

Supporting Information

Cationic Rhodium-BINAP complexes: full characterization of solvate- and arene bridged dimeric species.

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1. NMR data of complexes

Table S1. ^{31}P NMR data of rhodium/BINAP solvate complexes $[\text{Rh}(\text{BINAP})(\text{solvent})]\text{BF}_4$.

Solvent	$\delta^{31}\text{P}$ [ppm]	$J_{\text{P-Rh}}$ [Hz]	$\delta^{103}\text{Rh}$ [ppm]
MeOH-d ₄ ^[1]	54.4	205.8	327
THF-d ₈	54.1	206.0	350
acetone-d ₆	52.4	200.9	365
EtOH (non-deuterated)	55.1	205.8	n.d.
<i>i</i> -PrOH-d ₈	53.2	206.0	n.d.
propylene carbonate (non-deuterated)	54.5	215.7	n.d.

^[1] In contrast to Noyori's results, (cp. ref [12a] in the main manuscript) in our case only one species is observed in the ^{31}P and ^1H NMR spectra, vide infra.

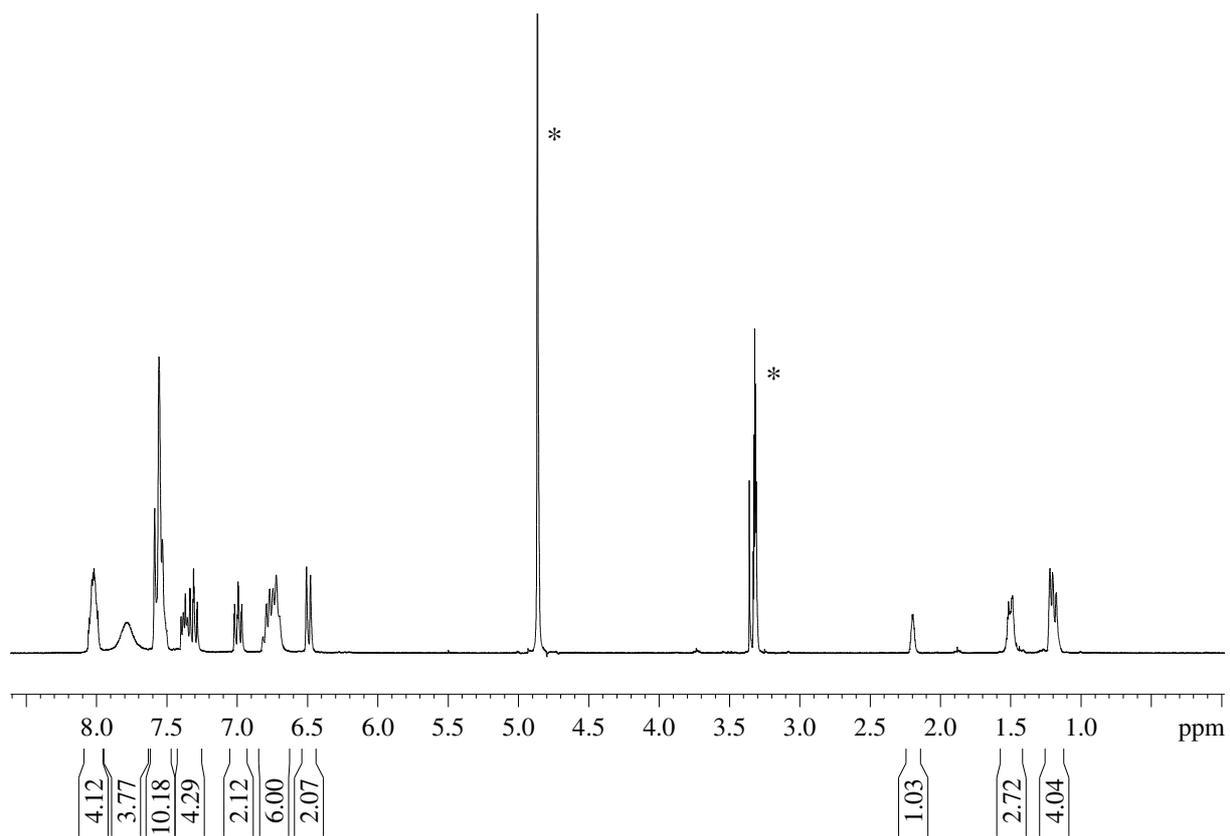


Figure S1: ^1H NMR of $[\text{Rh}(\text{BINAP})(\text{MeOH})_2]\text{BF}_4$ in MeOH-d_4 (solvent peaks are highlighted with an asterisk), prepared by hydrogenation of $[\text{Rh}(\text{BINAP})(\text{nbd})]\text{BF}_4$.

