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Supporting Information

Halogen Bonding Effects on the Outcome of Reactions at Metal Centres

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Supporting Information

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1. General Considerations:

All syntheses were carried out using chemicals as purchased from commercial sources unless otherwise stated. Air- and moisture-sensitive manipulations or reactions were performed under inert atmosphere, either in a glove box or with standard Schlenk techniques. Glassware was dried *in vacuo* before use with a hot air gun. All solvents were dried and deoxygenated by using a solvent purification system (SPS). Silica gel 60 (230-400 mesh) was used for column chromatography. NMR spectra were recorded at room temperature in 400 MHz or 500 MHz spectrometers in $CDCl_3$ or CD_2Cl_2 unless otherwise cited. ^{1}H and ^{13}C NMR chemical shifts are quoted in ppm relative to residual solvent peaks. $^{11}B\{^{1}H\}$ NMR chemical shifts are quoted in ppm relative to $BF_3{\cdot}(CH_3)_2O$ in $CDCl_3$. $^{19}F\{^{1}H\}$ NMR chemical shifts are quoted in ppm relative to $CFCl_3$ in $CDCl_3$. $^{31}P\{^{1}H\}$ NMR chemical shifts are quoted in ppm relative to 85% phosphoric acid in water. HRMS and MS spectra were recorded using ESI ionisation method in positive mode. IR spectra were recorded using Attenuated Total Reflection (ATR) technique. Ligands **1** and **2** were prepared according to previous literature reports.[1]

[1] L. Carreras, M. Serrano-Torné, P. W. N. M. van Leeuwen and A. Vidal-Ferran, *Chem. Sci.*, 2018, **9**, 3644-3648.

2. General Structural Comments on X-ray Crystals:

Crystal preparation. Crystals of **3**, **4**, **5**, **6**, **8** and **9** were grown by solvent diffusion, using CH_2Cl_2 and *n*-pentane at –20 ºC under inert atmosphere. (2-iodo-3,4,5,6-tetrafluorophenyl)-diphenylphosphine **2** was obtained as a thick oil that after some time evolved to a colourless solid, with crystals suitable for single crystal X-ray diffraction. The crystals used for structure determination were selected using a Zeiss stereomicroscope using polarised light and prepared under inert conditions immersed in perfluoropolyether as protecting oil for manipulation.

Data collection. Crystal structure determination for samples **2**, **3**, **4**, **5**, **6**, **8** and **9** were carried out using an Apex DUO Kappa 4-axis goniometer equipped with an APEX 2 4K CCD area detector, a Microfocus Source E025 IuS using MoK_α radiation, Quazar MX multilayer Optics as monochromator and an Oxford Cryosystems low temperature device Cryostream 700 plus (T = –173 °C). Full-sphere data collection was used with ω and φ scans. *Programs used:* Bruker Device: Data collection APEX-2,[2] data reduction Bruker Saint[3] V/.60A and absorption correction SADABS[4] or TWINABS.[5]

Structure solution and refinement. Crystal structure solution was achieved using the computer program SHELXT.[6] Visualisation was performed with the program SHELXle.[7] Missing atoms were subsequently located from difference Fourier synthesis and added to the atom list. Least-squares refinement on F^2 using all measured intensities was carried out using the program SHELXL 2015.[8] All non-hydrogen atoms were refined including anisotropic displacement parameters.

Comments to the structures. Complex **3**: The asymmetric unit contains two molecules of the metal complex, two BF_4^- anions and two highly disordered dichloromethane molecules. The BF_4^- anions are disordered in two orientations (ratios 62:38 and 56:44). The two dichloromethane molecules are disordered in respectively two and five positions

[2] Data collection with APEX II version v2013.4-1. Bruker (2007). Bruker AXS Inc., Madison, Wisconsin, USA.
[3] Data reduction with Bruker SAINT version V8.30c. Bruker (2007). Bruker AXS Inc., Madison, Wisconsin, USA.
[4] SADABS: V2012/1 Bruker (2001). Bruker AXS Inc., Madison, Wisconsin, USA. R. H. Blessing, *Acta Cryst.* 1995, **A51**, 33-38.
[5] TWINABS Version 2012/1 Bruker AXS scaling for twinned crystals. R. H. Blessing, *Acta Cryst.* 1995, **A51**, 33-38.
[6] SHELXT; V2014/4 (Sheldrick 2014). G. M. Sheldrick, *Acta Cryst*. 2015, **A71**, 3-8.
[7] SHELXle; C. B. Huebschle, G. M. Sheldrick and B. Dittrich, *J. Appl. Cryst.* 2011, **44**, 1281-1284.
[8] SHELXL; SHELXL-2014/7 (Sheldrick 2014). G. M. Sheldrick, *Acta Cryst*. 2015, **C71**, 3-8.

with ratios of 59:41 and 33:24:22:14:7. The measured sample is formed by a minimum of two crystals with a ratio of 57:43. The collected data were processed with TWINABS taking in account overlapping reflections.

Complex **5**: The asymmetric unit contains one molecule of the metal complex. The measured sample is formed by a minimum of two crystals with a ratio of 68:32. The collected data were processed with TWINABS taking in account overlapping reflections.

Complex **6**: The asymmetric unit contains one molecule of the metal complex. The pyridine ring present in the structure is disordered in two inverted orientations (ratio: 69:31).

Complex **8**: The asymmetric unit contains one molecule of the metal complex. This compound was measured three times and special tests (checking general remaining electron densities) were performed to ensure the location and presence of the nitrogen atoms in the complex.

Complex **9**: The asymmetric unit contains one molecule of the metal complex and two molecules of dichloromethane. One of the halogen atoms coordinated to the metal atom shows a shared occupancy of 83 % Chlorine and 17 % Iodine.

ORTEP figures for 2, 4, 5 and 8.

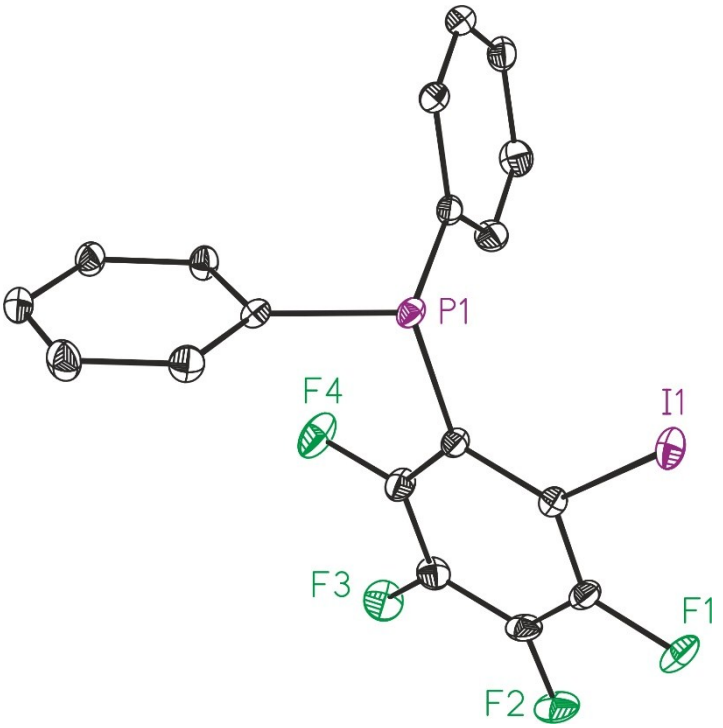


Figure SI 1. Crystal structure of **2**. Hydrogen atoms have been omitted for the sake of clarity. Colour scheme: C: black, P: purple, F: green, I: purple. Atomic displacement ellipsoids are drawn at a 50% probability.

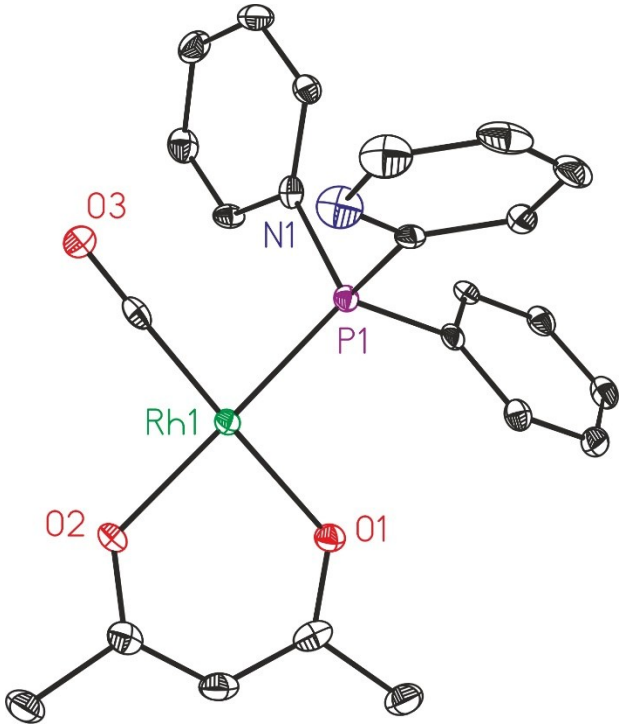


Figure SI 2. Crystal structure of **4**. Hydrogen atoms have been omitted for the sake of clarity. Colour scheme: C: black, P: purple, Rh: green, N: blue, O: red. Atomic displacement ellipsoids are drawn at a 50% probability.

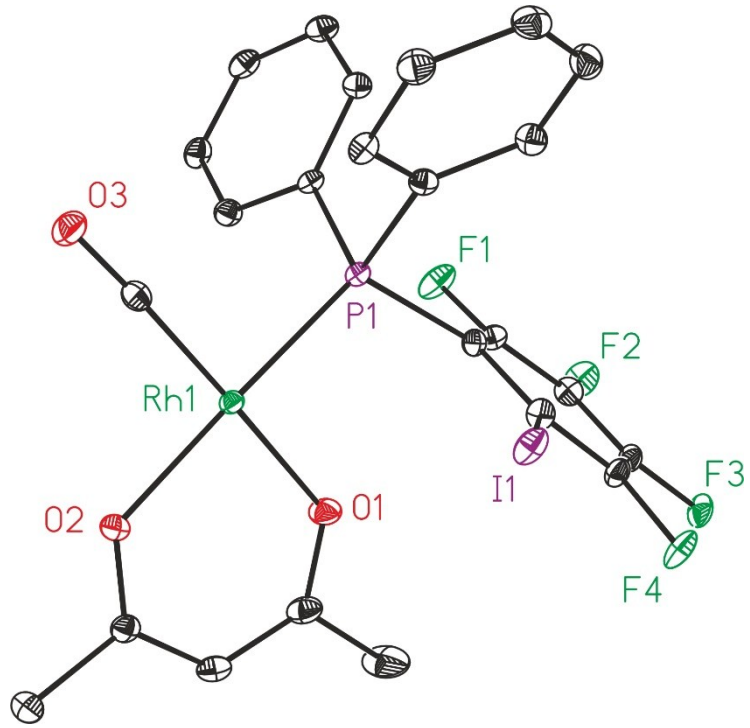


Figure SI 3. Crystal structure of **5**. Hydrogen atoms have been omitted for the sake of clarity. Colour scheme: C: black, P: purple, Rh: green, F: green, I: purple, O: red. Atomic displacement ellipsoids are drawn at a 50% probability.

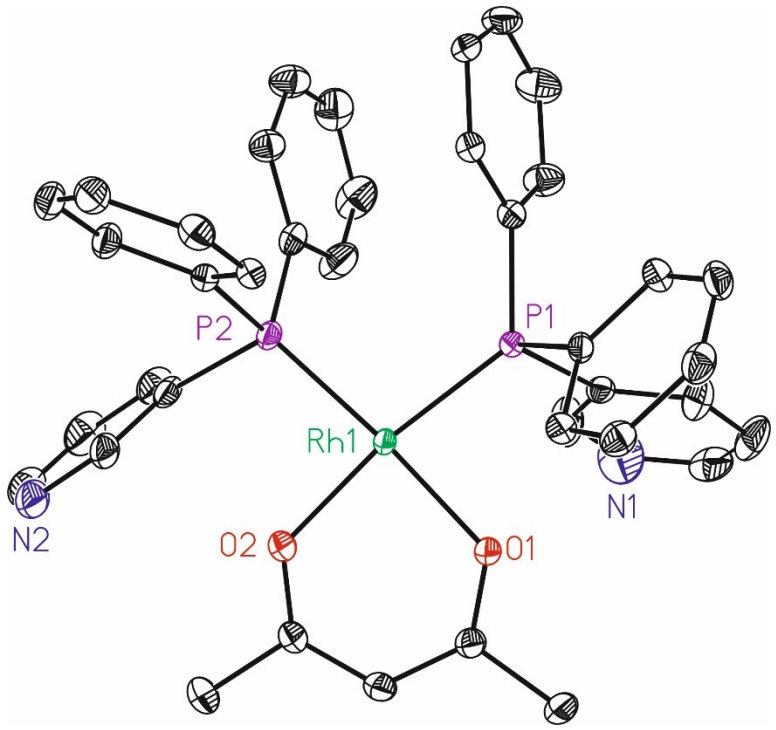
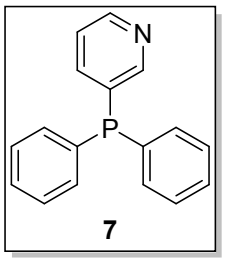


Figure SI 4. Crystal structure of **8**. Hydrogen atoms have been omitted for the sake of clarity. Colour scheme: C: black, P: purple, Rh: green, N: blue, O: red. Atomic displacement ellipsoids are drawn at a 50% probability.

3. Synthesis of Ligand 7:

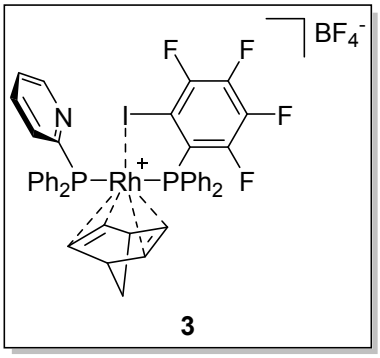


7

3-pyridyldiphenylphosphine (**7**): Ligand **7** was prepared according to a described procedure,[9] leading to 851.0 mg of white solid 3-diphenylphosphino pyridine (66.0% yield). ^{1}H NMR, ^{13}C{^{1}H} NMR and ^{31}P{^{1}H} NMR data were in agreement with those previously reported.[10] ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.49 (dt, J = 4.8, 1.5 Hz, 1 H), 8.44 (m, 1 H), 7.48 (m, 1 H), 7.31-7.20 (m, 10 H), 7.17 (m, 1 H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ: 154.3 (d, $J_{C–P}$ = 24.0 Hz), 149.7, 141.0 (d, $J_{C–P}$ = 15.7 Hz), 135.8 (d, $J_{C–P}$ = 10.3 Hz), 133.7 (d, $J_{C–P}$ = 19.9 Hz), 133.6 (d, $J_{C–P}$ = 16.0 Hz), 129.2, 128.8 (d, $J_{C–P}$ = 7.0 Hz), 123.5 (d, $J_{C–P}$ = 4.1 Hz) ppm. ^{31}P{^{1}H} NMR (202 MHz, $CDCl_3$) δ: −8.8 ppm. ESI-MS: $[M+H]^+$, 264.0.

[9] S. Ponsico, H. Gulyas, M. Martínez-Belmonte, E. C. Escudero-Adán, Z. Freixa and P. W. N. M. van Leeuwen, *Dalton Trans.*, 2011, **40**, 10686-10697.
[10] M. Sun, H.-Y. Zhang, Q. Han, K. Yang and S.-D. Yang, *Chem. - Eur. J.*, 2011, **17**, 9566-9570.

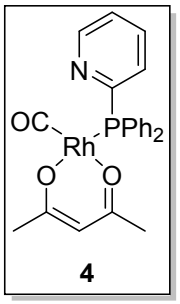
4. Syntheses of Complexes 3, 4, 5, 6, 8, 9, 10 and 11:



3

Norbornadiene diphenyl-2-pyridylphosphine (2-iodo-3,4,5,6-tetrafluorobenzene) diphenylphosphine rhodium(I) tetrafluoroborate, [Rh(nbd)(**1**)(**2**)]BF_4 (**3**): In a glovebox filled with N_2, 66.8 mg (0.18 mmol, 1 equiv.) of [Rh(nbd)$_2$]BF_4 were weighed in a glass vial provided with a magnetic stirrer and dissolved in 1 mL of CH_2Cl_2. Then, a solution of 2-PyPPh$_2$, **1** (46.1 mg, 0.18 mmol, 1 equiv.) and (2-iodo-3,4,5,6-tetrafluorobenzene)diphenyl-phosphine, **2** (80.5 mg, 0.18 mmol, 1 equiv.) in 1 mL of dichloromethane was prepared in a vial provided with a magnetic stirrer. The solution was stirred for 5 minutes at 25 °C. Afterwards, the ligands' solution was added dropwise to the rhodium solution. This mixture was stirred for 30 minutes at 25 °C. The resulting solution was evaporated, and then washed with *n*-pentane (3 x 2 mL) and dried under vacuum to afford 159.0 mg of **3** as an orange solid in 90.3% yield. ^{1}H NMR (500 MHz, CD_2Cl_2) δ: 7.94 (br m, 1 H), 7.52 (t, J = 7.3 Hz, 1 H), 7.48-7.18 (m, 14 H), 7.09 (m, 3 H), 7.02-6.88 (m, 4 H), 6.58 (dm, J = 7.9 Hz, 1 H), 3.80-3.60 (m, 6 H), 1.34 (s, 2 H) ppm. ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2) δ:[11] 156.5 (d, $J_{C–P}$ = 64.5 Hz, C_{Py}), 149.0 (d, $J_{C–P}$ = 18.7 Hz, C_{Py}), 136.8 (d, $J_{C–P}$ = 4.1 Hz, C_{Ph}), 134.7 (d, $J_{C–P}$ = 11.6 Hz, C_{Ph}), 132.7 (d, $J_{C–P}$ = 11.4 Hz, C_{Ph}), 131.6 (C_{Py}), 131.2 (C_{Ph}), 130.9 (C_{Ph}), 130.5 (d, $J_{C–P}$ = 8.8 Hz, C_{Ph}), 129.5-129.0 (C_{Ph}, C_{Py}), 128.0 (d, $J_{C–P}$ = 11.0 Hz, C_{Ph}), 125.2 (d, $J_{C–P}$ = 1.4 Hz, C_{Py}), 64.0 (C_{nbd}), 57.6 (C_{nbd}), 57.3 (C_{nbd}), 47.2 (C_{nbd}) ppm. ^{11}B{^{1}H} NMR (CD_2Cl_2, 160 MHz) δ: –1.1 ppm. ^{19}F{^{1}H} NMR (471 MHz, CD_2Cl_2) δ: –108.6 (m, 1 F), –112.9 (m, 1 F), –145.6 (m, 1 F), –149.0 (m, 1 F), –152.6 (s, 4 F) ppm. ^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2) δ: 77.3 (ddd, $J_{P–Rh}$ = 140.3 Hz, $J_{P–F}$ = 30.1, 15.3 Hz), 30.8 (br d, $J_{P–Rh}$ = 136.7 Hz) ppm. IR (neat): 3057, 2922, 1614, 1571, 1495, 1433, 1333, 1303, 1184, 1162, 1107, 1052, 1027, 996, 844, 777, 742, 719, 695, 514, 437, 415 cm^{-1}. HRMS ESI-MS (m/z): [M–BF_4]$^+$ calcd. for $C_{42}H_{32}F_4INP_2Rh^+$ 918.0040, found 918.0069.

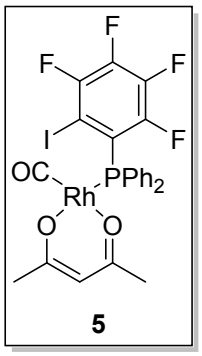
[11] A heavily overlapped ^{13}C{^{1}H} NMR spectrum was observed due to the splitting of the carbon signals with other NMR active nuclei present in the molecule. Whenever possible the carbons where assigned with the help of other NMR experiments as it follows: C_{nbd} (norbornadiene carbons), C_{Ph} (phenyl ring carbons), C_{Py} (pyridyl ring carbons), C_F (fluorine-containing ring carbons), C_{CO} (carbonyl carbon), C_{acac} (acetylacetonate carbons). This also applies for complexes **4**, **5**, **8**, **9**, **10** and **11**.



4

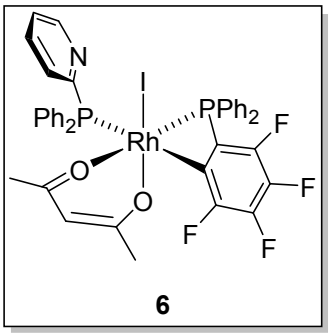
Acetylacetonato carbonyl diphenyl-2-pyridylphosphine rhodium(I), [Rh(acac)(CO)(**1**)] (**4**): In a glovebox filled with N_2, 14.8 mg (0.06 mmol, 1 equiv.) of [Rh(acac)$(CO)_2$] were weighed in a vial provided with a magnetic stirrer and dissolved in 0.5 mL of toluene. The green crystals turned into a yellow solution. Then a solution of 0.5 mL of (2-pyridyl)diphenylphosphine, **1** (15.8 mg, 0.06 mmol, 1 equiv.) in toluene was added dropwise to the rhodium precursor solution, observing some bubbling due to the release of CO and a change in the colour of the solution from yellow to orange. Finally, 0.5 mL of toluene were added and the solution was stirred for 2 hours. Precipitation with *n*-pentane yielded a yellow powder that after drying under vacuum resulted to be the desired complex (quantitative amounts). ^{1}H NMR, ^{13}C{^{1}H} NMR, ^{31}P{^{1}H} NMR and IR data were in agreement with those previously reported.[12] ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.68 (d, J = 4.7 Hz, 1 H), 7.93 (m, 1 H), 7.80-7.70 (m, 4 H), 7.59 (tq, J = 9.5, 1.8 Hz, 1 H), 7.40-7.25 (m, 6 H), 7.19 (m, 1 H), 5.34 (s, 1 H), 2.01 (s, 3 H), 1.44 (s, 3 H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ:[11] 188.9 (dd, $J_{C–Rh}$ = 75.4 Hz, $J_{C–P}$ = 24.5 Hz, C_{CO}), 187.6 (C_{acac}), 185.5 (C_{acac}), 157.7 (d, $J_{C–P}$ = 71.4 Hz, C_{Py}), 150.1 (d, $J_{C–P}$ = 14.5 Hz, C_{Py}), 135.5 (d, $J_{C–P}$ = 9.4 Hz, C_{Py}), 135.0 (d, $J_{C–P}$ = 11.4 Hz, C_{Ph}), 132.3 (d, $J_{C–P}$ = 51.6 Hz, C_{Ph}), 131.3 (d, $J_{C–P}$ = 27.0 Hz, C_{Py}), 130.4 (d, $J_{C–P}$ = 2.5 Hz, C_{Ph}), 128.0 (d, $J_{C–P}$ = 10.6 Hz, C_{Ph}), 123.9 (d, $J_{C–P}$ = 2.2 Hz, C_{Py}), 100.8 (d, $J_{C–Rh}$ = 2.2 Hz, C_{acac}), 27.7 (d, $J_{C–Rh}$ = 5.3 Hz, C_{acac}), 26.7 (C_{acac}) ppm. ^{31}P{^{1}H} NMR (202 MHz, $CDCl_3$): 53.6 (d, $J_{P–Rh}$ = 174.6 Hz) ppm. IR (neat): 1962 (CO), 1567, 1515, 1479, 1447, 1434, 1420, 1381, 1309, 1271, 1194, 1154, 1097, 1025, 999, 987, 930, 769, 743, 724, 709, 693, 590, 537, 526, 512, 496 cm^{-1}. ESI-MS: $[M+Na]^+$, 516.0.

