Synthesis and characterization of half-sandwich ruthenium complexes containing aromatic sulfonamides bearing pyridinyl rings: catalysts for transfer hydrogenation of acetophenone derivatives

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Abstract

N-quinoline-8-yl-Aryl-benzenesulfonamides (**1**-**6**) were successfully synthesized by the reaction of *8-aminoquinoline* and various benzenesulfonylchlorides. Then, a series of half-sandwich ruthenium complexes (**7**-**12**) were prepared from the reaction of (**1**-**6**) with $[RuCl_2(p\text{-cymene})]_2$. The synthesized compounds were characterized by NMR, FT-IR, EA and X-ray diffraction for compounds **8** and **9**. The complexes were screened for their efficiency as catalysts in the transfer hydrogenation (TH) of acetophenone derivatives to phenylethanols in the presence of KOH with 2-propanol (as hydrogen source) at 82 ^{o}C, and show good activity. Complexes **10** and **12** were the most active (turnover frequency values: **703** and **734** h^{-1}, respectively).

Introduction

Sulfonamides are widely used in the field of coordination chemistry [1-4] and have also been investigated for their luminescent and antimicrobial properties and for analytical applications [5-7]. Many sulfonamide derivatives and their complexes have been recently reported [8[a-d]]. Furthermore, complexes containing sulfonamide groups have been used to catalyze various organic reactions, for example olefin metathesis, asymmetric transfer hydrogenation, the nitroaldol (Henry) reaction etc. [9-11]. Sulfonamides containing 8-aminoquinoline have rarely been studied by the scientific community, mostly in relation to their luminescent properties [12-16]. Also, catalysis and molecular structural properties of sulfonamides have recently been studied in detail by our research team [17[a-d]].

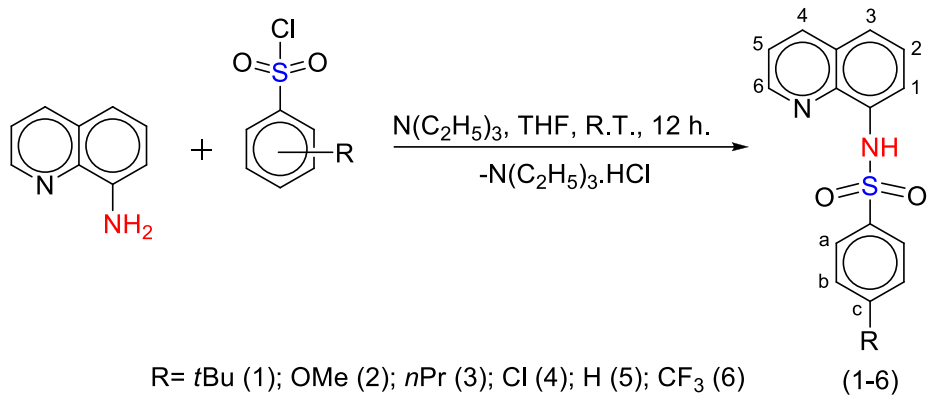
The ketone transfer hydrogenation (TH) catalyzed by Ru(II) complexes containing N-donors ligands has attracted increasing attention [18-32] since the success of Noyori's work using 1,2-diamine ligands [33]. Several diamine ligand modifications have been explored aimed at developing catalysts with increased activity. At the same time, half-sandwich ruthenium(II) complexes containing thioamides, 2-(diphenylphosphanyl)-aniline, ferrocenyl tosylamine-phosphine and pyridine-based chelating diamine ligands were also studied for the catalytic transfer hydrogenation of ketones [34-37]. Also, remarkable studies have been carried out in the TH of acetophenone derivatives [38-52].

Herein, a series of new half-sandwich Ru(II) complexes containing sulfonamide ligands were synthesized and characterized by various spectroscopic techniques. The synthesized complexes were used as catalysts for transfer hydrogenation of acetophenone derivatives.

Results and Discussion

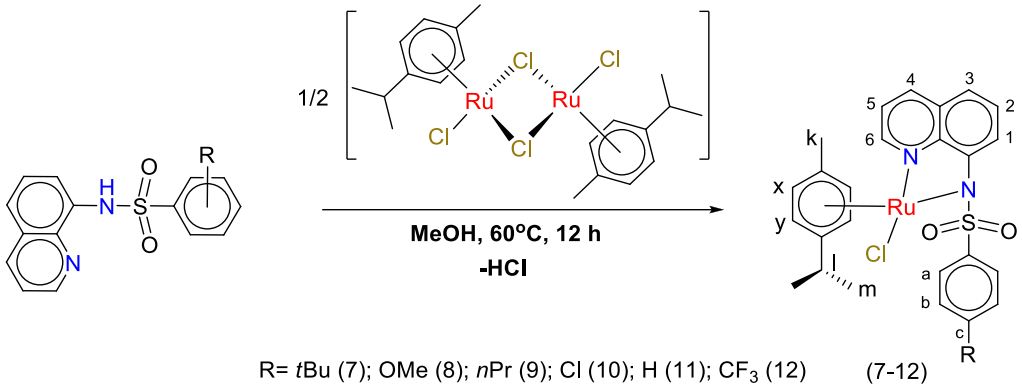
Syntheses

The synthesis and reaction routes to the ligands and to their corresponding Ru(II) complexes are presented in Figures 1 and 2. The ligands **1-6** were obtained by the reaction of 8-aminoquinoline with R-arylsulfonyl chlorides in the presence of triethylamine in THF (Figure 1). Then, the new ruthenium complexes (**7-12**) were synthesized by the reaction of **1-6** with $[RuCl_2(p\text{-cymene})]_2$ in methyl alcohol (Figure 2). All compounds were characterized by 1H-NMR, 13C-NMR and IR spectroscopy techniques. In addition, the solid state structures of complexes **8** and **9** were confirmed by X-ray crystallography.



R= *t*Bu (1); OMe (2); *n*Pr (3); Cl (4); H (5); CF_3 (6) (1-6)

Figure 1. Synthesis of the ligands together with NMR numbering scheme



R= *t*Bu (7); OMe (8); *n*Pr (9); Cl (10); H (11); CF_3 (12) (7-12)

Figure 2. Synthesis of the complexes together with NMR numbering scheme

Crystal Structures

Molecular views of compounds **8** and **9** are shown in Figure 3. In each complex the Ru atom has a pseudo-tetrahedral geometry with the η^6 π-bonded arene rings occupying one vertex of the tetrahedron, the three other vertices being occupied by the two N atoms of the pyridinyl ligands and the Cl atoms. Selected bond lengths and angles are shown in Table 1. Such geometry is common for all η^6-ruthenium arene complexes [56-58].

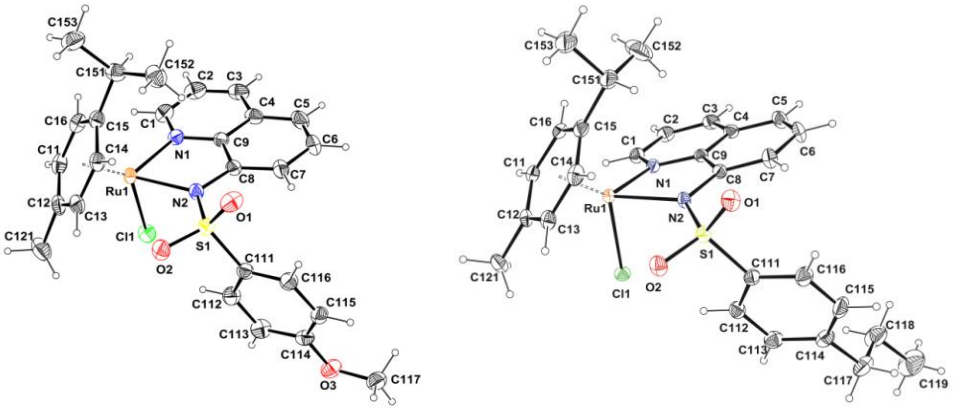


Figure 3: Molecular views of compounds **8** and **9** with the atoms labelling scheme. Ellipsoids are drawn at the 50% probability level. H atoms are represented as small spheres of arbitrary radii.

Table 1: Comparison of selected bond distances (Å) and bond angles (°) for both compounds **8** and **9**. Esds in parentheses refer to the last significant digit.

Compound 8		**Compound 9**	
Ru(1)-Cg(1)	1.6799(9)	Ru(1)-Cg(1)	1.6666(7)
Ru(1)-N(1)	2.0965(16)	Ru(1)-N(1)	2.0852(14)
Ru(1)-N(2)	2.1285(16)	Ru(1)-N(2)	2.1236(13)
Ru(1)-Cl(1)	2.4322(5)	Ru(1)-Cl(1)	2.3981(5)
S(1)-O(2)	1.4382(15)	S(1)-O(2)	1.4392(13)
S(1)-O(1)	1.4424(16)	S(1)-O(1)	1.4496(12)
S(1)-N(2)	1.6157(16)	S(1)-N(2)	1.6146(14)
S(1)-C(111)	1.768(2)	S(1)-C(111)	1.7774(17)
N(1)-C(1)	1.324(3)	N(1)-C(1)	1.330(2)
N(1)-C(9)	1.373(3)	N(1)-C(9)	1.377(2)
N(2)-C(8)	1.400(2)	N(2)-C(8)	1.406(2)
Cg(1)-Ru(1)-Cl(1)	127.01(4)	Cg(1)-Ru(1)-Cl(1)	127.27(3)
Cg(1)-Ru(1)-N(1)	131.54(5)	Cg(1)-Ru(1)-N(1)	130.32(4)
Cg(1)-Ru(1)-N(2)	131.93(5)	Cg(1)-Ru(1)-N(2)	130.13(4)
N(1)-Ru(1)-N(2)	76.86(6)	N(1)-Ru(1)-N(2)	77.10(5)
N(1)-Ru(1)-Cl(1)	84.31(5)	N(1)-Ru(1)-Cl(1)	85.09(4)
N(2)-Ru(1)-Cl(1)	87.46(5)	N(2)-Ru(1)-Cl(1)	90.18(4)
O(2)-S(1)-O(1)	116.55(10)	O(2)-S(1)-O(1)	116.60(8)
O(2)-S(1)-N(2)	107.43(9)	O(2)-S(1)-N(2)	107.34(7)
O(1)-S(1)-N(2)	111.55(9)	O(1)-S(1)-N(2)	112.02(7)
O(2)-S(1)-C(111)	107.18(10)	O(2)-S(1)-C(111)	108.86(8)
O(1)-S(1)-C(111)	106.93(9)	O(1)-S(1)-C(111)	106.36(8)
N(2)-S(1)-C(111)	106.70(9)	N(2)-S(1)-C(111)	105.03(7)
C(1)-N(1)-C(9)	118.80(17)	C(1)-N(1)-C(9)	119.04(15)
C(1)-N(1)-Ru(1)	125.07(14)	C(1)-N(1)-Ru(1)	125.18(11)
C(9)-N(1)-Ru(1)	116.10(12)	C(9)-N(1)-Ru(1)	115.69(11)
C(8)-N(2)-S(1)	118.75(13)	C(8)-N(2)-S(1)	119.50(11)
C(8)-N(2)-Ru(1)	115.35(12)	C(8)-N(2)-Ru(1)	114.30(10)
S(1)-N(2)-Ru(1)	125.75(9)	S(1)-N(2)-Ru(1)	126.19(8)
N(1)-C(1)-C(2)	122.4(2)	N(1)-C(1)-C(2)	122.31(16)

NMR Spectra

In the ^{1}H-NMR spectra of the ligands **1-6**, the -H_a, -H_b and -H_c protons were observed as a doublet and two triplets, respectively, in a 2:2:1 ratio at around δ 7.79-7.88 ppm in *N-quinoline-8-yl-benzenesulfonamide*. Similarly in other *N-quinoline-8-yl-arylsulfonamides* ligands, the -H_a and -H_b protons were observed as doublets in a 2:2 ratio at around δ 6.99-8.80 ppm. The *NH* protons were found at around δ 9.31-11.66 ppm.

In the ^{1}H-NMR spectra for **7-12**, the sulfonamide N*H* proton is no longer present while new resonances belonging to the *p*-cymene group. (-H_k, -H_x, -H_y, -H_l and -H_m) appear shown in Table 2.

Table 2. ^{1}H-NMR and ^{13}C-NMR data of ligands and complexes

Ligands	^{1}H-NMR / ^{13}C-NMR (ppm)						
	-H_a	-H_b	-H_c	NH	-p-C(CH_3)$_3$	-p-OCH_3	-p-$CH_2CH_2CH_3$
1	7.86		-	9.31	1.24 (^{1}H) 35.0, 30.9 (^{13}C)	-	-
2	7.80	6.99	-	10.02	-	3.74 (^{1}H) / 56.1 -^{13}C)	-
3	8.80	8.20	-	11.66	-	-	0.84, 3.12, 1.40 (^{1}H) 45.9, 24.0, 8.7 (^{13}C)
4	7.83	7.80	-	11.00	-	-	-
5	7.86	7.79	7.88	11.21	-	-	-
6	8.03	7.86	-	10.94	-	-	-

Complexes	-H_k	-H_x	-H_y	-H_l	-H_m	-p-C(CH_3)$_3$	-p-OCH_3	-p-$CH_2CH_2CH_3$
7	2.37	6.29	5.70	2.62	0.95-1.07	1.24 (^{1}H) 34.8, 31.1 (^{13}C)	-	-
8	2.36	6.26	5.67	2.62	0.92-1.08	-	3.72 (^{1}H)/ 55.3 (^{13}C)	-
9	2.34	6.24	5.86	2.61	0.92-1.07	-	-	0.83, 3.10, 1.37 (^{1}H) 46.1, 24.1, 8.7 (^{13}C)
10	2.36	6.23	5.67	2.63	0.94-1.09	-	-	-
11	2.37	6.26	5.69	2.62	0.93-1.08	-	-	-
12	2.36	6.23	5.68	2.63	0.94-1.09	-	-	-

Infrared Spectra

The sulfonamide *N-H* stretching band for the ligands **1-6** appears at 3260-3192 cm^{-1} see Table 3. This band disappears on going to the ruthenium complexes **7-12**. The frequencies of the SO_2 stretching and bending peaks are shown in Table 3. For **7-12**, there is a blue shift for the bending and asymmetric stretching are observed a general shift toward increase frequency as compared to their respective ligands. But, the symmetric stretching was also seen a general shift toward lower frequency as compared to their respective ligands.

Table 3. IR data of ligands and complexes

Ligand	IR (cm^{-1})			
	ν(NH)	$\nu_{as}(SO_2)^a$	$\nu_s(SO_2)^b$	$\Delta(SO_2)^c$
1	3258	1303	1162	570
2	3192	1332	1153	572
3	3260	1306	1156	560
4	3243	1303	1157	555
5	3217	1307	1169	557
6	3239	1307	1163	551
Complex	$\nu_{as}(SO_2)$	$\nu_s(SO_2)$		$\Delta(SO_2)$
7	1315	1145		577
8	1316	1140		572
9	1316	1139		577
10	1315	1140		567
11	1316	1139		582
12	1317	1144		563

[a] ν_{as}= asymmetric stretching. [b] ν_s= symmetric stretching. [c] Δ=bending

Catalytic Studies

As the starting point, the performances of the catalysts in the transfer hydrogenation were screened by using acetophenone as a model substrate and we screened the influence of the base. NaOH and KOH are known to yield better conversions when compared to K_2CO_3 and $KOBu^t$ in the TH reactions [36, 49]. The stronger the base the higher the general conversion rankings, KOH > NaOH > $KOBu^t$ > K_2CO_3. Indeed, the TH of acetophenone catalyzed by compound **10** leads to better results when using KOH, reaching 97% conversion within 120 min at a substrate/catalyst/base (S/C/base) molar ratio of 1: 0.002: 10 (Figure 4). In the absence of a base no transfer hydrogenation was observed. Therefore, KOH was selected as the base in all subsequent studies.

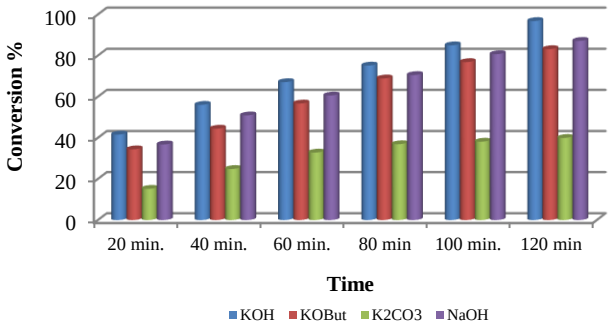


Figure 4. Effect of various bases in the TH of acetophenone catalyzed by **10** (0.2 mol %) in 2-propanol at 82 ^oC.

A variety of ketones was transformed to the corresponding secondary alcohols. Typical results are shown in Figure 5. The transformation of 4-chloroacetophenone is the fastest, giving complete conversion to the corresponding alcohol 120 min under the selected operating conditions (Figure 5, b). Among the tested catalysts, complexes **8**, **10** and **12** are more efficient than complexes **7**, **9** and **11**.

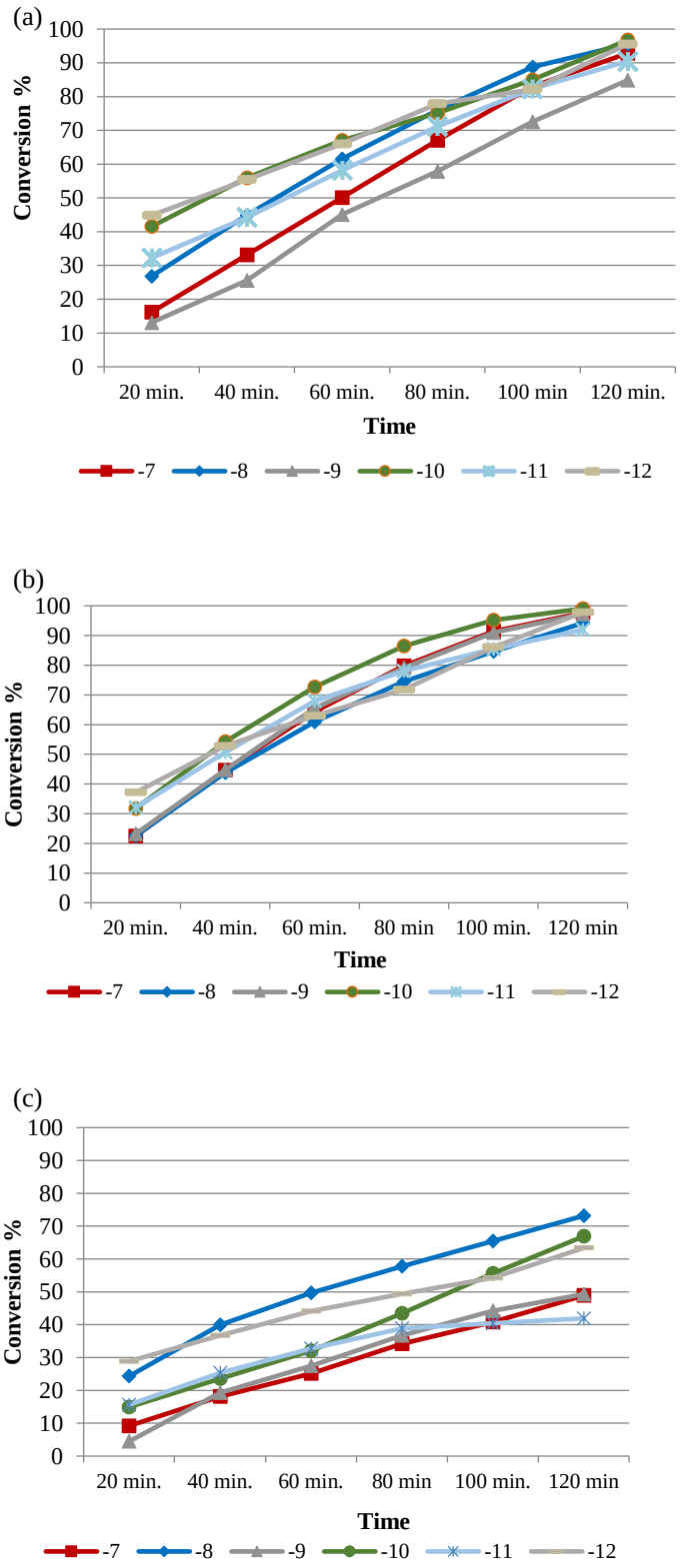
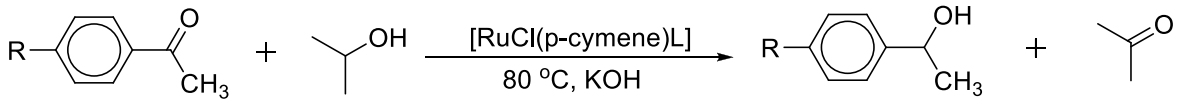
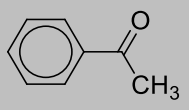
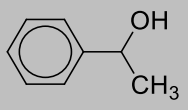
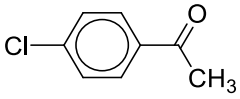
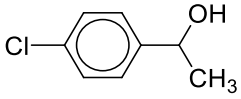
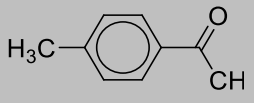
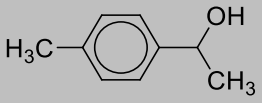


Figure 5. Catalytic activity as shown by the % conversion vs. time for the transfer hydrogenation of (**a**) acetophenone, (**b**) 4-chloro-acetophenone, (**c**) 4-methyl-acetophenone catalyzed by compounds **7-12** in isopropanol. Conditions: ketone/Ru/KOH, 1:0.002:10; T= 82 ºC

We have also examined the acetophenone TH at a (S/C/base) molar ratio of 1: 0.001: 10 (Figure 6). The results of the catalytic experiments show once again that complexes **10** and **12** are highly efficient. The highest measured TOF were in the 734-575 h^{-1} range for the S/C molar ratio of 1: 0.001, at 20 min. (Table 4).

Table-5 Initial TOF for the TH of various ketones catalyzed by compounds **7-12**.



Entry	Complex	Substrate	Product	S/C[a]	TOF/h^{-1}
1	7			500/1 (1000/1)	243 (610)
2	8				403 (653)
3	9				197 (575)
4	10				624 (703)
5	11				484 (697)
6	12				673 (734)
7	7			500/1	338
8	8				339
9	9				348
10	10				476
11	11				480
12	12				557
13	7			500/1	138
14	8				365
15	9				67
16	10				224
17	11				233
18	12				433

[a] Acetophenone/Ru molar ratio.

Conclusions

In summary, we have reported the preparation and characterization of the sulfonamide ligands **1-6**, and their neutral half-sandwich sulfonamido-Ru(II) complexes **7-12**. We have also reported the catalytic activity of these complexes in the transfer hydrogenation of some acetophenone derivatives with the use of 2-propanol in the presence of base. Complexes **10** and **12** are the most active complexes. The procedure is simple and efficient towards various aryl ketones. The catalyst efficiency depends not only on the ligand but also on the aromatic ketone substituent. Electron-withdrawing groups introduced at the *para* position of the acetophenone accelerate the transformation, whereas electron-donating groups slow it down. Likewise, the presence of electron-withdrawing groups on the sulfonamido-ring has a beneficial effect. The catalytic activity decreases in the order **10** > **12** > **8** > **7** > **9** > **11**, the best results being obtained in the presence of the –Cl and $–CF_3$ substituents at *para* position of the sulfonamido aryl

group. Ruthenium(II) arene complexes widely used in the TH of ketones. When examined to the literature, it is clear that the half-sandwich sulfonamido-Ru(II) complexes used herein have been a good efficiency in the TH [59-73].

Experimental Section

Materials and Methods. All reagents and solvents were obtained from commercial suppliers and used without any additional purification. NMR spectra were recorded in 5 mm tubes at 297 K on a Bruker Avance III 400 NMR spectrometer at 400 MHz (^{1}H) and 100.56 MHz (^{13}C). Signals are quoted in parts per million as δ downfield from tetramethylsilane (δ 0.00) as an internal standard. Coupling constants (*J*-values) are given in hertz. Abbreviations used for the NMR resonances are: br= broad, s = singlet, d = doublet, t = triplet, m = multiplet. Infrared spectra were measured with a Perkin-Elmer Spectrum 400 FTIR system and recorded using a universal ATR sampling accessory within the range 550-4000 cm^{-1}. Melting points were determined in open capillary tubes on a digital Electrothermal 9100 melting point apparatus. GC measurements for catalytic experiments were performed using Fisons 8000 Series instrument equipped with a DB-1MS column (30mx0.32mmx0.25m) & Younglin Acme 6100, OPTIMA 5 MS column (30mx0.32mmx0.25m).

TOF= moles of product / (moles of the catalyst)x(hour), measured on the basis of the conversion at 20 min for entries 1-18, at 30 min for entries 19-24. Conditions are given in the legends of Fig. 5 and 6.

General procedure for the synthesis of Ligands (L), 1-6

N-quinoline-8-yl-aryl-benzenesulfonamides **(1-6)** were prepared by modifying the published procedure [44]. A 50 ml Schlenk tube containing a magnetic stirring bar was charged with a solution of the suitable benzenesulfonylchloride derivative (10 mmol) in THF (10 ml). The slow addition of a solution of triethylamine (20 mmol) in THF (5 ml) and *8-aminoquinoline* (10 mmol) in THF (5 ml), respectively, gives rise to the immediate precipitation of a white solid ($HCl.N(C_2H_5)_3$). After being stirred for 12 hours at room temperature, the solid was removed by filtration using a fine sintered-glass filter. Then, the solvent was completely removed under reduced pressure. The crude product was used without further purification. An analytically pure sample was obtained by recrystallization from chloroform/diethyl ether (15 ml 1:3, v/v) (Fig. 1).

N- Quinoline-8-yl -4-t-butyl-benzenesulfonamide (1): Yield: 85 %. Orange solid, Mp: 155-157 ºC, ^{1}H-NMR ($CDCl_3$, δ ppm): 1.24 (s, 9H, -C(C*H*$_3$)$_3$, 7.37-7.48 (m, 4H, -*H*$_{2-5}$), 7.86 (dd, 4H, *J*=4 Hz, *J*=4 Hz, -*H*$_{a-b}$), 8.13 (d, 1H, *J*=8 Hz, -*H*$_1$), 8.77 (d, 1H, *J*=8 Hz, -*H*$_6$), 9.31 (br. 1H, -*NH*). ^{13}C-NMR ($CDCl_3$, ppm): 30.9 (-C(*C*H$_3$)$_3$), 35.0 (-*C*(CH$_3$)$_3$), 115.1 (Ar. -*C*), 121.9 (Ar. -*C*), 122.0 (Ar. -*C*), 125.9 (Ar. -*C*), 127.0 (Ar. -*C*), 128.2 (Ar. -*C*), 133.8 (Ar. -*C*), 136.4 (Ar. -*C*), 136.6 (Ar. -*C*), 138.2 (Ar. -*C*), 148.4 (Ar. -*C*), 148.5 (Ar. -*C*), 156.7 (Ar. -*C*). IR (cm^{-1}): 3258 (-NH), 3078, 2962, 2905, 2869, 1623, 1595, 1579, 1505, 1471, 1436, 1414, 1397, 1378, 1362, 1336, 1303 (-SO_2), 1266, 1236, 1206, 1194, 1162 (-SO_2),

1139, 1112, 1086, 1057, 1029, 1013, 984, 972, 962, 922, 894, 851, 824, 803, 792, 749, 734, 645, 637, 626, 600, 570 (-SO_2), 548, 515, 478, 466. $C_{19}H_{20}N_2O_2S$ (340.3): calcd. for: C:67.03, H:5.92, N:8.23, O:9.40, S:9.42, Found: C:67.15, H:5.84, N:8.18, S:9.47.

N-Quinoline-8-yl-4-methoxy-benzenesulfonamide (2): Yield: 78 %, brown solid, Mp: 145-147 ^oC, ^{1}H-NMR (DMSO, δ ppm): 3.74 (s, 3H, -OCH_3), 6.99 (d, 2H, *J*=8 Hz, -H_b), 7.55-7.77 (m, 4H, -H_{2-5}), 7.80 (d, 2H, *J*=8 Hz, -H_a), 8.55 (d, 1H, *J*=8 Hz, -H_1), 8.95 (d, 1H, *J*=8 Hz, -H_6), 10.02 (br. 1H, -*NH*). ^{13}C-NMR (DMSO, ppm): 56.1 (-OCH_3), 114.8 (Ar. -*C*), 119.7 (Ar. -*C*), 122.9 (Ar. -*C*), 124.3 (Ar. -*C*), 127.8 (Ar. -*C*), 128.9 (Ar. -*C*), 129.8 (Ar. -*C*), 130.9 (Ar. -*C*), 132.9 (Ar. -*C*), 138.0 (Ar. -*C*), 139.4 (Ar. -*C*), 149.1 (Ar. -*C*), 163.1 (Ar. -*C*). IR (cm^{-1}): 3192 (-NH), 3192 (-NH), 3045, 2971, 2872, 2776, 2731, 1629, 1590, 1576, 1543, 1489, 1465, 1436, 1425, 1408, 1375, 1347, 1332 (-SO_2), 1310, 1298, 1285, 1256, 1220, 1206, 1178, 1153 (-SO_2), 1138, 1113, 1089, 1061, 1025, 1006, 974, 935, 924, 909, 885, 849, 828, 803, 779, 768, 741, 698, 638, 627, 605, 572 (-SO_2), 555, 538, 516, 500, 484, 466. $C_{16}H_{14}N_2O_3S$ (314.2): Calcd. for: C: 61.13, H: 4.49, N:8.91, O: 15.27, S: 10.20, Found: C: 61.19, H: 4.39, N:8.81, S: 10.11.

N-Quinoline-8-yl-4-n-propyl-benzenesulfonamide (3): Yield: 82 %, light brown solid, Mp: 120-122 ^oC, ^{1}H-NMR ($CDCl_3$, δ ppm): 0.84 (t, 2H, *J*=8 Hz, -C$H_2$$CH_2CH_3$), 1.40 (t, 3H, *J*=8 Hz, -CH_2CH_2CH_3), 3.12 (m, 2H, -CH_2C$H_2$$CH_3$), 7.14-7.89 (m, 4H, -$H_{2-5}$), 8.20 (d, 2H, *J*=8 Hz, -H_b), 8.74 (d, 1H, *J*=8 Hz, -H_1), 8.80 (d, 2H, *J*=8 Hz, -H_a), 8.96 (d, 1H, *J*=8 Hz, -H_6), 11.66 (br. 1H, -*NH*). ^{13}C-NMR ($CDCl_3$, ppm): 8.7 (-$CH_2CH_2$$CH_3$), 24.0 (-$CH_2$$CH_2$$CH_3$), 45.9 (-$CH_2$$CH_2CH_2CH_3$), 116.5 (Ar. -*C*), 120.3 (Ar. -*C*), 121.8 (Ar. -*C*), 122.4 (Ar. -*C*), 125.9 (Ar. -*C*), 127.3 (Ar. -*C*), 128.3 (Ar. -*C*), 128.9 (Ar. -*C*), 131.3 (Ar. -*C*), 133.3 (Ar. -*C*), 136.6 (Ar. -*C*), 147.8 (Ar. -*C*), 148.4 (Ar. -*C*). IR (cm^{-1}): 3260 (-NH), 3068, 2959, 2932, 2866, 2605, 2498, 1662, 1623, 1593, 1543, 1504, 1471, 1446, 1435, 1429, 1408, 1378, 1367, 1330, 1306 (-SO_2), 1248, 1237, 1223, 1184, 1156 (-SO_2), 1119, 1112, 1086, 1058, 1029, 1018, 999, 970, 921, 883, 844, 829, 817, 806, 795, 758, 728, 690, 679, 637, 601, 575, 560 (-SO_2), 535, 526, 485, 470. $C_{18}H_{18}N_2O_2S$ (326.3): calcd. for: C:66.23, H: 5.56, N: 8.58, O: 9.80, S: 9.82, Found: C: 66.35, H: 5.61, N: 8.49, S: 9.95.

N-Quinoline-8-yl-4-chloro-benzenesulfonamide (4): Yield: 81 %, brown solid, Mp: 110-112 ^oC, ^{1}H-NMR ($CDCl_3$, δ ppm): 7.30-7.49 (m, 4H, -H_{2-5}), 7.80 (d, 2H, *J*=8 Hz, -H_b), 7.83 (d, 2H, *J*=8 Hz, -H_a), 8.10 (d, 1H, *J*=8 Hz, -H_1), 8.74 (d, 1H, *J*=8 Hz, -H_6), 11.00 (br. 1H, -*NH*). ^{13}C-NMR ($CDCl_3$, ppm): 115.4 (Ar. -*C*), 116.0 (Ar. -*C*), 122.1 (Ar. -*C*), 122.6 (Ar. -*C*), 126.8 (Ar. -*C*), 127.6 (Ar. -*C*), 128.3 (Ar. -*C*), 128.6 (Ar. -*C*), 129.2 (Ar. -*C*), 133.4 (Ar. -*C*), 136.3 (Ar. -*C*), 139.4 (Ar. -*C*), 148.9 (Ar. -*C*). IR (cm^{-1}): 3243 (-NH), 3089, 3019, 2978, 2947, 1618, 1581, 1504, 1470, 1435, 1412, 1396, 1366, 1334, 1303 (-SO_2), 1278, 1258, 1233, 1188, 1174, 1157 (-SO_2), 1135, 1122, 1083, 1057, 1031, 1005, 977, 920, 849, 822, 805, 794, 786, 751, 705, 647, 620, 574, 555 (-SO_2), 523, 480, 459. $C_{15}H_{11}ClN_2O_2S$ (318.7): calcd. for: C:56.52, H: 3.48, Cl: 11.12, N: 8.79, O:10.04, S: 10.06, Found: C: 56.43, H: 3.56, N: 8.67, S: 10.10.

N-Quinoline-8-yl-benzenesulfonamide (5): Yield: 75 %, brown solid, Mp: 90-92 ^{o}C, ^{1}H-NMR ($CDCl_3$, δ ppm): 7.32-7.43 (m, 4H, -H_{2-5}), 7.79 (t, 2H, J=8 Hz, -H_b), 7.86 (d, 2H, J=8 Hz, -H_a), 7.88 (t, 1H, J=8 Hz, -H_c), 8.07 (d, 1H, J=8 Hz, -H_1), 8.72 (d, 1H, J=8 Hz, -H_6), 11.21 (br. 1H, -*NH*). ^{13}C-NMR ($CDCl_3$, ppm): 115.0 (Ar. -*C*), 122.0 (Ar. -*C*), 122.3 (Ar. -*C*), 125.9 (Ar. -*C*), 126.8 (Ar. -*C*), 127.2 (Ar. -*C*), 128.2 (Ar. -*C*), 128.9 (Ar. -*C*), 129.8 (Ar. -*C*), 132.9 (Ar. -*C*), 136.3 (Ar. -*C*), 139.3 (Ar. -*C*), 148.5 (Ar. -*C*). IR (cm^{-1}): 3217 (-NH), 2980, 2947, 2883, 1618, 1597, 1505, 1472, 1446, 1431, 1406, 1398, 1371, 1358, 1333, 1307 (-SO_2), 1231, 1169 (-SO_2), 1123, 1086, 1072, 1057, 1033, 1016, 997, 952, 926, 852, 820, 805, 786, 750, 726, 685, 666, 611, 584, 568, 557 (-SO_2), 518, 462. $C_{15}H_{12}N_2O_2S$ (284.2): calcd. for: C:63.36, H: 4.25, N: 9.85, O:11.25, S: 11.28, Found: C:63.47, H: 4.16, N: 9.78, O:11.34 S: 11.24.

N-Quinoline-8-yl-4-(trifluoromethyl)-benzenesulfonamide (6): Yield: 71 %, brown solid, Mp: 128-130 ^{o}C, ^{1}H-NMR ($CDCl_3$, δ ppm): 7.42-7.63 (m, 4H, -H_{2-5}), 7.86 (d, 2H, J=8 Hz, -H_b), 8.03 (d, 2H, J=8 Hz, -H_a), 8.11 (d, 1H, J=8 Hz, -H_1), 8.75 (d, 1H, J=8 Hz, -H_6), 10.94 (br. 1H, -*NH*). ^{13}C-NMR ($CDCl_3$, ppm): 115.5 (Ar. -*C*), 116.0 (Ar. -*C*), 122.2 (Ar. -*C*), 122.9 (Ar. -*C*), 124.4 (Ar. -*C*), 126-126.2 (-*C*F_3), 126.6 (Ar. -*C*), 126.8 (Ar. -*C*), 127.7 (Ar. -*C*), 128.3 (Ar. -*C*), 133.1 (Ar. -*C*), 136.4 (Ar. -*C*), 138.5 (Ar. -*C*), 148.9 (Ar. -*C*). IR (cm^{-1}): 3239 (-NH), 3106, 3069, 3051, 2980, 2947, 1603, 1581, 1505, 1473, 1435, 1403, 1371, 1321, 1307 (-SO_2), 1255, 1238, 1163 (-SO_2), 1134, 1104, 1086, 1061, 1030, 1007, 972, 922, 830, 795, 759, 711, 656, 634, 603, 591, 575, 551 (-SO_2), 521, 492. $C_{16}H_{11}F_3N_2O_2S$ (353.8): calcd. for: C:54.54, H: 3.15, F: 16.18, N: 7.95, O:9.08, S: 9.10, Found: C:54.42, H: 3.21, N: 7.81, S: 9.13.

General procedure for the synthesis of [(p-cymene)RuLCl], 7-12: A solution of **1-6** (0.50 mmol) in methyl alcohol (5 ml) was added to a solution of $[RuCl_2(p\text{-}cymene)]_2$ (0.25 mmol) in methyl alcohol (5 ml) in a Schlenk tube. The reaction mixture was stirred for 12 hours at 60 ^{o}C. The volatiles were removed under reduced pressure. The residue was washed with diethyl ether (20 ml) and dried under vacuum. The desired products were recrystallized from MeOH to give orange or dark red-colored microcrystals (Figure 2).

{[N-Quinoline-8-yl-4-t-butyl-benzenesulfonamido]-(p-cymene)-chloro-ruthenium(II)} (7): Yield: 72 %, orange microcrystals, Mp: 291-292 ^{o}C, ^{1}H-NMR ($CDCl_3$, δ ppm): 0,95 and 1,07 (d, d, 6H, J=8 Hz, -H_m), 1.24 (s, 9H, -C(CH_3)$_3$), 2.37 (s, 3 H, -H_k), 2.62 (m, 1H, -H_l), 5.70 (d, 2H, J=4 Hz, -H_y), 6.29 (d, 2H, J=4 Hz, -H_x), 7.01-7.44 (m, 4H, -H_{2-5},), 8.07 (d, 1H, J=8 Hz, -H_1), 8.15 (dd, 4H, J=4 Hz, J=4 Hz, -H_{a-b}), 9.10 (d, 1H, J=8 Hz, -H_6). ^{13}C-NMR ($CDCl_3$, ppm): 19.3 (-CH_3), 22.1 (-CH(*C*H_3)$_2$), 30.9 (-*C*H(CH$_3$)$_2$), 31.1 (-C(*C*H_3)$_3$), 34.8 (-*C*(CH$_3$)$_3$), 82.3 (Ar. -*C*), 84.6 (Ar. -*C*), 86.2 (Ar. -*C*), 104.5 (Ar. -*C*), 115.7 (Ar. -*C*), 118.0 (Ar. -*C*), 121.9 (Ar. -*C*), 125.4 (Ar. -*C*), 128.3 (Ar. -*C*), 129.0 (Ar. -*C*), 129.5 (Ar. -*C*), 137.8 (Ar. -*C*), 137.9 (Ar. -*C*), 144.7 (Ar. -*C*), 147.4 (Ar. -*C*), 151.1 (Ar. -*C*), 154.6 (Ar. -*C*). IR (cm^{-1}): 3055, 2960, 2906, 2869, 1639, 1597, 1570, 1535, 1530, 1502, 1462, 1432, 1376, 1365, 1315 (-SO_2), 1298, 1285, 1273, 1261, 1212, 1204, 1190, 1145 (-SO_2), 1107, 1081, 1057, 1047, 1015, 947, 905, 877, 868, 822, 803, 787, 749, 735, 712, 690, 665, 649, 623, 577 (-SO_2), 549, 523, 470. $C_{29}H_{33}Cl$

N_2O_2RuS (609/9): calcd. for: C:56,90, H:5,76, Cl:5,79, N:4,58, O:5,23, Ru:16,51, S:5,24, Found: C:56,80, H:5,92, N:4,57, S:5,23.

{[N-Quinoline-8-yl-4-methoxy-benzenesulfonamido]-(p-cymene)-chloro-ruthenium(II)} (8): Yield: 82 %, Dark red microcrystals, Mp: 194-196 ^oC, ^1H-NMR ($CDCl_3$, δ ppm): 0,92 and 1,08 (d, d, 6H, *J*=8 Hz, -*H*$_m$), 2.36 (s, 3 H, -*H*$_k$), 2.62 (m, 1H, -*H*$_l$), 3.72 (s, 3H, -OC*H*$_3$), 5.67 (d, 2H, *J*=4 Hz, -*H*$_y$), 6.26 (d, 2H, *J*=4 Hz, -*H*$_x$), 6.77 (d, 2H, *J*=8 Hz, -*H*$_b$), 7.55-7.77 (m, 4H, -*H*$_{2-5}$), 8.06 (d, 1H, *J*=8 Hz, -*H*$_1$), 8.16 (d, 2H, *J*=8 Hz, -*H*$_a$), 9.10 (d, 1H, *J*=8 Hz, -*H*$_6$). ^{13}C-NMR ($CDCl_3$, ppm): 19.3 (-*C*H_3), 22.1 (-CH(*C*H_3)$_2$), 31.0 (-*C*H(CH$_3$)$_2$), 55.3 (-O*C*H_3), 80.6 (Ar. -*C*), 82.3 (Ar. -*C*), 84.4 (Ar. -*C*), 86.2 (Ar. -*C*), 113.5 (Ar. -*C*), 115.8 (Ar. -*C*), 117.9 (Ar. -*C*), 121.9 (Ar. -*C*), 128.9 (Ar. -*C*), 129.5 (Ar. -*C*), 130.6 (Ar. -*C*), 132.6 (Ar. -*C*), 137.8 (Ar. -*C*), 144.7 (Ar. -*C*), 147.4 (Ar. -*C*), 151.2 (Ar. -*C*), 161.8 (Ar. -*C*). IR (cm^{-1}): 3091, 3047, 2962, 2904, 2875, 1642, 1592, 1568, 1534, 1498, 1466, 1440, 1412, 1387, 1373, 1316 (-SO_2), 1292, 1285, 1274, 1252, 1216, 1191, 1182, 1157, 1140 (-SO_2), 1134, 1111, 1082, 1059, 1045, 1026, 1018, 1008, 990, 943, 902, 863, 840, 818, 805, 790, 779, 759, 720, 692, 660, 628, 590, 572 (-SO_2), 555, 527, 473. $C_{26}H_{27}Cl\ N_2O_3RuS$ (583.9): Calcd. for: C:53,28, H:4,99, Cl:6,05, N:4,78, O:8,19, Ru:17,24, S:5,47, Found: C:53,35, H:4,87, N:4,69, S:5,55.

{[N-Quinoline-8-yl-4-n-propyl-benzenesulfonamido]-(p-cymene)-chloro-ruthenium(II)} (9): Yield: 76 %, dark red microcrystals, Mp: 247-248 ^oC, ^1H-NMR ($CDCl_3$, δ ppm): 0.83 (t, 2H, *J*=8 Hz, -C*H*$_2$CH$_2$CH$_3$), 0,92 and 1,07 (d, d, 6H, *J*=8 Hz, -*H*$_m$), 1.37 (t, 3H, *J*=8 Hz, -CH$_2$CH$_2$C*H*$_3$), 2.34 (s, 3 H, -*H*$_k$), 2.61 (m, 1H, -*H*$_l$), 3.10 (m, 2H, -CH$_2$C*H*$_2$CH$_3$), 5.86 (d, 2H, *J*=4 Hz, -*H*$_y$), 6.24 (d, 2H, *J*=4 Hz, -*H*$_x$), 6.96-7.20 (m, 4H, -H$_{2-5}$), 7.37 (d, 2H, *J*=8 Hz, -*H*$_b$), 8.04 (d, 1H, *J*=8 Hz, -*H*$_1$), 8.11 (d, 2H, *J*=8 Hz, -*H*$_a$), 9.10 (d, 1H, *J*=8 Hz, -*H*$_6$). ^{13}C-NMR ($CDCl_3$, ppm): 8.7 (-CH$_2$CH$_2$*C*H_3), 19.3 (-*C*H_3), 22.3 (-CH(*C*H_3)$_2$), 24.1 (-CH$_2$*C*H_2CH$_3$), 30.9 (-*C*H(CH$_3$)$_2$), 46.1 (-*C*H_2CH$_2$CH$_3$), 80.6 (Ar. -*C*), 82.3 (Ar. -*C*), 84.5 (Ar. -*C*), 86.1 (Ar. -*C*), 115.8 (Ar. -*C*), 117.9 (Ar. -*C*), 121.9 (Ar. -*C*), 128.4 (Ar. -*C*), 128.5 (Ar. -*C*), 128.9 (Ar. -*C*), 129.5 (Ar. -*C*), 137.8 (Ar. -*C*), 138.1 (Ar. -*C*), 144.7 (Ar. -*C*), 146.2 (Ar. -*C*), 147.4 (Ar. -*C*), 151.3 (Ar. -*C*). IR (cm^{-1}): 3049, 2977, 2953, 2926, 2868, 2851, 1595, 1569, 1531, 1505, 1464, 1423, 1398, 1378, 1363, 1316 (-SO_2), 1289, 1269, 1235, 1214, 1201, 1189, 1158, 1136 (-SO_2), 1114, 1081, 1044, 1019, 990, 947, 905, 872, 842, 825, 806, 793, 785, 761, 675, 652, 635, 605, 589, 577, 540, 528, 516, 505, 465. $C_{28}H_{31}ClN_2O_2RuS$ (595.9): calcd. for: C:56,22, H:5,56, Cl:5,93 N:4,68, O:5,35, Ru:16,90, S:5,36, Found: C:56,31, H:5,48, N:4,60, S:5,40.

{[N-Quinoline-8-yl-4-chloro-benzenesulfonamido]-(p-cymene)-chloro-ruthenium(II)} (10): Yield: 83 %, dark red microcrystals, Mp: 171-172 ^oC, ^1H-NMR ($CDCl_3$, δ ppm): 0,94 and 1,09 (d, d, 6H, *J*=8 Hz, -*H*$_m$), 2.36 (s, 3 H, -*H*$_k$), 2.63 (m, 1H, -*H*$_l$), 5.67 (d, 2H, *J*=4 Hz, -*H*$_y$), 6.23 (d, 2H, *J*=4 Hz, -*H*$_x$), 7.03-7.28 (m, 4H, -*H*$_{2-5}$), 7.36 (d, 2H, *J*=8 Hz, -*H*$_b$), 8.10 (d, 1H, *J*=8 Hz, -*H*$_1$), 8.19 (d, 2H, *J*=8 Hz, -*H*$_a$), 9.12 (d, 1H, *J*=8 Hz, -*H*$_6$). ^{13}C-NMR ($CDCl_3$, ppm): 19.3 (-*C*H_3), 22.2-22.3 (-CH(*C*H_3)$_2$), 31.0 (-*C*H(CH$_3$)$_2$), 80.7 (Ar. -*C*), 82.4 (Ar. -*C*), 84.3 (Ar. -*C*), 85.9 (Ar. -*C*), 116.4 (Ar. -*C*), 117.9 (Ar. -*C*), 122.1 (Ar. -*C*), 127.7 (Ar. -*C*), 128.5 (Ar. -*C*), 128.9 (Ar. -*C*), 129.5 (Ar. -*C*), 130.2 (Ar. -*C*), 137.5 (Ar. -*C*), 137.9 (Ar. -*C*), 139.4 (Ar. -*C*), 144.7 (Ar. -*C*), 151.5 (Ar. -*C*). IR (cm^{-1}): 3055, 3010, 2960, 2869,

1572, 1532, 1532, 1502, 1465, 1446, 1422, 1392, 1377, 1315 (-SO_2), 1298, 1278, 1270, 1233, 1214, 1189, 1173, 1161, 1140 (-SO_2), 1111, 1080, 1044, 1031, 1013, 1005, 985, 965, 946, 905, 868, 833, 821, 805, 792, 781, 748, 708, 693, 666, 646, 614, 587, 567 (-SO_2), 541, 524, 501, 480, 470, 461, 455. $C_{25}H_{24}Cl_2N_2O_2RuS$ (588.4): calcd. for: C:50,85, H:4,44, Cl:12,01, N:4,74, O:5,42, Ru:17,12, S:5,43, Found: C:50,91, H:4,40, N:4,78, S:5,49.

{[N-Quinoline-8-yl-benzenesulfonamido]-(p-cymene)-chloro-ruthenium(II)} (11): Yield: 83 %, dark red microcrystals, Mp: 256-257 ^oC, ^{1}H-NMR ($CDCl_3$, δ ppm): 0,93 and 1,08 (d, d, 6H, *J*=8 Hz, -H_m), 2.37 (s, 3 H, -H_k), 2.62 (m, 1H, -H_l), 5.69 (d, 2H, *J*=4 Hz, -H_y), 6.26 (d, 2H, *J*=4 Hz, -H_x), 6.98-7.41 (m, 4H, -H_{2-5}, -$H_{b,c}$), 8.06 (d, 1H, *J*=8 Hz, -H_1), 8.23 (d, 2H, *J*=8 Hz, -H_a), 9.11 (d, 1H, *J*=8 Hz, -H_6). ^{13}C-NMR ($CDCl_3$, ppm): 19.3 (-CH_3), 22.1, 22.3 (-CH(CH_3)$_2$), 30.9 (-CH(CH_3)$_2$), 80.5 (Ar. -*C*), 82.3 (Ar. -*C*), 84.4 (Ar. -*C*), 86.1 (Ar. -*C*), 116.0 (Ar. -*C*), 117.9 (Ar. -*C*), 121.9 (Ar. -*C*), 128.4 (Ar. -*C*), 128.6 (Ar. -*C*), 128.9 (Ar. -*C*), 129.5 (Ar. -*C*), 131.3 (Ar. -*C*), 137.8 (Ar. -*C*), 140.9 (Ar. -*C*), 144.7 (Ar. -*C*), 147.2 (Ar. -*C*), 151.3 (Ar. -*C*). IR (cm^{-1}): 3058, 2964, 2935, 2870, 1570, 1531, 1503, 1475, 1464, 1445, 1423, 1378, 1316 (-SO_2), 1298, 1290, 1274, 1234, 1214, 1189, 1176, 1165, 1139 (-SO_2), 1112, 1087, 1044, 1028, 1010, 961, 946, 933, 898, 868, 850, 824, 817, 805, 795, 783, 777, 753, 714, 692, 662, 637, 614, 582 (-SO_2), 565, 539, 524, 502, 473, 463. $C_{25}H_{25}ClN_2O_2RuS$ (553.9): calcd. for: C:54,00, H:4,89, Cl:6,38, N:5,04, O:5,75, Ru:18,18, S:5,77, Found: C: 54,12, H:4,81, N:5,14, S:5,69.

{[N-Quinoline-8-yl-4-(trifluoromethyl)-benzenesulfonamido]-(p-cymene)-chloro-ruthenium(II)} (12): Yield: 83 %, dark red microcrystals, Mp: 245-247 ^oC, ^{1}H-NMR ($CDCl_3$, δ ppm): 0,94 and 1,09 (d, d, 6H, *J*=8 Hz, -H_m), 2.36 (s, 3 H, -H_k), 2.63 (m, 1H, -H_l), 5.68 (d, 2H, *J*=4 Hz, -H_y), 6.23 (d, 2H, *J*=4 Hz, -H_x), 7.05-7.41 (m, 4H, -H_{2-5}), 7.55 (d, 2H, *J*=8 Hz, -H_b), 8.10 (d, 1H, *J*=8 Hz, -H_1), 8.37 (d, 2H, *J*=8 Hz, -H_a), 9.12 (d, 1H, *J*=8 Hz, -H_6). ^{13}C-NMR ($CDCl_3$, ppm): 19.3 (-CH_3), 22.1–22.3 (-CH(CH_3)$_2$), 30.9 (-CH(CH_3)$_2$), 80.7 (Ar. -*C*), 82.4 (Ar. -*C*), 84.4 (Ar. -*C*), 85.9 (Ar. -*C*), 116.6 (Ar. -*C*), 117.9 (Ar. -*C*), 122.2 (Ar. -*C*), 125.3-125.5 (-CF_3), 126.5 (Ar. -*C*), 126.6 (Ar. -*C*), 128.9 (Ar. -*C*), 129.6 (Ar. -*C*), 133.0 (Ar. -*C*), 137.9 (Ar. -*C*), 138.7 (Ar. -*C*), 139.3 (Ar. -*C*), 144.6 (Ar. -*C*), 151.6 (Ar. -*C*). IR (cm^{-1}): 3035, 2967, 2929, 2872, 2812, 1607, 1573, 1538, 1505, 1468, 1402, 1379, 1317 (-SO_2), 1294, 1235, 1215, 1186, 1160, 1144 (-SO_2), 1129, 1107, 1086, 1061, 1016, 949, 910, 876, 852, 832, 821, 806, 793, 781, 770, 759, 736, 708, 666, 632, 609, 563 (-SO_2), 541, 524, 504, 472. $C_{26}H_{24}ClF_3N_2O_2RuS$ (621.9). Calcd. for: C:50,20, H:3,89, Cl:5,70, F:9.16, N:4,50, O:5,14, Ru:16,25, S:5,15, Found: C:50,12, H:3,96, N:4,40, S:5,22.

X-ray structural analyses. Single crystal of each compound **8** and **9** was mounted under inert perfluoropolyether at the tip of glass fiber and cooled in the cryostream of a Bruker APEX2 CCD diffractometer. The structures were solved by direct methods (SIR97[53]) and refined by least-squares procedures on F^2 using SHELXL-97[54]. All H atoms attached to carbon were introduced in calculation in idealised positions and treated as riding models. The drawing of the molecules was realised with the help of ORTEP32[55]. Crystal data and refinement parameters are shown in Table 5.

Table- 1. Crystal data for **8** and **9**.

Identification code	**8**	**9**
Empirical formula	C_{26} H_{27} Cl N_2 O_3 Ru S	C_{28} H_{31} Cl N_2 O_2 Ru S
Formula weight	584.08	596.13
Temperature, K	180(2)	180(2)
Wavelength, Å	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/c$
a, Å	14.4087(17)	10.5377(12)
b, Å	11.6057(14)	13.6881(14)
c, Å	16.2028(19)	17.987(2)
α (°)	90.0	90.0
β (°)	116.146(2)	95.771(5)
γ (°)	90.0	90.0
Volume, $Å^3$	2432.2(5)	2581.3(5)
Z	4	4
Density (calc), Mg/m^3	1.595	1.534
Abs. coefficient, mm^{-1}	0.872	0.821
F(000)	1192	1224
Crystal size, mm^3	0.50 x 0.45 x 0.25	0.48 x 0.48 x 0.10
Theta range, °	2.25 to 30.03	1.87 to 29.24
Reflections collected	49026	21457
Indpt reflections (R_{int})	7061 (0.0242)	6964 (0.0243)
Completeness, %	99.2	99.1
Absorption correction	Multi-scan	Multi-scan
Max. and min. transmission	0.7462 and 0.6219	0.7458 and 0.6462
Refinement method	F^2	F^2
Data /restraints/parameters	7061 / 0 / 311	6964 / 0 / 320
Goodness-of-fit on F^2	1.062	1.059
R1, wR2 [I>2σ(I)]	0.0292, 0.0624	0.0250, 0.0581
R1, wR2 (all data)	0.0404, 0.0706	0.0298, 0.0604
Residual density, $e.Å^{-3}$	1.066 and -0.586	0.477 and -0.496
CCDC deposition no.	925980	925981

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