Supporting Information for

Long-range C-H bond activation by Rh^{III}-carboxylates

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Experimental

General Considerations. Unless otherwise noted, all synthetic procedures were performed under anaerobic conditions in a nitrogen filled glovebox or by using standard Schlenk techniques. Glovebox purity was maintained by periodic nitrogen purges and was monitored by an oxygen analyzer (O_2 < 15 ppm for all reactions). Tetrahydrofuran, pentane and diethyl ether were dried by distillation from Na/benzophenone. Benzene, hexanes and methylene chloride were purified by passage through a column of activated alumina. Trifluoroacetic acid was degassed and stored under N_2 atmosphere. Benzene-d_6, chloroform-d_1, tetrahydrofuran-d_8 and nitromethane-d_3 were stored over 4 Å molecular sieves in a nitrogen atmosphere. Trifluoroacetic acid-d_1 was stored under N_2. ^{1}H NMR spectra and ^{13}C NMR spectra were recorded Varian Inova 500 MHz and Bruker DRX 600 MHz spectrometer. ^{19}F NMR spectra was recorded on a Varian Mercury Plus 300 MHz. All ^{1}H and ^{13}C NMR spectra are referenced against residual proton signals (^{1}H NMR) or the ^{13}C resonances of the deuterated solvent. $\{(COE)_2Rh(\mu\text{–}TFA)\}_2$[2] was prepared according to published literature procedures. All other reagents were used as purchased from commercial sources.

Synthesis of 8,8'-(4,5-*o*-xylene)diquinoline (Q_2X) (1). Quinolin-8-ylboronic acid (0.720 g, 4.00 x10^{-3} mol, 2.2 equiv.), 4,5-dibromo-*o*-xylene (0.478 g, 1.81 x10^{-3} mol, 1 equiv.), $Pd(PPh_3)_4$ (0.200 g, 2.18 x10^{-4} mol, 0.12 equivalents), and K_3PO_4 (15.0 g, 7.07 x10^{-2} mol, 39 equiv.) were combined into the 250 mL Schlenk flask. Under an inert atmosphere, degassed dimethylformaldehyde (20 mL) and degassed DI water (20 mL) were added to the Schlenk flask, and the flask was fitted with a glass stopper and sealed. The glass stopper was secured to the Schlenk flask with several rubber bands, and then the reaction mixture was heated in an oil bath at 100 °C with stirring. After 20 minutes, the sealed Schlenk flask was gently shaken to re-dissolve 4,5-dibromo-*o*-xylene, which sublimed along the walls of the flask. The reaction mixture was stirred vigorously with continued heating at 100 °C for 14 h, then heated for an additional 6 h at 120 °C. Afterwards, the reaction mixture was allowed to cool to room temperature, during which the aqueous and organic layers separated, and a red-white precipitate formed. The lower aqueous phase was separated from the organic phase by separatory funnel and discarded. The organic layer along with the solid precipitate was collected, and a copious amount of DI water (500 mL) was added to precipitate a light pink solid. The solid was collected by filtration and washed with water. The solid was triturated wth Et_2O (10 mL) and filtered (3x). The solid was collected and dried under vacuum for several hours. Afterwards, the solid was dissolved in toluene (50 mL) and filtered. The filtrate was reduced to 5 mL, and pentane (50 mL) was added to precipitate analytically pure **1** (0.247 g, Yield = 38%). ^{1}H NMR (C_6D_6, 500 MHz): δ = 8.75 (br, 2H, Ar–*H*), 7.58 (d, 2H, Ar–*H*, $^3J_{HH}$= 7 Hz), 7.54 (s, 2H, Ar–*H*), 7.44 (d, 2H, Ar–*H*, $^3J_{HH}$ = 8 Hz), 7.11 (d, 2H, Ar–*H*, $^3J_{HH}$ = 8 Hz), 6.79 (t, 2H, Ar–*H*, $^3J_{HH}$ = 8 Hz), 6.72 (m, 2H, Ar–*H*), and 2.17 (s, 6H, -C*H*$_3$) ppm. ^{13}C{^{1}H} NMR (C_6D_6, 150 HMz): δ = 150.0 (s, Ar–*C*), 147.0 (s, Ar–*C*), 137.1 (s, Ar–*C*), 135.8 (s, Ar–*C*), 135.3 (s, Ar–*C*), 133.0 (s, Ar–*C*), 131.1 (s, Ar–*C*), 128.1 (s, Ar–*C*), 126.6 (s, Ar–*C*), 125.5 (s, Ar–*C*), 120.4 (s, Ar–*C*), and 19.9 (s, –*C*H$_3$) ppm. Anal. Calcd. for $C_{26}H_{20}N_2$ (360.46 g/mol): C: 86.64%; H: 5.59%; N: 7.77%, Found; C: 86.79%; H: 5.64%; N: 7.93%.

Synthesis of (Q_2X)Rh(TFA)(COE) (2). Solid ligand **1** (0.220 g, 6.1 x10^{-4} mol) was added to a THF solution (20 mL) of $\{Rh(\mu\text{–}TFA)(COE)_2\}_2$ (0.266 g, 6.1 x10^{-4} mol) and stirred for 0.5 h. The solution was filtered and then reduced in vacuo to 5 mL. Pentane (25 mL) was added to the solution to precipitate an orange powder. The solid was collected by filtration, washed with pentane (2x 5 mL), and dried under

vacuum to afford the analytically pure **2** (0.351 g, yield = 90%). ^{1}H NMR (d_8-THF, 600 MHz): δ = 10.60 (s, 1H, Ar–*H*), 8.26 (s, 1H, Ar–*H*), 8.12 (d, 1H, Ar–*H*, $^{3}J_{HH}$ = 8 Hz), 7.98 (d, 1H, Ar–*H*, $^{3}J_{HH}$ = 8 Hz), 7.92 (s, 1H, Ar–*H*), 7.87 (br, 1H, Ar–*H*), 7.75 (d, 1H, Ar–*H*, $^{3}J_{HH}$ = 8 Hz), 7.55 (br, 3H, Ar–*H*), 7.44 (d, 1H, Ar–*H*, $^{3}J_{HH}$ = 8 Hz), 6.95 (br, 1H, Ar–*H*), 6.79-6.86 (br, 1H, Ar–*H*), 6.67 (s, 1H, Ar–*H*), 5.60 (br, 2H, =C*H*, COE), 2.77 (s, 1H, COE-*H*), 2.46 (s, 3H, -CH_3), 2.25 (s, 3H, -CH_3), 2.04-2.3 (m, 4H, COE-*H*), 1,12-1,77 (m, 7H, COE-*H*) ppm. ^{19}F NMR (d_8-THF, 282 MHz): δ = -75.9 (s, TFA, minor isomer- 28%) and -76.0 (s, TFA, major isomer- 72%) ppm. ^{13}C{^{1}H} NMR (d_8-THF, 150 HMz): δ = 157.5 (s, Ar–*C*), 156.6 (s, Ar–*C*), 152.5 (s, Ar–*C*), 150.9 (s, Ar–*C*), 142.3 (s, Ar–*C*), 141.6 (s, Ar–*C*), 137.1 (s, Ar–*C*), 136.8 (s, Ar–*C*), 136.0 (s, Ar–*C*), 134.5 (s, Ar–*C*), 134.1 (s, Ar–*C*), 133.7 (s, Ar–*C*), 133.4 (s, Ar–*C*), 132.4 (s, Ar–*C*), 131.8 (s, Ar–*C*), 131.7 (s, Ar–*C*), 130.9 (s, =C*H*, COE), 129.6 (s, Ar–*C*), 129.4 (s, Ar–*C*), 129.2 (s, Ar–*C*), 128.5 (s, Ar–*C*), 128.4 (s, Ar–*C*), 128.1 (s, Ar–*C*), 127.6 (s, Ar–*C*), 127.4 (s, Ar–*C*), 126.2 (s, Ar–*C*), 31.1 (s, COE-*C*), 30.6 (s, COE-*C*), 30.2 (s, COE-*C*), 28.5 (s, COE-*C*), 27.8 (s, COE-*C*), 27.6 (s, COE-*C*), 27.2 (s, COE-*C*), 26.6 (s, COE-*C*), 26.4 (s, COE-*C*), 26.0 (s, COE-*C*), 20.3 (s, –*C*H_3), and 19.7 (s, –*C*H_3) ppm. Anal. Calcd. for $C_{36}H_{34}F_3N_2O_2Rh$ (686.58 g/mol): C: 62.98%; H: 4.99%; N: 4.08%, Found; C: 63.04%; H: 5.05%; N: 4.06%.

Synthesis of $(Q_2X)Rh(TFA)_3$ (3). Complex **2** (0.100 g, 1.58 x10^{-4} mol) was dissolved HTFA (10 mL) and $Cu(TFA)_2(OH_2)_2$ (0.186 g, 5.71 x10^{-4} mol) was added. The reaction mixture was stirred for 2 h, and then the solvent was reduced in vacuo to 2 mL. The reaction solution was diluted with CH_2Cl_2 (10 mL), and then Et_2O (5 mL) and pentane (30 mL) were added to the solution in the corresponding order. An oil residue that precipitated was separated by filtration from a blue/purple solution. The oil was redissolved in CH_2Cl_2 (5 mL) along with 1 mL of HTFA. Again Et_2O (5 mL) and pentane (30 mL) in sequential order were added to precipitate a light brown powder. The solid was separated from a light blue solution by filtration. This process of dissolving in CH_2Cl_2/HTFA and adding Et_2O and pentane was continued two times more until a yellow precipitate forms and the corresponding filtrate is colorless. The isolated yield of **3** was 0.058 g (49%). ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 9.28 (s, 2H, Ar–*H*), 8.25 (s, 2H, Ar–*H*), 7.70 (s, 2H, Ar–*H*), 7.54 (s, 2H, Ar–*H*), 7.53 (s, 2H, Ar–*H*), 7.48 (s, 2H, Ar–*H*), 7.25 (s, 2H, Ar–*H*), and 2.42 (s, 6H, –CH_3) ppm. ^{19}F NMR ($CDCl_3$, 282 MHz): δ = -74.9 (s, 6F, TFA) and -75.0 (s, 3F, TFA) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 150 MHz): δ = 153.6 (s, Ar–*C*), 152.2 (s, Ar–*C*), 146.8 (s, Ar–*C*), 140.3 (s, Ar–*C*), 139.6 (s, Ar–*C*), 137.8 (s, Ar–*C*), 133.6 (s, Ar–*C*), 130.1 (s, Ar–*C*), 129.2 (s, Ar–*C*), 128.5 (s, Ar–*C*), 128.2 (s, Ar–*C*), and 20.0 (s, –*C*H_3) ppm. Anal. Calcd. for $C_{32}H_{20}F_9N_2O_6Rh$ (754.41 g/mol): C: 47.90%; H: 2.51%; N: 3.49%, Found; C: 47.84%; H: 2.33%; N: 3.37%.

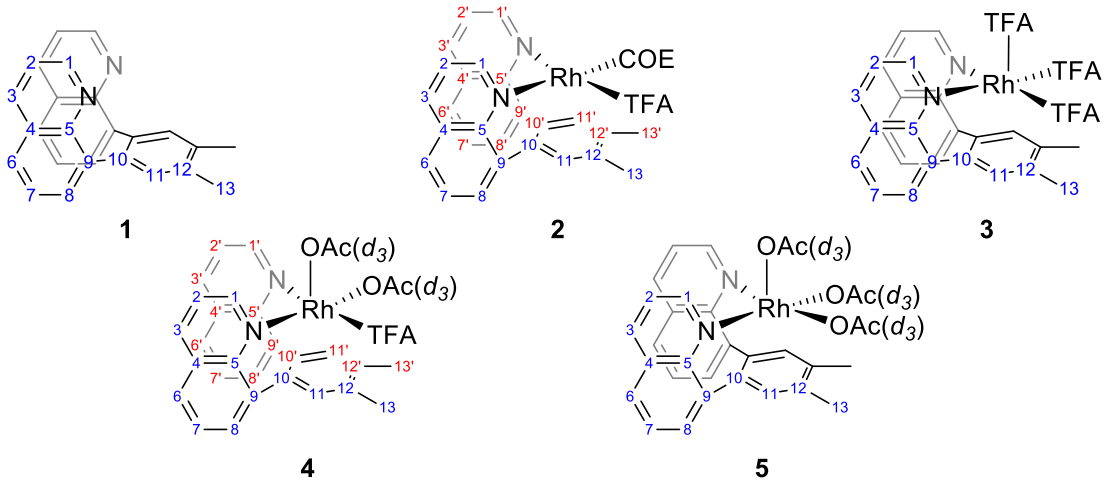


Table S1. Assigned ^{1}H and ^{13}C chemical shifts for complexes **1-6**.

	1		**2**		**3**		**4**		**5**	
Position	^{1}H	^{13}C	^{1}H	^{13}C	^{1}H	^{13}C	^{1}H	^{13}C	^{1}H	^{13}C
1	8.85	149.8	10.60	157.1	9.28	153.6	9.56	154.6	8.99	156.8
1'			8.27	156.4			8.66	153.2		
2	6.60	120.6	7.55	121.5	7.54	120.8	7.84	123.7	7.49	123.9
2'			6.67	121.6			7.49	123.3		
3	7.32	137.1	8.12	136.7	8.25	140.3	8.49	141.1	8.29	140.2
3'			7.74	135.2			8.40	141.7		
4		128.5		129.0	7.70	130.1		129.3		130.4
4'				129.6				130.3		
5		147.9		150.7	7.48	152.2		153.2		151.9
5'				152.4				151.7		
6	6.98	127.0	6.84	133.7	7.25	133.6	7.81	133.5	7.71	134.7
6'			7.55	127.1			7.14	135.9		
7	6.76	126.0	6.95	126.1		128.2	7.78	128.4	7.60	128.8
7'			7.55	127.1			7.39	129.2		
8	7.61	132.2	7.44	127.3		129.2	7.93	129.4	7.80	129.3
8'			7.86	137.3			7.78	129.7		
9		142.6		141.6		137.8		141.1		138.6
9'				142.3				141.4		
10		131.4		136.0		146.8		147.9		142.6
10'				136.0				145.4		
11	7.36	133.0	7.99	130.9	7.53	139.6	8.16	139.9	7.67	136.1
11'			7.93	132.7			7.45	140.6		
12		136.4		128.2		128.5		NA		128.8
12'				127.2				NA		
13	2.20	19.5	2.46	22.1	2.42	20.0	2.45	20.0	NA	19.7
13'			2.25	20.0			2.32	19.7		

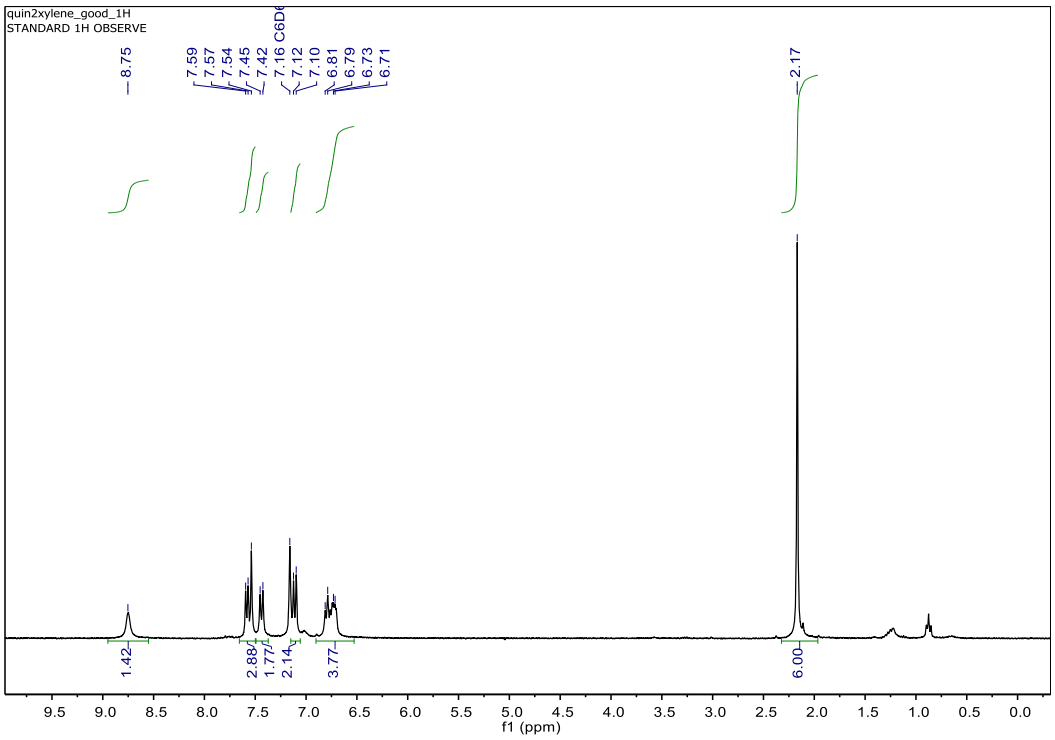


Figure S1. ^{1}H NMR (C_6D_6, 500 MHz) spectrum of **1**.

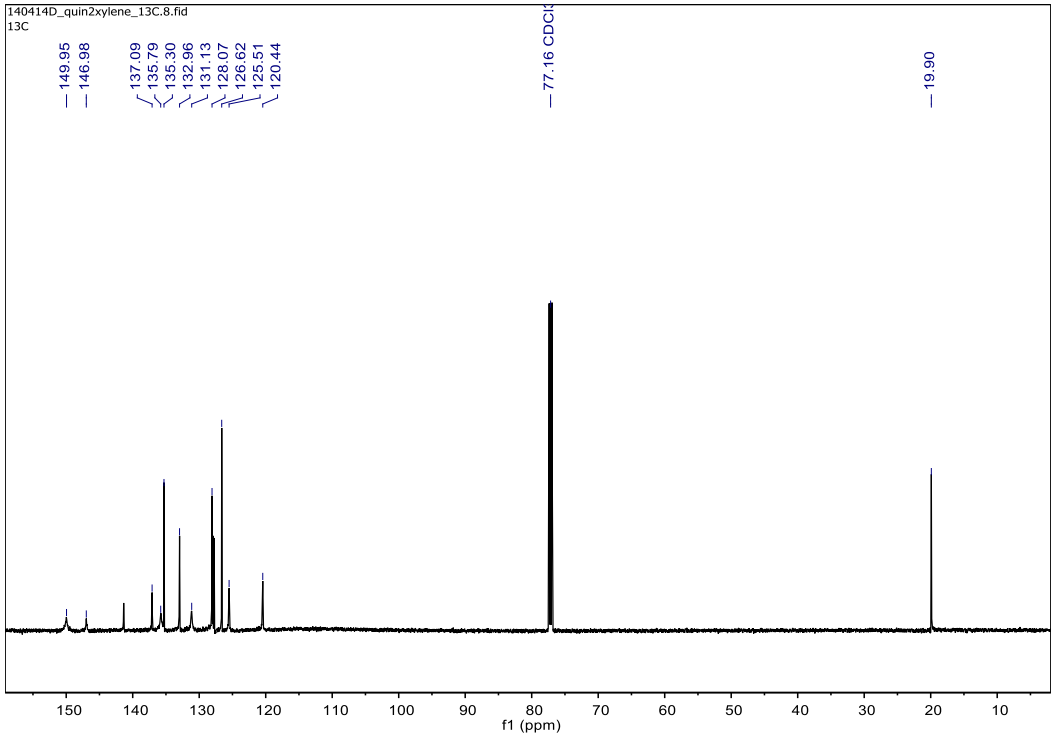


Figure S2. ^{13}C{^{1}H} NMR (C_6D_6, 150 MHz) spectrum of **1**.

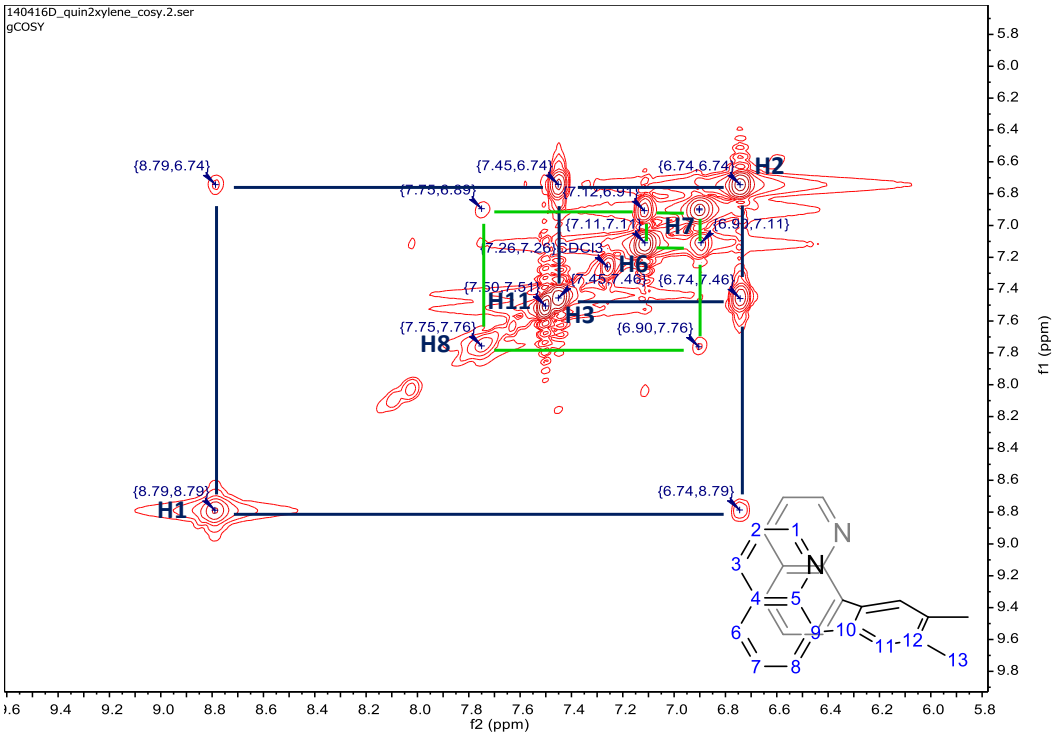


Figure S3. gCOSY NMR ($CDCl_3$, 600 MHz) spectrum of **1**.

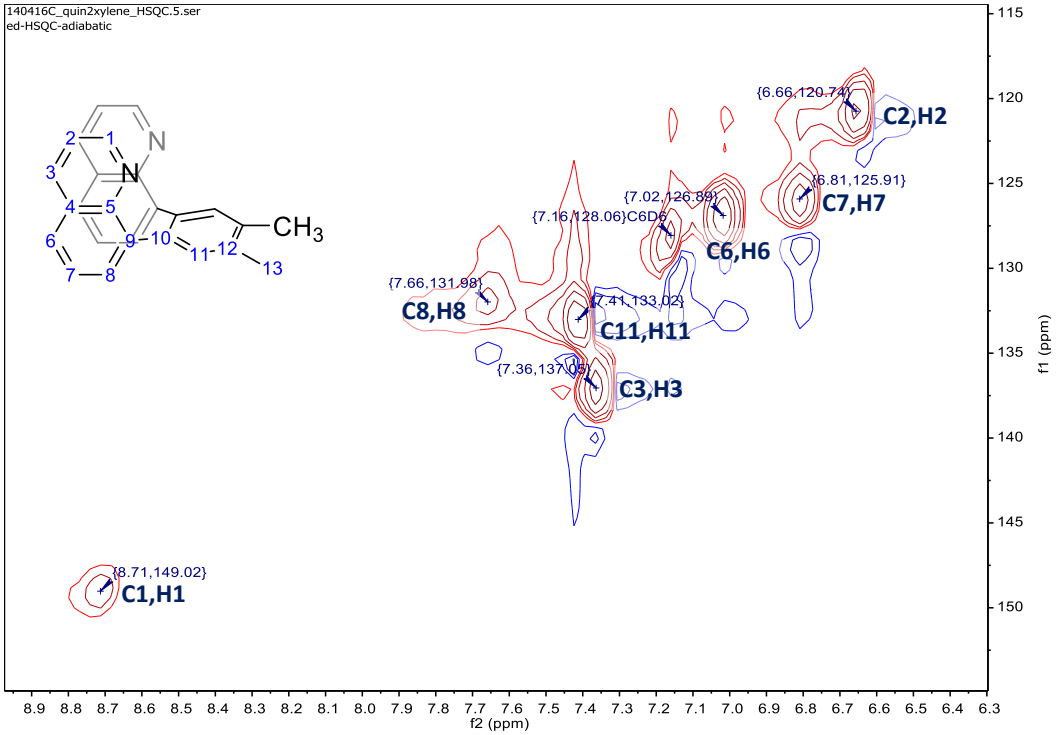


Figure S4. gHSQC NMR ($CDCl_3$, 600 MHz) spectrum of **1**.

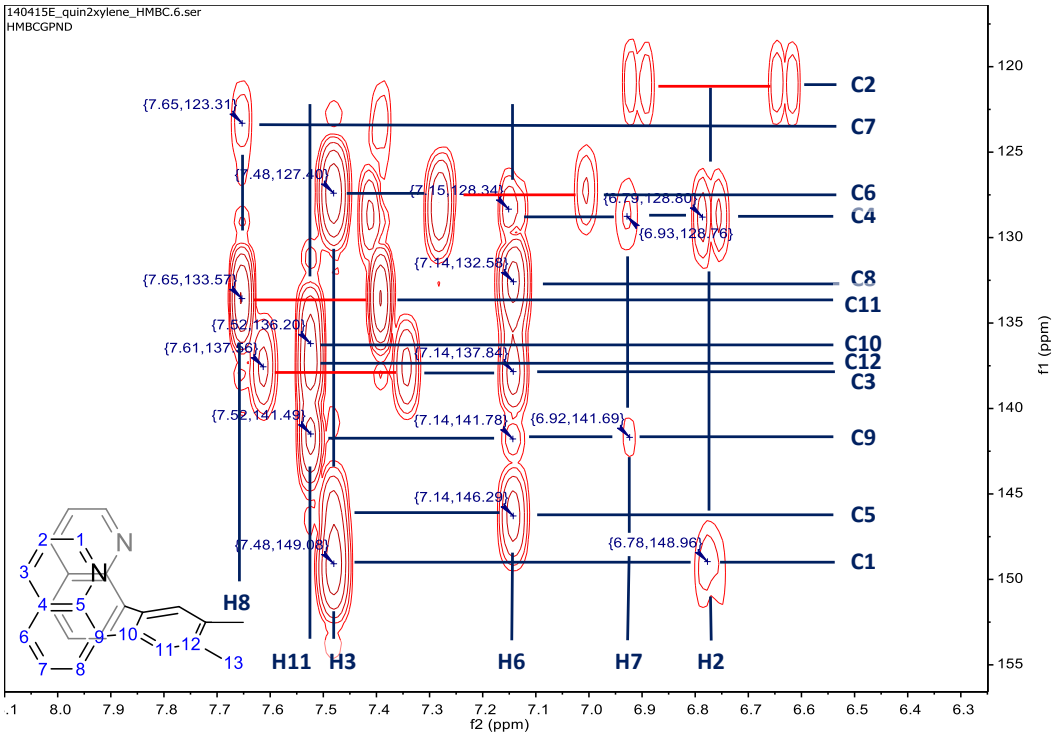


Figure S5. gHMBC NMR ($CDCl_3$, 600 MHz) spectrum of **1**.

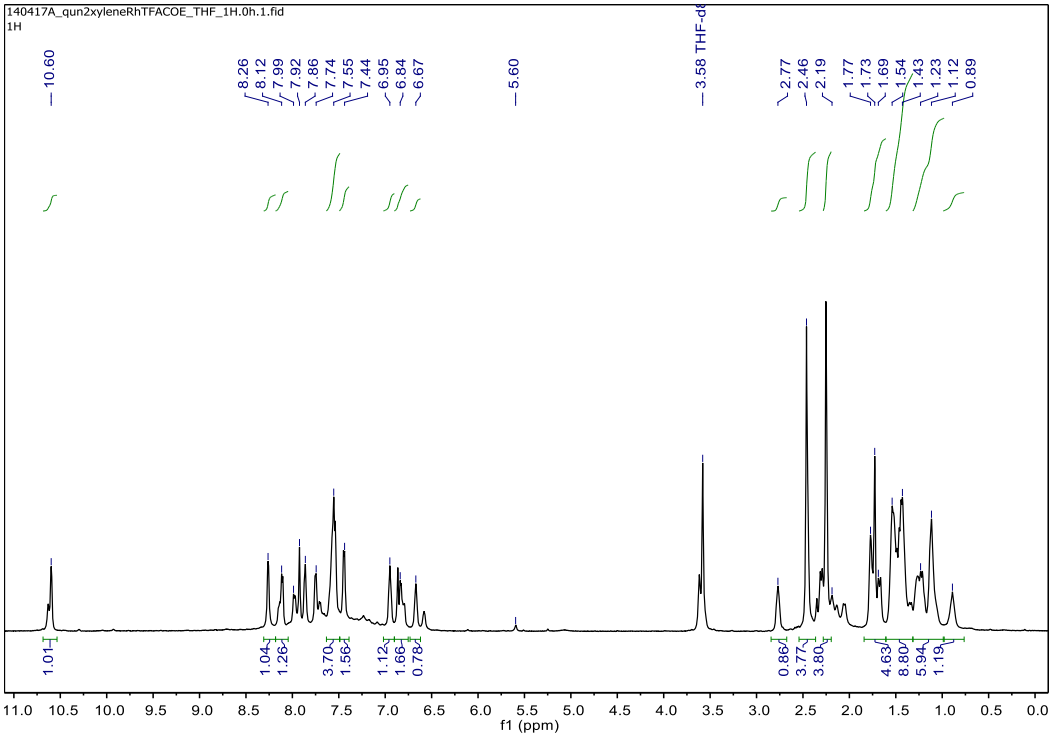


Figure S6. ^{1}H NMR (d_8-THF, 600 MHz) spectrum of **2**.

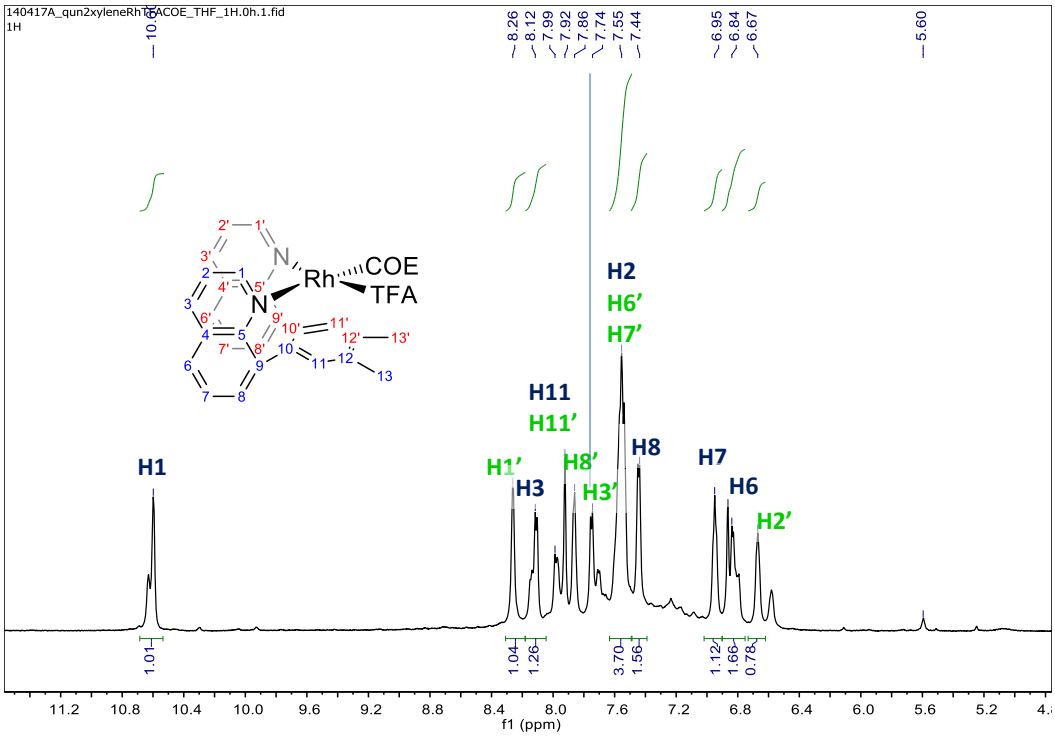


Figure S7. ^{1}H NMR (d_8-THF, 600 MHz) spectrum of **2** (expanded).

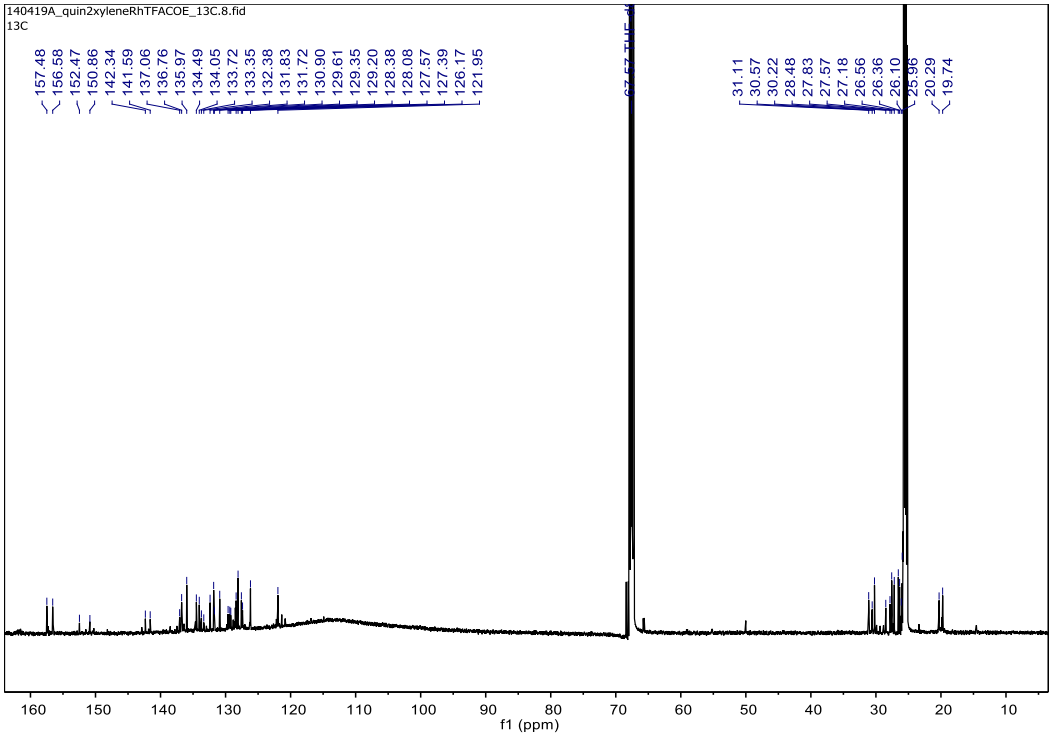


Figure S8. ^{13}C{^{1}H} NMR (d_8-THF, 126 MHz) spectrum of **2**.

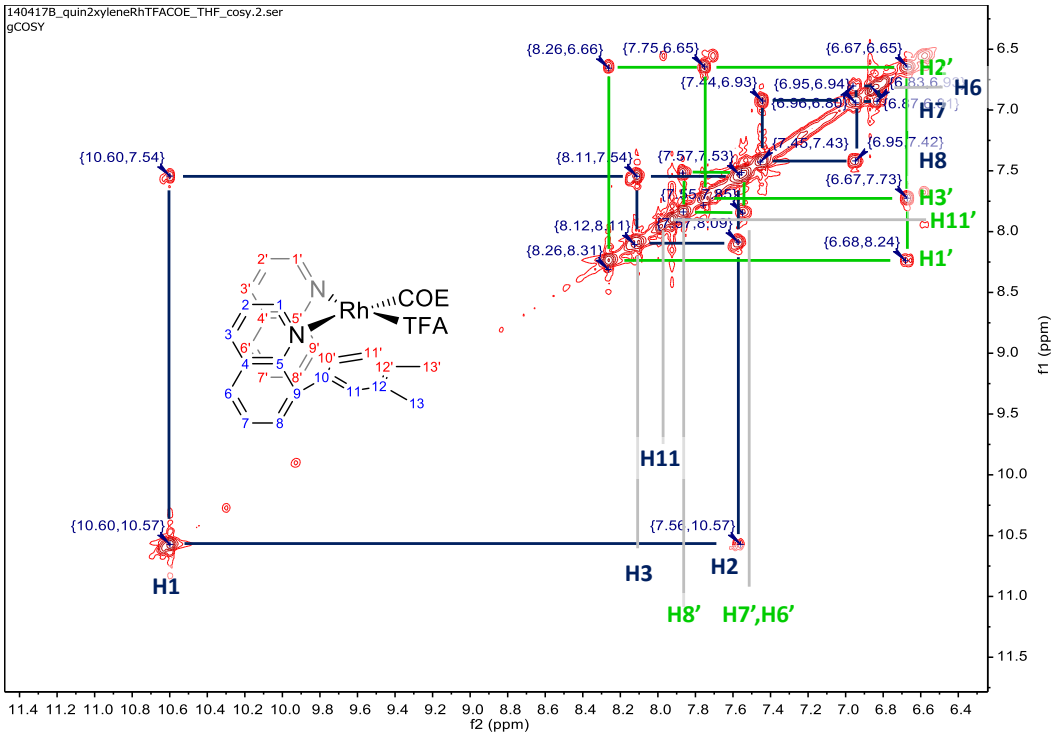


Figure S9. gCOSY NMR (d_8-THF, 600 MHz) spectrum of **2**.

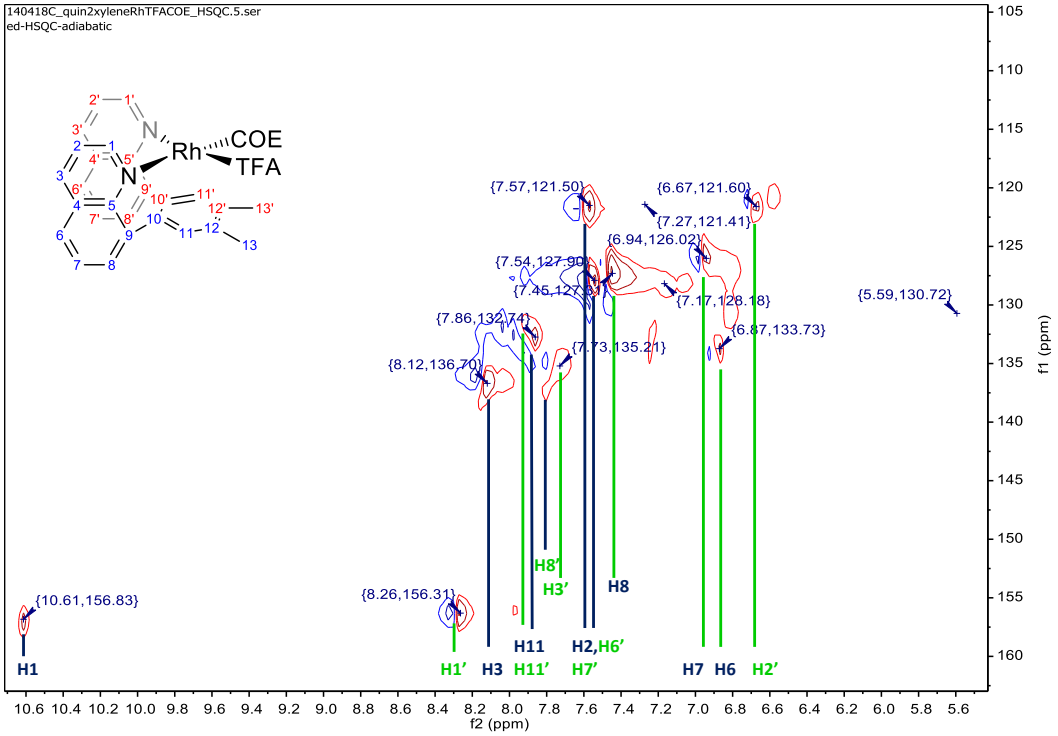


Figure S10. gHSQC NMR (d_8-THF, 600 MHz) spectrum of **2**.

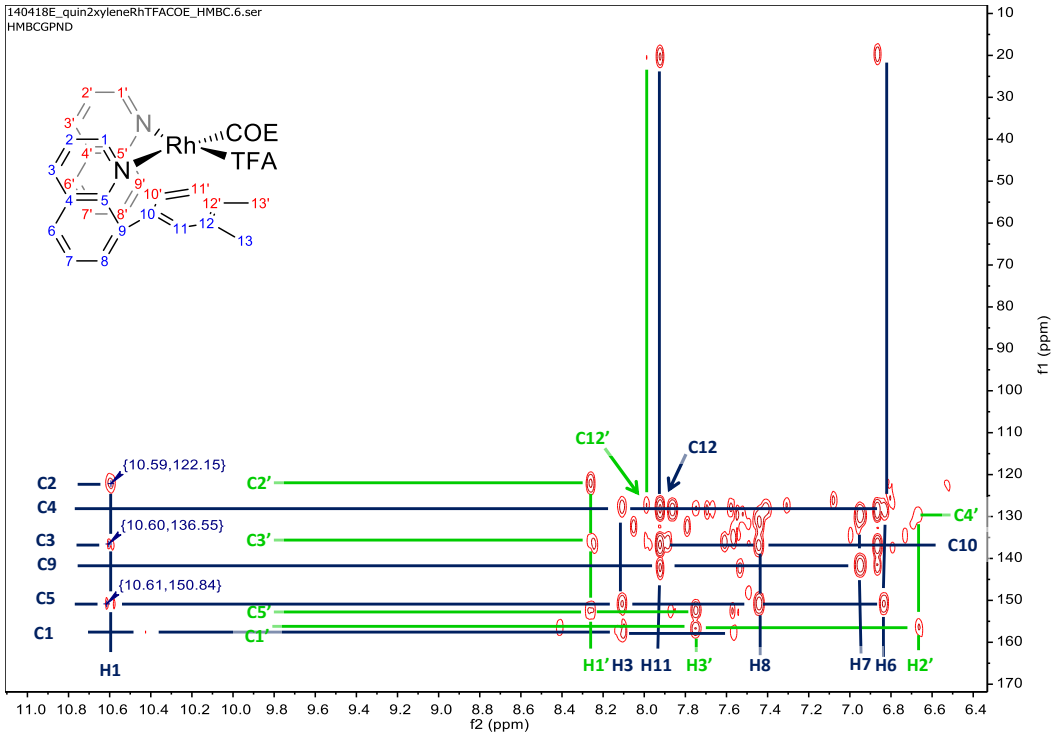


Figure S11. gHMBC NMR (d_8-THF, 600 MHz) spectrum of **2**.

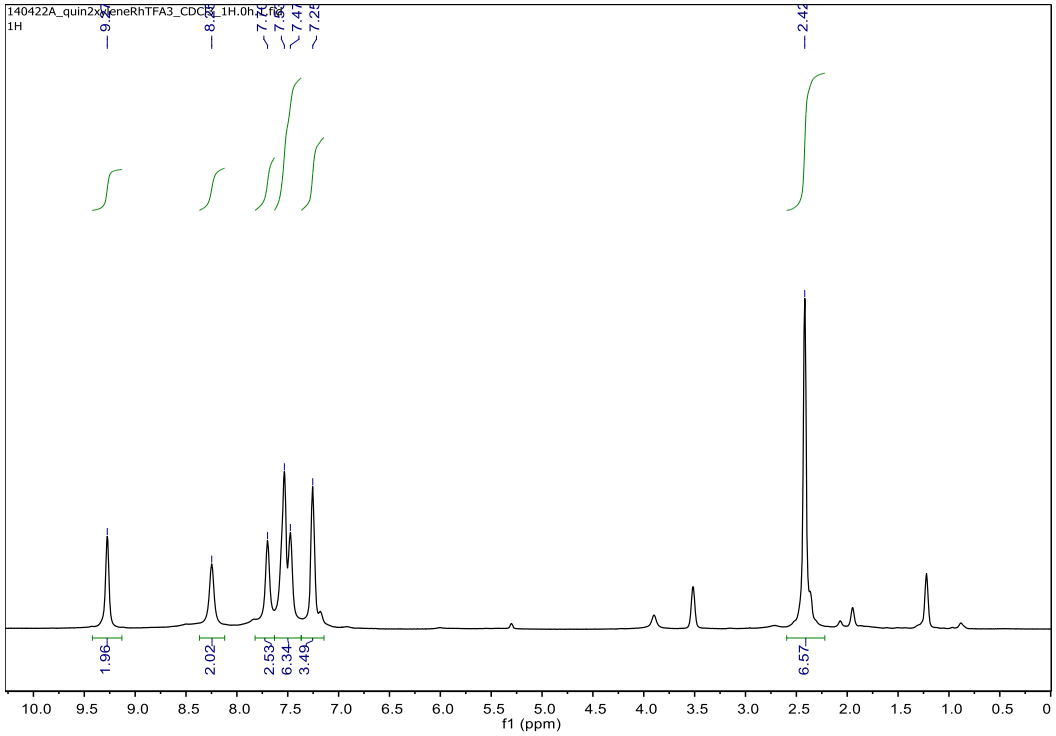


Figure S12. ^{1}H NMR ($CDCl_3$, 600 MHz) spectrum of **3**.

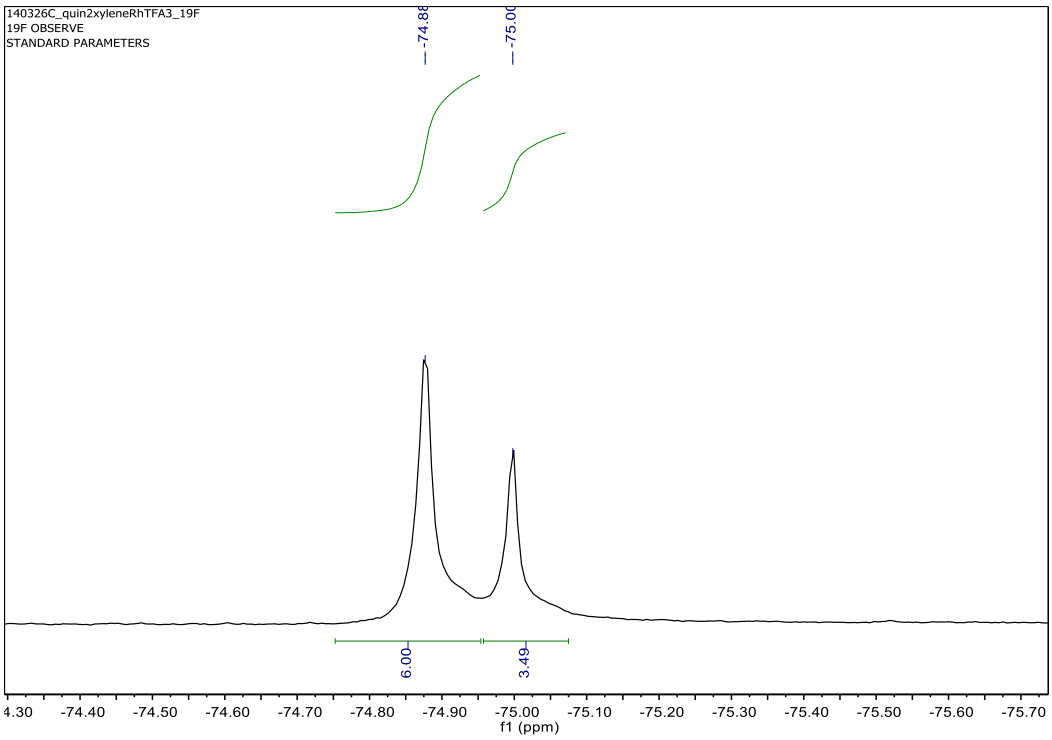


Figure S13. ^{19}F NMR ($CDCl_3$, 282 MHz) spectrum of **3**.

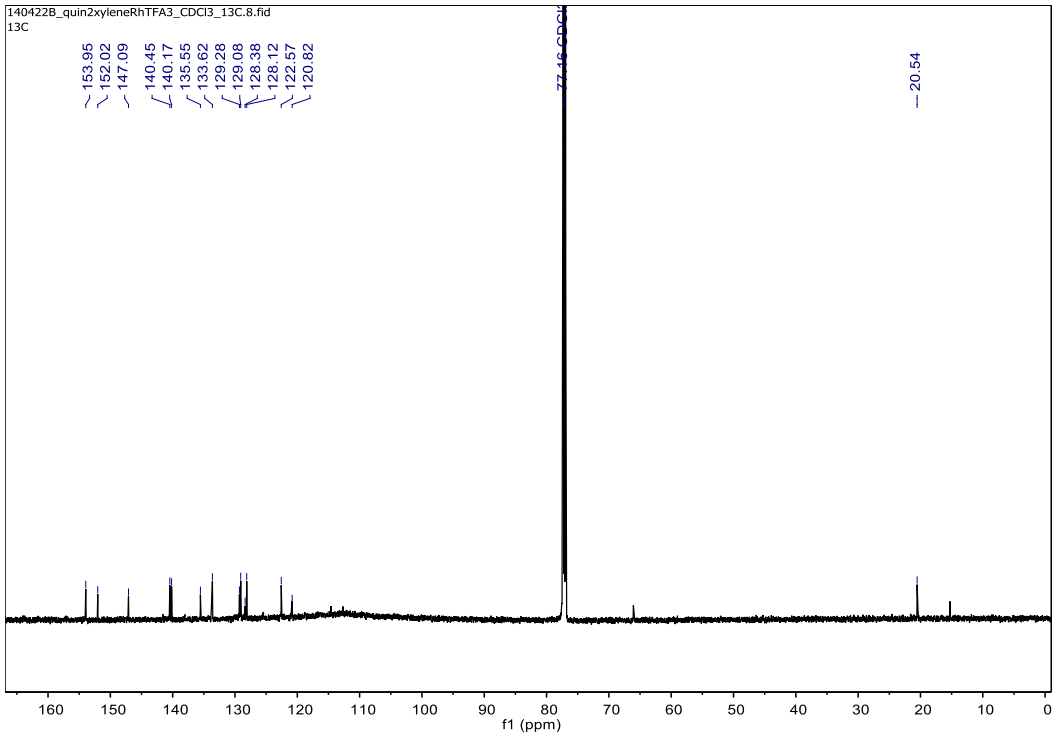


Figure S14. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 150 MHz) spectrum of **3**.

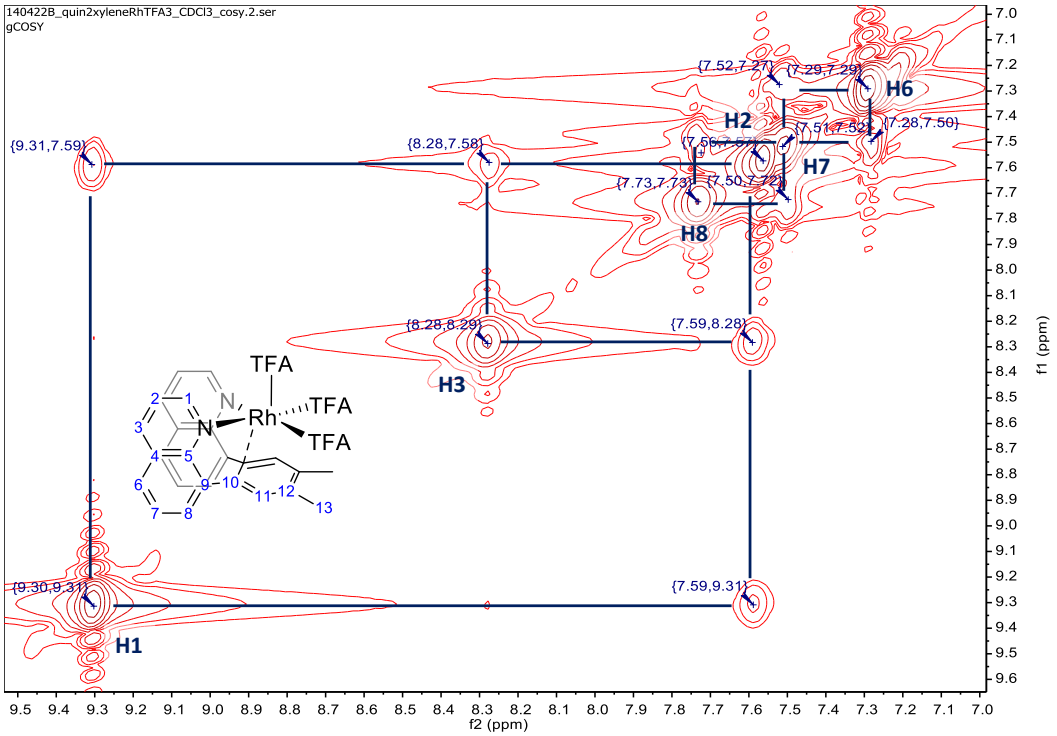


Figure S15. gCOSY NMR ($CDCl_3$, 600 MHz) spectrum of **3**.

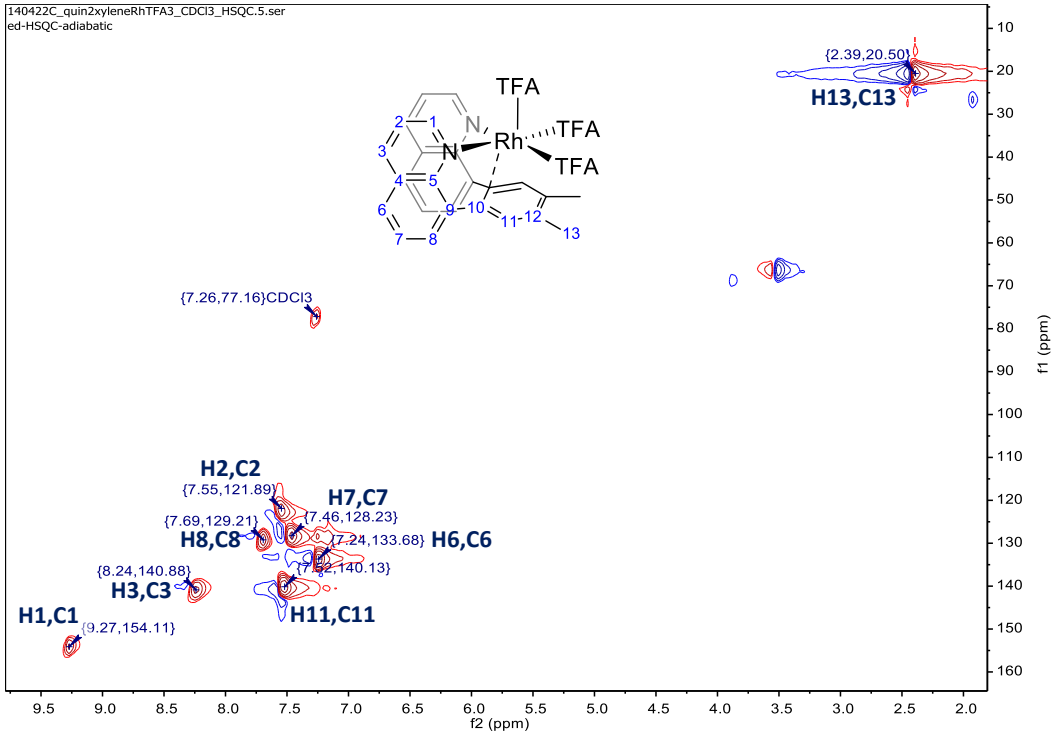


Figure S16. gHSQC NMR ($CDCl_3$, 600 MHz) spectrum of **3**.

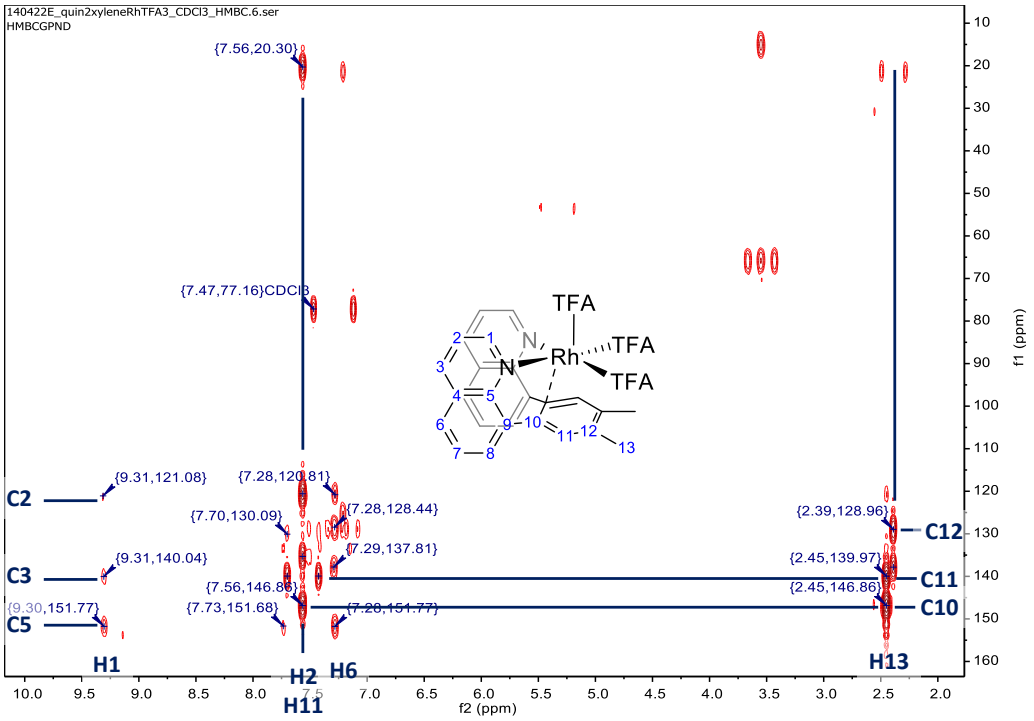


Figure S17.. gHMBC NMR ($CDCl_3$, 600 MHz) spectrum of **3**.

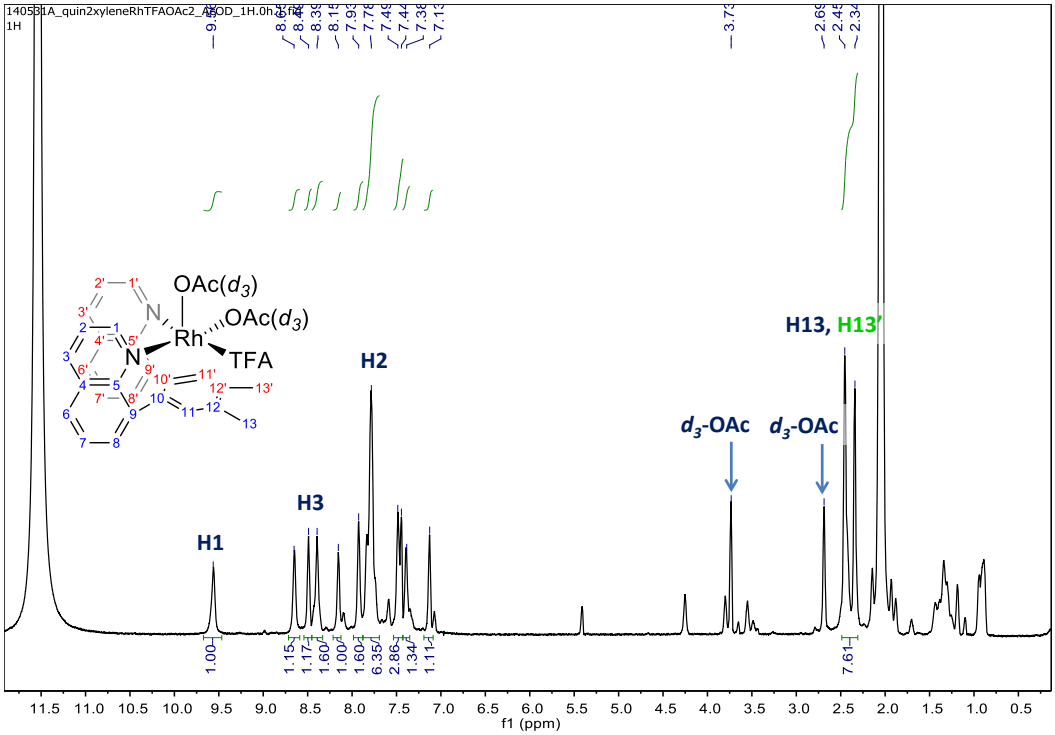


Figure S18. ^{1}H NMR (d_3-AcOD, 600 MHz) spectrum of **4**.

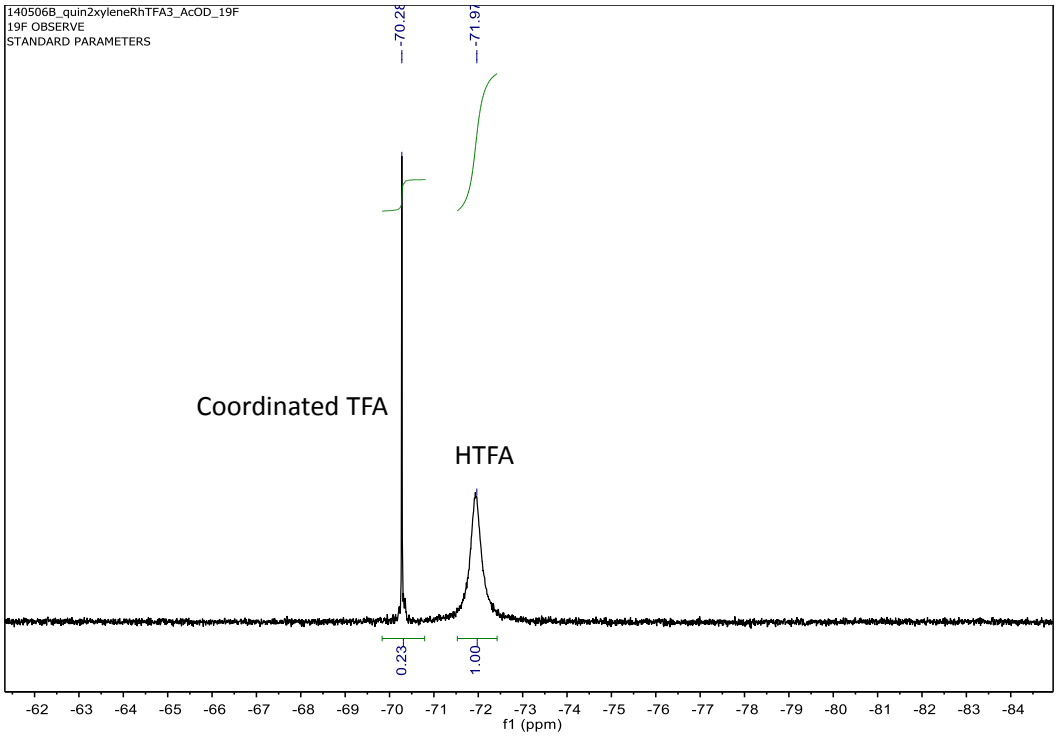


Figure S19. ^{19}F NMR (d_3-AcOD, 282 MHz) spectrum of **4**.

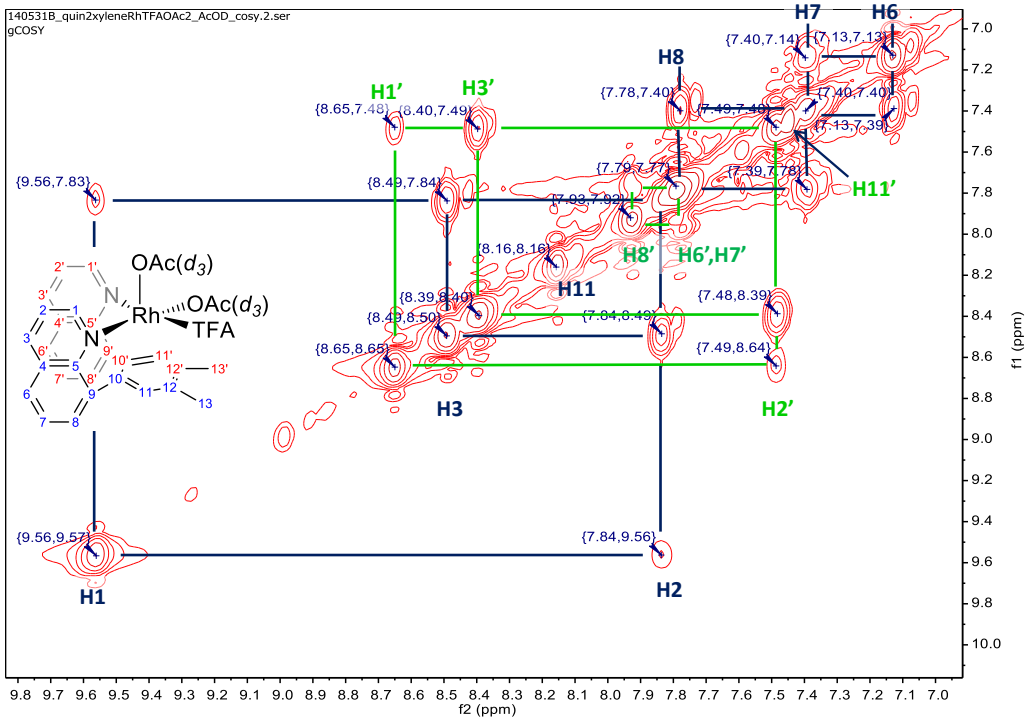


Figure S20. gCOSY NMR (d_3-AcOD, 600 MHz) spectrum of **4**.

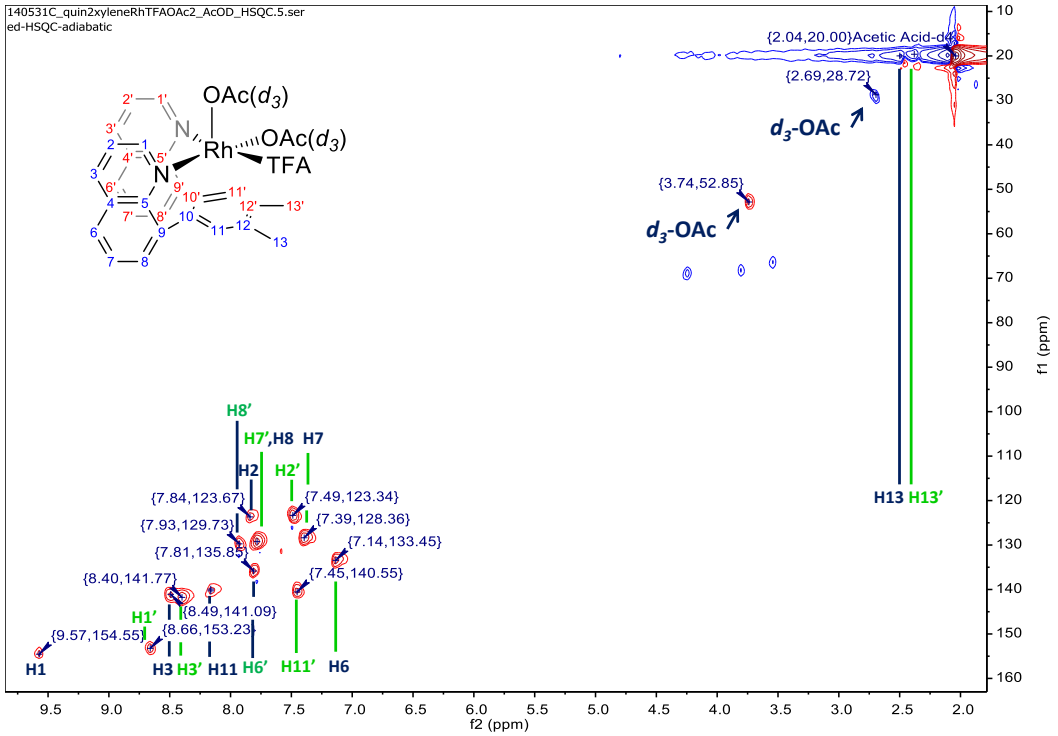


Figure S21. gHSQC NMR (d_3-AcOD, 600 MHz) spectrum of **4**.

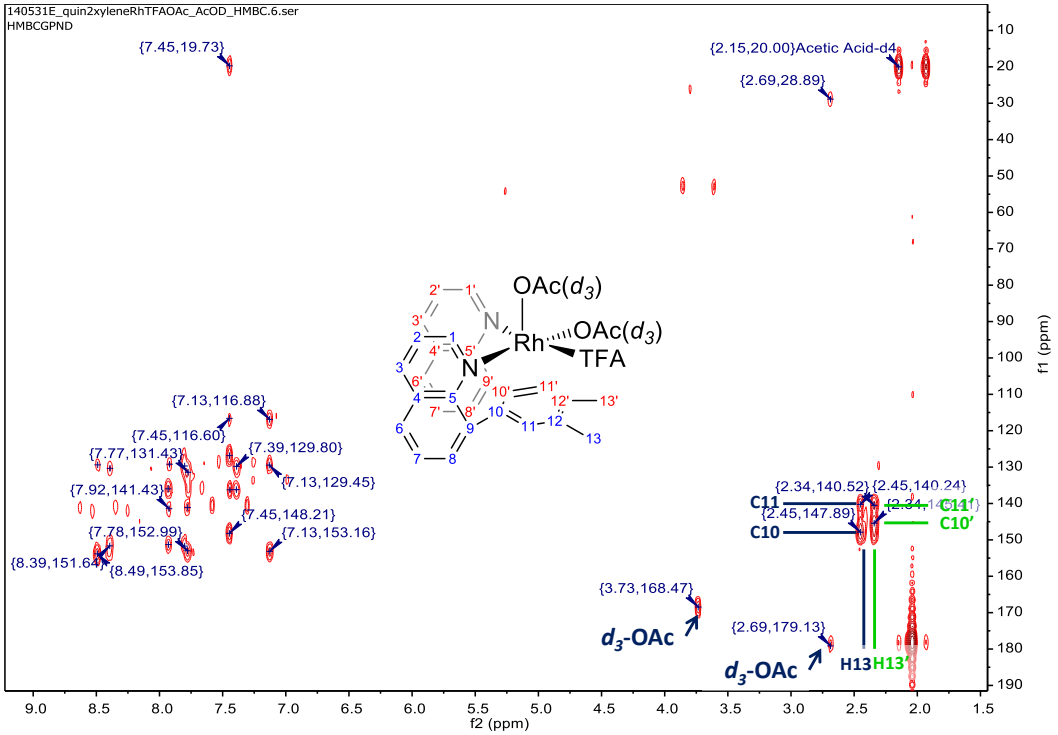


Figure S22. gHMBC NMR (d_3-AcOD, 600 MHz) spectrum of **4**.

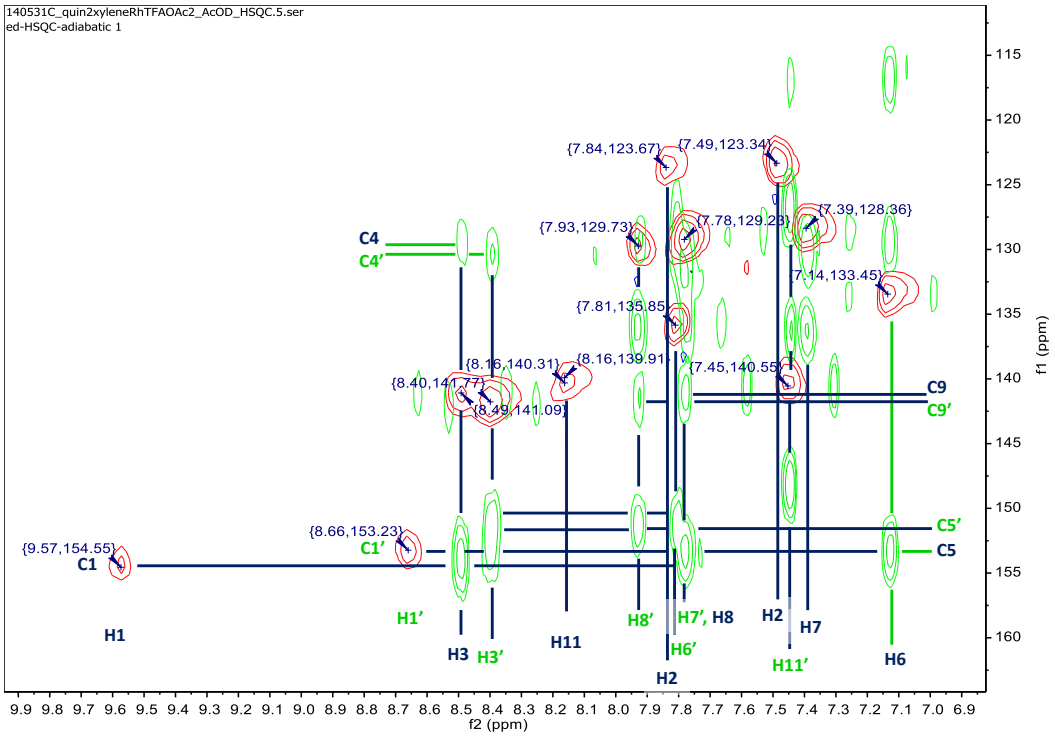


Figure S23. gHMBC (green) and gHSQC (red) NMR (d_3-AcOD, 600 MHz) spectrum of **4** (expanded).

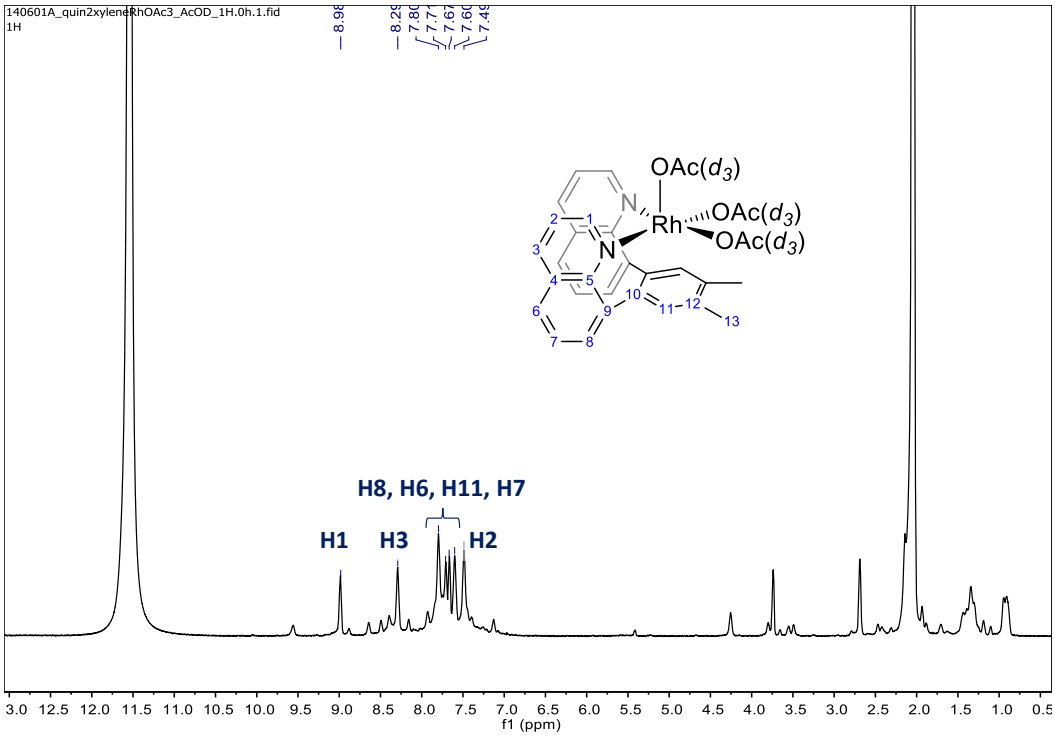


Figure S24. ^{1}H NMR (d_3-AcOD, 600 MHz) spectrum of **5**.

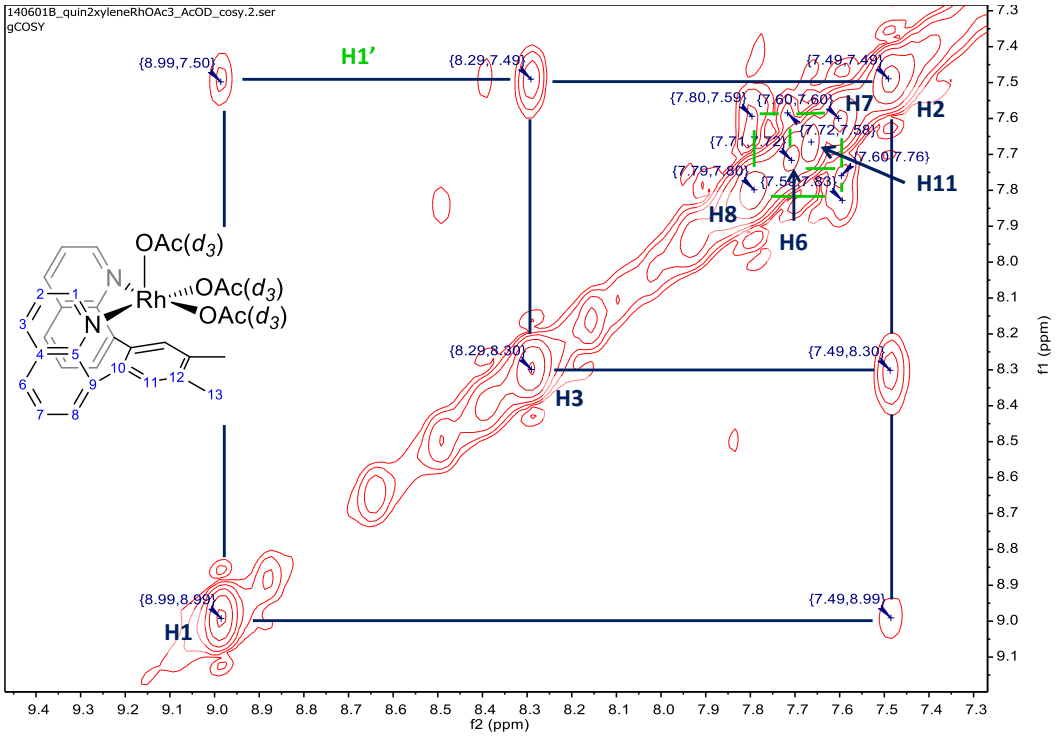


Figure S25. gCOSY NMR (d_3-AcOD, 600 MHz) spectrum of **5**.

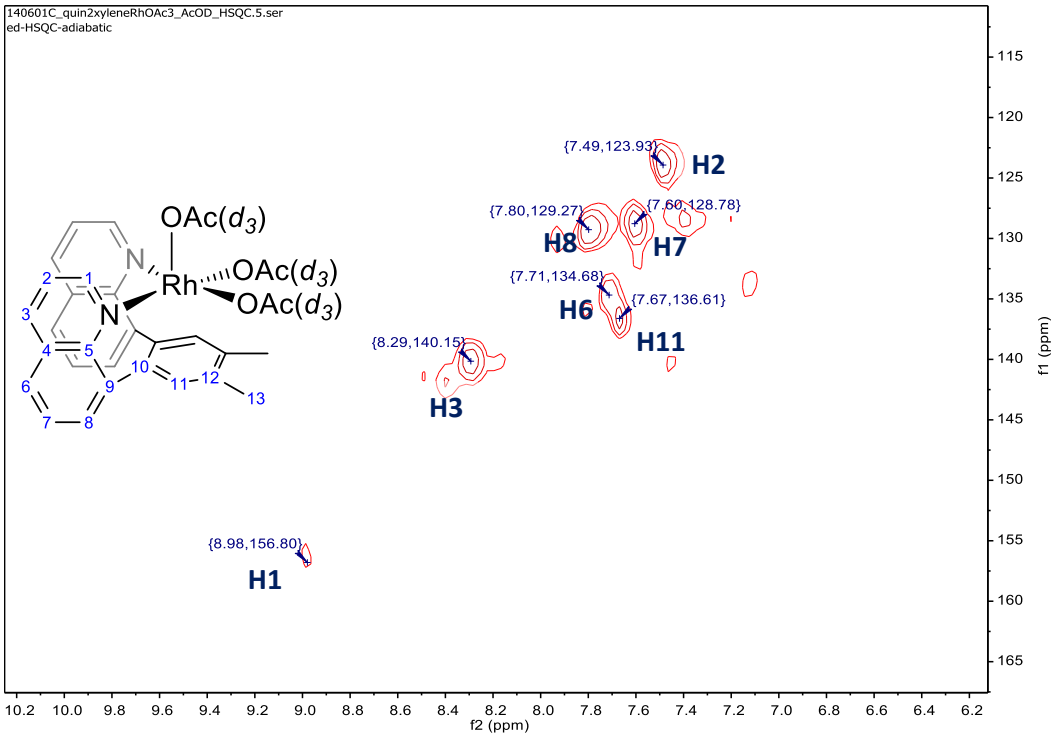


Figure S26. gHSQC NMR (d_3-AcOD, 600 MHz) spectrum of **5**.

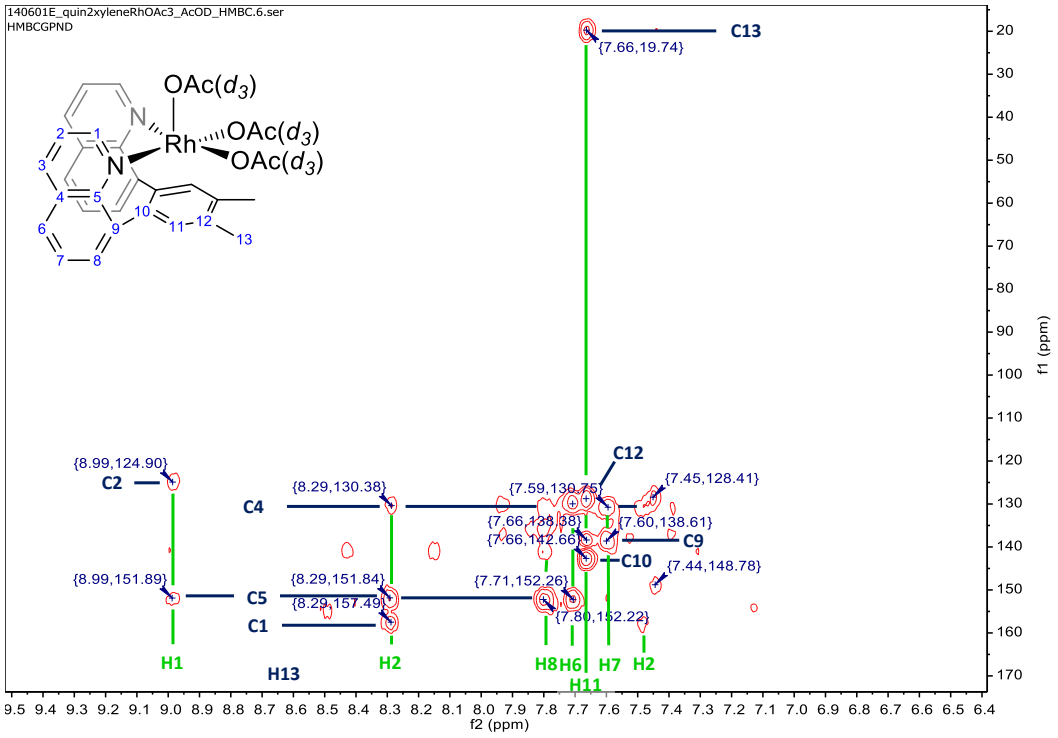


Figure S27. gHMBC NMR (d_3-AcOD, 600 MHz) spectrum of **5**.

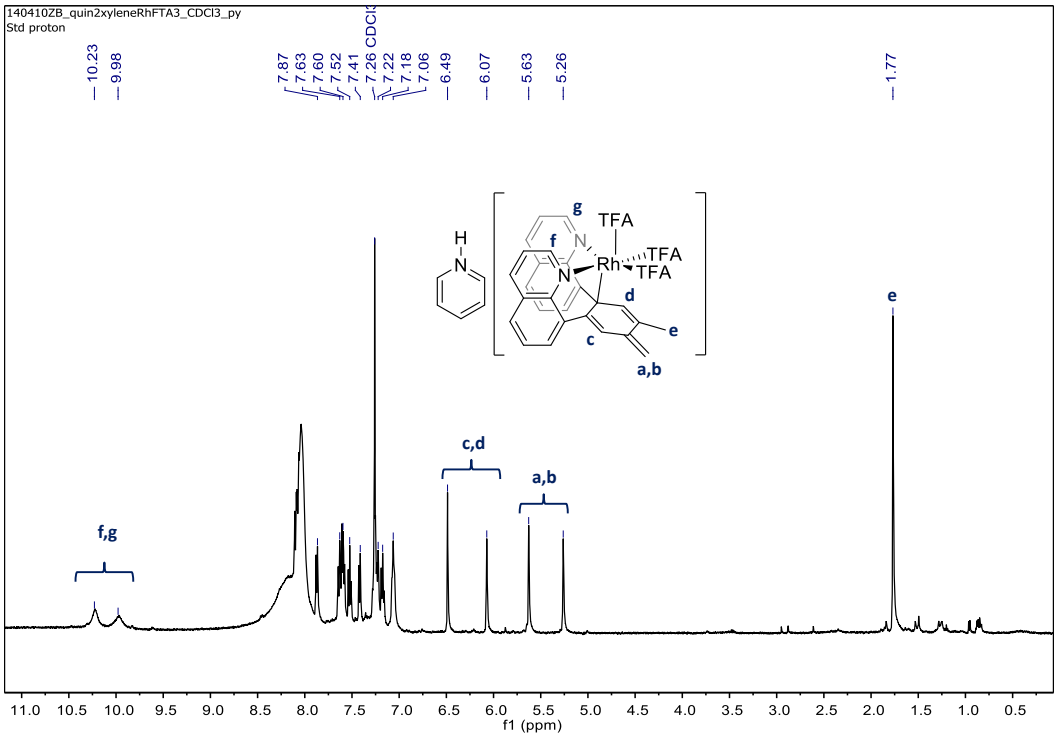


Figure S28. ^{1}H NMR ($CDCl_3$, 600 MHz) spectrum of in-situ **6**.

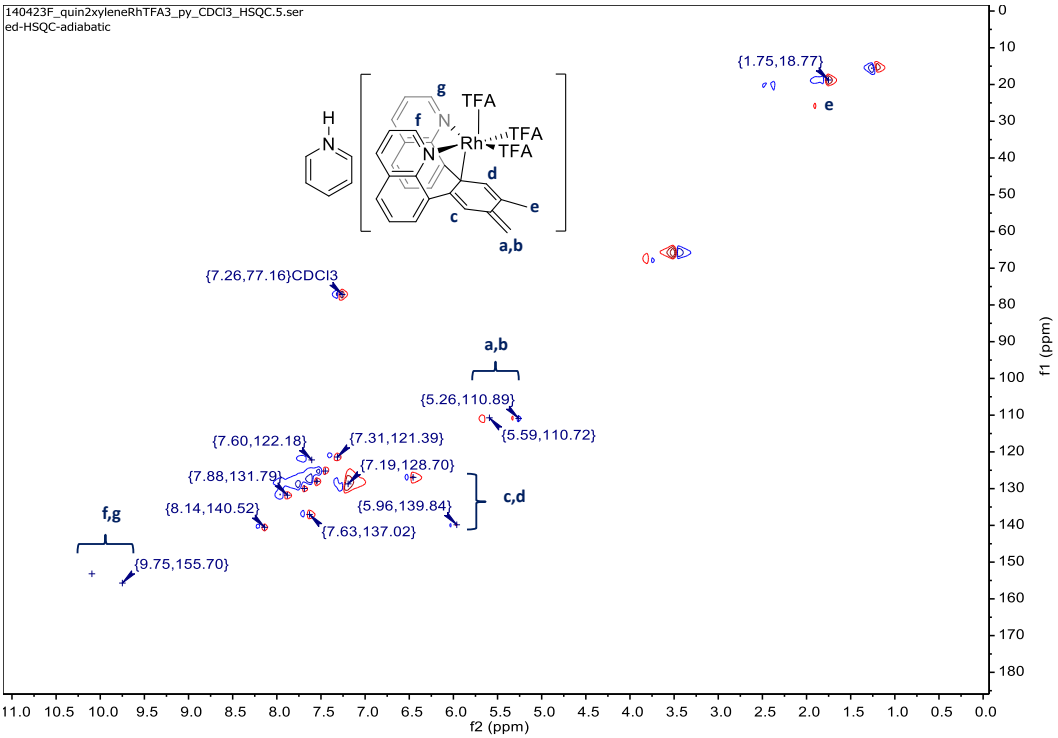


Figure S29. gHSQC NMR ($CDCl_3$, 600 MHz) spectrum of in-situ **6**. Attempts were made to obtain $^{13}C\{^1H\}$ NMR spectra at low temperatures. But, we could not obtain a satisfactory $^{13}C\{^1H\}$ NMR spectrum due to the poor signal-to-noise ratio. However, we were able to obtain a gHSQC spectrum of the complex. From these data, we have strong support for the assignment of complex **6**. For example, the four new singlets between 5.3 and 6.5 (olefinic region) are connected to three different olefinic carbon atoms whose resonances are at 110.7, 128.7, 139.6 ppm. Additionally, the integrations of the four olefinic peaks (1:1:1:1) and one remaining CH_3 group (3H) are consistent with the proposed complex. Due to the complexity of the ^1H and ^{13}C signals, we are not able to assign all the peaks, but we do observe 16-carbon signals directly attached to protons, which is consistent with the proposed structure.

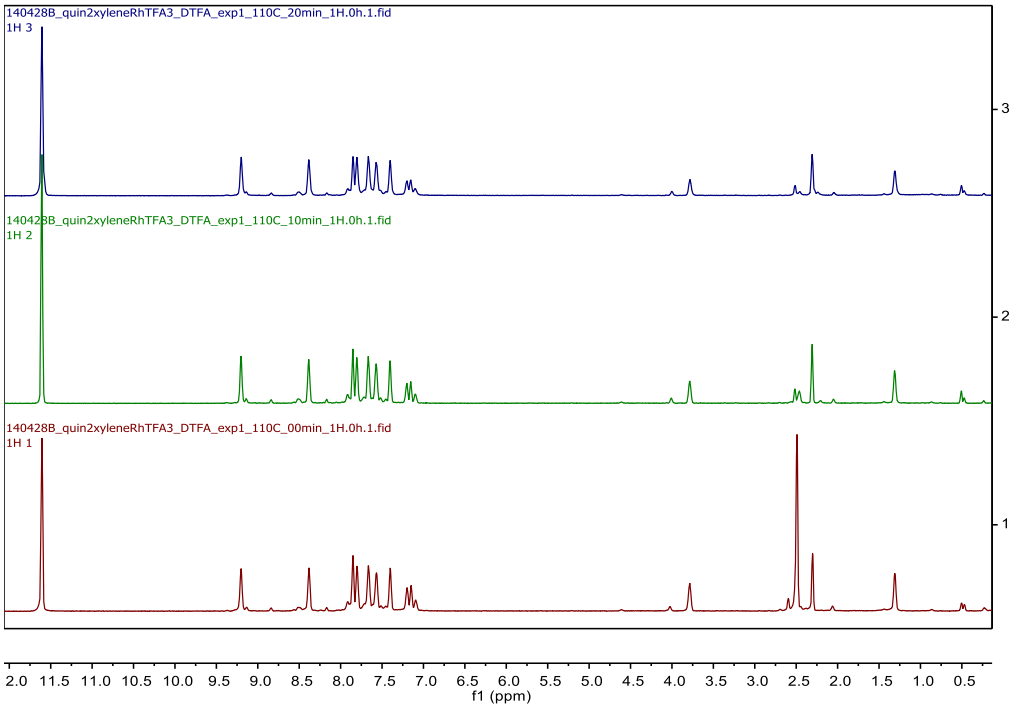


Figure S30. Changes in the ^{1}H NMR spectra of **3** at time intervals of 0, 10 and 20 minutes during the H/D exchange reaction with DTFA upon heating at 110 °C .

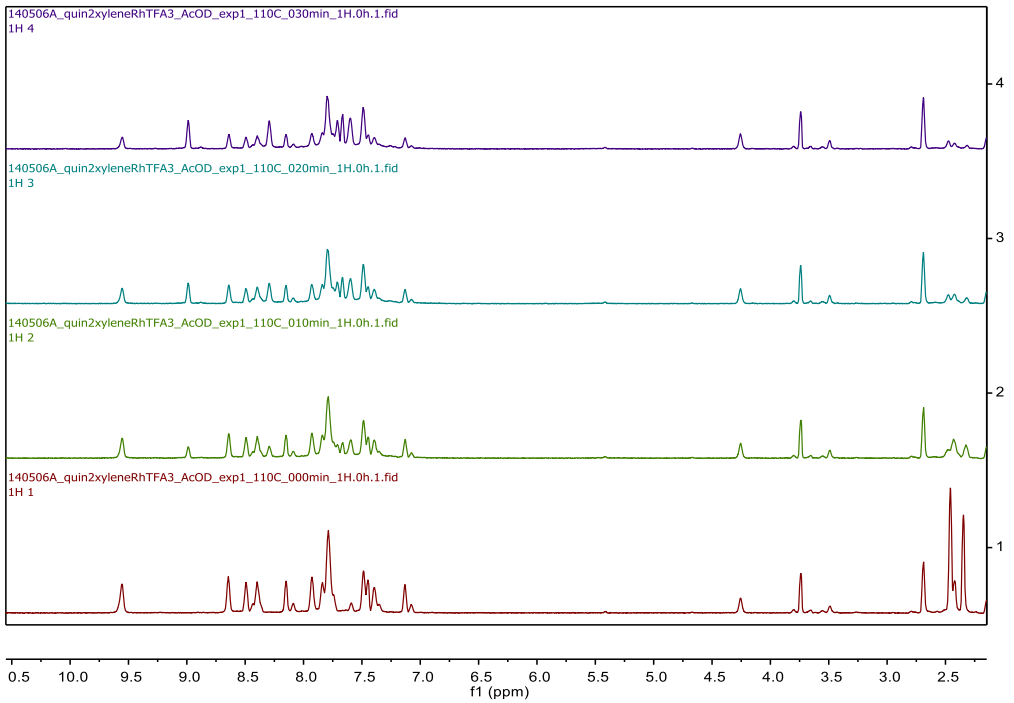


Figure S31. Changes in the ^{1}H NMR spectra of **4** at time intervals of 0, 10, 20 and 30 minutes during the H/D exchange reaction with d_3-AcOD upon heating at 110 °C .

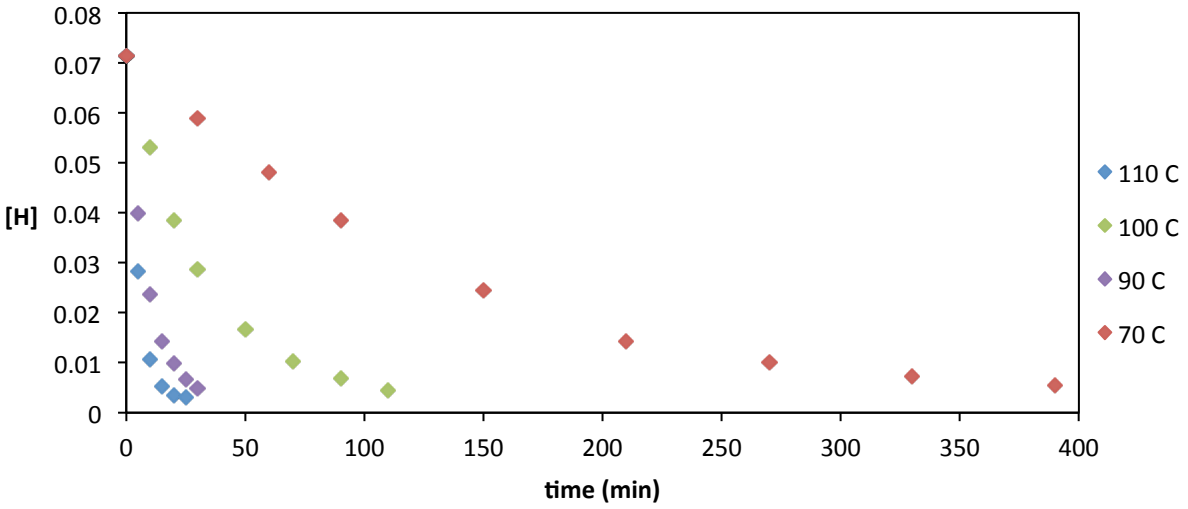


Figure S32. Average [H] {where [H] designates the methyl protons' conc.; e.g. initial [H] = 6×[**3**] } vs time (min) for H/D exchange of complex **3** with DTFA at temperature between 70 and 100 °C .

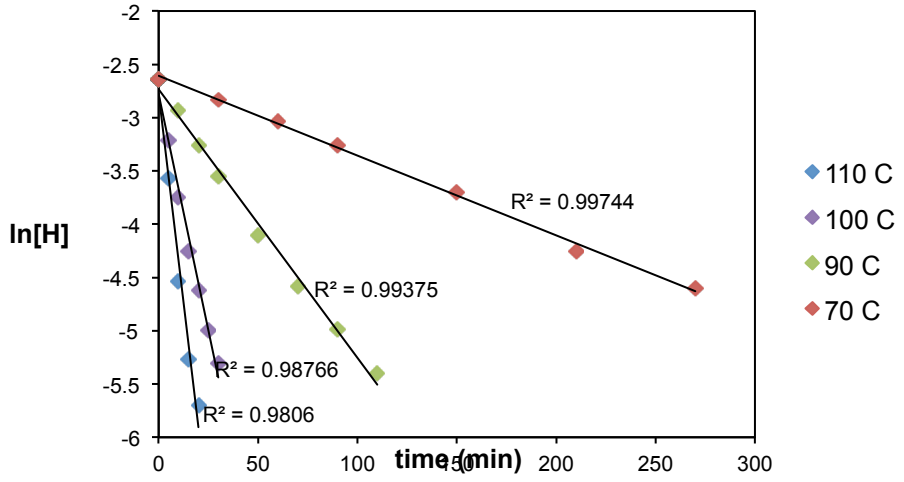


Figure S33. Average ln[H] {where [H] designates the methyl protons' conc.; e.g. initial [H] = 6×[**3**] } vs time (min) for H/D exchange of complex **3** with DTFA at temperature between 70 and 100 °C .

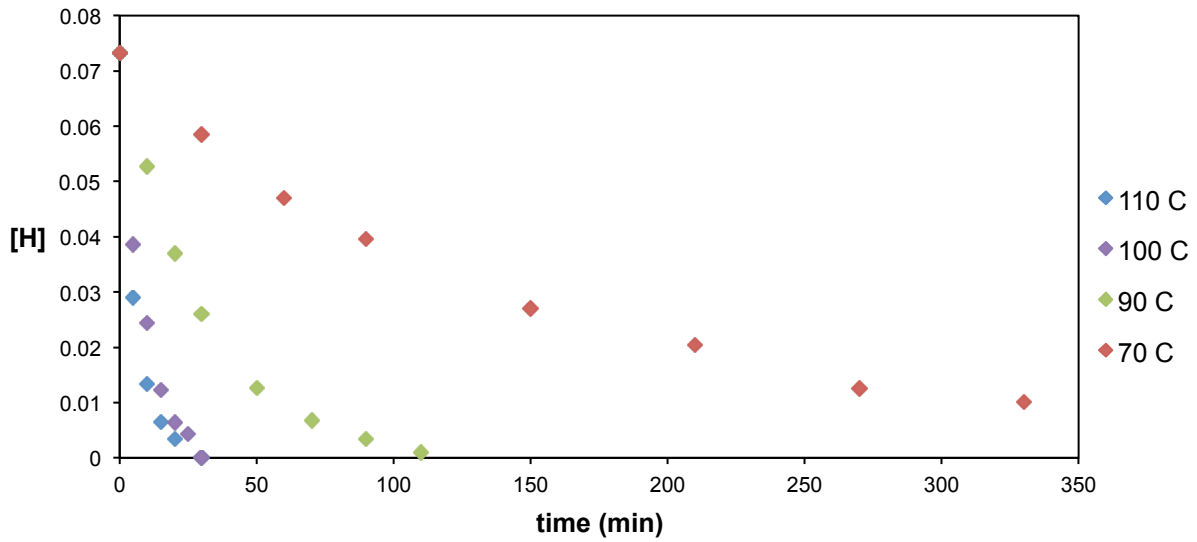


Figure S34. Average [H] {where [H] designates the methyl protons' conc.; e.g. initial [H] = 6×[**3**] } vs time (min) for H/D exchange of complex **4** with d_3-AcOD at temperature between 70 and 100 °C .

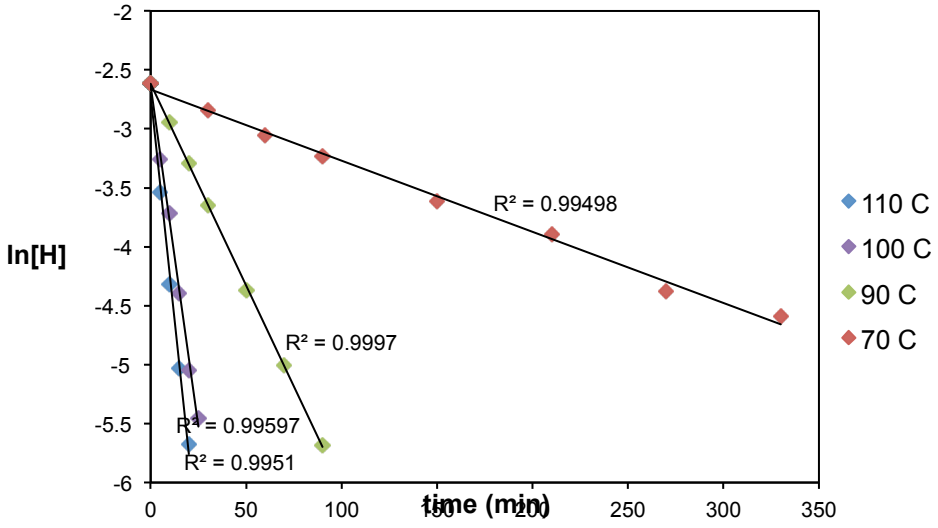


Figure S35. Average ln[H] {where [H] designates the methyl protons' conc.; e.g. initial [H] = 6×[**3**] } vs time (min) for H/D exchange of complex **4** with d_3-AcOD at temperature between 70 and 100 °C .

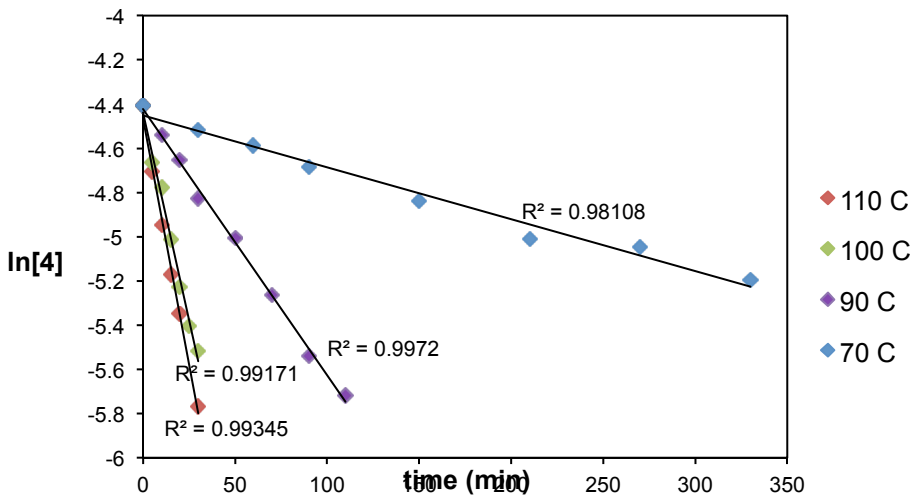


Figure S36. Average ln[**4**] vs time (min) for TFA/OAc exchange in d_3-AcOD at temperature between 70 and 100 °C .

Table S2. Crystal data and structure refinement for **2**.

Empirical formula	$C_{36}H_{34}F_3N_2O_2Rh$	
Formula weight	686.56	
Temperature	233(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 10.4419(19) Å	α= 84.562(4)°.
	b = 11.239(2) Å	β= 85.982(3)°.
	c = 13.655(3) Å	γ = 75.605(3)°.
Volume	1543.5(5) $Å^3$	
Z	2	
Density (calculated)	1.477 Mg/m^3	
Absorption coefficient	0.607 mm^{-1}	
F(000)	704	
Crystal size	0.350 x 0.180 x 0.090 mm^3	
Theta range for data collection	3.395 to 23.142°.	
Index ranges	-11<=h<=11, -12<=k<=12, -15<=l<=15	
Reflections collected	16485	
Independent reflections	4350 [R(int) = 0.0259]	
Completeness to theta = 23.000°	99.6 %	
Absorption correction	Empirical	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4350 / 164 / 434	
Goodness-of-fit on F^2	1.040	
Final R indices [I>2sigma(I)]	R1 = 0.0229, wR2 = 0.0482	
R indices (all data)	R1 = 0.0278, wR2 = 0.0500	
Largest diff. peak and hole	0.307 and -0.211 e.$Å^{-3}$	

Table S3. Atomic coordinates ($x10^4$) 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 Uij tensor.

	x	y	z	U(eq)
Rh	2038(1)	2682(1)	2825(1)	32(1)
F(1A)	5138(14)	5789(10)	1621(8)	108(3)
F(2A)	5787(8)	3919(8)	1421(8)	126(3)
F(3A)	5638(8)	4517(8)	2824(5)	123(3)
F(1B)	5107(16)	5779(11)	2000(8)	116(3)
F(2B)	5166(7)	4678(8)	862(4)	123(2)
F(3B)	5963(6)	3885(8)	2209(8)	122(3)
O(1)	3624(2)	3419(2)	2394(1)	39(1)
O(2)	2723(2)	5447(2)	2102(2)	78(1)
N(1)	703(2)	3763(2)	1711(2)	38(1)
N(2)	539(2)	1866(2)	3218(1)	37(1)
C(1)	1984(3)	3185(2)	4266(2)	42(1)
C(2)	2920(3)	2032(2)	4176(2)	38(1)
C(3)	4388(3)	1864(2)	4240(2)	44(1)
C(4)	4874(3)	1692(3)	5289(2)	55(1)
C(5)	4574(3)	2832(3)	5856(2)	65(1)
C(6)	3136(4)	3316(3)	6187(2)	73(1)
C(7)	2365(3)	4450(3)	5585(2)	70(1)
C(8)	2378(3)	4331(2)	4470(2)	53(1)
C(9)	-12(3)	4889(2)	1847(2)	46(1)
C(10)	-1155(3)	5446(3)	1340(2)	56(1)
C(11)	-1577(3)	4817(3)	685(2)	54(1)

C(12)	-856(2)	3623(2)	501(2)	44(1)
C(13)	-1200(3)	2921(3)	-194(2)	56(1)
C(14)	-436(3)	1795(3)	-356(2)	58(1)
C(15)	727(3)	1312(3)	154(2)	47(1)
C(16)	1119(2)	1951(2)	834(2)	34(1)
C(17)	311(2)	3122(2)	1026(2)	36(1)
C(18)	2473(2)	1504(2)	1240(2)	33(1)
C(19)	3506(2)	1820(2)	647(2)	36(1)
C(20)	4824(2)	1334(2)	818(2)	39(1)
C(21)	5158(2)	482(2)	1637(2)	40(1)
C(22)	4160(2)	156(2)	2218(2)	38(1)
C(23)	2806(2)	637(2)	2056(2)	33(1)
C(24)	1848(2)	-9(2)	2591(2)	34(1)
C(25)	2047(3)	-1257(2)	2572(2)	45(1)
C(26)	1136(3)	-1897(3)	3023(2)	58(1)
C(27)	2(3)	-1283(3)	3462(2)	60(1)
C(28)	-265(3)	8(2)	3513(2)	46(1)
C(29)	-1435(3)	702(3)	3942(2)	61(1)
C(30)	-1613(3)	1927(3)	3969(2)	65(1)
C(31)	-595(3)	2476(3)	3613(2)	52(1)
C(32)	697(2)	633(2)	3110(2)	35(1)
C(33)	5874(3)	1679(3)	115(2)	59(1)
C(34)	6582(3)	-79(3)	1879(2)	69(1)
C(35)	3623(3)	4521(3)	2149(2)	44(1)
C(36)	5021(3)	4698(3)	1903(3)	67(1)

Table S4. Bond lengths [Å] for **2**.

Bond	Length	Bond	Length
Rh-N(2)	2.0204(19)	C(1)-C(8)	1.501(4)
Rh-O(1)	2.0564(16)	C(2)-C(3)	1.506(4)
Rh-C(1)	2.091(3)	C(3)-C(4)	1.532(3)
Rh-C(2)	2.105(2)	C(4)-C(5)	1.514(4)
Rh-N(1)	2.200(2)	C(5)-C(6)	1.516(4)
Rh-C(23)	2.541(2)	C(6)-C(7)	1.527(4)
Rh-C(18)	2.597(2)	C(7)-C(8)	1.540(4)
F(1A)-F(1B)	0.52(2)	C(9)-C(10)	1.399(4)
F(1A)-C(36)	1.283(10)	C(10)-C(11)	1.350(4)
F(1A)-F(2B)	1.691(14)	C(11)-C(12)	1.402(4)
F(2A)-F(3B)	1.100(9)	C(12)-C(13)	1.408(4)
F(2A)-F(2B)	1.184(10)	C(12)-C(17)	1.422(3)
F(2A)-C(36)	1.236(6)	C(13)-C(14)	1.347(4)
F(3A)-F(3B)	1.131(10)	C(14)-C(15)	1.405(4)
F(3A)-C(36)	1.427(7)	C(15)-C(16)	1.368(3)
F(3A)-F(1B)	1.725(14)	C(16)-C(17)	1.412(3)
F(1B)-C(36)	1.260(10)	C(16)-C(18)	1.504(3)
F(2B)-C(36)	1.422(7)	C(18)-C(19)	1.400(3)
F(3B)-C(36)	1.231(6)	C(18)-C(23)	1.411(3)
O(1)-C(35)	1.252(3)	C(19)-C(20)	1.376(3)
O(2)-C(35)	1.216(3)	C(20)-C(21)	1.406(3)
N(1)-C(9)	1.322(3)	C(20)-C(33)	1.506(3)
N(1)-C(17)	1.374(3)	C(21)-C(22)	1.367(3)
N(2)-C(31)	1.319(3)	C(21)-C(34)	1.510(4)
N(2)-C(32)	1.376(3)	C(22)-C(23)	1.407(3)
C(1)-C(2)	1.425(4)	C(23)-C(24)	1.490(3)

C(24)-C(25)	1.369(3)	C(28)-C(29)	1.399(4)
C(24)-C(32)	1.419(3)	C(28)-C(32)	1.417(3)
C(25)-C(26)	1.405(4)	C(29)-C(30)	1.346(4)
C(26)-C(27)	1.346(4)	C(30)-C(31)	1.394(4)
C(27)-C(28)	1.415(4)	C(35)-C(36)	1.532(4)

Table S5. Bond angles [°] for **2**.

Bond	Length	Bond	Length
N(2)-Rh-O(1)	176.73(7)	C(2)-C(1)-C(8)	122.7(3)
N(2)-Rh-C(1)	89.21(10)	C(2)-C(1)-Rh	70.68(14)
O(1)-Rh-C(1)	92.74(9)	C(8)-C(1)-Rh	120.77(19)
N(2)-Rh-C(2)	90.96(9)	C(1)-C(2)-C(3)	123.2(2)
O(1)-Rh-C(2)	88.86(9)	C(1)-C(2)-Rh	69.60(14)
C(1)-Rh-C(2)	39.71(10)	C(3)-C(2)-Rh	119.38(17)
N(2)-Rh-N(1)	84.78(8)	C(2)-C(3)-C(4)	114.9(2)
O(1)-Rh-N(1)	96.36(7)	C(5)-C(4)-C(3)	116.5(2)
C(1)-Rh-N(1)	122.66(9)	C(4)-C(5)-C(6)	115.9(3)
C(2)-Rh-N(1)	162.09(8)	C(5)-C(6)-C(7)	116.1(3)
N(2)-Rh-C(23)	77.40(8)	C(6)-C(7)-C(8)	115.5(2)
O(1)-Rh-C(23)	99.36(7)	C(1)-C(8)-C(7)	111.2(2)
C(1)-Rh-C(23)	133.20(9)	N(1)-C(9)-C(10)	123.2(3)
C(2)-Rh-C(23)	95.20(9)	C(11)-C(10)-C(9)	119.6(3)
N(1)-Rh-C(23)	100.80(7)	C(10)-C(11)-C(12)	120.0(3)
N(2)-Rh-C(18)	88.61(8)	C(11)-C(12)-C(13)	123.7(3)
O(1)-Rh-C(18)	88.82(7)	C(11)-C(12)-C(17)	117.5(3)
C(1)-Rh-C(18)	164.74(9)	C(13)-C(12)-C(17)	118.8(3)
C(2)-Rh-C(18)	125.23(8)	C(14)-C(13)-C(12)	120.4(3)
N(1)-Rh-C(18)	72.15(7)	C(13)-C(14)-C(15)	120.5(3)
C(23)-Rh-C(18)	31.86(7)	C(16)-C(15)-C(14)	121.8(3)
F(1B)-F(1A)-C(36)	76(2)	C(15)-C(16)-C(17)	118.2(2)
F(1B)-F(1A)-F(2B)	131(2)	C(15)-C(16)-C(18)	120.2(2)
C(36)-F(1A)-F(2B)	55.1(5)	C(17)-C(16)-C(18)	120.9(2)
F(3B)-F(2A)-F(2B)	133.5(9)	N(1)-C(17)-C(16)	118.3(2)
F(3B)-F(2A)-C(36)	63.3(5)	N(1)-C(17)-C(12)	121.6(2)
F(2B)-F(2A)-C(36)	71.9(6)	C(16)-C(17)-C(12)	120.2(2)
F(3B)-F(3A)-C(36)	56.1(4)	C(19)-C(18)-C(23)	118.0(2)
F(3B)-F(3A)-F(1B)	91.9(7)	C(19)-C(18)-C(16)	115.5(2)
C(36)-F(3A)-F(1B)	45.9(4)	C(23)-C(18)-C(16)	125.5(2)
F(1A)-F(1B)-C(36)	81(2)	C(19)-C(18)-Rh	110.90(15)
F(1A)-F(1B)-F(3A)	127(3)	C(23)-C(18)-Rh	71.85(13)
C(36)-F(1B)-F(3A)	54.4(5)	C(16)-C(18)-Rh	98.52(14)
F(2A)-F(2B)-C(36)	55.7(4)	C(20)-C(19)-C(18)	123.6(2)
F(2A)-F(2B)-F(1A)	91.0(6)	C(19)-C(20)-C(21)	118.5(2)
C(36)-F(2B)-F(1A)	47.7(4)	C(19)-C(20)-C(33)	120.2(2)
F(2A)-F(3B)-F(3A)	136.7(10)	C(21)-C(20)-C(33)	121.3(2)
F(2A)-F(3B)-C(36)	63.8(5)	C(22)-C(21)-C(20)	118.5(2)
F(3A)-F(3B)-C(36)	74.2(7)	C(22)-C(21)-C(34)	119.9(2)
C(35)-O(1)-Rh	128.34(17)	C(20)-C(21)-C(34)	121.6(2)
C(9)-N(1)-C(17)	118.1(2)	C(21)-C(22)-C(23)	123.9(2)
C(9)-N(1)-Rh	121.78(18)	C(22)-C(23)-C(18)	117.4(2)
C(17)-N(1)-Rh	117.02(15)	C(22)-C(23)-C(24)	117.7(2)
C(31)-N(2)-C(32)	118.0(2)	C(18)-C(23)-C(24)	123.1(2)
C(31)-N(2)-Rh	121.76(17)	C(22)-C(23)-Rh	108.61(15)
C(32)-N(2)-Rh	120.20(15)	C(18)-C(23)-Rh	76.29(13)

C(24)-C(23)-Rh	98.41(14)	F(3B)-C(36)-F(1B)	114.5(9)
C(25)-C(24)-C(32)	117.9(2)	F(2A)-C(36)-F(1B)	127.2(8)
C(25)-C(24)-C(23)	120.0(2)	F(3B)-C(36)-F(1A)	121.7(8)
C(32)-C(24)-C(23)	122.1(2)	F(2A)-C(36)-F(1A)	111.3(8)
C(24)-C(25)-C(26)	122.0(3)	F(1B)-C(36)-F(1A)	23.4(9)
C(27)-C(26)-C(25)	120.4(3)	F(3B)-C(36)-F(2B)	104.4(6)
C(26)-C(27)-C(28)	120.5(3)	F(2A)-C(36)-F(2B)	52.4(5)
C(29)-C(28)-C(27)	123.3(3)	F(1B)-C(36)-F(2B)	100.6(6)
C(29)-C(28)-C(32)	118.1(2)	F(1A)-C(36)-F(2B)	77.2(6)
C(27)-C(28)-C(32)	118.6(3)	F(3B)-C(36)-F(3A)	49.7(5)
C(30)-C(29)-C(28)	119.8(3)	F(2A)-C(36)-F(3A)	102.0(6)
C(29)-C(30)-C(31)	119.3(3)	F(1B)-C(36)-F(3A)	79.6(7)
N(2)-C(31)-C(30)	123.6(3)	F(1A)-C(36)-F(3A)	100.0(6)
N(2)-C(32)-C(28)	120.8(2)	F(2B)-C(36)-F(3A)	148.2(5)
N(2)-C(32)-C(24)	118.9(2)	F(3B)-C(36)-C(35)	118.1(4)
C(28)-C(32)-C(24)	120.3(2)	F(2A)-C(36)-C(35)	117.1(4)
O(2)-C(35)-O(1)	131.2(3)	F(1B)-C(36)-C(35)	112.8(8)
O(2)-C(35)-C(36)	116.5(3)	F(1A)-C(36)-C(35)	117.8(7)
O(1)-C(35)-C(36)	112.3(2)	F(2B)-C(36)-C(35)	103.7(4)
F(3B)-C(36)-F(2A)	52.9(5)	F(3A)-C(36)-C(35)	105.4(4)

Table S6. 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}
Rh	33(1)	30(1)	32(1)	0(1)	1(1)	-8(1)
F(1A)	92(4)	86(4)	145(7)	55(4)	4(5)	-48(4)
F(2A)	82(6)	130(6)	186(8)	-79(6)	64(6)	-59(4)
F(3A)	106(6)	174(7)	120(5)	27(4)	-58(4)	-90(5)
F(1B)	128(6)	100(4)	154(8)	-32(5)	3(6)	-87(4)
F(2B)	118(6)	190(7)	77(3)	-14(4)	43(3)	-77(5)
F(3B)	45(3)	128(6)	183(8)	70(6)	-27(6)	-28(4)
O(1)	41(1)	37(1)	39(1)	2(1)	0(1)	-14(1)
O(2)	64(1)	48(1)	116(2)	20(1)	-14(1)	-9(1)
N(1)	34(1)	34(1)	41(1)	4(1)	1(1)	-6(1)
N(2)	36(1)	34(1)	39(1)	-3(1)	4(1)	-8(1)
C(1)	48(2)	41(2)	36(2)	-8(1)	6(1)	-10(1)
C(2)	53(2)	33(1)	28(1)	-1(1)	-1(1)	-13(1)
C(3)	55(2)	37(2)	38(2)	-2(1)	-7(1)	-4(1)
C(4)	65(2)	53(2)	44(2)	0(1)	-15(1)	-8(2)
C(5)	85(2)	65(2)	47(2)	-8(2)	-19(2)	-15(2)
C(6)	98(3)	85(2)	40(2)	-21(2)	-1(2)	-25(2)
C(7)	83(2)	62(2)	68(2)	-37(2)	2(2)	-11(2)
C(8)	63(2)	39(2)	56(2)	-14(1)	-3(1)	-4(1)
C(9)	43(2)	38(2)	53(2)	2(1)	5(1)	-6(1)
C(10)	40(2)	43(2)	72(2)	12(2)	10(2)	3(1)
C(11)	29(1)	58(2)	68(2)	24(2)	-3(1)	-6(1)
C(12)	30(1)	50(2)	50(2)	19(1)	-4(1)	-14(1)
C(13)	43(2)	72(2)	59(2)	23(2)	-20(1)	-27(2)
C(14)	62(2)	69(2)	53(2)	5(2)	-20(2)	-32(2)
C(15)	50(2)	50(2)	44(2)	1(1)	-10(1)	-16(1)
C(16)	34(1)	38(1)	32(1)	5(1)	-3(1)	-11(1)
C(17)	31(1)	39(1)	36(1)	10(1)	0(1)	-11(1)
C(18)	35(1)	30(1)	33(1)	-5(1)	-2(1)	-6(1)
C(19)	40(1)	35(1)	33(1)	1(1)	-2(1)	-7(1)
C(20)	37(1)	42(2)	40(2)	-11(1)	4(1)	-10(1)

C(21)	34(1)	48(2)	37(1)	-13(1)	-2(1)	-3(1)
C(22)	40(1)	39(1)	31(1)	-4(1)	-5(1)	-1(1)
C(23)	37(1)	32(1)	28(1)	-5(1)	-2(1)	-5(1)
C(24)	39(1)	34(1)	29(1)	0(1)	-8(1)	-9(1)
C(25)	54(2)	38(2)	42(2)	-4(1)	-6(1)	-9(1)
C(26)	81(2)	35(2)	63(2)	1(1)	-6(2)	-23(2)
C(27)	71(2)	54(2)	63(2)	4(2)	0(2)	-36(2)
C(28)	49(2)	48(2)	44(2)	3(1)	-1(1)	-22(1)
C(29)	50(2)	68(2)	70(2)	-3(2)	15(2)	-29(2)
C(30)	42(2)	64(2)	86(2)	-11(2)	24(2)	-13(2)
C(31)	44(2)	44(2)	64(2)	-6(1)	14(1)	-9(1)
C(32)	38(1)	37(1)	31(1)	2(1)	-5(1)	-11(1)
C(33)	44(2)	67(2)	63(2)	-1(2)	12(1)	-15(2)
C(34)	38(2)	97(3)	62(2)	2(2)	-5(1)	0(2)
C(35)	49(2)	45(2)	39(2)	7(1)	-7(1)	-17(1)
C(36)	62(2)	54(2)	89(3)	1(2)	4(2)	-28(2)

Table S7. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **2**.

	x	y	z	U(eq)
H(3A)	4638	2585	3897	53
H(3B)	4848	1143	3892	53
H(4A)	4482	1073	5665	66
H(4B)	5835	1357	5255	66
H(5A)	4861	3488	5443	78
H(5B)	5105	2648	6440	78
H(6A)	3104	3515	6873	87
H(6B)	2682	2653	6172	87
H(7A)	2729	5151	5686	85
H(7B)	1443	4640	5842	85
H(8A)	1764	5053	4163	64
H(8B)	3268	4307	4179	64
H(9)	261	5336	2306	55
H(10)	-1627	6252	1455	67
H(11)	-2355	5180	352	65
H(13)	-1968	3241	-548	68
H(14)	-683	1328	-813	70
H(15)	1252	529	23	57
H(19)	3287	2396	102	44
H(22)	4392	-424	2758	45
H(25)	2817	-1700	2247	54
H(26)	1321	-2758	3018	70
H(27)	-618	-1715	3736	71
H(29)	-2096	315	4210	74
H(30)	-2415	2407	4224	78
H(31)	-724	3327	3658	62
H(33A)	5461	2316	-375	89
H(33B)	6361	960	-210	89
H(33C)	6477	1984	476	89
H(34A)	6612	-613	2482	104
H(34B)	7016	571	1964	104
H(34C)	7034	-556	1345	104
H(1)	1120(30)	3170(20)	4554(18)	45(7)
H(2)	2650(20)	1320(20)	4415(15)	26(6)

Computational methods

All quantum mechanical calculations were carried out using the Jaguar software version 7.6 developed by Schrödinger Inc. [1] Geometry optimizations were carried out on initial guess structures, and vibrational frequencies were gathered to confirm the optimized geometries as intermediates or transition states and to construct a free energy profile. Solvation energies were calculated using the PBF Poisson-Boltzmann implicit continuum solvation model [2] in Jaguar, with a dielectric constant of 8.55 and a probe radius of 2.451 Å for TFAH.

Geometry optimization and vibrational data were calculated using the B3LYP density functional [3] with a smaller basis set, whereas single point gas-phase and solvated energies were calculated using the M06 functional [4] and a larger basis set. Here the "smaller basis set" consists of a modified double-ζ Los Alamos basis set and pseudopotential [5] that includes *f* functions for rhodium [6], and the 6-31G** basis set [7] for the other atoms; whereas the "larger basis set" consists of the triple-ζ Los Alamos basis set and pseudopotential (LACV3P**++) modified to include *f* functions and diffuse functions for rhodium, and the 6-311G**++ basis set [8] for the other atoms.

The free energy for each molecular species in solution was calculated using the formula

$$G = E_{gas} + \Delta G_{solv} + ZPE + H_{vib} + 6kT - T[S_{vib} + 0.54(S_{trans} + S_{rot} - 14.3 \text{ e.u.}) + 7.98 \text{ e.u.}]$$

where the last term is an empirical approximation of the change in the translational and rotational entropy of the molecule between the gas phase and the solution phase (due to the finite librational frequencies) derived from Wertz [9].

For pure liquids (e.g., trifluoroacetic acid), the Gibbs free energy was calculated using the formula

$$G_{liquid} = E_{gas} + ZPE + H_{tot} - TS_{tot} + \Delta G_{gas \to liquid}$$

where $\Delta G_{gas \to liquid} = G_{liquid} - G_{gas}(1 \text{ atm})$ is the free energy of condensation to liquid from 1 atm gas. We can solve for this by noting that

$$\Delta G_{gas \to liquid} = \Delta G_{exp} + \Delta G_{gas \to solv},$$

where $\Delta G_{exp} = G_{gas}(P) - G_{gas}(1 \text{ atm})$ is the expansion of the gas from 1 atm to the vapor pressure *P*, and $\Delta G_{gas \to solv}$ is the condensation of gas to liquid. Since a liquid is by definition at equilibrium with its vapor pressure, $\Delta G_{gas \to solv} = 0$, and we thus have

$$\Delta G_{gas \to liquid} = G_{gas}(P) - G_{gas}(1 \text{ atm}) = RTln\left(\frac{P}{1 \text{ atm}}\right).$$

We can find the vapor pressure *P* at a given temperature using the Antoine Equation:

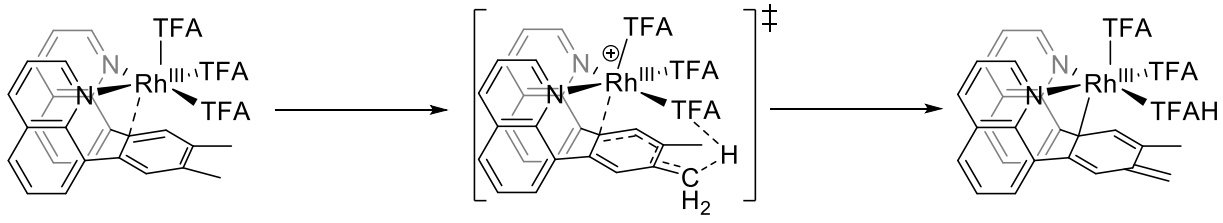
$$log_{10} P = A - \frac{B}{C + T},$$

where the empirical parameters *A*, *B*, and *C* vary with the solvent and temperature range and were taken from Table S2. Calculations were performed at nine temperature levels spaced by 25 K from 298.15 K to 498.15 K.

Table S8 Antoine equation parameters used for trifluoroacetic acid and water at each temperature point investigated. Numbers taken from [10] and are set such that *P* will be measured in bar.

Temperature	Trifluoroacetic acid		
	A	B	C
298.15 K	3.33963	1267.252	-52.958
323.15 K	3.33963	1267.252	-52.958
348.15 K	3.33963	1267.252	-52.958
373.15 K	3.33963	1267.252	-52.958
398.15 K	3.33963	1267.252	-52.958
423.15 K	3.33963	1267.252	-52.958
448.15 K	3.33963	1267.252	-52.958
473.15 K	3.33963	1267.252	-52.958
498.15 K	3.33963	1267.252	-52.958

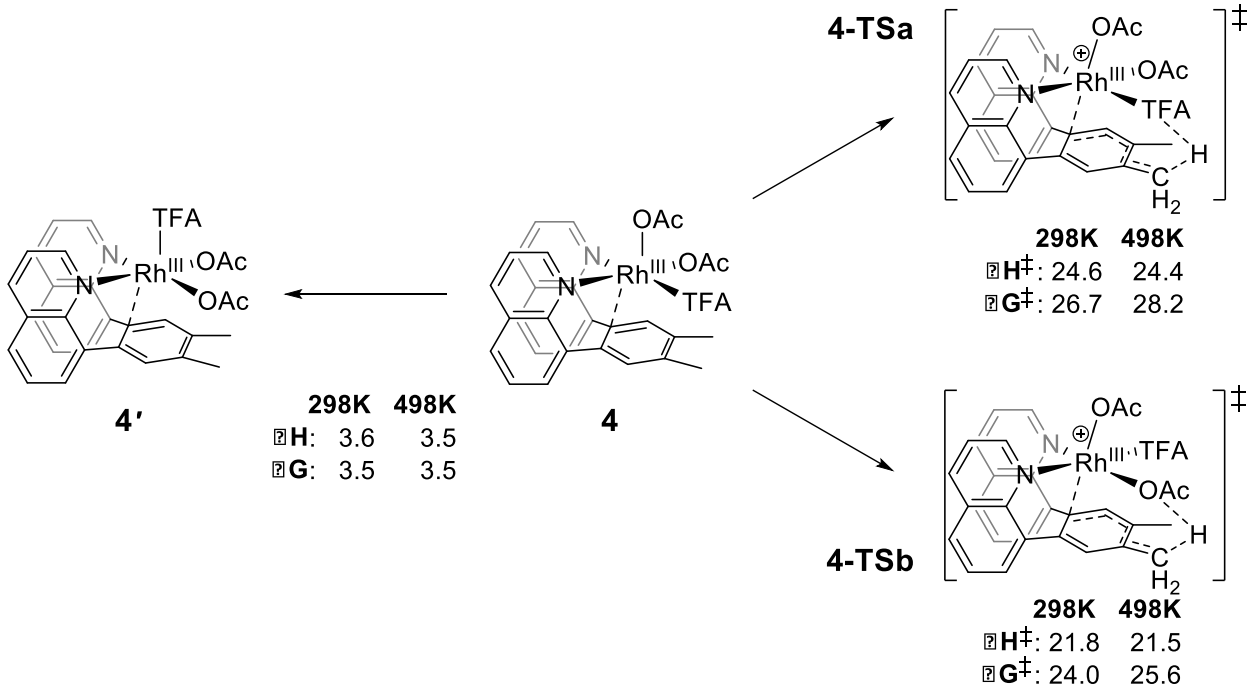
Computational results



	298K	498K
H‡	22.4	22.2
G‡	24.2	25.5
S‡	-6.0	-6.6

	298K	498K
H	3.8	3.2
G	4.8	5.1
S	-3.4	-3.7

Scheme S1. Reproduction of Scheme 4 in the main text, showing the enthalpy, free energy, and entropy of activation of **3**, as well as the enthalpy, free energy and entropy change of conversion to **3a**. All numbers are in kcal/mol.



Scheme S2. Comparison of **4** and its symmetric isomer **4′** (left) shows that **4′** is several kcal/mol higher in energy. Comparison of internal deprotonation by TFA and OAc ligands (right, also as in Scheme 7) shows that an OAc ligand is more likely to interact with the methyl group.

Tables of Cartesian coordinates and thermodynamic values

Table S9. Cartesian coordinates of complex **3**

Atom	x	y	z
Rh1	-1.63378	0.344652	-1.77592
N2	-2.36148	-0.84371	-0.20704
C3	-3.09572	-1.92149	-0.44146
C4	-3.47106	-2.81421	0.58254
C5	-3.03737	-2.58081	1.864981
C6	-6.33484	1.656454	-1.77943
C7	-5.77848	1.073588	-2.89178
C8	-4.3846	0.849526	-2.93692
N9	-3.577	1.224887	-1.95256
H10	-3.35524	-2.10012	-1.47915
H11	-4.07411	-3.68015	0.332882
H12	-3.28873	-3.26129	2.674112
O13	-2.32188	-1.06254	-3.04192
H14	-3.91428	0.343491	-3.7694
O15	-0.00765	-0.8571	-1.49827
C16	1.184524	-0.74545	-2.00444
O17	1.798507	0.221712	-2.40624
C18	1.88937	-2.13305	-1.9441
F19	3.033105	-2.13398	-2.63904
F20	2.193602	-2.43052	-0.65344
F21	1.113404	-3.12701	-2.41306
O22	-0.75531	1.556753	-3.14697
C23	-1.18407	1.755528	-4.34572
O24	-2.17417	1.324662	-4.9194
C25	-0.28562	2.779943	-5.09479
F26	-0.28334	2.556669	-6.41351
F27	-0.78261	4.030425	-4.8884
F28	0.991606	2.789152	-4.66931
C29	-1.63693	-1.57284	-4.03556

O30	-0.50825	-1.36794	-4.41295
C31	-2.56029	-2.58148	-4.77874
F32	-1.90881	-3.22613	-5.74642
F33	-3.05824	-3.50546	-3.9202
F34	-3.61492	-1.94071	-5.33148
C35	-4.08845	1.912535	-0.87612
C36	-5.49395	2.100087	-0.72694
C37	-5.98172	2.736068	0.443182
C38	-5.10654	3.197036	1.399651
C39	-3.71094	3.083303	1.202704
C40	-3.19352	2.461213	0.081386
H41	-7.05431	2.86269	0.56225
H42	-5.48178	3.6842	2.294517
H43	-3.02915	3.51878	1.927092
C44	-1.91905	-0.56575	1.063399
C45	-2.23375	-1.4473	2.142032
C46	-1.71718	-1.17736	3.434262
C47	-0.91402	-0.08126	3.640035
C48	-0.61843	0.792943	2.570868
C49	-1.11324	0.583868	1.294581
H50	-1.95609	-1.85705	4.247322
H51	-0.50476	0.122792	4.624777
H52	0.008757	1.661265	2.750856
H53	-6.38601	0.748353	-3.72911
H54	-7.40944	1.797304	-1.69719
C55	-1.73503	2.521123	-0.24376
C56	-0.77737	1.577091	0.222954
C57	0.590141	1.830127	-0.06153
C58	1.015639	2.921195	-0.8013
C59	0.052452	3.866224	-1.24441
C60	-1.28874	3.648711	-0.95343
H61	1.324312	1.11608	0.295541
H64	-2.02831	4.365798	-1.29846
C64	0.467263	5.074255	-2.04313
H65	-0.39031	5.709888	-2.27626
H66	1.206223	5.677761	-1.50305
H67	0.924763	4.768121	-2.98901
C67	2.46519	3.064153	-1.17904
H68	2.845958	4.072324	-0.98335
H69	3.087296	2.343421	-0.64491
H70	2.576705	2.856875	-2.24903

Table S10. Thermodynamic values for complex **3**

Temp	298.15	498.15
E_{gas}	-2799.82	-2799.82
E_{solv}	-2799.86	-2799.86
G	-2799.44	-2799.52
ZPE	299.754	299.754
H_{vib}	26.206	66.367
S_{trans}	45.924	48.474
S_{rot}	38.386	39.916
S_{vib}	172.777	274.180
solv	-22.0	-22.0

Table S11. Cartesian coordinates of transition state **3-TS**

Atom	x	y	z
Rh1	-1.67165	0.488932	-1.60779
N2	-2.25305	-0.76084	0.024667
C3	-2.87295	-1.88937	-0.30497
C4	-3.31156	-2.83179	0.644506
C5	-3.08519	-2.58842	1.975303
C6	-6.36613	1.516089	-1.6878
C7	-5.83009	0.746497	-2.69342
C8	-4.44069	0.493618	-2.72126
N9	-3.63096	1.008643	-1.80635
H10	-2.99202	-2.065	-1.36871
H11	-3.80731	-3.73311	0.301498
H12	-3.4006	-3.29392	2.739368
O13	-2.03348	-1.14006	-2.89961
H14	-3.97579	-0.13322	-3.47048
O15	0.308956	-0.29386	-1.31008
C16	1.400173	-0.33887	-1.91532
O17	2.207473	0.593391	-2.21294
C18	1.974332	-1.75127	-2.20487
F19	2.582902	-1.81897	-3.38896
F20	2.893575	-2.02547	-1.24454

F21	1.032372	-2.70198	-2.14181
O22	-0.94223	1.662408	-3.11071
C23	-1.47067	1.793486	-4.28069
O24	-2.51513	1.352631	-4.73563
C25	-0.61767	2.755241	-5.15467
F26	-0.83199	2.557546	-6.45975
F27	-0.97319	4.037117	-4.86679
F28	0.704024	2.648997	-4.92445
C29	-1.29735	-1.49334	-3.90507
O30	-0.20259	-1.09889	-4.26178
C31	-2.03316	-2.59759	-4.71563
F32	-1.30804	-3.04034	-5.74534
F33	-2.32486	-3.65836	-3.92332
F34	-3.20848	-2.13002	-5.20061
C35	-4.11971	1.829364	-0.81705
C36	-5.51514	2.082805	-0.70429
C37	-5.96887	2.875598	0.380165
C38	-5.06586	3.390867	1.283521
C39	-3.67765	3.167658	1.125469
C40	-3.18832	2.400868	0.08336
H41	-7.03304	3.068065	0.484175
H42	-5.41528	3.995518	2.115212
H43	-2.98202	3.625242	1.822638
C44	-2.00102	-0.48201	1.352801
C45	-2.41211	-1.40588	2.367009
C46	-2.12031	-1.14126	3.729302
C47	-1.42706	-0.00936	4.081531
C48	-1.01396	0.897796	3.084571
C49	-1.2903	0.696182	1.741215
H50	-2.44431	-1.85678	4.479796
H51	-1.19438	0.194431	5.122284
H52	-0.46964	1.793349	3.368728
H53	-6.45263	0.309239	-3.466
H54	-7.4361	1.699479	-1.63541
C55	-1.71602	2.258502	-0.22846
C56	-0.80667	1.689309	0.754723
C57	0.525494	2.004856	0.708138
C58	1.068106	2.858254	-0.30882
C59	0.147017	3.666007	-1.07788
C60	-1.18024	3.365637	-1.00366
H61	1.22232	1.468057	1.345634
H64	-1.88354	3.92849	-1.61159
C64	0.659653	4.7106	-2.0352
H65	-0.16173	5.311241	-2.43309
H66	1.3811	5.381251	-1.55516
H67	1.157759	4.239823	-2.89018
C67	2.421553	2.723983	-0.67386
H68	2.877355	3.473198	-1.31584
H69	3.100222	2.266522	0.045904
H70	2.186581	1.61273	-1.55999

Table S12. Thermodynamic values for transition state **3-TS**

Temp	298.15	498.15
E_{gas}	-2799.79	-2799.79
E_{solv}	-2799.82	-2799.82
G	-2799.40	-2799.48
ZPE	296.726	296.726
H_{vib}	25.482	65.421
S_{trans}	45.924	48.474
S_{rot}	38.380	39.910
S_{vib}	166.792	267.611
solv	-20.1	-20.1

Table S13. Cartesian coordinates of complex **3a**

Atom	x	y	z
Rh1	-1.72027	0.370111	-1.58718
N2	-2.12053	-0.85041	0.114672
C3	-2.69719	-2.01122	-0.19109
C4	-3.09648	-2.95537	0.771186
C5	-2.88724	-2.67365	2.09699
C6	-6.39758	1.482721	-1.46589
C7	-5.95631	0.587969	-2.4136
C8	-4.58281	0.266416	-2.48613
N9	-3.70088	0.819248	-1.66768
H10	-2.83499	-2.20655	-1.24802
H11	-3.55573	-3.8817	0.443959
H12	-3.17877	-3.37377	2.875361

O13	-2.123	-1.43962	-2.99388
H14	-4.19355	-0.45249	-3.19707
O15	0.348948	-0.03372	-1.26531
C16	1.327035	-0.46422	-1.89013
O17	1.414186	-0.99492	-3.04437
C18	2.695957	-0.36429	-1.17141
F19	3.45172	-1.44575	-1.41687
F20	3.356166	0.722018	-1.59925
F21	2.534289	-0.26272	0.158633
O22	-1.656	1.442078	-3.35014
C23	-0.59798	1.891809	-3.93821
O24	0.583266	1.749744	-3.66751
C25	-1.00414	2.803098	-5.13038
F26	0.042564	3.114616	-5.90339
F27	-1.94723	2.240535	-5.91015
F28	-1.5207	3.968734	-4.65063
C29	-1.61945	-1.64483	-4.12867
O30	-0.47038	-1.38886	-4.54583
C31	-2.57758	-2.34287	-5.12896
F32	-2.06446	-2.45742	-6.35501
F33	-2.88776	-3.57919	-4.68176
F34	-3.73928	-1.64854	-5.22751
C35	-4.09383	1.760157	-0.74878
C36	-5.4663	2.10329	-0.5941
C37	-5.81171	3.039125	0.412557
C38	-4.82679	3.601109	1.195415
C39	-3.46418	3.278518	0.99313
C40	-3.07926	2.368295	0.025438
H41	-6.85522	3.305664	0.551986
H42	-5.09307	4.317981	1.966677
H43	-2.70208	3.768735	1.59206
C44	-1.88963	-0.52966	1.436698
C45	-2.27467	-1.45298	2.466501
C46	-2.03285	-1.14766	3.829076
C47	-1.4235	0.034243	4.169793
C48	-1.04381	0.94171	3.161871
C49	-1.24714	0.696448	1.80907
H50	-2.33796	-1.86439	4.586195
H51	-1.23885	0.280792	5.211005
H52	-0.58287	1.88232	3.445346
H53	-6.64235	0.109925	-3.10417
H54	-7.45298	1.72749	-1.37984
C55	-1.6215	2.084192	-0.32414
C56	-0.76546	1.69401	0.827117
C57	0.479982	2.211171	0.968402
C58	1.052705	3.206316	0.074261
C59	0.178803	3.71422	-0.99137
C60	-1.06358	3.19981	-1.12826
H61	1.122975	1.836189	1.760447
H64	-1.70778	3.584688	-1.91261
C64	0.687417	4.777474	-1.9298
H65	-0.07551	5.049726	-2.66228
H66	0.995894	5.682095	-1.3914
H67	1.557742	4.409692	-2.48589
C67	2.332829	3.616537	0.246765
H68	2.799985	4.343931	-0.40612
H69	2.946511	3.209554	1.044469
H70	0.517162	-1.06271	-3.64164

Table S14. Thermodynamic values for complex **3a**

Temp	298.15	498.15
E_{gas}	-2799.83	-2799.83
E_{solv}	-2799.85	-2799.85
G	-2799.43	-2799.51
ZPE	299.193	299.193
H_{vib}	25.231	64.861
S_{trans}	45.924	48.474
S_{rot}	38.489	40.019
S_{vib}	169.361	270.403
solv	-16.1	-16.1

Table S15. Cartesian coordinates of complex **4**

Atom	x	y	z
Rh1	-1.7133	0.404582	-1.8208
N2	-2.37301	-0.80659	-0.1736
C3	-3.14604	-1.84876	-0.44433
C4	-3.54692	-2.78108	0.532481

C5	-3.10083	-2.62424	1.820857
C6	-6.39119	1.724874	-1.66677
C7	-5.88992	1.120857	-2.79434
C8	-4.50512	0.854409	-2.88612
N9	-3.6608	1.208124	-1.92744
H10	-3.42077	-1.96171	-1.48718
H11	-4.17974	-3.61324	0.243648
H12	-3.36778	-3.33368	2.599681
O13	-2.34429	-1.06177	-3.03726
H14	-4.05376	0.362018	-3.73834
O15	0.017656	-0.64719	-1.5452
C16	1.170863	-0.4447	-2.1007
O17	1.684739	0.560879	-2.55441
C18	2.018189	-1.74799	-2.02111
F19	3.066408	-1.70887	-2.85592
F20	2.509594	-1.88564	-0.75868
F21	1.311012	-2.85898	-2.29574
O22	-0.96206	1.579612	-3.27992
C23	-1.39337	1.624649	-4.51496
O24	-2.47098	1.209466	-4.94282
C25	-0.36613	2.268639	-5.43788
H26	-0.81151	2.460481	-6.41567
H27	0.021384	3.196934	-5.00904
H28	0.475274	1.576316	-5.53963
C29	-1.61373	-1.56012	-4.03393
O30	-0.48118	-1.25196	-4.34542
C31	-2.42168	-2.5936	-4.81619
H32	-1.73534	-3.23177	-5.37474
H33	-3.05527	-3.20002	-4.16368
H34	-3.0668	-2.06189	-5.52397
C35	-4.11286	1.899063	-0.82916
C36	-5.50546	2.134299	-0.63668
C37	-5.93542	2.763445	0.559115
C38	-5.0154	3.158006	1.503535
C39	-3.63182	2.985141	1.269284
C40	-3.16643	2.378723	0.116472
H41	-6.99823	2.930976	0.711779
H42	-5.34538	3.636232	2.421014
H43	-2.91511	3.363754	1.992231
C44	-1.93058	-0.59708	1.111518
C45	-2.26964	-1.52506	2.146999
C46	-1.76335	-1.3374	3.457579
C47	-0.946	-0.26896	3.734662
C48	-0.62895	0.656465	2.718032
C49	-1.10994	0.528174	1.424421
H50	-2.02743	-2.05645	4.227986
H51	-0.54722	-0.12369	4.73413
H52	0.000877	1.50939	2.953183
H53	-6.53648	0.817445	-3.61076
H54	-7.45741	1.90354	-1.55264
C55	-1.70452	2.383486	-0.22198
C56	-0.73911	1.572017	0.429532
C57	0.623525	1.878213	0.253353
C58	1.060497	2.916495	-0.55905
C59	0.100033	3.724553	-1.21931
C60	-1.24459	3.456044	-1.02218
H61	1.359269	1.240747	0.73408
H64	-1.98644	4.080537	-1.51207
C64	0.525026	4.831767	-2.15075
H65	-0.34201	5.344492	-2.57559
H66	1.147145	5.579854	-1.64467
H67	1.116792	4.427366	-2.97988
C67	2.533437	3.117069	-0.7925
H68	2.817829	4.174102	-0.77789
H69	3.129384	2.587604	-0.04457
H70	2.793403	2.701762	-1.77333

Table S16. Thermodynamic values for complex **4**

Temp	298.15	498.15
E_{gas}	-2204.35	-2204.35
E_{solv}	-2204.39	-2204.39
G	-2203.92	-2203.99
ZPE	328.174	328.174
H_{vib}	23.847	61.192
S_{trans}	45.493	48.043
S_{rot}	37.584	39.114
S_{vib}	156.221	250.429
solv	-22.0	-22.0

Table S17. Cartesian coordinates of complex **4′**

Atom	x	y	z
Rh1	-1.63226	0.384247	-1.80926
N2	-2.34616	-0.81523	-0.19554
C3	-3.09939	-1.87656	-0.44571
C4	-3.48719	-2.78811	0.55715
C5	-3.04694	-2.59098	1.842534
C6	-6.35192	1.681019	-1.75088
C7	-5.81669	1.09338	-2.87115
C8	-4.4241	0.860776	-2.94066
N9	-3.60155	1.229935	-1.96836
H10	-3.36641	-2.03073	-1.48529
H11	-4.10536	-3.63789	0.288791
H12	-3.30608	-3.28453	2.638263
O13	-2.3131	-1.05149	-3.0445
H14	-3.9599	0.369493	-3.7859
O15	0.020302	-0.77455	-1.55219
C16	1.237596	-0.57508	-2.0209
O17	1.764417	0.49067	-2.30434
C18	1.983134	-1.90066	-2.16944
H19	3.056805	-1.71582	-2.23978
H20	1.765924	-2.57768	-1.3388
H21	1.635573	-2.3759	-3.09223
O22	-0.79598	1.549635	-3.22618
C23	-1.22238	1.653125	-4.45936
O24	-2.28939	1.240151	-4.91199
C25	-0.20183	2.35862	-5.34557
H26	-0.65207	2.59763	-6.31049
H27	0.173967	3.266935	-4.86671
H28	0.649979	1.687	-5.49099
C29	-1.65566	-1.58617	-4.03679
O30	-0.52767	-1.41821	-4.4415
C31	-2.60753	-2.59293	-4.74853
F32	-1.97674	-3.27669	-5.70678
F33	-3.11443	-3.4904	-3.86491
F34	-3.65545	-1.95129	-5.30933
C35	-4.09241	1.905657	-0.87816
C36	-5.4926	2.109411	-0.70648
C37	-5.95408	2.733794	0.480134
C38	-5.05792	3.158695	1.434229
C39	-3.66685	3.019387	1.220754
C40	-3.1739	2.413712	0.079121
H41	-7.02267	2.876587	0.616531
H42	-5.41319	3.635926	2.34267
H43	-2.96913	3.422697	1.948766
C44	-1.90376	-0.57042	1.081629
C45	-2.22856	-1.47373	2.141503
C46	-1.71389	-1.24353	3.44215
C47	-0.90313	-0.16035	3.680104
C48	-0.60027	0.739022	2.63537
C49	-1.09037	0.569044	1.350784
H50	-1.96397	-1.94223	4.235712
H51	-0.49703	0.01595	4.671548
H52	0.026788	1.601361	2.841102
H53	-6.44077	0.774549	-3.69898
H54	-7.42397	1.833244	-1.65439
C55	-1.71366	2.453847	-0.25417
C56	-0.74025	1.591314	0.318992
C57	0.623009	1.901935	0.116835
C58	1.044622	2.983101	-0.64063
C59	0.070723	3.835601	-1.22159
C60	-1.27135	3.563689	-1.00537
H61	1.367196	1.240756	0.547585
H64	-2.02194	4.221136	-1.43565
C64	0.476358	5.007691	-2.08003
H65	-0.39917	5.540446	-2.46053
H66	1.095451	5.72458	-1.52716
H67	1.066872	4.671477	-2.93989
C67	2.513198	3.186303	-0.89951
H68	2.798835	4.24271	-0.8941
H69	3.121098	2.658854	-0.1599
H70	2.756598	2.759316	-1.87901

Table S18. Thermodynamic values for complex **4′**

Temp	298.15	498.15
E_{gas}	-2204.35	-2204.35

E_{solv}	-2204.38	-2204.38
G	-2203.91	-2203.99
ZPE	328.220	328.220
H_{vib}	23.860	61.205
S_{trans}	45.493	48.043
S_{rot}	37.635	39.166
S_{vib}	156.382	250.589
solv	-19.6	-19.6

Table S19. Cartesian coordinates of transition state **4-TSa**

Atom	x	y	z
Rh1	-1.68648	0.514609	-1.62397
N2	-2.25371	-0.75892	0.023915
C3	-2.88305	-1.87868	-0.31164
C4	-3.32019	-2.82914	0.63148
C5	-3.07982	-2.60172	1.962886
C6	-6.38618	1.522333	-1.62912
C7	-5.85537	0.763333	-2.64507
C8	-4.46433	0.521024	-2.68832
N9	-3.64836	1.031283	-1.77822
H10	-3.01189	-2.03271	-1.37826
H11	-3.82642	-3.72385	0.285825
H12	-3.39238	-3.31345	2.72253
O13	-2.03518	-1.10356	-2.91429
H14	-3.9919	-0.08713	-3.44682
O15	0.305694	-0.26359	-1.31722
C16	1.376303	-0.30143	-1.95323
O17	2.168015	0.642383	-2.27357
C18	1.978678	-1.70281	-2.22974
F19	2.590337	-1.77703	-3.41321
F20	2.909129	-1.9403	-1.26676
F21	1.06429	-2.67844	-2.14818
O22	-0.98548	1.693238	-3.11665
C23	-1.49701	1.741962	-4.32225
O24	-2.60726	1.342086	-4.6692
C25	-0.52616	2.360931	-5.32057
H26	-1.05817	2.637795	-6.23253
H27	-0.01995	3.232175	-4.89666
H28	0.235688	1.610363	-5.55392
C29	-1.24601	-1.44115	-3.90958
O30	-0.14264	-0.97136	-4.16483
C31	-1.8713	-2.51068	-4.8032
H32	-1.09339	-2.99154	-5.39823
H33	-2.4143	-3.25708	-4.21678
H34	-2.58433	-2.0253	-5.479
C35	-4.13228	1.839512	-0.77675
C36	-5.52863	2.084918	-0.64923
C37	-5.97888	2.865071	0.445562
C38	-5.07256	3.376522	1.347394
C39	-3.68486	3.161547	1.176344
C40	-3.19742	2.408459	0.122968
H41	-7.04349	3.050364	0.558721
H42	-5.41864	3.971686	2.187411
H43	-2.98635	3.615708	1.872741
C44	-1.99404	-0.49408	1.35174
C45	-2.3986	-1.42592	2.361263
C46	-2.0956	-1.17299	3.722999
C47	-1.39969	-0.04383	4.078918
C48	-0.99679	0.873444	3.086955
C49	-1.28379	0.683323	1.744334
H50	-2.41396	-1.89377	4.470534
H51	-1.15847	0.150852	5.11961
H52	-0.45182	1.767674	3.374087
H53	-6.48394	0.329119	-3.41473
H54	-7.45654	1.700378	-1.56491
C55	-1.72732	2.279539	-0.194
C56	-0.81088	1.686886	0.762782
C57	0.524895	1.993348	0.705501
C58	1.062955	2.861769	-0.29868
C59	0.134708	3.683781	-1.04009
C60	-1.19446	3.388037	-0.96011
H61	1.223813	1.438229	1.324688
H64	-1.9007	3.962811	-1.55333
C64	0.640279	4.74879	-1.97792
H65	-0.18614	5.34826	-2.36948
H66	1.349903	5.423306	-1.48459
H67	1.159699	4.300524	-2.83366
C67	2.413972	2.735801	-0.67737

H68	2.86865	3.503013	-1.29875
H69	3.096834	2.257232	0.024362
H70	2.158641	1.628663	-1.60796

Table S20. Thermodynamic values for transition state **4-TSa**

Temp	298.15	498.15
E_{gas}	-2204.31	-2204.31
E_{solv}	-2204.34	-2204.34
G	-2203.87	-2203.95
ZPE	325.203	325.203
H_{vib}	23.041	60.175
S_{trans}	45.493	48.043
S_{rot}	37.576	39.106
S_{vib}	149.138	242.788
solv	-18.8	-18.8

Table S21. Cartesian coordinates of transition state **4-TSb**

Atom	x	y	z
Rh1	-1.64903	0.487243	-1.61804
N2	-2.26108	-0.73341	0.026478
C3	-2.91589	-1.84207	-0.29873
C4	-3.36114	-2.78079	0.651464
C5	-3.09991	-2.55542	1.979125
C6	-6.36033	1.539364	-1.70169
C7	-5.81859	0.7946	-2.72249
C8	-4.42813	0.546323	-2.748
N9	-3.61966	1.041106	-1.82245
H10	-3.05517	-1.9991	-1.36349
H11	-3.88821	-3.66618	0.312881
H12	-3.41486	-3.26033	2.744063
O13	-2.05313	-1.13262	-2.88972
H14	-3.95028	-0.05842	-3.50645
O15	0.285604	-0.30568	-1.24076
C16	1.42254	-0.37596	-1.80296
O17	2.191637	0.588332	-2.1163
C18	1.966387	-1.7617	-2.0892
H19	1.63452	-2.02821	-3.09702
H20	3.057331	-1.76318	-2.05459
H21	1.551884	-2.48641	-1.38502
O22	-0.9315	1.65994	-3.12779
C23	-1.43965	1.749822	-4.30696
O24	-2.45864	1.266475	-4.78242
C25	-0.60781	2.729769	-5.18107
F26	-0.80333	2.514199	-6.48844
F27	-1.00576	4.003566	-4.911
F28	0.714449	2.667782	-4.94118
C29	-1.3133	-1.49719	-3.91577
O30	-0.1992	-1.08051	-4.20103
C31	-2.02514	-2.5238	-4.79718
H32	-1.29302	-3.04861	-5.41319
H33	-2.60363	-3.23803	-4.20453
H34	-2.71721	-1.98868	-5.45712
C35	-4.11531	1.841916	-0.82069
C36	-5.51294	2.086779	-0.70443
C37	-5.97516	2.851902	0.396125
C38	-5.07811	3.35136	1.313891
C39	-3.68851	3.141346	1.152767
C40	-3.19039	2.403017	0.093981
H41	-7.04094	3.035659	0.500638
H42	-5.43313	3.934743	2.158458
H43	-2.99671	3.588669	1.860288
C44	-1.98881	-0.46385	1.351813
C45	-2.39681	-1.38919	2.366694
C46	-2.07911	-1.13903	3.725747
C47	-1.3704	-0.01602	4.075094
C48	-0.97145	0.898368	3.07928
C49	-1.26958	0.710436	1.738446
H50	-2.39919	-1.85627	4.47589
H51	-1.11904	0.177535	5.113564
H52	-0.42189	1.791076	3.362214
H53	-6.43823	0.374406	-3.50708
H54	-7.43102	1.718662	-1.64745
C55	-1.71759	2.287266	-0.21122
C56	-0.80412	1.716369	0.757085
C57	0.527098	2.04738	0.711034
C58	1.059503	2.9025	-0.30209

C59	0.134773	3.687011	-1.08247
C60	-1.19369	3.380622	-1.00127
H61	1.22908	1.509724	1.341969
H64	-1.9009	3.932337	-1.61506
C64	0.637073	4.716959	-2.06121
H65	-0.18975	5.304554	-2.46804
H66	1.355427	5.401825	-1.59641
H67	1.136396	4.233114	-2.90796
C67	2.419342	2.765093	-0.67098
H68	2.86949	3.519674	-1.31149
H69	3.099117	2.346444	0.072007
H70	2.185463	1.661727	-1.48911

Table S22. Thermodynamic values for transition state **4-TSb**

Temp	298.15	498.15
E_{gas}	-2204.32	-2204.32
E_{solv}	-2204.35	-2204.35
G	-2203.88	-2203.95
ZPE	325.342	325.342
H_{vib}	23.035	60.154
S_{trans}	45.493	48.043
S_{rot}	37.583	39.113
S_{vib}	148.721	242.332
solv	-19.9	-19.9

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