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Wingtip substituents tailor the catalytic activity of ruthenium triazolylidene complexes in base-free alcohol oxidation

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1. Experimental procedures for the synthesis of the triazolium salts 1a–m

General. Butyl azide,[S1] 1-4-dihexyl-1,2,3-triazole,[S2] and the triazolium salts **1f**, **1h**, **1i**,[S3] were synthesized as described previously. All other reagents are commercially available and were used as received. Microwave reactions were carried out using a Biotage Initiator 2.5, operating at 100 W irradiation power.

1-ethyl-4-butyl-1,2,3-triazole. To a solution of ethyl azide, generated in situ by mixing iodoethane (3.73 g, 23.8 mmol) and sodium azide (6.22 g, 95.7 mmol) in *t*BuOH/H_2O (100 mL, 1:1 v/v) at RT for 48 h, was added 1-hexyne (1.95 g, 23.8 mmol), aqueous $CuSO_4$ (1 M, 5.1 mL, 5.1 mmol), and Cu powder (60 mg, 0.94 mmol). The reaction mixture was stirred for 15 h at 100 °C. Most *t*BuOH was evaporated under reduced pressure and the residue was extracted with CH_2Cl_2 (3 × 70 mL). The combined organic phases were washed with NH_4OH (25%, 2 × 50 mL), H_2O (2 × 100 mL), and, brine

(2 × 100 mL), dried over $MgSO_4$ and evaporated to dryness. The residue was washed with pentane (50 mL) and purified over a small pad of SiO_2. Elution with Et_2O afforded the title product as pale yellow oil (2.76 g, 76 %). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.28 (s, 1H, H_{trz}), 4.37 (q, $^3J_{HH}$ = 7.4 Hz, 2H, NCH_2), 2.72 (t, $^3J_{HH}$ = 7.3 Hz, 2H, C_{trz}–CH_2), 1.64 (quint, $^3J_{HH}$ = 7.3 Hz, 2H, C_{trz}–CH_2CH_2), 1.53 (t, $^3J_{HH}$ = 7.4 Hz, 3H, NCH_2CH_3), 1.38 (sext, $^3J_{HH}$ = 7.3 Hz, 2H, $CH_2CH_2CH_3$), 0.92 (t, $^3J_{HH}$ = 7.3 Hz, 3H, $CH_2CH_2CH_3$). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 148.8 (C_{trz}–Bu), 120.1 (C_{trz}–H), 45.4 (NCH_2), 31.8 (C_{trz}–CH_2), 25.6 (C_{trz}–CH_2CH_2), 22.5 (C_{trz}–$CH_2CH_2CH_2$), 15.7 (NCH_2CH_3), 14.0 ($CH_2CH_2CH_3$). Anal. Calcd for $C_8H_{15}N_3$ (153.13) × 1/8 H_2O: C, 61.80; H, 9.89; N, 27.03. Found: C, 61.67; H, 10.02; N, 26.90