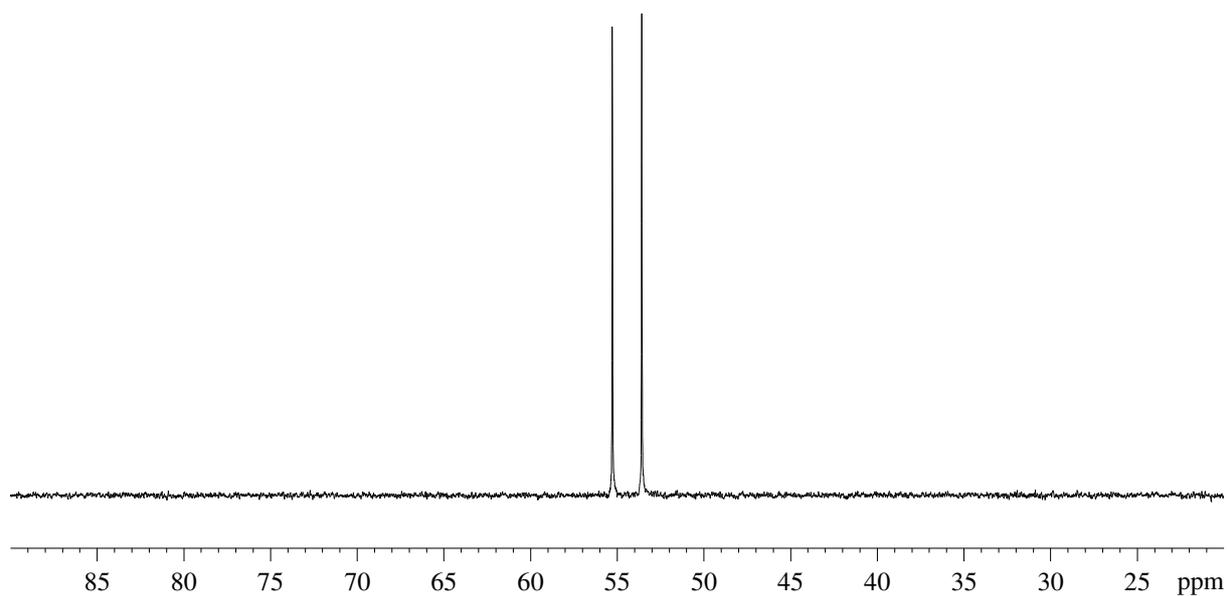


Figure S2: ^{31}P NMR of $[\text{Rh}(\text{BINAP})(\text{MeOH})_2]\text{BF}_4$ in MeOH-d_4 .

