

Supporting information for:

**Isocyanate Deinsertion from κ^1 -O Amidates: Facile Access
to Perfluoroaryl Rhodium(I) Complexes**

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1. Spectral data for Rh(I) amidate complexes	S-2
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The figure displays a ^1H NMR spectrum of a Rhodium complex. The chemical structure of the complex is shown as an inset. It features a Rhodium (Rh) center coordinated by two 1,5-cyclooctadiene (1,5-COD) ligands and two 1,1'-bis(2,4,6-trimethylphenyl)ferrocene (Fc) ligands. The Fc ligands are substituted with a C_6F_5 group. The spectrum shows several peaks in the aromatic region (6.5-7.5 ppm) and a cluster of peaks in the aliphatic region (1.5-2.5 ppm). The peaks are labeled with their corresponding chemical shifts in ppm.

Chemical Shift (ppm)
7.184
7.169
7.154
7.151
7.128
7.118
7.106
7.095
7.084
7.071
7.057
7.047
7.034
7.024
7.019
7.015
7.011
7.007
7.003
7.000
6.997
6.994
6.991
6.988
6.985
6.982
6.979
6.976
6.973
6.970
6.967
6.964
6.961
6.958
6.955
6.952
6.949
6.946
6.943
6.940
6.937
6.934
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6.310
6.307
6.304
6.301
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6.292
6.289
6.286
6.283
6.280
6.277
6.274
6.271
6.268
6.265
6.262
6.259
6.256
6.253
6.250
6.247
6.244
6.241
6.238
6.235
6.232
6.

The figure displays the ^{13}C NMR spectrum of a Rhodium complex. The chemical structure of the complex is shown above the spectrum. It features two Rhodium (Rh) centers coordinated by two chiral ligands (represented by 3D models) and two nitrogen atoms (N). The central part of the molecule contains two oxygen atoms (O) and two fluorine atoms (F), with a C_6F_5 group attached to one of the nitrogens.

The ^{13}C NMR spectrum shows several peaks in the aromatic region (135-145 ppm) and a large peak in the carbonyl region (155 ppm). The peak list is as follows:

Chemical Shift (ppm)
135.8990
140.5104
152.2207
152.7775
154.3343
154.8315
161.8076
162.3332
162.3523
162.3951
162.4107
162.4535
162.4750
163.2030

Figure S3. 2, $^{13}\text{C}\{^1\text{H}\}$ NMR, C_6D_6 , 150 MHz, 298 K

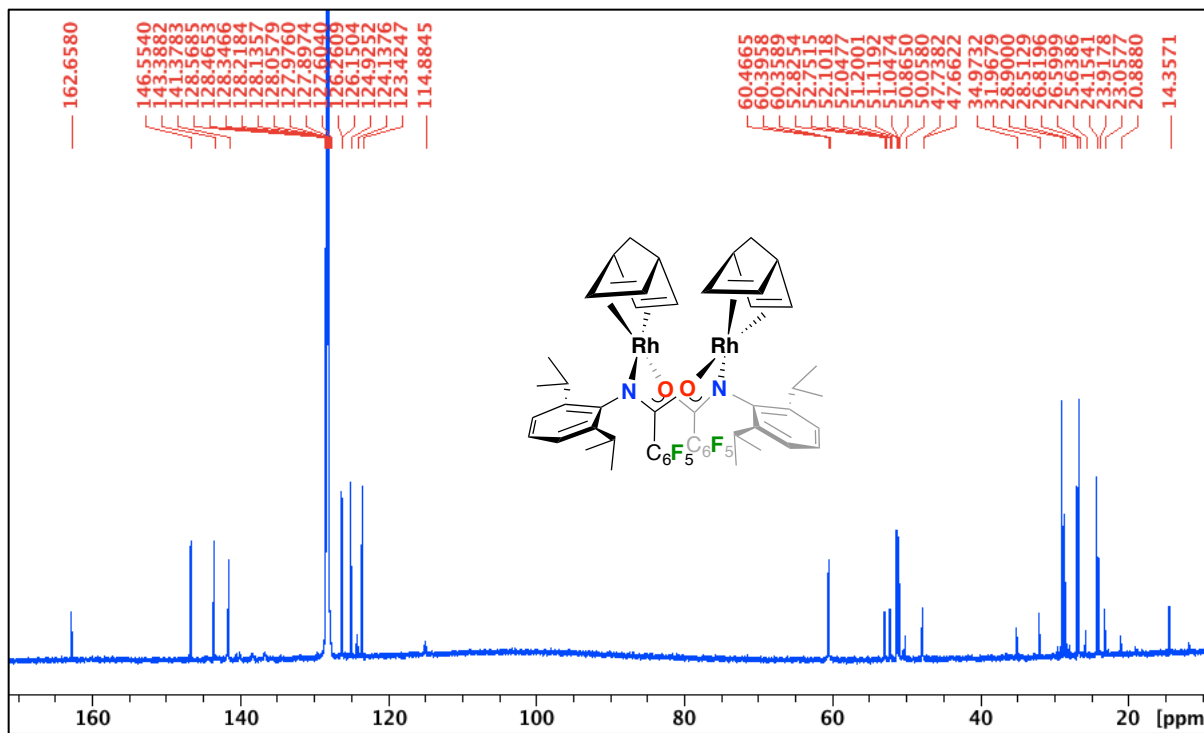


Figure S4. *E/Z*-3, ^1H NMR, $\text{tol-}d_8$, 300 MHz, 298 K

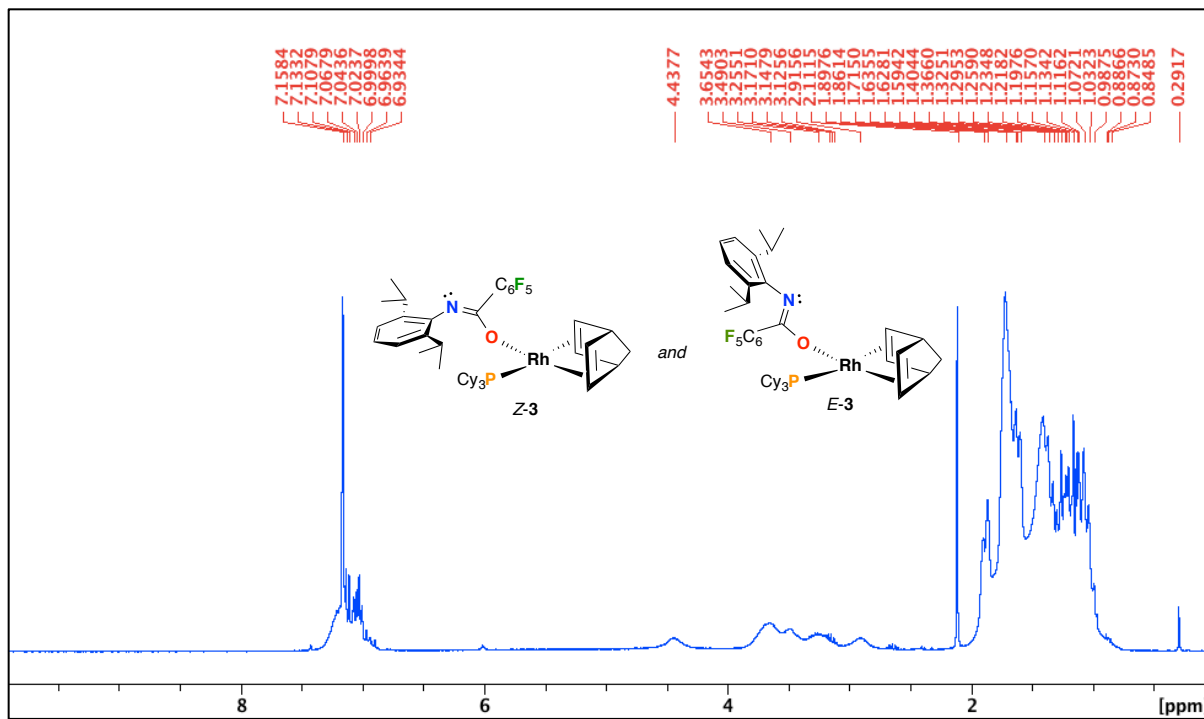


Figure S5. *E/Z*-3, VT ^1H NMR, $\text{tol-}d_8$, 300 MHz (* = residual $\text{Rh}(\eta^4\text{-NBD})(\text{PCy}_3)\text{Cl}$)

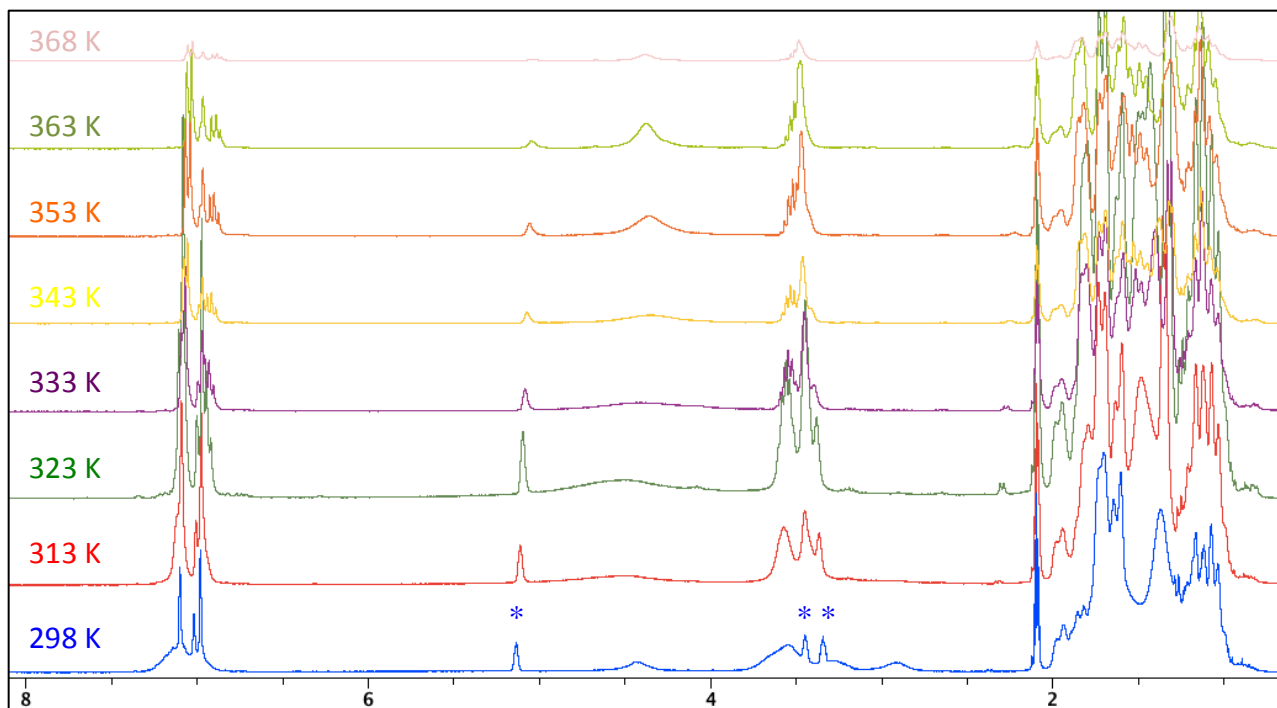


Figure S6. *E/Z*-3, $^{31}\text{P}\{^1\text{H}\}$ NMR, $\text{tol-}d_8$, C_6D_6 , 121 MHz, 298 K

