Supporting Information

To 'Rollover', or Not? Stereoelectronically Guided C–H Functionalization Pathways from Rhodium–Abnormal NHC Intermediates

Champak Dutta,[†] Debasish Ghorai,[†,§] and Joyanta Choudhury*[,†]

[†]Organometallics & Smart Materials Laboratory, Department of Chemistry, Indian Institute of Science Education and Research Bhopal, Bhopal 462 066, India.

[§]Present address: Institut für Organische und Biomolekulare Chemie, Georg-August-Universität, Tammannstraße 2, 37077 Goettingen, Germany.

*E-mail: joyanta@iiserb.ac.in

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1. General methods and materials

^{1}H, $^{13}C\{^{1}H\}$, ^{31}P and ^{19}F NMR spectra were recorded on Bruker AVANCE III 400, 500MHz NMR spectrometers at room temperature unless mentioned otherwise. Chemical shifts (δ) are expressed in ppm using the residual proton resonance of the solvent as an internal standard ($CHCl_3$: δ = 7.26 ppm for ^{1}H spectra, 77.2 ppm for $^{13}C\{^{1}H\}$ spectra; CH_3CN: δ = 1.94 ppm for ^{1}H spectra, 1.3 ppm for $^{13}C\{^{1}H\}$ spectra) and DMSO: 2.50 ppm for ^{1}H spectra, 39.5 ppm for $^{13}C\{^{1}H\}$ spectra). All coupling constants (J) are expressed in hertz (Hz) and only given for ^{1}H-^{1}H couplings unless mentioned otherwise. The following abbreviations were used to indicate multiplicity: s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublet), dt (doublet of triplets), ddd (doublet of doublet of doublets), m (multiplet). ESI mass spectrometry was performed on a Bruker microTOF QII spectrometer. Single-crystal X-ray diffraction data were collected using a Bruker SMART APEX II CCD diffractometer with graphite monochromated Mo Kα (λ = 0.71073 Å) radiation at different low temperatures for each crystal. Dry solvents and reagents were obtained from commercial suppliers and used without further purification. Deuterated solvents, $RhCl_3.xH_2O$ were purchased from Aldrich and used as received without further purification. $[RhCp^*Cl_2]_2$[1] and required aryl imidazoles were synthesized according to reported procedures[2].

2. General procedure for the synthesis of imidazolium salts:

The syntheses of N-substituted imidazoles were performed by following the literature procedure[2]. A mixture of CuI (5 mol%), benzotriazole (10 mol%), aryl halide (2 mmol), imidazole (1 equiv.) and KO^{t}Bu (1.4 equiv.) in DMSO (2 mL) was refluxed for 20 - 40 h. After completion of the reaction, EtOAc was added to the mixture and the whole solution was washed with water. Then organic layer was dried over anhydrous Na_2SO_4. The final product was separated by silica gel column chromatography. Further, the syntheses of imidazolium salts were performed according to the reported procedure[3] by stirring a mixture of *N*-aryl imidazole (2 mmol) and iodomethane (0.19 mL, 3 mmol) in dry THF (3 mL) for 24 h at room temperature[3]. The resultant precipitate of iodide salt was collected by filtration and washed with hexane and then dried *in vacuo*. Next, if required, the aqueous solution of the iodide salt (2 mmol) and an aqueous solution of KPF_6 (5 mmol) were mixed well[4]. The resulting white precipitate was washed with water and diethyl ether to yield the desired products.

2,3-dimethyl-1-(pyridin-2-yl)-1H-imidazolium hexafluorophosphate (1a): 88%, 56 mg. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (d, *J* = 3.8 Hz, 1H), 8.00 (td, *J* = 7.9, 1.6 Hz, 1H), 7.92 (d, *J* = 8.0 Hz, 1H), 7.81 (d, *J* = 2.0 Hz, 1H), 7.68 (d, *J* = 2.0 Hz, 1H), 7.49 (dd, *J* = 7.0, 5.1 Hz, 1H), 4.04 (s, 3H), 2.87 (s, 3H). HRMS (ESI, positive ion): M^+ = 170.1030 (calculated 170.1026 for $[C_{10}H_{12}N_3]^+$).

2,3-dimethyl-1-(6-methylpyridin-2-yl)-1H-imidazolium hexafluorophosphate (1b): 85%, 56 mg. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (t, *J* = 7.8 Hz, 1H), 7.81 (d, *J* = 2.1 Hz, 1H), 7.74 (d, *J* = 7.9 Hz, 1H), 7.62 (d, *J* = 2.1 Hz, 1H), 7.35 (d, *J* = 7.7 Hz, 1H) 4.08 (s, 3H), 2.90 (s, 3H), 2.55 (s,3H). HRMS (ESI, positive ion): M^+ = 188.1176 (calculated 188.1182 for $[C_{11}H_{14}N_3]^+$). HRMS (ESI, positive ion): M^+ = 188.1176 (calculated 188.1182 for $[C_{11}H_{14}N_3]^+$).

2,3-dimethyl-1-(6-methoxypyridin-2-yl)-1H-imidazolium hexafluorophosphate (1c): 75%, 54 mg. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 – 7.83 (m, 1H), 7.66 (d, *J* = 8.0 Hz, 1H), 7.55 (s, 1H), 7.51 (d, *J* = 7.5 Hz, 1H), 6.96 (d, *J* = 8.4 Hz, 1H), 4.10 (s, 3H), 3.94 (s, 3H), 2.96 (s, 3H). HRMS (ESI, positive ion): M^+ = 204.1115 (calculated 204.1131 for $[C_{11}H_{14}N_3O]^+$).

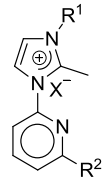
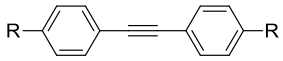
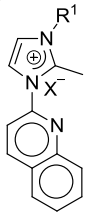
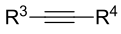
2,3-dimethyl-1-(quinolin-2-yl)-1H-imidazolium iodide (1d): 80%, 56 mg. ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.84 (d, *J* = 8.5 Hz, 1H), 8.25 (s, 1H), 8.22 (d, *J* = 8.0 Hz, 1H), 8.12 (d, *J* = 8.1 Hz, 1H), 7.99 – 7.91 (m, 3H), 7.82 (d, *J* = 7.4 Hz, 1H), 3.93 (s, 3H), 2.86 (s, 3H). HRMS (ESI, positive ion): M^+ =224.118 2 (calculated for 224.1182 for $[C_{14}H_{14}N_3]^+$).

2,3-dimethyl-1-(6-*tert*-butylpyridin-2-yl)-1H-imidazolium iodide (1e): 87%, 62 mg. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (t, *J* = 7.9 Hz, 1H), 7.83 (d, *J* = 2.0 Hz, 1H), 7.72 (d, *J* = 7.8 Hz, 1H), 7.68 (d, *J* = 2.1 Hz, 1H), 7.52 (d, *J* = 7.9 Hz, 1H), 4.12 (s, 3H), 2.96 (s, 3H), 1.35 (s, 9H). HRMS (ESI, positive ion): M^+ = 230.1649 (calculated 230.1652 for $[C_{14}H_{20}N_3]^+$).

General procedure for synthesis of 1f: In an oven dried screw cap sealed tube, 2-methyl-1-pyridylimidazole (2 mmol) and benzyl bromide (2.4 mmol) were taken and flushed with N_2. Then the mixture was stirred at 135 °C in an oil bath for 48 h. After cooling, the residue was washed with diethyl ether. Then it was dissolved in $CHCl_3$ (~15 mL) and to this solution diethyl ether (~80 mL) was added. The resulting sticky white ppt. was washed with Et_2O. Next this ppt. was dissolved in minimum volume of water and to that solution aqueous KPF_6 (4 mmol) was added with stirring. A white precipitate appeared after some time which was washed with water and diethyl ether to afford the desired product.

3-benzyl-2-methyl-1-(pyridin-2-yl)-1H-imidazolium hexafluorophosphate (1f): 90%, 71 mg. ^{1}H NMR (400 MHz, DMSO-d_6, 300K) δ 8.70 (d, *J* = 3.8 Hz, 1H), 8.21 (td, *J* = 7.9, 1.7 Hz, 1H), 8.17 (d, *J* = 2.1 Hz, 1H), 7.96 (d, *J* = 2.1 Hz, 1H), 7.85 (d, *J* = 8.1 Hz, 1H), 7.70 (dd, *J* = 7.2, 5.0 Hz, 1H), 7.49 – 7.40 (m, 5H), 5.54 (s, 2H), 2.77 (s, 3H). HRMS (ESI, positive ion): M^+ = 250.1331 (calculated 250.1339 for $[C_{16}H_{16}N_3]^+$).

3. Table of imidazolium salts and internal alkynes used (Table S1):

Imidazolium salts (**1**)	**Internal alkynes** (**2**)
1a, R^1 = Me, R_2= H, X= PF_6 **1b**, R^1 = Me, R_2= Me, X= PF_6 **1c**, R^1 = Me, R_2= OMe, X= PF_6 **1e**, R^1 = Me, R_2= t-Butyl, X= I **1f**, R^1 = CH_2Ph, R_2= H, X= PF_6 	 **2a**, R= H **2e**, R= NO_2
1d, R^1 = Me, X= I 	 **2b**, R^3= R^4= n-Pr **2c**, R^3= R^4= CO_2Me **2d**, R^3= Ph, R^4= Et

4. General procedure for the non-rollover alkenylation reactions:

To an oven dried Schlenk tube, **1** (0.11 mmol), NaOAc (0.5 mmol), $[RhCp^*Cl_2]_2$ (0.003 mmol), AgOTf (0.25 mmol) and **2** (0.1 mmol) were loaded and then the tube was kept under vacuum for 15 minutes. After that the tube was filled with Ar gas. To this mixture, dry and degassed DCE (1.5 mL) was added under

Schlenk technique and the reaction mixture was left with stirring at 110 °C in dark. After 24 h, the whole reaction mixture was passed through a short celite pad which was thereafter washed with dichloromethane (3×5 mL). The combined filtrate was concentrated under reduced pressure. The final product was separated by silica gel column chromatography, eluted with a $CHCl_3$/acetone solvent mixture.

5. Optimization studies: Following similar procedure as of **section 4** above, following reactions were performed. The crude reaction mixture was dried and sent for ^{1}H NMR analysis in presence of mesitylene as internal standard.

Scheme S1: General reaction conditions

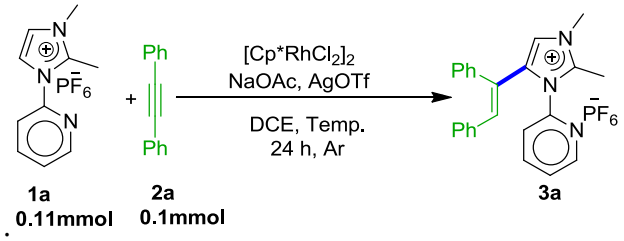
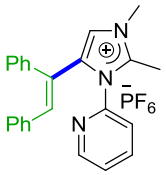


Table S2: Optimization studies

Entry	Conditions	Result (crude NMR yield)
1	Room Temperature	49% of **3a**
2	No AgOTf	No **3a**
3	No NaOAc	No **3a**
4	No $[Cp^*RhCl_2]_2$	No **3a**
5	O_2 balloon, No AgOTf	No **3a**

6. Experimental characterization data of the products (3a-3j):

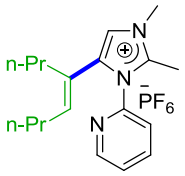
(*E*)-5-(1,2-diphenylvinyl)-2,3-dimethyl-1-(pyridin-2-yl)-1H-imidazolium hexafluorophosphate (3a):



86%, 44 mg. ^{1}H NMR (400 MHz, CD_3CN) δ 8.38 (dd, *J* = 4.8, 1.1 Hz, 1H), 7.75 (td, *J* = 7.8, 1.8 Hz, 1H), 7.51 (s, 1H), 7.40 – 7.33 (m, 1H), 7.21 (d, *J* = 8.0 Hz, 1H), 7.18 – 7.11 (m, 4H), 7.09 – 7.00 (m, 4H), 6.95 (s, 1H), 6.85 (d, *J* = 7.2 Hz, 2H), 3.83 (s, 3H), 2.40 (s, 3H). ^{13}C NMR (101 MHz, CD3CN) δ 150.7, 147.4, 147.2, 140.4, 137.1, 136.9, 136.2, 135.3, 130.5, 130.4, 129.4, 129.2, 129.1, 129.0, 128.4, 126.5, 123.6, 122.3, 35.9, 11.1. ^{19}F NMR (376 MHz, CD_3CN) δ -72.88 (d, *J* = 706.5 Hz). ^{31}P NMR (162 MHz, CD_3CN) δ -144.61 (hept, *J* = 706.8 Hz). HRMS (ESI, positive ion): M^+ = 352.1804 (calculated 352.1808 for $[C_{24}H_{22}N_3]^+$).

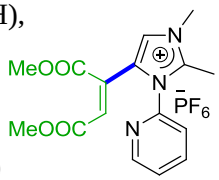
(*E*)-2,3-dimethyl-1-(pyridin-2-yl)-5-(oct-4-en-4-yl)-1H-imidazolium hexafluorophosphate (**3b**):

94%, 40 mg. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.59 (ddd, J = 4.8, 1.8, 0.7 Hz, 1H), 7.95 (td, *J* = 7.8, 1.9 Hz, 1H), 7.58 (d, *J* = 7.9 Hz, 1H), 7.53 (ddd, *J* = 7.6, 4.9, 1.0 Hz, 1H), 7.16 (s, 1H),

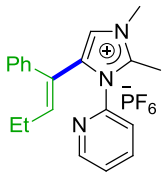


5.50 (t, *J* = 7.4 Hz, 1H), 3.89 (s, 3H), 2.48 (s, 3H), 1.92 (q, *J* = 7.4 Hz, 2H), 1.85 – 1.80 (m, 2H), 1.24 (dd, *J* = 13.6, 5.9 Hz, 2H), 1.17 (dd, *J* = 14.7, 7.4 Hz, 2H), 0.73 (dt, *J* = 14.9, 7.4 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.9, 147.1, 145.0, 139.9, 138.9, 136.2, 126.0, 125.5, 123.3, 119.5, 35.4, 31.8, 30.1, 22.1, 21.3, 13.6, 13.6 (peaks overlapping) 10.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ -73.54 (d, *J* = 712.3 Hz).^{31}P NMR (162 MHz, $CDCl_3$) δ -144.55 (hept, *J* = 712.3 Hz). HRMS (ESI, positive ion): M^+ = 284.2133 (calculated 284.2121 for $[C_{18}H_{26}N_3]^+$).

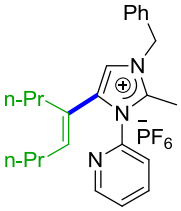
(*Z*)-5-(1,4-dimethoxy-1,4-dioxobut-2-en-2-yl)-2,3-dimethyl-1-(pyridin-2-yl)-1H-imidazol-3-ium hexafluorophosphate (3c): 47%, 22 mg. ^{1}H NMR (400 MHz, CD_3CN) δ 8.59 (dd, *J* = 4.7, 1.0 Hz, 1H), 8.05 (td, *J* = 7.8, 1.8 Hz, 1H), 7.62 – 7.57 (m, 1H), 7.50 (s, 1H), 7.43 (d, *J* = 8.0 Hz, 1H), 7.09 (s, 1H), 3.84 (s, 3H), 3.68 (s, 3H), 3.58 (s, 3H), 2.59 (s, 3H). ^{13}C NMR (101 MHz, CDCl3) δ 164.9, 164.6, 150.9, 147.3, 147.2, 141.0, 136.7, 129.9, 127.0, 126.6, 124.2, 122.5, 53.8, 53.2, 36.3, 11.7. ^{19}F NMR (376 MHz, CD_3CN) δ -72.90 (d, *J* = 706.5 Hz).^{31}P NMR (162 MHz, CD_3CN) δ -144.61 (hept, *J* = 706.6 Hz). HRMS (ESI, positive ion): M^+ = 316.1324 (calculated 316.1292 for $[C_{16}H_{18}N_3O_4]^+$).



(*Z*)-2,3-dimethyl-1-(pyridin-2-yl)-5-(1-phenylbut-1-en-2-yl)-1H-imidazolium hexafluorophosphate (3d): 78%, 35 mg. ^{1}H NMR (400 MHz, CD_3CN) δ 8.69 (dd, *J* = 4.7, 1.2 Hz, 1H), 8.07 (td, *J* = 7.8, 1.8 Hz, 1H), 7.63 (dd, *J* = 7.2, 4.9 Hz, 1H), 7.52 (d, *J* = 8.0 Hz, 1H), 7.44 (s, 1H), 7.34 (t, *J* = 7.3 Hz, 2H), 7.28 (dd, *J* = 8.6, 6.0 Hz, 1H), 7.14 (d, *J* = 7.2 Hz, 2H), 6.42 (s, 1H), 3.82 (s, 3H), 2.47 (s, 3H), 2.20 (q, *J* = 7.5 Hz, 2H), 0.99 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (101 MHz, CD_3CN) δ 151.2, 147.9, 146.9, 141.1, 136.5, 135.8, 135.8, 135.8 (peaks overlapping), 130.3, 129.4, 129.4 (peaks overlapping), 129.3, 128.8, 127.1 123.7, 121.4, 35.9, 24.5, 13.0, 11.2. ^{19}F NMR (376 MHz, CD_3CN) δ -72.88 (d, *J* = 706.5 Hz). ^{31}P NMR (162 MHz, CD_3CN) δ -144.61 (hept, *J* = 706.8 Hz). HRMS (ESI, positive ion): M^+ = 304.1825 (calculated 304.1808 for $[C_{20}H_{22}N_3]^+$).

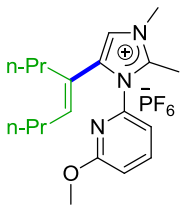


(*E*)-3-benzyl-2-methyl-1-(pyridin-2-yl)-5-(oct-4-en-4-yl)-1H-imidazolium hexafluorophosphate (3e): 80%, 40 mg. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 (dd, *J* = 4.7, 1.0 Hz, 1H), 7.99 (td, *J* = 7.8, 1.8 Hz, 1H), 7.61 – 7.54 (m, 2H), 7.47 – 7.40 (m, 3H), 7.37 – 7.32 (m, 2H), 6.92 (s, 1H), 5.55 (t, *J* = 7.4 Hz, 1H), 5.31 (s, 2H), 2.50 (s, 3H), 1.94 (q, *J* = 7.4 Hz, 2H), 1.88 – 1.81(m, 2H), 1.22 (ddd, *J* = 22.2, 15.0, 7.4 Hz, 4H), 0.76 (dt, *J* = 9.6, 7.4 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.9, 147.1, 145.0, 140.2, 139.4, 136.7, 132.3, 129.7, 129.5,

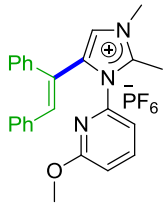


128.6, 126.2, 125.5, 123.7, 118.1, 52.4, 31.9, 30.3, 22.2, 21.4, 13.8, 13.8 (peaks overlapping), 11.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ -73.54(d, *J* = 712.3 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ -144.55 (hept, *J* = 712.3 Hz). HRMS (ESI, positive ion): M^+ = 360.2452 (calculated 360.2434 for $[C_{24}H_{30}N_3]^+$).

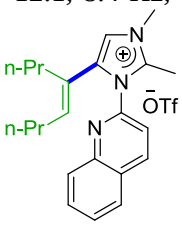
(*E*)-2,3-dimethyl-1-(6-methoxypyridin-2-yl)-5-(oct-4-en-4-yl)-1H-imidazolium hexafluorophosphate (3f): 86%, 39 mg. ^{1}H NMR (500 MHz, DMSO) δ 8.04 (dd, *J* = 8.3, 7.4 Hz, 1H), 7.76 (s, 1H), 7.20 (d, *J* = 7.0 Hz, 1H), 7.14 (d, *J* = 7.9 Hz, 1H), 5.41 (t, *J* = 7.4 Hz, 1H), 3.83 (s, 3H), 3.83 (s, 3H), 2.47 (s, 3H), 1.99 (ddd, *J* = 14.5, 8.9, 5.6 Hz, 4H), 1.32 – 1.24 (m, 2H), 1.15 (h, *J* = 7.3 Hz, 2H), 0.78 (t, *J* = 7.3 Hz, 3H), 0.69 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, DMSO) δ 163.8, 145.5, 144.1, 142.4, 136.5, 134.5, 125.9, 119.9, 115.6, 113.3, 54.0, 34.9, 31.3, 29.5, 21.9, 21.0, 13.6, 13.3, 10.5. ^{19}F NMR (471 MHz, DMSO) δ -70.18 (d, *J*= 711.2 Hz). ^{31}P NMR (202 MHz, DMSO) δ -144.21 (hept, *J* = 711.4 Hz). HRMS (ESI, positive ion): M^+ = 314.2233 (calculated 314.2227 for $[C_{19}H_{28}N_3O]^+$).



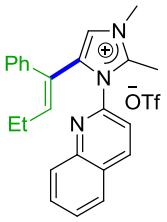
(*E*)-2,3-dimethyl-1-(6-methoxypyridin-2-yl)-5-(1,2-diphenylvinyl)-1H-imidazolium hexafluorophosphate (3g): 76%, 40 mg. ^{1}H NMR (500 MHz, DMSO) δ 7.99 (s, 1H), 7.78 – 7.70 (m, 1H), 7.18 – 7.14 (m, 4H), 7.13 – 7.09 (m, 2H), 7.01 – 6.97 (m, 3H), 6.95 (s, 1H), 6.85 (dd, *J* = 12.0, 4.9 Hz, 3H), 3.89 (s, 3H), 3.70 (s, 3H), 2.49 (s, 3H). ^{13}C NMR (126 MHz, DMSO) δ 163.2, 146.1, 143.5, 141.8, 135.7, 135.2, 135.0, 133.5, 129.3, 129.3, 128.5, 128.4, 128.3, 128.1, 127.5, 121.7, 115.4, 112.7, 53.8, 35.1, 10.5. ^{19}F NMR (471 MHz, DMSO) δ -70.16 (d, *J* = 711.2 Hz). ^{31}P NMR (202 MHz, DMSO) δ -144.20 (hept, *J* = 711.2 Hz). HRMS (ESI, positive ion): M^+ = 382.1907 (calculated 382.1914 for $[C_{25}H_{24}N_3O]^+$).



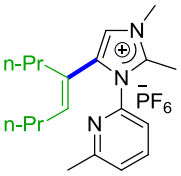
2-(5-((*E*)-but-2-en-2-yl)-2,3-dimethyl-1H-imidazol-1-yl)quinolinium trifluoromethane sulphonate (3h): 79%, 38 mg. ^{1}H NMR (400 MHz, CD_3CN) δ 8.60 (d, *J* = 8.6 Hz, 1H), 8.10 (dd, *J* = 12.1, 8.4 Hz, 2H), 7.95 – 7.89 (m, 1H), 7.83 – 7.75 (m, 1H), 7.50 (d, *J* = 8.6 Hz, 1H), 7.34 (s, 1H), 5.47 (t, *J* = 7.5 Hz, 1H), 3.81 (s, 3H), 2.48 (s, 3H), 2.01 – 1.94 (m, 4H), 1.34 (dd, *J* = 15.0, 7.5 Hz, 2H), 1.07 (dd, *J* = 14.6, 7.3 Hz, 2H), 0.80 (t, *J* = 7.3 Hz, 3H), 0.60 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, CD_3CN) δ 147.9, 147.3, 146.4, 141.6, 139.0, 136.4, 132.4, 129.9, 129.8, 129.3, 129.1, 126.8, 120.7, 120.4, 35.8, 32.4, 30.5, 22.7, 22.0, 13.8, 13.6, 11.3. ^{19}F NMR (376 MHz, CD_3CN) δ -79.29. HRMS (ESI, positive ion): M^+ = 334.2298 (calculated 334.2278 for $[C_{22}H_{28}N_3]^+$).



2-(2,3-dimethyl-5-((*Z*)-1-phenylbut-1-en-2-yl)-1H-imidazol-1-yl)quinolinium trifluoromethane sulphonate (3i): 73%, 38 mg. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (d, *J* = 8.6 Hz, 1H), 8.06 (d, *J* = 8.4 Hz, 1H), 7.95 (d, *J* = 8.1 Hz, 1H), 7.82 (dd, *J* = 15.8, 7.9 Hz, 2H), 7.70 (t, *J* = 7.4 Hz, 1H), 7.36 (s, 1H), 7.26 – 7.19 (m, 3H), 7.03 (d, *J* = 7.1 Hz, 2H), 6.62 (s, 1H), 4.00 (s, 3H), 2.63 (s, 3H), 2.14 (q, *J* = 7.4 Hz, 2H), 1.02 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.9, 146.3, 145.8, 140.6, 136.1, 135.7, 135.5, 131.4, 129.2, 129.0, 128.9, 128.5, 128.4, 128.3, 128.1, 127.8, 120.3, 119.9, 35.6, 23.9, 12.9, 11.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ -78.27. HRMS (ESI, positive ion): M^+ = 354.1970 (calculated 354.1965 for $[C_{24}H_{24}N_3]^+$).



2-(5-((*Z*)-but-2-en-2-yl)-2,3-dimethyl-1H-imidazol-1-yl)-6-methylpyridinyl hexafluorophosphate (3j): 35%, 14 mg. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (t, *J* = 7.8 Hz, 1H), 7.50 (d, *J* = 7.8 Hz, 1H), 7.37 (d, *J* = 7.7 Hz, 1H), 7.09 (s, 1H), 7.09 (s, 1H), 5.58 (t, *J* = 7.4 Hz, 1H), 3.91 (s, 1H), 2.59 (s, 1H), 2.53 (s, 1H), 1.97 (q, *J* = 7.3 Hz,1H), 1.91 – 1.85 (m, 1H), 1.25 (ddd, *J* = 29.8, 14.9, 7.4 Hz, 1H), 0.77 (dt, *J* = 14.8, 7.3 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.7, 146.5, 145.1, 140.1, 139.1, 136.5, 125.7, 125.6, 120.6, 119.3, 35.5, 32.0, 30.3, 24.2, 22.3, 21.4, 13.8, 13.7, 11.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ -73.54 (d, *J* = 712.3 Hz).^{31}P NMR (162 MHz, $CDCl_3$) δ -144.55 (hept, *J* = 712.3 Hz). HRMS (ESI, positive ion): M^+ = 298.2291 (calculated 298.2278 for $[C_{19}H_{28}N_3]^+$).

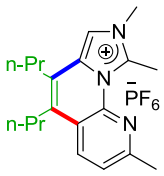


7. General procedure for the rollover annulation reactions:

To an oven dried Schlenk tube, **1** (0.11 mmol), NaOAc (0.6 mmol), $[RhCp^*Cl_2]_2$ (0.003 mmol), AgOTf (0.25 mmol) and **2** (0.1 mmol) were loaded and then the tube was kept under vacuum for 15 minutes. After that the tube was filled with Ar gas. To this mixture, dry and degassed DCE (1.5 mL) was added under Schlenk technique and the reaction mixture was left with stirring at 110 °C in dark. After 24 h, the whole reaction mixture was passed through a short celite pad which was thereafter washed with dichloromethane (3×5 mL). The combined filtrate was concentrated under reduced pressure. The final product was separated by silica gel column chromatography, eluted with a $CHCl_3$/acetone solvent mixture.

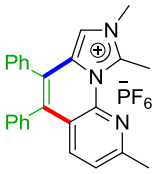
8. Experimental characterization data of the products (4a-4g)

2,9-dimethyl-5,6-dipropylimidazo[1,5-a][1,8]naphthyridinium hexafluorophosphate (4a) : 60%, 27 mg. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 8.3 Hz, 1H), 8.04 (s, 1H), 7.47 (d, *J* = 8.3 Hz, 1H), 4.23 (s, 3H), 3.48 (s, 3H), 2.87 – 2.76 (m, 4H), 2.70 (s, 3H), 1.68 (dd, *J* = 15.6, 7.7 Hz, 2H), 1.60 (dd, *J* = 15.7, 7.7 Hz, 2H), 1.07 (td, *J* = 7.3, 3.7 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.3, 142.2, 139.5, 134.6, 132.1, 130.7, 126.3, 123.8, 118.9, 115.2,

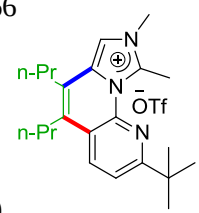


36.4, 30.9, 29.4, 24.3, 23.3, 23.0, 14.9, 14.5, 14.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ -73.54 (d, *J* = 712.3 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ -144.55 (hept, *J* = 712.3 Hz). HRMS (ESI, positive ion): M^+ = 296.2149 (calculated 296.2121 for $[C_{19}H_{26}N_3]^+$).

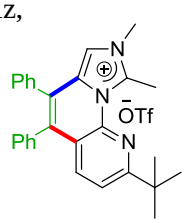
2,9-dimethyl-5,6-diphenylimidazo[1,5-a][1,8]naphthyridinium hexafluorophosphate (4b): 92%, 47 mg. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.2 Hz, 1H), 7.33 (d, *J* = 8.3 Hz, 1H), 7.30 – 7.27 (m, 4H), 7.25 (dd, *J* = 5.1, 1.8 Hz, 3H), 7.19 (dd, *J* = 7.1, 2.5 Hz, 2H), 7.09 (dd, *J* = 6.5, 2.9 Hz, 2H), 4.11 (s, 3H), 3.55 (s, 3H), 2.71 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 158.4, 142.3, 140.8, 137.3, 134.4, 134.1, 133.7, 130.8, 130.5, 129.8, 128.8, 128.7, 128.6, 128.4, 127.3, 123.8, 119.6, 116.9, 36.6, 24.5, 15.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ -73.54 (d, *J* = 712.3 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ -144.55 (hept, *J* = 712.3 Hz). HRMS (ESI, positive ion): M^+ = 364.1819 (calculated 364.1808 for $[C_{25}H_{22}N_3]^+$).



2-tert-butyl-9-methyl-5,6-dipropylimidazo[1,5-a][1,8]naphthyridinium trifluoromethanesulphonate (4c) : 79%, 38 mg. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, *J* = 8.5 Hz, 1H), 8.04 (s, 1H), 7.66 (d, *J* = 8.5 Hz, 1H), 4.23 (s, 3H), 3.51 (s, 3H), 2.87 – 2.76 (m, 4H), 1.63 (ddd, *J* = 23.0, 15.5, 7.6 Hz, 4H), 1.44 (s, 9H), 1.07 (q, *J* = 7.2 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.4, 141.7, 139.2, 134.9, 132.1, 130.8, 126.4, 120.0, 118.9, 115.3, 38.4, 36.4, 30.9, 30.2, 29.4, 23.3, 23.0, 15.2, 14.4, 14.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ -78.38. HRMS (ESI, positive ion): M^+ = 338.2609 (calculated 338.2591 for $[C_{22}H_{32}N_3]^+$).

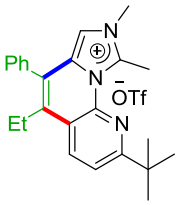


2-tert-butyl-9-methyl-5,6-diphenylimidazo[1,5-a][1,8]naphthyridinium trifluoromethanesulphonate (4d): 84%, 47 mg. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.5 Hz, 1H), 7.55 (d, *J* = 8.5 Hz, 1H), 7.33 (s, 1H), 7.32 – 7.29 (m, 3H), 7.28 – 7.25 (m, 3H), 7.20 (dd, *J* = 6.9, 2.5 Hz, 2H), 7.11 (dd, *J* = 6.4, 2.8 Hz, 2H), 4.15 (s, 3H), 3.60 (s, 3H), 1.46 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.6, 141.8, 140.5, 137.6, 134.5, 134.1, 133.7, 130.9, 130.6, 129.8, 128.8, 128.7, 128.4, 127.5, 120.0, 119.7, 119.2, 117.0, 38.6, 36.7, 30.2, 15.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ -78.38. HRMS (ESI, positive ion): M^+ = 406.2298 (calculated 406.2278 for $[C_{28}H_{28}N_3]^+$).

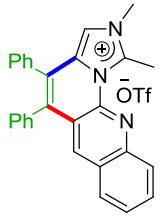


2-tert-butyl-5-ethyl-9-methyl-6-phenylimidazo[1,5-a][1,8]naphthyridinium trifluoromethanesulphonate (4e): 80%, 41 mg. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (d, *J* = 8.5 Hz, 1H), 7.72 (d, *J* = 8.5 Hz, 1H), 7.57 – 7.47 (m, 3H), 7.39 – 7.33 (m, 2H), 7.01 (s, 1H), 4.11 (s, 3H), 3.55 (s, 3H), 2.75 (q, *J* = 7.5 Hz, 2H), 1.48 (s, 9H), 1.18 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$)

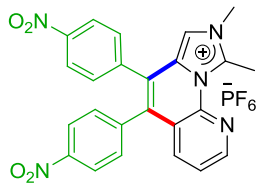
δ 169.4, 142.3, 140.1, 135.4, 134.8, 134.0, 131.4, 129.5, 129.3, 129.2, 126.8, 120.2, 118.4, 115.9, 38.6, 36.6, 30.2, 21.6, 15.3, 14.7. ^{19}F NMR (376 MHz, $CDCl_3$) δ -78.40. HRMS (ESI, positive ion): M^+ = 358.2289 (calculated 358.2278 for $[C_{24}H_{28}N_3]^+$).



1,2-dimethyl-4,5-diphenylbenzo[g]imidazo[1,5-a][1,8]naphthyridin-2-ium trifluoromethanesulphonate (4f): 88%, 48 mg. ^{1}H NMR (400 MHz, CD_3CN) δ 8.30 (s, 1H), 8.20 (d, *J* = 8.5 Hz, 1H), 7.94 (d, *J* = 8.2 Hz, 1H), 7.92 – 7.85 (m, 1H), 7.65 (t, *J* = 7.2 Hz, 1H), 7.44 – 7.40 (m, 3H), 7.36 (dd, *J* = 7.3, 4.4 Hz, 4H), 7.30 (td, *J* = 6.8, 2.9 Hz, 4H), 3.99 (s, 3H), 3.58 (s, 3H). ^{13}C NMR (101 MHz, CD_3CN) δ 145.7, 144.3, 143.1, 138.5, 135.5, 135.4, 135.1, 132.9, 131.6, 131.6, 130.8, 129.5, 129.5, 129.5, 129.5, 129.3, 128.9, 128.9, 128.0, 128.0, 122.1, 118.5, 36.6, 15.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ -78.40. HRMS (ESI, positive ion): M^+ = 400.1812 (calculated 400.1808 for $[C_{28}H_{22}N_3]^+$).

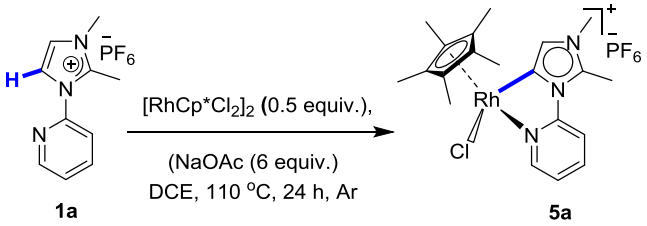


8,9-dimethyl-5,6-bis(4-nitrophenyl)imidazo[1,5-a][1,8]naphthyridinium hexafluorophosphate (4g): 75%, 44 mg. ^{1}H NMR (500 MHz, CD_3CN) δ 8.82 (dd, J = 4.6, 1.7 Hz, 1H), 8.22 – 8.16 (m, 4H), 7.85 (dd, J = 8.2, 1.7 Hz, 1H), 7.66 (dd, J = 8.1, 4.6 Hz, 1H), 7.50 (ddd, J = 9.0, 5.6, 2.2 Hz, 4H), 7.48 (s, 1H), 3.99 (s, 3H), 3.48 (s, 3H). ^{13}C NMR (126 MHz, CD_3CN) δ 149.7, 149.0, 148.9, 144.0, 143.1, 141.4, 140.9, 138.0, 134.1, 132.9, 132.1, 130.3, 127.7, 125.2, 124.8, 124.7, 122.1, 118.6, 36.8, 15.1. ^{19}F NMR (376 MHz, CD_3CN) δ -72.95 (d, *J* = 706.6 Hz). ^{31}P NMR (162 MHz, CD_3CN) δ -144.65 (hept, *J* = 706.7 Hz). HRMS (ESI, positive ion): M^+ = 440.1365 (calculated 440.1353 for $[C_{24}H_{18}N_5O_4]^+$).



9. Mechanistic studies:

(I) Synthesis of the aNHC-pyridine chelated Rh(III) intermediate 5a:



To an oven dried Schlenk tube, a mixture of **1a** (61 mg, 0.2 mmol), NaOAc (98.4 mg, 1.2 mmol) and $[RhCp^*Cl_2]_2$ (61.6 mg, 0.1 mmol) were loaded and then the tube was kept under vacuum for 15 minutes. After that the tube was filled with Ar gas. To this mixture, dry and degassed DCE (10 mL) was added

under Schlenk technique. After 24 h of reflux, the reaction mixture was allowed to cool down to room temperature and the solution was passed through a short celite pad followed by washing with dichloromethane (3×5 mL). The combined filtrate was concentrated under reduced pressure and the solid formed was re-dissolved in minimum quantity of CH_2Cl_2. To this solution hexane (~20 times) was added and resulting orange solid was separated and washed with hexane to produce the desired complex **5a** (109 mg, 92%) after drying under reduced pressure. ^{1}H NMR (500 MHz, CD_3CN) δ 8.75 (d, *J* = 5.3 Hz, 1H), 8.19 – 8.12 (m, 1H), 7.93 (d, *J* = 8.5 Hz, 1H), 7.57 (t, *J* = 6.4 Hz, 1H), 7.11 (s, 1H), 3.80 (s, 3H), 2.86 (s, 3H), 1.66 (s, 15H). ^{13}C NMR (126 MHz, CD_3CN) δ 155.2 (d, $J_{Rh\text{-}C(5)}$ = 44.6 Hz), 152.92, 152.05, 143.58, 142.09, 125.1, 123.5 (d, $J_{Rh\text{-}C(4)}$ = 2.9 Hz), 114.77, 98.20 (d, $J_{Rh\text{-}C(Cp^*)}$ = 6.8 Hz), 35.28, 12.86, 9.04. ^{19}F NMR (471 MHz, CD_3CN) δ -72.8(d, *J*= 703.58). ^{31}P NMR (202 MHz, CD_3CN) δ -144.70 (hept, *J* = 706.6 Hz). HRMS (ESI, positive ion): M^+ = 446.0876 (calculated 446.0865 for $[C_{20}H_{26}N_3ClRh]^+$).

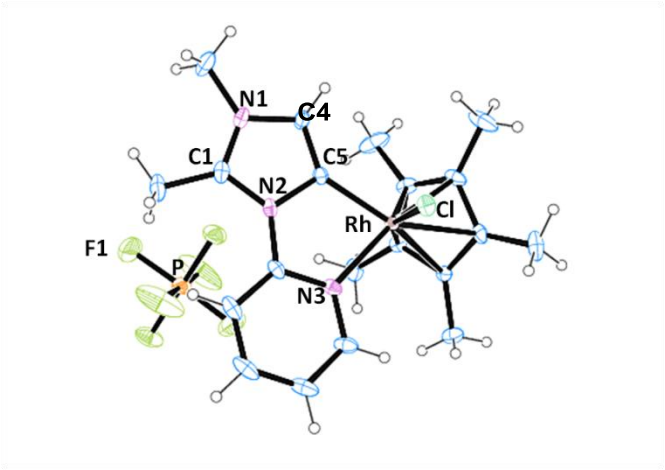
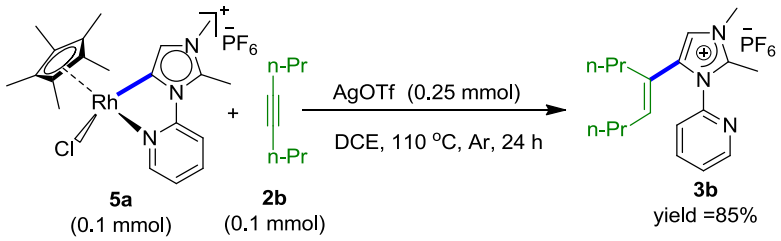


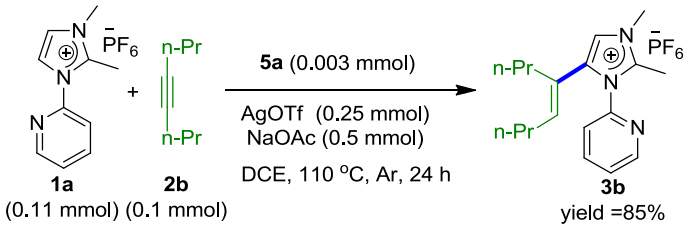
Figure S1: Molecular structure for 5a (30% probability ellipsoid): Selected bond lengths (Å) and bond angles (°): C5–Rh = 2.004(3); N3–Rh = 2.114(2); Cl–Rh = 2.428(7); C5–Rh–N3=77.39(10); N3–Rh–Cl = 88.47(6), C5–Rh–Cl = 88.87(8). **CCDC no.: 1431209**

(Ia): Stoichiometric reaction of 5a with alkyne 2b:

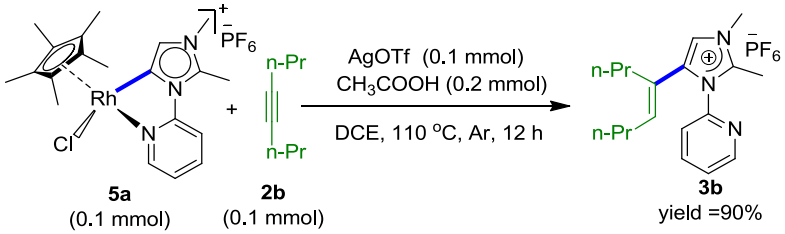
To an oven dried Schlenk tube, complex **5a** (0.1 mmol), AgOTf (0.25 mmol) and were loaded and then the tube was kept under vacuum for 15 minutes. After that the tube was filled with Ar gas. To this mixture, **2b** (0.1 mmol) and dry and degassed DCE (1.5 mL) was added under Schlenk technique and the reaction mixture was left with stirring at 110 °C in dark. After 24 h, the whole reaction mixture was passed through a short celite pad which was thereafter washed with dichloromethane (3×5 mL). The combined filtrate was concentrated under reduced pressure. The final product was separated by silica gel column chromatography, eluted with a $CHCl_3$/acetone solvent mixture.