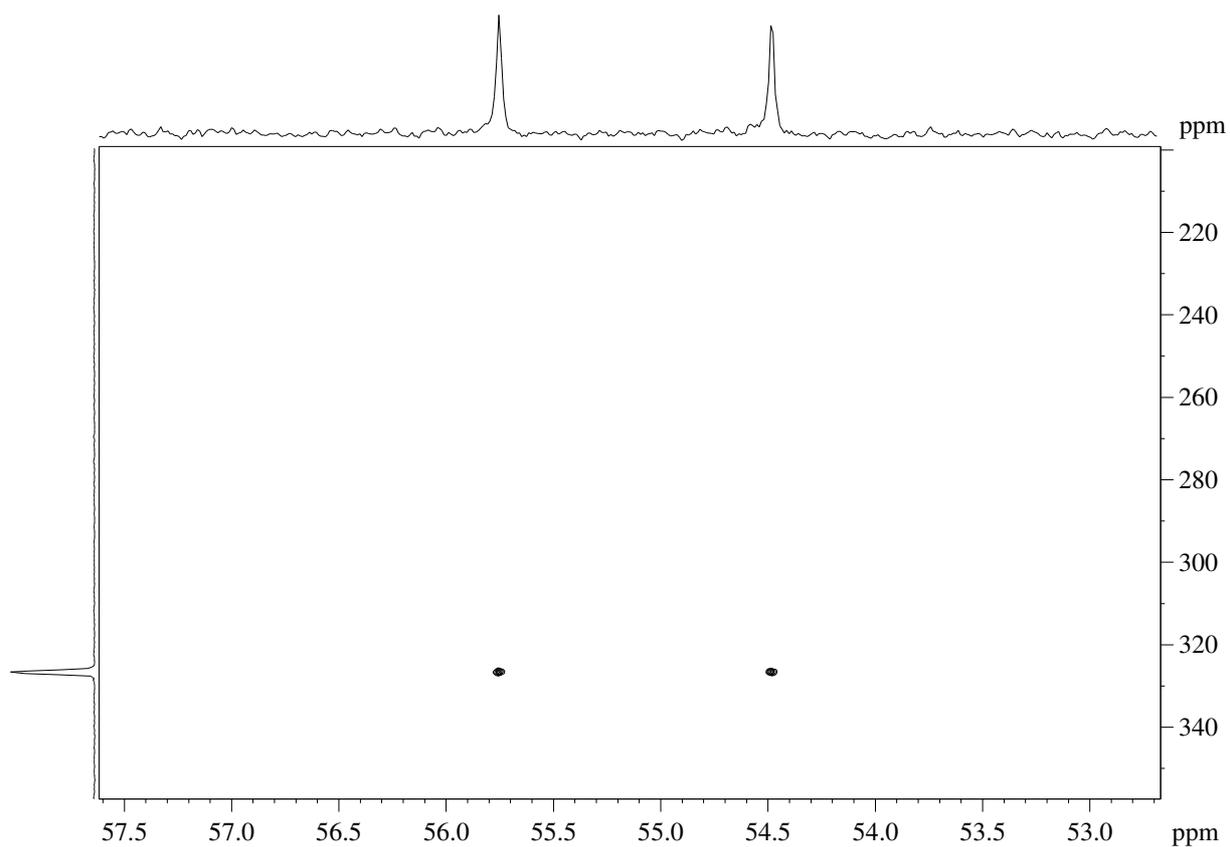


Figure S3: ^{31}P - $^{103}\text{Rh}\{^1\text{H}\}$ HMQC NMR (162 MHz) of $[\text{Rh}(\text{BINAP})(\text{MeOH})_2]\text{BF}_4$ in MeOH-d_4 . $\delta(^{31}\text{P})$ 55.1 ppm, $\delta(^{103}\text{Rh})$ 327 ppm ($\Xi = 3.161033$ MHz).

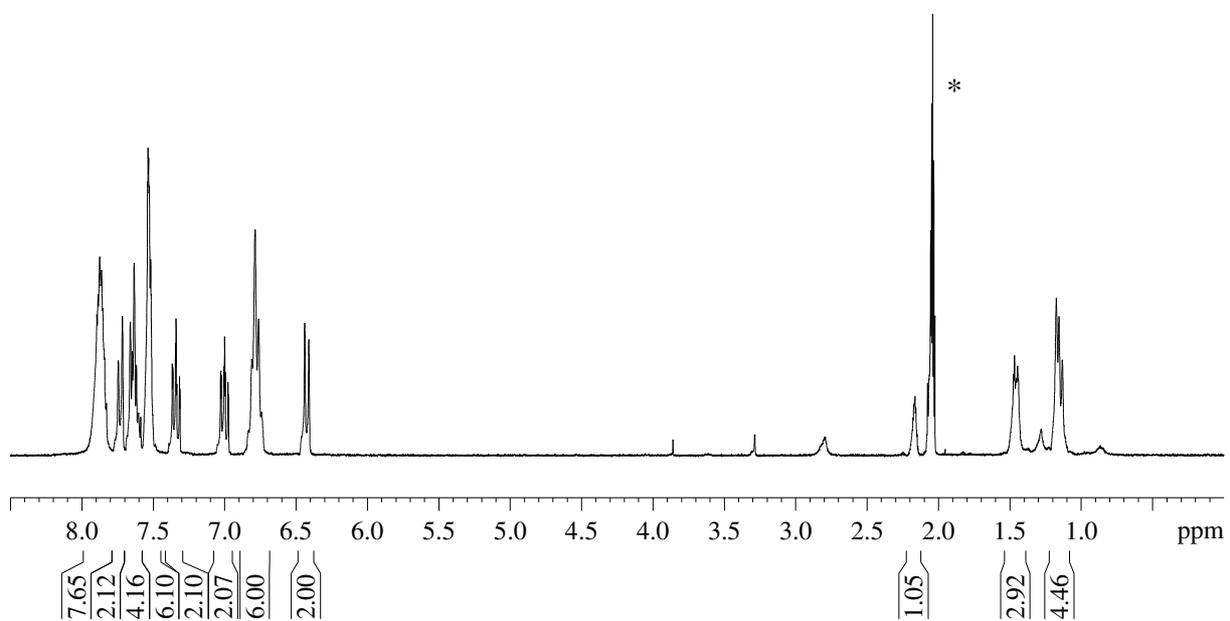


Figure S4: ^1H NMR of $[\text{Rh}(\text{BINAP})(\text{acetone})_2]\text{BF}_4$ in acetone-d_6 (solvent peaks are highlighted with an asterisk).

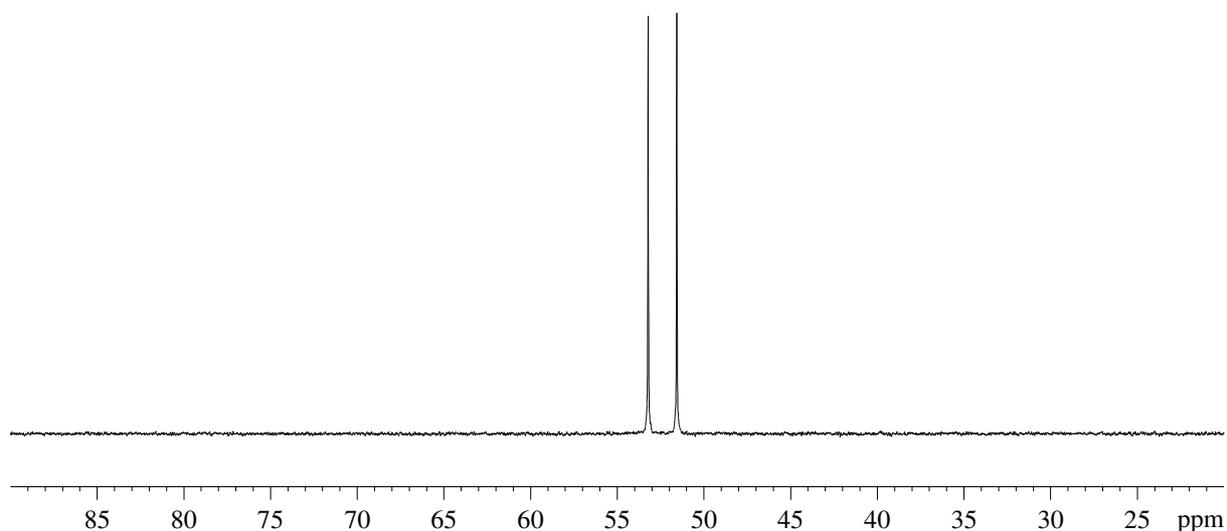


Figure S5: ^{31}P NMR of $[\text{Rh}(\text{BINAP})(\text{acetone})_2]\text{BF}_4$ in acetone- d_6 .

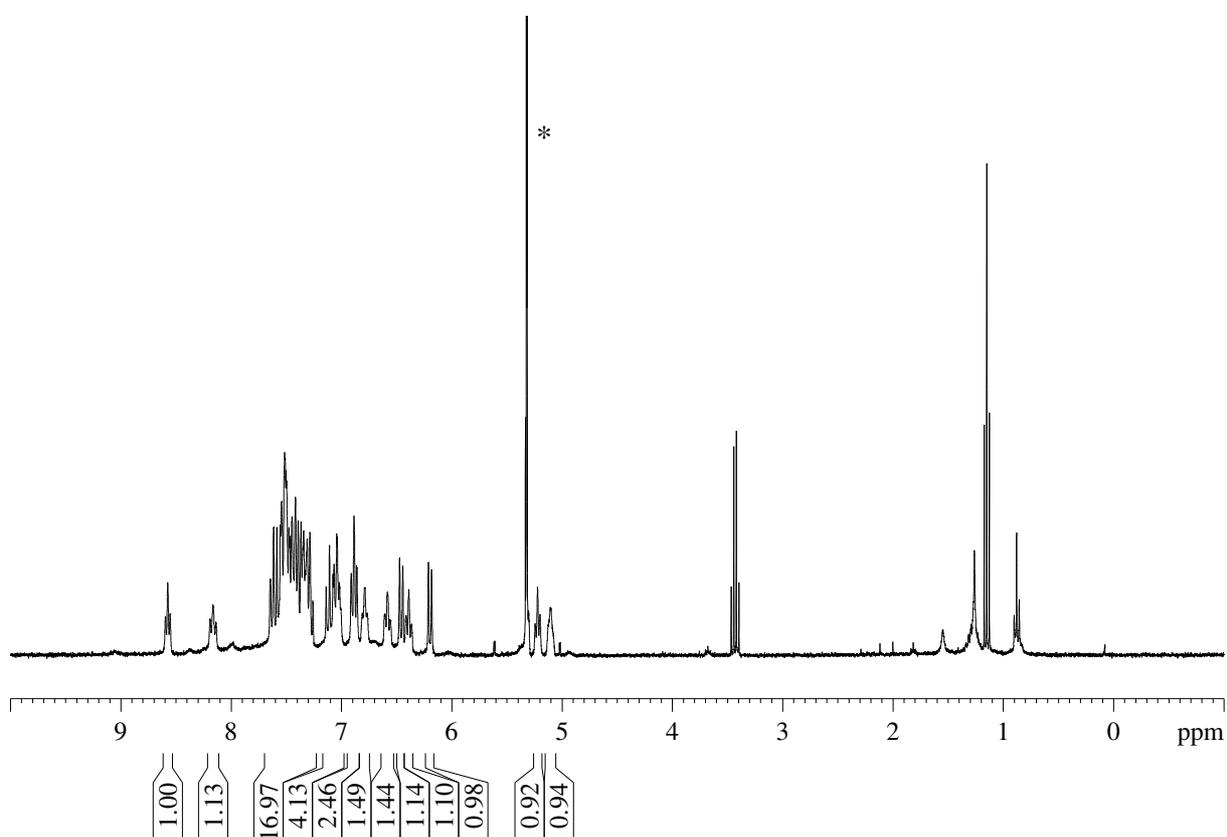


Figure S6: ^1H NMR of $[\text{Rh}(\text{BINAP})]_2(\text{BF}_4)_2$ in CD_2Cl_2 . (The signals at 1.2 and 3.4 ppm are assigned to residual diethyl ether remaining after crystal washing.) Signals of the minor diastereomer are mostly overlapped by signals of the major diastereomer (solvent peaks are highlighted with an asterisk).

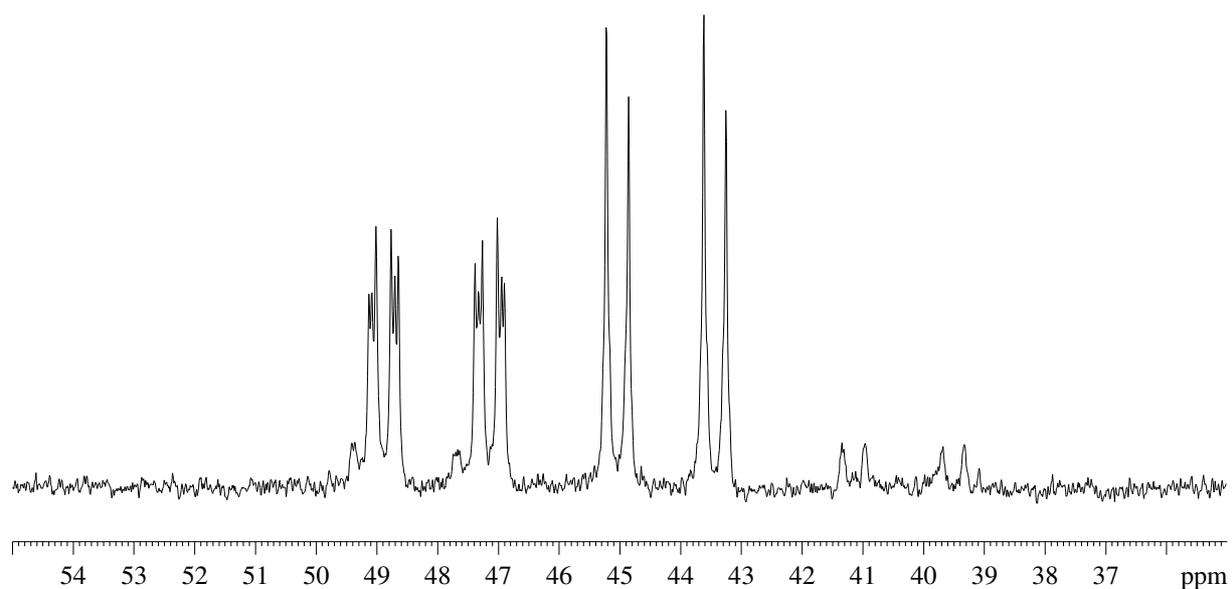


Figure S7: ^{31}P NMR of $[\text{Rh}(\text{BINAP})]_2(\text{BF}_4)_2$ in CD_2Cl_2 . The 2nd signal set of the minor diastereomer lies under the left signal set of the major diastereomer.

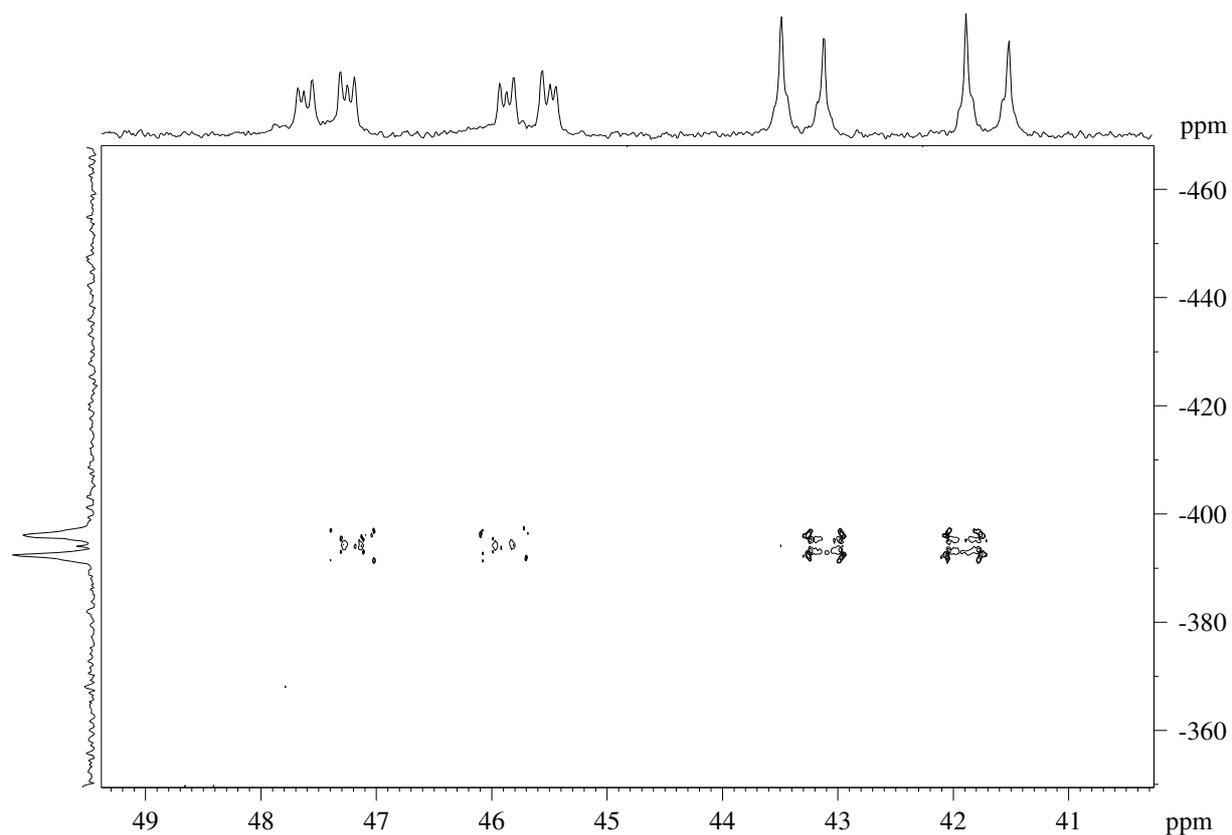


Figure S8: ^{31}P - $^{103}\text{Rh}\{^1\text{H}\}$ HMQC NMR of $[\text{Rh}(\text{BINAP})]_2(\text{BF}_4)_2$ in CD_2Cl_2 . $\delta(^{31}\text{P})$ 42.5 and 46.6 ppm, $\delta(^{103}\text{Rh})$ -394 ppm ($\Xi = 3.158755$ MHz). The minor diastereomer could not be detected.

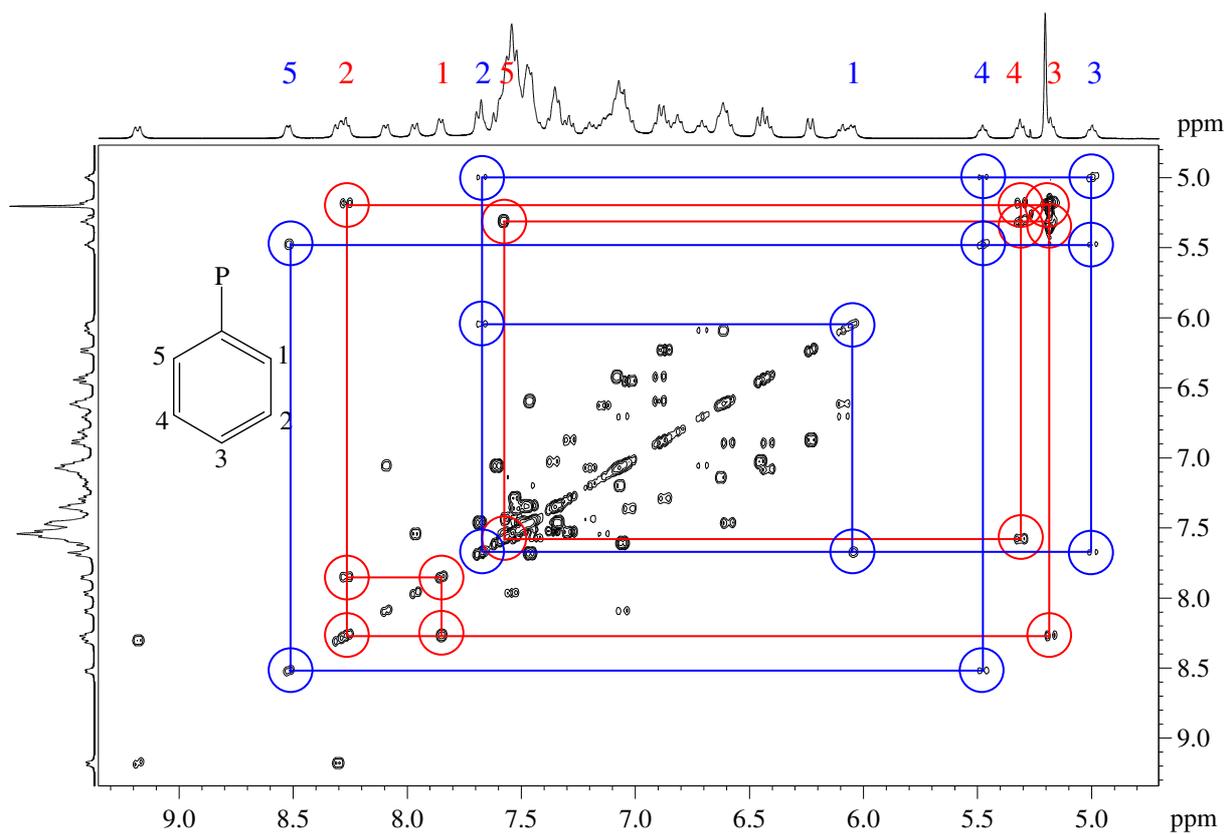


Figure S9: Detail of the ^1H ^1H COSY NMR spectrum of **4** in $\text{CF}_3\text{CD}_2\text{OD}$. The protons of the arene bridge of the more abundant diastereomer (red) and its diastereomer in slightly lower concentration (blue) are encircled.

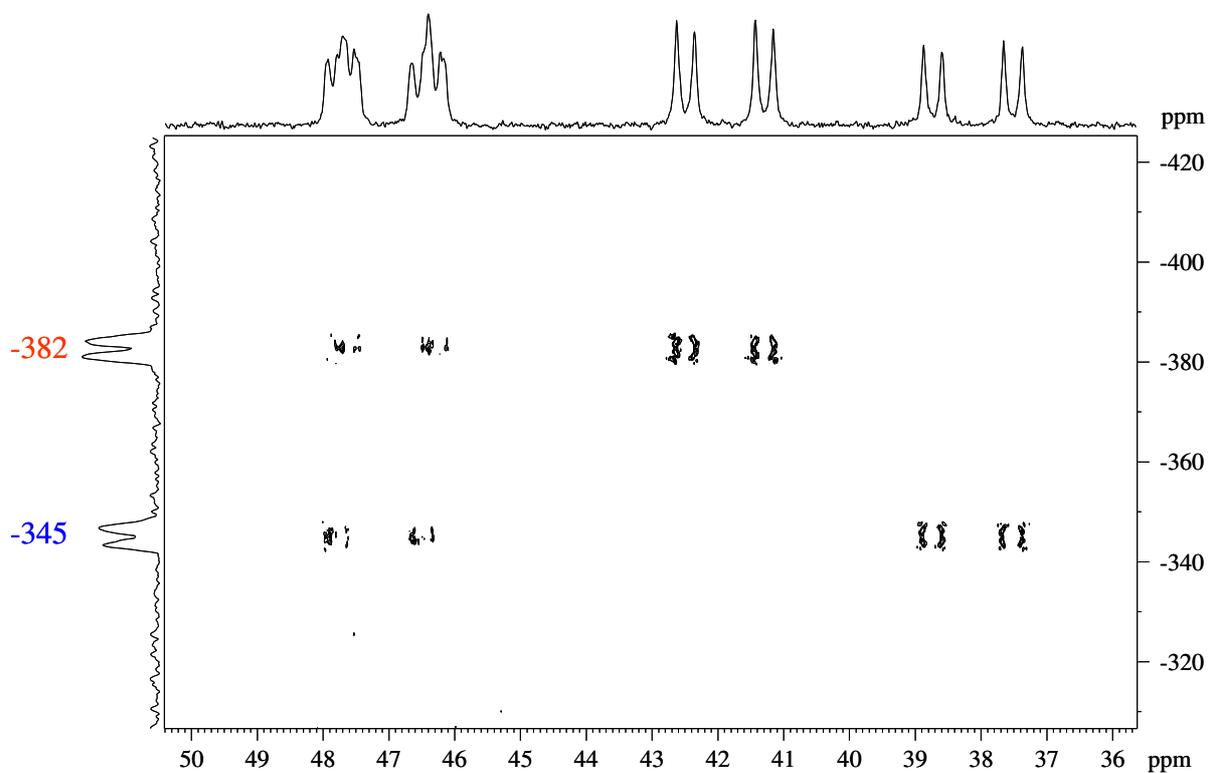


Figure S10: ^{31}P - $^{103}\text{Rh}\{^1\text{H}\}$ HMQC NMR of $[\text{Rh}(\text{BINAP})]_2(\text{BF}_4)_2$ in $\text{CF}_3\text{CD}_2\text{OD}$. Ξ frequencies are 3.158791 MHz (red) and 3.158910 MHz (blue).