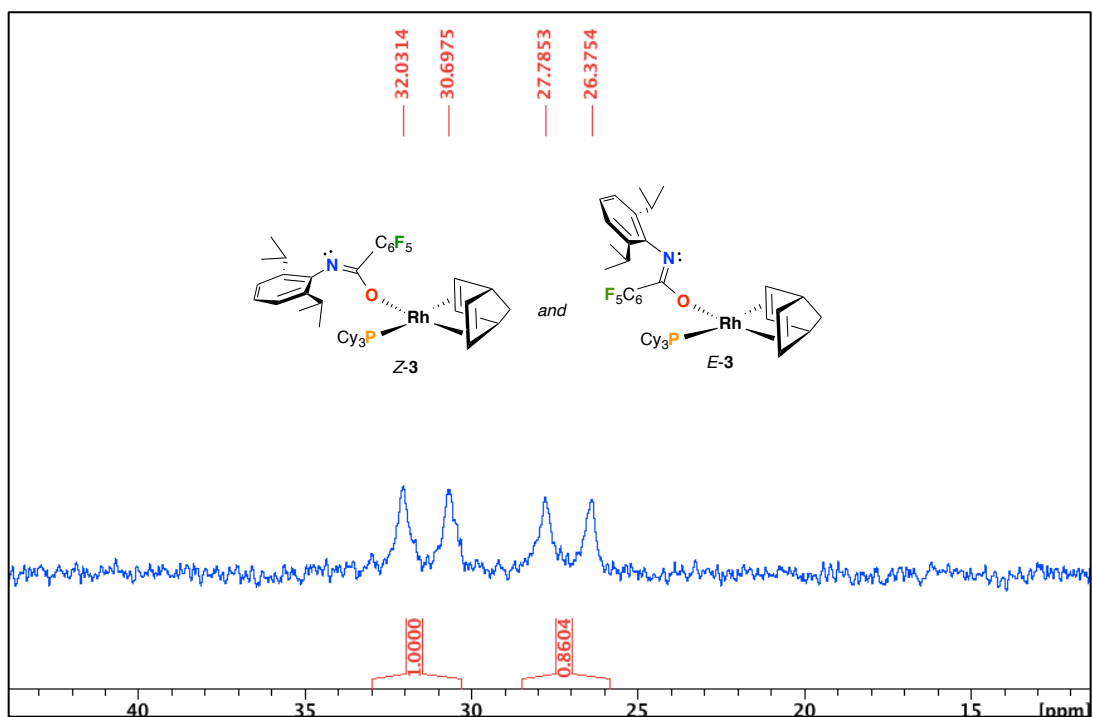


Figure S7. *E/Z*-3, VT $^{19}\text{F}\{^1\text{H}\}$ NMR, $\text{tol-}d_8$, 282 MHz

