylnaphthalene-1,4-dione
Metronidazole - 2-(2-methyl-5-nitro-1*H*-imidazol-1-yl)ethan-1-ol
MsCl - methanesulfonyl chloride
Sulfadiazine - 4-amino-*N*-(pyrimidin-2-yl)benzenesulfonamide
Sulfadoxine - 4-amino-*N*-(5,6-dimethoxypyrimidin-4-yl)benzenesulfonamide
Sulfamethoxazole - 4-amino-*N*-(5-methylisoxazol-3-yl)benzenesulfonamide
TEA – triethylamine
TFA – Trifluoroacetic acid
Triclosan - 5-chloro-2-(2,4-dichlorophenoxy)phenol
For the description of the NMR spectra: *Ar* – arene, *Cipro* – ciprofloxacin, *Im* – imidazole, *Napht* – naphthalen, *Tr* – triazole.

2. Synthesis of the di-ruthenium intermediates

The synthesis of the dithiolato intermediate **1**[2-3] ([(η^6-*p*-$MeC_6H_4Pr^i$)$_2$$Ru_2$($\mu_2$-$SCH_2C_6H_4$-*p*-$Bu^t$)$Cl_2$]), of the mixed trithiolato compounds **2**[3] ([(η^6-*p*-$MeC_6H_4Pr^i$)$_2$$Ru_2$($\mu_2$-$SCH_2C_6H_4$-*p*-$Bu^t$)$_2$($\mu_2$-$SC_6H_4$-*p*-$CH_2CO_2H$)]Cl), **3**[2-3] ([($\eta^6$-*p*-$MeC_6H_4Pr^i$)$_2$$Ru_2$($\mu_2$-$SCH_2C_6H_4$-*p*-$Bu^t$)$_2$($\mu_2$-$SC_6H_4$-*p*-OH)]Cl) and **4**[3] ([(η^6-*p*-$MeC_6H_4Pr^i$)$_2$$Ru_2$($\mu_2$-$SCH_2C_6H_4$-*p*-$Bu^t$)$_2$($\mu_2$-$SC_6H_4$-*p*-$NH_2$)]Cl), and of the symmetric trithiolato compounds **5** ([(η^6-*p*-$MeC_6H_4Pr^i$)$_2$$Ru_2$($\mu_2$-$SC_6H_4$-*p*-OH)$_3$]Cl)[3] and **6** ([($\eta^6$-*p*-$MeC_6H_4Pr^i$)$_2$$Ru_2$($\mu_2$-$SC_6H_4$-*p*-$NH_2$)]Cl)[4] were described previously.

Synthesis of [(η^6-*p*-$MeC_6H_4Pr^i$)$_2$$Ru_2$($\mu_2$-$SCH_2C_6H_4$-*p*-$Bu^t$)$_2$($\mu_2$-$SC_6H_4$-*p*-$CH_2$-(C=O)-NH-R)]Cl (R = CH_2-C≡CH) (7)

To a solution of **2** (1.00 g, 0.969 mmol, 1 equiv.) in dry CH_2Cl_2 (50 mL) at r.t. under inert atmosphere (N_2) were added successively EDCI (0.557 g, 2.907 mmol, 3 equiv.) and DIPEA (0.42 mL, 2.423 mmol, 2.5 equiv.). After 15 min were added HOBt·H_2O (0.320 g, 2.326 mmol, 2.4 equiv.), propargylamine (0.163 g, 2.907 mmol, 3 equiv.) and DIPEA (0.42 mL, 2.423 mmol, 2.5 equiv.). The reaction mixture was stirred at r.t. under inert atmosphere (N_2) for further 24 h and the reaction evolution was verified by TLC (CH_2Cl_2/CH_3OH 10:1 (v/v)). The reaction mixture was concentrated to dryness under reduced pressure and purified by column chromatography using CH_2Cl_2/CH_3OH mixture afforded 7 as an orange solid (0.861 g, 0.805 mmol, yield 83%).
^{1}H-NMR ($CDCl_3$) δ_H, ppm: 9.37 (1H, m br, S-(*Ar*)C-CH-CH-C-CH_2-(C=O)-N*H̲*), 7.53-7.62 (4H, m, 2xS-(*Ar*)C-CH-C*H̲*-C-CH_2-(C=O)-NH, 2xS-(*Ar*)C-C*H̲*-CH-C-CH_2-(C=O)-NH, $^3J_{H,H}$ = 8.1 Hz), 7.37-7.50 (8H, m, 4xCH_2-(*Ar*)C-C*H̲*-CH-C-C(CH_3)$_3$, 4xCH_2-(*Ar*)C-CH-C*H̲*-C-C(CH_3)$_3$, $^3J_{H,H}$ = 8.3 Hz), 5.00 (2H, d, 2xCH_3-(*Ar*)C-CH-C*H̲*-C, $^3J_{H,H}$ = 5.7 Hz), 4.89 (2H, d, 2xCH_3-(*Ar*)C-CH-C*H̲*-C, $^3J_{H,H}$ = 5.8 Hz), 4.77 (2H, d, 2xCH_3-(*Ar*)C-C*H̲*-CH-C, $^3J_{H,H}$ = 5.7 Hz), 4.59 (2H, d, 2xCH_3-(*Ar*)C-C*H̲*-CH-C, $^3J_{H,H}$ = 5.8 Hz), 3.98-4.02 (2H, m, (*Ar*)C-CH_2-(C=O)-NH-C*H̲₂*-C≡CH, $^4J_{H,H}$ = 1.9 Hz), 3.82 (2H, s, S-(*Ar*)C-CH-CH-C-C*H̲₂*-(C=O)-NH), 3.56 (2H, s, C*H̲₂*-(*Ar*)C-CH-CH-C-C(CH_3)$_3$), 3.36 (2H, s, C*H̲₂*-(*Ar*)C-CH-CH-C-C(CH_3)$_3$), 2.03-2.05 (1H, t br, (*Ar*)C-CH_2-(C=O)-NH-CH_2-C≡C*H̲*, $^4J_{H,H}$ = 2.1 Hz), 1.92 (2H, sept,

2x(*Ar*)C-CH-CH-C-C*H*(CH$_3$)$_2$, $^3J_{H,H}$ = 6.8 Hz), 1.68 (6H, s, 2xC*H$_3$*-(*Ar*)C-CH-CH-C), 1.36 (9H, s, S-CH$_2$-(*Ar*)C-CH-CH-C-C(C*H$_3$*)$_3$), 1.33 (9H, s, S-CH$_2$-(*Ar*)C-CH-CH-C-C(C*H$_3$*)$_3$), 0.94 (6H, d, 2x(*Ar*)C-CH-CH-C-CH(C*H$_3$*)$_2$, $^3J_{H,H}$ = 6.8 Hz), 0.90 (6H, d, 2x(*Ar*)C-CH-CH-C-CH(C*H$_3$*)$_2$, $^3J_{H,H}$ = 6.9 Hz).
^{13}C-NMR (CDCl$_3$) δ_C, ppm: 171.5 (1C, S-(*Ar*)C-CH-CH-C-CH$_2$-(*C*=O)-NH), 152.01, 151.95 (2C, 2xS-CH$_2$-(*Ar*)C-CH-CH-*C*-C(CH$_3$)$_3$), 138.3 (1C, S-(*Ar*)*C*-CH-CH-C-CH$_2$-(C=O)-NH), 136.8, 136.5 (2C, 2xS-CH$_2$-(*Ar*)*C*-CH-CH-C-C(CH$_3$)$_3$), 134.7 (1C, S-(*Ar*)C-CH-CH-*C*-CH$_2$-(C=O)-NH), 132.3 (2C, 2xS-(*Ar*)C-*C*H-CH-C-CH$_2$-(C=O)-NH), 130.8 (2C, 2xS-(*Ar*)C-CH-*C*H-C-CH$_2$-(C=O)-NH), 129.3, 129.1 (2C, 2xS-CH$_2$-(*Ar*)C-*C*H-CH-C-C(CH$_3$)$_3$), 125.7, 125.6 (2C, 2xS-CH$_2$-(*Ar*)C-CH-*C*H-C-C(CH$_3$)$_3$), 107.5 (2C, 2xCH$_3$-(*Ar*)C-CH-CH-*C*), 100.5 (2C, 2xCH$_3$-(*Ar*)*C*-CH-CH-C), 84.0 (2C, 2xCH$_3$-(*Ar*)C-CH-*C*H-C), 83.72 (2C, 2xCH$_3$-(*Ar*)C-*C*H-CH-C), 83.69 (2C, 2xCH$_3$-(*Ar*)C-CH-*C*H-C), 82.4 (2C, 2xCH$_3$-(*Ar*)C-*C*H-CH-C), 81.0 (1C, (*Ar*)C-CH$_2$-(C=O)-NH-CH$_2$-*C*≡CH), 70.0 (1C, (*Ar*)C-CH$_2$-(C=O)-NH-CH$_2$-C≡*C*H), 42.7 (1C, S-(*Ar*)C-CH-CH-C-*C*H$_2$-(C=O)-NH), 40.0 (1C, S-*C*H$_2$-(*Ar*)C-CH-CH-C-C(CH$_3$)$_3$), 39.4 (1C, S-*C*H$_2$-(*Ar*)C-CH-CH-C-C(CH$_3$)$_3$), 34.93 (1C, S-CH$_2$-(*Ar*)C-CH-CH-C-*C*(CH$_3$)$_3$), 34.90 (1C, S-CH$_2$-(*Ar*)C-CH-CH-C-*C*(CH$_3$)$_3$), 31.55, 31.53 (6C, 2xS-CH$_2$-(*Ar*)C-CH-CH-C-C(*C*H$_3$)$_3$), 31.0 (2C, 2x(*Ar*)CH-CH-C-*C*H(CH$_3$)$_2$), 29.1 (1C, (*Ar*)C-CH$_2$-(C=O)-NH-*C*H$_2$-C≡CH), 23.2 (2C, (*Ar*)CH-CH-C-CH(*C*H$_3$)$_2$), 22.9 (2C, (*Ar*)CH-CH-C-CH(*C*H$_3$)$_2$), 18.2 (2C, 2x*C*H$_3$-(*Ar*)C-CH-CH).
R$_f$ (CH$_2$Cl$_2$/CH$_3$OH 10:1) = 0.282.
ESI-MS(+): *m/z* found 1034.2565 [M-Cl]$^+$, calcd. for $C_{53}H_{68}NORu_2S_3^+$ 1034.2545.
Elemental analysis (%): calcd. for $C_{53}H_{68}ClNORu_2S_3 \cdot CH_2Cl_2$ C 56.12, H 6.12, N 1.21; found C 56.58, H 6.06, N 1.23.

3. Synthesis of the conjugates with sulfa-drugs (dapsone, sulfamethoxazole, sulfadiazine, sulfadoxine)

Synthesis of [(η^6-*p*-MeC$_6$H$_4$Pr^i)$_2$Ru$_2$(μ_2-SCH$_2$C$_6$H$_4$-*p*-Bu^t)$_2$(μ_2-SC$_6$H$_4$-*p*-CH$_2$-(C=O)-NH-R)]Cl (R = 4-((4-aminophenyl)sulfonyl)-*N*-aniline) (8)
To a solution of **2** (0.200 g, 0.194 mmol, 1 equiv.) in dry CH$_3$CN (50 mL) at r.t. under inert atmosphere (N$_2$), were added successively HOBt (0.064 g, 0.466 mmol, 2.4 equiv.), EDCI (0.112 g, 0.582 mmol, 3 equiv.), dapsone (0.074 g, 0.291 mmol, 1.5 equiv.) and DIPEA (0.17 mL, 0.970 mmol, 5 equiv.). The reaction mixture was stirred at r.t. under inert atmosphere (N$_2$) for further 24 h and the reaction evolution was verified by TLC (CH$_2$Cl$_2$/CH$_3$OH 9:1 (v/v)). The reaction mixture was filtered and concentrated to dryness under reduced pressure. Purification by column chromatography using CH$_2$Cl$_2$/CH$_3$OH mixture afforded **8** as an orange solid (0.072 g, 0.057 mmol, yield 29%).
^{1}H-NMR (CDCl$_3$) δ_H, ppm: 11.57 (1H, m br, S-(*Ar*)C-CH-CH-C-CH$_2$-(C=O)-N*H*), 8.13 (2H, d, 2x(C=O)-NH-(*Ar*)C-CH-C*H*-C-(SO$_2$), $^3J_{H,H}$ = 8.9 Hz), 7.73 (2H, d, 2x(C=O)-NH-(*Ar*)C-C*H*-CH-C-(SO$_2$), $^3J_{H,H}$ = 8.8 Hz), 7.56-7.66 (6H, m, 2xS-(*Ar*)C-CH-C*H*-C-CH$_2$-(C=O)-NH, 2xS-(*Ar*)C-C*H*-CH-C-CH$_2$-(C=O)-NH, 2x(SO$_2$)-(*Ar*)C-C*H*-CH-C-NH$_2$), 7.35-7.50 (8H, m, 4xCH$_2$-(*Ar*)C-C*H*-CH-C-C(CH$_3$)$_3$, 4xCH$_2$-(*Ar*)C-CH-C*H*-C-C(CH$_3$)$_3$, $^3J_{H,H}$ = 8.4 Hz), 6.81 (2H, d br, 2x(SO$_2$)-(*Ar*)C-CH-C*H*-C-NH$_2$, $^3J_{H,H}$ = 7.0 Hz), 5.00 (2H, d, 2xCH$_3$-(*Ar*)C-CH-C*H*-C, $^3J_{H,H}$ = 5.6 Hz), 4.86 (2H, d, 2xCH$_3$-(*Ar*)C-CH-C*H*-C, $^3J_{H,H}$ = 5.7 Hz), 4.78 (2H, d, 2xCH$_3$-(*Ar*)C-C*H*-CH-C, $^3J_{H,H}$ = 5.6 Hz), 4.56 (2H, d, 2xCH$_3$-(*Ar*)C-C*H*-CH-C, $^3J_{H,H}$ = 5.7 Hz), 4.00 (2H, s, S-(*Ar*)C-CH-CH-C-C*H$_2$*-(C=O)-NH), 3.56 (2H, s, C*H$_2$*-(*Ar*)C-CH-CH-C-C(CH$_3$)$_3$), 3.35 (2H, s, C*H$_2$*-(*Ar*)C-CH-CH-C-C(CH$_3$)$_3$), 1.85 (2H, sept, 2x(*Ar*)C-CH-CH-C-C*H*(CH$_3$)$_2$, $^3J_{H,H}$ = 6.8 Hz), 1.67 (6H, s, 2xC*H$_3$*-(*Ar*)C-CH-CH-C), 1.36 (9H, s, S-CH$_2$-(*Ar*)C-CH-CH-C-C(C*H$_3$*)$_3$), 1.34 (9H, s, S-CH$_2$-(*Ar*)C-CH-CH-C-C(C*H$_3$*)$_3$), 0.87 (6H, d, 2x(*Ar*)C-CH-CH-C-CH(C*H$_3$*)$_2$, $^3J_{H,H}$ = 6.9 Hz), 0.85 (6H, d, 2x(*Ar*)C-CH-CH-C-CH(C*H$_3$*)$_2$, $^3J_{H,H}$ = 6.9 Hz).
^{13}C-NMR (CDCl$_3$) δ_C, ppm: 171.0 (1C, S-(*Ar*)C-CH-CH-C-CH$_2$-(*C*=O)-NH), 152.00, 151.97 (2C, 2xS-CH$_2$-(*Ar*)C-CH-CH-*C*-C(CH$_3$)$_3$), 148.6 (1C, (SO$_2$)-(*Ar*)C-CH-CH-*C*-NH$_2$), 144.2 (1C, (C=O)-NH-

(*Ar*)$\underline{C}$-CH-CH-C-(SO$_2$)), 137.9 (1C, S-(*Ar*)C-CH-CH-$\underline{C}$-CH$_2$-(C=O)-NH), 136.8, 136.5 (2C, 2xS-CH$_2$-(*Ar*)$\underline{C}$-CH-CH-C-C(CH$_3$)$_3$), 135.8 (1C, (C=O)-NH-(*Ar*)C-CH-CH-$\underline{C}$-(SO$_2$)), 135.2 (1C, S-(*Ar*)$\underline{C}$-CH-CH-C-CH$_2$-(C=O)-NH), 132.5 (1C, (SO$_2$)-(*Ar*)$\underline{C}$-CH-CH-C-NH$_2$), 132.4 (2C, 2xS-(*Ar*)C-$\underline{C}$H-CH-C-CH$_2$-(C=O)-NH), 130.7 (2C, 2xS-(*Ar*)C-CH-$\underline{C}$H-C-CH$_2$-(C=O)-NH), 129.42, 129.35 (2C, 2xS-CH$_2$-(*Ar*)C-$\underline{C}$H-CH-C-C(CH$_3$)$_3$), 129.1 (2C, 2x(SO$_2$)-(*Ar*)C-$\underline{C}$H-CH-C-NH$_2$), 128.1 (2C, 2x(C=O)-NH-(*Ar*)C-C$\underline{H}$-CH-C-(SO$_2$)), 125.74, 125.65 (2C, 2xS-CH$_2$-(*Ar*)C-CH-$\underline{C}$H-C-C(CH$_3$)$_3$), 120.1 (2C, 2x(C=O)-NH-(*Ar*)C-CH-C$\underline{H}$-C-(SO$_2$)), 116.0 (2C, 2x(SO$_2$)-(*Ar*)C-CH-$\underline{C}$H-C-NH$_2$), 107.3 (2C, 2xCH$_3$-(*Ar*)C-CH-CH-$\underline{C}$), 100.7 (2C, 2xCH$_3$-(*Ar*)$\underline{C}$-CH-CH-C), 84.1 (2C, 2xCH$_3$-(*Ar*)C-CH-$\underline{C}$H-C), 83.7 (2C, 2xCH$_3$-(*Ar*)C-$\underline{C}$H-CH-C), 83.5 (2C, 2xCH$_3$-(*Ar*)C-CH-$\underline{C}$H-C), 82.5 (2C, 2xCH$_3$-(*Ar*)C-$\underline{C}$H-CH-C), 44.1 (1C, S-(*Ar*)C-CH-CH-C-$\underline{C}$H$_2$-(C=O)-NH), 40.0 (1C, S-$\underline{C}$H$_2$-(*Ar*)C-CH-CH-C-C(CH$_3$)$_3$), 39.4 (1C, S-$\underline{C}$H$_2$-(*Ar*)C-CH-CH-C-C(CH$_3$)$_3$), 34.9 (2C, 2xS-CH$_2$-(*Ar*)C-CH-CH-C-$\underline{C}$(CH$_3$)$_3$), 31.6 (6C, 2xS-CH$_2$-(*Ar*)C-CH-CH-C-C($\underline{C}$H$_3$)$_3$), 31.0 (2C, 2x(*Ar*)CH-CH-C-$\underline{C}$H(CH$_3$)$_2$), 23.2 (2C, (*Ar*)CH-CH-C-CH($\underline{C}$H$_3$)$_2$), 22.7 (2C, (*Ar*)CH-CH-C-CH($\underline{C}$H$_3$)$_2$), 18.2 (2C, 2x$\underline{C}$H$_3$-(*Ar*)C-CH-CH).
R$_f$ (CH$_2$Cl$_2$/CH$_3$OH 10:1) = 0.216.
ESI-MS(+): *m/z* found 1227.2786 [M-Cl]$^+$, calcd. for $C_{62}H_{75}N_2O_3Ru_2S_4^+$ 1227.2742.
Elemental analysis (%): calcd. for $C_{62}H_{75}ClN_2O_3Ru_2S_4\cdot1.2CH_3OH$ C 58.37, H 6.18, N 2.15; found C 58.37, H 6.14, N 2.20.

