



Carbonylative Annulation

Highly Selective and Modular Synthesis of 3-Aryl-4-(arylethynyl)-2*H*-chromen-2-ones from 2-lodoaryl 2-Arylacetates through a Carbonylative Sonogashira Coupling–Intramolecular Aldol Cascade Reaction

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Dedicated to Professor Dr. Henning Hopf on the occasion of his 75th birthday

Abstract: A modular method for the synthesis of 3-aryl-4-(arylethynyl)-2*H*-chromen-2-ones from 2-iodoaryl 2-arylacetates and arylacetylenes has been developed. The carbonylative Sonogashira coupling–intramolecular aldol casade reaction was carried out in the presence of $Pd(PPh_3)_2(Cl)_2$ as the catalyst. The onepot approach that involves the in situ formation of the 2-iodoaryl 2-arylacetates from the corresponding 2-iodophenols and 2-arylacetyl chlorides followed by the palladium-catalyzed carbonylative annulation in the presence of the arylacetylene has also been described for the formation of the 3-aryl-4-(aryl-ethynyl)-2*H*-chromen-2-ones.

Introduction

2H-Chromen-2-one (coumarin) and its derivatives are found in nature, especially in the plant kingdom.^[1] They are an important class of compounds as they display a wide range of biological activities^[2] and also have applications in materials chemistry as laser dyes, light-emitting diodes, and fluorescent probes.^[3] The conventional synthesis of 2H-chromen-2-one by using a Perkin^[4] or von Pechmann reaction^[5] involves the condensations of substituted phenols with various carbonyl compounds. Modern transition-metal-mediated catalytic methods involve carbonylative annulation reactions that use carbon monoxide as a one-carbon source. Cobalt(III)-catalyzed carbonylative annulations of 2-alkenylphenols to give coumarin derivatives have been reported,^[6] and this approach requires the synthesis of 2-alkenylphenols from the corresponding salicylaldehyde derivatives by a Wittig reaction. Palladium-catalyzed carbonylative annulations of internal alkynes and 2-iodophenols have been reported to give regioisomeric mixtures of 3,4-disubstituted coumarins from unsymmetrical internal alkynes.^[7] In a related work, two examples of the synthesis of 3,4disubstituted coumarins through a carbonylative annulation of 2-iodophenyl 3-alkenoate have been reported along with details of the formation of an aurone derivative as a byproduct.^[8] Herein, we report a general and modular synthetic method for the synthesis of 3-aryl-4-(arylethynyl)-2H-chromen-2-ones from

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Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejoc.201600569. 2-iodoaryl 2-arylacetate and arylacetylene in the presence of $Pd(PPh_3)_2(Cl)_2$ as the catalyst under carbon monoxide (1 atm). An earlier report^[9] of the synthesis of 4-arylethynyl-2*H*-chromen-2-ones used 4-hydroxycoumarin as the starting material. In that report, the tosylates of 4-hydroxycoumarins were generated in situ and subjected to palladium-catalyzed Sonogashira coupling reactions with terminal acetylenes.

Results and Discussion

The 2-iodoaryl 2-arylacetates 1a-g were synthesized according to a literature method by employing the reaction between the corresponding 2-iodophenol and 2-arylacetyl chloride derivatives.^[10] The carbonylative annulation reactions of **1a-g** with arylacetylenes 2a-e were then carried out in toluene at 80 °C, as there was no reaction at room temperature (Scheme 1). These reactions were performed in the presence of Pd(PPh₃)₂(Cl)₂ (1 mol-%) as the catalyst and a balloon filled with CO (1 atm), and the progress of the reactions was monitored by TLC analysis. Under these conditions, the reactions proceeded cleanly and selectively towards the formation of coumarin derivatives 3a-v and 3y (Scheme 1) in high yields, and the corresponding Sonogashira coupling products, namely the 2-(arylethynyl)phenyl 2-arylacetates, were not observed. The absence of the Sonogashira coupling product suggests that the carbonylation reaction that follows the oxidative addition of Pd⁰ across the C-I bond occurs much faster than the Sonogashira coupling reaction. Small amounts of 1,4-diarylbuta-1,3-diynes were obtained, presumably from the oxidative dimerization of the arylacetylenes.







Scheme 1. Synthesis of 3-aryl-4-(arylethynyl)-2H-chromen-2-ones from 2-iodoaryl 2-arylacetates.

The effect of the palladium source on the reaction between 1a and 2a was also examined by using Pd(OAc)₂. In this case, small amounts of the (noncarbonylative) Sonogashira coupling product were produced along with 3a in 72 % yield. The reaction of methoxy derivative **1b** was slower than that of the other substrates, and trace amounts of the starting material were recovered even after 24 h. The electron-donating nature of the methoxy substituent with the decreased acidity of the CH₂ protons provides an explanation for this change in the reaction rate. The synthesis is modular as the substituents of the three aromatic rings can be independently varied, which is illustrated by the examples shown in Scheme 1 and Table 1. In all of the cases, the products were purified by column chromatography on silica gel and characterized by spectroscopic data. The structures of **3h** and **3p** were unambiguously established by single crystal XRD data (Figure 1). Moreover, the reaction of 1a with

Table 1. Substrate scope for the synthesis of 3-aryl-4-(arylethynyl)-2*H*-chromen-2-ones **3a-v** and **3y** from 2-iodoaryl 2-arylacetates **1a-g**.

Entry	R ¹	R ²	R ³	Time [h]	% Yield 3
1	Н	Н	Н	4	91 (3a)
2	Н	4-OMe	Н	10	76 (3b)
3	Н	4-Br	Н	3	95 (3c)
4	Н	4-NO ₂	Н	6	70 (3d)
5	4-tBu	Н	Н	4	90 (3e)
6	4-tBu	4-Br	Н	3	92 (3f)
7	Н	Н	4-Me	4	90 (3g)
8	Н	4-OMe	4-Me	10	71 (3h)
9	Н	4-Br	4-Me	4	91 (3i)
10	4-tBu	Н	4-Me	5	89 (3j)
11	4-tBu	4-Br	4-Me	4	90 (3k)
12	Н	Н	2-Me	5	86 (3I)
13	Н	4-Br	2-Me	5	89 (3m)
14	Н	4-NO ₂	2-Me	6	74 (3n)
15	4-tBu	4-Br	2-Me	4	86 (30)
16	Н	Н	2,4,6-Me ₃	6	81 (3p)
17	4-tBu	Н	2,4,6-Me ₃	6	90 (3q)
18	Н	Н	4-OMe	8	79 (3r)
19	Н	4-Br	4-OMe	8	82 (3s)
20	Н	4-NO ₂	4-OMe	8	75 (3t)
21	4-tBu	Н	4-OMe	10	70 (3u)
22	4-tBu	4-Br	4-OMe	8	77 (3v)
23	4-Cl	Н	Н	5	87 (3y)

trimethylsilylacetylene (**2f**) proceeded smoothly to give **3w** in 78 % yield. Deprotection of the trimethylsilyl group of **3w** by using $(n-C_4H_9)_4NF$ gave the terminal acetylene derivative **3x** in 80 % yield (Scheme 2).



Figure 1. Ellipsoid representation (50 % probability) of the crystal structures of 3h (left) and 3p (right).



Scheme 2. Synthesis of 3w and then 3x from the reaction of 1a with trimethylsilylacetylene (TMS = trimethylsilyl).

The feasibility of a one-pot synthesis of **3** was then investigated by sequentially adding the reagents of the two steps. Initially, to a mixture of the 2-iodophenol and triethylamine (3 equiv.) in toluene was added 2-phenylacetyl chloride (1.1 equiv.). This mixture was stirred at room temperature for 30 min followed by the addition of phenylacetylene (1.1 equiv.) and Pd(PPh₃)₂(Cl)₂ (1 mol-%) and then finally CO. The one-pot strategy yielded (after chromatographic purification) 72 % of **3a** and 77 % of **3e** from the reactions of **2a** with iodophenol and 4-*tert*-butyl-2-iodophenol, respectively (Scheme 3).



Scheme 3. One-pot synthesis of **3a** and **3e** by the sequential addition of reagents.

From the results in Table 1, it is evident that this method is fairly general and modular in nature and allows for the independent variation of the substituents on the three aryl rings to synthesize a variety of coumarin derivatives (i.e., **3a–3y**) in good to excellent yields. Several functional groups such as the chloro, bromo, nitro, and methoxy substituents were tolerated under the reaction conditions. Compound **3x**, which contains a termi-





nal acetylene group, could serve as a starting material in a synthesis designed for further structural diversity.

The attempted synthesis of 4-(arylethynyl)-2*H*-chromen-2ones from 2-iodophenyl acetate (**4a**) and 4-*tert*-butyl-2-iodophenyl acetate (**4b**) under the conditions described in Scheme 1 gave only the carbonylative Sonogashira coupling products **5a** and **5b**, respectively, in nearly quantitative yields (Scheme 4). The anticipated carbonylative annulation products, namely the corresponding chromen-2-ones, were not observed in these reactions. The differences in the reactivities between **1a** and **4a** and those between **1b** and **4b** can be explained by higher acidities of the CH₂ protons of **1a** and **1b** compared with those of the CH₃ protons of **4a** and **4b** ($\Delta pK_a \approx 7.0$ units^[111]). The formation of the enolate and its intramolecular aldol reaction with the newly formed carbonyl group that results from the carbonylation reaction is facile in the cases of **1a** and **1b** compared with that of **4a** and **4b**.



Scheme 4. Attempted carbonylative annulation reaction of 2-iodoaryl acetates in toluene.

