Electronic Supplementary Information (ESI) for:

Ruthenium catalysts bearing a benzimidazolylidene ligand for the metathetical ring-closure of tetrasubstituted cycloolefins

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I. Experimental Procedures

1. General information

All the reactions were carried out using standard Schlenk techniques under a dry argon atmosphere. Solvents were distilled from appropriate drying agents and deoxygenated prior to use. The first-generation Hoveyda–Grubbs catalyst[1] and the substrates for RCM reactions[2] were prepared according to literature. Petroleum ether refers to the hydrocarbon fraction of bp 40–60 °C and was purchased from Labotec. Chromatography was performed on silica gel 60 (60 Å nominal pore diameter, 0.063–0.200 mm particle size) supplied by Biosolve. All the other chemicals were purchased from Aldrich and used as received. Unless otherwise specified, ^{1}H, $^{13}C\{^{1}H\}$, and $^{31}P\{^{1}H\}$ NMR spectra were recorded at 298 K with a Bruker DRX 400 or a Bruker Avance 250 spectrometer. Chemical shifts are listed in parts per million downfield from TMS and are referenced from the solvent peaks or TMS. Infrared spectra were recorded with a Perkin-Elmer Spectrum One FT-IR spectrometer. Elemental analyses were carried out in the Laboratory of Pharmaceutical Chemistry at the University of Liège.

2. Synthesis of 1,3-di(2-tolyl)benzimidazolium tetrafluoroborate (7)

To a 100 mL round-bottom flask fitted with a three-way stopcock and containing $Pd(OAc)_2$ (114.2 mg, 0.5 mmol) were added toluene (30 mL) and a 1 M solution of tri-*tert*-butylphosphine in toluene (1.53 mL, 1.53 mmol). The mixture was stirred until complete dissolution of the palladium salt. 1,2-Dibromobenzene (3.00 g, 12.7 mmol) and 2-toluidine (2.7 mL, 25.3 mmol) were then added to the flask and the resulting solution was transferred under argon into a second 100 mL round-bottom flask containing sodium *tert*-butoxide (3.67 g, 38 mmol). The resulting suspension was heated at 110 °C overnight. After cooling to room temperature, it was brought back to air and quenched with saturated aqueous NH_4Cl (50 mL). The organic phase was washed with deionized water (50 mL), dried over $MgSO_4$, and concentrated under vacuum to afford a dark green oil that was purified by column chromatography on silica gel using petroleum ether/ethyl acetate (70/30 v/v) as eluents. Upon acidification with concentrated aqueous hydrochloric acid and evaporation of the volatiles, crude *N,N′*-bis(2-tolyl)-*o*-phenylenediamine dihydrochloride was obtained as a hygroscopic pinkish powder that was immediately used for the next step.

To this intermediate diamine dihydrochloride (2.20 g, 6.1 mmol) in triethyl orthoformate (40 mL) was added concentrated aqueous hydrochloric acid (2 mL) and formic acid (5 drops). The suspension was refluxed overnight and the solvent evaporated under vacuum to afford 1,3-di(2-tolyl)benzimidazolium chloride as a highly hygroscopic oil. Addition of 48% aqueous HBF_4 (1.6 mL, 12.2 mmol, 2 equiv) to this salt dissolved in water (30 mL) afforded a white precipitate that was recrystallized from ethanol to give pure 1,3-di(2-tolyl)benzimidazolium tetrafluoroborate (**7**) as a white crystalline powder (1.83 g, 78% yield for the cyclization step). ^{1}H NMR (250 MHz, CD_2Cl_2): δ 9.33 (s, 1 H, H2), 7.73 (dd, J = 3.2 and 6.4 Hz, 2 H), 7.60–7.66 (m, 4 H), 7.50–7.56 (m, 4 H), 7.46 (dd, J = 3.2 and 6.4 Hz, 2 H), 2.18 (s, 6 H, Me) ppm. ^{13}C{^{1}H} NMR (62.5 MHz, CD_2Cl_2): δ 141.5, 135.0, 132.1, 132.0, 131.9, 131.2, 128.6, 128.0, 127.6, 113.9, 17.1 ppm.

3. Synthesis of 1,1',3,3'-tetra-*o*-tolyl-1,1',3,3'-tetrahydro-2,2'-bibenzo[*d*]imidazolylidene (8)

Under an inert atmosphere, a 0.5 M solution of potassium bis(trimethylsilyl)amide in toluene (0.65 mL, 0.32 mmol, 1.25 equiv) was added to a suspension of 1,3-di(2-tolyl)benzimidazolium tetrafluoroborate (**7**) (100 mg, 0.26 mmol) in toluene (2 mL). The reaction mixture was stirred for 30 min at room temperature. It was then filtered on a 0.45 μm membrane. The filtrate was further stirred for 2 h at room temperature, during which the solution progressively turned bright orange. The solvent was evaporated under vacuum to yield the $(BTol)_2$ carbene dimer as a bright orange powder (70 mg, 90% yield). ^{1}H NMR (400 MHz, C_6D_6, 333 K): δ 7.34 (s, 16 H), 6.65 (dd, J = 3.2 and 5.6 Hz, 4 H), 6.25 (dd, J = 3.2 and 5.6 Hz, 4 H), 1.83 (s, 12 H, o-CH_3) ppm. ^{13}C{^{1}H} NMR (101 MHz, C_6D_6): δ 143.6, 141.1, 137.7, 131.8, 129.7, 128.9, 127.5, 127.0, 121.3, 109.4, 17.9 ppm.

4. Synthesis of [RhCl(COD)(BTol)] (9)

In a 50 mL Schlenk flask, $[RhCl(COD)]_2$ (50.0 mg, 0.1 mmol) and potassium *tert*-butoxide (25.0 mg, 0.22 mmol, 2.2 equiv) were stirred for 45 min at room temperature in THF (25 mL). Next, 1,3-di(2-tolyl)benzimidazolium tetrafluoroborate (**7**) (82.1 mg, 0.22 mmol, 2.2 equiv) was added and the reaction mixture was stirred overnight at room temperature. It was brought back to air and filtered on a 0.45 μm membrane. The filtrate was evaporated under vacuum. The residue was dissolved in dichloromethane/pentane and purified by column chromatography on silica gel using petroleum ether/ethyl acetate (3/1 v/v) as eluents to afford the title compound (R_f = 0.39) as a yellow powder (89.4 mg, 82% yield). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 8.50–8.36 (m, 1.5 H),

7.63–7.39 (m, 6.5 H), 7.26–7.14 (m, 2 H), 7.04–6.94 (m, 1.5 H), 6.94– 6.85 (m, 0.5 H), 4.79–4.62 (m, 1.5 H), 4.57–4.40 (m, 0.5 H), 3.57–3.44 (m, 0.5 H), 2.99–2.82 (m, 1.5 H), 2.29 (s, 0.5 H), 2.25 (s, 1.25 H), 2.19–2.11 (m, 1 H), 2.11 (s, 1.25 H), 2.02 (s, 3 H), 1.97–1.82 (m, 1 H), 1.82–1.62 (m, 3 H), 1.62–1.38 (m, 3 H) ppm. $^{13}C\{^{1}H\}$ NMR (101 MHz, CD_2Cl_2): δ 198.4 (d, $J_{Rh–C}$ = 50.6 Hz), 197.9 (d, $J_{Rh–C}$ = 51.1 Hz), 138.0, 137.7, 137.1, 136.7, 136.7, 136.58, 135.55, 135.2, 134.6, 134.3, 134.1, 131.8, 131.7, 131.6, 130.7, 130.5, 129.6, 129.34, 129.30, 128.9, 128.6, 127.0, 126.9, 126.3, 126.2, 123.10, 123.07, 123.00, 111.1, 111.0, 110.7, 110.5, 98.9, 98.8, 98.73, 98.66, 98.5, 98.39, 98.35, 98.28, 69.2, 69.1, 68.8, 68.7, 67.9, 67.7, 67.0, 66.9, 32.4, 32.33, 32.26, 28.4, 28.3, 28.2, 28.0, 18.8, 18.1, 17.9 ppm. Anal. Calc. for $C_{29}H_{30}ClN_2Rh$ (544.92): C, 63.9; H, 5.6; N, 5.1%. Found: C, 64.3; H, 5.6, N, 5.0%.

5. Synthesis of [RhCl(CO)$_2$(BTol)] (10)

Carbon monoxide was bubbled into a solution of [RhCl(COD)(BTol)] (**9**) (50 mg, 0.09 mmol) in dichloromethane (10 mL) for 15 min at room temperature. The solvent was evaporated under vacuum and the residue was washed with a minimal amount of *n*-pentane at 0 °C, leaving a light yellow solid (30 mg, 71% yield). IR (NaCl, CH_2Cl_2): ν_{CO} 2080 (*trans*) and 1999 cm^{-1} (*cis*). ^1H NMR (250 MHz, CD_2Cl_2): δ 7.72–7.40 (m, 10 H), 7.35 (dd, *J* = 3.2 and 6.1 Hz, 2 H), 7.08 (dd, *J* = 3.2 and 6.1 Hz, 2 H), 2.17 (s, 3 H), 2.13 (s, 3 H) ppm. $^{13}C\{^{1}H\}$ NMR (62.5 MHz, CD_2Cl_2): δ 187.1 (dd, $J_{Rh–C}$ = 43.4 and 5.3 Hz), 185.7 (dd, $J_{Rh–C}$ = 54.3 and 1.9 Hz), 182.8 (dd, $J_{Rh–C}$ = 74.1 and 1.3 Hz), 135.9, 135.9, 135.2, 135.0, 131.43, 131.37, 130.2, 127.1, 124.49, 124.46, 111.72, 111.66, 17.8, 17.6 ppm.

6. Synthesis of [RuCl$_2$(=CHPh)(PCy$_3$)(BTol)] (11)

N,N′-bis(2-tolyl)benzimidazolium tetrafluoroborate (**7**) (100 mg, 0.26 mmol, 1.5 equiv) was weighed in a Schlenk tube and placed under an argon atmosphere. Toluene (3 mL) and a 0.5 M solution of potassium bis(trimethylsilyl)amide in toluene (0.62 mL, 0.31 mmol, 1.8 equiv) were added and the mixture was stirred for 15 min at room temperature. It was then cannulated under argon into a second flask containing a solution of [$RuCl_2$(=CHPh)(PCy_3)$_2$] (142 mg, 1 equiv) in toluene (12 mL). The mixture was stirred overnight at room temperature. The solvent was evaporated under vacuum and the residue was purified by column chromatography under argon. Tricyclohexylphosphine was first eluted with *n*-pentane. The desired product was then eluted as a dark orange band with *n*-pentane/diethyl ether (9/1 v/v) as eluents. The solvents were evaporated

and the solid was dried under high vacuum to yield the title compound as a red-brown powder (98 mg, 68%). ^{1}H NMR (400 MHz, CD_2Cl_2, 298 K): δ 19.26 (s, 0.6 H), 19.22 (s, 0.4 H), 8.25–8.13 (m, 1.2 H), 7.56–7.44 (m, 3.8 H), 7.44–6.98 (m, 7 H), 6.98–6.80 (m, 2.6 H), 6.76 (d, J = 7.9 Hz, 0.6 H), 6.62 (t, J = 7.3 Hz, 1.8 H), 2.39 (s, 1.8 H), 2.30 (s, 1.8 H), 2.26 (s, 1.2 H), 2.06 (s, 1.2 H), 2.15–1.75 (m, 7 H), 1.75– 0.65 (m, 26 H) ppm. ^{13}C{^{1}H} NMR (62.5 MHz, CD_2Cl_2, 298 K): δ 297.3 (Ru=*C*HPh), 294.5 (Ru=*C*HPh), 202.4 ($J_{P–C}$ = 80.8 Hz, $C2_{NHC}$), 201.5 ($J_{P–C}$ = 82.2 Hz, $C2_{NHC}$), 161.8, 149.4, 141.0, 139.6, 138.7, 137.6, 137.2, 136.2, 135.8, 135.6, 135.5, 135.3, 135.2, 134.8, 134.6, 133.6, 132.9, 131.3, 130.9, 130.4, 130.3, 130.0, 129.6, 129.5, 129.4, 129.2, 128.7, 128.6, 128.3, 127.9, 127.8, 127.5, 127.3, 127.1, 126.5, 126.1, 126.0, 125.7, 122.4, 121.1, 119.9, 119.7, 115.5, 110.5, 110.2, 109.4, 109.1, 33.7, 31.3, 31.2, 31.0, 30.9, 29.5, 28.2, 27.8, 27.1, 27.0, 25.5, 22.2, 18.4, 18.1, 17.4, 17.2, 16.9, 13.7 ppm. ^{31}P{^{1}H} NMR (101 MHz, CD_2Cl_2, 298 K): δ 29.2, 26.2 ppm. ^{1}H NMR (400 MHz, CD_2Cl_2, 223 K, benzylidene protons only): δ 19.11 (s, 0.5 H), 19.03 (s, 0.1 H), 18.96 (s, 0.3 H), 18.81 (s, 0.1 H) ppm. ^{31}P{^{1}H} NMR (101 MHz, CD_2Cl_2, 223 K): δ 31.0, 29.6, 27.2, 24.2 ppm. Calc. for $C_{46}H_{57}Cl_2N_2PRu$: C, 65.7; H, 6.8; N, 3.3%. Found: C, 65.5; H, 6.4, N, 3.7%.

7. Synthesis of [$RuCl_2$(=CH-*o*-O^{i}PrC_6H_4)(BTol)] (12)

N,N′-bis(2-tolyl)benzimidazolium tetrafluoroborate (**7**) (142 mg, 0.37 mmol, 1.2 equiv) was weighed in a Schlenk tube and placed under an argon atmosphere. Toluene (3 mL) and a 0.5 M solution of potassium bis(trimethylsilyl)amide in toluene (0.93 mL, 0.47 mmol, 1.5 equiv) were added and the mixture was stirred for 15 min at room temperature. It was then cannulated under argon into a second flask containing a solution of [$RuCl_2$(=CH-*o*-O^{i}PrC_6H_4)(PCy_3)] (185 mg, 0.31 mmol, 1 equiv) in toluene (15 mL). The reaction mixture was stirred for 1 h at 60 °C before copper(I) chloride (59.3 mg, 0.6 mmol) was added and stirring at 60 °C was resumed for 2 h. The suspension was cooled to room temperature and filtered on a 0.45 μm nylon membrane. The solvent was evaporated under vacuum. The residue was purified by column chromatography on silica gel with pentane/dichloromethane (9/1 v/v) as eluents to afford the title compound as a yellow-green microcrystalline powder (124 mg, 65%). ^{1}H NMR (250 MHz, CD_2Cl_2, 223 K): δ 16.41 (s, 0.4 H), 16.24 (s, 0.6 H), 8.52 (m, 1 H), 7.71–7.33 (m, 10 H), 7.20–7.10 (m, 2 H), 7.00–6.89 (m, 4 H), 5.03 (sept. J = 5.8 Hz, 1 H), 2.22–2.11 (m, 6 H), 1.48–1.18 (m, 6 H) ppm. ^{13}C{^{1}H} NMR (62.5 MHz, CD_2Cl_2, 223 K): δ 294.4, 292.7, 191.7, 191.1, 152.1, 151.8, 143.0, 142.7,

138.0, 137.8, 137.5, 137.0, 136.9, 136.7, 136.6, 136.5, 136.3, 135.4, 135.3, 134.9, 134.4, 134.2, 133.3, 133.2, 132.2, 131.4, 131.2, 131.1, 131.0, 130.8, 130.1, 130.0, 129.8, 129.7, 129.4, 128.9, 128.4, 127.9, 127.7, 127.5, 127.3, 127.0, 126.8, 124.3, 122.6, 122.12, 122.05, 121.9, 121.5, 121.3, 112.7, 111.7, 109.3, 109.1, 108.6, 108.3, 108.1, 74.9, 74.8, 21.1, 21.0, 20.9, 20.8, 18.6, 18.4, 17.6, 17.44, 17.35, 17.2 ppm. Calc. for $C_{31}H_{30}Cl_2N_2ORu$: C, 60.2; H, 4.9; N, 4.5%. Found: C, 60.3; H, 5.2, N, 4.3%.

8. RCM of α,ω-dienes 13 and 15

A 2 mL volumetric flask capped with a septum was charged with a ruthenium complex (3.2 μmol) under argon. Dried and degassed dichloromethane-d_2 (2 mL) was added with a dried syringe under argon. An NMR tube capped with a septum was charged with this stock solution (0.50 mL, 0.8 μmol of catalyst) and dichloromethane-d_2 (0.3 mL) under argon. The sample was thermostated at 30 °C in the NMR probe before the substrate (**13**: 19.3 μL or **15**: 20.5 μL, 0.08 mmol, 0.1 M) was added with a dried microsyringe under argon. Experimental data points were collected using the Bruker automation software. The conversion of diethyl 2,2-diallylmalonate (**13**) was computed from the integrals of the allyl methylene protons in the starting material (δ = 2.53, d) and the product (δ = 2.90, s). The conversion of diethyl 2-allyl-2-(2-methylallyl)-malonate (**15**) was determined similarly from the signals of the allyl methylene protons in the starting material (δ = 2.59, s and 2.56, m) and the product (δ = 2.79, m and 2.85, m).

9. RCM of α,ω-dienes 17 and 19

An NMR tube capped with a septum was charged with a ruthenium complex (4 μmol, 5 mol%) under argon. Dried and degassed benzene-d_6 (0.8 mL) was then introduced under argon. The sample was thermostated at 60 °C in the NMR probe before the substrate (**17**: 21.6 μL or **19**: 22.3 μL, 0.08 mmol, 0.1 M) was added with a dried microsyringe under argon. Experimental data points were collected using the Bruker automation software. The conversion of diethyl 2,2-bis(2-methylallyl)malonate (**17**) and 4-methyl-*N,N*-bis(2-methylallyl)benzenesulfonamide (**19**) were computed from the integrals of the allyl methylene protons in the starting material (δ = 2.65, s or 3.68, s, respectively) and the product (δ = 2.81, s or 3.88, s respectively).

II. X-Ray diffraction studies

1. General Information

Crystal data were collected on Bruker Smart CCD-1000 (**8**) or APEX II (**9**, **12**) diffractometers using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) from a fine-focus sealed tube source at 100 K. Computing data and reduction was made with the APEX II software.[3] The structures of **8** and **9** were solved using SIR[4] and the structure of **12** with DIRDIF.[5] They were refined by full-matrix, least-squares based on F^2 by SHELXL.[6] An empirical absorption correction was applied using SADABS.[7] All non-hydrogen atoms were anisotropically refined and the hydrogen atoms positions were included in the model by electronic density or were geometrically calculated and refined using a riding model.