[12] W. Purcell, J. Conradie, T. T. Chiweshe, J. A. Venter, H. G. Visser and M. P. Coetzee, *J. Mol. Struct.*, 2013, **1038**, 220-229.



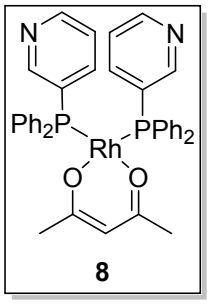
5

Acetylacetonato carbonyl (2-iodo-3,4,5,6-tetrafluorobenzene)-diphenylphosphine rhodium(I), [Rh(acac)(CO)(**2**)] (**5**): In a glovebox filled with N_2, 46.1 mg (0.18 mmol, 1 equiv.) of [Rh(acac)$(CO)_2$] were weighed in a vial provided with a magnetic stirrer and dissolved in 1 mL of toluene. The green crystals turned into a yellow solution. Then a solution of 1 mL of (2-iodo-3,4,5,6-tetrafluorobenzene)-diphenylphosphine **2** (81.4 mg, 0.18 mmol, 1 equiv.) in toluene was added dropwise to the rhodium precursor solution. The solution changed from yellow to orange, indicating that the ligand coordination was taking place. The solution was stirred overnight at room temperature. Precipitation with *n*-pentane yielded a yellow powder that after washing with *n*-pentane (3 x 2 mL) and drying under vacuum yielded the desired complex (75.8 mg, 62.1% yield). ^{1}H NMR (400 MHz, CD_2Cl_2) δ: 7.90-7.80 (m, 4 H), 7.55-7.40 (m, 6 H), 5.48 (s, 1 H), 2.09 (s, 3 H), 1.59 (s, 3 H) ppm. ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2) δ:[11] 189.8 (dd, $J_{C–Rh}$ = 75.4 Hz, $J_{C–P}$ = 24.5 Hz, C_{CO}), 188.2 (C_{acac}), 185.4 (C_{acac}), 149.4 (ddm, $J_{C–F}$ = 254.9 Hz, J = 11.5 Hz, C_F), 148.0 (dtm, $J_{C–F}$ = 242.0 Hz, J = 11.0 Hz, C_F), 140.8 (dm, $J_{C–F}$ = 256.1 Hz, C_F), 140.4 (dm, $J_{C–F}$ = 260.8 Hz, C_F), 134.6 (d, J = 12.8 Hz, C_{Ph}), 132.4 (dd, J = 53.0, 3.2 Hz, C_{Ph}), 131.3 (d, J = 2.5 Hz, C_{Ph}), 128.9 (d, J = 11.1 Hz, C_{Ph}), 120.0 (ddm, J = 40.7, 14.5 Hz, C_F), 100.8 (d, $J_{C–Rh}$ = 2.0 Hz, C_{acac}), 87.8 (m, C_F), 27.7 (d, $J_{C–Rh}$ = 6.5 Hz, C_{acac}), 27.0 (C_{acac}) ppm. ^{19}F{^{1}H} NMR (376 MHz, CD_2Cl_2) δ: −109.7 (dm, J = 24.0 Hz, 1 F), −121.9 (m, 1 F), −149.7 (m, 1 F), −153.5 (tm, J = 18.8 Hz, 1 F) ppm. ^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2): 66.3 (dt, $J_{P–Rh}$ = 183.9 Hz, $J_{P–F}$ = 7.7 Hz) ppm. IR (neat): 1968 (CO), 1571, 1552, 1517, 1483, 1427, 1377, 1332, 1301, 1271, 1233, 1186, 1121, 1103, 1088, 1026, 999, 782, 774, 758, 746, 717, 693, 504 cm^{-1}. HRMS ESI-MS (m/z): $[M–CO+H]^+$ calcd. for $C_{23}H_{18}F_4IO_2PRh$ 662.9075, found 662.9085.



6

Iodo acetylacetonato κ*C*,κ*P*-(3,4,5,6-tetrafluorobenzene)diphenylphosphine diphenyl-2-pyridylphosphine rhodium(III), [Rh(I)(acac)(κ^2-2-$C_6F_4PPh_2$)(**1**)] (**6**): In a glove box filled with N_2, 65.8 mg (0.21 mmol, 1 equiv.) of [Rh(acac)(cod)][13] were weighed in a vial provided with a magnetic stirrer and dissolved in 1 mL of diethyl ether, forming a yellow solution. Then a solution of 1 mL of (2-iodo-3,4,5,6-tetrafluorobenzene)diphenylphosphine, **2** (95.7 mg, 0.21 mmol, 1 equiv.) and 2-$PyPPh_2$, **1** (54.7 mg, 0.21 mmol, 1 equiv.) in Et_2O, previously stirred for five minutes, was added dropwise to the rhodium precursor solution. During the addition, it was observed a change from yellow to a deep orange/red colour. After *ca*. 15 minutes an orange precipitate was formed. Following stirring for 1 hour, the mother liquors were decanted, and the solid was washed with Et_2O (3 x 2 mL) and *n*-pentane (3 x 2 mL) and dried under vacuum, affording complex **6** as an orange solid (118.0 mg) in 61.4% yield. Spectroscopic data were in agreement with those previously reported by our group.[1]

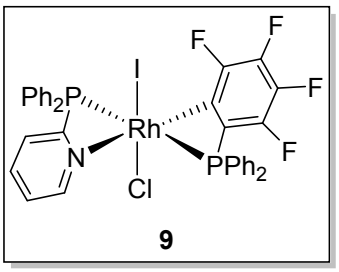


8

Acetylacetonato bis(diphenyl-3-pyridylphosphine) rhodium(I), [Rh(acac)(**7**)$_2$] (**8**): In a glove box filled with N_2, 65.3 mg (0.21 mmol, 1 equiv.) of [Rh(acac)(cod)][13] were weighed in a vial provided with a magnetic stirrer and dissolved in 1 mL of diethyl ether, forming a yellow solution. Then a solution of 1 mL of (2-iodo-3,4,5,6-tetrafluorobenzene)diphenylphosphine, **2** (94.9 mg, 0.21 mmol, 1 equiv.) and 3-$PyPPh_2$, **7** (54.3 mg, 0.21 mmol, 1 equiv.) in Et_2O, previously stirred for five minutes, was added dropwise to the rhodium precursor solution. During the addition, it was observed a change from yellow to a deep orange colour and approximately, after 15 minutes, a precipitate was formed. After stirring for 1 hour, the mother liquors were decanted, and the solid was washed with Et_2O (3 x 2 mL) and *n*-pentane (3 x 2 mL) and dried under vacuum, affording 48.1 mg of homocomplex **8** (32.0% yield) as a yellow solid. ^{1}H NMR (500 MHz, CD_2Cl_2) δ: 8.53 (d, *J* = 2.0 Hz, 2 H), 8.37 (d, *J* = 4.7 Hz, 2 H), 7.70-7.55 (m, 10 H), 7.27 (t, *J* = 7.4 Hz, 4 H), 7.14 (t, *J* = 7.4 Hz, 8 H), 6.99 (m, 2 H), 5.29 (s, 1 H), 1.43 (s, 6 H) ppm. ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2) δ:[11] 185.0 (C_{acac}),

[13] The reactivity observed for precursor [Rh(acac)(cod)] was identical to that observed for the analogous precursor [Rh(acac)(C_2H_4)$_2$].

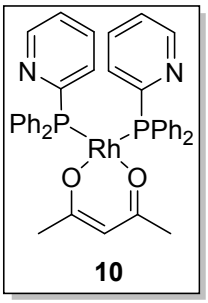
154.6 (t, J_{C-P} = 5.9 Hz, C_{Py}), 149.6 (C_{Py}), 141.5 (t, J_{C-P} = 4.6 Hz, C_{Py}), 135.1 (t, J_{C-P} = 5.9 Hz, C_{Ph}), 134.5 (t, J_{C-P} = 22.3 Hz, C_{Ph}), 132.2 (t, J_{C-P} = 19.3 Hz, C_{Py}), 129.7 (C_{Ph}), 127.8 (t, J_{C-P} = 4.9 Hz, C_{Ph}), 122.5 (t, J_{C-P} = 3.4 Hz, C_{Py}), 99.8 (d, J_{C-Rh} = 1.4 Hz, C_{acac}), 26.9 (d, J_{C-Rh} = 2.9 Hz, C_{acac}) ppm. $^{31}P\{^{1}H\}$ NMR (162 MHz, CD_2Cl_2): 54.3 (d, J_{P-Rh} = 193.1 Hz) ppm. IR (neat): 3046, 1567, 1515, 1477, 1433, 1395, 1270, 1179, 1090, 1021, 931, 794, 753, 692, 620, 599, 551, 525, 436 cm^{-1}. HRMS ESI-MS (m/z): $[M]^{+\bullet}$ calcd. for $C_{39}H_{35}N_2O_2P_2Rh$ 728.1223, found 728.1241.



9

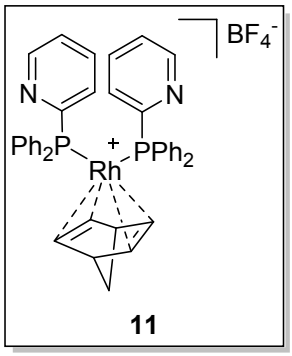
Iodo chloro κ*C*,κ*P*-(3,4,5,6-tetrafluorobenzene)diphenylphosphine diphenyl-2-pyridylphosphine rhodium(III), [Rh(I)(Cl)(κ^2-2-$C_6F_4PPh_2$)(**1**)] (**9**): In a glovebox filled with N_2, 25.5 mg (0.06 mmol, 0.5 equiv.) of $[Rh(Cl)(CO)_2]_2$ dimer were weighed in a vial provided with a magnetic stirrer and dissolved in 1 mL of CH_2Cl_2. Then, a solution of 2-$PyPPh_2$, **1** (34.5 mg, 0.12 mmol, 1 equiv.) and (2-iodo-3,4,5,6-tetrafluorobenzene)diphenylphosphine, **2** (61.6 mg, 0.12 mmol, 1 equiv.) in 2 mL of dichloromethane was prepared in a vial provided with a magnetic stirrer. The resulting solution was stirred for 5 minutes at 25 °C. Afterwards, the ligands' solution was added dropwise to the rhodium solution, observing some bubbling due to the release of CO. This mixture was stirred for 1 hour at 25 °C. The resulting red solution was evaporated and complex **9** was obtained after crystallisation using CH_2Cl_2 and *n*-pentane, obtaining 20.3 mg (18.5% yield) of the complex **9** as red crystals. ^{1}H NMR (500 MHz, CD_2Cl_2) δ: 8.74 (d, *J* = 5.0 Hz, 1 H), 8.02 (tt, *J* = 7.9, 1.8 Hz, 1 H), 7.90-7.65 (m, 10 H), 7.55-7.35 (m, 12 H) ppm. $^{13}C\{^{1}H\}$ NMR (126 MHz, CD_2Cl_2) δ:[11] 167.9 (d, J_{C-P} = 56.2 Hz, C_{Py}), 152.6 (dm, J_{C-P} = 17.9 Hz, C_{Py}), 137.7 (d, J_{C-P} = 3.4 Hz, C_{Py}), 135.3 (d, J_{C-P} = 9.7 Hz, C_{Ph}), 134.8 (d, J_{C-P} = 9.5 Hz, C_{Ph}), 134.1 (d, J_{C-P} = 10.0 Hz, C_{Ph}), 131.5 (dd, *J* = 15.5, 2.5 Hz, C_{Ph}), 131.2 (dd, *J* = 13.3, 2.6 Hz, C_{Ph}), 130.5 (m, C_{Py}), 128.9 (m, C_{Py}), 128.7 (d, J_{C-P} = 4.0 Hz, C_{Ph}), 128.6 (t, J_{C-P} = 3.6 Hz, C_{Ph}), 128.5 (d, J_{C-P} = 4.5 Hz, C_{Ph}) ppm. $^{19}F\{^{1}H\}$ NMR (471 MHz, CD_2Cl_2) δ: −131.3 (tm, *J* = 19.4 Hz, 1 F), −132.9 (m, 1 F), −148.7 (t, *J* = 22.0 Hz, 1 F), −161.5 (t, *J* = 20.2 Hz, 1 F) ppm. $^{31}P\{^{1}H\}$ NMR (202 MHz, CD_2Cl_2) δ: −17.7 (ddd, J_{P-P} = 568.6 Hz, J_{P-Rh} = 85.8 Hz, J_{P-F} = 17.7 Hz), −31.2 (dd, J_{P-P} = 568.4 Hz, J_{P-Rh} = 74.6 Hz) ppm. IR (neat): 3055, 2085, 1980, 1615, 1584, 1467, 1447, 1434, 1329,

1294, 1185, 1092, 1015, 843, 789, 740, 707, 688, 617, 526, 506, 434 cm^{-1}. HRMS ESI-MS (m/z): $[M+Na]^+$ calcd. for $C_{35}H_{24}ClF_4INNaP_2Rh$ 883.9001, found 883.8986.



Acetylacetonato bis(diphenyl-2-pyridylphosphine) rhodium(I), [Rh(acac)(**1**)$_2$] (**10**): In a glove box filled with N_2, 21.1 mg (0.07 mmol, 1 equiv.) of [Rh(acac)(cod)][13] were weighed in a vial provided with a magnetic stirrer and dissolved in 0.5 mL of diethyl ether, forming a yellow solution. Then a solution of 0.5 mL of 2-PyPPh$_2$, **2** (36.2 mg, 0.13 mmol, 2 equiv.) in Et_2O was added dropwise to the rhodium precursor solution. During the addition, a change from yellow to a deep orange colour was observed. 0.5 mL of Et_2O were further added to quantitatively transfer the ligand, and after *ca*. 15 minutes, a precipitate was formed. After stirring for 1 hour, the mother liquors were decanted. The solid was washed with Et_2O (3 x 2 mL) and *n*-pentane (3 x 2 mL) and dried under vacuum, affording 47.4 mg (97.6% yield) of **10** as an orange solid. ^1H NMR, $^{13}C\{^1H\}$ NMR, $^{31}P\{^1H\}$ NMR and IR data were in agreement with those previously reported.[14] ^1H NMR (500 MHz, CD_2Cl_2) δ: 8.38 (d, J = 4.5 Hz, 2 H), 8.14 (d, J = 7.7 Hz, 2 H), 7.70-7.60 (m, 8 H), 7.41 (tm, J = 7.7 Hz, 2 H), 7.21 (t, J = 7.3 Hz, 4 H), 7.10 (t, J = 7.5 Hz, 8 H), 7.03 (m, 2 H), 5.27 (s, 1 H), 1.42 (s, 6 H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, CD_2Cl_2) δ:[11] 184.8 (C_{acac}), 160.6 (t, J_{C-P} = 30.9 Hz, C_{Py}), 149.0 (t, J_{C-P} = 6.3 Hz, C_{Py}), 135.8 (t, J_{C-P} = 22.4 Hz, C_{Py}), 135.3 (t, J_{C-P} = 5.6 Hz, C_{Ph}), 134.6 (t, J_{C-P} = 4.7 Hz, C_{Ph}), 132.2 (t, J_{C-P} = 14.0 Hz, C_{Py}), 129.0 (C_{Ph}), 127.2 (t, J_{C-P} = 4.9 Hz, C_{Ph}), 122.9 (C_{Py}), 99.6 (d, J_{C-Rh} = 1.6 Hz, C_{acac}), 26.9 (t, J_{C-Rh} = 2.8 Hz, C_{acac}) ppm. $^{31}P\{^1H\}$ NMR (202 MHz, CD_2Cl_2): 59.2 (d, J_{P-Rh} = 192.8 Hz) ppm. IR (neat): 3046, 2985, 2911, 1567, 1513, 1478, 1445, 1433, 1418, 1393, 1308, 1268, 1194, 1181, 1152, 1127, 1091, 1045, 1026, 998, 986, 931, 791, 765, 740, 724, 693, 618, 597, 551, 526, 517, 510, 499, 461, 436, 417 cm^{-1}.

[14] K. Kartashova, S. Mallet-Ladeira and M. R. Axet, *J. Organomet. Chem.*, 2015, **799-800**, 226-231.



Norbornadiene bis(diphenyl-2-pyridylphosphine) rhodium(I) tetrafluoroborate, $[Rh(nbd)(\mathbf{1})_2]BF_4$ (**11**):[15] In a glovebox filled with N_2, 51.8 mg (0.14 mmol, 1 equiv.) of $[Rh(nbd)_2]BF_4$ were weighed in a glass vial provided with a magnetic stirrer and dissolved in 1 mL of CH_2Cl_2. Then, a solution of 2-$PyPPh_2$, **1** (75.2 mg, 0.28 mmol, 2 equiv.) in 1 mL of dichloromethane was prepared and then added dropwise to the rhodium solution. This mixture was stirred for 30 minutes at 25 °C. The resulting solution was evaporated and then washed with *n*-pentane (3 x 2 mL) and dried under vacuum to afford 98.0 mg of **11** as an orange solid in 87.9% yield. ^{1}H NMR (500 MHz, CD_2Cl_2) δ: 8.02 (d, J = 4.7 Hz, 2 H), 7.54-7.44 (m, 14 H), 7.42-7.34 (m, 8 H), 7.11 (t, J = 6.2 Hz, 2 H), 7.02 (d, J = 7.8 Hz, 2 H), 3.92 (d, J = 2.1 Hz, 4 H), 3.53 (s, 2 H), 1.30 (s, 2 H) ppm. ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2) δ:[11] 161.4 (d, J_{C-P} = 57.4 Hz, C_{Py}), 150.8 (d, J_{C-P} = 19.3 Hz, C_{Py}), 136.9 (d, J_{C-P} = 1.8 Hz, C_{Ph}), 134.1 (d, J_{C-P} = 13.5 Hz, C_{Ph}), 132.4 (d, J_{C-P} = 10.0 Hz, C_{Ph}), 131.3 (d, J_{C-P} = 32.4 Hz, C_{Py}), 131.1 (C_{Ph}), 129.3 (d, J_{C-P} = 9.7 Hz, C_{Ph}), 128.2 (d, J_{C-P} = 11.6 Hz, C_{Ph}), 125.3 (C_{Py}), 63.9 (C_{nbd}), 59.5 (d, J_{C-P} = 4.1 Hz, C_{nbd}), 49.7 (C_{nbd}) ppm. ^{11}B{^{1}H} NMR (CD_2Cl_2, 128 MHz) δ: −1.1 ppm. ^{19}F{^{1}H} NMR (376 MHz, CD_2Cl_2) δ: −153.0 (s) ppm. ^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2) δ: 10.4 (d, J_{P-Rh} = 124.2 Hz) ppm. IR (neat): 3053, 2989, 2926, 2861, 1585, 1570, 1479, 1449, 1434, 1422, 1305, 1280, 1159, 1090, 1049, 997, 741, 693, 504 cm^{-1}. HRMS ESI-MS (m/z): $[M-BF_4]^+$ calcd. for $C_{41}H_{36}N_2P_2Rh^+$ 721.1403, found 721.1393.

[15] The synthesis of homocomplex $[Rh(nbd)(\mathbf{2})_2]BF_4$ was also attempted but a complex mixture of products were obtained according to the ^{31}P{^{1}H} NMR.

5. DOSY NMR Experiments:[16]

Diffusion Ordered SpectroscopY (DOSY) NMR spectra were recorded at 298 K in a 500 MHz spectrometer equipped with a cryoprobe. All DOSY experiments were obtained with a longitudinal eddy-current delay (LED) bipolar gradient pulse pair and two spoil gradients pulse sequence (ledbpgp2s) in the standard Bruker pulse sequence library.[17] All experiments were processed with standard Bruker 1D and 2D DOSY software. $CDCl_3$ was used as solvent and the concentration of the ligands was chosen to be 0.3 M. Bis(2-diphenylphosphinophenyl)ether (DPEphos) was included as control bidentate ligand.

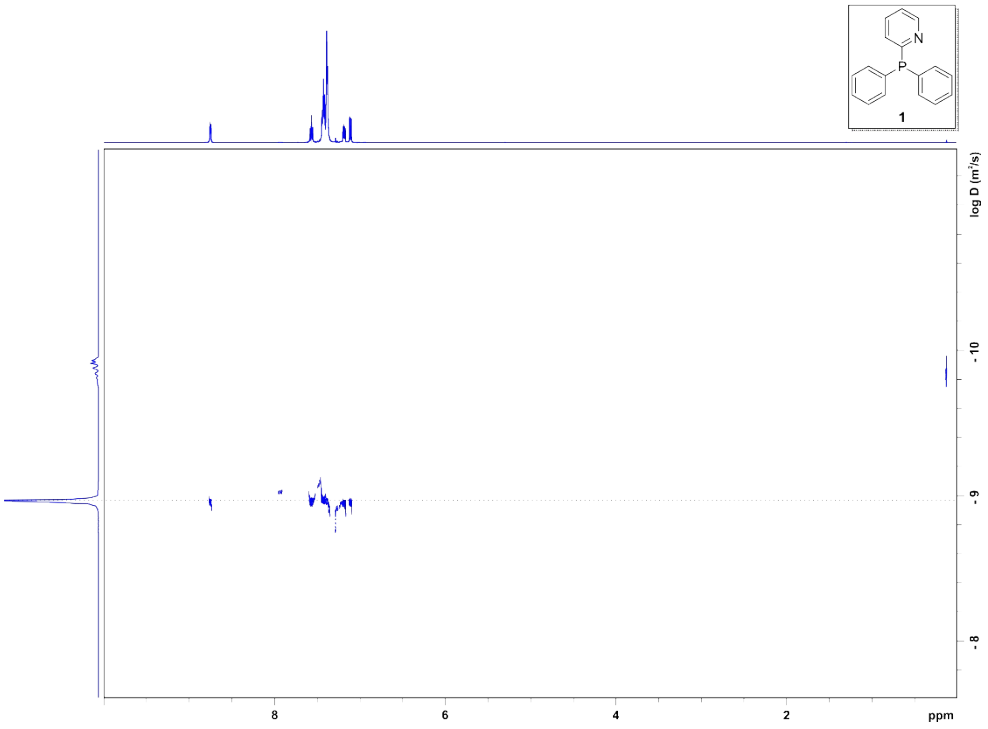


Figure SI 5. 2D DOSY for ligand **1**. Log D = −8.99±0.01 → D = 1.03±0.01·10^{-9} m^2/s.

[16] Reproducibility of DOSY experiments was proven by successfully repeating the experiments two times.
[17] *Bruker User Library* (accessed 23 October 2018); https://www.bruker.com/service/information-communication/nmr-pulse-program-lib/bruker-user-library.html

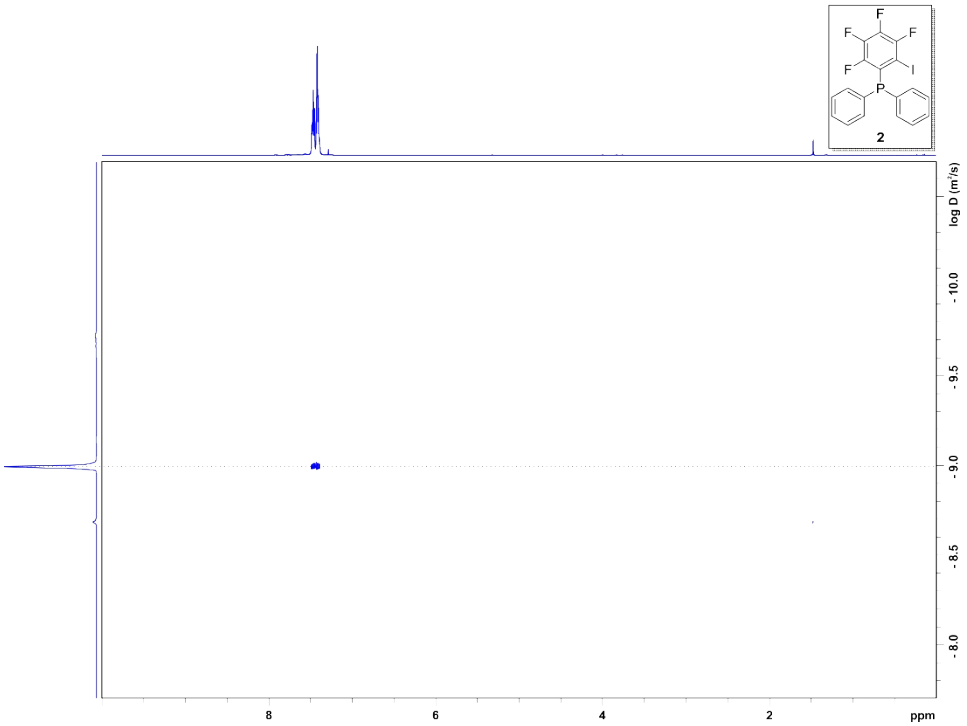


Figure SI 6. 2D DOSY for ligand **2**. Log D = −9.02±0.03 → D = 9.47±0.75·10^{-10} m^2/s.

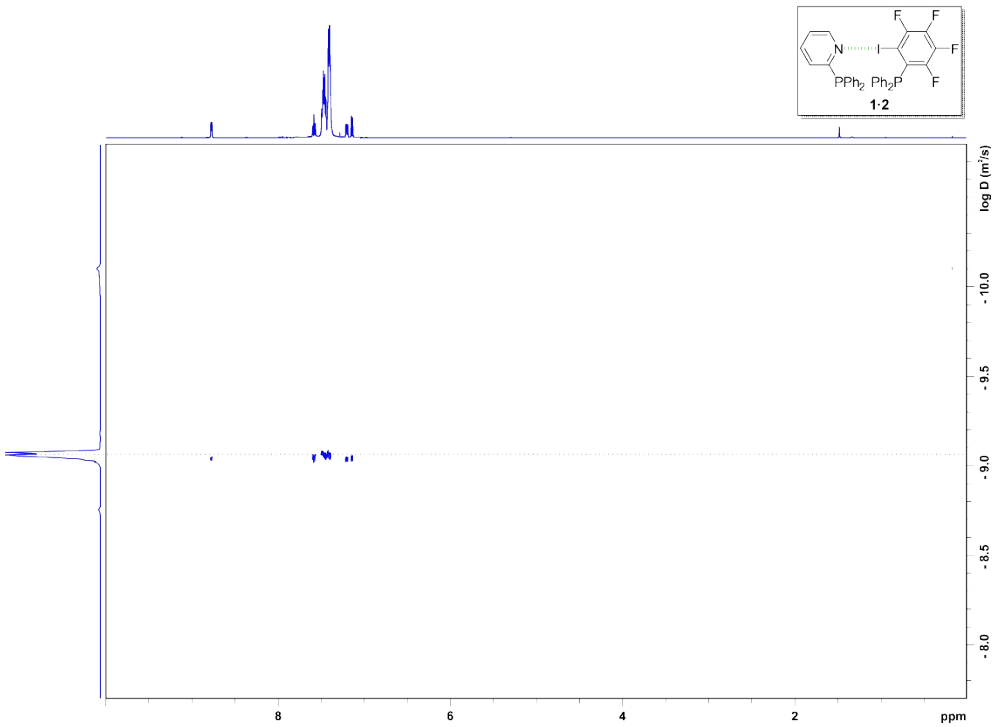


Figure SI 7. 2D DOSY for ligands **1·2**. Log D = −9.06±0.01 → D = 8.66±0.21·10^{-10} m^2/s.

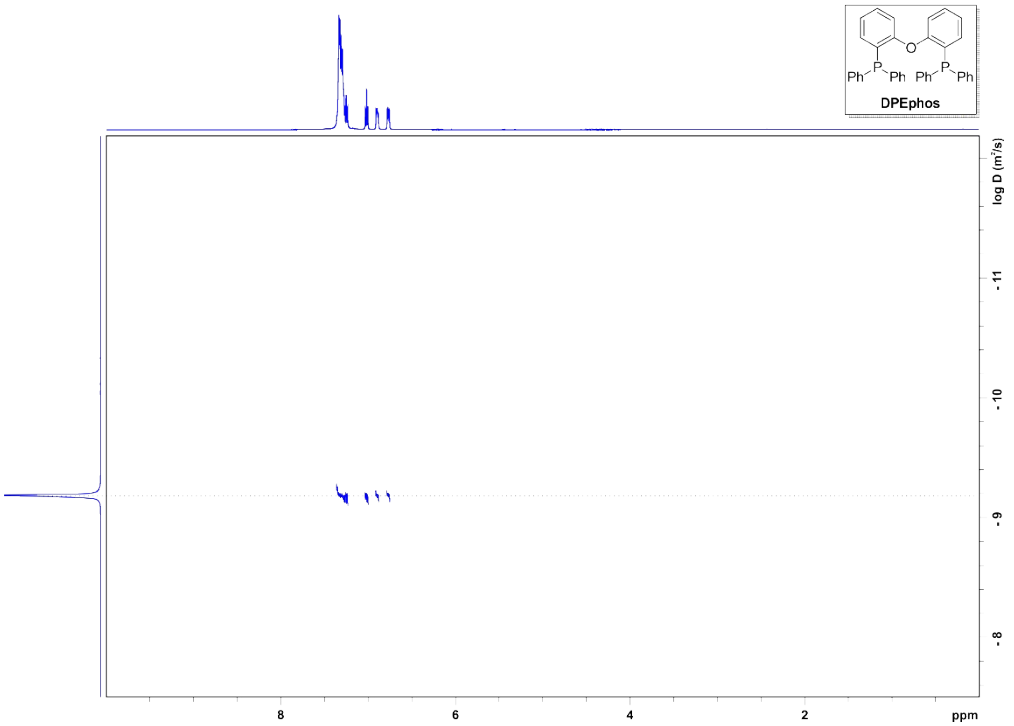


Figure SI 8. 2D DOSY for ligand DPEphos. Log D = −9.19 → D = $6.46 \cdot 10^{-10}$ m^2/s.

6. Tolman Electronic Parameter and Percent Buried Volume Calculation:

Tolman Electronic Parameter was measured considering the CO stretching frequencies of carbonylrhodium(I) complexes **4** (1962 cm^{-1}) and **5** (1968 cm^{-1}).[18]

Percent buried volume ($\%V_{Bur}$) was calculated using SambVca 2.0 web application.[19] Bond distances from the X-ray structures of **4** and **5** were used to determine $\%V_{Bur}$ of ligands **1** and **2** respectively.

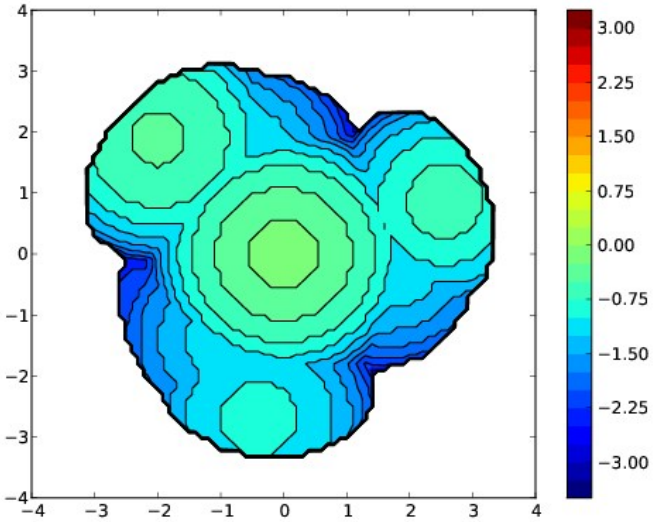


Figure SI 9. Generated steric map for ligand **1** ($\%V_{Bur}$ = 28.9).

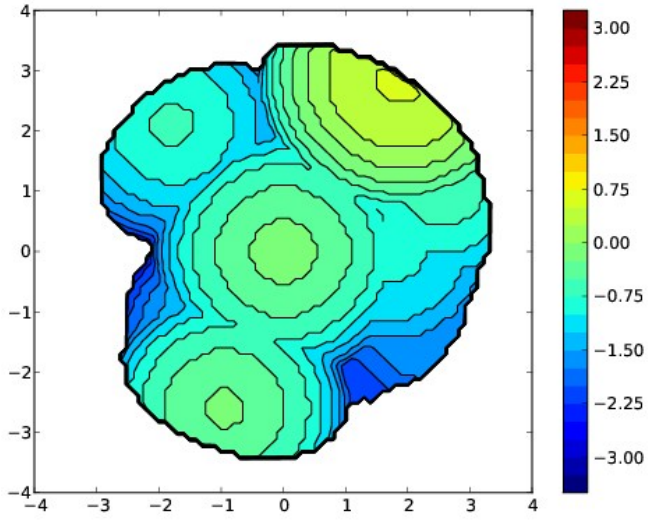


Figure SI 10. Generated steric map for ligand **2** ($\%V_{Bur}$ = 34.4).

[18] A. Roodt, S. Otto and G. Steyl, *Coord. Chem. Rev.*, 2003, **245**, 121-137.
[19] SambVca 2.0: https://www.molnac.unisa.it/OMtools/sambvca2.0/. For details see: L. Falivene, R. Credendino, A. Poater, A. Petta, L. Serra, R. Oliva, V. Scarano and L. Cavallo, *Organometallics*, 2016, **35**, 2286-2293.

7. ^{31}P NMR Reaction Monitoring:

In a glove box filled with N_2, 20.0 mg (0.06 mmol, 1 equiv.) of [Rh(acac)(cod)] were weighed in a flask provided with a magnetic stirrer and dissolved in 0.5 mL of diethyl ether, forming a yellow solution. Then a solution of 0.5 mL of (2-iodo-3,4,5,6-tetrafluorobenzene)diphenylphosphine **2** (29.1 mg, 0.06 mmol, 1 equiv.) and 2-PyPPh$_2$ **1** or 2-PyPPh$_2$ **7** (17.1 mg, 0.06 mmol, 1 equiv.) in Et_2O, previously stirred for five minutes, was added dropwise to the rhodium precursor solution. A change in colour from yellow to orange was observed during the addition. This solution was immediately transferred to a screw-capped NMR tube provided with a septum and a $(CD_3)_2CO$ insert. ^{31}P{^{1}H} NMR were recorded at 298 K in a 500 MHz spectrometer equipped with a cryoprobe every 10 minutes for 2 hours.

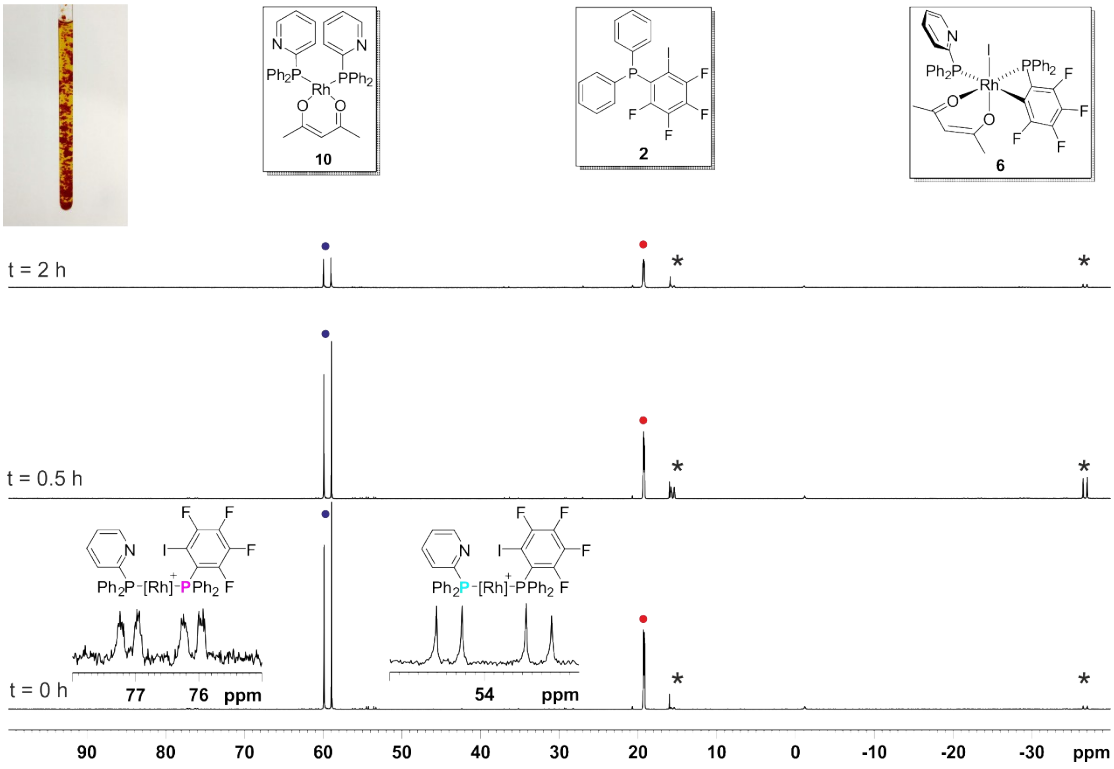


Figure SI 11. ^{31}P{^{1}H} NMR (202 MHz, CD_2Cl_2) stacked spectra for ligands **1**·**2**. Upon time consumption of **10** (●) and **2** (●) was observed, whilst **6** (*) was generated. After 0.5 hours, **6** started to crystallise (see figure), leading to the decrease of the signals intensity. Heterocomplexes were observed in the mixture (δ: 76.6 (dd, J = 207.5, 58.7 Hz), 53.9 (dd, J = 191.1, 54.9 Hz) ppm).

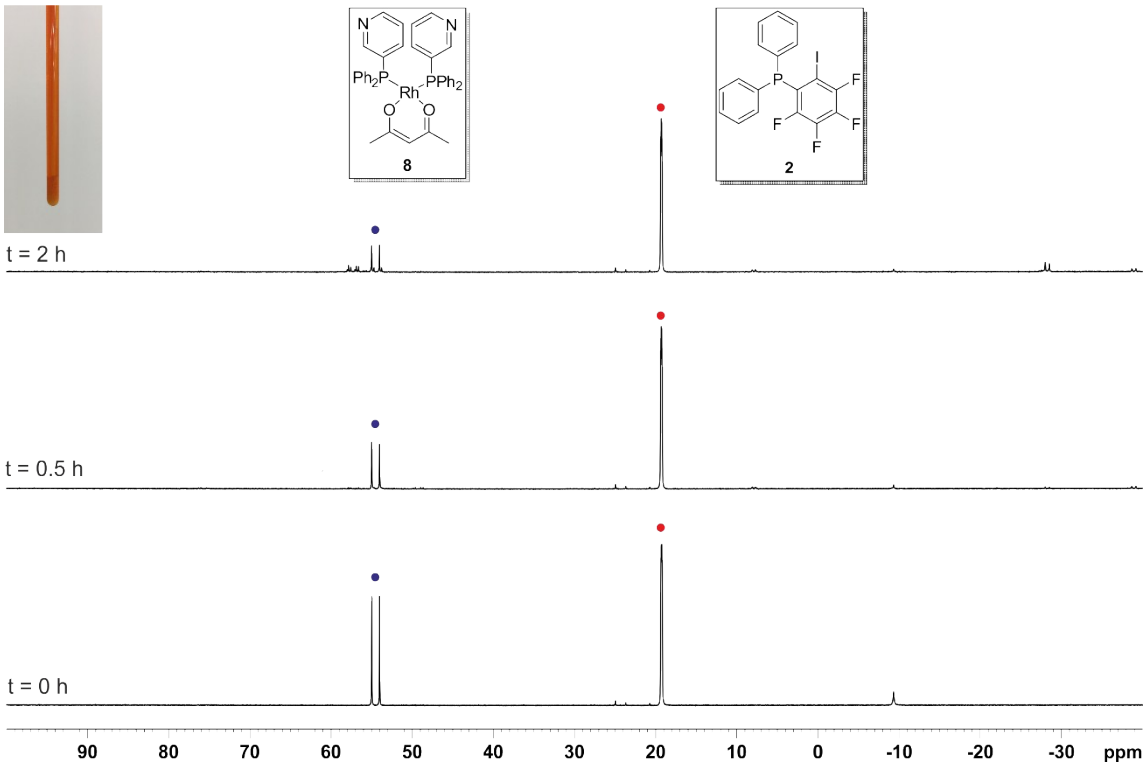


Figure SI 12. $^{31}P\{^{1}H\}$ NMR (202 MHz, CD_2Cl_2) stacked spectra for ligands **7**·**2**. Upon time consumption of **8** (●) was observed, whilst the concentration of **2** (●) was maintained. After 0.5 hours, **8** started to precipitate (see figure), leading to the decrease of the signals intensity.

8. Spectroscopic Data:

8.1. Spectroscopic NMR Data for ligand 7.

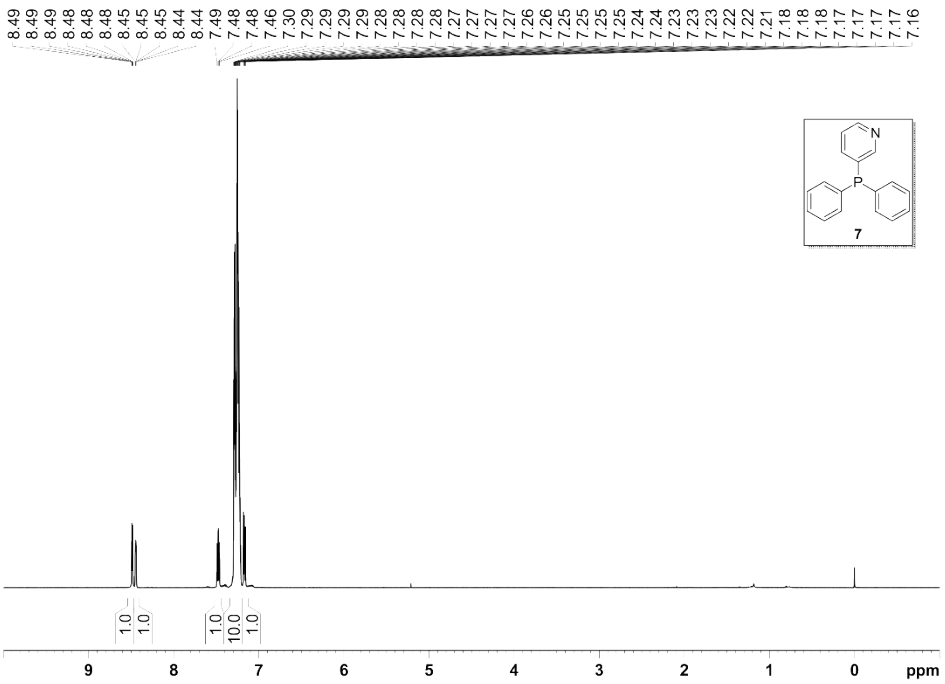


Figure SI 13. ^{1}H NMR (500 MHz, $CDCl_3$) for ligand **7**.

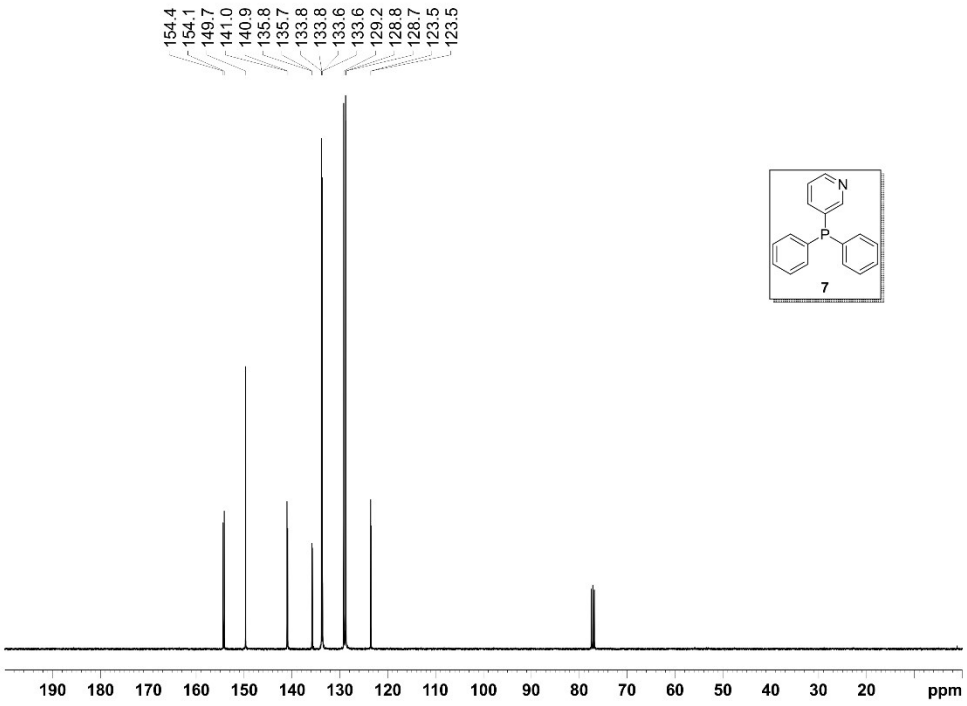


Figure SI 14. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) for ligand **7**.

