Supporting information for:

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

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Figure S1. 2, ^{1}H NMR, C_6D_6, 600 MHz, 298K

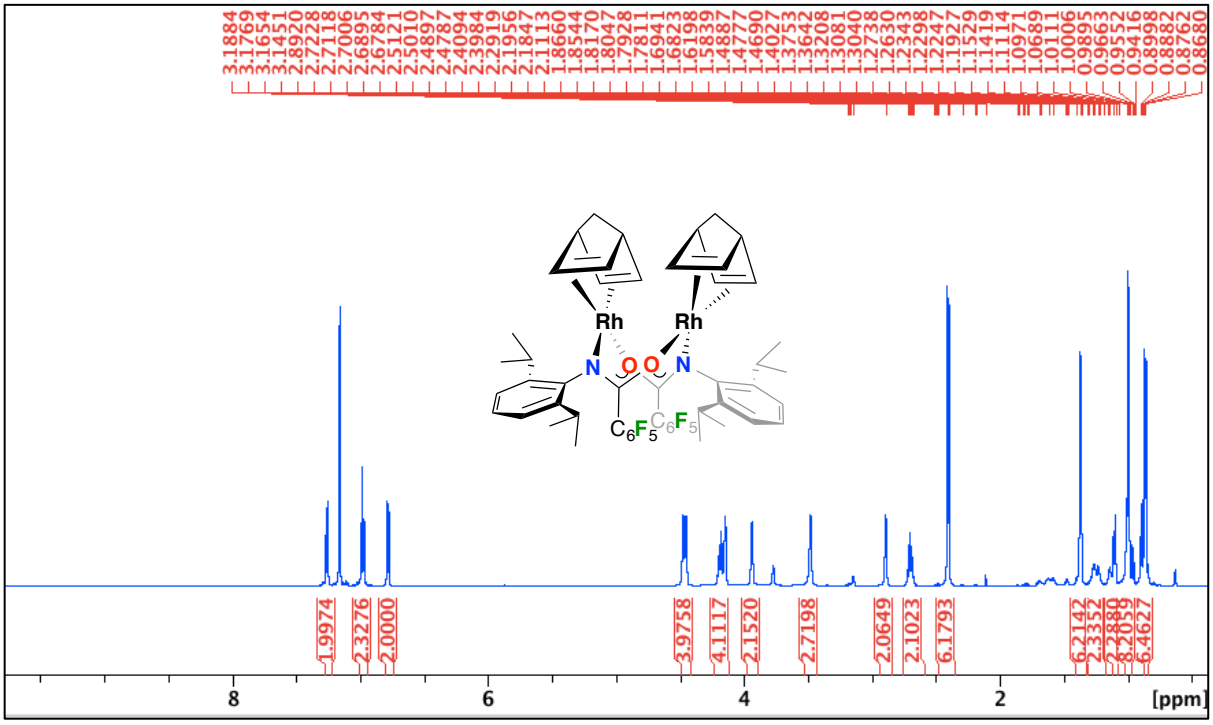

Figure S2. 2, $^{19}F\{^{1}H\}$ NMR, C_6D_6, 377 MHz, 298 K

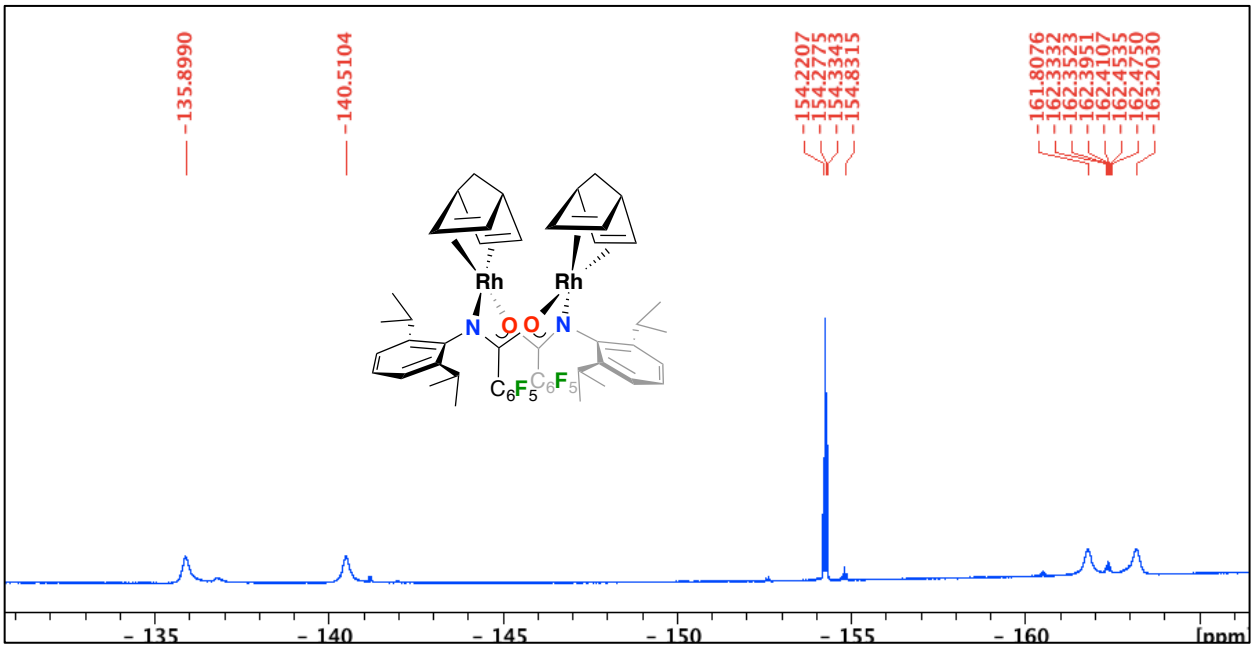

Figure S3. 2, $^{13}C\{^{1}H\}$ NMR, C_6D_6, 150 MHz, 298 K

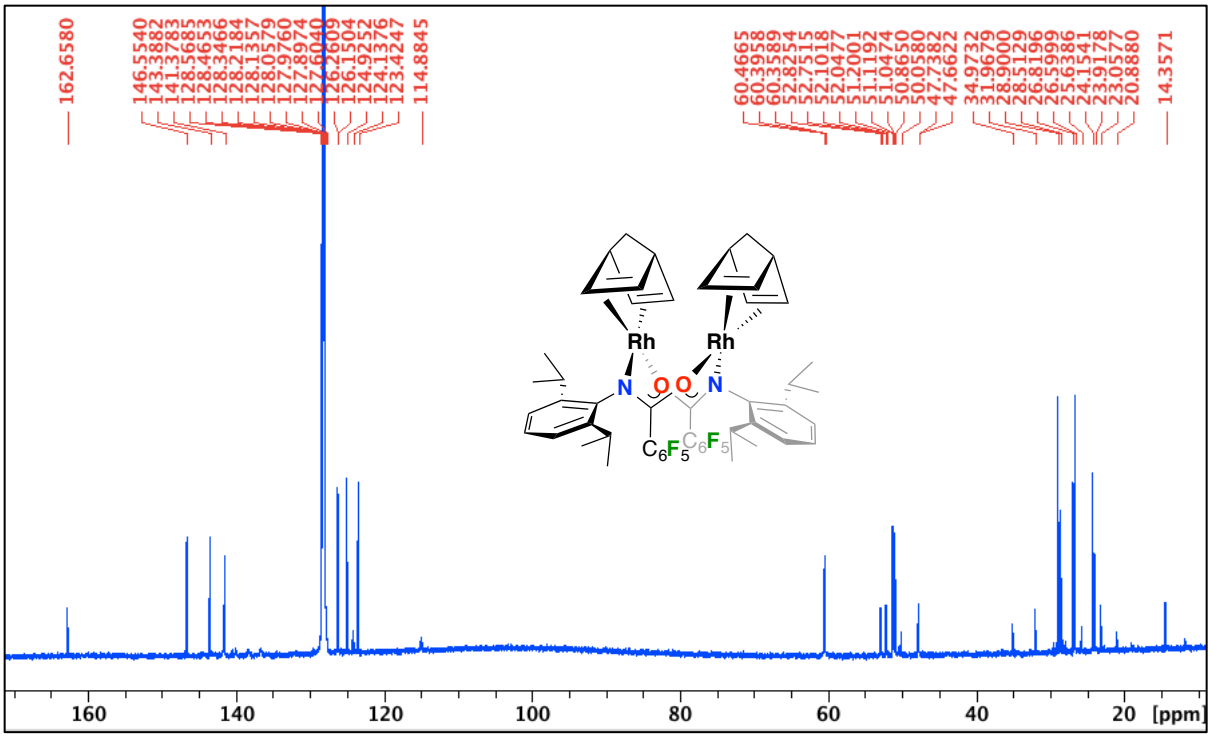

Figure S4. *E*/*Z*-3, ^{1}H NMR, tol-d_8, 300 MHz, 298 K

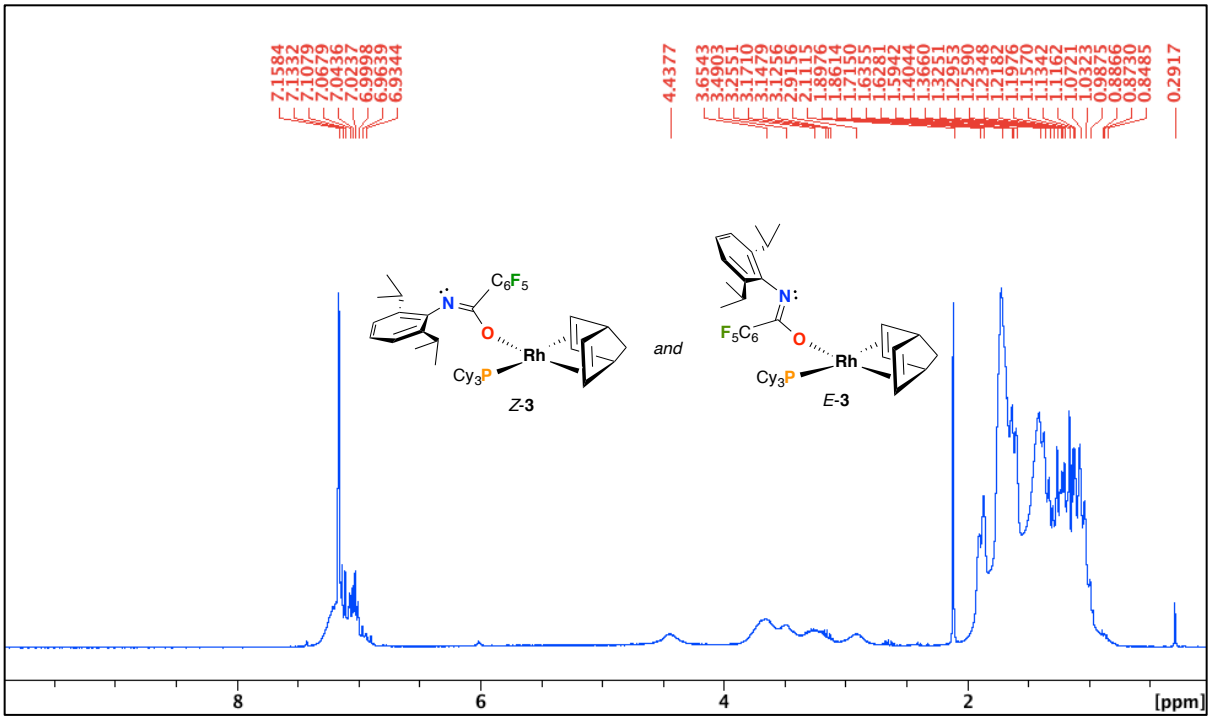

Figure S5. ***E*/*Z*-3**, VT ^{1}H NMR, tol-d_8, 300 MHz (* = residual Rh(η^4-NBD)(PCy$_3$)Cl))