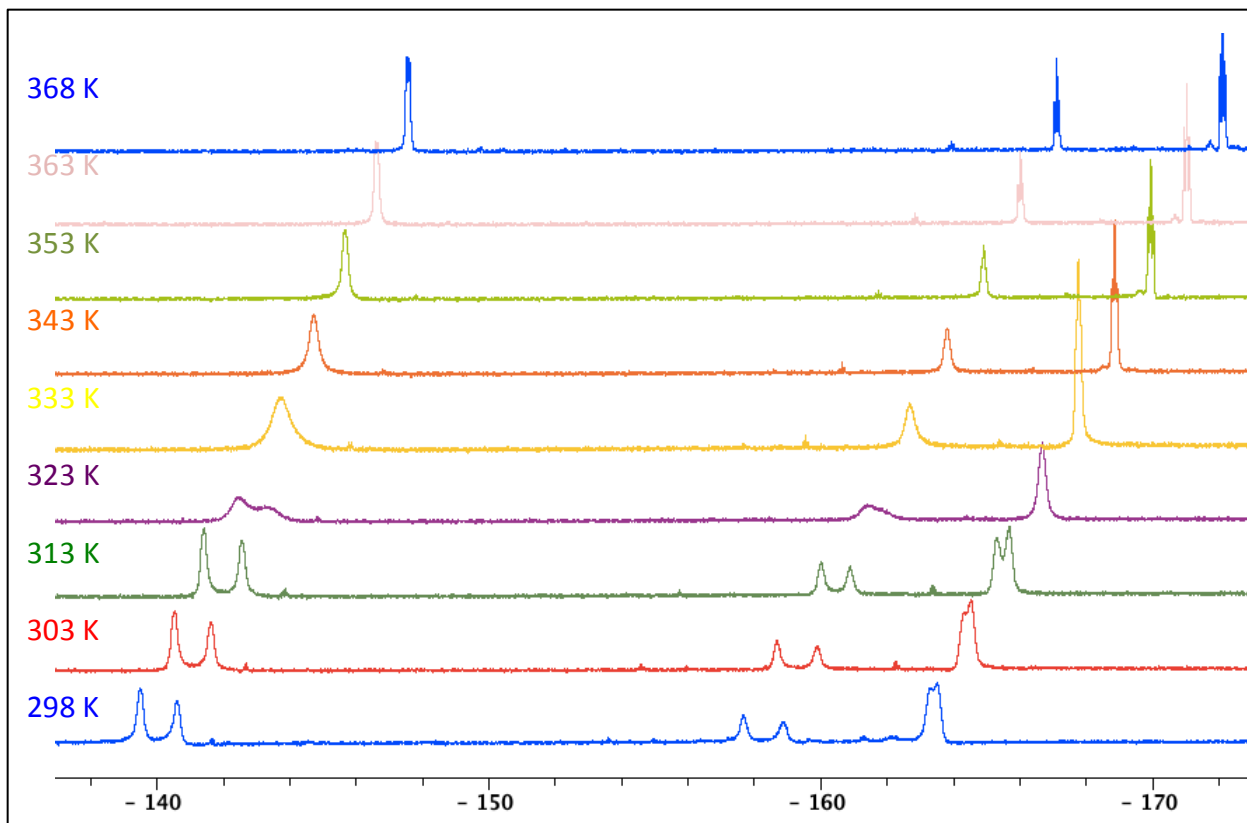


Figure S8. *E/Z*-3, solid-state IR (ATR) spectrum, 298 K

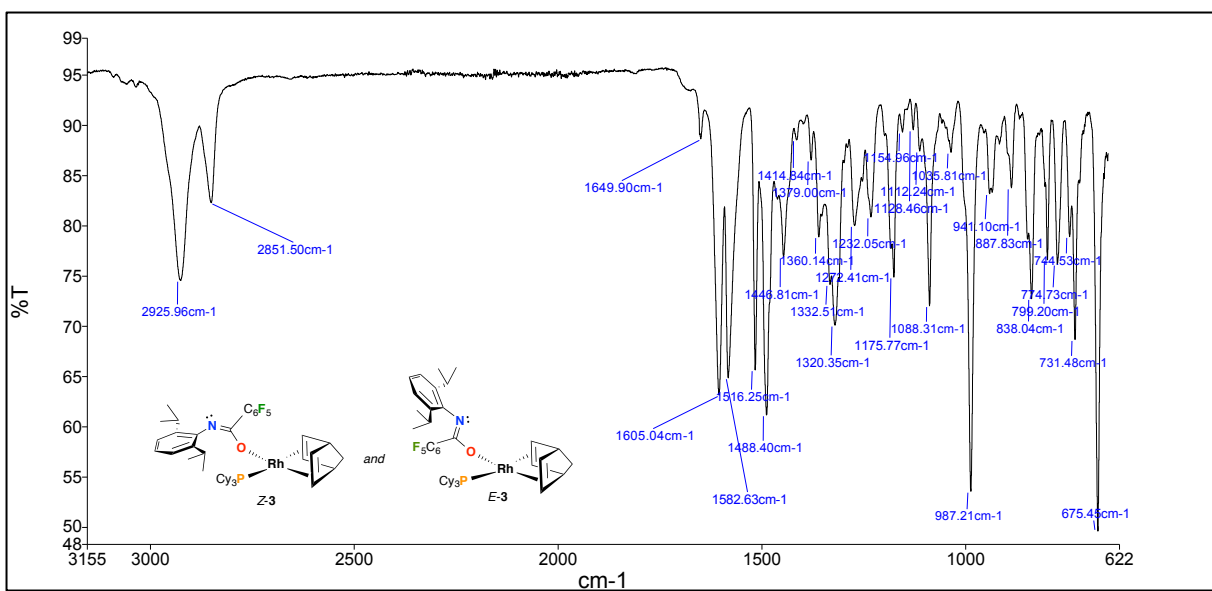


Figure S9. 5, ^1H NMR, C_6D_6 , 400 MHz, 298K

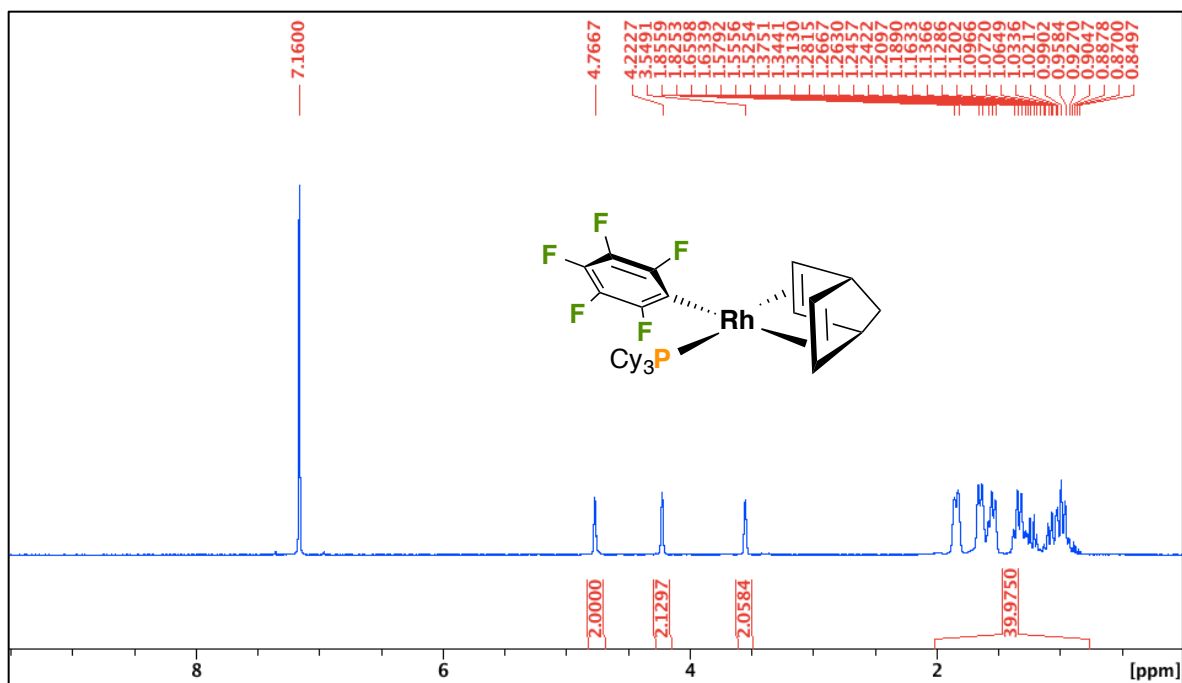


Figure S10. 5, $^{19}\text{F}\{^1\text{H}\}$ NMR, C_6D_6 , 377 MHz, 298 K

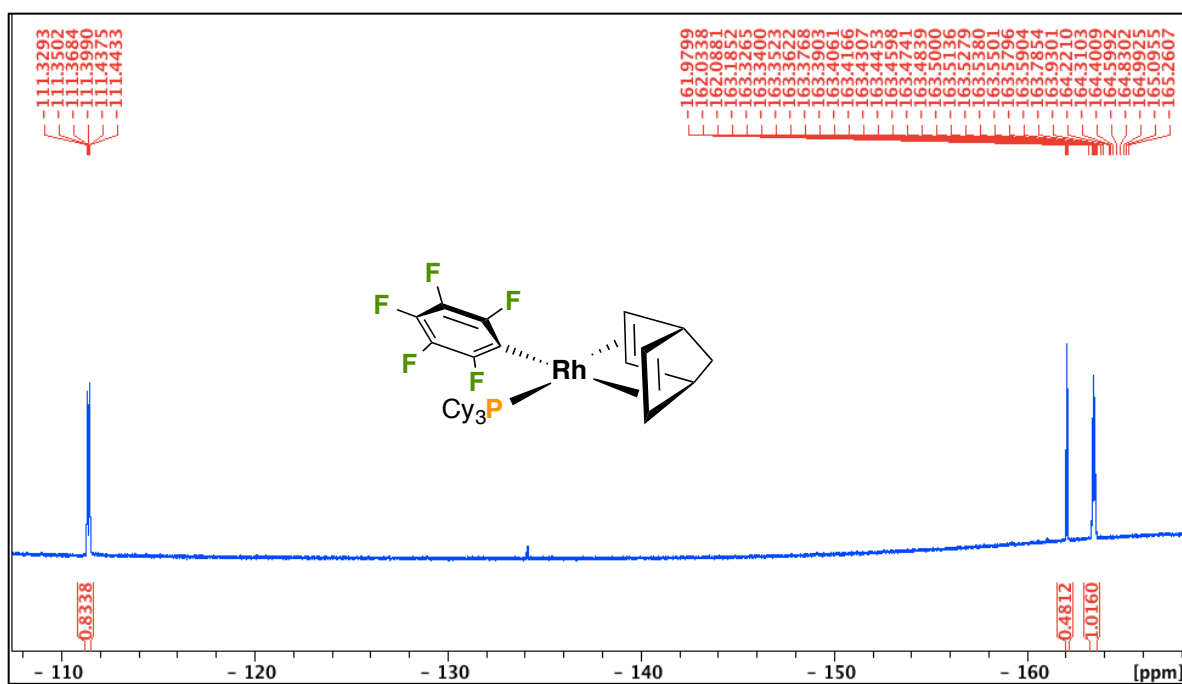


Figure S11. 5, $^{31}\text{P}\{^1\text{H}\}$ NMR, C_6D_6 , 162 MHz, 298 K

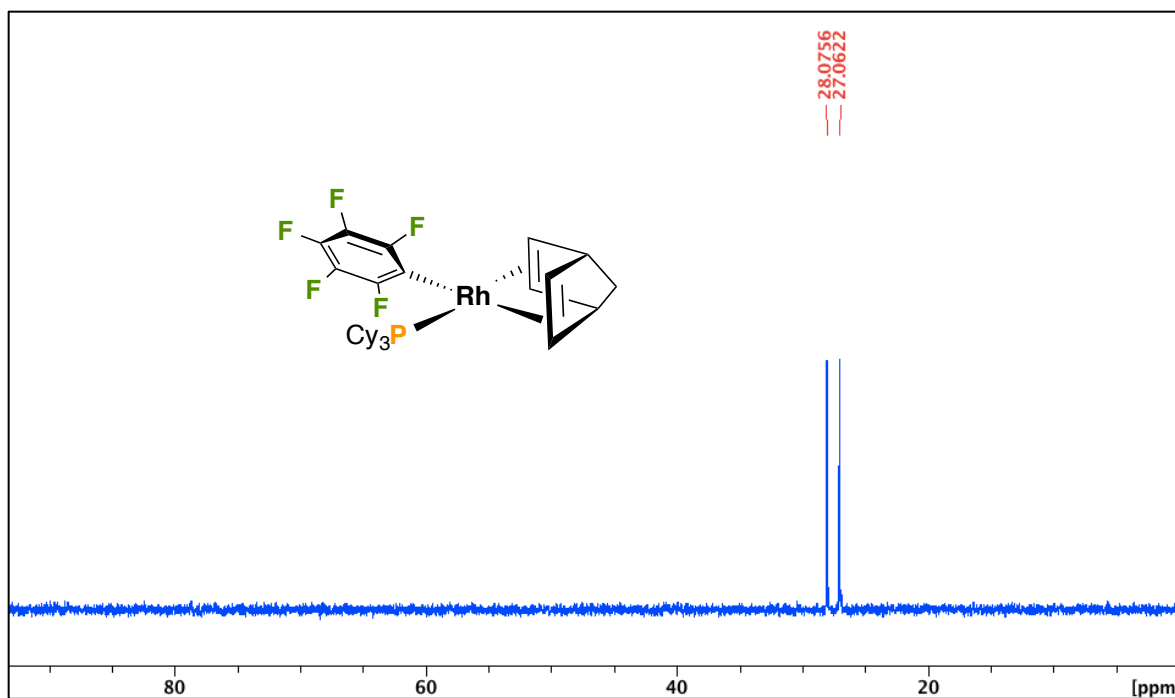


Figure S12. 5, $^{13}\text{C}\{^1\text{H}\}$ NMR, C_6D_6 , 100 MHz, 298 K

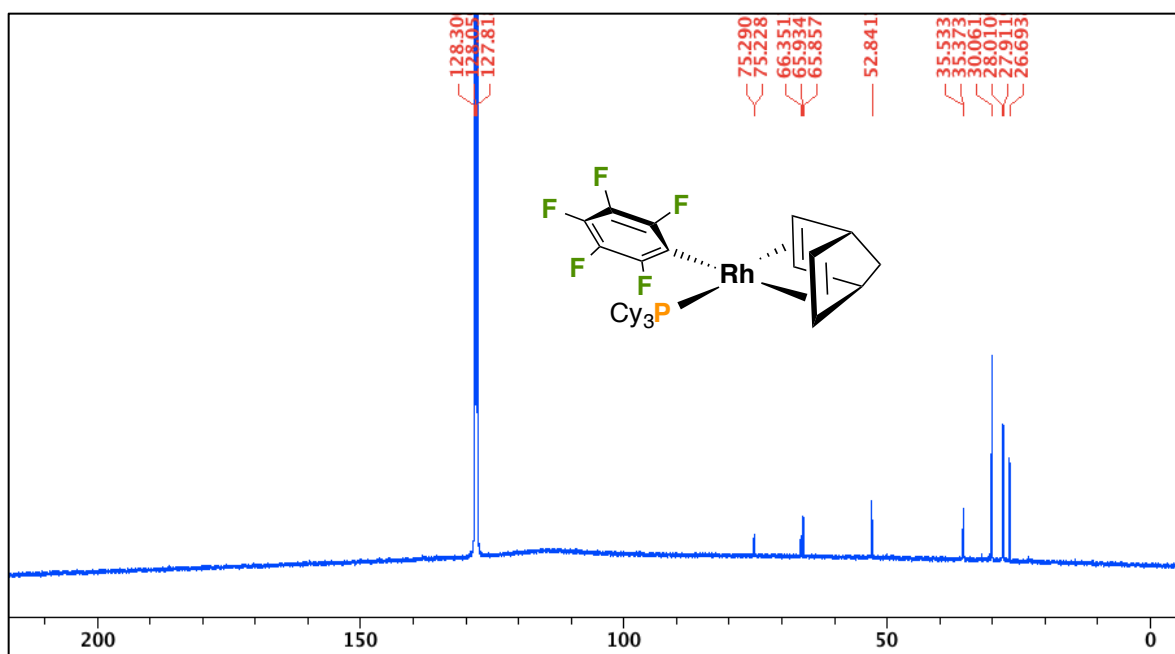


Figure S13. 6, ^1H NMR, C_6D_6 , 400 MHz, 298 K

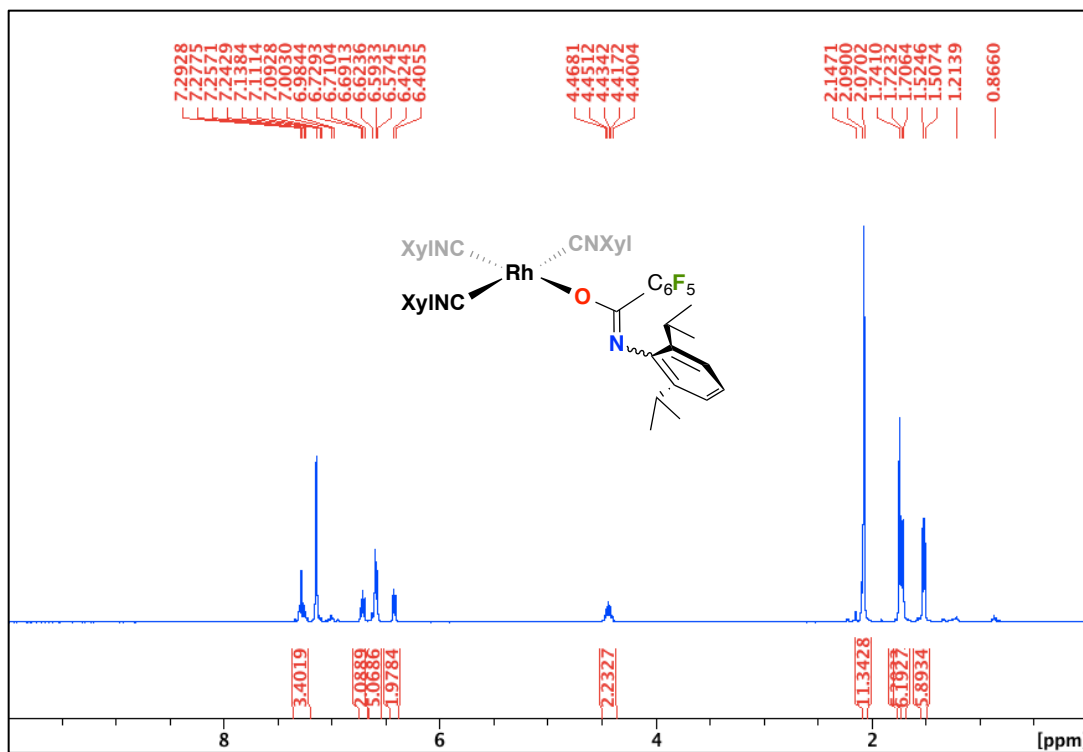
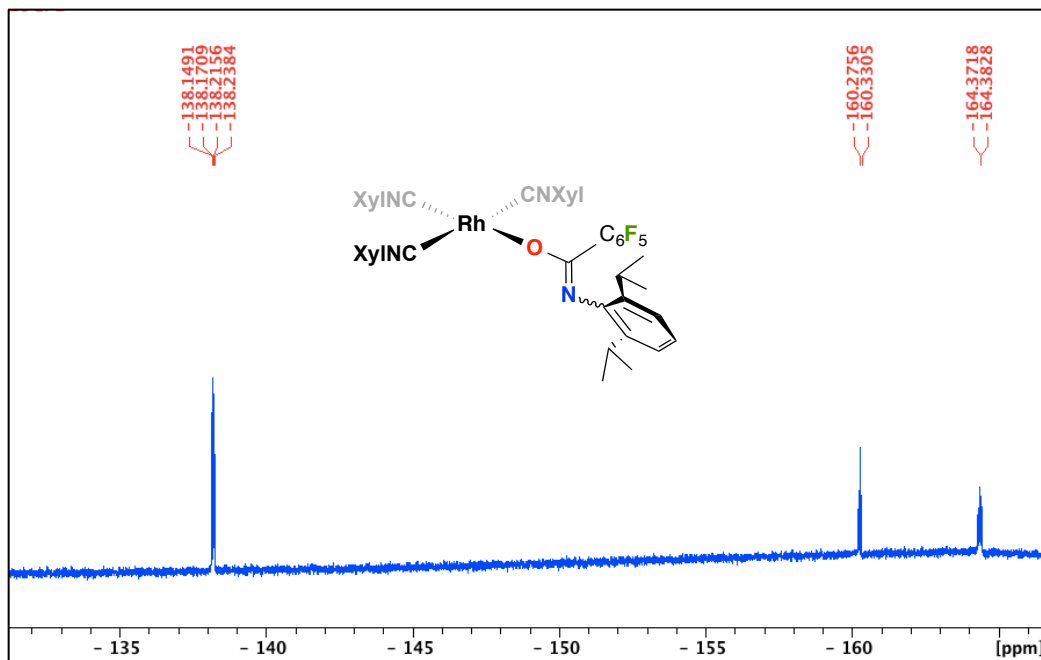


