Electronic Supplementary Material (ESI) for Dalton Transactions.

Solid-state structure, solution-state behaviour and catalytic activity of electronically divergent C, N-chelating palladium-N-heterocyclic carbene complexes

Electronic Supporting Information

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1. General Considerations

Where stated, manipulations were performed under an atmosphere of dry nitrogen by means of standard Schlenk line or Glovebox techniques. Anhydrous solvents were prepared by passing the solvent over activated alumina to remove water, copper catalyst to remove oxygen and molecular sieves to remove any remaining water, *via* the Dow-Grubbs solvent system. Deuterated chloroform and acetonitrile were dried over CaH_2, cannula filtered or distilled, and then freeze-pump-thaw degassed prior to use. All other reagents and solvents were used as supplied.

^{1}H and ^{13}C NMR spectra were recorded on a Bruker DPX300 spectrometer or a Bruker AV500 spectrometer. The values of chemical shifts are given in ppm and values for coupling constants (*J*) in Hz. Assignment of some ^{1}H NMR spectra was aided by the use of 2D $^{1}H^{1}H$ COSY experiments and the assignment of some $^{13}C\{^{1}H\}$ NMR spectra was aided by $^{13}C\{^{1}H\}$ dept 135 experiments. Mass spectra were collected on a Bruker Daltonics (micro TOF) instrument operating in the electrospray mode. Microanalyses were performed using a Carlo Erba Elemental Analyser MOD 1106 spectrometer. GC analyses were performed using a Bruker 430-GC equipped with a CP-8400 autosampler and a BR-5 column (30 m x 0.25 mm (ID) x 0.25 μm film thickness) with carrier gas flow rate of 2.0 $mL.min^{-1}$ and a temperature ramp from 50 to 310 °C at 20 °C min^{-1}. The injection volume was 5 μL with a split ratio of 10. The response factors for the internal standard, substrate and product were calculated using an appropriate calibration for this GC and column.

2. Preparation of imidazolium salts

General allylation procedure. 2-(1-Imidazol)-pyridine derivative (5.0 mmol), allyl bromide (2.0 mL, 23 mmol) and acetonitrile (40 mL) were added to a small round-bottomed flask and heated at reflux for 16 hours. After this time, the mixture was cooled to room temperature and the volume of solvent reduced *in vacuo* (to approx. 10 mL). Slow addition of diethyl ether (35 mL) to the stirring acetonitrile solution led to the precipitation of the product as an off-white crystalline solid, which was collected by vacuum filtration, washed repeatedly with diethyl ether and dried *in vacuo*.

General salt metathesis procedure. 1-Allyl-3-(2-pyridyl)imidazolium bromide derivative (2.00 mmol), ammonium hexafluorophosphate (0.98 g, 6.0 mmol) and water (40 mL) were added to a round-bottomed flask and stirred at room temperature for 2 hours. After this time, an off-white crystalline solid had developed which was isolated *via* vacuum filtration and washed with water (3 x 30 mL) followed by aliquots of cold diethyl ether (3 x 30 mL) and dried *in vacuo*.

1-Allyl-3-(2-pyridyl)imidazolium bromide (1a). 2-(Imidazole-1-yl)pyridine[1] (0.72 g, 5.0 mmol) was reacted according to the general allylation procedure (*vide supra*). Yield: 1.18 g, 4.45 mmol, 89 %. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 11.74 (s, 1H, NC*H*N), 8.57 – 8.47 (m, 2H, py*H*), 8.32 (t, *J* = 1.7 Hz, 1H, im*H*), 8.08 – 7.98 (m, 1H, py*H*), 7.52 (t, *J* = 1.7 Hz, 1H, im*H*), 7.48 – 7.42 (m, 1H, py*H*), 6.12 (ddt, *J* = 16.8, 10.1, 6.5 Hz, 1H, C*H*=CH_2), 5.57 (d, *J* = 16.8 Hz, 1H, HC=CHH_{trans}), 5.51 (dd, *J* = 10.1, 0.6 Hz, 1H, HC=CHH_{cis}), 5.24 (d, *J* = 6.5 Hz, 2H, NCH_2). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ (ppm) 149.1, 146.1, 140.8, 136.0, 129.7, 125.3, 123.5, 122.0, 119.1, 115.2, 52.8. HR-MS (ESI^+): *m/z* 186.1030 $[C_{11}H_{12}N_3]^+$, calcd. $[M - Br]^+$ 186.1026. These data are in agreement with those reported in the literature.[2]

1-Allyl-3-(2-(4-methyl)pyridyl)imidazolium bromide (1b). 2-(Imidazole-1-yl)-4-methylpyridine[3] (0.80 g, 5.0 mmol) was reacted according to the general allylation procedure (*vide supra*). Yield: 1.25 g, 4.46 mmol, 89 %. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 11.34 (s, 1H, NC*H*N), 8.42 – 8.21 (m, 3H, py*H*, im*H*), 7.67 (s, 1H, im*H*), 7.20 (d, *J* = 4.9 Hz, 1H, py*H*), 6.09 (ddt, *J* = 16.9, 10.1, 6.5 Hz, 1H, C*H*=CH_2), 5.56 (d, *J* = 16.9 Hz, 1H, C*H*=CHH_{trans}), 5.44 (d, *J* = 10.1 Hz, 1H, C*H*=CHH_{cis}), 5.21 (d, *J*

= 6.5 Hz, 2H, NCH_2), 2.48 (s, 3H, CH_3). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ (ppm) 152.9, 148.6, 146.1, 135.2, 129.8, 126.2, 123.2, 122.5, 119.2, 115.5, 52.6, 21.3. HR-MS (ESI^+): *m/z* 200.1180 $[C_{12}H_{14}N_3]^+$, calcd. $[M - Br]^+$ 200.1182. These data are in agreement with those reported in the literature.[2]

1-Allyl-3-(2-(5-nitro)pyridyl)imidazolium bromide (1c). 2-(Imidazole-1-yl)-5-nitropyridine[4] (0.95 g, 5.0 mmol) was reacted according to the general allylation procedure (*vide supra*). Yield: 1.37 g, 4.43 mmol, 86 %. ^1H NMR (300 MHz, $CDCl_3$): δ (ppm) 12.22 (s, 1H, NC*H*N), 9.34 (d, *J* = 2.4 Hz, 1H, py*H*), 9.12 (d, *J* = 9.0 Hz, 1H, py*H*), 8.84 (dd, *J* = 9.0, 2.4 Hz, 1H, py*H*), 8.42 (t, *J* = 1.8 Hz, 1H, im*H*), 7.51 (t, *J* = 1.8 Hz, 1H, im*H*), 6.15 (m, 1H, C*H*=CH_2), 5.64 (d, *J* = 16.7 Hz, 1H, CH=CHH_{trans}), 5.58 (d, *J* = 10.2 Hz, 1H, CH=CHH_{cis}), 5.22 (d, *J* = 6.6 Hz, 2H, NCH_2). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ (ppm) 149.2, 145.1, 144.6, 137.0, 136.3, 129.3, 124.1, 123.0, 119.6, 116.2, 53.1. HR-MS (ESI^+): *m/z* 231.0880 $[C_{11}H_{11}N_4O_2]^+$, calcd. $[M - Br]^+$ 231.0877. These data are in agreement with those reported in the literature.[2]

1-Allyl-3-(2-(4-methoxy)pyridyl)imidazolium bromide (1d). 2-(Imidazole-1-yl)-4-methoxypyridine[5] (0.88 g, 5.0 mmol) was reacted according to the general allylation procedure (*vide supra*). Yield: 1.24 g, 4.20 mmol, 84 %. ^1H NMR (300 MHz, $CDCl_3$) δ (ppm) 11.81 (s, 1H, NC*H*N), 8.29 (s, 1H, im*H*), 8.22 (d, *J* = 5.8 Hz, 1H, py*H*), 8.19 (d, *J* = 3.0 Hz, 1H, py*H*), 7.51 (s, 1H, im*H*), 6.90 (dd, *J* = 5.8, 3.0 Hz, 1H, py*H*), 6.14 (ddt, *J* = 16.8, 10.1, 6.5 Hz, 1H, C*H*=CH_2), 5.66 (d, *J* = 16.8 Hz, 1H, CH=CHH_{trans}), 5.55 (d, *J* = 10.1 Hz, 1H, CH=CHH_{cis}), 5.14 (d, *J* = 6.5 Hz, 2H, NCH_2), 4.10 (s, 3H, OCH_3). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ (ppm) 169.3, 150.0, 147.8, 136.1, 129.7, 123.3, 121.7, 119.4, 113.9, 100.1, 58.0, 52.9. HR-MS (ESI^+): *m/z* 216.1161 $[C_{12}H_{14}N_3O]^+$, calcd. $[M - Br]^+$ 216.1131. These data are in agreement with those reported in the literature.[2]

1-Allyl-3-(2-methylpyridyl)imidazolium bromide (1e). 2-Bromomethylpyridine hydrobromide (0.51 g, 2.00 mmol), 1-allylimidazole (0.23 g, 2.1 mmol) and potassium carbonate (1.40 g, 10.00 mmol) were charged to a round-bottomed flask and stirred vigorously in acetonitrile (30 mL) at 60 °C for 18 hours. After this time, the mixture was filtered and solvents removed *in vacuo* to furnish a pale orange oil. Dissolution in acetonitrile (20 mL) followed by reprecipitation with diethyl ether (50 mL)

(twice) delivered the pure product as a pale yellow oil. Yield: 0.25 g, 2.00 mmol, quantitative. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 10.92 (s, 1H, NC*H*N), 8.55 (d, *J* = 4.0 Hz, 1H, im*H*), 7.87 (d, *J* = 8.0 Hz, 1H, *meta*-C*H*), 7.76 (td, *J* = 8.0 Hz, 1H, *para*-C*H*), 7.63 (d, *J* = 4.0 Hz, 1H, im*H*), 7.30 (td, *J* = 8.0 Hz, 1H, *meta'*-C*H*), 7.16 (d, *J* = 8.0 Hz, 1H, *ortho*-C*H*), 6.02 (m, 1H, CH_2=C*H*C), 5.79 (s, 2H, CH_2), 5.49 (d, *J* = 12.0 Hz, 2H, CH_2=CH), 4.92 (d, *J* = 3.0 Hz, 2H, NCH_2). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ (ppm) 152.5, 150.0, 137.9, 137.6, 129.6, 124.3, 124.2, 123.1, 121.3, 110.1, 54.2, 52.4. HR-MS (ESI$^+$): *m/z* 200.1202 $[C_{12}H_{14}N_3]^+$, calcd. $[M - Br]^+$ 200.1182. These data are in agreement with those reported in the literature.[2]

1,3-*Bis*(2-methylpyridyl)imidazolium bromide (1f). 2-Bromomethylpyridine (1.20 g, 4.74 mmol), imidazole (0.21 g, 3.10 mmol) and potassium carbonate (1.65 g, 11.9 mmol) were charged to a round-bottomed flask and stirred vigorously in acetonitrile (50 mL) at 60 °C for 24 hours. After this time, the mixture was filtered and solvents removed *in vacuo* to give a crude brown oil. The residue was dissolved in acetonitrile (30 mL) followed by reprecipitation with diethyl ether (60 mL) (twice) to furnish a light brown oil, which was further washed with diethyl ether (3 x 30 mL) and dried *in vacuo* to afford spectroscopically pure title compound as a light-brown solid. Yield: 0.64 g, 2.00 mmol, 84 %. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 10.95 (br s, 1H, NC*H*N), 8.56 (d, *J* = 3.0 Hz, 2H, im*H*), 7.78 – 7.75 (m, 4H, py*CH*), 7.54 (br s, 2H, im*H*), 7.31 (td, *J* = 6.0 Hz, 2H, *meta*-C*H*), 5.67 (s, 4H, CH_2). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ (ppm) 152.3, 149.9, 137.8, 137.5, 124.1, 124.0, 122.4, 54.15. HR-MS (ESI$^+$): *m/z* 251.1297 $[C_{15}H_{15}N_4]^+$, calcd. $[M - Br]^+$ 251.1291. Anal. calcd. (%) for $C_{15}H_{15}N_4Br$: C 54.39, H 4.61, N 16.92; found C 54.00, H 5.00, N 16.90.

1-Allyl-3-(2-pyridyl)imidazolium hexafluorophosphate (2a). 1-Allyl-3-(2-pyridyl)imidazolium bromide (0.53 g, 2.0 mmol) was reacted according to the general salt metathesis reaction (*vide supra*). Yield: 0.66 g, 2.00 mmol, quantitative. ^{1}H NMR (300 MHz, CD_3CN): δ (ppm) 9.28 (s, 1H, NC*H*N), 8.61 (d, *J* = 4.8 Hz, 1H, im*H*), 8.34 – 8.08 (m, 2H, py*H*), 7.75 (d, *J* = 9.0 Hz, 1H, py*H*), 7.07 (d, *J* = 4.8 Hz, 1H, im*H*), 7.58 – 7.56 (m, 1H, py*H*), 6.16 (ddt, *J* = 15.9, 9.0, 1.5 Hz, 1H, C*H*=CH_2), 5.51 (d, *J* = 15.9 Hz, 1H, HC=CHH_{trans}), 5.47 (dd, *J* = 6.6, 0.9 Hz, 1H, HC=CHH_{cis}), 4.89 (d, *J* = 6.5 Hz, 2H, NCH_2). ^{13}C{^{1}H} NMR (75 MHz, CD_3CN): δ (ppm) 150.7, 148.1, 142.3, 136.0, 128.1, 125.2, 123.3,

120.9, 118.8, 115.1, 52.3. HR-MS (ESI^+): *m/z* 186.1020 $[C_{11}H_{12}N_3]^+$, calcd. $[M - PF_6]^+$ 186.1026. Anal. calcd. (%) for $C_{11}H_{12}N_3PF_6.{}^2/_3CH_2Cl_2$: C 35.97, H 3.46, N 10.80; found C 35.70, H 3.20, N 11.20.

1-Allyl-3-(2-(4-methyl)pyridyl)imidazolium hexafluorophosphate (2b). 1-Allyl-3-(2-(4-methyl)pyridyl)imidazolium bromide (0.56 g, 2.0 mmol) was reacted according to the general salt metathesis reaction (*vide supra*). Yield: 0.65 g, 1.88 mmol, 94 %. ^{1}H NMR (300 MHz, CD_3CN) δ (ppm) 9.26 (br s, 1H, NC*H*N), 8.44 (d, *J* = 5.1 Hz, 1H, py*H*), 8.07 (br t, *J* = 3.0, 1.5 Hz, 1H, im*H*), 7.61 (br s, 1H, py*H*), 7.57 (br t, *J* = 3.0, 1.5 Hz, 1H, im*H*), 7.42 (br d, *J* = 5.1 Hz, 1H, py*H*), 6.08 (ddt, *J* = 18.1, 10.1, 6.5 Hz, 1H, C*H*=CH_2), 5.47 (d, *J* = 18.1 Hz, 1H, C*H*=CHH_{trans}), 4.89 (d, *J* = 10.1 Hz, 1H, C*H*=CHH_{cis}), 2.50 (s, 3H, CH_3). ^{13}C{^{1}H} NMR (75 MHz, CD_3CN) δ (ppm) 149.9, 148.0, 135.0, 131.3, 127.2, 124.4, 122.5, 120.5, 118.6, 115.5, 53.1, 21.2. HR-MS (ESI^+): *m/z* 200.1163 $[C_{12}H_{14}N_3]^+$, calcd. $[M - PF_6]^+$ 200.1182. Anal. calcd. (%) for $C_{12}H_{14}N_3PF_6.CH_2Cl_2$: C 36.30, H 3.75, N 9.91; found C 36.25, H 3.50, N 10.10.

1-Allyl-3-(2-(5-nitro)pyridyl)imidazolium hexafluorophosphate (2c). 1-Allyl-3-(2-(5-nitro)pyridyl)imidazolium bromide (0.62 g, 2.0 mmol) was reacted according to the general salt metathesis reaction (*vide supra*). Yield: 0.74 g, 1.96 mmol, 98 %. ^{1}H NMR (300 MHz, CD_3CN) δ (ppm) 9.23 (br s, 1H, NC*H*N), 9.22 (br s, 1H, py*H*), 8.72 (d, *J* = 8.1 Hz, 1H, im*H*), 8.07 (s, 1H, py*H*), 7.87 (d, *J* = 8.1 Hz, 1H, im*H*), 7.51 (br s, 1H, py*H*), 6.08 – 5.91 (m, 1H, C*H*=CH_2), 5.41 (d, *J* = 6.3 Hz, 1H, CH=CHH_{trans}), 5.35 (br s, 1H, CH=CHH_{cis}), 4.81 (br d, *J* = 5.7 Hz, 2H, NCH_2). ^{13}C{^{1}H} NMR (75 MHz, CD_3CN): δ (ppm) 150.4, 146.3, 145.9, 137.2, 136.1, 130.9, 125.0, 123.0, 121.0, 115.8, 53.5. HR-MS (ESI^+): *m/z* 231.0888 $[C_{11}H_{11}N_4O_2]^+$, calcd. $[M - PF_6]^+$ 231.0877. Anal. calcd. (%) for $C_{11}H_{11}N_4O_2PF_6.{}^1/_2H_2O$: C 34.30, H 3.14, N 14.54; found C 34.15, H 2.80, N 14.20.

1-Allyl-3-(2-(4-methoxy)pyridyl)imidazolium hexafluorophosphate (2d). 1-Allyl-3-(2-(4-methoxy)pyridyl)imidazolium bromide (0.56 g, 2.00 mmol) was reacted according to the general salt metathesis reaction (*vide supra*). Yield: 0.72 g, 2.00 mmol, quantitative. ^{1}H NMR (300 MHz, CD_3CN) δ 9.28 (s, 1H, NC*H*N), 8.39 (d, *J* = 6.0 Hz, 1H, pyr*H*), 8.10 (br t, *J* = 3.9, 1.8 Hz, 1H, im*H*), 7.56 (br t, *J* = 3.9, 1.8 Hz, 1H, im*H*), 7.26 (d, *J* = 2.1 Hz, 1H, pyr*H*), 7.11 (dd, *J* = 5.7, 2.1 Hz, 1H, pyr*H*), 6.16 –

6.02 (ddt, *J* = 17.7, 12.6, 6.3 Hz, 1H, C*H*=CH_2), 5.50 (d, *J* = 17.7 Hz, 1H, CH=CHH_{trans}), 5.45 (d, *J* = 12.6 Hz, 1H, CH=CHH_{cis}), 4.88 (d, *J* = 6.3 Hz, 2H, NCH_2), 3.98 (s, 3H, OCH_3) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, CD_3CN): δ 169.7, 151.3, 149.0, 135.4, 131.4, 124.2, 122.5, 120.6, 112.6, 101.4, 57.5, 53.3 ppm. HR-MS (ESI^+): Calcd for $C_{12}H_{14}N_3O$ $[M\text{-}PF_6]^+$: 216.1131. Found: 216.1149.

1,3-*Bis*(2-methylpyridyl)imidazolium hexafluorophosphate (2f). 1,3-*Bis*(2-methylpyridyl)imidazolium bromide (0.66 g, 2.0 mmol) was reacted according to the general salt metathesis reaction (*vide supra*). Yield: 0.75 g, 1.90 mmol, 95 %. ^1H NMR (300 MHz, CD_3CN): δ (ppm) 8.82 (br s, 1H, NC*H*N), 8.62 (dd, *J* = 5.7, 1.8 Hz, 2H, im*H*), 8.06 (td, *J* = 15.6, 7.8, 1.8 Hz, 2H, py*H*), 7.59 – 7.55 (m, 4H, py*H*), 7.52 (d, *J* = 1.8 Hz, 2H, py*H*), 5.55 (s, 4H, CH_2). $^{13}C\{^1H\}$ NMR (100 MHz, CD_3CN): δ (ppm) 152.3, 149.0, 141.5, 138.4, 126.0, 125.0, 124.5, 53.7. HR-MS (ESI^+): *m/z* 251.1288 $[C_{15}H_{15}N_4]^+$, calcd. $[M - PF_6]^+$ 251.1291. These data are in agreement with those reported in the literature.[6]

3. ^{1}H NMR spectra of imidazolium salts

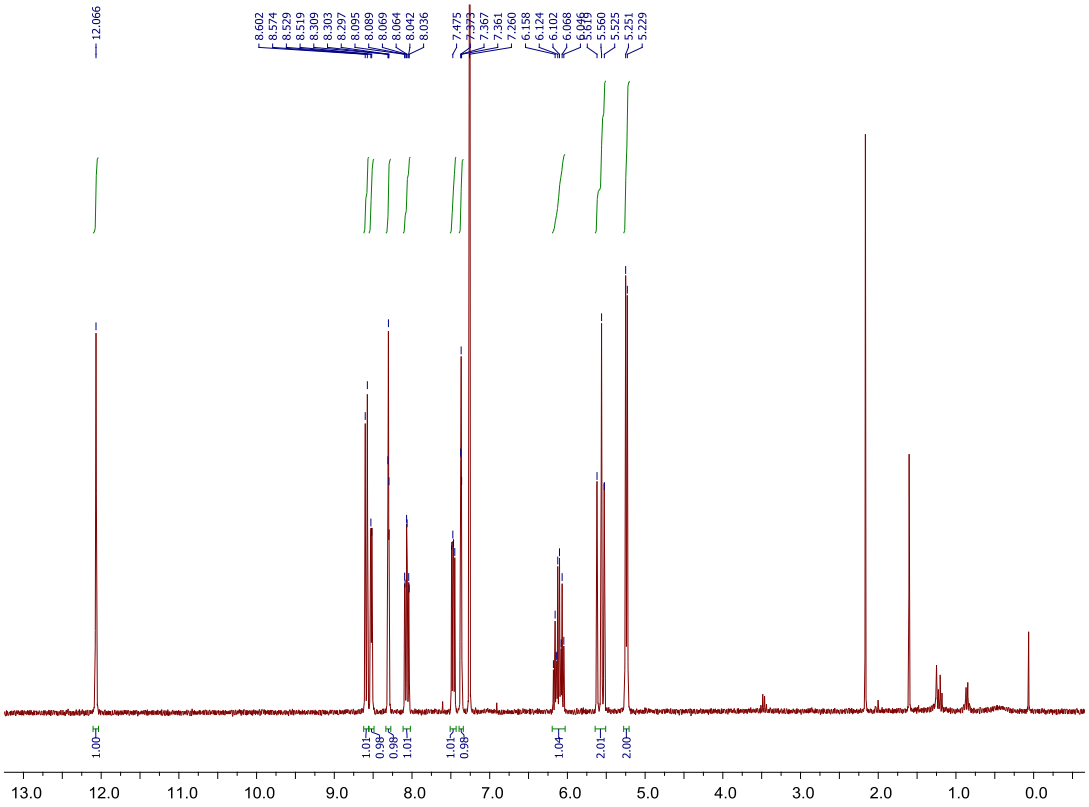


Figure 1. ^{1}H NMR spectrum of 1-allyl-3-(2-pyridyl)imidazolium bromide (**1a**).

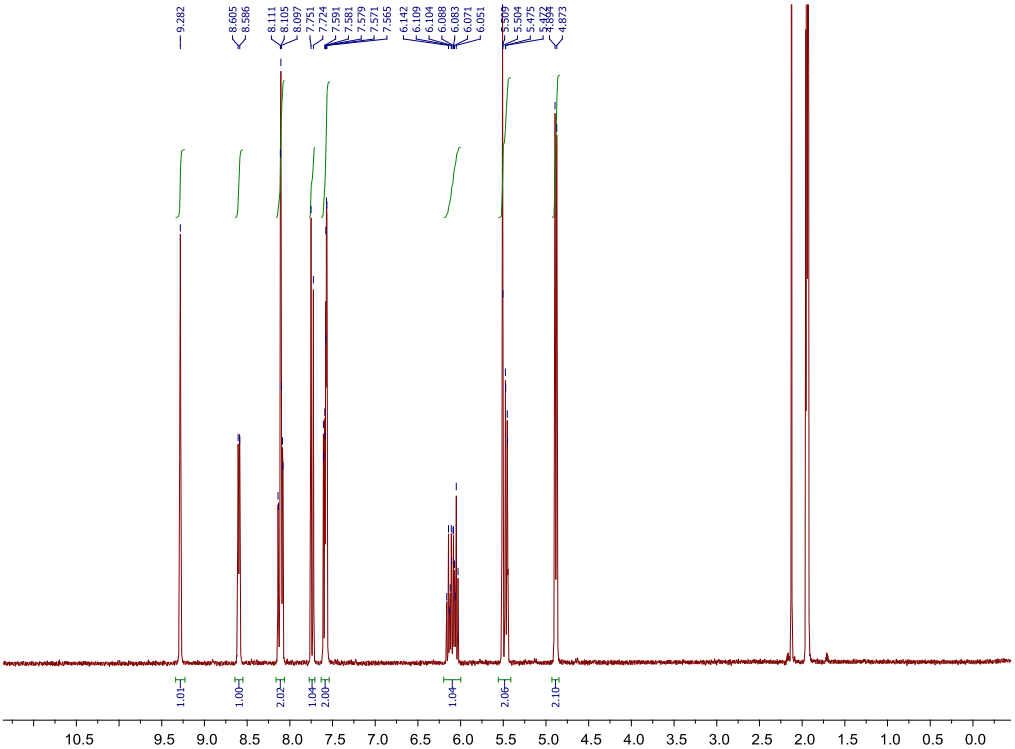


Figure 2. ^{1}H NMR spectrum of 1-allyl-3-(2-pyridyl)imidazolium hexafluorophosphate (**2a**).

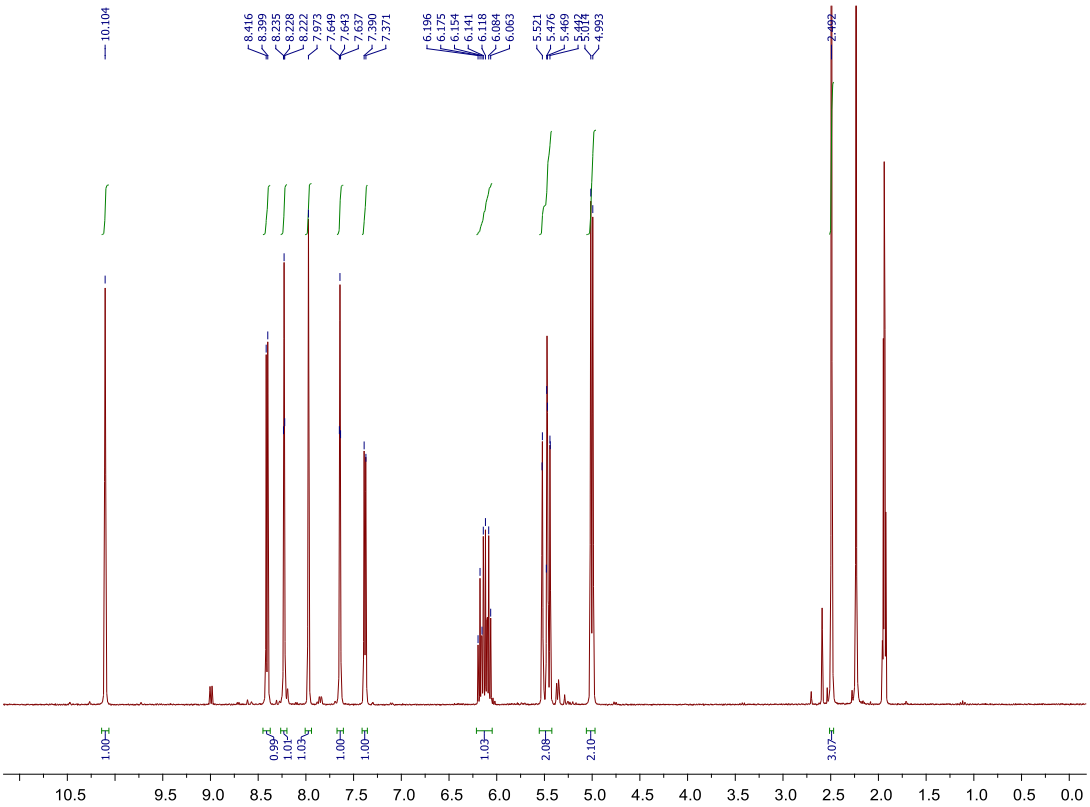


Figure 3. ^{1}H NMR spectrum of 1-allyl-3-(2-(4-methyl)pyridyl)imidazolium bromide (**1b**).

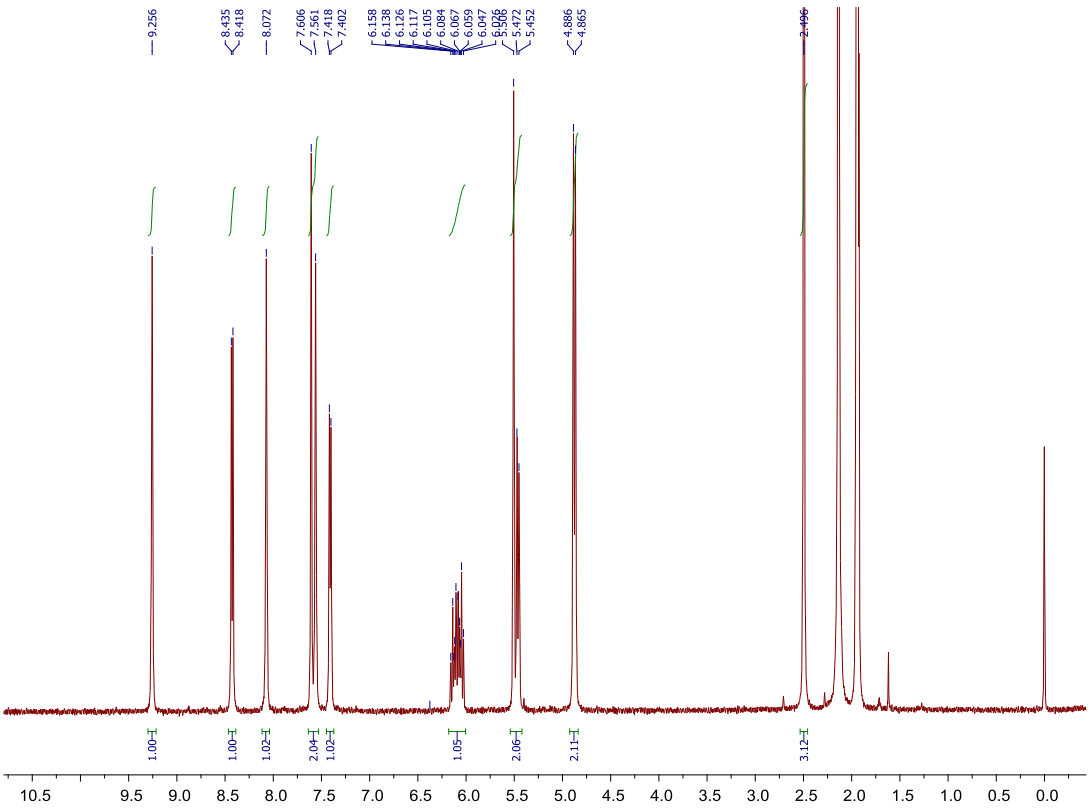


Figure 4. ^{1}H NMR spectrum of 1-allyl-3-(2-(4-methyl)pyridyl)imidazolium hexafluorophosphate (**2b**).

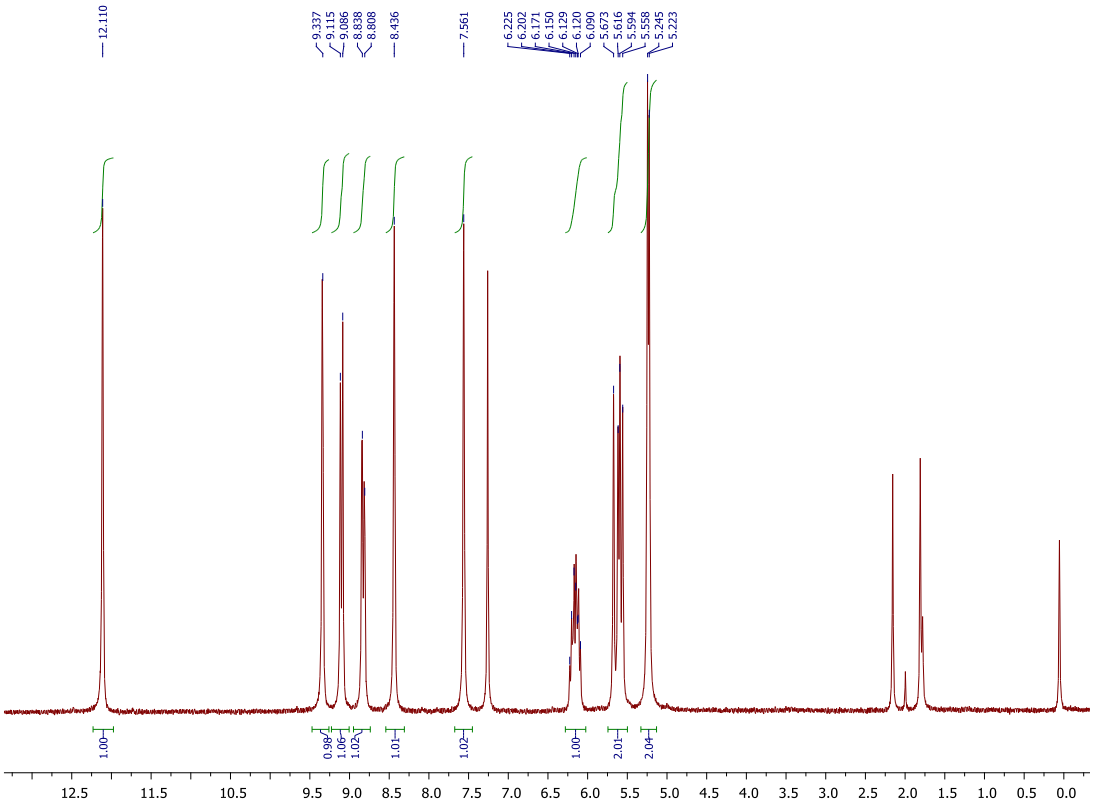


Figure 5. ^{1}H NMR spectrum of 1-allyl-3-(2-(5-nitro)pyridyl)imidazolium bromide (**1c**).

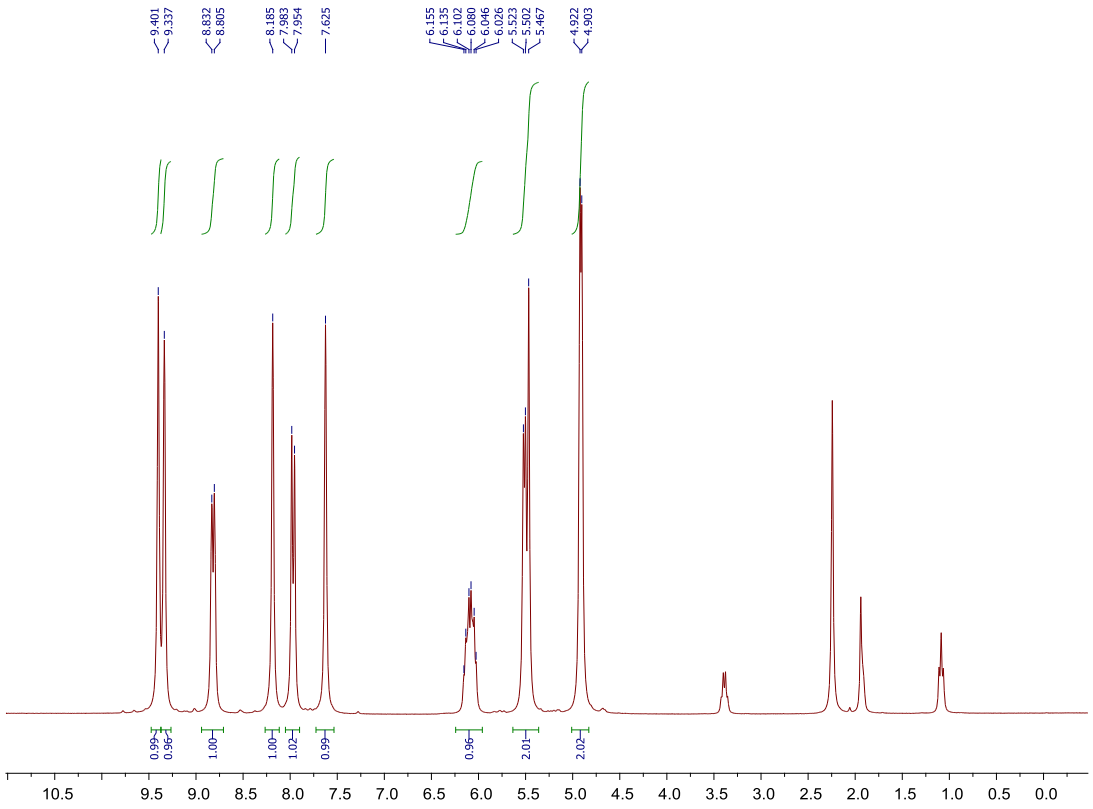


Figure 6. ^{1}H NMR spectrum of 1-allyl-3-(2-(5-nitro)pyridyl)imidazolium hexafluorophosphate (**2c**).

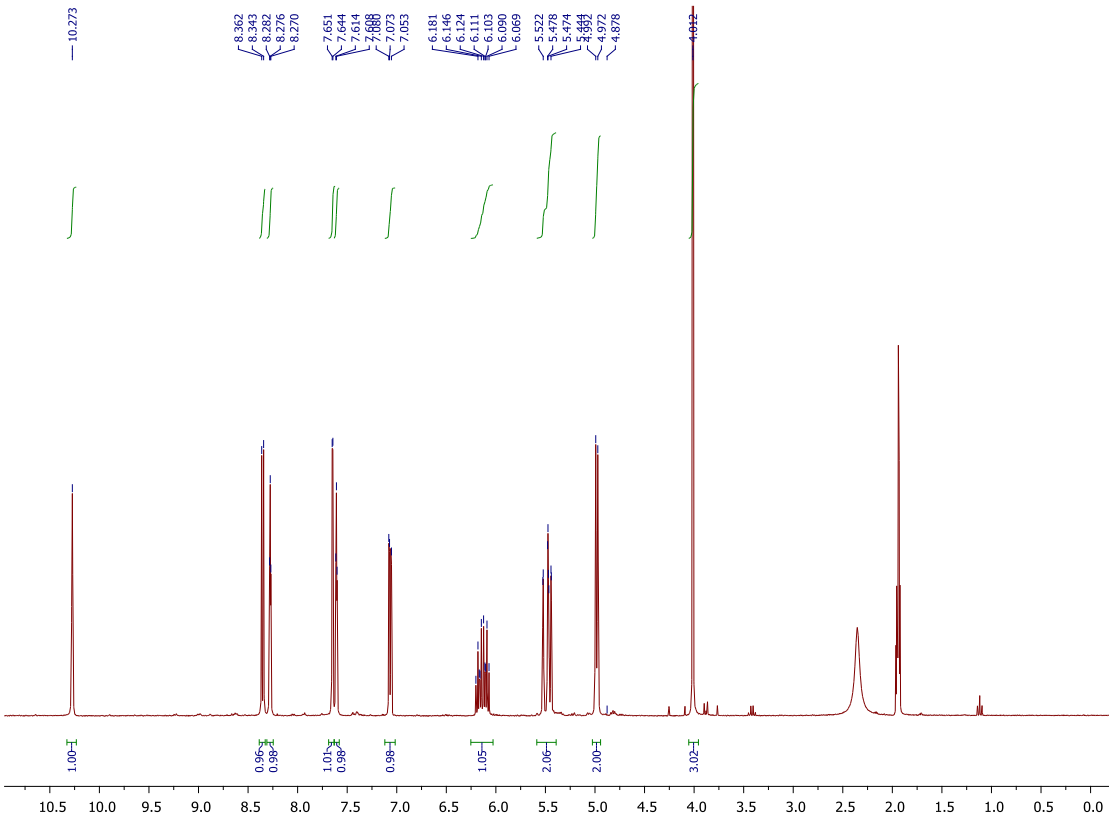


Figure 7. ^{1}H NMR spectrum of 1-allyl-3-(2-(4-methoxy)pyridyl)imidazolium bromide (**1d**).

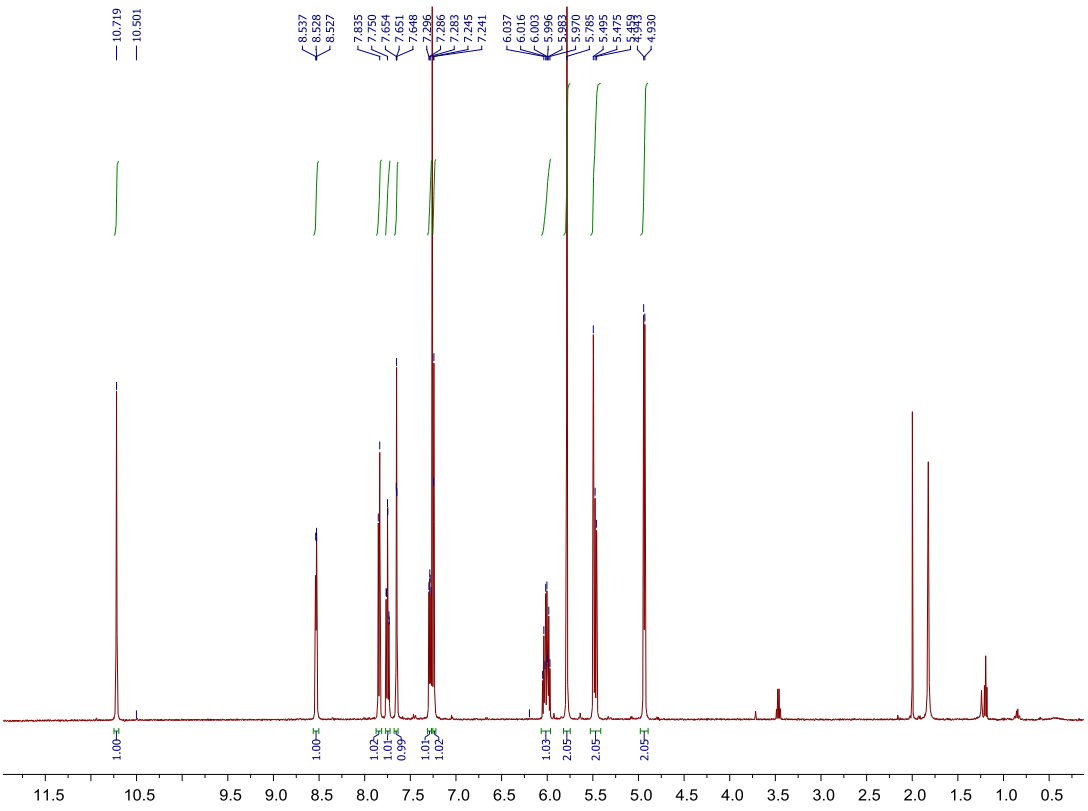


Figure 8. ^{1}H NMR spectrum of 1-allyl-3-(2-methylpyridyl)imidazolium bromide (**1e**).

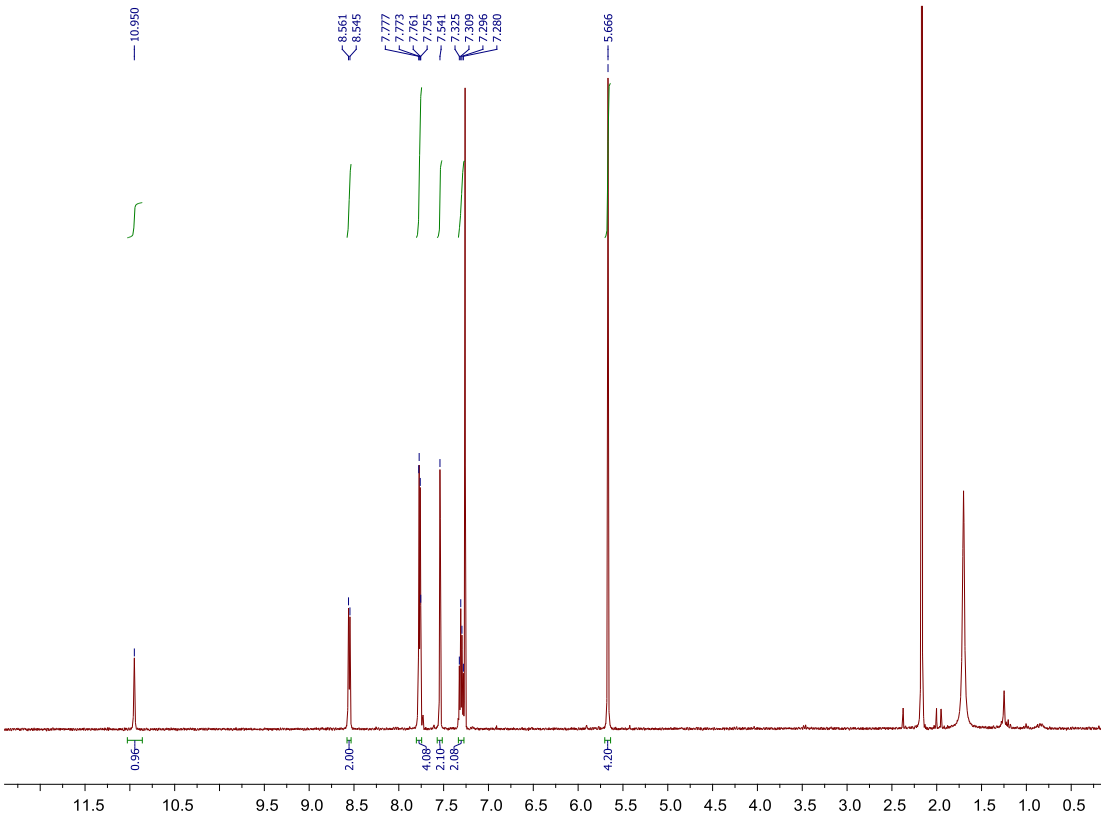


Figure 9. ^{1}H NMR spectrum of 1,3-bis(2-methylpyridyl)imidazolium bromide (**1f**).

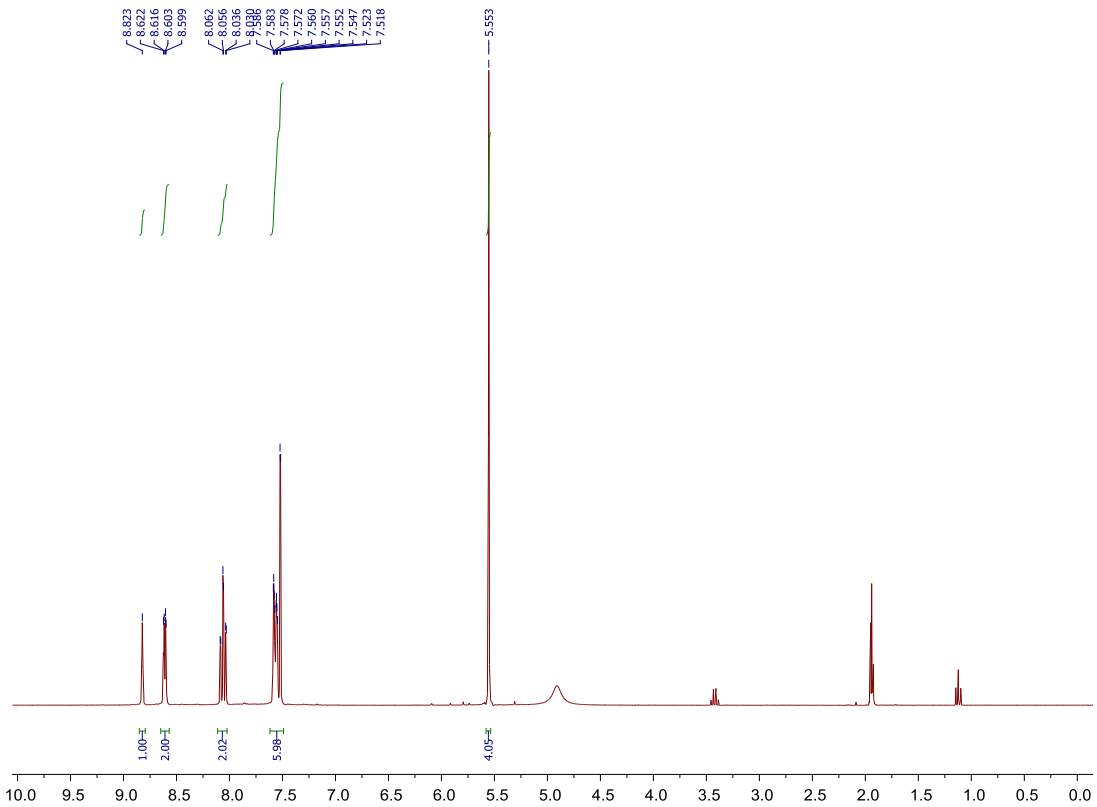


Figure 10. ^{1}H NMR spectrum of 1,3-bis(2-methylpyridyl)imidazolium hexafluorophosphate (**2f**).

5. Ligand exchange studies

5 mg of complexes **3a**, **3b** and **3c** were dissolved separately in 1 mL acetonitrile and subjected to ESI MS. Positive ions of [**3a**-Br]$^+$ 557.0109, [**3b**-Br]$^+$ 585.0401 and [**3c**-Br]$^+$ 646.9797 were observed. Three further acetonitrile solutions were made up of **3a**+**3b**, **3a**+**3c** and **3b**+**3c** (5mg each complex in 1mL) and allowed to stand for 5 minutes. ESI MS showed ions of only the starting complexes, with no ligand scrambling observed.

5. Crystallographic Details

X-ray diffraction data were collected on either a Bruker Nonius X8 diffractometer fitted with an Apex II detector with Mo-Kα radiation (λ = 0.71073 Å), or an Agilent SuperNova diffractometer fitted with an Atlas CCD detector with Mo-Kα radiation (λ = 0.71073 Å) or Cu- Kα radiation (λ = 1.5418 Å). Crystals were mounted under oil on nylon fibres. Data sets were corrected for absorption using a multiscan method, and the structures were solved by direct methods using SHELXS-97 and refined by full-matrix least squares on F2using ShelXL-97, interfaced through the program Olex2.[7] Molecular graphics for all structures were generated using POV-RAY in the X-Seed program.

Crystallographic details for 1f:

Identification code	mrc029
Empirical formula	$C_{15}H_{15}N_4Br$
Formula weight	331.22
Temperature/K	99.99(10)
Crystal system	monoclinic
Space group	$P2_1$
a/Å	8.1157(2)
b/Å	16.6921(4)
c/Å	10.8193(3)
α/°	90.00
β/°	98.625(3)
γ/°	90.00
Volume/Å^3	1449.09(6)
Z	4
ρ_{calc}g/cm^3	1.518
μ/mm^{-1}	2.832

F(000)	672.0
Crystal size/mm^3	0.44 × 0.23 × 0.18
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	5.88 to 57.4
Index ranges	-10 ≤ h ≤ 10, -22 ≤ k ≤ 20, -14 ≤ l ≤ 14
Reflections collected	11471
Independent reflections	6309 [R_{int} = 0.0322, R_{sigma} = 0.0524]
Data/restraints/parameters	6309/1/362
Goodness-of-fit on F^2	1.054
Final R indexes [I>=2σ (I)]	R_1 = 0.0363, wR_2 = 0.0765
Final R indexes [all data]	R_1 = 0.0417, wR_2 = 0.0790
Largest diff. peak/hole / e Å^{-3}	1.83/-0.48
Flack parameter	0.377(8)

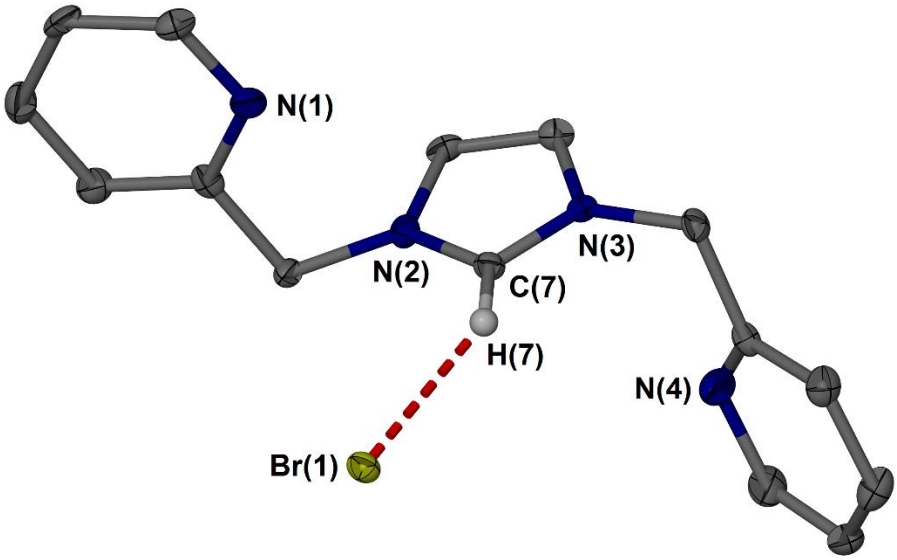


Figure 11. Molecular structure of **1f**.

Crystallographic details for 3a:

Identification code	brml290
Empirical formula	$C_{46}H_{52}N_{12}O_2Pd_2Br_4$
Formula weight	668.70
Temperature/K	100.15
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	23.0939(12)
b/Å	9.6206(5)

c/Å	25.3916(11)
α/°	90.00
β/°	112.426(5)
γ/°	90.00
Volume/Å^3	5214.8(4)
Z	4
ρ_{calc}g/cm^3	1.704
μ/mm^{-1}	9.546
F(000)	2640.0
Crystal size/mm^3	0.06 × 0.04 × 0.02
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	7.08 to 133.2
Index ranges	-26 ≤ h ≤ 19, -11 ≤ k ≤ 11, -30 ≤ l ≤ 30
Reflections collected	26524
Independent reflections	8977 [R_{int} = 0.1150, R_{sigma} = 0.1203]
Data/restraints/parameters	8977/0/600
Goodness-of-fit on F^2	1.003
Final R indexes [I>=2σ (I)]	R_1 = 0.0583, wR_2 = 0.1148
Final R indexes [all data]	R_1 = 0.1350, wR_2 = 0.1479
Largest diff. peak/hole / e Å^{-3}	1.14/-0.98

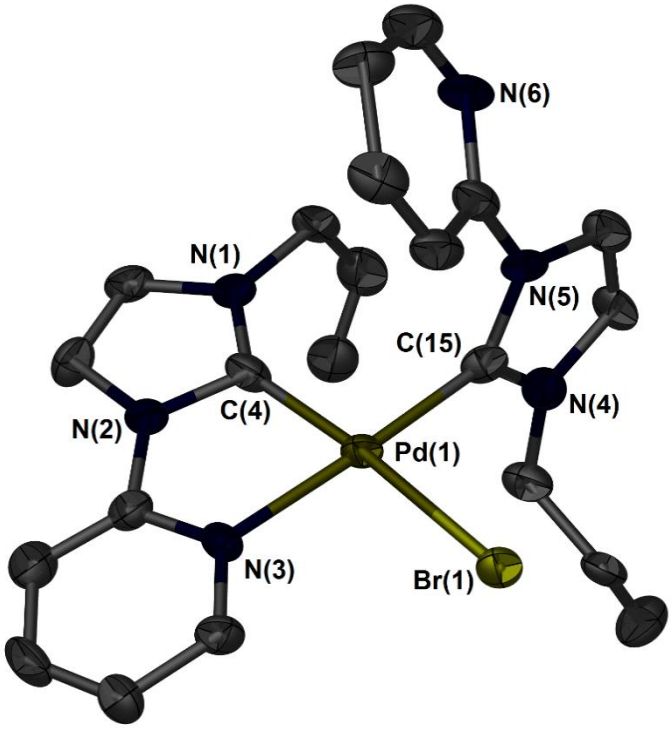


Figure 12. Molecular structure of **3a**.

Crystallographic details for 3c:

Identification code	BRML285
Empirical formula	$C_{22.5}H_{22}N_8O_{4.5}Br_2Pd$
Formula weight	1485.36
Temperature/K	100.15
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	7.3047(9)
b/Å	11.7658(11)
c/Å	31.200(3)
α/°	90.00
β/°	92.115(10)
γ/°	90.00
Volume/Å^3	2679.7(5)
Z	4
ρ_{calc}g/cm^3	1.841
μ/mm^{-1}	3.722
F(000)	1460.0
Crystal size/mm^3	0.16 × 0.04 × 0.02
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	6.26 to 50.12
Index ranges	$-8 \leq h \leq 8$, $-12 \leq k \leq 14$, $-37 \leq l \leq 33$
Reflections collected	11046
Independent reflections	4707 [R_{int} = 0.0951, R_{sigma} = 0.1411]
Data/restraints/parameters	4707/0/354
Goodness-of-fit on F^2	1.020
Final R indexes [I>=2σ (I)]	R_1 = 0.0678, wR_2 = 0.1184
Final R indexes [all data]	R_1 = 0.1272, wR_2 = 0.1364
Largest diff. peak/hole / e Å^{-3}	1.50/-0.96

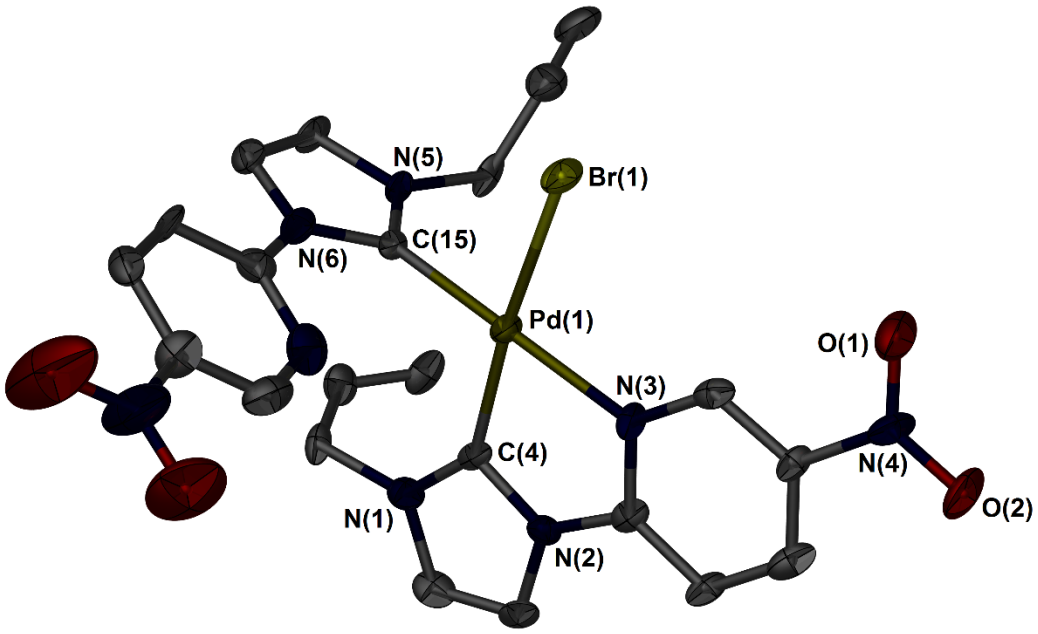


Figure 13. Molecular structure of **3c**.

Crystallographic details for 4b:

Identification code	MRC125_Mo_a
Empirical formula	$C_{12}H_{13}Br_2N_3Pd$
Formula weight	465.47
Temperature/K	120.0(2)
Crystal system	triclinic
Space group	P-1
a/Å	7.9713(7)
b/Å	9.1926(8)
c/Å	9.8150(4)
α/°	80.496(5)
β/°	79.638(6)
γ/°	87.116(7)
Volume/Å^3	697.61(9)
Z	2
ρ_{calc}g/cm^3	2.216
μ/mm^{-1}	7.043
F(000)	444.0
Crystal size/mm^3	0.09 × 0.05 × 0.04
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.12 to 56.56

Index ranges	$-10 \leq h \leq 10$, $-12 \leq k \leq 12$, $-13 \leq l \leq 12$
Reflections collected	14130
Independent reflections	3472 [R_{int} = 0.0413, R_{sigma} = 0.0366]
Data/restraints/parameters	3472/0/164
Goodness-of-fit on F^2	1.029
Final R indexes [I>=2σ (I)]	R_1 = 0.0330, wR_2 = 0.0732
Final R indexes [all data]	R_1 = 0.0435, wR_2 = 0.0778
Largest diff. peak/hole / e $Å^{-3}$	0.99/-1.02

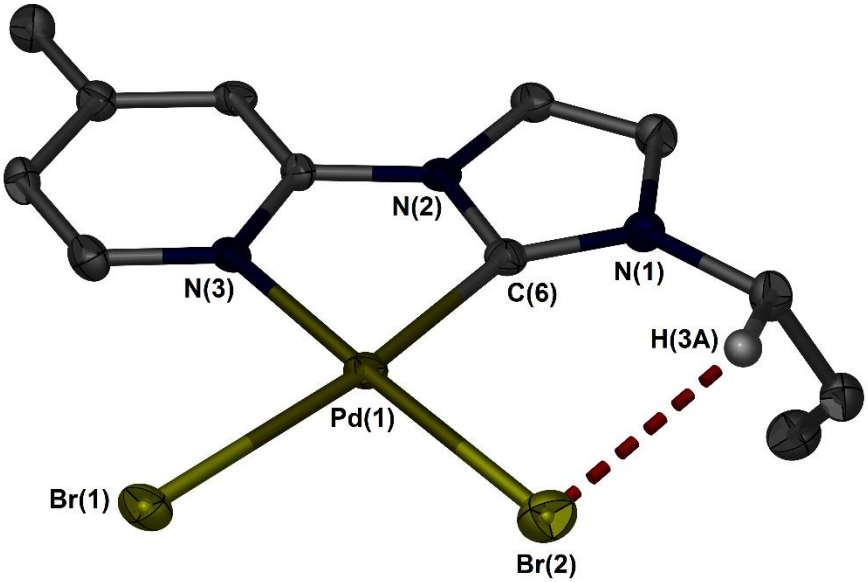
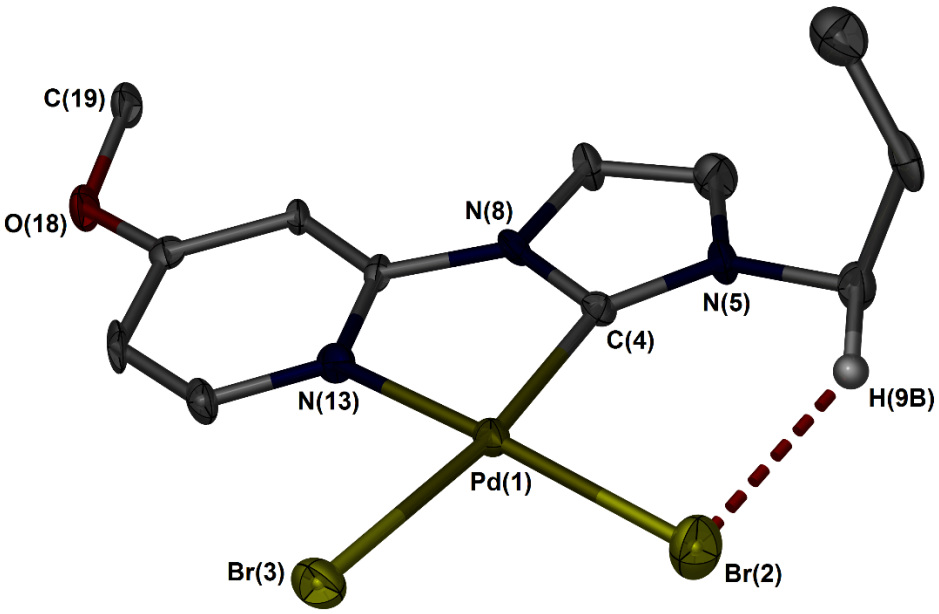


Figure 14. Molecular structure of **4b**.

Crystallographic details for 4d:

Identification code	MRC99_Mo
Empirical formula	$C_{12}H_{13}Br_2N_3OPd$
Formula weight	481.47
Temperature/K	120.01(11)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	13.5090(8)
b/Å	7.9393(3)
c/Å	13.9341(9)
α/°	90.00
β/°	108.376(6)
γ/°	90.00

Volume/Å^3	1418.25(14)
Z	4
ρ_{calc}mg/mm^3	2.255
m/mm^{-1}	6.937
F(000)	920.0
Crystal size/mm^3	0.13 × 0.09 × 0.04
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection	6.3 to 52.74°
Index ranges	-16 ≤ h ≤ 14, -8 ≤ k ≤ 9, -17 ≤ l ≤ 17
Reflections collected	8045
Independent reflections	2885 [R_{int} = 0.0658, R_{sigma} = 0.0789]
Data/restraints/parameters	2885/0/173
Goodness-of-fit on F^2	1.039
Final R indexes [I>=2σ (I)]	R_1 = 0.0569, wR_2 = 0.1154
Final R indexes [all data]	R_1 = 0.0828, wR_2 = 0.1280
Largest diff. peak/hole / e Å^{-3}	1.45/-1.11



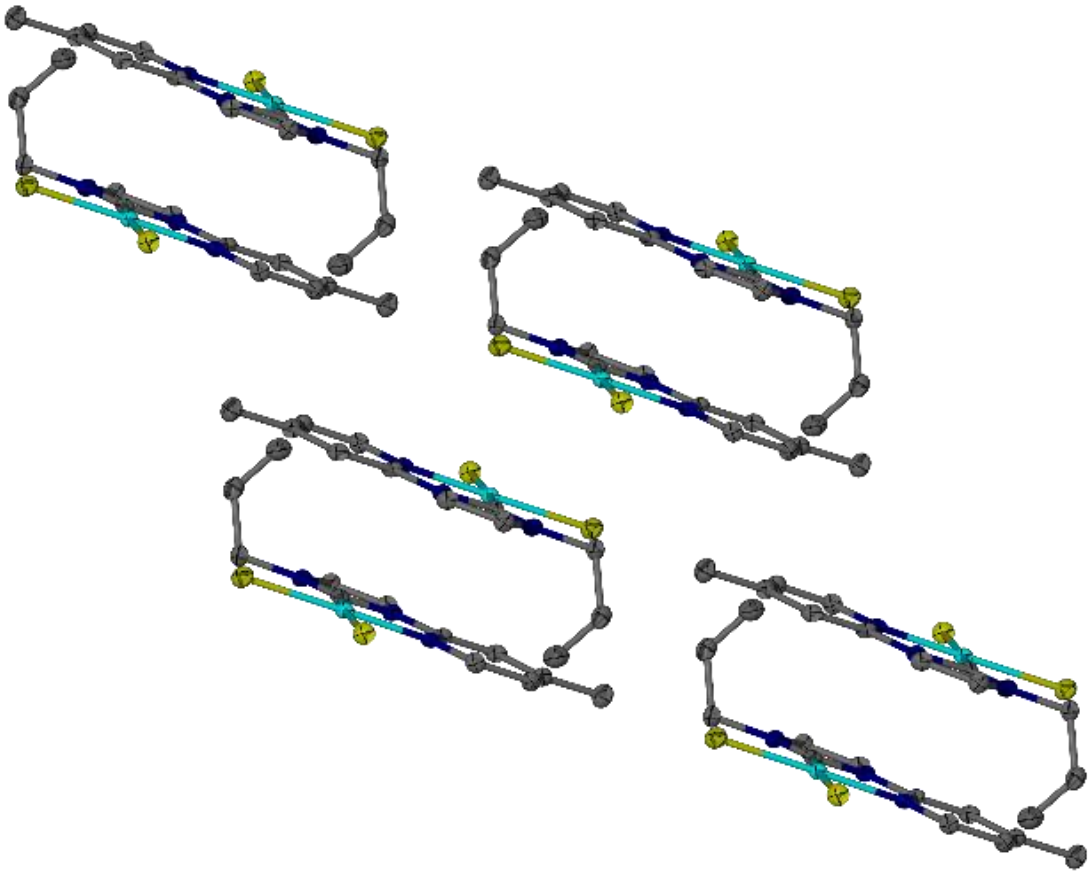


Figure 15. Molecular structure of **4d** and extended packing structure of **4d**, running along the crystallographic b axis.

Crystallographic details for 5c:

Identification code	MRC118_171114_Mo
Empirical formula	$C_{24}H_{23}F_{12}N_9O_4P_2Pd$
Formula weight	897.85
Temperature/K	120.00(13)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	11.9415(9)
b/Å	16.7247(9)
c/Å	16.7259(10)
α/°	90.00
β/°	102.857(6)
γ/°	90.00
Volume/Å^3	3256.7(4)
Z	4

ρ_{calc}g/cm^3	1.831
μ/mm^{-1}	0.785
F(000)	1784.0
Crystal size/mm^3	0.17 × 0.13 × 0.05
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.2 to 56.56
Index ranges	-15 ≤ h ≤ 13, -19 ≤ k ≤ 22, -21 ≤ l ≤ 22
Reflections collected	23620
Independent reflections	8072 [R_{int} = 0.0539, R_{sigma} = 0.0665]
Data/restraints/parameters	8072/0/470
Goodness-of-fit on F^2	1.043
Final R indexes [I>=2σ (I)]	R_1 = 0.0432, wR_2 = 0.0765
Final R indexes [all data]	R_1 = 0.0711, wR_2 = 0.0873
Largest diff. peak/hole / e Å^{-3}	0.54/-0.63

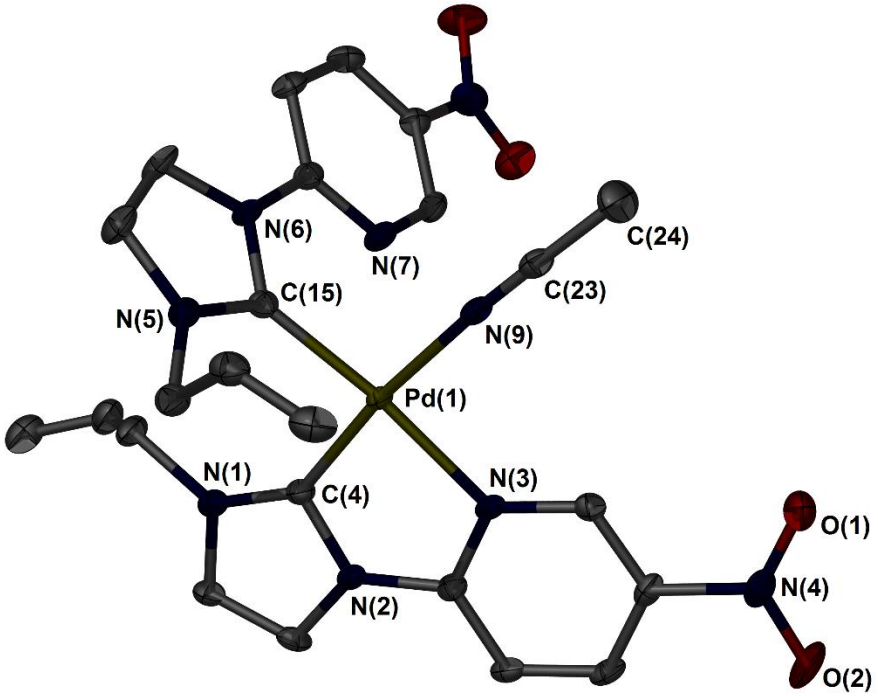


Figure 16. Molecular structure of **5c**.

Crystallographic details for 5d:

Identification code	MRC090a
Empirical formula	$C_{26}H_{29}N_7O_2F_{12}P_2Pd$
Formula weight	867.90
Temperature/K	100.0(5)

Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	17.4973(8)
b/Å	9.5790(5)
c/Å	20.1652(10)
α/°	90.00
β/°	98.859(4)
γ/°	90.00
Volume/$Å^3$	3339.5(3)
Z	4
$\rho_{calc}g/cm^3$	1.726
μ/mm^{-1}	0.757
F(000)	1736.0
Crystal size/mm^3	0.31 × 0.24 × 0.11
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.58 to 56.56
Index ranges	$-23 \leq h \leq 13$, $-12 \leq k \leq 12$, $-26 \leq l \leq 26$
Reflections collected	15136
Independent reflections	8234 [R_{int} = 0.0421, R_{sigma} = 0.0721]
Data/restraints/parameters	8234/0/454
Goodness-of-fit on F^2	1.030
Final R indexes [I>=2σ (I)]	R_1 = 0.0572, wR_2 = 0.1242
Final R indexes [all data]	R_1 = 0.0775, wR_2 = 0.1374
Largest diff. peak/hole / e $Å^{-3}$	2.99/-1.04

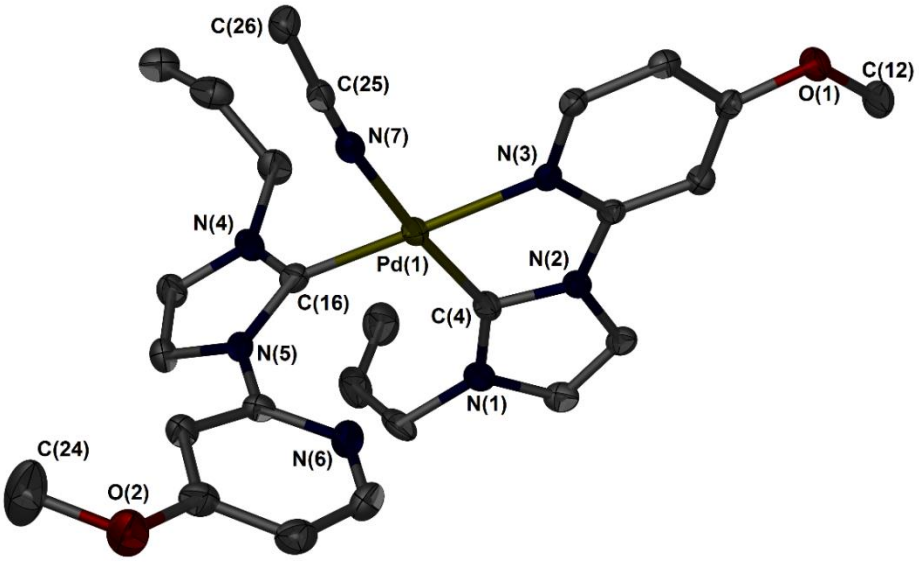


Figure 17. Molecular structure of **5d**.

Crystallographic details for 6f:

Identification code	MRC147_Mo
Empirical formula	$C_{32}H_{32}Br_2N_8OPdS$
Formula weight	842.94
Temperature/K	120.0(2)
Crystal system	monoclinic
Space group	C2/c
a/Å	30.370(4)
b/Å	12.2010(19)
c/Å	18.606(2)
α/°	90.00
β/°	107.066(14)
γ/°	90.00
Volume/Å^3	6590.9(16)
Z	8
ρ_{calc}g/cm^3	1.699
μ/mm^{-1}	3.091
F(000)	3360.0
Crystal size/mm^3	0.21 × 0.05 × 0.04
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.5 to 56.56
Index ranges	$-40 \leq h \leq 39$, $-16 \leq k \leq 15$, $-24 \leq l \leq 24$
Reflections collected	23167
Independent reflections	8170 [R_{int} = 0.0876, R_{sigma} = 0.1187]
Data/restraints/parameters	8170/0/403
Goodness-of-fit on F^2	1.017
Final R indexes [I>=2σ (I)]	R_1 = 0.0803, wR_2 = 0.1602
Final R indexes [all data]	R_1 = 0.1442, wR_2 = 0.1898
Largest diff. peak/hole / e Å^{-3}	1.46/-2.79

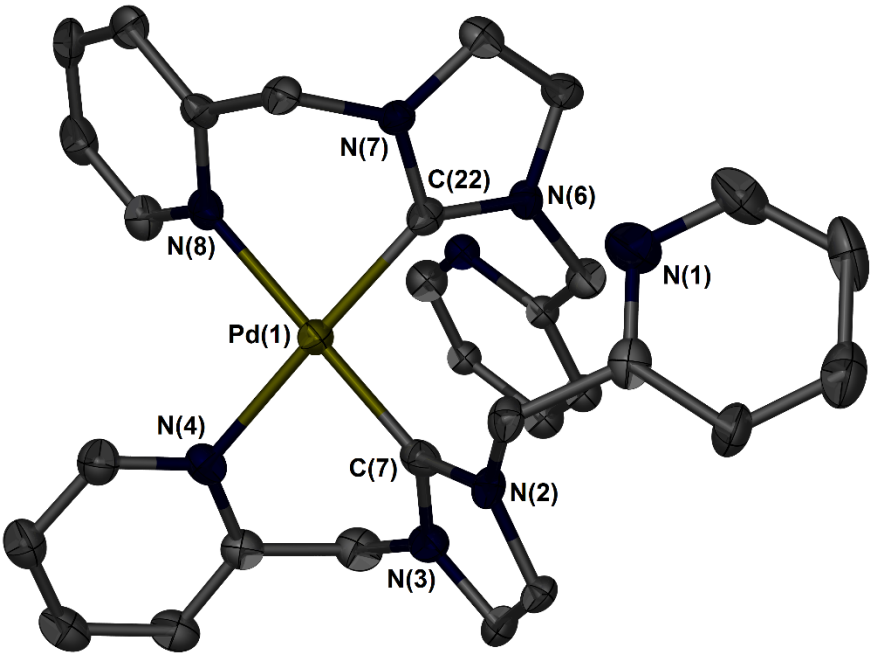


Figure 18. Molecular structure of **6f**.

Crystallographic details for 7e:

Identification code	mrc055
Empirical formula	$C_{24}H_{26}N_6F_{12}P_2Pd$
Formula weight	794.85
Temperature/K	99.9(4)
Crystal system	triclinic
Space group	P-1
a/Å	8.1012(3)
b/Å	10.9063(4)
c/Å	16.9064(7)
α/°	96.373(3)
β/°	98.659(3)
γ/°	97.265(3)
Volume/Å^3	1451.93(10)
Z	2
ρ_{calc}g/cm^3	1.818
μ/mm^{-1}	0.855
F(000)	792.0
Crystal size/mm^3	0.11 × 0.07 × 0.03
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.8 to 56.56

Index ranges	$-10 \leq h \leq 10$, $-13 \leq k \leq 14$, $-22 \leq l \leq 21$
Reflections collected	14671
Independent reflections	7152 [R_{int} = 0.0318, R_{sigma} = 0.0555]
Data/restraints/parameters	7152/0/406
Goodness-of-fit on F^2	1.047
Final R indexes [I>=2σ (I)]	R_1 = 0.0403, wR_2 = 0.0835
Final R indexes [all data]	R_1 = 0.0521, wR_2 = 0.0896
Largest diff. peak/hole / e $Å^{-3}$	1.14/-0.79

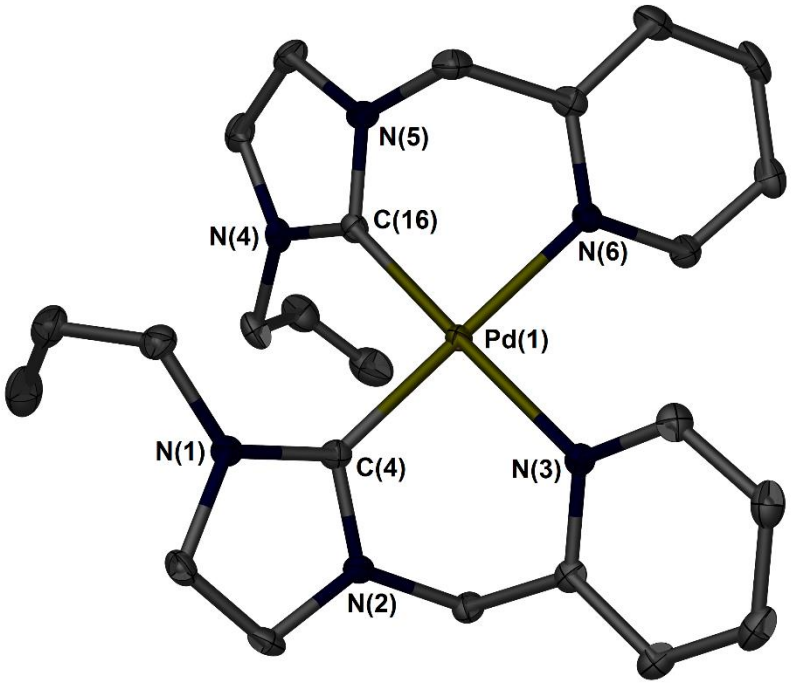


Figure 19. Molecular structure of **7e**.

Crystallographic details for 7f:

Identification code	MRC100_Mo
Empirical formula	$C_{30}H_{28}F_{12}N_8P_2Pd$
Formula weight	896.94
Temperature/K	119.99(13)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	8.0821(4)
b/Å	20.5140(10)
c/Å	20.6555(9)
α/°	90.00

β/°	96.704(4)
γ/°	90.00
Volume/Å^3	3401.2(3)
Z	4
ρ_{calc}g/cm^3	1.752
μ/mm^{-1}	0.743
F(000)	1792.0
Crystal size/mm^3	0.11 × 0.04 × 0.03
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.44 to 56.56
Index ranges	-10 ≤ h ≤ 10, -26 ≤ k ≤ 27, -27 ≤ l ≤ 27
Reflections collected	31660
Independent reflections	8440 [R_{int} = 0.0892, R_{sigma} = 0.1003]
Data/restraints/parameters	8440/16/474
Goodness-of-fit on F^2	1.041
Final R indexes [I>=2σ (I)]	R_1 = 0.0731, wR_2 = 0.1314
Final R indexes [all data]	R_1 = 0.1144, wR_2 = 0.1464
Largest diff. peak/hole / e Å^{-3}	1.76/-0.78

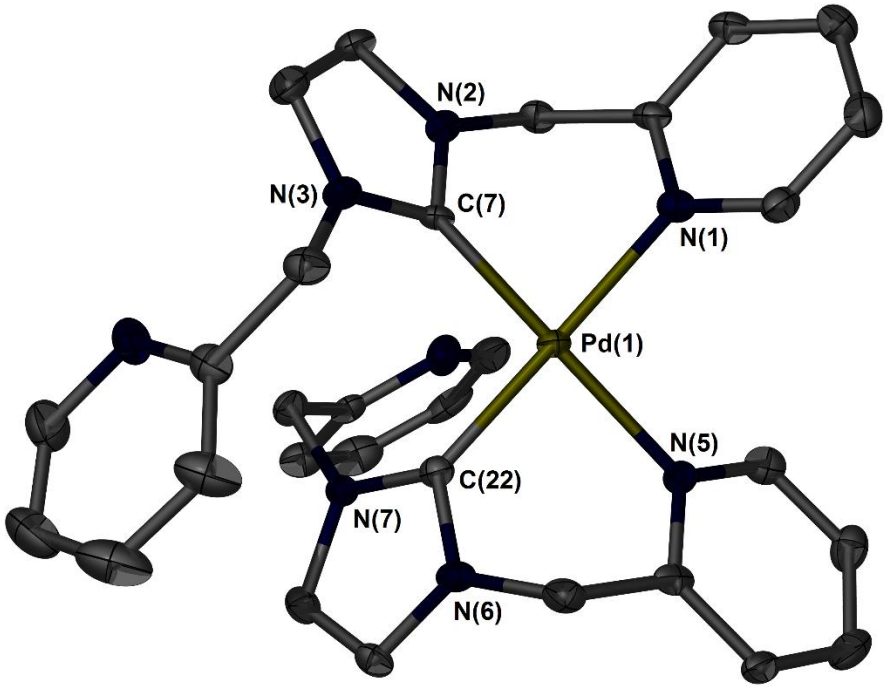


Figure 20. Molecular structure of **7f**.

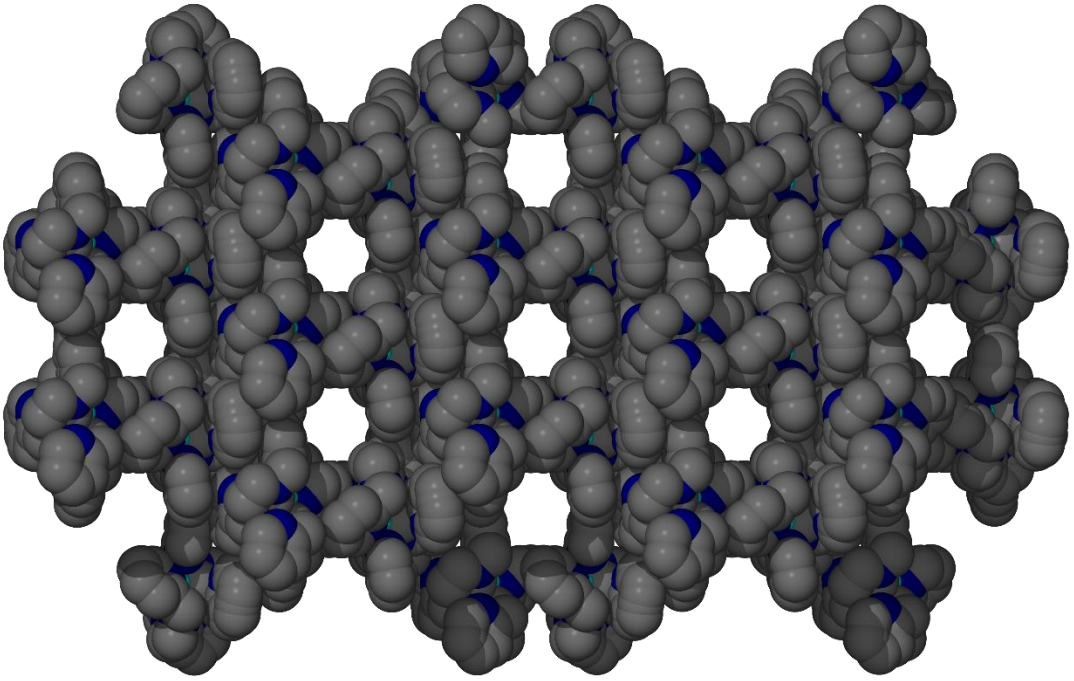


Figure 21. Packed structure of **7f**, illustrating extended network of solvent accessible channels.

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