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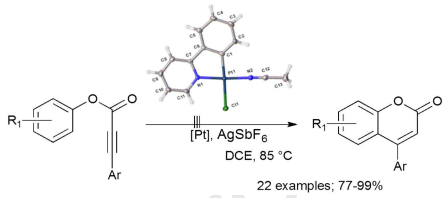

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Cyclization of Aryl 3-Arylpropynoates into 4-Arylcoumarins Catalyzed by Cyclometalated Platinum(II) Complexes

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Dedicated to Professor Léon Ghosez to acknowledge his many seminal research achievements, his unique contribution to *Tetrahedron* and his friendship.

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ABSTRACT

Cyclometalated (ppy)Pt^{II} complexes (ppy = 2-phenylpyridinato-C^2,*N*) catalyze the intramolecular cyclization of aryl propynoates to form coumarins and benzocoumarins. The complex [(ppy)PtCl(MeCN)] (5 mol %) was the most active and efficient catalyst for such reaction, especially in the presence of $AgSbF_6$ (15 mol %) in 1,2-dichloroethane. With this catalytic system, a wide range of substituents and functional groups proved compatible with the cyclization process, leading to a large variety of substituted coumarins and benzocoumarins (22 examples, 77−99%)

1. Introduction

Coumarins are natural products, isolated from a large range of organisms (Figure 1).[1] They exhibit a broad range of activity that has made the coumarin core a privileged scaffold found nowadays in numerous pharmaceutical, agrochemical and cosmetic compounds.[2] Due to their optical properties, coumarins are also widely employed in biology as fluorophores, fluorescent labels and probes for imaging,[3] as well as in material sciences as laser and as organic light-emitting diodes.[4] They further gained application as dyes and optical brighteners.[5]

As these various properties can be tuned by substituting the coumarin core, numerous syntheses have been proposed since the original Pechmann condensation,[6] and among them,[7] metal-catalyzed routes emerged as mild alternatives to the traditional methods requiring strongly acidic or basic conditions.[8] In particular, the metal-promoted cyclization of aryl propynoates offers a simple, convergent and modular access to coumarin derivatives. Within these methods, some of them relied on radical processes initiated by electron transfer from Ag^{I}, Cu^{II}, Fe^{III} salts or Ir^{III} complex.[9] Such cyclization required specific conditions, while leading to side-products. In contrast, cyclization promoted

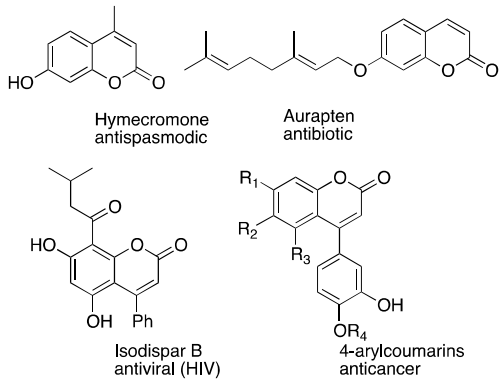
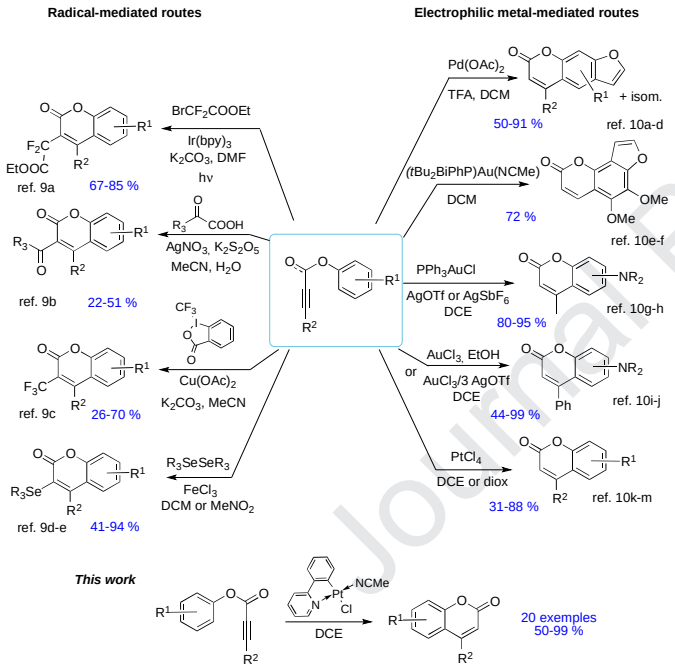


Figure 1. Representative examples of bioactive natural and non-natural coumarins

by π-electrophilic cations (Pd^{II}, Pt^{IV} and Au^{III} salts or Au^{I} complexes) provided reliable results.[10] Among the most efficient, Pd catalysts required trifluoroacetic acid as solvent, which could be deleterious for sensitive compounds.[10a-d] Au catalysts are also quite efficient, [10e-j] but they required Ag salts as cocatalyst, especially $AuCl_3$, which needs 3 equivalents of AgOTf. Au-catalyzed reactions are also sensitive to moisture, since water induces the formation of spiro compounds in competition with the expected coumarins.[10g] Despite solubility problem due to its polymeric structure, $PtCl_4$ is also known as catalyst for such cyclization, although modest to good yields have been observed depending on the substituents (Scheme 1).[10k-m] Although $PtCl_2$ has also been screened for this cyclization, it always gave lower yields (13-28 vs 73-78%).[10h, 10k-l] However, $PtCl_2$ usually exhibits similar and even better reactivity compared to that of $PtCl_4$, despite its lower electrophilicity.[11] It should thus compete with Au(I) and $PtCl_4$ catalysts in the cyclization of aryl propynoates.

We thus investigated Pt(II) derivatives, reasoning that Pt(II) reactivity and solubility could be tuned by using specific ligand. We showed here that cyclometalated platinum(II) complexes [(ppy)PtLCl, ppy = (2-phenylpyridinato-C^2,*N*)] offer an enhanced reactivity, providing various coumarins in good to high yields.



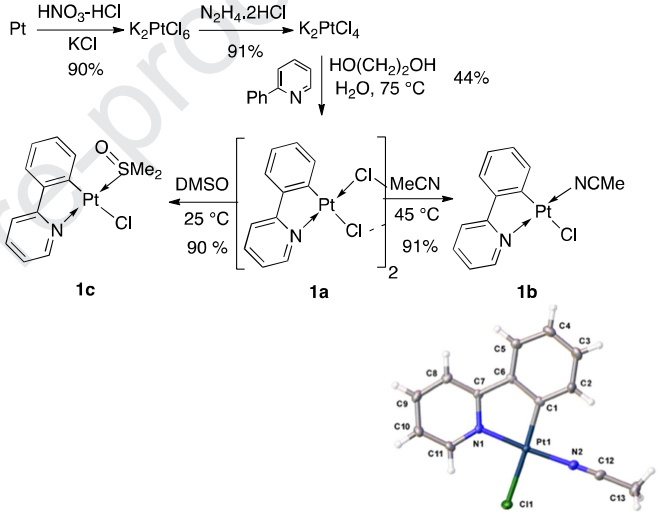
Scheme 1. Known metal-promoted cyclizations of aryl propynoates and the proposed new catalyzed version.

2. Results and discussion

2.1. Catalyst synthesis & study.

As a matter of fact, not many Pt(II) complexes have been developed for catalytic purposes in organic synthesis.[11-13] Nevertheless, numerous Pt(II) derivatives have been prepared as analogs to the well-known 'cisplatin' drug since the discovery of its anticancer property.[14] More recently, the increasing development of luminescent systems (sensors, switches, bioprobes, imaging tools and OLED) has also promoted the synthesis of Pt(II) derivatives.[15] Among the latter, platinacycles have often been employed due to the ease with which their photophysical properties could be modulated. Their electronic properties, as well as the control of the *cis/trans* complex geometry, can indeed easily be tuned.

Expecting similar tuning of catalytic properties, we explored the behavior of Pt(II) derivatives with cyclometalated ligands in the cyclization of aryl propynoates. Such ligand usually exhibits strong *trans*-influence, while increasing metal electrophilicity,[16] and both effects are required to allow coordination and activation of the propynoate substrate. Furthermore, platinacycles exhibit a remarkable stability of the Pt-C bond,[17] and they thus should give stable catalysts. In this context, one of the simplest cyclometalating ligand, *i.e.* 2-phenylpyridine (ppy), was initially selected. The corresponding platinacycles, (2- phenylpyridinato-C^2,*N*)Pt(II) complexes, have been reported,[18-19] but they were never used in catalysis. It was thus worth investigating them as catalysts. Such complexes could be obtained from 2-phenylpyridine and potassium tetrachloroplatinate, but their synthesis seems not so obvious.[18] Here, the chloro-bridged dimer [{(ppy)PtCl}$_2$] **1a** was readily produced in warm aqueous ethoxyethanol (Scheme 2). The mild heating of this dimer in acetonitrile afforded the analytically pure monomeric complex [(ppy)PtCl(MeCN)] **1b**, that was isolated in 91% yield. This complex **1b** was fully characterized by ESI-HRMS, FTIR, ^{1}H and ^{13}C NMR, and by single-crystal X-ray diffraction. Similarly, the monomeric complex **1c**[19] was obtained by dissociation of the dimeric **1a** in DMSO.



Scheme 2. Synthesis of 2-(pyridin-2-yl)phenyl Pt(II) complexes, and a XRD view of crystal of **1b** (Thermal ellipsoids drawn with 50% probability; hydrogen labels omitted for simplicity)

Complex **1b** is a stable solid in air at room temperature, but in CH_2Cl_2, $CHCl_3$ or MeOH solutions, **1b** is slowly transformed to the starting chloro-bridged dimer **1a** (the transformation was complete after 48 hours as showed by ^{1}H NMR monitoring). The presence of $[M-Cl]^+$ peaks in ESI-HRMS indicates the existence of small amount of the corresponding dechlorinated complex in equilibrium with the chloro-bridged dimer **1a** and acetonitrile in MeOH solutions. In contrast, the monomeric [(ppy)PtCl(DMSO)] complex **1c** is stable in solutions and does not evolve back to dimer **1a**. The large stability difference for these monomeric complexes in solution is clearly indicative of a weak coordinating bond between the nitrile ligand and the platinum center, which could be of interest in catalysis.

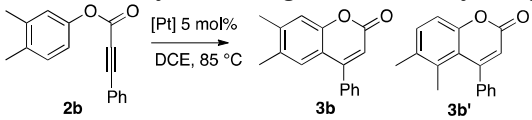
2.2. Catalysis set up

The simple phenyl 3-phenylpropynoate **2a** was first selected as model to study the catalytic ability of the above-mentioned Pt complexes. Unfortunately, almost no reaction could be detected with this substrate. Its dimethylated analog **2b** proved more reactive and although it gave a mixture of regioisomeric coumarins (**3b** and **3b'** in a 5:1 ratio), compound **2b** was used to screen Pt catalysts (Table 1).

While the absence of metal catalyst led to the recovery of the starting material **2b** (entry 1), simple platinum di- or tetrachloride salts provided the expected cyclized products, *i.e.* the coumarins **3b** and **3b'**, in non-coordinating solvent, but with low conversion and thus in low yields (entries 2 and 3), in agreement with some reports.[10h, 10k-l] More soluble complexes tended to slightly improve conversions and yields, but to the detriment of reaction time (entries 4 and 5). In sharp contrast, the (ppy)Pt(II) dimer **1a** provided coumarins in high yield after full conversion, but still after long reaction time (entry 6). As expected, the monomeric (ppy)Pt(II) complex in its acetonitrile form **1b** proved much more reactive, giving coumarins in almost quantitative yield within a day (entry 7). However, its DMSO form **1c** only induced very slow reaction, leading to only 37% after 3 days (entry 8). Such a large reactivity difference between these two monomeric (ppy)Pt(II) complexes clearly reflects the leaving ability of the ligand (see their respective stability, section 2.1).

It is worth noticing here that the cyclometalated platinum complexes **1a-b** efficiently provided the cyclized coumarinic product in high yields, while simple platinum chloride salts could only promote this cyclization with low yields (87-95% vs 14-20% respectively).

Table 1. Catalyst screening for the Pt-catalyzed cyclization of 3,4-dimethylphenyl 3-phenylpropynoate **2b**.



