Recyclable Iridium-Containing Copolymers for Homogeneous Photoredox Catalysis

Shweta Gaikwad, Argha Bhattacharjee, Stanley Baldwin, Steven Huss, Anna Griggs, Michael Spicuzza, Elizabeth Elacqua*

Department of Chemistry, The Pennsylvania State University, University Park, Pennsylvania 16802, United States

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1) Materials and Methods

All chemicals were purchased from Sigma Aldrich, Alfa Aesar, Oakwood Chemicals, Ambeed or TCI America, and used as received unless otherwise indicated. NMR spectroscopic characterization was conducted on a Bruker NEO-400 MHz spectrometer using $CDCl_3$, DMSO-d_6, or acetone-d_6. Chemical shifts are reported in ppm and referenced with respect to residual solvent. Ir complexes (i.e., Ir[(dF(CF_3)ppy_2)(dmbpy)](PF_6), [Ir(dmbpy)$(ppy)_2$](PF_6), and *fac*-Ir$(ppy)_3$, were synthesized according to modified procedures.[1-3] 1,3,5-Trimethoxybenzene was utilized as an internal standard to calculate conversion and yields for small molecule photoredox reactions.

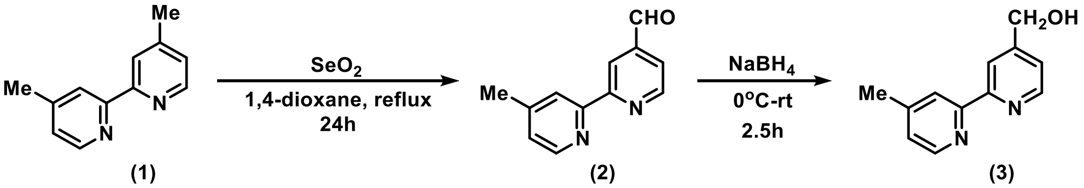
UV-Visible absorption spectra were obtained on a PerkinElmer LAMBDA 365 UV-Vis spectrometer (PerkinElmer, Inc) using a quartz cuvette (VWR). Fluorescence spectra were obtained on a PerkinElmer FL 6500 Fluorimeter (PerkinElmer, Inc) using a quartz cuvette (VWR).

The mass data were acquired on a Bruker Ultraflextreme MALDI-TOF mass spectrometer in positive reflector mode. The matrix was 10 mg/mL solution of DCTB in dichloromethane. Samples were mixed with the matrix in 1:1 volumetric ratio and applied to a polished steel target plate

Photoredox experiments were conducted using CFL lights or Kessil LED photoredox lights (PR-160; 440 nm, 456 nm, 427 nm, 100% intensity) using either 20 mL scintillation vials or 5 mL vials pending reaction scale. All reactions were irradiated with different light sources depending on the reactions at a vial-to-lamp distance of 6.5 cm have a total irradiance of 64.7 mW/cm^2 and a cooling fan positioned either adjacent to the reactions (household desk fan) or above the reactions (Kessil rig).

2) Synthesis of Iridium Monomers

Synthesis of (4'-methyl-[2,2'-bipyridin]-4-yl) methanol (3)[4]



A mixture of 4,4'-dimethyl-2,2'-bipyridine (6.15 g, 33.3 mmol) and selenium dioxide (6.15 g, 55.5 mmol) was dissolved in 300 mL of 1,4-dioxane and refluxed at 110 °C for 24 hours. After cooling to room temperature, the mixture was filtered and the 1,4-dioxane was evaporated under reduced pressure. The resulting solid was suspended in 300 mL of chloroform, filtered, and the chloroform was removed under reduced pressure. The solid was then treated with 50 mL of methanol and stirred on ice. Sodium borohydride (1.0 g in 8.8 mL of 0.2M aqueous NaOH) was added dropwise while stirring, and the mixture was kept on ice for 30 minutes then warmed to room temperature and stirred for 2 hours. Methanol was removed under reduced pressure, and 24 mL of saturated sodium bicarbonate was added. The aqueous layer was extracted with chloroform (4 x 80 mL), washed with brine (1 x 100 mL), dried over sodium sulfate, and concentrated. The resulting solid was purified by flash column chromatography (silica, 5% MeOH in CH_2Cl_2), yielding 3.12 g (47%) of the product as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.60 (d, *J* = 5.06 Hz, 1H), 8.50 (d, *J* = 4.97 Hz, 1H), 8.31 (s, 1H), 8.19 (s, 1H), 7.30 (d, *J* = 5.01 Hz, 1H), 7.13 (d, *J* = 4.87 Hz, 1H), 4.77 (s, 2H), 3.25 (br s, 1H), 2.43 (s, 3H) ppm

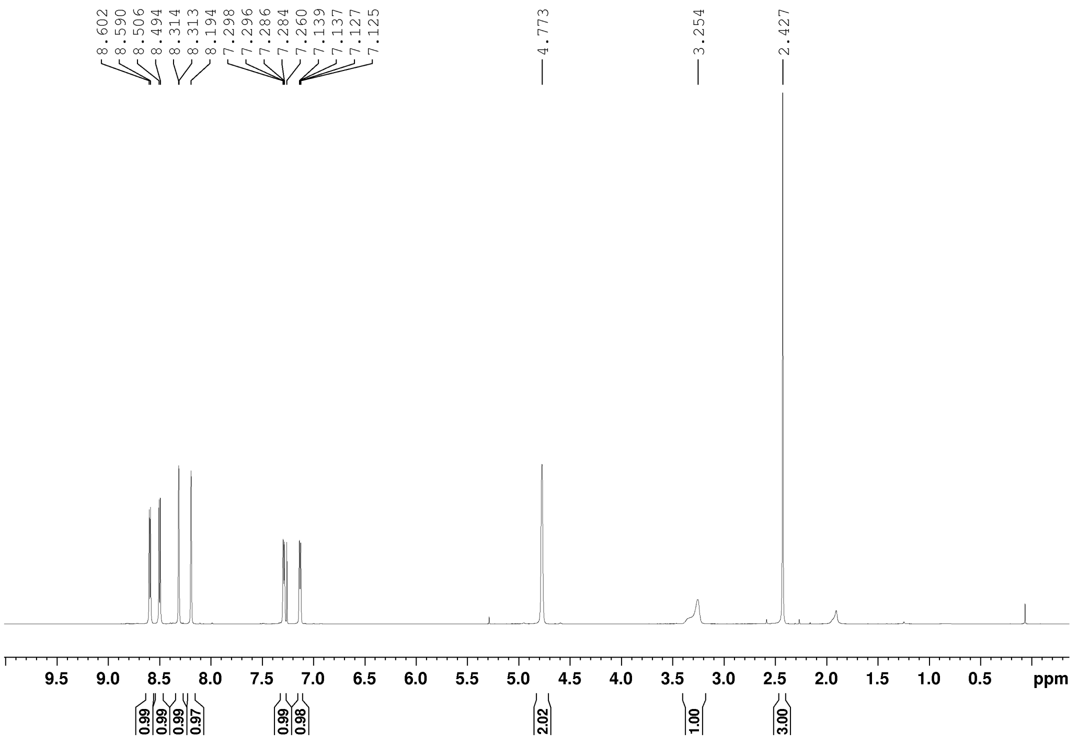
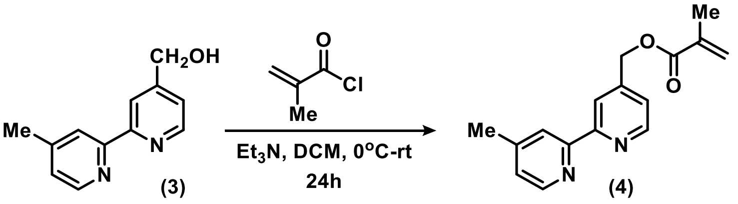


Figure S1. ^{1}H NMR spectrum of (3) ($CDCl_3$, 400 MHz)

Synthesis of (4'-methyl-[2,2'-bipyridin]-4-yl) methyl methacrylate (4)[4]



(4'-Methyl-[2,2'-bipyridin]-4-yl) methanol (3.00 g, 15.0 mmol) and triethylamine (2.33 mL, 16.7 mmol) were dissolved in 18 mL of chloroform and stirred. The solution was then cooled to 0 °C using an ice bath. Methacryloyl chloride (1.64 mL, 16.5 mmol) was added dropwise while stirring. Once the addition was complete, the mixture was allowed to stir at room temperature for 24 hours. The organic layer (reaction mixture) was washed sequentially with distilled water (3 x 50 mL), saturated sodium bicarbonate (3 x 30 mL), and brine (1 x 50 mL), then dried over sodium sulfate. After concentrating the solution, a brown oil was obtained. This oil was purified by flash column chromatography (silica, 5% MeOH:CH_2Cl_2), yielding 3.42 g (85%) of the product as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.68 (d, J = 5.16 Hz, 1H), 8.54 (d, J = 5.05 Hz, 1H), 8.38 (s, 1H), 8.23 (s, 1H), 7.30 (d, J = 4.98 Hz, 1H), 7 .15 (d, J = 4.98 Hz, 1H), 6.23 (s, 1H), 5.65 (s, 1H), 5.29 (s, 2H), 2.44 (s, 3H), 2.01 (s, 3H) ppm

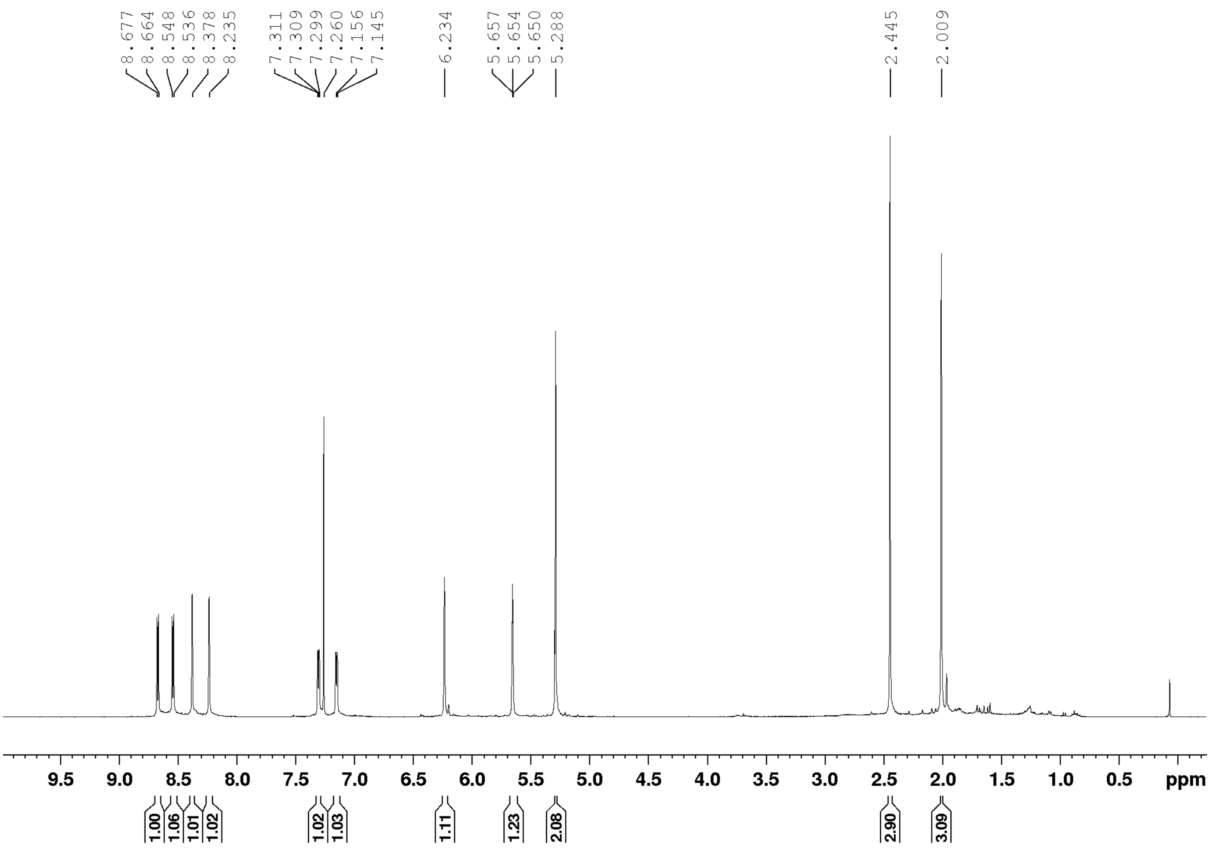
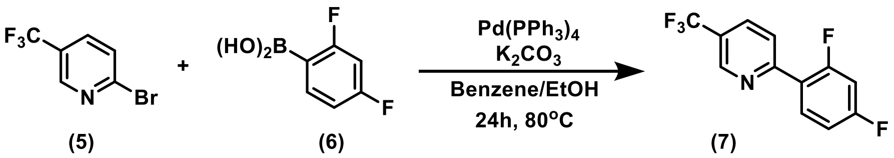


Figure S2. ^{1}H NMR spectrum of (4) ($CDCl_3$, 400 MHz)

Synthesis of 2-(2,4-Difluorophenyl)-5-(trifluoromethyl) pyridine, (dF(CF_3)ppy) (7)[5]



A three-necked round-bottomed flask was equipped with a coldwater reflux condenser, an argon inlet on top of the reflux condenser, and two stoppers. The flask was flushed with argon for 5 min before being sequentially charged with 2-chloro-5-(trifluoromethyl)pyridine (3.00 g, 0.017 mmol, 1.00 equiv), (2,4-difluorophenyl)boronic acid (2.87 g, 0.018 mmol, 1.10 equiv), $Pd(PPh_3)_4$ (1.22 g, 0.001 mmol, 0.064 equiv), benzene (18 mL), ethanol (3.6 mL) and 2.0 M aqueous sodium carbonate (15 mL) under argon. The reaction was then stirred and refluxed at 80 °C for 72 h and then allowed to cool to room temperature. Water (50 mL) was added, and then the whole mixture was added to a separatory funnel. The flask was rinsed with DCM as needed to ensure all contents were collected. The organic layer was separated, and the aqueous layer was extracted with DCM (1 × 100 mL). The combined organic layers were washed with water (1 × 25 mL) followed by brine (1 × 50 mL) and dried over anhydrous Na_2SO_4. The organic solvent was removed under vacuum, and the product was purified by column chromatography (silica, 2-3% EtOAc in Hexanes) to yield the product as a pink-white solid 3.37 g (80% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.96 (s, 1H), 8.10 (app td, J = 8.8, 6.8 Hz, 1H), 7.99 (dd, J = 8.3, 1.8 Hz, 1H), 7.91 (d, J = 8.3 Hz, 1H), 7.06 – 7.02 (m, 1H), 6.95 (ddd, J = 11.2, 8.7, 2.4 Hz, 1H).

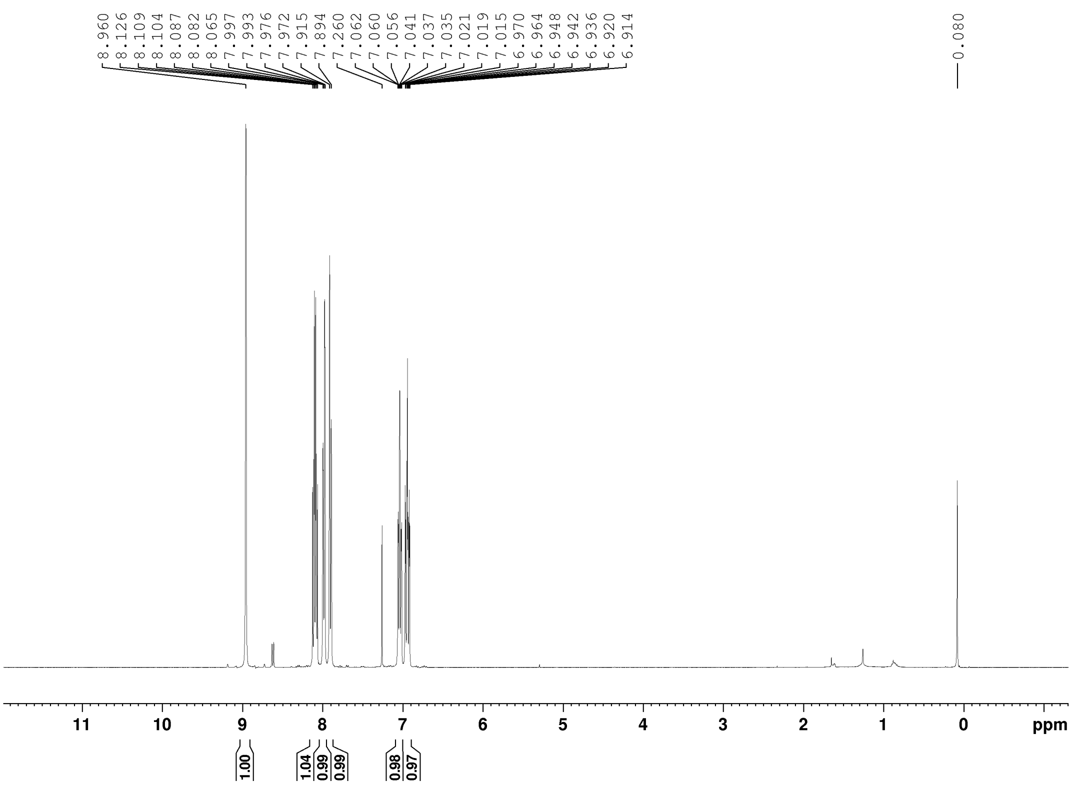
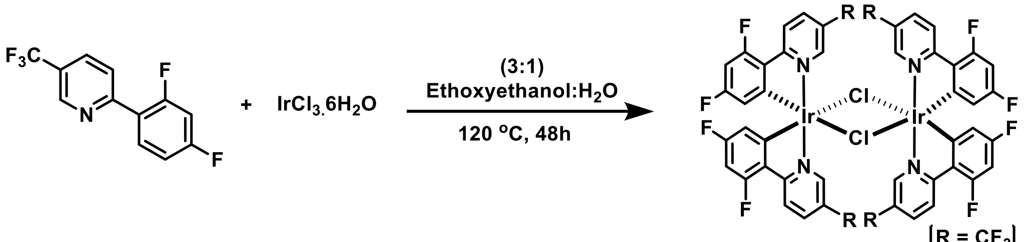


Figure S3. ^{1}H NMR spectrum of (7) ($CDCl_3$, 400 MHz)

Synthesis of $[(dF(CF_3)ppy)_2\text{-}Ir\text{-}\mu\text{-}Cl]_2$ complex (9)[5]



(7) (8) (9)

A three-necked round-bottomed flask was equipped with a cold water reflux condenser, an argon inlet and two stoppers. The flask was flushed with argon for 5 min before sequentially charged with iridium (III)chloride hydrate (8) (3.50 g, 11.1 mmol, 1.00 equiv), dF(CF_3)ppy (6.60 g, 25.4 mmol, 2.30 equiv), 2-ethoxyethanol (140 mL) and water (70 mL) under argon. The reaction mixture was refluxed at 120–125 °C, wherein the color changed from dark brown to orange within the first two hours of heating. Heating was stopped after 48 h and the flask was cooled to room temperature for over 45 min. Water (200 mL) was then added to the resulting yellow slurry after which, the flask was immersed in an ice bath for 30 min. The resulting yellow solid was collected by vacuum filtration. The reaction flask was rinsed with water (70 mL) and passed through the funnel followed by washing the yellow solid with 1:1 MeOH: H_2O (1 × 150 mL) and hexanes (100 mL) under vacuum. The yellow powder was then air dried overnight (15-18 h) to afford 6.27 g (38 % yield) of the desired complex.

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.51 (d, *J* = 2.0 Hz, 2 H), 8.46 (dd, *J* = 8.5 Hz, 2.5 Hz, 2 H), 8.05 (dd, *J* = 8.5 Hz, 2 H), 6.43 (ddd, *J* = 11.5 Hz, 8.5 Hz, 2.0 Hz, 2 H), 5.07 (dd, *J* = 8.5 Hz, 2.5 Hz, 2 H).

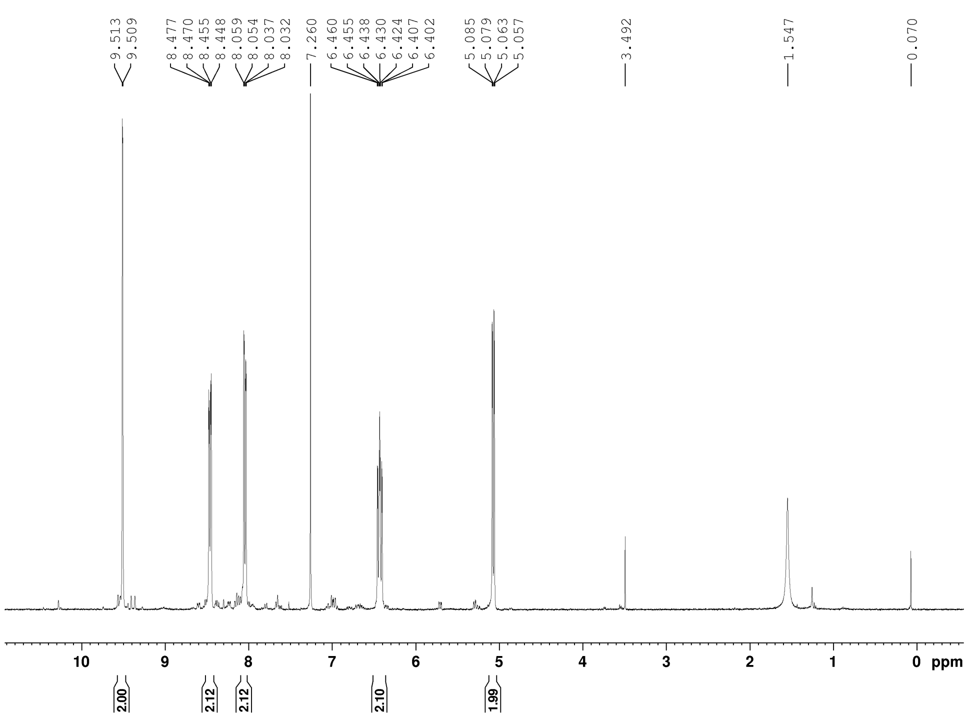
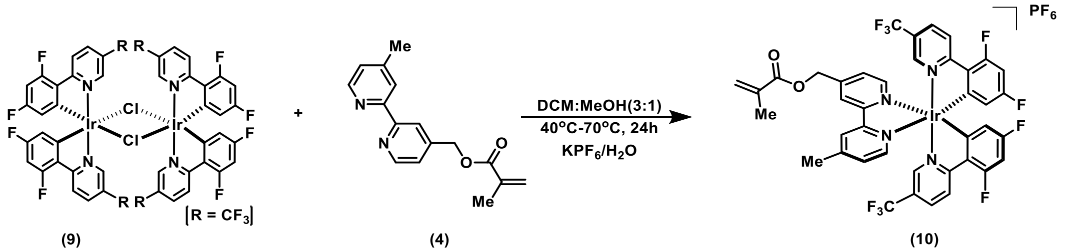


Figure S4. ^{1}H NMR spectrum of (9) ($CDCl_3$, 400 MHz)

Synthesis of [4-methacryloylmethyl-4’-methylbipyridine] bis [3,5-difluoro-2-[5-(trifluoromethyl)-2-pyridinyl]phenyl]Iridium(III)hexafluorophosphate (10)



(4'-Methyl-[2,2'-bipyridin]-4-yl) methyl methacrylate (272 mg, 1.01 mmol) in 50 mL of 3:1 DCM: MeOH was stirred at 40 °C. Separately, the dimer (500 mg, 0.338 mmol) was dissolved in 100 mL of 3:1 DCM: MeOH and added dropwise to the reaction mixture for over an hour. The resulting mixture was then refluxed until the reaction reached completion. The solvent was removed, and 50 mL of DI water was added along with a saturated solution of K_4PF_6 (5.8 g). The reaction was allowed to stir overnight (until the product precipitated). A bright yellow solid is obtained, washed with ether (6 x 10 mL) to remove any impurity, and dried under reduced pressure to give 620 mg (85%) of the product. MALDI-ToF MS [$C_{40}H_{26}F_{10}IrN_4O_2$, M^+]: $m/z = 977.17$

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.14 (s, 1H), 8.99 (s, 1H), 8.48 (dd, J = 8.61 Hz, 2.52 Hz , 2H), 8.06 (m, 2H), 7.86 (d, J = 5.86 Hz, 1H), 7.74 (d, J = 5.61 Hz, 1H), 7.56 (d, J = 15.32 Hz, 2H), 7.49 (d, J = 5.60 Hz, 1H), 7.39 (d, J = 5.45 Hz, 1H), 6.63 (m, 2H), 6.21 (s, 1H), 5.66-5.54 (m, 5H), 2.66 (s, 3H), 1.94 (s, 3H) ppm

^{13}C NMR coupled with ^{19}F (125 MHz, $CDCl_3$): δ 167.9, 167.8, 166.6, 166.2, 166.1, 163.9, 163.8, 163.6, 163.5, 161.3, 161.2, 155.6, 154.7, 154.6, 154.5, 154.4, 154.3, 152.2, 150.1, 149.3, 144.9, 136.7, 135.3, 129.9, 127.6, 127.2, 126.2, 126.1, 126.0, 124.6, 123.9, 123.7, 122.9, 120.5, 114.2, 114.1, 113.9, 100.3, 100.0, 99.8, 77.4, 77.1, 76.7, 63.6, 21.5, 18.2

^{19}F NMR decoupled with ^{1}H (376.5 MHz, $CDCl_3$): -105.70, -105.67, -105.66, -105.64, -101.52, -101.49, -73.52, -71.63, -62.78, -62.76.

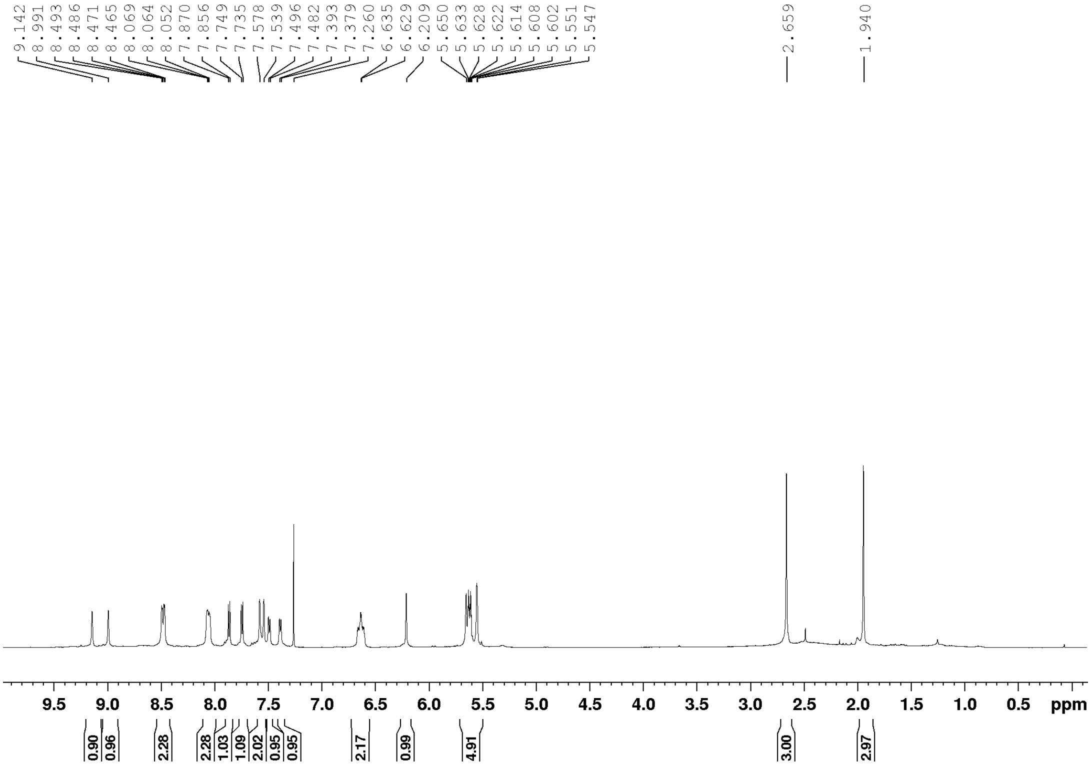


Figure S5. ^{1}H NMR spectrum of (10) ($CDCl_3$, 400 MHz)

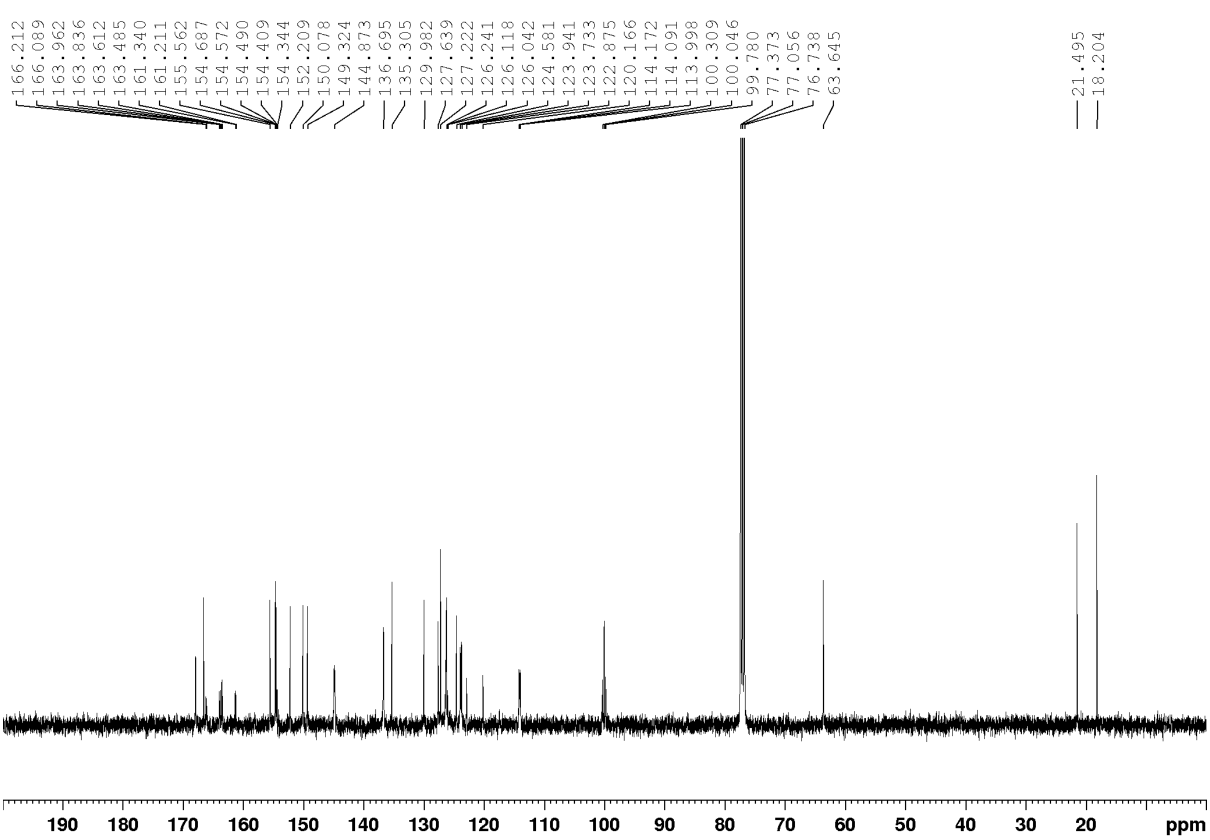


Figure S6. ^{13}C NMR spectrum of (10) ($CDCl_3$, 125 MHz)

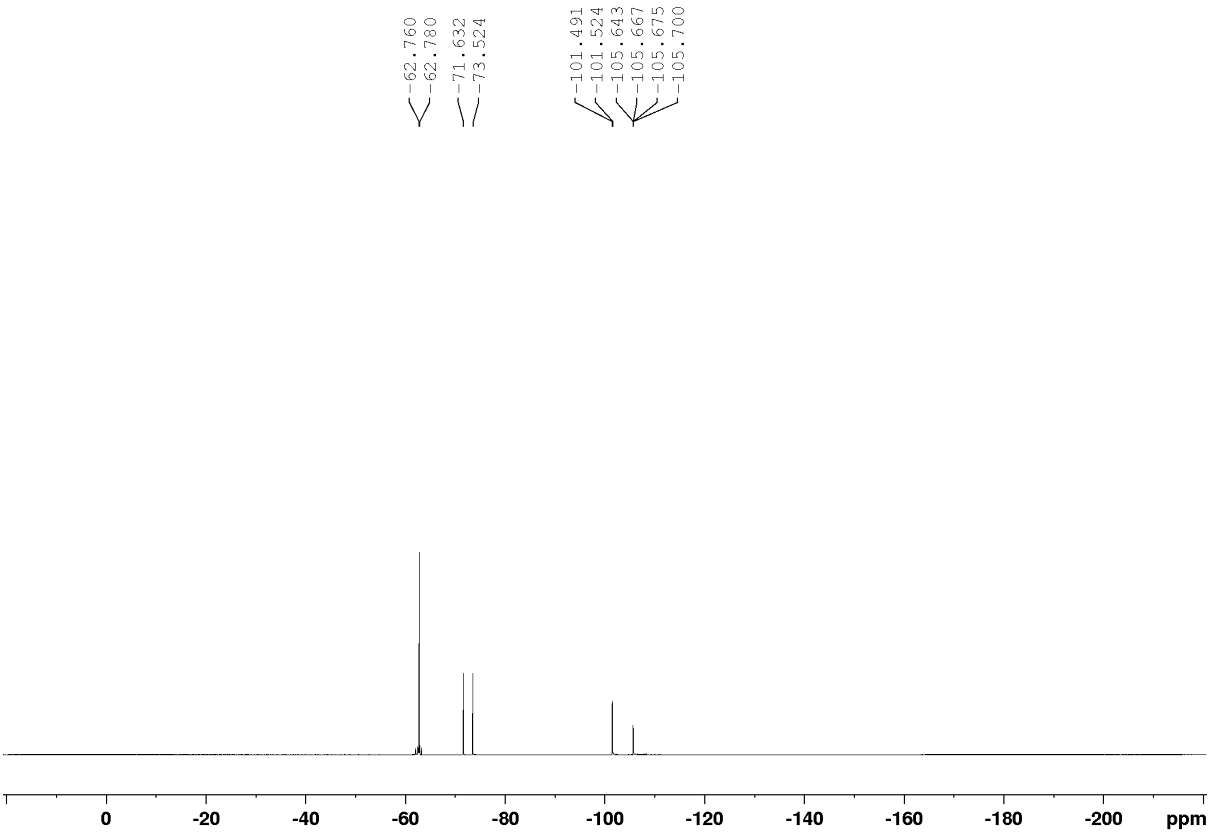
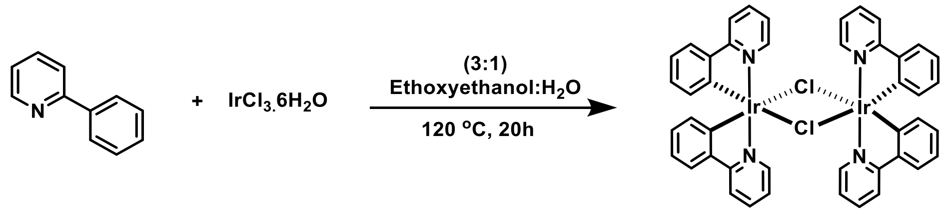


Figure S7. ^{19}F NMR spectrum of (10) ($CDCl_3$, 376.5 MHz)

Synthesis of Tetrakis[2-phenylpyridinato-N,C$^{2'}$]-bis(*μ*-chloro)diiridium(III) [$(ppy)_2$-Ir-μ-Cl]$_2$ complex (12)[6]



(11) **(8)** **(12)**

A three-necked round-bottomed flask was equipped with a cold-water reflux condenser, an argon inlet and two stoppers. The flask was flushed with argon for 5 min before being sequentially charged with iridium (III) chloride hydrate (500 mg, 1.58 mmol, 1.00 equiv), 2-phenyl pyridine (564 mg, 3.63 mmol, 2.3 equiv), 2-ethoxyethanol (20 mL) and water (7 mL) under argon. The reaction flask was refluxed at 120–125 °C. The color of the reaction changed from dark brown to orange within the first two hours of heating. After 24 h heating was stopped and the flask was allowed to cool to room temperature over 45 min. Water (50 mL) was then added to the resulting yellow slurry after which, the flask was immersed in an ice bath for 30 min. The resulting yellow solid was collected by vacuum filtration with the reaction flask being rinsed with water (20 mL) and passed through the funnel. The yellow solid was washed with 1:1 MeOH: H_2O (1 × 40 mL) and hexane (20 mL) under vacuum. The yellow powder is then air-dried overnight (15-18 h) to give 0.658 mg (68% yield) of [$(ppy)_2$-Ir-μ-Cl]$_2$ complex.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 9.24 (dd, *J* = 1.0, 5.5 Hz, 1H), 7.87 (d, *J* = 7.5 Hz, 1H), 7.73 (td, *J* = 1.5, 7.5 Hz, 1H), 7.48 (dd, *J* = 1.5, 7.5 Hz, 1H), 6.79 – 6.72 (m, 4H), 6.56 (td, *J* = 1.5, 7.5 Hz, 1H), 5.93 (dd, *J* = 1.0, 7.5 Hz, 1H)

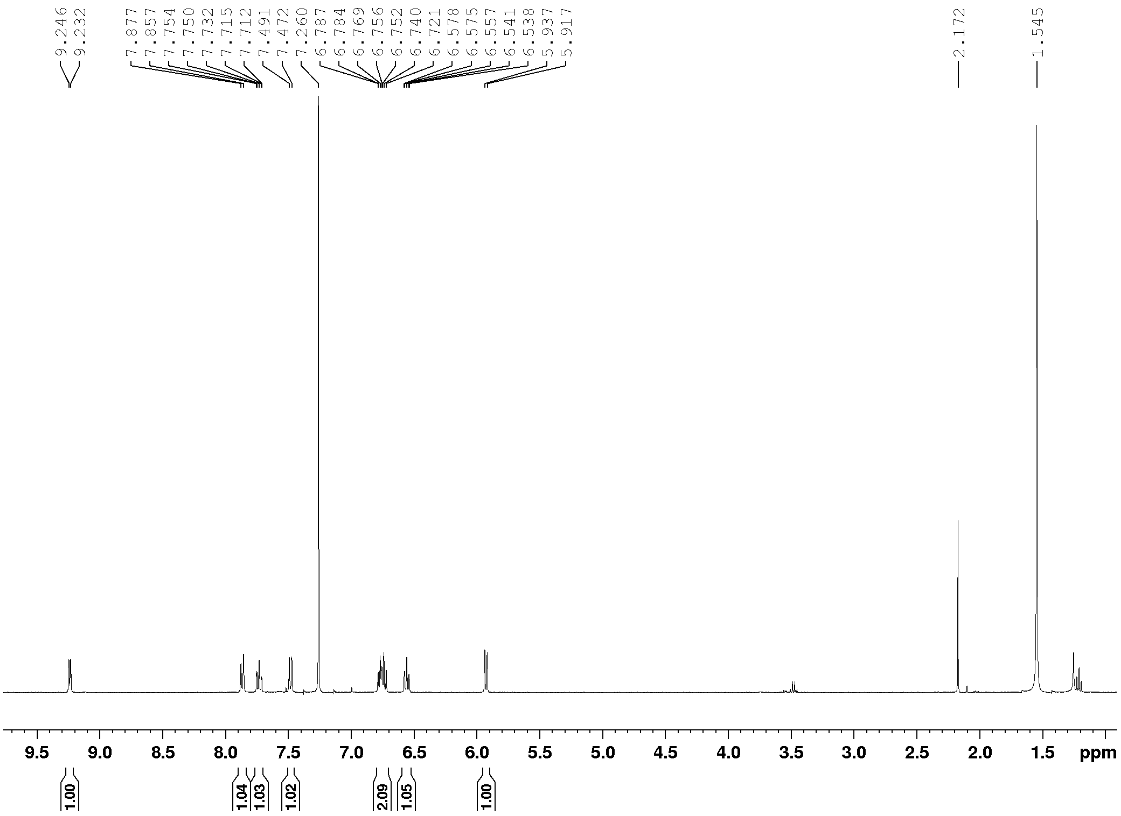
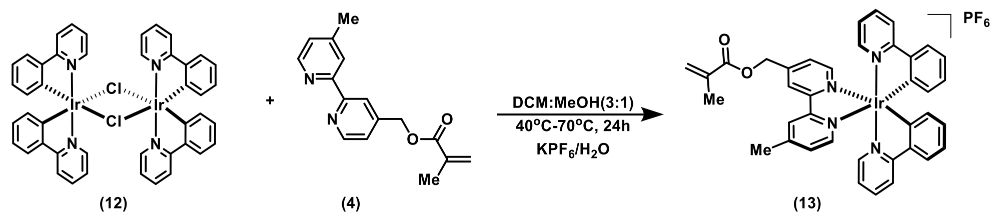


Figure S8. ^{1}H NMR spectrum of (12) ($CDCl_3$, 400MHz)

Synthesis of [4-methacryloylmethyl-4'-methylbipyridine] bis [2-phenylpyridinato-N,C$^{2'}$]Iridium(III)hexafluorophosphate (13)



(4'-Methyl-[2,2'-bipyridin]-4-yl) methyl methacrylate (125 mg, 0.47 mmol) in 25 mL of 3:1 DCM: MeOH was stirred at 40 °C. Separately, the dimer (250 mg, 0.233 mmol) was dissolved in 50 mL of 3:1 DCM: MeOH and added dropwise to the reaction mixture for over an hour. The resulting mixture was then refluxed until the reaction reached completion. The solvent was removed, and 25 mL of DI water was added along with a saturated solution of K_4PF_6 (2.9 g). The reaction was allowed to stir overnight (until the product precipitated). A bright yellow solid is obtained, washed with ether (6 x 10 mL) to remove any impurity, and dried under reduced pressure to give 300 mg (70%) of the product. MALDI-ToF MS [$C_{38}H_{32}IrN_4O_2$, M^+]: *m/z* = 769.22

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.54 (s, 1H), 8.44 (s, 1H), 7.88 (m, 3H), 8.06 (m, 2H), 7.86 (d, *J* = 5.86 Hz, 1H), 7.74 (m, 3H), 7.66 (d, *J* = 7.44 Hz, 2H), 7.53 (d, *J* = 5.62 Hz, 2H), 7.31 (d, *J* = 5.62 Hz, 1H), 7.19 (d, *J* = 5.79 Hz, 1H), 7.07-6.98 (m, 4H), 6.90-6.88 (m, 2H), 6.29-6.27 (m, 2H), 6.22 (s, 1H), 5.65 (br s, 1H), 5.45 (s, 2H), 2.57 (s, 3H), 1.95 (s, 3H) ppm

^{13}C NMR (125 MHz, $CDCl_3$): δ166.7, 166.6, 165.7, 154.9, 154.0, 151.3, 149.4, 149.3, 149.2, 148.9, 148.5, 147.7, 147.6, 142.5, 137.1, 137.0, 134.4, 130.7, 130.6, 129.7, 129.6, 128.0, 126.1, 125.0, 124.4, 123.7, 123.6, 122.5, 122.4, 121.9, 121.5, 118.5, 118.4, 76.3, 76.0, 75.7, 62.8, 20.4, 17.3

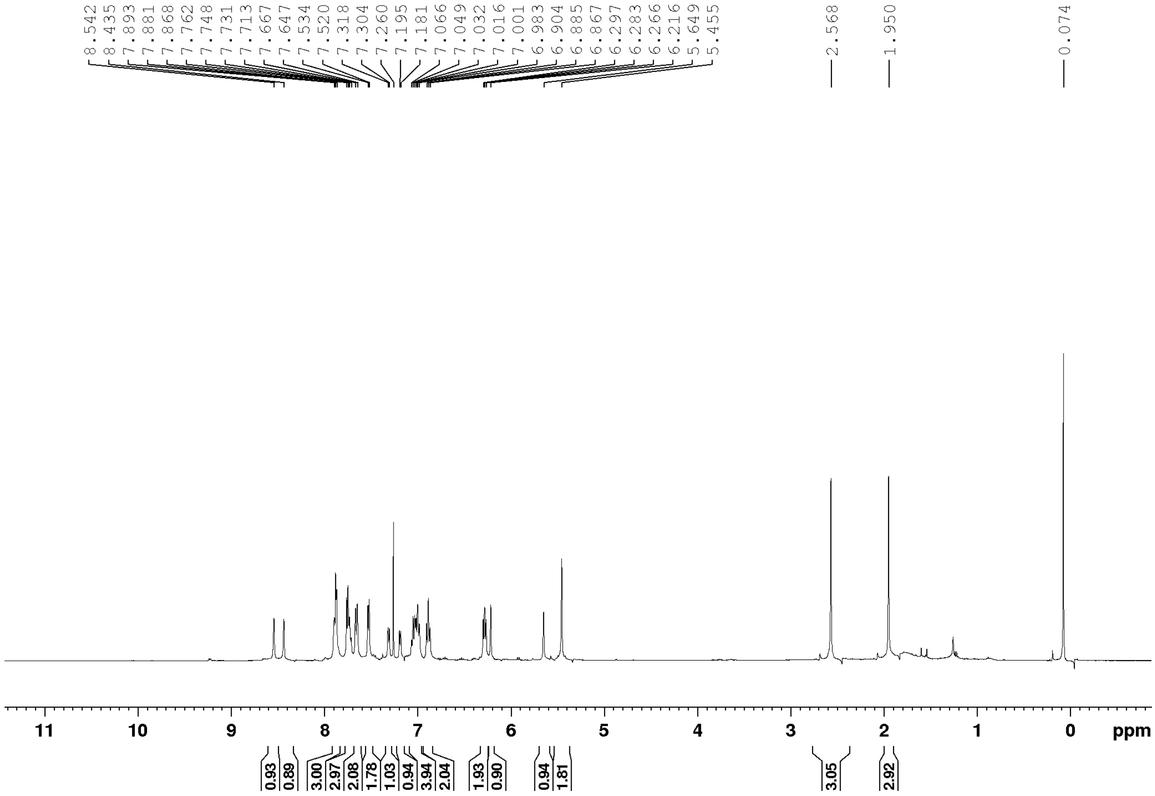


Figure S9. ^{1}H NMR spectrum of (13) ($CDCl_3$, 400 MHz)

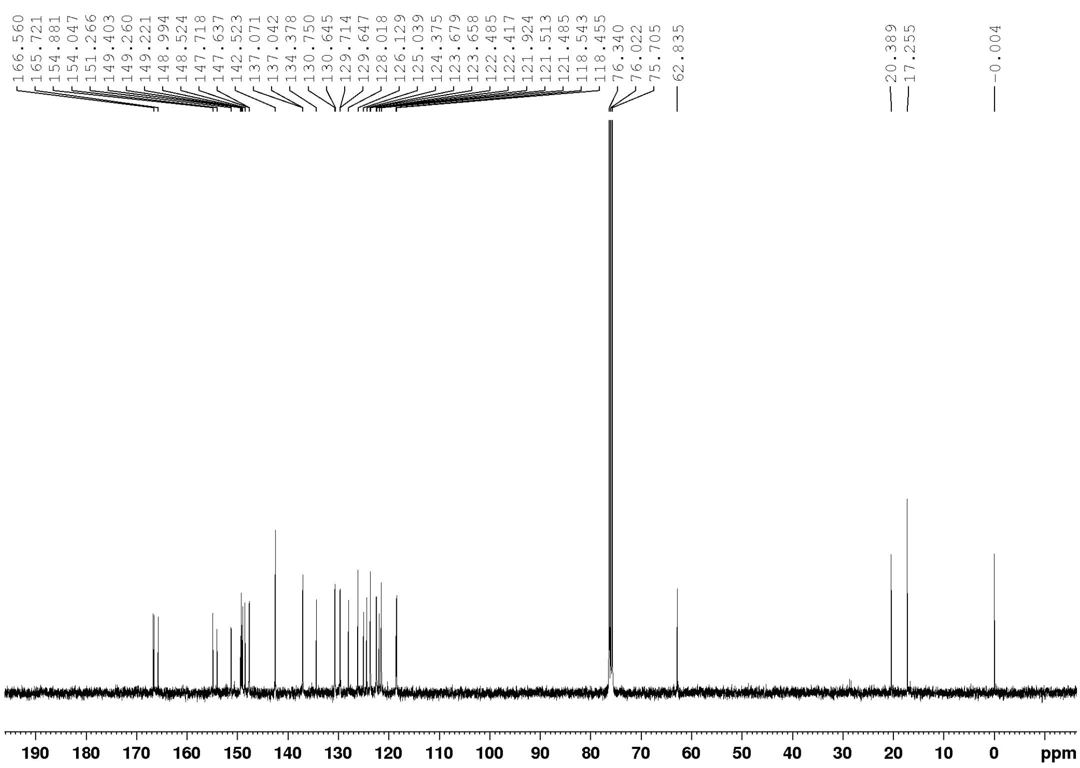
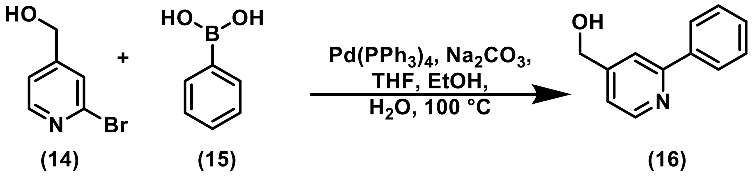


Figure S10. ^{13}C NMR spectrum of (13) ($CDCl_3$, 125 MHz)

Synthesis of 4-(hydroxymethyl)-2-phenylpyridine (16)[7,8]



A reaction mixture was prepared by combining 2-bromo-4-(hydroxymethyl)pyridine (1.88 g, 10.0 mmol, 1.00 equiv), phenylboronic acid (1.71 g, 14.0 mmol, 1.40 equiv), and sodium carbonate (3.97 g, 37.5 mmol, 3.75 equiv) in a solvent mixture of water (75 mL) and tetrahydrofuran (38 mL). The mixture was then sparged with nitrogen for 15 minutes. Pd(PPh3)$_4$ (231 mg, 0.20 mmol, 2 mol%) was added, and the reaction was heated to 100 °C. After 48 hours, the mixture was extracted with CH_2Cl_2 (3 × 75 mL), and the organic phases were combined, dried over Na_2SO_4, and concentrated. The resulting residue was purified by flash chromatography (silica gel, 40% ethyl acetate in hexanes), yielding a pale-yellow semisolid (810 mg, 44% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.60 (d, J = 6.6 Hz, 1H), 7.95 (d, J = 7.4 Hz, 2H), 7.69 (s, 1H), 7.44 (dt, J = 13.6, 7.0 Hz, 3H), 7.19 (d, J = 4.9 Hz, 1H), 4.76 (s, 2H).

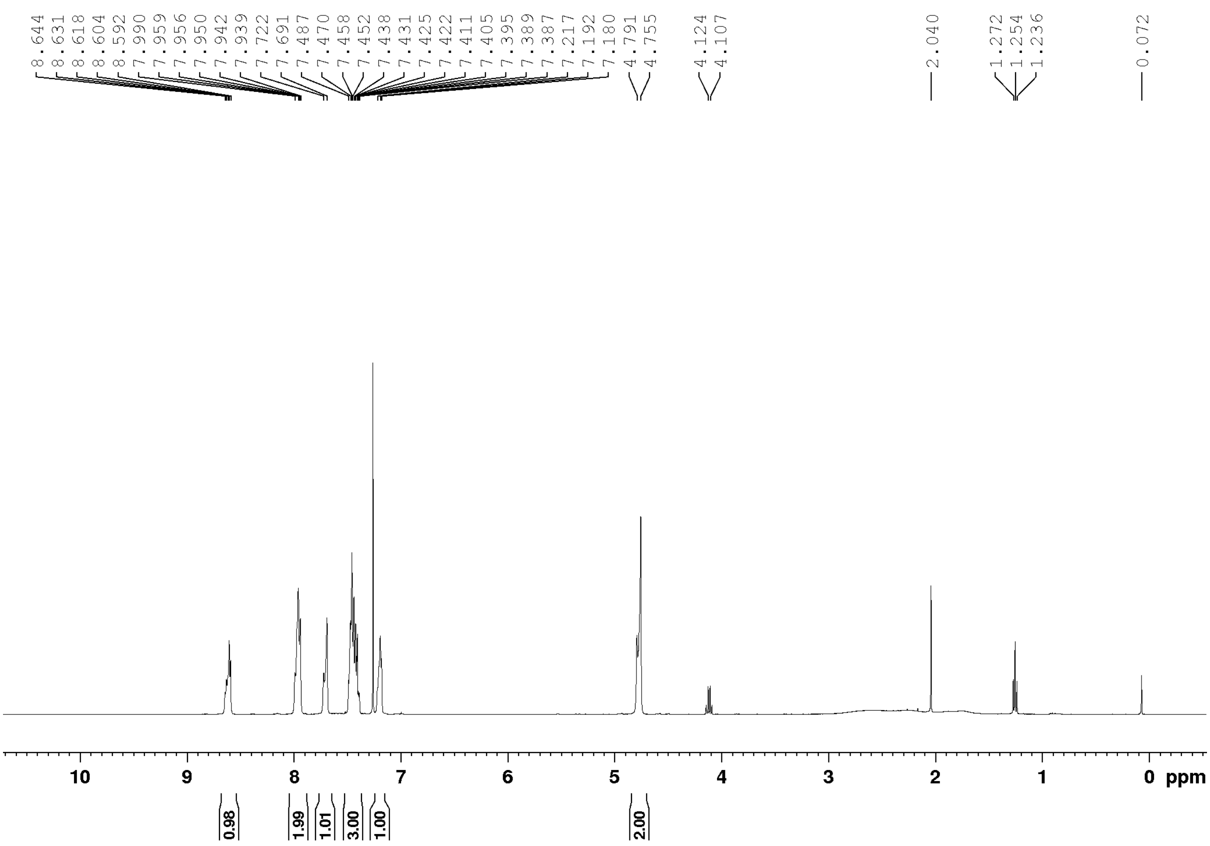
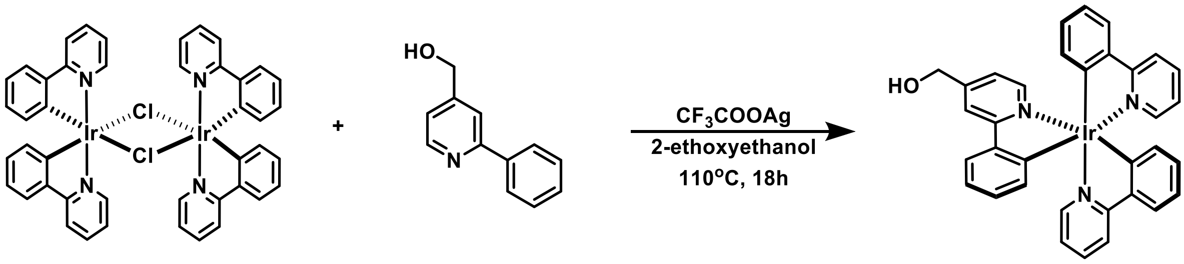


Figure S11. ^{1}H NMR spectrum of (16) ($CDCl_3$, 400 MHz)

Synthesis of [(4-hydroxymethyl-2-phenylpyridine)] bis [2-phenylpyridinatoN,C$^{2'}$]Iridium(17)[9]



(12) (16) (17)

The chloro-bridged dimer (0.69 g, 0.58 mmol) and 4-(hydroxymethyl)-2-phenylpyridine (0.27 g, 1.75 mmol) were dissolved in 2-ethoxyethanol (50 mL), then the solution was purged by nitrogen gas and silver trifluoroacetate (0.42 g, 1.90 mmol) was quickly added to the solution. The solution was heated at 110 °C for 18 h and evaporated under reduced pressure. The brown solid was dissolved in chloroform and excess silver trifluoroacetate was removed. The crude product was purified by silica-gel column chromatography using DCM:methanol (98:2 v/v) as the eluent. The product was obtained as a yellow powder (150 mg, 0.21 mmol, 18%). MALDI-ToF MS [$C_{34}H_{26}IrN_3O$, M^+]: *m/z* = 685.17

^{1}H NMR (400 MHz, DMSO-d$_6$) δ: 8.14 (dd, *J* = 8.26 Hz, 3.16 Hz, 2H), 8.03 (s, 1H), 7.82-7.70 (m, 5H), 7.54-7.48 (m, 2H), 7.42 (d, *J* = 5.68 Hz, 1H), 7.15- 7.11 (m, 2H), 7.08-7.07 (m, 1H) 7.13 (t, *J* = 8 Hz, 2H), 6.82-6.77 (m, 3H), 6.70-6.63 (m, 6H), 5.49 (t, *J* = 6 Hz, 1H), 4.62 (d, *J* = 4 Hz, 2H).

^{13}C NMR (150 MHz, DMSO-d$_6$) δ: 165.64, 161.40, 161.23, 153.06, 147.29, 147.27, 146.86, 144.34, 144.29, 144.26, 137.29, 136.84, 136.67, 129.56, 129.54, 129.47, 124.63, 124.59, 124.35, 123.21, 120.80, 120.06, 119.98, 119.51, 119.48, 116.43, 62.09

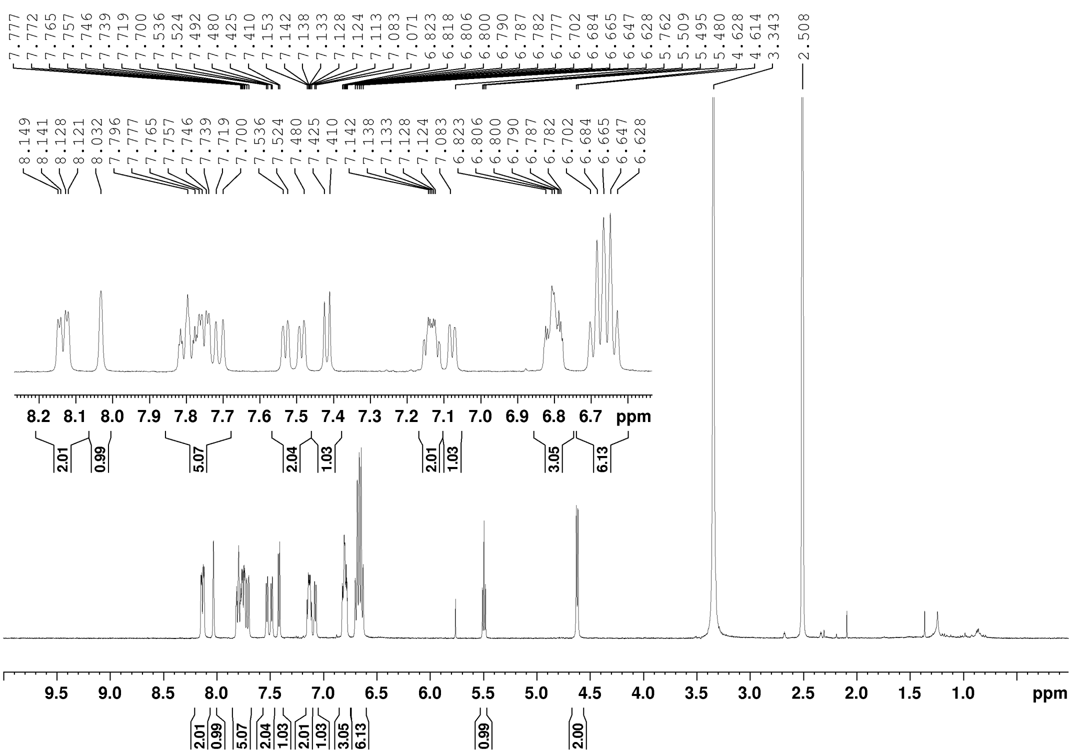


Figure S12. ^{1}H NMR spectrum of (17) (DMSO, 400 MHz)

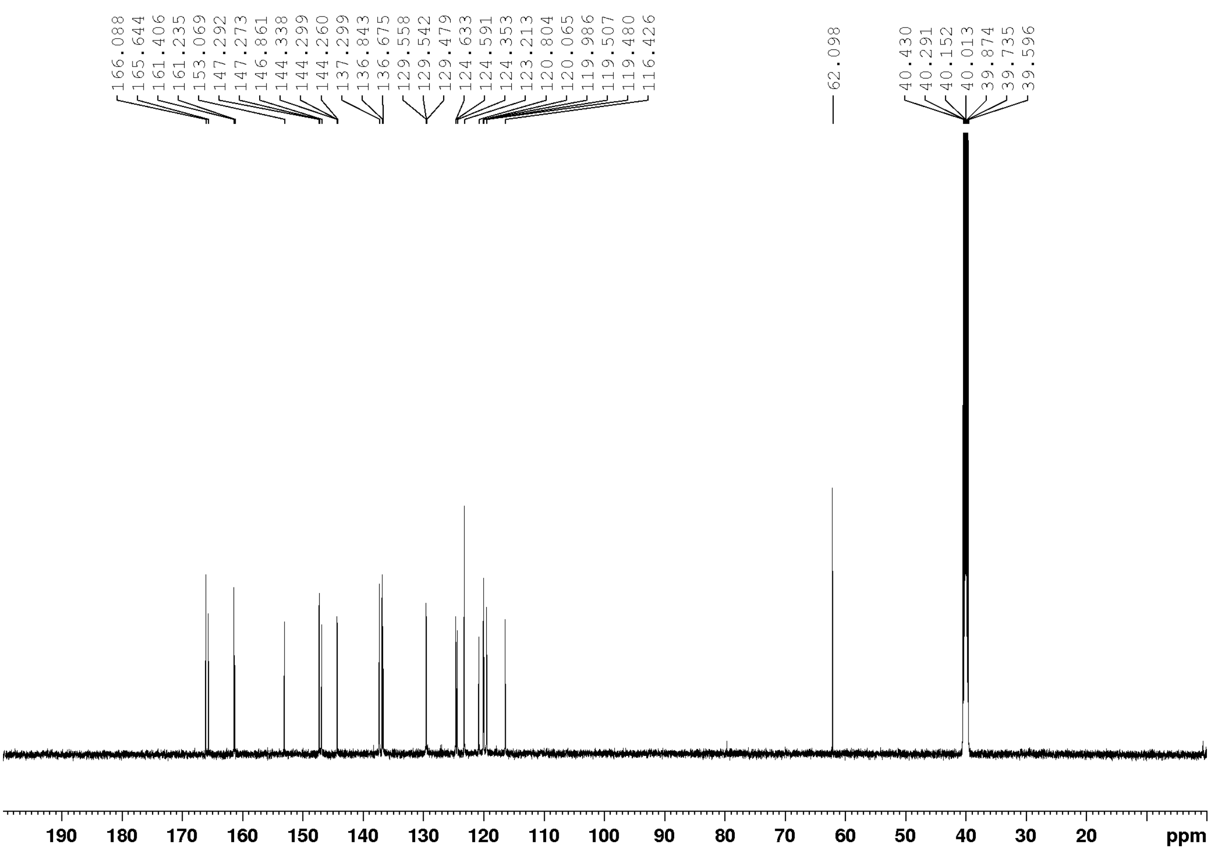
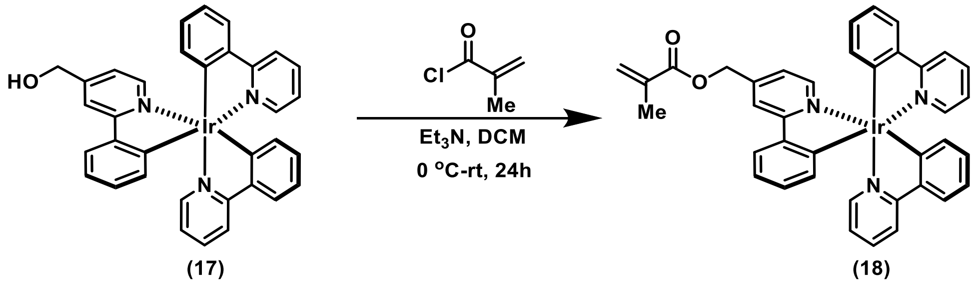


Figure S13. ^{13}C NMR spectrum of (17) (DMSO, 150 MHz)

Synthesis of [4-methacryloylmethyl-2-phenylpyridine] bis [2-phenylpyridinato-N,C$^{2'}$]Iridium (18)



(17)

(18)

To a dry round bottomed flask equipped with a magnetic stir bar and septum was added [(4-hydroxymethyl-2-phenylpyridine)] bis [2-phenylpyridinatoN,C$^{2'}$]Iridium(III) (100 mg, 0.146 mmol), DCM (6 mL, anhydrous) and TEA (203.49 µL, 1.46 mmol). The mixture was degassed with argon for 10 minutes and cooled to 0 °C, followed by addition of methacryloyl chloride (28.53 µL, 0.29 mmol). The reaction mixture was stirred at 0 °C for 10 minutes under argon then allowed to warm to room temperature and stirred for an additional hour. The resulting residue was purified by flash chromatography (silica gel, 1.0:0.99:0.01 Hex:DCM:TEA), concentrated, and then precipitated from DCM into hot hexanes to provide the desired product as a bright yellow powder after filtration (90 mg, 81% yield). MALDI-ToF MS [$C_{38}H_{30}IrN_3O_2$, M$^+$]: *m/z* = 753.21

^1H NMR (400 MHz, $CDCl_3$) δ 7.86-7.82 (m, 3H), 7.65 (dd, *J* = 6.75 Hz, 3H), 7.58-7.49 (m, 5H), 6.91-6.83 (m, 12Hz), 6.22 (s, 1H), 5.66 (s, 1H) 5.23 (s, 2H), 2.00 (s, 3H)

^{13}C NMR (125 MHz, $CDCl_3$) δ 165.9, 165.8, 165.6, 160.6, 160.1, 146.1, 146.0, 143.9, 142.6, 136.1, 136.0, 134.9, 134.7, 129.1, 128.9, 128.8, 125.6, 122.9, 122.8, 120.9, 119.1, 118.8, 118.7, 117.7, 115.6, 63.4, 28.7, 17.3.

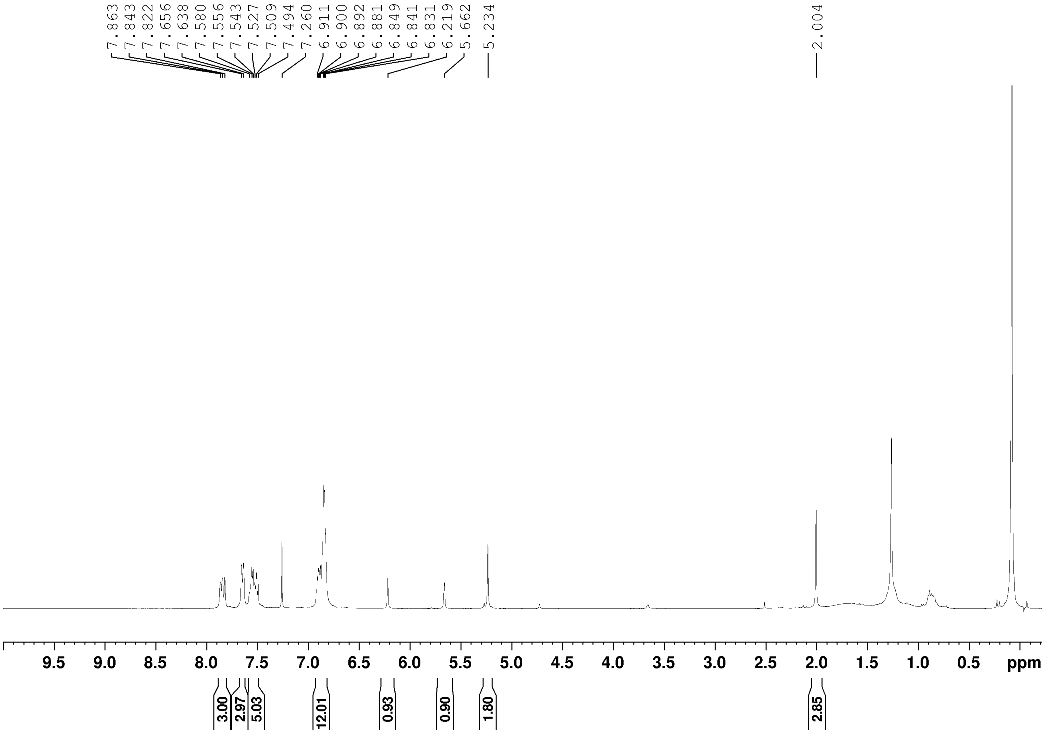


Figure S14. ^{1}H NMR spectrum of (18) ($CDCl_3$, 400 MHz)

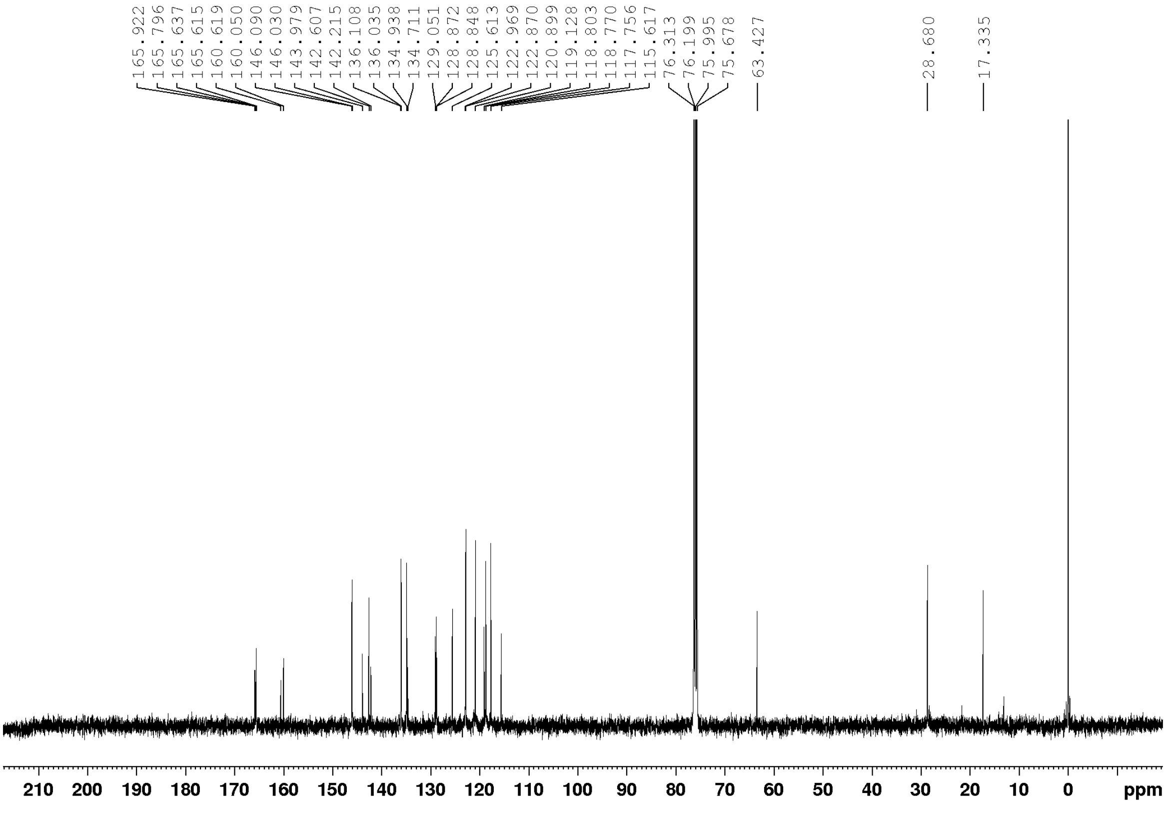
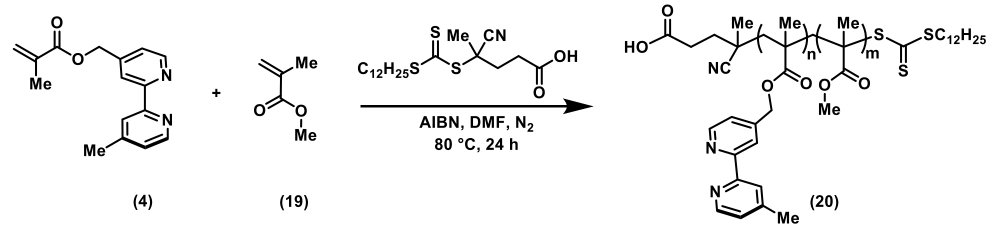


Figure S15. ^{13}C NMR spectrum of (18) ($CDCl_3$, 125 MHz)

3) Polymerization Procedures

dmbpy-co-MMA synthesis (20)



To a 20 mL scintillation vial equipped with a septum, 4-cyano-4-[(dodecylsulfanylthiocarbonyl)sulfanyl]pentanoic acid (35 mg, 0.086 mmol), 2,2′-azobis(2-methylpropionitrile) (2.8 mg, 0.017 mmol), dimethyl bipyridine monomer (4) (0.6 g, 2.2 mmol), methyl methacrylate (2.13 mL, 20 mmol), and dimethylformamide (3.8 mL) were added. The solution sparged with nitrogen for 15-20 minutes, using a vent needle. After sparging, the needles were removed, and the septum was sealed with electrical tape. The mixture was stirred at 80 °C for 24 hours, then cooled to room temperature. The resulting solution was poured into 200 mL of cold methanol, and the precipitate was collected by filtration. The solid was washed with methanol (2 × 20 mL) and dried under reduced pressure to afford 2.3 g of white powder. Percent incorporation for dmbpy units was determined using ^{1}H NMR spectroscopy.

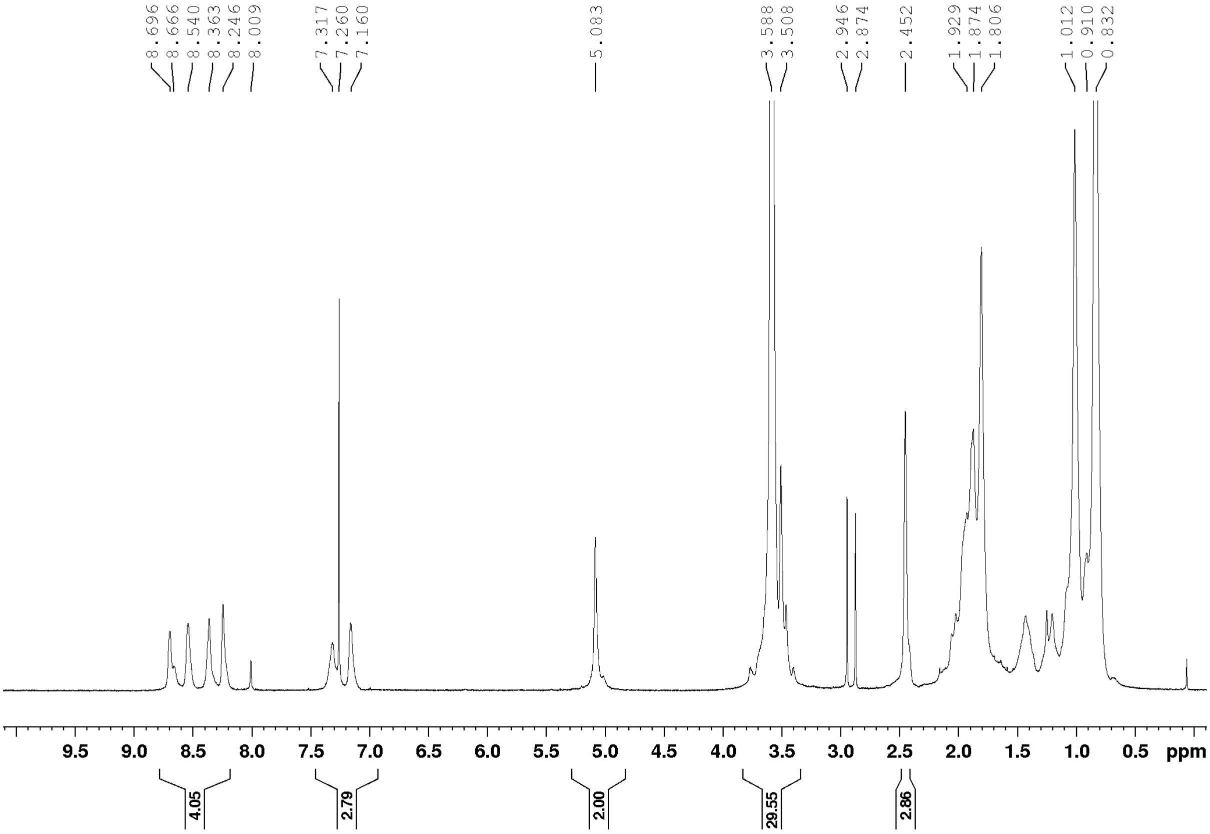
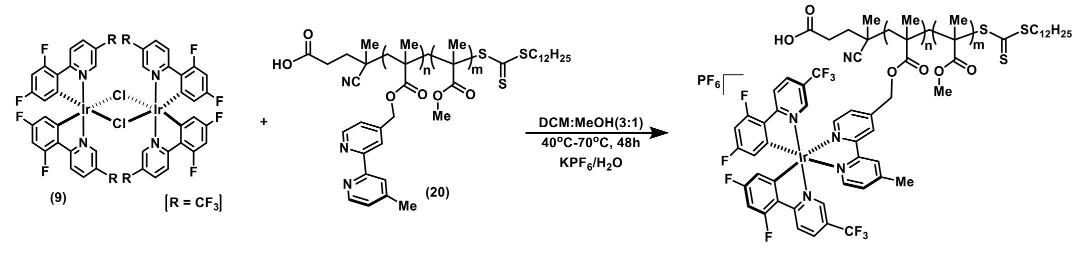


Figure S16. ^{1}H NMR spectrum of (20) ($CDCl_3$, 400 MHz)

IrCat synthesis using dmbpy-co-MMA



The polymer dmbpy-co-mma (300 mg-equivalent to 54 mg dimethyl bipyridine, 3 equiv.) was dissolved in 10 mL of 3:1 DCM: MeOH and stirred at 40 °C. Separately, the dimer (100 mg, 1 equiv.) was dissolved in 100 mL of 3:1 DCM: MeOH, and added dropwise to the reaction mixture for over an hour. The reaction mixture was then refluxed for the next 48 h, followed by removal of the solvent and addition of 20 mL of DI water and saturated K_4PF_6 (1.16 g). The resultant mixture was stirred overnight, until the product precipitated. The bright yellow solid was washed with MeOH (6 x 10 mL) to remove any impurity and dried under reduced pressure to give 180 mg of product. ^{1}H NMR spectroscopic analysis confirmed that the product had formed but not all dmbpy units could be coordinated.

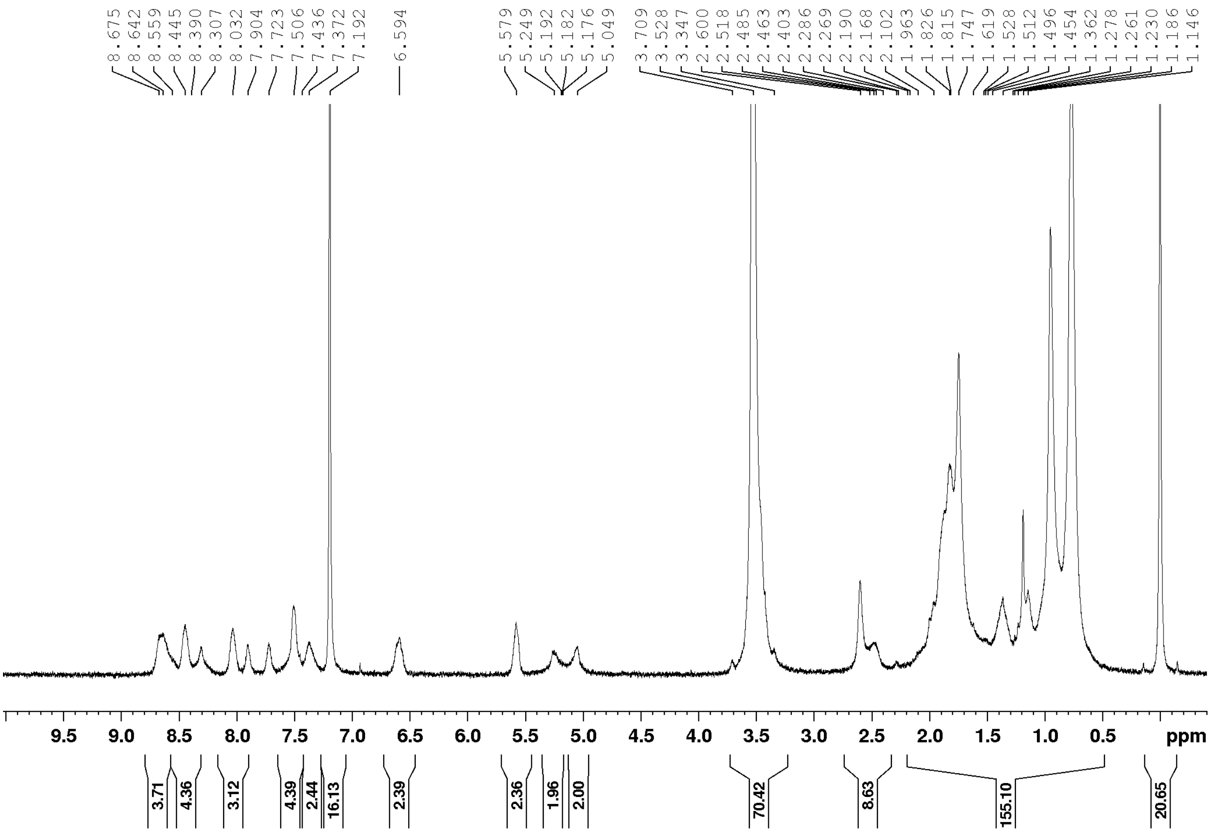
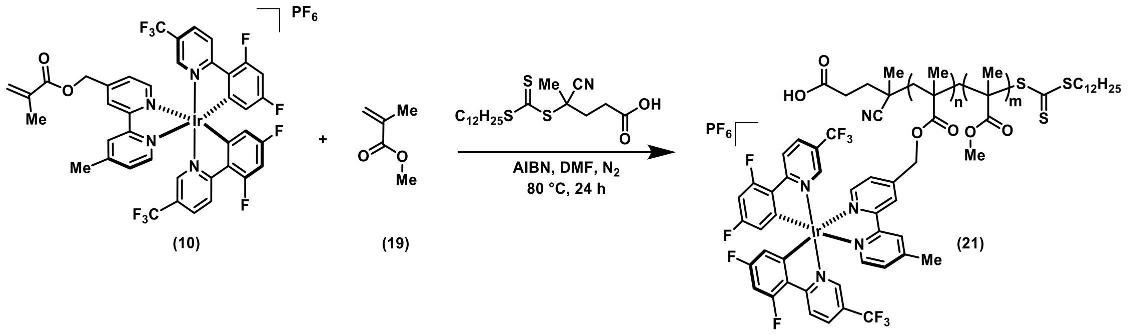


Figure S17. ^{1}H NMR spectrum of dmbpy-co-MMA after iridium incorporation ($CDCl_3$, 400 MHz)

IrCat1 synthesis using iridium monomer (21)



To a 20 mL scintillation vial equipped with a septum, 4-cyano-4-[(dodecylsulfanylthiocarbonyl)sulfanyl]pentanoic acid (35 mg, 0.086 mmol), 2,2′-azobis(2-methylpropionitrile) (2.87 mg, 0.017 mmol), iridium monomer (10) (0.26 g, 0.234 mmol), methyl methacrylate (2.48 mL, 23.37 mmol), and dimethylformamide (3.77 mL) were added. The solution sparged with nitrogen for 15-20 minutes, using a vent needle. After sparging, the needles were removed, and the septum was sealed with electrical tape. The mixture was stirred at 80 °C for 24 hours, then cooled to room temperature. The resulting solution was poured into 200 mL of cold methanol, and the precipitate was collected by filtration. The solid was washed with methanol (2 × 20 mL) and dried under reduced pressure to afford 1.2 g of yellow powder.

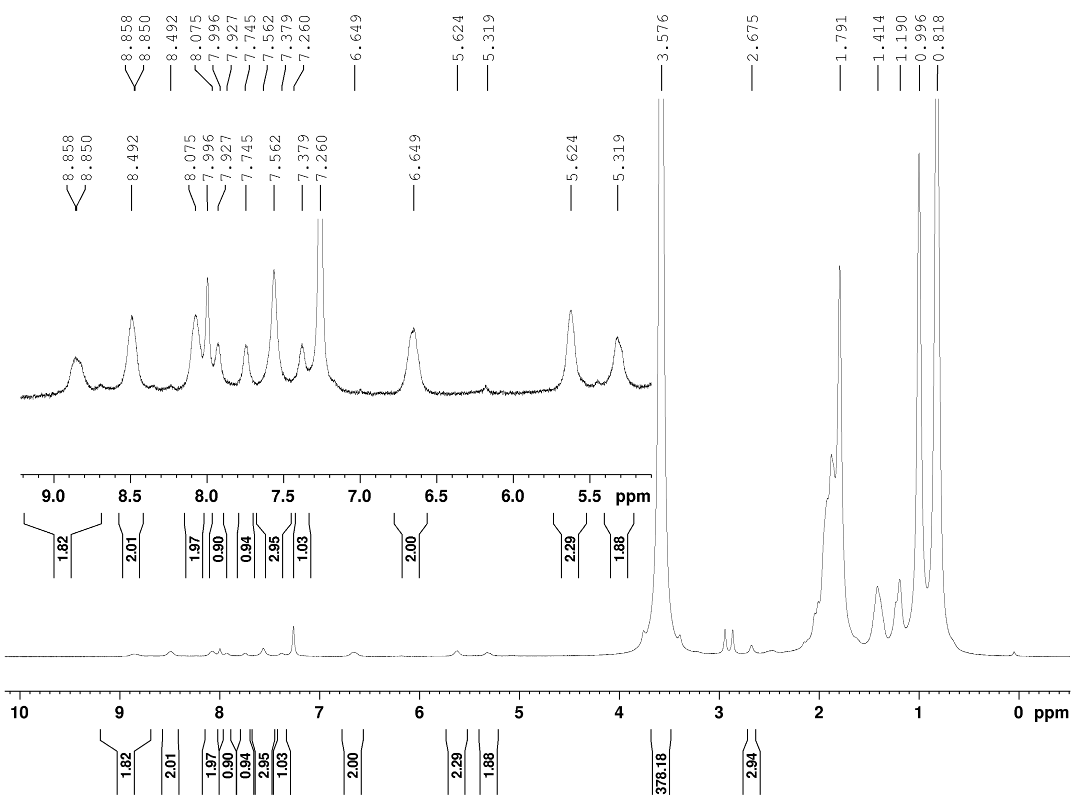


Figure S18. ^{1}H NMR spectrum of (21) ($CDCl_3$, 400 MHz)

IrCat1: Percent incorporation of iridium in polymer

Step 1: Calculate number of Iridium (Ir) side chains:

Choose any peak from ^{1}H NMR spectrum corresponding to iridium side chain.

$$\text{Ir side chains} = \frac{\mathbf{2}\ \text{[Integration of Ir (6.6 ppm from NMR spectrum)]}}{\mathbf{2}\ \text{[Total no. of protons for the selected peak]}} = 1$$

$$\text{MMA molecules} = \frac{\mathbf{378.2}\ \text{[Integration of MMA (3-4ppm from NMR spectrum)]}}{\mathbf{3}\ \text{[Total no. of protons in MMA per molecule]}} = 126$$

Step 2: Calculate mol% of each monomer:

a) $$\text{mol\% Ir} = \frac{\mathbf{1}\ \text{[No. of Ir side chains] (*100)}}{\mathbf{1}\ \text{[No. of Ir side chains]} + \mathbf{126}\ \text{[No. of MMA molecules]}}$$
$$= 0.8\ \%$$

b) $$\text{mol\% MMA} = \frac{\mathbf{126}\ \text{[No. of MMA molecules] (*100)}}{\mathbf{1}\ \text{[No. of Ir side chains]} + \mathbf{126}\ \text{[No. of MMA molecules]}}$$
$$= 99\ \%$$

Step 3: Calculate weight% for each monomer:

a) $$\text{Mass of Ir per mol polymer} = \frac{\mathbf{0.8}\ \text{[mol\% Ir]} * \mathbf{1160.6}\ \text{[MW of Ir monomer]}}{\mathbf{100}\ \text{[mol\% polymer]}} = 9.3\ \text{mg}$$

b) $$\text{Mass of MMA per mol polymer} = \frac{\mathbf{99}\ \text{[mol\% MMA]} * \mathbf{100.1}\ \text{[MW of MMA]}}{\mathbf{100}\ \text{[mol\% polymer]}}$$
$$= 99\ \text{mg}$$

Therefore,

$$\text{Weight \% Ir} = \frac{9.3\ (*100)}{9.3 + 99} = 8.6\%$$

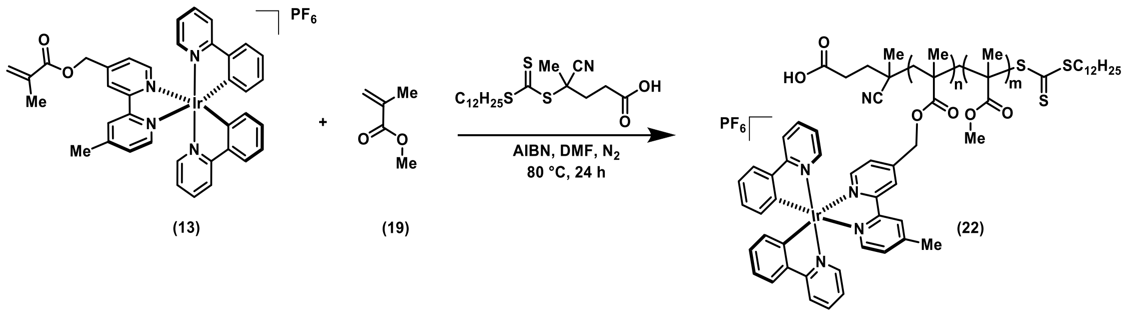
$$\text{Weight \% MMA} = \frac{99\ (*100)}{9.3 + 99} = 91.4\ \%$$

Step 4: Calculate the amount of polymer required for 1 mg iridium photocatalyst:

$$1\ \text{mg of Ir} = \frac{1\ \text{mg of polymer}}{0.086\ \text{mg of Ir monomer}} = 11.6\ \text{mg polymer}$$

11.62 mg of polymer corresponds to 1 mg iridium small molecule

IrCat2 synthesis (22)



To a 20 mL scintillation vial equipped with a septum, 4-cyano-4-[(dodecylsulfanylthiocarbonyl)sulfanyl]pentanoic acid (35 mg, 0.086 mmol), 2,2′-azobis(2-methylpropionitrile) (2.8 mg, 0.017 mmol), iridium monomer (13) (0.182 g, 0.2 mmol), methyl methacrylate (2.11 mL, 19.8 mmol), and dimethylformamide (3.8 mL) were added. The solution sparged with nitrogen for 15-20 minutes, using a vent needle. After sparging, the needles were removed, and the septum was sealed with electrical tape. The mixture was stirred at 80 °C for 24 hours, then cooled to room temperature. The resulting solution was poured into 200 mL of cold methanol, and the precipitate was collected by filtration. The solid was washed with methanol (2 × 20 mL) and dried under reduced pressure to afford 0.653 g of yellow powder.

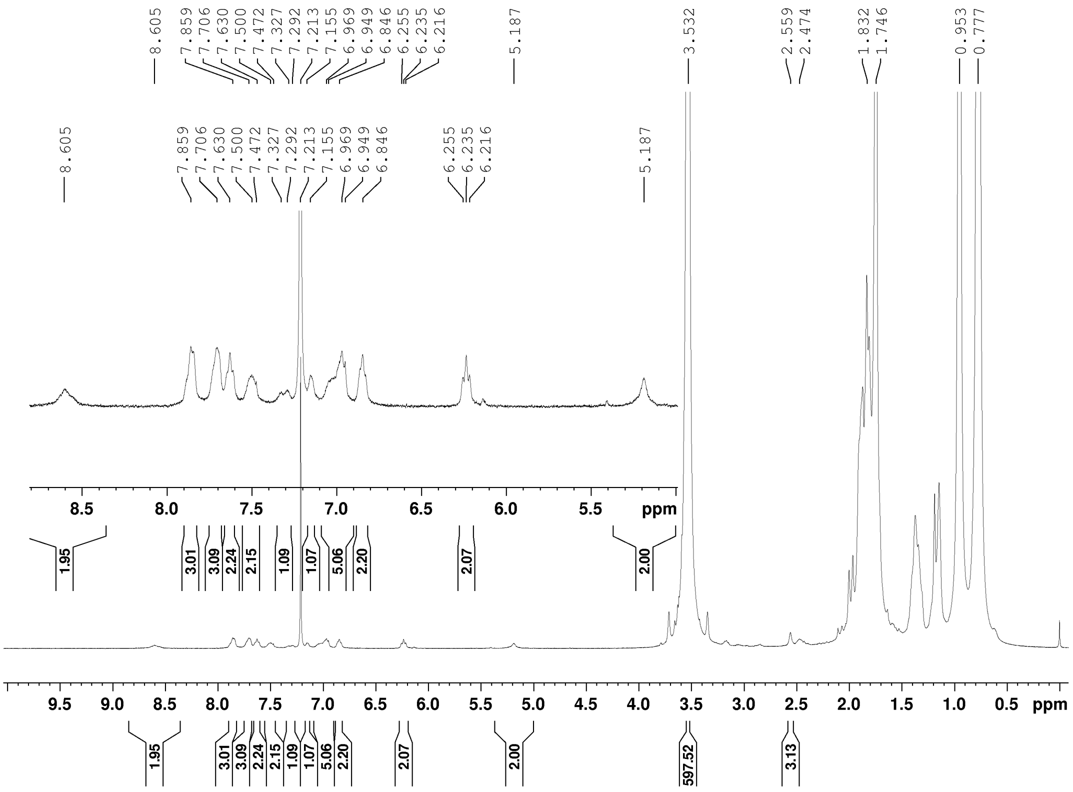


Figure S19. ^{1}H NMR spectrum of (22) ($CDCl_3$, 400 MHz)

IrCat2: Percent incorporation of iridium in polymer

Step 1: Calculate number of Iridium side chains:

Choose any peak from ^{1}H NMR spectrum corresponding to iridium side chain.

$$\text{Ir side chains} = \frac{\textbf{2}\ \text{[Integration of Ir (5.18 ppm from NMR spectrum)]}}{\textbf{2}\ \text{[Total no. of protons for the selected peak]}} = 1$$

$$\text{MMA molecules} = \frac{\textbf{597.5}\ \text{[Integration of MMA (3-4ppm from NMR spectrum)]}}{\textbf{3}\ \text{[Total no. of protons in MMA per molecule]}} = 199$$

Step 2: Calculate mol% of each monomer:

a) $$\text{mol\% Ir} = \frac{\textbf{1}\ \text{[No. of Ir side chains] (*100)}}{\textbf{1}\ \text{[No. of Ir side chains]} + \textbf{199}\ \text{[No. of MMA molecules]}}$$
$$= 0.5\ \%$$

b) $$\text{mol\% MMA} = \frac{\textbf{199}\ \text{[No. of MMA molecules] (*100)}}{\textbf{1}\ \text{[No. of Ir side chains]} + \textbf{199}\ \text{[No. of MMA molecules]}}$$
$$= 99.5\ \%$$

Step 3: Calculate weight% for each monomer:

a) $$\text{Mass of Ir per mol polymer} = \frac{\textbf{0.5}\ \text{[mol\% Ir]} * \textbf{913.8}\ \text{[MW of Ir monomer]}}{\textbf{100}\ \text{[mol\% polymer]}} = 4.6\ \text{mg}$$

b) $$\text{Mass of MMA per mol polymer} = \frac{\textbf{99.5}\ \text{[mol\% MMA]} * \textbf{100.1}\ \text{[MW of MMA]}}{\textbf{100}\ \text{[mol\% polymer]}}$$
$$= 99.6\ \text{mg}$$

Therefore,

$$\text{Weight \% Ir} = \frac{4.6\ (*100)}{4.6 + 99.6} = 4.4\ \%$$

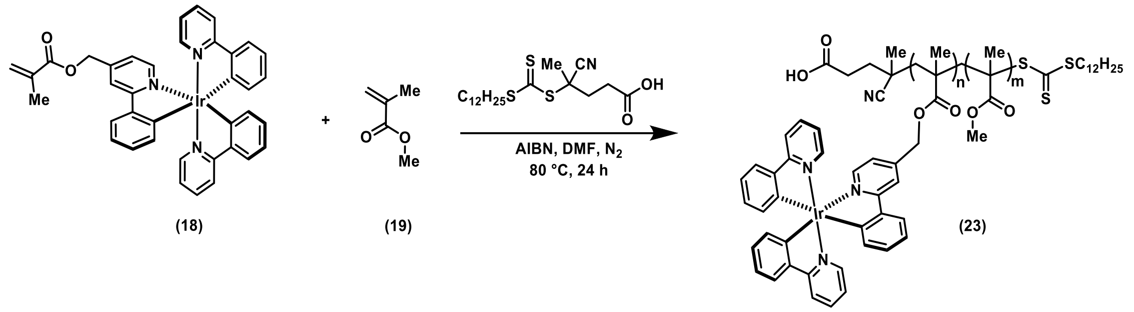
$$\text{Weight \% MMA} = \frac{99.6\ (*100)}{4.6 + 99} = 95.6\ \%$$

Step 4: Calculate the amount of polymer required for 1 mg iridium photocatalyst:

$$1\ \text{mg of Ir} = \frac{1\ \text{mg of polymer}}{0.044\ \text{mg of Ir monomer}} = 22.7\ \text{mg polymer}$$

22.7 mg of polymer corresponds to 1 mg iridium small molecule

IrCat3 synthesis (23)



To a 20 mL scintillation vial equipped with a septum, 4-cyano-4-[(dodecylsulfanylthiocarbonyl)sulfanyl]pentanoic acid (35 mg, 0.086 mmol), 2,2′-azobis(2-methylpropionitrile) (2.8 mg, 0.017 mmol), iridium monomer (18) (0.150 g, 0.2 mmol), methyl methacrylate (2.14 mL, 20 mmol), and dimethylformamide (3.8ml) were added. The solution sparged with nitrogen for 15-20 minutes, using a vent needle. After sparging, the needles were removed, and the septum was sealed with electrical tape. The mixture was stirred at 80 °C for 24 hours, then cooled to room temperature. The resulting solution was poured into 200 mL of cold methanol, and the precipitate was collected by filtration. The solid was washed with methanol (2 × 20 mL) and dried under reduced pressure to afford 0.710 g of yellow powder.

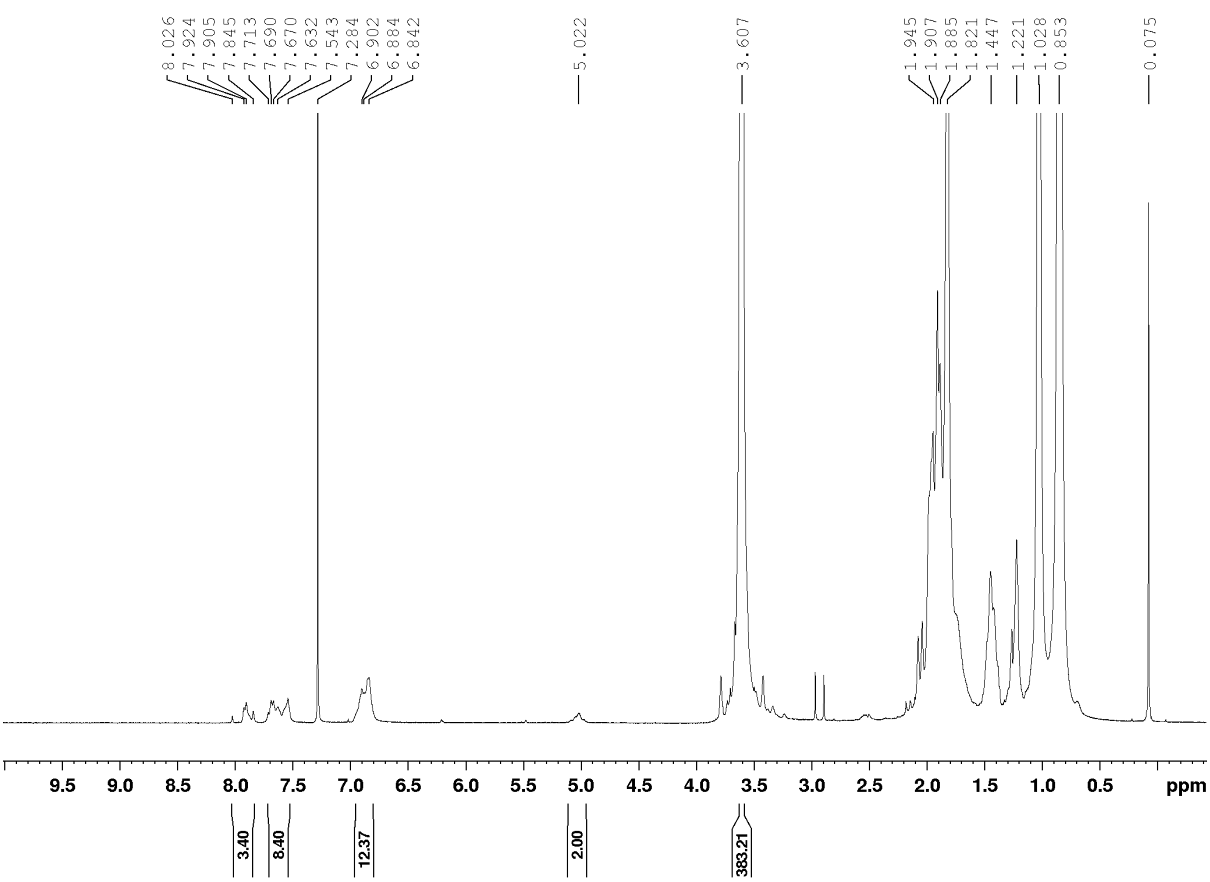


Figure S20. ^{1}H NMR spectrum of (23) (CDCl$_3$, 400 MHz)

IrCat3: Percent incorporation of iridium in polymer

Step 1: Calculate number of Iridium side chains:

Choose any peak from ^{1}H NMR spectrum corresponding to iridium side chain.

$$\text{Ir side chains} = \frac{\mathbf{2}\ \text{[Integration of Ir (5.02 ppm from NMR spectrum)]}}{\mathbf{2}\ \text{[Total no. of protons for the selected peak]}} = 1$$

$$\text{MMA molecules} = \frac{\mathbf{383.2}\ \text{[Integration of MMA (3-4ppm from NMR spectrum)]}}{\mathbf{3}\ \text{[Total no. of protons in MMA per molecule]}} = 127.7$$

Step 2: Calculate mol% of each monomer:

a) $$\text{mol\% Ir} = \frac{\mathbf{1}\ \text{[No. of Ir side chains] (*100)}}{\mathbf{1}\ \text{[No. of Ir side chains]} + \mathbf{127.7}\ \text{[No. of MMA molecules]}}$$
$$= 0.8\ \%$$

b) $$\text{mol\% MMA} = \frac{\mathbf{127.7}\ \text{[No. of MMA molecules] (*100)}}{\mathbf{1}\ \text{[No. of Ir side chains]} + \mathbf{127.7}\ \text{[No. of MMA molecules]}}$$
$$= 99.2\ \%$$

Step 3: Calculate weight% for each monomer:

a) $$\text{Mass of Ir per mol polymer} = \frac{\mathbf{0.8}\ \text{[mol\% Ir]} * \mathbf{752.9}\ \text{[MW of Ir monomer]}}{\mathbf{100}\ \text{[mol\% polymer]}} = 5.87\ \text{mg}$$

b) $$\text{Mass of MMA per mol polymer} = \frac{\mathbf{99.2}\ \text{[mol\% MMA]} * \mathbf{100.1}\ \text{[MW of MMA]}}{\mathbf{100}\ \text{[mol\% polymer]}}$$
$$= 99.3\ \text{mg}$$

Therefore,

$$\text{Weight \% Ir} = \frac{5.87\ (*100)}{5.87 + 99.3} = 5.6\ \%$$

$$\text{Weight \% MMA} = \frac{99.3\ (*100)}{5.87 + 99.3} = 94.4\ \%$$

Step 4: Calculate the amount of polymer required for 1 mg iridium photocatalyst:

$$1\ \text{mg of Ir} = \frac{1\ \text{mg of polymer}}{0.056\ \text{mg of Ir monomer}} = 17.9\ \text{mg polymer}$$

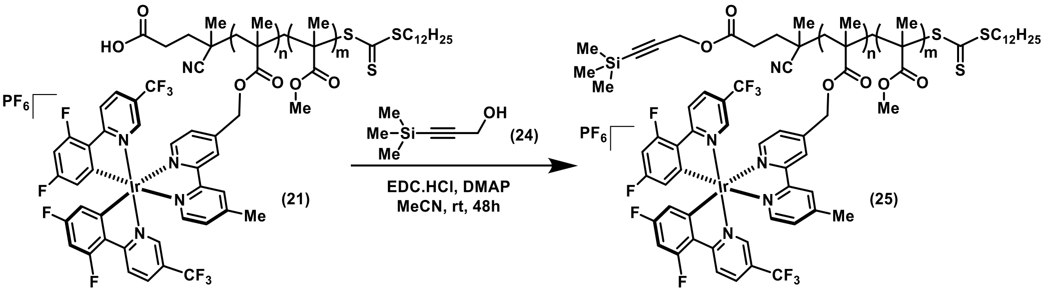
17.85 mg of polymer corresponds to 1 mg iridium small molecule

4) Example Molecular Weight Determination by GPC

Polymer	M_n	M_w	$Đ$
dmbpy-co-MMA (20)	16471	22327	1.35
IrCat1 (21)	9837	11407	1.16

5) Molecular Weight Determination by NMR Spectroscopic Chain-End Analysis

IrCat1 (21)



A solution of IrCat1 (21) (30 mg) and 3-trimethylsilylpropargyl alcohol (3 µL, 30 equivalents relative to the hypothetical –COOH group) was prepared in 200 µL of acetonitrile in a small vial. To this, *N*-(3-dimethylaminopropyl)-*N′*-ethylcarbodiimide hydrochloride (0.19 mg, 1.5 equivalents relative to the hypothetical –COOH group) and 4-(dimethylamino) pyridine (0.012 mg, 0.1 equivalent relative to the hypothetical –COOH group) were added from stock solutions. *N*-(3-dimethylaminopropyl)-*N′*-ethylcarbodiimide hydrochloride was introduced in two portions: 1 equivalent at the start and 0.5 equivalent after 24 hours of stirring. The reaction mixture was stirred for a total of 48 hours at room temperature. Afterward, acetonitrile was removed using a nitrogen stream. DCM (10 mL) was then added, and the solution was washed with distilled water (5 × 20 mL). The organic phase was separated and precipitated into an excess of diethyl ether (10 mL) to remove any unreacted small molecules. The polymer was further washed with ether (4 times), collected, and dried under reduced pressure.

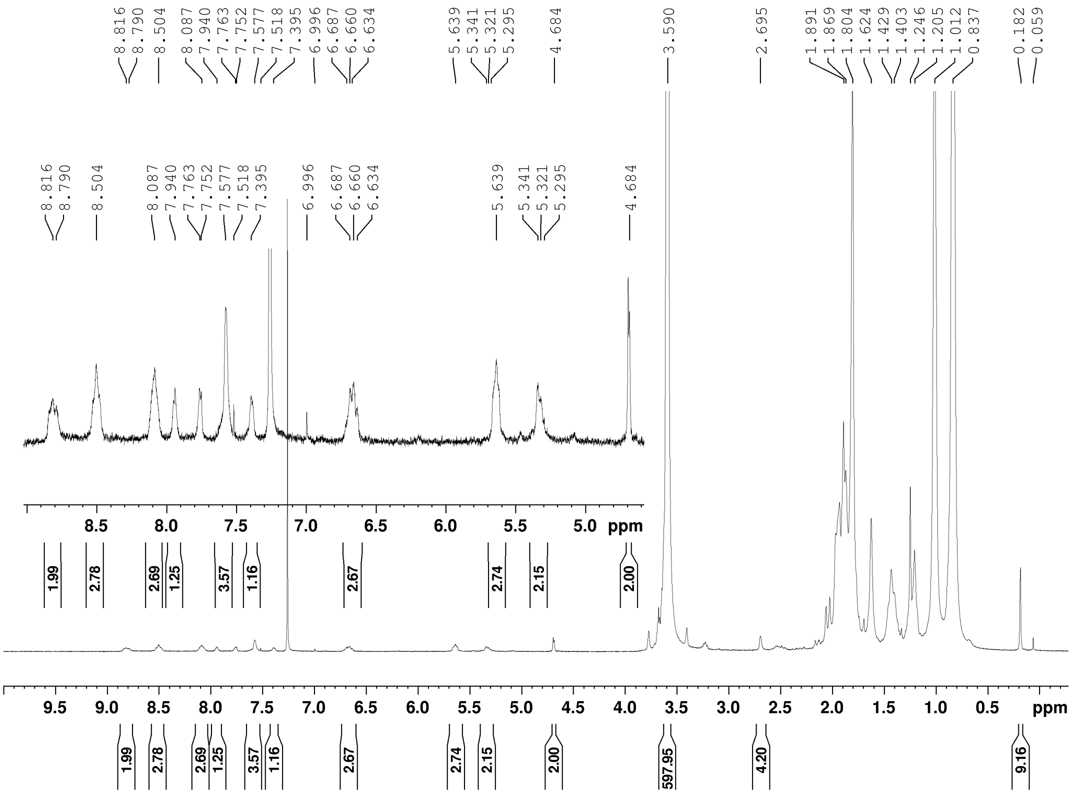


Figure S21. ^{1}H NMR spectrum of (25) ($CDCl_3$, 400 MHz)

Percent incorporation was calculated by calibrating the –TMS singlet at 0.059-0.182 ppm in Figure S13 to the theoretical value of 9. The ratios of the actual over theoretical integrations of $[Ir(dF(CF_3)ppy)_2(dmbpy)](PF_6)$ and MMA were calculated as shown below. The molecular weight was calculated by multiplying the actual incorporation numbers by their respective monomer molecular weights, the summation of those values is calculated to be the molecular weight of the polymer.

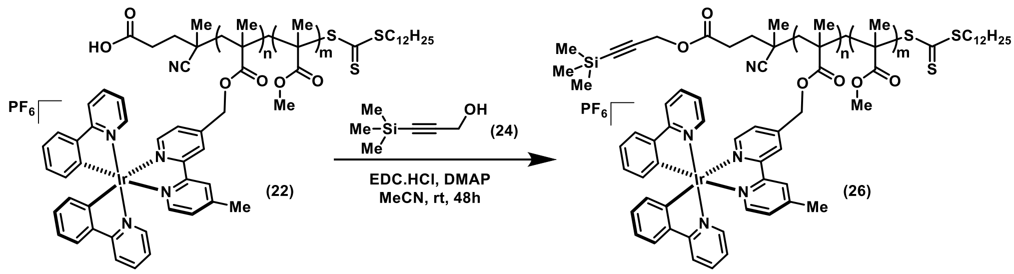
a) Incorporation of Ir $= \frac{2.67}{2} = 1.3$

b) Incorporation of MMA $= \frac{597.95}{3} = 199.3$

Incorporation number (m, n): 1.3 (Iridium complex), 199.3 (MMA)

$M_n = (1.3*1106.64) + (199.3*100.12) = 21{,}393\ Da\ (\sim 21\ kDa)$

IrCat2 (22)



A solution of IrCat2 (22) (30 mg) and 3-trimethylsilylpropargyl alcohol (3 μL, 30 equivalents relative to the hypothetical –COOH group) was prepared in 200 μL of acetonitrile in a small vial. To this, *N*-(3-dimethylaminopropyl)-*N*′-ethylcarbodiimide hydrochloride (0.19 mg, 1.5 equivalents relative to the hypothetical –COOH group) and 4-(dimethylamino) pyridine (0.012 mg, 0.1 equivalent relative to the hypothetical –COOH group) were added from stock solutions. *N*-(3-dimethylaminopropyl)-*N*′-ethylcarbodiimide hydrochloride was introduced in two portions: 1 equivalent at the start and 0.5 equivalent after 24 hours of stirring. The reaction mixture was stirred for a total of 48 hours at room temperature. Afterward, acetonitrile was removed using a nitrogen stream. DCM (10 mL) was then added, and the solution was washed with distilled water (5 × 20 mL). The organic phase was separated and precipitated into an excess of diethyl ether (10 mL) to remove any unreacted small molecules. The polymer was further washed with ether (4 times), collected, and dried under reduced pressure.

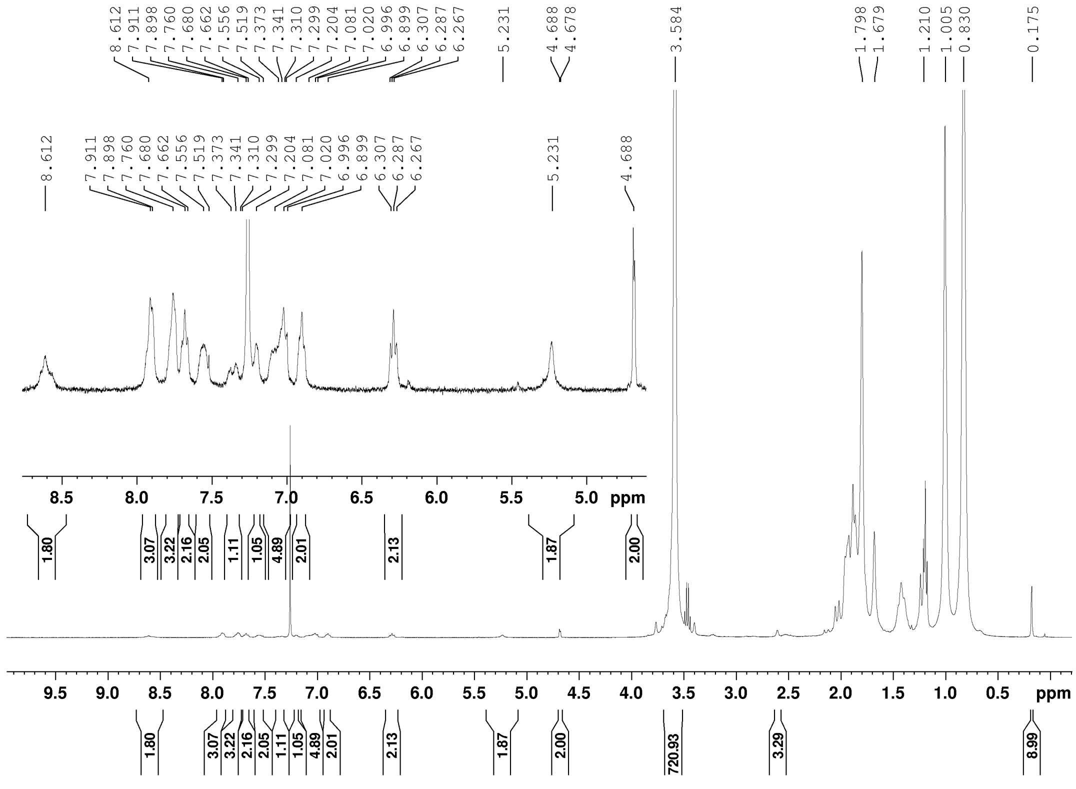


Figure S22. ^{1}H NMR spectrum of (26) ($CDCl_3$, 400 MHz)

Percent incorporation was calculated by calibrating the –TMS singlet at 0.175 ppm in Figure S13 to the theoretical value of 9. The ratios of the actual over theoretical integrations of $[Ir(ppy)_2(dmbpy)](PF_6)$ and MMA were calculated as shown below. The molecular weight was calculated by multiplying the actual incorporation numbers by their respective monomer molecular weights, the summation of those values is calculated to be the molecular weight of the polymer.

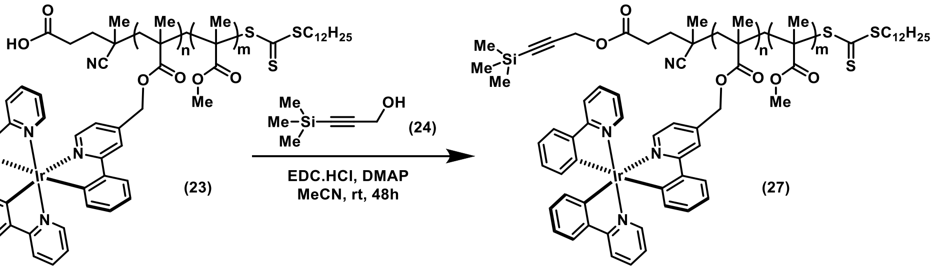
a) Incorporation of Ir $= \frac{2.13}{2} = 1.07$

b) Incorporation of MMA $= \frac{721}{3} = 240.3$

Incorporation number (m, n): 1.07 (Iridium complex), 240.3 (MMA)

$$M_n = (1.07*913.88) + (240.3*100.12) = 25{,}036\ Da\ (\sim 25\ kDa)$$

IrCat3 (27)



A solution of IrCat3 (27) polymer (30 mg) and 3-trimethylsilylpropargyl alcohol (3 µL, 30 equivalents relative to the hypothetical –COOH group) was prepared in 200 µL of acetonitrile in a small vial. To this, *N*-(3-dimethylaminopropyl)-*N*′-ethylcarbodiimide hydrochloride (0.19 mg, 1.5 equivalents relative to the hypothetical –COOH group) and 4-(dimethylamino) pyridine (0.012 mg, 0.1 equivalent relative to the hypothetical –COOH group) were added from stock solutions. *N*-(3-dimethylaminopropyl)-*N*′-ethylcarbodiimide hydrochloride was introduced in two portions: 1 equivalent at the start and 0.5 equivalent after 24 hours of stirring. The reaction mixture was stirred for a total of 48 hours at room temperature. Afterward, acetonitrile was removed using a nitrogen stream. DCM (10 mL) was then added, and the solution was washed with distilled water (5 × 20 mL). The organic phase was separated and precipitated into an excess of diethyl ether (10 mL) to remove any unreacted small molecules. The polymer was further washed with ether (4 times), collected, and dried under reduced pressure.

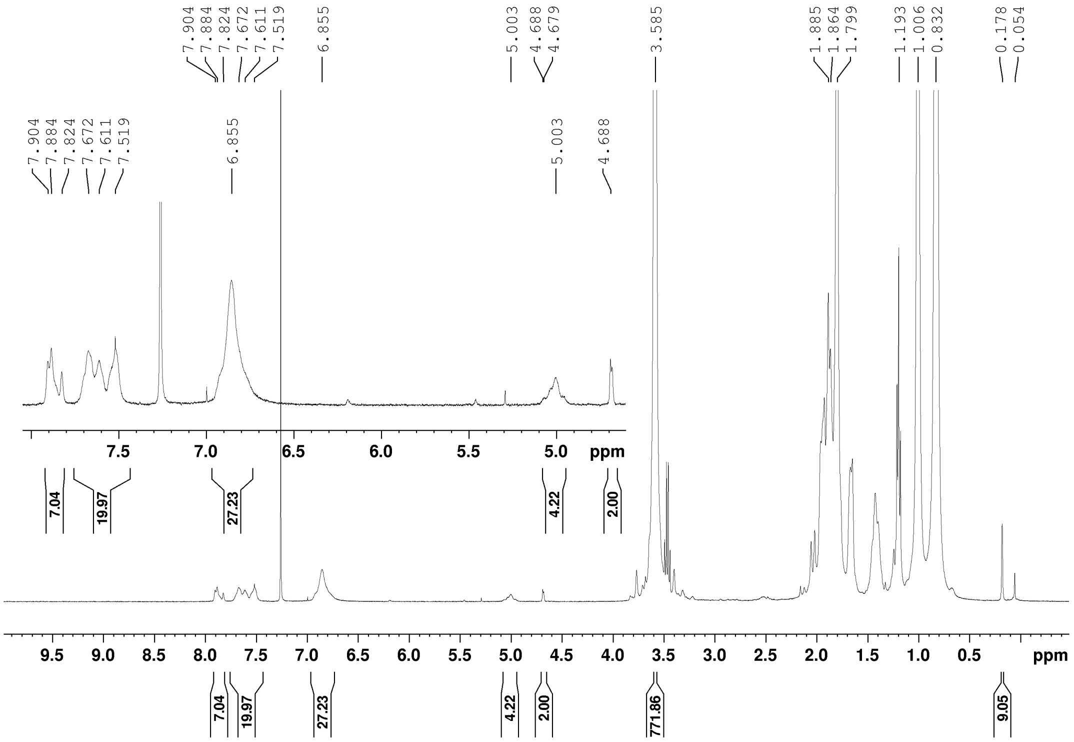


Figure S23. ^{1}H NMR spectrum of (27) (CDCl$_3$, 400 MHz)

Percent incorporation was calculated by calibrating the –TMS singlet at 0.175 ppm in Figure S13 to the theoretical value of 9. The ratios of the actual over theoretical integrations of [Ir(ppy)$_2$(mppy)](PF$_6$) and MMA were calculated as shown below. The molecular weight was calculated by multiplying the actual incorporation numbers by their respective monomer molecular weights, the summation of those values is calculated to be the molecular weight of the polymer.

a) Incorporation of Ir $= \frac{4.2}{2} = 2.1$

b) Incorporation of MMA $= \frac{772}{3} = 257.3$

Incorporation number (m, n): 2.1 (Iridium complex), 257.3 (MMA)

$M_n = (2.1*752.89) + (257.3*100.12) = 27{,}342\ Da\ (\sim 27\ kDa)$

6) Photophysical Characterization

A) UV-Visible Spectroscopy:

IrCat1 (21)

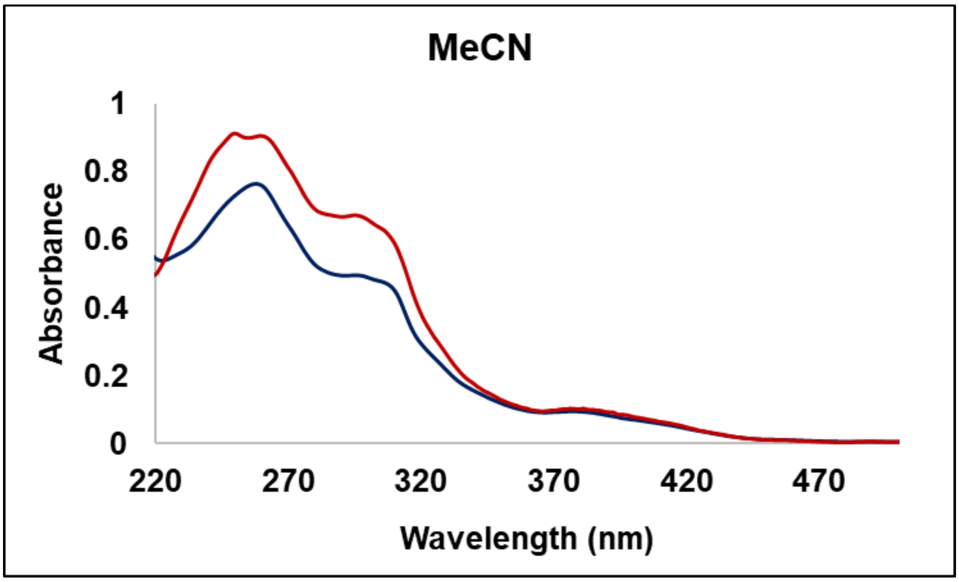


Figure S24. UV-Vis spectral overlay of [Ir(dF(CF$_3$)ppy)$_2$(dmbpy)]PF$_6$ (blue trace) and IrCat1 (red trace) in MeCN.

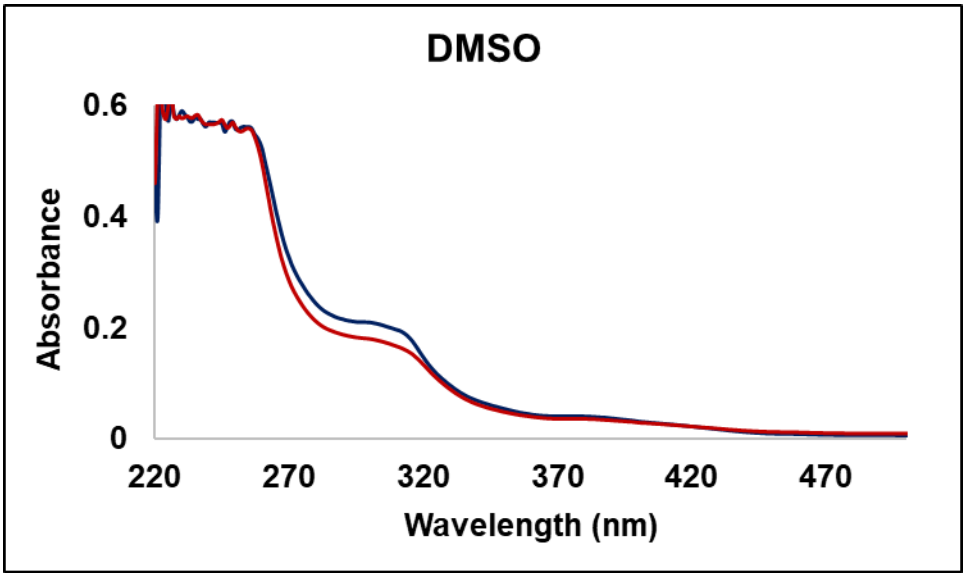


Figure S25. UV-Vis spectral overlay of [Ir(dF(CF$_3$)ppy)$_2$(dmbpy)]PF$_6$ (blue trace) and IrCat1 (red trace) in DMSO.

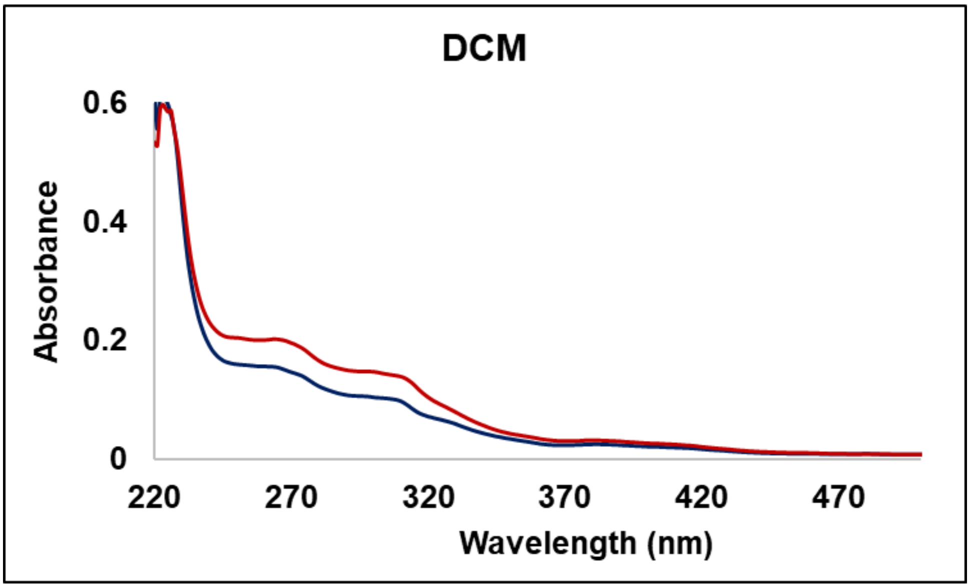


Figure S26. UV-Vis spectral overlay [Ir(dF(CF$_3$)ppy)$_2$(dmbpy)]PF$_6$ (blue trace) and IrCat (red trace) in DCM.

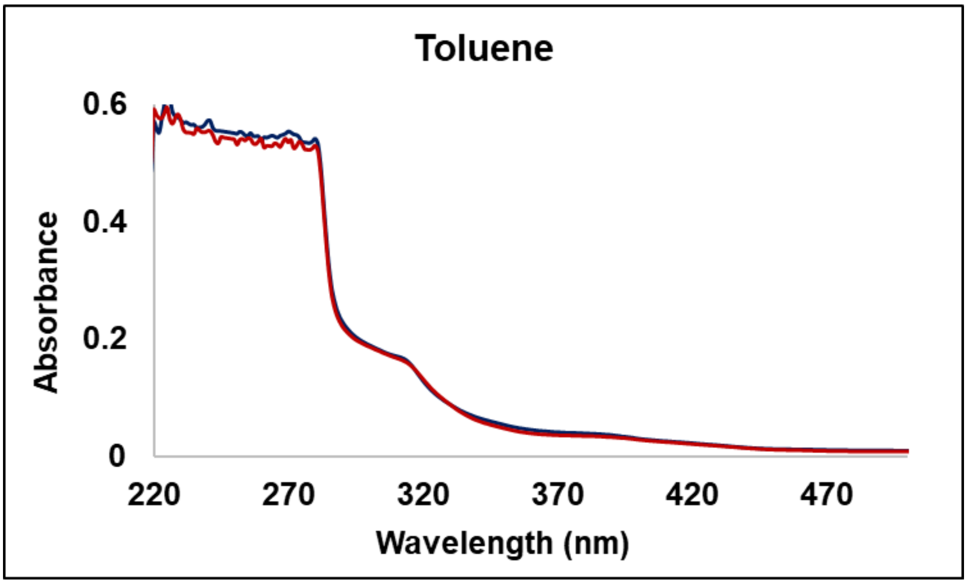


Figure S27. UV-Vis spectral overlay of [Ir(dF(CF$_3$)ppy)$_2$(dmbpy)]PF$_6$ (blue trace) and IrCat1 (red trace) in Toluene

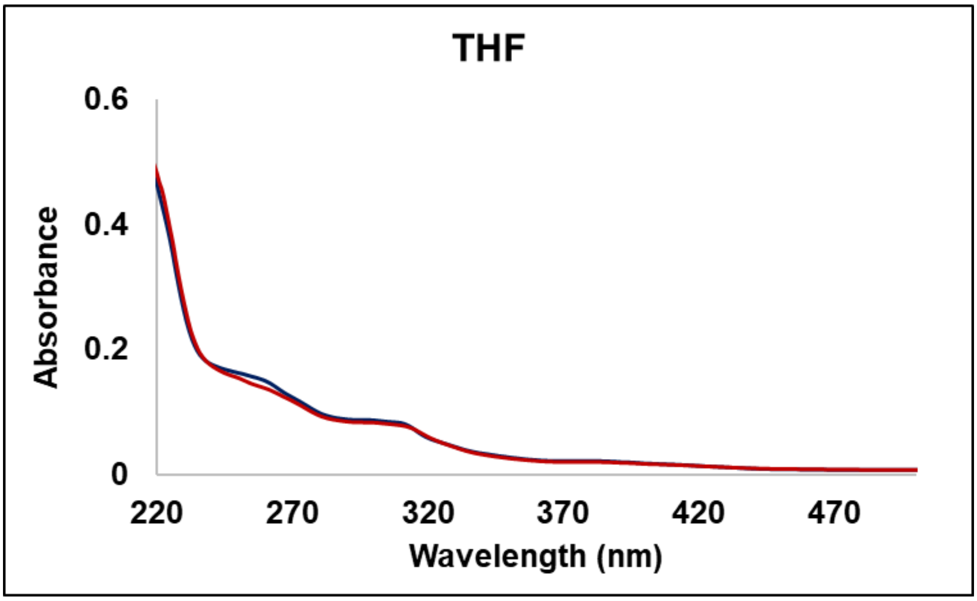


Figure S28. UV-Vis spectral overlay of [Ir(dF(CF$_3$)ppy)$_2$(dmbpy)]PF$_6$ (blue trace) and IrCat1 (red trace) in THF.

<u>**IrCat2 (22)**</u>

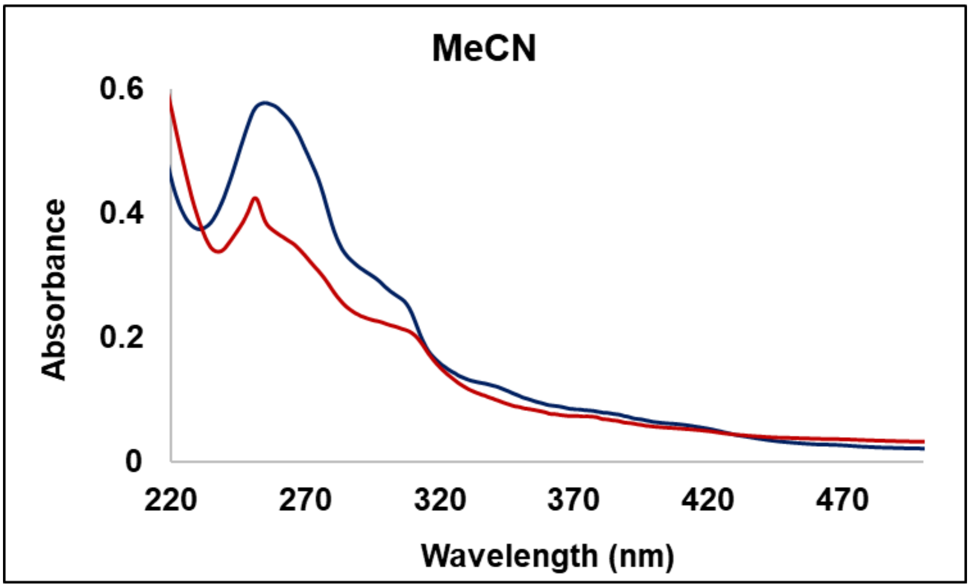


Figure S29. UV-Vis spectral overlay of [Ir(ppy)$_2$(dmbpy)](PF$_6$) (blue trace) and IrCat2 (red trace) in MeCN.

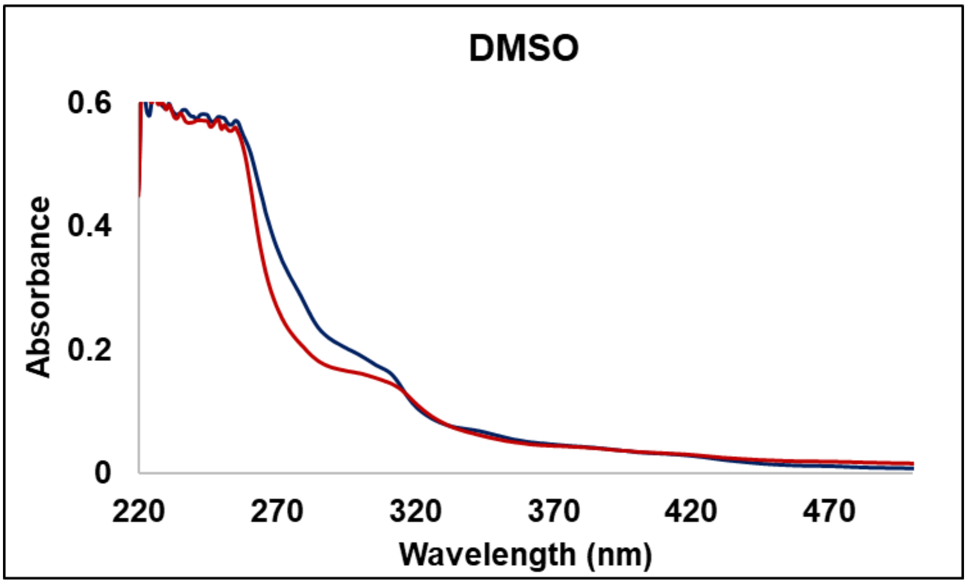


Figure S30. UV-Vis spectral overlay of [Ir(ppy)$_2$(dmbpy)](PF$_6$) (blue trace) and IrCat2 (red trace) in DMSO.

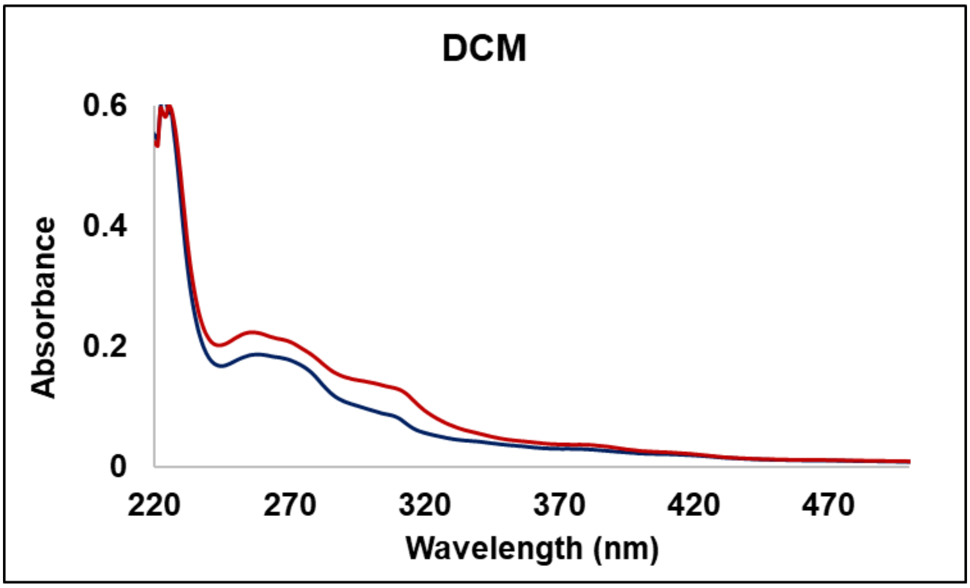


Figure S31. UV-Vis spectral overlay of [Ir(ppy)$_2$(dmbpy)](PF$_6$) (blue trace) and IrCat2 (red trace) in DCM.

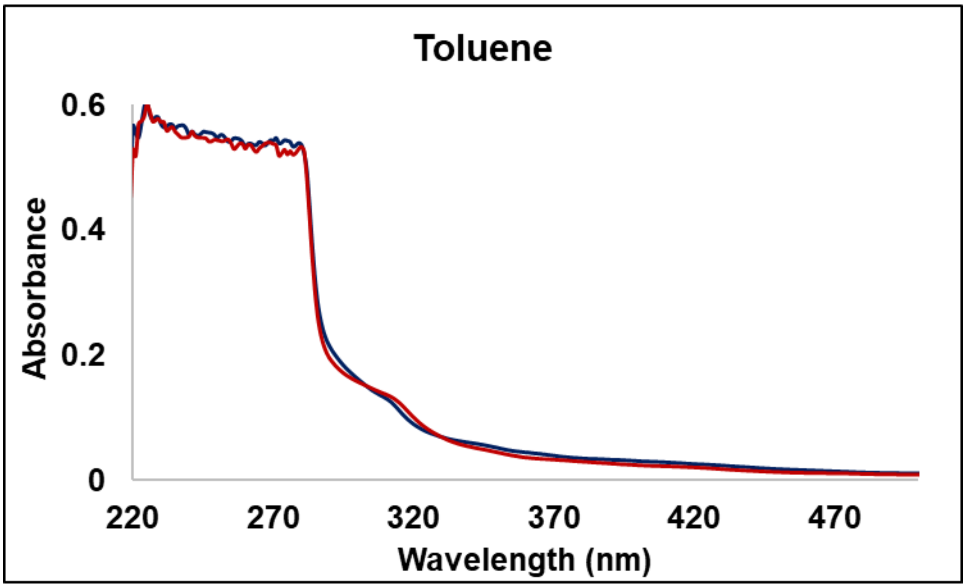


Figure S32. UV-Vis spectral overlay [Ir(ppy)$_2$(dmbpy)](PF$_6$) (blue trace) and IrCat2 (red trace) in Toluene.

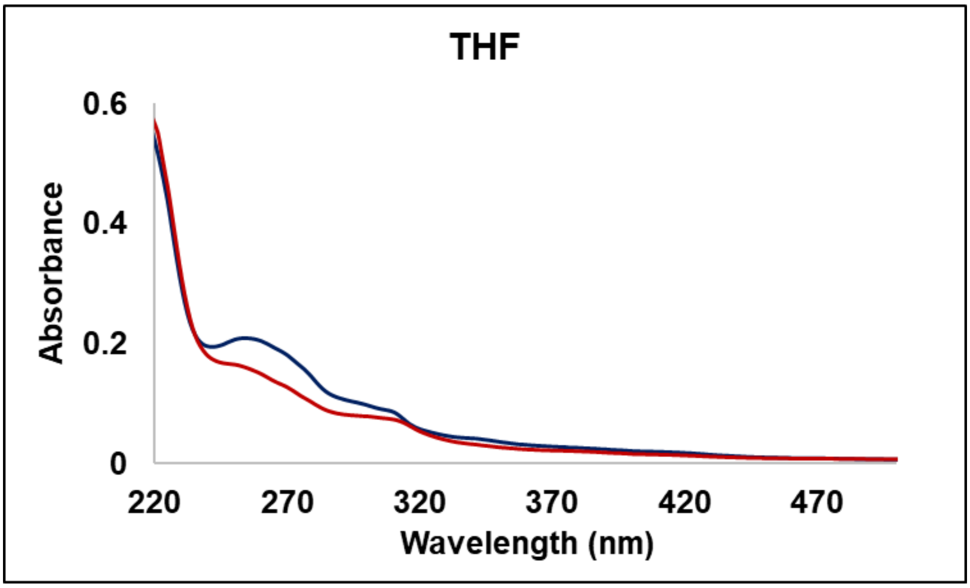


Figure S33. UV-Vis spectral overlay of [Ir(ppy)$_2$(dmbpy)](PF$_6$) (blue trace) and IrCat2 (red trace) in THF.

IrCat3 (23)

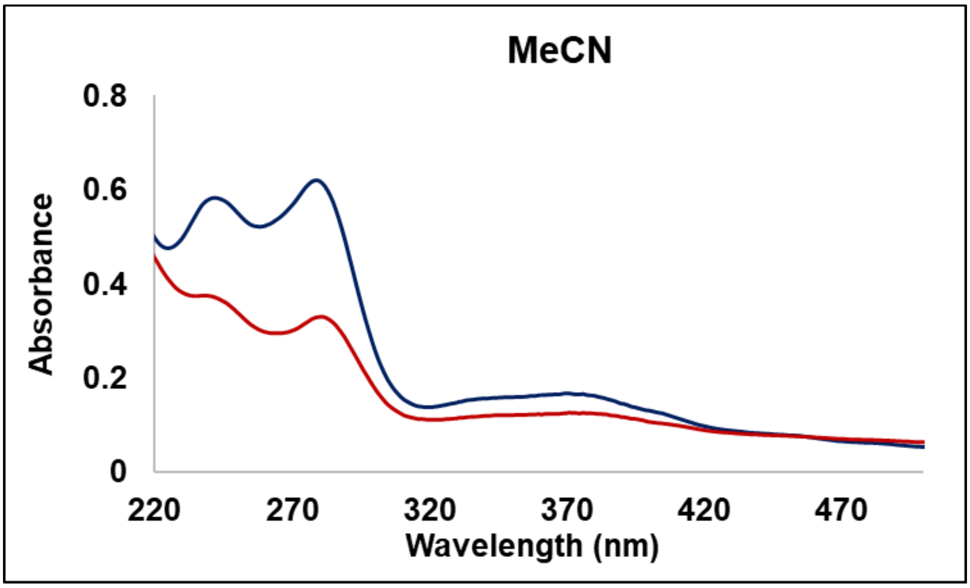


Figure S34. UV-Vis spectral overlay of *fac*-Ir(ppy)$_3$ (blue trace) and IrCat3 (red trace) in MeCN.

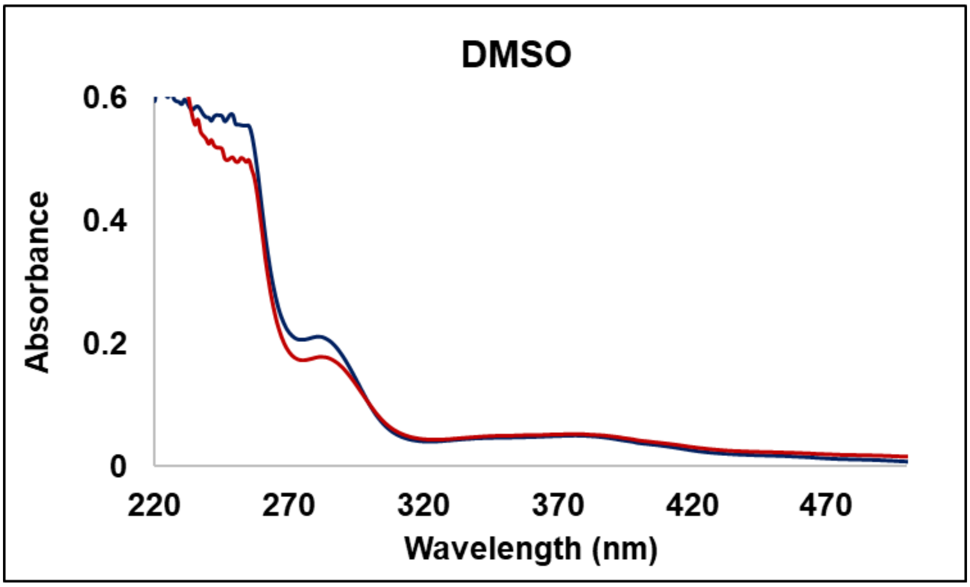


Figure S35. UV-Vis spectral overlay of *fac*-Ir(ppy)$_3$ (blue trace) and IrCat3 (red trace) in DMSO.

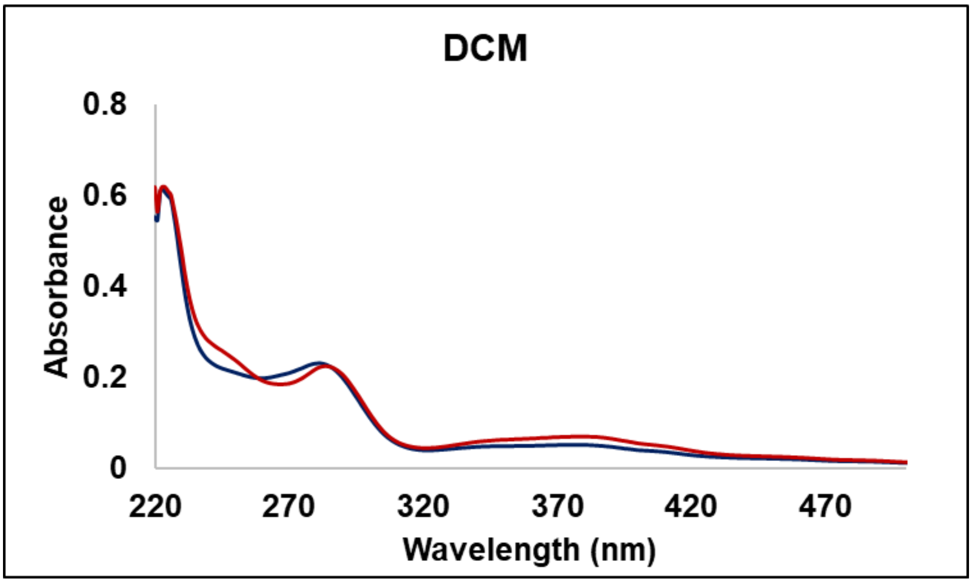


Figure S36. UV-Vis spectral overlay of *fac*-Ir(ppy)$_3$ (blue trace) and IrCat3 (red trace) in DCM.

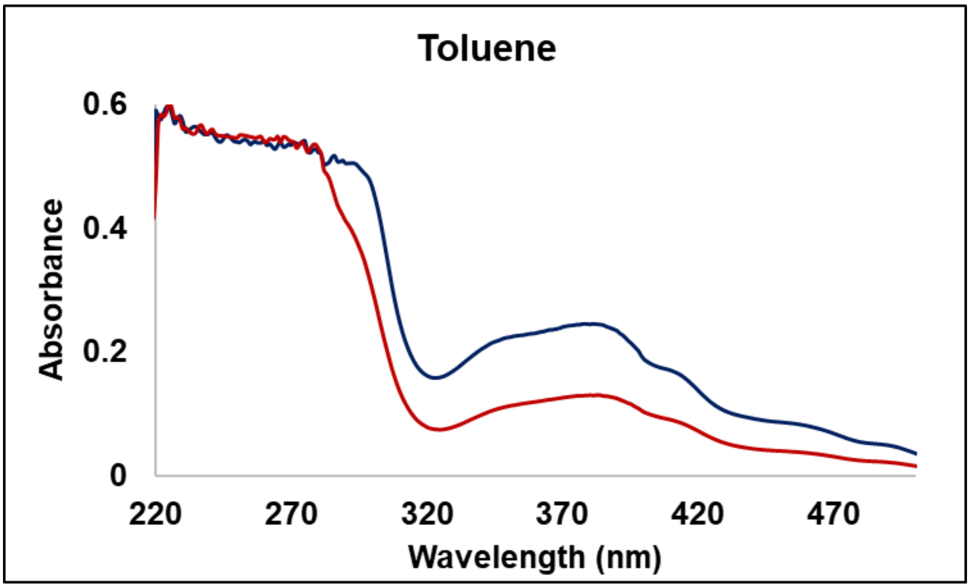


Figure S37. UV-Vis spectral overlay of *fac*-Ir(ppy)$_3$ (blue trace) and IrCat3 (red trace) in Toluene.

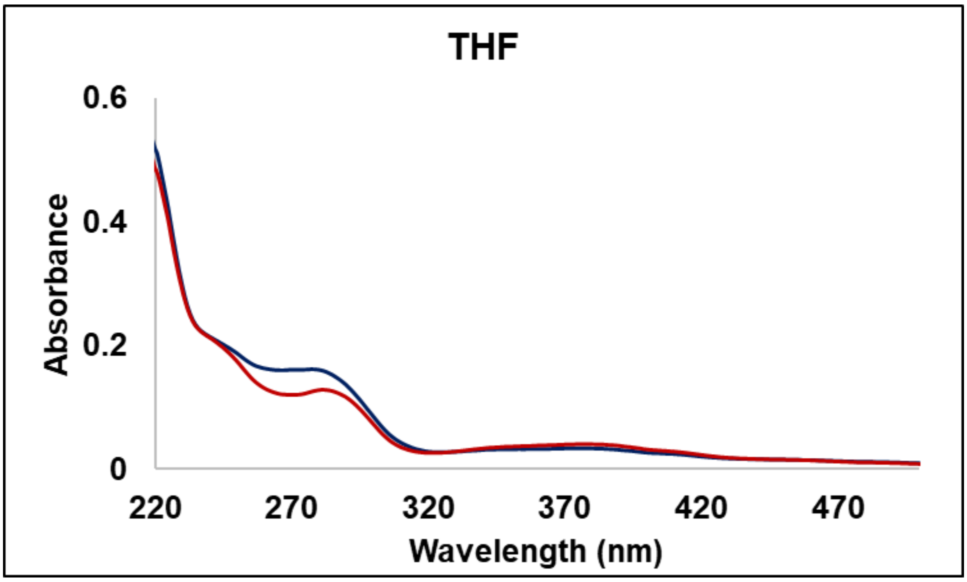


Figure S38. UV-Vis spectral overlay of *fac*-Ir(ppy)$_3$ (blue trace) and IrCat3 (red trace) in THF.

B) Fluorescence data

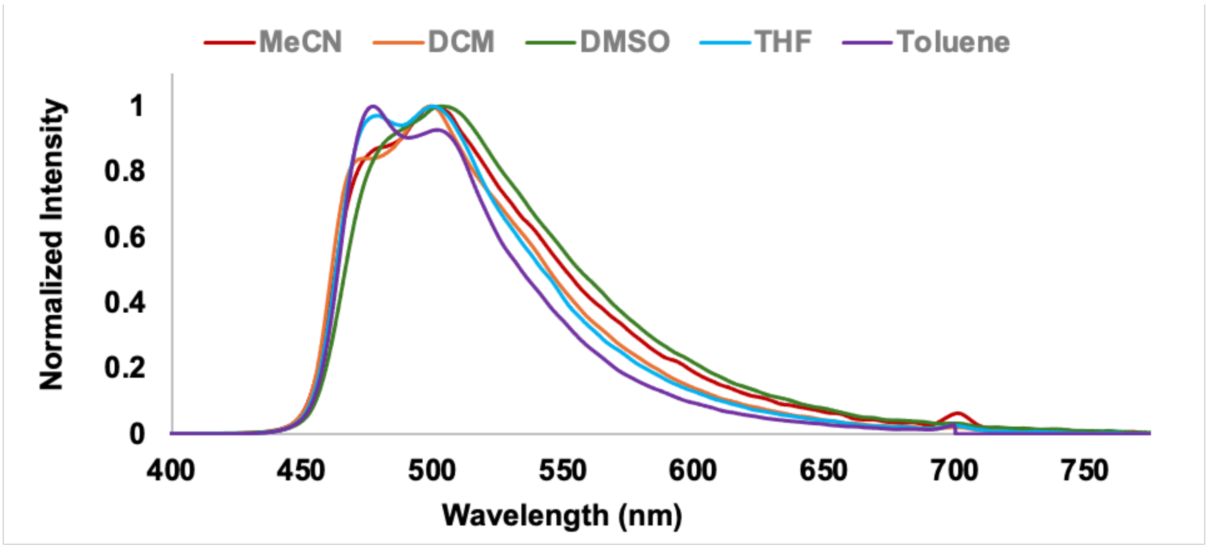


Figure S39. Fluorescence spectra of polymer IrCat1 obtained upon excitation at 350 nm in solvents with different dielectric constants.

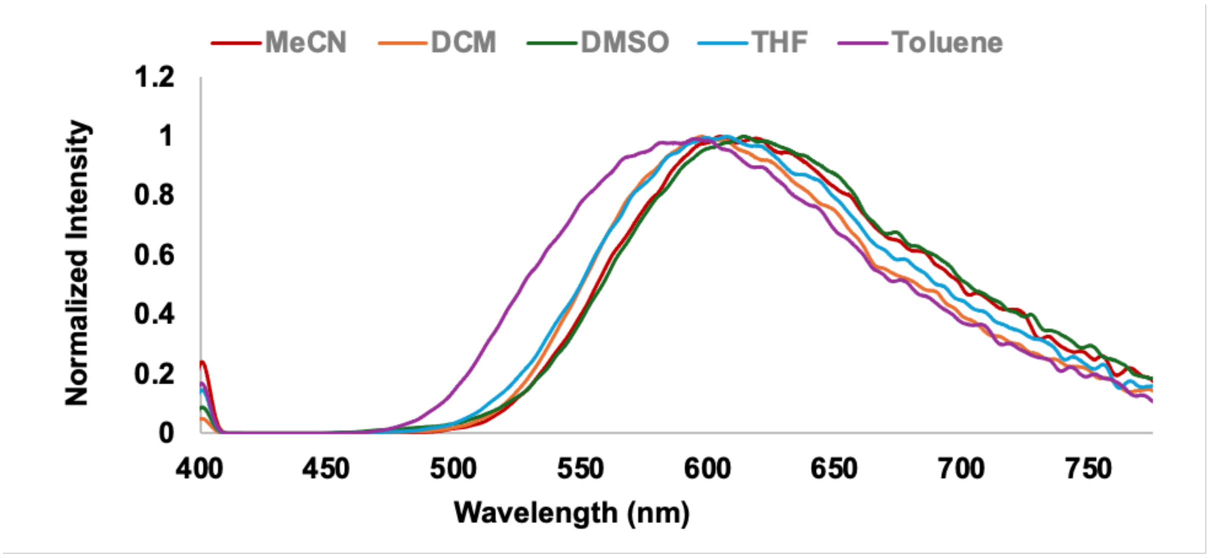


Figure S40. Fluorescence spectra of polymer IrCat2 obtained upon excitation at 400 nm in solvents with different dielectric constants.

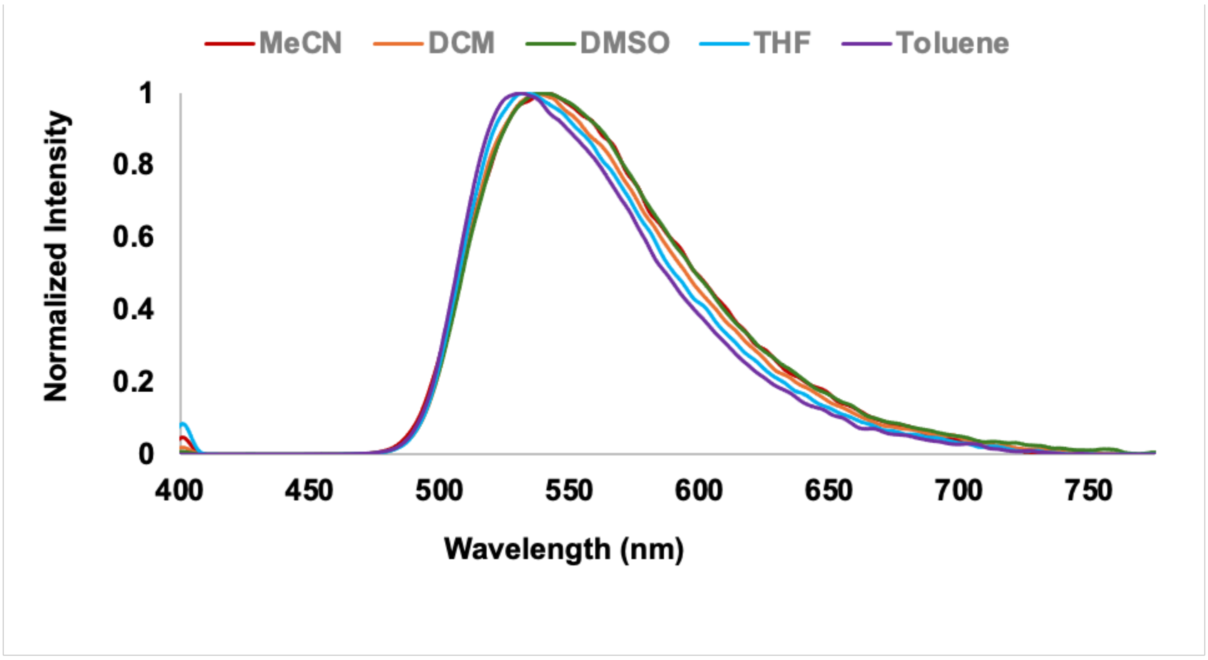
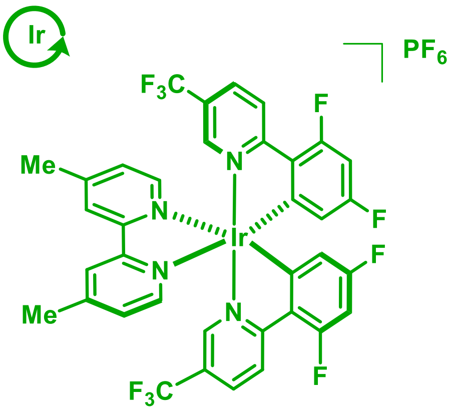


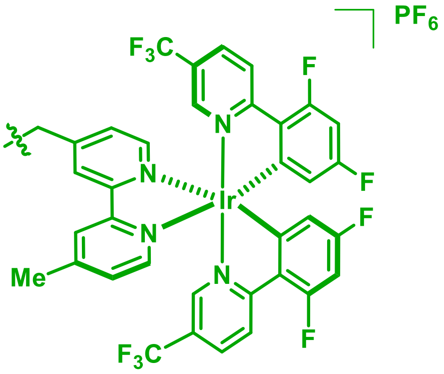
Figure S41. Fluorescence spectra of polymer IrCat3 obtained upon excitation at 400 nm in solvents with different dielectric constants.

7) Procedures and Characterization for Photoredox Applications:

IrCat1 (21)

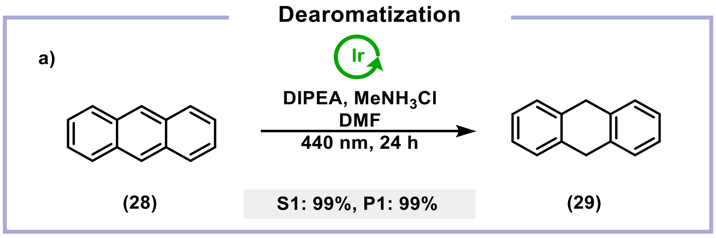


[Ir(dF(CF$_3$)ppy)$_2$(dmbpy)]PF$_6$
(S1)



IrCat1
(P1)

a) Dearomatization: The reaction was performed according to the reported procedure with some modifications.[10]



A vial was equipped with anthracene (17.8 mg, 0.1 mmol, 1 equiv.), DIPEA (34.8 μL, 0.2 mmol, 2 equiv.), $MeNH_3Cl$ (0.3 mg, 10 mol%) and the photocatalyst (1 mol%, 13 mg of IrCat1 or 1-2 mg of [Ir(dF(CF$_3$)ppy)$_2$(dmbpy)](PF$_6$)), along with a stirring bar. DMF (1 mL) was added as the solvent, and the vial was sealed under air. The reaction mixture was stirred and irradiated with a 456 nm LED for 24 hours at room temperature. After the reaction, the solvents were removed under reduced pressure to obtain the crude product. 1,3,5-trimethoxybenzene (TMB) was added as the internal standard to determine the yield. (IrCat1: 99%; [Ir(dF(CF$_3$)ppy)$_2$(dmbpy)](PF$_6$): 99%)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25−7.23 (m, 4H), 7.15−7.13 (m, 4H), 3.88 (s, 4H).

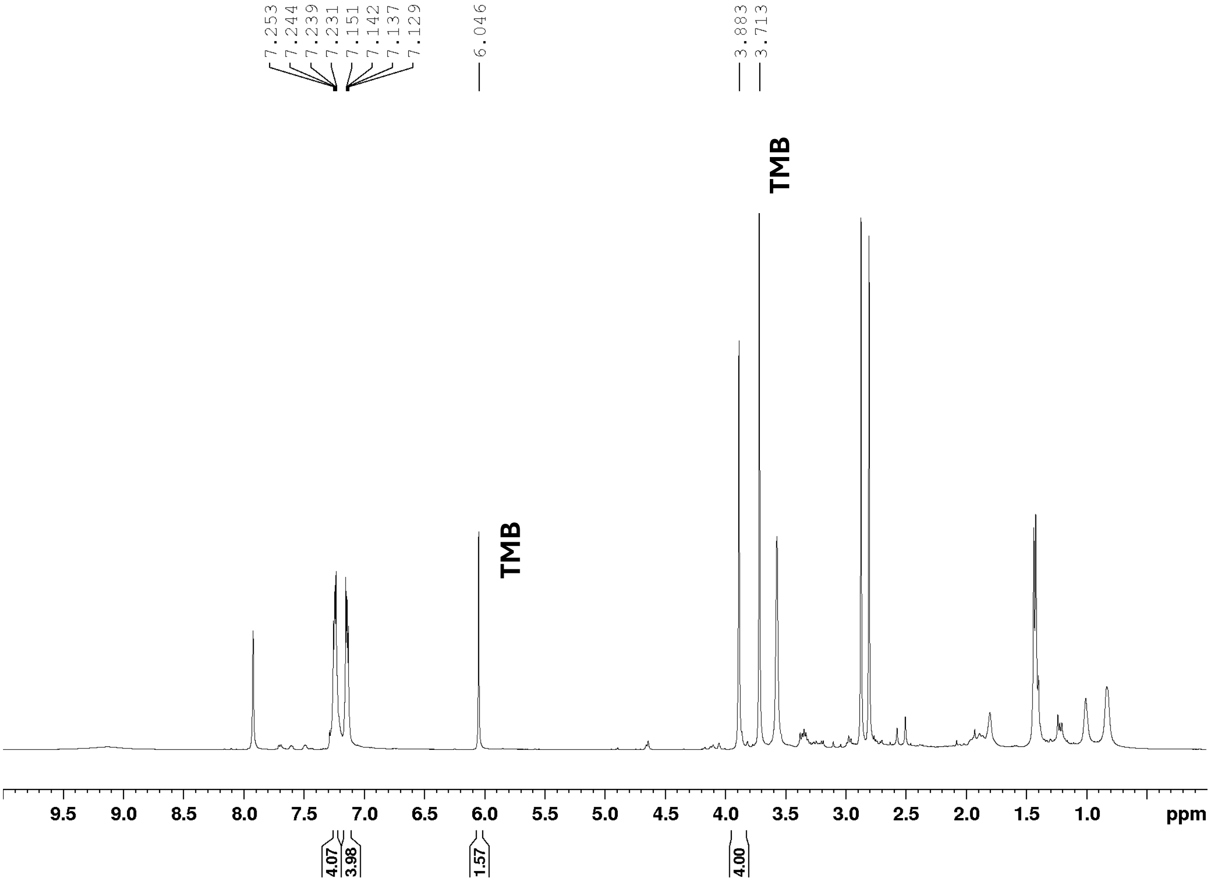
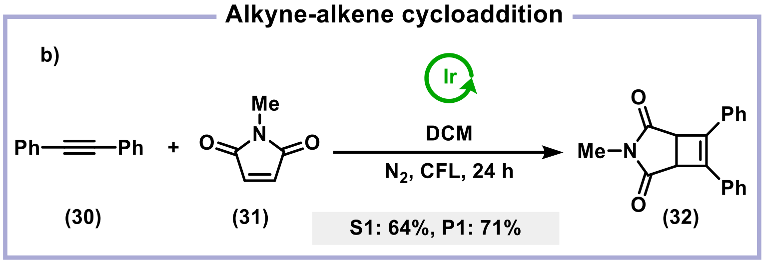


Figure S42. ^{1}H NMR spectrum of (29)

b) Alkyne-alkene cycloaddition: The reaction was performed according to the reported procedure with some modifications.[11]



1,2-Diphenylacetylene (17.65 uL, 0.1 mmol, 1.0 equiv.), *N*-methylmaleimide (16.67 mg, 0.15 mmol, 1.5 equiv.), photocatalyst (2.5 mol%, 0.025 equiv, 30 mg of IrCat1 or 3 mg of $[Ir(dF(CF_3)ppy)_2(dmbpy)](PF_6)$) and 2 mL DCM were added to a 5 mL vial equipped with a stir bar. The reaction mixture was then sparged with nitrogen for 20 mins and then irradiated by CFL lights at room temperature. After the reaction completion, the solution was concentrated under air stream. The yield was determined by using 1,3,5-trimethoxybenzene as the internal standard. (IrCat1: 71%; $[Ir(dF(CF_3)ppy)_2(dmbpy)](PF_6)$: 64%).

^{1}H NMR (400 MHz, CDCl3): δ 7.68 – 7.65 (m, 4H), 7.31 – 7.23 (m, 6H), 3.99 (s, 2H), 2.88 (s, 3H)

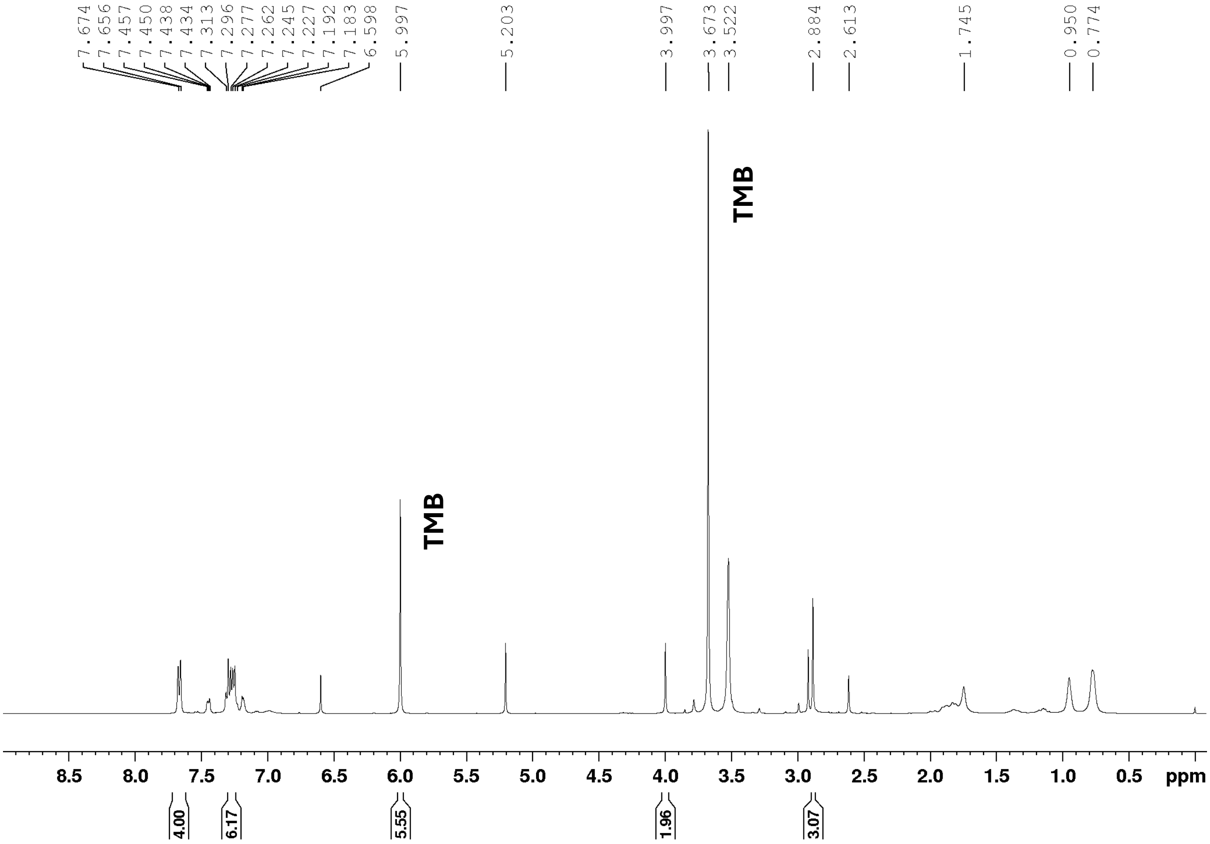
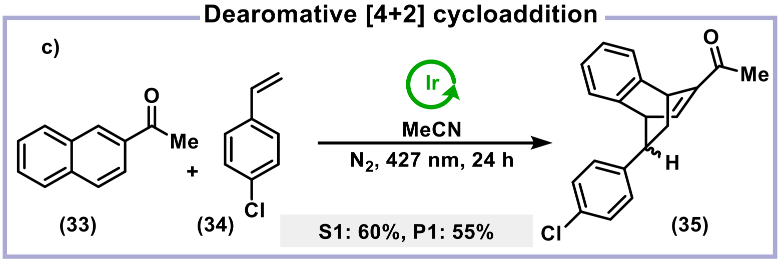


Figure S43. ^{1}H NMR spectrum of (32)

c) Dearomative [4+2] cycloaddition: The reaction was performed according to the reported procedure with some modifications.[12]



In a vial with septum, 2-acetyl naphthalene was added (0.1 mmol), along with photosensitizer (1 mol%, 0.01 equiv, 13 mg of IrCat1 or 1-2 mg of [Ir(dF(CF$_3$)ppy)$_2$(dmbpy)](PF$_6$)). The vial was evacuated and backfilled with nitrogen three times. Acetonitrile (2 mL) followed by 4-chlorostyrene (15 ul, 0.12 mmol, 1.2 equiv) was added under a nitrogen atmosphere. The vial was sealed, and the resulting solution was irradiated with 427 nm LED and irradiated for 24 h. Afterward, the mixture was diluted with CH$_2$Cl$_2$ (2 mL) and filtered the mixture through a small pack of silica gel, and then the solvent was evaporated under air stream. 1,3,5-trimethoxybenzene was added as the internal standard to determine the yield. (IrCat1: 60%; [Ir(dF(CF$_3$)ppy)$_2$(dmbpy)](PF$_6$): 55%). Two isomers form in this reaction, the major of which corresponds to the data supplied below.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (dd, *J* = 6.5, 1.8 Hz, 1H), 7.36 (d, *J* = 7.3 Hz, 1H), 7.23 – 7.19 (m, 1H), 7.10 – 7.00 (m, 3H), 6.85 (d, *J* = 7.3 Hz, 1H), 6.38 – 6.33 (m, 2H), 4.70 (q, *J* = S20 2.5 Hz, 1H), 3.91 (dd, *J* = 6.5, 2.3 Hz, 1H), 3.17 – 3.13 (m, 1H), 2.30 (s, 3H), 2.12 – 2.07 (m, 1H), 1.54 – 1.50 (m, 1H).

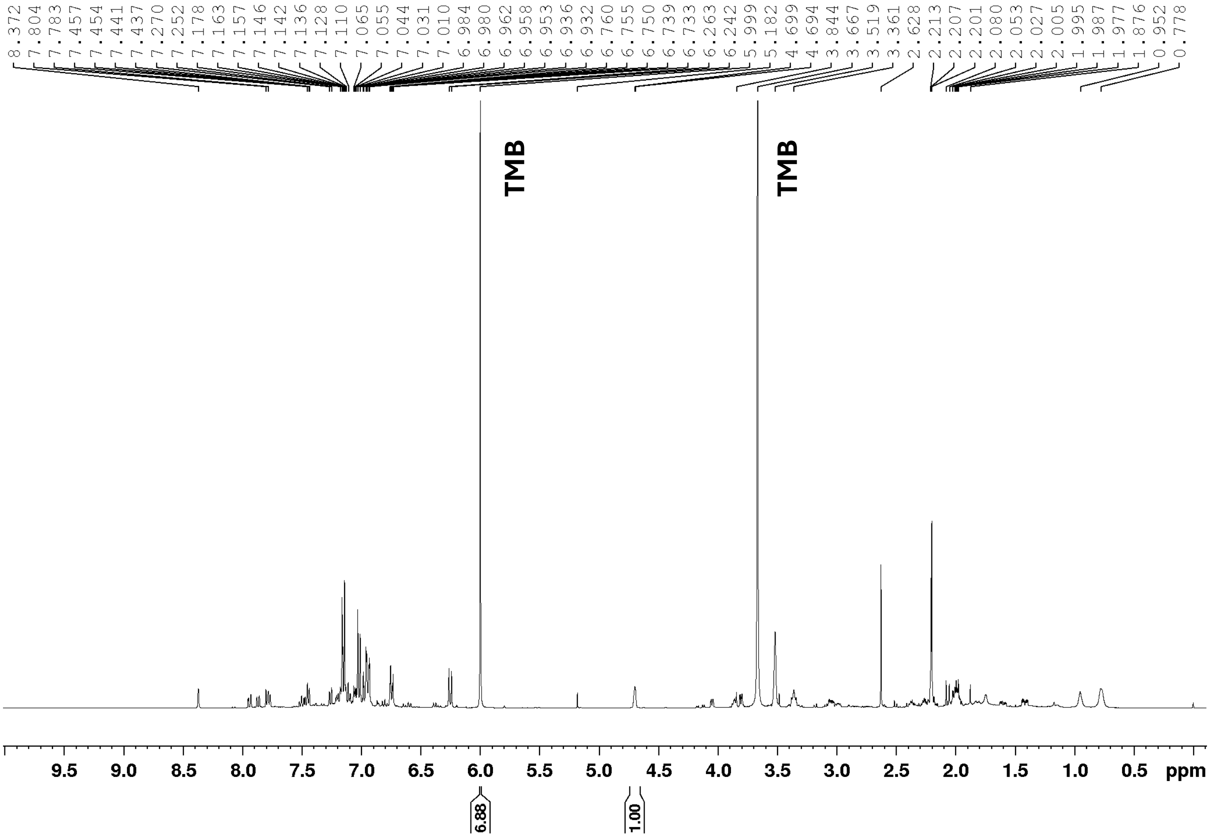
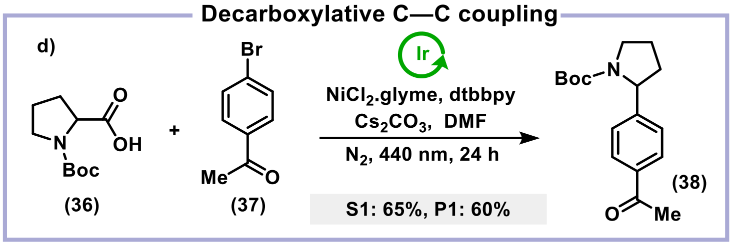


Figure S44. ^{1}H NMR spectrum of (35)

d) Decarboxylative C —C coupling: The reaction was performed according to the reported procedure with some modifications.[13]



In a vial with septum, was added photocatalyst (1.0 µmol, 0.01 equiv, 13 mg of IrCat1 or 1-2 mg of $[Ir(dF(CF_3)ppy)_2(dmbpy)](PF_6)$), $NiCl_2$.glyme (2.2 mg, 0.01 mmol, 0.1 equiv), 4,4′-di-tert-butyl-2,2′-bipyridyl (4 mg, 0.015 mmol, 0.15 equiv), 4-bromoacetophenone (24.8 mg, 0.1 mmol, 1.0 equiv), Boc-Pro-OH (32.3 mg, 0.15 mmol, 1.5 equiv), Cs_2CO_3 (48.87 mg, 0.15 mmol, 1.5 equiv), and 5 mL of DMF were used. The reaction mixture was purged with nitrogen for 20 minutes, after which it was stirred and exposed to 440 nm light from an LED for 24 hours. 1,3,5-trimethoxybenzene was added as the internal standard to determine the yield. (IrCat1: 60%; $[Ir(dF(CF_3)ppy)_2(dmbpy)](PF_6)$: 65%)

^{1}H NMR (400 MHz, $CDCl_3$) rotameric mixture: δ 7.92 (d, *J* = 8.1 Hz, 2H), 7.27 (d, *J* = 9.1 Hz, 2H), 4.98 and 4.82 (2 brs, 1H, rotamer), 3.66-3.62 (m, 2H), 2.62-2.56 (m, 3H), 2.46-2.27 (m, 1H), 1.90-1.79 (m, 3H), 1.48 (s, 3H), 1.19 (s, 6H).

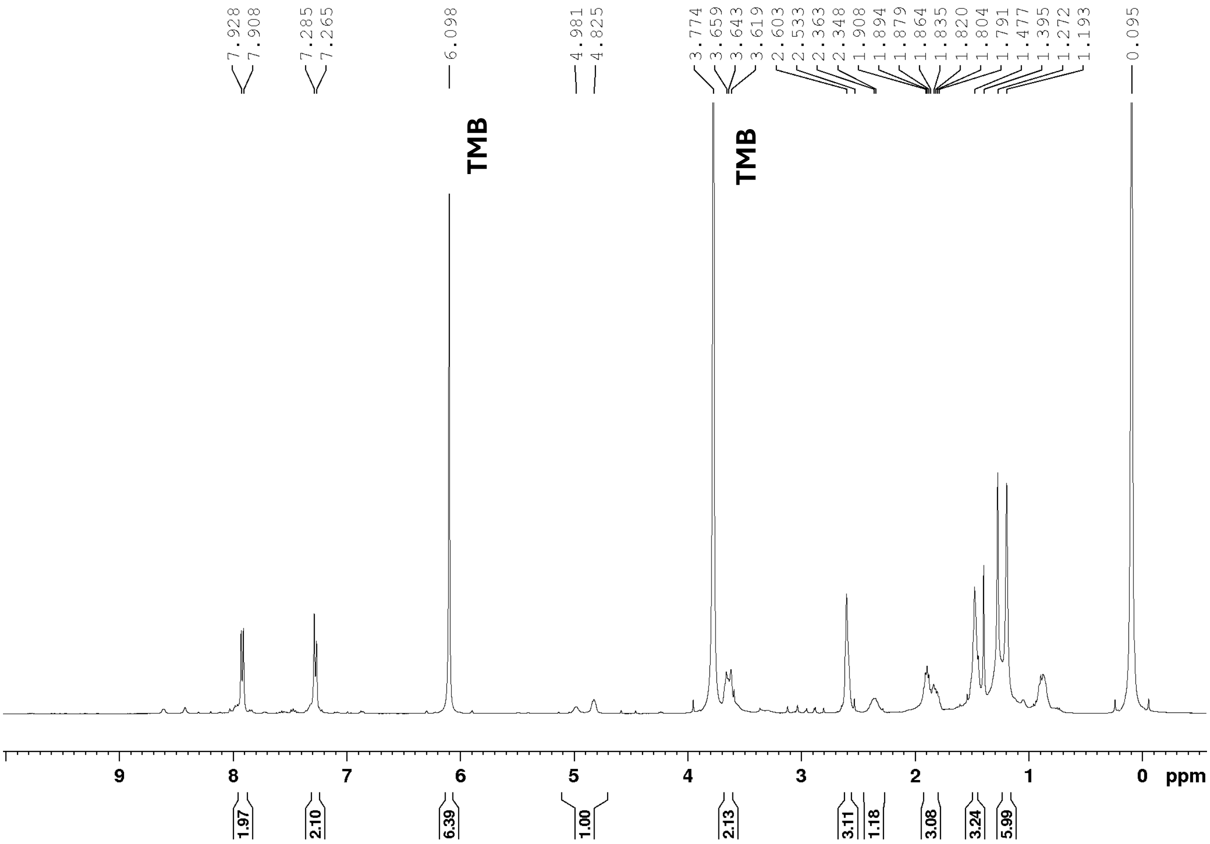
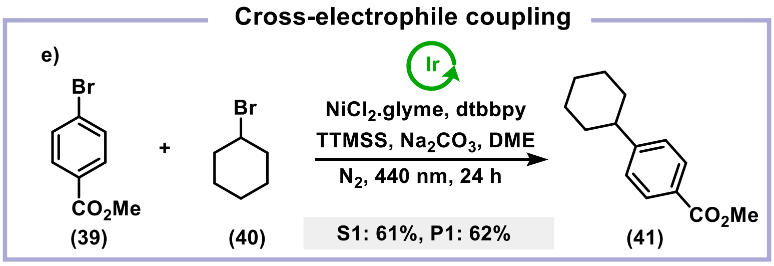


Figure S45. ^{1}H NMR spectrum of (38)

e) Cross-electrophile coupling: The reaction was performed according to the reported procedure with some modifications.[14a]



In a 5 mL vial equipped with a stir bar was added photocatalyst (1 mol%, 0.01 equiv, 13 mg of IrCat1 or 1-2 mg of $[Ir(dF(CF_3)ppy)_2(dmbpy)]PF_6$), methyl-4-bromobenzoate (21.6 mg, 0.1 mmol, 1 equiv.), bromocyclohexane (18.5 µL, 0.15 mmol, 1.5 equiv.), tris(trimethylsilyl)silane (31 µL, 0.1 mmol, 1.0 equiv.), and anhydrous sodium carbonate (21.2 mg, 0.2 mmol, 2 equiv.). The vial was capped and placed under nitrogen for 20 mins before 0.8 mL of DME was added. To a separate vial was added $NiCl_2$•glyme (1 mg, 5 µmol, 0.01 equiv.) and 4,4'-di-tert-butyl-2,2'-bipyridine (1.3 mg, 5 µmol, 0.01 equiv). The catalyst vial was sealed, purged with nitrogen then to it was added 2 mL of DME. The precatalyst solution was sonicated or stirred for 5 minutes, after which, 0.2 mL (0.1 mol% catalyst, 0.5 µmol, 0.005

equiv.) was syringed into the reaction vessel. The solution was degassed by sparging with nitrogen while stirring for 20 minutes. The reaction was stirred and irradiated with 440 nm LED lights for 24 hours, after which the solvent was evaporated under air stream. The yield was determined by using crude mixture and 1,3,5-trimethoxybenzene as the internal standard. (IrCat1: 62%; [Ir(dF(CF$_3$)ppy)$_2$(dmbpy)]PF$_6$: 61%).

^{1}H NMR (400 MHz, CDCl$_3$)[14b]: δ 7.77 (d, *J* = 8.12 Hz, 2H), 7.07 (d, *J* = 7.93 Hz, 2H), 3.70 (s, 3H), 2.37 (m, 1H), 1.63 – 1.71 (m, 5H), 1.29 – 1.16 (m, 5H)

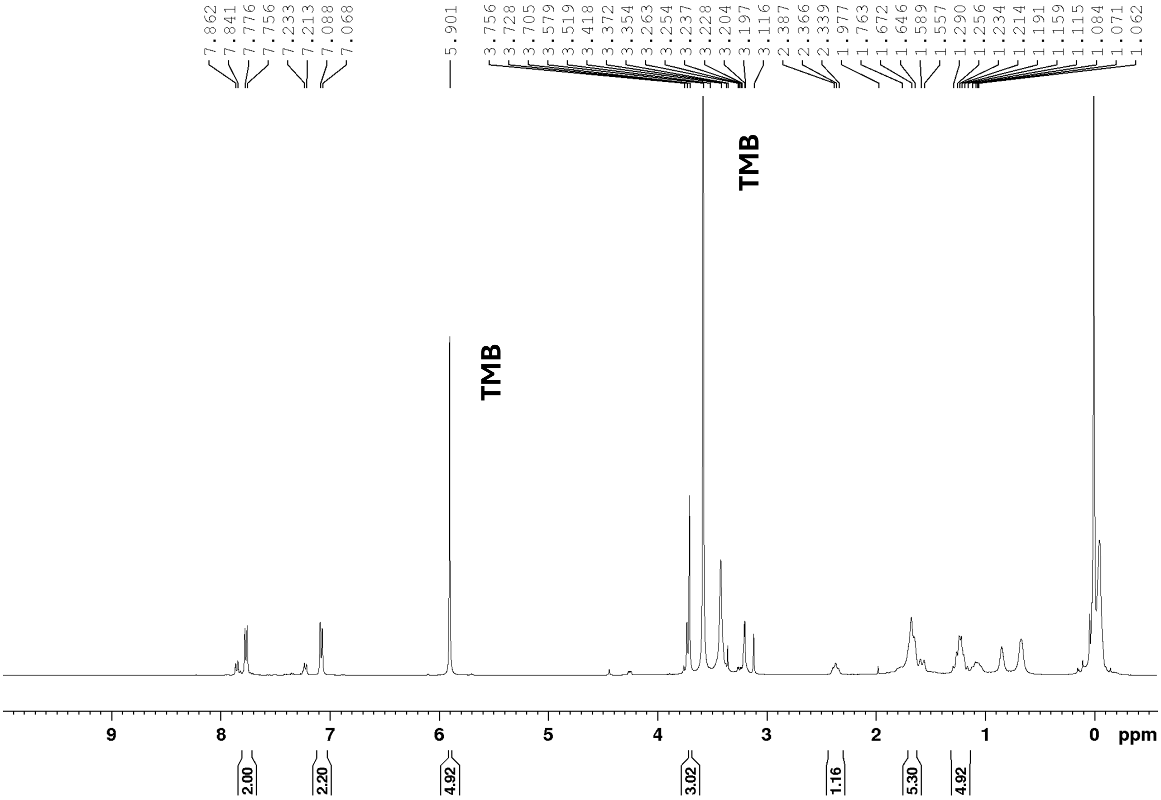
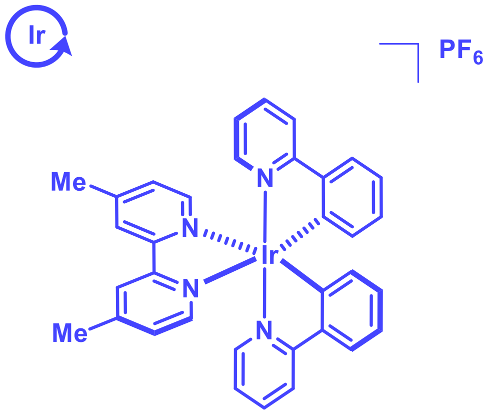
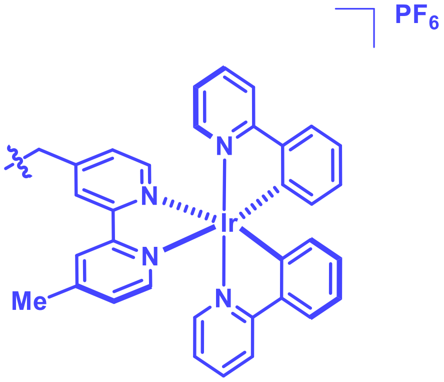


Figure S46. ^{1}H NMR spectrum of (41)

IrCat2 (22)

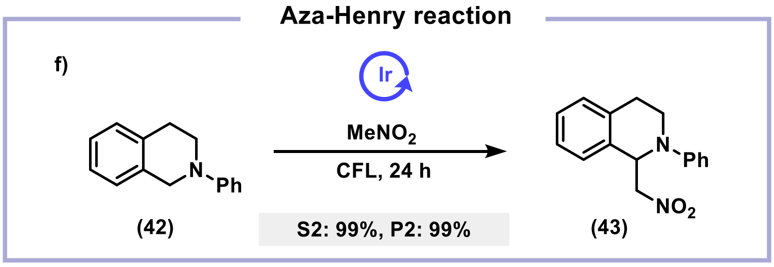


$[Ir(ppy)_2(dmbpy)]PF_6$
(S2)



IrCat2
(P2)

f) Aza-Henry: The reaction was performed according to the reported procedure with some modifications.[15]



In a 5 mL vial equipped with a stir bar, photocatalyst (0.01 equiv., 20 mg of IrCat2 or 1-2 mg of $[Ir(ppy)_2(dmbpy)](PF_6)$) 2-phenyl-1,2,3,4-tetrahydroisoquinoline (26.15 mg, 0.125 mmol, 1.0 equiv.), and nitromethane (1.0 mL) as the solvent were added. The reaction mixture was stirred under CFL lights for 24 hours. Afterward, the solvent was removed under reduced pressure. The residue was dissolved in a small amount of DCM, and a large volume of diethyl ether was added to the solution. The resulting suspension was filtered through a small silica plug and eluted with diethyl ether. The solvent was then evaporated from the crude mixture, and the yield was determined using 1,3,5-trimethoxybenzene as the internal standard. (IrCat2: 99%; $[Ir(ppy)_2(dmbpy)](PF_6)$: 99%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33-7.16 (m, 6H), 7.02 (d, J = 8.23 Hz, 2 H), 6.89 (t, J = 7.29 Hz, 1 H), 5.59 (t, J = 7.3 Hz, 1 H), 4.89 (dd, J = 11.8, 7.8 Hz, 1 H), 4.59 (dd, J = 11.8, 6.57 Hz, 1 H), 3.73-3.61(m, 2 H), 3.15-3.08 (m, 1 H), 2.81 (dt, J = 16.4, 5.0 Hz, 1H)

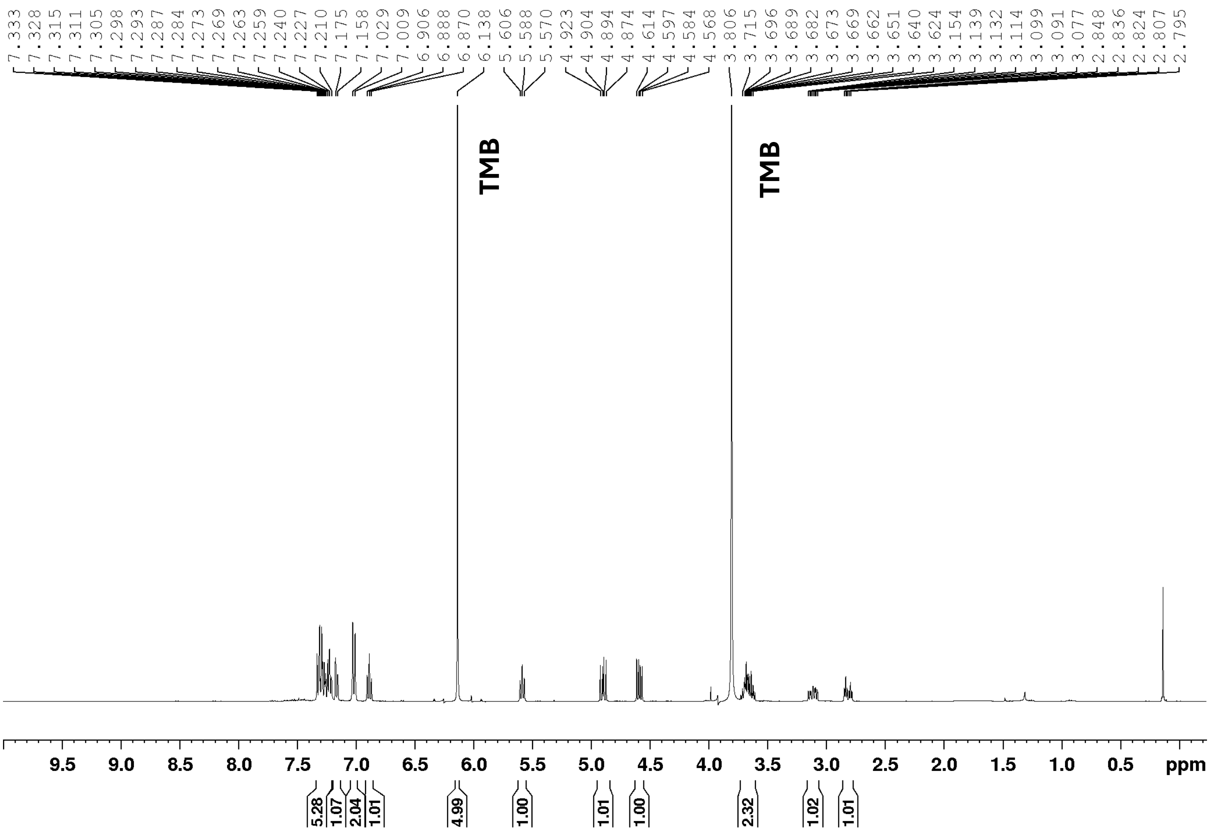
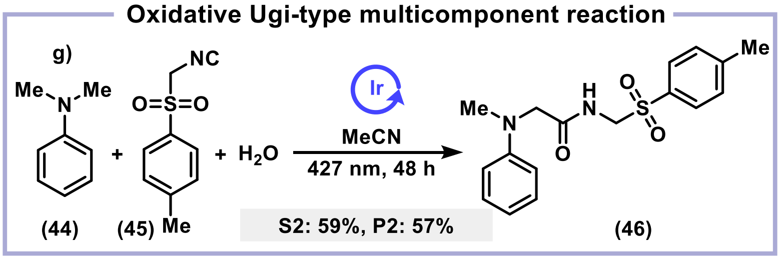


Figure S47. ^{1}H NMR spectrum of (43)

g) Oxidative Ugi-type multicomponent reaction: The reaction was performed according to the reported procedure with some modifications.[16]



In a vial with stir bar, the photoredox catalyst (0.01 equiv., 20 mg of IrCat2 or 1 mg of $[Ir(ppy)_2(dmbpy)](PF_6)$), isocyanide (45), *N*, *N*-dimethylaniline (13 uL, 0.1 mmol, 1 equiv.), H_2O (18 µL, 1 mmol, 10 equiv.) were dissolved in 1 mL of acetonitrile. The reaction mixture was stirred for 48 hours while being irradiated with 427 nm LED lights. Upon completion, the solvent was removed under reduced pressure, and the crude product was analyzed. The yield was determined using 1,3,5-trimethoxybenzene as the internal standard. (IrCat2: 57%; $[Ir(ppy)_2(dmbpy)](PF_6)$: 59%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67 (d, *J* = 8.14 Hz, 2H), 7.19-7.11 (m, 5H), 6.76 (t, *J* = 7.3, 1H), 6.55 (dd, *J* = 8.8, 1.83 Hz, 2H), 4.58 (d, *J* = 6.9 Hz, 2H), 3.66 (s, 2H), 2.89 (s, 3H), 2.41 (s, 3H) ppm

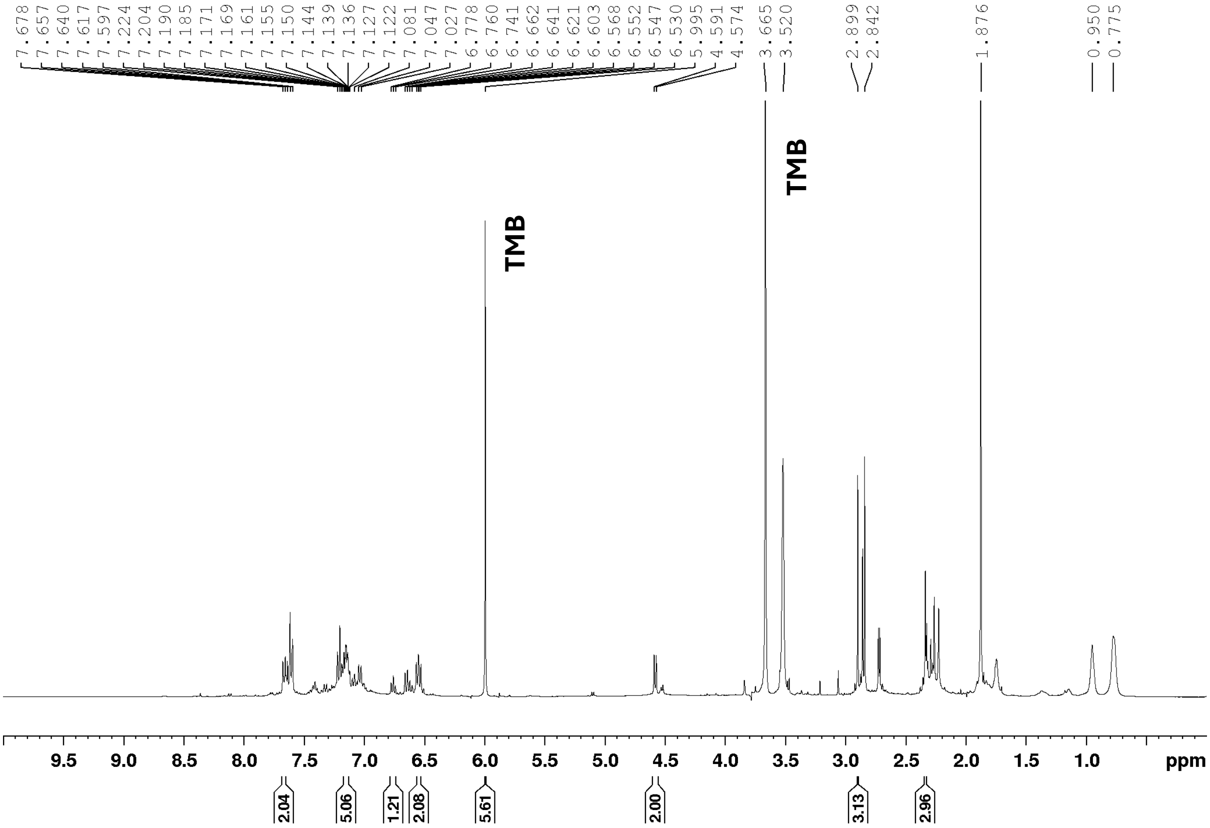
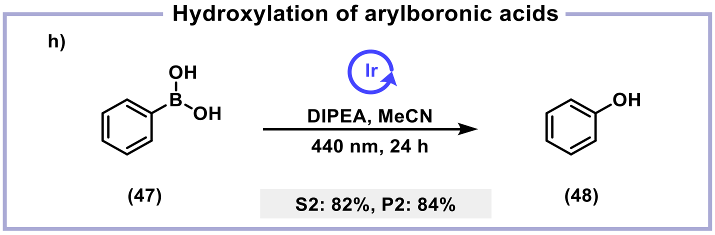


Figure S48. ^{1}H NMR spectrum of (46)

h) Hydroxylation of arylboronic acids: The reaction was performed according to the reported procedure with some modifications.[17a]



In a 20ml vial with stir bar, the photoredox catalyst (0.01 equiv., 20 mg of IrCat2 or 1 mg of [Ir(ppy)$_2$(dmbpy)](PF$_6$)), phenyl boronic acid (12.19 mg, 0.1 mmol, 1 equiv.) DIPEA (33 uL, 0.2 mmol, 2 equiv.), were dissolved in 1 mL of acetonitrile. The reaction mixture was stirred in air (using air ballon) for 24 hours while being irradiated with 440 nm LED lights. Upon completion, the solvent was removed under reduced pressure, and the crude product was analyzed. The yield was determined using 1,3,5-trimethoxybenzene as the internal standard. (IrCat2: 84%; [Ir(ppy)$_2$(dmbpy)](PF$_6$): 82%).

^{1}H NMR (400 MHz, CDCl$_3$):[17b] δ: 7.17 (t, J = 7.76 Hz, 2H), 6.85 (m, 3H), 3.26 (br s, 1H)

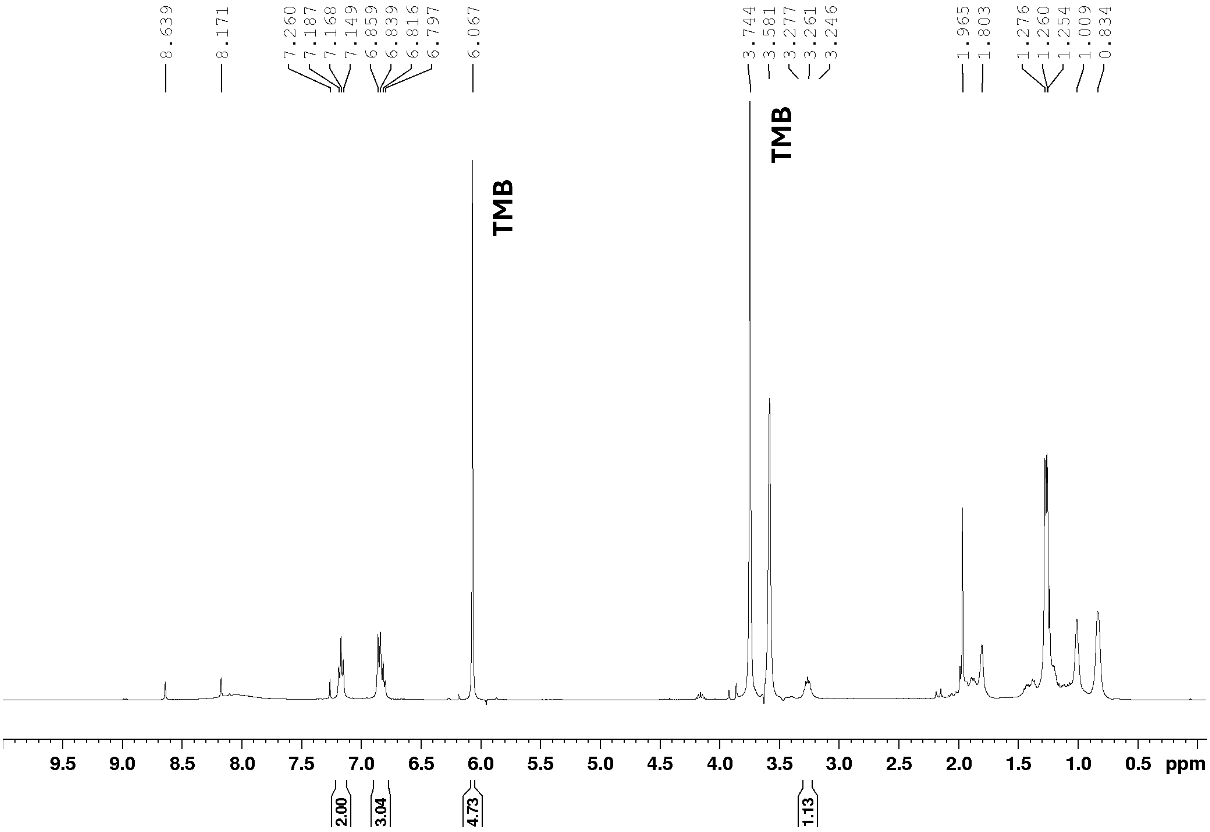
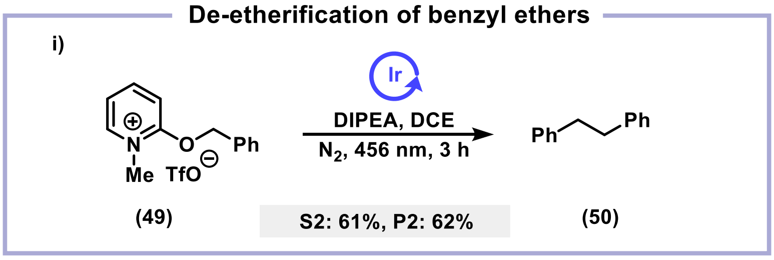


Figure S49. ^{1}H NMR spectrum of (48)

i) De-etherification of benzyl ethers: The reaction was performed according to the reported procedure with some modifications.[18]



In a 5 mL vial equipped with a stir bar, photocatalyst (0.02 equiv., 30 mg of IrCat2 or 2 mg of [Ir(ppy)$_2$(dmbpy)](PF$_6$)) was added, followed by 35 mg (0.1 mmol, 1 equiv.) of pyridinium salt (49). The mixture was degassed and then backfilled with nitrogen three times. Next, 52.25 µL (0.3 mmol, 3 equiv.) of DIPEA and 1 mL (0.1 M) of DCE were added, and the mixture was sparged with nitrogen for 20 minutes. The vial was then placed under 456 nm LEDs for 3h. After the reaction, the solvent was removed under reduced pressure. The crude product was analysed to determine the yield, using 1,3,5-trimethoxybenzene as the internal standard. (IrCat2: 62%; [Ir(ppy)$_2$(dmbpy)](PF$_6$): 61%).

^{1}H NMR (400 MHz, CDCl$_3$): δ 7.26-7.22 (m, 4H), 7.18-7.12 (m, 6H), 2.88 (s, 4H).

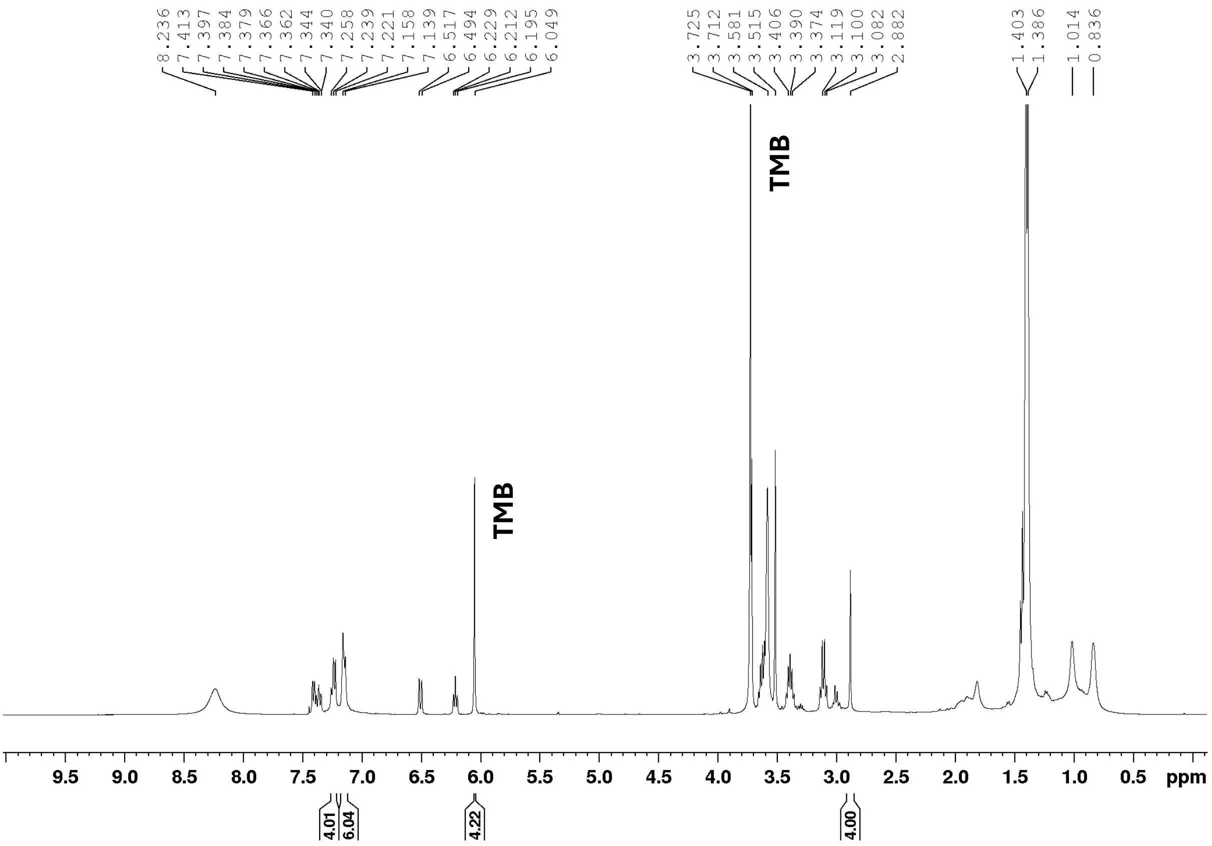
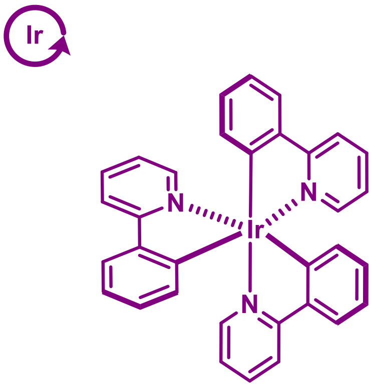
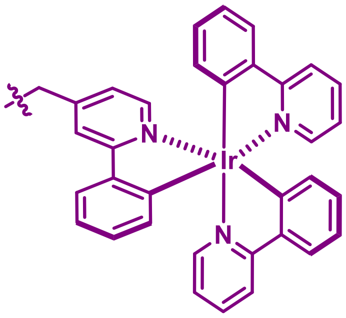


Figure S50. ^{1}H NMR spectrum of (50)

IrCat3 (23)

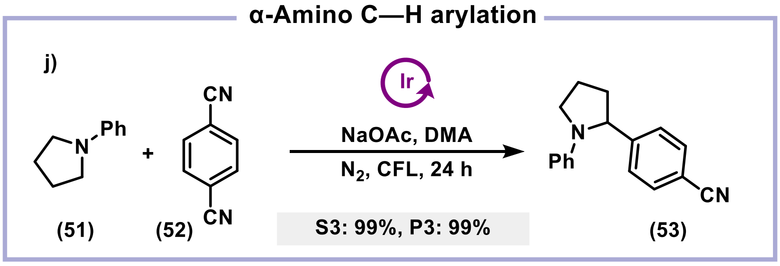


***Fac*-Ir(ppy)$_3$**
(S3)



IrCat3
(P3)

j) α-Amino C—H arylation: The reaction was performed according to the reported procedure with some modifications.[19a]



In a 5 ml vial with septum equipped with stir bar was added, the photocatalyst (0.005 equiv., 20 mg of IrCat3 or 1 mg of *fac*-Ir(ppy)$_3$), 1,4-dicyanobenzene (12.8 mg, 0.1 mmol, 1.0 equiv), sodium acetate (16.4 mg, 0.2 mmol, 2.0 equiv), *N*-phenyl pyrrolidine (43.38 ul, 0.3 mmol, 3.0 equiv) and 0.5 mL of DMA. The reaction mixture was sparged with nitrogen for 20mins and then subjected to the exposure of CFL lights for 24h. After the reaction completion, the solvent is evaporated and the yield is recorded using 1,3,5-trimethoxybenzene as the internal standard. (IrCat3: 99%; *fac*-Ir(ppy)$_3$: 99%).

^{1}H NMR (400 MHz, CDCl$_3$)[19b]: δ 7.45 (d, *J* = 8.02 Hz, 2H), 7.21 (d, *J* = 8.34 Hz, 2H), 7.04 (t, *J* = 7.75 Hz, 2H), 6.71 (t, *J* = 7.5 Hz, 1H), 6.45 (d, *J* = 7.7 Hz, 2H), 4.62 (dd, *J* = 8.6, 2.6 Hz , 1H), 3.75 (td, J = 8.7, 2.6 Hz, 1H), 3.33-3.29 (m, 1H), 2.26-2.33 (m, 2H), 2.19-2.02 (m, 2H)

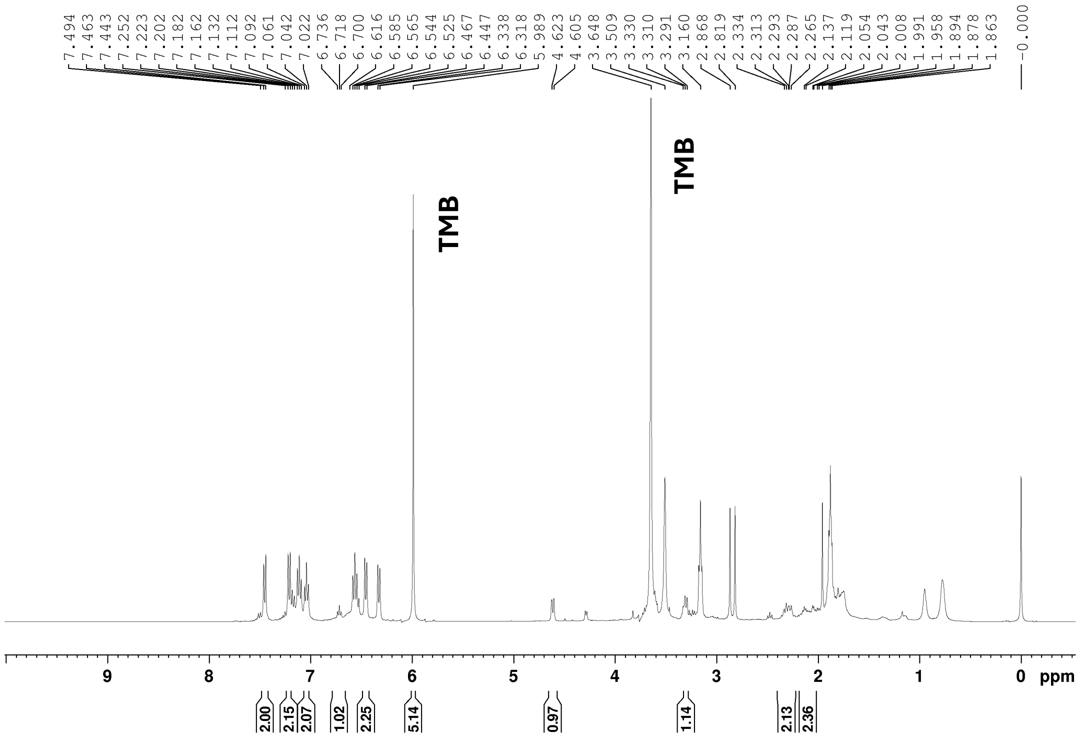
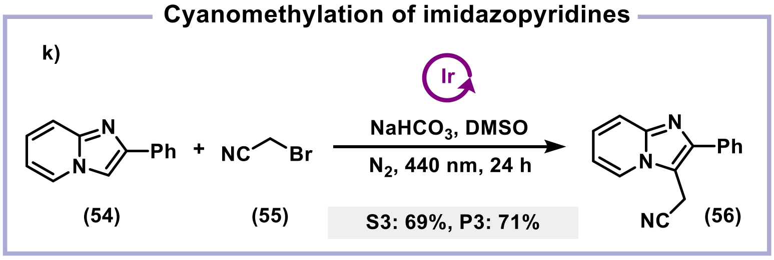


Figure S51. ^{1}H NMR spectrum of (53)

k) Cyanomethylation of imidazopyridines: The reaction was performed according to the reported procedure with some modifications.[20]



In a vial equipped with stir bar was charged with 2-phenylimidazo[1,2-*a*]pyridine (19.4 mg, 0.1 mmol, 1 equiv.), bromoacetonitrile (27.86 uL, 0.4 mmol, 4 equiv.), photocatalyst (0.002 equiv., 30 mg of IrCat3 or 1.3 mg of *fac*-Ir(ppy)$_3$), and NaHCO$_3$ (16.8 mg, 0.2 mmol, 2 equiv.). The flask was evacuated and backfilled with nitrogen 3 times, and then DMSO (1 mL) was added. The mixture was stirred under 440 nm lights irradiation for 24 h. When the reaction was completed, the mixture was diluted with water (10 mL) and extracted with DCM (15 mL × 3). The combined organic phases were washed with brine (15 mL), dried over anhydrous Na$_2$SO$_4$, filtered, and concentrated in *vacuo*. The product yield was determined by adding 1,3,5-trimethoxybenzene as the internal standard to the crude reaction mixture. (IrCat3: 68%; *fac*-Ir(ppy)$_3$: 71%).

^{1}H NMR (400 MHz, CDCl$_3$): δ (ppm) 8.19 (d, J = 5.94 Hz, 1H), 7.86 (d, J = 8.76 Hz, 1H), 7.68 (d, J = 7.09 Hz, 2H), 7.51–7.42 (m, 4H), 7.10 (t, J = 6.6 Hz, 1H), 4.22 (s, 2H)

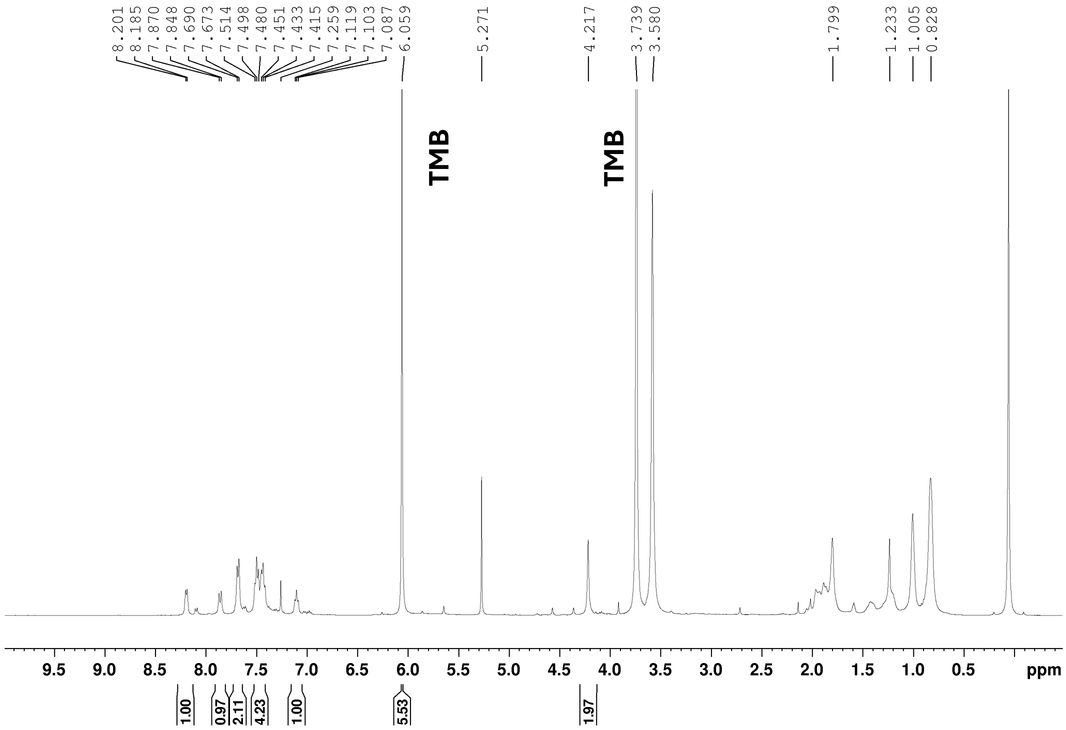
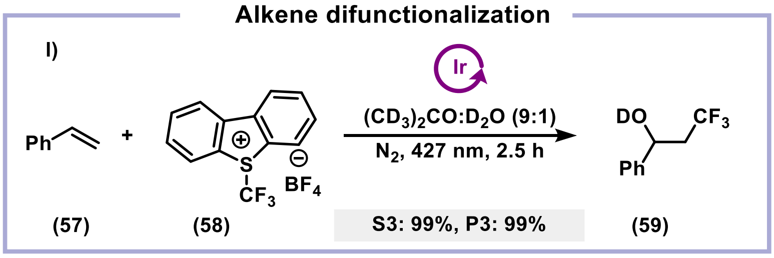


Figure S52. ^{1}H NMR spectrum of (56)

l) Alkene difunctionalization: The reaction was performed according to the reported procedure with some modifications.[21]



Under the nitrogen atmosphere, the photocatalyst (0.0025 equiv., 5 mg of IrCat3 or 0.3 mg of *fac*-Ir(ppy)_3), 5-(trifluoromethyl)dibenzothiophenium tetrafluoroborate (Umemoto's reagent) (13 mg, 0.026 mmol, 1.05 equiv.), styrene (2.86 uL, 0.0025 mmol, 1 equiv.), acetone-d6 (0.45 mL) and D_2O (50 µL) were added to the NMR tube. The reaction was carried out at room temperature under irradiation of 427 nm LED lights for 2.5 h to obtain the product. The product yield was determined by adding 1,3,5-trimethoxybenzene as the internal standard to the crude reaction mixture. (IrCat3: 99%; *fac*-Ir(ppy)_3: 99%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43-7.24 (m, 5 H), 5.00 (dd, *J* = 8.6, 4.2 Hz, 1 H), 2.72-2.45 (m, 2 H)

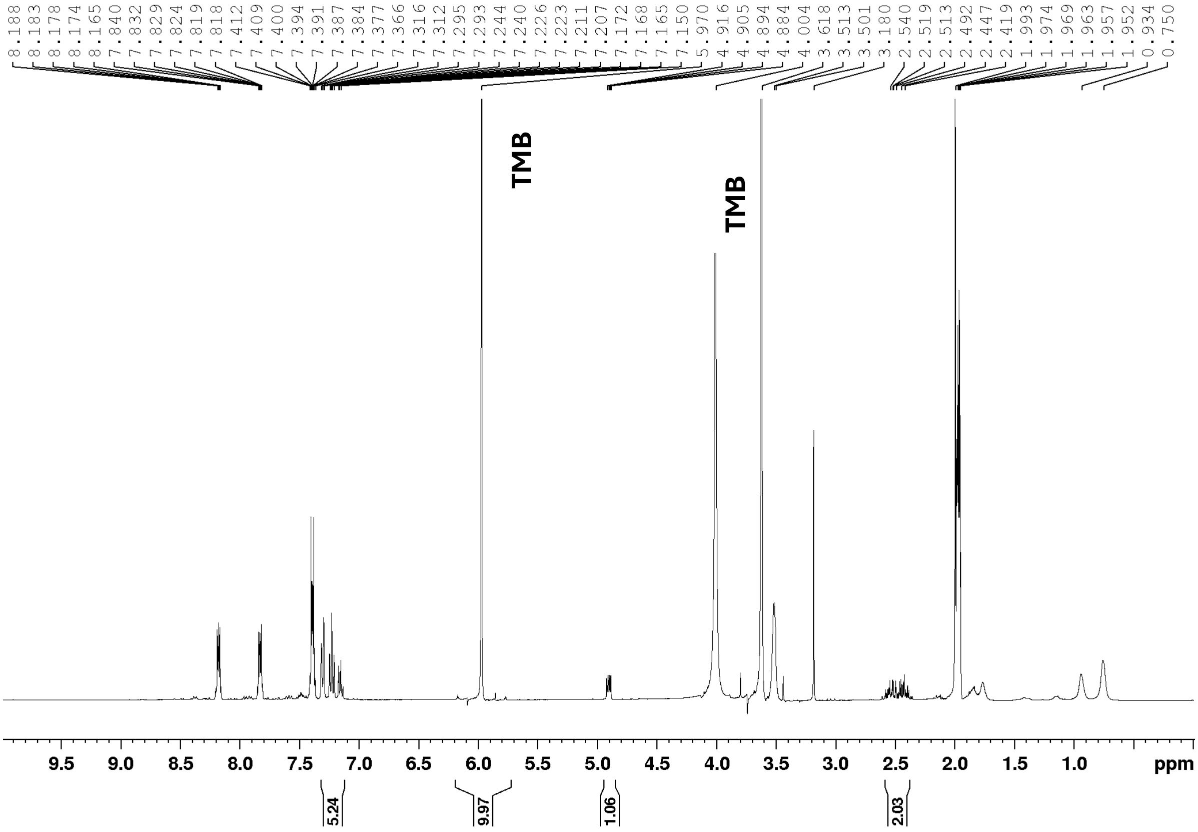
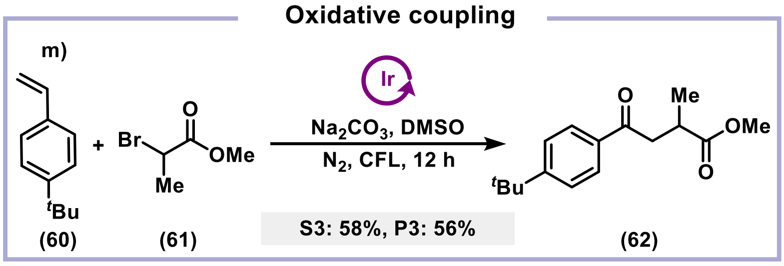


Figure S53. ^{1}H NMR spectrum of (59)

m) Oxidative coupling: The reaction was performed according to the reported procedure with some modifications.[22]



In a vial equipped with a stir bar, the photocatalyst (0.01 equiv., 20 mg of IrCat3 or 1 mg of *fac*-Ir(ppy)$_3$) and Na$_2$CO$_3$ (21.2 mg, 0.2 mmol, 2.00 equiv.) were added and purged by evacuating and backfilling with nitrogen three times. Next, DMSO (0.5 mL), 1-(tert-butyl)-4-vinylbenzene (18.3 µL, 0.1 mmol, 1.00 equiv.), and bromocarboxylate (22.26 µL, 0.2 mmol, 2.00 equiv.) were introduced. The reaction mixture was sparged with nitrogen for 20 minutes, then irradiated with CFL lights for 24 hours. After the reaction was complete, the mixture was transferred to 10 mL of water and extracted with ethyl acetate (10 mL) three times. The combined organic layers were dried with Na$_2$SO$_4$ and concentrated to yield a crude residue. 1,3,5-trimethoxybenzene was added to the crude product to calculate the yield (IrCat3: 56%; *fac*-Ir(ppy)$_3$: 58%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, J = 7.64 Hz, 2H), 7.51 (d, J = 7.5 Hz, 2H), 3.61 (s, 3H), 3.11-3.05 (m, 1H), 3.35-2.84 (m, 2H), 1.25-1.22 (m, 12H)

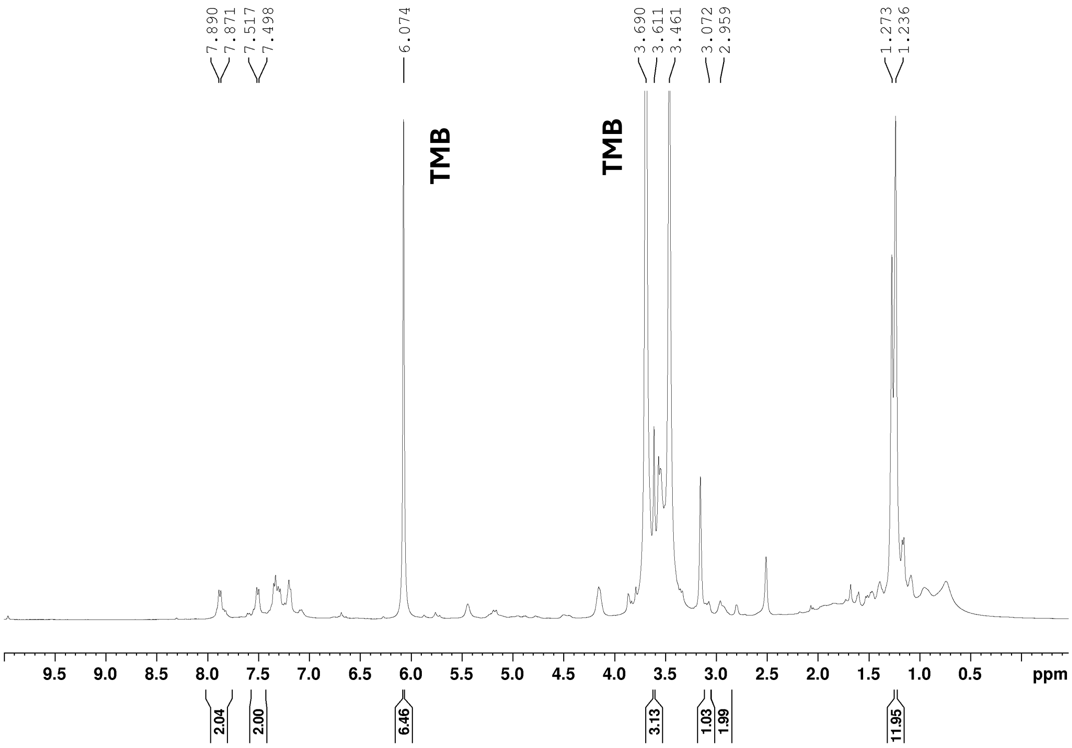
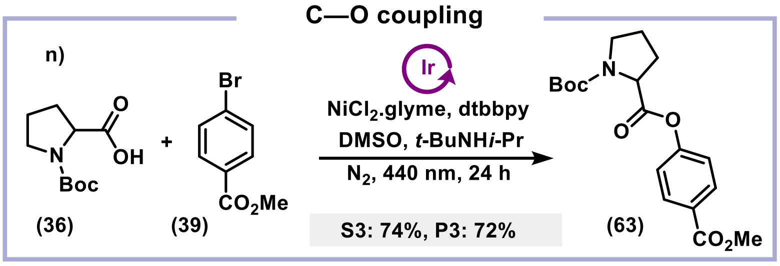


Figure S54. ^{1}H NMR spectrum of (62)

n) C —O coupling: The reaction was performed according to the reported procedure with some modifications.[23a, b]



In a vial equipped with a stir bar, nickel(II) chloride•diglyme (1.76 mg, 0.008 mmol, 0.08 equiv.), 4,4′-di-tert-butyl-2,2′-dipyridyl (1.3 mg, 0.005 mmol, 0.05 equiv.) were added, followed by the photocatalyst (0.0015 equiv., 26 mg of IrCat3 or 1 mg of *fac*-$Ir(ppy)_3$), bromoarene (21.5 mg, 0.1 mmol, 1.0 equiv.), Boc-Pro-OH (43mg, 0.2 mmol, 2.0 equiv.), and DMSO (0.5 mL) as the solvent. The reaction mixture was sonicated for 2 minutes until no solids remained. Next, *N*-tert-butyl-isopropylamine (32 µL, 0.2 mmol, 2 equiv.) was added, and the mixture was sparged with nitrogen for 20 minutes. The reaction was then irradiated with 440 nm light for 24 hours. Upon completion, the solution was poured into an aqueous lithium chloride solution (20% saturated aqueous LiCl, 80% water) and extracted with three portions of ethyl acetate (10 mL each). The combined organic phases were washed with a 50% saturated aqueous LiCl solution, dried over Na_2SO_4, and concentrated. The product yield was determined by adding 1,3,5-trimethoxybenzene as the internal standard to the crude reaction mixture. (IrCat3: 72%; *fac*-Ir(ppy)$_3$: 74%).

^{1}H NMR (400 MHz, DMSO-d_6)[23c] rotameric mixture δ 8.00-7.96 (m, 2H), 7.27–7.15 (m, 2H), 4.38 (m, 1H), 3.79 (s, 3H), 3.45–3.42 (m, 2H), 2.40–2.07 (m, 4H), 1.26–1.24 (m, 9H)

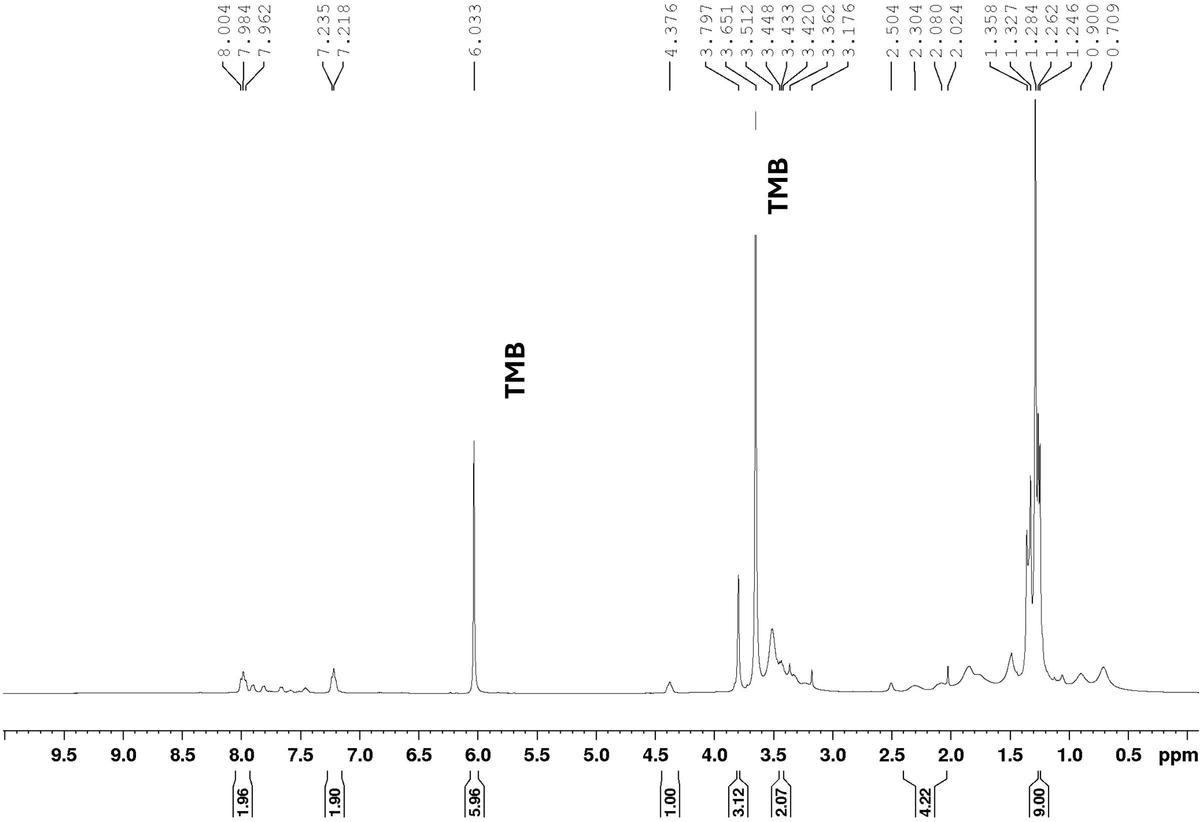
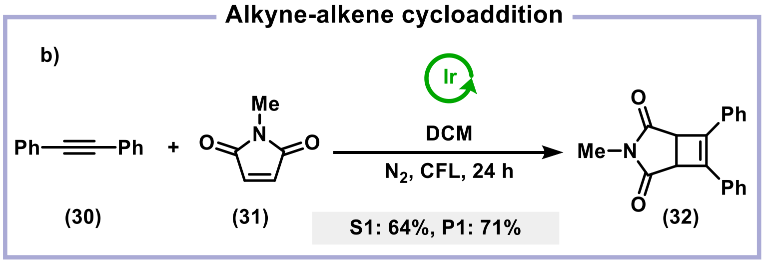


Figure S55. ^{1}H NMR spectrum of (63)

8) Recyclability Studies:

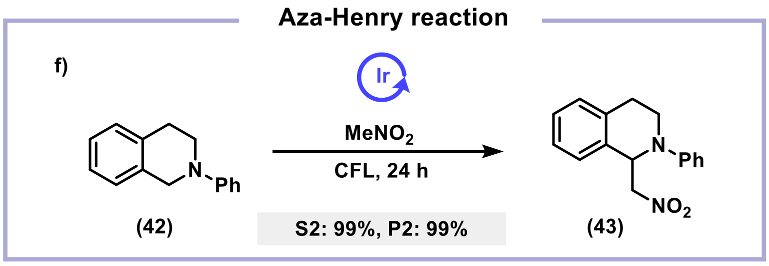
The recyclability of all three polymer-based iridium catalysts was studied using selected reactions for each catalyst, following the standard procedure outlined above. After the reaction is complete, the solvent is evaporated to isolate the desired product, which is then analyzed using ^{1}H-NMR spectroscopy. Yields are calculated using an internal standard. The $CDCl_3$ solvent from the samples is evaporated, and a few drops of dichloromethane (DCM) are added to dissolve the reaction mixture. The polymer catalyst is then precipitated by adding cold methanol, and the suspension is centrifuged to recover the catalyst as a film. This film is dried under air to remove any remaining solvent and is then reused for subsequent reactions. This process ensures the recovery and reuse of the polymer-based iridium catalysts for multiple cycles. In all cases, the recovered catalyst was weighed out after drying, and the starting material amount was adjusted as needed to account for mass loss.

A) **<u>IrCat1 (21):</u>** The recyclability of IrCat1 was investigated through alkyne-alkene cycloaddition using the standard procedure mentioned above. After calculating the yield, the polymer catalyst was reprecipitated, weighed, and adjusted for the next reaction cycle to keep the ratio of catalyst and reaction starting materials constant. This process was repeated for five cycles, and the following yields were recorded: 71% in the first cycle, 72% in the second cycle, 72% in the third cycle, 71% in the fourth cycle, and 70% in the fifth cycle.



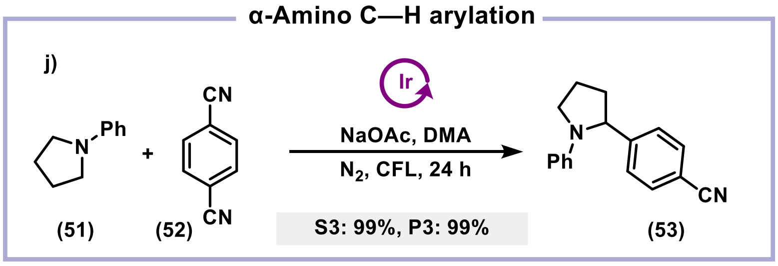
Cycle Number	Changes in mmol (30)	Yield (%)
1	0.2	71%
2	0.19	72%
3	0.18	72%
4	0.16	71%
5	0.14	70%

B) **<u>IrCat2 (22):</u>** The recyclability of IrCat2 was investigated through Aza-Henry reaction using the standard procedure mentioned above. After calculating the yield, the polymer catalyst was reprecipitated, weighed, and adjusted for the next reaction cycle to keep the ratio of catalyst and reaction starting materials constant. This process was repeated for five cycles, and the following yields were recorded: 99% in the first cycle, 99% in the second cycle, 99% in the third cycle, 99% in the fourth cycle, and 99% in the fifth cycle.



Cycle Number	Changes in mmol (42)	Yield (%)
1	0.2	99%
2	0.19	99%
3	0.17	99%
4	0.15	99%
5	0.14	99%

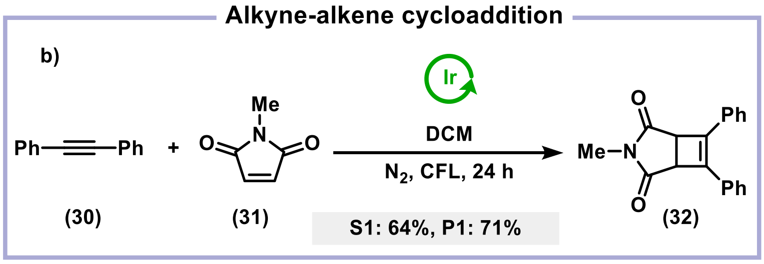
C) **IrCat3 (23):** The recyclability of IrCat3 was investigated through the α-amino C—H arylation reaction using the standard procedure mentioned above. After calculating the yield, the polymer catalyst was reprecipitated, weighed, and adjusted for the next reaction cycle to keep the ratio of catalyst and reaction starting materials constant. This process was repeated for five cycles, and the following yields were recorded: 99% in the first cycle, 99% in the second cycle, 98% in the third cycle, 99% in the fourth cycle, and 99% in the fifth cycle.



Cycle Number	Changes in mmol (52)	Yield (%)
1	0.2	99%
2	0.19	99%
3	0.18	98%
4	0.16	99%
5	0.14	99%

9) In Situ Catalyst Monitoring:

<u>IrCat1 (21):</u> IrCat1was monitored in the alkyne-alkene cycloaddition using the standard procedure mentioned above. At specific time intervals, aliquots were taken from the reaction mixture to measure emission intensity.



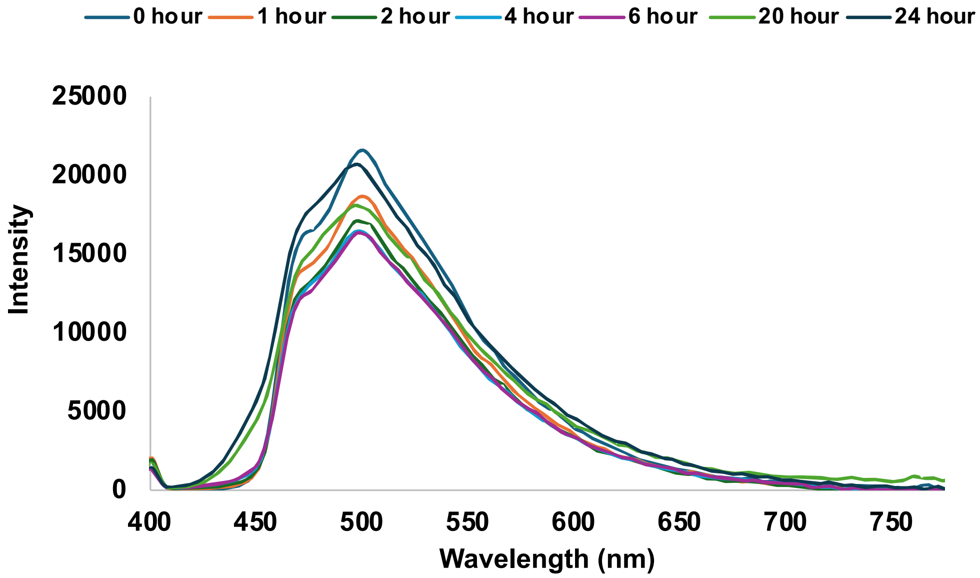
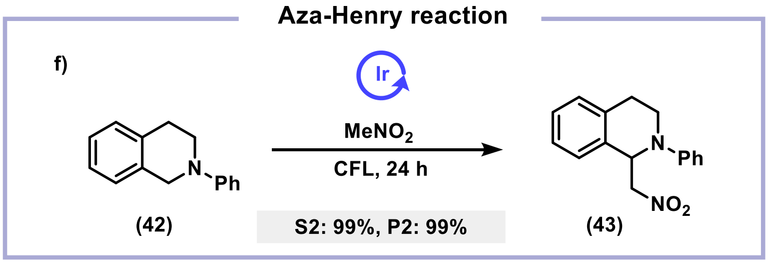


Figure S56. Fluorescence spectra of the reaction mixture recorded during the reaction with the excitation set at 400 nm.

<u>IrCat2 (22):</u> IrCat2 was monitored in the Aza-Henry reaction using the standard procedure mentioned above. At specific time intervals, aliquots were taken from the reaction mixture to measure emission intensity.



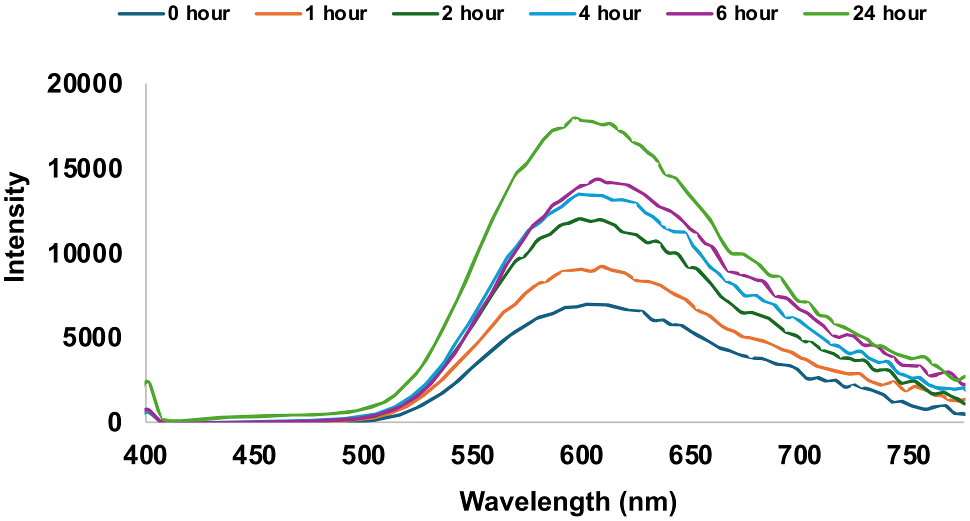
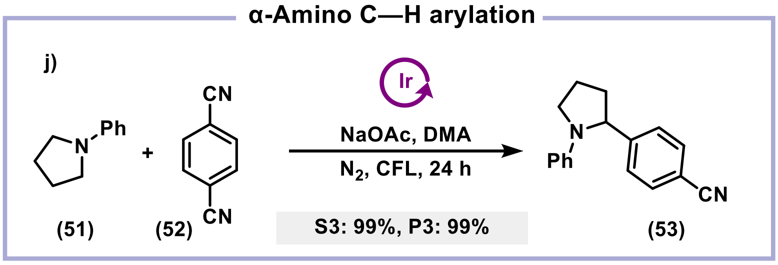


Figure S57. Fluorescence spectra of the reaction mixture with IrCat2 recorded during the reaction with the excitation set at 400 nm. The spectrum taken after 24 hours is recorded in DCM after recycling and removing the molecular components.

<u>IrCat3 (23):</u> IrCat3 was monitored in the α-amino C—H arylation using the standard procedure mentioned above. At specific time intervals, aliquots were taken from the reaction mixture to measure emission intensity.



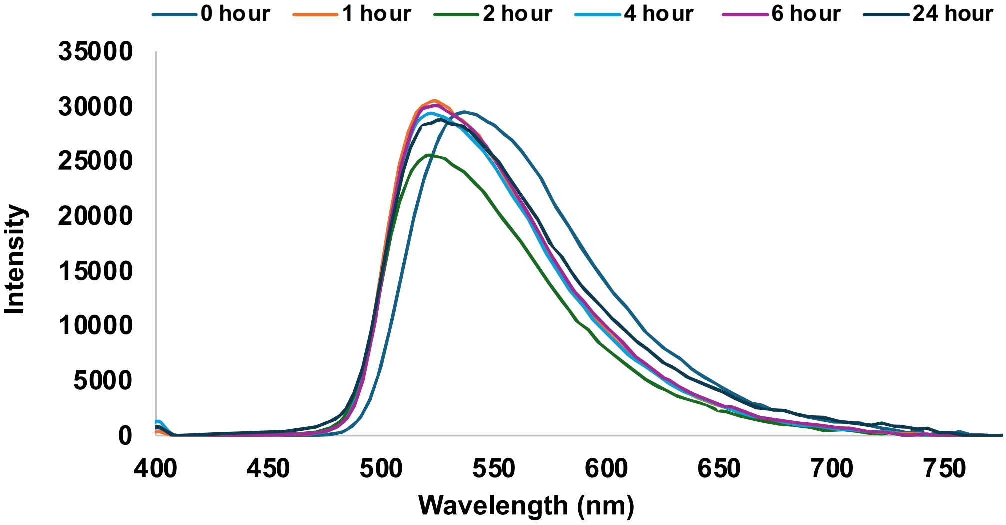


Figure S58. Fluorescence spectra of the reaction mixture with IrCat3 recorded during the reaction with the excitation set at 400 nm.

10) References:

1) Boyaala, R.; Peng, M.; Tai, W.-S.; Touzani, R.; Roisnel, T.; Dorcet, V.; Chi, Y.; Guerchais, V.; Doucet, H.; Soulé, J.-F. Exploiting the Reactivity of Fluorinated 2-Arylpyridines in Pd-Catalyzed C–H Bond Arylation for the Preparation of Bright Emitting Iridium(III) Complexes. *Inorg. Chem.* **2020**, *59* (19), 13898–13911.

2) Lepeltier, M.; Lee, T. K.; Lo, K. K.; Toupet, L.; Bozec, H. L.; Guerchais, V. Synthesis, Structure, and Photophysical and Electrochemical Properties of Cyclometallated Iridium(III) Complexes with Phenylated Bipyridine Ligands. *Eur. J. Inorg Chem.* **2004**, *2005* (1), 110–117.

3) Tamayo, A. B.; Alleyne, B. D.; Djurovich, P. I.; Lamansky, S.; Tsyba, I.; Ho, N. N.; Bau, R.; Thompson, M. E. Synthesis and Characterization of Facial and Meridional Tris-Cyclometalated Iridium(III) Complexes. *J. Am. Chem. Soc.* **2003**, *125* (24), 7377–7387.

4) Huss, S.; Walsh, A. R.; Griggs, A.; Rodriguez-Acevedo, D. A.; Arias-Rotondo, D. M.; Elacqua, E. Synthesis and Characterization of a Ruthenium-Containing Copolymer for Use as a Photoredox Catalyst. *Polym. Chem.* **2023**, *14* (39), 4560–4568.

5) Oderinde, M. S.; Johannes, J. W. Practical Syntheses of [2,2′-Bipyridine] *Bis* [3,5-Difluoro-2-[5-(Trifluoromethyl)-2-Pyridinyl]Phenyl]Iridium(III) Hexafluorophosphate, [$Ir\{DF(CF_3)ppy\}_2(Bpy)]PF_6$ and [4,4′- *Bis* (Tert-Butyl)-2,2′-Bipyridine] *Bis* [3,5-Difluoro-2-[5-(Trifluoromethyl)-2-Pyridinyl]Phenyl]Iridium(III) Hexafluorophosphate, [$Ir\{DF(CF_3)Ppy\}_2(Dtbbpy)]PF_6$. *Organic Syntheses* **2018**, 77–92.

6) Sprouse, S.; King, K. A.; Spellane, P. J.; Watts, R. J. Photophysical Effects of Metal-Carbon Sigma Bonds in Ortho-Metalated Complexes of Iridium(III) and Rhodium(III). *J. Am. Chem. Soc.* **1984**, *106* (22), 6647–6653.

7) Li, X.; Chen, Z.; Zhao, Q.; Shen, L.; Li, F.; Yi, T.; Cao, Y.; Huang, C. Nonconjugated Dendritic Iridium(III) Complexes with Tunable Pyridine-Based Ligands: Synthesis, Photophysical, Electrochemical, and Electroluminescent Properties. *Inorg. Chem.* **2007**, *46* (14), 5518–5527.

8) Nacsa, E. D.; MacMillan, D. W. C. Spin-Center Shift-Enabled Direct Enantioselective α-Benzylation of Aldehydes with Alcohols. *J. Am. Chem. Soc.* **2018**, *140* (9), 3322–3330.

9) Yoshihara, T.; Matsumura, N.; Tamura, T.; Shiozaki, S.; Tobita, S. Intracellular and Intravascular Oxygen Sensing of Pancreatic Tissues Based on Phosphorescence Lifetime Imaging Microscopy Using Lipophilic and Hydrophilic Iridium(III) Complexes. *ACS Sensors* **2022**, *7* (2), 545–554.

10) Chatterjee, A.; König, B. Birch-Type Photoreduction of Arenes and Heteroarenes by Sensitized Electron Transfer. *Angew. Chem. Int. Ed.* **2019**, *131* (40), 14427–14432.

11) Ha, S.; Lee, Y.; Kwak, Y.; Mishra, A.; Yu, E.; Ryou, B.; Park, C.-M. Alkyne–Alkene [2 + 2] Cycloaddition Based on Visible Light Photocatalysis. *Nat. Commun.* **2020**, *11* (1), 2509.

12) Rai, P.; Maji, K.; Jana, S. K.; Maji, B. Intermolecular Dearomative [4+2] Cycloaddition of Naphthalenes via Visible-Light Energy-Transfer-Catalysis. *Chem. Sci.* **2022**. *13*(42), 12503-12510.

13) Zuo, Z.; Ahneman, D. T.; Chu, L.; Terrett, J. A.; Doyle, A. G.; MacMillan, D. W. C. Merging Photoredox with Nickel Catalysis: Coupling of α-Carboxyl Sp^3-Carbons with Aryl Halides. *Science* **2014**, *345* (6195), 437–440.

14) a) Zhang, P.; Le, C.; MacMillan, D. W. C. Silyl Radical Activation of Alkyl Halides in Metallaphotoredox Catalysis: A Unique Pathway for Cross-Electrophile Coupling. . *J. Am. Chem. Soc.* **2016**, *138* (26), 8084–8087. b) Perry, I. B.; Brewer, T. F.; Sarver, P. J.; Schultz, D. M.; DiRocco, D. A.; MacMillan, D. W. C. Direct Arylation of Strong Aliphatic C–H Bonds. *Nature* **2018**, *560* (7716), 70–75.

15) Condie, A. G.; González-Gómez, J. C.; Stephenson, C. R. J. Visible-Light Photoredox Catalysis: Aza-Henry Reactions via C−H Functionalization. *J. Am. Chem. Soc.* **2010**, *132* (5), 1464–1465.

16) Rueping, M.; Vila, C. Visible Light Photoredox-Catalyzed Multicomponent Reactions. *Org. Lett.* **2013**, *15* (9), 2092–2095.

17) a) Xu, Z.-Y.; Luo, Y.; Zhang, D.-W.; Wang, H.; Sun, X.-W.; Li, Z.-T. Iridium Complex-Linked Porous Organic Polymers for Recyclable, Broad-Scope Photocatalysis of Organic Transformations. *Green Chem.* **2020**, *22* (1), 136–143. b) Gkizis, P. L.; Constantinou, C. T.; Kokotos, C. G. UVA-Light-Promoted Catalyst-Free Photochemical Aerobic Oxidation of Boronic Acids. *Eur. J. Org. Chem.* **2023**, *26* (44).

18) Chen, J.; Wang, F.; Li, X.; Wang, L.; Yu, W.; Sun, K.; Yang, J. Homocoupling of Benzyl Pyridyl Ethers *Via* Visible Light-Mediated Deoxygenation. *Chem. Commun.* **2023**, *59* (76), 11409–11412.

19) a) McNally, A.; Prier, C. K.; MacMillan, D. W. C. Discovery of an α-Amino C–H Arylation Reaction Using the Strategy of Accelerated Serendipity. *Science* **2011**, *334* (6059), 1114–1117. b) Gunasekera, D.; Mahajan, J. P.; Yanick Wanzi; Rodrigo, S.; Liu, W.; Tan, T.; Luo, L. Controlling One- or Two-Electron Oxidation for Selective Amine Functionalization by Alternating Current Frequency. *J. Am. Chem. Soc.* **2022**, *144* (22), 9874–9882.

20) Chang, Q.; Liu, Z.; Liu, P.; Yu, L.; Sun, P. Visible-Light-Induced Regioselective Cyanomethylation of Imidazopyridines and Its Application in Drug Synthesis. *J. Org. Chem.* **2017**, *82* (10), 5391–5397.

21) Yasu, Y.; Koike, T.; Akita, M. Three-Component Oxytrifluoromethylation of Alkenes: Highly Efficient and Regioselective Difunctionalization of C-C Bonds Mediated by Photoredox Catalysts. *Angew. Chem. Int. Ed.* **2012**, *51* (38), 9567–9571.

22) Fang, X.-X.; Wang, P.-F.; Yi, W.; Chen, W.; Lou, S.-C.; Liu, G.-Q. Visible-Light-Mediated Oxidative Coupling of Vinylarenes with Bromocarboxylates Leading to γ-Ketoesters. *J. Org. Chem.* **2019**, *84* (23), 15677–15684.

23) a) Malik, J. A.; Madani, A.; Pieber, B.; Seeberger, P. H. Evidence for Photocatalyst Involvement in Oxidative Additions of Nickel-Catalyzed Carboxylate *O*-Arylations. *J. Am. Chem. Soc.* **2020**, *142* (25), 11042–11049. b) Welin, E. R.; Le, C.; Arias-Rotondo, D. M.; McCusker, J. K.; MacMillan, D. W. C. Photosensitized, Energy Transfer-Mediated Organometallic Catalysis through Electronically Excited Nickel(II). *Science* **2017**, *355* (6323), 380–385. c) Yu, X.; He, M.; Yang, S.; Bao, M. 7,10-Dibromo-2,3-Dicyanopyrazinophenanthrene Aggregates as a Photosensitizer for Nickel-Catalyzed Aryl Esterification. *Synlett* **2021**, *33* (12), 1189–1193.