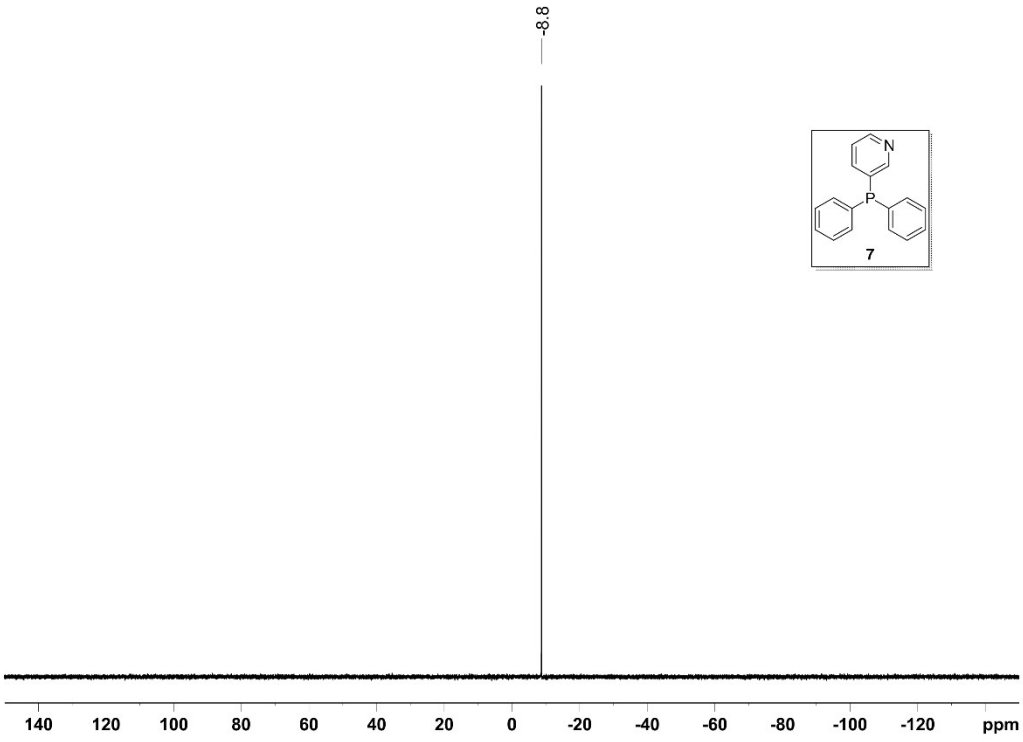


Figure SI 15. $^{31}P\{^{1}H\}$ NMR (202 MHz, $CDCl_3$) for ligand **7**.

8.2. Spectroscopic NMR and IR Data for Complexes 3, 4, 5, 8, 9, 10 and 11.

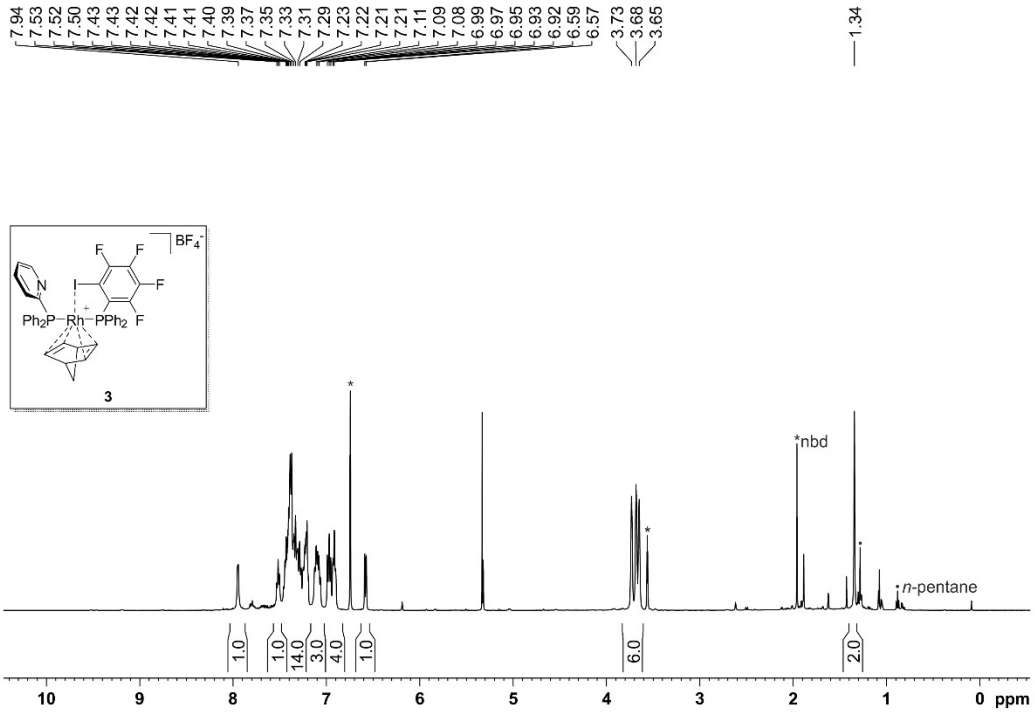


Figure SI 16. ^{1}H NMR (500 MHz, CD_2Cl_2) for complex **3**.

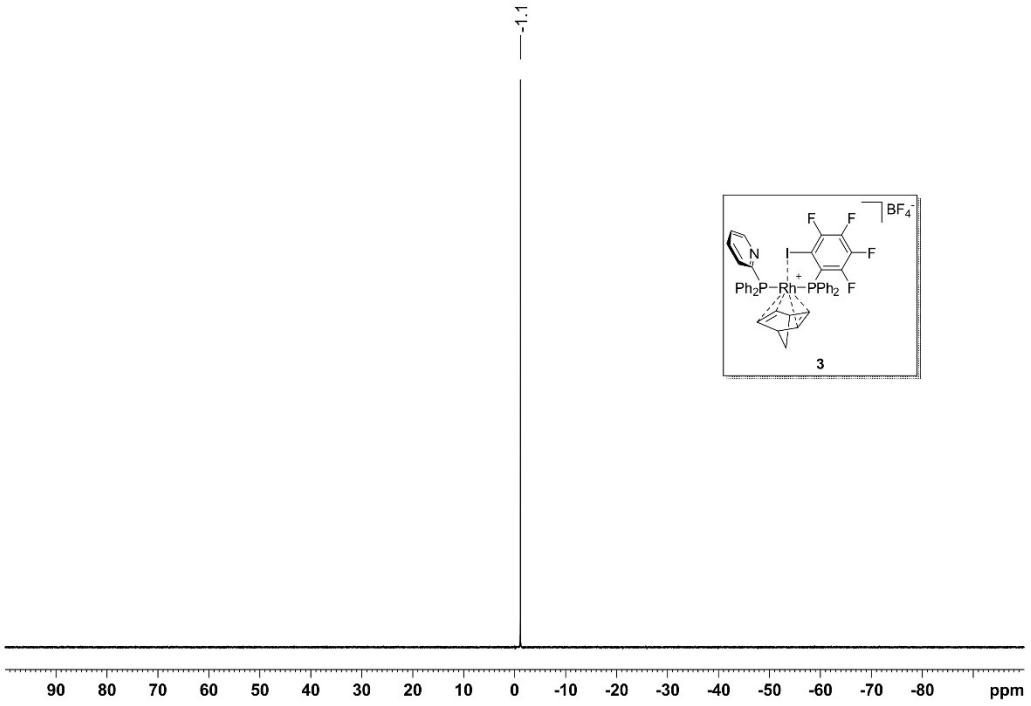


Figure SI 17. $^{11}B\{^{1}H\}$ NMR (160 MHz, CD_2Cl_2) for complex **3**.

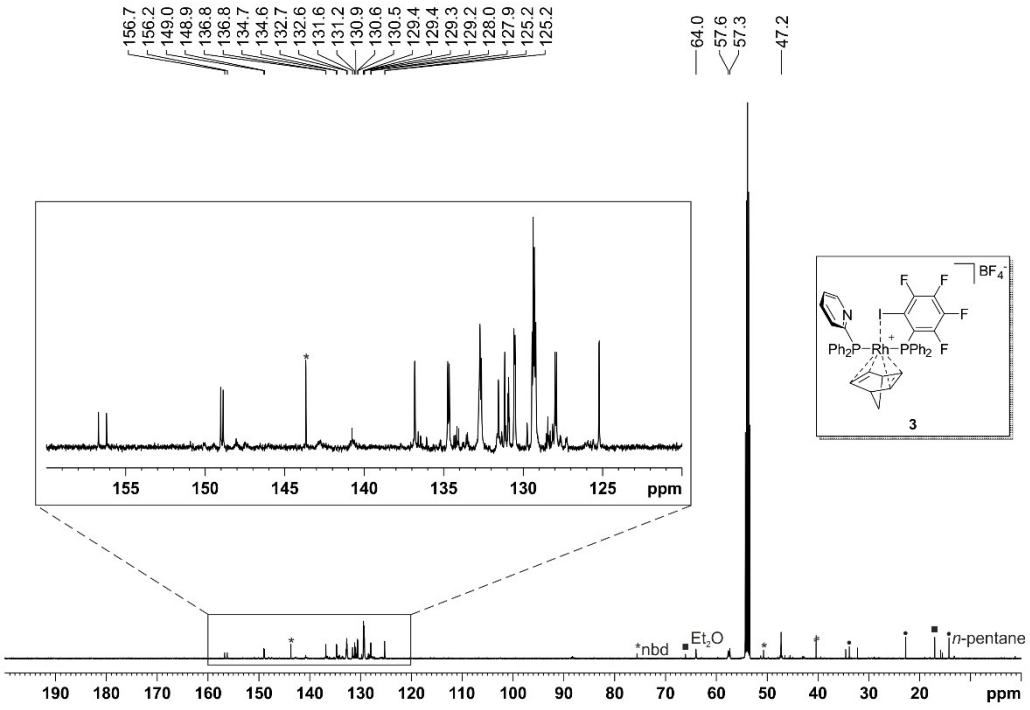


Figure SI 18. $^{13}C\{^{1}H\}$ NMR (126 MHz, CD_2Cl_2) for complex **3**.

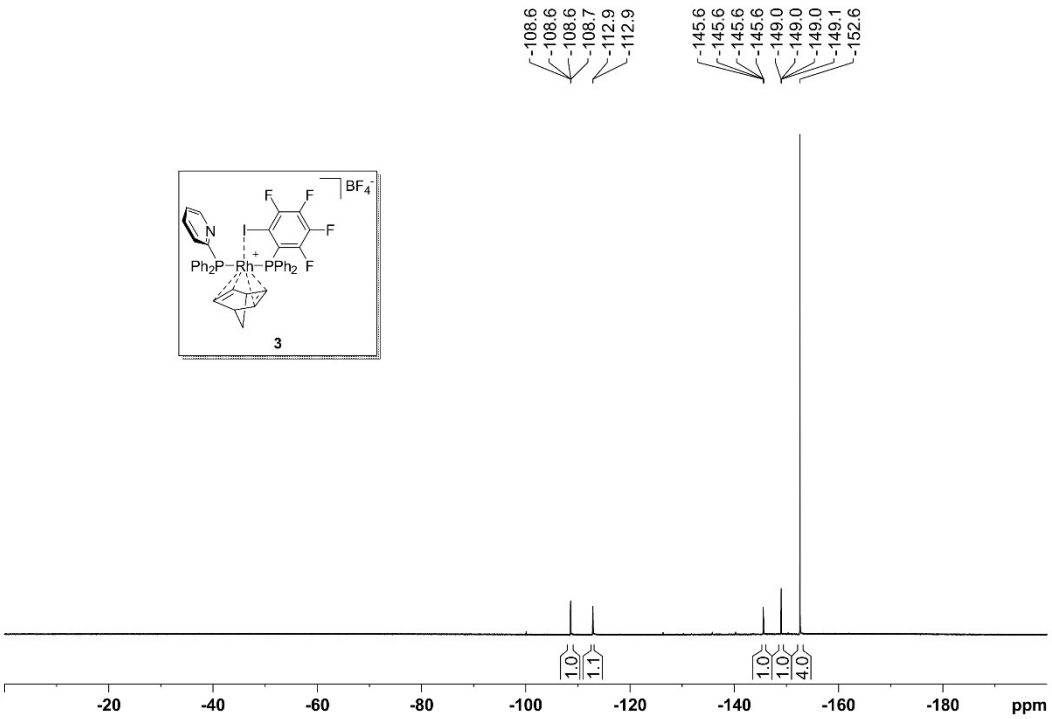


Figure SI 19. $^{19}F\{^{1}H\}$ NMR (471 MHz, CD_2Cl_2) for complex **3**.

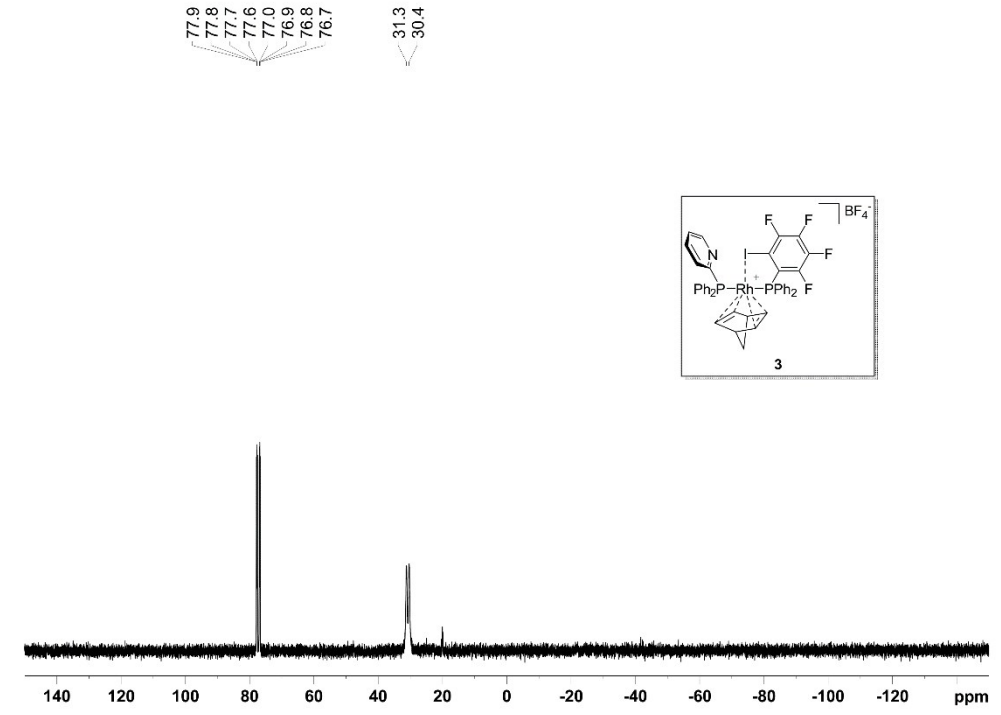


Figure SI 20. $^{31}P\{^{1}H\}$ NMR (162 MHz, CD_2Cl_2) for complex **3**.

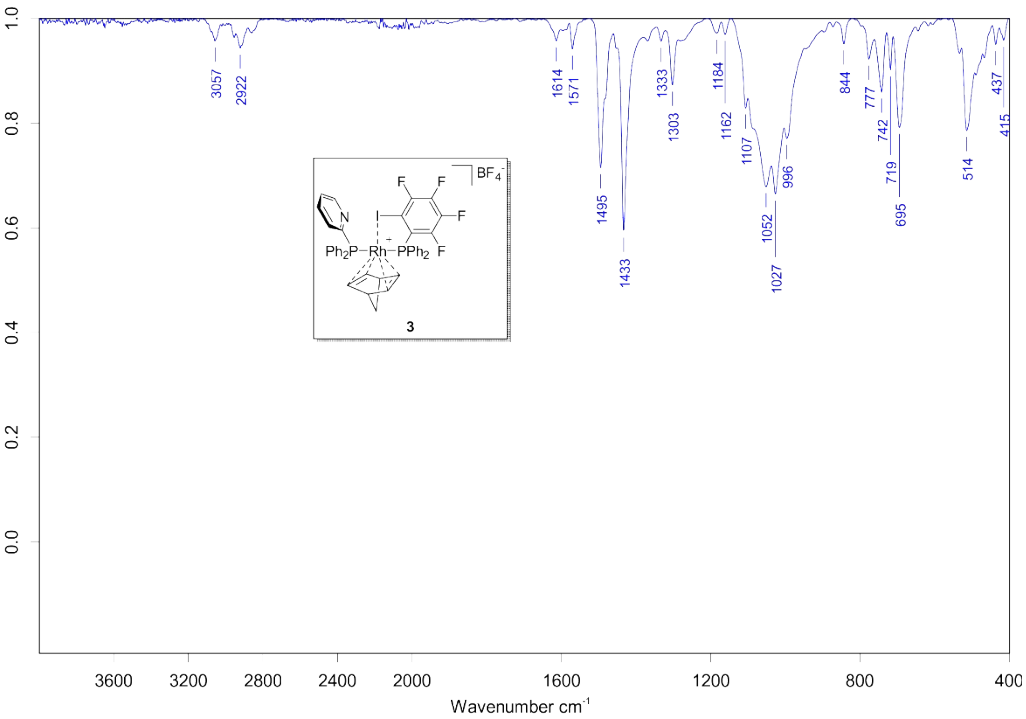


Figure SI 21. IR spectrum for complex **3**.

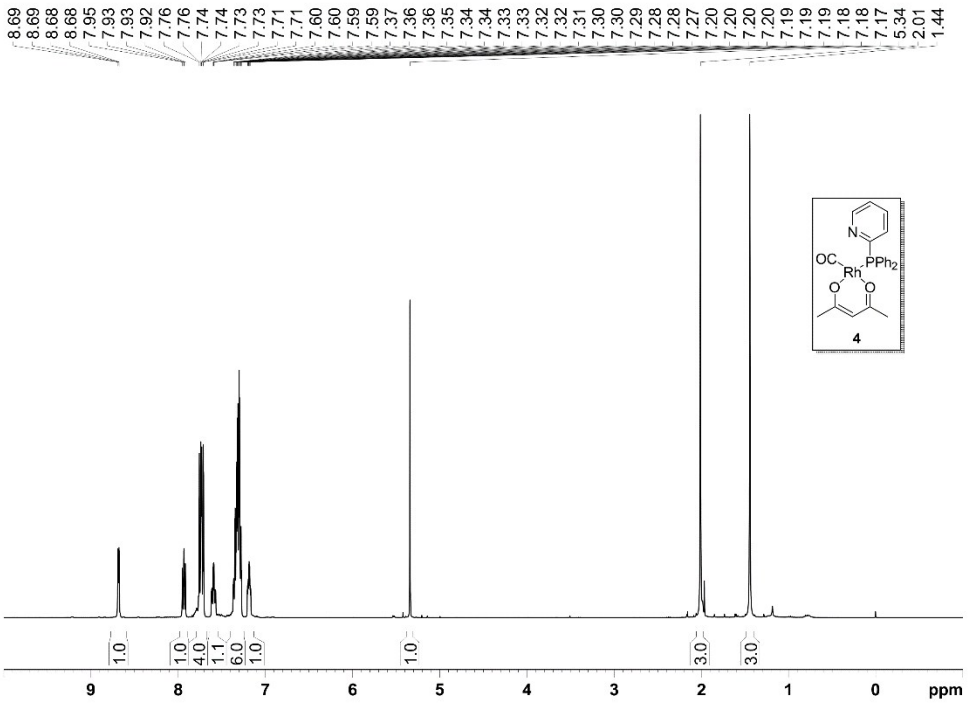


Figure SI 22. ^{1}H NMR (400 MHz, $CDCl_3$) for complex **4**.

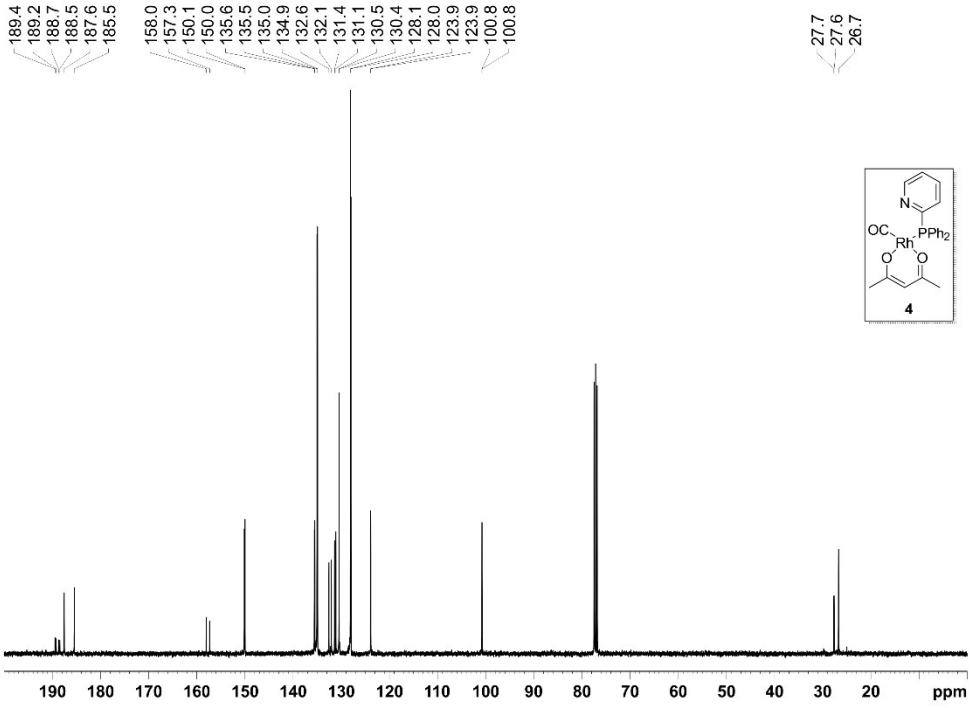


Figure SI 23. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) for complex **4**.

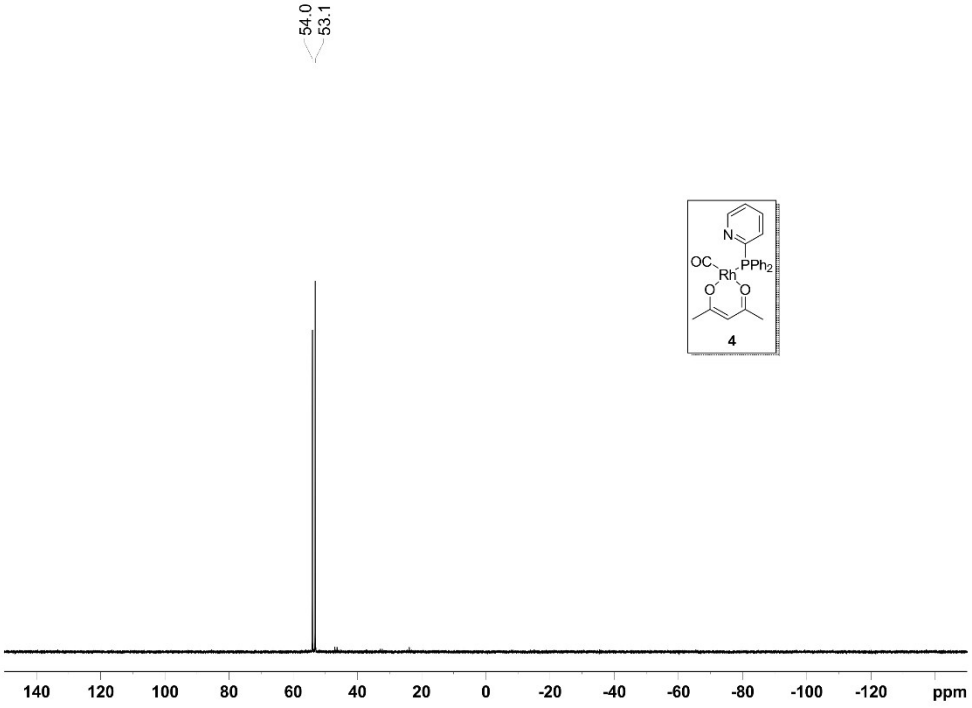


Figure SI 24. $^{31}P\{^{1}H\}$ NMR (202 MHz, $CDCl_3$) for complex **4**.