2. Crystal Data for the $(BTol)_2$ carbene dimer (8)

Orange crystals obtained by slow evaporation of a concentrated solution in toluene under an inert atmosphere. The crystal lattice contained 2 molecules of dimer and 5 molecules of solvent, $2(C_{42}H_{36}N_4)•5(C_7H_8)$, M = 1654.17, crystal dimensions: 0.5 × 0.25 × 0.06 mm, monoclinic, a = 11.6641(8), b = 31.857(3), c = 13.0216(10) Å, β = 110.406(3)°, V = 4534.9(6) Å^3, T = 100 K, space group $P2_1/n$, Z = 2, λ(Mo-$K\alpha$) = 0.7107 Å, 66779 reflections collected, 8289 independent reflections, R_{int} = 0.129, $R[F^2 > 2\sigma(F^2)]$ = 0.067, $wR(F^2)$ = 0.193.

3. Crystal Data for [RhCl(COD)(BTol)] (9)

Bright yellow crystals obtained by slow evaporation of a concentrated solution in dichloromethane under an inert atmosphere. The compound co-crystallized with one molecule of solvent, $C_{29}H_{30}ClN_2Rh•CH_2Cl_2$, M = 629.84, crystal dimensions: 0.22 × 0.11 × 0.08 mm, monoclinic, a = 12.303(2), b = 10.941(2), c = 21.492(4) Å, β = 106.131(2)°, V = 2779.0(9) Å^3, T = 100 K, space group $P2_1/n$, Z = 4, λ(Mo- $K\alpha$) = 0.7107 Å, 25154 measured reflections, 5706 independent reflections, R_{int} = 0.045, $R[F^2 > 2\sigma(F^2)]$ = 0.030, $wR(F^2)$ = 0.069.

4. Crystal Data for $[RuCl_2(=CH\text{-}o\text{-}O^iPrC_6H_4)(BTol)]$ (12)

Dark green crystals obtained by slow evaporation of a dichloromethane/cyclohexane solution under an inert atmosphere, $C_{31}H_{30}Cl_2N_2ORu$, M = 618.54.

Crystal A: crystal dimensions: 0.35 × 0.1 × 0.1 mm, monoclinic, a = 14.5764(6), b = 16.7449(7), c = 12.2037(5) Å, β = 112.151(2)°, V = 2758.8(2) Å^3, T = 100 K, space group $P2_1/c$, Z = 4, λ(Mo-$K\alpha$) = 0.7107 Å, 47107 measured reflections, 6856 independent reflections, R_{int} = 0.076, $R[F^2 > 2\sigma(F^2)]$ = 0.038, $wR(F^2)$ = 0.076.

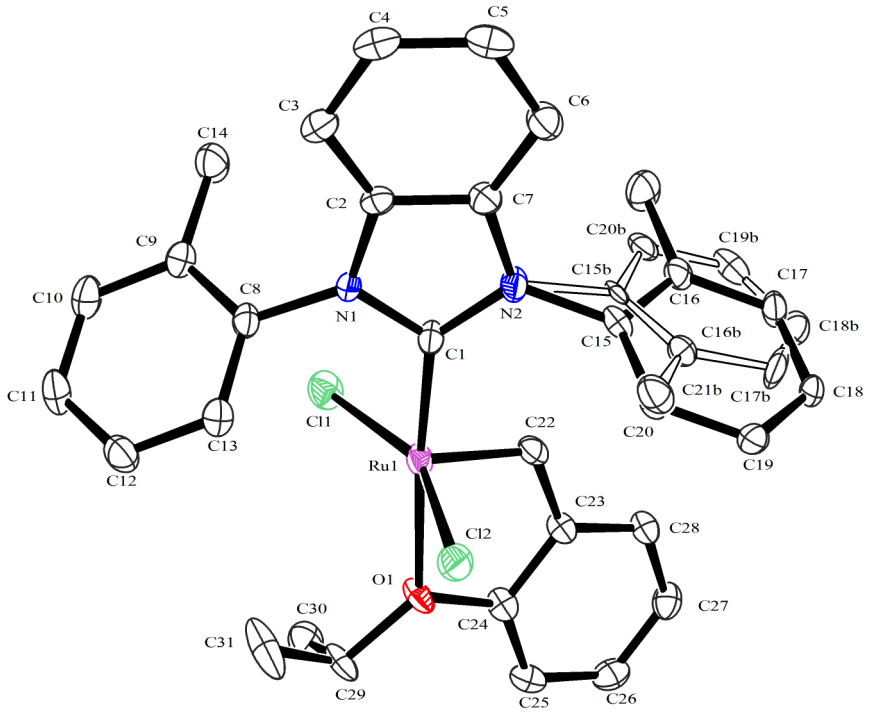

Figure S1. ORTEP representation of (S_a,R_a)-[$RuCl_2$(=CH-*o*-O^{i}PrC_6H_4)(BTol)] (**12b**) and (S_a,S_a)-[$RuCl_2$(=CH-*o*-O^{i}PrC_6H_4)(BTol)] (**12d**) in crystal **A**. Selected bond length (Å) and angles (deg): Ru1–C1 1.955(3), Ru1–Cl1 2.3362(7), Ru1–Cl2 2.3413(8), Ru1–O1 2.2675(18), Ru1–C22 1.817(3), N1–C1–N2 104.7(2), Cl1–Ru1–Cl2 155.81(3), C1–Ru1–O1 175.57(9), Cl2–Ru1–C22 104.04(9), Cl1–Ru1–C22 98.51(9).

Crystal B: crystal dimensions: 0.14 × 0.13 × 0.04 mm, monoclinic, a = 8.4640(4), b = 32.1234(14), c = 10.6949(5) Å, β = 108.894(3)°, V = 2751.2(2) Å^3, T = 100 K, space group $P2_1/n$, Z = 4, λ(Mo-$K\alpha$) = 0.7107 Å, 38665 measured reflections, 5677 independent reflections, R_{int} = 0.110, $R[F^2 > 2\sigma(F^2)]$ = 0.084, $wR(F^2)$ = 0.148.

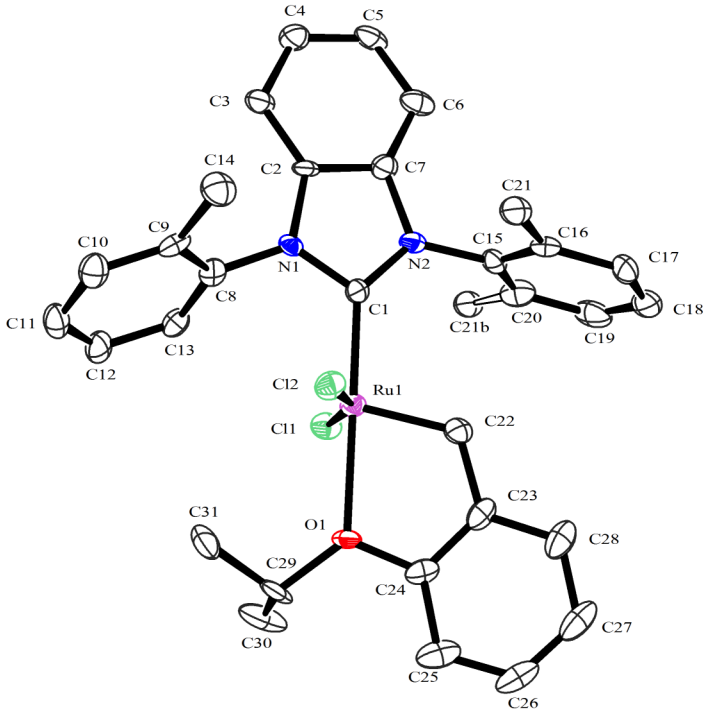

Figure S2. ORTEP representation of (R_a,R_a)-[$RuCl_2$(=CH-*o*-O^{i}PrC_6H_4)(BTol)] (**12c**) in crystal **B**. Selected bond length (Å) and angles (deg): Ru1–C1 1.966(7), Ru1–Cl1 2.3481(19), Ru1–Cl2 2.335(2), Ru1–O1 2.259(5), Ru1–C22 1.823(7), N1–C1–N2 105.2(6), Cl1–Ru1–Cl2 159.31(7), C1–Ru1–O1 179.1(2), Cl2–Ru1–C22 100.0(2), Cl1–Ru1–C22 99.7(2).

CCDC-1045783 (**12A**), 1045784 (**12B**), 1045785 (**8**) and 1045786 (**9**) contain the supplementary crystallographic data for these compounds. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

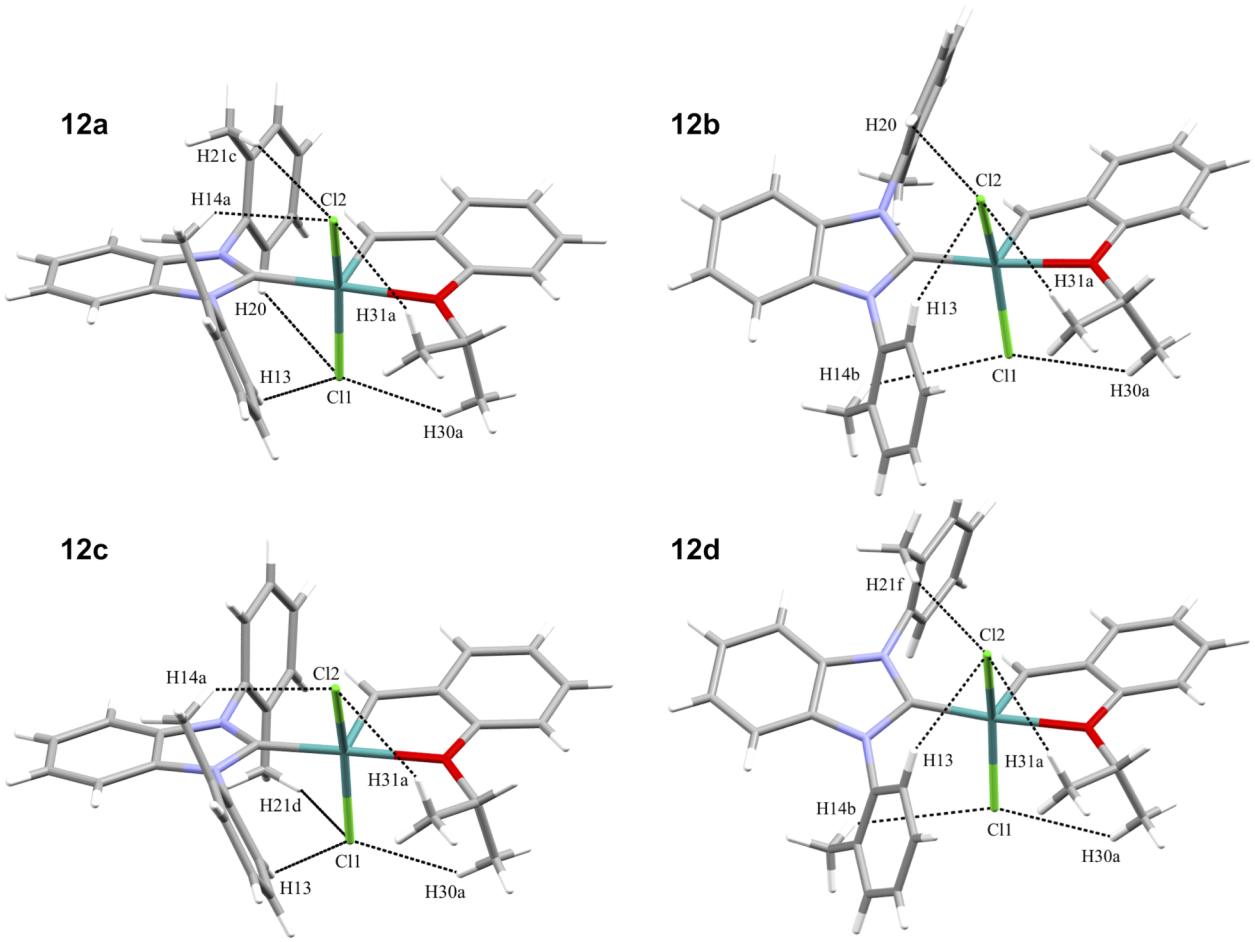

Figure S3. Short distance interactions within the molecular structures of [$RuCl_2$(=CH-*o*-O^{i}Pr-C_6H_4)(BTol)] (**12**).

Table S1. Hydrogen bond parameters derived from the molecular structures of complex **12**

Rotamer	Donor–H···Acceptor	D–H (Å)	H···A (Å)	D···A (Å)	D–H···A (°)
12c, **12a**	C(30)–H(30A)···Cl(1)	0.98	2.83	3.672(8)	144.3
12c, **12a**	C(31)–H(31A)···Cl(2)	0.98	2.85	3.579(8)	131.9
12c, **12a**	C(13)–H(13)···Cl(1)	0.95	2.74	3.500(8)	137.6
12c, **12a**	C(14)–H(14A)···Cl(2)	0.98	2.87	3.608(8)	133.3
12c	C(21B)–H(21D)···Cl(1)	0.98	2.61	3.48(4)	147.1
12c	C(16)–H(16)···Cl(2)	0.95	4.42	4.774(7)	106.1
12a	C(20)–H(20)···Cl(1)	0.95	3.65	4.3116(8)	113.4
12a	C(21)–H(21C)···Cl(2)	0.98	3.28	4.241(10)	167.4
12b, **12d**	C(30)–H(30A)···Cl(1)	0.98	3.08	3.861(3)	137.3
12b, **12d**	C(31)–H(31A)···Cl(2)	0.98	2.88	3.651(3)	136.4
12b, **12d**	C(13)–H(13)···Cl(2)	0.95	2.82	3.627(3)	143.4
12b, **12d**	C(14)–H(14B)···Cl(1)	0.98	3.40	3.894(3)	113.5
12b	C(20)–H(20)···Cl(2)	0.95	2.72	3.309(5)	120.6
12b	C(21)–H(21F)···Cl(1)	0.98	4.64	5.428(6)	139.6
12d	C(21B)–H(21F)···Cl(2)	0.98	2.62	3.547(7)	157.3
12d	C(20B)–H(20B)···Cl(1)	0.95	4.78	5.094(8)	103.7

Table S2. Analysis of X–H···Cg (π-ring) interactions within complex **12**

Rotamer		H···Cg (Å)	H–Perp (Å)	γ (°)	X–H···Cg (°)	X···Cg (Å)
12c, **12a**		2.49	2.33	20.39	158	3.390
12b	C(22)–H(22)···Cg	2.92	2.51	30.77	126	2.919
12d		2.59	2.32	26.13	141	3.369

Table S3. Malone categories of X–H···Cg (π-ring) interactions within complex **12**

Rotamer	$d\pi_C H$	d	Θ	α	Type
12c, **12a**	2.49	0.88	69.6	158	II
12b	2.92	1.49	59.2	126	VI
12d	2.59	1.15	63.9	141	III

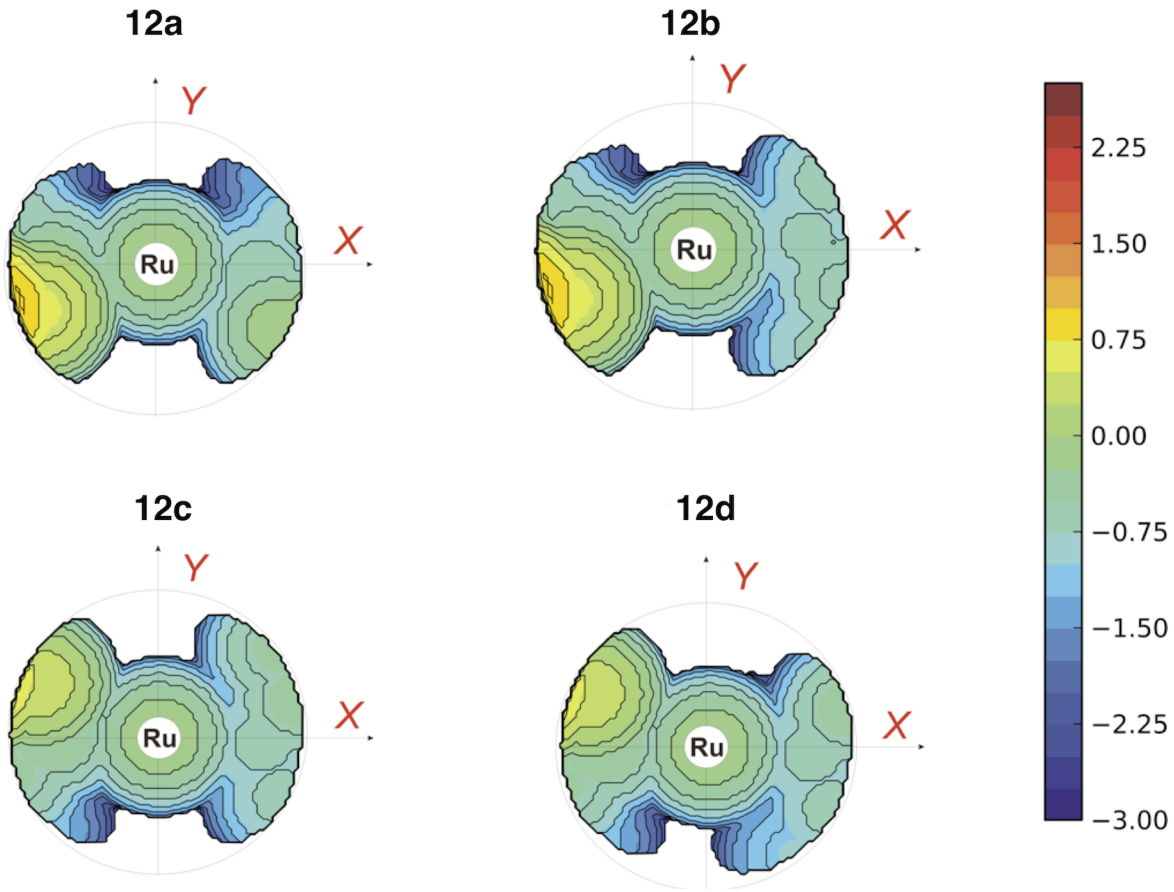

Figure S4. $\%V_{Bur}$ maps of the four possible rotamers of [$RuCl_2$(=CH-*o*-O^{i}PrC_6H_4)(BTol)] (**12**) derived from the molecular structures of crystals **A** and **B** with the color scale used to display the isocontour levels (in Å).

III. Bibliography

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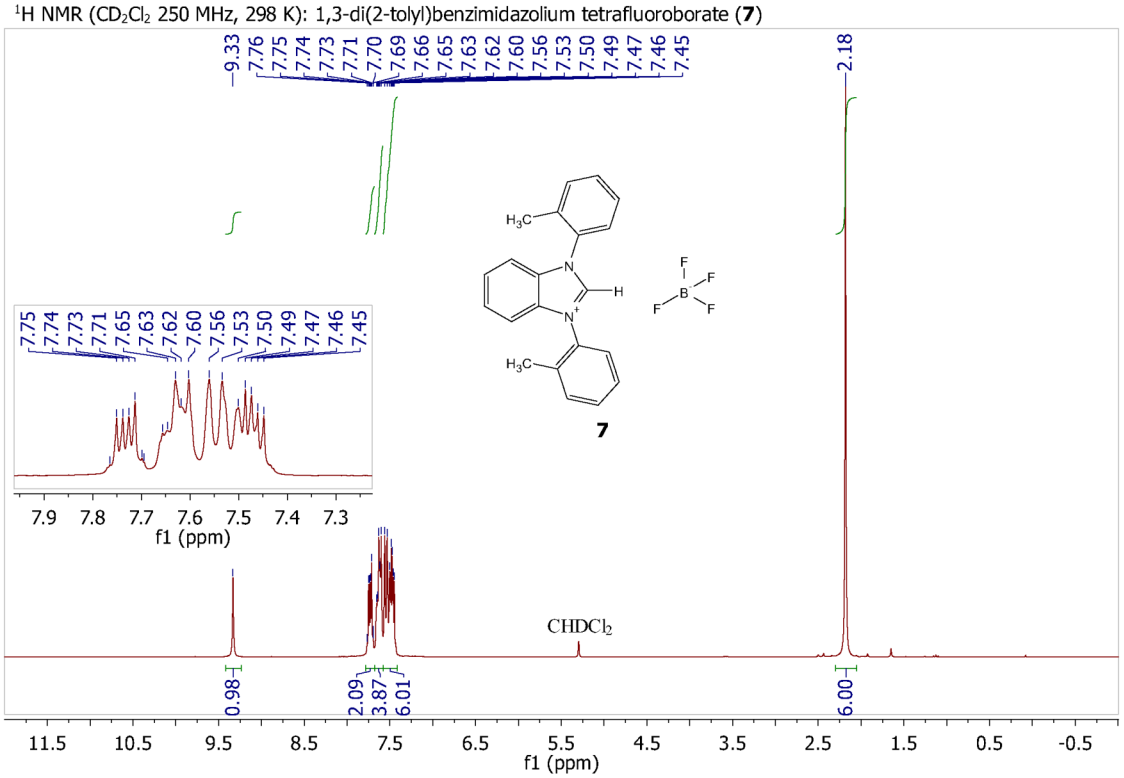
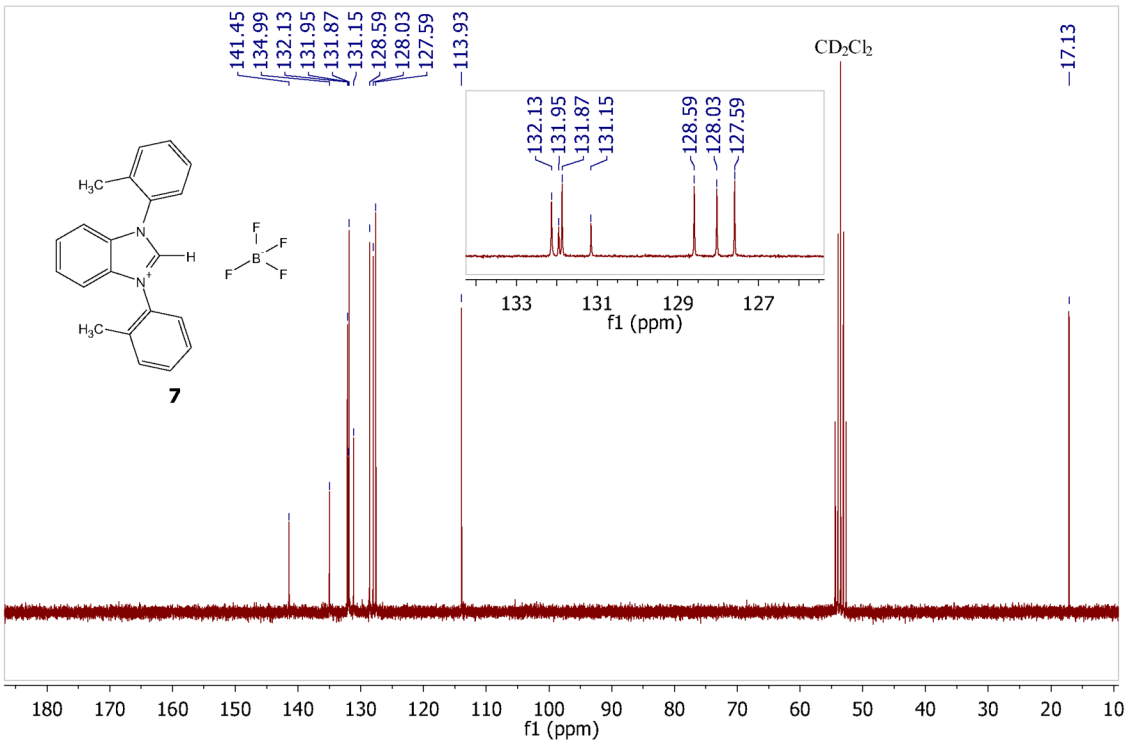
IV. NMR Spectra

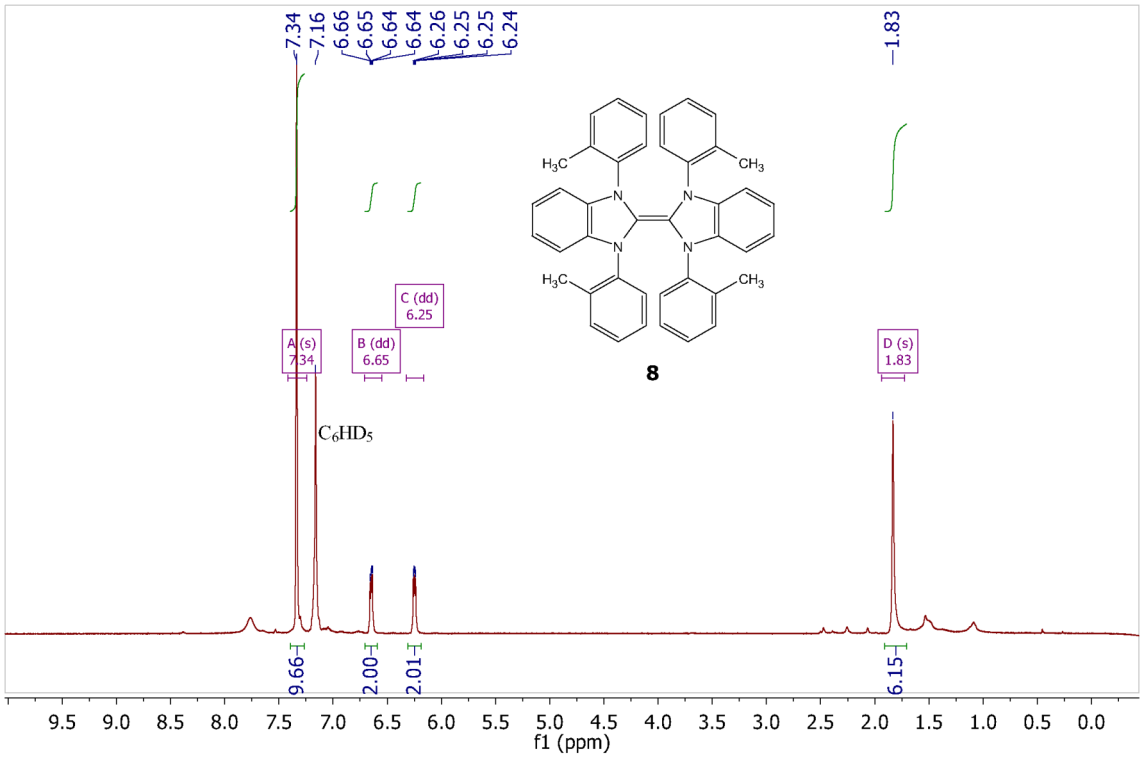
^{1}H NMR (CD_2Cl_2 250 MHz, 298 K): 1,3-di(2-tolyl)benzimidazolium tetrafluoroborate (**7**)



^{13}C NMR (CD_2Cl_2 63MHz, 298 K): 1,3-di(2-tolyl)benzimidazolium tetrafluoroborate (**7**)

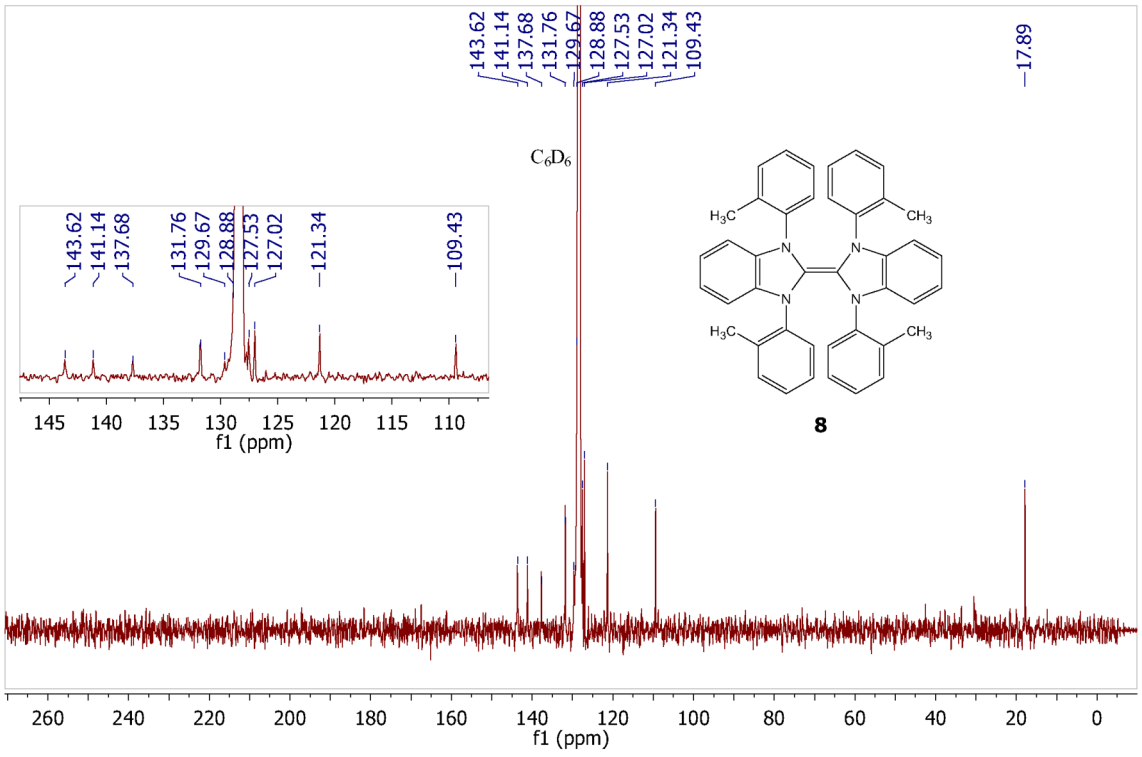


^{1}H NMR (C_6D_6 400 MHz, 333 K): 1,1',3,3'-tetra-*o*-tolyl-1,1',3,3'-tetrahydro-2,2'-bibenzo[*d*]imidazolylidene (**8**)



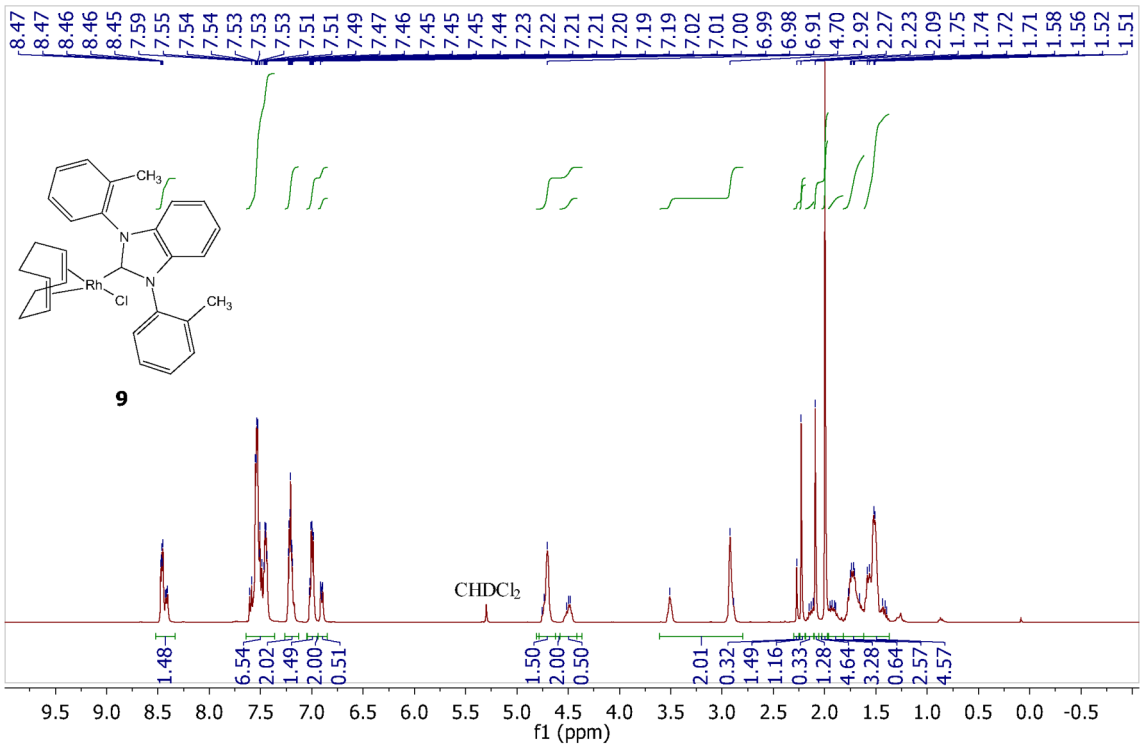
8

^{13}C NMR (C_6D_6 101 MHz, 333 K): 1,1',3,3'-tetra-*o*-tolyl-1,1',3,3'-tetrahydro-2,2'-bibenzo[*d*]imidazolylidene (**8**)

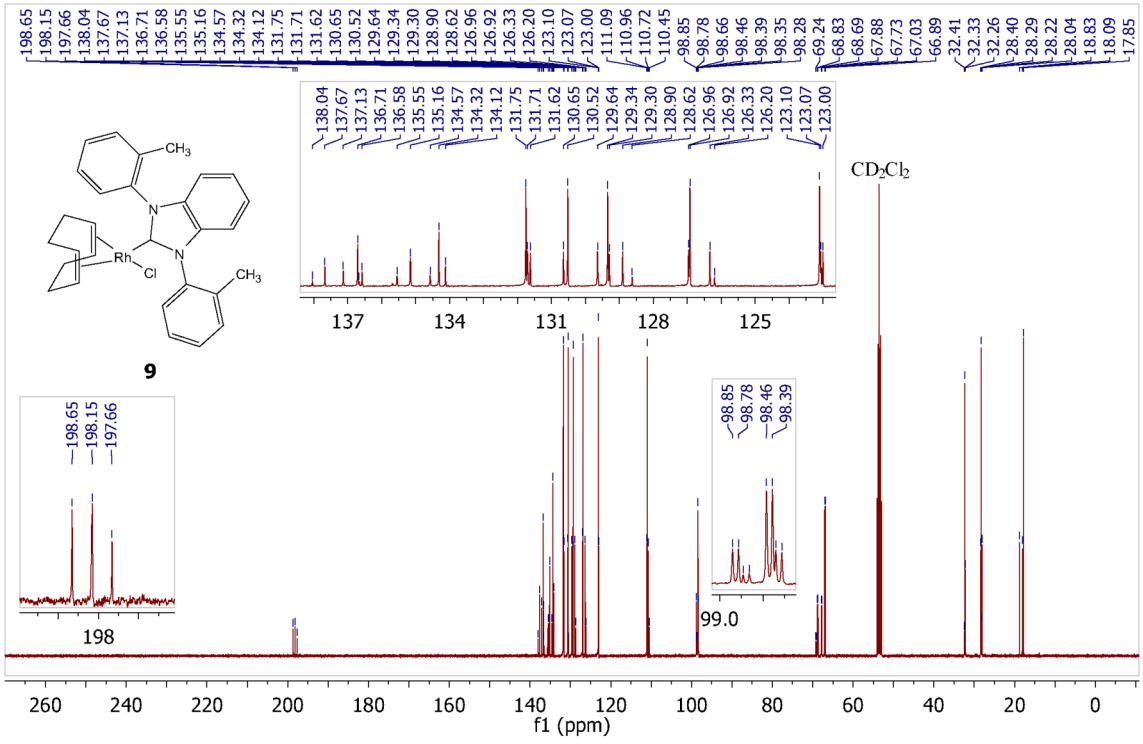


8

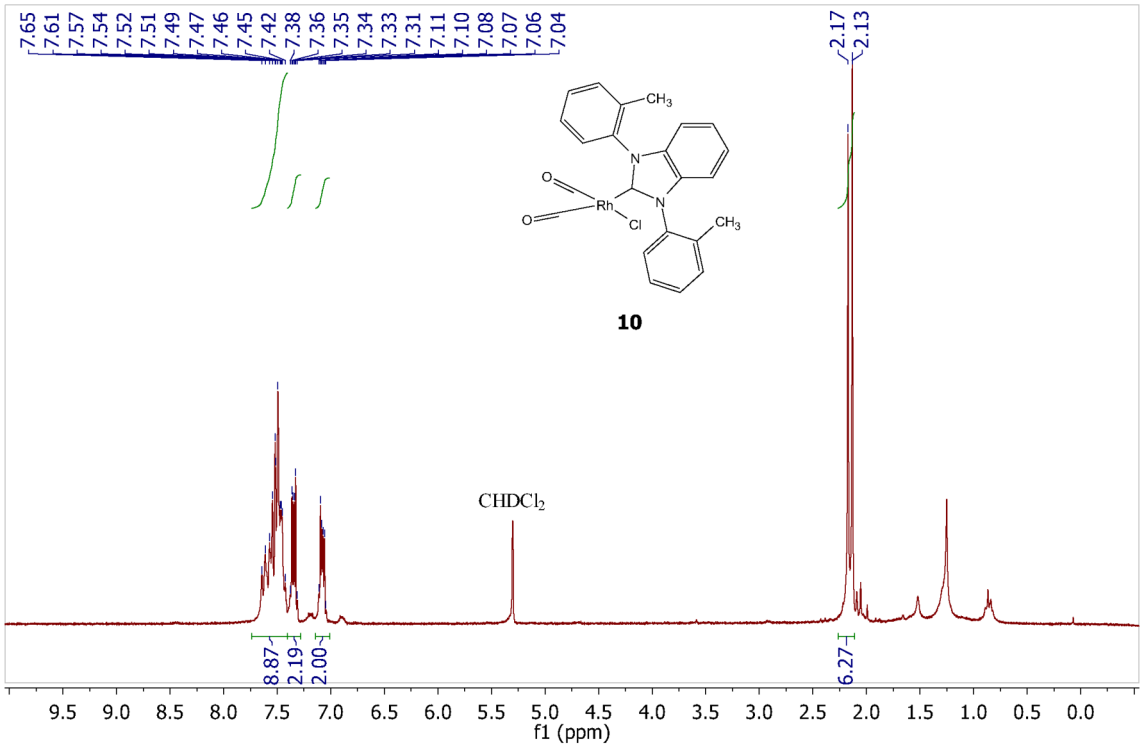
^{1}H NMR (CD_2Cl_2 400 MHz, 298 K): [RhCl(COD)(BTol)] (**9**)