2. Crystallographic data

Table S2: Crystallographic and refinement data for [Rh((*S*)-BINAP)(MeOH)₂BF₄ * 5MeOH, [Rh((*S*)-BINAP)(THF)₂BF₄ * thf, [Rh((*R*)-BINAP)(Aceton)₂BF₄ * ½ acetone * ½ diethylether and [Rh((*R*)-BINAP)]₂(BF₄)₂.

Compound	[Rh((<i>S</i>)-BINAP)(MeOH) ₂ BF ₄ * 5MeOH	[Rh((<i>S</i>)-BINAP)(THF) ₂ BF ₄ * thf
Empirical formula	C ₅₁ H ₆₀ BF ₄ O ₇ P ₂ Rh	C ₅₆ H ₅₈ O ₃ BF ₄ P ₂ Rh
Formula weight	1036.65	1030.68
Crystal system	orthorhombic	orthorhombic
Space group	P2 ₁ 2 ₁ 2 ₁	P2 ₁ 2 ₁ 2 ₁
a [Å]	12.351 (1)	11.918 (2)
b [Å]	13.064 (1)	15.845 (3)
c [Å]	31.480 (1)	26.245 (5)
α [°]	90	90
β [°]	90	90
γ [°]	90	90
V [Å ³]	5079.3 (2)	4956.1 (17)
d _c [Mg/m ³]	1.356	1.381
Z	4	4
μ [mm ⁻¹]	0.46	0.47
F(000)	2152	2136
Crystal size [mm]	0.5 x 0.5 x 0.5	0.3 x 0.3 x 0.3
Temperature [K]	200	200
Scan range (2θ) [°]	3.54 – 52.00	3.00 – 51.22
Index range (hkl)	-15/15, -16/16, -38/38	-14/14, -19/19, -31/31
Reflection collected	69847	68593
Independent reflections	9367	7951
Observed reflections	9957	9318
parameters	633	608
R1 (int)	0.0486	0.0428
R1 (2σ(I))	0.0255	0.0279
R1 (all data)	0.0279	0.0350
wR2 (all data)	0.0661	0.0588
Goodness of fit	1.026	0.862
Flack parameter	-0.02(2)	-0.02(2)
Largest difference peak and hole (e/ Å)	0.49/-0.29	0.37/-0.30

Compound	[Rh((<i>R</i>)-BINAP)(acetone) ₂] ₂ BF ₄ * ½ acetone * ½ diethylether	[Rh((<i>R</i>)-BINAP)] ₂ (BF ₄) ₂
Empirical formula	C _{53.5} H ₅₂ O ₃ BF ₄ P ₂ Rh	C ₈₈ H ₆₄ B ₂ F ₈ P ₄ Rh ₂
Formula weight	994.61	1624.71
Crystal system	orthorhombic	monoclinic
Space group	P2 ₁ 2 ₁ 2 ₁	C2
a [Å]	11.971 (1)	29.101 (6)
b [Å]	13.627 (1)	13.173 (3)
c [Å]	33.278 (1)	21.516 (4)
α [°]	90	90
β [°]	90	93.70 (3)
γ [°]	90	90
V [Å ³]	5428.4 (2)	8231 (3)
d _c [Mg/m ³]	1.217	1.311
Z	4	4
μ [mm ⁻¹]	0.43	0.54
F(000)	2052	3296
Crystal size [mm]	0.5 x 0.4 x 0.3	0.5 x 0.25 x 0.08
Temperature [K]	200	200
Scan range (2θ) [°]	3.62 – 50.00	2.80 – 49.50
Index range (hkl)	-14/14, -16/16, -39/39	-34/34, -15/14, -25/25
Reflection collected	70182	46285
Independent reflections	8050	6576
Observed reflections	9541	13581
parameters	565	937
R1 (int)	0.0501	0.1526
R1 (2σ(I))	0.0503	0.0460
R1 (all data)	0.0576	0.0992
wR2 (all data)	0.1337	0.0873
Goodness of fit	1.087	0.678
Flack parameter	-0.01(3)	-0.04 (3)
Largest difference peak and hole (e/ Å)	1.64/-0.74	0.40/-0.62