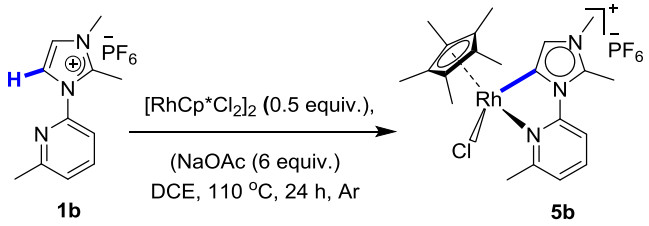
(Ib): Catalytic reaction of 5a with alkyne 2b: To an oven dried Schlenk tube, **1a** (0.11mmol), complex **5a** (0.003 mmol), NaOAc (0.5 mmol), AgOTf (0.25 mmol) and were loaded and then the tube was kept under vacuum for 15 minutes. After that the tube was filled with Ar gas. To this mixture **2b** (0.1 mmol), dry and degassed DCE (1.5 mL) was added under Schlenk technique and the reaction mixture was left with stirring at 110 °C in dark. After 24 h, the whole reaction mixture was passed through a short celite pad which was thereafter washed with dichloromethane (3×5 mL). The combined filtrate was concentrated under reduced pressure. The final product was separated by silica gel column chromatography, eluted with a $CHCl_3$/acetone solvent mixture.



(Ic): Control experiment in presence of acetic acid: To an oven dried Schlenk tube, complex **5a** (0.1 mmol), AgOTf (0.1 mmol) were loaded and then the tube was kept under vacuum for 15 minutes. After that the tube was filled with Ar gas. To this mixture, **2b** (0.1mmol), CH_3COOH (0.2mmol), dry and degassed DCE (1.5 mL) was added under Schlenk technique and the reaction mixture was left with stirring at 110 °C in dark. After 12 h, the whole reaction mixture was passed through a short celite pad which was thereafter washed with dichloromethane (3×5 mL). The combined filtrate was concentrated under reduced pressure. The final product was separated by silica gel column chromatography, eluted with a $CHCl_3$/acetone solvent mixture.

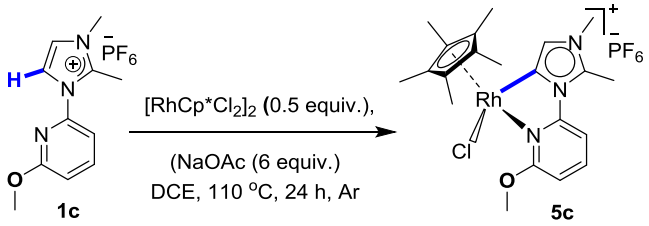


(II): Synthesis of the *a*NHC-pyridine chelated Rh(III) intermediate 4b:



To an oven dried Schlenk tube, a mixture of hexafluorophosphate salt of **1b** (33.3 mg, 0.1 mmol), NaOAc (49.2 mg, 0.6 mmol) and $[RhCp^*Cl_2]_2$ (30.8 mg, 0.05 mmol) were loaded and then the tube was kept under vacuum for 15 minutes. After that the tube was filled with Ar gas. To this mixture, dry and degassed DCE (5 mL) was added under Schlenk technique. After 24 h of reflux, the reaction mixture was allowed to cool down to room temperature and the solution was passed through a short celite pad followed by washing with dichloromethane (3×5 mL). The combined filtrate was concentrated under reduced pressure and the solid formed was re-dissolved in minimum quantity of CH_2Cl_2. To this solution hexane (~20 times) was added and resulting orange solid was separated and washed with hexane to produce the desired complex **5b** (54 mg, 89%) after drying under reduced pressure. ^{1}H NMR (500 MHz, CD_3CN) δ 8.00 (t, J = 8.0 Hz, 1H), 7.73 (d, J = 8.3 Hz, 1H), 7.51 (d, J = 7.7 Hz, 1H), 7.07 (s, 1H), 3.81 (s, 3H), 3.06 (s, 3H), 2.85 (s, 3H), 1.60 (s, 15H). ^{13}C NMR (126 MHz, CD_3CN) δ 163.7, 155.1 (d, $J_{Rh\text{-}C(5)}$ = 44.7 Hz), 152.4, 144.3, 141.7, 125.3, δ 124.4 (d, $J_{Rh\text{-}C(4)}$ = 2.9 Hz), 111.9, 98.9 (d, $J_{Rh\text{-}C(Cp^*)}$ = 6.7 Hz), 35.7, 28.3, 13.7, 9.9. ^{19}F NMR (471 MHz, CD_3CN) δ -72.96 (d, J = 706.0 Hz). HRMS (ESI, positive ion): M^+ = 460.1051 (calculated 460.1021 for $[C_{21}H_{27}N_3ClRh]^+$).

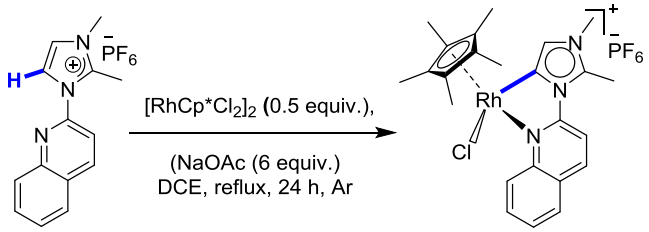
(III): Synthesis of the *a*NHC-pyridine chelated Rh(III) intermediate 5c:



To an oven dried Schlenk tube, a mixture of hexafluorophosphate salt of **1c** (36.9 mg, 0.1 mmol), NaOAc (49.2 mg, 0.6 mmol) and $[RhCp^*Cl_2]_2$ (30.8 mg, 0.05 mmol) were loaded and then the tube was kept under vacuum for 15 minutes. After that the tube was filled with Ar gas. To this mixture, dry and degassed DCE (5 mL) was added under Schlenk technique. After 24 h of reflux, the reaction mixture was allowed to cool down to room temperature and the solution was passed through a short celite pad followed by washing with dichloromethane (3×5 mL). The combined filtrate was concentrated under reduced pressure and the solid formed was re-dissolved in minimum quantity of CH_2Cl_2. To this solution hexane (~20 times) was

added and resulting orange solid was separated and washed with hexane to produce the desired complex **5c** (50 mg, 80%) after drying under reduced pressure. ^{1}H NMR (500 MHz, CD_3CN) δ 8.10 (t, *J* = 8.3 Hz, 1H), 7.49 (d, *J* = 8.1 Hz, 1H), 7.07 (t, *J* = 4.2 Hz, 2H), 4.15 (s, 3H), 3.80 (s, 3H), 2.85 (s, 3H), 1.66 (s, 15H). ^{13}C NMR (126 MHz, CD_3CN) δ 166.0, 154.4 (d, $J_{Rh\text{-}C(5)}$= 44.8 Hz),, 150.9, 144.8, 143.9, 123.6 (d, $J_{Rh\text{-}C(4)}$= 3.0 Hz), 107.1, 106.6, 98.6 (d, $J_{Rh\text{-}C(Cp^*)}$ = 6.9 Hz), 58.7, 35.7, 13.7, 10.0. ^{19}F NMR (471 MHz, CD_3CN) δ -72.96 (d, *J* = 706.0 Hz). ^{31}P NMR (202 MHz, CD_3CN) δ -144.63 (hept, *J* = 706.3 Hz). HRMS (ESI, positive ion): M^+ = 476.0997 (calculated 476.0970 for $[C_{21}H_{28}N_3OClRh]^+$).

(IV). Synthesis of the *a*NHC-pyridine chelated Rh(III) intermediate 5d :



To an oven dried Schlenk tube, a mixture of hexafluorophosphate salt of **1d** (35.8 mg, 0.1 mmol), NaOAc (49.2 mg, 0.6 mmol) and $[RhCp^*Cl_2]_2$ (30.8 mg, 0.05 mmol) were loaded and then the tube was kept under vacuum for 15 minutes. After that the tube was filled with Ar gas. To this mixture, dry and degassed DCE (5 mL) was added under Schlenk technique. After 24 h of reflux, the reaction mixture was allowed to cool down to room temperature and the solution was passed through a short celite pad followed by washing with dichloromethane (3×5 mL). The combined filtrate was concentrated under reduced pressure and the solid formed was re-dissolved in minimum quantity of CH_2Cl_2. To this solution hexane (~20 times) was added and resulting orange solid was separated and washed with hexane to produce the desired complex **5d** (55 mg, 85%) after drying under reduced pressure. ^{1}H NMR (500 MHz, CD_3CN) δ 8.69 (d, *J* = 9.0 Hz, 1H), 8.63 (d, *J* = 8.7 Hz, 1H), 8.13 (d, *J* = 8.1 Hz, 1H), 8.06 (ddd, *J* = 8.5, 8.0, 4.2 Hz, 2H), 7.80 (t, *J* = 7.6 Hz, 1H), 7.13 (s, 1H), 3.85 (s, 3H), 2.97 (s, 3H), 1.58 (s, 15H). ^{13}C NMR (126 MHz, CD_3CN) δ 156.59 (d, $J_{Rh\text{-}C(5)}$ = 44.9 Hz) 152.5, 146.4, 145.3, 143.4, 133.4, 130.9, 129.6, 129.3, 128.6, 124.7 (d, $J_{Rh\text{-}C(4)}$ = 2.9 Hz), 113.0, 99.1 (d, $J_{Rh\text{-}C(Cp^*)}$ = 6.7 Hz), 35.9, 13.8, 9.8. ^{19}F NMR (471 MHz, CD_3CN) δ -72.94 (d, *J* = 717.5 Hz). ^{31}P NMR (202 MHz, CD_3CN) δ -144.63 (hept, *J* = 706.3 Hz). HRMS (ESI, positive ion): M^+ = 496.1002 (calculated 496.1021 for $[C_{24}H_{28}N_3ClRh]^+$).

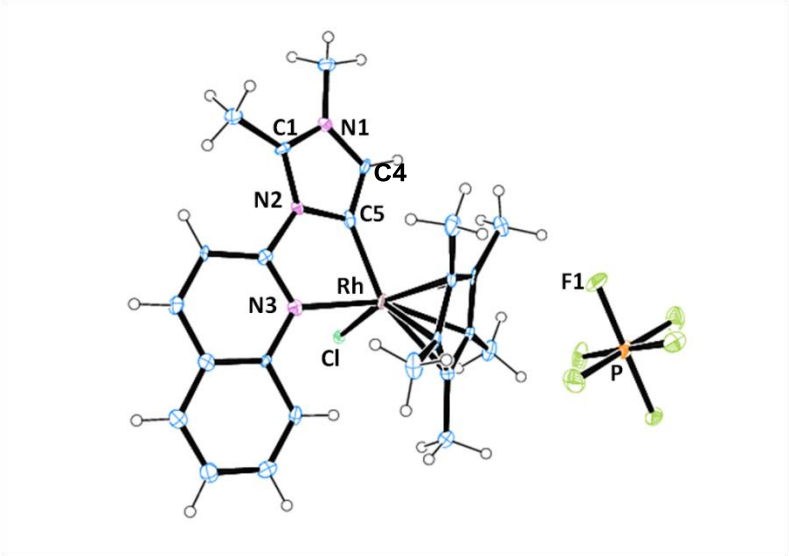
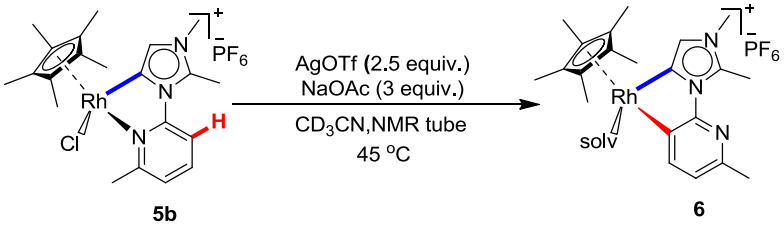


Figure S2: Molecular structure for 5d (30% probability ellipsoid): Selected bond lengths (Å) and bond angles (°): C5–Rh = 2.4386(15); N3–Rh = 2.135(5); Cl–Rh = 2.4386(15); C5–Rh–N3 = 76.7(2); N3–Rh–Cl = 86.86(13), C5–Rh–Cl = 94.89(17). **CCDC no.: 1587269**

10. Controlled studies: NMR tube experiment:

(a) In-situ generation of rollover abnormal cyclometalated intermediate 6: 0.005mmol, 3mg of complex **5b** was dissolved in CD_3CN in a NMR tube and to it 0.0125mmol, 3.2mg AgOTf and 0.015mmol, 1.2mg NaOAc was added and warmed at 45 ^oC for 30 minutes. Later, crude NMR data were collected to observe the changes.



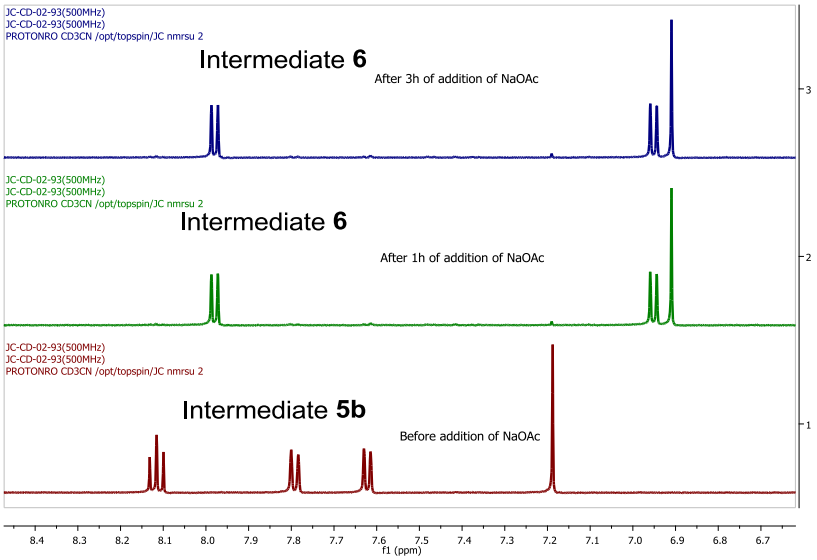


Figure S3: ^{1}H partial NMR of pre-rollover intermediate **5b** and post rollover intermediate **6** (500 MHz, CD_3CN, 300 K

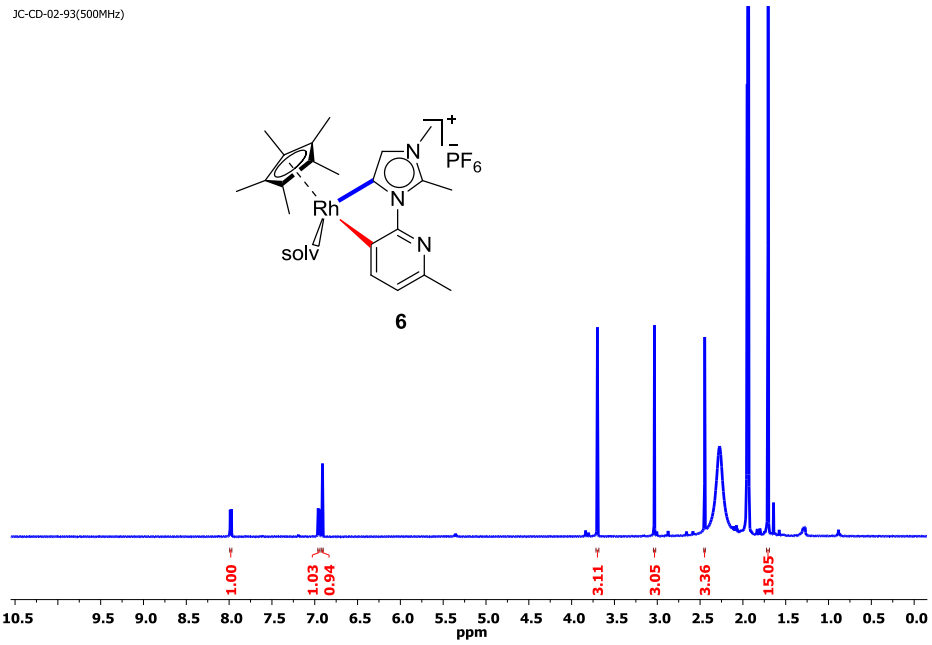


Figure S4: ^{1}H NMR of rollover intermediate **6** (500 MHz, CD_3CN, 300 K)

(b) Control experiment in absence of NaOAc: 0.005mmol, 3mg of complex **5b** is dissolved in CD_3CN in a NMR tube and to it 0.0125mmol, 3.2mg AgOTf is added and shaken well. NMR data were collected in intervals of 2h for 4 readings.

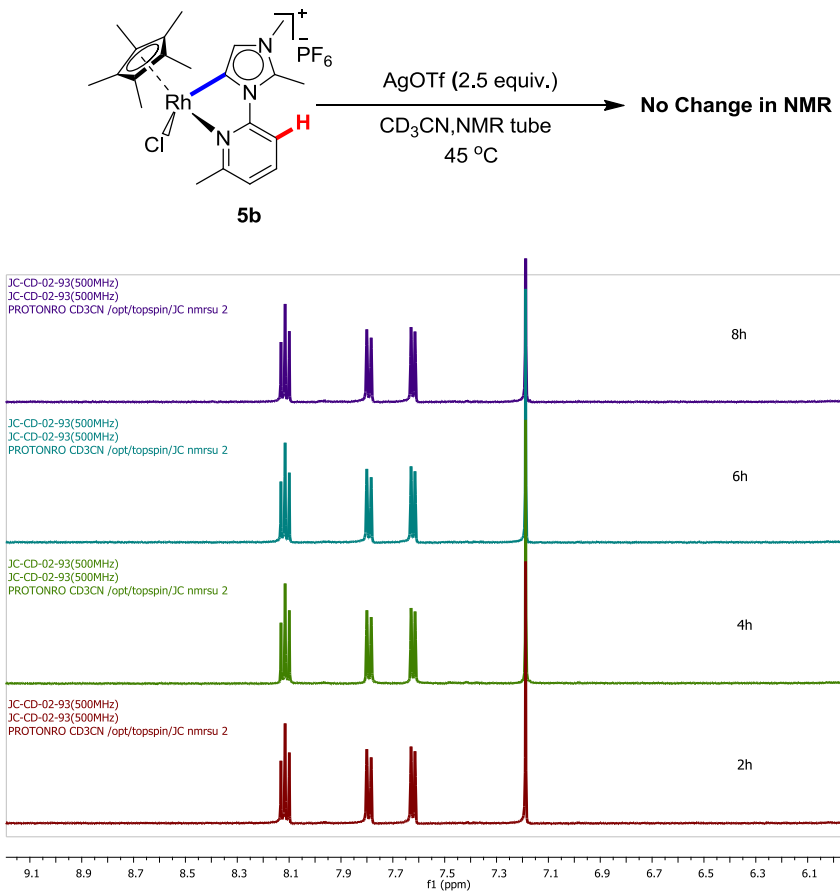


Figure S5: ^{1}H partial NMR of intermediate **5b** (500 MHz, CD_3CN, 300 K)

(c) Check for reversibility: To the NMR tube from experiment **10(a)**, 0.0125mmol, 1µL glacial Acetic acid was added and warmed for 30 minutes in water bath. Crude NMR data were collected in interval of 2h for 4 readings, first reading after 1 h of addition.

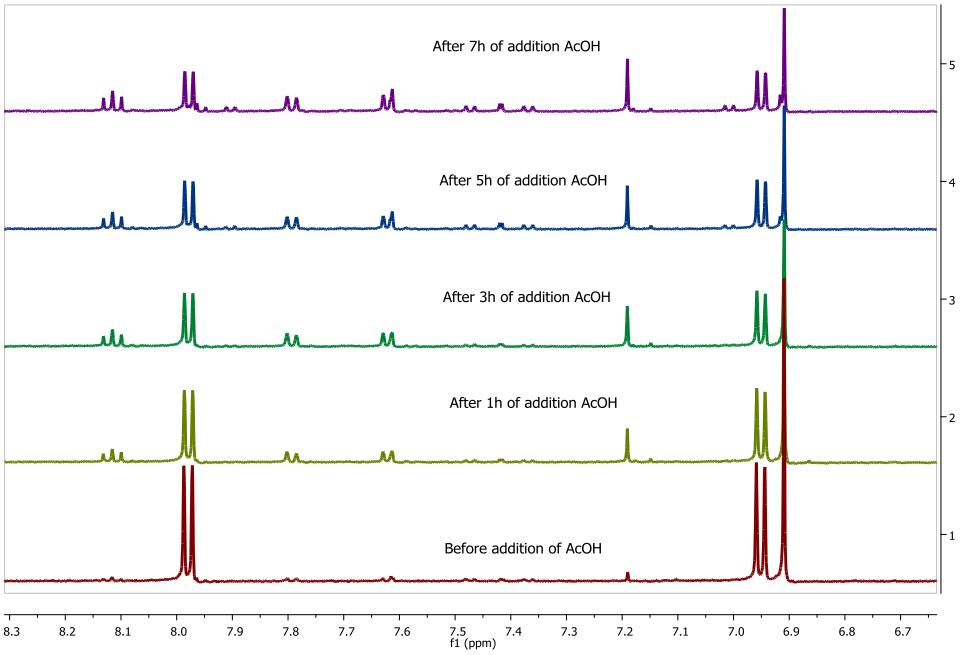
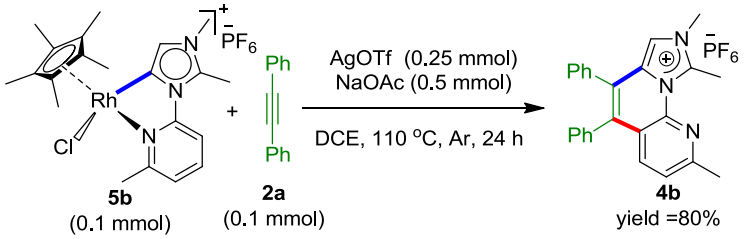


Figure S6: ^{1}H partial NMR for reversibility check (500 MHz, CD_3CN, 300 K)

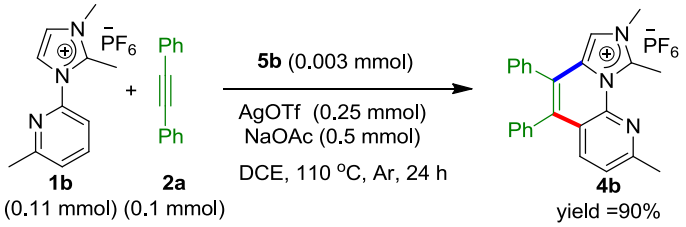
(d) Stoichiometric reaction of 5b with 2a:

To an oven dried Schlenk tube, complex **5b** (0.1 mmol), AgOTf (0.25 mmol), NaOAc (0.5mmol) and **2a** (0.1 mmol) were loaded and then the tube was kept under vacuum for 15 minutes. After that the tube was filled with Ar gas. To this mixture, dry and degassed DCE (1.5 mL) was added under Schlenk technique and the reaction mixture was left with stirring at 110 °C in dark. After 24 h, the whole reaction mixture was passed through a short celite pad which was thereafter washed with dichloromethane (3×5 mL). The combined filtrate was concentrated under reduced pressure. The final product was separated by silica gel column chromatography, eluted with a $CHCl_3$/acetone solvent mixture.



(e) Catalytic reaction of 5b with 2a: To an oven dried Schlenk tube, **1b** (0.11mmol), complex **5b** (0.003 mmol), NaOAc (0.5 mmol), AgOTf (0.25 mmol) and **2a** (0.1 mmol) were loaded and then the tube was kept under vacuum for 15 minutes. After that the tube was filled with Ar gas. To this mixture, dry and degassed DCE (1.5 mL) was added under Schlenk technique and the reaction mixture was left with stirring

at 110 °C in dark. After 24 h, the whole reaction mixture was passed through a short celite pad which was thereafter washed with dichloromethane (3×5 mL). The combined filtrate was concentrated under reduced pressure. The final product was separated by silica gel column chromatography, eluted with a $CHCl_3$/acetone solvent mixture.



(f) NMR tube control experiment for rollover in abnormal cyclometalated intermediate 5c: Similar procedure as in **section 10(a)**

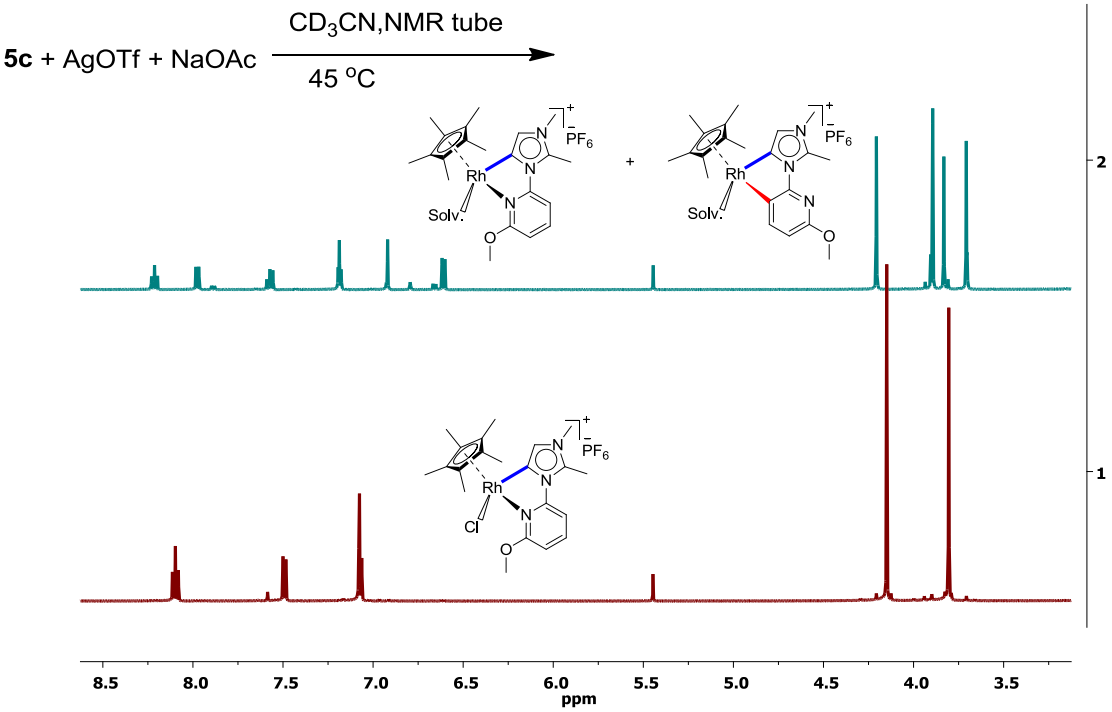


Figure S7: ^{1}H NMR for control experiment with intermediate **5c** (500 MHz, CD_3CN, 300 K)

(g) NMR tube control experiment for rollover in abnormal cyclometalated intermediate 5d: Similar procedure as in **section 10(a)**

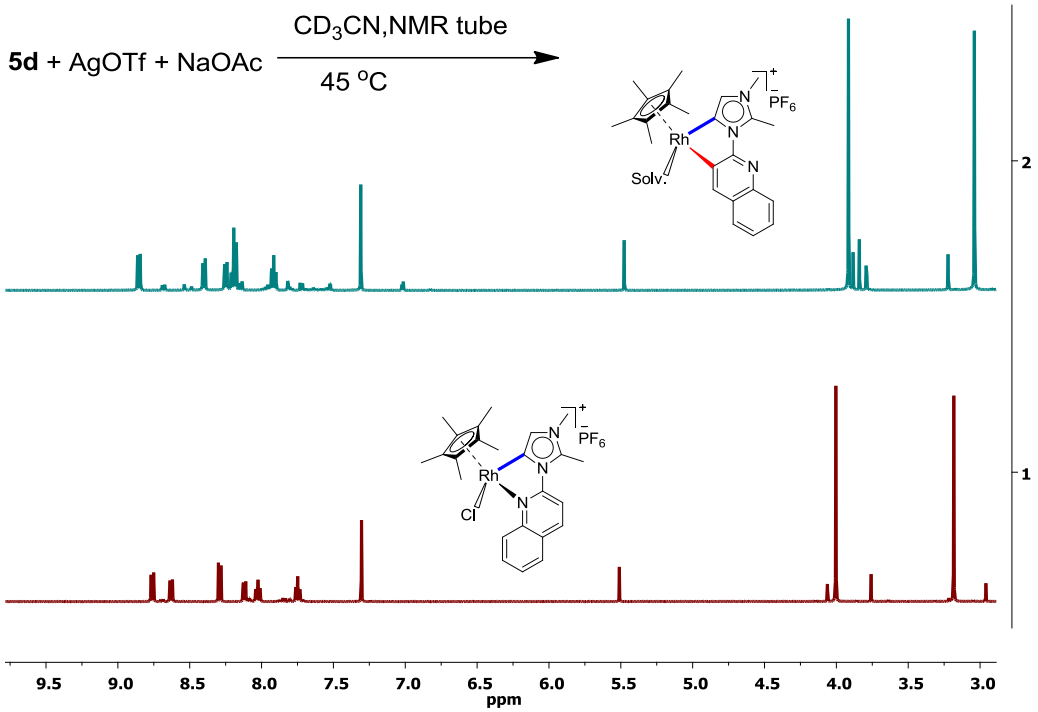


Figure S8: ^{1}H NMR for control experiment with intermediate **5d** (500 MHz, CD_3CN, 300 K)

11. Characterization data for imidazolium salts:

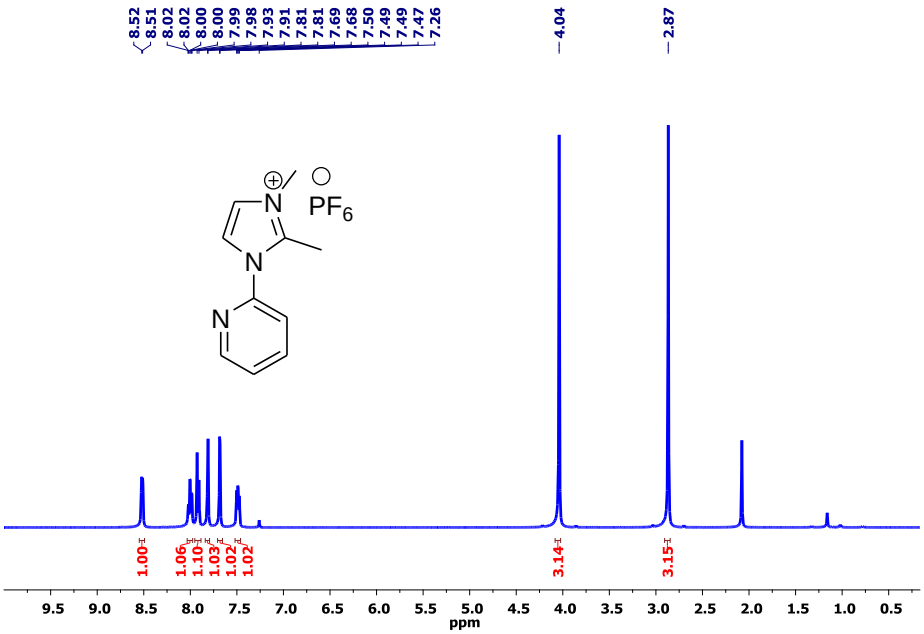


Figure S9. ^{1}H NMR spectrum of **1a** (400 MHz, $CDCl_3$, 300 K)

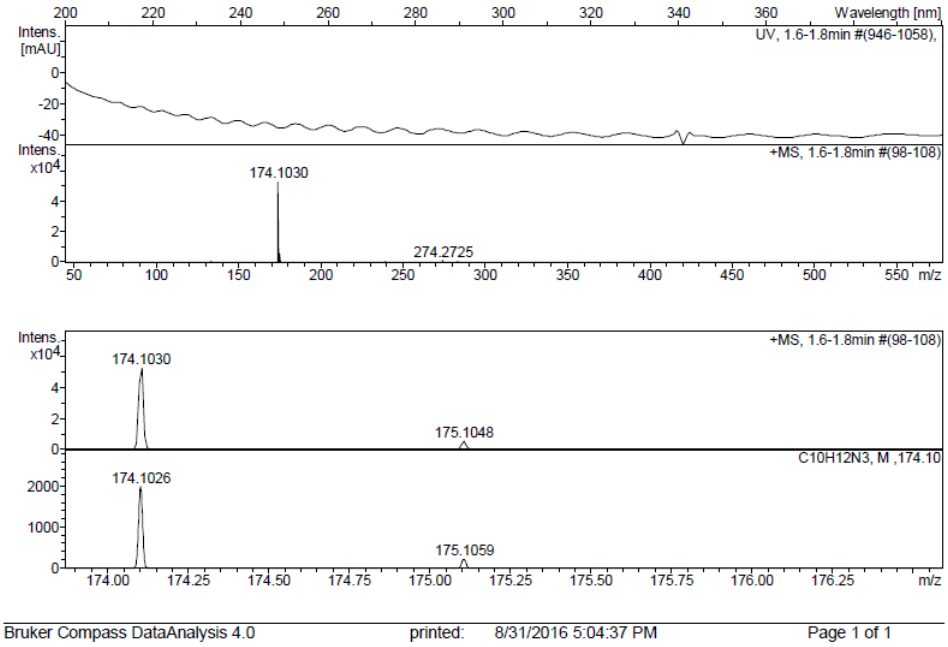


Figure S10. ESI-HRMS (positive ion mode) spectrum of **1a**

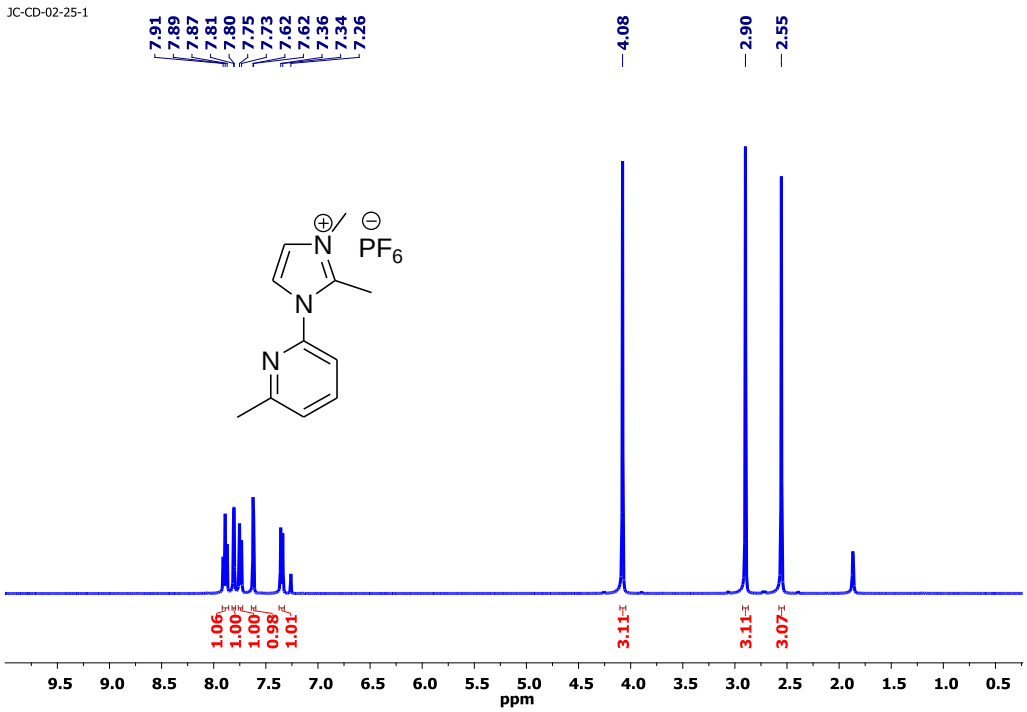


Figure S11. ^{1}H NMR spectrum of **1b** (400 MHz, $CDCl_3$, 300 K)

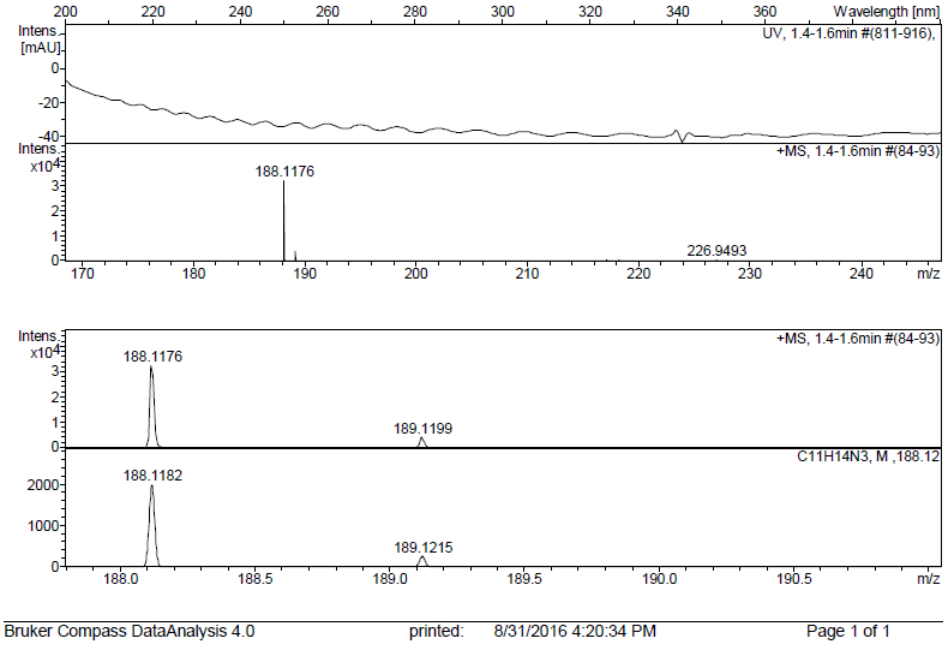


Figure S12. ESI-HRMS (positive ion mode) spectrum of **1b**

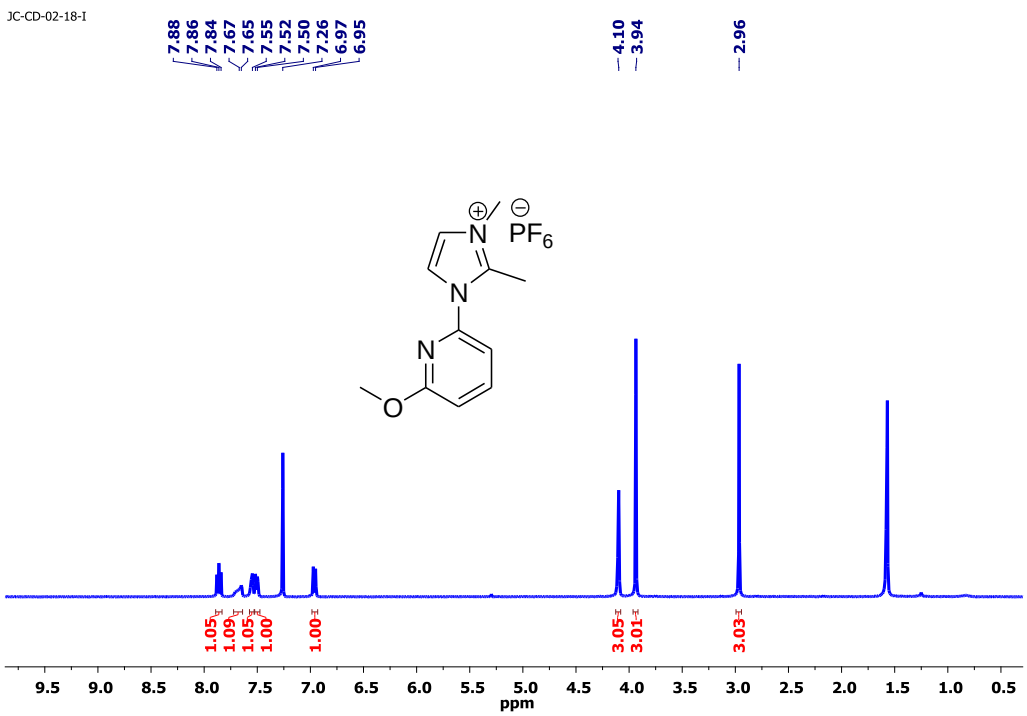


Figure S13. ^{1}H NMR spectrum of **1c** (400 MHz, $CDCl_3$, 300 K)

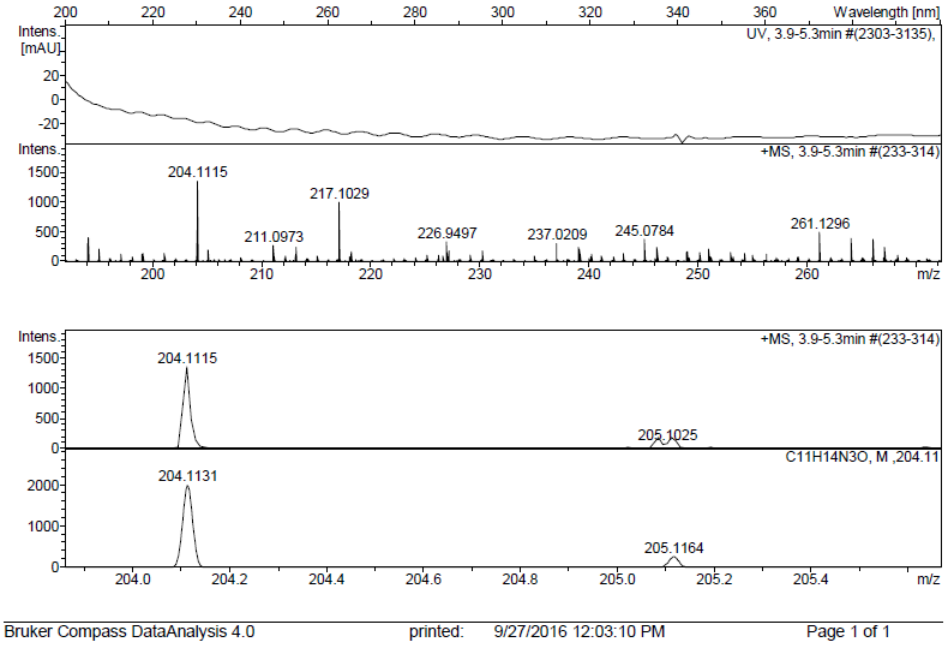


Figure S14. ESI-HRMS (positive ion mode) spectrum of **1c**

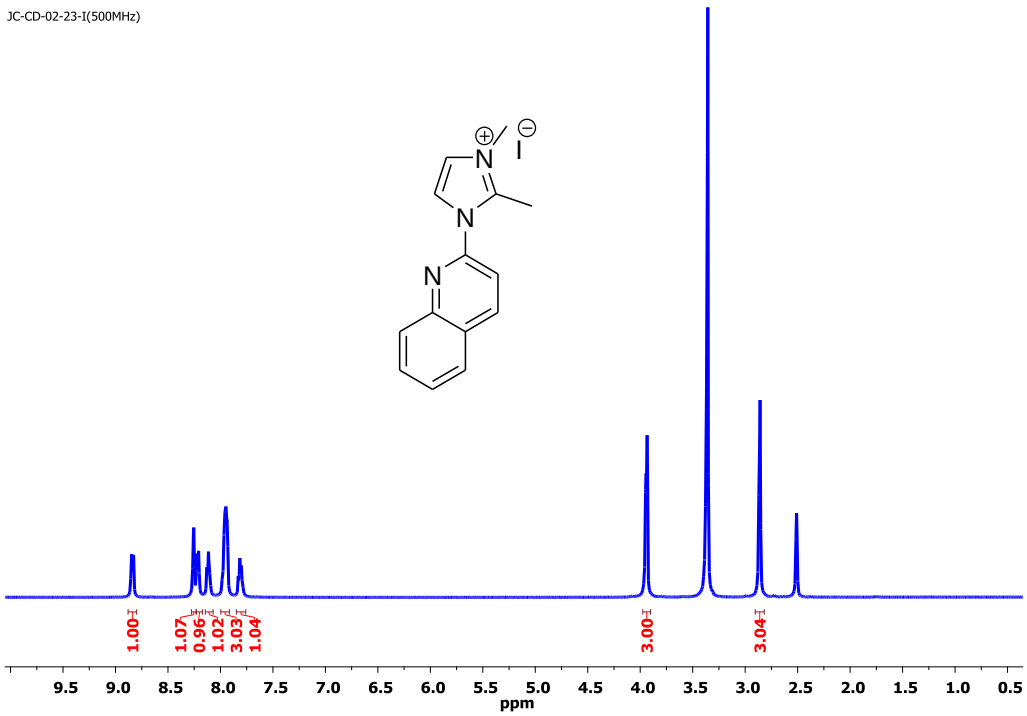


Figure S15. ^{1}H NMR spectrum of **1d** (500 MHz, DMSO-d6, 300 K)

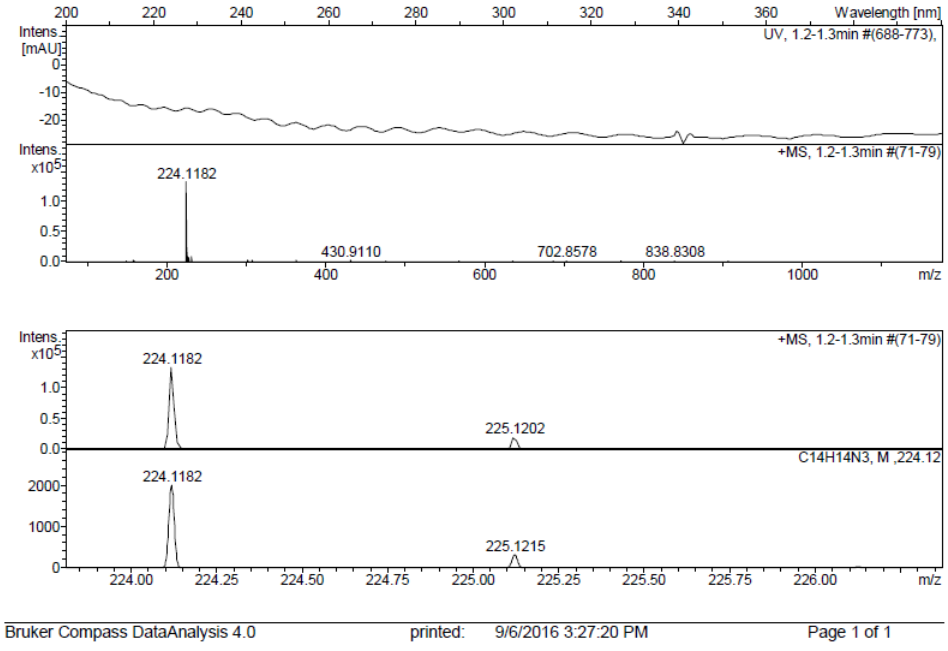


Figure S16. ESI-HRMS (positive ion mode) spectrum of **1d**

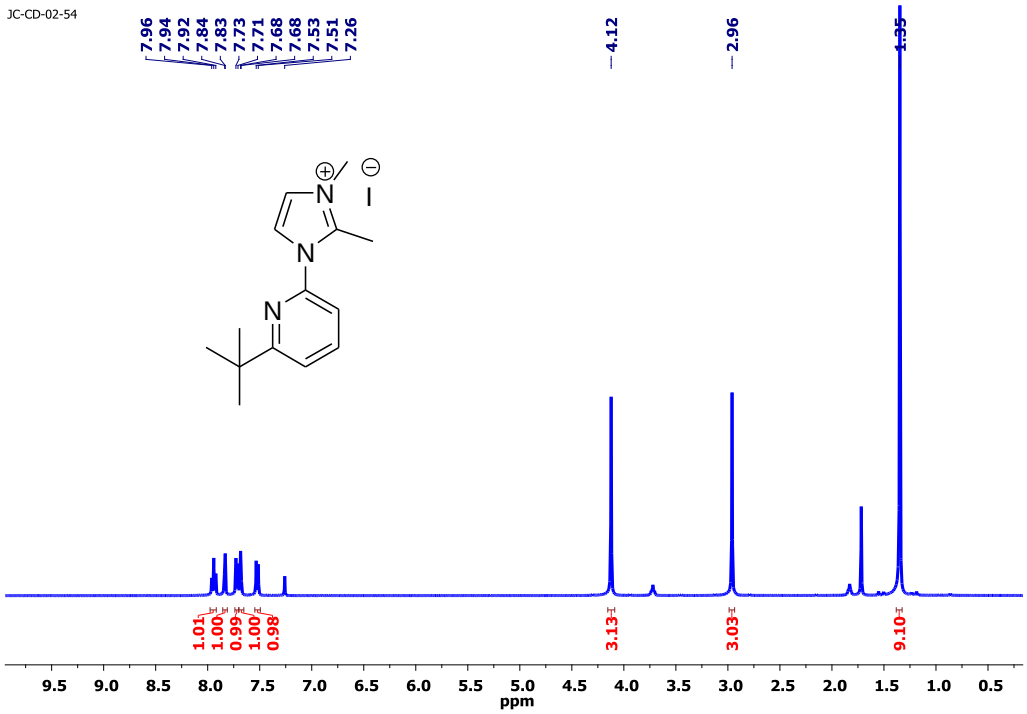


Figure S17. ^{1}H NMR spectrum of **1e** (400 MHz, $CDCl_3$, 300 K)

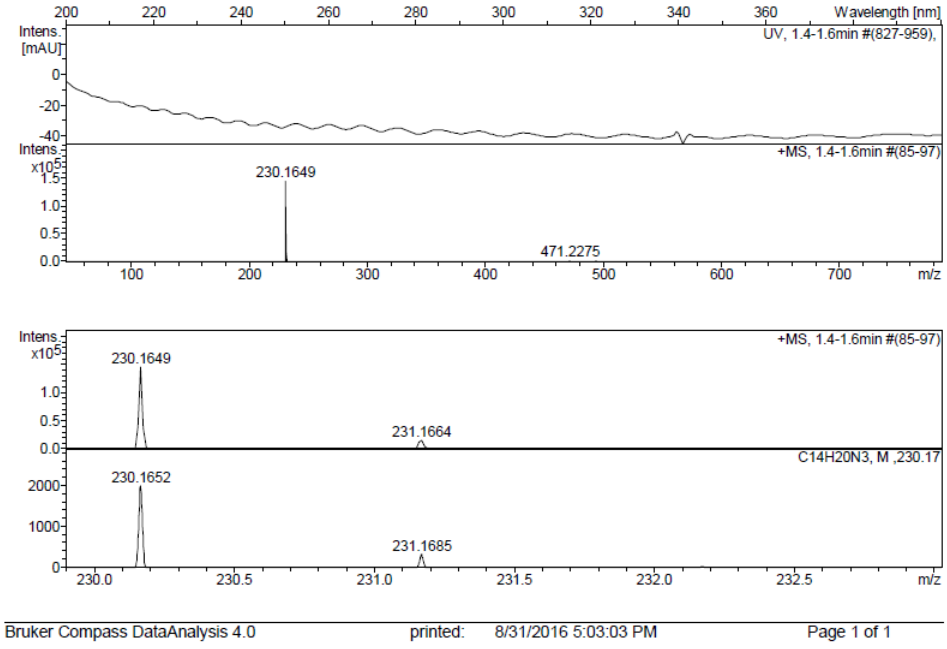


Figure S18. ESI-HRMS (positive ion mode) spectrum of **1e**

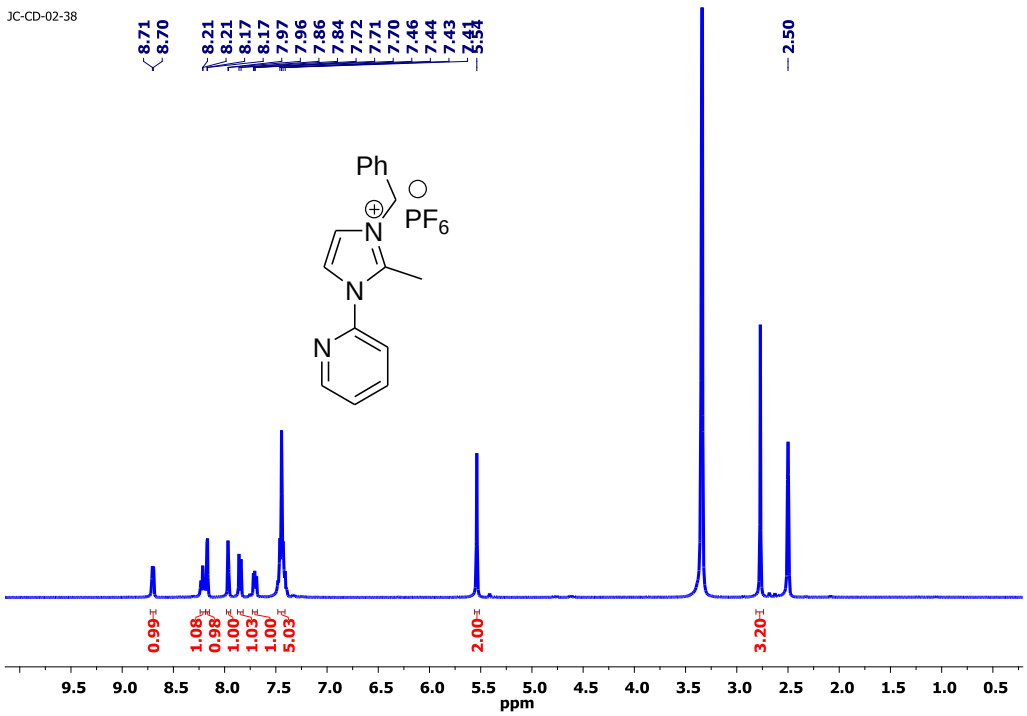


Figure S19. ^{1}H NMR spectrum of **1f** (400 MHz, DMSO-d6, 300 K)

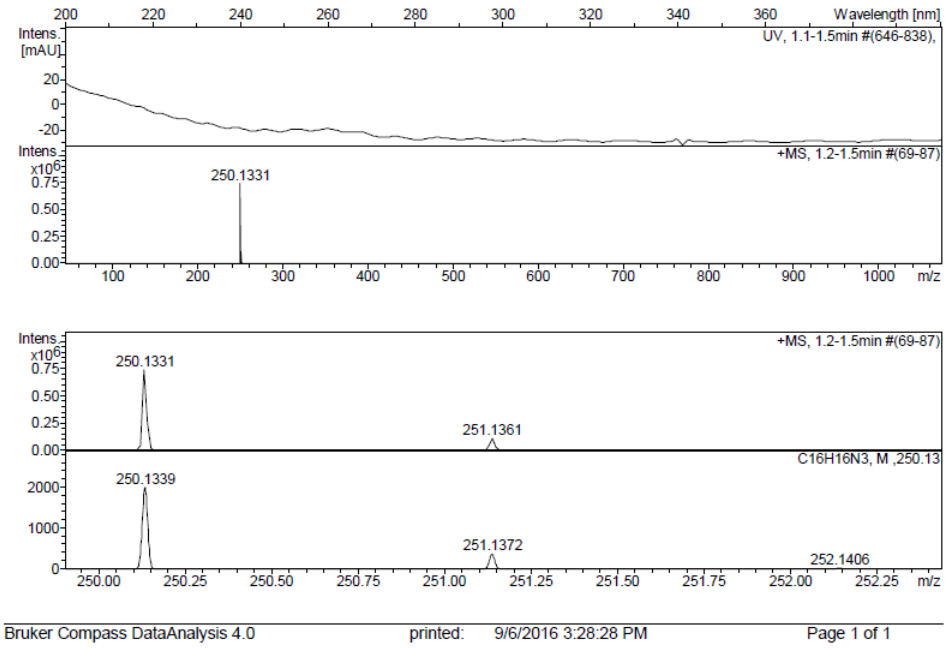


Figure S20. ESI-HRMS (positive ion mode) spectrum of **1f**

12. Characterization data for alkenylated products:

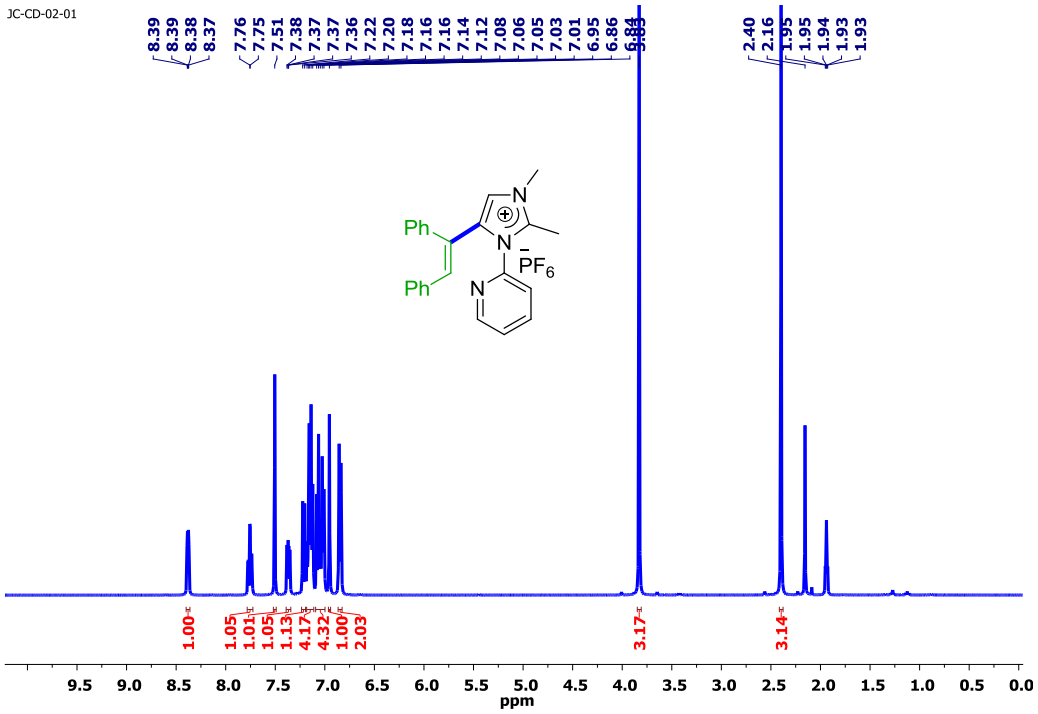


Figure S21. ^{1}H NMR spectrum of **3a** (400 MHz, CD_3CN, 300 K)

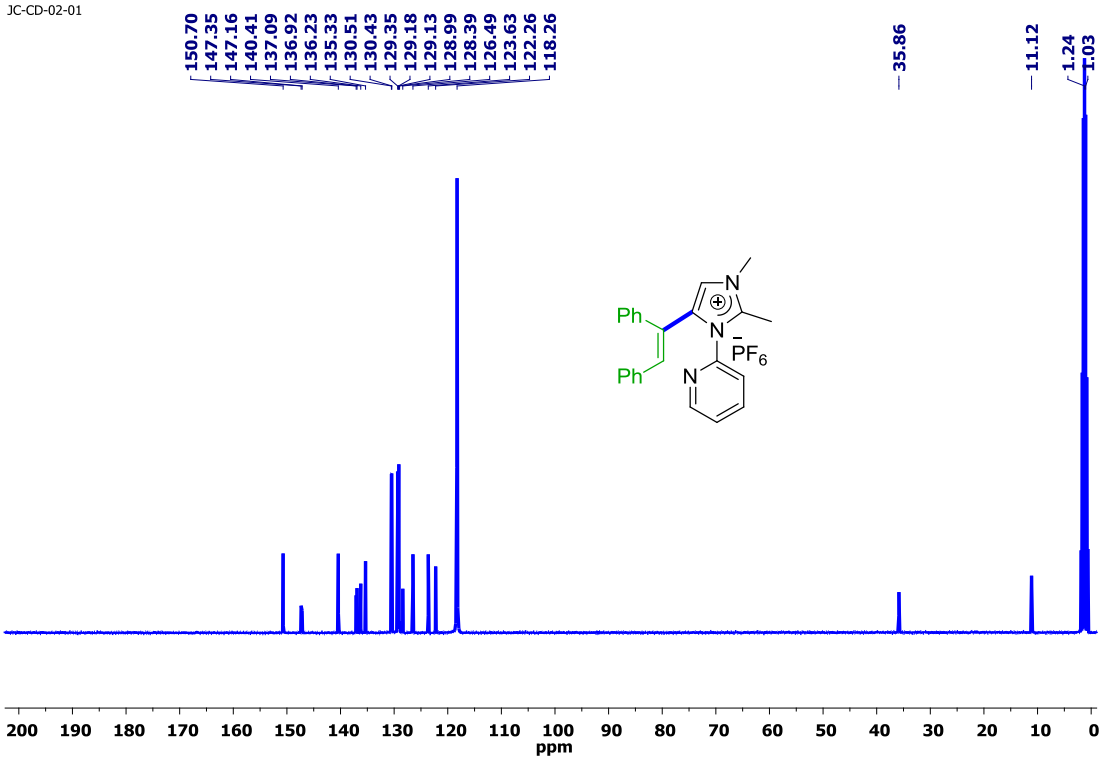


Figure S22. $^{13}C\{^{1}H\}$ NMR spectrum of **3a** (101 MHz, CD_3CN, 300 K)

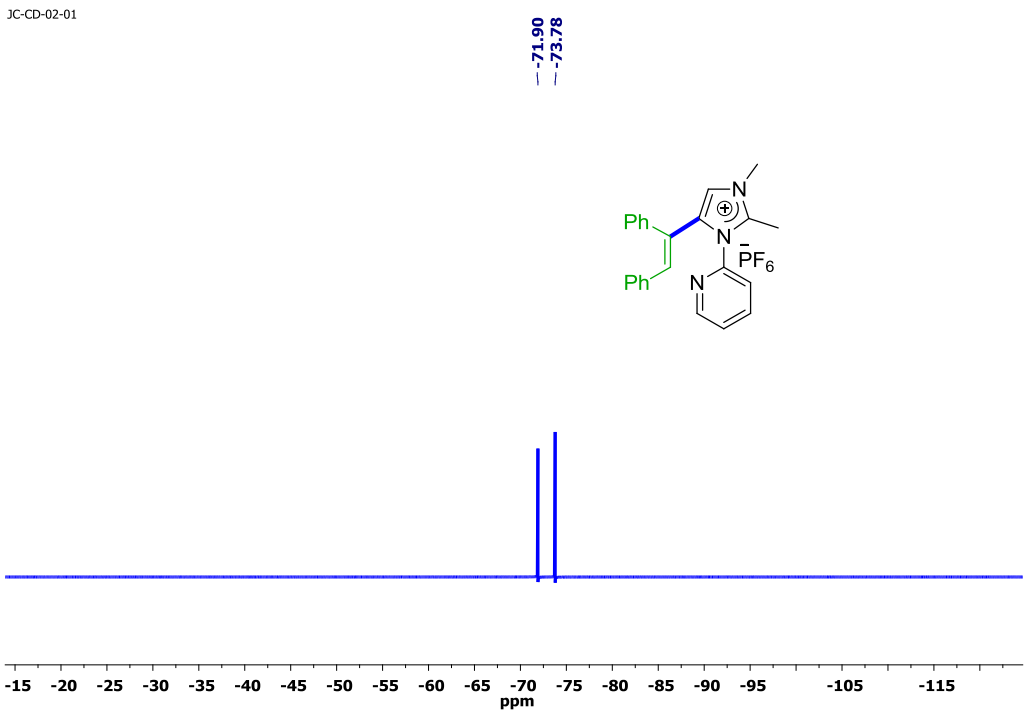


Figure S23. ^{19}F NMR spectrum of **3a** (376 MHz, CD_3CN, 300 K)

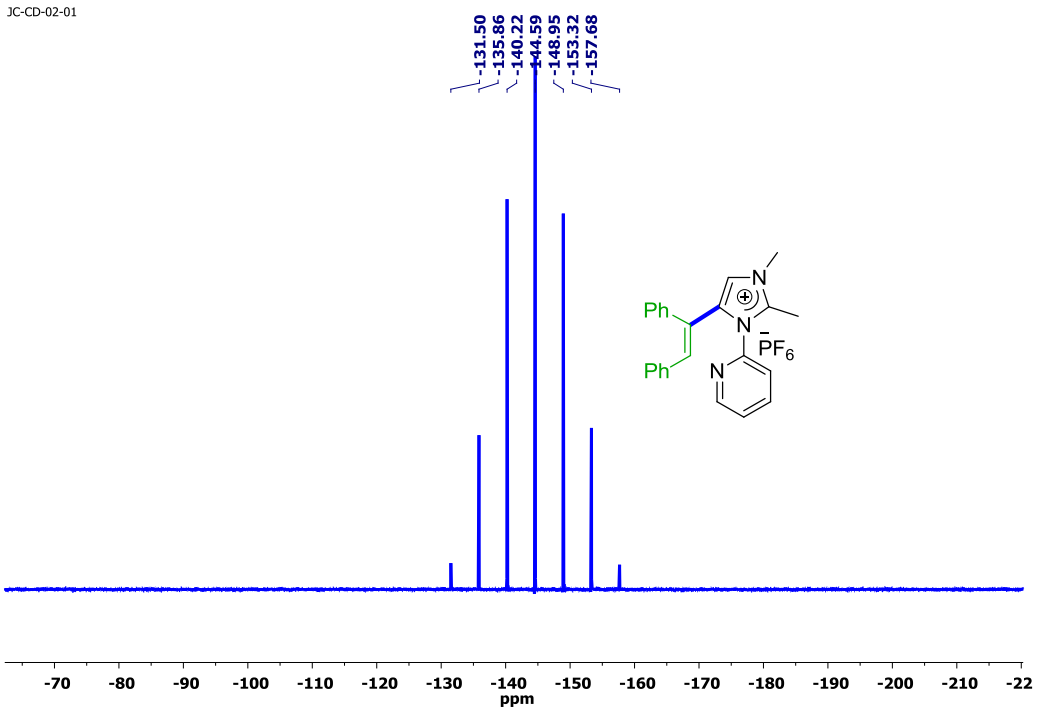


Figure S24. ^{31}P NMR spectrum of **3a** (162 MHz, CD_3CN, 300 K)

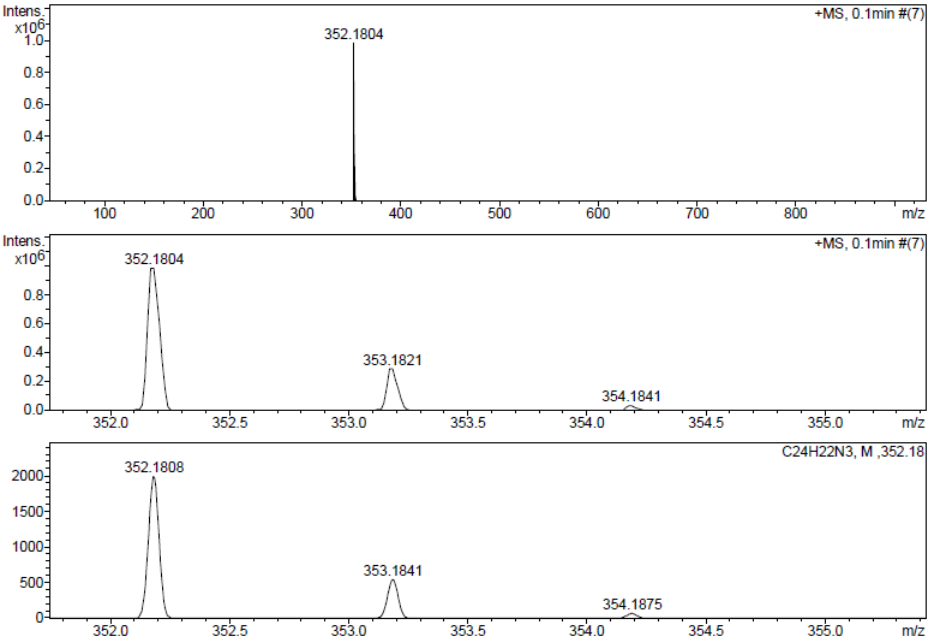


Figure S25. ESI-HRMS (positive ion mode) spectrum of **3a**

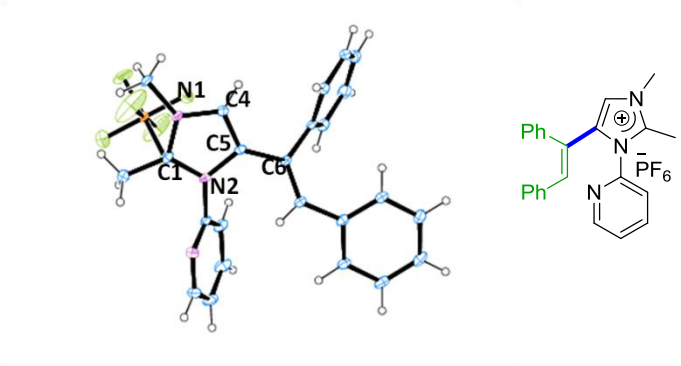


Figure S26. Molecular structure of product **3a** as hexafluorophosphate salt (30% probability level). Selected bond lengths (Å) and bond angles (°): C_1–N_1 = 1.329(4); C_1–N_2 = 1.342(3); C_5–C_6 = 1.473(4); N_1–C_1–N_2 = 107.9(2); N_2–C_5–C_6 = 125.5(2); C_4–C_5–C_6.= 129.8(3); **CCDC no.: 1587267**

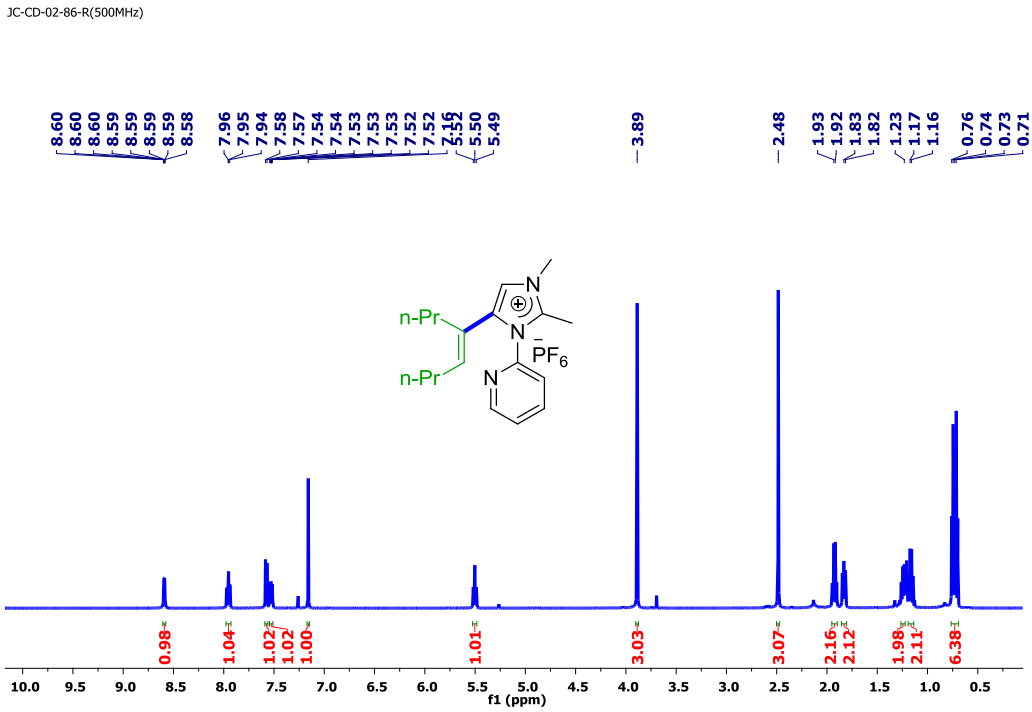


Figure S27. ^{1}H NMR spectrum of **3b** (500 MHz, $CDCl_3$, 300 K)

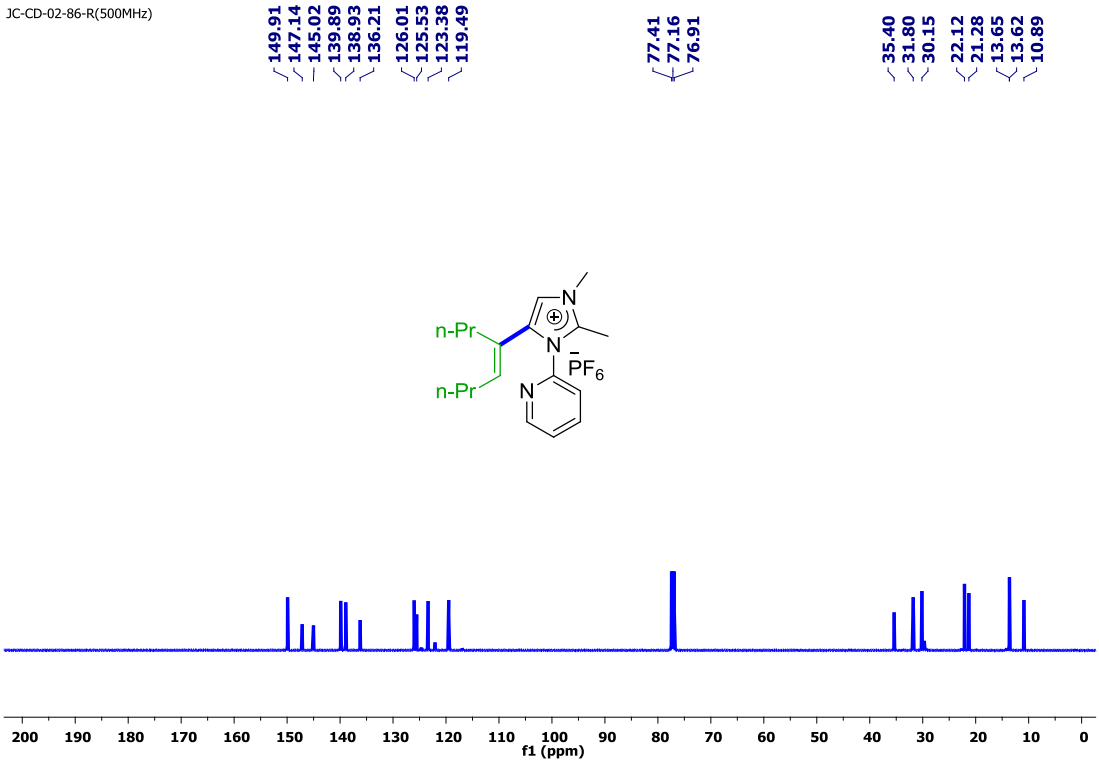


Figure S28. $^{13}C\{^{1}H\}$ NMR spectrum of **3b** (126 MHz, $CDCl_3$, 300 K) .

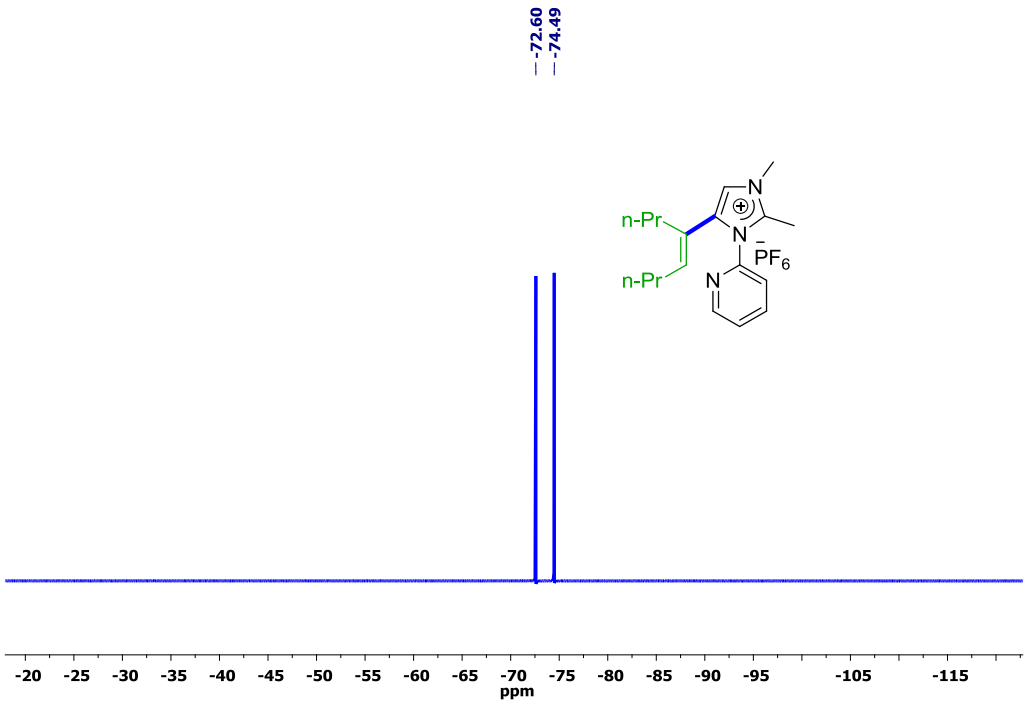


Figure S29. ^{19}F NMR spectrum of **3b** (471MHz, $CDCl_3$, 300 K)

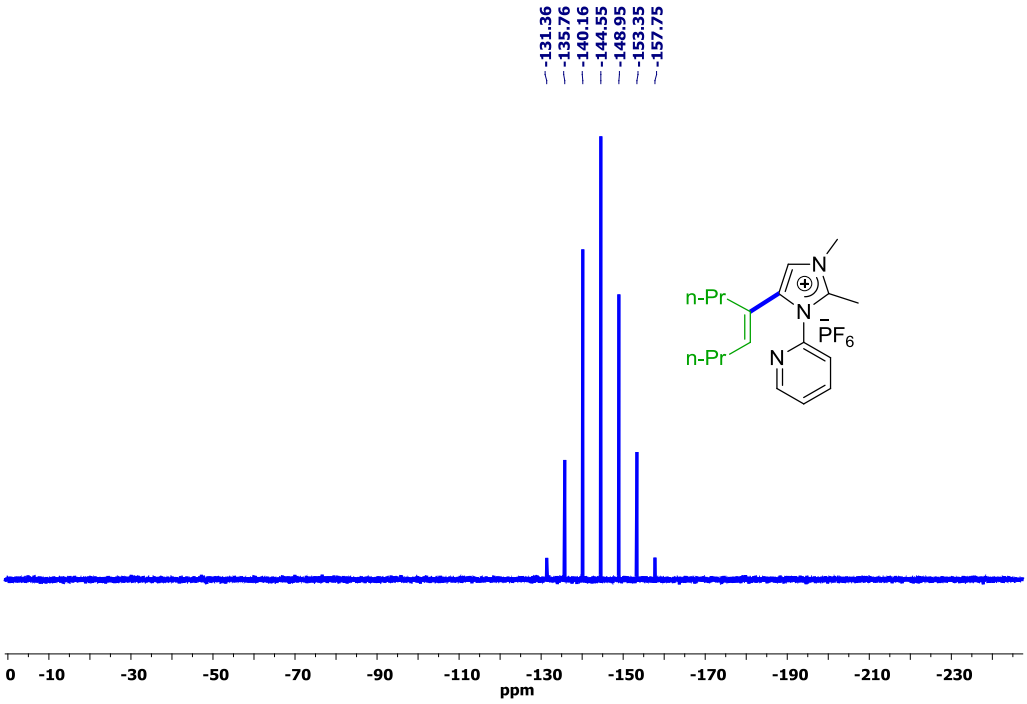


Figure S30. ^{31}P NMR spectrum of **3b** (202 MHz, $CDCl_3$, 300 K).

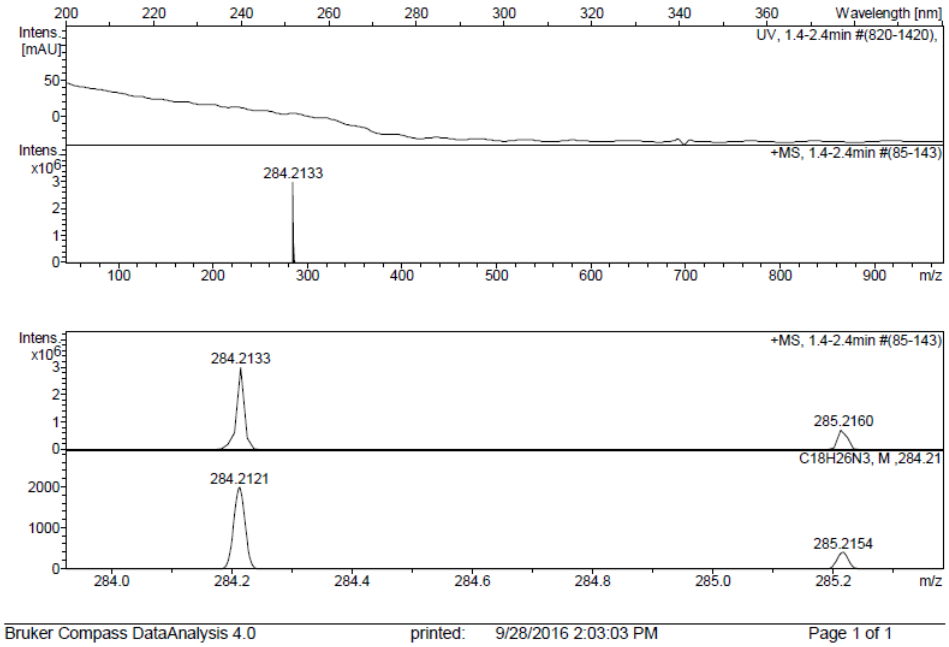


Figure S31. ESI-HRMS (positive ion mode) spectrum of **3b**

.

