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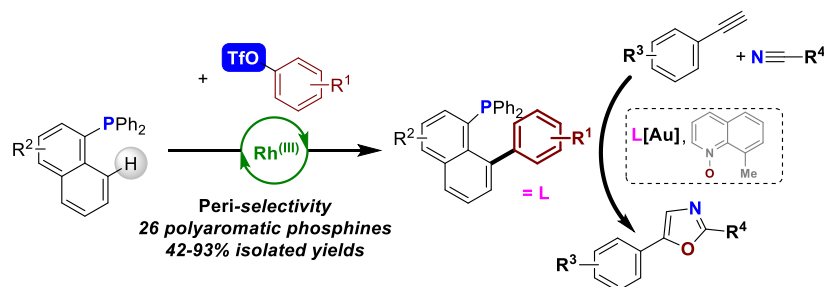
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# Aryl Triflates in Phosphorus-Directed Rhodium(III)-Catalyzed C–H Activation

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**Abstract** Aryl triflates were selected as suitable electrophile coupling partners for the *P*-directed rhodium(III) catalyzed *C*–*H* arylation of polyaromatic phosphines. We report herein simple conditions in the *peri*-*C*–*H* functionalization of polyarylphosphines, where the  $[Rh(III)Cl_2Cp^*]_2$  precatalyst is employed to provide a convenient access to polyarylated phosphines, up to 93% isolated yield. Our synthetic approach tolerates a scope of different aryl trifluoromethyl sulfonate derivatives bearing either electron-donating (COMe, CN, CF<sub>3</sub> or Cl) or electron-withdrawing substituents (Me, OMe) that are present in *para*-, *meta*- and *ortho*-position, and includes bulky polyaromatic triflate substrates. We further described the access to a large class of PAH phosphine ligands, their oxidized derivatives (i.e. their oxides and selenides), their coordination mode with Au(I) and Cu(I) coinage metal salts, and their use as efficient ligands in the atom-economic gold-catalyzed oxidative cyclisation of terminal alkynes with nitriles.

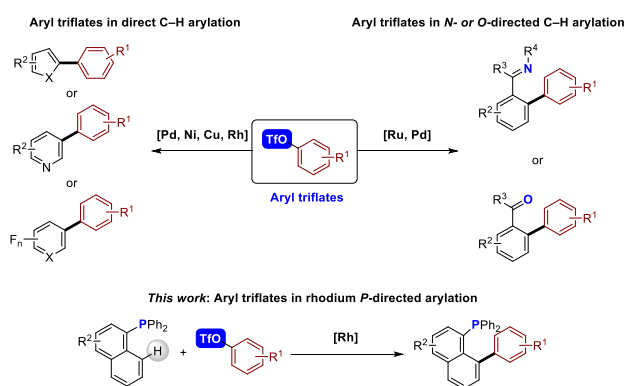
**Key words** Arylation, Catalysis, *P*-ligand directed *C*–*H* activation, Rhodium, Trifluoromethylsulfonates, Oxazoles

Selective transition-metal catalyzed *C*–*H* activation/functionalization reactions conducted with pseudo(halide)-coupling partners obtained from renewable resources, like alcohols and phenols,<sup>[1]</sup> complements advantageously the classical use of organic halides that are generally, transformed from fossil resources.<sup>[1a,b]</sup> The reactivity of some organic halides (iodides, fluorides) over phosphine leading preferentially to the formation of phosphonium salts,<sup>[1c,d]</sup> is sometimes a limitation to their direct use as ligands in transition metal catalysis. These findings are pertinent driving forces for the development of pseudo(halide) reactivity in direct *C*–*H* functionalization with transition metals. Many alcohols are directly available from bio-resources, with a wide availability, a rather low cost, while in addition the preparation of reactive alcohol derivatives is generally easy to achieve.<sup>[1d,e]</sup> In this context, the investigation on the use of electrophile alternatives to halogenated arenes, like crystalline purifiable, fairly robust phenolates, is appropriate.<sup>[1f]</sup>

Besides, the versatile phenolic group can be used for introducing further functionality on the aromatic ring of the substrate, and then be converted into a coupling function via the formation of the corresponding triflate.<sup>[1g]</sup>

Aryl trifluoromethyl sulfonates were successfully employed in the transition metals catalyzed *C*–*H* bond functionalization of heteroarenes. The direct *C*–*H* arylation of heteroarenes (mainly azole derivatives), pyridines and polyfluorinated arenes was achieved in the presence of palladium,<sup>[1g,2-4]</sup> and nickel precatalysts,<sup>[5]</sup> but remains limited to single studies for rhodium,<sup>[6]</sup> and copper (Scheme 1, top left).<sup>[7]</sup> Further, they were also fruitfully employed for the *nitrogen*-directed ruthenium catalyzed *ortho*-*C*–*H* arylation of heteroarenes,<sup>[8]</sup> and was extended to the *oxygen*-directed *C*–*H* activation/functionalization of aryl ketones with ruthenium,<sup>[9]</sup> and palladium catalysts (Scheme 1, top right).<sup>[10]</sup>

On the other hand, polycyclic aromatic hydrocarbons (PAH) incorporating phosphorus atoms are useful building blocks in organic electronic and medicine, with wide applications as pharmaceuticals,<sup>[11]</sup> in ligand design for catalysis,<sup>[12]</sup> and in material sciences.<sup>[13]</sup> New synthetic routes have been developed including catalyzed *C*–*H* activation/functionalization with transition metals using phosphorus as the directing group.<sup>[14,15]</sup> As a promising synthetic approach, the *P*-directed arylation, rhodium catalysts have demonstrated their high abilities for the direct *ortho*-arylation of biphenylphosphine,<sup>[16]</sup> and *peri*-arylation of naphthyl and related PAH such as pyrenylphosphines.<sup>[17,18]</sup> More recently, Shi *et al* reported the *ortho*-functionalization of triarylphosphine through a 4-membered rhodacycle.<sup>[19]</sup> These strategies mainly employed bromo- and chloroarenes as the electrophilic reagents. Thus, a general protocol for efficient *P*-ligand directed *peri*-arylation of polyaromatic hydrocarbons using phenolate derivatives remained to be developed.

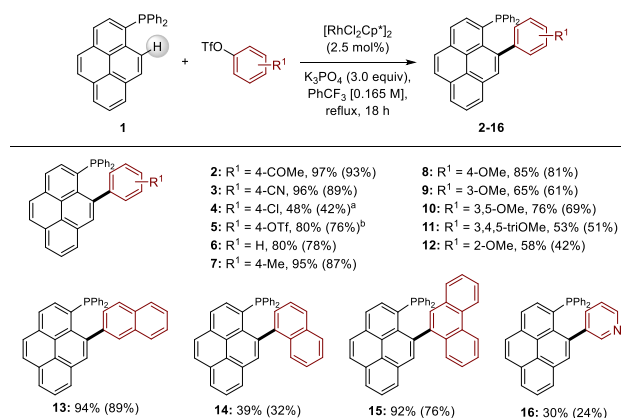


**Scheme 1** Previous works using aryl triflates as substrates in transition metals catalyzed C-H direct (hetero)arylation (top left) and *nitrogen*-, and *oxygen*-directed arylation (top right) and the present work of *phosphorus*-directed rhodium catalyzed C-H arylation of PAH phosphines (bottom).

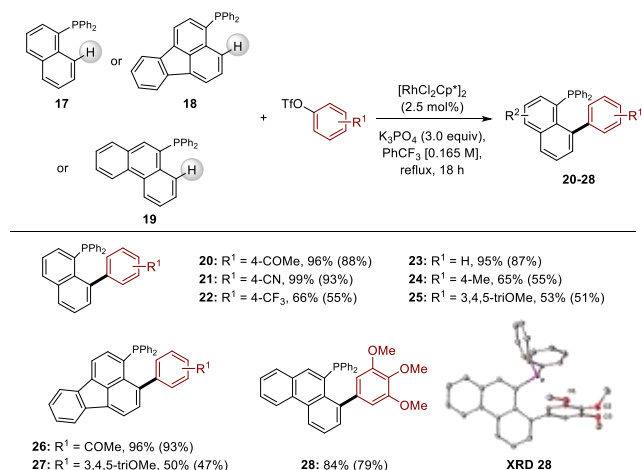
Based on our recent works on the *P*-directed C-H functionalization,<sup>[18]</sup> and the valuable use of aryl triflates as alternative electrophilic coupling partners in transition metals catalyzed C-H activation and functionalization,<sup>[18,8]</sup> we herein devised conditions for the exploitation of aryl trifluoromethyl sulfonates as substrates in rhodium-catalyzed *P*-ligands directing C-H activation/arylation.

Polyaromatic and biphenyl motifs are widely applied as pharmaceuticals, agrochemicals and in material sciences. We reported the efficiency of using rhodium(III) precatalysts to activate and functionalize selectively PAH by *P*-directed *peri*-C-H-arylation,<sup>[18]</sup> while a rhodium(I) was generally preferred.<sup>[13,17]</sup> We hypothesized that similarly the convenient and easy to handle  $[\text{Rh}(\text{III})\text{Cl}_2\text{Cp}^*]_2$  would be a suitable precatalyst to selectively perform the functionalization on the *K*-region of pyrene scaffold **1** with aryl triflates (Scheme 2, top and Table S-1 in the supporting information). After optimization, the 10-(4-acetylphenyl) pyrenyl diphenylphosphine **2** was indeed isolated in 93% yield using 2.5 mol% of  $[\text{RhCl}_2\text{Cp}^*]_2$  with 1.5 equiv of 4-acetylphenyl triflate, and  $\text{K}_3\text{PO}_4$  as the base in trifluoromethylbenzene ( $\text{PhCF}_3$ , 0.165 M based on **1**).

We then further investigated the scope of functionalized aryl triflates as coupling partners in the Rh(III)-catalyzed C-H arylation of 1-diphenylphosphine pyrene under the optimized conditions (Scheme 2). The reaction was successfully extended to *p*-benzonitrile triflate with 89% isolated yield (Scheme 2, **3**). With the 4-chlorophenyl triflate, 48% isolated yield was obtained for **4**, together with 7% of the side product 10-(4-trifluoromethyl sulfonate phenyl)-1-diphenylphosphine pyrene **5** (selectivity: 86/14 in favor of the C-OTf bond cleavage). Due to the higher reactivity of the C-Br bond compare to C-OTf in our reaction conditions, the 1-(diphenylphosphino)-10-(4-trifluoromethyl sulfonate phenyl) pyrene (**5**) was obtained in 76% isolated yield with a selectivity 91/9 (see also Table 2 in the Supporting Information).



**Scheme 2** *P*-directed C-H arylation of 1-diphenylphosphine pyrene **1** using functional aryl triflates. Conditions: 1-diphenylphosphine pyrene (0.5 mmol, 1 equiv), aryl triflate (1.5 equiv),  $[\text{RhCl}_2\text{Cp}^*]_2$  (2.5 mol%),  $\text{K}_3\text{PO}_4$  (3.0 equiv), in anhydrous trifluoromethylbenzene [0.165 M] at reflux, 18 h under argon. <sup>1</sup>H NMR yield, isolated yields are in bracket. <sup>a</sup> The corresponding 10-(4-trifluoromethyl sulfonate phenyl)-1-diphenylphosphine pyrene **5** was also detected in 14% yield. <sup>b</sup> The corresponding 10-(4-bromomethyl sulfonate phenyl)-1-diphenylphosphine pyrene **5'** was also detected in 8% yield.



**Scheme 3** Selected arylation of other polyaromatic hydrocarbon diphenylphosphine with aryl triflate. Conditions: 1-diphenylphosphine PAH (0.5 mmol, 1 equiv), aryl triflate (1.5 equiv),  $[\text{RhCl}_2\text{Cp}^*]_2$  (2.5 mol%),  $\text{K}_3\text{PO}_4$  (3.0 equiv), in anhydrous trifluoromethylbenzene [0.165 M] at reflux, 18 h under argon. <sup>1</sup>H NMR yield, isolated yields are in bracket.

The unsubstituted phenyl triflate was coupled to **1** to give **6** in 78% isolated yield. Electron-donating groups are also tolerated, such as methyl or methoxy groups, which can be present on the aryl triflate as one, two or three substituents in various *para*-, *meta*- or *ortho*-position. These coupling partners furnished lower yields (42 to 87% yield, Scheme 2, **7-13**) comparatively to the C-H arylation using substrates containing electron-withdrawing groups (Scheme 2, **2-5**). The steric congestion from polyaromatic triflates did not hampered the reaction, and in the presence of 2-naphthyl, 1-naphthyl or 9-phenanthrenyl groups the corresponding coupling products **13** (89%), **14** (32%) and **15** (76%) were obtained (Scheme 2). The 3-pyridinyl triflate was employed in our conditions and gave the 1-(diphenylphosphino)-10-(3-pyridinyl) pyrene **16** in 24% isolated yield.

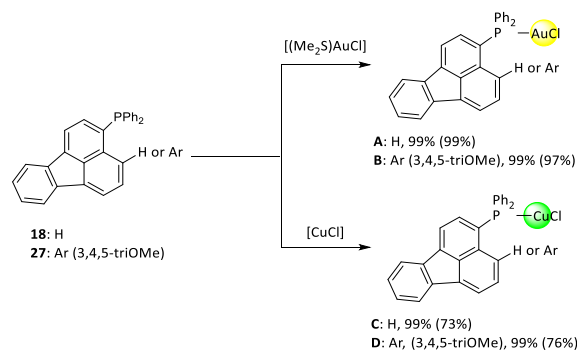
Our protocol was successfully extended to other PAH monophosphines (**17-19**, Scheme 3). 1-Naphthyl diphenylphosphine gave 88%, 93% and 55% isolated yield for **20**, **21** and **22**, respectively, in the presence of electron-withdrawing groups (with acetyl, nitrile and trifluoromethyl groups, respectively), and 87%, 55% and 51% for **23**, **24** and **25** respectively, in the presence of electron-rich triflate as coupling partners (with phenyl, methyl or trimethoxy substituents, respectively). 4-Fluoranthenyl and 9-phenanthrenyl phosphines as also found convenient partners for the *P*-directed C–H bond activation/arylation with 93%, 47% and 79% isolated yields for **26**, **27** and **28**, respectively. The X-ray diffraction structure of the [2-(3,4,5-trimethoxyphenyl)-3-phenanthryl]diphenyl phosphine **28** confirmed the expected selectivity of the C–H bond arylation at the *peri*-position of the polyaromatic hydrocarbon core.

We examined the impact on the donor-character of the phosphino groups that has the introduction of proximate aryl moieties (Table 1). This was achieved by the conversion of P(III) via oxidation or selenation, and measurement of the resulting  $^1J_{P,Se}$  nuclear spin-spin coupling constant.<sup>[20,21]</sup>

**Table 1**  $^{31}P$  NMR data (CDCl<sub>3</sub>, 202 MHz) for polyaromatic phosphines **16** and **25** and their corresponding oxide and selenium products, complexes with Au(I)Cl and Cu(I)Cl<sup>a</sup>

Phosphine	$^{31}P$ (ppm)	$^{31}PO$ (ppm)	$^{31}PSe$ (ppm)	$^1J_{P,Se}$ (Hz)	Au(I) / $^{31}P$ (ppm)	Cu(I) / $^{31}P$ (ppm)
<b>18</b>	-13.8	<b>18-O</b> : 30.7	<b>18-Se</b> : 29.8	724	24.5	-8.7 (br)
<b>27</b>	-6.8	<b>27-O</b> : 29.1	<b>27-Se</b> : 38.0	753	30.5	-6.4 (br)

<sup>a</sup> Benchmark  $^1J_{P,Se}$  value for Ph<sub>3</sub>P(Se) = 730 Hz;  $^{31}P$  NMR (CDCl<sub>3</sub>, 162 MHz) for [(Ph<sub>3</sub>P)AuCl] = 57.1 ppm.<sup>[22]</sup> The coordination to gold and copper were achieved in CH<sub>2</sub>Cl<sub>2</sub> by reacting the ligand with [(Me<sub>2</sub>S)AuCl] or CuCl respectively (Scheme 4).

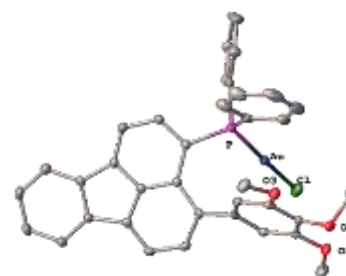


**Scheme 4** Au(I)Cl complexes **A** and **B**, and Cu(I)Cl complexes **C** and **D** stabilized by fluoranthenylphosphines **18** and **27**, respectively.

We examined both the polyaromatic diphenylphosphine **18** and its arylated derivative **27**, which incorporates several methoxy electron-donating group at the *peri*-aryl moiety. The  $^{31}P$  NMR spectroscopy data for these compounds and their corresponding oxides derivatives are collected in Table 1. The selenide phosphines **18-Se** and **27-Se** featured  $^{31}P$  NMR signals located at 29.8 and 38.0 ppm, while the corresponding phosphine oxides **18-O** and **27-O** showed signals at 30.7 and 29.1 ppm, respectively. The benchmark  $^1J_{P,Se}$  value for triphenylphosphine selenide Se=PPh<sub>3</sub> in CDCl<sub>3</sub> is 730 Hz, which was found higher than the  $^1J_{P,Se}$  = 724 Hz for the selenated 1-diphenylphosphine-

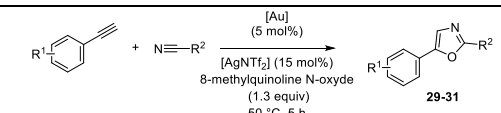
fluoranthene **18-Se**. The phosphine **18** is thus slightly more electron-donor (basic) than PPh<sub>3</sub>. Conversely, a notably less basic character for **25** (because  $^1J_{P,Se}$  = 753 Hz for **27-Se**) was suggested compared both with PPh<sub>3</sub> and the polyaromatic diphenylphosphine **18**.

We then achieved the complexation of the polyaromatic phosphines **18** and **27** to coinage metals with gold(I) chloride and copper(I) chloride salts (Table 1, Scheme 1).<sup>[23,24]</sup> For fluoranthenyl diphenylphosphines **18** and **27**, the reaction with [(Me<sub>2</sub>S)AuCl] quantitatively leads to complexes **A** and **B** that are characterized in  $^{31}P$  NMR spectroscopy (CDCl<sub>3</sub>, 202 MHz) by a singlet at 24.5 ppm and 30.5 ppm, respectively (Scheme 1, and XRD of **B** in Figure 4, XRD for **A** is reported in the Supporting Information). The complexation with Cu(I)Cl quantitatively leads to complexes **C** and **D**, respectively, which were obtained in 73% and 76% isolated yields after precipitation, and are characterized in  $^{31}P$  NMR spectroscopy (CDCl<sub>3</sub>, 202 MHz) by broad signals at -8.7 ppm and -6.4 ppm, respectively (see Scheme 4; XRD for **C**, as a classical cubane structure, is reported in the Supporting Information).



**Figure 1** Molecular structure of complex **B** (thermal ellipsoids at 30% probabilities, H atoms and one CH<sub>2</sub>Cl<sub>2</sub> are omitted for clarity).

The effect on gold catalysis activity of **18** and **27** used as ligands, for their corresponding gold complexes **A** and **B** were evaluated in the oxidative cyclisation of terminal alkynes with nitriles (Table 2).<sup>[25]</sup> The combination of AuClSMe<sub>2</sub> with both polyaromatic diphenylphosphines satisfactorily afforded the 2,5-disubstituted oxazole **29** (Table 2, entries 1-3). However, the introduction of an aryl group at the *peri*-position that is achieved with ligand **27** much enhanced the catalytic activity with a 97% conversion to **29**. A lower 76% conversion was achieved under similar conditions using the non-*peri*-arylated **18** (Table 2, entries 2 and 3). Consistent results were achieved with the corresponding preformed gold-complexes **A** and **B**, with 72% and 99% conversion, respectively (Table 2, entries 4 and 5), and similarly for the formation of the oxazoles **30** and **31** (Table 2, entries 6-9).

**Table 2** Gold-catalysed oxidative cyclisation of terminal alkynes with nitriles<sup>a</sup>


Entry	R <sup>1</sup>	R <sup>2</sup>	Catalyst	<sup>1</sup> H NMR Yield
1	4-OMe	Me	AuClSMe <sub>2</sub>	29: 9%
2	4-OMe	Me	18 + AuClSMe <sub>2</sub>	29: 76%
3	4-OMe	Me	27 + AuClSMe <sub>2</sub>	29: 97%
4	4-OMe	Me	[A]	29: 72%
5	4-OMe	Me	[B]	29: 99% (93%)
6	4-OMe	Ph	[A]	30: 97%
7	4-OMe	Ph	[B]	30: 99% (82%)
8	4-F	Me	[A]	31: 72%
9	4-F	Me	[B]	31: 92% (80%)

<sup>a</sup> Conditions: Aryl alkynes (0.6 mmol, 1 equiv), 8-methylquinoline oxide (1.3 equiv), [Au] (5 mol%), [AgNTf<sub>2</sub>] (15 mol%), in acetonitrile [0.2 M] at 50 °C, 5 h under argon. <sup>1</sup>H NMR yield based on the aryl alkynes consumption (isolated yields under brackets).

Overall, we showed that substituted aryl triflates are appropriate coupling partners in the rhodium-catalyzed direct C–H functionalization of polyaromatic phosphines. Trifluoromethyl sulfonates can be obtained from alcohols as resources issued of renewable biomass. We reported herein the practical synthesis of *peri*-functionalized polyaromatic hydrocarbon phosphines by using aryl phenolate derivatives as the coupling partner. Our rhodium-catalyzed *P*-directed C–H arylation tolerates aryl triflates incorporating varied electron-donating and electron-withdrawing groups at *ortho*-, *meta*- and *para*-position. This protocol provides a convenient access to novel polyarylated phosphines, ready-to-use for further modification, or as ligand for metal coordination and catalysis, as illustrated herein.

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#### General Conditions

All reagents were purchased from commercial suppliers and used without purifications. The polyarylated phosphines were synthesized according the literature.<sup>[18]</sup> All reactions were performed under an atmosphere of dry argon in oven-dried glassware materials using Schlenk and vacuum-line techniques. Flash chromatography was performed on silica gel (40–63 μm). The identity and purity of the products were established at the “Chemical Analysis Platform and Molecular Synthesis University of Burgundy” (PACSMUB Platform – SATT SAYENS) using high-resolution mass spectrometry, elemental analysis and multinuclear NMR. <sup>1</sup>H (500 MHz), <sup>31</sup>P (202 MHz), <sup>18</sup>F (407 MHz), <sup>13</sup>C (125 MHz) spectra were recorded on Bruker AVANCE III instrument in CDCl<sub>3</sub> solutions. Chemical shifts are reported in ppm relative to CDCl<sub>3</sub> (<sup>1</sup>H: 7.26 and <sup>13</sup>C: 77.16) and coupling constants *J* are given in Hz. Elemental analysis experiments were performed Thermo Electron Flash EA 1112 Series. High resolution mass spectra (HRMS) were obtained on a Thermo LTQ-Orbitrap XL with ESI source.

Accession Codes. CCDC XRD 28: 2214568; A: 2214569; B: 2214570; C: 2214571 contain the supplementary crystallographic data for the paper. These data can be obtained free of charge via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif), or by emailing [data\\_request@ccdc.cam.ac.uk](mailto:data_request@ccdc.cam.ac.uk), or by contacting The

Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

#### General procedures for the Synthesis of the aryalted diphenylphosphine PAH

An oven-dried Schlenk tube equipped with a magnetic stirring bar was charged with 1-diphenylphosphine PAH (0.5 mmol, 1 equiv), aryl triflate (0.75 mmol, 1.5 equiv), K<sub>3</sub>PO<sub>4</sub> (1.5 mmol, 3.0 equiv, 318 mg), and [RhCl<sub>2</sub>Cp\*]<sub>2</sub> (0.0125 mmol, 2.5 mol%, 7.7 mg), in anhydrous trifluoromethylbenzene (0.165 M, 3 ml). The mixture was stirred at reflux under argon during 18 h. After extraction using a CH<sub>2</sub>Cl<sub>2</sub>/H<sub>2</sub>O mixture, the organic layer was concentrated in *vacuum*. The crude product was purified by column chromatography on silica using as eluent a mixture pentane:dichloromethane.

#### 1-(Diphenylphosphino)-10-(4-acetylphenyl) pyrene (2)<sup>[18]</sup>

Pentane:dichloromethane (1:2); as a yellow solid (93%, 234 mg).

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ (ppm) = 8.22 (d, *J* = 7.5 Hz, 1H), 8.16 (dd, *J* = 7.4 Hz, 1H), 8.12 (d, *J* = 8.9 Hz, 1H), 8.09–8.00 (m, 3H), 7.96 (s, 1H), 7.79 (dd, *J* = 7.9, 4.1 Hz, 1H), 7.71 (d, *J* = 8.2 Hz, 2H), 7.37 (d, *J* = 8.2 Hz, 2H), 7.27 (t, *J* = 6.7 Hz, 2H), 7.21 (t, *J* = 7.4 Hz, 4H), 7.03 (t, *J* = 7.1 Hz, 4H), 2.60 (s, 3H).

<sup>31</sup>P{<sup>1</sup>H} NMR (202 MHz, CDCl<sub>3</sub>): δ (ppm) = –9.2 (s).

#### 1-(Diphenylphosphino)-10-(4-cyanophenyl) pyrene (3)

Pentane:dichloromethane (3:1); as a yellow solid (89%, 217 mg).

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ (ppm) = 8.26 (d, *J* = 7.5 Hz, 1H), 8.17 (dd, *J* = 15.8, 8.2 Hz, 2H), 8.07 (dt, *J* = 12.4, 7.8 Hz, 3H), 7.92 (s, 1H), 7.75 (dd, *J* = 8.0, 4.1 Hz, 1H), 7.38 (d, *J* = 8.3 Hz, 2H), 7.34 (d, *J* = 8.2 Hz, 2H), 7.29 (t, *J* = 7.3 Hz, 2H), 7.25–7.21 (m, 4H), 7.01 (t, *J* = 7.7 Hz, 4H).

<sup>31</sup>P{<sup>1</sup>H} NMR (202 MHz, CDCl<sub>3</sub>): δ (ppm) = –8.7 (s).

<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ (ppm) = 149.0 (d, *J*<sub>PC</sub> = 4.8 Hz), 138.8 (d, *J*<sub>PC</sub> = 15.0 Hz), 138.7, 135.8, 134.6 (d, *J*<sub>PC</sub> = 22.6 Hz), 133.7, (d, *J*<sub>PC</sub> = 20.3 Hz), 132.5 (d, *J*<sub>PC</sub> = 26.6 Hz), 132.1, 132.0, 131.7, 131.4, 131.2 (d, *J*<sub>PC</sub> = 7.3 Hz), 129.9, 128.6 (d, *J*<sub>PC</sub> = 15.6 Hz), 128.5, 128.4, 127.8, 126.6, 126.3, 126.2 (d, *J*<sub>PC</sub> = 5.5 Hz), 125.9, 125.7, 124.4 (d, *J*<sub>PC</sub> = 1.8 Hz), 119.5, 110.6.

Elemental analysis calcd (%) for C<sub>35</sub>H<sub>21</sub>NP: C, 85.23; H, 4.55; Found: C, 84.80; H, 4.69.

HRMS + p ESI (m/z) [M–H]<sup>+</sup> Calcd.: 486.14061, Found: 486.14031.

#### 1-(Diphenylphosphino)-10-(4-chlorophenyl) pyrene (4)<sup>[18]</sup>

Pentane:dichloromethane (4:1 then 2:1); as a yellow solid (42%, 104 mg).

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ (ppm) = 8.21 (d, *J* = 7.3 Hz, 1H), 8.14 (d, *J* = 7.4 Hz, 1H), 8.12 (d, *J* = 8.9 Hz, 1H), 8.06–7.99 (m, 3H), 7.92 (s, 1H), 7.74 (dd, *J* = 7.9, 4.0 Hz, 1H), 7.27 (t, *J* = 7.3 Hz, 2H), 7.22 (t, *J* = 7.4 Hz, 4H), 7.16 (d, *J* = 8.3 Hz, 2H), 7.09 (d, *J* = 8.3 Hz, 2H), 7.04 (t, *J* = 7.7 Hz, 4H).

<sup>31</sup>P{<sup>1</sup>H} NMR (202 MHz, CDCl<sub>3</sub>): δ (ppm) = –8.3 (s).

#### 1-(Diphenylphosphino)-10-(4-trifluoromethyl sulfonate phenyl) pyrene (5)

Pentane:dichloromethane (4:1 then 2:1); as a yellow solid (76%, 230 mg).

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ (ppm) = 8.16 (d, *J* = 7.5 Hz, 1H), 8.07 (dd, *J* = 13.0, 8.1 Hz, 2H), 7.97 (dd, *J* = 15.3, 7.4 Hz, 3H), 7.84 (s, 1H), 7.62 (dd, *J* = 8.0, 4.2 Hz, 1H), 7.31 (s, 1H), 7.22–7.18 (m, 3H), 7.12 (t, *J* = 7.4 Hz, 5H), 6.97–6.89 (m, 6H), 6.84 (d, *J* = 9.2 Hz, 1H).

<sup>31</sup>P{<sup>1</sup>H} NMR (202 MHz, CDCl<sub>3</sub>): δ (ppm) = –7.9 (s).

<sup>19</sup>F{<sup>1</sup>H} NMR (470 MHz, CDCl<sub>3</sub>): δ (ppm) = –72.8 (s).

<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ (ppm) = 142.4 (d, *J*<sub>PC</sub> = 5.2 Hz), 139.3 (d, *J*<sub>PC</sub> = 4.7 Hz), 139.1, 135.6, 135.1 (d, *J*<sub>PC</sub> = 21.5 Hz), 133.8 (d, *J*<sub>PC</sub> = 20.5 Hz), 133.3, 132.8 (d, *J*<sub>PC</sub> = 25.4 Hz), 132.0, 131.9 (d, *J*<sub>PC</sub> = 7.0 Hz), 131.8, 131.4, 130.2, 128.4, 128.3, 128.3, 128.2, 128.1, 127.8, 126.4, 126.2 (d, *J*<sub>PC</sub> = 5.2), 125.8 (d, *J*<sub>PC</sub> = 24.5 Hz), 125.4, 124.2 (d, *J*<sub>PC</sub> = 1.6 Hz).

Elemental analysis calcd (%) for C<sub>35</sub>H<sub>22</sub>F<sub>3</sub>O<sub>3</sub>PS: C, 68.85; H, 3.63; Found: C, 68.76; H, 3.59.

HRMS + p ESI (m/z) [M+H]<sup>+</sup> Calcd.: 611.10439, Found: 611.10521.

#### 1-(Diphenylphosphino)-10-(phenyl) pyrene (6)

Pentane:dichloromethane (4:1); as a yellow solid (78%, 200 mg).

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ (ppm) = 8.22 (d, *J* = 7.6 Hz, 1H), 8.15 (dd, *J* = 14.9, 8.1 Hz, 2H), 8.08–8.01 (m, 3H), 7.97 (s, 1H), 7.73 (dd, *J* = 8.0, 4.0 Hz,

<sup>1</sup>H, 7.30 (t, *J* = 7.4 Hz, 1H), 7.23 (d, *J* = 7.4 Hz, 3H), 7.22–7.12 (m, 7H), 7.02–6.97 (m, 4H).

<sup>31</sup>P{<sup>1</sup>H} NMR (202 MHz, CDCl<sub>3</sub>): δ (ppm) = –8.2 (s).

<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ (ppm) = 144.2 (d, *J*<sub>PC</sub> = 5.4 Hz), 140.5 (d, *J*<sub>PC</sub> = 5.1 Hz), 139.8 (d, *J*<sub>PC</sub> = 7.1 Hz), 135.7, 134.7 (d, *J*<sub>PC</sub> = 21.4 Hz), 133.8 (d, *J*<sub>PC</sub> = 20.6 Hz), 133.5 (d, *J*<sub>PC</sub> = 28.3 Hz), 132.0, 131.8, 131.4, 130.7 (d, *J*<sub>PC</sub> = 7.1 Hz), 130.4, 128.2, 128.2, 128.1, 127.8, 127.2, 126.4, 126.2 (d, *J*<sub>PC</sub> = 5.1 Hz), 125.5 (d, *J*<sub>PC</sub> = 5.0 Hz), 125.2, 124.3 (d, *J*<sub>PC</sub> = 1.7 Hz).

Elemental analysis calcd (%) for C<sub>34</sub>H<sub>23</sub>P: C, 88.29; H, 5.01; Found: C, 87.93; H, 4.81.

HRMS + p ESI (*m/z*) [M+H]<sup>+</sup> Calcd.: 463.16101, Found: 463.16070.

#### 1-(Diphenylphosphino)-10-(4-methylphenyl) pyrene (7)<sup>[18]</sup>

Pentane:dichloromethane (3:1); as a yellow solid (87%, 207 mg).

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ (ppm) = 8.11 (t, *J* = 7.9 Hz, 2H), 8.04 (d, *J* = 8.9 Hz, 1H), 8.00–7.95 (m, 3H), 7.93 (d, *J* = 7.6 Hz, 1H), 7.77 (dd, *J* = 7.9, 4.0 Hz, 1H), 7.24–7.15 (m, 8H), 7.05 (t, *J* = 6.9 Hz, 4H), 6.94 (d, *J* = 7.7 Hz, 2H), 2.38 (s, 3H).

<sup>31</sup>P{<sup>1</sup>H} NMR (202 MHz, CDCl<sub>3</sub>): δ (ppm) = –8.6 (s).

#### 1-(Diphenylphosphino)-10-(4-methoxyphenyl) pyrene (8)<sup>[18]</sup>

Pentane:dichloromethane (3:2 then 1:1); as a yellow solid (81%, 199 mg).

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ (ppm) = 8.20 (d, *J* = 7.4 Hz, 1H), 8.15 (d, *J* = 5.9 Hz, 1H), 8.12 (d, *J* = 8.8 Hz, 1H), 8.07–8.00 (m, 3H), 7.96 (sb, 1H), 7.73 (dd, *J* = 7.9, 4.0 Hz, 1H), 7.27–7.18 (m, 6H), 7.16 (d, *J* = 8.3 Hz, 2H), 7.04 (t, *J* = 6.5 Hz, 4H), 6.69 (d, *J* = 10.3 Hz, 2H), 3.82 (s, 3H).

<sup>31</sup>P{<sup>1</sup>H} NMR (202 MHz, CDCl<sub>3</sub>): δ (ppm) = –8.1 (s).

#### 1-(Diphenylphosphino)-10-(3-methoxyphenyl) pyrene (9)<sup>[18]</sup>

Pentane:dichloromethane (3:1 then 1:1); as a yellow solid (61%, 150 mg).

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ (ppm) = 8.04 (d, *J* = 7.5 Hz, 1H), 8.01 (d, *J* = 7.5 Hz, 1H), 7.96 (d, *J* = 8.8 Hz, 1H), 7.93–7.84 (m, 4H), 7.65 (dd, *J* = 8.0, 3.9 Hz, 1H), 7.13–7.00 (m, 7H), 6.95 (t, *J* = 7.5 Hz, 2H), 6.88 (q, *J* = 7.0 Hz, 3H), 6.76 (dd, *J* = 8.2, 2.3 Hz, 1H), 6.55 (s, 1H), 3.32 (s, 3H).

<sup>31</sup>P{<sup>1</sup>H} NMR (202 MHz, CDCl<sub>3</sub>): δ (ppm) = –8.6 (s).

#### 1-(Diphenylphosphino)-10-(3,5-dimethoxyphenyl) pyrene (10)

Pentane:dichloromethane (1:1); as a yellow solid (69%, 180 mg).

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ (ppm) = 8.20 (dd, *J* = 11.1, 7.5 Hz, 2H), 8.13 (d, *J* = 8.9 Hz, 1H), 8.10–8.02 (m, 4H), 7.85 (dd, *J* = 8.0, 3.7 Hz, 1H), 7.25 (q, *J* = 8.6, 7.4 Hz, 6H), 7.13–7.07 (m, 4H), 6.53 (t, *J* = 2.3 Hz, 1H), 6.50 (d, *J* = 2.2 Hz, 2H), 3.56 (s, 6H).

<sup>31</sup>P{<sup>1</sup>H} NMR (202 MHz, CDCl<sub>3</sub>): δ (ppm) = –9.1 (s).

<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ (ppm) = 160.7, 146.2 (d, *J*<sub>PC</sub> = 5.4 Hz), 140.5 (d, *J*<sub>PC</sub> = 18.9 Hz), 140.4 (d, *J*<sub>PC</sub> = 4.6 Hz), 136.2, 135.4 (d, *J*<sub>PC</sub> = 2.1 Hz), 133.5 (d, *J*<sub>PC</sub> = 20.7 Hz), 133.4 (d, *J*<sub>PC</sub> = 29.7 Hz), 132.1, 131.4, 131.1, 130.2, 128.3 (d, *J*<sub>PC</sub> = 6.0 Hz), 128.3, 128.0, 127.8, 126.4, 126.1 (d, *J*<sub>PC</sub> = 5.2 Hz), 125.6 (d, *J*<sub>PC</sub> = 12.3 Hz), 125.3, 124.3 (d, *J*<sub>PC</sub> = 1.8 Hz), 108.8 (d, *J*<sub>PC</sub> = 7.9 Hz), 108.7, 100.3, 55.2.

Elemental analysis calcd (%) for C<sub>36</sub>H<sub>27</sub>O<sub>2</sub>P: C, 82.74; H, 5.21; Found: C, 80.73; H, 5.10.

HRMS + p ESI (*m/z*) [M+H]<sup>+</sup> Calcd.: 523.18214, Found: 523.18154.

#### 1-(Diphenylphosphino)-10-(3,4,5-trimethoxyphenyl) pyrene (11)

Pentane:dichloromethane (1:2 then 1:4); as a yellow solid (51%, 141 mg).

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ (ppm) = 8.21 (d, *J* = 7.5 Hz, 1H), 8.18 (d, *J* = 7.4 Hz, 1H), 8.13 (d, *J* = 8.8 Hz, 1H), 8.09–8.01 (m, 4H), 7.80 (dd, *J* = 7.9, 3.7 Hz, 1H), 7.28–7.20 (m, 6H), 7.05 (t, *J* = 6.7 Hz, 4H), 6.49 (s, 2H), 3.98 (s, 3H), 3.52 (s, 6H).

<sup>31</sup>P{<sup>1</sup>H} NMR (202 MHz, CDCl<sub>3</sub>): δ (ppm) = –8.6 (s).

<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ (ppm) = 153.1, 140.5 (d, *J*<sub>PC</sub> = 19.1 Hz), 140.4 (d, *J*<sub>PC</sub> = 4.3 Hz), 139.6 (d, *J*<sub>PC</sub> = 5.4 Hz), 137.9, 136.1, 135.4 (d, *J*<sub>PC</sub> = 21.5 Hz), 133.4 (d, *J*<sub>PC</sub> = 21.0 Hz), 133.0, 132.1, 131.4, 131.2, 130.1, 128.4, 128.3, 128.3, 128.1, 127.8, 126.4, 126.1 (d, *J*<sub>PC</sub> = 2.1 Hz), 125.6, 125.4 (d, *J*<sub>PC</sub> = 13.0 Hz), 124.3 (d, *J*<sub>PC</sub> = 1.6 Hz), 108.1 (d, *J*<sub>PC</sub> = 8.0 Hz), 61.2, 55.7.

Elemental analysis calcd (%) for C<sub>37</sub>H<sub>29</sub>O<sub>3</sub>P: C, 80.42; H, 5.29; Found: C, 80.80; H, 5.49.

HRMS + p ESI (*m/z*) [M+H]<sup>+</sup> Calcd.: 551.17706, Found: 551.17629.

#### 1-(Diphenylphosphino)-10-(2-methoxyphenyl) pyrene (12)<sup>[18]</sup>

Pentane:dichloromethane (4:1); as a yellow solid (42%, 103 mg).

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ (ppm) = 8.21 (d, *J* = 7.5 Hz, 1H), 8.16 (d, *J* = 7.5 Hz, 1H), 8.16 (d, *J* = 8.9 Hz, 1H), 8.07–8.00 (m, 3H), 7.98 (s, 1H), 7.72 (dd, *J* = 7.3, 3.4 Hz, 1H), 7.40 (t, *J* = 7.6 Hz, 1H), 7.29 (sb, 3H), 7.22 (t, *J* = 7.0 Hz, 1H), 7.16–7.13 (m, 4H), 7.04 (d, *J* = 7.0 Hz, 1H), 6.87 (t, *J* = 6.9 Hz, 2H), 6.80 (t, *J* = 7.2 Hz, 2H), 3.48 (s, 3H).

<sup>31</sup>P{<sup>1</sup>H} NMR (202 MHz, CDCl<sub>3</sub>): δ (ppm) = –8.3 (s).

#### 1-(Diphenylphosphino)-10-(2-naphthyl) pyrene (13)<sup>[18]</sup>

Pentane:dichloromethane (4:1); as a yellow solid (89%, 227 mg).

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ (ppm) = 8.23 (d, *J* = 7.4 Hz, 1H), 8.18 (d, *J* = 8.2 Hz, 1H), 8.16 (d, *J* = 8.2 Hz, 1H), 8.09 (d, *J* = 7.6 Hz, 2H), 8.07–8.02 (m, 2H), 7.87 (d, *J* = 8.2 Hz, 1H), 7.82 (d, *J* = 8.3 Hz, 1H), 7.76 (dd, *J* = 8.0, 4.2 Hz, 1H), 7.65 (d, *J* = 8.3 Hz, 1H), 7.50–7.44 (m, 2H), 7.34 (q, *J* = 8.2, 7.7 Hz, 2H), 7.24–7.14 (m, 4H), 7.09 (t, *J* = 7.1 Hz, 2H), 6.93 (t, *J* = 6.9 Hz, 2H), 6.85 (t, *J* = 7.3 Hz, 2H).

<sup>31</sup>P{<sup>1</sup>H} NMR (202 MHz, CDCl<sub>3</sub>): δ (ppm) = –8.2 (s).

#### 1-(Diphenylphosphino)-10-(1-naphthyl) pyrene (14)<sup>[18]</sup>

Pentane:dichloromethane (4:1); as a yellow solid (32%, 82 mg).

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ (ppm) = 8.26 (d, *J* = 7.0 Hz, 1H), 8.18 (d, *J* = 8.2 Hz, 1H), 8.16 (d, *J* = 7.5 Hz, 1H), 8.12–8.03 (m, 4H), 7.92 (t, *J* = 6.4 Hz, 2H), 7.66 (t, *J* = 7.9, 3.6 Hz, 1H), 7.42 (t, *J* = 7.6 Hz, 2H), 7.25–7.12 (m, 7H), 7.07 (t, *J* = 7.4 Hz, 2H), 6.78 (t, *J* = 7.7 Hz, 2H), 6.67 (t, *J* = 6.8 Hz, 2H).

<sup>31</sup>P{<sup>1</sup>H} NMR (202 MHz, CDCl<sub>3</sub>): δ (ppm) = –7.7 (s).

#### 1-(Diphenylphosphino)-10-(9-phenanthryl) pyrene (15)<sup>[18]</sup>

Pentane:dichloromethane (4:1); as a yellow solid (76%, 202 mg).

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ (ppm) = 8.78 (d, *J* = 8.2 Hz, 1H), 8.74 (d, *J* = 8.3 Hz, 1H), 8.25 (d, *J* = 7.5 Hz, 1H), 8.19–8.13 (m, 3H), 8.12–8.07 (m, 2H), 8.03 (t, *J* = 7.6 Hz, 1H), 7.67–7.58 (m, 4H), 7.46 (t, *J* = 7.3 Hz, 1H), 7.39–7.30 (m, 3H), 7.19–7.09 (m, 2H), 7.09–6.98 (m, 4H), 6.68 (t, *J* = 6.8 Hz, 2H), 6.54 (t, *J* = 7.2 Hz, 2H).

<sup>31</sup>P{<sup>1</sup>H} NMR (202 MHz, CDCl<sub>3</sub>): δ (ppm) = –7.1 (s).

#### 1-(Diphenylphosphino)-10-(3-pyrinyl) pyrene (16)

Pentane:ethyl acetate (1:1); as a yellow solid (24%, 56 mg).

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ (ppm) = 8.65–8.56 (m, 2H), 8.27 (d, *J* = 7.5 Hz, 1H), 8.18 (dd, *J* = 13.9, 8.2 Hz, 2H), 8.08 (dd, *J* = 17.9, 7.8 Hz, 3H), 7.94 (s, 1H), 7.71 (dd, *J* = 8.0, 4.4 Hz, 1H), 7.44 (d, *J* = 7.7 Hz, 1H), 7.34–7.20 (m, 6H), 7.10 (dd, *J* = 7.5, 5.0 Hz, 1H), 7.01 (dt, *J* = 14.8, 7.2 Hz, 4H).

<sup>31</sup>P{<sup>1</sup>H} NMR (202 MHz, CDCl<sub>3</sub>): δ (ppm) = –6.1 (s).

<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ (ppm) = 151.3 (d, *J*<sub>PC</sub> = 3.0 Hz), 148.1, 139.6 (d, *J*<sub>PC</sub> = 5.5 Hz), 138.6 (d, *J*<sub>PC</sub> = 6.2, 5.6 Hz), 137.4 (d, *J*<sub>PC</sub> = 7.4 Hz), 136.8 (d, *J*<sub>PC</sub> = 3.9 Hz), 134.7, 134.1, 134.0 (d, *J*<sub>PC</sub> = 19.7, 5.3 Hz), 133.1, 132.9, 132.6, 132.0, 131.4, 130.1, 128.7 (d, *J*<sub>PC</sub> = 19.4 Hz), 128.5, 128.4 (d, *J*<sub>PC</sub> = 6.6 Hz), 128.2, 127.9, 126.5, 126.2 (d, *J*<sub>PC</sub> = 4.5 Hz), 126.0, 125.6 (d, *J*<sub>PC</sub> = 6.6 Hz), 124.4 (d, *J*<sub>PC</sub> = 1.7 Hz), 122.7.

Elemental analysis calcd (%) for C<sub>33</sub>H<sub>22</sub>NP: C, 85.51; H, 4.78; Found: C, 86.03; H, 4.80.

HRMS + p ESI (*m/z*) [M-H]<sup>+</sup> Calcd.: 462.14116, Found: 462.14103.

#### [8-(4-Acetylphenyl)-naphthalen-1-yl] diphenylphosphine (20)

Pentane:dichloromethane (1:3 then 0:1); as a yellow pale solid (88%, 189 mg).

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ (ppm) = 7.96 (d, *J* = 8.1 Hz, 2H), 7.67 (d, *J* = 8.2 Hz, 2H), 7.56–7.51 (m, 1H), 7.43–7.39 (m, 1H), 7.33 (dd, *J* = 7.0, 1.2 Hz, 1H), 7.29 (q, *J* = 6.7, 6.0 Hz, 3H), 7.25–7.19 (m, 6H), 7.02–6.96 (m, 4H), 2.62 (s, 3H).

<sup>31</sup>P{<sup>1</sup>H} NMR (202 MHz, CDCl<sub>3</sub>): δ (ppm) = –9.0 (s).

<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ (ppm) = 198.0, 148.7 (d, *J*<sub>PC</sub> = 4.6 Hz), 140.2 (d, *J*<sub>PC</sub> = 4.3 Hz), 138.9 (d, *J*<sub>PC</sub> = 5.5 Hz), 137.8, 135.5, 135.0, 134.9, 134.9, 134.8, 134.7, 131.0 (d, *J*<sub>PC</sub> = 7.0 Hz), 130.5 (d, *J*<sub>PC</sub> = 6.0 Hz), 129.5 (d, *J*<sub>PC</sub> = 1.6 Hz), 128.3, 128.2 (d, *J*<sub>PC</sub> = 6.5 Hz), 127.7, 125.6, 124.8, 26.7.

Elemental analysis calcd (%) for C<sub>30</sub>H<sub>23</sub>OP: C, 83.70; H, 5.39; Found: C, 84.51; H, 5.42.

HRMS + p ESI (*m/z*) [M+H]<sup>+</sup> Calcd.: 431.15593, Found: 431.15556.

#### [8-(4-Cyanophenyl)-naphthalen-1-yl] diphenylphosphine (21)

Pentane:dichloromethane (3:1); as a yellow pale solid (93%, 192 mg).

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ (ppm) = 7.92 (t, *J* = 8.5 Hz, 2H), 7.51–7.47 (m, 1H), 7.39–7.35 (m, 1H), 7.30 (d, *J* = 8.2 Hz, 2H), 7.27 (d, *J* = 9.4 Hz, 1H), 7.24

(d,  $J = 3.3$  Hz, 2H), 7.23–7.18 (m, 5H), 7.14 (d,  $J = 8.0$  Hz, 2H), 6.96–6.91 (m, 4H).

$^{31}\text{P}\{^1\text{H}\}$  NMR (202 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = -8.5 (s).

