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Supporting Information

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Tuning the Reactivity of Di-rhodium (II) Complexes with Axial NHC Ligands: The Arylation of Aldehydes

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General Remarks

Tetrahydrofuran (THF), dichloromethane (DMC), 1,2-dimethoxyethane (DME), *t*-amylalcohol were freshly distilled over calcium hydride prior to use. Ethyl acetate was distilled over potassium carbonate. All reactions were performed in oven-dried glassware under dry argon atmosphere. Flash chromatographies were carried out on silica gel 60 M purchased from MN (Ref. 815381), preparative thin layer chromatography plates were prepared with silica gel 60 GF_{254} MercK (Ref. 1.07730.1000). Reaction mixtures were analysed by TLC using ALUGRAM® SIL G/UV_{254} from MN (Ref. 818133, silica gel 60), and visualisation of TLC spots was effected using UV and phosphomolybdic acid solution.

NMR spectra were recorded in a Bruker AMX 400 using $CDCl_3$ as solvent and $(CH_3)_4Si$ (^1H) as internal standard. All coupling constants are expressed in Hz.

Dirhodium catalysts were purchased from Aldrich: $Rh_2(OAc)_4$ – Rhodium (II) acetate dimer; $Rh_2(pfb)_4$ – Rhodium (II) heptafluorobutyrate dimer.

NHC ligands used were prepared following reported procedures: 1,3-bis(*t*-butyl) imidazolium chloride **7**,[1] 1,3-bis(2,6-di*iso*propylphenyl) imidazolium chloride **4** and 1,3-bis(2,6-di*iso*propylphenyl) imidazolinium chloride **5**,[2] were prepared according to literature procedures, except 1,3-bis(2, 4, 6-trimethy-phenyl) imidazolinium chloride **6** which was purchased from Aldrich.

The aldehydes and boronic acids were purchased from Aldrich and used without further purification.

1.1 – Axial ligands evaluation – Table 1.

$Rh_2(OAc)_4$ (3.30 mg, 7.50×10^{-3} mmol, 3 mol %) was weighted into a flamed dried round bottom flask equipped with a condenser and under argon atmosphere. DME (0.5 mL) was added and the suspension was stirred at room temperature for 5 min. then, phenylboronic acid (61.00 mg, 0.50 mmol), NHC ligand (7.50×10^{-3} mmol, 3 mol %), KO^{t}Bu (28.00 mg, 0.25 mmol), water (120 μL) and 4-methoxybenzaldehyde (34.00 mg, 0.25 mmol) were successively added. The resulting mixture was stirred at 90 °C for different periods of time depending on the NHC ligand used. The reaction mixture was concentrated under reduced pressure and the residue was purified by preparative thin layer chromatography (ethyl acetate/hexane), yielding the desired secondary alcohol as a slightly yellow oil which crystallized upon standing at low temperature (fridge).

1.2 – Di-rhodium (II) catalyst evaluation – Table 1, Entries 9 and 10.

[1] Arduengo, A. J. III; Dias, H. V. R.; Harlow, R. L.; Kline M. *J. Am. Chem. Soc.*, **1992,** *114*, 5530-5534.

[2] Arduengo, A. J. III; Krafczyk, R.; Schmutzer, R. *Tetrahedron*, **1999,** *55*, 14523-14534.

Rh (II) catalyst (7.50×10^{-3} mmol, 3 mol %) was weighted into a flamed dried round bottom flask equipped with a condenser and under argon atmosphere. DME (0.5 mL) was added and the suspension was stirred at room temperature for 5 min. then, phenylboronic acid (61.00 mg, 0.50 mmol), 1,3-bis(2,6-di*iso*propylphenyl) imidazolinium chloride (3.20 mg, 7.50×10^{-3} mmol, 3 mol %), KO^{t}Bu (28.00 mg, 0.25 mmol), water (120 µL) and 4-methoxybenzaldehyde (34.00 mg, 0.25 mmol) were successively added. The resulting mixture was stirred at 60 or 90 °C for different periods of time depending on the catalyst used. The reaction mixture was concentrated under reduced pressure and the residue was purified by preparative thin layer chromatography (ethyl acetate/hexane), yielding the desired secondary alcohol as a slightly yellow oil which crystallized upon standing at low temperature (fridge).

1.3 – Solvent effect over the arylation of aldehyde 1 – Table 1, Entries 11 and 12.

Rh (II) catalyst (7.50×10^{-3} mmol, 3 mol %) was weighted into a flamed dried round bottom flask equipped with a condenser and under argon atmosphere. The solvent (0.5 mL, or 0.5 mL:0.12 mL when using solvent mixtures) was added and the suspension was stirred at room temperature for 5 min. then, phenylboronic acid (61.00 mg, 0.50 mmol), 1,3-bis(2,6-di*iso*propylphenyl) imidazolinium chloride (3.20 mg, 7.50×10^{-3} mmol, 3 mol %), KO^{t}Bu (28.00 mg, 0.25 mmol), water (120 µL) and 4-methoxybenzaldehyde (34.00 mg, 0.25 mmol) were successively added. The resulting mixture was stirred at 60 or 90 °C for different periods of time depending on the catalyst used. The reaction mixture was concentrated under reduced pressure and the residue was purified by preparative thin layer chromatography (ethyl acetate/hexane), yielding the desired secondary alcohol as a slightly yellow oil which crystallized upon standing at low temperature (fridge).

1.4 – Scope of the *in situ* methodology – Table 2, Entries 1-11.

$Rh_2(pfb)_4$ (7.90 mg, 7.50×10^{-3} mmol, 3 mol %) was weighted into a flamed dried round bottom flask equipped with a condenser and under argon atmosphere. *t*-Amylalcohol (0.5 mL) was added and the suspension was stirred at room temperature for 5 min. then, phenylboronic acid (61.00 mg, 0.50 mmol), 1,3-bis(2,6-di*iso*propylphenyl) imidazolinium chloride (3.20 mg, 7.50×10^{-3} mmol, 3 mol %), KO^{t}Bu (28.00 mg, 0.25 mmol) and the corresponding aldehyde (0.25 mmol) were successively added. The resulting mixture was stirred at 40, 60 or 80 °C for different periods of time. The reaction mixture was concentrated under reduced pressure and the residue was purified by preparative thin layer chromatography (ethyl acetate/hexane), yielding the desired secondary alcohol as a slightly yellow oil which, in most cases, crystallized upon standing at low temperature (fridge).

1.5 – Synthesis of complex 20 - $Rh_2(OAc)_4$-*i*PrNHC$_2$.

$Rh_2(OAc)_4$ (0.06 g, 1.36×10^{-4} mmol), 1,3-bis(2,6-di*iso*propylphenyl) imidazolinium chloride (0.17 g, 4.06×10^{-4} mmol, 3 eq) and KO^{t}Bu (0.06 g, 5.43×10^{-4} mmol, 4 eq) were weighted into a flamed dried Schlenk. DME (2 mL) was added and the suspension was stirred at 80 ºC, after 2 h at this temperature the solvent was removed under reduced pressure. The remaining solids were dissolved in dry toluene (1 mL) and filtered (celite) into a new Schlenk. The filtered toluene was removed under reduced pressure and the solids were dissolved in dry toluene (1 mL) and stored in the freezer (-20 ºC) over night to induce crystallization. The resulting crystals were collected by filtration and dried under vacuum (0.12 g, 72 %).

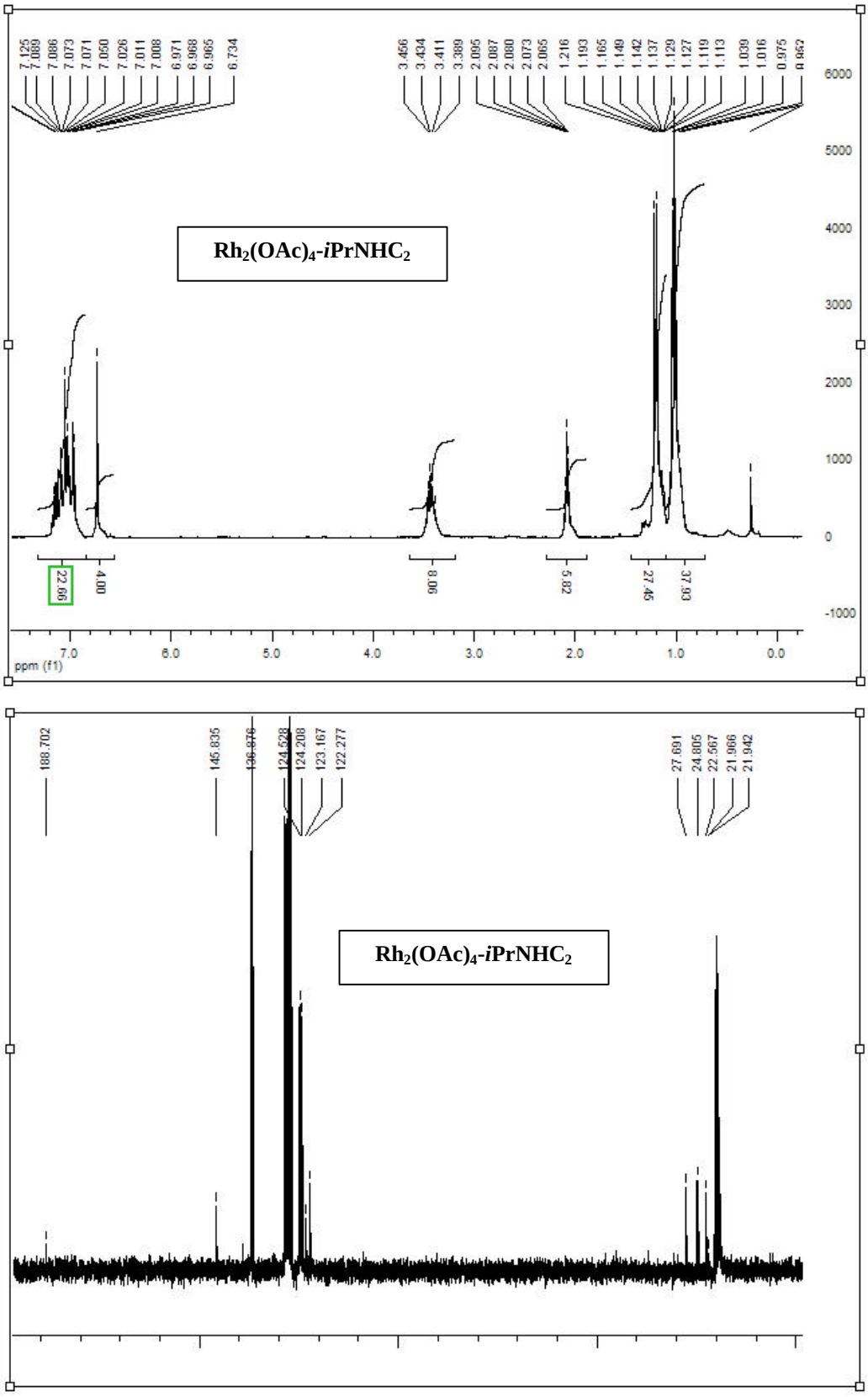
Further recristallizations from toluene afforded suitable orange-crystals for X-ray crystallography.