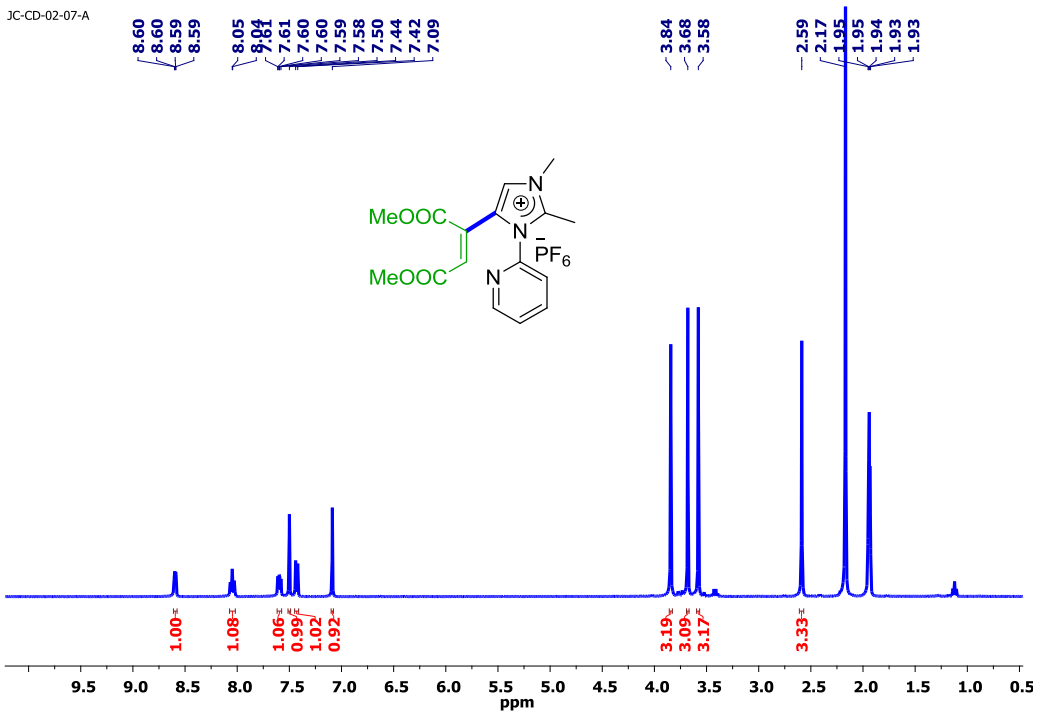


Figure S32. ^{1}H NMR spectrum of **3c** (400 MHz, CD_3CN, 300 K)

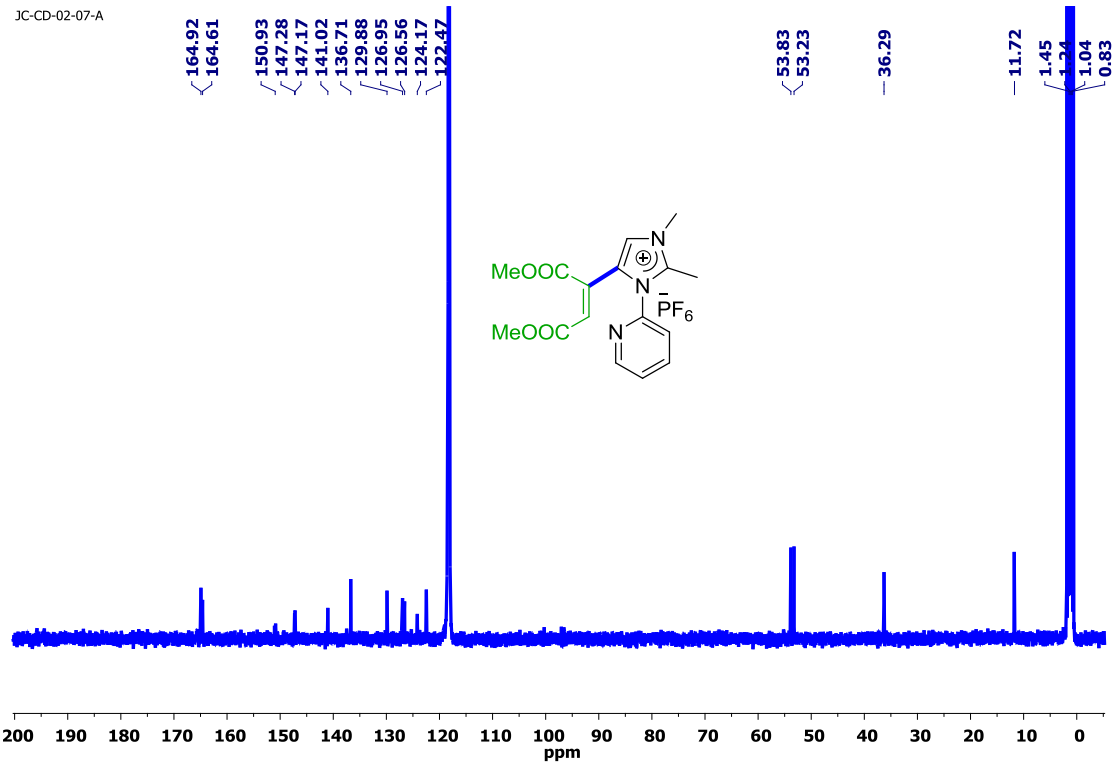


Figure S33. $^{13}C\{^{1}H\}$ NMR spectrum of **3c** (101 MHz, CD_3CN, 300 K).

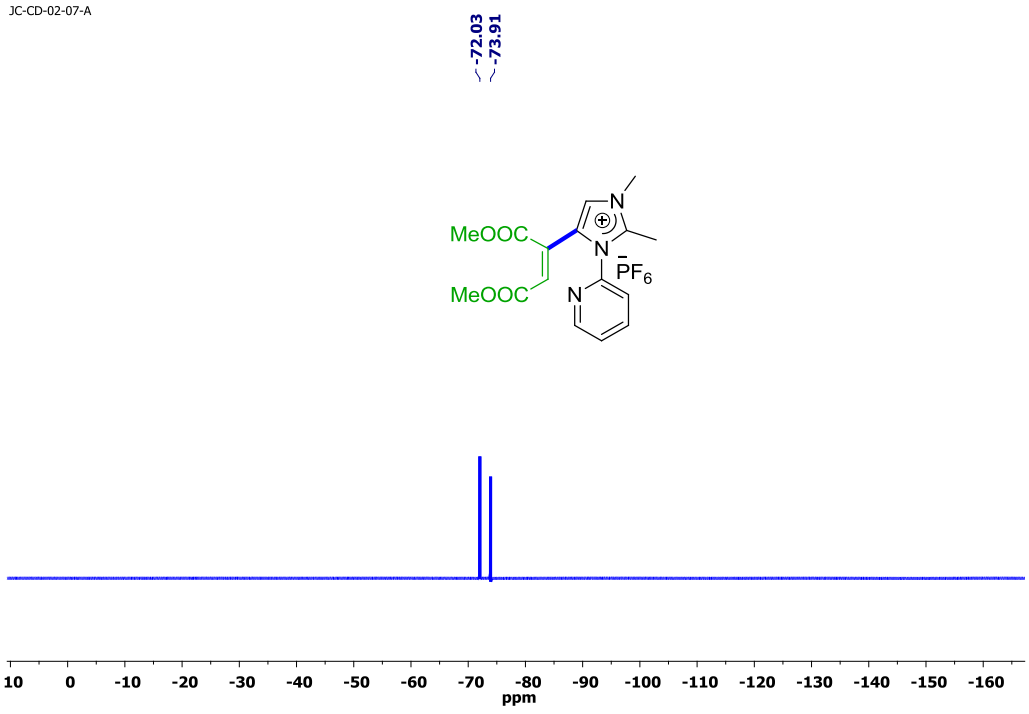


Figure S34. ^{19}F NMR spectrum of **3c** (376 MHz, CD_3CN, 300 K)

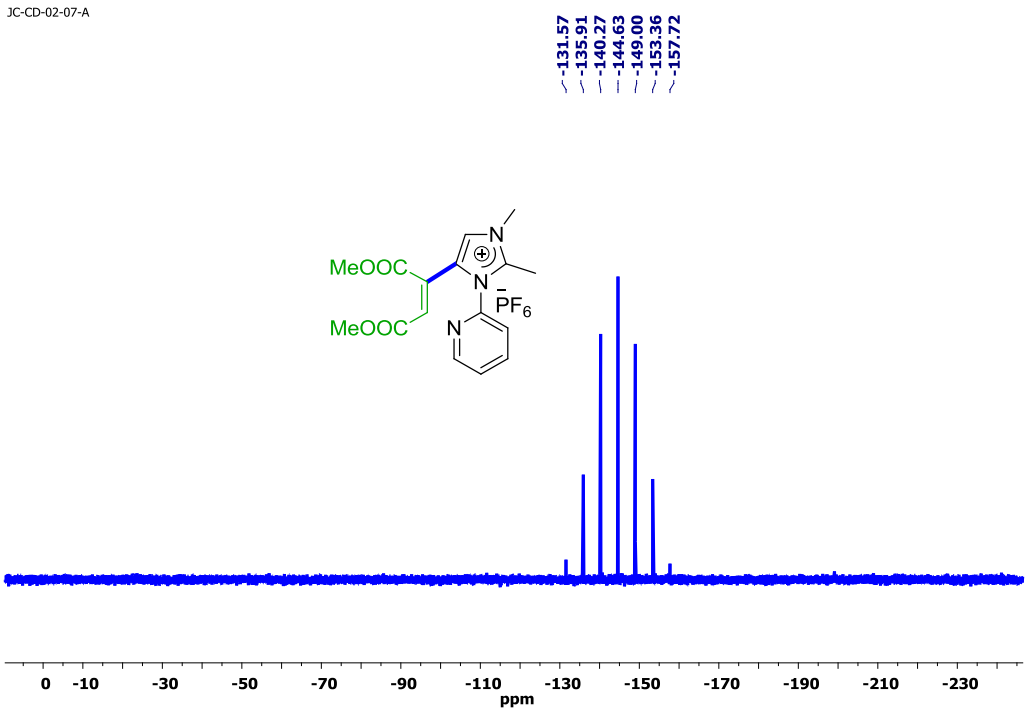


Figure S35. ^{31}P NMR spectrum of **3c** (162 MHz, CD_3CN, 300 K)

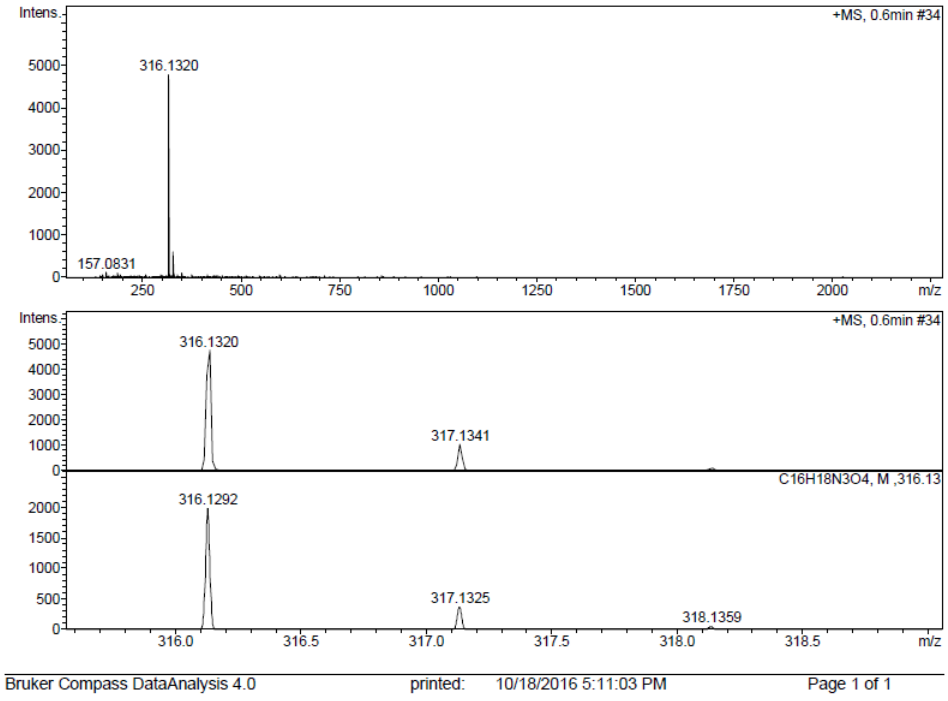


Figure S36. ESI-HRMS (positive ion mode) spectrum of **3c**

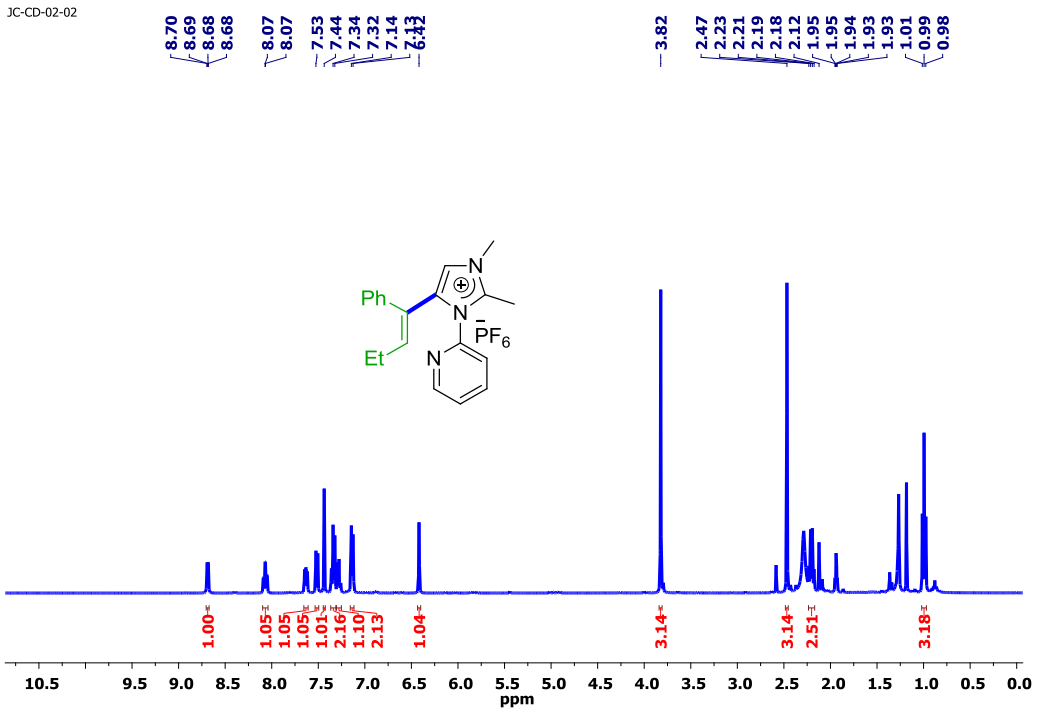


Figure S37. ^{1}H NMR spectrum of **3d** (400 MHz, CD_3CN, 300 K)

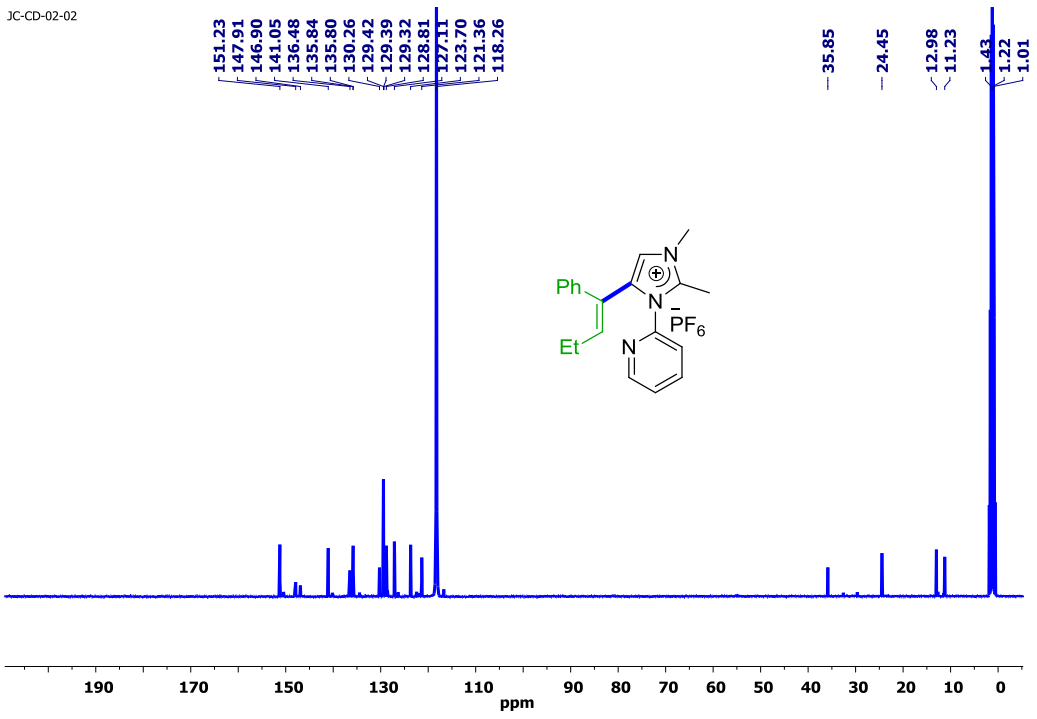


Figure S38. $^{13}C\{^{1}H\}$ NMR spectrum of **3d** (101 MHz, CD_3CN, 300 K).

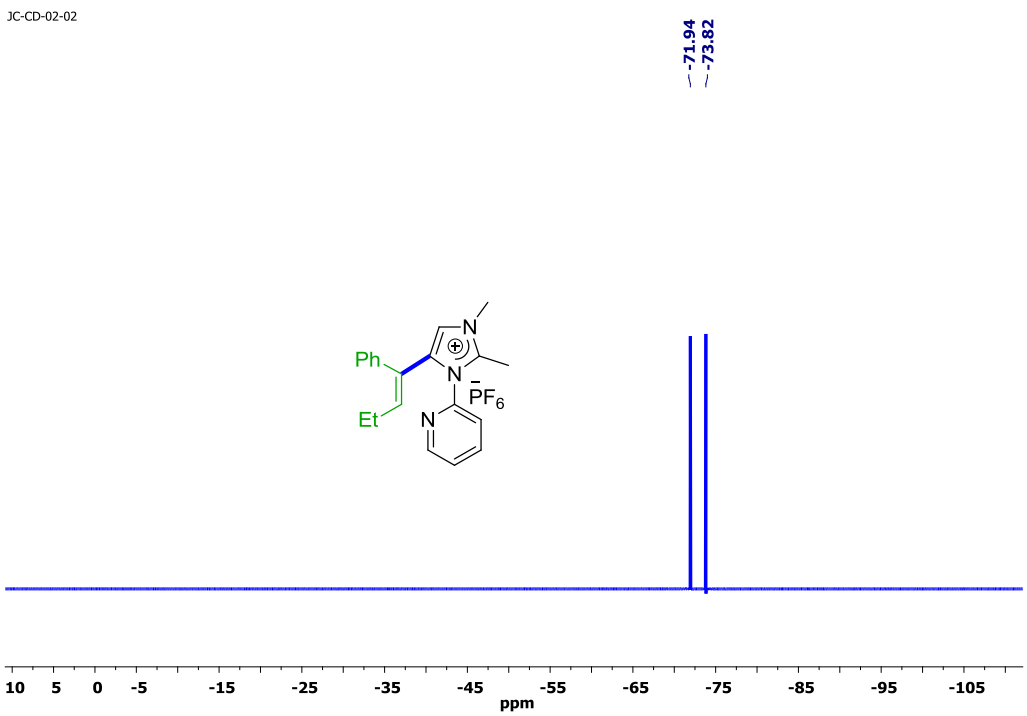


Figure S39. ^{19}F NMR spectrum of **3d** (376 MHz, CD_3CN, 300 K)

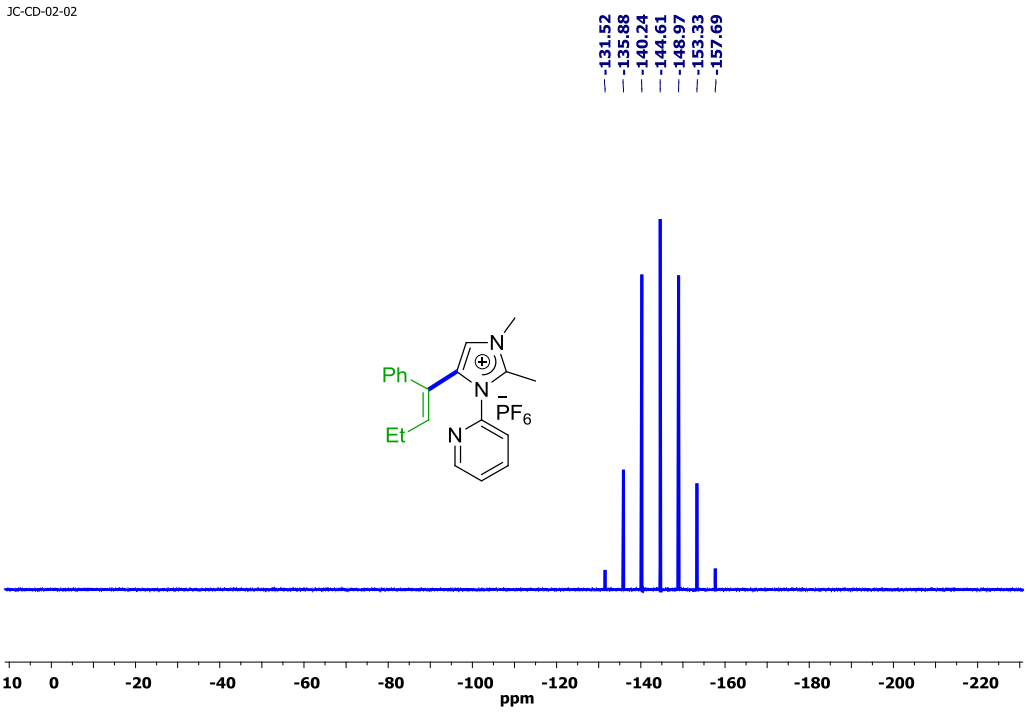


Figure S40. ^{31}P NMR spectrum of **3d** (162 MHz, CD_3CN, 300 K)

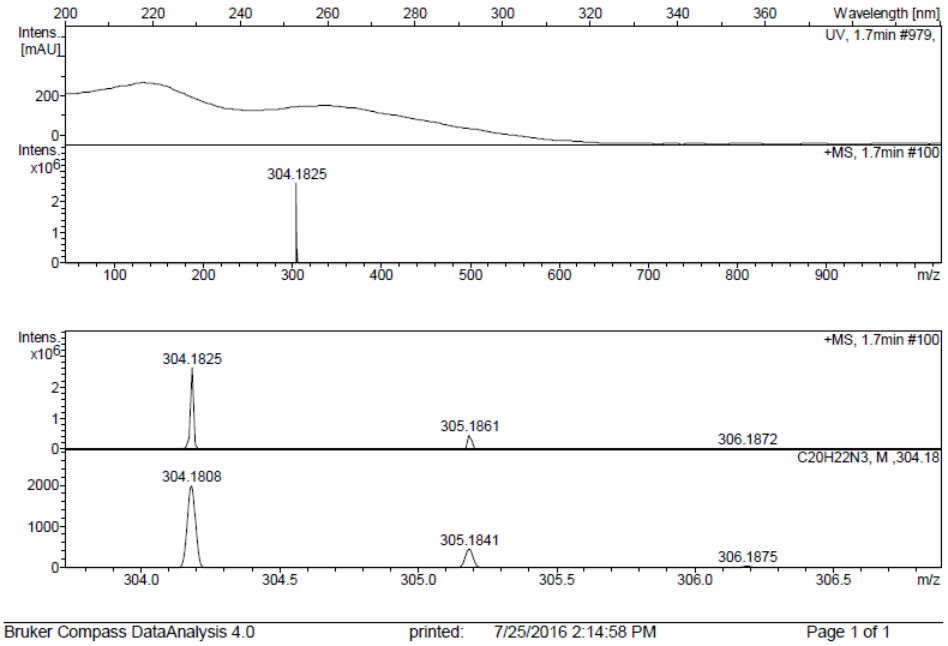


Figure S41. ESI-HRMS (positive ion mode) spectrum of **3d**

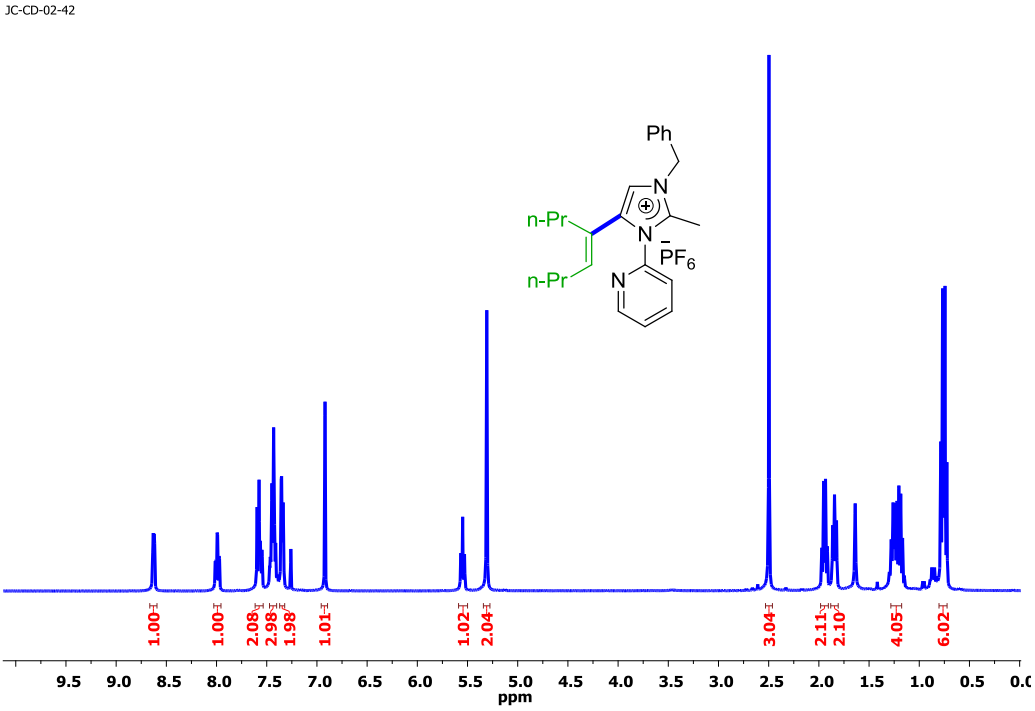


Figure S42. ^{1}H NMR spectrum of **3e** (400 MHz, $CDCl_3$, 300 K)

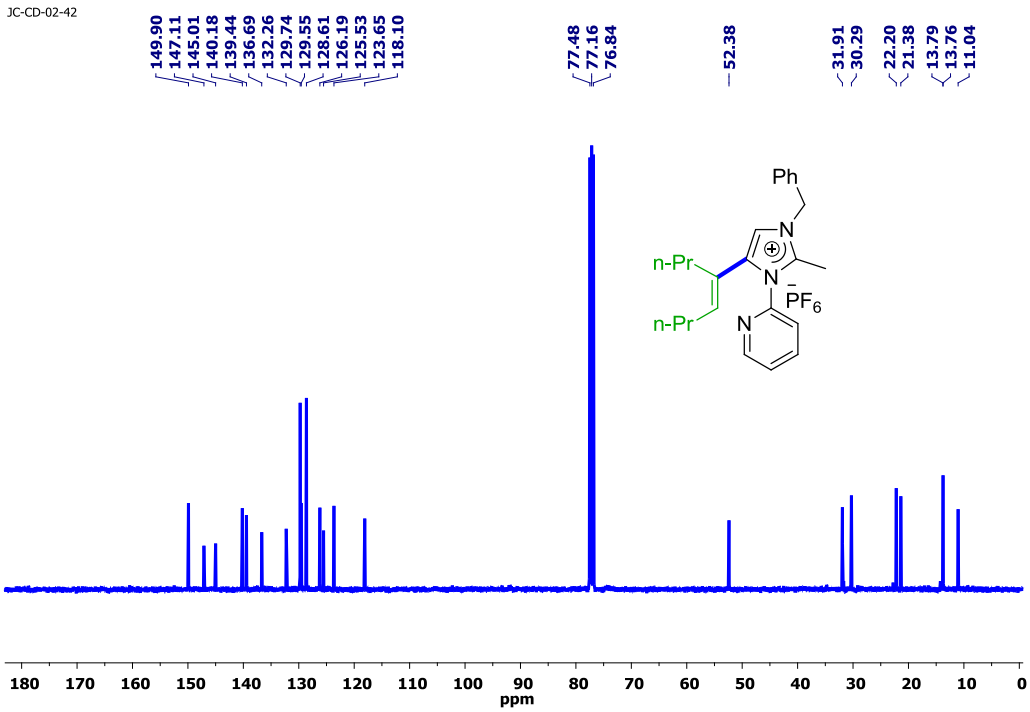


Figure S43. $^{13}C\{^{1}H\}$ NMR spectrum of **3e** (101 MHz, $CDCl_3$, 300 K).

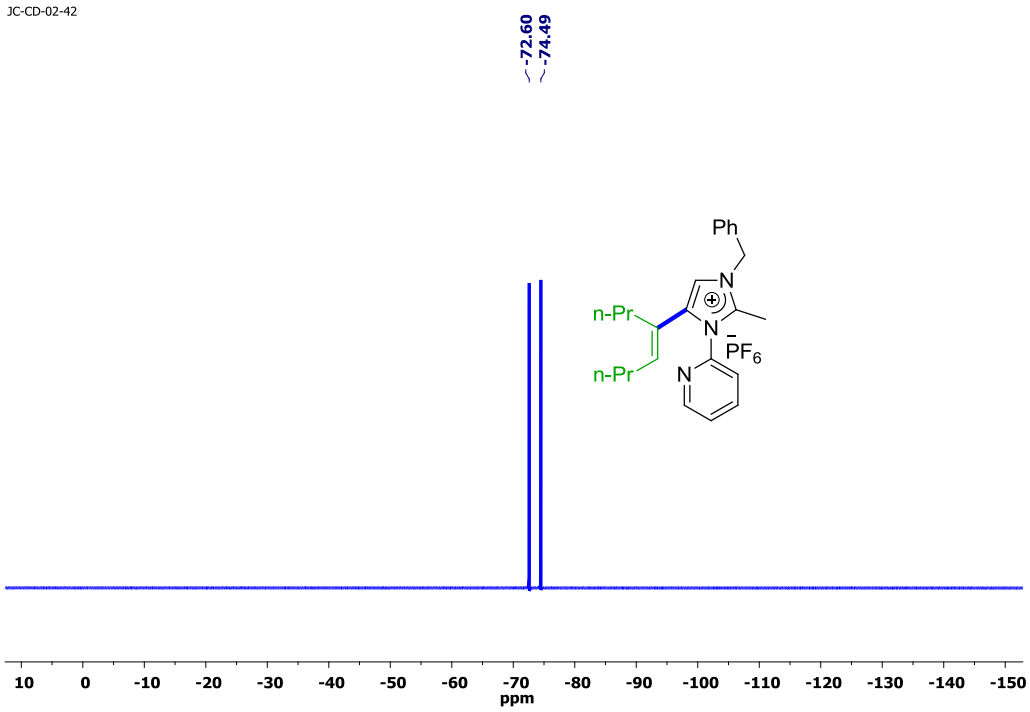


Figure S44. ^{19}F NMR spectrum of **3e** (376 MHz, $CDCl_3$, 300 K)

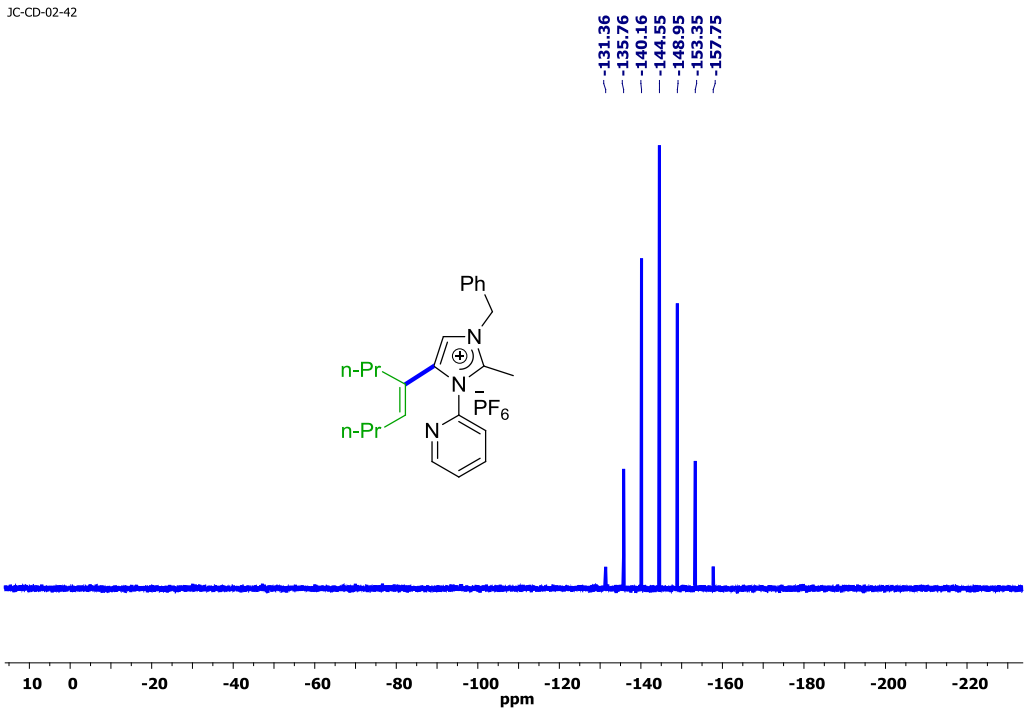


Figure S45. ^{31}P NMR spectrum of **3e** (162 MHz, $CDCl_3$, 300 K)

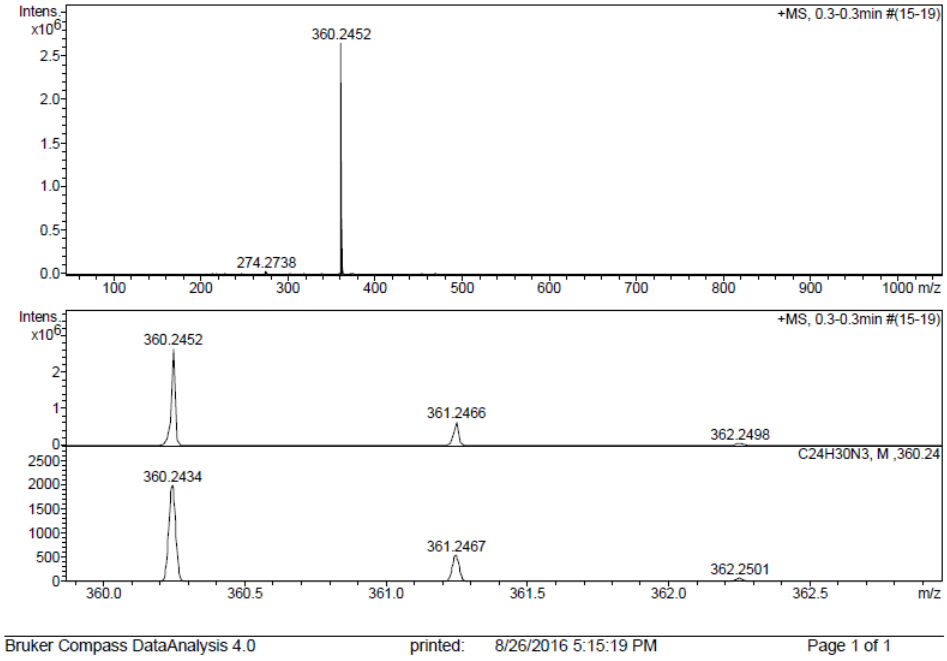


Figure S46. ESI-HRMS (positive ion mode) spectrum of **3e**

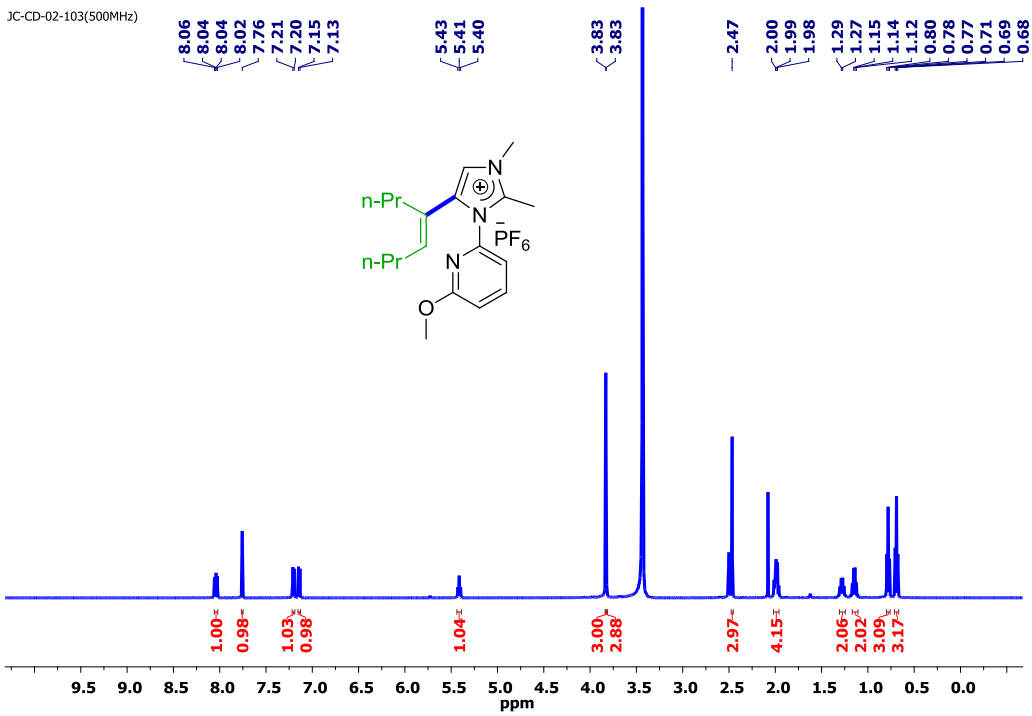


Figure S47. ^{1}H NMR spectrum of **3f** (500 MHz, DMSO-d_6, 300 K)

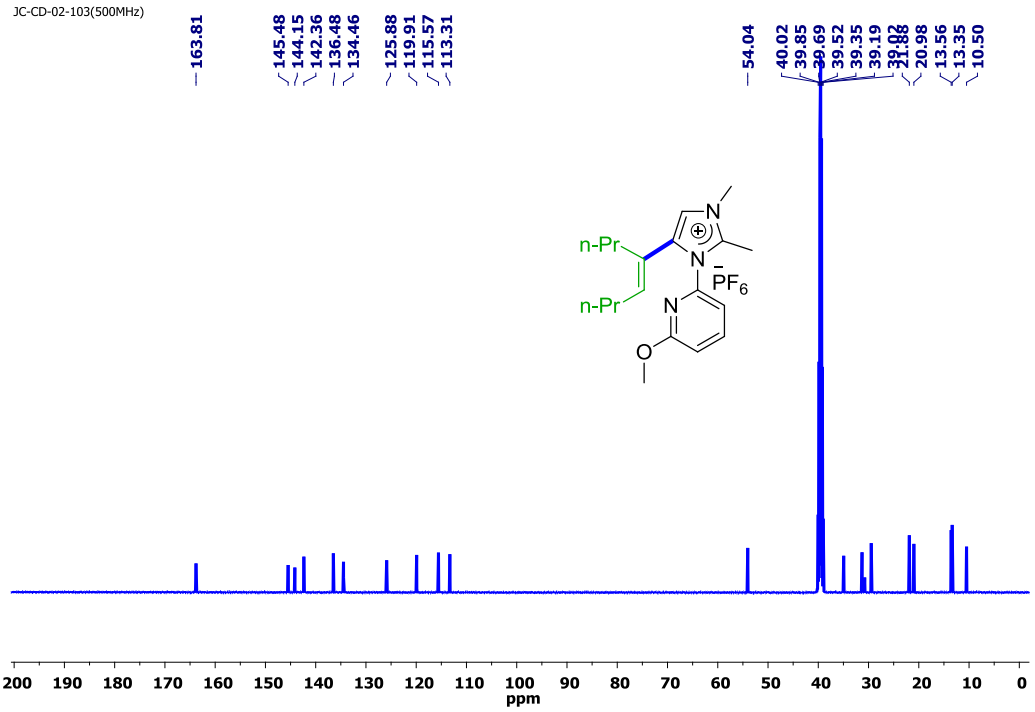


Figure S48. ^{13}C{^{1}H} NMR spectrum of **3f** (126 MHz, DMSO-d_6, 300 K).

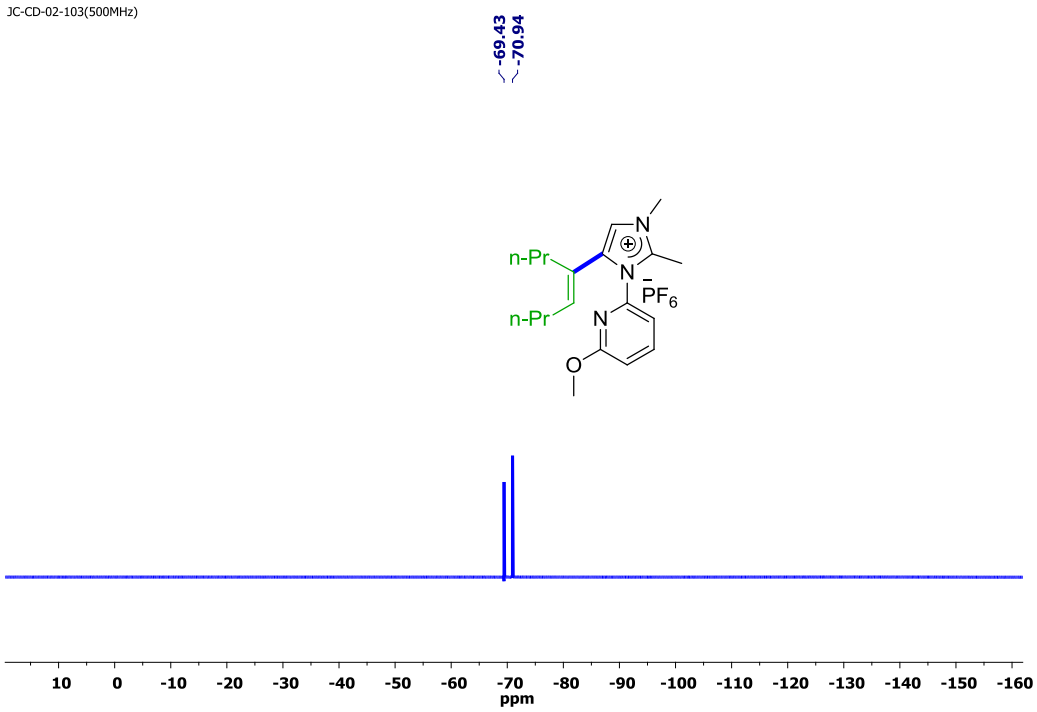


Figure S49. ^{19}F NMR spectrum of **3f** (471 MHz, DMSO-d_6, 300 K)

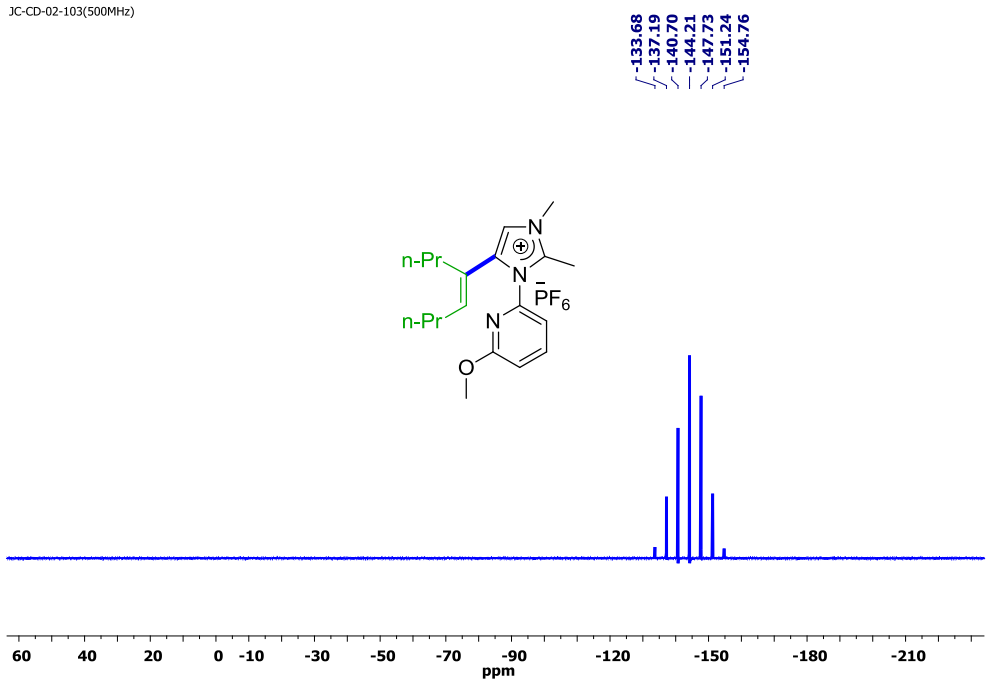


Figure S50. ^{31}P NMR spectrum of **3f** (202 MHz, DMSO-d_6, 300 K)

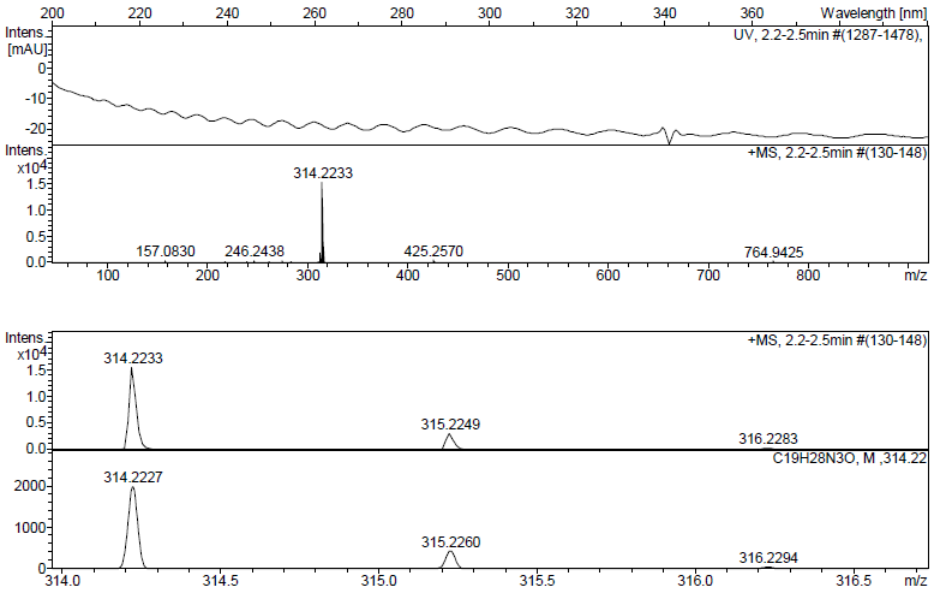


Figure S51. ESI-HRMS (positive ion mode) spectrum of **3f**

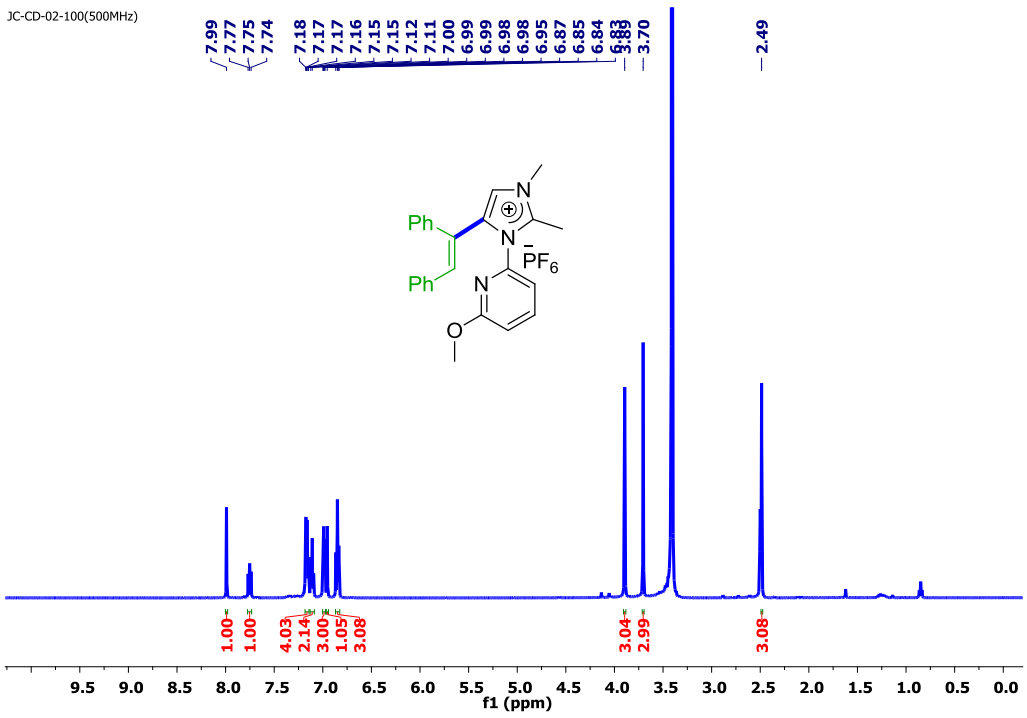


Figure S52. ^{1}H NMR spectrum of **3g** (500 MHz, DMSO-d_6, 300 K)

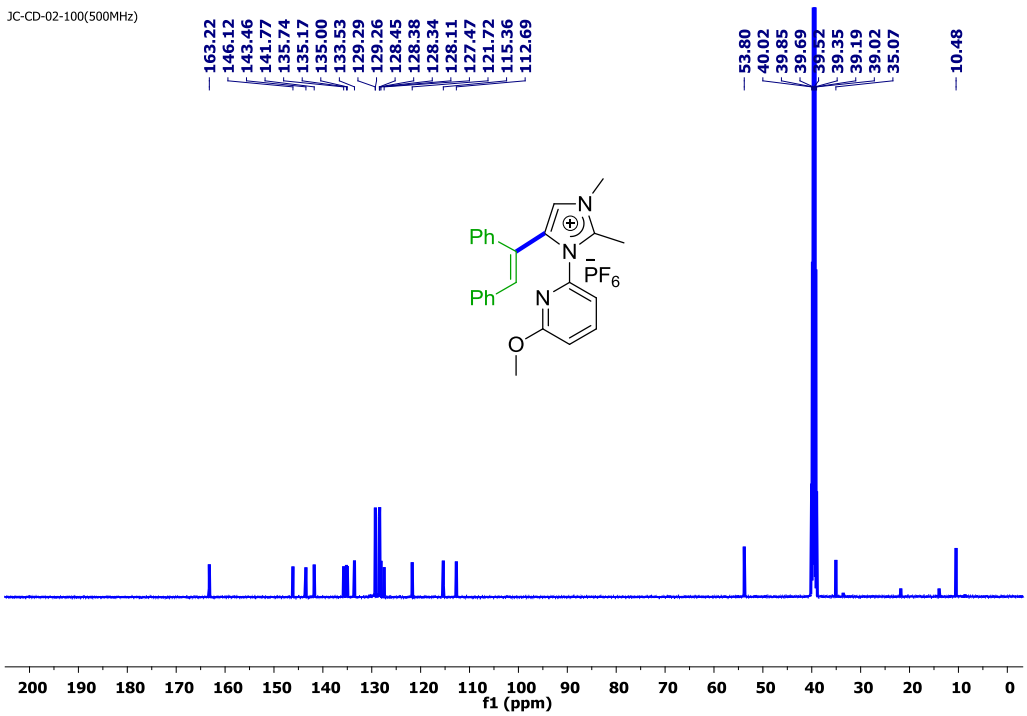


Figure S53. $^{13}C\{^{1}H\}$ NMR spectrum of **3g** (126 MHz, DMSO-d_6, 300 K).

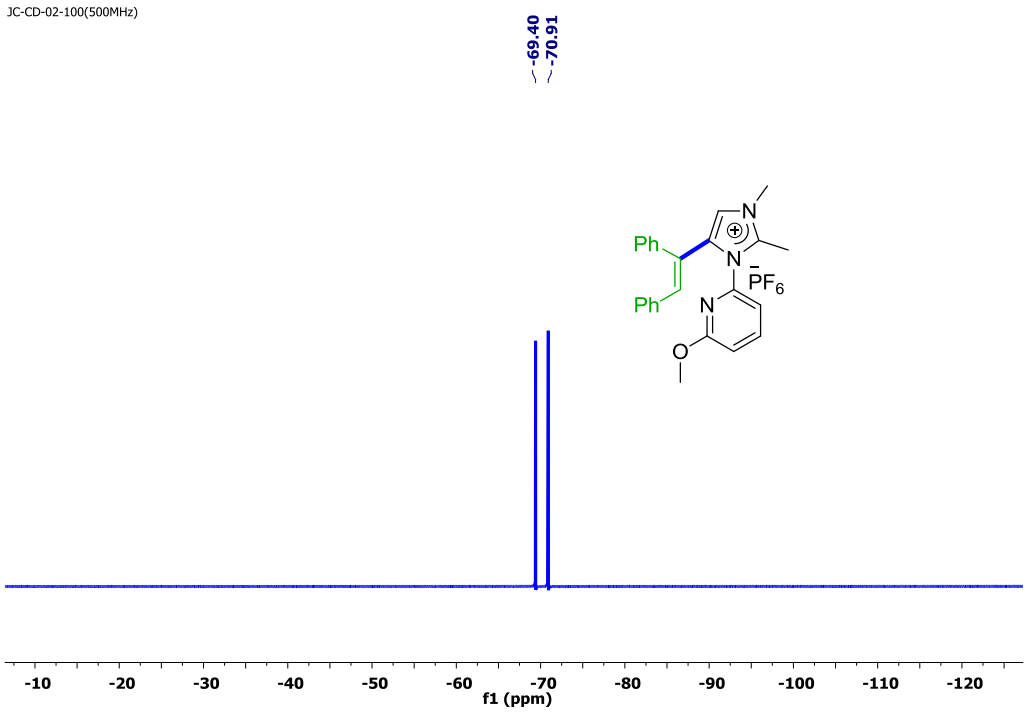


Figure S54. ^{19}F NMR spectrum of **3g** (471 MHz, DMSO-d_6, 300 K)

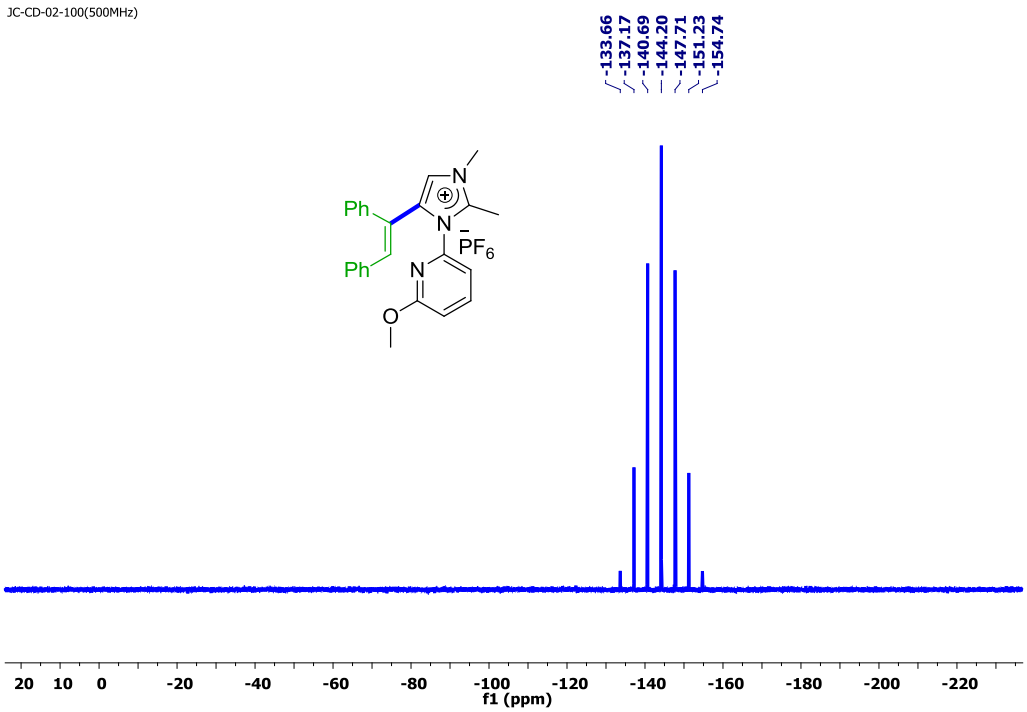


Figure S55. ^{31}P NMR spectrum of **3g** (202 MHz, DMSO-d_6, 300 K)

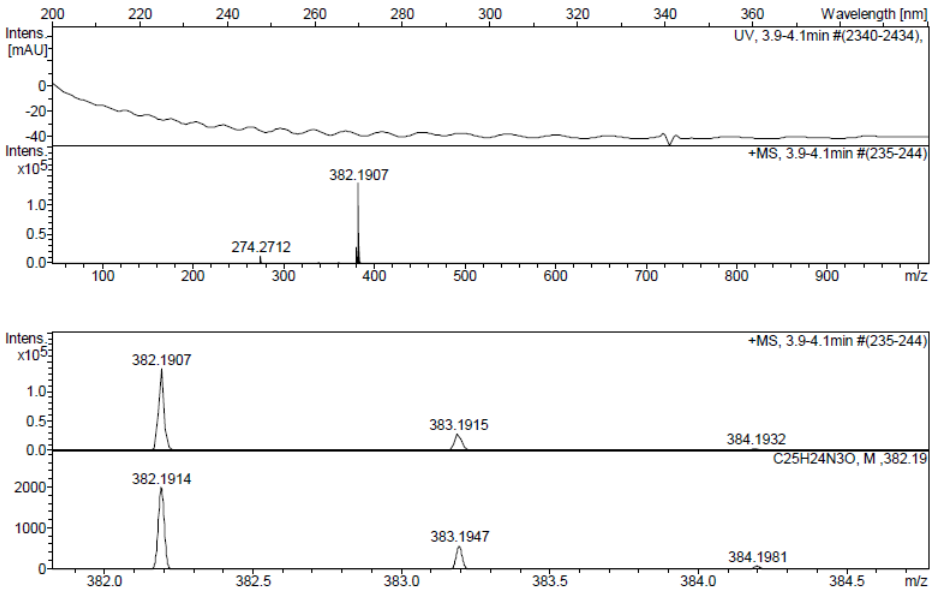


Figure S56. ESI-HRMS (positive ion mode) spectrum of **3g**

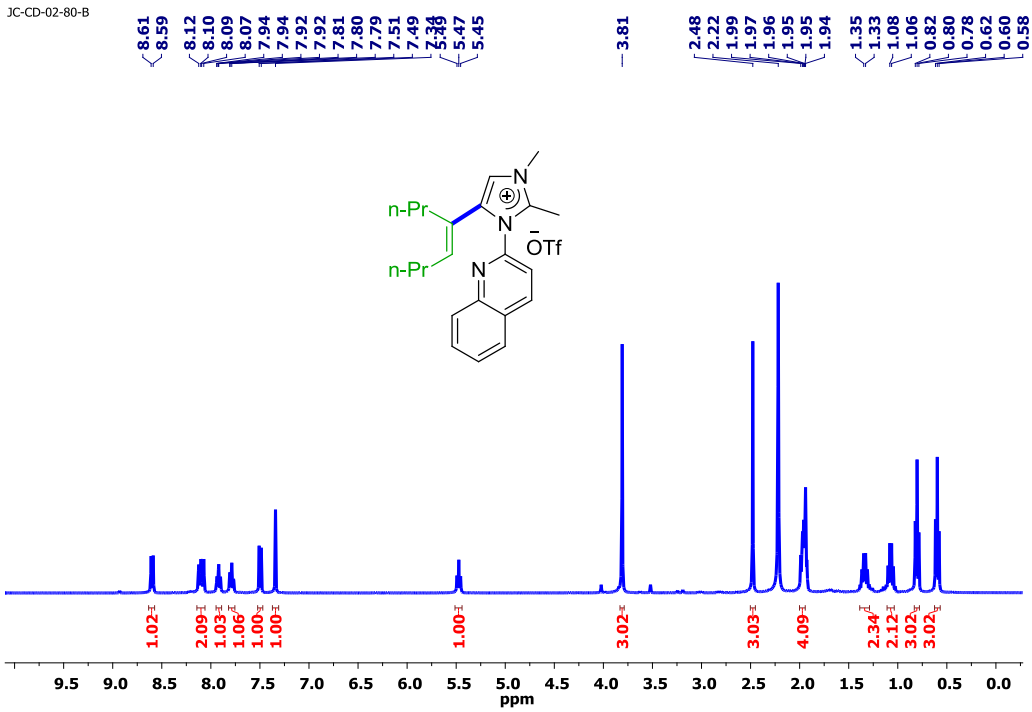


Figure S57. ^{1}H NMR spectrum of **3h** (400 MHz, CD_3CN, 300 K)

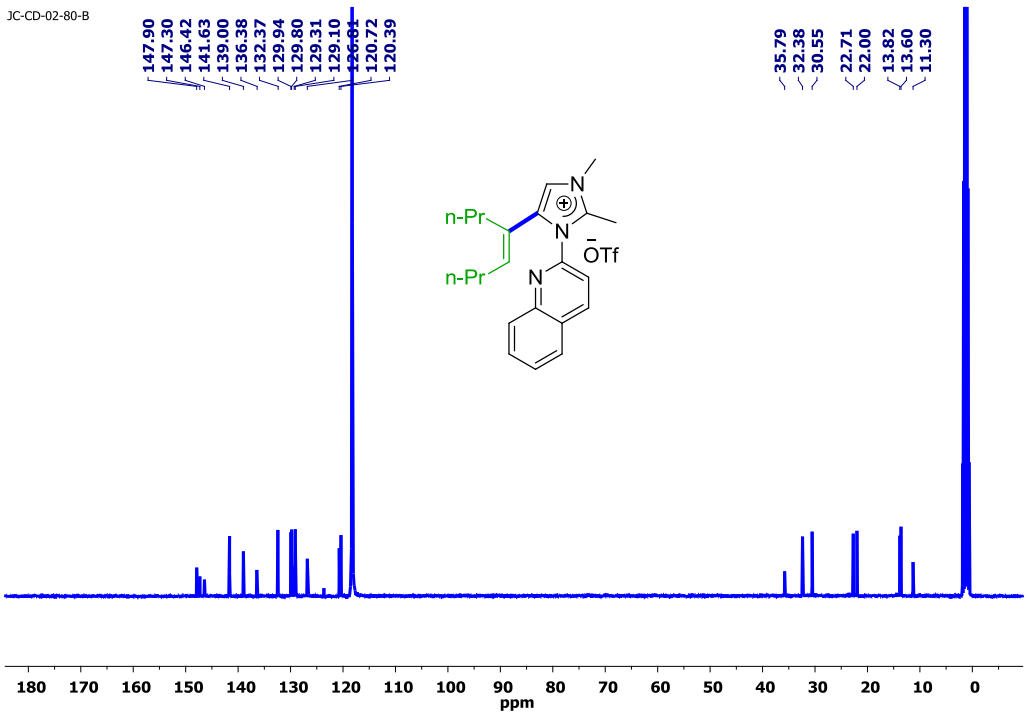


Figure S58. ^{13}C{^{1}H} NMR spectrum of **3h** (101 MHz, CD_3CN, 300 K).

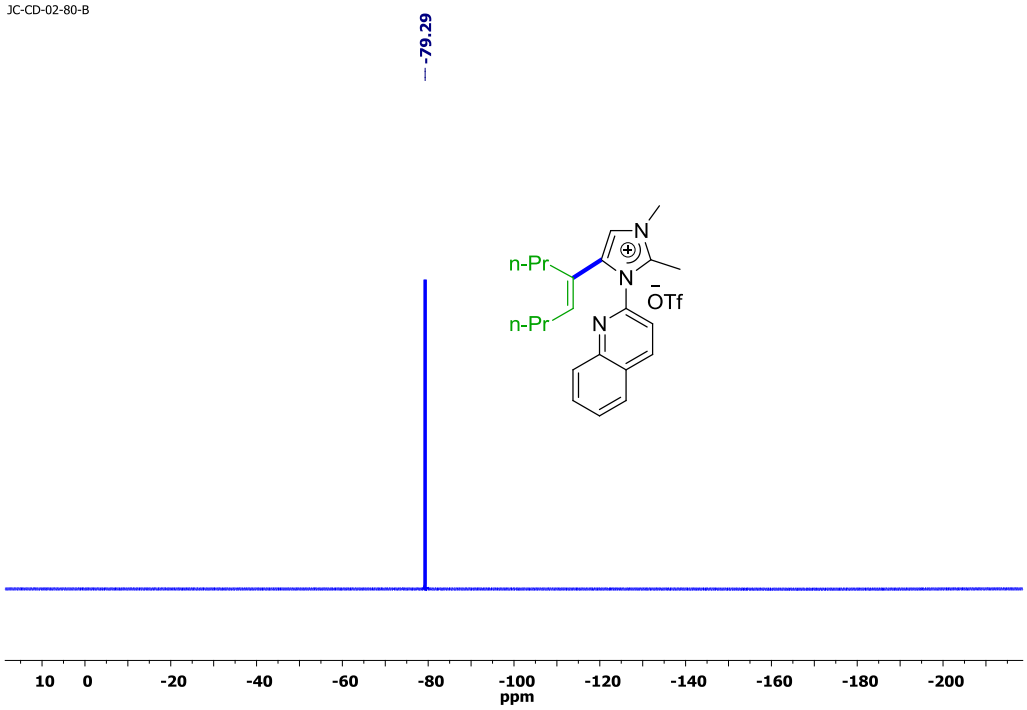


Figure S59. ^{19}F NMR spectrum of **3h** (376 MHz, CD_3CN, 300 K)

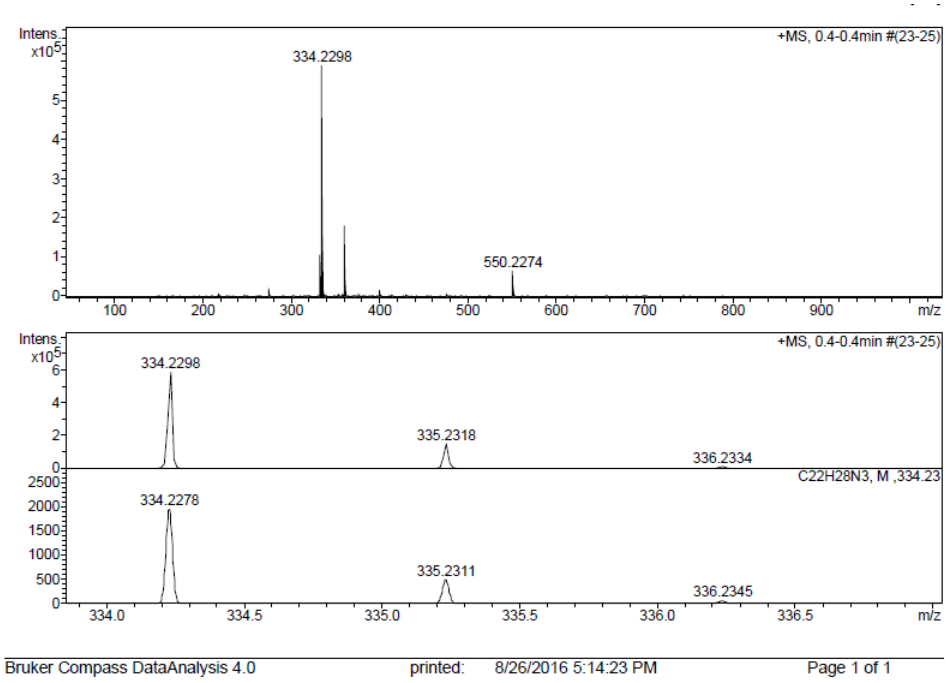


Figure S60. ESI-HRMS (positive ion mode) spectrum of **3h**

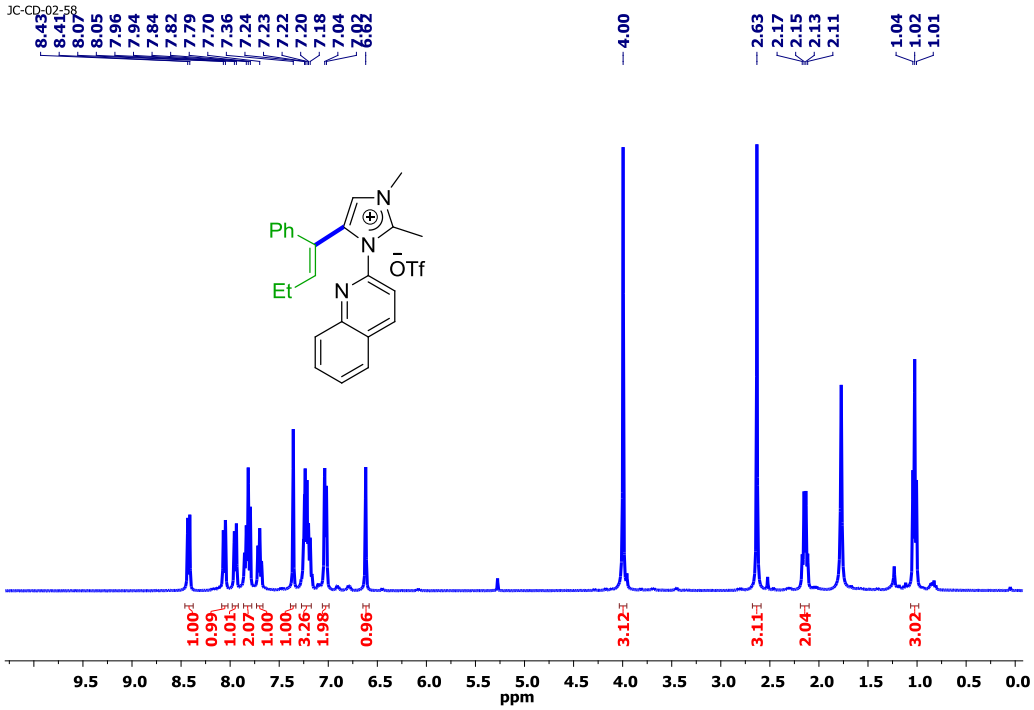


Figure S61. ^{1}H NMR spectrum of **3i** (400 MHz, $CDCl_3$, 300 K)

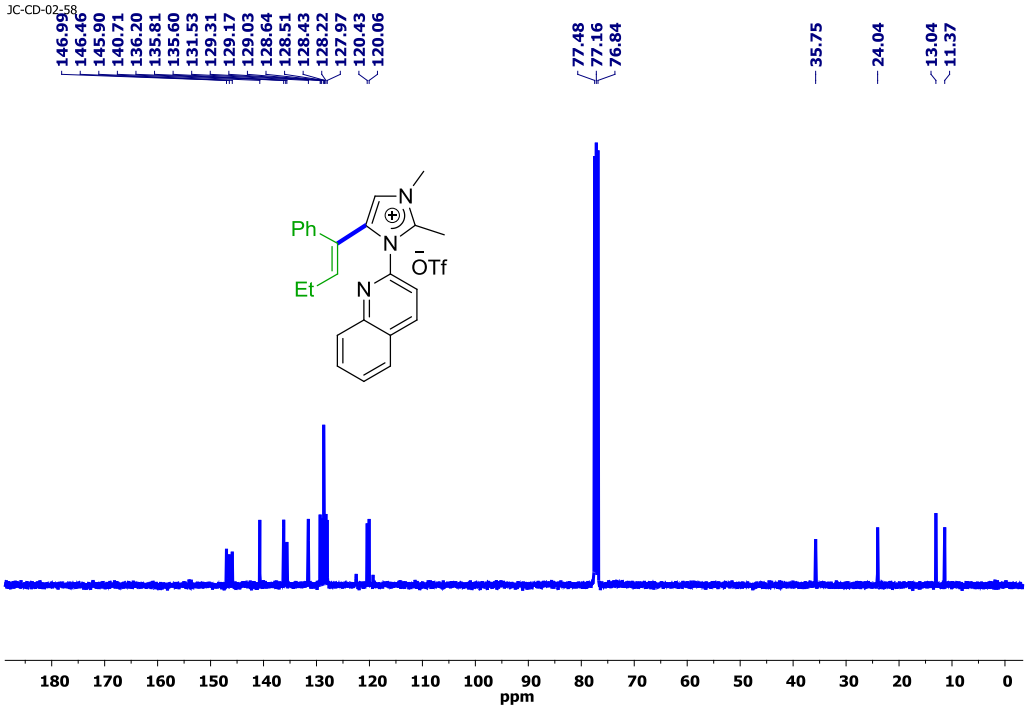


Figure S62. ^{13}C{^{1}H} NMR spectrum of **3i** (101 MHz, $CDCl_3$, 300 K).

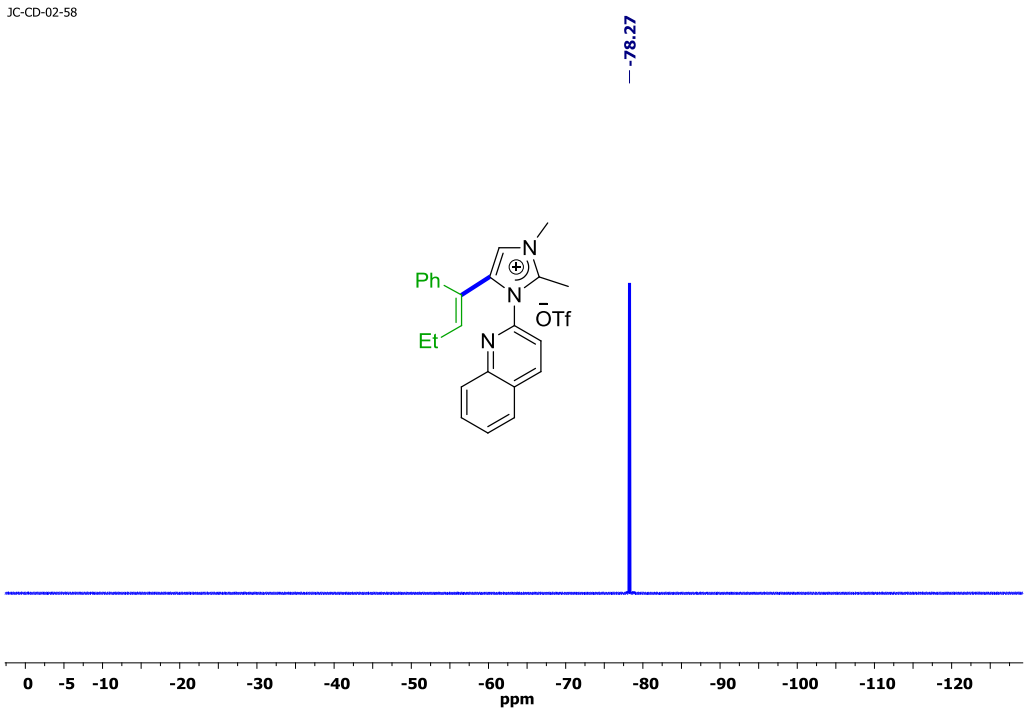


Figure S63. ^{19}F NMR spectrum of **3i** (376 MHz, $CDCl_3$, 300 K)

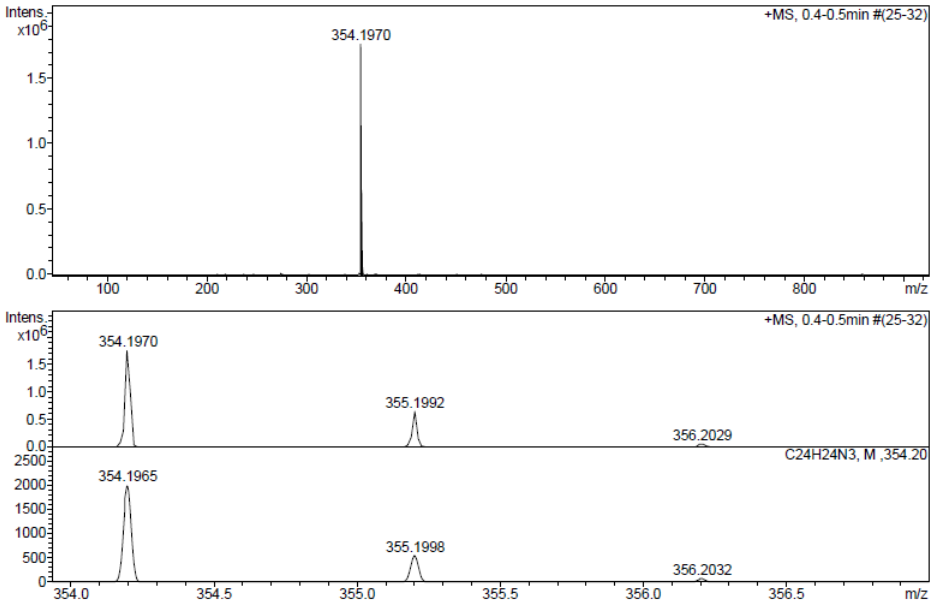


Figure S64. ESI-HRMS (positive ion mode) spectrum of **3i**

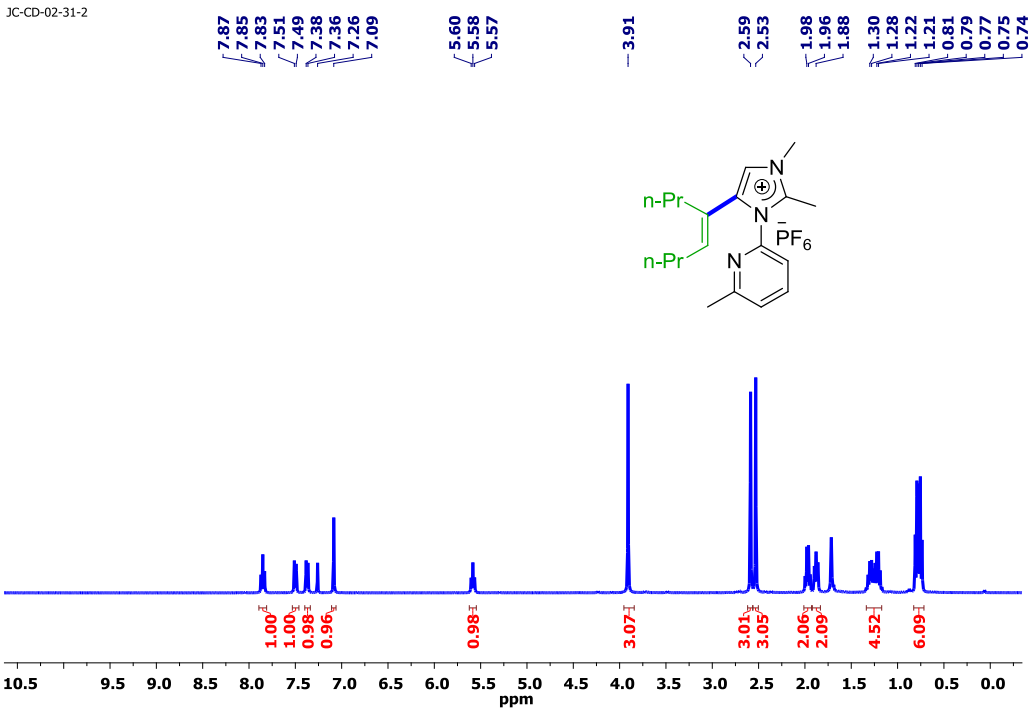


Figure S65. ^{1}H NMR spectrum of **3j** (400 MHz, $CDCl_3$, 300 K)

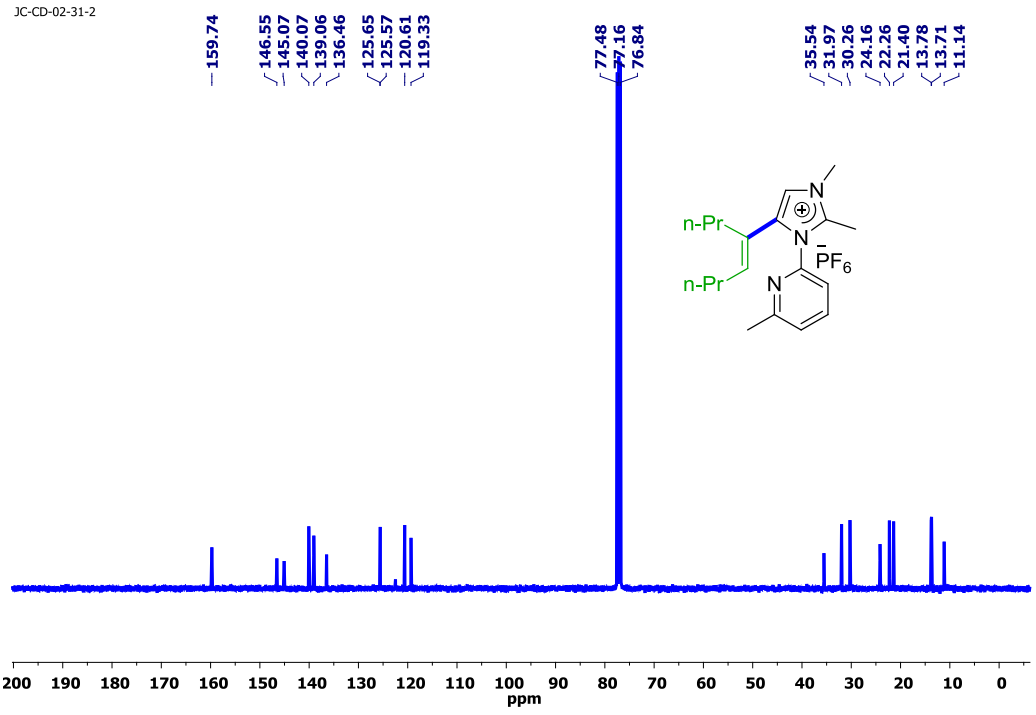


Figure S66. ^{13}C{^{1}H} NMR spectrum of **3j** (101 MHz, $CDCl_3$, 300 K).

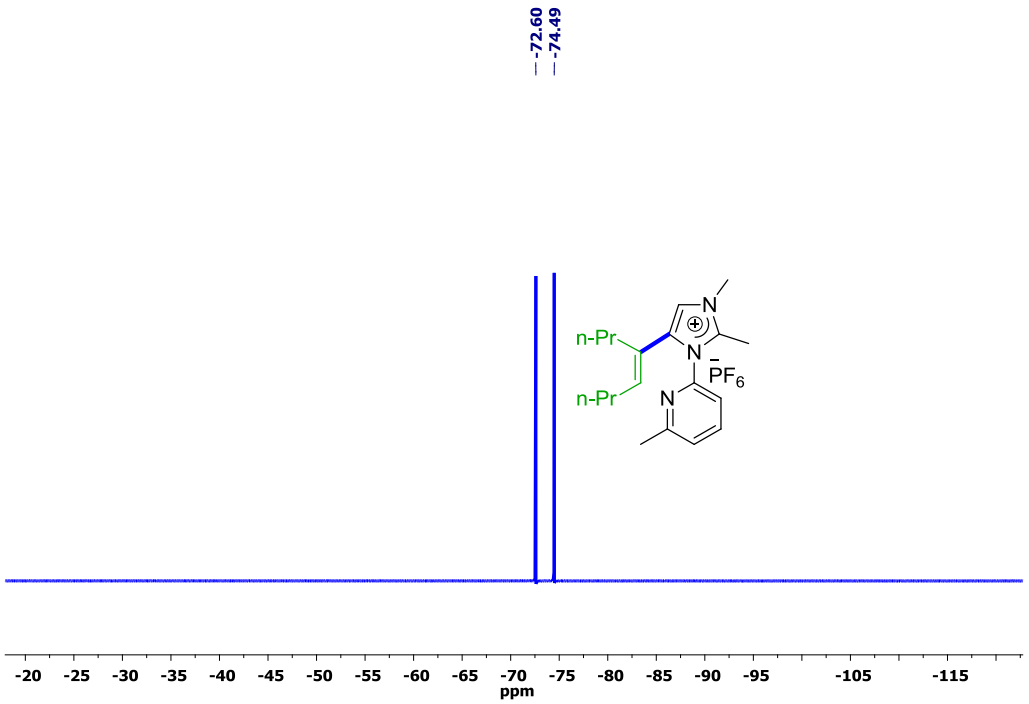


Figure S67. ^{19}F NMR spectrum of **3j**(376 MHz, $CDCl_3$, 300 K)

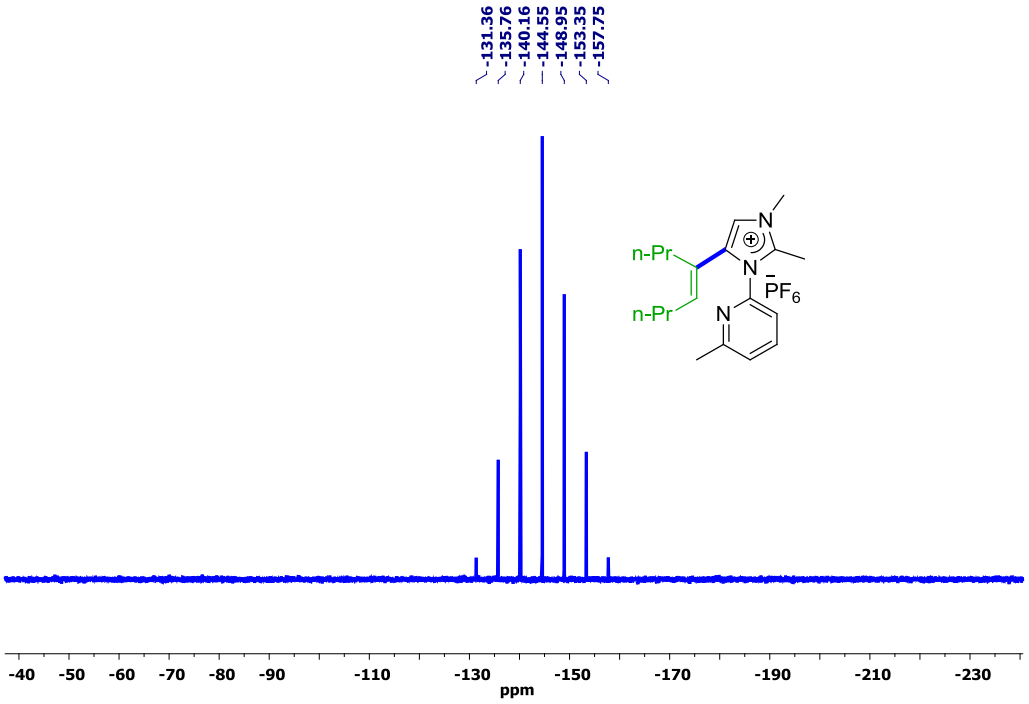


Figure S68. ^{1}H NMR spectrum of **3j** (162 MHz, $CDCl_3$, 300 K)

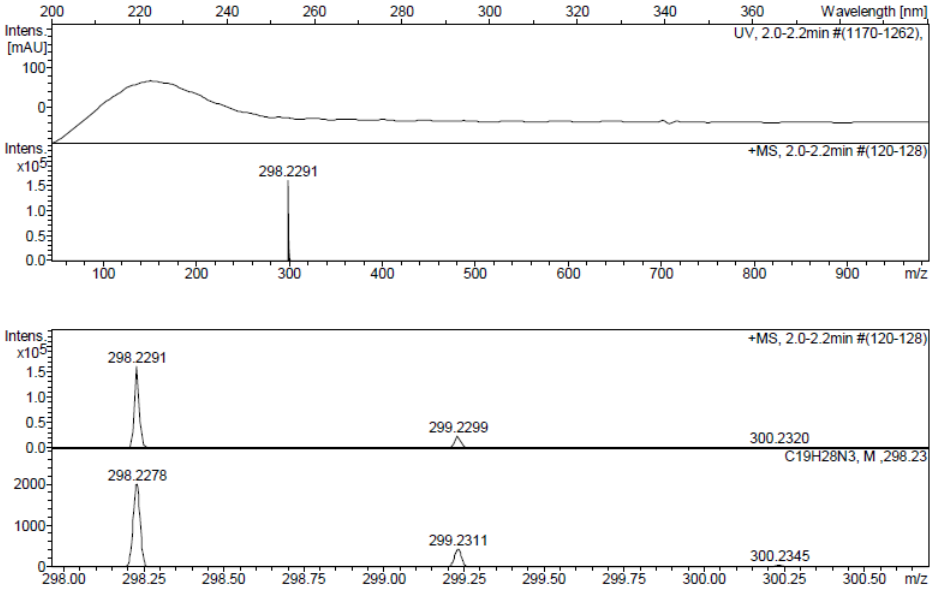


Figure S69. ESI-HRMS (positive ion mode) spectrum of **3j**

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13. Characterization data for annulated products:

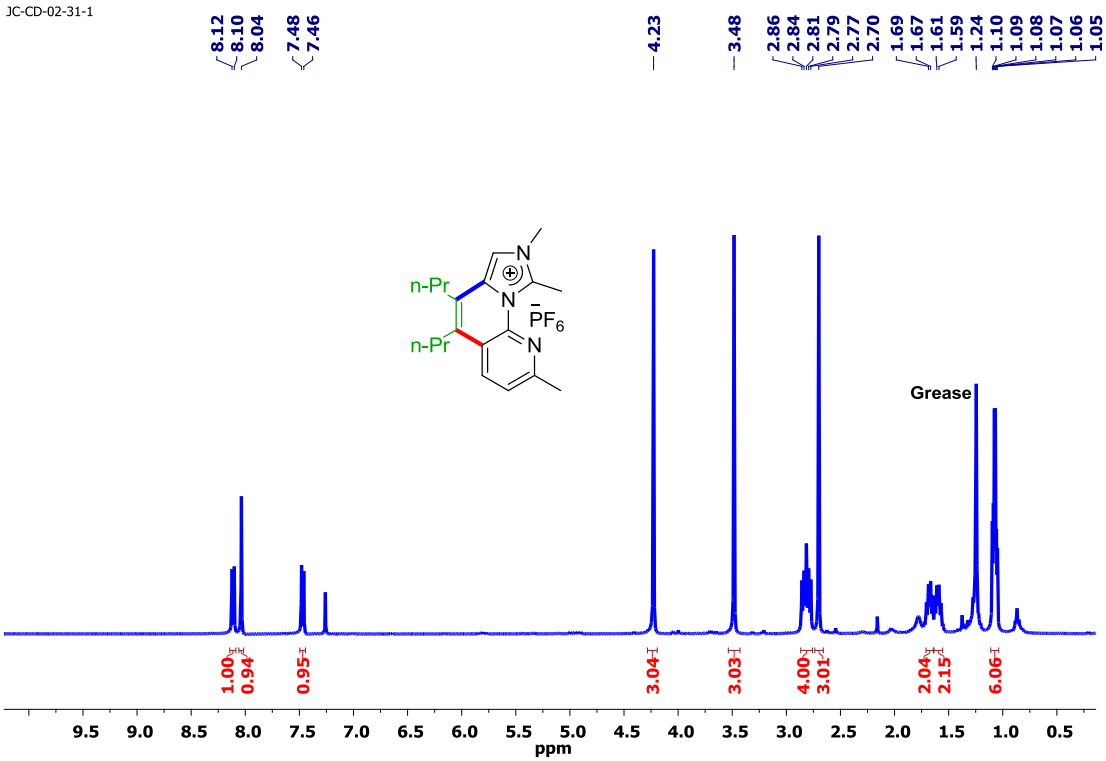

Figure S70. ^{1}H NMR spectrum of **4a** (400 MHz, $CDCl_3$, 300 K)

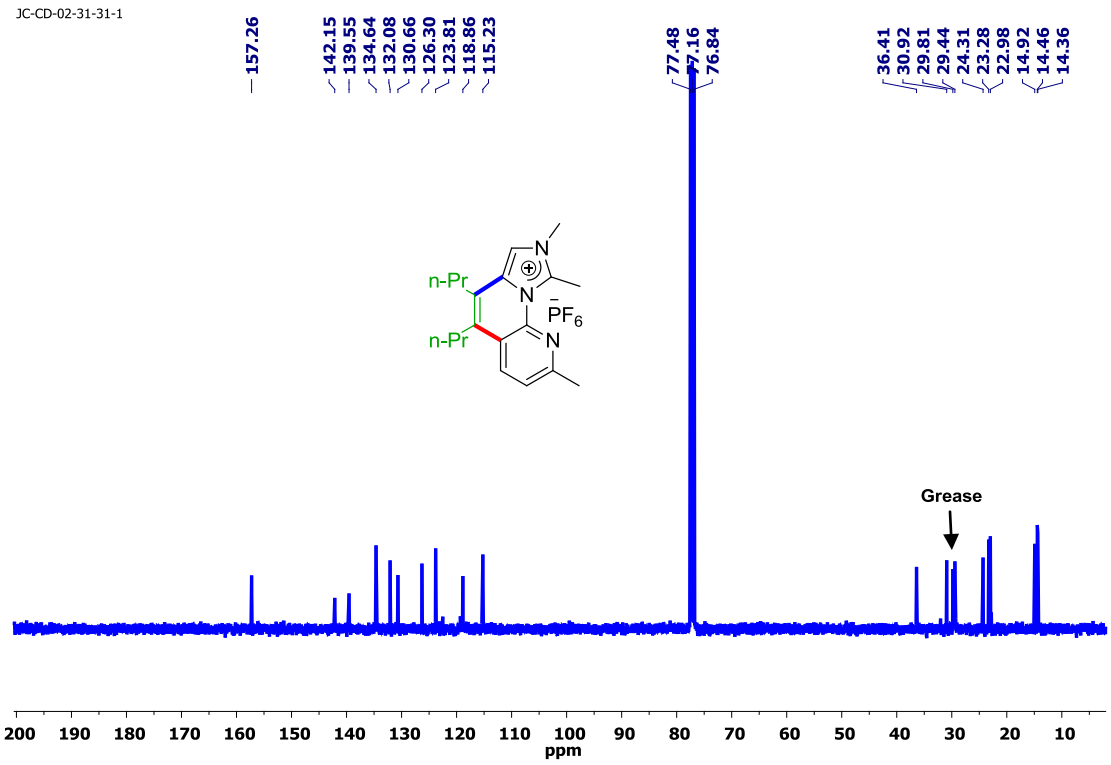

Figure S71. $^{13}C\{^{1}H\}$ NMR spectrum of **4a**(101 MHz, $CDCl_3$, 300 K).

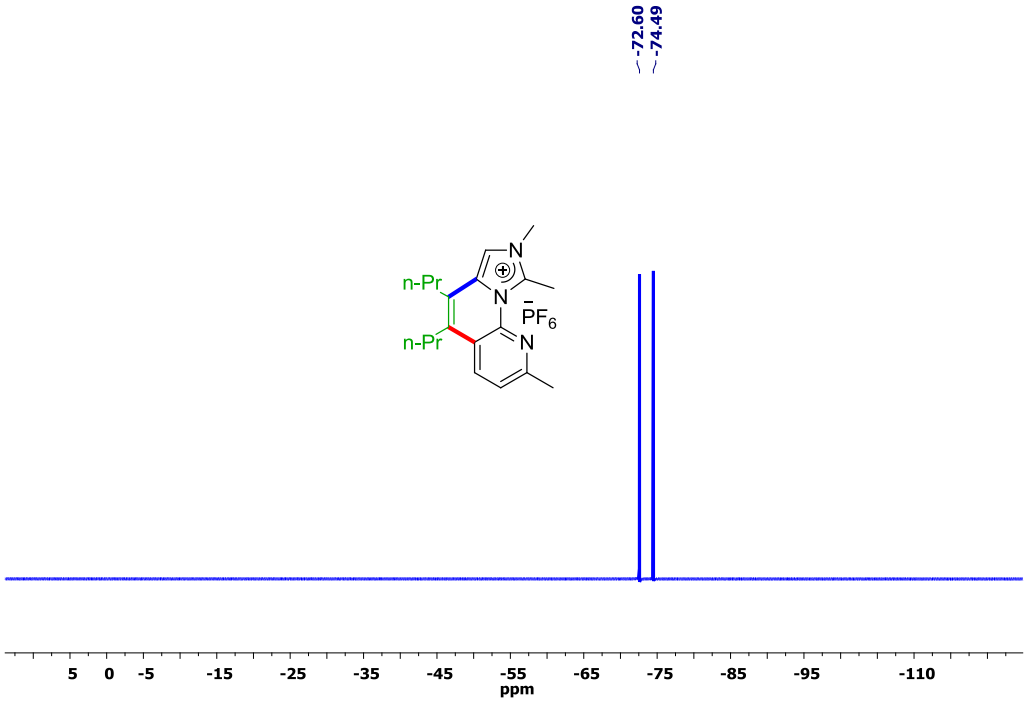

Figure S72. ^{19}F NMR spectrum of **4a** (376 MHz, $CDCl_3$, 300 K)

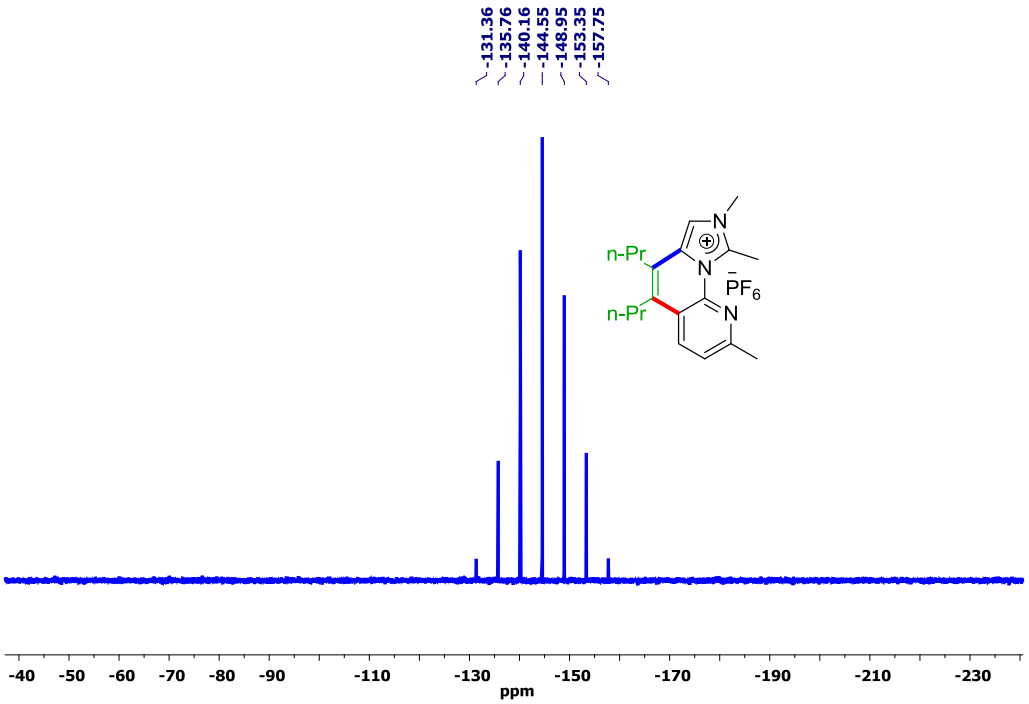

Figure S73. ^{31}P NMR spectrum of **4a** (162 MHz, $CDCl_3$, 300 K)

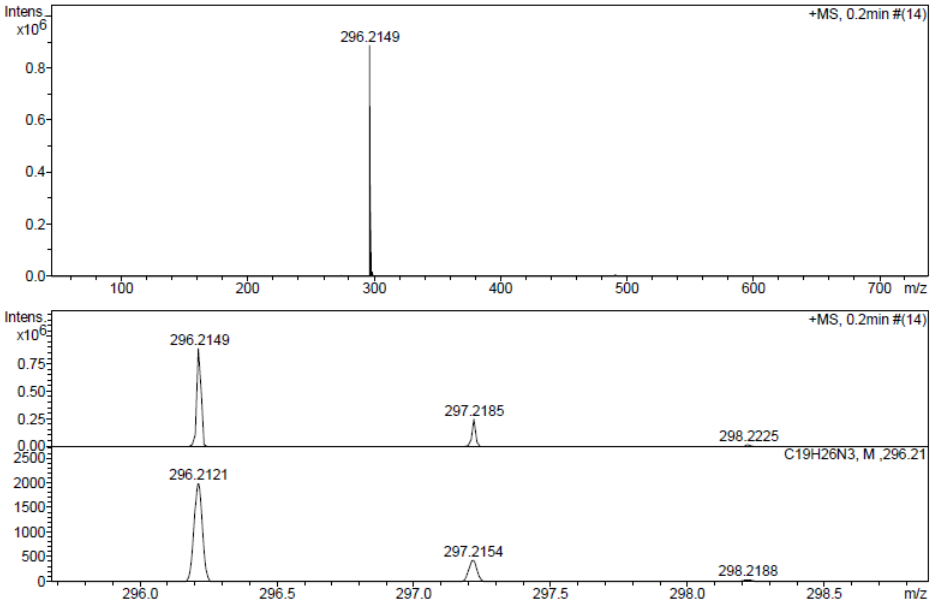

Figure S74. ESI-HRMS (positive ion mode) spectrum of **4a**

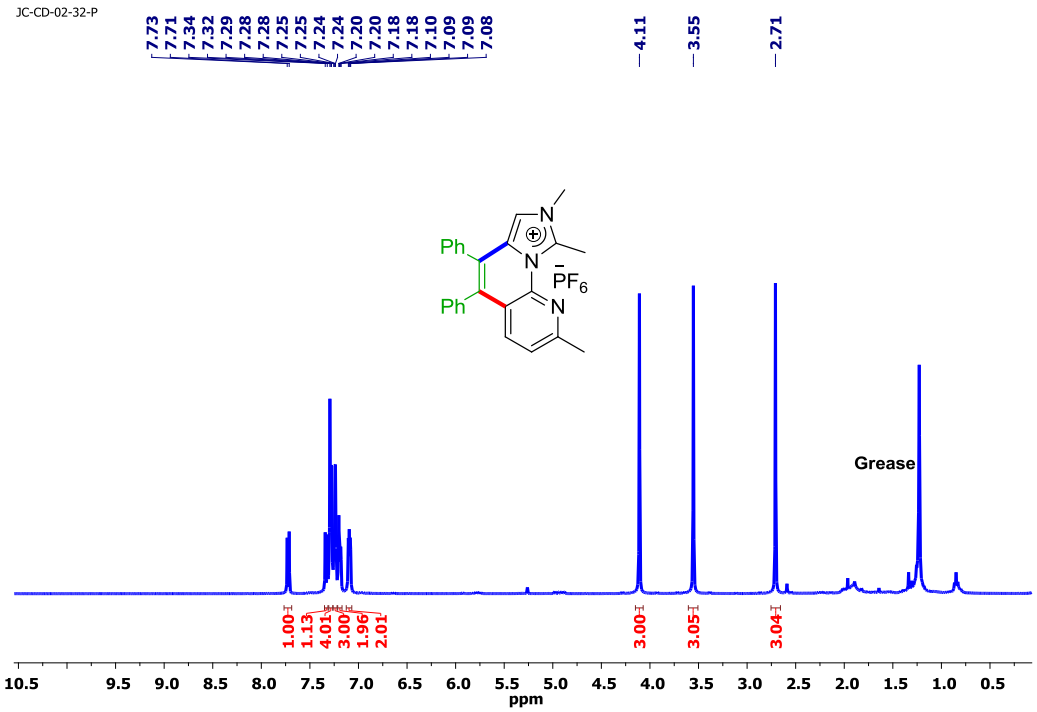

Figure S75. ^{1}H NMR spectrum of **4b** (400 MHz, $CDCl_3$, 300 K)

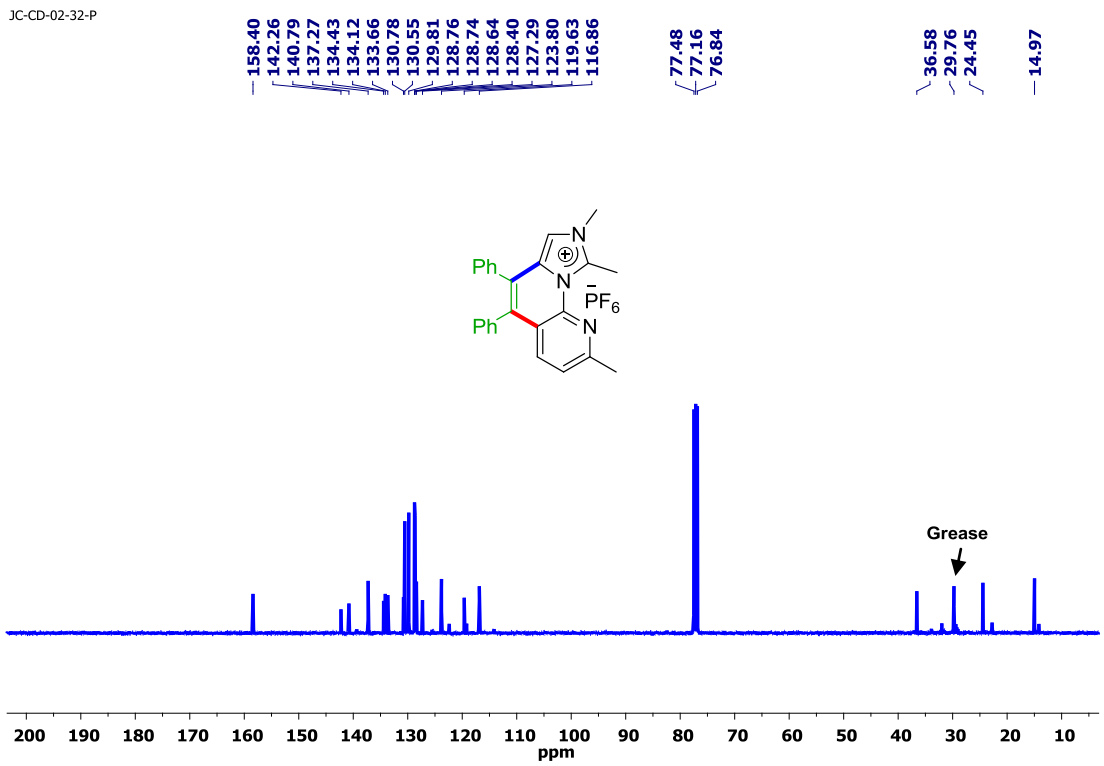

Figure S76. ^{13}C{^{1}H} NMR spectrum of **4b** (101 MHz, $CDCl_3$, 300 K).

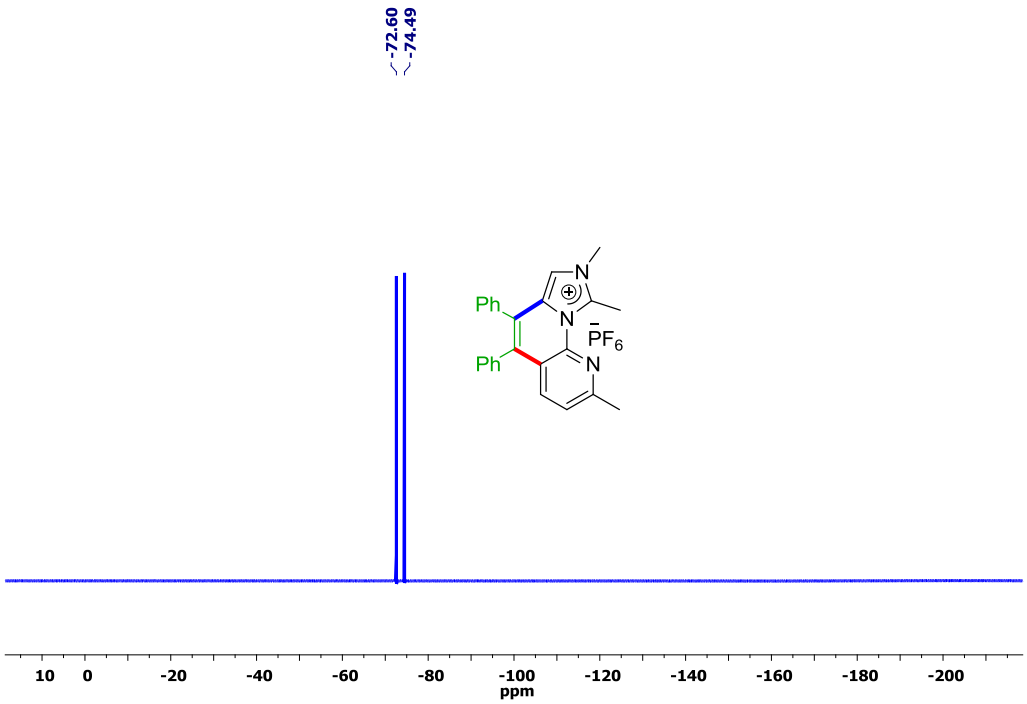

Figure S77. ^{19}F NMR spectrum of **4b** (376 MHz, $CDCl_3$, 300 K)

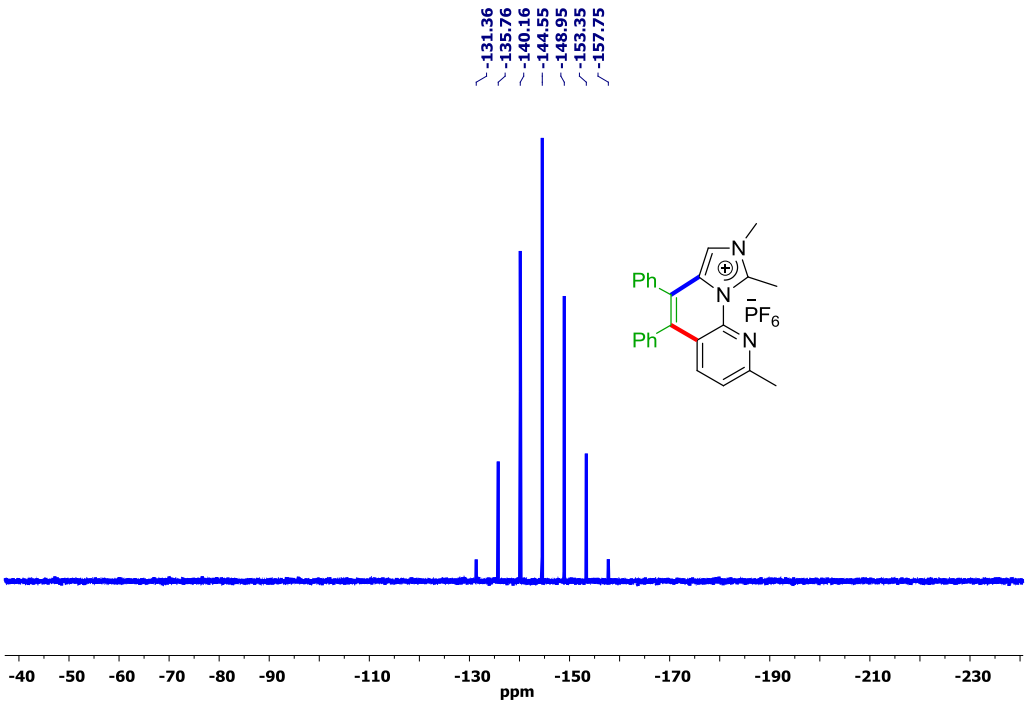

Figure S78. ^{31}P NMR spectrum of **4b** (162 MHz, $CDCl_3$, 300 K)

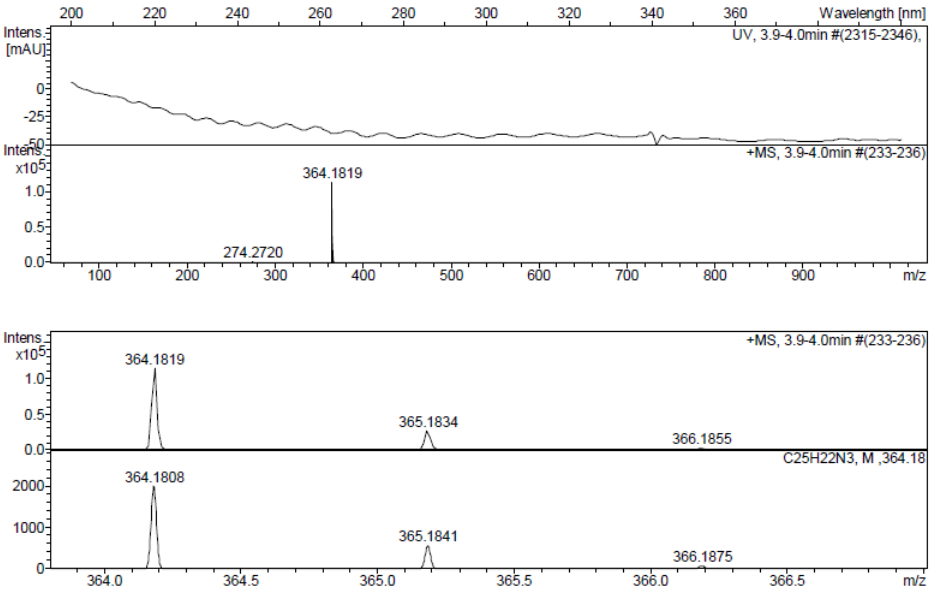

Figure S79. ESI-HRMS (positive ion mode) spectrum of **4b**

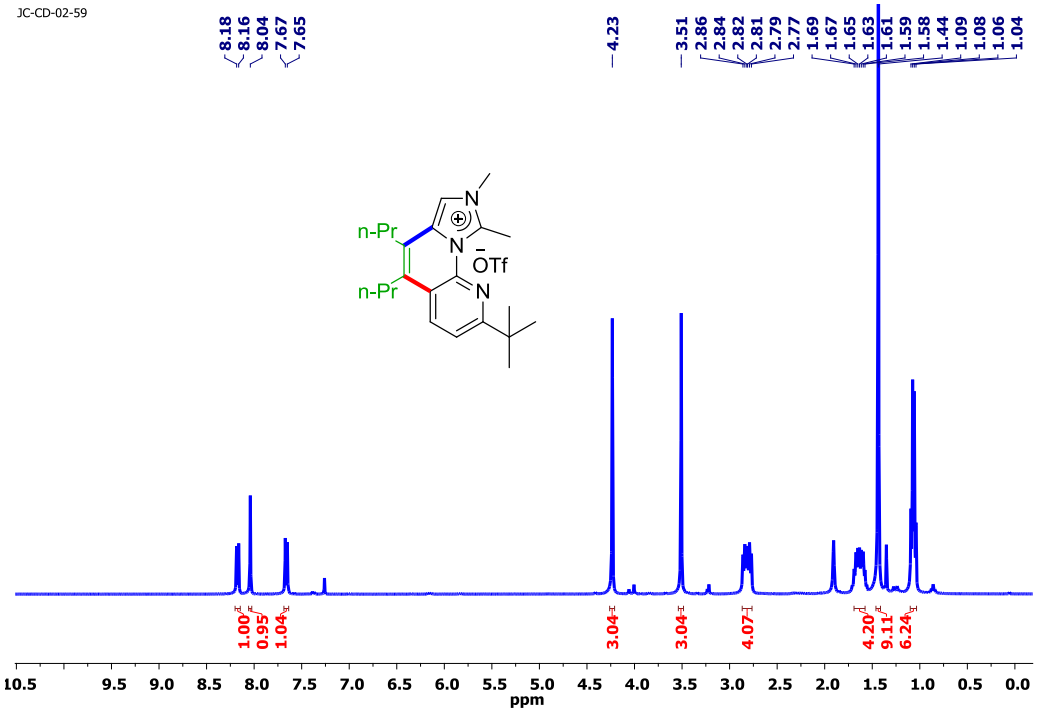

Figure S80. ^{1}H NMR spectrum of **4c** (400 MHz, $CDCl_3$, 300 K)

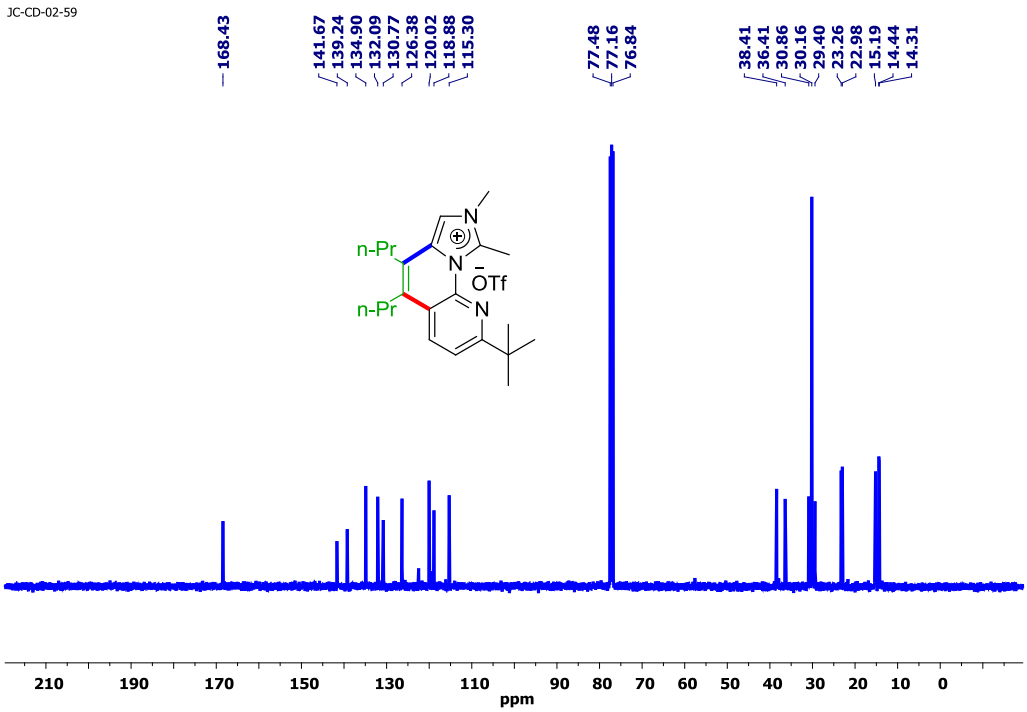

Figure S81. $^{13}C\{^{1}H\}$ NMR spectrum of **4c** (101 MHz, $CDCl_3$, 300 K).

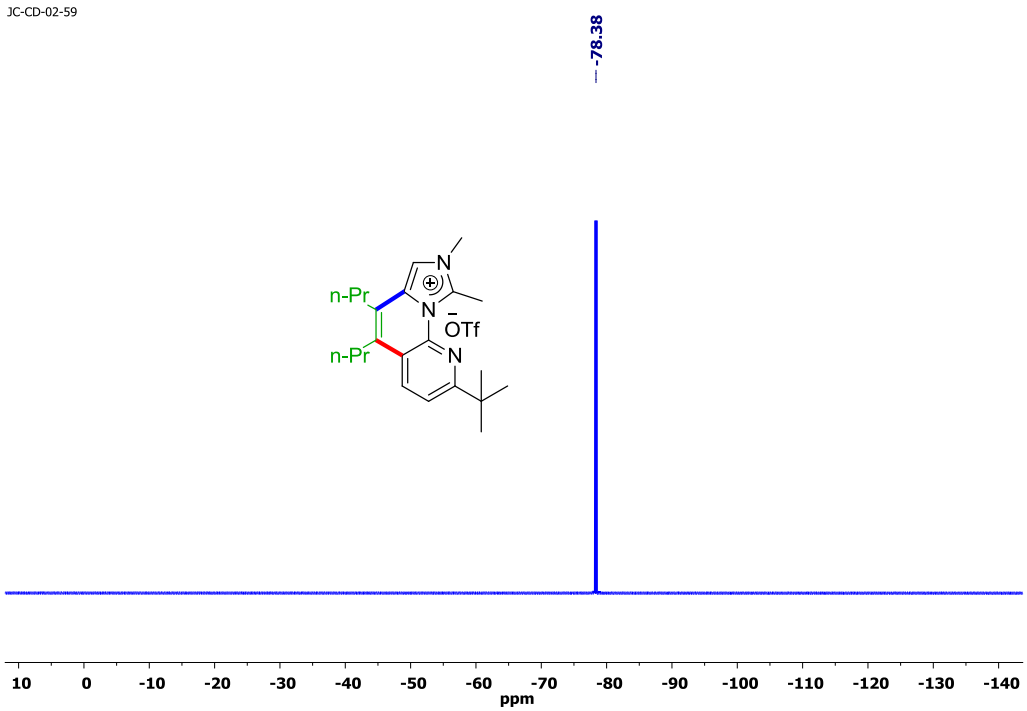

Figure S82. ^{1}H NMR spectrum of **4c** (376 MHz, $CDCl_3$, 300 K)

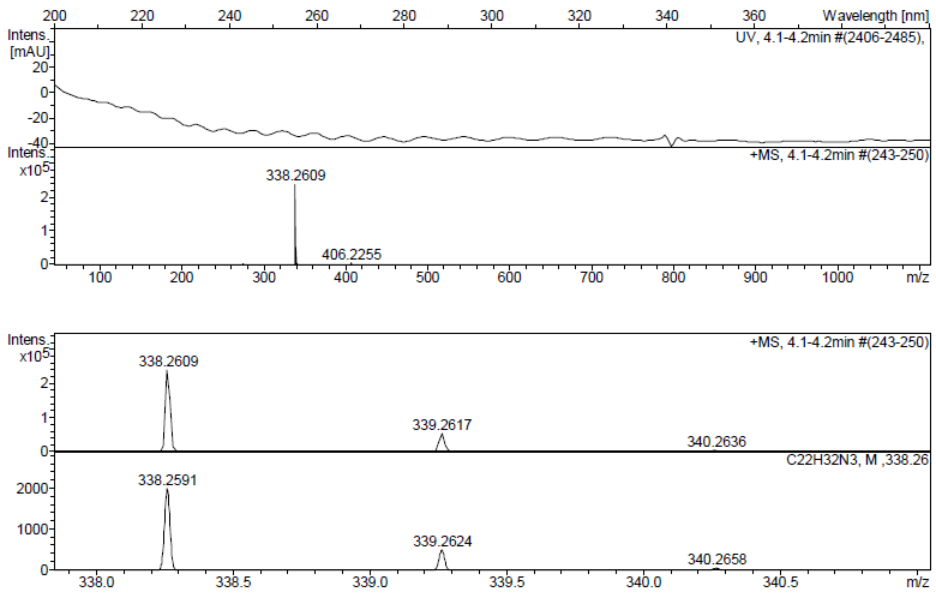

Figure S83. ESI-HRMS (positive ion mode) spectrum of **4c**

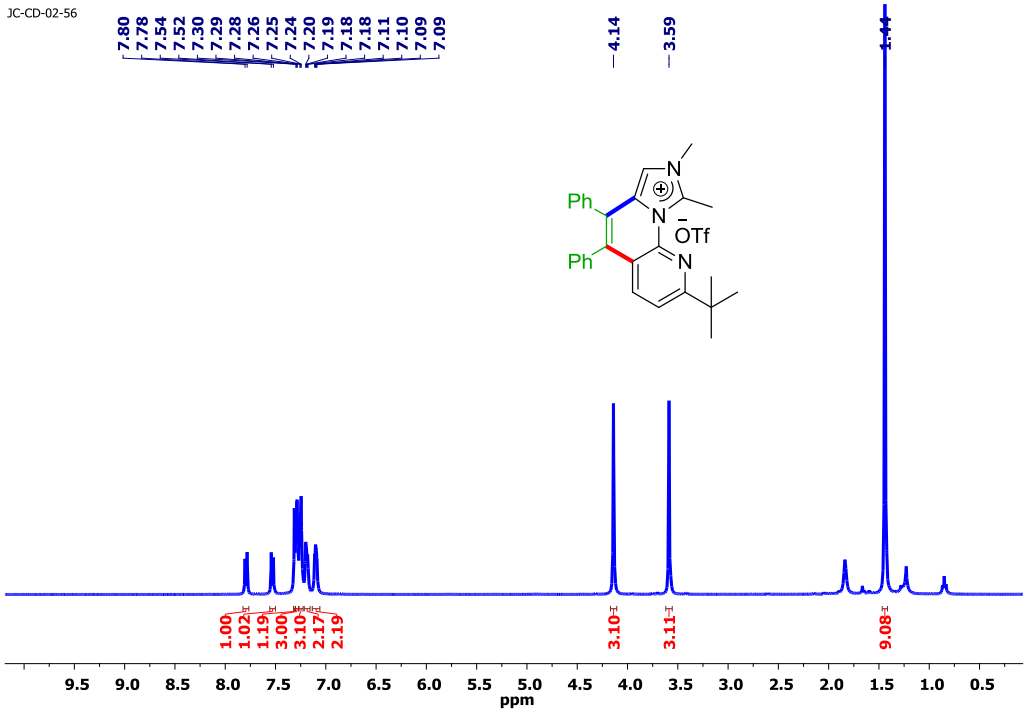

Figure S84. ^{1}H NMR spectrum of **4b** (400 MHz, $CDCl_3$, 300 K)

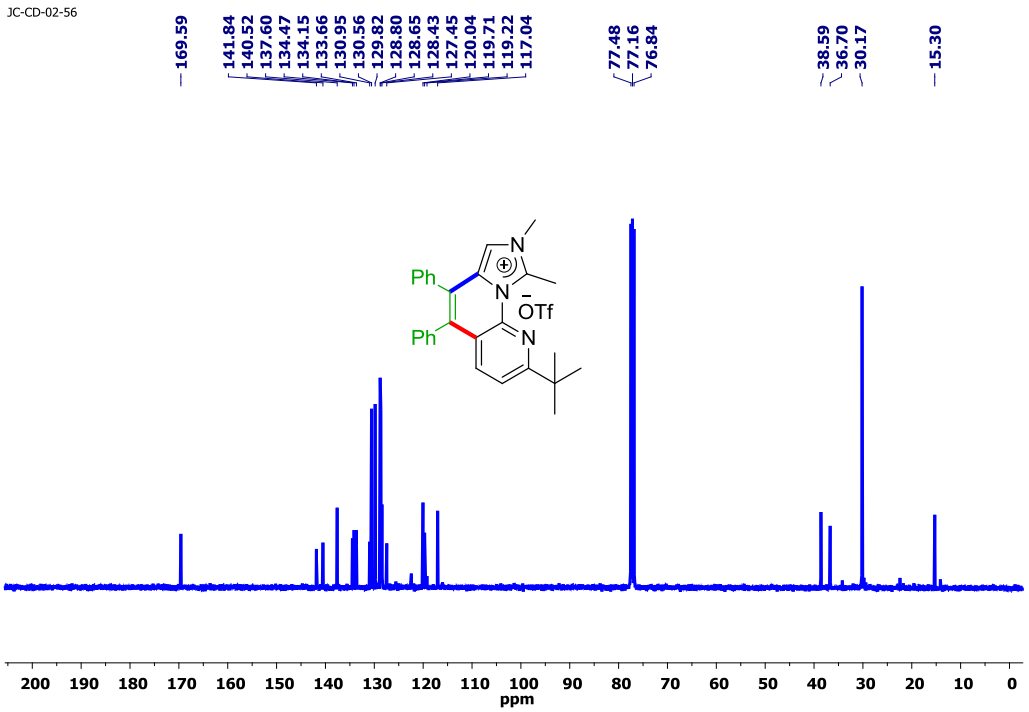

Figure S85. $^{13}C\{^{1}H\}$ NMR spectrum of **4d** (101 MHz, $CDCl_3$, 300 K).

