Phosphidoboratabenzene-Rhodium(I) complexes as catalysts for the hydrogenation of alkenes at room temperature and atmospheric pressure

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Supporting Information

1- NMR Characterization of complex **1**

Figure S1. ^{1}H NMR (benzene-d_6, 500 MHz) of $[Rh(C_2H_4)(DTBB)]_2$ (**1**)

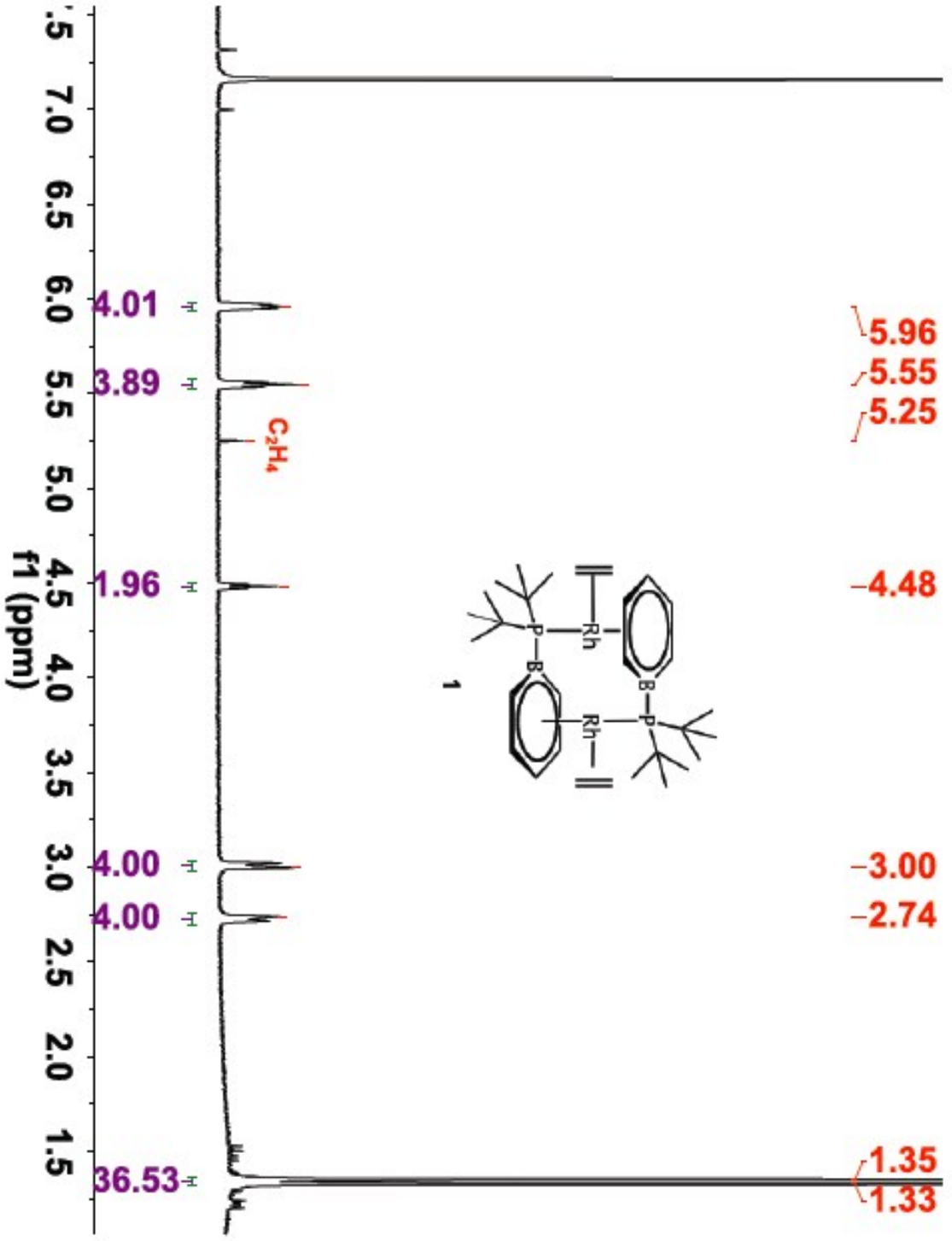


Figure S2. ^{31}P NMR (benzene-d_6, 202 MHz) of $[Rh(C_2H_4)(DTBB)]_2$ (1)

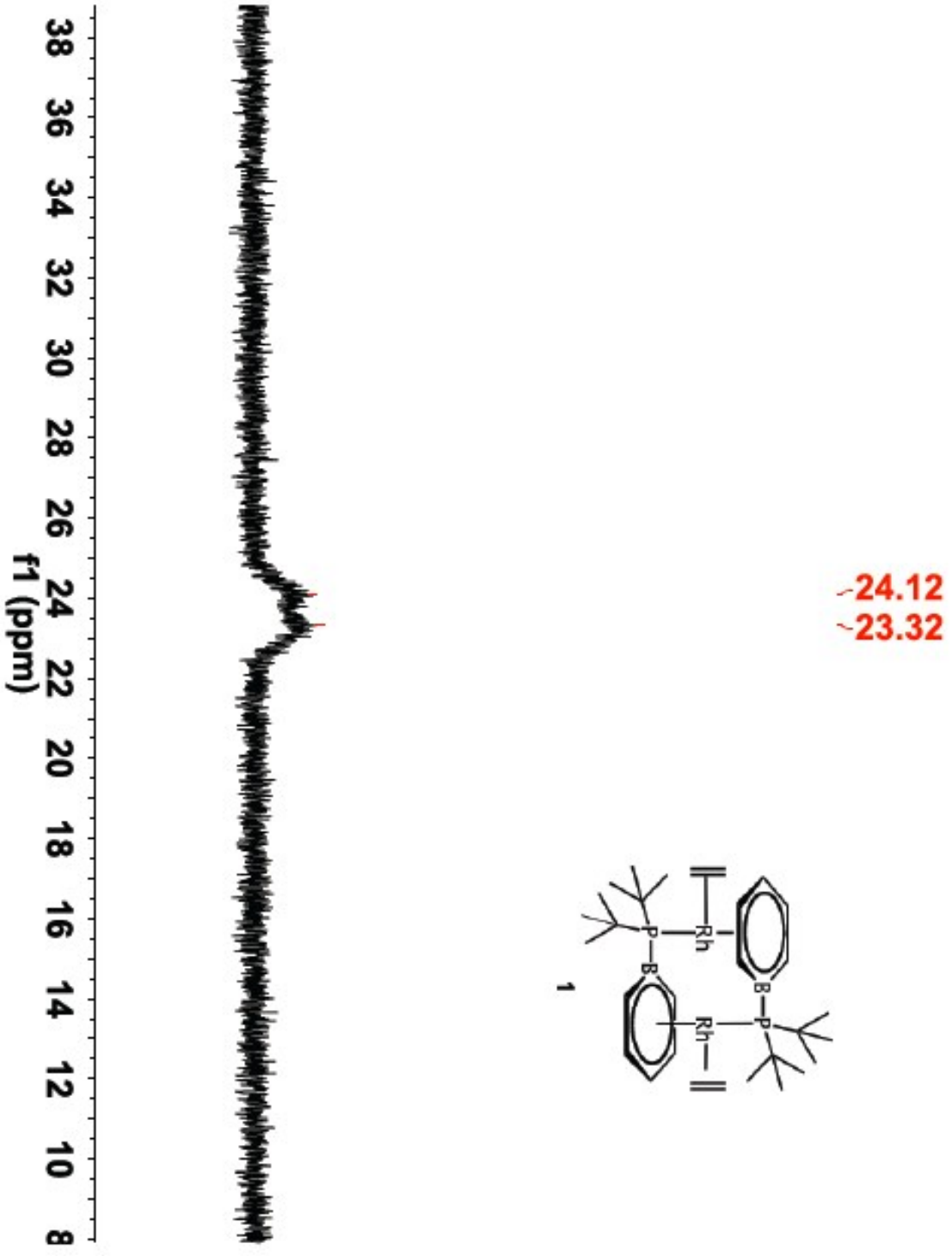


Figure S3. ^{11}B NMR (benzene-d_6, 160 MHz) of $[Rh(C_2H_4)(DTBB)]_2$ (**1**)

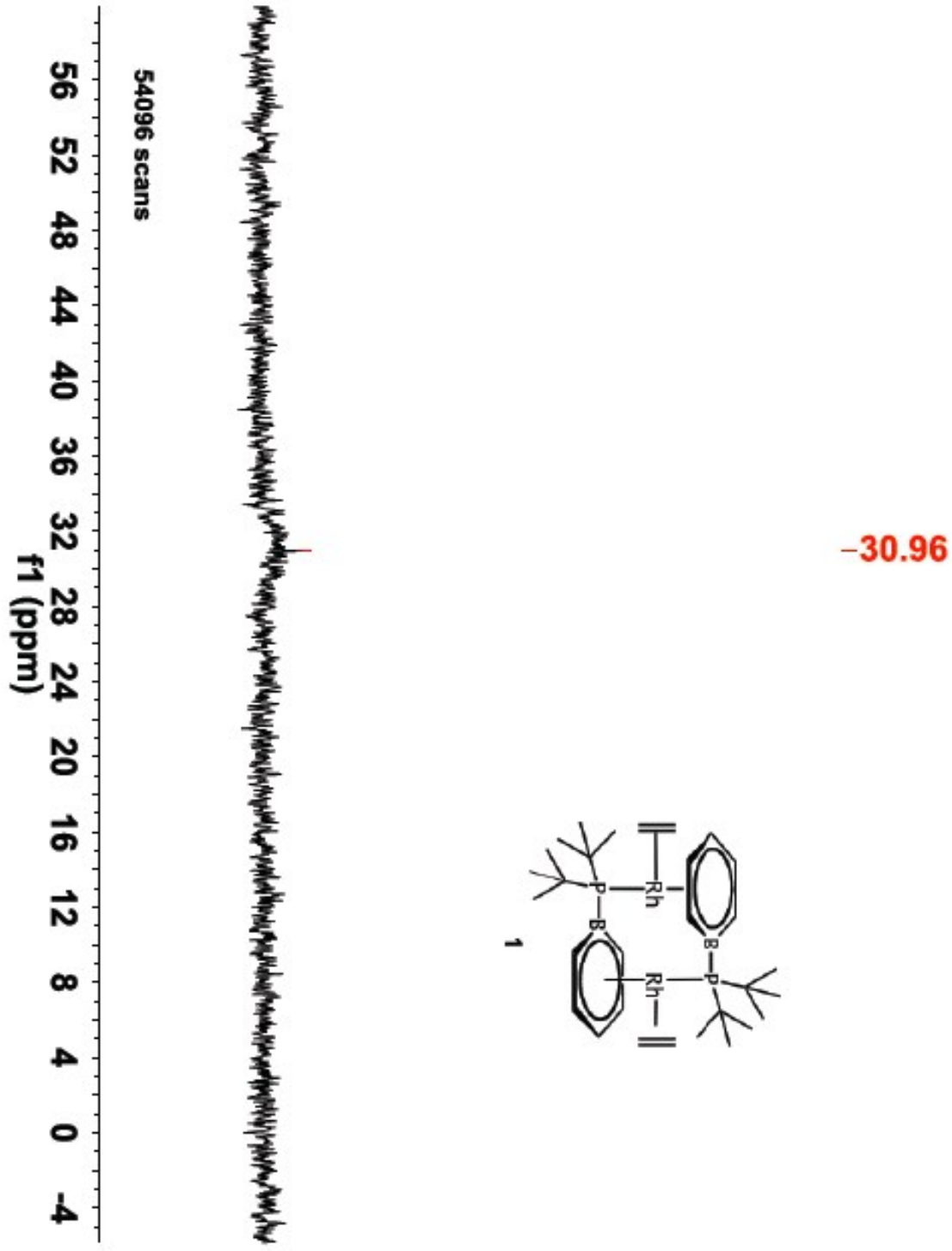


Figure S4. ^{13}C NMR (benzene-d_6, 125 MHz) of $[Rh(C_2H_4)(DTBB)]_2$ (**1**)

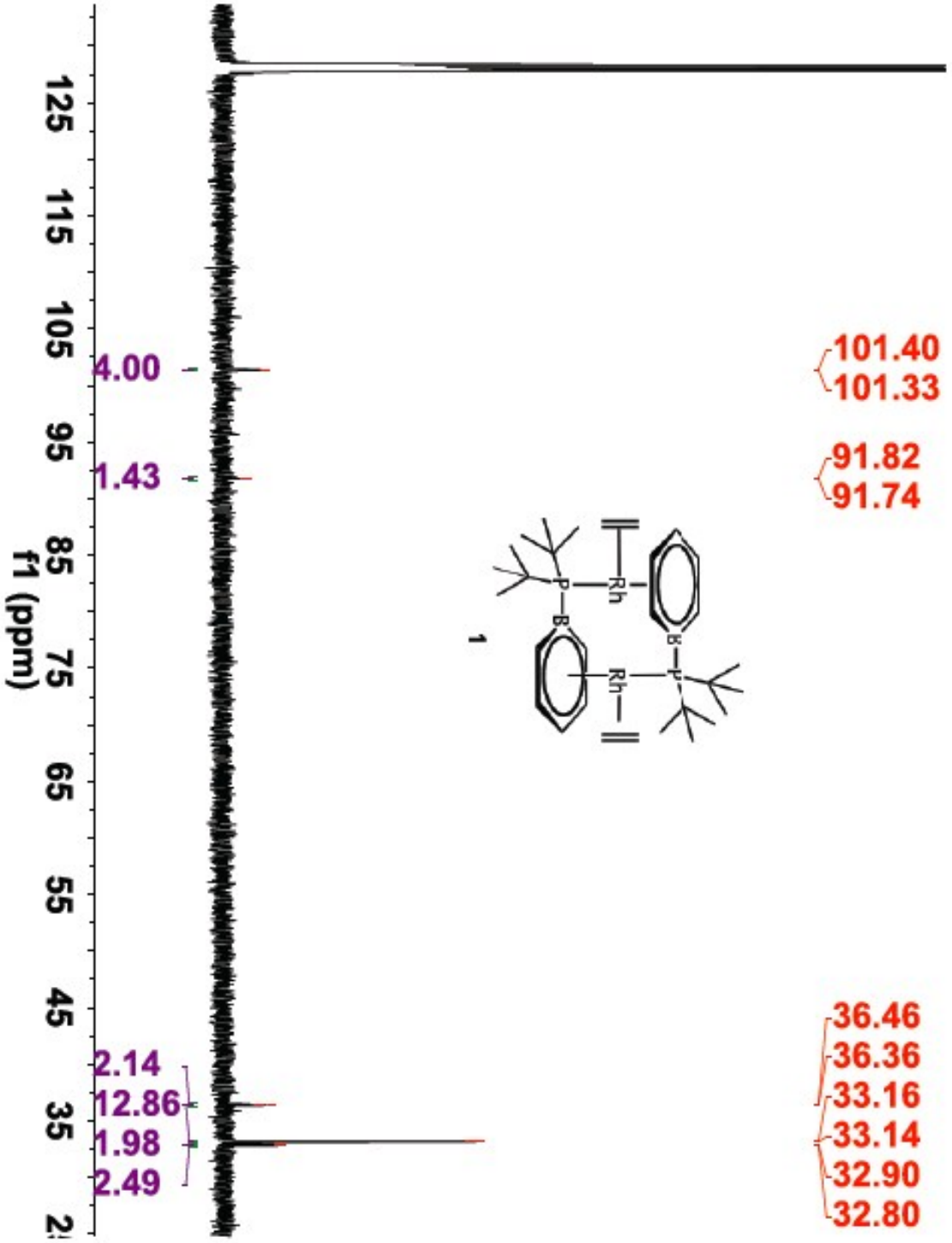


Figure S5. ^{1}H gCOSY NMR (benzene-d_6, 500 MHz) of $[Rh(C_2H_4)(DTBB)]_2$ (1)

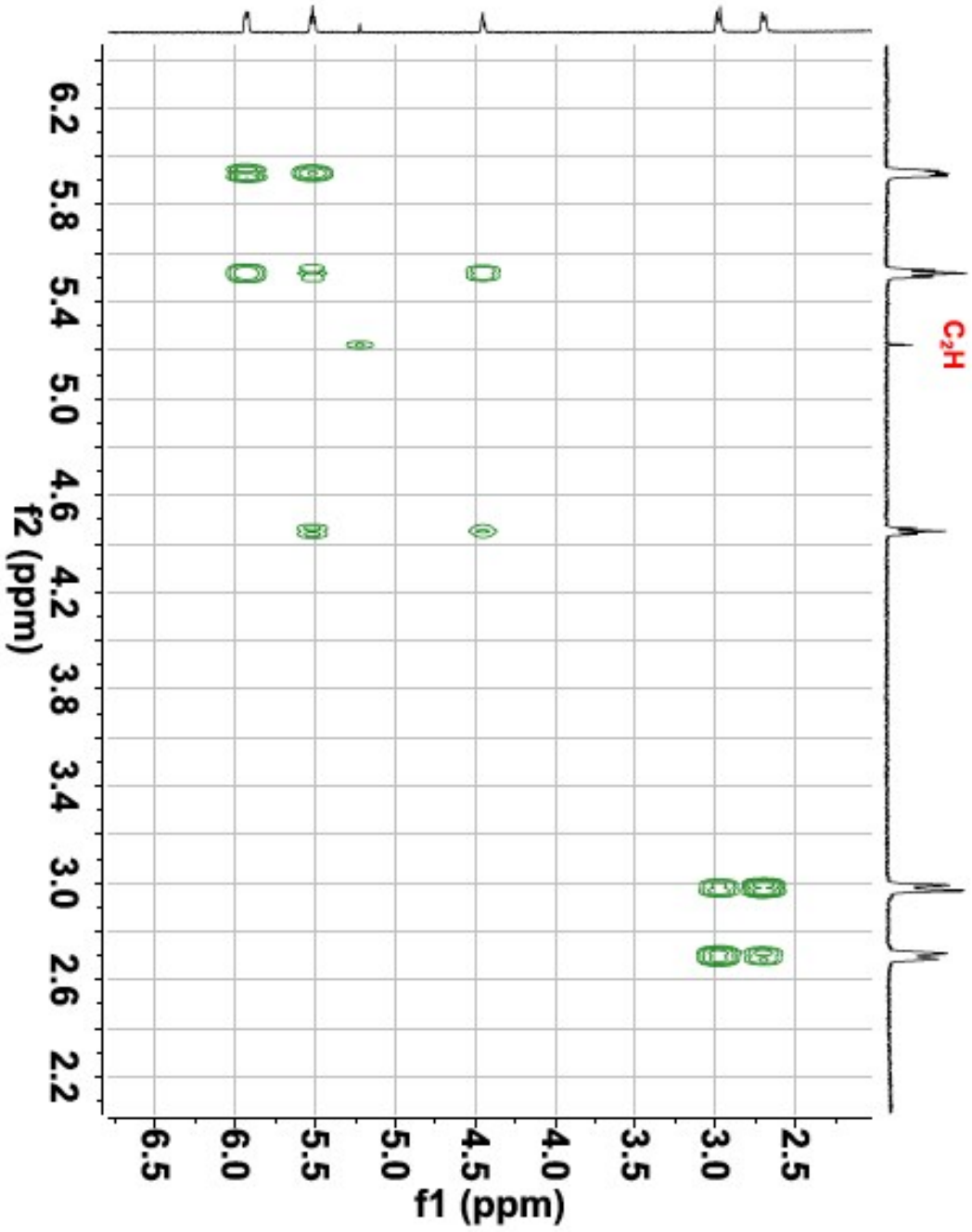
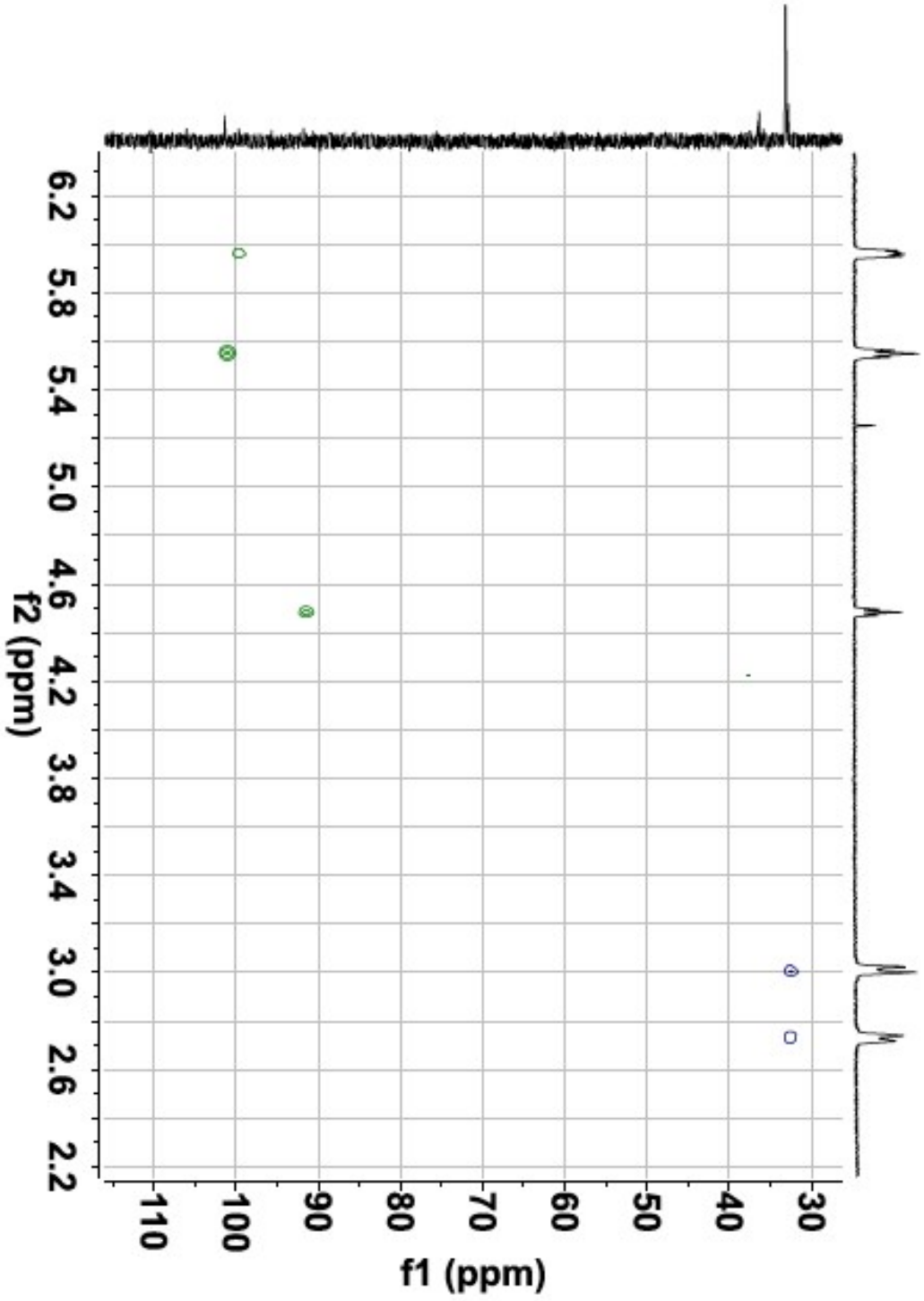


Figure S6. gHSQCAD (^{1}H-^{13}C) NMR (benzene-d_6) of $[Rh(C_2H_4)(DTBB)]_2$ (1)



2- NMR Characterization of complex **2**

Figure S7. ^{1}H NMR (benzene-d_6, 500 MHz) of species $[(DTBB)Rh(H)_2]_2$ (**2**)

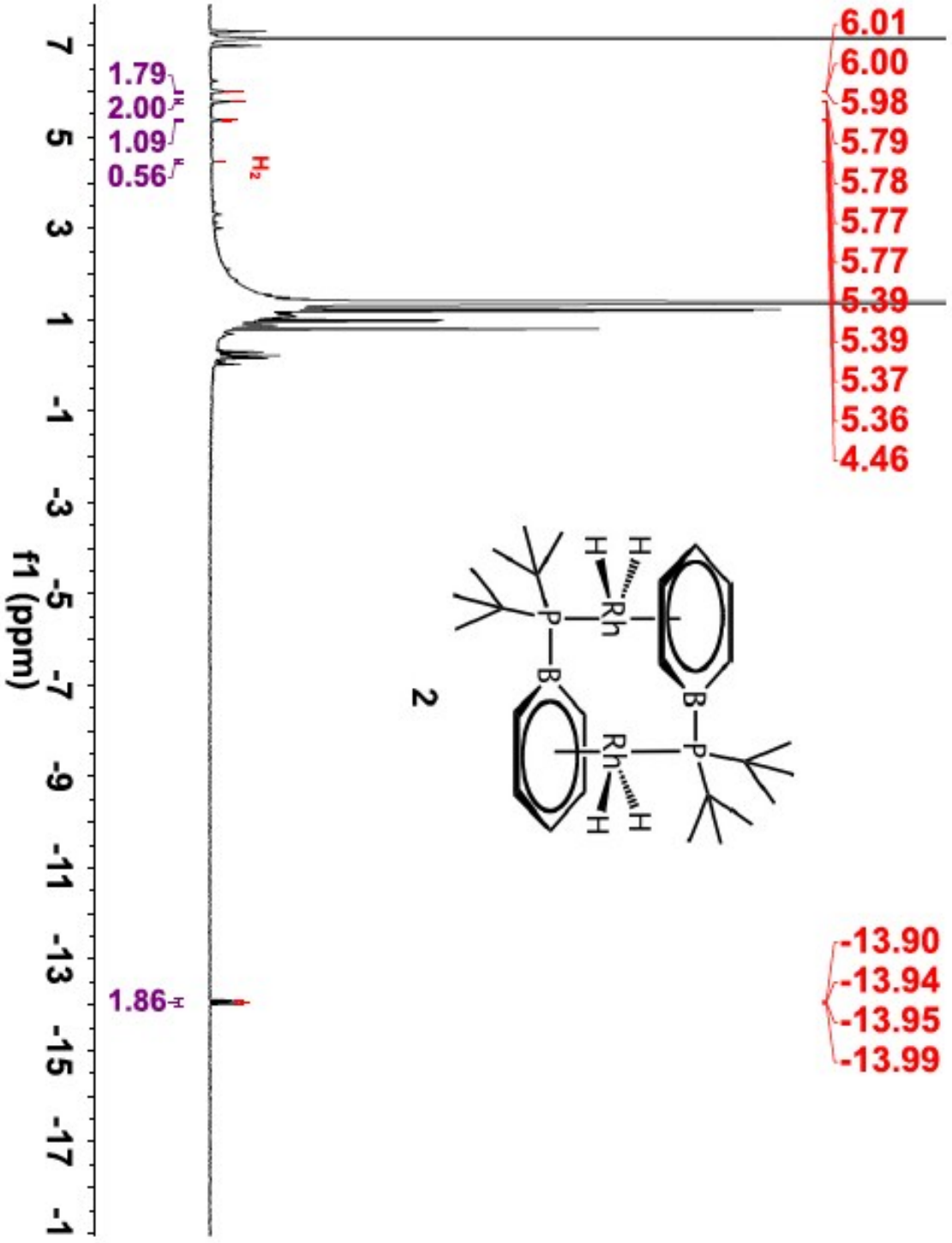
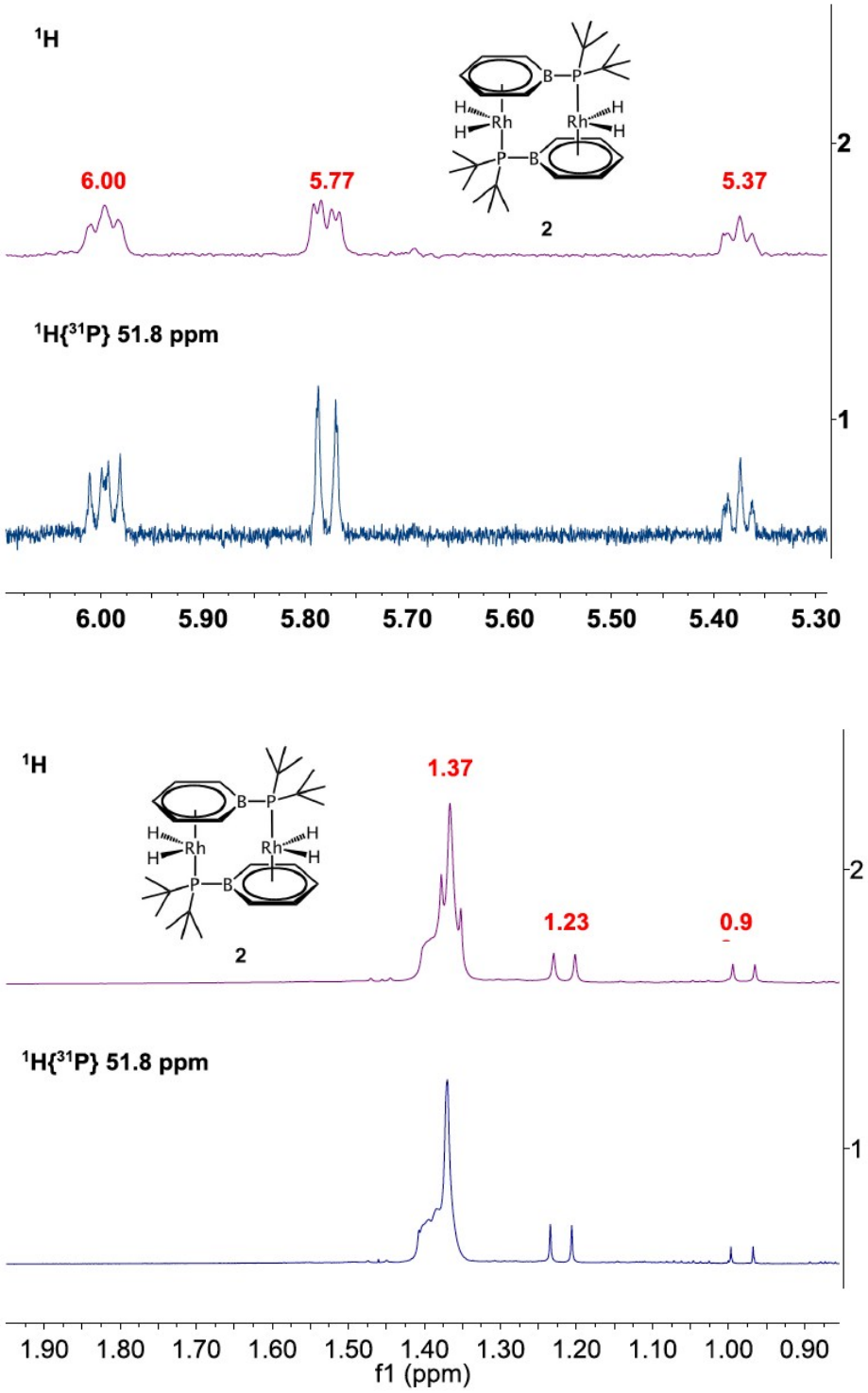


Figure S8. Selected area of the ^{1}H and $^{1}H\{^{31}P\}$ NMR (benzene-d_6, 500 MHz) {51.80 ppm} of species $[(DTBB)Rh(H)_2]_2$ (**2**)