2b **3b** **3b'**

Entry	Catalyst	Time (h)	Overall yield of **3b** and **3b'** (%)[a, b]
1	none	24	0
2	$PtCl_2$	24	20 (16[c])
3	$PtCl_4$	24	14 (7[c])
4	*cis*-$[PtCl_2(MeCN)_2]$	76	20
5	*cis*-$[PtCl_2(DMSO)_2]$	75	19
6	$[\{(ppy)PtCl\}_2]$ **1a**	56	87
7	[(ppy)PtCl(MeCN)] **1b**	24	95
8	[(ppy)PtCl(DMSO)] **1c**	75	37

[a] ^{1}H NMR yields.

[b] The **3b**:**3b'** ratios were always at 5:1 within experimental errors.

[c] Isolated yields.

To go further, we optimized the required amount of complex **1b**, while increasing the cationic nature of the metallic center by the addition of silver salts (Table 2). Silver salts are well known to abstract halide from metal halide complexes, thus liberating a coordination site on the metal and rendering the metal ion more electrophilic. This set up was performed on the cyclization of the more challenging *ortho*-substituted ester **2c**.

Without silver salt, the (ppy)Pt(II)-catalyzed cyclization of the relatively hindered 2-methylphenyl phenylpropynoate **2c** proved to be slow and only low conversion could be achieved within one hour, regardless the catalyst loading (entries 1 and 2). In the presence of silver tetrafluoroborate, the same slow transformation was observed (entry 3), but silver hexafluoroantimonate drastically increased it (~10 times; entry 4 vs 3). Increasing the amount of silver salt rewardingly increased further the conversion (entries 5−7), with an optimum observed around 15−20%, which led to complete conversion and high yields (entries 6 and 7). Control experiments revealed that silver salts alone were not efficient enough to drive the cyclization to completion within reasonable times (entry 8 vs 6−7).

These results clearly confirmed the requirement of at least one free coordination site on platinum, and probably two (after exchanging MeCN and removing Cl), to induce the expected cyclization (see the Mechanism section below).

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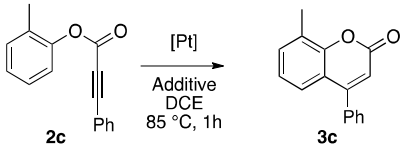
Table 2. Optimization of the catalyst loading and additive for the cyclization of 2-methylphenyl 3-phenylpropynoate **2c**.



2c **3c**

Entry	Catalyst (mol%)	Additive (mol%)	Yield (%)[a]
1	[(ppy)PtCl(MeCN)] **1b** (5)	-	8
2	**1b** (15)	-	11
3	**1b** (5)	$AgBF_4$ (5%)	4
4	**1b** (5)	$AgSbF_6$ (5%)	42
5	**1b** (5)	$AgSbF_6$ (10%)	91
6	**1b** (5)	$AgSbF_6$ (15%)	97
7	**1b** (5)	$AgSbF_6$ (20%)	100
8	-	$AgSbF_6$ (20%)	11

[a] Determined by ^{1}H NMR; the remaining part was the starting material.

2.3. Synthesis of coumarins: Scope and limitation

With a catalyst and conditions in hands, the influence of steric and electronic effects on the reaction course was examined with appropriately substituted aryl propynoates. The latter were prepared through classical esterification methods (See S. I.).

In a first set of experiments, aryl propynoates substituted at the ester moiety were investigated (Table 3). Reactions were monitored by TLC and stopped when full conversion of the starting material was reached, or after maximum 24h for slower cases. Esters carrying electron-rich substituents at the *O*-aryl residue gave higher conversions and yields of coumarins than those of the unsubstituted **2a** (entries 2−10 *vs* 1). Some variations nevertheless occurred depending on the nature of the substituent and on its position. A single methyl group induced a sharp increase in yield (entries 3-5 *vs* 1). Interestingly, the position of this group seems to play a role in the reaction time. The *ortho* isomer **2c** did not seem suffering much from steric hindrance, as similar conversion and yield were observed with its *para* isomer (entry 3 *vs* 4). As expected from mechanistic hypothesis (see section 2.5), the *meta* isomer **2e** gave a slightly faster reaction. The latter provided two regioisomeric coumarins, with the less hindered being the most abundant (~4:1 ratio; entry 5). It is worth noticing that the $Pd(OAc)_2$/TFA method[10a-c] provided lower selectivity (2:1), as well as lower yields in this series (75, 50, 78 vs 85, 89, 87 % for respectively the formation of **3c**, **3d**, **3e-e'**).

The dimethylated analog **2b** behave analogously in terms of efficacy and regioselectivity (entries 2 *vs* 4−5), but **2b** provided two isomers **3b** and **3b'** with a slightly better selectivity compared to **2e** (entry 2 *vs* 5). In contrast, the dimethylated **2f** proved more reactive than **2b** furnishing **3f** in only two hours (entry 6 *vs* 2). Here again the the $Pd(OAc)_2$/TFA method[10a-c] provided lower yields for similar compounds (75 vs 88 %).

Methoxylated or phenoxylated esters **2g-j** were as well efficiently cyclized with yields ranging from 82 to 94% (entries 7−10), with even faster reactions again for the *meta*-substituted isomers (entries 9-10 *vs* 7−8). In contrast, the electrodeficient bromo ester **2k** led to lower conversion and yield (entry 11 *vs* 1). For the methoxylated as well as for the bromo derivatives, the Au-catalyzed method provided similar or slightly higher yields,[10e, 10j] while simple Pt salts led to lower yields.[10k]

It is worth mentioning that the position of the substituent in the major products produced from *meta*-substituted aryl propynoates has been ascertained by establishing the structure of **3j** by XRD and NMR spectra comparison (See S. I.).

These results support the classically proposed mechanism based on nucleophilic addition of the aryl ester moiety to the metal-π-coordinated alkyne, for which the more electron rich the ester moiety, the more nucleophilic they are, inducing a more efficient cyclization (see the Mechanism section 2.5 below).

To confirm that hypothesis, the electronic density of the ynoate moiety was modulated by specific substituents. The fluoro derivative **2l** gave almost the same yield that the unsubstituted **2a** (entry 12 *vs* 1), while its methylated analog **2m** led to a slightly improved yield (entry 13 *vs* 1 *vs* 12). These results again support the proposed mechanism, but ynoate electronic effects seem to less affect the cyclization ability as compared to those observed with ester substituents (*e.g.* entry 13 *vs* 4). To check this aspect, compounds **2n−o** were prepared and submitted to cyclization. Acting on both sides also affected conversion and yield but the results showed that the substituent on the ester moiety indeed mostly drove the reaction efficacy (entry 15 *vs* 14).

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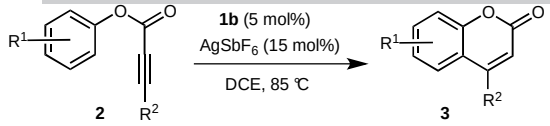
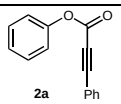
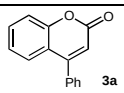
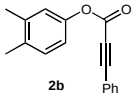
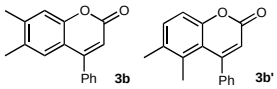
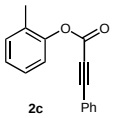
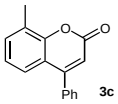
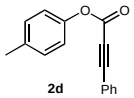
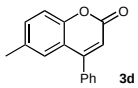
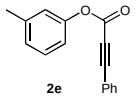
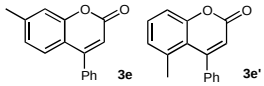
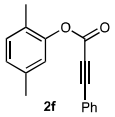
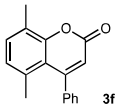
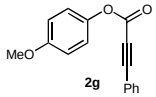
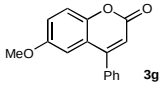
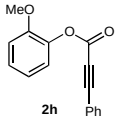
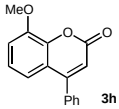
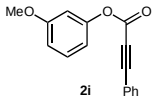
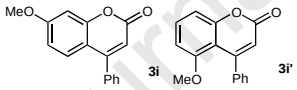
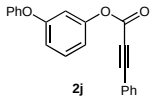
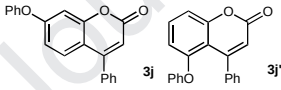
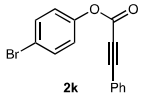
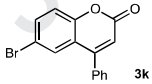
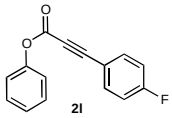
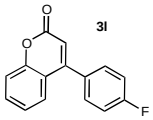
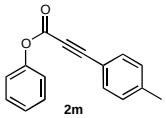
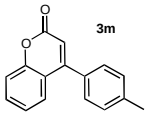
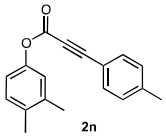
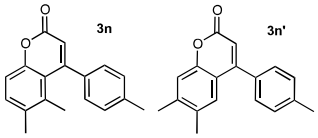
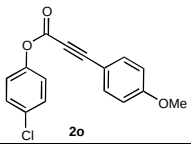
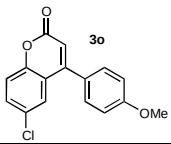
Table 3. [(ppy)PtCl(MeCN)]-catalyzed cyclization of aryl propynoates to coumarins.



Entry	Ynoate **2**	Coumarin **3**	Time (h)	Yield (%)[a]	Literature Yield (%)
1			24	54	
2			24	88 (5:1)	
3			24	85	75[10a]
4			24	89	50[10a]
5			20	87 (4.3:1)	75 (2:1) [10a]
6			2	88	75[b, 10a]
7			24	84	98[10j]
8			24	86	
9			1	94 (3.2:1)	50[10k]
10			2	82 (4:1)	
11			24	25	44[10j]
12			10	50	
13			24	59	
14			24	60 (3.8:1)	
15			24	50	

[a] Isolated yields.

2.4. Synthesis of benzocoumarins

Besides the biological activities associated to coumarins, benzocoumarins also constitute a promising family of photonic materials due to the extended nature of their π-electron system.[20] As only a limited number of such benzocoumarins have so far been reported,[21] we extended our strategy to the synthesis of a few benzocoumarins. A simple way to do so is to start from naphthyl ester derivatives.

Rewardingly, naphtyl esters **2p-t** proved very reactive under the set-up conditions. Full conversion and high yields were achieved within minutes (5−45 min; Table 4). The α isomer **2p** very rapidly gave the expected benzocoumarin **3p** in quantitative yield (entry 1). Interestingly, the β-naphtyl isomer required even shorter time and quantitatively provided a single regioisomer **3q** (entry 2 *vs* 1). Although the latter corresponds to the more hindered isomer among the two possible, it also corresponds to cyclization at the more nucleophilic α position in naphtyl derivatives. The structures of the products produced from the β-naphtyl propynoates have been ascertained by establishing the structure of **3r** and **3t** by XRD and NMR spectra comparison (See S. I.).

When substituents of different electron density were introduced on the phenyl propiolic moiety (**2r-t**), only variations of the reaction time were observed (entries 3−5 *vs* 2). No variations occurred regarding conversion and yields, except for the methyl substituted derivative **2r** (entry 3 *vs* 2). Surprisingly, the fluoro analog **2t** reacted as fast and as efficiently than the reference compound **2q** (entry 5 *vs* 2). These results, and especially the latter, confirm the prominent role of the ester moiety in such Pt(II)-catalyzed cyclization.

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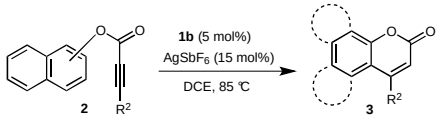
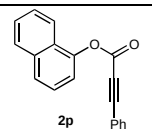
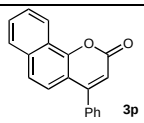
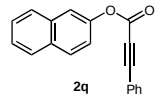
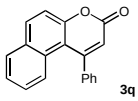
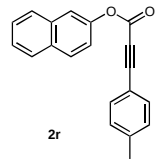
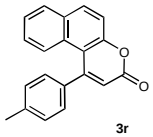
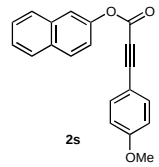
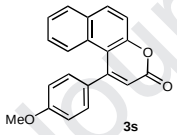
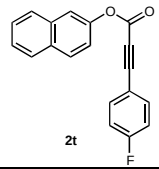
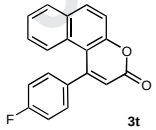
Table 4. [(ppy)PtCl(MeCN)]-catalyzed cyclization of naphtyl propynoates to benzocoumarins.