Figure S14. 6, $^{19}\text{F}\{^1\text{H}\}$ NMR, C_6D_6 , 377 MHz, 298 K



Chemical structure of the complex is shown with labels: XylNC, Rh, CNXyl, and C₆F₅.

Peak assignments (ppm):

- 29.3024
- 25.7530
- 24.5107
- 18.3683
- 18.2692

Chemical structure of compound 10 is shown as an inset. The structure features a Rhodium (Rh) center coordinated by two Xyl groups, a C₆F₅ group, and a C≡N group.

Key IR peaks (cm⁻¹):

- 2954.91
- 2865.99
- 2260.13
- 2173.32
- 2119.29
- 2094.04
- 1652.07
- 1595.19
- 1576.19
- 1493.78
- 1467.77
- 1439.52
- 1411.32
- 1382.11
- 1361.89
- 1283.85
- 1253.99
- 1178.78
- 1093.93
- 1037.04
- 940.91
- 891.19
- 877.89
- 814.95
- 800.12
- 773.48
- 733.95
- 720.00
- 695.54
- 680.02
- 652.30
- 986.36

Figure S17. 7, ^1H NMR, C_6D_6 , 400 MHz, 298 K

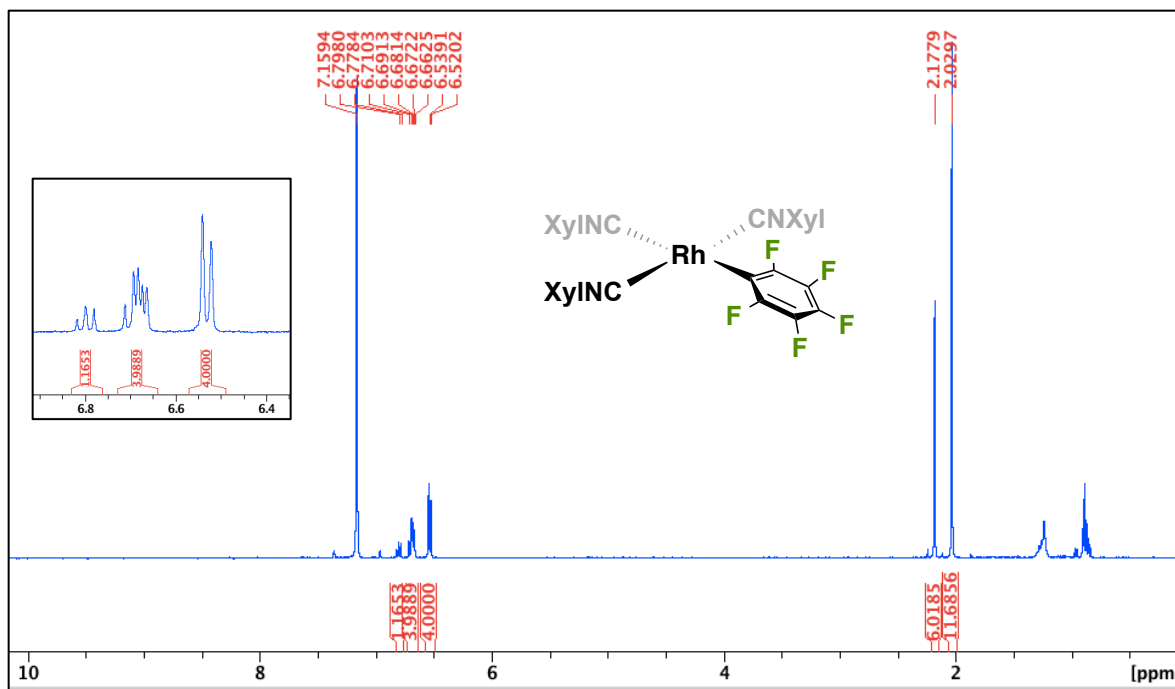


Figure S18. 7, $^{19}\text{F}\{^1\text{H}\}$ NMR, C_6D_6 , 377 MHz, 298 K

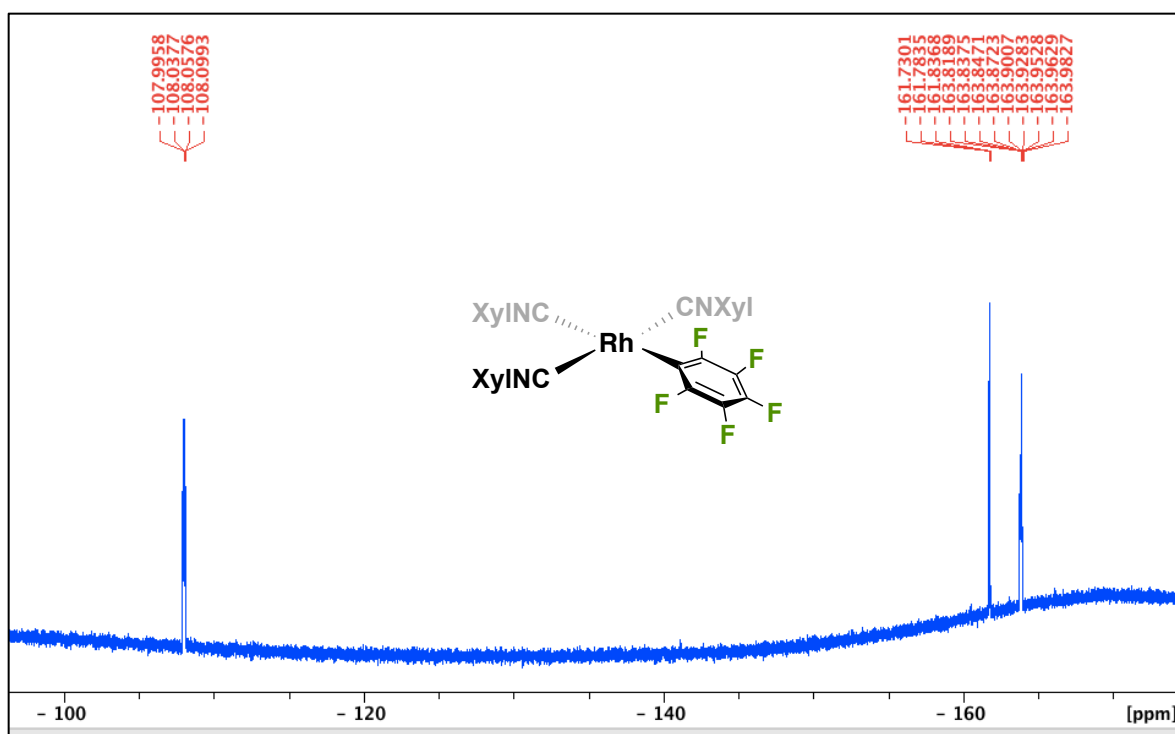