1-butyl-4-mesityl-1,2,3-triazole. Freshly synthesized butyl azide (450 mg, 4.53 mmol), and 1-ethynyl-mesitylene (720 mg, 4.99 mmol) were suspended in a mixture of water (7.0 mL) and THF (7.0 mL). Copper sulfate (20 mg, 0.09 mmol), and sodium ascorbate (180 mg, 0.90 mmol) were added and the mixture was stirred for 6 h at 100 °C under microwave irradiation. All volatiles were evaporated off and and the residue was extracted with CH_2Cl_2 (2 × 20 mL). The combined organic phases were washed with aqueous NH_4OH (25%, 2 × 20 mL), H_2O (2 × 50 mL), and brine (2 × 30 mL), dried over $MgSO_4$ and evaporated to dryness. The residue was washed with pentane (50 mL) to afford a red oil, which was filtered over a small pad of SiO_2. Elution with Et_2O gave the triazole as pale orange oil (700 mg, 60%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.40 (s, 1H, H_{trz}), 6.93 (s, 2H, H_{Mes}), 4.42 (t, $^3J_{HH}$ = 7.2 Hz, 2H, NCH_2), 2.31 (s, 3H, Mes–CH_3), 2.10 (s, 6H, Mes–CH_3), 1.95 (quint, 2H, $^3J_{HH}$ = 7.2 Hz, NCH_2CH_2), 1.38 (sext, $^3J_{HH}$ = 7.2 Hz, 2H, CH_2CH_3), 0.96 (t, $^3J_{HH}$ = 7.2 Hz, 2H, CH_2CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 145.7 (C_{trz}–Mes), 138.2, 137.9, 128.5, 127.5 (4 × C_{Mes}), 122.4 (C_{trz}–H), 50.2 (NCH_2), 31.3 (NCH_2CH_2), 21.3, 20.8 (2 × Mes–CH_3), 19.9 (CH_2CH_3), 13.7 (CH_2CH_3). Anal. Calcd for $C_{15}H_{21}N_3$ (243.34): C, 74.03; H, 8.70; N, 17.27. Found: C, 74.14; H, 8.75; N, 16.90.

General procedure for the synthesis of the triazolium iodides 1. To a MeCN solution of triazole was added MeI and the mixture was stirred under microwave irradiation at 90 °C for 5 h. All volatiles

were then removed in vacuo. The residue was washed with copious amounts of Et_2O several times and dried in vacuo to afford the crude triazolium salt **1**. Microanalytically pure samples were obtained by recrystallization from hot acetone.

1-ethyl-3-methyl-4-butyl-1,2,3-triazolium iodide 1a. Reaction of 1-ethyl-4-butyl-1,2,3-triazole (1.48 g, 9.68 mmol) and CH_3I (13.7 g, 96.8 mmol) in MeCN (8 mL) according to the general procedure gave **1a** as a yellow oil (2.50 g, 88%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.91 (s, 1H, H_{trz}), 4.71 (q, $^3J_{HH}$ = 7.4 Hz, 2H, NCH_2), 4.23 (s, 3H, NCH_3), 2.89 (m, 2H, C_{trz}–CH_2), 1.71 (quint, $^3J_{HH}$ = 7.3 Hz, 2H, C_{trz}–CH_2CH_2), 1.61 (t, $^3J_{HH}$ = 7.4 Hz, 3H, NCH_2CH_3), 1.40 (sext, $^3J_{HH}$ = 7.3 Hz, 2H, C_{trz}–$CH_2CH_2CH_2$), 0.89 (t, $^3J_{HH}$ = 7.3 Hz, 3H, C_{trz}–CH_2CH_2 CH_2CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz): δ 144.6 (C_{trz}–Bu), 128.9 (C_{trz}–H), 49.9 (NCH_2), 38.9 (NCH_3), 29.1 (C_{trz}–CH_2), 23.7 (C_{trz}–CH_2CH_2), 22.1 (C_{trz}–$CH_2CH_2CH_2$), 14.7 (NCH_2CH_3), 13.7 (C_{trz}–$CH_2CH_2CH_2CH_3$). Anal. Calcd for $C_9H_{18}IN_3$ (295.16): C, 36.62; H, 6.15; N, 14.24. Found: C, 36.72; H, 6.33; N, 13.92

1,4-dihexyl-3-methyl-1,2,3-triazolium iodide 1c. Reaction of 1,4-dihexyl-1,2,3-triazole (1.00 g, 4.21 mmol) and CH_3I (6.0 g, 42.12 mmol) in MeCN (10 mL) according to the general procedure gave **1c** as a yellow oil (1.4 g, 88%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 9.00 (s, 1H, H_{trz}), 4.63 (t, $^3J_{HH}$ = 7.4 Hz, 2H, NCH_2), 4.24 (s, 3H, NCH_3), 2.88 (m, 2H, C_{trz}-CH_2), 1.95 (quint, $^3J_{HH}$ = 7.4 Hz, 2H, NCH_2CH_2), 1.70 (quint, $^3J_{HH}$ = 7.7 Hz, 2H, C_{trz}-CH_2CH_2), 1.36 (m, 12H, CH_2 $_{hex}$), 0.80 (m, 6H, CH_3 $_{hex}$). ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz): δ 144.7 (C_{trz}–hex), 129.2 (C_{trz}–H), 54.4 (NCH_2), 38.9 (NCH_3), 31.2, 30.9, 29.4, 28.7, 27.2, 25.7, 24.0, 22.4, 22.3 (9 × CH_2, Hex), 14.0, 13.9 (2 × CH_3, Hex)

1-butyl-3-methyl-4-mesityl-1,2,3-triazolium iodide 1g. Reaction of 1-butyl-4-mesityl-1,2,3-triazole (1.00 g, 4.10 mmol) and CH_3I (5.4 g, 41 mmol) in MeCN (12 mL) according to the general procedure gave **1g** as a yellow solid (1.19 g, 75%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 9.51 (s, 1H, H_{trz}), 6.97 (s, 2H, H_{Mes}), 4.97 (t, $^3J_{HH}$ = 7.4 Hz, 2H, NCH_2), 3.98 (s, 3H, NCH_3), 2.31 (s, 3H, Mes–CH_3), 2.08 (m, 2H, NCH_2CH_2), 2.03 (s, 6H, Mes–CH_3), 1.42 (sext, $^3J_{HH}$ = 7.4 Hz, 2H, CH_2CH_3), 0.96 (t, $^3J_{HH}$ = 7.4 Hz, 2H, CH_2CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz): δ 142.6 (C_{trz}–Mes), 141.6, 138.2, 129.5, 128.4,

127.6, 117.6 (6 × C_{Mes}), 131.0 (C_{trz}–H), 54.8 (NCH_2), 38.1 (NCH_3), 31.3 (NCH_2CH_2), 21.4, 20.1 (2 × Mes–CH_3), 19.5 (CH_2CH_3), 13.5 (CH_2CH_3). Anal. Calcd for $C_{16}H_{24}IN_3$ (385.29): C, 49.88; H, 6.28; N, 10.91. Found: C, 49.59; H, 5.99; N, 11.20

Synthesis of (1-methyl-3-ethyl-4-phenyl-1,2,3-triazolium iodide) 1k. To a solution of 1-methyl-4-phenyl-1,2,3-triazole (800 mg, 5.0 mmol) in MeCN (20 mL) was added EtI (3.9 g, 25 mmol) and the mixture was heated to 75 °C for 48 h. All volatiles were then removed in vacuo. The solid residue was washed with Et_2O several times, and then dried recrystallized from acetone (1.10 g, 70%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 9.39 (s, 1H, H_{trz}), 7.65 (m, 2H, H_{ar}), 7.55 (m, 3H, H_{ar}), 4.57 (q, $^3J_{HH}$ = 7.4 Hz, 2H, NCH_2), 4.53 (s, 3H, NCH_3), 1.58 (t, $^3J_{HH}$ = 7.4 Hz, 3H, NCH_2CH_3). ^{13}C{1H} NMR ($CDCl_3$, 125 MHz): δ 142.4 (C_{trz}–Ph), 131.9, 130.9 (2 × C_{Ph}), 129.8 (C_{trz}–H), 129.7, 121.8 (2 × C_{Ph}), 47.7 (NCH_2), 41.5 (NCH_3), 14.4 (NCH_2CH_3). Anal. Calcd for $C_{11}H_{14}IN_3$ (315.53): C, 41.92; H, 4.48; N, 13.33. Found: C, 41.85; H, 4.55; N, 13.28.

Synthesis of (1,3-diethyl-4-phenyl-1,2,3-triazolium iodide) 1l. To a solution of 1-ethyl-4-phenyl-1,2,3-triazole (800 mg, 4.6 mmol) in MeCN (20 mL) was added EtI (3.6 g, 23 mmol) and the mixture was heated to 75 °C for 48 h. All volatiles were then removed in vacuo. The solid residue was washed with diethyl ether several times, then dried and finally recrystallized from acetone (1.20 g, 79%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 9.45 (s, 1H, H_{trz}), 7.69 (m, 2H, H_{Ph}), 7.53 (m, 3H, H_{Ph}), 4.87 (q, $^3J_{HH}$ = 7.4 Hz, 2H, NCH_2), 4.59 (q, $^3J_{HH}$ = 7.3 Hz, 2H, NCH_2), 1.71 (t, $^3J_{HH}$ = 7.4 Hz, 3H, NCH_2CH_3), 1.57 (t, $^3J_{HH}$ = 7.3 Hz, 3H, NCH_2CH_3). ^{13}C{1H} NMR ($CDCl_3$, 125 MHz): δ 142.4 (C_{trz}–Ph), 131.8, 130.6 (2 × C_{Ph}), 129.7 (C_{trz}–H), 129.1, 121.8 (2 × C_{Ph}), 50.2, 47.8 (2 × NCH_2), 14.7, 14.4 (2 × NCH_2CH_3). Anal. Calcd for $C_{12}H_{16}IN_3$ (329.18): C, 43.78; H, 4.90; N, 12.77. Found: C, 43.74; H, 4.97; N, 12.73.

Synthesis of (1-butyl-3-ethyl-4-phenyl-1,2,3-triazolium iodide) 1m. To a solution of 1-butyl-4-phenyl-1,2,3-triazole (800 mg, 4.0 mmol) in MeCN (20 mL) was added EtI (3.1 g, 20 mmol) and the mixture was heated to 75 °C for 48 h. All volatiles were then removed in vacuo. The solid residue was washed with diethyl ether several times, and dried. Pure **1m** was obtained by recrystallization from

CH_2Cl_2 (727 mg, 51%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 9.52 (s, 1H, H_{trz}), 7.69 (m, 2H, H_{Ph}), 7.55 (m, 3H, H_{Ph}), 4.84 (t, $^3J_{HH}$ = 7.4 Hz, 2H, NCH_2CH_2), 4.61 (q, $^3J_{HH}$ = 7.3 Hz, 2H, NCH_2CH_3), 2.08 (quint, $^3J_{HH}$ = 7.4 Hz, 2H, NCH_2CH_2), 1.59 (t, $^3J_{HH}$ = 7.3 Hz, 3H, NCH_2CH_3) 1.46 (sext, $^3J_{HH}$ = 7.4 Hz, 2H, $NCH_2CH_2CH_2$), 0.97 (t, $^3J_{HH}$ = 7.4 Hz, 3H, $NCH_2CH_2CH_2CH_3$). ^{13}C{1H} NMR ($CDCl_3$, 125 MHz): δ 142.3 (C_{trz}–Ph), 131.9, 130.0 (2 × C_{Ph}), 129.8 (C_{trz}–H), 129.7, 121.9 (2 × C_{Ph}), 54.4 (NCH_2CH_2), 47.8 (NCH_2CH_3), 31.3 (NCH_2CH_2), 19.5 ($NCH_2CH_2CH_2CH_3$), 14.4 (NCH_2CH_3), 13.3 ($NCH_2CH_2CH_2CH_3$). Anal. Calcd for $C_{14}H_{20}IN_3$ (357.23): C, 47.07; H, 5.64; N, 11.76. Found: C, 47.09; H, 5.75; N, 11.61.

2. Experimental procedures for the synthesis of the carbene silver complexes 2a–m

General procedure: To a solution of the triazolium salt **1** (1.0 eq) in CH_2Cl_2 was added Ag_2O (0.5 eq). The mixture was stirred in the dark at room temperature for the indicated time and filtered through Celite. The solvent was removed in vacuo at room temperature and the residue was washed with pentane (3 × 25 mL).

Complex 2a. According to the general procedure, **1a** (833 mg, 2.82 mmol) and Ag_2O (327 mg, 1.41 mmol) in CH_2Cl_2 (30 mL) were stirred for 2 h, affording **2a** as a yellow oil (691 mg, 61%). ^{1}H NMR (DMSO–D_6, 500 MHz): δ 4.50 (t, $^3J_{HH}$ = 7.3 Hz, 2H, NCH_2), 4.10 (s, 3H, NCH_3), 2.80 (t, $^3J_{HH}$ = 7.4 Hz, 2H, C_{trz}–CH_2), 1.72 (quint, $^3J_{HH}$ = 7.4 Hz, 2H, C_{trz}–CH_2CH_2), 1.53 (t, $^3J_{HH}$ = 7.3 Hz, 3H, NCH_2CH_3), 1.39 (sext, $^3J_{HH}$ = 7.4 Hz, 2H, C_{trz}–$CH_2CH_2CH_2$), 0.92 (t, $^3J_{HH}$ = 7.4 Hz, 3H, C_{trz}–$CH_2CH_2CH_2CH_3$).

Complex 2b. According to the general procedure from **1b** (520 mg, 1.6 mmol) and Ag_2O (187 mg, 0.80 mmol) in CH_2Cl_2 (30 mL) for 2 h, **2b** as a yellow oil (682 mg, 99%). ^{1}H NMR (DMSO–D_6, 300 MHz) δ 4.48 (t, $^3J_{HH}$ = 7.0 Hz, 2H, NCH_2), 4.01 (s, 3H, NCH_3), 2.81 (t, $^3J_{HH}$ = 7.6 Hz, 2H, C_{trz}–CH_2), 1.93 (quint, $^3J_{HH}$ = 7.0 Hz, 2H, NCH_2CH_2), 1.72 (quint, $^3J_{HH}$ = 7.6 Hz, 2H, C_{trz}–CH_2CH_2), 1.28 (m, 4H, CH_2CH_3), 0.89 (m, 6H, CH_2CH_3).

Complex 2c. According to the general procedure, reaction of **1c** (146 mg, 0.38 mmol) and Ag_2O (45 mg, 0.19 mmol) in CH_2Cl_2 (20 mL) for 48 h yielded **2c** as a yellow oil (162 mg, 98%). ^{1}H NMR (DMSO–D_6, 500 MHz) δ 4.45 (t, $^3J_{HH}$ = 7.0 Hz, 2H, NCH_2), 4.01 (s, 3H, NCH_3), 2.80 (m, 2H, C_{trz}-CH_2), 1.92 (quint, $^3J_{HH}$ = 7.0 Hz, 2H, NCH_2CH_2), 1.72 (quint, $^3J_{HH}$ = 7.6 Hz, 2H, C_{trz}-CH_2CH_2), 1.26 (m, 12H, $CH_{2\ hex}$), 0.83 (m, 6H, CH_2CH_3).

The carbene silver complex **2d** is reported elsewhere.[S3c]

The carbene silver complex **2e** is reported elsewhere.[S4]

Complex 2f. According to the general procedure from **1f** (500 mg, 1.46 mmol) and Ag_2O (169 mg, 0.73 mmol) in CH_2Cl_2 (30 mL) for 2 h gave **2f** as a white solid (362 mg, 55%). ^{1}H NMR (DMSO–D_6, 300 MHz): δ 7.73 (m, 2H, H_{Ph}), 7.53 (m, 3H, H_{Ph}), 4.50 (t, $^3J_{HH}$ = 7.3 Hz, 2H, NCH_2), 4.14 (s, 3H, NCH_3), 1.92 (quint, $^3J_{HH}$ = 7.3 Hz, 2H, NCH_2CH_2), 1.29 (sext, $^3J_{HH}$ = 7.3 Hz, 2H, CH_2CH_3), 0.87 (t, $^3J_{HH}$ = 7.3 Hz, 3H, CH_2CH_3).

Complex 2g. According to the general procedure, reaction of **1g** (362 mg, 0.94 mmol) and Ag_2O (109 mg, 0.47 mmol) in CH_2Cl_2 (30 mL) for 2 h yielded **2g** as a yellow oil (450 mg, 97%). ^{1}H NMR (DMSO–D_6, 500 MHz): δ 7.04 (s, 2H, H_{Ar}), 4.51 (t, $^3J_{HH}$ = 6.9 Hz, 2H, NCH_2), 3.81 (s, 3H, NCH_3), 2.32 (s, 3H, Mes–CH_3), 2.10 (m, 2H, NCH_2CH_2), 1.94 (s, 6H, Mes–CH_3), 1.25 (sext, $^3J_{HH}$ = 7.4 Hz, 2H, CH_2CH_3), 0.89 (t, $^3J_{HH}$ = 7.4 Hz, 2H, CH_2CH_3)

Complex 2h. According to the general procedure, reaction of **1h** (1.01 mg, 2.5 mmol) and Ag_2O (290 mg, 1.3 mmol) in CH_2Cl_2 (30 mL) for 2 h afforded **2h** as a white solid (1.02 mg, 79%). ^{1}H NMR (DMSO–D_6, 300 MHz): δ 7.67–7.49 (m, 5H, H_{Ar}), 7.07 (s, 2H, H_{Mes}), 4.23 (s, 3H, NCH_3), 2.39 (s, 3H, Mes–CH_3), 1.86 (s, 6H, Mes–CH_3).

Complex 2i. According to the general procedure, **1i** (199 mg, 0.45 mmol) and Ag_2O (57 mg, 0.22 mmol) in CH_2Cl_2 (30 mL) for 16 h gave **2i** as a white solid (246 mg, 99%). ^{1}H NMR (DMSO–D_6, 500

MHz): δ 7.04 (s, 2H, H_{Mes}), 7.03 (s, 2H, H_{Mes}), 3.90 (s, 3H, NCH_3), 2.39, 2.38 (2 × s, 3H, Mes–CH_3), 1.86, 1.79 (2 × s, 6H, Mes–CH_3)

Complex 2j. According to the general procedure, **1j** (500 mg, 1.38 mmol) and Ag_2O (159 mg, 0.68 mmol) in CH_2Cl_2 (30 mL) for 2 h afforded **2j** as a white solid (422 mg, 65%). ^{1}H NMR (DMSO–D_6, 500 MHz): δ 7.92 (m, 2H, H_{Ar}), 7.75 (m, 2H, H_{Ar}), 7.60 (m, 2H, H_{Ar}), 7.51 (m, 4H, H_{Ar}), 4.25 (s, 3H, NCH_3).

Complex 2k. According to the general procedure, **1k** (315 mg, 1.0 mmol) and Ag_2O (116 mg, 0.49 mmol) in CH_2Cl_2 (30 mL) for 2 h yielded **2k** as a white solid (169 mg, 40%). ^{1}H NMR (d_6-DMSO, 400 MHz): δ 7.66 (m, 2H, H_{Ph}), 7.56 (m, 3H, H_{Ph}), 4.48 (q, $^3J_{HH}$ = 7.3 Hz, 2H, NCH_2), 4.27 (s, 3H, NCH_3), 1.38 (t, $^3J_{HH}$ = 7.3 Hz, 3H, NCH_2CH_3).

Complex 2l. According to the general procedure, reaction of **1l** (500 mg, 1.52 mmol) and Ag_2O (176 mg, 0.76 mmol) in CH_2Cl_2 (35 mL) for 2 h gave **2l** as a white solid (291 mg, 44%). ^{1}H NMR (d_6-DMSO, 300 MHz): δ 7.67 (m, 2H, H_{Ph}), 7.55 (m, 3H, H_{Ph}), 4.60–4.45 (m, 4H, NCH_2), 1.54, 1.38 (2 × t, $^3J_{HH}$ = 7.3 Hz, 3H, NCH_2CH_3).

Complex 2m. According to the general procedure from **1m** (521 mg, 1.46 mmol) and Ag_2O (169 mg, 0.73 mmol) in CH_2Cl_2 (35 mL) for 2 h, yielding **2m** as a white solid (150 mg, 44%). ^{1}H NMR (d_6-DMSO, 300 MHz): δ 7.70 (m, 2H, H_{Ph}), 7.52 (m, 3H, H_{Ph}), 4.50 (t, $^3J_{HH}$ = 7.4 Hz, 2H, NCH_2CH_2), 4.16 (q, $^3J_{HH}$ = 7.3 Hz, 2H, NCH_2CH_3), 1.95 (quint, $^3J_{HH}$ = 7.4 Hz, 2H, NCH_2CH_2), 1.61 (t, $^3J_{HH}$ = 7.3 Hz, 2H, NCH_2CH_3), 1.29 (sext, $^3J_{HH}$ = 7.4 Hz, 2H, $NCH_2CH_2CH_2$), 0.86 (t, $^3J_{HH}$ = 7.4 Hz, 3H, $NCH_2CH_2CH_2CH_3$).

3. Time-conversion profiles for BnOH oxidation using complexes 3a–g

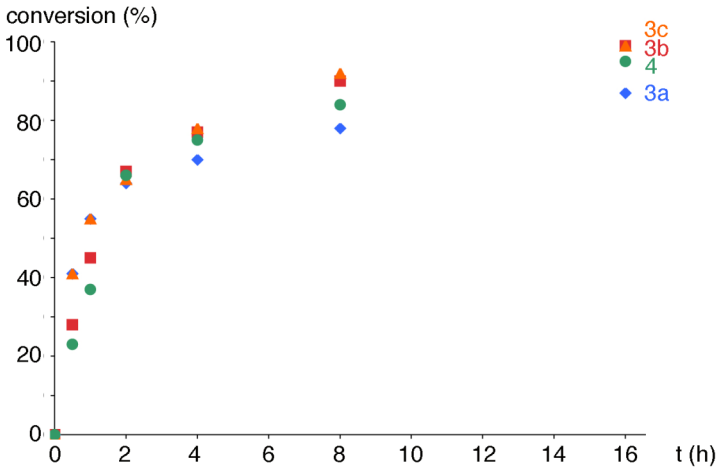

Figure S1. Time-conversion profile for the catalytic oxidation of benzyl alcohol (0.2 mmol) by triazolylidene ruthenium complexes **3a-3c** or **4** (5 mol%, 0.01 mmol) in toluene (2 mL) at 110 °C determined by ^{1}H NMR spectroscopy (anisole, 0.2 mmol, as internal standard).

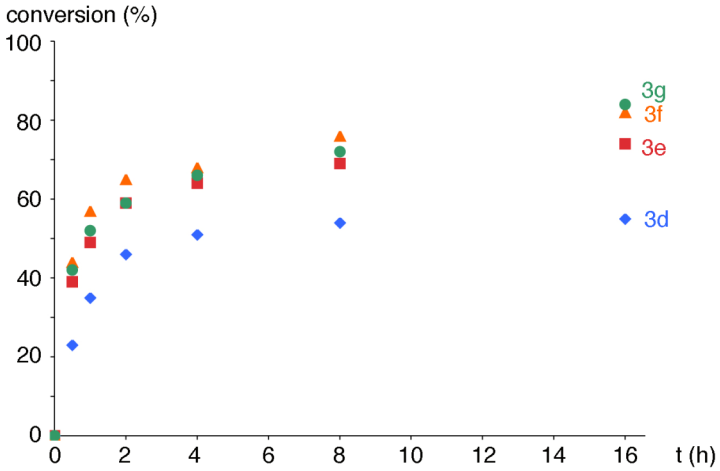

Figure S2. Time-conversion profile for the catalytic oxidation of benzyl alcohol (0.2 mmol) by triazolylidene ruthenium complexes **3d–3g** (5 mol%, 0.01 mmol) in toluene (2 mL) at 110 °C determined by ^{1}H NMR spectroscopy (anisole, 0.2 mmol, as internal standard).

4. References

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