

## Supporting Information

### Synthesis of Modified Fullerenes for Oxygen Reduction Reactions

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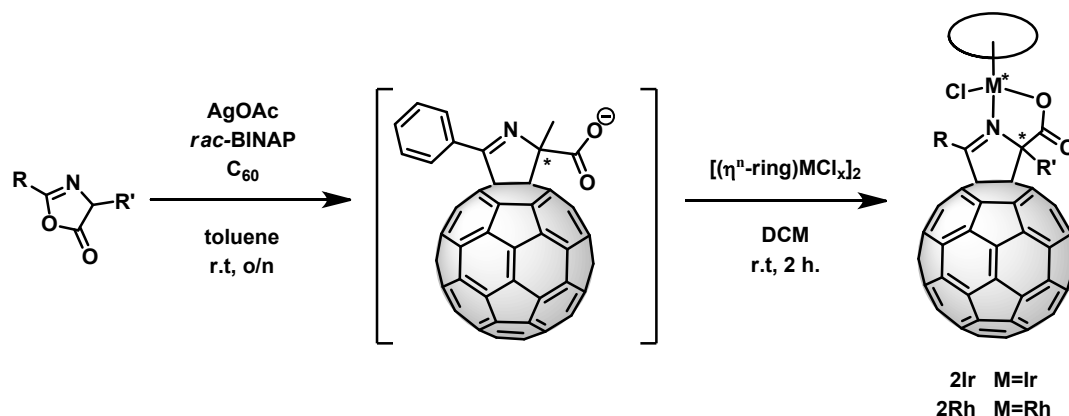
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## General Methods and Materials.

The commercially available reagents and solvents were used without further purification.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded on a BRUKER AVANCE AMX-700 in  $\text{CDCl}_3$  at  $23^\circ\text{C}$ , and referenced to  $\text{CDCl}_3$ ; coupling constants ( $J$ ) are reported in Hz and the chemical shifts ( $\delta$ ) in ppm. Mass spectra were reported on a HP1100EMD (ESI), and BRUKER-REFLEX (MALDI-TOF). Reactions were monitored by thin-layer chromatography carried out on 0.2 mm TLC-aluminum sheets of silica gel (Merck, TLC Silica gel 60 F<sub>254</sub>). Flash column chromatographs were performed using silica gel (230-400 mesh). For conversions, HPLC column *Buckyprep* (Waters) (4.6 × 250 mm) was used. All these values were monitored in a 320 nm spectrophotometer detector. FTIR spectra were carried out using ATR of the solid compounds. The instrument used was a Bruker TENSOR FTIR. The spectral range was 4000-550  $\text{cm}^{-1}$ . X-Ray analysis was carried out in an Agilent SuperNova Cu diffractometer, equipped with an Atlas CCD detector, at 100 K using a Cryostream 700 from Agilent Cryosystems (liquid  $\text{N}_2$ ).

## Experimental Procedures and Characterizations.

### General Procedure for the Synthesis of $[(\eta^n\text{-ring})\text{M}(\text{Pyrrolino}[3,4:1,2][60]\text{fullerene carboxylate})\text{Cl}]$ (2Ir and 2Rh).

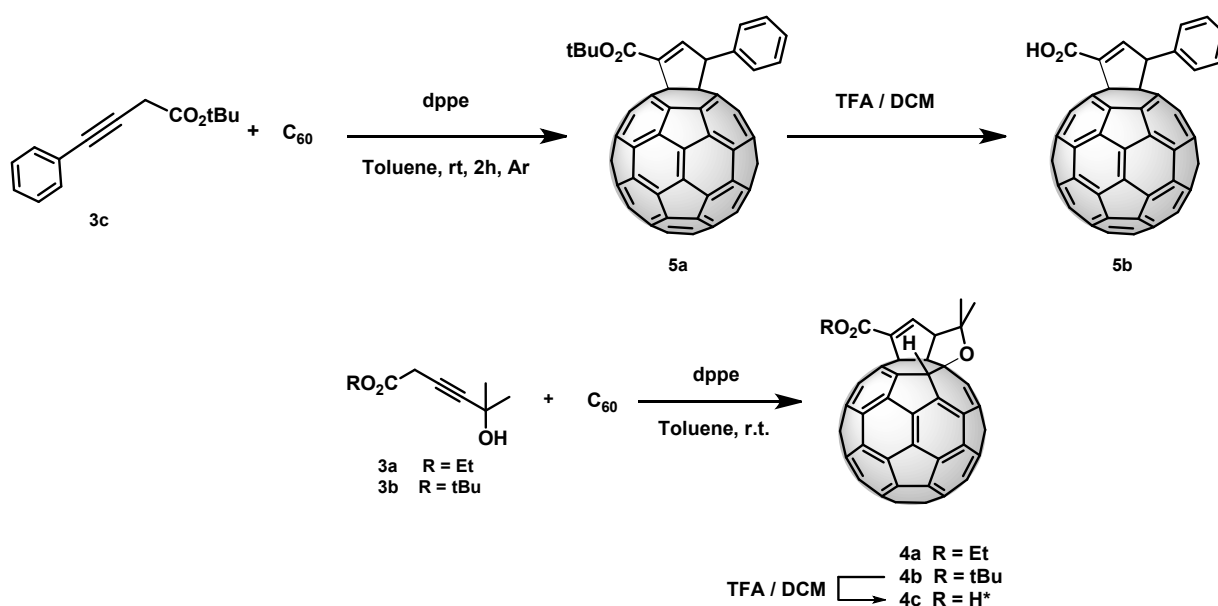


Starting pyrrolino[3,4:1,2][60]fullerene carboxylates were prepared “in situ” following a similar procedure described previously by our research group.<sup>1</sup>

<sup>1</sup> Marco-Martínez J, Reboredo S, Izquierdo M, Marcos V, López JL, Filippone S, *et al.* Enantioselective Cycloaddition of Münchnones onto [60]Fullerene: Organocatalysis versus Metal Catalysis. *J. Am. Chem. Soc.*, **136**, 2897-2904 (2014).

A suspension of a mixture of AgOAc (24mg, 0.143 mmol, 1 eq.) and (+/-)-2,2'-Bis(diphenylphosphino)-1,1'-binaphthyl (BINAP; 89 mg, 0.143 mmol, 1 eq.) in 50 mL of anhydrous toluene is prepared in an 100 ml one-neck round bottom flask. After 5-10 min of stirring at 25°C, azlactone **1** (0.143 mmol, 1 eq.) is added to the solution. Later, [60]fullerene (100 mg, 0.143 mmol, 1 eq.) is added and the purple mixture is stirred overnight at 25°C. Thereafter, a solution of the corresponding metal dimer (Ir or Rh, 0.5 eq.) in DCM (5 mL) is added to the brown solution and stirred for 2 h. Finally, the solvent is evaporated under vacuum and the dark residue is purified by silica-gel column chromatography using CS<sub>2</sub> as eluent (recovering unreacted [60]fullerene). Then, DCM and mixtures of DCM/MeOH (indicated in each case) were employed to obtain the desired products. In all cases, dark brown solids were obtained and centrifuged in dry MeOH (2 x 2 mL, 15 min at 6000 rpm) and dried under vacuum.

#### General Procedure for the Synthesis of **4a-b/5a**.



Starting alkynoates were prepared following the procedure described previously under copper catalysis.<sup>2</sup>

In an ordinary vial under Ar atmosphere, a suspension of the corresponding alkyne **3a-c** (1.0 eq.) and 1,2-bis(diphenylphosphino)ethane (0.2 eq.) in 8.0 mL of dry toluene is prepared. After 15 min. of stirring at room temperature, [60]fullerene (1.07 eq., 0.069 mmol) is added and the mixture is stirred at room temperature overnight. Finally, the solvent is evaporated under vacuum and dark residue is then purified by silica-gel column

<sup>2</sup> Andrés Suárez and Gregory C. Fu, A Straightforward and Mild Synthesis of Functionalized 3-Alkynoates. *Angew. Chem. Int. Ed.*, **43**, 3580-3582 (2004).

chromatography using CS<sub>2</sub> as eluent (for recovering unreacted [60]fullerene). Then, mixtures of solvents (indicated in each case) are used affording desired cyclopenteno[4,5:1,2][60]fullerene derivatives **4a-b/5a**. Conversions are determined by HPLC analysis using Buckyprep (Waters) (4.6 × 250 mm) as column (conditions and retention times are indicated in each case).

#### General Procedure for the Synthesis of **4c/5b**.

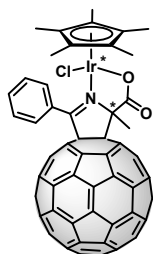
In an ordinary vial, a suspension of the corresponding alkyloxycarbonyl-3-phenyl-1-cyclopenteno[60]fullerene **5a/4b** (1.0 eq., 0,033 mmol) in 3.0 mL of dichloromethane is prepared. After trifluoroacetic acid (120 eq.) is added and the mixture is stirred at room temperature for five hours. Finally, the solvent is evaporated under vacuum and dark residue is then purified by precipitation in dichloromethane and separated by centrifugation (15 minutes at 6000 rpm); after that the residue is precipitated in methanol and separated by centrifugation (15 minutes at 6000 rpm) affording desired cyclopenteno[60]fullerene derivatives **4c/5b**.

#### General Procedure for the Synthesis of [(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>P]<sub>2</sub>Pt(η<sup>2</sup>-C<sub>60</sub>) (**6**).

This platinum-C<sub>60</sub> complex was prepared following the procedure described previously using [(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>P]<sub>2</sub>Pt(η<sup>2</sup>-C<sub>2</sub>H<sub>4</sub>) in toluene under a dinitrogen atmosphere.<sup>3</sup>

#### Characterization of compounds [(η<sup>n</sup>-ring)M(Pyrrolino[3,4:1,2][60]fullerene carboxylate)Cl] (2Ir and 2Rh).

##### Synthesis of [Cp\*Ir(Pyrrolino[3,4:1,2][60]fullerene carboxylate)Cl] (2Ir).

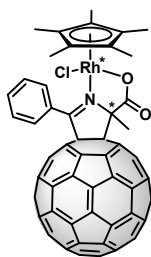


The product was obtained following the standard procedure as a brown solid after FC, eluent DCM and DCM/MeOH (100:1) in 40% isolated yield. <sup>1</sup>H NMR (700 MHz, CDCl<sub>3</sub>): δ 7.51 (m, 5H, Ph), 2.61 (s, 3H, Me), 1.57 (s, 15H, Cp\*) ppm. <sup>13</sup>C NMR (175MHz, CDCl<sub>3</sub>): δ 179.88 (HMBC, C=N), 177.73 (HMBC, C=O), 151.62, 151.19, 148.56, 148.12, 147.38, 147.27, 147.22, 147.18, 146.65, 146.60, 146.33, 146.20, 146.17, 146.15, 146.06, 146.00, 145.97, 145.88, 145.67, 145.63, 145.46, 145.38, 145.27, 145.22, 144.89, 144.82, 144.68, 144.36, 143.55, 143.11, 142.93, 142.87, 142.82, 142.75, 142.69, 142.61, 142.55, 142.07, 141.90, 141.67, 141.61, 141.36, 141.32, 140.05, 139.96,

<sup>3</sup> Paul J. Fagan, Joseph C. Calabrese and Brian Malone, The Chemical Nature of Buckminsterfullerene (C<sub>60</sub>) and the Characterization of a Platinum Derivative. *Science*, **252**, 1160-1161 (1991).

139.78, 139.16, 137.95, 137.40, 134.98, 134.66, 132.40, 130.49 (HSQC, CH-Ph), 90.82 (HMBC, C<sub>3</sub>sp<sup>3</sup>-adduct), 86.51 (C<sub>5</sub>sp<sup>3</sup>), 85.93 (HMBC, Cp\*), 72.46 (HMBC, C<sub>4</sub>sp<sup>3</sup>-adduct), 33.46 (HSQC, Me), 9.25 (HSQC, Me-Cp\*) ppm. HRMS (MALDI+) [M+Na]<sup>+</sup> Calc. for C<sub>80</sub>H<sub>23</sub>ClNNaO<sub>2</sub>Ir: 1280.0939; found: 1280.0934. ATR-FTIR  $\nu$  (C=O) = 1661 cm<sup>-1</sup>.

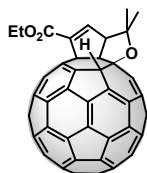
### Synthesis of [Cp\*Rh(Pyrrrolino[3,4:1,2][60]fullerene carboxylate)Cl] (2Rh).



The product was obtained following the standard procedure as a brown solid after FC, eluent DCM and DCM/MeOH (100:1 to 40:1) in 38% isolated yield. <sup>1</sup>H NMR (700 MHz, CDCl<sub>3</sub>):  $\delta$  7.53 (m, 5H, Ph), 2.61 (s, 3H, Me), 1.61 (s, 15H, Cp\*) ppm. <sup>13</sup>C NMR (175MHz, CDCl<sub>3</sub>):  $\delta$  180.27 (C=N), 176.44 (C=O), 151.95, 151.49, 148.74, 147.81, 147.54, 147.33, 147.17, 146.62, 146.56, 146.29, 146.21, 146.14, 146.11, 145.99, 145.95, 145.91, 145.83, 145.58, 145.42, 145.28, 145.23, 145.18, 145.13, 144.80, 144.68, 144.34, 143.53, 142.90, 142.87, 142.86, 142.72, 142.69, 142.57, 142.51, 142.04, 141.92, 141.89, 141.62, 141.43, 141.32, 140.07, 139.91, 139.71, 139.05, 137.85, 137.61, 134.82, 134.68, 132.57, 130.43 (CH-Ph), 94.34 (Cp\*), 94.30 (Cp\*), 91.62 (HMBC, C<sub>3</sub>sp<sup>3</sup>-adduct), 86.17 (C<sub>5</sub>sp<sup>3</sup>), 72.86 (HMBC, C<sub>4</sub>sp<sup>3</sup>-adduct), 33.85 (Me), 9.29 (Me-Cp\*) ppm. HRMS (MALDI+) [M+Na]<sup>+</sup> Calc. for C<sub>80</sub>H<sub>23</sub>ClNNaO<sub>2</sub>Rh: 1190.0365; found: 1190.0351. ATR-FTIR  $\nu$  (C=O) = 1642 cm<sup>-1</sup>.

### Characterization of compounds alkyloxycarbonyl-3-phenyl-1-cyclopenteno [60]fullerenes (4a-b/5a).

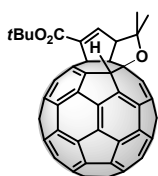
#### Synthesis of 4a.



The adduct **4a** was prepared according to the general procedure using ethyl-5-hydroxy-5-methyl-3-hexynoate **3a** (11.1 mg, 0.065 mmol), [60]fullerene (50 mg, 0.069 mmol) and 1,2-bis(diphenylphosphino)ethane (5.2 mg, 0.0130 mmol). Conversion: 37% (eluent: hexane:CH<sub>2</sub>Cl<sub>2</sub>, 1:1). <sup>1</sup>H NMR (700 MHz, CDCl<sub>3</sub>)  $\delta$  7.57 (s, 1H), 6.29 (s, 1H), 4.45 (d, J = 2.4 Hz, 1H), 4.45 – 4.37 (m, 2H), 1.96 (s, 3H), 1.85 (s, 3H), 1.41 (t, J = 7.1 Hz, 3H). <sup>13</sup>C NMR (176 MHz, CDCl<sub>3</sub>)  $\delta$  163.36, 151.10, 150.14, 149.18, 148.92, 148.87, 148.19, 148.10, 147.93, 147.85, 147.13, 147.11, 146.90, 146.76, 146.70, 146.48, 146.36, 146.06, 145.72, 145.34, 145.28, 145.12, 145.06, 145.00, 144.92, 144.84, 144.83, 144.80, 144.63, 144.39, 144.34, 144.29, 144.19, 144.17, 144.14, 143.91, 143.89, 143.75, 143.44, 143.10, 143.06, 142.91,

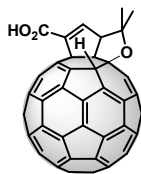
142.88, 142.74, 142.49, 142.48, 142.23, 141.60, 141.44, 140.88, 140.35, 139.06, 138.07, 138.01, 136.18, 136.10, 134.55, 97.16, 87.04, 77.21, 77.03, 76.84, 76.11, 73.32, 70.64, 61.43, 59.58, 32.01, 28.44, 14.25. HRMS (MALDI+): [M+Na]<sup>+</sup> Calc. for C<sub>69</sub>H<sub>14</sub>NaO<sub>3</sub>: 913.0841; found: 913.0821.

### Synthesis of 4b.



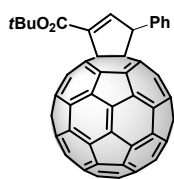
The adduct **4b** was prepared according to the general procedure using *tert*-butyl-5-hydroxy-5-methyl-3-hexynoate **3b** (12.9 mg, 0.065 mmol), [60]fullerene (50 mg, 0.069 mmol) and 1,2-bis(diphenylphosphino)ethane (5.2 mg, 0.0130 mmol). Conversion: 35% (eluent: hexane:CH<sub>2</sub>Cl<sub>2</sub>, 1:1). <sup>1</sup>H NMR (700 MHz, CDCl<sub>3</sub>) δ 7.47 (s, 1H), 6.29 (s, 1H), 4.40 (s, 1H), 1.95 (s, 3H), 1.83 (s, 3H), 1.58 (s, 9H). <sup>13</sup>C NMR (176 MHz, CDCl<sub>3</sub>) δ 162.67, 151.17, 150.32, 149.16, 148.91, 148.84, 148.16, 148.12, 148.10, 147.13, 147.10, 146.98, 146.90, 146.70, 146.46, 146.35, 146.02, 145.72, 145.35, 145.28, 145.19, 145.14, 145.09, 144.92, 144.82, 144.78, 144.61, 144.36, 144.29, 144.21, 144.14, 143.90, 143.89, 143.72, 143.11, 143.02, 142.88, 142.71, 142.66, 142.49, 142.47, 142.23, 141.51, 141.49, 140.87, 140.21, 139.64, 139.04, 138.02, 136.20, 136.10, 134.53, 97.15, 87.01, 82.76, 77.20, 77.02, 76.84, 76.34, 73.33, 70.33, 59.60, 32.02, 28.38, 28.28. HRMS (MALDI+): [M]<sup>+</sup> Calc. for C<sub>71</sub>H<sub>18</sub>O<sub>3</sub>: 918.1256; found: 918.1234.

### Synthesis of 4c.



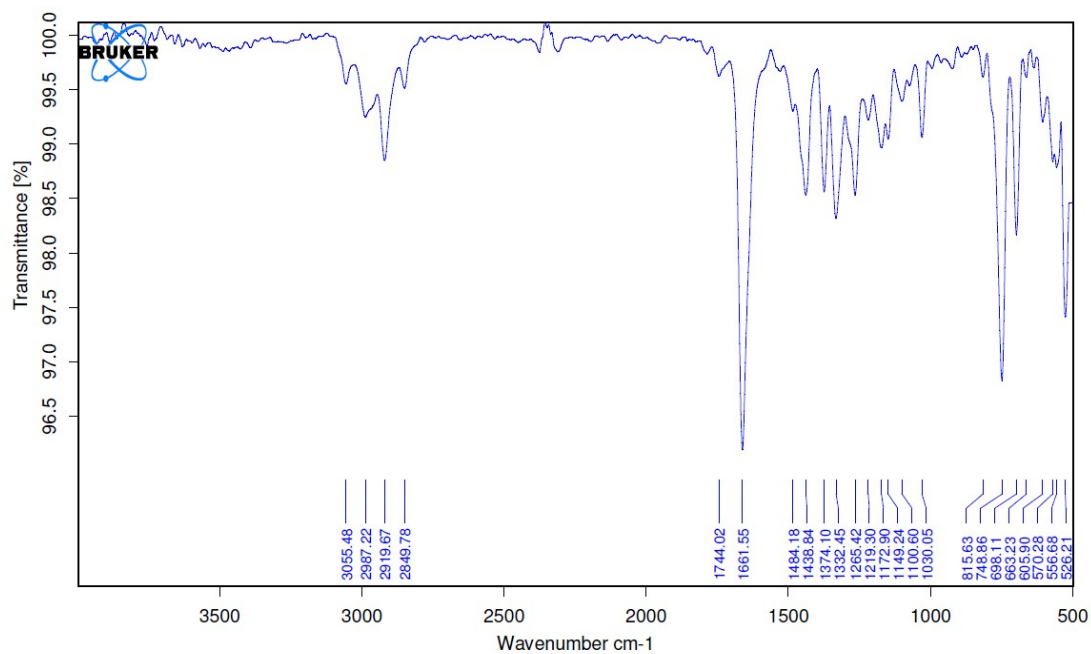
The adduct **4c** was prepared according to the general procedure using ethyl-5-hydroxy-5-methyl-3-hexynoate **4b** (30 mg, 0.033 mmol) and 0.3 mL of TFA. Yield: 77%. <sup>1</sup>H NMR (700 MHz, THF) δ 7.61 (s, 1H), 6.38 (s, 1H), 4.57 (s, 1H), 1.92 (s, 3H), 1.80 (s, 3H). <sup>13</sup>C NMR (176 MHz, THF) δ 161.87, 149.91, 148.96, 147.14, 147.06, 146.88, 146.83, 146.76, 146.33, 146.12, 145.76, 145.49, 145.07, 144.99, 144.88, 144.66, 144.42, 144.31, 144.23, 143.92, 143.85, 143.62, 143.42, 143.39, 143.27, 142.97, 142.78, 142.74, 142.73, 142.62, 142.38, 142.36, 142.25, 142.22, 142.20, 142.11, 142.07, 141.79, 141.77, 141.29, 140.91, 140.82, 140.79, 140.77, 140.39, 140.29, 139.55, 139.24, 138.69, 138.02, 136.84, 135.99, 135.62, 134.07, 133.89, 132.65, 95.16, 85.36, 74.49, 71.78, 68.89, 65.03, 64.91, 64.81, 64.74, 64.68, 64.62, 64.55, 64.43, 64.30, 57.78, 29.24, 25.63, 23.01, 22.92, 22.80, 22.70, 22.59, 22.47, 22.36, 22.25. HRMS (ESI): [M-H]<sup>-</sup> Calc. for C<sub>67</sub>H<sub>9</sub>O<sub>3</sub>: 861.0557; found: 861.0375.

Synthesis of (3R)-1-*tert*-butoxycarbonyl-3-phenyl-1-cyclopenteno[4,5:1,2][60]fullerene (**5a**).

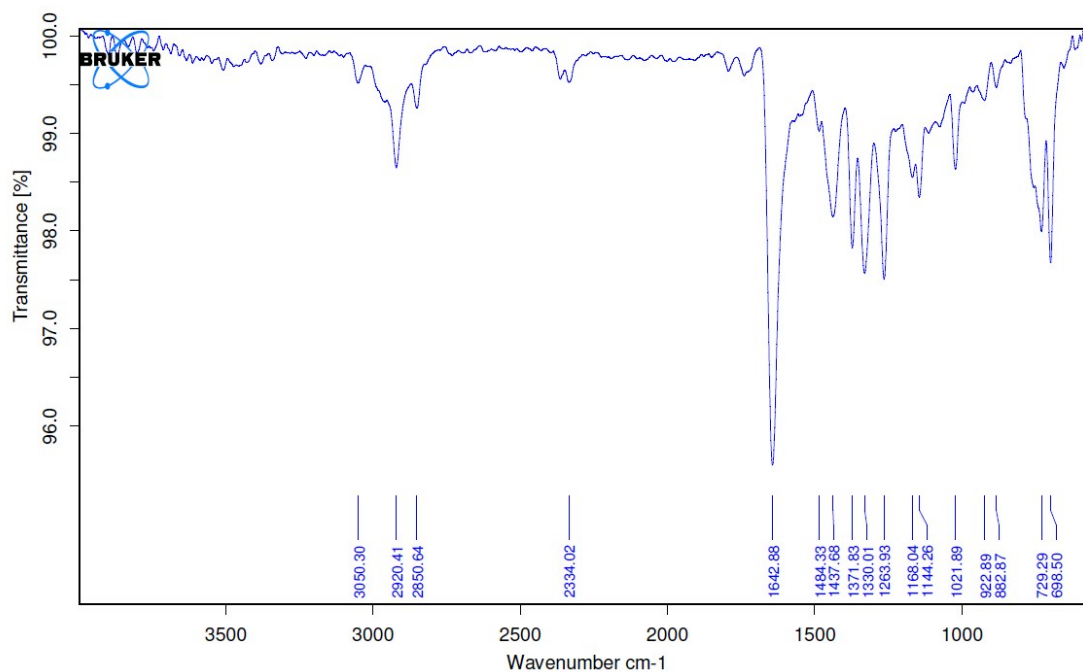


The adduct **5a** was prepared according to the general procedure using tert-butyl-4-phenyl-3-butynoate **3c** (3.4 mg, 0.016 mmol), [60]fullerene (12 mg, 0.017 mmol) and 1,2-bis(diphenylphosphino)ethane (1.6 mg, 0.004 mmol). Conversion: 49% (eluent: hexane:CH<sub>2</sub>Cl<sub>2</sub>, 3:1). <sup>1</sup>H NMR (700 MHz, CDCl<sub>3</sub>) δ 1.65 (s, 9H), 6.02 (d, J= 2.5 Hz, 1H), 7.39 (t, J= 7.5 Hz, 1H), 7.50 (t, J= 7.8 Hz, 2H), 7.72 (d, J= 7.2 Hz, 2H), 7.80 (d, J= 2.5 Hz, 1H) ppm. <sup>13</sup>C NMR (176 MHz, CDCl<sub>3</sub>) δ 28.4, 29.7, 63.3, 76.2, 76.4, 82.8, 128.2, 129.1, 129.8, 134.1, 135.5, 135.8, 135.9, 139.0, 139.3, 139.46, 139.50, 139.7, 140.2, 141.6, 141.6, 141.7, 141.8, 141.93, 141.94, 142.0, 142.1, 142.21, 142.22, 142.39, 142.42, 142.62, 142.64, 142.68, 142.70, 143.07, 143.12, 144.36, 144.43, 144.5, 144.8, 144.97, 144.99, 145.1, 145.30, 145.31, 145.34, 145.4, 145.5, 145.6, 145.7, 145.9, 145.98, 145.99, 146.1, 146.17, 146.20, 146.23, 146.3, 146.4, 147.3, 147.4, 148.1, 148.7, 150.6, 151.2, 153.9, 157.2, 163.0 ppm. HRMS (MALDI+): [M]<sup>+</sup> Calc. for C<sub>74</sub>H<sub>16</sub>O<sub>2</sub>: 936.1150; found: 936.1165.

## Representative IR spectra of compounds 2Ir, 2Rh



[Cp\*Ir(Pyrrolino[3,4:1,2][60]fullerene carboxylate)Cl] (2Ir).

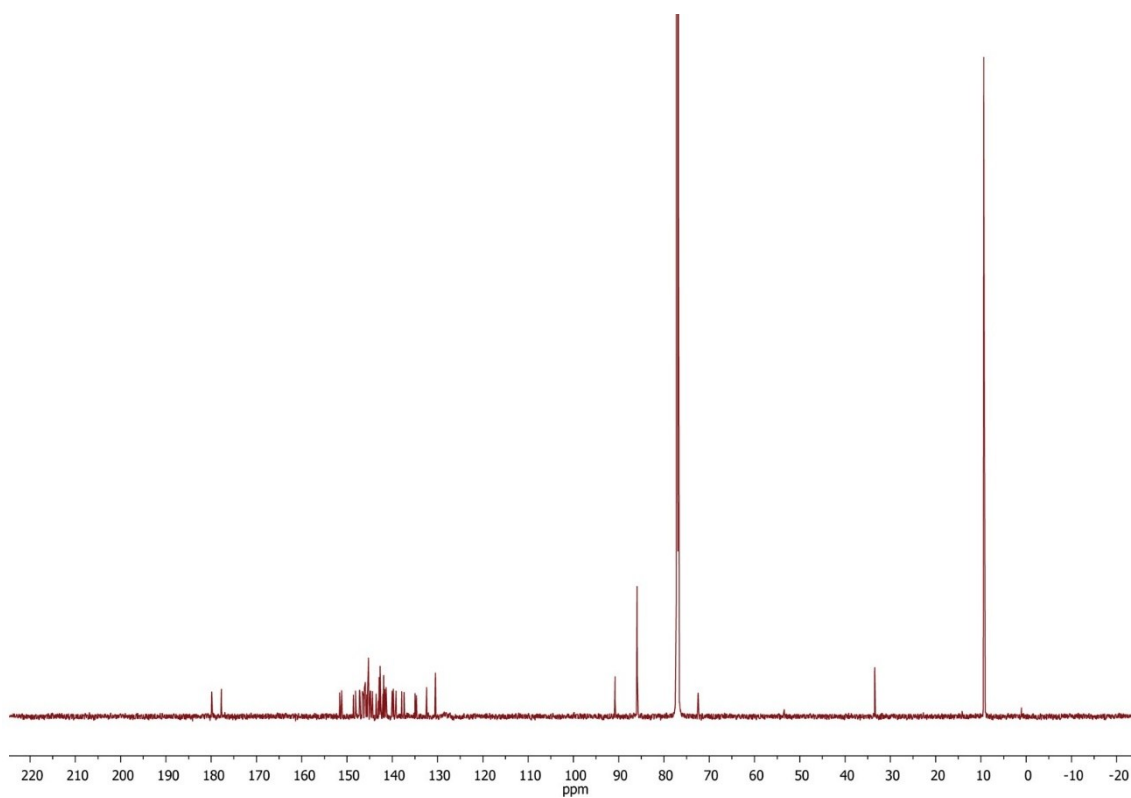
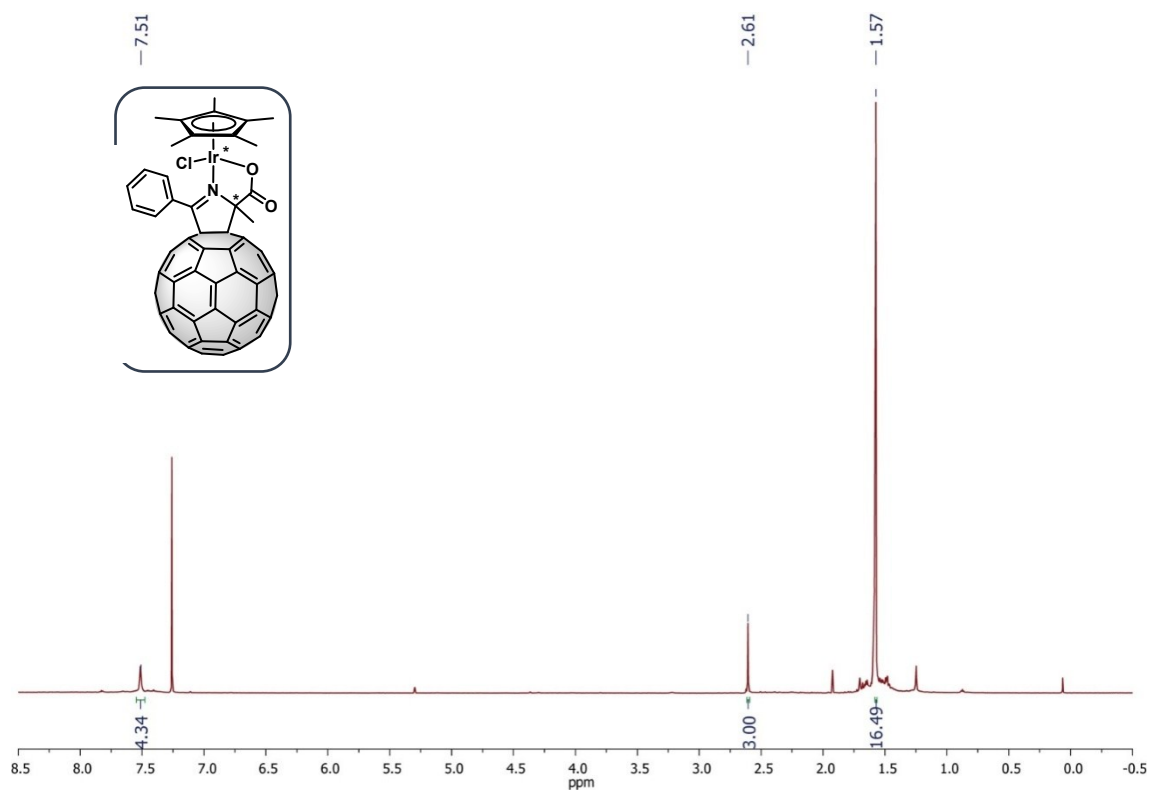


[Cp\*Rh(Pyrrolino[3,4:1,2][60]fullerene carboxylate)Cl] (2Rh).

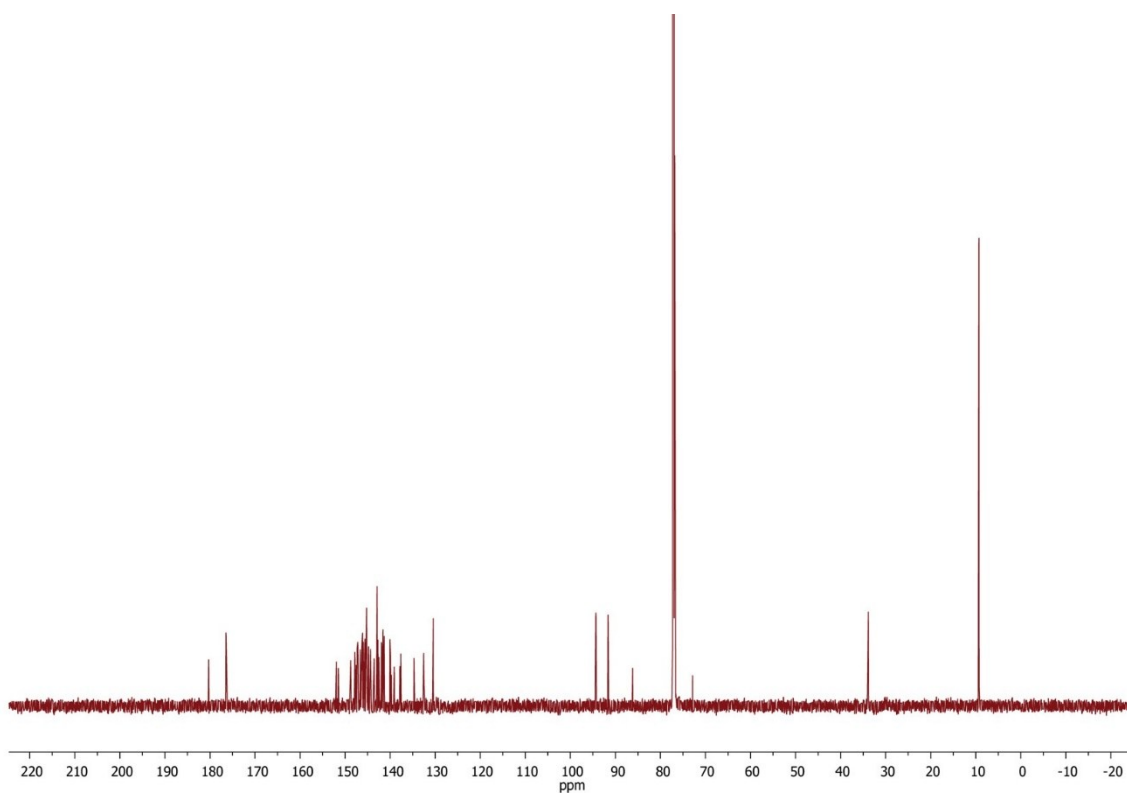
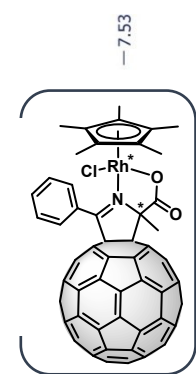
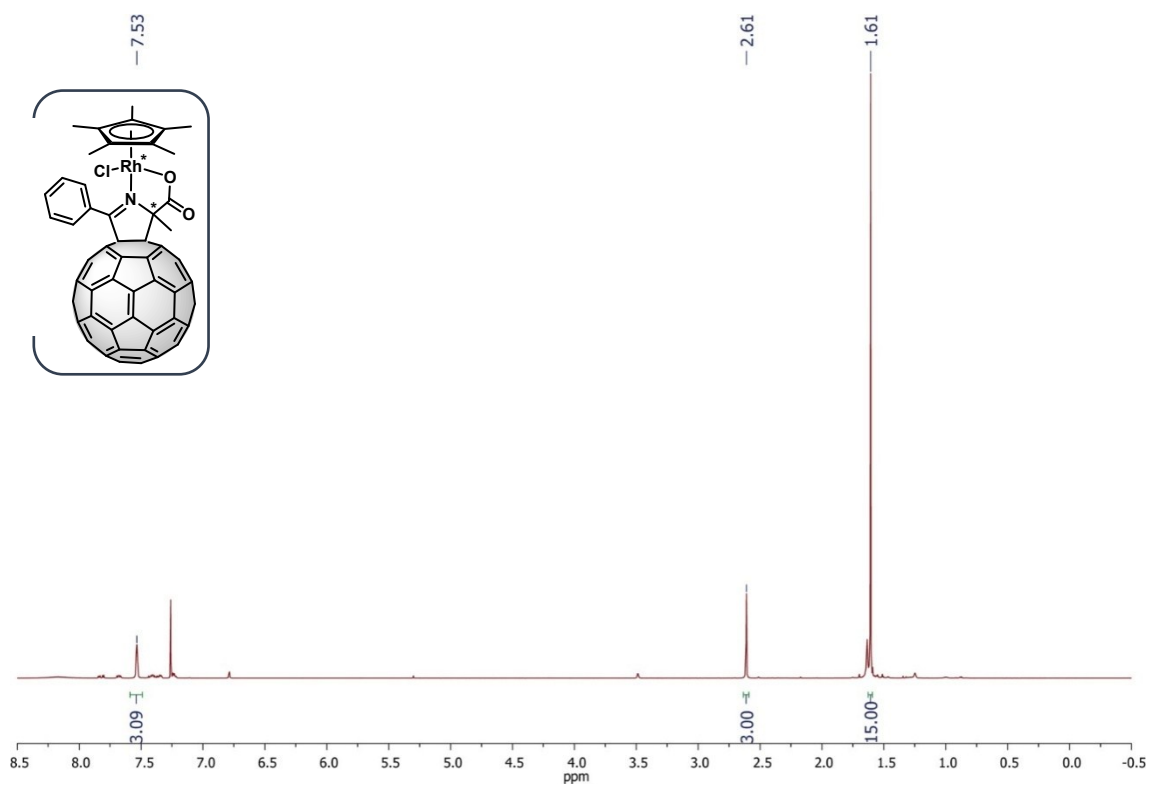


## Representative $^1\text{H}$ -NMR and $^{13}\text{C}$ -NMR spectra of compounds.

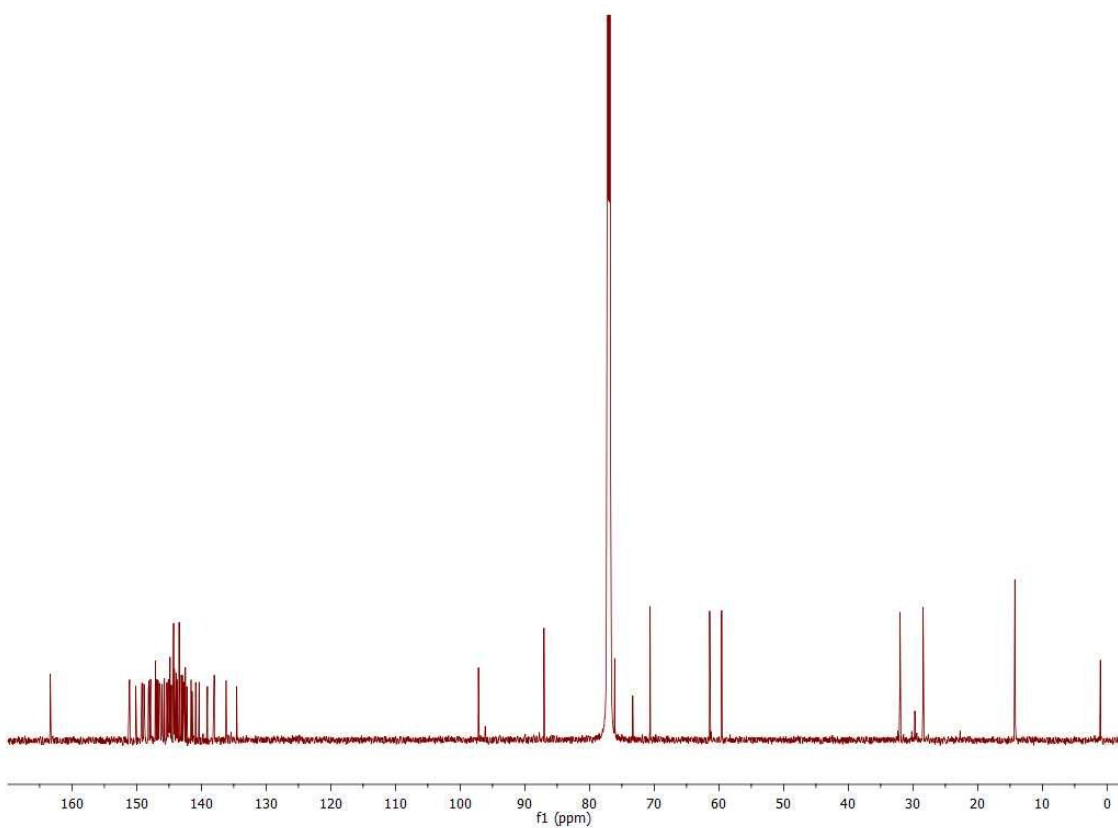
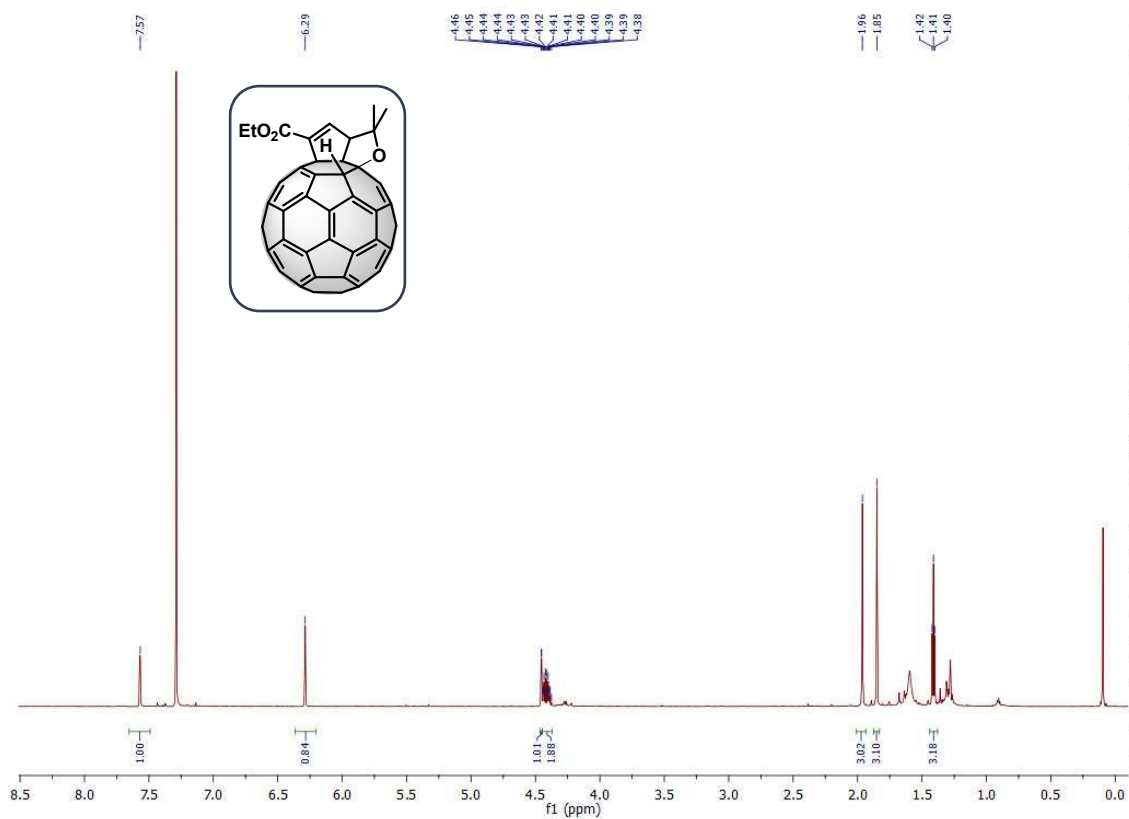
$[\text{Cp}^*\text{Ir}(\text{Pyrrolino}[3,4:1,2][60]\text{fullerene carboxylate})\text{Cl}] (2\text{Ir})$ .



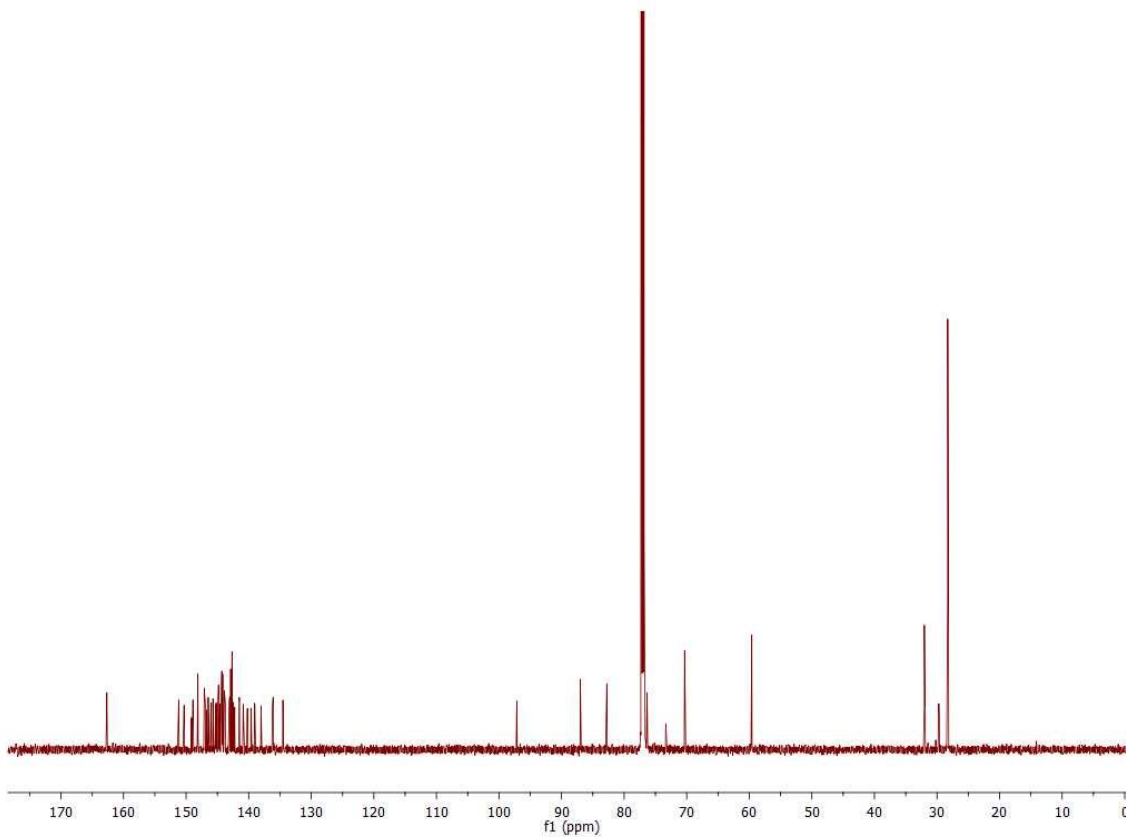
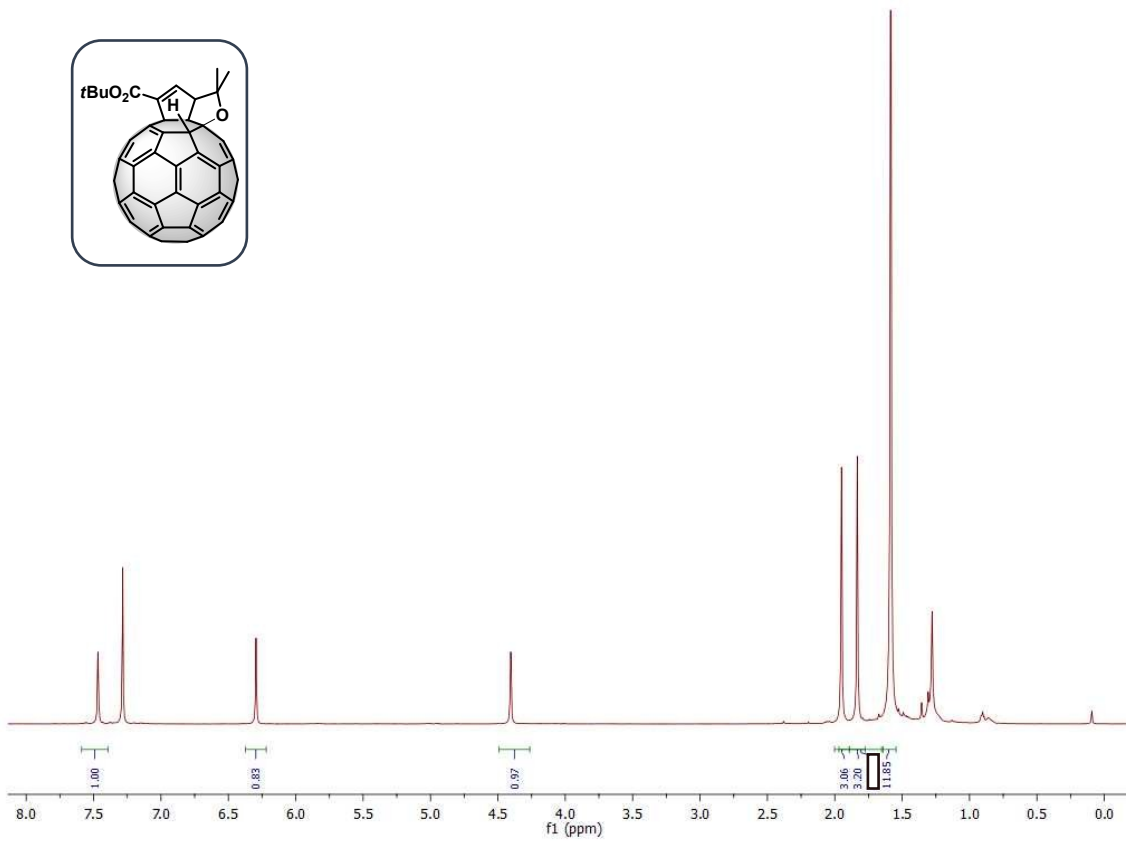
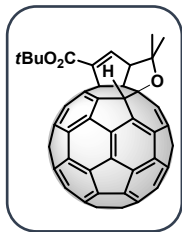
[Cp\*Rh(Pyrrolino[3,4:1,2][60]fullerene carboxylate)Cl] (2Rh).



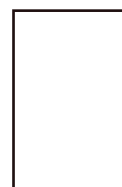
4a.

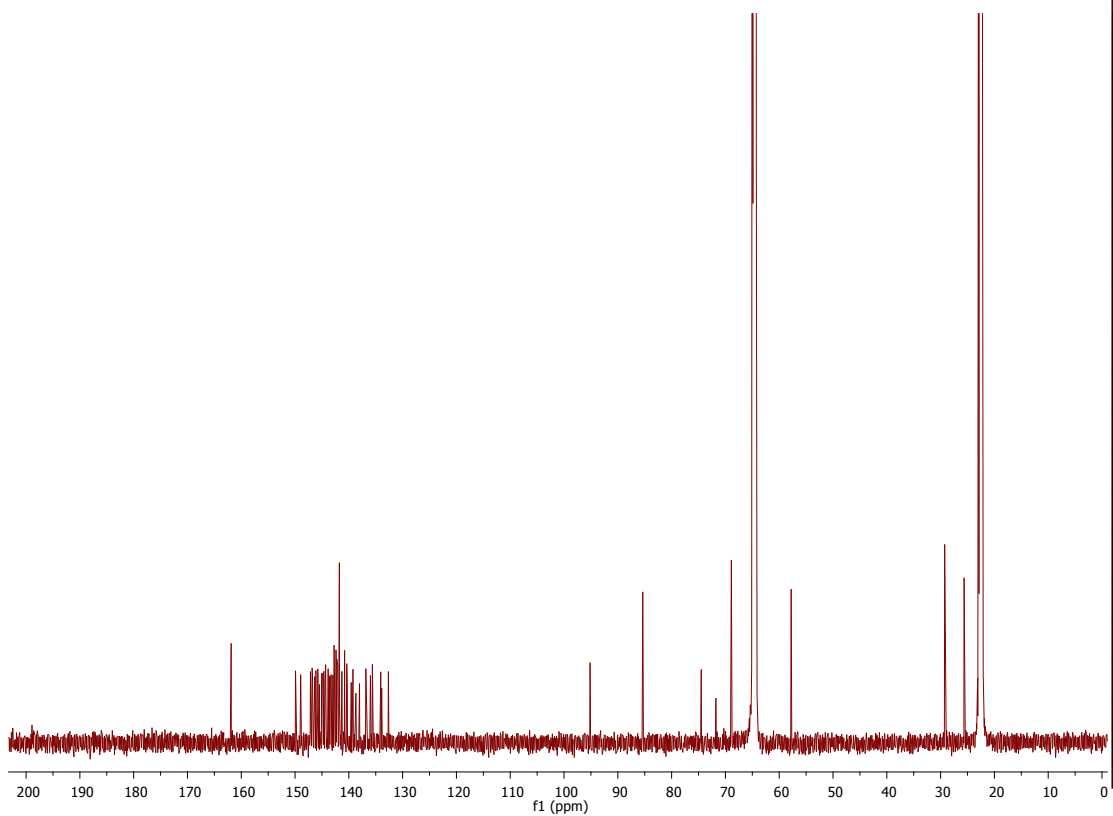
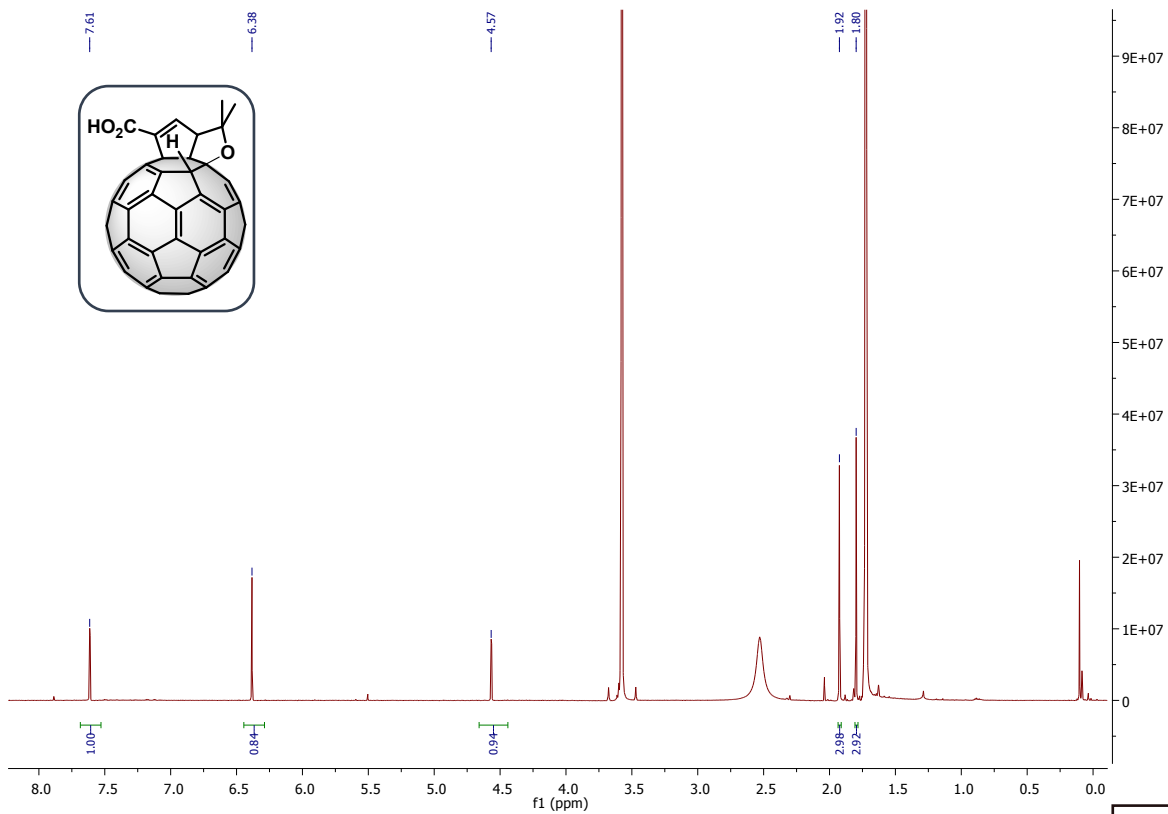


4b.



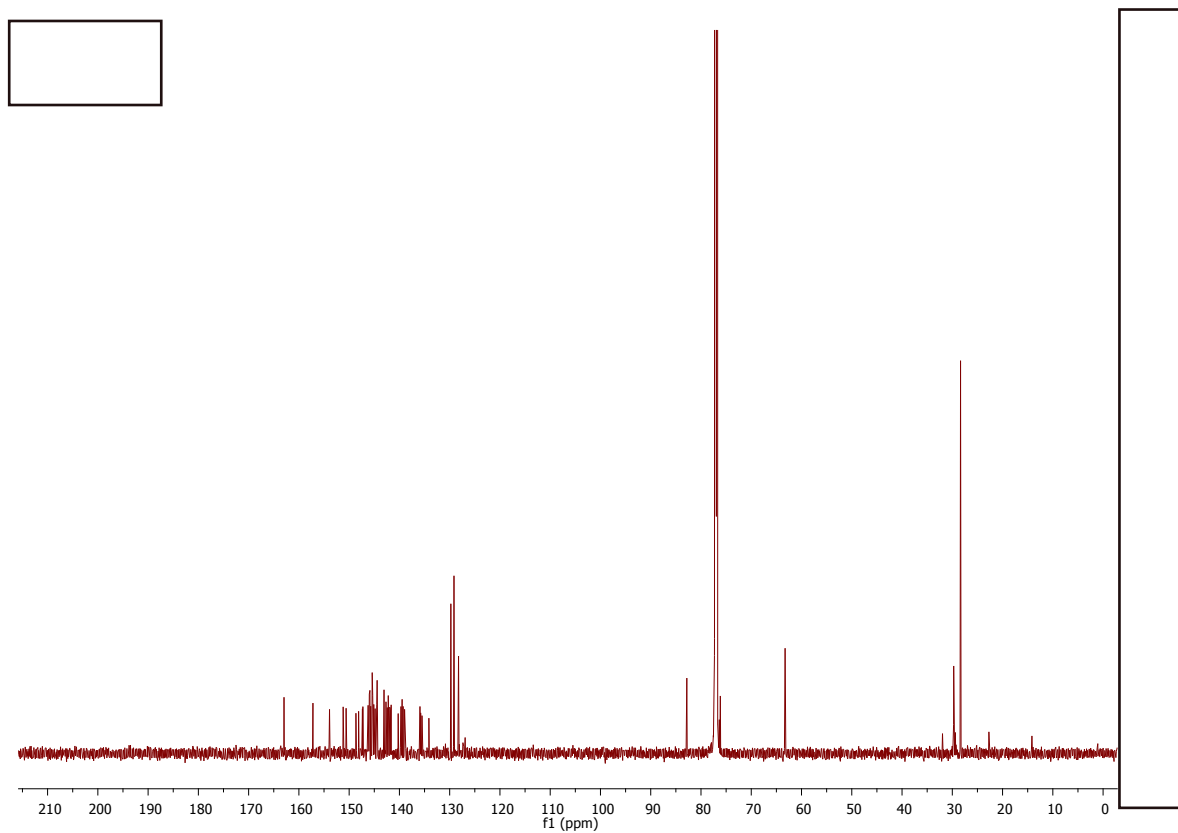
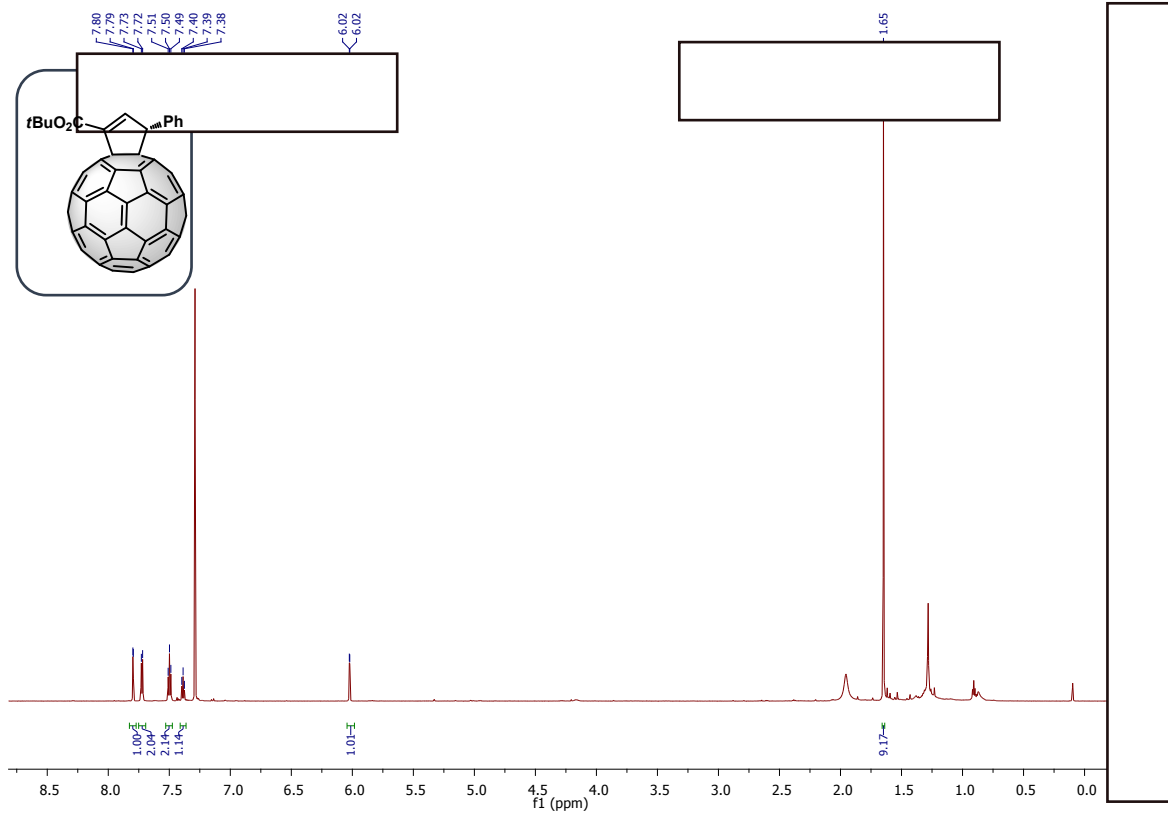
4c.





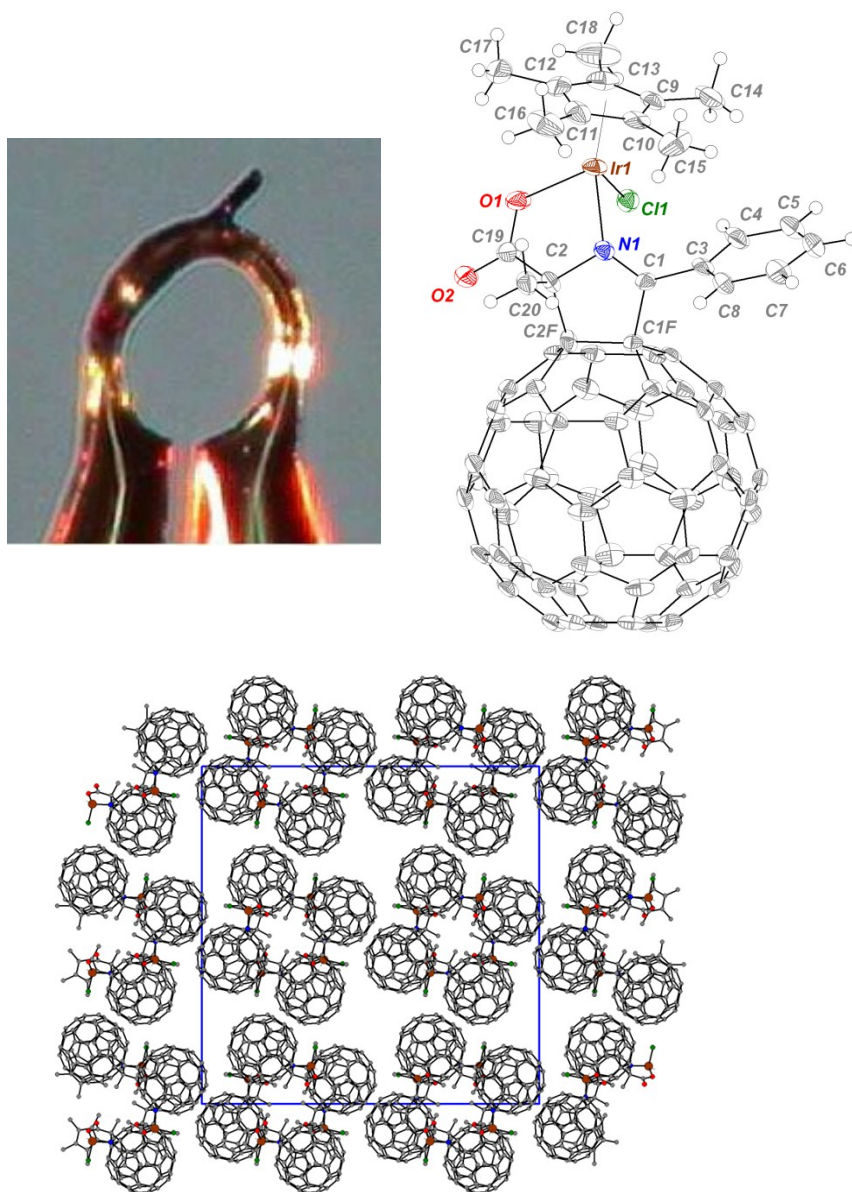
**1-tert-butoxycarbonyl-3-phenyl-1-cyclopenteno[4,5:1,2][60]fullerene**

**(5a).**



**Determination of the Configuration by X-Ray Analysis<sup>4</sup>**

The relative configuration of a single crystal (red small needles) of a sample of Ir-pyrrolino[60]fullerene hybrid **2Ir**, obtained by slow evaporation of a mixture of CS<sub>2</sub>/hexane, shows that iridium adopts a pseudotetrahedral geometry in a five member ring. Moreover, the metal is linked with a Cp\* group and a chlorine atom that is in a *trans* position with respect to the methyl group of pyrroline moiety.<sup>5</sup>



**Figure S1:** X-ray determined crystal structure and crystal structure over the coordinate axes for compound **2Ir**.

### Crystal data and structure refinement for compound **2Ir**

Empirical formula  $C_{80}H_{23}ClIrNO_2$

<sup>4</sup> SGIker technical support is gratefully acknowledged for X-ray analysis.

<sup>5</sup> Crystal structure has been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition number CCDC 960717.

|                                    |                                                                                                                     |
|------------------------------------|---------------------------------------------------------------------------------------------------------------------|
| Formula weight                     | 1257.64                                                                                                             |
| Temperature (K)                    | 100(1)°                                                                                                             |
| Wavelength (CuK $\alpha$ )         | 1.54184 Å                                                                                                           |
| Crystal system                     | Tetragonal                                                                                                          |
| Space group                        | I41/a                                                                                                               |
| Unit cell dimensions               | a = 34.7078(6) Å $\alpha = 90^\circ$<br>b = 34.7078(6) Å $\beta = 90^\circ$<br>c = 18.0586(3) Å $\gamma = 90^\circ$ |
| Volume                             | 21754.0(6) Å <sup>3</sup>                                                                                           |
| Z                                  | 16 (z'=1)                                                                                                           |
| Density (calculated)               | 1.536(1) g/cm <sup>3</sup>                                                                                          |
| Absorption coefficient             | 5.636 mm <sup>-1</sup>                                                                                              |
| F(000)                             | 9920                                                                                                                |
| Crystal size                       | 0.02 x 0.02 x 0.25 mm <sup>3</sup>                                                                                  |
| Theta range for data collection    | 2.55 to 72.46°.                                                                                                     |
| Index ranges                       | -29<=h<=30, 0<=k<=42, 0<=l<=22                                                                                      |
| Reflections collected              | 86819                                                                                                               |
| Independent reflections            | 10773 [R(int) = 0.149]                                                                                              |
| Absorption correction              | Analytical                                                                                                          |
| Refinement method:                 | SHELXL97                                                                                                            |
| Data / restraints / parameters     | 10773 / 0 / 772                                                                                                     |
| Goodness-of-fit on F <sup>2</sup>  | 0.918                                                                                                               |
| Final R indices [I>2 $\sigma$ (I)] | R1 = 0.0461, wR2 = 0.1022                                                                                           |
| R indices (all data)               | R1 = 0.00835, wR2 = 0.1129                                                                                          |
| Largest diff. peak and hole        | 1.646 and -1.434 eÅ <sup>-3</sup>                                                                                   |



## Photo-electrochemical cell preparation and characterization

SnO<sub>2</sub>:F (FTO) TEC 15 covered glass substrates (~200 μm, thickness, 15 Ω/sq resistance) were purchased from Dyesol. rr-P3HT (regio-regularity of 99.5 % ; average molecular weight 54,000-75,000 g/mol, Sigma-Aldrich), acting as electron donor in a BHJ configuration, was used without any further purification.

Blends with different fullerene electron acceptors synthesized in this work (P3HT:fullerene architecture) were realized by using chlorobenzene as the organic solvent for both components, dissolved at a concentration of 20 g/L and a relative ratio 1:1. The solutions were subsequently heated at 50 °C and stirred for 120 min, sonicated for 10 minutes at 50 °C and finally spin coated on top of previously cleaned FTO-covered glass substrates. Spinning parameters were properly optimized in order to obtain comparable film thicknesses, in the order of 140 nm.

Photoelectrodes with bilayer-like architecture (P3HT:PCBM/fullerene) were also fabricated. In these cases, the fullerene derivative was dissolved in dichlorometane (5g/L concentration), stirred for 120 min and sonicated for 10 minutes at room temperature, and finally deposited by spin coating on top of the underlying P3HT:PCBM layer.

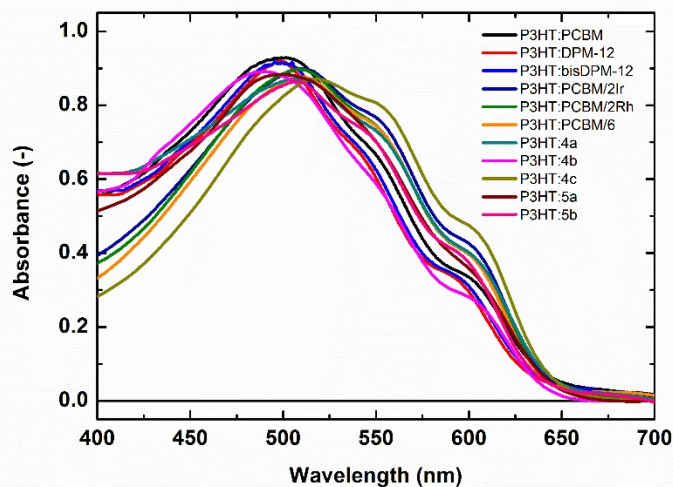
Post thermal annealing at 130° C for 10 minutes in a N<sub>2</sub> atmosphere was carried out on all devices, in order to evaporate residual solvent and to get properly phase segregation of the blend.

The optical properties of the samples in the range of 400–700 nm were measured with a UV/Vis/nIR spectrometer (Perkin Elmer Lambda 1050) in transmission and reflectance mode. Absorbance values of all fabricated devices are fully comparable (Figure S2).

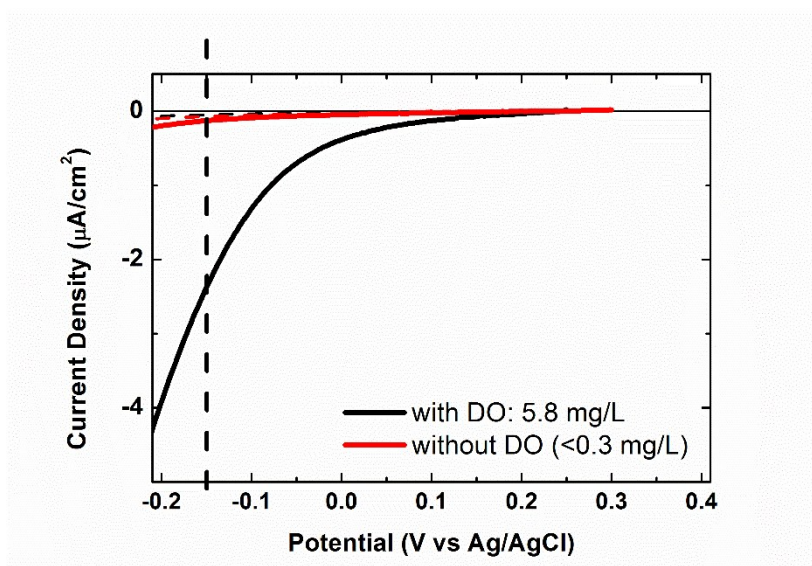
Electrochemical characterization was carried out in a quartz cell by using an Autolab potentiostat/galvanostat (PGSTAT 302N), in a three electrode configuration. A Pt wire was used as the counter electrode (CE) and an Ag/AgCl electrode filled with saturated KCl solution (0.197 V versus the standard hydrogen electrode at 25 °C) was used as the reference electrode (RE). All measurements were performed by employing phosphate buffered saline solution (PBS) at pH 7.4 (obtained by mixing 39 mL of 0.1 M sodium dihydrogen phosphate (NaH<sub>2</sub>PO<sub>4</sub>) and 61 mL of 0.1 M sodium hydrogen phosphate (Na<sub>2</sub>HPO<sub>4</sub>) and adjusting the final volume to 200 mL with deionized water) at room temperature 22 °C. A 300 W Xe light source equipped with AM filters (Lot Quantum

Design, model LS0306) calibrated to 1 sun on the electrode surface in the electrolyte was used to illuminate the photocathode.

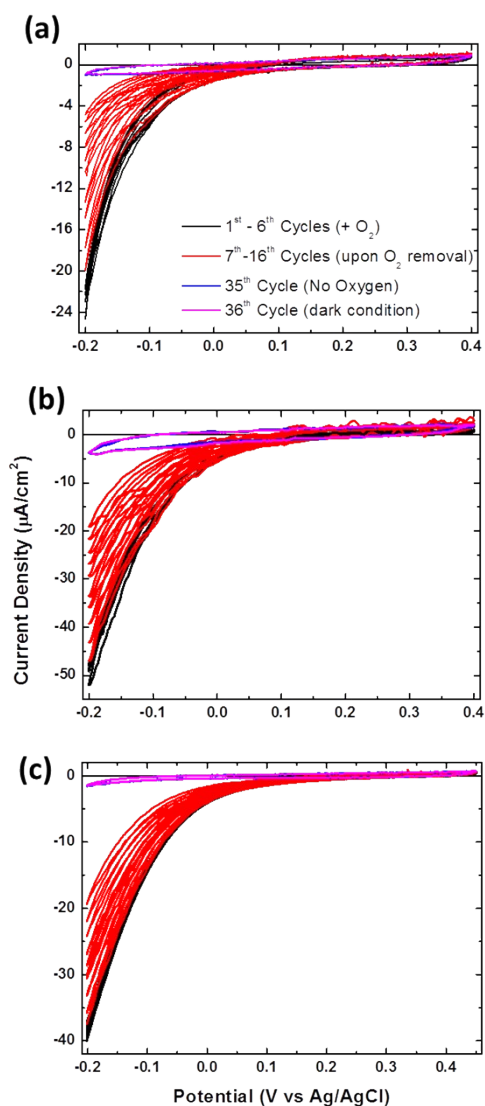
Linear Scan Voltammetry (LSV) and Cyclic Voltammetry (CV) techniques have been employed to evaluate the response of photocathodes. Linear Sweep Voltammetry (LSV) was performed with a scan rate of 10 mV/s while Cyclic Voltammetry has been done using 200 mV/s. DO concentration solution was monitored through a commercial D.O. sensor (Oxygen meter OXI 45+, Crison). Deoxygenation of the solution was achieved purging N<sub>2</sub> into the solution, while O<sub>2</sub>-saturated conditions were obtained purging O<sub>2</sub>. All the data were handled by NOVA 1.10.3 package software.



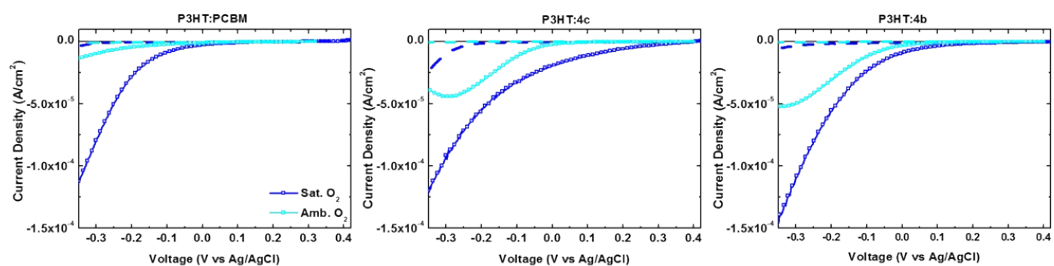
**Figure S2.** Optical absorption spectra of BHJ ( $P_3HT$ :fullerene) and bilayer ( $P_3HT$ :PCBM/fullerene) thin films based on  $P_3HT$  as electron donor and different fullerene derivatives as electron acceptors/catalysts for promotion of ORR. Fullerene compounds include PCBM (here used as benchmark, reference material), bis-adducts fullerenes (DPM-12 and bisDPM-12), fullerenes endowing metallic catalytic centers (**2Ir**; **2Rh**; **6**) and metal-free organo-fullerene catalysts (**4a**, **4b**, **4c**, **5a**, **5b**).



**Figure S3.** Linear Scan Voltammetry (LSV) measurements under dark (dashed lines) and upon visible light (1 SUN) (solid lines) on FTO/P<sub>3</sub>HT:PCBM in presence and in absence of dissolved oxygen (DO). As previously demonstrated for the organic blend APFO<sub>3</sub>:PCBM, the origin of the photocurrent can be unambiguously attributed to the occurrence of ORR at the polymer/electrolyte interface.



**Figure S4.** Cyclic Voltammetry (CV) measurements (scan rate 200 mV/s) for the best performing photoelectrochemical cells for ORR, based on BHJ thin films P<sub>3</sub>HT:6 (panel b) and P<sub>3</sub>HT:4c (panel c), as compared to the reference standard P<sub>3</sub>HT:PCBM (panel a). The first six cycles (dark lines) are performed at fixed dissolved oxygen concentration (5.8 mg/L), under 1 SUN illumination, showing optimal repeatability. Starting from the 7<sup>th</sup> cycle, oxygen is progressively removed from the solution, through nitrogen gas purging, and consistently photocurrent densities are substantially, progressively reduced (7<sup>th</sup>-16<sup>th</sup> cycles, red lines). When oxygen was completely removed (35<sup>th</sup> cycle, blue line) photocurrent values comparable to dark current (36<sup>th</sup> cycle, orange line) are recorded. The origin of the photocurrent signal is thus confirmed to be due to effective promotion of ORR in all cases, as previously demonstrated for the only case of P<sub>3</sub>HT:PCBM BHJ.



**Figure S5.** Linear Scan Voltammetry (LSV) measurements (scan rate, 10 mV/s) under dark (dashed lines) and upon visible light (1 SUN) (empty squares) on FTO/P<sub>3</sub>HT: PCBM (left panel), FTO/P<sub>3</sub>HT:4**c** (center panel) and FTO/P<sub>3</sub>HT:4**b** (right panel) for the O<sub>2</sub>-ambient equilibrated (5.8 mg/L) (cyan color) and for O<sub>2</sub>-saturated condition (blue color).

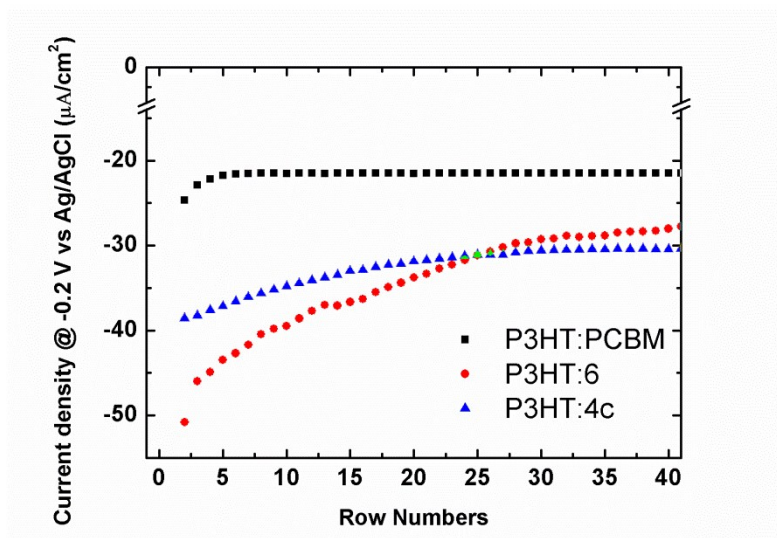


Figure S6. Current density recorded at -0.2V vs Ag/AgCl upon white light illumination (1 SUN) and constant 5.8 mg/L dissolved oxygen (DO) concentration for consecutive CV cycles (scan rate 200 mV/s).

**Scheme S1.** Four and two electron processes for oxygen reduction reaction (ORR) in both alkaline and acidic media.

Alkaline medium:



Acidic medium:

