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Indane-Fused Spiropentadiene Chromanones: A Pd-Catalyzed Spiro-Annulation Followed by Cyclization *via* C-H Activation Strategy

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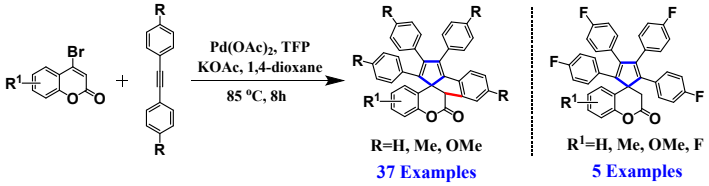


ABSTRACT

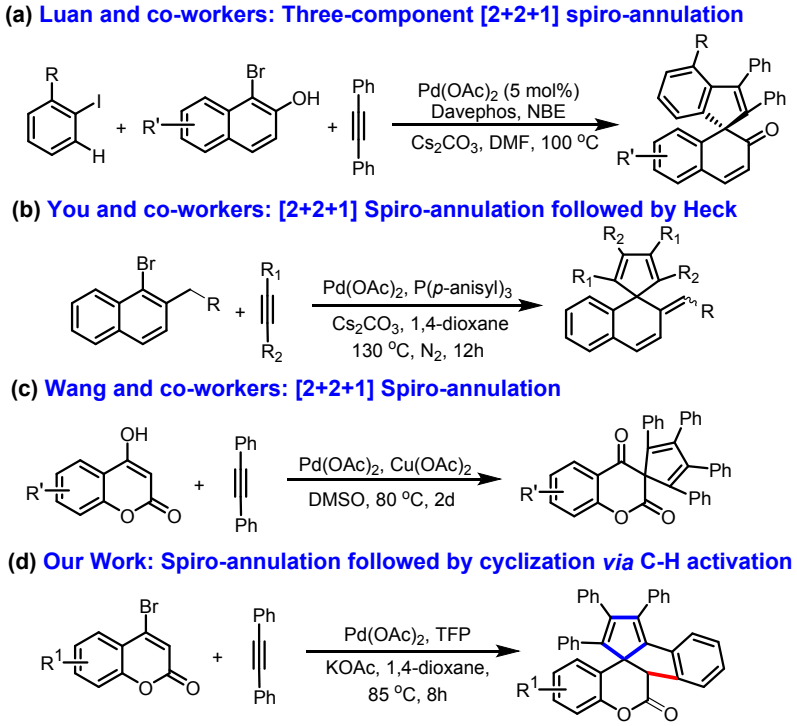
Pd-catalyzed spiroannulation of 4-bromocoumarin with alkynes have been illustrated. The reaction highlights an interesting process for cascade formation of two five-membered rings through spiro-annulation followed by cyclization *via* C-H activation. This method offers an attractive platform for the synthesis of a broad range of indane-fused spiropentadiene chromanones in good yields.

INTRODUCTION

The synthetic reaction strategies of simplicity towards complexity are significantly prevailing in the realm of polycyclic systems. Transition-metal catalyzed polycyclization has become a popular tactic to access highly functionalized and structurally diverse complex molecules. Particularly, spirocycles emerge as synthetically challenging and structurally important frameworks of many bioactive molecules[1] and optoelectronic materials.[2] In general, metal-catalyzed annulation has been recognized as an efficient and reliable synthetic route to access 3D-spirocyclic scaffolds from simple planar arenes. Transition-metal catalyzed annulative-dearomatization has been introduced by the pioneering and elegant works of Hamada,[3] Buchwald,[4] You,[5] Feringa,[6] and Tang[7] using phenol, indole, or pyrrole-based precursors. Later, various Ru(II)/Rh(III)[8] and Pd(0)/(II)[9] catalyzed dearomatizing [3+2] and [2+2+1] spiroannulations have been demonstrated through C-H bond activation followed by

oxidative annulation with alkynes. In particular, to achieve highly attractive chemo- and regio-selective spiroannulated derivatives, transition-metal catalyzed annulations of alkynes with haloarenes are considered as an attractive door with broad substrate compatibility. Additionally, annulation of alkynes with readily available arenes such as phenol diazonium salts,[10] napthols,[11] arylethers[12] , arylhalides[13] and heteroarenes[3b,14] have been widely explored.

Scheme 1. Pd-Catalyzed Spiro-Annulation



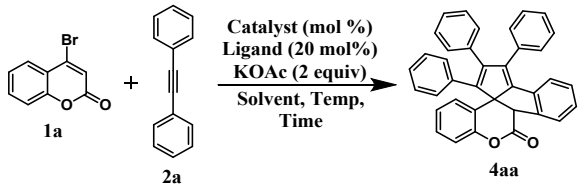
Nowadays, Pd-catalyzed processes gleam the synthetic world in a much effective approach. In this regard, some noteworthy Pd-catalyzed spiro-annulation reactions could be mentioned. Luan and co-workers described a three-component spiro-annulation of bromonaphthols with aryl iodides and alkynes in the presence of Pd(0)/norbornene system (Scheme 1a).[15] Whereas, You and co-workers reported the synthesis of a highly functionalized spiropentadienes with an exocyclic C-C double bond using alkyl bromoarenes with alkynes.[16] This reaction strategy discloses a Pd(0)-catalyzed dearomative [2+2+1] annulation reaction with high chemo-, regio-, and E/Z-selectivity *via* a Heck-type pathway (Scheme 1b). In most of the cases, simple aromatic precursors have been explored for the synthesis of sterically congested fused spirocyclic compounds. On the other hand, Pd-catalyzed spiro-annulation of heterocycle core unit with alkyne for the synthesis of spiro-annulated products is rare. In this regard, introduction of alternative precursor having immense potential in synthetic chemistry like coumarin or its derivatives could be an effective platform to access interesting spirocyclic

targets. With this view, Wang and co-workers utilizes 4-hydroxycoumarin for the synthesis of spiro cyclopentadiene-chroman derivatives employing Pd(II)-catalyzed cascade oxidative [2+2+1] cycloaddition reaction (Scheme 1c).[17]Although the reported methodologies have gained significant progress, further improvement for the synthesis of complex polycyclic systems is highly demanded in this field. Palladium catalyzed C-S bond activation of bromothiophenes[18] and our research work on coumarin moiety[19] encouraged us to design a new Pd-catalyzed cascade strategy followed by C-H activation for the synthesis of indane-fused spiropentadiene chromanones from 4-bromocoumarins and alkynes (Scheme 1d). This method offers the privilege to form a sterically congested spirocyclic core *via* multiple bond formations pathway providing a broad range of spirocyclic analogues. The present work in contrast, has distinctively enhanced the scope and utility of our method by constructing an additional five membered fused ring with spiropentadiene chromanone.

RESULTS AND DISCUSSION

At the onset, the envisioned reaction was optimized by considering 4-bromocoumarin **1a** and 1,2-diphenylethyne **2a** as model substrates for the synthesis of indane-fused spiropentadiene chromanone **4aa** (Table 1). In the initial study, we examine the reaction of 4-bromocoumarin **1a** (0.5 mmol) with 1,2-diphenylethyne **2a** (1 mmol) in the presence of $Pd(OAc)_2$ (10 mol%) as catalyst, $P(Cy)_3$ (20 mol%) as ligand and KOAc (1 mmol) as base in DCE at room temperature for 24h (Table 1, entry 1). Under these conditions, the desired product **4aa** was obtained in 22% yield. To improve the yield of **4aa**, we have investigated the solvent effect by screening some of the commonly used solvents such as DMF, DMSO, toluene, 1,4-dioxane and *t*-AmOH. These investigations reveal that 1,4-dioxane is optimal to give the desired product in 45% yield (Table 1, entries 1-6). To further improve the reaction efficiency, we next examined the reaction temperature as well as reaction time and found that the yield of the product **4aa** was improved to 55% on increasing the temperature to 85 ^{o}C for 8h (Table 1, entry 7). Furthermore, screening of ligands revealed that tri(2-furyl)phosphine (TFP) promoted the yield of the product **4aa** upto 78%, whereas other phosphine ligands such as $P(Ph)_3$, X-Phos, S-Phos, tri(*p*-tolyl)phosphine (TPTP), Ru-Phos and Dave-Phos were less effective (Table 1, entries 8-14). In addition to those, a series of Pd(II) catalysts were also screened, where $Pd(TFA)_2$ and $PdCl_2$ provided our desired product in 45% and 32% yields respectively, whereas $Pd[(PPh_3)_2]Cl_2$ failed to afford our desired product **4aa** (Table 1, entries 15-17).

Table 1. Optimization Studies[a]



entry	catalyst (mol %)	ligand (20 mol %)	solvent	time (h)	temp (ºC)	yield (%)[b]
1.	$Pd(OAc)_2$ (10)	$P(Cy)_3$	DCE	24	rt	22
2.	$Pd(OAc)_2$ (10)	$P(Cy)_3$	DMF	24	rt	ND
3.	$Pd(OAc)_2$ (10)	$P(Cy)_3$	DMSO	24	rt	ND
4.	$Pd(OAc)_2$ (10)	$P(Cy)_3$	Toluene	24	rt	trace
5.	$Pd(OAc)_2$ (10)	$P(Cy)_3$	1,4-dioxane	24	rt	45
6.	$Pd(OAc)_2$ (10)	$P(Cy)_3$	*t*-AmOH	24	rt	ND
7.	$Pd(OAc)_2$ (10)	$P(Cy)_3$	1,4-dioxane	8	85	55
8.	$Pd(OAc)_2$ (10)	$P(Ph)_3$	1,4-dioxane	8	85	41
9.	$Pd(OAc)_2$ (10)	X-Phos	1,4-dioxane	8	85	trace
10.	$Pd(OAc)_2$ (10)	S-Phos	1,4-dioxane	8	85	trace
11.	$Pd(OAc)_2$ (10)	TPTP	1,4-dioxane	8	85	40
12.	**$Pd(OAc)_2$ (10)**	**TFP**	**1,4-dioxane**	**8**	**85**	**78**
13.	$Pd(OAc)_2$ (10)	Ru-Phos	1,4-dioxane	8	85	ND
14.	$Pd(OAc)_2$ (10)	Dave-Phos	1,4-dioxane	8	85	ND
15.	$Pd(TFA)_2$ (10)	TFP	1,4-dioxane	8	85	45
16.	$Pd(Cl)_2$ (10)	TFP	1,4-dioxane	8	85	32
17.	$Pd[(PPh_3)_2]Cl_2$ (10)	TFP	1,4-dioxane	8	85	ND
18.	$Pd_2(dba)_3$ (10)	TFP	1,4-dioxane	8	85	ND
19.	$Pd(OAc)_2$ (5)	TFP	1,4-dioxane	8	85	56
20.	$Pd(OAc)_2$ (20)	TFP	1,4-dioxane	8	85	60
21.	--	TFP	1,4-dioxane	8	85	ND
22.	$Pd(OAc)_2$ (10)	--	1,4-dioxane	8	85	ND

[a]Conditions: **1a** (0.5 mmol), **2a** (1 mmol), KOAc (1 mmol), solvent (3 mL) stirred at rt to 85 [o]C; [b]Isolated yield; ND: Not detected

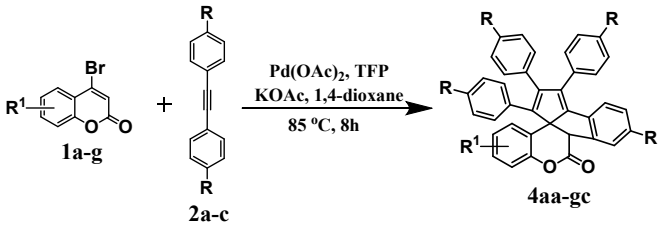
On the other hand, Pd(0) catalyst $Pd_2(dba)_3$ is unable to furnish our desired product **4aa** (Table 1, entry 18). In addition to these optimization studies, few more experiments were performed by changing the amount of $Pd(OAc)_2$ to 5 mol% and 20 mol% respectively, but no significant improvement of yield was observed (Table 1, entries 19 & 20). In a control experiment, the reaction was carried out in the absence of Pd-catalyst or ligand. However, the desired product **4aa** was not obtained (Table 1, entries 21 & 22). Finally, the optimal reaction conditions can

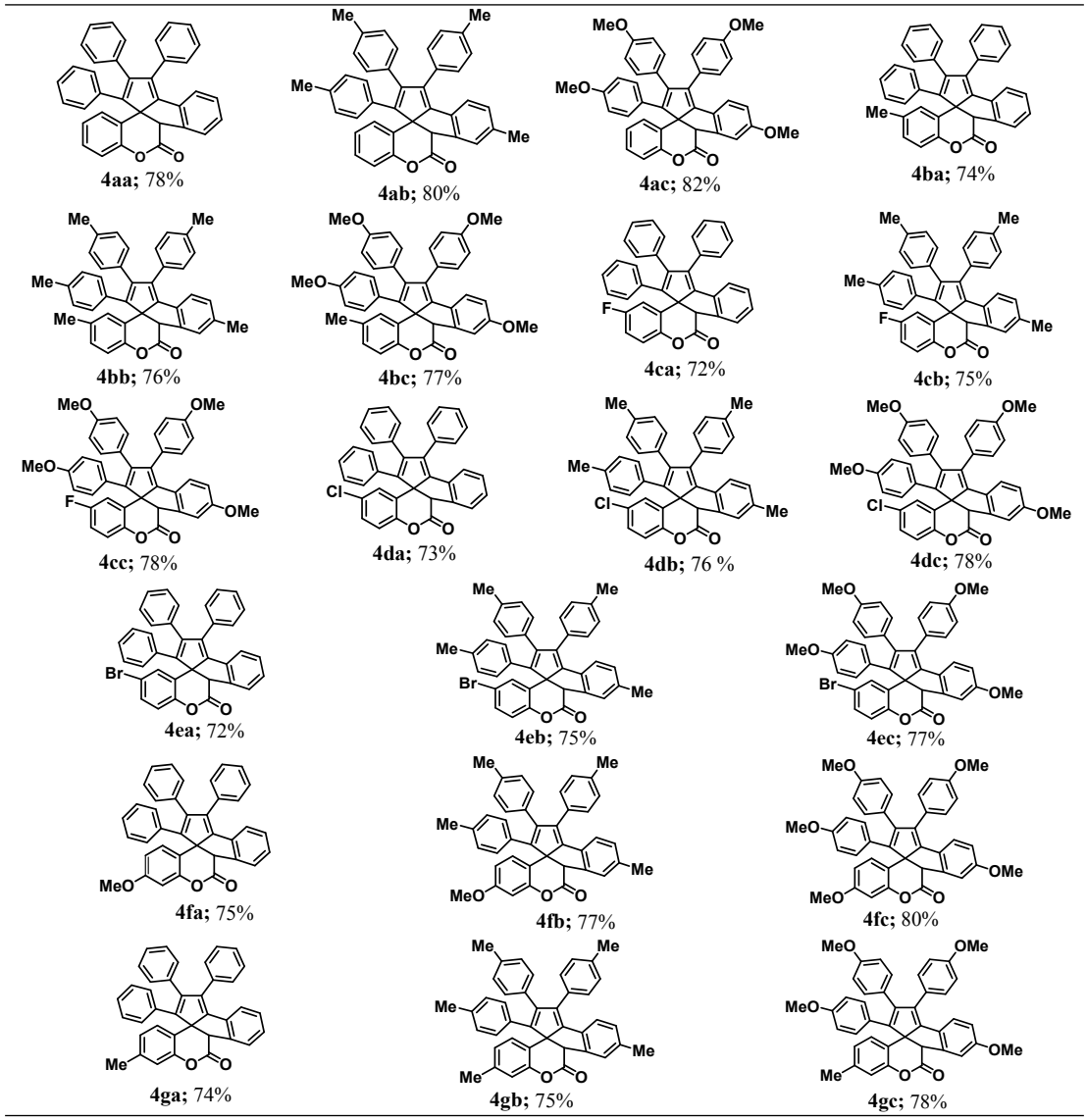
be summarized as follows: 4-bromocoumarin (0.5 mmol), 1,2-diphenylethyne (1 mmol), $Pd(OAc)_2$ (10 mol%), TFP (20 mol%) and KOAc (1 mmol) in 1,4-dioxane at 85 °C for 8h under argon atmosphere. The synthesized product **4aa** was characterized by NMR and HRMS analysis. In addition to basic spectroscopic analysis, the structure and configuration of the product **4aa** was confirmed unambiguously by single crystal X-ray diffraction analysis (See SI for details).[20]