Entry	Ynoate **2**	Coumarin **3**	Time (mn)	Yield (%)[a]
1			15	99
2			5	99
3			30	74
4			45	99
5			5	99

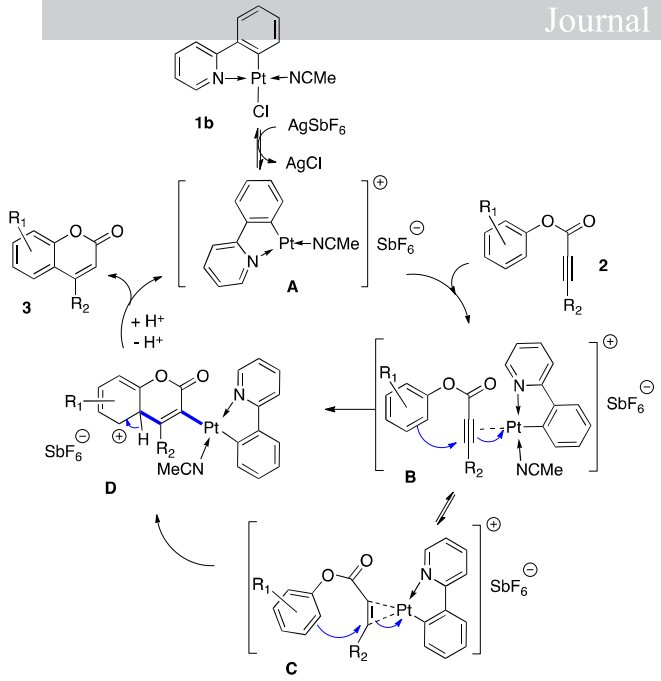
[a] Isolated yields.

2.5. Mechanism

As described above (see Section 2.2 and Table 1), a large reactivity difference was observed with (ppy)Pt(II) complexes compared to other Pt species. Among the former, the two monomeric (ppy)Pt(II) complexes **1b** and **1c** also exhibited a net activity difference as catalyst. These results as well as their respective stability (see section 2.1) clearly reflects the leaving ability of the ligand and the requirement for a free coordination site to induce the expected cyclization. The strong requirement for a free coordination site on platinum was further supported by the enhanced catalytic activity upon addition of silver salt (see Table 2).

Under the latter conditions, strongly electrophilic Pt(II) species (**A** in Sch. 3) would be *in situ* produced and π-coordination to the propynoate esters **2** would thus be facilitated (**B** in Sch. 3). Once activated, the alkynyl moiety could suffer from intramolecular nucleophilic addition of the phenolic ester moiety.

During our preliminary investigations, we observed in the presence of complex **1b** without additive a strong reactivity enhancement when an electrodonating substituent was located at the *meta*-position of the phenolic moiety of **2** (Sch. 4, top), and the more electrodonating this substituent, the more efficient and rapid was the cyclization (Sch. 4, bottom). Similar trend was also observed in the presence of silver additive (See Table 3, entry 9 vs 7-8). These results showed that the more nucleophilic is the *ortho* position in the phenolic moiety of **2**, the more efficient is the cyclization reaction. These results strongly suggest that the cyclization process is based on the nucleophilic addition of the phenolic moiety to the Pt-activated propynoate moiety.



Scheme 3. Proposed mechanism for the cyclisation of aryl propynoates to coumarins catalyzed by the (ppy)Pt(II) complex **1b**.

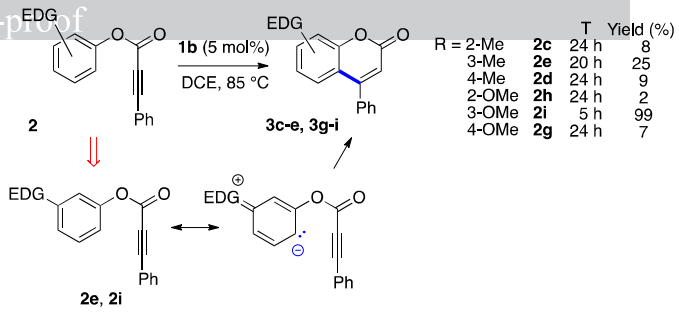
Although more Lewis acidic than gold,[22] platinum can easily form π-complexes (e.g. **B** in Sch. 3) and even platinacyclopropene-type complex (e.g. **C**), in agreement with the well-known strong back-donation of Pt(II) complexes.[12b, 23] The alkyne deformation induced by Pt(II) coordination[24] in **B** (or **C**) exposes the more nucleophilic *ortho* position of the phenolic moiety next to the more electrophilic carbon of the propynoate moiety and thus favors the 6-*endo-dig* cyclization. The latter should thus produce a cationic organoplatinum intermediate (**D**), which could then evolve through elimination of a proton to restore aromaticity. The so-liberated proton then allowed protodemetalation, which regenerates the catalyst and liberates the so-formed coumarin.

3. Conclusion

In this work, an efficient and mild access to coumarins has been developed, using monomeric or dimeric platinacycles as catalyst. Various substituents and functional groups proved compatible with the cyclization process, leading to a large variety of substituted coumarins. Benzocoumarins were also accessible in very high yields *via* the same platinacycle-catalyzed process.

Among the screened Pt(II) catalysts, the 2-(pyridin-2-yl)phenylPt(II)(acetonitrile) chloride complex **1b** was the most active and efficient. With this readily accessible complex, quantitative yields of benzocoumarins could be achieved and up to 94 % yield of coumarins was isolated. This platinacycle catalyst is thus highly competitive compared to other known catalysts, including the simple platinum chlorides.

The reactivity of the (ppy)Pt complexes reported here will be further explored and developed as a useful tool in organic synthesis.



Scheme 4. Cyclization of aryl propynoates, carrying electrodonating group (EDG) at the *O*-aryl residue, catalyzed by the monomeric catalyst **1b**.

4. Experimental section

NMR spectra were recorded on Bruker Avance 300, 400, or 500 instruments. Spectra were recorded in $CDCl_3$ solutions referenced to TMS or the solvent residual peak. IR spectra were recorded neat on Bruker Alpha ATR instrument. High-resolution mass spectra (HRMS) data were recorded on a microTOF spectrometer equipped with orthogonal electrospray interface (ESI). Chromatography was carried out using silica gel 60 (40–63 μm). Reagents and solvents were purified using standard methods. Anhydrous CH_2Cl_2, DCE, THF, and MeOH were dried by passing through activated alumina under a positive pressure of argon using GlassTechnology GTS100 devices. All other chemicals were used as received. All spectroscopies and analyses were performed at the Fédération de Chimie Le Bel, CNRS and University of Strasbourg.

4.1. Synthesis of platinum complexes

*4.1.1. Chlorido[2-(pyridin-2-yl)phenyl]Pt(II (**1a**)*[18]*:*

To a degassed water-ethoxyethanol (1:3) solution was added 0.58 g (3.7 mmol) of 2-phenylpyridine and 1.55 g (3.7 mmol) of dipotassium tetrachloroplatinate(II). The reaction mixture was heated at 75 °C for 24h. After cooling to room temperature, the reaction mixture was poured into 40 ml of distilled water. The resulting precipitate was filtered, washed with 10 ml of water and 5 ml of acetone, twice with 5 ml of dichloromethane and dried in air at room temperature. As a result, **1a** was obtained as a pale-yellow powder. Yield: 44%. ^{1}H NMR (300 MHz, DMSO-d^6): δ= 7.15 (t, 1H, *J* =7.2 Hz, $H_{arom.}$), 7.19 (t, 1H, *J* =7.2 Hz, $H_{arom.}$), 7.51 (t, 1H, *J* =7.2 Hz, $H_{arom.}$), 7.78 (d, 1H, *J* =6.0 Hz, $H_{arom.}$), 8.13-8.16 (m, 2H, $H_{arom.}$), 8.22 (d, 1H, *J* =6.1 Hz, $H_{arom.}$), 9.49 (d, 1H, *J* =6.1 Hz, $H_{arom.}$). Elemental analyses (C, H, N): calcd for $C_{22}H_{16}Cl_2N_2Pt_2$ 34.34%, 2.10%, 3.64%; found: 34.21%, 2.06%, 3.58%.

*4.1.2. (acetonitrile)chlorido[2-(pyridin-2-yl)phenyl]Pt(II) (**1b**)*

The dimeric complex [{(ppy)PtCl}]$_2$ **1a** (60 mg; 0.078 mmol) was stirred in acetonitrile (0.5 ml) at 45 °C for 16h. The resulting precipitate was filtered and dried in air at room temperature. **1b** was obtained as a yellow powder. Yield: 91%. IR (neat): 413, 480, 556, 628, 725, 743, 857, 1030, 1068, 1124, 1158, 1237, 1276, 1318, 1425, 1440, 1485, 1584, 1609, 2090, 3045 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ= 2.57 (s + ^{195}Pt satellites $^4J_{Pt-H}$ = 6.2 Hz, 3H, CH_3), 7.09-7.17 (m, 3H, $H_{arom.}$), 7.30 (dd, *J* = 6.3, 2.2, + ^{195}Pt satellites $^3J_{Pt-H}$ = 21.4 Hz, 1H, $H_{arom.}$), 7.43-7.46 (m, 1H, $H_{arom.}$), 7.60 (brd, *J* = 7.8 Hz, 1H, $H_{arom.}$), 7.82 (td, 1$H_{arom.}$, *J* = 8.0, 1.5 Hz, $H_{arom.}$), 9.55-9.72 (dd, *J* = 5.8, 1.5 Hz + ^{195}Pt satellites $^3J_{Pt-H}$ = 22.7 Hz, 1H, $H_{arom.}$). ^{13}C NMR (125MHz, $CDCl_3$): δ = 4.6, 116.5, 118.4, 122.0, 123.8, 124.3, 130.5, 132.0,

139.5, 139.6, 144.0, 151.0, 167.8. HRMS (ESI-µTOF): *m/z* [M–Cl+MeCN]$^+$ calcd for $C_{15}H_{14}N_3Pt$: 431.0831; found: 431.0841. Single crystal XRD structure (see S. I. and CCDC n° 1894192).

*4.2. General procedure for the synthesis of aryl propynoates (**2a-2t**).*

To a solution of propiolic acid derivative (6.8 mmol, 1eq) and phenol derivative (6.8 mmol, 1eq) in 10 mL of CH_2Cl_2 was added DCC (7.53 mmol, 1.1eq) and 10 drops of pyridine. The reaction mixture was stirred for 5-12 hours at 0 °C or rt. Upon reaction completion, the mixture was treated with water (50 ml), extracted with chloroform (3 × 50 ml). The combined organic phases were washed with 0.2 N NaOH (2 × 50 ml), water (2 × 50 ml) and dried over Na_2SO_4. After filtration, the solvent was removed under reduced pressure. The crude product was then purified by column chromatography on silica gel (eluent pentane : diethyl ether 95:5).

*4.2.1. 2,5-Dimethylphenyl 3-phenyl propynoate (**2f**)*

Yield: 74%. White solid; m.p =74.5–76 °C; R_f = 0.57 (10% diethyl ether/pentane). IR (neat): 451, 534, 557, 602, 689, 737, 758, 816, 904, 998, 1149, 1182, 1238, 1280, 1440, 1487, 1572, 1623, 1718, 2215, 2920 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ= 2.21 (s, 3H, CH_3), 2.34 (s, 3H, CH_3), 6.92 (s, 1H, $H_{arom.}$), 6.99 (d, 1H, *J* = 7.7 Hz, $H_{arom.}$), 7.14 (d, 1H, *J* = 7.7 Hz, $H_{arom.}$), 7.41 (t, 2H, *J* = 7.2 Hz, $H_{arom.}$), 7.49 (t, 1H, *J* = 7.4 Hz, $H_{arom.}$), 7.63 (d, 2H, *J* = 6.8 Hz, $H_{arom.}$). ^{13}C NMR (125MHz, $CDCl_3$): δ = 15.9, 21.0, 80.3, 88.5, 119.4, 122.3, 127.0, 127.5, 128.8, 131.1, 133.3, 137.2, 148.6, 152.4. HRMS (ESI): *m/z* [M+H]$^+$ calcd for $C_{17}H_{15}O_2$: 251.1067; found: 251.1068.

*4.2.2. 3,4-Dimethylphenyl 3-(4-methylphenyl)propynoate (**2n**)*

Yield: 53%. White solid; m.p =100.3–101.8°C; R_f = 0.6 (10% diethyl ether/pentane). IR (neat): 428, 536, 578, 710, 734, 819, 916, 1155, 1185, 1236, 1288, 1495, 1717, 2220, 2915 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.25 (s, 3H, CH_3), 2.27 (s, 3H, CH_3), 2.40 (s, 3H, CH_3), 6.91 (dd, 1H, *J* = 8.2, 2.5 Hz, $H_{arom.}$), 6.96 (d, 1H, *J* = 2.3 Hz, $H_{arom.}$), 7.15 (d, 1H, *J* = 8.2 Hz, $H_{arom.}$), 7.21 (d, 2H, *J* = 8.0 Hz, $H_{arom.}$), 7.52 (d, 2H, *J* = 8.1 Hz, $H_{arom.}$). ^{13}C NMR (125MHz, $CDCl_3$): δ = 19.3, 20.0, 21.8, 80.2, 89.1, 116.3, 118.6, 122.4, 129.5, 130.5, 133.3, 134.8, 138.2, 141.8, 148.1, 152.9. HRMS (ESI): *m/z* [M+K]$^+$ calcd for $C_{18}H_{16}KO_2$: 303.0782; found: 303.0789.

