Mechanism of the Rhodium(III)-Catalyzed Arylation of Imines via C–H Bond Functionalization: Inhibition by Substrate

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Supporting Information

I. Syntheses

General Information. 2-phenylpyridine (Sigma-Aldrich) was distilled under nitrogen and dried over activated molecular sieves (3 Å) prior to use. All other reagents were obtained from commercial suppliers and used without further purification. $[Cp^*RhCl_2]_2$,[1] **7**,[2] *iso*-propyl *N*-[-1-phenylmethylidene]carbamate **3d**,[3] *N-tert-butyl*-4-(trifluoromethyl)-benzylidenecarbamate **3c**[4] and *N*-benzylidene-4-methylbenzenesulfonamide **3a**[5] were synthesized according to published procedures. Dichloromethane and tetrahydrofuran (THF) were passed through a column of activated alumina under nitrogen. 1,2-Dichloroethane, *n*-pentane, CD_2Cl_2, and $CDCl_3$ were dried over activated molecular sieves (3 Å). All reactions involving $AgSbF_6$ (Strem) were carried out using syringe, cannula and/or inert atmosphere box techniques (N_2). All glassware was dried overnight

at 120 ˚C or flame-dried under vacuum immediately prior to use. Chromatography was performed on Merck 60 230-240 mesh silica gel. NMR chemical shifts are reported in ppm relative to $CHCl_3$ (7.26 ppm for ^1H, and 77.23 ppm for ^{13}C NMR) or CD_2Cl_2 (5.32 ppm for ^1H, and 53.84 ppm for ^{13}C NMR). IR spectra were recorded on a Nicolet 6700 FT-IR equipped with an attenuated total reflectance accessory (ATR), and only partial data are listed. Melting points were determined on a Mel-Temp apparatus and are reported uncorrected. Mass spectra (HRMS) were obtained by a 9.4T Bruker Qe FT-ICR MS at the Keck Center of Yale University.

Preparation of 1d. To a vial in a glovebox was combined $[Cp^*RhCl_2]_2$ (12.3 mg, 0.020 mmol, 0.1 equiv), $AgSbF_6$ (27.3 mg, 0.079 mmol, 0.4 equiv), **2** (71.3 mg, 0.459 mmol, 2.3 equiv), **3a** (38.5 mg, 0.201 mmol, 1.0 equiv), and CH_2Cl_2 (2.0 mL). The reaction mixture was transferred to a 5 mL Schlenk tube equipped with a magnetic stir bar, removed from the glovebox, and heated at 75 ˚C for 14 h with stirring. The reaction mixture was then cooled to room temperature, concentrated *in vacuo*, and purified by chromatography (5:1 hex:EtOAc) to yield a white solid (56.1 mg, 0.162 mmol, 81% yield). ^1H NMR (500 MHz, CD_2Cl_2) δ 8.56 (d, J = 4.2 Hz, 1H), 7.51 (t, J = 6.8 Hz, 2H), 7.44 (td, J = 7.4, 1.4 Hz, 1H), 7.40 (td, J = 7.4, 1.4 Hz, 1H), 7.33 (d, J = 7.2 Hz, 1H), 7.13 (dd, J = 6.7, 5.1 Hz, 1H), 7.06 – 6.96 (m, 5H), 6.90 (bs, 2H), 6.22 (d, J = 9.0 Hz, 1H), 4.87 (sep, J = 6.3 Hz, 1H), 1.25 (d, J = 5.2 Hz, 3H), 1.21 (d, J = 5.0 Hz, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2) δ 159.81, 155.50, 148.10, 142.02, 141.02, 140.41, 136.43, 130.90, 129.94, 128.62, 127.59 (3C), 126.10, 126.02 (2C), 124.22, 121.75, 67.85, 57.45, 21.90. M.p. = 135 ˚C. IR (neat) = 1699 (vs), 1584 (w), 1495 (vw), 1466 (m), 1442 (m),

1427 (m), 1395 (s), 1382 (s), 1339 (w), 1314 (s), 1286 (m), 1176 (w), 1150 (w), 1111 (s), 1025 (s), 753 (vs), 732 (vs), 698 (vs). HRMS: *m/z*: $[M + H]^+$ calculated for $C_{22}H_{22}N_2O_2$: 317.17540, found 317.17453 (-2.5 ppm).

Preparation of 4a. A 20 mL glass vial equipped with a magnetic stir bar was charged with **7** (96.8 mg, 0.226 mmol, 1.0 equiv) and $AgSbF_6$ (96.8 mg, 0.282 mmol, 1.3 equiv). To the vial was added a solution of **1a** (72.8 mg, 0.281 mmol, 1.3 equiv) in CH_2Cl_2 (4 mL) with stirring, and the resulting red slurry was stirred vigorously for 22 h. An orange solution over a grey precipitate was formed, which was separated by centrifugation and then extracted with CH_2Cl_2 (5 mL). The combined organic extracts were concentrated *in vacuo* and the resulting red resin was washed with Et_2O (2 x 10 mL) and hexane (5 mL), affording a red powder (147 mg, 0.165 mmol, 73%). ^{1}H NMR (500 MHz, CD_2Cl_2) δ 8.76 (d, *J* = 5.5 Hz, 1H), 8.22 (td, *J* = 7.8, 1.6 Hz, 1H), 7.77 – 7.70 (m, 2H), 7.51 – 7.43 (m, 2H), 7.37 (dd, *J* = 8.4, 1.7 Hz, 1H), 7.29 – 7.21 (m, 3H), 7.12 – 7.02 (m, 4H), 6.88 (d, *J* = 7.9 Hz, 1H), 5.20 (s, 1H), 2.32 (s, 3H), 1.36 (s, 15H). Two hydrogens not visible. $^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2) δ 161.89, 151.54, 143.66, 140.88, 140.79, 139.88, 139.63, 139.10, 132.25, 130.32, 130.31, 129.04, 128.66, 128.43, 128.18, 127.67, 125.71, 125.38, 95.60 (d, *J* = 9.1 Hz), 61.14, 21.18, 8.84. M.p. = 203 °C. IR (neat) = 1599 (w), 1478 (w), 1445 (w), 1252 (s), 1108 (m), 1052 (w), 1012 (m), 909 (m), 845 (s), 813 (s), 734 (m), 654 (vs), 593 (w). HRMS: *m/z*: $[M + H]^+$ calculated for $C_{35}H_{36}F_6N_2O_2RhSSb$: 887.05677, found 887.05693 (+0.2 ppm).

Preparation of 4c. A 20 mL glass vial equipped with a magnetic stir bar was charged with **7** (99.0 mg, 0.231 mmol, 1.0 equiv) and $AgSbF_6$ (95.6 mg, 0.278 mmol, 1.2 equiv). To the vial was added a solution of **3c** (77.3 mg, 0.282 mmol, 1.2 equiv) in CH_2Cl_2 (7.5 mL) with stirring, and the resulting red slurry was stirred vigorously for 2 h. The now orange mixture was filtered by syringe (0.45 μm, nylon) and concentrated *in vacuo*. The resulting red resin was washed with Et_2O (2 x 5 mL) and crystallized from CH_2Cl_2/pentane affording **4c** as red crystals suitable for X-ray diffraction (168 mg, 0.186 mmol, 81%). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.76 (d, J = 5.5 Hz, 1H), 8.17 (td, J = 7.8, 1.6 Hz, 1H), 8.00 – 7.84 (m, 2H), 7.69 – 7.57 (m, 3H), 7.52 (t, J = 7.5 Hz, 1H), 7.45 – 7.36 (m, 2H), 7.25 (d, J = 7.4 Hz, 1H), 6.73 (d, J = 8.0 Hz, 1H), 5.06 (s, 1H), 1.47 (s, 15H), 1.08 (s, 9H). ^{13}C{^{1}H} (101 MHz, CD_2Cl_2) δ 165.42 (d, J = 2.9 Hz), 162.79, 152.64, 146.39, 141.96, 141.01, 139.62, 133.12, 130.25, 129.83 (q, J = 32.2 Hz), 129.57, 128.85, 128.63, 128.47, 125.64, 125.37, 124.91 (q, J = 270.8 Hz), 94.52 (d, J = 8.8 Hz), 83.49, 61.42, 28.46, 9.26. ^{19}F{^{1}H} NMR (376 MHz, CD_2Cl_2, TFA) δ -63.57. M.p. = 187 °C. IR (neat) = 1506 (vw), 1474 (w), 1439 (s), 1368 (w), 1325 (s), 1161 (m), 1134 (s), 1106 (m), 1065 (m), 1019 (m), 862 (w), 822 (m), 768 (s), 712 (w), 654 (vs). HRMS: *m/z*: $[M - SbF_6]^+$ calculated for $C_{34}H_{37}F_3N_2O_2Rh$: 665.18567, found 665.18460 (-1.6 ppm).

Preparation of 4d. A 20 mL glass vial equipped with a magnetic stir bar was charged with a solution of **7** (40.4 mg, 0.0944 mmol, 1.0 equiv) and **3d** (23.0 mg, 0.120 mmol, 1.3 equiv) in CH_2Cl_2 (1 mL). $AgSbF_6$ (33.8 mg, 0.0984 mmol, 1 equiv) was added as a suspension in CH_2Cl_2 (1 mL), while the orange solution was stirred vigorously. A fluffy white precipitate formed quickly and the solution turned almost red. The mixture was

stirred for 10 minutes at room temperature and then filtered by syringe (0.45 μm, nylon). The filter was then flushed with CH_2Cl_2 (2 x 0.5 mL). The now red homogenous solution was overlaid with *n*-pentane and cooled to -20 ˚C for 3 d. Orange crystal plates formed, which were filtered, washed with *n*-pentane (2 x 1 mL) and dried *in vacuo*, yielding 51 mg (0.062 mmol, 66%) of crystals of **4d** suitable for X-ray diffraction analysis. ^{1}H NMR (500 MHz, CD_2Cl_2) δ 8.71 (dd, J = 6.0, 1.5 Hz, 1H), 8.11 (td, J = 7.7, 1.6 Hz, 1H), 7.75 (s, 1H), 7.62 – 7.57 (m, 3H), 7.45 (t, J = 7.5 Hz, 1H), 7.41 – 7.31 (m, 4H), 7.08 (s, 1H), 6.76 (d, J = 7.7 Hz, 1H), 5.04 (s, 1H), 4.54 (sept, J = 6.2 Hz, 1H), 1.44 (s, 15H), 0.93 (d, J = 6.3 Hz, 3H), 0.62 (d, J = 6.2 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2) δ 164.58 (d, J = 2.9 Hz), 164.56, 163.11, 152.29, 142.87, 141.73, 140.92, 139.54, 132.92, 130.12, 129.38, 129.18, 128.70, 128.19, 128.12 – 128.05 (m), 127.95, 125.29, 94.53 (d, J = 8.8 Hz), 71.18, 61.36, 22.24, 21.89, 9.31. M.p. = 183 ˚C. IR (neat) = 1599 (w), 1564 (m), 1471 (m), 1443 (s), 1374 (w), 1325 (w), 1138 (m), 1102 (m), 1075 (w), 1022 (m), 768 (s), 735 (s), 702 (m). HRMS: *m/z*: $[M - SbF_6]^+$ calculated for $C_{32}H_{36}N_2O_2Rh$: 583.18263, found 583.18260 (-0.1 ppm).

Preparation of 5. A 20 mL glass vial equipped with a magnetic stir bar was charged with **7** (99.0 mg, 0.231 mmol, 1.0 equiv), $AgSbF_6$ (82.8 mg, 0.241 mmol, 1.0 equiv), and **2** (78.0 mg, 0.503 mmol, 2.2 equiv). CH_2Cl_2 (5 mL) was added, and the resulting red slurry was stirred vigorously for 20 minutes. An orange solution over a white precipitate was formed, which was filtered off by syringe (0.45 μm, nylon). All volatiles were removed *in vacuo* yielding a sticky yellowish resin, which was stirred over night in hexane (5 mL). An orange powder emerged, which was washed with hexane and

pentane, and then dried *in vacuo* (180 mg, 0.230 mmol, 99%). ^{1}H NMR (500 MHz, CD_2Cl_2) δ 8.72 (bs, 1H), 7.93 (dd, *J* = 7.7, 0.6 Hz, 1H), 7.77 – 7.64 (m, 3H), 7.54 (dd, *J* = 7.7, 1.2 Hz, 1H), 7.52 – 7.50 (m, 1H), 7.47 – 7.39 (bs, 2H), 7.37 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.31 – 7.27 (bs, 1H), 7.25 (d, *J* = 5.4 Hz, 1H), 7.13 (td, *J* = 7.4, 1.2 Hz, 1H), 7.10 – 7.02 (m, 1H), 7.02 – 6.80 (bs, 1H), 6.75 (ddd, *J* = 7.2, 5.3, 1.9 Hz, 1H), 1.53 (s, 15H). One hydrogen not observed due to signal broadening. ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2) δ 176.93, 176.67, 164.85, 155.82 (broad signal), 151.54, 145.01, 141.08, 138.99, 137.85, 135.93, 131.87, 129.99, 129.70, 129.02 (broad signal), 127.87 (broad signal), 124.87, 124.25, 123.84, 119.65, 98.22 (d, *J* = 6.2 Hz), 9.29. One carbon not observed due to signal broadening. M.p. = 182 °C. IR (neat): 1601(m), 1567 (w), 1378 (vw), 1163 (m), 787 (m), 756 (s), 737 (s), 652 (vs). HRMS: *m/z*: $[M - SbF_6]^+$ calculated for $C_{32}H_{32}N_2Rh$: 547.16150, found 547.16173 (+0.4 ppm).