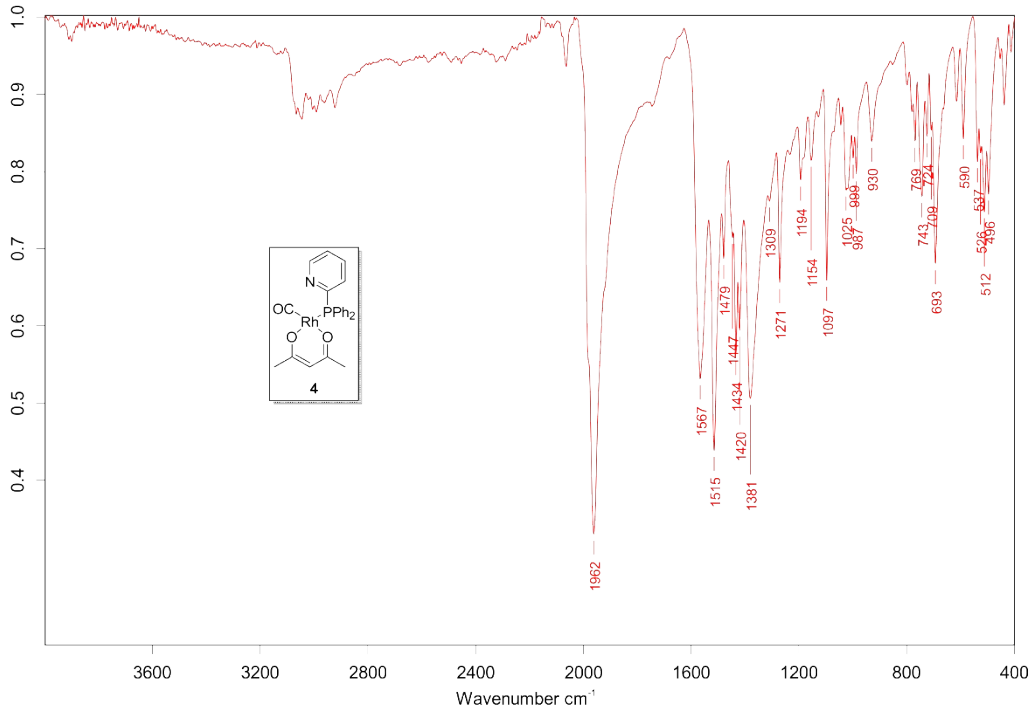


Figure SI 25. IR spectrum for complex **4**.

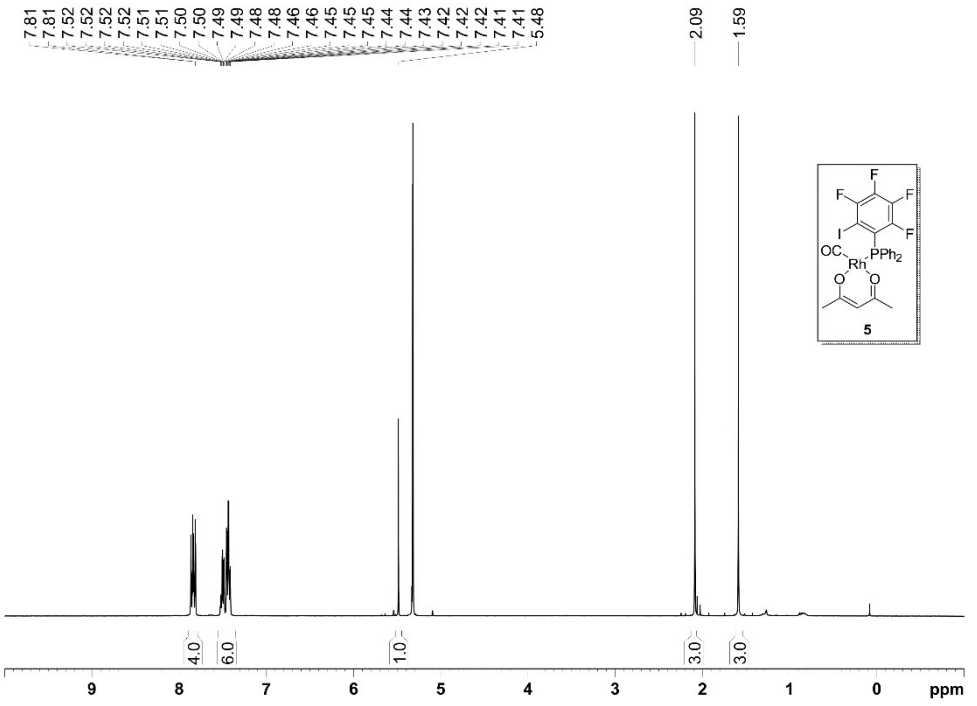


Figure SI 26. ^{1}H NMR (400 MHz, CD_2Cl_2) for complex **5**.

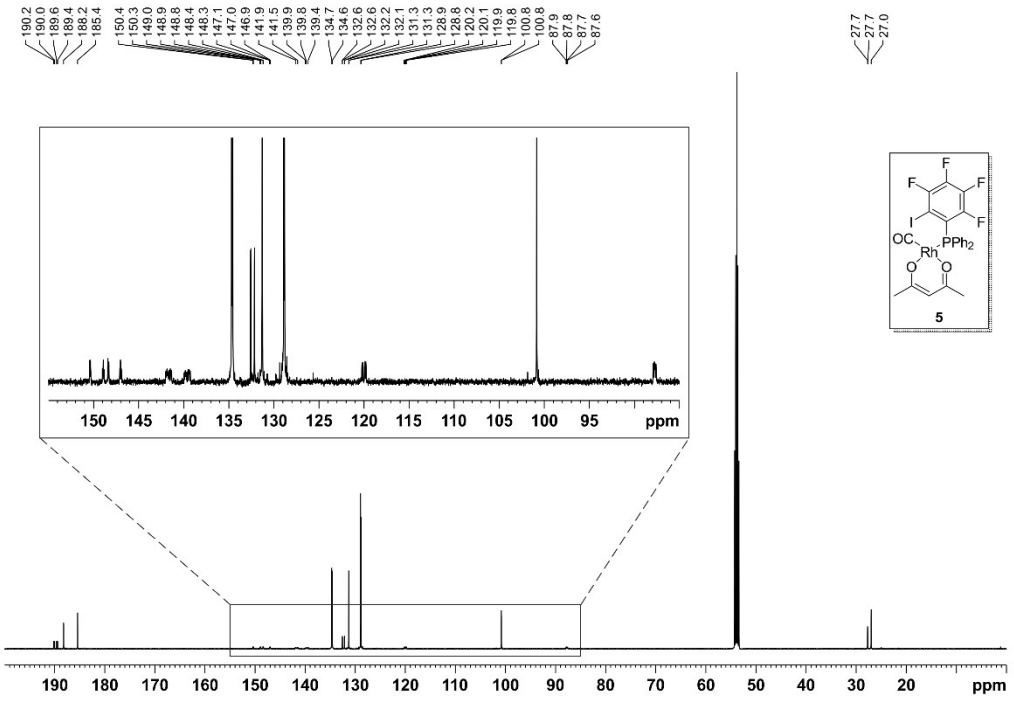


Figure SI 27. $^{13}C\{^{1}H\}$ NMR (126 MHz, CD_2Cl_2) for complex **5**.

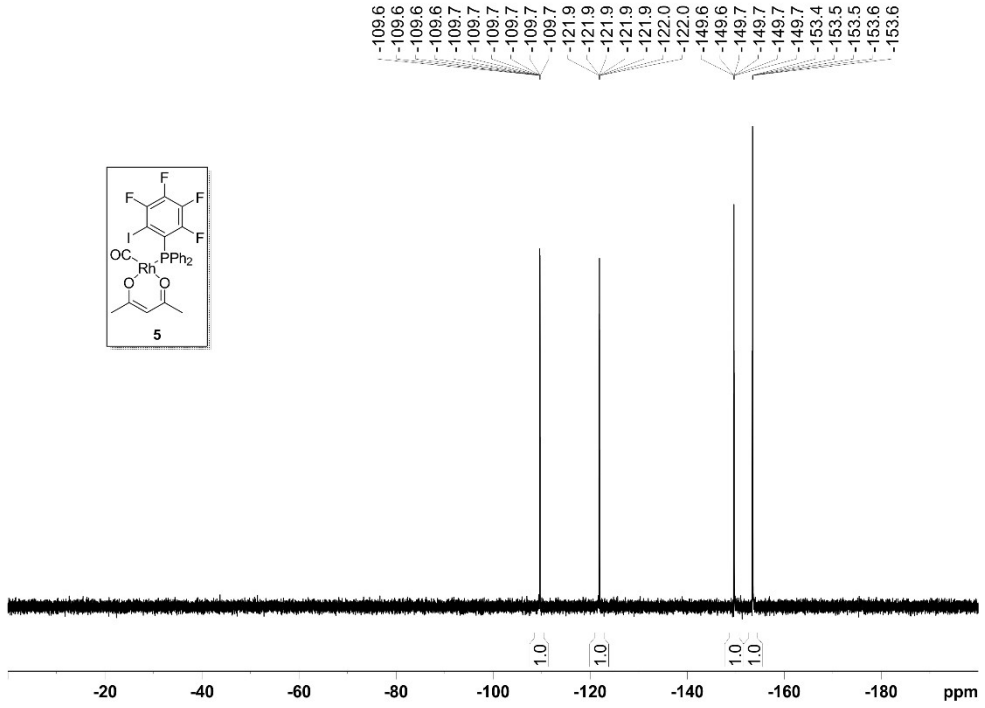


Figure SI 28. $^{19}F\{^{1}H\}$ NMR (376 MHz, CD_2Cl_2) for complex **5**.

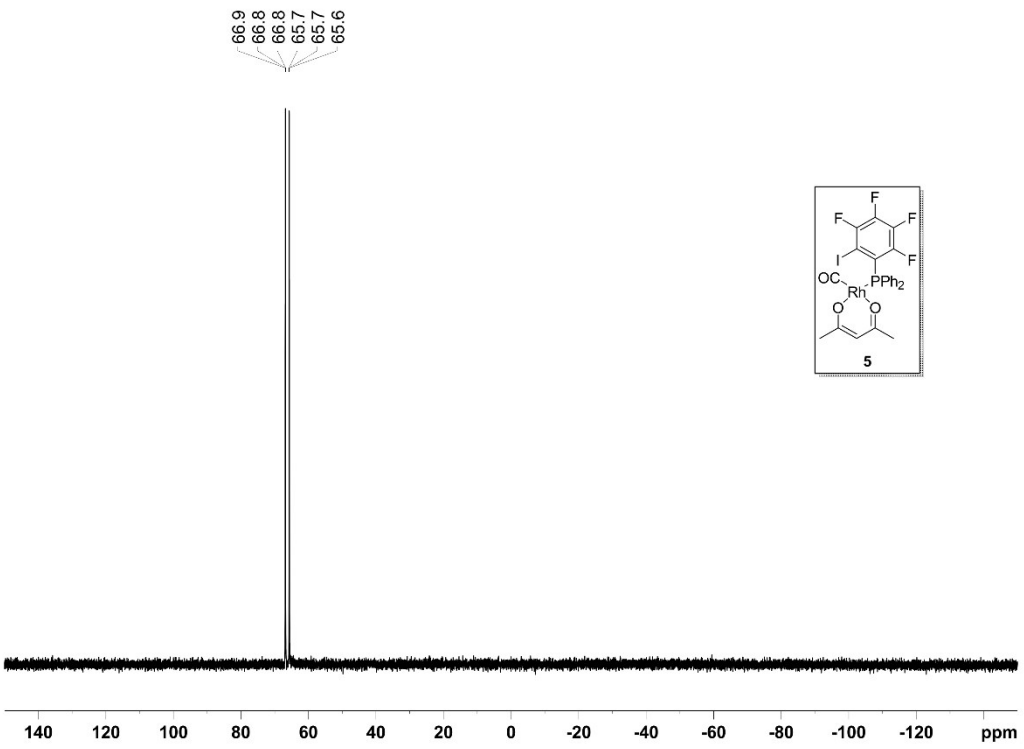


Figure SI 29. $^{31}P\{^{1}H\}$ NMR (162 MHz, CD_2Cl_2) for complex **5**.

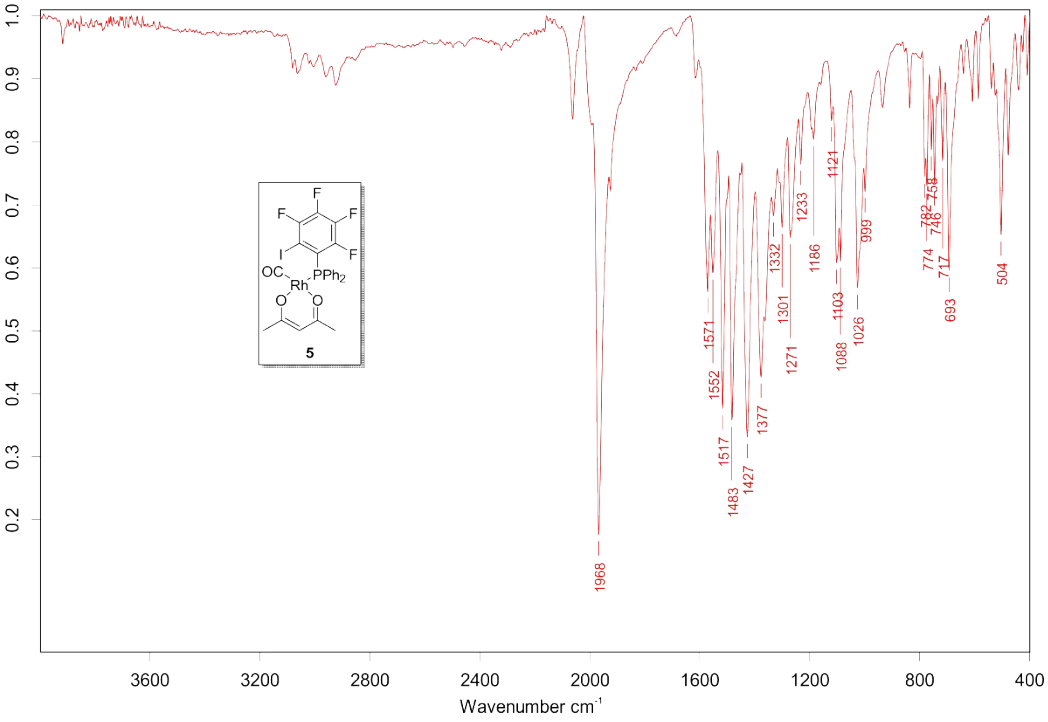


Figure SI 30. IR spectrum for complex **5**.

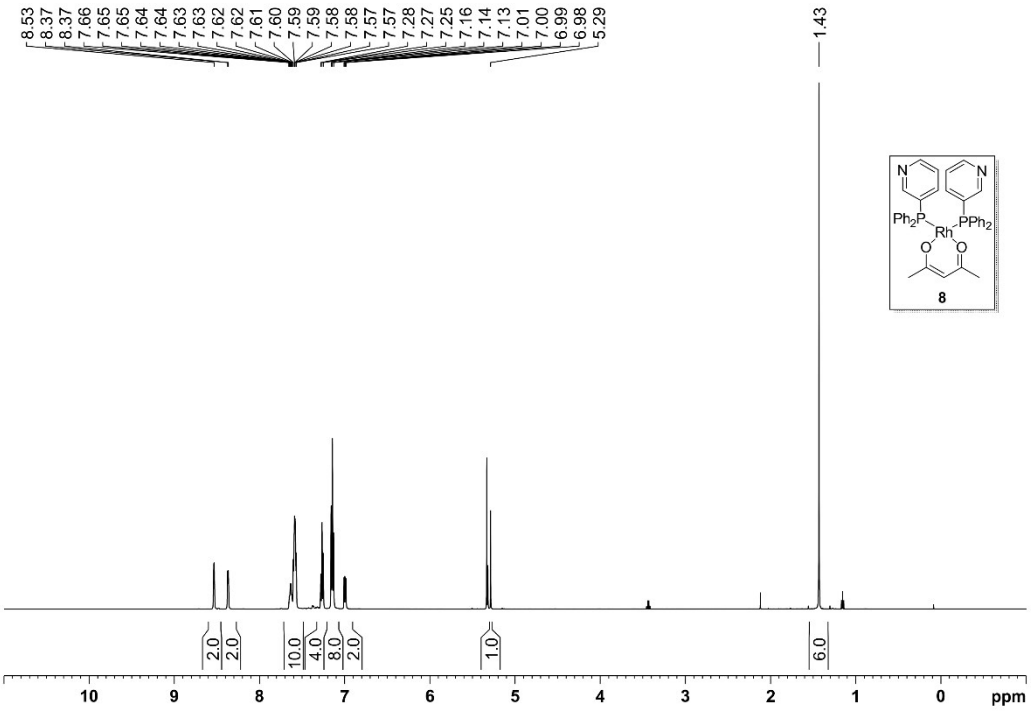


Figure SI 31. ^{1}H NMR (500 MHz, CD_2Cl_2) for complex **8**.

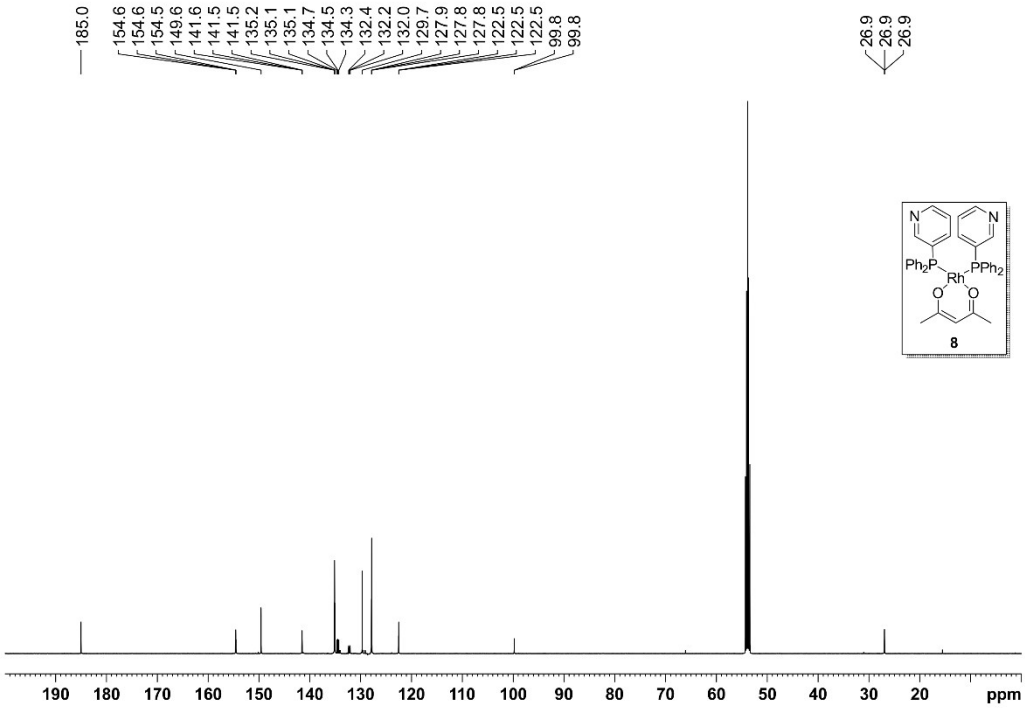


Figure SI 32. $^{13}C\{^{1}H\}$ NMR (126 MHz, CD_2Cl_2) for complex **8**.

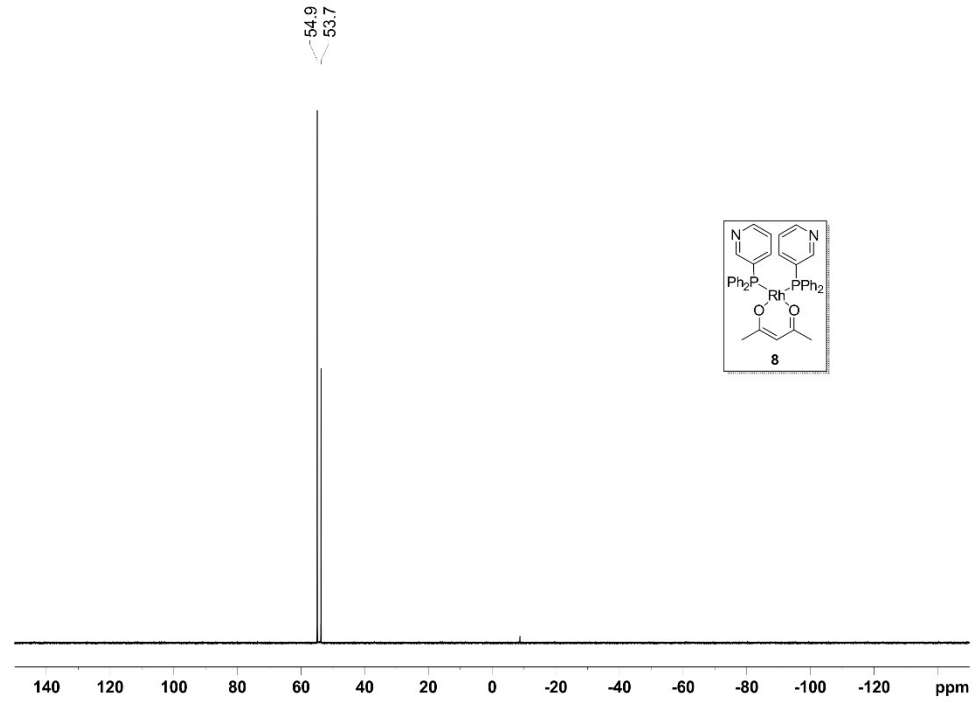


Figure SI 33. $^{31}P\{^{1}H\}$ NMR (162 MHz, CD_2Cl_2) for complex **8**.

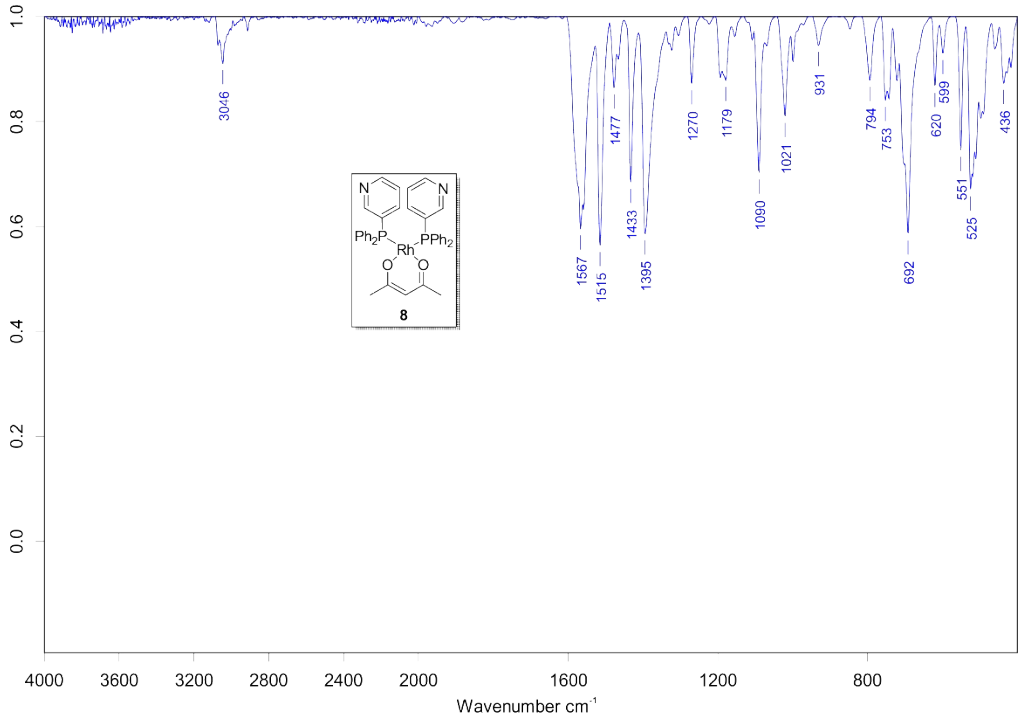


Figure SI 34. IR spectrum for complex **8**.

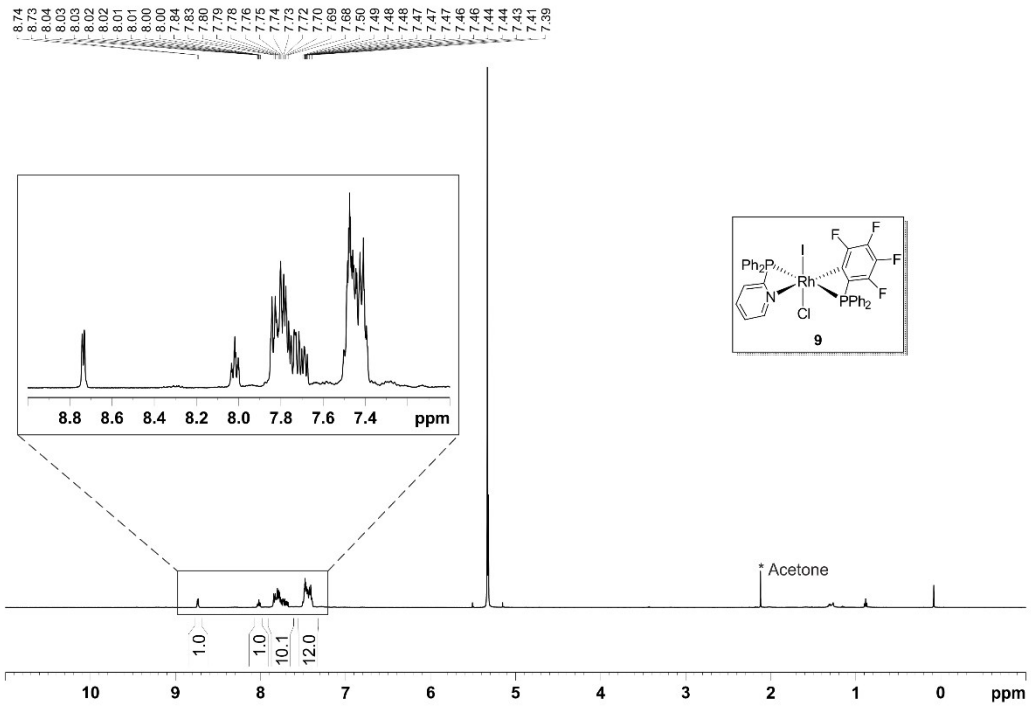


Figure SI 35. ^{1}H NMR (500 MHz, CD_2Cl_2) for complex **9**.

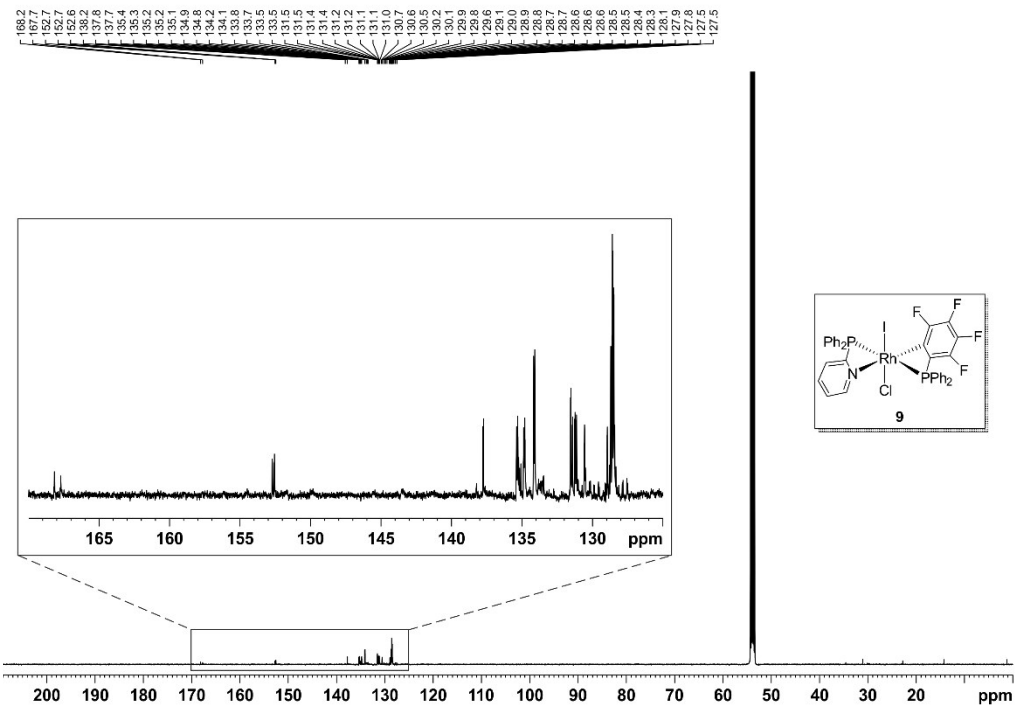


Figure SI 36. $^{13}C\{^{1}H\}$ NMR (126 MHz, CD_2Cl_2) for complex **9**.

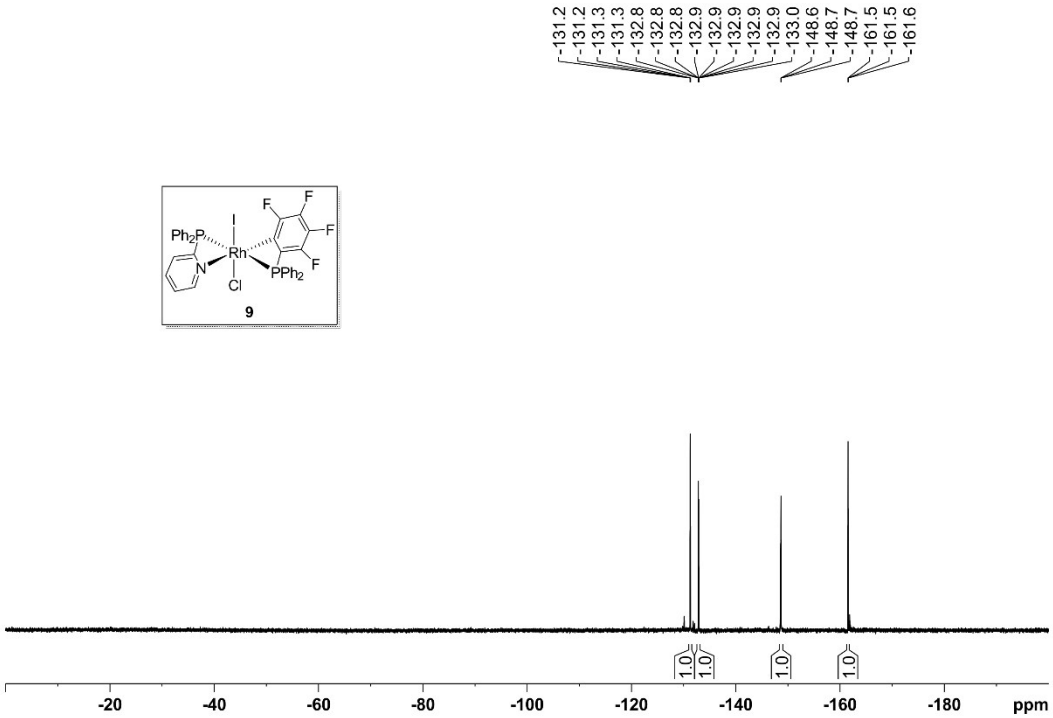


Figure SI 37. $^{19}F\{^{1}H\}$ NMR (471 MHz, CD_2Cl_2) for complex **9**.

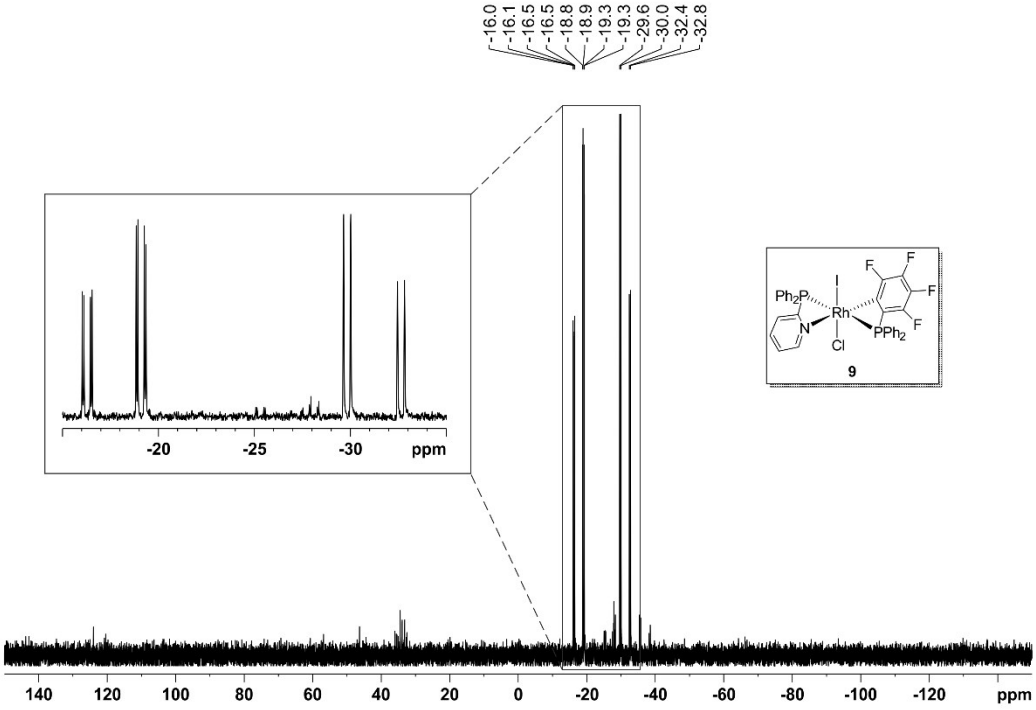


Figure SI 38. $^{31}P\{^{1}H\}$ NMR (202 MHz, CD_2Cl_2) for complex **9**.

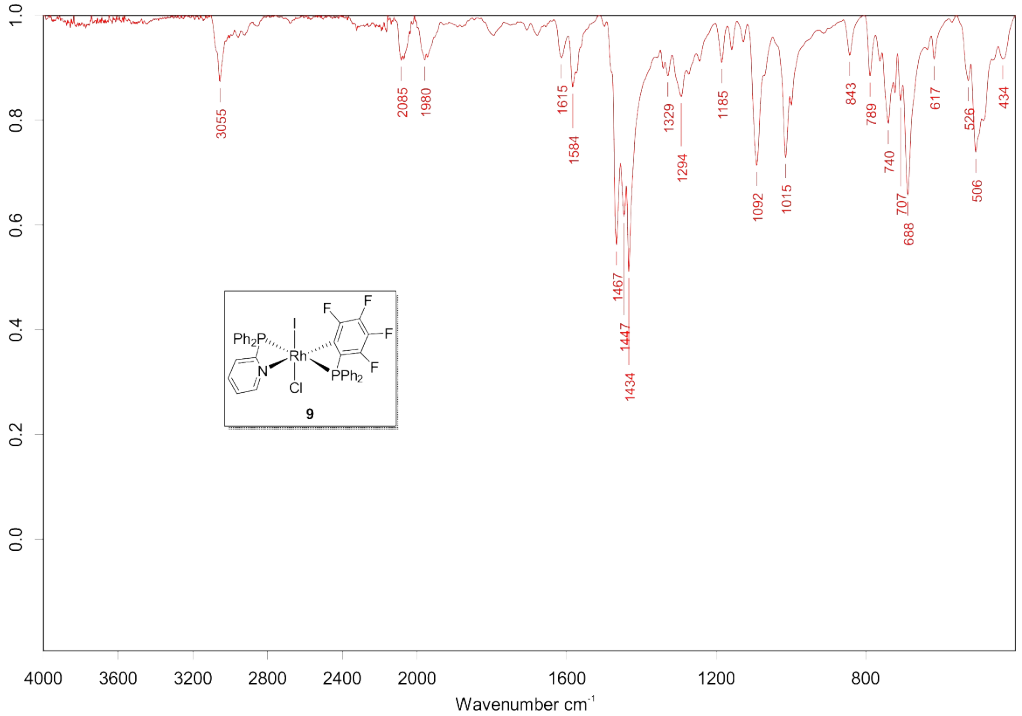


Figure SI 39. IR spectrum for complex **9**.

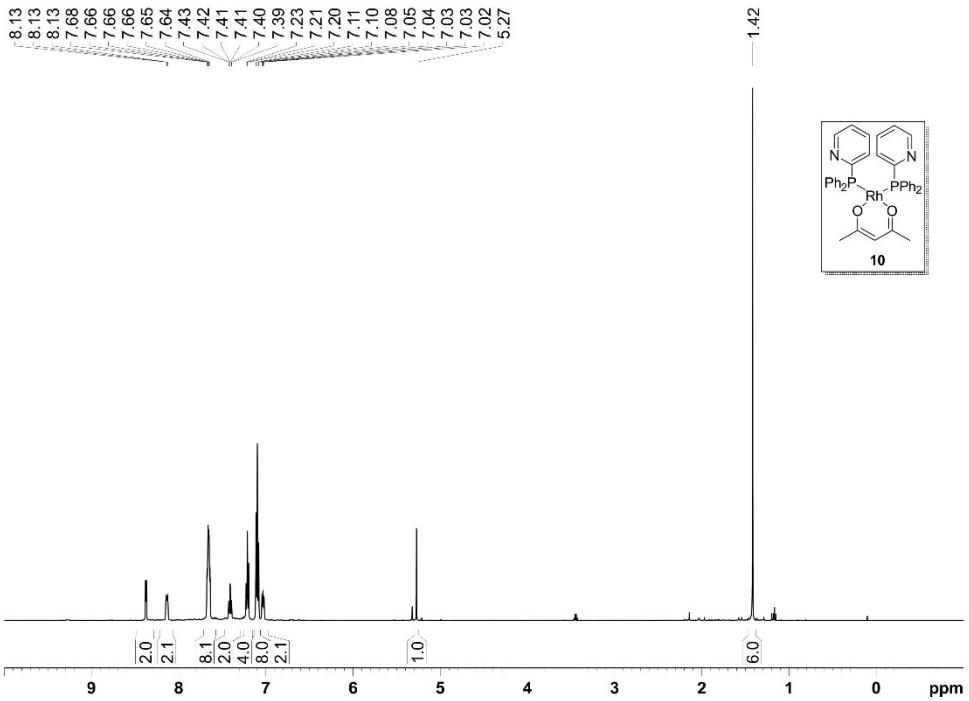


Figure SI 40. ^{1}H NMR (500 MHz, CD_2Cl_2) for complex **10**.

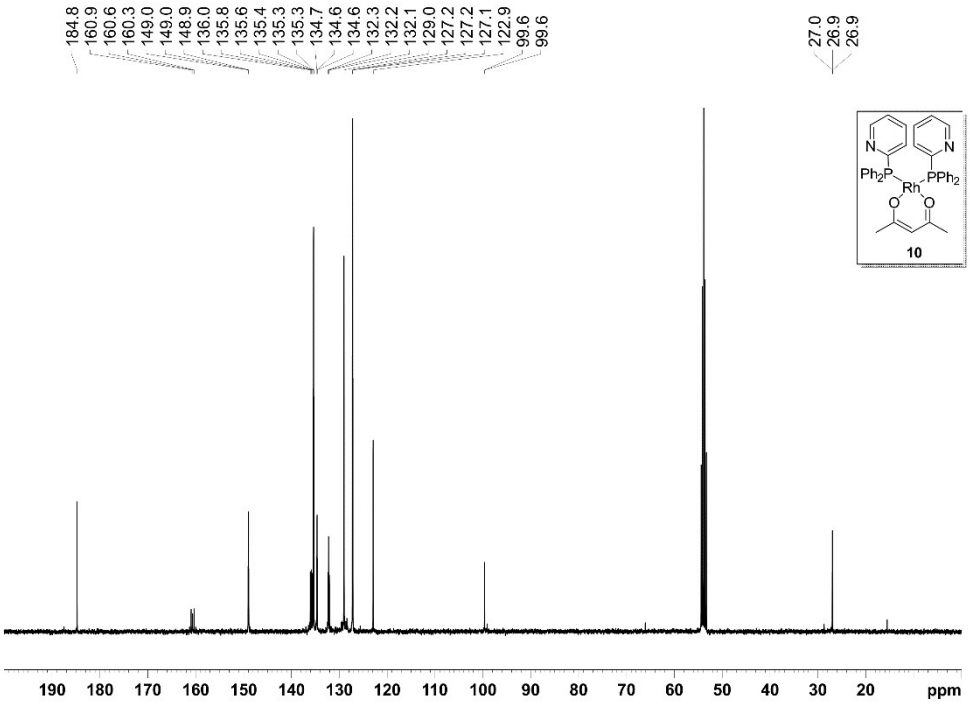


Figure SI 41. $^{13}C\{^{1}H\}$ NMR (100 MHz, CD_2Cl_2) for complex **10**.

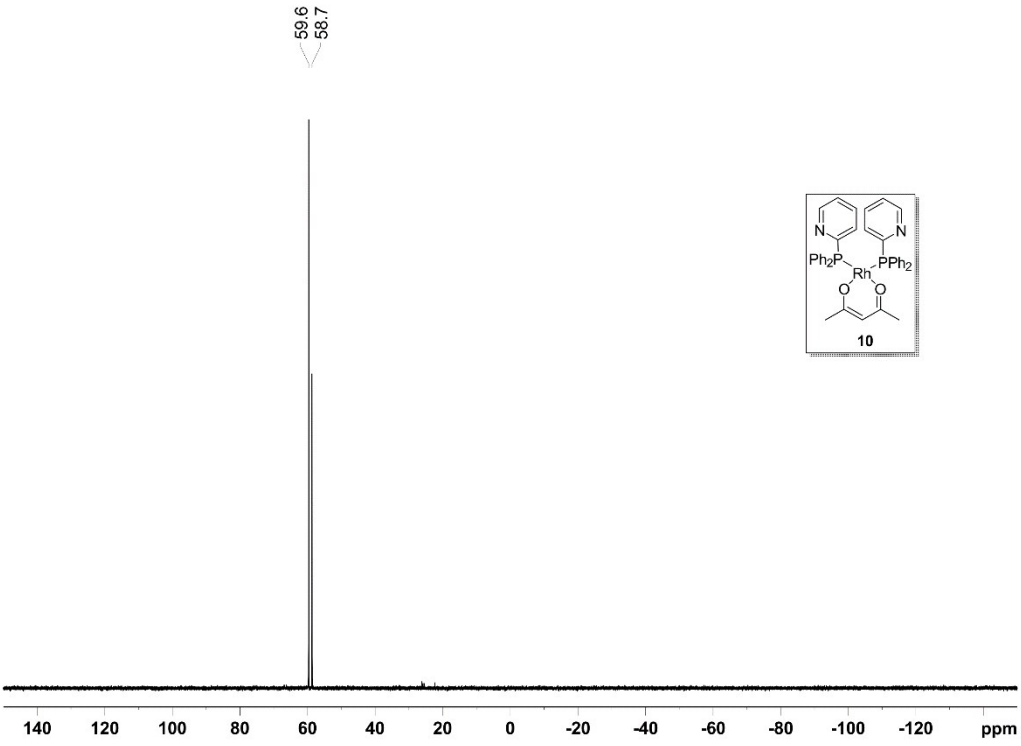


Figure SI 42. $^{31}P\{^{1}H\}$ NMR (202 MHz, CD_2Cl_2) for complex **10**.

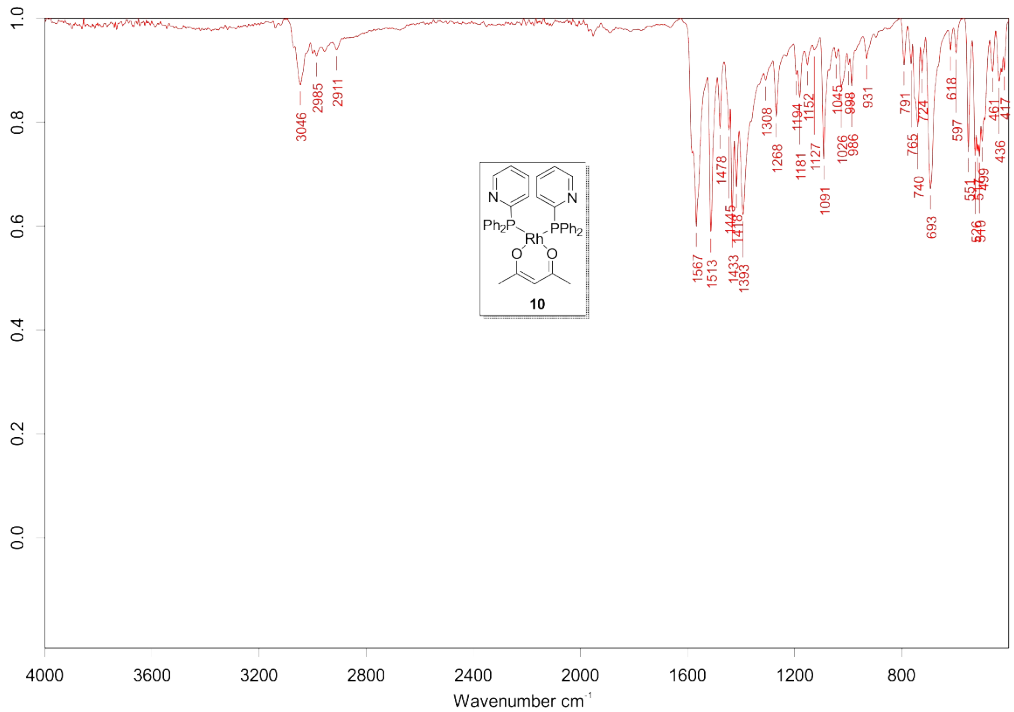


Figure SI 43. IR spectrum for complex **10**.

