Supporting Information for:

A Pentacoordinated Norbornenyl-Acyl-Rhodium(III) Complex as a Likely Intermediate in the Catalytic Hydroacylation of Norbornadiene

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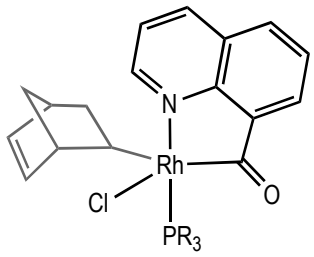
Characterization of New Compounds

Compound 1



R = (*p*-F-C_6H_4)

^{1}H NMR ($CDCl_3$)

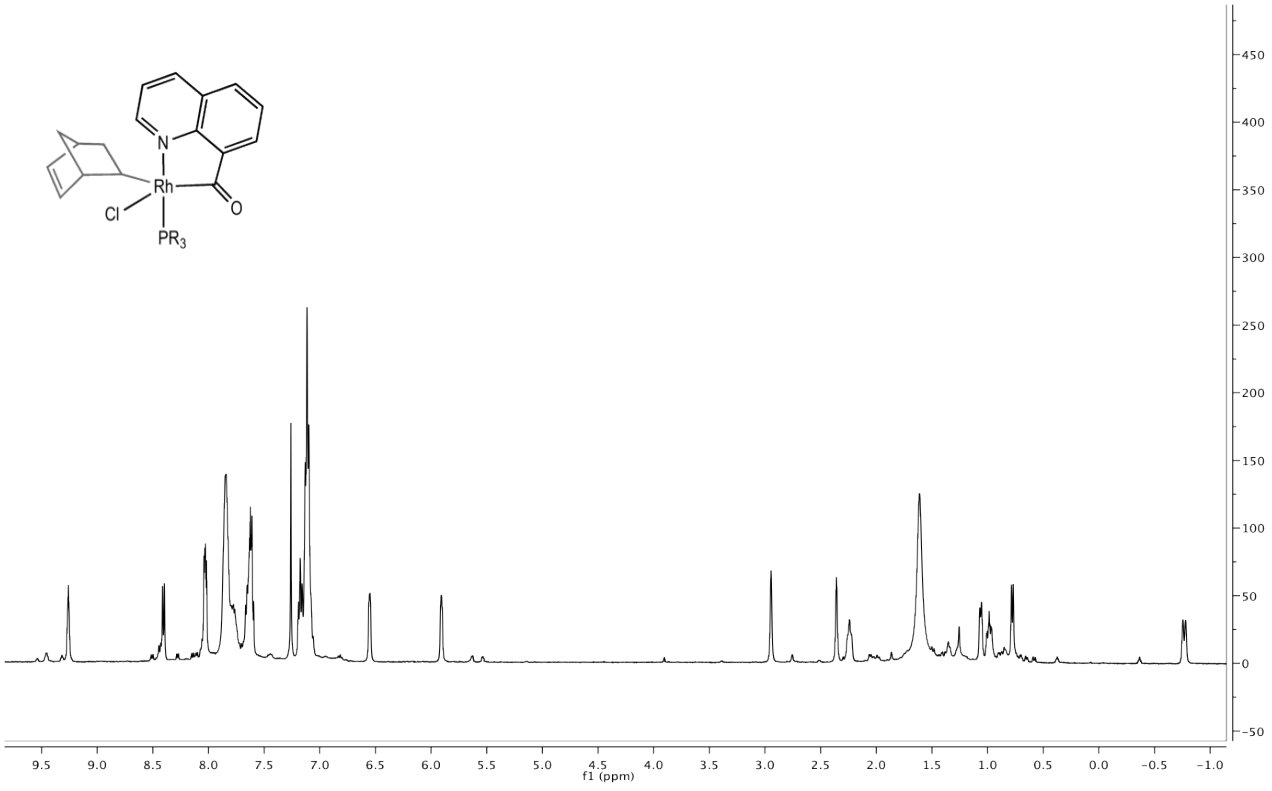


Figure S.1. ^{1}H NMR spectra of **1**.

$^{31}P\{^{1}H\}$ NMR ($CDCl_3$)

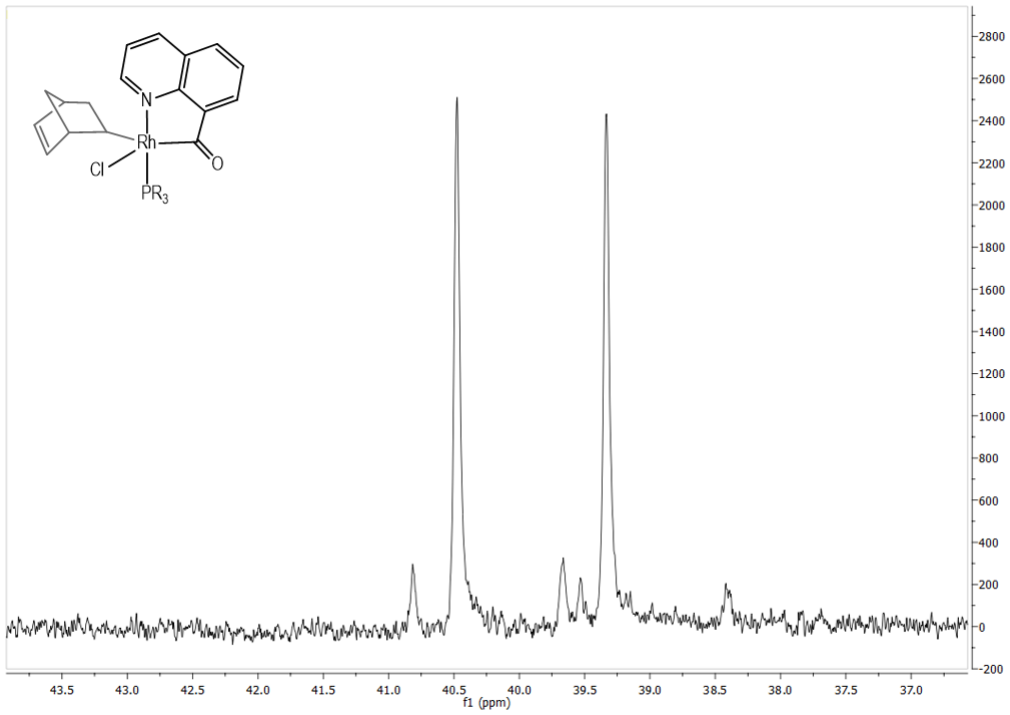


Figure S.2. $^{31}P\{^{1}H\}$ NMR spectra of **1**.

ESI-MS (MeOH) : $[M\text{-}Cl]^+$

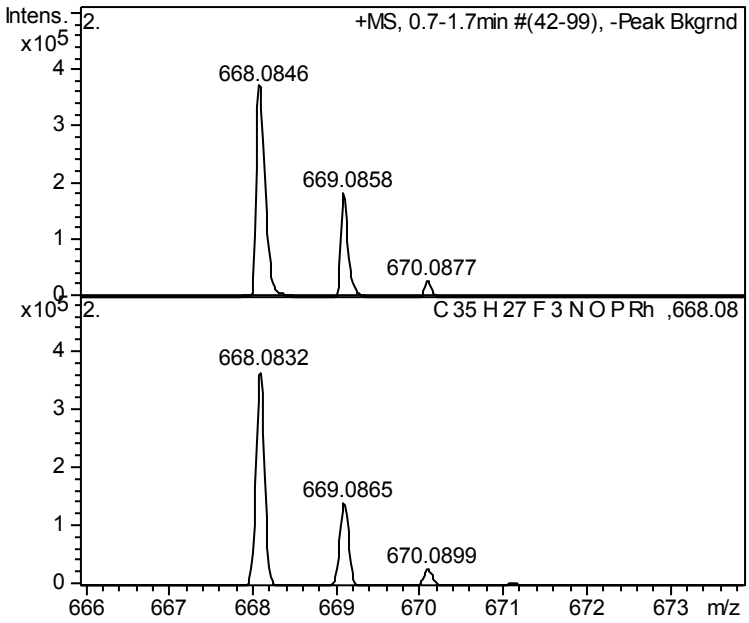
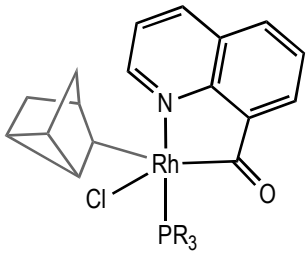


Figure S.3. ESI-MS of **1**. Found (top). Simulated (bottom).

Compound 2



R = (*p*-F-C_6H_4)

^{1}H NMR (CD_2Cl_2)

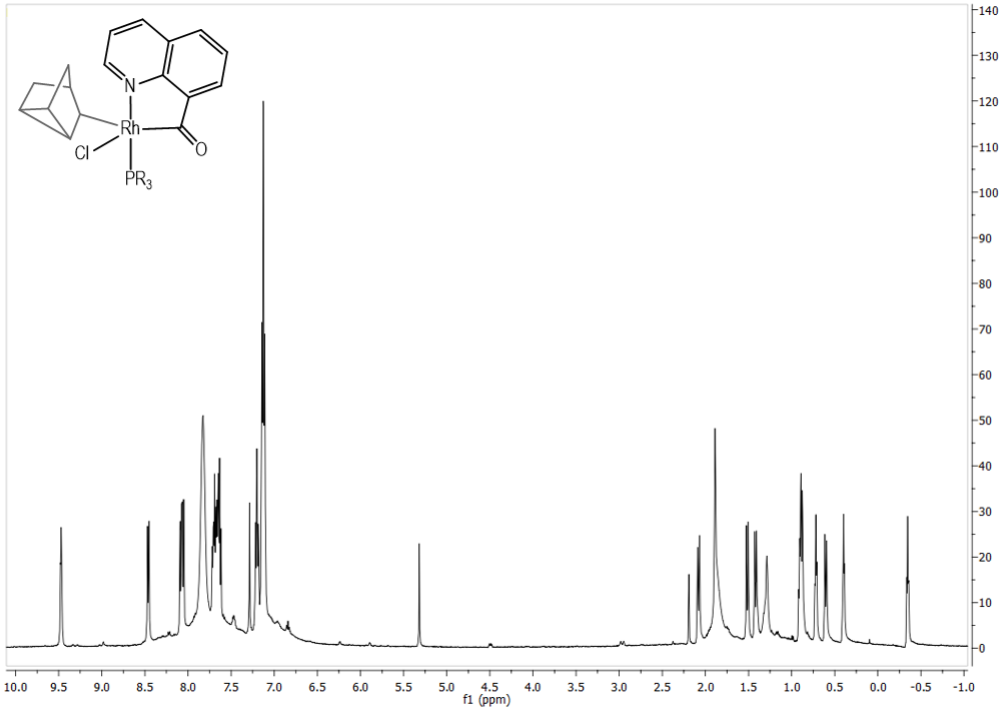


Figure S.4. ^{1}H NMR spectra of **2**.

$^{13}C\{^{1}H\}$ NMR ($CDCl_3$)

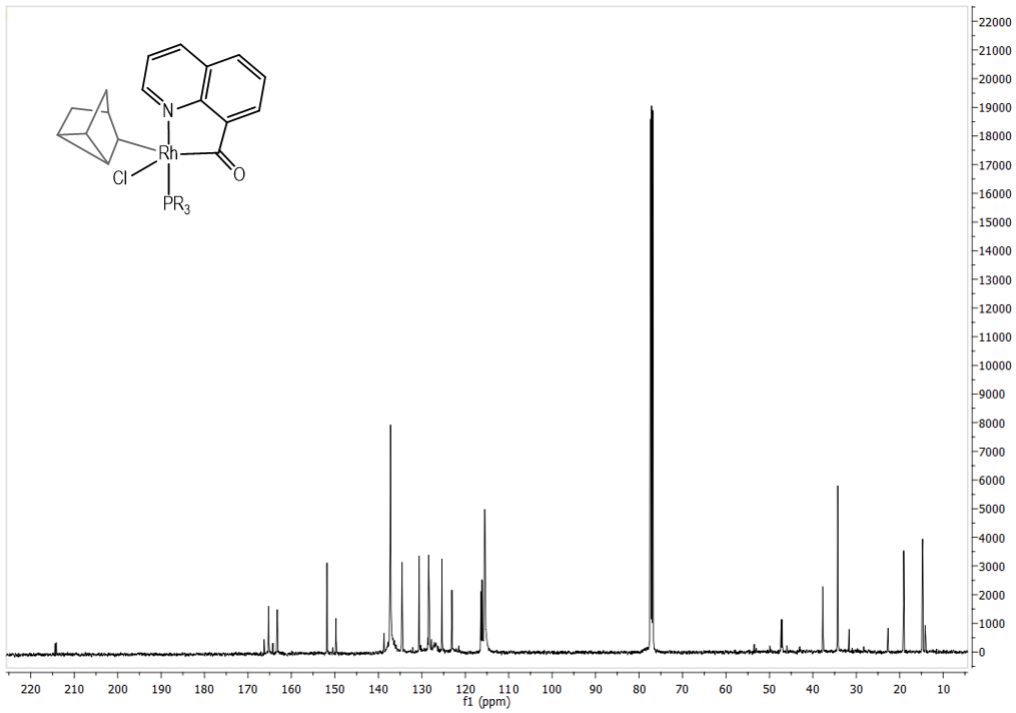


Figure S.5. $^{13}C\{^{1}H\}$ NMR spectra of **2**.

$^{31}P\{^{1}H\}$ NMR (CD_2Cl_2)

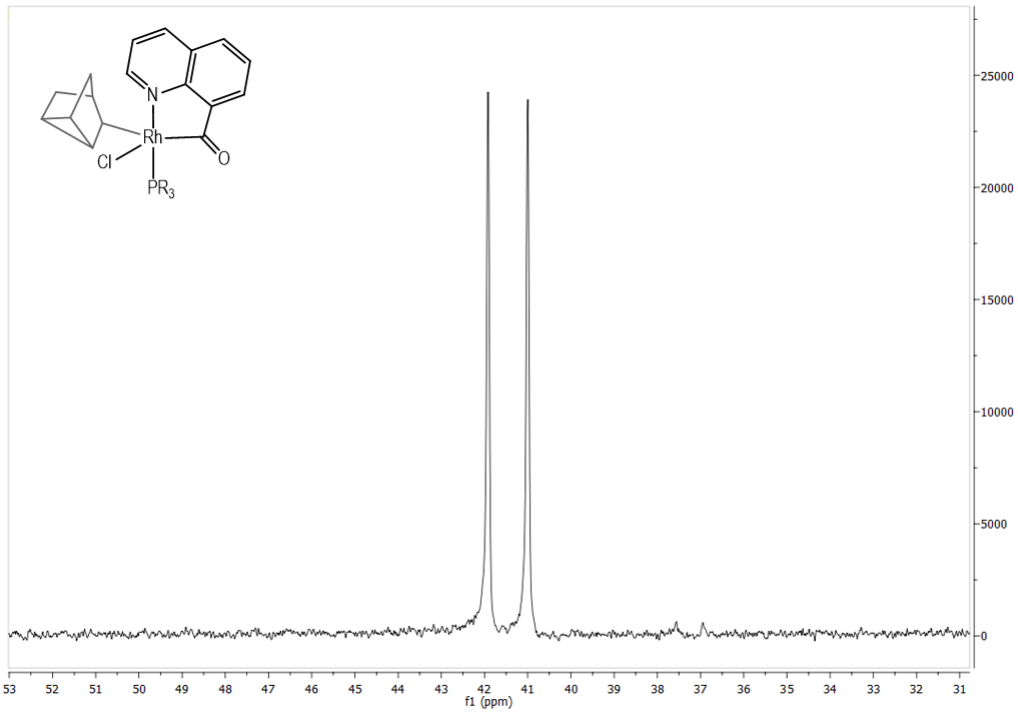


Figure S.6. $^{31}P\{^{1}H\}$ NMR spectra of **2**.

ESI-MS (MeOH) : $[M\text{-}Cl]^+$

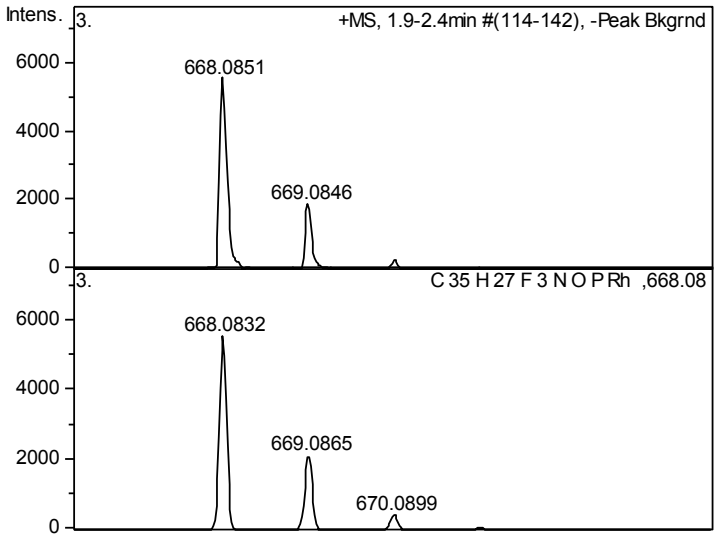
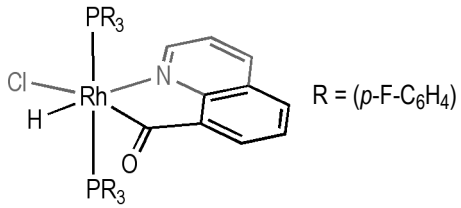


Figure S.7. ESI-MS of **2**. Found (top). Simulated (bottom).

Compound 3



^{1}H NMR (CD_2Cl_2)

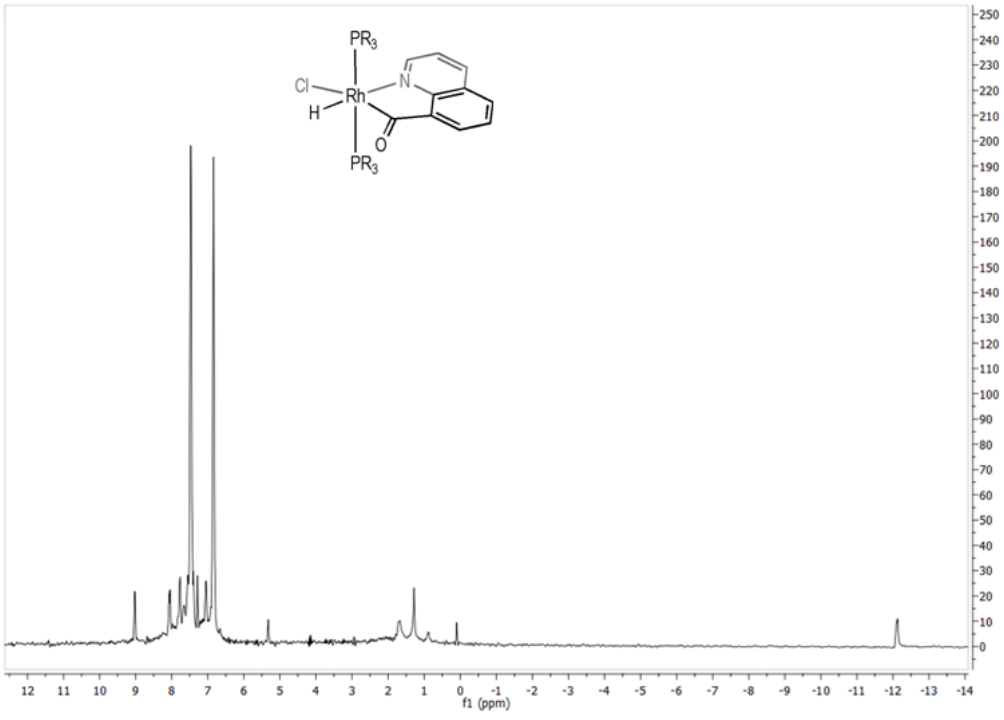


Figure S.8. ^{1}H NMR spectra of **3**.

$^{13}C\{^{1}H\}$ NMR (CD_2Cl_2)

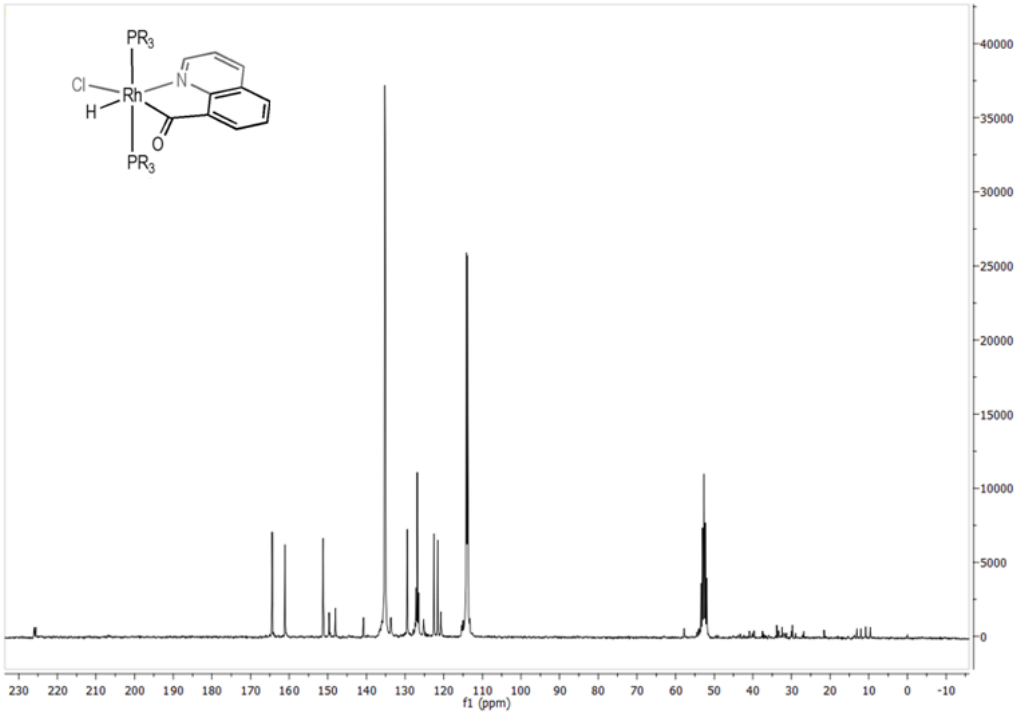


Figure S.9. $^{13}C\{^{1}H\}$ NMR spectra of **3**.

$^{31}P\{^{1}H\}$ NMR (CD_2Cl_2)

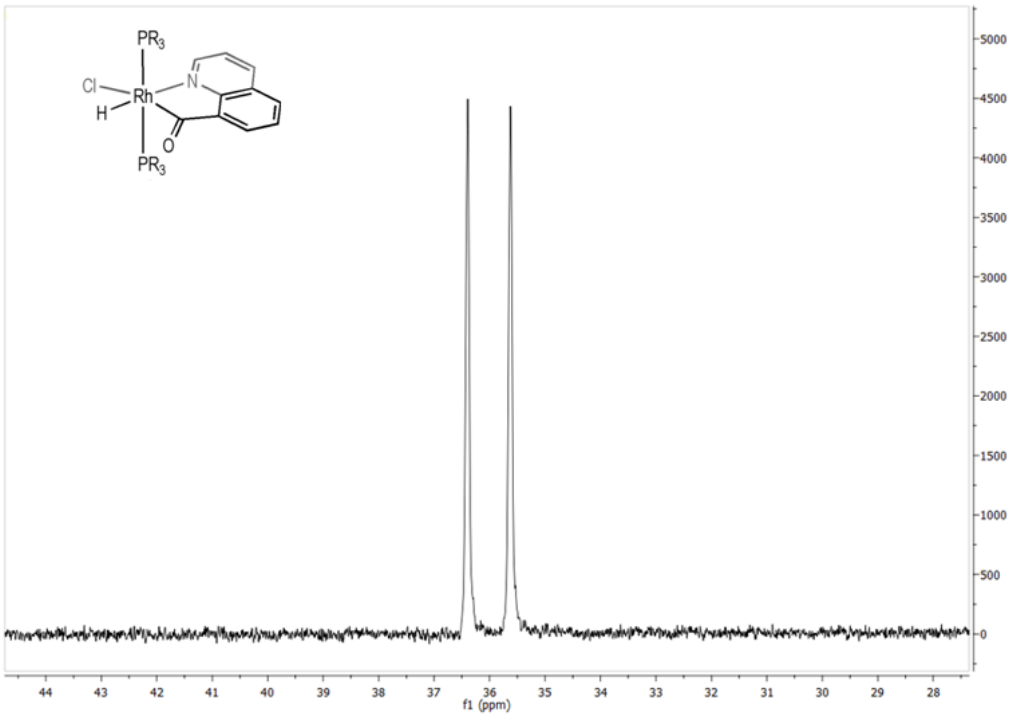


Figure S.10. $^{31}P\{^{1}H\}$ NMR spectra of **3**.

ESI-MS (MeOH) : $[M\text{-}Cl]^+$

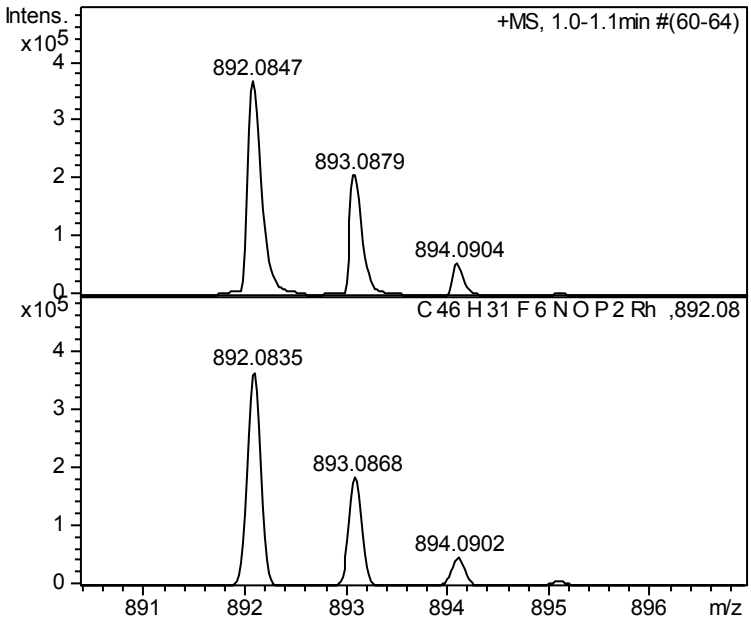


Figure S.11. ESI-MS of **3**. Found (top). Simulated (bottom).

4-ENDO:4-EXO

^{1}H NMR ($CDCl_3$)

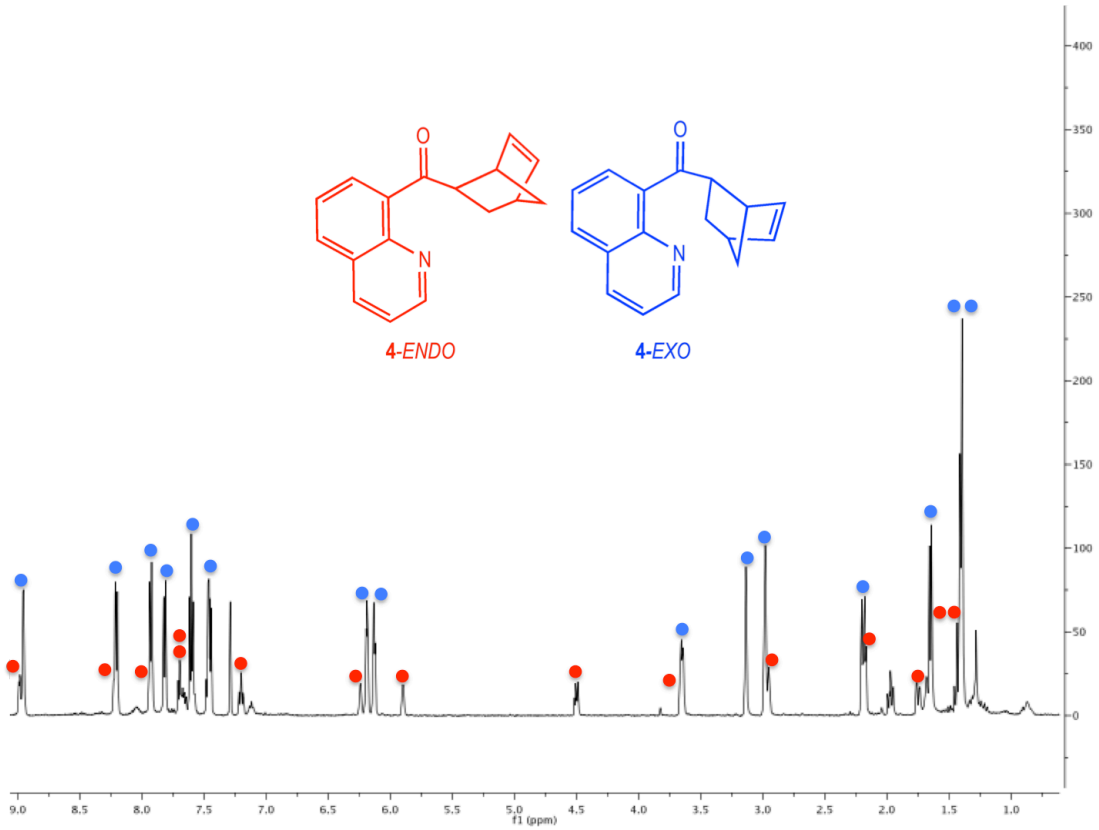


Figure S.12. ^{1}H NMR spectra of isomers mixture **4**-ENDO and **4**-EXO.

$^{13}C\{^{1}H\}$ NMR ($CDCl_3$)

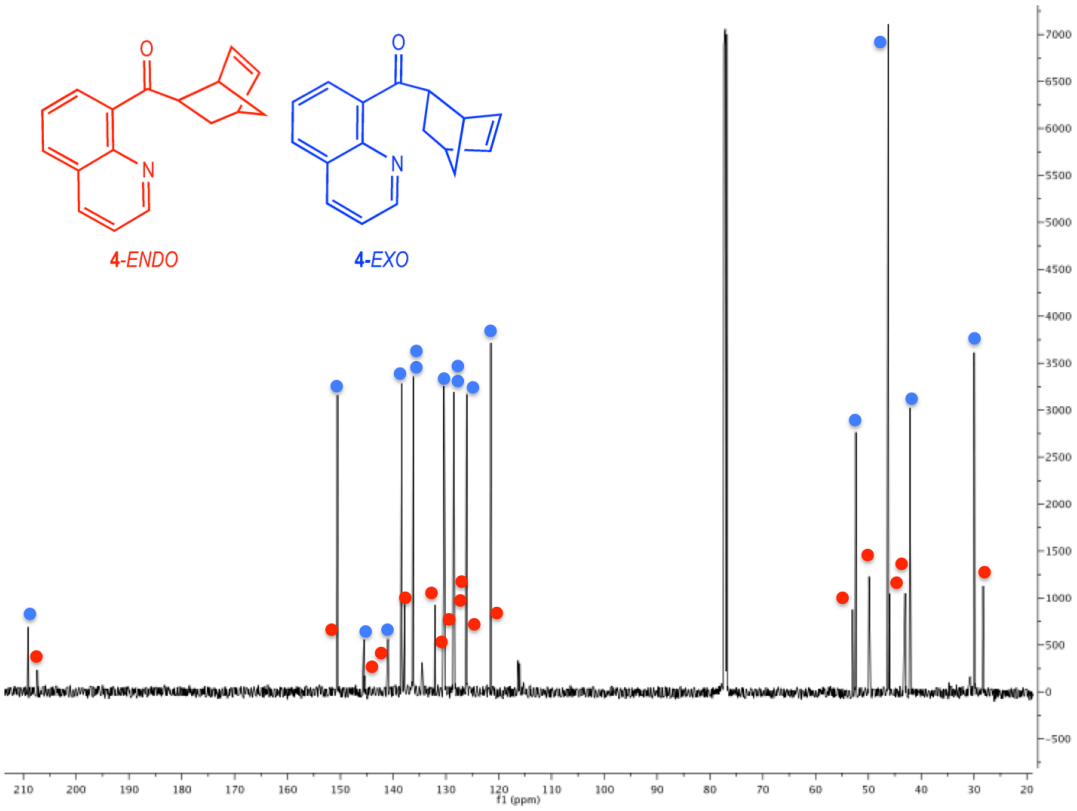
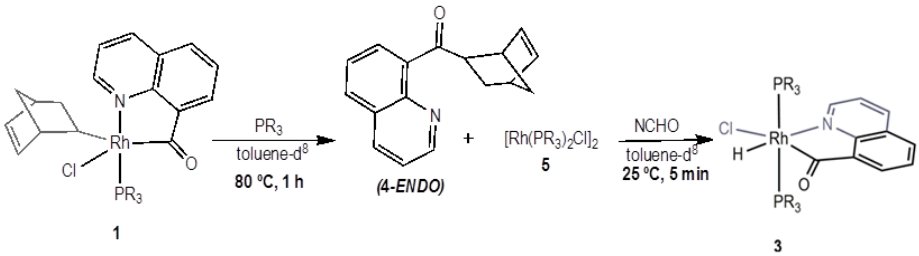


Figure S.13. $^{13}C\{^{1}H\}$ NMR spectra of isomers mixture **4**-ENDO and **4**-EXO.

Reaction of 1 with PR_3 (P = *p*-F-C_6H_4)

Stoichiometric reaction of compound **1** with the equimolar amount of PR_3 (R = *p*-F-C_6H_4) in toluene-d^8 at 80 ºC in a sealed Young NMR tube yields in 1 hour the hydroacylation product **4**-ENDO and $[Rh(PR_3)_2Cl]_2$ (R = *p*-F-C_6H_4) (**5**). This reaction was monitored by ^{1}H NMR (Figure S.14. top). In the same Young NMR tube an equivalent of NCHO (quinoline-8-carbaldehyde) was added and a ^{1}H NMR spectra was collected after 25 minutes at room temperature.



Scheme S.1. Reaction of **1** with PR_3 (R = *p*-F-C_6H_4) and consecutive addition of NCHO to the reaction mixture.

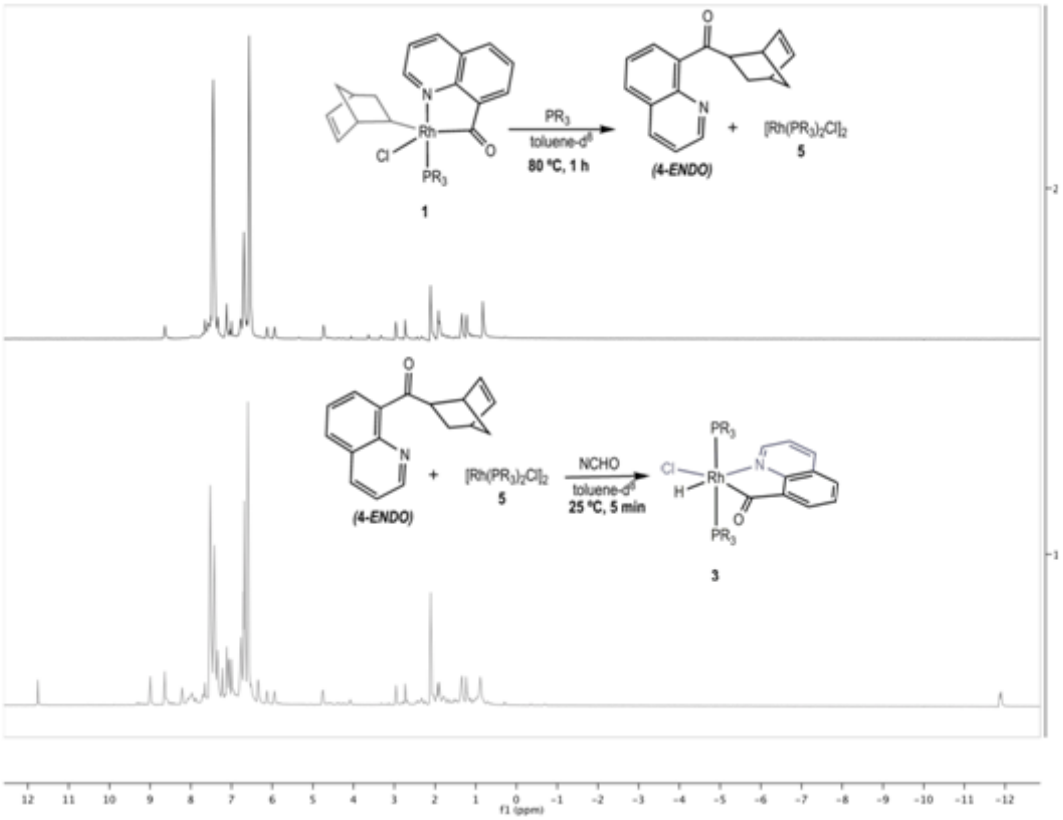


Figure S.14. ^{1}H NMR spectra of the reaction of **1** and PR_3 (R = *p*-F-C_6H_4) (top). ^{1}H NMR spectra of the reaction of **5** and NCHO (bottom).

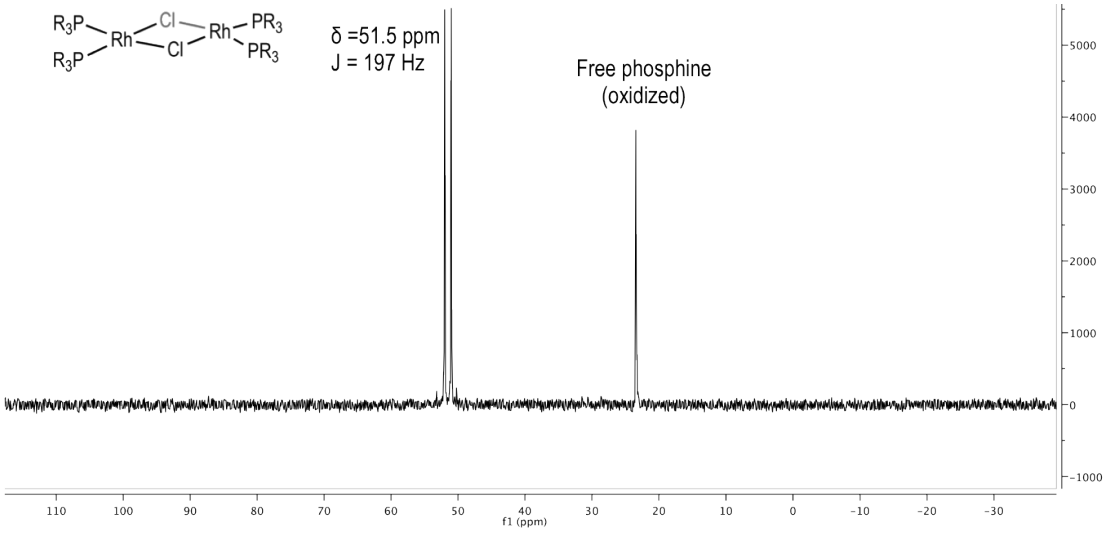


Figure S.15. ^{31}P{^{1}H} NMR of the reaction of **1** and PR_3 (R = *p*-F-C_6H_4) to give **5**.

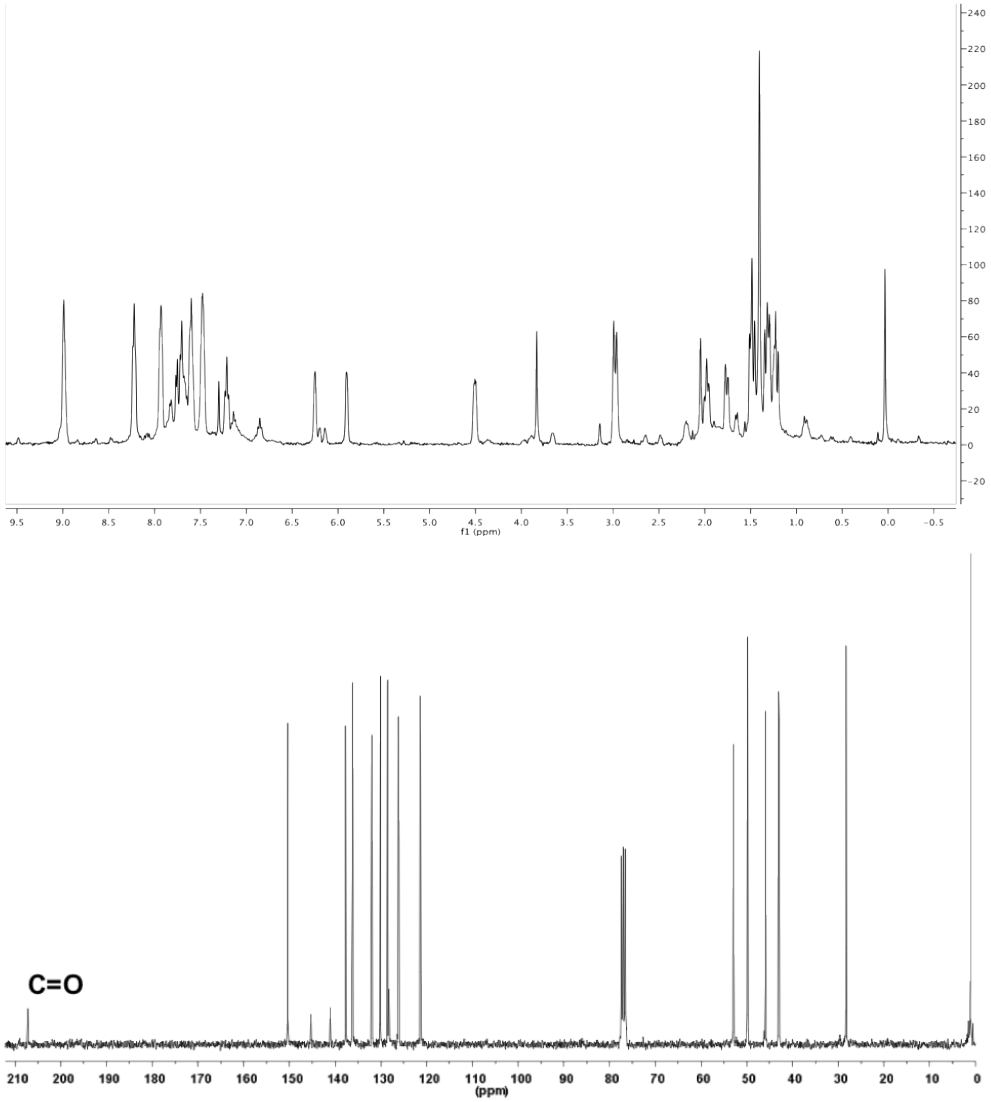
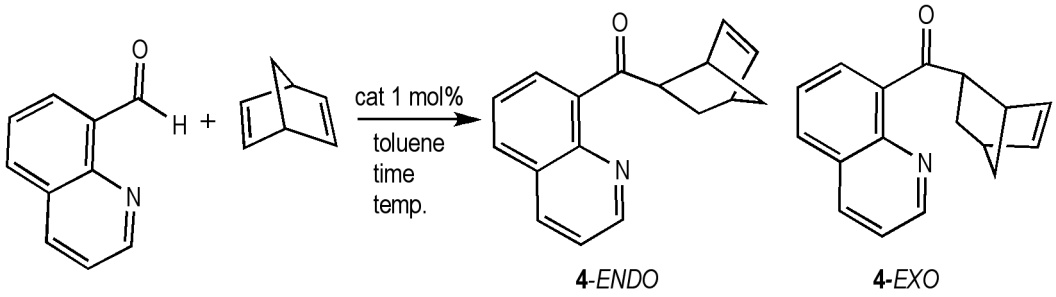


Figure S.16. ^{1}H NMR (top) and $^{13}C\{^{1}H\}$ NMR (bottom) of **4-ENDO**.

Catalytic Studies



Scheme S.2. Catalytic hydroacylation of norbornadiene with quinoline-8-carbaldehyde.

Catalyst: Compound **3**

50 ºC

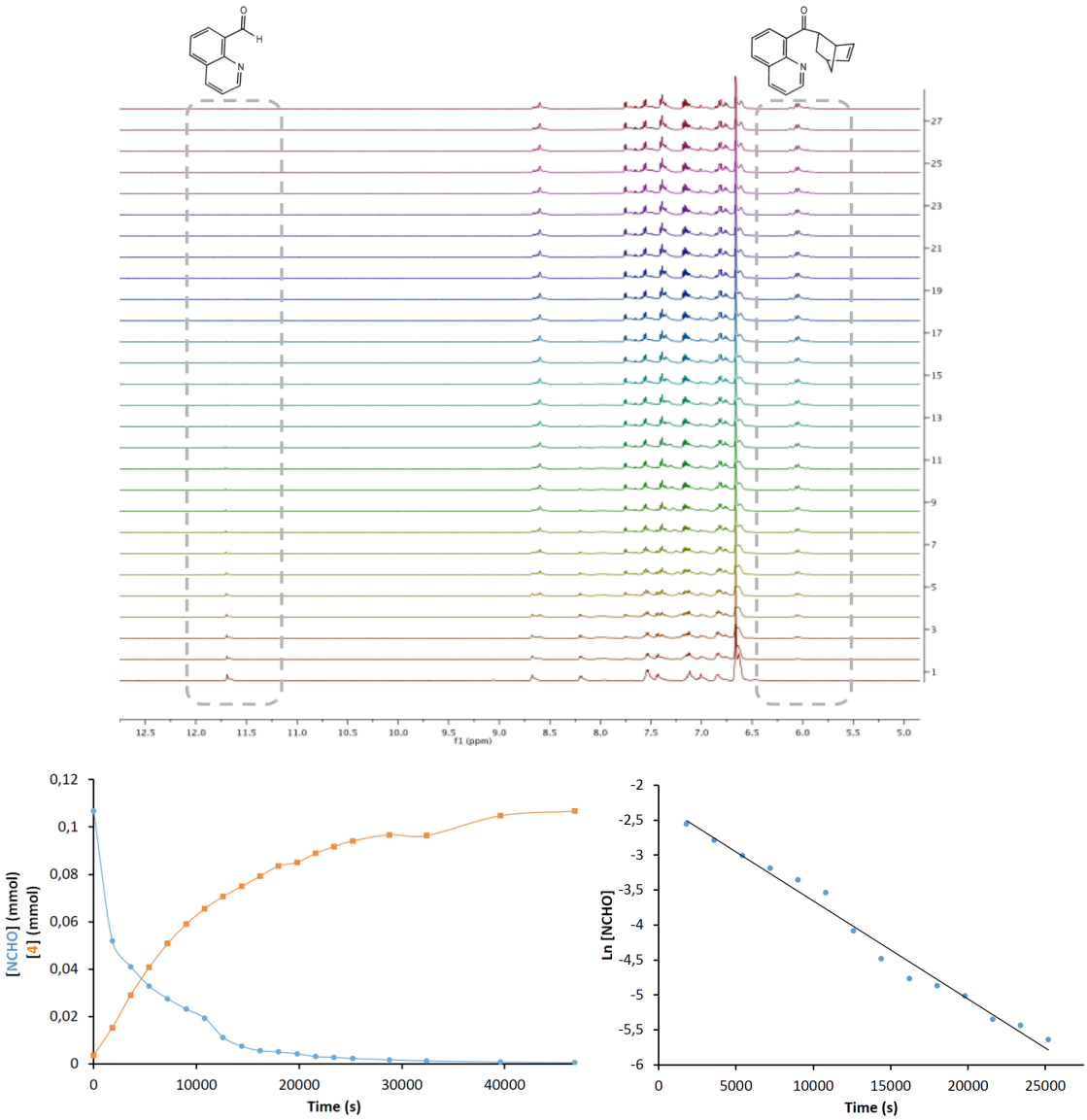


Figure S.17. ^{1}H NMR array of the catalytic hydroacylation of norbornadiene with NCHO (top). mmol of NCHO vs. time plot and Ln [NCHO] vs. time plot (bottom). k = 1.40 ± 0.02 × 10^{-4} s^{-1} ($t_{1/2}$ = 1926 s).

60 ºC

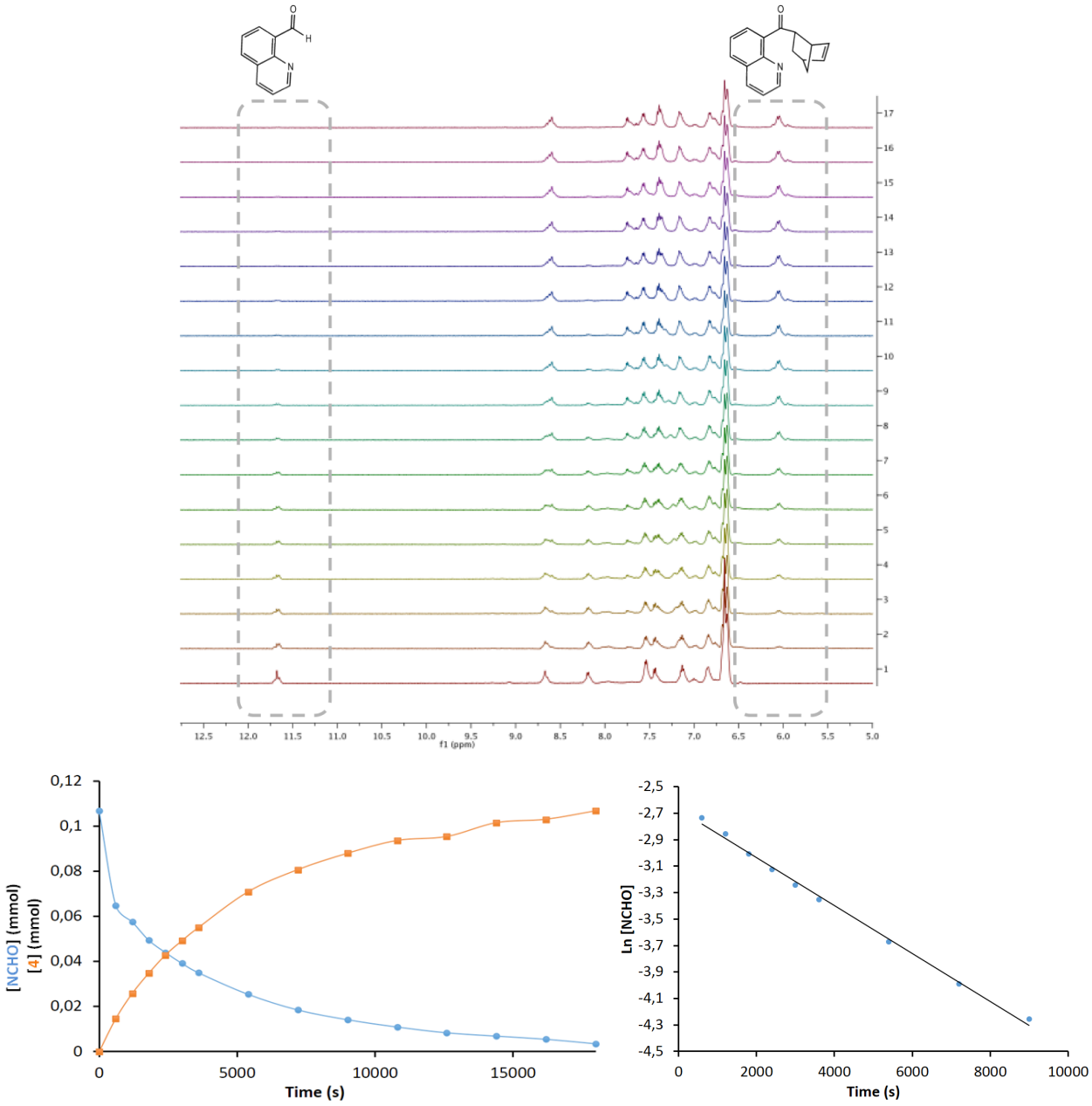


Figure S.18. ^{1}H NMR array of the catalytic hydroacylation of norbornadiene with NCHO (top). mmol of NCHO vs. time plot and Ln [NCHO] vs. time plot (bottom). k = 1.81 ± 0.04 × 10^{-4} s^{-1} ($t_{1/2}$ = 1431 s)

70 ºC

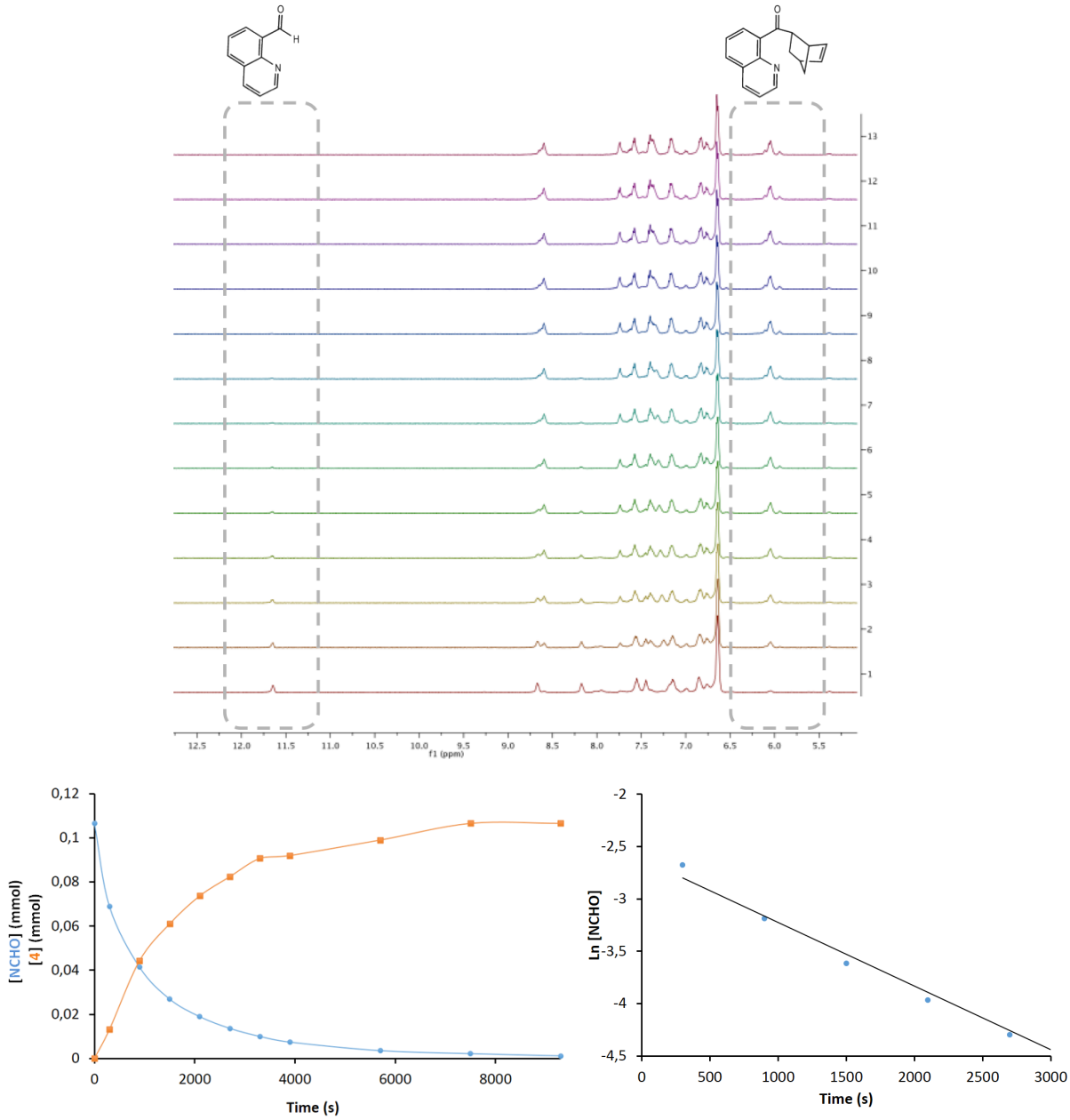


Figure S.19. ^{1}H NMR array of the catalytic hydroacylation of norbornadiene with NCHO (top). mmol of NCHO vs. time plot and Ln [NCHO] vs. time plot (bottom). k = 6.08 ± 0.27 × 10^{-4} s^{-1} ($t_{1/2}$ = 518 s)

80 ºC

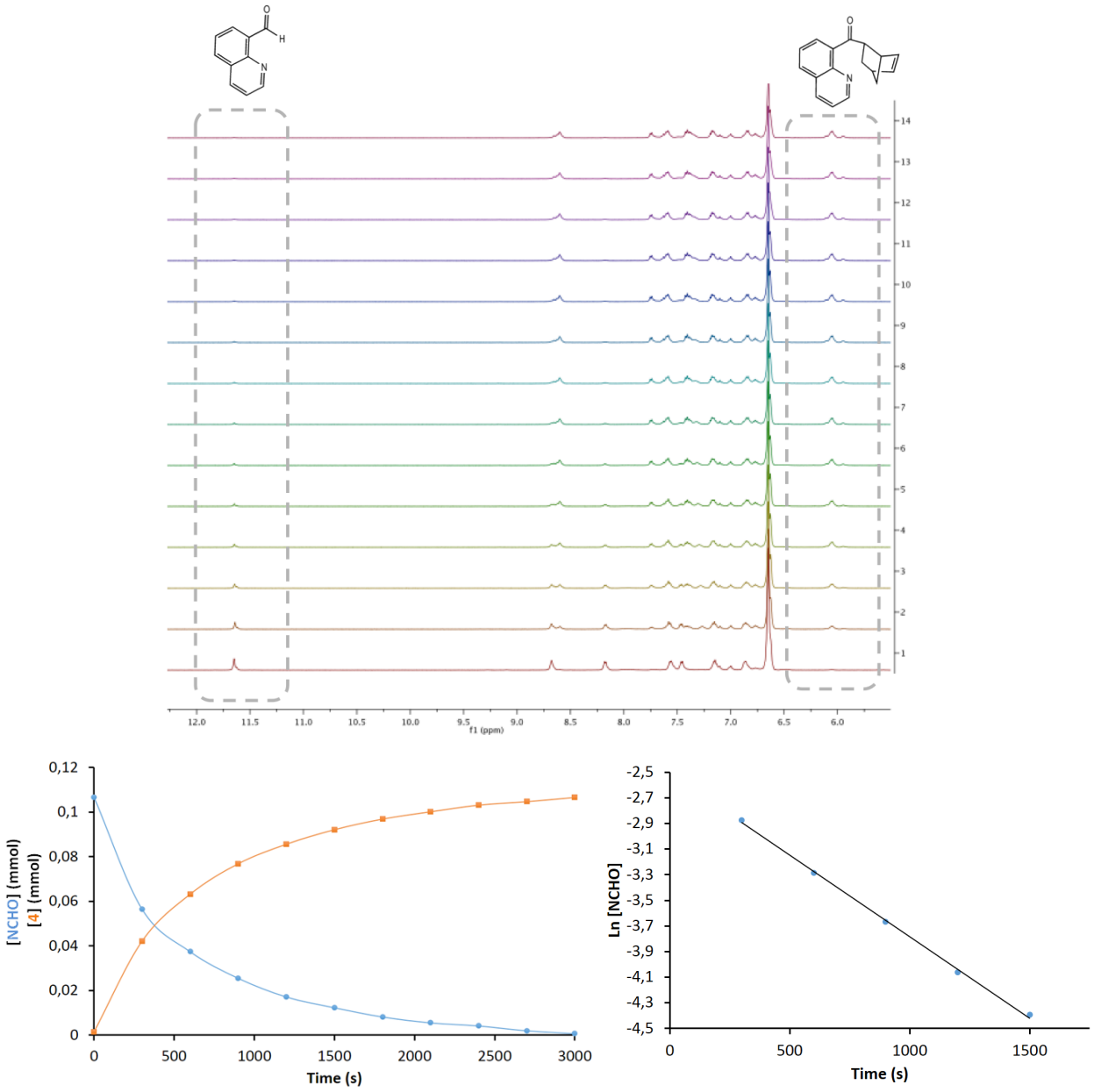
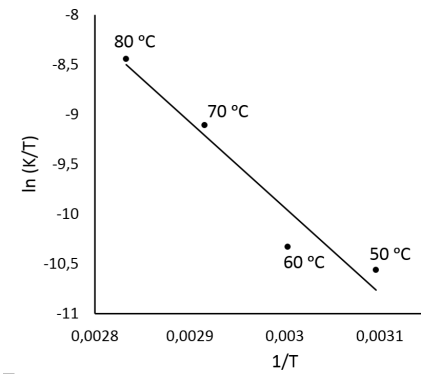


Figure S.20. ^{1}H NMR array of the catalytic hydroacylation of norbornadiene with NCHO (top). mmol of NCHO vs. time plot and Ln [NCHO] vs. time plot (bottom). k = 12.72 ± 0.26 × 10^{-4} s^{-1} ($t_{1/2}$ = 330 s)

Eyring Plot



ΔH‡ = 71.1 ± 12.9 kJ mol^{-1}

ΔS‡ = -100.9 ± 38.1 J mol^{-1} K^{-1}

ΔG‡ (298 K) = 101.2 ± 24.2 kJ mol^{-1}

Figure S.20. Eyring plot.

Catalyst: Compound **1**

70 ºC

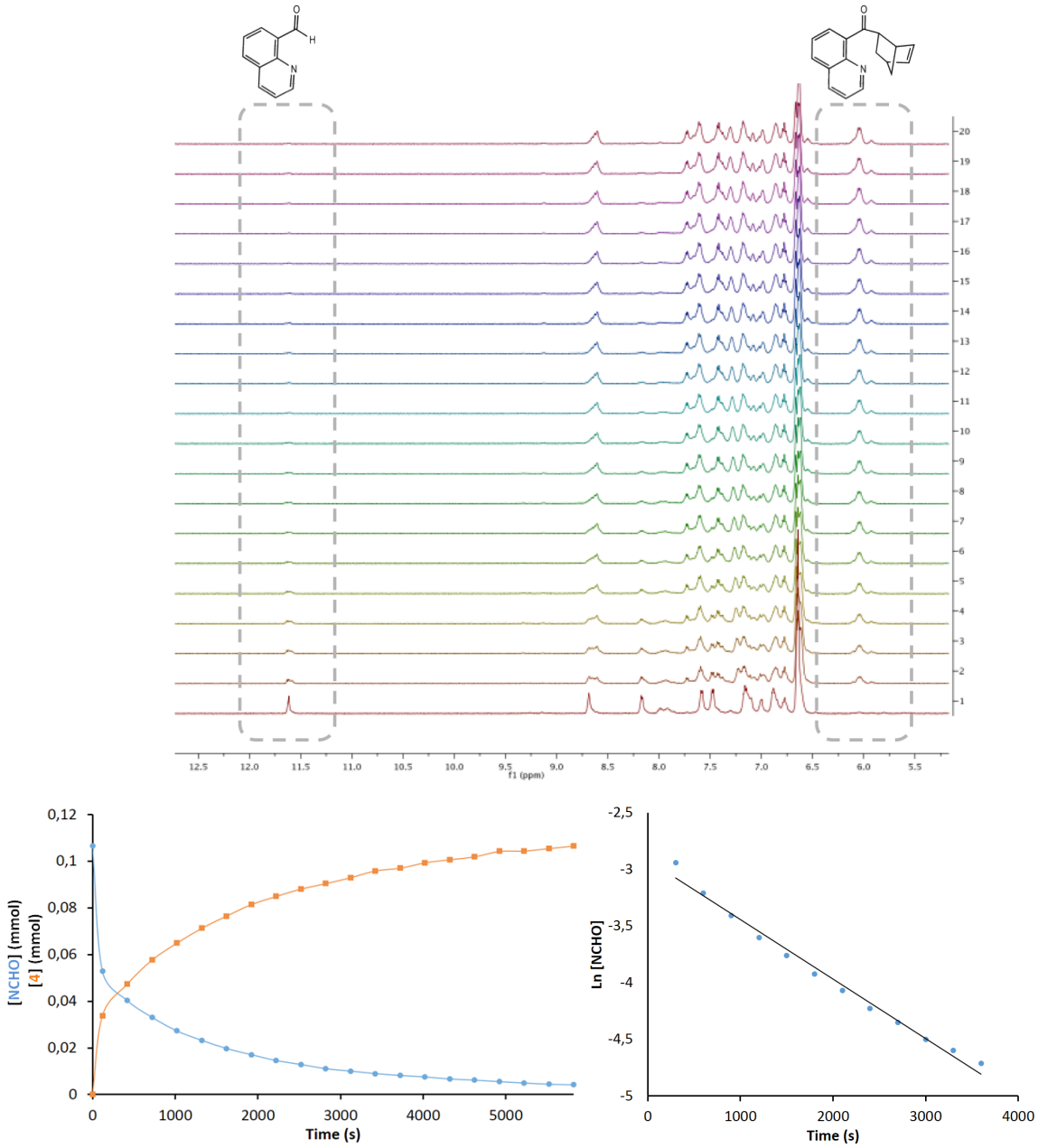


Figure S.21. ^{1}H NMR array of the catalytic hydroacylation of norbornadiene with NCHO (top). mmol of NCHO vs. time plot and Ln [NCHO] vs. time plot (bottom). k = 5.99 ± 0.46 × 10^{-4} s^{-1} ($t_{1/2}$ = 333 s)

X-Ray Structure of 3

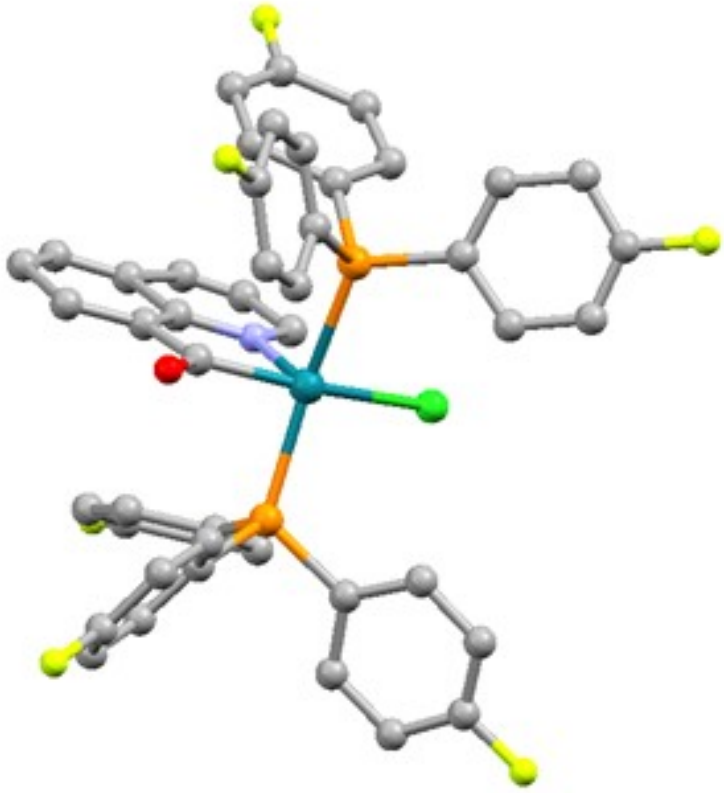


Figure S.22. Perspective view of molecular structure of **3**.

Crystallographic Tables

Table S1. Crystal data and structure refinement for compounds 1 - 3

	1	2	3
CCDC number	1505499	1505500	1505501
Formula	$C_{36}H_{29}Cl_3F_3NOPRh$	$C_{37}H_{31}Cl_5F_3NOPRh$	$C_{48}H_{34}Cl_5F_6NOP_2Rh$
M	788.83	873.76	1096.86
Crystal System	Triclinic	Triclinic	Orthorhombic
Space group	*P*-1	*P*-1	$Cmc2_1$
T [K]	100	100	100
a [Å]	12.3494(6)	10.2512(11)	48.335(4)
b [Å]	14.4492(7)	12.494(2)	10.4309(8)
c [Å]	20.1293(9)	13.7147(17)	15.6534(11)
α [deg]	69.671(2)	70.085(5)	90
β [deg]	79.770(2)	76.102(6)	90
γ [deg]	76.835(2)	76.715(6)	90
V [Å^3]	3260.5(3)	1582.0(4)	7892.1(10)
Z	4	2	4
Density [gcm^{-3}]	1.607	1.834	0.923
μ [mm^{-1}]	0.868	1.067	0.463
Observed reflections	163285	27007	49832
R_{int}	0.046	0.062	0.154
R_1 [I > 2σ(I)]	0.048	0.046	0.093
wR_2 [all data]	0.119	0.095	0.233
GoF	1.081	1.028	1.055
Largest diff. pk and hole [eÅ^{-3}]	1.970 and -2.021	0.836 and -0.641	1.655 and -4.627

[a] $\sum||F_o|-|F_c||/\sum|F_o|$ [b] $\{\sum [w(F_o^2-F_c^2)^2]/\sum [w(F_o^2)^2]\}^{1/2}$

Table S2. Bond distances (Å) for compounds 1 - 3

1	2	3
N1B Rh1B 2.111(3)	Rh1 C8 1.940(3)	Rh1 C1 1.973(18)
N1A Rh1A 2.100(3)	Rh1 C1 2.091(3)	Rh1 N1 2.164(15)
P1B Rh1B 2.2966(9)	Rh1 N1 2.100(2)	Rh1 P1 2.319(3)
P1A Rh1A 2.3006(8)	Rh1 P1 2.2891(8)	Rh1 P1 2.319(3)
Cl1B Rh1B 2.4186(9)	Rh1 Cl1 2.4296(8)	Rh1 Cl1 2.495(5)
Cl1A Rh1A 2.4372(8)		

Table S3. Bond angles (º) for compounds 1 - 3

1	2	3
C8B Rh1B C1B 81.27(14)	C8 Rh1 C1 81.89(12)	C1 Rh1 N1 80.6(7)
C8B Rh1B N1B 83.73(12)	C8 Rh1 N1 84.30(11)	C1 Rh1 P1 89.79(10)
C1B Rh1B N1B 95.37(12)	C1 Rh1 N1 93.81(11)	N1 Rh1 P1 96.58(7)
C8B Rh1B P1B 94.30(10)	C8 Rh1 P1 94.60(9)	C1 Rh1 P1 89.79(10)
C1B Rh1B P1B 91.02(10)	C1 Rh1 P1 91.19(9)	N1 Rh1 P1 96.58(8)
N1B Rh1B P1B 172.93(8)	N1 Rh1 P1 174.68(7)	P1 Rh1 P1 166.57(15)
C8B Rh1B Cl1B 127.60(11)	C8 Rh1 Cl1 124.75(9)	C1 Rh1 Cl1 165.6(6)
C1B Rh1B Cl1B 151.08(9)	C1 Rh1 Cl1 153.15(9)	N1 Rh1 Cl1 85.0(5)
N1B Rh1B Cl1B 87.24(8)	N1 Rh1 Cl1 86.51(7)	P1 Rh1 Cl1 91.87(8)
P1B Rh1B Cl1B 88.61(3)	P1 Rh1 Cl1 89.87(3)	P1 Rh1 Cl1 91.87(8)
C8A Rh1A C1A 82.96(13)		
C8A Rh1A N1A 83.73(12)		
C1A Rh1A N1A 94.40(12)		
C8A Rh1A P1A 94.12(10)		
C1A Rh1A P1A 90.98(9)		
N1A Rh1A P1A 173.91(8)		
C8A Rh1A Cl1A 126.04(10)		
C1A Rh1A Cl1A 150.85(9)		
N1A Rh1A Cl1A 86.94(8)		
P1A Rh1A Cl1A 89.76(3)		