JOC The Journal of Organic Chemistry

pubs.acs.org/joc Article

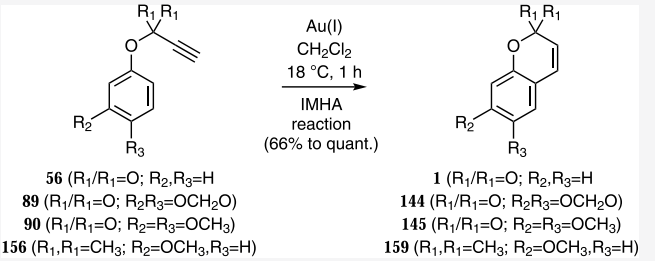
Gold(I)-Catalyzed Intramolecular Hydroarylation of Phenol-Derived Propiolates and Certain Related Ethers as a Route to Selectively Functionalized Coumarins and 2*H*-Chromenes

Aymeric Cervi, Yen Vo, Christina L. L. Chai, Martin G. Banwell,* Ping Lan, and Anthony C. Willis

Cite This: https://dx.doi.org/10.1021/acs.joc.0c02011 Read Online

ACCESS | Metrics & More | Article Recommendations | Supporting Information

ABSTRACT: Methods are reported for the efficient assembly of a series of phenol-derived propiolates, including the parent system **56**, and their Au(I)-catalyzed cyclization (intramolecular hydroarylation) to give the corresponding coumarins (e.g., **1**). Simple syntheses of natural products such as ayapin (**144**) and scoparone (**145**) have been realized by such means, and the first of these subject to single-crystal X-ray analysis. A related process is described for the conversion of propargyl ethers such as **156** into the isomeric 2*H*-chromene precocene I (**159**), a naturally occurring inhibitor of juvenile hormone biosynthesis.



INTRODUCTION

The coumarin framework **1** (Figure 1) is encountered not only in a wide range of biologically active natural products[1] but also in synthetically derived therapeutic agents,[2] in various useful materials and in devices.[3] As a consequence, a multitude of processes has been established for the synthesis of coumarins and these have been the subject of recent reviews.[4] For similar reasons, the structurally related 2*H*-chromene (**2**) and many derivatives of this, especially 2,2-dimethylated ones, have also been the subject of attention as synthetic targets.[5]

Earlier, we reported[6] that certain phenol-derived propiolates (e.g., **3**) engage in gold(I)-catalyzed[7] intramolecular hydroarylation (IMHA) reactions[8] and thereby forming the isomeric coumarins (e.g. **4**). Extensions of our originally reported processes have allowed for total syntheses of several coumarin-containing natural products including pimpinellin (**5**).[9] The pivotal cyclization process often proved to be an exceptionally effective one with a number of these proceeding in less than 1 h at ambient temperatures and in the presence of modest (1 mol %) catalyst loadings. Given the efficiencies of these IMHA reactions in a diverse range of settings, we were prompted to undertake a systematic study of their capacity to deliver site-specifically substituted coumarins through cyclization of the corresponding (isomeric) *O*-aryl propiolates. The outcomes of such studies, that have culminated in two-step syntheses of certain simple natural products, are reported herein and allow for the introduction of substituents at all possible positions on the coumarin framework. The results of an analogous but a more cursory study concerned with the equivalent cyclizations of certain aryl propargyl ethers (and leading to the corresponding 2*H*-chromenes) are also reported.

The present work is detailed against a backdrop of related studies,[10] including ones that have emerged in recent times. For example, in 2017, Kanan et al. detailed[10g] methods of electrostatic control in the Au(I)-catalyzed cyclization of aryl propargyl ethers and so enabling the regioselective assembly of 2*H*-chromenes.

RESULTS AND DISCUSSION

Synthesis of the *O*-Aryl Propiolates Required for the IMHA Reaction. The synthesis of the propiolates required for the present study proved to be more complicated than expected because of the propensity of certain of the target esters to engage in hetero-Michael addition reactions with the starting phenol. In the first approach used to access *O*-aryl propiolates, a chloroform solution of phenol and the parent acid **6** (*viz.* propiolic acid) was treated with dicyclohexylcarbodiimide (DCC) (Procedure A) and thus forming the required and parent ester in 64% yield. However, when same conditions were applied to the coupling of acid **6** with *p*-methoxyphenol (**7**), the anticipated product **3** was only obtained in 20% yield (Scheme 1). Furthermore, when this coupling agent was used in combination with 4-(*N*,*N*-dimethylamino)pyridine,[11] the major product obtained was the *E*-configured "2 + 1" adduct **8**, although this was only obtained in 30% yield. While the precise ordering of events

Received: August 20, 2020

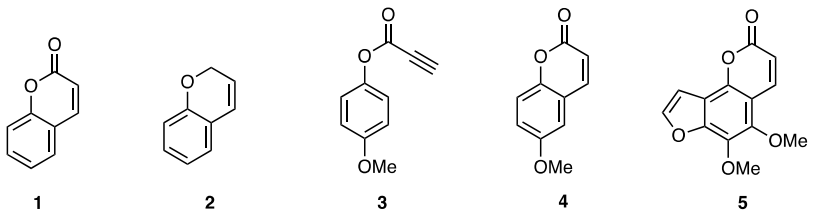
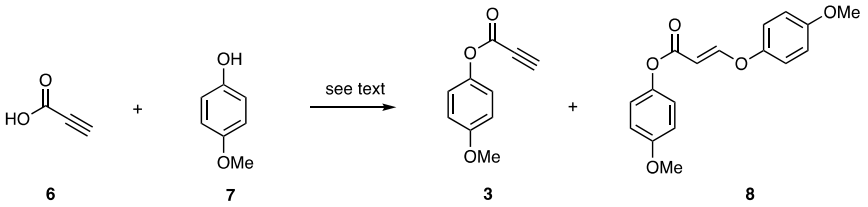


Figure 1. Structures of parent coumarin (**1**), parent 2*H*-chromene (**2**), propiolate **3**, its cyclization product, the substituted coumarin **4**, and the coumarin-containing natural product pimpinellin (**5**).

Scheme 1. Reaction of Propiolic Acid (6) with Phenol 7 Leading to the Target Ester 3 and/or Its Hetero-Michael Adduct 8



leading to the formation of compound **8** has not been determined, it is presumed that ester formation precedes a hetero-Michael addition reaction. Esterifications using other coupling agents including DMT-MM,[12] T3P,[13] and *N*-(3-dimethylaminopropyl)-*N*′-ethylcarbodiimide[14] along with a range of bases, such as pyridine, triethylamine, and 2,6-lutidine, failed to provide useful amounts of the target ester **3**. Further, upon using HATU[15] for the coupling process, compound **8** (rather than **3**) was obtained in 80% yield.

Because the DCC-promoted couplings produced fewer byproducts in the original suite of experiments, optimization studies were pursued using this reagent. Eventually, it was found that the most broadly useful protocol (Procedure B) for effecting the required coupling, including of "difficult" substrates such as compound **7**, involved using a combination of DCC and sodium hydride in tetrahydrofuran and wherein the phenol (**7**) was subjected to reaction with the base at the start of the process and the ensuing phenolate was then added to a magnetically stirred mixture of the propiolic acid and DCC in tetrahydrofuran maintained at 0 °C. Under such conditions, ester **3** was now obtained in 98% yield. Presumably, the DCC−propiolic acid adduct **9** (Figure 2) is the pivotal electrophile that reacts with

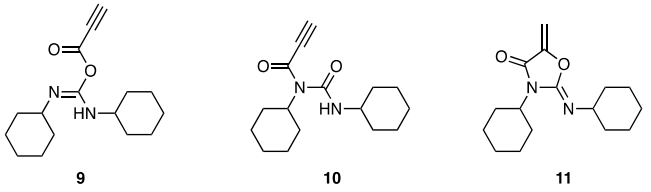


Figure 2. Structures of the DCC−propiolic acid adducts **9**, **10**, and **11**.

the phenolate in these successful conversions. Interestingly, small amounts of the crystalline and isomeric byproducts **10** and **11** (Figure 2) were also isolated from such reactions mixtures and the structure of each of these was established by single-crystal X-ray analysis (see the Experimental Section and Supporting Information for details). Urea **10** has been reported by Kulkarni and co-workers,[16] although not exhaustively characterized, while the previously undescribed isomer **11** is presumably the product of a 5-*exo*-dig cyclization reaction of the former compound.

Having defined optimal conditions for the coupling of two representative phenols with propiolic acid (**6**), the deployment of these in the esterification reactions of this and the related acids **12** and **13** (Figure 3) with a wide range of other phenols (**14**−**55**) was undertaken. Many of these phenols were commercially available but certain others had to be prepared by the straightforward methods detailed in the Experimental Section. The synthesis of a significant suite of variously substituted *O*-aryl propiolates (Figure 4) was realized through the application of the relevant coupling procedures, the outcomes of which are shown in Table 1. During the course of these studies, it was found that in two instances converting the acid into the corresponding acid chloride (using oxalyl chloride and DMF) and then reacting the latter with the relevant phenol (Procedure C) proved to be more effective than the DCC-mediated couplings. Details of all three procedures (A, B, and C) are provided in the Experimental Section.

The only notable failure involved efforts to prepare the monopropiolate ester of hydroquinone (**44**) (see entries 32 and 46, Table 1), although modest quantities (23%) of the corresponding and previously reported[17] bis-ester **99** (see entry 45, Table 1) could be obtained. The spectral data acquired on all the product esters were completely consistent with the assigned structures. In such instances where comparisons could be made with the analogous data sets reported in the literature (see the Experimental Section), then there was an excellent agreement. In the cases of compounds **66**, **76**, **78**, **84**, **85**, **87**, **89**, **93**, and **97**, it was possible to secure single-crystal X-ray data on them (details are presented in the Experimental Section and the Supporting Information).

Identification of the Optimal Catalyst and Conditions for the IMHA Reaction. With a suite of *O*-aryl propiolates in hand, a search was undertaken to identify the optimal catalyst and reaction conditions for effecting the IMHA reaction leading to the isomeric coumarins. The conversion used for this purpose is shown in Scheme 2 and was chosen because of the ready chromatographic separation of the substrate **93** from the product coumarin **100** as well as the ease of visualization of both compounds under UV light. It should be noted that the regioselectivity observed in the conversion **93** → **100** is consistent with preferential substitution at C1 in the intermolecular S_EAr reactions of 2-naphthol and naphthalenes

https://dx.doi.org/10.1021/acs.joc.0c02011
J. Org. Chem. XXXX, XXX, XXX−XXX

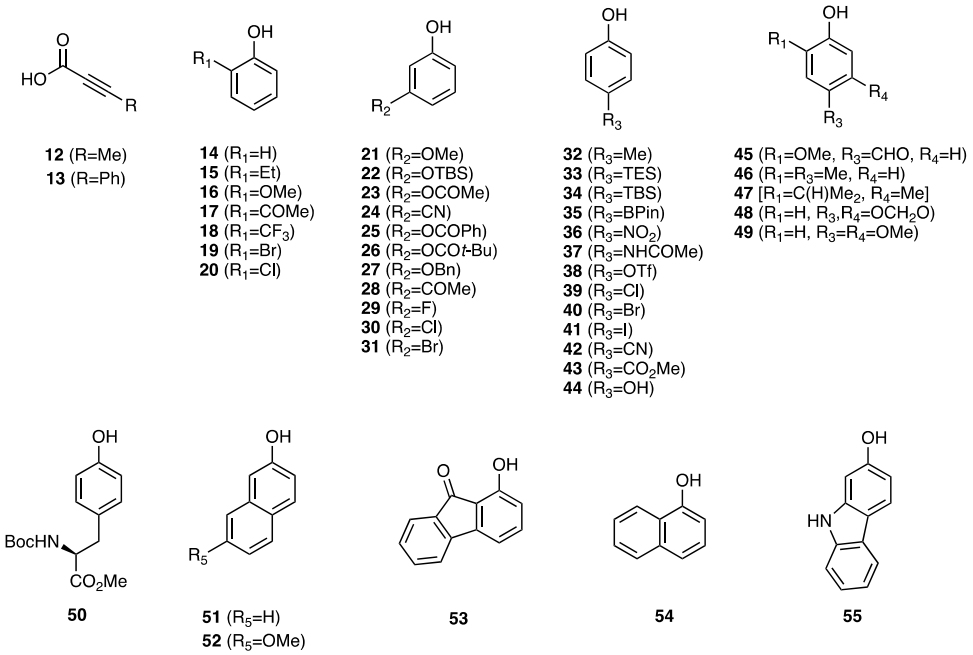


Figure 3. Structures of the additional propiolic acids (**12** and **13**) and phenols (**14**−**55**) used in the present study.

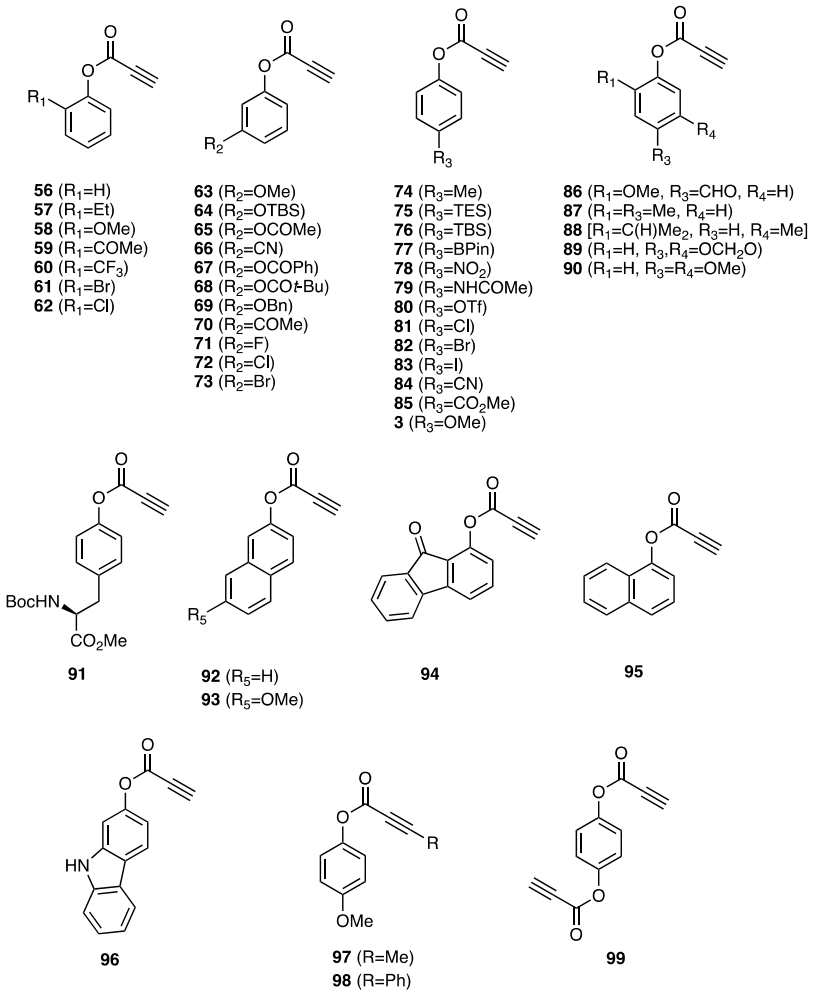


Figure 4. *O*-Aryl propiolates **56**−**99** generated through coupling of propiolic acids **6**, **12**, and **13** with phenols **14**−**55**.

more generally.[18] The structure of product **100** was confirmed by single-crystal X-ray analysis.

Informed by our earlier studies and the work reported by others in the intervening period,[10d−i] the major focus was on the

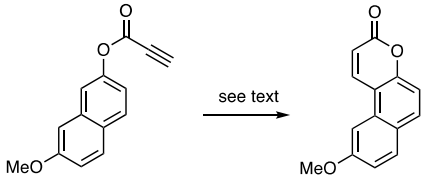
https://dx.doi.org/10.1021/acs.joc.0c02011
J. Org. Chem. XXXX, XXX, XXX−XXX

Table 1. Outcomes of the Esterification of Propiolic Acids 6, 12, and 13 with Phenols 7 and 14−55[a]

entry	acid	phenol	method[b]	ester	yield[c] (%)	entry	acid	phenol	method[b]	ester	yield[c] (%)
1	**6**	**7**	B	**3**	98	24	**6**	**36**	B	**78**	68
2	**6**	**14**	A	**56**	64	25	**6**	**37**	B	**79**	69
3	**6**	**15**	B	**57**	69	26	**6**	**38**	B	**80**	82
4	**6**	**16**	B	**58**	72	27	**6**	**39**	B	**81**	88
5	**6**	**17**	B	**59**	25	28	**6**	**40**	B	**82**	88
6	**6**	**18**	B	**60**	70	29	**6**	**41**	B	**83**	40
7	**6**	**19**	B	**61**	97	30	**6**	**43**	B	**84**	67
8	**6**	**20**	B	**62**	87	31	**6**	**43**	B	**85**	95
9	**6**	**21**	B	**63**	99	32	**6**	**44**	B	see entry 46	
10	**6**	**22**	B	**64**	80	33	**6**	**45**	B	**86**	86
11	**6**	**23**	B	**65**	45	34	**6**	**46**	B	**87**	79
12	**6**	**24**	B	**66**	70	35	**6**	**47**	B	**88**	78
13	**6**	**25**	B	**67**	42	36	**6**	**48**	B	**89**	76
14	**6**	**26**	B	**68**	40	37	**6**	**49**	B	**90**	93
15	**6**	**27**	B	**69**	78	38	**6**	**50**	B	**91**	82
16	**6**	**28**	B	**70**	79	39	**6**	**51**	B	**92**	96
17	**6**	**29**	B	**71**	79	40	**6**	**52**	B	**93**	89
18	**6**	**30**	B	**72**	95	41	**6**	**53**	B	**94**	90
19	**6**	**31**	B	**73**	96	42	**6**	**54**	B	**95**	90
20	**6**	**32**	B	**74**	85	43	**6**	**55**	B	**96**	46
21	**6**	**33**	B	**75**	52	44	**12**	7	C	**97**	98
22	**6**	**34**	B	**76**	58	45	**13**	7	C	**98**	9
23	**6**	**35**	B	77	70	46	**6**	**44**	B	**99**	23

[a]Formation of esters **3** and **56−99**. [b]Details of methods/procedures A, B, and C are provided in the Experimental Section. [c]Cited yields are for isolated and spectroscopically pure materials.

Scheme 2. Conversion of *O*-Aryl Propiolate 93 into the Isomeric Coumarin 100 Used for Developing Optimal Conditions for the IMHA Reaction



93 **100**

impact of the nature of the catalyst on this conversion (Table 2). Consistent with our earlier studies,[6,9] the most effective catalyst for this purpose proved to be the commercially available and relatively air-stable Au(I) species developed by Echavarren (see entry 7, Table 2). In contrast, most of the others, including various Au(III) species, were either completely ineffective, required higher catalyst loadings, longer reaction times, and/or provided lower yields of target **100**. Accordingly, all of our subsequent studies of the IMHA reaction were carried out using this commercially available system, namely, (acetonitrile)[(2-biphenyl)di-*tert*-butylphosphine]gold(I) hexafluoroantimonate (Echavarren's catalyst). The outcomes of such studies are detailed in the following sections.

Coumarin Formation Through Cyclization of *O*-Aryl Propiolates. In most instances, on subjecting esters **56−99** to treatment with Echavarren's catalyst in dichloromethane at ambient temperatures, the corresponding and isomeric coumarin or pair of (regioisomeric) coumarins was obtained. The structures of these cyclization products are shown in Figure 5 while the details of the outcomes of the reactions involving each of the substrate esters are presented in Table 3.

Table 2. Impact of Various Gold(I) and Gold(III) Catalysts on the Conversion of *O*-Aryl Propiolate 93 into Coumarin 100

entry	catalyst[a]	catalyst loading (mol %)	time	yield (of 100) (%)
1	gold(I) 1,3-bis(2,6-di-isopropyl phenyl)imidazole-2-ylidene	3−15	48 h	no reaction
2	gold(I) chlorotri-*tert*-butylphosphine	3−15	48 h	no reaction
3	gold(I) chloro tricyclohexylphosphine	3−15	48 h	3
4	gold(I) chloro triphenylphosphine	3−15	48 h	3
5	gold(I) chloride	3−15	48 h	18
6	gold(I) dicyclohexylphosphino-2′,4′,6′-triisopropylbiphenyl bistriflimide	3	8 h	95
7	Echavarren's catalyst[b]	3	10 min	quant.
8	gold(III) acetate	15	16 h	8
9	gold(III) chloride/AgOTf	3	8 h	89

[a]All reactions are run in CH_2Cl_2 at 18 °C at a ca. 0.1 mmol scale. [b](Acetonitrile)[(2-biphenyl)-di-*tert*-butylphosphine]gold(I) hexafluoroantimonate.

Isolation of the product coumarins normally just required passing the crude reaction mixture through a pad of TLC-grade silica gel contained in a sintered-glass filter funnel. In those cases where regioisomeric pairs of products had been generated (as a result of the presence of two nucleophilic sites within the meta-disubstituted aryl residues) they were, generally speaking, readily separated using flash chromatographic techniques. In such instances, there was always a strong preference for the formation of the C7- rather than the C8-substituted coumarin,

https://dx.doi.org/10.1021/acs.joc.0c02011
J. Org. Chem. XXXX, XXX, XXX−XXX

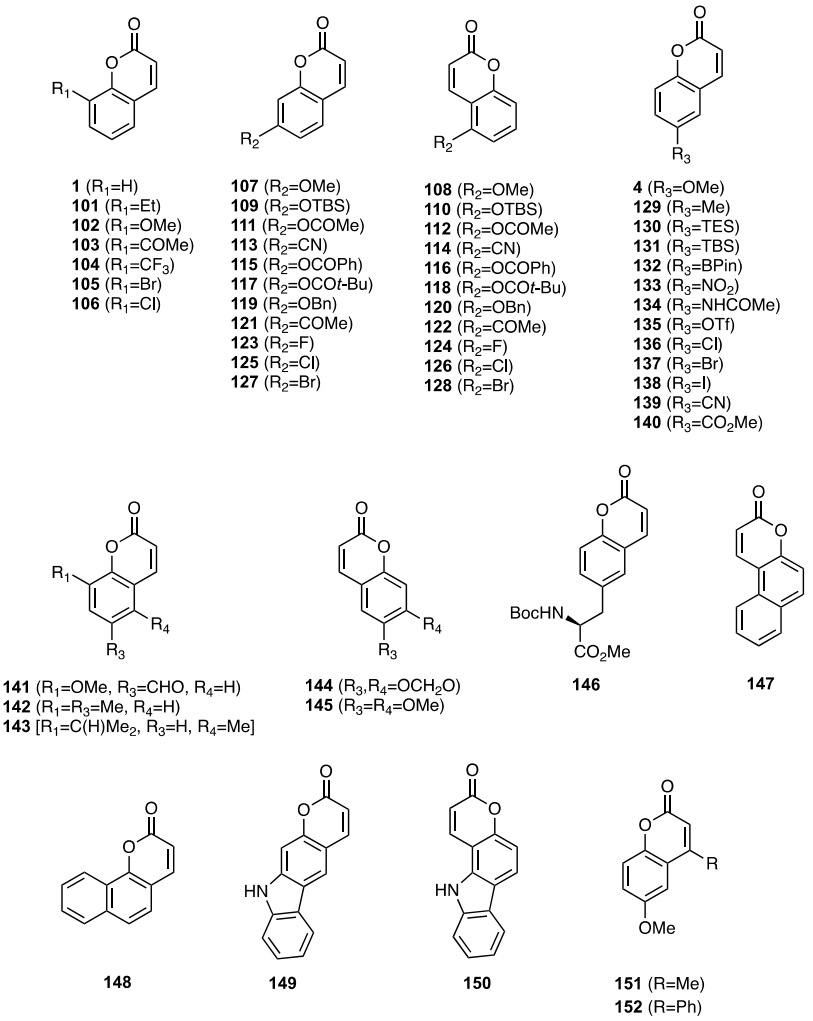


Figure 5. Structures of the coumarins anticipated from exposure of esters **3** and **56**–**99** to Echavarren's catalyst.

an outcome that presumably arises as a result of steric effects. All of the product coumarins were characterized by the usual means with the ^{1}H NMR spectrum of each generally being diagnostic by virtue of the presence, in the case of the C3- and C4-unsubstituted systems, of mutually coupled doublets (J = *ca.* 9–10 Hz) arising from the associated protons. Single-crystal X-ray analyses were carried out on the parent compound (**1**) as well as congeners **100**, **143**, and **144**. In many instances, the coumarins formed in these IMHA reactions had been reported previously and the derived spectral data matched those recorded in the literature (see the Experimental Section for details).

The product coumarins **107**, **144**, and **145** are naturally occurring systems named herniarin,[19] ayapin,[20] and scoparone,[21] respectively. The first of these natural products displays, inter alia, anti-inflammatory properties, the second hemostatic and antibiotic activity, while the last has been described as an immunosuppressant and vasorelaxant. Various other syntheses of these simple coumarins have been reported,[20,22] but the ones described here are notable for both their brevity and the very mild conditions employed in the assembly of the heterocyclic framework. As such they are competitive with those described earlier.[20,22]

The highest yielding IMHA reactions were those involving esters derived from electron-rich phenols. In contrast, those incorporating phenolic residues bearing strongly electron-withdrawing groups proceeded less effectively, if at all. In one instance, ester hydrolysis appeared to complete with the desired IMHA process (entry 28, Table 3) while in others decomposition (entries 26 and 45) of the substrate was observed. Substrates embodying polysubstituted and/or polynuclear aromatic residues also cyclize to give the isomeric coumarins and so providing access to variants (e.g. **151** and **152**) that have found applications in certain medicinal chemistry and materials science settings.[23] The efficient synthesis of various substituted coumarins including that derived from tyrosine, namely compound **146**, suggests that this form of IMHA displays a tolerance for various functional groups. As such, these protocols could allow for the introduction of coumarin fluorophores, via tyrosine residues, within peptides and proteins and so providing opportunities for cellular imaging.[24]

A diverse range of substituted coumarins is available by the IMHA-based pathway detailed above, and this could presumably be expanded upon by engaging the TES- and TBS-substituted systems such as in **130** and **131** in *ipso*-substitution reactions with a range of electrophiles.[25] So, for example, such processes could be employed in the synthesis of nitro-substituted coumarins such as compound **133** that are not available by direct cyclization (see entry 24, Table 3). In a related vein, the variously halogenated coumarins obtained as described above could be engaged in metal-catalyzed cross-coupling reactions so as to provide a range of additional substituted coumarins.[25,26]

https://dx.doi.org/10.1021/acs.joc.0c02011
J. Org. Chem. XXXX, XXX, XXX–XXX

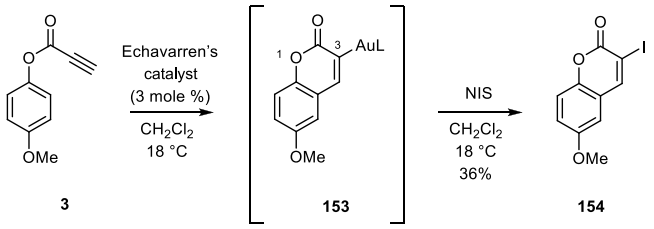
Table 3. Outcomes of the Reaction of Esters 3 and 56−99 with Echavarren's Catalyst[a]

entry	ester	product(s)	yield(s)[c]	entry	ester	product(s)	yield(s)[b]
1	**3**	**4**	quantitative	24	**78**	NR	0%
2	**56**	**1**	93%	25	**79**	**134**	52%
3	**57**	**101**	quantitative	26	**80**	decomp.[e]	0%
4	**58**	**102**	quantitative	27	**81**	**136**	66%[d]
5	**59**	NR[b]	0%	28	**82**	hydrol.[f]	0%
6	**60**	NR	0%	29	**83**	**138**	77%
7	**61**	**105**	70%	30	**84**	NR	0%
8	**62**	**106**	50%	31	**85**	**140**	18%
9	**63**	**107/108**	70%/15%	32	**86**	NR	0%
10	**64**	**109/110**	92%/4%	33	**87**	**142**	quant.
11	**65**	**111/112**	44%/14%	34	**88**	**143**	91%
12	**66**	NR[b]	0%	35	**89**	**144**	quant.
13	**67**	NR	0%	36	**90**	**145**	92%
14	**68**	**117/118**	36%/18%	37	**91**	**146**	68%
15	**69**	**119/120**	82%/17%	38	**92**	**147**	quant.
16	**70**	NR	0%	39	**93**	**100**	quant.
17	**71**	**123/124**	55%/5%[d]	40	**94**	NR	0%
18	**72**	**125/126**	83%/16%[d]	41	**95**	**148**	quant.
19	**73**	**127/128**	60%/14%[d]	42	**96**	**149/150**	60%/5%
20	**74**	**129**	quant.	43	**97**	**151**	80%
21	**75**	**130**	91%	44	**98**	**152**	75%
22	**76**	**131**	74%	45	**99**	decomp.[e]	0%
23	77	NR	0%				

[a]Formation of the isomeric coumarins. [b]NR = no reaction. [c]Cited yields are for isolated and spectroscopically pure coumarin(s). [d]Reaction run for 8 h. [e]Decomp. = decomposition. [f]hydrol. = ester hydrolysis.

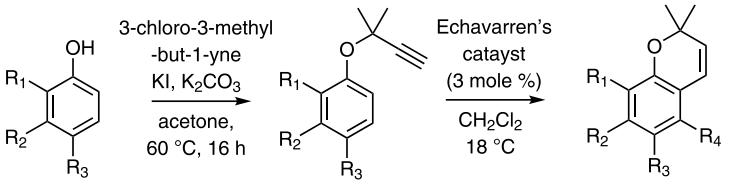
The IMHA reactions described here allow for the synthesis of coumarins that are substituted at all of positions C4 to C8. While C-3 is not an obviously accessible position, when one considers the primary product of cyclization of, say, substrate **3** (Scheme 3) to be the aurylated intermediate **153** and that related species have been intercepted with *N*-iodosuccinimide (NIS) so as to form, via an *ipso*-substitution process, the corresponding iodide,[27] we sought to establish if such chemistry could be applied in the current setting. In the event, when a solution of substrate **3** in dichloromethane containing a slight excess of NIS was treated with Echavarren's catalyst, then a smooth cyclization reaction took place and so affording the hoped-for 3-iodocoumarin **154** (36%) yield. This was accompanied by its chromatographically separable non-iodinated counterpart **4** (38%). Therefore, while this conversion clearly needs to be optimized for the former product, it does demonstrate that all positions on the coumarin framework can be functionalized in these types of IMHA reactions.

Scheme 3. Interception of the C-3 Aurylated Coumarin 153 with NIS: Formation of Its C-3 Iodinated Congener 154



Formation and Cyclization of *O*-Aryl Propargyl Ethers: The Synthesis of Some 2,2-Dimethylated 2*H*-Chromenes. A useful variation on the IMHA studies detailed above is one in which a phenol is converted into the

Scheme 4. Formation and Au(I)-Catalyzed IMHA Reactions of the Aryl Propargyl Ethers 155−157 Leading to the 2*H*-Chromenes 158−161



16 (R_1=OMe, R_2,R_3=H)
21 (R_1=R_3=H, R_2=OMe)
7 (R_1=R_2=H, R_3=OMe)

155 (R_1=OMe, R_2,R_3=H)
156 (R_1=R_3=H, R_2=OMe)
157 (R_1=R_2=H, R_3=OMe)

158 (R_1=OMe, R_2=R_3=R_4=H)
159 (R_1=R_3=R_4=H, R_2=OMe)
160 (R_1=R_2=R_4=H, R_3=OMe)
161 (R_1=R_2=R_3=H, R_4=OMe)

https://dx.doi.org/10.1021/acs.joc.0c02011
J. Org. Chem. XXXX, XXX, XXX−XXX

corresponding propargyl ether and the latter compound then subjected to a gold(I)-catalyzed IMHA and so delivering the corresponding 2*H*-chromene. In our earlier work,[6] we have shown the viability of these processes by engaging a series of simple aryl propargyl ethers in such cyclization reactions. However, while these proceeded under mild conditions, competing formation of the isomeric 2-methylbenzofurans was frequently observed.

Given the occurrence of oxygenated 2,2-dimethyl-2*H*-chromenes as natural products, we sought to establish methods for forming such heterocycles through gold(I)-catalyzed IMHA reactions of the isomeric, open-chain ethers. In particular, the implementation of the two-step sequence, as shown in Scheme 4, became the focus of our efforts in this regard.[28] So, following procedures reported by Ritchie et al.,[28a] treatment of the methoxylated phenols **7**, **16**, and **21** with 3-chloro-3-methylbut-1-yne under Finkelstein-type conditions and in the presence of potassium carbonate afforded the anticipated ethers **155**−**157** in 54−71% yield (Table 4). No evidence for the formation of the corresponding allenic ethers, through competing S_N'-type processes, was obtained.

Table 4. Outcomes of the Reactions Shown in Scheme 4 and Leading to 2*H*-Chromenes 158−161

entry	phenol	ether	yield (%)	2*H*-chromene	yield (%)
1	**16**	**155**	71	**158**	84
2	**21**	**156**	61	**159**/**161**	66/25[a]
3	**7**	**157**	54	**160**	99

[a]A mixture of chromatographically separable regioisomers **159** and **161** was obtained in this reaction.

The IMHA reactions of these product ethers were carried out under essentially the same conditions as employed for the cyclization of the *O*-aryl propiolates and, by such means, the anticipated heterocycles **158**−**161** were obtained. Substrates **155** and **157** each gave the single possible product in excellent yield, but the *m*-methoxylated one, **156**, cyclized by the two available pathways and so forming a mixture of 2*H*-chromenes **159** and **161**. These could be separated from one another by flash chromatography with the former thereby being obtained in 66% yield and latter in 25% yield. Once again, it is presumed that steric effects determine this product distribution. All of these compounds have been reported previously, and the C7- and C8-substituted systems are both naturally occurring compounds (the former, namely **159**, being named precocene I and acting as an inhibitor of juvenile hormone biosynthesis).[29,30] The spectroscopic data obtained on each of theses cyclization products were in complete accord with the assigned structures and matched those reported in the literature (see the Experimental Section for details). It is thus clear that the current procedure provides a means for 2*H*-chromene formation under particularly mild conditions.

CONCLUSIONS

The present study establishes that the commercially available and easily handled Echavarren's catalyst can affect the IMHA reactions of a wide range of *O*-aryl propiolates and aryl propargyl ethers and thereby generating the isomeric coumarins and 2*H*-chromenes, respectively. In the case of the former cyclization process, the ease (or otherwise) with which these proceed is dictated by the nature of the substituents on the aromatic ring in the substrate, with electron-donating ones facilitating the process and electron-withdrawing ones generally acting less favorably. Such observations are consistent with the electrophilic nature of the aurylated alkyne that is presumably the key intermediate and engaging in intramolecular S_EAr reactions.[8]

EXPERIMENTAL SECTION

General Experimental Procedures. Unless otherwise specified, proton (^{1}H) and proton-decoupled carbon (^{13}C) NMR spectra were recorded at room temperature in base-filtered $CDCl_3$ on a Varian spectrometer operating at 400 MHz for proton and 100 MHz for carbon nuclei. For ^{1}H NMR spectra, signals arising from the residual protio-forms of the solvent were used as the internal standards. ^{1}H NMR data are recorded as follows: chemical shift (δ) [multiplicity, coupling constant(s) J (Hz), relative integral], where multiplicity is defined as follows: s = singlet; d = doublet; t = triplet; q = quartet; m = multiplet; or combinations of the above. The signal due to residual $CHCl_3$ appearing at δ_H 7.26 and the central resonance of the $CDCl_3$ "triplet" appearing at δ_C 77.0 were used as reference for ^{1}H and ^{13}C NMR spectra, respectively. Infrared spectra (ν_{max}) were recorded on a PerkinElmer 1800 Series FTIR Spectrometer. Samples were analyzed as thin films on KBr plates. Low-resolution ESI mass spectra were recorded on a single-quadrupole liquid-chromatograph mass spectrometer, while high-resolution measurements were conducted on a time-of-flight instrument. Low- and high-resolution EI mass spectra were recorded on a magnetic-sector machine. Melting points were measured on an OptiMelt automated melting point system and are uncorrected. Analytical thin layer chromatography (TLC) was performed on aluminum-backed 0.2 mm thick silica gel 60 F_{254} plates as supplied by Merck. Eluted plates were visualized using a 254 nm UV lamp and/or by treatment with a suitable dip followed by heating. These dips included phosphomolybdic acid/ceric sulfate/sulfuric acid (conc.)/water (37.5 g:7.5 g:37.5 g:720 mL) or potassium permanganate/potassium carbonate/5% sodium hydroxide aqueous solution/water (3 g:20 g:5 mL:300 mL). Flash chromatographic separations were carried out following protocols defined by Still et al.[31] with silica gel 60 (0.040−0.063 μm) as the stationary phase and using the AR- or HPLC-grade solvents indicated. Starting materials and reagents were generally available from the Sigma-Aldrich, Merck, TCI, Strem or Lancaster Chemical Companies and were used as supplied. Drying agents and other inorganic salts were purchased from the AJAX, BDH, or Unilab Chemical Companies. Tetrahydrofuran, methanol, and dichloromethane were dried using a Glass Contour solvent purification system that is based upon a technology originally described by Grubbs et al.[32] Where necessary, reactions were performed under a nitrogen atmosphere, and when heating was required, this was achieved using an oil bath sitting on top of a stirrer hot-plate fitted with a temperature probe and controller.

Specific Chemical Transformations. *4-Methoxyphenyl (E)-3-(4-Methoxyphenoxy)acrylate (**8**).* Compound **8** (R_f = 0.6 in 1:4 v/v diethyl ether/pentane) was obtained as a clear, colorless oil in varying yields during the course of the optimization studies being undertaken in attempts to establish a synthesis of 4-methoxyphenyl propiolate (**3**). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 (d, J = 12.2 Hz, 1H), 7.01 (complex m, 4H), 6.88 (complex m, 4H), 5.60 (d, J = 12.2 Hz, 1H), 3.79 (s, 3H), 3.78 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 166.3, 162.0, 157.3, 149.6, 144.3, 122.6, 119.8, 115.1, 114.6, 100.6, 55.8, 55.7 (one signal obscured or overlapping); IR ν_{max} (KBr): 1725, 1646, 1502, 1223, 1178, 1095 cm^{-1}; MS (EI, 70 eV) m/z: 300 ($M^{+\bullet}$, 10%), 177 (100). HRMS data could not be acquired on this compound.

*N-Cyclohexyl-N-(cyclohexylcarbamoyl)propiolamide (**10**).* Compound **10**[16] (R_f = 0.5 in 1:4 v/v diethyl ether/pentane) was obtained, in varying yields, as a white, crystalline solid, mp 186−188 °C (lit.[16] mp 168−170 °C), during the course of the optimization studies being undertaken to establish a synthesis of 4-methoxyphenyl propiolate (**3**). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.09 (broad s, 1H), 4.38 (m, 1H), 3.68 (m, 1H), 3.34 (s, 1H), 2.30 (m, 2H), 1.99−1.89 (complex m, 2H), 1.89−1.74 (complex m, 4H), 1.74−1.56 (complex m, 4H), 1.47−1.05 (complex m, 8H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 155.3, 152.4, 81.8, 76.1, 60.4, 49.5, 32.7, 30.6, 26.6, 25.6, 25.1, 24.6; IR ν_{max} (KBr):

https://dx.doi.org/10.1021/acs.joc.0c02011
J. Org. Chem. XXXX, XXX, XXX−XXX

3304, 2990, 2934, 2105, 1694, 1632, 1529, 1453, 1394, 1347, 1304, 1258, 1235, 1077, 1066, 1058 cm^{-1}; MS (EI, 70 eV) *m/z*: 276 ($M^{+\bullet}$, 90%), 195 (100); HRMS (ESI) *m/z*: $[M + Na]^+$ calcd for $C_{16}H_{24}N_2O_2Na$, 299.1730; found, 299.1743. $[M + H]^+$ calcd for $C_{16}H_{25}N_2O_2$, 277.1911; found, 277.1914. This compound was subjected to single-crystal X-ray analysis. Details of this are presented in the Experimental Section and the Supporting Information.

*(Z)-3-Cyclohexyl-2-(cyclohexylimino)-4-methyleneoxazolidin-5-one (**11**).* Compound **11** (R_f = 0.6 in 1:4 v/v diethyl ether/pentane) was obtained, in varying yields, as a white, crystalline solid, mp 81−82 °C, during the course of the optimization studies being undertaken to establish a synthesis of 4-methoxyphenyl propiolate (**3**). ^1H NMR (400 MHz, $CDCl_3$): δ 5.22 (d, *J* = 2.9 Hz, 1H), 4.95 (d, *J* = 2.9 Hz, 1H), 4.00 (m, 1H), 3.65 (m, 1H), 2.24 (m, 2H), 1.88−1.57 (complex m, 10H), 1.44−1.12 (complex m, 8H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 161.1, 147.0, 141.7, 91.4, 54.1, 53.0, 34.2, 28.5, 25.8 (0), 25.7 (6), 25.1, 24.5; IR ν_{max} (KBr): 2930, 2856, 1713, 1669, 1451, 1404, 1388, 1347, 1286, 1075, 1053, 997 cm^{-1}; MS (ESI, +ve) *m/z*: 277 [$(M + H)^+$, 100%], 195 (70); HRMS (ESI) *m/z*: $[M + H]^+$ calcd for $C_{16}H_{25}N_2O_2$, 277.1911; found, 277.1918. This compound was subjected to single-crystal X-ray analysis. Details of this are presented in the Experimental Section and the Supporting Information.

Synthesis of Phenols 22, 23, 25, 26, 27, 33, 34, 38, and 50. *m-[(tert-Butyldimethylsilyl)oxy]phenol (**22**).* A magnetically stirred solution of resorcinol (1.00 g, 9.08 mmol, 1 equiv) in *N*,*N*-dimethylformamide (40 mL) maintained at 18 °C was treated with *tert*-butyldimethylchlorosilane (1.37 g, 9.08 mmol, 1 equiv) and imidazole (618 mg, 9.08 mmol, 1 equiv). The ensuing mixture was stirred at this temperature for 6 h before being concentrated under reduced pressure. The residue thus obtained was subjected to flash chromatography (silica gel, 1:4 v/v ethyl acetate/hexane elution), and concentration of the relevant fractions (R_f = 0.6) then gave compound **22**[33] (701 mg, 34%) as a clear, colorless oil. ^1H NMR (400 MHz, $CDCl_3$): δ 7.07 (t, *J* = 8.1 Hz, 1H), 6.46 (m, 2H), 6.39 (m, 1H), 1.00 (s, 9H), 0.21 (s, 6H) (signal due to OH group proton not observed); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 157.0, 156.6, 130.1, 112.8, 108.8, 107.9, 25.8, 18.3, −4.3; IR ν_{max} (KBr): 3676, 3390, 2988, 2971, 2930, 2901, 1592, 1491, 1473, 1407, 1394, 1294, 1170, 1146, 1075, 1066, 1057 cm^{-1}; MS (EI, 70 eV) *m/z*: 224 ($M^{+\bullet}$, 47%), 167 (100); HRMS (ESI) *m/z*: $[M + H]^+$ calcd for $C_{12}H_{21}O_2Si$, 225.1305; found, 225.1301.

*m-Hydroxyphenyl Acetate (**23**).* A magnetically stirred solution of resorcinol (1.00 g, 9.08 mmol, 1 equiv) in dichloromethane (40 mL) maintained at 18 °C was treated with acetyl chloride (650 μL, 9.08 mmol, 1 equiv). The ensuing mixture was stirred at this temperature for 4 h before being concentrated under reduced pressure. The residue thus obtained was subjected to flash chromatography (silica gel, 1:4 v/v ethyl acetate/hexane elution), and concentration of the relevant fractions (R_f = 0.2) afforded compound **23**[34] (712 mg, 52%) as a clear, colorless oil. ^1H NMR (400 MHz, $CDCl_3$): δ 7.18 (t, *J* = 8.2 Hz, 1H), 6.63 (m, 2H), 6.54 (d, *J* = 2.3 Hz, 1H), 6.10 (broad s, 1H), 2.29 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 170.5, 156.9, 151.5, 130.2, 113.5 (3), 113.4 (5), 109.3, 21.3; IR ν_{max} (KBr): 3676, 3404, 2988, 2901, 1765, 1735, 1602, 1486, 1460, 1372, 1226, 1134, 1075 cm^{-1}; MS (EI, 70 eV) *m/z*: 152 ($M^{+\bullet}$, 27%), 110 (100); HRMS (ESI) *m/z*: $[M + Na]^+$ calcd for $C_8H_8O_3Na$, 175.0366; found, 175.0358. $[M + H]^+$ calcd for $C_8H_9O_3$, 153.0546; found, 153.0542.

*m-Hydroxyphenyl Benzoate (**25**).* A magnetically stirred solution of resorcinol (1.00 g, 9.08 mmol, 1 equiv) in dichloromethane (40 mL) maintained at 18 °C was treated with benzoyl chloride (1.05 mL, 9.08 mmol, 1 equiv). The ensuing mixture was stirred at this temperature for 4 h before being concentrated under reduced pressure. The residue thus obtained was subjected to flash chromatography (silica gel, 1:4 v/v ethyl acetate/hexane elution), and concentration of the relevant fractions (R_f = 0.3) then gave compound **25**[35] (997 mg, 51%) as a colorless, crystalline solid, mp 133−134 °C (lit.[35] mp 133−136 °C). ^1H NMR (400 MHz, $CDCl_3$): δ 8.26 (d, *J* = 8.0 Hz, 2H), 7.70 (m, 1H), 7.57 (t, *J* = 8.0 Hz, 2H), 7.33 (m, 1H), 6.86 (d, *J* = 8.3 Hz, 1H), 6.79 (m, 2H), 5.24 (m, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 165.5, 156.8, 152.0, 133.8, 130.4, 130.3, 129.6, 128.8, 114.1, 113.4, 109.6; IR ν_{max} (KBr): 3676, 3406, 2988, 2972, 2901, 1734, 1715, 1601, 1484, 1453, 1406, 1394, 1382, 1264, 1139, 1066 cm^{-1}; MS (EI, 70 eV) *m/z*: 214 ($M^{+\bullet}$, 21%), 105 (100); HRMS (ESI) *m/z*: $[M + Na]^+$ calcd for $C_{13}H_{10}O_3Na$, 237.0522; found, 237.0526. $[M + H]^+$ calcd for $C_{13}H_{11}O_3$, 215.0703; found, 215.0702.

*m-Hydroxyphenyl Pivalate (**26**).* A magnetically stirred solution of resorcinol (1.00 g, 9.08 mmol, 1 equiv) in dichloromethane (40 mL) maintained at 18 °C was treated with pivaloyl chloride (1.12 mL, 9.08, 1 equiv). The ensuing mixture was stirred at this temperature for 4 h before being concentrated under reduced pressure. The residue thus obtained was subjected to flash chromatography (silica gel, 1:4 v/v ethyl acetate/hexane elution), and concentration of the relevant fractions (R_f = 0.5) then gave compound **26**[36] (860 mg, 49%) as a clear, colorless oil. ^1H NMR (400 MHz, $CDCl_3$): δ 7.16 (t, *J* = 8.1 Hz, 1H), 6.62 (m, 2H), 6.50 (t, *J* = 2.3 Hz, 1H), 2.07 (s, 9H) (signal due to OH group proton not observed); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 178.1, 157.0, 151.9, 130.1, 113.4, 113.3, 109.3, 39.3, 27.2; IR ν_{max} (KBr): 3676, 3418, 2973, 2901, 1730, 1604, 1479, 1461, 1395, 1271, 1229, 1139, 1114, 1075, 1066, 1057 cm^{-1}; MS (EI, 70 eV) *m/z*: 194 ($M^{+\bullet}$, 26%), 110 (100); HRMS (ESI) *m/z*: $[M + H]^+$ calcd for $C_{11}H_{15}O_3$, 195.1016; found, 195.1013.

*m-(Benzyloxy)phenol (**27**).* A magnetically stirred solution of resorcinol (1.00 g, 9.08 mmol, 1 equiv) in acetone (40 mL) maintained at 18 °C was treated with benzyl bromide (1.08 mL, 9.08 mmol, 1 equiv) and then with potassium carbonate (1.88 g, 13.62 mmol, 1.5 equiv). The ensuing mixture was stirred at this temperature for 6 h before being concentrated under reduced pressure, and the residue thus obtained was subjected to flash chromatography (silica gel, 1:4 v/v ethyl acetate/hexane elution). Concentration of the relevant fractions (R_f = 0.4) then gave compound **27**[37] (764 mg, 42%) as a clear, pink oil. ^1H NMR (400 MHz, $CDCl_3$): δ 7.45−7.32 (complex m, 5H), 7.14 (t, *J* = 8.1 Hz, 1H), 6.58 (m, 1H), 6.49 (t, *J* = 2.4 Hz, 1H), 6.44 (m, 1H), 5.04 (s, 2H), 5.00 (broad s, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 160.3, 156.9, 137.1, 130.3, 128.7, 128.1, 127.6, 108.3, 107.5, 102.7, 70.2; IR ν_{max} (KBr): 3676, 3390, 2988, 2973, 2901, 1595, 1491, 1454, 1406, 1394, 1284, 1172, 1147, 1076, 1066, 1050 cm^{-1}; MS (EI, 70 eV) *m/z*: 200 ($M^{+\bullet}$, 72%), 91 (100); HRMS (ESI) *m/z*: $[M + H]^+$ calcd for $C_{13}H_{13}O_3$, 201.0910; found, 201.0912.

*p-(Triethylsilyl)phenol (**33**).* A magnetically stirred solution of *p*-bromophenol (1.00 g, 5.78 mmol, 1 equiv) in dry tetrahydrofuran (50 mL) was treated with *n*-butyllithium (13 mL of a 1.33 M solution in tetrahydrofuran, 17.3 mmol, 3 equiv) at −78 °C. The resulting solution was stirred for 1 h at −78 °C then chlorotriethylsilane (17.3 mmol, 3 equiv) was added and the reaction mixture allowed to warm to 18 °C and then stirred at this temperature for 4 h before ammonium chloride (1 × 60 mL of a saturated aqueous solution) was added. The separated aqueous phase was extracted with ethyl acetate (3 × 50 mL), and the combined organic phases were washed with brine (1 × 50 mL) before being dried ($MgSO_4$), filtered, and concentrated under reduced pressure. The residue thus obtained was subjected to flash chromatography (silica gel, 1:8 v/v mixture of ethyl acetate/hexane elution), and concentration of the relevant fractions then gave compound **33**[38] (1.11 g, 92%) (R_f = 0.3 in 1:8 v/v ethyl acetate/hexane) as a yellow and low-melting solid, mp 29 °C (lit.[38] mp 31−32 °C). ^1H NMR (400 MHz, $CDCl_3$): δ 7.37 (d, *J* = 8.5 Hz, 2H), 6.84 (d, *J* = 8.5 Hz, 2H), 4.84 (s, 1H), 0.96 (t, *J* = 7.8 Hz, 9H), 0.77 (q, *J* = 7.8 Hz, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 156.3, 135.9, 128.6, 115.0, 7.5, 3.7; IR ν_{max} (KBr): 3341, 2954, 2875, 1599, 1583, 1503, 1458, 1416, 1361, 1256, 1237, 1179, 1107, 1054, 1033, 1007 cm^{-1}; MS (EI, 70 eV) *m/z*: 208 ($M^{+\bullet}$, 16%), 179 (90), 151 (92), 123 (100). HRMS data could not be acquired on this compound.

*p-(tert-Butyldimethylsilyl)phenol (**34**).* Following the same procedure as used in the preparation of compound **33** but using *tert*-butyldimethylchlorosilane in place of chlorotriethylsilane afforded, after work-up and column chromatography, compound **34**[39] (609 mg, 51%) (R_f = 0.3 in 1:8 v/v ethyl acetate/hexane) as a colorless, crystalline solid, mp 96−97 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 7.39 (d, *J* = 8.5 Hz, 2H), 6.83 (d, *J* = 8.5 Hz, 2H), 4.69 (s, 1H), 0.86 (s, 9H), 0.24 (s, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 156.4, 136.2, 129.1, 114.8, 26.6, 17.1, −5.9; IR ν_{max} (KBr): 3286, 2953, 2927, 2856, 1600, 1585, 1502, 1470, 1427, 1361, 1248, 1182, 1107, 1055, 1033, 1008 cm^{-1}; MS

https://dx.doi.org/10.1021/acs.joc.0c02011
J. Org. Chem. XXXX, XXX, XXX−XXX

(EI, 70 eV) m/z: 208 ($M^{+\bullet}$, 4%), 151 (100). HRMS data could not be acquired on this compound.

*p-Hydroxyphenyl Trifluoromethanesulfonate (**38**).* A magnetically stirred solution of hydroquinone (**44**) (2.00 g, 14.69 mmol, 1 equiv) in dichloromethane (150 mL) maintained at 0 °C was treated with trifluoromethanesulfonyl chloride (1.56 mL, 14.69 mmol, 1 equiv) and then with triethylamine (2.05 g, 14.69 mmol, 1 equiv). The resulting mixture was stirred for 4 h at 0 °C then quenched by the addition of hydrochloric acid (20 mL of a 2.0 M aqueous solution). The separated aqueous phase was extracted with dichloromethane (2 × 30 mL), and the combined organic phases were then dried ($MgSO_4$), filtered, and the filtrate was concentrated under reduced pressure. The residue thus obtained was subjected to flash chromatography (silica gel, 1:4 v/v ethyl acetate/hexane elution), and concentration of the relevant fractions (R_f = 0.3 in 1:4 v/v ethyl acetate/hexane) gave compound **38**[40] (580 mg, 19%) as a clear, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.15 (d, J = 9.1 Hz, 2H), 6.86 (d, J = 9.1 Hz, 2H), 5.17 (s, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 155.4, 143.3, 122.8, 120.4 (q, J_{C-F} = 322 Hz), 116.8; IR ν_{max} (KBr): 3277, 1600, 1505, 1420, 1249, 1212, 1167, 1138 cm^{-1}; MS (EI, 70 eV) m/z: 242 ($M^{+\bullet}$, 25%), 109 (100). HRMS data could not be acquired on this compound.

*Methyl (tert-Butoxycarbonyl)-L-tyrosinate (**50**).* A magnetically stirred solution of L-tyrosine methyl ester hydrochloride (1.00 g, 4.32 mmol, 1 equiv) in dichloromethane (50 mL) maintained at 0 °C was treated with triethylamine (1.20 mL, 8.63 mmol, 2 equiv). The ensuing mixture was stirred for 0.5 h at 0 °C before being treated with *tert*-butyloxycarbonyl anhydride (1.04 g, 4.75 mmol, 1.1 equiv). The resulting mixture was stirred at 0 °C for 16 h, warmed to room temperature, washed with citric acid (2 × 20 mL of a 1.0 M aqueous solution) and then brine (2 × 20 mL). The separated organic phase was dried (Na_2SO_4), filtered, and then concentrated under reduced pressure. The residue thus obtained was subjected to flash chromatography (silica gel, 1:4 v/v ethyl acetate/hexane elution), and concentration of the relevant fractions (R_f = 0.1) gave compound **50**[41] (1.20 g, 94%) as a colorless, crystalline solid, mp 102−103 °C (lit.[41] mp 100−102 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.96 (d, J = 8.0 Hz, 2H), 6.73 (d, J = 8.0 Hz, 2H), 5.68 (broad s, 1H), 5.00 (broad s, 1H), 4.53 (broad s, 1H), 3.71 (s, 3H), 3.00 (m, 2H), 1.42 (s, 9H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 172.6, 155.2, 155.0, 130.4, 127.7, 115.5, 80.1, 54.6, 52.2, 37.6, 28.3; IR ν_{max} (KBr): 3265, 2981, 1735, 1688, 1616, 1517, 1445, 1393, 1368, 1249, 1224, 1165, 1105, 1019 cm^{-1}; MS (ESI, +ve) m/z: 296 [$(M + H)^+$, 35%]; 282 (100); HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{15}H_{21}NO_5Na$, 318.1312; found, 318.1325.

General Protocols for the Synthesis of *O*-Aryl Propiolates 3 and 56−99. *Procedure A—Formation of Aryl Propiolates Using DCC.* A magnetically stirred solution of the relevant phenol (1 mmol, 1 equiv) and propiolic acid (1.2 mmol, 1.2 equiv) in chloroform (20 mL) maintained at 0 °C was treated with DCC (1.2 mmol, 1 equiv). The solution thus obtained was allowed to warm to 18 °C and then stirred at this temperature for 16 h before being concentrated under reduced pressure. The ensuing residue was taken up in acetonitrile (20 mL), and the mixture thus formed filtered. The filtrate was concentrated under reduced pressure, and the residue was subjected to flash chromatography (silica gel, 1:4 v/v mixture of diethyl ether/hexane elution). Concentration of the relevant fractions then gave the corresponding aryl propiolate.

Procedure B—Formation of Aryl Propiolates Using DCC/NaH. A magnetically stirred solution of the relevant phenol (1.0 mmol, 1.0 equiv) in tetrahydrofuran (10 mL) maintained at 0 °C was treated with sodium hydride (60% suspension in mineral oil, 1.1 mmol, 1.1 equiv). In a second flask, a magnetically stirred solution of propiolic acid (3.3 mmol, 3.3 equiv) in tetrahydrofuran (10 mL) was cooled to 0 °C and then treated with DCC (3.3 mmol, 3.3 equiv) followed by the mixture obtained by treating the phenol with NaH. The resulting mixture was allowed to warm to 18 °C and then stirred at this temperature for 16 h before being concentrated under reduced pressure. The residue so obtained was taken up in acetonitrile (10 mL) and filtered. The filtrate was concentrated under reduced pressure, and the residue thus obtained subjected to flash chromatography (silica gel, 1:4 v/v mixture of diethyl ether/hexane elution). Concentration of the relevant fractions gave the corresponding aryl propiolate.

Procedure C—Formation of Aryl Propiolates through In Situ Acyl Chloride Formation. A magnetically stirred solution of the carboxylic acid **12** or **13** (1 mmol, 1 equiv) and oxalyl chloride (1.1 mmol, 1.1 equiv) in dichloromethane (10 mL) maintained at 0 °C was treated with a few drops of *N*,*N*-dimethylformamide. After gas evolution had ceased (*ca.* 0.08 h), the reaction mixture was allowed to warm to 18 °C and then stirred at this temperature for 0.33 h before being treated with the requisite phenol (1.0 mmol, 1.0 equiv). The ensuing mixture was concentrated under reduced pressure, and the residue thus obtained was taken up in acetonitrile (10 mL) and filtered. The filtrate was concentrated under reduced pressure, and the residue so-formed was subjected to flash chromatography (silica gel, 1:4 v/v mixture of diethyl ether/hexane elution). Concentration of the relevant fractions then gave the corresponding aryl propiolate.

*p-Methoxyphenyl Propiolate (**3**).* Compound **3**[42] (278 mg, 98%) (R_f = 0.7 in 1:4 v/v diethyl ether/pentane) was prepared using General Procedure B and isolated as a clear, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.07 (d, J = 8.4 Hz, 2H), 6.90 (d, J = 8.4 Hz, 2H), 3.80 (s, 3H), 3.06 (s, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 157.8, 151.5, 143.4, 122.1, 114.7, 76.9, 74.4, 55.7; IR ν_{max} (KBr): 3260, 2123, 1727, 1597, 1504, 1465, 1442, 1251, 1199, 1177, 1103, 1031, 1009, 905 cm^{-1}; MS (EI, 70 eV) m/z: 176 ($M^{+\bullet}$, 80%), 124 (100), 123 (70), 120 (52), 109 (50), 95 (48), 91 (20); HRMS (EI) m/z: $M^{+\bullet}$ calcd for $C_{10}H_8O_3$, 176.0473; found, 176.0474.

*Phenyl Propiolate (**56**).* Compound **56**[43] (278 mg, 64%) (R_f = 0.9 in 1:4 v/v diethyl ether/hexane) was prepared using General Procedure A and isolated as clear, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32 (t, J = 7.7 Hz, 2H), 7.19 (t, J = 7.7 Hz, 1H), 7.07 (d, J = 7.7 Hz, 2H), 2.99 (s, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 151.1, 149.9, 129.8, 126.7, 121.4, 76.9, 74.4; IR ν_{max} (KBr): 3444, 3278, 3065, 2934, 2857, 2386, 2126, 1947, 1854, 1733, 1649, 1591, 1492, 1456, 1416, 1289, 1202, 1106, 1072, 1024, 1006, 929 cm^{-1}; MS (ESI, +ve) m/z: 169 [$(M + Na)^+$, 100%], 147 [$(M + H)^+$, 40]; HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_9H_6O_2Na$, 169.0265; found, 169.0262. $[M + H]^+$ calcd for $C_9H_7O_2$, 147.0446; found, 147.0443.

*o-Ethylphenyl Propiolate (**57**).* Compound **57** (198 mg, 69%) (R_f = 0.5 in 1:1 v/v chloroform/hexane) was prepared using General Procedure B and isolated as clear, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33 (d, J = 3.6 Hz, 1H), 7.26 (m, 2H), 7.11 (m, 1H), 3.10 (s, 1H), 2.64 (q, J = 7.6 Hz, 2H), 1.27 (t, J = 7.6 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 151.1, 148.0, 135.7, 129.7, 127.1, 127.0, 121.9, 76.9, 74.2, 23.1, 14.1; IR ν_{max} (KBr): 3271, 2973, 2937, 2126, 1730, 1489, 1454, 1193, 1168, 1114 cm^{-1}; MS (EI, 70 eV) m/z: 174 ($M^{+\bullet}$, 71%), 145 (100); HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{11}H_{11}O_2$, 175.0754; found, 175.0754.

*o-Methoxyphenyl Propiolate (**58**).* Compound **58** (510 mg, 72%) (R_f = 0.8 in chloroform) was prepared using General Procedure B and isolated as clear, yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.23 (m, 1H), 7.09 (m, 1H), 6.98 (m, 2H), 3.85 (s, 3H), 3.05 (s, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 151.1, 150.7, 139.0, 127.9, 122.7, 121.0, 112.9, 76.8, 74.4, 56.1; IR ν_{max} (KBr): 3270, 2125, 1733, 1499, 1309, 1281, 1260, 1193, 1171, 1159, 1110, 1042, 1024 cm^{-1}; MS (EI, 70 eV) m/z: 176 ($M^{+\bullet}$, 77%), 145 (85), 124 (100); HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{10}H_8O_3Na$, 199.0366; found, 199.0372. $[M + H]^+$ calcd for $C_{10}H_9O_3$, 177.0546; found, 177.0539.

*o-Acetylphenyl Propiolate (**59**).* Compound **59** (75 mg, 25%) (R_f = 0.3 in 1:4 v/v ethyl acetate/hexane) was prepared using General Procedure B and isolated as clear, yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82 (dd, J = 7.8 and 1.7 Hz, 1H), 7.54 (m, 1H), 7.36 (m, 1H), 7.16 (dd, J = 8.1 and 1.2 Hz, 1H), 3.13 (s, 1H), 2.56 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 197.0, 150.8, 147.9, 133.7, 130.5 (9), 130.5 (5), 127.0, 123.6, 77.4, 74.2, 29.5; IR ν_{max} (KBr): 3258, 2926, 2856, 2126, 1733, 1687, 1605, 1483, 1448, 1359, 1284, 1255, 1186, 1072 cm^{-1}; MS (EI, 70 eV) m/z: 188 ($M^{+\bullet}$, 16%), 173 (14), 145 (54), 121 (100); HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{11}H_8O_3Na$, 211.0366; found, 211.0369. $[M + H]^+$ calcd for $C_{11}H_9O_3$, 189.0546; found, 189.0551.

https://dx.doi.org/10.1021/acs.joc.0c02011
J. Org. Chem. XXXX, XXX, XXX−XXX

*o-(Trifluoromethyl)phenyl Propiolate (**60**).* Compound **60** (202 mg, 70%) (R_f = 0.6 in 1:2:3 v/v/v ethyl acetate/dichloromethane/hexane) was prepared using General Procedure B and isolated as clear, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70 (d, J = 8.0 Hz, 1H), 7.60 (m, 1H), 7.42 (m, 1H), 7.27 (d, J = 8.0 Hz, 1H), 3.12 (s, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 150.4, 147.1, 133.4, 127.3, 127.0, 124.2, 123.1 (q, J_{C-F} = 32 Hz), 122.9 (q, J_{C-F} = 272 Hz), 77.9, 73.7; IR ν_{max} (KBr): 3297, 2934, 2856, 2130, 1741, 1613, 1494, 1456, 1321, 1275, 1206, 1168, 1135, 1113, 1056 cm^{-1}; MS (ESI, +ve) m/z: 277 (100%), 214 ($M^{+\bullet}$, 18), 186 (22). HRMS data could not be acquired on this compound.

*o-Bromophenyl Propiolate (**61**).* Compound **61** (253 mg, 97%) (R_f = 0.7 in chloroform) was prepared using General Procedure B and isolated as clear, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64 (dd, J = 8.2 and 1.5 Hz, 1H), 7.36 (m, 1H), 7.18 (m, 2H), 3.11 (s, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 150.0, 147.4, 133.8, 128.8, 128.2, 123.6, 116.0, 77.6, 74.0; IR ν_{max} (KBr): 3284, 2973, 2866, 2127, 1734, 1470, 1445, 1179, 1046, 1033 cm^{-1}; MS (EI, 70 eV) m/z: 226 and 224 ($M^{+\bullet}$, both 13%), 198 and 196 (both 5), 174 and 172 (both 17), 145 (100); HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_9H_6{}^{79}BrO_2$, 224.9546; found, 224.9553.

*o-Chlorophenyl Propiolate (**62**).* Compound **62** (530 mg, 87%) (R_f = 0.3 in 1:9 v/v diethyl ether/hexane) was prepared using General Procedure B and isolated as clear, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59 (d, J = 7.6 Hz, 1H), 7.43 (m, 1H), 7.36 (m, 1H), 7.32 (d, J = 7.6 Hz, 1H), 3.24 (s, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 150.0, 146.0, 130.7, 128.1, 128.0, 126.8, 123.5, 77.6, 73.8; IR ν_{max} (KBr): 3286, 2128, 1738, 1583, 1474, 1448, 1262, 1181, 1062 cm^{-1}; MS (EI, 70 eV) m/z: 182 and 180 ($M^{+\bullet}$, 8 and 25%), 145 (100); HRMS (EI) m/z: $M^{+\bullet}$ calcd for $C_9H_5{}^{37}ClO_2$, 181.9949; found, 181.9942. $M^{+\bullet}$ calcd for $C_9H_5{}^{35}ClO_2$, 179.9978; found, 179.9972.

*m-Methoxyphenyl Propiolate (**63**).* Compound **63**[44] (280 mg, 99%) (R_f = 0.6 in 1:4 v/v diethyl ether/hexane) was prepared using General Procedure B and isolated as clear, yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30 (t, J = 8.2 Hz, 1H), 6.83 (dd, J = 8.2 and 2.4 Hz, 1H), 6.76 (dd, J = 8.2 and 2.4 Hz, 1H), 6.71 (broad s, 1H), 3.79 (s, 3H), 3.11 (s, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 160.6, 150.9, 150.7, 130.1, 113.4, 112.5, 107.3, 77.1, 74.2, 55.5; IR ν_{max} (KBr): 3267, 2120, 1727, 1609, 1588, 1488, 1468, 1453, 1439, 1315, 1286, 1263, 1183, 1128, 1077, 1037, 997, 945, 906 cm^{-1}; MS (EI, 70 eV) m/z: 176 ($M^{+\bullet}$, 80%), 124 (100), 123 (58); HRMS (EI) m/z: $M^{+\bullet}$ calcd for $C_{10}H_8O_3$, 176.0473; found, 176.0475.

*m-[(tert-Butyldimethylsilyl)oxy]phenyl Propiolate (**64**).* Compound **64** (196 mg, 80%) (R_f = 0.3 in 1:2 v/v chloroform/hexane) was prepared using General Procedure B and isolated as clear, yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.23 (t, J = 8.2 Hz, 1H), 6.76 (m, 2H), 6.65 (t, J = 2.3 Hz, 1H), 3.05 (s, 1H), 0.99 (s, 9H), 0.21 (s, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 156.8, 150.9, 150.7, 130.0, 118.5, 114.2, 113.6, 76.8, 74.5, 25.8, 18.3, −4.3; IR ν_{max} (KBr): 3272, 2957, 2931, 2860, 2126, 1767, 1735, 1604, 1587, 1485, 1282, 1258, 1182, 1130 cm^{-1}; MS (EI, 70 eV) m/z: 276 ($M^{+\bullet}$, 39%), 219 (54), 163 (100); HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{15}H_{20}O_3SiNa$, 299.1074; found, 299.1063. $[M + H]^+$ calcd for $C_{15}H_{21}O_3Si$, 277.1254; found, 277.1250.

*m-Acetoxyphenyl Propiolate (**65**).* Compound **65** (120 mg, 45%) (R_f = 0.6 in 1:2:3 v/v/v ethyl acetate/dichloromethane/hexane) was prepared using General Procedure B and isolated as clear, yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38 (t, J = 8.2 Hz, 1H), 7.05−6.95 (complex m, 3H), 3.11 (s, 1H), 2.26 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 168.9, 151.3, 150.5, 150.2, 129.9, 119.9, 118.7, 115.2, 77.4, 74.0, 21.0; IR ν_{max} (KBr): 3262, 2990, 2901, 2123, 1767, 1734, 1601, 1485, 1371, 1182, 1121 cm^{-1}; MS (EI, 70 eV) m/z: 204 ($M^{+\bullet}$, 25%), 162 (89), 134 (100); HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{11}H_8O_4Na$, 227.0315; found, 227.0305. $[M + H]^+$ calcd for $C_{11}H_9O_4$, 205.0495; found, 205.0488.

*m-Cyanophenyl Propiolate (**66**).* Compound **66** (202 mg, 70%) (R_f = 0.6 in 1:2:3 v/v/v ethyl acetate/dichloromethane/hexane) was prepared using General Procedure B and isolated as a colorless, crystalline solid, mp 112−113 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65−48 (complex m, 3H), 7.42 (m, 1H), 3.15 (s, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 150.2, 150.0, 130.8, 130.4, 126.3, 125.2, 117.6, 114.0, 78.1, 73.8; IR ν_{max} (KBr): 3269, 2990, 2901, 2236, 2122, 1735, 1584, 1481, 1433, 1394, 1234, 1186, 1066, 1058 cm^{-1}; MS (CI) m/z: 170 [$(M - H)^-$, 27%], 143 (24), 115 (24), 53 (100); HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{10}H_6NO_2$, 172.0393; found, 172.0397. This compound was subjected to single-crystal X-ray analysis. Details of this are presented in the Experimental Section and the Supporting Information.

*m-(Propioloyloxy)phenyl Benzoate (**67**).* Compound **67** (105 mg, 42%) (R_f = 0.4 in 1:4 v/v diethyl ether/hexane) was prepared using General Procedure B and isolated as a colorless, crystalline solid, mp 64−65 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.20 (dd, J = 8.2 and 1.0 Hz, 2H), 7.65 (m, 1H), 7.55−7.35 (complex m, 3H), 7.20−7.00 (complex m, 3H), 3.11 (s, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 164.7, 151.6, 150.6, 150.3, 133.9, 130.3, 130.1, 129.3, 128.7, 120.1, 118.8, 115.5, 77.3, 74.2; IR ν_{max} (KBr): 3262, 2990, 2901, 2122, 1734, 1699, 1483, 1452, 1262, 1235, 1189, 1124, 1079, 1061, 1025 cm^{-1}; MS (EI, 70 eV) m/z: 266 ($M^{+\bullet}$, 16%), 105 (100); HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{16}H_{10}O_4Na$, 289.0471; found, 289.0460. $[M + H]^+$ calcd for $C_{16}H_{11}O_4$, 267.0652; found, 267.0640.

*m-(Pivaloyloxy)phenyl Propiolate (**68**).* Compound **68** (102 mg, 40%) (R_f = 0.5 in 1:4 v/v ethyl acetate/hexane) was prepared using General Procedure B and isolated as clear, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38 (t, J = 8.2 Hz, 1H), 7.08−6.85 (complex m, 3H), 3.10 (s, 1H), 1.35 (s, 9H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 176.6, 151.8, 150.5, 150.3, 129.9, 119.8, 118.5, 115.2, 77.3, 74.1, 39.2, 27.1; IR ν_{max} (KBr): 3260, 2975, 2875, 2123, 1737, 1599, 1481, 1398, 1368, 1272, 1241, 1188, 1124, 1107, 1032, 1005 cm^{-1}; MS (EI, 70 eV) m/z: 246 ($M^{+\bullet}$, 16%), 162 (33), 134 (67), 57 (100); HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{14}H_{14}O_4Na$, 269.0784; found, 269.0789. $[M + H]^+$ calcd for $C_{14}H_{15}O_4$, 247.0965; found, 247.0969.

*m-(Benzyloxy)phenyl Propiolate (**69**).* Compound **69** (196 mg, 78%) (R_f = 0.6 in 1:4 v/v diethyl ether/hexane) was prepared using General Procedure B and isolated as clear, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45−7.30 (complex m, 6H), 6.90 (m, 1H), 6.80 (m, 2H), 5.06 (s, 2H), 3.06 (s, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 159.9, 150.8, 136.6, 130.2, 128.8, 128.3, 127.6, 113.8, 113.4, 108.4, 76.9, 74.4, 70.5 (one signal obscured or overlapping); IR ν_{max} (KBr): 3271, 2990, 2901, 2123, 1732, 1607, 1588, 1486, 1454, 1394, 1383, 1287, 1257, 1192, 1129, 1077, 1066, 1044, 1027 cm^{-1}; MS (EI, 70 eV) m/z: 252 ($M^{+\bullet}$, 10%), 91 (100); HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{16}H_{13}O_3$, 253.0859; found, 253.0854.

*m-Acetylphenyl Propiolate (**70**).* Compound **70** (219 mg, 79%) (R_f = 0.2 in 1:4 v/v ethyl acetate/hexane) was prepared using General Procedure B and isolated as a colorless, crystalline solid, mp 61−62 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86 (d, J = 7.9 Hz, 1H), 7.73 (m, 1H), 7.51 (t, J = 7.9 Hz, 1H), 7.36 (dm, J = 7.9 Hz, 1H), 3.11 (s, 1H), 2.60 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 196.7, 150.8, 150.2, 138.9, 130.0, 126.6, 126.1, 121.3, 77.4, 74.1, 26.8; IR ν_{max} (KBr): 3258, 2924, 2123, 1733, 1686, 1586, 1483, 1360, 1263, 1190 cm^{-1}; MS (EI, 70 eV) m/z: 188 ($M^{+\bullet}$, 25%), 187 (73), 173 (49), 160 (38), 145 (66), 121 (56), 53 (100); HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{11}H_8O_3Na$, 211.0366; found, 211.0369. $[M + H]^+$ calcd for $C_{11}H_9O_3$, 189.0546; found, 189.0551.

*m-Fluorophenyl Propiolate (**71**).* Compound **71** (575 mg, 79%) (R_f = 0.8 in chloroform) was prepared using General Procedure B and isolated as clear, yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37 (m, 1H), 7.05−6.85 (complex m, 3H), 3.09 (s, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 163.0 (d, J_{C-F} = 248 Hz), 150.7 (d, J_{C-F} = 11 Hz), 150.5, 130.6 (d, J_{C-F} = 9 Hz), 117.2 (d, J_{C-F} = 4 Hz), 113.8 (d, J_{C-F} = 21 Hz), 109.6 (d, J_{C-F} = 25 Hz), 77.3, 74.1; IR ν_{max} (KBr): 3291, 2981, 2126, 1735, 1603, 1486, 1450, 1254, 1187, 1117, 1073 cm^{-1}; MS (EI, 70 eV) m/z: 164 ($M^{+\bullet}$, 28%), 136 (52). HRMS data could not be acquired on this compound.

*m-Chlorophenyl Propiolate (**72**).* Compound **72** (670 mg, 95%) (R_f = 0.7 in chloroform) was prepared using General Procedure B and isolated as clear, yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36 (t, J = 8.1 Hz, 1H), 7.30 (m, 1H), 7.22 (broad s, 1H), 7.09 (m, 1H), 3.12 (s, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 150.5, 150.3, 135.1, 130.5, 127.1, 122.1, 119.8, 77.4, 74.1; IR ν_{max} (KBr): 3288, 2128, 1734, 1590,

https://dx.doi.org/10.1021/acs.joc.0c02011
J. Org. Chem. XXXX, XXX, XXX−XXX

1471, 1432, 1266, 1198, 1091, 1070, 1002 cm^{-1}; MS (EI, 70 eV) *m/z*: 182 and 180 ($M^{+\bullet}$, 21 and 63%), 53 (100); HRMS (ESI) *m/z*: $[M + H]^+$ calcd for $C_9H_6{}^{37}ClO_2$, 183.0021; found, 183.0023. $[M + H]^+$ calcd for $C_9H_6{}^{35}ClO_2$, 181.0051; found, 181.0053.

*m-Bromophenyl Propiolate (**73**).* Compound **73** (251 mg, 96%) (R_f = 0.8 in chloroform) was prepared using General Procedure B and isolated as clear, colorless oil. ^1H NMR (400 MHz, $CDCl_3$): δ 7.42 (m, 1H), 7.36 (broad s, 1H), 7.27 (t, *J* = 8.0 Hz, 1H), 7.11 (m, 1H), 3.09 (s, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 150.5, 150.4, 130.8, 130.0, 124.9, 122.7, 120.3, 77.4, 74.1; IR ν_{max} (KBr): 3285, 2973, 2127, 1733, 1586, 1470, 1427, 1193, 1063, 1033, 1000 cm^{-1}; MS (EI, 70 eV) *m/z*: 226 and 224 ($M^{+\bullet}$, both 35%), 196 and 198 (both 23), 172 and 174 (both 23), 145 (73), 53 (100). HRMS data could not be acquired on this compound.

*p-Tolyl Propiolate (**74**).* Compound **74**[45] (253 mg, 85%) (R_f = 0.5 in 1:4 v/v diethyl ether/hexane) was prepared using General Procedure B and isolated as clear, colorless oil. ^1H NMR (400 MHz, $CDCl_3$): δ 7.22 (d, *J* = 8.4 Hz, 2H), 7.06 (d, *J* = 8.4 Hz, 2H), 3.10 (s, 1H), 2.38 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 151.2, 147.6, 136.3, 130.1, 120.9, 77.0, 74.3, 20.8; IR ν_{max} (KBr): 3273, 2125, 1729, 1505, 1217, 1191, 1019, 910 cm^{-1}; MS (EI, 70 eV) *m/z*: 160 ($M^{+\bullet}$, 70%), 145 (18), 132 (32), 108 (75), 107 (100), 104 (80), 91 (12), 77 (48); HRMS (EI) *m/z*: $M^{+\bullet}$ calcd for $C_{10}H_8O_2$, 160.0524; found, 160.0522.

*p-Triethylsilylphenyl Propiolate (**75**).* Compound **75** (130 mg, 52%) (R_f = 0.9 in chloroform) was prepared using General Procedure B and isolated as clear, colorless oil. ^1H NMR (400 MHz, $CDCl_3$): δ 7.54 (d, *J* = 8.5 Hz, 2H), 7.16 (d, *J* = 8.5 Hz, 2H), 3.08 (s, 1H), 0.99 (t, *J* = 7.8 Hz, 9H), 0.82 (q, *J* = 7.8 Hz, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 151.0, 150.6, 136.3, 135.7, 120.6, 76.7, 74.5, 7.5, 3.5; IR ν_{max} (KBr): 3275, 2956, 2911, 2876, 2127, 1734, 1616, 1589, 1496, 1457, 1416, 1389, 1288, 1262, 1191, 1124, 1102, 1009 cm^{-1}; MS (EI, 70 eV) *m/z*: 260 ($M^{+\bullet}$, 7%), 231 (100), 203 (93), 175 (73); HRMS (ESI) *m/z*: $[M + H]^+$ calcd for $C_{15}H_{21}O_2Si$, 261.1305; found, 261.1299.

*p-tert-Butyldimethylsilylphenyl Propiolate (**76**).* Compound **76** (145 mg, 58%) (R_f = 0.9 in chloroform) was prepared using General Procedure B and isolated as clear, colorless oil. ^1H NMR (400 MHz, $CDCl_3$): δ 7.54 (d, *J* = 8.5 Hz, 2H), 7.13 (d, *J* = 8.5 Hz, 2H), 3.06 (s, 1H), 0.88 (s, 9H), 0.27 (s, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 151.0, 150.7, 136.6, 135.9, 120.4, 76.8, 74.5, 26.6, 17.0, −6.0; IR ν_{max} (KBr): 3236, 2953, 2928, 2855, 2127, 2109, 1721, 1589, 1497, 1470, 1463, 1389, 1361, 1260, 1209, 1165, 1102, 1019, 1010 cm^{-1}; MS (EI, 70 eV) *m/z*: 260 ($M^{+\bullet}$, 5%), 203 (100), 175 (20); HRMS (ESI) *m/z*: $[M + Na]^+$ calcd for $C_{15}H_{20}O_2SiNa$, 283.1125; found, 283.1129. This compound was subjected to single-crystal X-ray analysis. Details of this are presented in the Experimental Section and the Supporting Information.

*p-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl Propiolate (**77**).* Compound **77** (150 mg, 70%) (R_f = 0.5 in 1:4 v/v diethyl ether/hexane) was prepared using General Procedure B and isolated as a colorless, crystalline solid, mp 72−75 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 7.86 (d, *J* = 7.9 Hz, 2H), 7.16 (d, *J* = 7.9 Hz, 2H), 3.13 (s, 1H), 1.33 (s, 12H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 152.3, 150.7, 136.4, 127.5, 120.6, 84.0, 77.2, 74.2, 24.9; IR ν_{max} (KBr): 3272, 3046, 2980, 2934, 2859, 2126, 1733, 1635, 1603, 1583, 1517, 1470, 1400, 1361, 1321, 1271, 1200, 1143, 1088, 1019, 962, 915 cm^{-1}; MS (EI, 70 eV) *m/z*: 272 ($M^{+\bullet}$, 80%), 257 [$(M - CH_3^{\bullet})^+$, 60], 173 (100), 158 (20); HRMS (EI) *m/z*: $M^{+\bullet}$ calcd for $C_{15}H_{17}{}^{11}BO_4$, 272.1220; found, 272.1218. $(M - CH_3^{\bullet})^+$ calcd for $C_{14}H_{14}{}^{11}BO_4$, 257.0985; found, 257.0990.

*p-Nitrophenyl Propiolate (**78**).* Compound **78**[46] (140 mg, 68%) (R_f = 0.5 in 1:4 v/v diethyl ether/hexane) was prepared using General Procedure B and isolated as a colorless, crystalline solid, mp 126−128 °C (lit.[46] mp 132−133 °C). ^1H NMR (400 MHz, $CDCl_3$): δ 8.30 (d, *J* = 9.0 Hz, 2H), 7.36 (d, *J* = 9.0 Hz, 2H), 3.17 (s, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 154.3, 149.8, 146.0, 125.6, 122.4, 78.2, 73.7; IR ν_{max} (KBr): 3266, 2124, 1730, 1616, 1592, 1518, 1491, 1351, 1290, 1194, 1111, 918 cm^{-1}; MS (EI, 70 eV) *m/z*: 191 ($M^{+\bullet}$, 100%), 190 (48), 174 (65), 163 (72), 144 (30), 133 (50), 123 (25), 117 (40), 89 (30); HRMS (EI) *m/z*: $M^{+\bullet}$ calcd for $C_9H_5NO_4$, 191.0219; found, 191.0220. This compound was subjected to single-crystal X-ray analysis. Details of this are presented in the Experimental Section and the Supporting Information.

*p-Acetamidophenyl Propiolate (**79**).* Compound **79** (462 mg, 69%) (R_f = 0.3 in 1:1 v/v ethyl acetate/hexane) was prepared using General Procedure B and isolated as a colorless, crystalline solid, mp 118−121 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 7.53 (d, *J* = 8.9 Hz, 2H), 7.29 (broad s, 1H), 7.10 (d, *J* = 8.9 Hz, 2H), 3.07 (s, 1H), 2.17 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 168.4, 151.2, 146.1, 136.4, 121.9, 121.0, 77.0, 74.4, 24.7; IR ν_{max} (KBr): 3273, 2981, 2125, 1729, 1671, 1612, 1544, 1506, 1407, 1371, 1315, 1187, 1017 cm^{-1}; MS (EI, 70 eV) *m/z*: 203 ($M^{+\bullet}$, 52%), 161 (44), 151 (26), 108 (100); HRMS (ESI) *m/z*: $[M + Na]^+$ calcd for $C_{11}H_9NO_3Na$, 226.0475; found, 226.0484. $[M + H]^+$ calcd for $C_{11}H_{10}NO_3$, 204.0655; found, 204.0658.

*p-{[(Trifluoromethyl)sulfonyl]oxy}phenyl Propiolate (**80**).* Compound **80** (500 mg, 82%) (R_f = 0.8 in chloroform) was prepared using General Procedure B and isolated as clear, yellow oil. ^1H NMR (400 MHz, $CDCl_3$): δ 7.33 (d, *J* = 9.2 Hz, 2H), 7.27 (d, *J* = 9.2 Hz, 2H), 3.12 (s, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 150.4, 149.3, 147.3, 123.3, 122.8, 118.9 (q, *J* = 321 Hz), 77.7, 73.9; IR ν_{max} (KBr): 3289, 2129, 1737, 1497, 1427, 1251, 1207, 1188, 1136, 1017 cm^{-1}; MS (EI, 70 eV) *m/z*: 294 ($M^{+\bullet}$, 12%), 53 (100). HRMS data could not be acquired on this compound.

*p-Chlorophenyl Propiolate (**81**).* Compound **81**[47] (618 mg, 88%) (R_f = 0.8 in chloroform) was prepared using General Procedure B and isolated as a colorless, crystalline solid, mp 41−42 °C (lit.[47] mp 41−43 °C). ^1H NMR (400 MHz, $CDCl_3$): δ 7.29 (d, *J* = 8.9 Hz, 2H), 7.03 (d, *J* = 8.9 Hz, 2H), 3.01 (s, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 150.7, 148.4, 132.2, 129.8, 122.8, 77.3, 74.2; IR ν_{max} (KBr): 3278, 2981, 2889, 2124, 1722, 1487, 1402, 1382, 1197, 1164, 1088, 1016 cm^{-1}; MS (EI, 70 eV) *m/z*: 182 and 180 ($M^{+\bullet}$, 9 and 27%), 145 (100); HRMS (EI) *m/z*: $M^{+\bullet}$ calcd for $C_9H_5{}^{37}ClO_2$, 181.9949; found, 181.9944. $M^{+\bullet}$ calcd for $C_9H_5{}^{35}ClO_2$, 179.9978; found, 179.9974.

*p-Bromophenyl Propiolate (**82**).* Compound **82** (230 mg, 88%) (R_f = 0.8 in chloroform) was prepared using General Procedure B and isolated as a clear, colorless solid, mp 56−57 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 7.54 (d, *J* = 8.9 Hz, 2H), 7.07 (d, *J* = 8.9 Hz, 2H), 3.11 (s, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 150.6, 149.0, 132.9, 123.2, 119.9, 77.3, 74.2; IR ν_{max} (KBr): 3277, 2967, 2939, 2124, 1723, 1482, 1201, 1066, 1033, 1014 cm^{-1}; MS (EI, 70 eV) *m/z*: 226 and 224 ($M^{+\bullet}$, both 37%), 198 and 196 (both 26), 174 and172 (both 52), 145 (44), 53 (100). HRMS data could not be acquired on this compound.

*p-Iodophenyl Propiolate (**83**).* Compound **83** (250 mg, 40%) (R_f = 0.7 in 1:4 v/v diethyl ether/hexane) was prepared using General Procedure B and isolated as a colorless, crystalline solid, mp 72−73 °C. ^1H NMR (300 MHz, $CDCl_3$): δ 7.72 (d, *J* = 7.8 Hz, 2H), 6.93 (d, *J* = 7.8 Hz, 2H), 3.09 (s, 1H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 150.6, 149.7, 138.8, 123.5, 91.0, 77.4, 74.1; IR ν_{max} (KBr): 3280, 2125, 1728, 1478, 1396, 1273, 1186, 1055, 1009, 910 cm^{-1}; MS (EI, 70 eV) *m/z*: 272 ($M^{+\bullet}$, 90%), 244 (30), 220 (100); HRMS (EI) *m/z*: $M^{+\bullet}$ calcd for $C_9H_5IO_2$, 271.9334; found, 271.9334.

*p-Cyanophenyl Propiolate (**84**).* Compound **84**[44] (192 mg, 67%) (R_f = 0.5 in 1:2:3 v/v/v ethyl acetate/dichloromethane/hexane) was prepared using General Procedure B and isolated as a clear, yellow solid, 148−149 °C (lit.[44] mp 154−155 °C). ^1H NMR (400 MHz, $CDCl_3$): δ 7.72 (d, *J* = 8.9 Hz, 2H), 7.31 (d, *J* = 8.9 Hz, 2H), 3.14 (s, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 153.0, 149.9, 134.0, 122.6, 118.0, 110.9, 78.0, 73.8; IR ν_{max} (KBr): 3237, 2990, 2901, 2239, 2123, 1730, 1604, 1498, 1411, 1394, 1219, 1194, 1166, 1066, 1058 cm^{-1}; MS (EI, 70 eV) *m/z*: 171 ($M^{+\bullet}$, 23%), 53 (100); HRMS (ESI) *m/z*: $[M + H]^+$ calcd for $C_{10}H_6NO_2$, 172.0393; found, 172.0396. This compound was subjected to single-crystal X-ray analysis. Details of this are presented in the Experimental Section and the Supporting Information.

*Methyl p-(Propioloyloxy)benzoate (**85**).* Compound **85** (220 mg, 95%) (R_f = 0.4 in 1:4 v/v ethyl acetate/hexane) was prepared using General Procedure B and isolated as a colorless, crystalline solid, mp 88−89 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 8.10 (d, *J* = 8.8 Hz, 2H), 7.24 (d, *J* = 8.8 Hz, 2H), 3.92 (s, 3H), 3.11 (s, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 166.3, 153.5, 150.4, 131.6, 128.7, 121.5, 77.5, 74.2, 52.5; IR ν_{max} (KBr): 3261, 2958, 2131, 2116, 1716, 1681, 1600, 1503, 1438, 1273, 1219, 1158, 1111, 1098, 1098, 1014 cm^{-1}; MS (EI, 70 eV)

https://dx.doi.org/10.1021/acs.joc.0c02011
J. Org. Chem. XXXX, XXX, XXX−XXX

m/*z*: 204 ($M^{+\bullet}$, 40%), 173 (60), 145 (100); HRMS (EI) *m*/*z*: $M^{+\bullet}$ calcd for $C_{11}H_8O_4$, 204.0423; found, 204.0425. This compound was subjected to single-crystal X-ray analysis. Details of this are presented in the Experimental Section and the Supporting Information.

*4-Formyl-2-methoxyphenyl Propiolate (**86**).* Compound **86** (230 mg, 86%) (R_f = 0.6 in chloroform) was prepared using General Procedure B and isolated as a clear, colorless solid, mp 73−74 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.94 (s, 1H), 7.50 (m, 2H), 7.26 (d, *J* = 8.0 Hz, 1H), 3.91 (s, 3H), 3.12 (s, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 190.9, 151.8, 149.7, 143.6, 136.0, 124.6, 123.2, 111.3, 77.5, 73.8, 56.3; IR ν_{max} (KBr): 3258, 2942, 2856, 2126, 1733, 1700, 1602, 1502, 1465, 1423, 1393, 1323, 1287, 1273, 1183, 1146, 1119, 1030 cm^{-1}; MS (EI, 70 eV) *m*/*z*: 204 ($M^{+\bullet}$, 61%), 173 (96), 151 (100); HRMS (ESI) *m*/*z*: $[M + H]^+$ calcd for $C_{11}H_9O_4$, 205.0495; found, 205.0487.

*2,4-Dimethylphenyl Propiolate (**87**).* Compound **87**[44] (225 mg, 79%) (R_f = 0.7 in 1:4 v/v diethyl ether/hexane) was prepared using General Procedure B and isolated as a colorless, crystalline solid, mp = 53−55 °C (lit.[44] mp 51−53 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.05 (s, 1H), 7.02 (d, *J* = 8.2 Hz, 1H), 6.94 (d, *J* = 8.2 Hz, 1H), 3.04 (s, 1H), 2.31 (s, 3H), 2.18 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 151.2, 146.4, 136.6, 132.1, 129.6, 127.8, 121.4, 76.6, 74.4, 21.0, 16.2; IR ν_{max} (KBr): 3271, 2127, 1736, 1500, 1250, 1206, 1193, 1114 cm^{-1}; MS (EI, 70 eV) *m*/*z*: 174 ($M^{+\bullet}$, 100%), 122 (96); HRMS (ESI) *m*/*z*: $[M + Na]^+$ calcd for $C_{11}H_{10}O_2Na$, 197.0573; found, 197.0581. $[M + H]^+$ calcd for $C_{11}H_{11}O_2$, 175.0754; found, 175.0758. This compound was subjected to single-crystal X-ray analysis. Details of this are presented in the Experimental Section and the Supporting Information.

*2-iso-Propyl-5-methylphenyl Propiolate (**88**).* Compound **88** (210 mg, 78%) (R_f = 0.5 in 3:7 v/v dichloromethane/hexane) was prepared using General Procedure B and isolated as clear, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.22 (d, *J* = 7.9 Hz, 1H), 7.07 (d, *J* = 7.9 Hz, 1H), 6.87 (s, 1H), 3.06 (s, 1H), 3.02 (sept, *J* = 6.0 Hz, 1H), 2.33 (s, 3H), 1.22 (d, *J* = 6.0 Hz, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 151.5, 147.2, 137.1, 137.0, 128.0, 126.9, 122.5, 76.7, 74.5, 27.3, 23.2, 20.9; IR ν_{max} (KBr): 3265, 2967, 2871, 2123, 1732, 1507, 1455, 1193, 1084, 1058, 1033, 1011, 909 cm^{-1}; MS (EI, 70 eV) *m*/*z*: 202 ($M^{+\bullet}$, 21%), 187 (16), 159 (71), 149 (100), 135 (61); HRMS (ESI) *m*/*z*: $[M + Na]^+$ calcd for $C_{13}H_{14}O_2Na$, 225.0886; found, 225.0889. $[M + H]^+$ calcd for $C_{13}H_{15}O_2$, 203.1067; found, 203.1067.

*Benzo[d][1,3]dioxol-5-yl Propiolate (**89**).* Compound **89**[44] (210 mg, 76%) (R_f = 0.6 in 1:4 v/v diethyl ether/hexane) was prepared using General Procedure B and isolated as a colorless, crystalline solid, mp 82−84 °C (lit.[44] mp 80−82 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.78 (d, *J* = 8.4 Hz, 1H), 6.66 (d, *J* = 2.4 Hz, 1H), 6.59 (dd, *J* = 8.4 and 2.4 Hz, 1H), 6.00 (s, 2H), 3.06 (s, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 151.4, 148.3, 146.1, 144.1, 113.9, 108.2, 103.5, 102.0, 77.0, 74.3; IR ν_{max} (KBr): 3228, 2906, 2118, 1723, 1504, 1486, 1444, 1364, 1245, 1203, 1173, 1120, 1095, 1037, 947, 934, 924, 905 cm^{-1}; MS (EI, 70 eV) *m*/*z*: 190 ($M^{+\bullet}$, 65%), 138 (100), 137 (95), 134 (48), 107 (40), 79 (30); HRMS (EI) *m*/*z*: $M^{+\bullet}$ calcd for $C_{10}H_6O_4$, 190.0266; found, 190.0268. This compound was subjected to single-crystal X-ray analysis. Details of this are presented in the Experimental Section and the Supporting Information.

*3,4-Dimethoxyphenyl Propiolate (**90**).* Compound **90** (498 mg, 93%) (R_f = 0.3 in 3:7 v/v diethyl ether/hexane) was prepared using General Procedure B and isolated as a colorless, crystalline solid, mp 79−80 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.81 (s, 1H), 6.73−6.54 (complex m, 2H), 3.84 (s, 3H), 3.83 (s, 3H), 3.09 (s, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 151.4, 149.5, 147.4, 143.4, 112.7, 111.2, 105.3, 77.0, 74.3, 56.2, 56.0; IR ν_{max} (KBr): 3219, 2120, 1722, 1609, 1514, 1472, 1451, 1416, 1269, 1211, 1125, 1026 cm^{-1}; MS (EI, 70 eV) *m*/*z*: 206 ($M^{+\bullet}$, 100%), 191 (15), 175 (14), 163 (31), 153 (78); HRMS (EI) *m*/*z*: $M^{+\bullet}$ calcd for $C_{11}H_{10}O_4$, 206.0579; found, 206.0579.

*(S)-4-{2-[(tert-Butoxycarbonyl)amino]-3-methoxy-3-oxopropyl}-phenyl Propiolate (**91**).* Compound **91** (500 mg, 82%) (R_f = 0.2 in 1:4 v/v ethyl acetate/hexane) was prepared using General Procedure B and isolated as clear, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.14 (d, *J* = 8.5 Hz, 2H), 7.05 (d, *J* = 8.5 Hz, 2H), 5.04 (broad s, 1H), 4.54 (broad s, 1H), 3.67 (s, 3H), 3.11 (s, 1H), 3.08 (d, *J* = 5.8 Hz, 1H), 2.99 (m, 1H), 1.38 (s, 9H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 172.2, 155.1, 150.9, 148.9, 134.7, 130.5, 121.3, 80.1, 77.1, 74.3, 54.4, 52.3, 37.8, 28.3; IR ν_{max} (KBr): 3265, 2981, 2124, 1733, 1506, 1438, 1393, 1367, 1213, 1189, 1059, 1019 cm^{-1}; MS (ESI, +ve) *m*/*z*: 370 $[(M + Na)^+$, 40%], 348 $[(M + H)^+$, 100]; HRMS (ESI) *m*/*z*: $[M + Na]^+$ calcd for $C_{18}H_{21}NO_6Na$, 370.1261; found, 370.1269. $[M + H]^+$ calcd for $C_{18}H_{22}NO_6$, 348.1442; found, 348.1443.

*Naphthalen-2-yl Propiolate (**92**).* Compound **92**[43] (260 mg, 96%) (R_f = 0.5 in 1:4 v/v diethyl ether/hexane) was prepared using General Procedure B and isolated as a colorless, crystalline solid, mp 52−53 °C (lit.[43] mp 51−53 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90−7.75 (complex m, 3H), 7.64 (d, *J* = 2.3 Hz, 1H), 7.57−7.45 (complex m, 2H), 7.28 (dd, *J* = 8.9 and 2.3 Hz, 1H), 3.10 (s, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 151.2, 147.6, 133.8, 131.9, 129.8, 128.0, 127.9, 127.0, 126.3, 120.5, 118.7, 77.0, 74.5; IR ν_{max} (KBr): 3676, 3247, 2988, 2121, 1713, 1228, 1066 cm^{-1}; MS (EI, 70 eV) *m*/*z*: 196 ($M^{+\bullet}$, 66%), 168 (29), 144 (100); HRMS (ESI) *m*/*z*: $[M + H]^+$ calcd for $C_{13}H_9O_2$, 197.0597; found, 197.0594.

*7-Methoxynaphthalen-2-yl Propiolate (**93**).* Compound **93** (230 mg, 89%) (R_f = 0.5 in 1:4 v/v diethyl ether/hexane) was prepared using General Procedure B and isolated as a colorless, crystalline solid, mp 142−143 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79 (d, *J* = 8.8 Hz, 1H), 7.74 (d, *J* = 8.8 Hz, 1H), 7.52 (s, 1H), 7.17−7.08 (complex m, 3H), 3.92 (s, 3H), 3.10 (s, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 158.4, 151.1, 148.1, 135.0, 129.4, 129.3, 127.2, 119.1, 117.9, 117.4, 105.7, 76.8, 74.3, 55.3; IR ν_{max} (KBr): 3245, 2126, 1733, 1720, 1633, 1514, 1482, 1468, 1390, 1251, 1218, 1200, 1176, 1143, 1027, 918 cm^{-1}; MS (EI, 70 eV) *m*/*z*: 226 ($M^{+\bullet}$, 100%), 198 (30), 174 (85), 170 (70), 155 (30), 145 (50), 140 (25), 131 (35), 102 (50); HRMS (EI) *m*/*z*: $M^{+\bullet}$ calcd for $C_{14}H_{10}O_3$, 226.0630; found, 226.0630. This compound was subjected to single-crystal X-ray analysis. Details of this are presented in the Experimental Section and the Supporting Information.

*9-Oxo-9H-fluoren-1-yl Propiolate (**94**).* Compound **94** (245 mg, 90%) (R_f = 0.2 in 2:3 v/v chloroform/hexane) was prepared using General Procedure B and isolated as a clear, yellow solid, mp 154−155 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62 (m, 1H), 7.52−7.40 (complex m, 4H), 7.30 (m, 1H), 6.97 (d, *J* = 7.4 Hz, 1H), 3.14 (s, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 190.4, 150.0, 146.6, 146.2, 143.5, 136.5, 134.9, 134.1, 129.8, 124.6, 124.4, 123.0, 120.8, 118.9, 77.3, 74.1; IR ν_{max} (KBr): 3232, 2917, 2122, 1725, 1713, 1615, 1591, 1471, 1453, 1220, 1191, 1148, 1109 cm^{-1}; MS (EI, 70 eV) *m*/*z*: 248 ($M^{+\bullet}$, 27%), 220 (100), 196 (37); HRMS (ESI) *m*/*z*: $[M + Na]^+$ calcd for $C_{16}H_8O_3Na$, 271.0366; found, 271.0363.

*Naphthalen-1-yl Propiolate (**95**).* Compound **95**[44] (245 mg, 90%) (R_f = 0.5 in 1:4 v/v diethyl ether/hexane) was prepared using General Procedure B and isolated as a colorless, crystalline solid, mp 43−44 °C (lit.[44] mp 41−42 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97−7.86 (complex m, 2H), 7.79 (d, *J* = 8.3 Hz, 1H), 7.60−7.51 (complex m, 2H), 7.48 (t, *J* = 8.3 Hz, 1H), 7.33 (m, 1H), 3.14 (s, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 151.1, 145.9, 134.8, 128.2, 127.0, 126.9 (4), 126.8 (6), 126.4, 125.4, 121.1, 118.1, 77.2, 74.4; IR ν_{max} (KBr): 3676, 3276, 2988, 2125, 1732, 1390, 1190, 1155, 1066 cm^{-1}; MS (EI, 70 eV) *m*/*z*: 196 ($M^{+\bullet}$, 59%), 168 (49), 144 (81), 115 (100); HRMS (ESI) *m*/*z*: $[M + H]^+$ calcd for $C_{13}H_9O_2$, 197.0597; found, 197.0594.

*9H-Carbazol-1-yl Propiolate (**96**).* Compound **96** (118 mg, 46%) (R_f = 0.3 in 1:1 v/v ethyl acetate/hexane) was prepared using General Procedure B and isolated as a colorless, crystalline solid, mp 166−167 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.12 (broad s, 1H), 8.02 (d, *J* = 8.2 Hz, 2H), 7.45−7.41 (complex m, 2H), 7.30−7.18 (complex m, 2H), 7.01 (dd, *J* = 8.5 and 2.1 Hz, 1H), 3.10 (s, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 151.5, 148.2, 140.1, 139.6, 126.0, 122.7, 121.9, 121.0, 120.3, 119.9, 112.8, 110.7, 103.6, 76.8, 74.4; IR ν_{max} (KBr): 3404, 3284, 2932, 2856, 2133, 1714, 1631, 1610, 1461, 1442, 1337, 1327, 1227, 1118 cm^{-1}; MS (EI, 70 eV) *m*/*z*: 235 ($M^{+\bullet}$, 100%), 195 (48), 183 (65), 179 (71); HRMS (EI) *m*/*z*: $M^{+\bullet}$ calcd for $C_{15}H_9NO_2$, 235.0633; found, 235.0639.

*p-Methoxyphenyl But-2-ynoate (**97**).* Compound **97**[45] (300 mg, 98%) (R_f = 0.4 in 1:4 v/v diethyl ether/hexane) was prepared using General Procedure C and isolated as a colorless, crystalline solid, mp 59−60 °C (lit.[45] mp 58−60 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.05

https://dx.doi.org/10.1021/acs.joc.0c02011
J. Org. Chem. XXXX, XXX, XXX−XXX

(d, J = 9.2 Hz, 2H), 6.89 (d, J = 9.2 Hz, 2H), 3.80 (s, 3H), 2.06 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 157.7, 152.5, 143.7, 122.3, 114.7, 88.1, 72.3, 55.7, 4.1; IR ν_{max} (KBr): 2959, 2838, 2277, 2231, 1721, 1503, 1229, 1179, 1035 cm^{-1}; MS (EI, 70 eV) m/z: 190 ($M^{+\bullet}$, 60%), 148 (60), 124 (100), 109 (60); HRMS (EI) m/z: $M^{+\bullet}$ calcd for $C_{11}H_{10}O_3$, 190.0630; found, 190.0634. This compound was subjected to single-crystal X-ray analysis. Details of this are presented in the Experimental Section and the Supporting Information.

*p-Methoxyphenyl 3-Phenylpropiolate (**98**).* Compound **98**[48] (35 mg, 9%) (R_f = 0.5 in 1:4 v/v diethyl ether/hexane) was prepared using General Procedure C and isolated as a colorless, crystalline solid, mp 64−66 °C (lit.[48] mp 67−69 °C). ^1H NMR (400 MHz, $CDCl_3$): δ 7.63 (d, J = 7.5 Hz, 2H), 7.49 (m, 1H), 7.41 (t, J = 7.5 Hz, 2H), 7.12 (d, J = 9.1 Hz, 2H), 6.92 (d, J = 9.1 Hz, 2H), 3.81 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 157.8, 152.9, 143.8, 133.3, 131.1, 128.8, 122.4, 119.5, 114.7, 88.7, 80.4, 55.8; IR ν_{max} (KBr): 2952, 2837, 2233, 1723, 1504, 1282, 1250, 1188, 1165, 1143 cm^{-1}; MS (EI, 70 eV) m/z: 252 ($M^{+\bullet}$, 30%), 129 (100), 105 (58); HRMS (EI) m/z: $M^{+\bullet}$ calcd for $C_{16}H_{12}O_3$, 252.0786; found, 252.0787.

*1,4-Phenylene Dipropiolate (**99**).* Compound **99**[17] (90 mg, 23%) (R_f = 0.6 in chloroform) was prepared using General Procedure B and isolated as a colorless, crystalline solid, mp 158−159 °C (lit.[17] mp 159 °C). ^1H NMR (400 MHz, $CDCl_3$): δ 7.20 (s, 4H), 3.09 (s, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 150.7, 147.8, 122.6, 77.3, 74.2; IR ν_{max} (KBr): 3279, 2929, 2126, 1720, 1500, 1295, 1220, 1177, 1100, 1019, 920 cm^{-1}; MS (EI, 70 eV) m/z: 214 ($M^{+\bullet}$, 18%), 162 (36), 134 (14), 110 (23); 53 (100); HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{12}H_6O_4Na$, 237.0158; found, 237.0156. $[M + H]^+$ calcd for $C_{12}H_7O_4$, 215.0339; found, 215.0345.

Synthesis of Coumarins 1, 4, and 100−152. *General Procedure D—Gold(I)-Catalyzed Cyclization of Aryl Propiolates.* A magnetically stirred solution of the requisite aryl propiolate (1 mmol, 1 equiv) in dichloromethane (50 mL) was treated with Echavarren's gold(I) catalyst (23 mg, 0.03 mmol, 0.03 equiv). The resulting solution was stirred at 18 °C for 1 h then filtered through a pad of TLC-grade silica gel and the filtrate concentrated under reduced pressure. The light yellow oil thus obtained was subjected to flash chromatography (silica gel, 3:7 v/v ethyl acetate/hexane elution), and concentration of the relevant fractions then gave the anticipated coumarin.

*2H-Chromen-2-one (**1**).* Compound **1** (28 mg, 93%) (R_f = 0.9 in 1:4 v/v diethyl ether/hexane) was prepared from aryl propiolate **56** using General Procedure D and isolated as a colorless, crystalline solid, mp 70−72 °C (lit.[49] mp 68−73 °C). ^1H NMR (400 MHz, $CDCl_3$): δ 7.64 (d, J = 9.6 Hz, 1H), 7.45 (t, J = 7.9 Hz, 1H), 7.42 (d, J = 7.9 Hz, 1H), 7.25 (d, J = 7.9 Hz, 1H), 7.21 (t, J = 7.9 Hz, 1H), 6.39 (d, J = 9.6 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 160.9, 154.2, 143.5, 132.0, 128.0, 124.6, 119.0, 117.0, 116.9; IR ν_{max} (KBr): 1708, 1619, 1604, 1563, 1453, 1398, 1278, 1259, 1229, 1177, 1121, 1108 cm^{-1}; MS (EI, 70 eV) m/z: 146 ($M^{+\bullet}$, 90%), 118 (100); HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_9H_7O_2$, 147.0446; found, 147.0443. This compound was subjected to single-crystal X-ray analysis. Details of this are presented in the Experimental Section and the Supporting Information.

*6-Methoxy-2H-chromen-2-one (**4**).* Compound **4**[49] (20 mg, quantitative) (R_f = 0.2 in 1:3:6 v/v/v ethyl acetate/dichloromethane/hexane) was prepared from aryl propiolate **3** using General Procedure D and isolated as a colorless, crystalline solid, mp 99−100 °C (lit.[49] mp 101 °C). ^1H NMR (400 MHz, $CDCl_3$): δ 7.65 (d, J = 9.6 Hz, 1H), 7.26 (d, J = 9.0 Hz, 1H), 7.11 (dd, J = 9.0 and 2.9 Hz, 1H), 6.91 (d, J = 2.9 Hz, 1H), 6.42 (d, J = 9.6 Hz, 1H), 3.85 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 161.1, 156.3, 148.7, 143.3, 119.6, 119.4, 118.1, 117.3, 110.3, 56.0; IR ν_{max} (KBr): 1702, 1570, 1492, 1453, 1284, 1121, 1048 cm^{-1}; MS (EI, 70 eV) m/z: 176 ($M^{+\bullet}$, 100%), 161 (39), 148 (33), 133 (49); HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{10}H_8O_3Na$, 199.0366; found, 199.0373. $[M + H]^+$ calcd for $C_{10}H_9O_3$, 177.0546; found, 177.0548.

*9-Methoxy-3H-benzo[f]chromen-3-one (**100**).* Compound **100**[50] (20 mg, quantitative) (R_f = 0.2 in chloroform) was prepared from aryl propiolate **93** using General Procedure D and isolated as a colorless, crystalline solid, mp 141−143 °C (lit.[50] mp 143−144 °C). ^1H NMR (400 MHz, $CDCl_3$): δ 8.44 (d, J = 9.8 Hz, 1H), 7.91 (d, J = 8.9 Hz, 1H), 7.81 (d, J = 8.9 Hz, 1H), 7.51 (d, J = 2.4 Hz, 1H), 7.32 (d, J = 8.9 Hz, 1H), 7.22 (dd, J = 8.9 and 2.4 Hz, 1H), 6.55 (d, J = 9.8 Hz, 1H), 4.00 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 161.3, 160.0, 154.8, 139.4, 133.1, 131.0, 130.8, 125.7, 117.9, 115.2, 114.7, 112.5, 101.5, 55.7; IR ν_{max} (KBr): 2995, 1729, 1708, 1632, 1614, 1593, 1571, 1514, 1471, 1461, 1434, 1396, 1377, 1327, 1286, 1248, 1228, 1209, 1173, 1137, 1115, 1031, 1017, 911 cm^{-1}; MS (EI, 70 eV) m/z: 226 ($M^{+\bullet}$, 100%), 195 (20); HRMS (EI) m/z: $M^{+\bullet}$ calcd for $C_{14}H_{10}O_3$, 226.0630; found, 226.0630. This compound was subjected to single-crystal X-ray analysis. Details of this are presented in the Experimental Section and the Supporting Information.

*8-Ethyl-2H-chromen-2-one (**101**).* Compound **101**[51] (100 mg, quant) (R_f = 0.7 in chloroform) was prepared from aryl propiolate **57** using General Procedure D and isolated as a clear, colorless oil. ^1H NMR (400 MHz, $CDCl_3$): δ 7.65 (d, J = 9.5 Hz, 1H), 7.34 (d, J = 7.5 Hz, 1H), 7.27 (d, J = 7.5 Hz, 1H), 7.15 (t, J = 7.5 Hz, 1H), 6.34 (d, J = 9.5 Hz, 1H), 2.82 (q, J = 7.5 Hz, 2H), 1.23 (t, J = 7.5 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 160.9, 151.9, 143.9, 132.1, 131.6, 125.6, 124.2, 118.6, 116.2, 22.4, 14.1; IR ν_{max} (KBr): 3422, 2969, 2934, 2876, 1717, 1601, 1452, 1401, 1235, 1179, 1163, 1118, 1090, 1059, 1013 cm^{-1}; MS (EI, 70 eV) m/z: 174 ($M^{+\bullet}$, 76%), 159 (100), 131 (68); HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{11}H_{10}O_2Na$, 197.0573; found, 197.0565. $[M + H]^+$ calcd for $C_{11}H_{11}O_2$, 175.0754; found, 175.0749.

*8-Methoxy-2H-chromen-2-one (**102**).* Compound **102**[52] (100 mg, quantitative) (R_f = 0.3 in 1:3:6 v/v/v of ethyl acetate/dichloromethane/hexane) was prepared from aryl propiolate **58** using General Procedure D and isolated as a colorless, crystalline solid, mp 90−91 °C (lit.[52] mp 90−91 °C). ^1H NMR (400 MHz, $CDCl_3$): δ 7.70 (d, J = 9.6 Hz, 1H), 7.23 (t, J = 8.0 Hz, 1H), 7.10 (dd, J = 8.0 and 1.3 Hz, 1H), 7.08 (dd, J = 8.0 and 1.3 Hz, 1H), 6.45 (d, J = 9.6 Hz, 1H), 3.99 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 160.3, 147.5, 144.0, 143.7, 124.4, 119.7, 119.4, 117.2, 114.0, 56.5; IR ν_{max} (KBr): 1727, 1609, 1572, 1478, 1469, 1439, 1401, 1276, 1258, 1237, 1200, 1168, 1134, 1078 cm^{-1}; MS (EI, 70 eV) m/z: 176 ($M^{+\bullet}$, 100%), 161 (9), 148 (24), 133 (33); HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{10}H_8O_3Na$, 199.0366; found, 199.0366. $[M + H]^+$ calcd for $C_{10}H_9O_3$, 177.0546; found, 177.0543.

*8-Bromo-2H-chromen-2-one (**105**).* Compound **105**[53] (70 mg, 70%) (R_f = 0.4 in chloroform) was prepared from aryl propiolate **61** using General Procedure D and isolated as a colorless, crystalline solid, mp 136 °C (lit.[53] mp 135−138 °C). ^1H NMR (400 MHz, $CDCl_3$): δ 7.72 (dd, J = 7.9 and 1.5 Hz, 1H), 7.67 (d, J = 9.5 Hz, 1H), 7.43 (dd, J = 7.9 and 1.5 Hz, 1H), 7.14 (t, J = 7.9 Hz, 1H), 6.42 (d, J = 9.5 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 159.6, 150.9, 143.2, 135.4, 127.3, 125.2, 120.2, 117.4, 110.5; IR ν_{max} (KBr): 1732, 1617, 1594, 1552, 1438, 1399, 1236, 1168, 1146, 1109, 1069 cm^{-1}; MS (EI, 70 eV) m/z: 226 and 224 ($M^{+\bullet}$, both 100), 198 and 196 (both 85); HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_9H_5{}^{79}BrO_2Na$, 246.9365; found, 246.9368. $[M + H]^+$ calcd for $C_9H_6{}^{79}BrO_2$, 224.9546; found, 224.9546.

*8-Chloro-2H-chromen-2-one (**106**).* Compound **106**[54] (40 mg, 50%) (R_f = 0.3 in 0.5:3:6.5 v/v/v of ethyl acetate/dichloromethane/hexane) was prepared from aryl propiolate **62** using General Procedure D and isolated as a colorless, crystalline solid, mp 145−146 °C (lit.[54] mp 146−147 °C). ^1H NMR (400 MHz, $CDCl_3$): δ 7.70 (d, J = 9.6 Hz, 1H), 7.59 (dd, J = 7.9 and 1.5 Hz, 1H), 7.40 (dd, J = 7.9 and 1.5 Hz, 1H), 7.22 (t, J = 7.9 Hz, 1H), 6.46 (d, J = 9.6 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 159.6, 149.9, 143.2, 132.4, 126.5, 124.8, 121.9, 120.3, 117.5; IR ν_{max} (KBr): 1734, 1599, 1558, 1444, 1400, 1171, 1111 cm^{-1}; MS (EI, 70 eV) m/z: 182 and 180 ($M^{+\bullet}$, 36 and 100%), 154 and 152 (33 and 98); HRMS (EI) m/z: $M^{+\bullet}$ calcd for $C_9H_5{}^{37}ClO_2$, 181.9949; found, 181.9947. $M^{+\bullet}$ calcd for $C_9H_5{}^{35}ClO_2$, 179.9978; found, 179.9975.

*7-Methoxy-2H-chromen-2-one (Herniarin) (**107**).* Compound **107**[22a] (14 mg, 70%) (R_f = 0.4 in chloroform) was prepared from aryl propiolate **63** using General Procedure D and isolated as a colorless, crystalline solid, mp 115−117 °C (lit.[22a] mp 117−118 °C). ^1H NMR (400 MHz, $CDCl_3$): δ 7.63 (d, J = 9.5 Hz, 1H), 7.37 (d, J = 8.5 Hz, 1H), 6.84 (dd, J = 8.5 and 2.5 Hz, 1H), 6.81 (d, J = 2.5 Hz, 1H), 6.24 (d, J = 9.5 Hz, 1H), 3.87 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 163.0, 161.3, 156.1, 143.5, 128.9, 113.2, 112.7 (2), 112.6 (7), 101.0, 55.9; IR ν_{max} (KBr): 1704, 1611, 1505, 1399, 1351, 1282, 1232,

https://dx.doi.org/10.1021/acs.joc.0c02011
J. Org. Chem. XXXX, XXX, XXX−XXX

1205, 1123 cm^{-1}; MS (EI, 70 eV) m/z: 176 ($M^{+\bullet}$, 100%), 148 (70), 133 (65); HRMS (EI) m/z: $M^{+\bullet}$ calcd for $C_{10}H_8O_3$, 176.0473; found, 176.0475. This compound was co-produced with **108** and separated from it by flash chromatography.

*5-Methoxy-2H-chromen-2-one (**108**).* Compound **108**[55] (3 mg, 15%) (R_f = 0.4 in chloroform) was prepared from aryl propiolate **63** using General Procedure D and isolated as a colorless, crystalline solid, mp 118−119 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.09 (d, J = 9.8 Hz, 1H), 7.44 (t, J = 8.4 Hz, 1H), 6.93 (d, J = 8.4 Hz, 1H), 6.71 (d, J = 8.4 Hz, 1H), 6.34 (d, J = 9.8 Hz, 1H), 3.94 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 161.1, 156.3, 155.3, 138.7, 132.5, 114.8, 109.8, 109.4, 105.3, 56.2; IR ν_{max} (KBr): 1731, 1605, 1470, 1399, 1187, 1114, 1090 cm^{-1}; MS (EI, 70 eV) m/z: 176 ($M^{+\bullet}$, 100%), 148 (70), 133 (69); HRMS (EI) m/z: $M^{+\bullet}$ calcd for $C_{10}H_8O_3$, 176.0473; found, 176.0475.

*7-[(tert-Butyldimethylsilyl)oxy]-2H-chromen-2-one (**109**).* Compound **109**[56] (92 mg, 92%) (R_f = 0.6 in 1:8 v/v of ethyl acetate/toluene) was prepared from aryl propiolate **64** using General Procedure D and isolated as a colorless, crystalline solid, mp 53 °C (lit.[56] mp 53−55 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39 (d, J = 9.5 Hz, 1H), 7.09 (d, J = 7.4 Hz, 1H), 6.52 (m, 2H), 6.00 (d, J = 9.5 Hz, 1H), 0.75 (s, 9H), 0.01 (s, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 161.2, 159.5, 155.7, 143.4, 128.8, 117.5, 113.5, 113.3, 107.8, 25.7, 18.4, −4.3; IR ν_{max} (KBr): 3444, 2961, 2930, 2858, 1729, 1618, 1507, 1473, 1464, 1405, 1332, 1296, 1252, 1242, 1191, 1143 cm^{-1}; MS (EI, 70 eV) m/z: 276 ($M^{+\bullet}$, 61%), 219 (99), 163 (100); HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{15}H_{20}O_3SiNa$, 299.1074; found, 299.1068. $[M + H]^+$ calcd for $C_{15}H_{21}O_3Si$, 277.1254; found, 277.1250. This compound was co-produced with **110** and separated from it by flash chromatography.

*5-((tert-Butyldimethylsilyl)oxy)-2H-chromen-2-one (**110**).* Compound **110** (4 mg, 4%) (R_f = 0.7 in 1:8 v/v of ethyl acetate/toluene) was prepared from aryl propiolate **64** using General Procedure D and isolated as a colorless, crystalline solid, mp 91−93 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00 (d, J = 9.7 Hz, 1H), 7.35 (t, J = 8.3 Hz, 1H), 6.93 (d, J = 8.3 Hz, 1H), 6.68 (d, J = 8.3 Hz, 1H), 6.34 (d, J = 9.7 Hz, 1H), 1.04 (s, 9H), 0.29 (s, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 161.1, 155.5, 153.0, 139.0, 132.1, 115.0, 113.6, 112.4, 109.8, 25.9, 18.5, −4.2; IR ν_{max} (KBr): 2956, 2931, 2859, 1736, 1616, 1606, 1472, 1463, 1392, 1318, 1298, 1250, 1229, 1183, 1104, 1074, 1062 cm^{-1}; MS (EI, 70 eV) m/z: 276 ($M^{+\bullet}$, 41%), 219 (100), 191 (93); HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{15}H_{20}O_3SiNa$, 299.1074; found, 299.1072. $[M + H]^+$ calcd for $C_{15}H_{21}O_3Si$, 277.1254; found, 277.1252.

*2-Oxo-2H-chromen-7-yl Acetate (**111**).* Compound **111**[57] (22 mg, 44%) (R_f = 0.4 in 1:2:3 v/v/v of ethyl acetate/dichloromethane/pentane) was prepared from aryl propiolate **65** using General Procedure D and isolated as a colorless, crystalline solid, mp 137 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68 (d, J = 9.6 Hz, 1H), 7.48 (d, J = 8.4 Hz, 1H), 7.12 (d, J = 2.2 Hz, 1H), 7.06 (dd, J = 8.4 and 2.2 Hz, 1H), 6.40 (d, J = 9.6 Hz, 1H), 2.34 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 168.8, 160.4, 154.9, 153.4, 142.9, 128.7, 118.5, 116.8, 116.3, 110.6, 21.3; IR ν_{max} (KBr): 3077, 2988, 1735, 1617, 1403, 1372, 1272, 1223, 1236, 1148, 1123, 1105, 1046, 1017 cm^{-1}; MS (EI, 70 eV) m/z: 204 ($M^{+\bullet}$, 16%), 162 (100), 134 (90); HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{11}H_8O_4Na$, 227.0315; found, 227.0309. $[M + H]^+$ calcd for $C_{11}H_9O_4$, 205.0495; found, 205.0495. This compound was co-produced with **112** and separated from it by flash chromatography.

*2-Oxo-2H-chromen-5-yl Acetate (**112**).* Compound **112**[58] (7 mg, 14%) (R_f = 0.4 in 1:2:3 v/v/v of ethyl acetate/dichloromethane/hexane) was prepared from aryl propiolate **65** using General Procedure D and isolated as a colorless, crystalline solid, mp 86 °C (lit.[58] mp 88−89 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74 (d, J = 9.7 Hz, 1H), 7.52 (t, J = 8.3 Hz, 1H), 7.23 (d, J = 8.3 Hz, 1H), 7.08 (d, J = 8.3 Hz, 1H), 6.44 (d, J = 9.7 Hz, 1H), 2.41 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 168.7, 160.1, 154.9, 147.2, 137.3, 131.9, 117.8, 117.1, 114.7, 112.9, 21.0; IR ν_{max} (KBr): 1773, 1735, 1622, 1615, 1461, 1371, 1197, 1164, 1110, 1044 cm^{-1}; MS (EI, 70 eV) m/z: 204 ($M^{+\bullet}$, 25%), 162 (100); HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{11}H_9O_4$, 205.0495; found, 205.0499.

*2-Oxo-2H-chromen-7-yl Pivalate (**117**).* Compound **117**[58] (36 mg, 36%) (R_f = 0.4 in 1:8 v/v ethyl acetate/toluene) was prepared from aryl propiolate **68** using General Procedure D and isolated as a colorless, crystalline solid, mp 136−138 °C (lit.[58] mp 139 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69 (d, J = 9.6 Hz, 1H), 7.48 (d, J = 8.6 Hz, 1H), 7.08 (d, J = 2.2 Hz, 1H), 7.01 (dd, J = 8.6 and 2.2 Hz, 1H), 6.39 (d, J = 9.6 Hz, 1H), 1.37 (s, 9H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 176.5, 160.5, 154.9, 153.9, 143.0, 128.6, 118.5, 116.6, 116.1, 110.5, 39.4, 27.2; IR ν_{max} (KBr): 2976, 1717, 1616, 1484, 1427, 1264, 1232, 1129, 1115, 1104, 1038 cm^{-1}; MS (ESI, +ve) m/z: 310 (100%), 247 [$(M + H)^+$, 95]; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{14}H_{15}O_4$, 247.0970; found, 247.0971. This compound was co-produced with isomer **118** and separated from it by flash chromatography.

*2-Oxo-2H-chromen-5-yl Pivalate (**118**).* Compound **118** (18 mg, 18%) (R_f = 0.4 in 1:8 v/v ethyl acetate/toluene) was prepared from aryl propiolate **68** using General Procedure D and isolated as a colorless, crystalline solid, mp 86−87 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69 (d, J = 9.8 Hz, 1H), 7.52 (t, J = 8.3 Hz, 1H), 7.22 (d, J = 8.3 Hz, 1H), 7.02 (d, J = 8.3 Hz, 1H), 6.44 (d, J = 9.8 Hz, 1H), 1.44 (s, 9H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 176.5, 160.1, 154.8, 147.7, 137.2, 131.9, 117.7, 117.1, 114.4, 113.0, 39.7, 27.3; IR ν_{max} (KBr): 2973, 1747, 1734, 1622, 1613, 1460, 1240, 1186, 1097, 1040 cm^{-1}; MS (ESI, +ve) m/z: 247 [$(M + H)^+$, 100%]; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{14}H_{15}O_4$, 247.0970; found, 247.0972.

*7-(Benzyloxy)-2H-chromen-2-one (**119**).* Compound **119**[55] (82 mg, 82%) (R_f = 0.6 in 1:8 v/v of ethyl acetate/toluene) was prepared from aryl propiolate **69** using General Procedure D and isolated as a colorless, crystalline solid, mp 153−154 °C (lit.[55] mp 155 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60 (d, J = 9.4 Hz, 1H), 7.47−7.27 (complex m, 6H), 6.90 (dd, J = 8.6 and 2.4 Hz, 1H), 6.85 (d, J = 2.4 Hz, 1H), 6.22 (d, J = 9.4 Hz, 1H), 5.10 (s, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 161.9, 161.1, 155.8, 143.4, 135.8, 128.9, 128.8, 128.4, 127.5, 113.1 (9), 113.1 (7), 112.8, 102.0, 70.5; IR ν_{max} (KBr): 2918, 1726, 1609, 1464, 1457, 1387, 1349, 1278, 1256, 1229, 1198, 1155, 1125, 1107, 1075, 1013 cm^{-1}; MS (EI, 70 eV) m/z: 252 ($M^{+\bullet}$, 72%), 91 (100); HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{16}H_{12}O_3Na$, 275.0679; found, 275.0667. $[M + H]^+$ calcd for $C_{16}H_{13}O_3$, 253.0859; found, 253.0847. This compound was co-produced with isomer **120** and separated from it by flash chromatography.

*5-(Benzyloxy)-2H-chromen-2-one (**120**).* Compound **120**[55] (17 mg, 17%) (R_f = 0.7 in 1:8 v/v of ethyl acetate/toluene) was prepared from aryl propiolate **69** using General Procedure D and isolated as a colorless, crystalline solid, mp 101−102 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.13 (d, J = 9.8 Hz, 1H), 7.49−7.31 (complex m, 6H), 6.93 (d, J = 8.4 Hz, 1H), 6.79 (d, J = 8.4 Hz, 1H), 6.33 (d, J = 9.8 Hz, 1H), 5.17 (s, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 161.0, 155.4 (2), 155.3 (6), 138.7, 136.1, 132.4, 128.9, 128.5, 127.6, 114.9, 110.1, 109.6, 106.6, 71.0; IR ν_{max} (KBr): 2917, 2849, 1733, 1619, 1607, 1498, 1482, 1463, 1381, 1328, 1287, 1255, 1228, 1185, 1107, 1074, 1029 cm^{-1}; MS (EI, 70 eV) m/z: 252 ($M^{+\bullet}$, 48%), 91 (100); HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{16}H_{12}O_3Na$, 275.0679; found, 275.0677. $[M + H]^+$ calcd for $C_{16}H_{13}O_3$, 253.0859; found, 253.0849.

*7-Fluoro-2H-chromen-2-one (**123**).* Compound **123**[59] (55 mg, 55%) (R_f = 0.2 in 1:6 v/v ethyl acetate/toluene) was prepared from aryl propiolate **71** using General Procedure D and isolated as a colorless, crystalline solid, mp 133 °C (lit.[59] mp 132−133 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67 (d, J = 9.7 Hz, 1H), 7.46 (m, 1H), 7.05−6.93 (complex m, 2H), 6.34 (d, J = 9.7 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 164.5 (d, J_{C-F} = 254 Hz), 160.2, 155.3 (d, J_{C-F} = 13 Hz), 142.8, 129.3 (d, J_{C-F} = 10 Hz), 115.6 (d, J_{C-F} = 3 Hz), 115.5 (d, J_{C-F} = 3 Hz), 112.5 (d, J_{C-F} = 23 Hz), 104.5 (d, J_{C-F} = 26 Hz); IR ν_{max} (KBr): 1726, 1700, 1626, 1498, 1427, 1401, 1280, 1228, 1147, 1120, 1102 cm^{-1}; MS (EI, 70 eV) m/z: 164 ($M^{+\bullet}$, 92%), 136 (100); HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_9H_6FO_2$, 165.0346; found, 165.0353. This compound was co-produced with isomer **124** and separated from it by flash chromatography.

*5-Fluoro-2H-chromen-2-one (**124**).* Compound **124** (5 mg, 5%) (R_f = 0.3 in 1:6 v/v of ethyl acetate/toluene) was prepared from aryl propiolate **71** using General Procedure D and isolated as a colorless, crystalline solid, mp 111 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 (d, J = 9.7 Hz, 1H), 7.48 (m, 1H), 7.07 (d, J = 8.5 Hz, 1H), 6.92 (t, J = 8.5 Hz, 1H), 6.38 (d, J = 9.7 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 159.9 (s), 156.0 (d, J_{C-F} = 261 Hz), 136.2 (d, J_{C-F} = 4 Hz), 132.2 (d,

https://dx.doi.org/10.1021/acs.joc.0c02011
J. Org. Chem. XXXX, XXX, XXX−XXX

J_{C-F} = 10 Hz), 128.7 (d, J_{C-F} = 81 Hz), 116.8 (d, J_{C-F} = 2 Hz), 112.8 (d, J_{C-F} = 4 Hz), 110.4 (d, J_{C-F} = 20 Hz), 109.1 (d, J_{C-F} = 19 Hz); IR ν_{max} (KBr): 1733, 1628, 1617, 1461, 1239, 1187, 1107, 1039 cm^{-1}; MS (EI, 70 eV) *m/z*: 164 ($M^{+\bullet}$, 90%), 136 (100); HRMS (ESI) *m/z*: $[M + Na]^+$ calcd for $C_9H_5FO_2Na$, 187.0171; found, 187.0172. $[M + H]^+$ calcd for $C_9H_6FO_2$, 165.0352; found, 165.0352.

*7-Chloro-2H-chromen-2-one (**125**).* Compound **125**[49] (83 mg, 83%) (R_f = 0.4 in 1:3:6 v/v/v of ethyl acetate/dichloromethane/hexane) was prepared from aryl propiolate **72** using General Procedure D and isolated as a colorless, crystalline solid, mp 128−129 °C (lit.[49] mp 129 °C). ^1H NMR (400 MHz, $CDCl_3$): δ 7.67 (d, *J* = 9.5 Hz, 1H), 7.41 (d, *J* = 8.3 Hz, 1H), 7.35 (d, *J* = 2.0 Hz, 1H), 7.26 (dd, *J* = 8.3 and 2.0 Hz, 1H), 6.41 (d, *J* = 9.5 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 160.0, 154.6, 142.7, 138.0, 128.8, 125.2, 117.6, 117.4, 116.8; IR ν_{max} (KBr): 3081, 1721, 1683, 1619, 1604, 1488, 1394, 1267, 1247, 1221, 1180, 1139, 1106, 1076 cm^{-1}; MS (EI, 70 eV) *m/z*: 182 and 180 ($M^{+\bullet}$, 23 and 78), 154 and 152 (32 and 100); HRMS (ESI) *m/z*: $[M + Na]^+$ calcd for $C_9H_5{}^{35}ClO_2Na$, 202.9870; found, 202.9871. $[M + H]^+$ calcd for $C_9H_6{}^{35}ClO_2$, 181.0051; found, 181.0051. This compound was co-produced with isomer **126** and separated from it by flash chromatography.

*5-Chloro-2H-chromen-2-one (**126**).* Compound **126**[49] (16 mg, 16%) (R_f = 0.7 in 1:8 v/v ethyl acetate/toluene) was prepared from aryl propiolate **72** using General Procedure D and isolated as a colorless, crystalline solid, mp 89−90 °C (lit.[49] mp 91−94 °C). ^1H NMR (400 MHz, $CDCl_3$): δ 8.10 (d, *J* = 9.8 Hz, 1H), 7.45 (t, *J* = 8.2 Hz, 1H), 7.32 (d, *J* = 8.2 Hz, 1H), 7.25 (d, *J* = 8.2 Hz, 1H), 6.50 (d, *J* = 9.8 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 160.0, 155.1, 139.8, 132.6, 132.0, 125.2, 117.7, 117.6, 115.9; IR ν_{max} (KBr): 1738, 1615, 1599, 1447, 1265, 1235, 1185, 1113 cm^{-1}; MS (EI, 70 eV) *m/z*: 182 and 180 ($M^{+\bullet}$, 23 and 70%), 154 and 152 (33 and 100); HRMS (ESI) *m/z*: $[M + Na]^+$ calcd for $C_9H_5{}^{35}ClO_2Na$, 202.9870; found, 202.9872. $[M + H]^+$ calcd for $C_9H_6{}^{35}ClO_2$, 181.0051; found, 181.0060.

*7-Bromo-2H-chromen-2-one (**127**).* Compound **127**[53] (30 mg, 60%) (R_f = 0.5 in chloroform) was prepared from aryl propiolate **73** using General Procedure D and isolated as a colorless, crystalline solid, mp 122−123 °C (lit.[53] mp 120−124 °C). ^1H NMR (400 MHz, $CDCl_3$): δ 7.65 (d, *J* = 9.6 Hz, 1H), 7.49 (d, *J* = 1.8 Hz, 1H), 7.40 (dd, *J* = 8.3 and 1.8 Hz, 1H), 7.33 (d, *J* = 8.3 Hz, 1H), 6.42 (d, *J* = 9.6 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 159.9, 154.4, 142.8, 128.9, 128.0, 125.9, 120.3, 117.9, 117.0; IR ν_{max} (KBr): 1719, 1618, 1598, 1390, 1266, 1247, 1178, 1138, 1105, 1067 cm^{-1}; MS (EI, 70 eV) *m/z*: 226 and 224 ($M^{+\bullet}$, both 80%), 198 and 196 (98 and 100). HRMS data could not be acquired on this compound. This compound was co-produced with isomer **128** and separated from it by flash chromatography.

*5-Bromo-2H-chromen-2-one (**128**).* Compound **128**[53] (7 mg, 14%) (R_f = 0.3 in 3:2 v/v chloroform/hexane) was prepared from aryl propiolate **73** using General Procedure D and isolated as a colorless, crystalline solid, mp 94−95 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 8.06 (d, *J* = 9.8 Hz, 1H), 7.51 (d, *J* = 8.3 Hz, 1H), 7.37 (t, *J* = 8.3 Hz, 1H), 7.29 (d, *J* = 8.3 Hz, 1H), 6.49 (d, *J* = 9.8 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 160.0, 155.0, 142.3, 132.3, 128.6, 122.5, 119.0, 117.9, 116.6; IR ν_{max} (KBr): 1734, 1617, 1594, 1558, 1443, 1389, 1314, 1264, 1233, 1203, 1184, 1139, 1112 cm^{-1}; MS (EI, 70 eV) *m/z*: 226 and 224 ($M^{+\bullet}$, 94 and 94%), 198 and 196 (98 and 100); HRMS (ESI) *m/z*: $[M + Na]^+$ calcd for $C_9H_5{}^{81}BrO_2Na$ 248.9350; found, 248.9352. $[M + Na]^+$ calcd for $C_9H_5{}^{79}BrO_2Na$, 246.9371; found, 246.9372. $[M + H]^+$ calcd for $C_9H_6{}^{81}BrO_2$, 226.9531; found, 226.9533. $[M + H]^+$ calcd for $C_9H_6{}^{79}BrO_2$, 224.9551; found, 224.9552.

*6-Methyl-2H-chromen-2-one (**129**).* Compound **129**[49] (20 mg, quantitative) (R_f = 0.6 in chloroform) was prepared from aryl propiolate **74** using General Procedure D and isolated as a colorless, crystalline solid, mp 75−76 °C (lit.[49] mp 76.5 °C). ^1H NMR (400 MHz, $CDCl_3$): δ 7.60 (d, *J* = 9.5 Hz, 1H), 7.25 (d, *J* = 8.4 Hz, 1H), 7.20 (s, 1H), 7.14 (d, *J* = 8.4 Hz, 1H), 6.32 (d, *J* = 9.5 Hz, 1H), 2.40 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 161.2, 152.3, 143.5, 134.3, 133.0, 127.8, 118.7, 116.9, 116.7, 20.9; IR ν_{max} (KBr): 3081, 1760, 1714, 1684, 1623, 1612, 1575, 1487, 1430, 1380, 1278, 1262, 1246, 1189, 1168, 1131, 1106, 913 cm^{-1}; MS (EI, 70 eV) *m/z*: 160 ($M^{+\bullet}$, 100%), 132 (70); HRMS (EI) *m/z*: $M^{+\bullet}$ calcd for $C_{10}H_8O_2$, 160.0524; found, 160.0523.

*6-(Triethylsilyl)-2H-chromen-2-one (**130**).* Compound **130** (64 mg, 91%) (R_f = 0.5 in chloroform) was prepared from aryl propiolate **75** using General Procedure D and isolated as a colorless, crystalline solid, mp 48−50 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 7.64 (d, *J* = 9.5 Hz, 1H), 7.56 (dd, *J* = 8.2 and 1.5 Hz, 1H), 7.49 (d, *J* = 1.5 Hz, 1H), 7.25 (d, *J* = 8.2 Hz, 1H), 6.34 (d, *J* = 9.5 Hz, 1H), 0.90 (t, *J* = 7.7 Hz, 9H), 0.75 (q, *J* = 7.7 Hz, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 160.9, 154.8, 143.8, 137.7, 134.0 (4), 134.0 (2), 118.7, 116.7, 116.4, 7.4, 3.5; IR ν_{max} (KBr): 2955, 2910, 2875, 1733, 1618, 1594, 1562, 1457, 1418, 1363, 1283, 1259, 1225, 1183, 1131, 1111, 1085, 1008 cm^{-1}; MS (EI, 70 eV) *m/z*: 260 ($M^{+\bullet}$, 33%), 231 (100), 203 (100), 175 (100); HRMS (ESI) *m/z*: $[M + Na]^+$ calcd for $C_{15}H_{20}O_2SiNa$, 283.1125; found, 283.1118. $[M + H]^+$ calcd for $C_{15}H_{21}O_2Si$, 261.1305; found, 261.1296.

*6-(tert-Butyldimethylsilyl)-2H-chromen-2-one (**131**).* Compound **131** (37 mg, 74%) (R_f = 0.5 in chloroform) was prepared from aryl propiolate **76** using General Procedure D and isolated as a colorless, crystalline solid, mp 84−87 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 7.72 (d, *J* = 9.5 Hz, 1H), 7.63 (dd, *J* = 8.2 and 1.6 Hz, 1H), 7.57 (d, *J* = 1.6 Hz, 1H), 7.29 (d, *J* = 8.2 Hz, 1H), 6.40 (d, *J* = 9.5 Hz, 1H), 0.87 (s, 9H), 0.29 (s, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 160.8, 154.8, 143.8, 137.8, 134.3, 134.2, 118.4, 116.6, 116.0, 26.5, 16.9, −6.0; IR ν_{max} (KBr): 1752, 1728, 1622, 1607, 1564, 1454, 1400, 1276, 1260, 1228, 1178, 1120, 1102 cm^{-1}; MS (EI, 70 eV) *m/z*: 260 ($M^{+\bullet}$, 11%), 203 (100); HRMS (ESI) *m/z*: $[M + H]^+$ calcd for $C_{15}H_{21}O_2Si$, 261.1305; found, 261.1293.

*N-(2-Oxo-2H-chromen-6-yl)acetamide (**134**).* Compound **134**[60] (52 mg, 52%) (R_f = 0.5 in ethyl acetate) was prepared from aryl propiolate **79** using General Procedure D and isolated as a colorless, crystalline solid, mp 217 °C (lit.[60] mp 223−224 °C). ^1H NMR [400 MHz, $(CD_3)_2CO$]: δ 9.31 (broad s, 1H), 8.07 (s, 1H), 7.94 (d, *J* = 9.6 Hz, 1H), 7.69 (d, *J* = 8.9 Hz, 1H), 7.26 (d, *J* = 8.9 Hz, 1H), 6.40 (d, *J* = 9.6 Hz, 1H), 2.10 (s, 3H); $^{13}C\{^1H\}$ NMR [100 MHz, $(CD_3)_2CO$]: δ 169.0, 160.7, 150.9, 144.6, 137.0, 123.9, 119.9, 118.6, 117.7, 117.4, 24.2; IR ν_{max} (KBr): 3305, 3105, 2981, 2889, 1721, 1664, 1624, 1577, 1497, 1489, 1442, 1376, 1348, 1270, 1259, 1251, 1192, 1168, 1135, 1099 cm^{-1}; MS (EI, 70 eV) *m/z*: 203 ($M^{+\bullet}$, 57%), 161 (100), 133 (63); HRMS (ESI) *m/z*: $[M + Na]^+$ calcd for $C_{11}H_9NO_3Na$, 226.0475; found, 226.0480. $[M + H]^+$ calcd for $C_{11}H_{10}NO_3$, 204.0655; found, 204.0662.

*6-Chloro-2H-chromen-2-one (**136**).* Compound **136**[51] (33 mg, 66%) (R_f = 0.6 in chloroform) was prepared from aryl propiolate **81** using General Procedure D and isolated as a colorless, crystalline solid, mp 146−147 °C (lit.[51] mp 148−150 °C). ^1H NMR (400 MHz, $CDCl_3$): δ 7.63 (d, *J* = 9.6 Hz, 1H), 7.50−7.43 (complex m, 2H), 7.25 (partially obscured d, 1H), 6.45 (d, *J* = 9.6 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 159.9, 152.5, 142.2, 131.7, 129.7, 127.1, 119.8, 118.3, 117.9; IR ν_{max} (KBr): 1757, 1724, 1678, 1605, 1561, 1479, 1428, 1373, 1259, 1223, 1187, 1118, 1076 cm^{-1}; MS (EI, 70 eV) *m/z*: 182 and 180 ($M^{+\bullet}$, 30 and 89%), 154 and 152 (36 and 100); HRMS (ESI) *m/z*: $[M + H]^+$ calcd for $C_9H_6{}^{37}ClO_2$, 183.0024; found, 183.0021. $[M + H]^+$ calcd for $C_9H_6{}^{35}ClO_2$, 181.0051; found, 181.0051.

*6-Iodo-2H-chromen-2-one (**138**).* Compound **138**[61] (77 mg, 77%) (R_f = 0.4 in chloroform) was prepared from aryl propiolate **83** using General Procedure D and isolated as a colorless, crystalline solid, mp 164−165 °C (lit.[61] mp 165 °C). ^1H NMR (800 MHz, $CDCl_3$): δ 7.82 (d, *J* = 2.4 Hz, 1H), 7.80 (dd, *J* = 8.8 and 2.4 Hz, 1H), 7.61 (d, *J* = 8.8 Hz, 1H), 7.11 (d, *J* = 8.8 Hz, 1H), 6.44 (d, *J* = 8.8 Hz, 1H); $^{13}C\{^1H\}$ NMR (200 MHz, $CDCl_3$): δ 159.9, 153.7, 141.9, 140.4, 136.3, 120.9, 118.9, 117.7, 87.2; IR ν_{max} (KBr): 2923, 1726, 1594, 1555, 1472, 1419, 1364, 1259, 1216, 1180, 1107 cm^{-1}; MS (ESI, +ve) *m/z*: 273 [$(M + H)^+$, 100%]; HRMS (ESI) *m/z*: $[M + H]^+$ calcd for $C_9H_6IO_2$, 272.9413; found, 272.9415.

*Methyl 2-Oxo-2H-chromene-6-carboxylate (**140**).* Compound **140**[62] (9 mg, 18%) (R_f = 0.5 in 1:99 v/v chloroform/acetone) was prepared from aryl propiolate **85** using General Procedure D and isolated as a colorless, crystalline solid, mp 174−175 °C (lit.[62] mp 175−176 °C). ^1H NMR (400 MHz, $CDCl_3$): δ 8.20 (m, 2H), 7.75 (d, *J* = 9.6 Hz, 1H), 7.37 (d, *J* = 8.4 Hz, 1H), 6.48 (d, *J* = 9.6 Hz, 1H), 3.95 (s, 3H);

https://dx.doi.org/10.1021/acs.joc.0c02011
J. Org. Chem. XXXX, XXX, XXX−XXX

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 165.8, 160.0, 157.1, 143.2, 132.9, 130.1, 126.8, 118.7, 117.7, 117.3, 52.6; IR ν_{max} (KBr): 1747, 1717, 1628, 1605, 1445, 1428, 1379, 1284, 1265, 1217, 1179, 1129, 1094 cm^{-1}; MS (EI, 70 eV) m/z: 204 ($M^{+\bullet}$, 100%), 173 (99), 145 (60); HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{11}H_9O_4$, 205.0495; found, 205.0495.

*6,8-Dimethyl-2H-chromen-2-one (**142**).* Compound **142**[44] (20 mg, quantitative) (R_f = 0.5 in 1:4 v/v ethyl acetate/hexane) was prepared from aryl propiolate **87** using General Procedure D and isolated as a colorless, crystalline solid, mp 67−68 °C (lit.[44] mp 71−73 °C). ^1H NMR (400 MHz, $CDCl_3$): δ 7.63 (d, J = 9.5 Hz, 1H), 7.19 (s, 1H), 7.09 (s, 1H), 6.38 (d, J = 9.5 Hz, 1H), 2.42 (s, 3H), 2.36 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 161.4, 150.7, 143.9, 134.4, 133.7, 126.1, 125.5, 118.5, 116.4, 20.8, 15.4; IR ν_{max} (KBr): 1720, 1608, 1586, 1429, 1381, 1254, 1161, 1116, 1057 cm^{-1}; MS (EI, 70 eV) m/z: 174 ($M^{+\bullet}$, 100%), 146 (56), 131 (56); HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{11}H_{10}O_2Na$, 197.0573; found, 197.0573. $[M + H]^+$ calcd for $C_{11}H_{11}O_2$, 175.0754; found, 175.0754.

*8-iso-Propyl-5-methyl-2H-chromen-2-one (**143**).* Compound **143** (73 mg, 91%) (R_f = 0.6 in chloroform) was prepared from aryl propiolate **88** using General Procedure D and isolated as a colorless, crystalline solid, mp 56−57 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 7.92 (d, J = 9.8 Hz, 1H), 7.34 (d, J = 7.8 Hz, 1H), 7.06 (d, J = 7.8 Hz, 1H), 6.42 (d, J = 9.8 Hz, 1H), 3.60 (sept, J = 6.9 Hz, 1H), 2.49 (s, 3H), 1.29 (d, J = 6.9 Hz, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 161.1, 152.0, 141.0, 134.7, 133.4, 128.8, 125.7, 117.6, 115.7, 26.4, 22.9, 18.2; IR ν_{max} (KBr): 2965, 2930, 2872, 1731, 1594, 1485, 1458, 1384, 1239, 1185, 1159, 1124, 1052 cm^{-1}; MS (EI, 70 eV) m/z: 202 ($M^{+\bullet}$, 90%), 187 (100); HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{13}H_{15}O_2$, 203.1067; found, 203.1061. This compound was subjected to single-crystal X-ray analysis. Details of this are presented in the Experimental Section and the Supporting Information.

*6H-[1,3]Dioxolo[4,5-g]chromen-6-one (Ayapin) (**144**).* Compound **144**[55] (20 mg, quantitative) (R_f = 0.3 in chloroform) was prepared from aryl propiolate **89** using General Procedure D and isolated as a colorless, crystalline solid, mp 229−230 °C (lit.[55] mp 231−232 °C). ^1H NMR (400 MHz, $CDCl_3$): δ 7.58 (d, J = 9.5 Hz, 1H), 6.83 (s, 2H), 6.28 (d, J = 9.5 Hz, 1H), 6.07 (s, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 161.4, 151.5, 145.1, 143.7, 113.6, 112.9, 105.2, 102.6, 98.6 (one signal obscured or overlapping); IR ν_{max} (KBr): 1705, 1684, 1633, 1581, 1494, 1455, 1419, 1385, 1273, 1258, 1225, 1045, 941 cm^{-1}; MS (EI, 70 eV) m/z: 190 ($M^{+\bullet}$, 100%); HRMS (EI) m/z: $M^{+\bullet}$ calcd for $C_{10}H_6O_4$, 190.0266; found, 190.0264. This compound was subjected to single-crystal X-ray analysis. Details of this are presented in the Experimental Section and the Supporting Information.

*6,7-Dimethoxy-2H-chromen-2-one (Scoparone) (**145**).* Compound **145**[50] (45 mg, 92%) (R_f = 0.3 in 1:1 v/v of ethyl acetate/hexane) was prepared from aryl propiolate **90** using General Procedure D and isolated as a colorless, crystalline solid, mp 144−145 °C (lit.[50] mp 145−146 °C). ^1H NMR (400 MHz, $CDCl_3$): δ 7.59 (d, J = 9.5 Hz, 1H), 6.83 (s, 1H), 6.78 (s, 1H), 6.23 (d, J = 9.5 Hz, 1H), 3.90 (s, 3H), 3.88 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 161.4, 152.9, 150.0, 146.4, 143.4, 113.5, 111.5, 108.0, 100.0, 56.4 (1), 56.3 (9); IR ν_{max} (KBr): 1713, 1614, 1558, 1514, 1463, 1450, 1423, 1383, 1277, 1248, 1205, 1170, 1139, 1095, 1004 cm^{-1}; MS (EI, 70 eV) m/z: 206 ($M^{+\bullet}$, 100%); HRMS (EI) m/z: $M^{+\bullet}$ calcd for $C_{11}H_{10}O_4$, 206.0579; found, 206.0579.

*Methyl (S)-2-((tert-Butoxycarbonyl)amino)-3-(2-oxo-2H-chromen-6-yl)propanoate (**146**).* Compound **146** (34 mg, 68%) (R_f = 0.4 in 1:1 v/v ethyl acetate/hexane) was prepared from aryl propiolate **91** using General Procedure D and isolated as a clear, colorless oil. ^1H NMR (400 MHz, $CDCl_3$): δ 7.58 (d, J = 9.6 Hz, 1H), 7.25−7.16 (complex m, 3H), 6.34 (d, J = 9.6 Hz, 1H), 4.98 (broad s, 1H), 4.52 (broad s, 1H), 3.66 (s, 3H), 3.13 (dd, J = 14.0 and 6.0 Hz, 1H), 2.99 (dd, J = 14.0 and 6.7 Hz, 1H), 1.33 (s, 9H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 172.2, 171.3, 160.8, 155.2, 153.3, 143.3, 133.0, 132.9, 128.5, 119.0, 117.2, 80.4, 54.6, 52.6, 38.0, 28.5 (additional signals observed due to carbamate rotamers); IR ν_{max} (KBr): 2980, 1725, 1626, 1574, 1508, 1438, 1391, 1367, 1280, 1249, 1217, 1166, 1101, 1058, 1021 cm^{-1}; MS (ESI, +ve) m/z: 348 [$(M + H)^+$, 97%], 333 (65), 292 (100), 282 (76); HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{18}H_{21}NO_6Na$, 370.1261; found, 370.1278. $[M + H]^+$ calcd for $C_{18}H_{22}NO_6$, 348.1442; found, 348.1453.

*3H-Benzo[f]chromen-3-one (**147**).* Compound **147**[51] (20 mg, quantitative) (R_f = 0.2 in 1:4 v/v ethyl acetate/hexane) was prepared from aryl propiolate **92** using General Procedure D and isolated as a colorless, crystalline solid, mp 116−117 °C (lit.[51] mp 110−111 °C). ^1H NMR (400 MHz, $CDCl_3$): δ 8.50 (d, J = 9.8 Hz, 1H), 8.24 (d, J = 8.5 Hz, 1H), 7.99 (d, J = 9.0 Hz, 1H), 7.92 (d, J = 8.5 Hz, 1H), 7.70 (ddd, J = 8.5, 7.0 and 1.3 Hz, 1H), 7.58 (ddd, J = 8.5, 7.0 and 1.3 Hz, 1H), 7.47 (d, J = 9.0 Hz, 1H), 6.58 (d, J = 9.8 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 161.0, 154.1, 139.2, 133.3, 130.5, 129.2 (3), 129.1 (8), 128.4, 126.2, 121.5, 117.3, 115.9, 113.2; IR ν_{max} (KBr): 3710, 3681, 2973, 2923, 2866, 2844, 2827, 1719, 1566, 1516, 1337, 1176, 1112, 1055, 1033, 1013 cm^{-1}; MS (ESI, +ve) m/z: 196 ($M^{+\bullet}$, 84%), 168 (100), 139 (63); HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{13}H_8O_2Na$, 219.0417; found, 219.0419. $[M + H]^+$ calcd for $C_{13}H_9O_2$, 197.0597; found, 197.0603.

*2H-Benzo[h]chromen-2-one (**148**).* Compound **148**[49] (20 mg, quantitative) (R_f = 0.2 in 1:4 v/v ethyl acetate/hexane) was prepared from aryl propiolate **95** using General Procedure D and isolated as a colorless, crystalline solid, mp 140−141 °C (lit.[49] mp 141−142 °C). ^1H NMR (400 MHz, $CDCl_3$): δ 8.52 (m, 1H), 7.85 (m, 1H), 7.80 (d, J = 9.5 Hz, 1H), 7.66 (d, J = 8.7 Hz, 1H), 7.63 (dd, J = 6.8 and 3.5 Hz, 1H), 7.62 (d, J = 3.5 Hz, 1H), 7.43 (d, J = 8.7 Hz, 1H), 6.49 (d, J = 9.5 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 161.0, 151.5, 144.3, 135.0, 128.8, 127.9, 127.3, 124.5, 123.7, 123.2, 122.4, 116.1, 114.4; IR ν_{max} (KBr): 2361, 2342, 1716, 1637, 1605, 1564, 1504, 1472, 1381, 1345, 1279, 1119, 1033, 1009 cm^{-1}; MS (EI, 70 eV) m/z: 196 ($M^{+\bullet}$, 87%), 168 (100), 139 (67); HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{13}H_8O_2Na$, 219.0417; found, 219.0421. $[M + H]^+$ calcd for $C_{13}H_9O_2$, 197.0597; found, 197.0601.

*Pyrano[2,3-b]carbazol-2(10H)-one (**149**).* Compound **149** (120 mg, 60%) (R_f = 0.3 in 1:2 v/v ethyl acetate/hexane) was prepared from aryl propiolate **96** using General Procedure D and isolated as a yellow, crystalline powder, mp 235−236 °C. ^1H NMR [400 MHz, $(CD_3)_2CO$] δ 10.72 (s, 1H), 8.38 (s, 1H), 8.16 (dd, J = 8.0 and 1.0 Hz, 1H), 8.10 (d, J = 9.5 Hz, 1H), 7.56 (d, J = 8.0 Hz, 1H), 7.45 (ddd, J = 8.0, 7.1 and 1.0 Hz, 1H), 7.39 (s, 1H), 7.26 (ddd, J = 8.0, 7.1 and 1.0 Hz, 1H), 6.26 (d, J = 9.5 Hz, 1H); $^{13}C\{^1H\}$ NMR [100 MHz, $(CD_3)_2CO$]: δ 161.4, 154.3, 145.8, 143.4, 142.14, 127.3, 123.5, 121.9, 121.2, 120.9, 120.8, 113.2, 112.9, 112.1, 98.3; IR ν_{max} (KBr): 3310, 2917, 1716, 1637, 1615, 1458, 1441, 1347, 1227, 1173, 1116 cm^{-1}; MS (EI, 70 eV) m/z: 235 ($M^{+\bullet}$, 20%), 207 (100); HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{15}H_9NO_2Na$, 258.0525; found, 258.0536. $[M + H]^+$ calcd for $C_{15}H_{10}NO_2$, 236.0706; found, 236.0709. This compound was co-produced with isomer **150** and separated from it by flash chromatography.

*Pyrano[3,2-a]carbazol-3(11H)-one (**150**).* Compound **150** (10 mg, 5%) (R_f = 0.3 in 1:2 v/v ethyl acetate/hexane) was prepared from aryl propiolate **96** using General Procedure D and isolated as a yellow, crystalline powder, mp 261−262 °C. ^1H NMR [400 MHz, $(CD_3)_2CO$]: δ 11.12 (s, 1H), 8.50 (d, J = 9.6 Hz, 1H), 8.30 (d, J = 8.4 Hz, 1H), 8.14 (d, J = 7.4 Hz, 1H), 7.58 (d, J = 8.4 Hz, 1H), 7.43 (ddd, J = 8.4, 7.4 and 1.1 Hz, 1H), 7.26 (ddd, J = 8.4, 7.4 and 1.1 Hz, 1H), 7.15 (d, J = 8.4 Hz, 1H), 6.46 (d, J = 9.6 Hz, 1H); $^{13}C\{^1H\}$ NMR [100 MHz, $(CD_3)_2CO$]: δ 161.1, 154.6, 141.3, 139.8, 137.3, 126.6, 124.9, 123.9, 121.1, 120.9, 120.3, 115.6, 112.3, 109.1, 105.3; IR ν_{max} (KBr): 3361, 2923, 1706, 1637, 1610, 1460, 1326, 1239, 1142 cm^{-1}; MS (EI, 70 eV) m/z: 235 ($M^{+\bullet}$, 35%), 207 (100); HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{15}H_9NO_2Na$, 258.0525; found, 258.0533. $[M + H]^+$ calcd for $C_{15}H_{10}NO_2$, 236.0706; found, 236.0708.

*6-Methoxy-4-methyl-2H-chromen-2-one (**151**).* Compound **151**[63] (16 mg, 80%) (R_f = 0.3 in 1:3:6 v/v/v ethyl acetate/dichloromethane/hexane) was prepared from aryl propiolate **97** using General Procedure D and isolated as a colorless, crystalline solid, mp 164−165 °C (lit.[63] mp 164−166 °C). ^1H NMR (400 MHz, $CDCl_3$): δ 7.26 (d, J = 9.0 Hz, 1H), 7.10 (dd, J = 9.0 and 2.9 Hz, 1H), 7.01 (d, J = 2.9 Hz, 1H), 6.29 (d, J = 1.4 Hz, 1H), 3.86 (s, 3H), 2.41 (d, J = 1.4 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 161.0, 156.1, 152.0, 148.1, 120.6, 118.8, 118.1,

https://dx.doi.org/10.1021/acs.joc.0c02011
J. Org. Chem. XXXX, XXX, XXX−XXX

115.7, 107.9, 56.0, 18.8; IR ν_{max} (KBr): 2923, 2866, 1709, 1576, 1494, 1467, 1425, 1384, 1366, 1280, 1262, 1247, 1169, 1055, 1033, 1010 cm^{-1}; MS (EI, 70 eV) *m/z*: 190 ($M^{+\bullet}$, 100%); HRMS (ESI) *m/z*: $[M + H]^+$ calcd for $C_{11}H_{11}O_3$, 191.0703; found, 191.0704.

*6-Methoxy-4-phenyl-2H-chromen-2-one (**152**).* Compound **152**[64] (15 mg, 75%) (R_f = 0.5 in 1:4 v/v ethyl acetate/hexane) was prepared from aryl propiolate **98** using General Procedure D and isolated as a colorless, crystalline solid, mp 149−150 °C (lit.[64] mp 148−149 °C). ^1H NMR (400 MHz, $CDCl_3$): δ 7.53 (m, 3H), 7.46 (m, 2H), 7.34 (d, *J* = 9.0 Hz, 1H), 7.13 (dd, *J* = 9.0 and 3.0 Hz, 1H), 6.93 (d, *J* = 3.0 Hz, 1H), 6.38 (s, 1H), 3.74 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 161.1, 156.1, 155.5, 148.8, 135.5, 129.8, 129.1, 128.5, 119.6, 119.1, 118.4, 115.8, 110.2, 55.9; IR ν_{max} (KBr): 2921, 2845, 1713, 1562, 1483, 1447, 1425, 1361, 1270, 1240, 1179, 1054, 1033, 951 cm^{-1}; MS (EI, 70 eV) *m/z*: 252 ($M^{+\bullet}$, 100%), 224 (49), 181 (18); HRMS (ESI) *m/z*: $[M + Na]^+$ calcd for $C_{16}H_{12}O_3Na$, 275.0679; found, 275.0682. $[M + H]^+$ calcd for $C_{16}H_{13}O_3$, 253.0859; found, 253.0857.

*3-Iodo-6-methoxy-2H-chromen-2-one (**154**).* Compound **154** (123 mg, 36%) (R_f = 0.4 in 1:4 v/v diethyl ether/dichloromethane) was prepared from aryl propiolate **3** using General Procedure D except that NIS (1.1 equiv) was added to the reaction mixture before the gold catalyst. This product was isolated as a colorless, crystalline solid, mp 186−188 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 8.32 (s, 1H), 7.26 (d, *J* = 9.1 Hz, 1H), 7.14 (dd, *J* = 9.1 and 2.9 Hz, 1H), 6.85 (d, *J* = 2.9 Hz, 1H), 3.84 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 157.9, 156.5, 152.2, 148.7, 120.7, 120.3, 118.1, 108.9, 87.3, 56.1; IR ν_{max} (KBr): 1719, 1557, 1491, 1466, 1420, 1337, 1257, 1180, 1140, 1121, 1097, 1024 cm^{-1}; MS (EI, 70 eV) *m/z*: 302 ($M^{+\bullet}$, 100%), 175 (30), 119 (35); HRMS (EI) *m/z*: $M^{+\bullet}$ calcd for $C_{10}H_7IO_3$, 301.9440; found, 301.9443. This compound was co-produced with its de-iodinated congener **4** (38%) and separated from it by flash chromatography.

General Procedure E—Formation of Aryl Propargyl Ethers 155−157. A magnetically stirred solution of the relevant methoxyphenol (500 mg, 4.0 mmol, 1 equiv) in acetone (20 mL) was treated with 3-chloro-3-methylbut-1-yne (1.14 g, 8.1 mmol, 2 equiv), potassium carbonate (3.06 g, 22.2 mmol, 5.5 equiv), and potassium iodide (5.01 g, 30.2 mmol, 7.5 equiv). The resulting mixture was stirred at 60 °C for 16 h before being cooled and filtered. Hydrochloric acid (20 mL of 2.0 M aqueous solution) was then added to the filtrate, and the aqueous phase was extracted with diethyl ether (3 × 40 mL). The combined organic phases were washed with brine (1 × 50 mL) before being dried ($MgSO_4$), filtered, and concentrated under reduced pressure to give a yellow oil. This oil was subjected to flash chromatography (silica gel, 1:4 v/v diethyl ether/hexane elution), and concentration of the relevant fractions then gave the title propargyl ether.

*1-Methoxy-2-((2-methylbut-3-yn-2-yl)oxy)benzene (**155**).* Compound **155**[28e] (542 mg, 71%) (R_f = 0.6 in 1:4 v/v diethyl ether/hexane) was prepared from *o*-methoxyphenol (**16**) using General Procedure E and isolated as a clear, colorless oil. ^1H NMR (400 MHz, $CDCl_3$): δ 7.46 (dd, *J* = 8.0 and 1.7 Hz, 1H), 7.05 (m, 1H), 6.90 (complex m, 2H), 3.82 (s, 3H), 2.51 (s, 1H), 1.67 (s, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 153.2, 144.9, 124.2, 123.5, 120.5, 112.4, 86.6, 74.1, 73.4, 55.9, 29.5; IR ν_{max} (KBr): 1593, 1499, 1463, 1456, 1439, 1381, 1363, 1298, 1255, 1215, 1179, 1139, 1114, 1046, 1029 cm^{-1}; MS (EI, 70 eV) *m/z*: 190 ($M^{+\bullet}$, 40%), 175 (100), 160 (45); HRMS (ESI) *m/z*: $[M + Na]^+$ calcd for $C_{12}H_{14}O_2Na$, 213.0886; found, 213.0885. $[M + H]^+$ calcd for $C_{12}H_{15}O_2$, 191.1067; found, 191.1067.

*1-Methoxy-3-((2-methylbut-3-yn-2-yl)oxy)benzene (**156**).* Compound **156**[28a] (470 mg, 61%) (R_f = 0.5 in 1:4 v/v diethyl ether/hexane) was prepared from *m*-methoxyphenol (**21**) using General Procedure E and isolated as a clear, colorless oil. ^1H NMR (400 MHz, $CDCl_3$): δ 7.17 (t, *J* = 8.2 Hz, 1H), 6.86−6.76 (complex m, 2H), 6.61 (m, 1H), 3.79 (s, 3H), 2.57 (s, 1H), 1.65 (s, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 160.3, 156.8, 129.2, 113.5, 108.5, 107.3, 86.2, 73.8, 72.3, 55.2, 29.6; IR ν_{max} (KBr): 1601, 1591, 1487, 1466, 1452, 1382, 1364, 1313, 1282, 1264, 1225, 1196, 1134, 1077, 1043 cm^{-1}; MS (EI, 70 eV) *m/z*: 190 ($M^{+\bullet}$, 24%), 175 (100); HRMS (ESI) *m/z*: $[M + H]^+$ calcd for $C_{12}H_{15}O_2$, 191.1067; found, 191.1069.

*1-Methoxy-4-((2-methylbut-3-yn-2-yl)oxy)benzene (**157**).* Compound **157**[28a] (410 mg, 54%) (R_f = 0.8 in 1:4 v/v diethyl ether/hexane) was prepared from *p*-methoxyphenol (**7**) using General Procedure E and isolated as a clear, colorless oil. ^1H NMR (400 MHz, $CDCl_3$): δ 7.13 (d, *J* = 9.0 Hz, 2H), 6.81 (d, *J* = 9.0 Hz, 2H), 3.78 (s, 3H), 2.52 (s, 1H), 1.60 (s, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 156.0, 149.1, 123.8, 114.0, 86.6, 73.7, 73.1, 55.7, 29.7; IR ν_{max} (KBr): 1505, 1465, 1442, 1381, 1363, 1294, 1232, 1214, 1182, 1138, 1101, 1036 cm^{-1}; MS (EI, 70 eV) *m/z*: 190 ($M^{+\bullet}$, 24%), 175 (100); HRMS (ESI) *m/z*: $[M + H]^+$ calcd for $C_{12}H_{15}O_2$, 191.1067; found, 191.1069.

Synthesis of Chromenes 158−161. *General Procedure F—Gold(I)-Catalyzed Cyclization of Aryl Propargyl Ethers **155−157**.* A magnetically stirred solution of the requisite aryl propargyl ether (1 mmol, 1 equiv) in dichloromethane (50 mL) was treated with Echavarren's gold(I) catalyst (23 mg, 0.03 mmol, 0.03 equiv). The resulting solution was stirred at 18 °C for 1 h, then filtered through a pad of TLC-grade silica gel, and the filtrate concentrated under reduced pressure. The light yellow oil thus obtained was subjected to flash chromatography (silica gel, 3:7 v/v ethyl acetate/hexane elution), and concentration of the relevant fractions then gave the anticipated chromene(s).

*8-Methoxy-2,2-dimethyl-2H-chromene (**158**).* Compound **158**[5a] (84 mg, 84%) (R_f = 0.6 in 1:3 v/v ethyl acetate/hexane) was prepared from propargyl ether **155** using General Procedure F and isolated as a clear, colorless oil. ^1H NMR (400 MHz, $CDCl_3$): δ 6.78 (m, 2H), 6.64 (m, 1H), 6.31 (d, *J* = 9.8 Hz, 1H), 5.61 (d, *J* = 9.8 Hz, 1H), 3.86 (s, 3H), 1.48 (s, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 148.5, 142.2, 131.0, 122.5, 122.2, 120.4, 119.0, 112.7, 76.5, 56.5, 28.0; IR ν_{max} (KBr): 1575, 1480, 1459, 1393, 1377, 1361, 1269, 1208, 1165, 1131, 1082 cm^{-1}; MS (EI, 70 eV) *m/z*: 190 ($M^{+\bullet}$, 41%), 175 (100); HRMS (ESI) *m/z*: $[M + Na]^+$ calcd for $C_{12}H_{14}O_2Na$, 213.0886; found, 213.0889. $[M + H]^+$ calcd for $C_{12}H_{15}O_2$, 191.1067; found, 191.1069.

*7-Methoxy-2,2-dimethyl-2H-chromene (Precocene I) (**159**).* Compound **159**[5a,65] (99 mg, 66%) (R_f = 0.6 in 1:1 v/v toluene/hexane) was prepared from propargyl ether **156** using General Procedure F and isolated as a clear, colorless oil. ^1H NMR (400 MHz, $CDCl_3$): δ 6.88 (d, *J* = 8.2 Hz, 1H), 6.39 (m, 2H), 6.27 (d, *J* = 9.7 Hz, 1H), 5.47 (d, *J* = 9.7 Hz, 1H), 3.77 (s, 3H), 1.43 (s, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 160.8, 154.3, 128.0, 127.1, 122.1, 114.8, 106.8, 102.2, 76.5, 55.4, 28.2; IR ν_{max} (KBr): 1616, 1569, 1504, 1464, 1444, 1390, 1375, 1361, 1316, 1279, 1266, 1240, 1196, 1159, 1130, 1120, 1034 cm^{-1}; MS (EI, 70 eV) *m/z*: 190 ($M^{+\bullet}$, 36%), 175 (100); HRMS (ESI) *m/z*: $[M + H]^+$ calcd for $C_{12}H_{15}O_2$, 191.1067; found, 191.1069. This compound was co-produced with regioisomer **161** and separated from it by flash chromatography.

*6-Methoxy-2,2-dimethyl-2H-chromene (**160**).* Compound **160**[66] (99 mg, 99%) (R_f = 0.6 in 1:1 v/v chloroform/hexane) was prepared from propargyl ether **157** using General Procedure F and isolated as a clear, colorless oil. ^1H NMR (400 MHz, $CDCl_3$): δ 6.71−6.66 (complex m, 2H), 6.55 (m, 1H), 6.28 (d, *J* = 9.8 Hz, 1H), 5.63 (d, *J* = 9.8 Hz, 1H), 3.75 (s, 3H), 1.41 (s, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 153.9, 146.9, 131.9, 122.5, 122.1, 116.9, 114.4, 111.7, 75.9, 55.9, 27.8; IR ν_{max} (KBr): 2980, 1611, 1577, 1492, 1465, 1432, 1383, 1370, 1361, 1310, 1266, 1258, 1208, 1167, 1120, 1108, 1040 cm^{-1}; MS (EI, 70 eV) *m/z*: 190 ($M^{+\bullet}$, 52%), 175 (100); HRMS (ESI) *m/z*: $[M + H]^+$ calcd for $C_{12}H_{15}O_2$, 191.1067; found, 191.1071.

*5-Methoxy-2,2-dimethyl-2H-chromene (**161**).* Compound **161**[67] (38 mg, 25%) (R_f = 0.7 in 1:1 v/v toluene/hexane) was prepared from propargyl ether **156** using General Procedure F and isolated as a clear, colorless oil. ^1H NMR (400 MHz, $CDCl_3$): δ 7.05 (t, *J* = 8.2 Hz, 1H), 6.68 (d, *J* = 10.0 Hz, 1H), 6.45 (d, *J* = 8.2 Hz, 1H), 6.41 (d, *J* = 8.2, 1H), 5.56 (d, *J* = 10.0 Hz, 1H), 3.82 (s, 3H), 1.43 (s, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 155.4, 153.9, 129.0, 117.0, 110.8, 109.7, 103.1, 75.8, 55.8, 27.9 (one signal obscured or overlapping); IR ν_{max} (KBr): 1635, 1602, 1579, 1483, 1466, 1439, 1391, 1376, 1361, 1314, 1283, 1254, 1245, 1214, 1198, 1163, 1117, 1093 cm^{-1}; MS (EI, 70 eV) *m/z*: 190 ($M^{+\bullet}$, 41%), 175 (100); HRMS (ESI) *m/z*: $[M + H]^+$ calcd for $C_{12}H_{15}O_2$, 191.1067; found, 191.1069.

X-ray Crystallographic Studies. Crystallographic Data. *Crystallographic Data for Compound **1**.* $C_9H_6O_2$, *M* = 146.15, *T* =

https://dx.doi.org/10.1021/acs.joc.0c02011
J. Org. Chem. XXXX, XXX, XXX−XXX

200 K, orhorhombic, space group $Pca2_1$, $Z = 4$, $a = 15.5001(5)$ Å, $b = 5.6360(1)$ Å, $c = 7.8224(3)$ Å; $V = 683.35(4)$ Å^3, $D_x = 1.420$ Mg m^{-3}, 1064 unique data ($2\theta_{max} = 60°$), $R = 0.033$ [for 947 reflections with $I > 2.0\sigma(I)$]; Rw = 0.093 (all data), $S = 1.00$.[68]

Crystallographic Data for Compound ***10****.* $C_{16}H_{24}N_2O_2$, $M = 276.38$, $T = 150$ K, monoclinic, space group $P2_1/n$, $Z = 4$, $a = 10.4085(1)$ Å, $b = 15.1263(2)$ Å, $c = 10.7316(1)$ Å; $\beta = 107.1435(13)°$; $V = 1614.54(3)$ Å^3, $D_x = 1.137$ Mg m^{-3}, 3185 unique data ($2\theta_{max} = 144.8°$), $R = 0.038$ [for 2968 reflections with $I > 2.0\sigma(I)$]; Rw = 0.098 (all data), $S = 1.00$.

Crystallographic Data for Compound ***11****.* $C_{16}H_{24}N_2O_2$, $M = 276.38$, $T = 200$ K, triclinic, space group $P\bar{1}$, $Z = 4$, $a = 6.6046(2)$ Å, $b = 15.2228(8)$ Å, $c = 16.3344(8)$ Å; $\alpha = 108.4733(16)°$, $\beta = 90.541(3)°$, $\gamma = 98.291(3)°$; $V = 1538.70(12)$ Å^3, $D_x = 1.193$ Mg m^{-3}, 5408 unique data ($2\theta_{max} = 50°$), $R = 0.091$ [for 2757 reflections with $I > 2.0\sigma(I)$]; Rw = 0.264 (all data), $S = 0.96$.

Crystallographic Data for Compound ***66****.* $C_{10}H_5NO_2$, $M = 171.16$, $T = 150$ K, orthorhombic, space group $P2_12_12_1$, $Z = 4$, $a = 6.75067(9)$ Å, $b = 7.39783(8)$ Å, $c = 16.4098(2)$ Å; $V = 819.51(2)$ Å^3, $D_x = 1.387$ Mg m^{-3}, 1617 unique data ($2\theta_{max} = 144.6°$), $R = 0.026$ [for 1598 reflections with $I > 2.0\sigma(I)$]; Rw = 0.066 (all data), $S = 1.01$.

Crystallographic Data for Compound ***76****.* $C_{15}H_{20}O_2Si$, $M = 260.41$, $T = 150$ K, monoclinic, space group $P2_1/c$, $Z = 4$, $a = 12.2384(1)$ Å, $b = 10.9882(1)$ Å, $c = 12.8362(1)$ Å; $\beta = 117.4991(14)°$; $V = 1531.16(3)$ Å^3, $D_x = 1.130$ Mg m^{-3}, 3031 unique data ($2\theta_{max} = 145.4°$), $R = 0.033$ [for 2965 reflections with $I > 2.0\sigma(I)$]; Rw = 0.089 (all data), $S = 1.01$.

Crystallographic Data for Compound ***78****.* $C_9H_5NO_4$, $M = 191.14$, $T = 200$ K, monoclinic, space group Cc, $Z = 4$, $a = 3.7967(3)$ Å, $b = 17.9840(18)$ Å, $c = 12.4359(13)$ Å; $\beta = 96.435(6)°$; $V = 843.77(14)$ Å^3, $D_x = 1.505$ Mg m^{-3}, 751 unique data ($2\theta_{max} = 50.2°$), $R = 0.038$ [for 684 reflections with $I > 2.0\sigma(I)$]; Rw = 0.100 (all data), $S = 1.05$.

Crystallographic Data for Compound ***84****.* $C_{10}H_5NO_2$, $M = 171.16$, $T = 150$ K, monoclinic, space group $P2_1/n$, $Z = 4$, $a = 3.7480(1)$ Å, $b = 17.3981(5)$ Å, $c = 12.5878(3)$ Å; $\beta = 92.916(2)°$; $V = 819.76(4)$ Å^3, $D_x = 1.387$ Mg m^{-3}, 2057 unique data ($2\theta_{max} = 59.6°$), $R = 0.043$ [for 1586 reflections with $I > 2.0\sigma(I)$]; Rw = 0.111 (all data), $S = 1.01$.

Crystallographic Data for Compound ***85****.* $C_{11}H_8O_4$, $M = 204.18$, $T = 200$ K, triclinic, space group $P\bar{1}$, $Z = 4$, $a = 6.6091(1)$ Å, $b = 11.8349(3)$ Å, $c = 13.2614(3)$ Å; $\alpha = 70.6450(11)°$, $\beta = 85.7766(16)°$, $\gamma = 89.8209(14)°$; $V = 975.75(4)$ Å^3, $D_x = 1.390$ Mg m^{-3}, 4439 unique data ($2\theta_{max} = 55°$), $R = 0.054$ [for 3806 reflections with $I > 2.0\sigma(I)$]; Rw = 0.146 (all data), $S = 1.02$.

Crystallographic Data for Compound ***87****.* $C_{11}H_{10}O_2$, $M = 174.20$, $T = 200$ K, monoclinic, space group $P2_1/c$, $Z = 4$, $a = 6.2253(3)$ Å, $b = 19.1850(4)$ Å, $c = 8.2327(2)$ Å; $\beta = 104.6106(14)°$; $V = 951.46(3)$ Å^3, $D_x = 1.216$ Mg m^{-3}, 2179 unique data ($2\theta_{max} = 55°$), $R = 0.042$ [for 1710 reflections with $I > 2.0\sigma(I)$]; Rw = 0.107 (all data), $S = 0.96$.

Crystallographic Data for Compound ***89****.* $C_{10}H_6O_4$, $M = 190.16$, $T = 200$ K, monoclinic, space group $P2_1/c$, $Z = 4$, $a = 6.1545(1)$ Å, $b = 18.9599(5)$ Å, $c = 7.4521(2)$ Å; $\beta = 99.4936(13)°$; $V = 857.67(4)$ Å^3, $D_x = 1.473$ Mg m^{-3}, 2528 unique data ($2\theta_{max} = 60.2°$), $R = 0.038$ [for 1915 reflections with $I > 2.0\sigma(I)$]; Rw = 0.098 (all data), $S = 0.95$.

Crystallographic Data for Compound ***93****.* $C_{14}H_{10}O_3$, $M = 226.23$, $T = 200$ K, monoclinic, space group $P2_1/c$, $Z = 4$, $a = 8.3713(2)$ Å, $b = 6.1080(1)$ Å, $c = 21.7217(4)$ Å; $\beta = 95.2892(12)°$; $V = 1105.94(4)$ Å^3, $D_x = 1.359$ Mg m^{-3}, 2520 unique data ($2\theta_{max} = 55°$), $R = 0.040$ [for 1954 reflections with $I > 2.0\sigma(I)$]; Rw = 0.105 (all data), $S = 0.97$.

Crystallographic Data for Compound ***97****.* $C_{11}H_{10}O_3$, $M = 190.20$, $T = 150$ K, monoclinic, space group $P2_1/c$, $Z = 4$, $a = 3.9118(1)$ Å, $b = 10.6613(1)$ Å, $c = 22.5081(2)$ Å; $\beta = 92.0236(9)°$; $V = 938.11(3)$ Å^3, $D_x = 1.347$ Mg m^{-3}, 1853 unique data ($2\theta_{max} = 144.8°$), $R = 0.034$ [for 1817 reflections with $I > 2.0\sigma(I)$]; Rw = 0.094 (all data), $S = 1.01$.

Crystallographic Data for Compound ***100****.* $C_{14}H_{10}O_3$, $M = 226.23$, $T = 200$ K, monoclinic, space group $P2_1$, $Z = 2$, $a = 3.9570(2)$ Å, $b = 10.1776(6)$ Å, $c = 13.1193(7)$ Å; $\beta = 97.119(4)°$; $V = 524.28(5)$ Å^3, $D_x = 1.433$ Mg m^{-3}, 1261 unique data ($2\theta_{max} = 55°$), $R = 0.078$ [for 1147 reflections with $I > 2.0\sigma(I)$]; Rw = 0.239 (all data), $S = 1.02$.

Crystallographic Data for Compound ***143****.* $C_{13}H_{14}O_2$, $M = 202.25$, $T = 150$ K, monoclinic, space group $P2_1/c$, $Z = 8$, $a = 18.7210(4)$ Å, $b = 6.8676(1)$ Å, $c = 16.9360(3)$ Å; $\beta = 97.6555(3)°$; $V = 2158.03(7)$ Å^3, $D_x = 1.245$ Mg cm^{-3}, 4275 unique data ($2\theta_{max} = 145.2°$), $R = 0.043$ [for 3789 reflections with $I > 2.0\sigma(I)$]; Rw = 0.123 (all data), $S = 0.99$.

Crystallographic Data for Compound ***144****.* $C_{10}H_6O_4$, $M = 190.16$, $T = 200$ K, orthorhombic, space group $Pnma$, $Z = 4$, $a = 6.8358(4)$ Å, $b = 6.4527(5)$ Å, $c = 18.4109(12)$ Å; $V = 812.09(9)$ Å^3, $D_x = 1.555$ Mg cm^{-3}, 1011 unique data ($2\theta_{max} = 55°$), $R = 0.049$ [for 759 reflections with $I > 2.0\sigma(I)$]; Rw = 0.118 (all data), $S = 1.05$.

Structure Determinations. Images for compounds **1**, **11**, **78**, **85**, **87**, **89**, **93**, **100**, and **144** were measured on a Nonius KappaCCD diffractometer using Mo Kα radiation ($\lambda = 0.71073$ Å) and a graphite monochromator; images for compound **84** were measured on an Agilent Technologies SuperNova Dual Source diffractometer using Mo Kα radiation ($\lambda = 0.71073$ Å) and a mirror monochromator, while those for compounds **10**, **66**, **76**, **97**, and **143** were measured on the same diffractometer but using Cu Kα radiation ($\lambda = 1.54180$ Å) and a mirror monochromator. Data were normally extracted using DENZO[69] or CrysAlis PRO[70] as appropriate while structure solutions were achieved by direct methods (SIR92)[71] and refined using the CRYSTALS program package.[72] Atomic coordinates, bond lengths and angles, and displacement parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC depositions 2021338−2021352). These data can be obtained free-of-charge via www.ccdc.cam.ac.uk/data_request/cif, by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44 1223 336033.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.joc.0c02011.

X-ray-derived plots for compounds **1**, **10**, **11**, **66**, **76**, **78**, **84**, **85**, **87**, **89**, **93**, **97**, **100**, **143**, and **144**, copies of the ^{1}H and ^{13}C NMR spectra of compounds **1**, **3**, **4**, **8**, **10**, **11**, **22**, **23**, **25**, **26**, **27**, **33**, **34**, **38**, **50**, and **56**−**99** and **100**−**102**, **105**−**112**, **117**−**120**, **123**−**131**, **134**, **136**, **138**, **140**, **142**−**152**, and **154**−**161**, and X-ray crystallographic data for compound **1**, **10**, **11**, **66**, **76**, **78**, **84**, **85**, **87**, **89**, **93**, **97**, **100**, **143**, and **144** (PDF)

Accession Codes

CCDC 2021338−2021352 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

■ AUTHOR INFORMATION

Corresponding Author

Martin G. Banwell − *Research School of Chemistry, Institute of Advanced Studies, The Australian National University, Canberra, Australian Capital Territory 2601, Australia; Institute for Advanced and Applied Chemical Synthesis, Jinan University, Guangzhou, Guangdong 510632, China;* orcid.org/0000-0002-0582-475X; Email: martin.banwell@anu.edu.au

Authors

Aymeric Cervi − *Research School of Chemistry, Institute of Advanced Studies, The Australian National University, Canberra, Australian Capital Territory 2601, Australia; Institute of Chemical and Engineering Sciences, 138665, Singapore*

Yen Vo − *Research School of Chemistry, Institute of Advanced Studies, The Australian National University, Canberra, Australian Capital Territory 2601, Australia*

https://dx.doi.org/10.1021/acs.joc.0c02011
J. Org. Chem. XXXX, XXX, XXX−XXX

Christina L. L. Chai − *Institute of Chemical and Engineering Sciences, 138665, Singapore; Department of Pharmacy, National University of Singapore, 117543, Singapore;* orcid.org/0000-0002-9199-851X

Ping Lan − *Institute for Advanced and Applied Chemical Synthesis, Jinan University, Guangzhou, Guangdong 510632, China;* orcid.org/0000-0002-9285-3259

Anthony C. Willis − *Research School of Chemistry, Institute of Advanced Studies, The Australian National University, Canberra, Australian Capital Territory 2601, Australia*

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.joc.0c02011

Author Contributions

The manuscript was written through contributions from all of the authors. All of the authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

CCDC depositions 2021338−2021352 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by e-mailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K.; Fax: +44 1223 336033.

REFERENCES

(1) (a) Sarkar, S. D.; Nahar, L. Progress in the Chemistry of Naturally Occurring Coumarins. *Prog. Chem. Org. Nat. Prod.* **2017**, *106*, 241−304. (b) Stefanachi, A.; Leonetti, F.; Pisani, L.; Catto, M.; Carotti, A. Coumarin: A Natural, Privileged and Versatile Scaffold for Bioactive Compounds. *Molecules* **2018**, *23*, 250−283.

(2) See, for example, (a) Sandhu, S.; Bansal, Y.; Silakari, O.; Bansal, G. Coumarin Hybrids as Novel Therapeutic Agents. *Bioorg. Med. Chem.* **2014**, *22*, 3806−3814. (b) Awale, S.; Okada, T.; Dibwe, D. F.; Maruyama, T.; Takahara, S.; Okada, T.; Endo, S.; Toyooka, N. Design and Synthesis of Functionalized Coumarins as Potential Anti-Austerity Agents that Eliminates Cancer Cells' Tolerance to Nutrition Starvation. *Bioorg. Med. Chem. Lett.* **2019**, *29*, 1779−1784 and references cited therein.

(3) See, for example, (a) Trenor, S. R.; Shultz, A. R.; Love, B. J.; Long, T. E. Coumarins in Polymers: From Light Harvesting to Photo-Cross-Linkable Tissue Scaffolds. *Chem. Rev.* **2004**, *104*, 3059−3078. (b) Mertens, M. D.; Gütschow, M. Clickable Coumarins as Fluorescent Labels for Amino Acids. *Synthesis* **2014**, *46*, 2191−2200. (c) Mertens, M. D.; Hinz, S.; Müller, C. E.; Gütschow, M. Alkynyl-Coumarinyl Ethers as MAO-B Inhibitors. *Bioorg. Med. Chem.* **2014**, *22*, 1916−1928. (d) Delcourt, M.-L.; Reynaud, C.; Turcaud, S.; Favereau, L.; Crassous, J.; Micouin, L.; Benedetti, E. 3D Coumarin Systems Based on [2.2]Paracyclophane: Synthesis and Spectroscopic Characterization, and Chiroptical Properties. *J. Org. Chem.* **2019**, *84*, 888−899.

(4) For useful points-of-entry into the literature of this topic see: (a) Priyanka; Sharma, R. K.; Katiyar, D. Recent Advances in Transition-Metal-Catalyzed Synthesis of Coumarins. *Synthesis* **2016**, *48*, 2303−2322. (b) Salem, M. A.; Helal, M. H.; Gouda, M. A.; Ammar, Y. A.; El-Gaby, M. S. A.; Abbas, S. Y. An Overview on Synthetic Strategies to Coumarins. *Synth. Commun.* **2018**, *48*, 1534−1550. (c) Lončarić, M.; Gašo-Sokač, D.; Jokić, S.; Molnar, M. Recent Advances in the Synthesis of Coumarin Derivatives from Different Starting Materials. *Biolmolecules* **2020**, *10*, 151−185.

(5) (a) Nicolaou, K. C.; Pfefferkorn, J. A.; Roecker, A. J.; Cao, G.-Q.; Barluenga, S.; Mitchell, H. J. Natural Product-like Combinatorial Libraries Based on Privileged Structures. 1. General Principles and Solid-Phase Synthesis of Benzopyrans. *J. Am. Chem. Soc.* **2000**, *122*, 9939−9953. (b) Majumdar, N.; Paul, N. D.; Mandal, S.; de Bruin, B.; Wulff, W. D. Catalytic Synthesis of 2H-Chromenes. *ACS Catal.* **2015**, *5*, 2329−2366.

(6) Menon, R. S.; Findlay, A. D.; Bissember, A. C.; Banwell, M. G. The Au(I)-Catalyzed Intramolecular Hydroarylation of Terminal Alkynes Under Mild Conditions: Application to the Synthesis of 2H-Chromenes, Coumarins, Benzofurans, and Dihydroquinolines. *J. Org. Chem.* **2009**, *74*, 8901−8903.

(7) For a useful introductions to gold-catalyzed reactions see: (a) Li, Z.; Brouwer, C.; He, C. Gold-Catalyzed Organic Transformations. *Chem. Rev.* **2008**, *108*, 3239−3265. (b) Ranieri, B.; Escofet, I.; Echavarren, A. M. Anatomy of Gold Catalysts: Facts and Myths. *Org. Biomol. Chem.* **2015**, *13*, 7103−7118.

(8) For a general overview of both inter- and intra-molecular variants of this type of process see: Boyarskiy, V. P.; Ryabukhin, D. S.; Bokach, N. A.; Vasilyev, A. V. Alkenylation of Arenes and Heteroarenes with Alkynes. *Chem. Rev.* **2016**, *116*, 5894−5986.

(9) Cervi, A.; Aillard, P.; Hazeri, N.; Petit, L.; Chai, C. L. L.; Willis, A. C.; Banwell, M. G. Total Syntheses of the Coumarin-Containing Natural Products Pimpinellin and Fraxetin Using Au(I)-Catalyzed Intramolecular Hydroarylation (IMHA) Chemistry. *J. Org. Chem.* **2013**, *78*, 9876−9882.

(10) (a) Trost, B. M.; Toste, F. D.; Greenman, K. Atom Economy. Palladium-Catalyzed Formation of Coumarins by Addition of Phenols and Alkynoates via a Net C−H Insertion. *J. Am. Chem. Soc.* **2003**, *125*, 4518−4526. (b) Shi, Z.; He, C. Efficient Functionalization of Aromatic C-H Bonds Catalyzed by Gold(III) under Mild and Solvent Free Conditions. *J. Org. Chem.* **2004**, *69*, 3669−3671. (c) Wegner, H. A.; Ahles, S.; Neuburger, M. A New Gold-Catalyzed Domino Cyclization and Oxidative Coupling Reaction. *Chem.—Eur. J.* **2008**, *14*, 11310−11313. (d) Lykakis, I. N.; Efe, C.; Gryparis, C.; Stratakis, M. $Ph_3PAuNTf_2$ as a Superior Catalyst for the Selective Synthesis of 2H-Chromenes: Application to the Concise Synthesis of Benzopyran Natural Products. *Eur. J. Org. Chem.* **2011**, 2334−2338. (e) Kitamura, T.; Otsubo, K. Palladium-Catalyzed Intramolecular Hydroarylation of 4-Benzofuranyl Alkynoates. Approach to Angelicin Derivatives. *J. Org. Chem.* **2012**, *77*, 2978−2982. (f) Zhang, X.-S.; Li, Z.-W.; Shi, Z.-J. Palladium-catalyzed base-accelerated direct C-H bond alkenylation of phenols to synthesize coumarin derivatives. *Org. Chem. Front.* **2014**, *1*, 44. (g) Lau, V. M.; Pfalzgraff, W. C.; Markland, T. E.; Kanan, M. W. Electrostatic Control of Regioselectivity in Au(I)-Catalyzed Hydroarylation. *J. Am. Chem. Soc.* **2017**, *139*, 4035−4041. (h) Vacala, T.; Bejcek, L. P.; Williams, C. G.; Williamson, A. C.; Vadola, P. A. Gold-Catalyzed Hydroarylation of N-Aryl Alkynamides for the Synthesis of 2-Quinolinones. *J. Org. Chem.* **2017**, *82*, 2558−2569. (i) Nakamura, Y.; Sakata, Y.; Hosoya, T.; Yoshida, S. Synthesis of Functionalized Benzopyran/Coumarin-Derived Aryne Precursors and Their Applications. *Org. Lett.* **2020**, *22*, 8505−8510.

(11) Neises, B.; Steglich, W. Simple Method for the Esterification of Carboxylic Acids. *Angew. Chem., Int. Ed.* **1978**, *17*, 522−524.

(12) Kaminski, Z. J. 2-Chloro-4,6-dimethoxy-1,3,5-triazine. A New Coupling Reagent for Peptide Synthesis. *Synthesis* **1987**, 917.

(13) Dunetz, J. R.; Xiang, Y.; Baldwin, A.; Ringling, J. General and Scalable Amide Bond Formation with Epimerization-prone Substrates Using T3P and Pyridine. *Org. Lett.* **2011**, *13*, 5048−5051.

(14) Sheehan, J.; Cruickshank, P.; Boshart, G. Notes- A Convenient Synthesis of Water-Soluble Carbodiimides. *J. Org. Chem.* **1961**, *26*, 2525−2528.

(15) Carpino, L. A.; El-Faham, A.; Albericio, F. Racemization studies during solid-phase peptide synthesis using azabenzotriazole-based coupling reagents. *Tetrahedron Lett.* **1994**, *35*, 2279−2282.

(16) Deshmukh, A. R. A. S.; Joshi, G. D.; Gore, K. G.; Kulkarni, G. H. A Simple Short Synthesis of Isotachin 'C'. *Synth. Commun.* **1990**, *20*, 2259−2265.

(17) Wehler, J. R.; Feld, W. A. The synthesis of bis(propynoyloxy) aromatics. *J. Chem. Eng. Data* **1989**, *34*, 142−143.

(18) Bruckner, R. Organic Mechanisms. In *Reactions, Stereochemistry and Synthesis*; Harmata, M., Ed.; Springer-Verlag: Berlin Heidelberg, 2010; pp 209−215.

(19) Lesage-Meessen, L.; Bou, M.; Sigoillot, J.-C.; Faulds, C. B.; Lomascolo, A. Essential Oils and Distilled Straws of Lavender and Lavandin: A Review of Current Use and Potential Application in White Biotechnology. *Appl. Microbiol. Biotechnol.* **2015**, *99*, 3375−3385. and references cited therein

(20) Riveiro, M. E.; Maes, D.; Vázquez, R.; Vermeulen, M.; Mangelinckx, S.; Jacobs, J.; Debenedetti, S.; Shayo, C.; De Kimpe, N.; Davio, C. Toward Establishing Structure-Activity Relationships for Oxygenated Coumarins as Differentiation Inducers of Promonocytic Leukemic Cells. *Bioorg. Med. Chem.* **2009**, *17*, 6547−6559. and references cited therein

(21) Wu, C.; Li, T.; Zhu, B.; Zhu, R.; Zhang, Y.; Xing, F.; Chen, Y. Scoparone Protects Neuronal Cells from Oxygen Glucose Deprivation/Reoxygenation Injury. *RSC Adv.* **2019**, *9*, 2302−2308. and references cited therein

(22) For representative recent syntheses see: (a) Boeck, F.; Blazejak, M.; Anneser, M. R.; Hintermann, L. Cyclization of ortho-Hydroxycinnamates to Coumarins Under Mild Conditions: A Nucleophilic Organocatalysis Approach. *Beilstein J. Org. Chem.* **2012**, *8*, 1630−1636. (b) Gao, W.; Li, Q.; Chen, J.; Wang, Z.; Hua, C. Total Synthesis of Six 3,4-Unsubstituted Coumarins. *Molecules* **2013**, *18*, 15613−15623. (c) Gadakh, S. K.; Dey, S.; Sudalai, A. Rh-Catalyzed Synthesis of Coumarin Derivatives from Phenolic Acetates and Acrylates via C-H Bond Activation. *J. Org. Chem.* **2015**, *80*, 11544−11550.

(23) See, for example, (a) Francisco, C. S.; Rodrigues, L. R.; Cerqueira, N. M. F. S. A.; Oliveira-Campos, A. M. F.; Rodrigues, L. M.; Esteves, A. P. Synthesis of Novel Psoralen Analogues and their In Vitro Antitumor Activity. *Bioorg. Med. Chem.* **2013**, *21*, 5047−5053. (b) Vronteli, A.; Hadjipavlou-Litina, D. J.; Konstantinidou, M.; Litinas, K. E. Synthesis of Fused Pyranocarbazolones with Biological Interest. *ARKIVOC* **2015**, *iii*, 111−123. (c) Fujimoto, K.; Sasago, S.; Mihara, J.; Nakamura, S. DNA Photo-cross-linking Using Pyranocarbazole and Visible Light. *Org. Lett.* **2018**, *20*, 2802−2805.

(24) (a) Zhao, Y.; Zheng, Q.; Dakin, K.; Xu, K.; Martinez, M. L.; Li, W.-H. New Caged Coumarin Fluorophores with Extraordinary Uncaging Cross Sections Suitable for Biological Imaging Applications. *J. Am. Chem. Soc.* **2004**, *126*, 4653−4663. (b) Tomohiro, T.; Kato, K.; Masuda, S.; Kishi, H.; Hatanaka, Y. Photochemical Construction of Coumarin Fluorophore on Affinity-Anchored Protein. *Bioconjugate Chem.* **2011**, *22*, 315−318.

(25) For some indication of the diverse range of possibilities in this regard, see: Zhao, Z.; Snieckus, V. Directed ortho Metalation-Based Methodology. Halo-, Nitroso- and Boro-Induced ipso-Desilyation. Link to an in situ Suzuki Reaction. *Org. Lett.* **2005**, *7*, 2523−2526 and references cited therein.

(26) See, for example, Zhang, L.; Meng, T.; Fan, R.; Wu, J. General and Efficient Route for the Synthesis of 3,4-Disubstituted Coumarins via Pd-Catalyzed Site-Selective Cross-Coupling Reactions. *J. Org. Chem.* **2007**, *72*, 7279−7286 and references cited therein.

(27) Yu, M.; Zhang, G.; Zhang, L. Gold-Catalyzed Efficient Preparation of Linear α-Iodoenones from Propargylic Acetates. *Org. Lett.* **2007**, *9*, 2147−2150 and references cited therein.

(28) For descriptions of related routes to 2,2-dimethylated-2H-chromenes see: (a) Hlubucek, J.; Ritchie, E.; Taylor, W. Synthesis of 2,2-dimethylchromens. *Aust. J. Chem.* **1971**, *24*, 2347−2354. (b) Anderson, W. K.; LaVoie, E. J.; Whitkop, P. G. Steric and Electronic Factors Which Effect the Thermal Cyclization of Meta-Substituted Aryl Propargyl Ethers. Synthesis of 5- and 7-Substituted 3-Chromenes. *J. Org. Chem.* **1974**, *39*, 881−884. (c) Chauder, B. A.; Lopes, C. C.; Lopes, R. S. C.; da Silva, A. J. M.; Snieckus, V. Phenylboronic Acid-Mediated Synthesis of 2H-Chromenes. *Synthesis* **1998**, 279−282. (d) Bogaert-Alvarez, R. J.; Demena, P.; Kodersha, G.; Polomski, R. E.; Soundararajan, N.; Wang, S. S. Y. Continuous Processing to Control a Potentially Hazardous Process: Conversion of Aryl 1,1-Dimethylpropargyl Ethers to 2,2-Dimethylchromenes. *Org. Process Res. Dev.* **2001**, *5*, 636−645. (e) Babu, K. S.; Raju, B. C.; Praveen, B.; Kishore, K. H.; Murty, U. S.; Rao, J. M. Microwave Assisted Synthesis and Anti Microbial Activity of 2,2-Dimethyl Chromenes. *Heterocycl. Commun.* **2003**, *9*, 519−526. (f) Madabhushi, S.; Jillella, R.; Godala, K. R.; Mallu, K. K. R.; Beeram, C. R.; Chinthala, N. An Efficient and Simple Method for Synthesis of 2,2-Disubstituted-2H-chromenes by Condensation of a Phenol with a 1,1-Disubstitiuted Propargyl Alcohol Using $BF_3{\cdot}Et_2O$ as the Catalyst. *Tetrahedron Lett.* **2012**, *53*, 5275−5279. (g) Dimakos, V.; Singh, T.; Taylor, M. S. Boronic Acid/Brønsted Acid Co-Catalyst Systems for the Synthesis of 2H-Chromenes from Phenols and α,β-Unsaturated Carbonyls. *Org. Biomol. Chem.* **2016**, *14*, 6703.

(29) Fraga, B. M.; Cabrera, I. The Oligomerization and Acylation of Precocene I. *Tetrahedron* **2016**, *72*, 8078−8084.

(30) Kulkarni, M. M.; Nagasampagi, B. A.; Deshpande, S. G.; Sharma, R. N. Five Chromenes from Blepharispermum Subsessile. *Phytochem* **1987**, *26*, 2969−2971.

(31) Still, W. C.; Kahn, M.; Mitra, A. Rapid Chromatographic Technique for Preparative Separations with Moderate Resolution. *J. Org. Chem.* **1978**, *43*, 2923−2925.

(32) Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. Safe and Convenient Procedure for Solvent Purification. *Organometallics* **1996**, *15*, 1518−1520.

(33) Strych, S.; Trauner, D. Biomimetic Synthesis of Santalin A,B and Santarubin A,B, the Major Colorants of Red Sandalwood. *Angew. Chem., Int. Ed.* **2013**, *52*, 9509−9512.

(34) Schmidt, N. G.; Kroutil, W. Acyl Donors and Additives for the Biocatalytic Friedel-Crafts Acylation. *Eur. J. Org. Chem.* **2017**, 5865−5871.

(35) Bell, K. Selective Aminolysis of Benzoates and Acetates of α-Hydroxy Acids and Phenols With Benzylamine and Butan-1-amine. *Aust. J. Chem.* **1987**, *40*, 1723−1735.

(36) Okano, K.; Okuyama, K.-i.; Fukuyama, T.; Tokuyama, H. Mild Debenzylation of Aryl Benzyl Ether with BCl_3 in the Presence of Pentamethylbenzene as a Non-Lewis Basic Cation Scavenger. *Synlett* **2008**, 1977−1980.

(37) Khandelwal, A.; Hall, J. A.; Blagg, B. S. J. Synthesis and Structure-Activity Relationships of EGCG Analogues, a Recently Identified Hsp90 Inhibitor. *J. Org. Chem.* **2013**, *78*, 7859−7884.

(38) Fujii, S.; Miyajima, Y.; Masuno, H.; Kagechika, H. Increased Hydrophobicity and Estrogenic Activity of Simple Phenols with Silicon and Germanium-Containing Substituents. *J. Med. Chem.* **2013**, *56*, 160−166.

(39) Fässler, J.; McCubbin, J. A.; Roglans, A.; Kimachi, T.; Hollett, J. W.; Kunz, R. W.; Tinkl, M.; Zhang, Y.; Wang, R.; Campbell, M.; Snieckus, V. Highly Enantioselective (−)-Sparteine-Mediated Lateral Metalation-Functionalization of Remote Silyl Protected ortho-Ethyl N,N-Dialkyl Aryl O-Carbamates. *J. Org. Chem.* **2015**, *80*, 3368−3386.

(40) Endo, Y.; Shudo, K.; Okamoto, T. Acid-Catalyzed Solvolysis of N-Sulfonyl- and N-Acyl-O-arylhydroxylamines. Phenoxenium Ions. *J. Am. Chem. Soc.* **1982**, *104*, 6393−6397.

(41) Papst, S.; Noisier, A. F. M.; Brimble, M. A.; Yang, Y.; Krissansen, G. W. Synthesis and biological evaluation of tyrosine modified analogues of the α4β7 integrin inhibitor biotin-R_8ERY. *Bioorg. Med. Chem.* **2012**, *20*, 5139−5149.

(42) Aparece, M. D.; Vadola, P. A. Gold-Catalyzed Dearomative Spirocyclization of Aryl Alkynoate Esters. *Org. Lett.* **2014**, *16*, 6008−6011.

(43) Nagel, M.; Hansen, H.-J. Synthesis of Polyalkylphenyl Prop-2-ynoates and Their Flash Vacuum Pyrolysis to Polyalkylcyclohepta[b]-furan-2(2H)-ones. *Helv. Chim. Acta* **2000**, *83*, 1022−1048.

(44) Wegner, H. A.; Ahles, S.; Neuburger, M. A New Gold-Catalyzed Domino Cyclization and Oxidative Coupling Reaction. *Chem.—Eur. J.* **2008**, *14*, 11310−11313.

(45) Alvaro, M.; Garcia, H.; Iborra, S.; Miranda, M.; A Miranda, J. New photochemical approaches to the synthesis of chromones. *Tetrahedron* **1987**, *43*, 143−148.

(46) Balfour, W. J.; Greig, C. C.; Visaisouk, S. Preparation and characterization of propiolyl chloride. *J. Org. Chem.* **1974**, *39*, 725−726.

(47) Bloomfield, J.; Fuchs, R. Notes- Rates of Hydrolysis of cis and trans-3- and 4-Substituted Ethyl Cinnamates. *J. Org. Chem.* **1961**, *26*, 2991−2993.

https://dx.doi.org/10.1021/acs.joc.0c02011
J. Org. Chem. XXXX, XXX, XXX−XXX

(48) Garcia, H.; Iborra, S.; Primo, J.; Miranda, M. A. 6-Endo-Dig vs. 5-Exo-Dig ring closure in o-hydroxyaryl phenylethynyl ketones. A new approach to the synthesis of flavones and aurones. *J. Org. Chem.* **1986**, *51*, 4432−4436.
(49) Sharma, U.; Naveen, T.; Maji, A.; Manna, S.; Maiti, D. Palladium-Catalyzed Synthesis of Benzofurans and Coumarins from Phenols and Olefins. *Angew. Chem., Int. Ed.* **2013**, *52*, 12669−12673.
(50) Kitamura, T.; Tatemoto, K.; Sakai, M.; Oyamada, J. Cascade synthesis of 3-alkenylcoumarins by palladium-catalyzed reaction of phenols and ethyl propiolate. *Chem. Lett.* **2012**, *41*, 705−707.
(51) Reddy, M. S.; Thirupathi, N.; Haribabu, M. Tandem aldehyde-alkyne-amine coupling/cycloisomerization: A new synthesis of coumarins. *Beilstein J. Org. Chem.* **2013**, *9*, 180−184.
(52) Zeitler, K.; Rose, C. A. An Efficient Carbene-Catalyzed Access to 3,4-Dihydrocoumarins. *J. Org. Chem.* **2009**, *74*, 1759−1762.
(53) Valizadeh, H.; Vaghefi, S. One-Pot Wittig and Knoevenagel Reactions in Ionic Liquid as Convenient Methods for the Synthesis of Coumarin Derivatives. *Synth. Commun.* **2009**, *39*, 1666−1678.
(54) Bratulescu, G. A Quick and Advantageous Synthesis of 2H-1-Benzopyran-2-ones Unsubstituted on the Pyranic Nucleus. *Synthesis* **2008**, 2871−2873.
(55) Leão, R. A. C.; de Moraes, P. F.; Pedro, M. C. B. C.; Costa, P. R. R. Synthesis of Coumarins and Neoflavins Through Zinc Chloride Catalyzed Hydroarylation of Acetylenic Esters with Phenols. *Synthesis* **2011**, 3692−3696.
(56) Carta, F.; Maresca, A.; Scozzafava, A.; Supuran, C. T. Novel coumarins and 2-thioxo-coumarins as inhibitors of the tumor-associated carbonic anhydrases IX and XII. *Bioorg. Med. Chem.* **2012**, *20*, 2266−2273.
(57) Amin, K. M.; Awadalla, F. M.; Eissa, A. A. M.; Abou-Seri, S. M.; Hassan, G. S. Design, synthesis and vasorelaxant evaluation of novel coumarin-pyrimidine hybrids. *Bioorg. Med. Chem.* **2011**, *19*, 6087−6097.
(58) Bensel, N.; Reymond, M. T.; Reymond, J.-L. Pivalase Catalytic Antibodies: Towards Abzymatic Activation of Prodrugs. *Chem.—Eur. J.* **2001**, *7*, 4604−4612.
(59) Dubuffet, T.; Loutz, A.; Lavielle, G. An Efficient Large Scale Synthesis of Coumarins by a Dealkylative Boron-Mediated Ring Closure of 3-(Ortho-methoxyaryl)propenoic Esters. *Synth. Commun.* **1999**, *29*, 929−936.
(60) Reppel, L.; Schmollack, W. Beiträge zur Kenntnis der Cumarine. 4. Mitt.: Die Darstellung von Acylaminocumarinen und Sulfanilamidocumarinen. *Arch. Pharm. Ber. Dtsch. Pharm. Ges.* **1964**, *297*, 711−718.
(61) Dey, B. B.; Row, K. K. LXXI. − Action of Sodium Sulphite on Coumarins. *J. Chem. Soc., Trans.* **1924**, *125*, 554−564.
(62) Takeuchi, Y.; Ueda, N.; Uesugi, K.; Abe, H.; Nishioka, H.; Harayama, T. Convenient Synthesis of a Simple Coumarin from Salicylaldehyde and Wittig Reagent. IV: Improved Synthetic Method of Substituted Coumarins. *Heterocycles* **2003**, *59*, 217−224.
(63) Kumar, S.; Saini, A.; Sandhu, J. S. LiBr-mediated, solvent free von Pechmann reaction: facile and efficient method for the synthesis of 2H-chromen-2-ones. *ARKIVOC* **2007**, *2007*, 18−23.
(64) Li, Y.; Qi, Z.; Wang, H.; Fu, X.; Duan, C. Palladium-Catalyzed Oxidative Heck Coupling Reaction for Direct Synthesis of 4-Arylcoumarins Using Coumarins and Arylboronic Acids. *J. Org. Chem.* **2012**, *77*, 2053−2057.
(65) Adler, M. J.; Baldwin, S. W. Direct, regioselective synthesis of 2,2-dimethyl-2H-chromenes. Total syntheses of octandrenolone and precocenes I and II. *Tetrahedron Lett.* **2009**, *50*, 5075−5079.
(66) Nicolaou, K. C.; Pfefferkorn, J. A.; Cao, G.-Q. Selenium-Based Solid-Phase Synthesis of Benzopyrans I: Applications to Combinatorial Synthesis of Natural Products. *Angew. Chem., Int. Ed.* **2000**, *39*, 734−739.
(67) Chauder, B. A.; Kalinin, A. V.; Snieckus, V. Directed ortho Metalation Reactions of Aryl O-Carbamates; A Regiospecific Synthesis of 2,2-Disubstituted 2H-1-Benzopyrans. *Synthesis* **2001**, 140−144.
(68) A single-crystal X-ray analysis of compound **1** has been reported recently: Hsieh, T.-J.; Su, C.-C.; Chen, C.-Y.; Liou, C.-H.; Lu, L.-H. Using experimental studies and theoretical calculations to analyze the molecular mechanism of coumarin, p-hydroxybenzoic acid, and cinnamic acid. *J. Mol. Struct.* **2005**, *741*, 193−199.
(69) Otwinowski, Z.; Minor, W. Processing of X-ray diffraction data collected in oscillation mode. In *Methods in Enzymology*; Carter, C. W., Jr., Sweet, R. M., Eds.; Academic Press: New York, 1997; Vol. *276*: Macromolecular Crystallography, Part A, pp 307−326.
(70) Agilent. *CrysAlis PRO*; Agilent Technologies Ltd.: Yarnton, Oxfordshire, England, 2014.
(71) Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A.; Burla, M. C.; Polidori, G.; Camalli, M. SIR92 - a program for automatic solution of crystal structures by direct methods. *J. Appl. Crystallogr.* **1994**, *27*, 435.
(72) Betteridge, P. W.; Carruthers, J. R.; Cooper, R. I.; Prout, K.; Watkin, D. J. CRYSTALS version 12: software for guided crystal structure analysis. *J. Appl. Crystallogr.* **2003**, *36*, 1487.

https://dx.doi.org/10.1021/acs.joc.0c02011
J. Org. Chem. XXXX, XXX, XXX−XXX