Figure S19. 7, solid-state IR (ATR) spectrum, 298 K

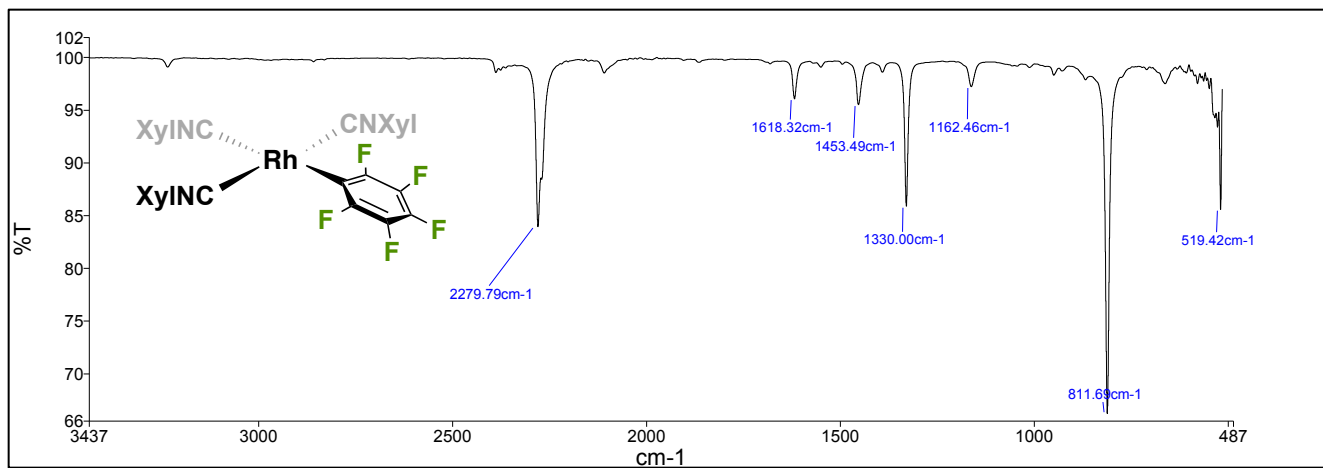


Figure S20. 8+PPh₃, ¹H NMR, C₆D₆, 400 MHz, 298 K

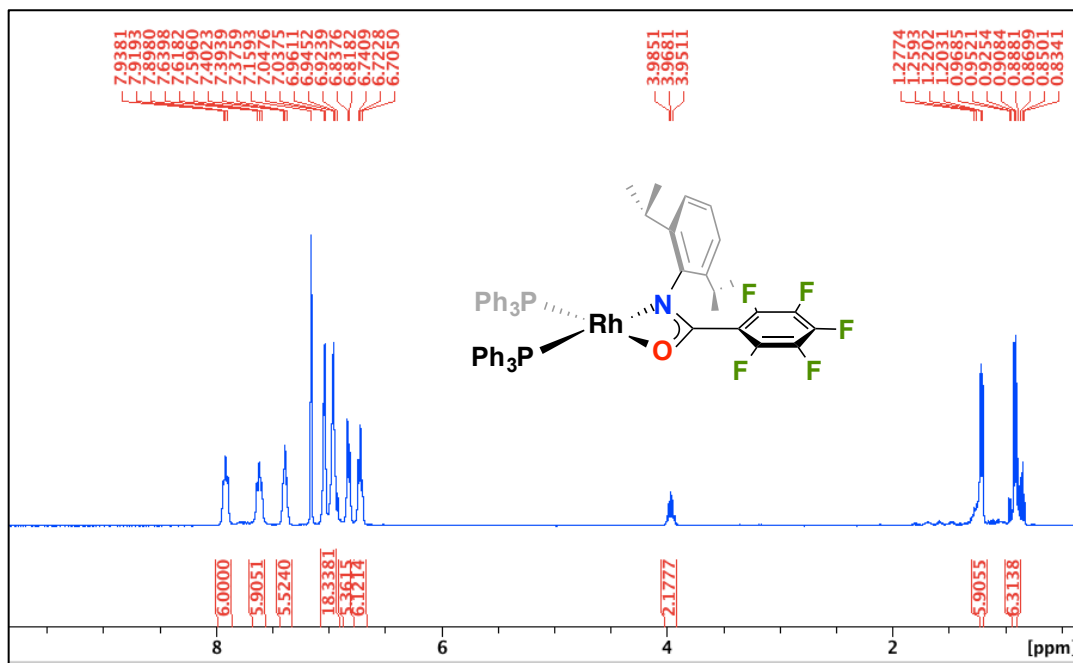


Figure S21. **8+PPh₃,** ³¹P{¹H} NMR, C₆D₆, 162 MHz, 298 K

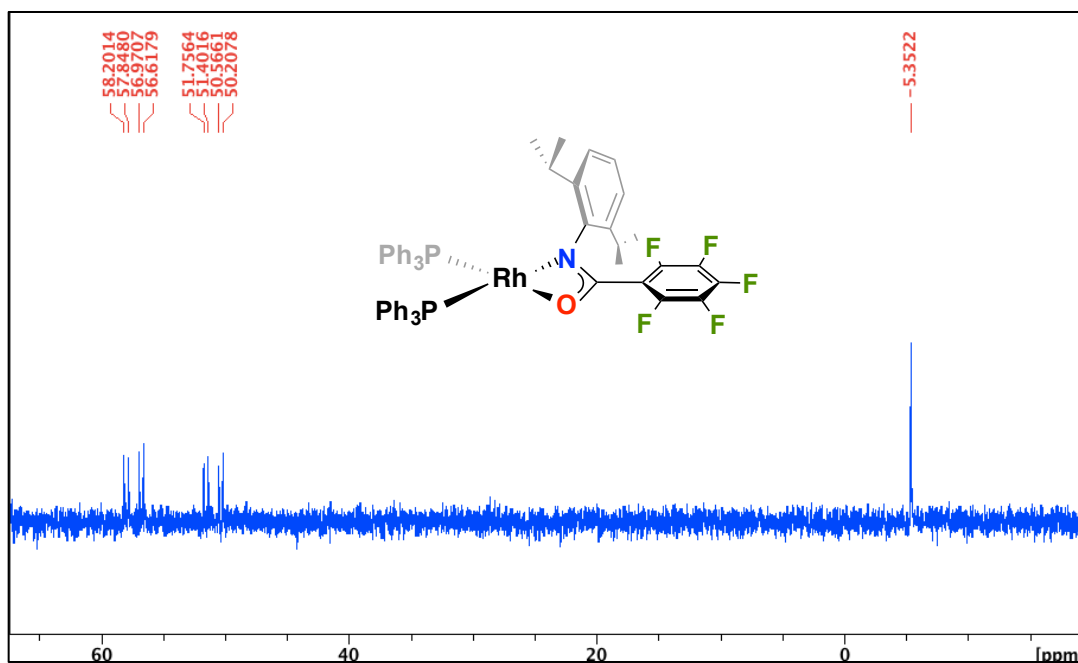


Figure S22. **8+PPh₃,** ¹⁹F{¹H} NMR, C₆D₆, 377 MHz, 298 K

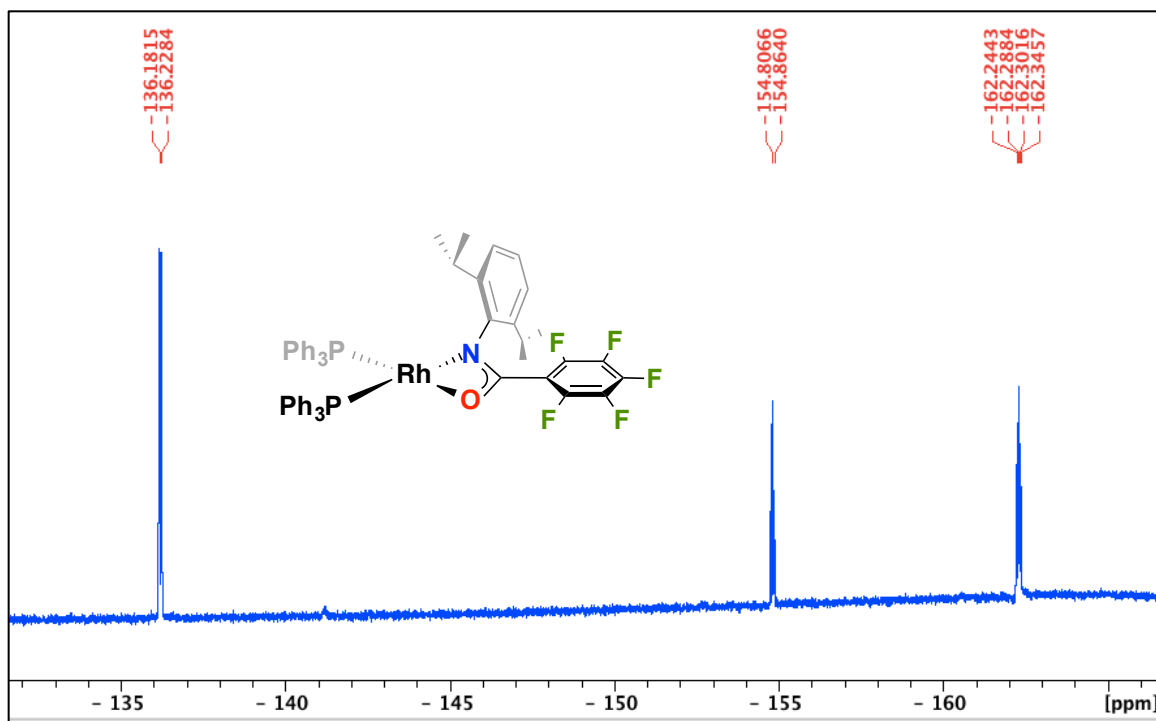


Figure S23. 8+PPh₃, ¹³C{¹H} NMR, tol-*d*₈, 100 MHz, 298 K

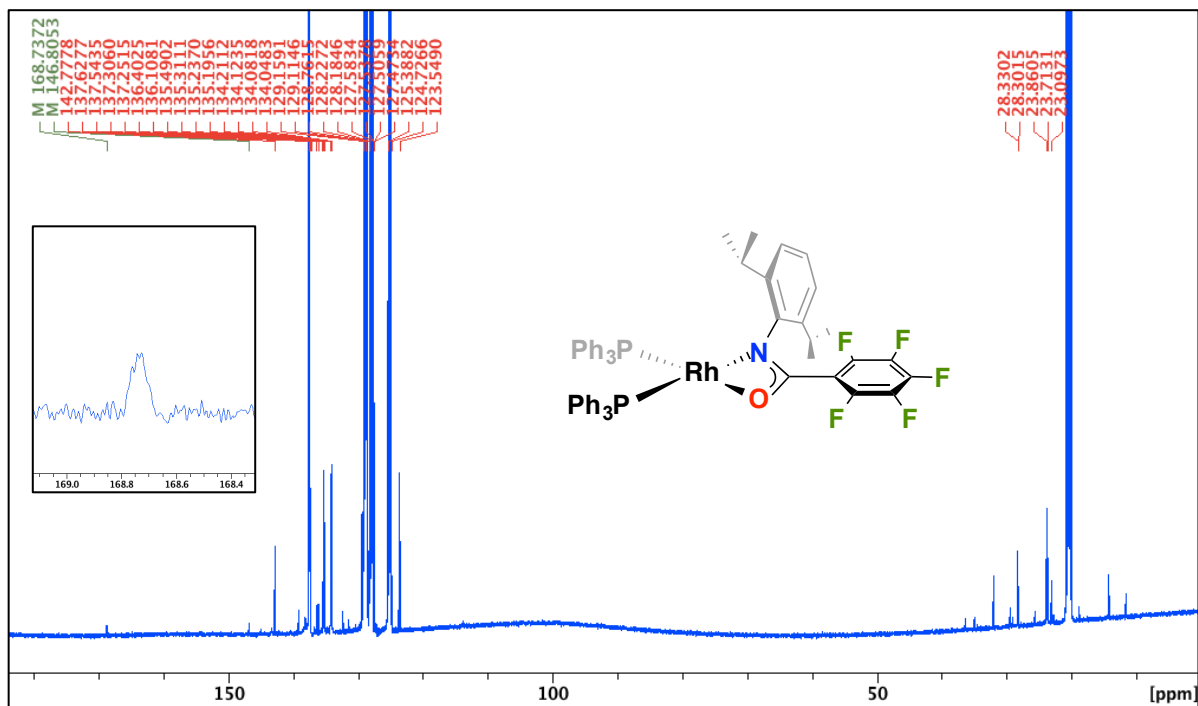


Figure S24. 8+PPh₃, VT ¹H NMR, tol-*d*₈, 400 MHz

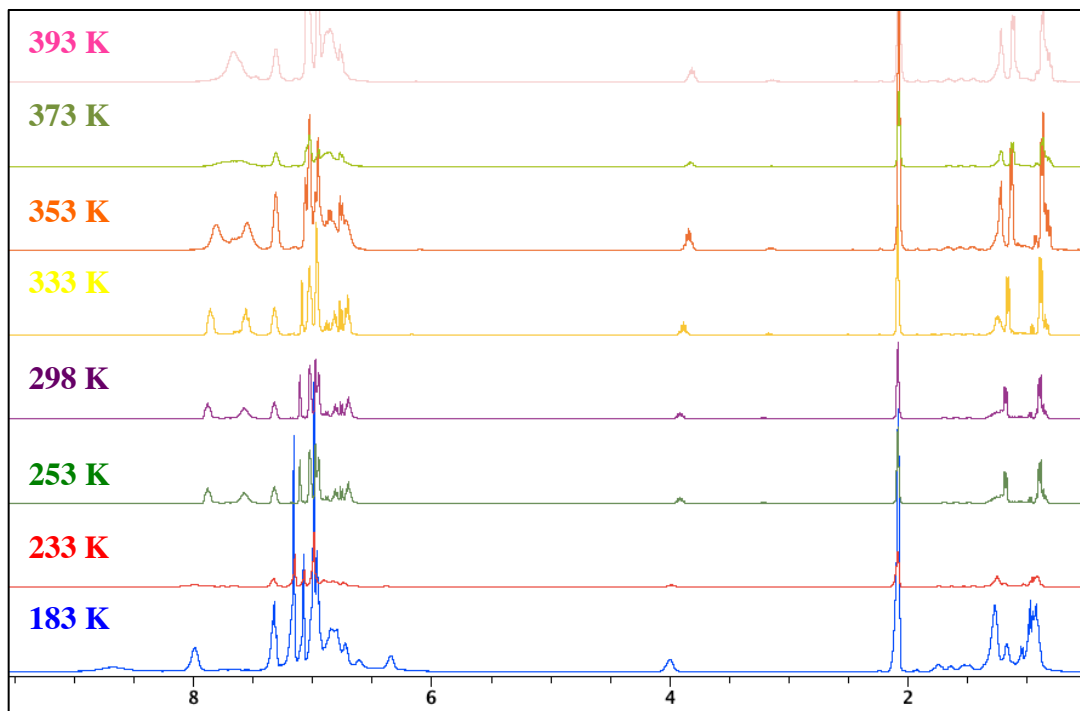


Figure S25. **8**+PPh₃, VT ³¹P{¹H} NMR, tol-*d*₈, 400 MHz

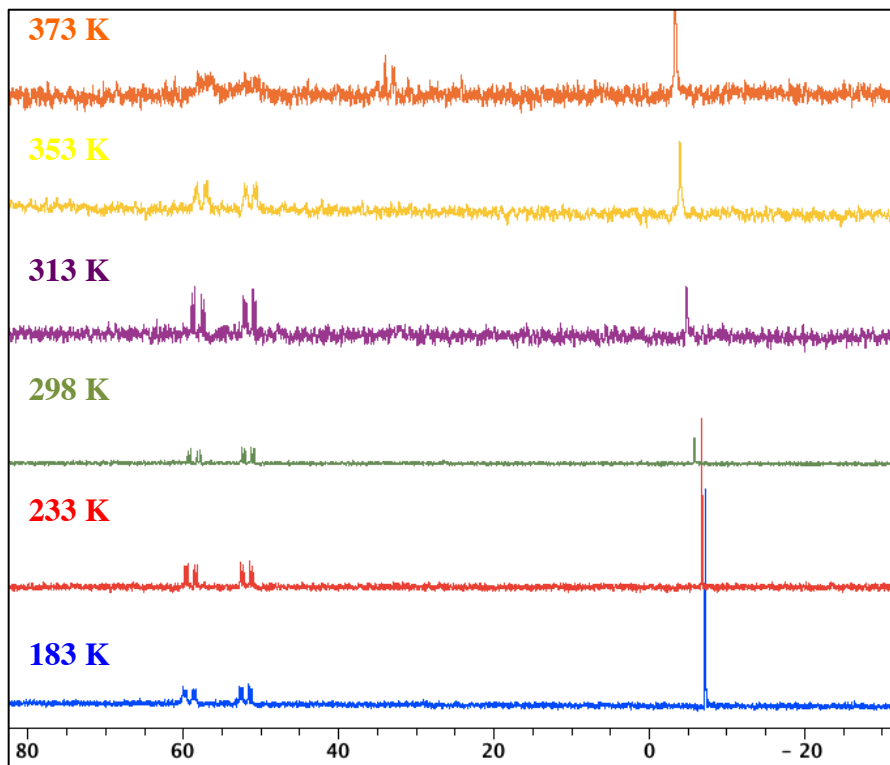


Figure S26. **8**+PPh₃, solid-state IR (ATR) spectrum, 298 K

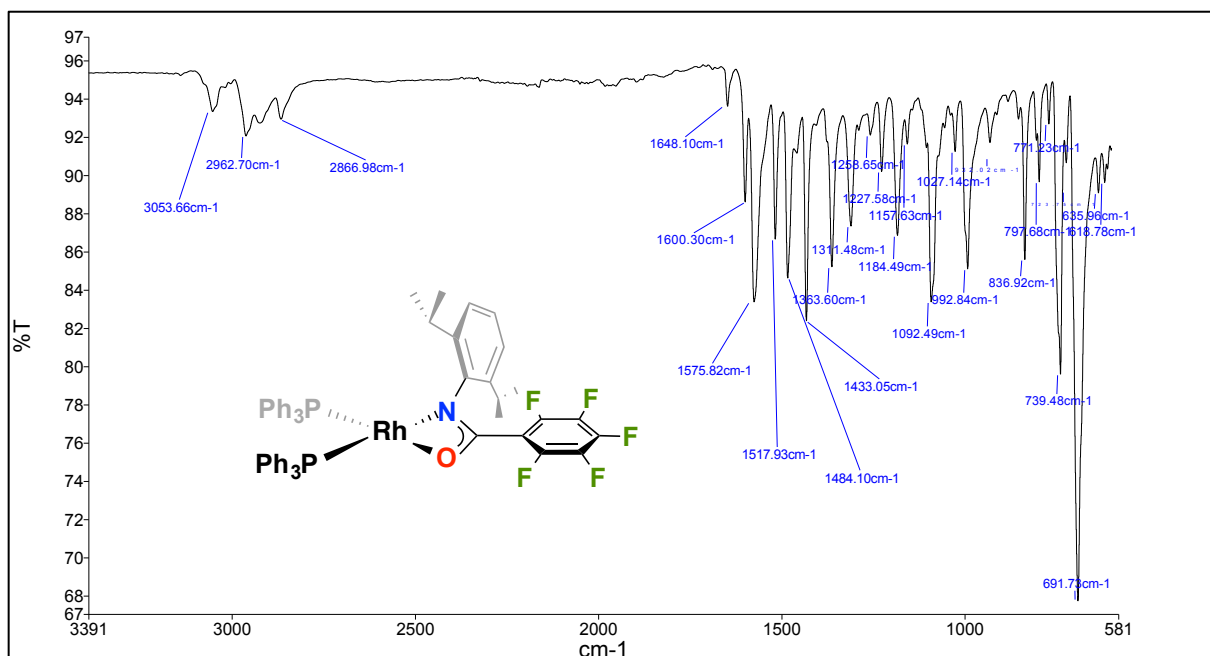


Figure S27. 10, ^1H NMR, C_6D_6 , 400 MHz, 298 K (* = trace solvent impurity (THF, Et_2O))

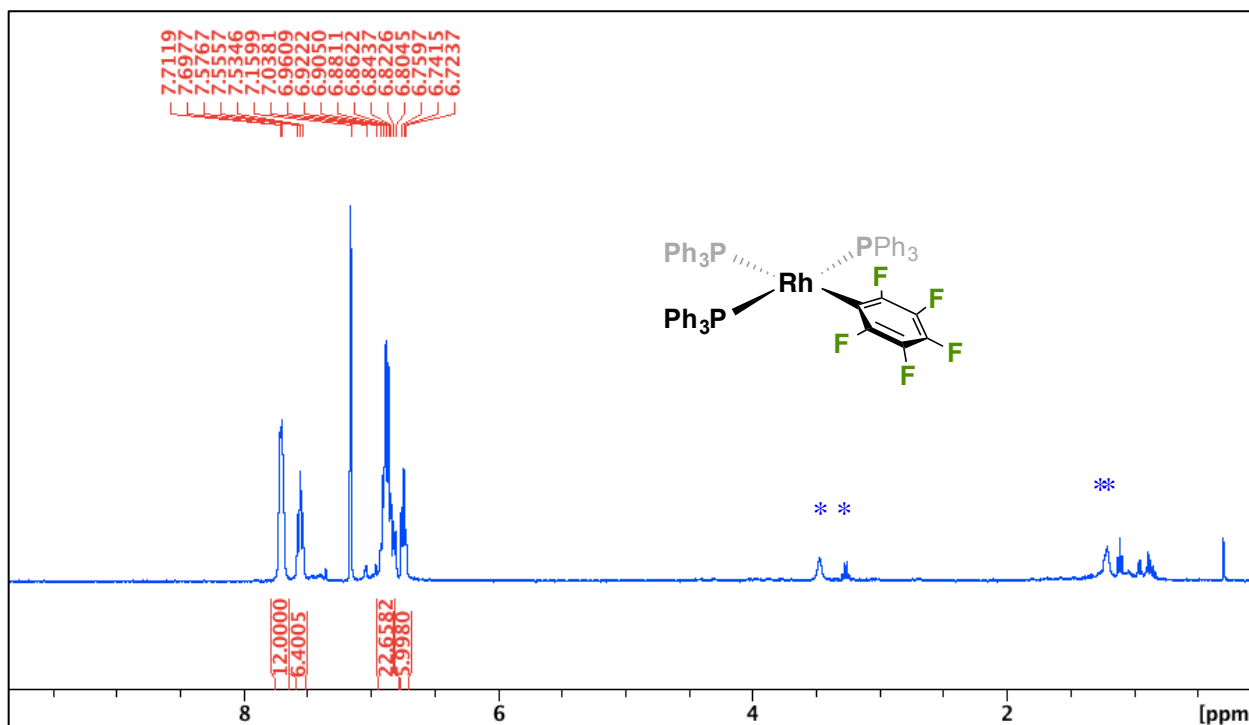
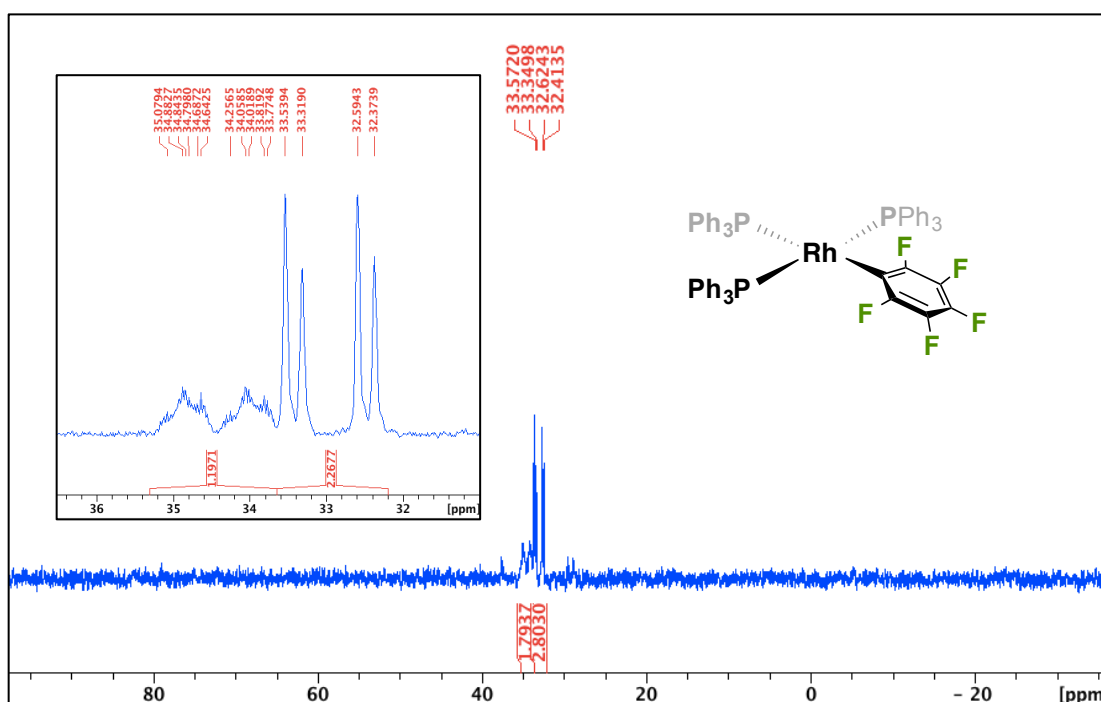