^{1}H NMR (C_7D_8) d (ppm) = 7.11-6.91 (m, toluene), 6.58 (s, 4H), 3.42-3-35 (m, 8H, *J* = 6.6 and 6.8 Hz), 2.06-2.02 (toluene), 1.16 (d, 24H, *J* = 6.9 Hz), 0.98 (d, 36H, *J* = 6.6 Hz); ^{13}C NMR (C_7D_8) d (ppm) = 189.29, 146.42, 139.61, 129.18, 123.75, 122.86, 28.26, 25.37, 23.14, 22.51.

MS (FAB$^+$): m/z = 830.1, 389.3. HMRS (FAB$^+$): m/z calcd. 1221.463398, found 1221.462541.

Anal Cal. for $C_{62}H_{84}N_4O_8Rh_2$: C, 61.08; H, 6.94; N, 4.60. Found: C, 61.12; H, 7.21; N, 4.39.

Additional NMR experiments such as DEPT and HMQC were carried out and confirmed the characterization described.



1.6 – Synthesis of complex $Rh_2(OAc)_4$-SIPrNHC$_2$ and caracterization of **$Rh_2(OAc)_4$-SIPrNHC.**

$Rh_2(OAc)_4$ (0.06 g, 1.36×10^{-4} mmol), 1,3-bis(2,6-di*iso*propylphenyl) imidazolinium chloride **5** (0.17 g, 4.06×10^{-4} mmol, 3 eq) and KO^{t}Bu (0.05 g, 4.35×10^{-4} mmol, 3.2 eq) were weighted into a flamed dried Schlenk. DME (2 mL) was added and the suspension was stirred at 60 ºC, after 1 h at this temperature the solvent was removed under reduced pressure. The remaining solids were dissolved in dry toluene (1 mL) and filtered (celite) into a new Schlenk. The filtered toluene was removed under reduced pressure and the solids were dissolved in dry toluene (1 mL) and stored in the freezer (-20 ºC) over night to induce crystallization. The resulting crystals were collected by filtration and dried under vacuum (0.10 g, 60 %).

Anal Cal. for $C_{62}H_{88}N_4O_8Rh_2$: C, 60.88; H, 7.25; N, 4.58. Found: C, 60.63; H, 7.28; N, 4.39.

MS (FAB$^+$): m/z = 1222.2, 832.0, 391.2. HMRS (FAB$^+$): m/z calcd. 1223.479048, found 1223.480968.

Further recristallizations from toluene afforded suitable orange-crystals for X-ray crystallography.

In solution at room temperature, the dimer is unstable and readily converts into the mono complex with the following data:

^{1}H NMR (C_7D_8) d (ppm) = 7.09-6.97 (m, toluene), 3.81 (s, 2H), 3.72-3-69 (m, 8H), 2.09-2.08 (toluene), 1.32-1.30 (m, 24H), 1.09 (d, 12H); ^{13}C NMR (C_7D_8) d (ppm) = 188.29, 145.98, 139.02, 123.43, 54.40, 28.07, 25.31, 24.13.

Additional NMR experiments such as HMQC were carried out and confirmed the characterization described.

1.7 – Scope of methodology using complex 20 as the catalyst – Table 2, Entries 12-18.

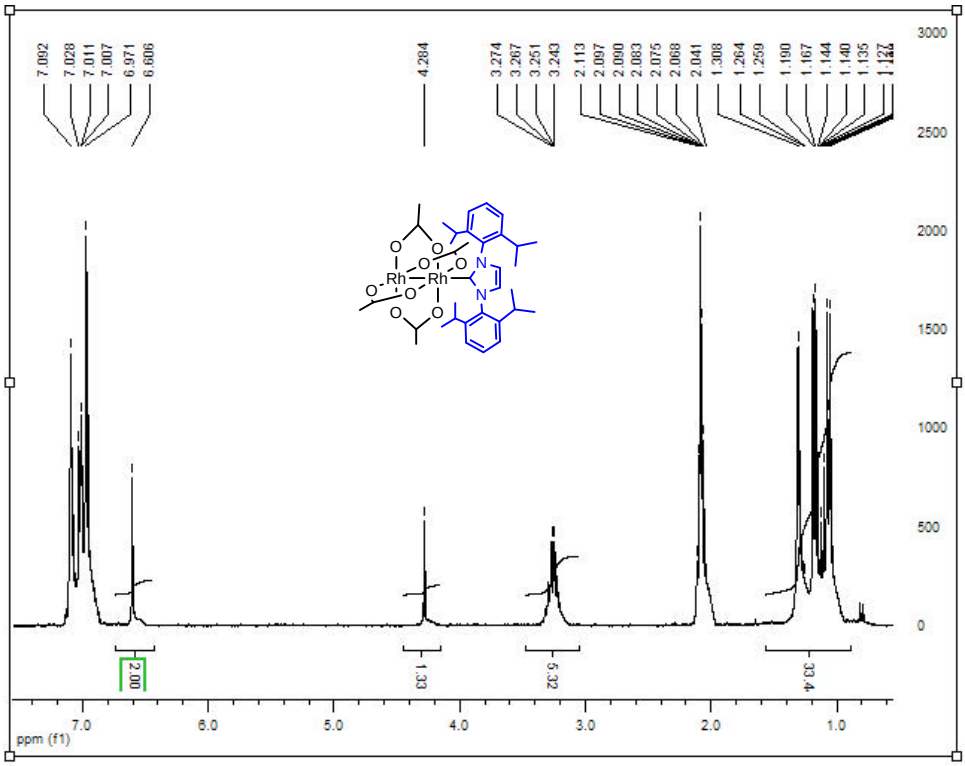
Complex **20** (3.00 mg, 2.50×10^{-3} mmol, 1 mol %) was weighted into a flamed dried round bottom flask equipped with a condenser and under argon atmosphere. *t*-Amylalcohol (0.5 mL), phenylboronic acid (61.00 mg, 0.50 mmol) and KO^{t}Bu (2.80 mg, 0.025 mmol, 10 mol %) were successively added, the resulting suspension was stirred at room temperature for 15 min. after which the corresponding aldehyde (0.25 mmol) were added. The resulting mixture was stirred at 90 °C for different periods of time. The reaction mixture was concentrated under reduced pressure and the residue was purified by preparative thin layer chromatography (ethyl acetate/hexane), yielding the desired secondary alcohol as a slightly yellow oil which, in most cases, crystallized upon standing at low temperature (fridge).

1.8 – Identification of the mono-complex: $Rh_2(OAc)_4$*i*PrNHC.

Complex **20** (6.0 mg, 5.00×10^{-3} mmol, 4.5 mol %) was weighted into a flamed dried round bottom flask equipped with a condenser and under argon atmosphere. *t*-Amylalcohol (0.3 mL), phenylboronic acid (27.00 mg, 0.22 mmol) and KO^{t}Bu (2.80 mg, 0.025 mmol, 10 mol %) were successively added, the resulting suspension was stirred at room temperature for 15 min. after which the corresponding 4-MeC_6H_5COH (0.11 mmol) were added. The resulting mixture was stirred at 90 °C for 1 h. The reaction mixture was concentrated under reduced pressure and the residue was purified by preparative thin layer chromatography (ethyl acetate/hexane), yielding the desired secondary alcohol quantitatively as a slightly yellow oil and a red-wine colored solid (3.0 mg, 75 % based on the initial amount of **20** used) which was identified as the $Rh_2(OAc)_4$*i*PrNHC.

The mono-complex $Rh_2(OAc)_4$*i*PrNHC (1.00 mg, 1.25×10^{-3} mmol, 1 mol %) was reused in a similar reaction affording the secondary alcohol **11** in 95 % isolated yield.

^{1}H NMR (C_7D_8) d (ppm) = 7.09-6.97 (m, toluene), 6.60 (s, 2H), 4.28 (s), 3.27-3.24 (m, 4H), 2.11-2.07 (toluene), 1.31 (s, 12H), 1.18 (d, 12H, *J* = 9.2 Hz), 1.06 (d, 12H, *J* = 9.0 Hz); ^{13}C NMR (C_7D_8) d (ppm) = 188.20, 145.61, 122.79, 28.10, 25.06, 22.83, 22.60.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7.028
7.011
7.007
6.971
6.606
4.284
3.274
3.267
3.251
3.243
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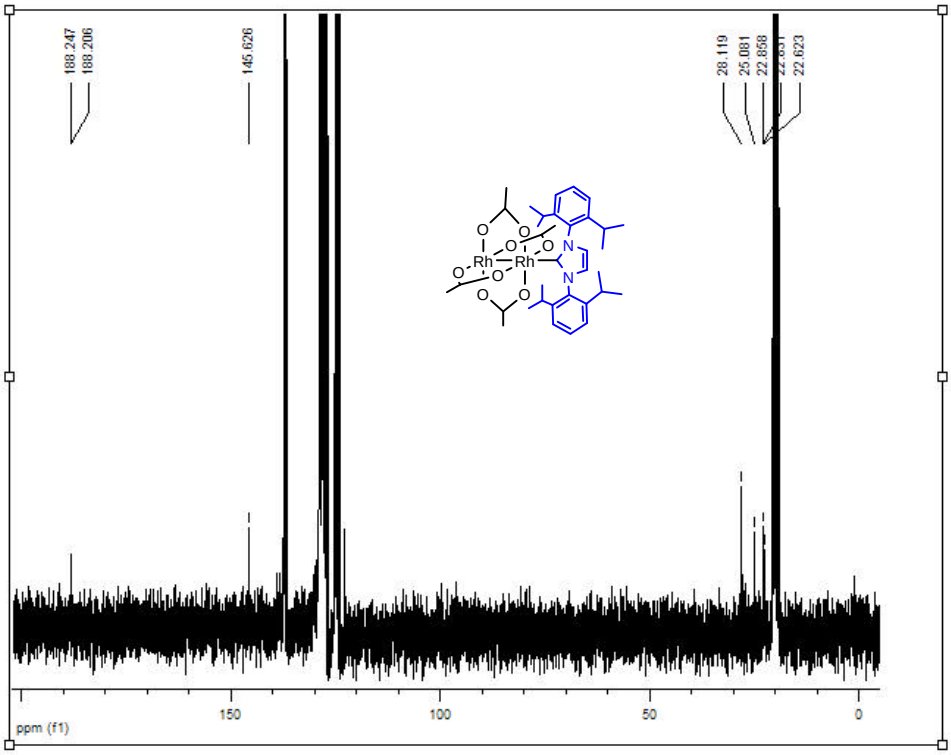
2.097
2.090
2.083
2.075
2.068
2.041
1.308
1.264
1.259
1.190
1.167
1.144
1.140
1.135
3000
2500
2000
1500
1000
500
0
2.00
1.33
6.32
33.4
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (f1)


188.247
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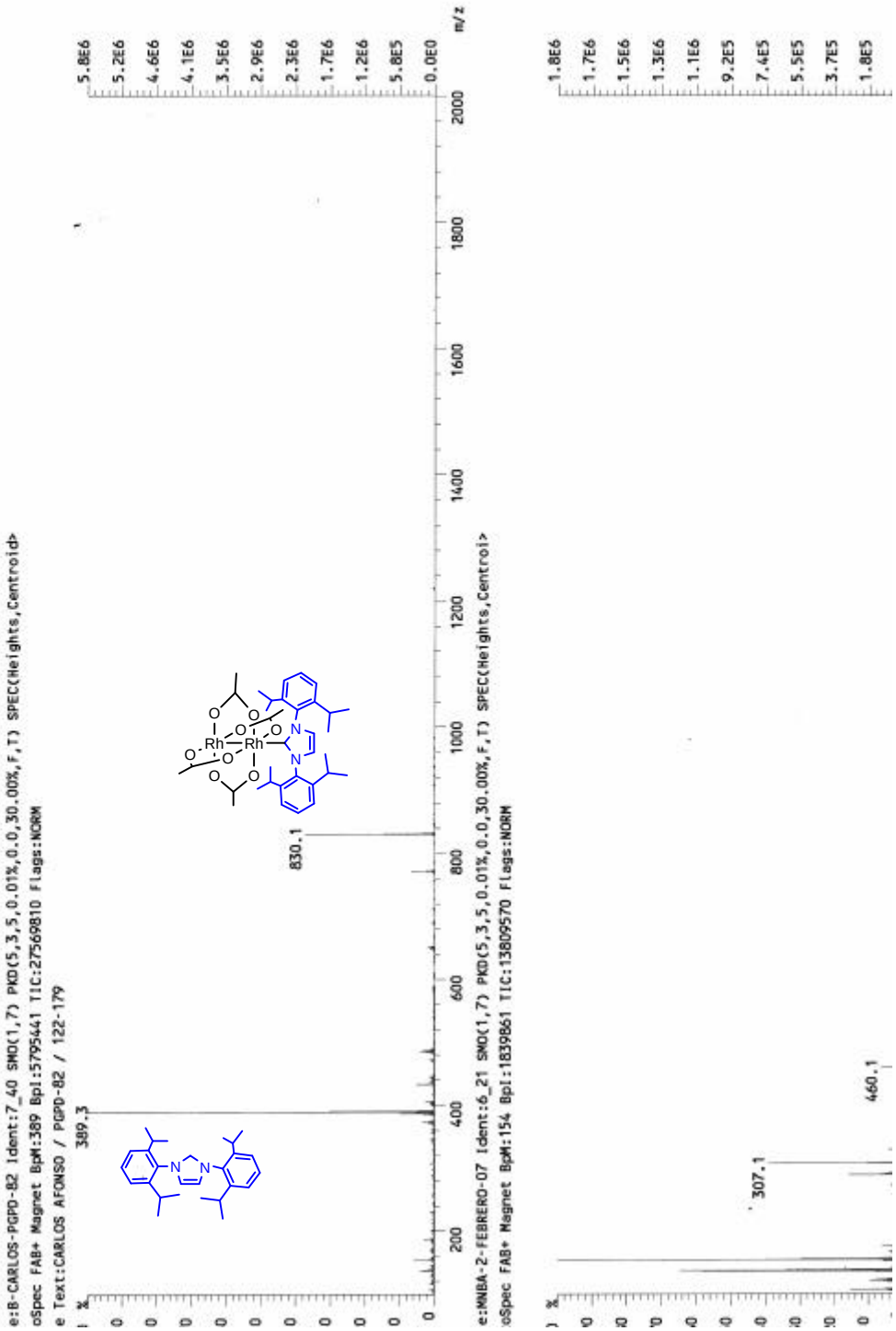
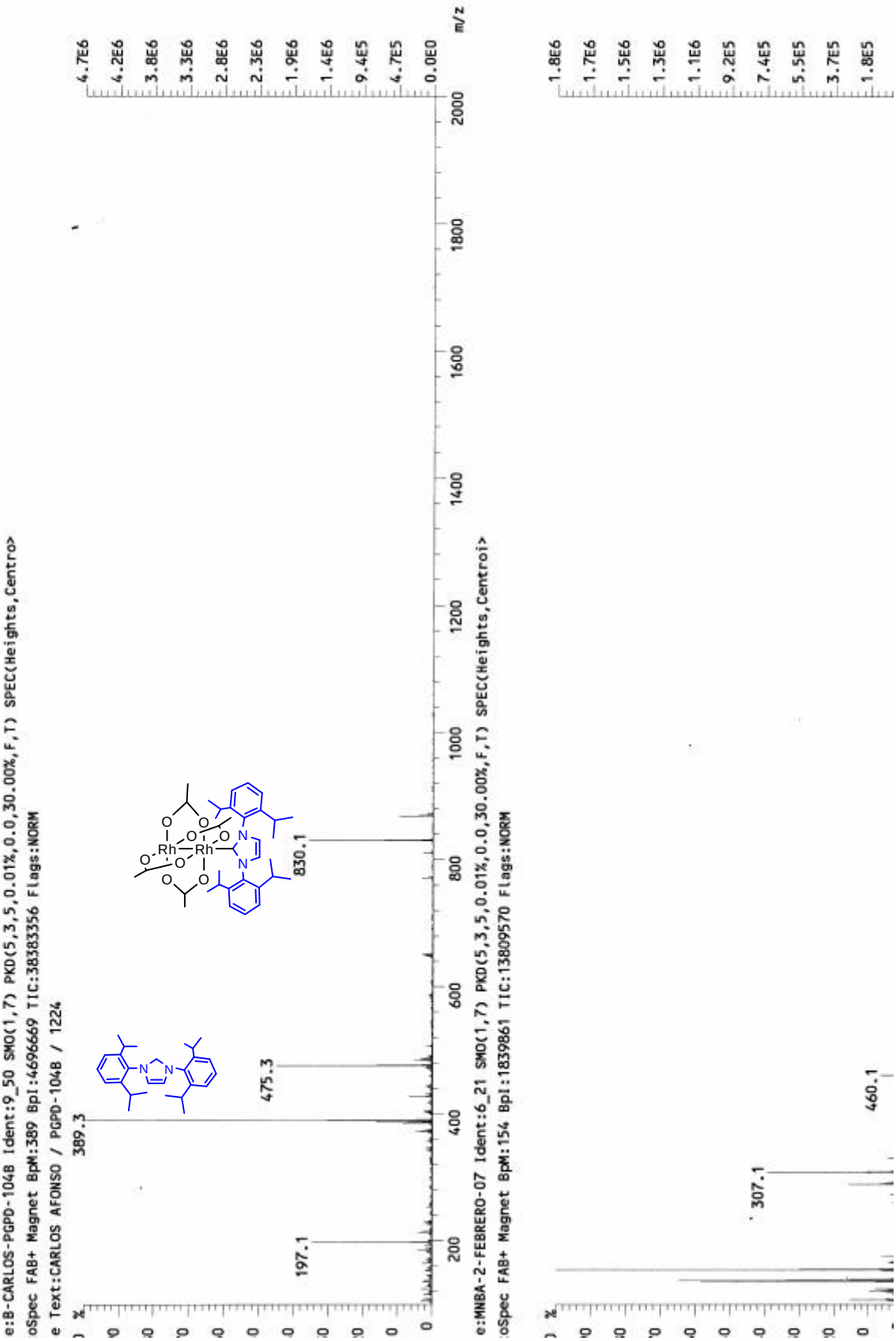
145.626
28.119
25.081
22.858
22.623
150
100
50
0
ppm (f1)

1.9 – Mass spectra of isolated complex 20 (A $Rh_2(OAc)_4$-*i*PrNHC$_2$) and reaction crude mixture of a reaction in which complex 20 (B $Rh_2(OAc)_4$-*i*PrNHC) was used, affording the secondary alcohol quantitatively.

A – MS of $Rh_2(OAc)_4$-*i*PrNHC$_2$ 20



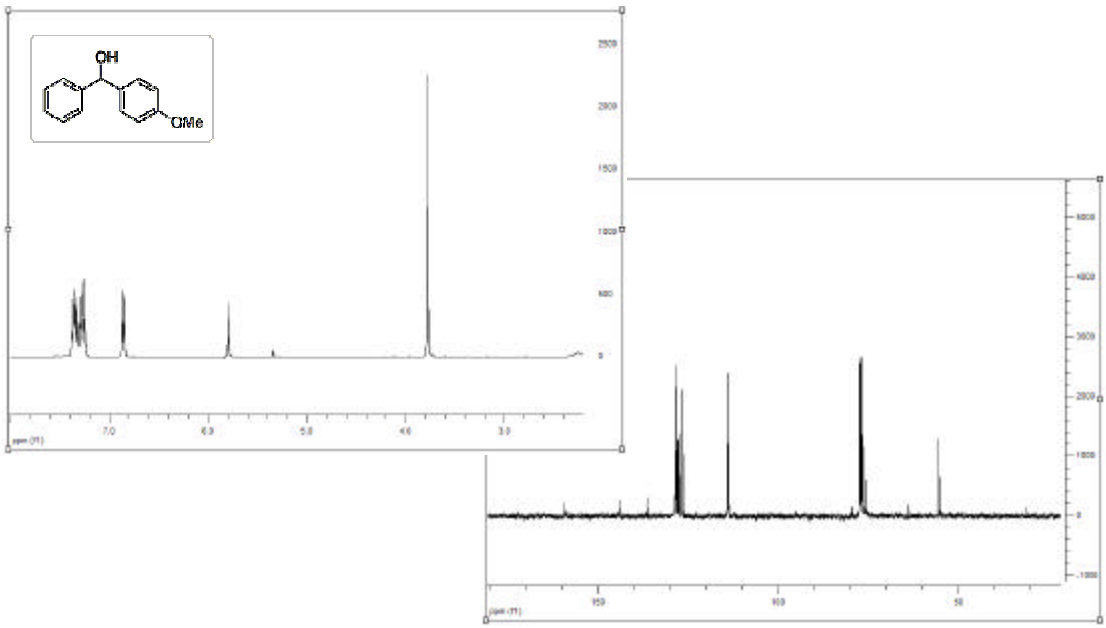
B - Reaction Crude Mixture



2– Compounds characterization

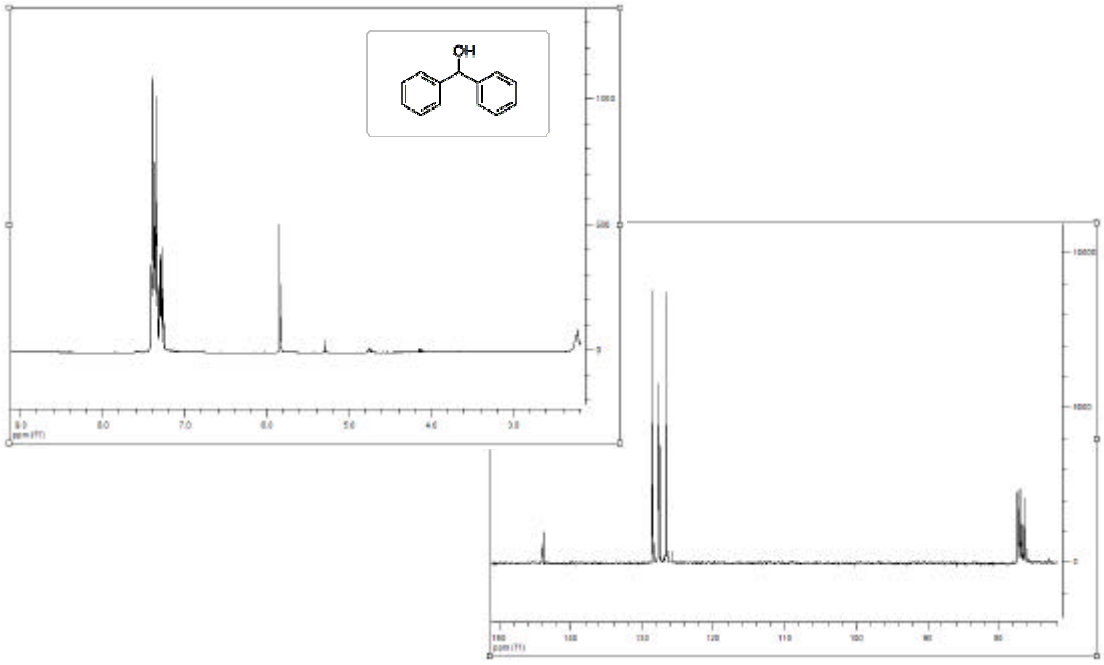
4-Methoxyphenyl-phenylmethanol 3[3]

Obtained in 94 % isolated yield after 30 min. at 90 ºC (Table 1, entry 3; ^{1}H NMR ($CDCl_3$) d (ppm) = 7.37-7.23 (m, 7H), 6.86 (d, 2H, *J* = 8.6 Hz), 5.79 (s, 1H), 3.78 (s, 3H), 2.25 (bs, 1H); ^{13}C NMR ($CDCl_3$) d (ppm) = 159.05, 144.02, 136.19, 128.56, 127.91, 127.41, 126.39, 113.87, 75.80, 55.26.



4-Phenyl-phenylmethanol 10

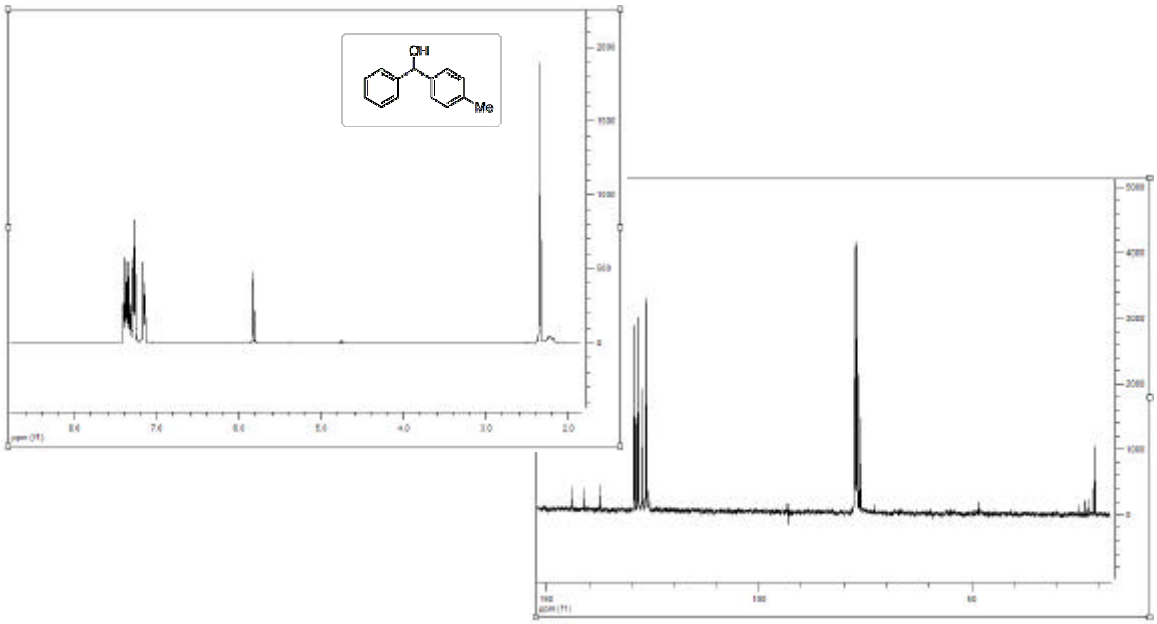
Obtained in 99 % isolated yield after 1 h at 60 ºC (Table 2, entry 1); ^{1}H NMR ($CDCl_3$) d (ppm) = 7.40-7.26 (m, 7H), 5.84 (s, 1H), 2.22 (bs, 1H); ^{13}C NMR ($CDCl_3$) d (ppm) = 143.79, 128.47, 127.54, 126.53, 72.80.



[3] Fürstner, A.; Krause, H. *Adv. Synth. Catal.* **2001**, *343*, 343-350.

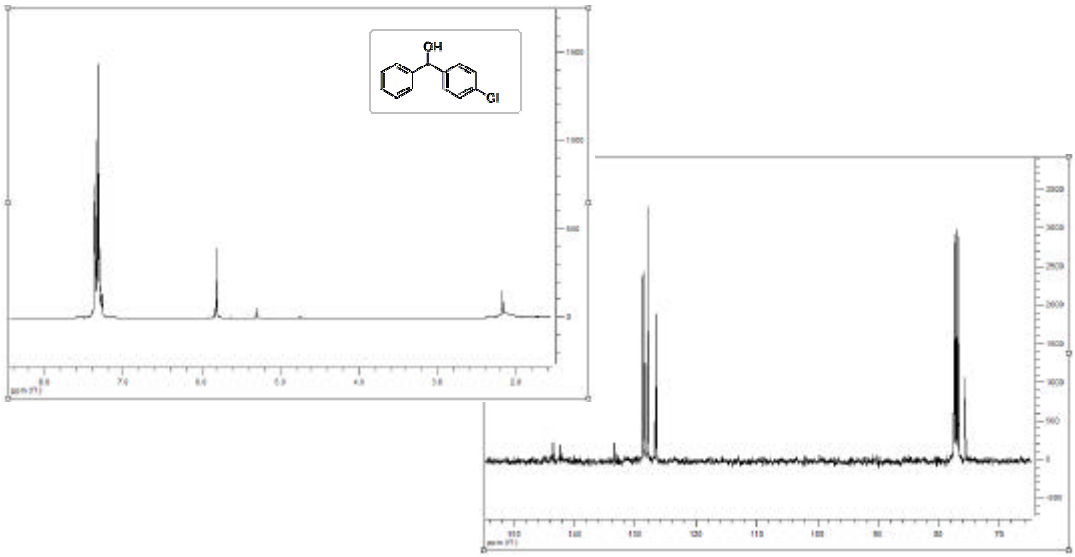
4-Tolyl-phenylmethanol 11[6]

Obtained in 91 % isolated yield after 4 h at 60 ºC (Table 2, entry 2); ^{1}H NMR ($CDCl_3$) d (ppm) = 7.39-7.24 (m, 7H), 7.16-7.14 (m, 2H), 5.81 (s, 1H), 2.34 (s, 3H), 2.21 (bs, 1H); ^{13}C NMR ($CDCl_3$) d (ppm) = 143.96, 140.96, 137.28, 129.18, 128.45, 127.45, 126.52, 125.86, 72.82, 21.10.



4-Chlorophenyl-phenylmethanol 12[4]

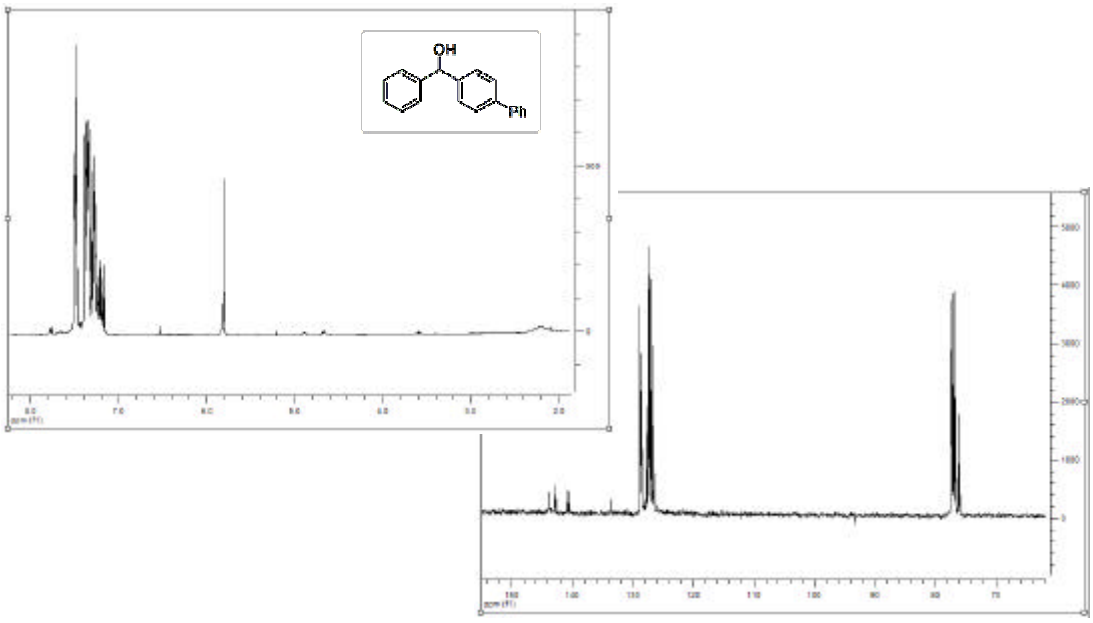
Obtained in 95 % isolated yield after 40 min. at 60 ºC (Table 2, entry 3); ^{1}H NMR ($CDCl_3$) d (ppm) = 7.35-7.27 (m, 9H), 5.81 (s, 1H), 2.17 (bs, 1H); ^{13}C NMR ($CDCl_3$) d (ppm) = 143.42, 142.19, 133.26, 128.63, 128.58, 127.85, 126.50, 75.60.



[4] Jagt, R. B. C.; de Vries, J. G. ; Feringa, B. L.; Minnard, A. *J. Org. Biomol. Chem.* **2006**, *4*, 773-775.

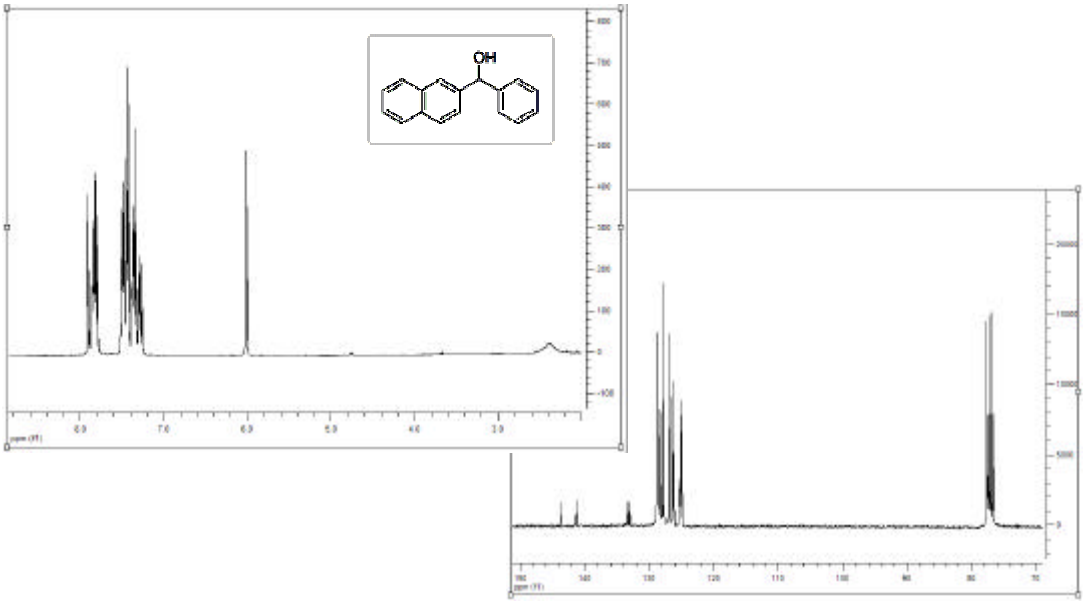
4-Benzylphenyl-phenylmethanol 13[6]

Obtained in 99 % isolated yield after 1 h at 60 ºC (Table 2, entry 5); ^{1}H NMR ($CDCl_3$) d (ppm) = 7.77-7.17 (m, 14H), 5.80 (s, 1H), 2.20 (bs, 1H); ^{13}C NMR ($CDCl_3$) d (ppm) = 143.73, 142.81, 140.77, 140.49, 133.47, 128.74, 128.55, 127.64, 127.25, 127.07,126.96, 126.53, 76.04.



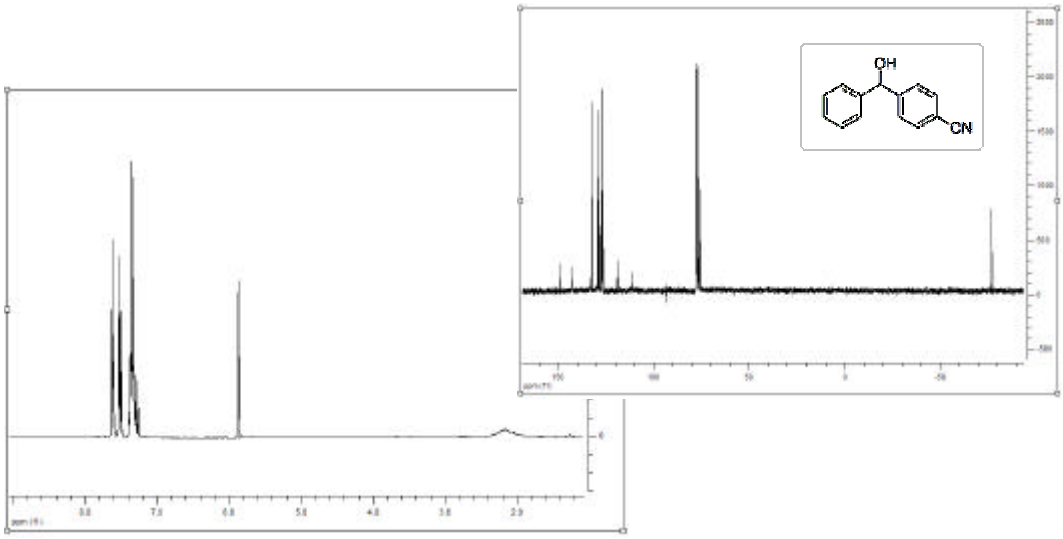
2-Naphtyl-phenylmethanol 14[6]

Obtained in 94 % isolated yield after 5 h at 80 ºC (Table 2, entry 6); ^{1}H NMR ($CDCl_3$) d (ppm) = 7.90-7.26 (m, 12H), 6.01 (s, 1H), 2.38 (bs, 1H); ^{13}C NMR ($CDCl_3$) d (ppm) = 143.62, 141.10, 133.23, 132.86, 128.52, 128.31, 128.05, 127.65, 126.70, 126.17, 125.95, 125.01, 124.75, 76.35.



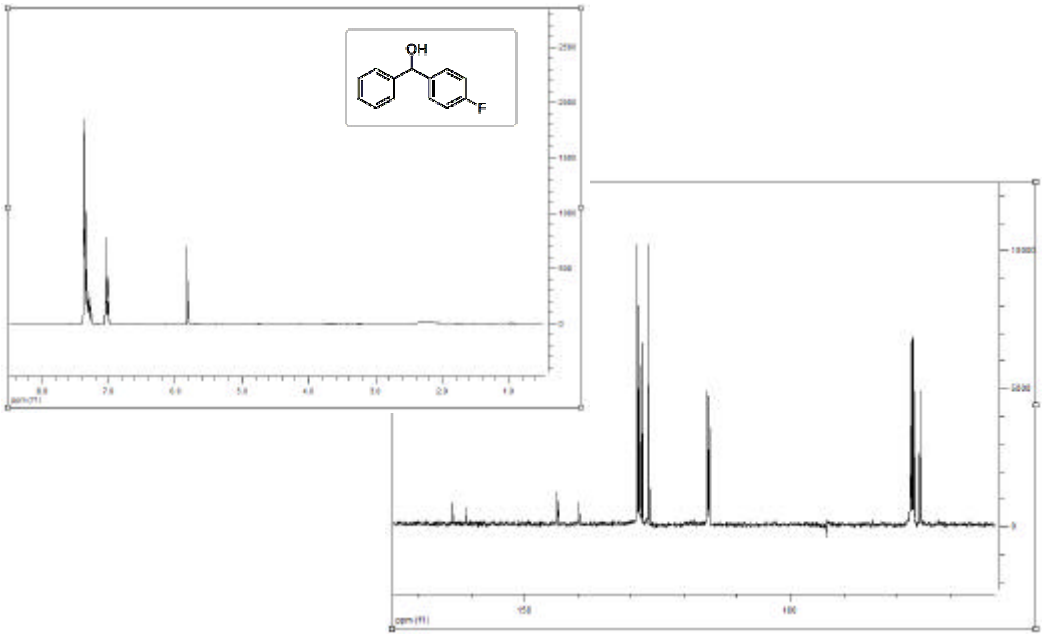
4-Cyanophenyl-phenylmethanol 15[5]

Obtained in 80 % isolated yield after 5 h at 80 ºC (Table 2, entry 7); ^{1}H NMR ($CDCl_3$) d (ppm) = 7.61 (d, 2H, *J* = 8.0 Hz), 7.51 (d, 2H, *J* = 8.0 Hz), 7.38-7.26 (m, 5H), 5.86 (s, 1H), 2.16 (bs, 1H); ^{13}C NMR ($CDCl_3$) d (ppm) = 148.78, 142.78, 132.24, 128.86, 128.28, 126.97, 126.66, 118.78, 111.14, 75.61.



4-Fluorophenyl-phenylmethanol 16[6]

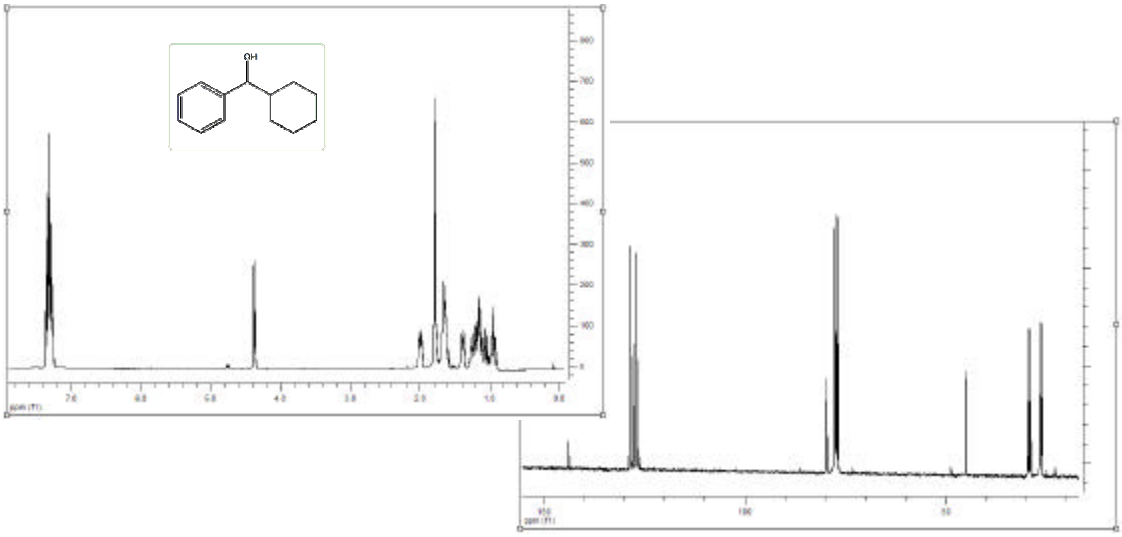
Obtained in 67 % isolated yield after 2 h at 60 ºC (Table 2, entry 9); ^{1}H NMR ($CDCl_3$) d (ppm) = 7.36-7.26 (m, 7H), 7.04-7.00 (m, 2H), 5.81 (s, 1H), 2.15 (bs, 1H); ^{13}C NMR ($CDCl_3$) d (ppm) = 163.35, 160.90, 143.60, 139.51, 128.55, 128.23, 127.70, 126.42, 115.36, 115.14, 75.56.



[5] Uchiyama, M.; Kameda, M.; Mishima, O.; Yokoyama, N. *J. Am. Chem. Soc.* **1998**, *120*, 4934-4946.
[6] Huang, R.; Shaughnessy, K. H. *Chem. Commun.* **2005**, 4484-4486.

