Electronic supplementary information (ESI)

Ruthenium – Sulfoxide Catalysts for Olefin Metathesis: Investigation on Synthesis and Activation Screening of New Family Dormant Initiators

Anna Szadkowska,[a] Anna Makal,[c] Krzysztof Woźniak,[c] Renat Kadyrov,[b] Karol Grela[a]

[a] Institute of Organic Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, 01-224 Warsaw, Poland; Fax: +48-22-343-21-09; E-mail: klgrela@gmail.com

[b] Evonik-Degussa GmbH, Rodenbacher Chaussee 4, 63457 Hanau, Germany. Fax: +49-6181-59-78712; E-mail: renat.kadyrov@degussa.com

[c] Department of Chemistry, Warsaw University, Pasteura 1, 02-093 Warsaw, Poland.

1. Equipment and chemicals used

All reactions were carried out under Ar in pre-dried glassware using Schlenk techniques. The solvents: dichloromethane (Merck), ethyl acetate (Merck), *n*-pentane (Fluka) were distilled over CaH_2, toluene (Fluka) was distilled over Na and methanol (Fluka) was distilled over Mg. All distillations were made under argon and all solvents were stored under argon. Flash column were performed using silica gel 60 (230–400 mesh). NMR spectra were recorded in $CDCl_3$; chemical shifts (δ) are given in ppm relative to TMS, coupling

constants are (*J*) in Hz. IR spectra: wavenumbers are in cm^{-1}. MS (EI) spectra were recorded on AMD 604 Intectra GmbH spectrometer. MS (ESI) spectra were recorded on Mariner Perseptive Biosystems, Inc. IR spectra were recorded on a Perkin-Elmer Spectrum One FTIR spectrometer with diamond ATR accessory. Melting point was recorded by EZ-Melt Automated Melting Point Apparatus. Micro-analyses were provided by Institute of Organic Chemistry, PAS, Warsaw.

CatMetium™ (**Ind-II'**) was obtained from Degussa-Evonik. Other ruthenium initiators and other reagents was purchased from Aldrich or Strem.

2. X-Ray crystallographic details

The data for **20c**, **20d** and **20f** were collected using the BRUKER KAPPA APEXII ULTRA controlled by APEXII software (Bruker, 2007) and equipped with MoKα rotating anode X-ray source and APEX-II CCD detector. The beam was monochromatized and collimated by a set of multi-layer focusing optics. The experiments were carried out using the Oxford Cryostream cooling device. The crystals were mounted on thin cactus needles with a droplet of Pantone-N oil and immediately cooled. The generator settings were 50kV and 22mA and the crystal to detector distance was set to 40mm. Indexing, integration and initial scaling were performed with *SAINT* and *SADABS* software (Bruker, 2007). The unit cell parameters were obtained and refined based on the whole datasets. The absorption correction from crystal faces was applied before scaling for each sample. The average mosaicity was refined to the value of 0.6°. No decay of the samples during the measurements was observed.

2.1. Structure solution and refinement

The structures were solved by direct methods approach using the *SHELXS-97* program (Sheldrick, 1990) and than refinements based on F^2 except reflections with negative intensities were carried out with the *SHELXL-97* (Sheldrick, 1997).[1] Weighted R factors wR and all goodness-of-fit S values were based on F^2, whereas conventional R factors were based on the amplitudes, with F set to zero for negative F^2. The $F_0^2 > 2\sigma(F_0^2)$ criterion was applied only for R factors calculation and was not relevant to the choice of reflections for the refinement. The R factors based on F^2 are for both structures about twice as large as those based on F. Scattering factors were taken from Tables 4.2.6.8 and 6.1.1.4 from the International Crystallographic Tables Vol. C. (Wilson, 1992) In the final refinement all non-hydrogen atoms for both structures were refined with anisotropic thermal displacement parameters. Hydrogen atoms were located directly from the Fourier map but then their positions and isotropic thermal displacement parameters were refined as 'riding' on the coordinates of the connected non-hydrogen atoms. No extinction correction was needed.

[1] a) L. J. Farrugia, *J. Appl. Crystallogr.* 1997, *30*, 565; b) CrysAlis CCD, Oxford Diffraction Ltd. (compiled Oct 25 2005,08:50:05); c) CrysAlis RED, Oxford Diffraction Ltd., (compiled Oct 25 2005,08:50:05), Analytical numeric absorption correction using a multifaceted crystal model based on expressions derived by R.C. Clark & J.S. Reid.; d) APEXII-2008v1.0 Bruker Nonius 2007; e) SAINT V7.34A Bruker Nonius 2007; f) SADABS-2004/1 Bruker Nonius area detector scaling and absorption correction, 2007; g) G. M. Sheldrick, *Acta Crystallogr.* 1990, *A46*, 467; h) G. M. Sheldrick, SHELXL93. *Program for the Refinement of Crystal Structures.,* Univ. of Göttingen, Germany; i) *International Tables for Crystallography*, Ed. A. J. C. Wilson, Kluwer: Dordrecht, 1992, Vol.C.

2.2. Preparation of crystals of the ruthenium complexes: 20c, 20d and 20f for X-Ray measurements

Crystals suitable of **20d** and **20f** for X-Ray structures determination of were grown from a solution of HPLC-grade methylene chloride and *n*-pentane at +4 ºC over a few days. X-Ray structures determination for **20c** were obtained form solution of HPLC-grade ethyl acetate and *n*-pentane at room temperature.

3. Preparative experiments

3.1. Synthesis of ligands 10 − 12

3.1.1. Synthesis of ligands 10a − f

Preparation of 10a. To a suspension of K_2CO_3 (0.74 g, 5.35 mmol) and Cs_2CO_3 (0.24 g, 0.75 mmol) in DMF (9 ml), 2-bromothiophenol (0.5 g, 3.57 mmol) was added. After stirring for 30 min, 2-iodopropane (0.41 mL, 0.7 g, 7.49 mmol) was added and reaction mixture was stirred for 1 h at RT. Then mixture was poured into water (5 mL), extracted with diethyl ether (3 × 6 mL), combined organic phases were washed with water, brine and dried. Solvent was evaporated to dryness to obtain **10a** as an yellow oil (0.62 g, 3.39 mmol, yield 96%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 1.26 − 1.45 (d, *J* = 6.7 Hz, 6H), 3.50 (septet, *J* = 6.7 Hz, 1H), 7.01 − 7.08 (m, 1H), 7.23 7.29 (m, 1H), 7.34−7.38 (m, 1H), 7.55 − 7.59 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 22.8, 37.2, 125.4, 127.2, 127.6, 130.8, 133.1, 137.3; MS

(EI) (*m/z*) (rel intensity): 39 (13), 41 (21), 43 (32), 69 (16), 108 (45), 109 (98), 110 (10), 188 (97), 189 (10), 190 (100), 230 (46), 232 (47); HRMS (EI): calcd. for $[M]^{+\bullet}$ ($C_9H_{11}S^{79}Br$) 231.16581; found 231.16572; IR (film): *v* 3118, 3050, 2968, 2929, 2868, 2302, 2254, 1909, 1815, 1687, 1605, 1574, 1449, 1428, 1386, 1368, 1314, 1239, 1156, 1124, 1104, 1052, 1039, 1020, 909, 650, 630 cm^{-1}; Anal. calcd. for $C_9H_{11}S^{79}Br$: C, 46.70, H, 4.77, S, 13.80, Br, 34.50; found: C, 46.55, H, 4.72, S, 13.82, Br, 34.62.