Figure S28. 10, $^{31}\text{P}\{^1\text{H}\}$ NMR, C_6D_6 , 162 MHz, 298 K



Chemical structure of the complex: P(c1ccccc1)(c1ccccc1)Rh(c1ccccc1)(c1ccccc1)c2cc(F)c(F)c(F)c(F)c2F

³¹P NMR chemical shifts (ppm):

- 107.7788
- 107.8266
- 107.8636
- 107.8876
- 163.5128
- 163.5686
- 163.6434
- 165.0837
- 165.1385
- 165.1941

Chemical structure of the complex: P(c1ccccc1)(c1ccccc1)Rh(P(c1ccccc1)(c1ccccc1)c1ccccc1)c2cc(F)c(F)c(F)c(F)c2F

¹³C NMR spectrum (CDCl₃) showing peaks for the complex. The inset shows the aromatic region (125-140 ppm) with peaks corresponding to the pentafluorophenyl ligand.

Peak list (ppm): 156.00, 155.75, 155.51, 155.26, 155.01, 154.76, 154.51, 154.26, 154.01, 153.76, 153.51, 153.26, 153.01, 152.76, 152.51, 152.26, 152.01, 151.76, 151.51, 151.26, 151.01, 150.76, 150.51, 150.26, 150.01, 149.76, 149.51, 149.26, 149.01, 148.76, 148.51, 148.26, 148.01, 147.76, 147.51, 147.26, 147.01, 146.76, 146.51, 146.26, 146.01, 145.76, 145.51, 145.26, 145.01, 144.76, 144.51, 144.26, 144.01, 143.76, 143.51, 143.26, 143.01, 142.76, 142.51, 142.26, 142.01, 141.76, 141.51, 141.26, 141.01, 140.76, 140.51, 140.26, 140.01, 139.76, 139.51, 139.26, 139.01, 138.76, 138.51, 138.26, 138.01, 137.76, 137.51, 137.26, 137.01, 136.76, 136.51, 136.26, 136.01, 135.76, 135.51, 135.26, 135.01, 134.76, 134.51, 134.26, 134.01, 133.76, 133.51, 133.26, 133.01, 132.76, 132.51, 132.26, 132.01, 131.76, 131.51, 131.26, 131.01, 130.76, 130.51, 130.26, 130.01, 129.76, 129.51, 129.26, 129.01, 128.76, 128.51, 128.26, 128.01, 127.76, 127.51, 127.26, 127.01, 126.76, 126.51, 126.26, 126.01, 125.76, 125.51, 125.26, 125.01, 124.76, 124.51, 124.26, 124.01, 123.76, 123.51, 123.26, 123.01, 122.76, 122.51, 122.26, 122.01, 121.76, 121.51, 121.26, 121.01, 120.76, 120.51, 120.26, 120.01, 119.76, 119.51, 119.26, 119.01, 118.76, 118.51, 118.26, 118.01, 117.76, 117.51, 117.26, 117.01, 116.76, 116.51, 116.26, 116.01, 115.76, 115.51, 115.26, 115.01, 114.76, 114.51, 114.26, 114.01, 113.76, 113.51, 113.26, 113.01, 112.76, 112.51, 112.26, 112.01, 111.76, 111.51, 111.26, 111.01, 110.76, 110.51, 110.26, 110.01, 109.76, 109.51, 109.26, 109.01, 108.76, 108.51, 108.26, 108.01, 107.76, 107.51, 107.26, 107.01, 106.76, 106.51, 106.26, 106.01, 105.76, 105.51, 105.26, 105.01, 104.76, 104.51, 104.26, 104.01, 103.76, 103.51, 103.26, 103.01, 102.76, 102.51, 102.26, 102.01, 101.76, 101.51, 101.26, 101.01, 100.76, 100.51, 100.26, 100.01, 99.76, 99.51, 99.26, 99.01, 98.76, 98.51, 98.26, 98.01, 97.76, 97.51, 97.26, 97.01, 96.76, 96.51, 96.26, 96.01, 95.76, 95.51, 95.26, 95.01, 94.76, 94.51, 94.26, 94.01, 93.76, 93.51, 93.26, 93.01, 92.76, 92.51, 92.26, 92.01, 91.76, 91.51, 91.26, 91.01, 90.76, 90.51, 90.26, 90.01, 89.76, 89.51, 89.26, 89.01, 88.76, 88.51, 88.26, 88.01, 87.76, 87.51, 87.26, 87.01, 86.76, 86.51, 86.26, 86.01, 85.76, 85.51, 85.26, 85.01, 84.76, 84.51, 84.26, 84.01, 83.76, 83.51, 83.26, 83.01, 82.76, 82.51, 82.26, 82.01, 81.76, 81.51, 81.26, 81.01, 80.76, 80.51, 80.26, 80.01, 79.76, 79.51, 79.26, 79.01, 78.76, 78.51, 78.26, 78.01, 77.76, 77.51, 77.26, 77.01, 76.76, 76.51, 76.26, 76.01, 75.76, 75.51, 75.26, 75.01, 74.76, 74.51, 74.26, 74.01, 73.76, 73.51, 73.26, 73.01, 72.76, 72.51, 72.26, 72.01, 71.76, 71.51, 71.26, 71.01, 70.76, 70.51, 70.26, 70.01, 69.76, 69.51, 69.26, 69.01, 68.76, 68.51, 68.26, 68.01, 67.76, 67.51, 67.26, 67.01, 66.76, 66.51, 66.26, 66.01, 65.76, 65.51, 65.26, 65.01, 64.76, 64.51, 64.26, 64.01, 63.76, 63.51, 63.26, 63.01, 62.76, 62.51, 62.26, 62.01, 61.76, 61.51, 61.26, 61.01, 60.76, 60.51, 60.26, 60.01, 59.76, 59.51, 59.26, 59.01, 58.76, 58.51, 58.26, 58.01, 57.76, 57.51, 57.26, 57.01, 56.76, 56.51, 56.26, 56.01, 55.76, 55.51, 55.26, 55.01, 54.76, 54.51, 54.26, 54.01, 53.76, 53.51, 53.26, 53.01, 52.76, 52.51, 52.26, 52.01, 51.76, 51.51, 51.26, 51.01, 50.76, 50.51, 50.26, 50.01, 49.76, 49.51, 49.26, 49.01, 48.76, 48.51, 48.26, 48.01, 47.76, 47.51, 47.26, 47.01, 46.76, 46.51, 46.26, 46.01, 45.76, 45.51, 45.26, 45.01, 44.76, 44.51, 44.26, 44.01, 43.76, 43.51, 43.26, 43.01, 42.76, 42.51, 42.26, 42.01, 41.76, 41.51, 41.26, 41.01, 40.76, 40.51, 40.26, 40.01, 39.76, 39.51, 39.26, 39.01, 38.76, 38.51, 38.26, 38.01, 37.76, 37.51, 37.26, 37.01, 36.76, 36.51, 36.26, 36.01, 35.76, 35.51, 35.26, 35.01, 34.76, 34.51, 34.26, 34.01, 33.76, 33.51, 33.26, 33.01, 32.76, 32.51, 32.26, 32.01, 31.76, 31.51, 31.26, 31.01, 30.76, 30.51, 30.26, 30.01, 29.76, 29.51, 29.26, 29.01, 28.76, 28.51, 28.26, 28.01, 27.76, 27.51, 27.26, 27.01, 26.76, 26.51, 26.26,

Figure S31. 2,6-diisopropylphenylisocyanate (**4**) following heating of **8**+PPh₃ at 100 °C for 1 h in tol-*d*₈, ¹H NMR, tol-*d*₈, 300 MHz, 298 K

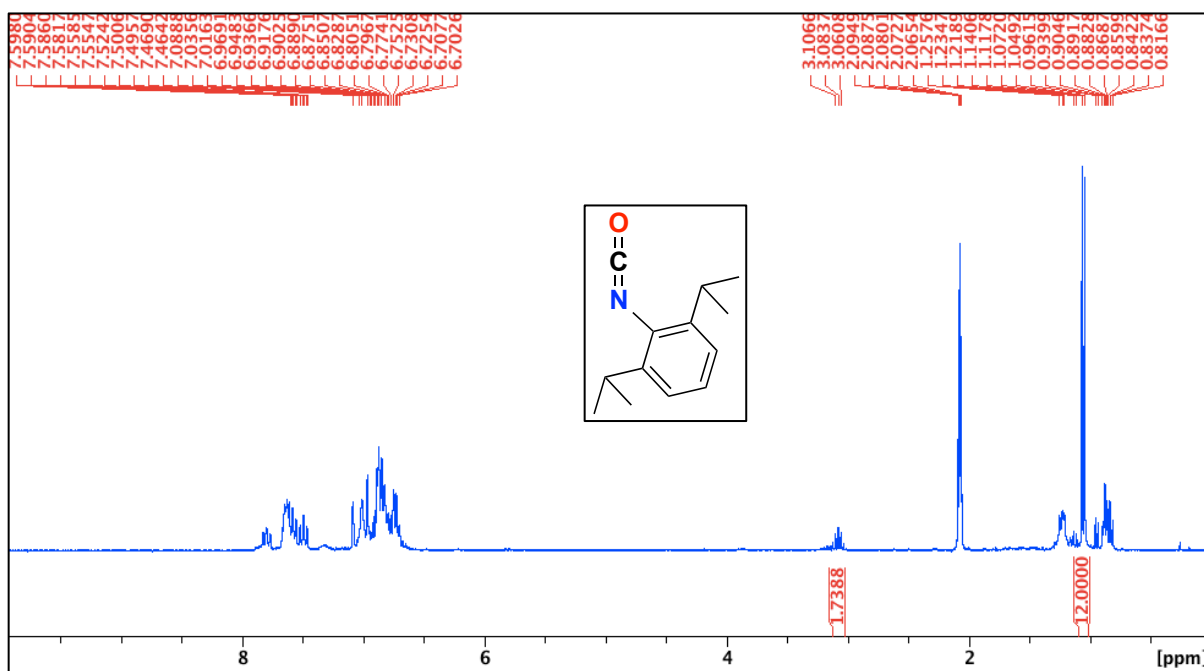


Figure S32. 2,6-diisopropylphenylisocyanate (**4**) formation following heating of **8**+PPh₃ at 100 °C for 1 h in tol-*d*₈, ¹H NMR, tol-*d*₈, 400 MHz, 373 K

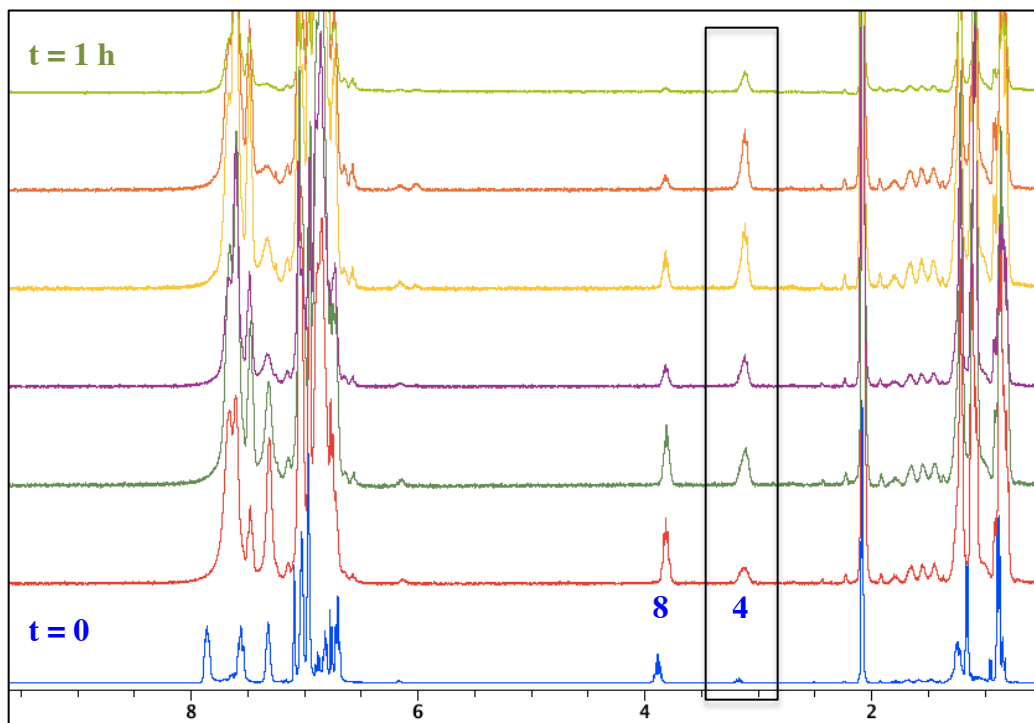


Figure S33. $\text{Rh}(\text{C}_6\text{F}_5)(\text{PPh}_3)_3$ formation following heating of **8**+ PPh_3 at 100 °C for 1 h in $\text{tol-}d_8$. $^{31}\text{P}\{^1\text{H}\}$ NMR, $\text{tol-}d_8$, 162 MHz, 373 K

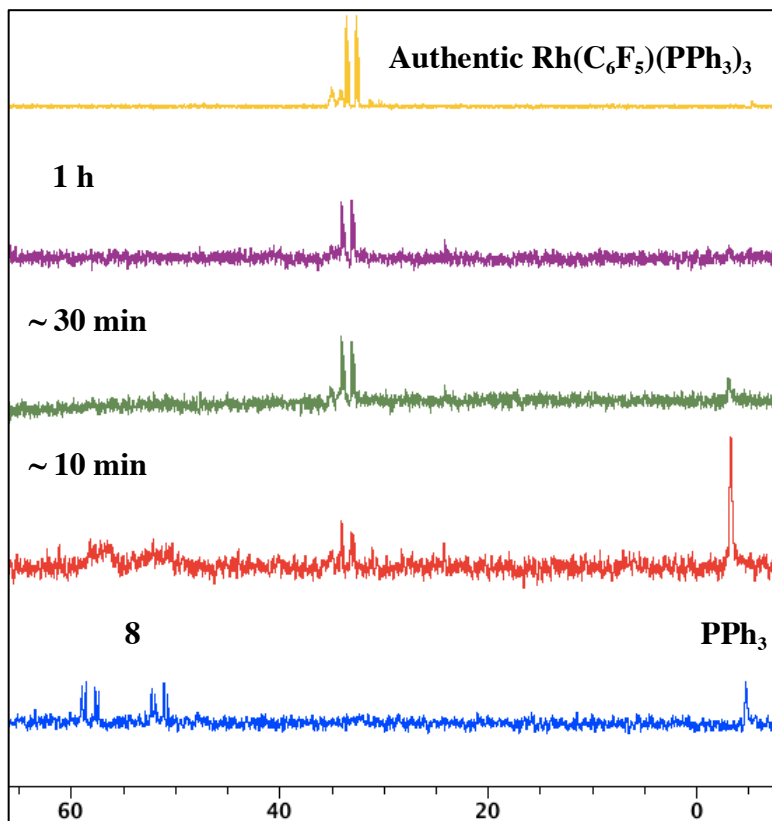


Figure S34. 2,6-diisopropylphenylisocyanate (**4**) in $\text{tol-}d_8$, IR (ATR), 298 K

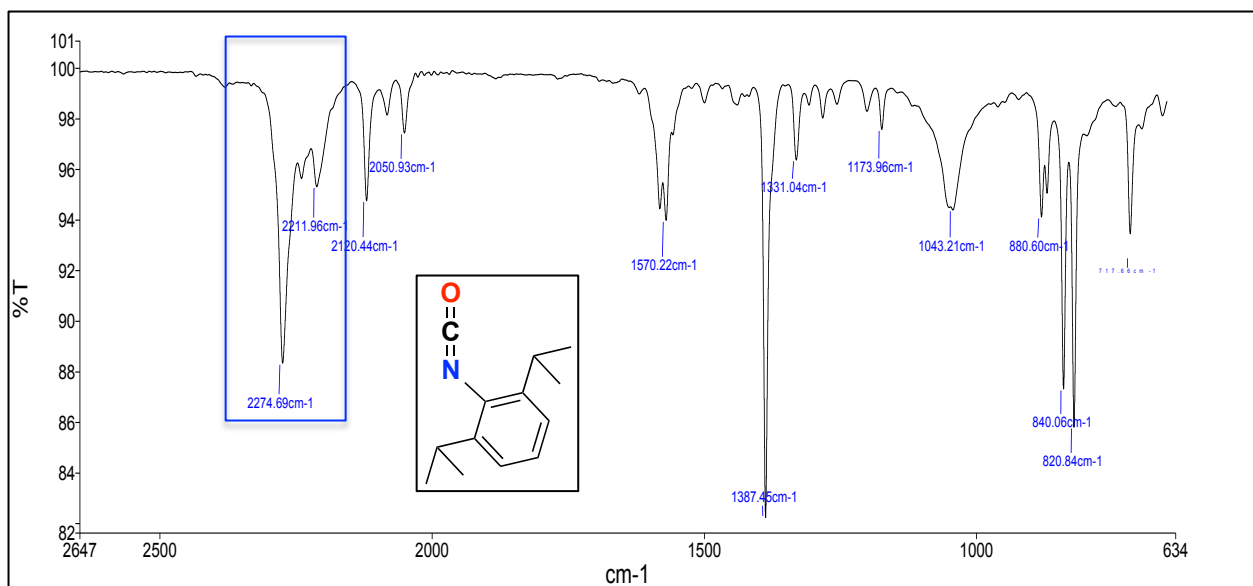


Table S1. Crystallographic data for **2** and *E/Z-3*

Compound	2	<i>E/Z-3</i>
Empirical formula	C ₅₂ H ₅₀ F ₁₀ N ₃ O ₄ Rh ₂	C _{45.5} H _{61.5} F ₅ NOPRh
Formula weight	1176.77	867.33
Temperature/K	90	90
Crystal system	Monoclinic	Triclinic
Space group	P2 ₁ /c	P-1
a/Å	18.4133(19)	9.9058(8)
b/Å	13.6493(13)	21.0289(17)
c/Å	20.839(2)	21.6355(16)
α/°	90	102.878(3)
β/°	101.855(3)	99.532(3)
γ/°	90	90.372(3)
Volume/Å ³	5125.7(9)	4328.4(6)
Z	4	4
ρ _{calc} /cm ³	1.525	1.331
μ/mm ⁻¹	0.727	0.487
F(000)	2380.0	1818.0
Crystal size/mm ³	0.31 × 0.16 × 0.09	0.41 × 0.21 × 0.13
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2θ range for data collection/°	3.59 to 60.282	2.454 to 50.802
Index ranges	-25 ≤ h ≤ 25, -19 ≤ k ≤ 19, - 28 ≤ l ≤ 29	-11 ≤ h ≤ 11, -25 ≤ k ≤ 24, 0 ≤ l ≤ 26
Reflections collected	14974	15659
Independent reflections	14974 [R _{sigma} = 0.0835]	15659 [R _{sigma} = 0.0779]
Data/restraints/parameters	14974/0/613	15659/0/991
Goodness-of-fit on F ²	0.961	1.057
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0449, wR ₂ = 0.0824	R ₁ = 0.0528, wR ₂ = 0.1349
Final R indexes [all data]	R ₁ = 0.0780, wR ₂ = 0.0908	R ₁ = 0.0798, wR ₂ = 0.1457

Table S2. Crystallographic data for **5** and **10**

Compound	5	10
Empirical formula	C ₃₁ H ₄₁ F ₅ PRh	C _{65.94} H _{58.87} F ₅ P ₃ Rh
Formula weight	642.52	1142.12
Temperature/K	90	90
Crystal system	Monoclinic	Monoclinic
Space group	P2 ₁ /n	P2 ₁ /n
a/Å	11.6503(12)	11.1408(7)
b/Å	20.980(2)	37.184(2)
c/Å	11.7247(13)	12.9377(8)
α /°	90	90
β /°	91.257(2)	96.3810(10)
γ /°	90	90
Volume/Å ³	2865.2(5)	5326.4(6)
Z	4	4
$\rho_{\text{calc}}/\text{cm}^3$	1.490	1.424
μ/mm^{-1}	0.704	0.471
F(000)	1328.0	2358.0
Crystal size/mm ³	0.4 × 0.27 × 0.07	0.43 × 0.14 × 0.12
Radiation	Mo K α (λ = 0.71073)	Mo K α (λ = 0.71073)
2 θ range for data collection/°	3.882 to 61.118	3.84 to 52.12
Index ranges	-16 ≤ h ≤ 16, -29 ≤ k ≤ 29, - 16 ≤ l ≤ 16	-13 ≤ h ≤ 13, -45 ≤ k ≤ 45, - 15 ≤ l ≤ 15
Reflections collected	35522	49268
Independent reflections	8756 [R _{int} = 0.0326, R _{sigma} = 0.0247]	10500 [R _{int} = 0.0827, R _{sigma} = 0.0669]
Data/restraints/parameters	8756/0/343	10500/711/733
Goodness-of-fit on F ²	1.054	1.012
Final R indexes [I ≥ 2 σ (I)]	R ₁ = 0.0355, wR ₂ = 0.0891	R ₁ = 0.0414, wR ₂ = 0.0765
Final R indexes [all data]	R ₁ = 0.0400, wR ₂ = 0.0927	R ₁ = 0.0694, wR ₂ = 0.0853