With the optimized reaction parameters in hand, we explored the substrate scope for the synthesis of indane-fused spiropentadiene chromanones **4**. A wide variety of 4-bromocoumarins **1** and alkynes **2** participated in our cascade process to afford **4** in good yields (Table 2). Initially, three different alkynes **2a**, **2b** and **2c** having -Me and -OMe functionalities at the peripheral aryl ring were allowed to react with 4-bromocoumarin **1a** under our optimized reaction conditions leading to our desired indane-fused spiropentadiene chromanones **4aa**, **4ab** and **4ac** in good yields. On the other hand, 4-bromocoumarins with various substituents at the aryl ring were also examined and a series of indane-fused spiropentadiene chromanones were synthesized in good yields (Table 2, **4ba-4gc**). The configuration of compound **4ba** was also established by X-ray crystallographic analysis (See SI for details).[21] Notably, both electron-donating and electron-withdrawing substituents at the aryl ring of 4-bromocoumarins were equally participated in our cascade reaction. Interestingly 4,6-dibromocoumarin **1e** undergoes chemoselective coupling with the bromo- moiety prevailing in 4-position without effecting the other bromo- group when treated with diaryl alkynes under our optimized conditions (Table 2, **4ea-4ec**). Additionally, other coupling prone chloro-functionality was also well tolerated during our Pd-catalyzed process. As a result, several such halo-functionalized indane-fused spiropentadiene chromanones were synthetized in good yields (Table 2, **4da-4dc**).

Furthermore, the scope of our spiro-annulation strategy was explored by applying unsymmetrically substituted alkynes as coupling partners. In this investigation, unsymmetrical alkyne 1-methoxy-4-(phenylethynyl) benzene **2d** was initially treated with 4-bromocoumarin **1a** under our optimized reaction conditions. Not surprisingly, the alkyne **2d** gave mixture of regio-isomers in 70% yield (Scheme 2a, **$4ad_1$-$4ad_4$**). The regio-isomers were difficult to separate into individual isomers using column chromatography and they are represented as mixture of regio-isomers.

Table 2. Synthesis of indane-fused spiropentadiene chromanones 4[a]



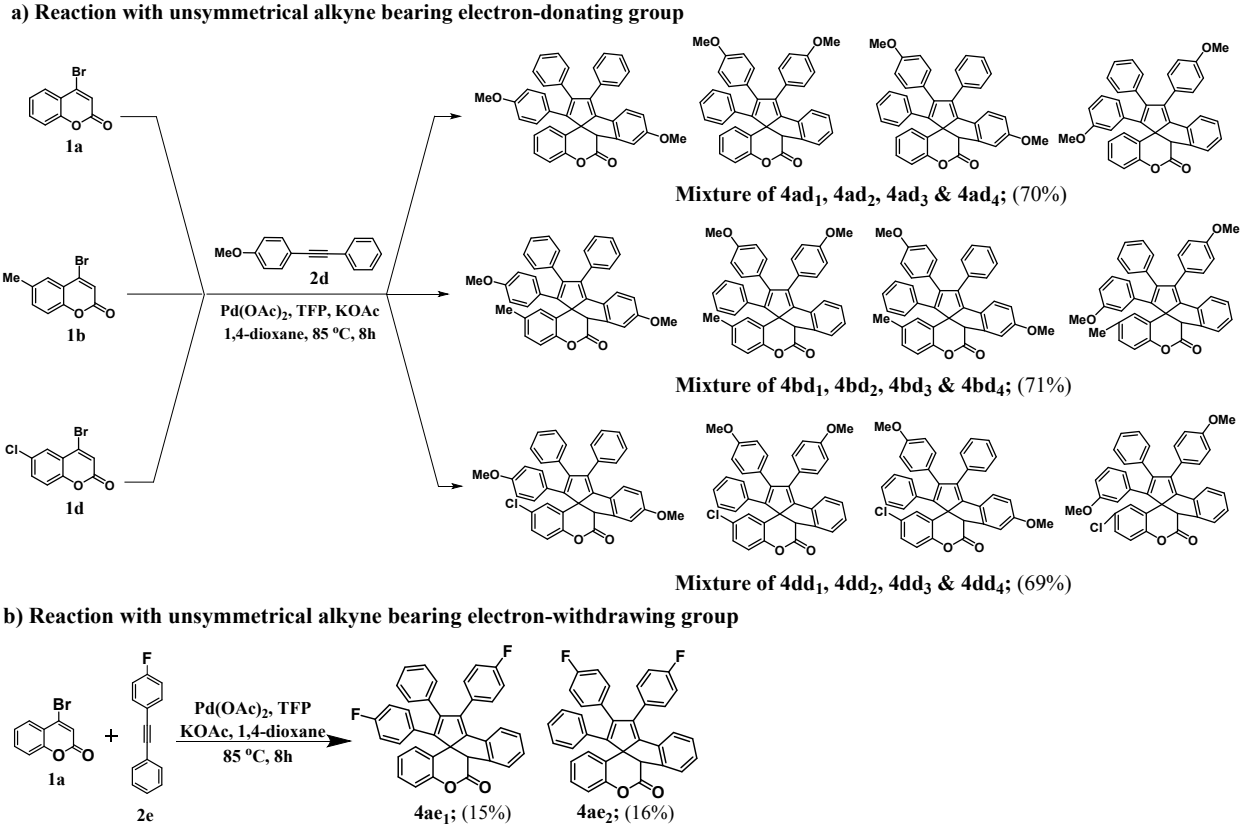


[a]Conditions: **1** (0.5 mmol), **2** (1.0 mmol), $Pd(OAc)_2$ (10 mol%), TFP (20 mol%), KOAc (1.0 mmol), 1,4-dioxane (3 mL) stirred at 85 °C for 8h

Under similar reaction conditions, two other bromocoumarins **1b** and **1d** effectively reacted with **2d** to afford the corresponding regio-isomers of indane-fused spiropentadiene chromanones in 71% and 69% yields respectively (Scheme 2a, **$4bd_1$-$4bd_4$** & **$4dd_1$-$4dd_4$**). Similarly, another unsymmetrical alkyne having electron withdrawing group at aryl ring 1-fluoro-4-(phenylethynyl) benzene **2e** was also investigated as coupling partner with 4-bromocoumarin **1a**. Under our optimized reaction conditions, it furnishes two regio-isomers

4ae$_1$ and **4ae$_2$**. The regio-isomers were separable under column chromatography and isolated into individual isomers with 15% and 16% yields respectively (Scheme 2b). Additionally, significant amount of both the starting materials were also recovered after the reaction time of 8h. This result indicates that C-H activation of the fluorophenyl group failed to occur, which resulted in the formation of only two regio-isomers.

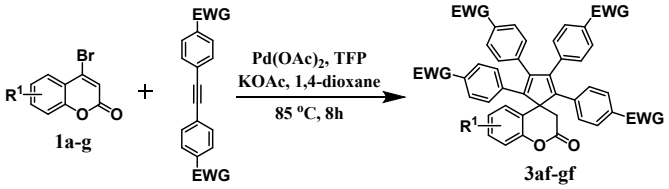
Scheme 2. Synthesis of indane-fused spiropentadiene chromanone from unsymmetrical alkyne

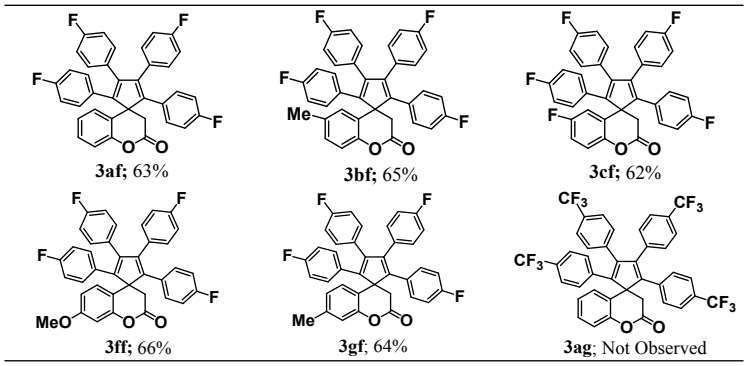


In order to explore the alkyne reactivity for our cascade process, symmetrical alkynes bearing electron withdrawing groups such as -F and -CF_3 were considered. In this regard, the alkyne 1,2-bis(4-fluorophenyl)ethyne **2f** was treated with 4-bromocoumarin **1a** under our optimized conditions. Interestingly, a spiropentadiene chromanone **3af** was isolated instead of indane-fused spiropentadiene chromanone **4af**, which was characterized by NMR and HRMS analysis (Table 3). Similarly, alkyne **2f** was further explored as reactive partner for the synthesis of other spiropentadiene chromanones by considering various substituted bromocoumarins. As a result, a series of spiropentadiene chromanones **3bf**, **3cf**, **3ff** and **3gf** were synthetized in good yields (Table 3). Next, we considered another alkyne 1,2-bis[4-(trifluoro-methyl)phenyl]ethyne **2g** as reactive partner for our cascade process. Unfortunately, the alkyne **2g** neither gave **3ag** nor the cyclized product **4ag** under our optimized reaction

conditions even after prolong reaction time. However, we recovered both the starting materials without significant loss. Under our experimental conditions, alkynes substituted with electron withdrawing groups did not proceed for the penultimate C–H functionalization, which could be due to weak interaction between carbopalladium intermediate and the C-H bond.

Table 3. Synthesis of spiropentadiene chromanones 3[a]

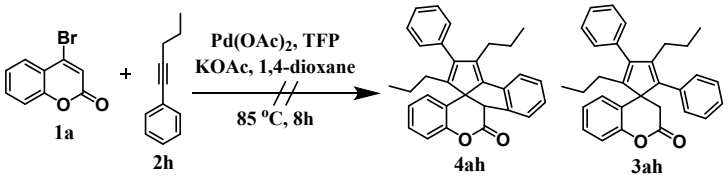




[a]Conditions: **1** (0.5 mmol), **2** (1.0 mmol), $Pd(OAc)_2$ (10 mol%), TFP (20 mol%), KOAc (1.0 mmol), 1,4-dioxane (3 mL) stirred at 85 °C for 8h.

Additionally, another interesting internal alkyne bearing a phenyl group and an alkyl group was considered as reactive partner for our annulation process. As shown in Scheme 3, alkyne **2h** was treated with 4-bromocoumarin **1a** under our optimized reaction conditions. This alkyne **2h** neither gave indane-fused spiropentadiene chromanone **4ah** nor spiropentadiene chromanone **3ah**.

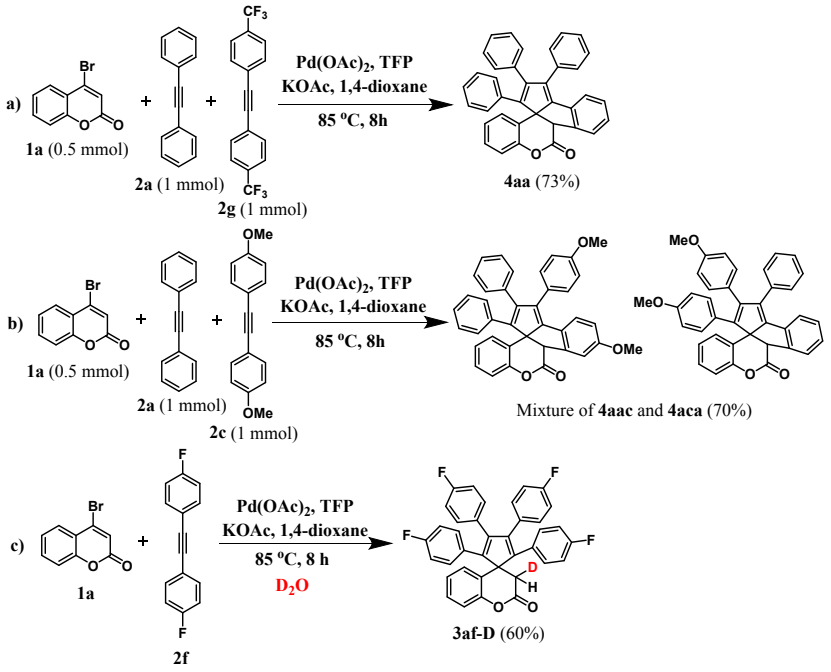
Scheme 3. Reaction Behavior of Internal Alkyne 2h



Furthermore, we planned some competition reactions of 4-bromocoumarin **1a** with two different alkynes in a single reaction vessel as shown in Scheme 4. In an initial experiment, 4-bromocoumarin **1a** (0.5 mmol) was treated with a mixture of alkynes **2a** (1 mmol) and **2g** (1 mmol) under our optimized conditions. Interestingly, 4-bromocoumarin **1a** predominantly coupled with alkyne **2a** instead of **2g** to form **4aa** in 73% yield (Scheme 4a). On the other hand, when **1a** (0.5 mmol) was treated with **2a** (1 mmol) along with alkyne **2c** (1 mmol), a mixture

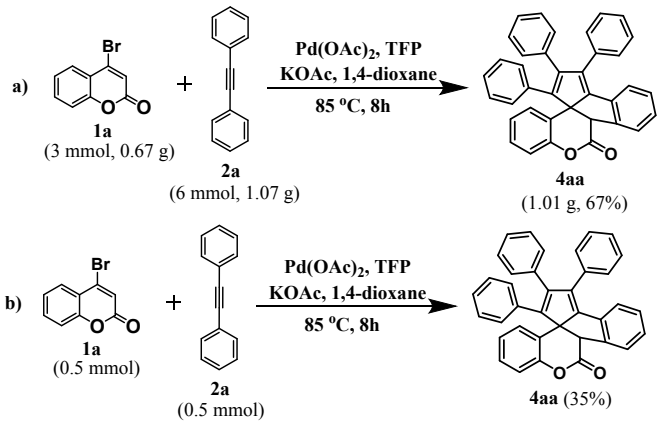
of hybrid products **4aac** and **4aca** were formed in 70% yield (Scheme 4b). This results reveal that diaryl alkynes having electron neutral or electron rich substituents were more favourable to form our desired indane-fused spiropentadiene chromanones. In addition to those, an independent experiment was also performed to gain insight into the reaction mechanism. Here, the reaction of **1a** with **2f** was studied in the presence of D_2O as fourth component under our optimized reaction conditions. To our delight, this experiment gives a deuterium incorporated product at the C-3 position of **3af-D** which could be due to the quenching of carbopalladium intermediate with deuterium oxide (Scheme 4c). Reasonably, this observation reveals that C-H activation failed to occur in presence of fluorophenyl group to give our desired indane-fused spiropentadiene chromanone.

Scheme 4. Competition Experiments and Deuterium Labeling Experiment



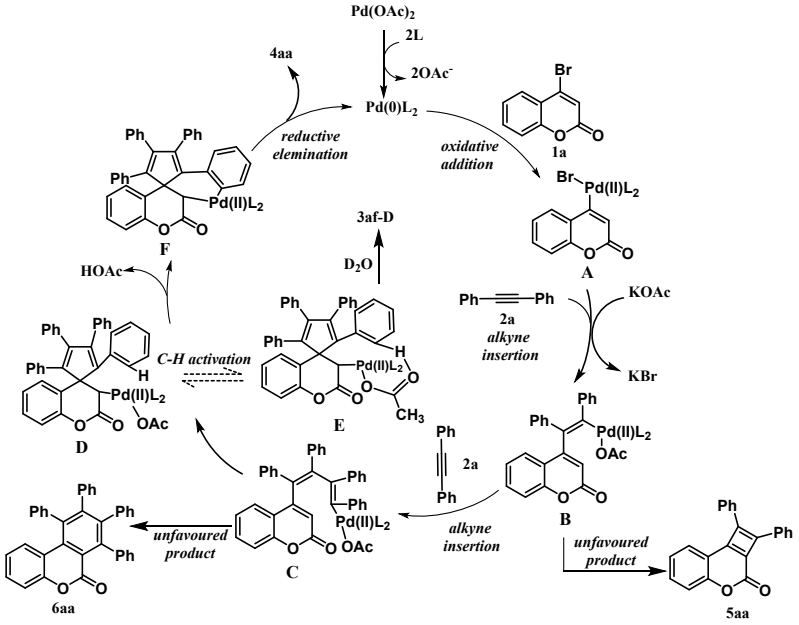
To demonstrate the practical utility of our cascade annulation process, a scale-up experiment was carried out under the optimized reaction conditions. As shown in Scheme 5a, the reaction of 4-bromocoumarin **1a** (3 mmol) with 1,2-diphenylethyne **2a** (6 mmol) was performed on a gram-scale to give our desired product **4aa** (1.01 g) in 67% yield. In addition, a control experiment with 1:1 ratio of 4-bromcoumarin **1a** and 1,2-diphenylethyne **2a** was performed to elucidate the nature and amount of product formed. Interestingly, our cyclized product **4aa** was obtained in only 35% yield (Scheme 5b).

Scheme 5. Scale-Up Experiment and Control Experiment



Based on our experiments and literature precedents, a plausible catalytic cycle for the formation of **4aa** was proposed and shown in Scheme 6. The catalytic cycle starts from $Pd(0)L_2$ (L=TFP), which was generated *in situ* from $Pd(OAc)_2$ and TFP.

Scheme 6. Plausible Reaction Mechanism for the Synthesis of 4



Subsequently, the oxidative addition of Pd(0) into the C-Br bond of **1a** takes place to form the intermediate **A**. Then, insertion of 1,2-diphenylacetylene **2a** into Pd-C bond would occur to produce intermediate **B**, which subsequently undergoes second insertion of 1,2-diphenylacetylene **2a** to generate intermediate **C**. Next, a unique ring contraction phenomenon takes place to generate a spiropentadiene chromanone intermediate **D**, which then undergoes C-H activation to form the complex **F**. Finally, reductive elimination from **F** gave our desired product **4aa** and concomitantly regenerates Pd(0) to complete the catalytic cycle. However, direct reductive elimination from intermediate **B** and **C** to form the unwanted product **5aa** and

6aa was not observed. The deuterium labelling product **3af-D** could be achieved by quenching **E** with deuterium oxide.

In conclusion, we have developed a Pd(0)-catalyzed spiro-annulation reaction of 4-bromocoumarin with alkynes to provide a wide range of indane-fused spiropentadiene chromanone derivatives in good yields. In comparison to previous reports, our synthetic protocol resulted in the formation of diverse sterically congested spirocyclic core bearing two-fused five membered rings in a single operation.

EXPERIMENTAL SECTION:

General Information: All reactions involving oxygen- or moisture-sensitive compounds were carried out under argon atmosphere using oven-dried or flame-dried glassware. All other solvents and reagents were purified according to standard procedures or were used as received from TCI, Aldrich, Merck and Spectrochem. Reactions were monitored by thin-layer chromatography (TLC) using aluminium-backed silica gel plates (0.2 mm thickness); the chromatograms were visualized with ultraviolet light (254 nm). Flash column chromatography was performed with silica gel 60 (100-200 or 200-400 mesh). HRMS data were recorded by electronspray ionization with a Q-TOF mass analyzer.

General procedure for the synthesis of 4-bromocoumarins:

An oven-dried round bottomed flask (50 mL capacity) equipped with a magnetic stir bar was evacuated and purged with argon. 4-Hydroxycoumarin (1 equiv), TBAB (1.16 equiv), P_2O_5 (2.4 equiv) and toluene (4 mL/mmol) was stirred at 94 ^oC (preheated oil-bath) for 1.5 h. Upon completion, the reaction mixture was washed with toluene (2x30 mL). The combined organic phases were washed with saturated $NaHCO_3$ and H_2O and dried over sodium sulfate. The solvent was removed under reduced pressure to obtain 4-bromocoumarin **1a**. Compounds **1b-g** was prepared using the same experimental procedure.

4,6-Dibromo-2*H*-chromen-2-one; **1e**

Using the general experimental procedure on 6-bromo-4-hydroxycoumarin (5 mmol, 1 equiv), TBAB (5.8 mmol, 1.16 equiv), P_2O_5 (12 mmol, 2.4 equiv) in toluene (20 mL), compound **1e** was obtained as light brown solid (1.033 g, 68% yield); mp: 166-168 ^oC; **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.93 (d, J=2.3 Hz, 1H), 7.66 (dd, J_1=2.3 Hz, J_2=8.7 Hz, 1H), 7.20 (d, J=8.7 Hz, 1H),

6.87 (s, 1H); **$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$)**: δ 157.8, 151.2, 139.7, 135.9, 130.3, 120.4, 120.3, 118.7, 117.7; **IR ($CHCl_3$):** 3425, 1756, 1649, 1546, 1329, 1266, 1187, 882, 772 cm^{-1}; **HRMS (+ESI) m/z: $[M+H]^+$ Calcd for $C_9H_5O_2Br_2$** 302.8656; found 302.8653.

General procedure for the synthesis of indane-fused spiropentadiene chromanone 4:

An oven-dried round bottomed flask (50 mL capacity) equipped with a magnetic stir bar was evacuated and purged with argon. 4-Bromocoumarin (0.5 mmol, 1 equiv), diaryl alkyne (1 mmol, 2 equiv), $Pd(OAc)_2$ (10 mol%), TFP (20 mol%), KOAc (1 mmol, 2 equiv) and 1,4-dioxane (3 mL) were added successively at room temperature. The reaction mixture was stirred at 85 °C (preheated oil-bath) for 8 h and then allowed to cool to room temperature. Saturated NH_4Cl solution (10 mL) was added to the reaction mixture, and the organic layer was extracted with EtOAc (2x30 mL). The combined organic phases were washed with brine and dried over sodium sulfate. The solvent was removed and the residue was purified by column chromatography on silica gel using hexane/ethyl acetate as eluent.

General procedure for gram scale experiment:

An oven-dried round bottomed flask (100 mL capacity) equipped with a magnetic stir bar was evacuated and purged with argon. 4-Bromocoumarin **1a** (3 mmol, 0.67 g), diaryl alkyne **2a** (6 mmol, 1.07 g), $Pd(OAc)_2$ (0.3 mmol, 67 mg), TFP (0.6 mmol, 140 mg), KOAc (6 mmol, 0.59 g) and 1,4-dioxane (20 mL) were added successively at room temperature. The reaction mixture was stirred at 85 °C (preheated oil-bath) for 8 h and then allowed to cool to room temperature. Upon completion, saturated NH_4Cl solution (50 mL) was added to the reaction mixture, and the organic layer was extracted with EtOAc (2x90 mL). The combined organic phases were washed with brine and dried over sodium sulfate. The solvent was removed and the residue was purified by column chromatography on silica gel to afford the corresponding indane-fused spiropentadiene chromanone **4aa** (1.01 g, 67%).

7,8,9-Triphenylcyclopenta[2,3]indeno[1,2-*c*]chromen-1(13b*H*)-one; **4aa**

Using the general experimental procedure on 4-bromocoumarin (0.112 g; 0.5 mmol, 1 equiv), diphenylacetylene (0.178 g; 1 mmol, 2 equiv), $Pd(OAc)_2$ (0.012 g; 0.05 mmol, 10 mol%), TFP (0.023 g; 0.1 mmol, 20 mol%), and KOAc (0.098 g; 1 mmol, 2 equiv) in 1,4-dioxane (3 mL), compound **4aa** was obtained as white solid (0.195 g, 78% yield) after purification by flash column chromatography using hexane/EtOAc (19:1) as an eluent; mp: 218-220 °C; **^1H NMR**

(500 MHz, $CDCl_3$): δ 7.41 (d, *J*= 7.5 Hz, 1H), 7.29 (d, *J*= 7.6 Hz, 1H), 7.16-7.24 (m, 6H), 6.82-7.08 (m, 14H), 6.73 (dd, J_1= 1.2 Hz, J_2= 8.0 Hz, 1H), 4.52 (s, 1H); **$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$)**: δ 166.3, 154.4, 151.4, 148.8, 145.7, 145.6, 140.7, 135.1, 134.9, 134.4, 134.0, 129.9, 129.8, 128.8, 128.7, 128.6, 128.2, 128.0, 127.9, 127.8, 127.7, 127.4, 127.3, 125.6, 124.7, 124.4, 122.3, 119.2, 117.7, 71.6, 48.8; **IR ($CHCl_3$):** 3420, 2918, 2853, 1753, 1601, 1504, 1485, 1443, 1219, 837, 772 cm^{-1}; **HRMS (+ESI) m/z: $[M+H]^+$ Calcd for $C_{37}H_{25}O_2$** 501.1855; found 501.1859.

12-Methyl-7,8,9-tri-*p*-tolylcyclopenta[2,3]indeno[1,2-*c*]chromen-1(13b*H*)-one; **4ab**

Using the general experimental procedure on 4-bromocoumarin (0.112 g; 0.5 mmol, 1 equiv), 1,2-di-*p*-tolylethyne (0.206 g; 1 mmol, 2 equiv), $Pd(OAc)_2$ (0.012 g; 0.05 mmol, 10 mol%), TFP (0.023 g; 0.1 mmol, 20 mol%), and KOAc (0.098 g; 1 mmol, 2 equiv) in 1,4-dioxane (3 mL), compound **4ab** was obtained as yellow solid (0.222 g, 80% yield) after purification by flash column chromatography using hexane/EtOAc (19:1) as an eluent; mp: 253-255 °C; **^1H NMR (500 MHz, $CDCl_3$):** δ 7.29 (d, *J*= 7.8 Hz, 1H), 7.15 (dd, J_1= 1.7 Hz, J_2= 7.8 Hz, 1H), 7.09 (s, 1H), 7.03 (s, 4H), 6.90-6.93 (m, 1H), 6.84-6.87 (m, 3H), 6.78-6.81 (m, 5H), 6.70-6.73 (m, 3H), 4.44 (s, 1H), 2.26 (s, 3H), 2.18 (s, 3H), 2.17 (s, 3H), 2.08 (s, 3H); **$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$)**: δ 166.7, 153.8, 151.4, 147.9, 145.6, 145.2, 139.9, 138.1, 137.3, 136.8, 136.7, 132.5, 131.8, 131.4, 129.8, 129.7, 129.3, 128.9, 128.6, 128.5, 128.4, 128.3, 125.8, 125.0, 124.5, 122.0, 119.9, 117.5, 71.6, 48.7, 21.4, 21.3, 21.2, 21.1 (One peak is missing due to overlap); **IR ($CHCl_3$):** 3421, 2920, 2855, 1754, 1606, 1484, 1447, 1244, 1211, 820, 770 cm^{-1}; **HRMS (+ESI) m/z: $[M+H]^+$ Calcd for $C_{41}H_{33}O_2$** 557.2481; found 557.2486.

12-Methoxy-7,8,9-tris(4-methoxyphenyl)cyclopenta[2,3]indeno[1,2-*c*]chromen-1(13b*H*)-one; **4ac**

Using the general experimental procedure on 4-bromocoumarin (0.112 g; 0.5 mmol, 1 equiv), 1,2-bis(4-methoxyphenyl)ethyne (0.238 g; 1 mmol, 2 equiv), $Pd(OAc)_2$ (0.012 g; 0.05 mmol, 10 mol%), TFP (0.023 g; 0.1 mmol, 20 mol%), and KOAc (0.098 g; 1 mmol, 2 equiv) in 1,4-dioxane (3 mL), compound **4ac** was obtained as brown solid (0.254 g, 82% yield) after purification by flash column chromatography using hexane/EtOAc (4:1) as an eluent; mp: 170-172 °C; **^1H NMR (500 MHz, $CDCl_3$):** δ 7.38 (d, *J*= 8.4 Hz, 1H), 7.21 (dd, J_1= 1.6 Hz, J_2= 7.8 Hz, 1H), 7.14 (d, *J*= 8.6 Hz, 2H), 7.01-7.04 (m, 1H), 6.91-6.97 (m, 4H), 6.82-6.86 (m, 5H), 6.69 (d, *J*= 8.8 Hz, 2H), 6.63-6.65 (m, 1H), 6.61 (d, *J*= 8.8 Hz, 2H), 4.52 (s, 1H), 3.82 (s, 3H),

3.75 (s, 3H), 3.74 (s, 3H), 3.69 (s, 3H); **$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)**: δ 166.8, 159.8, 158.9, 158.5, 158.3, 152.7, 151.3, 147.0, 146.7, 144.6, 138.3, 131.2, 131.0, 129.8, 128.5, 128.1, 128.0, 127.2, 126.9, 125.7, 124.6, 122.9, 120.2, 117.5, 115.0, 113.6, 113.3, 113.0, 109.5, 71.6, 55.5, 55.1, 55.0, 54.9, 49.0; **IR ($CHCl_3$):** 3420, 2932, 2836, 1757, 1605, 1510, 1479, 1247, 1176, 1030, 834, 771 cm^{-1}; **HRMS (+ESI) m/z: $[M+H]^+$ Calcd for $C_{41}H_{33}O_6$** 621.2277; found 621.2272.

5-Methyl-7,8,9-triphenylcyclopenta[2,3]indeno[1,2-*c*]chromen-1(13b*H*)-one; **4ba**

Using the general experimental procedure on 4-bromo-6-methylcoumarin (0.120 g; 0.5 mmol, 1 equiv), diphenylacetylene (0.178 g; 1 mmol, 2 equiv), $Pd(OAc)_2$ (0.012 g; 0.05 mmol, 10 mol%), TFP (0.023 g; 0.1 mmol, 20 mol%), and KOAc (0.098 g; 1 mmol, 2 equiv) in 1,4-dioxane (3 mL), compound **4ba** was obtained as light brown solid (0.190 g, 74% yield) after purification by flash column chromatography using hexane/EtOAc (19:1) as an eluent; mp: 238-240 °C; **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.49 (d, *J*= 7.4 Hz, 1H), 7.36 (d, *J*= 7.5 Hz, 1H), 7.24-7.32 (m, 5H), 7.06-7.17 (m, 8H), 6.99-7.01 (m, 3H), 6.90-6.91 (m, 2H), 6.81 (dd, J_1= 1.7 Hz, J_2= 8.3 Hz, 1H), 6.71 (d, *J*= 8.3 Hz, 1H), 4.54 (s, 1H), 2.20 (s, 3H); **$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)**: δ 166.6, 154.4, 149.4, 148.8, 145.7, 145.5, 140.6, 135.2, 135.0, 134.5, 134.2, 134.1, 130.0, 129.8, 129.6, 128.7, 128.6, 128.2, 128.0, 127.9, 127.8, 127.7, 127.3, 127.2, 125.5, 124.4, 122.4, 118.7, 117.3, 71.7, 48.9, 20.9; **IR ($CHCl_3$):** 3423, 3055, 3023, 2920, 2853, 1751, 1607, 1494, 1444, 1247, 1209, 752, 697 cm^{-1}; **HRMS (+ESI) m/z: $[M+H]^+$ Calcd for $C_{38}H_{27}O_2$** 515.2011; found 515.2017.

5,12-Dimethyl-7,8,9-tri-*p*-tolylcyclopenta[2,3]indeno[1,2-*c*]chromen-1(13b*H*)-one; **4bb**

Using the general experimental procedure on 4-bromo-6-methylcoumarin (0.120 g; 0.5 mmol, 1 equiv), 1,2-di-*p*-tolylethyne (0.206 g; 1 mmol, 2 equiv), $Pd(OAc)_2$ (0.012 g; 0.05 mmol, 10 mol%), TFP (0.023 g; 0.1 mmol, 20 mol%), and KOAc (0.098 g; 1 mmol, 2 equiv) in 1,4-dioxane (3 mL), compound **4bb** was obtained as yellow solid (0.216 g, 76% yield) after purification by flash column chromatography using hexane/EtOAc (19:1) as an eluent; mp: 254-256 °C; **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.39 (dd, J_1= 1.6 Hz, J_2= 7.7 Hz, 1H), 7.18 (s, 1H), 7.13 (s, 4H), 6.95-6.98 (m, 3H), 6.88-6.92 (m, 5H), 6.80-6.82 (m, 3H), 6.72 (d, *J*= 8.3 Hz, 1H), 4.49 (s, 1H), 2.37 (s, 3H), 2.28 (s, 3H), 2.26 (s, 3H), 2.20 (s, 3H), 2.19 (s, 3H); **$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)**: δ 166.9, 153.8, 149.3, 147.9, 145.7, 145.0, 139.8, 138.0, 137.2, 136.7, 133.9, 132.5, 131.8, 131.4, 129.8, 129.7, 129.4, 129.3, 128.9, 128.6, 128.4, 128.3, 125.6,

125.0, 122.0, 119.4, 117.2, 71.6, 48.8, 21.4, 21.3, 21.2, 21.1, 20.9 (Two peaks are missing due to overlap); **IR ($CHCl_3$):** 3421, 3023, 2920, 1754, 1605, 1493, 1250, 1218, 818, 772 cm^{-1}; **HRMS (+ESI) m/z: $[M+H]^+$ Calcd for $C_{42}H_{35}O_2$** 571.2637; found 571.2639.

12-Methoxy-7,8,9-tris(4-methoxyphenyl)-5-methylcyclopenta[2,3]indeno[1,2-*c*]chromen-1(13b*H*)-one; **4bc**

Using the general experimental procedure on 4-bromo-6-methylcoumarin (0.120 g; 0.5 mmol, 1 equiv), 1,2-bis(4-methoxyphenyl)ethyne (0.238 g; 1 mmol, 2 equiv), $Pd(OAc)_2$ (0.012 g; 0.05 mmol, 10 mol%), TFP (0.023 g; 0.1 mmol, 20 mol%), and KOAc (0.098 g; 1 mmol, 2 equiv) in 1,4-dioxane (3 mL), compound **4bc** was obtained as brown solid (0.244 g, 77% yield) after purification by flash column chromatography using hexane/EtOAc (4:1) as an eluent; mp: 155-157 ^oC; **^1H NMR (500 MHz, $CDCl_3$):** 7.40 (d, *J*= 8.4 Hz, 1H), 7.16 (d, *J*= 8.7 Hz, 2H), 6.80-6.97 (m, 9H), 6.61-6.73 (m, 6H), 4.49 (s, 1H), 3.81 (s, 3H), 3.74 (s, 3H), 3.73 (s, 3H), 3.68 (s, 3H), 2.19 (s, 3H); **$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$)**: δ 166.9, 159.7, 158.8, 158.4, 158.2, 152.6, 149.2, 147.1, 146.7, 144.4, 138.2, 134.0, 131.2, 131.0, 129.7, 129.3, 128.1, 128.0, 127.2, 126.9, 125.5, 122.8, 119.7, 117.1, 114.9, 113.6, 113.3, 113.0, 109.5, 71.6, 55.4, 55.1, 55.0, 54.9, 49.0, 20.9; **IR ($CHCl_3$):** 3421, 2931, 2836, 1741, 1605, 1509, 1288, 1247, 1175, 1030, 835, 772 cm^{-1}; **HRMS (+ESI) m/z: $[M+H]^+$ Calcd for $C_{42}H_{35}O_6$** 635.2434; found 635.2438.

5-Fluoro-7,8,9-triphenylcyclopenta[2,3]indeno[1,2-*c*]chromen-1(13b*H*)-one; **4ca**

Using the general experimental procedure on 4-bromo-6-fluorocoumarin (0.122 g; 0.5 mmol, 1 equiv), diphenylacetylene (0.178 g; 1 mmol, 2 equiv), $Pd(OAc)_2$ (0.012 g; 0.05 mmol, 10 mol%), TFP (0.023 g; 0.1 mmol, 20 mol%), and KOAc (0.098 g; 1 mmol, 2 equiv) in 1,4-dioxane (3 mL), compound **4ca** was obtained as white solid (0.187 g, 72% yield) after purification by flash column chromatography using hexane/EtOAc (19:1) as an eluent; mp: 261-263 ^oC; **^1H NMR (500 MHz, $CDCl_3$):** δ 7.43 (d, *J*= 7.4 Hz, 1H), 7.29 (d, *J*= 7.5 Hz, 1H), 7.24-7.26 (m, 3H), 7.16-7.18 (m, 2H), 7.00-7.11 (m, 8H), 6.91 (dd, J_1= 1.4 Hz, J_2= 8.0 Hz, 2H), 6.84-6.87 (m, 3H), 6.69-6.72 (m, 1H), 6.62-6.67 (m, 1H), 4.52 (s, 1H); **$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$)**: δ 166.0, 159.1 (d, *J*= 243.2 Hz), 154.0, 148.2, 147.5, 146.0, 145.2, 141.0, 134.8 (d, *J*= 7.5 Hz), 134.1, 133.8, 129.9, 129.8, 128.8, 128.6, 128.4, 128.2, 128.1, 128.0, 127.8, 127.5, 127.4, 124.4, 122.4, 121.4 (d, *J*= 7.5 Hz), 119.0 (d, *J*= 8.5 Hz), 116.0 (d, *J*= 23.9 Hz), 111.6 (d, *J*= 24.2 Hz), 71.6, 48.4 (One peak is missing due to overlap); **IR ($CHCl_3$):** 3420,

2922, 2853, 1755, 1599, 1488, 1219, 1177, 817, 772 cm^{-1}; **HRMS (+ESI) m/z: $[M+H]^+$ Calcd for $C_{37}H_{24}O_2F$** 519.1760; found 519.1768.

5-Fluoro-12-methyl-7,8,9-tri-*p*-tolylcyclopenta[2,3]indeno[1,2-*c*]chromen-1(13b*H*)-one; **4cb**

Using the general experimental procedure on 4-bromo-6-fluorocoumarin (0.122 g; 0.5 mmol, 1 equiv), 1,2-di-*p*-tolylethyne (0.206 g; 1 mmol, 2 equiv), $Pd(OAc)_2$ (0.012 g; 0.05 mmol, 10 mol%), TFP (0.023 g; 0.1 mmol, 20 mol%), and KOAc (0.098 g; 1 mmol, 2 equiv) in 1,4-dioxane (3 mL), compound **4cb** was obtained as yellow solid (0.215 g, 75% yield) after purification by flash column chromatography using hexane/EtOAc (19:1) as an eluent; mp: 265-267 °C; **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.40 (d, *J*= 7.8 Hz, 1H), 7.18 (s, 1H), 7.12 (s, 4H), 6.88-6.97 (m, 8H), 6.78-6.82 (m, 3H), 6.70-6.74 (m, 1H), 4.53 (s, 1H), 2.37 (s, 3H), 2.28 (s, 3H), 2.27 (s, 3H), 2.20 (s, 3H); **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)**: δ 166.4, 159.1 (d, *J*= 242.7 Hz), 153.4, 147.4, 145.6, 145.3, 140.2, 138.3, 137.5, 136.9 (d, *J*=7.5 Hz), 132.3, 132.2, 131.5, 131.1, 129.8, 129.7, 129.5, 129.0, 128.7, 128.4, 125.0, 121.1, 122.0, 118.9 (d, *J*=8.3 Hz), 115.7 (d, *J*=23.9 Hz), 111.7 (d, *J*=24.1 Hz), 71.6, 48.3, 21.4, 21.3, 21.2, 21.1; **IR ($CHCl_3$):** 3401, 3023, 2920, 2855, 1758, 1600, 1489, 1418, 1248, 1177, 817, 744 cm^{-1}; **HRMS (+ESI) m/z: $[M+H]^+$ Calcd for $C_{41}H_{32}O_2F$** 575.2386; found 575.2384.

5-Fluoro-12-methoxy-7,8,9-tris(4-methoxyphenyl)cyclopenta[2,3]indeno[1,2-*c*]chromen-1(13b*H*)-one; **4cc**

Using the general experimental procedure on 4-bromo-6-fluorocoumarin (0.122 g; 0.5 mmol, 1 equiv), 1,2-bis(4-methoxyphenyl)ethyne (0.238 g; 1 mmol, 2 equiv), $Pd(OAc)_2$ (0.012 g; 0.05 mmol, 10 mol%), TFP (0.023 g; 0.1 mmol, 20 mol%), and KOAc (0.098 g; 1 mmol, 2 equiv) in 1,4-dioxane (3 mL), compound **4cc** was obtained as brown solid (0.249 g, 78% yield) after purification by flash column chromatography using hexane/EtOAc (4:1) as an eluent; mp: 126-128 °C; **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.41 (d, *J*= 8.4 Hz, 1H), 7.15 (d, *J*= 8.8 Hz, 2H), 6.78-6.94 (m, 9H), 6.62-6.74 (m, 6H), 4.54 (s, 1H), 3.81 (s, 3H), 3.75 (s, 3H), 3.74 (s, 3H), 3.69 (s, 3H); **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)**: δ 166.4, 159.9, 159.2 (d, *J*=242.8 Hz), 158.9, 158.6, 158.4, 152.2, 147.3, 146.7, 146.2, 144.9, 138.6, 131.2, 131.0, 129.8, 127.9, 127.7, 126.9, 126.6, 122.9, 122.4 (d, *J*= 7.8 Hz), 118.9 (d, *J*=8.3 Hz), 115.7 (d, *J*=24.1 Hz), 115.1, 113.7, 113.4, 113.1, 111.6 (d, *J*=24.2 Hz), 109.6, 71.6, 55.4, 55.1, 55.0, 54.9, 48.6; **IR ($CHCl_3$):** 3419, 2933, 2836, 1734, 1604, 1509, 1248, 1175, 1030, 837, 772 cm^{-1}; **HRMS (+ESI) m/z: $[M+H]^+$ Calcd for $C_{41}H_{32}O_6F$** 639.2183; found 639.2181.

5-Chloro-7,8,9-triphenylcyclopenta[2,3]indeno[1,2-*c*]chromen-1(13b*H*)-one; **4da**

Using the general experimental procedure on 4-bromo-6-chlorocoumarin (0.129 g; 0.5 mmol, 1 equiv), diphenylacetylene (0.178 g; 1 mmol, 2 equiv), $Pd(OAc)_2$ (0.012 g; 0.05 mmol, 10 mol%), TFP (0.023 g; 0.1 mmol, 20 mol%), and KOAc (0.098 g; 1 mmol, 2 equiv) in 1,4-dioxane (3 mL), compound **4da** was obtained as yellow solid (0.195 g, 73% yield) after purification by flash column chromatography using hexane/EtOAc (19:1) as an eluent; mp: 246-248 ^oC; **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.52 (d, *J*= 7.1 Hz, 1H), 7.32-7.36 (m, 4H), 7.24-7.26 (m, 2H), 7.09-7.19 (m, 9H), 6.99-7.01 (m, 2H), 6.97 (dd, J_1= 2.5 Hz, J_2= 8.7 Hz, 1H), 6.92-6.94 (m, 2H), 6.75 (d, *J*= 8.7 Hz, 1H), 4.59 (s, 1H); **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)**: δ 165.8, 153.9, 150.0, 148.3, 146.0, 145.1, 141.1, 134.8, 134.7, 134.0, 133.0, 129.9, 129.8, 129.7, 129.0, 128.9, 128.5, 128.4, 128.2, 128.0, 127.7, 127.5, 127.4, 125.3, 124.3, 122.5, 121.3, 119.1, 71.4, 48.5 (One peak is missing due to overlap); **IR ($CHCl_3$):** 3421, 2920, 2853, 1755, 1600, 1477, 1217, 1111, 933, 771 cm^{-1}; **HRMS (+ESI) m/z: $[M+H]^+$ Calcd for $C_{37}H_{24}O_2Cl$** 535.1465; found 535.1467.

5-Chloro-12-methyl-7,8,9-tri-*p*-tolylcyclopenta[2,3]indeno[1,2-*c*]chromen-1(13b*H*)-one; **4db**

Using the general experimental procedure on 4-bromo-6-chlorocoumarin (0.129 g; 0.5 mmol, 1 equiv), 1,2-di-*p*-tolylethyne (0.206 g; 1 mmol, 2 equiv), $Pd(OAc)_2$ (0.012 g; 0.05 mmol, 10 mol%), TFP (0.023 g; 0.1 mmol, 20 mol%), and KOAc (0.098 g; 1 mmol, 2 equiv) in 1,4-dioxane (3 mL), compound **4db** was obtained as yellow solid (0.224 g, 76% yield) after purification by flash column chromatography using hexane/EtOAc (19:1) as an eluent; mp: 242-244 ^oC; **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.41 (dd, J_1= 1.6 Hz, J_2= 7.8 Hz, 1H), 7.15-7.17 (m, 2H), 7.13 (d, *J*= 1.6 Hz, 4H), 6.89-6.98 (m, 8H), 6.81 (dd, J_1= 2.1 Hz, J_2= 8.1 Hz, 2H), 6.76 (d, *J*= 8.7 Hz, 1H), 4.52 (s, 1H), 2.37 (s, 3H), 2.28 (s, 3H), 2.27 (s, 3H), 2.20 (s, 3H); **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)**: δ 166.2, 153.2, 149.9, 147.5, 145.6, 145.2, 140.4, 138.3, 137.5, 137.0, 136.9, 132.3, 132.2, 131.4 131.1, 129.8, 129.7, 129.5, 129.1, 128.7, 128.6, 128.4, 125.4, 125.0, 122.1, 122.0, 118.9, 71.4, 48.5, 21.4, 21.3, 21.2, 21.1 (Two peaks are missing due to overlap); **IR ($CHCl_3$):** 3400, 2920, 2853, 1762, 1606, 1475, 1256, 1212, 816, 748 cm^{-1}; **HRMS (+ESI) m/z: $[M+H]^+$ Calcd for $C_{41}H_{32}O_2Cl$** 591.2091; found 591.2098.

5-Chloro-12-methoxy-7,8,9-tris(4-methoxyphenyl)cyclopenta[2,3]indeno[1,2-*c*]chromen-1(13b*H*)-one; **4dc**

Using the general experimental procedure on 4-bromo-6-chlorocoumarin (0.129 g; 0.5 mmol, 1 equiv), 1,2-bis(4-methoxyphenyl)ethyne (0.238 g; 1 mmol, 2 equiv), $Pd(OAc)_2$ (0.012 g; 0.05 mmol, 10 mol%), TFP (0.023 g; 0.1 mmol, 20 mol%), and KOAc (0.098 g; 1 mmol, 2 equiv) in 1,4-dioxane (3 mL), compound **4dc** was obtained as brown solid (0.256 g, 78% yield) after purification by flash column chromatography using hexane/EtOAc (4:1) as an eluent; mp: 118-120 °C; **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.42 (d, *J*= 8.4 Hz, 1H), 7.13-7.16 (m, 3H), 6.96-6.99 (m, 1H), 6.93-6.94 (m, 2H), 6.89-6.90 (m, 1H), 6.84-6.87 (m, 4H), 6.77 (d, *J*=8.7 Hz, 1H), 6.70 (d, *J*=8.7 Hz, 2H), 6.64-6.68 (m, 1H), 6.64 (d, *J*=8.8 Hz, 2H), 4.52 (s, 1H), 3.82 (s, 3H), 3.75 (s, 3H), 3.74 (s, 3H), 3.69 (s, 3H); **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)**: δ 166.1, 159.9, 159.0, 158.6, 158.4, 152.1, 149.9, 146.7, 146.3, 144.9, 138.8, 131.4, 131.3, 129.8, 129.6, 128.7, 127.9, 127.7, 126.9, 126.6, 125.3, 123.0, 122.4, 118.9, 115.1, 113.7, 113.4, 113.1, 109.6, 71.4, 55.5, 55.1, 55.0, 54.9, 48.7; **IR ($CHCl_3$):** 3421, 2930, 2837, 1734, 1603, 1509, 1475, 1249, 1176, 1029, 834, 770 cm^{-1}; **HRMS (+ESI) m/z: $[M+H]^+$ Calcd for $C_{41}H_{32}O_6Cl$** 655.1887; found 655.1883.

5-Bromo-7,8,9-triphenylcyclopenta[2,3]indeno[1,2-*c*]chromen-1(13b*H*)-one; **4ea**

Using the general experimental procedure on 4,6-dibromocoumarin (0.152 g; 0.5 mmol, 1 equiv), diphenylacetylene (0.178 g; 1 mmol, 2 equiv), $Pd(OAc)_2$ (0.012 g; 0.05 mmol, 10 mol%), TFP (0.023 g; 0.1 mmol, 20 mol%), and KOAc (0.098 g; 1 mmol, 2 equiv) in 1,4-dioxane (3 mL), compound **4ea** was obtained as yellow solid (0.208 g, 72% yield) after purification by flash column chromatography using hexane/EtOAc (19:1) as an eluent; mp: 264-266 °C; **^{1}H NMR (500 MHz, $CDCl_3$):** 7.45 (d, *J*= 7.2 Hz, 1H), 7.23-7.29 (m, 5H), 7.17-7.19 (m, 2H), 7.02-7.12 (m, 9H), 6.91-6.93 (m, 2H), 6.84-6.86 (m, 2H), 6.63 (d, *J*= 8.7 Hz, 1H), 4.50 (s, 1H); **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)**: δ 165.7, 153.9, 150.5, 148.3, 146.0, 145.1, 141.2, 134.8, 134.7, 134.1, 133.7, 131.8, 130.0, 129.8, 128.9, 128.5, 128.4, 128.3, 128.2, 128.0, 127.8, 127.5, 127.4, 124.3, 122.5, 121.8, 119.4, 117.2, 71.4, 48.5 (One peak is missing due to overlap); **IR ($CHCl_3$):** 3401, 2921, 2853, 1757, 1601, 1473, 1251, 854, 772, 699 cm^{-1}; **HRMS (+ESI) m/z: $[M+H]^+$ Calcd for $C_{37}H_{24}O_2Br$** 579.0960; found 579.0953.

5-Bromo-12-methyl-7,8,9-tri-*p*-tolylcyclopenta[2,3]indeno[1,2-*c*]chromen-1(13b*H*)-one; **4eb**

Using the general experimental procedure on 4,6-dibromocoumarin (0.152 g; 0.5 mmol, 1 equiv), 1,2-di-*p*-tolylethyne (0.206 g; 1 mmol, 2 equiv), $Pd(OAc)_2$ (0.012 g; 0.05 mmol, 10 mol%), TFP (0.023 g; 0.1 mmol, 20 mol%), and KOAc (0.098 g; 1 mmol, 2 equiv) in 1,4-

dioxane (3 mL), compound **4eb** was obtained as yellow solid (0.238 g, 75% yield) after purification by flash column chromatography using hexane/EtOAc (19:1) as an eluent; mp: 258-260 °C; **^{1}H NMR (500 MHz, $CDCl_3$):** 7.40 (d, *J*= 7.8 Hz, 1H), 7.28 (d, *J*= 1.7 Hz, 1H), 7.16 (s, 1H), 7.12 (s, 5H), 6.89-6.97 (m, 7H), 6.80 (d, *J*= 7.9 Hz, 2H), 6.70 (d, *J*= 8.7 Hz, 1H), 4.51 (s, 1H), 2.36 (s, 3H), 2.28 (s, 3H), 2.27 (s, 3H), 2.20 (s, 3H); **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)**: δ 166.1, 153.2, 150.5, 147.5, 145.6, 145.2, 140.4, 138.3, 137.5, 137.0, 136.9, 132.3, 132.1, 131.6, 131.4, 131.1, 129.8, 129.7, 129.5, 129.1, 128.7, 128.5, 128.4, 125.0, 122.5, 122.1, 119.3, 117.1, 71.4, 48.5, 21.4, 21.3, 21.2, 21.1 (One peak is missing due to overlap); **IR ($CHCl_3$):** 3420, 2920, 2854, 1763, 1604, 1473, 1213, 1110, 816, 771 cm^{-1}; **HRMS (+ESI) m/z: $[M+H]^+$ Calcd for $C_{41}H_{32}O_2Br$** 635.1586; found 635.1590.

5-Bromo-12-methoxy-7,8,9-tris(4-methoxyphenyl)cyclopenta[2,3]indeno[1,2-*c*]chromen-1(13b*H*)-one; **4ec**

Using the general experimental procedure on 4,6-dibromocoumarin (0.152 g; 0.5 mmol, 1 equiv), 1,2-bis(4-methoxyphenyl)ethyne (0.238 g; 1 mmol, 2 equiv), $Pd(OAc)_2$ (0.012 g; 0.05 mmol, 10 mol%), TFP (0.023 g; 0.1 mmol, 20 mol%), and KOAc (0.098 g; 1 mmol, 2 equiv) in 1,4-dioxane (3 mL), compound **4ec** was obtained as brown solid (0.269 g, 77% yield) after purification by flash column chromatography using hexane/EtOAc (4:1) as an eluent; mp: 109-111 °C; **^{1}H NMR (500 MHz, $CDCl_3$):** 7.42 (d, *J*= 8.4 Hz, 1H), 7.27 (d, *J*= 2.2 Hz, 1H), 7.15 (d, *J*= 8.7 Hz, 2H), 7.10-7.13 (m, 1H), 6.93 (d, *J*= 8.8 Hz, 2H), 6.89-6.90 (m, 1H), 6.83-6.87 (m, 4H), 6.67-6.72 (m, 3H), 6.66-6.69 (m, 1H), 6.64 (d, *J*= 8.8 Hz, 2H), 4.51 (s, 1H), 3.82 (s, 3H), 3.75 (s, 3H), 3.74 (s, 3H), 3.69 (s, 3H); **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)**: δ 166.1, 159.9, 159.0, 158.6, 158.4, 152.1, 150.4, 146.6, 146.3, 144.9, 138.9, 131.6, 131.3, 131.1, 129.8, 128.4, 127.9, 127.7, 126.9, 126.6, 123.0, 122.8, 119.3, 117.1, 115.1, 113.8, 113.4, 113.1, 109.7, 71.4, 55.2, 55.1, 55.0, 54.9, 48.8; **IR ($CHCl_3$):** 3421, 2931, 2836, 1734, 1604, 1509, 1473, 1248, 1175, 1029, 834, 771 cm^{-1}; **HRMS (+ESI) m/z: $[M+H]^+$ Calcd for $C_{41}H_{32}O_6Br$** 699.1382; found 699.1379.

4-Methoxy-7,8,9-triphenylcyclopenta[2,3]indeno[1,2-*c*]chromen-1(13b*H*)-one; **4fa**

Using the general experimental procedure on 4-bromo-7-methoxycoumarin (0.127 g; 0.5 mmol, 1 equiv), diphenylacetylene (0.178 g; 1 mmol, 2 equiv), $Pd(OAc)_2$ (0.012 g; 0.05 mmol, 10 mol%), TFP (0.023 g; 0.1 mmol, 20 mol%), and KOAc (0.098 g; 1 mmol, 2 equiv) in 1,4-dioxane (3 mL), compound **4fa** was obtained as light brown solid (0.199 g, 75% yield) after

purification by flash column chromatography using hexane/EtOAc (9:1) as an eluent; mp: 210-212 °C; **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.42 (d, *J*= 7.4 Hz, 1H), 7.29 (d, *J*= 7.4 Hz, 1H), 7.23-7.24 (m, 3H), 7.15-7.18 (m, 2H), 7.00-7.10 (m, 9H), 6.90-6.92 (m, 2H), 6.83-6.85 (m, 2H), 6.47 (dd, J_1= 2.6 Hz, J_2= 8.7 Hz, 1H), 6.26 (d, *J*= 2.6 Hz, 1H), 4.48 (s, 1H), 3.55 (s, 3H); **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)**: δ 166.5, 159.5, 154.3, 152.1, 148.8, 145.6, 145.3, 140.3, 135.2, 134.9, 134.5, 134.1, 130.0, 129.8, 128.7, 128.6, 128.2, 128.0, 127.9, 127.8, 127.7, 127.3, 127.2, 126.4, 124.3, 122.4, 112.1, 110.7, 101.9, 71.2, 55.2, 48.8; **IR ($CHCl_3$):** 3417, 2918, 2850, 1754, 1623, 1219, 823, 772 cm^{-1}; **HRMS (+ESI) m/z: $[M+H]^+$ Calcd for $C_{38}H_{27}O_3$** 531.1960; found 531.1964.

4-Methoxy-12-methyl-7,8,9-tri-*p*-tolylcyclopenta[2,3]indeno[1,2-*c*]chromen-1(13b*H*)-one; **4fb**

Using the general experimental procedure on 4-bromo-7-methoxycoumarin (0.127 g; 0.5 mmol, 1 equiv), 1,2-di-*p*-tolylethyne (0.206 g; 1 mmol, 2 equiv), $Pd(OAc)_2$ (0.012 g; 0.05 mmol, 10 mol%), TFP (0.023 g; 0.1 mmol, 20 mol%), and KOAc (0.098 g; 1 mmol, 2 equiv) in 1,4-dioxane (3 mL), compound **4fb** was obtained as yellow solid (0.226 g, 77% yield) after purification by flash column chromatography using hexane/EtOAc (9:1) as an eluent; mp: 212-214 °C; **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.39 (d, *J*= 7.8 Hz, 1H), 7.18 (s, 1H), 7.12 (s, 4H), 7.10 (s, 1H), 6.95 (d, *J*= 7.9 Hz, 2H), 6.89 (dd, J_1= 2.1 Hz, J_2= 8.2 Hz, 5H), 6.81 (d, *J*= 8.1 Hz, 2H), 6.53 (dd, J_1= 2.6 Hz, J_2= 8.7 Hz, 1H), 6.34 (d, *J*= 2.6 Hz, 1H), 4.50 (s, 1H), 3.62 (s, 3H), 2.36 (s, 3H), 2.28 (s, 3H), 2.27 (s, 3H), 2.19 (s, 3H); **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)**: δ 166.9, 159.3, 153.7, 152.1, 147.9, 145.7, 144.9, 139.6, 138.0, 137.2, 136.7, 132.6, 132.5, 131.8, 131.5, 129.8, 129.7, 129.3, 128.9, 128.6, 128.4, 128.3, 126.5, 125.0, 122.0, 111.9, 111.4, 101.8, 71.1, 55.1, 48.8, 21.4, 21.3, 21.2, 21.1 (One peak is missing due to overlap); **IR ($CHCl_3$):** 3442, 3023, 2920, 2854, 1754, 1621, 1502, 1249, 1159, 1036, 824, 759 cm^{-1}; **HRMS (+ESI) m/z: $[M+H]^+$ Calcd for $C_{42}H_{35}O_3$** 587.2586; found 587.2583.

4,12-Dimethoxy-7,8,9-tris(4-methoxyphenyl)cyclopenta[2,3]indeno[1,2-*c*]chromen-1(13b*H*)-one; **4fc**

Using the general experimental procedure on 4-bromo-7-methoxycoumarin (0.127 g; 0.5 mmol, 1 equiv), 1,2-bis(4-methoxyphenyl)ethyne (0.238 g; 1 mmol, 2 equiv), $Pd(OAc)_2$ (0.012 g; 0.05 mmol, 10 mol%), TFP (0.023 g; 0.1 mmol, 20 mol%), and KOAc (0.098 g; 1 mmol, 2 equiv) in 1,4-dioxane (3 mL), compound **4fc** was obtained as light brown solid (0.260 g, 80% yield) after purification by flash column chromatography using hexane/EtOAc (4:1) as an

eluent; mp: 194-196 °C; **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.39 (d, *J*= 8.4 Hz, 1H), 7.13 (d, *J*= 8.8 Hz, 2H), 7.07 (d, *J*= 8.7 Hz, 1H), 6.82-6.92 (m, 7H), 6.51-6.69 (m, 5H), 6.52 (dd, J_1= 2.6 Hz, J_2= 8.7 Hz, 1H), 6.34 (d, *J*= 2.6 Hz, 1H), 4.92 (s, 1H), 3.81 (s, 3H), 3.74 (s, 3H), 3.73 (s, 3H), 3.69 (s, 3H), 3.63 (s, 3H); **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)**: δ 166.9, 159.7, 159.3, 158.8, 158.4, 158.2, 152.5, 152.0, 147.1, 146.7, 144.2, 138.0, 131.2, 131.0, 129.8, 128.2, 128.1, 127.2, 126.9, 126.5, 122.9, 115.0, 113.6, 113.3, 113.0, 112.0, 111.7, 109.5, 101.7, 71.1, 55.4, 55.2, 55.1, 55.0, 54.9, 49.0; **IR ($CHCl_3$):** 3440, 2933, 2835, 1753, 1606, 1502, 1247, 1176, 1030, 835, 759 cm^{-1}; **HRMS (+ESI) m/z: $[M+H]^+$ Calcd for $C_{42}H_{35}O_7$** 651.2383; found 651.2390.

4-Methyl-7,8,9-triphenylcyclopenta[2,3]indeno[1,2-*c*]chromen-1(13b*H*)-one; **4ga**

Using the general experimental procedure on 4-bromo-7-methylcoumarin (0.120 g; 0.5 mmol, 1 equiv), diphenylacetylene (0.178 g; 1 mmol, 2 equiv), $Pd(OAc)_2$ (0.012 g; 0.05 mmol, 10 mol%), TFP (0.023 g; 0.1 mmol, 20 mol%), and KOAc (0.098 g; 1 mmol, 2 equiv) in 1,4-dioxane (3 mL), compound **4ga** was obtained as yellow solid (0.191 g, 74% yield) after purification by flash column chromatography using hexane/EtOAc (19:1) as an eluent; mp: 181-183 °C; **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.48 (d, *J*= 7.4 Hz, 1H), 7.36 (d, *J*= 7.5 Hz, 1H), 7.30-7.31 (m, 3H), 7.23-7.25 (m, 2H), 7.05-7.16 (m, 9H), 6.98-7.00 (m, 2H), 6.91-6.93 (m, 2H), 6.76 (d, *J*= 8.0 Hz, 1H), 6.61 (s, 1H), 4.57 (s, 1H), 2.12 (s, 3H); **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)**: δ 166.7, 154.5, 151.2, 148.7, 145.7, 145.5, 140.4, 138.9, 135.2, 134.9, 134.5, 134.1, 129.9, 129.8, 128.7, 128.6, 128.2, 128.0, 127.9, 127.8, 127.7, 127.2, 125.7, 125.3, 124.3, 122.3, 117.9, 115.9, 71.4, 48.9, 20.9 (One peak is missing due to overlap); **IR ($CHCl_3$):** 3420, 2921, 2850, 1751, 1622, 1442, 1219, 1155, 822, 771 cm^{-1}; **HRMS (+ESI) m/z: $[M+H]^+$ Calcd for $C_{38}H_{27}O_2$** 515.2011; found 515.2007.

4,12-Dimethyl-7,8,9-tri-*p*-tolylcyclopenta[2,3]indeno[1,2-*c*]chromen-1(13b*H*)-one; **4gb**

Using the general experimental procedure on 4-bromo-7-methylcoumarin (0.120 g; 0.5 mmol, 1 equiv), 1,2-di-*p*-tolylethyne (0.206 g; 1 mmol, 2 equiv), $Pd(OAc)_2$ (0.012 g; 0.05 mmol, 10 mol%), TFP (0.023 g; 0.1 mmol, 20 mol%), and KOAc (0.098 g; 1 mmol, 2 equiv) in 1,4-dioxane (3 mL), compound **4gb** was obtained as light brown solid (0.214 g, 75% yield) after purification by flash column chromatography using hexane/EtOAc (19:1) as an eluent; mp: 205-207 °C; **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.26 (dd, J_1= 1.6 Hz, J_2= 7.7 Hz, 1H), 7.06 (s, 1H), 6.97-7.00 (m, 5H), 6.69-6.82 (m, 9H), 6.60 (d, *J*= 7.8 Hz, 1H), 6.48 (s, 1H), 4.40 (s, 1H),

2.21 (s, 3H), 2.13 (s, 3H), 2.11 (s, 3H), 2.02 (s, 3H), 1.96 (s, 3H); **$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$)**: δ 167.0, 153.8, 151.1, 147.8, 145.7, 145.1, 139.7, 138.6, 137.9, 137.1, 136.6, 132.6, 132.5, 131.8, 131.4, 129.8, 129.7, 129.3, 128.9, 128.6, 128.4, 128.3, 125.6, 125.4, 124.9, 121.9, 117.7, 116.6, 71.3, 48.9, 21.3, 21.2, 21.1, 21.0, 20.8 (One peak is missing due to overlap); **IR ($CHCl_3$):** 3421, 3023, 2920, 2853, 1752, 1607, 1502, 1454, 1184, 1110, 823, 771 cm^{-1}; **HRMS (+ESI) m/z: $[M+H]^+$ Calcd for $C_{42}H_{35}O_2$** 571.2637; found 571.2635.

12-Methoxy-7,8,9-tris(4-methoxyphenyl)-4-methylcyclopenta[2,3]indeno[1,2-*c*]chromen-1(13b*H*)-one; **4gc**

Using the general experimental procedure on 4-bromo-7-methylcoumarin (0.120 g; 0.5 mmol, 1 equiv), 1,2-bis(4-methoxyphenyl)ethyne (0.238 g; 1 mmol, 2 equiv), $Pd(OAc)_2$ (0.012 g; 0.05 mmol, 10 mol%), TFP (0.023 g; 0.1 mmol, 20 mol%), and KOAc (0.098 g; 1 mmol, 2 equiv) in 1,4-dioxane (3 mL), compound **4gc** was obtained as light brown solid (0.247 g, 78% yield) after purification by flash column chromatography using hexane/EtOAc (4:1) as an eluent; mp: 161-163 °C; **^1H NMR (500 MHz, $CDCl_3$):** δ 7.39 (d, *J*= 8.4 Hz, 1H), 7.14 (d, *J*= 8.6 Hz, 2H), 7.08 (d, *J*= 7.9 Hz, 1H), 6.93 (d, *J*= 8.7 Hz, 2H), 6.91-6.92 (m, 1H), 6.85 (d, *J*= 8.7 Hz, 4H), 6.74 (dd, J_1= 1.0 Hz, J_2= 8.0 Hz, 1H), 6.69 (d, *J*= 8.8 Hz, 2H), 6.60-6.64 (m, 4H), 4.51 (s, 1H), 3.81 (s, 3H), 3.74 (s, 3H), 3.73 (s, 3H), 3.68 (s, 3H), 2.14 (s, 3H); **$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$)**: δ 167.0, 159.7, 158.8, 158.4, 158.2, 152.7, 151.1, 147.1, 146.6, 144.4, 138.7, 138.0, 131.2, 131.0, 129.8, 128.1, 127.3, 126.9, 125.7, 125.4, 122.8, 117.7, 117.0, 115.0, 113.6, 113.3, 113.0, 109.5, 71.3, 55.4, 55.1, 55.0, 54.9, 49.1, 20.9 (One peak is missing due to overlap); **IR ($CHCl_3$):** 3421, 2929, 2836, 1751, 1605, 1509, 1247, 1175, 1030, 834, 771 cm^{-1}; **HRMS (+ESI) m/z: $[M+H]^+$ Calcd for $C_{42}H_{35}O_6$** 635.2434; found 635.2439.

12-Methoxy-7-(4-methoxyphenyl)-8,9-diphenylcyclopenta[2,3]indeno[1,2-*c*]chromen-1(13b*H*)-one; (**$4ad_1$**) 8,9-bis(4-methoxyphenyl)-7-phenylcyclopenta[2,3]indeno[1,2-*c*]chromen-1(13b*H*)-one; (**$4ad_2$**) 12-methoxy-8-(4-methoxyphenyl)-7,9-diphenylcyclopenta[2,3]indeno[1,2-*c*]chromen-1(13b*H*)-one; (**$4ad_3$**) 7-(3-methoxyphenyl)-9-(4-methoxyphenyl)-8-phenylcyclopenta[2,3]indeno [1,2-*c*]chromen-1(13b*H*)-one; (**$4ad_4$**)

Using the general experimental procedure on 4-bromocoumarin (0.112 g; 0.5 mmol, 1 equiv), 1-methoxy-4-(phenylethynyl)benzene (0.208 g; 1 mmol, 2 equiv), $Pd(OAc)_2$ (0.012 g; 0.05 mmol, 10 mol%), TFP (0.023 g; 0.1 mmol, 20 mol%), and KOAc (0.098 g; 1 mmol, 2 equiv) in 1,4-dioxane (3 mL), compounds **$4ad_1$, $4ad_2$, $4ad_3$** & **$4ad_4$** were obtained as light brown solid (0.197 g, 70% yield) after purification by flash column chromatography using hexane/EtOAc

(4:1) as an eluent; mp: 114-116 °C; **^{1}H NMR (500 MHz, $CDCl_3$):** δ 6.81-7.40 (m, 74H), 6.59-6.69 (m, 10H), 4.56 (s, 4H), 3.82 (s, 3H), 3.80 (s, 3H), 3.74 (s, 6H), 3.73 (s, 6H), 3.68 (s, 3H), 3.67 (s, 3H); **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)**: δ 166.7, 166.6 x 2, 166.5, 160.9, 160.1, 160.0, 159.1, 158.6, 158.5, 158.4, 154.2, 154.1, 153.7, 153.4, 152.9, 151.4, 151.3, 148.5, 148.4, 147.8, 147.6, 147.4, 147.3, 146.9, 145.3, 145.2, 145.0, 144.9, 141.9, 140.5, 138.5, 135.6, 135.5, 135.3, 135.2, 134.8, 134.4, 134.3, 131.8, 131.3, 131.2 x 2, 131.1, 130.0, 129.9, 129.8 x 2, 129.7 x 2, 128.6 x 2, 128.2, 128.0, 127.9, 127.8 x 2, 127.7 x 2, 127.6 x 2, 127.5, 127.1 x 2, 127.0, 126.8 x 2, 126.5 x 2, 126.3, 125.7, 125.6 x 2, 124.7 x 2, 124.6 x 2, 124.3 x 2, 123.1, 123.0, 122.2, 122.1, 119.9, 119.8, 119.7, 119.5, 117.6, 117.5, 115.1, 114.4, 113.7, 113.3 x 2, 113.1 x 2, 112.3, 111.5, 109.6, 71.8, 71.6, 71.5, 71.4, 55.5, 55.1 x 2, 55.0, 54.9, 49.0, 48.9, 48.8 x 2 (Several peaks are missing due to overlap); **IR ($CHCl_3$):** 3436, 2922, 2852, 1756, 1606, 1508, 1485, 1247, 1219, 1029, 837, 771 cm^{-1}; **HRMS (+ESI) m/z: $[M+H]^+$ Calcd for $C_{39}H_{29}O_4$** 561.2066; found 561.2065.

12-Methoxy-7-(4-methoxyphenyl)-5-methyl-8,9-diphenylcyclopenta[2,3]indeno[1,2-*c*]chromen-1(13b*H*)-one; (**4bd$_1$**) 8,9-bis(4-methoxyphenyl)-5-methyl-7-phenylcyclopenta[2,3]indeno[1,2-*c*]chromen-1(13b*H*)-one; (**4bd$_2$**) 12-methoxy-8-(4-methoxyphenyl)-5-methyl-7,9-diphenylcyclopenta[2,3]indeno[1,2-*c*]chromen-1(13b*H*)-one; (**4bd$_3$**) 7-(3-methoxyphenyl)-9-(4-methoxyphenyl)-5-methyl-8-phenylcyclopenta[2,3]indeno [1,2-*c*]chromen-1(13b*H*)-one; (**4bd$_4$**)

Using the general experimental procedure on 4-bromo-6-methylcoumarin (0.120 g; 0.5 mmol, 1 equiv), 1-methoxy-4-(phenylethynyl)benzene (0.208 g; 1 mmol, 2 equiv), $Pd(OAc)_2$ (0.012 g; 0.05 mmol, 10 mol%), TFP (0.023 g; 0.1 mmol, 20 mol%), and KOAc (0.098 g; 1 mmol, 2 equiv) in 1,4-dioxane (3 mL), compounds **4bd$_1$, 4bd$_2$, 4bd$_3$** & **4bd$_4$** were obtained as brown solid (0.204 g, 71% yield) after purification by flash column chromatography using hexane/EtOAc (4:1) as an eluent; mp: 115-117 °C; **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.41 (d, *J*= 7.3 Hz, 2H), 7.32 (d, *J*= 8.4 Hz, 2H), 6.73-7.33 (m, 64H), 6.55-6.66 (m, 10H), 6.53 (d, *J*= 8.4 Hz, 2H), 4.44 (s, 4H), 3.74 (s, 3H), 3.73 (s, 3H), 3.66 (s, 6H), 3.65 (s, 6H), 3.60 (s, 3H), 3.59 (s, 3H), 2.12 (s, 6H), 2.11 (s, 6H); **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)**: δ 166.9, 166.8, 166.7 x 2, 161.1, 160.0 x 2, 159.0, 158.6, 158.4 x 2, 154.1, 153.7, 153.4, 152.9, 149.3, 149.2, 148.5, 147.8 x 2, 147.5, 147.4, 146.9, 145.4, 145.3, 145.2, 145.1 x 2, 144.8, 144.7, 141.9, 140.4, 138.4, 135.6, 135.5, 135.3 x 2, 134.9, 134.4 x 2, 134.1, 134.0 x 2, 133.9, 132.8, 131.3, 131.2 x 2, 131.1, 130.0 x 2, 129.8 x 2, 129.7 x 2, 129.4 x 2, 128.6 x 2, 128.2, 128.0, 127.9, 127.8 x 2, 127.7 x 2, 127.6 x 2, 127.4, 127.0, 126.9 x 2, 126.8, 126.6 x 2, 126.1, 125.6, 125.5 x 2, 125.4

x 2, 123.1, 123.0, 122.2, 122.1, 119.4, 119.3, 119.2, 119.0, 117.3, 117.2, 115.1, 114.3, 113.6, 113.3 x 2, 113.1, 113.0, 112.3, 111.6, 109.5, 71.8, 71.6, 71.5, 71.4, 55.5, 55.1 x 2, 55.0, 54.9, 49.0 x 2, 48.9 x 2, 21.2, 20.9 x 2 (Several peaks are missing due to overlap); **IR ($CHCl_3$):** 3421, 2920, 2853, 1754, 1605, 1506, 1487, 1247, 1217, 1177, 834, 771 cm^{-1}; **HRMS (+ESI) m/z: $[M+H]^+$ Calcd for $C_{40}H_{31}O_4$** 575.2222; found 575.2221.

5-Chloro-12-methoxy-7-(4-methoxyphenyl)-8,9-diphenylcyclopenta[2,3]indeno[1,2-*c*]chromen-1(13b*H*)-one; (**4dd$_1$**) 5-chloro-8,9-bis(4-methoxyphenyl)-7-phenylcyclopenta[2,3]indeno[1,2-*c*]chromen-1(13b*H*)-one; (**4dd$_2$**) 5-Chloro-12-methoxy-8-(4-methoxyphenyl)-7,9-diphenylcyclopenta[2,3]indeno[1,2-*c*]chromen-1(13b*H*)-one; (**4dd$_3$**) 5-chloro-7-(3-methoxyphenyl)-9-(4-methoxyphenyl)-8-phenylcyclopenta[2,3]indeno [1,2-*c*]chromen-1(13b*H*)-one; (**4dd$_4$**)

Using the general experimental procedure on 4-bromo-6-chlorocoumarin (0.129 g; 0.5 mmol, 1 equiv), 1-methoxy-4-(phenylethynyl)benzene (0.208 g; 1 mmol, 2 equiv), $Pd(OAc)_2$ (0.012 g; 0.05 mmol, 10 mol%), TFP (0.023 g; 0.1 mmol, 20 mol%), and KOAc (0.098 g; 1 mmol, 2 equiv) in 1,4-dioxane (3 mL), compounds **4dd$_1$, 4dd$_2$, 4dd$_3$** & **4dd$_4$** were obtained as light brown solid (0.204 g, 69% yield) after purification by flash column chromatography using hexane/EtOAc (4:1) as an eluent; mp: 110-112 ^oC; **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.43 (d, *J*= 7.0 Hz, 2H), 7.34 (d, *J*= 8.4 Hz, 2H), 6.75-7.26 (m, 62H), 6.64-6.70 (m, 4H), 6.58-6.61 (m, 8H), 6.54 (d, *J*= 8.6 Hz, 2H), 4.47 (s, 4H), 3.73 (s, 3H), 3.71 (s, 3H), 3.64 (s, 6H), 3.63 (s, 6H), 3.59 (s, 6H); **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)**: δ 166.1, 166.0, 165.9 x 2, 160.1 x 2, 159.2, 158.7, 158.6, 158.5, 153.6, 153.1, 152.8, 152.6, 152.3, 149.9, 149.8, 148.1, 147.9, 147.3, 147.2, 146.9, 146.8, 146.4, 145.7, 145.6, 145.3, 145.2, 144.9, 144.8, 141.0, 140.8, 138.9, 135.2, 135.1 x 2, 135.0, 134.5, 134.1, 134.0, 132.1, 131.7, 131.3, 131.2 x 2, 131.6, 130.0, 129.9, 129.8, 129.7 x 2, 129.6 x 2, 129.5 x 2, 128.8, 128.6, 128.5, 128.4, 128.0 x 2, 127.9, 127.8, 127.7 x 2, 127.6 x 2, 127.5, 127.3 x 2, 127.2 x 2, 126.4 x 2, 126.2 x 2, 126.0, 125.4, 125.3, 125.2, 124.2, 123.3, 123.2, 122.3, 122.8, 122.1, 121.9, 121.8, 121.7, 119.0, 118.9, 118.8, 115.1, 114.6, 113.7, 113.4, 113.3, 113.1 x 2, 112.5, 112.1, 109.6, 71.6, 71.5, 71.4, 71.2, 55.5, 55.1 x 2, 55.0, 54.9, 48.7 x 2, 48.5 x 2 (Several peaks are missing due to overlap); **IR ($CHCl_3$):** 3421, 2927, 2835, 1761, 1605, 1508, 1476, 1248, 1217, 1175, 837, 770 cm^{-1}; **HRMS (+ESI) m/z: $[M+H]^+$ Calcd for $C_{39}H_{28}O_4Cl$** 595.1676; found 595.1672.

7,9-Bis(4-fluorophenyl)-8-phenylcyclopenta[2,3]indeno[1,2-*c*]chromen-1(13b*H*)-one; (**4ae$_1$**) 8,9-bis(4-fluorophenyl)-7-phenylcyclopenta[2,3]indeno[1,2-*c*]chromen-1(13b*H*)-one; (**4ae$_2$**)

Using the general experimental procedure on 4-bromocoumarin (0.112 g; 0.5 mmol, 1 equiv) 1-fluoro-4-(phenylethynyl)benzene (0.196 g; 1 mmol, 2 equiv), $Pd(OAc)_2$ (0.012 g; 0.05 mmol, 10 mol%), TFP (0.023 g; 0.1 mmol, 20 mol%), and KOAc (0.098 g; 1 mmol, 2 equiv) in 1,4-dioxane (3 mL), compound **4ae$_1$** was obtained as white solid (0.041 g, 15% yield); mp: 171-173 ^oC and compound **4ae$_2$** was obtained as off-white solid (0.044 g, 16% yield); mp: 172-174 ^oC; after purification by flash column chromatography using hexane/EtOAc (4:1) as an eluent; For **4ae$_1$: ^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.44 (d, *J*= 7.4 Hz, 1H), 7.38 (d, *J*= 7.5 Hz, 1H), 6.96-7.22 (m, 14H), 6.84-7.88 (m, 3H), 6.78 (t, *J*= 8.7 Hz, 2H), 4.56 (s, 1H); **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)**: δ 166.2, 162.3 (d, *J*=247.9 Hz), 161.8 (d, *J*=247.9 Hz), 154.5, 151.4, 147.8, 145.8, 145.4, 139.4, 134.8, 134.0, 131.5 (d, *J*=8.1 Hz), 131.1 (d, *J*=3.1 Hz), 130.3 (d, *J*=8.0 Hz), 130.0 (d, *J*=3.2 Hz), 129.9, 128.9, 128.8, 128.3, 128.2, 127.6, 125.4, 124.8, 124.5, 122.3, 119.0, 117.8, 115.4 (d, *J*=21.6 Hz), 114.9 (d, *J*=21.8 Hz), 71.7, 48.7; **IR ($CHCl_3$):** 3422, 2932, 2835, 1751, 1603, 1505, 1245, 1173, 831, 771 cm^{-1}; **HRMS (+ESI) m/z: $[M+H]^+$ Calcd for $C_{37}H_{23}F_2O_2$** 537.1666; found 537.1671.

For **4ae$_2$: ^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.43 (d, *J*= 7.5 Hz, 1H), 7.39 (d, *J*= 7.6 Hz, 1H), 7.17-7.23 (m, 4H), 7.09-7.14 (m, 4H), 7.02-7.06 (m, 3H), 6.94-6.99 (m, 3H), 6.82-6.90 (m, 5H), 4.57 (s, 1H); **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)**: δ 166.2, 162.3 (d, *J*=248.0 Hz), 162.0 (d, *J*=247.7 Hz), 154.7, 151.4, 149.0, 145.5, 145.3, 139.2, 134.8, 134.7, 131.7 (d, *J*=8.0 Hz), 131.5 (d, *J*=8.1 Hz), 130.2 (d, *J*=3.4 Hz), 129.9 (d, *J*=3.1 Hz), 128.9, 128.8, 128.5, 128.4, 128.2, 127.6, 125.4, 124.7, 124.5, 122.2, 118.9, 117.8, 115.2 (d, *J*=26.8 Hz), 115.0 (d, *J*=27.0 Hz), 71.7, 48.8; **IR ($CHCl_3$):** 3425, 2928, 2830, 1751, 1602, 1512, 1252, 1172, 832, 770 cm^{-1}; **HRMS (+ESI) m/z: $[M+H]^+$ Calcd for $C_{37}H_{23}F_2O_2$** 537.1666; found 537.1670.

General procedure for the synthesis of spiropentadiene chromanone 3:

2',3',4',5'-Tetrakis(4-fluorophenyl)spiro[chromane-4,1'-cyclopentane]-2',4'-dien-2-one; **3af**

Using the general experimental procedure on 4-bromocoumarin (0.112 g; 0.5 mmol, 1 equiv), 1,2-bis(4-fluorophenyl)ethyne (0.214 g; 1 mmol, 2 equiv), $Pd(OAc)_2$ (0.012 g; 0.05 mmol, 10 mol%), TFP (0.023 g; 0.1 mmol, 20 mol%), and KOAc (0.098 g; 1 mmol, 2 equiv) in 1,4-dioxane (3 mL), compound **3af** was obtained as yellow solid (0.181 g, 63% yield) after purification by flash column chromatography using hexane/EtOAc (19:1) as an eluent; mp: 100-102 ^oC; **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.46 (dd, J_1= 1.6 Hz, J_2= 7.7 Hz, 1H), 7.29-7.32

(m, 1H), 7.21 (td, J_1= 1.2 Hz, J_2= 7.5 Hz, 1H), 6.88-6.92 (m, 5H), 6.74-6.82 (m, 12H), 2.96 (s, 2H); **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)**: δ 166.7, 162.5 (d, *J*=248.3 Hz), 161.8 (d, *J*=247.7 Hz), 152.7, 147.3, 142.7, 131.5 (d, *J*=11.5 Hz), 131.4 (d, *J*=11.6 Hz), 130.1 (d, *J*=3.4 Hz), 129.6, 129.5 (d, *J*=3.4 Hz), 125.4, 125.2, 120.0, 118.0, 115.3 (d, *J*=38.4 Hz), 115.1 (d, *J*=38.7 Hz), 60.8, 34.6; **IR ($CHCl_3$):** 3400, 2918, 2850, 1768, 1600, 1503, 1220, 1158, 834, 772 cm^{-1}; **HRMS (+ESI) m/z: $[M+H]^+$ Calcd for $C_{37}H_{23}O_2F_4$** 575.1634; found 575.1642.

2',3',4',5'-Tetrakis(4-fluorophenyl)-6-methylspiro[chromane-4,1'-cyclopentane]-2',4'-dien-2-one; **3bf**

Using the general experimental procedure on 4-bromo-6-methylcoumarin (0.120 g; 0.5 mmol, 1 equiv), 1,2-bis(4-fluorophenyl)ethyne (0.214 g; 1 mmol, 2 equiv), $Pd(OAc)_2$ (0.012 g; 0.05 mmol, 10 mol%), TFP (0.023 g; 0.1 mmol, 20 mol%), and KOAc (0.098 g; 1 mmol, 2 equiv) in 1,4-dioxane (3 mL), compound **3bf** was obtained as white solid (0.191 g, 65% yield) after purification by flash column chromatography using hexane/EtOAc (19:1) as an eluent; mp: 229-231 ^{o}C; **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.17 (d, *J*= 1.4 Hz, 1H), 7.09-7.11 (m, 1H), 6.89-6.92 (m, 4H), 6.75-6.83 (m, 13H), 2.92 (s, 2H), 2.38 (s, 3H); **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)**: δ 166.9, 162.1 (d, *J*=248.4 Hz), 161.8 (d, *J*=247.7 Hz), 150.7, 147.3, 142.6, 134.8, 131.5 (d, *J*=11.4 Hz), 131.4 (d, *J*=11.5 Hz), 130.3, 130.1 (d, *J*=3.3 Hz), 129.6 (d, *J*=3.4 Hz), 125.3, 119.6, 117.7, 115.2 (d, *J*=35.7 Hz), 115.1 (d, *J*=35.8 Hz), 60.8, 34.8, 21.0; **IR ($CHCl_3$):** 3420, 2921, 2850, 1768, 1600, 1502, 1221, 1158, 832, 771 cm^{-1}; **HRMS (+ESI) m/z: $[M+H]^+$ Calcd for $C_{38}H_{25}O_2F_4$** 589.1791; found 589.1787.

6-Fluoro-2',3',4',5'-tetrakis(4-fluorophenyl)spiro[chromane-4,1'-cyclopentane]-2',4'-dien-2-one; **3cf**

Using the general experimental procedure on 4-bromo-6-fluorocoumarin (0.122 g; 0.5 mmol, 1 equiv), 1,2-bis(4-fluorophenyl)ethyne (0.214 g; 1 mmol, 2 equiv), $Pd(OAc)_2$ (0.012 g; 0.05 mmol, 10 mol%), TFP (0.023 g; 0.1 mmol, 20 mol%), and KOAc (0.098 g; 1 mmol, 2 equiv) in 1,4-dioxane (3 mL), compound **3cf** was obtained as white solid (0.183 g, 62% yield) after purification by flash column chromatography using hexane/EtOAc (19:1) as an eluent; mp: 173-175 ^{o}C; **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.11 (dd, J_1= 2.9 Hz, J_2= 8.5 Hz, 1H), 6.99-7.03 (m, 1H), 6.87-6.91 (m, 4H), 6.76-6.85 (m, 13H), 2.96 (s, 2H); **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)**: δ 166.2, 162.2 (d, *J*=248.8 Hz), 161.9 (d, *J*=247.9 Hz), 159.5 (d, *J*=244.5 Hz), 148.8 (d, *J*=2.2 Hz), 149.6, 143.1, 131.4 (d, *J*=15.3 Hz), 131.4 (d, *J*=15.4 Hz), 129.8 (d, *J*=3.3 Hz), 129.3 (d, *J*=3.4 Hz), 122.0 (d, *J*=7.3 Hz), 119.5 (d, *J*=8.3 Hz), 116.7 (d, *J*=23.7 Hz), 115.4 (d,

J=47.8 Hz), 115.2 (d, *J*=47.7 Hz), 111.4 (d, *J*=24.2 Hz), 60.7, 34.1; **IR ($CHCl_3$):** 3420, 2923, 2853, 1773, 1600, 1503, 1221, 1158, 833, 771 cm^{-1}; **HRMS (+ESI) m/z: $[M+H]^+$ Calcd for $C_{37}H_{22}O_2F_5$** 593.1540; found 593.1536.

2',3',4',5'-Tetrakis(4-fluorophenyl)-7-methoxyspiro[chromane-4,1'-cyclopentane]-2',4'-dien-2-one; **3ff**

Using the general experimental procedure on 4-bromo-7-methoxycoumarin (0.127 g; 0.5 mmol, 1 equiv), 1,2-bis(4-fluorophenyl)ethyne (0.214 g; 1 mmol, 2 equiv), $Pd(OAc)_2$ (0.012 g; 0.05 mmol, 10 mol%), TFP (0.023 g; 0.1 mmol, 20 mol%), and KOAc (0.098 g; 1 mmol, 2 equiv) in 1,4-dioxane (3 mL), compound **3ff** was obtained as yellow solid (0.200 g, 66% yield) after purification by flash column chromatography using hexane/EtOAc (19:1) as an eluent; mp: 170-172 °C; **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.29 (d, *J*= 8.6 Hz, 1H), 6.86-6.89 (m, 4H), 6.76-6.83 (m, 13H), 6.44 (d, *J*= 2.6 Hz, 1H), 3.80 (s, 3H), 2.92 (s, 2H); **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)**: δ 166.8, 162.1 (d, *J*=248.2 Hz), 161.8 (d, *J*=247.5 Hz), 160.3, 153.6, 147.5, 142.4, 131.5 (d, *J*=11.1 Hz), 131.4 (d, *J*=11.2 Hz), 130.1 (d, *J*=3.3 Hz), 129.7 (d, *J*=3.5 Hz), 126.2, 115.2 (d, *J*=41.3 Hz), 115.1 (d, *J*=41.3 Hz), 112.2, 111.2, 102.4, 60.3, 55.5, 34.7; **IR ($CHCl_3$):** 3414, 2920, 2850, 1767, 1601, 1503, 1220, 1158, 834, 772 cm^{-1}; **HRMS (+ESI) m/z: $[M+H]^+$ Calcd for $C_{38}H_{25}O_3F_4$** 605.1740; found 605.1748.

2',3',4',5'-Tetrakis(4-fluorophenyl)-7-methylspiro[chromane-4,1'-cyclopentane]-2',4'-dien-2-one; **3gf**

Using the general experimental procedure on 4-bromo-7-methylcoumarin (0.120 g; 0.5 mmol, 1 equiv), 1,2-bis(4-fluorophenyl)ethyne (0.214 g; 1 mmol, 2 equiv), $Pd(OAc)_2$ (0.012 g; 0.05 mmol, 10 mol%), TFP (0.023 g; 0.1 mmol, 20 mol%), and KOAc (0.098 g; 1 mmol, 2 equiv) in 1,4-dioxane (3 mL), compound **3gf** was obtained as yellow solid (0.188 g, 64% yield) after purification by flash column chromatography using hexane/EtOAc (19:1) as an eluent; mp: 101-103 °C; **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.30 (d, *J*= 8.6 Hz, 1H), 7.01 (dd, J_1= 0.9 Hz, J_2= 7.8 Hz, 1H), 6.88-6.91 (m, 4H), 6.76-6.82 (m, 12H), 6.72 (s, 1H), 2.92 (s, 2H), 2.35 (s, 3H); **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)**: δ 166.9, 162.1 (d, *J*=248.3 Hz), 161.7 (d, *J*=247.6 Hz), 152.6, 147.4, 142.6, 140.0, 131.4 (d, *J*=10.1 Hz), 131.4 (d, *J*=10.0 Hz), 130.1 (d, *J*=3.2 Hz), 129.7 (d, *J*=3.4 Hz), 126.1, 125.1, 120.0, 118.2, 116.7, 115.2 (d, *J*=37.5 Hz), 115.0 (d, *J*=37.7 Hz), 60.6, 34.7, 21.1; **IR ($CHCl_3$):** 3421, 2920, 2853, 1773, 1600, 1502, 1222, 1158, 833, 770 cm^{-1}; **HRMS (+ESI) m/z: $[M+H]^+$ Calcd for $C_{38}H_{25}O_2F_4$** 589.1791; found 589.1788.

7,8,9-Triphenylcyclopenta[2,3]indeno[1,2-*c*]chromen-1(13b*H*)-one; **4aa**

Using the general experimental procedure on 4-bromocoumarin (0.112 g; 0.5 mmol, 1 equiv), diphenylacetylene (0.178 g; 1 mmol, 2 equiv), 1,2-bis(4-(trifluoromethyl)phenyl)ethyne (0.314 g; 1 mmol, 2 equiv), $Pd(OAc)_2$ (0.012 g; 0.05 mmol, 10 mol%), TFP (0.023 g; 0.1 mmol, 20 mol%), and KOAc (0.098 g; 1 mmol, 2 equiv) in 1,4-dioxane (3 mL), compound **4aa** was obtained as white solid (0.182 g, 73% yield) after purification by flash column chromatography using hexane/EtOAc (19:1) as an eluent; mp: 218-220 ^oC; **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.45 (d, *J*= 7.4 Hz, 1H), 7.37 (d, *J*= 7.7 Hz, 1H), 7.24-7.32 (m, 6H), 6.90-7.16 (m, 14H), 6.81 (dd, J_1= 1.2 Hz, J_2= 8.0 Hz, 1H), 4.60 (s, 1H); **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)**: δ 166.4, 154.4, 151.4, 148.8, 145.7, 145.6, 140.7, 135.1, 134.9, 134.4, 130.4, 129.9, 129.8, 128.8, 128.7, 128.6, 128.2, 128.0, 127.9, 127.8, 127.7, 127.4, 127.3, 125.6, 124.7, 124.4, 122.3, 119.2, 117.7, 71.6, 48.8; **IR ($CHCl_3$):** 3421, 2928, 2852, 1757, 1605, 1508, 1487, 1219, 836, 771 cm^{-1}; **HRMS (+ESI) m/z: $[M+H]^+$ Calcd for $C_{37}H_{25}O_2$** 501.1855; found 501.1854.

12-Methoxy-9-(4-methoxyphenyl)-7,8-diphenylcyclopenta[2,3]indeno[1,2-c]chromen-1(13b*H*)-one; (**4aac)** 7,8-bis(4-methoxyphenyl)-9-phenylcyclopenta[2,3]indeno[1,2-c]chromen-1(13b*H*)-one; (**4aca)**

Using the general experimental procedure on 4-bromocoumarin (0.112 g; 0.5 mmol, 1 equiv), diphenylacetylene (0.178 g; 1 mmol, 2 equiv), 1,2-bis(4-methoxyphenyl)ethyne (0.238 g; 1 mmol, 2 equiv), $Pd(OAc)_2$ (0.012 g; 0.05 mmol, 10 mol%), TFP (0.023 g; 0.1 mmol, 20 mol%), and KOAc (0.098 g; 1 mmol, 2 equiv) in 1,4-dioxane (3 mL), compounds **4aac** & **4aca** were obtained as light brown solid (0.196 g, 70% yield) after purification by flash column chromatography using hexane/EtOAc (4:1) as an eluent; mp: 126-128 ^oC; **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.47 (d, *J*= 7.4 Hz, 1H), 7.41 (d, *J*= 8.4 Hz, 1H), 7.25-7.36 (m, 8H), 7.21 (dd, J_1= 1.4 Hz, J_2= 7.8 Hz, 1H), 7.12-7.16 (m, 5H), 7.00-7.09 (m, 8H), 6.80-6.98 (m, 13H), 6.61-6.68 (m, 5H), 4.57 (s, 1H), 4.55 (s, 1H), 3.80 (s, 3H), 3.74 (s, 3H), 3.73 (s, 3H), 3.68 (s, 3H); **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)**: δ 166.6, 166.5, 159.9, 158.9, 158.5, 158.4, 153.8, 153.3, 151.4, 151.3, 147.8, 147.7, 147.3, 145.9, 145.3, 144.3, 140.9, 138.0, 135.3, 135.1, 134.7, 134.3, 131.2, 131.0, 130.0, 129.9, 129.8, 128.7, 128.6, 128.5, 128.2, 127.9, 127.8 x 2, 127.7, 127.1 x 2, 126.9, 126.6, 125.7, 125.6, 124.3, 123.0, 122.2, 119.8, 119.7, 117.6, 117.5, 115.1, 113.7, 113.4, 113.1, 109.6, 71.6, 71.5, 55.5, 55.1, 55.0, 54.9, 48.9, 48.8 (Several peaks are missing due to overlap); **IR ($CHCl_3$):** 3427, 2924, 2853, 1757, 1606, 1511, 1483, 1247, 1210, 1175, 1029, 837, 769 cm^{-1}; **HRMS (+ESI) m/z: $[M+H]^+$ Calcd for $C_{39}H_{29}O_4$** 561.2066; found 561.2068.

2',3',4',5'-Tetrakis(4-fluorophenyl)spiro[chromane-4,1'-cyclopentane]-2',4'-dien-2-one-3-*d*; **3af-(D)**

Using the general experimental procedure on 4-bromocoumarin (0.112 g; 0.5 mmol, 1 equiv), 1,2-bis(4-fluorophenyl)ethyne (0.214 g; 1 mmol, 2 equiv), $Pd(OAc)_2$ (0.012 g; 0.05 mmol, 10 mol%), TFP (0.023 g; 0.1 mmol, 20 mol%), and KOAc (0.098 g; 1 mmol, 2 equiv) in 1,4-dioxane (3 mL) and D_2O (10.0 μL, 0.5 mmol), compound **3af-(D)** was obtained as yellow solid (0.173 g, 60% yield) after purification by flash column chromatography using hexane/EtOAc (19:1) as an eluent; mp: 108-110 °C; **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.43 (dd, J_1= 1.5 Hz, J_2= 7.7 Hz, 1H), 7.29-7.32 (m, 1H), 7.20 (td, J_1= 1.2 Hz, J_2= 7.5 Hz, 1H), 6.88-6.92 (m, 5H), 6.74-6.83 (m, 12H), 2.95 (d, *J*=6.4 Hz, 1H); **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)**: δ 166.7, 162.1 (d, *J*=248.4 Hz), 161.9 (d, *J*=247.6 Hz), 152.7, 147.3 (m), 142.7 (t, *J*=6.5 Hz), 131.5 (d, *J*=11.9 Hz), 131.4 (d, *J*=11.9 Hz), 130.0 (d, *J*=4.7 Hz), 129.7, 129.6 (d, *J*=3.2 Hz), 125.4, 125.2, 120.0, 118.0, 115.3 (d, *J*=38.8 Hz), 115.1 (d, *J*=38.6 Hz), 60.7 (t, *J*=7.9 Hz), 34.6; **IR ($CHCl_3$):** 3407, 2922, 2853, 1767, 1604, 1507, 1218, 1159, 832, 771 cm^{-1}; **HRMS (+ESI) m/z: $[M+H]^+$ Calcd for $C_{37}H_{22}DO_2F_4$** 576.1697; found 576.1696.

ASSOCIATED CONTENT

Supporting Information

Copies of NMR (^{1}H and ^{13}C), HRMS spectra and X-ray data for compound **4aa** and **4ba** (CIF). This material is available free of charge *via* the internet at http://pubs.acs.org.

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(20) CCDC-2002414 (compound **4aa**) contains the supplementary crystallographic data for this paper. This data can be obtained free of charge from the Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/conts/retrieving.html.

(21) CCDC-2002417 (compound **4ba**) contains the supplementary crystallographic data for this paper. This data can be obtained free of charge from the Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/conts/retrieving.html.