Synthesis of [(η^6-*p*-MeC$_6$H$_4$Pr^i)$_2$Ru$_2$(μ_2-SCH$_2$C$_6$H$_4$-*p*-Bu^t)$_2$(μ_2-SC$_6$H$_4$-*p*-CH$_2$-(C=O)-NH-R)]Cl (R = 4-amino-*N*-(5-methylisoxazol-3-yl)benzenesulfonamide) (9)

To a solution of **2** (0.200 g, 0.194 mmol, 1 equiv.) in dry CH$_2$Cl$_2$ (50 mL) at r.t. under inert atmosphere (N$_2$) were added EDCI (0.112 g, 0.582 mmol, 3 equiv.) and DIPEA (0.09 mL, 0.485 mmol, 2.5 equiv.). After 10 min, HOBt (0.063 g, 0.446 mmol, 2.4 equiv.), sulfamethoxazole (0.049 g, 0.194 mmol, 1 equiv.) and DIPEA (0.09 mL, 0.485 mmol, 2.5 equiv.), were successively added. The reaction mixture was stirred at r.t. under inert atmosphere (N$_2$) for further 24 h and the reaction evolution was verified by TLC (CH$_2$Cl$_2$/CH$_3$OH 9.5:0.5 (v/v)). The reaction mixture was concentrated to dryness under reduced pressure. Purification by column chromatography followed by purification on analytical TLCs using CH$_2$Cl$_2$/CH$_3$OH mixture afforded **9** as an orange solid (0.060 g, 0.047 mmol, yield 24%).
^{1}H-NMR (CDCl$_3$) δ_H, ppm: 11.49 (1H, s, (S=O)$_2$-N$\underline{H}$-(*Ar*)C-N-O-C-CH$_3$), 8.12 (2H, d, 2xNH-(*Ar*)C-CH-C$\underline{H}$-C-(S=O)$_2$, $^3J_{H,H}$ = 8.9 Hz), 7.65 (2H, d, 2xNH-(*Ar*)C-C$\underline{H}$-CH-C-(S=O)$_2$, $^3J_{H,H}$ = 8.9 Hz), 7.61-7.63 (4H, m, 2xS-(*Ar*)C-C$\underline{H}$-CH-C-CH$_2$-(C=O)-NH, 2xS-(*Ar*)C-CH-C$\underline{H}$-C-CH$_2$-(C=O)-NH), 7.36-7.49 (8H, m, 4xCH$_2$-(*Ar*)C-C$\underline{H}$-CH-C-C(CH$_3$)$_3$, 4xCH$_2$-(*Ar*)C-CH-C$\underline{H}$-C-C(CH$_3$)$_3$, $^3J_{H,H}$ = 8.4 Hz), 6.16 (1H, s, N-O-C(CH$_3$)-C$\underline{H}$-C), 5.00 (2H, d, 2xCH$_3$-(*Ar*)C-CH-C$\underline{H}$-C, $^3J_{H,H}$ = 5.7 Hz), 4.87 (2H, d, 2xCH$_3$-(*Ar*)C-C$\underline{H}$-CH-C, $^3J_{H,H}$ = 5.8 Hz), 4.79 (2H, d, 2xCH$_3$-(*Ar*)C-CH-C$\underline{H}$-C, $^3J_{H,H}$ = 5.8 Hz), 4.57 (2H, d, 2xCH$_3$-(*Ar*)C-C$\underline{H}$-CH-C, $^3J_{H,H}$ = 5.8 Hz), 4.05 (2H, s, S-(*Ar*)C-CH-CH-C-C$\underline{H_2}$-(C=O)-NH), 3.56 (2H, s, C$\underline{H_2}$-(*Ar*)C-CH-CH-C-C(CH$_3$)$_3$), 3.35 (2H, s, C$\underline{H_2}$-(*Ar*)C-CH-CH-C-C(CH$_3$)$_3$), 2.29 (3H, s, N-O-C-C$\underline{H_3}$), 1.85 (2H, sept, 2x(*Ar*)C-CH-CH-C-C$\underline{H}$(CH$_3$)$_2$, $^3J_{H,H}$ = 6.9 Hz), 1.68 (6H, s, 2xC$\underline{H_3}$-(*Ar*)C-CH-CH-C), 1.36 (9H, s, S-CH$_2$-(*Ar*)C-CH-CH-C-C(C$\underline{H_3}$)$_3$), 1.33 (9H, s, S-CH$_2$-(*Ar*)C-CH-CH-C-C(C$\underline{H_3}$)$_3$), 0.87 (6H, d, 2x(*Ar*)C-CH-CH-C-CH(C$\underline{H_3}$)$_2$, $^3J_{H,H}$ = 6.9 Hz), 0.85 (6H, d, 2x(*Ar*)C-CH-CH-C-CH(C$\underline{H_3}$)$_2$, $^3J_{H,H}$ = 6.9 Hz).
^{13}C-NMR (CDCl$_3$) δ_C, ppm: 171.2 (1C, S-(*Ar*)C-CH-CH-C-CH$_2$-($\underline{C}$=O)-NH), 170.6 (1C, N-O-$\underline{C}$(CH$_3$)-CH-C), 157.9 (1C, N-O-C(CH$_3$)-CH-$\underline{C}$), 152.0, 151.9 (2C, 2xS-CH$_2$-(*Ar*)C-CH-CH-$\underline{C}$-C(CH$_3$)$_3$), 144.7 (1C, NH-(*Ar*)$\underline{C}$-CH-CH-C-(S=O)$_2$), 137.5 (1C, S-(*Ar*)C-CH-CH-$\underline{C}$-CH$_2$-(C=O)-NH), 136.7, 136.5 (2C, 2xS-CH$_2$-(*Ar*)$\underline{C}$-CH-CH-C-C(CH$_3$)$_3$), 135.4 (1C, S-(*Ar*)$\underline{C}$-CH-CH-C-CH$_2$-(C=O)-NH), 132.4 (2C, 2xS-(*Ar*)C-$\underline{C}$H-CH-C-CH$_2$-(C=O)-NH), 132.3 (1C, NH-(*Ar*)C-CH-CH-$\underline{C}$-(S=O)$_2$), 130.7 (2C, 2xS-(*Ar*)C-CH-$\underline{C}$H-C-CH$_2$-(C=O)-NH), 129.3, 129.1 (2C, 2xS-CH$_2$-(*Ar*)C-$\underline{C}$H-CH-C-C(CH$_3$)$_3$), 128.1 (2C, 2xNH-

(*Ar*)C-CH-$\underline{C}$H-C-(S=O)$_2$), 125.7, 125.6 (2C, 2xS-CH$_2$-(*Ar*)C-CH-$\underline{C}$H-C-C(CH$_3$)$_3$), 119.9 (2C, 2xNH-(*Ar*)C-$\underline{C}$H-CH-C-(S=O)$_2$), 107.3 (2C, 2xCH$_3$-(*Ar*)C-CH-CH-$\underline{C}$), 100.7 (2C, 2xCH$_3$-(*Ar*)$\underline{C}$-CH-CH-C), 95.7 (1C, N-O-C(CH$_3$)-$\underline{C}$H-C), 84.1 (2C, 2xCH$_3$-(*Ar*)C-CH-$\underline{C}$H-C), 83.7 (2C, 2xCH$_3$-(*Ar*)C-CH-$\underline{C}$H-C), 83.5 (2C, 2xCH$_3$-(*Ar*)C-$\underline{C}$H-CH-C), 82.5 (2C, 2xCH$_3$-(*Ar*)C-$\underline{C}$H-CH-C), 43.9 (1C, S-(*Ar*)C-CH-CH-C-$\underline{C}$H$_2$-(C=O)-NH), 40.0 (1C, S-$\underline{C}$H$_2$-(*Ar*)C-CH-CH-C-C(CH$_3$)$_3$), 39.4 (1C, S-$\underline{C}$H$_2$-(*Ar*)C-CH-CH-C-C(CH$_3$)$_3$), 34.91 (1C, S-CH$_2$-(*Ar*)C-CH-CH-C-$\underline{C}$(CH$_3$)$_3$), 34.88 (1C, S-CH$_2$-(*Ar*)C-CH-CH-C-$\underline{C}$(CH$_3$)$_3$), 31.5 (6C, 2xS-CH$_2$-(*Ar*)C-CH-CH-C-C($\underline{C}$H$_3$)$_3$), 30.9 (2C, 2x(*Ar*)CH-CH-C-$\underline{C}$H(CH$_3$)$_2$), 23.2 (2C, (*Ar*)CH-CH-C-CH($\underline{C}$H$_3$)$_2$), 22.7 (2C, (*Ar*)CH-CH-C-CH($\underline{C}$H$_3$)$_2$), 18.2 (2C, 2x$\underline{C}$H$_3$-(*Ar*)C-CH-CH), 12.8 (1C, N-O-C-$\underline{C}$H$_3$).
R$_f$ (CH$_2$Cl$_2$/CH$_3$OH 10:1) = 0.396.
ESI-MS(+): *m/z* found 1232.2660 [M-Cl]$^+$, calcd. for $C_{60}H_{74}N_3O_4Ru_2S_4^+$ 1232.2644.
Elemental analysis (%): calcd. for $C_{60}H_{74}ClN_3O_4Ru_2S_4\cdot 2.7CH_3OH$ C 55.64, H 6.31, N 3.10; found C 55.74, H 6.56, N 3.03.

Synthesis of [(η^6-*p*-MeC$_6$H$_4$Pr^i)$_2$Ru$_2$(μ_2-SCH$_2$C$_6$H$_4$-*p*-Bu^t)$_2$(μ_2-SC$_6$H$_4$-*p*-CH$_2$-(C=O)-NH-R)]Cl (R = 4-amino-*N*-(pyrimidin-2-yl)benzenesulfonamide) (10)
To a solution of **2** (0.300 g, 0.291 mmol, 1 equiv.) in dry DMF (10 mL) at r.t. under inert atmosphere (N$_2$) were added EDCI (0.167 g, 0.873 mmol, 3 equiv.) and DIPEA (0.13 mL, 0.728 mmol, 2.5 equiv.). After 5 min HOBt (0.096 g, 0.698 mmol, 2.4 equiv.), sulfadiazine (0.087 g, 0.349 mmol, 1.2 equiv.) and DIPEA (0.13 mL, 0.728 mmol, 2.5 equiv.), were successively added. The reaction mixture was stirred at r.t. under inert atmosphere (N$_2$) for further 48 h and the reaction evolution was verified by TLC (CH$_2$Cl$_2$/CH$_3$OH 9.5:0.5 (v/v)). The reaction mixture was filtered and the filtrate concentrated to dryness under reduced pressure. Purification by column chromatography using CH$_2$Cl$_2$/CH$_3$OH mixture afforded **10** as an orange solid (0.088 g, 0.070 mmol, yield 24%).
^{1}H-NMR (CDCl$_3$) δ_H, ppm: 11.44 (1H, s br, (S=O)$_2$-N$\underline{H}$-(*Ar*)C-N-CH), 8.94 (1H, s, S-(*Ar*)C-CH-CH-C-CH$_2$-(C=O)-N$\underline{H}$), 8.60 (2H, d, (S=O)$_2$-NH-(*Ar*)C-N-C$\underline{H}$-CH-C$\underline{H}$, $^3J_{H,H}$ = 4.9 Hz), 7.89 (2H, d, 2xNH-(*Ar*)C-CH-C$\underline{H}$-C-(S=O)$_2$, $^3J_{H,H}$ = 9.0 Hz), 7.84 (2H, d, 2xNH-(*Ar*)C-C$\underline{H}$-CH-C-(S=O)$_2$, $^3J_{H,H}$ = 9.0 Hz), 7.66 (2H, d, 2xS-(*Ar*)C-CH-C$\underline{H}$-C-CH$_2$-(C=O)-NH, $^3J_{H,H}$ = 7.8 Hz), 7.36-7.48 (10H, m, 4xCH$_2$-(*Ar*)C-C$\underline{H}$-CH-C-C(CH$_3$)$_3$, 4xCH$_2$-(*Ar*)C-CH-C$\underline{H}$-C-C(CH$_3$)$_3$, 2xS-(*Ar*)C-C$\underline{H}$-CH-C-CH$_2$-(C=O)-NH, $^3J_{H,H}$ = 8.3 Hz), 6.93 (1H, t, (S=O)$_2$-NH-(*Ar*)C-N-CH-C$\underline{H}$-CH, $^3J_{H,H}$ = 4.9 Hz), 5.02 (2H, d, 2xCH$_3$-(*Ar*)C-CH-C$\underline{H}$-C, $^3J_{H,H}$ = 5.6 Hz), 4.89 (2H, d, 2xCH$_3$-(*Ar*)C-C$\underline{H}$-CH-C, $^3J_{H,H}$ = 5.8 Hz), 4.80 (2H, d, 2xCH$_3$-(*Ar*)C-CH-C$\underline{H}$-C, $^3J_{H,H}$ = 5.6 Hz), 4.56 (2H, d, 2xCH$_3$-(*Ar*)C-C$\underline{H}$-CH-C, $^3J_{H,H}$ = 5.7 Hz), 3.79 (2H, s, S-(*Ar*)C-CH-CH-C-C$\underline{H_2}$-(C=O)-NH), 3.57 (2H, s, C$\underline{H_2}$-(*Ar*)C-CH-CH-C-C(CH$_3$)$_3$), 3.36 (2H, s, C$\underline{H_2}$-(*Ar*)C-CH-CH-C-C(CH$_3$)$_3$), 1.86 (2H, sept, 2x(*Ar*)C-CH-CH-C-C$\underline{H}$(CH$_3$)$_2$, $^3J_{H,H}$ = 6.8 Hz), 1.69 (6H, s, 2xC$\underline{H_3}$-(*Ar*)C-CH-CH-C), 1.36 (9H, s, S-CH$_2$-(*Ar*)C-CH-CH-C-C(C$\underline{H_3}$)$_3$), 1.33 (9H, s, S-CH$_2$-(*Ar*)C-CH-CH-C-C(C$\underline{H_3}$)$_3$), 0.88 (6H, d, 2x(*Ar*)C-CH-CH-C-CH(C$\underline{H_3}$)$_2$, $^3J_{H,H}$ = 6.8 Hz), 0.85 (6H, d, 2x(*Ar*)C-CH-CH-C-CH(C$\underline{H_3}$)$_2$, $^3J_{H,H}$ = 6.9 Hz).
^{13}C-NMR (CDCl$_3$) δ_C, ppm: 170.3 (1C, S-(*Ar*)C-CH-CH-C-CH$_2$-($\underline{C}$=O)-NH), 158.8 (2C, (S=O)$_2$-NH-(*Ar*)C-N-$\underline{C}$H-CH-$\underline{C}$H), 156.9 (1C, (S=O)$_2$-NH-(*Ar*)$\underline{C}$-N-CH-CH-CH), 151.93, 151.90 (2C, 2xS-CH$_2$-(*Ar*)C-CH-CH-$\underline{C}$-C(CH$_3$)$_3$), 143.5 (1C, NH-(*Ar*)$\underline{C}$-CH-CH-C-(S=O)$_2$), 136.8, 136.6 (2C, 2xS-CH$_2$-(*Ar*)$\underline{C}$-CH-CH-C-C(CH$_3$)$_3$), 136.3 (1C, S-(*Ar*)$\underline{C}$-CH-CH-C-CH$_2$-(C=O)-NH), 136.1 (1C, S-(*Ar*)C-CH-CH-$\underline{C}$-CH$_2$-(C=O)-NH), 133.4 (1C, NH-(*Ar*)C-CH-CH-$\underline{C}$-(S=O)$_2$), 132.7 (2C, 2xS-(*Ar*)C-CH-$\underline{C}$H-C-CH$_2$-(C=O)-NH), 130.2 (2C, 2xS-(*Ar*)C-$\underline{C}$H-CH-C-CH$_2$-(C=O)-NH), 129.5, 129.4 (2C, 2xS-CH$_2$-(*Ar*)C-$\underline{C}$H-CH-C-C(CH$_3$)$_3$), 129.1 (2C, 2xNH-(*Ar*)C-CH-$\underline{C}$H-C-(S=O)$_2$), 125.7, 125.6 (2C, 2xS-CH$_2$-(*Ar*)C-CH-$\underline{C}$H-C-C(CH$_3$)$_3$), 119.2 (2C, 2xNH-(*Ar*)C-$\underline{C}$H-CH-C-(S=O)$_2$), 116.0 (1C, (S=O)$_2$-NH-(*Ar*)C-N-CH-$\underline{C}$H-CH), 107.3 (2C, 2xCH$_3$-(*Ar*)C-CH-CH-$\underline{C}$), 100.7 (2C, 2xCH$_3$-(*Ar*)$\underline{C}$-CH-CH-C), 84.1 (2C, 2xCH$_3$-(*Ar*)C-CH-$\underline{C}$H-C), 83.7 (2C, 2xCH$_3$-(*Ar*)C-CH-$\underline{C}$H-C), 83.5 (2C, 2xCH$_3$-(*Ar*)C-$\underline{C}$H-CH-C), 82.5

(2C, 2xCH_3-(*Ar*)C-$\underline{C}$H-CH-C), 44.0 (1C, S-(*Ar*)C-CH-CH-C-$\underline{C}H_2$-(C=O)-NH), 40.0 (1C, S-$\underline{C}H_2$-(*Ar*)C-CH-CH-C-$C(CH_3)_3$), 39.5 (1C, S-$\underline{C}H_2$-(*Ar*)C-CH-CH-C-$C(CH_3)_3$), 34.92 (1C, S-CH_2-(*Ar*)C-CH-CH-C-$\underline{C}(CH_3)_3$), 34.89 (1C, S-CH_2-(*Ar*)C-CH-CH-C-$\underline{C}(CH_3)_3$), 31.6 (6C, 2xS-CH_2-(*Ar*)C-CH-CH-C-$C(\underline{C}H_3)_3$), 31.0 (2C, 2x(*Ar*)CH-CH-C-$\underline{C}H(CH_3)_2$), 23.2 (2C, (*Ar*)CH-CH-C-$CH(\underline{C}H_3)_2$), 22.7 (2C, (*Ar*)CH-CH-C-$CH(\underline{C}H_3)_2$), 18.2 (2C, 2x$\underline{C}H_3$-(*Ar*)C-CH-CH).
R_f (CH_2Cl_2/CH_3OH 10:1) = 0.284.
ESI-MS(+): *m/z* found 1229.2645 $[M-Cl]^+$, calcd. for $C_{60}H_{73}N_4O_3Ru_2S_4^+$ 1229.2647.
Elemental analysis (%): calcd. for $C_{60}H_{73}ClN_4O_3Ru_2S_4\cdot0.2CH_2Cl_2\cdot0.5CH_3OH$ C 56.21, H 5.86, N 4.32; found C 56.25, H 5.84, N 4.03.

Synthesis of $[(\eta^6\text{-}p\text{-}MeC_6H_4Pr^i)_2Ru_2(\mu_2\text{-}SCH_2C_6H_4\text{-}p\text{-}Bu^t)_2(\mu_2\text{-}SC_6H_4\text{-}p\text{-}CH_2\text{-}(C{=}O)\text{-}NH\text{-}R)]Cl$ (R = 4-amino-*N*-(5,6-dimethoxypyrimidin-4-yl)benzenesulfonamide) (11)

To a solution of **2** (0.400 g, 0.388 mmol, 1 equiv.) in dry CH_2Cl_2 (50 mL) at r.t. under inert atmosphere (N_2) were added EDCI (0.223 g, 1.164 mmol, 3 equiv.) and DIPEA (0.17 mL, 0.970 mmol, 2.5 equiv.). After 10 min, HOBt (0.126 g, 0.930 mmol, 2.4 equiv.), sulfadoxine (0.120 g, 0.388 mmol, 1 equiv.) and DIPEA (0.17 mL, 0.970 mmol, 2.5 equiv.), were successively added. The reaction mixture was stirred at r.t. under inert atmosphere (N_2) for further 24 h and the reaction evolution was verified by TLC (CH_2Cl_2/CH_3OH 9.5:0.5 (v/v)). The reaction mixture was concentrated to dryness under reduced pressure. Purification by column chromatography followed by purification on analytical TLCs using CH_2Cl_2/CH_3OH mixture afforded **11** as an orange solid (0.181 g, 0.137 mmol, yield 35%).

^{1}H-NMR ($CDCl_3$) δ_H, ppm: 11.82 (1H, s, $(S{=}O)_2$-N$\underline{H}$-(*Ar*)C-C-O-CH_3), 8.18 (2H, d, 2xNH-(*Ar*)C-CH-C$\underline{H}$-C-$(S{=}O)_2$, $^3J_{H,H}$ = 8.9 Hz), 8.11 (1H, s, $(S{=}O)_2$-NH-(*Ar*)C-N-C$\underline{H}$-N-C-O-CH_3), 7.95 (2H, d, 2xNH-(*Ar*)C-C$\underline{H}$-CH-C-$(S{=}O)_2$, $^3J_{H,H}$ = 8.9 Hz), 7.65 (2H, d, 2xS-(*Ar*)C-CH-C$\underline{H}$-C-CH_2-(C=O)-NH, $^3J_{H,H}$ = 8.1 Hz), 7.59 (2H, d, 2xS-(*Ar*)C-C$\underline{H}$-CH-C-CH_2-(C=O)-NH, $^3J_{H,H}$ = 8.2 Hz), 7.34-7.49 (8H, m, 4xCH_2-(*Ar*)C-C$\underline{H}$-CH-C-$C(CH_3)_3$, 4xCH_2-(*Ar*)C-CH-C$\underline{H}$-C-$C(CH_3)_3$, $^3J_{H,H}$ = 8.2 Hz), 4.98 (2H, d, 2xCH_3-(*Ar*)C-CH-C$\underline{H}$-C, $^3J_{H,H}$ = 5.7 Hz), 4.85 (2H, d, 2xCH_3-(*Ar*)C-C$\underline{H}$-CH-C, $^3J_{H,H}$ = 5.9 Hz), 4.76 (2H, d, 2xCH_3-(*Ar*)C-CH-C$\underline{H}$-C, $^3J_{H,H}$ = 5.7 Hz), 4.54 (2H, d, 2xCH_3-(*Ar*)C-C$\underline{H}$-CH-C, $^3J_{H,H}$ = 5.8 Hz), 4.03 (2H, s, S-(*Ar*)C-CH-CH-C-$C\underline{H_2}$-(C=O)-NH), 3.93 (3H, s, $(S{=}O)_2$-NH-(*Ar*)C-N-CH-N-C-O-$C\underline{H_3}$), 3.78 (3H, s, $(S{=}O)_2$-NH-(*Ar*)C-C-O-$C\underline{H_3}$), 3.55 (2H, s, $C\underline{H_2}$-(*Ar*)C-CH-CH-C-$C(CH_3)_3$), 3.34 (2H, s, $C\underline{H_2}$-(*Ar*)C-CH-CH-C-$C(CH_3)_3$), 1.84 (2H, sept, 2x(*Ar*)C-CH-CH-C-$C\underline{H}(CH_3)_2$, $^3J_{H,H}$ = 6.9 Hz), 1.68 (6H, s, 2x$C\underline{H_3}$-(*Ar*)C-CH-CH-C), 1.35 (9H, s, S-CH_2-(*Ar*)C-CH-CH-C-$C(C\underline{H_3})_3$), 1.32 (9H, s, S-CH_2-(*Ar*)C-CH-CH-C-$C(C\underline{H_3})_3$), 0.86 (6H, d, 2x(*Ar*)C-CH-CH-C-$CH(C\underline{H_3})_2$, $^3J_{H,H}$ = 7.0 Hz), 0.84 (6H, d, 2x(*Ar*)C-CH-CH-C-$CH(C\underline{H_3})_2$, $^3J_{H,H}$ = 7.0 Hz).

^{13}C-NMR ($CDCl_3$) δ_C, ppm: 171.2 (1C, S-(*Ar*)C-CH-CH-C-CH_2-($\underline{C}$=O)-NH), 160.8 (1C, $(S{=}O)_2$-NH-(*Ar*)C-N-CH-N-$\underline{C}$-O-CH_3), 152.0 (2C, 2xS-CH_2-(*Ar*)C-CH-CH-$\underline{C}$-$C(CH_3)_3$), 151.2 (1C, $(S{=}O)_2$-NH-(*Ar*)C-N-$\underline{C}$H-N-C-O-CH_3), 150.1 (1C, $(S{=}O)_2$-NH-(*Ar*)$\underline{C}$-N-CH-N-C-O-CH_3), 145.0 (1C, NH-(*Ar*)$\underline{C}$-CH-CH-C-$(S{=}O)_2$), 137.9 (1C, S-(*Ar*)C-CH-CH-$\underline{C}$-CH_2-(C=O)-NH), 136.7, 136.4 (2C, 2xS-CH_2-(*Ar*)$\underline{C}$-CH-CH-C-$C(CH_3)_3$), 135.1 (1C, S-(*Ar*)$\underline{C}$-CH-CH-C-CH_2-(C=O)-NH), 132.3 (3C, 2xS-(*Ar*)C-$\underline{C}$H-CH-C-CH_2-(C=O)-NH, NH-(*Ar*)C-CH-CH-$\underline{C}$-$(S{=}O)_2$), 130.8 (2C, 2xS-(*Ar*)C-CH-$\underline{C}$H-C-CH_2-(C=O)-NH), 129.3, 129.2 (2C, 2xS-CH_2-(*Ar*)C-$\underline{C}$H-CH-C-$C(CH_3)_3$), 128.1 (2C, 2xNH-(*Ar*)C-CH-$\underline{C}$H-C-$(S{=}O)_2$), 126.6 (1C, $(S{=}O)_2$-NH-(*Ar*)C-$\underline{C}$-O-CH_3), 125.7, 125.6 (2C, 2xS-CH_2-(*Ar*)C-CH-$\underline{C}$H-C-$C(CH_3)_3$), 119.6 (2C, 2xNH-(*Ar*)C-$\underline{C}$H-CH-C-$(S{=}O)_2$), 107.3 (2C, 2xCH_3-(*Ar*)C-CH-CH-$\underline{C}$), 100.6 (2C, 2xCH_3-(*Ar*)$\underline{C}$-CH-CH-C), 84.0 (2C, 2xCH_3-(*Ar*)C-CH-$\underline{C}$H-C), 83.6 (2C, 2xCH_3-(*Ar*)C-CH-$\underline{C}$H-C), 83.4 (2C, 2xCH_3-(*Ar*)C-$\underline{C}$H-CH-C), 82.5 (2C, 2xCH_3-(*Ar*)C-$\underline{C}$H-CH-C), 60.6 (1C, s, $(S{=}O)_2$-NH-(*Ar*)C-C-O-$\underline{C}H_3$), 54.1 (1C, s, $(S{=}O)_2$-NH-(*Ar*)C-N-CH-N-C-O-$\underline{C}H_3$), 44.0 (1C, S-(*Ar*)C-CH-CH-C-$\underline{C}H_2$-(C=O)-NH), 39.9 (1C, S-$\underline{C}H_2$-(*Ar*)C-CH-CH-C-$C(CH_3)_3$), 39.4 (1C, S-$\underline{C}H_2$-(*Ar*)C-CH-CH-C-$C(CH_3)_3$), 34.89 (1C, S-

CH$_2$-(*Ar*)C-CH-CH-C-C(CH$_3$)$_3$), 34.87 (1C, S-CH$_2$-(*Ar*)C-CH-CH-C-C(CH$_3$)$_3$), 31.5 (6C, 2xS-CH$_2$-(*Ar*)C-CH-CH-C-C(CH$_3$)$_3$), 30.9 (2C, 2x(*Ar*)CH-CH-C-CH(CH$_3$)$_2$), 23.1 (2C, (*Ar*)CH-CH-C-CH(CH$_3$)$_2$), 22.7 (2C, (*Ar*)CH-CH-C-CH(CH$_3$)$_2$), 18.2 (2C, 2xCH$_3$-(*Ar*)C-CH-CH).
R$_f$ (CH$_2$Cl$_2$/CH$_3$OH 10:1) = 0.339.
ESI-MS(+): *m/z* found 1289.2848 [M-Cl]$^+$, calcd. for $C_{62}H_{77}N_4O_5Ru_2S_4^+$ 1289.2858.
Elemental analysis (%): calcd. for $C_{62}H_{77}ClN_4O_5Ru_2S_4$·2.5CH$_3$OH C 55.17, H 6.25, N 3.99; found C 55.27, H 6.29, N 3.78.

4. Synthesis of the conjugates with triclosan and with metronidazole

Synthesis of [(η^6-*p*-MeC$_6$H$_4$Pr^i)$_2$Ru$_2$(μ_2-SCH$_2$C$_6$H$_4$-*p*-Bu^t)$_2$(μ_2-SC$_6$H$_4$-*p*-CH$_2$-(C=O)-O-R)]Cl (R = 5-chloro-2-(2,4-dichlorophenoxy)phenoxy) (12)

To a solution of **2** (0.200 g, 0.194 mmol, 1 equiv.) in dry CH$_2$Cl$_2$ (50 mL) at r.t. under inert atmosphere (N$_2$), were added successively EDCI (0.074 g, 0.388 mmol, 2 equiv.), triclosan (0.067 g, 0.233 mmol, 1.2 equiv.) and DMAP (0.012 g, 0.097 mmol, 0.5 equiv.). The reaction mixture was stirred at r.t. under inert atmosphere (N$_2$) for further 24 h and the reaction evolution was verified by TLC (CH$_2$Cl$_2$/CH$_3$OH 9:1 (v/v)). The reaction mixture was filtered and concentrated to dryness under reduced pressure. Purification by column chromatography using CH$_2$Cl$_2$/CH$_3$OH mixture afforded **12** as an orange solid (0.102 g, 0.078 mmol, yield 40%).
^{1}H-NMR (CDCl$_3$) δ_H, ppm: 7.72 (2H, d, S-(*Ar*)C-CH-C*H*-C-CH$_2$-(C=O)-O, $^3J_{H,H}$ = 8.2 Hz), 7.50 (1H, CH$_2$-(C=O)-O-(*Ar*)C-C*H*-C(Cl)-CH-CH, $^4J_{H,H}$ = 2.5 Hz), 7.39-7.49 (8H, m, 4xS-CH$_2$-(*Ar*)C-C*H*-CH-C-C(CH$_3$)$_3$, 4xS-CH$_2$-(*Ar*)C-CH-C*H*-C-C(CH$_3$)$_3$, $^3J_{H,H}$ = 8.7 Hz), 7.23 (2H, d, S-(*Ar*)C-C*H*-CH-C-CH$_2$-(C=O)-O, $^3J_{H,H}$ = 8.2 Hz), 7.19 (1H, dd, CH$_2$-(C=O)-O-(*Ar*)C-CH-C(Cl)-C*H*-CH, $^3J_{H,H}$ = 8.7 Hz, $^4J_{H,H}$ = 2.5 Hz), 7.18 (1H, d, O-(*Ar*)C-C(Cl)-C*H*-C(Cl)-CH-CH, $^4J_{H,H}$ = 2.4 Hz), 7.17 (1H, dd, O-(*Ar*)C-C(Cl)-CH-C(Cl)-C*H*-CH, $^3J_{H,H}$ = 7.1 Hz, $^4J_{H,H}$ = 2.5 Hz), 6.89 (1H, d, CH$_2$-(C=O)-O-(*Ar*)C-CH-C(Cl)-CH-C*H*, $^3J_{H,H}$ = 8.8 Hz), 6.84 (1H, d, O-(*Ar*)C-C(Cl)-CH-C(Cl)-CH-C*H*, $^3J_{H,H}$ = 9.4 Hz), 5.09 (2H, d, 2xCH$_3$-(*Ar*)C-CH-C*H*-C, $^3J_{H,H}$ = 5.8 Hz), 4.98 (2H, d, 2xCH$_3$-(*Ar*)C-CH-C*H*-C, $^3J_{H,H}$ = 5.8 Hz), 4.88 (2H, d, 2xCH$_3$-(*Ar*)C-C*H*-CH-C, $^3J_{H,H}$ = 5.8 Hz), 4.60 (2H, d, 2xCH$_3$-(*Ar*)C-C*H*-CH-C, $^3J_{H,H}$ = 5.8 Hz), 3.81 (2H, s, S-(*Ar*)C-CH-CH-C-C*H$_2$*-(C=O)-O), 3.60 (2H, s, S-C*H$_2$*-(*Ar*)C-CH-CH-C-(CH$_3$)$_3$, 3.42 (2H, s, S-C*H$_2$*-(*Ar*)C-CH-CH-C-(CH$_3$)$_3$, 1.88 (2H, sept, 2x(*Ar*)C-CH-CH-C-C*H*(CH$_3$)$_2$, $^3J_{H,H}$ = 6.9 Hz), 1.71 (6H, s, 2xC*H$_3$*-(*Ar*)C-CH-CH-C), 1.35 (9H, s, S-CH$_2$-(*Ar*)C-CH-CH-C-C(C*H$_3$*)$_3$), 1.32 (9H, s, S-CH$_2$-(*Ar*)C-CH-CH-C-C(C*H$_3$*)$_3$), 0.90 (6H, d, 2x(*Ar*)C-CH-CH-C-CH(C*H$_3$*)$_2$, $^3J_{H,H}$ = 6.9 Hz), 0.86 (6H, d, 2x(*Ar*)C-CH-CH-C-CH(C*H$_3$*)$_2$, $^3J_{H,H}$ = 6.9 Hz).
^{13}C-NMR (CDCl$_3$) δ_C, ppm: 168.7 (1C, S-(*Ar*)C-CH-CH-C-CH$_2$-(C=O)-O), 151.9, 151.7 (2C, 2xS-CH$_2$-(*Ar*)C-CH-CH-C-C(CH$_3$)$_3$), 151.1 (1C, CH$_2$-(C=O)-O-(*Ar*)C-CH-C(Cl)-CH-CH-C-O), 146.7 (1C, CH$_2$-(C=O)-O-(*Ar*)C-CH-C(Cl)-CH-CH), 141.8 (1C, O-(*Ar*)C-C(Cl)-CH-C(Cl)-CH-CH), 137.2 (1C, S-(*Ar*)C-CH-CH-C-CH$_2$-(C=O)-O), 136.80, 136.76 (2C, 2xS-CH$_2$-(*Ar*)C-CH-CH-C-C(CH$_3$)$_3$), 133.5 (1C, S-(*Ar*)C-CH-CH-C-CH$_2$-(C=O)-O), 133.0 (2C, 2xS-(*Ar*)C-CH-CH-C-CH$_2$-(C=O)-O), 130.6 (1C, CH$_2$-(C=O)-O-(*Ar*)C-CH-C(Cl)-CH-CH), 130.1 (2C, 2xS-(*Ar*)C-CH-CH-C-CH$_2$-(C=O)-O), 129.7 (1C, CH$_2$-(C=O)-O-(*Ar*)C-CH-C(Cl)-CH-CH), 129.5 (1C, O-(*Ar*)C-C(Cl)-CH-C(Cl)-CH-CH), 129.4, 129.2 (4C, 4xS-CH$_2$-(*Ar*)C-CH-CH-C-C(CH$_3$)$_3$), 128.4 (1C, CH$_2$-(C=O)-O-(*Ar*)C-CH-C(Cl)-CH-CH), 127.3 (1C, O-(*Ar*)C-C(Cl)-CH-C(Cl)-CH-CH), 125.9 (1C, O-(*Ar*)C-C(Cl)-CH-C(Cl)-CH-CH), 125.7, 125.5 (4C, 4xS-CH$_2$-(*Ar*)C-CH-CH-C-C(CH$_3$)$_3$), 124.4 (1C, O-(*Ar*)C-C(Cl)-CH-C(Cl)-CH-CH), 120.6 (1C, CH$_2$-(C=O)-O-(*Ar*)C-CH-C(Cl)-CH-CH), 120.3 (1C, O-(*Ar*)C-C(Cl)-CH-C(Cl)-CH-CH), 107.2 (2C, 2xCH$_3$-(*Ar*)C-CH-CH-C), 100.6 (2C, 2xCH$_3$-(*Ar*)C-CH-CH-C), 84.1 (2C, 2xCH$_3$-(*Ar*)C-CH-CH-C), 83.84 (2C, 2xCH$_3$-(*Ar*)C-CH-CH-C), 83.80 (2C, 2xCH$_3$-(*Ar*)C-CH-CH-C), 82.5 (2C, 2xCH$_3$-(*Ar*)C-CH-CH-C), 40.1 (2C, S-CH$_2$-(*Ar*)C-CH-CH-C-C(CH$_3$)$_3$, S-(*Ar*)C-CH-CH-C-CH$_2$-(C=O)-O), 39.6 (1C, S-CH$_2$-

(*Ar*)C-CH-CH-C-C(CH_3)$_3$), 34.91, 34.86 (2C, 2xS-CH_2-(*Ar*)C-CH-CH-C-$\underline{C}$(CH_3)$_3$), 31.53, 31.55 (6C, 2xS-CH_2-(*Ar*)C-CH-CH-C-C($\underline{C}H_3$)$_3$), 30.9 (2C, 2x(*Ar*)CH-CH-C-$\underline{C}$H(CH_3)$_2$), 23.1 (2C, (*Ar*)CH-CH-C-CH($\underline{C}H_3$)$_2$), 22.8 (2C, (*Ar*)CH-CH-C-CH($\underline{C}H_3$)$_2$), 18.2 (2C, 2x$\underline{C}H_3$-(*Ar*)C-CH-CH).
R_f (CH_2Cl_2/CH_3OH 10:1) = 0.324.
ESI-MS(+): *m/z* found 1267.1651 [M-Cl]$^+$, calcd. for $C_{62}H_{70}Cl_3O_3Ru_2S_3^+$ 1267.1634.
Elemental analysis (%): calcd. for $C_{62}H_{70}Cl_4O_3Ru_2S_3\cdot 2.5CH_3OH$ C 56.00, H 5.83; found C 55.97, H 5.87.

Synthesis of [(η^6-*p*-$MeC_6H_4Pr^i$)$_2$$Ru_2$($\mu_2$-$SCH_2C_6H_4$-*p*-$Bu^t$)$_2$($\mu_2$-$SC_6H_4$-*p*-$CH_2$-(C=O)-O-R)]Cl (R = 2-(2-methyl-5-nitro-1*H*-imidazol-1-yl)ethan-1-oate) (13)
To a solution of **2** (0.200 g, 0.194 mmol, 1 equiv.) in dry CH_2Cl_2 (50 mL) at r.t. under inert atmosphere (N_2) were added successively EDCI (0.074 g, 0.388 mmol, 2 equiv.), metronidazole (0.040 g, 0.233 mmol, 1.2 equiv.) and DMAP (0.012 g, 0.097 mmol, 0.5 equiv.). The reaction mixture was stirred at r.t. under inert atmosphere (N_2) for further 24 h and the reaction evolution was verified by TLC (CH_2Cl_2/CH_3OH 9:1 (v/v)). The reaction mixture was concentrated to dryness under reduced pressure and purified by column chromatography followed by purification on analytical TLCs using CH_2Cl_2/CH_3OH mixture afforded **13** as an orange solid (0.117 g, 0.099 mmol, yield 51%).
^{1}H-NMR ($CDCl_3$) δ_H, ppm: 7.98 (1H, s, CH_3-(*Im*)C-N-C$\underline{H}$-C-(NO_2), 7.72 (2H, d, S-(*Ar*)C-CH-C$\underline{H}$-C-CH_2-(C=O)-O, $^3J_{H,H}$ = 7.5 Hz), 7.38-7.51 (8H, m, 4xS-CH_2-(*Ar*)C-C$\underline{H}$-CH-C-C(CH_3)$_3$, 4xS-CH_2-(*Ar*)C-CH-C$\underline{H}$-C-C(CH_3)$_3$, $^3J_{H,H}$ = 8.4 Hz), 7.17 (2H, d, S-(*Ar*)C-C$\underline{H}$-CH-C-CH_2-(C=O)-O, $^3J_{H,H}$ = 7.5 Hz), 5.10 (2H, d, 2xCH_3-(*Ar*)C-CH-C$\underline{H}$-C, $^3J_{H,H}$ = 5.3 Hz), 4.98 (2H, d, 2xCH_3-(*Ar*)C-CH-C$\underline{H}$-C, $^3J_{H,H}$ = 5.6 Hz), 4.93 (2H, d, 2xCH_3-(*Ar*)C-C$\underline{H}$-CH-C, $^3J_{H,H}$ = 5.2 Hz), 4.77 (2H, t, (*Im*)N-CH_2-C$\underline{H_2}$-O, $^3J_{H,H}$ = 4.7 Hz), 4.61 (2H, d, 2xCH_3-(*Ar*)C-C$\underline{H}$-CH-C, $^3J_{H,H}$ = 5.7 Hz), 4.48 (2H, t, (*Im*)N-C$\underline{H_2}$-CH_2-O, $^3J_{H,H}$ = 4.7 Hz), 3.60 (2H, s, S-C$\underline{H_2}$-(*Ar*)C-CH-CH-C-(CH_3)$_3$, 3.59 (2H, s, S-(*Ar*)C-CH-CH-C-C$\underline{H_2}$-(C=O)-O), 3.41 (2H, s, S-C$\underline{H_2}$-(*Ar*)C-CH-CH-C-(CH_3)$_3$, 2.62 (3H, s, C$\underline{H_3}$-(*Im*)C-N-CH-C-(NO_2), 1.89 (2H, sept, 2x(*Ar*)C-CH-CH-C-C$\underline{H}$(CH_3)$_2$, $^3J_{H,H}$ = 6.8 Hz), 1.73 (6H, s, 2xC$\underline{H_3}$-(*Ar*)C-CH-CH-C), 1.37 (9H, s, S-CH_2-(*Ar*)C-CH-CH-C-C(C$\underline{H_3}$)$_3$), 1.34 (9H, s, S-CH_2-(*Ar*)C-CH-CH-C-C(C$\underline{H_3}$)$_3$), 0.93 (6H, d, 2x(*Ar*)C-CH-CH-C-CH(C$\underline{H_3}$)$_2$, $^3J_{H,H}$ = 6.8 Hz), 0.88 (6H, d, 2x(*Ar*)C-CH-CH-C-CH(C$\underline{H_3}$)$_2$, $^3J_{H,H}$ = 6.8 Hz).
^{13}C-NMR ($CDCl_3$) δ_C, ppm: 170.6 (1C, S-(*Ar*)C-CH-CH-C-CH_2-(C=O)-O), 152.0, 151.90 (2C, 2xS-CH_2-(*Ar*)C-CH-CH-$\underline{C}$-C(CH_3)$_3$), 151.87 (1C, CH_3-(*Im*)$\underline{C}$-N-CH-C-NO_2), 138.8 (1C, CH_3-(*Im*)C-N-CH-$\underline{C}$-NO_2), 136.9 (1C, S-(*Ar*)$\underline{C}$-CH-CH-C-CH_2-(C=O)-O), 136.7 (2C, 2xS-CH_2-(*Ar*)$\underline{C}$-CH-CH-C-C(CH_3)$_3$), 134.0 (1C, S-(*Ar*)C-CH-CH-$\underline{C}$-CH_2-(C=O)-O), 133.0 (2C, 2xS-(*Ar*)C-CH-$\underline{C}$H-C-CH_2-(C=O)-O), 132.7 (1C, CH_3-(*Im*)C-N-$\underline{C}$H-C-NO_2), 130.2 (2C, 2xS-(*Ar*)C-$\underline{C}$H-CH-C-CH_2-(C=O)-O), 129.4, 129.2 (4C, 4xS-CH_2-(*Ar*)C-$\underline{C}$H-CH-C-C(CH_3)$_3$), 125.8, 125.6 (4C, 4xS-CH_2-(*Ar*)C-CH-$\underline{C}$H-C-C(CH_3)$_3$), 107.2 (2C, 2xCH_3-(*Ar*)C-CH-CH-$\underline{C}$), 100.7 (2C, 2xCH_3-(*Ar*)$\underline{C}$-CH-CH-C), 84.2 (2C, 2xCH_3-(*Ar*)C-CH-$\underline{C}$H-C), 83.82 (2C, 2xCH_3-(*Ar*)C-$\underline{C}$H-CH-C), 83.78 (2C, 2xCH_3-(*Ar*)C-CH-$\underline{C}$H-C), 82.6 (2C, 2xCH_3-(*Ar*)C-$\underline{C}$H-CH-C), 63.2 (1C, (*Im*)N-CH_2-$\underline{C}H_2$-O-(C=O)), 45.4 (1C, (*Im*)N-$\underline{C}H_2$-CH_2-O-(C=O)), 40.5 (1C, S-(*Ar*)C-CH-CH-C-$\underline{C}H_2$-(C=O)-O), 40.1 (1C, S-$\underline{C}H_2$-(*Ar*)C-CH-CH-C-C(CH_3)$_3$), 39.6 (1C, S-$\underline{C}H_2$-(*Ar*)C-CH-CH-C-C(CH_3)$_3$), 34.94, 34.90 (2C, 2xS-CH_2-(*Ar*)C-CH-CH-C-$\underline{C}$(CH_3)$_3$), 31.57, 31.55 (6C, 2xS-CH_2-(*Ar*)C-CH-CH-C-C($\underline{C}H_3$)$_3$), 31.0 (2C, 2x(*Ar*)CH-CH-C-$\underline{C}$H(CH_3)$_2$), 23.2 (2C, (*Ar*)CH-CH-C-CH($\underline{C}H_3$)$_2$), 22.8 (2C, (*Ar*)CH-CH-C-CH($\underline{C}H_3$)$_2$), 18.3 (2C, 2x$\underline{C}H_3$-(*Ar*)C-CH-CH), 14.8 (1C, $\underline{C}H_3$-(*Im*)C-N-CH-C-NO_2).
R_f (CH_2Cl_2/CH_3OH 10:1) = 0.235.
ESI-MS(+): *m/z* found 1150.2798 [M-Cl]$^+$, calcd. for $C_{56}H_{72}N_3O_4Ru_2S_3^+$ 1150.2766.
Elemental analysis (%): calcd. for $C_{56}H_{72}ClN_3O_4Ru_2S_3\cdot 1.2CH_3OH$ C 56.16, H 6.33, N 3.43; found C 56.18, H 6.32 N 3.40.