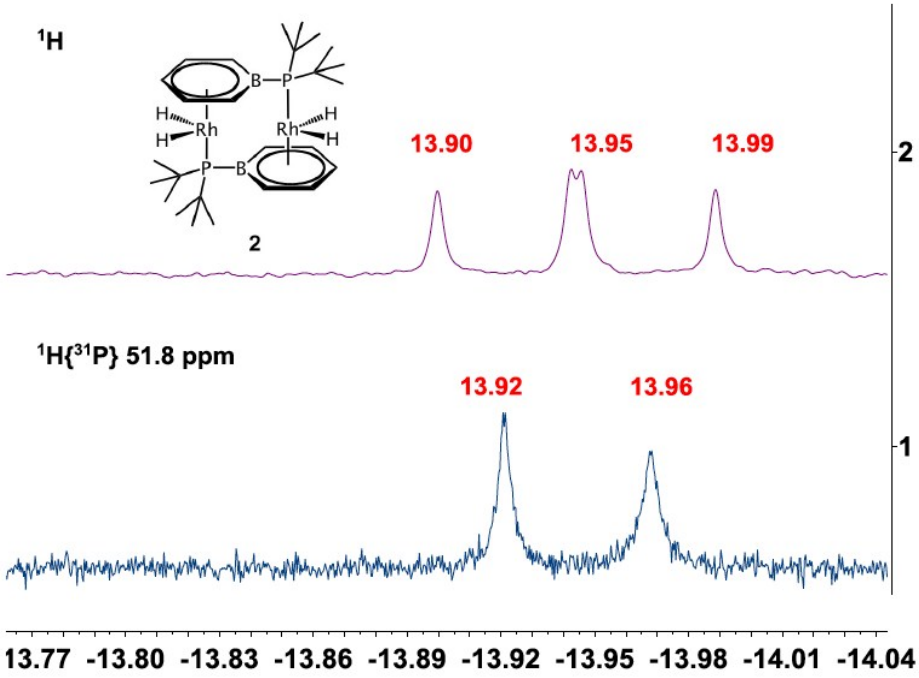

^{1}H
13.90
13.95
13.99
2
2
^{1}H{^{31}P} 51.8 ppm
13.92
13.96
1
13.77 -13.80 -13.83 -13.86 -13.89 -13.92 -13.95 -13.98 -14.01 -14.04

Figure S9. ^{1}H gCOSY NMR (benzene-d_6, 500 MHz) of species $[(DTBB)Rh(H)_2]_2$ (**2**)

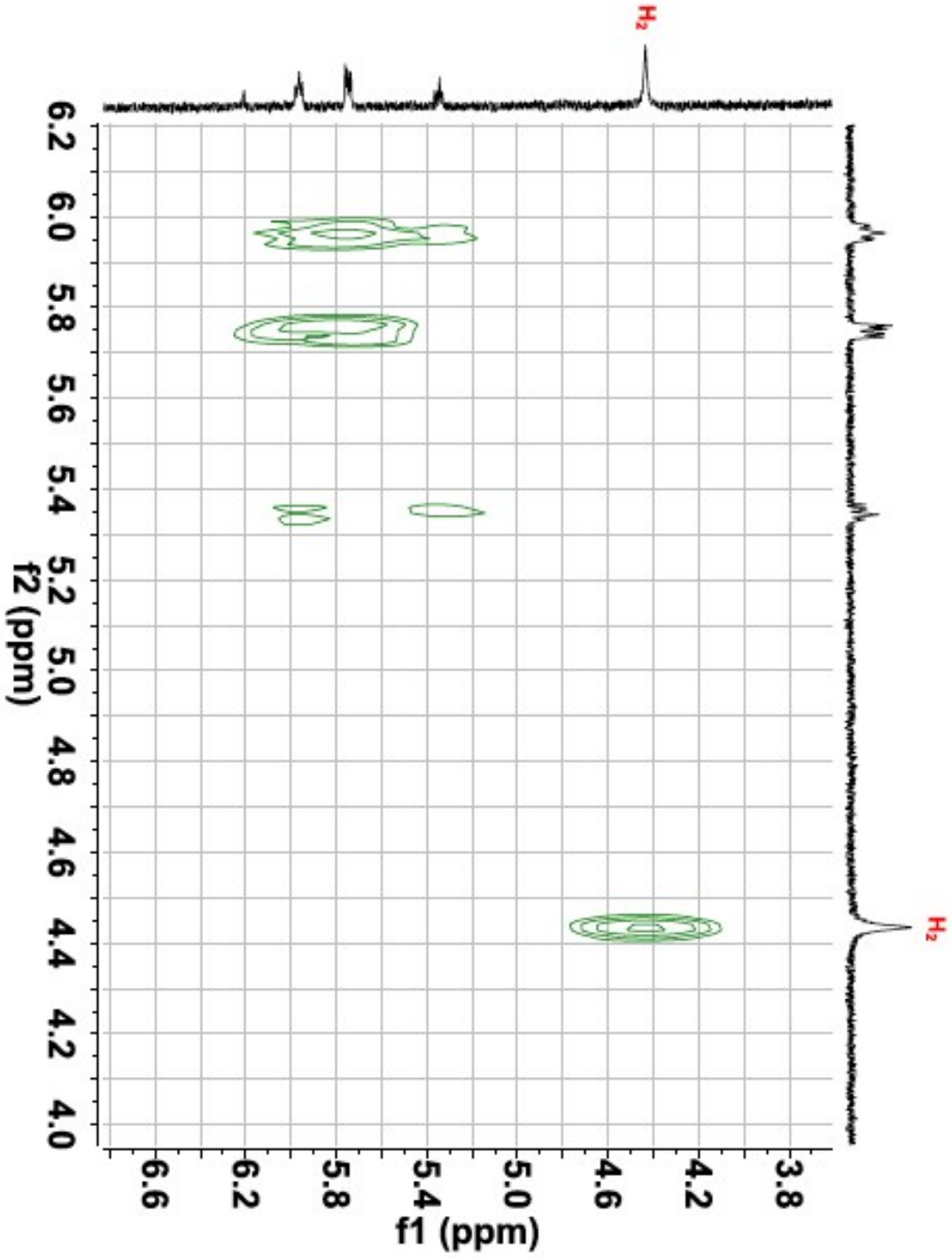


Figure S10. ^{31}P NMR (benzene-d_6, 202 MHz) of species $[(DTBB)Rh(H)_2]_2$ (**2**)

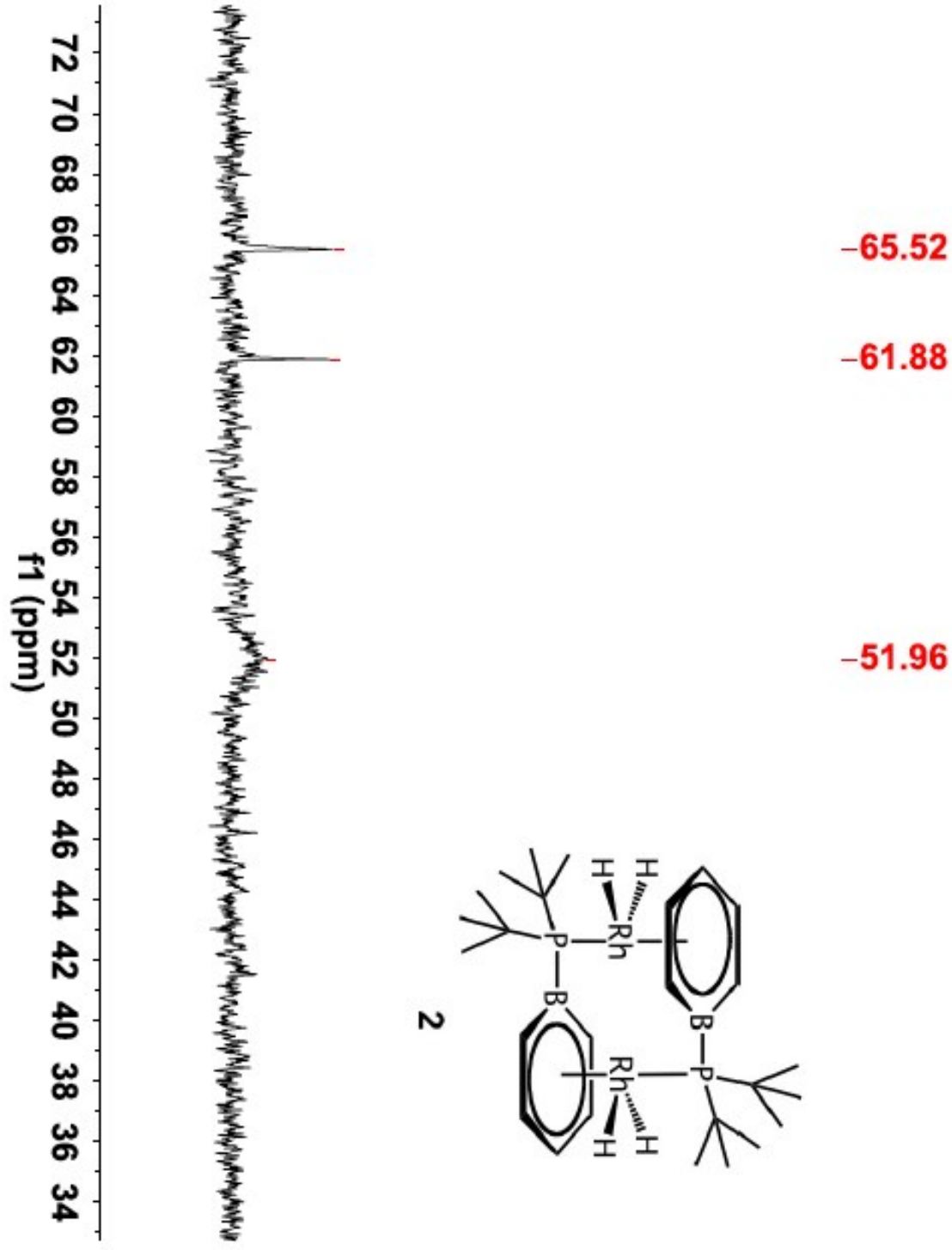


Figure S11. ^{11}B NMR (benzene-d_6, 160 MHz) of species $[(DTBB)Rh(H)_2]_2$ (**2**) after 34 000 scans

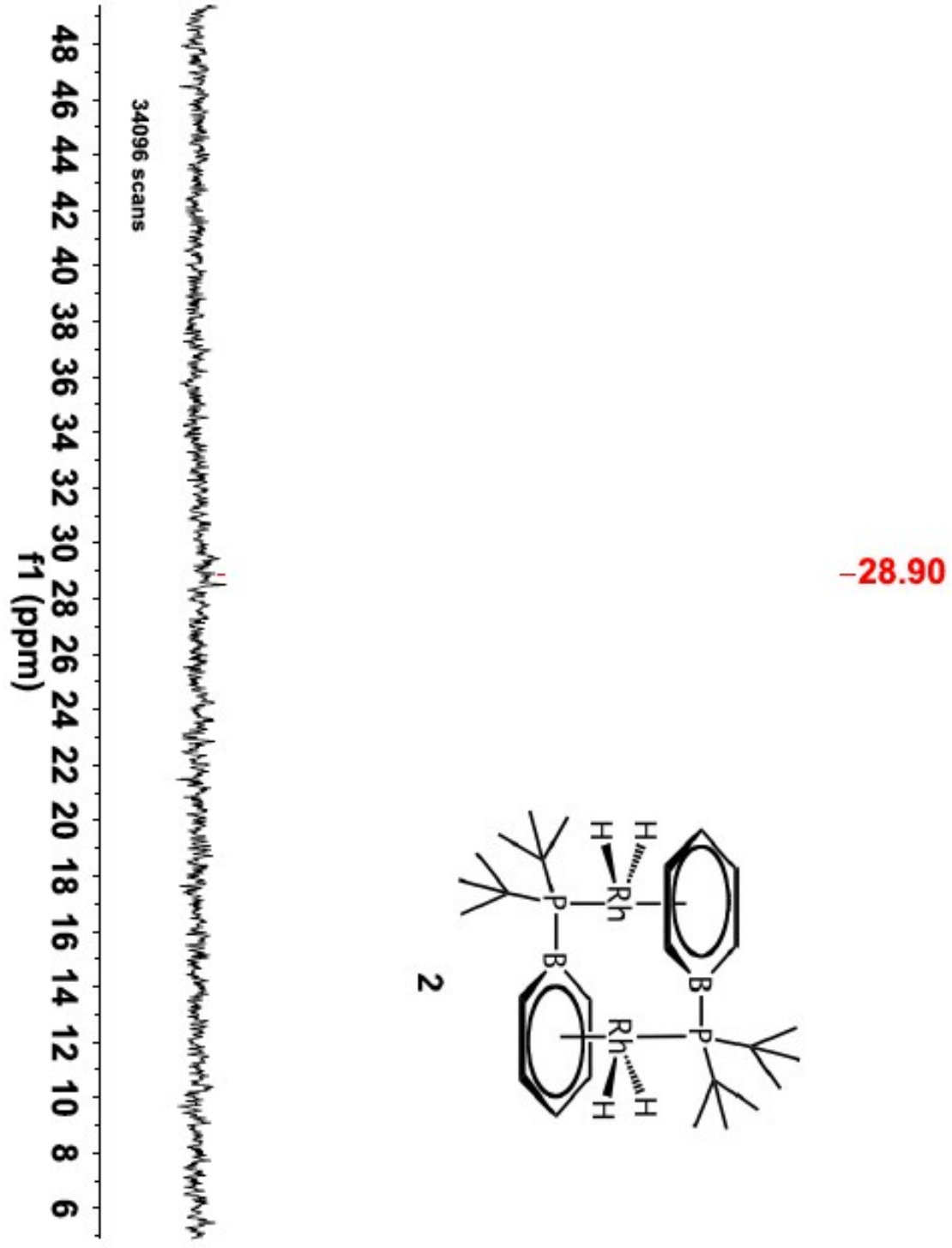


Figure S12. ^{13}C NMR (benzene-d_6, 125 MHz) of species $[(DTBB)Rh(H)_2]_2$ (**2**) (12 hours acquisition)

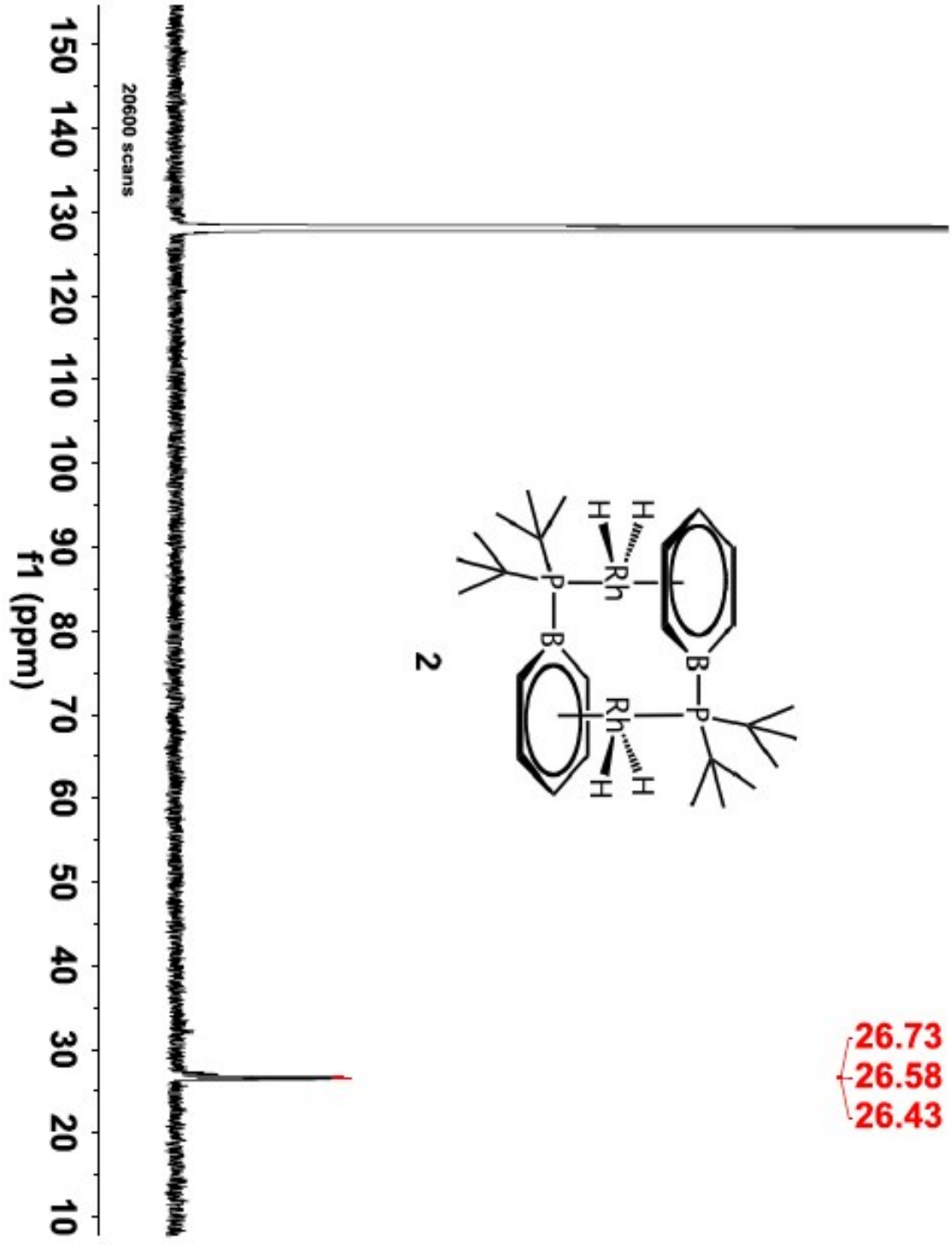
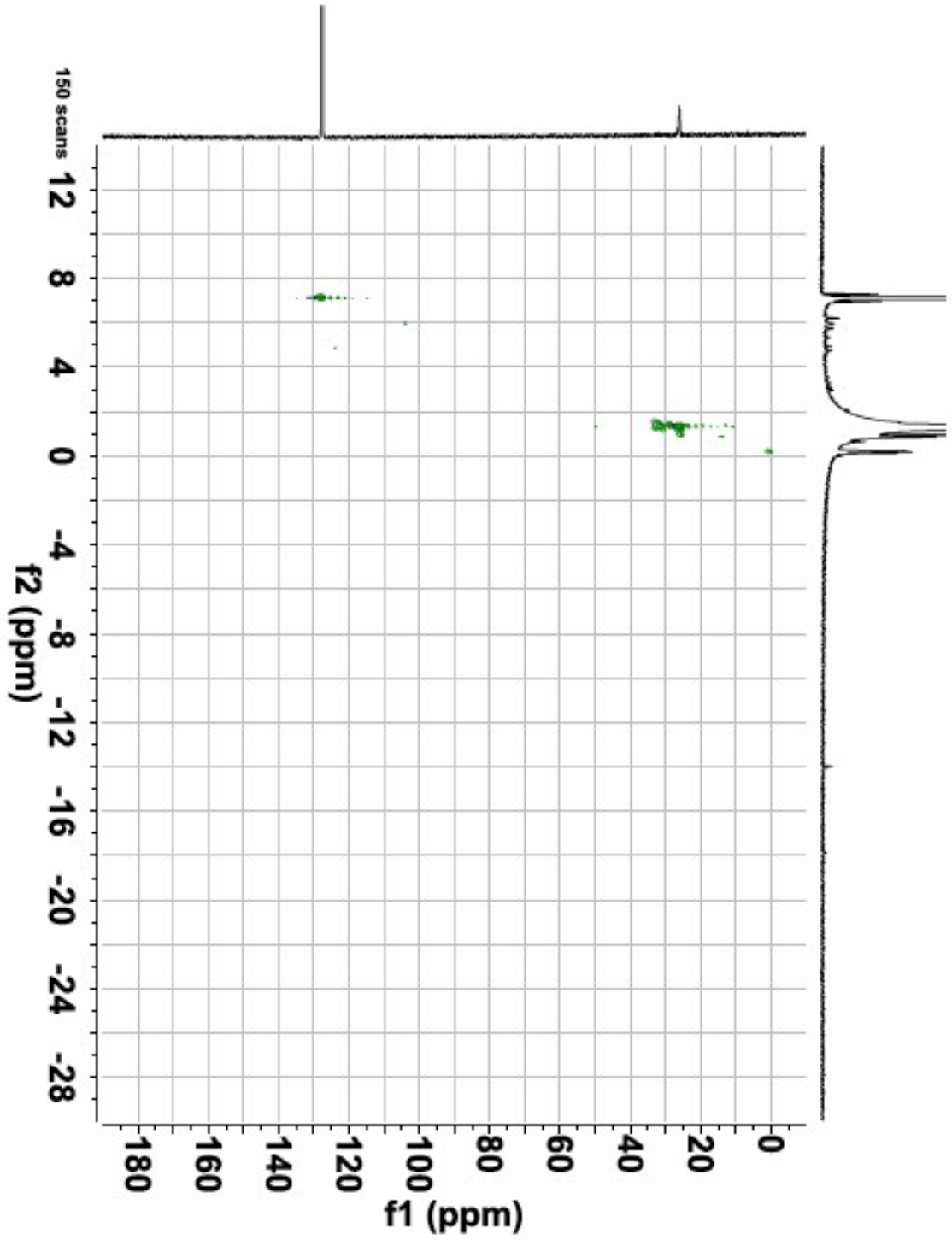


Figure S13. HSQCAD (^{1}H-^{13}C) NMR (benzene-d_6) of species $[(DTBB)Rh(H)_2]_2$ (**2**)



3- NMR Characterization of complex **3**

Figure S14. ^{1}H NMR (benzene-d_6, 500 MHz) of species $[(DTBB)Rh(H)]_2$ (**3**)

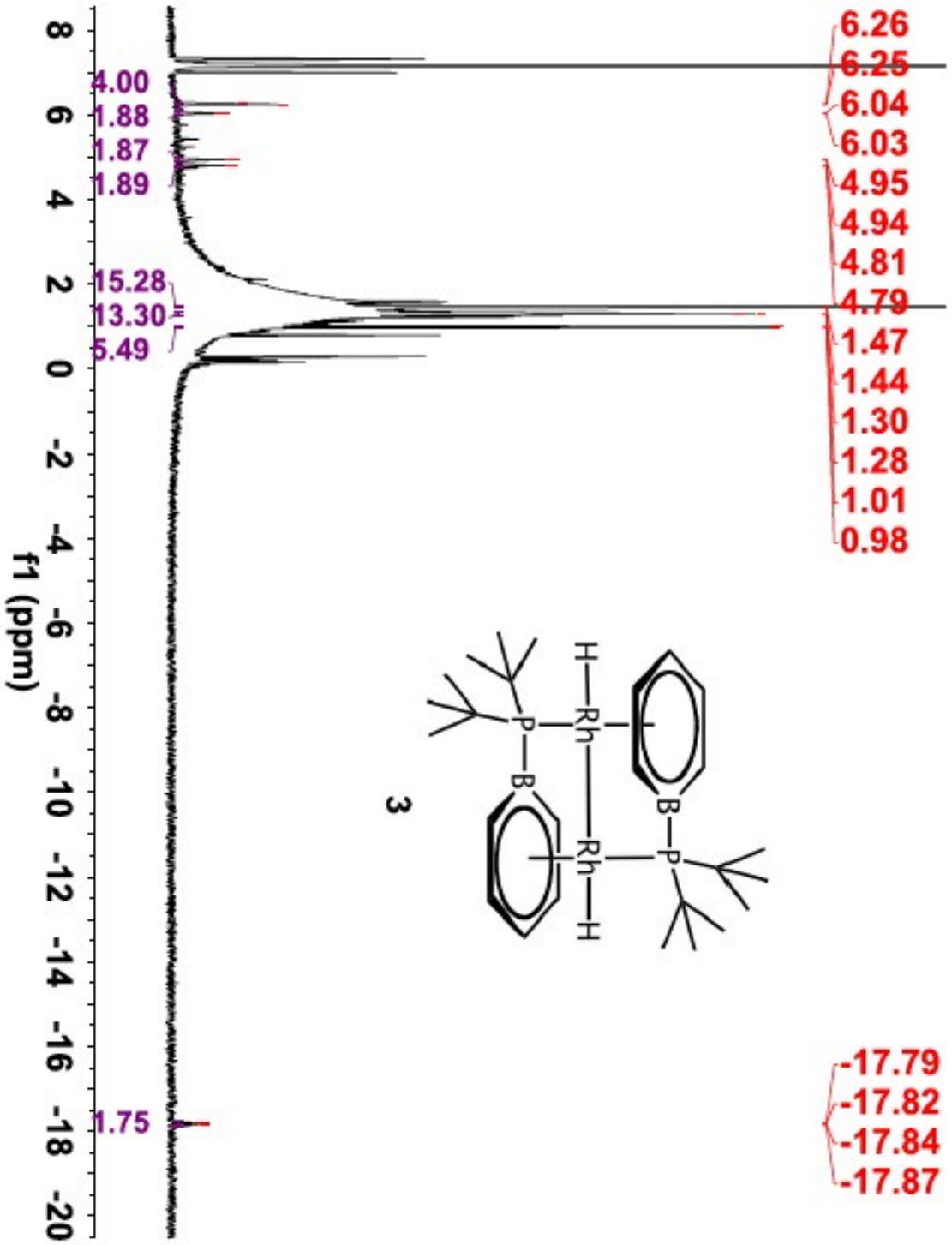
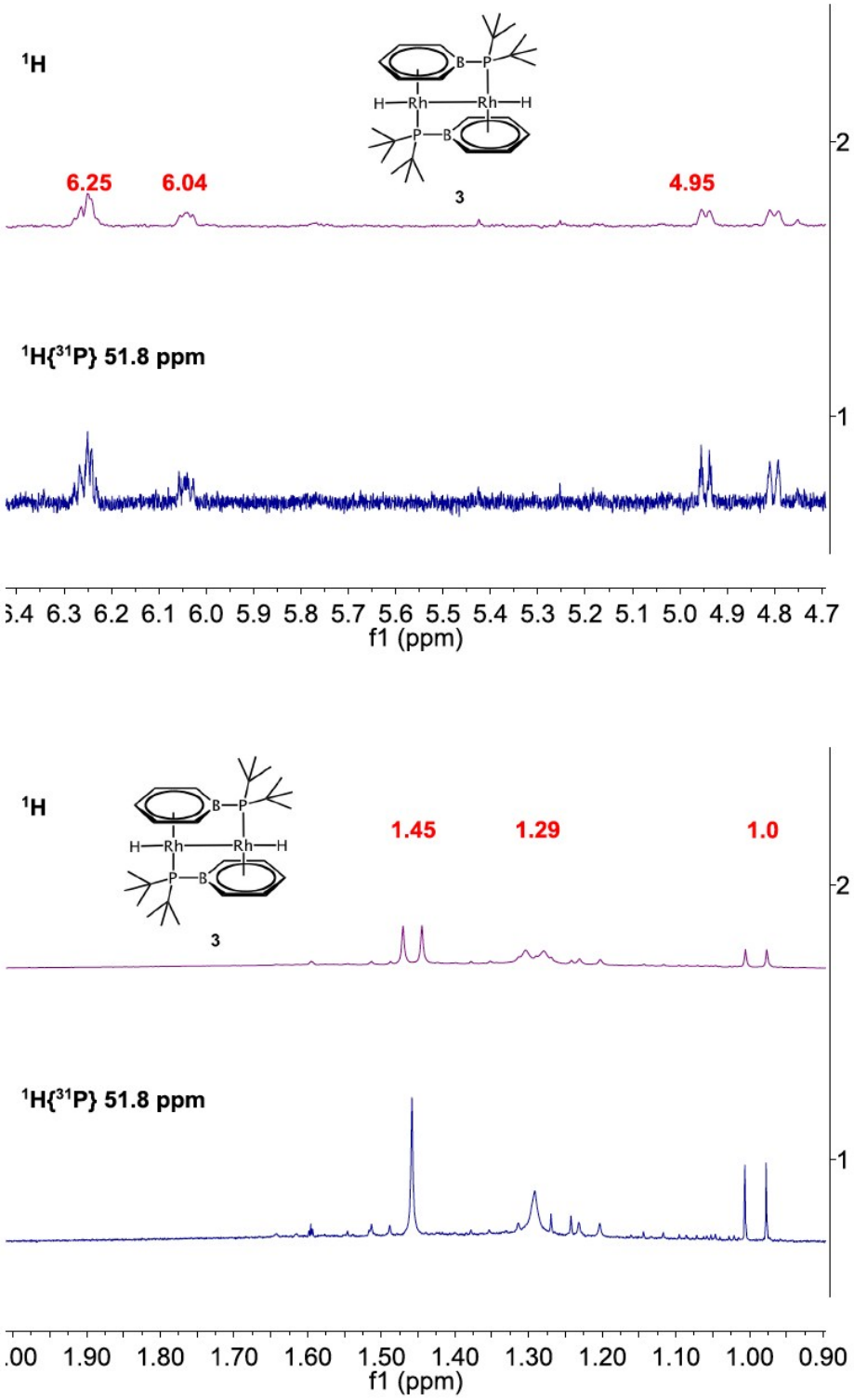


Figure S15. Selected area of the ^{1}H and $^{1}H\{^{31}P\}$ NMR (benzene-d_6, 500 MHz) {54.2 ppm} of species $[(DTBB)Rh(H)]_2$ (**3**)



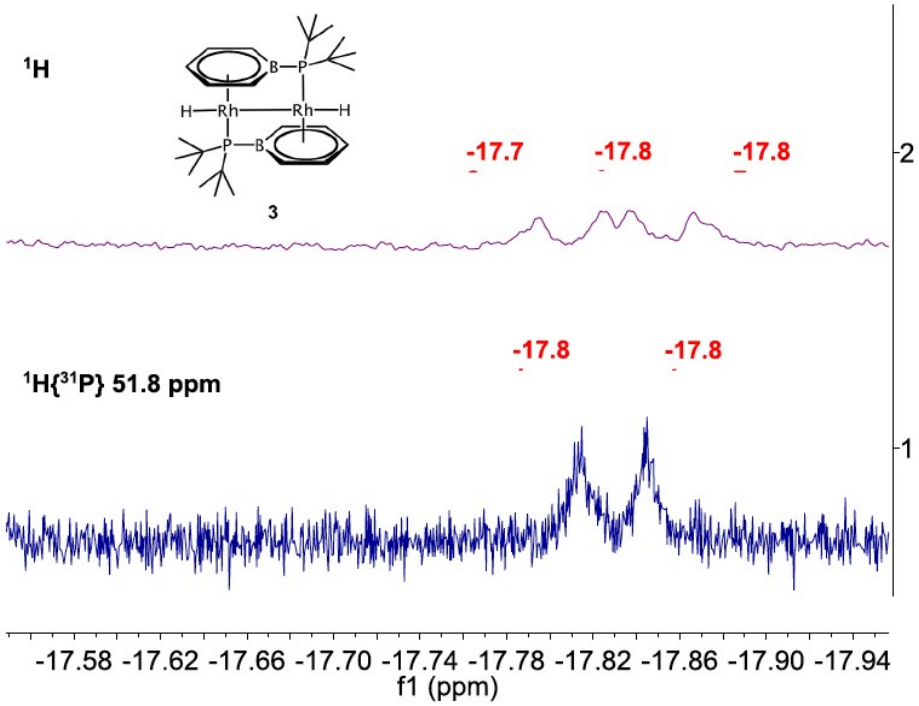

^{1}H
B—P
H—Rh—Rh—H
P—B
3
-17.7
-17.8
-17.8
2
-17.8
-17.8
^{1}H{^{31}P} 51.8 ppm
1
-17.58 -17.62 -17.66 -17.70 -17.74 -17.78 -17.82 -17.86 -17.90 -17.94
f1 (ppm)

Figure S16. ^{1}H gCOSY NMR (benzene-d_6, 500 MHz) of species $[(DTBB)Rh(H)]_2$ (**3**)

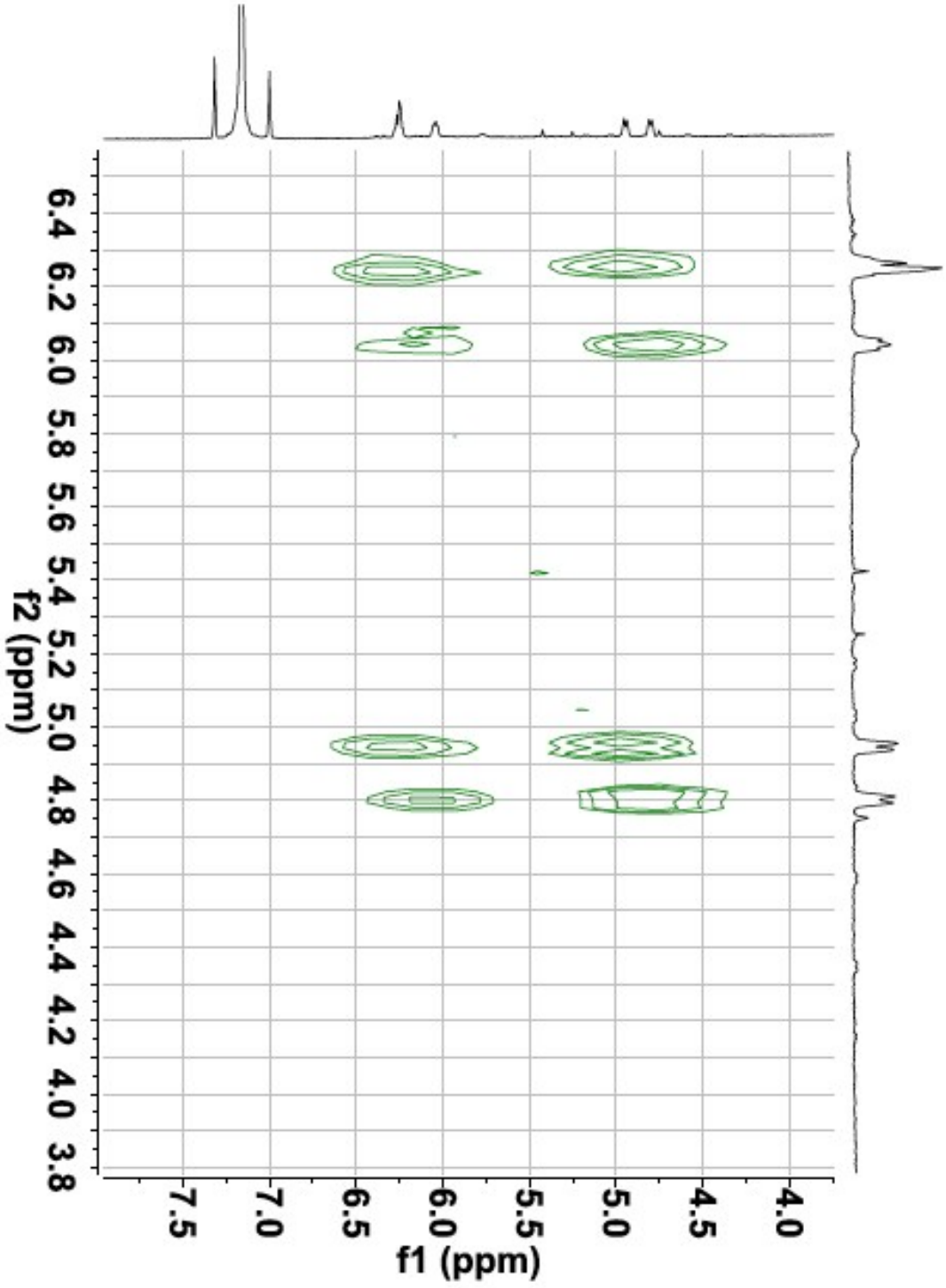


Figure S17. ^{31}P NMR (benzene-d_6, 202 MHz) of species $[(DTBB)Rh(H)]_2$ (**3**)

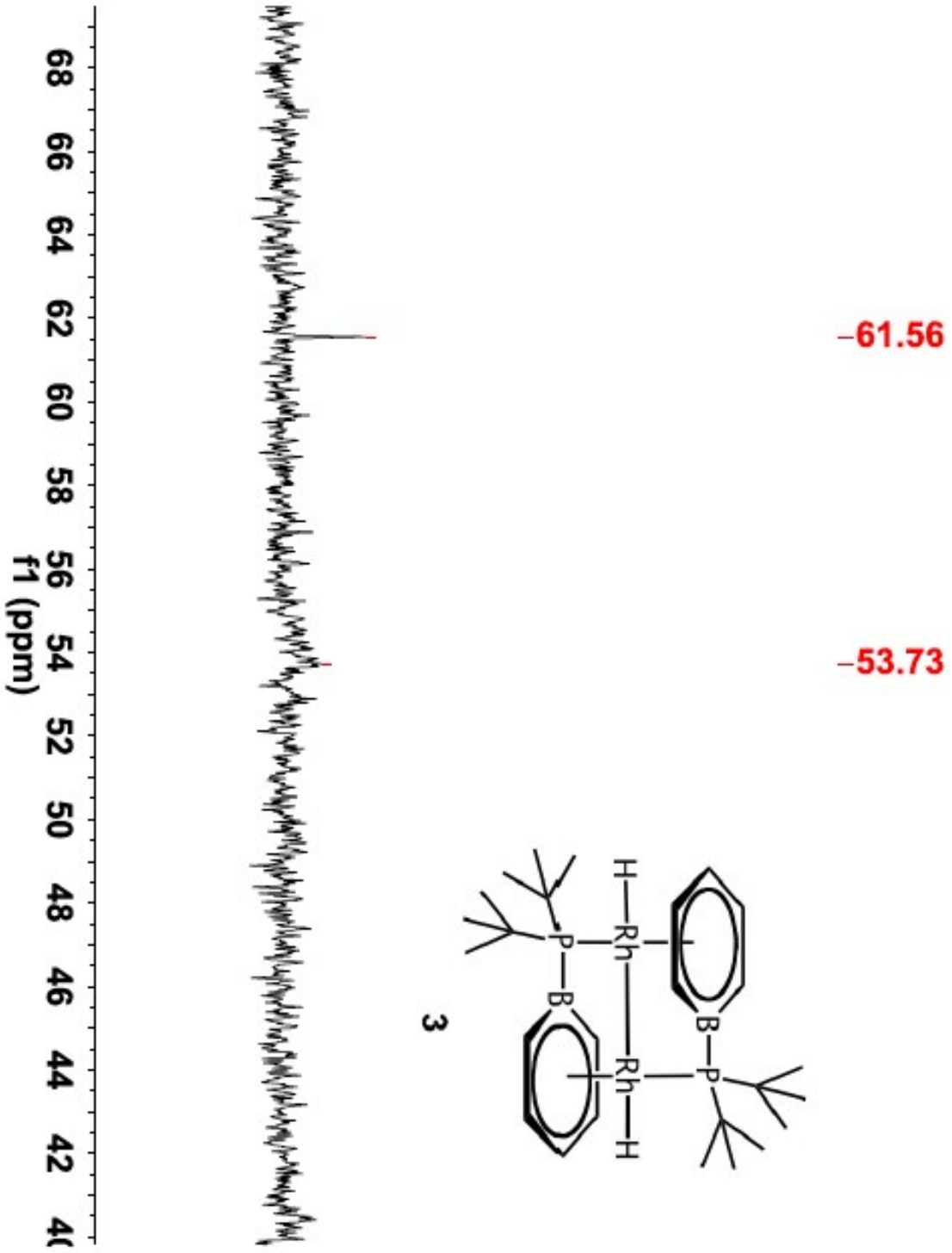


Figure S18. ^{13}C NMR (benzene-d_6, 125 MHz) of species $[(DTBB)Rh(H)]_2$ (**3**)

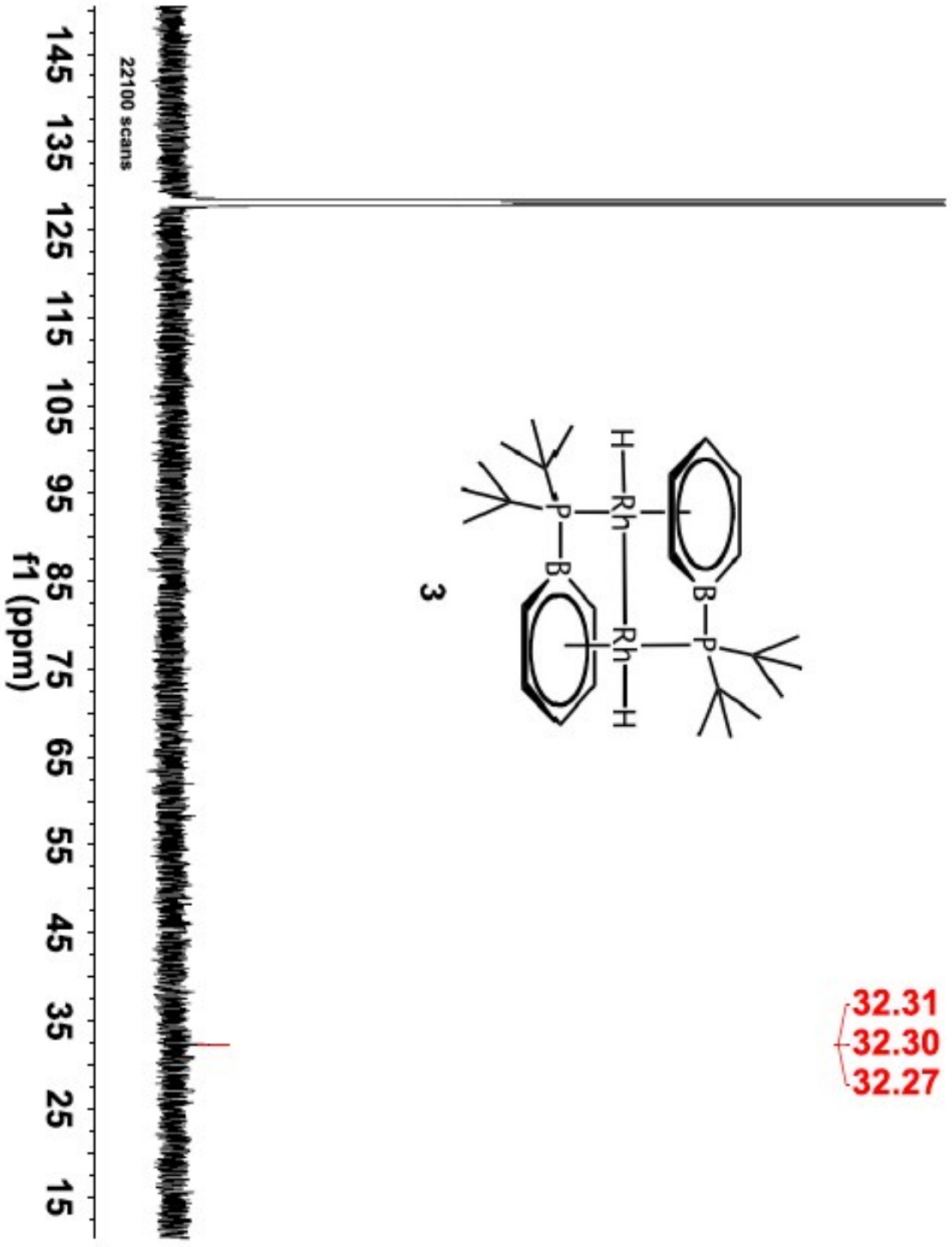


Figure S19. HSQCAD (^{1}H-^{13}C) NMR (benzene-d_6) of species [(DTBB)Rh(H)]$_2$ (**3**).

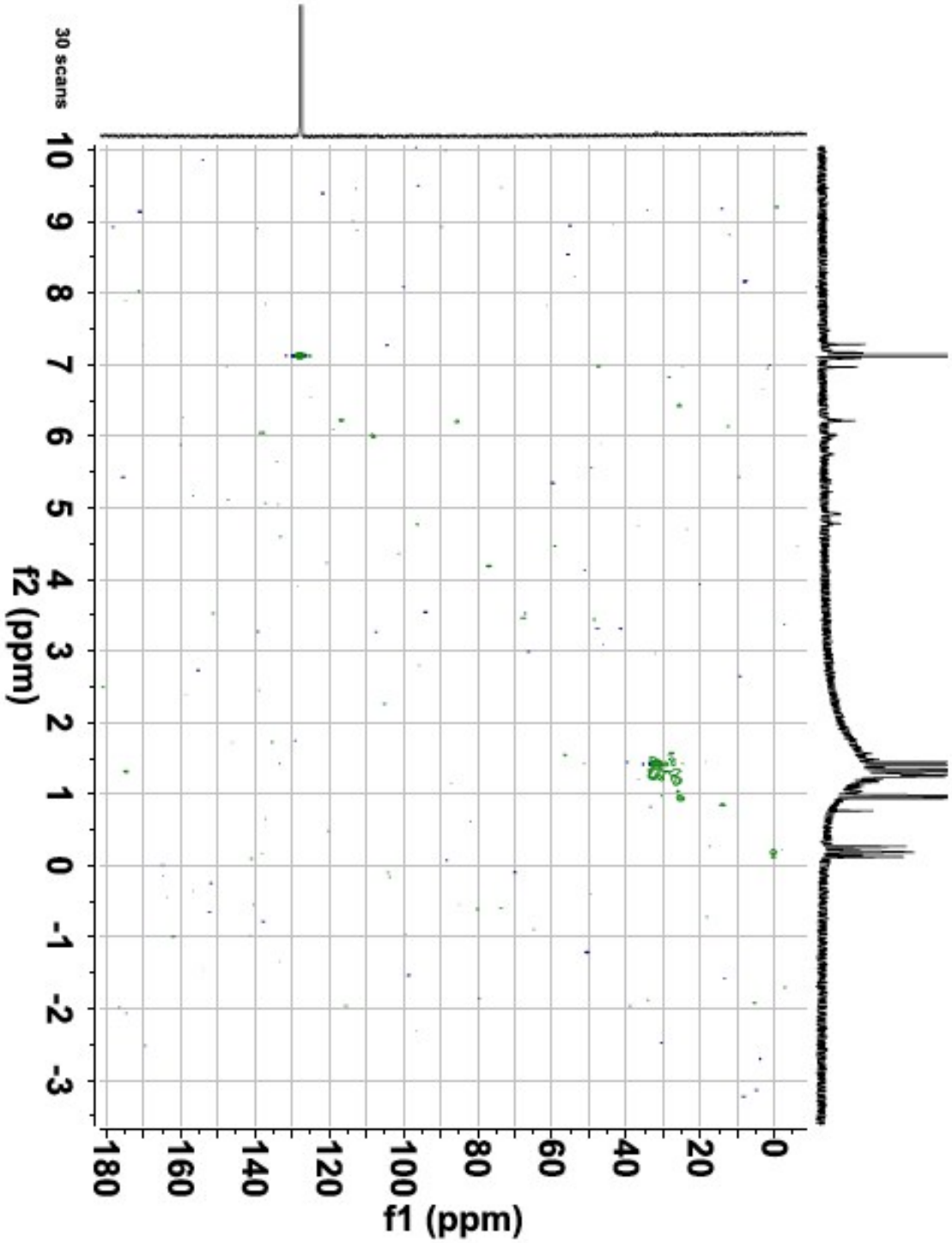


Figure S20. IR of the oil obtained from reaction of **1** with H_2

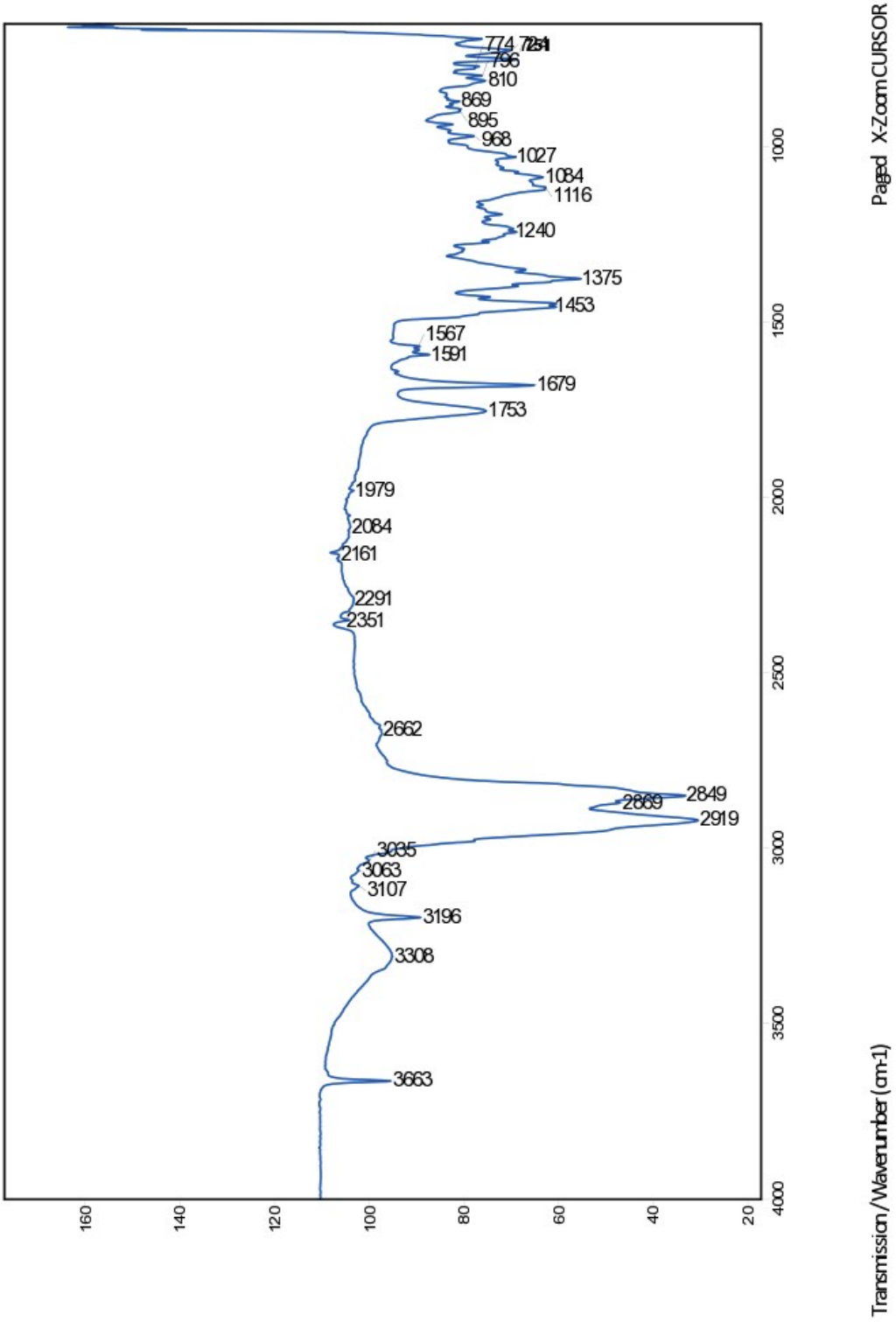


Table S1. T1(s) measurements for complexes $[(DTBB)Rh(H)_2]_2$ (2) and $[(DTBB)Rh(H)]_2$ (**3**) at different temperatures.

Temperature (K)	**2** T1 (s)[a]	**3** T1 (s)[a]
183	4.49	4.81
193	5.30	5.35
203	5.70	6.41
213	6.58	6.02
223	6.77	6.16
233	7.91	6.25
243	7.42	5.38
253	7.56	5.60
263	7.75	6.18
273	8.13	7.01
283	8.62	6.34
295	0.87[b]	6.75

[a]All measurements were carried in a 500 MHz NMR, 5 seconds were allowed between each pulse to avoid NOE effects.
[b]Measurement in a C_6D_6.

Table S2. Crystal data and structure refinement for $[(C_2H_4)Rh(DTBB)]_2$ (1).

Empirical formula	C30 H54 B2 P2 Rh2	
Formula weight	704.11	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/n	
Unit cell dimensions	a = 8.3211(8) Å	⟨= 90°.
	b = 19.9816(19) Å	®= 110.3513(14)°.
	c = 9.8002(10) Å	© = 90°.
Volume	1527.8(3) $Å^3$	
Z	2	
Density (calculated)	1.531 Mg/m^3	
Absorption coefficient	1.203 mm^{-1}	
F(000)	728	
Crystal size	0.260 x 0.100 x 0.080 mm^3	
Theta range for data collection	2.038 to 28.291°.	
Index ranges	-11<=h<=11, -26<=k<=26, -13<=l<=13	
Reflections collected	16042	
Independent reflections	3786 [R(int) = 0.0561]	
Completeness to theta = 25.242°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.908 and 0.866	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3786 / 0 / 185	
Goodness-of-fit on F^2	1.037	
Final R indices [I>2sigma(I)]	R1 = 0.0346, wR2 = 0.0758	
R indices (all data)	R1 = 0.0551, wR2 = 0.0849	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.079 and -0.438 $e.Å^{-3}$	