Preparation of 6. Within a glovebox, **2** (233 mg, 1.50 mmol, 1.4 equiv) and $AgSbF_6$ (363 mg, 1.06 mmol, 1.0 equiv) were dissolved in THF (5 mL) in a 50 mL three-necked round bottom flask equipped with a magnetic stir bar. The flask was sealed with a rubber septa and a gas flow adapter. Outside the glovebox, *t*BuCl (0.25 mL, 2.3 mmol, 2.2 equiv) was added via syringe. The colorless solution was stirred for 1 h at room temperature. During this time a white precipitate formed. The solution was filtered off, employing filter cannula technique, and concentrated to dryness *in vacuo*. The resulting colorless solid was washed thoroughly with CH_2Cl_2 (2 x 1.5 mL) and dried *in vacuo* yielding **6** as a white powder (108 mg, 0.276 mmol, 26%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.78 (d, *J* = 5.0 Hz, 1H), 8.24 (s, 1H), 8.21 – 8.14 (m, 1H), 8.05 (d, *J* = 6.4 Hz, 2H),

7.71 – 7.63 (m, 1H), 7.63 – 7.51 (m, 3H). ^{1}H NMR (300 MHz, THF-d_8) δ 8.86 (d, J = 5.8 Hz, 1H), 8.62 (td, J = 8.1, 1.4 Hz, 1H), 8.34 (d, J = 8.2 Hz, 1H), 8.04 – 7.94 (m, 3H), 7.67 – 7.59 (m, 3H). ^{13}C NMR (75 MHz, THF) δ 153.79, 147.64, 143.83, 133.07, 132.80, 130.67, 129.12, 126.70, 126.54. M.p. = 129 – 134 ˚C. IR (neat) = 3297 (w), 1634 (m), 1611 (s), 1581 (w), 1535 (m), 1496 (m), 1441 (w), 1276 (m), 1170 (m), 790 (w), 748 (s).

***In situ* observation of 8d.** A solution of **3d** (5.1 mg, 0.027mmol, 1.1 equiv) in CD_2Cl_2 (0.7 mL) was added to a mixture of **7** (10.4 mg, 0.0243 mmol, 1.0 equiv) and $AgSbF_6$ (9.3 mg, 0.027 mmol, 1.1 equiv). The resulting red suspension was stirred vigorously for 10 min in a 20 mL glass vial and then transferred to an oven dried J-Young tube. An ^{1}H NMR was taken within 30 min at room temperature and displayed a **4d**:**8d** ratio of 1:2.7. ^{1}HNMR (500 MHz, CD_2Cl_2, only resonances of **8d** are reported): 8.77 (d, J = 3.6 Hz, 1H), 8.32 (s, 1H), 7.97 (t, J = 6.6 Hz, 1H), 7.92 (m, 1H), 7.83 (d, J = 6.5 Hz, 1H), 7.72 (d, J = 6.7 Hz, 1H), 7.59 (m, 2H), 7.50 (m, 2H), 7.45 (m, 2H), 7.34 (t, J = 6.5 Hz, 1H), 7.26 (t, 6.5 Hz, 1H), 4.43 (sept, J = 5.8 Hz, 1H), 1.63 (s, 15H), 0.71 (d, J = 5.9 Hz, 3H), 0.68 (d, J = 5.9 Hz, 3H).

II. Stoichiometric conversions with complexes 4 and 5 (^{1}H NMR experiments)

General procedure for reaction of 2-phenylpyridine with complexes 4a, c, and d. Within a glovebox a 5 mL glass vial was charged with complex **4** (10 μmol, 1 equiv), 2-phenylpyridine (4.7 mg, 30 μmol, 3 equiv), and hexamethylbenzene (2.5 mg, 15 μmol,

1.5 equiv). CD_2Cl_2 (0.8 mL) was added and the red solution was transferred to an oven-dried J-Young tube, and the reaction was monitored by ^1H NMR.

Reaction of imine 3c with complex 5.

Within a glove box a 5 mL glass vial was charged with complex **5** and hexamethylbenzene as an internal standard. A solution in CD_2Cl_2 (0.7 mL) of imine **3** and 2-phenylpyridine **2** was added and the red solution then transferred to an oven-dried J-Young NMR tube. The reaction was monitored by ^1H NMR spectroscopy. The proportions of each compound are indicated in Table S1.

Table S1. Reaction of **3** and **2** with complex **5**.

entry	run	*t*	imine	**2** [equiv]	**5** [%]	**4** [%]	**8** [%]	**1** [%]
1	A[a)]	10 min	**3d**	-	56	6	38	0
2	A [a)]	20 h	**3d**	-	51	48	1	50
3	B[b)]	15 h	**3d**	1.0	100	0	0	60
4	C[c)]	10 min	**3c**	-	96	4	0	0
5	C[c)]	20 h	**3c**	-	45	55	0	22
6	D[d)]	15 h	**3c**	2.0	83	17	0	30

[a)] 0.02 mmol (1 equiv) of **5**, 0.04 mmol (2.2 equiv) of **3d**, 0.03 mmol (1.5 equiv) of C_6Me_6. [b)] 0.014 mmol (1 equiv) of **5**, 0.02 mmol (1 equiv) of **3d**, 0.02 mmol (1 equiv) of **2**, 0.03 mmol (2.4 equiv) of C_6Me_6. [c)] 0.013 mmol (1 equiv) of **5**, 0.013 mmol (1 equiv) **3c**. [d)] 0.014 mmol (1 equiv) of **5**, 0.02 mmol (1 equiv) of **3d**, 0.02 mmol (1 equiv) of **2**, 0.03 mmol (2.4 equiv) of C_6Me_6.

Arylation of 3a with 2 employing 4a as a catalyst

Within a glove box a 5 mL glass vial was charged with complex **4a** (8.9 mg, 0.010 mmol, 0.2 equiv), imine **3a** (14.3 mg, 0.0551 mmol, 1.2 equiv), and heterocycle **2** (7.5 mg, 0.048mmol, 1 equiv). CH_2Cl_2 (0.70 mL) was added, and the resulting red solution was transferred to an oven dried NMR tube equipped with a capillary containing C_6D_6. The tube was closed with a Cajon adapter and flame sealed under active vacuum outside the box. A ^1H NMR was taken and the tube placed into a preheated oil bath (75 ˚C). The conversion was monitored by ^1H NMR as outlined in Table S2.

Table S2. Arylation of **3a** with **2** employing **4a** as a catalyst.

entry	*t* [h]	**1a** [%]	**3a** [%]	**4a** : **5**
1	0	19	81	1.8 : 1.0
2	1	22	78	0.1 : 1.0
3	2	25	75	0.2 : 1.0
4	3	28	72	0.2 : 1.0
5	4	35	65	0.4 : 1.0
6	6	42	58	0.5 : 1.0

III. Kinetic studies

All glass equipment was oven-dried (120 ˚C) over night prior to use. NMR-experiments were performed on a 400 MHz Bruker NMR spectrometer at 298 K. The samples were heated by submerging them completely in a heated water bath (75.0 ˚C, Endocal circulating bath RTE-9, Neslab). NMR data was processed with MestReNova (6.2.0): solvent suppression (DCE, 3.04 ppm), metabonomics and BL optimization (phasing), Whitacker smoother (baseline correction).

A typical kinetic experiment with ^{1}H NMR monitoring was performed as follows. Within a glovebox a 5 mL glass vial was charged with the appropriate amount of additive (if applicable) and a stock solution (0.30 mL) containing 2-phenylpyridine (0.30 mmol), imine **3d** (0.050 mmol) and hexamethylbenzene (C_6Me_6, 0.050 mmol) in DCE. The vial was gently shaken to insure thorough mixing. Next, a freshly prepared solution of the catalyst **5** in DCE (0.20 mL, 5.6 μmol) was added, and the vial again carefully shaken. The reaction mixture was then transferred to an NMR tube equipped with a capillary containing DMSO-d_6 with a glass pipette. To secure quantitative transfer of the reagents to the NMR tube, the glass vial was flushed twice with DCE (2 x 0.10 mL). The NMR-

tube was closed with a Cajon-adapter and flame-sealed outside the glovebox under active vacuum resulting in a total tube length of 17 cm. A ^{1}H NMR was taken within 20 minutes. After the indicated time of heating the NMR tube was submerged into an ice bath for approximately 10 seconds. Complete cooling was demonstrated by solidification of DMSO in the capillary.

III-1 Reaction monitoring with 5, $[Cp^*RhCl_2]_2$/$AgSbF_6$, and additives

Table S3. Stock solutions employed.

	m [mg]	n [mmol]	M [mol/L]	Stock Solution
2-phenylpyridine **2**	775.8	4.999	1.000	A[a]
Imine **3d**	159.2	0.8321	0.1664	A[a]
C_6Me_6	135.2	0.1833	0.1666	A[a]
5	21.8	0.028	0.0278	B[b]
$[Cp^*RhCl_2]_2$	8.6 mg	0.014	0.0093	C[c]

a) Solution in DCE, total volume 5.00 mL. *b)* Solution in DCE, total volume 1.00 mL. *c)* Solution in DCE, total volume 1.50 mL.

Table S4. Reaction setup "additives"[a]

Run #	A [mL]	B [mL]	C [mL]	**6** [mg]	$AgSbF_6$ [mg]
1	0.30	0.20[b]	-	-	-
2	0.30	0.20[b]	-	1.0[c]	-
3	0.30	0.20[b]	-	2.0[d]	-
4	0.30	0.20[b]	-	4.0[e]	-
5	0.30	0.20[b]	-	7.7[f]	-
6	0.30	0.20[b]	-	-	2.2[g]
7	0.30	-	0.20[h]	-	4.0[i]

[a] 0.300 mmol of **2**, 0.050 mmol of **3d**, 0.050 mol of C_6Me_6, DCE, total volume of 0.70 mL. [b] 5.6 μmol, 0.11 equiv. [c] 2.6 μmol, 0.05 equiv. [d] 5.1 μmol, 0.10 equiv. [e] 10.2 μmol, 0.20 equiv. [f] 19.6 μmol, 0.39 equiv. [g] 6.4 μmol, 0.13 equiv. [h] 2.8 μmol, 0.056 equiv. [i] 12 μmol, 0.23 equiv.

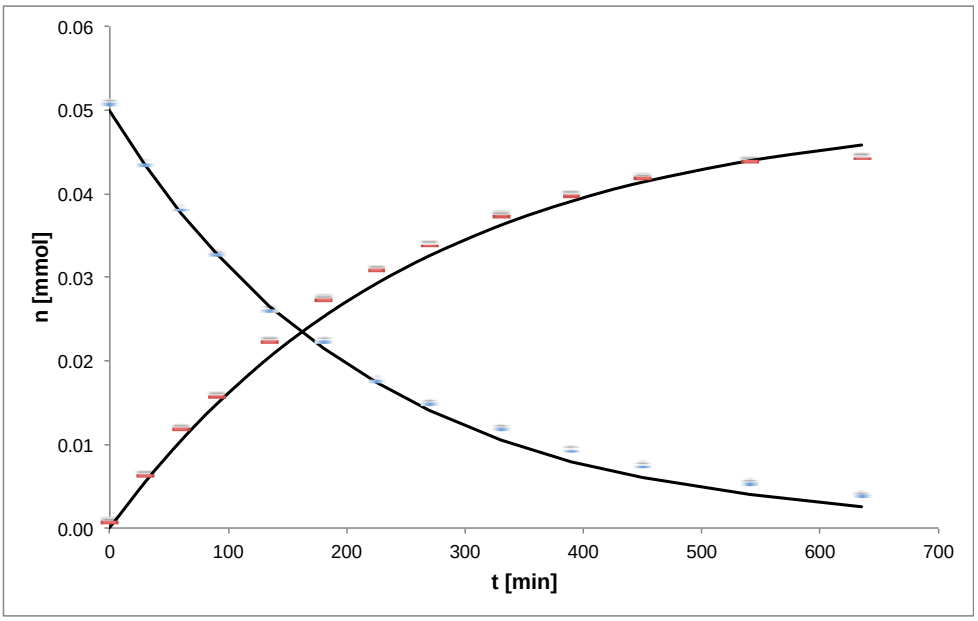

Figure S1. Monitoring run #1. Squares: **1d** formation (black line k = 0.0040 min^{-1}), diamonds: **3d** consumption (black line k = 0.0047 min^{-1}).

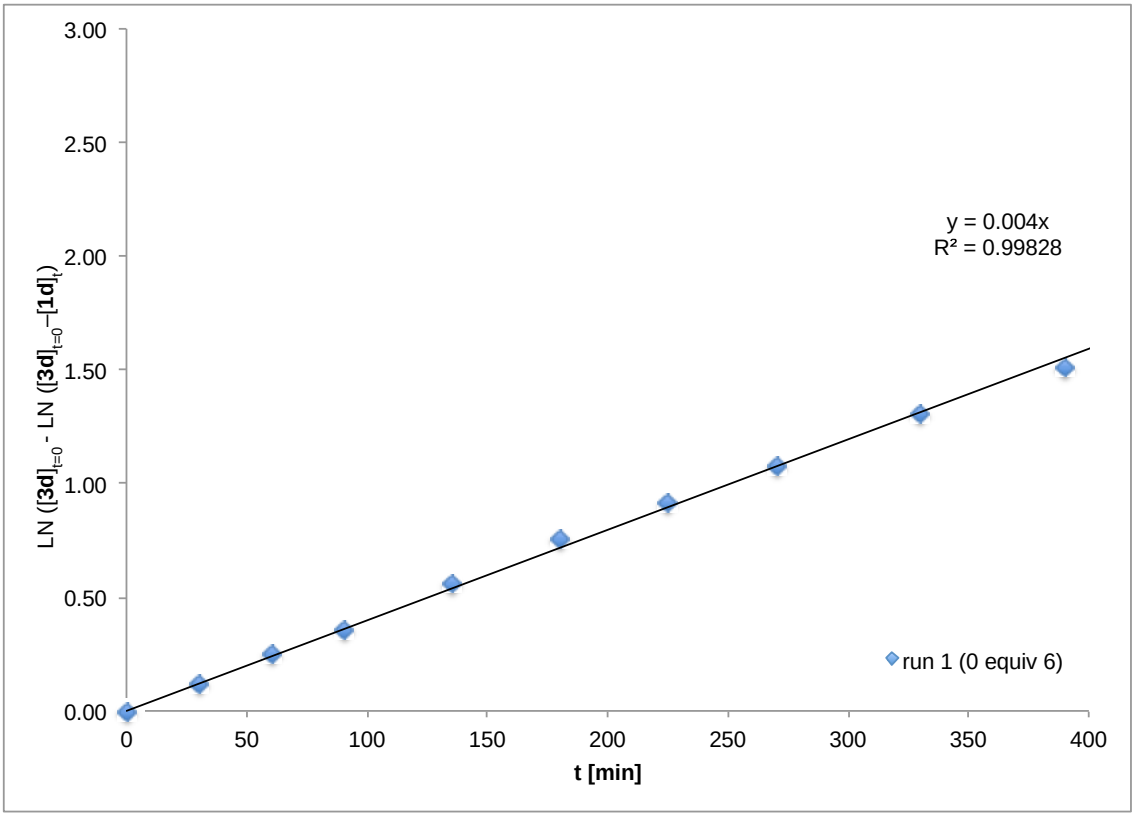

Figure S2. Logarithmic plot of **1d** formation in run 1 (no additive).

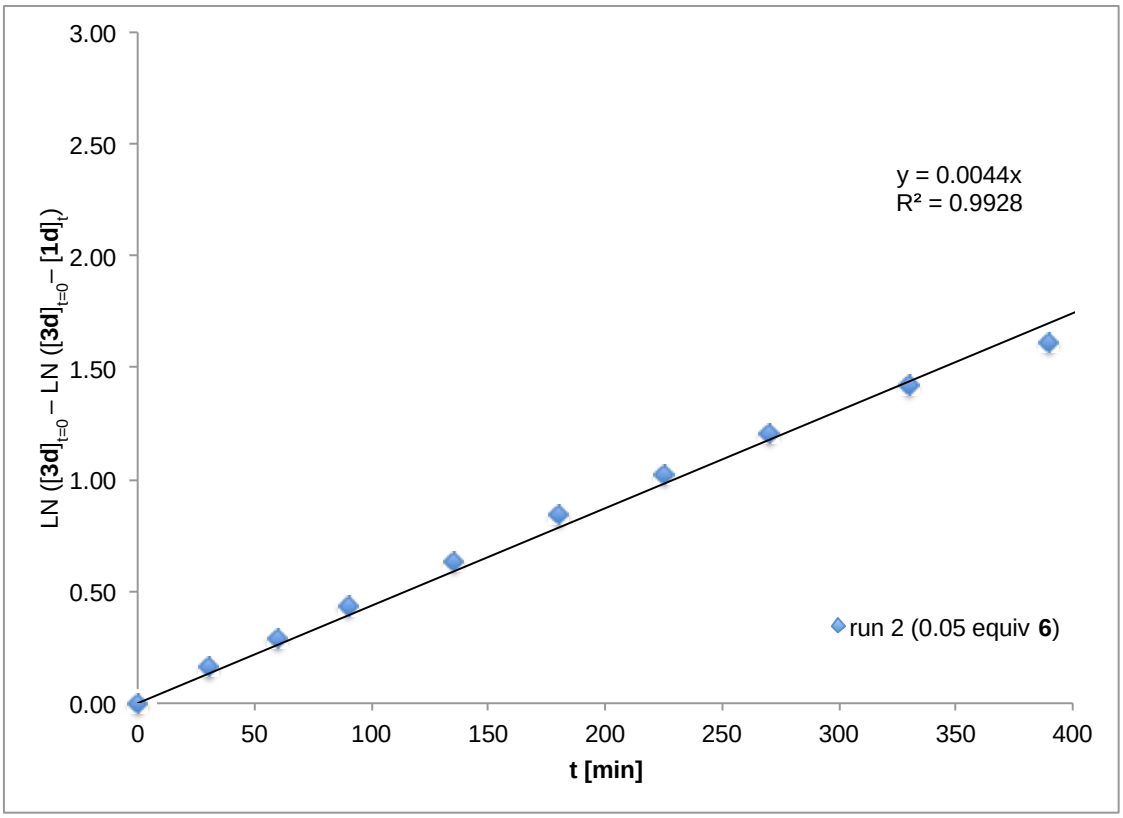

Figure S3. Logarithmic plot of **1d** formation in run 2 (additive: 0.05 equiv of **6**).

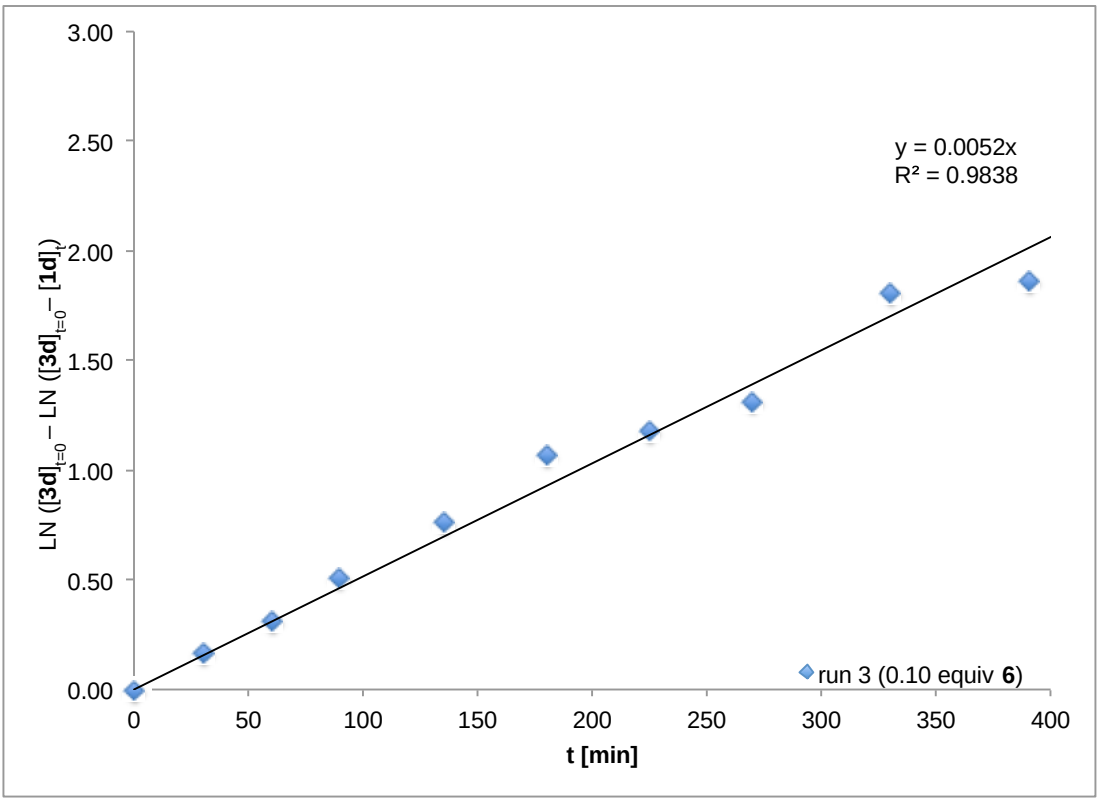

Figure S4. Logarithmic plot of **1d** formation in run 3 (additive: 0.10 equiv of **6**).

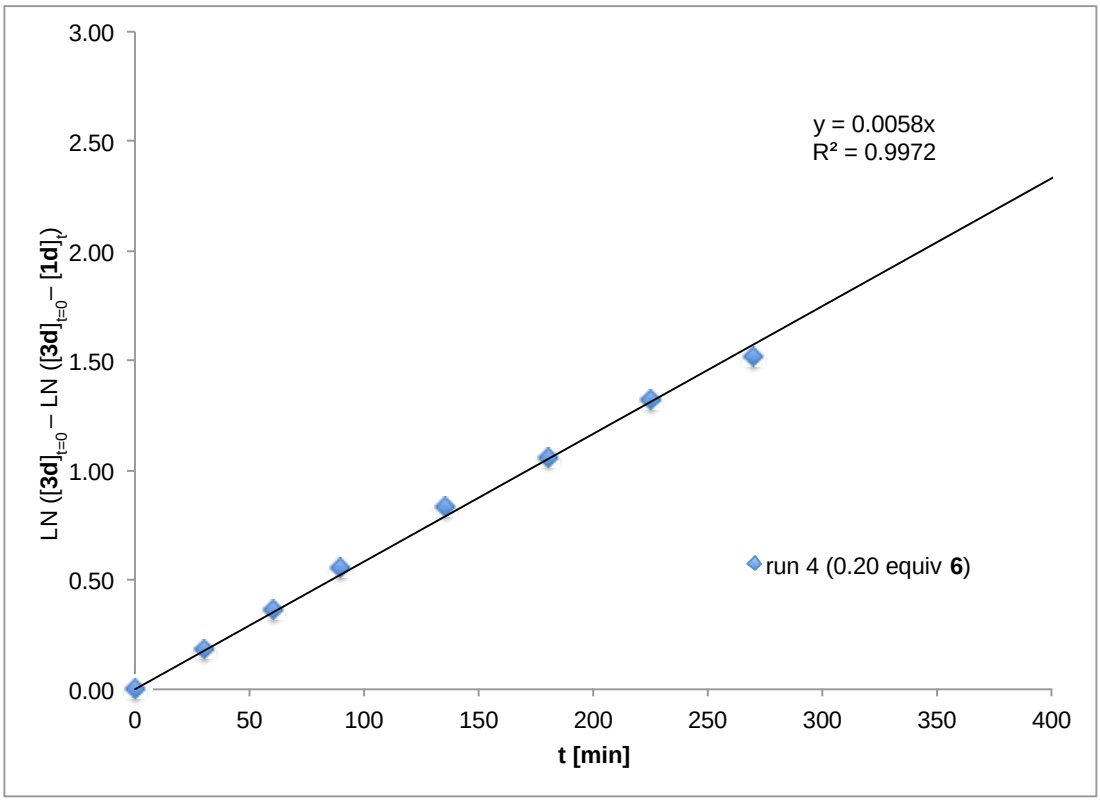

Figure S5. Logarithmic plot of **1d** formation in run 4 (additive: 0.20 equiv of **6**).

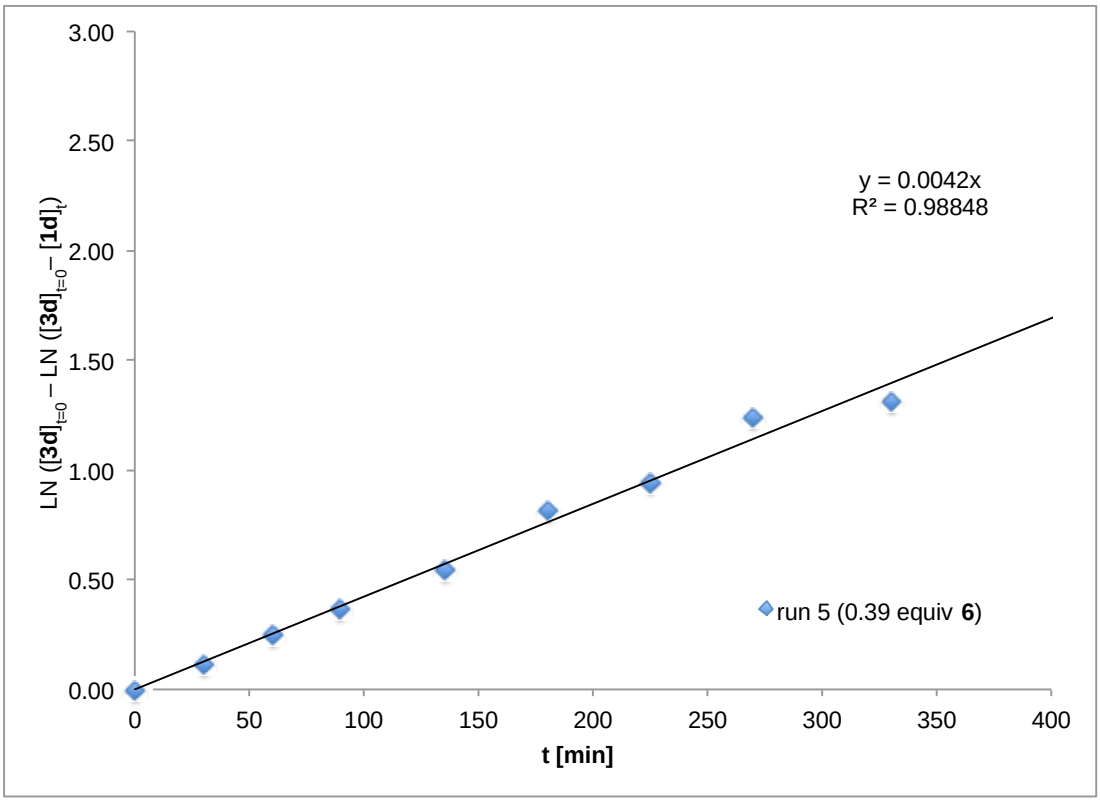

Figure S6. Logarithmic plot of **1d** formation in run 5 (additive: 0.39 equiv of **6**).

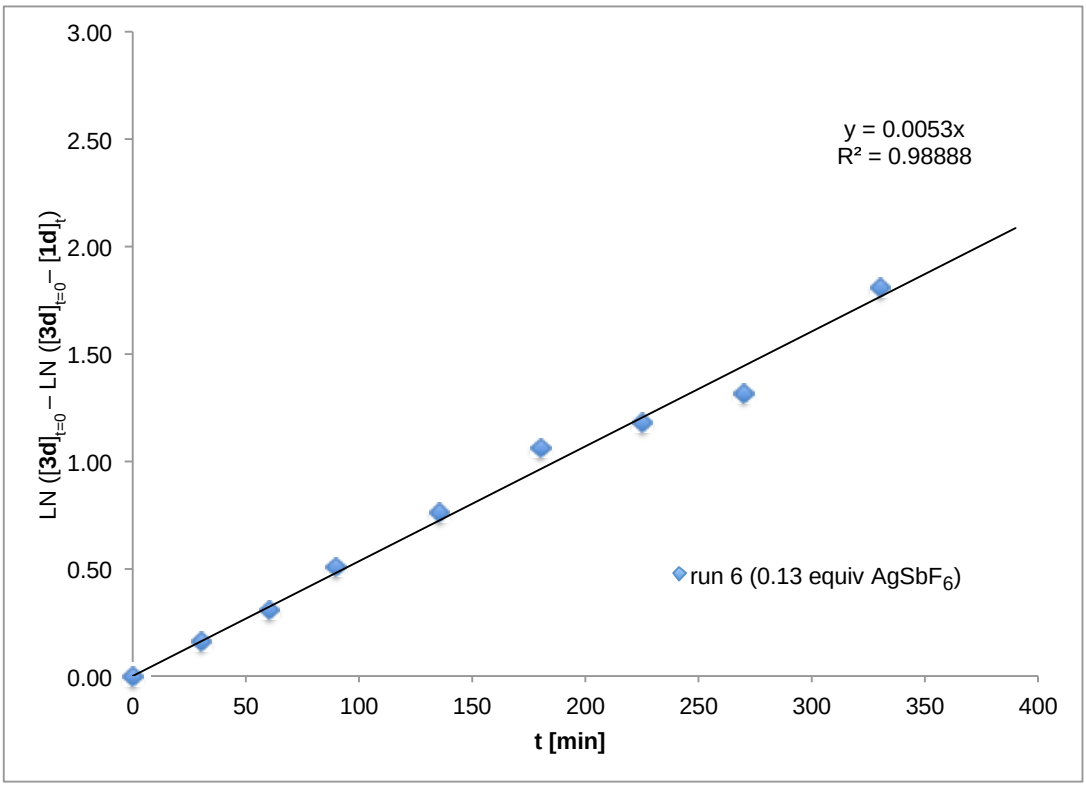

Figure S7. Logarithmic plot of **1d** formation in run 6 (additive: 0.13 equiv of $AgSbF_6$).

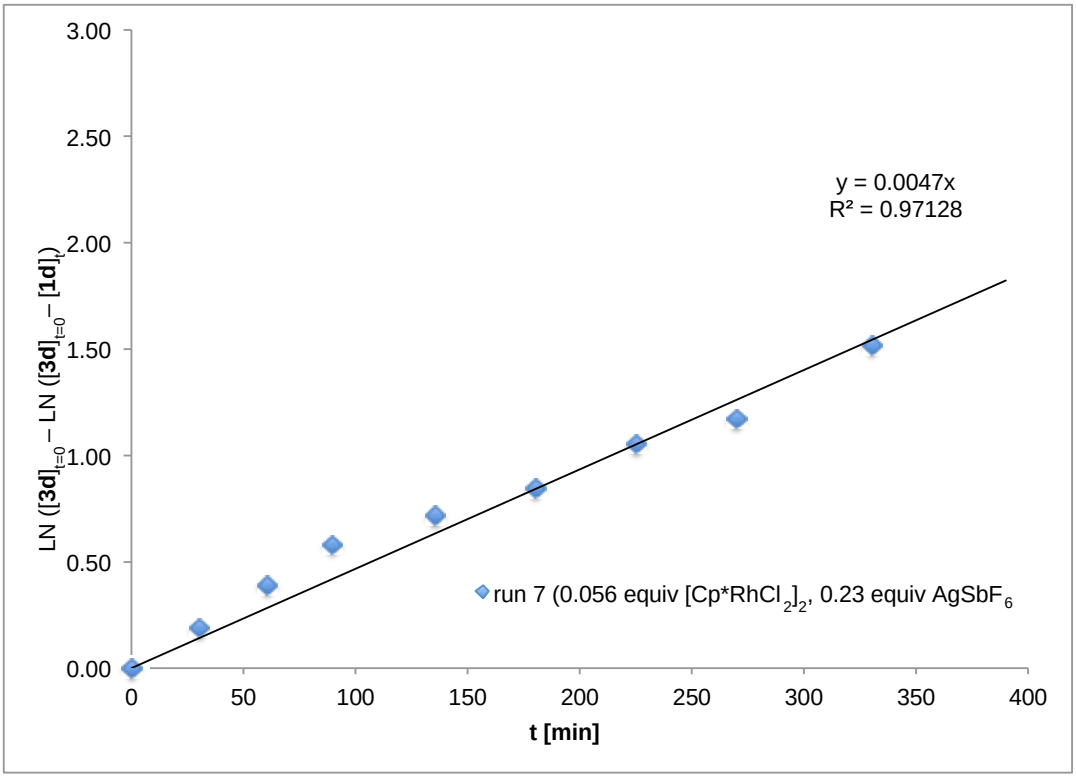

Figure S8. Logarithmic plot of **1d** formation in run 7 (0.056 equiv of $[Cp^*RhCl_2]_2$ and 0.23 equiv of $AgSbF_6$ as catalyst).

III-2 Order in catalyst (5)

Table S5. Stock solutions employed.

	m [mg]	n [mmol]	M [mol/L]	Stock Solution
2-phenylpyridine **2**	775.5	4.997	0.9940	A[a]
Imine **3d**	159.3	0.8326	0.1665	A[a]
C_6Me_6	134.9	0.1813	0.1663	A[a]
5	19.6	0.025	0.025	B[b]

[a] Solution in DCE, total volume of 5.00 mL. [b] Solution in DCE, total volume of 1.00 mL.

Table S6. Reaction setup "catalyst order"[a]

Run #	A [mL]	B [mL]	DCE [mL]	**5** [equiv]	k [min^{-1}]
8	0.30	0.30	0.10	0.15	0.0063
9	0.30	0.15	0.25	0.075	0.0026
10	0.30	0.20	0.20	0.10	0.0037
11	0.30	0 [b]	0.40	0.20	0.0089

[a] 0.300 mmol of **2**, 0.050 mmol of **3d**, 0.050 mol of C_6Me_6, DCE, total volume of 0.70 mL. [b] 8.1 mg (0.010 mmol) neat.

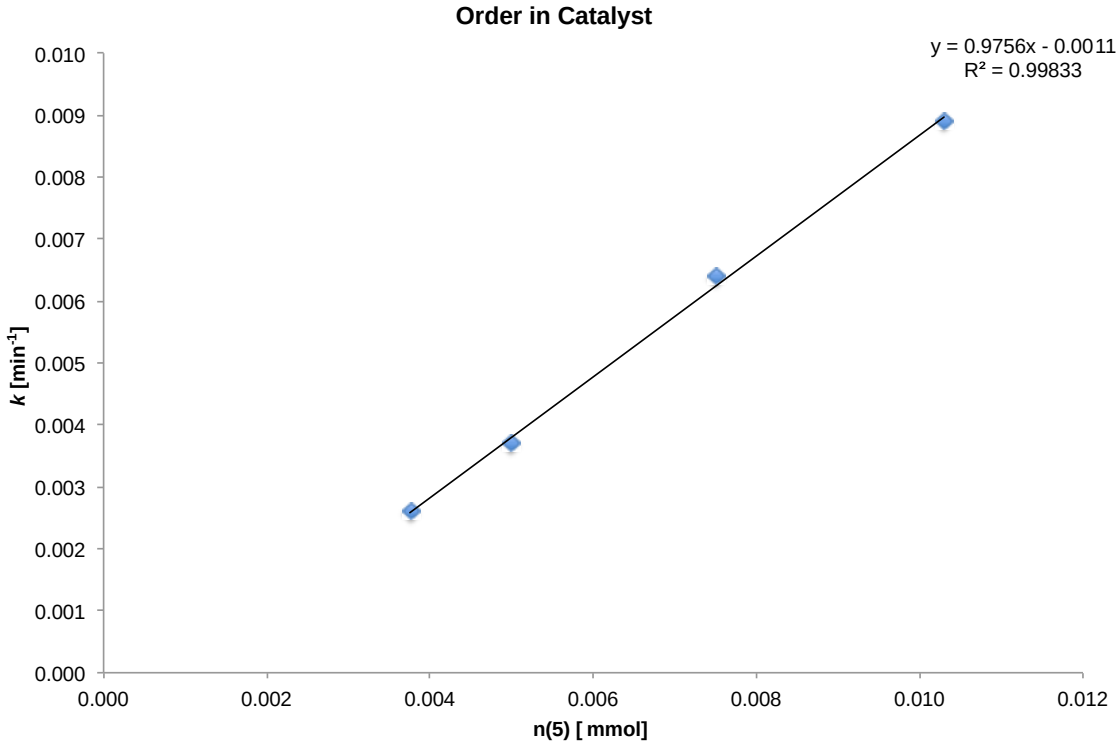

Figure S9. Rate constants k (runs 8-11) versus catalyst (**5**) concentration.

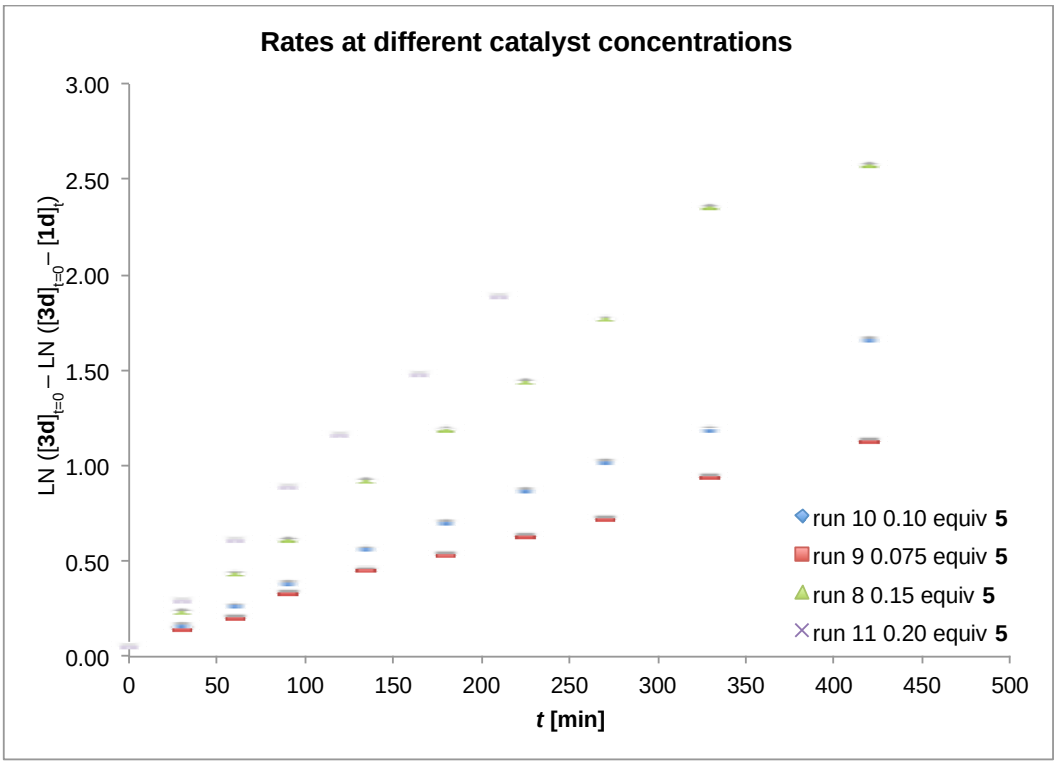

Figure S10. . Logarithmic plot of **1d** formation in runs 9-11.

III-3 Order in 2-phenylpyridine (2)

Table S7. Stock solutions employed.

	m [mg]	n [mmol]	M [mol/L]	Stock Solution
2-phenylpyridine **2**	775.5	4.997	0.9940	A[a)]
Imine **3d**	159.3	0.8326	0.1665	A[a)]
C_6Me_6	134.9	0.1813	0.1663	A[a)]
5	19.6	0.025	0.025	B[b)]
2-phenylpyridine **2**	103.6	0.668	0.668	C[b)]
Imine **3d**	32.1	0.168	0.168	C[b)]
C_6Me_6	27.0	0.166	0.166	C[b)]

[a)] Solution in DCE, total volume of 5.00 mL. [b)] Solution in DCE, total volume of 1.00 mL.

Table S8. Reaction setup "order in 2-phenylpyridine"[a)]

Run #	A [mL]	C [mL]	**2** [mg]	**2** [equiv][b)]	k [min^{-1}]
12	-	0.30	-	3.98	0.0056
13	-	0.30	7.6	4.94	0.0043
14	0.30	-	8.1	7.05	0.0030
15	0.30	-	15.9	8.06	0.0024

[a)] 0.050 mmol of **3d**, 0.050 mol of C_6Me_6, 0.20 mL of stock solution B **(**5.0 μmol of **5**), 0.20 mL of DCE. [b)] with regard to **3d**.

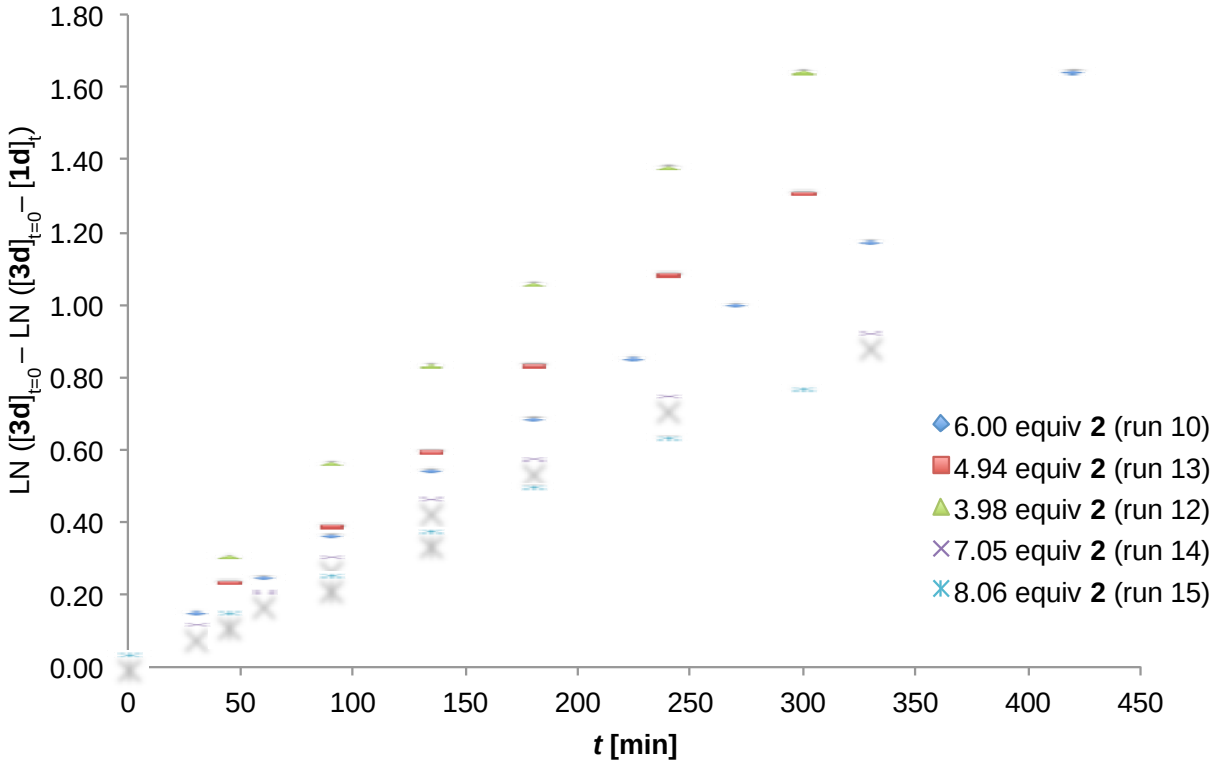

Figure S11. Logarithmic plot of **1d** formation in runs 10, 12-15.

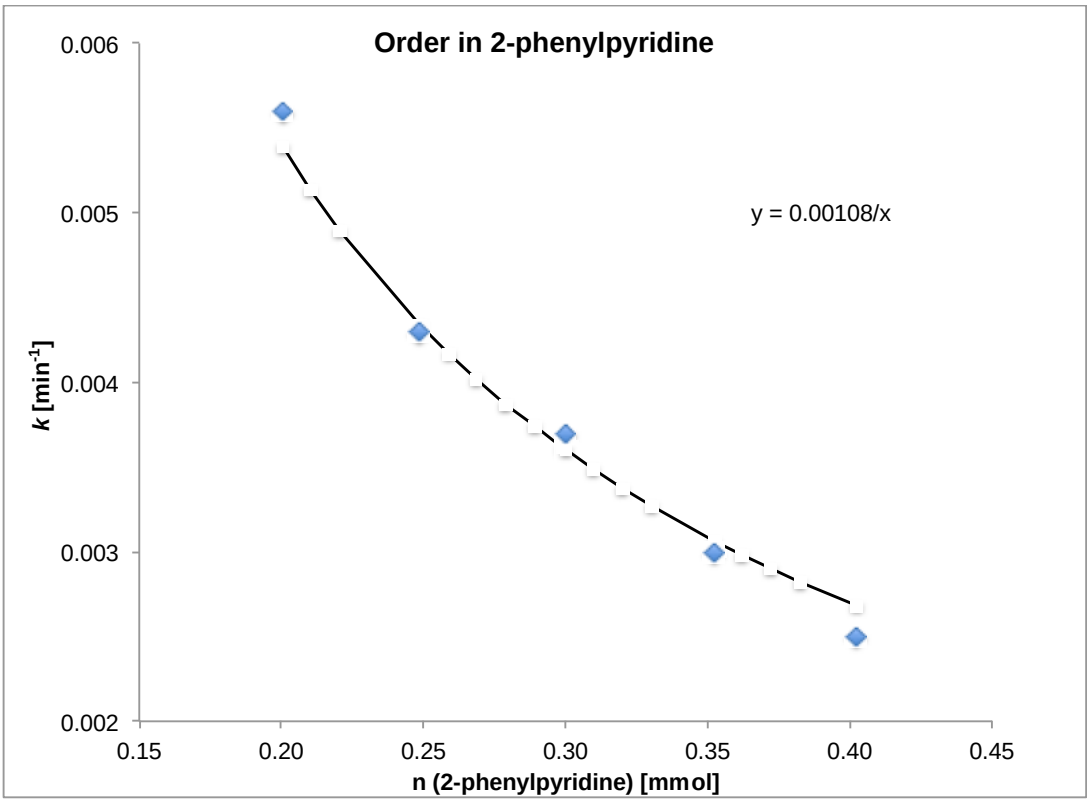

Figure S12. Rate constants *k* (runs 10, 12-15) versus 2-phenylpyridine concentration.

IV. X-ray structures

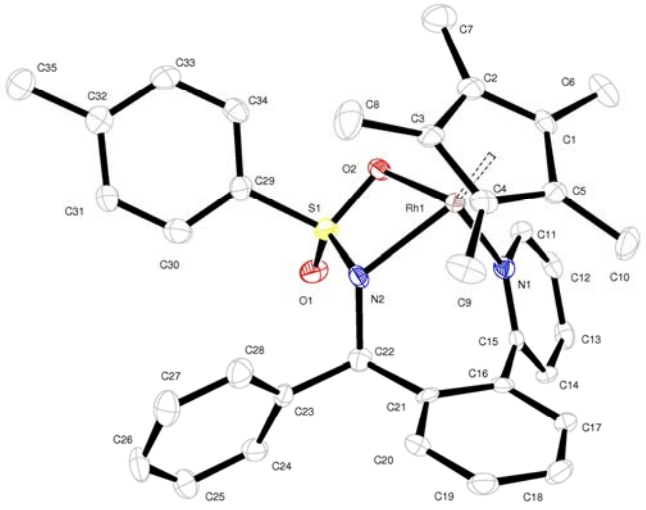

Figure S13. Thermal ellipsoid plot of **4a** depicted at the 50% probability level. Hydrogen atoms and SbF_6 anion are omitted for clarity.

Table S9. Crystal data and structure refinement for **4a.**

Empirical formula	C35 H36 F6 N2 O2 Rh S Sb
Formula weight	887.38
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P2(1)/c
Unit cell dimensions	a = 18.4587(8) Å □= 90°. b = 10.7989(5) Å □= 103.395(2)°. c = 17.5940(9) Å □ = 90°.
Volume	3411.7(3) $Å^3$
Z	4
Density (calculated)	1.728 Mg/m^3
Absorption coefficient	1.405 mm^{-1}
F(000)	1768
Crystal size	0.06 x 0.03 x 0.02 mm^3
Crystal color/habit	yellow plate
Theta range for data collection	2.20 to 25.42°.
Index ranges	-21<=h<=22, -11<=k<=12, -21<=l<=21
Reflections collected	22273
Independent reflections	6210 [R(int) = 0.0601]
Completeness to theta = 25.00°	99.3 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9725 and 0.9205
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6210 / 0 / 439
Goodness-of-fit on F^2	1.013
Final R indices [I>2sigma(I)]	R1 = 0.0374, wR2 = 0.0608
R indices (all data)	R1 = 0.0643, wR2 = 0.0686
Largest diff. peak and hole	0.707 and -0.630 $e.Å^{-3}$

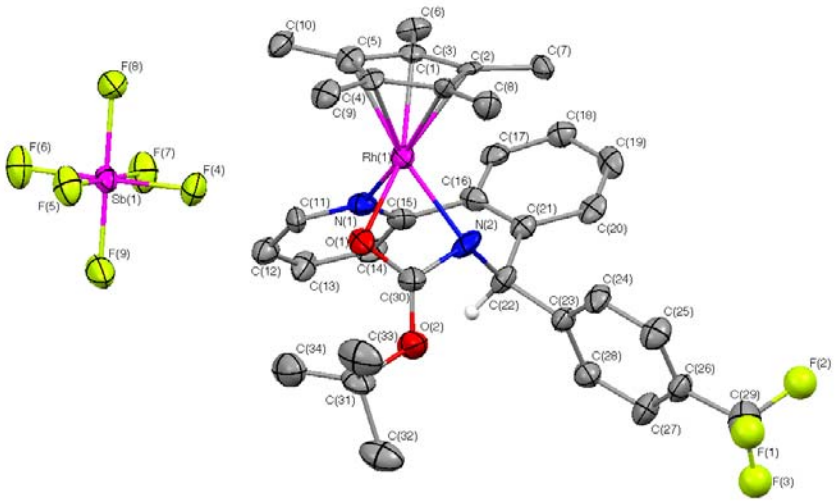

Figure S14. Thermal ellipsoid plot of **4c** depicted at the 50% probability level. Hydrogen atoms are omitted for clarity.

Table S10. Crystal data and structure refinement for **4c.**

Empirical formula	C34 H37 F9 N2 O2 Rh Sb	
Formula weight	901.32	
Temperature	93 K	
Wavelength	1.54187 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 20.9479(15) Å	α= 90°
	b = 10.8946(3) Å	β= 110.357(8)°
	c = 17.4188(4) Å	γ = 90°
Volume	3727.0(3) $Å^3$	
Z	4	
Density (calculated)	1.606 g/cm^3	
Absorption coefficient	10.000 mm^{-1}	
F(000)	1792	
Crystal size	0.20 x 0.20 x 0.08 mm^3	
Theta range for data collection	2.20 to 25.45°	
Index ranges	-25<=h<=25, -8<=k<=13, -20<=l<=19	
Reflections collected	22948	
Independent reflections	6705 [R(int) = 0.1290]	
Absorption correction	Multi-scan	
Max. and min. transmission	0.449 and 0.131	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6705 / 0 / 440	
Goodness-of-fit on F^2	1.035	
Final R indices [I>2sigma(I)]	R1 = 0.0922, wR2 = 0.2446	
R indices (all data)	R1 = 0.1409, wR2 = 0.2456	
Largest diff. peak and hole	1.82 and -1.29 e $Å^{-3}$	

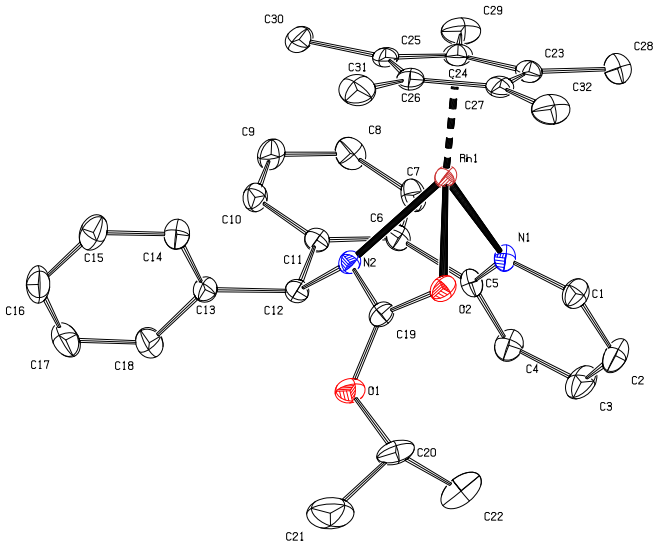

Figure S15. Thermal ellipsoid plot of **4d** depicted at the 50% probability level. Hydrogen atoms, SbF_6-anion and one molecule of crystal CH_2Cl_2 are omitted for clarity.

Table S11. Crystal data and structure refinement for **4d.**

Empirical formula	C33 H38 Cl2 F6 N2 O2 Rh Sb	
Formula weight	904.21	
Temperature	123(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 18.8446(9) Å	α= 90°
	b = 9.9469(4) Å	β= 100.0660(10)°
	c = 19.9152(9) Å	γ = 90°
Volume	3675.5(3) $Å^3$	
Z	4	
Density (calculated)	1.634 g/cm^3	
Absorption coefficient	1.391 mm^{-1}	
F(000)	1800	
Crystal size	0.37 x 0.30 x 0.08 mm^3	
Theta range for data collection	2.20 to 25.45°	
Index ranges	-22<=h<=22, -7<=k<=11, -23<=l<=24	
Reflections collected	33709	
Independent reflections	6747 [R(int) = 0.0328]	
Completeness to theta = 25.00°	100.0 %	
Absorption correction	Multi-scan	
Max. and min. transmission	0.8969 and 0.6271	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6747 / 0 / 431	
Goodness-of-fit on F^2	1.059	
Final R indices [I>2sigma(I)]	R1 = 0.0225, wR2 = 0.0636	

R indices (all data)	R1 = 0.0289, wR2 = 0.0681
Largest diff. peak and hole	0.775 and -0.671 e Å^{-3}

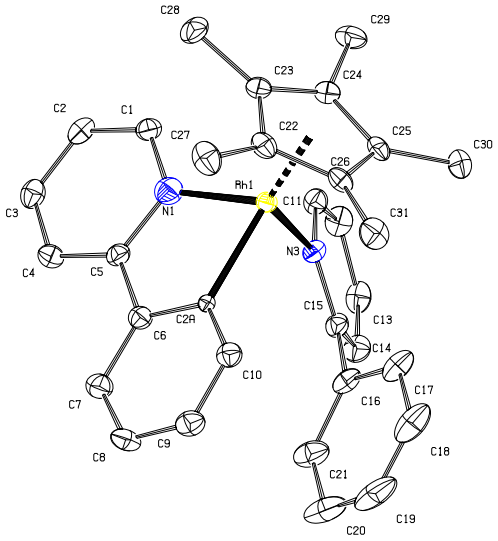

Figure S16. Thermal ellipsoid plot of **5** depicted at the 50% probability level. Hydrogen atoms and SbF_6 anion are omitted for clarity.

Table S12. Crystal data and structure refinement for **5.**

Empirical formula	C32 H32 F6 N2 Rh Sb	
Formula weight	783.26	
Temperature	100(2)	
Wavelength	0.71073 Å	
Crystal system	orthorhombic	
Space group	P2(1)2(1)2(1)	
Unit cell dimensions	a = 13.046(3) Å	α = 90°
	b = 13.991(3) Å	β = 90°
	c = 16.446(3) Å	γ = 90°
Volume	3002.0(10) Å^3	
Z	4	
Density (calculated)	1.733 g/cm^3	
Absorption coefficient	1.512 mm^{-1}	
F(000)	1552	
Crystal size	0.3 x 0.3 x 0.1 mm^3	
Theta range for data collection	1.91 to 30.55 °	
Index ranges	-18<=h<=18, -19<=k<=19, -20<=l<=23	
Reflections collected	153584	
Independent reflections	9171 [R(int) = 0.0300]	
Absorption correction	Empirical	
Max. and min. transmission	0.7461 and 0.6632	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	9171 / 0 / 384	
Goodness-of-fit on F^2	1.080	

Final R indices [I>2sigma(I)]	R1 = 0.0198, wR2 = 0.0453
R indices (all data)	R1 = 0.0215, vR2 = 0.0468
Largest diff. peak and hole	0.857 and -0.381 e $Å^{-3}$

V. References

(1) Kang, J. W.; Moseley, K.; Maitlis, P. M. *J. Am. Chem. Soc.* **1969**, *91*, 5970.
(2) Li, L.; Brennessel, W. W.; Jones, W. D. *J. Am. Chem. Soc.* **2008**, *130*, 12414.
(3) Trost, B. M.; Jonasson, C. *Angew. Chem., Int. Ed.* **2003**, *42*, 2063.
(4) Tsai, A. S.; Tauchert, M. E.; Bergman, R. G.; Ellman, J. A. *J. Am. Chem. Soc.* **2011**, *133*, 1248.
(5) Wu, X. F.; Vovard-Le Bray, C.; Bechki, L.; Darcel, C. *Tetrahedron* **2009**, *65*, 7380.

VI. Spectral Data

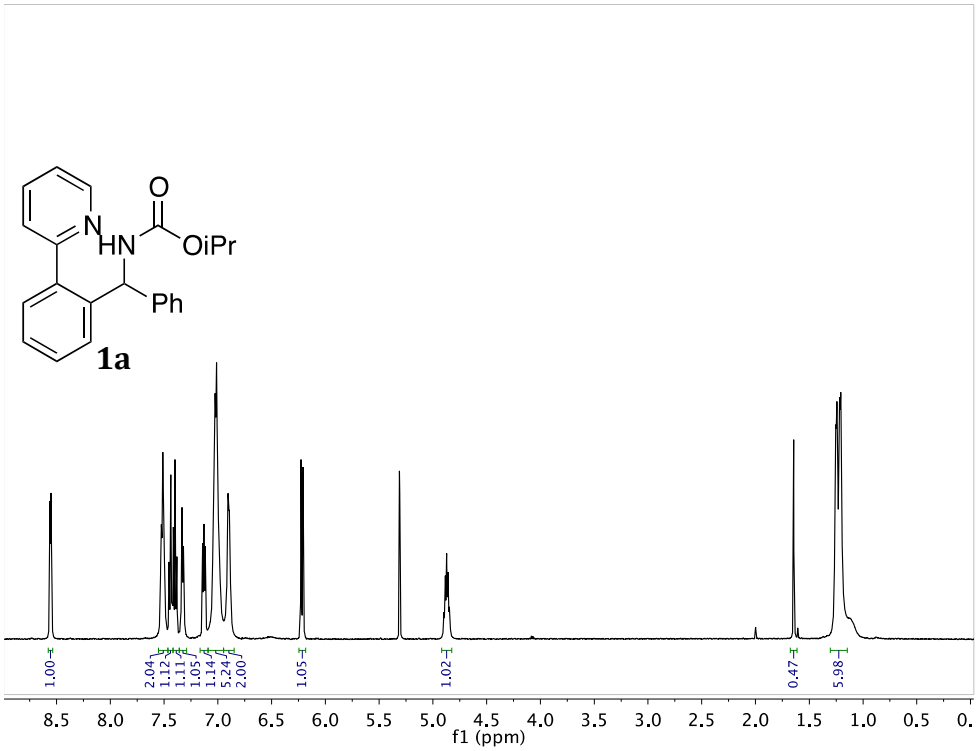

Figure S17. ^{1}H NMR (500 MHz) spectra of **1d** in CD_2Cl_2 at room temperature.

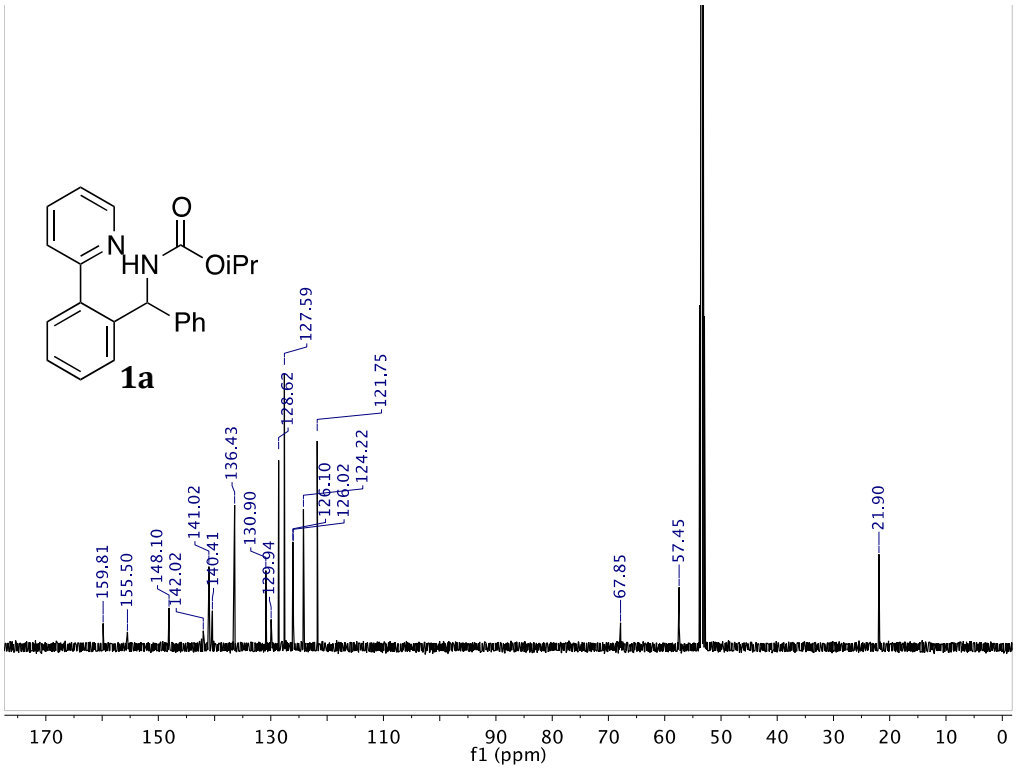

Figure S18. $^{13}C\{^{1}H\}$ NMR (126 MHz) spectra of **1d** in CD_2Cl_2 at room temperature.

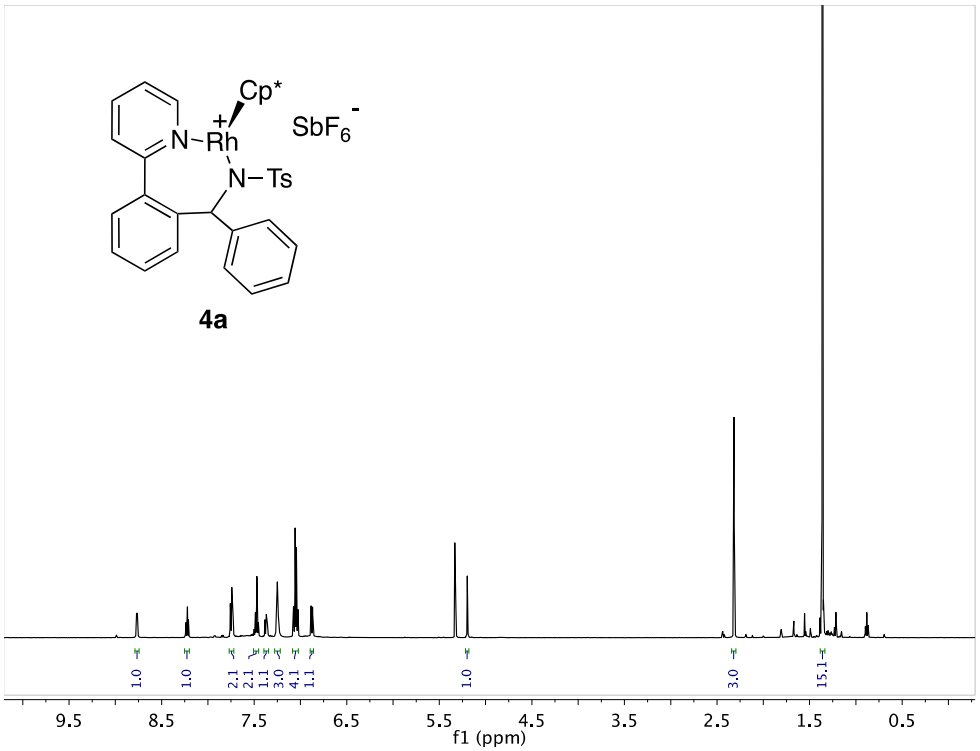

Figure S19. ^{1}H NMR (500 MHz) spectra of **4a** in CD_2Cl_2 at room temperature.

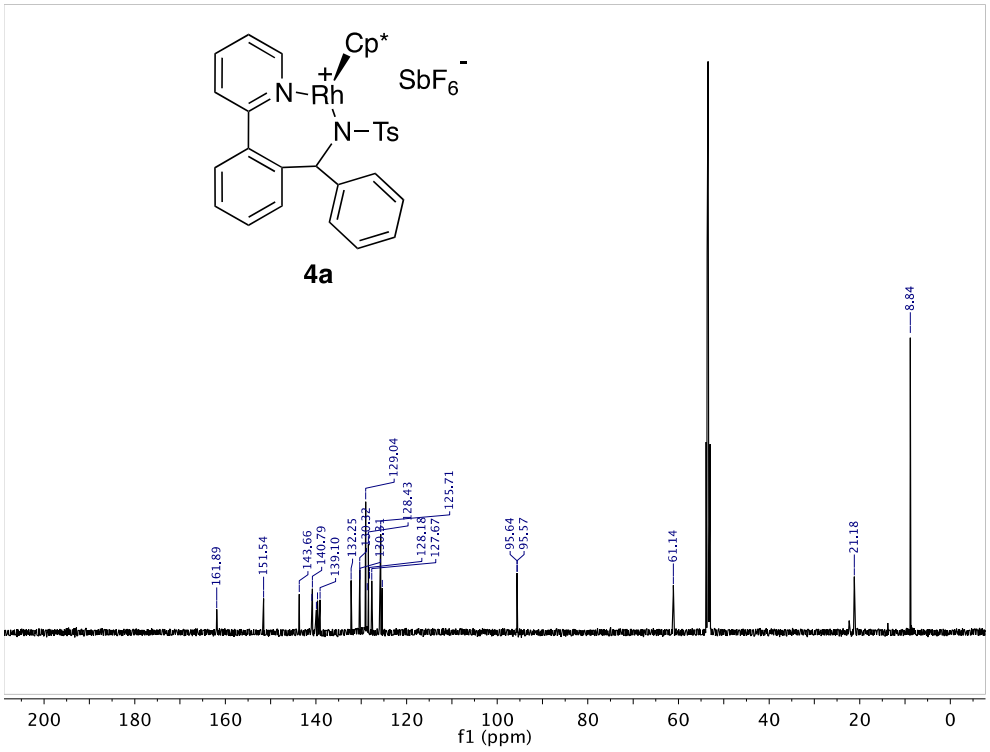

Figure S20. $^{13}C\{^{1}H\}$ NMR (126 MHz) spectra of **4a** in CD_2Cl_2 at room temperature.

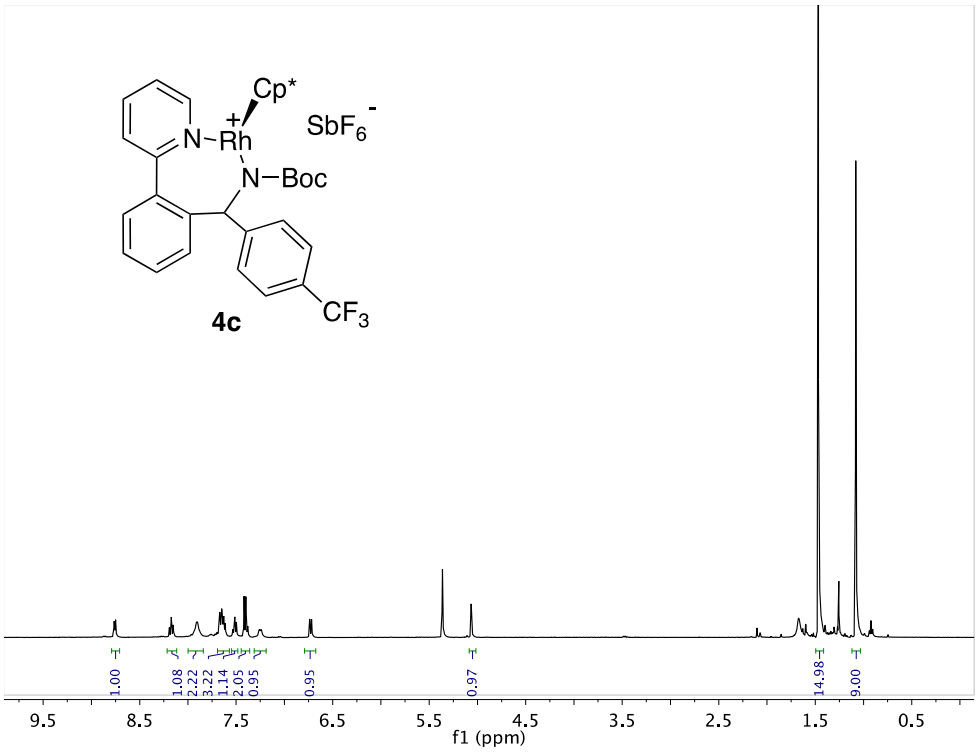

Figure S21. ^{1}H NMR (500 MHz) spectra of **4c** in CD_2Cl_2 at room temperature.

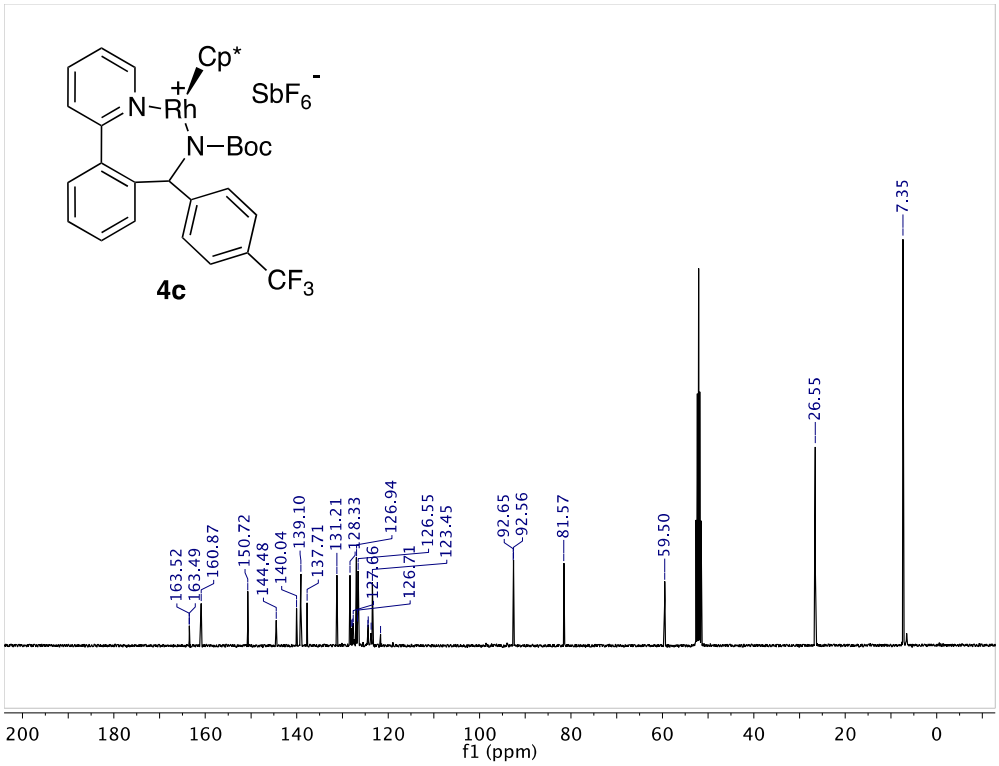

Figure S22. $^{13}C\{^{1}H\}$ NMR (101 MHz) spectra of **4c** in CD_2Cl_2 at room temperature.

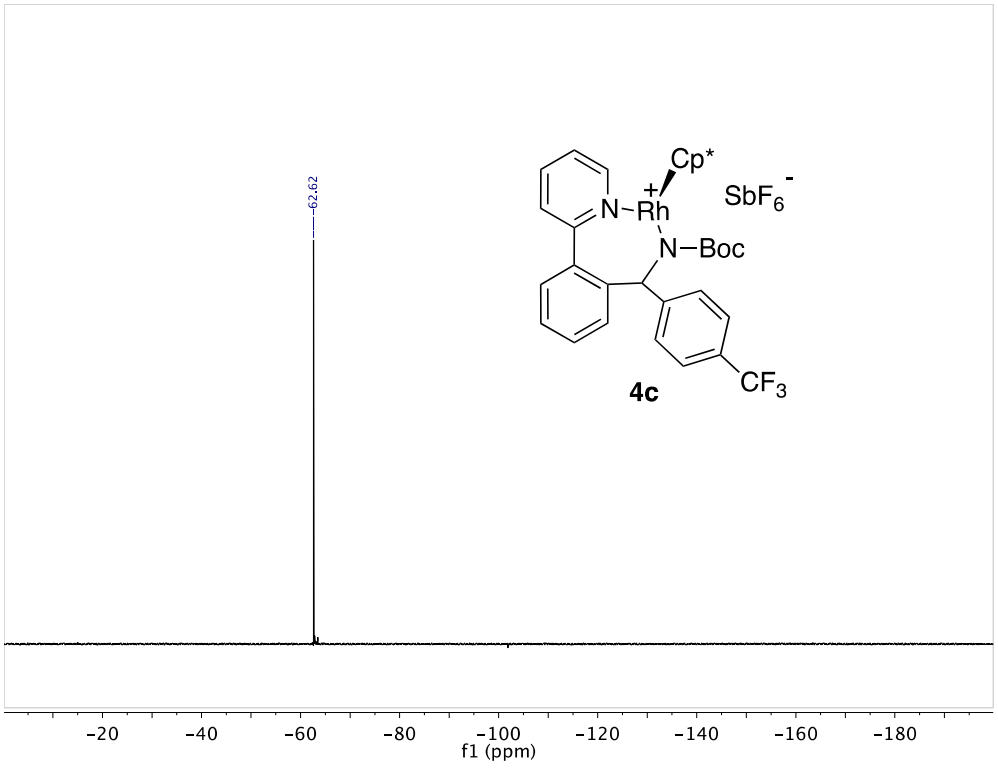

Figure S23. $^{19}F\{^{1}H\}$ NMR (376 MHz) spectra of **4c** in CD_2Cl_2 at room temperature.

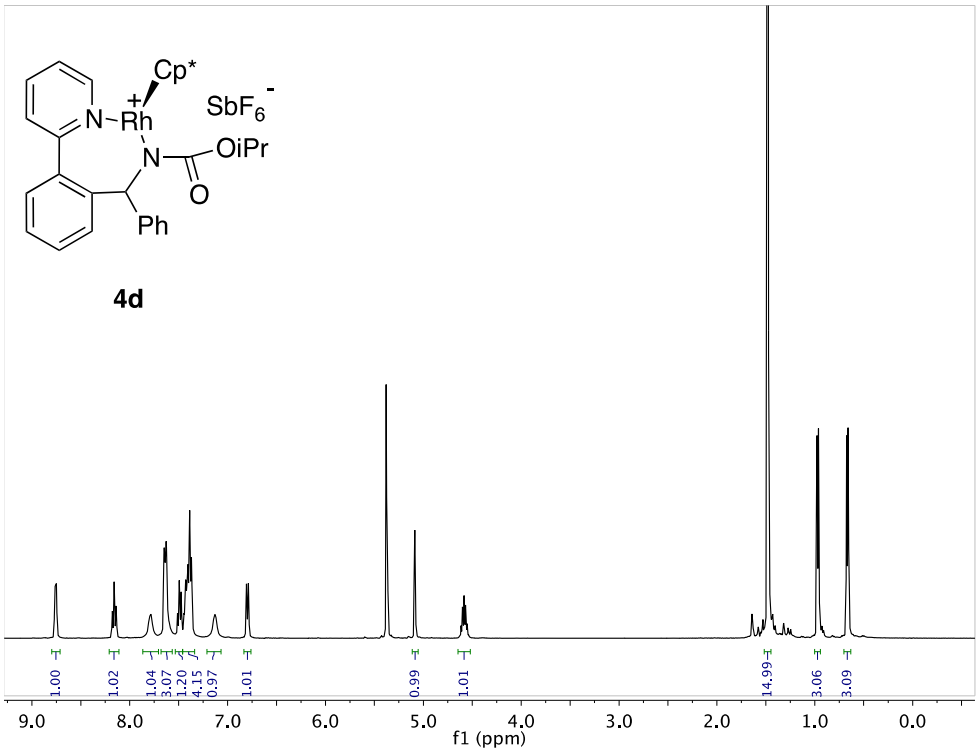

Figure S24. ^{1}H NMR (500 MHz) spectra of **4d** in CD_2Cl_2 at room temperature.

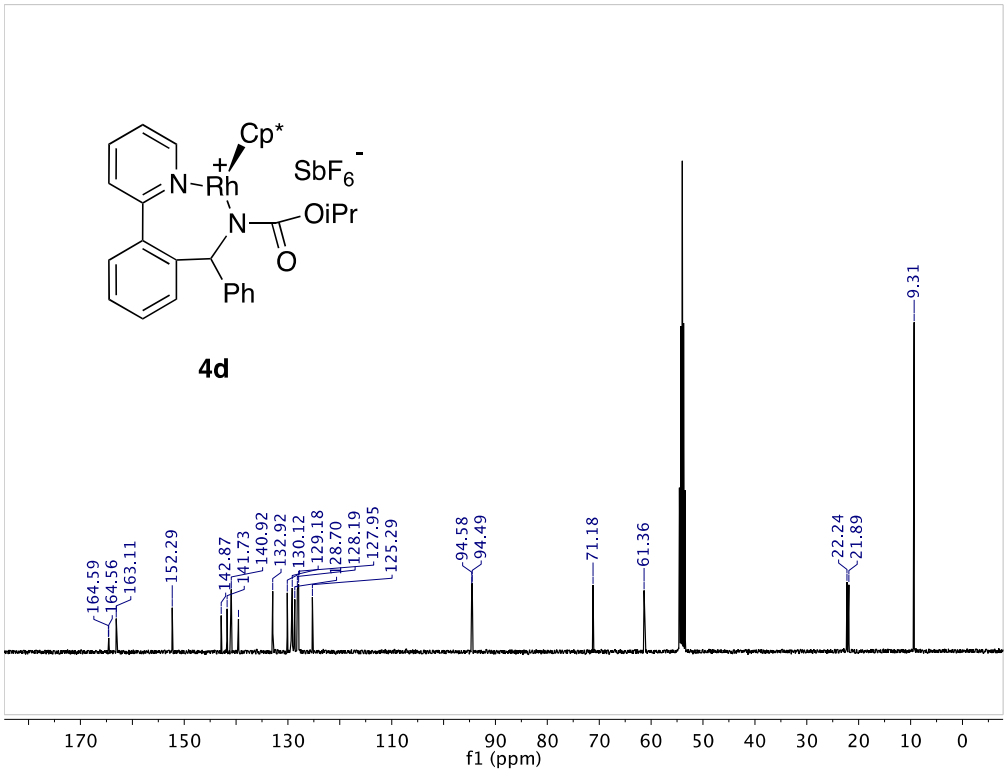

Figure S25. $^{13}C\{^{1}H\}$ NMR (126 MHz) spectra of **4d** in CD_2Cl_2 at room temperature.

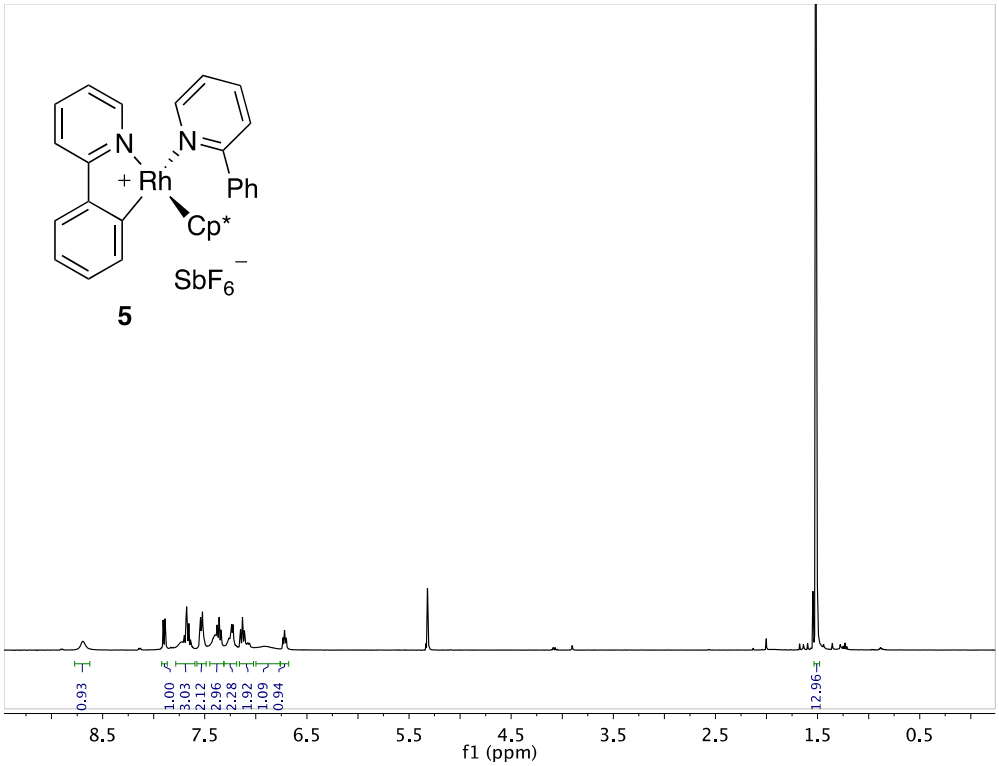

Figure S26. ^{1}H NMR (500 MHz) spectra of **5** in CD_2Cl_2 at room temperature.

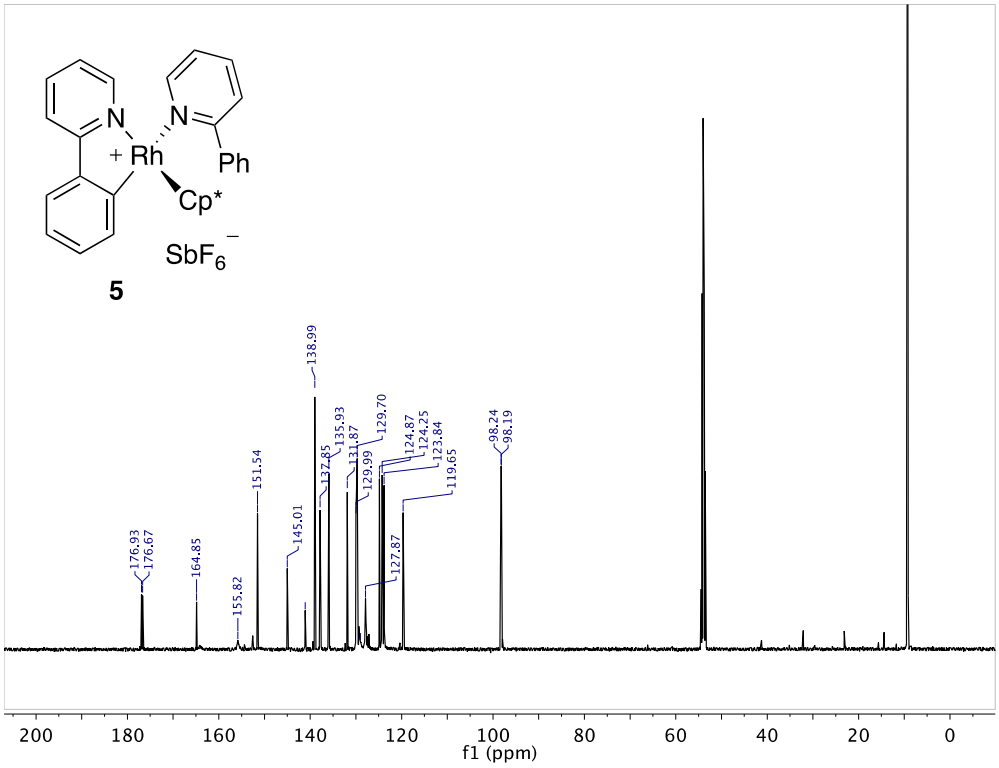

Figure S27. $^{13}C\{^{1}H\}$ NMR (126 MHz) spectra of **5** in CD_2Cl_2 at room temperature.

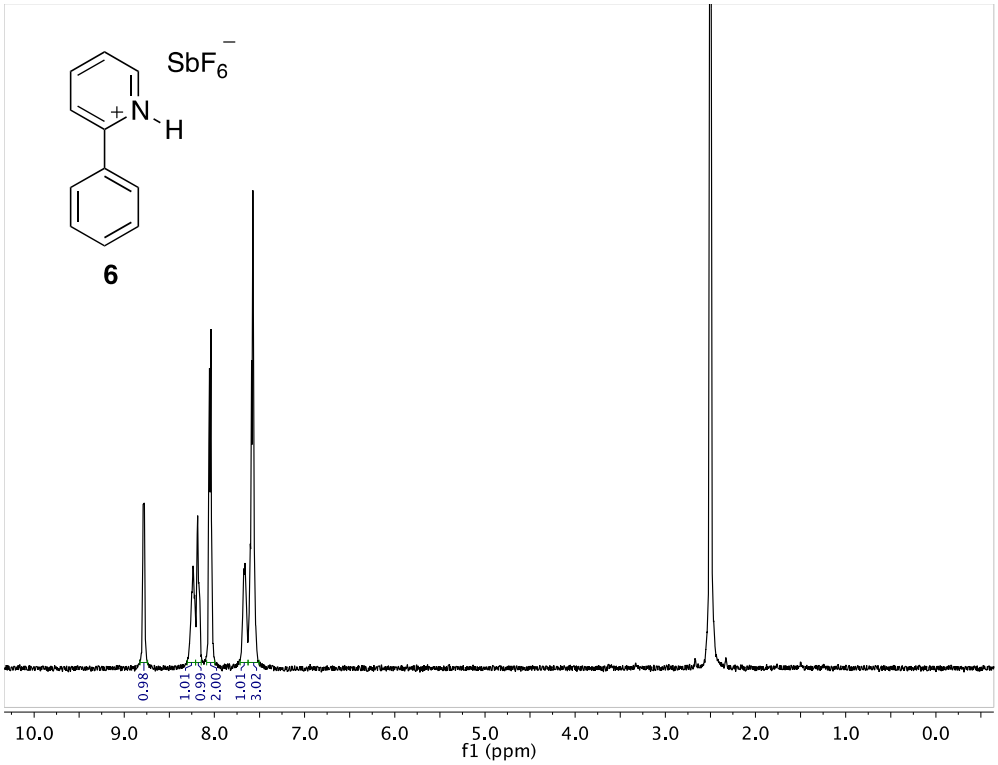

Figure S28. ^{1}H NMR (400 MHz) spectra of **6** in DMSO-d_6 at room temperature.

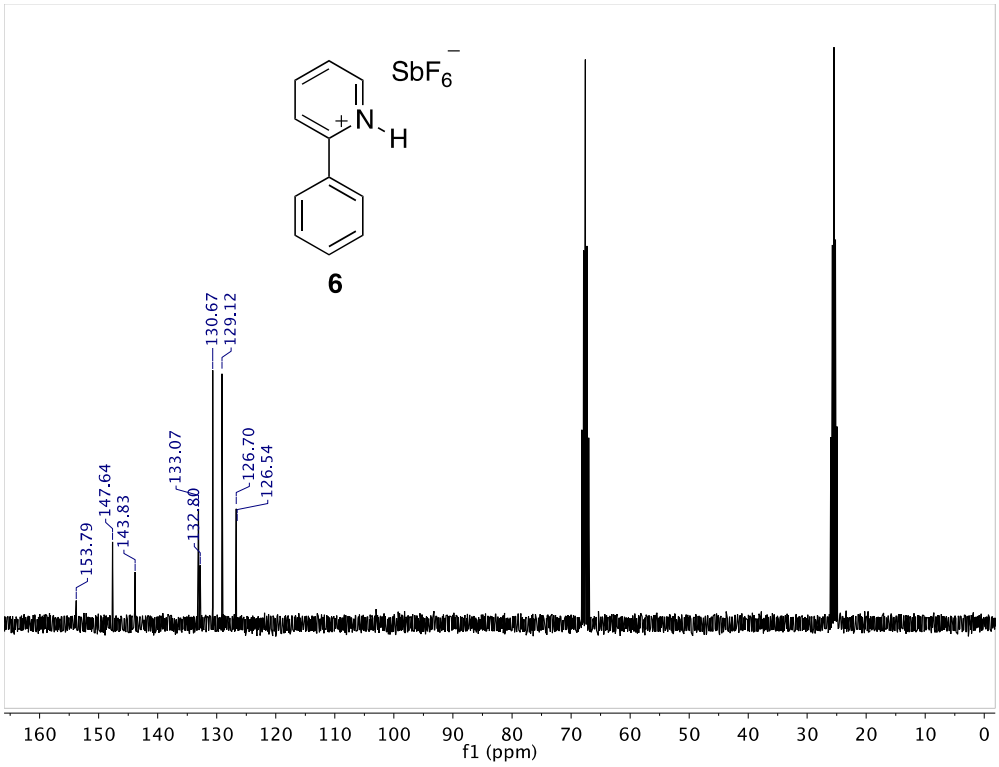

Figure S29. $^{13}C\{^{1}H\}$ NMR (75 MHz) spectra of **6** in THF-d_8 at room temperature.

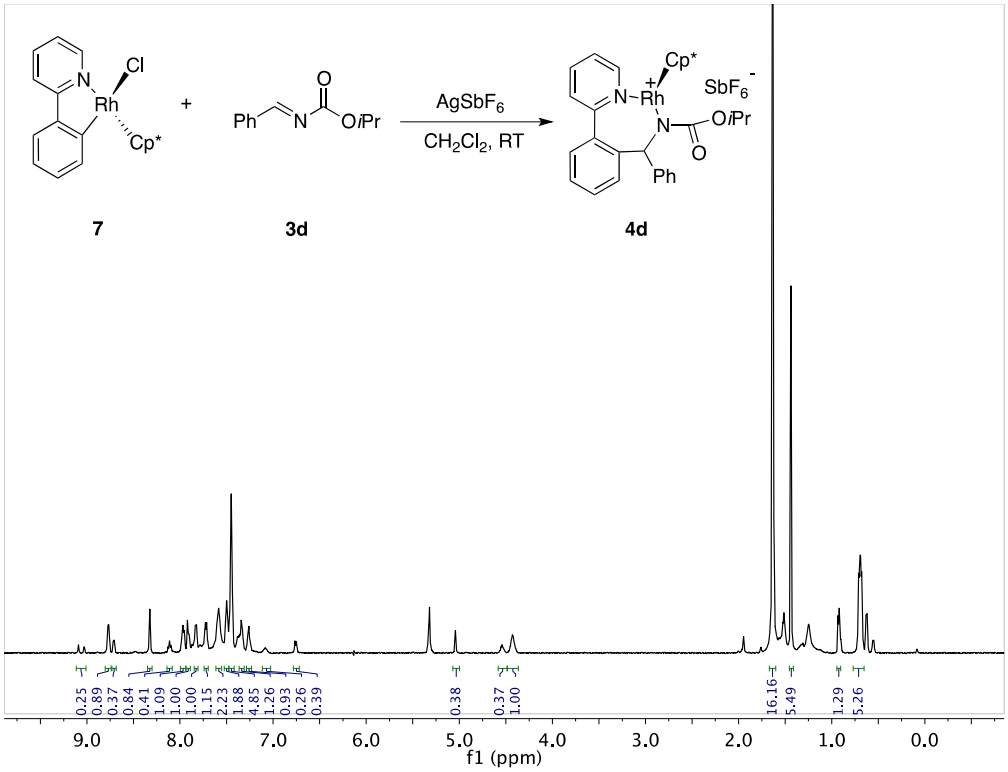

Figure S30. ^{1}H NMR (500 MHz) spectra of **4d** and **8d** (1:2.7) in CD_2Cl_2 at RT.