$^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = 148.4 (d,  $J_{\text{PC}} = 4.6$  Hz), 139.5 (d,  $J_{\text{PC}} = 4.2$  Hz), 138.5 (d,  $J_{\text{PC}} = 14.7$  Hz), 137.8, 135.0 (d,  $J_{\text{PC}} = 4.7$  Hz), 135.7 (d,  $J_{\text{PC}} = 1.1$  Hz), 134.6, 134.5 (d,  $J_{\text{PC}} = 4.8$  Hz), 133.8, 133.7, 131.5 (d,  $J_{\text{PC}} = 7.1$  Hz), 131.2, 130.6 (d,  $J_{\text{PC}} = 6.5$  Hz), 130.0 (d,  $J_{\text{PC}} = 1.6$  Hz), 128.6, 128.4, 128.3, 125.8, 124.9, 119.4.

Elemental analysis calcd (%) for  $\text{C}_{29}\text{H}_{20}\text{NP}$ : C, 84.24; H, 4.88; Found: C, 83.71; H, 4.76.

HRMS + p ESI (m/z)  $[\text{M}-\text{H}]^+$  Calcd.: 412.12496, Found: 412.12470.

#### [8-(4-Trifluoromethylphenyl)-naphthalen-1-yl] diphenylphosphine (22)

Pentane:dichloromethane (4:1); as a yellow pale solid (55%, 125 mg).

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = 7.95–7.91 (m, 2H), 7.76 (d,  $J = 8.7$  Hz, 1H), 7.50 (t,  $J = 7.6$  Hz, 1H), 7.43 (d,  $J = 8.7$  Hz, 1H), 7.40–7.36 (m, 1H), 7.28 (d,  $J = 8.2$  Hz, 1H), 7.26–7.18 (m, 8H), 7.15 (d,  $J = 7.9$  Hz, 2H), 6.94 (t,  $J = 7.4$  Hz, 4H).

$^{31}\text{P}\{^1\text{H}\}$  NMR (202 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = -8.9 (s).

$^{19}\text{F}\{^1\text{H}\}$  NMR (470 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = -62.4 (s).

#### Diphenyl-(8-phenyl-naphthalen-1-yl) phosphine (23)<sup>[17]</sup>

Pentane:dichloromethane (4:1); as a yellow solid (87%, 169 mg).

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = 7.99–7.91 (m, 2H), 7.56–7.51 (m, 1H), 7.42–7.36 (m, 2H), 7.33–7.21 (m, 8H), 7.14 (d,  $J = 6.6$  Hz, 4H), 7.05–6.99 (m, 4H).

$^{31}\text{P}\{^1\text{H}\}$  NMR (202 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = -8.2 (s).

#### Diphenyl-[8-(4-tolyl)-naphthalen-1-yl] phosphine (24)<sup>[17]</sup>

Pentane:dichloromethane (4:1); as a yellow solid (55%, 110 mg).

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = 7.92 (t,  $J = 8.5$  Hz, 2H), 7.51 (t,  $J = 7.5$  Hz, 1H), 7.36 (q,  $J = 7.5$  Hz, 2H), 7.24 (dt,  $J = 13.9, 7.1$  Hz, 7H), 7.03–6.96 (m, 5H), 6.90 (d,  $J = 4.8$  Hz, 2H), 2.38 (s, 3H).

$^{31}\text{P}\{^1\text{H}\}$  NMR (202 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = -8.7 (s).

#### [8-(3,4,5-Trimethoxyphenyl)-naphthalen-1-yl] diphenylphosphine (25)

Pentane:dichloromethane (1:3); as a yellow solid (51%, 122 mg).

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = 8.78 (d,  $J = 8.2$  Hz, 1H), 8.74 (d,  $J = 8.3$  Hz, 1H), 8.25 (d,  $J = 7.5$  Hz, 1H), 8.19–8.13 (m, 3H), 8.12–8.07 (m, 2H), 8.03 (t,  $J = 7.6$  Hz, 1H), 7.67–7.58 (m, 4H), 7.46 (t,  $J = 7.3$  Hz, 1H), 7.39–7.30 (m, 3H), 7.19–7.09 (m, 2H), 7.09–6.98 (m, 4H), 6.68 (t,  $J = 6.8$  Hz, 2H), 6.54 (t,  $J = 7.2$  Hz, 2H).

$^{31}\text{P}\{^1\text{H}\}$  NMR (202 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = -7.1 (s).

$^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = 152.6, 141.3 (d,  $J_{\text{PC}} = 3.3$  Hz), 140.3 (d,  $J_{\text{PC}} = 18.5$  Hz), 139.0 (d,  $J_{\text{PC}} = 5.1$  Hz), 137.8, 137.7, 135.5 (d,  $J_{\text{PC}} = 23.5$  Hz), 135.2 (d,  $J_{\text{PC}} = 13.2$  Hz), 135.0 (d,  $J_{\text{PC}} = 4.4$  Hz), 133.6 (d,  $J_{\text{PC}} = 21.1$  Hz), 130.6, 130.3, 129.3 (d,  $J_{\text{PC}} = 1.8$  Hz), 128.4 (d,  $J_{\text{PC}} = 6.3$  Hz), 128.1, 125.4, 124.8, 108.4 (d,  $J_{\text{PC}} = 7.8$  Hz), 61.2, 55.7.

Elemental analysis calcd (%) for  $\text{C}_{31}\text{H}_{27}\text{O}_3\text{P}$ : C, 77.81; H, 5.69; Found: C, 76.78; H, 5.34.

HRMS + p ESI (m/z)  $[\text{M}-\text{H}]^+$  Calcd.: 477.161958, Found: 477.16090.

#### [4-(4-Acetylphenyl)-3-fluoranthenyl]diphenyl phosphine (26)

Pentane:dichloromethane (1:3); as a yellow solid (93%, 234 mg).

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = 7.98–7.91 (m, 2H), 7.89 (dd,  $J = 6.3, 1.3$  Hz, 1H), 7.83 (d,  $J = 7.2$  Hz, 1H), 7.73 (d,  $J = 8.2$  Hz, 2H), 7.43 (qd,  $J = 7.0, 1.2$  Hz, 2H), 7.38 (d,  $J = 7.1$  Hz, 1H), 7.34–7.27 (m, 3H), 7.27–7.20 (m, 6H), 7.01 (t,  $J = 7.8$  Hz, 4H), 2.66 (s, 3H).

$^{31}\text{P}\{^1\text{H}\}$  NMR (202 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = -9.2 (s).

$^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = 147.6 (d,  $J_{\text{PC}} = 3.7$  Hz), 140.8 (d,  $J_{\text{PC}} = 2.1$  Hz), 139.2, 139.0, 138.5 (d,  $J_{\text{PC}} = 5.3$  Hz), 138.3, 137.9, 137.8 (d,  $J_{\text{PC}} = 1.7$  Hz), 136.3 (d,  $J_{\text{PC}} = 29.3$  Hz), 135.8, 134.1, 134.0, 133.5 (d,  $J_{\text{PC}} = 5.4$  Hz), 132.0 (d,  $J_{\text{PC}} = 21.3$  Hz), 131.8, 131.2 (d,  $J_{\text{PC}} = 6.1$  Hz), 128.6, 128.4 (d,  $J_{\text{PC}} = 6.7$  Hz), 128.3, 127.9, 127.6, 121.7 (d,  $J_{\text{PC}} = 25.2$  Hz), 120.1, 119.6, 26.9.

Elemental analysis calcd (%) for  $\text{C}_{36}\text{H}_{25}\text{P}$ : C, 85.70; H, 4.99; Found: C, 81.79; H, 4.88.

HRMS + p ESI (m/z)  $[\text{M}+\text{H}]^+$  Calcd.: 505.17213, Found: 505.17099.

#### [2-(3,4,5-Dimethoxyphenyl)-3-fluoranthenyl]diphenyl phosphine (27)

Pentane:dichloromethane (1:3); as a yellow solid (47%, 130 mg).

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = 7.94 (d,  $J = 7.1$  Hz, 1H), 7.89 (dd,  $J = 21.2, 7.1$  Hz, 2H), 7.81 (d,  $J = 7.2$  Hz, 1H), 7.47 (d,  $J = 7.1$  Hz, 1H), 7.43–7.36 (m, 2H), 7.28–7.25 (m, 3H), 7.22 (t,  $J = 7.3$  Hz, 4H), 7.01 (t,  $J = 7.0$  Hz, 4H), 6.32 (d,  $J = 1.4$  Hz, 2H), 3.94 (s, 3H), 3.53 (s, 6H).

$^{31}\text{P}\{^1\text{H}\}$  NMR (202 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = -8.9 (s).

$^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = 152.0, 142.0, 141.9, 139.5 (d,  $J_{\text{PC}} = 16.6$  Hz), 139.3, 139.0, 138.4, 138.0, 137.8, 137.7 (d,  $J_{\text{PC}} = 4.1$  Hz), 137.3 (d,  $J_{\text{PC}} = 1.7$  Hz), 136.7 (d,  $J_{\text{PC}} = 31.4$  Hz), 133.7 (d,  $J_{\text{PC}} = 21.0$  Hz), 133.3 (d,  $J_{\text{PC}} = 5.2$  Hz), 132.4 (d,  $J_{\text{PC}} = 20.7$  Hz), 131.6, 128.5 (d,  $J_{\text{PC}} = 6.6$  Hz), 128.4, 127.7, 121.6, 121.4, 120.0, 119.6, 108.5 (d,  $J_{\text{PC}} = 6.7$  Hz), 61.2, 55.8.

Elemental analysis calcd (%) for  $\text{C}_{37}\text{H}_{29}\text{O}_3\text{P}$ : C, 80.42; H, 5.29; Found: C, 80.20; H, 5.22.

HRMS + p ESI (m/z)  $[\text{M}+\text{Na}]^+$  Calcd.: 575.17465, Found: 575.17341.

#### [2-(3,4,5-Dimethoxyphenyl)-3-phenanthryl]diphenyl phosphine (28)

Pentane:dichloromethane (1:3); as a yellow solid (79%, 208 mg).

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = 8.72 (d,  $J = 8.4$  Hz, 1H), 8.61 (d,  $J = 8.4$  Hz, 1H), 7.59–7.52 (m, 2H), 7.48–7.35 (m, 4H), 7.12 (dt,  $J = 14.8, 7.5$  Hz, 6H), 6.92 (t,  $J = 6.9$  Hz, 4H), 6.22 (s, 2H), 3.83 (s, 3H), 3.43 (s, 6H).

$^{31}\text{P}\{^1\text{H}\}$  NMR (202 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = -7.1 (s).

$^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = 152.6, 142.1 (d,  $J_{\text{PC}} = 3.3$  Hz), 140.1 (d,  $J_{\text{PC}} = 18.6$  Hz), 139.4, 139.1 (d,  $J_{\text{PC}} = 5.3$  Hz), 137.8, 134.2 (d,  $J_{\text{PC}} = 31.4$  Hz), 133.6 (d,  $J_{\text{PC}} = 21.4$  Hz), 132.9 (d,  $J_{\text{PC}} = 19.3$  Hz), 131.6 (d,  $J_{\text{PC}} = 4.7$  Hz), 131.0, 130.9, 130.8, 128.7, 128.4 (d,  $J_{\text{PC}} = 6.4$  Hz), 128.2, 127.8, 126.9, 125.4, 123.0, 122.8 (d,  $J_{\text{PC}} = 1.0$  Hz), 108.7 (d,  $J_{\text{PC}} = 7.8$  Hz), 61.2, 55.8.

Elemental analysis calcd (%) for  $\text{C}_{35}\text{H}_{29}\text{O}_3\text{P}$ : C, 79.53; H, 5.53; Found: C, 78.87; H, 5.47.

HRMS + p ESI (m/z)  $[\text{M}-\text{H}]^+$  Calcd.: 527.17706, Found: 527.17636.

#### Synthesis of the 1-diphenylphosphine HAP oxides

A round flask equipped with a magnetic stirring bar was charged with 1-diphenylphosphine HAP (0.05 mmol, 1 equiv),  $\text{H}_2\text{O}_2$  in excess and  $\text{CH}_2\text{Cl}_2$  (0.025 M, 2 ml). The solution was stirred at room temperature overnight. After extraction ( $\text{CH}_2\text{Cl}_2/\text{H}_2\text{O}$ ), the organic layer was removed in vacuum to give the corresponding product.

#### 2-(Diphenylphosphino)fluoranthene oxide (18-O)

As a yellow solid (99%, 21 mg)

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = 8.31 (d,  $J = 8.5$  Hz, 1H), 7.89–7.86 (m, 3H), 7.83 (dd,  $J = 7.1, 1.3$  Hz, 1H), 7.74–7.70 (m, 4H), 7.58–7.51 (m, 4H), 7.49–7.46 (m, 4H), 7.43–7.36 (m, 2H).

$^{31}\text{P}\{^1\text{H}\}$  NMR (202 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = 30.7 (s).

$^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = 141.7 (d,  $J_{\text{PC}} = 2.9$  Hz), 140.4, 138.4, 137.6, 135.5 (d,  $J_{\text{PC}} = 2.4$  Hz), 133.6, 133.0 (d,  $J_{\text{PC}} = 10.0$  Hz), 132.8, 132.3, 132.2, 132.1 (d,  $J_{\text{PC}} = 2.8$  Hz), 131.1 (d,  $J_{\text{PC}} = 8.2$  Hz), 129.5, 129.4, 129.1, 128.8 (d,  $J_{\text{PC}} = 12.3$  Hz), 128.0, 127.4 (d,  $J_{\text{PC}} = 4.0$  Hz), 122.4, 121.8, 120.9, 118.5 (d,  $J_{\text{PC}} = 14.1$  Hz).

Elemental analysis calcd (%) for  $\text{C}_{28}\text{H}_{19}\text{OP}$ : C, 83.57; H, 4.76; Found: C, 82.89; H, 4.39.

HRMS + p ESI (m/z)  $[\text{M}+\text{Na}]^+$  Calcd.: 425.10657, Found: 425.10661.

#### 2-(3,4,5-Dimethoxyphenyl)3-fluoranthenyl]diphenylphosphine oxide (27-O)

As a yellow solid (99%, 22 mg)

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = 7.91 (dd,  $J = 7.6, 10.9$  Hz, 3H), 7.87–7.78 (m, 2H), 7.45 (t,  $J = 7.6$  Hz, 2H), 7.39 (m, 7H), 7.29 (m, 4H), 6.26 (s, 2H), 3.95 (s, 3H), 3.80 (s, 6H).

$^{31}\text{P}\{^1\text{H}\}$  NMR (202 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = 29.1 (s).

$^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = 152.0, 142.1, 142.1, 141.9 (d,  $J_{\text{PC}} = 3.1$  Hz), 141.0, 140.9 (d,  $J_{\text{PC}} = 1.5$  Hz), 139.8, 138.1, 137.2, 137.0 (d,  $J_{\text{PC}} = 5$  Hz), 135.9, 135.1, 134.2, 130.8 (d,  $J_{\text{PC}} = 9.3$  Hz), 129.3, 128.4 (d,  $J_{\text{PC}} = 12.1$  Hz), 128.0, 122.3, 121.5, 120.5, 118.7 (d,  $J_{\text{PC}} = 14.7$  Hz), 107.9, 60.8, 55.7.

Elemental analysis calcd (%) for  $\text{C}_{37}\text{H}_{29}\text{O}_4\text{P}$ : C, 78.16; H, 5.14; Found: C, 78.66; H, 5.32.

HRMS + p ESI (m/z)  $[\text{M}+\text{H}]^+$  Calcd.: 569.18762, Found: 569.18568.

#### Synthesis of the fluoranthenylphosphine selenides<sup>[21]</sup>

A round flask equipped with a magnetic stirring bar was charged with 1-diphenylphosphine HAP (1 equiv, 0.055 mmol) and excess of selenium

powder in CH<sub>2</sub>Cl<sub>2</sub> (0.025 M, 2 ml). The solution was stirred at room temperature overnight, and the mixture was filtrated on Celite and washed with CH<sub>2</sub>Cl<sub>2</sub>. The solvent was removed under vacuum to give the corresponding selenide as a yellow solid.

### 2-(Diphenylphosphino)fluoranthene selenide (18-Se)

As a yellow solid (99%, 25 mg)

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ (ppm) = 8.25 (d, *J* = 8.5 Hz, 1H), 7.90–7.82 (m, 7H), 7.75 (d, *J* = 7.2 Hz, 1H), 7.55 (m, 2H), 7.49–7.45 (m, 5H), 7.44–7.32 (m, 3H).

<sup>31</sup>P{<sup>1</sup>H} NMR (202 MHz, CDCl<sub>3</sub>): δ (ppm) = 29.5 (singlet with doublet satellites, *J*<sub>P-Se</sub> = 724 Hz).

<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ (ppm) = 141.6 (d, *J*<sub>PC</sub> = 3.5 Hz), 140.4, 138.4, 137.8, 134.6 (d, *J*<sub>PC</sub> = 10.8 Hz), 133.7, 133.6, 133.2 (d, *J*<sub>PC</sub> = 11.0 Hz), 131.9, 131.9 (d, *J*<sub>PC</sub> = 3.0 Hz), 131.3, 130.1 (d, *J*<sub>PC</sub> = 9.8 Hz), 129.1, 128.8 (d, *J*<sub>PC</sub> = 12.7 Hz), 128.6, 128.2, 128.0, 127.5 (d, *J*<sub>PC</sub> = 5.1 Hz), 122.3, 121.7, 120.9, 118.7 (d, *J*<sub>PC</sub> = 14.1 Hz).

Elemental analysis calcd (%) for C<sub>28</sub>H<sub>19</sub>PSe: C, 72.26; H, 4.12; Found: C, 71.87; H, 4.02.

HRMS + p ESI (m/z) [M+Na]<sup>+</sup> Calcd.: 489.02818, Found: 489.02837.

### [2-(3,4,5-Dimethoxyphenyl)3-fluoranthenyl]diphenylphosphine selenide (27-Se)

As a white solid (99%, 22 mg)

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ (ppm) = 8.03 (dd, *J* = 19.0, 7.3 Hz, 1H), 7.94–7.87 (m, 4H), 7.58 (dd, *J* = 12.9, 7.8 Hz, 3H), 7.45 (t, *J* = 7.3 Hz, 1H), 7.41 (t, *J* = 6.8 Hz, 2H), 7.29 (t, *J* = 7.0 Hz, 2H), 7.21 (m, 4H), 6.12 (s, 2H), 3.94 (s, 3H), 3.81 (s, 6H).

<sup>31</sup>P{<sup>1</sup>H} NMR (202 MHz, CDCl<sub>3</sub>): δ (ppm) = 38.0 (singlet with doublet satellites, *J*<sub>P-Se</sub> = 753 Hz).

<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ (ppm) = 152.3, 141.7 (d, *J*<sub>PC</sub> = 1.6 Hz), 141.2, 140.8, 140.7, 139.7, 138.2, 137.2, 137.1, 134.1, 132.0, 131.9, 130.5, 129.2, 128.2 (d, *J*<sub>PC</sub> = 12.5 Hz), 122.3, 121.5, 120.6, 119.2, 60.9, 55.9.

Elemental analysis calcd (%) for C<sub>37</sub>H<sub>29</sub>O<sub>3</sub>PSe: C, 70.36; H, 4.63; Found: C, 70.82; H, 4.81.

HRMS + p ESI (m/z) [M+Na]<sup>+</sup> Calcd.: 655.09117, Found: 655.08922.

### Synthesis of the Au(I)Cl and Cu(I)Cl complexes (A-D)<sup>[23]</sup>

A round flask (50 ml) equipped with a magnetic stirring bas was charged with 1-diphenylphosphine HAP (0.055 mmol, 1 equiv) and gold chloride [(Me<sub>2</sub>S)AuCl] or copper chloride CuCl (0.055 mmol, 1 equiv) and CH<sub>2</sub>Cl<sub>2</sub> (0.025 M, 2 ml). The solution was stirred at room temperature overnight, and the mixture was filtrated on Celite and washed with CH<sub>2</sub>Cl<sub>2</sub>. The solvent was removed under vacuum to give the corresponding complex. Crystallization or precipitation was operated using CH<sub>2</sub>Cl<sub>2</sub> solution and the slow addition of minimum pentane.

### Gold complex stabilized by 2-(diphenylphosphino)fluoranthene (A)

As a white solid (99%, 362 mg)

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ (ppm) = 8.23 (d, *J* = 8.4 Hz, 1H), 7.89 (d, *J* = 6.9 Hz, 1H), 7.86 (d, *J* = 7.5 Hz, 2H), 7.79 (d, *J* = 7.1 Hz, 1H), 7.63 (dd, *J* = 13.5, 7.6 Hz, 4H), 7.57 (t, *J* = 7.2 Hz, 2H), 7.53 (d, *J* = 8.1 Hz, 1H), 7.50 (dt, *J* = 7.1, 3.9 Hz, 4H), 7.40 (m, 2H), 7.17 (dd, *J* = 14.4, 7.1 Hz, 1H).

<sup>31</sup>P{<sup>1</sup>H} NMR (202 MHz, CDCl<sub>3</sub>): δ (ppm) = 24.5 (s).

<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ (ppm) = 141.8 (d, *J*<sub>PC</sub> = 2.3 Hz), 140.1, 138.2, 138.0 (d, *J*<sub>PC</sub> = 1.3 Hz), 135.3 (d, *J*<sub>PC</sub> = 8.5 Hz), 134.9 (d, *J*<sub>PC</sub> = 14.1 Hz), 133.1 (d, *J*<sub>PC</sub> = 9.4 Hz), 132.4 (d, *J*<sub>PC</sub> = 1.7 Hz), 130.5 (d, *J*<sub>PC</sub> = 12.1 Hz), 129.8, 129.6 (d, *J*<sub>PC</sub> = 12.1 Hz), 129.3, 128.7 (d, *J*<sub>PC</sub> = 63.6 Hz), 128.2, 125.3 (d, *J*<sub>PC</sub> = 9.7 Hz), 124.8 (d, *J*<sub>PC</sub> = 62.4 Hz), 122.4, 121.9, 121.2, 119.1 (d, *J*<sub>PC</sub> = 11.5 Hz).

Elemental analysis calcd (%) for C<sub>28</sub>H<sub>19</sub>AuClP: C, 54.34; H, 3.09; Found: C, 53.47; H, 2.93.

HRMS + p ESI (m/z) [M+Na]<sup>+</sup> Calcd.: 641.04706, Found: 641.04800.

### Gold complex stabilized by [2-(3,4,5-dimethoxyphenyl)3-fluoranthenyl]diphenyl phosphine (B)

As a yellow solid (97%, 41 mg)

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ (ppm) = 7.94 (d, *J* = 7.1 Hz, 1H), 7.89 (dd, *J* = 14.2, 7.4 Hz, 2H), 7.83 (d, *J* = 7.3 Hz, 1H), 7.50–7.43 (d, *J* = 7.1 Hz, 1H), 7.41–7.36 (m, 4H), 7.38 (m, 9H), 6.30 (s, 2H), 3.93 (s, 3H), 3.58 (s, 6H).

<sup>31</sup>P{<sup>1</sup>H} NMR (202 MHz, CDCl<sub>3</sub>): δ (ppm) = 30.4 (s).

<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ (ppm) = 153.0, 141.6 (d, *J*<sub>PC</sub> = 2.9 Hz), 141.1 (d, *J*<sub>PC</sub> = 3.5 Hz), 140.8 (d, *J*<sub>PC</sub> = 7.1 Hz), 139.7, 138.1, 138.0, 137.6, 137.5 (d,

*J*<sub>PC</sub> = 1.9 Hz), 134.5, 134.3 (d, *J*<sub>PC</sub> = 9.7 Hz), 133.9 (d, *J*<sub>PC</sub> = 14.0 Hz), 132.3, 131.8, 131.6 (d, *J*<sub>PC</sub> = 2.3 Hz), 131.3 (d, *J*<sub>PC</sub> = 11.8 Hz), 129.5, 129.3 (d, *J*<sub>PC</sub> = 11.8 Hz), 128.2, 125.8, 125.4, 122.3, 121.7, 120.7, 119.0 (d, *J*<sub>PC</sub> = 11.0 Hz), 108.4, 61.3, 56.0.

Elemental analysis calcd (%) for C<sub>37</sub>H<sub>29</sub>AuClO<sub>3</sub>P: C, 56.61; H, 3.72; Found: C, 53.06; H, 3.35.

HRMS + p ESI (m/z) [M+Na]<sup>+</sup> Calcd.: 807.11006, Found: 807.11375.

### Copper complex stabilized by 2-(diphenylphosphino)fluoranthene (C)

As a white solid (73%, 37 mg)

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ (ppm) = 8.33 (d, *J* = 8.1 Hz, 1H), 7.81 (d, *J* = 6.5 Hz, 1H), 7.73 (d, *J* = 6.5 Hz, 1H), 7.67 (d, *J* = 6.8 Hz, 1H), 7.57 (s, 3H), 7.48 (d, *J* = 6.8 Hz, 1H), 7.36–7.27 (m, 4H), 7.17 (t, *J* = 7.4 Hz, 4H), 7.08 (s, 1H), 6.92 (s, 1H).

<sup>31</sup>P{<sup>1</sup>H} NMR (202 MHz, CDCl<sub>3</sub>): δ (ppm) = -8.7 (sb).

<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ (ppm) = 140.1, 139.3, 138.8, 137.0, 134.7, 134.6, 134.2 (d, *J*<sub>PC</sub> = 2.8 Hz), 132.8 (d, *J*<sub>PC</sub> = 6.7 Hz), 132.2 (d, *J*<sub>PC</sub> = 36.0 Hz), 131.4, 131.3, 130.1, 128.8 (d, *J*<sub>PC</sub> = 8.9 Hz), 128.6 (d, *J*<sub>PC</sub> = 36.1 Hz), 127.6, 127.2 (d, *J*<sub>PC</sub> = 11.0 Hz), 121.9, 121.5, 120.6, 119.3 (d, *J*<sub>PC</sub> = 5.6 Hz).

Elemental analysis calcd (%) for C<sub>28</sub>H<sub>19</sub>ClCuP: C, 69.28; H, 3.92; Found: C, 70.06; H, 4.02.

HRMS + p ESI (m/z) [2M+H]<sup>+</sup> Calcd.: 969.04961, Found: 969.21468.

### Copper complex stabilized by [2-(3,4,5-dimethoxyphenyl)3-fluoranthenyl]diphenyl phosphine (D)

As a yellow solid (76%, 26 mg)

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ (ppm) = 7.89 (d, *J* = 7.1 Hz, 1H), 7.86–7.82 (m, 2H), 7.81 (d, *J* = 7.3 Hz, 1H), 7.43 (d, *J* = 7.0 Hz, 4H), 7.38 (t, *J* = 10.2 Hz, 10H), 6.29 (s, 2H), 3.92 (s, 3H), 3.22 (s, 6H).

<sup>31</sup>P{<sup>1</sup>H} NMR (202 MHz, CDCl<sub>3</sub>): δ (ppm) = -5.3 (sb).

<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ (ppm) = 154.0, 140.7, 140.3 (d, *J*<sub>PC</sub> = 8.6 Hz), 139.5, 138.4, 137.9, 137.5, 136.7 (d, *J*<sub>PC</sub> = 2.2 Hz), 133.7, 133.7 (d, *J*<sub>PC</sub> = 15.6 Hz), 132.9, 132.0 (d, *J*<sub>PC</sub> = 16.8 Hz), 130.4, 129.1 (d, *J*<sub>PC</sub> = 9.9 Hz), 128.9, 128.0, 122.0, 121.6, 120.2, 119.5 (d, *J*<sub>PC</sub> = 6.1 Hz), 104.0, 61.2, 55.5.

Elemental analysis calcd (%) for C<sub>37</sub>H<sub>29</sub>ClCuO<sub>3</sub>P: C, 68.20; H, 4.49; Found: C, 67.84; H, 4.30.

HRMS + p ESI (m/z) [M-Cl]<sup>+</sup> Calcd.: 615.11448, Found: 615.11487.

### General procedures for the Synthesis of the 2,5-disubstituted oxazoles

An oven-dried Schlenk tube equipped with a magnetic stirring bar was charged with terminal alkynes (0.6 mmol, 1 equiv), 8-methylquinoline N-oxide (0.78 mmol, 1.3 equiv), [Au] (0.03 mmol, 5 mol%), AgNTf<sub>2</sub> (0.09 mmol, 15 mol%), in acetonitrile or benzonitrile (0.2 M, 3 ml). The mixture was stirred at 50°C under argon during 5 h. The crude product was purified by column chromatography on silica using as eluent a mixture pentane:ethyl acetate.

### 5-(4-methoxyphenyl)-2-methyloxazole (29)<sup>[25a]</sup>

As a yellow solid (93%, 105 mg)

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ (ppm) = 7.87 (d, *J* = 8.9 Hz, 3H), 7.19 (s, 1H), 6.87 (d, *J* = 8.9 Hz, 3H), 3.80 (s, 3H), 2.49 (s, 3H).

### 5-(4-methoxyphenyl)-2-phenyloxazole (30)<sup>[26]</sup>

As a yellow solid (82%, 123 mg)

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ (ppm) = 8.10 (d, *J* = 6.6 Hz, 2H), 7.65 (d, *J* = 8.8 Hz, 2H), 7.50–7.43 (m, 3H), 7.32 (s, 1H), 6.97 (d, *J* = 8.8 Hz, 2H), 3.85 (s, 3H).

### 5-(4-fluorophenyl)-2-methyloxazole (31)<sup>[27]</sup>

As a white solid (80%, 85 mg)

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ (ppm) = 7.50 (dd, *J* = 8.8, 5.2 Hz, 2H), 7.07 (s, 1H), 7.03 (t, *J* = 8.7 Hz, 2H), 2.45 (s, 3H).

<sup>19</sup>F{<sup>1</sup>H} NMR (470 MHz, CDCl<sub>3</sub>): δ (ppm) = -112.9 (s).

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## Supporting Information

YES (this text will be updated with links prior to publication)

## Primary Data

NO.

## Conflict of Interest

The authors declare no conflict of interest.

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