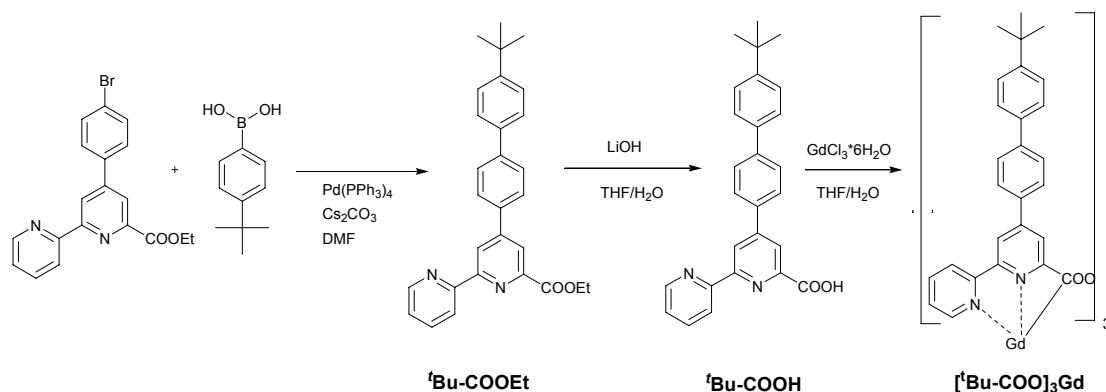


Supplementary Material for Dalton Transactions

Sensitized Near-infrared Emission from Ytterbium(III) via Direct Energy Transfer from Iridium(III) in a Heterometallic Complex

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Scheme S1. Synthetic procedure for the preparation of [**tBu-COO**]₃Yb.

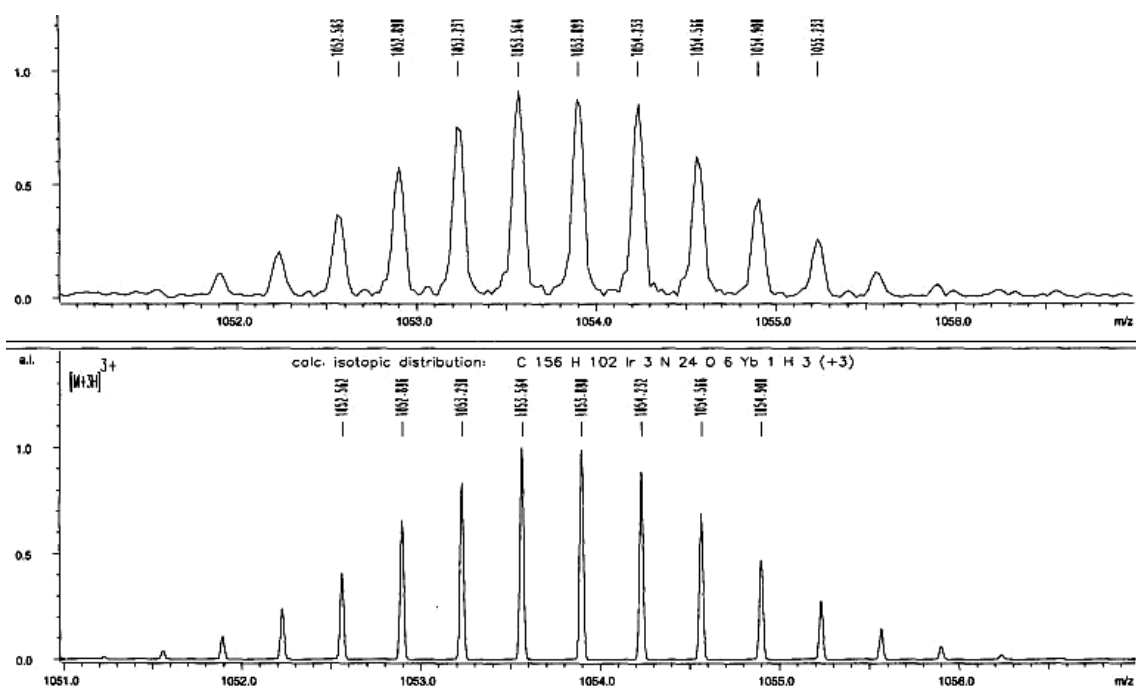


Figure S1. High resolution mass spectrum of $[\text{Ir}_3\text{Yb} + 3\text{H}]^{3+}$ (top) and calculated isotopic distribution (bottom).

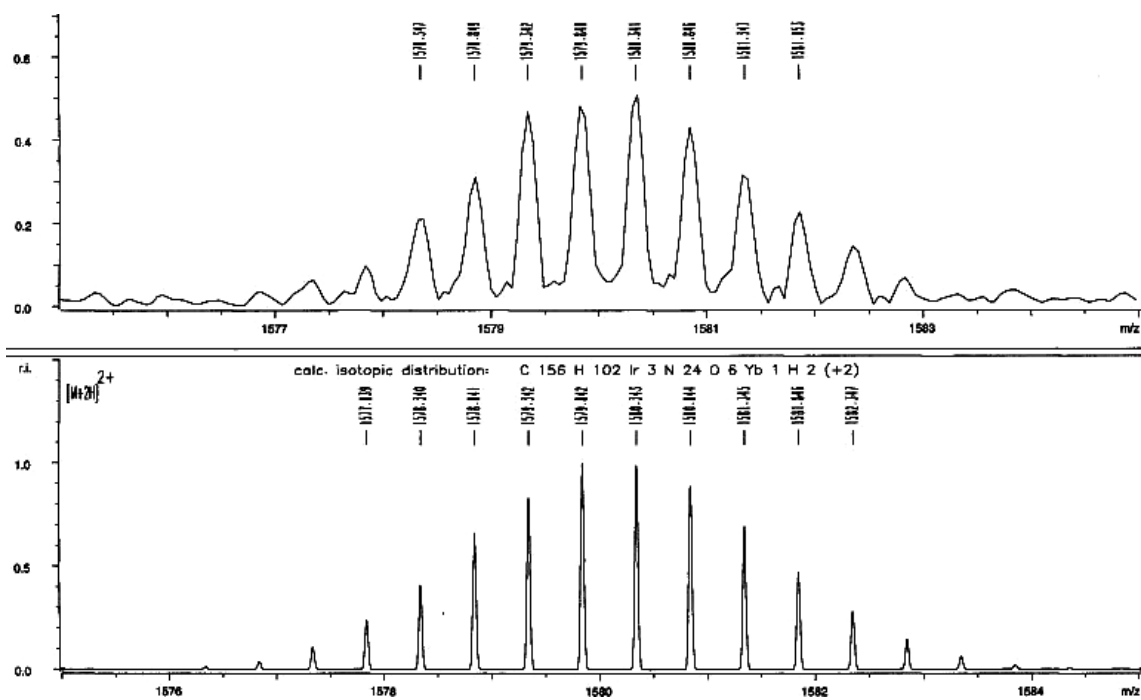


Figure S2. High resolution mass spectrum of $[\text{Ir}_3\text{Yb} + 2\text{H}]^{2+}$ (top) and calculated isotopic distribution (bottom).

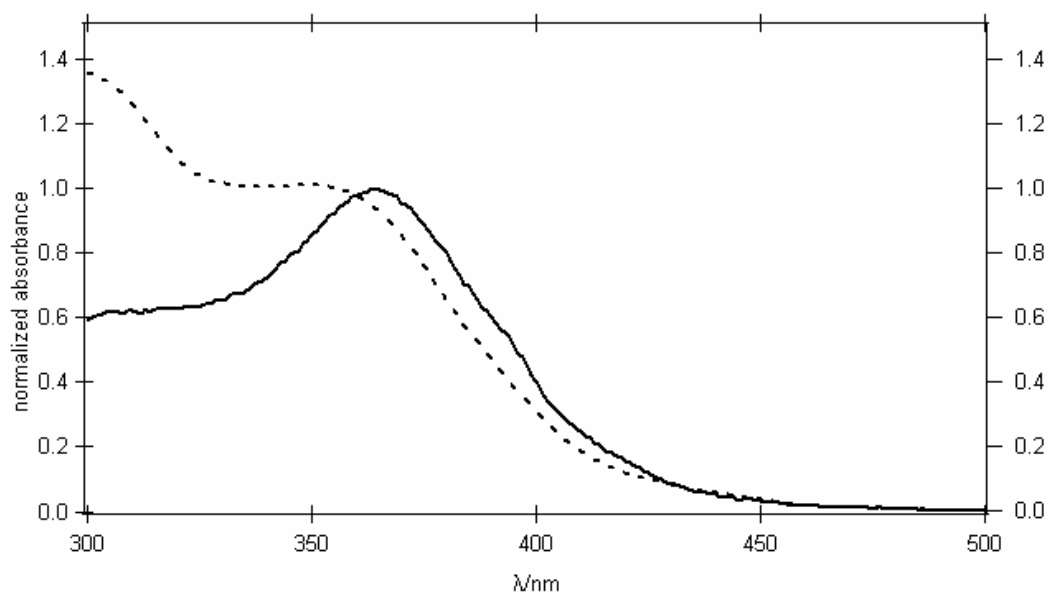


Figure S3. Normalized excitation (solid line) and absorption (dashed line) spectrum of Ir_3Yb in degassed CH_2Cl_2 ($\lambda_{\text{em}} = 976 \text{ nm}$).

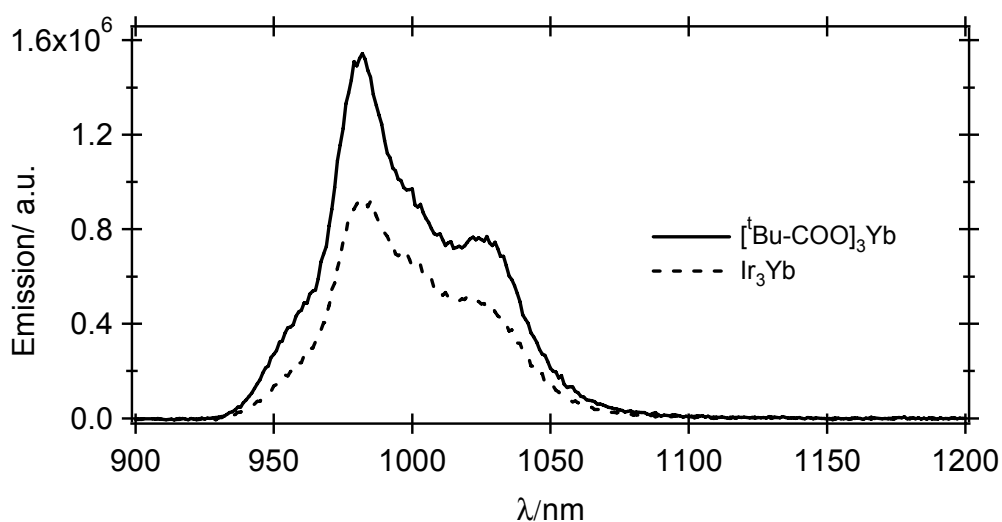


Figure S4. Emission spectra of Ir_3Yb and $[\text{tBu-COO}]_3\text{Yb}$ after excitation at 370 nm in deaerated CH_2Cl_2 . The concentrations were adjusted such that the individual solutions were isoabsorptive at 370 nm.

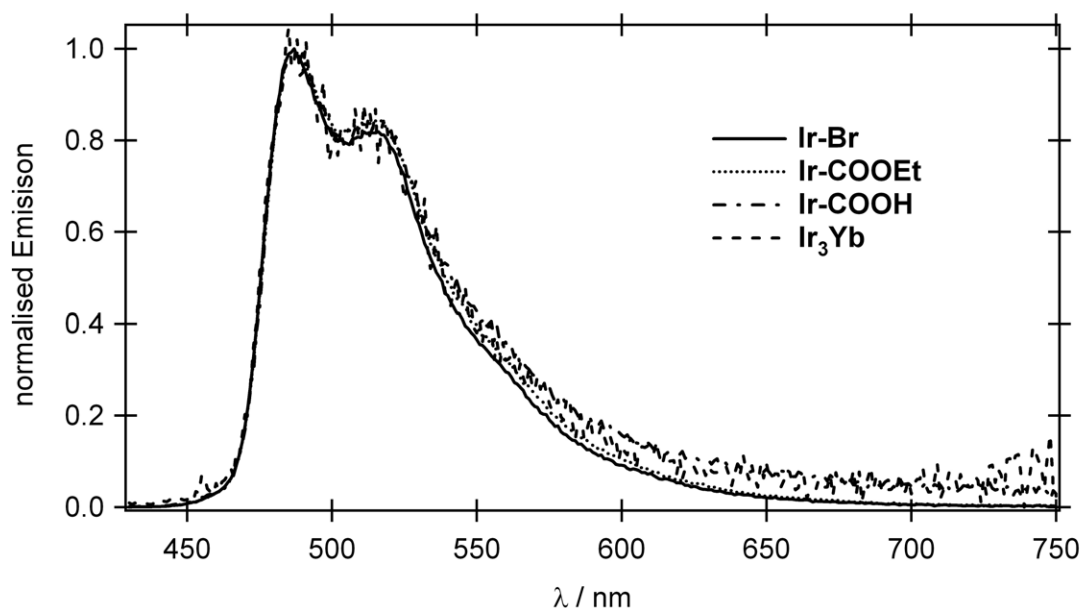


Figure S5. Normalised emission spectra of **Ir-Br**, **Ir-COOEt**, **Ir-COOH**, and **Ir₃Yb**. All compounds were excited at 400 nm and measured in deaerated CH₂Cl₂.

Experimental Section

Photophysics: Absorption spectra were measured on a Varian Cary 5000 double-beam UV-Vis-NIR spectrometer and baseline corrected. Steady-state emission spectra were recorded on a HORIBA Jobin-Yvon IBH FL-322 Fluorolog 3 spectrometer equipped with a 450 W xenon arc lamp, double grating excitation and emission monochromators (2.1 nm/mm dispersion; 1200 grooves/mm) and a Hamamatsu R928 photomultiplier tube or a TBX-4-X single-photon-counting detector. Emission and excitation spectra were corrected for source intensity (lamp and grating) and emission spectral response (detector and grating) by standard correction curves. Time-resolved measurements up to ~5 μs were performed using the time-correlated single-photon counting (TCSPC) option on the Fluorolog 3. A NanoLED (402 nm; FWHM < 750 ps) with repetition rates between 10 kHz and 1 MHz was used to excite the sample. The excitation source was mounted directly on the sample chamber at 90° to a double

grating emission monochromator (2.1 nm/mm dispersion; 1200 grooves/mm) and collected by a TBX-4-X single-photon-counting detector. The photons collected at the detector are correlated by a time-to-amplitude converter (TAC) to the excitation pulse. Signals were collected using an IBH DataStation Hub photon counting module and data analysis was performed using the commercially available DAS6 software (HORIBA Jobin Yvon IBH). The goodness of fit was assessed by minimizing the reduced chi squared function (χ^2) and visual inspection of the weighted residuals.

Excited-state lifetimes $>10 \mu\text{s}$ using the FL-1040 phosphorescence module with a 70-W xenon flash tube (full-width at half maximum, FWHM = 3 ms) with a variable flash rate (0.05 – 25 Hz). The signals were recorded on the TBX-4-X single-photon-counting detector and collected with a multichannel scaling (MCS) card in the IBH DataStation Hub photon counting module and data analysis was performed as described above.

Steady-state NIR measurements were performed using the Fluorolog 3 equipped with an air-cooled Hamamatsu H9170-75 (InP/InGaAs) PMT in the spectral range 930 – 1700 nm. Emission spectra were corrected for source intensity (lamp and grating) and emission spectral response (detector and grating) by standard correction curves.

Time-resolved NIR measurements were measured on an FL900CDT time-resolved T-Geometry fluorometer equipped with a LTB MSG 400 nitrogen laser (337 nm; pulse energy=20 mJ, repetition rate=10 Hz) and a North Coast EO 817P liquid-nitrogen-cooled germanium detector with a time resolution of 0.3 ns. The signals were averaged using a digitized Tektronix oscilloscope and then analyzed using standard fitting software.

Luminescence quantum yields (Φ_{em}) were measured in optically dilute solutions (O.D. < 0.1 at excitation wavelength) and compared to reference emitters by the following equation:¹

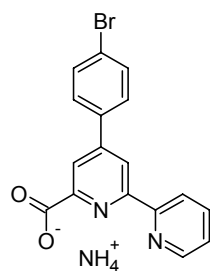
$$\Phi_x = \Phi_r \left[\frac{A_r(\lambda_r)}{A_x(\lambda_x)} \right] \left[\frac{I_r(\lambda_r)}{I_x(\lambda_x)} \right] \left[\frac{n_x^2}{n_r^2} \right] \left[\frac{D_x}{D_r} \right]$$

where A is the absorbance at the excitation wavelength (λ), I is the intensity of the excitation light at the excitation wavelength (λ), n is the refractive index of the

solvent, D is the integrated intensity of the luminescence and Φ is the quantum yield. The subscripts r and x refer to the reference and the sample, respectively. All quantum yields were performed at identical excitation wavelength for the sample and the reference, canceling the $I(\lambda_r)/I(\lambda_x)$ term in the equation. All solvents were spectrometric grade; dichloromethane was dried over calcium hydride and distilled prior to use. All solutions were filtered through 0.2 μm syringe filter before measurement. Deaerated samples were prepared by the freeze-pump-thaw technique.

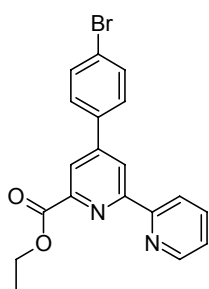
Synthesis: All reagents were analytical grade and used as received. Solvents were purified according to the standard procedures.² All reactions were performed under inert atmosphere (Schlenk-line techniques). All chromatography was performed with silica gel 60 (particle size 63 – 200 μm , 230 – 400 mesh, Merck) using common flash procedures.³ NMR spectra were recorded on an ARX 300 (Bruker Analytische Messtechnik, Karlsruhe, Germany) or on a Unity Plus 600 MHz (Varian, Palo Alto, CA, USA) spectrometer. The chemical shifts (δ) of the signals are given in ppm and referenced to residual protons in the deuterated solvents. The signal splitting was abbreviated as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. All coupling constants (J) are given in Hertz (Hz). The abbreviation C_q in the ^{13}C -NMR describes quaternary carbon atoms. Electrospray ionization (ESI) mass spectra were recorded on a Waters Micromass (Manchester, UK) Quattro LCZ with nanospray inlet or a Bruker Daltonics (Bremen, Germany) MicroTof with loop injection. Mass spectrometry measurements, elemental (CHN) analyses and NMR measurements were performed in the Department of Chemistry, University of Münster.

Ammonium 4-(4-Bromophenyl)-6-(pyridin-2-yl)pyridine-2-carboxylate –



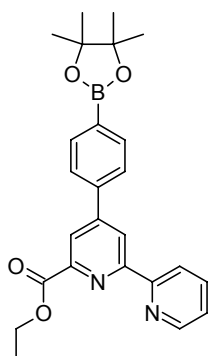
Synthesized according to the literature procedure.⁴ The resulting gray solid was used without further purification. δ_{H} (300 MHz, d_6 -DMSO) 8.72 – 8.70 (m, 1 H, py), 8.58 – 8.56 (m, 1 H, py), 8.48 (d, $J = 8.0$, 1 H), 8.18 – 8.15 (m, 1 H, py), 8.02 – 7.93 (m, 1 H, py), 7.82 (d, $J = 8.4$, 2 H, Ph), 7.74 (d, $J = 8.4$, 2 H, Ph), 7.52 – 7.43 (m, 1 H, py). MS (ESI): m/z 353.0 (100 %, $[\text{M} - \text{H}]^-$).

Ethyl-4-(4-bromophenyl)-6-(pyridin-2-yl)pyridine-2-carboxylate (Br-COOEt) –



To 500 mg (1.5 mmol) of 4-(4-Bromophenyl)-6-(pyridin-2-yl)pyridine-2-carboxylic acid in 50 mL of absolute EtOH was added ~5 – 10 drops of conc. H₂SO₄. The mixture was heated to reflux, at which time all solids went into solution (more H₂SO₄ was added if this was not the case). After 6 h, the solution was cooled to room temperature and poured over ice (50 mL). With stirring, 2 M K₂CO₃ was slowly added until the mixture was basic, causing a white precipitate to form. The solid was filtered, washed with water and air dried, giving 450 mg (48%) of an off-white solid, which could be used without further purification. Analytically pure compound was obtained by chromatography on silica gel (5:2:1 hexane:EtOAc:Et₃N) followed by recrystallization from hexane as white needles. Mp: 138 – 139 °C. δ_{H} (300 MHz, CDCl₃) 8.86 (d, J = 1.6, 1 H, py), 8.72 (d, J = 8.0, 1 H, py), 8.62 (d, J = 7.8, 1 H, py), 8.32 (d, J = 1.8, 1 H, py), 7.88 (dd, J = 8.1, J = 1.8, 1 H, py), 7.70 (d, J = 8.7, 2 H, Ph), 7.66 (d, J = 8.7, 2 H, Ph), 7.38 (dd, 1 H, py), 4.53 (q, J = 7.2, 2 H, OCH₂CH₃), 1.49 (t, J = 7.2, 3 H, OCH₂CH₃). δ_{C} (300 MHz, CDCl₃) 192.7 (C=O), 165.2, 156.6, 154.8, 149.2, 148.8, 137.4, 136.2, 132.3 (Ph), 128.8 (Ph), 124.4, 124.0, 122.5, 122.0, 121.5, 62.0 (OCH₂CH₃), 14.3 (OCH₂CH₃). MS (ESI⁺, MeOH) m/z 353 (5 %, [M – CH₂CH₃]⁺), 369.0 (4, [M – CH₂]⁺), 383.0 (40, [M + H]⁺), 391.0 (15, [M – CH₂ + Na]⁺), 405.0 (100, [M + Na]⁺). Anal. Calcd. for C₁₉H₁₅O₂N₂Br: C, 59.55; H, 3.95; N, 7.31. Found: C, 59.50; H, 3.80; N, 7.21.

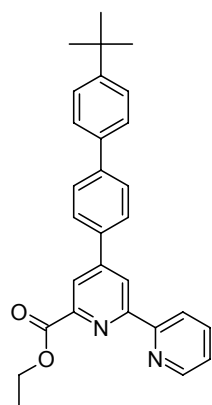
Ethyl-4-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-6-(pyridin-2-yl)pyridine-2-carboxylate -



To a dry, 25 mL Schlenk flask was added 200 mg (0.52 mmol) of ethyl-4-(4-bromophenyl)-6-(pyridin-2-yl)pyridine-2-carboxylate, 146 mg (0.57 mmol) of 4,4,5,5-tetramethyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,3,2-dioxaborolane and 154 mg (1.6 mmol) of potassium acetate. The flask was evacuated for 10 min. before being backfilled with nitrogen, at which time 10 mL of DMSO was added. The solution was degassed by freeze-pump-thaw technique and 13 mg (0.016 mmol) of PdCl₂(dppf) was added. The solution was heated to 80 °C for 16 h at which time TLC (5:2:1 hexane:EtOAc:Et₃N) indicated the absence of starting material. After cooling

to room temperature, the mixture was filtered through celite, washing with chloroform. The chloroform was removed by rotary evaporation and the DMSO by Kügelrohr distillation, resulting in a black solid. The solid was stirred for one hour in refluxing hexanes and filtered hot, washing twice with boiling hexanes. Removal of the solvent gave 202 mg (90%) of a white solid that was stored cold (0 °C) and used without further purification or recrystallized from hexanes. δ_{H} (300 MHz, CDCl_3) 9.03 (br s, 1 H, py), 8.76 (br s, 1 H, py), 8.70 – 8.66 (m, 1 H, py), 8.42 (s, 1 H, py), 8.05 – 7.90 (m, 3 H, py + Ph), 7.88 (d, $J = 7.5$, 2 H, Ph), 7.46 (br s, 1 H, py), 4.53 (q, $J = 7.2$, 2 H, OCH_2CH_3), 1.49 (t, $J = 7.2$, 3 H, OCH_2CH_3), 1.38 (s, 12 H, CH_3). MS (ESI⁺) m/z 417.4 ($[\text{M} - \text{CH}_2 + \text{H}]^+$), 431.4 ($[\text{M} + \text{H}]^+$), 453.4 ($[\text{M} + \text{Na}]^+$).

^tBu-COOEt – To a flame-dried, nitrogen-purged 20 mL Schlenk flask was added 250

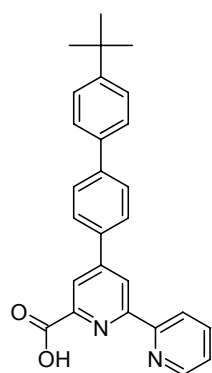


mg (0.65 mmol) of 4-bromophenyl-6-(ethyl carboxylato)-2,2'-bipyridine, 139 mg (0.78 mmol) of 4-*tert*-butylphenylboronic acid, and 255 mg (0.78 mmol) of Cs_2CO_3 . The flask was evacuated for 10 min. before backfilling with nitrogen, at which time 10 mL of dry DMF was added. The mixture was degassed by bubbling nitrogen through it for 20 min. and 38 mg (0.033 mmol) of $\text{Pd}(\text{PPh}_3)_4$ was added under a flow of nitrogen. The mixture was heated to 100 °C for 16 hours, at which point TLC (10:2:1

hexane:EtOAc:Et₃N) showed the absence of starting material. After cooling to room temperature, 20 mL of Et₂O and 20 mL of H₂O were added and biphasic solution stirred. After transferring to a separatory funnel and separating, the aqueous phase was washed twice more with Et₂O (20 mL), and the combined organic phases four times with water (20 mL) and once with brine (20 mL), dried over sodium sulfate, filtered and rotovapped to an oily solid. The crude product was chromatographed on silica with 10:2:1 hexane:EtOAc:Et₃N to yield the product as a white solid. The solid was crystallized from hexanes to give 250 mg (88%) of **^tBu-COOEt** as small white needles. Mp: 174 – 175 °C. δ_{H} (600 MHz, CDCl_3) 8.93 (d, $J = 1.7$, 1 H), 8.72 (m, $J = 0.8$, $J = 4.7$, 1 H), 8.63 (d, $J = 7.9$, 1 H), 8.42 (d, $J = 1.7$, 1 H), 7.91 (d, $J = 8.4$, 2 H), 7.87 (dt, $J = 1.8$, $J = 7.7$, 1 H), 7.75 (d, $J = 8.4$, 2 H), 7.62 (d, $J = 8.5$, 2 H), 7.51 (d, $J = 8.4$, 2 H), 7.36 (ddd, $J = 1.1$, $J = 4.8$, $J = 7.5$, 1 H), 4.54 (q, $J = 7.1$, 2 H, OCH_2), 1.51 (t, $J = 7.1$, 3 H, OCH_2CH_3), 1.38 (s, 9 H, *t*-Bu). δ_{C} /APT (600 MHz, CDCl_3)

165.4 (CO), 156.9 (C_{Ar}), 155.3 (C_{Ar}), 150.9 (C_{Ar}), 149.9 (C_{Ar}), 149.0 (C_{Ar}H), 148.5 (C_{Ar}), 142.2 (C_{Ar}), 137.2 (C_{Ar}H), 137.1 (C_{Ar}), 135.9 (C_{Ar}), 127.6 (C_{Ar}H), 127.5 (C_{Ar}H), 126.7 (C_{Ar}H), 125.9 (C_{Ar}H), 124.2 (C_{Ar}H), 122.6 (C_{Ar}H), 121.9 (C_{Ar}H), 121.5 (C_{Ar}H), 61.9 (OCH₂), 34.6 (C(CH₃)₃), 31.3 (C(CH₃)₃), 14.4 (OCH₂CH₃). MS (ESI⁺, MeCN/DMF) *m/z* 437.3 ([M + H]⁺), 459.2 ([M + Na]⁺), 873.4 ([2M + H]⁺), 895.3 ([2M + Na]⁺). Anal. Calcd. for C₂₉H₂₈O₂N₂: C, 79.79; H, 6.46; N, 6.42. Found: C, 79.85; H, 6.48; N, 6.31.

^tBu-COOH – To 200 mg of **^tBu-COOEt** (0.46 mmol) in 20 mL of THF and 5 mL of H₂O was added 13 mg (0.55 mmol, 1.2 eq.) of LiOH in 5 mL of H₂O. With vigorous stirring, the solution was stirred at room temperature for 16 h, at which time TLC (10:2:1 hexane:EtOAc:Et₃N) indicated the complete disappearance of starting material. After addition of several drop of HCl (2 M in H₂O), the reaction was partitioned between 20 mL of CH₂Cl₂ and 20 mL of H₂O, transferred to a separatory funnel and separated.

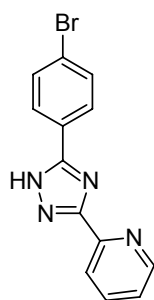


The aqueous phase was washed twice (20 mL) with CH₂Cl₂ and the combined organic phases three times (20 mL) with water. The organic phase was concentrated under reduced pressure to yield a pale yellow solid or oil. The crude product was crystallized from hot hexanes to give 170 mg (91%) of **^tBu-COOH** as a white crystalline solid and used without further purification. Mp: 200 – 201 °C. δ_H (500 MHz, CDCl₃) 8.99 (d, *J* = 1.4, 1 H), 8.79 (d, *J* = 4.2, 1 H), 8.55 (d, *J* = 1.6, 1 H), 8.41 (d, *J* = 7.9, 1 H), 7.95 – 7.87 (m, 3 H), 7.76 (d, *J* = 8.4, 2 H), 7.60 (d, *J* = 8.4, 2 H), 7.51 (d, *J* = 8.4, 2 H), 7.43 (dd, *J* = 5.2, *J* = 7.0, 1 H), 1.38 (s, 9 H). δ_C (500 MHz, CDCl₃) 164.4, 155.5, 153.9, 151.5, 151.1, 149.5, 146.4, 142.7, 137.3, 137.0, 135.2, 127.7, 127.6, 126.7, 125.9, 124.7, 122.7, 121.3, 121.2, 34.6, 31.3. MS (ESI⁻, MeOH): *m/z* 407.4 (100, [M – H]⁻), 443.3 (15, [M + Cl]⁻). Anal. Calcd. for C₂₇H₂₄O₂N₂: C, 79.39; H, 5.92; N, 6.86. Found: C, 79.05; H, 5.87; N, 6.75.

[^tBu-COO]₃Yb – To 100 mg (0.25 mmol, 3 eq.) of **^tBu-COOH** in 10 mL of THF and 2 mL of H₂O was added dropwise 6 mg (0.25 mmol, 3 eq.) of LiOH in 2 mL of H₂O at room temperature. The solution was then cooled to 0 °C and YbCl₃·6H₂O (0.083 mmol, 1 eq.) dissolved in 5 mL of H₂O was added dropwise. Immediately a white

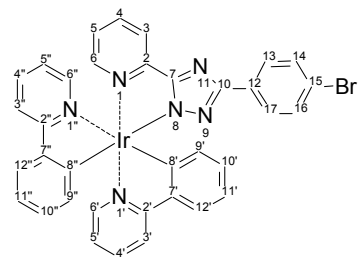
precipitate formed. The mixture was allowed to warm to room temperature overnight, at which time 30 mL of water was added. The white solid was filtered, washed with copious water and air dried. The off-white powder was further purified by the slow evaporation of CH₂Cl₂ from a CH₂Cl₂/CH₃CN solution to give 107 mg (88%) of [**Bu-COO**]₃**Yb** as a semi-crystalline white solid. MS (ESI⁺, MeCN): Calcd: 1418.5 ([L₃Yb + Na]⁺). Found: 1418.4. Anal. Calcd. for C₈₁H₆₉N₆O₆Yb·CH₂Cl₂: C, 66.53; H, 4.79; N, 5.68. Found: C, 66.24; H, 5.13; N, 5.64.

2-(5-(4-bromophenyl)-2H-1,2,4-triazol-3-yl)pyridine⁵ – To a flame-dried, nitrogen



purged 30 mL Schlenk tube was added of (pyridine-2-yl)amidrazone⁶ (2.0 g, 15 mmol) and of sodium carbonate (1.6 g, 15 mmol). The flask was evacuated and gently heated. After cooling, the flask was purged with nitrogen. Next, 15 mL of dry dimethylacetamide (DMAA) and 5 mL of dry THF was added, yielding a pale yellow suspension that was cooled to 0 °C. In a separate, dry 10 mL Schlenk flask, 3.2 g (15 mmol) of 4-bromobenzoyl chloride was dissolved in 5 mL of DMAA. This solution was then added to pre-cooled amidrazone mixture dropwise, which caused it to turn bright yellow. The mixture was slowly warmed to room temperature and stirred for an additional 5 h, yielding a thick yellow mixture. The contents were filtered, the solid washed with water and EtOH and the resulting pale yellow solid (3.85 g) allowed to air dry. The solid was suspended in 20 mL of ethylene glycol and heated to 200 °C for 30 min., yielding a pale yellow solution. Upon cooling to room temperature, a white solid formed and was collected on a glass frit, washing with ethanol. The solid was dried under vacuum to yield 3.2 g (73%) of a grey-white solid, which was used without further purification. Mp: 238 – 239 °C (lit.⁷ 230 – 231 °C). δ_H (300 MHz, d₆-DMSO) 8.73 (d, *J* = 4.5, 1 H, py), 8.18 (d, *J* = 7.8, 1 H, py), 8.10 (d, *J* = 12.9, 2 H, Ph), 8.02 (t, *J* = 7.5, 1 H, py), 7.60 – 7.40 (m, 4 H). MS (ESI⁻) *m/z* 301.0 ([M – H]⁻).

Ir-Br – The iridium dimer complex⁸ (1 eq., 142 mg, 0.13 mmol) and 2.5 eq. of 2-(5-(4-bromophenyl)-2H-1,2,4-triazol-3-yl)pyridine (102 mg, 0.33 mmol) were dissolved into 5 mL of CH₂Cl₂ and 1.5 mL of EtOH. The solution was stirred at room temperature for 12 h (after 1 hour everything went into solution and the reaction



solution became slightly green), turning yellow. The yellow solution was precipitated with hexanes while stirring. The precipitate was filtered and washed with hexanes. The yellow powder was dissolved with CH_2Cl_2 and chromatographed on silica gel (10:1 $\text{CHCl}_3/\text{EtOH}$) to yield 192 mg (90%) of a yellow solid. δ_{H} (600 MHz, d_6 -DMSO) 8.20 – 8.14 (m, 3 H, H-6, H-6', H-6''), 8.04 (dt, $J = 7.8$, $J = 1.6$, 1 H, H-4), 7.88 (d, $J = 8.7$, 2 H, H-13, H-17), 7.86-7.82 (m, 3 H, H-4', H-4'', H-12''), 7.80 (d, $J = 7.7$, 1 H, H-12'), 7.65 (d, $J = 5.8$, 1 H, H-3''), 7.62 (d, $J = 5.5$, 1 H, H-3), 7.59 (d, $J = 5.9$, 1 H, H-3'), 7.53 (d, $J = 8.7$, 2 H, H-14, H-16), 7.37 (dt, $J = 5.5$, $J = 1.4$, 1 H, H-5), 7.17 (dt, $J = 5.8$, $J = 1.4$, 1 H, H-5''), 7.13 (dt, $J = 5.9$, $J = 1.4$, 1 H, H-5'), 6.96 (dt, $J = 1.3$, $J = 7.5$, 1 H, H-10''), 6.89 (dt, $J = 7.3$, $J = 1.2$, 1 H, H-11''), 6.86 (dt, $J = 7.4$, $J = 1.3$, 1 H, H-10'), 6.76 (dt, $J = 7.4$, $J = 1.3$, 1 H, H-11'), 6.20 (dd, $J = 7.9$, $J = 1.2$, 1 H, H-9''), 6.19 (dd, $J = 7.7$, $J = 1.2$, 1 H, H-9'). The protons were assigned according to the following NMR-experiments: gHSQC, gCOSY, gHMBC.

δ_{C} (500 MHz, d_6 -DMSO) 167.6 (C_q), 167.3 (C_q), 163.3 (C_q), 162.8 (C_q), 153.7 (C-Br), 150.6 (C_q), 149.7 (C_q), 149.1 (C-3, C-3''), 148.6 (C-3'), 144.6 (C-Ir), 143.9 (C-Ir), 139.4 (C-4), 138.1 (C-4''), 137.6 (C-4'), 131.4 (C-14, C-16, C-9', C-9''), 129.9 (C-11''), 129.1 (C-11'), 127.5 (C-13, C-17), 125.3 (C-5), 124.8 (C-12''), 124.3 (C-12'), 123.5 (C-5''), 123.2 (C-5'), 121.7 (C-10''), 121.1 (C_q), 120.8 (C-10'), 120.7 (C_q), 119.5 + 119.4 (C-6/C-6'/C-6''). MS (ESI⁺) m/z 801.1 (100 % $[\text{M} + \text{H}]^+$), 823.1 (10, $[\text{M} + \text{Na}]^+$). HRMS calcd. For $\text{C}_{35}\text{H}_{25}\text{N}_6\text{BrIr}$ 801.0933 ($[\text{M} + \text{H}]^+$); found 801.0925. Anal. Calcd. for $\text{C}_{35}\text{H}_{24}\text{IrN}_6\cdot\text{CH}_2\text{Cl}_2$: C, 48.82; H, 2.96; N, 9.49. Found: C, 48.99; H, 3.05; N, 9.52.

Ir-COOEt – To a flame-dried 20 mL Schlenk flask was added 60.0 mg (0.075 mmol) of **Ir-Br**, 48.4 mg (0.112 mmol) of ethyl-4-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-6-(pyridin-2-yl)pyridine-2-carboxylate and 245 mg (0.75 mmol) of Cs_2CO_3 and dissolved in 10 mL of anhydrous DMF. The solution was degassed by the freeze-pump-thaw technique and 5 mg $\text{Pd}(\text{PPh}_3)_4$ was added under nitrogen. The reaction mixture was heated at 95 °C for 6 h. The solvent was reduced by adding toluene and evaporating the azeotropic mixture under reduced pressure. The residue was extracted with water and CH_2Cl_2 , the organic phases were dried over

MgSO₄, filtered and the solvent was evaporated under reduced pressure. The yellow solid was dissolved in CH₂Cl₂ and chromatographed on silica gel (10:1.5 CHCl₃:EtOH) to yield 65 mg (84%) of **Ir-COOEt** as a yellow solid. δ_{H} (400 MHz, CDCl₃) 8.92 (s, 1 H), 8.72 (d, $J = 1.6$, 1 H), 8.61 (d, $J = 8.0$, 1 H), 8.41 (s, 1 H), 8.34 (bd, $J = 6.4$, 1 H), 8.26 (d, $J = 8.0$, 2 H), 7.95 (d, $J = 5.2$, 1 H), 7.90 – 7.60 (m, 16 H), 7.56 (d, $J = 5.2$, 1 H), 7.35 (m, 1 H), 7.09 (t, 1 H), 7.01 – 6.81 (m, 6 H), 6.41 (t, 1 H), 4.54 (q, $J = 7.2$, 2 H, -OCH₂), 1.50 (t, $J = 7.2$, 3 H, -OCH₂CH₃). δ_{C} (500 MHz, CDCl₃) 167.6, 167.3, 164.7, 163.4, 163.3, 156.3, 154.3, 153.8, 150.8, 149.8, 149.5, 149.1, 148.6, 144.5, 143.9, 141.1, 139.4, 138.1, 137.9, 137.6, 137.5, 135.3, 132.6, 131.4, 129.9, 129.1, 127.6, 127.3, 126.7, 126.2, 125.2, 124.9, 124.8, 124.3, 123.5, 123.2, 122.0, 121.7, 121.0, 120.8, 120.4, 119.5, 119.4, 79.2, 61.5. MS (ESI⁺) m/z 1025.3 (100 %, [M + H]⁺), 1047.3 (98, [M + Na]⁺), 1011.2 ([M - CH₂ + H]⁺). HRMS Calcd. for C₅₄H₃₉IrN₈O₂ 1047.2727 ([M₂Na₂]²⁺); found 1047.2703.

Ir-COOH – To a solution of 67.2 mg (65.6 μmol) of **Ir-COOEt** in 15 mL THF was added 1.5 mL of 1 M aq. NaOH solution. The reaction mixture was stirred for 12 h at room temperature during which time a yellow precipitate formed. The THF was evaporated under reduced pressure. Upon addition of water the precipitate dissolved and the solution was extracted with CH₂Cl₂ (3 \times 30 mL) and the organic layers were washed with water (3 \times 30 mL) (with the negatively charged carboxylate **Ir-COO⁻** remaining in the basic water phase). After careful acidification of the aqueous layer with dilute HCl, the carboxylic acid **Ir-COOH** was extracted from the aqueous phase with CH₂Cl₂ (3 \times 30 mL). The organic phase was washed with water (3 \times 30 mL) and evaporated under reduced pressure (drying with basic drying agents is not recommended). The yellow compound was obtained in 90% yield (58.8 mg) and used without further purification. δ_{H} (300 MHz, CDCl₃) 8.99 (m, 2 H), 8.75 (m, 2 H), 8.53 (m, 2 H), 8.39 (m, 2 H), 8.33 (d, $J = 8.4$, 2 H), 7.96 (m, 2 H), 7.90 (d, 4 H), 7.77 (d, 4 H), 7.66 (m, 6 H), 7.53 (m, 1 H), 7.40 (m, 2 H), 7.16 (t, 1 H), 6.97 (m, 2 H), 6.87 (m, 1 H), 6.40 (m, 2 H). MS (ESI⁻) m/z 995.4 (100 %, [M - H]⁺). Anal. Calcd. for C₅₂H₃₅IrN₈O₂·EtOH: C, 58.88; H, 3.45; N, 10.37. Found: C, 58.95; H, 3.69; N, 10.00.

Ir₃Yb – The iridium acid (87 mg, 87 μmol) **Ir-COOH** was dissolved in water, which was brought to pH 9 with Et₃N. YbCl₃·6 H₂O (12 mg, 29 μmol) was dissolved in the

minimum amount of water and then added dropwise under stirring to the reaction mixture. After stirring overnight and then heating to 50 °C for 1 h, a yellow precipitate formed. The precipitate was filtered and washed with basic water in order to remove unreacted **Ir-COOH**, which stayed in the basic aqueous phase. The solid is then dissolved in CH₂Cl₂, again extracted with basic water, and then evaporated. The solid was dried under vacuum to yield **Ir₃Yb** in 80% yield (74 mg). HRMS (ESI⁺), *m/z* 997.259 (100%, [**Ir-COOH** + H]⁺), 1053.564 (90, [**Ir₃Yb** + 3H]³⁺), 1203.420 (20), 1580.341 (50, [**Ir₃Yb** + 2H]²⁺), 1656.820 (10) (see Figures S4 and S5).

References for Supporting Information

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