Supplementary Information

Room-Temperature Combinatorial Screening of Cylometallated Iridium (III) Complexes for a Step Towards Molecular Control of Color Purity

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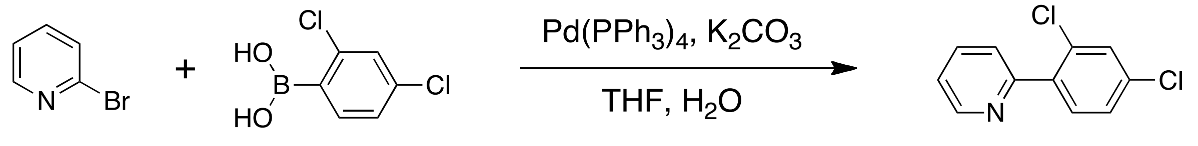
General Considerations.

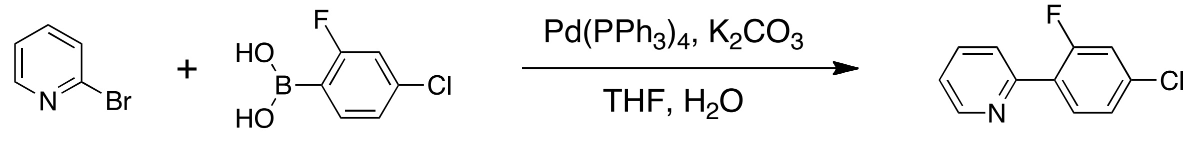
The solvents (puriss. grade) and commercially available starting materials were used as received. UV-vis spectra were recorded in a 1 cm path length quartz cell on a Cary 5 spectrophotometer. Emission spectra were recorded on a Spex Fluorolog 112 using a 90° optical geometry. The emitted light was detected with a Hamamatsu R2658 photomultiplier operated in single photon-counting mode. The emission spectra were photometrically corrected using a NBS calibrated 200 W tungsten lamp as reference source. Data collections for X-ray crystal structures were performed at low temperature on an Oxford Diffraction Sapphire/KM4 CCD (**EB183**, **EB95**, **N977** and **EB43**) and on a Bruker APEX II CCD (**EB73**, **N995** and **N995dimer**) both equipped with a kappa geometry goniometer. Data were treated for cell refinement; then integrated and corrected for absorption (using semi-empirical methods). Structure solutions and refinements were carried out by SHELXTL. Crystal structures were refined using the full-matrix on F^2. H atoms were placed in calculated positions by means of the "riding" model. NMR spectra were measured with AV-400 spectrometers, and the reported chemical shifts were referenced to TMS.

Synthesis of ligands.



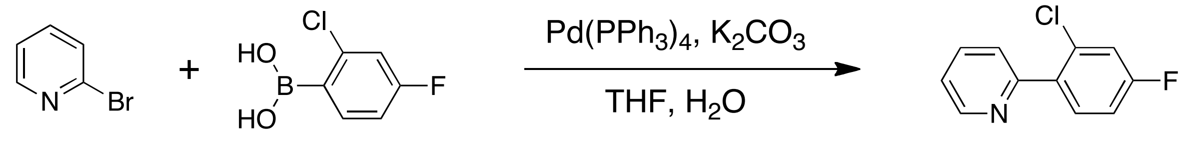
Cl$_2$-ppy

2-(2,4-Dichlorophenyl)pyridine (Cl$_2$-ppy). To a mixture of 2-bromopyridine (0.61 ml, 6.31 mmol, 1.1 eq.), 2,4-dichlorophenylboronic acid (1.1 g, 5.76 mmol), potassium carbonate (1.58 g, 11.5 mmol, 2 eq), and $Pd(PPh_3)_4$ (0.135 g, 0.11 mmol, 2 mol %) were added degassed THF and water. The solution was refluxed overnight under argon, and then cooled down to room temperature. Water (50 ml) was added and the organic compounds extracted with dichloromethane (3 times). The organic phase was washed by brine (50 ml) and dried over $MgSO_4$. After filtration the solvents were removed under vacuum. The crude product was purified by silica gel column chromatography using a mixture of ethylacetate/hexane (1:2) as the eluent. **Cl$_2$-ppy** was obtained as a pale yellow powder ($R_f = 0.2$, 0.73 g, 56%.); ^{1}H NMR (400 MHz, $CDCl_3$): 8.71 (d, $J = 4.8$ Hz, 1H), 7.76 (td, $J = 8.0$, 2.0 Hz, 1H), 7.64 (d, $J = 8.0$ Hz, 1H), 7.56 (d, $J = 8.0$ Hz, 1H), 7.50 (d, $J = 2.0$ Hz, 1H), 7.35 (dd, $J = 8.0$, 2.0 Hz, 1H), 7.30 (dd, $J = 8.0$, 4.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): 155.90, 149.81, 137.81, 136.08, 134.96, 133.00, 132.58, 130.00, 127.50, 124.92, 122.78. MS (GC-EI): *m/z*: calcd for $C_{11}H_7Cl_2N$: 223, found: 223.



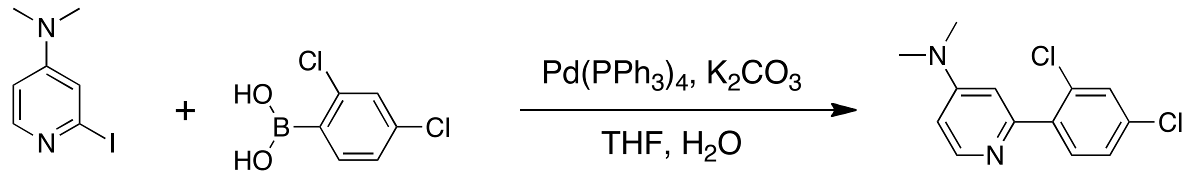
FCl-ppy

2-(4-Chloro-2-fluorophenyl)pyridine (FCl-ppy). Synthesized by a procedure similar to **Cl_2-ppy** as follow: 2-bromopyridine (0.61 ml, 6.31 mmol, 1.1 eq.), 2-fluoro-4-chlorophenylboronic acid (1 g, 5.73 mmol), potassium carbonate (1.58 g, 11.5 mmol, 2 eq), and $Pd(PPh_3)_4$ (0.135 g, 0.11 mmol, 2 mol %) were used. The product was purified by column chromatography on silica gel with a 1:2 mixture of dichloromethane/hexane as the eluent to yield as a white powder (R_f = 0.3, 0.52 g, 44 %.); ^{1}H NMR (400 MHz, $CDCl_3$): 8.73 (d, J = 8.4 Hz, 1H), 7.99 (t, J = 8.4 Hz, 1H), 7.77-7.75 (m, 2H), 7.28-7.26 (m, 2H), 7.21 (dd, J = 10.8, 4.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): 160.29 (d, J = 251.8 Hz), 152.37 (d, J = 2.5 Hz), 149.92, 136.59, 135.45 (d, J = 10.3 Hz), 131.92 (d, J = 4.0 Hz), 126.65 (d, J = 11.5 Hz), 125.26 (d, J = 3.6 Hz), 124.88 (d, J = 9.6 Hz), 122.77, 116.98 (d, J = 26.5 Hz). MS (GC-EI): *m/z*: calcd for $C_{11}H_7ClFN$: 207 found: 207.



ClF-ppy

2-(2-Chloro-4-fluorophenyl)pyridine (ClF-ppy). Synthesized by a procedure similar to **Cl_2-ppy** as follow: 2-bromopyridine (0.61 ml, 6.31 mmol, 1.1 eq.), 2-chloro-4-fluorophenylboronic acid (1 g, 5.73 mmol), potassium carbonate (1.58 g, 11.5 mmol, 2 eq), and $Pd(PPh_3)_4$ (0.135 g, 0.11 mmol, 2 mol %) were used. The product was purified by column chromatography on silica gel with a 1:2 mixture of dichloromethane/hexane as the eluent to yield as a white powder (R_f = 0.3, 0.50 g, 42 %.); ^{1}H NMR (400 MHz, $CDCl_3$): 8.69 (dq, J = 4.8, 0.8 Hz, 1H), 7.73 (td, J = 7.6, 2.0 Hz, 1H), 7.60 (dt, J = 7.2, 1.2 Hz, 1H), 7.60 (dd, J = 8.8, 6.4 Hz, 1H), 7.26 (dd, J = 7.6, 4.8 Hz, 1H), 7.21 (dd, J = 8.4, 6.4 Hz, 1H), 7.07 (td, J = 8.0, 2.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): 162.40 (d, J = 249.6 Hz), 156.00, 149.66, 136.00, 135.58 (d, J = 3.6 Hz), 133.04 (d, J = 10.3 Hz), 132.91 (d, J = 8.8 Hz), 124.89, 122.55, 117.47 (d, *J* = 24.5 Hz), 114.44 (d, *J* = 21.0 Hz). MS (GC-EI): *m/z*: calcd for $C_{11}H_7ClFN$: 207, found: 207.



Cl$_2$-NMe$_2$-ppy

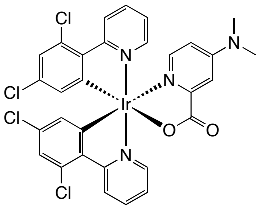
2-(2,4-Dichlorophenyl)-N,N-dimethylpyridin-4-amine (Cl$_2$-NMe$_2$-ppy). Synthesized by a procedure similar to **Cl$_2$-ppy** as follow: 2-iodo-4-dimethylpyridine (0.8 g, 3.23 mmol), 2,4-dichlorophenylboronic acid (0.68 g, 3.56 mmol, 1.1 eq.), potassium carbonate (0.89 g, 6.45 mmol, 2 eq), and $Pd(PPh_3)_4$ (0.075 g, 0.065 mmol, 2 mol %) were used. The product was purified by column chromatography on silica gel with a 1:2 mixture of ethylacetate/hexane as the eluent to yield as a pale yellow powder (R_f = 0.2, 0.32 g, 37%.); ^{1}H NMR (400 MHz, $CDCl_3$): 8.27 (d, *J* = 6.0 Hz, 1H), 7.48 (d, *J* = 8.0 Hz, 1H), 7.43 (d, *J* = 2.0 Hz, 1H), 7.27 (dd, *J* = 8.4, 2.0 Hz, 1H), 6.74 (d, *J* = 2.4 Hz, 1H), 6.47 (dd, *J* = 6.0, 2.8 Hz, 1H), 2.99 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): 155.90, 154.29, 149.52, 138.91, 134.23, 132.91, 132.33, 129.67, 127.10, 107.66, 105.71, 39.19. MS (GC-EI): *m/z*: calcd for $C_{11}H_7ClFN$: 266, found: 266.

Synthesis of iridium complexes.

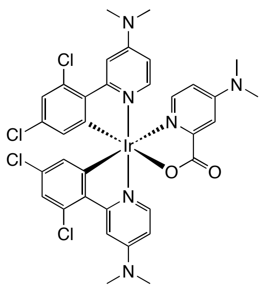
General method for syntheses of chloro-bridged dimers: a solution of $IrCl_3$, x H_2O (about 0.9 mmol) in a mixture of 2-ethoxyethanol/water (50 mL/15 mL) was degassed by bubbling argon for 30 minutes while heating at 70 °C. **Ligand** (about 2.1 mmol) was added as a solid and the mixture heated at 135 °C for 20 hours. After cooling down to room temperature, water (150 mL) was added and the mixture kept in the fridge for 2 hours. The precipitate was filtered on fritted glass, washed with water (6 x 50 mL), MeOH (50 mL) and hexane (3 x 50 mL) and dried under vacuum to afford the chloro-bridged iridium dimer used without further purification.

Parallel synthesis and emission characterization protocol. Stock solutions of dimer, ligand and tetrabutyl ammonium hydroxide (TBAOH) were prepared in dichloromethane (about 0.25 mM each). For each combination, 1 mL of dimer solution, 2 mL of ligand solution and 2 mL of TBAOH solution (or 2 mL of dichloromethane when neutral complex is used) were mixed in a vial, sonicated 10 seconds and left at room temperature on the bench overnight. About 0.5 mL of the solution is then taken and diluted to 5 mL with dichloromethane and emission spectra were directly recorded.

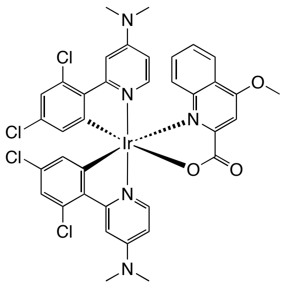
General method for neutral complexes syntheses: to a solution of the corresponding dimer in dichloromethane were added the desired ancillary ligand (3 equivalents) and tetrabutyl ammonium hydroxide (5 equivalents). The solution was gently refluxed (about 40 °C) under argon overnight. After cooling down to room temperature, the solution was evaporated to dryness to give a yellow viscous oil which precipitate upon addition of methanol and deionized water. The suspension was kept in the fridge for 2 hours, filtered off and washed with water. The solid was adsorbed on silica, deposited on the top of a silica gel chromatography column and eluted with dichloromethane/methanol mixture. Finally, the main fraction was dissolved in a minimum amount of dichloromethane and slowly precipitated with hexane. The suspension was filtered off, washed with hexane and dried to afford complexes as solids.



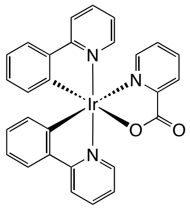
EB73



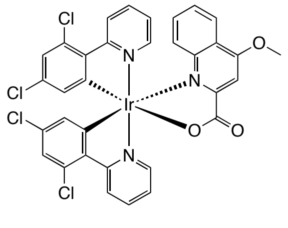
EB112



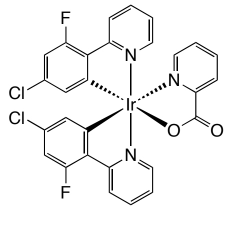
EB102



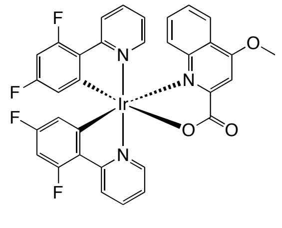
EB183



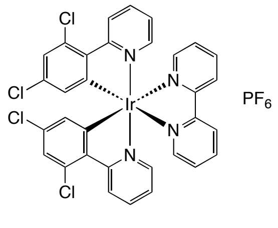
EB95



EB117



EB96



EB76

EB73: obtained as a yellow solid (135 mg, yield 92%).

^{1}H NMR (CDCl$_3$, 400 MHz): δ 9.08 (1H, ddd, J=8.4, 1.2, 0.8 Hz); 8.99 (1H, ddd, J=8.4, 1.2, 0.8 Hz); 8.83 (1H, ddd, J=5.6, 2.0, 0.8 Hz); 7.82-7.75 (2H, m); 7.67 (1H, ddd, J=5.6, 2.0, 0.8 Hz); 7.52 (1H, d, J=3.2 Hz); 7.23 (1H, ddd, J=7.6, 5.6, 1.2 Hz); 7.19 (1H, d, J=6.8 Hz); 7.06-

7.02 (2H, m); 6.98 (1H, d, J=2.0 Hz); 6.46 (1H, dd, J=6.8, 3.2 Hz); 6.14 (1H, d, J=2.0 Hz); 5.90 (1H, d, J=2.0 Hz); 3.08 (6H, s).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 173.26, 165.86, 164.25, 154.39, 154.34, 152.72, 149.74, 148.41, 148.11, 146.47, 138.79, 138.31, 136.87, 136.73, 134.25, 133.92, 130.82, 130.76, 130.14, 130.01, 124.24, 123.78, 123.53, 123.26, 122.69, 122.49, 110.28, 109.03, 38.88.

TOF MS ES: MH$^+$ *m/z*: calc. 803.0105 found: 803.0109

EB112: obtained as a yellow solid (32 mg, yield 47%).

^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.29 (1H, d, J=2.8 Hz); 8.27 (1H, d, J=6.8 Hz); 8.21 (1H, d, J=2.8 Hz); 7.50 (1H, d, J=2.8 Hz); 7.24 (1H, d, J=6.4 Hz); 7.15 (1H, d, J=6.4 Hz); 6.97 (1H, d, J=2.0 Hz); 6.92 (1H, d, J=2.0 Hz); 6.40 (2H, m); 6.32 (1H, d, J=2.0 Hz); 6.23 (1H, dd, J=6.8, 2.8 Hz); 6.12 (1H, d, J=2.0 Hz); 3.14 (6H, s); 3.13 (6H, s); 3.05 (6H, s).

TOF MS ES: MH$^+$ *m/z*: calc. 889.0970 found: 889.0980

EB102: obtained as a yellow solid (72 mg, yield 58%).

^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.30 (1H, d, J=2.8 Hz); 8.19-8.15 (3H, m); 7.93 (1H, s); 7.72 (1H, d, J=8.4 Hz); 7.47 (1H, ddd, J=8.4, 6.8, 1.2 Hz); 7.30 (1H, ddd, J=8.8, 6.8, 1.6 Hz); 7.24 (1H, d, J=10.0 Hz); 7.02 (1H, d, J=2.0 Hz); 6.96 (1H, d, J=2.0 Hz); 6.42 (1H, d, J=2.0 Hz); 6.35 (1H, dd, J=6.8, 2.8 Hz); 6.11 (1H, dd, J=6.8, 2.8 Hz); 5.99 (1H, d, J=2.0 Hz); 4.15 (3H, s); 3.11 (6H, s); 3.08 (6H, s).

TOF MS ES: MH$^+$ *m/z*: calc. 926.0810 found: 926.0790

EB95: obtained as a yellow solid (126 mg, yield 74%).

^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.09 (1H, dd, J=8.8, 0.8 Hz); 8.95 (1H, dd, J=8.8, 0.8 Hz); 8.72 (1H, ddd, J=6.0, 2.0, 0.8 Hz); 8.22 (1H, dd, J=8.4, 1.6 Hz); 7.95 (1H, s); 7.82-7.69 (3H, m); 7.61 (1H, d, J= 9.2 Hz); 7.50 (1H, ddd, J= 8.0, 7.2, 0.8 Hz); 7.33 (1H, ddd, J= 9.2, 6.8, 1.2 Hz); 7.14 (1H, ddd, J=7.6, 6.0, 1.2 Hz); 7.10 (1H, d, J= 2.0 Hz); 7.02 (1H, d, J=2.0 Hz); 6.93 (1H, ddd, J=7.6, 6.0, 1.2 Hz); 6.23 (1H, d, J=2.0 Hz); 5.75 (1H, d, J=2.0 Hz); 4.18 (3H, s).

TOF MS ES: MH$^+$ *m/z*: calc. 839.9966 found: 839.9986

EB96: obtained as a bright yellow solid (32 mg, yield 68%).

^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.68 (1H, d, J=6.0 Hz); 8.29 (1H, d, J=8.4 Hz); 8.22 (1H, d, J=7.2 Hz); 8.18 (1H, d, J=8.4 Hz); 7.96 (1H, s); 7.78-7.64 (4H, m); 7.52 (1H, ddd, J=8.0, 6.8, 1.2 Hz); 7.32 (1H, ddd, J=8.0, 6.8, 1.6 Hz); 7.11 (1H, ddd, J=8.8, 6.0, 1.6 Hz); 6.85 (1H, ddd, J=8.8, 6.4, 1.2 Hz); 6.48 (1H, ddd, J=12.4, 9.2, 2.4 Hz); 6.41 (1H, ddd, J=12.4, 9.2, 2.4 Hz); 5.92 (1H, dd, J=9.2, 2.0 Hz); 5.44 (1H, dd, J=8.8, 2.4 Hz); 4.19 (3H, s).

TOF MS ES: MH^+ *m/z*: calc. 776.1148 found: 776.1138

EB117: obtained as a bright yellow solid (82 mg, yield 81%).

^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.74 (1H, d, J=5.6 Hz); 8.33 (1H, d, J=8.0 Hz); 8.29 (1H, d, J=8.4 Hz); 8.23 (1H, d, J=8.4 Hz); 7.95 (1H, t, J=7.6 Hz); 7.70 (3H, m); 7.42 (2H, m); 7.18 (1H, t, J=6.0 Hz); 6.96 (1H, t, J=6.0 Hz); 6.47 (1H, ddd, J=12.0, 9.2, 2.4 Hz); 6.39 (1H, ddd, J=12.0, 9.2, 2.4 Hz); 5.82 (1H, dd, J=8.8, 2.0 Hz); 5.56 (1H, dd, J=8.8, 2.0 Hz).

TOF MS ES: MH^+ *m/z*: calc. 728.0295 found: 728.0282

EB183: obtained as orange solid (323 mg, yield 89%).

^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.79 (1H, dd, J=6.4, 0.8 Hz); 8.32 (1H, dt, J=8.0, 1.2 Hz); 7.88 (3H, m); 7.77 (dd, 1H, J=5.2, 0.8 Hz); 7.70 (2H, m); 7.60 (1H, dd, J=8.0, 1.2 Hz); 7.58 (1H, dd, J=7.6, 1.2 Hz); 7.46 (1H, dd, J=6.0, 0.8 Hz); 7.32 (1H, ddd, J=7.6, 5.6, 1.2 Hz); 7.12 (1H, ddd, J=7.6, 6.0, 1.6 Hz); 6.92 (2H, m); 6.86 (dt, 1H, J=6.0, 1.2 Hz); 6.80 (dt, 1H, J=5.6, 1.2 Hz); 6.74 (dt, 1H, J=6.0, 1.2 Hz); 6.41 (1H, dd, J=7.6, 0.8 Hz); 6.18 (1H, dd, J=7.6, 1.2 Hz).

TOF MS ES: MH^+ *m/z*: calc. 624.1265 found: 624.1263

N977: obtained as light yellow solid (183 mg, yield 64%).

^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.23 (1H, d, J=6.8 Hz); 7.51 (1H, d, J=3.2 Hz); 7.46 (1H, t, J=3.6 Hz); 7.40 (1H, t, J=3.2 Hz); 7.28 (1H, d, J=6.4 Hz); 7.10 (1H, d, J=6.8 Hz); 6.42-6.25 (m, 4 H); 6.19 (1H, dd, J=6.8, 2.8 Hz); 5.94 (1H, dd, J=9.2, 2.4 Hz); 5.79 (1H, dd, J=8.8, 2.4 Hz); 3.12 (6H, s); 3.11 (6H, s); 3.05 (6H, s).

TOF MS ES: MH^+ *m/z*: calc. 825.2152 found: 825.2149

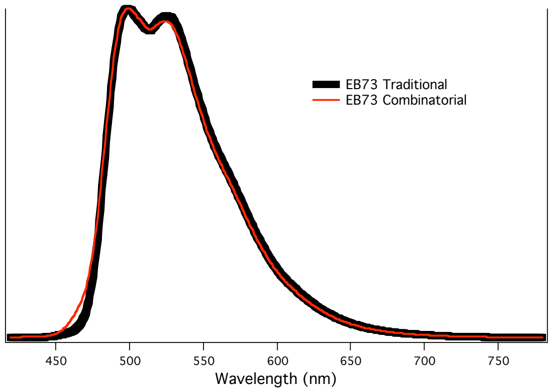
General method for synthesizing cationic complexes: to a solution of the corresponding dimer in dichloromethane was added the desired ancillary ligand (3 equivalents) and the solution was gently refluxed (about 40 °C) under argon overnight. After cooling down to room temperature, the solution was reduced under vacuum and poured into cold diethylether. The precipitate was filtered off and washed extensively with diethylether. The chloride salt obtained was dissolved in the minimum amount of methanol. A saturated solution of KPF_6 in water was added to precipitate the complex as the PF_6 salt. The precipitate was filtered off, washed with water and cold methanol and dried to afford the complexes as solids.

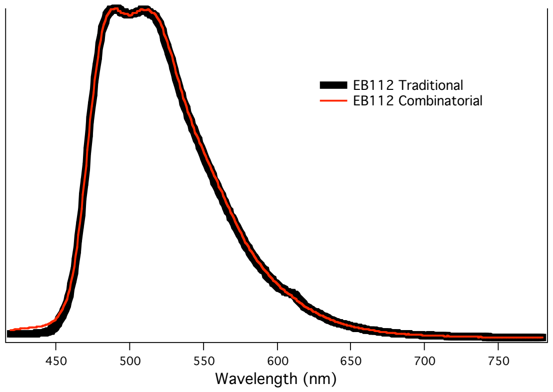
EB76: obtained as a pale orange solid (36 mg, yield 50%).

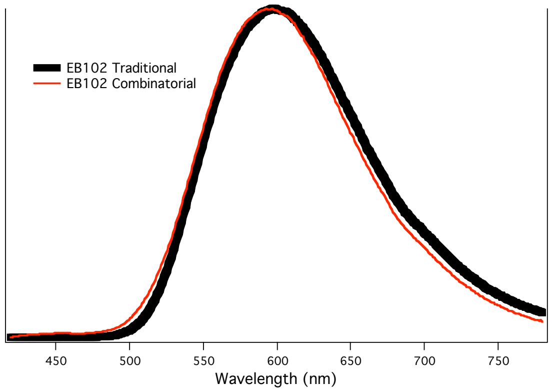
^{1}H NMR (acetone-*d6*, 400 MHz): δ 9.20 (2H, ddd, J=8.4, 1.6, 0.8 Hz); 8.89 (2H, d, J=8.4 Hz); 8.35 (2H, ddd, J=9.6, 8.0, 1.6 Hz); 8.20 (2H, ddd, J=9.6, 1.6, 0.8 Hz); 8.11 (2H, ddd, J=9.2, 6.8, 1.6 Hz); 8.02 (2H, ddd, J=6.0, 1.6, 0.8 Hz); 7.75 (2H, ddd, J=7.6, 5.2, 1.2 Hz); 7.31 (2H, ddd, J=7.6, 5.6, 1.2 Hz); 7.24 (2H, d, J=2.0 Hz); 6.12 (2H, d, J=2.0 Hz).

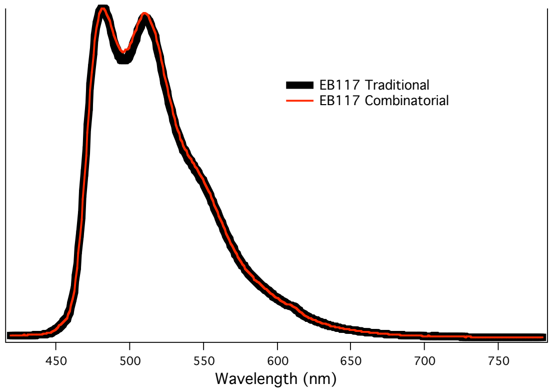
TOF MS ES: $M\text{-}PF_6^+$ *m/z*: calc. 793.0050 found: 793.0078

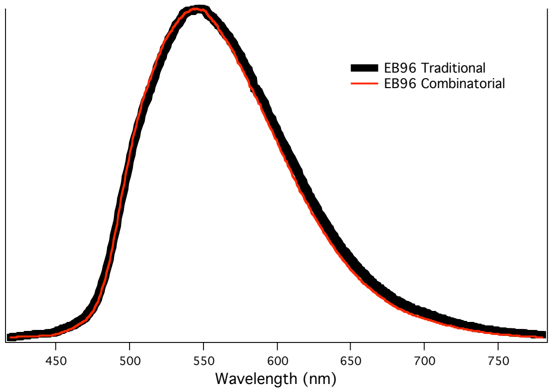
Comparison of emission spectra from traditional *vs.* combinatorial syntheses

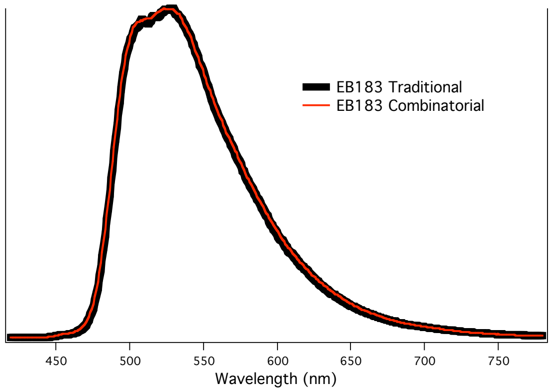


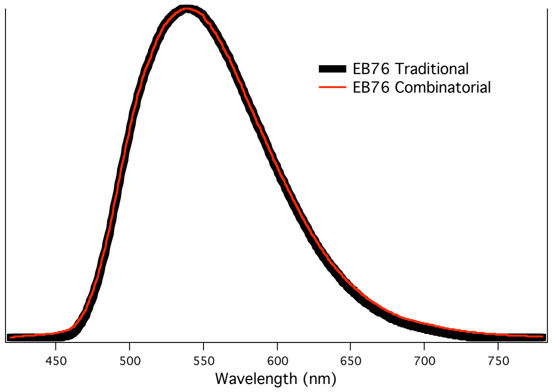


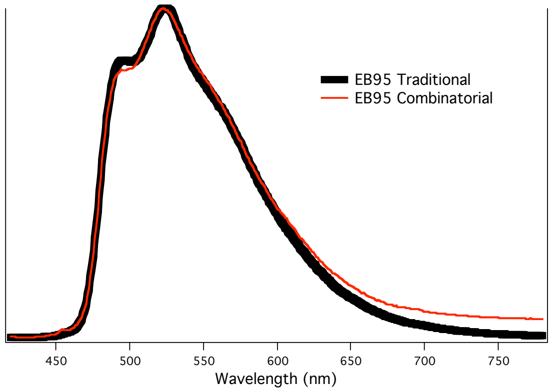




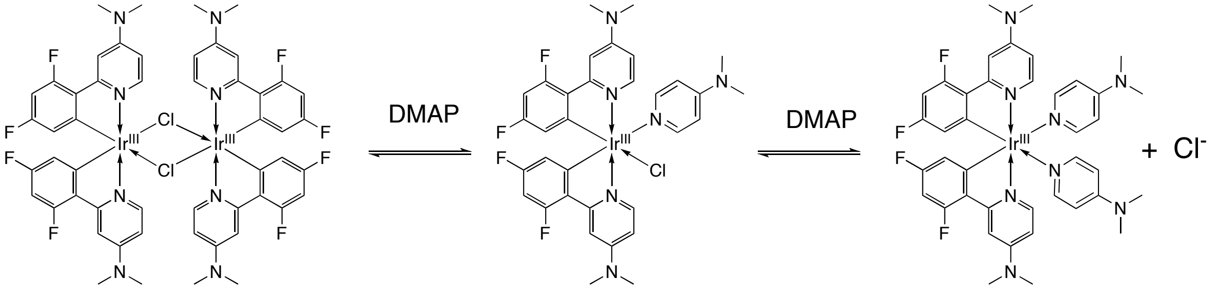








^{1}H NMR spectra of the N995 study



EB39 **EB40** **EB43**

The iridium dimer EB39

$IrCl_3$.x H_2O (558 mg, from Heraeus) was dissolved in a mixture of 2-ethoxy-ethanol and deionized water (60 mL/20 mL) in a two-necked 250 mL round bottom flask. While heating to 80 °C, argon was bubbled directly into the mixture. When the mixture reached 80-90 °C, the ligand 2-(2,4-difluorophenyl)-4-*N,N*-dimethylaminopyridine (690 mg) was added as a solid. The mixture was heated overnight at 125 °C. After cooling to room temperature, deionized water (150 mL) was added and the yellow precipitate filtered off, washed with deionized water, methanol, hexane and diethyl ether, and dried under vacuum. All steps were carried out with aluminium foil as a protection against light. **EB39** was obtained as a yellow powder (660 mg, 60% yield based on $IrCl_3$. 3 H_2O)

^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.78 (d, 4H), 7.50 (t, 4H), 6.24 (td, 4H), 6.13 (dd, 4H), 5.47 (dd, 4H), 3.21 (s, 24H).

EB40 first method, precipitation with Et_2O: **EB39** was stirred with excess **DMAP** in CH_2Cl_2 overnight. The solvent was reduced under vacuum and Et_2O was added, the precipitate filtered off and washed with Et_2O. This purity is difficult to reproduce.

EB40 second method, **using NBu_4Cl: EB39** (20 mg), **DMAP** (10 mg), **NBu_4Cl** (30 mg) were stirred overnight at RT in CH_2Cl_2 puriss. (10 mL). The solution was filtered on cellite and the solvent evaporated under vacuum.

N995: EB39 (69 mg), **DMAP** (45 mg) and **NBu_4Cl** (180 mg) were dissolved in dichloromethane (50 mL). Argon was bubbled into the solution for 5 min and the flask was sealed with a cap and parafilm, covered with aluminium foil, and stirred 20 hours at room temperature. **NBu_4CN** (94 mg) dissolved in a mixture of MeOH/acetone/CH_2Cl_2 (5 mL/5 mL/5 mL) was added all at once in the crude solution of **EB40** and the solution stirred at room temperature for 20 hours. After evaporation of the solvents, the remaining wax was dissolved in a minimum of acetone/hexane (55/45 mixture) and deposited at the top of a column of neutral alumina and eluted first with the same mixture as eluent, followed by acetone/CH_2Cl_2. The fractions containing the blue luminescent product were gathered and the solvents evaporated. **N995** product was precipitated by addition of deionized water, filtered off, wash with water, hexane and ether.

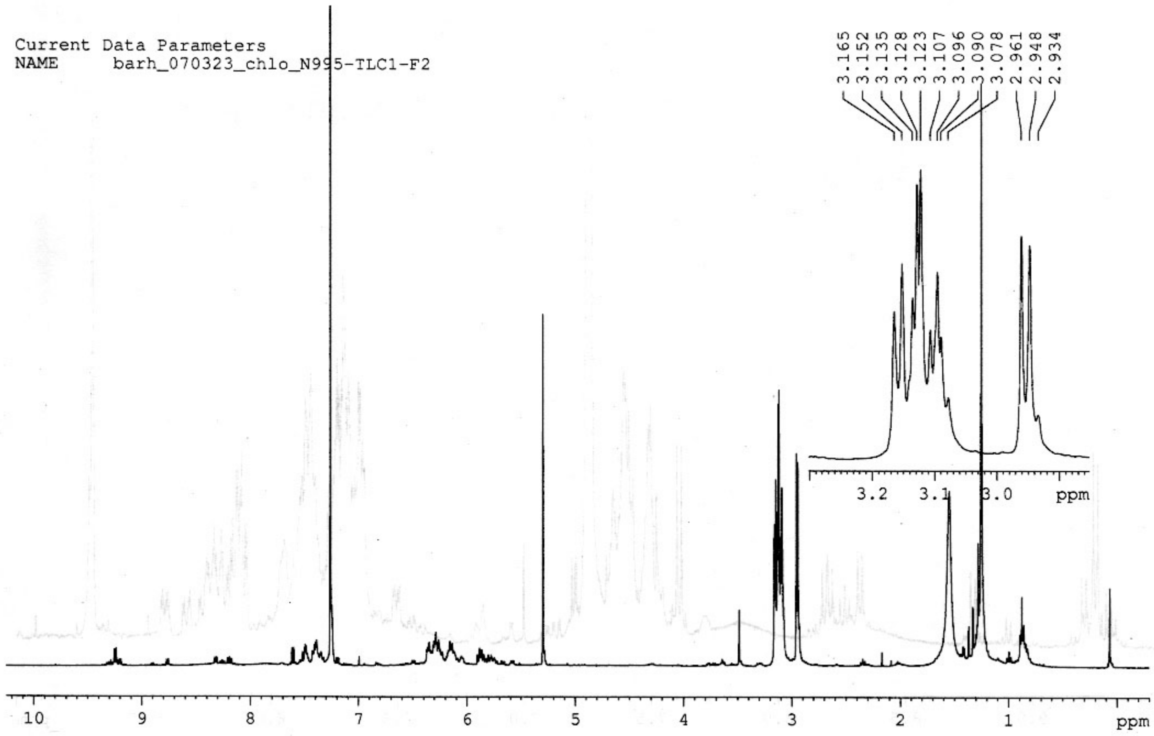
^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.24 (1H, d, J=6.8 Hz); 8.35 (2H, very broad singlet); 7.61 (1H, d, J=6.8 Hz); 7.49 (1H, t, J=3.2 Hz); 7.39 (1H, t, J=3.2 Hz); 6.30 (6H, m); 5.89 (1H, dd, J=4.0, 2.4 Hz); 5.86 (1H, dd, J=9.2, 1.6 Hz); 3.13 (6H, s); 3.12 (6H, s); 2.96 (6H, s).

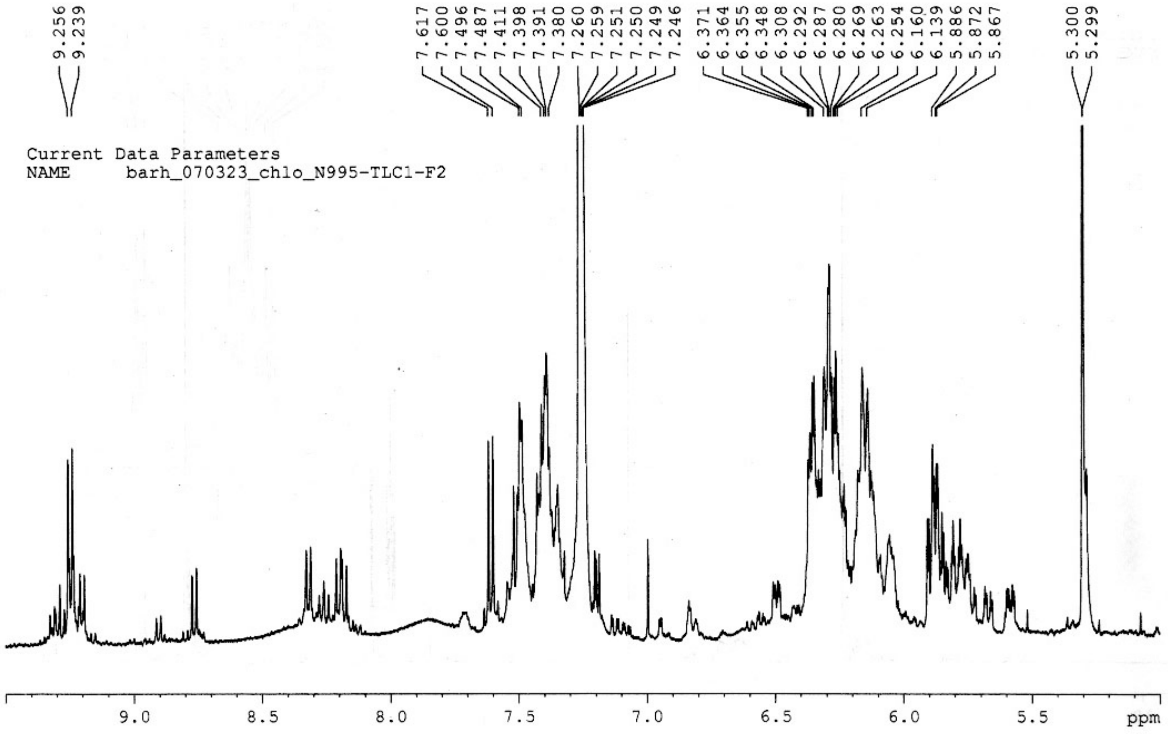
EB43: EB39 (20 mg) and **DMAP** (40 mg) were dissolved in CH_2Cl_2 (10 mL) and refluxed overnight. The solvents were evaporated, 5 mL methanol were used to dissolve the crude mixture and a saturated solution of NH_4PF_6 in MeOH added (10 mL). Water (50 mL) was added and extracted with dichloromethane. The organic phase was washed with water and the volume reduced to the minimum and then methanol was added. The precipitated complex was filtered off and washed with cold methanol, hexane and Et_2O and dried under vacuum. **EB43** was obtained as a slightly yellow solid (19 mg, 63 %) as the PF_6 salt.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.00 (d, 2H), 7.76 (d, 4H), 7.36 (t, 2H), 6.55 (dd, 2H), 6,43 (d, 4H), 6.32 (dt, 2H), 5.91 (dd, 2H), 3.15 (s, 12H), 2.99 (s, 12H).

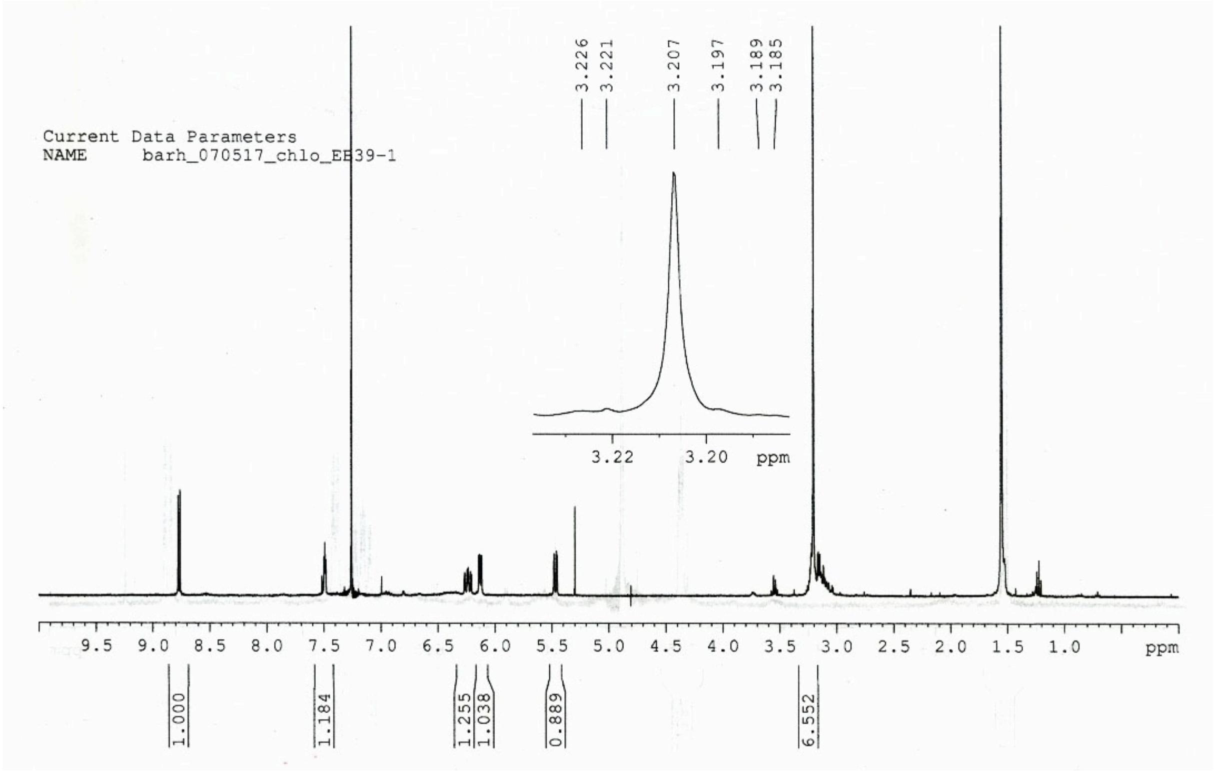
^{1}H NMR ($CDCl_3$, 400 MHz):

Initial **N995** isolated using standard synthetic methods.





EB39: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3.197
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5.5
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4.0
3.5
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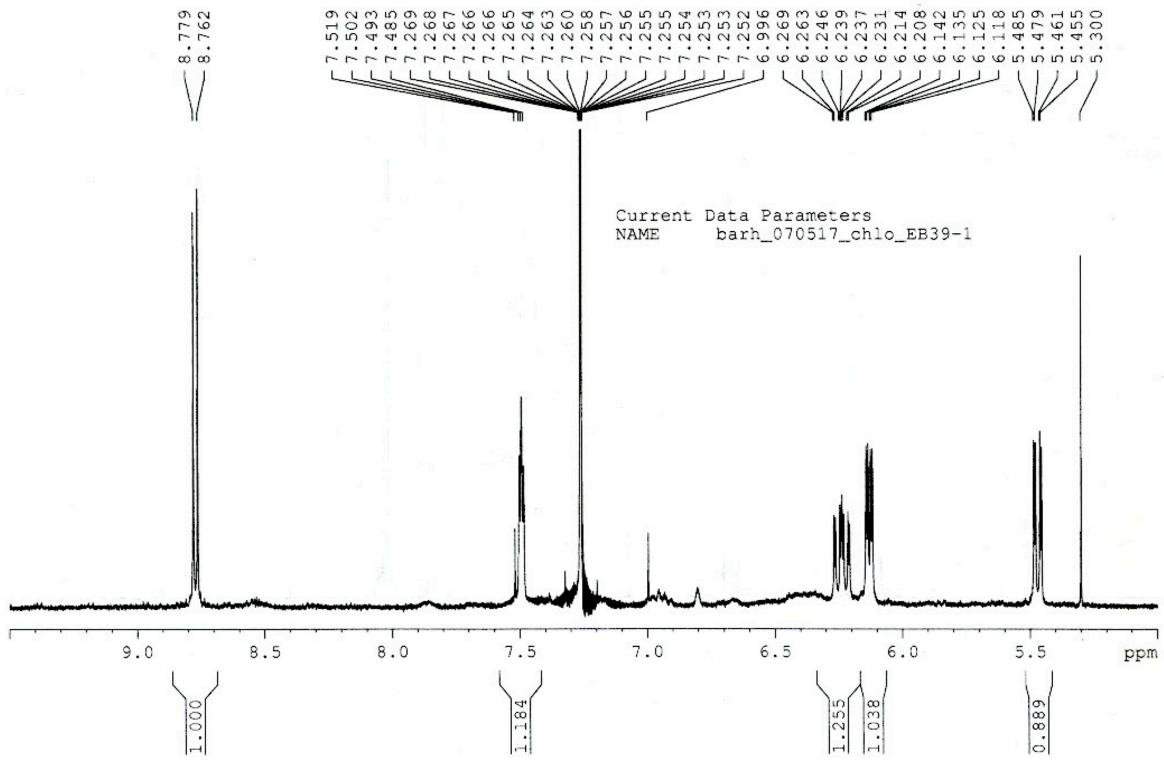
1.255
1.038
0.889
6.552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7.258
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7.256
7.255
7.255
7.254
7.253
7.253
7.252
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6.269
6.263
6.246
6.239
6.237
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ppm
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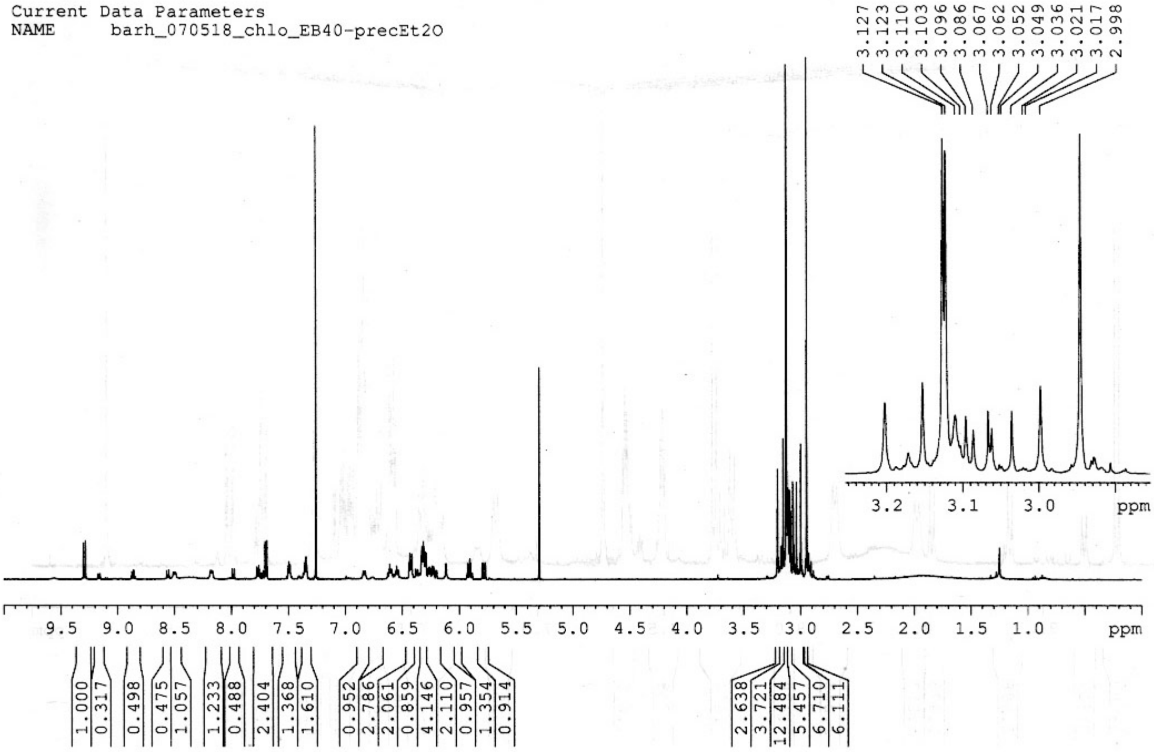
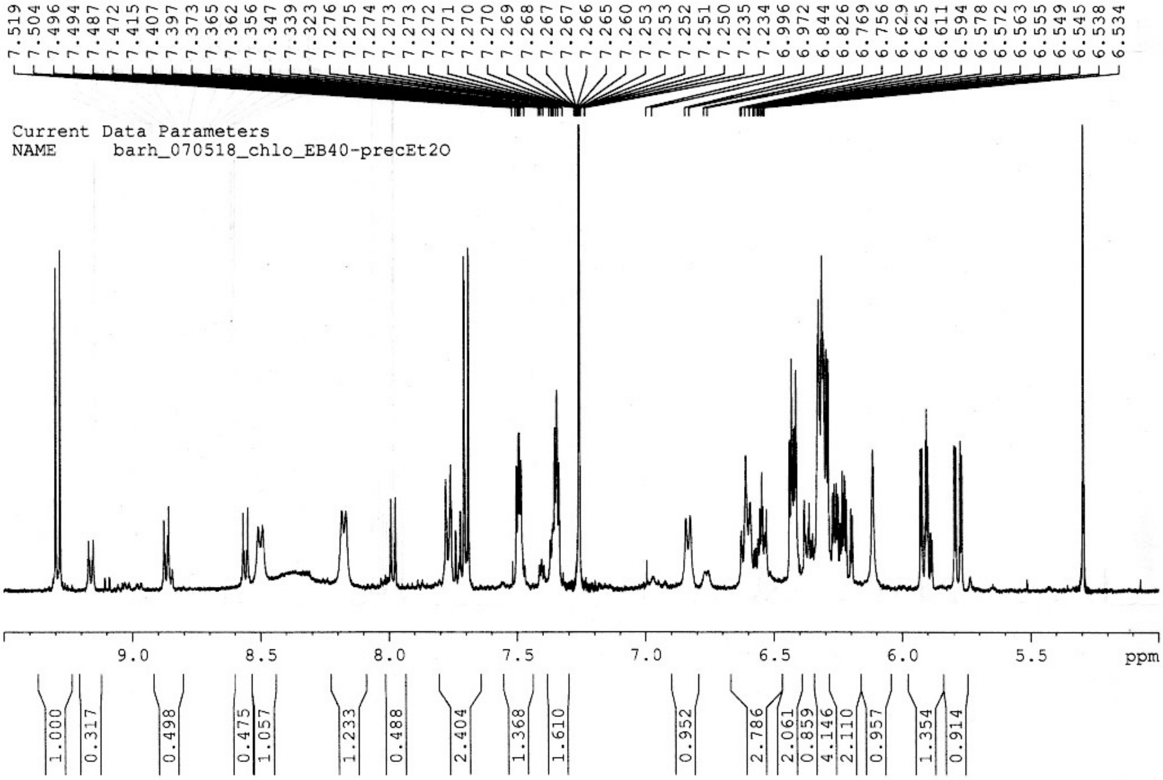
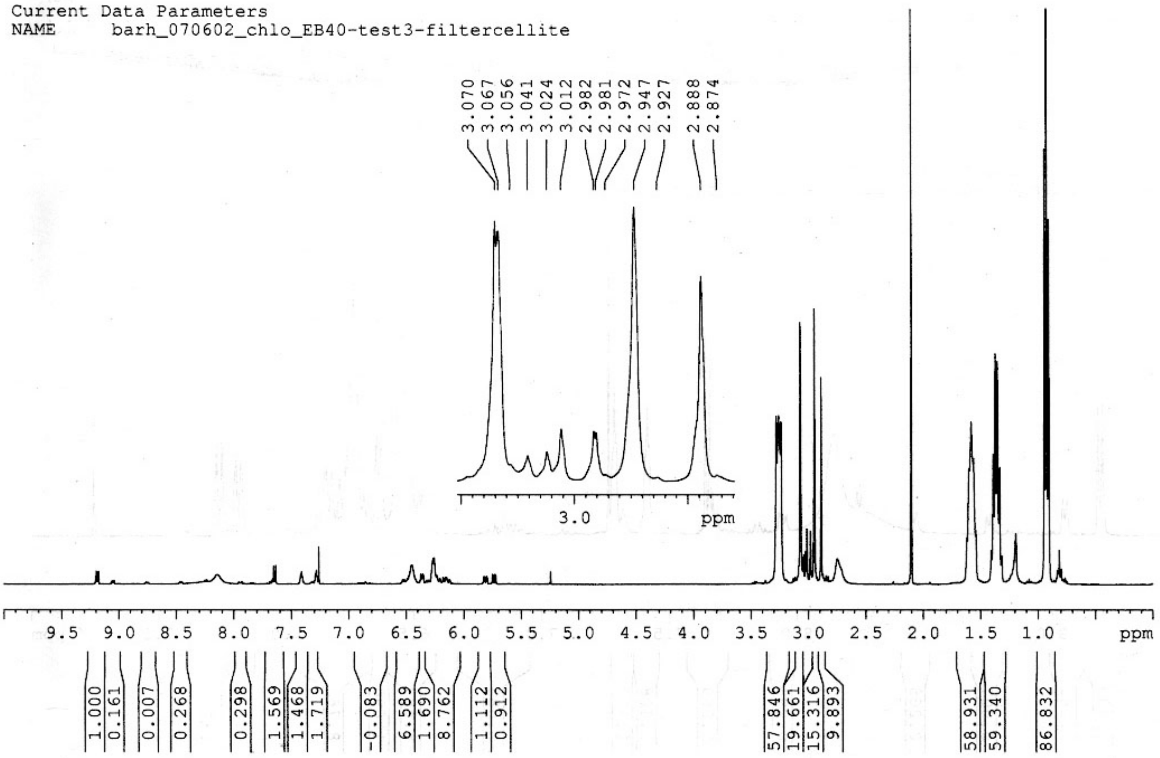
1.038
0.889

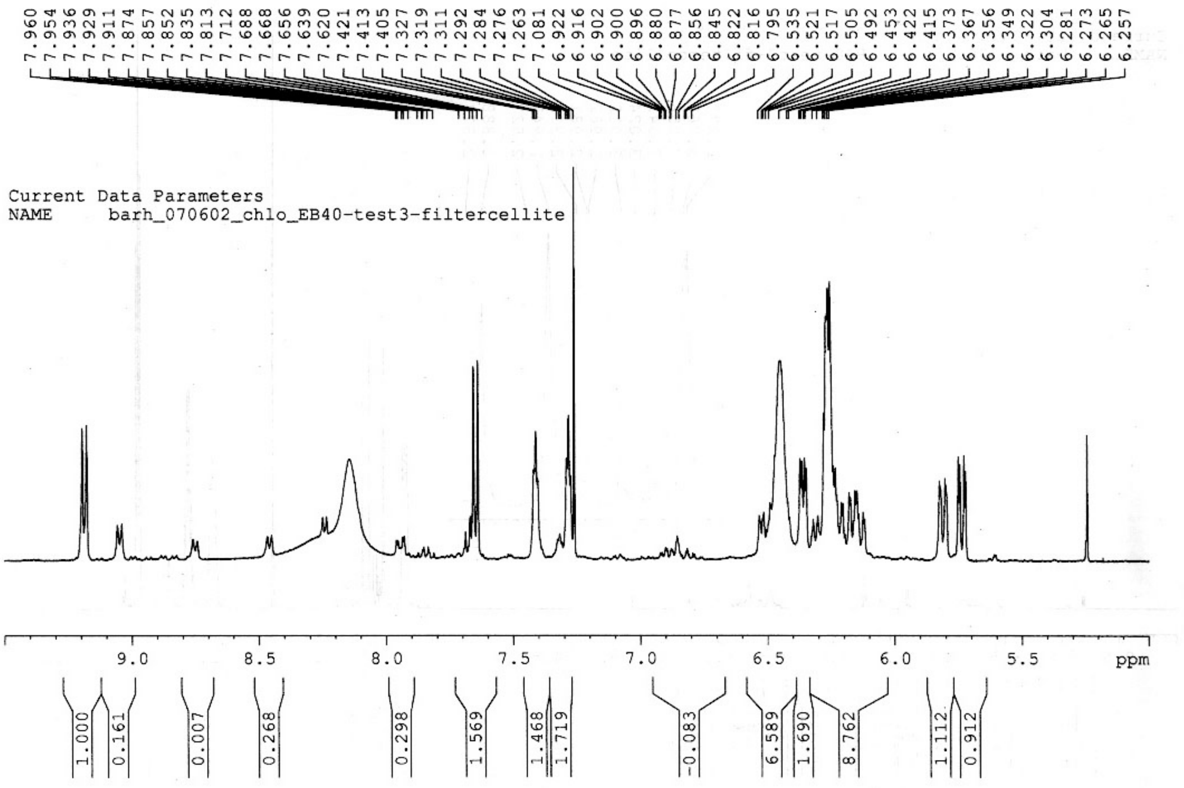
EB40 classical synthetic method, precipitation with Et_2O:



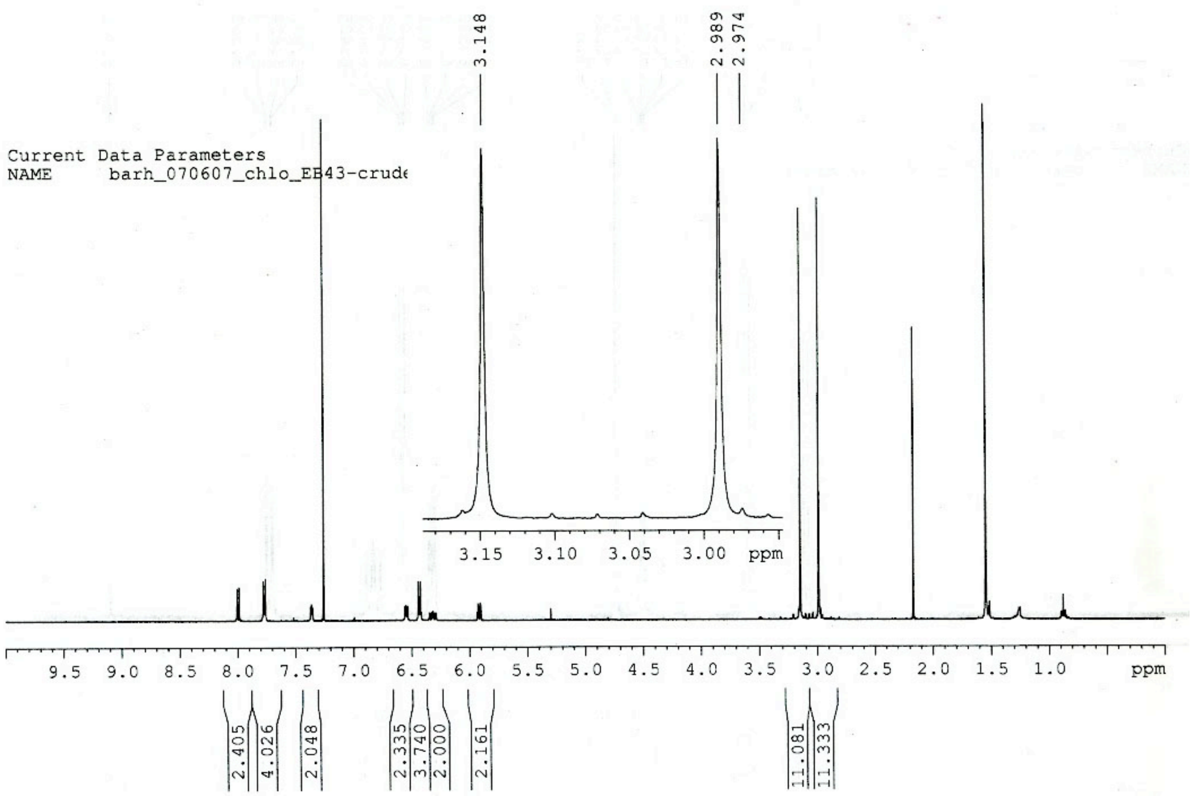


EB40 prepared using **NBu$_4$Cl**:





EB43: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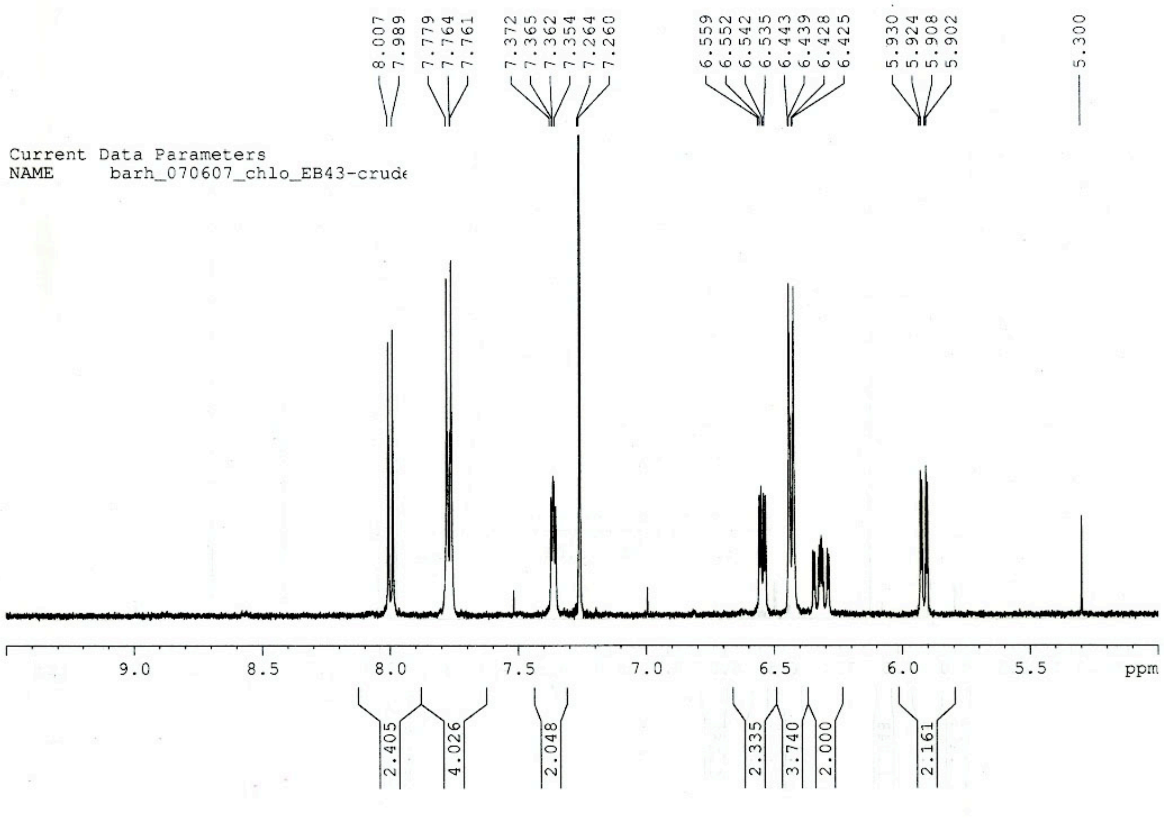
11.333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5.902
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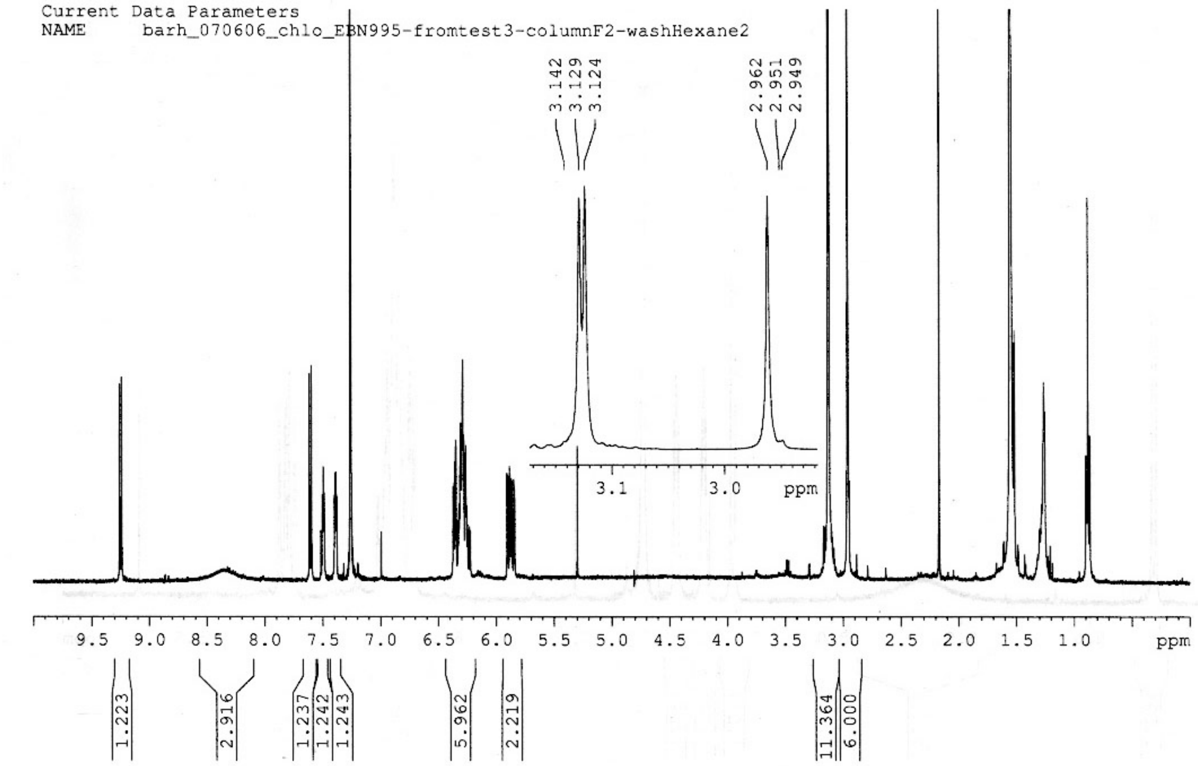
2.000
2.161

N995 final: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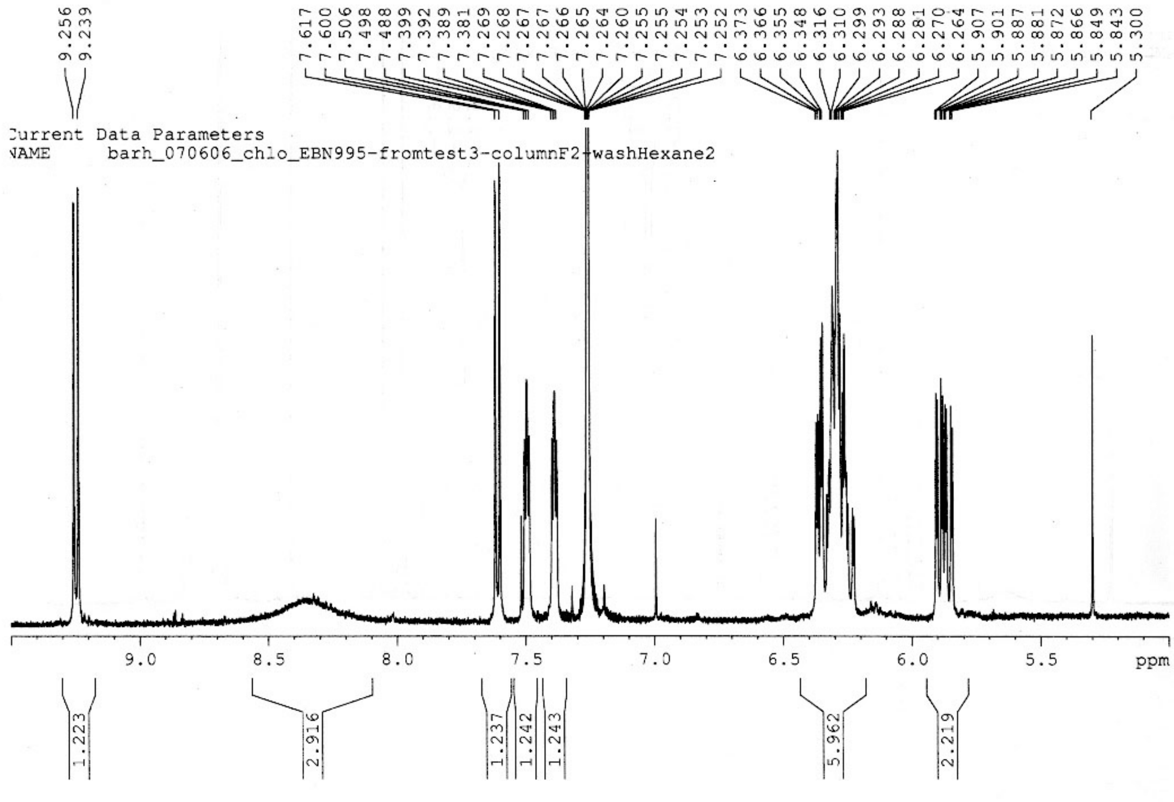
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6.0
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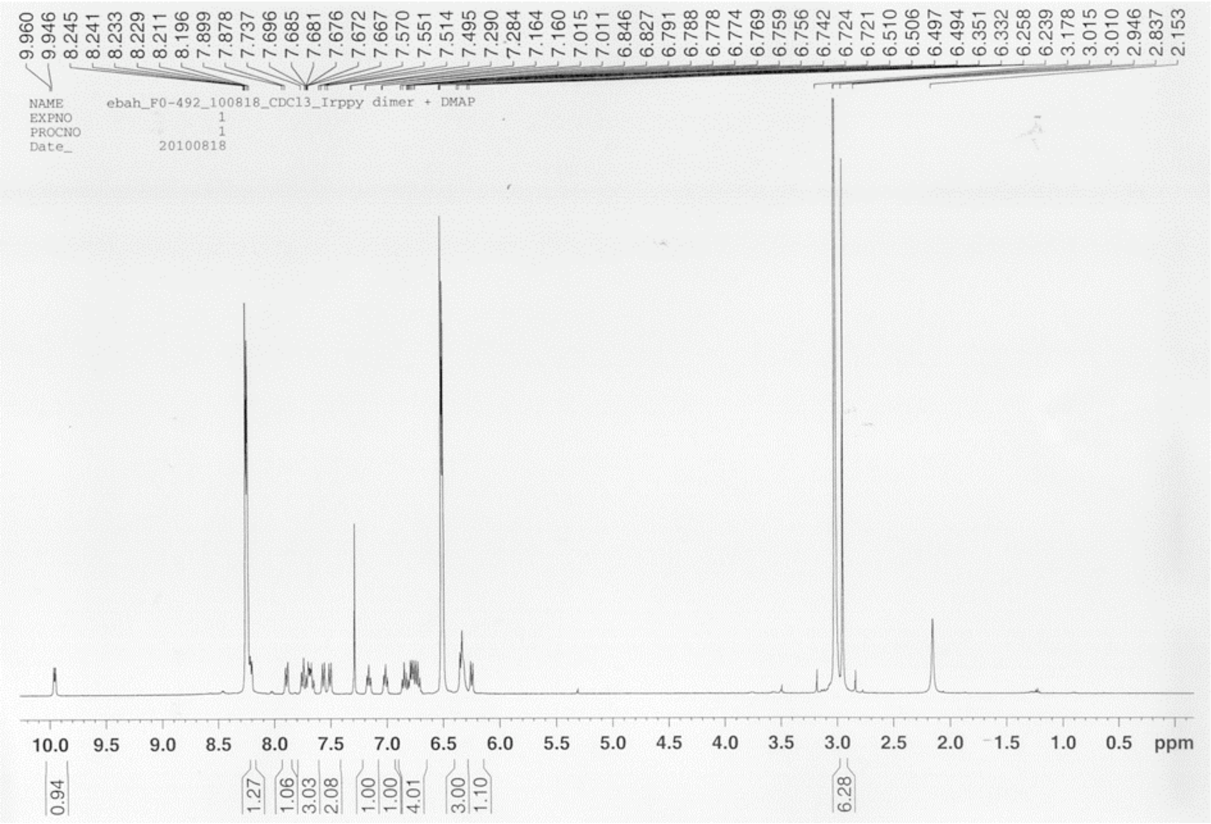
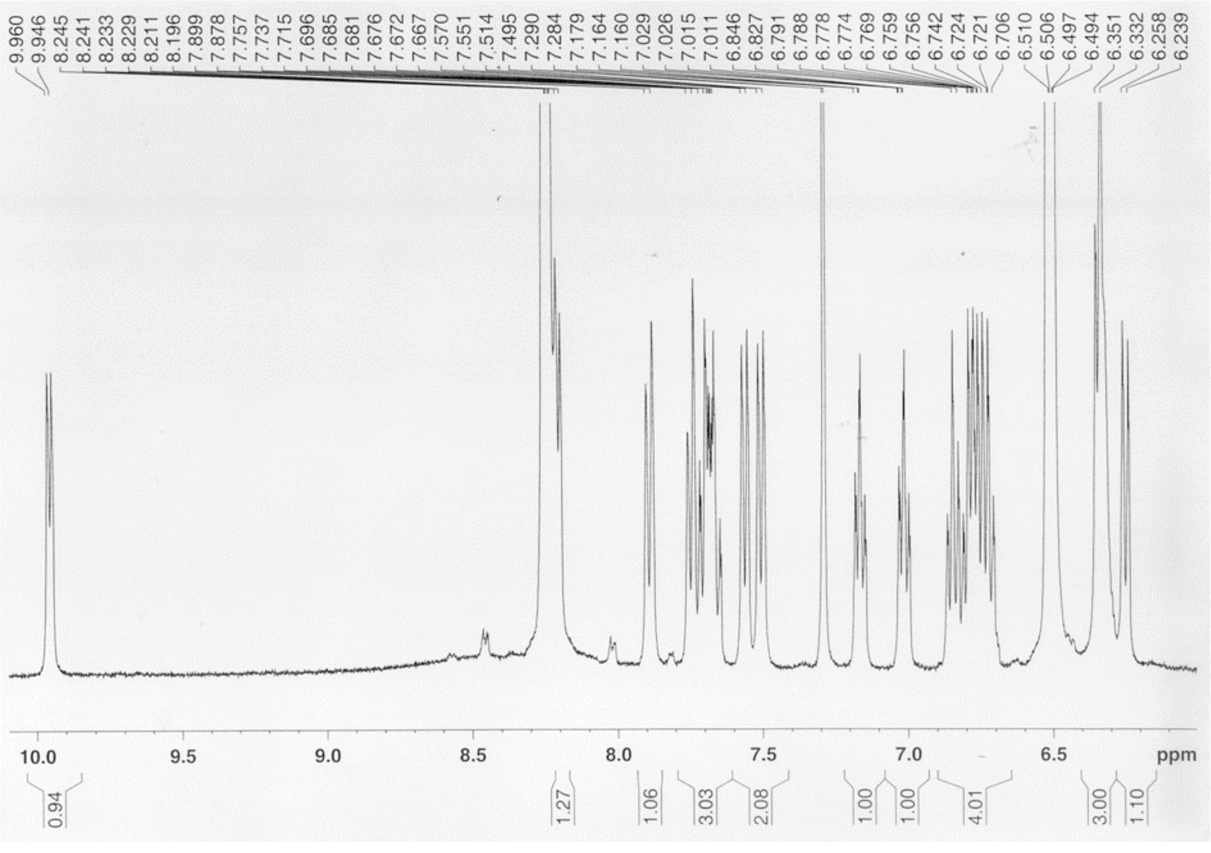
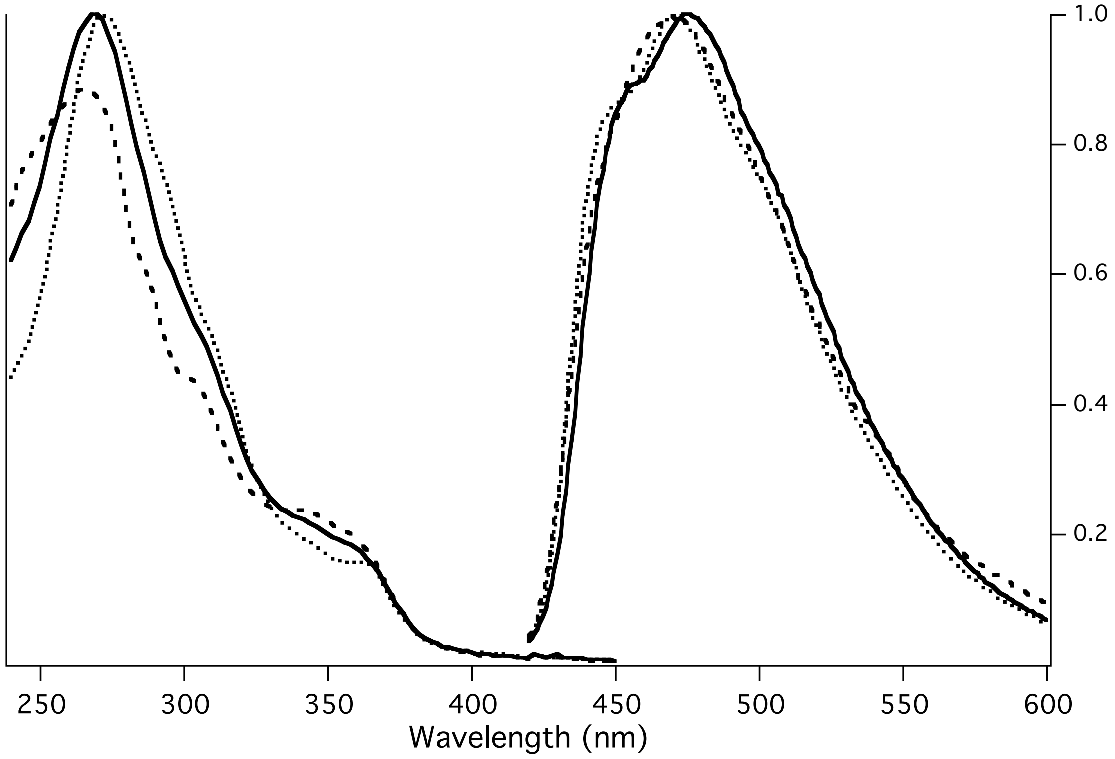
5.962
2.219

[Ir(ppy)$_2$Cl(DMAP)] from [Ir(ppy)$_2$Cl]$_2$ with excess of DMAP:







Absorption (left) and normalized emission (right) spectra of **N995** (CN-DMAP; solid line), **N959** (CN_2; dashed line) and **EB43** ($DMAP_2$; dotted line) in dichloromethane solution at room temperature.

X-ray crystal structures data

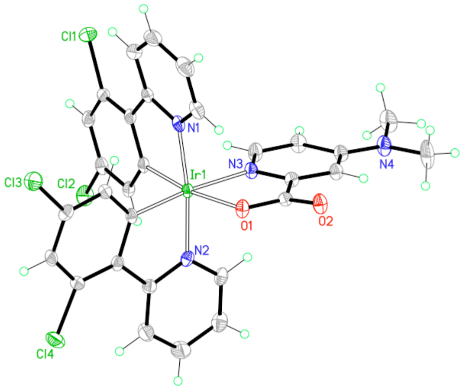


Table S1. Crystal data and structure refinement for **EB73**.

Identification code	eb73	
Empirical formula	$C_{30}H_{21}Cl_4Ir\ N_4O_2$	
Formula weight	803.51	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	*P*-1	
Unit cell dimensions	a = 9.9283(13) Å	α= 88.213(10)°.
	b = 11.5891(10) Å	β= 78.226(13)°.
	c = 14.914(3) Å	γ = 64.844(9)°.
Volume	1517.6(4) $Å^3$	
Z	2	
Density (calculated)	1.758 Mg/m^3	
Absorption coefficient	4.786 mm^{-1}	
F(000)	780	
Crystal size	0.36 x 0.28 x 0.23 mm^3	
Theta range for data collection	3.33 to 27.50°.	
Index ranges	-12<=h<=12, -14<=k<=15, -19<=l<=19	
Reflections collected	33984	
Independent reflections	6926 [R(int) = 0.0414]	
Completeness to theta = 27.50°	99.4 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.0000 and 0.6511	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6926 / 0 / 370	
Goodness-of-fit on F^2	1.123	
Final R indices [I>2sigma(I)]	R1 = 0.0245, wR2 = 0.0508	
R indices (all data)	R1 = 0.0298, wR2 = 0.0527	
Largest diff. peak and hole	0.724 and -0.696 e.$Å^{-3}$	

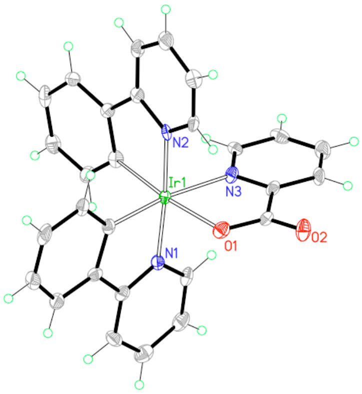


Table S2. Crystal data and structure refinement for **EB183**.

Identification code	eb183b	
Empirical formula	$C_{28}H_{20}IrN_3O_2$	
Formula weight	622.67	
Temperature	140(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1$	
Unit cell dimensions	a = 9.1602(9) Å	α= 90°.
	b = 14.1871(9) Å	β= 117.348(13)°.
	c = 9.5929(10) Å	γ = 90°.
Volume	1107.31(18) $Å^3$	
Z	2	
Density (calculated)	1.868 Mg/m^3	
Absorption coefficient	6.061 mm^{-1}	
F(000)	604	
Crystal size	0.28 x 0.18 x 0.15 mm^3	
Theta range for data collection	2.87 to 26.37°.	
Index ranges	-11<=h<=10, -17<=k<=17, -11<=l<=11	
Reflections collected	9835	
Independent reflections	4283 [R(int) = 0.0367]	
Completeness to theta = 26.37°	99.1 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.66460	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4283 / 1 / 307	
Goodness-of-fit on F^2	1.039	
Final R indices [I>2sigma(I)]	R1 = 0.0300, wR2 = 0.0728	
R indices (all data)	R1 = 0.0348, wR2 = 0.0739	
Absolute structure parameter	0.000(12)	
Largest diff. peak and hole	3.179 and -1.080 e.$Å^{-3}$	

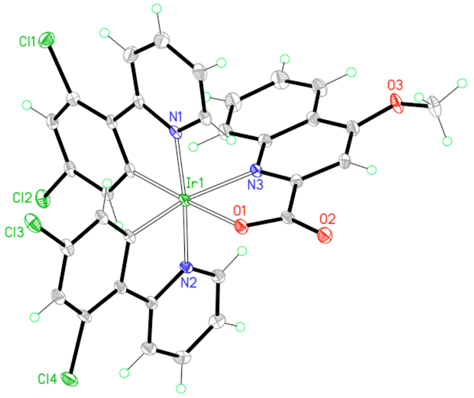


Table S3. Crystal data and structure refinement for **EB95**.

Identification code	eb95h	
Empirical formula	$C_{33}H_{20}Cl_4IrN_3O_3$	
Formula weight	840.52	
Temperature	140(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	*P*-1	
Unit cell dimensions	a = 10.9629(3) Å	α= 90.525(2)°.
	b = 11.1318(3) Å	β= 91.673(2)°.
	c = 12.1713(3) Å	γ = 102.779(2)°.
Volume	1447.75(7) Å^3	
Z	2	
Density (calculated)	1.928 Mg/m^3	
Absorption coefficient	5.023 mm^{-1}	
F(000)	816	
Crystal size	0.34 x 0.30 x 0.20 mm^3	
Theta range for data collection	2.91 to 26.02°.	
Index ranges	-13<=h<=13, -13<=k<=13, -15<=l<=14	
Reflections collected	11733	
Independent reflections	5655 [R(int) = 0.0167]	
Completeness to theta = 26.02°	99.2 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.60029	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5655 / 0 / 397	
Goodness-of-fit on F^2	1.030	
Final R indices [I>2sigma(I)]	R1 = 0.0186, wR2 = 0.0472	
R indices (all data)	R1 = 0.0203, wR2 = 0.0477	
Largest diff. peak and hole	0.846 and -0.541 e.Å^{-3}	

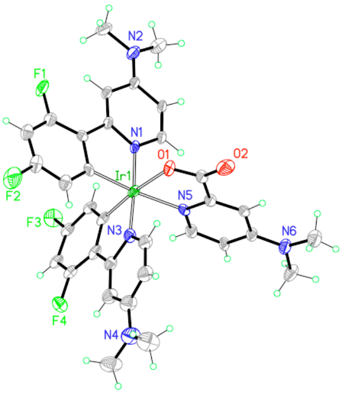


Table S4. Crystal data and structure refinement for **N977**.

Identification code	n977	
Empirical formula	$C_{35}H_{35}F_4IrN_6O_3$	
Formula weight	855.89	
Temperature	140(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	*P*-1	
Unit cell dimensions	a = 9.4762(8) Å	α= 108.231(7)°.
	b = 13.8917(9) Å	β= 93.780(7)°.
	c = 15.4205(14) Å	γ = 107.916(7)°.
Volume	1804.8(3) Å^3	
Z	2	
Density (calculated)	1.575 Mg/m^3	
Absorption coefficient	3.762 mm^{-1}	
F(000)	848	
Crystal size	0.15 x 0.10 x 0.04 mm^3	
Theta range for data collection	2.90 to 22.99°.	
Index ranges	-10<=h<=10, -14<=k<=15, -16<=l<=16	
Reflections collected	9199	
Independent reflections	4465 [R(int) = 0.1066]	
Completeness to theta = 22.99°	89.1 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.97653	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4465 / 270 / 442	
Goodness-of-fit on F^2	0.938	
Final R indices [I>2sigma(I)]	R1 = 0.0667, wR2 = 0.1024	
R indices (all data)	R1 = 0.1127, wR2 = 0.1129	
Largest diff. peak and hole	1.689 and -1.845 e.Å^{-3}	

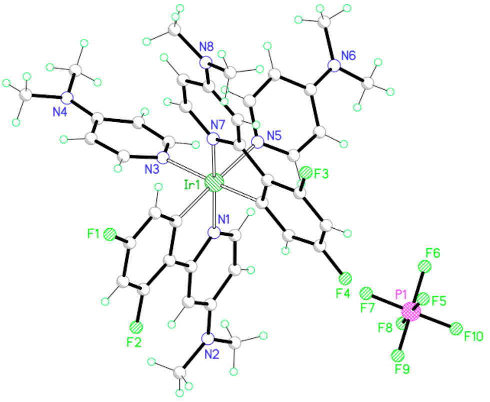


Table S5. Crystal data and structure refinement for **EB43**.

Identification code	eb43	
Empirical formula	$C_{40}H_{42}F_{10}IrN_8P$	
Formula weight	1047.99	
Temperature	140(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	*P*-1	
Unit cell dimensions	a = 9.8685(3) Å	α= 82.031(2)°.
	b = 12.1840(3) Å	β= 74.703(2)°.
	c = 18.1833(5) Å	γ = 82.763(2)°.
Volume	2079.33(10) Å^3	
Z	2	
Density (calculated)	1.674 Mg/m^3	
Absorption coefficient	3.335 mm^{-1}	
F(000)	1040	
Crystal size	0.36 x 0.30 x 0.19 mm^3	
Theta range for data collection	2.95 to 26.02°.	
Index ranges	-12<=h<=11, -15<=k<=14, -22<=l<=22	
Reflections collected	19019	
Independent reflections	8132 [R(int) = 0.0194]	
Completeness to theta = 26.02°	99.3 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.73889	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8132 / 0 / 541	
Goodness-of-fit on F^2	1.037	
Final R indices [I>2sigma(I)]	R1 = 0.0279, wR2 = 0.0715	
R indices (all data)	R1 = 0.0323, wR2 = 0.0727	
Largest diff. peak and hole	1.829 and -1.178 e.Å^{-3}	

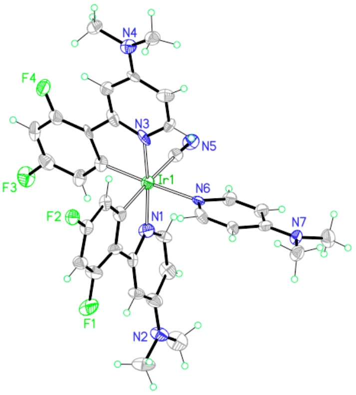


Table S6. Crystal data and structure refinement for **N995**.

Identification code	n995-b	
Empirical formula	$C_{35}H_{34}Cl_2F_4IrN_7$	
Formula weight	891.79	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	*P*-1	
Unit cell dimensions	a = 9.753(5) Å	α= 73.78(3)°.
	b = 12.791(6) Å	β= 85.69(4)°.
	c = 15.288(6) Å	γ = 69.36(3)°.
Volume	1713.2(13) Å^3	
Z	2	
Density (calculated)	1.729 Mg/m^3	
Absorption coefficient	4.112 mm^{-1}	
F(000)	880	
Crystal size	0.33 x 0.19 x 0.18 mm^3	
Theta range for data collection	3.36 to 25.00°.	
Index ranges	-11<=h<=11, -15<=k<=15, -18<=l<=18	
Reflections collected	22003	
Independent reflections	5957 [R(int) = 0.0981]	
Completeness to theta = 25.00°	98.5 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.0000 and 0.4409	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5957 / 42 / 477	
Goodness-of-fit on F^2	1.149	
Final R indices [I>2sigma(I)]	R1 = 0.0879, wR2 = 0.2070	
R indices (all data)	R1 = 0.1186, wR2 = 0.2299	
Largest diff. peak and hole	3.861 and -2.324 e.Å^{-3}	

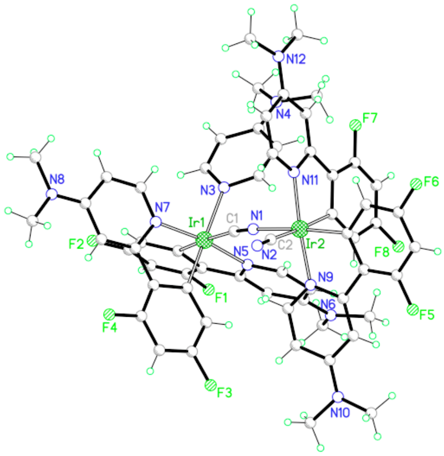
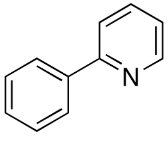
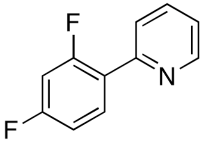
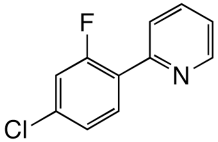
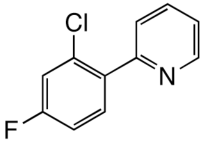
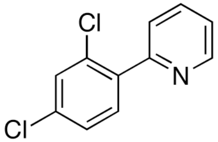
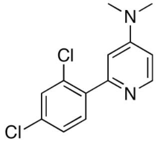
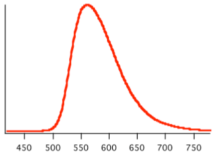
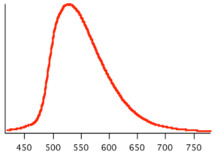
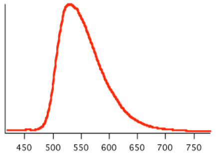
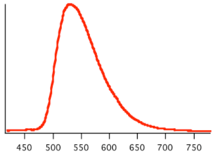
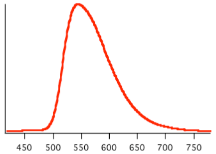
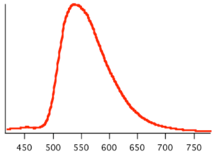
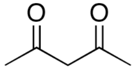
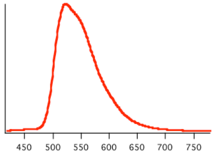
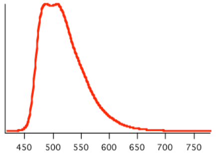
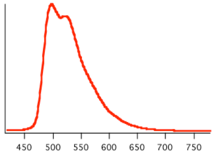
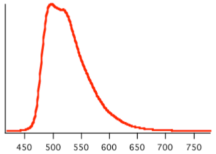
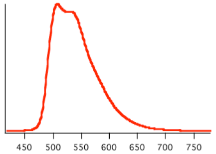
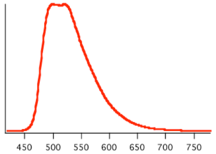
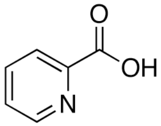
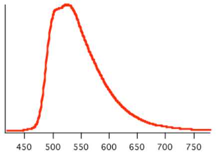
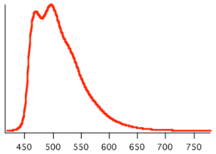
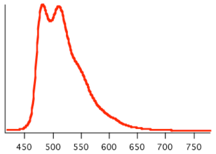
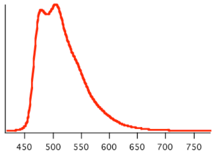
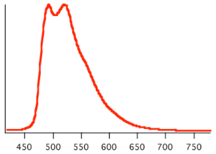
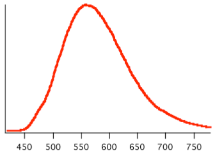
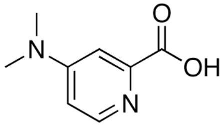
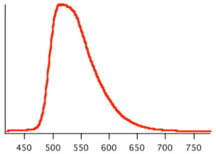
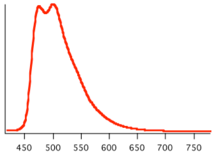
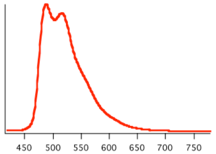
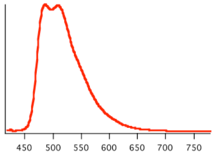
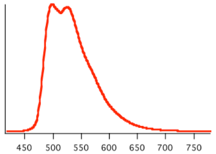
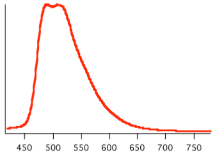
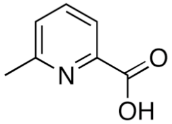
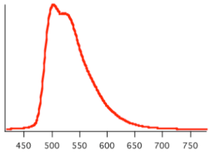
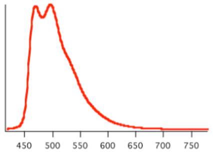
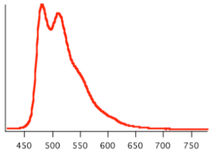
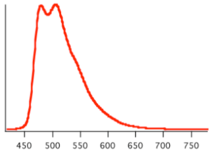
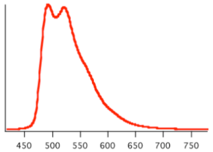
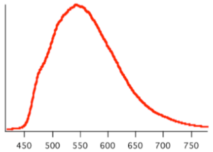
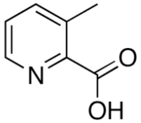
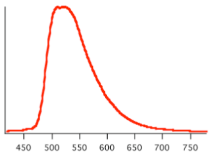
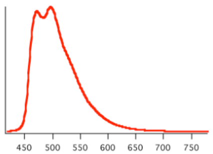
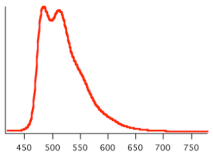
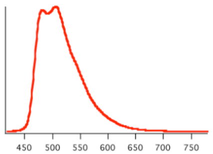
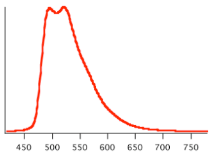
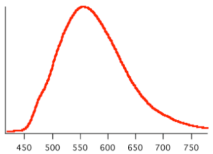
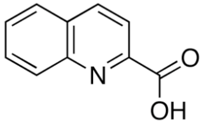
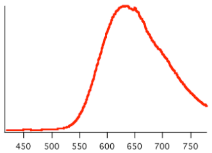
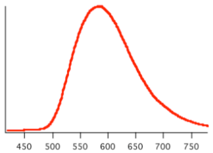
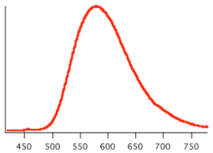
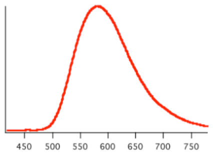
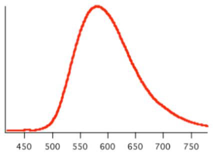
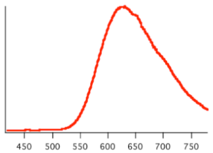
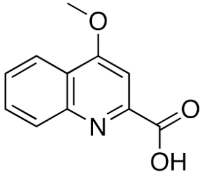
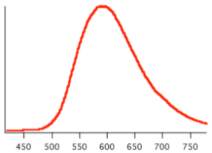
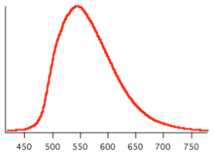
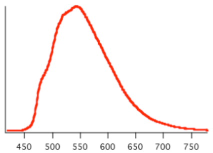
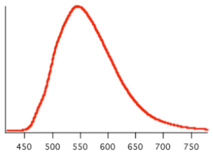
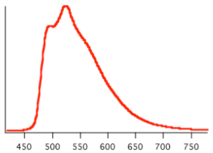
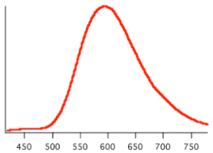
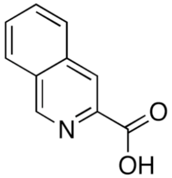
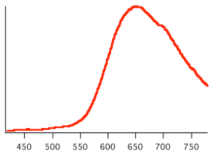
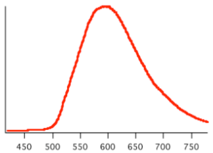
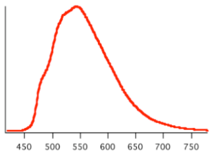
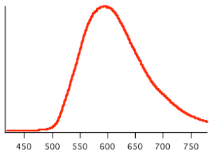
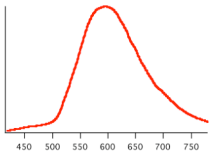
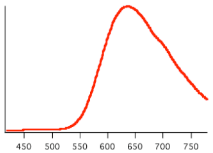
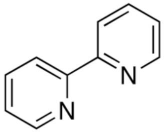
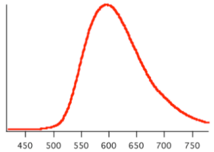
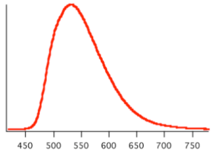
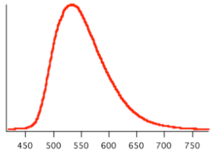
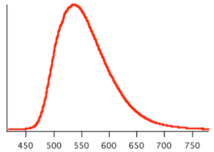
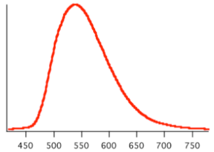
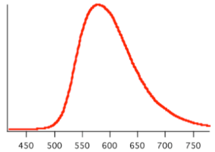
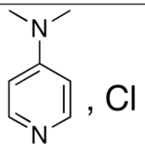
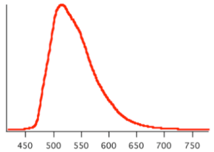
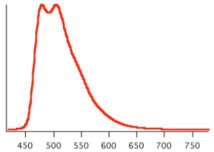
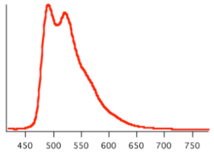
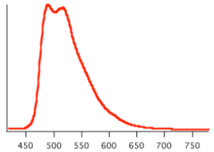
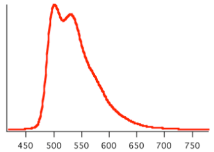
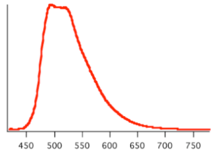
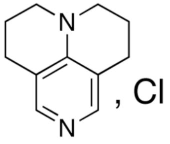
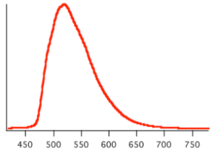
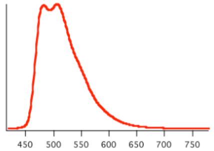
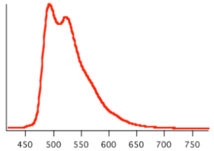
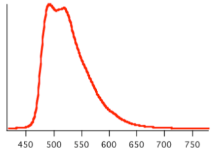
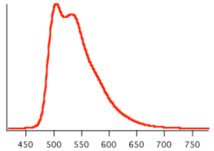
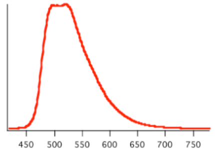
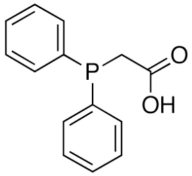
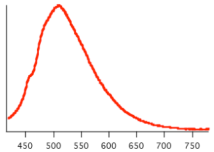
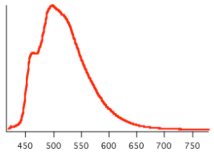
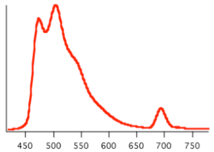
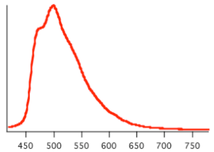
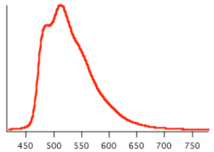
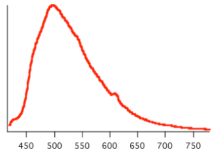
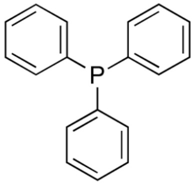
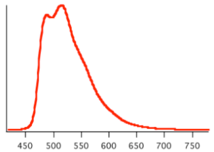
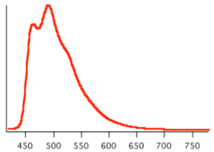
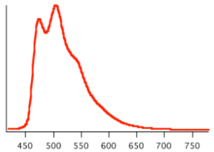
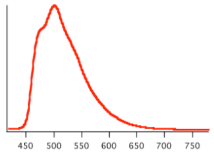
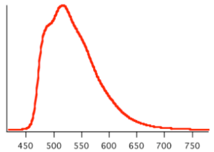
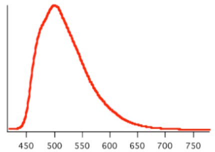


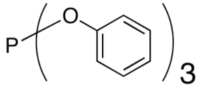
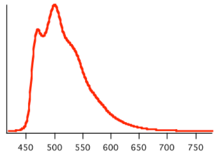
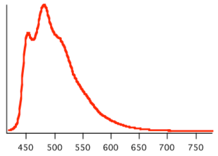
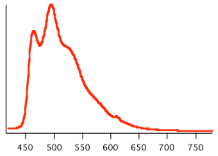
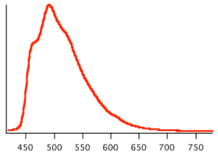
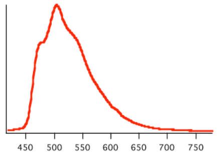
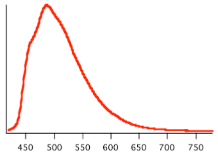
Table S7. Crystal data and structure refinement for **N995dimer**.

Identification code	n995	
Empirical formula	C61H54F8Ir2N12	
Formula weight	1491.56	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	*P*-1	
Unit cell dimensions	a = 17.450(2) Å	a= 80.953(10)°.
	b = 18.5594(19) Å	b= 76.281(12)°.
	c = 24.439(4) Å	g = 68.024(8)°.
Volume	7109.5(16) Å^3	
Z	4	
Density (calculated)	1.394 Mg/m^3	
Absorption coefficient	3.802 mm^{-1}	
F(000)	2920	
Crystal size	0.37 x 0.29 x 0.21 mm^3	
Theta range for data collection	3.31 to 27.50°.	
Index ranges	-22<=h<=22, -24<=k<=24, -31<=l<=31	
Reflections collected	161099	
Independent reflections	31819 [R(int) = 0.0428]	
Completeness to theta = 27.50°	97.4 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.0000 and 0.6696	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	31819 / 0 / 1495	
Goodness-of-fit on F2	1.070	
Final R indices [I>2sigma(I)]	R1 = 0.0395, wR2 = 0.0906	
R indices (all data)	R1 = 0.0584, wR2 = 0.1000	
Largest diff. peak and hole	2.654 and -1.413 e.Å^{-3}	

Ancillary ligand	**Main Ligand**					
						
TBAOH	 λ_{max}:560 nm fwhm:2716 cm^{-1}	 λ_{max}:527 nm fwhm:3383 cm^{-1}	 λ_{max}:531 nm fwhm:2719 cm^{-1}	 λ_{max}:530 nm fwhm:2789 cm^{-1}	 λ_{max}:544 nm fwhm:2822 cm^{-1}	 λ_{max}:539 nm fwhm:2987 cm^{-1}
	 λ_{max}:524 nm fwhm:2656 cm^{-1}	 λ_{max}:487 nm fwhm:3183 cm^{-1}	 λ_{max}:498 nm fwhm:2755 cm^{-1}	 λ_{max}:498 nm fwhm:2896 cm^{-1}	 λ_{max}:509 nm fwhm:2910 cm^{-1}	 λ_{max}:501 nm fwhm:3269 cm^{-1}
	 λ_{max}:524 nm fwhm:3221 cm^{-1}	 λ_{max}: 470, 497 nm fwhm:3518 cm^{-1}	 λ_{max}:483, 511 nm fwhm:3011 cm^{-1}	 λ_{max}:479, 506 nm fwhm:3187 cm^{-1}	 λ_{max}:493, 520 nm fwhm:3154 cm^{-1}	 λ_{max}:558 nm fwhm:4027 cm^{-1}
	 λ_{max}:518 nm fwhm:2844 cm^{-1}	 λ_{max}:476, 500 nm fwhm:3164 cm^{-1}	 λ_{max}:488, 516 nm fwhm:2798 cm^{-1}	 λ_{max}:486, 509 nm fwhm:3049 cm^{-1}	 λ_{max}:499, 526 nm fwhm:3078 cm^{-1}	 λ_{max}:490 nm fwhm:3301 cm^{-1}

	 λ_{max}:503 nm fwhm:2779 cm^{-1}	 λ_{max}:471, 498 nm fwhm:3204 cm^{-1}	 λ_{max}:482, 511 nm fwhm:2796 cm^{-1}	 λ_{max}:481, 507 nm fwhm:3169 cm^{-1}	 λ_{max}:493, 521 nm fwhm:3076 cm^{-1}	 λ_{max}:544 nm fwhm:4671 cm^{-1}
	 λ_{max}:521 nm fwhm:3017 cm^{-1}	 λ_{max}:472, 497 nm fwhm:3226 cm^{-1}	 λ_{max}:484, 513 nm fwhm:2965 cm^{-1}	 λ_{max}:482, 507 nm fwhm:3117 cm^{-1}	 λ_{max}:496, 522 nm fwhm:3061 cm^{-1}	 λ_{max}:556 nm fwhm:4195 cm^{-1}
	 λ_{max}:634 nm fwhm:3282 cm^{-1}	 λ_{max}:585 nm fwhm:3512 cm^{-1}	 λ_{max}:579 nm fwhm:3329 cm^{-1}	 λ_{max}:580 nm fwhm:3346 cm^{-1}	 λ_{max}:580 nm fwhm:3365 cm^{-1}	 λ_{max}:624 nm fwhm:3233 cm^{-1}
	 λ_{max}:593 nm fwhm:3461 cm^{-1}	 λ_{max}:545 nm fwhm:3710 cm^{-1}	 λ_{max}:544 nm fwhm:3941 cm^{-1}	 λ_{max}:546 nm fwhm:3802 cm^{-1}	 λ_{max}:523 nm fwhm:3676 cm^{-1}	 λ_{max}:593 nm fwhm:3451 cm^{-1}
	 λ_{max}:651 nm fwhm:3504 cm^{-1}	 λ_{max}:597 nm fwhm:3537 cm^{-1}	 λ_{max}:592 nm fwhm:3462 cm^{-1}	 λ_{max}:595 nm fwhm:3439 cm^{-1}	 λ_{max}:594 nm fwhm:3519 cm^{-1}	 λ_{max}:637 nm fwhm:3390 cm^{-1}

	 λ_{max}:596 nm fwhm:3165 cm^{-1}	 λ_{max}:534 nm fwhm:3556 cm^{-1}	 λ_{max}:532 nm fwhm:3412 cm^{-1}	 λ_{max}:538 nm fwhm:3402 cm^{-1}	 λ_{max}:540 nm fwhm:3630 cm^{-1}	 λ_{max}:580 nm fwhm:3142 cm^{-1}
	 λ_{max}:517 nm fwhm:2924 cm^{-1}	 λ_{max}:479, 506 nm fwhm:3166 cm^{-1}	 λ_{max}:492, 521 nm fwhm:2780 cm^{-1}	 λ_{max}:490, 517 nm fwhm:3028 cm^{-1}	 λ_{max}:502, 531 nm fwhm:2841 cm^{-1}	 λ_{max}:494 nm fwhm:3291 cm^{-1}
	 λ_{max}:520 nm fwhm:3062 cm^{-1}	 λ_{max}:483, 507 nm fwhm:3192 cm^{-1}	 λ_{max}:493, 523 nm fwhm:2728 cm^{-1}	 λ_{max}:493, 520 nm fwhm:3007 cm^{-1}	 λ_{max}:506, 534 nm fwhm:2895 cm^{-1}	 λ_{max}:499 nm fwhm:3324 cm^{-1}
	 λ_{max}:511 nm fwhm:3945 cm^{-1}	 λ_{max}:462, 499 nm fwhm:4008 cm^{-1}	 λ_{max}:474, 505 nm fwhm:3315 cm^{-1}	 λ_{max}:500 nm fwhm:3481 cm^{-1}	 λ_{max}:512 nm fwhm:3385 cm^{-1}	 λ_{max}:498 nm fwhm:4271 cm^{-1}
	 λ_{max}:488, 514 nm fwhm:3228	 λ_{max}:464, 491 nm fwhm:3446 cm^{-1}	 λ_{max}:474, 505 nm fwhm:3351 cm^{-1}	 λ_{max}:502 nm fwhm:3426 cm^{-1}	 λ_{max}:518 nm fwhm:3645 cm^{-1}	 λ_{max}:502 nm fwhm:3626 cm^{-1}

	 λ_{max}:471, 500 nm fwhm:3463 cm^{-1}	 λ_{max}:454, 482 nm fwhm:3610 cm^{-1}	 λ_{max}:465, 494 nm fwhm:3552 cm^{-1}	 λ_{max}:492 nm fwhm:3709 cm^{-1}	 λ_{max}:505 nm fwhm:3595 cm^{-1}	 λ_{max}:488 nm fwhm:3959 cm^{-1}
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