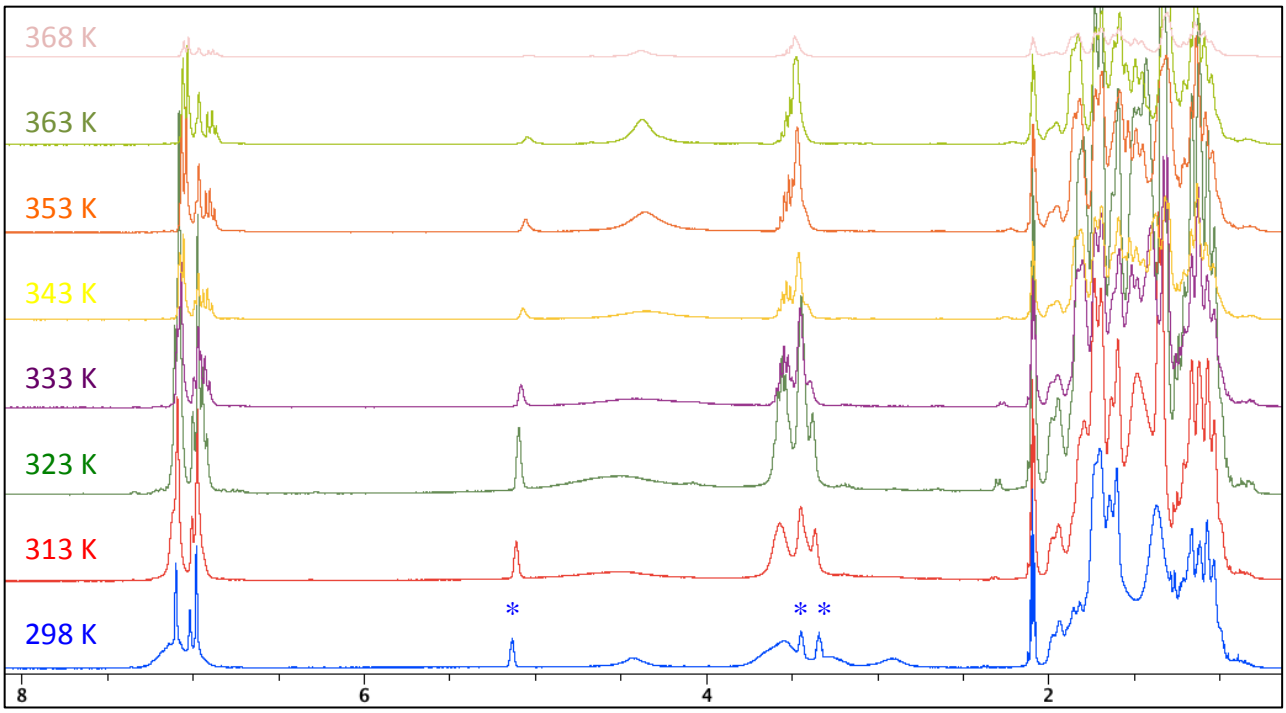

Figure S6. ***E*/*Z*-3,** ^{31}P{^{1}H} NMR, tol-d_8, C_6D_6, 121 MHz, 298 K

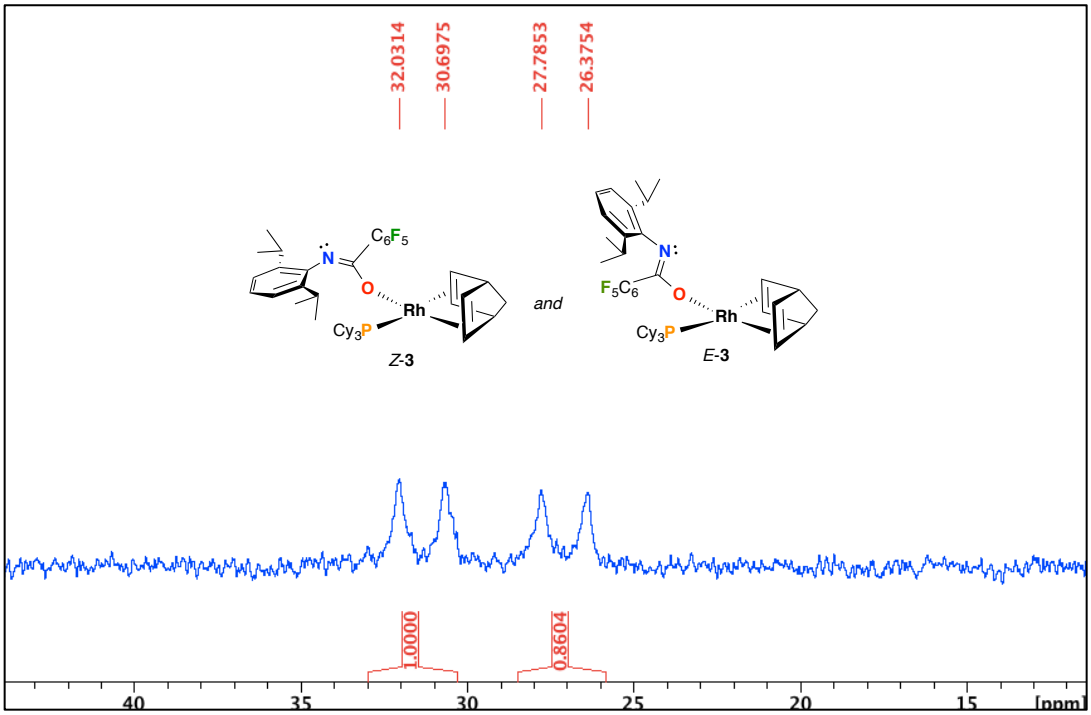

Figure S7. ***E*/*Z*-3**, VT $^{19}F\{^{1}H\}$ NMR, tol-d_8, 282 MHz

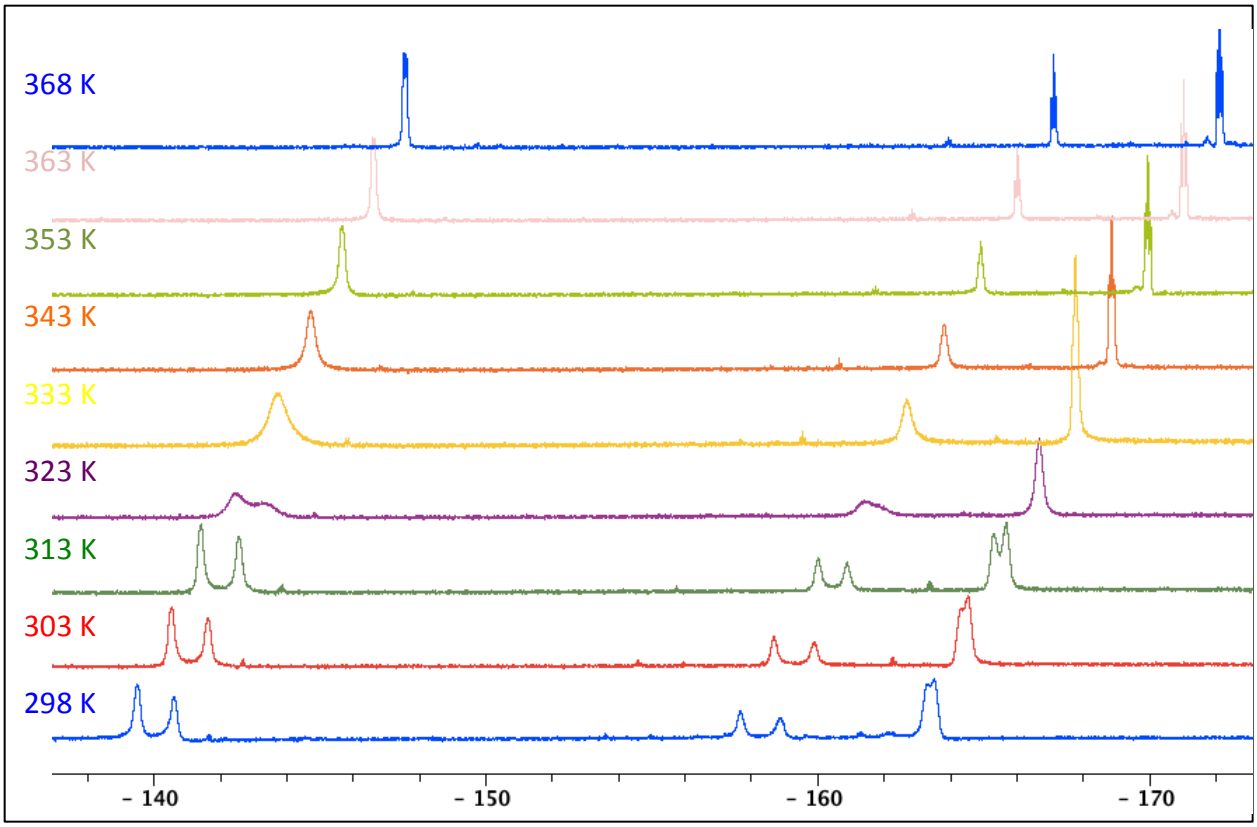

Figure S8. ***E*/*Z*-3**, solid-state IR (ATR) spectrum, 298 K

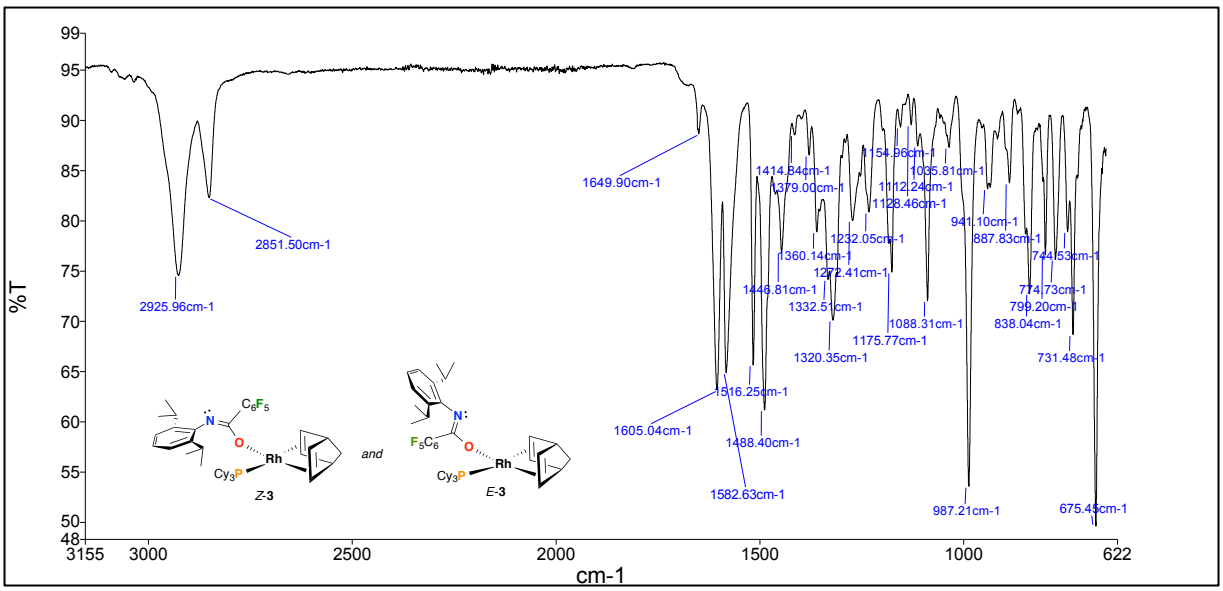

Figure S9. 5, ^{1}H NMR, C_6D_6, 400 MHz, 298K

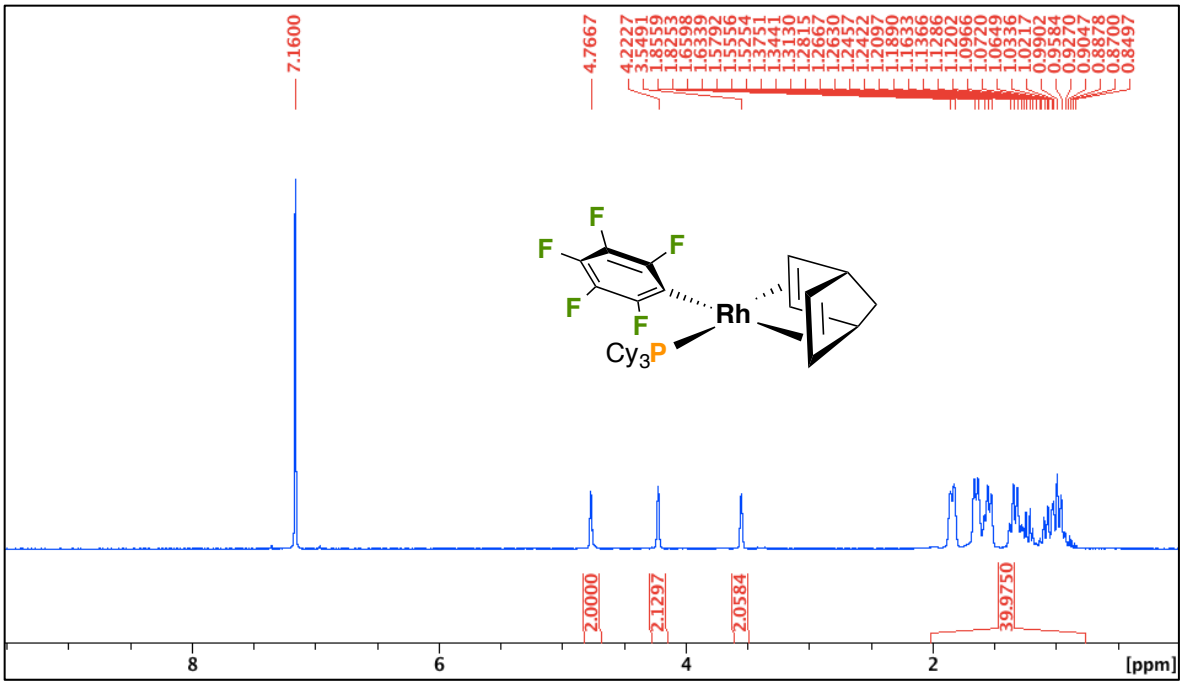

