# S U P P L E M E N T A R Y  M A T E R I A L

**Table S1 -** Crystal Data and Structure Refinement for **2.**

**Table S2** - Atomic coordinates ( x $10^4$) and equivalent isotropic displacement parameters (Å$^2$ x $10^3$) for **2**.

**Table S3** - Bond lengths (Å) and angles (degrees) for **2.**

**Table S4** - Anisotropic Displacement Parameters (Å$^2$ x $10^3$) for **2.**

**Table S5** - Hydrogen coordinates ( x $10^4$) and isotropic displacement parameters (Å$^2$ x $10^3$) for **2.**

**Table S1' -** Crystal Data and Structure Refinement for **4C.**

**Table S2' -** Atomic coordinates ( x $10^4$) and equivalent isotropic displacement parameters (Å$^2$ x $10^3$) for **4C**.

**Table S3' -** Bond lengths (Å) and angles (degrees) for **4C.**

**Table S4**' - Anisotropic Displacement Parameters (Å$^2$ x $10^3$) for **4C.**

**Table S5' -** Hydrogen coordinates ( x $10^4$) and isotropic displacement parameters (Å$^2$ x $10^3$) for **4C.**

**Table S6 -** Distances and angles for the intramolecular hydrogen bonds found in complexes **2** and **4C**.

**Table S7 -** Complete catalytic data for the evolution with time of the transfer hydrogenation of benzophenone (1000 equivalents) in 2-propanol, using as precatalyst [RuCl(Arene)(NN)][$BPh_4$], without the addition of base.

**Table S8 -** Complete catalytic data for the evolution with time of the transfer hydrogenation of benzophenone (1000 equivalents) in 2-propanol, using as precatalyst [RuCl(*p*-cymene)(bpz*m)][X], without the addition of base.

**Table S9 -** Complete catalytic data for the evolution with time of the transfer hydrogenation of different carbonyl compounds (1000 equivalents) in 2-propanol, using as precatalyst [RuCl(*p*-cymene)(NN)][$BPh_4$], without the addition of base.

**Table S10 -** Transfer hydrogenation of benzophenone with different changes in the reaction media, using as precatalyst [RuCl(*p*-cymene)(NN)][$BPh_4$].

**Table S11 -** Evolution with time of the NMR signals obtained for each precatalyst in refluxing 2-propanol.

**Figure S1 -** Evolution with time of the yield of product for the transfer hydrogenation of benzophenone when [RuCl(benzene)(NN)][$BPh_4$] complexes are used.

**Figure S2 -** Evolution with time of the yield of product for the transfer hydrogenation of benzophenone when [RuCl(*p*-cymene)(NN)][$BPh_4$] complexes are used.

**Figure S3** - Evolution with time of the yield of product for the transfer hydrogenation of benzophenone. Comparison between the results obtained for [RuCl(*p*-cymene)(bpz*mArOH)][$BPh_4$] complex (**2**) and when the catalyst is generated in situ in the reaction medium.

**Figure S4** - Evolution with time of the yield of product for the transfer hydrogenation of benzophenone. Comparison between the results obtained for [RuCl(*p*-

cymene)(bpz*mArNO$_2$)][BPh$_4$] complex (**14**) and when the catalyst is generated in situ in the reaction medium.

**Figure S5** - Evolution with time of the yield of product for the transfer hydrogenation of benzophenone. Comparison between the results obtained for [RuCl(*p*-cymene)(bpz*m)][BPh$_4$] complex (**8**) and when the catalyst is generated in situ in the reaction medium.

**Figure S6 -** Evolution with time of the yield of product for the transfer hydrogenation of benzophenone when [RuCl(*p*-cymene)(bpz*m)][X] complexes are used.

**Figure S7** - Evolution with time of the yield of product for the transfer hydrogenation of benzophenone when [RuCl(*p*-cymene)(bpz*mPh)][BPh$_4$] complex (**10**) ise used as precatalyst, with different incubation times.

**Figure S8** - Evolution with time of the yield of product for the transfer hydrogenation of benzophenone when [RuCl(*p*-cymene)(bpz*mArOH)][BPh$_4$] complex (**2**) is used as precatalyst, with different incubation times.

**Figure S9** - Evolution with time of the yield of product for the transfer hydrogenation of benzophenone when [RuCl(*p*-cymene)(bpz*m)][BPh$_4$] complex (**8**) is used as precatalyst, with different incubation times.

**Figure S10** - Evolution with time of the yield of product for the transfer hydrogenation of benzophenone when [RuCl(*p*-cymene)(bpz*mArOH)][BPh$_4$] (**2**) is used as precatalyst in two catalytic cycles.

**Figure S11** - Evolution with time of the yield of product for the transfer hydrogenation of benzophenone when [RuCl(*p*-cymene)(bpz*mArOH)][BPh$_4$] (**2**) is used as precatalyst and a excess of *p*-cymene is added.

**Figure S12**. $^1$H NMR spectra (hydride region) obtained after a treatment of 4 hours at 82ºC of complex **2** in 2-propanol.

**Figure S13**. $^{1}H$ NMR spectra (hydride region) obtained after a treatment of 16 hours at 82ºC of complex **14** in 2-propanol.

**Figure S14** - Representation of Ln (K) versus Ln [Ru] for the transfer hydrogenation of acetophenone with [RuCl(*p*-cymene)(bpz*mArOH)][$BPh_4$] (**2**) as precatalyst.

**Table S1 -** Crystal data and structure refinement for **2**.

| | | |
|---|---|---|
| Empirical formula | $[C_{27}H_{34}ClN_4ORu][C_{24}H_{20}B]$ | |
| Formula weight | 886.31 | |
| Temperature | 150(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Monoclinic | |
| Space group | $P2_1/c$ | |
| Unit cell dimensions | a = 13.9184(7) Å | α= 90.0° |
| | b = 16.6271(8) Å | β= 104.071(2)°. |
| | c = 20.0114(9) Å | γ = 90.0° |
| Volume | 4492(2) $Å^3$ | |
| Z | 4 | |
| Density (calculated) | 1.311 $Mg/m^3$ | |
| Absorption coefficient | 0.450 $mm^{-1}$ | |
| F(000) | 1848 | |
| Crystal size | 0.46 x 0.19 x 0.04 $mm^3$ | |
| Theta range for data collection | 1.51 to 25.00°. | |
| Index ranges | $-16 \leq h \leq 16$, $-19 \leq k \leq 19$, $-23 \leq l \leq 23$ | |
| Reflections collected | 31454 | |
| Independent reflections | 7885 [R(int) = 0.0888] | |
| Completeness to theta = 25.00° | 99.7 % | |
| Absorption correction | Semi-empirical from equivalents | |
| Max. and min. transmission | 0.932 and 0.783 | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 7885 / 0 / 540 | |
| Goodness-of-fit on $F^2$ | 1.037 | |
| Final R indices [$I>2\sigma(I)$] | R1 = 0.0541, wR2 = 0.1334 | |
| R indices (all data) | R1 = 0.1053, wR2 = 0.1760 | |
| Largest diff. peak and hole | 0.733 and -0.478 $e.Å^{-3}$ | |

**Table 2 -** Atomic coordinates ( x $10^4$) and equivalent isotropic displacement parameters ($Å^2$x $10^3$) for **2**. U(eq) is defined as one third of the trace of the orthogonalized $U^{ij}$ tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| Ru(1) | 1637(1) | 3651(1) | 1354(1) | 41(1) |
| Cl(1) | 1244(1) | 3975(1) | 156(1) | 62(1) |
| O(13) | 2655(3) | 781(2) | 2009(2) | 63(1) |
| N(1) | 279(3) | 2999(3) | 1066(2) | 45(1) |
| N(2) | 231(3) | 2187(2) | 952(2) | 46(1) |
| N(3) | 2322(3) | 2635(3) | 1034(2) | 46(1) |
| N(4) | 1898(3) | 1887(3) | 951(2) | 47(1) |
| B(1) | 7017(5) | 3090(4) | 2888(4) | 60(2) |
| C(1) | -707(4) | 1947(3) | 667(3) | 55(2) |
| C(2) | -1278(4) | 2620(4) | 589(3) | 59(2) |
| C(3) | -659(4) | 3262(3) | 826(3) | 50(1) |
| C(4) | -980(4) | 1103(4) | 495(4) | 72(2) |
| C(5) | -954(4) | 4125(3) | 835(4) | 71(2) |
| C(6) | 1071(3) | 1674(3) | 1238(3) | 45(1) |
| C(7) | 2384(4) | 1390(3) | 606(3) | 57(2) |
| C(8) | 3132(4) | 1837(4) | 472(3) | 64(2) |
| C(9) | 3064(4) | 2596(4) | 727(3) | 59(2) |
| C(10) | 2078(5) | 550(4) | 420(4) | 79(2) |
| C(11) | 3716(5) | 3294(4) | 670(4) | 85(2) |
| C(12) | 1274(3) | 1591(3) | 2009(3) | 46(1) |
| C(13) | 612(4) | 1893(3) | 2366(3) | 53(1) |
| C(14) | 726(4) | 1749(4) | 3058(4) | 68(2) |
| C(15) | 1507(5) | 1278(4) | 3403(3) | 68(2) |
| C(16) | 2147(4) | 952(4) | 3056(3) | 63(2) |
| C(17) | 2041(4) | 1108(3) | 2371(3) | 49(1) |
| C(18) | 2500(4) | 3635(3) | 2457(3) | 49(1) |
| C(19) | 1530(4) | 3886(3) | 2409(3) | 52(1) |
| C(20) | 1112(4) | 4550(4) | 1988(3) | 58(2) |
| C(21) | 1640(4) | 4959(3) | 1597(3) | 57(2) |
| C(22) | 2612(4) | 4685(4) | 1612(3) | 59(2) |
| C(23) | 3028(4) | 4051(4) | 2042(3) | 52(1) |
| C(24) | 1205(5) | 5651(4) | 1140(3) | 77(2) |

| | | | | |
|---|---|---|---|---|
| C(25) | 2971(4) | 2996(4) | 2960(3) | 60(2) |
| C(26) | 3330(6) | 3394(6) | 3669(3) | 106(3) |
| C(27) | 3798(4) | 2541(4) | 2752(4) | 76(2) |
| C(28) | 8153(4) | 3417(3) | 3179(3) | 53(2) |
| C(29) | 8803(4) | 3035(4) | 3745(3) | 67(2) |
| C(30) | 9767(4) | 3282(5) | 4011(3) | 76(2) |
| C(31) | 10132(5) | 3928(5) | 3735(4) | 73(2) |
| C(32) | 9532(5) | 4331(4) | 3193(4) | 73(2) |
| C(33) | 8569(4) | 4066(4) | 2922(3) | 62(2) |
| C(34) | 6393(4) | 3763(3) | 2343(4) | 61(2) |
| C(35) | 6518(5) | 3795(4) | 1673(4) | 74(2) |
| C(36) | 6048(6) | 4371(5) | 1194(4) | 92(2) |
| C(37) | 5448(6) | 4934(5) | 1389(6) | 102(3) |
| C(38) | 5294(5) | 4928(5) | 2029(5) | 94(3) |
| C(39) | 5744(4) | 4349(4) | 2498(4) | 73(2) |
| C(40) | 6578(4) | 2935(4) | 3572(3) | 63(2) |
| C(41) | 6549(4) | 3559(4) | 4036(4) | 74(2) |
| C(42) | 6246(5) | 3462(6) | 4638(4) | 97(3) |
| C(43) | 5984(5) | 2726(7) | 4810(5) | 101(3) |
| C(44) | 6011(5) | 2086(5) | 4386(5) | 89(2) |
| C(45) | 6306(4) | 2192(4) | 3769(4) | 71(2) |
| C(46) | 6987(4) | 2264(3) | 2442(3) | 56(2) |
| C(47) | 6106(5) | 1904(4) | 2106(4) | 78(2) |
| C(48) | 6029(6) | 1216(5) | 1713(4) | 92(2) |
| C(49) | 6894(8) | 859(4) | 1638(4) | 93(2) |
| C(50) | 7776(7) | 1194(5) | 1956(4) | 86(2) |
| C(51) | 7828(5) | 1879(4) | 2345(3) | 67(2) |

**Table S3 -** Bond lengths [Å] and angles [°] for **2.**

| | |
|---|---|
| Ru(1)-N(3) | 2.113(4) |
| Ru(1)-N(1) | 2.133(4) |
| Ru(1)-C(22) | 2.173(5) |
| Ru(1)-C(19) | 2.187(6) |
| Ru(1)-C(23) | 2.189(5) |
| Ru(1)-C(20) | 2.198(5) |
| Ru(1)-C(21) | 2.228(6) |
| Ru(1)-C(18) | 2.241(5) |
| Ru(1)-Cl(1) | 2.3889(16) |
| O(13)-C(17) | 1.360(6) |
| N(1)-C(3) | 1.350(6) |
| N(1)-N(2) | 1.368(5) |
| N(2)-C(1) | 1.352(6) |
| N(2)-C(6) | 1.448(6) |
| N(3)-C(9) | 1.325(6) |
| N(3)-N(4) | 1.370(6) |
| N(4)-C(7) | 1.358(7) |
| N(4)-C(6) | 1.450(6) |
| B(1)-C(46) | 1.633(9) |
| B(1)-C(28) | 1.639(8) |
| B(1)-C(40) | 1.649(10) |
| B(1)-C(34) | 1.654(9) |
| C(1)-C(2) | 1.360(8) |
| C(1)-C(4) | 1.472(8) |
| C(2)-C(3) | 1.381(7) |
| C(3)-C(5) | 1.493(8) |
| C(6)-C(12) | 1.506(7) |
| C(7)-C(8) | 1.358(8) |
| C(7)-C(10) | 1.481(8) |
| C(8)-C(9) | 1.374(8) |
| C(9)-C(11) | 1.495(8) |
| C(12)-C(13) | 1.389(7) |
| C(12)-C(17) | 1.390(7) |
| C(13)-C(14) | 1.376(8) |
| C(14)-C(15) | 1.381(9) |
| C(15)-C(16) | 1.367(8) |

