Supporting Information for:

Ion-tagged π-acidic alkene ligands promote Pd-catalysed allyl-aryl couplings in an ionic liquid

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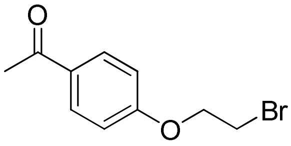
Table of contents

General Details

All chemicals were purchased from Aldrich, Acros or Merck and used as received. The liquids bought were degassed and the catalytical experiments were carried out under an atmosphere of dry argon or nitrogen using standard Schlenk techniques. NMR spectra were recorded on a Jeol ECX400, Jeol ECX270 or Mercury-400 NMR spectrometer, ^{1}H NMR and ^{13}C NMR spectra were referenced using residual solvent peaks (*e.g.* $CHCl_3$ in $CDCl_3$). ^{19}F NMR spectra were referenced externally. Electrospray ionisation (ESI) and chemical ionisation (CI) measurements were performed on a Bruker microTOF instrument. The ionic liquids were synthesised using modified literature procedures and characterization obtained agrees with the literature.[1] Halide and water content were minimised by repeated washing of the IL with water, until an $AgNO_3$ test proved negative, and by drying *in vacuo* (~10^{-3} mbar, at 70 °C, overnight). Final halide and water contents are usually well below 100 ppm and 50 ppm respectively using these proceedures. The ionic liquids were stored under N_2 before being employed. The ligand characterisation data agrees with similar compounds reported in literature .[2] Samples for elemental analysis were dried *in vacuo* (vacuum oven at 50 °C) for several hours prior to analysis.

Experimental

1-(4-(2-Bromoethoxy)phenyl)ethanone



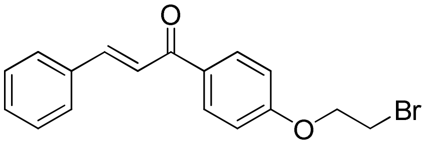
To a solution of 4-hydroxyacetophenone (5 g, 36.7 mmol, 1 eq.) in 3-pentanone (100 mL) was added K_2CO_3 (15.2 g, 0.11 mol, 3 eq.). The mixture was stirred for 30 minutes, then 1,2-dibromoethane (9.5 mL, 0.11 mol) was added. The reaction mixture was stirred at 100 °C for 16 hours. The pentanone and the dibromoethane were removed under reduced pressure. The remaining slurry was then diluted in EtOAc (1 x 50 mL) and washed with water (3 x 50 mL). The organic layer was dried over $MgSO_4$, filtered and then concentrated *in vacuo* to give a pale brown product. If the product was not shown to be pure by ^{1}H NMR spectroscopy, it was recrystallised from ethanol to yield a colourless solid (7.16 g, 80.3%).

^{1}H NMR ($CDCl_3$) δ: 7.93 (d, 2H, J=8.9 Hz), 6.96 (d, 2H, J=8.9 Hz), 4.36 (t, 2H, J= 6.2 Hz), 3.67 (t, 2H, J= 6.2 Hz), 2.56 (s, 3H).

^{13}C NMR: 197.3, 162.3, 131.1, 130.9, 114.4, 67.7, 28.3, 26.1.

MS: (m/z) 264.9835 $[M+Na]^+$ (Br^{79}), calc. 264.98.

(*E*)-1 -(4-(2-Bromoethoxy)phenyl)-3-phenylprop-2-en-1-one (5a)



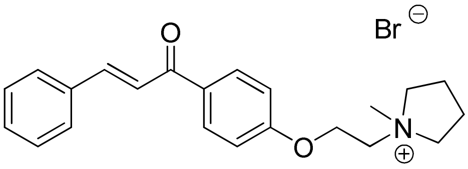
To an aqueous alcoholic solution of EtOH:H_2O (1:2, *v*/*v*, 12 mL) of NaOH (0.3 g, 7.5 mmol, 1.25 eq.) was added bromoethoxyacetophenone (1.44 g, 5.92 mmol, 1 eq.). The reaction mixture was cooled in ice and benzaldehyde (0.6 mL, 5.92 mmol, 1 eq.) was added dropwise. The reaction mixture was stirred at 25 °C for 16 hours. The solid formed was removed by filtration, washed with water (10 mL) and then recrystallised from hot EtOH to afford a solid (1.80 g, 92 %).

^{1}H NMR ($CDCl_3$) *δ:* 8.03 (d, 2H, *J*=8.9 Hz), 7.79 (d, 1H, *J*=15.6 Hz), 7.64-7.62 (m, 2H), 7.52 (d, 1H, *J*=15.6 Hz), 7.41-7.39 (m, 3H), 6.98 (d, 2H, *J*=8.9 Hz), 4.35 (t, 2H, *J*=6.2 Hz), 3.65 (t, 2H, *J*=6.2 Hz).

^{13}C NMR: 189.5, 162.6, 144.8, 135.6, 132.6, 131.5, 131.0, 129.5, 129.0, 122.3, 114.9, 68.1, 28.7.

MS: (*m/z*) $[M+Na]^+$ 353.0148 (Br^{79}), calc. 353.02.

(*E*)-1 -(2-(4-Cinnamoylphenoxy)ethyl)-1-methylpyrrolidinium bromide [1a]Br



To compound **5a** (1.0 g, 3.01 mmol) in toluene (15 mL) at room temperature was slowly added *N*-methylpyrrolidine (3 mL, excess). The mixture was stirred at 60 °C overnight. A solid formed, which was collected and washed with ether (3 x 10 mL) several times and then dried *in vacuo* (0.88 g, 70 %).

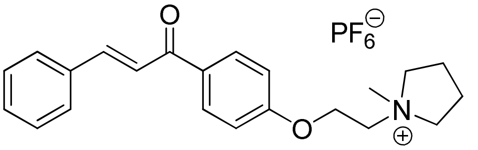
^{1}H NMR ($CDCl_3$) *δ:* 8.02 (d, 2H, *J*=8.9 Hz), 7.77 (d, 1 H, *J*=15.7 Hz), 7.64-7.62 (m, 2H), 7.51 (d, 2H, *J*=15.7 Hz), 7.41-7.40 (m, 3H), 7.04-7.02 (d, 2H, *J*=8.9 Hz), 4.62-4.60 (m, 2H), 4.44-4.41 (m, 2H), 4.06-4.04 (m, 2H), 3.93-3.90 (m, 2H), 3.43 (s, 3H), 2.38-2.15 (br, 4H).

^{13}C NMR: 189.1, 161.0, 144.9, 135.1, 132.6, 131.2, 130.8, 129.2, 128.7, 121.7, 114.6, 65.7, 62.9, 62.5, 48.7, 21.3.

M.p. 160 °C.

MS: (*m/z*) 336.20 $[M]^+$, calc. 336.20.

(*E*)-1 -(2-(4-Cinnamoylphenoxy)ethyl)-1-methylpyrrolidinium hexafluorophosphate [1a]PF$_6$



To **[1a]Br** (0.5 g, 1.2 mmol) dissolved in water (5 mL) was added KPF$_6$ (0.24 g, 1.1 eq.) dissolved in water (5 mL). A white solid was formed almost instantly, which was collected and washed with water (10 mL) and dried *in vacuo* (0.52 g, 90.1%).

^{1}H NMR {$(CD_3)_2CO$} *δ:* 8.19 (d, 2H, *J*=9.0 Hz), 7.87 (d, 1H, *J*=15.6 Hz), 7.83-7.81 (m, 2H), 7.77 (d, 1H, *J*=15.6), 7.47-7.45 (m, 3H), 7.18 (d, 2H, 9.0 Hz), 4.79 (m, 2H), 4.16-4.13 (m, 2H), 3.95-3.93 (m, 4H), 3.45 (s, 3H), 2.43-2.35 (m, 4H).

^{13}C NMR {$(CD_3)_2CO$}: 190.4, 164.3, 146.3 , 134.8, 133.9, 133.6, 133.2, 131.7, 131.0, 124.5, 117.3, 82.4, 67.9, 65.1, 48.8, 23.6.

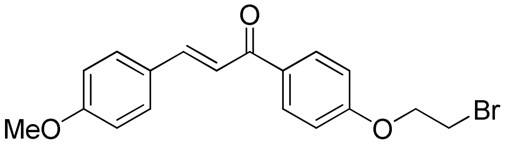
^{19}F NMR {$(CD_3)_2CO$}: - 72.53 ($^1J_{PF}$ = 707.8 Hz)

M.p. 184 °C.