When **4a** and **4b** were treated with phenylacetylene in triethylamine as the solvent, a mixture of products **6–8** were formed (Scheme 5). This type of carbonylative annulation that yields 2-(aryl)-4*H*-chromen-4-one has been previously reported^[12] to result from the reaction of 2-(3-arylpropiolyl)phenyl acetate under basic conditions. Products **6–8** were separated by column chromatography and characterized by spectroscopic methods. Compounds **6a** and **7b** were characterized by single crystal XRD data. The stereochemistry of **8b** was assigned by comparing the ¹H and ¹³C NMR spectroscopic data of similar aurone derivatives reported in the literature.^[13]



Scheme 5. Carbonylative annulation reaction of 2-iodoaryl acetates in trimethylamine.

The attempted synthesis of a naphthalene analogue by treating **9** with phenylacetylene under the identical reaction conditions in Scheme 1 failed to furnish the expected naphthyl-fused 2H-chromen-2-one derivative. Instead, the reaction yielded the product of deiodination (i.e., 10) in almost guantitative yield (Scheme 6). A control experiment revealed that the deiodination of 9 also occurred in the absence of CO (under N₂). The reaction of 1-iodo-2-naphthyl acetate (11) under identical conditions gave only the corresponding Sonogashira coupling product 12, and neither the carbonylative Sonogashira coupling product nor the carbonylative annulation product was observed in this reaction (Scheme 6). In the case of 4a and 4b, the oxidative addition and carbonvlation reaction sequence occurred faster than the Sonogashira coupling of the alkyne, whereas in the case of **11**, the latter process was faster than the carbonylation reaction. The absence of the carbonylation reaction in the cases of 9 and 11 is attributed to steric hindrance at the 1-naphthyl position. The deiodination of 9 competes with the Sonogashira coupling as well as the carbonylation reaction and occurs by protonation of the C-Pd bond by either Et₃NH⁺ or an intramolecular proton transfer from the acidic CH₂ moiety of 9. Because of the lower acidity of 11 compared with 9, the protonation did not occur, and the Sonogashira coupling effectively proceeded to form 12 (Scheme 7). A similar deiodination reaction has been previously reported for



Scheme 6. Attempted synthesis of naphthyl-fused 2H-chromen-2-one.



Scheme 7. Plausible reaction mechanism for the formation of 10 and 12.





the Pd-catalyzed carbonylative annulation of 1-iodo-2-naphthol to yield 2-naphthol.^[7b]

Finally, the reaction of another sterically hindered iodide, namely 2-iodo-3,5-dimethylphenyl 2-phenylacetate (**13**), under the standard reaction conditions gave only 8 % of the Sonogashira coupled product **14** after 12 h, and neither the corresponding carbonylative Sonogashira coupled product nor the expected chromen-2-one derivative was obtained. Upon chromatographic separation, the starting material **13** was recovered in 77 % yield (Scheme 8).



Scheme 8. Attempted carbonylative Sonogashira coupling-aldol cascade reaction of sterically hindered iodide **13**.

Conclusions

We have developed a modular carbonylative annulation method for the synthesis of 3-aryl-4-(arylethynyl)-2*H*-chromen-2-ones from 2-iodoaryl 2-arylacetates and arylacetylenes under CO (1 atm) in toluene at 80 °C in the presence of 1 mol-% of readily available Pd(PPh₃)₂(Cl)₂ as the catalyst. By starting from readily available 2-iodophenols, the one-pot synthesis of the 2*H*-chromen-2-one derivatives has also been demonstrated by the sequential addition of reagents. This is a general method for use with phenyl derivatives as demonstrated by the synthesis of 24 different 3,4-disubstitued 2*H*-chromen-2-ones in good to excellent yields. Sterically hindered iodides **9** and **13**, however, did not yield the expected coumarin derivatives, which might be a limitation of the present method.

Experimental Section

General Methods: Infrared (IR) spectra were recorded on an FTIR spectrometer. The ¹H NMR spectroscopic data were recorded with 400 and 500 MHz spectrometers. Chemical shifts are reported in ppm, and tetramethylsilane was used as the internal standard. The ¹³C NMR spectroscopic data were recorded with 100 and 125 MHz spectrometers with complete proton decoupling. Chemical shifts are reported in ppm, and the residual solvent signals were used as the internal standard. High resolution mass spectrometry was performed with an ESI Q-TOF micromass spectrometer equipped with a Harvard apparatus syringe pump. X-ray crystallographic data were collected on a charge-coupled device (CCD) diffractometer with graphite-monochromator Mo- K_{α} radiation ($\lambda = 0.71073$ Å). CCDC 1478489 (for 3h), 1478490 (for 3p), 1478491 (for 7b), and 1478492 (for 6a) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre. Precoated TLC plates (silica gel 60 F254 grade, 0.25 mm) were used for thin-layer chromatography.

General Procedure for the Synthesis 2-Iodophenyl 2-Arylacetates: To a stirred solution of 2-iodophenol (1 equiv.) and triethylamine (2 equiv.) in CH₂Cl₂/tetrahydrofuran (THF; 1:1, 20 mL) was added acyl chloride (1.5 equiv.) at 0 °C under N₂. The reaction mixture was stirred at room temperature for 3–5 h and then quenched with water. The resulting mixture was extracted with CH₂Cl₂. The isolated organic layer was washed with brine and dried with Na₂SO₄, and the solvent was removed under vacuum. The crude product was purified by flash column chromatography (EtOAc/hexane, 1:19 v/v) on silica gel.

2-lodophenyl 2-Phenylacetate (1a): 2-lodophenol (1 g, 4.5 mmol), 2-phenylacetyl chloride (1.06 g, 6.9 mmol), and Et₃N (1.3 mL) afforded **1a** (1.5 g, 98 % yield) as a yellow oil, ¹H NMR (400 MHz, CDCl₃): δ = 7.81 (dd, *J* = 8, 1.6 Hz, 1 H), 7.45–7.32 (m, 6 H), 7.07 (dd, *J* = 8, 1.2 Hz, 1 H), 6.98–6.94 (m, 1 H), 3.94 (s, 2 H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 169.2, 151.3, 139.5, 133.1, 129.8, 129.5, 128.8, 127.7, 127.5, 123.0, 90.3, 41.5 ppm. IR: \tilde{v} = 1758 cm⁻¹. HRMS (ESI): calcd. for C₁₄H₁₁O₂IK [M + K]⁺ 376.9441; found 376.9422.

2-lodophenyl 2-(4-Methoxyphenyl)acetate (1b): 2-lodophenol (1 g, 4.5 mmol), 4-nitrophenylacetyl chloride (1.3 g, 6.9 mmol), and Et₃N (1.3 mL) afforded **1b** (1.5 g, 91 % yield) as a pale yellow oil. ¹H NMR (400 MHz, CDCl₃): $\delta = 7.80$ (dd, J = 8, 1.6 Hz, 1 H), 7.35–7.31 (m, 3 H), 7.05 (dd, J = 8, 1.2 Hz, 1 H), 6.97–6.93 (m, 1 H), 6.97–6.88 (m, 2 H), 3.87 (s, 2 H), 3.81 (s, 3 H) ppm. ¹³C NMR (100 MHz, CDCl₃): $\delta = 169.6$, 159.0, 151.2, 139.5, 130.8, 129.5, 127.7, 125.1, 123.0, 114.1, 90.5, 55.4, 40.6 ppm. IR (KBr): $\tilde{v} = 1759$ cm⁻¹. HRMS (ESI): calcd. for C₁₅H₁₃O₃INa [M + Na]⁺ 390.9807; found 390.9813.

2-Iodophenyl 2-(4-Bromophenyl)acetate (1c): 2-Iodophenol (1 g, 4.5 mmol), 4-bromophenylacetyl chloride (1.6 g, 6.9 mmol), and Et₃N (1.3 mL) afforded **1c** (1.8 g, 94 % yield) as a pale yellow solid; m.p. 66 °C. ¹H NMR (400 MHz, CDCl₃): δ = 7.81 (dd, *J* = 8, 1.6 Hz, 1 H), 7.52–7.48 (m, 2 H), 7.36–7.29 (m, 3 H), 7.06 (dd, *J* = 8.4, 1.6 Hz, 1 H), 6.99–6.95 (m, 1 H), 3.89 (s, 2 H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 168.7, 151.1, 139.5, 132.0, 131.9, 131.5, 129.5, 127.9, 122.9, 121.6, 90.3, 40.9 ppm. IR (KBr): \tilde{v} = 1766 cm⁻¹. HRMS (ESI): calcd. for C₁₄H₁₀O₂BrINa [M + Na]⁺ 438.8807; found 438.8805.

2-lodophenyl 2-(4-Nitrophenyl)acetate (1d): 2-lodophenol (1 g, 4.5 mmol), 4-nitrophenylacetyl chloride (1.37 g, 6.9 mmol), and Et₃N (1.3 mL) afforded **1d** (1.6 g, 90 % yield) as a white solid; m.p. 68 °C. ¹H NMR (400 MHz, CDCl₃): δ = 8.23 and 7.60 (AA'BB' pattern, *J* = 8.8 Hz, 2 H), 7.81 (dd, *J* = 8, 1.6 Hz, 1 H), 7.62–7.59 (m, 2 H), 7.38–7.33 (m, 1 H), 7.08 (dd, *J* = 8, 1.2 Hz, 1 H), 7.01–6.96 (m, 1 H), 4.05 (s, 2 H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 167.9, 150.9, 147.5, 140.3, 139.6, 130.8, 129.6, 128.0, 123.9, 122.9, 90.2, 41.1 ppm. IR (KBr): \tilde{v} = 1760 cm⁻¹. HRMS (ESI): calcd. for C₁₄H₁₀NO₄INa [M + Na]⁺ 405.9552; found 405.9570.

4-tert-Butyl-2-iodophenyl 2-Phenylacetate (1e): 4-tert-Butyl-2-iodophenol (1 g, 3.6 mmol), phenylacetyl chloride (0.84 g, 5.4 mmol), and Et₃N (1 mL) afforded **1e** (1.3 g, 95 % yield) as a white solid; m.p. 57 °C. ¹H NMR (500 MHz, CDCl₃): δ = 7.78 (d, *J* = 2 Hz, 1 H), 7.44–7.33 (m, 6 H), 6.97 (d, *J* = 8.5 Hz, 1 H), 3.93 (s, 2 H), 1.29 (s, 9 H) ppm. ¹³C NMR (125 MHz, CDCl₃): δ = 169.4, 151.0, 148.9, 136.5, 133.2, 129.8, 128.7, 127.5, 126.6, 122.2, 90.0, 41.5, 34.5, 31.3 ppm. IR (KBr): \tilde{v} = 1765 cm⁻¹. HRMS (ESI): calcd. for C₁₈H₁₉O₂INa [M + Na]⁺ 417.0328; found 417.0320.

4-tert-Butyl-2-iodophenyl 2-(4-Bromophenyl)acetate (1f): 4-tert-Butyl-2-iodophenol (1 g, 3.6 mmol), 4-bromophenylacetyl chloride (1.27 g, 5.4 mmol), and Et₃N (1 mL) afforded **1f** (1.6 g, 95 % yield) as a white solid; m.p. 81 °C. ¹H NMR (400 MHz, CDCl₃): δ = 7.77 (d, J = 2 Hz, 1 H), 7.512–7.47 (m, 2 H), 7.35–7.28 (m, 3 H), 6.96 (d, J = 8.8 Hz, 1 H), 3.87 (S, 2 H), 1.29 (S, 9 H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 168.9, 151.2, 148.7, 136.5, 132.1, 131.9, 131.5, 126.7, 122.1, 121.6, 90.0, 40.9, 34.6, 31.3 ppm. IR (KBr): \tilde{v} = 1765 cm⁻¹.





HRMS (ESI): calcd. for $C_{18}H_{18}O_2BrINa$ [M + Na]⁺ 494.9433; found 494.9412.

4-Chloro-2-iodophenyl 2-Phenylacetate (1g): 4-Chloro-2-iodophenol (0.5 g, 1.96 mmol), phenylacetyl chloride (0.45 g, 2.9 mmol), and Et₃N (0.6 mL) afforded **1g** (0.73 g, 90 % yield) as a colorless oil. ¹H NMR (400 MHz, CDCl₃): δ = 7.78 (d, *J* = 2.4 Hz, 1 H), 7.43–7.35 (m, 4 H), 7.33–7.29 (m, 2 H), 6.98 (d, *J* = 8.8 Hz, 1 H), 3.91 (s, 2 H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 169.1, 150.0, 138.7, 132.8, 132.2, 129.7, 129.5, 128.8, 127.6, 123.6, 90.7, 41.5 ppm. IR: \tilde{v} = 1765 cm⁻¹. HRMS (ESI): calcd. for C₁₄H₁₁O₂ClI [M + H]⁺ 372.9492; found 372.9512.

1-Iodo-2-naphthyl 2-Phenylacetate (9): 1-Iodo-2-naphthol (1 g, 3.7 mmol), phenylacetyl chloride (0.86 g, 5.5 mmol), and Et₃N (1 mL) afforded **9** (1.3 g, 89 % yield) as a pale yellow solid; m.p. 80 °C. ¹H NMR (500 MHz, CDCl₃): δ = 8.15 (d, *J* = 8.5 Hz, 1 H), 7.82–7.78 (m, 2 H), 7.60–7.57 (m, 1 H), 7.52–7.47 (m, 3 H), 7.41–7.38 (m, 2 H), 7.35–7.32 (m, 2 H), 4.02 (s, 2 H) ppm. ¹³C NMR (125 MHz, CDCl₃): δ = 169.5, 150.1, 135.3, 133.1, 132.2, 132.1, 130.2, 129.8, 128.8, 128.4, 128.3, 127.6, 126.5, 121.4, 94.5, 41.7 ppm. IR (KBr): \tilde{v} = 1763 cm⁻¹. HRMS (ESI): calcd. for C₁₈H₁₃O₂INa [M + Na]⁺ 410.9858; found 410.9883.

1-Iodo-2-naphthyl Acetate (11):^[14] 1-Iodonaphthalene-2-ol (1 g, 3.7 mmol) was employed to give **11** (1.1 g, 95 % yield) as a yellow oil. ¹H NMR (400 MHz, CDCl₃): δ = 8.17 (dd, *J* = 8.4, 0.4 Hz, 1 H), 7.84 (d, *J* = 8.8 Hz, 1 H), 7.80 (td, *J* = 8, 0.8 Hz, 1 H), 7.61–7.57 (m, 1 H), 7.53–7.49 (m, 1 H), 7.23 (d, *J* = 8.8 Hz, 1 H), 2.45 (s, 3 H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 169.0, 150.1, 135.3, 132.2, 132.1, 130.2, 128.4, 128.3, 126.5, 121.5, 94.6, 21.5 ppm. IR (KBr): \tilde{v} = 1766 cm⁻¹.

2-lodo-3,5-dimethylphenyl 2-Phenylacetate (13): 2-lodo-3,5-dimethylphenol (0.5 g, 2.0 mmol), phenylacetyl chloride (0.46 g, 3.0 mmol), and Et₃N (0.6 mL) afforded **13** (0.68 g, 93 % yield) as a colorless oil. ¹H NMR (400 MHz, CDCl₃): δ = 7.44–7.42 (m, 2 H), 7.39–7.35 (m, 2 H), 7.33–7.31 (m, 1 H), 6.94 (d, *J* = 0.8 Hz, 1 H), 6.68 (s, 1 H), 3.93 (s, 2 H), 2.43 (s, 3 H), 2.26 (s, 3 H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 169.5, 151.2, 143.3, 139.1, 133.3, 129.8, 128.7, 128.4, 127.4, 120.7, 93.2, 41.6, 28.4, 20.86 ppm. IR: \tilde{v} = 1762 cm⁻¹. HRMS (ESI): calcd. for C₁₆H₁₆O₂I [M + H]⁺ 367.0195; found 367.0178.

3,5-Dimethyl-2-(phenylethynyl)phenyl 2-Phenylacetate (14): 2-lodo-3,5-dimethylphenyl 2-phenylacetate (**13**, 110 mg, 0.3 mmol), phenylacetylene (36 μ L, 0.33 mmol), PdCl₂(PPh₃)₂ (2 mg, 0.01 mmol), and Et₃N (0.13 mL, 0.9 mmol) afforded **14** as a pale yellow oil. ¹H NMR (400 MHz, CDCl₃): δ = 7.40–7.36 (m, 4 H), 7.32–7.31 (m, 3 H), 7.26–7.24 (m, 3 H), 6.93 (d, *J* = 0.4 Hz, 1 H), 6.74 (s, 1 H), 3.91 (s, 2 H), 2.46 (s, 3 H), 2.30 (S, 3 H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 169.7, 151.5, 141.9, 139.4, 133.4, 132.6, 131.6, 129.5, 128.7, 128.4, 128.1, 127.3, 123.4, 120.1, 114.3, 97.5, 83.4, 41.3, 29.8, 20.8 ppm. IR: \tilde{v} = 2195, 1762 cm⁻¹. HRMS (ESI): calcd. for C₂₄H₂₀O₂Na [M + Na]⁺ 363.1362; found 363.1365.

2-lodophenyl Acetate (4a):^[15] 2-lodophenol (1 g, 4.5 mmol) was employed to afford **4a** (1.15 g, 96 % yield) as a colorless oil. ¹H NMR (400 MHz, CDCl₃): δ = 7.82 (d, *J* = 8 Hz, 1 H), 7.36 (t, *J* = 7.2 Hz, 1 H), 7.10 (d, *J* = 8 Hz, 1 H), 6.97 (t, *J* = 7.6 Hz, 1 H), 2.36 (s, 3 H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 168.7, 151.3, 139.5, 129.5, 127.7, 123.1, 90.6, 21.3 ppm.

4-tert-Butyl-2-iodophenyl Acetate (4b):⁽¹⁶⁾ 4-tert-Butyl-2-iodophenol (1 g, 3.6 mmol) was employed to afford **4b** (1.062 g, 92 % yield) as a colorless oil. ¹H NMR (400 MHz, CDCl₃): δ = 7.79 (d, *J* = 2.4 Hz, 1 H), 7.36 (dd, *J* = 8.4, 2.4 Hz, 1 H), 7.00 (d, *J* = 8.4 Hz, 1 H), 2.35 (s, 3 H), 1.30 (s, 9 H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 168.9, 151.0, 148.9, 136.5, 126.7, 122.3, 90.3, 34.5, 31.4, 21.3 ppm.

General Procedure for Carbonylative Annulation Reactions in Toluene: To an oven-dried Schlenk tube under N₂ were added $PdCl_2(PPh_3)_2$ (0.01 equiv.) and toluene (5 mL) followed by 2-iodophenyl 2-phenylacetate (1 equiv.). Then, phenylacetylene (1.1 equiv.) was added along with triethylamine (3 equiv.). The reaction mixture was flushed with CO from a balloon and stirred at 80 °C under CO (1 atm, balloon). After stirring for the period of time reported in Table 1, the reaction mixture was cooled to room temperature and then passed through a pad of Celite. The filter cake was washed with dichloromethane, and the combined filtrates were concentrated under vacuum. The crude product was purified by column chromatography (hexane/EtOAc, of varying ratios) on silica gel to afford the pure product.

3-Phenyl-4-(phenylethynyl)-2H-chromen-2-one (3a): 2-lodophenyl 2-phenylacetate **(1a,** 101 mg, 0.3 mmol), phenylacetylene **(2a,** 36 μL, 0.33 mmol), PdCl₂(PPh₃)₂ (2 mg, 0.01 mmol), and Et₃N (0.13 mL, 0.9 mmol) were stirred for 4 h to give **3a** (87 mg, 91 % yield) as a white solid; m.p. 161 °C. ¹H NMR (400 MHz, CDCl₃): δ = 8.07 (dd, *J* = 8.4, 2 Hz, 1 H), 7.70–7.67 (m, 2 H), 7.60–7.55 (m, 1 H), 7.51–7.45 (m, 3 H), 7.40–7.32 (m, 7 H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 160.6, 152.9, 134.0, 133.1, 132.2, 131.8, 130.5, 130.4, 130.1, 129.0, 128.7, 127.9, 127.2, 124.6, 121.6, 119.1, 116.8, 104.8, 83.7 ppm. IR (KBr): \tilde{v} = 2207, 1711, 1596 cm⁻¹. HRMS (ESI): calcd. for C₂₃H₁₄O₂Na [M + Na]⁺ 345.0891; found 345.0920.

3-(4-Methoxyphenyl)-4-(phenylethynyl)-2H-chromen-2-one (3b): 2-lodophenyl 2-(4-methoxyphenyl)acetate (**1b**, 110 mg, 0.3 mmol), phenylacetylene (**2a**, 36 μL, 0.33 mmol), PdCl₂(PPh₃)₂ (2 mg, 0.01 mmol), and Et₃N (0.13 mL, 0.9 mmol) were stirred for 10 h to afford **3b** (80 mg, 76 % yield) as a yellow solid; m.p. 186 °C. ¹H NMR (400 MHz, CDCl₃): δ = 8.06 (dd, *J* = 8, 1.6 Hz, 1 H), 7.68 and 7.02 (AA'BB' pattern, *J* = 8.8 Hz, 4 H), 7.58–7.53 (m, 1 H), 7.45–7.34 (m, 7 H), 3.88 (s, 3 H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 160.2, 152.7, 132.2, 132.0, 131.5, 130.0, 129.9, 128.77, 128.74, 127.1, 126.3, 124.5, 121.7, 119.3, 116.7, 113.4, 104.4, 84.0, 76.9 (merged with CDCl₃ signals), 55.5 ppm. IR (KBr): \tilde{v} = 2205, 1719, 1606 cm⁻¹. HRMS (ESI): calcd. for C₂₄H₁₆O₃Na [M + Na]⁺ 375.0997; found 375.0981.

3-(4-Bromophenyl)-4-(phenylethynyl)-2*H***-chromen-2-one (3c):** 2-lodophenyl 2-(4-bromophenyl)acetate (1c, 125 mg, 0.3 mmol), phenylacetylene (2a, 36 μL, 0.33 mmol), PdCl₂(PPh₃)₂ (2 mg, 0.01 mmol), and Et₃N (0.13 mL, 0.9 mmol) were stirred for 3 h to afford 3c (114 mg, 95 % yield) as a pale yellow solid; m.p. 178 °C. ¹H NMR (500 MHz, CDCl₃): δ = 8.06 (dd, *J* = 8, 1.5 Hz, 1 H), 7.63– 7.57 (m, 5 H), 7.43–7.37 (m, 7 H) ppm. ¹³C NMR (125 MHz, CDCl₃): δ = 160.3, 152.9, 133.2, 132.9, 132.27, 132.25, 132.1, 131.2, 130.3, 129.0, 128.8, 127.3, 124.7, 123.3, 121.4, 119.0, 116.9, 105.4, 83.4 ppm. IR (KBr): \tilde{v} = 2201, 1714, 1592 cm⁻¹. HRMS (ESI): calcd. for C₂₃H₁₃O₂BrNa [M + Na]⁺ 422.9997; found 423.0016.

3-(4-Nitrophenyl)-4-(phenylethynyl)-2*H***-chromen-2-one (3d): 2lodophenyl 2-(4-nitrophenyl)acetate (1d, 115 mg, 0.3 mmol), phenylacetylene (2a, 36 µL, 0.33 mmol), PdCl₂(PPh₃)₂ (2 mg, 0.01 mmol), and Et₃N (0.13 mL, 0.9 mmol) were stirred for 6 h to afford 3d** (77 mg, 70 % yield) as a pale yellow solid; m.p. 241 °C. ¹H NMR (400 MHz, CDCl₃): δ = 8.35 and 7.89 (AA'BB' pattern, *J* = 9.2, 8.8 Hz, 4 H), 8.08 (dd, *J* = 8.4, 1.6 Hz, 1 H), 7.66–7.62 (m, 1 H), 7.46–7.38 (m, 7 H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 159.9, 153.1, 147.9, 140.8, 134.5, 132.8, 132.2, 131.8, 130.7, 128.9, 127.6, 125.0, 123.1, 120.9, 118.8, 117.0, 106.4, 82.9, 77.3 ppm. IR (KBr): \tilde{v} = 2199, 1709, 1595 cm⁻¹. HRMS (ESI): calcd. for C₂₃H₁₃NO₄Na [M + Na]⁺ 390.0742; found 390.0770.

6-tert-Butyl-3-phenyl-4-(phenylethynyl)-2H-chromen-2-one (3e): 4-tert-Butyl-2-iodophenyl 2-phenylacetate (1e, 118 mg,





0.3 mmol), phenylacetylene (**2a**, 36 μL, 0.33 mmol), PdCl₂(PPh₃)₂ (2 mg, 0.01 mmol), and Et₃N (0.13 mL, 0.9 mmol) were stirred for 4 h to afford **3e** (102 mg, 90 % yield) as a white solid; m.p. 167 °C. ¹H NMR (500 MHz, CDCl₃): δ = 8.08 (d, *J* = 2.5 Hz, 1 H), 7.69–7.67 (m, 2 H), 7.62 (dd, *J* = 8.5, 2 Hz, 1 H), 7.51–7.45 (m, 3 H), 7.41–7.32 (m, 6 H), 1.42 (s, 9 H) ppm. ¹³C NMR (125 MHz, CDCl₃): δ = 160.9, 151.0, 147.6, 134.2, 133.4, 132.2, 130.5, 130.1, 130.0, 129.6, 128.9, 128.7, 127.9, 123.4, 121.7, 118.4, 116.4, 104.8, 83.9, 34.8, 31.5 ppm. IR (KBr): \tilde{v} = 2201, 1713, 1594 cm⁻¹. HRMS (ESI): calcd. for C₂₇H₂₂O₂Na [M + Na]⁺ 401.1517; found 401.1531.

3-(4-Bromophenyl)-6-*tert*-**butyl-4-(phenylethynyl)**-2*H*-**chromen-2-one (3f):** 4-*tert*-Butyl-2-iodophenyl 2-(4-bromophenyl)acetate (1f, 142 mg, 0.3 mmol), phenylacetylene (**2a**, 36 µL, 0.33 mmol), PdCl₂(PPh₃)₂ (2 mg, 0.01 mmol), and Et₃N (0.13 mL, 0.9 mmol) were stirred for 3 h to afford **3f** (102 mg, 92 % yield) as a white solid; m.p. 193 °C. ¹H NMR (400 MHz, CDCl₃): δ = 8.08 (d, *J* = 2.4 Hz, 1 H), 7.65–7.56 (m, 5 H), 7.46–7.38 (m, 5 H), 7.32 (d, *J* = 8.4 Hz, 1 H), 1.42 (s, 9 H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 160.6, 150.9, 147.8, 133.6, 133.1, 132.29, 132.22, 131.1, 130.3, 129.8, 128.9, 128.6, 123.4, 123.2, 121.5, 118.3, 116.4, 105.4, 83.6, 34.8, 31.5 ppm. IR (KBr): \tilde{v} = 2209, 1703, 1596 cm⁻¹. HRMS (ESI): calcd. for C₂₇H₂₁O₂BrNa [M + Na]⁺ 479.0623; found 479.0651.

3-Phenyl-4-(*p*-tolylethynyl)-2*H*-chromen-2-one (3g): 2-lodophenyl 2-phenylacetate (**1a**, 101 mg, 0.3 mmol), 4-ethynyltoluene (**2b**, 42 μL, 0.33 mmol), PdCl₂(PPh₃)₂ (2 mg, 0.01 mmol), and Et₃N (0.13 mL, 0.9 mmol) were stirred for 4 h to afford **3g** (91 mg, 90 % yield) as a white solid; m.p. 165 °C. ¹H NMR (400 MHz, CDCl₃): δ = 8.06 (dd, *J* = 8, 1.6 Hz, 1 H), 7.69–7.66 (m, 2 H), 7.59–7.54 (m, 1 H), 7.50–7.41 (m, 3 H), 7.39–7.35 (m, 2 H), 7.27–7.25 (m, 2 H), 7.16–7.14 (m, 2 H), 1.36 (s, 3 H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 160.7, 152.9, 140.7, 134.1, 133.3, 132.1, 131.8, 130.5, 129.5, 128.9, 127.9, 127.3, 124.5, 119.2, 118.5, 116.7, 105.4, 83.4, 77.3, 21.8 ppm. IR (KBr): \tilde{v} = 2201, 1722, 1593 cm⁻¹. HRMS (ESI): calcd. for C₂₄H₁₆O₂Na [M + Na]⁺ 359.1048; found 359.1021.

3-(4-Methoxyphenyl)-4-(*p***-tolylethynyl)-2***H***-chromen-2-one (3h):** 2-lodophenyl 2-(4-methoxyphenyl)acetate **(1b**, 110 mg, 0.3 mmol), 4-ethynyltoluene **(2b**, 42 µL, 0.33 mmol), PdCl₂(PPh₃)₂ (2 mg, 0.01 mmol), and Et₃N (0.13 mL, 0.9 mmol) were stirred for 10 h to afford **3h** (78 mg, 71 % yield) as a white solid; m.p. 186 °C. ¹H NMR (400 MHz, CDCl₃): δ = 8.05 (d, *J* = 7.2 Hz, 1 H), 7.68–8.08 (d, *J* = 8.8 Hz, 2 H), 7.55–8.08 (t, *J* = 6.8 Hz, 1 H), 7.38–7.32 (m, 4 H), 7.17 (d, *J* = 7.6 Hz, 2 H), 7.01 (d, *J* = 8.4 Hz, 2 H), 3.88 (s, 3 H), 2.38 (s, 3 H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 160.1, 152.7, 140.6, 132.3, 132.1, 132.0, 131.5, 129.5, 127.2, 126.3, 124.5, 119.3, 118.6, 116.7, 113.3, 105.0, 83.6, 77.3, 55.5, 21.8 ppm. IR (KBr): \tilde{v} = 2201, 1720, 1593 cm⁻¹. HRMS (ESI): calcd. for C₂₅H₁₈O₃Na [M + Na]⁺ 389.1154; found 389.1171.

3-(4-Bromophenyl)-4-(*p***-tolylethynyl)-2***H***-chromen-2-one (3i): 2lodophenyl 2-(4-bromophenyl)acetate (1c, 125 mg, 0.3 mmol), 4ethynyltoluene (2b**, 42 µL, 0.33 mmol), PdCl₂(PPh₃)₂ (2 mg, 0.01 mmol), and Et₃N (0.13 mL, 0.9 mmol) were stirred for 4 h to afford **3i** (113 mg, 91 % yield) as a white solid; m.p. 201 °C. ¹H NMR (400 MHz, CDCl₃): δ = 8.06 (dd, *J* = 8.4, 1.6 Hz, 1 H), 7.63–7.56 (m, 5 H), 7.40–7.36 (m, 2 H), 7.30 (d, *J* = 8 Hz, 2 H), 7.19 (d, *J* = 8 Hz, 2 H), 2.39 (s, 3 H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 160.4, 152.9, 141.0, 133.5, 133.0, 132.2, 132.1, 132.19, 131.10, 129.6, 128.5, 127.4, 124.7, 123.2, 119.0, 118.3, 116.8, 106.0, 83.1, 21.8 ppm. IR (KBr): \tilde{v} = 2205, 1721, 1593 cm⁻¹. HRMS (ESI): calcd. for C₂₄H₁₅O₂BrNa [M + Na]⁺ 437.0153; found 437.0136.

6-tert-Butyl-3-phenyl-4-(p-tolylethynyl)-2H-chromen-2-one (3): 4-tert-Butyl-2-iodophenyl 2-phenylacetate (1e, 118 mg, 0.3 mmol), 4-ethynyltoluene (**2b**, 42 μL, 0.33 mmol), PdCl₂(PPh₃)₂ (2 mg, 0.01 mmol), and Et₃N (0.13 mL, 0.9 mmol) were stirred for 5 h to afford **3j** (105 mg, 89 % yield) as a white solid; m.p. 186 °C. ¹H NMR (400 MHz, CDCl₃): δ = 8.07 (d, *J* = 2.4 Hz, 1 H), 7.69–7.66 (m, 2 H), 7.61 (dd, *J* = 8.8, 2.4 Hz, 1 H), 7.50–7.43 (m, 3 H), 7.31 (d, *J* = 8.8 Hz, 1 H), 7.27–7.25 (m, 2 H), 7.16 (dd, *J* = 8.4, 0.4 Hz, 2 H), 2.37 (s, 3 H), 1.42 (s, 9 H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 161.0, 150.9, 147.5, 140.7, 134.2, 133.6, 132.1, 130.58, 130.50, 130.4, 129.5, 128.8, 127.9, 123.4, 118.6, 118.4, 116.3, 105.4, 83.5, 34.8, 31.5, 21.8 ppm. IR (KBr): \tilde{v} = 2203, 1714, 1595 cm⁻¹. HRMS (ESI): calcd. for C₂₈H₂₅O₂ [M + H]⁺ 393.1855; found 393.1861.

3-(4-Bromophenyl)-6-*tert*-**butyl-4-**(*p*-**tolylethynyl**)-*2H*-**chromen-2-one (3k):** 4-*tert*-Butyl-2-iodophenyl 2-(4-bromophenyl)acetate (1f, 142 mg, 0.3 mmol), 4-ethynyltoluene (**2b**, 42 μL, 0.33 mmol), PdCl₂(PPh₃)₂ (2 mg, 0.01 mmol), and Et₃N (0.13 mL, 0.9 mmol) were stirred for 4 h to afford **3k** (127 mg, 90 % yield) as a white solid; m.p. 218 °C. ¹H NMR (400 MHz, CDCl₃): δ = 8.06 (d, *J* = 2 Hz, 1 H), 7.64–7.56 (m, 5 H), 7.33–7.29 (m, 3 H), 7.20 (d, *J* = 7.6 Hz, 2 H), 2.39 (s, 3 H), 1.42 (s, 9 H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 160.7, 150.9, 147.7, 141.0, 133.8, 133.1, 132.3, 132.1, 131.1, 129.8, 129.6, 128.1, 123.5, 123.1, 118.4, 116.4, 106.0, 83.2, 34.8, 31.5, 21.8 ppm. IR (KBr): \tilde{v} = 2202, 1707, 1593 cm⁻¹. HRMS (ESI): calcd. for C₂₈H₂₃O₂BrK [M + K]⁺ 509.0518; found 509.0547.

3-Phenyl-4-(o-tolylethynyl)-2H-chromen-2-one (3I): 2-lodophenyl 2-phenylacetate (**1a**, 101 mg, 0.3 mmol), 2-ethynyltoluene (**2c**, 42 µL, 0.33 mmol), PdCl₂(PPh₃)₂ (2 mg, 0.01 mmol), and Et₃N (0.13 mL, 0.9 mmol) were stirred for 5 h to afford **3I** (86 mg, 86 % yield) as a white solid; m.p. 176 °C. ¹H NMR (400 MHz, CDCl₃): δ = 8.08 (dd, *J* = 8.4, 1.6 Hz, 1 H), 7.64–7.56 (m, 3 H), 7.49–7.36 (m, 6 H), 7.31–7.27 (m, 1 H), 7.20–7.15 (m, 2 H), 2.22 (s, 3 H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 160.7, 152.9, 141.2, 134.3, 133.5, 132.9, 131.8, 130.3, 130.2, 129.8, 128.9, 128.2, 127.2, 125.9, 124.6, 121.4, 119.2, 116.8, 104.1, 87.2, 76.8 (merged with CDCl₃ signals), 20.6 ppm. IR (KBr): \tilde{v} = 2197, 1720, 1592 cm⁻¹. HRMS (ESI): calcd. for C₂₄H₁₇O₂ [M + H]⁺ 337.1229; found 337.1222.

3-(4-Bromophenyl)-4-(*o***-tolylethynyl)-2***H***-chromen-2-one (3**m): 2-lodophenyl 2-(4-bromophenyl)acetate (**1c**, 125 mg, 0.3 mmol), 2ethynyltoluene (**2c**, 42 μL, 0.33 mmol), PdCl₂(PPh₃)₂ (2 mg, 0.01 mmol), and Et₃N (0.13 mL, 0.9 mmol) were stirred for 5 h to afford **3m** (111 mg, 89 % yield) as a white solid; m.p. 216 °C. ¹H NMR (400 MHz, CDCl₃): δ = 8.07 (dd, *J* = 8.4, 1.6 Hz, 1 H), 7.61–7.52 (m, 5 H), 7.41–7.37 (m, 3 H), 7.32 (t, *J* = 7.6 Hz, 1 H), 7.23–7.18 (m, 2 H), 2.26 (s, 3 H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 160.4, 153.0, 141.2, 133.7, 133.2, 132.9, 132.1, 131.4, 130.4, 130.0, 128.9, 127.3, 126.0, 124.7, 123.2, 121.2, 119.1, 116.9, 104.7, 86.9, 77.3, 20.6 ppm. IR (KBr): \tilde{v} = 2195, 1719, 1593 cm⁻¹. HRMS (ESI): calcd. for C₂₄H₁₆O₂Br [M + H]⁺ 415.0334; found 415.0338.

3-(4-Nitrophenyl)-4-(*o***-tolylethynyl)-2***H***-chromen-2-one (3n): 2lodophenyl 2-(4-nitrophenyl)acetate (1d, 115 mg, 0.3 mmol), 2-ethynyltoluene (2c, 42 µL, 0.33 mmol), PdCl₂(PPh₃)₂ (2 mg, 0.01 mmol), and Et₃N (0.13 mL, 0.9 mmol) were stirred for 6 h to afford 3n** (85 mg, 74 % yield) as a white solid; m.p. 253 °C. ¹H NMR (400 MHz, CDCl₃): δ = 8.34 and 7.85 (AA'BB' pattern, *J* = 9.2, 9.2 Hz, 4 H), 8.10 (dd, *J* = 8, 1.6 Hz, 1 H), 7.66–7.62 (m, 1 H), 7.44–7.41 (m, 2 H), 7.36– 7.31 (m, 2 H), 7.23–7.18 (m, 2 H), 2.26 (s, 3 H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 160.0, 153.1, 147.9, 141.1, 141.0, 134.8, 132.9, 132.7, 131.7, 130.8, 130.1, 127.6, 127.5, 126.2, 125.0, 123.3, 120.8, 118.8, 117.1, 105.7, 86.4, 20.7 ppm. IR (KBr): \tilde{v} = 2192, 1714, 1595 cm⁻¹. HRMS (ESI): calcd. for C₂₄H₁₅O₄NK [M + K]⁺ 420.0638; found 420.0638.

3-(4-Bromophenyl)-6-tert-butyl-4-(o-tolylethynyl)-2H-chromen-2-one (30): 4-tert-Butyl-2-iodophenyl 2-(4-bromophenyl)acetate (1f,





142 mg, 0.3 mmol), 2-ethynyltoluene (**2c**, 42 μL, 0.33 mmol), PdCl₂(PPh₃)₂ (2 mg, 0.01 mmol), and Et₃N (0.13 mL, 0.9 mmol) were stirred for 4 h to afford **3o** (121 mg, 86 % yield) as a white solid; m.p. 203 °C. ¹H NMR (400 MHz, CDCl₃): δ = 8.09 (d, *J* = 2 Hz, 1 H), 7.65–7.59 (m, 3 H), 7.54–7.51 (m, 2 H), 7.34–7.30 (m, 3 H), 7.25–7.19 (m, 2 H), 2.34 (s, 3 H), 1.41 (s, 9 H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 160.6, 151.0, 147.8, 141.1, 134.1, 133.4, 132.9, 132.1, 131.3, 130.4, 129.9, 129.8, 128.6, 126.1, 123.5, 123.1, 121.4, 118.3, 116.5, 104.6, 87.2, 34.9, 31.5, 20.7 ppm. IR (KBr): \tilde{v} = 2200, 1709, 1594 cm⁻¹. HRMS (ESI): calcd. for C₂₈H₂₃O₂BrK [M + K]⁺ 509.0518; found 509.0501.

4-(Mesitylethynyl)-3-phenyl-2H-chromen-2-one (3p): 2-lodophenyl 2-phenylacetate (**1a**, 101 mg, 0.3 mmol), mesitylacetylene (**2d**, 52 μL, 0.33 mmol), PdCl₂(PPh₃)₂ (2 mg, 0.01 mmol), and Et₃N (0.13 mL, 0.9 mmol) were stirred for 6 h to afford **3p** (88 mg, 81 % yield) as a white solid; m.p. 193 °C. ¹H NMR (400 MHz, CDCl₃): δ = 8.12 (dd, *J* = 8, 1.2 Hz, 1 H), 7.60–7.55 (m, 3 H), 7.46–7.35 (m, 5 H), 6.84 (d, *J* = 0.4 Hz, 2 H), 2.27 (s, 3 H), 2.18 (s, 6 H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 160.8, 153.0, 141.5, 140.2, 134.7, 134.1, 131.7, 130.1, 129.9, 128.8, 128.4, 128.0, 127.2, 124.5, 119.4, 118.5, 116.9, 103.5, 90.9, 21.5, 20.9 ppm. IR (KBr): \tilde{v} = 2196, 1714, 1598 cm⁻¹. HRMS (ESI): calcd. for C₂₆H₂₀O₂Na [M + Na]⁺ 387.1361; found 387.1374.

6-*tert*-**Butyl**-4-(**mesitylethynyl**)-3-phenyl-2*H*-**chromen-2-one** (**3q**): 4-*tert*-Butyl-2-iodophenyl 2-phenylacetate (**1e**, 118 mg, 0.3 mmol), mesitylacetylene (**2d**, 52 µL, 0.33 mmol), PdCl₂(PPh₃)₂ (2 mg, 0.01 mmol), and Et₃N (0.13 mL, 0.9 mmol) were stirred for 6 h to afford **3q** (113 mg, 90 % yield) as a white solid; m.p. 179 °C. ¹H NMR (400 MHz, CDCl₃): δ = 8.12 (d, *J* = 2.4 Hz, 1 H), 7.63 (dd, *J* = 8.8, 2.4 Hz, 1 H), 7.54–7.52 (m, 2 H), 7.46–7.40 (m, 3 H), 7.34 (d, *J* = 8.8 Hz, 1 H), 6.85 (s, 2 H), 2.28 (s, 3 H), 2.17 (s, 6 H), 1.40 (s, 9 H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 161.1, 151.0, 147.6, 140.1, 134.9, 134.5, 130.1, 129.9, 129.4, 128.7, 128.48, 128.44, 123.6, 118.67, 118.64, 116.4, 103.4, 91.1, 76.8 (merged with CDCl₃ signals), 34.9, 31.6, 21.5, 20.9 ppm. IR (KBr): \tilde{v} = 2188, 1719, 1595 cm⁻¹. HRMS (ESI): calcd. for C₃₀H₂₉O₂ [M + H]⁺ 421.2168; found 421.2198.

4-(4-Methoxyphenylethynyl)-3-phenyl-2*H***-chromen-2-one (3r):** 2-lodophenyl 2-phenylacetate (**1a**, 101 mg, 0.3 mmol), 4-ethynylanisole (**2e**, 43 μL, 0.33 mmol), PdCl₂(PPh₃)₂ (2 mg, 0.01 mmol), and Et₃N (0.13 mL, 0.9 mmol) were stirred for 8 h to afford **3r** (83 mg, 79 % yield) as a yellow solid; m.p. 118 °C. ¹H NMR (400 MHz, CDCl₃): $\delta = 8.06$ (dd, J = 8, 1.6 Hz, 1 H), 7.69–7.67 (m, 2 H), 7.59–7.55 (m, 1 H), 7.49–7.45 (m, 2 H), 7.39–7.35 (m, 3 H), 7.31 and 6.86 (AA'BB' pattern, J = 8.8, 9.2 Hz, 4 H), 3.83 (s, 3 H) ppm. ¹³C NMR (100 MHz, CDCl₃): $\delta = 161.1$, 152.9, 135.3, 134.2, 134.0, 131.8, 130.5, 129.4, 128.9, 127.9, 127.3, 124.5, 119.2, 116.8, 114.4, 113.6, 105.9, 83.1, 77.3, 55.5 ppm. IR (KBr): $\tilde{v} = 2198$, 1719, 1598 cm⁻¹. HRMS (ESI): calcd. for C₂₄H₁₆O₃Na [M + Na]⁺ 375.0997; found 375.1006.

3-(4-Bromophenyl)-4-(4-methoxyphenylethynyl)-2H-chromen-2-one (3s): 2-lodophenyl 2-(4-bromophenyl)acetate (**1c**, 125 mg, 0.3 mmol), 4-ethynylanisole (**2e**, 43 µL, 0.33 mmol), PdCl₂(PPh₃)₂ (2 mg, 0.01 mmol), and Et₃N (0.13 mL, 0.9 mmol) were stirred for 8 h to afford **3s** (101 mg, 82 % yield) as a pale yellow solid; mp. 206 °C. ¹H NMR (400 MHz, CDCl₃): δ = 8.05 (dd, *J* = 8.4, 1.6 Hz, 1 H), 7.63–7.56 (m, 5 H), 7.40–7.34 (m, 4 H), 6.90 (AA'BB' pattern, *J* = 8.8 Hz, 2 H), 3.84 (s, 3 H) ppm. ¹³C NMR (400 MHz, CDCl₃): δ = 161.3, 152.9, 134.0, 133.6, 133.1, 132.3, 132.0, 131.1, 128.0, 127.3, 124.6, 123.1, 119.0, 116.8, 114.5, 113.3, 106.3, 82.8, 76.8 (merged with CDCl₃ signals), 55.5 ppm. IR (KBr): \tilde{v} = 2197, 1721, 1593 cm⁻¹. HRMS (ESI): calcd. for C₂₄H₁₆O₃Br [M + H]⁺ 431.0283; found 431.0312.

4-(4-Methoxyphenylethynyl)-3-(4-nitrophenyl)-2H-chromen-2one (3t): 2-lodophenyl 2-(4-nitrophenyl)acetate (1d, 115 mg, 0.3 mmol), 4-ethynylanisole (**2e**, 43 μ L, 0.33 mmol), PdCl₂(PPh₃)₂ (2 mg, 0.01 mmol), and Et₃N (0.13 mL, 0.9 mmol) were stirred for 8 h to afford **3t** (89 mg, 75 % yield) as a yellow solid; m.p. 276 °C. ¹H NMR (500 MHz, CDCl₃): δ = 8.35, 7.89, 7.33 and 6.90 (AA'BB' pattern, *J* = 8.5, 9, 8.5, 8.5 Hz, 8 H), 8.08 (dd, *J* = 8.5, 1.5 Hz, 1 H), 7.64–7.61 (m, 1 H), 7.43–7.40 (m, 2 H), 3.84 (s, 3 H) ppm. ¹³C NMR (125 MHz, CDCl₃): δ = 161.6, 160.0, 153.1, 147.8, 141.0, 134.9, 134.1, 132.7, 131.8, 127.6, 126.8, 124.9, 123.1, 118.8, 117.0, 114.7, 112.9, 107.4, 82.5, 55.6 ppm. IR (KBr): \tilde{v} = 2194, 1707, 1598 cm⁻¹. HRMS (ESI): calcd. for C₂₄H₁₅O₅NK [M + K]⁺ 436.0587; found 436.0582.

6-*tert*-**Butyl-4**-(**4**-methoxyphenylethynyl)-3-phenyl-2*H*chromen-2-one (**3u**): 4-*tert*-Butyl-2-iodophenyl 2-phenylacetate (**1e**, 118 mg, 0.3 mmol), 4-ethynylanisole (**2e**, 43 μL, 0.33 mmol), PdCl₂(PPh₃)₂ (2 mg, 0.01 mmol), and Et₃N (0.13 mL, 0.9 mmol) were stirred for 10 h to afford **3u** (86 mg, 70 % yield) as a pale yellow solid; m.p. 158 °C. ¹H NMR (400 MHz, CDCl₃): δ = 8.07 (d, *J* = 2 Hz, 1 H), 7.69–7.67 (m, 2 H), 7.61 (dd, *J* = 8.8, 2.4 Hz, 1 H), 7.51–7.44 (m, 3 H), 7.33–7.30 (m, 3 H), 6.88 (AA'BB' pattern, *J* = 8.8 Hz, 2 H), 3.83 (s, 3 H), 1.42 (s, 9 H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 161.1, 150.9, 147.5, 134.4, 133.9, 133.8, 130.5, 129.4, 129.0, 128.8, 127.9, 123.4, 118.4, 116.3, 114.4, 113.7, 105.7, 83.3, 77.3, 55.5, 34.8, 31.5 ppm. IR (KBr): \tilde{v} = 2198, 1709, 1596 cm⁻¹. HRMS (ESI): calcd. for C₂₈H₂₅O₃ [M + H]⁺ 409.1804; found 409.1790.

3-(4-Bromophenyl)-6-*tert***-butyl-4-(4-methoxyphenylethynyl)**-**2H-chromen-2-one (3v):** 4-*tert*-Butyl-2-iodophenyl 2-(4-bromophenyl)acetate (**1f**, 142 mg, 0.3 mmol), 4-ethynylanisole (**2e**, 43 µL, 0.33 mmol), PdCl₂(PPh₃)₂ (2 mg, 0.01 mmol), and Et₃N (0.13 mL, 0.9 mmol) were stirred for 8 h to afford **3v** (112 mg, 77 % yield) as a white solid; m.p. 203 °C. ¹H NMR (400 MHz, CDCl₃): δ = 8.06 (d, J = 2.4 Hz, 1 H), 7.64–7.56 (m, 5 H), 7.34 and 6.91 (AA'BB' pattern, J = 8.8, 8.8 Hz, 4 H), 7.31 (d, J = 8.8 Hz, 1 H), 3.85 (s, 3 H), 1.42 (s, 9 H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 161.3, 160.7, 150.9, 147.6, 133.9, 133.3, 132.3, 131.1, 129.7, 127.6, 123.4, 123.0, 118.3, 116.8, 116.4, 114.6, 113.4, 106.3, 83.0, 55.5, 34.8, 31.5 ppm. IR (KBr): \tilde{v} = 2195, 1699, 1595 cm⁻¹. HRMS (ESI): calcd. for C₂₈H₂₅O₃Br [M + H]⁺ 487.0909; found 487.0915.

6-Chloro-3-phenyl-4-(phenylethynyl)-2H-chromen-2-one (3y): 4-chloro-2-iodophenyl 2-phenylacetate (**1g**, 110 mg, 0.3 mmol), phenylacetylene (36 μL, 0.33 mmol), PdCl₂(PPh₃)₂ (2 mg, 0.01 mmol), and Et₃N (0.13 mL, 0.9 mmol) were stirred for 5 h to afford **3y** (90 mg, 87 % yield) as a pale yellow solid; m.p. 159 °C. ¹H NMR (400 MHz, CDCl₃): δ = 8.01 (d, *J* = 2.8 Hz, 1 H), 7.68–7.66 (m, 2 H), 7.53–7.46 (m, 4 H), 7.42–7.32 (m, 6 H) ppm. ¹³C NMR (125 MHz, CDCl₃): δ = 160.0, 151.3, 133.7, 132.3, 131.9, 131.8, 131.2, 130.4, 130.3, 130.0, 129.3, 128.7, 128.0, 126.7, 121.3, 120.3, 118.2, 105.4, 83.2 ppm. IR (KBr): \tilde{v} = 2203, 1722, 1266 cm⁻¹. HRMS (ESI): calcd. for C₂₃H₁₄O₂Cl [M + H]⁺ 357.0682; found 357.0675.

3-Phenyl-4-[(trimethylsilyl)ethynyl]-2H-chromen-2-one (3w): 2-lodophenyl 2-phenylacetate (**1a**, 101 mg, 0.3 mmol), trimethylsilyl-acetylene (**2f**, 0.17 mL, 1.2 mmol), PdCl₂(PPh₃)₂ (2 mg, 0.01 mmol), and Et₃N (0.13 mL, 0.9 mmol) were stirred for 12 h to afford **3w** (74 mg, 78 % yield) as a white solid; m.p. 99 °C. ¹H NMR (400 MHz, CDCl₃): δ = 7.95 (dd, *J* = 8.4, 1.6 Hz, 1 H), 7.62–7.59 (m, 2 H), 7.57–7.53 (m, 1 H), 7.46–7.40 (m, 3 H), 7.36–7.32 (m, 2 H), 0.176 (s, 9 H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 160.6, 152.9, 133.7, 132.7, 131.8, 131.4, 130.3, 128.9, 127.8, 127.4, 124.6, 119.0, 116.6, 112.6, 98.0, –0.5 ppm. IR (KBr): \tilde{v} = 1712, 1401 cm⁻¹. HRMS (ESI): calcd. for C₂₀H₁₈O₂Na [M + Na]⁺ 341.0974; found 341.0991.

4-Ethynyl-3-phenyl-2H-chromen-2-one (3x): Tetra-*n*-butylammonium fluoride (1 M in THF, 0.2 mL, 0.69 mmol) was added to a solution of 3-phenyl-4-[(trimethylsilyl)ethynyl]-2H-chromen-2-one



(**3w**, 200 mg, 0.62 mmol) in THF (8 mL) under anhydrous conditions at 0 °C, and the resulting mixture was stirred at room temperature for 10 min. The solvent was removed under reduced pressure, and the residue was then dissolved in EtOAc. The solution was washed with brine, and the organic layer was dried with Na₂SO₄ and concentrated under reduced pressure. The crude product was purified by flash chromatography (EtOAc/hexane, 10:90 v/v) on silica gel to give **3x** (124 mg, 80 % yield) as a pale pink solid; m.p. 166 °C. ¹H NMR (400 MHz, CDCl₃): δ = 7.98 (d, *J* = 8 Hz, 1 H), 7.60–7.55 (m, 3 H), 7.46–7.41 (m, 3 H), 7.37–7.34 (m, 2 H), 3.69 (s, 1 H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 160.3, 152.8, 133.5, 132.3, 132.0, 131.9, 130.2, 129.2, 128.1, 127.2, 124.7, 119.0, 116.7, 92.4, 77.1 (merged with CDCl₃ signals) ppm. IR (KBr): \tilde{v} = 2102, 1717, 1599 cm⁻¹. HRMS (ESI): calcd. for C₁₇H₁₀O₂Na [M + Na] 269.0578; found 269.0558.

Procedure for One-Pot Synthesis of 3a and 3e: A mixture of the corresponding 2-iodophenol (110 mg, 0.5 mmol) and Et₃N (0.2 mL, 1.5 mmol) was placed in an oven-dried Schlenk tube under N₂, and toluene (8 mL) was added followed by a solution of 2-phenylacetyl chloride (93 mg, 0.6 mmol) in toluene (4 mL). The reaction mixture was stirred at 25 °C for 30 min, and then phenylacetylene (60 μ L, 0.55 mmol) and PdCl₂(PPh₃)₂ (4 mg, 1 mol-%) were added. The resulting mixture was flushed with CO and then stirred under CO (1 atm, balloon) at 80 °C for 6 or 8 h to give **3a** or **3e**, respectively (Scheme 3). The mixture was cooled to room temperature and filtered through a pad of Celite. The filter cake was washed with dichloromethane several times. The combined filtrates were concentrated under vacuum. The crude product was purified by column chromatography (hexane/EtOAc, 9.7:0.3 v/v) on silica gel to afford the corresponding pure product [**3a** (72 % yield), **3e** (77 % yield)].

2-Naphthyl 2-Phenylacetate (10): 1-lodo-2-naphthyl 2-phenylacetate (**9**, 116 mg, 0.3 mmol), phenylacetylene (**2a**, 36 μ L, 0.33 mmol), PdCl₂(PPh₃)₂ (2 mg, 0.01 mmol), and Et₃N (0.13 mL, 0.9 mmol) were stirred for 5 h to give **10** (75 mg, 96 % yield) as a pale orange solid; m.p. 86 °C, ¹H NMR (400 MHz, CDCl₃): δ = 7.84 (d, *J* = 9.2 Hz, 2 H), 7.83–7.79 (m, 1 H), 7.57 (d, *J* = 2.4 Hz, 1 H), 7.51–7.40 (m, 6 H), 7.37–7.33 (m, 1 H), 7.22 (dd, *J* = 8.8, 2.4 Hz, 1 H), 3.94 (s, 2 H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 170.2, 148.4, 133.8, 133.5, 131.5, 129.4, 128.8, 127.8, 127.7, 127.5, 126.6, 125.8, 121.1, 118.5, 41.6 ppm. IR (KBr): \tilde{v} = 1757 cm⁻¹. HRMS (ESI): calcd. for C₁₈H₁₄O₂Na [M + Na]⁺ 285.0891; found 285.0918.

1-(Phenylethynyl)-2-naphthyl Acetate (12): 1-lodo-2-naphthyl acetate **(11,** 94 mg, 0.3 mmol), phenylacetylene **(2a,** 36 μ L, 0.33 mmol), PdCl₂(PPh₃)₂ (2 mg, 0.01 mmol), and Et₃N (0.13 mL, 0.9 mmol) were stirred for 5 h to afford **12** (84 mg, 98 % yield) as a yellow solid; m.p. 97 °C. ¹H NMR (400 MHz, CDCl₃): δ = 8.41 (d, *J* = 8.4 Hz, 1 H), 7.87–7.85 (m, 2 H), 7.64–7.60 (m, 3 H), 7.55–7.51 (m, 1 H), 7.41–7.40 (m, 3 H), 7.29 (d, *J* = 8.8 Hz, 1 H), 2.45 (s, 3 H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 169.2, 150.4, 133.8, 131.7, 131.4, 129.8, 128.8, 128.6, 128.3, 127.5, 126.35, 126.31, 123.2, 121.2, 113.3, 99.5, 82.5, 21.1 ppm. IR (KBr): \tilde{v} = 2200, 1766 cm⁻¹. HRMS (ESI): calcd. for C₂₀H₁₅O₂ [M + H]⁺ 287.1072; found 287.1063.

