

Recycling of Brush Polymer Containing Iridium Photocatalyst supported on Glass Balls

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General conditions

All commercial compounds were purchased from chemical suppliers and were used as received unless stated otherwise. All reactions were carried out using standard Schleck technique. All air and water sensitive reactions were carried out under dry argon atmosphere. Solvents were purchased from Carlo Erba and degassed prior to their use by bubbling argon gas directly in the solvent.

Liquid NMR spectra were recorded at room temperature on 400 MHz, 500 MHz and 600 MHz Brücker spectrometers at 298 K unless stated otherwise. Proton (^1H) NMR information is given in the following format: multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; quin, quintet; sex, sextet; sept, septet; m, multiplet), coupling constant(s) (J) in Hertz (Hz), number of protons. The prefix br indicates the signal is broadened. Carbon (^{13}C) NMR spectra are reported in ppm (δ). For both ^1H and ^{13}C , ppm values are relative to residual solvents: CDCl_3 , 7.26 (^1H) and 77.2 (^{13}C); CD_2Cl_2 , 5.32 (^1H) and 53.8 (^{13}C); $\text{DMSO-}d_6$, 2.50 (^1H), 39.5 (^{13}C). Phosphorous (^{31}P) and Fluoride (^{19}F) NMR spectra are reported in the following format: multiplicity, coupling constant(s), number of atoms.

Solid-state MAS NMR spectra were recorded on a Bruker Avance III-HD 500 (11.7 T) spectrometer using 4 mm-OD zirconia rotors. ^1H and an ^1H echo ($\pi/2-\tau-\pi$) was performed for ^1H MAS NMR with a recycle delay of 5 s and a spinning speed of 14 kHz. CPMAS $\{^1\text{H}\}$ - ^{13}C was done with a contact time of 2 ms, a recycle delay of 5 s and a spinning frequency of 14 kHz. Tetra-methylsilane (TMS) was used as chemical shift reference for ^1H and ^{13}C nucleus.

HRMS (ESI-TOF) m/z analysis were performed on an Acquity UPLC H-Class Xevo G2-XS QToF (WATERS). Infrared (IR) spectra were recorded over a PerkinElmer Spectrum 100 FT-IR Spectrometer using neat conditions and wavenumbers are reported in cm^{-1} .

IC-MS analyses were performed in Agilent's 7700 Series. Before, samples were mineralized in *aqua regia* using a microwave digestion system. After dilution, iridium was dosed using a calibration curve with 7 points.

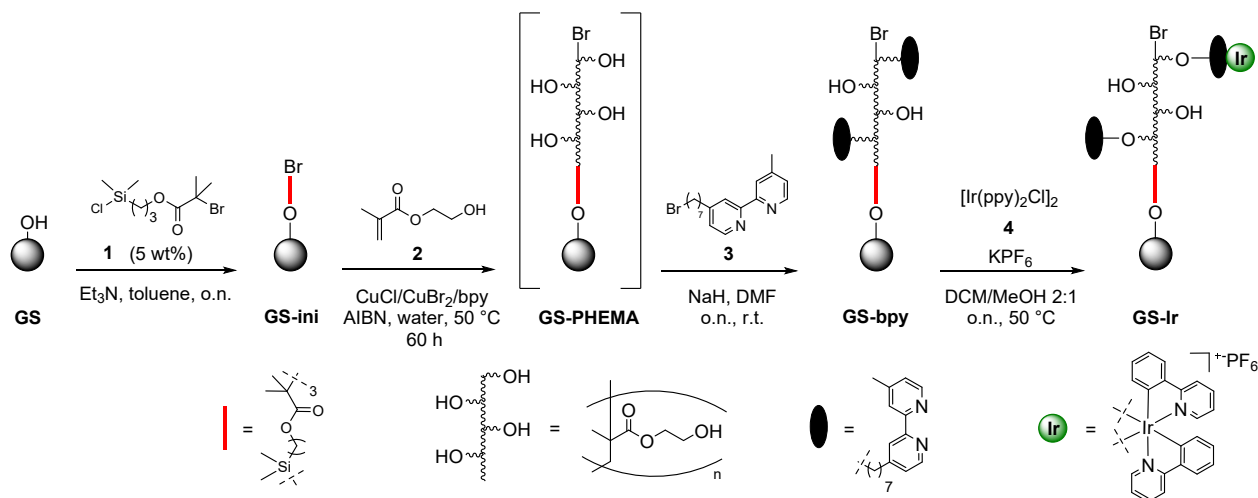
GC-FID analyses were performed on a Shimadzu GC2014 using an automated sampler AOC20i, an injection split (ratio 1/100 at 280°C), a column SPBS type (100% methylsiloxane, 15 m, 0.25 μm film thickness and 0.32 mm diameter) and a detector FID at 300°C .

UV-visible absorption spectrum in solution was measured at room temperature in dichloromethane solution (concentration = $1.0 \times 10^{-5} \text{ mol.L}^{-1}$) on a Perkin Elmer Lambda 40 UV-visible spectrometer. Emission spectra were measured at room temperature in liquid (concentration = $1.0 \times 10^{-5} \text{ mol.L}^{-1}$) or in solid state with FS5 Spectrofluorometer (Edinburgh Instruments Ltd.). Wavelengths are given in nm.

Cyclic voltammetry experiments were carried out on an Autolab PGSTAT101 potentiostat unit from Metrohm with the Nova software package. A glassy carbon working electrode, a platinum wire auxiliary electrode and an Ag/AgCl electrode (3 M KCl) were used in a standard three-electrode

configuration. Cyclic voltammetry was performed in a 0.1 M anhydrous degassed solution of $n\text{Bu}_4\text{NPF}_6$ in acetonitrile. Values were calibrated using ferrocene as reference.

Synthesis procedure for the preparation of GS-Ir



Scheme S1. General synthesis of GS-Ir.

Preparation of organic precursors

Synthesis of 2-bromo-2-methylpropanoyloxypropyldimethylchlorosilane 1

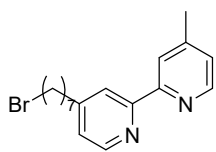
2-Bromo-2-methylpropanoyloxypropyldimethylchlorosilane was synthesized in a two-step procedure.¹ Under argon atmosphere, in a solution of allyl alcohol (1.00 equiv.) and bromoisobutyryl bromide (1.00 equiv.), triethylamine (1.50 equiv.) was added dropwise. The resulting solution was stirred at room temperature for 1 hour. Water and hydrochloric acid were added until $pH = 7$. Then, aqueous layer was extracted three times with dichloromethane. Combined organic layers were washed with water, dried over MgSO_4 , filtrated and concentrated under vacuum. The crude product was pure enough to be engaged in the next step. Analyses of the allyl 2-bromo-2-methylpropionate intermediate were in agreement with the literature.²

$^1\text{H NMR}$ (CDCl_3 , 500 MHz) δ 5.93 (ddt, $J = 17.3, 10.5, 5.6$ Hz, 1H), 5.37 (dq, $J = 17.2, 1.5$ Hz, 1H), 5.26 (dq, $J = 10.5, 1.3$ Hz, 1H), 4.66 (dt, $J = 5.6$ Hz, 1.5 Hz, 2H), 1.94 (s, 6H).

In a glove box, allyl 2-bromo-2-methylpropionate (1.00 equiv.) was added to a solution of hexachloroplatinic acid (1 mol%, 0.5 wt% in xylene). Finally, chlorodimethylsilane (9.00 equiv.) was added. The resulting solution was stirred at 100 °C overnight (a brown solution was obtained). After cooling down to room temperature, the solvent was evaporated and the product was distilled under reduced pressure to give the 2-bromo-2-methylpropanoyloxypropyldimethylchlorosilane **1** as a transparent liquid (90%). Analysis was in agreement with the literature.³

$^1\text{H NMR}$ (CDCl_3 , 500 MHz) δ 4.71 (t, $J = 6.7$ Hz, 2H, CH_2), 1.94 (s, 6H, 2CH_3), 1.83 – 1.77 (m, 2H, CH_2), 0.91 – 0.86 (m, 2H, CH_2), 0.44 (s, 6H, 2CH_3).

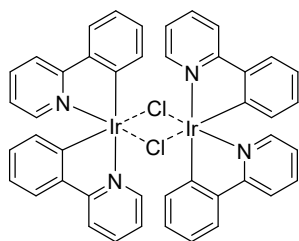
Synthesis of 4'-(7-bromoheptyl)-4-methyl-[2,2']-bipyridine 3



4'-(7-Bromoheptyl)-4-methyl-[2,2']-bipyridine was synthesized according to a reported procedure.⁴ Under argon and at $-78\text{ }^{\circ}\text{C}$, *n*-BuLi (2.5 M solution in hexane, 1.05 equiv.) was added dropwise into a solution of distilled *N,N*-di-*iso*-propylamine (1.20 equiv.) in dry THF (1.5 M). After the addition, the reaction mixture was warmed to $0\text{ }^{\circ}\text{C}$ and stirred for 15 minutes to give a yellow solution. Then, the reaction mixture was cooled down at $-78\text{ }^{\circ}\text{C}$ and 4,4'-dimethylpyridine (1 equiv.) dissolved in dry THF (0.25 M) was added and the resulting brown solution was stirred for 1 h at $0\text{ }^{\circ}\text{C}$. At $0\text{ }^{\circ}\text{C}$, 1,6-dibromohexane (5.10 equiv.) dissolved in dry THF was added and the solution was stirred for 1.5 h at room temperature. The blue solution turned to yellow during this step and a precipitate appeared. Then, water and a solution of 2 M hydrochloric acid were added until $\text{pH} = 7$. The aqueous layer was extracted once with diethyl ether and three times with DCM. Combined organic layers were dried over MgSO_4 , filtrated and concentrated under vacuum to give a yellow oil. After addition of diethyl ether, a white precipitate was filtrated on fritted glass. The filtrate was concentrated and pentane was added for a second filtration. The filtrate was concentrated and a first silica gel column chromatography was carried out to remove the excess of 1,6-dibromohexane using a deactivated silica gel and a gradient of pentane/ethyl-acetate from 1/0 to 50/50 to afford an off-white solid. Then, a second column chromatography was carried out with silica using a gradient of DCM/acetone from 1/0 to 8/2 to afford the pure 4'-(7-bromoheptyl)-4-methyl-[2,2']-bipyridine **3** (32%) as an off-white solid. Analysis was in agreement with the literature.⁴

$^1\text{H NMR}$ (CDCl_3 , 500 MHz) δ 8.55 (dd, $J = 5.1, 7.4\text{ Hz}$, 2H, H_{py}), 8.23 (*br d*, $J = 5.3\text{ Hz}$, 2H, H_{py}), 7.15-7.12 (m, 2H, H_{py}), 3.40 (t, $J = 6.8\text{ Hz}$, 2H, CH_2), 2.69 (dd, $J = 7.5\text{ Hz}, 7.5\text{ Hz}$, 2H, CH_2), 2.44 (s, 3H), 1.89-1.80 (m, 2H, CH_2), 1.74-1.66 (m, 2H, CH_2), 1.46-1.32 (m, 6H, 3 CH_2).

Synthesis of bis-[μ -chloro-bis-(2-phenylpyridinato- C^2, N)iridium(III)] 4



Bis-[μ -chloro-bis-(2-phenylpyridinato- C^2, N)iridium(III)] was synthesized according to a reported procedure.⁵ In a dry Schlenk tube under an argon atmosphere, $\text{IrCl}_3 \cdot x\text{H}_2\text{O}$ (1.00 equiv.) and 2-phenylpyridine (2.20 equiv.) were introduced in a degassed 3:1 mixture of ethylene glycol monomethylated/water (16 mL). The resulting reaction mixture was heated at $120\text{ }^{\circ}\text{C}$ overnight. After cooling down to room temperature, water was added. The resulting precipitate was filtered, successively washed with water, diethyl ether and pentane and dried under vacuum to afford the bis-[μ -chloro-bis-(2-phenylpyridinato- C^2, N)iridium(III)] **4** (88%) as a yellow powder. Analysis was in agreement with the literature.⁵

$^1\text{H NMR}$ (CDCl_3 , 500 MHz) δ 9.24 (*br d*, $J = 5.8\text{ Hz}$, 4H, 4CH), 7.87 (d, $J = 7.9\text{ Hz}$, 4H, 4CH), 7.74 (dt, $J = 7.5, 1.5\text{ Hz}$, 4H, 4CH), 7.48 (dd, $J = 7.7, 1.2\text{ Hz}$, 4H, 4CH), 6.79-6.72 (m, 8H, 8CH), 6.56 (dt, $J = 7.7, 1.3\text{ Hz}$, 4H, 4CH), 5.93 (dd, $J = 7.9, 0.9\text{ Hz}$, 4H, 4CH).

Preparation of grafted iridium complexes on brush polymer

Pre-treatment and synthesis of initiator grafted glass spheres **GS-ini**

The surface of the glass sphere **GS** (9-13 μm particle size) was cleaned with a piranha solution ($\text{H}_2\text{SO}_4:\text{H}_2\text{O}_2$ 3:1) to remove organic or metal residues.⁶ Then, 5 w/w% of initiator **1** and distilled triethylamine (0.2 mL) was added to 10 g of cleaned **GS** in anhydrous toluene (25 mL). The resulting mixture was stirred at room temperature overnight. The solid was filtered, washed with water and diethyl ether and dried under vacuum to afford **GS-ini**.

Brush-polymerization synthesis of **GS-PHEMA**

Following reported procedure,³ a mixture of CuCl (1.0 equiv.), CuBr_2 (0.3 equiv.), 2,2-bipyridine (3.0 equiv.) and 2-hydroxyethyl methacrylate **2** (60 equiv.) in water (7 mL) was added to initiator-grafted glass spheres **GS-ini** under argon atmosphere. Then, 5 w/w% of azo-bis-iso-butyronitrile AIBN was added to initiate the polymerization. The resulting suspension was stirred for 2.5 days at 50 °C. The resulting material was washed with methanol (50 mL) and chloroform (50 mL) until brown/red color disappeared and dried under reduced pressure for 24 h. Of note, mixture of grafted and non-grafted polymer was obtained and engaged in the next step without further purification.

Synthesis of ligand-functionalized brush polymer on glass sphere **GS-bipy**.

A suspension of sodium hydride (60 %w/w) dispersed in mineral oil (10 mg) in DMF (1 mL) was added in Schlenk tube containing **GS-PHEM** (50 mg). After addition of the bromo ligand **3** (50 mg), the resulting suspension was stirred overnight at room temperature. The reaction mixture was quenched with water (0.5 ml), after centrifugation, the liquid phase was removed and the resulting solid material was washed with diethyl ether (10 mL) and dried for 24 h under reduced pressure to furnish pure **GS-bipy**.

Synthesis of iridium-functionalized brush polymer on glass sphere **GS-Ir**.

In a Schlenk tube under argon, iridium complex **4** and the immobilized and functionalized ligand **GS-bipy** (see manuscript for the different ratio used) were dispersed in a dichloromethane/MeOH mixture (2:1). Finally, the suspension was heated at 50 °C overnight and a large excess of potassium hexafluorophosphate was added. The solid was filtrated, washed with dichloromethane and methanol until colorless filtrate was obtained and then dried for 24 h under reduced pressure.

Determination of metal leaching in solution

The **GS-Ir**₅₁₈ (0.52 wt% of iridium) was suspended either into dichloromethane or acetonitrile overnight, then solvents were removed. No iridium leaching was detected in the filtrate whatever the solvent used.

Characterization of Glass ball material by solid NMR spectroscopy

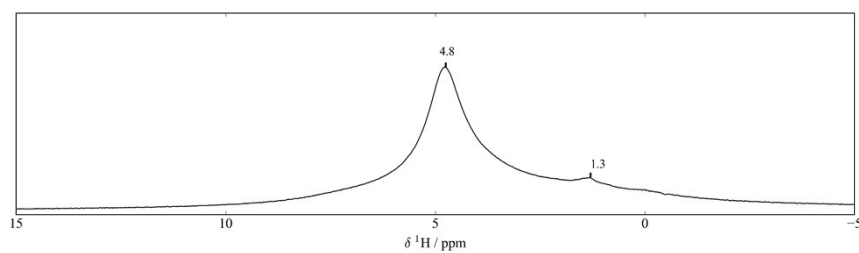


Figure S1. ^1H MAS NMR of GS.

Silanol content was evaluated in the free glass sphere from ^1H MAS NMR analysis (**Figure S1**) using adamantane, as reference. Thus, a silanol content of $6.4 \mu\text{mol/g}$ of sample was estimated, corresponding to the peak at 1.3 ppm.

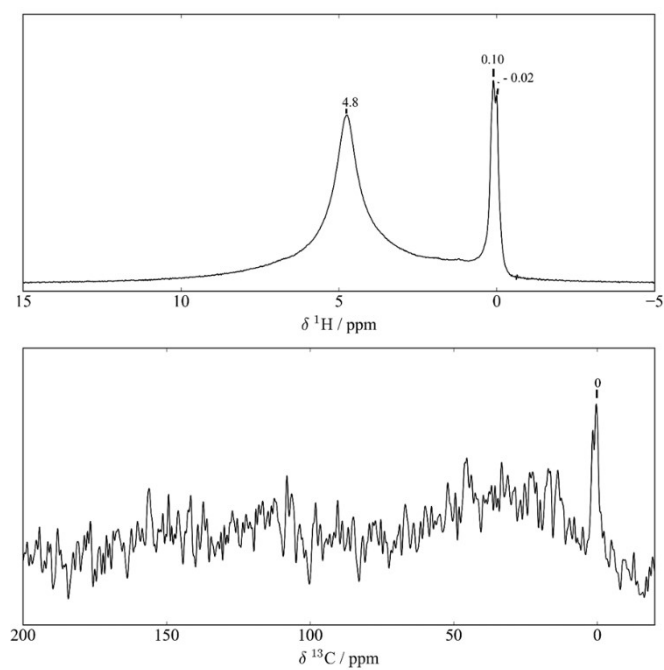


Figure S2. ^1H (top) et ^{13}C (bottom) MAS NMR of GS-*ini*.

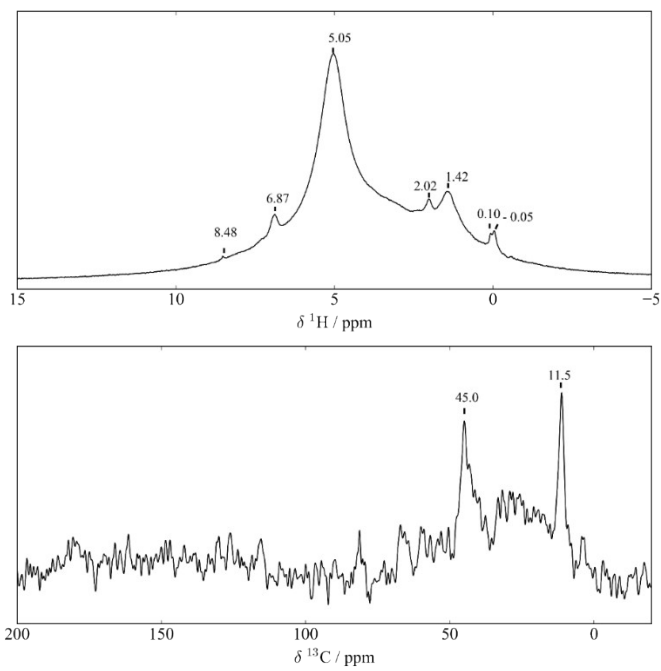


Figure S3. ^1H (top) et ^{13}C (bottom) MAS NMR of GS-bipy.

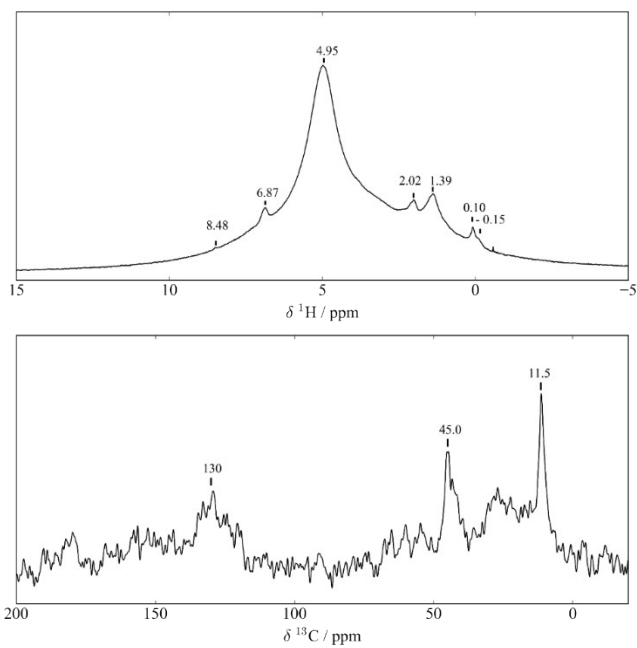


Figure S4. ^1H (top) et ^{13}C (bottom) MAS NMR of GS-Ir₅₁₈.

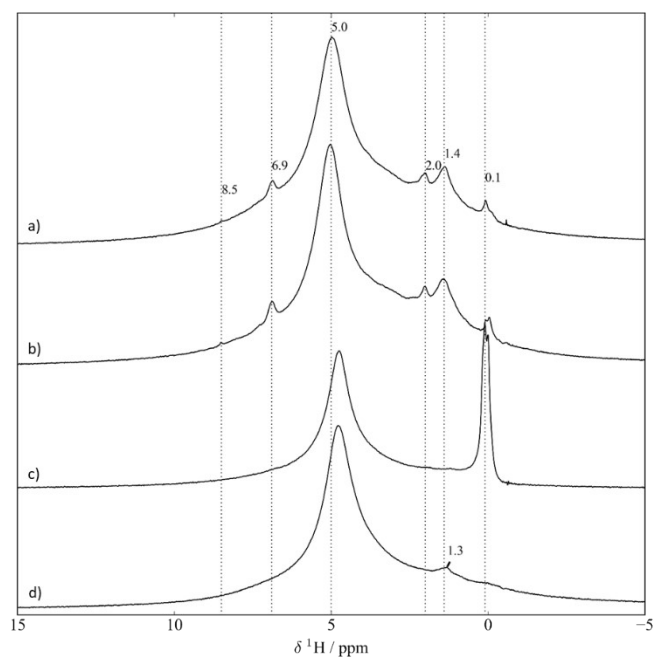


Figure S5. ^1H MAS NMR Comparison between **GS-Ir₅₁₈** (a), **GS-bipy** (b), **GS-ini** (c) and **GS** (d).

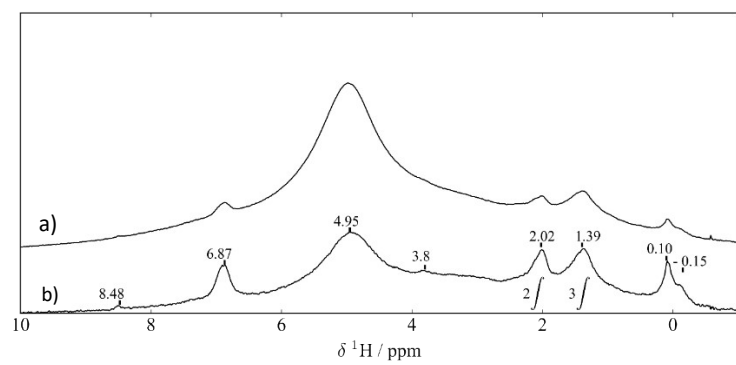


Figure S6. a) ^1H MAS NMR and b) ^1H echo MAS NMR of **GS-Ir₅₁₈**.

The grafting rate of the final sample was estimated from the CPMAS $\{^1\text{H}\}\text{-}^{29}\text{Si}$ NMR analysis (**Figure S7**). Experimental peaks are an addition of two different components corresponding to the Si-O-H (centered at -100 ppm) and the Si-O-Si (centered at -103 ppm). An important decrease of the Si-OH component was observed in the **GS-Ir** spectrum (**Figure S7, b**). After deconvolution of the **GS-Ir** experimental peak using DMfit software, 66 % of silanols were functionalized.

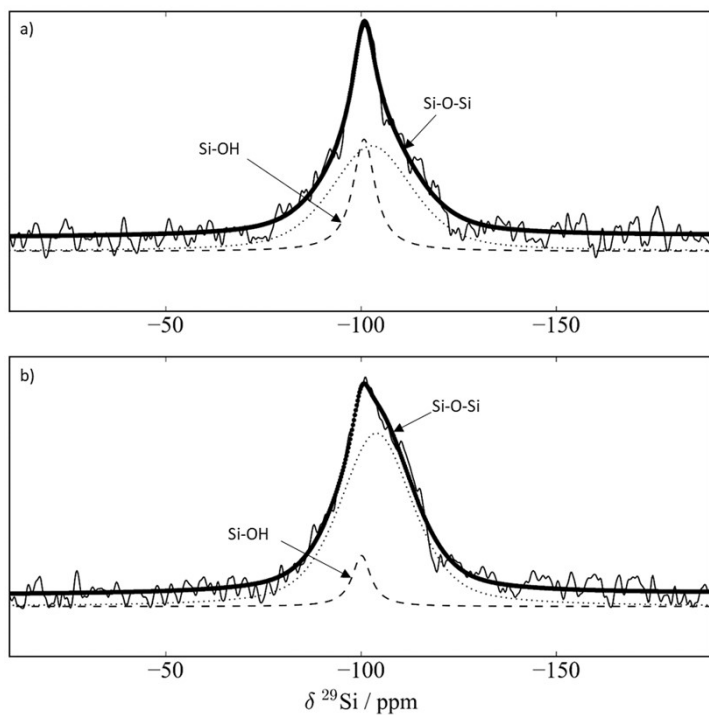
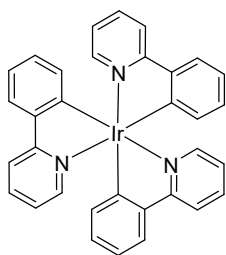


Figure S7. CPMAS $\{^1\text{H}\}\text{-}^{29}\text{Si}$ NMR of glass sphere **GS** (a.) and **GS-Ir** (b.)

Synthesis of iridium complexes 5-7

Both *fac*-[Ir(ppy)₃] **5** and [Ir(ppy)₂(dtbbpy)]Cl **6** are well-known complexes and were synthesized following reported procedures.⁵ In a Schlenk tube under argon, **4** (1.00 equiv.) and 4,4'-di-*tert*-butyl-2,2'-dipyridine **dtbbpy** or 2-phenylpyridine **ppy** (2.20 equiv.) were introduced in DCM/methanol (2:1). The resulting reaction mixture was stirred overnight at 60 °C. Solvents were evaporated and the resulting solid was washed several times with methanol and ether to obtain both products as yellow powders.

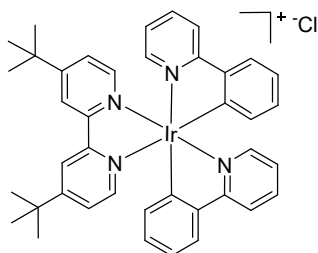
Tris[2-phenylpyridinato-C²,N]iridium(III) **5**



Yield: 72%. Analyses were in agreement with the literature.⁷

¹H NMR (CDCl₃, 500 MHz) δ 7.87 (d, *J* = 8.2 Hz, 3H), 7.65 (d, *J* = 7.6 Hz, 3H), 7.58 (t, *J* = 7.7 Hz, 3H), 7.53 (d, *J* = 5.2 Hz, 3H), 6.92 - 6.82 (m, 12H).

[4,4'-Di-*tert*-butyl-2,2'-bipyridine-N1,N1']bis[2-(2-pyridinyl-N)phenyl-C]iridium(III) chloride **6**

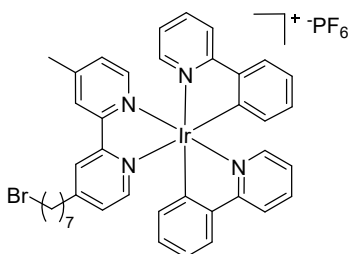


Yield: 95%. Analyses were in agreement with the literature.⁸

Hz, 2H), 1.39 (s, 18H).

¹H NMR (DMSO-*d*₆, 400 MHz) δ 8.86 (d, *J* = 1.5 Hz, 2H), 8.26 (d, *J* = 8.2 Hz, 2H), 7.97 - 7.88 (m, 4H), 7.76 (d, *J* = 5.9 Hz, 2H), 7.70 (dd, *J* = 5.9, 1.5 Hz, 2H), 7.60 (*br* d, *J* = 5.7 Hz, 2H), 7.18 (*br* t, *J* = 7.1 Hz, 2H), 7.01 (*br* t, *J* = 7.3 Hz, 2H), 6.89 (*br* t, *J* = 7.5 Hz, 2H), 6.17 (*br* d, *J* = 7.5

[4'-(7-Bromoheptyl)-4-methyl-2,2'-bipyridine-N1,N1']bis[2-(2-pyridinyl-N)phenyl-C]iridium(III) hexafluorophosphate **7**



A mixture of **4** (145 mg, 0.13 mmol, 1.00 equiv.) and 4'-(7-bromoheptyl)-4-methyl-[2,2']-bipyridine (103 mg, 0.29 mmol, 2.20 equiv.) in 14 mL of dichloromethane/methanol (2:1 v/v) was refluxed under inert atmosphere overnight. Then, the yellow solution was cooled down to room temperature and solvents were evaporated under vacuum. The resulting yellow solid was diluted in 14 mL of dichloromethane and KPF₆ (249 mg, 1.35 mmol, 10.0 equiv.) was added. The suspension was stirred for an hour and the excess of KPF₆ was filtrated and washed several times with dichloromethane. The solvent was evaporated under vacuum to give a yellow solid which was then triturated in diethyl ether, filtered and dried to afford [4'-(7-bromoheptyl)-4-methyl-2,2'-bipyridine-N1,N1']bis[2-(2-pyridinyl-

N)phenyl-*C*]iridium(III) hexafluorophosphate **[Ir(ppy)₂(Br-bpy)]PF₆** (213 mg, 0.22 mmol, 80%) as a yellow powder. A mixture of two diastereoisomers was obtained (major 65%, minor 35%).

¹H NMR (CD₂Cl₂, 600 MHz) δ 8.30 (dd, *J* = 19.0, 2.5 Hz, 2H, CH), 7.95 (d, *J* = 8.2 Hz, 2H, CH), 7.84 (dd, *J* = 13.2, 5.7 Hz, 2H, CH), 7.76 (*br* d, *J* = 7.8 Hz, 2H, CH), 7.51 (*br* dd, *J* = 14.1, 5.8 Hz, 2H, CH), 7.24 (dd, *J* = 5.5, 0.8 Hz, 2H, CH), 7.06 (dt, *J* = 7.6, 1.1 Hz, 2H, CH), 7.02 – 6.98 (m, 2H, CH), 6.93 (dt, *J* = 7.5, 1.1 Hz, 2H, CH), 6.31 (*br* t, *J* = 7.0 Hz, 2H, CH), 3.54 (t, *J* = 6.7 Hz, 2H, CH₂, 65%), 3.42 (t, *J* = 6.8 Hz, CH₂-py, 35%), 2.83 (t, *J* = 7.8 Hz, 2H, CH₂-Br), 2.59 (s, 3H, CH₃), 1.84 (quin, *J* = 7.1 Hz, 2H, CH₂, 35%), 1.76 (quin, *J* = 7.1 Hz, 2H, CH₂, 65%), 1.74 – 1.68 (m, 2H, CH₂), 1.46 – 1.34 (m, 6H); **¹³C NMR (CD₂Cl₂, 151 MHz)** δ 168.2 (Cq, 100%), 168.2 (Cq, 100%), 156.7 (Cq, 100%), 155.9 (Cq, 100%), 155.8 (Cq, 100%), 152.4 (Cq, 100%), 150.8 (Cq, 2C, 100%), 150.5 (CH, 100%), 150.3 (CH, 100%), 148.9 (CH, 100%), 148.9 (CH, 100%), 144.2 (Cq, 100%), 144.1 (Cq, 100%), 138.5 (CH, 2C, 100%), 132.1 (CH, 100%), 132.0 (CH, 100%), 131.0 (CH, 100%), 131.0 (CH, 100%), 129.4 (CH, 100%), 128.5 (CH, 100%), 125.6 (CH, 100%), 125.2 (CH, 100%), 125.2 (CH, 100%), 124.8 (CH, 100%), 123.6 (CH, 100%), 123.5 (CH, 100%), 122.9 (CH, 2C, 100%), 120.1 (CH, 100%), 120.0 (CH, 100%), 45.7 (CH₂, 65%), 35.8 (CH₂, 100%), 34.7 (CH₂, 35%), 33.1 (CH₂, 35%), 32.9 (CH₂, 65%), 30.4 (CH₂, 100%), 29.5 (CH₂, 65%), 29.4 (CH₂, 35%), 28.9 (CH₂, 65%), 28.8 (CH₂, 35%), 28.3 (CH₂, 35%), 27.0 (CH₂, 65%), 21.6 (CH₃, 100%); **³¹P NMR (CD₂Cl₂, 202 MHz)** δ -144.3 (hept, *J* = 714 Hz, 1P, PF₆); **¹⁹F NMR (CD₂Cl₂, 564 MHz)** δ -72.9 (d, *J* = 714 Hz, 6F, PF₆); **HRMS** calcd for C₄₀H₃₉N₄BrIr [M – PF₆]⁺: 847.1987; found 847.1963; **IR (cm⁻¹)** 3060, 3040, 2931, 2857, 1607, 1583, 1478, 1421, 835, 757, 556.

Photophysical characterization of GS-Ir and iridium complex 7

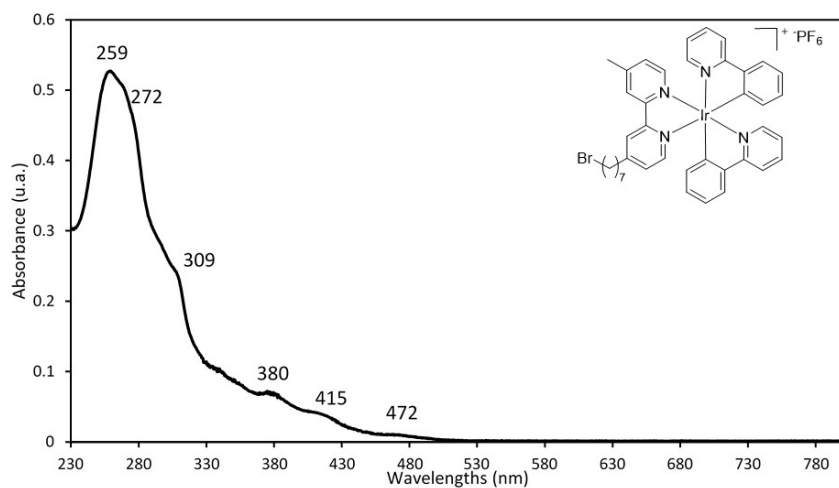


Figure S8. UV-vis absorption spectra of $[\text{Ir}(\text{ppy})_2(\mathbf{3})][\text{PF}_6]$ **7** in dichloromethane ($C = 10^{-5}$ M).

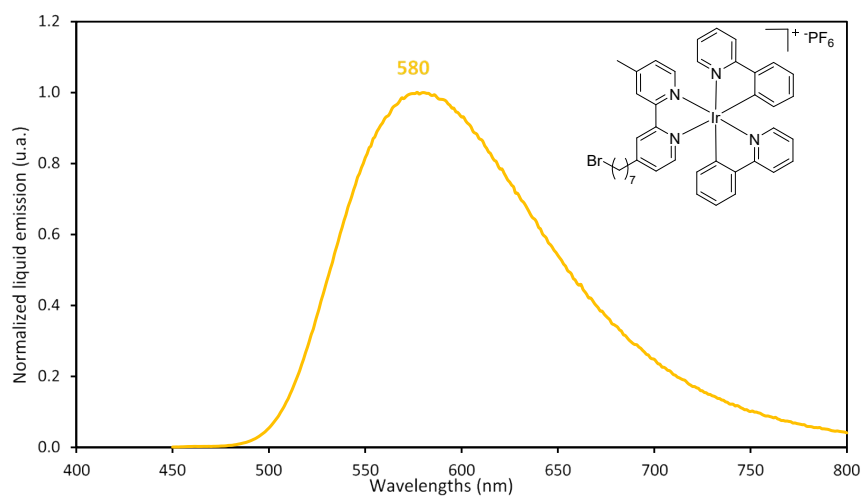


Figure S9. Normalized liquid emission of $[\text{Ir}(\text{ppy})_2(\mathbf{3})][\text{PF}_6]$ **7** in dichloromethane ($C = 10^{-5}$ M, $\lambda_{\text{ex}} = 380$ nm).

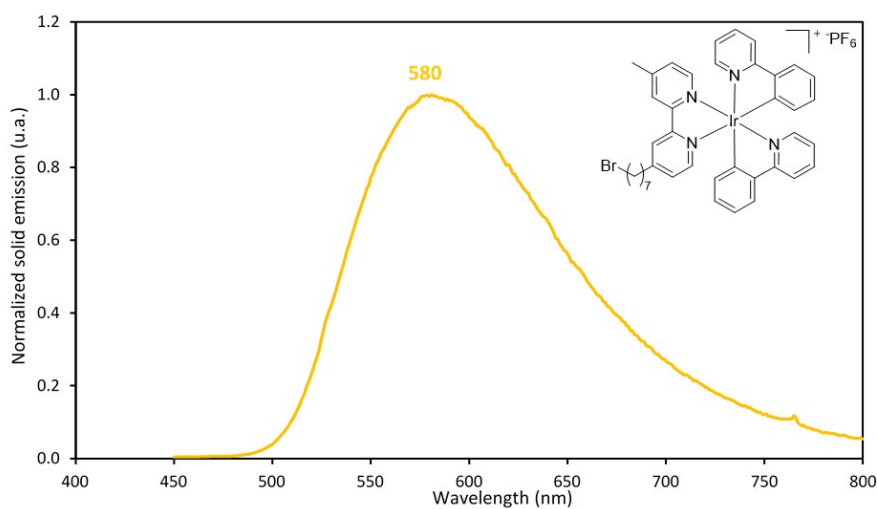


Figure S10. Normalized solid emission of $[\text{Ir}(\text{ppy})_2(\mathbf{3})][\text{PF}_6]$ **7** ($\lambda_{\text{ex}} = 380$ nm).

Emission of **GS-Ir₅₁₈** was measured for each iridium contents (518 to 4750 ppm). Only the **GS-Ir₅₁₈** gave a low emission (**Figure S11**). At higher iridium content, emission is quenched probably due to a self-absorption by the iridium complex framework itself.

Due to the low emission of the support, emission spectrum of **GS-Ir₅₁₈** (blue curve in **figure S11**) contains numerous scattering peaks (**Figure S11**). Despite this issue, peaks centered at 515 nm in the **GS-Ir₅₁₈** (blue curve in **figure S11**) was not observed in unfunctionalized **GS** (dashed orange curve in **figure S11**). In order to have a better visualization of the emission peak, baseline and deconvolution were performed using literature procedure.^{9,10}

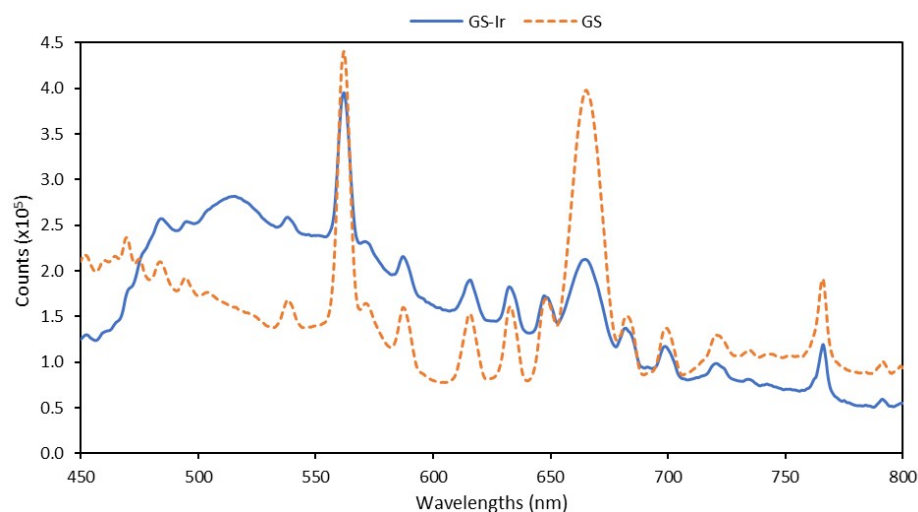


Figure S11. Emission spectra of **GS** (dashed orange curve) and **GS-Ir₅₁₈** (blue curve)

First, baseline of both curves was computed using the airPLS method (adaptive iteratively reweighted penalized least squares).⁹ Thanks to this method, both spectra are easily comparable and all scattering peaks are observed (**Figure S11**).

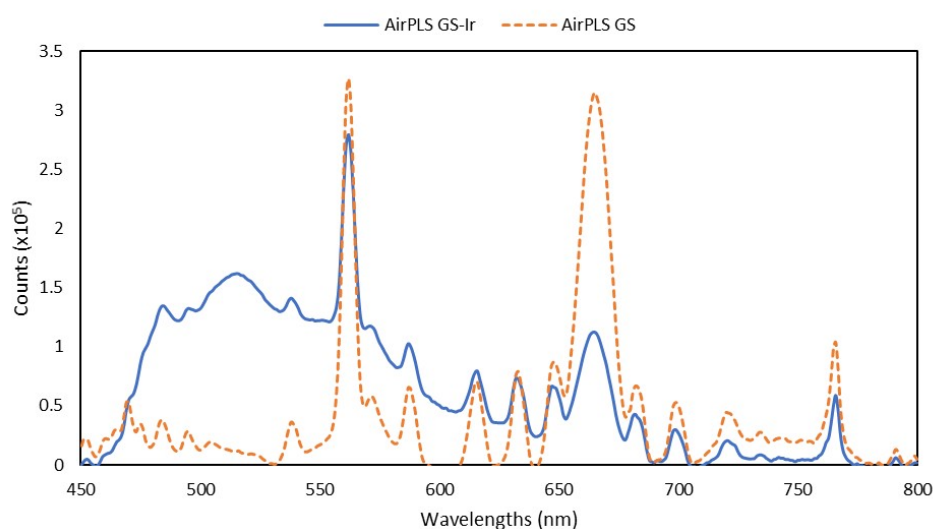


Figure S12. Emission spectra of **GS** (dashed yellow curve) and **GS-Ir₅₁₈** (blue curve) after airPLS correction

Then, a deconvolution was done to remove scattering peaks using an EMG function (exponentially modified gaussian) for the emission peak and pseudo-Voigt profiles for the scattering peaks. This leads to the spectrum in **Figure S13** after normalization.¹⁰ As observed previously in the **Figure S12**, the emission peak is centered at 515 nm. All scattering peaks are observed in **Figure S14**.

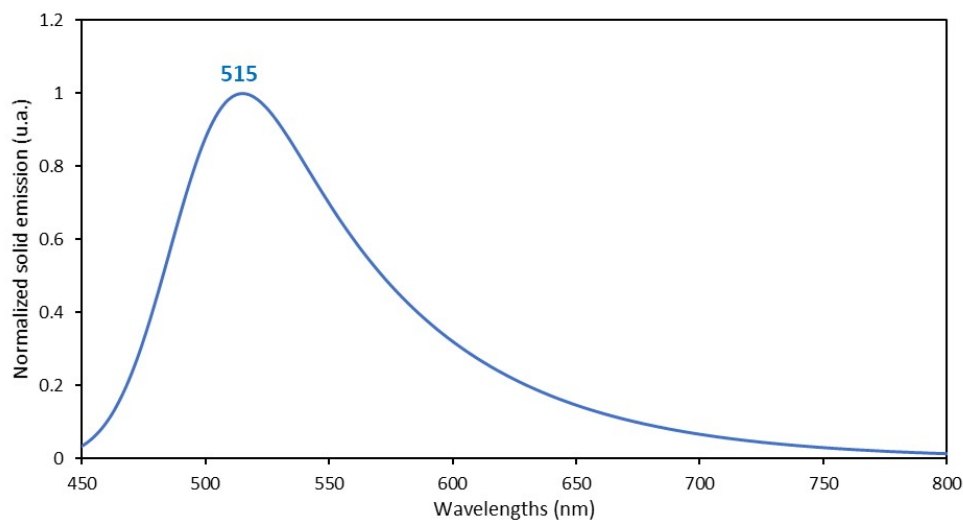


Figure S13. Final curve of the normalized solid emission of **GS-Ir₅₁₈**.

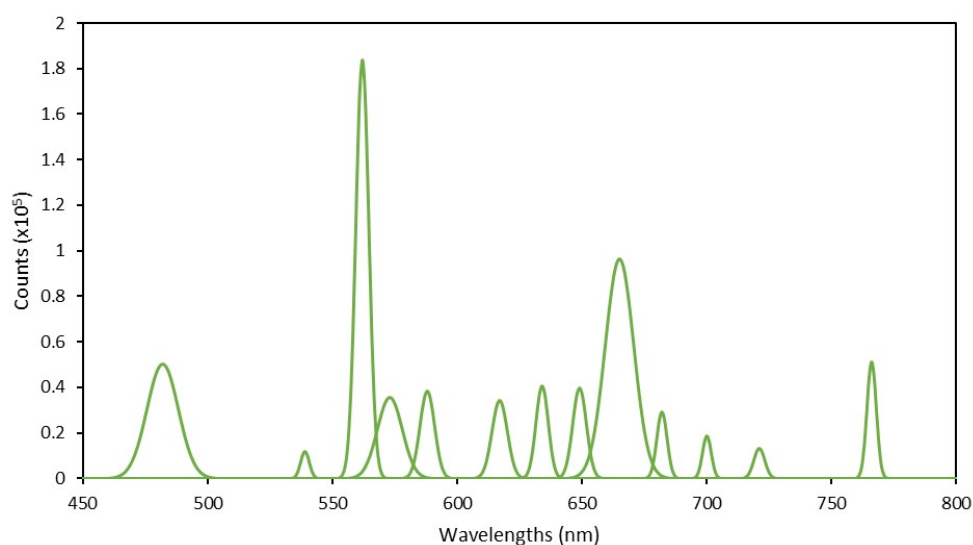


Figure S14. Representation of scattering peaks deconvoluted using pseudo-Voigt profiles.

The final modified emission spectra of **GS-Ir₅₁₈** presented in **figure S13** and all deconvoluted scattering peaks (**Figure S14**) were added (blue curve in **Figure S15**) and compared with the initial emission spectra of **GS-Ir₅₁₈** obtained without any modification (orange dashed curve in **Figure S15**) to confirm the correctness of the deconvolution. The mean absolute error (MAE) was calculated between the airPLS curve and the final deconvoluted curve using the equation (equiv. 1) and gave an error of $\pm 1.5\%$.

$$MAE = \frac{\sum_{i=1}^n |y_i - x_i|}{n} \quad (\text{eq. 1})$$

with n = total number of data (350), y_i = deconvoluted values, x_i = airPLS values

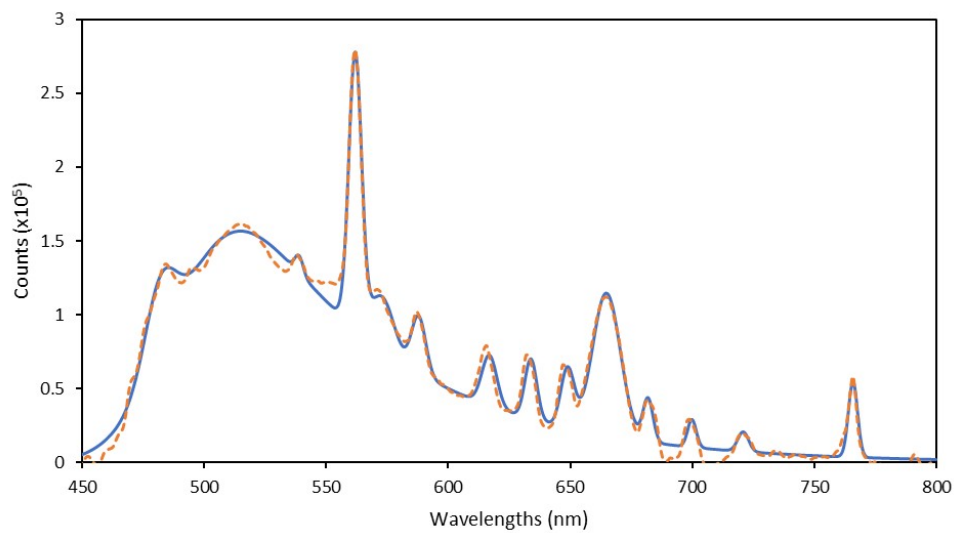


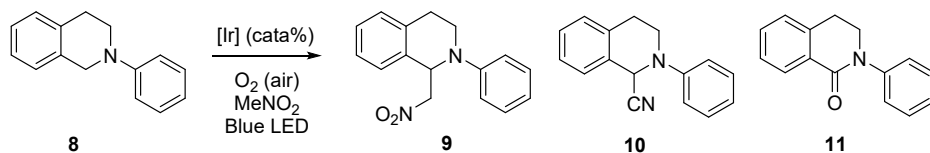
Figure S15. Comparison between the final deconvoluted **GS-Ir₅₁₈** after airPLC correction (with addition of scattering peaks, blue curve) and the unmodified emission spectra of **GS-Ir₅₁₈** (dashed yellow curve).

Cross dehydrogenative coupling (CDC)

All photocatalytic reactions were performed in a Hepatochem HCK1006-01-025 photoredox box under blue light irradiation from a 150 W Tuna Blue Kessil lamp ($\lambda_{\text{abs, max}} = 455 \text{ nm}$) (Figure S16).



Figure S16. Picture of the photochemical setup for CDC reaction under blue light irradiation.



Scheme S2. Formation of compounds 9-10 from 8 by CDC reaction.

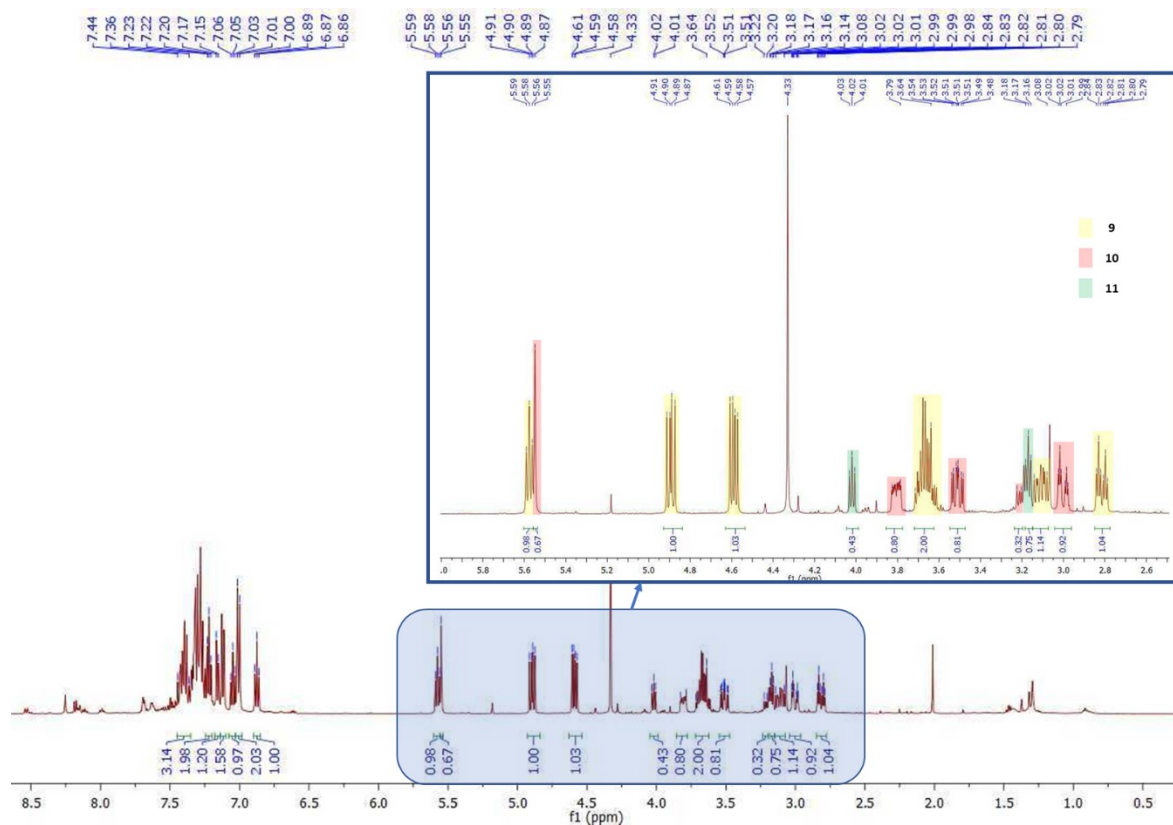


Figure S17. ^1H NMR spectroscopy of crude CDC reaction using **GS-Ir**₂₂₅₁. Inset shows signals assignment for compounds **9**, **10** and **11** in the aliphatic area.

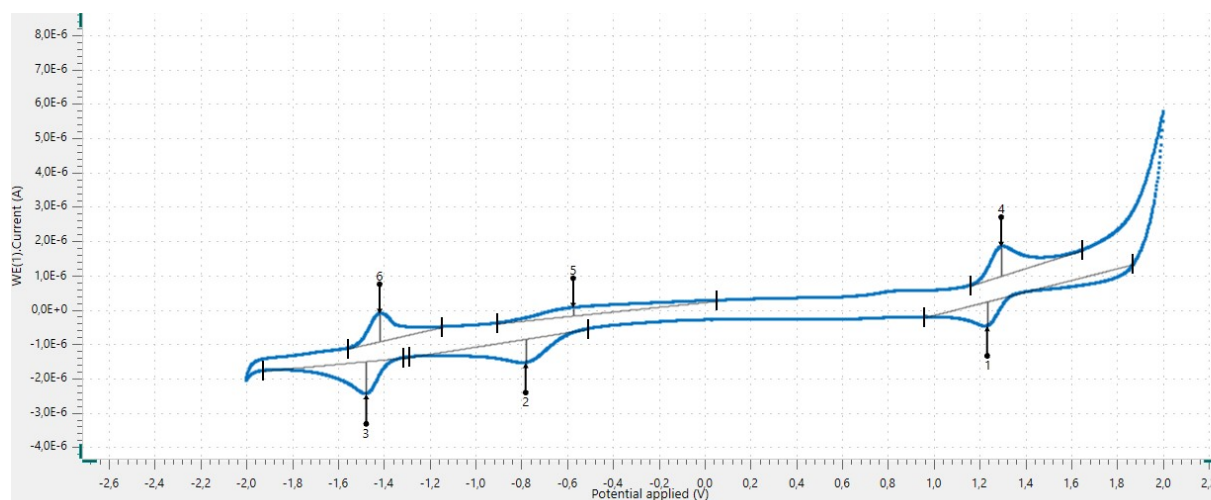


Figure S18. Cyclic voltammetry in $n\text{Bu}_4\text{NPF}_6$ acetonitrile solution (0.1 M) of $[\text{Ir}(\text{ppy})_2(\text{Br-bpy})][\text{PF}_6]$ **7**, rate of $100 \text{ mV}\cdot\text{s}^{-1}$.

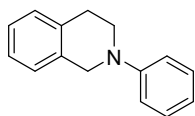
Table S1. Redox potential at ground state and estimation of redox potential at the excited state for complex **7**.

$E_0(\text{Ir(III)/Ir(II)})$	$E_0(\text{Ir(IV)/Ir(III)})$	λ_{max} Em (nm)	E_{00}^a	$E^*(\text{Ir(IV)/Ir(III)})$	$E^*(\text{Ir(III)/Ir(II)})$
-1.49	1.22	580	2.14	-0.92	0.65

^a Estimated using the maximum emission wavelength using the formula $E_{00} = hc/\lambda$.

Synthesis of starting materials

Synthesis of 2-phenyltetrahydroisoquinoline



2-Phenyltetrahydroisoquinoline was synthesized according to a known procedure.⁵

In a dry Schlenk tube under argon atmosphere, a solution of tetrahydroisoquinoline (1.00 equiv.), iodobenzene (1.50 equiv.), copper iodide (10 mol%), L-proline (20 mol%) and potassium carbonate (2.00 equiv.) in dry and degassed DMSO was stirred at 90 °C for a weekend. After few minutes, the yellow solution turned green. After cooling down to room temperature, water and ethyl acetate were added. The organic layer was separated and the aqueous layer was extracted two more times with ethyl acetate. Then, combined organic layers were washed with NH₄Cl, dried and concentrated under vacuum to afford the crude solid. Pure 2-phenyltetrahydroisoquinoline (71%) was obtained as a white solid after a column chromatography on silica gel (pentane/ethyl acetate 96/4). Analyses were in agreement with the literature.⁵

¹H NMR (CDCl₃, 500 MHz) δ 7.32 – 7.27 (m, 2H, 2CH), 7.20 – 7.14 (m, 4H, 4CH), 6.99 (d, *J* = 7.7 Hz, 2H, 2CH), 6.83 (t, *J* = 6.9 Hz, 1H, CH), 4.42 (s, 2H), 3.57 (t, *J* = 5.9 Hz, 2H), 2.99 (t, *J* = 5.9 Hz, 2H).

1. Procedures for CDC reaction

General procedure: 2-phenyltetrahydroisoquinoline (0.1 mmol) and iridium catalyst (1.0 or 0.1 mol%) were stirred in nitromethane (1 mL) under air in 10 mL capped vials. After closing the vial, the reaction mixture was irradiated under blue light (455 nm) for 24-30 hours. Then, methyl 3,5-dinitrobenzoate (25 mol%) was dissolved in the reaction mixture as external standard. Two different work-up were performed depending on the iridium catalyst.

Homogeneous catalysts: the resulting reaction mixture was filtrated over celite with acetonitrile and solvents were evaporated. The resulting crude was analyzed by ¹H NMR spectroscopy to evaluate the reaction conversion of **8**.

Heterogeneous catalyst: the suspension was centrifuged for 5 minutes and the reaction mixture was removed. The solid was washed 3 times with 5 mL of acetonitrile, centrifuged for 5 minutes after each washing to separate solid and reaction mixture and then dried under vacuum. Finally, ¹H NMR yields were evaluated as above.

Recycling: 2-phenyltetrahydroisoquinoline (0.1 mmol) and iridium catalyst (1.0 or 0.1 mol%) were stirred in nitromethane (1 mL) under air in 10 mL capped vials. After closing the vial, the reaction mixture was irradiated under blue light (455 nm) for 24-30 hours. Then, methyl 3,5-dinitrobenzoate (25 mol%) was dissolved in the reaction mixture as external standard. The suspension was centrifuged for 5 minutes and the reaction mixture was removed. The solid was washed 3 times with 5 mL of

acetonitrile, centrifuged for 5 minutes between each washing to separate solid and reaction mixture and then dried under vacuum. **GS-Ir₅₁₈** catalyst was kept in the vial and used for the next run (until the 10th, see manuscript figure 4).

Kinetics

Protocol: 2-phenyltetrahydroisoquinoline (0.1 mmol) and iridium catalyst (1.0 mol% or 20 mg) were stirred in nitromethane (1 mL) under air atmosphere and in 10 mL vials. After closing the vial, the reaction mixture was irradiated. 10 μ L of the reaction mixture was collected and injected into the GC-MS for each reaction and times. After 30h of irradiation, all reactions were analyzed in ¹H NMR to confirm results.

Reactions were conducted: with 20 mg of **GS-Ir₅₁₈**, **GS-Ir₂₂₅₁**, or **GS-Ir₄₇₉₅**, one with the complex **5** at 1 mol% and one without photocatalyst (PC). All catalyst loadings are reported in the **Table S2**. and the GC-FID conversions as the function of time are reported in the **Figure 8** and **Figure 9** in the manuscript.

Table S2. Catalyst loading engaged in kinetic studies for each catalyst

Catalyst	No PC	<i>Fac</i> -[Ir(ppy) ₃]	GS-Ir₅₁₈	GS-Ir₂₂₅₁	GS-Ir₄₇₉₅
Ir loading (mol%)	-	1.00	0.05	0.23	0.50

}

Liquid NMR Spectra

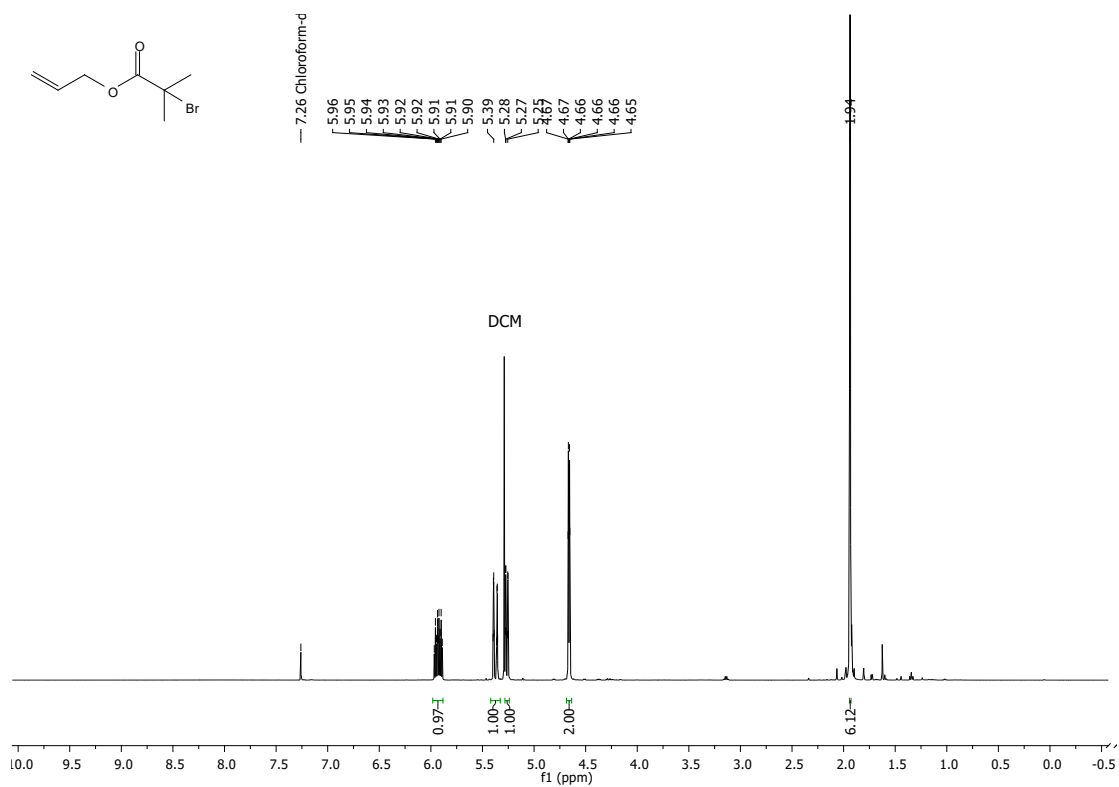


Figure S19. ^1H NMR (500 MHz, CDCl_3) spectra of 2-bromo-2-methylpropionate.

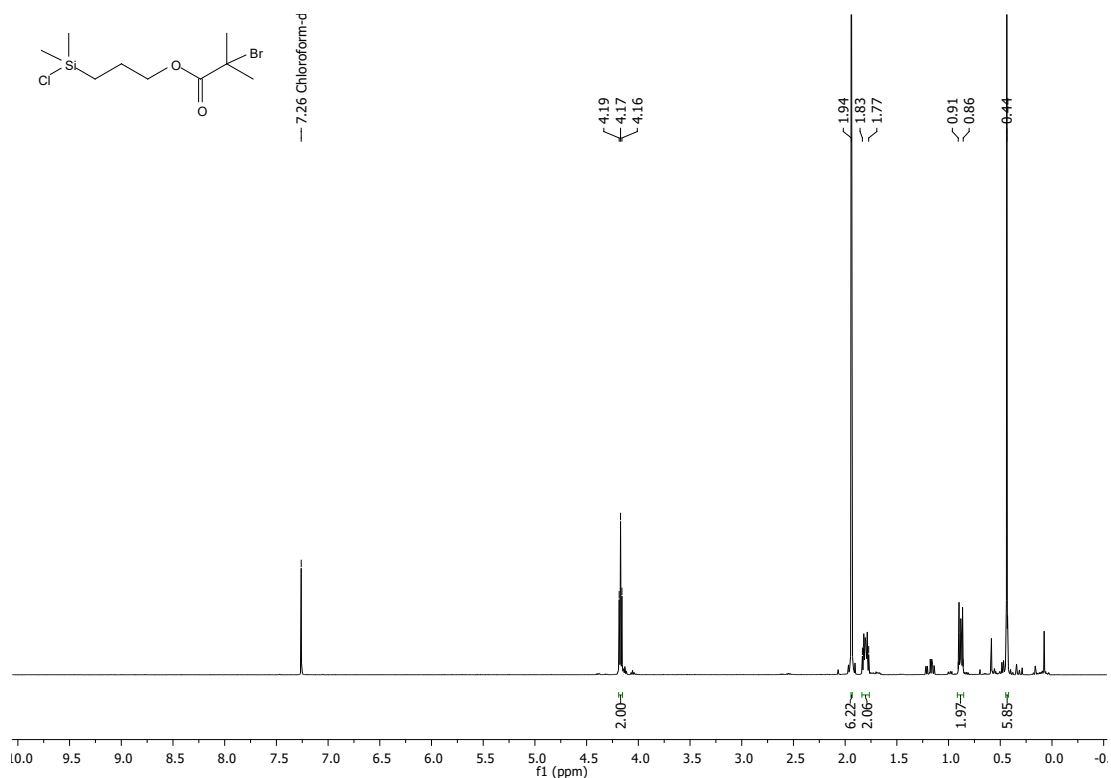


Figure S20. ^1H NMR (500 MHz, CDCl_3) spectra of 2-bromo-2-methylpropanoxypropyl dimethylchlorosilane **1**.

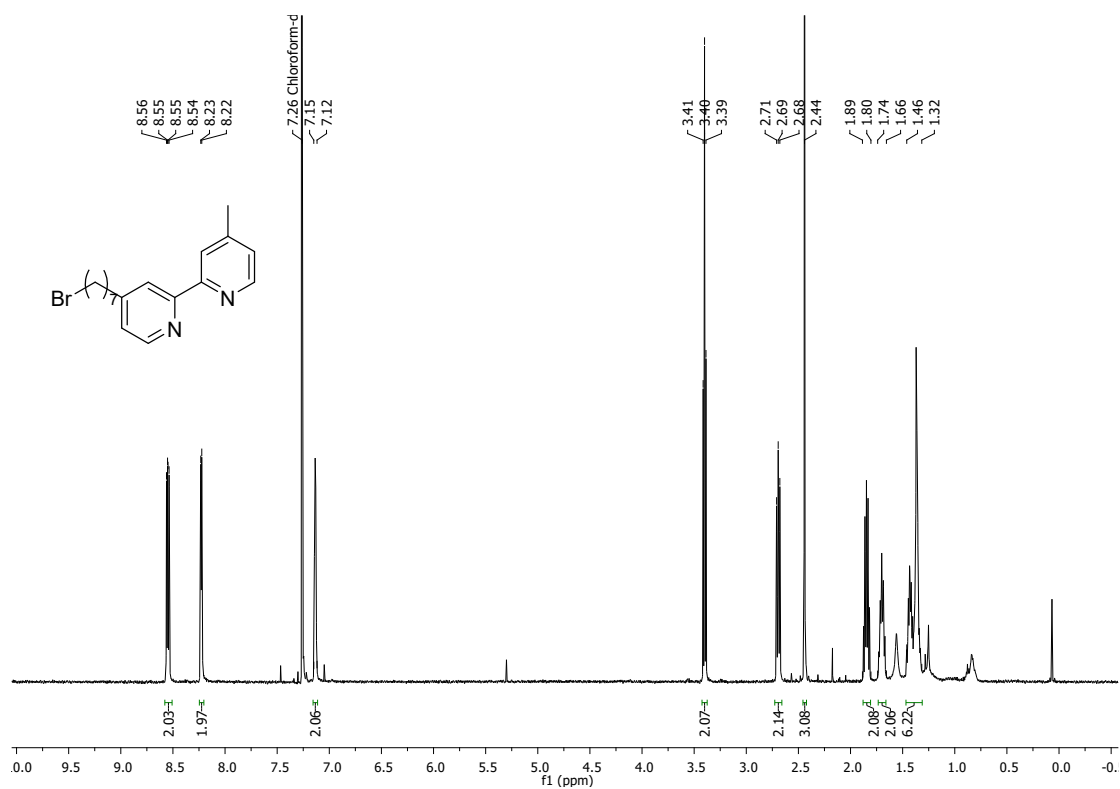


Figure S21. ^1H NMR (500 MHz, CDCl_3) spectra of 3.

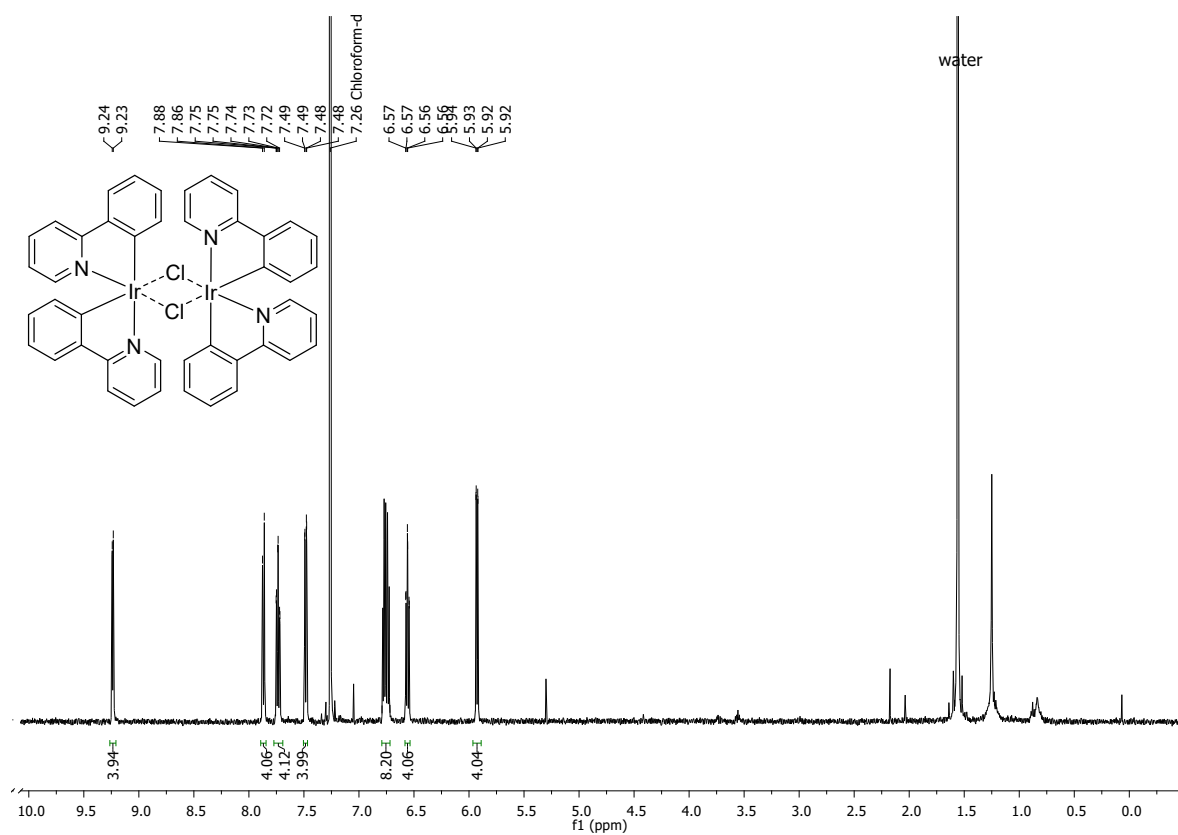


Figure S22. ^1H NMR (500 MHz, CDCl_3) spectra of 4.

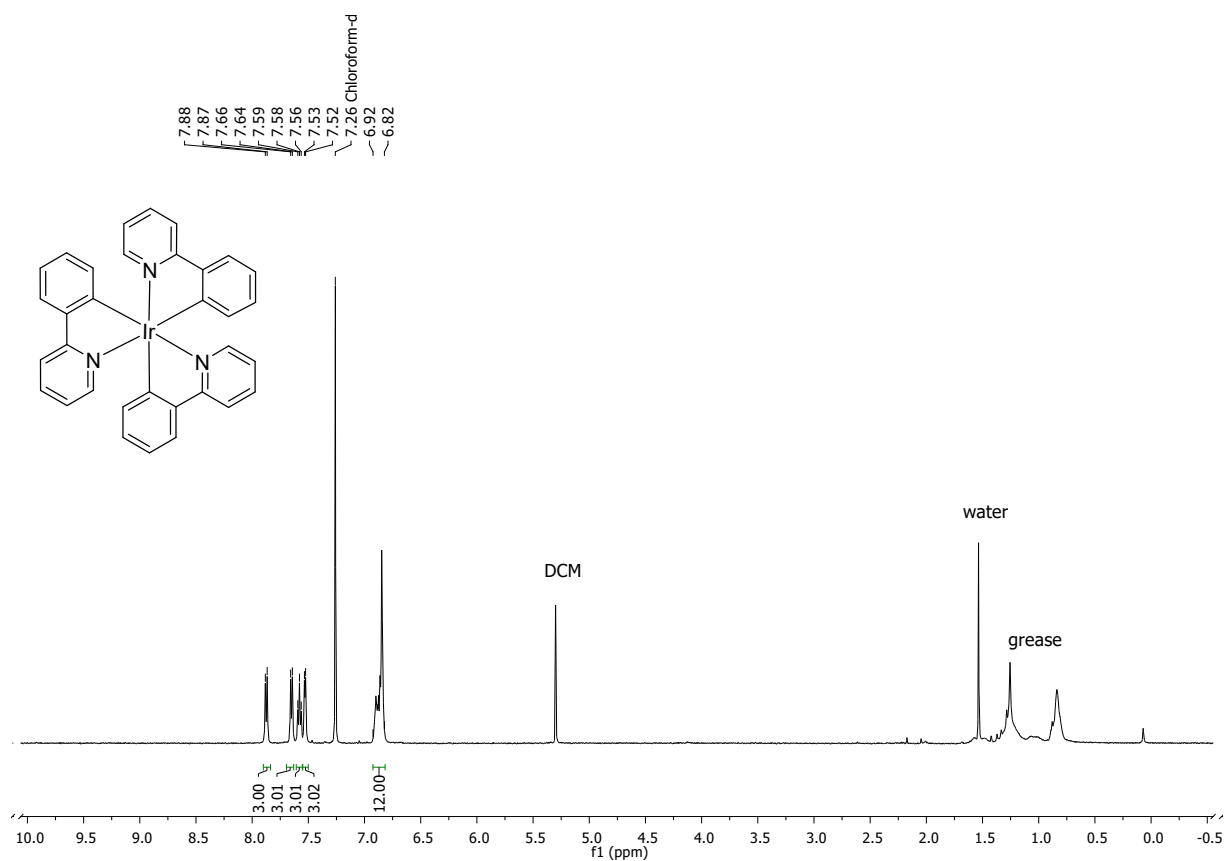


Figure S23. ^1H NMR (500 MHz, CDCl_3) spectra of $[\text{Ir}(\text{ppy})_3]$

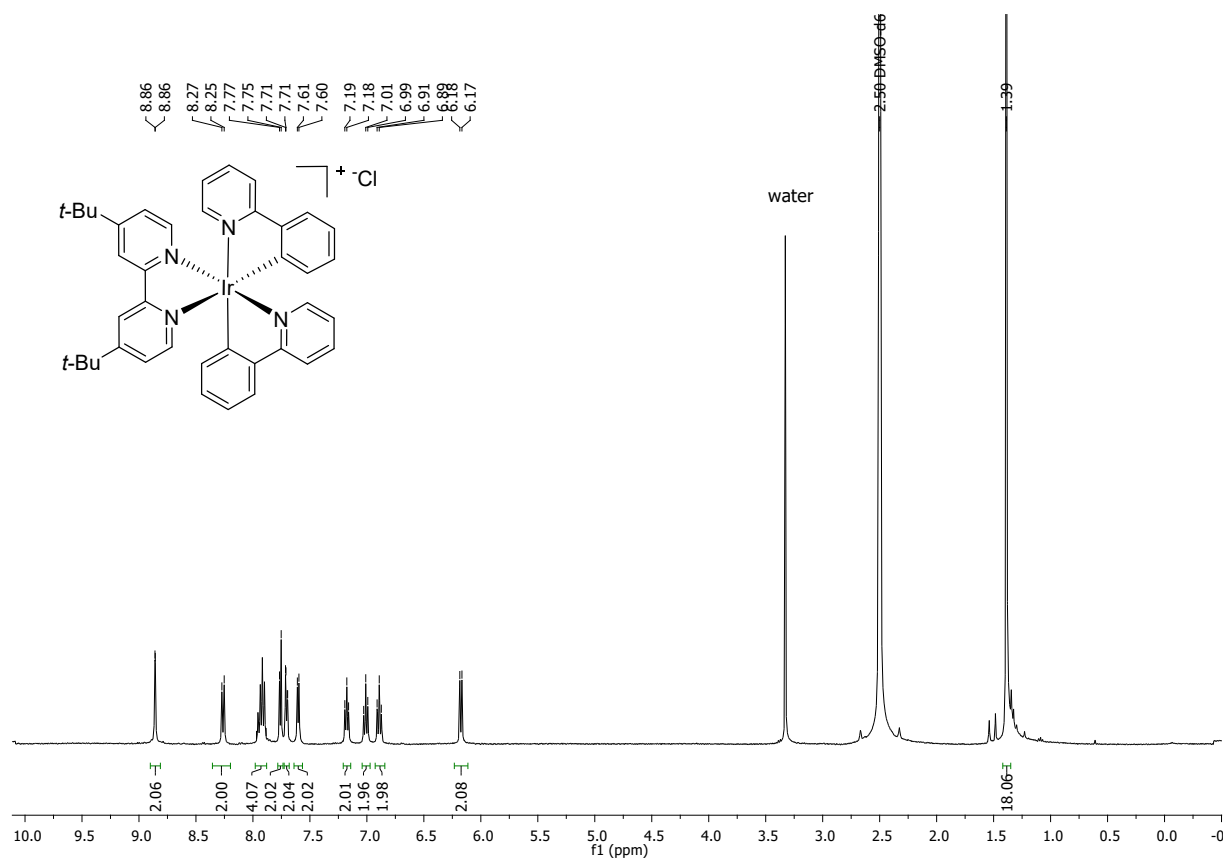


Figure S24. ^1H NMR (400 MHz, $\text{DMSO}-d_6$) spectra of $[\text{Ir}(\text{ppy})_2(\text{dtbbpy})]\text{Cl}$.

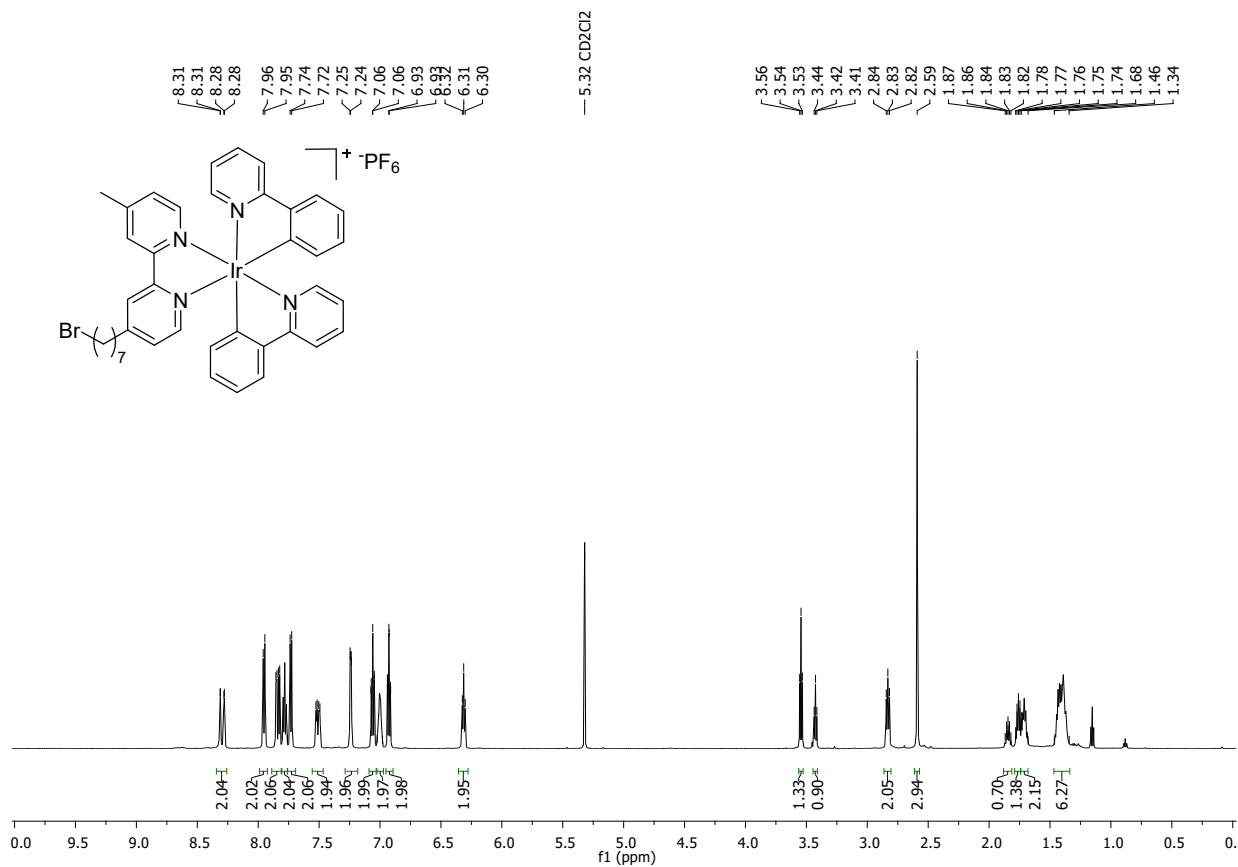


Figure S25. ¹H NMR (600 MHz, CD₂Cl₂) spectra of complex 7.

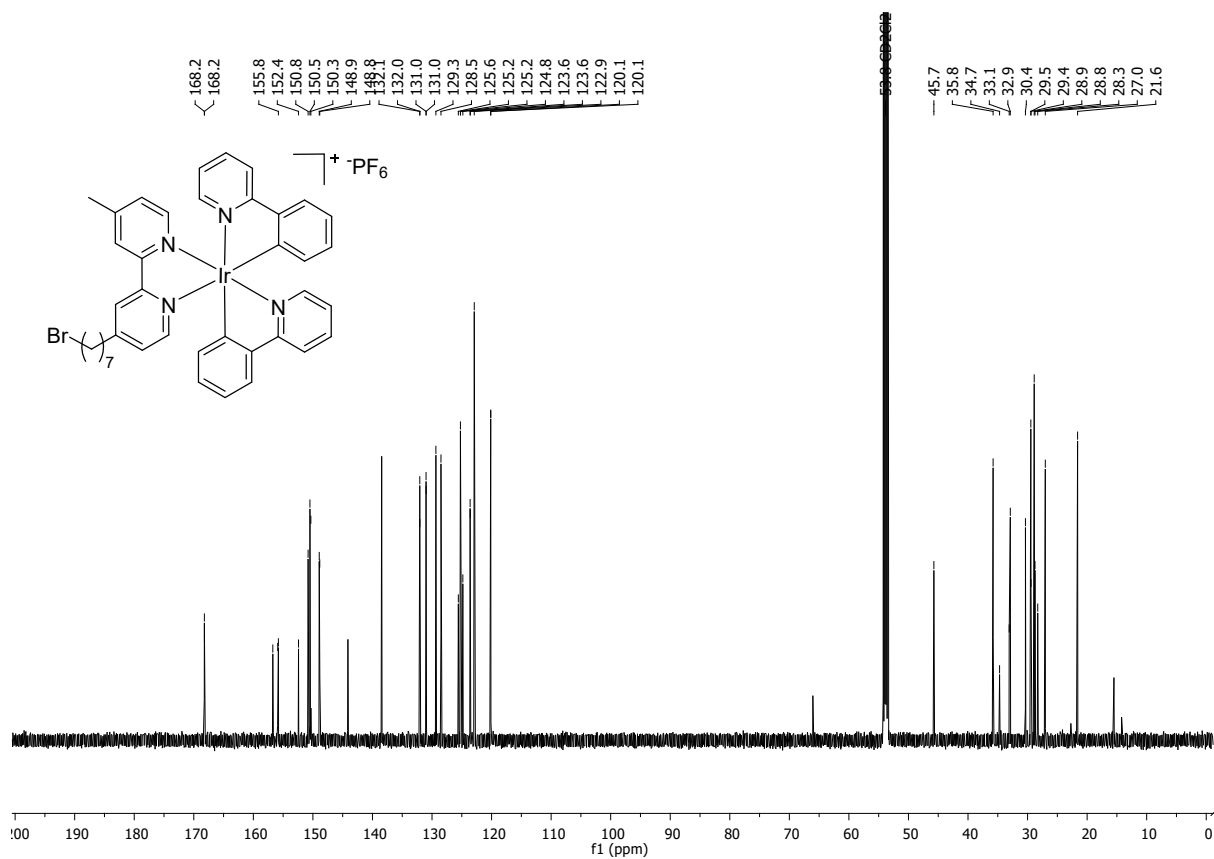


Figure S26. ¹³C NMR (CD₂Cl₂, 151 MHz) spectra of complex 7.

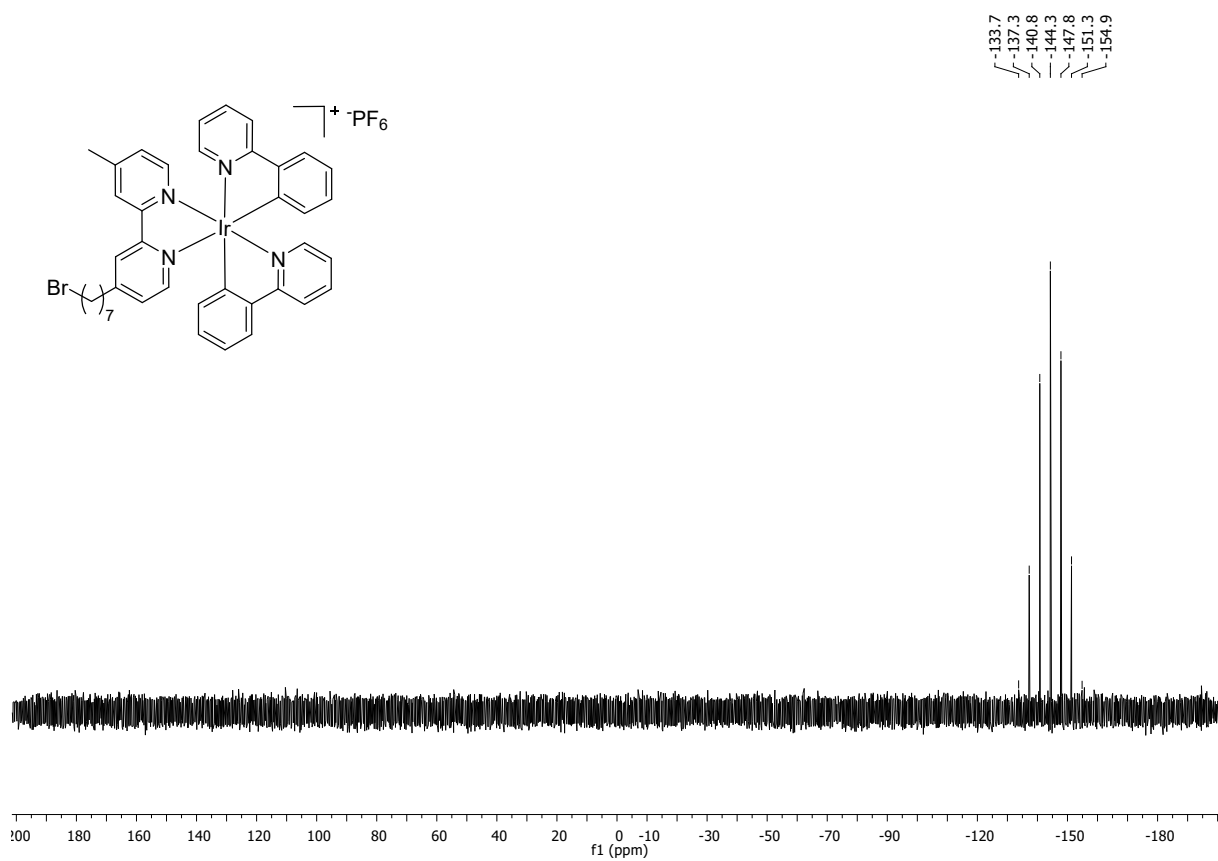


Figure S27. ³¹P NMR (CD₂Cl₂, 202 MHz) spectra of complex 7.



Figure S28. ¹⁹F NMR (CD₂Cl₂, 564 MHz) spectra of complex 7.

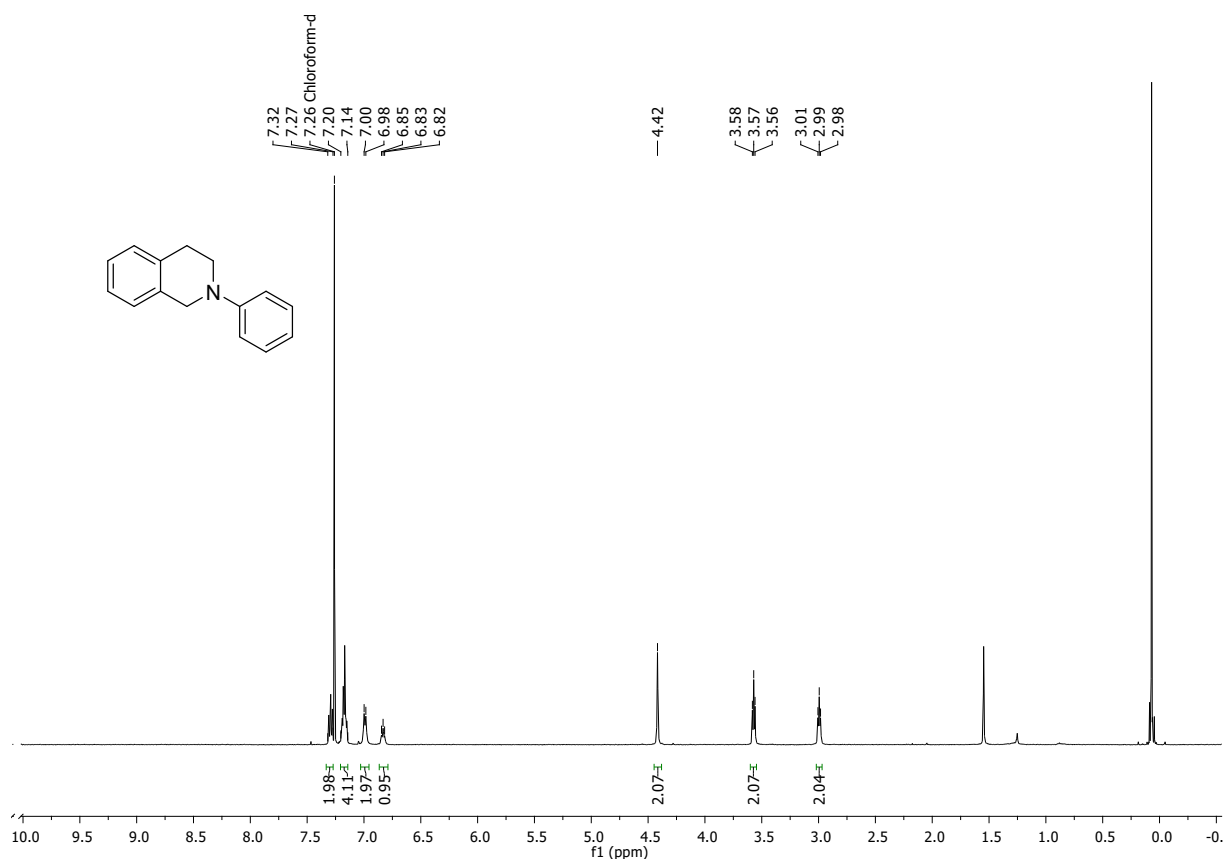


Figure S29. ^1H NMR (500 MHz, CDCl_3) spectra of 2-phenyltetrahydroisoquinoline **8**.

References

1. H. Oikawa, M. Yamahiro, K. Yoshida, N. Ootake, K. Watanabe, K. Ohno, Y. Tsujii and T. Fukuda, EP1650214 (A2), April 26, 2006.
2. T. von Werne and T. E. Patten, *J. Am. Chem. Soc.*, 2001, **123**, 7497.
3. A. E. Fernandes, A. Dirani, C. d'Haese, G. Deumer, W. Guo, P. Hensenne, F. Nahra, X. Laloyaux, V. Haufrond, B. Nysten, O. Riant and A. M. Jonas, *Chem. Eur. J.*, 2012, **18**, 16226.
4. U. Schatzschneider and J. K. Barton, *J. Am. Chem. Soc.*, 2004, **126**, 8630.
5. E. Sauvageot, R. Marion, F. Sguerra, A. Grimault, R. Daniellou, M. Hamel, S. Gaillard and J.-L. Renaud, *Org. Chem. Front.*, 2014, **1**, 639.
6. S. Tugulu, A. Arnold, I. Sielaff, K. Johnsson and H.-A. Klok, *Biomacromolecules*, 2005, **6**, 1602.
7. A. B. Tamayo, B. D. Alleyne, P. I. Djurovich, S. Lamansky, I. Tsyba, N. N. Ho, R. Bau and M. E. Thompson, *J. Am. Chem. Soc.*, 2003, **125**, 7377.
8. J. D. Slinker, A. A. Gorodetsky, M. S. Lowry, J. Wang, S. Parker, R. Rohl, S. Bernhard and G. G. Malliaras, *J. Am. Chem. Soc.*, 2004, **126**, 2763.
9. Z.-M. Zhang, S. Chen and Y.-Z. Liang, *Analyst*, 2010, **135**, 1138.
10. K. J. Goodman and J. Thomas. Brenna, *Anal. Chem.*, 1994, **66**, 1294.