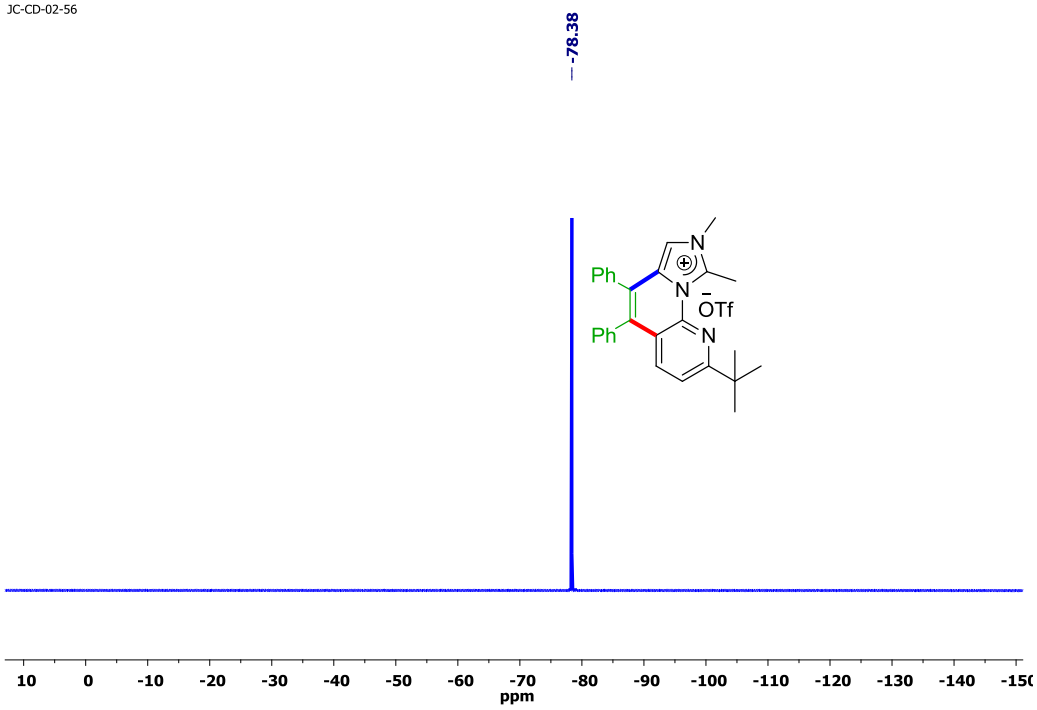

Figure S86. ^{19}F NMR spectrum of **4d** (376 MHz, $CDCl_3$, 300 K)

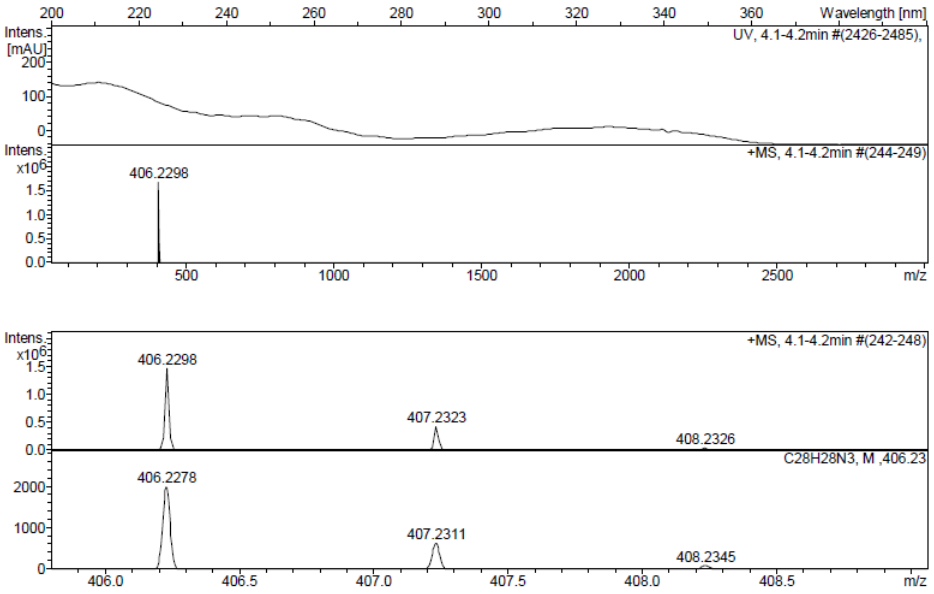

Figure S87. ESI-HRMS (positive ion mode) spectrum of **4d**

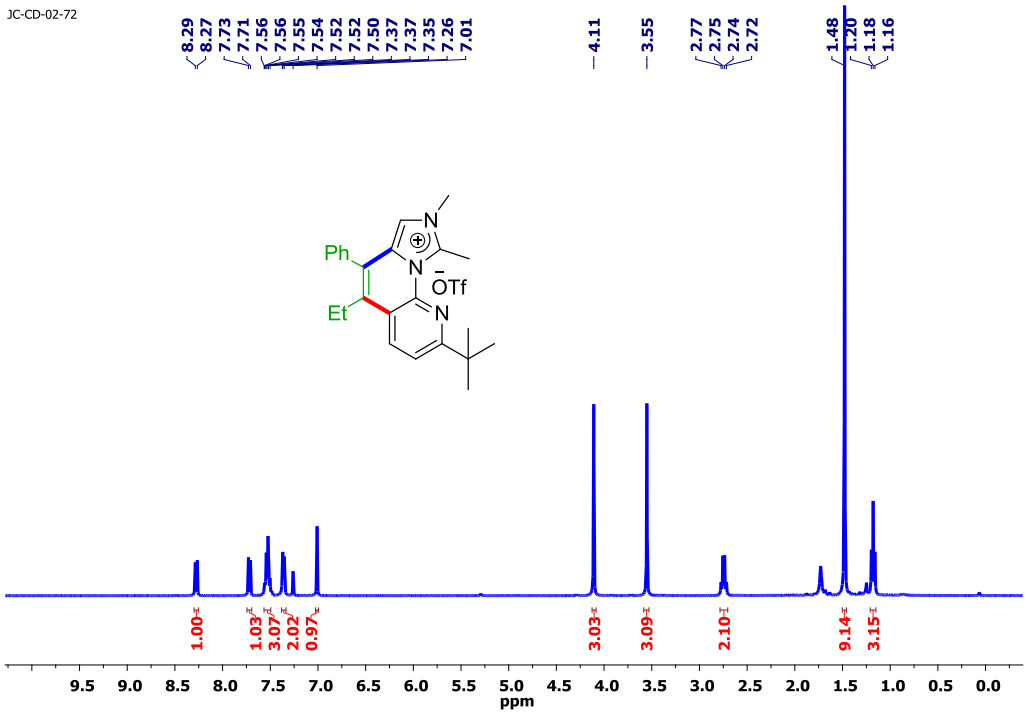

Figure S88. ^{1}H NMR spectrum of **4e** (400 MHz, $CDCl_3$, 300 K)

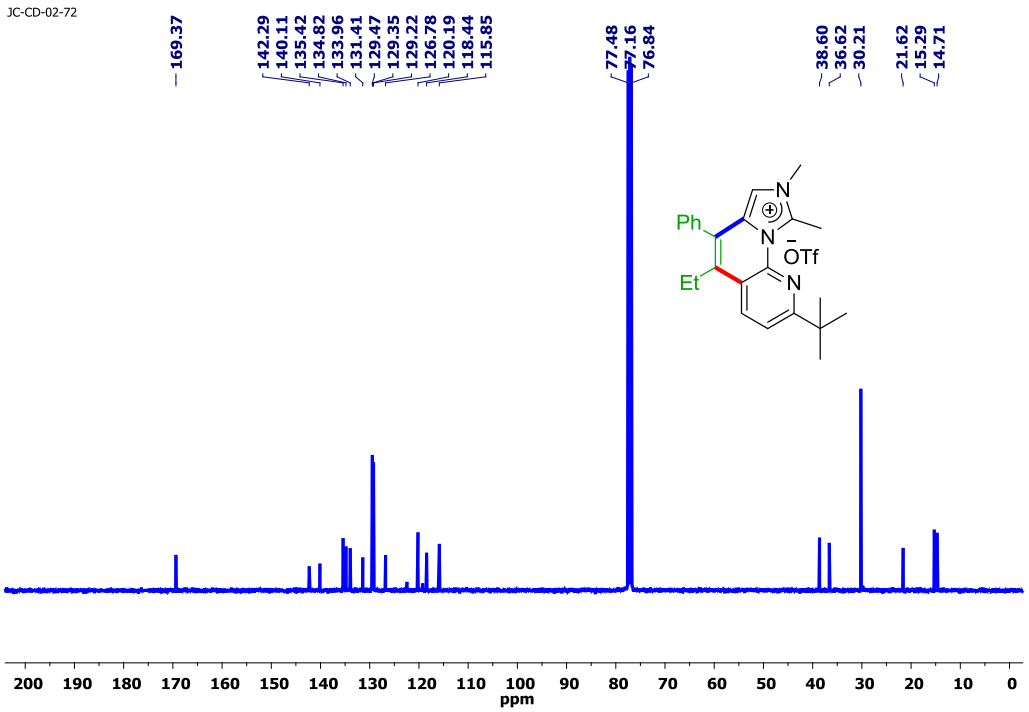

Figure S89. $^{13}C\{^{1}H\}$ NMR spectrum of **4e** (101 MHz, $CDCl_3$, 300 K).

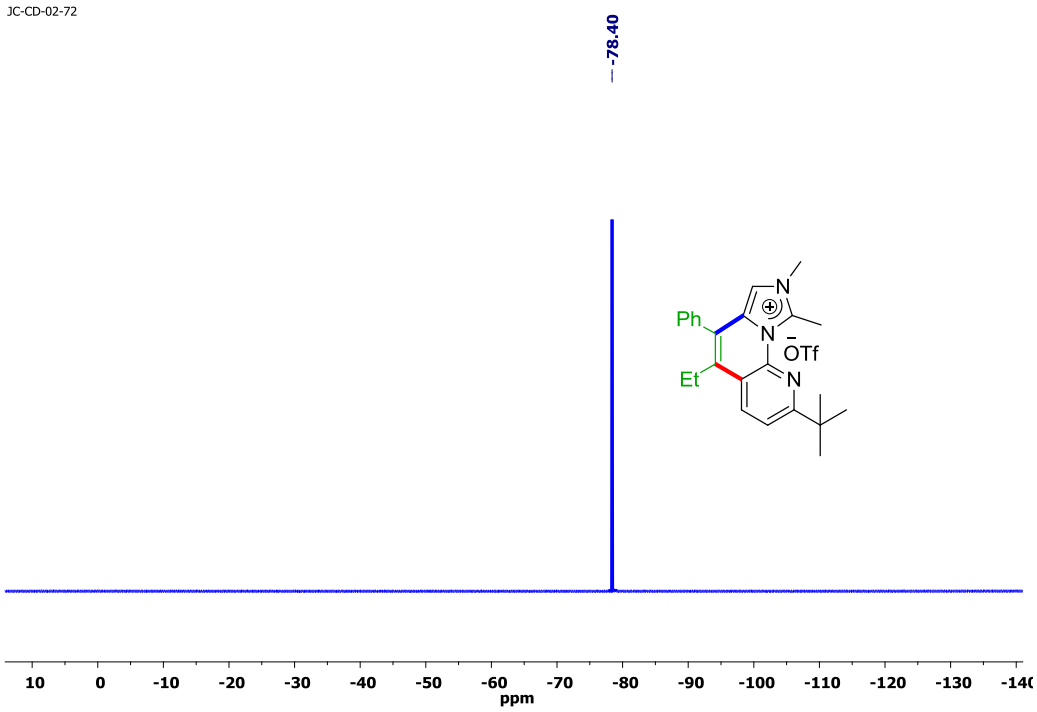

Figure S90. ^{19}F NMR spectrum of **4e** (400 MHz, $CDCl_3$, 300 K)

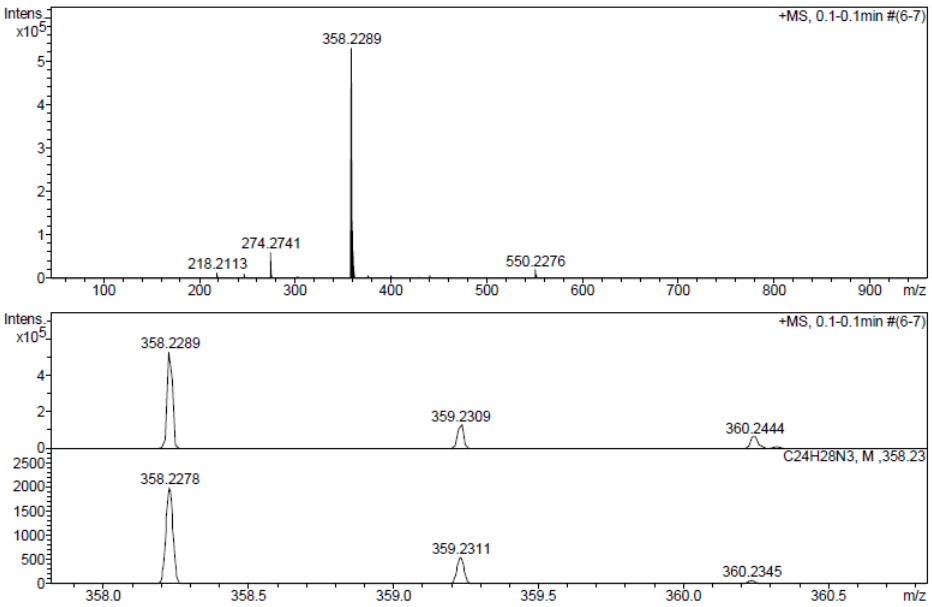

Figure S91. ESI-HRMS (positive ion mode) spectrum of **4e**

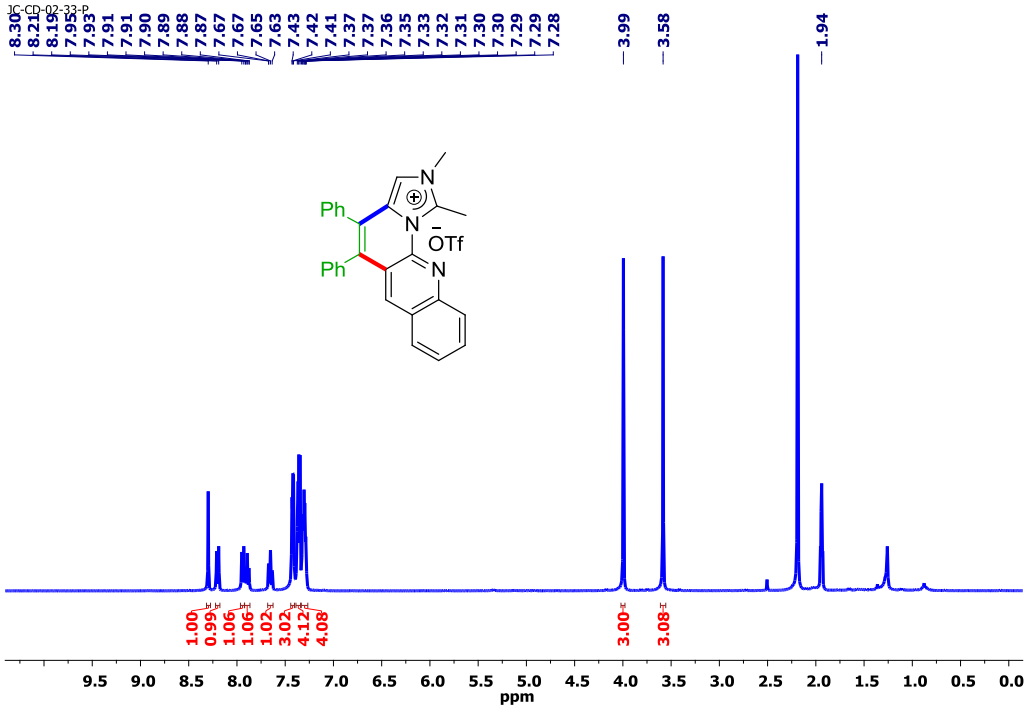

Figure S92. ^{1}H NMR spectrum of **4f** (400 MHz, CD_3CN, 300 K)

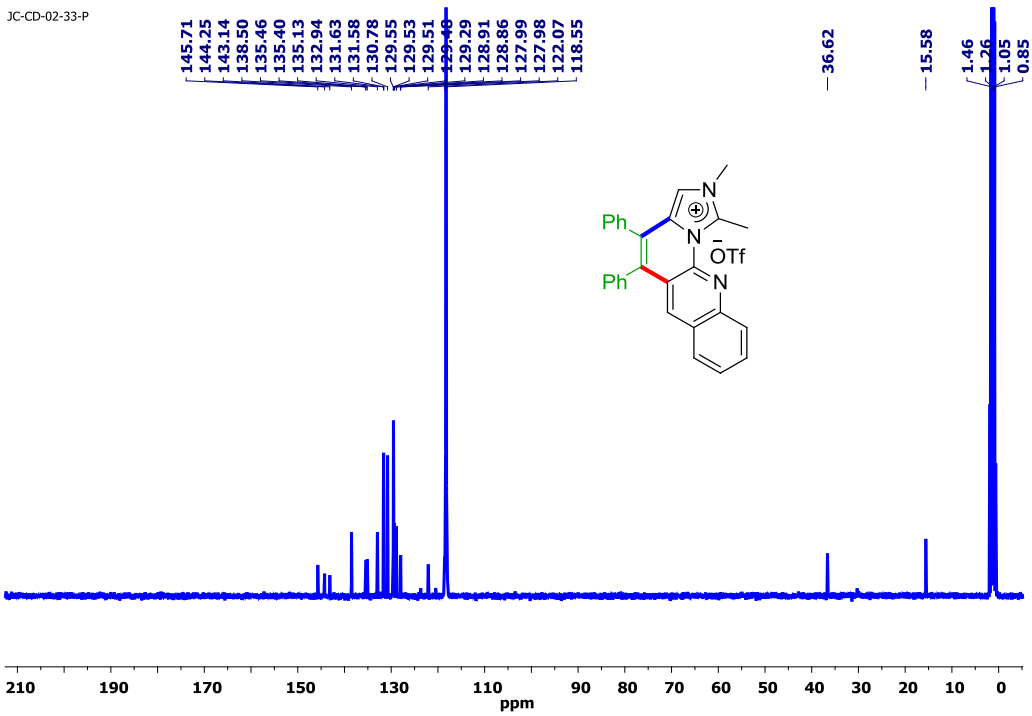

Figure S93. $^{13}C\{^{1}H\}$ NMR spectrum of **4f** (101 MHz, CD_3CN, 300 K).

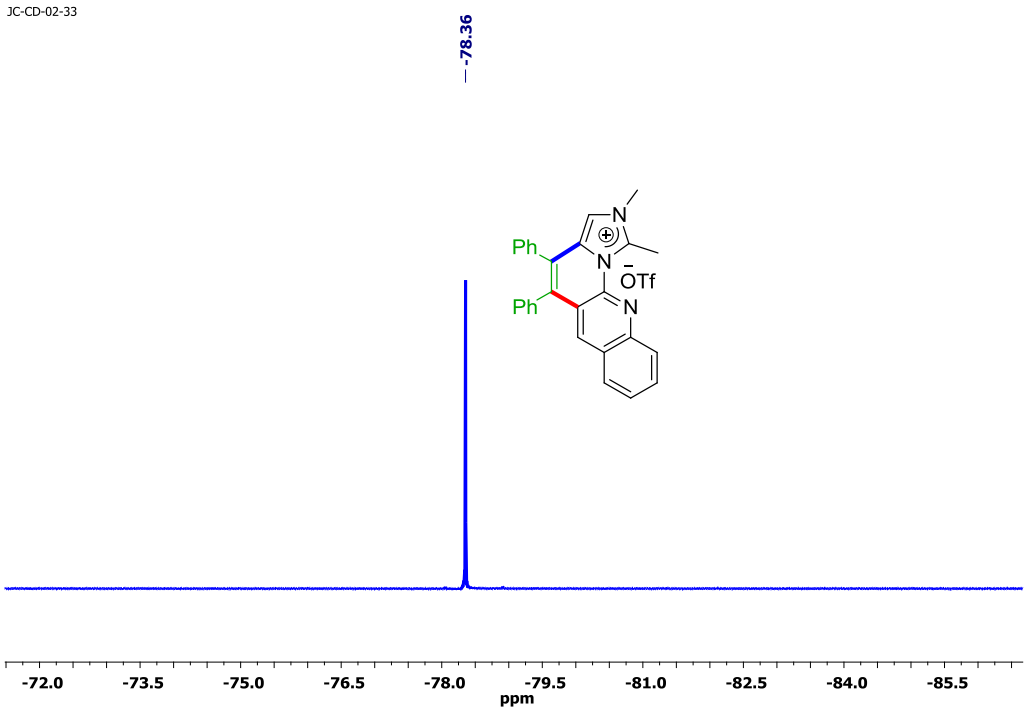

Figure S94. ^{19}F NMR spectrum of **4f** (376 MHz, CD_3CN, 300 K)

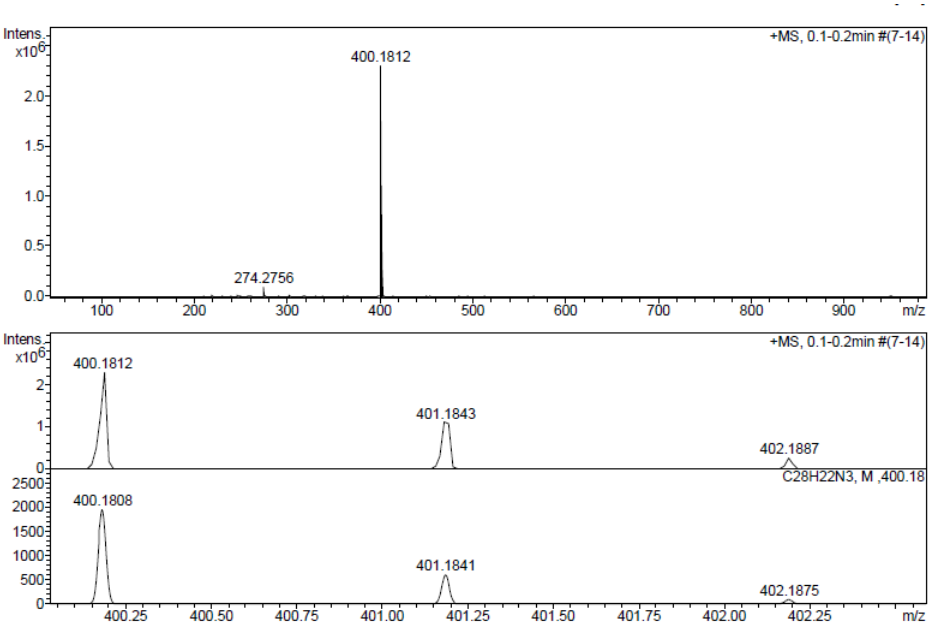

Figure S95. ESI-HRMS (positive ion mode) spectrum of **4f**

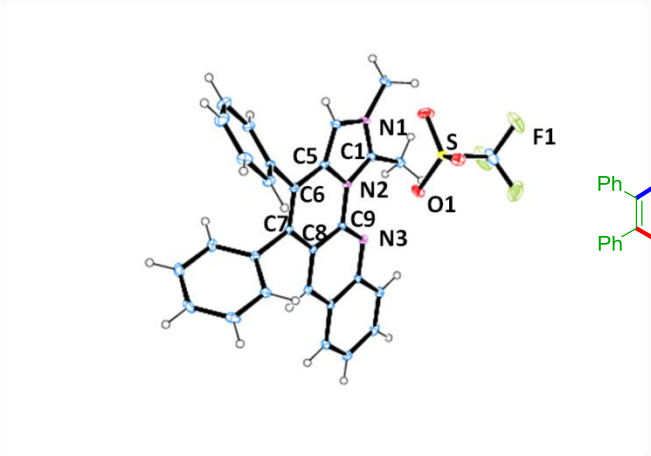

Figure S96. Molecular structure of **4f as** trifluoromethanesulfonate salt (30% probability ellipsoid). Selected bond lengths (Å) and bond angles (°):C_1–N_1 = 1.329(4); C_1–N_2 = 1.358(4); C_5–C_6 = 1.436(5); N_1–C_1–N_2 = 107.7(3); N_2–C_5–C_6 = 121.4(3); N_2–C_9–C_8.= 116.4(3); **CCDC NO.:1587268**

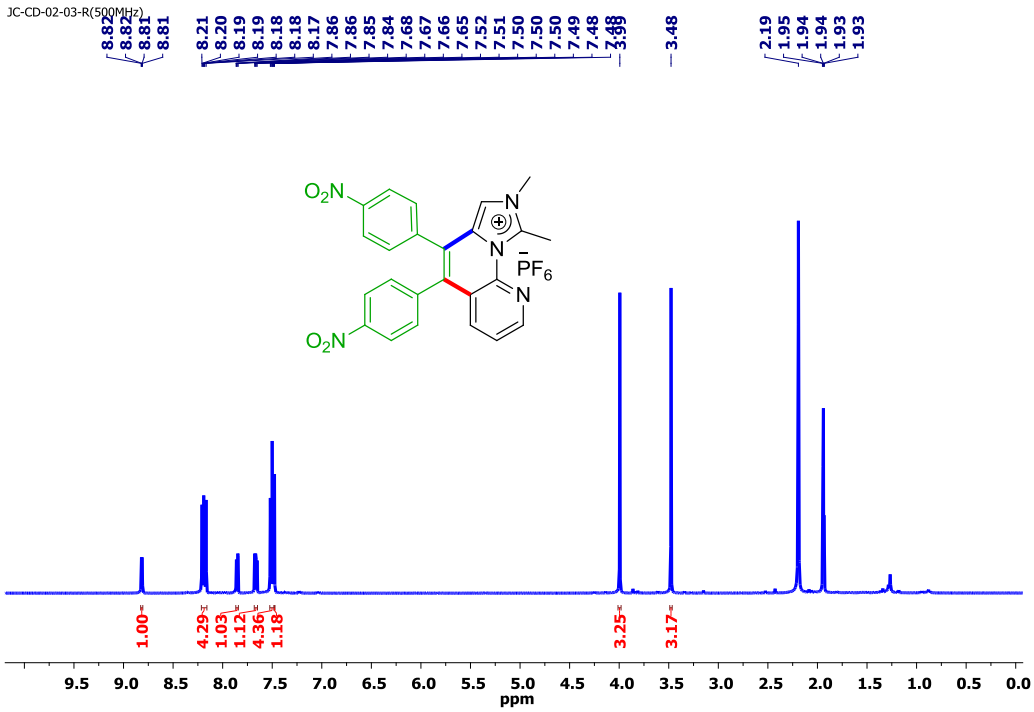

Figure S97. ^{1}H NMR spectrum of **4g** (500 MHz, CD_3CN, 300 K)

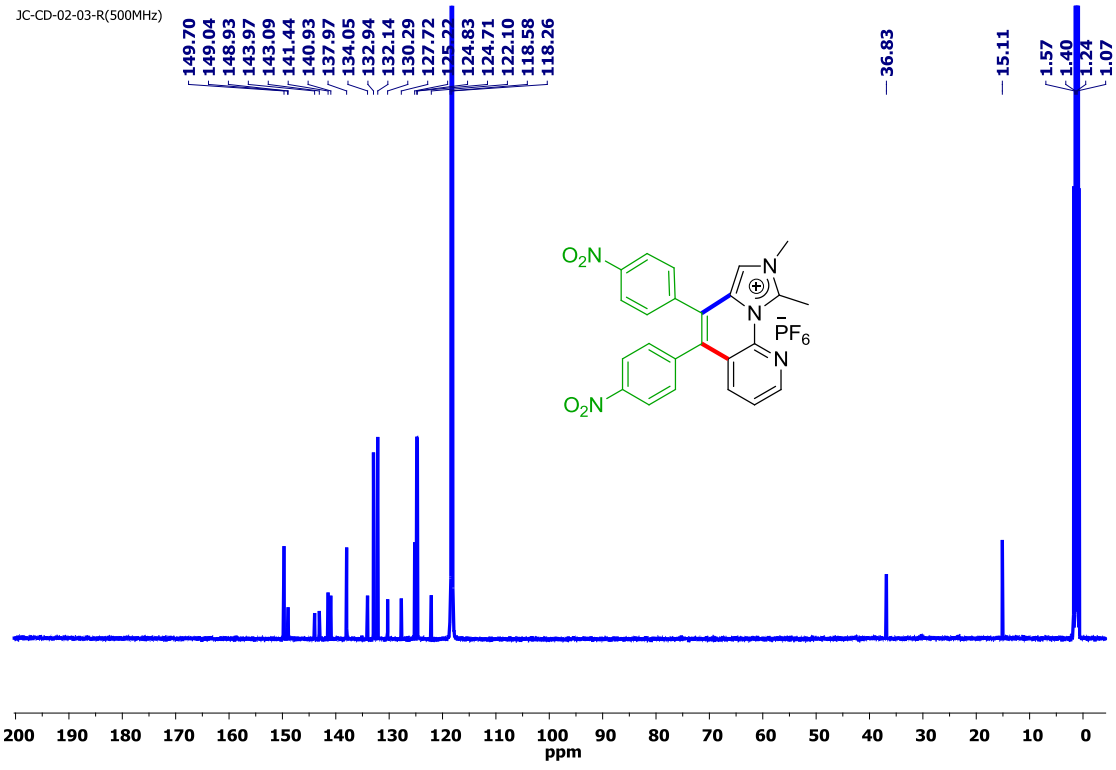

Figure S98. $^{13}C\{^{1}H\}$ NMR spectrum of **4g** (126 MHz, CD_3CN, 300 K).

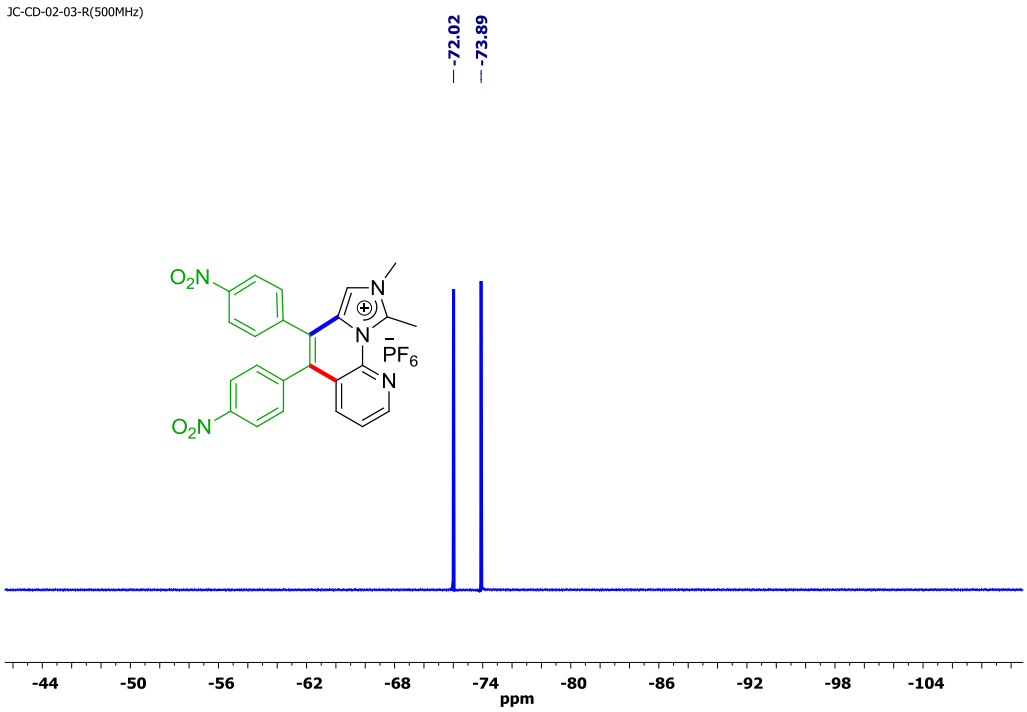

Figure S99. ^{19}F NMR spectrum of **4g** (471 MHz, CD_3CN, 300 K)

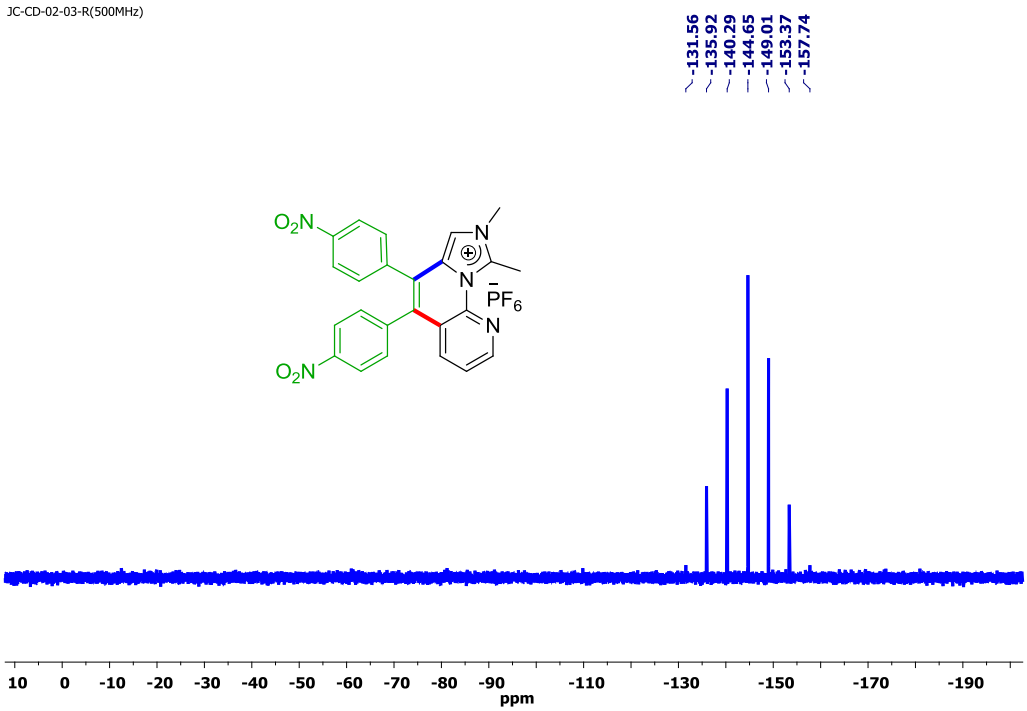

Figure S100. ^{31}P NMR spectrum of **4g** (500 MHz, CD_3CN, 300 K)

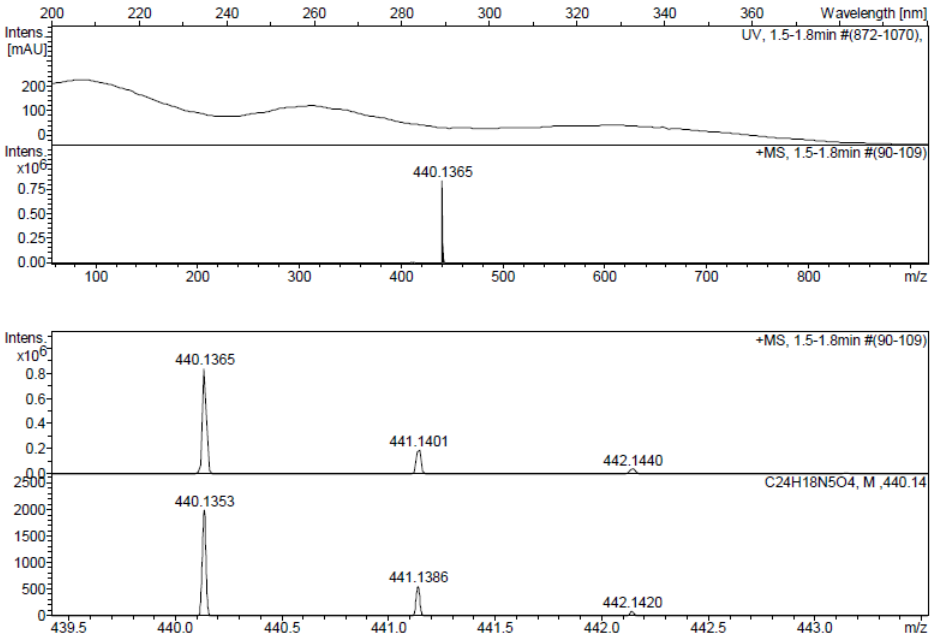

Figure S101. ESI-HRMS (positive ion mode) spectrum of **4g**

14. Characterization data for *a*NHC pre-rollover intermediates

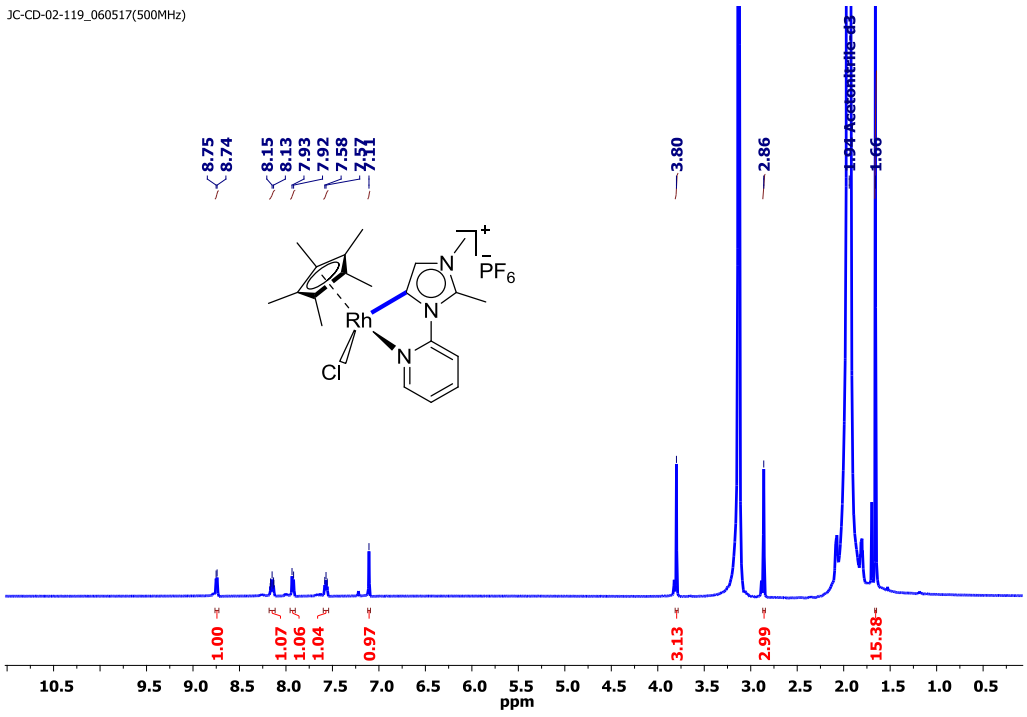

Figure S102. ^{1}H NMR spectrum of **5a** (500 MHz, CD_3CN, 300 K)

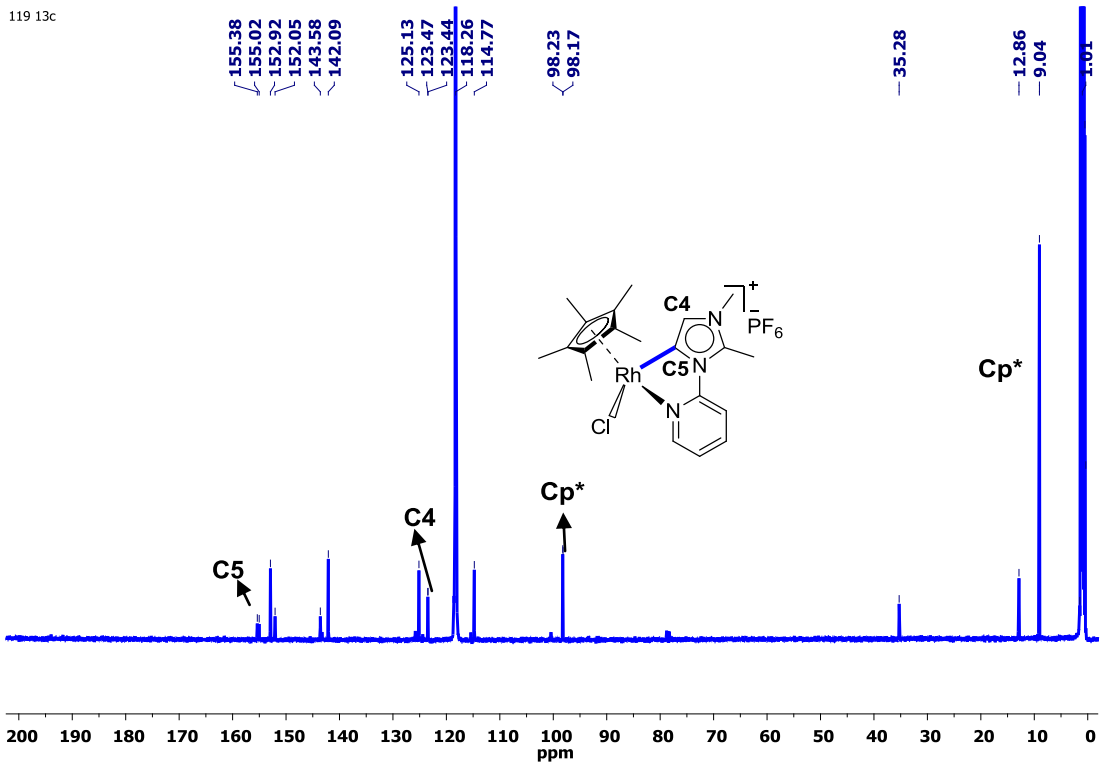

Figure S103. $^{13}C\{^{1}H\}$ NMR spectrum of **5a** (126 MHz, CD_3CN, 300 K)

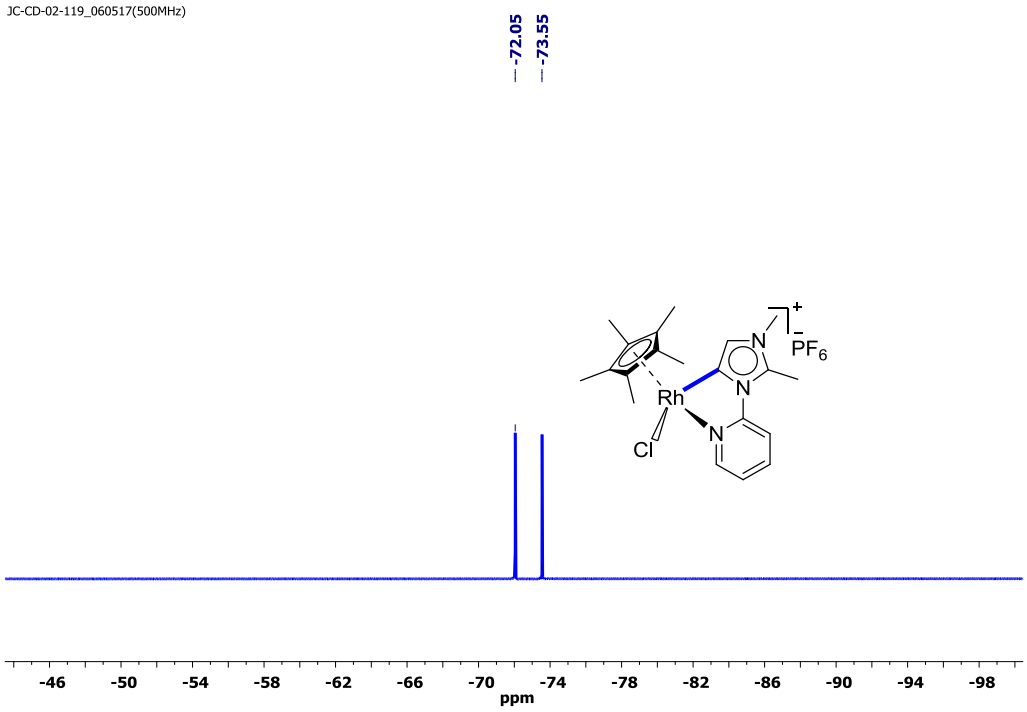

Figure S104. ^{19}F NMR spectrum of **5a** (471 MHz, CD_3CN, 300 K)

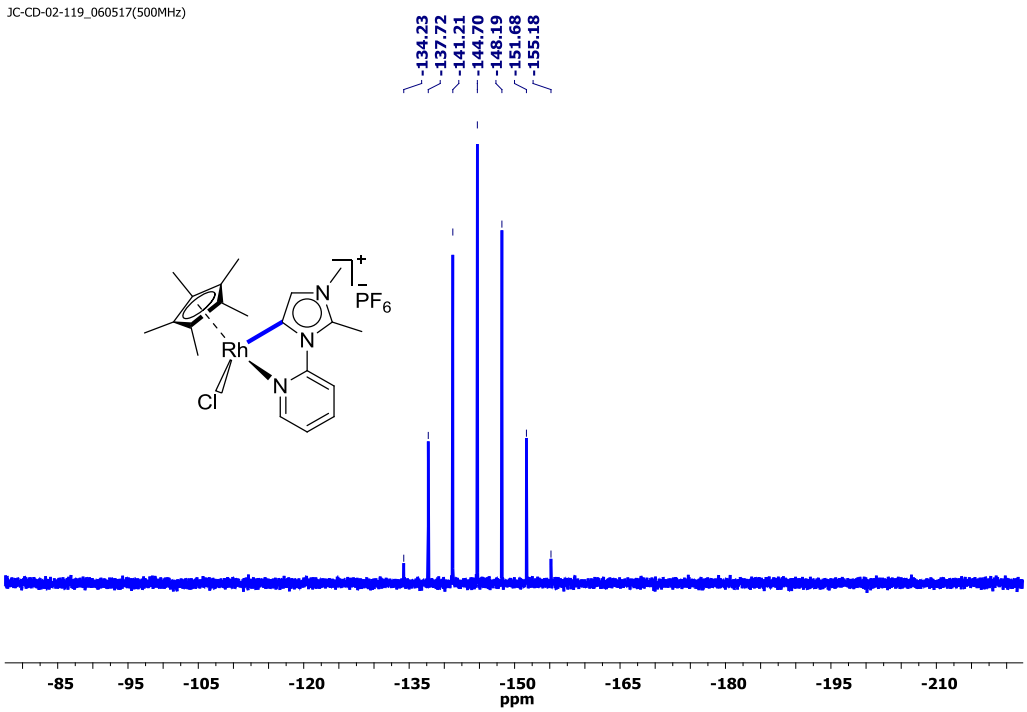

Figure S105. ^{31}P NMR spectrum of **5a** (202 MHz, CD_3CN, 300 K)

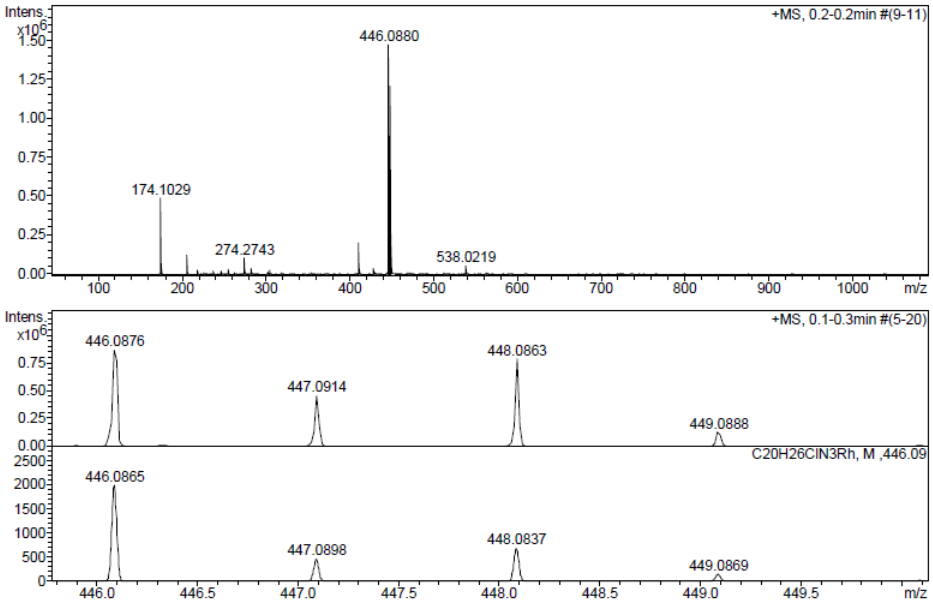

Figure S106. ESI-HRMS (positive ion mode) spectrum of **5a**

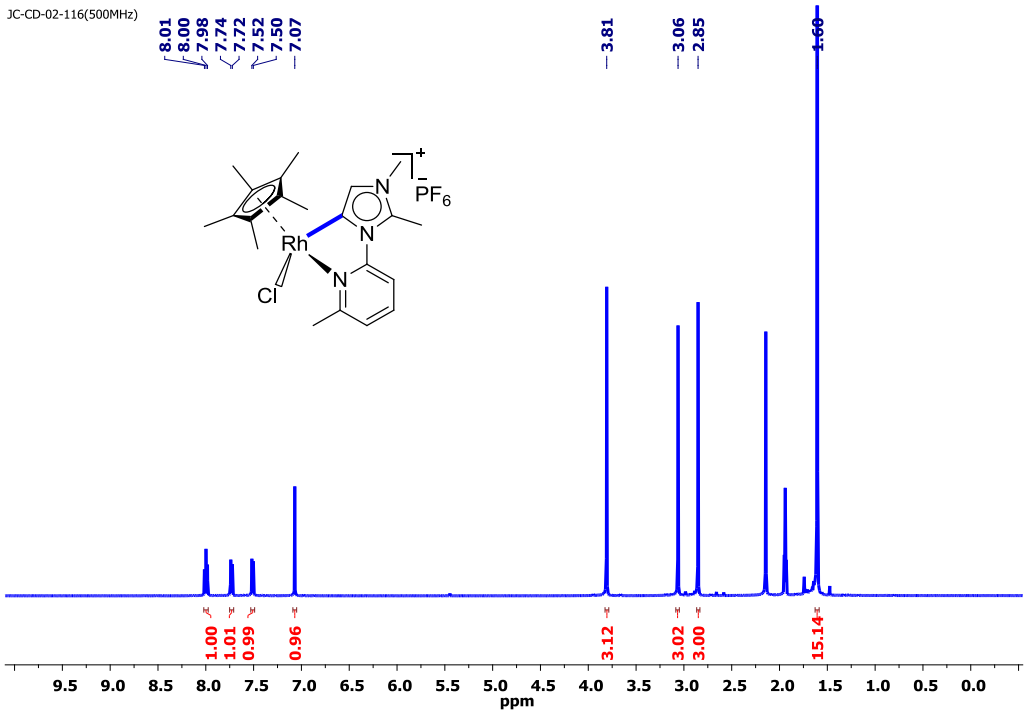

Figure S107. ^{1}H NMR spectrum of **5b** (500 MHz, CD_3CN, 300 K)

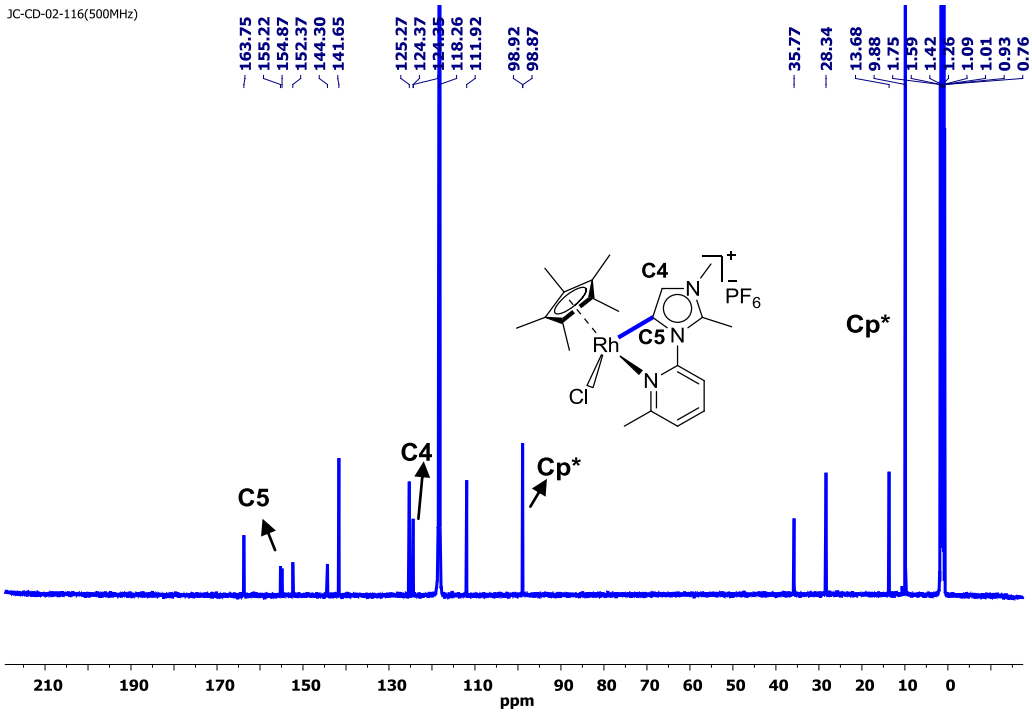

Figure S108. ^{13}C{^{1}H} NMR spectrum of **5b** (126 MHz, CD_3CN, 300 K)

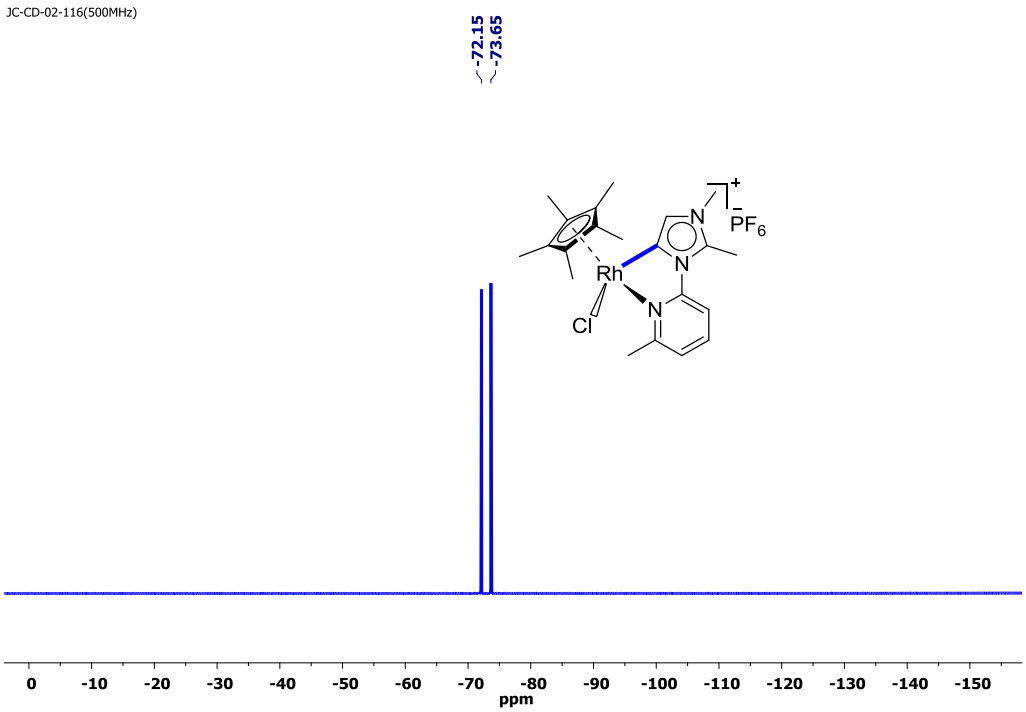

Figure S109. ^{19}F NMR spectrum of **5b** (471 MHz, CD_3CN, 300 K)

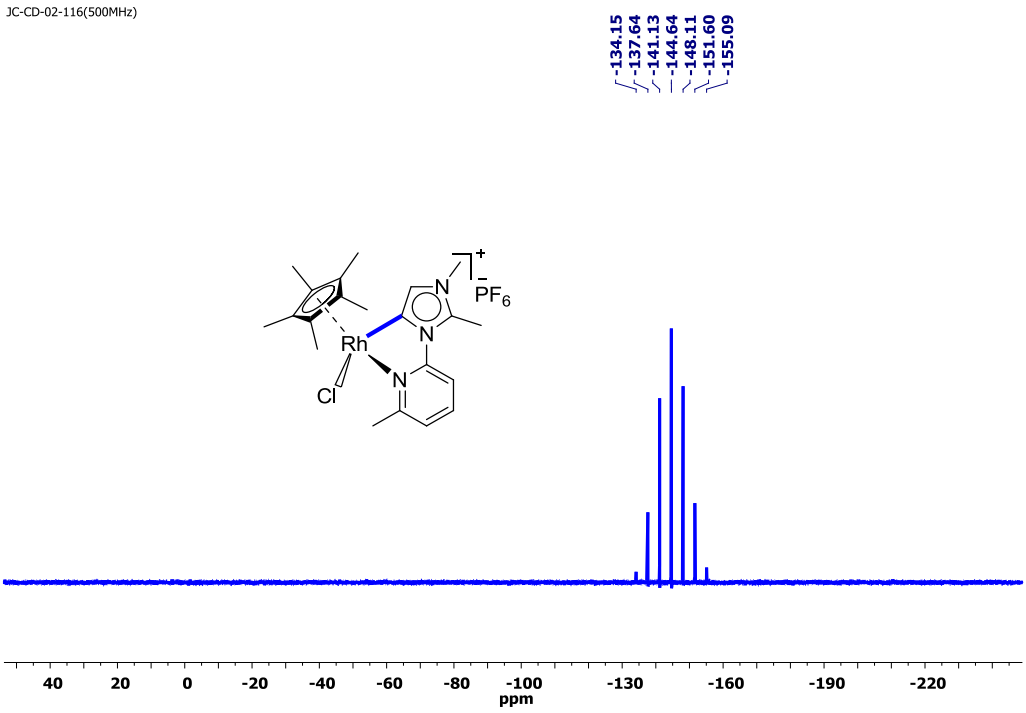

Figure S110. ^{31}P NMR spectrum of **5b** (202 MHz, CD_3CN, 300 K)

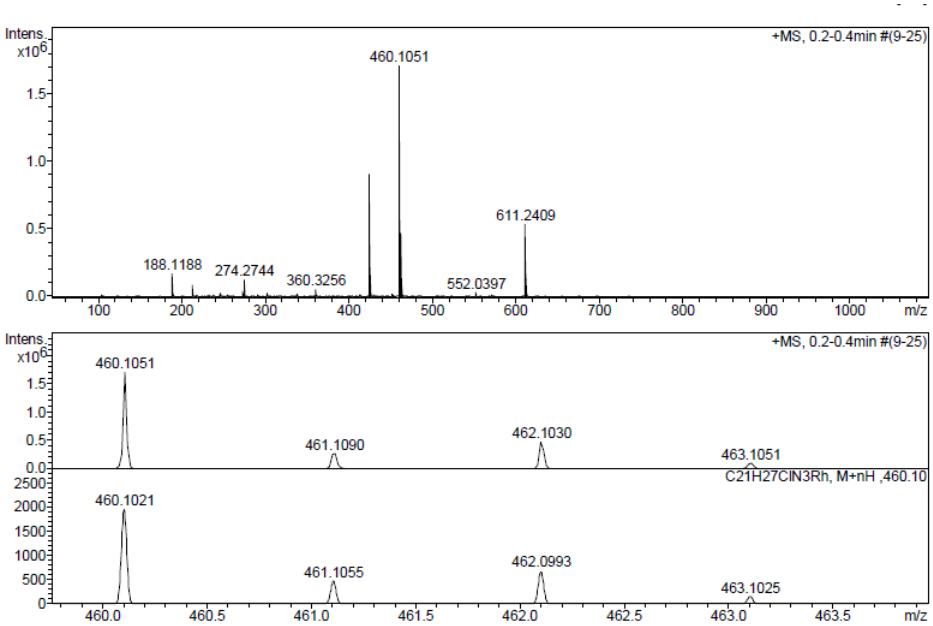

Figure S111. ESI-HRMS (positive ion mode) spectrum of **5b**

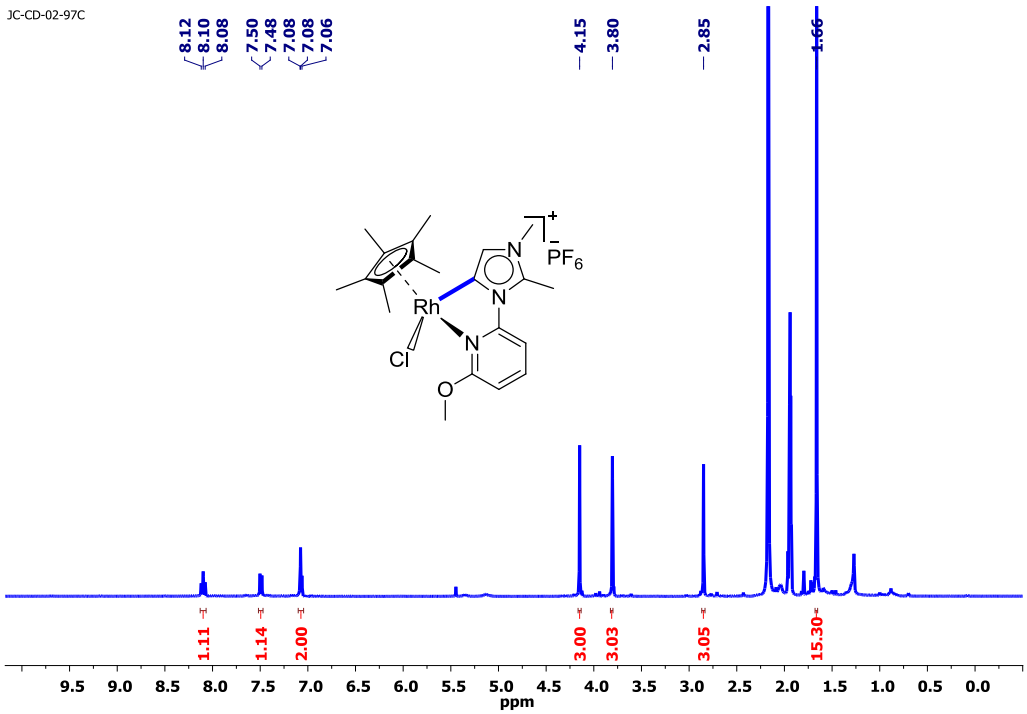

Figure S112. ^{1}H NMR spectrum of **5c** (500 MHz, CD_3CN, 300 K)

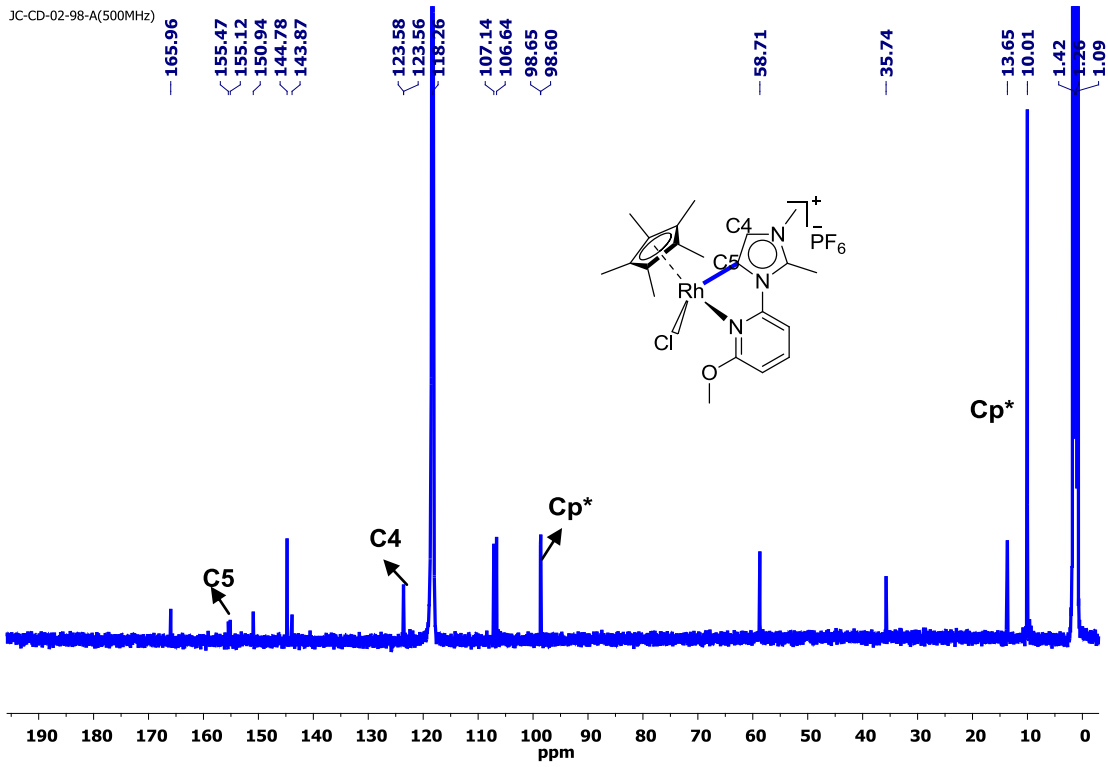

Figure S113. $^{13}C\{^{1}H\}$ NMR spectrum of **5c** (126 MHz, CD_3CN, 300 K)

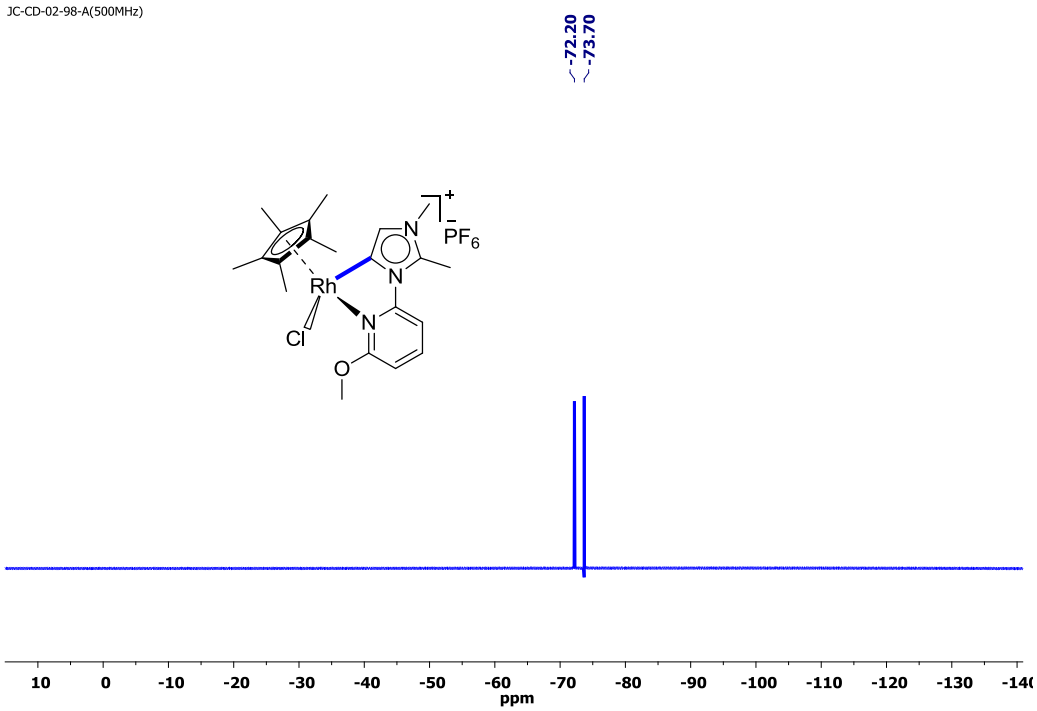

Figure S114. ^{19}F NMR spectrum of **5c** (471 MHz, CD_3CN, 300 K)

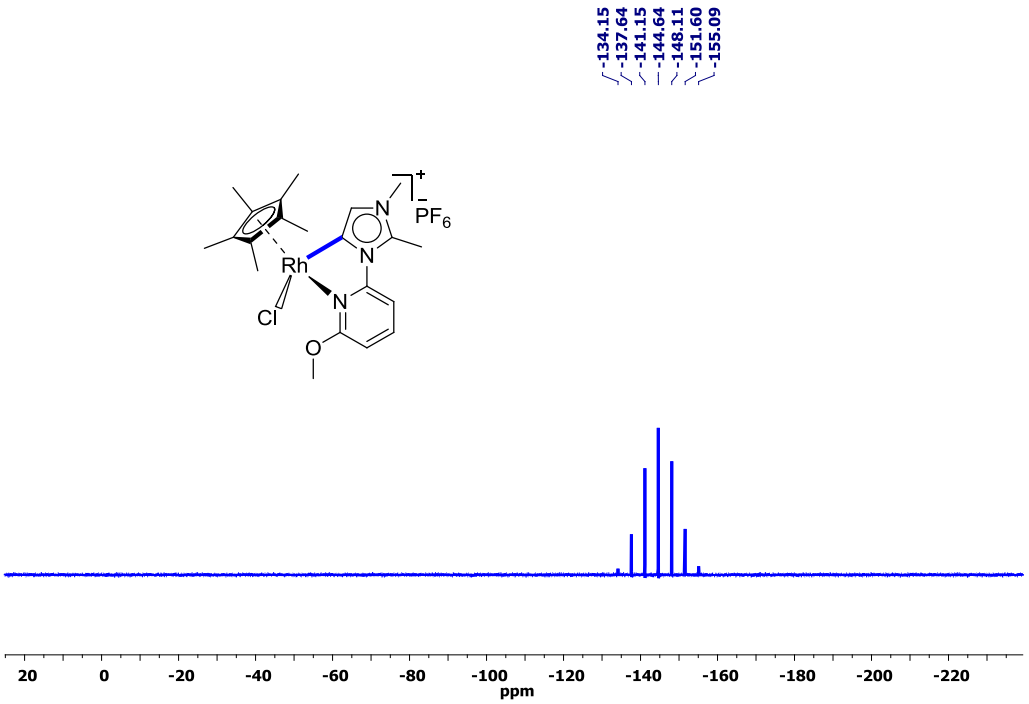

Figure S115. ^{31}P NMR spectrum of **5c (**202 MHz, CD_3CN, 300 K)

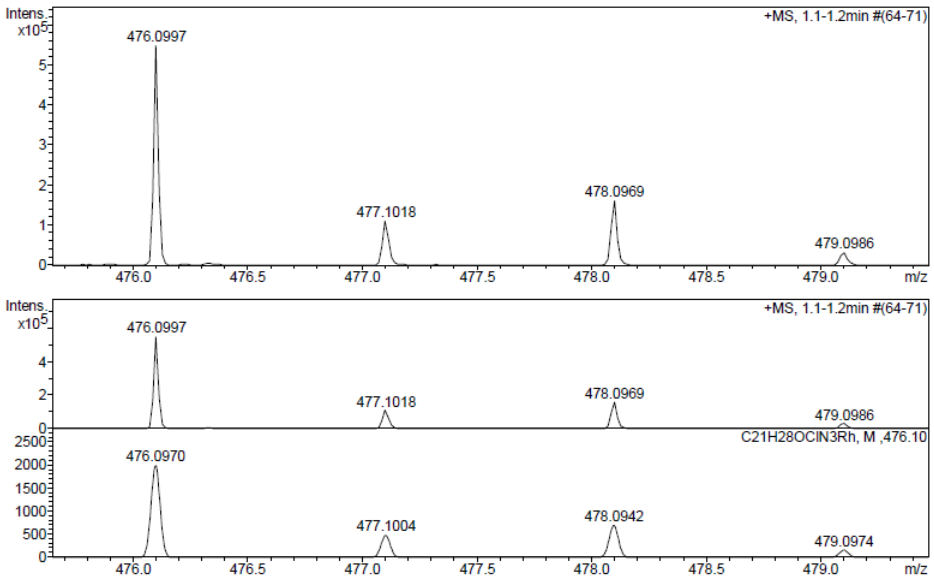

Figure S116. ESI-HRMS (positive ion mode) spectrum of **5c**

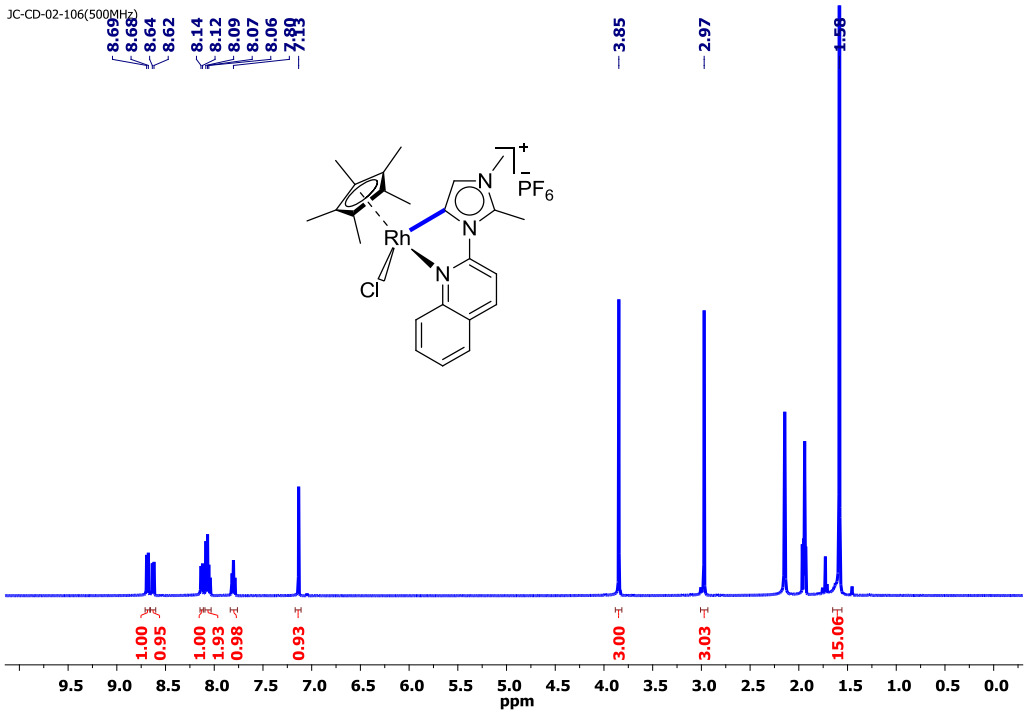

Figure S117. ^{1}H NMR spectrum of **5d** (500 MHz, CD_3CN, 300 K)

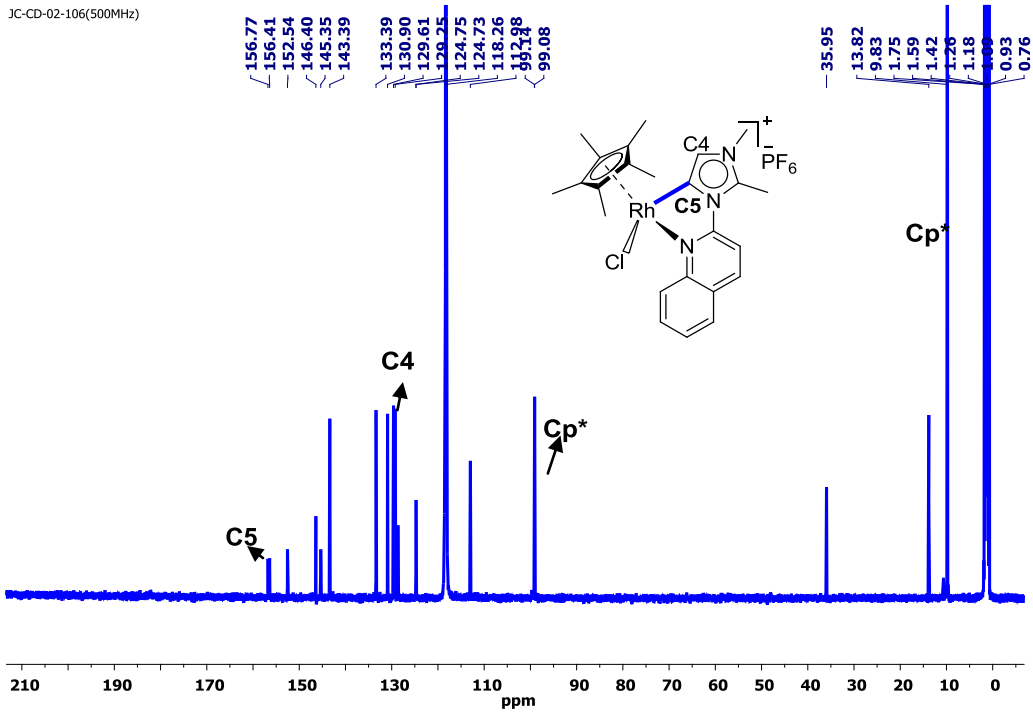

Figure S118. ^{13}C{^{1}H} NMR spectrum of **5d**(126 MHz, CD_3CN, 300 K).

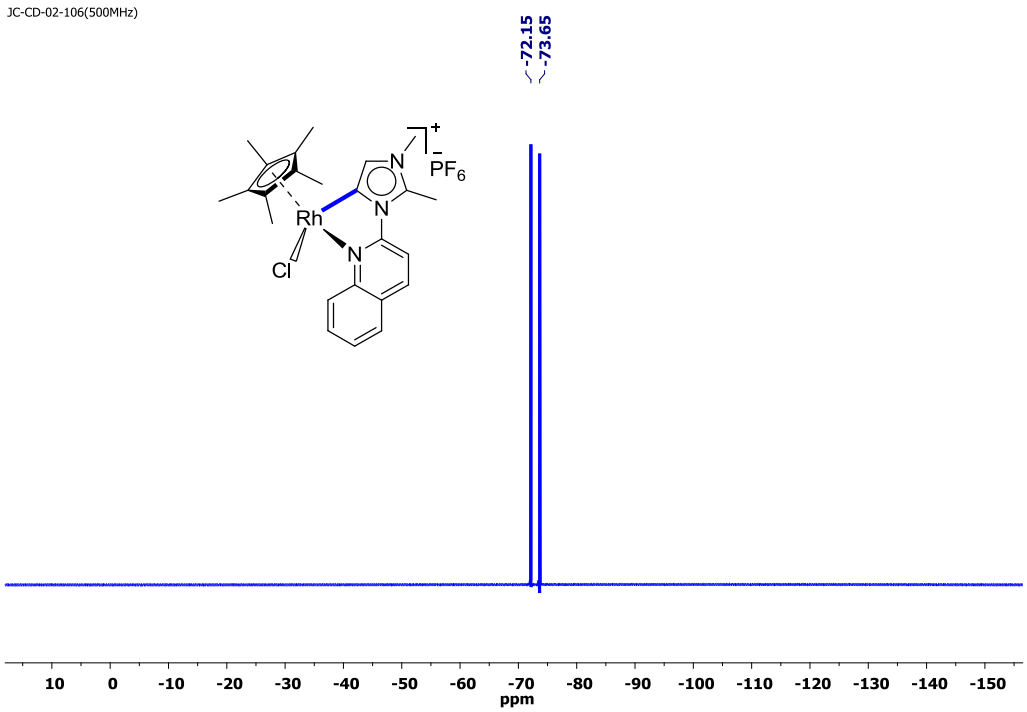

Figure S119. ^{19}F NMR spectrum of **5d** (471 MHz, CD_3CN, 300 K)

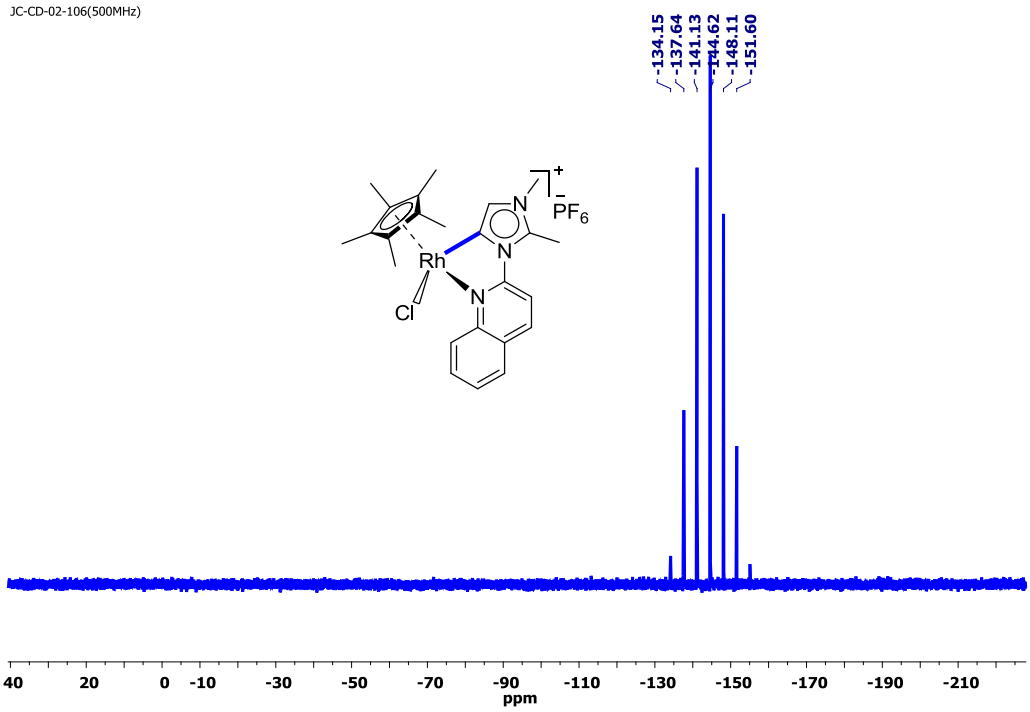

Figure S120. ^{31} P NMR spectrum of **5d (**202 MHz, CD_3CN, 300 K)

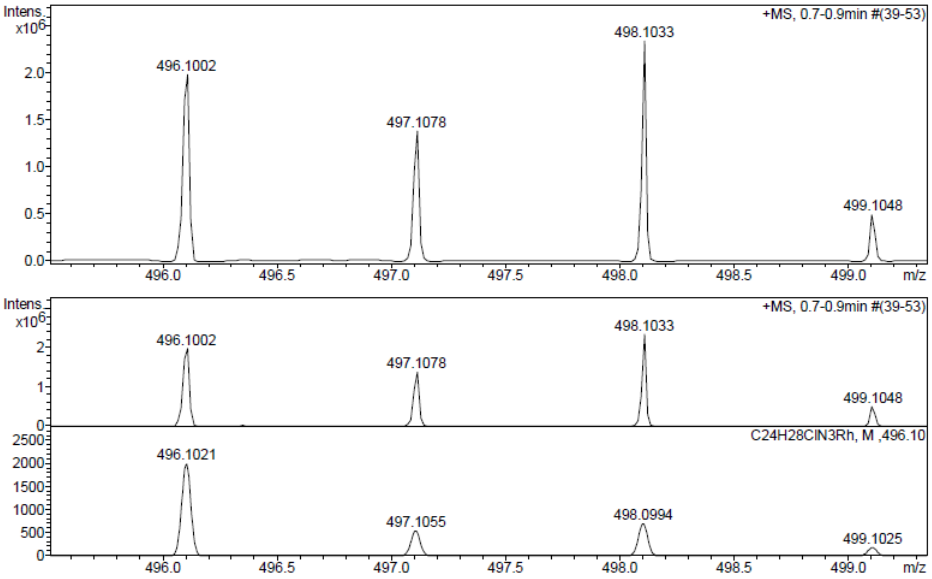

Figure S121. ESI-HRMS (positive ion mode) spectrum of **5d**

15. References

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4. Ghorai, D.; Dutta, C.; Choudhury, J. Switching of "Rollover Pathway" in Rhodium(III)-Catalyzed C–H Activation of Chelating Molecules. *ACS Catal.* **2016**, *6*, 709−713