Electronic Supplementary Material (ESI) for Dalton Transactions.

Electronic Supporting Information:

Luminescence from open-shell first-row transition metal dipyrrinato complexes

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Experimental Details

Ligand syntheses were performed under an atmosphere of air, and all subsequent manipulations were carried out in the absence of water and dioxygen in an MBraun inert atmosphere drybox under a dinitrogen atmosphere. All glassware was oven dried for a minimum of 1 h and cooled in an evacuated antechamber prior to use in the glovebox. Ethyl acetate was purchased from VWR and used as received. Chloroform-*d* was purchased from Cambridge Isotope Labs and used as received. Dichloromethane, benzene, *n*-hexane and tetrahydrofuran were dried and deoxygenated on a Glass Contour System (SG Water) and stored over 4 Å molecular sieves prior to use. Hexamethyldisiloxane (Aldrich) and benzene-d_6 (Cambridge Isotope Labs) were degassed by 3 free-pump-thaw cycles and stored over 4 Å molecular sieves prior to use. Pyridinium *p*-toluenesulfonate and lithium hexamethyldisilazide were purchased from Aldrich and used as received. Iron(II) chloride, manganese(II) chloride, copper(I) chloride, copper(II) chloride, and zinc(II) chloride were purchased from Strem and used as received. N-bromosuccinimide and N-iodosuccinimide were purchased from Aldrich and recrystallized from boiling deionized water prior to use. 2-(2′,4′,6′-Triphenylphenyl)-1H-pyrrole,[1] mesitaldehyde dimethyl acetal,[2] $(^{Ar}L)H$, $(^{Ar}L)Li(THF)_2$, and $(^{Ar}L)FeCl(THF)_3$ were synthesized according to literature procedures.

UV/Visible spectra were recorded on a Varian Cary 50 UV/Visible spectrometer, with a scan rate of 300 nm/min. Extinction coefficients were calculated from a minimum of four samples of different concentration and calculated by linear regression of the absorbance at λ_{max}. ^1H and ^{13}C NMR spectra were recorded on a Varian Unity/Inova 500 MHz spectrometer. ^1H and ^{13}C NMR chemical shifts are reported relative to $SiMe_4$ using the chemical shift of residual solvent peaks as reference. Spectra were processed using the ACDLabs SpecManager v. 12 software package. Mass spectrometry was performed at the Harvard University FAS Center for Systems Biology Mass

Spectrometry and Proteomics Resource Laboratory on an Agilent 6210 TOF LC/MS with a dual nebulizer ESI source. Elemental analyses were carried out at Complete Analysis Laboratories, Inc. (Parsippany, NJ).

2,3,7,8-tetrabromo-1,9-bis(2′,4′,6′-triphenyl)phenyl-5-mesityl-dipyrrin ((^{BrAr}L)H). To a stirring solution of (^{Ar}L)H (0.115 mmol) in tetrahydrofuran was added N-bromosuccinimide (0.471 mmol). After 12 hours, the solvent was removed in vacuo, the residue was taken up in ethyl acetate, washed with saturated aqueous sodium bicarbonate and water, and the solid suspended in the organic layer was collected by vacuum filtration to afford the clean product in 72% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 1.92 (s, 6H), 2.33 (s, 3H), 6.88 (s, 2H), 7.00 - 7.08 (m, 16H), 7.11 - 7.20 (m, 4H), 7.45 (t, J = 7.4 Hz, 2H), 7.54 (t, J = 7.5 Hz, 4H), 7.77 - 7.89 (m, 8H), 12.07 (br. s., 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm 19.35, 21.61, 117.06, 127.56, 127.61, 127.94, 128.05, 128.26, 128.79, 129.04, 129.27, 129.35, 129.90, 134.44, 136.54, 139.88, 139.95, 140.39, 140.69, 142.88, 143.64, 151.75. HR-MS (ESI$^+$, $^m/_z$ for $[M+H]^+$) calc'd for $[C_{66}H_{46}Br_4N_2+H]$: 1183.04673, found 1183.04968. UV/Vis (CH_2Cl_2, 25 °C) λ_{max} = 519 nm, ε = 35,300 $M^{-1}cm^{-1}$.

2,3,7,8-tetraiodo-1,9-bis(2′,4′,6′-triphenyl)phenyl-5-mesityl-dipyrrin ((^{IAr}L)H). To a darkened, stirring solution of (^{Ar}L)H (0.173 mmol) in anhydrous tetrahydrofuran was added N-iodo-succinimide (0.706 mmol) and catalytic camphor sulfonic acid. After stirring for 1 week at ambient temperature, the solvent was removed in vacuo. The residue was taken up in ethyl acetate, washed with saturated aqueous sodium bicarbonate, water, and brine, then dried over magnesium sulfate, filtered, and concentrated in vacuo. The residue was purified by passage through a neutral alumina plug eluting with dichloromethane, and dried in vacuo to afford the clean product in 65%

yield. ^{1}H NMR (500 MHz, C_6D_6) δ ppm 2.10 (s, 6H), 2.21 (s, 3H), 6.89 (s, 2H), 6.92 - 7.03 (m, 8H), 7.14 (s, 12H), 7.21 (d, *J* = 7.0 Hz, 6H), 7.35 - 7.45 (m, 4H), 7.74 (s, 4H), 12.80 (br. s., 1H). ^{13}C NMR (125 MHz) δ ppm 19.77, 21.44, 96.39, 99.20, 127.54, 128.06, 128.20, 129.03, 129.70, 130.95, 138.48, 139.67, 140.20, 140.35, 140.90, 142.10, 142.99, 143.77, 157.09. UV/Vis (CH_2Cl_2, 25 °C) λ_{max} = 539 nm, ε = 34,900 M^{-1}cm^{-1}.

Lithium Salts ((^{Ar}L)Li(THF)$_n$, (^{BrAr}L)Li(THF)$_n$, (^{IAr}L)Li(THF)$_n$). To stirring solutions of the protio dipyrrin in anhydrous THF was added lithium hexamethyldisilazide as a 1.0 *M* solution in hexanes via syringe, and the solution was allowed to stir for 4-12 hours. The solvent was removed in vacuo to afford the lithium salts as dark pinkish-purple powders. Depending on length of time on the vacuum line, the resulting salts had 1, 1.5, or 2 equivalents of THF bound, which varied between batches.

(^{BrAr}L)Li(THF) (1 equiv. THF). ^{1}H NMR (500 MHz, C_6D_6) δ ppm 1.20 (br. s., 4H), 2.22 (s, 3H), 2.25 (s, 6H), 3.24 (br. s., 4H), 6.95 (s, 2H), 6.95 - 7.01 (m, 8H), 7.03 (d, *J* = 7.3 Hz, 4H), 7.14 (s, 6H), 7.22 (d, *J* = 7.3 Hz, 12H), 7.45 (d, *J* = 7.3 Hz, 4H), 7.69 (s, 4H).

(^{IAr}L)Li(THF)$_{1.5}$ (1.5 equiv. THF). ^{1}H NMR (500 MHz, C_6D_6) δ ppm 1.31 (br. s., 6H), 2.18 (s, 6H), 2.26 (s, 3H), 3.43 (br. s., 6H), 6.89 - 6.97 (m, 10H), 7.00 (q, *J* = 7.5 Hz, 6H), 7.14 (s, 8H), 7.19 - 7.26 (m, 12H), 7.45 (d, *J* = 7.3 Hz, 4H), 7.72 (s, 4H).

1,9-bis(2′,4′,6′-triphenyl)phenyl-5-mesityl-dipyrrinato manganese(II) chloride (THF adduct) ((^{Ar}L)MnCl(THF)). To a stirring solution of (^{Ar}L)Li(THF)$_2$ (0.191 mmol) in tetrahydrofuran was added $MnCl_2$ (0.200 mmol), and the resulting solution was allowed to stir at room temperature for 16 hours. The solvent was removed in vacuo, and the residue was taken up in benzene, filtered through Celite, and concentrated to dryness to afford the NMR-silent manganese complex as a purple-green solid in 92% yield. Crystals suitable for X-ray diffraction analysis were grown from hexanes/THF at -35° C. Anal. calc'd for $C_{70}H_{57}ClMnN_2O$: C, 81.42; H, 5.56; N, 2.71. Found: C, 81.36; H, 5.63; N, 2.59.

1,9-bis(2′,4′,6′-triphenyl)phenyl-5-mesityl-dipyrrinato zinc(II) chloride (THF adduct) ((^{Ar}L)ZnCl(THF)). To a stirring solution of (^{Ar}L)Li(THF)$_2$ (0.101 mmol) in tetrahydrofuran was added $ZnCl_2$ (0.111 mmol), and the resulting solution was allowed to stir at room temperature for 16 hours. The solvent was removed in vacuo, and the residue was taken up in benzene, filtered through Celite, and concentrated to dryness to afford the zinc complex as a purple solid in 90% yield. ^{1}H NMR (500 MHz, C_6D_6) δ ppm 1.32 (br. s., 4H), 1.94 (s, 6H), 2.17 (s, 3H), 3.53 (br. s., 4H), 5.86 (d, J = 4.0 Hz, 2H), 6.12 (d, J = 4.0 Hz, 2H), 6.73 (s, 2H), 6.99 - 7.24 (m, 19H), 7.33 - 7.46 (m, 12H), 7.71 (s, 4H); the residual solvent peak was buried beneath the ligand aryl proton peaks, so referencing to the solvent peak is potentially inaccurate. Anal. calc'd for $C_{70}H_{57}ClZnN_2O$: C, 80.61; H, 5.51; N, 2.69. Found: C, 80.49; H, 5.44; N, 2.56.

1,9-bis(2′,4′,6′-triphenyl)phenyl-5-mesityl-dipyrrinato copper(II) chloride ((^{Ar}L)Cu^{II}Cl). To a stirring solution of (^{Ar}L)Li(THF)$_2$ (0.255 mmol) in tetrahydrofuran was added $CuCl_2$ (0.268 mmol), and the resulting solution was allowed to stir at room temperature for 16 hours. The solvent was removed in vacuo, and the residue was taken up in benzene, filtered through Celite, frozen, and lyophilized to dryness to afford the NMR-silent copper(II) complex as a maroon solid in 65%

yield. Crystals suitable for X-ray characterization were grown from saturated hexane solution at -35° C. Anal. calc'd for $C_{66}H_{49}ClCuN_2$: C, 81.80; H, 5.10; N, 2.89. Found: C, 81.68; H, 4.99; N, 2.83.

1,9-bis(2′,4′,6′-triphenyl)phenyl-5-mesityl-dipyrrinato copper(I) ((^{Ar}L)Cu^{I}). To a stirring solution of (^{Ar}L)Li(THF)$_2$ (1.23 mmol) in tetrahydrofuran was added CuCl (1.29 mmol), and the resulting solution was allowed to stir at room temperature for 16 hours. The solvent was removed in vacuo, and the residue was taken up in benzene, filtered through Celite, and concentrated to dryness to afford the copper(I) complex as a dichroic bluish-purple/brown solid in 88% yield. Crystals suitable for X-ray diffraction analysis were obtained from concentrated hexanes solutions at -35° C. ^{1}H NMR (500 MHz, C_6D_6) δ ppm 2.15 (s, 6H), 2.17 (s, 3H), 5.86 (d, *J* = 4.0 Hz, 2H), 6.20 (d, *J* = 4.0 Hz, 2H), 6.74 (s, 2H), 6.90 - 7.00 (m, 12H), 7.10 (dd, *J* = 8.1, 1.4 Hz, 8H), 7.17 (d, *J* = 7.3 Hz, 2H), 7.20 - 7.26 (m, 4H), 7.47 - 7.55 (m, 4H), 7.69 (s, 4H). ^{13}C NMR (125 MHz, C_6D_6), δ ppm 19.82, 21.06, 121.37, 135.17, 126.10, 127.36, 127.56, 127.77, 127.81, 128.29, 128.44, 129.09, 134.23, 136.43, 136.53, 136.75, 137.64, 140.52, 140.62, 140.74, 142.75, 145.13, 155.48. Anal. calc'd for $C_{66}H_{49}CuN_2$: C, 84.90; H, 5.29; N, 3.00. Found: C, 84.81; H, 5.38; N, 2.95.

2,3,7,8-tetraiodo-1,9-bis(2′,4′,6′-triphenyl)phenyl-5-mesityl-dipyrrinato manganese(II) chloride ((^{IAr}L)MnCl(THF)). To a stirring solution of (^{IAr}L)Li(THF)$_{1.5}$ (0.038 mmol) in tetrahydrofuran was added $MnCl_2$ (0.042 mmol) and the solution was allowed to stir at room temperature for 16 hours. The solvent was then removed in vacuo, the residue was taken up in benzene, filtered through Celite, and concentrated in vacuo to afford the NMR-silent title compound as a dark purple powder in 71% yield. Only clean free ligand was observed in the HR-MS, and elemental analysis was hampered by the extreme water- and air-sensitivity of the material.

Figure S1. ^{1}HNMR Spectrum of (^{Ar}L)ZnCl(THF)

as-4-9_h1.esp, processed on **09/01/2013** at **13:03**

Acquisition Time (sec)	2.1853	***Comment***	STANDARD CARBON PARAMETERS			***Date***	Sep 26 2011
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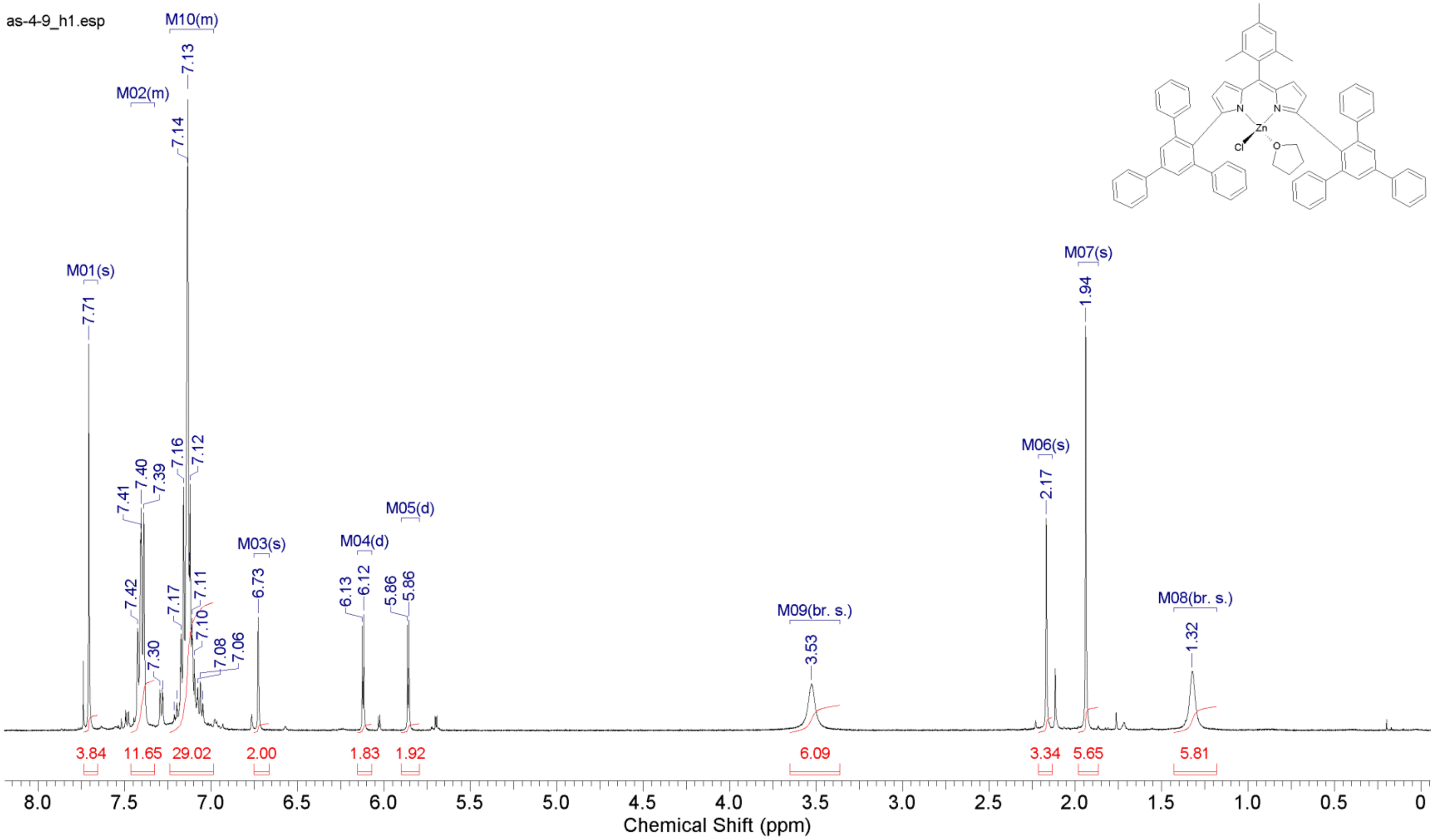
Frequency (MHz)	499.88	***Nucleus***	1H	***Number of Transients***	32	***Pulse Sequence***	s2pul
Receiver Gain	46.00	***Solvent***	BENZENE-d6	***Spectrum Offset (Hz)***	3299.2378	***Spectrum Type***	STANDARD
Sweep Width (Hz)	9995.00	***Temperature (degree C)***	25.000				

^{1}H NMR (500 MHz, BENZENE-d_6) δ ppm 1.32 (br. s., 4 H) 1.94 (s, 5 H) 2.17 (s, 3 H) 3.53 (br. s., 4 H) 5.86 (d, *J*=3.97 Hz, 2 H) 6.12 (d, *J*=3.97 Hz, 2 H) 6.73 (s, 2 H) 6.99 - 7.24 (m, 19 H) 7.33 - 7.46 (m, 12 H) 7.71 (s, 4 H)



as-4-9_h1.esp

Figure S2. ^{1}HNMR Spectrum of (^{Ar}L)Cu^{I}

as-4-38_h1.esp, processed on **09/01/2013** at **13:14**

Acquisition Time (sec)	2.1853	***Comment***	S/N = 351	***Date***	Jul 26 2012	***Date Stamp***	Jul 26 2012
File Name	\\rcfs1.rc.fas.harvard.edu\betley_lab\Users\ascharf\Betley\Characterization Data\as-4-38\as-4-38_h1.fid\fid					***Frequency (MHz)***	499.88
Nucleus	1H	***Number of Transients***	64	***Pulse Sequence***	s2pul	***Receiver Gain***	28.00
Solvent	Benzene	***Spectrum Offset (Hz)***	3299.4590	***Spectrum Type***	STANDARD	***Sweep Width (Hz)***	9995.00
Temperature (degree C)	25.000						

^{1}H NMR (500 MHz, Benzene) δ ppm 2.15 (s, 6 H) 2.17 (s, 3 H) 5.86 (d, J=3.97 Hz, 2 H) 6.20 (d, J=3.97 Hz, 2 H) 6.74 (s, 2 H) 6.90 - 7.00 (m, 12 H) 7.10 (dd, J=8.08, 1.37 Hz, 8 H) 7.17 (d, J=7.32 Hz, 2 H) 7.20 - 7.26 (m, 4 H) 7.47 - 7.55 (m, 4 H) 7.69 (s, 4 H)

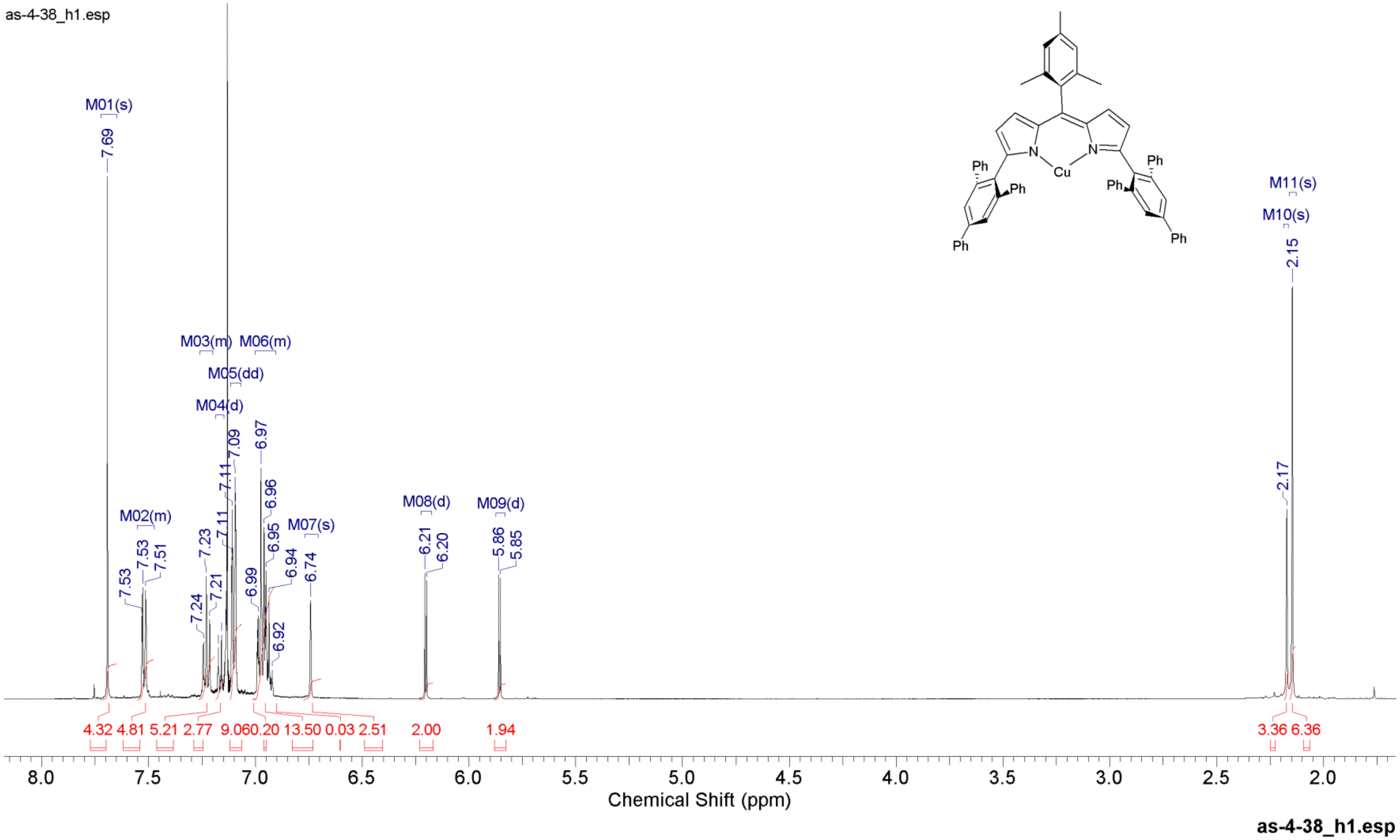
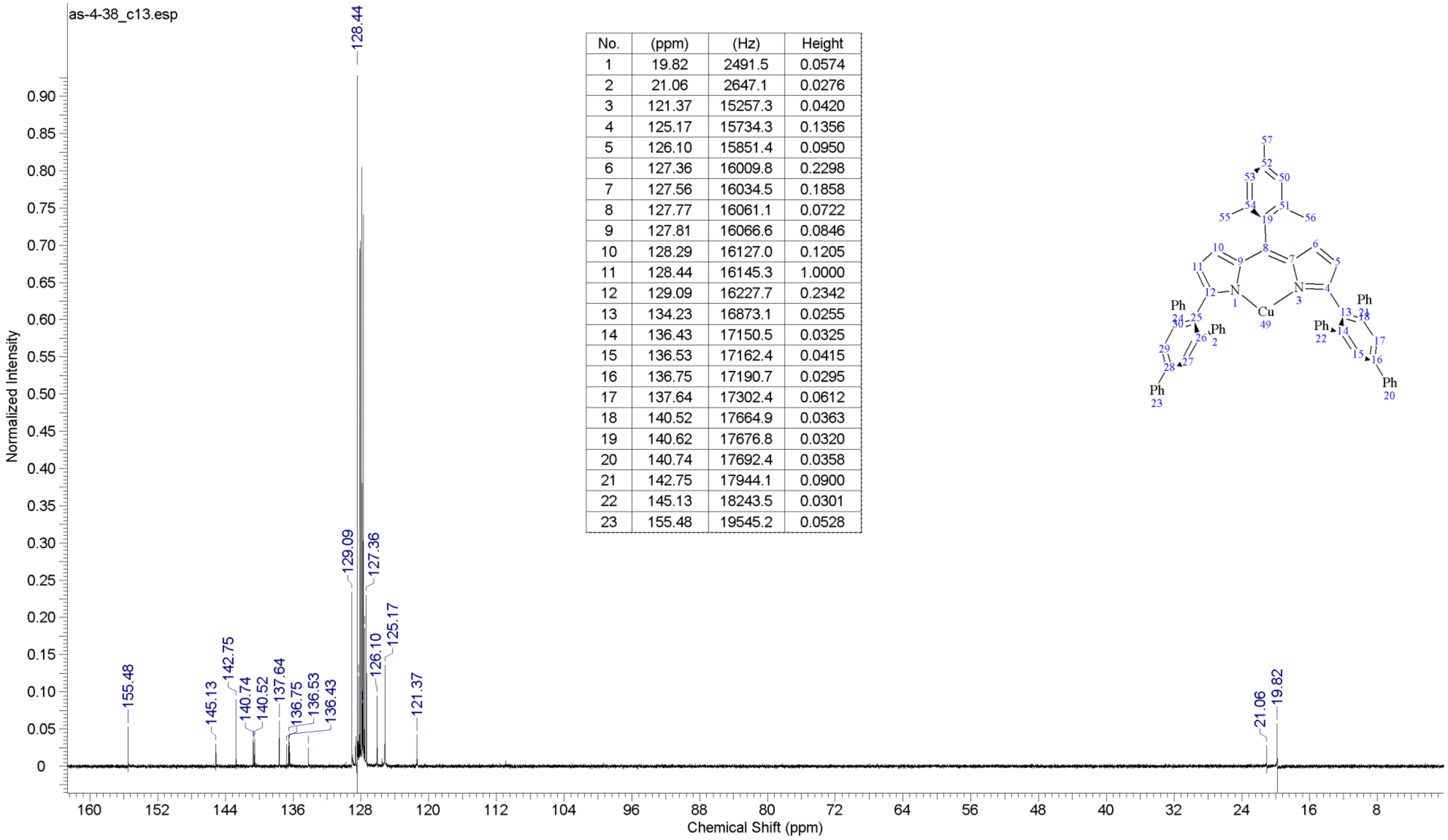


Figure S3. ^{13}CNMR Spectrum of (^{Ar}L)Cu^{I}

1/9/2013 1:16:35 PM

Formula $C_{66}H_{49}CuN_2$	**FW** 933.6547

Acquisition Time (sec)	1.0924	**Comment**	STANDARD CARBON PARAMETERS			**Date**	Jul 26 2012
Date Stamp	Jul 26 2012	**File Name**	\\rcfs1.rc.fas.harvard.edu\betley_lab\Users\ascharf\Betley\Characterization Data\as-4-38\as-4-38_c13.fid\fid				
Frequency (MHz)	125.71	**Nucleus**	13C	**Number of Transients**	1024	**Original Points Count**	32768
Points Count	32768	**Pulse Sequence**	s2pul	**Receiver Gain**	60.00	**Solvent**	Benzene
Spectrum Offset (Hz)	13942.2891	**Spectrum Type**	STANDARD	**Sweep Width (Hz)**	29996.25	**Temperature (degree C)**	25.000



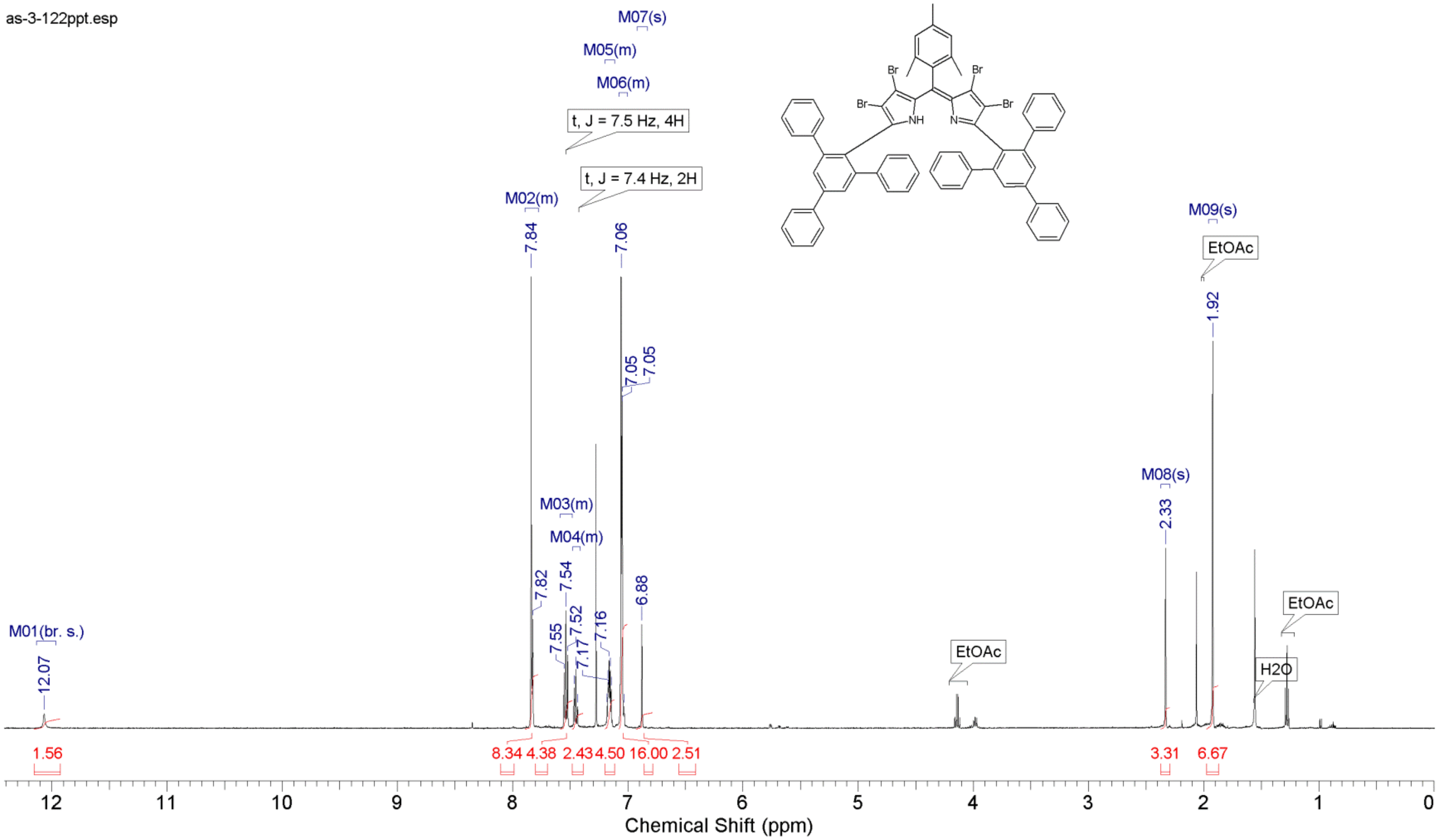
No.	(ppm)	(Hz)	Height
1	19.82	2491.5	0.0574
2	21.06	2647.1	0.0276
3	121.37	15257.3	0.0420
4	125.17	15734.3	0.1356
5	126.10	15851.4	0.0950
6	127.36	16009.8	0.2298
7	127.56	16034.5	0.1858
8	127.77	16061.1	0.0722
9	127.81	16066.6	0.0846
10	128.29	16127.0	0.1205
11	128.44	16145.3	1.0000
12	129.09	16227.7	0.2342
13	134.23	16873.1	0.0255
14	136.43	17150.5	0.0325
15	136.53	17162.4	0.0415
16	136.75	17190.7	0.0295
17	137.64	17302.4	0.0612
18	140.52	17664.9	0.0363
19	140.62	17676.8	0.0320
20	140.74	17692.4	0.0358
21	142.75	17944.1	0.0900
22	145.13	18243.5	0.0301
23	155.48	19545.2	0.0528

Figure S4. ^{1}HNMR Spectrum of (^{BrAr}L)H

as-3-122ppt.esp, processed on **09/01/2013** at **12:00**

Acquisition Time (sec)	2.1853	***Comment***	S/N = 351	***Date***	Jul 21 2011	***Date Stamp***	Jul 21 2011
File Name	\\rcfs1.rc.fas.harvard.edu\betley_lab\Users\ascharf\Betley\Characterization Data\as-3-122\as-3-122ppt.fid\fid					***Frequency (MHz)***	499.87
Nucleus	1H	***Number of Transients***	16	***Pulse Sequence***	s2pul	***Receiver Gain***	46.00
Solvent	CHLOROFORM-d			***Spectrum Offset (Hz)***	3299.4473	***Spectrum Type***	STANDARD
Sweep Width (Hz)	9995.00	***Temperature (degree C)***	25.000				

^{1}H NMR (500 MHz, CHLOROFORM-*d*) δ ppm 1.92 (s, 6 H) 2.33 (s, 3 H) 6.88 (s, 2 H) 7.00 - 7.08 (m, 16 H) 7.11 - 7.20 (m, 4 H) 7.41 - 7.48 (m, 2 H) 7.48 - 7.59 (m, 4 H) 7.77 - 7.89 (m, 8 H) 12.07 (br. s., 1 H)



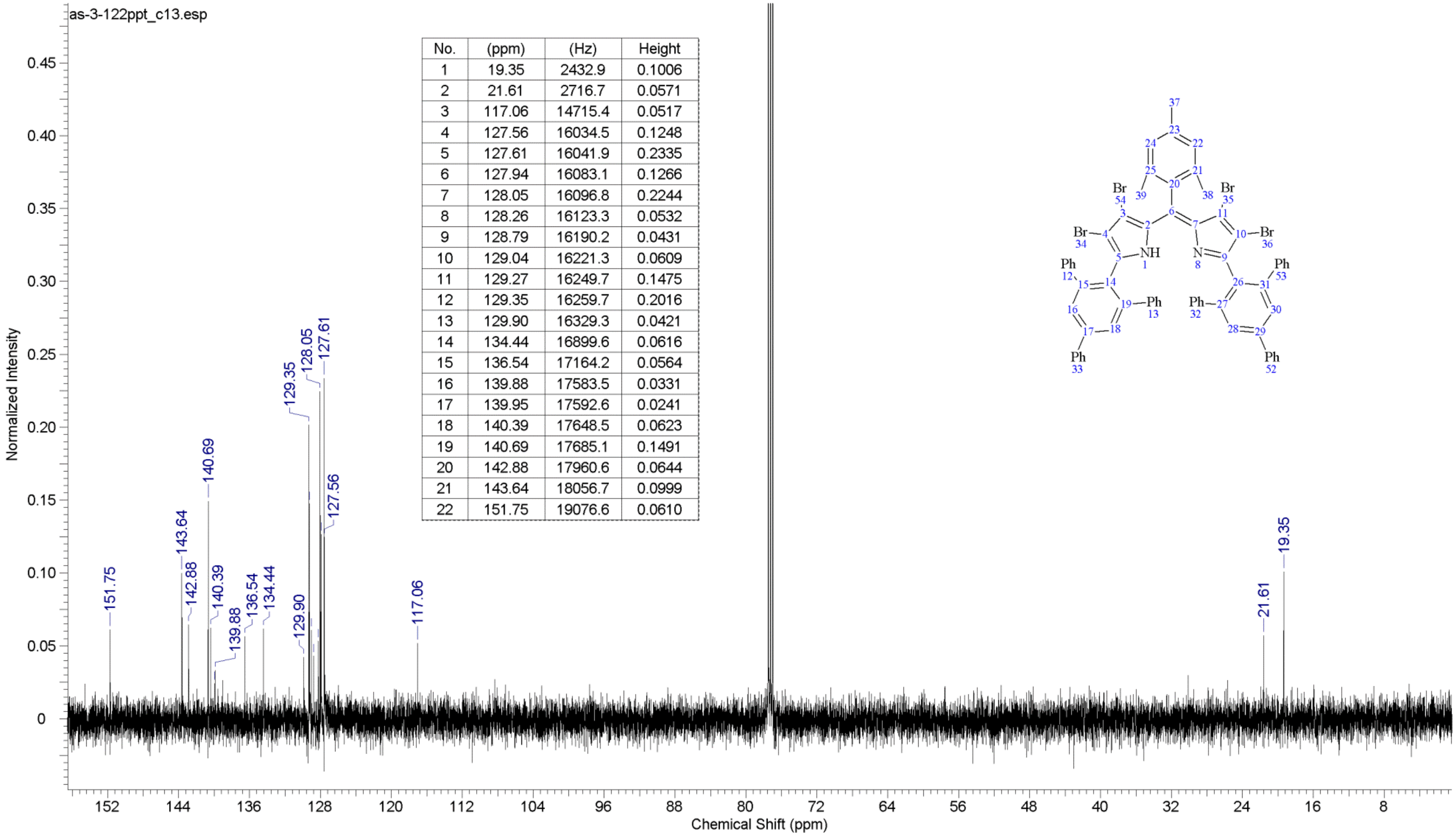
as-3-122ppt.esp

Figure S5. ^{13}CNMR Spectrum of (^{BrAr}L)H

1/9/2013 2:18:47 PM

Formula $C_{66}H_{46}Br_4N_2$	**FW** 1186.7008

Acquisition Time (sec)	1.0924	**Comment**	STANDARD CARBON PARAMETERS			**Date**	Jul 21 2011
Date Stamp	Jul 21 2011	**File Name**	\\rcfs1.rc.fas.harvard.edu\betley_lab\Users\ascharf\Betley\Characterization Data\as-3-122\as-3-122ppt_c13.fid\fid				
Frequency (MHz)	125.71	**Nucleus**	13C	**Number of Transients**	1024	**Original Points Count**	32768
Points Count	32768	**Pulse Sequence**	s2pul	**Receiver Gain**	60.00	**Solvent**	CHLOROFORM-d
Spectrum Offset (Hz)	13942.3018	**Spectrum Type**	STANDARD	**Sweep Width (Hz)**	29996.25	**Temperature (degree C)**	25.000



No.	(ppm)	(Hz)	Height
1	19.35	2432.9	0.1006
2	21.61	2716.7	0.0571
3	117.06	14715.4	0.0517
4	127.56	16034.5	0.1248
5	127.61	16041.9	0.2335
6	127.94	16083.1	0.1266
7	128.05	16096.8	0.2244
8	128.26	16123.3	0.0532
9	128.79	16190.2	0.0431
10	129.04	16221.3	0.0609
11	129.27	16249.7	0.1475
12	129.35	16259.7	0.2016
13	129.90	16329.3	0.0421
14	134.44	16899.6	0.0616
15	136.54	17164.2	0.0564
16	139.88	17583.5	0.0331
17	139.95	17592.6	0.0241
18	140.39	17648.5	0.0623
19	140.69	17685.1	0.1491
20	142.88	17960.6	0.0644
21	143.64	18056.7	0.0999
22	151.75	19076.6	0.0610

Figure S6. ^{1}HNMR Spectrum of ($^{\text{BrAr}}$L)Li(THF)

as-3-153b.esp, processed on **09/01/2013** at **13:54**

Acquisition Time (sec)	2.1853	***Comment***	S/N = 351	***Date***	Sep 20 2011	***Date Stamp***	Sep 20 2011
File Name	\\rcfs1.rc.fas.harvard.edu\betley_lab\Users\ascharf\Betley\Characterization Data\as-3-153\as-3-153b.fid\fid					***Frequency (MHz)***	499.88
Nucleus	1H	***Number of Transients***	16	***Pulse Sequence***	s2pul	***Receiver Gain***	46.00
Solvent	Benzene	***Spectrum Offset (Hz)***	3299.4590	***Spectrum Type***	STANDARD	***Sweep Width (Hz)***	9995.00
Temperature (degree C)	25.000						

^{1}H NMR (500 MHz, Benzene) δ ppm 1.20 (br. s., 4 H) 2.22 (s, 3 H) 2.25 (s, 6 H) 3.24 (br. s., 4 H) 6.95 (s, 2 H) 6.95 - 7.01 (m, 8 H) 7.03 (d, *J*=7.32 Hz, 4 H) 7.14 (s, 6 H) 7.22 (d, *J*=7.32 Hz, 12 H) 7.45 (d, *J*=7.32 Hz, 4 H) 7.69 (s, 4 H)

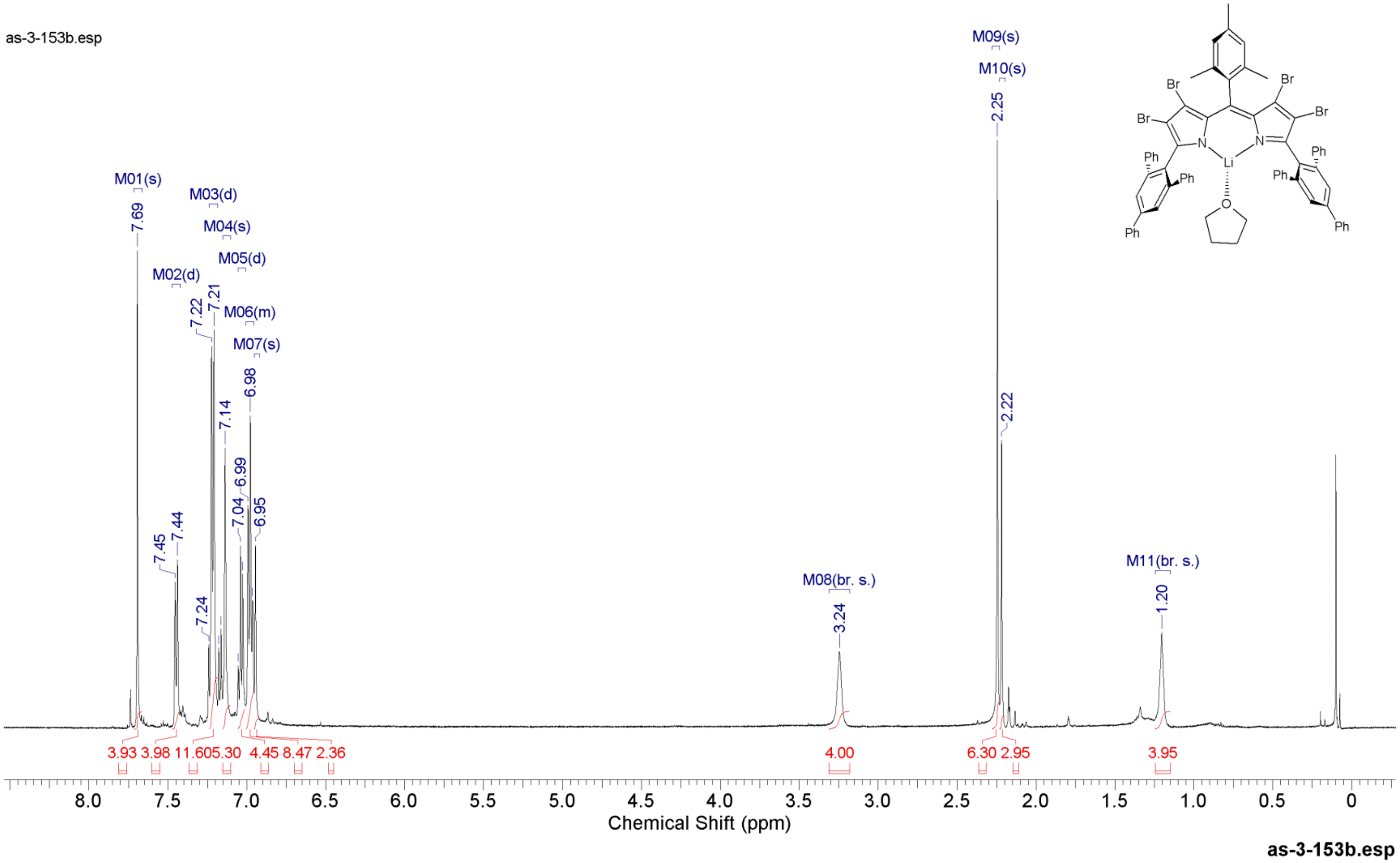
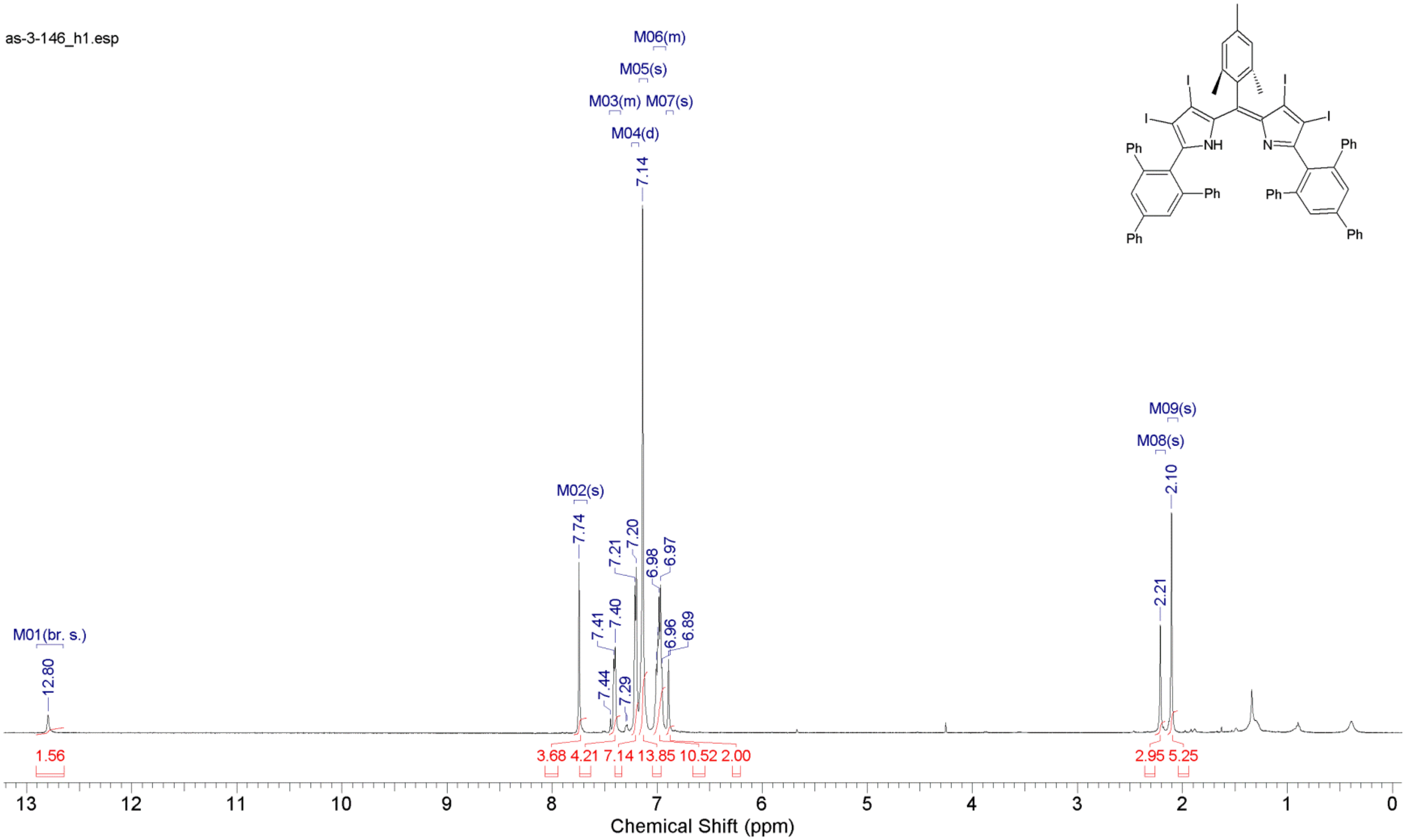


Figure S7. ^{1}HNMR Spectrum of (^{IAr}L)H

as-3-146_h1.esp, processed on **09/01/2013** at **12:25**

Acquisition Time (sec)	2.1853	***Comment***	S/N = 351	***Date***	Sep 6 2011	***Date Stamp***	Sep 6 2011
File Name	\\rcfs1.rc.fas.harvard.edu\betley_lab\Users\ascharf\Betley\Characterization Data\as-3-146\as-3-146_h1.fid\fid					***Frequency (MHz)***	499.88
Nucleus	1H	***Number of Transients***	16	***Pulse Sequence***	s2pul	***Receiver Gain***	40.00
Solvent	Benzene	***Spectrum Offset (Hz)***	3299.4590	***Spectrum Type***	STANDARD	***Sweep Width (Hz)***	9995.00
Temperature (degree C)	25.000						

^{1}H NMR (500 MHz, Benzene) δ ppm 2.10 (s, 6 H) 2.21 (s, 3 H) 6.89 (s, 2 H) 6.92 - 7.03 (m, 8 H) 7.14 (s, 12 H) 7.21 (d, *J*=7.02 Hz, 6 H) 7.35 - 7.45 (m, 4 H) 7.74 (s, 4 H) 12.80 (br. s., 1 H)



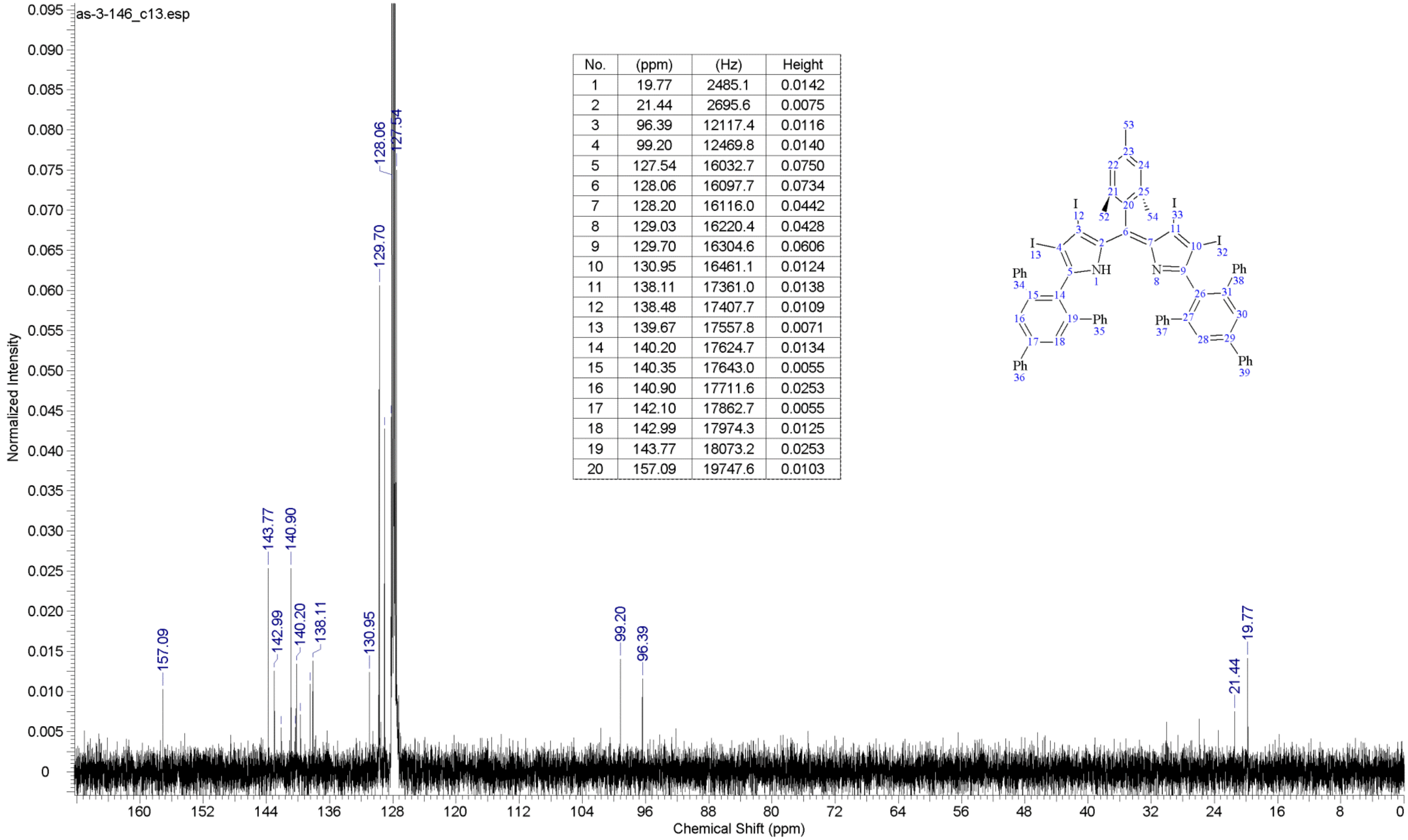
as-3-146_h1.esp

Figure S9. ^{13}CNMR Spectrum of (^{IAr}L)H

1/9/2013 2:14:12 PM

Formula $C_{66}H_{46}I_4N_2$	**FW**	1374.7027

Acquisition Time (sec)	1.0924	**Comment**	STANDARD CARBON PARAMETERS			**Date**	Sep 6 2011
Date Stamp	Sep 6 2011	**File Name**	\\rcfs1.rc.fas.harvard.edu\betley_lab\Users\ascharf\Betley\Characterization Data\as-3-146\as-3-146_c13.fid\fid				
Frequency (MHz)	125.71	**Nucleus**	13C	**Number of Transients**	1024	**Original Points Count**	32768
Points Count	32768	**Pulse Sequence**	s2pul	**Receiver Gain**	60.00	**Solvent**	Benzene
Spectrum Offset (Hz)	13942.2891	**Spectrum Type**	STANDARD	**Sweep Width (Hz)**	29996.25	**Temperature (degree C)**	25.000



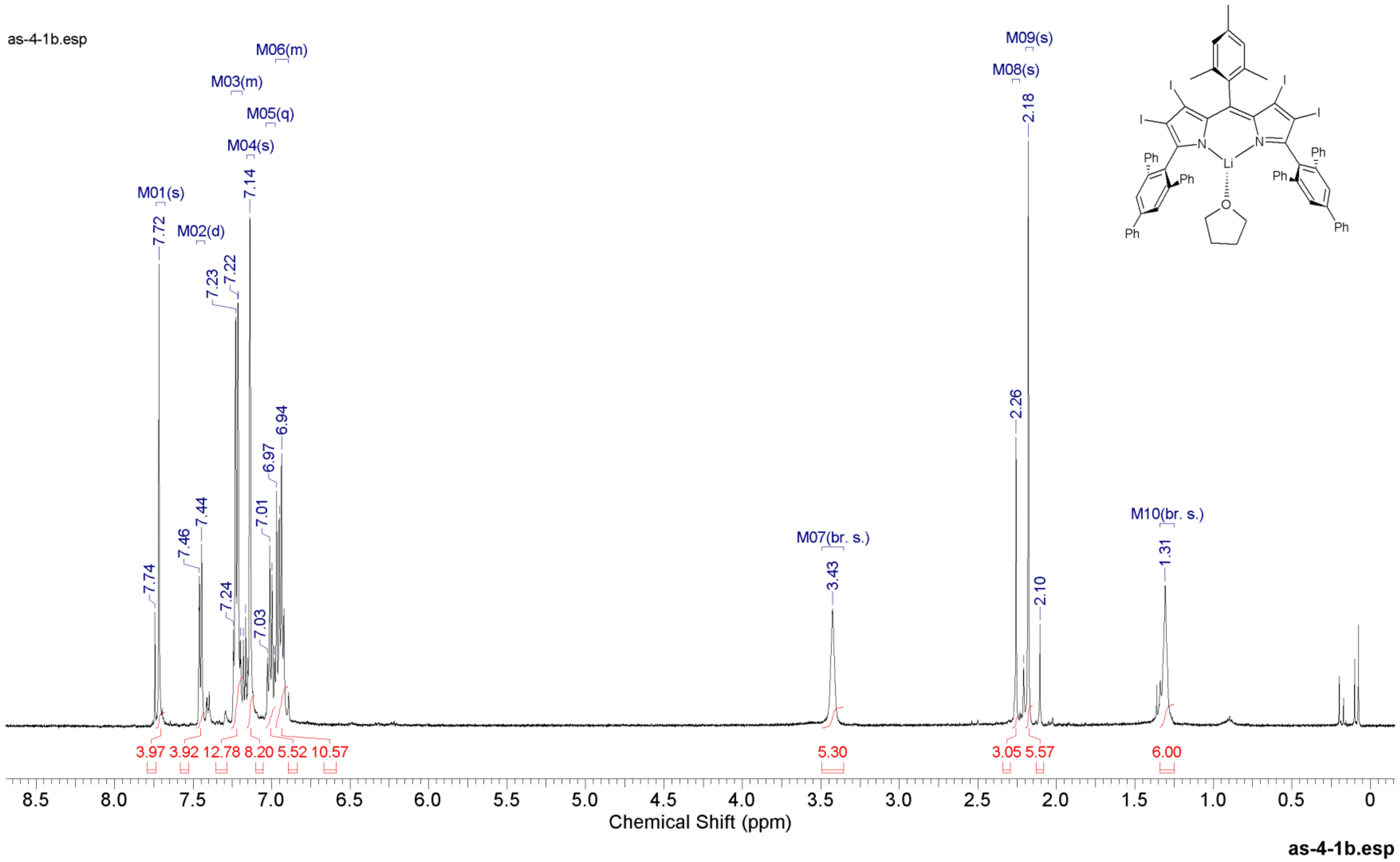
No.	(ppm)	(Hz)	Height
1	19.77	2485.1	0.0142
2	21.44	2695.6	0.0075
3	96.39	12117.4	0.0116
4	99.20	12469.8	0.0140
5	127.54	16032.7	0.0750
6	128.06	16097.7	0.0734
7	128.20	16116.0	0.0442
8	129.03	16220.4	0.0428
9	129.70	16304.6	0.0606
10	130.95	16461.1	0.0124
11	138.11	17361.0	0.0138
12	138.48	17407.7	0.0109
13	139.67	17557.8	0.0071
14	140.20	17624.7	0.0134
15	140.35	17643.0	0.0055
16	140.90	17711.6	0.0253
17	142.10	17862.7	0.0055
18	142.99	17974.3	0.0125
19	143.77	18073.2	0.0253
20	157.09	19747.6	0.0103

Figure S10. ^{1}HNMR Spectrum of ($^{\mathrm{IAr}}$L)Li(THF)$_{1.5}$

as-4-1b.esp, processed on **09/01/2013** at **13:49**

Acquisition Time (sec)	2.1853	***Comment***	S/N = 351	***Date***	Sep 20 2011	***Date Stamp***	Sep 20 2011
File Name	\\rcfs1.rc.fas.harvard.edu\betley_lab\Users\ascharf\Betley\Characterization Data\as-4-1\as-4-1b.fid\fid					***Frequency (MHz)***	499.88
Nucleus	1H	***Number of Transients***	16	***Pulse Sequence***	s2pul	***Receiver Gain***	50.00
Solvent	Benzene	***Spectrum Offset (Hz)***	3299.4590	***Spectrum Type***	STANDARD	***Sweep Width (Hz)***	9995.00
Temperature (degree C)	25.000						

^{1}H NMR (500 MHz, Benzene) δ ppm 1.31 (br. s., 6 H) 2.18 (s, 6 H) 2.26 (s, 3 H) 3.43 (br. s., 6 H) 6.89 - 6.97 (m, 10 H) 7.00 (q, *J*=7.52 Hz, 6 H) 7.14 (s, 8 H) 7.19 - 7.26 (m, 12 H) 7.45 (d, *J*=7.32 Hz, 4 H) 7.72 (s, 4 H)



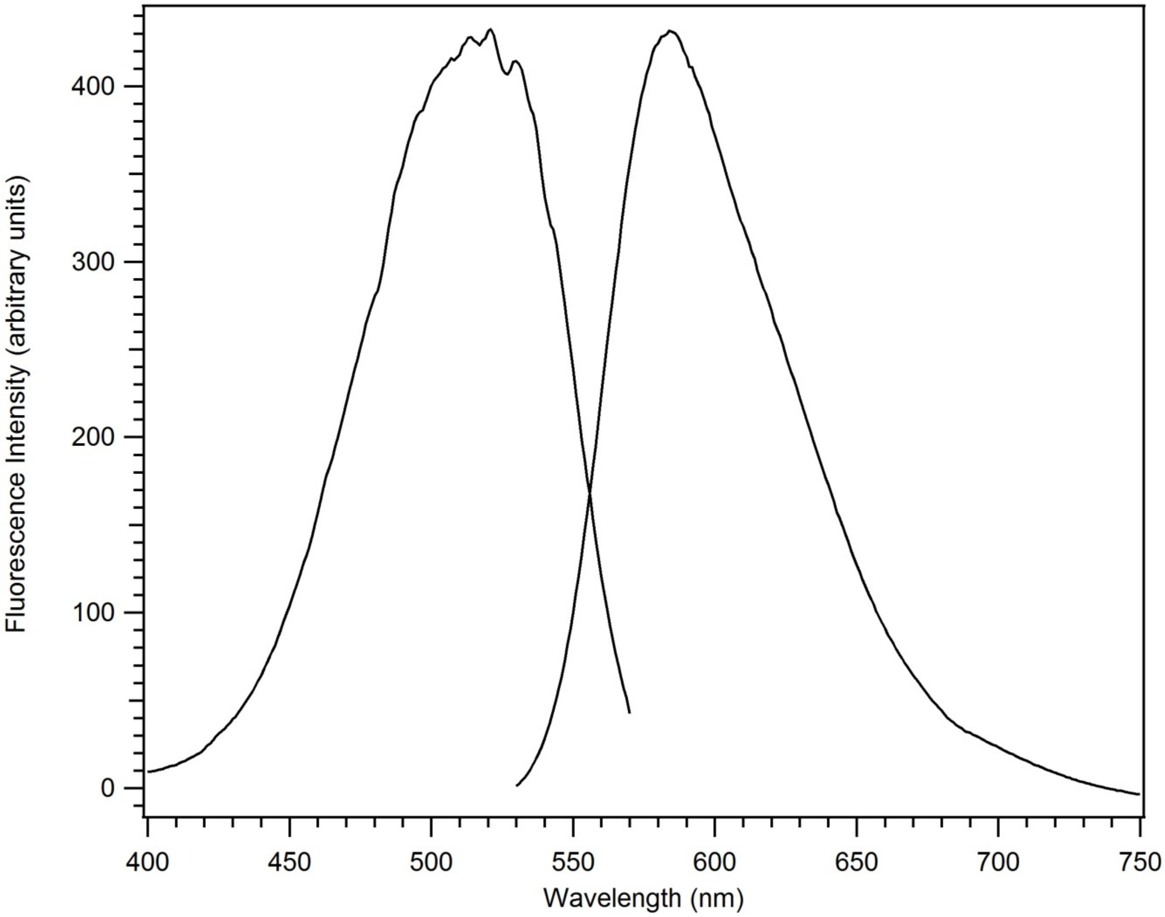
Luminescence Spectra

Luminescence measurements were performed on a Varian Cary Eclipse fluorescence spectrophotometer operating with a scan rate of 600 nm/min, a data interval of 1 nm, and an averaging time of 0.10 seconds. Other instrument settings (emission and excitation slit widths, PMT detector voltage) were optimized for each individual sample. Relative quantum yields of optically dilute solutions (absorbance < 0.1, concentrations ~10^{-6} – 10^{-7} *M*) were calculated in comparison to dilute solutions of Rhodamine 6G in absolute ethanol ($\Phi = 0.95 \pm 0.005$)[4] according to the equation[5]

$$\Phi_x = \Phi_r \left(\frac{A_r}{A_x}\right)\left(\frac{I_r}{I_x}\right)\left(\frac{D_x}{D_r}\right)\left(\frac{n_x}{n_r}\right)^2$$

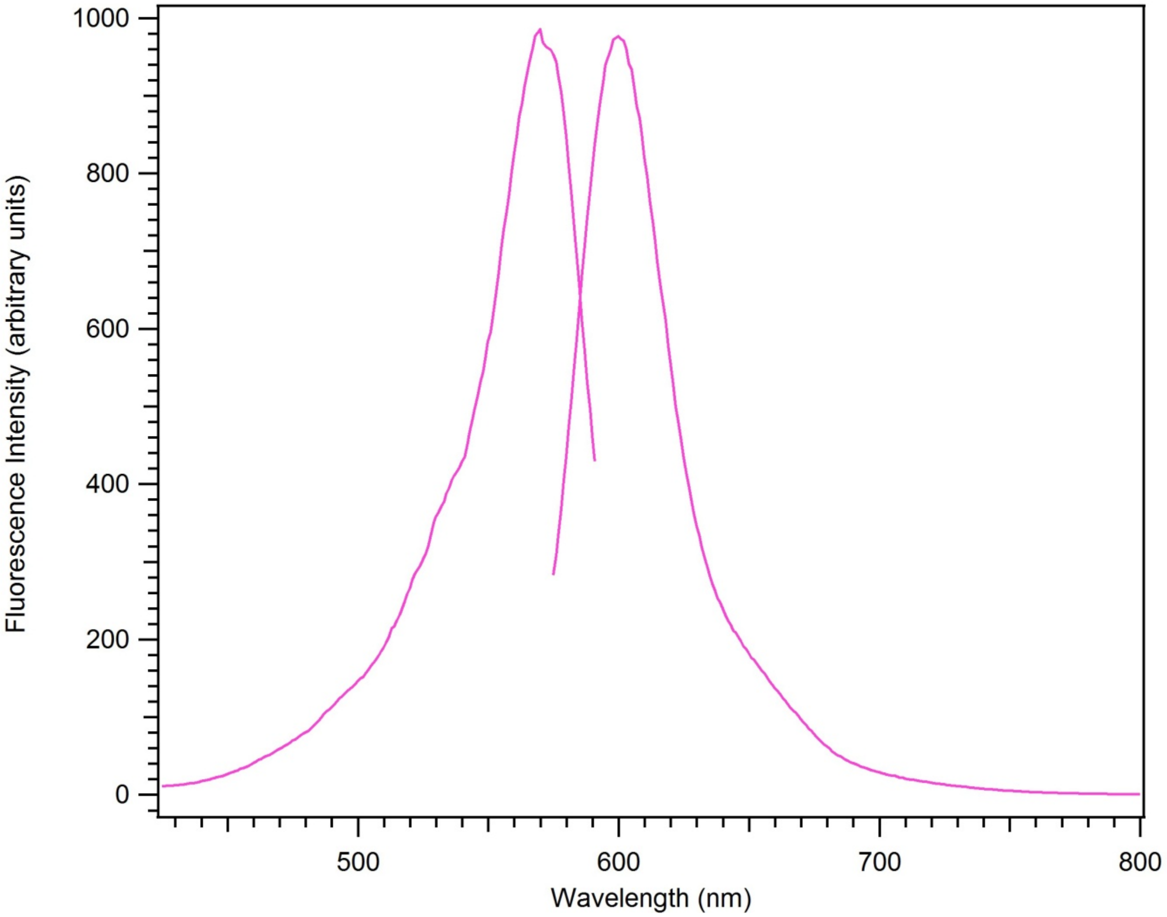
where A is the absorbance at the excitation wavelength, I is the intensity of the incident light, D is the integrated area under the emission curve (calculated by trapezoidal numerical integration of the spectrum in Microsoft Excel), n is the refractive index of the solvent, and subscripts x and r denote the analyte and reference solutions, respectively. For identical instrument configurations between analyte and reference solutions, I_r/I_x was considered to be unity. However, for weakly-emitting samples ($\Phi < 0.05$), the instrument settings used to obtain acceptable excitation and emission spectra of the analyte gave over-range fluorescence intensities for the Rhodamine 6G reference solution. In these cases, either the voltage of the PMT detector was lowered or the slit widths were decreased for the reference solution measurement, and the intensity ratios I_r/I_x were calculated by linear calibration of the instrument response to the altered measurement conditions. Quantum yields are reported with ±0.10 intervals.

Figure S11. $(^{Ar}L)H$



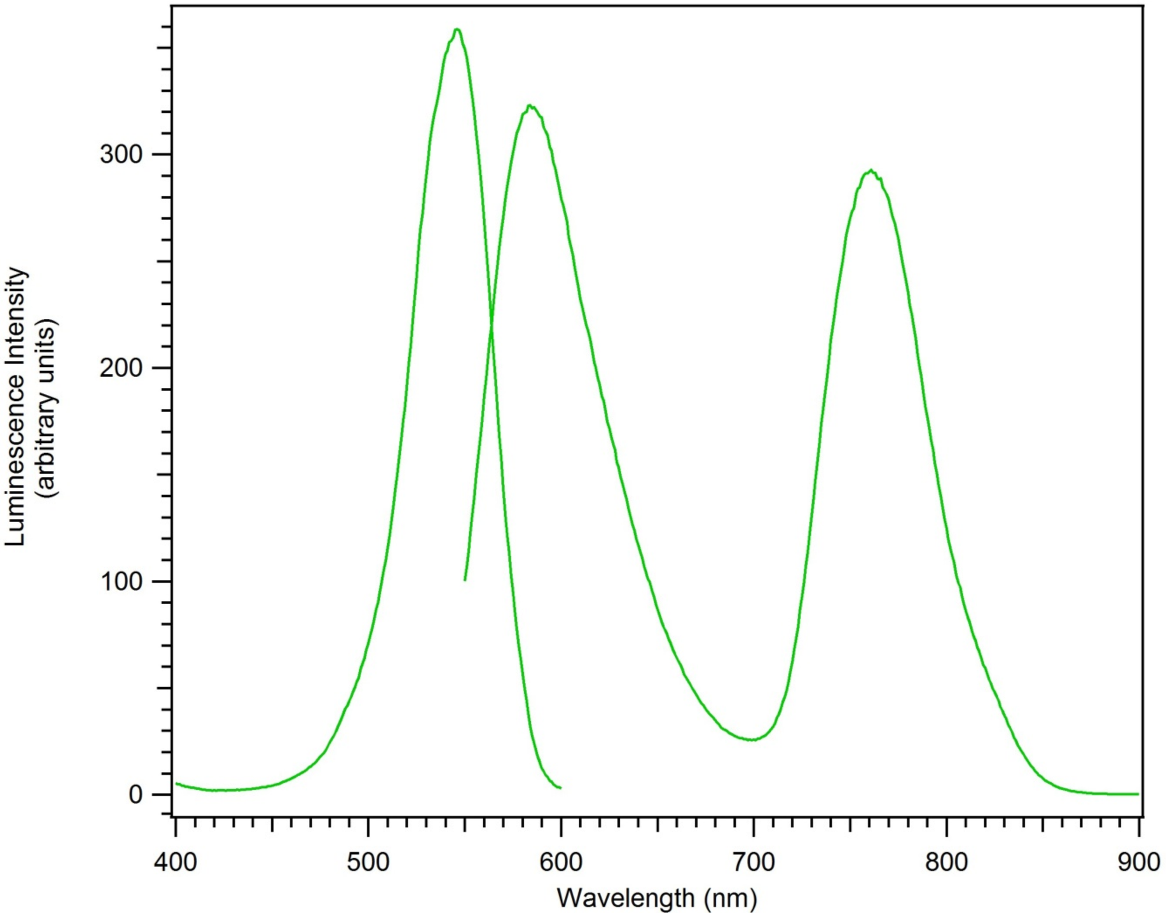
Excitation maximum: 520 nm
Emission maximum: 584 nm
Stokes shift: 64 nm
Absorbance at 520 nm: 0l087
Φ = 0.16
Ex/Em slit widths: 5/5 nm
PMT detector voltage: 600 V

Figure S12. (^{Ar}L)Li(THF)$_2$



Excitation maximum: 570 nm
Emission maximum: 600 nm
Stokes shift: 30 nm
Absorption at 540 nm: 0.026
Φ = 0.51
Ex/Em slit widths: 5/5 nm
Detector voltage: 600 V

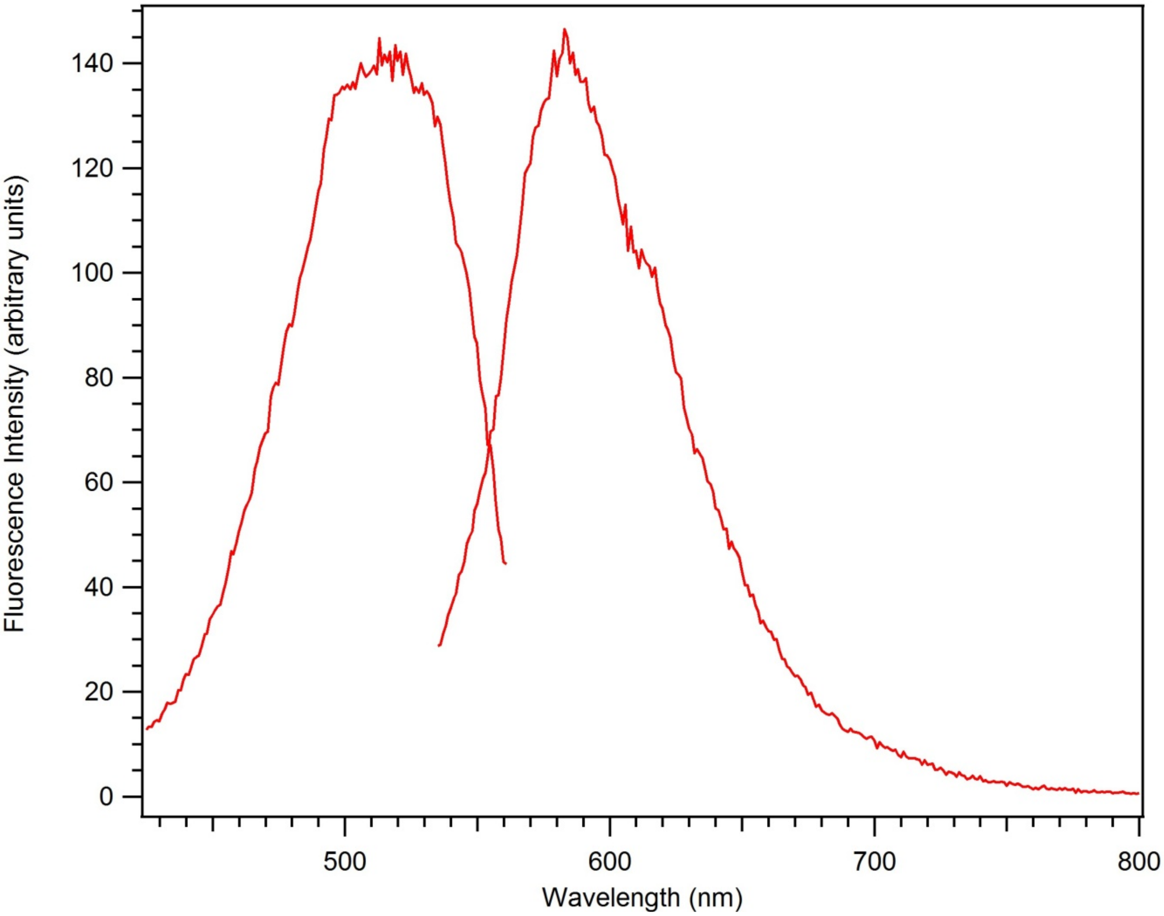
Figure S13. (^{Ar}L)MnCl(THF)



This spectrum was obtained without added THF; see next section for spectrum with THF added.

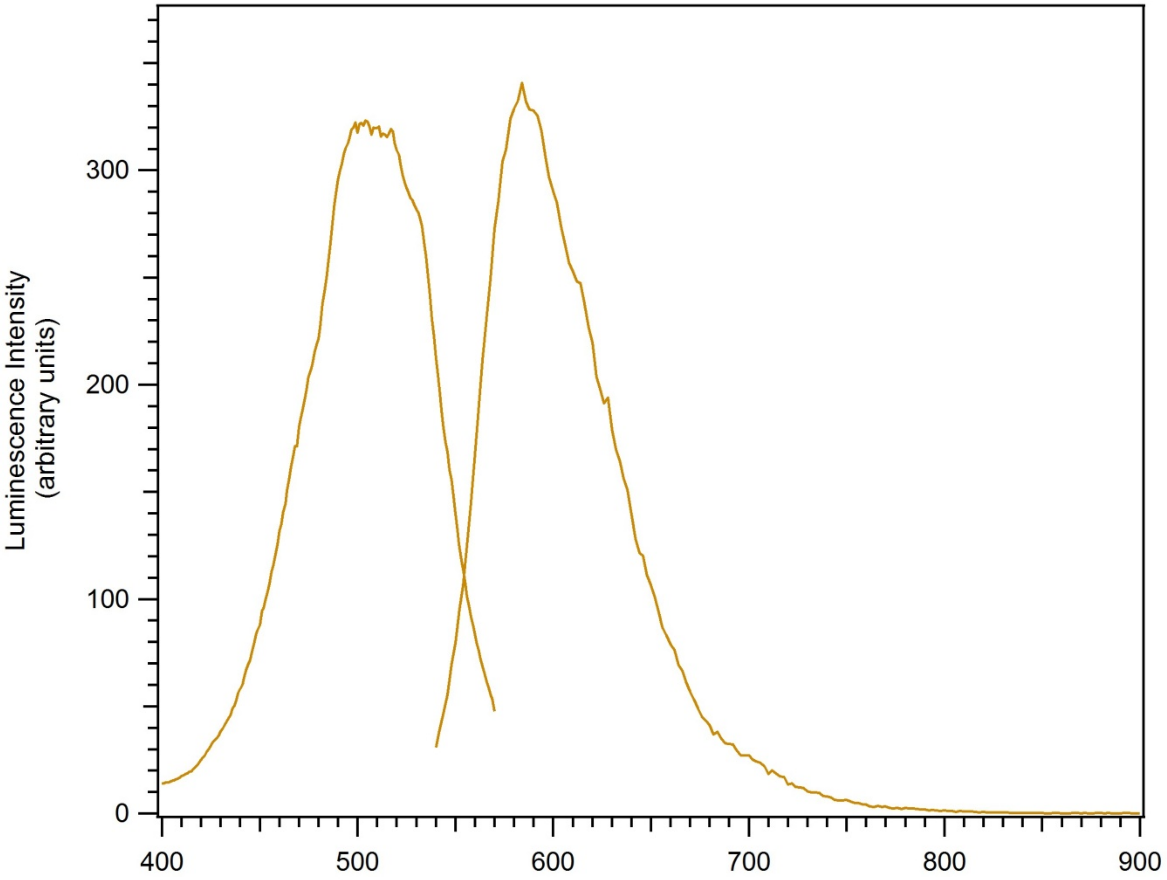
Fluorescence excitation maximum: 532 nm
Fluorescence emission maximum: 579 nm
Fluorescence Stokes shift: 47 nm
Phosphorescence excitation maximum: 546 nm
Phosphorescence emission maximum: 761 nm
Phosphorescence Stokes shift: 215 nm
Absorbance at 545 nm: 0.059
Φ(total) = 0.03
Ex/Em slid widths: 10/10 nm
PMT Detector voltage: 800 V

Figure S14. (^{Ar}L)FeCl(THF)



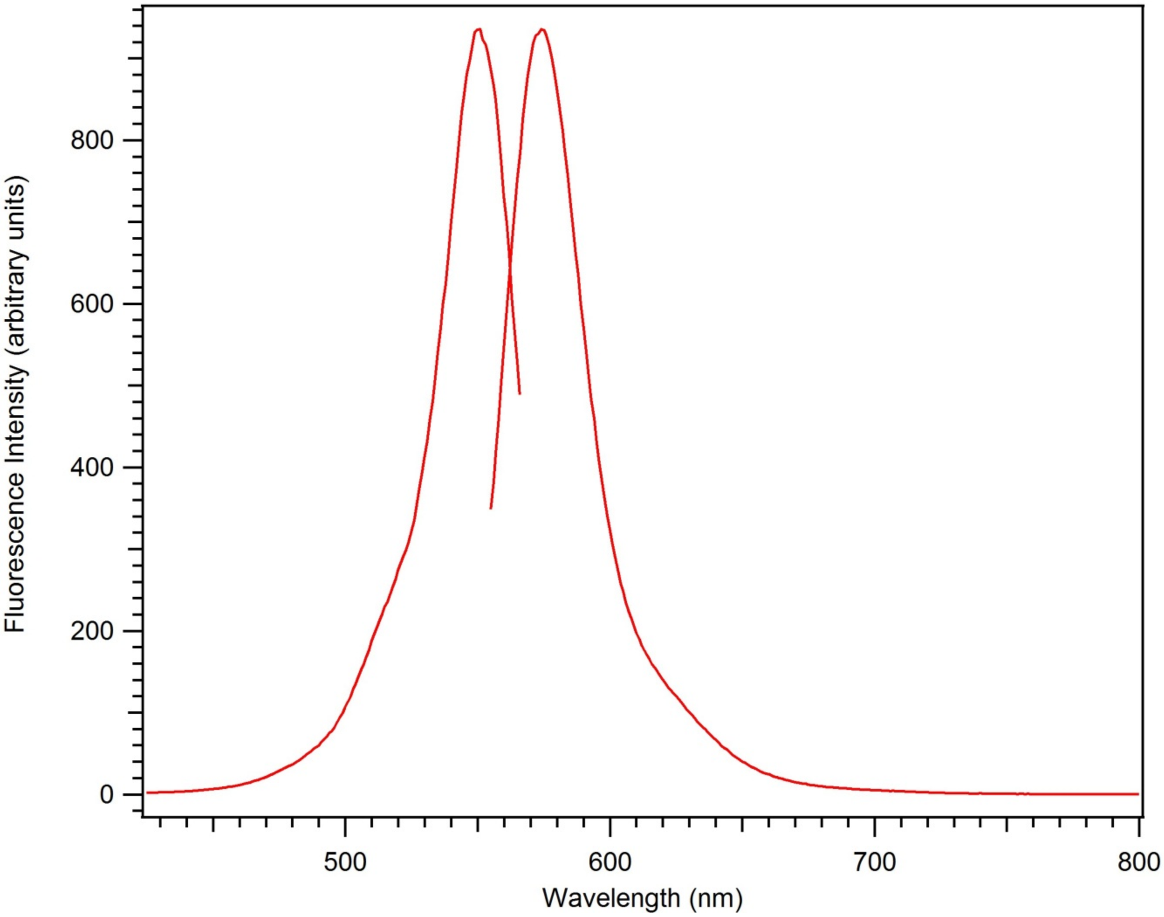
Excitation maximum: 519 ± 4 nm
Emission maximum: 583 nm
Stokes shift: 64 ± 4 nm
Absorbance at 530 nm: 0.033
$\Phi < 0.001$
Ex/Em slit widths: 5/10 nm
PMT Detector voltage: 800 V

Figure S15. $(^{Ar}L)Cu^{II}Cl$



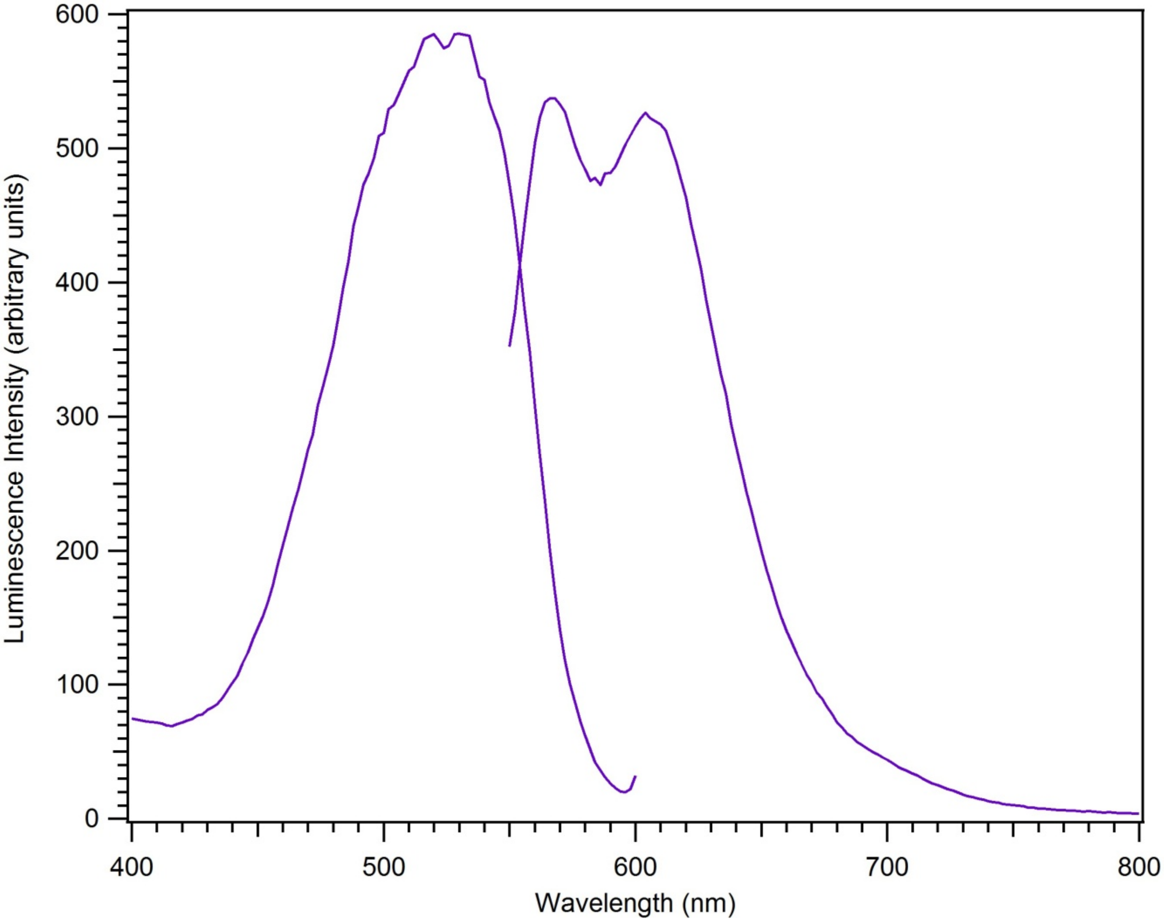
Excitation maximum: 504 nm
Emission maximum: 588 nm
Stokes shift: 84 nm
$\Phi = 0.03$
Ex/Em slit widths: 5/5 nm
PMT Detector voltage: 600 V

Figure S16. (^{Ar}L)ZnCl(THF)



Excitation maximum: 550 nm
Emission maximum: 574 nm
Stokes shift: 24 nm
Absorption at 550 nm: 0.027
$\Phi = 0.67$
Ex/Em slit widths: 5/5 nm
PMT Detector voltage: 600 V

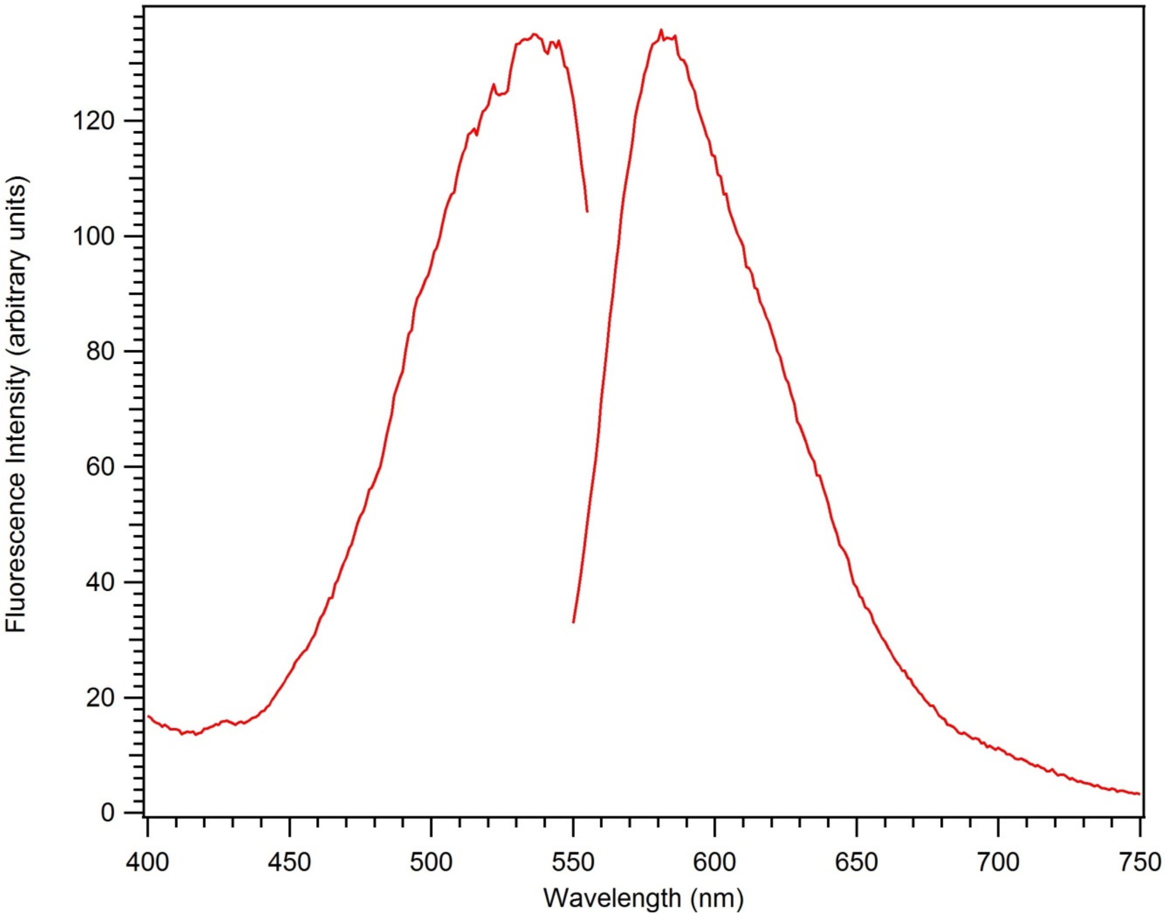
Figure S17. $(^{Ar}L)Cu^I$



This spectrum was taken with no acetonitrile added; see the next section for more details.

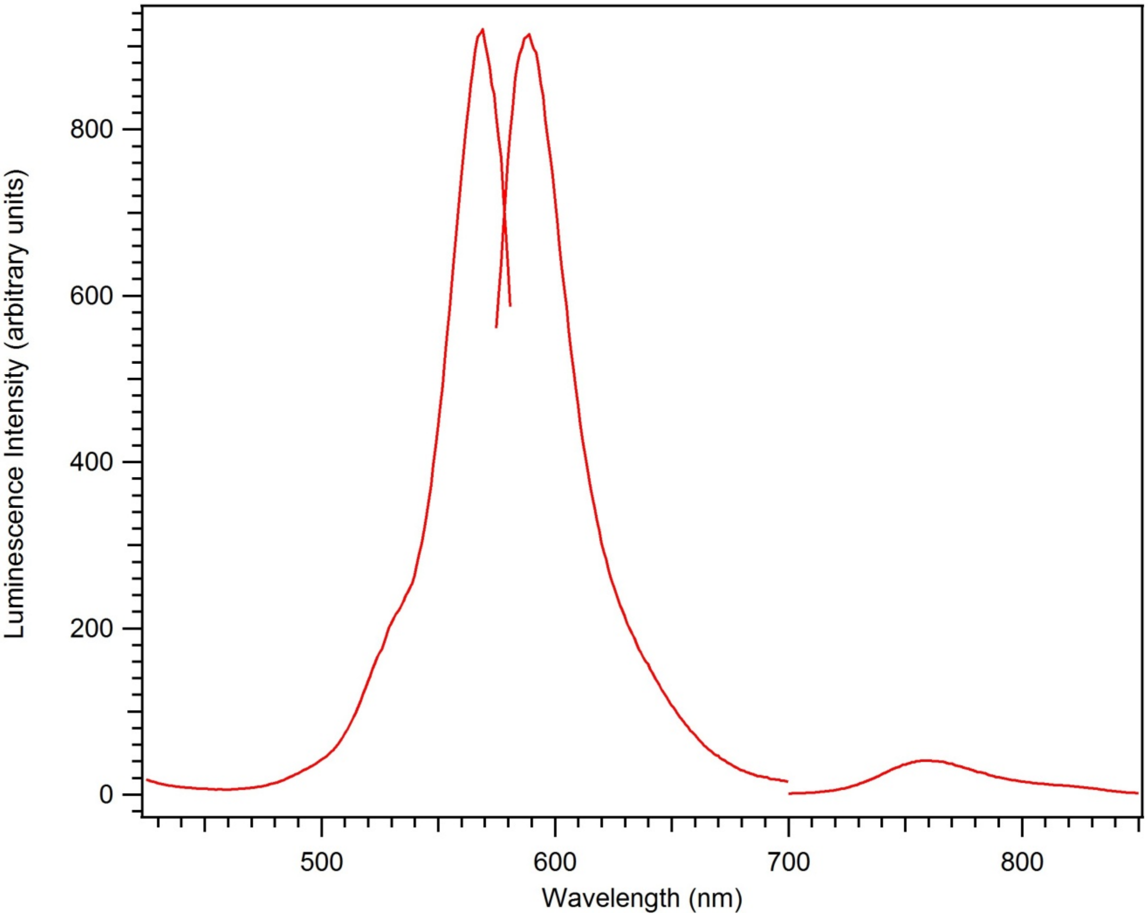
Excitation maxima: 532 & 544 nm
Emission maxima: 567 & 605 nm
Stokes shifts: 35 & 61 nm
Φ(total) ~ 0.03 vs. Rhodamine 6G in EtOH
Ex/Em slit widths: 5/10 nm
PMT Detector voltage: 600 V

Figure S18. (^{BrAr}L)H



Excitation maximum: 535 nm
Emission maximum: 583 nm
Stokes shift: 48 nm
Φ = 0.005
Ex/Em slit widths: 5/5 nm
PMT Detector voltage: 800 V

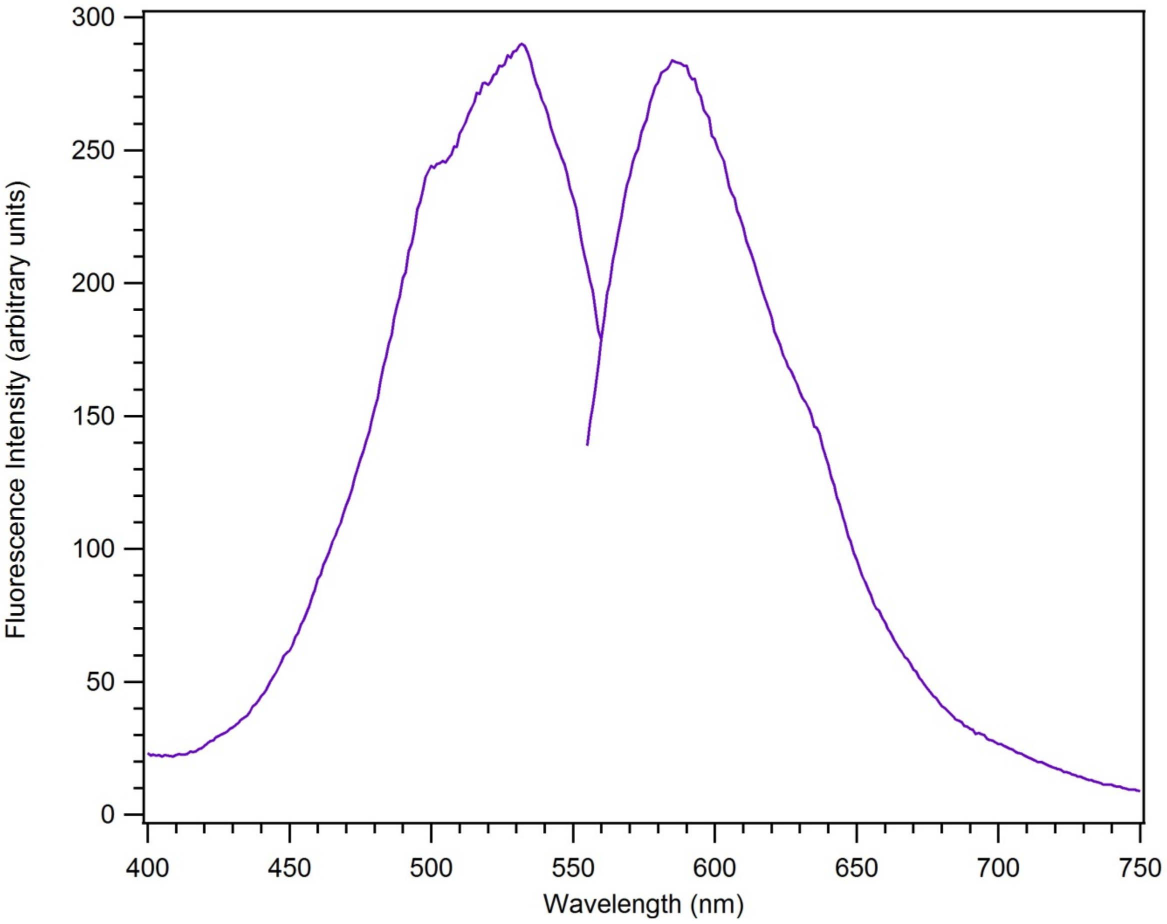
Figure S19. (^{BrAr}L)Li(THF)



The fluorescence and phosphorescence emission curves are NOT shown to scale; the phosphorescence curve is magnified by ~10x in order to be able to be seen.

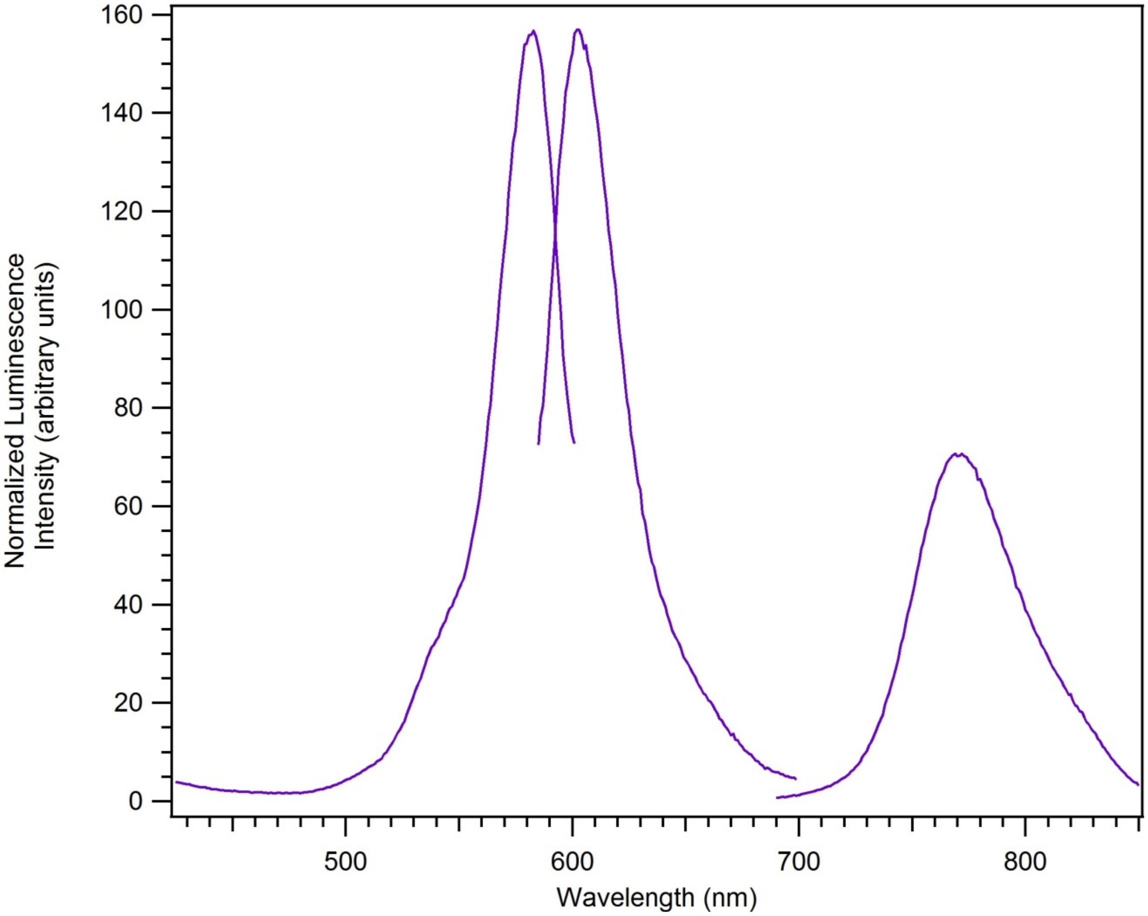
Fluorescence excitation maximum: 569 nm
Fluorescence emission maximum: 589 nm
Phosphorescence emission maximum: 760 nm
Stokes shift of fluorescence: 20 nm
Stokes shift of phosphorescence 171 nm
Φ(fluor) = 0.21
Φ(phos) = 0.002
Ex/Em slit widths (fluorescence): 2.5/5 nm
Ex/Em slit widths (phosphorescence): 5/10 nm
PMT Detector voltage (fluorescence): 600 V
PMT Detector voltage (phosphorescence): 800 V

Figure S20. (^{IAr}L)H



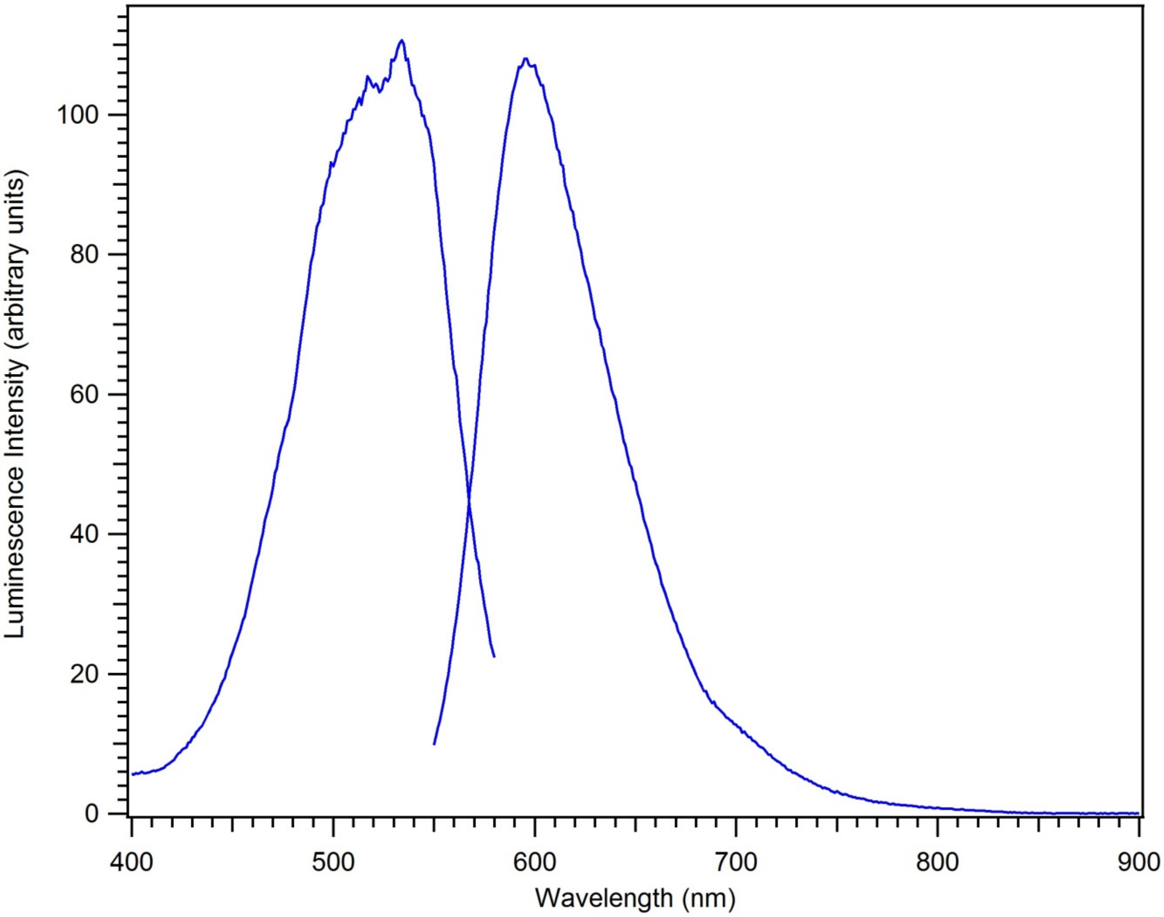
Excitation maximum: 532 nm
Emission maximum: 585 nm
Stokes shift: 53 nm
$\Phi = 0.002$
Ex/Em slit widths: 10/10 nm
PMT Detector voltage: 800 V

Figure S21. $(^{IAr}L)Li(THF)_{1.5}$



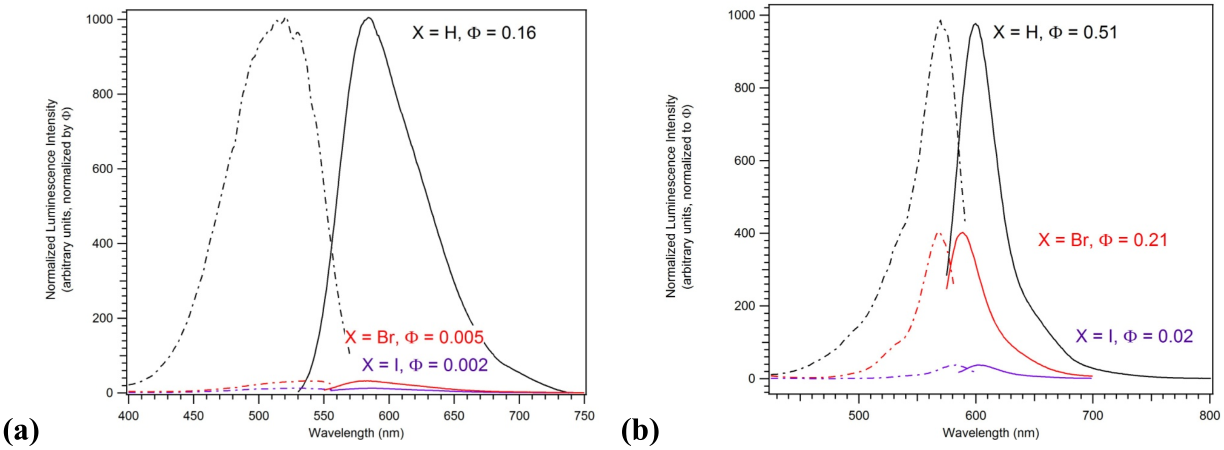
Fluorescence excitation maximum: 583 nm
Fluorescence emission maximum: 603 nm
Phosphorescence emission maximum: 772 nm
Stokes shift of fluorescence: 20 nm
Stokes shift of phosphorescence: 189 nm
Φ(fluor) = 0.017
Φ (phos) = 0.008
Ex/Em slit widths (fluorescence): 5/5 nm
Ex/Em slit widths (phosphorescence): 5/10 nm
PMT Detector voltage (fluorescence): 600 V
PMT Detector voltage (phosphorescence): 800 V

Figure S22. $(^{IAr}L)MnCl(THF)$



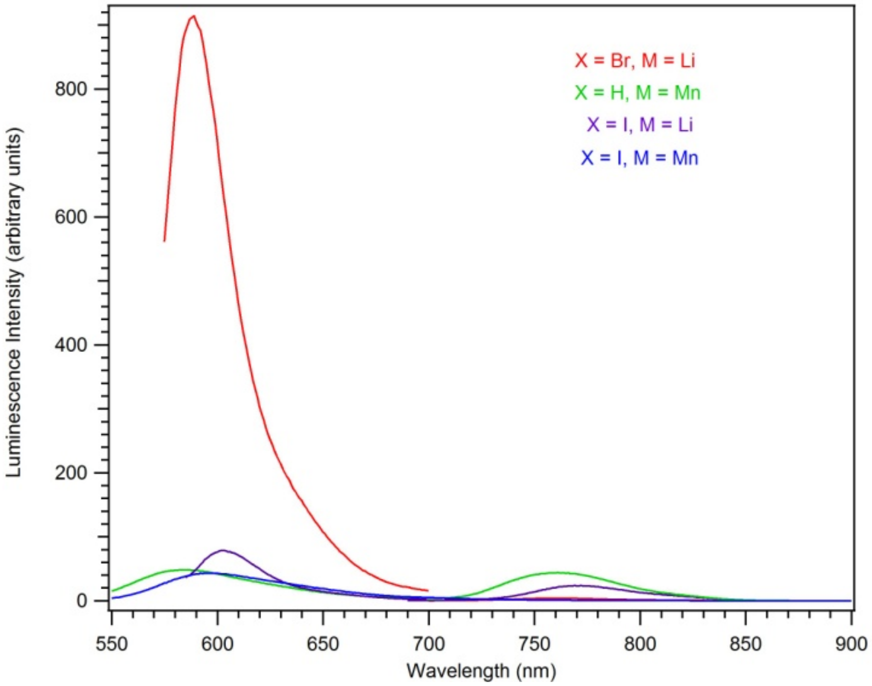
Excitation maximum: 534 nm
Emission maximum: 595 nm
Stokes shift: 61 nm
$\Phi = 0.020$
Ex/Em slit widths: 10/5 nm
PMT Detector voltage: 600 V

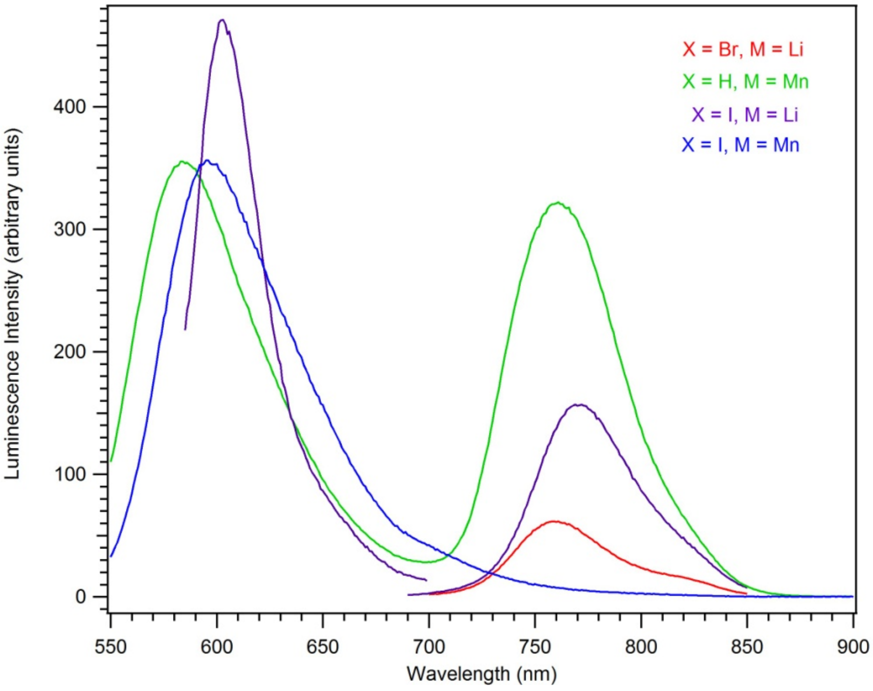
Figure S23. Fluorescence Spectra of Halogenated Species



(a) Black, $(^{Ar}L)H$; red, $(^{BrAr}L)H$; purple $(^{IAr}L)H$. (b) Black, $(^{Ar}L)Li(THF)_2$; red, $(^{BrAr}L)Li(THF)$; purple $(^{IAr}L)Li(THF)_{1.5}$. Intensities are normalized to Φ and are reported on an arbitrary y-axis.

Figure S24. Emission Spectra of Phosphorescent Samples

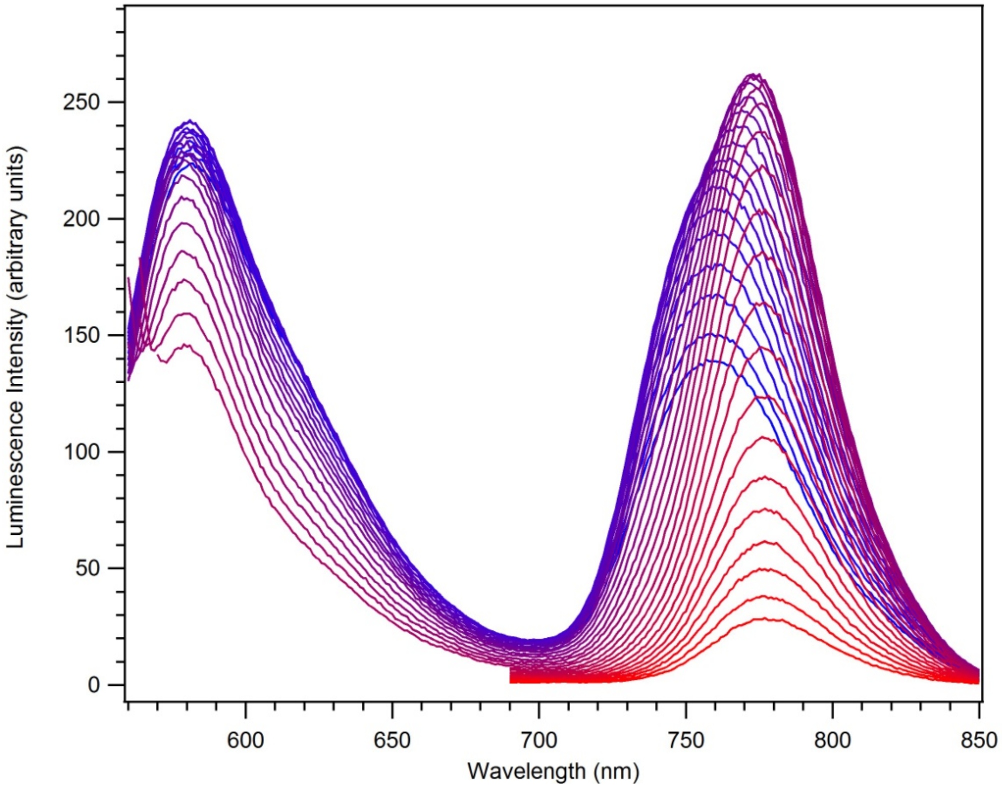




Red, (^{BrAr}L)Li(THF); purple, (^{IAr}L)Li(THF)$_{1.5}$; green, (^{Ar}L)MnCl(THF); blue, (^{IAr}L)MnCl(THF). Top: normalized emission spectra for all species; bottom: magnified emission spectra of all species, omitting the fluorescence emission curve of (^{BrAr}L)Li(THF), which dwarfs the other emission intensities.

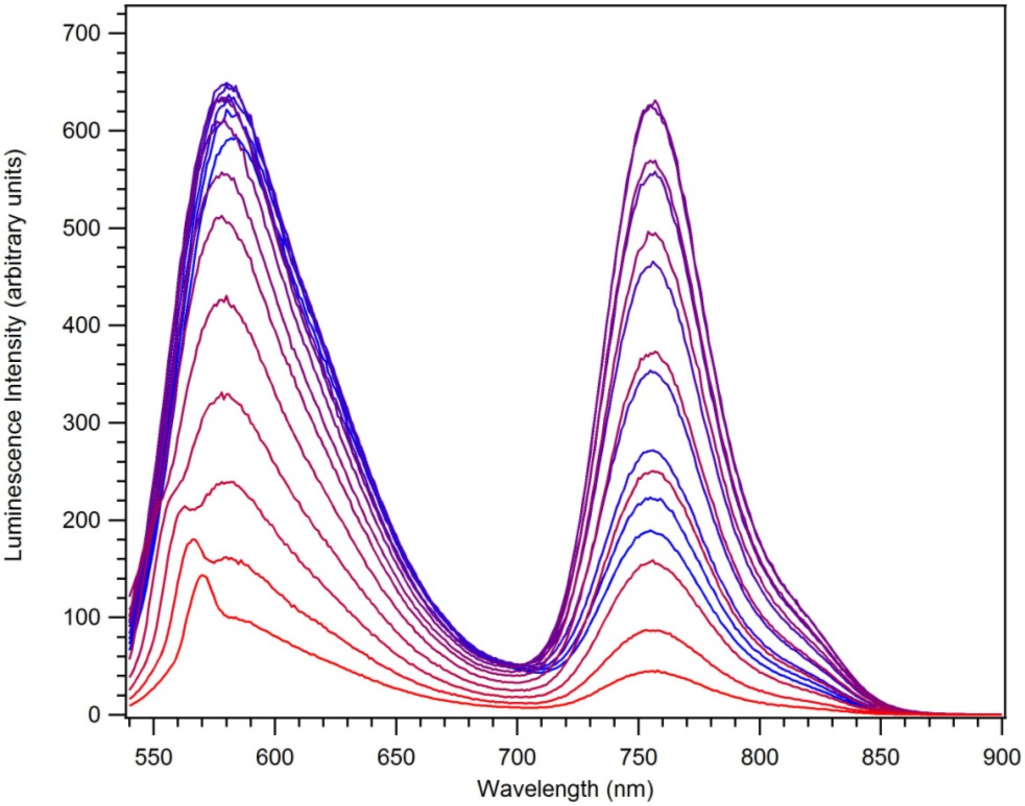
Excitation Wavelength Dependence

Figure S25. Excitation-dependent emission spectra of (^{Ar}L)MnCl(THF) without added THF



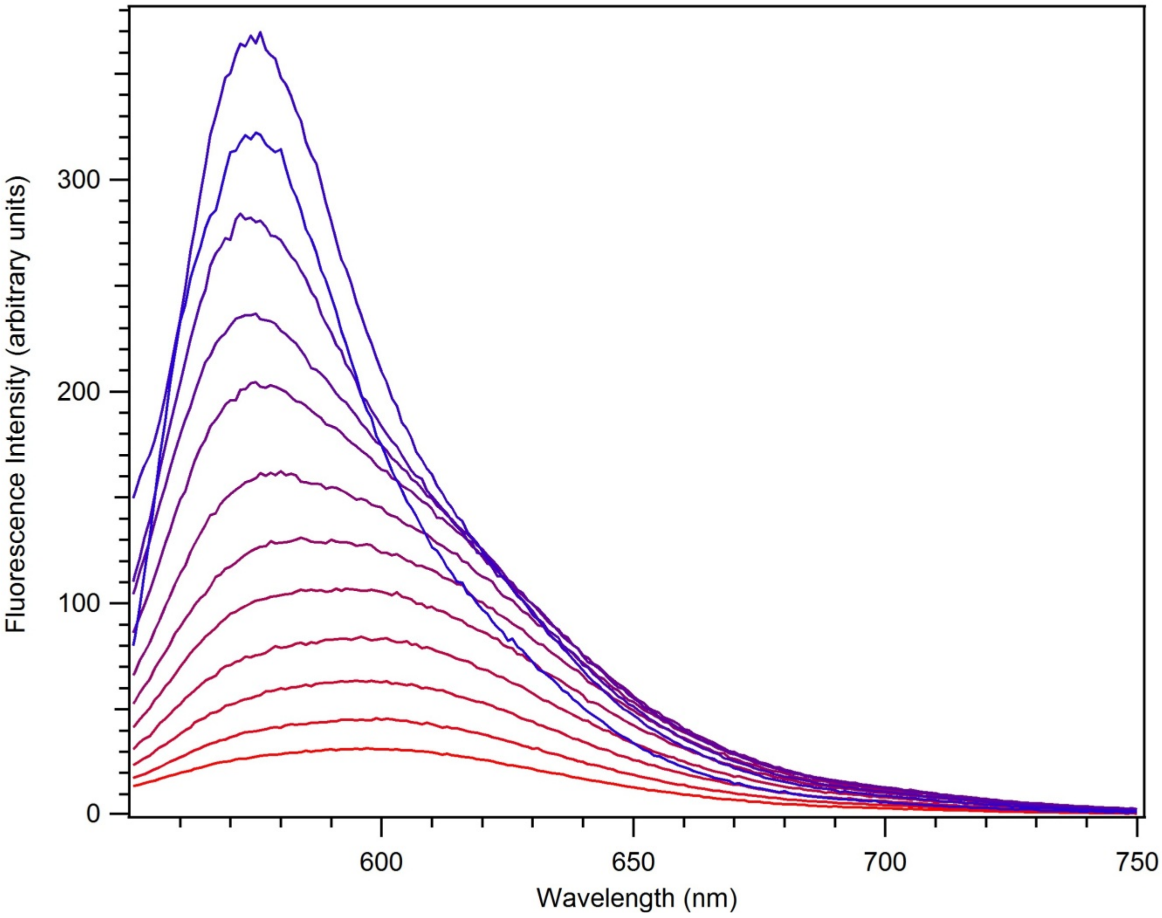
Emission spectra were collected for excitation wavelengths in 1 nm increments from 520 nm (blue traces) to 580 nm (red traces). λ_{max}(fluorescence) = 579 ± 1 nm for all excitation wavelengths; λ_{max} (phosphorescence) = 757 nm for excitation at 520 nm; λ_{max} (phosphorescence) = 777 nm for excitation at 580 nm.

Figure S26. Excitation-dependent emission spectra of $(^{Ar}L)MnCl(THF)$ with added THF



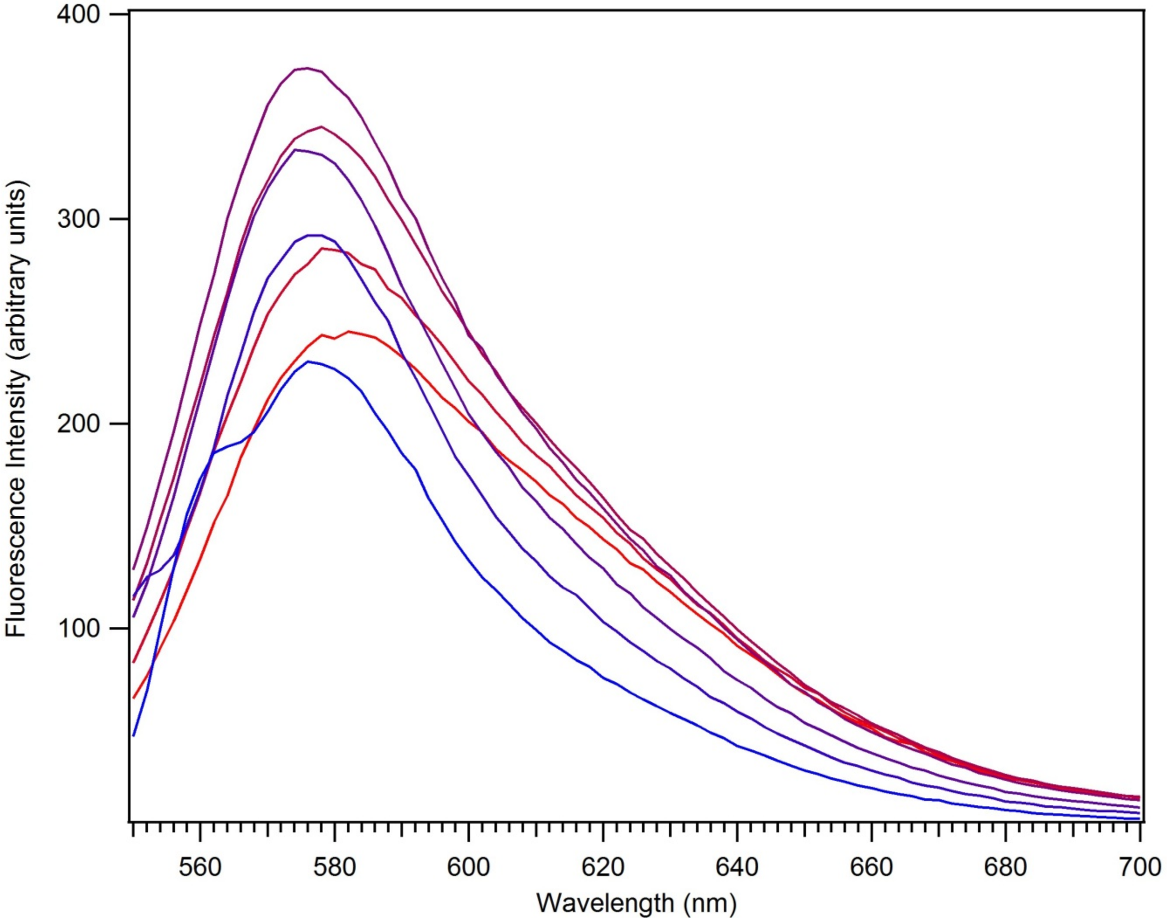
Emission spectra were collected for excitation wavelengths in 2 nm increments from 520 nm (blue traces) to 580 nm (red traces). λ_{max} (fluorescence) = 579 ± 1 nm and λ_{max} (phosphorescence) = 757 nm for all excitation wavelengths. The small shoulders in the fluorescence emission curves at long excitation wavelengths are due to bleed-over from the excitation source.

Figure S27. Excitation-dependent fluorescence spectra of (^{Ar}L)Cu^{I} without coordinating solvent



Spectra were recorded in 10 nm increments of excitation wavelength from 450 nm (red traces) to 560 nm (blue traces). λ_{max} (fluorescence) = 597 nm for excitation at 450 nm; λ_{max} (fluorescence) = 575 nm for excitation at 560 nm.

Figure S28. Excitation-dependent fluorescence spectra of (^{Ar}L)Cu^{I} with added acetonitrile

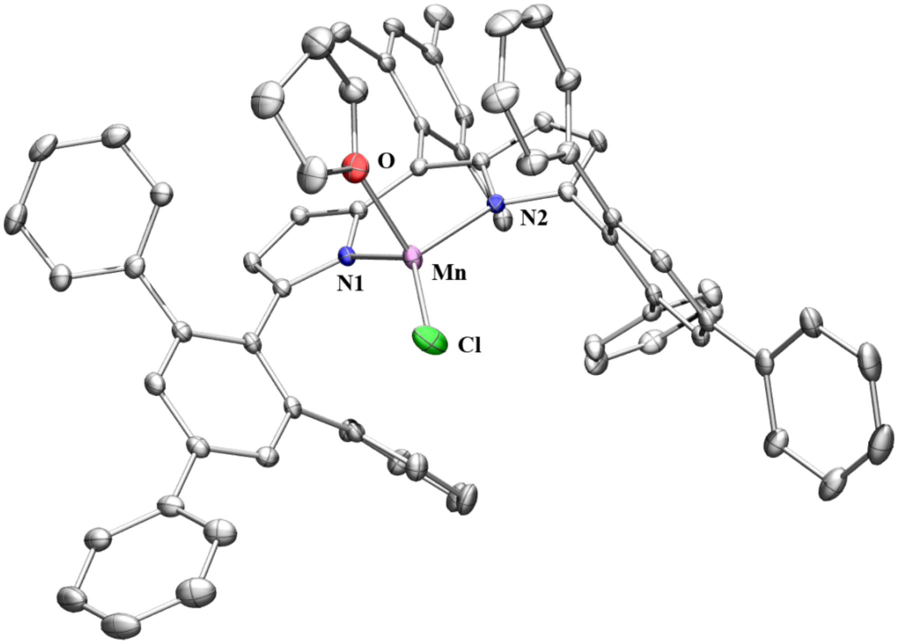


Spectra were recorded in 10 nm increments of excitation wavelength from 500 nm (red traces) to 560 nm (blue traces). λ_{max} (fluorescence) = 576 ± 1 nm for all excitation wavelengths. The complex with acetonitrile bound is markedly less luminescent than the unsolvated complex (Figure S27). Some peak shape dependence on the excitation wavelength can be seen, but we attribute this to the broad excitation/absorption spectra of this species rather than an equilibrium mixture of various adducts.

X-ray Crystallography

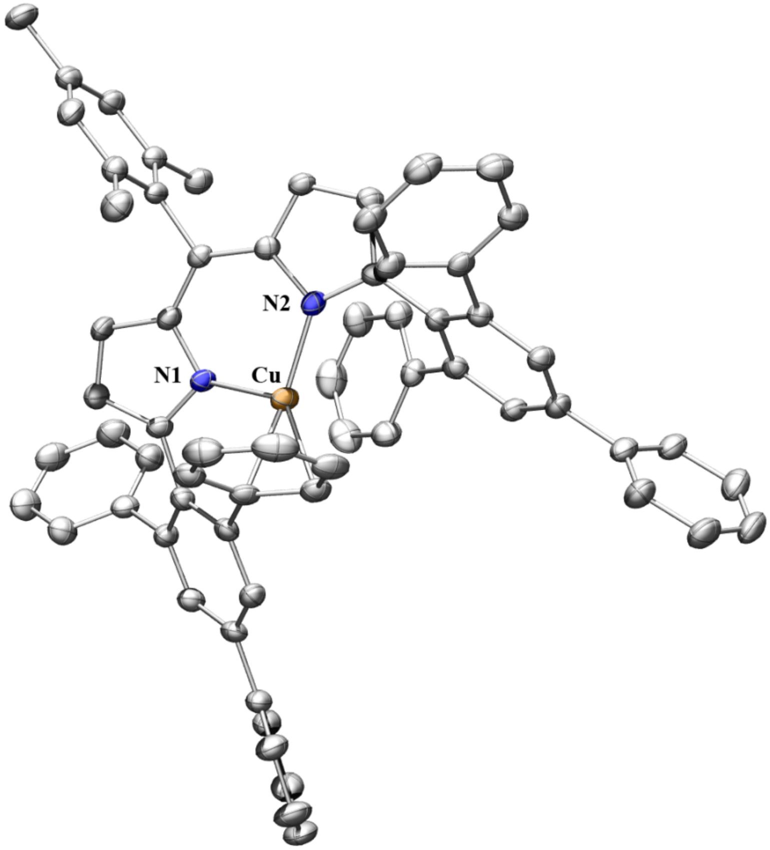
X-ray crystallography was performed at the Harvard Center for Crystallographic Studies. Data was obtained on a Bruker three-circle platform goniometer equipped with an Apex II CCD and an Oxford cryostream cooling device. Radiation was from a graphite fine focus sealed tube Mo Kα (0.71073 Å) source. Crystals were mounted on a cryoloop or glass fiber pin using Paratone N oil. Structures were collected at 100 K. All data was collected as a series of φ and ω scans. Data was integrated using SAINT and scaled with a multi-scan absorption correction using SADABS.[6] The structures were solved by direct methods or Patterson maps using SHELXS-97 and refined against F^2 on all data by full matrix least squares with SHELXL-97.[7] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed at idealized positions and refined using a riding model.

Figure S29. Solid-state structure of (^{Ar}L)MnCl(THF)



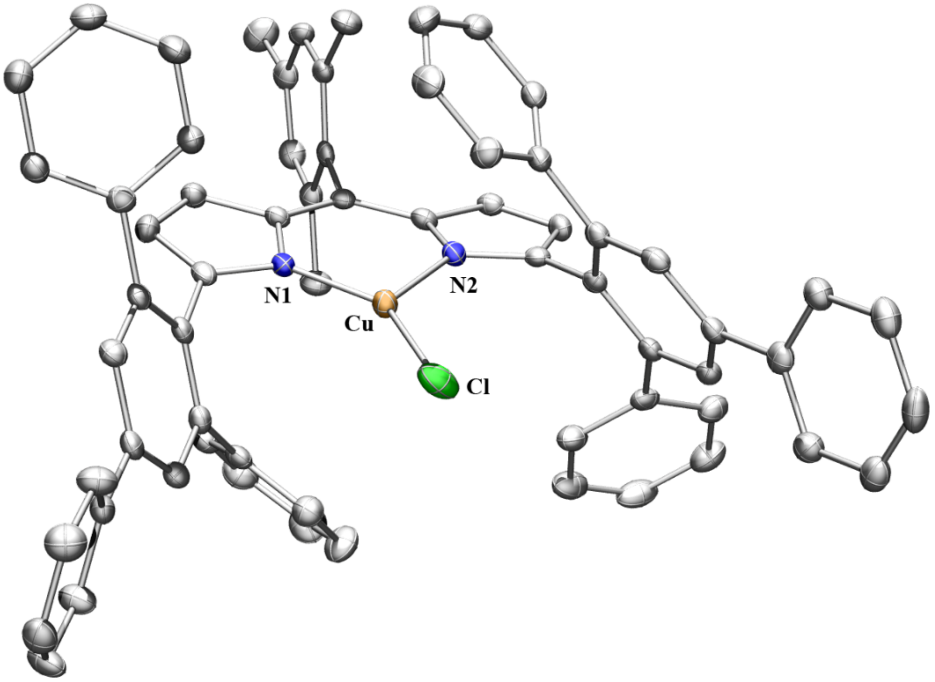
ORTEP drawing of (^{Ar}L)MnCl(THF); ellipsoids set at 50% probability. Gray, carbon; blue, nitrogen; green, chlorine; red, oxygen; orchid, manganese.

Figure S30. Solid-state structure of (^{Ar}L)Cu^{I}



ORTEP drawing of (^{Ar}L)Cu^{I}; ellipsoids set at 50% probability. Hydrogen atoms and solvent molecules are omitted for clarity. Gray, carbon; blue, nitrogen; light orange, copper.

Figure S31. Solid-state structure of (^{Ar}L)Cu^{II}Cl



ORTEP drawing of (^{Ar}L)Cu^{II}Cl; ellipsoids set at 30% probability. Hydrogen atoms have been omitted for clarity. Gray, carbon; blue, nitrogen; green, chlorine; light orange, copper.

References.

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(2) N. Ji, H. O'Dowd, B. M. Rosen, A. G. Myers, *J. Am. Chem. Soc.* 2006, **128**, 14825.
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(6) Bruker AXS: Milwaukee, WI, 2009.
(7) G. M. Sheldrick, *Acta Crystallogr., Sect. A* 2008, **64**, 112.