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|---|---|
| C(16)-C(17) | 1.367(8) |
| C(18)-C(19) | 1.394(7) |
| C(18)-C(23) | 1.416(8) |
| C(18)-C(25) | 1.499(8) |
| C(19)-C(20) | 1.424(8) |
| C(20)-C(21) | 1.377(8) |
| C(21)-C(22) | 1.420(8) |
| C(21)-C(24) | 1.503(8) |
| C(22)-C(23) | 1.395(8) |
| C(25)-C(27) | 1.518(8) |
| C(25)-C(26) | 1.535(8) |
| C(28)-C(33) | 1.382(8) |
| C(28)-C(29) | 1.416(8) |
| C(29)-C(30) | 1.380(8) |
| C(30)-C(31) | 1.362(10) |
| C(31)-C(32) | 1.371(9) |
| C(32)-C(33) | 1.390(8) |
| C(34)-C(35) | 1.394(10) |
| C(34)-C(39) | 1.413(8) |
| C(35)-C(36) | 1.399(10) |
| C(36)-C(37) | 1.373(11) |
| C(37)-C(38) | 1.350(11) |
| C(38)-C(39) | 1.383(10) |
| C(40)-C(45) | 1.378(9) |
| C(40)-C(41) | 1.401(9) |
| C(41)-C(42) | 1.379(10) |
| C(42)-C(43) | 1.344(11) |
| C(43)-C(44) | 1.368(11) |
| C(44)-C(45) | 1.404(10) |
| C(46)-C(47) | 1.383(8) |
| C(46)-C(51) | 1.389(8) |
| C(47)-C(48) | 1.377(10) |
| C(48)-C(49) | 1.383(10) |
| C(49)-C(50) | 1.358(10) |
| C(50)-C(51) | 1.372(9) |

| | |
|---|---|
| N(3)-Ru(1)-N(1) | 86.99(16) |
| N(3)-Ru(1)-C(22) | 113.7(2) |

| | |
|---|---|
| N(1)-Ru(1)-C(22) | 158.0(2) |
| N(3)-Ru(1)-C(19) | 125.31(19) |
| N(1)-Ru(1)-C(19) | 95.06(19) |
| C(22)-Ru(1)-C(19) | 79.3(2) |
| N(3)-Ru(1)-C(23) | 92.21(19) |
| N(1)-Ru(1)-C(23) | 156.2(2) |
| C(22)-Ru(1)-C(23) | 37.3(2) |
| C(19)-Ru(1)-C(23) | 66.2(2) |
| N(3)-Ru(1)-C(20) | 163.0(2) |
| N(1)-Ru(1)-C(20) | 96.01(19) |
| C(22)-Ru(1)-C(20) | 66.5(2) |
| C(19)-Ru(1)-C(20) | 37.9(2) |
| C(23)-Ru(1)-C(20) | 78.3(2) |
| N(3)-Ru(1)-C(21) | 150.3(2) |
| N(1)-Ru(1)-C(21) | 120.62(19) |
| C(22)-Ru(1)-C(21) | 37.6(2) |
| C(19)-Ru(1)-C(21) | 67.2(2) |
| C(23)-Ru(1)-C(21) | 67.2(2) |
| C(20)-Ru(1)-C(21) | 36.2(2) |
| N(3)-Ru(1)-C(18) | 96.70(18) |
| N(1)-Ru(1)-C(18) | 119.20(18) |
| C(22)-Ru(1)-C(18) | 67.8(2) |
| C(19)-Ru(1)-C(18) | 36.68(19) |
| C(23)-Ru(1)-C(18) | 37.3(2) |
| C(20)-Ru(1)-C(18) | 67.3(2) |
| C(21)-Ru(1)-C(18) | 79.9(2) |
| N(3)-Ru(1)-Cl(1) | 83.44(13) |
| N(1)-Ru(1)-Cl(1) | 82.61(12) |
| C(22)-Ru(1)-Cl(1) | 92.12(17) |
| C(19)-Ru(1)-Cl(1) | 151.12(15) |
| C(23)-Ru(1)-Cl(1) | 120.98(16) |
| C(20)-Ru(1)-Cl(1) | 113.49(17) |
| C(21)-Ru(1)-Cl(1) | 89.20(17) |
| C(18)-Ru(1)-Cl(1) | 158.19(14) |
| C(3)-N(1)-N(2) | 104.9(4) |
| C(3)-N(1)-Ru(1) | 130.4(4) |
| N(2)-N(1)-Ru(1) | 123.4(3) |
| C(1)-N(2)-N(1) | 111.4(4) |

| | |
|---|---|
| C(1)-N(2)-C(6) | 126.7(4) |
| N(1)-N(2)-C(6) | 120.9(4) |
| C(9)-N(3)-N(4) | 105.1(4) |
| C(9)-N(3)-Ru(1) | 129.8(4) |
| N(4)-N(3)-Ru(1) | 123.3(3) |
| C(7)-N(4)-N(3) | 111.2(4) |
| C(7)-N(4)-C(6) | 126.5(5) |
| N(3)-N(4)-C(6) | 122.3(4) |
| C(46)-B(1)-C(28) | 111.5(5) |
| C(46)-B(1)-C(40) | 110.9(5) |
| C(28)-B(1)-C(40) | 106.1(5) |
| C(46)-B(1)-C(34) | 105.6(5) |
| C(28)-B(1)-C(34) | 108.4(5) |
| C(40)-B(1)-C(34) | 114.3(5) |
| N(2)-C(1)-C(2) | 106.4(5) |
| N(2)-C(1)-C(4) | 123.2(5) |
| C(2)-C(1)-C(4) | 130.3(5) |
| C(1)-C(2)-C(3) | 107.4(5) |
| N(1)-C(3)-C(2) | 109.9(5) |
| N(1)-C(3)-C(5) | 123.5(5) |
| C(2)-C(3)-C(5) | 126.6(5) |
| N(2)-C(6)-N(4) | 110.0(4) |
| N(2)-C(6)-C(12) | 113.0(4) |
| N(4)-C(6)-C(12) | 117.3(4) |
| N(4)-C(7)-C(8) | 105.6(5) |
| N(4)-C(7)-C(10) | 123.6(6) |
| C(8)-C(7)-C(10) | 130.8(6) |
| C(7)-C(8)-C(9) | 107.7(5) |
| N(3)-C(9)-C(8) | 110.5(5) |
| N(3)-C(9)-C(11) | 123.5(5) |
| C(8)-C(9)-C(11) | 126.0(6) |
| C(13)-C(12)-C(17) | 117.5(5) |
| C(13)-C(12)-C(6) | 120.7(4) |
| C(17)-C(12)-C(6) | 121.0(5) |
| C(14)-C(13)-C(12) | 121.7(5) |
| C(13)-C(14)-C(15) | 119.0(6) |
| C(16)-C(15)-C(14) | 120.2(6) |
| C(15)-C(16)-C(17) | 120.6(6) |

| | |
|---|---|
| O(13)-C(17)-C(16) | 122.0(5) |
| O(13)-C(17)-C(12) | 117.1(5) |
| C(16)-C(17)-C(12) | 120.9(5) |
| C(19)-C(18)-C(23) | 116.5(5) |
| C(19)-C(18)-C(25) | 121.1(5) |
| C(23)-C(18)-C(25) | 122.3(5) |
| C(19)-C(18)-Ru(1) | 69.6(3) |
| C(23)-C(18)-Ru(1) | 69.4(3) |
| C(25)-C(18)-Ru(1) | 135.3(4) |
| C(18)-C(19)-C(20) | 121.5(5) |
| C(18)-C(19)-Ru(1) | 73.8(3) |
| C(20)-C(19)-Ru(1) | 71.5(3) |
| C(21)-C(20)-C(19) | 121.4(5) |
| C(21)-C(20)-Ru(1) | 73.1(3) |
| C(19)-C(20)-Ru(1) | 70.6(3) |
| C(20)-C(21)-C(22) | 117.8(6) |
| C(20)-C(21)-C(24) | 122.2(6) |
| C(22)-C(21)-C(24) | 119.9(6) |
| C(20)-C(21)-Ru(1) | 70.7(3) |
| C(22)-C(21)-Ru(1) | 69.1(3) |
| C(24)-C(21)-Ru(1) | 129.5(4) |
| C(23)-C(22)-C(21) | 120.4(6) |
| C(23)-C(22)-Ru(1) | 72.0(3) |
| C(21)-C(22)-Ru(1) | 73.3(3) |
| C(22)-C(23)-C(18) | 122.2(5) |
| C(22)-C(23)-Ru(1) | 70.7(3) |
| C(18)-C(23)-Ru(1) | 73.4(3) |
| C(18)-C(25)-C(27) | 114.0(5) |
| C(18)-C(25)-C(26) | 107.9(5) |
| C(27)-C(25)-C(26) | 111.7(5) |
| C(33)-C(28)-C(29) | 113.8(5) |
| C(33)-C(28)-B(1) | 125.6(5) |
| C(29)-C(28)-B(1) | 120.6(5) |
| C(30)-C(29)-C(28) | 123.2(6) |
| C(31)-C(30)-C(29) | 120.0(6) |
| C(30)-C(31)-C(32) | 119.4(6) |
| C(31)-C(32)-C(33) | 119.8(6) |
| C(28)-C(33)-C(32) | 123.7(6) |

| | |
|---|---|
| C(35)-C(34)-C(39) | 114.9(6) |
| C(35)-C(34)-B(1) | 119.4(6) |
| C(39)-C(34)-B(1) | 125.7(6) |
| C(34)-C(35)-C(36) | 122.6(7) |
| C(37)-C(36)-C(35) | 119.1(8) |
| C(38)-C(37)-C(36) | 120.9(8) |
| C(37)-C(38)-C(39) | 119.9(8) |
| C(38)-C(39)-C(34) | 122.7(8) |
| C(45)-C(40)-C(41) | 114.8(6) |
| C(45)-C(40)-B(1) | 124.1(6) |
| C(41)-C(40)-B(1) | 120.7(6) |
| C(42)-C(41)-C(40) | 123.9(7) |
| C(43)-C(42)-C(41) | 119.3(8) |
| C(42)-C(43)-C(44) | 120.0(9) |
| C(43)-C(44)-C(45) | 120.4(8) |
| C(40)-C(45)-C(44) | 121.6(7) |
| C(47)-C(46)-C(51) | 114.2(6) |
| C(47)-C(46)-B(1) | 122.1(5) |
| C(51)-C(46)-B(1) | 123.6(5) |
| C(48)-C(47)-C(46) | 125.0(7) |
| C(47)-C(48)-C(49) | 118.0(7) |
| C(50)-C(49)-C(48) | 119.0(7) |
| C(49)-C(50)-C(51) | 121.6(7) |
| C(50)-C(51)-C(46) | 122.1(7) |

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Symmetry transformations used to generate equivalent atoms:

**Table S4 -** Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **2**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2 a^{*2} U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| Ru(1) | 40(1) | 41(1) | 42(1) | -4(1) | 8(1) | 1(1) |
| Cl(1) | 81(1) | 60(1) | 45(1) | 3(1) | 14(1) | 4(1) |
| O(13) | 63(2) | 65(3) | 61(3) | 11(2) | 14(2) | 27(2) |
| N(1) | 43(2) | 40(3) | 49(3) | 4(2) | 5(2) | 2(2) |
| N(2) | 41(2) | 36(2) | 53(3) | 2(2) | -4(2) | -2(2) |
| N(3) | 44(2) | 46(3) | 48(3) | -6(2) | 10(2) | 1(2) |
| N(4) | 47(2) | 44(3) | 48(3) | 2(2) | 10(2) | 8(2) |
| B(1) | 49(3) | 54(4) | 76(5) | -3(4) | 11(3) | 0(3) |
| C(1) | 51(3) | 52(4) | 55(4) | 1(3) | 2(3) | -9(3) |
| C(2) | 39(3) | 62(4) | 69(4) | 7(3) | 1(3) | -2(3) |
| C(3) | 42(3) | 49(3) | 56(4) | 7(3) | 4(3) | 3(3) |
| C(4) | 60(4) | 63(4) | 80(5) | 1(4) | -6(3) | -13(3) |
| C(5) | 57(3) | 55(4) | 92(5) | 7(4) | 4(3) | 18(3) |
| C(6) | 44(3) | 39(3) | 48(3) | 1(3) | 0(2) | 8(2) |
| C(7) | 72(4) | 49(4) | 47(4) | -7(3) | 10(3) | 13(3) |
| C(8) | 68(4) | 72(4) | 59(4) | 0(4) | 27(3) | 20(3) |
| C(9) | 56(3) | 64(4) | 62(4) | -8(3) | 25(3) | 3(3) |
| C(10) | 105(5) | 55(4) | 75(5) | -9(4) | 22(4) | 17(4) |
| C(11) | 79(4) | 82(5) | 110(6) | -13(5) | 57(4) | -11(4) |
| C(12) | 42(3) | 44(3) | 51(4) | 4(3) | 9(2) | 2(2) |
| C(13) | 44(3) | 54(4) | 59(4) | 7(3) | 10(3) | 2(3) |
| C(14) | 60(4) | 76(5) | 72(5) | 9(4) | 25(3) | 3(3) |
| C(15) | 85(4) | 75(5) | 44(4) | 16(3) | 17(3) | 3(4) |
| C(16) | 68(4) | 68(4) | 51(4) | 13(3) | 8(3) | 13(3) |
| C(17) | 46(3) | 47(3) | 51(4) | 3(3) | 8(3) | 2(2) |
| C(18) | 48(3) | 54(3) | 39(3) | -7(3) | 0(2) | -8(3) |
| C(19) | 50(3) | 58(4) | 45(3) | -5(3) | 7(3) | 3(3) |
| C(20) | 58(3) | 60(4) | 50(4) | -18(3) | 5(3) | 9(3) |
| C(21) | 70(4) | 43(3) | 51(4) | -14(3) | 1(3) | 4(3) |
| C(22) | 69(4) | 51(4) | 56(4) | -7(3) | 12(3) | -15(3) |
| C(23) | 43(3) | 62(4) | 50(4) | -8(3) | 6(3) | -6(3) |
| C(24) | 111(5) | 42(4) | 69(5) | -5(3) | 3(4) | 12(3) |
| C(25) | 56(3) | 69(4) | 48(4) | 4(3) | -2(3) | 4(3) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C(26) | 129(7) | 119(7) | 52(5) | -13(4) | -12(5) | 27(5) |
| C(27) | 61(4) | 74(4) | 86(5) | 4(4) | 2(3) | 10(3) |
| C(28) | 52(3) | 52(3) | 57(4) | -13(3) | 15(3) | 1(3) |
| C(29) | 61(4) | 69(4) | 69(5) | -4(4) | 11(3) | -3(3) |
| C(30) | 59(4) | 100(6) | 61(4) | -18(4) | -2(3) | 12(4) |
| C(31) | 49(3) | 99(6) | 74(5) | -27(4) | 21(3) | -18(4) |
| C(32) | 67(4) | 77(5) | 81(5) | -15(4) | 31(4) | -18(4) |
| C(33) | 55(3) | 67(4) | 67(4) | -2(4) | 21(3) | 1(3) |
| C(34) | 46(3) | 54(4) | 81(5) | -6(3) | 10(3) | -7(3) |
| C(35) | 72(4) | 60(4) | 83(6) | -3(4) | 3(4) | -4(3) |
| C(36) | 95(5) | 80(6) | 86(6) | 9(5) | -6(4) | -20(5) |
| C(37) | 75(5) | 58(5) | 144(9) | 7(6) | -29(6) | -2(4) |
| C(38) | 51(4) | 61(5) | 157(9) | -21(6) | 1(5) | -7(3) |
| C(39) | 45(3) | 60(4) | 110(6) | -7(4) | 10(3) | -6(3) |
| C(40) | 45(3) | 63(4) | 76(5) | -9(4) | 8(3) | -13(3) |
| C(41) | 58(4) | 77(5) | 88(6) | -12(4) | 22(4) | -7(3) |
| C(42) | 66(4) | 142(9) | 86(6) | -29(6) | 21(4) | -14(5) |
| C(43) | 59(4) | 160(9) | 79(6) | -7(7) | 7(4) | -19(5) |
| C(44) | 71(4) | 102(6) | 87(6) | 25(5) | 5(4) | -21(4) |
| C(45) | 59(4) | 85(5) | 66(5) | -3(4) | 8(3) | -17(3) |
| C(46) | 60(3) | 48(3) | 57(4) | 6(3) | 9(3) | -6(3) |
| C(47) | 75(4) | 72(5) | 86(5) | -19(4) | 20(4) | -7(4) |
| C(48) | 107(6) | 88(6) | 80(6) | -22(5) | 23(5) | -29(5) |
| C(49) | 155(8) | 54(5) | 69(5) | -8(4) | 26(5) | -12(5) |
| C(50) | 116(6) | 74(5) | 76(5) | 6(4) | 38(5) | 24(5) |
| C(51) | 79(4) | 61(4) | 59(4) | -2(3) | 16(3) | 8(3) |

**Table S5 -** Hydrogen coordinates ( x $10^4$) and isotropic displacement parameters (Å$^2$x $10^3$) for **2**.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(13) | 3011 | 444 | 2247 | 95 |
| H(2) | -1960 | 2644 | 410 | 71 |
| H(4A) | -656 | 918 | 152 | 107 |
| H(4B) | -1685 | 1063 | 320 | 107 |
| H(4C) | -779 | 778 | 902 | 107 |
| H(5A) | -937 | 4283 | 1299 | 106 |
| H(5B) | -1612 | 4193 | 551 | 106 |
| H(5C) | -502 | 4452 | 660 | 106 |
| H(6) | 870 | 1136 | 1058 | 54 |
| H(8) | 3606 | 1660 | 248 | 77 |
| H(10A) | 2156 | 235 | 831 | 118 |
| H(10B) | 2484 | 330 | 139 | 118 |
| H(10C) | 1397 | 541 | 168 | 118 |
| H(11A) | 3321 | 3772 | 563 | 127 |
| H(11B) | 4050 | 3193 | 312 | 127 |
| H(11C) | 4197 | 3367 | 1100 | 127 |
| H(13A) | 78 | 2201 | 2131 | 63 |
| H(14) | 283 | 1966 | 3291 | 81 |
| H(15) | 1597 | 1181 | 3872 | 81 |
| H(16) | 2659 | 622 | 3288 | 76 |
| H(19) | 1095 | 3547 | 2608 | 62 |
| H(20) | 398 | 4648 | 1905 | 69 |
| H(22) | 2953 | 4891 | 1273 | 71 |
| H(23) | 3648 | 3816 | 1984 | 63 |
| H(24A) | 502 | 5669 | 1092 | 116 |
| H(24B) | 1338 | 5582 | 694 | 116 |
| H(24C) | 1497 | 6145 | 1340 | 116 |
| H(25) | 2455 | 2607 | 2991 | 72 |
| H(26A) | 3779 | 3823 | 3640 | 158 |
| H(26B) | 3662 | 3001 | 3997 | 158 |
| H(26C) | 2772 | 3605 | 3815 | 158 |
| H(27A) | 3567 | 2345 | 2290 | 114 |

| | | | | |
|---|---|---|---|---|
| H(27B) | 4000 | 2095 | 3059 | 114 |
| H(27C) | 4352 | 2894 | 2777 | 114 |
| H(29) | 8569 | 2597 | 3947 | 80 |
| H(30) | 10168 | 3007 | 4379 | 91 |
| H(31) | 10781 | 4095 | 3912 | 87 |
| H(32) | 9770 | 4780 | 3007 | 88 |
| H(33) | 8183 | 4340 | 2546 | 75 |
| H(35) | 6929 | 3419 | 1540 | 89 |
| H(36) | 6142 | 4372 | 750 | 110 |
| H(37) | 5143 | 5324 | 1075 | 122 |
| H(38) | 4886 | 5313 | 2155 | 112 |
| H(39) | 5614 | 4345 | 2932 | 88 |
| H(41) | 6745 | 4069 | 3932 | 88 |
| H(42) | 6223 | 3901 | 4922 | 117 |
| H(43) | 5785 | 2653 | 5217 | 121 |
| H(44) | 5833 | 1577 | 4507 | 107 |
| H(45) | 6318 | 1750 | 3486 | 85 |
| H(47) | 5521 | 2144 | 2150 | 93 |
| H(48) | 5414 | 999 | 1504 | 110 |
| H(49) | 6872 | 396 | 1373 | 111 |
| H(50) | 8360 | 953 | 1910 | 104 |
| H(51) | 8447 | 2093 | 2550 | 80 |

**Table S1' -** Crystal data and structure refinement for **4C**.

| | | |
|---|---|---|
| Empirical formula | $[C_{23}H_{25}N_4ORu][BC_{24}H_{20}] \times C_2H_4Cl_2$ | |
| Formula weight | 892.70 | |
| Temperature | 180(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Monoclinic | |
| Space group | $P2_1/c$ | |
| Unit cell dimensions | a = 12.0756(10) Å | $\alpha$= 90°. |
| | b = 14.3033(11) Å | $\beta$= 93.8760(10)°. |
| | c = 24.6336(19) Å | $\gamma$ = 90°. |
| Volume | 4245.0(6) $Å^3$ | |
| Z | 4 | |
| Density (calculated) | 1.397 $Mg/m^3$ | |
| Absorption coefficient | 0.538 $mm^{-1}$ | |
| F(000) | 1848 | |
| Crystal size | 0.52 x 0.28 x 0.21 $mm^3$ | |
| Theta range for data collection | 2.18 to 28.29°. | |
| Index ranges | $-15 \leq h \leq 16$, $-18 \leq k \leq 18$, $-32 \leq l \leq 32$ | |
| Reflections collected | 32582 | |
| Independent reflections | 10273 [R(int) = 0.0778] | |
| Completeness to theta = 28.29° | 97.5 % | |
| Absorption correction | Semi-empirical from equivalents | |
| Max. and min. transmission | 0.8954 and 0.7673 | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 10273 / 0 / 526 | |
| Goodness-of-fit on $F^2$ | 0.899 | |
| Final R indices [$I>2\sigma(I)$] | R1 = 0.0506, wR2 = 0.1048 | |
| R indices (all data) | R1 = 0.0809, wR2 = 0.1140 | |
| Largest diff. peak and hole | 1.217 and -1.181 $e.Å^{-3}$ | |

**Table S2' -** Atomic coordinates ( x $10^4$) and equivalent isotropic displacement parameters ($Å^2$x $10^3$) for **4C**. U(eq) is defined as one third of the trace of the orthogonalized $U^{ij}$ tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| Ru(1) | -1950(1) | -406(1) | 3280(1) | 29(1) |
| O(1) | -1628(2) | -1459(2) | 3834(1) | 38(1) |
| N(1) | -469(2) | -767(2) | 2925(1) | 30(1) |
| N(2) | 540(2) | -591(2) | 3185(1) | 32(1) |
| N(3) | 93(2) | 119(2) | 4013(1) | 30(1) |
| N(4) | -956(2) | 372(2) | 3843(1) | 33(1) |
| C(1) | 1346(3) | -669(2) | 2835(2) | 40(1) |
| C(2) | 864(3) | -881(2) | 2341(2) | 42(1) |
| C(3) | -261(3) | -940(2) | 2411(1) | 34(1) |
| C(4) | -1207(3) | 1056(2) | 4180(1) | 37(1) |
| C(5) | -354(3) | 1238(2) | 4559(1) | 37(1) |
| C(6) | 461(3) | 633(2) | 4448(1) | 36(1) |
| C(7) | 675(2) | -655(2) | 3778(1) | 32(1) |
| C(8) | 382(2) | -1600(2) | 3987(1) | 30(1) |
| C(9) | -723(3) | -1913(2) | 4011(1) | 31(1) |
| C(10) | -865(3) | -2780(2) | 4261(1) | 39(1) |
| C(11) | 15(3) | -3314(2) | 4466(1) | 45(1) |
| C(12) | 1098(3) | -3012(3) | 4423(1) | 44(1) |
| C(13) | 1266(3) | -2163(2) | 4190(1) | 36(1) |
| C(14) | -2722(3) | 693(3) | 2734(2) | 44(1) |
| C(15) | -2723(3) | -134(3) | 2473(2) | 53(1) |
| C(16) | -3156(3) | -957(3) | 2673(2) | 55(1) |
| C(17) | -3649(3) | -963(3) | 3204(2) | 51(1) |
| C(18) | -3637(2) | -81(2) | 3482(1) | 31(1) |
| C(19) | -3182(2) | 700(2) | 3235(1) | 34(1) |
| C(20) | -4059(3) | -1814(3) | 3465(2) | 81(2) |
| C(21) | -2228(3) | 1583(3) | 2493(2) | 63(1) |
| C(22) | -3101(3) | 1937(4) | 2052(2) | 76(2) |
| B(1) | 3480(3) | 2026(3) | 3621(1) | 28(1) |
| C(23) | -1131(3) | 1502(3) | 2317(2) | 77(2) |
| C(24) | 3181(2) | 1622(2) | 2997(1) | 29(1) |
| C(25) | 2170(2) | 1774(2) | 2694(1) | 32(1) |

| | | | | |
|---|---|---|---|---|
| C(26) | 1949(3) | 1424(3) | 2173(1) | 41(1) |
| C(27) | 2730(3) | 897(3) | 1931(2) | 47(1) |
| C(28) | 3734(3) | 728(3) | 2211(2) | 46(1) |
| C(29) | 3958(3) | 1093(2) | 2727(1) | 39(1) |
| C(30) | 2632(2) | 2866(2) | 3761(1) | 31(1) |
| C(31) | 2932(3) | 3810(2) | 3820(1) | 36(1) |
| C(32) | 2178(3) | 4499(3) | 3940(1) | 47(1) |
| C(33) | 1089(3) | 4279(3) | 4013(1) | 49(1) |
| C(34) | 760(3) | 3367(3) | 3963(1) | 46(1) |
| C(35) | 1513(3) | 2676(2) | 3840(1) | 37(1) |
| C(36) | 4765(2) | 2418(2) | 3676(1) | 30(1) |
| C(37) | 5250(3) | 2883(2) | 3251(2) | 39(1) |
| C(38) | 6303(3) | 3273(2) | 3302(2) | 45(1) |
| C(39) | 6936(3) | 3207(3) | 3786(2) | 49(1) |
| C(40) | 6504(3) | 2752(3) | 4220(2) | 43(1) |
| C(41) | 5441(2) | 2364(2) | 4163(1) | 34(1) |
| C(42) | 3391(2) | 1177(2) | 4069(1) | 30(1) |
| C(43) | 3153(2) | 1368(3) | 4607(1) | 36(1) |
| C(44) | 3169(3) | 695(3) | 5010(2) | 46(1) |
| C(45) | 3435(3) | -210(3) | 4898(2) | 53(1) |
| C(46) | 3681(3) | -438(3) | 4376(2) | 48(1) |
| C(47) | 3648(2) | 242(2) | 3971(1) | 35(1) |
| C(51) | 4131(6) | 3785(5) | 5401(3) | 149(3) |
| C(52) | 3830(6) | 4703(5) | 5536(3) | 142(3) |
| Cl(1) | 2370(2) | 4894(1) | 5365(1) | 108(1) |
| Cl(2) | 5537(2) | 3543(2) | 5596(1) | 130(1) |

**Table S3' -** Bond lengths [Å] and angles [°] for **4C**.

| | |
|---|---|
| Ru(1)-O(1) | 2.053(2) |
| Ru(1)-N(4) | 2.093(3) |
| Ru(1)-N(1) | 2.107(2) |
| Ru(1)-C(16) | 2.164(3) |
| Ru(1)-C(19) | 2.169(3) |
| Ru(1)-C(15) | 2.172(4) |
| Ru(1)-C(18) | 2.180(3) |
| Ru(1)-C(17) | 2.198(3) |
| Ru(1)-C(14) | 2.230(4) |
| O(1)-C(9) | 1.320(4) |
| N(1)-C(3) | 1.331(4) |
| N(1)-N(2) | 1.362(3) |
| N(2)-C(1) | 1.347(4) |
| N(2)-C(7) | 1.463(4) |
| N(3)-C(6) | 1.349(4) |
| N(3)-N(4) | 1.356(3) |
| N(3)-C(7) | 1.452(4) |
| N(4)-C(4) | 1.332(4) |
| C(1)-C(2) | 1.349(5) |
| C(2)-C(3) | 1.383(4) |
| C(4)-C(5) | 1.367(4) |
| C(5)-C(6) | 1.353(4) |
| C(7)-C(8) | 1.498(4) |
| C(8)-C(13) | 1.402(4) |
| C(8)-C(9) | 1.412(4) |
| C(9)-C(10) | 1.399(4) |
| C(10)-C(11) | 1.376(5) |
| C(11)-C(12) | 1.388(5) |
| C(12)-C(13) | 1.365(5) |
| C(14)-C(15) | 1.346(5) |
| C(14)-C(19) | 1.386(5) |
| C(14)-C(21) | 1.542(5) |
| C(15)-C(16) | 1.393(6) |
| C(16)-C(17) | 1.473(6) |
| C(17)-C(18) | 1.435(5) |
| C(17)-C(20) | 1.477(5) |

| | |
|---|---|
| C(18)-C(19) | 1.401(4) |
| C(21)-C(23) | 1.426(5) |
| C(21)-C(22) | 1.546(5) |
| B(1)-C(30) | 1.630(5) |
| B(1)-C(36) | 1.648(4) |
| B(1)-C(42) | 1.648(5) |
| B(1)-C(24) | 1.658(5) |
| C(24)-C(25) | 1.405(4) |
| C(24)-C(29) | 1.407(4) |
| C(25)-C(26) | 1.385(4) |
| C(26)-C(27) | 1.375(5) |
| C(27)-C(28) | 1.374(5) |
| C(28)-C(29) | 1.385(5) |
| C(30)-C(31) | 1.403(5) |
| C(30)-C(35) | 1.405(4) |
| C(31)-C(32) | 1.388(5) |
| C(32)-C(33) | 1.376(5) |
| C(33)-C(34) | 1.367(5) |
| C(34)-C(35) | 1.389(4) |
| C(36)-C(37) | 1.402(4) |
| C(36)-C(41) | 1.406(4) |
| C(37)-C(38) | 1.387(4) |
| C(38)-C(39) | 1.375(5) |
| C(39)-C(40) | 1.385(5) |
| C(40)-C(41) | 1.396(4) |
| C(42)-C(47) | 1.397(4) |
| C(42)-C(43) | 1.404(4) |
| C(43)-C(44) | 1.380(4) |
| C(44)-C(45) | 1.366(5) |
| C(45)-C(46) | 1.379(5) |
| C(46)-C(47) | 1.392(5) |
| C(51)-C(52) | 1.408(8) |
| C(51)-Cl(2) | 1.768(8) |
| C(52)-Cl(1) | 1.806(8) |

| | |
|---|---|
| O(1)-Ru(1)-N(4) | 82.78(10) |
| O(1)-Ru(1)-N(1) | 88.17(9) |
| N(4)-Ru(1)-N(1) | 86.61(10) |

| | |
|---|---|
| O(1)-Ru(1)-C(16) | 106.25(15) |
| N(4)-Ru(1)-C(16) | 168.79(13) |
| N(1)-Ru(1)-C(16) | 100.08(12) |
| O(1)-Ru(1)-C(19) | 131.84(10) |
| N(4)-Ru(1)-C(19) | 90.42(11) |
| N(1)-Ru(1)-C(19) | 139.15(11) |
| C(16)-Ru(1)-C(19) | 78.63(13) |
| O(1)-Ru(1)-C(15) | 142.20(14) |
| N(4)-Ru(1)-C(15) | 134.69(15) |
| N(1)-Ru(1)-C(15) | 89.37(12) |
| C(16)-Ru(1)-C(15) | 37.48(15) |
| C(19)-Ru(1)-C(15) | 64.65(14) |
| O(1)-Ru(1)-C(18) | 98.16(10) |
| N(4)-Ru(1)-C(18) | 103.77(11) |
| N(1)-Ru(1)-C(18) | 168.39(11) |
| C(16)-Ru(1)-C(18) | 68.85(13) |
| C(19)-Ru(1)-C(18) | 37.59(11) |
| C(15)-Ru(1)-C(18) | 79.65(13) |
| O(1)-Ru(1)-C(17) | 85.61(12) |
| N(4)-Ru(1)-C(17) | 137.67(14) |
| N(1)-Ru(1)-C(17) | 133.60(14) |
| C(16)-Ru(1)-C(17) | 39.46(15) |
| C(19)-Ru(1)-C(17) | 68.07(13) |
| C(15)-Ru(1)-C(17) | 69.30(15) |
| C(18)-Ru(1)-C(17) | 38.27(13) |
| O(1)-Ru(1)-C(14) | 166.02(11) |
| N(4)-Ru(1)-C(14) | 102.88(13) |
| N(1)-Ru(1)-C(14) | 104.79(11) |
| C(16)-Ru(1)-C(14) | 66.83(15) |
| C(19)-Ru(1)-C(14) | 36.70(12) |
| C(15)-Ru(1)-C(14) | 35.57(14) |
| C(18)-Ru(1)-C(14) | 68.17(12) |
| C(17)-Ru(1)-C(14) | 81.64(14) |
| C(9)-O(1)-Ru(1) | 134.13(19) |
| C(3)-N(1)-N(2) | 105.1(2) |
| C(3)-N(1)-Ru(1) | 131.3(2) |
| N(2)-N(1)-Ru(1) | 121.15(19) |
| C(1)-N(2)-N(1) | 110.3(3) |

| | |
|---|---|
| C(1)-N(2)-C(7) | 126.7(3) |
| N(1)-N(2)-C(7) | 119.6(2) |
| C(6)-N(3)-N(4) | 110.5(3) |
| C(6)-N(3)-C(7) | 126.1(3) |
| N(4)-N(3)-C(7) | 123.2(2) |
| C(4)-N(4)-N(3) | 104.6(2) |
| C(4)-N(4)-Ru(1) | 131.3(2) |
| N(3)-N(4)-Ru(1) | 123.0(2) |
| N(2)-C(1)-C(2) | 108.0(3) |
| C(1)-C(2)-C(3) | 105.6(3) |
| N(1)-C(3)-C(2) | 111.0(3) |
| N(4)-C(4)-C(5) | 111.8(3) |
| C(6)-C(5)-C(4) | 105.4(3) |
| N(3)-C(6)-C(5) | 107.7(3) |
| N(3)-C(7)-N(2) | 109.0(2) |
| N(3)-C(7)-C(8) | 114.8(3) |
| N(2)-C(7)-C(8) | 112.7(3) |
| C(13)-C(8)-C(9) | 120.1(3) |
| C(13)-C(8)-C(7) | 116.6(3) |
| C(9)-C(8)-C(7) | 123.2(3) |
| O(1)-C(9)-C(10) | 117.2(3) |
| O(1)-C(9)-C(8) | 126.4(3) |
| C(10)-C(9)-C(8) | 116.3(3) |
| C(11)-C(10)-C(9) | 122.6(3) |
| C(10)-C(11)-C(12) | 120.5(3) |
| C(13)-C(12)-C(11) | 118.5(3) |
| C(12)-C(13)-C(8) | 122.0(3) |
| C(15)-C(14)-C(19) | 116.4(4) |
| C(15)-C(14)-C(21) | 121.9(4) |
| C(19)-C(14)-C(21) | 121.8(4) |
| C(15)-C(14)-Ru(1) | 69.9(2) |
| C(19)-C(14)-Ru(1) | 69.3(2) |
| C(21)-C(14)-Ru(1) | 131.1(2) |
| C(14)-C(15)-C(16) | 124.2(4) |
| C(14)-C(15)-Ru(1) | 74.6(2) |
| C(16)-C(15)-Ru(1) | 70.9(2) |
| C(15)-C(16)-C(17) | 120.2(3) |
| C(15)-C(16)-Ru(1) | 71.6(2) |

| | |
|---|---|
| C(17)-C(16)-Ru(1) | 71.52(18) |
| C(18)-C(17)-C(16) | 115.2(3) |
| C(18)-C(17)-C(20) | 120.7(4) |
| C(16)-C(17)-C(20) | 124.0(4) |
| C(18)-C(17)-Ru(1) | 70.19(17) |
| C(16)-C(17)-Ru(1) | 69.02(19) |
| C(20)-C(17)-Ru(1) | 126.9(3) |
| C(19)-C(18)-C(17) | 119.0(3) |
| C(19)-C(18)-Ru(1) | 70.79(17) |
| C(17)-C(18)-Ru(1) | 71.54(18) |
| C(14)-C(19)-C(18) | 125.0(3) |
| C(14)-C(19)-Ru(1) | 74.1(2) |
| C(18)-C(19)-Ru(1) | 71.62(18) |
| C(23)-C(21)-C(14) | 116.2(4) |
| C(23)-C(21)-C(22) | 114.7(4) |
| C(14)-C(21)-C(22) | 106.2(3) |
| C(30)-B(1)-C(36) | 109.5(3) |
| C(30)-B(1)-C(42) | 109.4(2) |
| C(36)-B(1)-C(42) | 107.4(2) |
| C(30)-B(1)-C(24) | 110.6(2) |
| C(36)-B(1)-C(24) | 109.8(2) |
| C(42)-B(1)-C(24) | 110.1(3) |
| C(25)-C(24)-C(29) | 114.5(3) |
| C(25)-C(24)-B(1) | 124.5(3) |
| C(29)-C(24)-B(1) | 121.0(3) |
| C(26)-C(25)-C(24) | 122.9(3) |
| C(27)-C(26)-C(25) | 120.3(3) |
| C(28)-C(27)-C(26) | 119.1(3) |
| C(27)-C(28)-C(29) | 120.3(3) |
| C(28)-C(29)-C(24) | 122.8(3) |
| C(31)-C(30)-C(35) | 114.6(3) |
| C(31)-C(30)-B(1) | 124.7(3) |
| C(35)-C(30)-B(1) | 120.7(3) |
| C(32)-C(31)-C(30) | 122.5(3) |
| C(33)-C(32)-C(31) | 120.8(4) |
| C(34)-C(33)-C(32) | 118.7(3) |
| C(33)-C(34)-C(35) | 120.5(3) |
| C(34)-C(35)-C(30) | 122.9(3) |

| | |
|---|---|
| C(37)-C(36)-C(41) | 114.5(3) |
| C(37)-C(36)-B(1) | 122.7(3) |
| C(41)-C(36)-B(1) | 122.7(3) |
| C(38)-C(37)-C(36) | 123.3(3) |
| C(39)-C(38)-C(37) | 120.3(3) |
| C(38)-C(39)-C(40) | 119.0(3) |
| C(39)-C(40)-C(41) | 120.0(3) |
| C(40)-C(41)-C(36) | 122.8(3) |
| C(47)-C(42)-C(43) | 114.3(3) |
| C(47)-C(42)-B(1) | 124.4(3) |
| C(43)-C(42)-B(1) | 121.0(3) |
| C(44)-C(43)-C(42) | 123.3(3) |
| C(45)-C(44)-C(43) | 120.5(4) |
| C(44)-C(45)-C(46) | 118.7(4) |
| C(45)-C(46)-C(47) | 120.4(4) |
| C(46)-C(47)-C(42) | 122.7(3) |
| C(52)-C(51)-Cl(2) | 112.2(6) |
| C(51)-C(52)-Cl(1) | 110.5(5) |

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Symmetry transformations used to generate equivalent atoms:

**Table S4' -** Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **4C**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2 a^{*2} U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| Ru(1) | 23(1) | 39(1) | 24(1) | -7(1) | -5(1) | 6(1) |
| O(1) | 26(1) | 49(2) | 38(1) | 6(1) | -3(1) | 0(1) |
| N(1) | 30(1) | 33(2) | 27(1) | 0(1) | 0(1) | 4(1) |
| N(2) | 25(1) | 37(2) | 32(2) | 2(1) | 0(1) | 2(1) |
| N(3) | 27(1) | 30(2) | 31(2) | 0(1) | -7(1) | 1(1) |
| N(4) | 28(1) | 40(2) | 30(2) | -4(1) | -6(1) | 8(1) |
| C(1) | 28(2) | 43(2) | 49(2) | 6(2) | 11(2) | 3(2) |
| C(2) | 45(2) | 45(2) | 39(2) | -1(2) | 17(2) | 6(2) |
| C(3) | 42(2) | 30(2) | 30(2) | -4(2) | 3(2) | 5(2) |
| C(4) | 44(2) | 38(2) | 30(2) | -6(2) | -2(2) | 8(2) |
| C(5) | 52(2) | 32(2) | 25(2) | -5(2) | -5(2) | -7(2) |
| C(6) | 42(2) | 33(2) | 30(2) | 0(2) | -14(2) | -13(2) |
| C(7) | 22(2) | 38(2) | 34(2) | 1(2) | -7(1) | 5(1) |
| C(8) | 32(2) | 30(2) | 26(2) | -2(1) | -7(1) | 3(1) |
| C(9) | 35(2) | 35(2) | 23(2) | -5(2) | -1(1) | -3(2) |
| C(10) | 42(2) | 37(2) | 37(2) | -2(2) | -3(2) | -6(2) |
| C(11) | 72(3) | 26(2) | 37(2) | -3(2) | 0(2) | 1(2) |
| C(12) | 51(2) | 38(2) | 42(2) | -4(2) | -5(2) | 15(2) |
| C(13) | 35(2) | 36(2) | 35(2) | -7(2) | -4(2) | 7(2) |
| C(14) | 33(2) | 57(3) | 42(2) | 4(2) | -5(2) | 12(2) |
| C(15) | 39(2) | 77(3) | 43(2) | 5(2) | -2(2) | 6(2) |
| C(16) | 33(2) | 62(3) | 64(3) | -28(2) | -7(2) | 6(2) |
| C(17) | 26(2) | 35(2) | 87(3) | 2(2) | -15(2) | -2(2) |
| C(18) | 19(2) | 41(2) | 32(2) | 4(2) | -3(1) | 3(1) |
| C(19) | 25(2) | 42(2) | 33(2) | 1(2) | -5(1) | 6(2) |
| C(20) | 46(2) | 49(3) | 143(5) | 20(3) | -21(3) | -13(2) |
| C(21) | 58(3) | 74(3) | 57(3) | 29(2) | 11(2) | 7(2) |
| C(22) | 62(3) | 109(4) | 57(3) | 42(3) | 1(2) | 21(3) |
| B(1) | 30(2) | 27(2) | 28(2) | 5(2) | -2(2) | 2(2) |
| C(23) | 60(3) | 47(3) | 123(4) | 22(3) | -6(3) | -5(2) |
| C(24) | 29(2) | 30(2) | 28(2) | 7(1) | 4(1) | 1(1) |
| C(25) | 30(2) | 32(2) | 34(2) | 4(2) | -1(1) | 1(1) |
| C(26) | 36(2) | 47(2) | 39(2) | 6(2) | -7(2) | -4(2) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C(27) | 48(2) | 61(3) | 32(2) | -7(2) | 1(2) | -10(2) |
| C(28) | 44(2) | 52(3) | 42(2) | -7(2) | 7(2) | 6(2) |
| C(29) | 36(2) | 45(2) | 34(2) | 3(2) | -1(2) | 4(2) |
| C(30) | 36(2) | 33(2) | 23(2) | 7(1) | 0(1) | 5(2) |
| C(31) | 47(2) | 34(2) | 28(2) | 2(2) | 3(2) | 5(2) |
| C(32) | 79(3) | 32(2) | 31(2) | 0(2) | 3(2) | 10(2) |
| C(33) | 65(3) | 47(3) | 35(2) | 1(2) | 10(2) | 23(2) |
| C(34) | 44(2) | 59(3) | 35(2) | 11(2) | 11(2) | 14(2) |
| C(35) | 40(2) | 33(2) | 37(2) | 7(2) | 7(2) | 8(2) |
| C(36) | 31(2) | 23(2) | 36(2) | 2(1) | -2(1) | 2(1) |
| C(37) | 32(2) | 37(2) | 49(2) | 13(2) | 2(2) | 3(2) |
| C(38) | 37(2) | 37(2) | 61(3) | 12(2) | 12(2) | 0(2) |
| C(39) | 34(2) | 40(2) | 72(3) | -12(2) | 8(2) | -8(2) |
| C(40) | 35(2) | 43(2) | 49(2) | -13(2) | -6(2) | -1(2) |
| C(41) | 33(2) | 33(2) | 35(2) | -5(2) | 1(2) | 0(2) |
| C(42) | 23(2) | 33(2) | 32(2) | 6(2) | -7(1) | -1(1) |
| C(43) | 33(2) | 40(2) | 35(2) | 9(2) | -5(2) | 1(2) |
| C(44) | 33(2) | 66(3) | 38(2) | 20(2) | -5(2) | 0(2) |
| C(45) | 33(2) | 69(3) | 57(3) | 40(2) | -5(2) | -5(2) |
| C(46) | 31(2) | 32(2) | 78(3) | 20(2) | -10(2) | -1(2) |
| C(47) | 25(2) | 38(2) | 42(2) | 5(2) | -5(1) | -4(2) |
| C(51) | 217(9) | 92(5) | 138(6) | 7(5) | 25(6) | -64(6) |
| C(52) | 179(7) | 131(6) | 128(6) | -61(5) | 97(5) | -97(5) |
| Cl(1) | 173(2) | 82(1) | 64(1) | 11(1) | -24(1) | -48(1) |
| Cl(2) | 124(1) | 194(2) | 75(1) | -7(1) | 17(1) | -68(1) |

**Table S5' -** Hydrogen coordinates ( x $10^4$) and isotropic displacement parameters ($Å^2$x $10^3$) for **4C.**

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(1) | 2119 | -590 | 2922 | 48 |
| H(2) | 1221 | -970 | 2013 | 51 |
| H(3) | -811 | -1084 | 2129 | 40 |
| H(4) | -1896 | 1379 | 4160 | 45 |
| H(5) | -337 | 1694 | 4840 | 45 |
| H(6) | 1166 | 580 | 4641 | 43 |
| H(7) | 1483 | -560 | 3881 | 38 |
| H(10) | -1597 | -3008 | 4290 | 47 |
| H(11) | -121 | -3894 | 4637 | 54 |
| H(12) | 1708 | -3388 | 4554 | 53 |
| H(13) | 2005 | -1947 | 4163 | 43 |
| H(15) | -2408 | -157 | 2130 | 64 |
| H(16) | -3134 | -1517 | 2467 | 66 |
| H(18) | -3933 | -27 | 3828 | 37 |
| H(19) | -3190 | 1277 | 3425 | 40 |
| H(20A) | -4018 | -1728 | 3861 | 121 |
| H(20B) | -3600 | -2349 | 3375 | 121 |
| H(20C) | -4831 | -1929 | 3334 | 121 |
| H(21) | -2192 | 2061 | 2789 | 75 |
| H(22A) | -2808 | 2484 | 1870 | 114 |
| H(22B) | -3781 | 2111 | 2223 | 114 |
| H(22C) | -3267 | 1441 | 1785 | 114 |
| H(23A) | -623 | 1313 | 2625 | 116 |
| H(23B) | -895 | 2106 | 2177 | 116 |
| H(23C) | -1121 | 1031 | 2029 | 116 |
| H(25) | 1613 | 2132 | 2852 | 39 |
| H(26) | 1255 | 1549 | 1982 | 49 |
| H(27) | 2578 | 653 | 1575 | 56 |
| H(28) | 4276 | 359 | 2049 | 55 |
| H(29) | 4667 | 982 | 2907 | 46 |
| H(31) | 3680 | 3984 | 3775 | 44 |
| H(32) | 2417 | 5131 | 3973 | 57 |

| | | | | |
|---|---|---|---|---|
| H(33) | 575 | 4752 | 4097 | 58 |
| H(34) | 11 | 3204 | 4012 | 55 |
| H(35) | 1259 | 2049 | 3807 | 44 |
| H(37) | 4836 | 2934 | 2910 | 47 |
| H(38) | 6589 | 3587 | 3002 | 54 |
| H(39) | 7660 | 3471 | 3822 | 58 |
| H(40) | 6930 | 2703 | 4557 | 51 |
| H(41) | 5162 | 2052 | 4465 | 40 |
| H(43) | 2971 | 1992 | 4700 | 43 |
| H(44) | 2993 | 863 | 5367 | 55 |
| H(45) | 3451 | -673 | 5175 | 64 |
| H(46) | 3873 | -1063 | 4292 | 57 |
| H(47) | 3808 | 63 | 3613 | 42 |
| H(51A) | 4002 | 3697 | 5003 | 178 |
| H(51B) | 3653 | 3337 | 5582 | 178 |
| H(52A) | 4271 | 5155 | 5336 | 170 |
| H(52B) | 3995 | 4807 | 5931 | 170 |

**Table S6 -** Distances and angles for the intramolecular hydrogen bonds found in complexes **2** and **4C**.

| **Complex** | **Hydrogen bond D–H···A** | **H···A (Å)** | **D···A (Å)** | **DHA angle (º)** |
|---|---|---|---|---|
| **2** | C10– H10A···O13 | 2.463(4) | 3.109(8) | 124.5(3) |
| **2** | C24– H24B···Cl1 | 2.872(2) | 3.420(7) | 117.3(4) |
| **2** | C27– H27A···O13 | 2.889(4) | 3.487(8) | 121.4(4) |
| **2** | C5– H5C···Cl1 | 2.956(2) | 3.645(7) | 129.7(4) |
| **2** | C11– H11A···Cl1 | 2.827(2) | 3.530(7) | 130.8(4) |
| **4C** | C20– H20A···O1 | 2.916(2) | 3.056(4) | 88.7(2) |

**Table S7 -** Complete catalytic data for the evolution with time of the transfer hydrogenation of benzophenone (1000 equivalents) in 2-propanol, using as precatalyst [RuCl(Arene)(NN)][$BPh_4$], without the addition of base.

| Run | Arene | NN-Ligand (**complex**) | t = 1.5 h | | t = 3 h | | t = 6 h | | t = 9 h | | t = 24 h | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | Yield[a] /% | TOF / $h^{-1}$ | Yield[a] /% | TOF / $h^{-1}$ | Yield[a] /% | TOF / $h^{-1}$ | Yield[a] /% | TOF / $h^{-1}$ | Yield[a] /% | TOF / $h^{-1}$ |
| 1a | - | - | 0 | - | 0 | - | 0 | - | 0 | - | 0 | - |
| 1b | benzene[b] | - | - | - | - | - | - | - | - | - | 12 | 5 |
| 1c | *p*-cymene[c] | - | - | - | - | - | - | - | - | - | 34 | 14 |
| 2a | benzene | bpz*m (**7**) | 5 | 28 | 10 | 33 | 18 | 30 | 29 | 32 | 45 | 19 |
| 3a | *p*-cymene | bpz*m (**8**) | 0 | 0 | 21 | 69 | 85 | 142 | 94 | 104 | 96 | 40 |
| 4a | benzene | bpz*mPh (**9**) | 2 | 16 | 5 | 17 | 6 | 10 | 7 | 8 | 20 | 8 |
| 5a | *p*-cymene | bpz*mPh (**10**) | 10 | 67 | 19 | 62 | 49 | 81 | 61 | 68 | 96 | 40 |
| 6a | benzene | bpzmPh (**11**) | 22 | 147 | 35 | 117 | 42 | 64 | 44 | 48 | 54 | 22 |
| 7a | *p*-cymene | bpzmPh (**12**) | 32 | 214 | 39 | 130 | 51 | 85 | 58 | 65 | 87 | 36 |
| 8a | benzene | bpz*mAr$NO_2$ (**13**) | 4 | 24 | 12 | 41 | 23 | 38 | 27 | 30 | 41 | 17 |
| 9a | *p*-cymene | bpz*mAr$NO_2$ (**14**) | 45 | 300 | 61 | 204 | 86 | 143 | 94 | 104 | 96 | 40 |
| 10a | benzene | bpzmAr$NO_2$ (**15**) | 11 | 75 | 30 | 99 | 52 | 86 | 61 | 68 | 65 | 27 |
| 11a | *p*-cymene | bpzmAr$NO_2$ (**16**) | 47 | 313 | 65 | 215 | 78 | 130 | 95 | 106 | 95 | 39 |
| 12a | benzene | bpz*mAr$NH_2$ (**17**) | 10 | 67 | 16 | 53 | 21 | 36 | 22 | 24 | 25 | 10 |
| 13a | *p*-cymene | bpz*mAr$NH_2$ (**18**) | 20 | 133 | 34 | 112 | 55 | 91 | 75 | 84 | 91 | 38 |
| 14a | benzene | bpz*mArOH (**1**) | 5 | 34 | 6 | 20 | 7 | 10 | 8 | 9 | 9 | 4 |
| 15a | *p*-cymene | bpz*mArOH (**2**) | 45 | 300 | 65 | 215 | 86 | 143 | 94 | 104 | 96 | 40 |
| 16a | benzene | bpzmArOH (**3**) | 6 | 39 | 7 | 23 | 8 | 13 | 9 | 9 | 31 | 13 |
| 17a | *p*-cymene | bpzmArOH (**4**) | 2 | 13 | 2 | 7 | 3 | 5 | 6 | 7 | 14 | 6 |

[a] Determined by $^1$H-NMR. [b] 0.002 mmol of [$RuCl_2(C_6H_6)(CH_3CN)$] added. [c] 0.001 mmol of [$RuCl_2$(*p*-cymene)]$_2$ added.

**Table S8 -** Complete catalytic data for the evolution with time of the transfer hydrogenation of benzophenone (1000 equivalents) in 2-propanol, using as precatalyst [RuCl(*p*-cymene)(bpz*m)][X], without the addition of base.

| Run | Anion (**complex**) | t = 1.5 h | | t = 3 h | | t = 6 h | | t = 9 h | | t = 24 h | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Yield[a] /% | TOF / $h^{-1}$ | Yield[a] /% | TOF / $h^{-1}$ | Yield[a] /% | TOF / $h^{-1}$ | Yield[a] /% | TOF / $h^{-1}$ | Yield[a] /% | TOF / $h^{-1}$ |
| 3a | $BPh_4$ (**8**) | 0 | 0 | 21 | 69 | 85 | 142 | 94 | 104 | 96 | 40 |
| 21a | $BF_4$ (**5**) | 4 | 24 | 27 | 88 | 78 | 129 | 85 | 94 | 94 | 39 |
| 22a | Cl (**6**) | 20 | 133 | 35 | 113 | 55 | 92 | 72 | 83 | 90 | 38 |

[a] Determined by $^1$H-NMR.

**Table S9 -** Complete catalytic data for the evolution with time of the transfer hydrogenation of different carbonyl compounds (1000 equivalents) in 2-propanol, using as precatalyst [RuCl(*p*-cymene)(NN)][$BPh_4$], without the addition of base.

| Run | NN-Ligand (**complex**) | Substrate | Susbstrate/Catalyst Ratio[a] | t = 1.5 h | | t = 3 h | | t = 6 h | | t = 9 h | | t = 24 h | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | Yield[d] /% | TOF / $h^{-1}$ | Yield[d] /% | TOF / $h^{-1}$ | Yield[d] /% | TOF / $h^{-1}$ | Yield[d] /% | TOF / $h^{-1}$ | Yield[d] /% | TOF / $h^{-1}$ |
| 23a | bpz*mArOH (**2**) | Acetofenone | 1000/1 | 43 | 287 | 69 | 230 | 89 | 148 | 95 | 106 | 98 | 41 |
| 24a | bpz*mAr$NO_2$ (**14**) | Acetofenone | 1000/1 | 46 | 307 | 71 | 237 | 91 | 152 | 96 | 107 | >99 | 41 |
| 25a | bpz*mArOH (**2**) | Benzylphenylketone | 1000/1 | - | - | - | - | - | - | - | - | 15 | 6 |
| 26a | bpz*mAr$NO_2$ (**14**) | Benzylphenylketone | 1000/1 | - | - | - | - | - | - | - | - | 34 | 14 |
| 27a | bpz*mArOH (**2**) | Benzylphenylketone | 167/1[b] | 8 | 9 | 19 | 11 | 25 | 7 | 36 | 7 | 60 | 4 |
| 28a | bpz*mAr$NO_2$ (**14**) | Benzylphenylketone | 167/1[b] | 15 | 17 | 30 | 17 | 59 | 16 | 84 | 16 | 98 | 7 |
| 29a | bpz*mArOH (**2**) | Cyclohexanone | 1000/1 | - | - | - | - | - | - | - | - | 9 | 4 |
| 30a | bpz*mAr$NO_2$ (**14**) | Cyclohexanone | 1000/1 | - | - | - | - | - | - | - | - | 11 | 5 |
| 31a | bpz*mArOH (**2**) | Cyclohexanone | 250/1[c] | 0 | - | 11 | 9 | 30 | 12 | 52 | 14 | 74 | 8 |
| 32a | bpz*mAr$NO_2$ (**14**) | Cyclohexanone | 250/1[c] | 38 | 63 | 67 | 56 | 86 | 36 | >99 | 28 | >99 | 10 |
| 33a | bpz*mArOH (**2**) | Benzaldehyde | 1000/1 | 19 | 127 | 81 | 270 | 85 | 142 | 97 | 108 | - | - |
| 34a | bpz*mAr$NO_2$ (**14**) | Benzaldehyde | 1000/1 | 56 | 373 | 85 | 285 | 93 | 155 | 96 | 107 | - | - |
| 35a | bpz*mArOH (**2**) | 2-Phenylpropanal | 1000/1 | - | - | - | - | - | - | - | - | 10 | 4 |
| 36a | bpz*mAr$NO_2$ (**14**) | 2-Phenylpropanal | 1000/1 | - | - | - | - | - | - | - | - | 13 | 5 |
| 37a | bpz*mArOH (**2**) | 2-Phenylpropanal | 125/1[c] | 31 | 26 | 45 | 19 | 84 | 17 | 91 | 5 | >99 | 5 |
| 38a | bpz*mAr$NO_2$ (**14**) | 2-Phenylpropanal | 125/1[c] | 46 | 38 | 80 | 33 | 84 | 17 | 87 | 5 | >99 | 5 |

[a]Reaction conditions: solvent: 10 mL of 2-propanol, 0.002 mmol of precatalyst, no base. [b]Precatalyst: 0.006 mmol used. [c]Precatalyst: 0.004 mmol used. [d]Determined by $^1$H-NMR.

**Table S10** - Transfer hydrogenation of benzophenone with different changes in the reaction media, using as precatalyst [RuCl(*p*-cymene)(NN)][$BPh_4$].

| Run[a] | NN- Ligand (**complex**) | Special fact | Yield[b] (%) | TOF ($h^{-1}$)[c] | Sample (Time in hours / Yield in %) | | | |
|---|---|---|---|---|---|---|---|---|
| 9c | bpz*mAr$NO_2$[e] (**14**) | 2 equivalents of precatalyst used | 96 | 192 | 0.5 / 40 | 1.5 / 56 | 5 / 71 | 8 / 92 |
| 15c | bpz*mArOH[e] (**2**) | 2 equivalents of precatalyst used | 97 | 417 | 0.5 / 49 | 1.5 / 69 | 5 / 87 | 8 / 97 |
| 18a | bpz*mArOH (**2**) | "In situ" precatalyst | 47 | - | 1.5 / 15 | 3 / 26 | 6 / 37 | 9 / 43 |
| 19a | bpz*mAr$NO_2$ (**14**) | "In situ" precatalyst | 69 | 172 | 1.5 / 34 | 3 / 52 | 6 / 63 | 9 / 67 |
| 20a | bpz*m (**8**) | "In situ" precatalyst | 75 | 62 | 1.5 / 16 | 3 / 30 | 6 / 45 | 9 / 57 |
| 39a | bpz*mArOH (**2**) | 300 equivalents of Hg added | 74 | 51 | 1 / 12 | 4 / 35 | 10 / 53 | |
| 40a | bpz*mArOH[d] (**2**) | 2 hours of incubation | 57 | 119 | 1 /16 | 2 / 30 | 4 / 46 | |
| 41a | | 16 hours of incubation | 19 | - | 1 / 6 | 2 / 11 | 4 / 16 | |
| 42a | | 24 hours of incubation | 4 | - | 1 /1 | 2 / 2 | 4 / 3 | |
| 43a | bpz*m[d] (**8**) | 1.5 hours of incubation | 22 | - | 1 / 4 | 2 / 9 | 4 / 16 | |
| 44a | | 2 hours of incubation | 13 | - | 1 / 5 | 2 / 5 | 4 / 9 | |
| 45a | | 16 hours of incubation | 6 | - | 1 / 1 | 2 / 2 | 4 / 4 | |
| 46a | bpz*mPh[d] (**10**) | 1 hour of incubation | 44 | - | 1 / 25 | 2 / 36 | 4 / 43 | |
| 47a | | 24 hours of incubation | 15 | - | 1 / 4 | 2 / 7 | 4 / 15 | |
| 48a | bpz*mArOH[f] (**2**) | 4 mmols of ketone added | 66 | 40 | 24 / 48 | 26 / 51 | 32 / 64 | 48 / 66 |
| 49a | bpz*mArOH (**2**) | 20 equivalents of *p*-cymene added | 54 | 48 | 1.5 / 18 | 3 / 28 | 6 / 37 | 9 / 45 |
| 50a | bpz*mAr$NO_2$ (**14**) | 20 equivalents of *p*-cymene added | 32 | - | 1.5 / 20 | 3 / 29 | 6 / 29 | 9 / 31 |

[a] Reaction conditions: benzophenone/catalyst = 1000/1, solvent: 2-propanol, no base. [b]Determined by $^1$H-NMR at t = 24 hours. [c]TOF calculated at Yield = 50 %. [d]Yield determined at t = 6 hours. [e]Yield determined at t = 8 hours. [f] After 24 hours of normal conditions, 2 mmols of ketone are added. Yield over 4 mmol of ketone calculated at t = 48 hours. TOF calculated at 32 hours.

**Table S11 -** Evolution with time of the NMR signals obtained for each precatalyst in refluxing 2-propanol.

| Precatalyst | Time (h) | NMR signals (higher to lower intensity order) (ppm) |
|---|---|---|
| [RuCl(*p*-cymene)(bpz*mArNO$_2$)][BPh$_4$] **14** | 2 | -10.27 -13.46 |
| | 4 | -13.46 -10.27 -8.84 |
| | 16 | -13.46 |
| [RuCl(*p*-cymene)(bpz*mArOH)][BPh$_4$] **2** | 2 | -8.84 |
| | 4 | -8.84 -12.07 |
| | 16 | -12.07 -8.84 |
| [RuCl(*p*-cymene)(bpz*mPh)][BPh$_4$] **12** | 2 | -8.84 -9.64 -9.62 |
| | 4 | -8.84 |
| | 6 | -9.77 |
| | 16 | -10.04 -8.81 -13.41 -13.44 |
| [RuCl$_2$(*p*-cymene)]$_2$ | 16 | -10.26 |

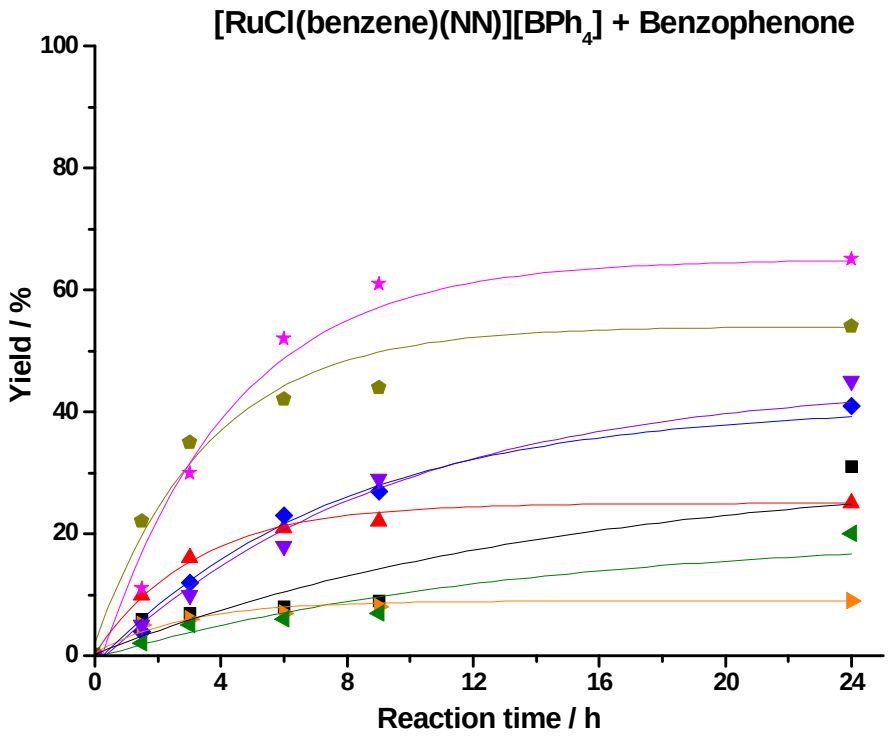


**Figure S1.** Evolution with time of the yield of product for the reaction of transfer hydrogenation of benzophenone when [RuCl(benzene)(NN)][$BPh_4$] complexes are used. ▼**7** (bpz*m) ⬟ **11** (bpzmPh) ◀ **9** (bpz*mPh) ■ **3** (bpzmArOH) ▶ **1** (bpz*mArOH) ★ **15** (bpzmAr$NO_2$) ◆ **13** (bpz*mAr$NO_2$) ▲ **17** (bpz*mAr$NH_2$)

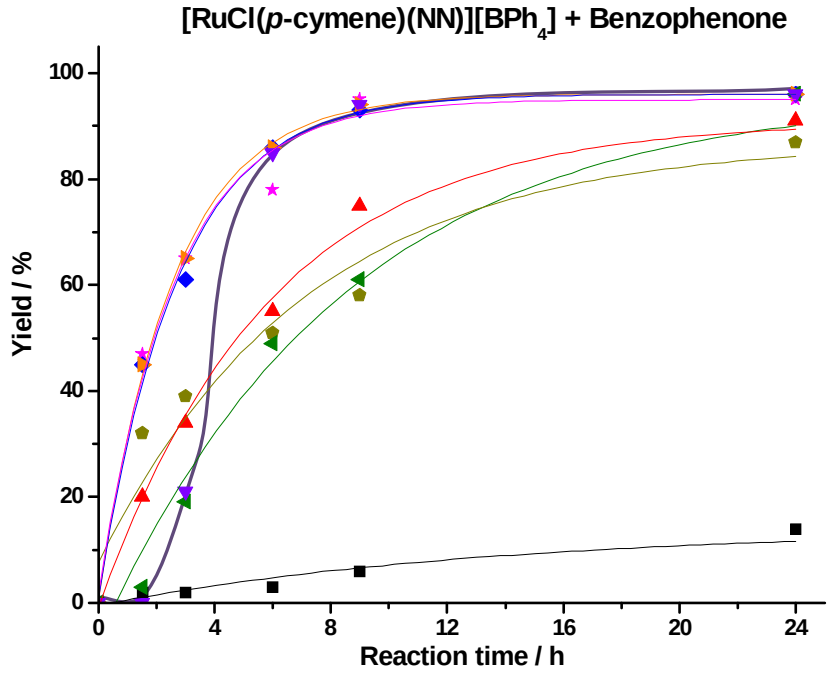


**Figure S2.** Evolution with time of the yield of product for the reaction of transfer hydrogenation of benzophenone when [RuCl(*p*-cymene)(NN)][$BPh_4$] complexes are used. ▼ **8** (bpz*m) ⬟ **12** (bpzmPh) ◀ **10** (bpz*mPh) ■ **4** (bpzmArOH) ▶ **2** (bpz*mArOH) ★ **16** (bpzmAr$NO_2$) ◆ **14** (bpz*mAr$NO_2$) ▲ **18** (bpz*mAr$NH_2$)

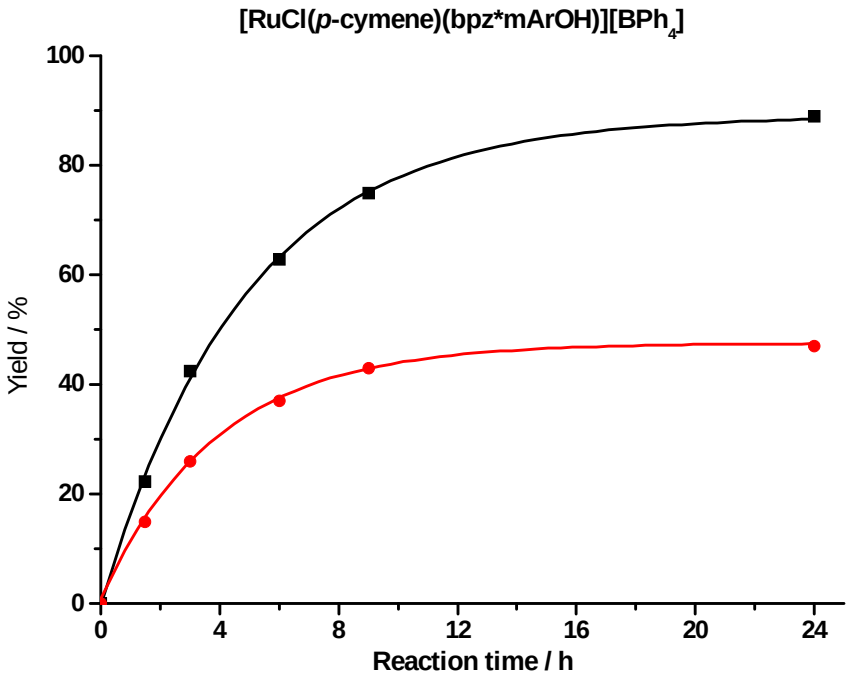


**Figure S3** - Evolution with time of the yield of product for the reaction of transfer hydrogenation of benzophenone. Comparison between the results obtained for [RuCl(*p*-

cymene)(bpz*mArOH)][$BPh_4$] complex (**2**) and when the catalyst is generated in situ in the reaction medium. ■ Normal test ● "In situ" precatalyst

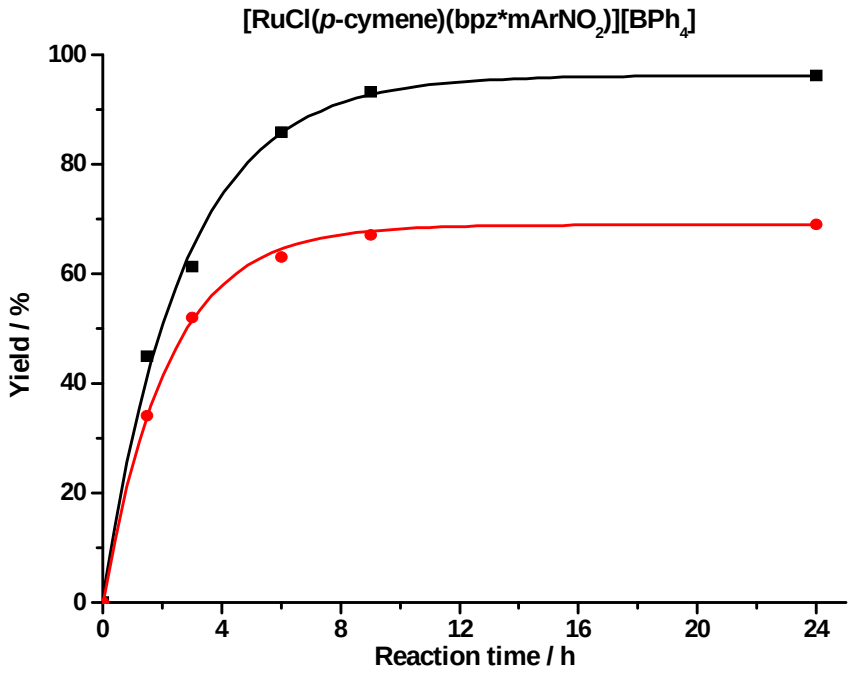


**Figure S4** - Evolution with time of the yield of product for the reaction of transfer hydrogenation of benzophenone. Comparison between the results obtained for [RuCl(*p*-cymene)(bpz*mAr$NO_2$)][$BPh_4$] complex (**14**) and when the catalyst is generated in situ in the reaction medium. ■ Normal test ● "In situ" precatalyst

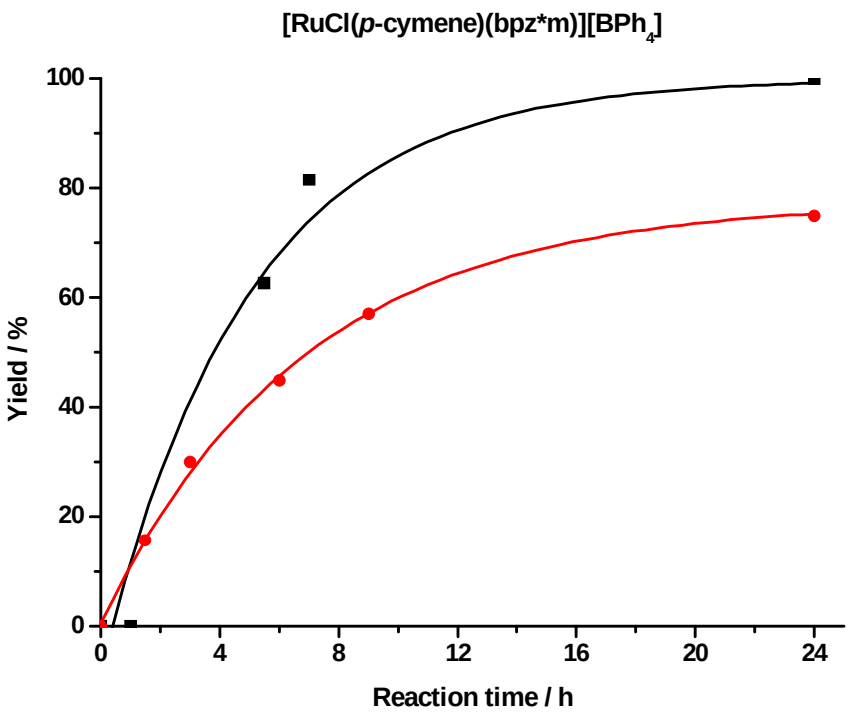


**Figure S5** - Evolution with time of the yield of product for the reaction of transfer hydrogenation of benzophenone. Comparison between the results obtained for [RuCl(*p*-cymene)(bpz*m)][$BPh_4$] complex (**8**) and when the catalyst is generated in situ in the reaction medium. ■ Normal test ● "In situ" precatalyst

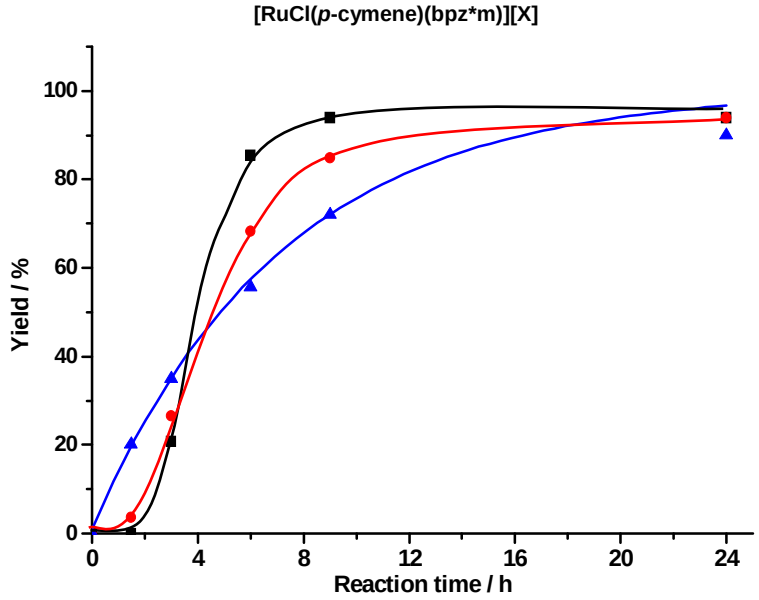


**Figure S6 -** Evolution with time of the yield of product for the reaction of transfer hydrogenation of benzophenone when [RuCl(*p*-cymene)(bpz*m)][X] complexes are used. X = ■$BPh_4$ (**8**), ●$BF_4$ (**5**), and ▲Cl (**6**)

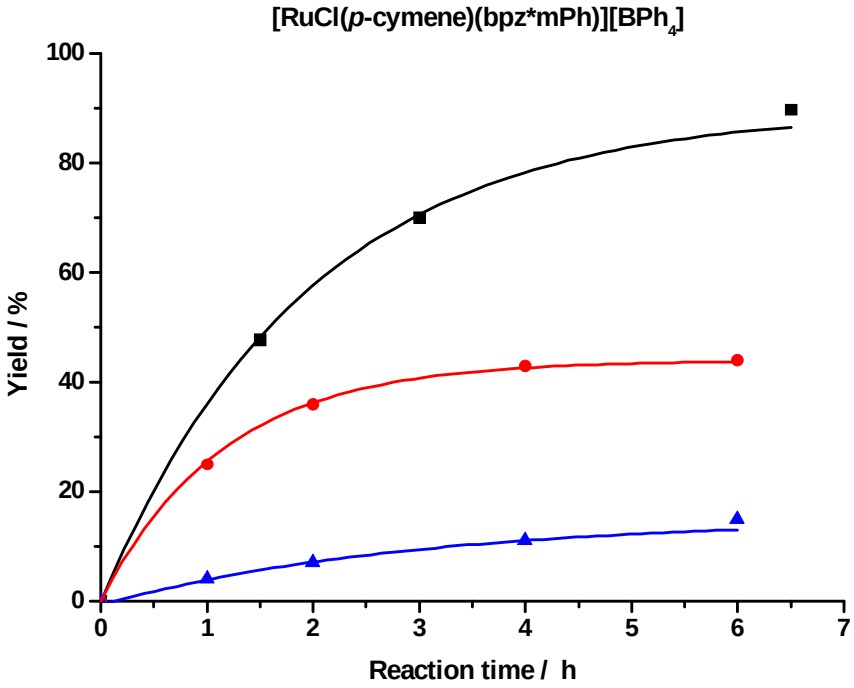


**Figure S7** - Evolution with time of the yield of product for the reaction of transfer hydrogenation of benzophenone when [RuCl(*p*-cymene)(bpz*mPh)][$BPh_4$] complex (**10**) is used as precatalyst, with different incubation times.

■ No incubation ● 1 hour of incubation ▲ 24 hours of incubation

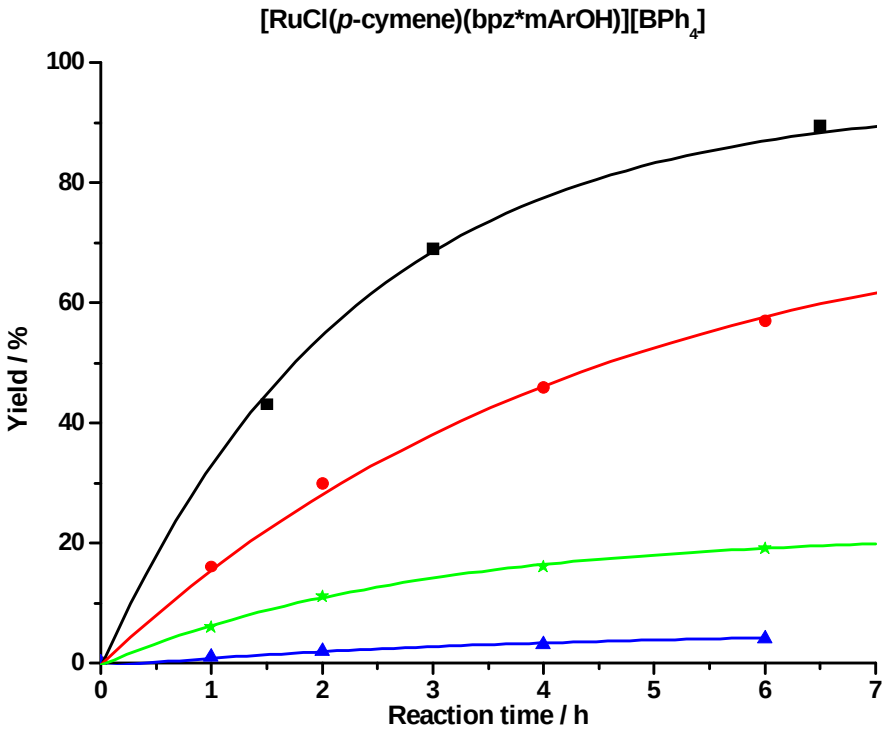


**Figure S8** - Evolution with time of the yield of product for the reaction of transfer hydrogenation of benzophenone when [RuCl(*p*-cymene)(bpz*mArOH)][$BPh_4$] complex (**2**) is used as precatalyst, with different incubation times.

■ No incubation ● 2 hours of incubation ★ 16 hours of incubation ▲ 24 hours of incubation

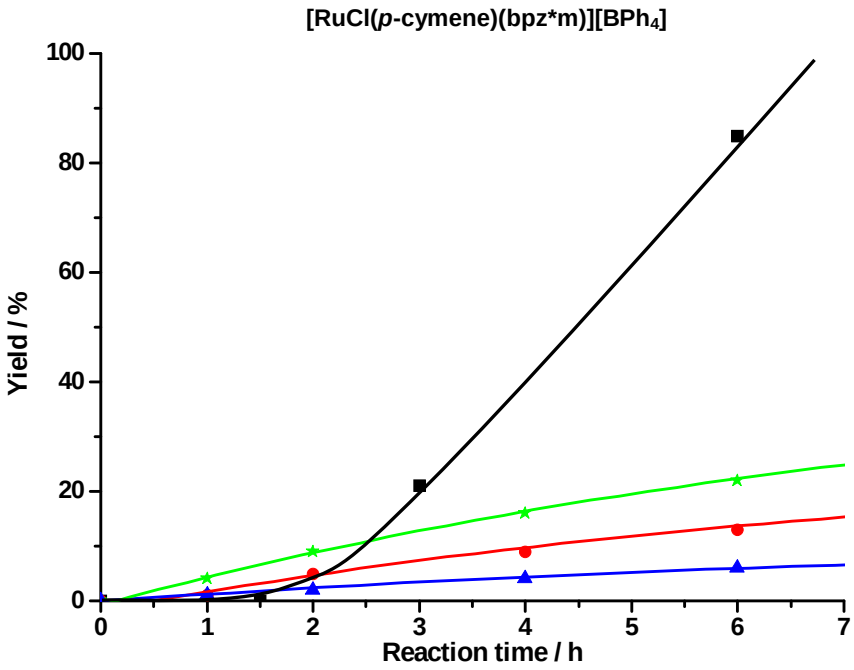


**Figure S9** - Evolution with time of the yield of product for the reaction of transfer hydrogenation of benzophenone when [RuCl(*p*-cymene)(bpz*m)][$BPh_4$] complex (**8**) is used as precatalyst, with different incubation times.

■ No incubation ● 1.5 hour of incubation ★ 2 hours of incubation ▲ 16 hours of incubation

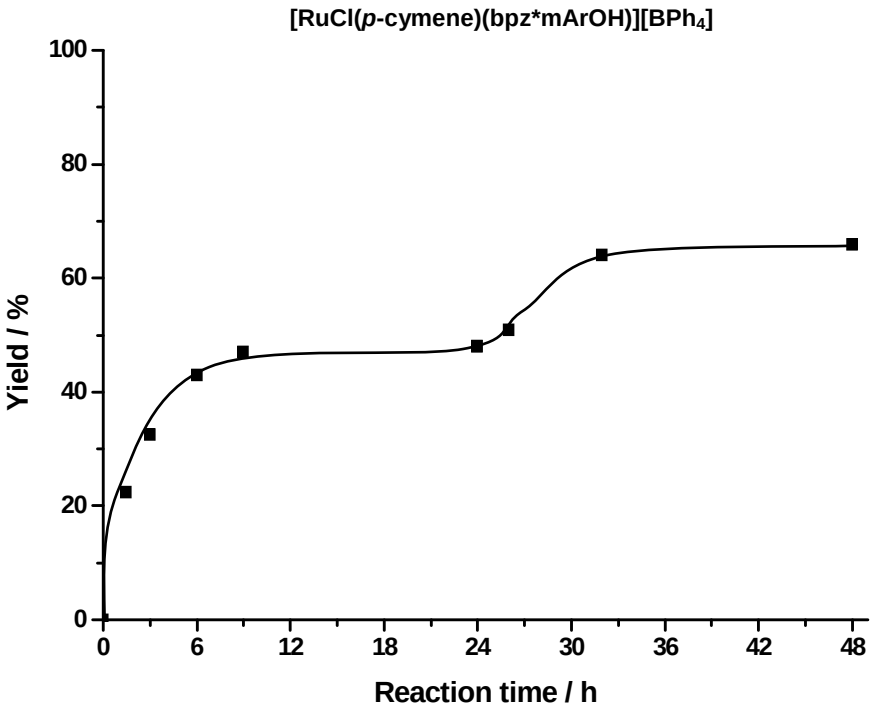


**Figure S10** - Evolution with time of the yield of product for the reaction of transfer hydrogenation of benzophenone when [RuCl(*p*-cymene)(bpz*mArOH)][$BPh_4$] (**2**) is used as precatalyst in two catalytic cycles. 2 additional mmol of benzophenone are added at 24 hours of reaction.

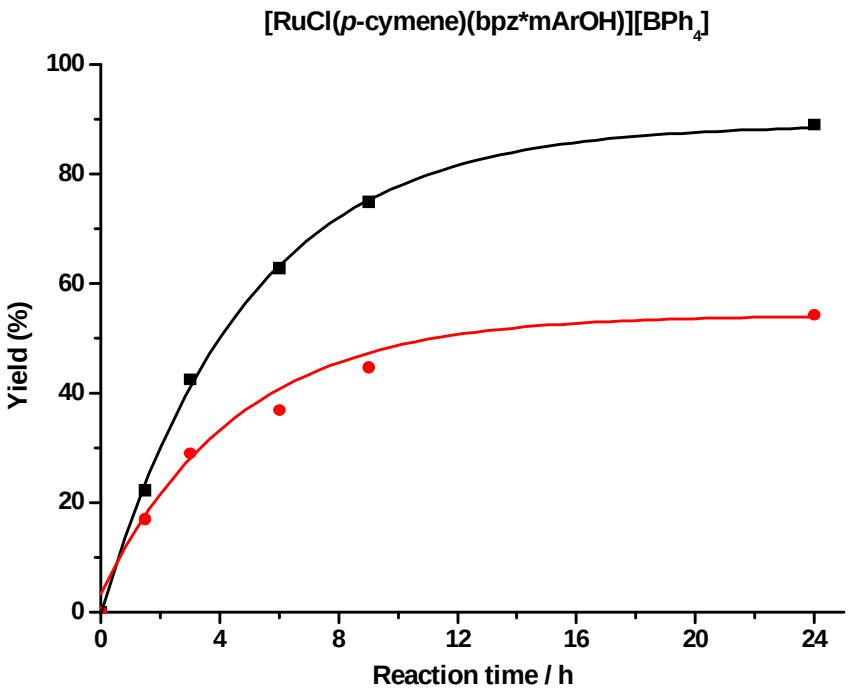


**Figure S11** - Evolution with time of the yield of product for the reaction of transfer hydrogenation of benzophenone when [RuCl(*p*-cymene)(bpz*mArOH)][$BPh_4$] (**2**) is used as precatalyst and a excess of *p*-cymene is added. ■ Normal test ● 20 eq of *p*-cymene added.

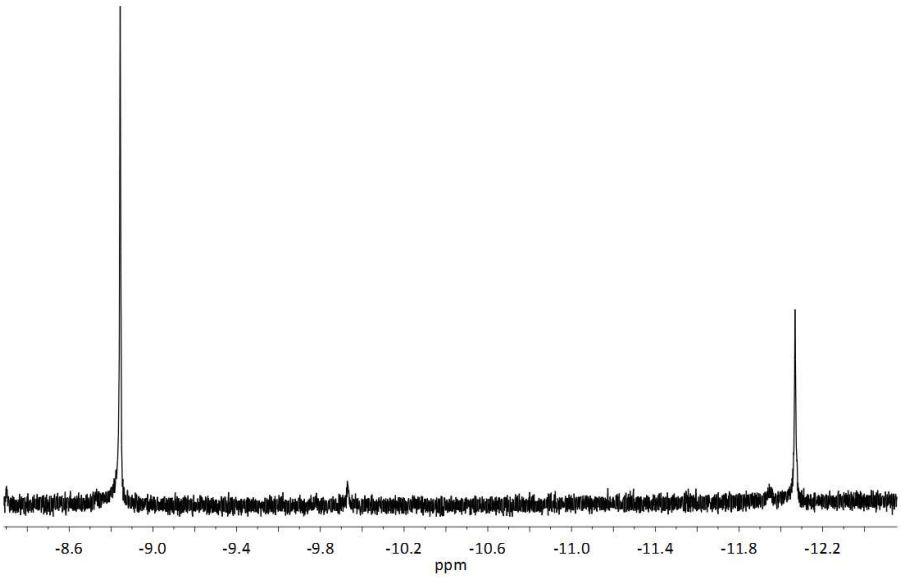


**Figure S12**. $^1$H NMR spectra (hydride region) obtained after a treatment of 4 hours at 82ºC of complex **2** in 2-propanol.

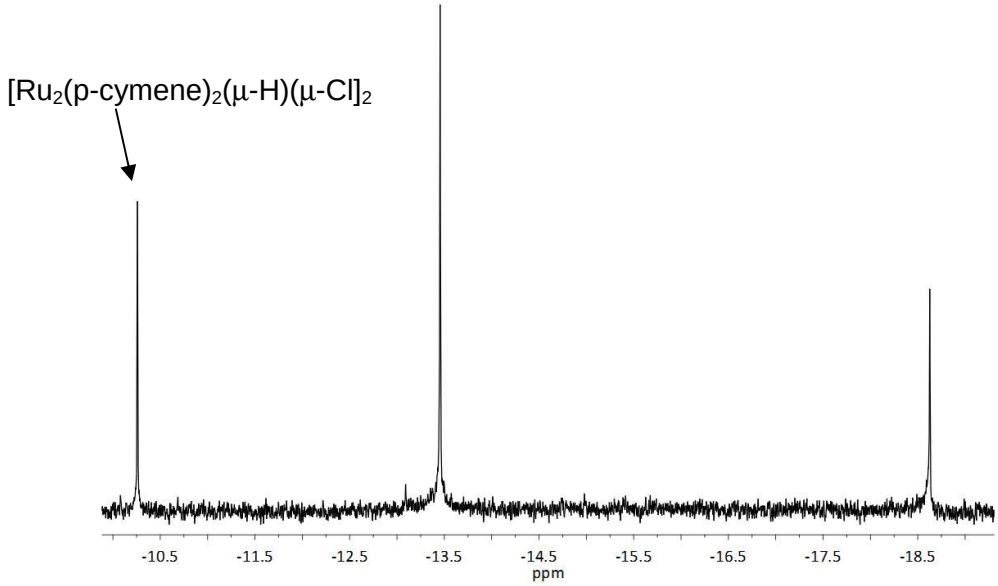


**Figure S13**. $^{1}$H NMR spectra (hydride region) obtained after a treatment of 16 hours at 82ºC of complex **14** in 2-propanol.

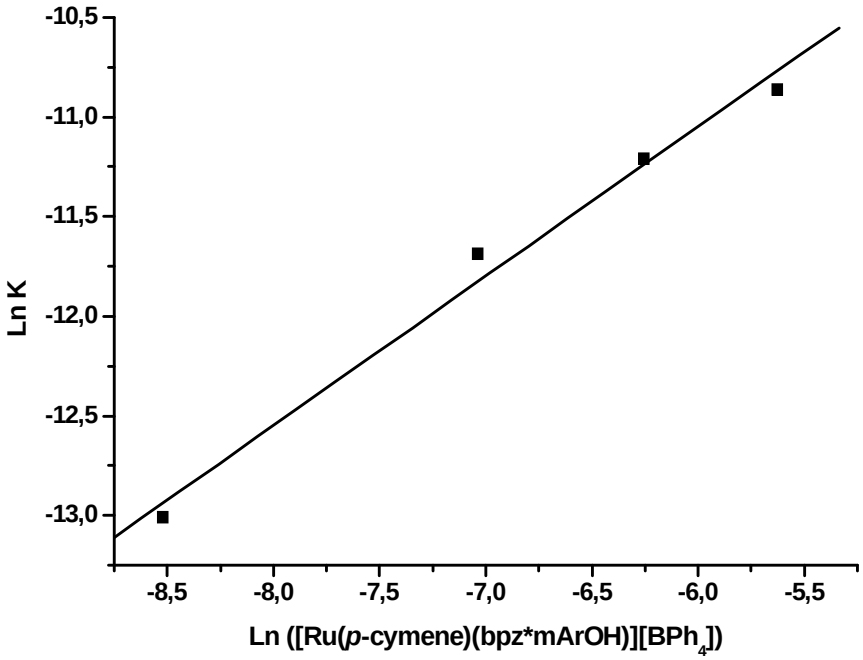


**Figure S14 -** Representation of Ln (K) versus Ln [Ru] for the reaction of transfer hydrogenation of acetophenone with [RuCl(*p*-cymene)(bpz*mArOH)][$BPh_4$] (**2**) as precatalyst.