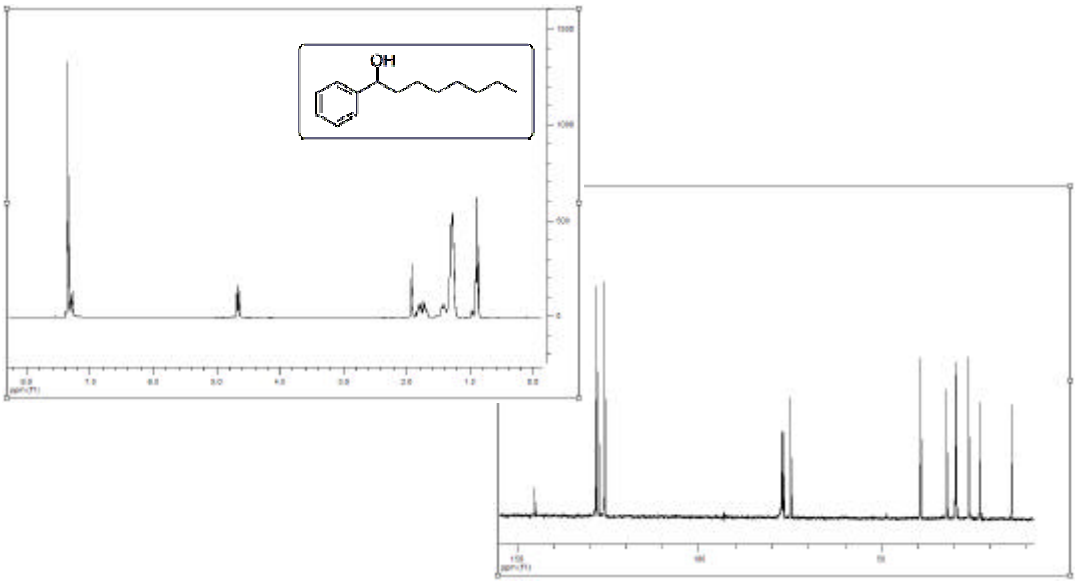
Cyclohexyl-(phenyl)-methanol 17[7]

Obtained in 88 % isolated yield after 3 h at 60 ºC (Table 2, entry 10); ^{1}H NMR ($CDCl_3$) d (ppm) = 7.35-7.25 (m, 5H), 4.37 (d, 1H, *J* = 7.2 Hz), 2.00-1.97 (m, 1H), 1.78-1.75, 1.68-1.57, 1.39-1.36, 1.28-0.89 (several multiples accounting for 10H); ^{13}C NMR ($CDCl_3$) d (ppm) = 143.60, 128.17, 127.39, 126.61, 79.38, 44.95, 29.29, 28.81, 26.41, 26.08, 26.00.



1-Phenyl-octanol 18[8]

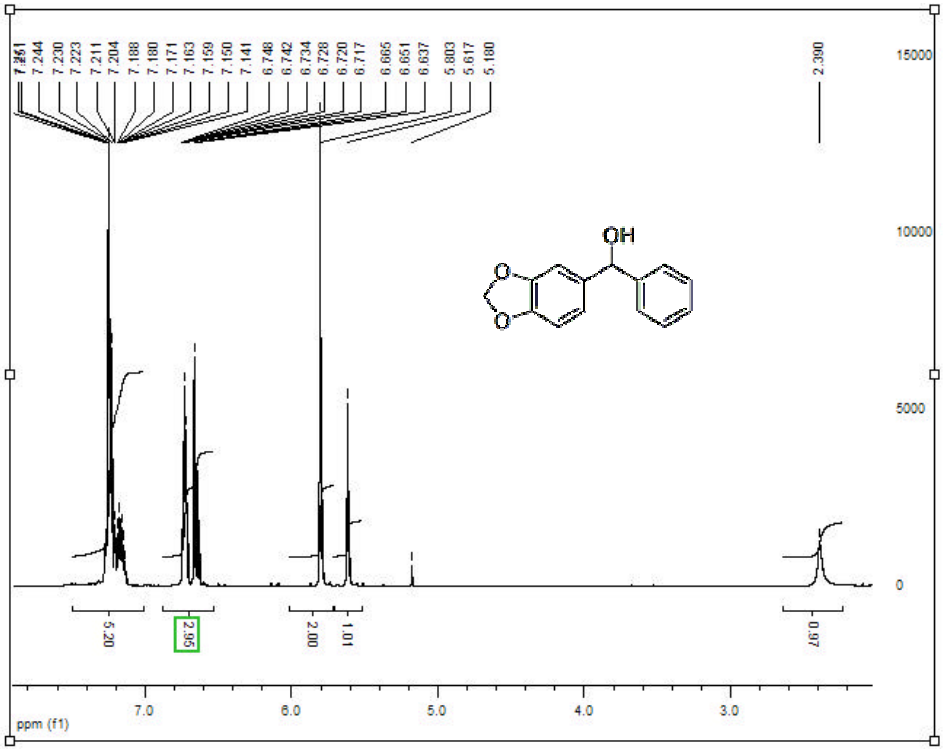
Obtained in 77 % isolated yield after 3 h at 60 ºC (Table 2, entry 11); ^{1}H NMR ($CDCl_3$) d (ppm) = 7.37-7.25 (m, 5H), 4.67-4.64 (m, 1H), 1.91 (bs, 1H), 1.81-1.77 (m, 1H), 1.74-1.68 (m, 1H), 1.43-1.39 (m, 10H), 0.88 (t, 3H, *J* = 8.0 Hz); ^{13}C NMR ($CDCl_3$) d (ppm) = 144.93, 128.38, 127.43, 125.87, 74.67, 39.09, 31.78, 29.47, 29.19, 25.81, 22.61, 14.05.

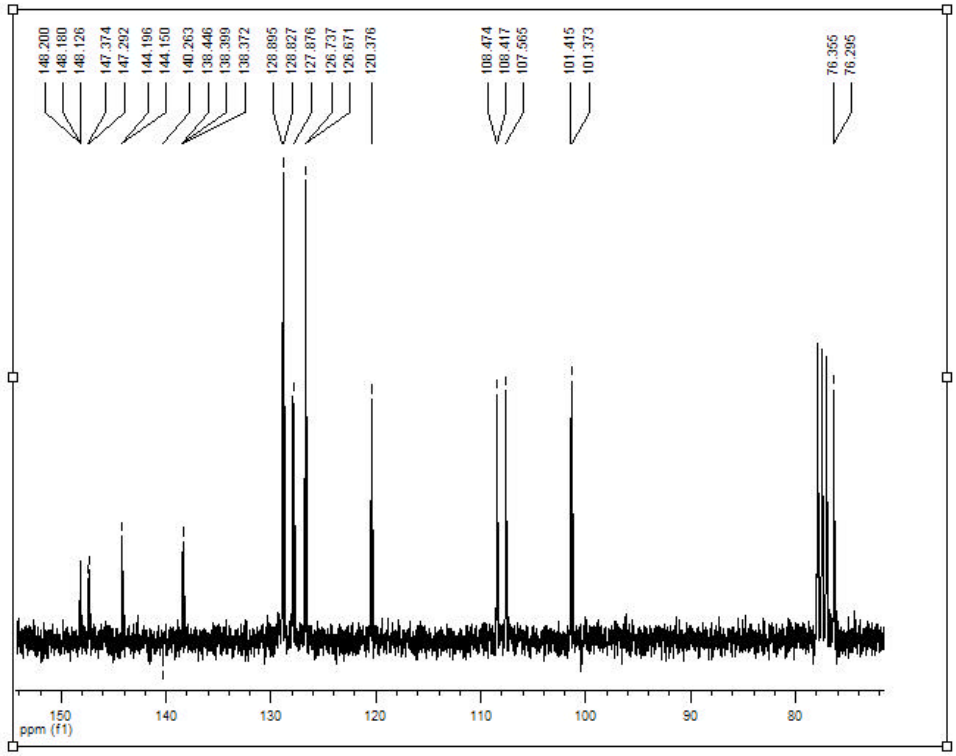


[7] Batey, R. A.; Thadani, A. N.; Smil, D. V. *Org. Lett.* **1999**, *1*, 1683-1686.
[8] Li, C.-J.; Meng, Y. *J. Am. Chem. Soc.* **2000**, *122*, 9538-9539.

1,3-benzodioxol-5-yl-phenylmethanol 19[9]

Obtained in 96 % isolated yield after 3 h at 90 ºC (Table 2, entry 13); ^{1}H NMR ($CDCl_3$) d (ppm) = 7.26-7.14 (m, 5H), 6.75-6.64 (m, 3H), 5.80 (s, 1H), 5.62 (s, 1H); ^{13}C NMR ($CDCl_3$) d (ppm) = 148.18, 147.37, 144.19, 140.26, 138.39, 128.89, 127.88, 126.73, 120.38, 108.47, 107.56, 101.41, 76.35.





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3- Computational Details

All calculations were performed using the Gaussian 98 software package,[10] and the B3PW91 hybrid functional, without symmetry constraints. That functional includes a mixture of Hartree-Fock[11] exchange with DFT[12] exchange-correlation, given by Becke's three parameter functional[13] with Perdew and Wang's 1991 gradient-corrected correlation functional.[14] The LanL2DZ basis set[15] augmented with a f-polarization function[16] was used for Rh, and a standard 6-31G(d,p)[17] for the remaining elements. A Natural Population Analysis (NPA)[18] and the resulting Wiberg indices[19] were used for a detailed study of the electronic structure and bonding of the optimised species. Orbital representations were obtained using the program MOLEKEL 4.0.[20]

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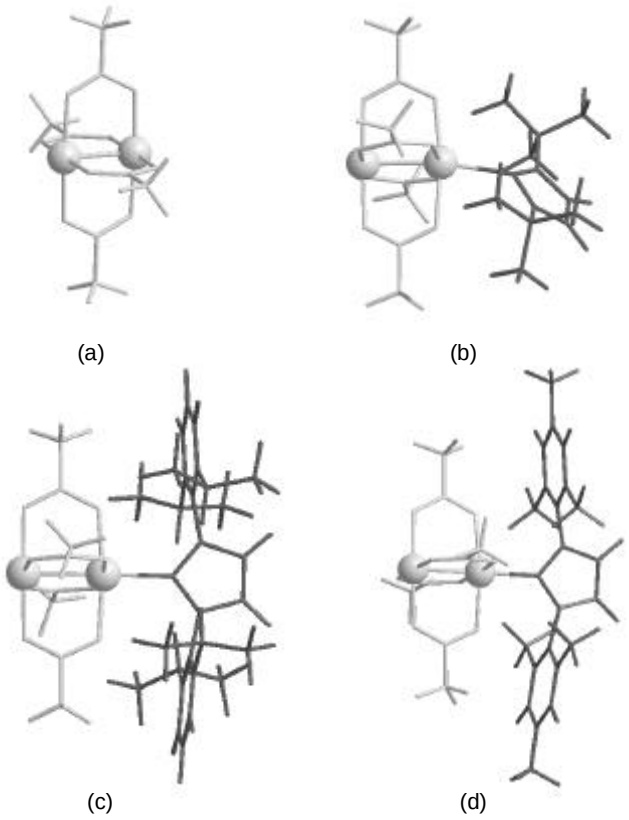

Figure S1. Optimized geometries (B3PW91) for $Rh_2(OAc)_4$ (a) and the three NHC complexes, $Rh_2(OAc)_4$(NHC), with NHC-**7** (b), NHC-**4** (c) and NHC-**6** (d). NHC are darkened.

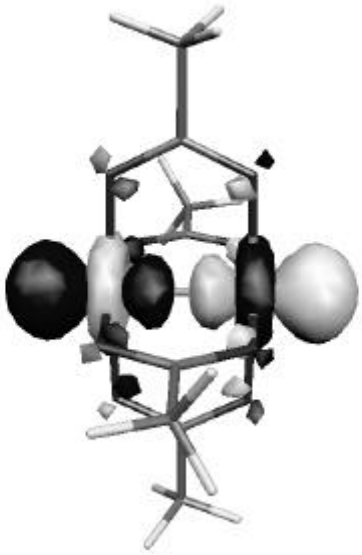

Figure S2. LUMO of $Rh_2(OAc)_4$.

4.1- X-ray Crystallography data for complexes 20 and 21.

Crystals of the complexes, suitable for X-ray diffraction study were mounted on a loop with protective oil. X-ray data was collected, for both, at 150K on a Bruker AXS-KAPPA APEX II diffractometer using graphite monochromated Mo-Kα radiation (λ=0.71069 Å) and operating at 50kV and 30 mA. Data was collected over the complete sphere by a combination of four sets, using omega scans of 0.5º per frame. The data was collected to a maximum 2θ value of 50.82º, 42.6º. Each frame exposure time was 10s. A total of 56487, 30833 oscillation images were collected. Cell parameters were retrieved using Bruker SMART[21] software and refined using Bruker SAINT[22] on all observed reflections. Absorption corrections were applied using SADABS[23]. Structure solution and refinement were performed using direct methods with program SIR97[24] and SHELXL97[25], both included in the package of programs WINGX-Version 1.70.01[26]. Non-hydrogen atoms were refined anisotropically. A full-matrix least-squares refinement was used for the non-hydrogen atoms with anisotropic thermal parameters All hydrogens were inserted in idealised positions and allowed to refine riding in the parent carbon atom. In both structures disordered solvent toluene molecules were found.

4.2- Selected bond lengths (Å)obtained for complexes 20 and 21.

	20	**21**
Rh(1)-O(5)	2.044(2)	2.030(5)
Rh(1)-O(1)	2.049(2)	2.044(5)
Rh(1)-O(8)	2.050(2)	2.030(5)
Rh(1)-O(4)	2.060(2)	2.037(5)
Rh(1)-C(9)	2.228(3)	2.243(7)
Rh-Rh	2.4731(3)	2.4627(12)
O(1)-C(7)	1.272(4)	1.249(9)
O(5)-C(1)	1.269(4)	1.272(9)
C(9)-N(2)	1.356(4)	1.325(9)
C(9)-N(1)	1.382(4)	1.334(9)
N(2)-C(11)	1.388(4)	1.486(10)
N(1)-C(10)	1.391(4)	1.469(10)
C(10)-C(11)	1.343(4)	1.495(12)
N(1)-C(12)	1.453(4)	1.435(10)
N(2)-C(24)	1.457(4)	1.439(10)

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Atomic Coordinates for all the optimized structures

NHC-4

C	-0.014081	0.056764	-0.286913
N	-0.270965	-0.520988	0.930166
N	-0.362015	1.361350	-0.045767
C	-0.808908	1.580714	1.254270
H	-1.116910	2.551880	1.609953
H	-1.009881	0.087608	2.882763
C	-0.753267	0.379463	1.876057
C	-0.055783	-1.911632	1.212871
H	4.268654	-0.851755	1.863021
H	3.915108	-2.582855	1.916905
C	1.111598	-2.294199	1.896188
H	3.402135	-1.622725	0.521090
H	1.413798	-0.970921	4.320835
H	3.100730	-0.477784	4.096291
H	2.688747	-2.191632	4.233439
H	2.177137	-3.974626	2.713077
C	1.283792	-3.651956	2.185113
C	0.337482	-4.592547	1.800583
H	0.490297	-5.643432	2.031220
H	-1.534075	-4.935775	0.813709
C	-0.804148	-4.190858	1.115293
H	1.868373	-0.306629	1.960771
C	-1.029736	-2.845825	0.811208
H	-4.397941	-2.748308	-0.074376
H	-3.702461	-3.140292	1.507618
H	-2.862450	-2.225738	-2.058599
H	-1.767136	-3.585858	-1.751949
H	-1.134374	-1.922817	-1.762926
C	-0.277061	2.401883	-1.030671
C	-1.442810	2.789542	-1.713913
H	-2.645643	1.339268	-0.726489
H	-2.222171	4.142210	-3.194287
H	-2.435217	-1.362897	0.238827
C	-1.336893	3.822844	-2.650894
H	-0.056123	5.238996	-3.637381
C	-0.118853	4.439896	-2.903618
H	-4.205945	0.875213	-2.575383
H	1.970341	4.517574	-2.432802
C	1.022463	4.032167	-2.221621
H	1.922758	2.044690	0.362723
H	-3.486832	-4.238845	0.135125
C	0.969804	3.011206	-1.268972
H	3.862820	1.144801	-0.911197
H	3.265357	1.933841	-2.382108
H	2.306389	0.646927	-1.614065
H	3.987817	3.309951	0.446054
H	2.641052	4.461272	0.413246
H	3.616365	4.179449	-1.037681
H	-2.527033	0.682340	-3.114340
H	-3.448696	2.121903	-3.574470
C	2.185495	-1.296902	2.300839
H	-4.782708	2.575480	-0.764744
C	2.354033	-1.231861	3.824885
H	-4.047130	3.887651	-1.692459
C	3.519268	-1.609144	1.608230
H	-3.514065	3.575188	-0.036466
C	-2.260091	-2.423240	0.025672
C	-1.987733	-2.546831	-1.481735
C	-3.527903	-3.184063	0.427764
C	-2.784752	2.111620	-1.488622
C	-3.267097	1.407244	-2.764319
C	-3.839686	3.095511	-0.964882
C	2.231597	2.545191	-0.561540
C	2.961309	1.501650	-1.421899
C	3.164952	3.694044	-0.165815

NHC-6

C	0.216470	0.197270	0.589811
N	-0.050755	-0.378460	1.804977
N	-0.157845	1.496039	0.819037
C	-0.631919	1.714063	2.110260
H	-0.959274	2.681643	2.458871
H	-0.839354	0.226204	3.741372
C	-0.566376	0.517167	2.738516
C	0.178749	-1.765078	2.079804
C	1.263221	-2.132225	2.887829
H	2.291366	-3.785607	3.786951
C	1.451717	-3.489553	3.161473
C	0.604097	-4.470371	2.646247
C	0.844555	-5.930307	2.927246
H	-1.128187	-4.816202	1.419490
C	-0.458577	-4.065474	1.834416
C	-0.691724	-2.722441	1.536983
C	-0.065621	2.523239	-0.174467
C	-1.237276	2.988851	-0.787889
H	-2.027457	4.368877	-2.225554
C	-1.124508	4.005186	-1.739258
C	0.203334	5.667123	-3.099659
C	0.110309	4.551772	-2.092087
H	2.229912	4.448069	-1.748044
C	1.256324	4.046667	-1.474342
C	1.194925	3.036298	-0.512988
C	2.216999	-1.101106	3.428308
C	-1.835910	-2.313465	0.651418
C	-2.578764	2.389814	-0.461446
C	2.446505	2.501576	0.126083
H	-0.095093	-6.465742	3.095757
H	1.476332	-6.070222	3.808862
H	1.346924	-6.416958	2.082428
H	1.150991	5.635745	-3.645232
H	0.141402	6.647319	-2.610877
H	-0.609685	5.616402	-3.829849
H	3.099952	-1.579423	3.859611
H	1.757562	-0.484102	4.208601
H	2.543741	-0.420280	2.636462
H	-2.396279	-3.187393	0.309802
H	-1.466255	-1.764119	-0.219788
H	-2.529299	-1.647541	1.177558
H	-3.340361	2.743542	-1.160909
H	-2.910253	2.646965	0.550748
H	-2.540561	1.297412	-0.514647
H	3.332391	2.999497	-0.276030
H	2.533155	1.424543	-0.046661
H	2.435203	2.650789	1.211802

NHC-7

C	-0.306518	0.393955	0.168470
C	-1.109743	1.801209	-2.075500
N	0.284809	0.076979	-1.021959
C	1.222426	-1.298317	0.406816
N	0.296186	-0.474801	1.033990
C	-0.516611	-0.295270	-3.309513
C	1.216349	-0.946297	-0.900536
C	1.253521	1.433731	-2.819410
C	-0.021408	0.752195	-2.302357
C	-1.037196	0.527658	2.835444
C	1.279131	-0.313968	3.275807
C	-0.012049	-0.548710	2.479255
H	1.803344	-2.052796	0.915179
C	-0.589822	-1.936782	2.790545
H	1.792309	-1.341273	-1.723567
H	-1.326862	2.296057	-3.028114
H	-0.791254	2.547678	-1.345595
H	-2.024115	1.343988	-1.692209
H	0.243423	-1.056117	-3.513491
H	-0.769726	0.184766	-4.260026
H	-1.409965	-0.798558	-2.928163
H	2.055179	0.710854	-3.001571
H	1.614832	2.168003	-2.093373
H	1.050662	1.950993	-3.762485
H	-1.261628	0.461374	3.905390
H	-1.958891	0.398783	2.265258
H	-0.655075	1.525544	2.610791
H	1.069779	-0.343250	4.349647
H	1.704995	0.664175	3.033592
H	2.034386	-1.077296	3.063654
H	-0.839874	-2.013587	3.853396
H	0.122544	-2.734333	2.556328
H	-1.499343	-2.110390	2.207912

$Rh_2(OAc)_4$

Rh	1.025225	-0.197066	0.550788
Rh	-1.025231	0.197066	-0.550788
O	0.940526	1.707212	1.282498
C	-0.051732	2.434419	0.963618
O	-0.940532	-1.707212	-1.282498
C	0.051726	-2.434419	-0.963619
O	1.022883	-2.082531	-0.224268
C	-0.070564	3.835203	1.514852
O	-1.022889	2.082531	0.224268
C	0.070558	-3.835203	-1.514851
O	-0.030234	-0.856660	2.169290
O	0.030227	0.856661	-2.169290
H	-0.950902	4.374425	1.166132
O	1.993889	0.480899	-1.111197
O	-1.993896	-0.480900	1.111197
H	0.837797	4.358214	1.203760
C	1.299664	0.854466	-2.107344
C	-1.299670	-0.854466	2.107344
C	2.040129	1.336436	-3.326104
C	-2.040136	-1.336436	3.326104
H	-0.065623	3.794056	2.607542
H	0.950895	-4.374424	-1.166132
H	0.065614	-3.794057	-2.607541
H	-0.837803	-4.358214	-1.203758
H	3.116636	1.301313	-3.160763
H	1.729411	2.358395	-3.559377
H	1.772927	0.710484	-4.181998
H	-3.116643	-1.301313	3.160762
H	-1.772934	-0.710484	4.181998
H	-1.729418	-2.358396	3.559377

$Rh_2(OAc)_4$(NHC-4)

Rh	1.328670	-1.782198	-3.231180
Rh	0.311407	-0.761873	-1.264316
C	-0.522211	0.120474	0.489629
N	-0.797259	-0.476917	1.693083
O	0.225757	-2.670132	-0.487111
O	1.410512	0.062261	-4.101039
H	0.974166	3.203358	-3.441725
N	-0.842953	1.433384	0.716638
H	0.047663	2.463699	-4.756988
O	0.485462	1.032684	-2.272664
C	-1.297682	1.637096	2.010905
O	1.207057	-3.600379	-2.305949
H	-1.595459	2.613034	2.358615
H	-1.542323	0.134482	3.622972
O	-1.519978	-1.083498	-2.165042
C	-1.269910	0.435963	2.624414
O	3.159199	-1.454210	-2.368656
H	1.814327	2.445294	-4.841044
O	2.224495	-0.512973	-0.527724
O	-0.560394	-2.045465	-3.982983
C	0.961674	1.050964	-3.453871
C	0.680092	-3.652739	-1.158795
C	-0.699964	-1.859767	2.097970
H	1.313485	-5.686256	-0.919253
H	-0.434976	-5.430970	-0.793514
H	3.829777	-1.438320	2.536003
H	3.216736	-2.961656	3.178118
C	0.469785	-2.291584	2.745917
H	2.905594	-2.525509	1.485450
H	0.914766	-0.275852	4.610733
H	2.673895	-0.202092	4.430092
H	1.907391	-1.669596	5.058532
H	1.356345	-3.943489	3.797420
C	0.470594	-3.583011	3.282423
H	0.599134	-4.945677	0.556818
C	-0.643123	-4.408867	3.176680
H	-0.623380	-5.405946	3.608763
H	-2.922786	-1.644319	-4.947622
H	-2.645781	-4.609899	2.433643
C	-1.780506	-3.958240	2.517288
H	-3.691496	-1.381439	-3.349270
H	1.585374	-0.560718	2.214751
C	-1.836469	-2.675098	1.965286
H	-3.123901	-2.997353	-3.835855
H	-5.157703	-1.680440	1.764151
H	-4.006910	-1.342631	3.067711
H	-4.377857	-2.761634	-0.397682
H	-3.738279	-4.154064	0.481217
H	-2.678649	-3.224479	-0.601526
C	0.544320	-5.017646	-0.529919
C	0.963003	2.384194	-4.160939
H	4.554582	-0.005018	0.198120
C	-0.790926	2.570692	-0.170767
H	5.244517	-0.256944	-1.436485
C	-1.952362	2.916822	-0.881507
H	5.012614	-1.633409	-0.359465
H	-2.974766	1.118013	-0.378192
H	-2.817646	4.411344	-2.162680
H	-2.906440	-1.231319	0.824459
C	-1.933338	4.112448	-1.607001
H	-0.820689	5.861975	-2.175708
C	-0.810420	4.930606	-1.615635
H	-4.593519	1.088134	-2.205847
H	1.198145	5.206751	-0.915312
C	0.325709	4.559413	-0.904493
H	1.513091	1.964781	0.940264
H	-4.512693	-3.005275	2.743083
C	0.363929	3.371467	-0.168730
H	3.743612	2.737320	0.328348
C	3.212530	-0.894543	-1.237780
C	-1.551985	-1.658294	-3.302379
C	-2.917453	-1.923865	-3.891638
C	4.591832	-0.670267	-0.664167
H	3.089296	4.099957	-0.579932
H	2.776194	2.439533	-1.126636
H	2.636513	3.600365	2.445457
H	0.878418	3.791186	2.526562
H	1.849787	4.942181	1.599508
H	-2.948523	1.250056	-2.846063
H	-4.037600	2.652861	-2.801777
C	1.694658	-1.404988	2.901290
H	-5.209187	2.128678	0.024873
C	1.800212	-0.855803	4.332392
H	-4.595338	3.720250	-0.449125
C	2.983645	-2.132249	2.501474
H	-3.980232	2.936051	1.011341
C	-3.105247	-2.210396	1.270089
C	-3.494154	-3.148679	0.120669
C	-4.259327	-2.049542	2.270761
C	-3.216844	2.073355	-0.852775
C	-3.724020	1.751835	-2.263518
C	-4.311046	2.754579	-0.016267
C	1.612121	3.005149	0.617475
C	2.876301	3.078331	-0.246637
C	1.749016	3.884907	1.869593

$Rh_2(OAc)_4$(NHC-6)

Rh	0.621978	-2.042653	-3.178501
Rh	-0.353028	-1.004326	-1.199147
C	-1.184668	-0.118655	0.544411
N	-1.452293	-0.707679	1.750226
O	-0.567796	-2.920051	-0.471801
O	0.817234	-0.188658	-4.009619
H	0.840679	2.922888	-3.231831
N	-1.561246	1.180957	0.740685
H	-0.371490	2.444039	-4.420535
O	-0.035823	0.796789	-2.154586
C	-2.045350	1.388706	2.024638
O	0.396860	-3.866879	-2.290693
H	-2.386507	2.358680	2.350151
H	-2.245689	-0.095899	3.661563
O	-2.191871	-1.193448	-2.120126
C	-1.976844	0.199952	2.659833
O	2.461246	-1.829976	-2.291799
H	1.342353	2.133552	-4.769073
O	1.562304	-0.882729	-0.436945
O	-1.279024	-2.189959	-3.942625
C	0.455943	0.813176	-3.328479
C	-0.153241	-3.911841	-1.154029
C	-1.277345	-2.075063	2.166495
H	0.057759	-6.047434	-1.190679
H	-1.407336	-5.449396	-0.357246
C	-0.080993	-2.444400	2.789478
H	0.935994	-4.049370	3.783570
C	0.012145	-3.744438	3.296336

H	0.155131	-5.305107	0.437635
C	-1.045053	-4.651138	3.205225
C	-0.936751	-6.032284	3.796931
H	-3.838705	-0.854197	-4.388697
H	-3.050444	-4.935752	2.476640
C	-2.219443	-4.239030	2.567745
H	-4.380696	-1.990055	-3.145894
C	-2.358605	-2.956744	2.037428
H	-3.640470	-2.595266	-4.664828
C	-0.342757	-5.274547	-0.534634
C	0.591474	2.167970	-3.978836
H	3.976755	-0.351780	0.131746
C	-1.504909	2.297645	-0.165567
H	4.671377	-1.196480	-1.291491
C	-2.623646	2.584685	-0.953876
H	4.072907	-2.119526	0.097698
H	-3.454916	3.991974	-2.341808
C	-2.592772	3.751624	-1.723197
C	-1.509984	5.896319	-2.504182
C	-1.498835	4.617896	-1.707611
H	0.468434	4.942357	-0.895404
C	-0.398014	4.283950	-0.912251
C	-0.375769	3.126509	-0.134159
C	2.534381	-1.316165	-1.141760
C	-2.248459	-1.736340	-3.273708
C	-3.617892	-1.812224	-3.906208
C	3.905632	-1.227607	-0.515419
C	1.070769	-1.484518	2.902779
C	-3.613801	-2.544779	1.319968
C	-3.814827	1.667451	-0.981405
C	0.829834	2.762622	0.686813
H	-1.378151	-6.786307	3.137467
H	-1.465550	-6.093245	4.755944
H	0.105127	-6.310374	3.978602
H	-0.541395	6.081795	-2.979164
H	-1.724037	6.758764	-1.861039
H	-2.272563	5.874280	-3.287579
H	1.904455	-1.944712	3.439611
H	0.785833	-0.574374	3.442842
H	1.418788	-1.179692	1.909904
H	-4.351002	-3.351605	1.334561
H	-3.392681	-2.295063	0.276912
H	-4.073329	-1.660190	1.774930
H	-4.601680	2.075760	-1.621014
H	-4.236819	1.524150	0.019851
H	-3.532850	0.679321	-1.360827
H	1.602608	3.531035	0.602717
H	1.248377	1.809265	0.347251
H	0.581774	2.648245	1.747988

$Rh_2(OAc)_4$(NHC-7)

Rh	0.345938	-1.007589	-0.065139
Rh	-1.984723	-0.321616	0.120699
C	2.397231	-2.062032	-0.343901
O	-0.222134	-2.750366	0.903212
C	2.359655	-0.338802	-2.830908
N	2.905241	-2.438763	-1.571165
C	3.570166	-4.011944	-0.193420
N	2.883082	-3.036497	0.505247
O	-2.382399	-2.087897	1.065981
C	2.344580	-2.557648	-3.967980
O	0.652259	0.846883	-0.938688
C	3.583671	-3.640390	-1.484865
C	4.508294	-1.511355	-3.175464
O	-1.534562	1.425738	-0.824106
C	3.009668	-1.707983	-2.877497
C	2.297700	-1.927885	2.676459
O	0.631359	0.089251	1.672516
C	4.449183	-3.108991	2.388748
C	2.958170	-3.113840	2.001565
O	-1.567388	0.581720	1.898142
H	4.003110	-4.878225	0.277447
C	2.280496	-4.411520	2.459965
O	-0.206452	-1.947954	-1.829210
H	4.030223	-4.126463	-2.335660
H	-2.863005	-4.310081	2.035022
O	-2.351914	-1.238446	-1.667198
C	-1.440863	-2.911974	1.238366
H	-1.313706	-4.238677	2.911031
C	-1.783116	-4.213645	1.922657
H	-1.386659	-5.053040	1.345923
H	-0.888423	3.573576	-1.873064
H	0.533117	2.836889	-2.672060
H	0.699507	3.521163	-1.056587
C	-0.321102	1.644500	-1.111347
H	-0.904334	1.978555	3.843098
C	0.015632	2.984226	-1.720329
H	0.824392	2.032867	3.371422
H	0.213846	0.676297	4.319476
H	-2.807288	-2.534249	-3.721978
H	-1.381486	-3.593129	-3.496692
C	-0.355475	0.630797	2.260792
H	-1.211088	-2.060790	-4.356822
C	-0.043430	1.388247	3.528890
C	-1.410709	-1.859339	-2.236201
C	-1.733849	-2.559194	-3.534603
H	2.600321	0.184186	-3.762498
H	2.723450	0.257229	-1.993460
H	1.279744	-0.417115	-2.744869
H	2.845549	-3.519775	-4.114851
H	2.378445	-2.020571	-4.921107
H	1.302509	-2.741233	-3.700154
H	5.052004	-2.454155	-3.279164
H	4.982808	-0.927490	-2.380773
H	4.618586	-0.962120	-4.115379
H	2.515841	-1.979324	3.748254
H	1.220529	-1.945919	2.538242
H	2.672197	-0.979919	2.289184
H	4.537699	-3.151320	3.478552
H	4.931092	-2.189560	2.042418
H	5.001083	-3.959815	1.980282
H	2.291478	-4.462878	3.553241
H	2.787311	-5.305870	2.084030
H	1.245340	-4.422235	2.114277