Synthesis of 2-(2-methyl-5-nitro-1*H*-imidazol-1-yl)ethyl methanesulfonate (14a)

To a solution of metronidazole (0.500 g, 2.921 mmol, 1 equiv.) in dry CH_2Cl_2 (50 mL) at 0°C under inert atmosphere (N_2) were added dropwise MsCl (0.27 mL, 3.505 mmol, 1.2 equiv.) and TEA (0.61 mL, 4.382 mmol, 1.5 equiv.). The reaction mixture was stirred at 0°C under inert atmosphere (N_2) for further 2 h and the reaction evolution was verified by TLC (CH_2Cl_2/CH_3OH 10:1 (v/v)). The reaction was quenched with water (50 mL). The isolated aqueous phase was further extracted with CH_2Cl_2 (2×30 mL). The combined organic phases were washed with brine (50 mL), dried over anhydrous Na_2SO_4, filtered and concentrated to dryness under reduced pressure. The product **14a** isolated as a white solid (0.444 g, 1.781 mmol, yield 61%) was used in next step without further purification.

^{1}H-NMR (DMSO-d$_6$) δ_H, ppm: 8.09 (1H, s, CH_3-(*Im*)C-N-C<u>*H*</u>-C-(NO_2)), 4.66 (2H, t, (*Im*)N-C<u>*H_2*</u>-CH_2-O-(S=O)-CH_3, $^3J_{H,H}$ = 5.1 Hz), 4.55 (2H, t, (*Im*)N-CH_2-C<u>*H_2*</u>-O-(S=O)-CH_3, $^3J_{H,H}$ = 5.1 Hz), 3.15 (3H, s, (*Im*)N-CH_2-CH_2-O-(S=O)-C<u>*H_3*</u>), 2.47 (3H, s, C<u>*H_3*</u>-(*Im*)C-N-CH-C-(NO_2).

^{13}C-NMR (DMSO-d$_6$) δ_C, ppm: 151.7 (1C, CH_3-(*Im*)<u>*C*</u>-N-CH-C-NO_2), 138.4 (1C, CH_3-(*Im*)C-N-CH-<u>*C*</u>-NO_2), 132.8 (1C, CH_3-(*Im*)C-N-<u>*C*</u>H-C-NO_2), 68.4 (1C, (*Im*)N-CH_2-<u>*C*</u>H_2-O-(S=O)-CH_3), 45.1 (1C, (*Im*)N-<u>*C*</u>H_2-CH_2-O-(S=O)-CH_3), 36.7 (1C, (*Im*)N-CH_2-CH_2-O-(S=O)-<u>*C*</u>H_3), 14.0 (1C, <u>*C*</u>H_3-(*Im*)C-N-CH-C-NO_2).

R$_f$ (CH_2Cl_2/CH_3OH 10:1) = 0.624.

ESI-MS(+): *m/z* found 250.0495 $[M+H]^+$, calcd. for $C_7H_{12}N_3O_5S^+$ 250.0492.

Elemental analysis (%): calcd. for $C_7H_{11}N_3O_5S\cdot0.2CH_2Cl_2\cdot0.4H_2O$ C 31.63, H 4.50, N 15.37; found C 31.61, H 4.55, N 15.39.

Synthesis of 1-(2-azidoethyl)-2-methyl-5-nitro-1*H*-imidazole (14)

To a solution of **14a** (0.444 g, 1.781 mmol, 1 equiv.) in dry DMF (5 mL) was added NaN_3 (0.232 mL, 3.562 mmol, 2 equiv.) and the reaction mixture was heated at 60°C under inert atmosphere (N_2) for 24 h. The mixture was allowed to cool to r.t., Et_2O (150 mL) was added and the mixture was washed with H_2O (2×200 mL). The organic phase was washed with brine (100 mL), dried over anhydrous Na_2SO_4, filtered and concentrated to dryness under reduced pressure. **14** was isolated as a white solid (0.165 g, 0.841 mmol, yield 47%) and was used in next step without further purification.

^{1}H-NMR (CDCl$_3$) δ_H, ppm: 8.00 (1H, s, CH_3-(*Im*)C-N-C<u>*H*</u>-C-NO_2), 4.44 (2H, t, (*Im*)N-C<u>*H_2*</u>-CH_2-N_3, $^3J_{H,H}$ = 5.6 Hz), 3.79 (2H, t, (*Im*)N-CH_2-C<u>*H_2*</u>-N_3, $^3J_{H,H}$ = 5.6 Hz), 2.56 (3H, s, C<u>*H_3*</u>-(*Im*)C-N-CH-C-NO_2).

^{13}C-NMR (CDCl$_3$) δ_C, ppm: 151.4 (1C, CH_3-(*Im*)<u>*C*</u>-N-CH-C-NO_2), 138.4 (1C, CH_3-(*Im*)C-N-CH-<u>*C*</u>-NO_2), 133.4 (1C, CH_3-(*Im*)C-N-<u>*C*</u>H-C-NO_2), 51.1 (1C, (*Im*)N-CH_2-<u>*C*</u>H_2-N_3), 45.7 (1C, (*Im*)N-<u>*C*</u>H_2-CH_2-N_3), 14.7 (1C, <u>*C*</u>H_3-(*Im*)C-N-CH-C-NO_2).

R$_f$ (CH_2Cl_2/CH_3OH 10:1) = 0.699.

ESI-MS(+): *m/z* found 197.0787 $[M+H]^+$, calcd. for $C_6H_9N_6O_2^+$ 197.0781.

Elemental analysis (%): calcd. for $C_6H_8N_6O_2$ C 36.74, H 4.11, N 42.84; found C 38.43, H 4.45, N 40.47.

Synthesis of [(η^6-*p*-MeC$_6$H$_4$Pr^i)$_2$Ru$_2$(μ_2-SCH$_2$C$_6$H$_4$-*p*-Bu^t)$_2$(μ_2-SC$_6$H$_4$-*p*-CH$_2$-(C=O)-NH-R)]Cl (R = *N*-((1-(2-(2-methyl-5-nitro-1*H*-imidazol-1-yl)ethyl)-1*H*-1,2,3-triazol-4-yl)methyl)amine) (15)

To a solution of **7** (0.200 g, 0.187 mmol, 1 equiv.) in dry DMF (10 mL) at r.t. under inert atmosphere (N_2) were successively added **14** (0.044 g, 0.224 mmol, 1.2 equiv.), $CuSO_4\cdot5H_2O$ (0.047 g, 0.187 mmol, 1 equiv.) and sodium L-ascorbate (0.074 g, 0.374 mmol, 2 equiv.). The reaction mixture was stirred at r.t. under inert atmosphere (N_2) for 48 h and the reaction evolution was verified by TLC (CH_2Cl_2/CH_3OH 10:1 (v/v)). The reaction mixture was filtered, solubilized in EtOAc (100 mL) and washed with H_2O

(3×100 mL). The unified aqueous phases were extracted with EtOAc (100 mL) and the combined organic phases were further washed with brine (100 mL), dried over anhydrous Na_2SO_4, filtered and concentrated to dryness under reduced pressure. Purification by column chromatography using CH_2Cl_2/CH_3OH mixture afforded **15** as an orange solid (0.078 g, 0.061 mmol, yield 33%).

^{1}H-NMR (DMSO-d$_6$) δ_H, ppm: 8.64 (1H, t br, S-(*Ar*)C-CH-CH-C-CH$_2$-(C=O)-N*H*), 8.18 (1H, s br, (*Tr*)C-N=N-N-C*H*), 7.88 (1H, s, CH$_3$-(*Im*)C-N-C*H*-C-NO$_2$), 7.69 (2H, d, 2xS-(*Ar*)C-CH-C*H*-C-CH$_2$-(C=O)-NH, $^3J_{H,H}$ = 7.9 Hz), 7.47-7.52 (4H, m, 4xS-CH$_2$-(*Ar*)C-CH-C*H*-C-C(CH$_3$)$_3$, $^3J_{H,H}$ = 8.6 Hz), 7.37-7.45 (4H, m, 4xS-CH$_2$-(*Ar*)C-C*H*-CH-C-C(CH$_3$)$_3$, $^3J_{H,H}$ = 8.3 Hz), 7.21 (2H, d, 2xS-(*Ar*)C-C*H*-CH-C-CH$_2$-(C=O)-NH, $^3J_{H,H}$ = 8.0 Hz), 5.37 (2H, d, 2xCH$_3$-(*Ar*)C-CH-C*H*-C, $^3J_{H,H}$ = 5.3 Hz), 5.25 (4H, d, 2xCH$_3$-(*Ar*)C-CH-C*H*-C, 2xCH$_3$-(*Ar*)C-C*H*-CH-C, $^3J_{H,H}$ = 5.8 Hz), 4.78-4.84 (2H, t br, (*Im*)N-C*H$_2$*-CH$_2$-(*Tr*)N), 4.66-4.75 (4H, m, (*Im*)N-CH$_2$-C*H$_2$*-(*Tr*)N, 2xCH$_3$-(*Ar*)C-C*H*-CH-C), 4.25 (2H, d, (C=O)-NH-C*H$_2$*-(*Tr*)C-N=N-N-CH$_2$, $^3J_{H,H}$ = 5.2 Hz), 3.63 (2H, s, S-C*H$_2$*-(*Ar*)C-CH-CH-C-(CH$_3$)$_3$), 3.43 (4H, s, S-(*Ar*)C-CH-CH-C-C*H$_2$*-(C=O)-NH, S-C*H$_2$*-(*Ar*)C-CH-CH-C-(CH$_3$)$_3$), 1.86 (3H, s, C*H$_3$*-(*Im*)C-N-CH-C-NO$_2$), 1.72-1.81 (2H, m, 2x(*Ar*)C-CH-CH-C-C*H*(CH$_3$)$_2$), 1.75 (6H s, 2xC*H*$_3$-(*Ar*)C-CH-CH-C), 1.33 (9H, s, S-CH$_2$-(*Ar*)C-CH-CH-C-C(C*H$_3$*)$_3$), 1.29 (9H, s, S-CH$_2$-(*Ar*)C-CH-CH-C-C(C*H$_3$*)$_3$), 0.79 (6H, d, 2x(*Ar*)C-CH-CH-C-CH(C*H$_3$*)$_2$, $^3J_{H,H}$ = 6.8 Hz), 0.74 (6H, d, 2x(*Ar*)C-CH-CH-C-CH(C*H$_3$*)$_2$, $^3J_{H,H}$ = 6.7 Hz).

^{13}C-NMR (DMSO-d$_6$) δ_C, ppm: 169.6 (1C, S-(*Ar*)C-CH-CH-C-CH$_2$-(*C*=O)-NH), 150.5, 150.3 (2C, 2xS-CH$_2$-(*Ar*)C-CH-CH-*C*-C(CH$_3$)$_3$), 145.2 (2C, (*Tr*)*C*-N=N-N-CH, CH$_3$-(*Im*)*C*-N-CH-C-NO$_2$), 137.0, 136.8 (2C, 2xS-CH$_2$-(*Ar*)*C*-CH-CH-C-C(CH$_3$)$_3$), 136.1 (1C, S-(*Ar*)*C*-CH-CH-C-CH$_2$-(C=O)-NH), 135.2 (1C, S-(*Ar*)C-CH-CH-*C*-CH$_2$-(C=O)-NH), 133.2 (1C, s, CH$_3$-(*Im*)C-N-CH-*C*-NO$_2$), 132.2 (2C, 2xS-(*Ar*)C-CH-*C*H-C-CH$_2$-(C=O)-NH), 129.29 (2C, 2xS-(*Ar*)C-*C*H-CH-C-CH$_2$-(C=O)-NH), 129.25, 128.9 (4C, 4xS-CH$_2$-(*Ar*)C-*C*H-CH-C-C(CH$_3$)$_3$), 125.2, 125.0 (4C, 4xS-CH$_2$-(*Ar*)C-CH-*C*H-C-C(CH$_3$)$_3$), 123.8 (2C, (*Tr*)C-N=N-N-*C*H, CH$_3$-(*Im*)C-N-C*H*-C-NO$_2$), 105.2 (2C, 2xCH$_3$-(*Ar*)C-CH-CH-*C*), 101.3 (2C, 2xCH$_3$-(*Ar*)*C*-CH-CH-C), 85.1 (2C, 2xCH$_3$-(*Ar*)C-CH-*C*H-C), 82.6 (2C, 2xCH$_3$-(*Ar*)C-*C*H-CH-C), 82.4 (2C, 2xCH$_3$-(*Ar*)C-CH-*C*H-C), 82.3 (2C, 2xCH$_3$-(*Ar*)C-*C*H-CH-C), 48.6 (2H, m, (*Im*)N-CH$_2$-*C*H$_2$-(*Tr*)N), 46.3 (2H, m, (*Im*)N-*C*H$_2$-CH$_2$-(*Tr*)N), 41.6 (1C, S-(*Ar*)C-CH-CH-C-*C*H$_2$-(C=O)-NH), 39.7 (1C, S-*C*H$_2$-(*Ar*)C-CH-CH-C-C(CH$_3$)$_3$), 39.5 (1C, S-*C*H$_2$-(*Ar*)C-CH-CH-C-C(CH$_3$)$_3$), 34.39, 34.34 (2C, 2xS-CH$_2$-(*Ar*)C-CH-CH-C-*C*(CH$_3$)$_3$), 34.1 (1C, (C=O)-NH-*C*H$_2$-(*Tr*)C-N=N-N-CH$_2$), 31.2, 31.1 (6C, 2xS-CH$_2$-(*Ar*)C-CH-CH-C-C(*C*H$_3$)$_3$), 29.9 (2C, 2x(*Ar*)CH-CH-C-*C*H(CH$_3$)$_2$), 23.0 (2C, (*Ar*)CH-CH-C-CH(*C*H$_3$)$_2$), 21.8 (2C, (*Ar*)CH-CH-C-CH(*C*H$_3$)$_2$), 17.5 (2C, 2x*C*H$_3$-(*Ar*)C-CH-CH), 12.9 (1C, *C*H$_3$-(*Im*)C-N-CH-C-NO$_2$).

R$_f$ (CH_2Cl_2/CH_3OH 10:1) = 0.117.

ESI-MS(+): *m/z* found 1231.3262 [M-Cl]$^+$, calcd. for $C_{59}H_{75}N_6O_4Ru_2S_3^+$ 1231.3093.

Elemental analysis (%): calcd. for $C_{59}H_{75}ClN_6O_4Ru_2S_3\cdot CH_2Cl_2\cdot 1.8H_2O$ C 52.09, H 5.87, N 6.07; found C 52.04, H 5.95, N 6.56.

5. Synthesis of the conjugates with ciprofloxacin

Synthesis of 7-(4-(*tert*-butoxycarbonyl)piperazin-1-yl)-1-cyclopropyl-6-fluoro-4-oxo-1,4-dihydroquinoline-3-carboxylic acid (16)

To a suspension of ciprofloxacin (0.505 g, 15.04 mmol, 1 equiv.) in dry CH_2Cl_2 (30 mL) under N_2, at r.t. were added successively di-*tert*-butyl decarbonate (0.396 g, 1.78 mmol, 1.2 equiv.) and TEA (0.459 g, 6.20 mmol, 3 equiv.). The reaction mixture was further stirred under N_2 at r.t. for 72 h. The reaction mixture was concentrated to dryness to afford **16** as a pale-yellow solid in quantitative yield.

^{1}H-NMR (CDCl$_3$) δ_H, ppm: 14.92 (1H, s br, (C=O)-O*H*), 8.73 (1H, s, N-C*H*-C-(C=O)-OH), 7.99 (1H, d, F-(*Ar*)C-C*H*-C-C, $^3J_{H,F}$ = 12.9 Hz), 7.36 (1H, d, F-(*Ar*)C-CH-C-C-C*H*-C-N, $^4J_{H,F}$ = 7.1 Hz), 3.64-3.69

(4H, m, 2xF-(*Ar*)C-C-N-CH_2-C$\underline{H_2}$-N, $^3J_{H,H}$ = 5.2 Hz), 3.51-3.58 (1H, m, N-C$\underline{H}$-CH_2-CH_2, $^3J_{H,H}$ = 3.8 Hz), 3.27-3.32 (4H, m, 2xF-(*Ar*)C-C-N-C$\underline{H_2}$-CH_2-N, $^3J_{H,H}$ = 5.2 Hz), 1.49 (9H, s, N-(C=O)-O-C(C$\underline{H_3}$)$_3$), 1.37-1.42 (2H, m, N-CH-C$\underline{H_2}$-C$\underline{H_2}$), 1.18-1.23 (2H, m, N-CH-C$\underline{H_2}$-C$\underline{H_2}$).

^{13}C-NMR ($CDCl_3$) δ_C, ppm: 177.2 (1C, d, N-CH-$\underline{C}$-(C=O)-OH, $^4J_{C,F}$ = 2.6 Hz), 167.0 (1C, N-CH-C-($\underline{C}$=O)-OH), 154.7 (1C, N-($\underline{C}$=O)-O-C(CH_3)$_3$), 153.8 (1C, d, F-(*Ar*)$\underline{C}$-CH-C-C, $^1J_{C,F}$ = 251.4 Hz), 147.6 (1C, N-$\underline{C}$H-C-(C=O)-OH), 145.9 (1C, d, F-(*Ar*)C-$\underline{C}$-N-CH_2, $^2J_{C,F}$ = 10.4 Hz), 139.2 (1C, F-(*Ar*)C-CH-C-$\underline{C}$-CH-C-N), 120.3 (1C, d, F-(*Ar*)C-CH-$\underline{C}$-C-CH-C-N, $^3J_{C,F}$ = 7.9 Hz), 112.7 (1C, d, F-(*Ar*)C-$\underline{C}$H-C-C-CH-C-N, $^2J_{C,F}$ = 23.4 Hz), 108.3 (1C, N-CH-$\underline{C}$-(C=O)-OH), 105.2 (1C, F-(*Ar*)C-CH-C-C-$\underline{C}$H-C-N, $^3J_{C,F}$ = 3.2 Hz), 80.5 (1C, N-(C=O)-O-$\underline{C}$(CH_3)$_3$), 49.9 (2C, 2xF-(*Ar*)C-C-N-$\underline{C}H_2$-CH_2-N), 43.8 (2C,br, 2xF-(*Ar*)C-C-N-CH_2-$\underline{C}H_2$-N), 35.4 (1C, N-$\underline{C}$H-CH_2-CH_2), 28.5 (3C, N-(C=O)-O-C($\underline{C}H_3$)$_3$), 8.4 (2C, N-CH-$\underline{C}H_2$-$\underline{C}H_2$).

^{19}F-NMR ($CDCl_3$) δ_F, ppm: -121.80 (1F, dd, $^3J_{F,H}$ = 12.6 Hz, $^4J_{F,H}$ = 7.6 Hz).

R_f (CH_2Cl_2/CH_3OH 10:1) = 0.611.

ESI-MS(+): *m/z* found 332.1399 [M-Boc+H]$^+$, 376.1295 [M-*t*BuOH+H]$^+$, 432.1918 [M+H]$^+$, 454.1736 [M+Na]$^+$ and 885.3594 [2M+Na]$^+$, calcd. for $C_{17}H_{19}FN_3O_3^+$ 332.1405, $C_{18}H_{19}FN_3O_5^+$ 376.1303, $C_{22}H_{27}FN_3O_5^+$ 432.1929, $C_{22}H_{26}FN_3NaO_5^+$ 454.1749 and $C_{44}H_{52}F_2N_6NaO_{10}^+$ 885.3605.

Elemental analysis (%): calcd. for $C_{22}H_{26}FN_3O_5\cdot0.05CH_2Cl_2$ C 60.78, H 6.04, N 9.64; found C 60.71, H 6.04 N 9.69.

Synthesis of [(η^6-*p*-Me$C_6H_4{}^i$Pr)$_2$Ru$_2$(SCH$_2$-*p*-$C_6H_4{}^t$Bu)$_2$(SC_6H_4-*p*-O-R)]Cl (R = 7-(4-(*tert*-butoxycarbonyl)piperazin-1-yl)-1-cyclopropyl-6-fluoro-4-oxo-1,4-dihydroquinoline-3-carboxylate) (17)

To a solution of **3** (0.250 g, 0.253 mmol, 1 equiv.) in dry CH_2Cl_2 (30 mL), at r.t. under inert atmosphere (N_2) was added **16** (0.127 g, 0.328 mmol, 1.3 equiv.), HOBt·H_2O (0.082 g, 0.555 mmol, 2.4 equiv.), EDCI (0.145 g, 0.756 mmol, 3 equiv.) and DIPEA (0.163 g, 1.261 mmol, 5 equiv.). After 30 min, HBTU (0.230 g, 0.606 mmol, 2.4 equiv.) was added and the reaction mixture was stirred for further 72 h. The reaction evolution was verified by TLC (CH_2Cl_2/CH_3OH 10:1 (v/v)). The mixture was concentrated to dryness and purification by column chromatography using CH_2Cl_2/CH_3OH mixture afforded **17** as an orange solid (0.242 g, 0.172 mmol, yield 68%).

^{1}H-NMR ($CDCl_3$) δ_H, ppm: 8.52 (1H, s, (*Cipro*)N-C$\underline{H}$-C-(C=O)-O), 7.98 (1H, d, (*Cipro*)F-(*Ar*)C-C$\underline{H}$-C-C, $^3J_{H,F}$ = 13.1 Hz), 7.52 (2H, m, 2xS-(*Ar*)C-C$\underline{H}$-CH-C-O-(C=O), $^3J_{H,H}$ = 8.6 Hz), 7.37-7.47 (8H, m, 4xS-CH_2-(*Ar*)C-C$\underline{H}$-CH-C-C(CH_3)$_3$, 4xS-CH_2-(*Ar*)C-CH-C$\underline{H}$-C-C(CH_3)$_3$, $^3J_{H,H}$ = 8.9 Hz, $^3J_{H,H}$ = 8.4 Hz), 7.29 (1H, d, (*Cipro*)F-(*Ar*)C-CH-C-C-C$\underline{H}$-C-N, $^4J_{H,F}$ = 7.1 Hz), 6.87 (2H, d, 2xS-(*Ar*)C-CH-C$\underline{H}$-C-O-(C=O), $^3J_{H,H}$ = 8.7 Hz), 5.00 (2H, d, 2xCH_3-(*Ar*)C-CH-C$\underline{H}$-C, $^3J_{H,H}$ = 5.8 Hz), 4.89 (2H, d, 2xCH_3-(*Ar*)C-CH-C$\underline{H}$-C, $^3J_{H,H}$ = 5.8 Hz), 4.74 (2H, d, 2xCH_3-(*Ar*)C-C$\underline{H}$-CH-C, $^3J_{H,H}$ = 5.8 Hz), 4.55 (2H, d, 2xCH_3-(*Ar*)C-C$\underline{H}$-CH-C, $^3J_{H,H}$ = 5.8 Hz), 3.60-3.66 (4H, m, 2x(*Cipro*)F-(*Ar*)C-C-N-CH_2-C$\underline{H_2}$-N, $^3J_{H,H}$ = 5.2 Hz), 3.54 (2H, s, S-C$\underline{H_2}$-(*Ar*)C-CH-CH-C-C(CH_3)$_3$), 3.42-3.49 (1H, m, (*Cipro*)N-C$\underline{H}$-CH_2-CH_2, $^3J_{H,H}$ = 3.7 Hz), 3.35 (2H, s, S-C$\underline{H_2}$-(*Ar*)C-CH-CH-C-C(CH_3)$_3$), 3.18-3.24 (4H, m, 2xF-(*Ar*)C-C-N-C$\underline{H_2}$-CH_2-N, $^3J_{H,H}$ = 5.1 Hz), 1.91 (2H, sept, 2x(*Ar*)C-CH-CH-C-C$\underline{H}$(CH_3)$_2$, $^3J_{H,H}$ = 6.9 Hz), 1.69 (6H, s, 2xC$\underline{H_3}$-(*Ar*)C-CH-CH-C), 1.50 (9H, s, N-(C=O)-O-C(C$\underline{H_3}$)$_3$), 1.34 (9H, s, S-CH_2-(*Ar*)C-CH-CH-C-C(C$\underline{H_3}$)$_3$), 1.32 (9H, s, S-CH_2-(*Ar*)C-CH-CH-C-C(C$\underline{H_3}$)$_3$), 1.25-1.31 (2H, m, N-CH-C$\underline{H_2}$-C$\underline{H_2}$), 1.06-1.13 (2H, m, N-CH-C$\underline{H_2}$-C$\underline{H_2}$), 0.94 (6H, d, (*Ar*)C-CH-CH-C-CH(C$\underline{H_3}$)$_2$, $^3J_{H,H}$ = 6.9 Hz), 0.89 (6H, d, (*Ar*)C-CH-CH-C-CH(C$\underline{H_3}$)$_2$, $^3J_{H,H}$ = 6.9 Hz).

^{13}C-NMR ($CDCl_3$) δ_C, ppm: 173.2 (1C, d, (*Cipro*)N-CH-$\underline{C}$-(C=O)-O, $^4J_{C,F}$ = 1.6 Hz), 165.8 (1C, (*Cipro*)N-CH-C-($\underline{C}$=O)-O), 154.7 (1C, (*Cipro*)N-($\underline{C}$=O)-O-C(CH_3)$_3$), 153.5 (1C, d, (*Cipro*)F-(*Ar*)$\underline{C}$-CH-C-C, $^1J_{C,F}$ = 248.3 Hz), 151.7, 151.8 (2C, 2xS-CH_2-(*Ar*)C-CH-CH-$\underline{C}$-C(CH_3)$_3$), 148.3 (1C,

(*Cipro*)N-*C*H-C-(C=O)-O), 144.7 (1C, d, (*Cipro*)F-(*Ar*)C-*C*-N, $^2J_{C,F}$ = 10.4 Hz), 144.3 (1C, S-(*Ar*)C-CH-CH-*C*-O-(C=O)), 138.3 (1C, (*Cipro*)F-(*Ar*)C-CH-C-*C*-CH-C-N), 138.3 (1C, S-(*Ar*)*C*-CH-CH-C-O-(C=O)), 136.8, 136.9 (2C, 2xS-CH_2-(*Ar*)*C*-CH-CH-C-C(CH_3)$_3$), 133.9 (2C, 2xS-(*Ar*)C-*C*H-CH-C-O-(C=O), 129.1, 129.3 (4C, 4xS-CH_2-(*Ar*)C-*C*H-CH-C), 125.5, 125.6 (4C, 4xS-CH_2-(*Ar*)C-CH-*C*H-C), 123.0 (1C, d, (*Cipro*)F-(*Ar*)C-CH-*C*-C-CH-C-N, $^3J_{C,F}$ = 7.0 Hz), 116.4 (2C, 2xS-(*Ar*)C-CH-*C*H-C-O-(C=O)), 113.3 (1C, d, (*Cipro*)F-(*Ar*)C-*C*H-C-C-CH-C-N, $^2J_{C,F}$ = 23.1 Hz), 110.2 (1C, (*Cipro*)N-CH-*C*-(C=O)-O), 107.1 (2C, 2xCH_3-(*Ar*)C-CH-CH-*C*), 105.2 (1C, (*Cipro*)F-(*Ar*)C-CH-C-C-*C*H-C-N, $^3J_{C,F}$ = 2.6 Hz), 100.4 (2C, 2xCH_3-(*Ar*)*C*-CH-CH-C), 83.8 (4C, 2xCH_3-(*Ar*)C-*C*H-CH-C, 2xCH_3-(*Ar*)C-CH-*C*H-C), 83.5 (2C, 2xCH_3-(*Ar*)C-CH-*C*H-C), 82.3 (2C, 2xCH_3-(*Ar*)C-*C*H-CH-C), 80.3 (1C, (*Cipro*)N-(C=O)-O-*C*(CH_3)$_3$), 50.0 (2C, (*Cipro*)2xF-(*Ar*)C-C-N-*C*H_2-CH_2-N), 43.6 (2C, br, (*Cipro*)2xF-(*Ar*)C-C-N-CH_2-*C*H_2-N), 39.8 (1C, S-*C*H_2-(*Ar*)C-CH-CH-C-C(CH_3)$_3$), 39.2 (1C, S-*C*H_2-(*Ar*)C-CH-CH-C-C(CH_3)$_3$), 34.85 (1C, S-CH_2-(*Ar*)C-CH-CH-C-*C*(CH_3)$_3$), 34.81 (2C, S-CH_2-(*Ar*)C-CH-CH-C-*C*(CH_3)$_3$, (*Cipro*)N-*C*H-CH_2-CH_2), 31.49, 31.50 (6C, 2xS-CH_2-(*Ar*)C-CH-CH-C-C(*C*H_3)$_3$), 30.9 (2C, 2x(*Ar*)CH-CH-C-*C*H(CH_3)$_2$), 28.5 (3C, (*Cipro*)N-(C=O)-O-C(*C*H_3)$_3$), 23.2 (2C, (*Ar*)CH-CH-C-CH(*C*H_3)$_2$), 22.8 (2C, (*Ar*)CH-CH-C-CH(*C*H_3)$_2$), 18.1 (2C, 2x*C*H_3-(*Ar*)C-CH-CH-C), 8.3 (2C, (*Cipro*)N-CH-*C*H_2-*C*H_2).
R_f (CH_2Cl_2/CH_3OH 10:1) = 0.667.
^{19}F-NMR ($CDCl_3$) δ_F, ppm: -124.5 (1F, dd, $^3J_{F,H}$ = 12.5 Hz, $^4J_{F,H}$ = 7.1 Hz).
ESI-MS(+): *m/z* found 1368.3875 [M-Cl]$^+$, calcd. for $C_{70}H_{87}FN_3O5Ru_2S_3^+$ 1368.3873.

Synthesis of [(η^6-*p*-$MeC_6H_4Pr^i$)$_2$$Ru_2$($\mu_2$-$SCH_2C_6H_4$-*p*-$Bu^t$)$_2$($\mu_2$-$SC_6H_4$-*p*-NH-R)]Cl (R = 7-(4-(tert-butoxycarbonyl)piperazin-1-yl)-1-cyclopropyl-6-fluoro-4-oxo-1,4-dihydroquinoline-3-carboxylate) (18)

To a solution of **4** (0.250 g, 0.253 mmol, 1 equiv.) in CH_2Cl_2 (50 mL) were added at r.t. under N_2, DIPEA (0.163 g, 1.261 mmol, 5 equiv.) and EDCI (0.145 g, 0.756 mmol, 3 equiv.). After 10 min HOBt·H_2O (0.082 g, 0.555 mmol, 2.4 equiv.) and **16** (0.127 g, 0.328 mmol, 1.3 equiv.) were successively added. The reaction mixture was stirred for 2 h then HBTU (0.230 g, 0.606 mmol, 2.4 equiv.) was added. The reaction was further stirred at r.t for 72 h and the evolution was verified by TLC (CH_2Cl_2/CH_3OH 10:1 (v/v)). The mixture was concentrated to dryness and purified by column chromatography using CH_2Cl_2/CH_3OH mixture to afford **18** as an orange solid (0.307 g, 0,219 mmol, yield 87%).
^{1}H-NMR ($CDCl_3$) δ_H, ppm: 12.49 (1H, s, S-(*Ar*)C-CH-CH-C-N*H*-(C=O)), 8.90 (1H, s, (*Cipro*)N-C*H*-C-(C=O)-NH), 8.07 (1H, d, F-(*Ar*)C-C*H*-C-C, $^3J_{H,F}$ = 13.1 Hz), 7.69-7.74 (4H, m, 2xS-(*Ar*)C-CH-C*H*-C-NH-(C=O), 2xS-(*Ar*)C-C*H*-CH-C-NH-(C=O), $^3J_{H,H}$ = 9.1 Hz), 7.40-7.50 (9H, m, F-(*Ar*)C-CH-C-C-C*H*-C-N, 4xS-CH_2-(*Ar*)C-C*H*-CH-C-C(CH_3)$_3$, 4xS-CH_2-(*Ar*)C-CH-C*H*-C-C(CH_3)$_3$, $^3J_{H,H}$ = 8.7 Hz), 5.04 (2H, d, 2xCH_3-(*Ar*)C-CH-C*H*-C, $^3J_{H,H}$ = 5.7 Hz), 4.95 (2H, d, 2xCH_3-(*Ar*)C-CH-C*H*-C, $^3J_{H,H}$ = 5.8 Hz), 4.80 (2H, d, 2xCH_3-(*Ar*)C-C*H*-CH-C, $^3J_{H,H}$ = 5.7 Hz), 4.61 (2H, d, 2xCH_3-(*Ar*)C-C*H*-CH-C, $^3J_{H,H}$ = 5.8 Hz), 3.65-3.69 (4H, m, 2xF-(*Ar*)C-C-N-CH_2-C*H_2*-N, $^3J_{H,H}$ = 4.6 Hz), 3.59-3.64 (1H, m, N-CH-CH_2-CH_2, $^3J_{H,H}$ = 3.9 Hz), 3.59 (2H, s, S-C*H_2*-(*Ar*)C-CH-CH-C-C(CH_3)$_3$), 3.40 (2H, s, S-C*H_2*-(*Ar*)C-CH-CH-C-C(CH_3)$_3$), 3.27-3.32 (4H, m, 2xF-(*Ar*)C-C-N-C*H_2*-CH_2-N, $^3J_{H,H}$ = 4.9 Hz), 1.93 (2H, sept, 2x(*Ar*)C-CH-CH-C-C*H*(CH_3)$_2$, $^3J_{H,H}$ = 6.9 Hz), 1.74 (6H, s, 2xC*H_3*-(*Ar*)C-CH-CH-C), 1.50 (9H, s, N-(C=O)-O-C(C*H_3*)$_3$), 1.41-1.48 (2H, m, N-CH-C*H_2*-C*H_2*), 1.36 (9H, s, S-CH_2-(*Ar*)C-CH-CH-C-C(C*H_3*)$_3$), 1.34 (9H, s, S-CH_2-(*Ar*)C-CH-CH-C-C(C*H_3*)$_3$), 1.14-1.18 (2H, m, N-CH-C*H_2*-C*H_2*), 0.95 (6H, d, (*Ar*)C-CH-CH-C-CH(C*H_3*)$_2$, $^3J_{H,H}$ = 6.9 Hz), 0.91 (6H, d, (*Ar*)C-CH-CH-C-CH(C*H_3*)$_2$, $^3J_{H,H}$ = 6.9 Hz).
^{13}C-NMR ($CDCl_3$) δ_C, ppm: 175.7 (1C, d, (*Cipro*)N-CH-*C*-(C=O)-NH, $^4J_{C,F}$ = 2.1 Hz), 165.9 (1C, (*Cipro*)N-CH-C-(*C*=O)-NH), 154.8 (1C, (*Cipro*)N-(*C*=O)-O-C(CH_3)$_3$), 153.8 (1C, d, (*Cipro*)F-(*Ar*)*C*-CH-C-C, $^1J_{C,F}$ = 249.7 Hz), 151.8, 151.9 (2C, 2xS-CH_2-(*Ar*)C-CH-CH-*C*-C(CH_3)$_3$), 147.2 (1C,

(*Cipro*)N-$\underline{C}$H-C-(C=O)-NH), 145.4 (1C, d, (*Cipro*)F-(*Ar*)C-$\underline{C}$-N, $^{2}J_{C,F}$ = 10.4 Hz), 139.6 (1C, (*Cipro*)F-(*Ar*)C-CH-C-$\underline{C}$-CH-C-N), 138.8 (1C, S-(*Ar*)$\underline{C}$-CH-CH-C-NH-(C=O)), 136.7, 136.8 (2C, 2xS-CH$_2$-(*Ar*)$\underline{C}$-CH-CH-C-C(CH$_3$)$_3$), 133.4 (2C, 2xS-(*Ar*)C-$\underline{C}$H-CH-C-NH-(C=O), 132.0 (1C, S-(*Ar*)C-CH-CH-$\underline{C}$-NH-(C=O)), 129.2, 129.4 (4C, 4xS-CH$_2$-(*Ar*)C-$\underline{C}$H-CH-C), 125.6, 125.7 (4C, 4xS-CH$_2$-(*Ar*)C-CH-$\underline{C}$H-C), 121.7 (1C, d, (*Cipro*)F-(*Ar*)C-CH-$\underline{C}$-C-CH-C-N, $^{3}J_{C,F}$ = 7.2 Hz), 120.5 (2C, 2xS-(*Ar*)C-CH-$\underline{C}$H-C-NH-(C=O)), 112.7 (1C, d, (*Cipro*)F-(*Ar*)C-$\underline{C}$H-C-C-CH-C-N, $^{2}J_{C,F}$ = 23.3 Hz), 111.0 (1C, (*Cipro*)N-CH-$\underline{C}$-(C=O)-NH), 107.4 (2C, 2xCH$_3$-(*Ar*)C-CH-CH-$\underline{C}$), 105.5 (1C, (*Cipro*)F-(*Ar*)C-CH-C-C-$\underline{C}$H-C-N, $^{3}J_{C,F}$ = 2.8 Hz), 100.5 (2C, 2xCH$_3$-(*Ar*)$\underline{C}$-CH-CH-C), 83.9 (2C, 2xCH$_3$-(*Ar*)C-CH-$\underline{C}$H-C), 83.8 (2C, 2xCH$_3$-(*Ar*)C-$\underline{C}$H-CH-C), 83.7 (2C, 2xCH$_3$-(*Ar*)C-CH-$\underline{C}$H-C), 82.4 (2C, 2xCH$_3$-(*Ar*)C-$\underline{C}$H-CH-C), 80.4 (1C, (*Cipro*)N-(C=O)-O-$\underline{C}$(CH$_3$)$_3$), 50.0 (2C, (*Cipro*)2xF-(*Ar*)C-C-N-$\underline{C}$H$_2$-CH$_2$-N), 43.5 (2C, br, (*Cipro*)2xF-(*Ar*)C-C-N-CH$_2$-$\underline{C}$H$_2$-N), 40.0 (1C, S-$\underline{C}$H$_2$-(*Ar*)C-CH-CH-C-C(CH$_3$)$_3$), 39.4 (1C, S-$\underline{C}$H$_2$-(*Ar*)C-CH-CH-C-C(CH$_3$)$_3$), 35.4 (1C, (*Cipro*)N-$\underline{C}$H-CH$_2$-CH$_2$), 34.91 (1C, S-CH$_2$-(*Ar*)C-CH-CH-C-$\underline{C}$(CH$_3$)$_3$), 34.88 (1C, S-CH$_2$-(*Ar*)C-CH-CH-C-$\underline{C}$(CH$_3$)$_3$), 31.53, 31.55 (6C, 2xS-CH$_2$-(*Ar*)C-CH-CH-C-C($\underline{C}$H$_3$)$_3$), 31.0 (2C, 2x(*Ar*)CH-CH-C-$\underline{C}$H(CH$_3$)$_2$), 28.5 (3C, (*Cipro*)N-(C=O)-O-C($\underline{C}$H$_3$)$_3$), 23.2 (2C, (*Ar*)CH-CH-C-CH($\underline{C}$H$_3$)$_2$), 22.8 (2C, (*Ar*)CH-CH-C-CH($\underline{C}$H$_3$)$_2$), 18.2 (2C, 2x$\underline{C}$H$_3$-(*Ar*)C-CH-CH-C), 8.4 (2C, (*Cipro*)N-CH-$\underline{C}$H$_2$-$\underline{C}$H$_2$).

^{19}F-NMR (CDCl$_3$) δ_F, ppm: -122.45 (1F, m).

R$_f$ (CH$_2$Cl$_2$/CH$_3$OH 10:1) = 0.713.

ESI-MS(+): *m/z* found 1367.4036 [M-Cl]$^+$, calcd. for $C_{70}H_{88}FN_4O_4Ru_2S_3^+$ 1367.4033.

Elemental analysis (%): calcd. for $C_{70}H_{88}ClFN_4O_4Ru_2S_3\cdot 1.1CH_2Cl_2\cdot 2.5H_2O$ C 55.43, H 6.23, N 3.64; found C 55.45, H 6.23, N 4.29.

Synthesis of [(η^6-*p*-MeC$_6$H$_4$Pr^i)$_2$Ru$_2$(μ_2-SCH$_2$C$_6$H$_4$-*p*-Bu^t)$_2$(μ_2-SC$_6$H$_4$-*p*-NH-R)]Cl (R = 1-cyclopropyl-6-fluoro-4-oxo-7-(piperazin-1-yl)-1,4-dihydroquinoline-3-carboxylate) (19)

TFA (3 mL) was dropwise added to a solution of **18** (0.200 g, 0.128 mmol) in dry CH$_2$Cl$_2$ (15 mL) at r.t.. The mixture was stirred for 2 h at r.t. and the reaction progression was verified by TLC. The reaction mixture was concentrated under reduced pressure and the crude was resolubilised in MeOH (3×50 mL) and re-concentrated to afford **19** the product as an orange solid (0.108 g, 0.082 mmol, yield 64%).

^{1}H-NMR (MeOD-d$_4$) δ_H, ppm: 8.93 (1H, s, (*Cipro*)N-C$\underline{H}$-C-(C=O)-NH), 8.04 (1H, d, F-(*Ar*)C-C$\underline{H}$-C-C, $^{3}J_{H,F}$ = 13.0 Hz), 7.87 (2H, d, 2xS-(*Ar*)C-CH-C$\underline{H}$-C-NH-(C=O), $^{3}J_{H,H}$ = 8.4 Hz), 7.73 (2H, d, 2xS-(*Ar*)C-C$\underline{H}$-CH-C-NH-(C=O), $^{3}J_{H,H}$ = 8.4 Hz), 7.68 (1H, d, F-(*Ar*)C-CH-C-C-C$\underline{H}$-C-N, $^{4}J_{H,F}$ = 7.2 Hz), 7.45-7.59 (8H, m, 4xS-CH$_2$-(*Ar*)C-C$\underline{H}$-CH-C-C(CH$_3$)$_3$, 4xS-CH$_2$-(*Ar*)C-CH-C$\underline{H}$-C-C(CH$_3$)$_3$, $^{3}J_{H,H}$ = 8.0 Hz), 5.27 (2H, d, 2xCH$_3$-(*Ar*)C-CH-C$\underline{H}$-C, $^{3}J_{H,H}$ = 5.4 Hz), 5.16 (2H, d, 2xCH$_3$-(*Ar*)C-CH-C$\underline{H}$-C, $^{3}J_{H,H}$ = 5.6 Hz), 5.05 (2H, d, 2xCH$_3$-(*Ar*)C-C$\underline{H}$-CH-C, $^{3}J_{H,H}$ = 5.4 Hz), 4.77 (2H, d, 2xCH$_3$-(*Ar*)C-C$\underline{H}$-CH-C, $^{3}J_{H,H}$ = 5.5 Hz), 3.75-3.83 (1H, m, N-C$\underline{H}$-CH$_2$-CH$_2$), 3.70 (2H, s, S-C$\underline{H_2}$-(*Ar*)C-CH-CH-C-C(CH$_3$)$_3$), 3.60-3.66 (4H, m, 2xF-(*Ar*)C-C-N-C$\underline{H_2}$-CH$_2$-NH), 3.52 (2H, s, S-C$\underline{H_2}$-(*Ar*)C-CH-CH-C-C(CH$_3$)$_3$), 3.46-3.52 (4H, m, 2xF-(*Ar*)C-C-N-CH$_2$-C$\underline{H_2}$-NH), 1.96 (2H, sept, 2x(*Ar*)C-CH-CH-C-C$\underline{H}$(CH$_3$)$_2$, $^{3}J_{H,H}$ = 6.8 Hz), 1.80 (6H, s, 2xC$\underline{H_3}$-(*Ar*)C-CH-CH-C), 1.41-1.47 (2H, m, N-CH-C$\underline{H_2}$-C$\underline{H_2}$), 1.39 (9H, s, S-CH$_2$-(*Ar*)C-CH-CH-C-C(C$\underline{H_3}$)$_3$), 1.35 (9H, s, S-CH$_2$-(*Ar*)C-CH-CH-C-C(C$\underline{H_3}$)$_3$), 1.21-1.29 (2H, m, N-CH-C$\underline{H_2}$-C$\underline{H_2}$), 0.96 (6H, d, (*Ar*)C-CH-CH-C-CH(C$\underline{H_3}$)$_2$, $^{3}J_{H,H}$ = 6.8 Hz), 0.93 (6H, d, (*Ar*)C-CH-CH-C-CH(C$\underline{H_3}$)$_2$, $^{3}J_{H,H}$ = 6.8 Hz).

^{13}C-NMR (MeOD-d$_4$) δ_C, ppm: 176.8 (1C, d, (*Cipro*)N-CH-$\underline{C}$-(C=O)-NH, $^{4}J_{C,F}$ = 2.4 Hz), 167.5 (1C, (*Cipro*)N-CH-C-($\underline{C}$=O)-NH), 154.9 (1C, d, (*Cipro*)F-(*Ar*)$\underline{C}$-CH-C-C, $^{1}J_{C,F}$ = 248.6 Hz), 152.6, 152.7 (2C, 2xS-CH$_2$-(*Ar*)C-CH-CH-$\underline{C}$-C(CH$_3$)$_3$), 149.0 (1C, (*Cipro*)N-$\underline{C}$H-C-(C=O)-NH), 145.4 (1C, d, (*Cipro*)F-(*Ar*)C-$\underline{C}$-N, $^{2}J_{C,F}$ = 10.8 Hz), 140.2 (1C, (*Cipro*)F-(*Ar*)C-CH-C-$\underline{C}$-CH-C-N), 140.1 (1C, S-(*Ar*)$\underline{C}$-CH-CH-C-NH-(C=O)), 138.5, 138.6 (2C, 2xS-CH$_2$-(*Ar*)$\underline{C}$-CH-CH-C-C(CH$_3$)$_3$), 135.0 (2C, 2xS-

(*Ar*)C-C̲H-CH-C-NH-(C=O), 134.1 (1C, S-(*Ar*)C-CH-CH-C̲-NH-(C=O)), 130.3, 130.7 (4C, 4xS-CH_2-(*Ar*)C-C̲H-CH-C), 126.6, 126.8 (4C, 4xS-CH_2-(*Ar*)C-CH-C̲H-C), 123.5 (1C, d, (*Cipro*)F-(*Ar*)C-CH-C̲-C-CH-C-N, $^3J_{C,F}$ = 7.4 Hz), 121.4 (2C, 2xS-(*Ar*)C-CH-C̲H-C-NH-(C=O)), 113.2 (1C, d, (*Cipro*)F-(*Ar*)C-C̲H-C-C-CH-C-N, $^2J_{C,F}$ = 23.3 Hz), 111.6 (1C, (*Cipro*)N-CH-C̲-(C=O)-NH), 108.1 (2C, 2xCH_3-(*Ar*)C-CH-CH-C̲), 108.0 (1C, (*Cipro*)F-(*Ar*)C-CH-C-C-C̲H-C-N, $^3J_{C,F}$ = 1.8 Hz), 102.3 (2C, 2xCH_3-(*Ar*)C̲-CH-CH-C), 85.7 (2C, 2xCH_3-(*Ar*)C-CH-C̲H-C), 84.7 (4C, 2xCH_3-(*Ar*)C-CH-C̲H-C, 2xCH_3-(*Ar*)C-C̲H-CH-C), 83.9 (2C, 2xCH_3-(*Ar*)C-C̲H-CH-C), 48.2 (2C, 2x(*Cipro*)F-(*Ar*)C-C-N-C̲H_2-CH_2-N), 44.7 (2C, 2x(*Cipro*)F-(*Ar*)C-C-N-CH_2-C̲H_2-N), 41.2 (1C, S-C̲H_2-(*Ar*)C-CH-CH-C-C$(CH_3)_3$), 40.7 (1C, S-C̲H_2-(*Ar*)C-CH-CH-C-C$(CH_3)_3$), 36.7 (1C, (*Cipro*)N-C̲H-CH_2-CH_2), 35.63 (1C, S-CH_2-(*Ar*)C-CH-CH-C-C̲$(CH_3)_3$), 35.58 (1C, S-CH_2-(*Ar*)C-CH-CH-C-C̲$(CH_3)_3$), 32.1 (2C, 2x(*Ar*)CH-CH-C-C̲H$(CH_3)_2$), 31.8, 31.9 (6C, 2xS-CH_2-(*Ar*)C-CH-CH-C-C(C̲$H_3)_3$), 23.6 (2C, (*Ar*)CH-CH-C-CH(C̲$H_3)_2$), 23.0 (2C, (*Ar*)CH-CH-C-CH(C̲$H_3)_2$), 18.3 (2C, 2xC̲H_3-(*Ar*)C-CH-CH-C), 8.6 (2C, (*Cipro*)N-CH-C̲H_2-C̲H_2).
R$_f$ (CH_2Cl_2/CH_3OH 9:1) = 0.142.
ESI-MS(+): *m/z* found 1267.3498 $[M-Cl]^+$, calcd. for $C_{65}H_{80}FN_4O_2Ru_2S_3^+$ 1267.3509.
Elemental analysis (%): calcd. for $C_{65}H_{80}ClFN_4O_2Ru_2S_3\cdot 4.35CH_2Cl_2$ C 49.83, H 5.35, N 3.35; found C 49.82, H 5.32, N 4.51.

6. Synthesis of the conjugates with menadione

Synthesis of 3-(3-methyl-1,4-dioxo-1,4-dihydronaphthalen-2-yl)propanoic acid (20)

The synthesis was adapted after literature procedures[5-8]. To a solution of 2-methyl-1,4-naphthoquinone (1.00 g, 5.808 mmol, 1 equiv.) and butanedioic acid (2.058 g, 17.427 mmol, 3 equiv.) in a mixture CH_3CN/H_2O (25 mL, 2:1 (v/v)) at 65°C, were successively added $AgNO_3$ (0.296 g, 1.742 mmol, 0.3 equiv.) and a solution of $(NH_4)_2S_2O_8$ (1.723 g, 7.550 mmol, 1.3 equiv.) in aq. CH_3CN (12 mL) over 2 h. The mixture was further stirred at 65°C for 1 h, then it was cooled to r.t. and extracted with CH_2Cl_2 (3×150 mL). The organic phase was washed with water (2×150 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated. Purification by column chromatography using CH_2Cl_2/CH_3OH (9.5:0.5 (v/v)) mixture afforded **20** as a white solid (0.987 g, 4.041 mmol, yield 70%).
^{1}H-NMR ($CDCl_3$) δ_H, ppm: 8.05-8.11 (2H, m, (*Ar*)C-CH-C*H̲*-C*H̲*-CH, $^3J_{H,H}$ = 3.9 Hz), 7.68-7.72 (2H, m, (*Ar*)C-C*H̲*-CH-CH-C*H̲*, $^3J_{H,H}$ = 4.1 Hz), 2.98 (2H, t, (C=O)-C-CH_2-C*H̲*$_2$-CO_2H), $^3J_{H,H}$ = 8.0 Hz), 2.61 (2H, t, (C=O)-C-C*H̲*$_2$-CH_2-CO_2H, $^3J_{H,H}$ = 8.1 Hz), 2.23 (3H, s, (C=O)-C-C*H̲*$_3$).
^{13}C-NMR ($CDCl_3$) δ_C, ppm: 185.2 (1C, (C̲=O)-C-CH_3), 184.6 (1C, (C̲=O)-C-$(CH_2)_2$-(C=O)-OH), 178.0 (1C, (C=O)-C-$(CH_2)_2$-(C̲=O)-OH), 144.9 (1C, (C=O)-C̲-CH_3), 144.7 (1C, (C=O)-C̲-$(CH_2)_2$-(C=O)-OH), 133.7 (2C, (*Ar*)C-CH-C̲H-C̲H-CH-C), 132.24, 132.19 (2C, (*Ar*)C̲-CH-CH-CH-CH-C̲), 126.52, 126.48 (2C, (*Ar*)C-C̲H-CH-CH-C̲H-C), 32.6 (1C, (C=O)-C-CH_2-C̲H_2-CO_2H), 22.7 (1C, (C=O)-C-C̲H_2-CH_2-CO_2H), 12.9 (1C, (C=O)-C-C̲H_3).
R$_f$ (CH_2Cl_2/CH_3OH 10:1) = 0.343.
ESI-MS(-): *m/z* found 243.0667 $[M-H]^-$, 487.1403 $[2M-H]^-$, calcd. for $C_{14}H_{11}O_4^-$ 243.0663, and for $C_{28}H_{23}O_8^-$ 487.1398.
Elemental analysis (%): calcd. for $C_{14}H_{12}O_4$ C 68.85, H 4.95, found C 71.01, 4.85.

Synthesis of 5-(3-methyl-1,4-dioxo-1,4-dihydronaphthalen-2-yl)pentanoic acid (21)

The synthesis was adapted after literature procedures[5-8]. To a solution of 2-methyl-1,4-naphthoquinone (0.600 g, 3.505 mmol,1 equiv.) and hexanedioic acid (1.528 g, 10.46 mmol, 3 equiv.) in a mixture CH_3CN/H_2O (25 mL, 2:1 (v/v) at 65°C, were successively added $AgNO_3$ (0.178 g, 1.048 mmol, 0.3 equiv.) and a solution of $(NH_4)_2S_2O_8$ (1.034 g, 4.521 mmol, 1.3 equiv.) in aq. CH_3CN (15 mL) over 2 h.

The mixture was further stirred at 65°C for 1 h, then it was cooled to r.t. and extracted with CH_2Cl_2 (3×150 mL). The organic phase was then washed with water (2×150 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated. Purification by column chromatography using CH_2Cl_2/CH_3OH (9.5:0.5 (v/v)) mixture afforded **21** as a white solid (0.584 g, 2.144 mmol, yield 61%).

^{1}H-NMR ($CDCl_3$) δ_H, ppm: 8.05-8.07 (2H, m, (*Ar*)C-CH-C$\underline{H}$-C$\underline{H}$-CH, $^3J_{H,H}$ = 3.5 Hz), 7.66-7.70 (2H, m, (*Ar*)C-C$\underline{H}$-CH-CH-C$\underline{H}$, $^3J_{H,H}$ = 4.1 Hz), 2.66 (2H, t, (C=O)-C-C$\underline{H_2}$-$(CH_2)_3$-CO_2H), $^3J_{H,H}$ = 7.8 Hz), 2.41 (2H, t, (C=O)-C-$(CH_2)_3$-C$\underline{H_2}$-CO_2H), $^3J_{H,H}$ = 7.4 Hz), 2.19 (3H, s, (C=O)-C-C$\underline{H_3}$), 1.75 (2H, qvint, (C=O)-C-$(CH_2)_2$-C$\underline{H_2}$-CH_2-CO_2H), $^3J_{H,H}$ = 7.5 Hz), 1.50-1.58 (2H, m, (C=O)-C-CH_2-C$\underline{H_2}$-$(CH_2)_2$-CO_2H), $^3J_{H,H}$ = 8.0 Hz).

^{13}C-NMR ($CDCl_3$) δ_C, ppm: 185.4 (1C, ($\underline{C}$=O)-C-CH_3), 184.8 (1C, ($\underline{C}$=O)-C-$(CH_2)_4$-(C=O)-OH), 179.4 (1C, (C=O)-C-$(CH_2)_4$-($\underline{C}$=O)-OH), 146.9 (1C, (C=O)-$\underline{C}$-$(CH_2)_4$-(C=O)-OH), 143.6 (1C, (C=O)-$\underline{C}$-CH_3), 133.52, 133.50 (2C, (*Ar*)C-CH-$\underline{C}$H-$\underline{C}$H-CH-C), 132.26, 132.25 (2C, (*Ar*)$\underline{C}$-CH-CH-CH-CH-$\underline{C}$), 126.43, 126.36 (2C, (*Ar*)C-$\underline{C}$H-CH-CH-$\underline{C}$H-C), 33.8 (1C, (C=O)-C-$(CH_2)_3$-$\underline{C}H_2$-CO_2H), 28.1 (1C, (C=O)-C-CH_2-$\underline{C}H_2$-$(CH_2)_2$-CO_2H), 26.8 (1C, (C=O)-C-$(CH_2)_2$-$\underline{C}H_2$-CH_2-CO_2H), 24.9 (1C, (C=O)-C-$\underline{C}H_2$-$(CH_2)_3$-CO_2H), 12.8 (1C, (C=O)-C-$\underline{C}H_3$).

R_f (CH_2Cl_2/CH_3OH 10:1) = 0.583.

ESI-MS(+): *m/z* found 273.1123 $[M+H]^+$, 295.0941 $[M+Na]^+$, 567.1979 $[2M+Na]^+$, 583.1639 $[2M+K]^+$, calcd. for $C_{16}H_{17}O_4^+$ 273.1121, for $C_{16}H_{16}NaO_4^+$ 295.0941, for $C_{32}H_{32}NaO_8^+$ 567.1989 and for $C_{32}H_{32}KO_8^+$ 583.1729.

Elemental analysis (%): calcd. for $C_{16}H_{16}O_4{\cdot}0.1CH_3OH$ C 70.19, H, 6.00; found C 70.15, H 6.04.

Synthesis of 7-(3-methyl-1,4-dioxo-1,4-dihydronaphthalen-2-yl)heptanoic acid (22)

The synthesis was adapted after literature procedures[5-8]. To a solution of 2-methyl-1,4-naphthoquinone (0.600 g, 3.485 mmol, 1 equiv.) and octanedioic acid (1.821 g, 10.45 mmol, 3 equiv.) in a mixture CH_3CN/H_2O (25 mL, 2:1, v/v) at 65°C, were successively added $AgNO_3$ (0.178 g, 1.048 mmol, 0.3 equiv.) and a solution of $(NH_4)_2S_2O_8$ (1.034 g, 4.521 mmol, 1.3 equiv.) in CH_3CN (12 mL) over 2 h. The mixture was further stirred at 65°C for 1 h, then it was cooled to r.t. and extracted with CH_2Cl_2 (3×300 mL). The organic phase was then washed with water (2×150 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated to dryness. Purification by column chromatography using CH_2Cl_2/CH_3OH (9.5:0.5 (v/v)) mixture afforded **22** as a white solid (0.544 g, 1.810 mmol, yield 52%).

^{1}H-NMR ($CDCl_3$) δ_H, ppm: 8.05-8.09 (2H, m, (*Ar*)C-CH-C$\underline{H}$-C$\underline{H}$-CH, $^3J_{H,H}$ = 3.6 Hz), 7.66-7.72 (2H, m, (*Ar*)C-C$\underline{H}$-CH-CH-C$\underline{H}$, $^3J_{H,H}$ = 3.3 Hz), 2.63 (2H, t, (C=O)-C-C$\underline{H_2}$-$(CH_2)_5$-CO_2H, $^3J_{H,H}$ = 7.6 Hz), 2.36 (2H, t, (C=O)-C-$(CH_2)_5$-C$\underline{H_2}$-CO_2H, $^3J_{H,H}$ = 7.4 Hz), 2.18 (3H, s, (C=O)-C-C$\underline{H_3}$), 1.65 (2H, qvint, (C=O)-C-$(CH_2)_4$-C$\underline{H_2}$-CH_2-CO_2H, $^3J_{H,H}$ = 7.0 Hz), 1.35-1.53 (6H, m, (C=O)-C-CH_2-$(C\underline{H_2})_{\underline{3}}$-$(CH_2)_2$-$CO_2H$).

^{13}C-NMR ($CDCl_3$) δ_C, ppm: 185.5 (1C, ($\underline{C}$=O)-C-CH_3), 184.9 (1C, ($\underline{C}$=O)-C-$(CH_2)_6$-(C=O)-OH), 179.2 (1C, (C=O)-C-$(CH_2)_6$-($\underline{C}$=O)-OH), 147.5 (1C, (C=O)-$\underline{C}$-$(CH_2)_6$-(C=O)-OH), 143.3 (1C, (C=O)-$\underline{C}$-CH_3), 133.48, 133.45 (2C, (*Ar*)C-CH-$\underline{C}$H-$\underline{C}$H-CH-C), 132.33, 132.31 (2C, (*Ar*)$\underline{C}$-CH-CH-CH-CH-$\underline{C}$), 126.4, 126.3 (2C, (*Ar*)C-$\underline{C}$H-CH-CH-$\underline{C}$H-C), 34.0 (1C, (C=O)-C-$(CH_2)_5$-$\underline{C}H_2$-CO_2H), 29.7 (1C, (C=O)-C-$(CH_2)_2$-$\underline{C}H_2$-$(CH_2)_3$-CO_2H), 29.0 (1C, (C=O)-C-$(CH_2)_3$-$\underline{C}H_2$-$(CH_2)_2$-CO_2H), 28.6 (1C, (C=O)-C-CH_2-$\underline{C}H_2$-$(CH_2)_4$-CO_2H), 27.1 (1C, (C=O)-C-$(CH_2)_4$-$\underline{C}H_2$-CH_2-CO_2H), 24.7 (1C, (C=O)-C-$\underline{C}H_2$-$(CH_2)_5$-CO_2H), 12.8 (1C, (C=O)-C-$\underline{C}H_3$).

R_f (CH_2Cl_2/CH_3OH 10:1) = 0.705.

ESI-MS(-): *m/z* found 299.1290 $[M-H]^-$, 599.2655 $[2M-H]^-$; calcd. for $C_{18}H_{19}O_4^-$ 299.1278 and for $C_{36}H_{39}O_8^-$ 599.2639.

Elemental analysis (%): calcd. for $C_{18}H_{20}O_4{\cdot}0.1CH_3OH$ C 71.62, H 6.77, found C 71.62, H 6.79.

Synthesis of [(η^6-*p*-MeC$_6$H$_4$Pr^i)$_2$Ru$_2$(SCH$_2$-*p*-C$_6$H$_4$Bu^t)$_2$(SC$_6$H$_4$-*p*-O-R)]Cl (R = 3-(3-methyl-1,4-dioxo-1,4-dihydronaphthalen-2-yl)propanoate) (23)

To a solution of **20** (0.081 g, 0.330 mmol, 1.3 equiv.) in dry CH_2Cl_2 (50 mL), at r.t. under inert atmosphere (N_2) was added EDCI (0.063 g, 0.329 mmol, 1.3 equiv.). After 10 min were successively added **3** (0.250 g, 0.253 mmol, 1 equiv.) and DMAP (0.009 g, 0.074 mmol, 0.3 equiv.). The mixture was further stirred for 24 h at r.t., and the reaction evolution was verified by TLC (CH_2Cl_2/CH_3OH 10:1 (v/v)). The mixture was concentrated to dryness and purification by column chromatography using CH_2Cl_2/CH_3OH mixture as eluent afforded **23** as an orange solid (0.183 g, 0.150 mmol, yield 59%).

^{1}H-NMR ($CDCl_3$) δ_H, ppm: 8.09-8.15 (2H, m, (*Napht*)C-CH-C$\underline{H}$-C$\underline{H}$-CH, $^3J_{H,H}$ = 3.2 Hz), 7.78 (2H, d, 2xS-(*Ar*)C-C$\underline{H}$-CH-C-O-(C=O), $^3J_{H,H}$ = 8.6 Hz), 7.71-7.76 (2H, m, (*Napht*)C-C$\underline{H}$-CH-CH-C$\underline{H}$, $^3J_{H,H}$ = 2.8 Hz), 7.38-7.52 (8H, m, 4xS-CH$_2$-(*Ar*)C-C$\underline{H}$-CH-C-C(CH$_3$)$_3$, 4xS-CH$_2$-(*Ar*)C-CH-C$\underline{H}$-C-C(CH$_3$)$_3$, $^3J_{H,H}$ = 8.5 Hz), 7.06 (2H, d, 2xS-(*Ar*)C-CH-C$\underline{H}$-C-O-(C=O), $^3J_{H,H}$ = 8.6 Hz), 5.11 (2H, d, 2xCH$_3$-(*Ar*)C-CH-C$\underline{H}$-C, $^3J_{H,H}$ = 6.0 Hz), 4.99 (2H, d, 2xCH$_3$-(*Ar*)C-CH-C$\underline{H}$-C, $^3J_{H,H}$ = 5.7 Hz), 4.89 (2H, d, 2xCH$_3$-(*Ar*)C-C$\underline{H}$-CH-C, $^3J_{H,H}$ = 5.8 Hz), 4.63 (2H, d, 2xCH$_3$-(*Ar*)C-C$\underline{H}$-CH-C, $^3J_{H,H}$ = 5.8 Hz), 3.61 (2H, s, S-C$\underline{H_2}$-(*Ar*)C-CH-CH-C-C(CH$_3$)$_3$), 3.43 (2H, s, S-C$\underline{H_2}$-(*Ar*)C-CH-CH-C-C(CH$_3$)$_3$), 3.18 (2H, t, (*Napht*)(C=O)-C-C$\underline{H_2}$-CH$_2$-(C=O)-O, $^3J_{H,H}$ = 6.7 Hz), 3.10 (2H, t, (*Napht*)(C=O)-C-CH$_2$-C$\underline{H_2}$-(C=O)-O, $^3J_{H,H}$ = 7.9 Hz), 2.29 (3H, s, (*Napht*)(C=O)-C-C$\underline{H_3}$), 1.89 (2H, sept, 2x(*Ar*)C-CH-CH-C-C$\underline{H}$(CH$_3$)$_2$, $^3J_{H,H}$ = 6.7 Hz), 1.77 (6H, s, 2xC$\underline{H_3}$-(*Ar*)C-CH-CH-C), 1.37 (9H, s, S-CH$_2$-(*Ar*)C-CH-CH-C-C(C$\underline{H_3}$)$_3$), 1.33 (9H, s, S-CH$_2$-(*Ar*)C-CH-CH-C-C(C$\underline{H_3}$)$_3$), 0.95 (6H, d, (*Ar*)C-CH-CH-C-CH(C$\underline{H_3}$)$_2$, $^3J_{H,H}$ = 6.8 Hz), 0.90 (6H, d, (*Ar*)C-CH-CH-C-CH(C$\underline{H_3}$)$_2$, $^3J_{H,H}$ = 6.8 Hz).

ESI-MS(+): *m/z* found 1181.2770 [M-Cl]+, calcd. for $C_{62}H_{73}O_4Ru_2S_3^+$ 1181.2752.

Synthesis of [(η^6-*p*-MeC$_6$H$_4$Pr^i)$_2$Ru$_2$(SCH$_2$-*p*-C$_6$H$_4$Bu^t)$_2$(SC$_6$H$_4$-*p*-NH-R)]Cl (R = 3-(3-methyl-1,4-dioxo-1,4-dihydronaphthalen-2-yl)propanoate) (24)

To a solution of **20** (0.081 g, 0.303 mmol, 1.3 equiv.) in dry CH_2Cl_2 (20 mL), at r.t. under inert atmosphere (N_2) was added HOBt·H_2O (0.095 g, 0.703 mmols, 3 equiv.) and DIPEA (0.055 g, 0.507 mmol, 2 equiv.). After 10 min were added successively EDCI (0.121 g, 0.631 mmol, 2.5 equiv.), **4** (0.250 g, 0.253 mmol, 1 equiv.) and DIPEA (0.055 g, 0.507 mmol, 2 equiv.). The reaction mixture was stirred for further 24 h and the reaction evolution was verified by TLC (CH_2Cl_2/CH_3OH 10:1 (v/v)). The mixture was concentrated to dryness and purification by column chromatography using CH_2Cl_2/CH_3OH mixture afforded **24** as an orange solid (0.166 g, 0.136 mmol, yield 54%).

^{1}H-NMR ($CDCl_3$) δ_H, ppm: 11.29 (1H, s, 2xS-(*Ar*)C-CH-CH-C-N$\underline{H}$-(C=O)), 8.08 (2H, d, 2xS-(*Ar*)C-CH-C$\underline{H}$-C-NH-(C=O), $^3J_{H,H}$ = 8.7 Hz), 8.00-8.07 (2H, m, (*Napht*)C-CH-C$\underline{H}$-C$\underline{H}$-CH), 7.60-7.65 (2H, m, (*Napht*)C-C$\underline{H}$-CH-CH-C$\underline{H}$), 7.56 (2H, d, 2xS-(*Ar*)C-C$\underline{H}$-CH-C-NH-(C=O), $^3J_{H,H}$ = 8.7 Hz), 7.36-7.48 (8H, m, 4xS-CH$_2$-(*Ar*)C-C$\underline{H}$-CH-C-C(CH$_3$)$_3$, 4xS-CH$_2$-(*Ar*)C-CH-C$\underline{H}$-C-C(CH$_3$)$_3$, $^3J_{H,H}$ = 8.4 Hz), 4.97 (2H, d, 2xCH$_3$-(*Ar*)C-CH-C$\underline{H}$-C, $^3J_{H,H}$ = 5.7 Hz), 4.88 (2H, d, 2xCH$_3$-(*Ar*)C-CH-C$\underline{H}$-C, $^3J_{H,H}$ = 5.8 Hz), 4.69 (2H, d, 2xCH$_3$-(*Ar*)C-C$\underline{H}$-CH-C, $^3J_{H,H}$ = 5.7 Hz), 4.60 (2H, d, 2xCH$_3$-(*Ar*)C-C$\underline{H}$-CH-C, $^3J_{H,H}$ = 5.8 Hz), 3.54 (2H, s, S-C$\underline{H_2}$-(*Ar*)C-CH-CH-C-C(CH$_3$)$_3$), 3.34 (2H, s, S-C$\underline{H_2}$-(*Ar*)C-CH-CH-C-C(CH$_3$)$_3$), 3.11 (2H, t, (*Napht*)(C=O)-C-C$\underline{H_2}$-CH$_2$-(C=O)-NH, $^3J_{H,H}$ = 8.2 Hz), 2.92 (2H, t, (*Napht*)(C=O)-C-CH$_2$-C$\underline{H_2}$-(C=O)-NH, $^3J_{H,H}$ = 8.3 Hz), 2.25 (3H, s, (*Napht*)(C=O)-C-C$\underline{H_3}$), 1.97 (2H, sept, 2x(*Ar*)C-CH-CH-C-C$\underline{H}$(CH$_3$)$_2$, $^3J_{H,H}$ = 6.9 Hz), 1.65 (6H, s, 2xC$\underline{H_3}$-(*Ar*)C-CH-CH-C), 1.35 (9H, s, S-CH$_2$-(*Ar*)C-CH-CH-C-C(C$\underline{H_3}$)$_3$), 1.33 (9H, s, S-CH$_2$-(*Ar*)C-CH-CH-C-C(C$\underline{H_3}$)$_3$), 0.97 (6H, d, (*Ar*)C-CH-CH-C-CH(C$\underline{H_3}$)$_2$, $^3J_{H,H}$ = 6.8 Hz), 0.92 (6H, d, (*Ar*)C-CH-CH-C-CH(C$\underline{H_3}$)$_2$, $^3J_{H,H}$ = 6.9 Hz).

^{13}C-NMR ($CDCl_3$) δ_C, ppm: 185.5 (1C, (*Napht*) ($\underline{C}$=O)-C-CH$_3$), 184.4 (1C, (*Napht*) ($\underline{C}$=O)-C-(CH$_2$)$_2$-(C=O)-NH), 172.0 (1C, (*Napht*) (C=O)-C-(CH$_2$)$_2$-($\underline{C}$=O)-NH), 151.88, 151.94 (2C, 4xS-CH$_2$-(*Ar*)C-CH-CH-$\underline{C}$-C(CH$_3$)$_3$), 146.6 (1C, (*Napht*)(C=O)-$\underline{C}$-(CH$_2$)$_2$-(C=O)-NH), 144.3 (1C, (*Napht*)(C=O)-$\underline{C}$-

CH_3), 141.3 (1C, S-(*Ar*)$\underline{C}$-CH-CH-C-NH-(C=O)), 136.5, 136.8 (2C, 2xS-CH_2-(*Ar*)$\underline{C}$-CH-CH-C-$C(CH_3)_3$), 133.1, 133.2 (2C, (*Napht*)C-CH-$\underline{C}$H-$\underline{C}$H-CH-C), 132.7 (2C, 2xS-(*Ar*)C-$\underline{C}$H-CH-C-NH-(C=O), 132.4, 132.5 (2C, (*Napht*)$\underline{C}$-CH-CH-CH-CH-$\underline{C}$), 129.4 (1C, S-(*Ar*)C-CH-CH-$\underline{C}$-NH-(C=O)), 129.0, 129.3 (4C, 4xS-CH_2-(*Ar*)C-$\underline{C}$H-CH-C-$C(CH_3)_3$), 126.1, 126.4 (2C, (*Napht*)C-$\underline{C}$H-CH-CH-$\underline{C}$H-C), 125.6, 125.7 (4C, 4xS-CH_2-(*Ar*)C-CH-$\underline{C}$H-C-$C(CH_3)_3$), 120.4 (2C, 2xS-(*Ar*)C-CH-$\underline{C}$H-C-NH-(C=O)), 107.7 (2C, 2xCH_3-(*Ar*)C-CH-CH-$\underline{C}$), 100.1 (2C, 2xCH_3-(*Ar*)$\underline{C}$-CH-CH-C), 84.2 (2C, 2xCH_3-(*Ar*)C-CH-$\underline{C}$H-C), 83.8 (2C, 2xCH_3-(*Ar*)C-$\underline{C}$H-CH-C), 83.2 (2C, 2xCH_3-(*Ar*)C-CH-$\underline{C}$H-C), 82.2 (2C, 2xCH_3-(*Ar*)C-$\underline{C}$H-CH-C), 39.9 (1C, S-$\underline{C}H_2$-(*Ar*)C-CH-CH-C-$C(CH_3)_3$), 39.3 (1C, S-$\underline{C}H_2$-(*Ar*)C-CH-CH-C-$C(CH_3)_3$), 35.8 (1C, (*Napht*)(C=O)-C-CH_2-$\underline{C}H_2$-(C=O)-NH), 34.89 (1C, S-CH_2-(*Ar*)C-CH-CH-C-$\underline{C}(CH_3)_3$), 34.86 (1C, S-CH_2-(*Ar*)C-CH-CH-C-$\underline{C}(CH_3)_3$), 31.50, 31.51 (6C, 2xS-CH_2-(*Ar*)C-CH-CH-C-$C(\underline{C}H_3)_3$), 31.1 (2C, 2x(*Ar*)CH-CH-C-$\underline{C}H(CH_3)_2$), 23.4 (1C, (*Napht*)(C=O)-C-$\underline{C}H_2$-CH_2-(C=O)-NH), 23.1 (2C, (*Ar*)CH-CH-C-$CH(\underline{C}H_3)_2$), 23.0 (2C, (*Ar*)CH-CH-C-$CH(\underline{C}H_3)_2$), 18.1 (2C, 2x$\underline{C}H_3$-(*Ar*)C-CH-CH-C), 13.0 (1C, (*Napht*) (C=O)-C-$\underline{C}H_3$).
R_f (CH_2Cl_2/CH_3OH 10:1) = 0.406.
ESI-MS(+): *m/z* found 1180.2926 [M-Cl]$^+$, calcd. for $C_{62}H_{74}NO_3Ru_2S_3^+$ 1180.2912.
Elemental analysis (%): calcd. for $C_{62}H_{74}ClNO_3Ru_2S_3\cdot0.1CH_3OH\cdot1.3H_2O$ C 60.07, H 6.25, N 1.13, found C 60.07, H 6.24, N 1.35.

[(η^6-*p*-$MeC_6H_4Pr^i$)$_2$$Ru_2$($\mu_2$-$SC_6H_4$-*p*-OH)$_2$($\mu_2$-$SC_6H_4$-*p*-O-R)]Cl (R = 3-(3-methyl-1,4-dioxo-1,4-dihydronaphthalen-2-yl)propanoate) (25)

To a solution of **20** (0.480 g, 1.965 mmol, 6.9 equiv.) in dry CH_2Cl_2 (50 mL), at r.t. under inert atmosphere (N_2) was added HOBt·H_2O (0.340 g, 2.516 mmols, 8.9 equiv.) and DIPEA (0.279 g, 2.155 mmol, 7.6 equiv.). After 10 min were added successively EDCI (0.386 g, 2.014 mmol, 7.1 equiv.), **5** (0.250 g, 0.284 mmol, 1 equiv.) and DIPEA (0.279 g, 2.155 mmol, 7.6 equiv.). The reaction mixture was stirred for further 24 h and the reaction evolution was verified by TLC (CH_2Cl_2/CH_3OH 10:1 (v/v)). The mixture was concentrated to dryness and purification by column chromatography using CH_2Cl_2/CH_3OH mixture afforded **25** as an orange solid (0.120 g, 0.077 mmol, yield 27%).

^{1}H-NMR ($CDCl_3$) δ_H, ppm: 8.01-8.08 (2H, m, (*Napht*)C-CH-C$\underline{H}$-C$\underline{H}$-CH), 7.78 (2H, d, 2xS-(*Ar*)C-C$\underline{H}$-CH-C-O-(C=O), $^3J_{H,H}$ = 8.7 Hz), 7.64-7.72 (2H, m, (*Napht*)C-C$\underline{H}$-CH-CH-C$\underline{H}$, $^3J_{H,H}$ = 3.2 Hz), 7.60 (2H, m, 2xS-(*Ar*)C-C$\underline{H}$-CH-C-OH, $^3J_{H,H}$ = 8.8 Hz), 7.57 (2H, m, 2xS-(*Ar*)C-C$\underline{H}$-CH-C-OH, $^3J_{H,H}$ = 8.8 Hz), 7.01 (2H, m, 2xS-(*Ar*)C-CH-C$\underline{H}$-C-O-(C=O), $^3J_{H,H}$ = 8.7 Hz), 6.80 (4H, d, 4xS-(*Ar*)C-CH-C$\underline{H}$-C-OH, $^3J_{H,H}$ = 8.5 Hz), 5.16 (2H, d, 2xCH_3-(*Ar*)C-CH-C$\underline{H}$-C, $^3J_{H,H}$ = 5.8 Hz), 5.11 (2H, d, 2xCH_3-(*Ar*)C-CH-C$\underline{H}$-C, $^3J_{H,H}$ = 5.8 Hz), 5.00 (2H, d, 2xCH_3-(*Ar*)C-C$\underline{H}$-CH-C, $^3J_{H,H}$ = 5.7 Hz), 4.94 (2H, d, 2xCH_3-(*Ar*)C-C$\underline{H}$-CH-C, $^3J_{H,H}$ = 5.9 Hz), 3.05 (2H, t, (*Napht*)(C=O)-C-C$\underline{H_2}$-CH_2-(C=O)-O, $^3J_{H,H}$ = 7.7 Hz), 2.79 (2H, t, (*Napht*)(C=O)-C-CH_2-C$\underline{H_2}$-(C=O)-O, $^3J_{H,H}$ = 7.7 Hz), 2.23 (3H, s, (*Napht*)(C=O)-C-C$\underline{H_3}$), 1.88 (2H, m, 2x(*Ar*)C-CH-CH-C-C$\underline{H}$$(CH_3)_2$, $^3J_{H,H}$ = 6.9 Hz), 1.55 (6H, s, 2xC$\underline{H_3}$-(*Ar*)C-CH-CH-C), 0.84 (6H, d, (*Ar*)C-CH-CH-C-CH(C$\underline{H_3}$)$_2$, $^3J_{H,H}$ = 6.9 Hz), 0.76 (6H, d, (*Ar*)C-CH-CH-C-CH(C$\underline{H_3}$)$_2$, $^3J_{H,H}$ = 6.9 Hz).
^{13}C-NMR ($CDCl_3$) δ_C, ppm: 185.2 (1C, (*Napht*)($\underline{C}$=O)-C-CH_3), 184.7 (1C, (*Napht*)($\underline{C}$=O)-C-$(CH_2)_2$-(C=O)-O), 170.9 (1C, (*Napht*)(C=O)-C-$(CH_2)_2$-($\underline{C}$=O)-O), 158.2 (2C, 2xS-(*Ar*)C-CH-CH-$\underline{C}$-OH), 150.7 (1C, S-(*Ar*)C-CH-CH-$\underline{C}$-O-(C=O)), 144.8 (1C, (*Napht*)(C=O)-$\underline{C}$-$(CH_2)_2$-(C=O)-O), 144.7 (1C, (*Napht*)(C=O)-$\underline{C}$-CH_3), 135.8 (1C, S-(*Ar*)$\underline{C}$-CH-CH-C-O-(C=O)), 132.80 (2C, 2xS-(*Ar*)C-$\underline{C}$H-CH-C-O-(C=O)), 133.76 (4C, 4xS-(*Ar*)C-$\underline{C}$H-CH-C-OH), 133.4, 133.6 (2C, (*Napht*)C-CH-$\underline{C}$H-$\underline{C}$H-CH-C),

132.0, 132.1(2C, (*Napht*)(*Ar*)C-CH-CH-CH-CH-C), 126.4, 126.5 (2C, (*Napht*)C-CH-CH-CH-CH-C), 126.3 (2C, 2xS-(*Ar*)C-CH-CH-C-OH), 122.1 (2C, 2S-(*Ar*)C-CH-CH-C-O-(C=O)), 116.3 (4C, 4xS-(*Ar*)C-CH-CH-C-OH), 107.4 (2C, 2xCH_3-(*Ar*)C-CH-CH-C), 99.7 (2C, 2xCH_3-(*Ar*)C-CH-CH-C), 85.2 (2C, 2xCH_3-(*Ar*)C-CH-CH-C), 84.6 (2C, 2xCH_3-(*Ar*)C-CH-CH-C), 84.5 (2C, 2xCH_3-(*Ar*)C-CH-CH-C), 83.5 (2C, 2xCH_3-(*Ar*)C-CH-CH-C), 32.9 (1C, (*Napht*)(C=O)-C-CH_2-CH_2-(C=O)-O), 30.6 (2C, 2x(*Ar*)CH-CH-C-CH(CH_3)$_2$), 27.7 (1C, (*Napht*)(C=O)-C-CH_2-CH_2-(C=O)-O), 22.4 (2C, (*Ar*)CH-CH-C-CH(CH_3)$_2$), 22.1 (2C, (*Ar*)CH-CH-C-CH(CH_3)$_2$), 17.6 (2C, 2xCH_3-(*Ar*)C-CH-CH-C), 12.8 (1C, (*Napht*)(C=O)-C-CH_3).
R$_f$ (CH_2Cl_2/CH_3OH 10:1) = 0.132.
ESI-MS(+): *m/z* found 1073.1077 $[M-Cl]^+$, calcd. for $C_{52}H_{53}O_6Ru_2S_3^+$ 1073.1086.