MS: (*m/z*) 336.1958 [M]$^+$, calc. 336.20.

Elemental Analysis: calculated for $C_{22}H_{27}F_6NO_{2.5}P$ (includes ½ H_2O per molecule): %C 53.88, %H 5.55, %N 2.73, found: %C 54.25, %H 5.19, %N 2.73.

(*E*)-1 -(4-(2-Bromoethoxy)phenyl)-3-(4-methoxyphenyl)prop-2-en-1-one (5b)



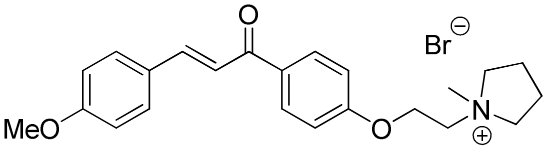
To a suspension of 4-bromoethoxyacetophenone (3.0 g, 12.5 mmol, 1 eq.) in MeOH (25 mL) was added crushed NaOH pellets (0.64 g, 16.0 mmol, 1.28 eq.). The reaction mixture was cooled in ice and 4-methoxybenzaldehyde (1.7 g, 12.5 mmol, 1 eq.) was added slowly. Then, on complete addition, stirred at 25 °C for 16 hours. A solid formed which was removed by filtration and washed with MeOH (3 x 5 mL) and dried *in vacuo* (3.30 g, 73%).

^{1}H NMR ($CDCl_3$) *δ:* 7.96 (d, 2H, *J*=8.9 Hz), 7.70 (d, 1H, *J*=15.6 Hz), 7.54 (d, 2H, *J*=8.7 Hz), 7.35 (d, 1H, *J*=15.6 Hz), 6.93 (d, 2H, *J*=8.9 Hz), 6.88 (d, 2H, *J*=8.8 Hz), 4.30 (t, 2H, *J*= 6.2 Hz), 3.79 (s, 3H), 3.61 (t, 2H, *J*=6.2 Hz).

^{13}C NMR ($CDCl_3$): 188.7, 161.6, 161.5, 144.0, 131.9, 130.7, 130.1, 127.7, 119.4, 114.4, 114.2, 67.8, 55.4, 28.6.

MS: (*m/z*) 383.0253 $[M+Na]^+$ (Br^{79}), calc. 383.03.

(4-Methoxyphenyl)acryloyl)phenoxy)ethyl)-1-methylpyrrolidinium bromide ([1b]Br)



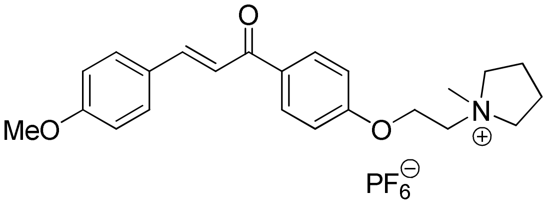
To **5b (**1 g, 2.77 mmol) in toluene (15 mL) was added *N*-methylpyrrolidine (2 mL, excess). The mixture was then stirred at 60 °C overnight. A slightly brown solid was formed which was removed by filtration, and washed with ether (3 x 10 mL) and dried *in vacuo* (0.69 g, 55.8%).

^{1}H NMR (CD_3OD) *δ:* 8.09 (d, 2H, *J*=8.9 Hz), 7.71 (d, 1H, *J*=15.6 Hz), 7.68–7.67 (d, 2H, *J*=8.8 Hz*),* 7.60 (d, 1H, *J*=15.6 Hz), 7.60 (d, 2H, *J*=8.9 Hz), 7.12 (d, 2H, *J*=8.9 Hz), 6.96 (d, 2H, *J*=8.8 Hz), 4.57 (m, 2H), 3.92-3.89 (m, 2H), 3.80 (s, 3H), 3.70-3.66 (m, 4H), 3.19 (s, 3H), 2.26-2.23 (m, 4H).

^{13}C NMR (CD_3OD): 191.5, 164.1, 163.38, 146.4, 133.8, 132.6, 132.1, 129.3, 120.6, 116.1, 116.0, 66.7, 64.01, 63.9, 56.0, 49.3, 22.3.

MS: (*m/z*) 366.21 $[M]^+$, calc. 366.21.

(4-Methoxyphenyl)acryloyl)phenoxy)ethyl)-1-methylpyrrolidinium hexafluorophosphate ([1b]PF_6)



To compound **[1b]Br** (0.5 g, 1.12 mmol, 1 eq.) in water (10 mL) was added potassium hexafluorophosphate (0.25 g, 1.34 mmol, 1.2 eq.). The solution was stirred at room temperature for 1 hour. A solid formed which was collected and washed with ether (3 x 5 mL) and water (3 x 5 mL) then dried *in vacuo* (0.39 g, 68.4%).

^{1}H NMR {$(CD_3)_2CO$} δ: 8.17 (d, 2H, *J*=8.9 Hz), 7.79-7.75 (m, 4H), 7.16 (d, 2H, *J*=8.9 Hz), 7.02 (d, 2H, *J*=8.8 Hz), 4.82-4.76 (b, 2H), 4.16-4.14 (m, 2H), 3.94-3.92 (m, 4H), 3.87 (s, 3H), 3.45 (s, 3H), 2.47-2.32 (m, 4H).

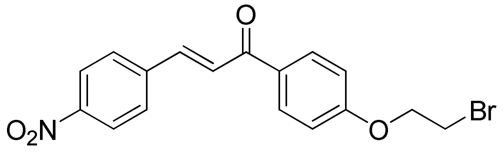
^{13}C NMR {$(CD_3)_2CO$}: 189.4, 163.8, 163.2, 145.3, 132.5, 132.2, 130.6, 129.6, 121.0, 116.3, 116.1, 69.0, 66.9, 64.2, 56.4, 40.1, 22.6.

^{19}F NMR {$(CD_3)_2CO$}: -72.51 ($^1J_{PF}$ = 707.8 Hz).

MS: (*m/z*) 366.21 $[M]^+$, calc. 366.21.

Elemental Analysis: calculated for $C_{23}H_{28}F_6NO_3P$: %C 54.01, %H 5.52, %N 2.74, found: %C 53.83, %H 5.40, %N 2.48.

(*E*)-1-(4-(2-Bromoethoxy)phenyl)-3-(4-nitrophenyl)prop-2-en-1-one (5c)



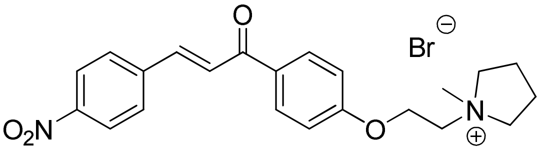
To a ice-cooled suspension of 4-bromoethoxyacetophenone (3.0 g, 12.34 mmol, 1 eq.) in methanol/ ethanol (25:5, *v/v*, 30 mL) was added crushed NaOH pellets (0.62 g, 15.42 mmol, 1.25 eq.) and *p*-nitrobenzaldehyde (1.87 g, 12.34 mmol, 1 eq.). The suspension was stirred at 25 °C for 16 hours. A yellowish solid formed which was removed by filtration and washed with MeOH (3 x 10 mL) and then dried *in vacuo* (3.50 g, 75.4%).

^{1}H NMR ($CDCl_3$) δ: 8.27 (d, 2H, *J*=8.9 Hz), 8.05 (d, 2H, *J*=8.8 Hz), 7.83-7.77 (m, 3H), 7.64 (d, 1H, *J*=15.6 Hz), 7.02 (d, 2H, *J*=8.9 Hz), 4.38 (t, 2H, *J*=6.2 Hz), 3.68 (t, 2H, *J*=6.2 Hz).

^{13}C NMR ($CDCl_3$): One 4° carbon not observed, 188.6, 163.0, 148.4, 141.8, 141.6, 131.6, 129.4, 126.0, 124.8, 115.0, 68.2, 28.6.

MS: (*m/z*) 376.20 $[MH]^+$ (^{79}Br), calc. 376.20.

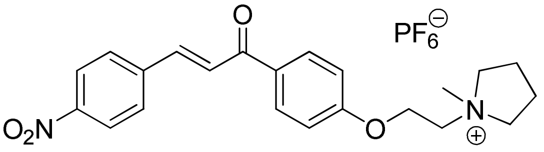
1 -Methyl-1-(2-(4-(3-(4-nitrophenyl)acryloyl)phenoxy)ethyl) pyrrolidinium bromide ([1c]Br)



To compound **5c** (1.0 g, 2.66 mmol, 1 eq.) in toluene (10 mL) was added *N*-methylpyrrolidine (0.91 g, 10.64 mmol, 4 eq.). The solution was stirred at 70 °C for 24 h. The solid that was formed was collected by filtration and washed with ether (3 x 10 mL) and then dried *in vacuo* (0.72 g, 58.3 %).

^{1}H NMR ($CDCl_3$) *δ:* 8.14 (d, 2H, *J*=8.4 Hz), 7.96 (d, 1H, *J*=8.8 Hz), 7.70 (d, 2H, *J*=8.8 Hz), 7.67 (d, 1H, *J*=16.4 Hz), 7.57 (d, 1H, *J*=15.6 Hz) 6.97 (d, 1H, *J*=8.8 Hz), 4.48-4.46 (m, 2H), 3.95 (m, 2H), 3.69-3.57 (m,4H), 3.12 (s, 3H), 2.44-2.09 (m, 4H).

(1-Methyl-1-(2-(4-(3-(4-nitrophenyl)acryloyl)phenoxy)ethyl)pyrrolidinium hexafluorophosphate ([1c]PF$_6$)



To compound **[1c]Br (**1.0 g, 1.96 mmol, 1 eq.) in water (10 mL) was added potassium hexalfluorophosphate (0.40 g, 2.16 mmol, 1.1 eq.). The solution was stirred at room temperature for 1 hour. A solid formed which was collected by filteration, washed with ether (3 x 10 mL) and water (3 x 10 mL), then dried *in vacuo* (0.83 g, 80.4%).

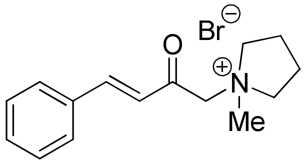
^{1}H NMR {$(CD_3)_2CO$} *δ:* 8.30 (d, 2H, *J*=8.8 Hz), 8.23 (d, 2H, *J*=9.0 Hz), 8.13-8.08 (m, 3H), 7.84 (d, 1H, *J*=15.7 Hz), 7.20 (d, 2H, *J*=9.0 Hz), 4.82-4.79 (b, 2H), 4.18-4.16 (m, 2H), 3.97-3.93 (m, 4H), 3.46 (s, 3H), 2.43-2.36 (m, 4H).

^{13}C NMR {$(CD_3)_2CO$}: 190.0, 164.6, 151.4, 144.4, 143.3, 133.8, 132.2, 128.5, 126.7, 117.4, 67.9, 65.3, 65.1, 50.9, 23.5. (One carbon environment not visible in spectrum, likely due to the solubility of this material)

^{19}F NMR {$(CD_3)_2CO$}: -72.55 ($^{1}J_{PF}$ = 707.68 Hz).

Elemental Analysis: calculated for $C_{22}H_{25}F_6N_2O_4P$: %C 50.20, %H 4.79, %N 5.32, found: %C 50.25, %H 4.64, %N 4.78.

(*E*)-1-Methyl-1-(2-oxo-4-phenylbut-3-enyl)pyrrolidinium bromide ([2]Br)[3]



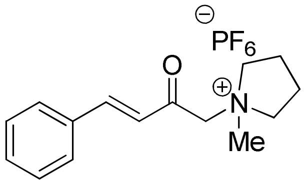
Styryl methyl ketone (2.0 g, 13.68 mmol, 1 eq.) was dissolved in dry THF (30 mL). Pyrrolidone hydrotribromide (8.0 g, 16.36 mmol, 1.2 eq.) was dissolved in dry THF (50 mL). Both solutions were combined and stirred at room temperature for 1 hour. The THF was then removed *in vacuo*. The product was subjected to column chromatography of silica-gel (Et_2O:PE, *v/v*, 1:6). Combining the collected fractions corresponding to the product and removing the organic solvents *in vacuo* gave a liquid. The product was then dissolved in toluene (10 mL), then *N*-methylpyrrolidine (1.28 g, 15.05 mmol, 1.1 eq.) was added until no further solid was formed. The solid formed was collected by filteration, washed with ether (3 x 10 mL) and then dried *in vacuo* (3.78 g, 89%).

^{1}H NMR ($CDCl_3$) δ: 8.05 (d, 1H, *J*=16.4 Hz), 7.61 (m, 2H), 7.40-7.33 (m, 3H), 6.78 (d, 1H, *J*=16.4 Hz), 5.66 (s, 2H), 4.15-4.03 (m, 4H), 3.42 (s, 3H), 2.35-2.30 (m, 2H), 2.17-2.12 (m, 2H).

^{13}C NMR ($CDCl_3$): 191.2, 147.3, 133.5, 131.5, 129.0, 128.9, 122.8, 68.0, 65.2, 48.7, 20.7.

MS: (*m/z*) 230.1539 $[M]^+$, 230.15 calc.

(*E*)-1-Methyl-1-(2-oxo-4-phenylbut-3-enyl)pyrrolidinium hexafluorophosphate ([2]PF_6)



Compound **[2]Br** (2.0 g, 6.45 mmol) was dissolved in water (10 mL) and potassium hexafluorophosphate (1.3 g, 7.1 mmol, 1.1 eq.) added. A white precipitate was formed immediately and collected by filtration (2.00 g, 82.7 %).

^{1}H NMR {$(CD_3)_2CO$} δ: 7.73 (d, 1H, *J*=16.0 Hz), 7.65-7.63 (m, 2H), 7.41-7.36 (m, 3H), 6.90 (d, 1H, *J*=16.4 Hz), 4.97 (s, 2H), 3.93-3.91 (m, 2H), 3.80-3.77 (m, 2H), 3.37 (s, 3H), 2.26-2.24 (m, 4H).

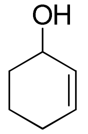
^{13}C NMR {$(CD_3)_2CO$}: 193.5, 147.9, 136.8, 134.2, 132.0, 131.6, 125.9, 82.4, 68.2, 51.9, 23.8.

^{19}F NMR {$(CD_3)_2CO$}: -72.6 ($^1J_{PF\,=}$ 684.5 Hz).

MS: (*m/z*) 230.1539 $[M]^+$, 230.15 calc.

Elemental Analysis: calculated for $C_{15}H_{21}F_6NO_{1.5}P$ (includes ½ H_2O per molecule): %C 46.88, %H 5.51, %N 3.64, found: %C 47.16, %H 4.98, %N 3.46.

Cyclohex-2-en-1-ol [3]

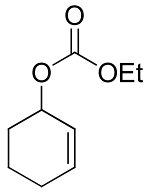


To a dry THF (100 mL) solution of 1-cyclohexenone (25 mL, 0.24 mol, 1 eq.) was added $LiAlH_4$ (4.57 g, 0.12 mol, 0.5 eq.). The suspension was stirred for 2 hours at 20 °C. The THF was removed under reduced pressure and the remaining slurry was quenched with $MgSO_4$ (5 g) and water (100 mL). The water layer was extracted with ethyl acetate (3 x 50 mL) and the organic layer was dried with $MgSO_4$, filtered, and then concentrated *in vacuo* to give an oil (18.84 g, 80%).

^1H NMR ($CDCl_3$) *δ:* 5.81 (m, 1H), 5.73 (m, 1H), 4.31 (m, 1H), 2.81 (s, 1H), 2.02-1.88 (m, 2H), 1.74 (m, 1H), 1.62 -1.57 (m, 2H).

^{13}C NMR ($CDCl_3$): 130.4, 130.0, 65.3, 32.1, 25.2, 19.3.

Allyl carbonate (7) [4]

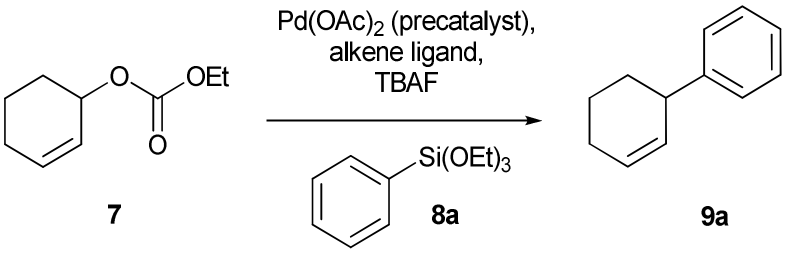


To 2-cyclohexen-1-ol (5 g, 50.9 mmol, 1 eq.) in CH_2Cl_2 (45 mL) and pyridine (6.15 mL, 76.3 mmol, 1.5 eq.) was added ethyl chloroformate (7.58 mL, 76.3 mmol, 1.5 eq.) dropwise via glass syringe under argon. The reaction mixture was allowed to stir at room temperature for 5 days. The mixture was quenched with water (100 mL) and extracted with CH_2Cl_2 (3 x 50 mL), dried over $MgSO_4$, filtered and concentrated *in vacuo* to give an oil (7.8 g, 90%).

^1H NMR ($CDCl_3$) *δ:* 5.92-5.89 (m, 1H), 5.72-5.71 (m, 1H), 5.04 (m, 1H), 4.13-4.09 (q, 2H, *J*=7.1), 2.00-1.58 (br, 6H), 1.24-1.22 (t, 3H, *J*=7.1).

^{13}C NMR ($CDCl_3$): 155.3, 133.6, 125.8, 71.6, 63.8, 28.0, 24.6, 18.3, 14.0.

Hiyama cross-coupling: General procedure



To the ionic liquid (4 mL) was added 1 M TBAF solution in THF (2.84 mL, 2.84 mmol, 4 eq.). The THF was then removed *in vacuo*. To this mixture was added of compound **7** (121 mg, 0.712 mmol, 1 eq.) and the aryl siloxane (342 mg, 1.42 mmol, 2 eq.). This was followed by the addition of the ion-tagged ionic alkene ligand (0.142 mmol, 0.2 eq.) and palladium(II) acetate (16 mg, 0.0712 mmol, 0.1 eq.). The reaction mixture was stirred at 50 °C for 20 h under N_2. The product was extracted with Et_2O* (4 x 10 mL) and the organic layer concentrated *in vacuo*. The oily product was dissolved in Et_2O (3 mL) and then subjected to a silica-gel plug (0.4 g, 5 mm diameter column) filtration. The Et_2O was removed *in vacuo* to give the product as a colourless oil.

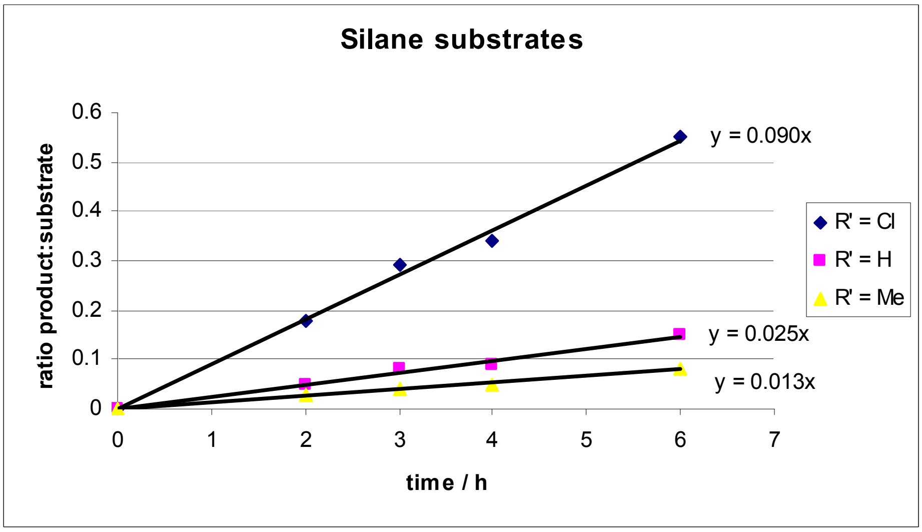
*N.B. The product can also be extracted with hexane, before filtration through silica-gel or Celite™ to remove any traces of the ionic liquid and/or reactants. Alternately, the product can be obtained by Kugelrohr distillation at 55 °C (0.5 mbar).

Hiyama cross-coupling: Aryl siloxane competition experiment

To the ionic liquid (4 mL) was added 1 M TBAF solution in THF (2.84 mL, 2.84 mmol, 4 eq.). The THF was removed *in vacuo*. To this mixture was added compound **7** (121 mg, 0.712 mmol, 1 eq.) and 0.47 mmol of the three aryl siloxanes ($4\text{-}RC_6H_4Si(OEt)_3$; R = Me, H, Cl). This was followed by the addition of ligand **1a** (0.142 mmol, 0.2 eq.) and palladium(II) acetate (0.0712 mmol, 0.1 eq.). The reaction was stirred at 50 °C for 6 h under N_2. Each data point was determined by high resolution GC analysis. The corresponding cross-coupled products were verified by GC/MS analysis.

Table 1:

Time (hours)	Cyclohex-2-enyl ethyl carbonate GC integration	Product; R'=Me GC integration	Product; R'=H GC integration	Product; R'=Cl GC integration
2	141467	3950	6983	26190
3	32332	1393	2475	9306
4	77512	3941	7005	26538
6	57529	4783	8605	31613
Average relative rate:		0.55	1.00	3.67

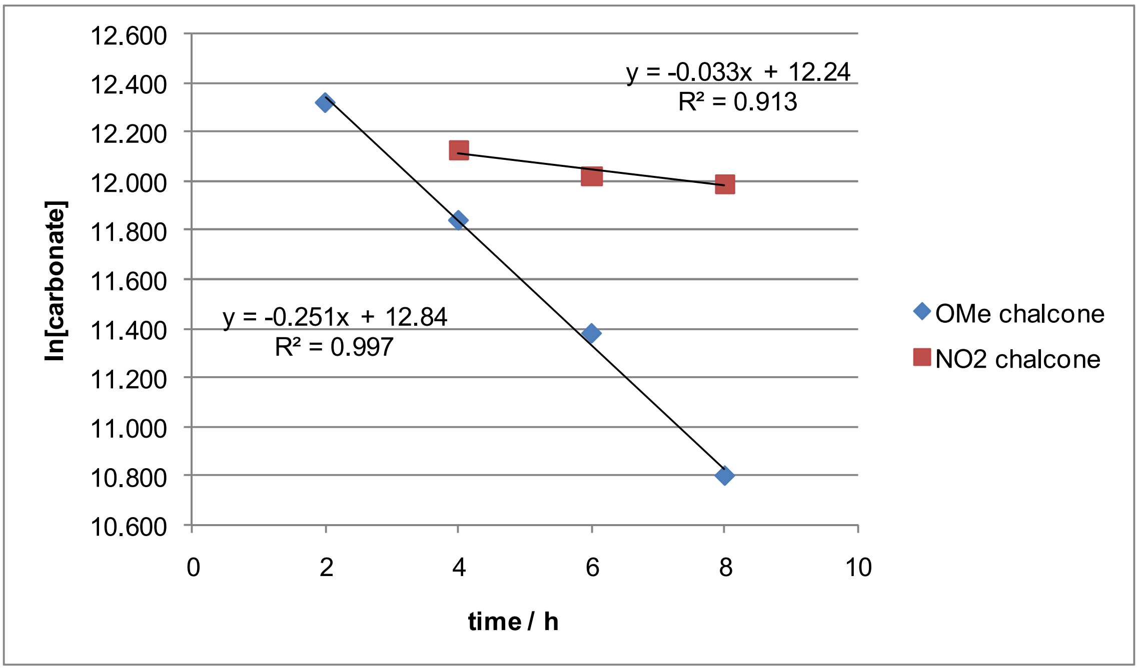


Hiyama cross-coupling: Kinetic analysis with ligands 1b and 1c

To the ionic liquid (4 mL) was added 1 M TBAF solution in THF (2.84 mL, 2.84 mmol, 4 eq.). The THF was then removed *in vacuo*. Compound **7** **(**121 mg, 0.712 mmol, 1 eq.) was added to this mixture, followed by $PhSi(OEt_3)_3$ (0.47 mmol), ligand **1b** or **1c** (0.1422 mmol, 0.2 eq.) and palladium(II) acetate (0.0712 mmol, 0.1 eq.). The reaction mixture was stirred at 50 °C for 6 h under N_2. Each data point was determined by high resolution GC analysis. The corresponding cross-coupled products were verified by GC/MS analysis.

Table 2:

Ligand	**Time (hours)**	**Carbonate GC integration**	**Product GC integration**	**ln(carbonate GC integration)**
OMe substituted	2	224105	72808	12.320
	4	138647	77833	11.840
	6	87438	88039	11.379
	8	48911	86432	10.798
NO_2 substituted	2	151877	44198	11.931
	4	184315	74061	12.124
	6	166601	83361	12.023
	8	161537	93302	11.992



Kinetic plots for the coupling reaction using ligands **1b** and **1c**. Note: The GC integral at 2 h for the NO_2-substituted chalcone (**1c**) was removed during this analysis, as it appears to be an outlier.

3-Phenyl-1-cyclohexene (9a) [5]

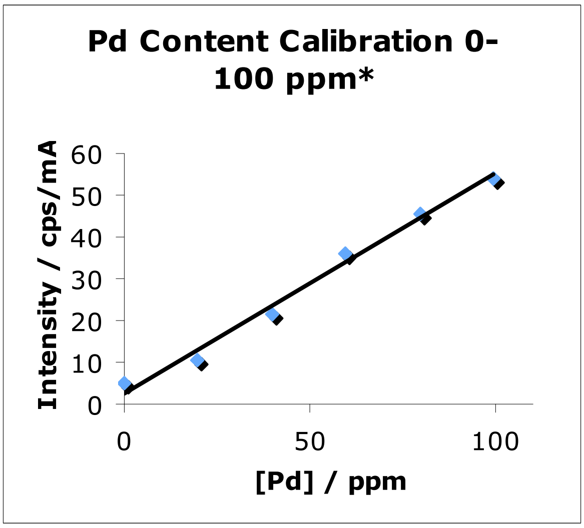
^{1} H NMR ($CDC1_3$) *δ:* 7.22-7.20 (m, 2H), 7.15-7.13 (m, 3H), 5.80 (m, 1H), 5.65 (m, 1H), 3.32-3.31 (b, 1H), 2.08-1.84 (b, 3H), 1.70-1.55 (b, 3H).

^{13}C NMR ($CDCl_3$): 146.6, 130.4, 128.6, 128.5, 127.9, 126.2, 41.6, 32.3, 24.7, 20.9.

Pd analysis of 3-phenyl-1-cyclohexene (9a) by X-Ray Fluorescence (XRF)

Palladium content in product **9a** was analysed by X-Ray Fluorescence (XRF) (Horiba XGT7000 X-ray Analytical Microscope). For the Pd content calibration, standard solutions were made by serial dilution of a 1020µg/mL Pd in 5% HCl stock solution in water (supplied by Aldrich). Product samples were run as hexane solutions. All analyses were taken under partial vacuum, using an X-Ray source operating at 50kV with a Ni filter. Calibration data is given in Table 3, with accompanying graph. Product **9a** Pd content is given in Table 4.

Table 3: Pd content XRF calibration.



[Pd] / ppm	Intensity / cps / mA
995	218.19
99.5	30.70
9.95	9.39*
0 (water)	5.00*
0 (hexane)	3.91*

*Spectrometer forced to identify palladium content at 20, 10 and 0 ppm.

Table 4: Product **9a** analysis.

Product 9a	Intensity / cps/mA	[Pd] / ppm†
After Et_2O extraction and silica-gel filtration	0.85*	< 1
After Et_2O extraction and silica-gel filtration	5.08*	3.9
After extraction with hexane only	4.66*	4.7

* Spectrometer forced to identify palladium content. † Values determined from the calibration curve.

The palladium content deviates from linearity at lower concentrations (<50 ppm). As a result of this outcome, we are confident that the Pd content is below 50 ppm.

Transmission Electron Microscopy (TEM) details

A JEOL 2011 TEM, operating with a tungsten filament at 120 kV and 125 mA emission was used for all TEM measurement. Samples were prepared by diluting a drop of the reaction mixture in acetone, redispersing via ultra-sonication and mounting this solution on a holey carbon grid (Agar Scientific), which was air dried before being placed in the vacuum chamber. Micrographs were recorded using a Gatan digital camera and Digital Microscope software. The poor image contrast in some of these images may be due to residual IL that covers the particles and is not removed in the vacuum of the microscope.

References

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2. B.E. Moulton, A.-K. Duhme-Klair, I. J. S. Fairlamb, J. M. Lynam and A. C. Whitwood, *Organometallics*, **2007**, *26*, 6354.
3. P. Saravanan, A. DattaGupta, D. Bhuniya and Vinod K. Singh, *Tetrahedron*, **1997**, *53*, 1855.
4. N.G. Clemo, D. R. Gedge and G. Pattenden, *J. Chem. Soc., Perkin Trans. 1*, **1981**, 1448.
5. K. H. Shukla and P. DeShong, *J. Org. Chem.*, **2008**, *73*, 6283.

Selected X-ray diffraction data

Table 5. Crystal data and structure refinement for jms0805m. **[2]Br** (CCDC deposition 726739)

Identification code	jms0805m	
Empirical formula	C15 H20 Br N O	
Formula weight	310.23	
Temperature	383(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 10.6662(18) Å	α= 90°.
	b = 13.109(2) Å	β= 115.960(3)°.
	c = 11.3363(18) Å	γ = 90°.
Volume	1425.2(4) Å^3	
Z	4	
Density (calculated)	1.446 Mg/m^3	
Absorption coefficient	2.873 mm^{-1}	
F(000)	640	
Crystal size	0.12 x 0.09 x 0.09 mm^3	
Theta range for data collection	2.19 to 28.34°.	
Index ranges	-13<=h<=14, -17<=k<=17, -14<=l<=15	
Reflections collected	13289	
Independent reflections	3504 [R(int) = 0.0457]	
Completeness to theta = 28.34°	98.2 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.772 and 0.593	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3504 / 0 / 164	
Goodness-of-fit on F^2	0.985	
Final R indices [I>2sigma(I)]	R1 = 0.0357, wR2 = 0.0886	
R indices (all data)	R1 = 0.0481, wR2 = 0.0923	
Largest diff. peak and hole	0.998 and -0.324 e.Å^{-3}	

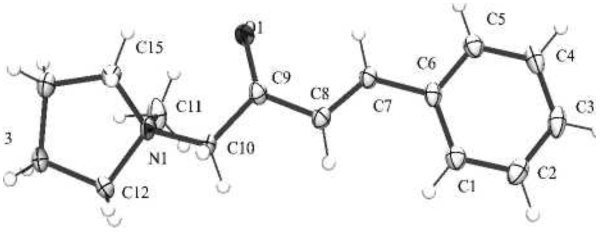


Table 6. Crystal data and structure refinement for jms0803m. **[1a]Br** (CCDC deposition 726740)

Identification code	jms0803m	
Empirical formula	C22 H26 N O2 Br	
Formula weight	416.35	
Temperature	110(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 8.2923(5) Å	α= 102.082(10)°.
	b = 10.5937(6) Å	β= 94.398(10)°.
	c = 13.0176(8) Å	γ = 112.711(10)°.
Volume	1015.67(10) Å^3	
Z	2	
Density (calculated)	1.361 Mg/m^3	
Absorption coefficient	2.039 mm^{-1}	
F(000)	432	
Crystal size	0.13 x 0.12 x 0.08 mm^3	
Theta range for data collection	2.16 to 28.32°.	
Index ranges	-11<=h<=11, -13<=k<=14, -17<=l<=17	
Reflections collected	10520	
Independent reflections	4982 [R(int) = 0.0167]	
Completeness to theta = 28.32°	98.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.849 and 0.765	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4982 / 0 / 246	
Goodness-of-fit on F^2	1.111	
Final R indices [I>2sigma(I)]	R1 = 0.0393, wR2 = 0.1174	
R indices (all data)	R1 = 0.0446, wR2 = 0.1203	
Largest diff. peak and hole	1.006 and -0.326 e.Å^{-3}	

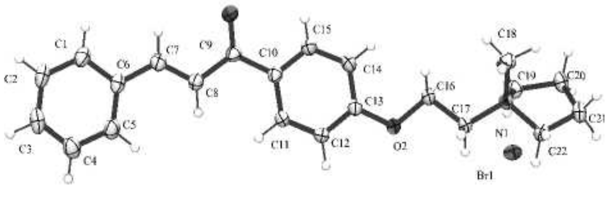


Table 7. Crystal data and structure refinement for jms0810. **[1a]PF$_6$** (CCDC deposition 726742)

Identification code	jms0810	
Empirical formula	C22 H26 F6 N O2 P	
Formula weight	481.41	
Temperature	110(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 9.9133(4) Å	α= 90°.
	b = 21.1994(7) Å	β= 94.152(4)°.
	c = 10.4816(4) Å	γ = 90°.
Volume	2196.99(14) Å^3	
Z	4	
Density (calculated)	1.455 Mg/m^3	
Absorption coefficient	1.756 mm^{-1}	
F(000)	1000	
Crystal size	0.26 x 0.1 x 0.08 mm^3	
Theta range for data collection	4.17 to 70.56°.	
Index ranges	-11<=h<=12, -25<=k<=24, -12<=l<=12	
Reflections collected	18215	
Independent reflections	4086 [R(int) = 0.0483]	
Completeness to theta = 70.56°	97.2 %	
Absorption correction	Multi-scan	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4086 / 0 / 400	
Goodness-of-fit on F^2	1.034	
Final R indices [I>2sigma(I)]	R1 = 0.0827, wR2 = 0.2053	
R indices (all data)	R1 = 0.0971, wR2 = 0.2166	
Largest diff. peak and hole	0.853 and -0.472 e.Å^{-3}	

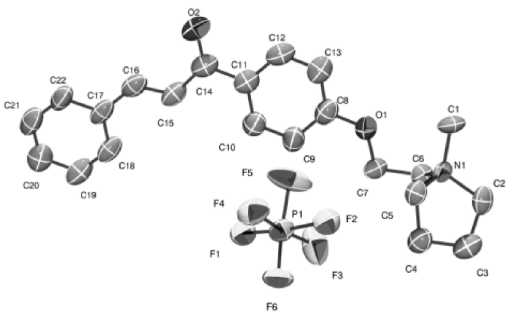
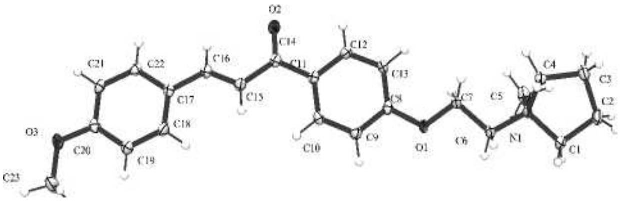


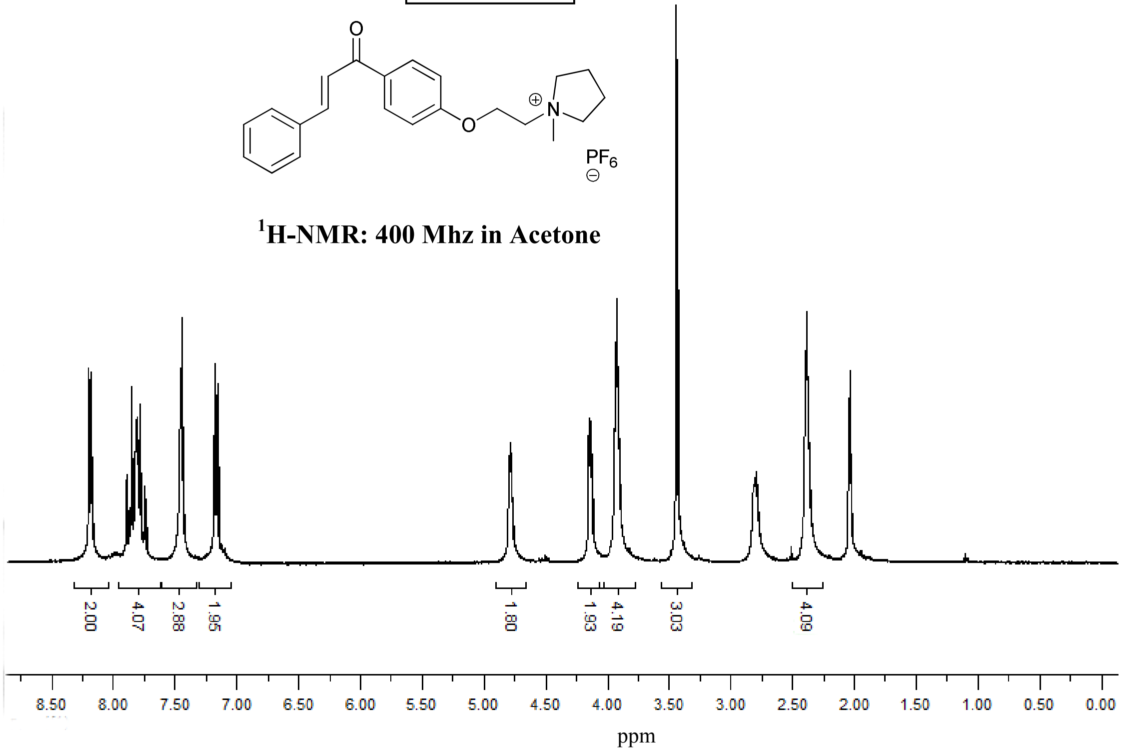
Table 8. Crystal data and structure refinement for jms0809a. **[1b]Br** (CCDC deposition 726741)

Identification code	jms0809a	
Empirical formula	C23 H28 Br N O3	
Formula weight	446.37	
Temperature	110(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P21/c	
Unit cell dimensions	a = 10.5509(6) Å	α= 90°.
	b = 25.7087(16) Å	β= 111.2720(10)°.
	c = 8.2257(5) Å	γ = 90°.
Volume	2079.2(2) Å^{3}	
Z	4	
Density (calculated)	1.426 Mg/m^{3}	
Absorption coefficient	2.001 mm^{-1}	
F(000)	928	
Crystal size	0.33 x 0.13 x 0.04 mm^{3}	
Theta range for data collection	1.58 to 28.29°.	
Index ranges	-14<=h<=13, -34<=k<=34, -10<=l<=10	
Reflections collected	21232	
Independent reflections	5141 [R(int) = 0.0383]	
Completeness to theta = 28.29°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Refinement method	Full-matrix least-squares on F^{2}	
Data / restraints / parameters	5141 / 0 / 255	
Goodness-of-fit on F^{2}	1.021	
Final R indices [I>2sigma(I)]	R1 = 0.0329, wR2 = 0.0747	
R indices (all data)	R1 = 0.0454, wR2 = 0.0794	
Largest diff. peak and hole	0.510 and -0.265 e.Å^{-3}	



NMR spectra of key compounds

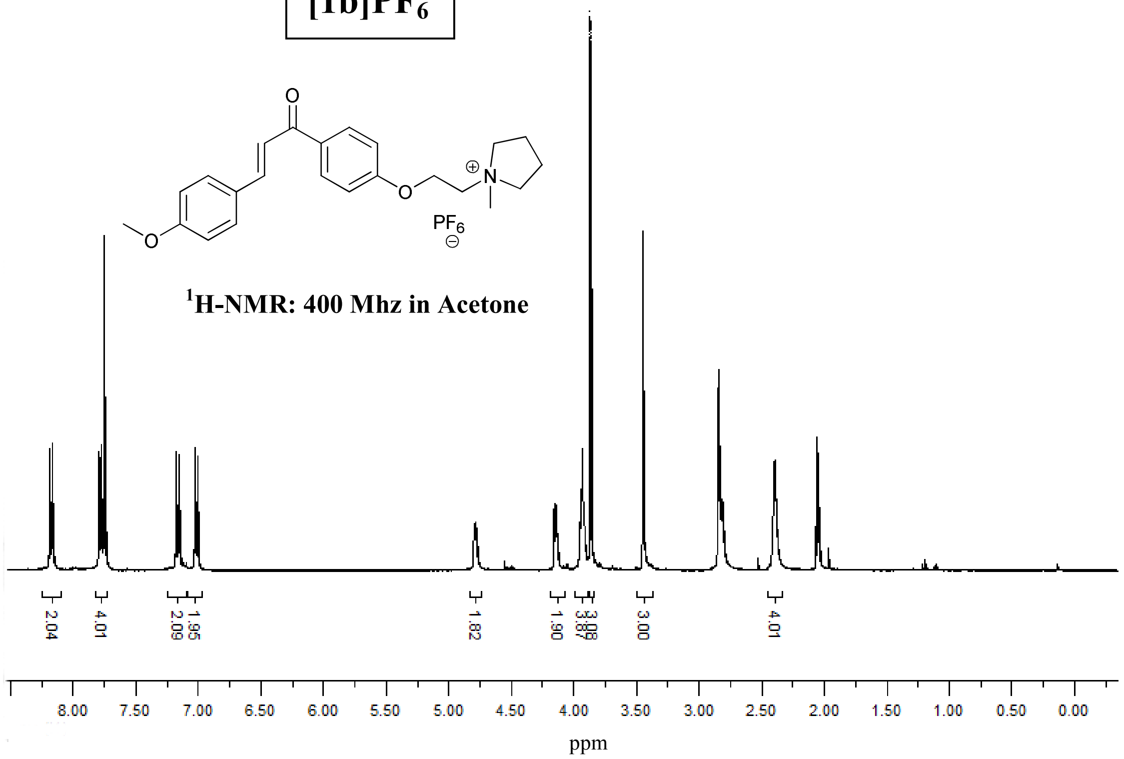
[1a]PF$_6$



^{1}H-NMR: 400 Mhz in Acetone

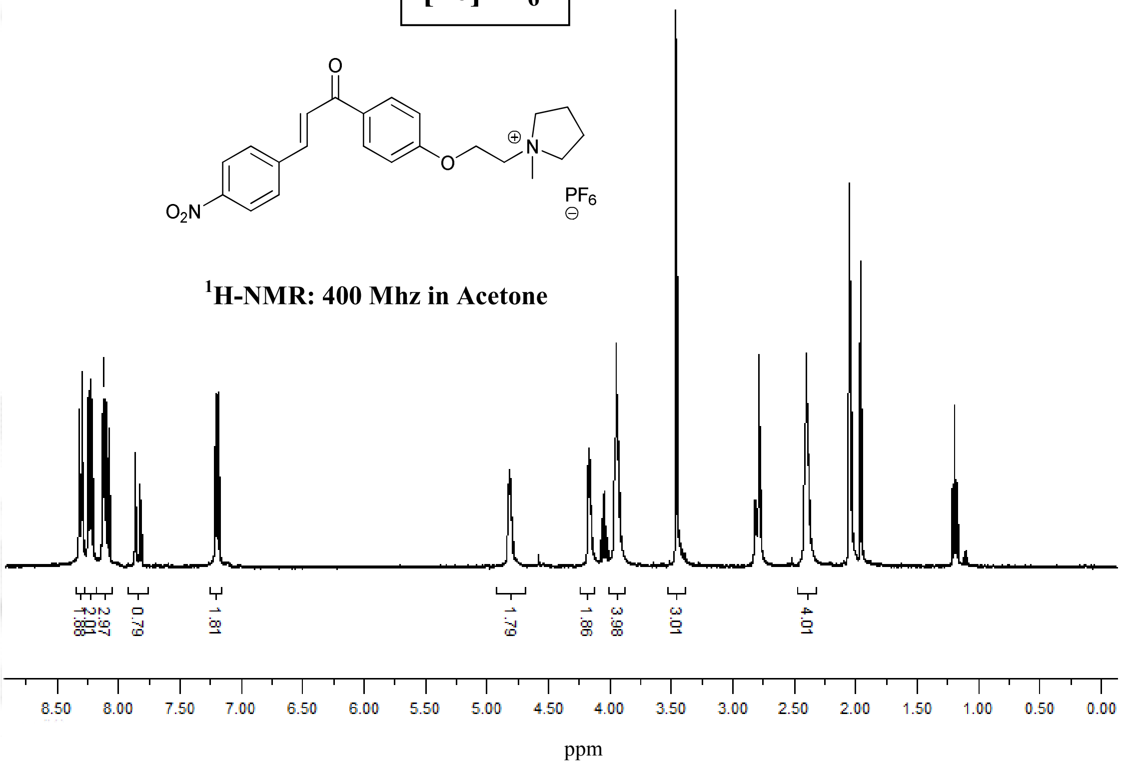
This sample carries a small acetone impurity.

[1b]PF$_6$



^{1}H-NMR: 400 Mhz in Acetone

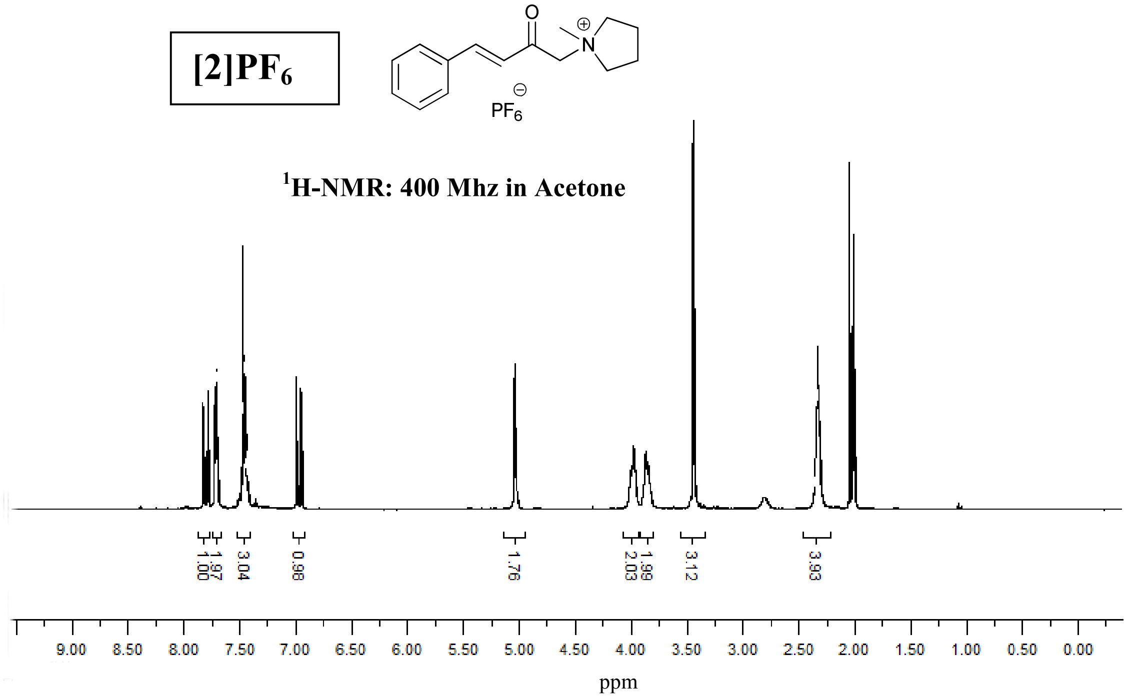
[1c]PF$_6$



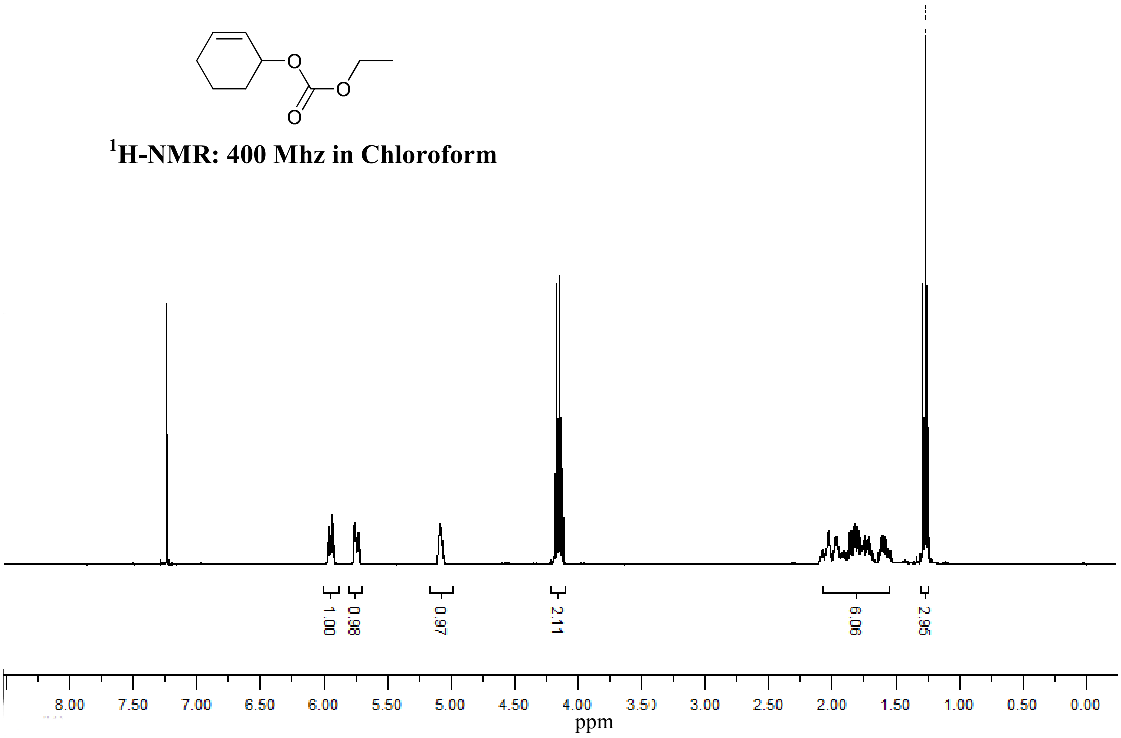
^{1}H-NMR: 400 Mhz in Acetone

This sample carries a small EtOAc impurity.

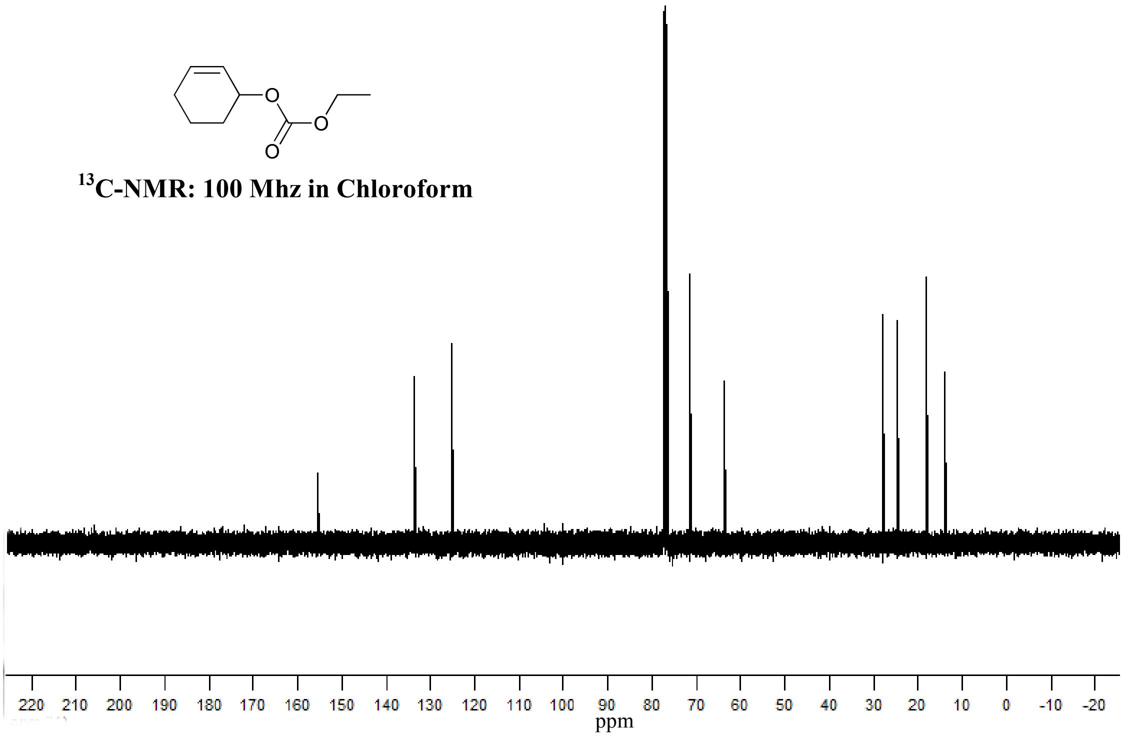
[2]PF$_6$



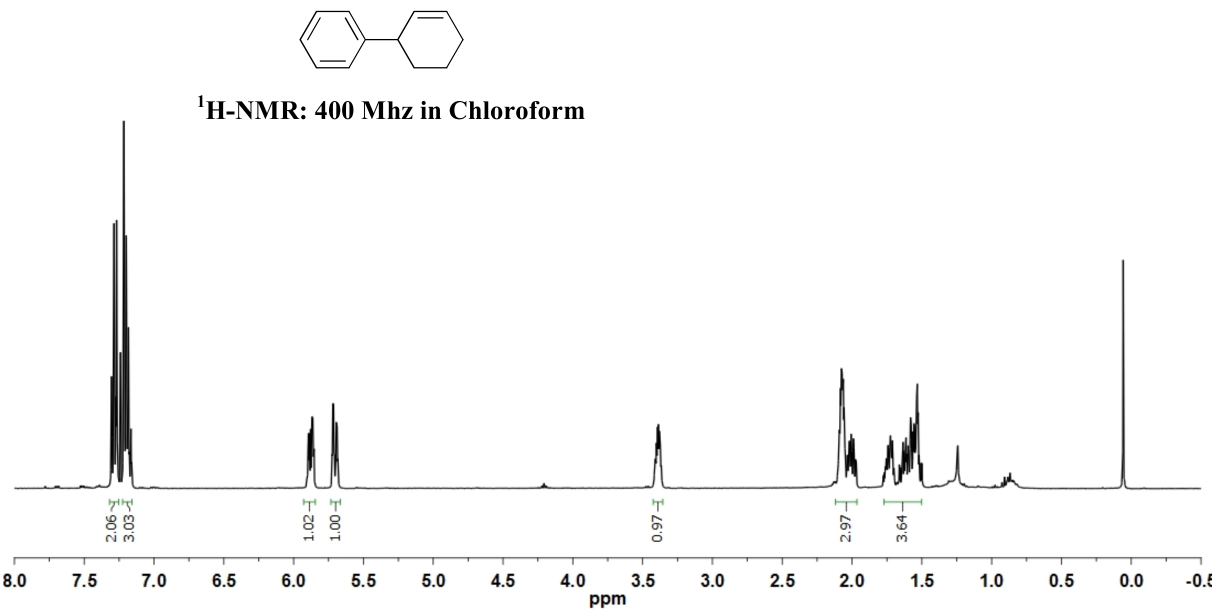
^{1}H-NMR: 400 Mhz in Acetone



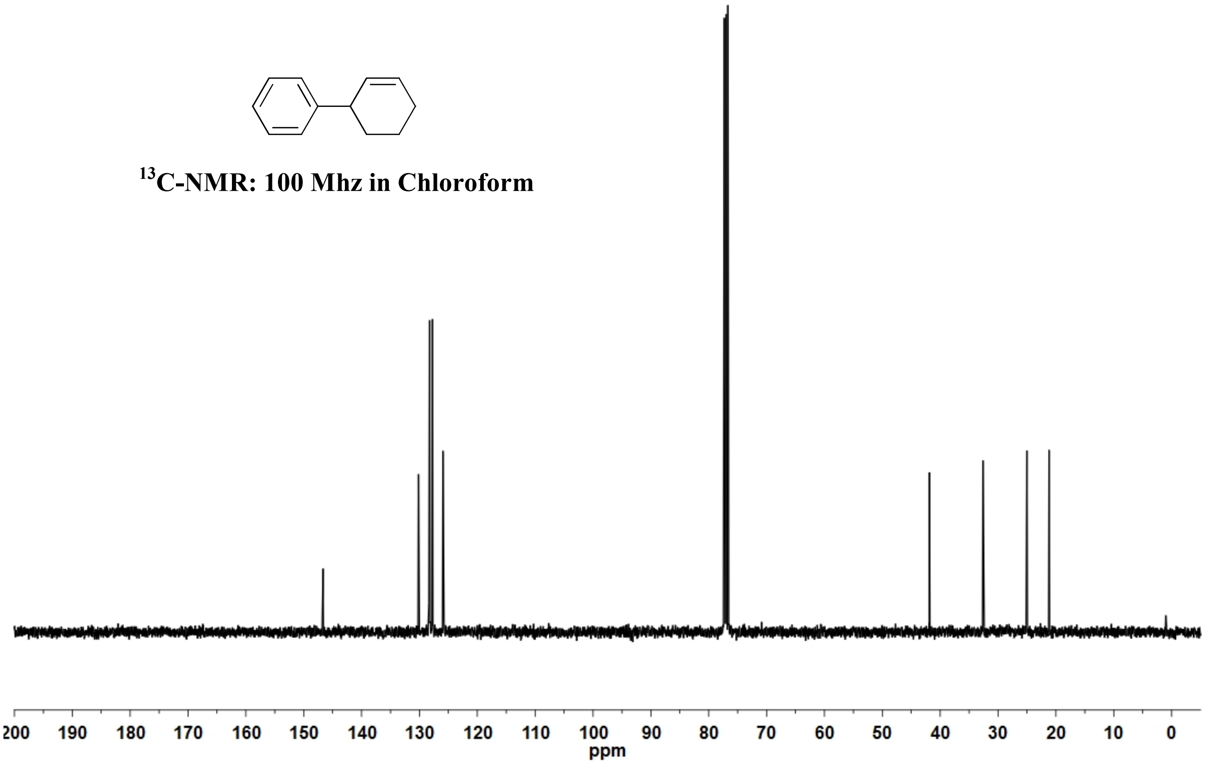
^{1}H-NMR: 400 Mhz in Chloroform



^{13}C-NMR: 100 Mhz in Chloroform



^{1}H-NMR: 400 Mhz in Chloroform
2.06
3.03
1.02
1.00
0.97
2.97
3.64
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.
ppm



^{13}C-NMR: 100 Mhz in Chloroform
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm