Electronic Supplementary Information for:

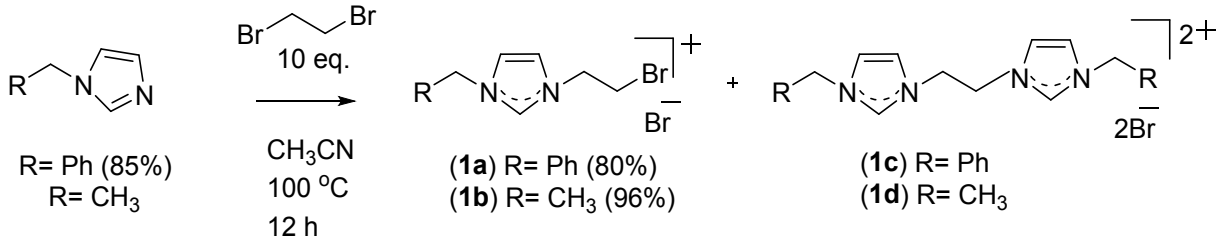
Luminescent Iridium(III) Complexes of N-Heterocyclic Carbene Ligands Prepared Using the 'Click Reaction'

Rebecca E. Karmis, [a] Serena Carrara, [a] Amy A. Baxter,[b] Conor F. Hogan, [a] Mark D. Hulett[b] and Peter J. Barnard [a] *

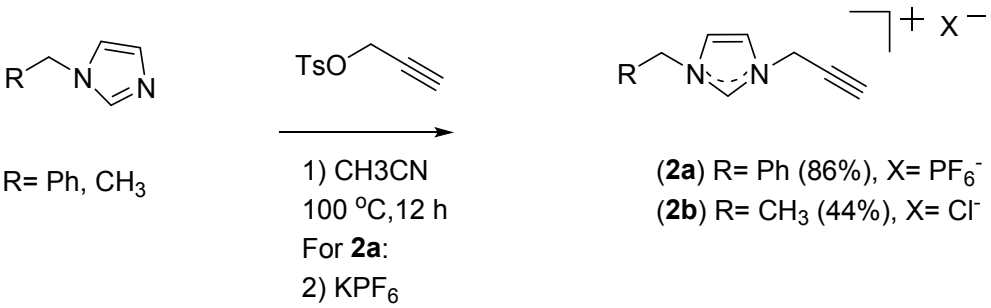
[a]*Department of Chemistry and Physics, La Trobe Institute for Molecular Science, La Trobe University, Victoria, 3086, Australia, Fax: (+)61 3 9479 1266, E-mail: p.barnard@latrobe.edu.au*

[b]*Department of Biochemistry and Genetics, La Trobe Institute for Molecular Science, La Trobe University, Victoria, 3086, Australia.*

Ligand Synthesis



Scheme S1. Synthesis of imidazolium salts **1a** and **1b** (with their corresponding bis-imidazolium salt biproducts **1c** and **1d**, respectively).



Scheme S2. Synthesis of the alkyne functionalized imidazolium salts **2a** and **2b**.

1-benzyl-1H-imidazole ^{1}H NMR (400 Hz, $CDCl_3$): δ 5.11 (s, 2H, CH_2), 6.92 (s, 1H, H_{imi}), 7.11 (s, 1H, H_{imi}), 7.16-7.18 (m, 2H, H_{Ar}), 7.32-7.38 (m, 3H, H_{Ar}), 7.72 (s, 1H, H_{Ar}). ^{13}C NMR (100 Hz, $CDCl_3$): δ 51.2 (CH_2), 119.5 (C_{imi}), 127.5 (C_{Ar}), 128.5 (C_{imi}), 129.1 (C_{Ar}), 129.2 (C_{Ar}), 136.0 (C_q), 137.4 (C_{imi}). HRESI-MS$^+$ (CH_3OH): *m*/z 181.0735 $[C_{10}H_{10}N_2]Na^+$ calcd. 181.0736.

Propargyl tosylate A solution of toluenesulfonyl chloride (4.86 g, 25.5 mmol) in acetone (10 mL) was cooled in an ice bath and propargyl alcohol (1.48 mL, 25.5 mmol) in 10% NaOH (25 mL) was added with stirring over 15 min. The reaction mixture was extracted with CH_2Cl_2 (3 × 10 mL) and the combined organic layers washed with water (3 × 10 mL), dried over $MgSO_4$ and the solvent removed *in vacuo* to give the product as a colorless liquid (5.03 g, 94%). ^{1}H NMR (400 Hz, $CDCl_3$): δ 2.42 (s, 3H, CH_3), 3.66 (t, 1H, *J*= 2.42 Hz, C≡C*H*), 4.85 (d, 2H, *J*= 2.42 Hz, CH_2), 7.48 (dd, 2H, *J*= 2.60, 8.58 Hz, H_{Ar}), 7.82 (dd, 2H, *J*= 1.67, 6.55 Hz, H_{Ar}). ^{13}C NMR (100 Hz, $CDCl_3$): δ 21.7 (CH_3), 57.5 (CH_2), 75. 4 (*C*≡CH), 77.4 (C≡*C*H), 128.1 (C_{Ar}), 130.0 (C_{Ar}), 132.9 (C_q), 145.4 (C_q).

1a To a solution of 1-benzylimidazole (2.40 g, 15.2 mmol) in acetonitrile (50 mL) was added 1,2-dibromoethane (13.0 mL, 152 mmol) and the mixture was refluxed at 100 °C overnight. The mixture was concentrated *in vacuo* and the resulting white solid corresponding to the disubstituted compound (**1c**) was collected. To the filtrate was added ether and an off-white solid formed after scratching. This solid was collected, giving the title compound (4.20 g, 80%). ^{1}H NMR (500 Hz, d_6- DMSO): δ 3.97 (t, 2H, *J*=5.85 Hz, CH_2), 4.65 (t, 2H, *J*= 5.83 Hz, CH_2), 5.50 (s, 2H, Bn-CH_2), 7.39-7.44 (m, 5H, H_{Ar}), 7.89 (d, 2H, *J*= 1.95 Hz, H_{imi}), 9.45 (s, 1H, H_{imi}). ^{13}C NMR (125 Hz, d_6- DMSO): δ 31.5 (CH_2), 50.2 (CH_2), 51.9 (CH_2), 122.7 (C_{imi}), 122.8 (C_{imi}), 128.1 (C_{Ar}), 128.7 (C_{Ar}), 129.0 (C_{Ar}), 134.7 (C_q), 136.7 (C_{imi}). HRESI-MS$^+$ (CH_3OH): *m*/z 265.0336 $[C_{12}H_{14}BrN_2]^+$ calcd. 265.0335.

1b This compound was prepared using the same procedure as that described for **1a** from 1-ethylimidazole (1.01 mL, 10.4 mmol) in acetonitrile (40 mL), 1,2-dibromoethane (8.96 mL, 104 mmol). The reaction mixture was concentrated *in vacuo* and the resulting white solid was collected (**1d**). To the filtrate was added ether and the title compound was obtained as a brown oil (2.82 g, 96%). ^{1}H NMR (400 Hz, d_6- DMSO): δ 1.43 (t, 3H, J= 7.29 Hz, CH_3), 3.97 (t, 2H, *J*= 5.98 Hz, CH_2), 4.25 (q, 2H, *J*= 7.46, 14.62 Hz, CH_2), 4.63 (t, 2H, *J*= 5.88 Hz, CH_2), 7.89 (s, 2H, H_{imi}), 9.38 (d, 1H, *J*= 4.30 Hz, H_{imi}). ^{13}C NMR (100 Hz, d_6- DMSO): δ 15.1 (CH_3), 31.5 (CH_2), 44.3 (CH_2), 50.1 (CH_2), 122.3 (C_{imi}), 122.5 (C_{imi}), 136.3 (C_{imi}). HRESI-MS$^+$ (CH_3OH): *m*/z 203.0181 $[C_7H_{12}BrN_2]^+$ calcd. 203.0814.

2a To a solution of 1-benzylimidazole (2.0 g, 12.6 mmol) in acetonitrile (50 mL) was added propargyl tosylate (2.16 mL, 12.6 mmol) and the mixture was heated at 100 °C for 12 h. The reaction mixture was concentrated *in vacuo* and to the residue was added ether and the formed oil was dissolved in

water (15 mL). A saturated aqueous solution of KPF_6 (~1 mL) was then added and after 30 min the white solid was collected and washed several times with water and dried to give the title product (4.05 g, 86%). ^{1}H NMR (400 Hz, *d*$_6$- DMSO): δ 3.84 (d, 1H, *J*= 4.0 Hz, C≡C*H*), 5.17 (d, 2H, *J*= 4.0 Hz, CH_2), 5.44 (s, 2H, Bn-CH_2), 7.39-7.44 (m, 5H, H_{Ar}), 7.83 (dt, 2H, *J*= 1.95, 10.32 Hz, H_{imi}), 9.38 (s, 1H, H_{imi}) . ^{13}C NMR (100 Hz, *d*$_6$- DMSO): δ 38.8 (*C*H$_2$), 52.2 (Bn-*C*H$_2$), 76.0 (*C*≡CH), 79.1 (C≡*C*H), 122.8 (C_{imi}), 122.9 (C_{imi}), 128.4 (C_{Ar}), 128.9 (C_{Ar}), 129.1 (C_{Ar}), 134.7 (C_q), 136.3 (C_{imi}). HRESI-MS$^+$ (CH$_3$OH): *m*/z 197.1077 $[C_{13}H_{13}N_2]^+$ calcd. 197.1073.

2b This compound was prepared using the same procedure as that described for **2a** from 1-ethyl imidazole (0.585 g, 6.09 mmol), propargyl tosylate (1.28 g, 6.09 mmol) and acetonitrile (50 mL) (0.710 g, 42%). ^{1}H NMR for tosylate anion (500 Hz, *d*$_6$- DMSO): δ 1.41 (t, 3H, *J*= 7.60 Hz, CH_3), 2.28 (s, 3H, CH_3), 3.84 (t, 1H, *J*= 2.58 Hz, C≡C*H*), 4.21 (q, 2H, *J*= 7.25, 14.98 Hz, CH_2), 5.17 (d, 2H, *J*= 2.50 Hz, CH_2), 7.10 (d, 2H, *J*= 8.09 Hz, H_{Ar}), 7.46 (d, 2H, *J*= 8.43 Hz, H_{Ar}), 7.81 (t, 1H, *J*= 1.78 Hz, H_{imi}), 7.86 (t, 1H, *J*= 1.90 Hz, H_{imi}), 9.28 (s, 1H, H_{imi}). ^{13}C NMR (125 Hz, *d*$_6$- DMSO): δ 15.0 (*C*H$_3$), 20.7 (*C*H$_3$), 38.5 (*C*H$_2$), 44.4 (*C*H$_2$), 76.1 (*C*≡CH), 78.9 (C≡*C*H), 122.3 (C_{imi}), 122.5 (C_{imi}), 125.5 (C_{Ar}), 128.0 (C_{Ar}), 135.8 (C_q), 137.5 (C_q), 145.8 (C_{imi}). HRESI-MS$^+$ (CH$_3$OH): *m*/z 135.0917 $[C_8H_{11}N_2]^+$ calcd. 135.0917. ^{1}H NMR for PF_6^- anion (400 Hz, *d*$_6$- DMSO): δ 1.41 (d, 3H, *J*= 7.36 Hz, CH_3), 3.77 (t, 1H, *J*= 2.68 Hz, C≡C*H*), 4.22 (q, 2H, *J*= 7.28, 15.83 Hz, CH_2), 5.16 (d, 2H, *J*= 2.64 Hz, CH_2), 7.78-7.81 (m, 2H, H_{imi}), 9.25 (s, 1H, H_{imi}). To exchange the anion from hexafluorophosphate to chloride, a solution of tetrabutylammonium chloride in THF was added to a solution of **2b** (1.00 g, 4.35 mmol) in THF (10 mL) and the mixture was stirred for 30 min, during which time an oil separated from the mixture. The solvent was decanted the residue was washed several times with THF and then dried *in vacuo* (0.456 g, 44%). ^{1}H NMR for **2b·Cl** (500 Hz, *d*$_6$- DMSO): δ 1.43 (t, 3H, *J*= 7.08 Hz, CH_3), 3.85 (t, 1H, *J*= 2.56 Hz, C≡C*H*), 4.25 (q, 2H, *J*= 7.23, 15.77 Hz, CH_2), 5.23 (d, 2H, *J*= 2.55 Hz, CH_2), 7.85 (t, 1H, *J*= 1.75 Hz, H_{imi}), 7.89 (t, 1H, *J*= 1.84 Hz, H_{imi}), 9.43 (s, 1H, H_{imi}).

X ray crystallography

Single crystals of the pro-ligands **4a** and **5b** and Ir(III) complex **11** suitable for X-ray diffraction studies were grown by slow diffusion of ether into DCM solutions (**4a** and **11**) and slow diffusion of ether into acetonitrile solution (**5b**). Crystallographic data for all structures determined are given in Table S1. For all samples, crystals were removed from the crystallisation vial and immediately coated with paratone oil on a glass slide. A suitable crystal was mounted in Paratone oil on a glass fibre and cooled rapidly to 173 K in a stream of cold N_2 using an Oxford low temperature device. Diffraction data were measured using an Oxford Gemini diffractometer mounted with Mo-Kα λ = 0.71073 Å and Cu-Kα λ = 1.54184. Data were reduced and corrected for absorption using the CrysAlis Pro program. The SHELXL2013-2 program was used to solve the structures with Direct Methods, with refinement by the Full-Matrix Least-Squares refinement techniques on F2. The non-hydrogen atoms were refined anisotropically and hydrogen atoms were placed geometrically and refined using the riding model. Coordinates and anisotropic thermal parameters of all non-hydrogen atoms were refined. All calculations were carried out using the program Olex2. Further XRD details are provided in the Supporting Information. CCDC 1905286-1905288 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via https://www.ccdc.cam.ac.uk/structures/

Table S1. Crystallographic refinement data for compounds **4a**, **5b** and **11**.

Identification code	**4a**	**5b**	**11**
Empirical formula	$C_{20}H_{20}F_6N_5P$	$C_{16}H_{21}I_2N_5$	$C_{39}H_{37}Cl_2F_6IrN_7P$
Formula weight	475.38	537.18	1011.82
Temperature/K	172.99(10)	173	173.01(10)
Crystal system	orthorhombic	triclinic	monoclinic
Space group	$P2_12_12_1$	P-1	$P2_1/c$
a/Å	9.64361(15)	11.1054(5)	17.1602(5)
b/Å	16.6534(4)	11.9823(9)	12.9309(4)
c/Å	26.2220(4)	15.3663(9)	17.8048(5)
α/°	90	99.443(5)	90
β/°	90	92.342(4)	92.613(3)
γ/°	90	101.879(5)	90
Volume/Å^3	4211.22(13)	1968.0(2)	3946.7(2)
Z	8	4	4
ρ_{calc}g/cm^3	1.5	1.813	1.703
μ/mm^{-1}	1.813	3.202	3.627
F(000)	1952	1032	2000
Crystal size/mm^3	0.25 × 0.15 × 0.1	0.2 × 0.18 × 0.12	0.08 × 0.06 × 0.05
Radiation	CuKα (λ = 1.54184)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.288 to 130.126	5.888 to 52.742	5.702 to 52.744
Index ranges	$-11 \le h \le 6$, $-18 \le k \le 18$, $-30 \le l \le 28$	$-13 \le h \le 13$, $-14 \le k \le 14$, $-19 \le l \le 19$	$-21 \le h \le 19$, $-16 \le k \le 16$, $-22 \le l \le 22$
Reflections collected	14267	19296	45853
Independent reflections	6850 [R_{int} = 0.0226, R_{sigma} = 0.0303]	8038 [R_{int} = 0.0272, R_{sigma} = 0.0345]	8063 [R_{int} = 0.0304, R_{sigma} = 0.0205]
Data/restraints/parameters	6850/0/577	8038/0/419	8063/0/507
Goodness-of-fit on F^2	1.06	1.04	1.07
Final R indexes [I>=2σ (I)]	R_1 = 0.0530, wR_2 = 0.1451	R_1 = 0.0245, wR_2 = 0.0539	R_1 = 0.0328, wR_2 = 0.0849
Final R indexes [all data]	R_1 = 0.0575, wR_2 = 0.1498	R_1 = 0.0308, wR_2 = 0.0575	R_1 = 0.0392, wR_2 = 0.0896
Largest diff. peak/hole / e Å^{-3}	0.68/-0.35	0.72/-0.68	2.18/-1.69
Flack parameter	0.505(11)		

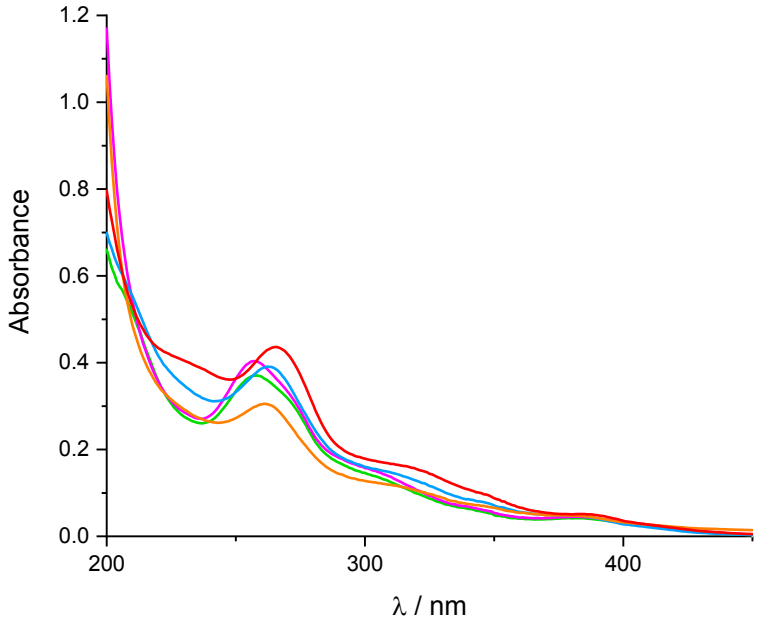


Figure S1. Absorbance spectra of 1 x 10^{-5} solutions of complexes **7-11.** (green) **7**; (pink) **8**; (blue) **9**; (orange) **10**; (red) **11**.

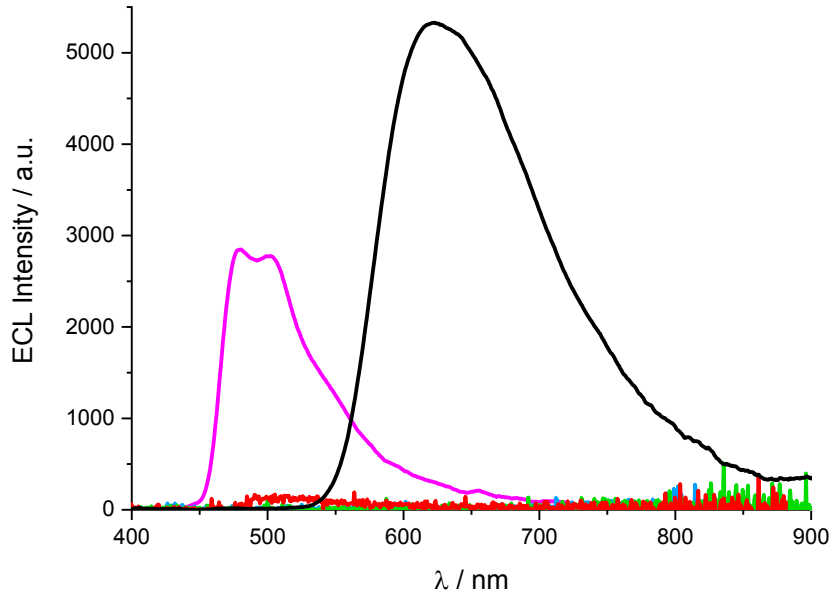


Figure S2. Co-reactant ECL spectra for the complexes **7-9** and **11** (1 mM) in acetonitrile containing 0.1 M $[Bu_4N][PF_6]$ as supporting electrolyte and 10 mM tripropylamine (TPA) as the co-reactant. (green) **7**; (pink) **8**; (blue) **9**; (red) **11**; (black) $[Ru(bpy)_3]^{2+}$.