*4.2.3. Naphthalen-2-yl 3-(4-methylphenyl)propynoate (**2r**)*

Yield: 53%. Pale yellow solid; m.p = 104.5–106.9 °C; R_f = 0.5 (10% diethyl ether/pentane). IR (neat): 404, 481, 533, 570, 733, 761, 814, 896, 960, 1141, 1184, 1206, 1238, 1288, 1355, 1506, 1600, 1715, 2209, 2913 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ= 2.40 (s, 3H, CH_3), 7.21 (d, 2H, *J* =7.9 Hz, $H_{arom.}$), 7.32 (dd, 1H$_{arom.}$, *J* = 8.9, 2.4 Hz, $H_{arom.}$), 7.48-7.55 (m, 4H, $H_{arom.}$), 7.66 (d, 1H, *J* =2.5 Hz, $H_{arom.}$), 7.82-7.90 (m, 3H, $H_{arom.}$). ^{13}C NMR (125MHz, $CDCl_3$): δ = 21.9, 80.1, 89.6, 116.2, 118.7, 120.9, 126.1, 126.8, 127.9, 129.6, 129.7, 131.8, 133.3, 133.8, 142.0, 147.9, 152.7. HRMS (ESI): *m/z* [M+H]$^+$ calcd for $C_{20}H_{15}O_2$: 287.1067; found: 287.1074.

*4.2.4. Naphthalen-2-yl 3-(4-methoxyphenyl)propynoate (**2s**)*

Yield: 48%. Pale beige solid; m.p=91–93°C; R_f = 0.2 (10% diethyl ether/pentane). IR (neat): 468, 536, 577, 729, 759, 800, 827, 853, 889, 965, 1024, 1138, 1185, 1211, 1257, 1289, 1509, 1603, 1710, 2204, 2847, 2928, 3008, 3063, 3283 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ= 3.85 (s, 3H, CH_3), 6.91 (d, 2H, *J* =6.8 Hz, $H_{arom.}$), 7.32 (dd, 1H, *J* = 8.8, 2.3 Hz, $H_{arom.}$), 7.45-7.54 (m, 2H, $H_{arom.}$), 7.59 (d, 2H, *J* =8.9 Hz, $H_{arom.}$), 7.66 (d, 1H, *J* =2.3 Hz, $H_{arom.}$), 7.81-7.90 (m, 3H, $H_{arom.}$). ^{13}C NMR (125MHz, $CDCl_3$): δ = 55.6, 80.0, 90.0, 111.1, 114.5, 118.8, 120.9, 126.1, 126.8, 127.91, 127.94, 129.7, 131.7, 133.8, 135.4, 147.9, 152.8, 162.0. HRMS (ESI): *m/z* [M+H]$^+$ calcd for $C_{20}H_{15}O_3$: 303.1016; found: 303.0995.

*4.2.5. Naphthalen-2-yl 3-(4-fluorophenyl)propynoate (**2t**)*

Yield: 59%. Pale yellow solid; m.p =103–105.9 °C; Rf = 0.5 (10% diethyl ether/pentane). IR (neat): 470, 536, 573, 731, 762, 776, 821, 839, 865, 896, 938, 962, 1153, 1174, 1204, 1227, 1291, 1502, 1597, 1708, 2215, 3066, 3408 cm-1. ^{1}H NMR (500 MHz, $CDCl_3$): δ= 7.09 - 7.14 (m, 2H, $H_{arom.}$), 7.32 (dd, 1H, *J* = 8.8, 2.3 Hz, $H_{arom.}$), 7.48 - 7.53 (m, 2H, $H_{arom.}$), 7.63 - 7.67 (m, 3H, $H_{arom.}$), 7.82 - 7.90 (m, 3H, $H_{arom.}$). ^{13}C NMR (125MHz, $CDCl_3$): δ = 80.3, 87.9, 115.50, 115.53, 116.3, 116.5, 118.7, 120.8, 126.2, 126.9, 127.92, 127.96, 129.8, 131.8, 133.7, 135.6, 135.7, 147.8, 152.5, 163.3, 165.3. HRMS (ESI): *m/z* [M+H]$^+$ calcd for $C_{19}H_{12}FO_2$: 291.0816; found: 291.0810.

*4.3. General procedure for the Pt-catalyzed cyclization (**3a – 3t**).*

In a sealed tube (with a screw cap) filled with 2 ml of 1,2-DCE was added (ppy)PtCl(MeCN) (0.05 eq) and $AgSbF_6$ (0.15 eq), and after 5 min of mixing, was added O-aryl esters of 3-arylpropynoic acid (30 mg, 1eq). The reaction was performed at 85 °C with stirring, during 5 min - 24 h. At the end of the reaction, the mixture was filtered and the solvent was removed under reduced pressure. The resulting reaction product was purified by column chromatography on silica gel (eluents cyclohexane : diethyl ether 80:20).

*4.3.1. 5,8-dimethyl-4-phenyl-2H-chromen-2-one (**3f**)*

Yield: 88%. White solid; m.p =97.4–99.4 °C; Rf = 0.25 (20% diethyl ether /pentane). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.39 (s, 3H, CH_3), 2.42 (s, 3H, CH_3), 6.30 (s, 1H, =CH-), 7.03 (d, 1H, J = 8.2 Hz, H_{arom}), 7.20 (d, 1H, J = 8.2 Hz, $H_{arom.}$), 7.41 – 7.45 (m, 2H, H_{arom}), 7.48 – 7.52 (m, 3H, H_{arom}). ^{13}C NMR (125MHz, $CDCl_3$): δ = 11.8, 20.6, 113.8, 116.9, 124.0, 125.1, 125.7, 128.6, 128.9, 129.6, 135.9, 141.8, 152.5, 156.3, 161.4. IR (neat): 424, 497, 570, 619, 638, 699, 712, 757, 778, 817, 890, 953, 1090, 1176, 1258, 1370, 1448, 1597, 1707, 2853, 2921, 2973, 3059 cm-1. HRMS (ESI- µTOF): m/z [M+K]+ calcd for $C_{17}H_{14}KO_2$: 289.0625; found: 289.0588.

*4.3.2. 7-Phenoxy-4-phenyl-2H-chromen-2-one (**3j**)*

Yield: 82%. R_f = 0.3 (20% diethyl ether / cyclohexane). IR (neat): 404, 429, 466, 496, 570, 614, 644, 689, 731, 771, 797, 818, 836, 850, 868, 936, 999, 1049, 1072, 1113, 1147, 1182, 1241, 1271, 1339, 1374, 1449, 1484, 1550, 1586, 1712, 2853, 2923, 3051, 3088 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.23 (s, 0.25H, =CH-), 6.26 (s, 1H, =CH-), 6.42 – 6.45 (m, 0.5H, $H_{arom.}$), 6.77 (dd, 0.26H, *J* = 8.2, 1.1 Hz $H_{arom.}$), 6.87 (dd, 1H, *J* = 8.8, 2.5 Hz, $H_{arom.}$), 6.92 (d, 1H, *J* = 2.4 Hz, $H_{arom.}$), 6.96 – 6.99 (m, 0.26H, $H_{arom.}$), 7.07 – 7.15 (m, 2.54H, $H_{arom.}$), 7.20 – 7.25 (m, 2.26H, $H_{arom.}$), 7.38 – 7.48 m (5.22H, $H_{arom.}$), 7.50 – 7.54 (m, 3H, $H_{arom.}$). HRMS (ESI-µTOF): *m/z* [M+H]$^+$ calcd for $C_{21}H_{15}O_3$: 315.1016; found: 315.1001. Single crystal XRD structure (see S. I. and CCDC n° 1970640).

*4.3.3. 6,7-Dimethyl-4-(p-tolyl)-2H-chromen-2-one (**3n**)*

Yield: 60%. White solid; R_f = 0.2(20% diethyl ether /pentane). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.23 (s, 3H, CH_3), 2.35 (s, 3H, CH_3), 2.46 (s, 3H, CH_3), 6.27 (s, 1H, =CH-), 7.19 (s, 1H, $H_{arom.}$), 7.23 (s, 1H, $H_{arom.}$), 7.31-7.37 (m, 4H, $H_{arom.}$). ^{13}C NMR (125MHz, $CDCl_3$): δ = 19.5, 20.3, 21.5, 114.0, 116.8, 118.0, 127.1, 128.5, 129.6, 132.8, 133.0, 139.8, 142.1, 152.7, 155.9, 161.6. HRMS (ESI-μTOF): *m/z* $[M+H]^+$ calcd for $C_{18}H_{17}O_2$: 265.1223; found: 265.1219.

4.3.4. 4-(4-Methylphenyl)-2H-benzo[f]chromen-2-one (**3r**).

Yield: 74%. White solid; m.p=124.8–126.6°C. Rf=0.19 (20% diethyl ether /pentane). IR (neat): 408, 459, 566, 603, 747, 811, 933, 996, 1055, 1454, 1509, 1546, 1622, 1721, 2852, 2921 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.50 (s, 3H, CH_3), 6.37 (s, 3H, =CH-), 7.17 – 7.22 (m, 1H, H_{arom}), 7.25 (d, 2H, J = 8.2 Hz, H), 7.31 – 7.37 (m, 3H, H), 7.40 – 7.45 (m, 1H, H), 7.51 (d, 1H, J = 8.9 Hz, H), 7.85 (dd, 1H, J = 8.1, 1.3 Hz H), 7.99 (d, 1H, J = 8.9 Hz, H). ^{13}C NMR (125MHz, $CDCl_3$): δ = 21.6, 113.3, 116.8, 117.6, 125.4, 126.2, 126.8, 127.5, 129.1, 129.6, 129.9, 131.4, 134.0, 136.8, 139.4, 154.9, 156.8, 160.6. HRMS (ESI-μTOF): m/z [M+H]+ calcd for $C_{20}H_{15}O_2$: 287.1067; found: 287.1093. Single crystal XRD structure (see S. I. and CCDC).

4.3.5. 1-(4-Fluorophenyl)-2H-benzo[f]chromen-2-one (**3t**)

Yield: 99%. White solid; m.p=116.5–121.4°C; Rf=0.15 (20% diethyl ether /pentane). IR (neat): 402, 503, 532, 565, 600, 685, 698, 723, 750, 817, 848, 893, 933, 996, 1074, 1092, 1154, 1182, 1214, 1267, 1319, 1394, 1430, 1454, 1503, 1546, 1599, 1622, 1717, 2849, 2920, 3069 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.37 (s, 1H, =CH-), 7.17 – 7.28 (m, 4H, $H_{arom.}$), 7.33 – 7.39 (m, 2H, $H_{arom.}$), 7.40 – 7.46 (m, 1H, $H_{arom.}$), 7.54 (d, 1H, *J* = 9.0 Hz, $H_{arom.}$), 7.87 (dd, 1H, *J* = 8.1, 1.2 Hz $H_{arom.}$), 8.02 (d, 1H, *J* = 8.9 Hz, $H_{arom.}$). ^{13}C NMR (125MHz, $CDCl_3$): δ = 113.0, 116.4, 116.6, 117.2, 117.7, 125.6, 125.9, 127.0, 129.3, 129.4, 129.5, 129.6, 131.5, 134.3, 135.6, 135.7, 155.0, 155.6, 160.4, 162.4, 164.4. HRMS (ESI-μTOF): *m/z* $[M+H]^+$ calcd for $C_{19}H_{12}FO_2$: 291.0816; found: 291.0817. Single crystal XRD structure (see S. I. and CCDC).

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Supplementary Material

Experimental details for the synthesis of Pt(II) complexes, for all starting aryl propynoates and coumarin products, as well as copy of ^{1}H, ^{13}C and ^{19}F NMR spectra and XRD data and structures for some compounds, are provided.

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Highlights

- The synthesis of dimeric and monomeric cyclometalated Platinum(II) complexes is reported.
- The cyclization of aryl propynoates to coumarins and benzocoumarins is reported
- 2- phenylpyridinato-C^2,*N*)Pt(II) complexe is a very efficient catalyst for these cyclizations

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: