

## SUPPORTING INFORMATION

### Catalytic Synthesis of "Super" Linear Alkenyl Arenes Using a Rh(I) Catalyst Supported by a "Capping Arene" Ligand: Access to Aerobic Catalysis

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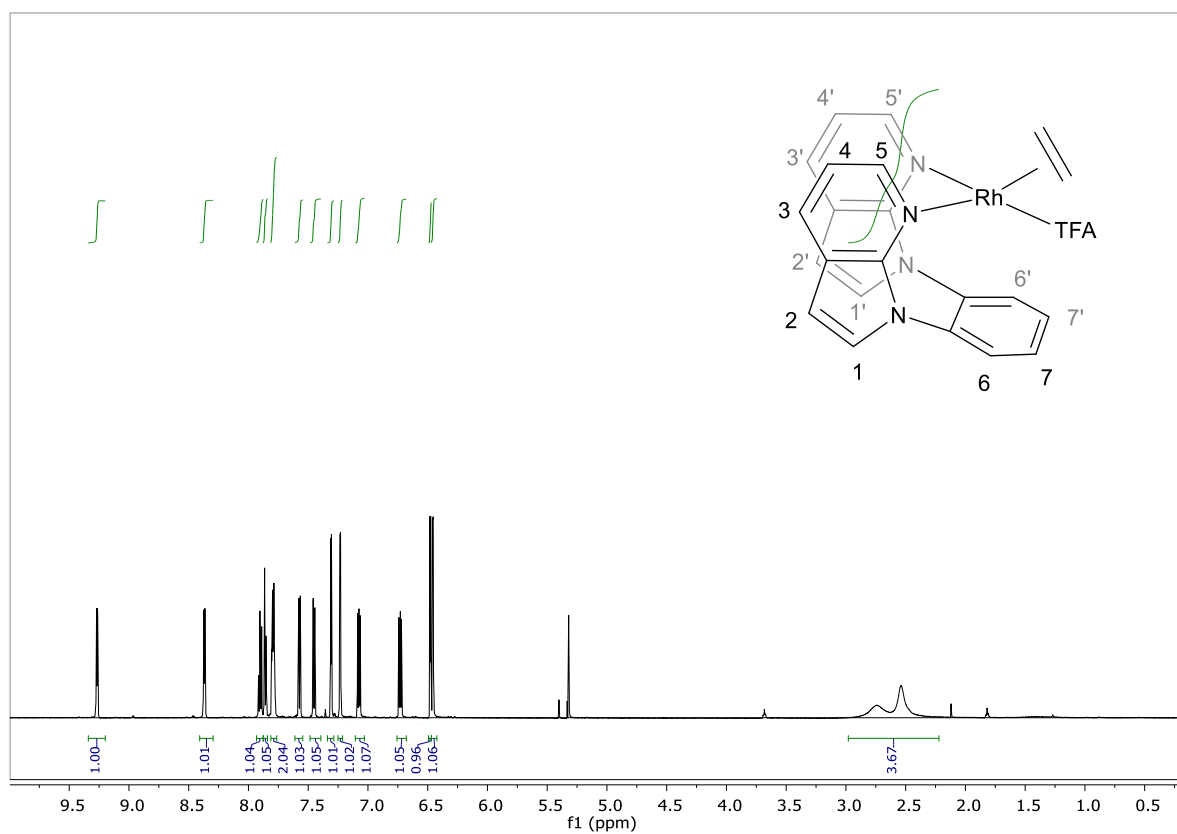
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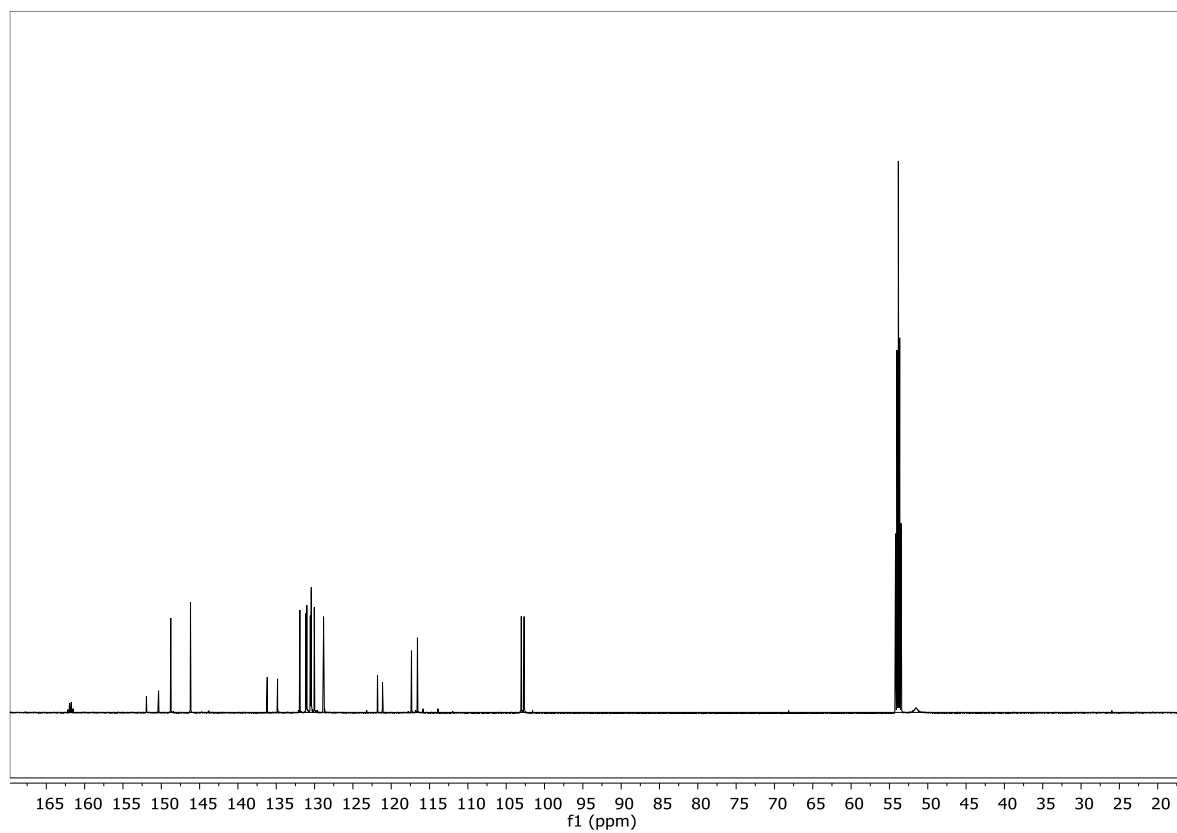
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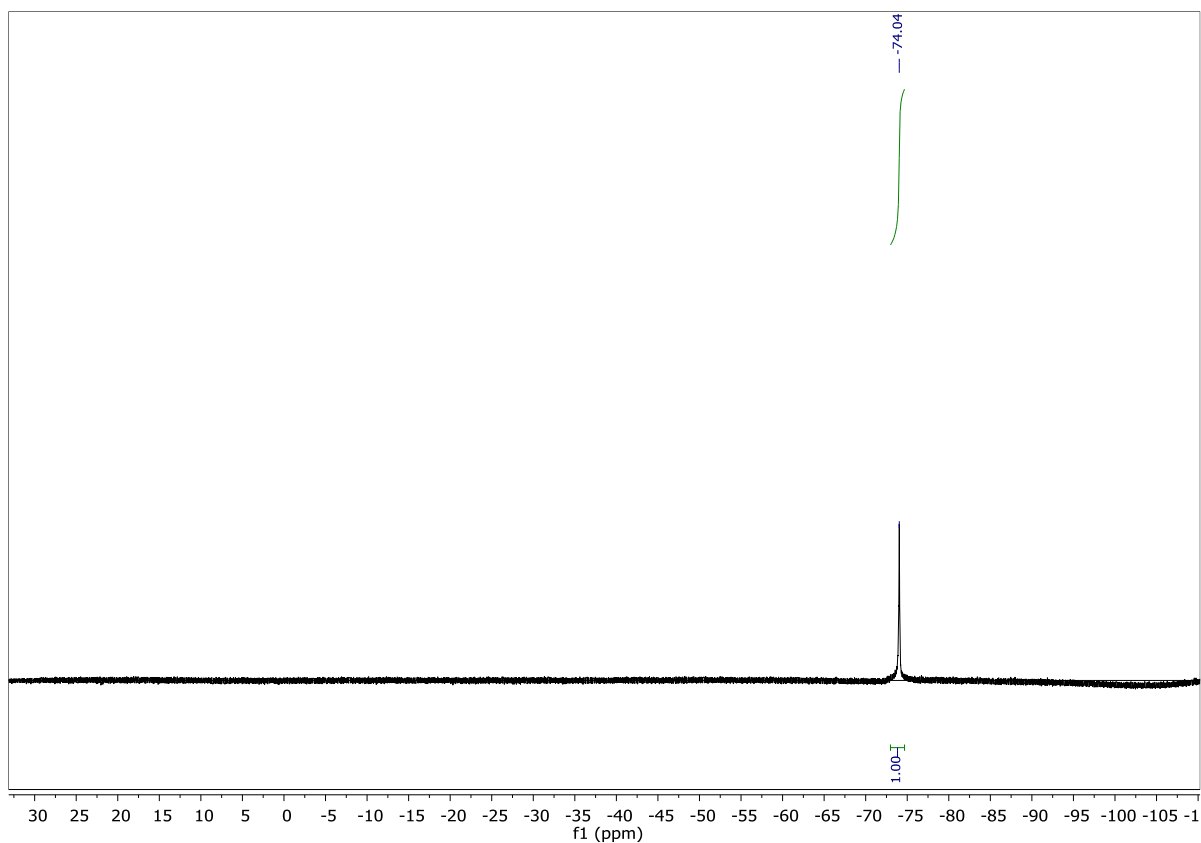
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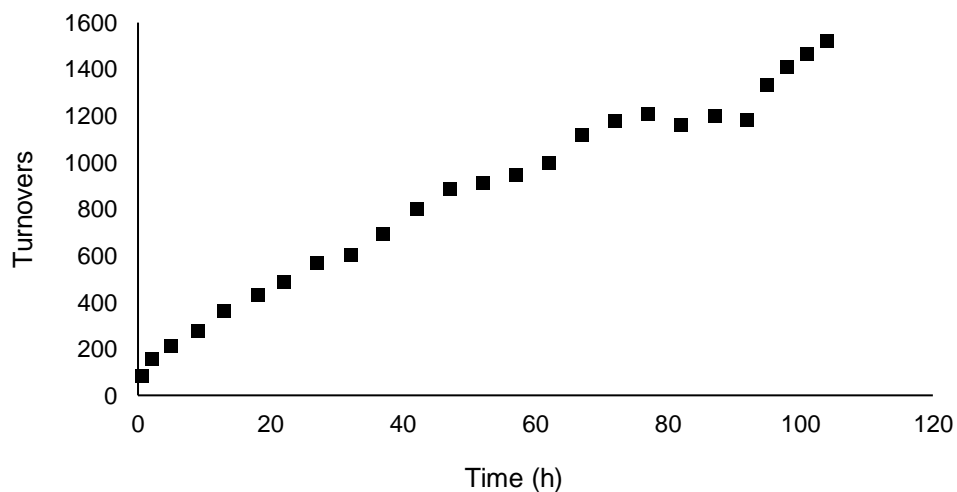
**Figure S1.**  $^1\text{H}$  NMR spectrum of  $(5\text{-FP})\text{Rh}(\text{TFA})(\eta^2\text{-C}_2\text{H}_4)$  (**1**) (includes some solvent residue).



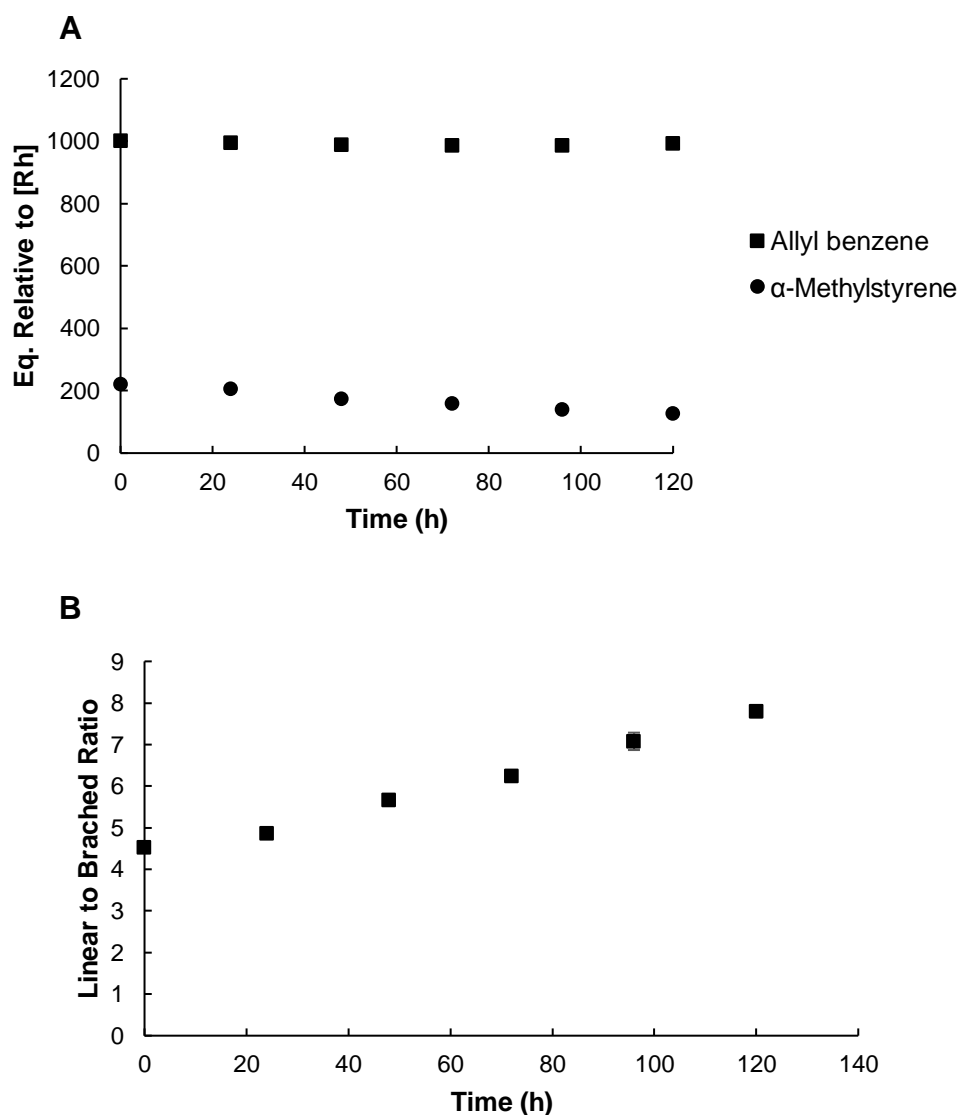
**Figure S2.**  $^{13}\text{C}$  NMR spectrum of  $(5\text{-FP})\text{Rh}(\text{TFA})(\eta^2\text{-C}_2\text{H}_4)$  (**1**) (includes some solvent residue).



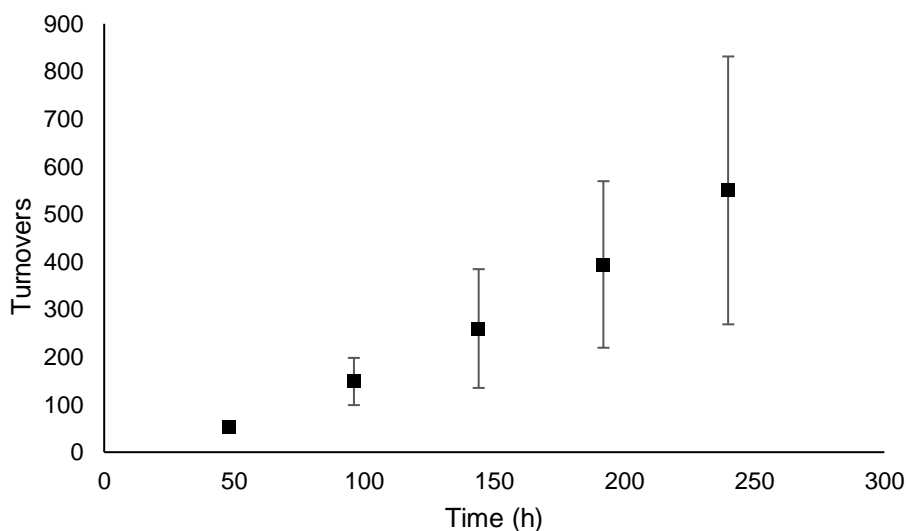
**Figure S3.**  $^{19}\text{F}$  NMR spectrum of  $(5\text{-FP})\text{Rh}(\text{TFA})(\eta^2\text{-C}_2\text{H}_4)$  (**1**).



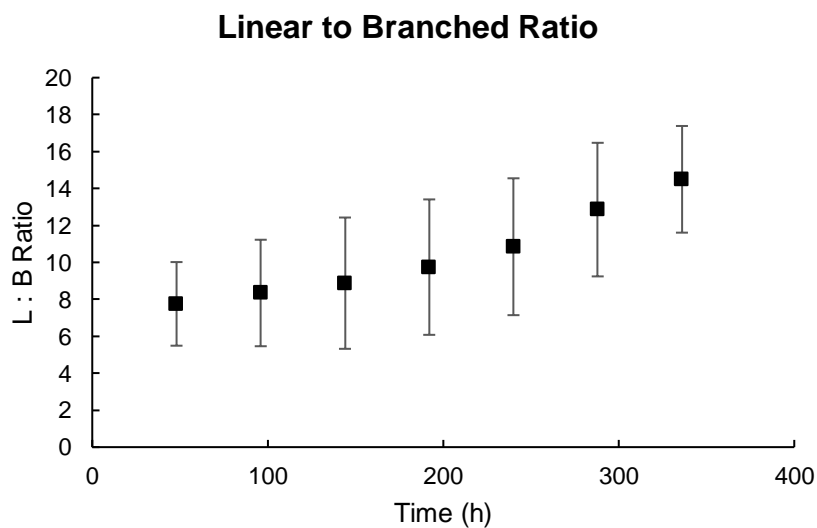
**Figure S4.** Plot of turnovers versus time for catalytic oxidative hydrophenylation of propylene with  $\text{Cu}(\text{II})$  oxidant that is regenerated *in situ* (using  $(5\text{-FP})\text{Rh}(\text{TFA})(\eta^2\text{-C}_2\text{H}_4)$  (**1**) as catalyst). Reaction conditions: 0.001 mol % Rh, 240 equiv.  $\text{Cu}(\text{OPiv})_2$ , 480 equiv.  $\text{HOPIv}$ , 30 psig propylene, at 150 °C. After sampling at the 92 h time point, an additional 480 equiv.  $\text{HOPIv}$  were added.



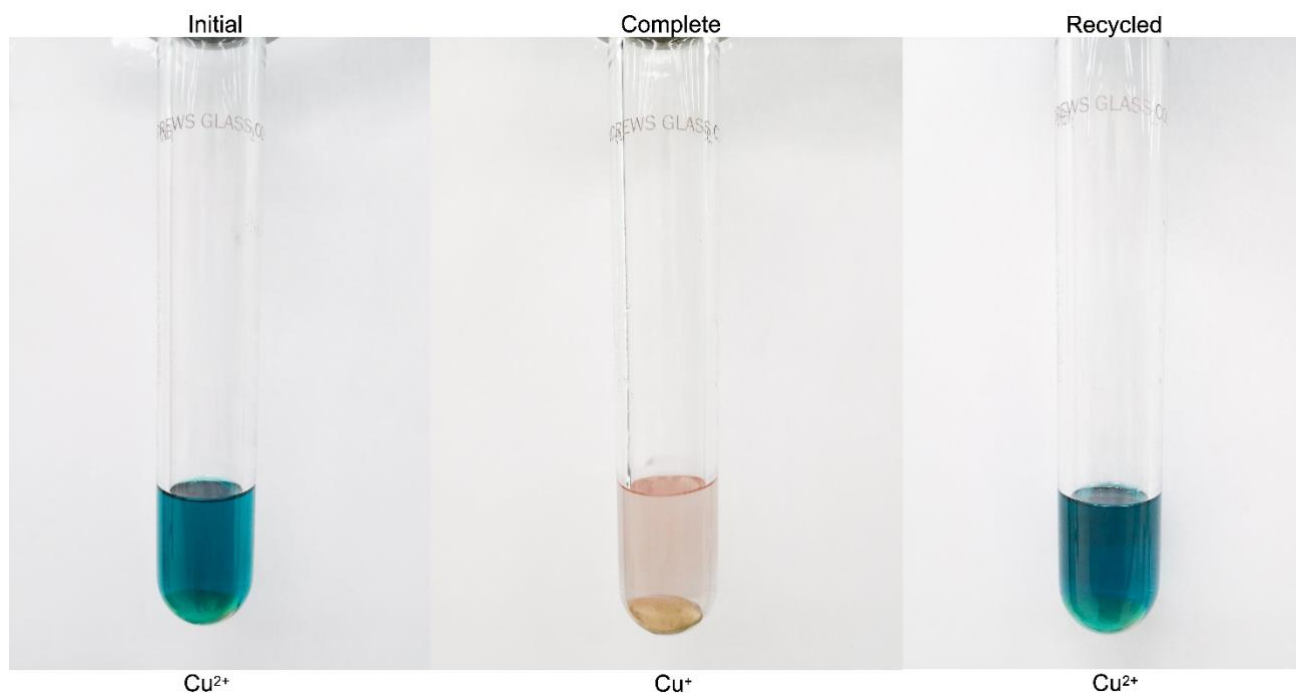
**Figure S5.** Alkenyl arenes products decomposition study with (5-FP)Rh(TFA)( $\eta^2$ -C<sub>2</sub>H<sub>4</sub>) (**1**). (A) Plot of alkenyl arenes versus time. Reaction conditions: 0.001 mol % Rh, 1 atm unpurified air, and 85 psig N<sub>2</sub> at 150 °C with initial allyl benzene (~1000 equivalents to [Rh]) and  $\alpha$ -methylstyrene (~200 equivalents to [Rh]) addition. Reactions were sampled every 24 hours and air was purged into reactor at every sample point. The data are from three separate experiments with standard deviations given (Note: most standard deviations are too small to be observed on the plot). (B) Plot of L:B ratio versus time under the reaction condition listed in Part A.



**Figure S6.** Catalytic oxidative hydrophenylation of propylene using air as oxidant with (5-FP)Rh(TFA)( $\eta^2$ -C<sub>2</sub>H<sub>4</sub>) (**1**). Reaction conditions: 0.001 mol % Rh, 4800 equiv. HOPiv, 1 atm unpurified air, 30 psig propylene, at 150 °C. Reactions were sampled every 48 hours and air was purged into reactor at every sample point. The data are from three separate experiments with standard deviations given.



**Figure S7.** Plot of L:B ratio versus time for (5-FP)Rh(TFA)( $\eta^2$ -C<sub>2</sub>H<sub>4</sub>) (**1**). Reaction conditions: 0.0001 mol % Rh, 2400 equiv. Cu(OPiv)<sub>2</sub>, 48000 equiv. HOPiv, 1 atm unpurified air, 30 psig propylene, at 150 °C. Air was purged into the reactor every 24 h, and the reaction mixture was sampled every 48 hours. The data are from four separate experiments with standard deviations given.



**Figure S8.** Photographs of reaction solution over the course of the reaction.

### Computational Methods

Free energies of organometallic compounds were computed at 423 K according to

$$G(C) = E_{M06} + G_{solv} + ZPE + 3kT + H_{vib} - T(S_{vib} + S_{elec} + S_{lib}) + kT \ln(C/C_0).$$

Structures were first optimized in vacuum with the B3LYP functional<sup>1-2</sup> including the Grimme-Becke-Johnson D3 empirical correction for dispersion<sup>3</sup>, using the 6-31G\*\* basis set<sup>4-5</sup> for organic elements and for rhodium the pseudopotential and triple- $\zeta$  valence functions of Hay and Wadt<sup>6</sup> (augmented with diffuse functions). Frequencies calculated at these geometries were used to compute ZPE,  $H_{vib}$  and  $S_{vib}$ . Librational entropies in solution  $S_{lib}$  were estimated from ideal gas translational and rotational values using

$$S_{lib} \text{ (e.u.)} = .78 * (S_{t,r,I.G.} - 12) + 5$$

where the constants are derived for benzene as Wertz<sup>7</sup> derived them for aqueous solution. Structures were then reoptimized using the M06<sup>8</sup> functional and the triple- $\zeta$  Los Alamos Effective Core Potential (pseudopotential) augmented with two  $f$ -functions<sup>9</sup> (for Rh) and the 6-311G\*\*++ basis,<sup>10-11</sup> including continuum solvation with the PBF method.<sup>12</sup> The dielectric constant 2.284 and probe radius 2.6Å were used to represent benzene. Free energies calculated at  $C^0 = 1$  atm were corrected to nonstandard concentrations representative of reaction conditions: 53mM pivalic acid, 4.4 atm  $C_2H_4$ , 1 atm  $O_2$ , 10mM styrene and ethylbenzene, 11M (liquid) benzene, and 0.11mM for all rhodium complexes. Pivalic acid's free energy is the ideal gas free energy plus the PBF solvation energy and concentration adjustment. The free energy of the solvent benzene is the computed ideal gas free energy plus the free energy of condensation (1.48kcal/mol), derived from the measured vapor pressure of benzene at 423K

(5.84 atm<sup>13</sup>). Based on their chemical similarity, the empirical free energy of condensation of benzene was also used for ethylbenzene and styrene, rather than computed solvation energies. All calculations were performed with Jaguar<sup>14</sup> version 9.4.

### Single Crystal X-ray Diffraction Study of (5-FP)Rh(TFA)( $\eta^2$ -C<sub>2</sub>H<sub>4</sub>) (1).

A brown plate-like specimen of C<sub>24</sub>H<sub>18</sub>F<sub>3</sub>N<sub>4</sub>O<sub>2</sub>Rh,  $M_r = 554.34$  g/mol, approximate dimensions 0.170 mm x 0.181 mm x 0.212 mm, was coated with Paratone oil and mounted on a MiTeGen MicroLoop. The X-ray intensity data were measured on a Bruker Kappa APEXII Duo system equipped with a graphite monochromator and a Mo K $\alpha$  fine-focus sealed tube ( $\lambda = 0.71073$  Å).

The total exposure time was 5.78 hours. A total of 2081 frames were collected. The frames were integrated with the Bruker SAINT software package<sup>[15]</sup> using a narrow-frame algorithm. The integration of the data using a triclinic unit cell yielded a total of 25479 reflections to a maximum  $\theta$  angle of 28.34° (0.75 Å resolution), of which 6354 were independent (average redundancy 4.010, completeness = 99.9%,  $R_{int} = 4.16\%$ ,  $R_{sig} = 4.07\%$ ) and 5310 (83.57%) were greater than  $2\sigma(F^2)$ . The final cell constants of  $a = 7.9741(6)$  Å,  $b = 12.0163(9)$  Å,  $c = 14.0689(11)$  Å,  $\alpha = 76.5870(10)^\circ$ ,  $\beta = 77.5760(10)^\circ$ ,  $\gamma = 80.2600(10)^\circ$ , volume = 1270.46(17) Å<sup>3</sup>, are based upon the refinement of the XYZ-centroids of 7202 reflections above  $20 \sigma(I)$  with  $5.082^\circ < 2\theta < 51.88^\circ$ . Data were corrected for absorption effects using the Multi-Scan method (SADABS).<sup>[1]</sup> The ratio of minimum to maximum apparent transmission was 0.925. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.8620 and 0.8870.

The structure was solved and refined using the Bruker SHELXTL Software Package<sup>[16]</sup> within APEX3<sup>[15]</sup> and OLEX2,<sup>[17]</sup> using the space group P -1, with  $Z = 2$  for the formula unit, C<sub>24</sub>H<sub>18</sub>F<sub>3</sub>N<sub>4</sub>O<sub>2</sub>Rh. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in geometrically calculated positions with  $U_{iso} = 1.2U_{equiv}$  of the parent atom. During the structure solution, electron density difference maps revealed that there was disordered solvent that could not be successfully modeled with or without restraints. Thus, the structure factors were modified using the PLATON SQUEEZE<sup>[18]</sup> technique, in order to produce a “solvate-free” structure factor set. PLATON reported a total electron density of 48 e<sup>-</sup> and total solvent accessible volume of 237 Å<sup>3</sup>, likely representing one pentane molecule per asymmetric unit. The final anisotropic full-matrix least-squares refinement on  $F^2$  with 307 variables converged at  $R1 = 3.77\%$ , for the observed data and  $wR2 = 9.64\%$  for all data. The goodness-of-fit was 1.040. The largest peak in the final difference electron density synthesis was 1.186 e<sup>-</sup>/Å<sup>3</sup> and the largest hole was -0.828 e<sup>-</sup>/Å<sup>3</sup> with an RMS deviation of 0.087 e<sup>-</sup>/Å<sup>3</sup>. On the basis of the final model, the calculated density was 1.449 g/cm<sup>3</sup> and F(000), 556 e<sup>-</sup>.

**Table S1.** Sample and crystal data for (5-FP)Rh(TFA)( $\eta^2$ -C<sub>2</sub>H<sub>4</sub>).

<b>Identification code</b>	(5-FP)Rh(TFA)( $\eta^2$ -C <sub>2</sub> H <sub>4</sub> )	
<b>Chemical formula</b>	C <sub>24</sub> H <sub>18</sub> F <sub>3</sub> N <sub>4</sub> O <sub>2</sub> Rh	
<b>Formula weight</b>	554.33 g/mol	
<b>Temperature</b>	150(2) K	
<b>Wavelength</b>	0.71073 Å	
<b>Crystal size</b>	0.170 x 0.181 x 0.212 mm	
<b>Crystal habit</b>	brown plate	
<b>Crystal system</b>	triclinic	
<b>Space group</b>	P -1	
<b>Unit cell dimensions</b>	a = 7.9741(6) Å	$\alpha = 76.5870(10)^\circ$
	b = 12.0163(9) Å	$\beta = 77.5760(10)^\circ$
	c = 14.0689(11) Å	$\gamma = 80.2600(10)^\circ$
<b>Volume</b>	1270.46(17) Å <sup>3</sup>	
<b>Z</b>	2	
<b>Density (calculated)</b>	1.449 g/cm <sup>3</sup>	
<b>Absorption coefficient</b>	0.720 mm <sup>-1</sup>	
<b>F(000)</b>	556	

**Table S2.** Data collection and structure refinement for (5-FP)Rh(TFA)( $\eta^2$ -C<sub>2</sub>H<sub>4</sub>).

<b>Diffractometer</b>	Bruker Kappa APEXII Duo
<b>Radiation source</b>	fine-focus sealed tube, Mo K $\alpha$
<b>Theta range for data collection</b>	1.51 to 28.34°
<b>Index ranges</b>	-10 ≤ h ≤ 10, -15 ≤ k ≤ 16, -18 ≤ l ≤ 18
<b>Reflections collected</b>	25479
<b>Independent reflections</b>	6354 [R(int) = 0.0416]
<b>Coverage of independent reflections</b>	99.9%
<b>Absorption correction</b>	Multi-Scan
<b>Max. and min. transmission</b>	0.8870 and 0.8620
<b>Structure solution technique</b>	direct methods
<b>Structure solution program</b>	SHELXT 2014/5 (Sheldrick, 2014)
<b>Refinement method</b>	Full-matrix least-squares on F <sup>2</sup>
<b>Refinement program</b>	SHELXL-2016/6 (Sheldrick, 2016)
<b>Function minimized</b>	$\Sigma w(F_o^2 - F_c^2)^2$
<b>Data / restraints / parameters</b>	6354 / 0 / 307
<b>Goodness-of-fit on F<sup>2</sup></b>	1.040



$\Delta/\sigma_{\max}$	0.001
<b>Final R indices</b>	5310 data; $I > 2\sigma(I)$ R1 = 0.0377, wR2 = 0.0907
	all data R1 = 0.0514, wR2 = 0.0964
<b>Weighting scheme</b>	$w=1/[\sigma^2(F_o^2)+(0.0511P)^2+0.7886P]$ where $P=(F_o^2+2F_c^2)/3$
<b>Largest diff. peak and hole</b>	1.186 and -0.828 eÅ <sup>-3</sup>
<b>R.M.S. deviation from mean</b>	0.087 eÅ <sup>-3</sup>

**Table S3.** Atomic coordinates and equivalent isotropic atomic displacement parameters (Å<sup>2</sup>) for (5-FP)Rh(TFA)( $\eta^2$ -C<sub>2</sub>H<sub>4</sub>). U(eq) is defined as one third of the trace of the orthogonalized U<sub>ij</sub> tensor.

	x/a	y/b	z/c	U(eq)
Rh1	0.37164(3)	0.34681(2)	0.26769(2)	0.02236(7)
O1	0.3324(3)	0.52222(19)	0.21248(16)	0.0393(5)
N1	0.4183(3)	0.36918(18)	0.40550(16)	0.0202(4)
N2	0.7295(3)	0.34998(19)	0.35697(16)	0.0219(4)
N4	0.4243(3)	0.1753(2)	0.31863(19)	0.0299(5)
N3	0.7353(3)	0.1649(2)	0.26003(18)	0.0295(5)
C13	0.7531(3)	0.2788(2)	0.2040(2)	0.0252(5)
F2	0.1925(5)	0.7807(2)	0.2531(2)	0.0967(11)
O2	0.0804(3)	0.5614(2)	0.3122(2)	0.0568(7)
C4	0.6207(3)	0.3468(2)	0.51964(19)	0.0222(5)
C5	0.5785(3)	0.3558(2)	0.42550(18)	0.0189(5)
C2	0.3167(3)	0.3698(2)	0.5796(2)	0.0259(6)
C9	0.7656(3)	0.4800(3)	0.1958(2)	0.0276(6)
C1	0.2900(3)	0.3770(2)	0.4837(2)	0.0235(5)
C8	0.7463(3)	0.3701(2)	0.25136(19)	0.0218(5)
C6	0.8057(3)	0.3354(3)	0.5051(2)	0.0282(6)
C7	0.8665(3)	0.3389(3)	0.4068(2)	0.0274(6)
C3	0.4836(4)	0.3549(2)	0.5989(2)	0.0268(6)
C10	0.7931(4)	0.4994(3)	0.0928(2)	0.0343(7)
C12	0.7867(4)	0.2985(3)	0.1006(2)	0.0333(7)
C23	0.2036(4)	0.5827(3)	0.2456(2)	0.0359(7)
C17	0.5865(4)	0.1188(2)	0.3089(2)	0.0319(6)
C11	0.8043(4)	0.4085(3)	0.0461(2)	0.0376(7)
F1	0.3187(7)	0.7343(3)	0.1171(3)	0.144(2)
C21	0.3777(4)	0.3225(4)	0.1238(2)	0.0431(8)
C22	0.2089(4)	0.3221(4)	0.1776(2)	0.0448(9)
C20	0.2989(5)	0.1104(3)	0.3698(3)	0.0467(9)

	x/a	y/b	z/c	U(eq)
C14	0.8727(5)	0.0761(3)	0.2667(3)	0.0465(9)
C16	0.6313(5)	0.0005(3)	0.3485(3)	0.0557(11)
C15	0.8152(6)	0.9775(3)	0.3203(4)	0.0667(13)
C19	0.3315(6)	0.9933(3)	0.4114(4)	0.0721(15)
F3	0.0577(8)	0.7469(4)	0.1519(4)	0.169(2)
C24	0.1993(7)	0.7125(4)	0.1932(3)	0.0642(13)
C18	0.4985(7)	0.9385(3)	0.4010(4)	0.0838(18)

**Table S4.** Bond lengths (Å) for (5-FP)Rh(TFA)( $\eta^2$ -C<sub>2</sub>H<sub>4</sub>).

Bond	Length	Bond	Length
Rh1-N4	2.022(2)	Rh1-O1	2.065(2)
Rh1-C22	2.096(3)	Rh1-C21	2.101(3)
Rh1-N1	2.134(2)	O1-C23	1.225(4)
N1-C1	1.341(3)	N1-C5	1.342(3)
N2-C5	1.374(3)	N2-C7	1.393(3)
N2-C8	1.429(3)	N4-C20	1.349(4)
N4-C17	1.350(4)	N3-C17	1.372(4)
N3-C14	1.396(4)	N3-C13	1.425(4)
C13-C12	1.392(4)	C13-C8	1.398(4)
F2-C24	1.293(5)	O2-C23	1.219(4)
C4-C3	1.392(4)	C4-C5	1.411(4)
C4-C6	1.432(4)	C2-C3	1.389(4)
C2-C1	1.392(4)	C2-H2	0.95
C9-C8	1.385(4)	C9-C10	1.388(4)
C9-H9	0.95	C1-H1	0.95
C6-C7	1.356(4)	C6-H6	0.95
C7-H7	0.95	C3-H3	0.95
C10-C11	1.381(5)	C10-H10	0.95
C12-C11	1.378(5)	C12-H12	0.95
C23-C24	1.560(5)	C17-C16	1.416(4)
C11-H11	0.95	F1-C24	1.279(6)
C21-C22	1.396(5)	C21-H21A	0.99
C21-H21B	0.99	C22-H22A	0.99
C22-H22B	0.99	C20-C19	1.397(5)
C20-H20	0.95	C14-C15	1.343(6)
C14-H14	0.95	C16-C18	1.377(6)

C16-C15	1.431(6)	C15-H15	0.95
C19-C18	1.376(7)	C19-H19	0.95
F3-C24	1.341(6)	C18-H18	0.95

**Table S5.** Bond angles (°) for (5-FP)Rh(TFA)( $\eta^2$ -C<sub>2</sub>H<sub>4</sub>).

Bond Angle	Degree	Bond Angle	Degree
N4-Rh1-O1	176.79(9)	N4-Rh1-C22	92.28(13)
O1-Rh1-C22	89.30(13)	N4-Rh1-C21	91.64(13)
O1-Rh1-C21	87.83(13)	C22-Rh1-C21	38.85(13)
N4-Rh1-N1	86.92(9)	O1-Rh1-N1	92.99(9)
C22-Rh1-N1	152.10(11)	C21-Rh1-N1	168.97(10)
C23-O1-Rh1	121.6(2)	C1-N1-C5	114.9(2)
C1-N1-Rh1	121.85(17)	C5-N1-Rh1	122.19(17)
C5-N2-C7	107.7(2)	C5-N2-C8	127.0(2)
C7-N2-C8	124.6(2)	C20-N4-C17	115.3(3)
C20-N4-Rh1	121.7(2)	C17-N4-Rh1	122.95(19)
C17-N3-C14	107.6(3)	C17-N3-C13	128.4(2)
C14-N3-C13	123.8(3)	C12-C13-C8	119.4(3)
C12-C13-N3	119.6(3)	C8-C13-N3	120.9(2)
C3-C4-C5	117.1(2)	C3-C4-C6	136.3(3)
C5-C4-C6	106.5(2)	N1-C5-N2	125.5(2)
N1-C5-C4	126.1(2)	N2-C5-C4	108.5(2)
C3-C2-C1	120.3(2)	C3-C2-H2	119.8
C1-C2-H2	119.8	C8-C9-C10	119.9(3)
C8-C9-H9	120.0	C10-C9-H9	120.0
N1-C1-C2	123.8(2)	N1-C1-H1	118.1
C2-C1-H1	118.1	C9-C8-C13	120.1(2)
C9-C8-N2	119.3(2)	C13-C8-N2	120.5(2)
C7-C6-C4	107.2(2)	C7-C6-H6	126.4
C4-C6-H6	126.4	C6-C7-N2	110.1(2)
C6-C7-H7	124.9	N2-C7-H7	124.9
C2-C3-C4	117.7(3)	C2-C3-H3	121.2
C4-C3-H3	121.2	C11-C10-C9	119.8(3)
C11-C10-H10	120.1	C9-C10-H10	120.1
C11-C12-C13	119.9(3)	C11-C12-H12	120.1
C13-C12-H12	120.1	O2-C23-O1	132.5(3)
O2-C23-C24	114.3(3)	O1-C23-C24	113.2(3)
N4-C17-N3	126.5(3)	N4-C17-C16	125.1(3)

N3-C17-C16	108.3(3)	C12-C11-C10	120.8(3)
C12-C11-H11	119.6	C10-C11-H11	119.6
C22-C21-Rh1	70.39(18)	C22-C21-H21A	116.6
Rh1-C21-H21A	116.6	C22-C21-H21B	116.6
Rh1-C21-H21B	116.6	H21A-C21-H21B	113.6
C21-C22-Rh1	70.76(18)	C21-C22-H22A	116.5
Rh1-C22-H22A	116.5	C21-C22-H22B	116.5
Rh1-C22-H22B	116.5	H22A-C22-H22B	113.5
N4-C20-C19	123.4(3)	N4-C20-H20	118.3
C19-C20-H20	118.3	C15-C14-N3	110.3(3)
C15-C14-H14	124.8	N3-C14-H14	124.8
C18-C16-C17	117.3(4)	C18-C16-C15	136.5(4)
C17-C16-C15	106.2(3)	C14-C15-C16	107.6(3)
C14-C15-H15	126.2	C16-C15-H15	126.2
C18-C19-C20	119.9(4)	C18-C19-H19	120.0
C20-C19-H19	120.0	F1-C24-F2	110.4(5)
F1-C24-F3	100.9(4)	F2-C24-F3	106.0(4)
F1-C24-C23	114.9(3)	F2-C24-C23	113.6(3)
F3-C24-C23	110.0(4)	C19-C18-C16	119.0(4)
C19-C18-H18	120.5	C16-C18-H18	120.5

**Table S6.** Torsion angles ( $^{\circ}$ ) for (5-FP)Rh(TFA)( $\eta^2$ -C<sub>2</sub>H<sub>4</sub>).

Torsion Angle	Degree	Torsion Angle	Degree
C17-N3-C13-C12	-103.4(4)	C14-N3-C13-C12	70.7(4)
C17-N3-C13-C8	80.0(4)	C14-N3-C13-C8	-105.9(3)
C1-N1-C5-N2	-177.5(2)	Rh1-N1-C5-N2	13.9(3)
C1-N1-C5-C4	1.6(4)	Rh1-N1-C5-C4	-167.0(2)
C7-N2-C5-N1	178.5(2)	C8-N2-C5-N1	7.8(4)
C7-N2-C5-C4	-0.8(3)	C8-N2-C5-C4	-171.4(2)
C3-C4-C5-N1	-1.5(4)	C6-C4-C5-N1	-179.2(3)
C3-C4-C5-N2	177.8(2)	C6-C4-C5-N2	0.1(3)
C5-N1-C1-C2	-1.2(4)	Rh1-N1-C1-C2	167.4(2)
C3-C2-C1-N1	0.7(4)	C10-C9-C8-C13	-0.5(4)
C10-C9-C8-N2	175.9(2)	C12-C13-C8-C9	2.7(4)
N3-C13-C8-C9	179.3(2)	C12-C13-C8-N2	-173.6(2)
N3-C13-C8-N2	3.0(4)	C5-N2-C8-C9	91.6(3)
C7-N2-C8-C9	-77.6(3)	C5-N2-C8-C13	-92.0(3)
C7-N2-C8-C13	98.8(3)	C3-C4-C6-C7	-176.4(3)

C5-C4-C6-C7	0.6(3)	C4-C6-C7-N2	-1.1(3)
C5-N2-C7-C6	1.2(3)	C8-N2-C7-C6	172.1(3)
C1-C2-C3-C4	-0.5(4)	C5-C4-C3-C2	0.8(4)
C6-C4-C3-C2	177.6(3)	C8-C9-C10-C11	-1.2(4)
C8-C13-C12-C11	-3.2(4)	N3-C13-C12-C11	-179.9(3)
Rh1-O1-C23-O2	1.5(5)	Rh1-O1-C23-C24	-179.8(2)
C20-N4-C17-N3	179.6(3)	Rh1-N4-C17-N3	-3.9(4)
C20-N4-C17-C16	-0.6(5)	Rh1-N4-C17-C16	175.9(3)
C14-N3-C17-N4	-178.9(3)	C13-N3-C17-N4	-4.1(5)
C14-N3-C17-C16	1.2(4)	C13-N3-C17-C16	176.1(3)
C13-C12-C11-C10	1.5(5)	C9-C10-C11-C12	0.7(5)
C17-N4-C20-C19	0.7(5)	Rh1-N4-C20-C19	-175.9(3)
C17-N3-C14-C15	-1.7(4)	C13-N3-C14-C15	-176.9(3)
N4-C17-C16-C18	0.0(7)	N3-C17-C16-C18	179.9(4)
N4-C17-C16-C15	179.8(4)	N3-C17-C16-C15	-0.4(5)
N3-C14-C15-C16	1.5(5)	C18-C16-C15-C14	179.0(6)
C17-C16-C15-C14	-0.7(5)	N4-C20-C19-C18	-0.1(8)
O2-C23-C24-F1	-173.6(5)	O1-C23-C24-F1	7.5(6)
O2-C23-C24-F2	58.0(5)	O1-C23-C24-F2	-120.9(4)
O2-C23-C24-F3	-60.5(5)	O1-C23-C24-F3	120.5(4)
C20-C19-C18-C16	-0.5(9)	C17-C16-C18-C19	0.6(8)
C15-C16-C18-C19	-179.1(6)		

**Table S7.** Anisotropic atomic displacement parameters ( $\text{\AA}^2$ ) for (5-FP)Rh(TFA)( $\eta^2$ -C<sub>2</sub>H<sub>4</sub>). The anisotropic atomic displacement factor exponent takes the form:  $-2\pi^2 [h^2 a^{*2} U_{11} + \dots + 2 h k a^* b^* U_{12}]$ .

	U <sub>11</sub>	U <sub>22</sub>	U <sub>33</sub>	U <sub>23</sub>	U <sub>13</sub>	U <sub>12</sub>
Rh1	0.01845(10)	0.02702(12)	0.02263(11)	-0.00553(8)	-0.00519(7)	-0.00315(7)
O1	0.0373(12)	0.0359(12)	0.0332(12)	0.0026(9)	0.0012(9)	0.0037(9)
N1	0.0186(10)	0.0217(11)	0.0214(10)	-0.0064(8)	-0.0013(8)	-0.0059(8)
N2	0.0182(10)	0.0288(12)	0.0175(10)	-0.0049(9)	-0.0004(8)	-0.0034(8)
N4	0.0292(12)	0.0276(12)	0.0347(13)	-0.0119(10)	0.0004(10)	-0.0086(10)
N3	0.0287(12)	0.0264(12)	0.0324(13)	-0.0089(10)	-0.0031(10)	-0.0002(10)
C13	0.0186(12)	0.0331(15)	0.0241(13)	-0.0080(11)	-0.0030(10)	-0.0025(10)
F2	0.190(4)	0.0469(15)	0.0514(15)	-0.0132(12)	-0.0219(19)	-0.0070(18)
O2	0.0344(13)	0.0607(17)	0.0699(19)	-0.0218(14)	0.0080(13)	-0.0021(12)
C4	0.0210(12)	0.0242(13)	0.0215(12)	-0.0050(10)	-0.0018(10)	-0.0052(10)
C5	0.0177(11)	0.0182(12)	0.0207(12)	-0.0046(9)	-0.0012(9)	-0.0045(9)
C2	0.0191(12)	0.0301(14)	0.0271(14)	-0.0093(11)	0.0047(10)	-0.0059(10)

	U <sub>11</sub>	U <sub>22</sub>	U <sub>33</sub>	U <sub>23</sub>	U <sub>13</sub>	U <sub>12</sub>
C9	0.0216(12)	0.0336(15)	0.0261(14)	-0.0053(12)	0.0006(10)	-0.0067(11)
C1	0.0170(11)	0.0256(13)	0.0289(14)	-0.0096(11)	-0.0003(10)	-0.0048(10)
C8	0.0157(11)	0.0318(14)	0.0184(12)	-0.0055(10)	-0.0018(9)	-0.0054(10)
C6	0.0208(12)	0.0410(17)	0.0238(13)	-0.0056(12)	-0.0065(10)	-0.0051(11)
C7	0.0161(12)	0.0402(16)	0.0261(14)	-0.0078(12)	-0.0035(10)	-0.0029(11)
C3	0.0292(14)	0.0317(15)	0.0197(13)	-0.0055(11)	-0.0014(10)	-0.0075(11)
C10	0.0297(15)	0.0424(18)	0.0273(15)	0.0035(13)	-0.0022(12)	-0.0133(13)
C12	0.0293(14)	0.0481(19)	0.0256(14)	-0.0145(13)	-0.0018(11)	-0.0074(13)
C23	0.0336(16)	0.053(2)	0.0224(14)	-0.0076(14)	-0.0082(12)	-0.0042(14)
C17	0.0329(15)	0.0237(14)	0.0378(17)	-0.0108(12)	0.0003(12)	-0.0025(11)
C11	0.0334(16)	0.060(2)	0.0188(13)	-0.0055(14)	0.0001(12)	-0.0141(15)
F1	0.239(5)	0.0477(17)	0.089(2)	0.0037(16)	0.066(3)	-0.014(2)
C21	0.0326(16)	0.073(2)	0.0299(16)	-0.0221(16)	-0.0098(13)	-0.0022(16)
C22	0.0296(16)	0.078(3)	0.0339(17)	-0.0144(17)	-0.0137(13)	-0.0130(16)
C20	0.0416(18)	0.0351(18)	0.063(2)	-0.0163(16)	0.0084(16)	-0.0169(14)
C14	0.0364(17)	0.0392(19)	0.061(2)	-0.0190(17)	-0.0042(16)	0.0096(14)
C16	0.058(2)	0.0226(17)	0.075(3)	-0.0083(17)	0.006(2)	-0.0003(15)
C15	0.058(2)	0.032(2)	0.095(3)	-0.011(2)	0.001(2)	0.0164(17)
C19	0.071(3)	0.034(2)	0.098(4)	-0.013(2)	0.028(3)	-0.029(2)
F3	0.238(6)	0.107(3)	0.169(4)	-0.005(3)	-0.144(4)	0.064(3)
C24	0.098(3)	0.050(2)	0.0312(19)	-0.0042(17)	-0.014(2)	0.022(2)
C18	0.090(4)	0.0204(19)	0.117(4)	-0.004(2)	0.025(3)	-0.011(2)

**Table S8.** Hydrogen atomic coordinates and isotropic atomic displacement parameters ( $\text{\AA}^2$ ) for (5-FP)Rh(TFA)( $\eta^2$ -C<sub>2</sub>H<sub>4</sub>).

	x/a	y/b	z/c	U(eq)
H2	0.2202	0.3751	0.6322	0.031
H9	0.7600	0.5421	0.2281	0.033
H1	0.1741	0.3881	0.4731	0.028
H6	0.8731	0.3269	0.5550	0.034
H7	0.9854	0.3344	0.3764	0.033
H3	0.5035	0.3505	0.6640	0.032
H10	0.8042	0.5750	0.0545	0.041
H12	0.7975	0.2363	0.0677	0.04
H11	0.8244	0.4219	-0.0244	0.045
H21A	0.4001	0.3894	0.0686	0.052
H21B	0.4376	0.2480	0.1079	0.052

	x/a	y/b	z/c	U(eq)
H22A	0.1615	0.2474	0.1957	0.054
H22B	0.1240	0.3888	0.1564	0.054
H20	0.1825	0.1463	0.3779	0.056
H14	0.9902	0.0843	0.2374	0.056
H15	0.8841	-0.0944	0.3365	0.08
H19	0.2384	-0.0485	0.4469	0.087
H18	0.5219	-0.1410	0.4295	0.101

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