Preparation of 10b.[2] 2-bromothiophenol (0.41 mL, 0.66 g, 3.5 mmol) was reacted with cyclohexyl bromide (0.47 mL, 0.63 g, 3.85 mmol) and KF (0.81g, 14 mmol) with catalytic CsF (0.03 g, 0.21 mmol) in DMF at reflux during 8.5 h. The reaction was then cooled to ambient temperature, diluted with hexane and washed with 10 % KOH, 5 % HCl and brine. Organic extracts were combined and dried over $MgSO_4$. Solvent was removed in vacuo and then the crude product was purified on column chromatography, using as eluent first pure cyclohexane and later cyclohexane : ethyl acetate (20 : 1 v/v) to yield **10b** as a yellow solid (0.5 g, 1.84 mmol, yield 53%). Analysis are in accordance with the analytical data form cited literature.

Preparation of 10c.[3] In air, 2-bromothiophenol (0.4 mL, 0.64 g, 3.4 mmol) was added dropwise to a vigorously stirred solution of *tert*-butyl alcohol (0.5 g, 5.1 mol), H_2O (2.3 mL), and concentrated H_2SO_4 (3.3 mL) at −10 ºC. Following addition, the reaction was allowed to come to ambient temperature and stirring was continued for 18 h, at which time diethyl ether (5 mL) was added to the reaction mixture. The organic phase was washed with 1 M aq. K_2CO_3 solution (20 mL) and water (3 × 4 mL) and dried over Mg-

[2] M. Lamothe, M. B. Anderson, P. L. Fuchs. *Syn. Comm*, **1991**, *21*, 1675.

[3] S. B. Harkins, J. C. Peters. *J. Am. Chem. Soc.* **2004**, *126*, 2890.

SO_4. The solvent was removed in vacuo. The residue was distilled (90 °C /0.01 mmHg) affording colorless oil (0.48 g, 1.97 mmol, 58%). Analysis are in accordance with the analytical data form cited literature.

Preparation of 10d. To a suspension of K_2CO_3 (1.1 g, 8 mmol) and Cs_2CO_3 (0.27 g, 0.84 mmol) in DMF (10 ml), 1-bromo-2-thiophenol (0.47 mL, 0.76 g, 4 mmol) was added. After stirring for 30 min, benzyl chloride (0.69 mL, 0.76 g, 6 mmol) was added and the reaction mixture was stirred for 1 h at RT. Then the mixture was poured into water (5 mL), extracted with diethyl ether and the combined organic phases were washed with water, brine and dried. Solvent was removed in vacuo and then the crude product was purified on column chromatography, using as eluent first pure cyclohexane and later cyclohexane : ethyl acetate (15 : 1 v/v) to yield **10d** as a yellow oil (1.05 g, yield 94%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 4.08 − 4.20 (m, 2H), 6.97 − 7.05 (m, 1H), 7.16 − 7.22 (m, 2H), 7.23 − 7.33 (m, 3H), 7.34 − 7.39 (m, 2H), 7.51 − 7.57 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 37.9, 123.6, 126.9, 127.4, 127.7, 128.6, 128.8, 128.9, 132.9, 136.1, 137.8; MS (EI) (*m/z*) (rel intensity): 39 (3), 40 (3), 63 (2), 65 (8), 91 (100), 92 (8), 108 (6), 278 (12), 280 (12); HRMS (EI): calcd. for [$M^{+\bullet}$] ($C_{13}H_{11}S^{79}Br$) 277.97648; found 277.97584; IR (KBr): *v* 3345, 3084, 3060, 3029, 2925, 2850, 1948, 1900, 1806, 1676, 1601, 1575, 1557, 1494, 1449, 1427, 1385, 1319, 1256, 1237, 1199, 1159, 1107, 1090, 1070, 1039, 1020, 920, 845, 814, 778, 744, 717, 697, 650, 620, 566, 507, 485, 449, 428 cm^{-1}; Anal. calcd. for $C_{13}H_{11}S^{79}Br$: C, 55.93, H, 3.97, S, 11.48, Br, 28.62; found: C, 55.99, H, 3.92, S, 11.60, Br, 28.48; M.p. 41 − 43 ºC.

Preparation of 10e. To a suspension of K_2CO_3 (0.53 g, 3.83 mmol) and Cs_2CO_3 (0.18 g, 0.54 mmol) in DMF (15 ml), 1-bromo- 2-thiophenol (0.3 mL, 0.48 g, 2.55 mmol) was added. After stirring for 30 min, iodomethane (0.54 g, 0.24 mL, 3.83 mmol) was added and reaction mixture was stirred for 1 h at RT. Then mixture was poured into water (8 mL), extracted with diethyl ether, combined organic phases were washed with water, brine and dried. Solvent was removed in vacuo and then the crude product was purified on column chromatography, using as eluent first pure cyclohexane and later cyclohexane : ethyl acetate (10 : 1 v/v) to yield **10e** as a yellow oil (0.48 g, yield 92%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 2.5 (s, 3H), 6.97 − 7.03 (m, 1H), 7.11 − 7.16 (m, 1H), 7.27 − 7.33 (m, 1H), 7.50 − 7.55 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 15.7, 121.7, 125.4, 125.7, 125.8, 132.6, 139.6; MS (EI) (*m/z*) (rel intensity): 45 (47), 50 (22), 51 (14), 63 (16), 69 (28), 74 (13), 75 (13), 77 (26), 82 (13), 108 (86), 121 (14), 122 (15), 123 (16), 156 (11), 158 (11), 169 (24), 171 (24), 187 (10), 202 (98), 204 (100); HRMS (EI): cald. for $[M]^{+\bullet}$ ($C_7H_7S^{79}Br$) 201.94518; found 201.94480. IR (film): *v* 3058, 2985, 2919, 2836, 2549, 2283, 1941, 1813, 1778, 1671, 1576, 1557, 1450, 1435, 1428, 1355, 1319, 1274, 1250, 1163, 1111, 1041, 1020, 953, 934, 848, 743, 706, 649, 429 cm^{-1}; Anal. calcd. for $C_7H_7S^{79}Br$: C, 41.40, H, 3.47, S, 15.79, Br, 39.34; found: C, 41.59, H, 3.32, S, 15.63, Br, 39.48.

Preparation of 10f. To a solution of 4-nitro-fluorobenzene (0.43 mL, 4 mmol,) in EtOH (20 mL), a solution of 1-bromo-2-thiophenol (0.53 mL, 4.5 mmol,) in 4 mL of EtOH was added, followed by addition of K_2CO_3 (0.63 g, 4.50 mmol,). Reaction mixture was left for overnight stirring under reflux at 70°C. After this time, mixture was poured into water (30 mL), 10% HCl aq. was added to reached: 7.5 − 8.0 pH. Reaction mixture was extract-

ed using system of solvents: cyclohexane : ethyl acetate (5 : 1 v/v), (3 × 70 mL). Combined extracts were washed with 10% NaOH aq. until the inorganic phase was almost colorless. All inorganic phases were acidified and extracted with AcOEt (3 × 50 mL). Organic extracts were dried over $MgSO_4$ and evaporated to dryness. The crude product was purified by column chromatography, using as eluent first pure cyclohexane and later cyclohexane : ethyl acetate (20 : 1 v/v) to yield **10f** as a yellow solid (1.17 g, 3.8 mmol, yield 84%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.18 − 7.23 (m, 2H), 7.28 − 7.41 (m, 2H), 7.55 − 7.60 (m, 1H), 7.72 − 7.77 (m, 1H), 8.08 − 8.14 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 124.2, 127.5, 128.6, 129.2, 131.0, 132.3, 134.2, 136.2, 145.8, 146.0; MS (EI) (*m/z*) (rel intensity): 50 (10), 69 (13), 108 (26), 139 (23), 152 (11), 171 (10), 172 (12), 183 (16), 184 (100), 185 (14), 309 (92), 311 (95), 312 (13); HRMS (EI): calcd. for $[M]^{+\bullet}$ ($C_{12}H_8O_2NS^{79}Br$) 308.94591; found 308.94659; IR (KBr): *v* 3181, 3094, 3064, 2905, 2825, 2682, 2597, 2437, 2214, 2181, 1931, 1908, 1808, 1698, 1646, 1621, 1592, 1575, 1504, 1474, 1446, 1429, 1399, 1362, 1334, 1249, 1219, 1178, 1159, 1112, 1107, 1082, 1018, 1004, 948, 866, 851, 822, 753, 742, 728, 701, 680, 645, 624, 542, 524, 472, 434 cm^{-1}; Anal. calcd. for $C_{12}H_{18}O_2NS^{79}Br$: C, 46.47, H, 2.60, N, 4.52, S, 10.34, Br, 25.76; found: C, 46.32, H, 2.79, N, 4.31, S, 10.36, Br, 25.68; M.p. 94 − 96 ºC.

3.1.2. Synthesis of ligands 11a − f [4]

To a three-necked, round-bottomed flask, equipped with a stirrer, thermometer, and addition funnel with sidearm were added Oxone™ (1.29 g, 2.1 mmol) and water (4 mL). The mixture is cooled to 5 °C and a solution of the appropriate sulfide (2.1 mmol) in methanol (4 mL) was placed in the addition funnel and added dropwise to the stirring slurry. After addition of the sulfide, the reaction mixture was stirred at room temperature for 1 − 4 hr, and the methanol is removed on the rotary evaporator. The remaining solution is extracted with methylene chloride (2 × 5 mL). The combined organic layers were dried over magnesium sulfate, concentrated to ca. 3 mL, filtered through a plug of silica gel and washed with an additional 3 mL of methylene chloride. The colorless filtrate was concentrated and the resulting oil or solid was dried under vacuum at room temperature to provide a suitable sulfoxide (yield 62 − 78%).

11a ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.97 − 1.07, 1.42 − 1.52 (AB, J = 7.2 Hz, 6H, CH_3), 3.21 (septet, J = 7.0 Hz, 1H), 7.32 − 7.39 (m, 1H), 7.53 − 7.59 (m, 2H), 7.76 − 7.81 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.9, 17.7, 51.3, 119.2, 127.5, 127.9, 132.0, 132.9, 142.2; HRMS (ESI) (*m/z*): $[M + Na]^{+\bullet}$ calcd. for ($C_9H_{11}ONaS^{79}Br$) 268.96062; found 268.9595; IR (film): *v* 3486, 3059, 2971, 2931, 2868, 2726, 2580, 2323, 2084, 1958, 1820, 1641, 1566, 1462, 1447, 1383, 1364, 1284, 1241, 1158, 1125, 1091, 1060, 1025, 1015, 955, 929, 874, 760, 715, 702, 647, 580, 541, 505, 488, 441 cm^{-1}; Anal. calcd. for

[4] J. R. McCarthy, D. P. Matthews, J. P. Paolini. *Organic Syntheses, Coll. Vol. 9*, p. 446 (**1998**).

$C_9H_{11}OS^{79}Br$: C, 43.74, H, 4.49, S, 10.34, Br, 32.33; found: C, 43.82, H, 4.65, S, 10.30, Br, 32.48.

11b ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.13 − 1.27 (m, 2H), 1.28 − 1.44 (m, 2H), 1.51 − 1.62 (m, 1H), 1.63 − 1.77 (m, 2H), 1.79 − 1.86 (m, 1H), 1.87 − 1.97 (m, 1H), 2.05 − 2.16 (m, 1H), 2.86 − 2.96 (m, 1H), 7.31 − 7.38 (m, 1H), 7.50 − 7.58 (m, 2H), 7.76 − 7.81 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.8, 25.2, 25.3, 26.0, 27.6, 59.8, 119.5, 127.7, 127.9, 132.0, 132.9, 141.7; MS (EI) (*m/z*) (rel intensity): 41 (14), 55 (36), 83 (13), 96 (7), 125 (8), 156 (9), 158 (9), 204 (97), 206 (100), 207 (8); HRMS (EI): calcd. for $[M]^{+\bullet}$ ($C_{12}H_{15}OS^{79}Br$) 286.00270; found 286.00192; IR (film): *v* 3476, 3058, 2932, 2854, 2654, 2108, 1633, 1565, 1425, 1342, 1296, 1264, 1243, 1179, 1159, 1122, 1092, 1057, 1014, 992, 918, 892, 848, 759, 716, 647, 538, 511, 486, 442 cm^{-1}; Anal. calcd. for $C_{12}H_{15}OS^{79}Br$: C, 50.18, H, 5.26, S, 11.16, Br, 27.82; found: C, 50.09, H, 5.38, S, 11.36, Br, 27.61.

11c ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.28 (s, 9H), 7.31 − 7.40 (m, 1H), 7.46 − 7.55 (m, 1H), 7.56 − 7.61 (m, 1H), 7.77 − 7.86 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 23.2, 59.0, 122.6, 127.6, 128.9, 132.5, 133.0, 141.1; HRMS (ESI) (*m/z*): $[M + Na]^+$ calcd. for ($C_{10}H_{13}ONaS^{79}Br$) 282.97756; found 282.97627; IR (film): *v* 3467, 3059, 2976, 2927, 2900, 2865, 2609, 2328, 2090, 1958, 1821, 1633, 1564, 1472, 1447, 1425, 1363, 1391, 1363, 1281, 1245, 1169, 1127, 1090, 1048, 1015, 941, 870, 759, 715, 646, 563, 526, 464, 450 cm^{-1}; Anal. calcd. for $C_{10}H_{13}OS^{79}Br$: C, 45.99, H, 5.02, S, 12.28, Br, 30.59; found: C, 45.82, H, 4.95, S, 12.16, Br, 30.34.

11d ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.97 − 4.11, 4.24 − 4.37 (AB, J = 13 Hz, 2H, CH_2), 7.03 − 7.12 (m, 2H), 7.20 − 7.32 (m, 3H), 7.33 − 7.47 (m, 3H), 7.53 − 7.60 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 59.7, 118.8, 127.2, 128.1, 128.3, 129.4, 130.4, 132.2, 132.6, 142.4; MS (EI) (*m/z*) (rel intensity): 39 (2), 63 (2), 65 (8), 89 (2), 91 (100), 92 (8), 169 (2), 171 (2), 292 (5), 293 (8); HRMS (EI): calcd. for $[M]^{+\bullet}$ ($C_{13}H_{11}OS^{79}Br$) 293.97140; found 293.97079; IR (film): *v* 3448, 3061, 3030, 2922, 2852, 2320, 2108, 1947, 1812, 1602, 1566, 1495, 1446, 1433, 1323, 1285, 1244, 1198, 1158, 1126, 1092, 1071, 1057, 1015, 915, 869, 818, 757, 712, 697, 647, 616, 593, 507, 487, 468, 440 cm^{-1}; Anal. calcd. for $C_{13}H_{11}OS^{79}Br$: C, 52.89, H, 3.76, S, 10.86, Br, 27.07; found: C, 52.63, H, 3.82, S, 10.93, Br, 27.13.

11e ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.83 (s, 3H), 7.31 − 7.45 (m, 1H), 7.51 − 7.65 (m, 2H), 7.90 − 8.01 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 41.9, 118.4, 125.7, 128.7, 132.2, 132.9, 145.3; MS (EI) (*m/z*) (rel intensity): 45 (12), 50 (30), 74 (13), 75 (30), 76 (24), 96 (43), 108 (14), 139 (27), 155 (13), 157 (13), 171 (10), 175 (18), 177 (17), 203 (99), 204 (12), 205 (100), 218 (71), 220 (72); HRMS (EI): calcd. for $[M]^{+\bullet}$ ($C_7H_7OS^{79}Br$) 217.93914; found 217.94010; IR (film): *v* 3480, 3060, 2997, 2915, 2351, 2110, 1955, 1638, 1566, 1447, 1423, 1316, 1291, 1244, 1154, 1126, 1093, 1059, 1015, 915, 873, 758, 712, 100, 672, 646, 517, 481, 440 cm^{-1}; Anal. calcd. for $C_7H_7OS^{79}Br$: C, 38.37, H, 3.22, S, 14.63, Br, 36.47; found: C, 38.22, H, 3.39, S, 14.46, Br, 36.61.

11f ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.19 − 7.23 (m, 1H), 7.53 − 7.60 (m, 2H), 7.95 − 7.99 (m, 1H), 8.00 − 8.04 (m, 2H), 8.28 − 8.34 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 119.8, 124.4, 126.3, 126.5, 129.0, 133.0, 133.4, 144.3, 149.4, 151.9; MS (EI) (*m/z*) (rel intensity): 50 (58), 51 (12), 63 (21), 69 (20), 70 (11), 74 (21), 75 (53), 76 (55), 92 (10),

96 (30), 108 (100), 110 (10), 138 (13), 139 (16), 143 (27), 145 (24), 152 (30), 155 (24), 157 (23), 171 (42), 173 (41), 183 (12), 187 (87), 189 (90), 200 (18), 203 (39), 205 (38), 229 (15), 277 (13), 279(18), 325 (56), 327 (58); HRMS (EI): calcd. for $[M]^{+\bullet}$ ($C_{12}H_8O_3NS^{79}Br$) 324.94083; found 324.93997. IR (KBr): *v* 3100, 3083, 3058, 2855, 2455, 2101, 1942, 1811, 1687, 1627, 1602, 1566, 1524, 1469, 1448, 1431, 1395, 1363, 1342, 1314, 1245, 1160, 1122, 1095, 1076, 1055, 1006, 951, 866, 853, 760, 742, 720, 696, 680, 645, 604, 568, 545, 534, 507, 460, 440 cm^{-1}; Anal. calcd. for $C_{12}H_8O_3NS^{79}Br$: C, 44.19, H, 2.47, N, 4.29, S, 9.83, Br, 24.50; found: C, 44.37, H, 2.62, N, 4.38, S, 9.66, Br, 24.48; M.p. 88 − 90 ºC.

3.1.3. Synthesis of ligands 12a − f [5]

A solution of potassium vinyltrifluroborate (0.2 g, 1.5 mmol), $PdCl_2(PPh_3)_2$ (0.02 g, 0.03 mmol), PPh_3 (0.03g, 0.12 mmol), Cs_2CO_3 (1.46 g, 4.5 mmol) and suitable sulfoxide (1.5 mmol) in THF/H_2O (9 : 1 v/v) (7 mL) was heated at 85 ºC under argon atmosphere in Schlenk tube. The reaction mixture was stirred at this temperature for 22 h, then cooled to room temperature and diluted with H_2O (6 mL) followed by extraction with methylene chloride (3 × 10 mL). Organic phases were dried over $MgSO_4$. The solvent was removed in vacuo and the crude product was purified by silica gel column chromatography (using eluents: cyclohexane/ethyl acetate 10 : 1 to 1 : 1 v/v) to obtain a corresponding styrene (67 − 74% yield).

[5] G. A. Molander, A. R. Brown. *J. Org. Chem.* **2006,** *71*, 9681.

12a ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.03 − 1.10, 1.30 − 1.32 (AB, *J* = 7.0 Hz, 3H), 2.83-2.93 (septet, *J* = 7.1Hz, 1H), 5.36 − 5.43 (dd, *J* = 0.83, 11 Hz, 1H), 5.72 − 5.80 (dd, *J* = 0.96, 17.3 Hz, 1H), 6.93 − 7.02 (m, 1H), 7.44 − 7.58 (m, 2H), 7.86 − 7.89 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.1, 17.1, 53.2, 117.8, 124.8, 125.7, 128.3, 130.7, 131.6, 135.9, 139.8; MS (EI) (*m/z*) (rel intensity): 39 (8), 41 (9), 43 (11), 45 (8), 51 (7), 77 (11), 91 (21), 135 (100), 136 (11), 137 (10),152 (13), 194 (4·); HRMS (EI): calcd. for $[M]^{+\bullet}$ ($C_{11}H_{14}OS$): 194.07654; found 194.07703; IR (film): *v* 3686, 3603, 3411, 2982, 2933, 2870, 2543, 2049, 1969, 1940, 1856, 1727, 1628, 1606, 1562, 1465, 1440, 1414, 1384, 1366, 1193, 1158, 1125, 1069, 1024, 990, 956, 926, 891, 875, 638, 582, 549, 506 cm^{-1}; Anal. calcd. for $C_{11}H_{14}OS$: C, 68.00, H, 7.26, S, 16.50; found: C, 67.85, H, 7.51, S, 16.57.

12b ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.11 − 1.34 (m, 3H), 1.40 − 1.57 (m, 2H), 1.58 − 1.71 (m, 2H), 1.72 − 1.95 (m, 3H), 2.54 − 2.67 (m, 1H), 5.35 − 5.45 (dd, *J* = 0.92, 11 Hz, 1H), 5.72 − 5.84 (dd, *J* = 0.92, 17.2 Hz, 1H), 6.91 − 7.05 (m, 1H), 7.42 − 7.53 (m, 2H), 7.54 − 7.62 (m, 1H), 7.83 − 7.94 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 23.4, 24.1, 25.2, 25.3, 25.4, 25.7, 27.0, 117.7, 125.0, 125.6, 126.9, 128.3, 128.5, 130.7, 131.6, 136.1, 139.6; MS (EI) (*m/z*) (rel intensity): 41 (7), 55 (14), 77 (5), 83 (4), 91 (8), 134 (7), 135 (100), 136 (11), 137 (10), 152 (21); HRMS (EI): calcd. for $[M]^{+\bullet}$ ($C_{14}H_{18}OS$) 234.10784; found 234.10831; IR (film): *v* 3452, 3087, 3057, 3015, 2932, 2855, 2655, 1963, 1841, 1626, 1589, 1561, 1465, 1451, 1413, 1343, 1296, 1265, 1193, 1179, 1158, 1124, 1064, 1034, 991, 920, 892, 848, 772, 745, 698, 678, 646, 576, 544, 517, 489, 442, 421 cm^{-1}; Anal. calcd. for $C_{14}H_{18}OS$: C, 71.75, H, 7.74, S, 13.68; found: C, 71.89, H, 7. 81, S, 13.49.

12c ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.18 (s, 9H), 5.29 − 5.44 (dd, *J* = 0.92, 11 Hz, 1H), 5.68 − 5.84 (dd, *J* = 0.92, 17.4 Hz, 1H), 7.05 − 7.23 (m, 1H), 7.36 − 7.53 (m, 2H), 7.55 −

7.67 (m, 1H), 7.82 − 7.95 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 23.2, 116.8, 125.4, 126.3, 127.9, 131.0, 132.8, 138.0, 138.1; HRMS (ESI) (*m/z*): $[M + Na]^{+\bullet}$ calcd. for ($C_{12}H_{16}ONaS^{79}$) 231.08141; found 231.908148; IR (film): *v* 3468, 3087, 3059, 3015, 2978, 2927, 2901, 2866, 2083, 1959, 1841, 1627, 1589, 1466, 1414, 1391, 1364, 1309, 1275, 1195, 1171, 1124, 1060, 1033, 991, 920, 773, 745, 698, 678, 646, 567, 539, 464, 450 cm^{-1}; Anal. calcd. for $C_{12}H_{16}OS$: C, 69.19, H, 7.74, S, 15.39; found: C, 69.38, H, 7.78, S, 15.12.

12d ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.91 − 3.99, 4.01 − 4.10 (AB, *J* = 12.9 Hz, 2H, CH_2), 5.31 − 5.37 (dd, *J* = 1.0, 11 Hz, 1H), 5.65 − 5.73 (dd, *J* = 0.93, 17.2 Hz, 1H), 6.80 − 6.89 (m, 1H), 6.93 − 6.98 (m, 2H), 7.18 − 7.22 (m, 1H), 7.23 − 7.24 (m, 1H), 7.25 − 7.27 (m, 2H), 7.34 − 7.39 (m, 1H), 7.40 − 7.45 (m, 1H), 7.48 − 7.50 (m, 1H), 7.60 − 7.62 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 24.1, 25.4, 61.3, 65.3, 118.0, 124.2, 125.5, 127.9, 127.6, 128.3, 128.5, 129.3, 130.3, 130.9, 135.7, 140.1; MS (EI) (*m/z*) (rel intensity): 39 (2), 45 (2), 65 (7), 77 (2), 89 (2), 91 (100), 92 (6), 134 (3), 135 (8), 225 (3), 242 (10); HRMS (EI): calcd. for $[M]^{+\bullet}$ ($C_{15}H_{14}OS$) 242.07654; found 242.07544; IR (film): *v* 3420, 3086, 3061, 3030, 2980, 2928, 2854, 2627, 2091, 1949, 1835, 1748, 1627, 1603, 1585, 1563, 1495, 1466, 1454, 1413, 1365, 1310, 1292, 1231, 1194, 1158, 1127, 1074, 1062, 1036, 987, 923, 887, 769, 743, 698, 618, 594, 577, 520, 495, 470, 411, 436 cm^{-1}; Anal. calcd. for $C_{15}H_{14}OS$: C, 74.34, H, 5.82, S, 13.23; found: C, 74.27, H, 5.72, S, 13.39.

12e ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.7 (s, 3H), 5.34 − 5.53 (dd, *J* = 0.92, 11 Hz, 1H), 5.67 − 5.88 (dd, *J* = 0.92, 17.2 Hz, 1H), 6.82 − 7.00 (m, 1H), 7.39 − 7.64 (m, 3H), 7.94 − 8.07 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 42.4, 118.5, 122.8, 125.9, 129.1, 130.9, 131.1, 134.9, 143.0; MS (EI) (*m/z*) (rel intensity): 39 (17), 45 (100), 50 (19), 51 (45), 63

(16), 75 (10), 76 (11), 77 (50), 79 (15), 89 (12), 91 (54), 102 (15), 116 (12), 123 (77), 134 (48), 135 (40), 136 (12), 137 (16), 138 (87), 149 (17), 151 (28), 166 (71), 167 (10); HRMS (EI): calcd. for $[M]^{+\bullet}$ ($C_9H_{10}OS$) 166.04524; found 166.04556; IR (film): *v* 3469, 3057, 2997, 2914, 1852, 2095, 1959, 1847, 1627, 1564, 1466, 1447, 1415, 1294, 1244, 1194, 1158, 1126, 1092, 1069, 1034, 1016, 988, 951, 935, 772, 744, 713, 682, 669, 646, 575, 525, 483, 439 cm^{-1}; Anal. calcd. for $C_9H_{10}OS$: C, 65.02, H, 6.06, S, 19.29; found: C, 64.93, H, 6.29, S, 19.36.

12f ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.48-5.55 (dd, *J* = 0.83, 11 Hz, 1H), 5.76 − 5.84 (dd, *J* = 0.80, 17.2 Hz, 1H), 7.28 − 7.35 (m, 1H), 7.42 − 7.51 (m, 2H), 7.56 − 7.61 (m, 1H), 7.76 − 7.81 (m, 2H), 7.84 − 7.88 (m, 1H), 8.24 − 8.29 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 119.2, 124.3, 124.6, 125.5, 126.6, 129.4, 131.5, 131.9, 136.5, 141.7, 149.0, 152.8; MS (EI) (*m/z*) (rel intensity): 45 (9), 51 (10), 77 (39), 91 (19), 137 (100), 184 (14), 197 (11), 210 (12), 256 (17), 273 (26); HRMS (EI): calcd. for $[M]^{+\bullet}$ ($C_{14}H_{11}O_3NS$) 273.04597; found 273.04627; IR (KBr): *v* 3444, 3098, 3077, 3054, 3024, 2966, 2852, 2441, 1968, 1938, 1861, 1823, 1724, 1626, 1601, 1578, 1525, 1467, 1436, 1414, 1395, 1371, 1339, 1318, 1261, 1192, 1163, 1126, 1104, 1088, 1059, 1037, 1020, 1004, 985, 953, 926, 860, 852, 829, 802, 771, 748, 738, 720, 683, 648, 622, 574, 551, 516, 489, 475, 435, 421, 407 cm^{-1}; Anal. calcd. for $C_{14}H_{11}O_3NS$: C, 61.52, H, 4.06, N, 5.12, S, 11.73; found: C, 61.32, H, 4.19, N, 5.32, S, 11.67. M.p. 84 − 86 ºC.

3.2. Synthesis of catalysts

3.2.1. Synthesis of catalyst 13a

A Schlenk tube equipped with a stirring bar charged with ruthenium complex **Ind-II** (0.15 g, 0.2 mmol) and CuCl (0.039g, 0.4 mmol). The tube was flushed with argon and charged with anhydrous toluene (10 mL). Styrene **12a** (0.078g, 0.4 mmol) in anhydrous toluene (5 mL) was added and the resulting mixture was stirred at 80 °C for 30 minutes. After this time, TLC indicated complete conversion of the substrate. The resulting mixture was concentrated in vacuo, and the residue was re-dissolved in AcOEt and the solution was passed through a Paster pipette containing a small amount of cotton and evaporated to dryness. Concentrated crude mixture was purified by column chromatography (using eluents: cyclohexane/ethyl acetate 10 : 1 to 1 : 1 v/v). The solid was collected and washed a few times with AcOEt and with cold *n*-pentane (0.094 g, 0.14 mmol, yield 72%).

13a, green crystals. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.05 (m, 6H), 2.29 (m, 3H), 2.35 − 2.45 (m, 12H), 2.55 (s, 6H), 3.61 (septet, J = 6.7 Hz, 1H), 4.15 (s, 4H), 6.74 (m, 1H), 6.95 − 7.05 (m, 4H), 7.34 (m, 1H), 7. 65 − 7.70 (m, 1H) 7.72 − 7.78 (m, 1H), 16.81 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 21.0, 51.7, 121.0, 127.5, 128.9, 129.4, 129.6, 129.7, 133.9, 135.4, 138.1, 138.5, 138.9, 139.0, 156.2, 207.2, 301.3; HRMS (ESI) (*m/z*): 658 $[M–Cl+CH_3CN]^{+\bullet}$. The molecular formula was confirmed by comparing the theoretical and experimental isotope patterns, which were found to be identical within the experimental error limits; IR (KBr): *v* 3447, 2963, 2917, 2738, 1702, 1628, 1607, 1482, 1439, 1380, 1264, 1227, 1183, 1158, 1121, 1105, 1037, 992, 950, 932, 852, 803, 751, 697, 635, 593, 578, 535, 506, 446, 418 cm^{-1}; Anal. calcd. for $C_{31}H_{38}Cl_2ON_2RuS$: C, 56.53, H, 5.81, N, 4.87, S, 4.87, Cl, 10.76; found: C, 56.32, H, 5.79, N, 4.51, S, 5.01, Cl, 10.68.

3.2.2. General synthesis of catalysts 20a − f

A Schlenk tube equipped with a stirring bar charged with ruthenium catalyst (**Ind−II'**) (0.17 g, 0.2 mmol) and CuCl (0.03 g, 0.24 mmol). The tube was flushed with argon and charged with anhydrous toluene (10 mL). A corresponding styrene (0.4 mmol) in anhydrous toluene (5 mL) was added. The resulted solution was stirred at 80 ºC for 20 - 30 minutes. After this all manipulations can be done without a protective atmosphere of argon. The resulting mixture was concentrated in vacuum, and the residue was re-dissolved in AcOEt and the solution was passed through a Paster pipette containing a small amount of cotton and evaporated to dryness. Concentrated crude mixture was purifed by column chromatography (using eluents: cyclohexane/ethyl acetate 10 : 1 to 1 : 1 v/v). The solid was collected and washed a few times with mixture of solvents: AcOEt or methylene chloride with cold *n*-pentane (yield 33 - 60%).

20a, green crystals, yield 60% ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.96 − 1.00 (m, 3H), 1.10 − 1.14 (m, 3H), 1.25 − 1.35 (m, 2H), 2.32 − 2.36 (m, 10H), 2.42 − 2.44 (m, 8H), 3.58 − 3.62 (m, 1H), 7.00 − 7.05 (m, 3H), 7.12 − 7.14 (m, 2H), 7.32 − 7.38 (m, 1H), 7.62 − 7.66 (m, 1H), 7.76 − 7.78 (m, 1H). 16.88 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 18.9, 21.0, 21.1, 26.3, 52.2, 53.2, 120.7, 122.2, 124.6, 124.8, 127.3, 128.3, 128.5, 129.0, 129.4, 129.5, 133.8, 134.5, 135.0, 135.8, 137.2, 137.5, 139.5, 156.4, 176.2, 298.5; MS (FD/FI; *m/z*): $[M]^+$ 656.03883 (calcd. 656.03865); IR (KBr): *ν* 3374, 3161, 3120, 3091, 2920, 2854, 2737, 1736, 1643, 1607, 1563, 1486, 1443, 1398, 1381, 1363, 1314, 1263, 1228, 1162, 1162, 1121, 1106, 1037, 973, 962, 853, 801, 745, 700, 637, 593, 577, 535, 508, 479, 448 cm^{-1}; Anal. calcd. for $C_{31}H_{38}Cl_2ON_2RuS$: C, 56.70, H, 5.53, N, 4.27, S, 4.88, Cl, 10.80; found: C, 56.60, H, 5.45, N, 4.31, S, 4.79, Cl, 10.61.

20b, light green crystals, yield 57% ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.90 − 1.90 (m, 11H), 2.08 − 2.12 (m, 2H), 2.32 − 2.36 (m, 10H), 2.42 − 2.46 (m, 8H), 6.74 − 6.80 (m, 1H), 7.00 − 7.20 (m, 4H), 7.32 − 7.38 (m, 1H), 7.60 − 7.66 (m, 1H), 7.74 − 7.78 (m, 1H), 16.88 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 17.7, 18.8, 18.9, 21.0, 21.1, 25.2, 25.3, 25.4, 26.0, 59.9, 120.4, 122.2, 124.6, 127.5, 128.3, 129.1, 129.4, 129.5, 129.9, 133.5, 134.5, 135.0, 136.1, 137.2, 137.5, 139.5, 140.1, 156.5, 176.3, 300.5; MS (FD/FI; *m/z*): $[M]^+$ 696.18983 (calcd. 696.18965); IR (KBr): *v* 3432, 3161, 3124, 3094, 3061, 2922, 2853, 2738, 1941, 1734, 1643, 1607, 1485, 1447, 1397, 1381, 1341, 1313, 1263, 1229, 1163, 1119, 1105, 1042, 997, 972, 962, 925, 892, 852, 801, 770, 744, 701, 592, 578, 546, 500, 462, 449 cm^{-1}; Anal. calcd. for $C_{34}H_{40}Cl_2ON_2RuS$: C, 58.61, H, 5.79, N, 4.02, S, 4.60, Cl, 10.18; found: C, 58.37, H, 5.59, N, 4.27, S, 4.62, Cl, 10.28.

20c, dark green crystals, yield 57% ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.90 − 1.0 (m, 9H), 2.10 − 2.46 (m, 18H), 6.70 − 6.72 (m, 2H), 7.02 − 7.06 (m, 4H), 7.10 − 7.14 (m, 2H), 7.30 − 7.34 (m, 1H), 7.58 − 7.62 (m, 1H), 7.72 − 7.76 (m, 1H), 16.99 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 14.2, 18.7, 18.9, 21.1, 23.5, 23.6, 60.3, 63.5, 119.0, 124.7, 124.8, 126.9, 127.9, 129.1, 129.2, 129.4, 129.5 133.0, 136.5, 137.3, 137.4, 139.4, 141.4, 157.6, 174.7, 304.9; MS (FD/FI; *m/z*): $[M]^+$ 670.71237 (calcd. 670.71185); IR (KBr): *v* 3453, 2916, 2853, 2734, 1936, 1732, 1668, 1628, 1606, 1590, 1573, 1496, 1481, 1416, 1401, 1378, 1262, 1211, 1175, 1154, 1132, 1093, 1034, 914, 850, 833, 789, 773, 697, 645, 591, 578, 512, 467, 426, 414 cm^{-1}; Anal. calcd. for $C_{32}H_{38}Cl_2ON_2RuS$: C, 57.30, H, 5.71, N, 4.18, S, 4.78, Cl, 10.57; found: C, 57.24, H, 5.79, N, 4.37, S, 4.62, Cl, 10.81.

20d, green crystals, yield 57% ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.10 − 2.26 (m, 12H), 2.33 − 2.34 (m, 6H), 2.35 − 2.45 (m, 2H), 3.98 − 4.01, 4.72 − 4.75 (m, AB, 2H, CH_2),

6.95 − 6.99 (m, 1H), 7.04 − 7.06 (m, 1H), 7.08 − 7.09 (m, 1H), 7.14 − 7.19 (m, 6H), 7.22 − 7.23 (m, 2H), 7.24 − 7.25 (m, 3H), 7.26 − 7.30 (m, 2H), 7.30 − 7.32 (m, 1), 16.88 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 17.7, 18.9, 21.1, 21.2, 57.0, 120.9, 122.2, 124.8, 127.3, 128.0, 128.1, 128.4, 128.9, 129.2, 129.5, 129.6, 131.9, 134.1, 134.5, 137.2, 137.4, 139.5, 139.6, 155.0, 175.9, 297.7; MS (FD/FI; *m/z*): $[M]^+$ 704.74590 (calcd. 704.74513); IR (KBr): *v* 3441, 3160, 3060, 3027, 2976, 2946, 2915, 2855, 2736, 2618, 2415, 1947, 1776, 1755, 1722, 1700, 1676, 1607, 1581, 1543, 1486, 1454, 1445, 1399, 1380, 1341, 1314, 1283, 1264, 1234, 1163, 1143, 1108, 1076, 1035, 962, 930, 900, 863, 800, 764, 743, 701, 641, 605, 592, 577, 523, 479, 466, 447, 421 cm^{-1}; Anal. calcd. for $C_{35}H_{36}Cl_2ON_2RuS$: C, 59.65, H, 5.15, N, 3.98, S, 4.55, Cl, 10.06; found: C, 59.60, H, 5.02, N, 3.73, S, 4.32, Cl, 10.24.

20e, dark green crystals, yield 33% ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.26-2.30 (m, 12H), 2.44 (s, 6H), 2.97 (s, 3H), 6.78 − 6.80 (m, 1H), 7.04 − 7.08 (m, 4H), 7.14 − 7.19 (m, 2H), 7.36 − 7.38 (m, 2H), 7.70 − 7.72 (m, 1H), 7.84 − 7.86 (m, 1H), 16.81 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 14.1, 18.7, 18.7, 18.9, 20.9, 21.1, 40.9, 60.2, 121.1, 124.8, 124.9, 129.1, 129.5, 129.6, 129.8, 134.2, 135.9, 137.1, 137.3 139.6, 141.8, 154.6, 171.0, 175.8, 296.6; MS (FD/FI; *m/z*): $[M]^+$ 628.36950 (calcd. 628.36941); IR (KBr): *v* 3412, 3162, 3123, 3092, 2984, 2922, 2859, 2738, 1775, 1729, 1700, 1605, 1564, 1484, 1459, 1443, 1396, 1312, 1264, 1227, 1120, 1108, 1051, 1039, 954, 926, 853, 798, 754, 716, 701, 669, 589, 540, 466, 442, 420, 404 cm^{-1}; Anal. calcd. for $C_{29}H_{32}Cl_2ON_2RuS$: C, 55.41, H, 5.13, N, 4.46, S, 5.10, Cl, 11.28; found: C, 55.32, H, 5.19, N, 4.35, S, 5.26, Cl, 11.18.

20f, light green crystals, yield 60% ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.10 − 2.22 (m, 6H), 2.31 − 2.43 (m, 12H), 6.84 − 6.88 (m, 1H), 7.00 − 7.10 (m, 5H), 7.14 − 7.18 (m, 2H),

7.28 − 7.30 (m, 2H), 7.31 − 7.33 (m, 1H), 7.46 − 7.50 (m, 1H), 7.60 − 7.64 (m, 2H), 8.04 − 8.08 (m, 2H), 16.77 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 17.7, 18.8, 21.2, 22.3, 26.1, 26.9, 27.8, 29.9, 121.1, 122.3, 124.1, 125.1, 126.8, 128.9, 129.2, 129.6, 130.2, 131.4, 134.5, 134.8, 135.9, 137.0, 137.4, 139.7, 141.9, 145.5, 148.9, 156.4, 173.9, 295.0; MS (FD/FI; *m/z*): $[M]^+$ 735.10708 (calcd. 628.10297); IR (KBr): *v* 3444, 3165, 3131, 3098, 3060, 3024, 2918, 2857, 2737, 1698, 1644, 1604, 1581, 1526, 1485, 1455, 1443, 1397, 1381, 1344, 1312, 1264, 1224, 1165, 1128, 1103, 1081, 1067, 1036, 1011, 972, 961, 925, 852, 796, 743, 724, 699, 680, 593, 555, 514, 455, 419, 404 cm^{-1}; Anal. calcd. for $C_{34}H_{33}Cl_2O_3N_3RuS$: C, 55.51, H, 4.52, N, 5.71, S, 4.36, Cl, 9.64; found: C, 55.67, H, 4.69, N, 4.48, S, 4.51, Cl, 9.82.

3.3. General procedure for preparative RCM reactions of using 13a and 20a-f.

At 24 ºC and 40 ºC: Cyclization of *N*,*N*-diallyltosylamine **14** was used as a test to compare the activity of catalysts in methylene chloride at 24 ºC and at 40 ºC. Typically 1 mol % of the catalyst (0.008 mmol) was added to a solution of substrate (0.150 mmol) and an internal standard in 7.5 mL methylene chloride at 24 ºC and at 40 ºC. The reaction was running at 24 ºC and at 40 ºC under argon and samples were taken after 5 min, 10 min, 20 min, 30 min, 1 h, 2 h, 4 h, 6 h, 24 h and analyzed by TLC and GC.

At 40 ºC: Cycloisomerisation of enyne **18** was used as a test to compare the activity of catalysts in methylene chloride at 40 ºC. Typically 5 mol % of the catalyst (0.008 mmol) was added to a solution of substrate (0.150 mmol) and an internal standard in 7.5 mL or methylene chloride at 40 ºC. The reaction was running at 40 ºC under argon and samples

were taken after 1 h, 2 h, 4 h, and analyzed by GC. The same procedure was applied for cyclization of *N*,*N*-diallyltosylamine, using 1 mol % of the catalysts (0.003 mmol, 0.25 mmol substrate scale and 12.5 mL of solvent). The reaction was running at 40 ºC under argon and samples were taken after 5 min, 10 min, 20 min, 30 min, 1 h, 1.5 h, 2 h, 4 h and analyzed by TLC and GC.

At 80 ºC: Cyclization of diethylallyl(2-methylallyl)malonate **16** was used as a test to compare the activity of catalysts in toluene at 80 ºC. Typically 5 mol % of the catalyst (0.005 mmol) was added to a solution of substrate (0.1 mmol) and an internal standard in 5 mL of solvent at 80 ºC. The reaction was running at 80 ºC under argon and samples were taken after 5 min, 10 min, 20 min, 30 min, 1 h, 2 h, 4 h, 6 h and analyzed by GC.

At 110 ºC: Typically 1 mol % of the catalyst (0.0035 mmol) was added to the solution of substrate diethyldi(2-methylallyl)malonate (3.5 mmol) **21** and an internal standard in 45 mL of toluene at RT. The reaction was running at 110 °C under argon atmosphere for 6 h and samples were taken for GC after: 5 min, 10 min, 15 min, 30 min, 1 h, 2 h, 3 h, 4 h, 5 h, 6 h and 20 h.

3.4. Results for preparative RCM reactions of using 20a-f.

Table 1. Kinetic measurements (conversions) of RCM reaction of *N*,*N*-diallyltosylamine in CH_2Cl_2 at 40 ºC (presented as a plot in article).

Time [h]	**20a**	**20b**	**20c**	**20d**	**20e**	**20f**
2 h	0	0	0	0	0	2
4 h	19	16	24	9	12	28
6 h	41	32	47	19	26	57

|**Table 2.** Kinetic measurements (conversions) of RCM reaction of diethyl(methylallyl)-malonate in toluene at 80 ºC (presented as a plot in article).

Time [h]	**20a**	**20b**	**20c**	**20d**	**20e**	**20f**
0.08 h	0	0	2	0	0	3
0.17 h	0	0	34	0	0	37
0.33 h	3	2	57	2	5	54
0.5 h	9	6	72	5	7	77
1 h	18	16	79	78	13	85
2 h	30	28	87	12	18	91
4 h	32	30	92	13	19	99
6 h	32	31	92	13	19	99

Table 3. Kinetic measurements (conversions) of RCM reaction of 2,2-diphenyl-3-vinyl-2,5-dihydrofuran in CH_2Cl_2 at 40 ºC (presented as a plot in article).

Time [h]	**20a**	**20b**	**20c**	**20d**	**20e**	**20f**
0.08 h	5	4	5	2	3	6
0.17 h	12	10	13	5	9	13
0.33 h	29	29	32	7	24	35
0.5 h	46	41	49	9	31	53
1 h	60	55	82	14	41	88
1.25 h	65	60	89	17	46	96
1.5 h	69	63	92	20	50	99
2 h	70	66	95	23	55	99
4 h	71	68	95	23	56	99