Electronic Supplementary Information

cis-Oxoruthenium complexes supported by chiral tetradeutate amine (N₄) ligands for hydrocarbon oxidations

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Experimental Section

Materials
Solvents were purified according to reported methods. Ligands N,N'-dimethyl-N,N'-bis(pyridin-2-ylmethyl)cyclohexane-1,2-diamine (mcp), N,N'-dimethyl-N,N'-bis((6-methylpyridin-2-yl)methyl)cyclohexane-1,2-diamine (Me2mcp), 1,1'-bis(pyridin-2-ylmethyl)-2,2'-bipyrrolidine (pdp), 1,1'-bis((6-methylpyridin-2-yl)methyl)-2,2'-bipyrrolidine (Me2pdp), N,N'-dimethyl-N,N'-di(quinolin-8-yl)cyclohexane-1,2-diamine (bqcn), and N,N'-dimethyl-N,N'-bis(2-methylquinolin-8-yl)cyclohexane-1,2-diamine (Me2bqcn), and ruthenium complex [Ru(II)(OH)26](OTs)2 were prepared as reported. Silver trifluoro-methanesulfonate (99+, Acros) was used as received. Cerium(IV) ammonium nitrate (CAN) was purchased from Acros Organics; its purity was determined by iodometric titration to be > 98%. Ce(IV)(ClO4)4 (~ 0.5 N in perchloric acid) was obtained from Aldrich; its [Ce(IV)] and [H+] were determined to be 0.485 M and 7 M, respectively, by iodometric and acid-base titrations. Organic substrates were obtained from commercial sources and used as received, except that S310 S5 (racemic), S611 S7,11 and S811 were prepared using published protocols.

Instrumentation
NMR spectra were obtained using Bruker DPX-300, Advance 400, 500, or 600 FT-NMR spectrometers. Chemical shifts in ppm were referenced to residual non-deuterated solvents. Infrared spectra were recorded as a KBr disc or Nujol mull on a Nicolet 20 SXC FT-IR spectrophotometer. UV-visible absorption spectra were recorded on a Hewlett-Packard 8453A diode array spectrophotometer. Fast atom bombardment mass spectrometry (FAB-MS) was performed with a Thermo Scientific DFS high resolution spectrometer or a Finnigan MAT 95 mass spectrometer. Electrospray ionization mass spectrometry (ESI-MS) was performed with a Finnigan MAT LCQ spectrometer or a Waters Micromass Q-Tof Premier quadrupole time-of-flight tandem mass spectrometer (Waters Corporation, Milford, USA). Elemental analyses were performed at the Institute of Chemistry of the Chinese Academy of Sciences. Gas chromatography-mass spectrometry (GC-MS) analyses were performed with an Agilent Technologies 7890B Network GC System
with an Agilent Technologies 5977A Network Mass Selective Detector (MSD). An Agilent Technologies HP-5MS Ultra Inert (30.0 m × 0.25 mm, 0.25 micron) capillary column was used to analyze the reaction mixture in oxidation reactions. Helium was used as carrier gas. Chlorobenzene or 1,4-dichlorobenzene, depending on the molecular weight/retention time of oxidized products, was used as internal standard for quantification. The X-ray diffraction data of single crystals were collected on MAR, Bruker D8 VENTURE Dual Source Photon100 CMOS, or Bruker APEX-II CCD diffractometers.

**Synthesis of ruthenium complexes**

cis-\[(\text{mcp})\text{Ru}^{\text{III}}\text{Cl}_2\]\text{ClO}_4 (1a). An ethanolic solution of mcp (0.5 g, in 250 mL) was added dropwise over 3 h to a stirred ethanolic suspension (250 mL) of K$_2$[RuCl$_5$(OH$_2$)] (0.5 g) under refluxing condition. Upon complete addition of ligand, the mixture was further refluxed for 15 h. The reaction mixture was then cooled, with addition of a few drops of concentrated HCl, filtered, and evaporated to dryness. The residue was dissolved in water (5 mL), followed by addition of saturated NaClO$_4$ solution (10 mL). The crude product was recrystallized from hot HCl (0.1 M, 100 mL) to afford 1a as a red crystalline solid. Yield: 55%. Anal. Calcd. for C$_{20}$H$_{28}$N$_4$O$_4$Cl$_3$Ru: C, 40.31; H, 4.74; N, 9.40. Found: C, 40.34; H, 4.76; N, 9.43. FAB-MS: m/z 496.1 (M$^+$). UV-Vis (MeCN) $\lambda_{\text{max}}$/nm ($\varepsilon_{\text{max}}$/dm$^3$mol$^{-1}$cm$^{-1}$): 415 (1920), 299 (7440).

cis-\[(\text{mcp})\text{Ru}^{\text{III}}(\text{O}_2\text{CCF}_3)_2\]\text{ClO}_4 (1b). A mixture of [(mcp)Ru$^{\text{III}}$Cl$_2$]ClO$_4$ (1a, 0.3 g) and zinc amalgam (1 g) in distilled water (30 mL) was heated at 80 °C for 30 min, giving a dark green solution. Zinc amalgam was removed, and the remaining solution was treated with CF$_3$CO$_2$H (0.2 M, 20 mL) and silver trifluoromethanesulfonate (0.3 g). Insoluble AgCl was removed by filtration, and the volume was slowly reduced to ca. 15 mL by heating at 80 °C to give a yellow solution. Addition of saturated NaClO$_4$ solution (5 mL) induced precipitation of 1b as a pale yellow solid. The crude product was recrystallized in aqueous CF$_3$CO$_2$H (0.1 M, 20 mL). Yield: 20%. Anal. Calcd. for C$_{24}$H$_{28}$F$_6$O$_8$N$_4$ClRu: C, 38.38; H, 3.76; N, 7.46. Found: C, 38.53; H, 3.84; N, 7.53. IR (KBr): 1712, 1613 and 1393 cm$^{-1}$. FAB-MS: m/z 652.1 (M$^+$). UV-Vis (MeCN) $\lambda_{\text{max}}$/nm ($\varepsilon_{\text{max}}$/dm$^3$mol$^{-1}$cm$^{-1}$): 269 (7040).
cis-[(mcp)Ru^{IV}(NCMe)_{2}](ClO_{4})_{2} (1d). This complex was obtained as a by-product in the stoichiometric oxidation of hydrocarbons by cis-[(mcp)Ru^{VI}(O)_{2}](ClO_{4})_{2} (1e), after diethyl ether diffusion into an acetonitrile solution. Anal. Calcd. for C_{22}H_{32}N_{6}O_{6}Cl_{3}Ru: C 40.80; H, 4.85; N 11.89. Found: C 40.31; H, 4.74; N 11.96. UV-Vis (MeCN) \( \lambda_{\text{max}}/\text{nm} (\varepsilon_{\text{max}}/\text{dm}^{3} \text{ mol}^{-1} \text{cm}^{-1}) \): 245 (9900), 347 (9750). FAB-MS: m/z 607.2 ([M + ClO_{4}]^{+}). \(^{1}H\) NMR (300 MHz, CD_{3}CN): \( \delta \) 0.93–1.02 (m, 2H), 1.12–1.26 (m, 2H), 1.60–1.62 (m, 2H), 2.06–2.16 (m, 2H), 2.21–2.31 (m, 2H), 2.32 (s, 6H), 2.45 (s, 6H), 4.24 (d, 2H, \( J = 16.0 \) Hz), 4.50 (d, 2H, \( J = 16.0 \) Hz), 7.50 (t, 2H, \( J = 6.6 \) Hz), 7.59 (d, 2H, \( J = 7.8 \) Hz), 7.93 (t, 2H, \( J = 7.7 \) Hz), 8.94 (d, 2H, \( J = 5.6 \) Hz).

cis-[(mcp)Ru^{VI}(O)_{2}](ClO_{4})_{2} (1e). To an ice-cooled solution of 1b (0.1 g) in H_{2}O (10 mL) was added a solution of (NH_{4})_{2}[Ce^{IV}(NO_{3})_{6}] (1 g, in 2 mL water). The solution gradually turned pale green. Upon addition of a saturated solution of NaClO_{4} (4 mL), a pale green solid was formed. The solid was collected on a frit and air-dried. Yield: 66\%. UV-Vis (MeCN) \( \lambda_{\text{max}}/\text{nm} (\varepsilon_{\text{max}}/\text{dm}^{3} \text{ mol}^{-1} \text{cm}^{-1}) \): 261 (8700), 344 (2210). FAB-MS: m/z 458.1 (M\(^{+}\)). \(^{1}H\) NMR (300 MHz, CD_{3}CN): \( \delta \) 0.91–0.96 (m, 2H), 1.14–1.22 (m, 2H), 1.51–1.62 (m, 2H), 1.90–1.98 (m, 2H), 2.05–2.15 (m, 2H), 2.20 (s, 6H), 3.87 (d, 2H, \( J = 16 \) Hz), 4.44 (d, 2H, \( J = 16 \) Hz), 7.40 (t, 2H, \( J = 6.4 \) Hz), 7.53 (d, 2H, \( J = 7.4 \) Hz), 7.84 (t, 2H, \( J = 7.7 \) Hz), 8.79 (d, 2H, \( J = 5.6 \) Hz).

cis-[(Me_{2}mcp)Ru^{III}Cl_{3}]ClO_{4} (2a). The procedure was similar to that for the preparation of 1a, except that 6-Me_{2}mcp, instead of mcp, was employed as ligand. Recrystallization of the crude product by slow diffusion of diethyl ether into an acetonitrile solution afforded 2a as an orange-red crystalline solid. Yield: 32\%. Anal. Calcd. for C_{22}H_{32}N_{6}O_{6}Cl_{3}Ru: C, 42.35; H, 5.17; N, 8.98. Found: C, 42.32; H, 5.37; N, 8.71. FAB-MS: m/z 524.1 (M\(^{+}\)). UV-Vis (MeCN) \( \lambda_{\text{max}}/\text{nm} (\varepsilon_{\text{max}}/\text{dm}^{3} \text{ mol}^{-1} \text{cm}^{-1}) \): 430 (1850), 277 (7785).

cis-[(pdp)Ru^{III}Cl_{3}]Cl (3a-Cl). An ethanolic solution (200 mL) of pdp (0.523 g) was added dropwise over 3 h to a stirred ethanolic suspension (250 mL) of K_{2}[RuCl_{6}(OH_{2})] (0.761 g) under refluxing condition. Upon complete addition of ligand, the mixture was further refluxed for 15 h. The reaction mixture was then cooled, with addition of 5 drops of concentrated HCl, filtered, and evaporated to dryness. The brown oil thus
obtained was re-dissolved in methanol followed by addition of excess diethyl ether. Complex 3a·Cl was isolated as a brown hygroscopic solid. Yield: 78%. Anal. Calcd. (%) for C_{29}H_{26}N_{4}RuCl_{3}·3HCl: C 37.58, H 4.57, N 8.76; found: C 37.29, H 4.53, N 8.42. ESI-MS (H_{2}O): m/z 494.1 (M^+). UV-Vis (MeCN) \( \lambda_{\text{max}}/\text{nm} \) (\( \epsilon_{\text{max}}/\text{dm}^3\text{mol}^{-1}\text{cm}^{-1} \)): 301 (7220), 404 (2070).

cis-[(pdp)Ru^{III}Cl_{2}]ClO_{4} (3a·ClO_{4}). This complex was prepared by recrystallizing 3a·Cl (0.6 g) by vapor diffusion of diethyl ether into its acetonitrile solution in the presence of 0.1 M LiClO_{4}. The product was obtained as a yellow crystalline solid including a diffraction-quality crystal suitable for X-ray crystallography. Yield: 82%. Anal. Calcd. (%) for C_{32}H_{30}N_{4}RuCl_{3}ClO_{4}: C 40.45, H 4.41, N 9.43; found: C 40.20, H 4.41, N 9.45. ESI-MS (MeCN): m/z 494.1 (M^+). UV-Vis (MeCN) \( \lambda_{\text{max}}/\text{nm} \) (\( \epsilon_{\text{max}}/\text{dm}^3\text{mol}^{-1}\text{cm}^{-1} \)): identical to that of 3a·Cl.

cis-[(pdp)Ru^{II}(OH)_{2}]_{2}(OTs)_{2} (3c·OTs). The pdp ligand (129 mg) was dissolved in distilled THF (40 mL). [(Ru^{II}(OH)_{2})Cl(OTs)] (265 mg) was then added under positive pressure of argon. The resultant mixture was heated under argon for 1 h. After cooling and evacuation of solvent under vacuum, the crude product was dissolved in dichloromethane, filtered to remove excess [Ru^{II}(OH)_{2}]Cl(OTs), and vacuum-dried. The product thus obtained was generally pure analytically. In rare cases where ESI-MS analysis showed the presence of unreacted ligand (detected as m/z LH^+), the product was further purified by washing its aqueous solution (40 mL) with chloroform (40 mL × 3) using a separating funnel. Complex 3c·OTs was obtained as a green micro-crystalline solid upon evaporation of the aqueous solution under vacuum. Yield: 68%. Anal. Calcd. (%) for C_{34}H_{44}N_{4}RuS_{2}O_{8}: C 50.92, H 5.53, N 6.99; found: C 51.24, H 5.69, N 6.81. ESI-MS (H_{2}O): m/z 595.1 ([((pdp)Ru^{II}(OTs)])^+). UV-Vis (H_{2}O) \( \lambda_{\text{max}}/\text{nm} \) (\( \epsilon_{\text{max}}/\text{dm}^3\text{mol}^{-1}\text{cm}^{-1} \)): 249 (10043), 394 (6880). UV-Vis (MeCN) \( \lambda_{\text{max}}/\text{nm} \) (\( \epsilon_{\text{max}}/\text{dm}^3\text{mol}^{-1}\text{cm}^{-1} \)): 248 (11560), 362 (6730). UV-Vis (CH_{2}Cl_{2}) \( \lambda_{\text{max}}/\text{nm} \) (\( \epsilon_{\text{max}}/\text{dm}^3\text{mol}^{-1}\text{cm}^{-1} \)): 251 (9930), 414 (7270). ^1H NMR (300 MHz, CD_{3}CN): \( \delta \) 1.31–1.37 (m, 2H), 1.80–1.84 (m, 2H), 2.10–2.19 (m, 4H), 2.42 (s, 6H), 2.43–2.48 (m, 2H), 2.64–2.65 (m, 2H), 3.20–3.28 (m, 2H), 4.07–4.12 (d, 2H, \( J = 15.4 \text{ Hz} \)), 4.28–4.33 (d, 2H, \( J = 15.5 \text{ Hz} \)), 7.48–7.54 (m, 4H), 7.88–7.94 (dt, 2H, \( J = 7.8 \text{ Hz} \)), , 8.99–9.01 (d, 2H, \( J = 5.4 \text{ Hz} \)).
cis-[(pdp)Ru^{II}(OH)_2](CF_3SO_3)_2 (3c·CF_3SO_3). A mixture of 3a·Cl (0.25 g) and zinc amalgam (0.8 g) in distilled water (23.5 mL) was heated at 80 °C for 30 min under argon to give a dark green solution. The reaction mixture was cooled to room temperature, filtered under argon, and treated with silver trifluoromethanesulfonate (0.363 g). After heating at 80 °C for another 30 min under argon, the reaction mixture was cooled to room temperature and filtered under argon to remove AgCl. After removal of solvents under vacuum followed by exhaustive vacuum-drying, the product was isolated as a highly hygroscopic dark-green solid. Yield: 88%. ESI-MS (H_2O): m/z 573.1 ([(pdp)Ru^{II}(O_3SCF_3)])^+. UV-Vis (H_2O) \( \lambda_{max}/\text{nm} \) (\( \varepsilon_{max}/\text{dm}^3\text{mol}^{-1}\text{cm}^{-1} \)): 249 (9600), 395 (6850). Cautious note: This complex was not fully characterized and may contain Zn(CF_3SO_3)_2 as an impurity.

cis-[(pdp)Ru^{III}(O_3SCF_3)_2]CF_3SO_3 (3c'). Following the procedure for the synthesis of 3c·CF_3SO_3, after Zn reduction and dechlorination by Ag^+, the reaction mixture was exposed to air and cooled to room temperature. Insoluble AgCl was removed by filtration, and the solvents were evaporated under vacuum. The resulting green oil was washed thoroughly with diethyl ether and dried under vacuum for 24 h to produce 3c' as a highly hygroscopic green solid. Yield: 83%. Anal. Calcd. (%) for C_{23}H_{26}F_{9}N_{4}O_{9}RuS_{5}·5H_{2}O: C 28.75, H 3.78, N 5.83; found: C 28.70, H 3.83, N 5.71. ESI-MS (H_2O): m/z 458.1 ([(pdp)Ru^{III}(OH)_2])^+. UV-Vis (H_2O) \( \lambda_{max}/\text{nm} \) (\( \varepsilon_{max}/\text{dm}^3\text{mol}^{-1}\text{cm}^{-1} \)): 246 (9190), 296 (5400).

cis-[(Me_2pdp)Ru^{III}Cl_2]Cl (4a·Cl). This complex was prepared in a manner similar to that of 3a·Cl from Me_2pdp (0.42 g) and K_2[RuCl_5(OH)_2] (0.54 g). The product was isolated as a brown solid. Yield: 97%. Anal. Calcd. (%) for C_{22}H_{30}N_{4}RuCl_3·H_2O: C 45.88, H 5.60, N 9.73; found: C 45.44, H 5.80, N 9.26. ESI-MS (MeOH or H_2O): m/z 522 (M^+). UV-Vis (MeCN) \( \lambda_{max}/\text{nm} \) (\( \varepsilon_{max}/\text{dm}^3\text{mol}^{-1}\text{cm}^{-1} \)): 258 (8320), 383 (3000).

cis-[(Me_2pdp)Ru^{II}(OH)_2](OTs)_2 (4c·OTs). This complex was prepared in a manner similar to that of 3c·OTs except that Me_2pdp (70 mg), instead of pdp, was used as ligand. Complex 4c·OTs was obtained as a brown-green solid. Yield: 76%. Anal. Calcd. (%) for C_{36}H_{48}N_{4}RuS_2O_6: C 52.10, H 5.83, N 6.75; found: C 51.96, H 6.03, N 6.74. ESI-MS (H_2O): m/z 623.2 ([(Me_2pdp)Ru^{II}(OTs)])^+. UV-Vis (H_2O) \( \lambda_{max}/\text{nm} \)
cis-[(bqcn)Ru\textsuperscript{II}(OH)\textsubscript{2}](OTs)\textsubscript{2} (5c-OTs). This complex was prepared in a manner similar to that of 3c-OTs except that bqcn (158 mg, 0.4 mmol), instead of pdp, was used as ligand. The reaction was conducted at room temperature and the reaction time was extended to 18 h. Complex 5c-OTs was obtained as a red microcrystalline solid. Yield: 71\%. Anal. Calcd. (%) for C\textsubscript{50}H\textsubscript{46}N\textsubscript{8}O\textsubscript{8}RuS\textsubscript{2}·H\textsubscript{2}O: C 53.74, H 5.41, N 6.27; found: C 53.65, H 5.29, N 5.90. ESI-MS (H\textsubscript{2}O): m/z 669.1 ([(bqcn)Ru\textsuperscript{II}(OTs)]\textsuperscript{+}). UV-Vis (H\textsubscript{2}O) \(\lambda_{\text{max}}\)/nm \(\varepsilon_{\text{max}}/\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}\): 287 (11220), 477 (6880).

cis-[(bqcn)Ru\textsuperscript{II}(NCMe)\textsubscript{2}](ClO\textsubscript{4})\textsubscript{2} (5d). This complex was prepared by successive vapor diffusion of diethyl ether into an acetonitrile solution of 5c-OTs in the presence of 0.1 M LiClO\textsubscript{4}. The product 5d was obtained as a yellow crystalline solid. Yield: 70\%. Anal. Calcd. (%) for C\textsubscript{36}H\textsubscript{34}N\textsubscript{6}RuCl\textsubscript{2}O\textsubscript{8}Cl\textsubscript{2}·CH\textsubscript{3}CN: C 46.89, H 4.55, N 8.65; found: C 47.01, H 4.55, N 8.77. ESI-MS (MeCN): m/z 290.1 ([M]\textsuperscript{2+}). UV-Vis (MeCN) \(\lambda_{\text{max}}\)/nm \(\varepsilon_{\text{max}}/\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}\): 278 (12100), 415 (6900). \(^1\)H NMR (400 MHz, CD\textsubscript{3}CN): this compound exists as a mixture of cis-\(\alpha\) and cis-\(\beta\) isomers which gives highly complicated NMR signals, see in-text discussion.

cis-[(Me\textsubscript{2}bqcn)Ru\textsuperscript{II}(OH)\textsubscript{2}](OTs)\textsubscript{2} (6c-OTs). This complex was prepared in a manner similar to that of 3c-OTs except that Me\textsubscript{2}bqcn (170 mg), instead of pdp, was used as ligand. The reaction was conducted at room temperature and the reaction time was extended to 18 h. Complex 6c-OTs was obtained as a reddish-brown solid. Yield: 41\%. Anal. Calcd. (%) for C\textsubscript{52}H\textsubscript{50}N\textsubscript{4}RuS\textsubscript{2}O\textsubscript{8}: C 55.80, H 5.57, N 6.20; found: C 55.33, H 5.70, N 5.90. ESI-MS (H\textsubscript{2}O): m/z 697.1 ([(Me\textsubscript{2}bqcn)Ru\textsuperscript{II}(OTs)]\textsuperscript{+}). UV-Vis (H\textsubscript{2}O) \(\lambda_{\text{max}}\)/nm \(\varepsilon_{\text{max}}/\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}\): 287 (13680), 453 (4690).

cis-[(Me\textsubscript{2}bqcn)Ru\textsuperscript{II}(NCMe)\textsubscript{2}](ClO\textsubscript{4})\textsubscript{2} (6d). This complex was prepared by successive vapor diffusion of diethyl ether into an acetonitrile solution of 6c-OTs in the presence of 0.1 M LiClO\textsubscript{4}.
of 0.1 M LiClO₄. The product 6d was obtained as a yellow crystalline solid. Yield: 70%. Anal. Calcd. (%) for C₃₂H₃₈N₆RuCl₂O₈Cl₂: C 47.65, H 4.75, N 10.42; found: C 47.86, H 4.80, N 10.36. ESI-MS (MeCN): m/z 304.1 ([M]²⁺). UV-Vis (MeCN) λ_max/nm (ε_max/dm³ mol⁻¹ cm⁻¹): 272 (14685), 402 (5500). ¹H NMR (400 MHz, CD₃CN): δ 0.77–0.82 (m, 2H), 1.50–1.53 (m, 2H), 1.58–1.60 (m, 2H), 1.96–2.00 (m, 2H), 2.85–2.88 (m, 2H), 3.07 (s, 6H), 3.50 (s, 6H), 7.57–7.58 (d, 2H, J = 8.5 Hz), 7.66–7.70 (t, 2H, J = 8.0 Hz), 7.93–7.95 (d, 2H, J = 8.1 Hz), 8.0–8.02 (d, 2H, J = 7.7 Hz), 8.34–8.36 (d, 2H, J = 8.5 Hz).

Stoichiometric organic oxidations by 1e
To a 100-mL Schlenck flask was added alkene (30 mmol), tert-butanol (10 mL) and distilled water (2 mL). The mixture was degassed by three freeze-pump-thaw cycles and filled with argon. The cis-dioxoruthenium complex 1e (300 µmol) was added under a positive pressure of argon, and the reaction mixture was stirred magnetically at room temperature for 30 min. To work-up, the organic products were separated from the reaction mixture by diethyl ether extraction (3 × 50 mL). After washing with brine (2 × 10 mL) and drying over MgSO₄, the volume of the ethereal extract was reduced to about 3 mL for GC analysis and/or column chromatographic purification. Similar experimental procedures were employed when acetonitrile was used as solvent for the alkene oxidation. The organic products (e.g. cis/trans-diols, carbonyl compounds) were identified by ¹H and ¹³C NMR spectroscopy by comparing with authentic or literature data. Enantiomeric excess of the diol products was determined by chiral HPLC.

Similar procedures were employed in the oxidation of alcohols and alkanes (Table 3 in main text), whereas acetonitrile was used as solvent.

Catalytic studies

Catalytic alkene oxidation by 1b
To a mixture of tert-butanol (2 mL) and distilled water (1 mL) containing substrate (0.5 mmol) was added catalyst 1b (1 mol%). Then, NaIO₄ (1.1 mmol, 2.2 equiv.) was added to the reaction mixture all at once. The reaction mixture was reacted at room temperature for 1 h. To work-up, any unreacted oxidant was quenched by saturated
Na$_2$SO$_3$ solution (2 mL), followed by extraction with ethyl acetate (3 × 10 mL). The combined organic extracts were dried over MgSO$_4$, and subjected to GC analysis and/or column chromatographic purification. The organic products were identified by GC by comparing with authentic sample and/or NMR spectroscopy of the isolated product.

**Catalytic alcohol oxidation by 1b**

In a 25-mL flask, alcohol (1 mmol) was dissolved in aqueous tert-butanol (3 mL, tert-butanol/water = 2:1 v/v), followed by addition of 1b (7.5 mg, 10 μmol) into the solution. The reaction mixture was then heated to reflux. Under refluxing condition, H$_2$O$_2$ solution (0.35 mL, 4 equiv.) was added via syringe pump over 8 h. Upon complete H$_2$O$_2$ addition, the mixture was further refluxed for 4 h. To work-up, any unreacted H$_2$O$_2$ was quenched by saturated NaHSO$_3$ solution (2 mL), followed by extraction with diethyl ether (5 × 20 mL). The combined ethereal extracts were dried over MgSO$_4$, and subjected to GC analysis and/or column chromatographic purification. The organic products were identified by GC by comparing with authentic sample and/or NMR spectroscopy of the isolated product.

**Catalytic alkane oxidation by cis-[(N$_4$)Ru$^{II}$(OH)$_2$]$_2^{2+}$ complexes**

To a mixture of substrate (0.2–0.25 mmol) and Ru catalyst (2–5 mol%) in tert-butanol (2 mL) and distilled water (2 mL) was added CAN (3 equiv.). In some entries depicted in the Tables, after the intense orange-red color of CAN had disappeared (in 10 min to 1 h), another portion of CAN (3 equiv.) was added to the system. The reaction mixture was stirred at room temperature for the time specified in each entry. To work-up, the mixture was treated with saturated Na$_2$SO$_3$ solution (2 mL), followed by extraction with ethyl acetate (3 × 10 mL). Organic products were identified and quantified by GC-MS (internal standard = 1,4-dichlorobenzene) by comparing with authentic samples, or by NMR spectroscopy after purification/isolation by chromatography on silica gel.
**Scheme S1** Preparation of 3c'.

![Scheme S1](image)

**Table S1** Selected bond lengths (Å) and angles (°) for 1a, 2a, and 3a·ClO₄⁻

|          | 1a        | 2a (I)    | 2a (II)   | 3a·ClO₄⁻   |
|----------|-----------|-----------|-----------|------------|
| Ru–N₁    | 2.070(2)  | 2.125(3)  | 2.161(3)  | 2.090(2)   |
| Ru–N₄    | 2.079(2)  | 2.125(3)  | 2.161(3)  | 2.087(2)   |
| Ru–N₂    | 2.112(2)  | 2.142(6)  | 2.137(6)  | 2.108(2)   |
| Ru–N₃    | 2.117(2)  | 2.142(6)  | 2.137(6)  | 2.113(2)   |
| Ru–Cl₁   | 2.3373(8) | 2.3571(16)| 2.3445(16)| 2.3499(8)  |
| Ru–Cl₂   | 2.3331(8) | 2.3571(16)| 2.3445(16)| 2.3378(7)  |
| α        | 92.67(3)  | 95.25(8)  | 93.52(9)  | 95.64(3)   |
| β        | 83.85(9)  | 83.5(3)   | 82.2(3)   | 82.59(9)   |
**Table S2** Crystallographic data of 1a and 2a.

|                      | 1a                           | 2a                           |
|----------------------|------------------------------|------------------------------|
| **Empirical Formula**| $\text{C}_{20}\text{H}_{28}\text{Cl}_{3}\text{N}_{4}\text{O}_{4}\text{Ru}$ | $\text{C}_{22}\text{H}_{32}\text{Cl}_{3}\text{N}_{4}\text{O}_{4}\text{Ru}$ |
| **Formula weight**   | 595.88                       | 623.94                       |
| **Temperature/K**    | 200                          | 253                          |
| **Crystal system**   | Monoclinic                   | Monoclinic                   |
| **Space group**      | $\text{P} 2_1/c$            | $\text{P} 2$                |
| $a$ (Å)              | 11.0085(6)                   | 10.505(2)                    |
| $b$ (Å)              | 13.2457(7)                   | 10.579(2)                    |
| $c$ (Å)              | 15.8552(9)                   | 11.649(2)                    |
| $\alpha$ (°)        | 90                           | 90                           |
| $\beta$ (°)         | 92.636(2)                    | 101.09(3)                    |
| $\gamma$ (°)        | 90                           | 90                           |
| $V$ (Å³)             | 2309.5(2)                    | 1270.4(4)                    |
| **Z**                | 4                            | 2                            |
| **Diffractometer**  | Bruker D9 Venture            | MAR                          |
| $D_c$ (g cm⁻³)       | 1.714                        | 1.631                        |
| $\mu$ (mm⁻¹)        | 1.06                         | 0.969                        |
| $F(000)$             | 1212                         | 638                          |
| **Crystal size (mm³)** | 0.35 × 0.23 × 0.21          | 0.6 × 0.25 × 0.15            |
| **Radiation**        | MoKα ($\lambda = 0.71073$)  | MoKα ($\lambda = 0.71073$)  |
| $2\theta$ range for data collection/° | 4.8 to 50.0                 | 0 to 50.94                   |
| Index ranges         | $-12 \leq h \leq 13, -15 \leq k \leq 15,$ | $-12 \leq h \leq 12, -12 \leq k \leq 15,$ |
|                      | $-18 \leq l \leq 18$        | $12, -14 \leq l \leq 14$    |
| Refractions collected | 24259                       | 7611                         |
| Independent reflections | 4088                        | 4197                         |
| No. of parameters    | 291                          | 337                          |
| $R_1^{[a]}$          | 0.029                        | 0.0291                       |
| $wR_2^{[a]}$         | 0.066                        | 0.082                        |
| Goodness-of-fit      | 1.03                         | 1.037                        |
| Flack parameter      | 0.02(4)                      |                               |

[a] $R_1 = \sum ||F_o|| - |F_c| \Sigma |F_o|$, $wR_2 = [\Sigma_w((F_o) - |F_c|)^2/\Sigma wF_o^2]^{1/2}$, in which $w = 4F_o^2/\sigma^2(F_o^2)$.
|                          | 3a·ClO₄·MeCN          | 5d·MeCN          | 6d                               |
|--------------------------|-----------------------|------------------|----------------------------------|
| **Empirical formula**    | C₂₂H₂₅Cl₃N₅O₄Ru      | C₂₁H₂₇Cl₃N₅O₄Ru | C₂₁H₃₈Cl₃N₆O₄Ru                 |
| **Formula weight**       | 634.92                | 819.65           | 806.65                           |
| **Temperature/K**        | 100                   | 100              | 100                              |
| **Crystal system**       | Orthorhombic          | Triclinic        | Monoclinic                       |
| **Space group**          | P₂₁/2₁/2₁             | P-1              | P₂₁                             |
| **a (Å)**                | 8.6233(10)            | 9.9120(7)        | 8.1503(6)                       |
| **b (Å)**                | 12.5838(16)           | 17.5103(14)      | 16.4241(13)                     |
| **c (Å)**                | 23.552(4)             | 21.2883(17)      | 12.8050(11)                     |
| **α (°)**                | 90                    | 81.245(5)        | 90                              |
| **β (°)**                | 90                    | 80.941(6)        | 99.016(3)                       |
| **γ (°)**                | 90                    | 83.022(6)        | 90                              |
| **V (Å³)**               | 2555.8(6)             | 3588.2(5)        | 1692.9(2)                       |
| **Z**                    | 4                     | 4                | 2                               |
| **Dc (g cm⁻³)**          | 1.650                 | 1.517            | 1.582                           |
| **μ (mm⁻¹)**             | 8.185                 | 5.409            | 5.712                           |
| **F(000)**               | 1292.0                | 1680.0           | 828.0                           |
| **Crystal size (mm³)**   | 0.3 × 0.05 × 0.04     | 0.2 × 0.05 × 0.01| 0.25 × 0.12 × 0.02              |
| **Radiation**            | CuKα (λ = 1.54178)    | CuKα (λ = 1.54178)| CuKα (λ = 1.54178)             |
| **2Θ range for data collection/°** | 7.506 to 135.434     | 4.242 to 101.422 | 6.99 to 135.37                   |
| **Index ranges**         | -10 ≤ h ≤ 9, -14 ≤ k ≤ 14, -7 ≤ h ≤ 9, -17 ≤ k ≤ 16, -21 ≤ h ≤ 9, -19 ≤ k ≤ 19, -27 ≤ l ≤ 28 | l ≤ 21, -15 ≤ l ≤ 15 |                                |
| **Reflections collected**| 36238                 | 15663            | 27030                           |
| **Independent reflections** | 4555 [Rint = 0.0491, Rsigma = 0.0278] | 7361 [Rint = 0.0653, Rsigma = 0.0923] | 5959 [Rint = 0.0493, Rsigma = 0.0382] |
| **No. of parameters**    | 317                   | 950              | 458                             |
| **Goodness-of-fit**      | 1.068                 | 1.031            | 1.055                           |
| **Final R indexes (I>=2σ(I))** | R₁ = 0.0188, wR₂ = 0.0483 R₁ = 0.0684, wR₂ = 0.1769 | R₁ = 0.0273, wR₂ = 0.0688 |                                    |
| **Final R indexes [all data]** | R₁ = 0.0188, wR₂ = 0.0485 R₁ = 0.0967, wR₂ = 0.1946 | R₁ = 0.0274, wR₂ = 0.0689 |                                    |
| **Flack parameter**      | 0.051(3)              |                  | 0.028(5)                        |

**Table S3** Crystallographic data of 3a·ClO₄, 5d and 6d.
Table S4: Oxidation of racemic 2-phenylhexane with CAN catalyzed by cis-[(N₂)Ru[H(OH)₂]²⁺] complexes.a

| Entry | Catalyst     | Product TON | Product ee |
|-------|--------------|-------------|------------|
| 1     | 1b           | 9           | 1%         |
| 2     | 3c·OTs       | 14          | 5%         |
| 3     | 4c·OTs       | trace       | 1%         |
| 4     | 5c·OTs       | 10          | 2%         |
| 5     | 6c·OTs       | trace       | 0%         |

a Substrate (0.5 mmol), catalyst (0.005 mmol), CAN (0.75 mmol), tBuOH/H₂O (1:1 v/v, 4 mL), 0 °C, 30 min.

Oxidation of racemic 2-phenylhexane by “(R,R)-3c + CAN” was conducted at 0 °C and compared with other ruthenium catalysts (1b, 4c–6c). Complex 3c gave the best result which afforded the tertiary alcohol product in quantitative yield based on 14% conversion (TON = 14). However, none of the catalysts gave product with significant enantiomeric excess (ee <5%).
Table S5 Catalytic alkene oxidations by cis-[(mcp)Ru^{III}(O_2CCF_3)_2]ClO_4 (1b) in aqueous tert-butanol with NaIO_4.\textsuperscript{a}

| Entry | Substrates | Conversion (%) | C=O Products | Yield (%)\textsuperscript{b} | Epoxidation products | Yield (%)\textsuperscript{b} |
|-------|------------|----------------|--------------|-----------------|----------------------|-----------------|
| 1     |            | 100            | benzaldehyde | 89\textsuperscript{c} |          |                  |
| 2     | MeO        | 83             | benzaldehyde | 98              |          |                  |
| 3     | F          | 100            | benzaldehyde | 97              |          |                  |
| 4     |            | 96             | benzaldehyde | 99              |          |                  |
| 5     |            | 84             | benzaldehyde | 90              |          |                  |
| 6     | COOMe      | 88             | benzaldehyde | 100             |          |                  |
| 7     |            | 77             | benzaldehyde | 0               | oxide     | 83              |
| 8     |            | 100            | benzaldehyde | 0               | epoxide   | 95              |

\textsuperscript{a} Reaction conditions: To a mixture of tert-butanol (2 mL) and distilled water (1 mL) containing substrate (0.5 mmol) was added catalyst 1b (0.005 mmol, 1 mol%). NaIO_4 (1.1 mmol, 2.2 equiv.) was added to the reaction mixture all at once. The reaction mixture was reacted at room temperature for 1 h. \textsuperscript{b} Yield based on conversion. \textsuperscript{c} When 2.2 mmol of NaIO_4 (4.4 equiv.) was used, the product yield of benzaldehyde dropped to 43%; with concomitant formation of benzoic acid in 55% yield.
Catalytic alcohol oxidations by cis-[[(mcp)Ru^{III}(O_{2}CCF_{3})_{2}]ClO_{4} (1b) in aqueous tert-butanol with H_{2}O_{2}.\textsuperscript{a}

| Entry | Substrates | Conversion (%) | Product(s)\textsuperscript{b} | Yield (%) | Entry | Substrates | Conversion (%) | Product(s)\textsuperscript{b} | Yield (%) |
|-------|------------|----------------|-------------------------------|-----------|-------|------------|----------------|-------------------------------|-----------|
| 1\textsuperscript{c} | Ph-OH      | 20             | PhCHO                         | 78        | 9     | HO_{2}C-COOH | 100            | COOH                        | 95        |
| 2     | Ph-OH      | 100            | PhCO_{2}H                     | 91        | 10    | HO_{2}C-COOH | 100            | COOH                        | 80        |
| 3     | Ph-OH      | 100            | PhCHO                         | 5         | 11    | HO_{2}C-COOH | 100            | COOH                        | 90        |
| 4     | Ph-OH      | 100            | PhCO_{2}H                     | 85        | 12    | HO_{2}C-COOH | 100            | COOH                        | 87        |
| 5     | Ph-OH      | 100            | PhCO_{2}H                     | 85        | 13    | HO_{2}C-COOH | 100            | COOH                        | 91        |
| 6     | Ph-OH      | 100            | PhCHO                         | 98        | 14    | HO_{2}C-COOH | 100            | COOH                        | 65        |
| 7     | Ph-OH      | 100            | PhCHO                         | 57        | 15    | HO_{2}C-COOH | 100            | COOH                        | 80        |
| 8     | Ph-OH      | 100            | PhCHO                         | 32        |       | PhCHO         | 100            | PhCO_{2}H                   | 15        |

\textsuperscript{a} Reaction conditions: To a mixture of tert-butanol (2 mL) and distilled water (1 mL) containing substrate (1 mmol) was added catalyst 1b (0.01 mmol, 1 mol%). Aqueous H_{2}O_{2} (2.2 equiv. for entries 1–9; 4 equiv. for entries 10–15) was added to the refluxing reaction mixture over 8 h. The reaction mixture was further refluxed for 4 h. \textsuperscript{b} Aldehydes / ketones were identified and quantified by GC; while carboxylic acids were obtained by column chromatography and characterized by \textsuperscript{1}H NMR spectroscopy. \textsuperscript{c} H_{2}O_{2} was added all at once instead of added dropwise.

Catalytic alcohol oxidations by cis-[Ru^{III}(mcp)(O_{2}CCF_{3})_{2}]ClO_{4} (1b) with H_{2}O_{2}

Previously, we showed that [Ru^{III}(Me_{3}tacn)(O_{2}CCF_{3})_{2}(OH_{2})]CF_{3}CO_{2} is an effective catalyst for the oxidation of alcohols using tert-butylhydroperoxide or hydrogen peroxide as terminal oxidant.\textsuperscript{13,14} Prompted by these findings and the reactivity of 1e, we have examined the catalytic activities of 1b for oxidation of alcohols using H_{2}O_{2} as a terminal oxidant. When 35\% aqueous H_{2}O_{2} (0.22 mL, 2.2 mmol) was added dropwise via syringe pump to a mixture of benzyl alcohol (1 mmol) and 1b (10 \mu mol; 1 mol%) in refluxing aqueous tert-butanol, benzoic acid (91\%) and benzaldehyde (5\%) were formed with 100\% substrate conversion (Table S6, entry 2). However, when the reaction was conducted without dropwise addition of H_{2}O_{2}, the substrate conversion was markedly reduced to only 20\% with benzaldehyde obtained in 78\% yield (based on conversion, Table S6, entry 1).
Secondary alcohols such as 1-phenylethanol and 1-phenyl-1-propanol were converted to the corresponding ketones in 85% and 88% yields with complete substrate consumption (Table S6, entries 3 and 4). Likewise, the catalytic oxidation of 2-cyclohexen-1-ol and cyclohexanol produced 2-cyclohexen-1-one (83% yield) and cyclohexanone (98% yield), respectively (Table S6, entries 5 and 6). Oxidation of trans-cinnamyl alcohol produced 57% yield of cinnamyl aldehyde along with 32% yield of benzaldehyde, presumably via C=C bond cleavage reaction (Table S6, entry 7). Terminal alcohols such as 1-heptanol and 1-octanol were effectively oxidized to the corresponding carboxylic acids in 85–95% yields (Table S6, entries 8 and 9). When cis-cyclooctane-1,2-diol was treated with aqueous H₂O₂ (4 equiv.) and 1b (1 mol%) in refluxing aqueous tert-butanol solution for 12 h, octane-1,8-dicarboxylic acid was obtained in 80% yield (Table S6, entry 10). Other 1,2-diols such as trans-cyclopentane-1,2-diol, trans-cyclohexane-1,2-diol, trans-cycloheptane-1,2-diol and docecane-1,2-diol also underwent oxidative cleavage to form terminal carboxylic acids in 65-91% yields under the Ru-catalyzed conditions (Table S6, entries 11-14). Oxidation of 1,2-diphenylethane-1,2-diol gave predominantly benzaldehyde in 80% yield (Table S6, entry 15).

ESI-MS analysis of a mixture of 1b (1 x 10⁻⁴ M) and H₂O₂ (10 equiv.) in water gave an intense signal attributable to [(mcp)Ru₃(OH)₂]⁺. No signals assignable to [Ru⁶(O)₂], [Ru⁵(O)₂], [Ru⁴(O)], or [Ru₃(OOH)] species could be detected.
**Fig. S1** ORTEP drawing of the cation of \(cis-[(mcp)\text{Ru}^{III}\text{Cl}_2]\text{ClO}_4\) (1a). Thermal ellipsoids are at 50% probability level.

**Fig. S2** ORTEP drawing of one (I) of the two crystallographically independent cations present in the crystals of \(cis-[(\text{Me}_2\text{mcp})\text{Ru}^{III}\text{Cl}_2]\text{ClO}_4\) (2a). Thermal ellipsoids are at 30% probability level.
Fig. S3 ORTEP drawing of one (II) of the two crystallographically independent cations present in the crystals of \( \text{cis}^{-}\text{[(Me}_2\text{mcp)}\text{Ru}^{\text{III}}\text{Cl}_2]\text{ClO}_4 \) (2a). Thermal ellipsoids are at 30% probability level.

Fig. S4 ORTEP drawing of the cation of \( \text{cis}^{-}\text{[(pdp)}\text{Ru}^{\text{III}}\text{Cl}_2]\text{ClO}_4 \) \( (3a\cdot\text{ClO}_4) \). Thermal ellipsoids are at 50% probability level.

Fig. S5 ORTEP drawings of the cation of \( \text{cis}^{-}\text{[(Me}_2\text{bqcn)}\text{Ru}^{\text{II}}\text{(NCMe)}_2]\text{(ClO}_4)_2 \) (6d). Thermal ellipsoids are at 50% probability level.
Fig. S6 UV-Vis absorption spectra of 1a and 2a (left) and 3a and 4a (right) in acetonitrile.

Fig. S7 UV-Vis absorption spectra of 3c and 5c (left) and 4c and 6c (right) in water.

Fig. S8 Cyclic voltammograms of cis-dichlororuthenium(III) complexes in DMF (0.1 M TBAPF$_6$ as supporting electrolyte). Working electrode: glassy carbon; scan rate: 0.1 V s$^{-1}$. Initial potential: 0.8 V. Initial scan direction: reduction.
**Fig. S9** Cyclic voltammograms of *cis*-dichlororuthenium(III) complexes 1a – 4a in acetonitrile (0.1 M TBAPF₆ as supporting electrolyte). Working electrode: glassy carbon; scan rate: 0.1 V s⁻¹. Initial potential: 0.8 – 1.0 V. Initial scan direction: reduction.

**Fig. S10** Cyclic voltammograms of 2a in acetonitrile (0.1 M TBAPF₆ as supporting electrolyte) at different scan rates (0.1–5.0 V s⁻¹).
Fig. S11 Cyclic voltammograms of 5d and 6d in acetonitrile (0.1 M TBAPF₆ as supporting electrolyte). Working electrode: glassy carbon; scan rate: 0.1 V s⁻¹.

Fig. S12 Cyclic voltammogram of cis-[(mcp)RuIII(O₂CCF₃)₂]ClO₄ (1b) at pH 5 (acetate buffer). Working electrode: edge-plane pyrolytic graphite.
**Fig. S13** Cyclic voltammograms of 3c’ in 0.1 M CF₃SO₃H (pH 1) at 0.1 V s⁻¹ in the absence or presence of propan-2-ol (IPA; top), ethanol (EtOH; middle) and tosyllic acid (TsOH; bottom). Working electrode: edge-plane pyrolytic graphite.
Fig. S14 Cyclic voltammograms in 0.1 M CF$_3$SO$_3$H (pH 1) of (a) cis-[(pdp)Ru$^{II}$(OH)$_2$](OTs)$_2$ (3c·OTs), (b) cis-[(bqcn)Ru$^{II}$(OH)$_2$](OTs)$_2$ (5c·OTs) and (c) cis-[(Me$_2$bqcn)Ru$^{II}$(OH)$_2$](OTs)$_2$ (6c·OTs); scan rate: 0.1 V s$^{-1}$.
Fig. S15 Cyclic voltammograms at 0.1 V s⁻¹ of 3c' in Britton-Robinson buffer at pH 2.56 (top), pH 5.02 (middle) and pH 6.37 (bottom).
Fig. S16 (Top) Simulation of [(mcp)Ru VI(O)2]2+. (Bottom) Experimental ESI-MS signals of 1e in water.

Fig. S17 (Top) Simulation of [(pdp)Ru V(O)(OH)]2+. (Middle) Simulation of [(pdp)Ru IV(O)]2+. (Bottom) Experimental ESI-MS signals for a reaction mixture of 3c-CF3SO3 and 4 equiv. of CeIV(ClO4)4, [Ru] = 1 × 10^{-4} M.
Fig. S18 Time trace from 0 to 3 min of the signal intensity of $m/z = 555.05$ ion.

Fig. S19 (a) (Top-left) Simulation of $[(pdp)Ru^{V}(O)_{2}]^{+}$. (Bottom-left) Experimental ESI-MS signals for a reaction mixture of $3c·CF_{3}SO_{3}$ and 6 equiv. of Ce$^{IV}$(ClO$_{4}$)$_{4}$, [Ru] $= 1 \times 10^{-3}$ M. (b) (Right) Time trace from 0 to 3 min of the signal intensity of $m/z = 456.10$ ion.
Fig. S20. (Top) Simulation of \([(\text{Me}_2\text{pdp})\text{Ru}^{\text{V}}(\text{O})_2]^{+}\). (Middle) Experimental ESI-MS signals for a reaction mixture of 4c·OTs and 6 equiv. of CAN, [Ru] = 1 × 10^{-4} M. (Bottom) Experimental ESI-MS signals for a reaction mixture of 4c·OTs and 10 equiv. of CAN, [Ru] = 1 × 10^{-4} M.

When an aqueous solution of cis-\([(\text{Me}_2\text{pdp})\text{Ru}^{\text{II}}(\text{OH})_2]_2(\text{OTs})_2\) (4c·OTs) was treated with CAN (6 equiv.), a new signal was detected at \(m/z\) 484.3 assignable to \([(\text{Me}_2\text{pdp})\text{Ru}^{\text{V}}(\text{O})_2]^{+}\) (see middle of Fig. S20). Subsequent increase of the CAN concentration to 10 equiv. did not produce signals attributed to Ru(VI) species. Instead, a shift of the \(m/z\) 484.3 signal to \(m/z\) 483.2 was observed (see bottom of Fig. S20). We propose that intramolecular oxidation of the ortho-methyl group has occurred via a highly reactive cis-dioxoruthenium(VI) intermediate:

![Chemical Structure Diagram]

Similar oxygenation of aliphatic C–H bond adjacent to pyridine ring has been documented.\(^{15}\)
NMR spectra of oxidation products P11–P14

P11: Matches with reported NMR data (ref. 16).
**P12**: $^1$H NMR (400 MHz, CDCl$_3$): δ 8.07–8.10 (d, 2H), 7.70–7.78 (m, 6H), 3.43–3.48 (m, 1H), 1.85–1.92 (m, 1H), 1.51–1.58 (m, 1H), 1.24–1.25 (d, 3H), 0.94–0.98 (t, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$): δ 203.8, 144.4, 143.2, 136.6, 132.7, 129.1, 127.9, 127.5, 118.7, 111.9, 42.3, 26.7, 16.7, 11.8.
P13: $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 9.54 (s, 1H), 6.51 (s, 1H), 2.66–2.74 (m, 1H), 1.21–1.28 (d, 6 H). $^{13}$C NMR (100 MHz, CDCl$_3$): 158.2, 133.4, 122.8, 24.4, 20.2. MS (EI): 127.0
P14: \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 5.26 (s, 1H), 1.93 (s, 3H), 1.89 (s, 2H), 1.58–1.64 (m, 4H), 1.29–1.45 (m, 5H), 1.09–1.18 (m, 2H), 0.94 (s, 6H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): 169.5, 70.3, 55.2, 50.4, 49.5, 47.7, 46.5, 34.2, 29.2, 24.6.
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