Synthesis of [(η^6-*p*-$MeC_6H_4Pr^i$)$_2$$Ru_2$($\mu_2$-$SC_6H_4$-*p*-NH-R)$_3$]Cl (R = 3-(3-methyl-1,4-dioxo-1,4-dihydronaphthalen-2-yl)propanoate) (26)

To a solution of **20** (0.843 g, 3.437 mmol, 4 equiv.), in dry CH_2Cl_2 (50 mL) at r.t. under N_2 were added HOBt·H_2O (0.574 g, 4.248 mmol, 5 equiv.) and DIPEA (0.500 g, 3.869 mmol, 4.5 equiv.). After 10 min were successively added EDCI (0.741 g, 3.866 mmol, 4.5 equiv.), **6** (0.750 g, 0.859 mmol, 1 equiv.) and DIPEA (0.500 g, 3.869 mmol, 4.5 equiv.). The mixture was further stirred under N_2 at r.t. for 24 h and the reaction evolution was verified by TLC (CH_2Cl_2/CH_3OH 10:1 (v/v)). The mixture was concentrated under reduced pressure and purification by column chromatography using CH_2Cl_2/CH_3OH mixture afforded the **26** as an orange brown solid (0.102 g, 0.065 mmol, yield 8%).
^{1}H-NMR ($CDCl_3$) δ_H, ppm: 10.00 (3H, s br, 3xS-(*Ar*)C-CH-CH-C-N*H*), 7.95-8.01 (6H, m, 3x(*Napht*)C-CH-C*H*-C*H*-CH), 7.83 (6H, m, 6xS-(*Ar*)C-CH-C*H*-C-NH-(C=O), $^3J_{H,H}$ = 8.4 Hz), 7.70 (6H, m, 6xS-(*Ar*)C-C*H*-CH-C-NH-(C=O), $^3J_{H,H}$ = 8.4 Hz), 7.59-7.65 (6H, m, 3x(*Napht*)C-C*H*-CH-CH-C*H*), 5.21 (2H, d, 2xCH_3-(*Ar*)C-CH-C*H*-C, $^3J_{H,H}$ = 6.8 Hz), 5.19 (2H, d, 2xCH_3-(*Ar*)C-CH-C*H*-C, $^3J_{H,H}$ = 6.9 Hz), 5.05 (2H, d, 2xCH_3-(*Ar*)C-C*H*-CH-C, $^3J_{H,H}$ = 5.6 Hz), 5.01 (2H, d, 2xCH_3-(*Ar*)C-C*H*-CH-C, $^3J_{H,H}$ = 5.7 Hz), 3.03 (6H, t br, 3x(*Napht*)(C=O)-C-CH_2-CH_2-(C=O)-NH, $^3J_{H,H}$ = 6.9 Hz), 2.77 (6H, t br, 3x(*Napht*)(C=O)-C-CH_2-CH_2-(C=O)-NH, $^3J_{H,H}$ = 6.8 Hz), 2.21 (9H, s, 3x(*Napht*)(C=O)-C-CH_3), 1.99 (2H, sept, 2x(*Ar*)C-CH-CH-C-C*H*(CH_3)$_2$, $^3J_{H,H}$ = 6.7 Hz), 1.56 (6H, s, 2xCH_3-(*Ar*)C-CH-CH-C), 0.89 (6H, d, (*Ar*)C-CH-CH-C-CH(CH_3)$_2$, $^3J_{H,H}$ = 6.8 Hz), 0.81 (6H, d, (*Ar*)C-CH-CH-C-CH(CH_3)$_2$, $^3J_{H,H}$ = 6.7 Hz).
^{13}C-NMR ($CDCl_3$) δ_C, ppm: 185.2 (3C, 3x(*Napht*)(C=O)-C-CH_3), 184.6 (3C, 3x(*Napht*)(C=O)-C-(CH_2)$_2$-(C=O)-NH), 171.3 (3C, 3x(*Napht*)(C=O)-C-(CH_2)$_2$-(C=O)-NH), 145.9 (3C, 3x(*Napht*)(C=O)-C-(CH_2)$_2$-(C=O)-NH), 144.4 (3C, 3x(*Napht*)(C=O)-C-CH_3), 139.9 (3C, 3xS-(*Ar*)C-CH-CH-C-NH-(C=O)), 133.5 (6C, 3x(*Napht*)C-CH-CH-CH-CH-C), 133.0 (6C, 6xS-(*Ar*)C-CH-CH-C-NH-(C=O), 132.3 (6C, 3x(*Napht*)C-CH-CH-CH-CH-C), 131.6 (3C, 3xS-(*Ar*)C-CH-CH-C-NH-(C=O)), 126.3, 126.4 (6C, 3x(*Napht*)C-CH-CH-CH-CH-C), 120.2 (6C, 6xS-(*Ar*)C-CH-CH-C-NH-(C=O)), 108.0 (2C, 2xCH_3-(*Ar*)C-CH-CH-C), 99.2 (2C, 2xCH_3-(*Ar*)C-CH-CH-C), 85.9 (2C, 2xCH_3-(*Ar*)C-CH-CH-C), 85.2 (2C, 2xCH_3-(*Ar*)C-CH-CH-C), 84.1 (2C, 2xCH_3-(*Ar*)C-CH-CH-C), 83.3 (2C, 2xCH_3-(*Ar*)C-CH-CH-C), 35.8 (3C, 3x(*Napht*)(C=O)-C-CH_2-CH_2-(C=O)-NH), 30.8 (2C, 2x(*Ar*)CH-CH-C-CH(CH_3)$_2$), 23.5 (3C, 3x(*Napht*)(C=O)-C-CH_2-CH_2-(C=O)-NH), 22.9 (2C, (*Ar*)CH-CH-C-CH(CH_3)$_2$), 22.2 (2C, (*Ar*)CH-CH-C-CH(CH_3)$_2$), 17.8 (2C, 2xCH_3-(*Ar*)C-CH-CH-C), 13.0 (3C, 3x(*Napht*)(C=O)-C-CH_3).
R$_f$ (CH_2Cl_2/CH_3OH 10:1) = 0.396.
ESI-MS(+): *m/z* found 1522.2912 $[M-Cl]^+$, calcd. for $C_{80}H_{76}N_3O_9Ru_2S_3^+$ 1522.2825.
Elemental analysis (%): calcd. for $C_{80}H_{76}ClN_3O_9Ru_2S_3$ C 61.70, H 4.92, N 2.70, found C 61.80, H 4.81, N 3.41.

Synthesis of [(η^6-*p*-MeC$_6$H$_4$Pr^i)$_2$Ru$_2$(μ_2-SC$_6$H$_4$-*p*-NH-R)$_3$]Cl (R = 5-(3-methyl-1,4-dioxo-1,4-dihydronaphthalen-2-yl)pentanoate) 27

To a solution of **21** (0.312 g, 1.146 mmol, 4 equiv.) in dry CH_2Cl_2 (50 mL), at r.t. under N_2 were added HOBt·H_2O (0.186 g, 1.377 mmol, 5 equiv.) and DIPEA (0.167 g, 1.289 mmol, 4.5 equiv.). After 10 min, were added successively EDCI (0.247 g, 1.289 mmol, 4.5 equiv.), **6** (0.250 g, 0.286 mmol, 1 equiv.) and DIPEA (0.167 g, 1.289 mmol, 4.5 equiv.). The reaction mixture was stirred for further 48 h under N_2 at r.t. and the reaction evolution was monitored by TLC (CH_2Cl_2/CH_3OH 9:1 (v/v)). The mixture was then concentrated to dryness. Purification by column chromatography using CH_2Cl_2/CH_3OH mixture afforded **27** as an orange solid (0.136 g, 0.083 mmol, yield 33%).

^{1}H-NMR (CDCl$_3$) δ_H, ppm: 9.88 (3H, s br, 3xS-(*Ar*)C-CH-CH-C-N<u>*H*</u>), 7.96-8.02 (6H, m, 3x(*Napht*)C-CH-C<u>*H*</u>-C<u>*H*</u>-CH, $^3J_{H,H}$ = 3.8 Hz), 7.87 (6H, m, 6xS-(*Ar*)C-CH-C<u>*H*</u>-C-NH-(C=O), $^3J_{H,H}$ = 8.5 Hz), 7.70 (6H, m, 6xS-(*Ar*)C-C<u>*H*</u>-CH-C-NH-(C=O), $^3J_{H,H}$ = 8.5 Hz), 7.60-7.66 (6H, m, 3x(*Ar*)C-C<u>*H*</u>-CH-CH-C<u>*H*</u>, $^3J_{H,H}$ = 3.4 Hz), 5.18 (2H, d, 2xCH$_3$-(*Ar*)C-CH-C<u>*H*</u>-C, $^3J_{H,H}$ = 5.7 Hz), 5.18 (2H, d, 2xCH$_3$-(*Ar*)C-CH-C<u>*H*</u>-C, $^3J_{H,H}$ = 5.8 Hz), 5.03 (2H, d, 2xCH$_3$-(*Ar*)C-C<u>*H*</u>-CH-C, $^3J_{H,H}$ = 5.6 Hz), 4.98 (2H, d, 2xCH$_3$-(*Ar*)C-C<u>*H*</u>-CH-C, $^3J_{H,H}$ = 5.8 Hz), 2.58-2.69 (12H, m, 3x(*Napht*)(C=O)-C-(CH$_2$)$_3$-C<u>*H$_2$*</u>-(C=O)-NH, 3x(*Napht*)(C=O)-C-C<u>*H$_2$*</u>-(CH$_2$)$_3$-(C=O)-NH, $^3J_{H,H}$ = 7.2 Hz), 2.15 (9H, s, 3x(*Napht*)(C=O)-C-C<u>*H$_3$*</u>), 1.97 (2H, sept, 2x(*Ar*)C-CH-CH-C-C<u>*H*</u>(CH$_3$)$_2$, $^3J_{H,H}$ = 6.8 Hz), 1.83 (6H, qvint, 3x(*Napht*)(C=O)-C-(CH$_2$)$_2$-C<u>*H$_2$*</u>-CH$_2$-(C=O)-NH), $^3J_{H,H}$ = 7.3 Hz), 1.51-1.63 (6H, m, 3x(*Napht*)(C=O)-C-CH$_2$-C<u>*H$_2$*</u>-(CH$_2$)$_2$-(C=O)-NH), 1.56 (6H, s, 2xC<u>*H$_3$*</u>-(*Ar*)C-CH-CH-C), 0.87 (6H, d, (*Ar*)C-CH-CH-C-CH(C<u>*H$_3$*</u>)$_2$, $^3J_{H,H}$ = 6.8 Hz), 0.80 (6H, d, (*Ar*)C-CH-CH-C-CH(C<u>*H$_3$*</u>)$_2$, $^3J_{H,H}$ = 6.8 Hz).

^{13}C-NMR (CDCl$_3$) δ_C, ppm: 185.3 (3C, 3x(*Napht*)(<u>*C*</u>=O)-C-CH$_3$), 184.8 (3C, 3x(*Napht*)(<u>*C*</u>=O)-C-(CH$_2$)$_4$-(C=O)-NH), 172.6 (3C, 3x(*Napht*)(C=O)-C-(CH$_2$)$_4$-(<u>*C*</u>=O)-NH), 147.1 (3C, 3x(*Napht*)(C=O)-<u>*C*</u>-(CH$_2$)$_4$-(C=O)-NH), 143.6 (3C, 3x(*Napht*)(C=O)-<u>*C*</u>-CH$_3$), 140.0 (3C, 3xS-(*Ar*)<u>*C*</u>-CH-CH-C-NH-(C=O)), 133.4 (6C, 3x(*Napht*)C-CH-<u>*C*</u>H-<u>*C*</u>H-CH-C), 132.9 (6C, 6xS-(*Ar*)C-<u>*C*</u>H-CH-C-NH-(C=O), 132.2 (6C, 3x(*Napht*)<u>*C*</u>-CH-CH-CH-CH-<u>*C*</u>), 131.4 (3C, 3xS-(*Ar*)C-CH-CH-<u>*C*</u>-NH-(C=O)), 126.25, 126.30 (6C, 3x(*Napht*)C-<u>*C*</u>H-CH-CH-<u>*C*</u>H-C), 120.2 (6C, 6xS-(*Ar*)C-CH-<u>*C*</u>H-C-NH-(C=O)), 108.0 (2C, 2xCH$_3$-(*Ar*)C-CH-CH-<u>*C*</u>), 99.1 (2C, 2xCH$_3$-(*Ar*)<u>*C*</u>-CH-CH-C), 85.8 (2C, 2xCH$_3$-(*Ar*)C-CH-<u>*C*</u>H-C), 85.1 (2C, 2xCH$_3$-(*Ar*)C-<u>*C*</u>H-CH-C), 84.0 (2C, 2xCH$_3$-(*Ar*)C-CH-<u>*C*</u>H-C), 83.3 (2C, 2xCH$_3$-(*Ar*)C-<u>*C*</u>H-CH-C), 37.1 (3C, 3x(*Napht*)(C=O)-C-(CH$_2$)$_3$-<u>*C*</u>H$_2$-(C=O)-NH), 30.8 (2C, 2x(*Ar*)CH-CH-C-<u>*C*</u>H(CH$_3$)$_2$), 28.2 (3C, 3x(*Napht*)(C=O)-C-CH$_2$-<u>*C*</u>H$_2$-(CH$_2$)$_2$-(C=O)-NH), 26.9 (3C, 3x(*Napht*)(C=O)-C-<u>*C*</u>H$_2$-(CH$_2$)$_3$-(C=O)-NH), 26.0 (3C, 3x(*Napht*)(C=O)-C-(CH$_2$)$_2$-<u>*C*</u>H$_2$-CH$_2$-(C=O)-NH), 22.8 (2C, (*Ar*)CH-CH-C-CH(<u>*C*</u>H$_3$)$_2$), 22.2 (2C, (*Ar*)CH-CH-C-CH(<u>*C*</u>H$_3$)$_2$), 17.8 (2C, 2x<u>*C*</u>H$_3$-(*Ar*)C-CH-CH-C), 12.8 (3C, 3x(*Napht*)(C=O)-C-<u>*C*</u>H$_3$).

R$_f$ (CH_2Cl_2/CH_3OH 10:1) = 0.406.

ESI-MS(+): *m/z* found 1606.3881 [M-Cl]$^+$, calcd. for $C_{86}H_{88}N_3O_9Ru_2S_3^+$ 1606.3764.

Elemental analysis (%): calcd. for $C_{86}H_{88}ClN_3O_9Ru_2S_3 \cdot CH_3OH$ C 62.44, H 5.54, N 2.51; found C 62.44, H 5.70, N, 2.60.

[(η^6-*p*-MeC$_6$H$_4$Pr^i)$_2$Ru$_2$(μ_2-SC$_6$H$_4$-*p*-NH$_2$)$_2$(μ_2-SC$_6$H$_4$-*p*-NH-R)]Cl (R = 7-(3-methyl-1,4-dioxo-1,4-dihydronaphthalen-2-yl)heptanoate) 28

To a solution of **22** (0.344 g, 1.145 mmol, 4 equiv.) in dry CH_2Cl_2 (50 mL), at r.t. under N_2 were added HOBt·H_2O (0.186 g, 1.377 mmol, 5 equiv.) and DIPEA (0.167 g, 1.289 mmol, 4.5 equiv.). After 10 min, were added successively EDCI (0.247 g, 1.289 mmol, 4.5 equiv.), **6** (0.250 g, 0.286 mmol, 1 equiv.) and DIPEA (0.167 g, 1.289 mmol, 4.5 equiv.). The reaction mixture was stirred for 24 h under N_2 at r.t. and the reaction evolution was monitored by TLC (CH_2Cl_2/CH_3OH 10:1 (v/v)). The mixture was concentrated to dryness and purification by column chromatography using CH_2Cl_2/CH_3OH mixture afforded **28** as an orange solid (0.144 g, 0.124 mmol, yield 50%).

^{1}H-NMR ($CDCl_3$) δ_H, ppm: 10.88 (1H, s, S-(*Ar*)C-CH-CH-C-N$\underline{H}$-(C=O), 8.09 (2H, d, 2xS-(*Ar*)C-CH-C$\underline{H}$-C-NH-(C=O), $^3J_{H,H}$ = 8.4 Hz), 8.02-8.07 (2H, m, (*Napht*)C-CH-C$\underline{H}$-C$\underline{H}$-CH, $^3J_{H,H}$ = 3.3 Hz), 7.67 (2H, d, 2xS-(*Ar*)C-C$\underline{H}$-CH-C-NH-(C=O), $^3J_{H,H}$ = 7.7 Hz), 7.63-7.67 (2H, m, (*Napht*)C-C$\underline{H}$-CH-CH-C$\underline{H}$, $^3J_{H,H}$ = 3.4 Hz), 7.59 (4H, d, 4xS-(*Ar*)C-C$\underline{H}$-CH-C-NH_2, $^3J_{H,H}$ = 8.2 Hz), 6.74 (4H, d, 4xS-(*Ar*)C-CH-C$\underline{H}$-C-NH_2, $^3J_{H,H}$ = 7.9 Hz), 5.13 (2H, d, 2xCH_3-(*Ar*)C-CH-C$\underline{H}$-C, $^3J_{H,H}$ = 4.3 Hz), 5.11 (2H, d, 2xCH_3-(*Ar*)C-CH-C$\underline{H}$-C, $^3J_{H,H}$ = 4.5 Hz), 5.01 (2H, d, 2xCH_3-(*Ar*)C-C$\underline{H}$-CH-C, $^3J_{H,H}$ = 5.6 Hz), 4.95 (2H, d, 2xCH_3-(*Ar*)C-C$\underline{H}$-CH-C, $^3J_{H,H}$ = 5.7 Hz), 2.70 (2H, t, (*Napht*)(C=O)-C-C$\underline{H_2}$-$(CH_2)_5$-(C=O)-NH, $^3J_{H,H}$ = 7.3 Hz), 2.62 (2H, t br, (*Napht*)(C=O)-C-$(CH_2)_5$-C$\underline{H_2}$-(C=O)-NH, $^3J_{H,H}$ = 6.2 Hz), 2.17 (3H, s, (*Napht*)(C=O)-C-C$\underline{H_3}$), 2.00 (2H, qvint, (*Napht*)(C=O)-C-$(CH_2)_4$-C$\underline{H_2}$-CH_2-(C=O)-NH, $^3J_{H,H}$ = 6.8 Hz), 1.75 (2H, m, 2x(*Ar*)C-CH-CH-C-C$\underline{H}$$(CH_3)_2$, $^3J_{H,H}$ = 6.8 Hz), 1.60 (6H, s, 2xC$\underline{H_3}$-(*Ar*)C-CH-CH-C), 1.42-1.52 (6H, m, (*Napht*)(C=O)-C-CH_2-(C$\underline{H_2}$$)_3$-$(CH_2)_2$-(C=O)-NH), 0.91 (6H, d, (*Ar*)C-CH-CH-C-CH(C$\underline{H_3}$$)_2$, $^3J_{H,H}$ = 6.8 Hz), 0.85 (6H, d, (*Ar*)C-CH-CH-C-CH(C$\underline{H_3}$$)_2$, $^3J_{H,H}$ = 6.8 Hz).

^{13}C-NMR ($CDCl_3$) δ_C, ppm: 185.6 (1C, (*Napht*)($\underline{C}$=O)-C-CH_3), 184.8 (1C, (*Napht*)($\underline{C}$=O)-C-$(CH_2)_6$-(C=O)-NH), 173.8 (1C, (*Napht*)(C=O)-C-$(CH_2)_6$-($\underline{C}$=O)-NH), 147.8 (1C, (*Napht*)(C=O)-$\underline{C}$-$(CH_2)_6$-(C=O)-NH), 146.8 (2C, 2xS-(*Ar*)C-CH-CH-$\underline{C}$-NH_2), 143.3 (1C, (*Napht*)(C=O)-$\underline{C}$-CH_3), 141.0 (1C, S-(*Ar*)$\underline{C}$-CH-CH-C-NH-(C=O)), 133.6, 133.7 (4C, 4xS-(*Ar*)C-$\underline{C}$H-CH-C-NH_2), 133.3, 133.4 (2C, (*Napht*)C-CH-$\underline{C}$H-$\underline{C}$H-CH-C), 132.6 (2C, 2xS-(*Ar*)C-$\underline{C}$H-CH-C-NH-(C=O)), 132.3, 132.4 (2C, (*Napht*)(*Ar*)$\underline{C}$-CH-CH-CH-CH-$\underline{C}$), 130.3 (1C, S-(*Ar*)C-CH-CH-$\underline{C}$-NH-(C=O)), 126.2, 126.4 (2C, (*Napht*)C-$\underline{C}$H-CH-CH-$\underline{C}$H-C), 125.9 (2C, 2xS-(*Ar*)$\underline{C}$-CH-CH-C-NH_2), 120.4 (2C, 2S-(*Ar*)C-CH-$\underline{C}$H-C-NH-(C=O)), 115.9 (4C, 4xS-(*Ar*)C-CH-$\underline{C}$H-C-NH_2), 107.6 (2C, 2xCH_3-(*Ar*)C-CH-CH-$\underline{C}$), 99.1 (2C, 2xCH_3-(*Ar*)$\underline{C}$-CH-CH-C), 85.6 (2C, 2xCH_3-(*Ar*)C-CH-$\underline{C}$H-C), 84.9 (2C, 2xCH_3-(*Ar*)C-$\underline{C}$H-CH-C), 84.0 (2C, 2xCH_3-(*Ar*)C-CH-$\underline{C}$H-C), 83.3 (2C, 2xCH_3-(*Ar*)C-$\underline{C}$H-CH-C), 37.4 (1C, (*Napht*)(C=O)-C-$(CH_2)_5$-$\underline{C}$$H_2$-(C=O)-NH), 30.7 (2C, 2x(*Ar*)CH-CH-C-$\underline{C}$H$(CH_3)_2$), 30.1 (1C, (*Napht*)(C=O)-C-$(CH_2)_2$-$\underline{C}$$H_2$-$(CH_2)_3$-(C=O)-NH), 29.3 (1C, (*Napht*)(C=O)-C-$(CH_2)_3$-$\underline{C}$$H_2$-$(CH_2)_2$-(C=O)-NH), 28.8 (1C, (*Napht*)(C=O)-C-CH_2-$\underline{C}$$H_2$-$(CH_2)_4$-(C=O)-NH), 27.3 (1C, (*Napht*)(C=O)-C-$\underline{C}$$H_2$-$(CH_2)_5$-(C=O)-NH), 25.8 (1C, (*Napht*)(C=O)-C-$(CH_2)_4$-$\underline{C}$$H_2$-$CH_2$-(C=O)-NH), 22.8 (2C, (*Ar*)CH-CH-C-CH($\underline{C}$$H_3$$)_2$), 22.4 (2C, (*Ar*)CH-CH-C-CH($\underline{C}$$H_3$$)_2$), 17.8 (2C, 2x$\underline{C}$$H_3$-(*Ar*)C-CH-CH-C), 12.8 (1C, (*Napht*)(C=O)-C-$\underline{C}$$H_3$).

R_f (CH_2Cl_2/CH_3OH 10:1) = 0.277.

ESI-MS(+): *m/z* found 1126.2203 $[M-Cl]^+$ and 1158.1806 $[M+CH_3OH-Cl]^+$, calcd. for $C_{56}H_{64}N_3O_3Ru_2S_3^+$ 1126.2191 and for $C_{57}H_{68}N_3O_4Ru_2S_3^+$ 1158.2453.

Elemental analysis (%): calcd. for $C_{57}H_{68}ClN_3O_4Ru_2S_3\cdot CH_3OH$ C 57.39, H 5.75, N, 3.52; found C 57.45, H 5.75, N 3.46.

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