Figure S10. 5, ^{19}F{^{1}H} NMR, C_6D_6, 377 MHz, 298 K

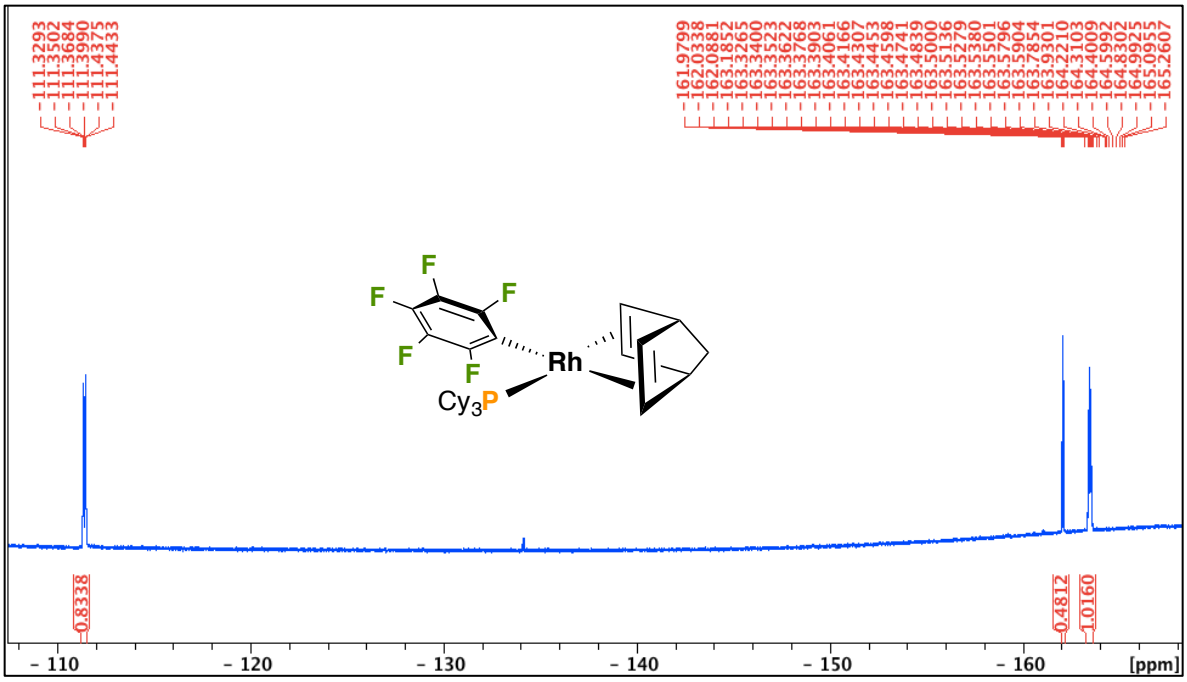

Figure S11. 5, $^{31}P\{^{1}H\}$ NMR, C_6D_6, 162 MHz, 298 K

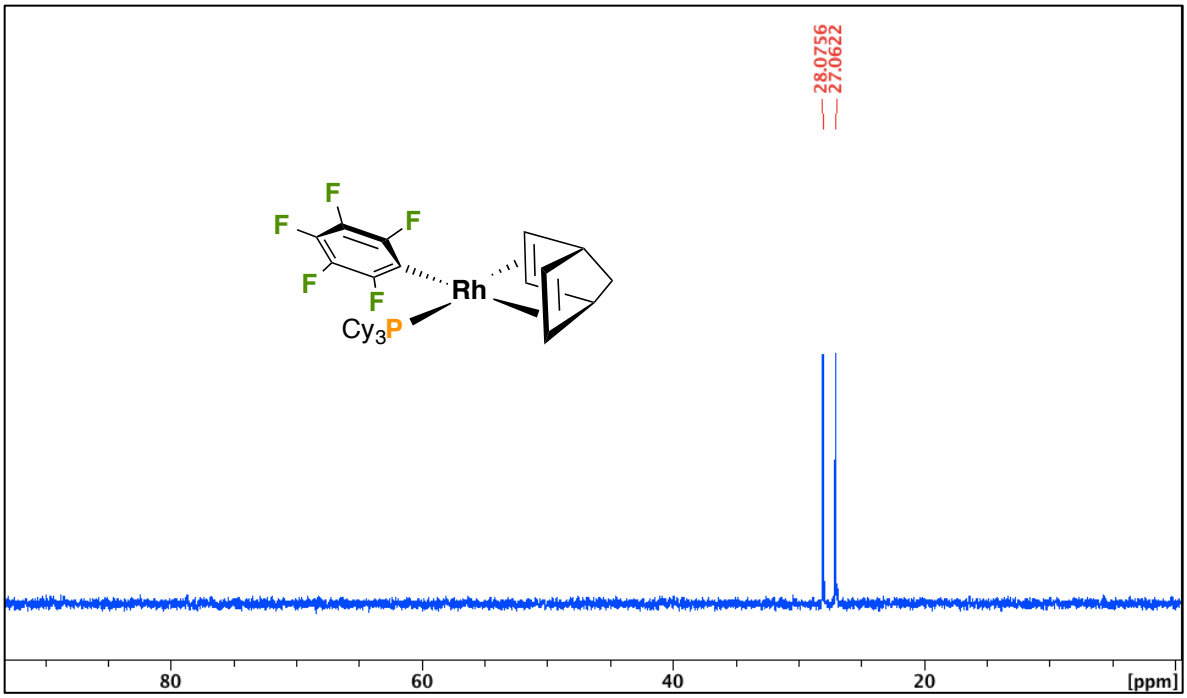

Figure S12. 5, $^{13}C\{^{1}H\}$ NMR, C_6D_6, 100 MHz, 298 K

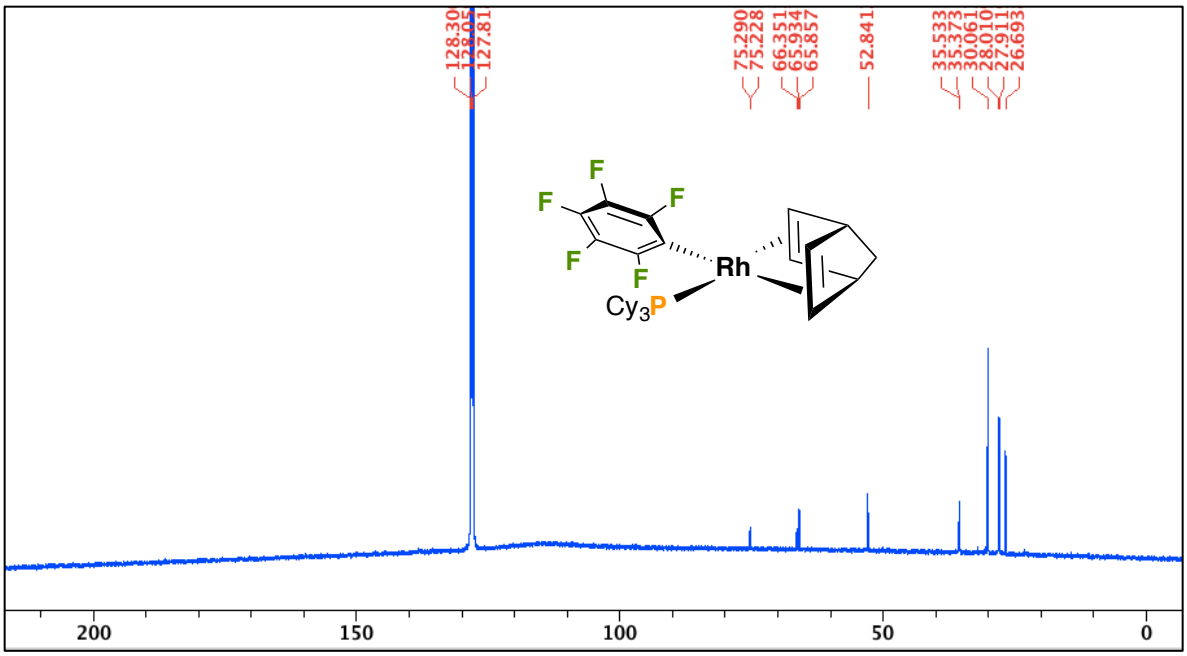

Figure S13. 6, ^{1}H NMR, C_6D_6, 400 MHz, 298 K

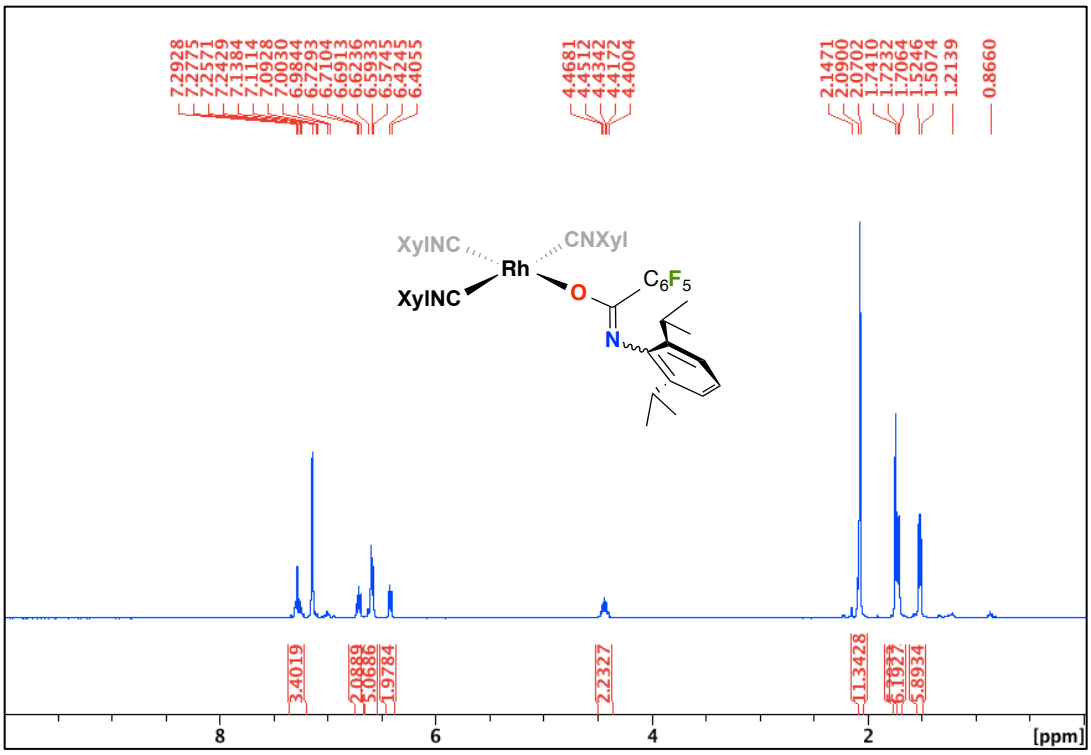

Figure S14. 6, $^{19}F\{^{1}H\}$ NMR, C_6D_6, 377 MHz, 298 K

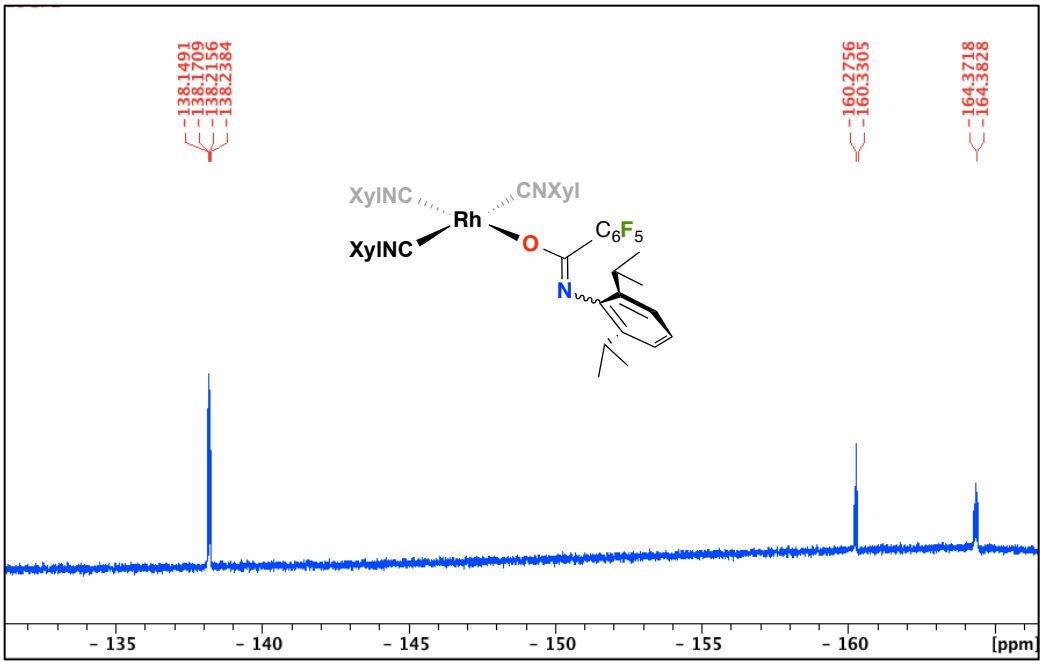

Figure S15. 6, $^{13}C\{^{1}H\}$ NMR, C_6D_6, 100 MHz, 298 K

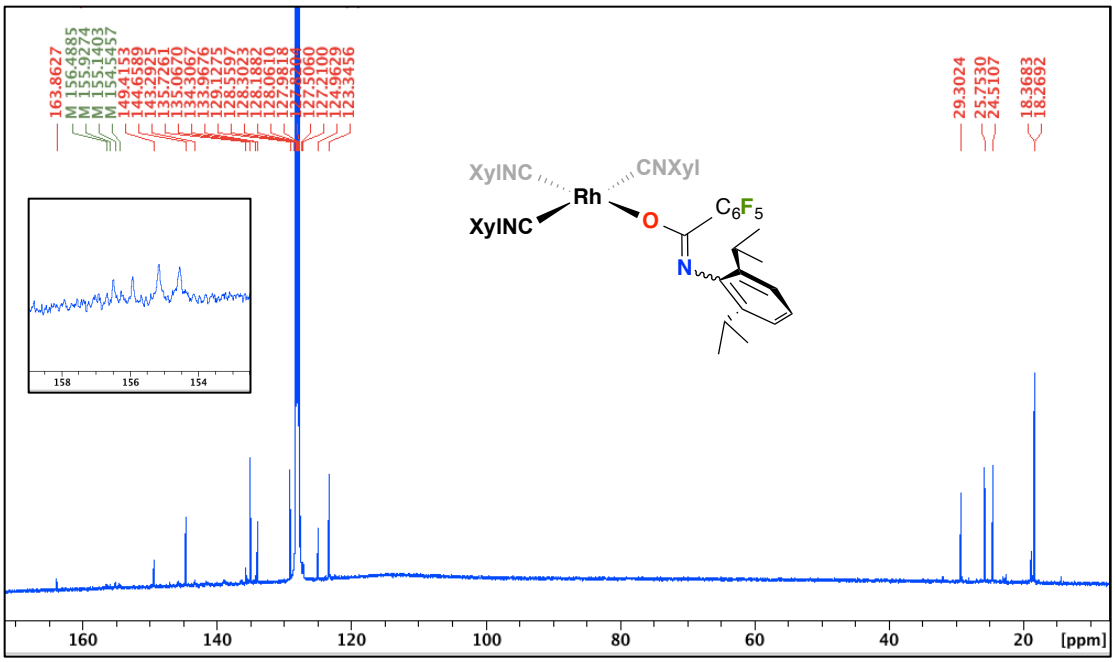

Figure S16. 6, solid-state IR (ATR) spectrum, 298 K

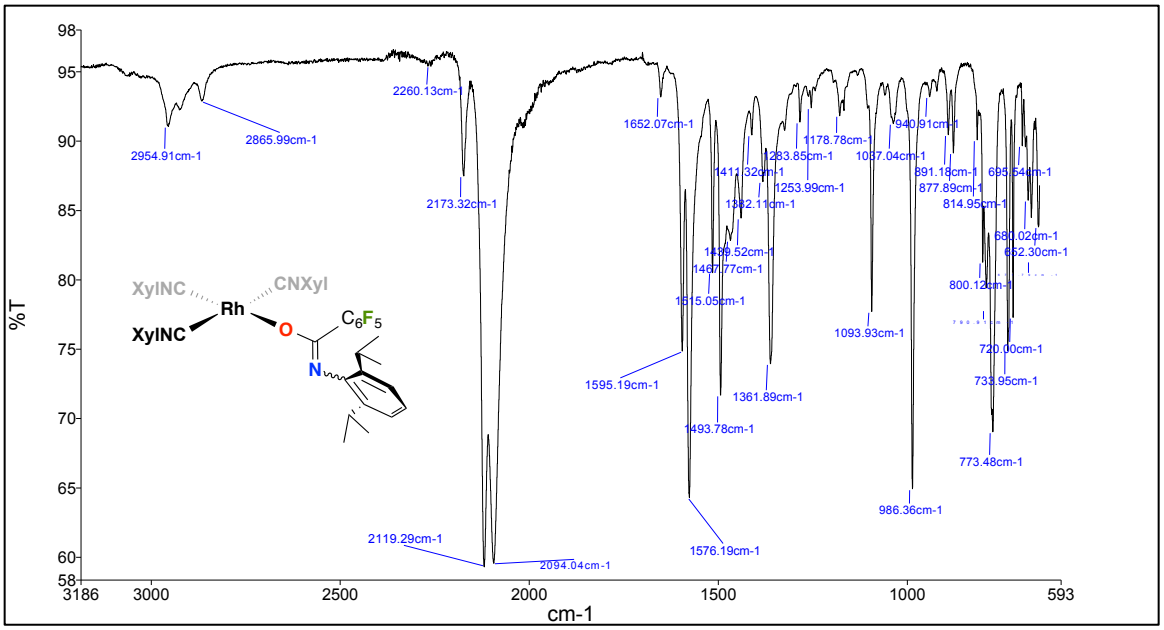

Figure S17. 7, ^{1}H NMR, C_6D_6, 400 MHz, 298 K

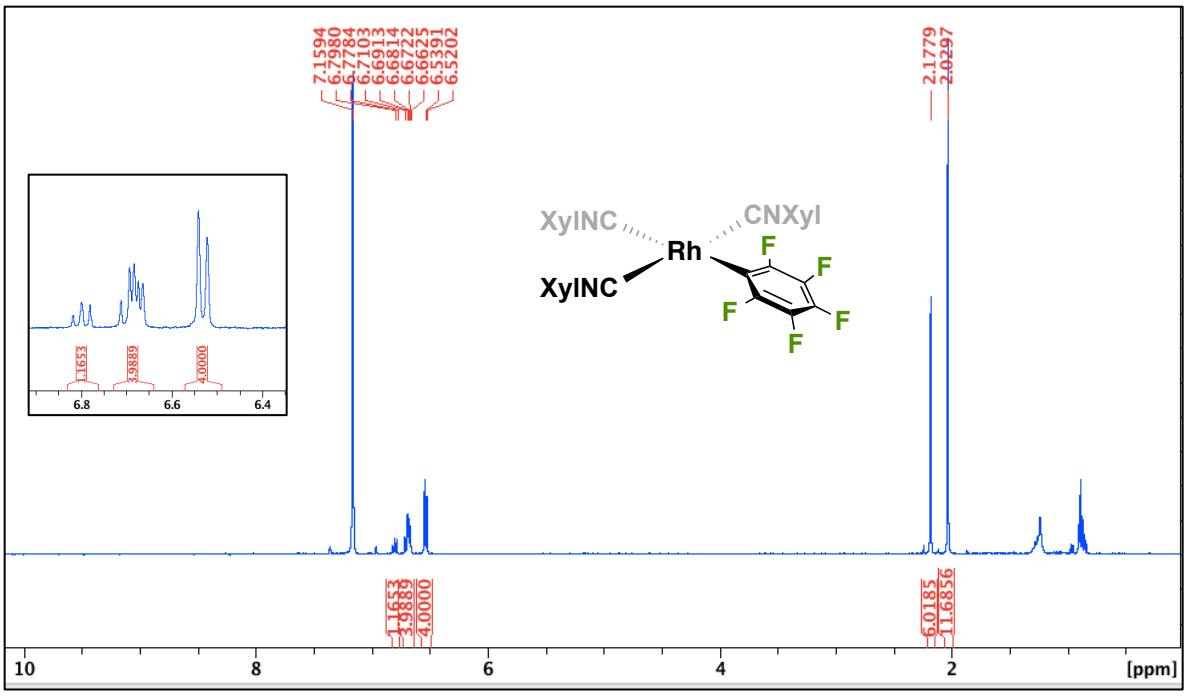

Figure S18. 7, ^{19}F{^{1}H} NMR, C_6D_6, 377 MHz, 298 K

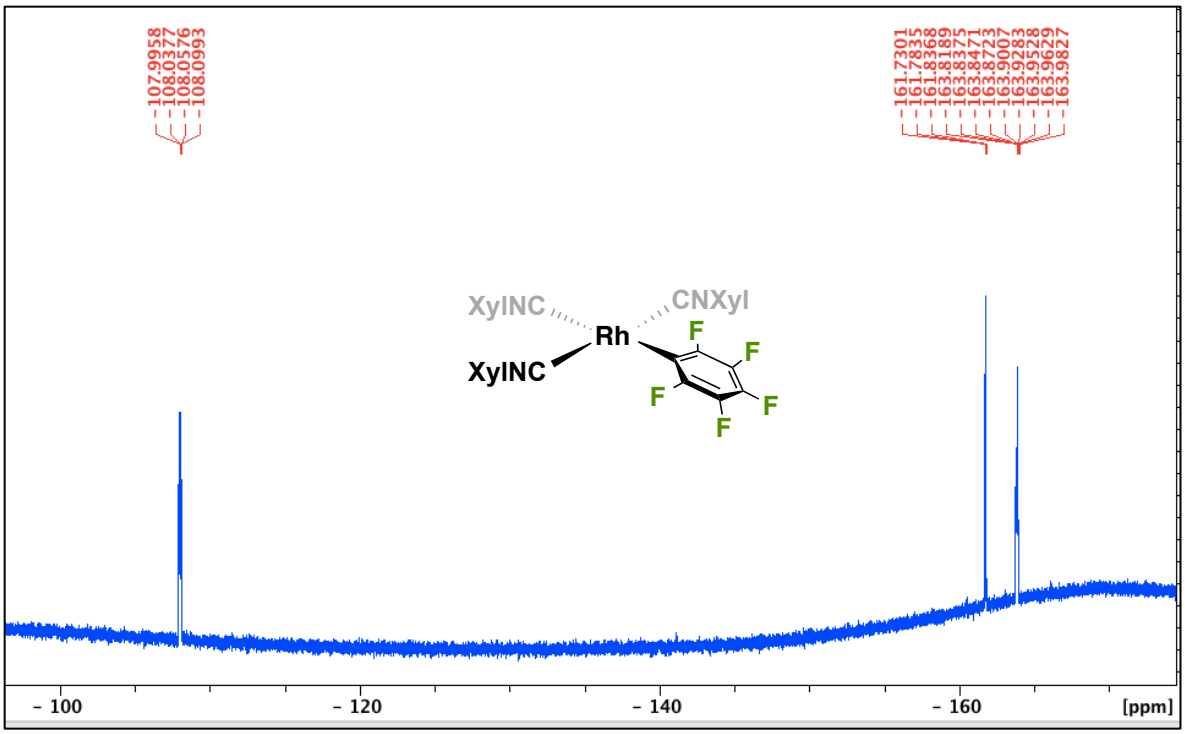

Figure S19. 7, solid-state IR (ATR) spectrum, 298 K

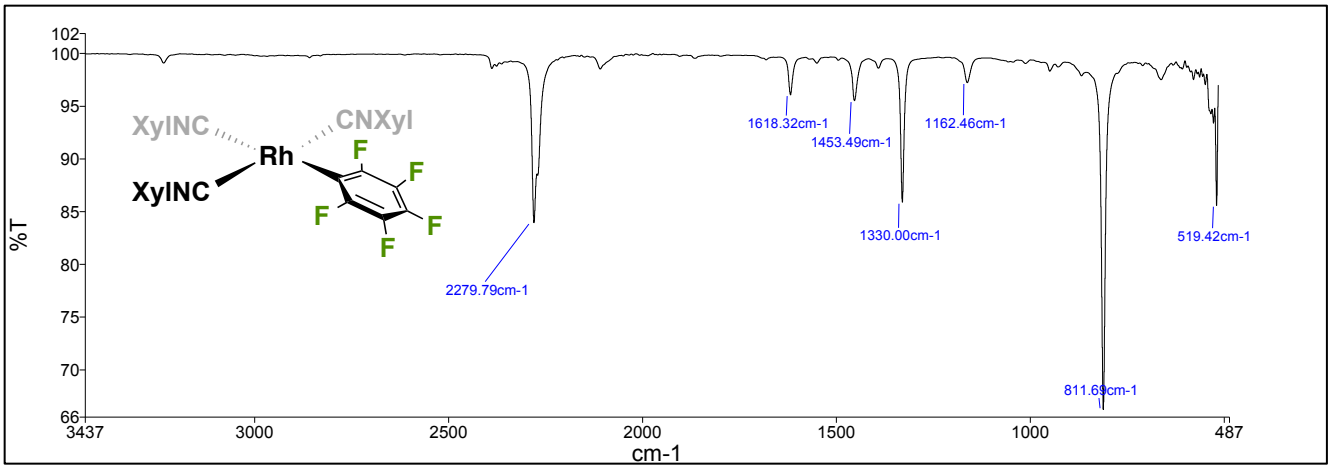

Figure S20. 8+PPh$_3$, ^{1}H NMR, C_6D_6, 400 MHz, 298 K

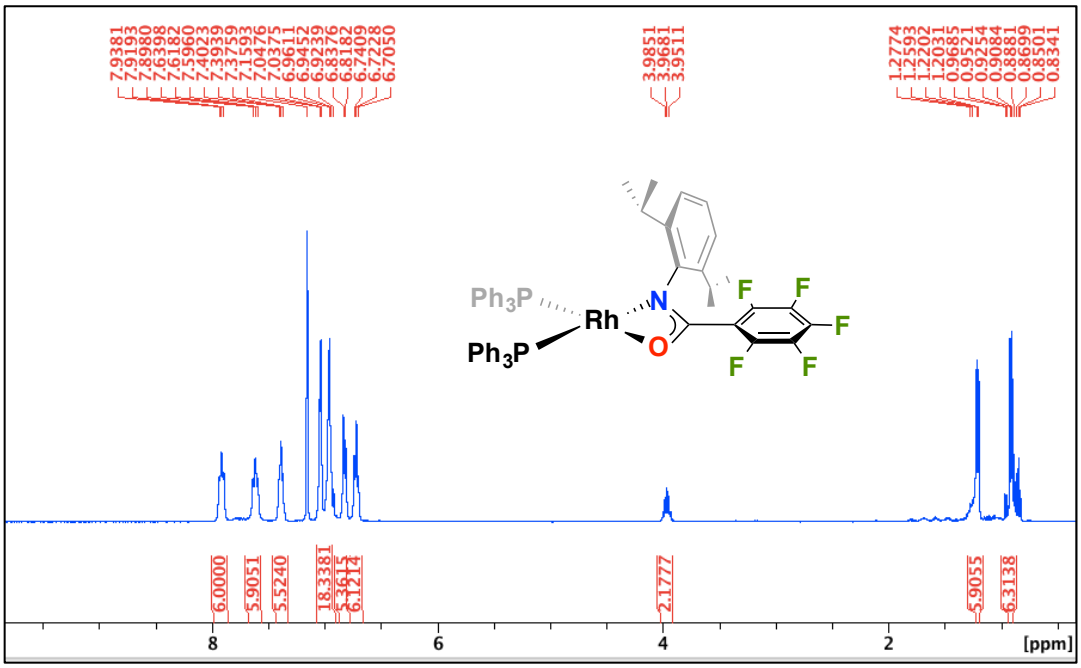

Figure S21. 8+PPh$_3$, ^{31}P{^{1}H} NMR, C_6D_6, 162 MHz, 298 K

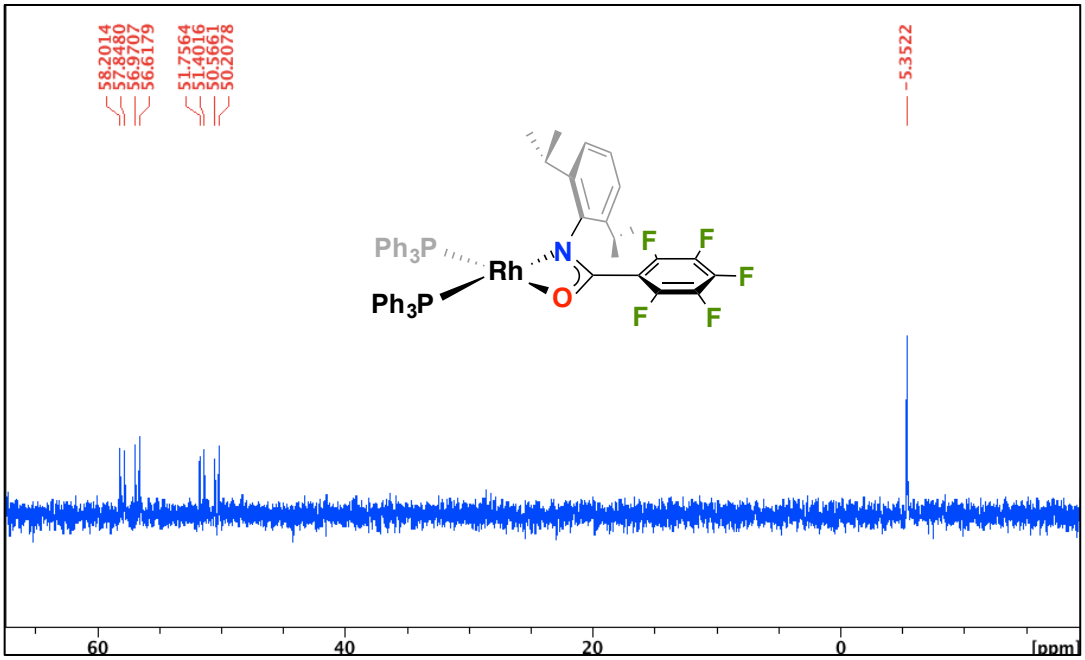

Figure S22. 8+PPh$_3$, ^{19}F{^{1}H} NMR, C_6D_6, 377 MHz, 298 K

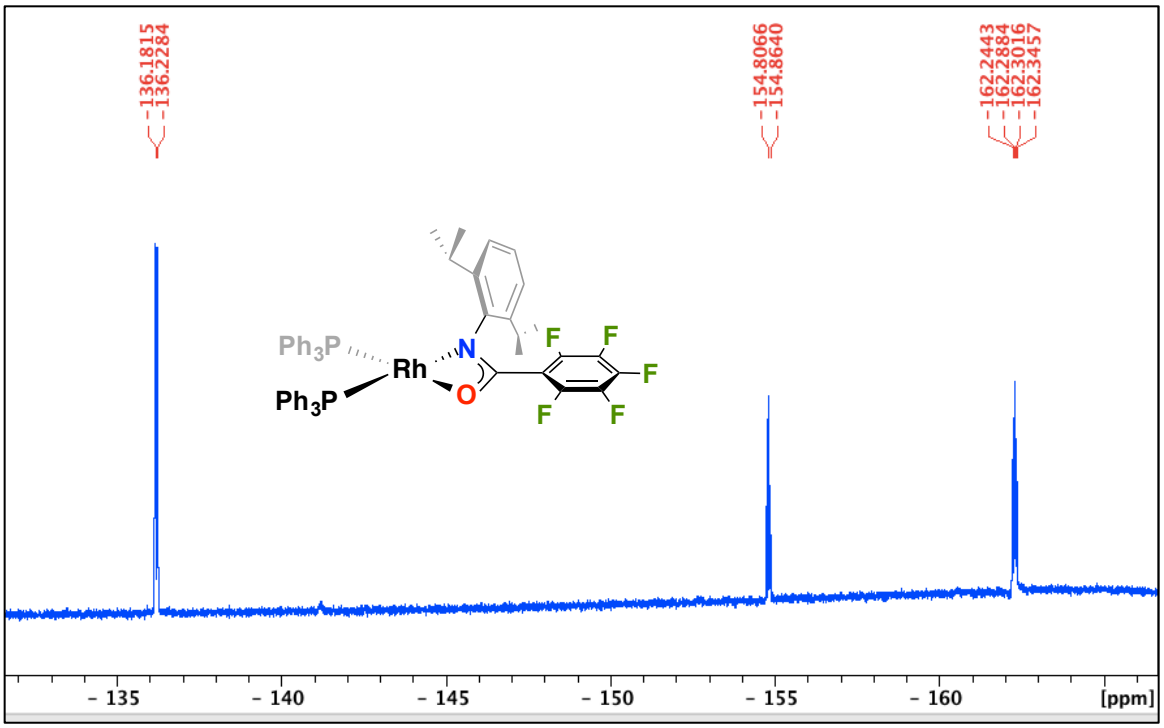

Figure S23. 8+PPh$_3$, $^{13}C\{^1H\}$ NMR, tol-d_8, 100 MHz, 298 K

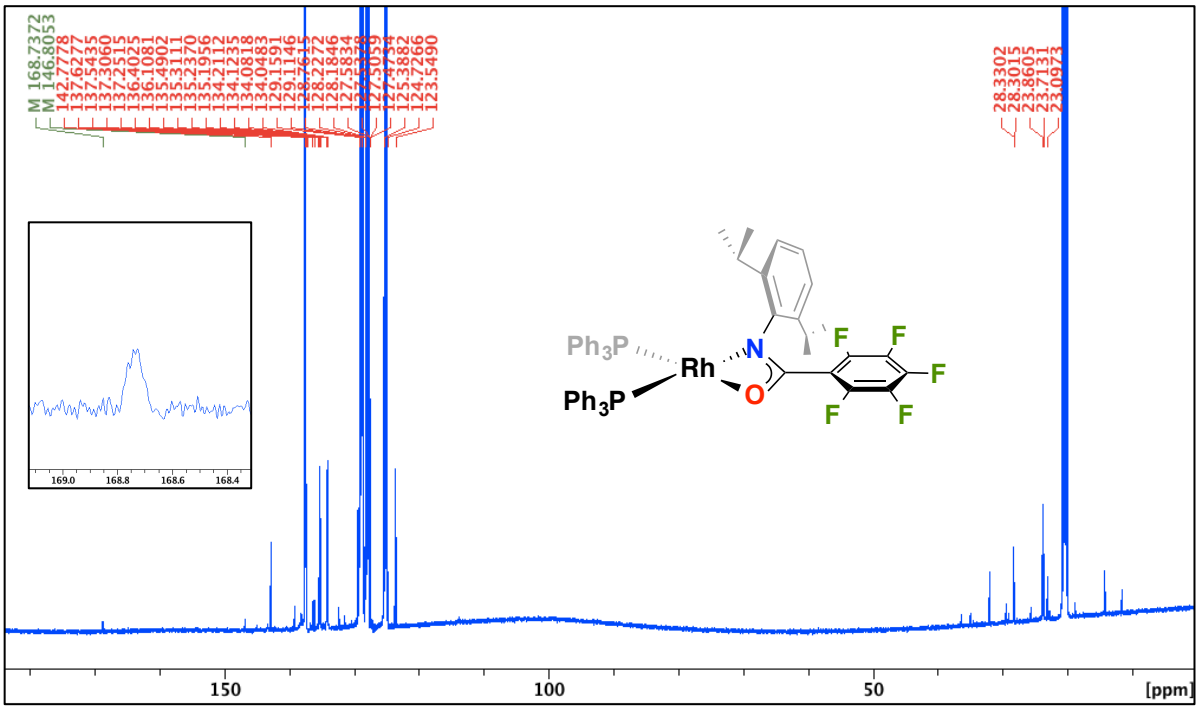

Figure S24. 8+PPh$_3$, VT ^1H NMR, tol-d_8, 400 MHz

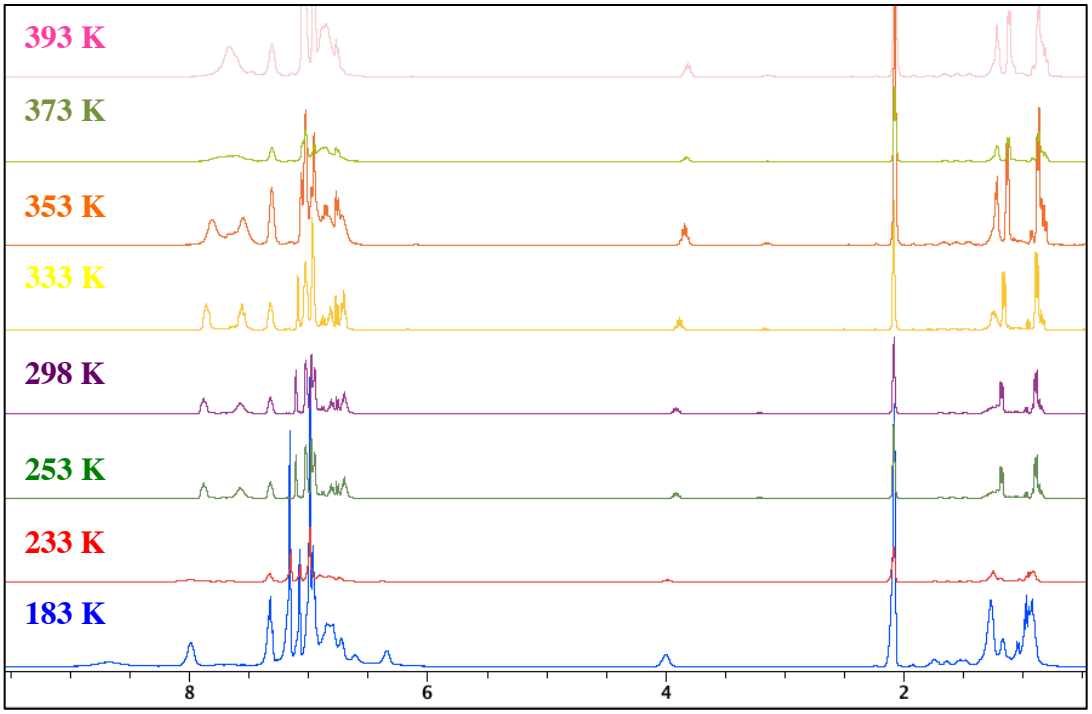

Figure S25. 8+PPh$_3$, VT ^{31}P{^{1}H} NMR, tol-d_8, 400 MHz

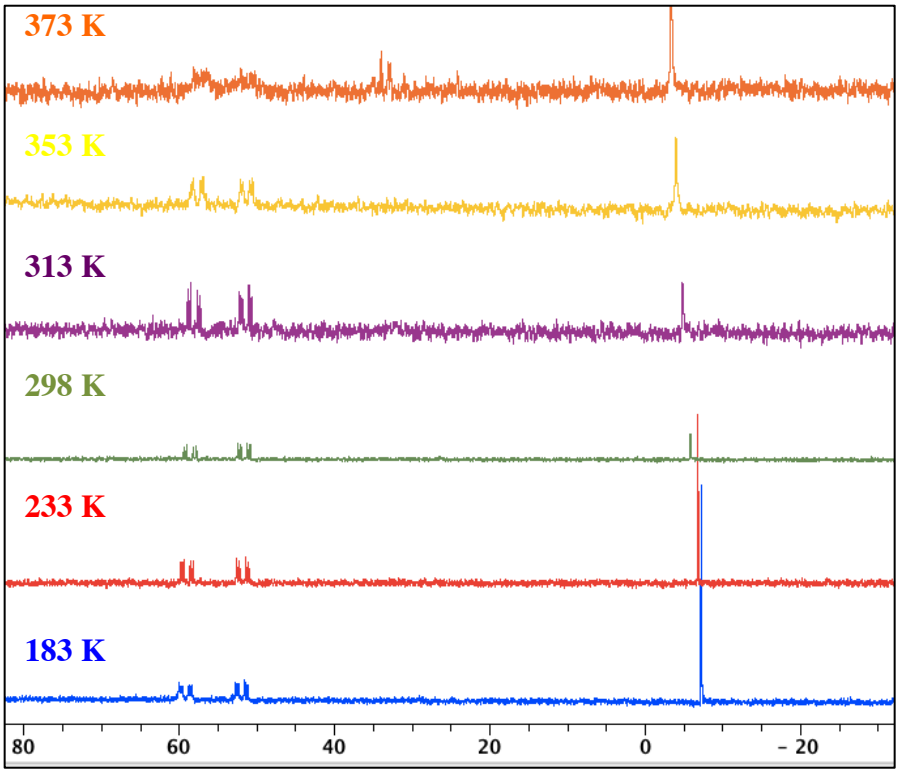

Figure S26. 8+PPh$_3$, solid-state IR (ATR) spectrum, 298 K

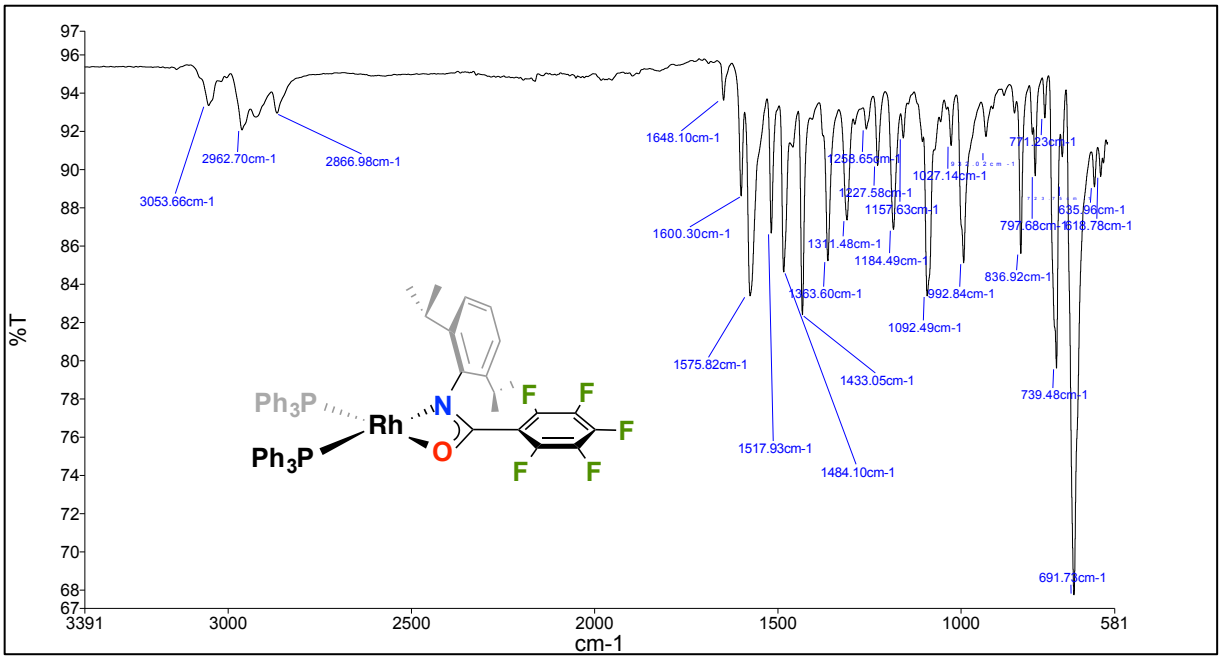

Figure S27. 10, ^{1}H NMR, C_6D_6, 400 MHz, 298 K (* = trace solvent impurity (THF, Et_2O))

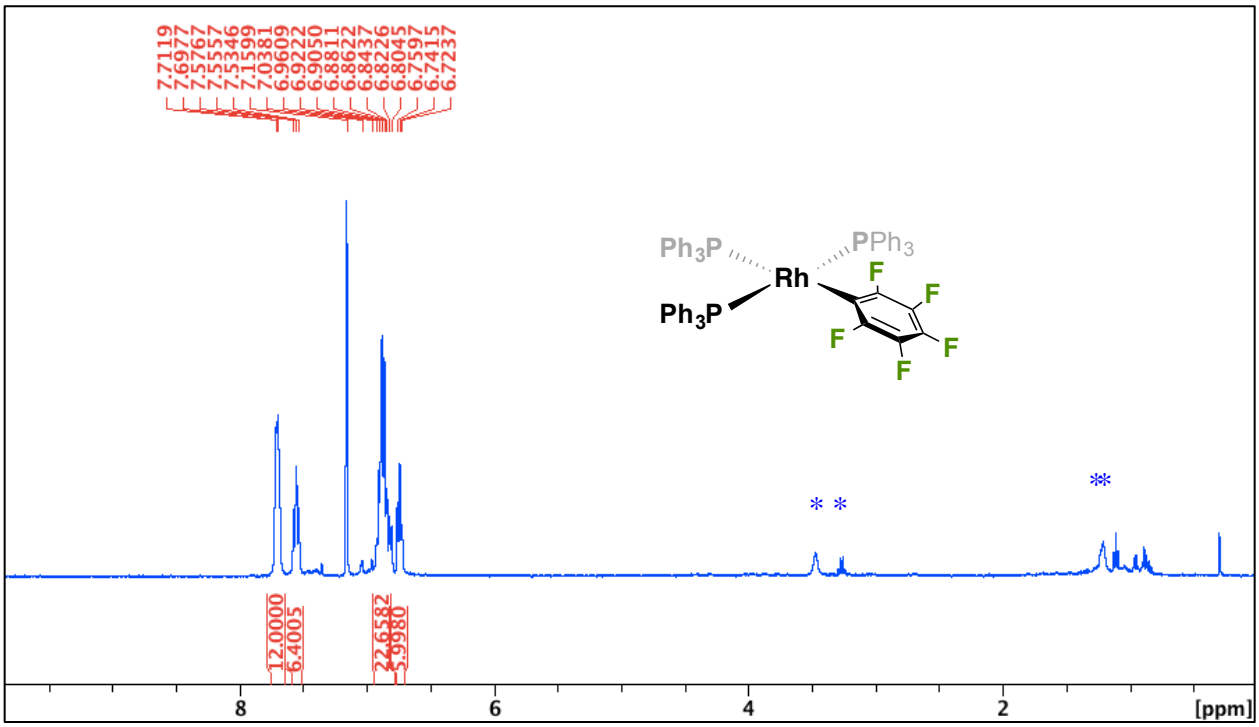

Figure S28. 10, $^{31}P\{^{1}H\}$ NMR, C_6D_6, 162 MHz, 298 K

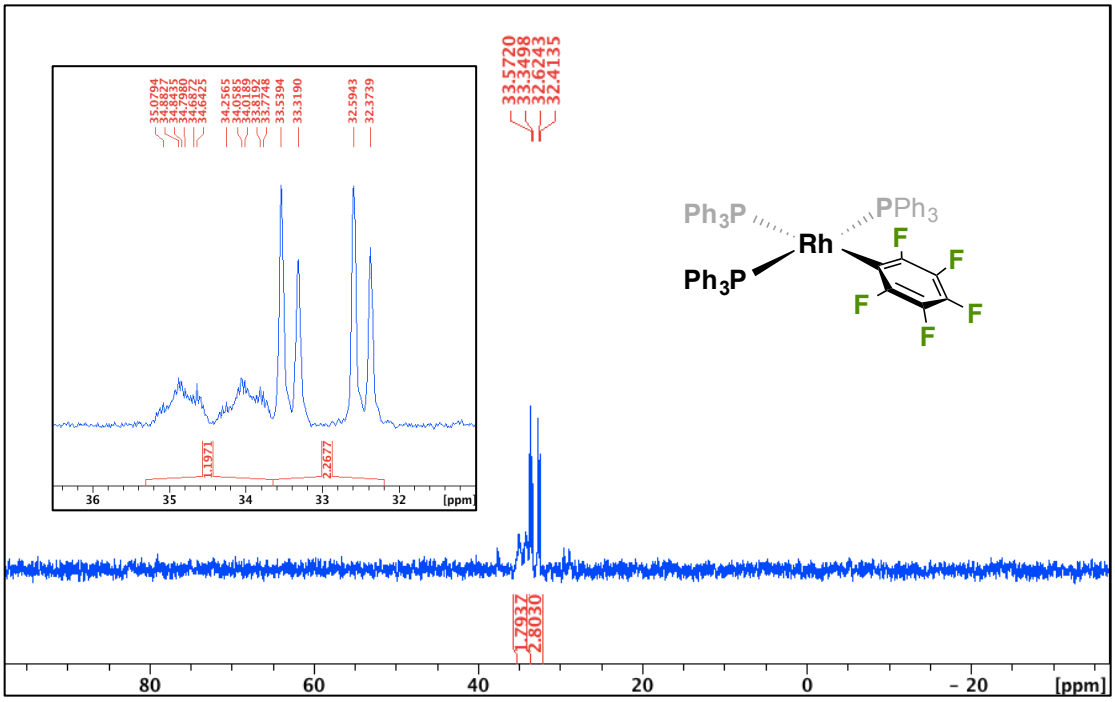

Figure S29. 10, $^{19}F\{^{1}H\}$ NMR, C_6D_6, 377 MHz, 298 K

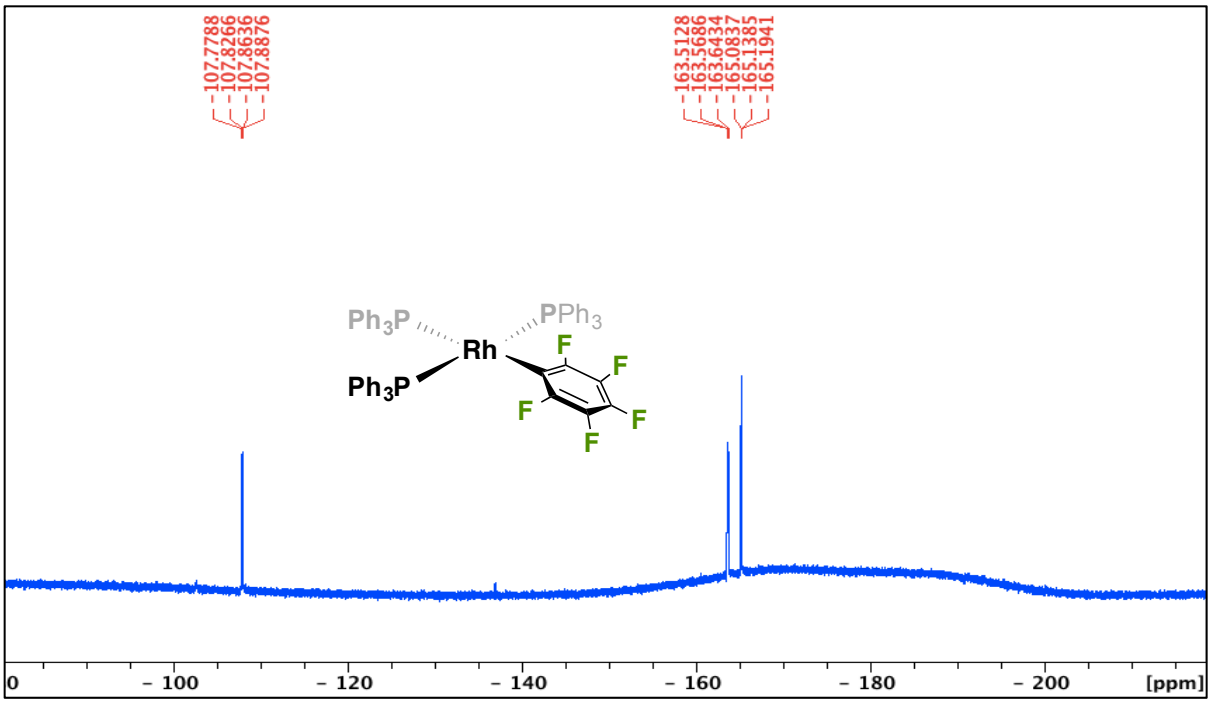

Figure S30. 10, $^{13}C\{^{1}H\}$ NMR, C_6D_6, 100 MHz, 298 K

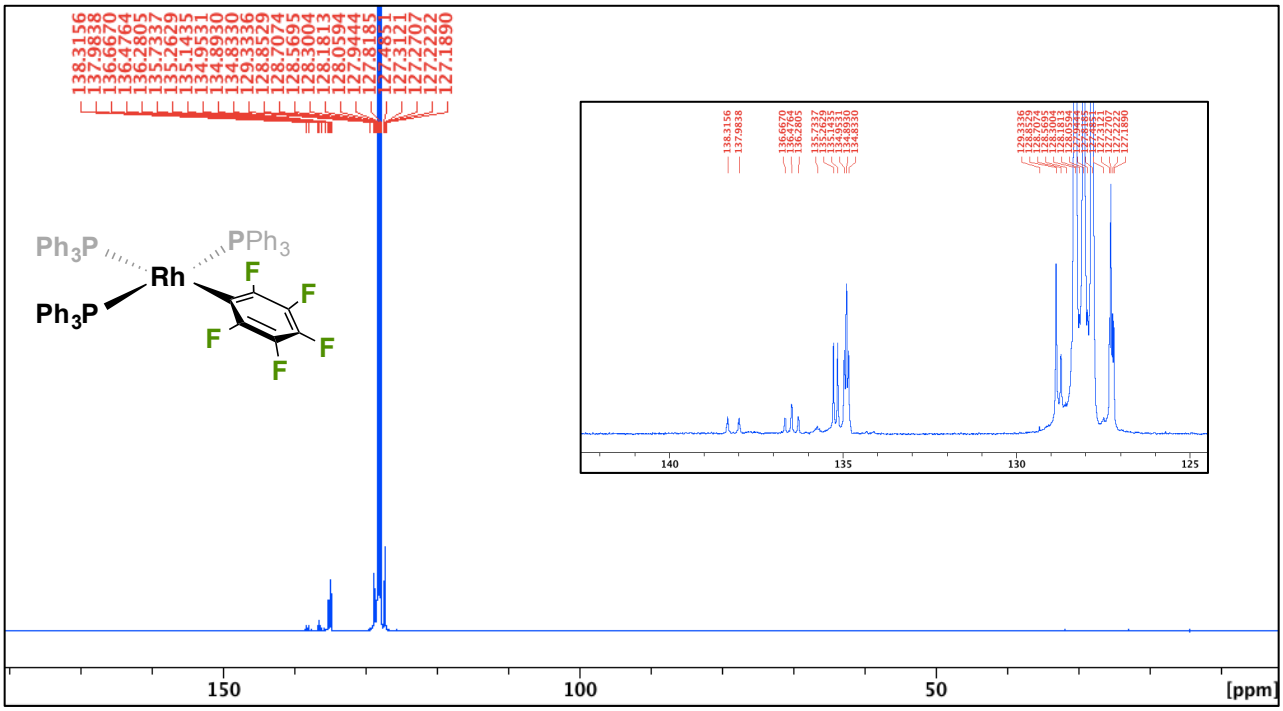

Figure S31. 2,6-diisopropylphenylisocyanate (4) following heating of 8+PPh$_3$ at 100 ^{o}C for 1 h in tol-d$_8$, ^{1}H NMR, tol-d_8, 300 MHz, 298 K

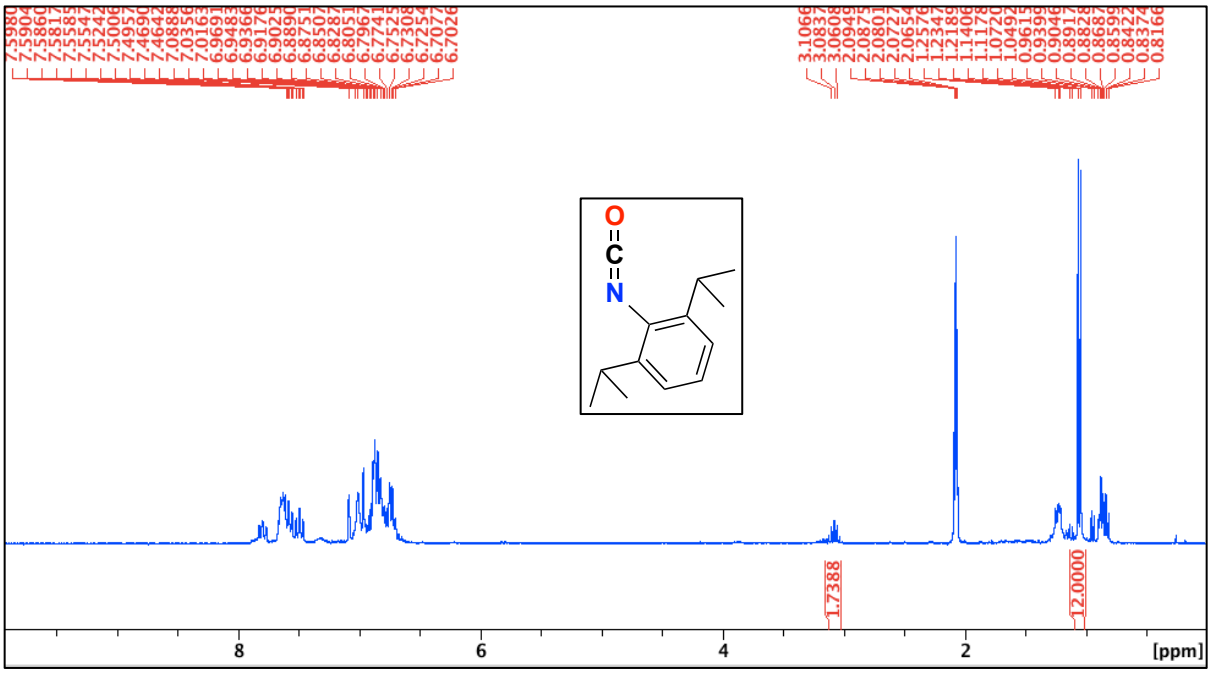

Figure S32. 2,6-diisopropylphenylisocyanate (4) formation following heating of 8+PPh$_3$ at 100 ^{o}C for 1 h in tol-d_8. ^{1}H NMR, tol-d_8, 400 MHz, 373 K

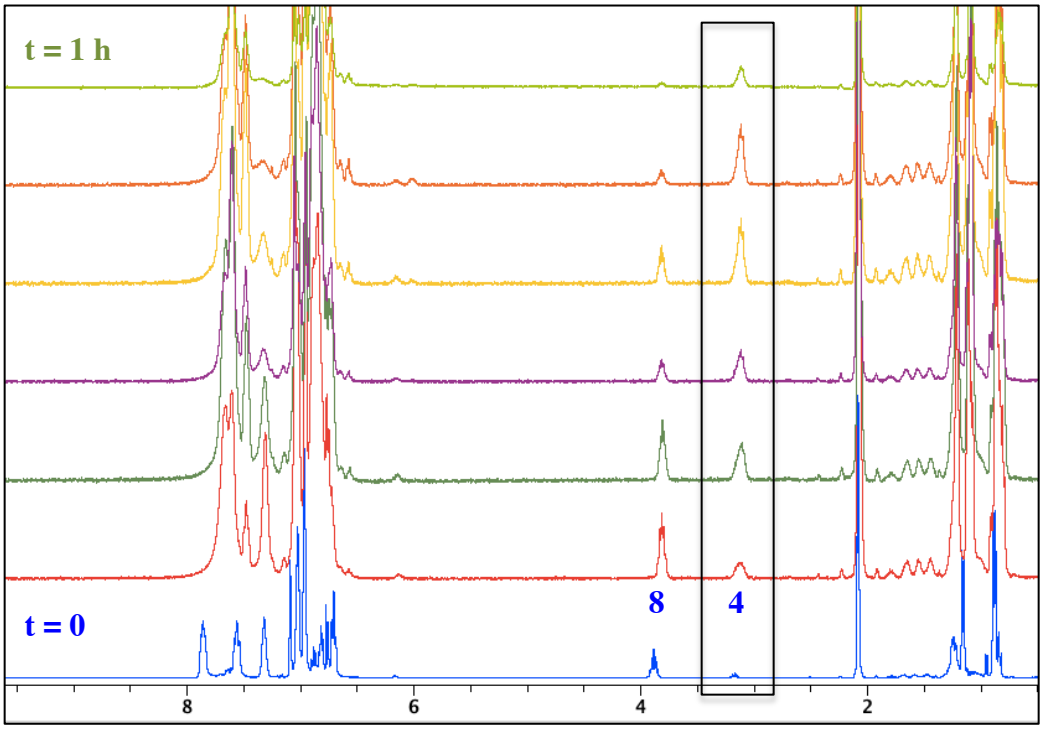

Figure S33. $Rh(C_6F_5)(PPh_3)_3$ formation following heating of 8+PPh_3 at 100 °C for 1 h in tol-d_8. $^{31}P\{^1H\}$ NMR, tol-d_8, 162 MHz, 373 K

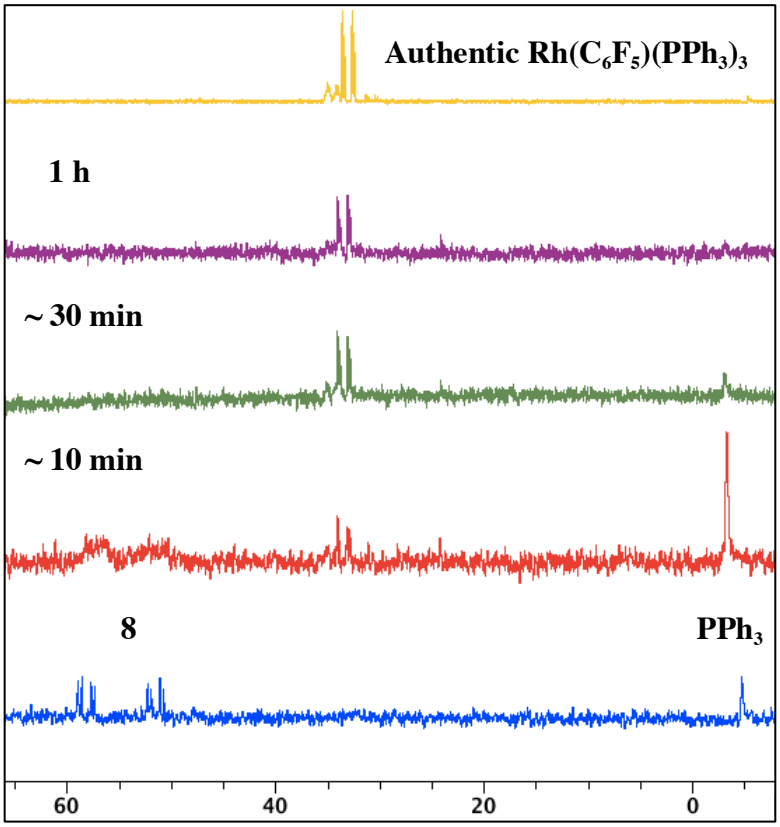

Figure S34. 2,6-diisopropylphenylisocyanate (4) in tol-d_8, IR (ATR), 298 K

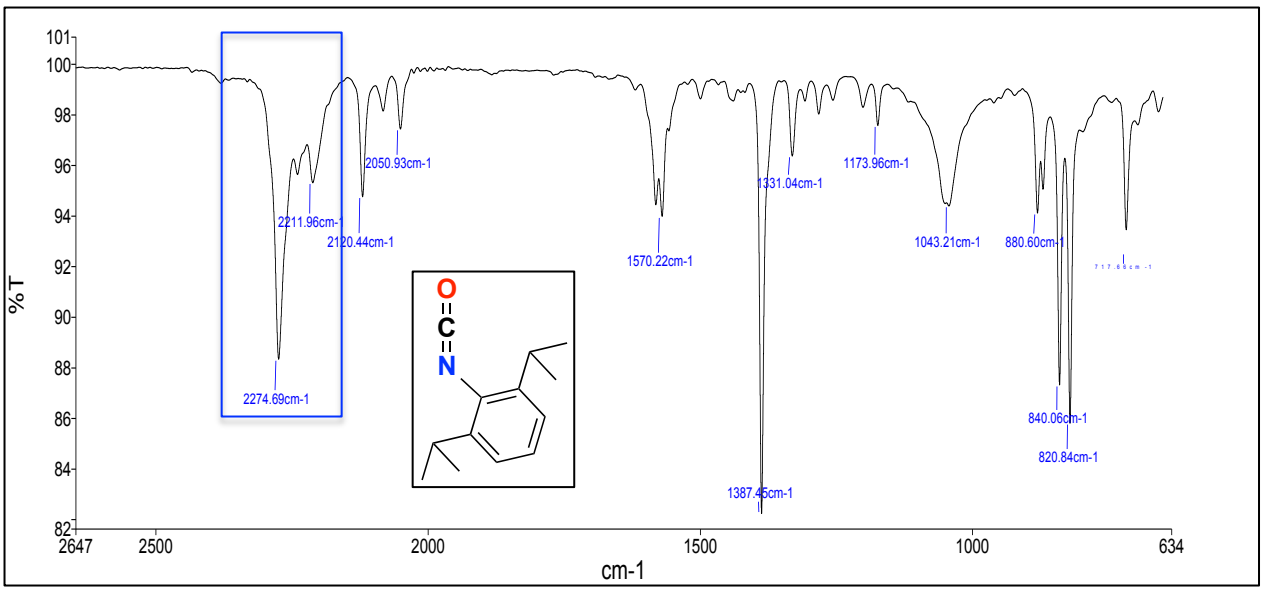

Table S1. Crystallographic data for **2** and *E*/*Z*-**3**

Compound	**2**	*E*/*Z*-**3**
Empirical formula	$C_{52}H_{50}F_{10}N_3O_4Rh_2$	$C_{45.5}H_{61.5}F_5NOPRh$
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}g/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	$-25 \leq h \leq 25$, $-19 \leq k \leq 19$, $-28 \leq l \leq 29$	$-11 \leq h \leq 11$, $-25 \leq k \leq 24$, $0 \leq l \leq 26$
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	$C_{31}H_{41}F_5PRh$	$C_{65.94}H_{58.87}F_5P_3Rh$
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
ρ_{calc}g/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 Kα (λ = 0.71073)	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	3.882 to 61.118	3.84 to 52.12
Index ranges	$-16 \leq h \leq 16$, $-29 \leq k \leq 29$, $-16 \leq l \leq 16$	$-13 \leq h \leq 13$, $-45 \leq k \leq 45$, $-15 \leq l \leq 15$
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>=2σ (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