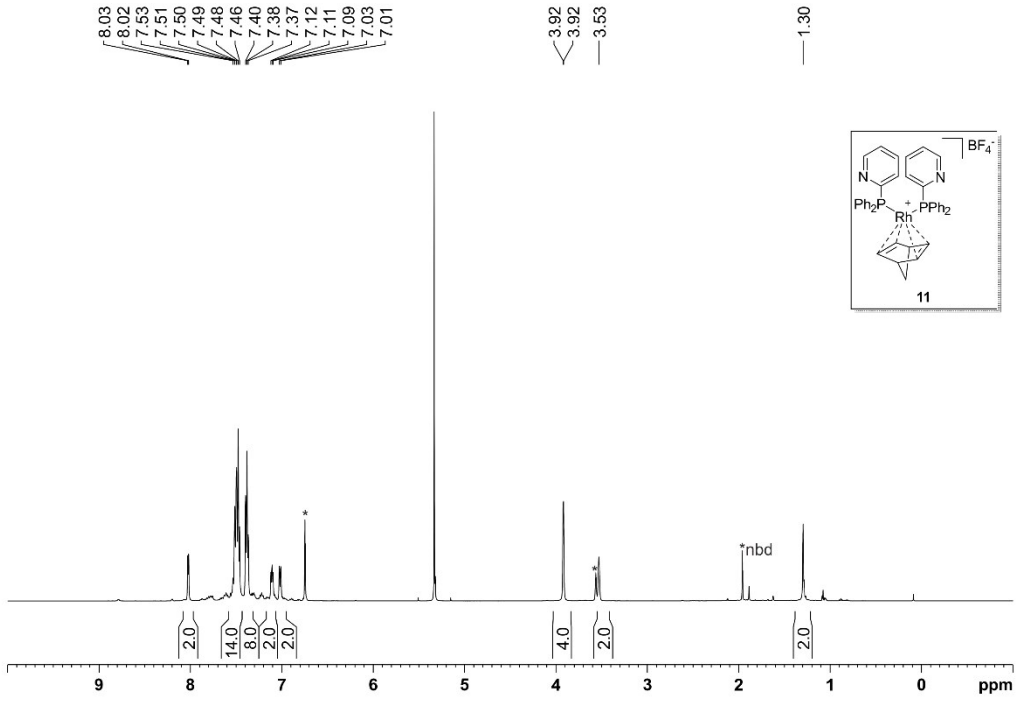


Figure SI 44. ^{1}H NMR (500 MHz, CD_2Cl_2) for complex **11**.

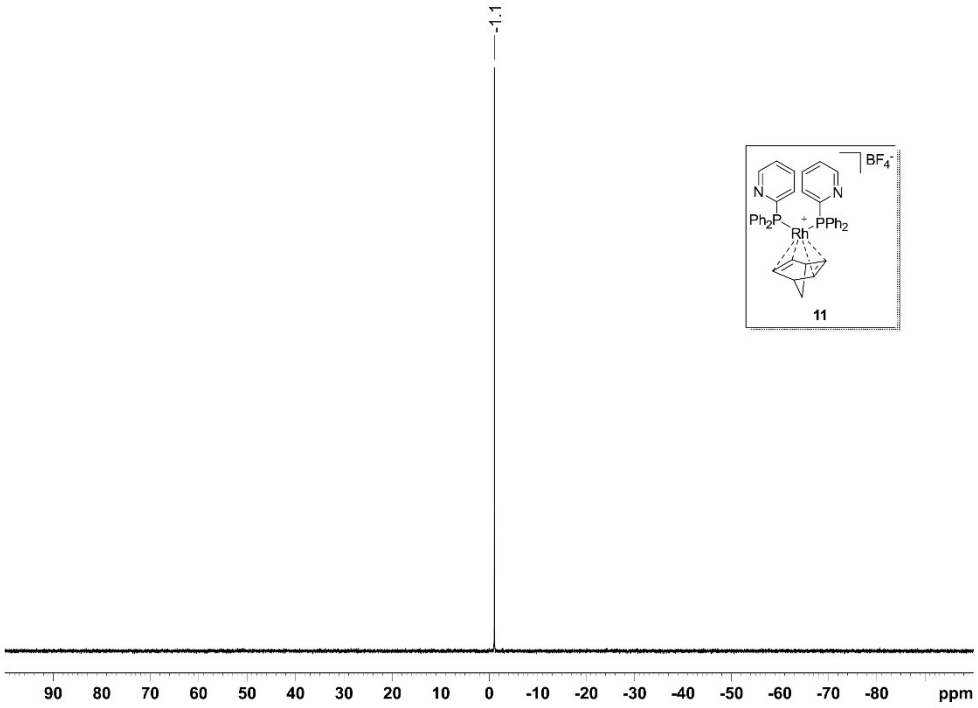


Figure SI 45. $^{11}B\{^{1}H\}$ NMR (128 MHz, CD_2Cl_2) for complex **11**.

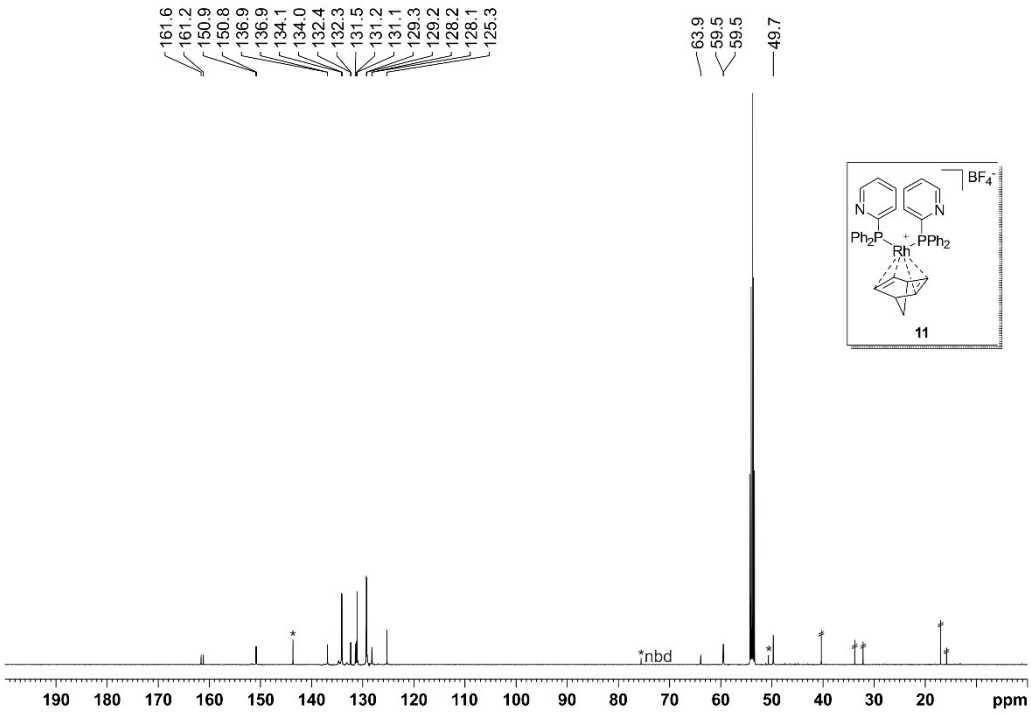


Figure SI 46. $^{13}C\{^{1}H\}$ NMR (126 MHz, CD_2Cl_2) for complex **11**.

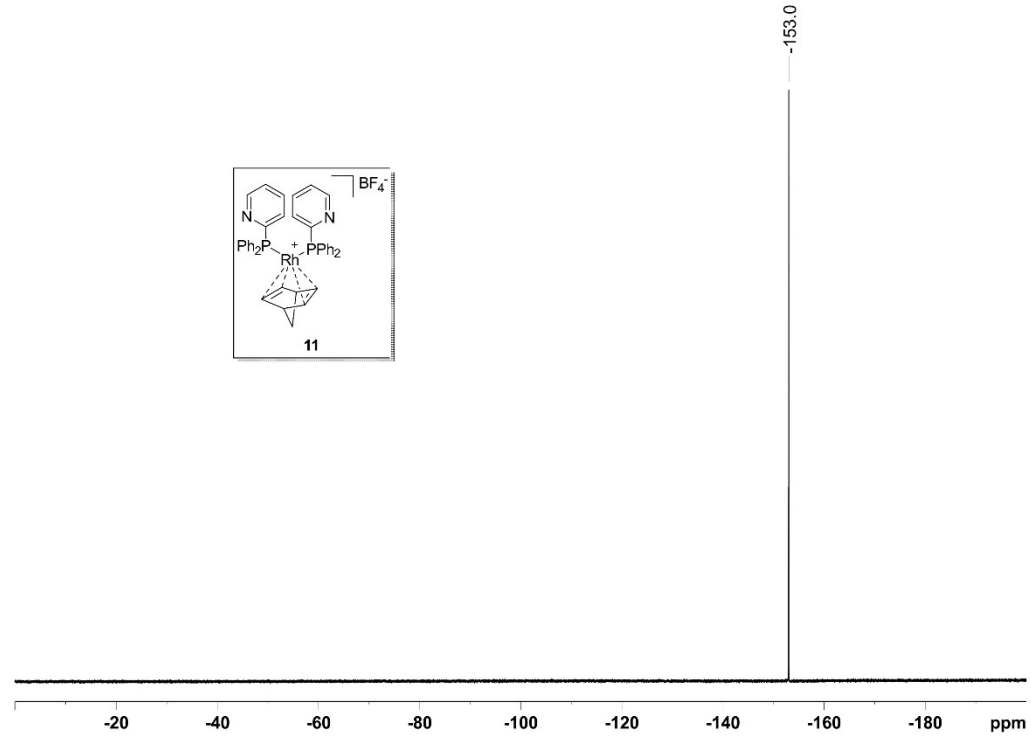


Figure SI 47. $^{19}F\{^{1}H\}$ NMR (376 MHz, CD_2Cl_2) for complex **11**.

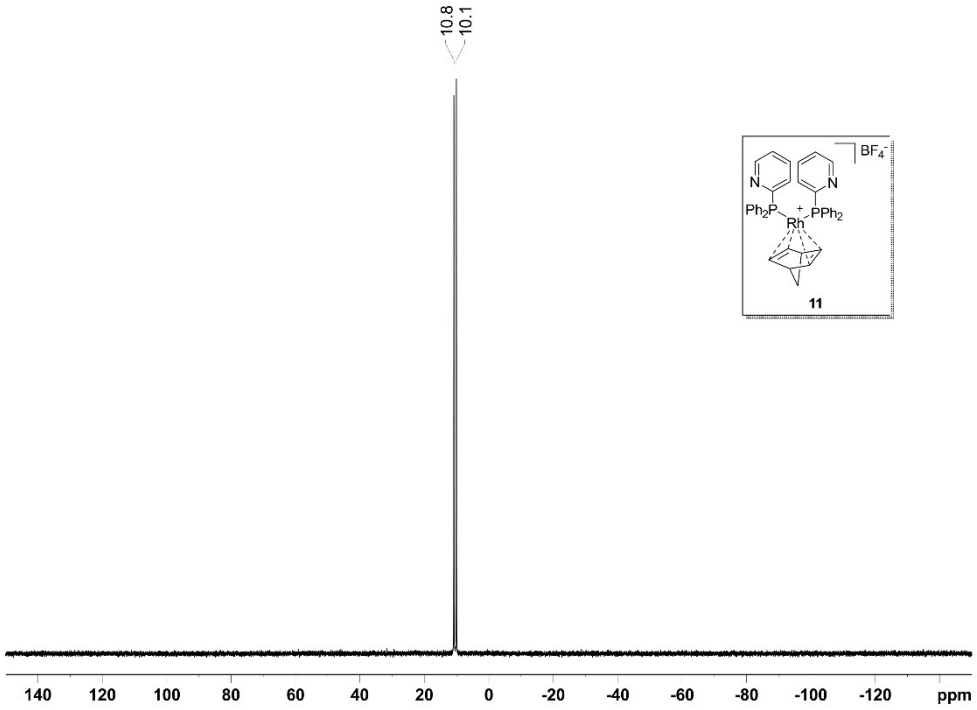


Figure SI 48. $^{31}P\{^{1}H\}$ NMR (162 MHz, CD_2Cl_2) for complex **11**.

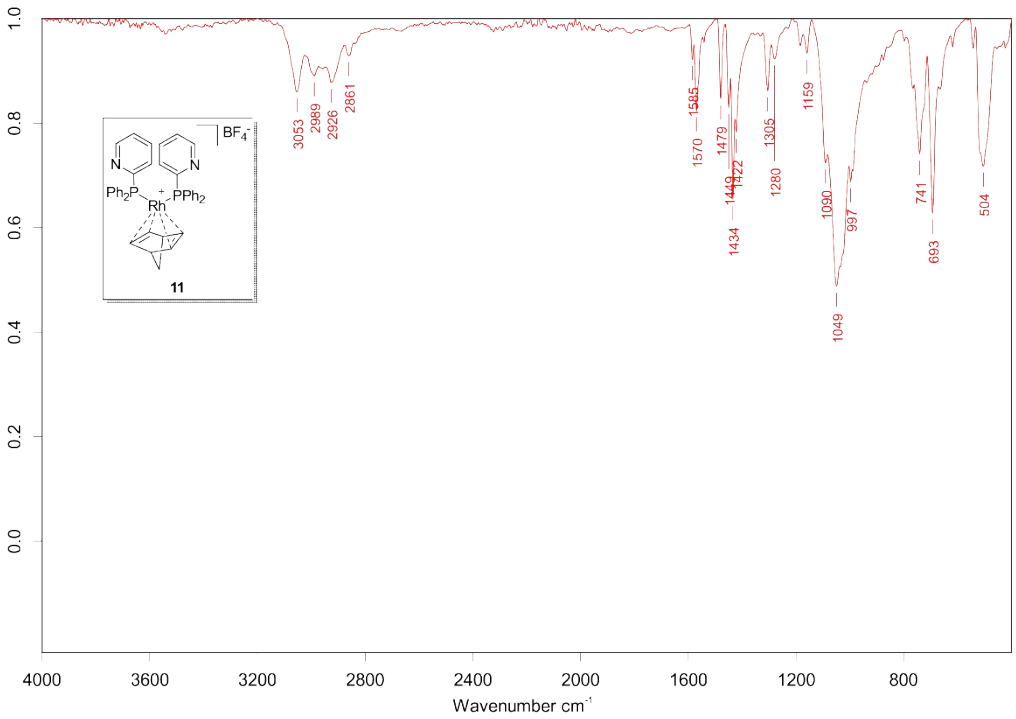


Figure SI 49. IR spectrum for complex **11**.

9. Computational Methods:

All geometry optimisations were carried out using the M06-2X hybrid functional[20] at LANL2DZ level of theory implemented in Gaussian 09 package.[21] Analysis of corresponding frequencies were performed to characterise structures of minima (N_{imag} = 0) or transition states (N_{imag} = 1). Product of oxidative addition (**6**) was optimised from X-ray structure as jumping-off place and transition state connecting reagent/intermediate and products was calculated using the quadratic synchronous transit (QST3) approach[22] and verified by having only one imaginary frequency.

Molecular Electrostatic Potential (MEP) surfaces (isosurface, 0.001 a.u.) have been computed at the same level for optimisations. Solvent effects (diethyl ether) on the energies (kcal·mol^{-1}) were considered using the polarisable continuum model (PCM) with the integral equation formalism variant (IEFPCM).[23]

The NCIplot[24] isosurfaces have been used to confirm the halogen bonding interaction in the transition state. The favourable or unfavourable interaction is evaluated by the isosurface colour from red for ρ^{+}cut (repulsive) to blue for ρ^{-}cut (attractive).

9.1. MEP Surfaces.

In Figure SI 50 we show the MEP surfaces of phosphine **1** (left) and **2** (right) and it can be observed that the MEP at the N atom of **1** is large and negative (–38 kcal/mol) and at the extension of the C–I bond in **2** is large and positive, thus anticipating a strong halogen bonding interaction between both ligands.

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[20] Y. Zhao and D. G. Truhlar, *Theor. Chem. Acc.*, 2008, **120**, 215-241.

[21] Gaussian 09, Revision C.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford, CT, 2009.

[22] J. B. Foresman and Æ. Frisch, Exploring Chemistry with Electronic Structure Methods, 3rd Ed. (Gaussian, Inc., Wallingford, CT, 2015). ISBN: 978-1-935522-03-4.

[23] J. Tomasi, B. Mennucci, and R. Cammi, *Chem. Rev.*, 2005, **105**, 2999-3093.

[24] J. Contreras-García, E. R. Johnson, S. Keinan, R. Chaudret, J.-P. Piquemal, D. N. Beratan and W. Yang, *J. Chem. Theory Comput.*, 2011, **7**, 625-632.

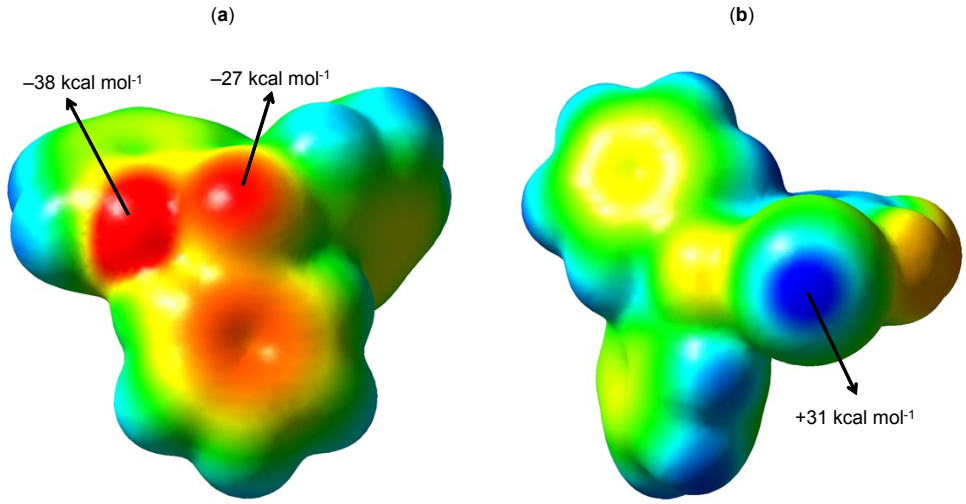

Figure SI 50. Molecular electrostatic potential (MEP) of ligands: (a) **1** and (b) **2**, computed on the 0.001 a.u. contour of the electronic density at M06-2X/LANL2DZ level.

9.2. Optimised Structure of the Intermediate Using Phosphine 7.

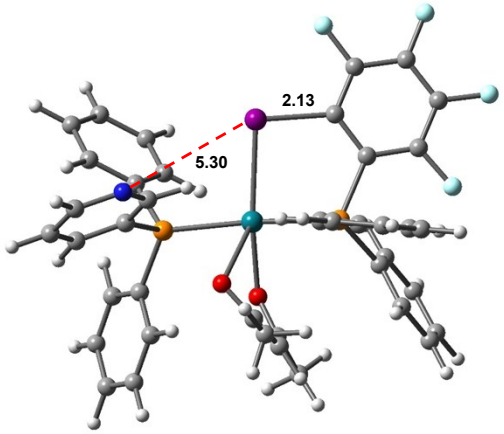

Figure SI 51. Optimised intermediate (N_{imag} = 0) derived from ligand **7** at M06-2X/LANL2DZ level.

9.3. NCIplot Index

We have also computed the "Non-Covalent Interaction plot" (NCIplot) index in order to characterise the halogen bonding interaction in the TS. The NCIplot is an intuitive visualisation index that enables the identification of non-covalent interactions efficiently. The NCIplot is convenient to analyse host-guest interactions since it clearly shows which molecular regions interact. The colour scheme is a red-yellow-green-blue scale with red (repulsive) and blue (attractive). Yellow and green surfaces correspond to weak repulsive and weak attractive interactions, respectively. The representation of the NCIplot is shown in Figure SI 52. As noted, the intermolecular C–I···N contact is characterised by a small and green isosurfaces located between both donor N-atom and the iodine.

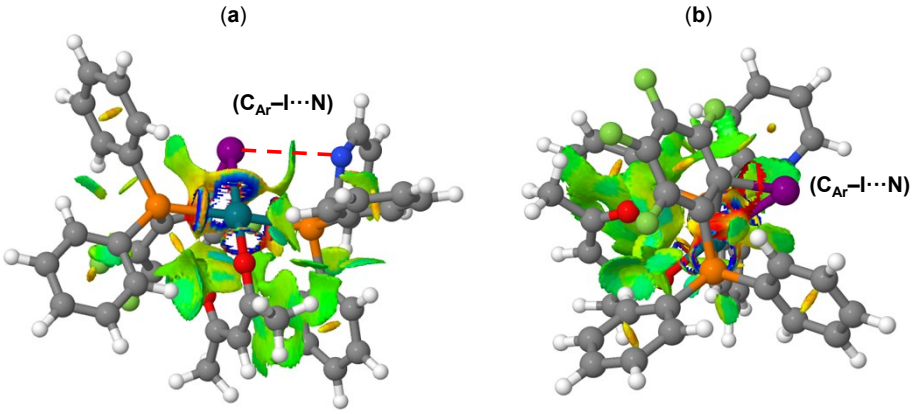

Figure SI 52. NCI surface of transition state (TS) at two point of views. The gradient cut-off is s = 0.50 a.u., and the colour scale is $-0.04 < \rho < 0.04$ a.u.

9.4. Cartesian Coordinates of Optimised Reactants, Intermediates, TS and Products.

Ligand **1**:

P	0.03715300	0.01758800	-1.28137400
C	0.68988100	1.54650000	-0.38961600
C	-0.12928100	2.42856000	0.33971500
C	2.54811400	2.92045200	-0.06080900
C	0.43691100	3.59383200	0.87701800
H	-1.18041400	2.20762800	0.48316400
C	1.80154100	3.84821200	0.67938500
H	3.60562700	3.07354100	-0.24706500
H	-0.17782600	4.28726700	1.44123700
H	2.27574600	4.73693200	1.07851500
N	2.00758700	1.80278100	-0.59109700
C	0.98875900	-1.37246900	-0.43202600
C	0.33414100	-2.59664400	-0.19119100
C	2.36150200	-1.26093100	-0.14557900
C	1.03515600	-3.68401600	0.34967900
H	-0.72362700	-2.70370400	-0.41679100
C	3.05809100	-2.35026300	0.40149500
H	2.87681200	-0.32880600	-0.35206000
C	2.40017300	-3.56331000	0.65223200
H	0.51669800	-4.61993700	0.53226700
H	4.11590700	-2.24988400	0.62366900
H	2.94294000	-4.40432300	1.07191600
C	-1.63564500	-0.15142800	-0.44388300
C	-1.78042900	-0.41850700	0.93214900
C	-2.78624400	0.02540000	-1.23064000
C	-3.05462700	-0.50480200	1.50844600
H	-0.89510700	-0.56419900	1.54686400
C	-4.06641700	-0.05748600	-0.65516500
H	-2.68076400	0.22443900	-2.29362000
C	-4.20091600	-0.32267300	0.71439900
H	-3.15517800	-0.71274800	2.56887000

H	-4.94767700	0.07988800	-1.27338600
H	-5.18780700	-0.39194500	1.16104200

Ligand **2**:

P	-0.92845700	0.65319700	-0.86233300
C	-1.73569700	1.62558200	0.53173200
C	-1.25482600	2.93766200	0.70408700
C	-2.74682700	1.14266900	1.38260300
C	-1.75954600	3.75273100	1.72821100
H	-0.48916400	3.32283500	0.03508800
C	-3.25926600	1.96333000	2.39768400
H	-3.12934700	0.13475100	1.25994800
C	-2.76408900	3.26518500	2.57678000
H	-1.37697700	4.75989000	1.85576300
H	-4.03712300	1.58330500	3.05171400
H	-3.16073600	3.89390800	3.36739300
C	-2.18343400	-0.67075200	-1.27835600
C	-1.78096900	-1.98437700	-1.57346200
C	-3.53120300	-0.30880800	-1.45289500
C	-2.71655800	-2.93065700	-2.01377200
H	-0.73972800	-2.27821200	-1.46335600
C	-4.46674200	-1.25601500	-1.89467900
H	-3.85650100	0.70780200	-1.24579500
C	-4.06305500	-2.57001900	-2.17414700
H	-2.39483100	-3.94363000	-2.23244400
H	-5.50476800	-0.96655200	-2.02162000
H	-4.78672000	-3.30243200	-2.51622900
C	0.34348600	-0.34006100	0.14443100
C	1.73099400	-0.16556400	-0.06640400
C	-0.04061400	-1.23115600	1.15263800
C	2.64829700	-0.87775100	0.71180200
C	0.87358500	-1.94279800	1.92533100
C	2.23261600	-1.76295800	1.70254900
I	2.53226100	1.15549000	-1.50802300
F	-1.37418700	-1.44481500	1.42740000
F	0.44627600	-2.80853900	2.89950000
F	3.15091400	-2.44815700	2.45414100
F	4.00321900	-0.72382600	0.52395100

Intermediate, σ-hole:

I	0.17012900	-2.33449000	-0.71428300
Rh	-0.45604200	0.24522800	-0.12187100
P	1.87177800	0.69336500	-0.02114700
P	-2.79727100	-0.22335400	0.07886500
F	2.35148400	-4.56181600	-0.25583300
F	4.93793400	-4.53311500	0.64591700
F	6.15546800	-2.12952700	1.27587800
F	4.81012600	0.20792600	0.97795100

O	-0.74479100	2.31584400	-2.13504800
O	-0.94937500	2.04208200	0.85166300
C	2.81423600	-0.93588300	0.24055600
C	2.20579200	-2.16642600	-0.07806900
C	2.93294400	-3.34862100	0.05680400
C	4.24888100	-3.35542500	0.51037700
C	4.85815100	-2.14732000	0.82842100
C	4.14166600	-0.96228100	0.67729200
C	0.57346500	4.19887600	-2.85722600
H	0.23142100	5.23961600	-2.82800100
H	0.36664500	3.77003200	-3.84028000
H	1.65804500	4.19465800	-2.68672500
C	-0.12380700	3.37063400	-1.78371500
C	-0.02539200	3.87330900	-0.43895200
H	0.41605600	4.85922700	-0.32798800
C	-0.48120500	3.25800700	0.73054800
C	-0.42696200	4.02251400	2.03898500
H	-0.01869300	5.02847300	1.91558100
H	0.19251500	3.46289300	2.75140700
H	-1.43893700	4.08845900	2.45401900
C	-3.48891700	-1.53594800	-1.06859300
C	-4.79564900	-1.51405700	-1.57926300
C	-3.01978900	-3.52891000	-2.19838600
C	-5.20963900	-2.55171100	-2.42942700
H	-5.46222200	-0.69764100	-1.32390600
C	-4.31182500	-3.58166900	-2.74149600
H	-2.28378700	-4.29526600	-2.41756700
H	-6.21371500	-2.55262700	-2.83944600
H	-4.59364400	-4.40040000	-3.39250100
N	-2.61877400	-2.52669400	-1.38889300
C	2.75028700	1.32035500	-1.54064900
C	4.06447700	1.82581300	-1.52648600
C	2.05474600	1.19289400	-2.75652600
C	4.67526900	2.20512900	-2.72934600
H	4.61010900	1.91637800	-0.59239900
C	2.67850200	1.56267000	-3.95832900
H	1.02324600	0.84870600	-2.75573800
C	3.98556600	2.06948200	-3.94654700
H	5.68757700	2.59565100	-2.71763300
H	2.13671500	1.46732400	-4.89335400
H	4.46505900	2.36027000	-4.87591500
C	2.41527300	1.72852300	1.42328100
C	2.85421100	3.05188300	1.27006100
C	2.27902400	1.17849800	2.70927300
C	3.18833200	3.81129800	2.40178700
H	2.91849000	3.49682100	0.28143700
C	2.62007700	1.93653900	3.83731800
H	1.89560100	0.16741900	2.83143500
C	3.08104800	3.25448400	3.68459900
H	3.52801300	4.83448000	2.27938600

H	2.51989900	1.50504900	4.82782100
H	3.34519900	3.84264400	4.55751900
C	-4.01745700	1.16831000	-0.07098100
C	-5.22023200	1.17766800	0.65631600
C	-3.69753100	2.23053600	-0.93440900
C	-6.11924300	2.24344200	0.50527400
H	-5.44520700	0.37148300	1.35080500
C	-4.60401900	3.29272300	-1.08255300
H	-2.74133500	2.23174800	-1.45689600
C	-5.81251900	3.29952100	-0.36855000
H	-7.04517900	2.25409900	1.07118800
H	-4.35630100	4.11713400	-1.74311100
H	-6.50601000	4.12714800	-0.48132200
C	-3.15197000	-0.92402300	1.76895100
C	-3.94918200	-2.05451900	2.00028700
C	-2.55840200	-0.24255000	2.85046200
C	-4.16150200	-2.50466500	3.31423400
H	-4.40175600	-2.59084000	1.16985500
C	-2.78398600	-0.68860300	4.15930000
H	-1.92796900	0.62411000	2.65224400
C	-3.58389000	-1.82046100	4.39325600
H	-4.77389300	-3.38295200	3.49177300
H	-2.33144800	-0.16116300	4.99277200
H	-3.75034700	-2.16836300	5.40780300

Intermediate, **INT 2**:

I	0.46948000	2.40011300	0.56841400
Rh	-0.40608700	-0.06787300	-0.18094000
P	1.85562000	-0.74977700	-0.06302600
P	-2.75456300	0.40732900	-0.19127400
F	2.87053800	4.41428200	0.32702400
F	5.52766000	4.11771500	-0.28480400
F	6.55067400	1.60273400	-0.80680400
F	4.94945800	-0.58063700	-0.70436000
O	-1.51844900	-1.97158900	1.62847500
O	-0.87196900	-1.79710700	-1.25264300
C	3.00908800	0.75888100	-0.17967500
C	2.51104700	2.04617900	0.09308200
C	3.35802600	3.15336200	0.06021200
C	4.70993400	3.01979900	-0.24451900
C	5.22090900	1.75483300	-0.51049200
C	4.37347200	0.64938400	-0.46271200
C	-0.70685800	-3.95806600	2.72132100
H	-1.30249100	-4.87781400	2.68042100
H	-0.98476200	-3.38987300	3.61197600
H	0.35004000	-4.24321200	2.78056300
C	-0.96237800	-3.11102300	1.48210800
C	-0.58570600	-3.68999800	0.22221700
H	-0.27624500	-4.73054200	0.23832100

C	-0.64894700	-3.06339800	-1.02911600
C	-0.45124900	-3.88116500	-2.28919400
H	-0.16655500	-4.91385600	-2.07206100
H	0.31729600	-3.40755100	-2.91159900
H	-1.38903300	-3.87474400	-2.85751000
C	-3.55475500	0.43996900	1.48738600
C	-4.94178800	0.31204900	1.66214100
C	-5.47012700	0.34513000	2.95996000
H	-5.59201900	0.16869300	0.80232700
C	-4.58847800	0.50618300	4.03964800
H	-6.53459200	0.24383800	3.13576700
H	-4.95459300	0.54327400	5.06007600
C	2.41923500	-1.46576600	1.56178200
C	3.69802600	-2.02792500	1.74437900
C	1.52617300	-1.37423300	2.64341100
C	4.07651100	-2.49506300	3.00943200
H	4.39118100	-2.10476000	0.91195700
C	1.91546400	-1.83878600	3.91025800
H	0.52793700	-0.96875700	2.49076200
C	3.18788000	-2.39781100	4.09424000
H	5.06108900	-2.92934200	3.14914400
H	1.22130200	-1.76801700	4.74095900
H	3.48700300	-2.75785900	5.07336400
C	2.47632100	-1.87250100	-1.40345400
C	2.74538600	-3.22734600	-1.16144400
C	2.58080000	-1.35429900	-2.70505900
C	3.15490300	-4.05480400	-2.21829500
H	2.62162700	-3.64094100	-0.16492300
C	2.99415400	-2.18139300	-3.75695100
H	2.32904600	-0.31399300	-2.90098300
C	3.28782700	-3.53347300	-3.51344500
H	3.36314900	-5.10262100	-2.02889100
H	3.07932200	-1.77740000	-4.76014700
H	3.60713300	-4.17458200	-4.32853700
C	-3.86081200	-0.77150100	-1.11765400
C	-4.65689800	-0.36541200	-2.19859700
C	-3.86626100	-2.11650200	-0.70076200
C	-5.46331400	-1.30415100	-2.86473300
H	-4.65496700	0.67092700	-2.52526200
C	-4.67592000	-3.04600500	-1.36449500
H	-3.23634200	-2.41912100	0.13219600
C	-5.47472800	-2.64260700	-2.44899900
H	-6.07733600	-0.98806400	-3.70201200
H	-4.67763500	-4.08196700	-1.04073100
H	-6.09815600	-3.36641900	-2.96457500
C	-3.17392100	2.07201700	-0.93233600
C	-4.15379600	2.94043600	-0.42420700
C	-2.43677300	2.44993700	-2.07264800
C	-4.39689300	4.17358300	-1.05184400
H	-4.71867000	2.66943700	0.46299100

C	-2.68773900	3.67508000	-2.70511000
H	-1.66469800	1.78296500	-2.45210200
C	-3.66906000	4.54023400	-2.19371600
H	-5.14907300	4.84372600	-0.64854900
H	-2.11673600	3.95647900	-3.58379800
H	-3.85833200	5.49368900	-2.67615600
N	-3.24878800	0.60862600	3.88641400
C	-2.74897800	0.56277600	2.63220100
H	-1.66707900	0.58616500	2.54086900

Transition state, **TS** (frequency: –145.41 cm^{-1}):

I	-0.26791600	-2.64315100	0.69098000
Rh	0.09897000	-0.25092300	-0.66779100
P	-2.40553600	-0.28003800	-0.79467000
P	2.45181500	-0.16939700	-0.34746400
F	0.69588900	-0.84214600	3.21931800
F	-0.63358500	0.99746100	4.74397800
F	-3.08017800	1.99593300	3.92702900
F	-4.11179300	1.27210000	1.49770500
O	-0.65212700	2.10167200	0.76809100
O	0.41069800	1.46048900	-1.90110500
C	-2.24605200	-0.17999300	1.07254400
C	-1.03502200	-0.75278800	1.53870200
C	-0.51265700	-0.34534500	2.76152900
C	-1.18481900	0.58596800	3.55290000
C	-2.40937400	1.08911600	3.14068200
C	-2.92267300	0.70076500	1.90206000
C	-0.34661900	4.35417400	1.52947600
H	0.44916000	5.10208300	1.46842100
H	-0.37111600	3.91295200	2.53099500
H	-1.30912800	4.85336700	1.36013700
C	-0.17420600	3.25117500	0.49599800
C	0.48264600	3.59003200	-0.73235000
H	0.84188800	4.60818300	-0.83121600
C	0.74687500	2.72258700	-1.79664000
C	1.49233600	3.25656700	-3.00650500
H	1.67428000	4.33139300	-2.93860800
H	0.91630700	3.03583500	-3.91152100
H	2.45339600	2.73355700	-3.09288200
C	3.26035900	-1.44035700	0.76733500
C	3.78861200	-1.14513200	2.03098700
C	3.78859100	-3.69413800	0.98500100
C	4.33023800	-2.19419200	2.79197000
H	3.77974600	-0.13045300	2.41030700
C	4.33438200	-3.49086600	2.26372100
H	3.76970100	-4.67948300	0.53224500
H	4.73838900	-1.99751600	3.77734700
H	4.74404500	-4.32611600	2.81942300
N	3.25609800	-2.69442600	0.25532100

C	-3.47350200	1.13035900	-1.35057600
C	-4.85603500	0.98939900	-1.55256300
C	-2.84176500	2.36217800	-1.58954000
C	-5.61085500	2.09085500	-1.97806300
H	-5.34366300	0.03466200	-1.37708200
C	-3.60364200	3.46247500	-2.00778200
H	-1.76948500	2.45259600	-1.45276800
C	-4.98697800	3.32953500	-2.20008300
H	-6.67987600	1.98459300	-2.13091000
H	-3.11312900	4.41420000	-2.18444900
H	-5.57606700	4.18210500	-2.52348600
C	-3.42109100	-1.80517700	-1.09989200
C	-3.24251900	-2.48094700	-2.31891000
C	-4.34523800	-2.28824400	-0.15863200
C	-3.99084400	-3.63303300	-2.59928900
H	-2.51341100	-2.11590200	-3.03798100
C	-5.08932500	-3.44472800	-0.43790100
H	-4.47574900	-1.77030500	0.78857900
C	-4.91414100	-4.11611100	-1.65811500
H	-3.84900400	-4.15316500	-3.54066200
H	-5.79903500	-3.81943300	0.29235100
H	-5.48910100	-5.01112800	-1.87262800
C	3.00348200	1.45996900	0.36017100
C	3.93268600	2.28023000	-0.29853400
C	2.41912300	1.89434000	1.56468400
C	4.27699800	3.52797800	0.24430600
H	4.37943700	1.95888200	-1.23534500
C	2.77939400	3.13081100	2.11501300
H	1.65816900	1.28865400	2.05247000
C	3.70595400	3.95259400	1.45250100
H	4.98667600	4.16279100	-0.27631100
H	2.32475700	3.45737000	3.04505100
H	3.97482600	4.91660900	1.87282000
C	3.42346400	-0.36224000	-1.92030900
C	4.79227900	-0.68374600	-1.88695700
C	2.77265500	-0.17817500	-3.15133500
C	5.51115200	-0.81765000	-3.08186200
H	5.29229300	-0.83833700	-0.93385300
C	3.49760600	-0.31307700	-4.34709000
H	1.71803900	0.08588200	-3.16474500
C	4.86287700	-0.63178500	-4.31465700
H	6.56626900	-1.06969800	-3.05352400
H	2.99422400	-0.17174200	-5.29796000
H	5.41853100	-0.73908500	-5.24093500

Compound **6**:

I	-0.02591500	-0.55893700	-2.78274500
Rh	0.05901200	-0.83111600	-0.08200500
P	-1.60306500	0.91210500	0.24384300

P	2.20257000	0.39517100	-0.02610400
F	-1.51445700	-4.03209100	-0.41833400
F	-4.21330100	-4.41189400	-0.27832500
F	-5.93754600	-2.31021500	0.10734400
F	-4.95043900	0.26820800	0.37284600
O	1.05854200	-2.63462500	-0.26211200
O	0.06801200	-1.04137200	1.97885800
C	-2.70359700	-0.57701900	0.11892400
C	-1.80154500	-1.64386900	-0.09141100
C	-2.32040700	-2.92382500	-0.22079600
C	-3.70161400	-3.14056700	-0.15355700
C	-4.58140600	-2.07530500	0.04356300
C	-4.07251500	-0.78334100	0.18101500
C	1.68114400	-4.86017500	0.21403300
H	1.93626700	-5.51437900	1.04940300
H	2.55571800	-4.70821100	-0.42552500
H	0.90123600	-5.33295900	-0.39318300
C	1.15884500	-3.52175900	0.67356900
C	0.82400200	-3.33142300	2.03898300
H	0.97155900	-4.17571700	2.69958000
C	0.34059300	-2.14368600	2.61628300
C	0.13055400	-2.05325500	4.10928600
H	0.27775300	-3.01374600	4.60630700
H	-0.87908800	-1.68020300	4.30671500
H	0.83372600	-1.31644600	4.51628600
C	2.08658600	1.99171500	-0.97948600
C	2.85777600	2.25119600	-2.12077600
C	0.90856300	3.98010800	-1.22633300
C	2.61751900	3.43399300	-2.83602400
H	3.60654600	1.53973900	-2.44980700
C	1.62924600	4.31637700	-2.38205100
H	0.13171300	4.63206800	-0.84575300
H	3.18565200	3.65412000	-3.73316400
H	1.40762700	5.23676400	-2.90875100
N	1.12083500	2.83657700	-0.54130400
C	-2.30443700	2.19459200	-0.89770200
C	-2.29921500	3.54428000	-0.50982200
C	-2.85291000	1.81816100	-2.13488900
C	-2.83816900	4.51859000	-1.36222200
H	-1.88710300	3.83328000	0.45346700
C	-3.38566300	2.79646100	-2.98527800
H	-2.85496300	0.77596700	-2.44060100
C	-3.37793300	4.14688900	-2.60285200
H	-2.84185000	5.55983900	-1.05519100
H	-3.80558500	2.50194200	-3.94099500
H	-3.79587900	4.90020300	-3.26283900
C	-1.79019300	1.63342100	1.93965300
C	-0.65367100	1.79265000	2.74487400
C	-3.05676700	2.02837200	2.40802700
C	-0.78053800	2.35415500	4.02483700

H	0.31619400	1.46539400	2.38715700
C	-3.17903800	2.58278700	3.68980900
H	-3.93622700	1.91210100	1.77961100
C	-2.04128600	2.74706100	4.49802800
H	0.10322500	2.47546500	4.64337000
H	-4.15534700	2.88464800	4.05389100
H	-2.14049000	3.17735600	5.48973400
C	3.72686400	-0.42713100	-0.71278900
C	3.59656400	-1.51007700	-1.59964200
C	5.00641900	0.04670400	-0.36396800
C	4.74758300	-2.10787800	-2.14002000
H	2.61198800	-1.88830600	-1.85643300
C	6.15051600	-0.55367800	-0.90551300
H	5.10696600	0.87436600	0.33418600
C	6.02125300	-1.63225900	-1.79706400
H	4.64307500	-2.94136300	-2.82667000
H	7.13424800	-0.18564300	-0.63322400
H	6.90749700	-2.09792900	-2.21642100
C	2.77573100	0.90036900	1.67691600
C	3.06813400	-0.14109600	2.57875300
C	2.89945800	2.23438300	2.09464900
C	3.48677900	0.15064600	3.88312400
H	2.98091600	-1.17829200	2.25838400
C	3.31462600	2.52516500	3.40509200
H	2.65869400	3.04403300	1.41432800
C	3.60827900	1.48694400	4.30092000
H	3.71802900	-0.65900000	4.56807600
H	3.40846100	3.55934500	3.72041100
H	3.93144800	1.71409300	5.31180200

Product from "**INT 2**" (not observed experimentally):

I	-0.02145300	-0.40793800	-2.76947000
Rh	-0.00038000	-0.85578200	-0.09785800
P	-1.50994000	1.00165600	0.30525900
P	2.21054000	0.23791200	0.03408500
F	-1.87526000	-3.86633800	-0.72897800
F	-4.59472300	-4.00237100	-0.57354100
F	-6.11109900	-1.79053900	0.01124000
F	-4.87628500	0.66235400	0.45575600
O	0.85233800	-2.73448600	-0.36823000
O	-0.10803300	-1.24102000	1.94291300
C	-2.72964200	-0.37574900	0.10643800
C	-1.92889800	-1.50041700	-0.19081800
C	-2.56968700	-2.70906100	-0.42077400
C	-3.96476600	-2.79988100	-0.35096000
C	-4.74027400	-1.67747600	-0.05367800
C	-4.11134700	-0.45325900	0.17424800
C	1.11594500	-5.06611700	-0.09151900
H	1.23260800	-5.81832000	0.69043700

H	2.04134900	-4.97495000	-0.66705800
H	0.32371700	-5.38070800	-0.78030200
C	0.73065300	-3.71811400	0.46331300
C	0.27572100	-3.61772700	1.80437300
H	0.22858900	-4.53755200	2.37231000
C	-0.07400000	-2.43193900	2.47232300
C	-0.40498500	-2.45939600	3.94568200
H	-0.45406500	-3.47650700	4.33812400
H	-1.36016400	-1.95103000	4.10917800
H	0.36248400	-1.89539400	4.48923800
C	2.10601300	2.02622400	-0.46951400
C	2.41451100	2.42070200	-1.78356400
C	2.22576900	3.75866200	-2.15294400
H	2.78295200	1.69501500	-2.50251800
C	1.74007500	4.66365800	-1.19780800
H	2.44294400	4.09327500	-3.16006500
H	1.58640900	5.70898500	-1.44213900
C	-2.01675400	2.35466100	-0.85324100
C	-1.67638300	3.68504700	-0.55763900
C	-2.72116600	2.04612200	-2.02920500
C	-2.03700100	4.70739500	-1.44673300
H	-1.13797000	3.93504600	0.35167600
C	-3.08646000	3.07359600	-2.90795700
H	-2.96977500	1.01584600	-2.26703700
C	-2.74271600	4.40425600	-2.62043600
H	-1.76801200	5.73300200	-1.21557900
H	-3.63259400	2.83394500	-3.81379000
H	-3.02546800	5.19736100	-3.30506100
C	-1.65442400	1.73076700	2.00411200
C	-0.62662000	1.54129300	2.94240600
C	-2.79604300	2.48163900	2.34110300
C	-0.73530200	2.11898400	4.21656800
H	0.22971300	0.91882000	2.69818400
C	-2.90145700	3.04888300	3.61795700
H	-3.59200300	2.62396700	1.61493600
C	-1.86949500	2.87256800	4.55449000
H	0.06200200	1.97584700	4.93850700
H	-3.78218800	3.62576600	3.87903300
H	-1.95224500	3.31810300	5.54070100
C	3.61353700	-0.41349300	-1.00990300
C	3.43618800	-1.56972200	-1.78523700
C	4.85869200	0.24230900	-0.98905200
C	4.50994100	-2.06231200	-2.54692400
H	2.47585600	-2.07636500	-1.79604500
C	5.92382300	-0.25176700	-1.75102700
H	4.99680300	1.13318400	-0.37966300
C	5.74857300	-1.40699700	-2.53277900
H	4.37122200	-2.95245300	-3.15157300
H	6.88235300	0.25639600	-1.73470200
H	6.57350000	-1.79032500	-3.12501400

C	2.98780100	0.25961800	1.73498900
C	2.95214800	-0.95658000	2.44309800
C	3.63564300	1.36988400	2.30141900
C	3.54265900	-1.05720800	3.70942300
H	2.47693700	-1.82854800	1.99830500
C	4.21789200	1.27103400	3.57558900
H	3.69748900	2.31005300	1.76120800
C	4.16926200	0.06112400	4.28320200
H	3.51614500	-2.00238700	4.24231700
H	4.71297700	2.13464200	4.00736100
H	4.62288000	-0.01354800	5.26625900
N	1.43153100	4.29691800	0.06630900
C	1.60193900	3.00094800	0.41147500
H	1.32563200	2.75094000	1.43320500