EurJIC European Journal of Inorganic Chemistry
ChemPubSoc Europe
FULL PAPER

DOI:10.1002/ejic.201300266

Synthesis and Characterization of Half-Sandwich Ruthenium Complexes Containing Aromatic Sulfonamides Bearing Pyridinyl Rings: Catalysts for Transfer Hydrogenation of Acetophenone Derivatives

Serkan Dayan,[a] Nilgun Ozpozan Kalaycioglu,*[a] Jean-Claude Daran,[b,c] Agnès Labande,[b] and Rinaldo Poli[b,c,d]

Keywords: Transfer hydrogenation / Sulfonamides / Ruthenium / N ligands

N-(Quinoline-8-yl-aryl)benzenesulfonamides **1–6** were successfully synthesized by the reaction of 8-aminoquinoline and various benzenesulfonyl chlorides. Then, half-sandwich ruthenium complexes **7–12** were prepared from the reactions of **1–6** with $[RuCl_2(p\text{-cymene})]_2$. The synthesized compounds were characterized by NMR and FTIR spectroscopy and elemental analysis, and compounds **8** and **9** were further analyzed by X-ray diffraction. The complexes were screened for their efficiency as catalysts in the transfer hydrogenation of acetophenone derivatives to phenylethanols in the presence of KOH with 2-propanol (as hydrogen source) at 82 °C, and they all showed 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.[8a–8d] Furthermore, complexes containing sulfonamide groups have been used to catalyze various organic reactions, for example, olefin metathesis, asymmetric transfer hydrogenation (TH), the nitroaldol (Henry) reaction, and so on.[9–11] Sulfonamides containing 8-aminoquinoline have rarely been studied by the scientific community, and mostly only in relation to their luminescent properties.[12–16] Also, catalysis and the molecular structural properties of sulfonamides have recently been studied in detail by our research team.[17a–17d]

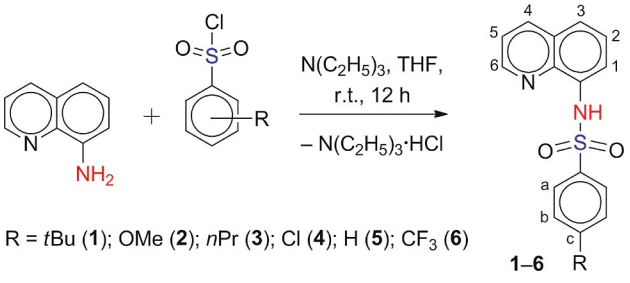
Ketone TH catalyzed by Ru^{II} complexes containing N-donor ligands has attracted increasing attention[18–32] since the success of Noyori's work using 1,2-diamine ligands.[33] Several diamine ligand modifications have been explored aimed at developing catalysts with increased activity. At the same time,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

Herein, a series of half-sandwich Ru^{II} complexes containing sulfonamide ligands were synthesized and characterized by various spectroscopic techniques. The synthesized complexes were used as catalysts for the TH 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 Fig-



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

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

[a] Department of Chemistry, Faculty of Science, Erciyes University,
38039 Kayseri, Turkey
Fax: +90-352-437-4933
E-mail: nozpozan@erciyes.edu.tr
Homepage: http://aves.erciyes.edu.tr/SorguKimlikBilgileri.aspx?Sorgu=789
[b] CNRS, LCC,
31077 Toulouse, France
[c] Univ. Toulouse, UPS, INPT,
31077 Toulouse, France
[d] Inst. Univ. France,
75005 Paris, France

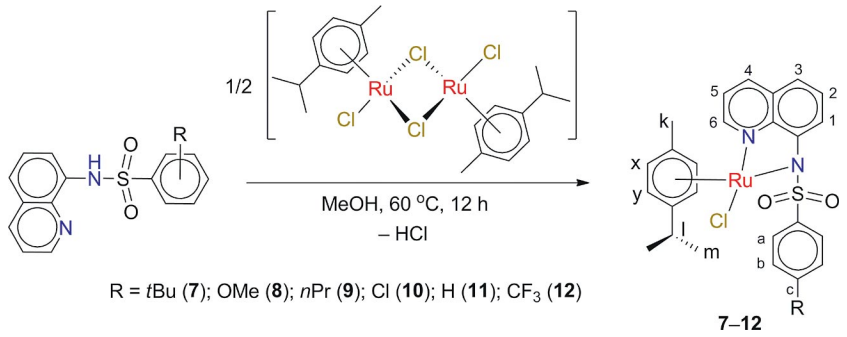


Figure 2. Synthesis of the complexes together with their NMR numbering scheme.

ures 1 and 2. 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, ruthenium complexes **7**–**12** were synthesized by the reactions of **1**–**6** with $[RuCl_2(p\text{-cymene})]_2$ in methyl alcohol (Figure 2). All compounds were characterized by ^1H NMR, ^{13}C NMR, and IR spectroscopy. In addition, the solid-state structures of complexes **8** and **9** were confirmed by X-ray crystallography.

Crystal Structures

Molecular views of compounds **8** and **9** are shown in Figure 3. In each complex, the Ru atom has a pseudotetrahedral geometry; the η^6-π-bonded arene rings occupy one vertex of the tetrahedron, and the three other vertices are 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]

NMR Spectra

In the ^1H NMR spectra of 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-arylsulfonamide 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 ^1H NMR spectra of **7**–**12**, the sulfonamide NH proton is no longer present, whereas new resonances belonging to the *p*-cymene group (H^k, H^x, H^y, H^l, and H^m) appear (Table 2).

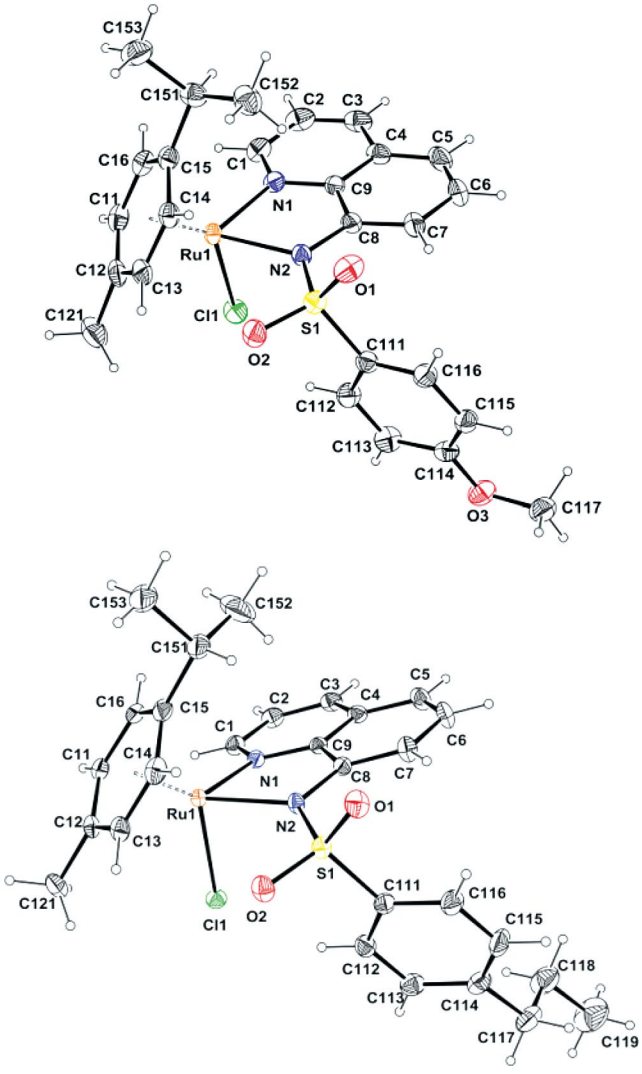


Figure 3. Molecular views of compounds **8** and **9** with the atom labeling scheme; ellipsoids are drawn at the 50% probability level. H atoms are represented as small spheres of arbitrary radii.

Infrared Spectra

The sulfonamide N–H stretching band for ligands **1**–**6** appears at 3260–3192 cm^{-1} (Table 3). This band disappears on going to ruthenium complexes **7**–**12**. The frequencies of the SO_2 stretching and bending peaks are shown in Table 3. For **7**–**12**, the bending and asymmetric stretching bands are observed at higher frequencies than their respective ligands. However, the symmetric stretches also underwent a general shift toward lower frequencies as compared to their respective ligands.

Table 1. Comparison of selected bond lengths and bond angles for both compounds **8** and **9**. Estimated standard deviations in parentheses refer to the last significant digit.

Compound **8**		Compound **9**	
Bond length [Å]			
Ru1–Cg1	1.6799(9)	Ru1–Cg1	1.6666(7)
Ru1–N1	2.0965(16)	Ru1–N1	2.0852(14)
Ru1–N2	2.1285(16)	Ru1–N2	2.1236(13)
Ru1–Cl1	2.4322(5)	Ru1–Cl1	2.3981(5)
S1–O2	1.4382(15)	S1–O2	1.4392(13)
S1–O1	1.4424(16)	S1–O1	1.4496(12)
S1–N2	1.6157(16)	S1–N2	1.6146(14)
S1–C111	1.768(2)	S1–C111	1.7774(17)
N1–C1	1.324(3)	N1–C1	1.330(2)
N1–C9	1.373(3)	N1–C9	1.377(2)
N2–C8	1.400(2)	N2–C8	1.406(2)
Bond angle [°]			
Cg1–Ru1–Cl1	127.01(4)	Cg1–Ru1–Cl1	127.27(3)
Cg1–Ru1–N1	131.54(5)	Cg1–Ru1–N1	130.32(4)
Cg1–Ru1–N2	131.93(5)	Cg1–Ru1–N2	130.13(4)
N1–Ru1–N2	76.86(6)	N1–Ru1–N2	77.10(5)
N1–Ru1–Cl1	84.31(5)	N1–Ru1–Cl1	85.09(4)
N2–Ru1–Cl1	87.46(5)	N2–Ru1–Cl1	90.18(4)
O2–S1–O1	116.55(10)	O2–S1–O1	116.60(8)
O2–S1–N2	107.43(9)	O2–S1–N2	107.34(7)
O1–S1–N2	111.55(9)	O1–S1–N2	112.02(7)
O2–S1–C111	107.18(10)	O2–S1–C111	108.86(8)
O1–S1–C111	106.93(9)	O1–S1–C111	106.36(8)
N2–S1–C111	106.70(9)	N2–S1–C111	105.03(7)
C1–N1–C9	118.80(17)	C1–N1–C9	119.04(15)
C1–N1–Ru1	125.07(14)	C1–N1–Ru1	125.18(11)
C9–N1–Ru1	116.10(12)	C9–N1–Ru1	115.69(11)
C8–N2–S1	118.75(13)	C8–N2–S1	119.50(11)
C8–N2–Ru1	115.35(12)	C8–N2–Ru1	114.30(10)
S1–N2–Ru1	125.75(9)	S1–N2–Ru1	126.19(8)
N1–C1–C2	122.4(2)	N1–C1–C2	122.31(16)

Table 3. IR data of ligands and complexes.

Ligand	IR band [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		$\nu_{as}(SO_2)$[a]	$\nu_{s}(SO_2)$[b]	$\Delta(SO_2)$[c]
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 TH 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 than K_2CO_3 and KO*t*Bu in TH reactions.[36,49] The stronger the base, the higher the general conversion rankings: KOH > NaOH > KO*t*Bu > K_2CO_3. Indeed, the TH of acetophenone catalyzed by **10** led to better results when using KOH, and the reaction reached 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 base, no TH was

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

Ligand	$\delta(^1H)/\delta(^{13}C)$ [ppm]							
	H^a	H^b	H_c	NH		*p*-C(CH$_3$)$_3$	*p*-OCH$_3$	*p*-CH$_2$CH$_2$CH$_3$
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		–	–	–
Complex	H^k	H^x	H^y	H^l	H^m	*p*-C(CH$_3$)$_3$	*p*-OCH$_3$	*p*-CH$_2$CH$_2$CH$_3$
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	–	–	–

observed. Therefore, KOH was selected as the base in all subsequent studies.

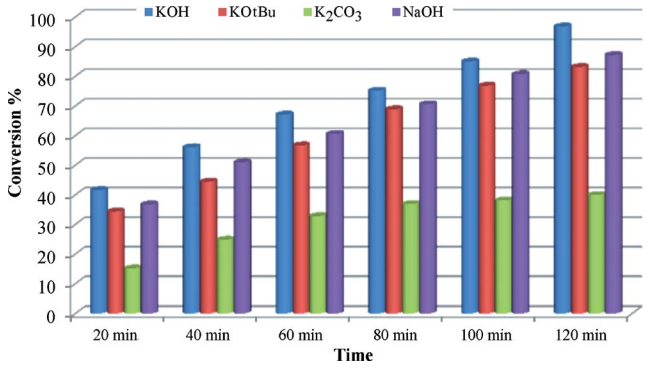


Figure 4. Effect of various bases in the TH of acetophenone catalyzed by **10** (0.2 mol-%) in 2-propanol at 82 °C.

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

We also examined the TH of acetophenone 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 turnover frequency (TOF) was in the 734–575 h^{-1} range for a S/C molar ratio of 1:0.001 at 20 min (Table 4).

Conclusions

In summary, we have reported the preparation and characterization of 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 TH 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 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**, and the best results are obtained in the presence of the Cl and CF_3 substituents at the *para* position to the sulfonamido aryl group. Ruthenium(II) arene complexes are widely used in the TH of ketones. When examined in the context of the literature, it is clear that the half-sandwich sulfonamido–Ru^{II} complexes used herein show good efficiency in TH reactions.[59–73]

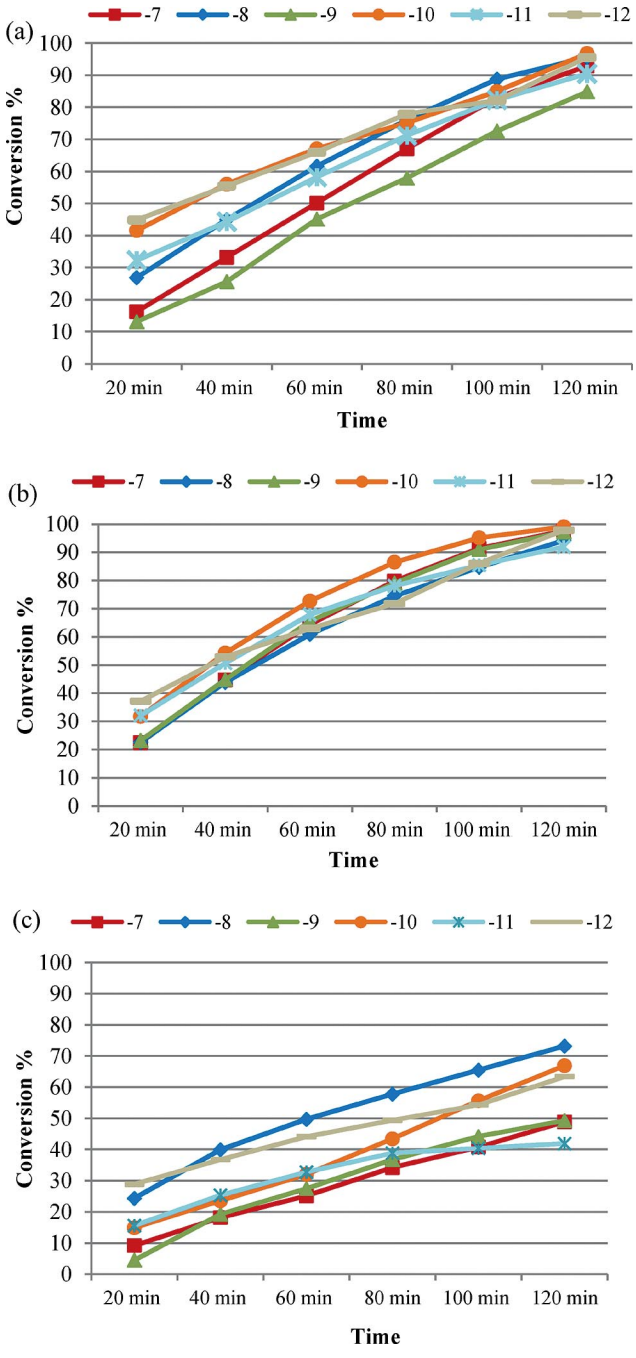


Figure 5. Catalytic activity as shown by the %conversion versus time plot for the TH of (a) acetophenone, (b) 4-chloroacetophenone, and (c) 4-methylacetophenone catalyzed by **7**–**12** in 2-propanol. Conditions: ketone/Ru/KOH = 1:0.002:10, T = 82 °C.

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 with a Bruker Avance III 400 NMR spectrometer at 400 (for ^1H) and 100.56 MHz (for ^{13}C). Signals are quoted relative to tetramethylsilane (δ = 0.00 ppm). 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 by using a universal ATR sampling accessory

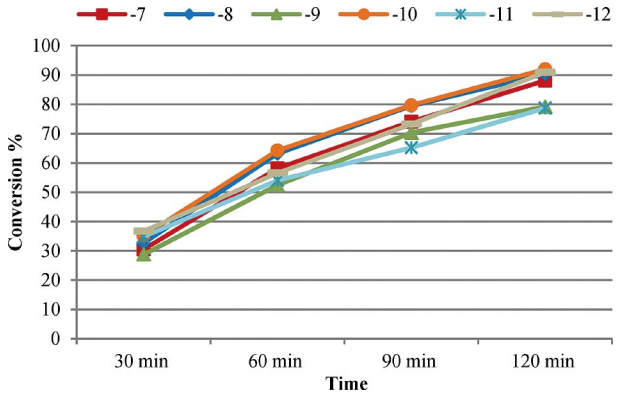
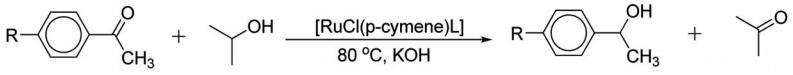


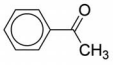
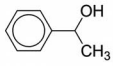
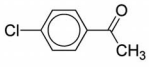
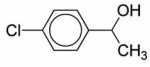
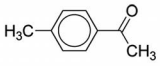
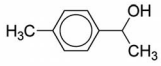
Figure 6. Catalytic activity as shown by the %conversion versus time plot for the TH of acetophenone catalyzed by **7**–**12** in 2-propanol at a S/C/KOH ratio of 1:0.001:10, T = 82 °C.

slow addition of a solution of triethylamine (20 mmol) in THF (5 mL) followed by a solution of 8-aminoquinoline (10 mmol) in THF (5 mL) gave rise to the immediate precipitation of a white solid [HCl·N(C_2H_5)$_3$]. After being stirred for 12 h at room temperature, the solid was removed by filtration by 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; Figure 1).

***N*-Quinoline-8-yl-4-*tert*-butylbenzenesulfonamide (1):** Yield 85%. orange solid, m.p. 155–157 °C. ^{1}H NMR ($CDCl_3$): δ = 1.24 [s, 9 H, -C(CH_3)$_3$], 7.37–7.48 (m, 4 H, -H^{2-5}), 7.86 (dd, J = 4, 4 Hz, 4 H, -H^{a-b}), 8.13 (d, J = 8 Hz, 1 H, -H^1), 8.77 (d, J = 8 Hz, 1 H, -H^6), 9.31 (br. 1 H, -NH) ppm. ^{13}C NMR ($CDCl_3$): δ = 30.9 [-C(*C*H$_3$)$_3$], 35.0 [-*C*(CH$_3$)$_3$], 115.1 (aryl-*C*), 121.9 (aryl-*C*), 122.0 (aryl-*C*), 125.9 (aryl-*C*), 127.0 (aryl-*C*), 128.2 (aryl-*C*), 133.8 (aryl-*C*), 136.4 (aryl-*C*), 136.6 (aryl-*C*), 138.2 (aryl-*C*), 148.4 (aryl-*C*), 148.5 (aryl-*C*), 156.7 (aryl-*C*) ppm. IR: $\tilde{\nu}$ = 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 cm^{-1}. $C_{19}H_{20}N_2O_2S$ (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.

Table 4. Initial TOF for the TH of various ketones catalyzed by **7**–**12**.[a]



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.

within the range 550–4000 cm^{-1}. Melting points were determined in open capillary tubes with a digital Electrothermal 9100 melting point apparatus. GC measurements for catalytic experiments were performed by using Fisons 8000 Series instrument equipped with a DB-1MS column (30 m × 0.32 mm × 0.25 m) and Younglin Acme 6100, OPTIMA 5 MS column (30m × 0.32mm × 0.25 m).

TOF = mol of product/(mol of catalyst) × (hour), measured on the basis of the conversion at 20 min for entries 1–18 and at 30 min for entries 19–24. Conditions are given in the legends of Figures 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 a published procedure.[44] A 50 mL Schlenk tube containing a magnetic stirring bar was charged with a solution of the suitable benzenesulfonyl chloride derivative (10 mmol) in THF (10 mL). The

***N*-Quinoline-8-yl-4-methoxybenzenesulfonamide (2):** Yield 78%, brown solid, m.p. 145–147 °C. ^{1}H NMR (DMSO): δ = 3.74 (s, 3 H, -OCH_3), 6.99 (d, J = 8 Hz, 2 H, -H^b), 7.55–7.77 (m, 4 H, -H^{2-5}), 7.80 (d, J = 8 Hz, 2 H, -H^a), 8.55 (d, J = 8 Hz, 1 H, -H^1), 8.95 (d, J = 8 Hz, 1 H, -H^6), 10.02 (br. 1 H, -NH) ppm. ^{13}C NMR (DMSO): δ = 56.1 (-OCH$_3$), 114.8 (aryl-*C*), 119.7 (aryl-*C*), 122.9 (aryl-*C*), 124.3 (aryl-*C*), 127.8 (aryl-*C*), 128.9 (aryl-*C*), 129.8 (aryl-*C*), 130.9 (aryl-*C*), 132.9 (aryl-*C*), 138.0 (aryl-*C*), 139.4 (aryl-*C*),

149.1 (aryl-*C*), 163.1 (aryl-*C*) ppm. IR: ṽ = 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 cm^{-1}. $C_{16}H_{14}N_2O_3S$ (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, N8.81, S 10.11.

***N*-Quinoline-8-yl-4-*n*-propylbenzenesulfonamide (3):** Yield 82%, light-brown solid, m.p. 120–122 °C. ^{1}H NMR ($CDCl_3$): δ = 0.84 (t, J = 8 Hz, 2 H, -$CH_2CH_2CH_3$), 1.40 (t, J = 8 Hz, 3 H, -$CH_2CH_2CH_3$), 3.12 (m, 2 H, -$CH_2CH_2CH_3$), 7.14–7.89 (m, 4 H, -$H^{2\text{-}5}$), 8.20 (d, J = 8 Hz, 2 H, -H^b), 8.74 (d, J = 8 Hz, 1 H, -H^1), 8.80 (d, J = 8 Hz, 2 H, -H^a), 8.96 (d, J = 8 Hz, 1 H, -H^6), 11.66 (br. 1 H, -N*H*) ppm. ^{13}C NMR ($CDCl_3$): δ = 8.7 (-$CH_2CH_2CH_3$), 24.0 (-$CH_2CH_2CH_3$), 45.9 (-$CH_2CH_2CH_3$), 116.5 (aryl-*C*), 120.3 (aryl-*C*), 121.8 (aryl-*C*), 122.4 (aryl-*C*), 125.9 (aryl-*C*), 127.3 (aryl-*C*), 128.3 (aryl-*C*), 128.9 (aryl-*C*), 131.3 (aryl-*C*), 133.3 (aryl-*C*), 136.6 (aryl-*C*), 147.8 (aryl-*C*), 148.4 (aryl-*C*) ppm. IR: ṽ = 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 cm^{-1}. $C_{18}H_{18}N_2O_2S$ (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-chlorobenzenesulfonamide (4)**: Yield 81%, brown solid, m.p. 110–112 °C. ^{1}H NMR ($CDCl_3$): δ = 7.30–7.49 (m, 4 H, -$H^{2\text{-}5}$), 7.80 (d, J = 8 Hz, 2 H, -H^b), 7.83 (d, J = 8 Hz, 2 H, -H^a), 8.10 (d, J = 8 Hz, 1 H, -H^1), 8.74 (d, J = 8 Hz, 1 H, -H^6), 11.00 (br. 1 H, -N*H*) ppm. ^{13}C NMR ($CDCl_3$): δ = 115.4 (aryl-*C*), 116.0 (aryl-*C*), 122.1 (aryl-*C*), 122.6 (aryl-*C*), 126.8 (aryl-*C*), 127.6 (aryl-*C*), 128.3 (aryl-*C*), 128.6 (aryl-*C*), 129.2 (aryl-*C*), 133.4 (aryl-*C*), 136.3 (aryl-*C*), 139.4 (aryl-*C*), 148.9 (aryl-*C*) ppm. IR: ṽ = 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 cm^{-1}. $C_{15}H_{11}ClN_2O_2S$ (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, m.p. 90–92. ^{1}H NMR ($CDCl_3$): δ = 7.32–7.43 (m, 4 H, -$H^{2\text{-}5}$), 7.79 (t, J = 8 Hz, 2 H, -H^b), 7.86 (d, J = 8 Hz, 2 H, -H^a), 7.88 (t, J = 8 Hz, 1 H, -H^c), 8.07 (d, J = 8 Hz, 1 H, -H^1), 8.72 (d, J = 8 Hz, 1 H, -H^6), 11.21 (br., 1 H, N*H*) ppm. ^{13}C NMR ($CDCl_3$): δ = 115.0 (aryl-*C*), 122.0 (aryl-*C*), 122.3 (aryl-*C*), 125.9 (aryl-*C*), 126.8 (aryl-*C*), 127.2 (aryl-*C*), 128.2 (aryl-*C*), 128.9 (aryl-*C*), 129.8 (aryl-*C*), 132.9 (aryl-*C*), 136.3 (aryl-*C*), 139.3 (aryl-*C*), 148.5 (aryl-*C*) ppm. IR: ṽ = 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 cm^{-1}. $C_{15}H_{12}N_2O_2S$ (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, m.p. 128–130 °C. ^{1}H NMR ($CDCl_3$): δ = 7.42–7.63 (m, 4 H, -$H^{2\text{-}5}$), 7.86 (d, J = 8 Hz, 2 H, -H^b), 8.03 (d, J = 8 Hz, 2 H, -H^a), 8.11 (d, J = 8 Hz, 1 H, -H^1), 8.75 (d, J = 8 Hz, 1 H, -H^6), 10.94 (br. 1 H, -N*H*) ppm. ^{13}C NMR ($CDCl_3$): δ = 115.5 (aryl-*C*), 116.0 (aryl-*C*), 122.2 (aryl-*C*), 122.9 (aryl-*C*), 124.4 (aryl-*C*), 126–126.2 (-CF_3), 126.6 (aryl-*C*), 126.8 (aryl-*C*), 127.7 (aryl-*C*), 128.3 (aryl-*C*), 133.1 (aryl-*C*), 136.4 (aryl-*C*), 138.5 (aryl-*C*), 148.9 (aryl-*C*) ppm. IR: ṽ = 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 cm^{-1}. $C_{16}H_{11}F_3N_2O_2S$ (353.8): calcd. for C 54.54, H3.15, 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*-cymene)]$_2$ (0.25 mmol) in methyl alcohol (5 mL) in a Schlenk tube. The reaction mixture was stirred for 12 h at 60 °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-*tert*-butylbenzenesulfonamido)(*p*-cymene)chlororuthenium(II)] (7): Yield 72%, orange microcrystals, m.p. 291–292 °C. ^{1}H NMR ($CDCl_3$): δ = 0:95 and 1:07 (d and d, J = 8 Hz, 6 H, -H^m), 1.24 [s, 9 H, -C(CH_3)$_3$], 2.37 (s, 3 H, -H^k), 2.62 (m, 1 H, -H^l), 5.70 (d, J = 4 Hz, 2 H, -H^y), 6.29 (d, J = 4 Hz, 2 H, -H^x), 7.01–7.44 (m, 4 H, -$H^{2\text{-}5}$), 8.07 (d, J = 8 Hz, 1 H, -H^1), 8.15 (dd, J = 4, 4 Hz, 4 H, -$H^{a\text{-}b}$), 9.10 (d, J = 8 Hz, 1 H, -H^6) ppm. ^{13}C NMR ($CDCl_3$): δ = 19.3 (-CH_3), 22.1 [-CH(CH_3)$_2$], 30.9 [-CH(CH_3)$_2$], 31.1 [-C(CH_3)$_3$], 34.8 [-C(CH_3)$_3$], 82.3 (aryl-*C*), 84.6 (aryl-*C*), 86.2 (aryl-*C*), 104.5 (aryl-*C*), 115.7 (aryl-*C*), 118.0 (aryl-*C*), 121.9 (aryl-*C*), 125.4 (aryl-*C*), 128.3 (aryl-*C*), 129.0 (aryl-*C*), 129.5 (aryl-*C*), 137.8 (aryl-*C*), 137.9 (aryl-*C*), 144.7 (aryl-*C*), 147.4 (aryl-*C*), 151.1 (aryl-*C*), 154.6 (aryl-*C*) ppm. IR: ṽ = 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 cm^{-1}. $C_{29}H_{33}ClN_2O_2RuS$ (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-methoxybenzenesulfonamido)(*p*-cymene)chlororuthenium(II)] (8): Yield 82%, dark red microcrystals, m.p. 194–196 °C. ^{1}H NMR ($CDCl_3$): δ = 0:92 and 1:08 (d and d, J = 8 Hz, 6 H, -H^m), 2.36 (s, 3 H, -H^k), 2.62 (m, 1 H, -H^l), 3.72 (s, 3 H, -OCH_3), 5.67 (d, J = 4 Hz, 2 H, -H^y), 6.26 (d, J = 4 Hz, 2 H, -H^x), 6.77 (d, J = 8 Hz, 2 H, -H^b), 7.55–7.77 (m, 4 H, -$H^{2\text{-}5}$), 8.06 (d, J = 8 Hz, 1 H, -H^1), 8.16 (d, J = 8 Hz, 2 H, -H^a), 9.10 (d, J = 8 Hz, 1 H, -H^6) ppm. ^{13}C NMR ($CDCl_3$): δ = 19.3 (-CH_3), 22.1 [-CH(CH_3)$_2$], 31.0 [-CH(CH_3)$_2$], 55.3 (-OCH_3), 80.6 (aryl-*C*), 82.3 (aryl-*C*), 84.4 (aryl-*C*), 86.2 (aryl-*C*), 113.5 (aryl-*C*), 115.8 (aryl-*C*), 117.9 (aryl-*C*), 121.9 (aryl-*C*), 128.9 (aryl-*C*), 129.5 (aryl-*C*), 130.6 (aryl-*C*), 132.6 (aryl-*C*), 137.8 (aryl-*C*), 144.7 (aryl-*C*), 147.4 (aryl-*C*), 151.2 (aryl-*C*), 161.8 (aryl-*C*) ppm. IR: ṽ = 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 cm^{-1}. $C_{26}H_{27}ClN_2O_3RuS$ (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*-propylbenzenesulfonamido)(*p*-cymene)-chlororuthenium(II)] (9): Yield 76%, dark red microcrystals, m.p. 247–248 °C. ^{1}H NMR ($CDCl_3$): δ = 0.83 (t, J = 8 Hz, 2 H, -$CH_2CH_2CH_3$), 0.92 and 1.07 (d and d, J = 8 Hz, 6 H, -H^m), 1.37 (t, J = 8 Hz, 3 H, -$CH_2CH_2CH_3$), 2.34 (s, 3 H, -H^k), 2.61 (m, 1 H, -H^l), 3.10 (m, 2 H, -$CH_2CH_2CH_3$), 5.86 (d, J = 4 Hz, 2 H, -H^y), 6.24 (d, J = 4 Hz, 2 H, -H^x), 6.96–7.20 (m, 4 H, -$H^{2\text{-}5}$), 7.37

(d, J = 8 Hz, 2 H, -H^b), 8.04 (d, J = 8 Hz, 1 H, -H^l), 8.11 (d, J = 8 Hz, 2 H, -H^a), 9.10 (d, J = 8 Hz, 1 H, -H^6) ppm. ^{13}C NMR ($CDCl_3$): δ = 8.7 (-$CH_2CH_2CH_3$), 19.3 (-CH_3), 22.3 [-CH(CH_3)$_2$], 24.1 (-$CH_2CH_2CH_3$), 30.9 [-$CH(CH_3)_2$], 46.1 (-$CH_2CH_2CH_3$), 80.6 (aryl-C), 82.3 (aryl-C), 84.5 (aryl-C), 86.1 (aryl-C), 115.8 (aryl-C), 117.9 (aryl-C), 121.9 (aryl-C), 128.4 (aryl-C), 128.5 (aryl-C), 128.9 (aryl-C), 129.5 (aryl-C), 137.8 (aryl-C), 138.1 (aryl-C), 144.7 (aryl-C), 146.2 (aryl-C), 147.4 (aryl-C), 151.3 (aryl-C) ppm. IR: $\tilde{\nu}$ = 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 cm^{-1}. $C_{28}H_{31}ClN_2O_2RuS$ (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-chlorobenzenesulfonamido)(*p*-cymene)chlororuthenium(II)] (10): Yield 83%, dark red microcrystals, m.p. 171–172 °C. ^{1}H NMR ($CDCl_3$): δ = 0.94 and 1.09 (d and d, J = 8 Hz, 6 H, -H^m), 2.36 (s, 3 H, -H^k), 2.63 (m, 1 H, -H^l), 5.67 (d, J = 4 Hz, 2 H, -H^y), 6.23 (d, J = 4 Hz, 2 H, -H^x), 7.03–7.28 (m, 4 H, -$H^{2\text{-}5}$), 7.36 (d, J = 8 Hz, 2 H, -H^b), 8.10 (d, J = 8 Hz, 1 H, -H^l), 8.19 (d, J = 8 Hz, 2 H, -H^a), 9.12 (d, J = 8 Hz, 1 H, -H^6) ppm. ^{13}C NMR ($CDCl_3$): δ = 19.3 (-CH_3), 22.2–22.3 [-CH(CH_3)$_2$], 31.0 [-$CH(CH_3)_2$], 80.7 (aryl-C), 82.4 (aryl-C), 84.3 (aryl-C), 85.9 (aryl-C), 116.4 (aryl-C), 117.9 (aryl-C), 122.1 (aryl-C), 127.7 (aryl-C), 128.5 (aryl-C), 128.9 (aryl-C), 129.5 (aryl-C), 130.2 (aryl-C), 137.5 (aryl-C), 137.9 (aryl-C), 139.4 (aryl-C), 144.7 (aryl-C), 151.5 (aryl-C) ppm. IR: $\tilde{\nu}$ = 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 cm^{-1}. $C_{25}H_{24}Cl_2N_2O_2RuS$ (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)chlororuthenium(II)] (11): Yield 83%, dark red microcrystals, m.p. 256–257 °C. ^{1}H NMR ($CDCl_3$): δ = 0.93 and 1.08 (d and d, J = 8 Hz, 6 H, -H^m), 2.37 (s, 3 H, -H^k), 2.62 (m, 1 H, -H^l), 5.69 (d, J = 4 Hz, 2 H, -H^y), 6.26 (d, J = 4 Hz, 2 H, -H^x), 6.98–7.41 (m, 4 H, -$H^{2\text{-}5}$, -$H^{b,c}$), 8.06 (d, J = 8 Hz, 1 H, -H^l), 8.23 (d, J = 8 Hz, 2 H, -H^a), 9.11 (d, J = 8 Hz, 1 H, -H^6) ppm. ^{13}C NMR ($CDCl_3$): δ = 19.3 (-CH_3), 22.1, 22.3 [-CH(CH_3)$_2$], 30.9 [-$CH(CH_3)_2$], 80.5 (aryl-C), 82.3 (aryl-C), 84.4 (aryl-C), 86.1 (aryl-C), 116.0 (aryl-C), 117.9 (aryl-C), 121.9 (aryl-C), 128.4 (aryl-C), 128.6 (aryl-C), 128.9 (aryl-C), 129.5 (aryl-C), 131.3 (aryl-C), 137.8 (aryl-C), 140.9 (aryl-C), 144.7 (aryl-C), 147.2 (aryl-C), 151.3 (aryl-C) ppm. IR: $\tilde{\nu}$ = 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 cm^{-1}. $C_{25}H_{25}ClN_2O_2RuS$ (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)chlororuthenium(II)} (12): Yield 83%, dark red microcrystals, m.p. 245–247 °C. ^{1}H NMR ($CDCl_3$): δ = 0.94 and 1.09 (d and d, J = 8 Hz, 6 H, -H^m), 2.36 (s, 3 H, -H^k), 2.63 (m, 1 H, -H^l), 5.68 (d, J = 4 Hz, 2 H, -H^y), 6.23 (d, J = 4 Hz, 2 H, -H^x), 7.05–7.41 (m, 4 H, -$H^{2\text{-}5}$), 7.55 (d, J = 8 Hz, 2 H, -H^b), 8.10 (d, J = 8 Hz, 1 H, -H^l), 8.37 (d, J = 8 Hz, 2 H, -H^a), 9.12 (d, J = 8 Hz, 1 H, -H^6) ppm. ^{13}C NMR ($CDCl_3$): δ = 19.3 (-CH_3), 22.1–22.3 [-CH(CH_3)$_2$], 30.9 [-$CH(CH_3)_2$], 80.7 (aryl-C), 82.4 (aryl-C), 84.4 (aryl-C), 85.9 (aryl-C), 116.6 (aryl-C), 117.9 (aryl-C), 122.2 (aryl-C), 125.3–125.5 (-CF_3), 126.5 (aryl-C), 126.6 (aryl-C), 128.9 (aryl-C), 129.6 (aryl-C), 133.0 (aryl-C), 137.9 (aryl-C), 138.7 (aryl-C), 139.3 (aryl-C), 144.6 (aryl-C), 151.6 (aryl-C) ppm. IR: $\tilde{\nu}$ = 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 cm^{-1}. $C_{26}H_{24}ClF_3N_2O_2RuS$ (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 crystals of compounds **8** and **9** were mounted under inert perfluoropolyether at the tip of a 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 by using SHELXL-97.[54] All H atoms attached to carbon atoms were introduced in the calculation in idealized positions and treated as riding models. The drawing of the molecules was realized with the help of ORTEP32.[55] Crystal data and refinement parameters are shown in Table 5.

Table 5. Crystal data for **8** and **9**.

	8	**9**
Empirical formula	$C_{26}H_{27}ClN_2O_3RuS$	$C_{28}H_{31}ClN_2O_2RuS$
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 (calcd.) [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 × 0.45 × 0.25	0.48 × 0.48 × 0.10
θ range [°]	2.25 to 30.03	1.87 to 29.24
Reflns collected	49026	21457
Independent reflns (R_{int})	7061 (0.0242)	6964 (0.0243)
Completeness [%]	99.2	99.1
Absorption correction	multiscan	multiscan
Max./min. transmission	0.7462/0.6219	0.7458/0.6462
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
R_1, wR_2 [$I > 2\sigma(I)$]	0.0292, 0.0624	0.0250, 0.0581
R_1, wR_2 (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-925980 (for **8**) and -925981 (for **9**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgments

Financial support granted by Erciyes University (ERUBAP) (FBY-12-3909, ID: 3909) is acknowledged.

[1] M. Tabatabaee, M. A.-Abbasnejad, N. Nozari, S. Sadegheian, M. Ghasemzadeh, *Acta Crystallogr. Sect. E* **2007**, *63*, o2099–o2100.
[2] G. E. Camí, M. E. Chacón Villalba, P. Colinas, G. A. Echeverría, G. Estiu, D. B. Soria, *J. Mol. Struct.* **2012**, *1024*, 110–116.
[3] J. B. Tommasino, G. Pilet, F. N. R. Renaud, G. Novitchi, V. Robert, D. Luneau, *Polyhedron* **2012**, *37*, 27–34.
[4] W. Wang, T. Zhang, F. Wang, M. Shi, *Tetrahedron* **2011**, *67*, 1523–1529.
[5] A. S. Culf, J. T. Gerig, P. G. Williams, *J. Biomol. NMR* **1997**, *10*, 293–299.
[6] a) S. S. Krasnikova, I. K. Yakushchenko, S. N. Shamaev, *Mol. Cryst. Liq. Cryst.* **2007**, *468*, 439–445; b) J. Zhao, D. Zhao, H. Zhao, *Huaxue Shiji* **1997**, *19*, 257–260; c) F. P. Dininno, R. N. Guthikonda, *US Patent Publication*, **1994**, US 5294610 A 19940315.
[7] E. Kremer, G. Facchin, E. Estevez, P. Albores, E. J. Baran, E. J. Ellena, M. H. Torre, *J. Inorg. Biochem.* **2006**, *100*, 1167–1175.
[8] a) I. Beloso, J. Castro, J. A. Garcia-Vazquez, P. Perez-Lourido, J. Romero, A. Sousa, *Polyhedron* **2003**, *22*, 1099–1111; b) I. Beloso, J. Castro, J. A. Garcia-Vazquez, P. Perez-Lourido, J. Romero, A. Sousa, *Eur. J. Inorg. Chem.* **2004**, 635–645; c) I. Beloso, J. Castro, J. A. Garcia-Vazquez, P. Perez-Lourido, J. Romero, A. Sousa, *Inorg. Chem.* **2005**, *44*, 336–351; d) I. Beloso, J. Castro, J. A. Garcia-Vazquez, P. Perez-Lourido, J. Romero, A. Sousa, *Polyhedron* **2006**, *25*, 2673–2682.
[9] A. Szadkowska, K. Zukowska, A. E. Pazio, K. Wozniak, R. Kadyrov, K. Grela, *Organometallics* **2011**, *30*, 1130–1138.
[10] W. Jin, X. Li, B. Wan, *J. Org. Chem.* **2011**, *76*, 484–491.
[11] N. A. Cortez, G. Aguirre, M. Parra-Hake, R. Somanathan, *Tetrahedron Lett.* **2009**, *50*, 2228–2231.
[12] B. Macíasa, I. García, M. V. Villa, J. Borrás, A. Castiñeiras, F. Sanz, *Polyhedron* **2002**, *21*, 1229–1234.
[13] B. Macíasa, I. García, M. V. Villa, J. Borrás, A. Castiñeiras, F. Sanz, *Z. Anorg. Allg. Chem.* **2003**, *629*, 255–260.
[14] L. E. da Silva, P. T. de S. A. C. Joussef Jr., C. Piovezan, A. Neves, *Quim. Nova* **2008**, *31*, 1161–1164.
[15] H. Xu, L. F. Huang, L. M. Guo, Y. G. Zhang, X. M. Ren, Y. Song, J. Xie, *J. Lumin.* **2008**, *128*, 1665–1672.
[16] M. Yan, T. Li, Z. Yang, *Inorg. Chem. Commun.* **2011**, *14*, 463–465.
[17] a) S. Dayan, N. Özpozan Kalaycıoğlu, *Appl. Organomet. Chem.* **2013**, *27*, 52–58; b) N. Özdemir, S. Dayan, O. Dayan, M. Dinçer, N. Özpozan Kalaycıoğlu, *Mol. Phys.* **2013**, *111*, 707–723; c) S. Dayan, N. Özpozan Kalaycıoğlu, O. Dayan, N. Özdemir, M. Dinçer, O. Büyükgüngör, *Dalton Trans.* **2013**, *42*, 4957–4969; d) S. Dayan, N. Özpozan Kalaycıoğlu, O. Dayan, E. Çırçır Öztürk, *Inorg. Chim. Acta* **2013**, *401*, 107–113.
[18] M. K. O'Neill, A. F. Trappey, P. Battle, C. L. Boswell, D. N. Blauch, *Dalton Trans.* **2009**, 3391–3394.
[19] C. Deraeve, A. Maraval, L. Vendier, V. Faugeroux, M. Pitié, B. Meunier, *Eur. J. Inorg. Chem.* **2008**, 5622–5631.
[20] M. K. Paira, J. Dinda, T.-H. Lu, A. R. Paital, C. Sinha, *Polyhedron* **2007**, *26*, 4131–4140.
[21] I. Yamada, R. Noyori, *Org. Lett.* **2000**, *2*, 3425.
[22] S. W. Seidel, T. J. Deming, *Macromolecules* **2003**, *4*, 96439.
[23] A. M. Hayes, D. J. Morris, G. J. Clarkson, M. Wills, *J. Am. Chem. Soc.* **2005**, *20*, 7318.
[24] J. Canivet, G. Labat, H. Stoeckli-Evans, G. Suss-Fink, *Eur. J. Inorg. Chem.* **2005**, 4493.
[25] T. Ohkuma, N. Utsumi, K. Tsutsumi, K. Murata, C. Sandoval, R. Noyori, *J. Am. Chem. Soc.* **2006**, *27*, 8724.
[26] T. Ohkuma, K. Tsutsumi, N. Utsumi, N. Arai, R. Noyori, K. Murata, *Org. Lett.* **2007**, *9*, 255–257.
[27] J. E. D. Martins, D. J. Morris, B. Tripathi, M. Wills, *J. Organomet. Chem.* **2008**, *23*, 3527–3532.
[28] A. Çetin, O. Dayan, *Chin. J. Chem.* **2009**, *5*, 978–982.
[29] J. E. D. Martins, G. J. Clarkson, M. Wills, *Org. Lett.* **2009**, *11*, 847.
[30] F. K. Cheung, A. J. Clarke, G. J. Clarkson, D. J. Fox, M. A. Graham, C. Lin, A. L. Criville, M. Wills, *Dalton Trans.* **2010**, *5*, 1395.
[31] O. Dayan, B. Çetinkaya, *J. Mol. Catal. A* **2007**, *271*, 134–141.
[32] O. Dayan, N. Özdemir, Z. Şerbetçi, M. Dinçer, B. Çetinkaya, O. Büyükgüngör, *Inorg. Chim. Acta* **2012**, *392*, 246–253.
[33] R. Noyori, S. Hashiguchi, *Acc. Chem. Res.* **1997**, *30*, 97.
[34] H. Turkmen, I. Kani, B. Cetinkaya, *Eur. J. Inorg. Chem.* **2012**, 4494–4499.
[35] A. Bacchi, M. Balordi, R. Cammi, L. Elviri, C. Pelizzi, F. Picchioni, V. Verdolino, K. Goubitz, R. Peschar, P. Pelagatti, *Eur. J. Inorg. Chem.* **2008**, 4462–4473.
[36] M. M. Wei, M. Garcia-Melchor, J. C. Daran, C. Audin, A. Lledós, R. Poli, E. Deydier, E. Manoury, *Organometallics* **2012**, *31*, 6669–6680.
[37] D. Pandiarajan, R. Ramesh, *J. Organomet. Chem.* **2013**, *723*, 26–35.
[38] A. A. Mikhailine, R. H. Morris, *Inorg. Chem.* **2010**, *49*, 11039–11044.
[39] A. A. Mikhailine, M. I. Maishan, A. J. Lough, R. H. Morris, *J. Am. Chem. Soc.* **2012**, *134*, 12266–12280.
[40] X. Guo, Y. Tang, X. Zhang, M. Lei, *J. Phys. Chem. A* **2011**, *115*, 12321–12330.
[41] D. E. Prokopchuk, J. F. Sonnenberg, N. Meyer, M. Z. Iuliis, A. J. Lough, R. H. Morris, *Organometallics* **2012**, *31*, 3056–3064.
[42] J. Dimroth, U. Schedler, J. Keilitz, R. Haag, R. Schomäcker, *Adv. Synth. Catal.* **2011**, *353*, 1335–1344.
[43] R. Noyori, S. Hashiguchi, *Acc. Chem. Res.* **1997**, *30*, 97.
[44] S. Günnaz, N. Özdemir, S. Dayan, O. Dayan, B. Çetinkaya, *Organometallics* **2011**, *30*, 4165–4173.
[45] N. Gurbuz, E. O. Ozcan, I. Ozdemir, B. Cetinkaya, O. Sahin, O. Buyukgungor, *Dalton Trans.* **2012**, *41*, 82330–2339.
[46] T. Marimuthu, H. B. Friedrich, *ChemCatChem* **2012**, *4*, 2090–2095.
[47] M. Aydemir, F. Durap, C. Kayan, A. Baysal, Y. Turgut, *Synlett* **2012**, *19*, 2777–2784.
[48] C. Aliende, M. Perez-Manrique, F. A. Jalon, B. R. Manzano, A. M. Rodriguez, G. Espino, *Organometallics* **2012**, *31*, 6106–6123.
[49] A. Zirakzadeh, R. Schuecker, N. Gorgas, K. Mereiter, F. Spindler, W. Weissensteiner, *Organometallics* **2012**, *31*, 4241–4250.
[50] J. Vaclavik, P. Kacer, M. Kuzma, L. Cerveny, *Molecules* **2011**, *16*, 5460–5495.
[51] S. Gulcemal, *Appl. Organomet. Chem.* **2012**, *26*, 246–251.
[52] S. Gulcemal, J. C. Daran, B. Cetinkaya, *Inorg. Chim. Acta* **2011**, *365*, 264–268.
[53] A. Altomare, M. Burla, M. Camalli, G. Cascarano, C. Giacovazzo, A. Guagliardi, A. Moliterni, G. Polidori, R. Spagna, *J. Appl. Crystallogr.* **1999**, *32*, 115–119.
[54] G. M. Sheldrick, *Acta Crystallogr. Sect. A* **2008**, *64*, 112–122.
[55] L. J. Farrugia, *J. Appl. Crystallogr.* **1997**, *30*, 565.
[56] D. Carmona, M. P. Lamata, F. Viguri, R. Rodriguez, F. J. Lahoz, I. T. Dobrinovitch, L. A. Oro, *Dalton Trans.* **2008**, 3328.
[57] A. Singh, N. Singh, D. S. Pandey, *J. Organomet. Chem.* **2002**, *642*, 48.
[58] B. Therrien, G. Suss-Fink, P. Govindaswamy, C. Said-Mohamed, *Polyhedron* **2007**, *26*, 4065.
[59] A. Bacchi, P. Pelagatti, C. Pelizzi, D. Rogolino, *J. Organomet. Chem.* **2009**, *694*, 3200–3211.
[60] C. A. Madrigal, A. García-Fernández, J. Gimeno, E. Lastra, *J. Organomet. Chem.* **2008**, *693*, 2535–2540.
[61] P. Kumar, A. K. Singh, R. Pandey, P. Z. Li, S. K. Singh, Q. Xu, D. S. Pandey, *J. Organomet. Chem.* **2010**, *695*, 2205–2212.
[62] M. Aydemir, N. Meric, A. Baysal, Y. Turgut, C. Kayan, S. Seker, M. Toğrul, B. Gümgüm, *J. Organomet. Chem.* **2011**, *696*, 1541–1546.

[63] D. Elma, F. Durap, M. Aydemir, A. Baysal, N. Meric, B. Ak, Y. Turgut, B. Gümgüm, *J. Organomet. Chem.* **2013**, *729*, 46–52.
[64] B. T. Kırkar, H. Turkmen, I. Kani, B. Cetinkaya, *Tetrahedron* **2012**, *68*, 8655–8662.
[65] N. A. Cortez, G. Aguirre, M. Parra-Hake, R. Somanathan, *Tetrahedron: Asymmetry* **2008**, *19*, 1304–1309.
[66] J. E. D. Martins, M. A. C. Redondo, M. Wills, *Tetrahedron: Asymmetry* **2010**, *21*, 2258–2264.
[67] A. Grabulosa, A. Mannu, E. Alberico, S. Denurra, S. Gladiali, G. Muller, *J. Mol. Catal. A* **2012**, *363*, 49–57.
[68] M. U. Raja, E. Sindhuja, R. Ramesh, *Inorg. Chem. Commun.* **2010**, *13*, 1321–1324.
[69] M. C. Carrión, F. A. Jalón, B. R. Manzano, A. M. Rodríguez, F. Sepúlveda, M. Maestro, *Eur. J. Inorg. Chem.* **2007**, 3961–3973.
[70] T. Glöge, D. Petrovic, C. Hrib, P. G. Jones, M. Tamm, *Eur. J. Inorg. Chem.* **2009**, 4538–4546.
[71] D. J. Morris, A. M. Hayes, M. Wills, *J. Org. Chem.* **2006**, *71*, 7035–7044.
[72] P. Singh, A. K. Singh, *Organometallics* **2010**, *29*, 6433–6442.
[73] M. Ito, Y. Shibata, A. Watanabe, T. Ikariya, *Synlett* **2009**, *10*, 1621–1626.

Received: February 25, 2013
Published Online: May 14, 2013