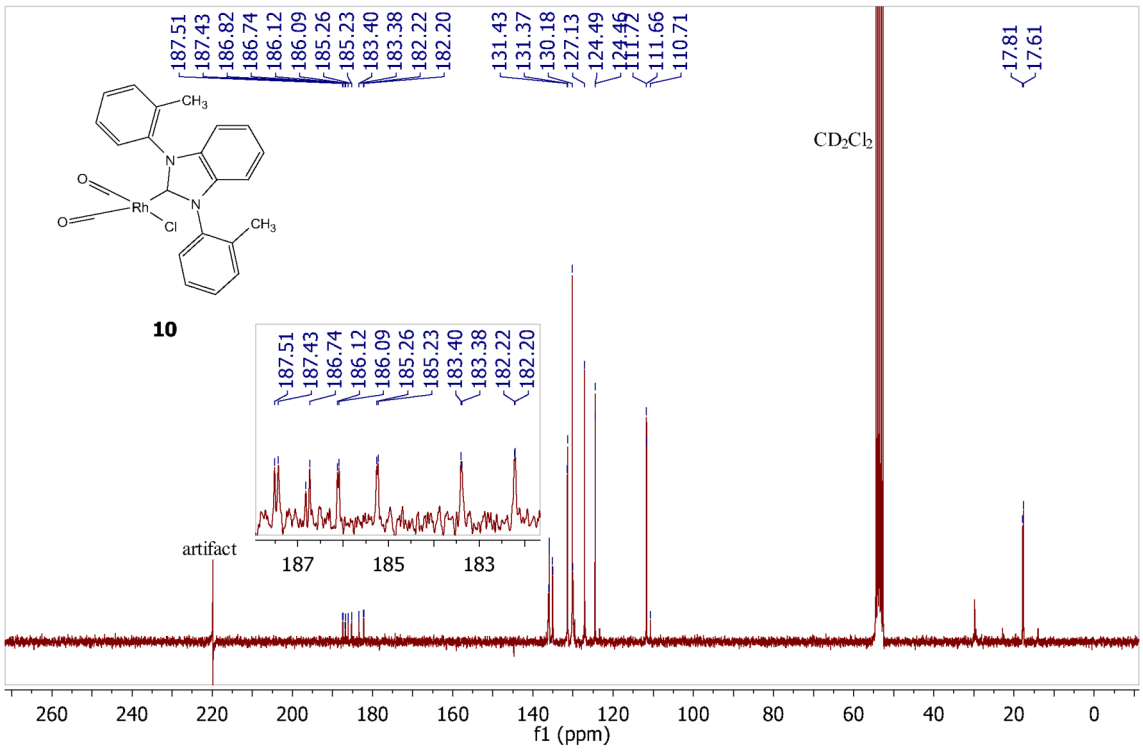
^{13}C NMR (CD_2Cl_2 101 MHz, 298 K): [RhCl(COD)(BTol)] (**9**)



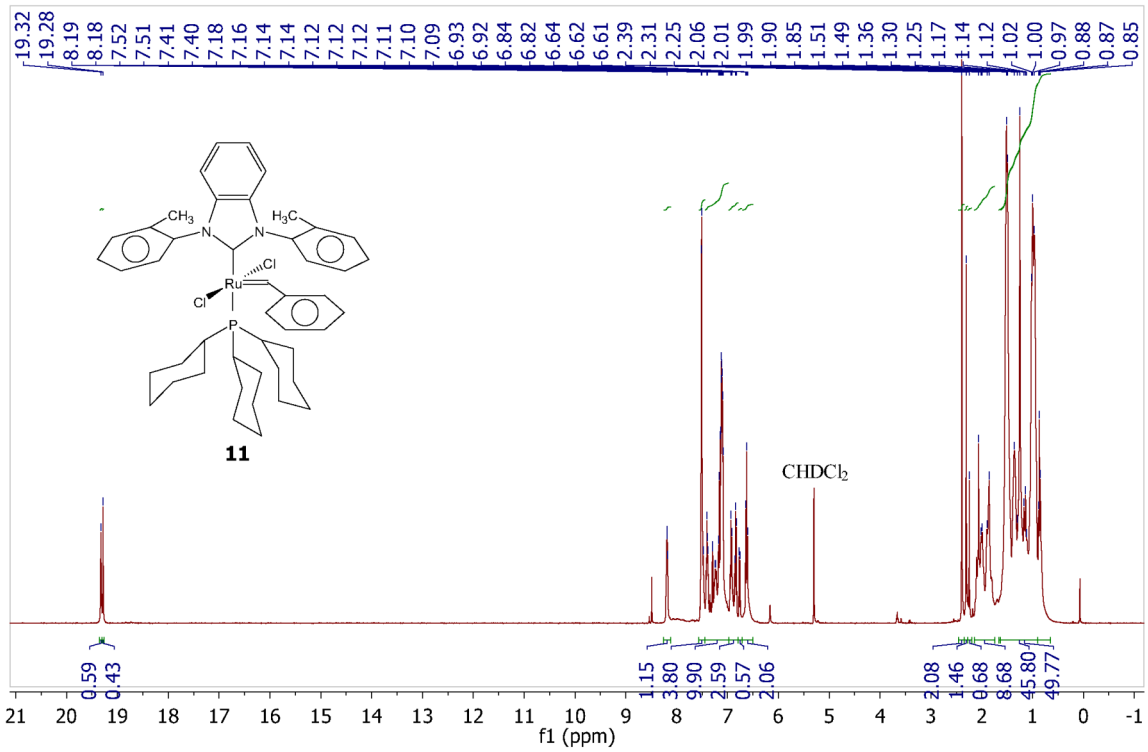
^{1}H NMR (CD_2Cl_2 250 MHz, 298 K): [RhCl(CO)$_2$(BTol)] (**10**)



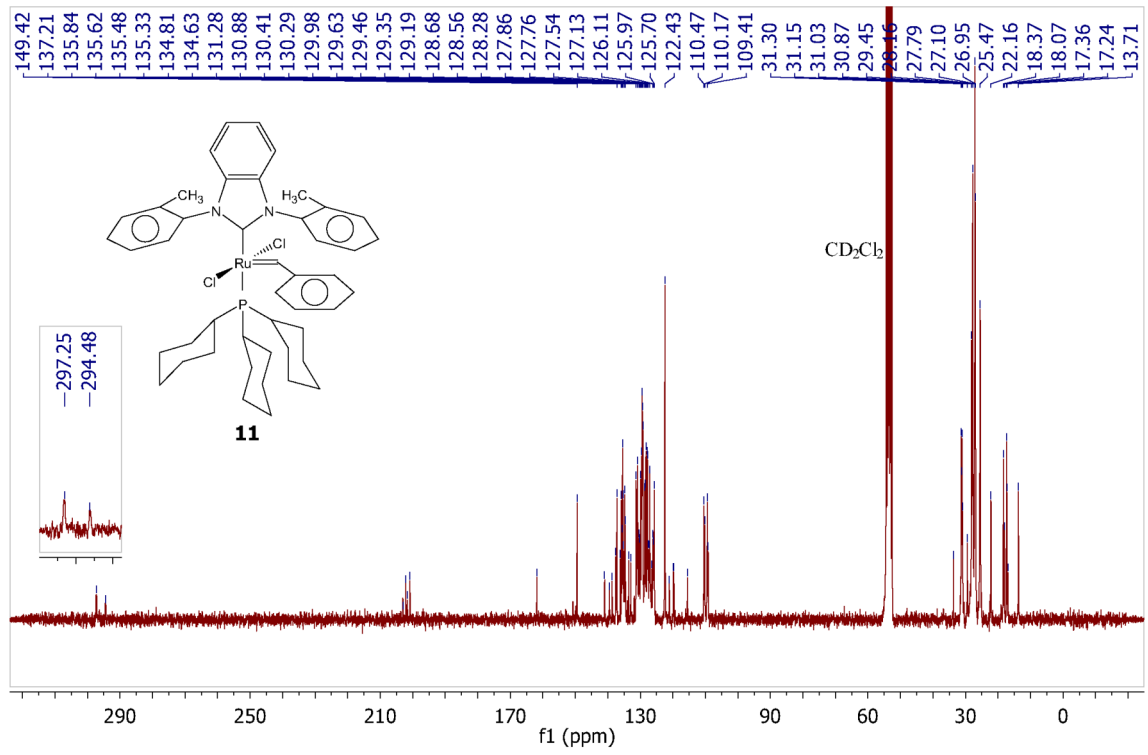
^{13}C NMR (CD_2Cl_2 63 MHz, 298 K): [RhCl(CO)$_2$(BTol)] (**10**)



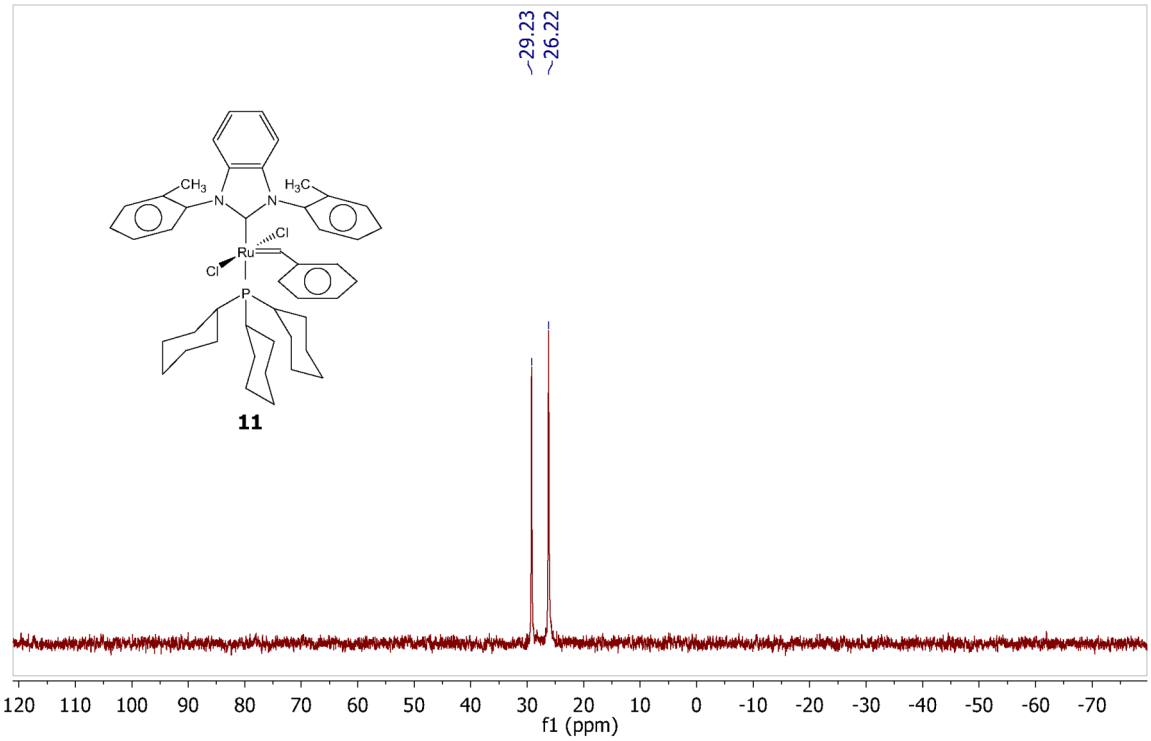
^{1}H NMR (CD_2Cl_2 400 MHz, 298 K): [$RuCl_2$(=CHPh)(PCy_3)(BTol)] (**11**)



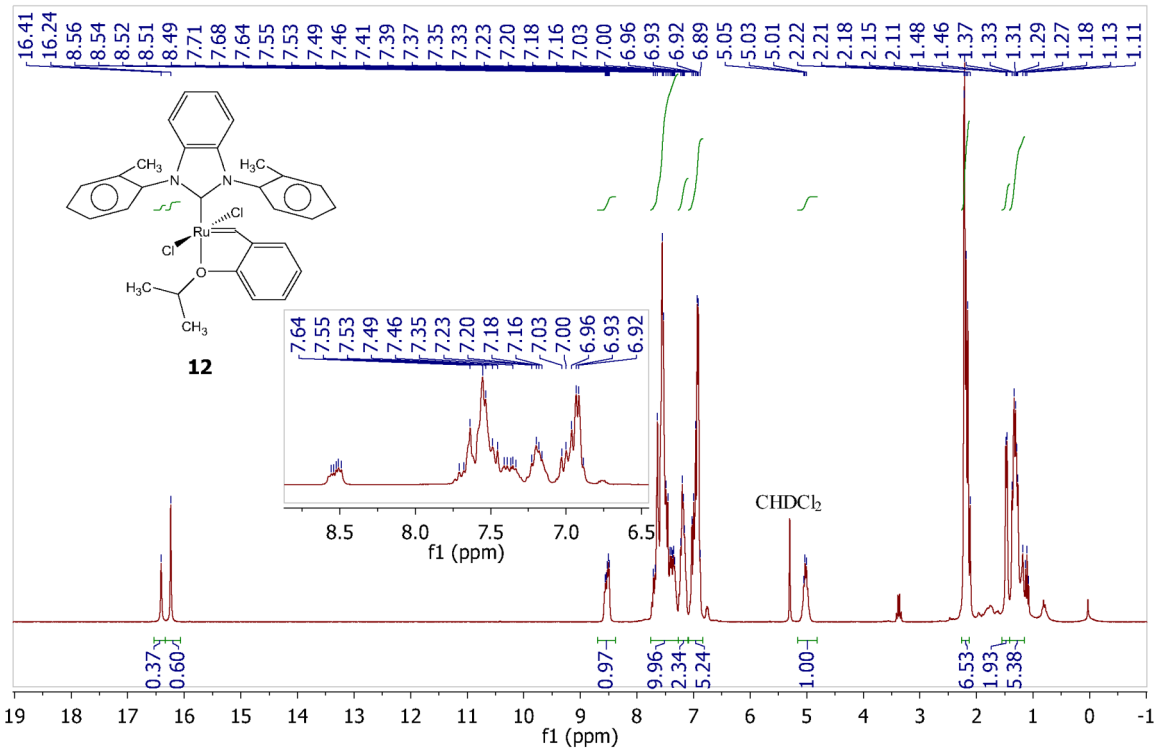
^{13}C NMR (CD_2Cl_2 63 MHz, 223 K): [$RuCl_2$(=CHPh)(PCy_3)(BTol)] (**11**)



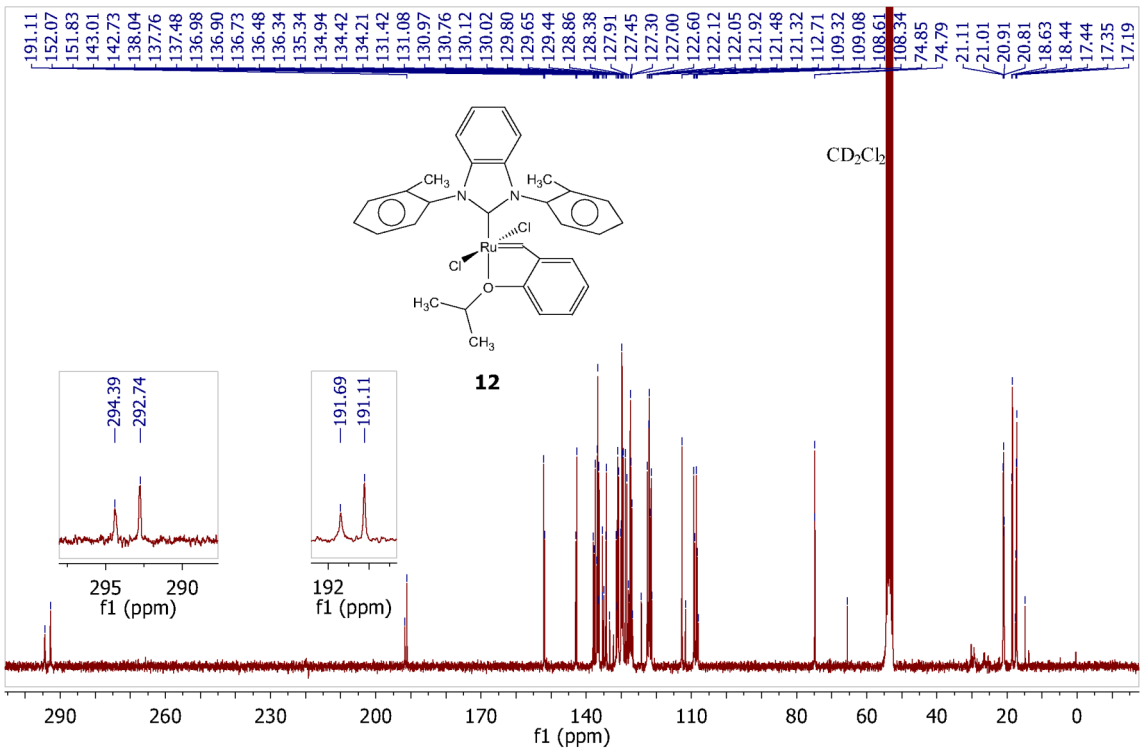
^{31}P NMR (CD_2Cl_2 101 MHz, 298 K): [$RuCl_2$(=CHPh)(PCy_3)(BTol)] (**11**)



^{1}H NMR (CD_2Cl_2 250 MHz, 223 K): [$RuCl_2$(=CH-*o*-$O^{i}PrC_6H_4$)(BTol)] (**12**)



^{13}C NMR (CD_2Cl_2 63 MHz, 223 K): [$RuCl_2$(=CH-*o*-*O* ^{i}PrC_6H_4)(BTol)] (**12**)



^{13}C NMR (CD_2Cl_2 63 MHz, 223 K): [$RuCl_2$(=CH-*o*-*O* ^{i}PrC_6H_4)(BTol)] (**12**)