2-(3-Phenylpropynoyl)phenyl Acetate (5a):^[12a] 2-lodophenyl acetate (4a, 79 mg, 0.3 mmol), phenylacetylene (2a, 36 μ L, 0.33 mmol), PdCl₂(PPh₃)₂ (2 mg, 0.01 mmol), and Et₃N (0.13 mL, 0.9 mmol) were combined to afford 5a (80 mg, 100 % yield) as a yellow oil. ¹H NMR (400 MHz, CDCl₃): δ = 8.27 (dd, *J* = 8, 1.6 Hz, 1 H), 7.65–7.60 (m, 3 H), 7.49–7.46 (m, 1 H), 7.42–7.39 (m, 3 H), 7.14 (dd, *J* = 8, 1.2 Hz, 1 H), 2.35 (s, 3 H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 176.1, 169.7, 150.2, 134.8, 133.2, 133.1, 131.0, 129.6, 128.8, 126.2, 124.1, 120.0, 92.7, 87.8, 21.2 ppm. IR: \tilde{v} = 2196, 1767 cm⁻¹. HRMS (ESI): calcd. for C₁₇H₁₃O₃ [M + H]⁺ 265.0865; found 265.0844.



4-*tert*-**Butyl-2-(3-phenylpropynoyl)phenyl Acetate** (**5b**): 4-*tert*-Butyl-2-iodophenyl acetate (**4b**, 96 mg, 0.3 mmol), phenylacetylene (**2a**, 36 μL, 0.33 mmol), PdCl₂(PPh₃)₂ (2 mg, 0.01 mmol), and Et₃N (0.13 mL, 0.9 mmol) were combined to afford **5b** (95 mg, 99 % yield) as a pale yellow oil. ¹H NMR (400 MHz, CDCl₃): δ = 8.29 (d, *J* = 2.4 Hz, 1 H), 7.65–7.62 (m, 3 H), 7.50–7.46 (m, 1 H), 7.43–7.39 (m, H), 7.06 (d, *J* = 8 Hz, 1 H), 2.33 (s, 3 H), 1.38 (s, 9 H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 176.5, 169.9, 149.2, 147.9, 133.2, 132.0, 131.0, 130.1, 128.9, 123.6, 120.2, 92.6, 87.9, 77.1 (merged with CDCl₃ signals), 34.8, 31.3, 21.2 ppm. IR: \tilde{v} = 2197, 1764, 1644 cm⁻¹. HRMS (ESI): calcd. for C₂₁H₂₀O₃Na [M + Na]⁺ 343.1310; found 343.1332.

General Procedure for Carbonylative Annulation Reaction of 2-Iodoaryl Acetates in Triethylamine: To a Schlenk flask were added PdCl₂(PPh₃)₂ (0.02 mmol) and triethylamine (10 mL). To this suspension was added 2-iodophenyl acetate (4a) or 4b (1 equiv.) followed by addition of phenylacetylene (2a, 1.2 equiv.). The reaction mixture was flushed with CO and then stirred under CO (1 atm, balloon) at 80 °C for 72 h. The progress of the reaction was monitored by TLC. Within 4 h, the starting materials were consumed, and the carbonylative Sonogashira coupling product (5a or 5b) was formed, as observed by the formation of a distinct spot on the TLC plate. Upon a prolonged reaction time (72 h), a mixture of compounds was formed. After cooling the reaction mixture to room temperature, the solvent was evaporated. The residue was partitioned between brine and CH₂Cl₂ and then extracted with CH₂Cl₂. The organic layer was concentrated under vacuum, and crude mixture was purified by column chromatography on silica gel (CH₂Cl₂/hexane, 10:1 v/v) to give **6a** and **7a** and (EtOAc/hexane, 1:30 v/v) to give **6b**, **7b**, and **8b**.

2-lodophenyl acetate (**4a**, 105 mg, 0.4 mmol), phenylacetylene (**2a**, 53 μ L, 0.48 mmol), and PdCl_2(PPh_3)_2 (5.6 mg, 0.02 mmol) afforded **6a** and **7a**.

3-Acetyl-2-phenyl-4*H***-chromen-4-one (6a):**^{(12]} White solid (29 mg, 27 % yield); m.p. 109 °C. ¹H NMR (400 MHz, CDCl₃): δ = 8.19–8.17 (m, 1 H), 7.93–7.90 (m, 2 H), 7.73–7.68 (m, 1 H), 7.61–7.56 (m, 1 H), 7.49–7.40 (m, 4 H), 2.38 (s, 3 H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 175.9, 165.5, 156.1, 137.1, 134.2, 133.9, 129.5, 128.89, 128.85, 126.1, 125.6, 123.5, 123.2, 117.9, 19.2 ppm. IR (KBr): \tilde{v} = 1675, 1641, 1575 cm⁻¹. HRMS (ESI): calcd. for C₁₇H₁₃O₃ [M + H]⁺ 265.0865; found 265.0862.

2-Phenyl-4H-chromen-4-one (7a):^[17] White solid (37 mg, 42 % yield); m.p. 83 °C. ¹H NMR (400 MHz, CDCl₃): δ = 8.23 (dd, *J* = 8, 1.6 Hz, 1 H), 7.94–7.91 (m, 2 H), 7.72–7.68 (m, 1 H), 7.58–7.49 (m, 4 H), 7.44–7.40 (m, 1 H), 6.83 (s, 1 H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 178.6, 163.5, 156.4, 133.9, 131.9, 131.7, 129.1, 126.4, 125.8, 125.3, 124.1, 118.2, 107.7 ppm. IR (KBr): \tilde{v} = 1645, 1603, 1563 cm⁻¹. HRMS (ESI): calcd. for C₁₅H₁₀O₂Na [M + Na]⁺ 245.0578; found 245.0551.

4-*tert*-Butyl-2-iodophenyl acetate (**4b**, 160 mg, 0.5 mmol), phenyl-acetylene (**2a**, 66 μ L, 0.6 mmol), and PdCl₂(PPh₃)₂ (7 mg, 0.02 mmol) afforded **6b**, **7b**, and **8b**.

3-Acetyl-6-*tert***-butyl-2-phenyl-4***H***-chromen-4-one** (6b): White solid (19 mg, 12 % yield); m.p. 116 °C. ¹H NMR (400 MHz, CDCl₃): $\delta = 8.23$ (d, J = 2.4 Hz, 1 H), 7.78 (dd, J = 8.8, 2.8 Hz, 1 H), 7.65–7.63 (m, 2 H), 7.54–7.45 (m, 4 H), 2.46 (s, 3 H), 1.39 (s, 9 H) ppm. ¹³C NMR (100 MHz, CDCl₃): $\delta = 200.8$, 176.3, 162.5, 154.2, 149.2, 132.4, 132.1, 131.5, 128.9, 128.7, 124.9, 122.9, 121.8, 117.8, 35.0, 32.4, 31.4 ppm. IR (KBr): $\tilde{v} = 1707$, 1639, 1616 cm⁻¹. HRMS (ESI): calcd. for C₂₁H₂₁O₃ [M + H]⁺ 321.1491; found 321.1508.

6-*tert*-**Butyl**-**2**-**phenyl**-**4***H*-**chromen**-**4**-**one** (7b): White solid (66 mg, 47 % yield); m.p. 126 °C. ¹H NMR (400 MHz, CDCl₃): δ = 8.22 (d, *J* = 2.4 Hz, 1 H), 7.94–7.91 (m, 2 H), 7.76 (dd, *J* = 8.8, 2.8 Hz, 1





H), 7.53–7.50 (m, 4 H), 6.83 (s, 1 H), 1.39 (s, 9 H) ppm. ^{13}C NMR (100 MHz, CDCl₃): δ = 178.9, 163.3, 154.6, 148.7, 132.0, 131.8, 131.6, 129.1, 126.4, 123.4, 121.6, 117.8, 107.6, 35.0, 31.4 ppm. IR (KBr): $\tilde{\nu}$ = 1652, 1615 cm $^{-1}$. HRMS (ESI): calcd. for $C_{19}H_{18}O_2Na$ [M + Na]+ 301.1204; found 301.1176.

(*Z*)-2-Benzylidene-5-*tert*-butylbenzofuran-3(2*H*)-one (8b): White solid (48 mg, 34 % yield); m.p. 121 °C. ¹H NMR (400 MHz, CDCl₃): δ = 7.93–7.91 (m, 2 H), 7.81 (d, *J* = 2 Hz, 1 H), 7.72 (dd, *J* = 8.4, 2.0 Hz, 1 H), 7.48–7.37 (m, 3 H), 7.26 (d, *J* = 8.8 Hz, 1 H), 6.88 (s, 1 H), 1.35 (s, 9 H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 185.4, 164.6, 147.6, 147.0, 135.0, 132.5, 131.6, 129.9, 129.0, 121.3, 120.9, 112.8, 112.4, 34.8, 31.5 ppm. IR (KBr): \tilde{v} = 1707, 1651 cm⁻¹. HRMS (ESI): calcd. for C₁₉H₂₀O₂ [M + H]⁺ 279.1385; found 279.1364.

Supporting Information (see footnote on the first page of this article): Copies of ¹H and ¹³C NMR spectra of all new compounds.

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Carbonylative Annulation

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Highly Selective and Modular Synthesis of 3-Aryl-4-(arylethynyl)-2Hchromen-2-ones from 2-lodoaryl 2-Arylacetates through a Carbonylative Sonogashira Coupling–Intramolecular Aldol Cascade Reaction



A modular approach for the synthesis of 3-aryl-4-(arylethynyl)-2*H*-chromen-2-ones from iodoaryl 2-arylacetates and arylacetylenes has been developed. This highly selective general method was used to prepare 24 different 3,4-disubstitued 2*H*-chromen-2one derivatives in good to excellent yields.

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