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Modular Copper-Catalyzed Synthesis of Chromeno[4,3-*b*]quinolines with the Utilization of Diaryliodonium Salts

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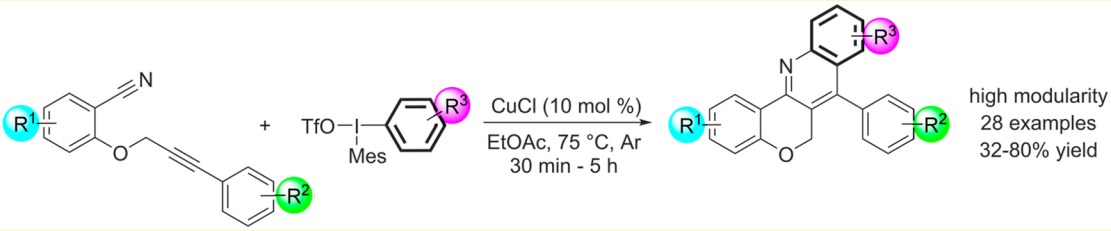
Supporting Information



ABSTRACT: A novel, highly modular synthetic method with high functional group tolerance was developed for the construction of chromenoquinoline derivatives from arylpropynyloxy-benzonitriles and diaryliodonium triflates via an oxidative arylation−cyclization path. The copper(I) chloride catalyzed reaction is presumed to involve the formation of highly active arylcopper(III) species.

INTRODUCTION

Copper-catalyzed syntheses of aromatic and heteroaromatic systems are intensively studied areas of current organic chemistry.[1] In the past few years, triple bond activation via the intermediacy of Cu(III) species[2,3] using diaryliodonium salts[4] as arylating agents has become an efficient method for the construction of diverse heterocyclic skeletons. The highly electrophilic arylcopper(III) intermediates can activate triple bonds or generate carbocationic species from alkynes and nitriles. These copper complexes and the carbocationic intermediates can easily undergo ring closure when in the close proximity to nucleophilic functional groups. For example, Gaunt and co-workers[2b] developed several copper-catalyzed transformations for the synthesis of dihydronaphthalene, chromene, and dihydroquinoline derivatives from function-alized electron-rich alkynes and diaryliodonium salts via vinyl cation intermediates. Besides the transformation of alkynes, the activation of a nitrile group with copper catalysts and iodonium salts is also possible, and the construction of heterocyclic skeletons such as quinolines,[3a,c] quinazolines,[3b] and tetrahy-droacridines[3a] through the formation of iminium cations was described by Chen et al. Utilizing the strategy of triple bond activation with the aid of Cu(III) species, our research group also developed novel copper-catalyzed cyclizations for the synthesis of benzoxazine,[5a] iminobenzoxazine,[5b] and dihydroox-azole[5c] derivatives (Scheme 1). Considering the activation ability of Cu(III)-aryl species toward triple bonds, we aimed to develop a novel, highly modular catalytic strategy for the construction of complex heterocyclic systems from substrates equipped with both nitrile and alkyne functional groups.

RESULT AND DISCUSSION

To realize the concept, we synthesized arylpropynyloxy-benzonitriles as model substrates from the appropriate 2-hydroxybenzonitrile derivatives. In the presence of a C≡C triple bond *ortho* to the nitrile moiety, a ring closure reaction can occur, which should provide chromeno[4,3-*b*]-quinolines[6a−c] through two sequential cyclization paths (Scheme 2).

Beyond the importance of the conceptual aspects of this transformation, the realization of this chemical approach would provide a new synthetic route to chromenoquinolines, an important and synthetically useful class of heterocyclic compounds.

Chromenoquinolines are significant due to their biological activity and their applications in medical chemistry. For example, 6*H*-chromeno[4,3-*b*]quinolines act as estrogen receptor β-selective ligands,[7a] and they can be used also for bioimaging due to their fluorescent properties.[7b,c] Moreover, the spiro analogues of benzothiazolylchromeno derivatives have shown cytotoxic activity against MCF-7 (breast cancer) and HeLa (cervical cancer) cell lines.[7d]

To optimize the reaction conditions, we chose 2-((3-phenylprop-2-yn-1-yl)oxy)benzonitrile (**1a**) as a substrate and phenylmesityliodonium triflate (**2a**) as the arylating agent, while the oxidative coupling was performed at 75 °C for 1 h.[8] Examination of the solvent effect on the conversion showed that the reaction is slow in DMF, CH_2Cl_2, THF, PhMe, and

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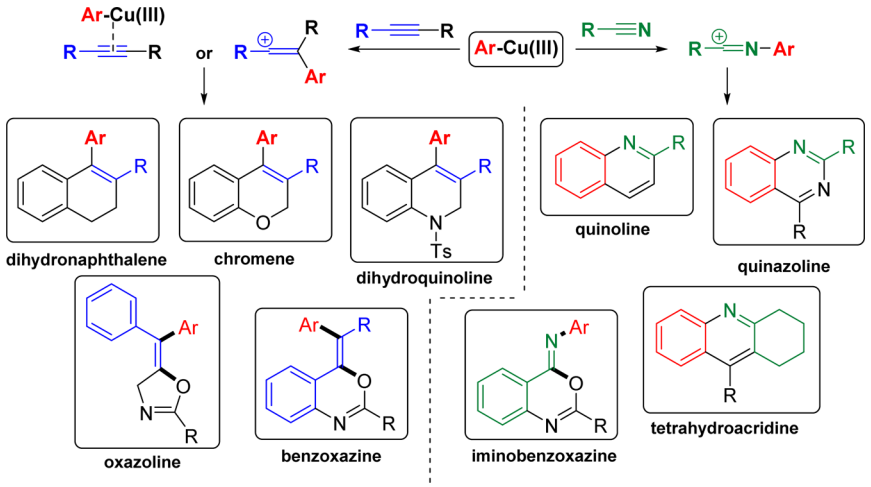
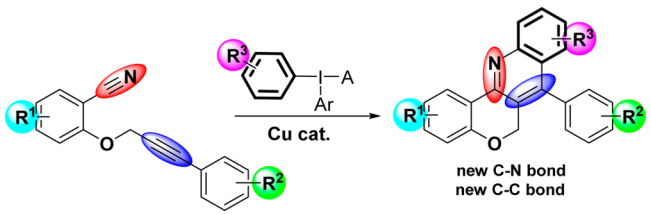
Scheme 1. Utilization of Arylation−Ring Closure Strategy

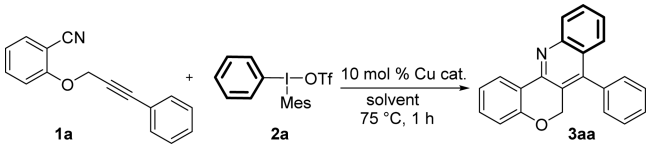


Scheme 2. Highly Modular Synthesis of Chromenoquinolines via Arylation−Ring Closure



DCE, and no reaction occurs in MeOH (Table 1, entries 1−6). In contrast, full conversion was reached in 1 h when the reaction was conducted in EtOAc (entry 7). Comparison of the activity of different copper catalysts showed that CuCl and CuBr are suitable for the transformation (entries 7−8). In the case of CuI or CuO, no reaction occurs in 1 h (entries 9−10), while the reaction was slow when $Cu(OTf)_2$, $CuSO_4$, $Cu(acac)_2$, or $(MeCN)_4Cu(OTf)$ were used (entries 11−14). No reaction was observed in the absence of catalyst (entry 15).

Table 1. Optimization Studies[a]



entry	catalyst	solvent	conversion[b] (%)
1	CuCl	MeOH	0
2	CuCl	DMF	5
3	CuCl	CH_2Cl_2	19
4	CuCl	THF	29
5	CuCl	PhMe	35
6	CuCl	DCE	41
7	CuCl	EtOAc	100
8	CuBr	EtOAc	100
9	CuI	EtOAc	0
10	CuO	EtOAc	0
11	$Cu(OTf)_2$	EtOAc	3
12	$CuSO_4$	EtOAc	10
13	$Cu(acac)_2$	EtOAc	12
14	$(MeCN)_4Cu(OTf)$	EtOAc	40
15		EtOAc	0

[a]2-((3-Phenylprop-2-yn-1-yl)oxy)benzonitrile (0.125 mmol), phenyl-mesityliodonium triflate (0.150 mmol, 1.20 equiv), copper catalyst (0.013 mmol, 0.10 equiv); solvent (250 μL), Ar, 75 °C, 1 h. [b]Conversion of the starting material to desired product was determined by GCFID analysis.

With optimal conditions in hand, we aimed to explore the scope and limitations of the method. First, we reacted 2-((3-phenylprop-2-yn-1-yl)oxy)benzonitrile (**1a**) with phenylmesityliodonium triflate (**2a**) using 10 mol % of CuCl in EtOAc at 75 °C, and **3aa** was obtained in 78% yield (Scheme 3). When a methyl substituent was present in the *ortho* position of the phenyl group of the iodonium salt, the reaction was slower (5 h reaction time was needed) and the desired product (**3ab**) was isolated in 32% yield. In contrast, when the methyl group was *meta* or *para* to the iodonium salt, the reaction was fast, and the desired compounds (**3ac** and **3ad**) were obtained in 65% and 50% yields, respectively. When the aryl part of the iodonium salt contained a halogen atom (F, Cl, or Br) *ortho* to the iodine, the ring closure reaction was retarded and the desired compounds were detected only with GC−MS (5−8% GC−MS conversion, not shown). When the reaction was attempted with diaryliodonium salts containing halogens in the *meta* or *para* positions, **1a** was transformed to the appropriate chromenoquinoline derivatives (**3af**−**3al**) in 47−65% yield. Diaryliodonium salt bearing a *para* COOEt group provided the desired product (**3am**) in 70% yield. In the case of *meta* substituted iodonium salts, chromenoquinolines **3ac**, **3ah**, and **3ak** were obtained as 1:1 mixtures of possible regioisomers that originated from the aromatic electrophilic substitution step of the transformation (for mechanism, see Scheme 6.)

Next, we investigated the scope of this transformation by studying the reactivity of different nitriles in the ring closure reaction (Scheme 4). Nitriles **1b**−**1l** bearing different aryl groups on the alkyne moiety were reacted with phenyl-mesityliodonium triflate (**2a**) to prepare the desired chromenoquinoline derivatives (**3ba**−**3la**). Two more examples (**3im** and **3lm**) are given where the applicability of the ring closure reaction is demonstrated with 4-ethoxycarbonyl-phenylmesity-liodonium triflate (**2m**). When the arylpropynyloxy-benzonitrile contained a thiophenyl group (**1b**), the appropriate product (**3ba**) was isolated in 48% yield, respectively. When the reaction was performed with nitrile derivatives bearing electron-donating groups (**1c** and **1d**) in the *para* position, the desired

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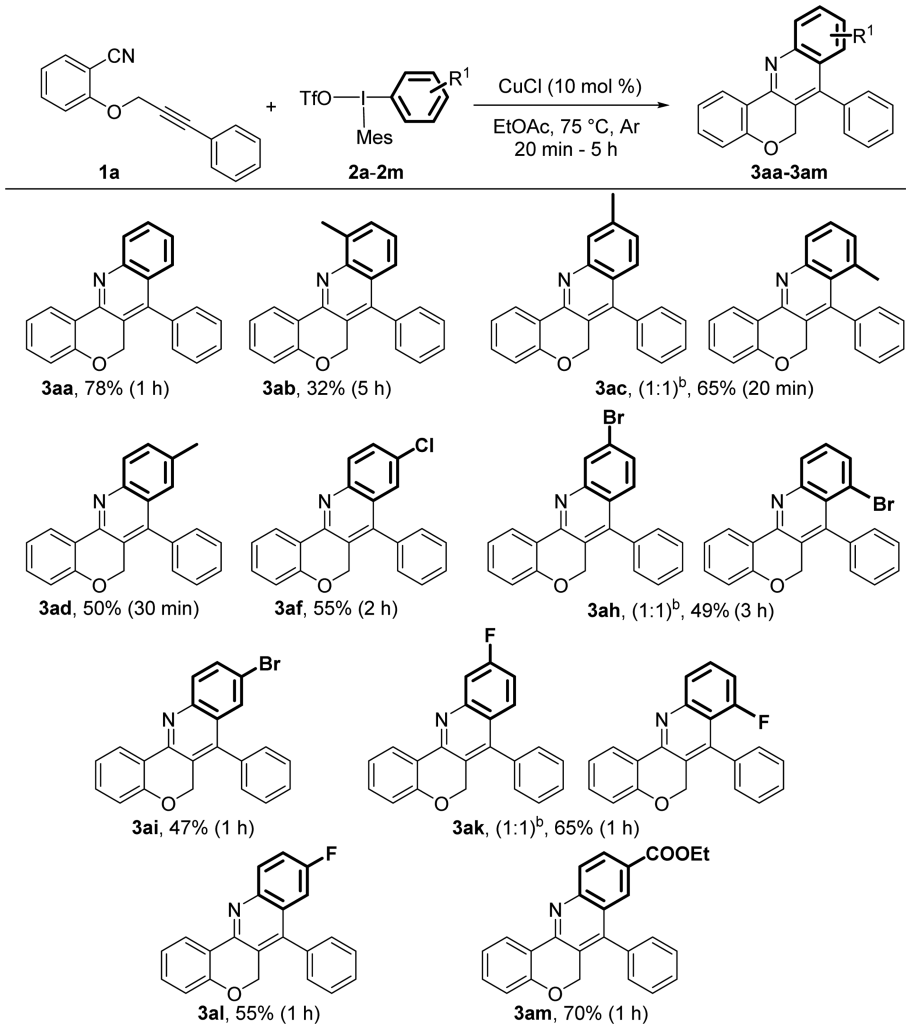
Scheme 3. Synthesis of Chromeno[4,3-*b*]quinolines 1[a]



[a]2-((3-Phenylprop-2-yn-1-yl)oxy)benzonitrile (0.5 mmol, 1.0 equiv), arylmesityliodonium triflate (0.6 mmol, 1.2 equiv), CuCl (0.05 mmol, 0.10 equiv), EtOAc (1.0 mL), Ar, 75 °C, % isolated yield. [b]Isolated as 1:1 mixture of regioisomers.

compounds (**3ca** and **3da**) were obtained in 71% and 34% yields. The presence of halogens (**1e**−**1i**) on the aromatic ring of the nitrile was well-tolerated in the *ortho*, *meta*, and *para* positions, and the appropriate products (**3ea**−**3ia**) were isolated in 60−75% yield. Reaction with nitriles bearing electron-withdrawing groups (**1j** and **1k**) in the *para* position afforded the desired chromenoquinoline derivatives (**3ja** and **3ka**) in 72% and 48% yields. In the presence of an ester group on the aromatic ring of the arylpropynyloxy-benzonitrile derivative (**1l**), we could isolate product **3la** with good yield (80%). The reaction of substrate **1i** and **1l** with the *para*-ester derivative (**2m**) of the iodonium salt led to the appropriate products (**3im** and **3lm**) in 51% and 67% yields.

Finally, the cyclization was performed with substrates bearing halogen and phenyl substituents (**1m**−**1p**) on the hydroxybenzonitrile moiety. The presence of halogens (**1m**, **1n**, and **1o**) on the aromatic ring of the nitrile was well-tolerated, and the desired chloro (**3ma**) and bromo (**3na** and **3oa**) substituted chromenoquinolines were isolated with 78, 80, and 67% yields, respectively. The phenyl substituted derivative (**1p**) of the nitrile was also active in the ring closure reaction and afforded the appropriate product (**3pa**) in 70% yield.

The reactivity of substrate **1q** was conceptually important in establishing the preferential site of activation and comparing the reactivity of the acetylene and the nitrile groups toward the highly electrophilic arylcopper species (Scheme 5). The *ortho* ethynyl anilide motif could undergo cylization in which the amide moiety is involved, providing benzoxazines through acetylene activation, as we demonstrated earlier.[5a] The *N*-aryliminium ion formation via the activation of nitrile could provide quinolines or condensed benzoxazines. The reaction of **1q** with phenylmesityliodonium triflate afforded the appropriate chromenoquinoline product (**3qa**) in 46% yield. While we were not able to detect the formation of any other byproducts, we can conclude that the nitrile function has preferential reactivity over the alkyne moiety, and that electrophilic substitution of the presumed vinyl cation intermediate by the aromatic ring is preferable to attack by the amide part.

The geometry of the chromenoquinoline frame was established by single-crystal X-ray diffraction in the case of compound **3aa** (Figure 1).

Regarding a possible mechanism for the transformation, on the basis of the literature reports,[2,3,5] we suppose that diaryliodonium salts (**1**) generate highly electrophilic

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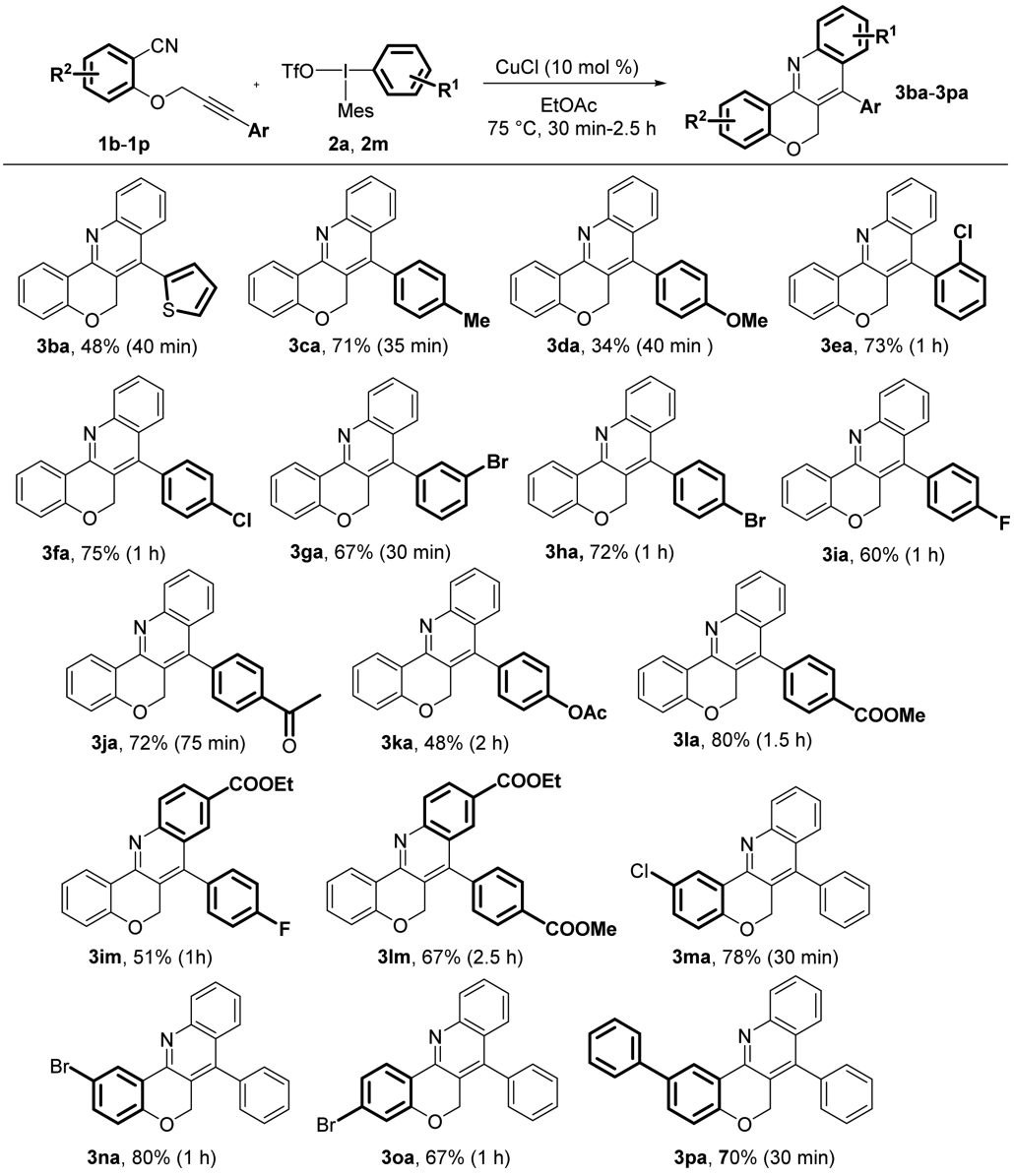
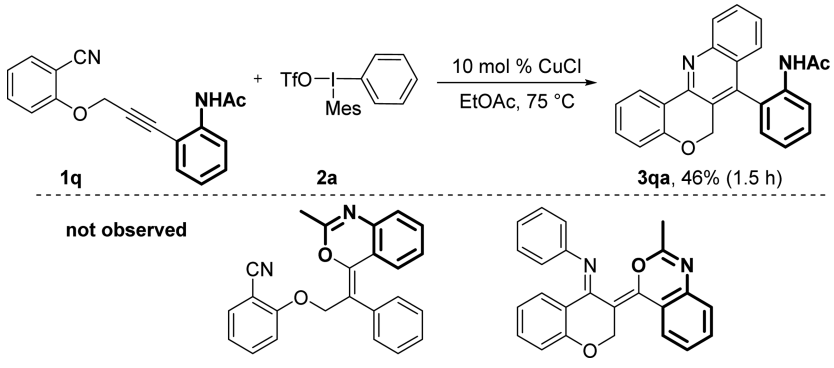
Scheme 4. Synthesis of Chromeno[4,3-*b*]quinolines 2[a]



[a]2-((3-Phenylprop-2-yn-1-yl)oxy)benzonitrile (0.5 mmol, 1.0 equiv), arylmesityliodonium triflate (0.6 mmol, 1.2 equiv), CuCl (0.05 mmol, 0.10 equiv), EtOAc (1.0 mL), Ar, 75 °C, % isolated yield.

Scheme 5. Ring Closure of Trifunctional Substrate



arylcopper(III) species **4** in the presence of the copper catalyst (Scheme 6). This copper(III)-intermediate interacts with the nitrile function (**2**) and forms a cationic species (**5**) and Cu(I). The arylnitrilium intermediate **5** can be readily attacked in an

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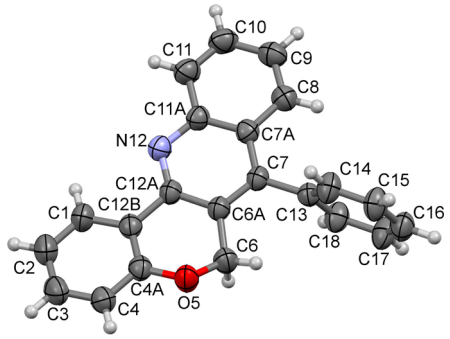
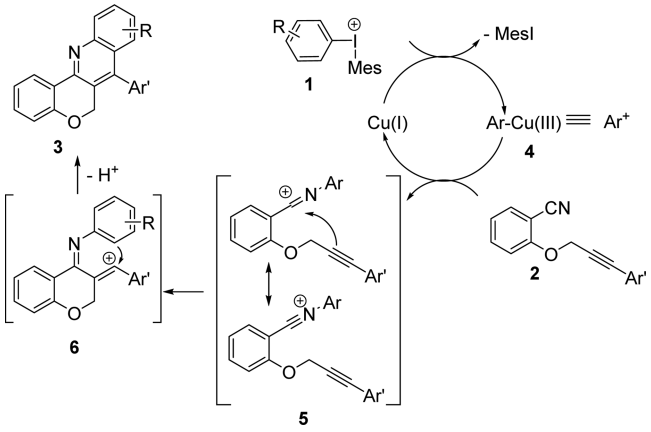


Figure 1. Molecular structure ORTEP representation of compound **3aa**.[8,9] Displacement ellipsoids are drawn at the 50% probability level.

Scheme 6. Plausible Mechanism for the Arylation–Cyclization Reaction



intramolecular fashion by the acetylene moiety, resulting in the formation of the chromene ring with an *exo* vinyl cation (**6**). The resulting intermediate **6** can undergo an intramolecular cyclization via electrophilic aromatic substitution, providing the chromenoquinoline product (**3**).

CONCLUSION

In conclusion, we have demonstrated in a novel reaction that the ring closing strategy based on electrophilic Ar–Cu(III) activation can be extended to substrates containing both nitrile and acetylene functional groups. Herein, we report the development of a new copper-catalyzed oxidative transformation for the construction of chromenoquinoline derivatives from arylpropynyloxy-benzonitriles and diaryliodonium salts. The overall transformation includes two sequential cyclizations which are accompanied by the formation of new C–C and C–N bonds. The developed method enables the synthesis of chromenoquinoline derivatives with high modularity due to the ease with which variable functional groups can be built into the reaction. Further applications of the oxidative ring closure–arylation concept for the construction of novel heterocyclic systems are in progress in our laboratory.

EXPERIMENTAL SECTION

General Methods. Ring closure reactions of substrates **1a–1q** with the appropriate iodonium salt (**2a–2m**) were performed under an argon atmosphere. All solvents used were distilled using standard methods. Ethyl acetate was distilled from calcium hydride. *m*CPBA was dried under high vacuum at room temperature and was stored under argon. Unless otherwise noted, all reagents were ordered and used without further purification. ^{1}H NMR and ^{13}C NMR spectra were recorded at 250 and 62.5 MHz using $CDCl_3$ or DMSO-d_6 as solvent. Chemical shifts are given in ppm relative to TMS for $CDCl_3$, or the residual solvent peak of DMSO as internal standards. Coupling constants (J) are reported in hertz (Hz). Infrared spectra were recorded on a single-reflection diamond ATR spectrometer as solids or thin films. In the IR spectra, only the strongest/structurally most important peaks (ν, cm^{-1}) are listed. HRMS data for new compounds were obtained using a Q-TQF high-resolution mass spectrometer equipped with an electrospray ion source. The measured melting points are uncorrected.

General Procedure 1 for the Synthesis of 2-(Prop-2-yn-1-yloxy)benzonitriles. 2-(Prop-2-yn-1-yloxy)benzonitriles were synthesized from the appropriate 2-hydroxybenzonitrile derivatives and propargyl bromide according to the procedure of Lingam.[10] 2-Hydroxybenzonitrile (1.12 g; 10.0 mmol) and potassium carbonate (2.76 g; 20.0 mmol) were added to a 100 mL round-botton flask fitted with a rubber septum; then, the system was charged with argon. Dimethylformamide (60 mL) was added under an argon atmosphere; then, propargyl bromide (80% toluene solution) (1.93 g; 13.0 mmol; 1.45 mL) was added dropwise. After that, the mixture was stirred at 50 °C for 16 h. Dichloromethane (50 mL) and distilled water (50 mL) were added to the reaction mixture, the aqueous phase was extracted with dichloromethane (3 × 50 mL), and the combined organics were washed with saturated LiCl solution (5 × 50 mL), dried over anhydrous magnesium sulfate, filtered, and evaporated. The crude residue was purified by column chromatography.

*2-(Prop-2-yn-1-yloxy)benzonitrile (**1a′**).*[10] Prepared according to the general procedure from 2-hydroxybenzonitrile. Purification of the crude product by column chromatography on silica gel afforded the product as a white crystalline solid (1.48 g, 9.42 mmol, 94%). Mp 77–78 °C; R_f = 0.35 (hexane–ethyl acetate, 5:1). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.49 (dd, J = 10.1, 4.0 Hz, 2H), 7.07 (d, J = 8.9 Hz, 1H), 6.98 (t, J = 7.6 Hz, 1H), 4.75 (d, J = 2.3 Hz, 1H), 2.50 (t, J = 2.2 Hz, 1H); ^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 159.4, 134.6, 134.3, 122.1, 116.6, 113.4, 102.9, 78.0, 77.6, 56.9; IR ν_{max}/cm^{-1} (solid): 2941, 2573, 2237, 1600, 1490, 1454, 1290, 1233, 1017, 740.

*5-Chloro-2-(prop-2-yn-1-yloxy)benzonitrile (**1b′**).* Prepared according to the general procedure from 5-chloro-2-hydroxybenzonitrile (500 mg, 3.27 mmol). Purification of the crude product by column chromatography on silica gel afforded the product as a white crystalline solid (488 mg, 2.56 mmol, 78%). Mp 125–126 °C; R_f = 0.60 (hexane–ethyl acetate, 4:1). ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.51 (d, J = 8.1 Hz, 2H), 7.10 (d, J = 8.8 Hz, 1H), 4.82 (d, J = 1.9 Hz, 2H), 2.59 (s, 1H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 158.1, 134.6, 133.5, 127.0, 115.2, 114.8, 104.3, 77.7, 77.1, 57.3; IR ν_{max}/cm^{-1} (solid): 2930, 1488, 1285, 1266, 1234, 1135, 1018; HRMS m/z [M-H] Calculated for $C_{10}H_5NOCl$: 190.0060; found 190.0069.

*5-Bromo-2-(prop-2-yn-1-yloxy)benzonitrile (**1c′**).* Prepared according to the general procedure from 5-bromo-2-hydroxybenzonitrile (1.00 g, 5.05 mmol). Purification of the crude product by column chromatography on silica gel afforded the product as a white crystalline solid (1.13 g, 4.81 mmol, 95%). Mp 128–129 °C; R_f = 0.32 (hexane–ethyl acetate, 5:1). ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.66–7.52 (m, 2H), 6.98 (d, J = 8.7 Hz, 1H), 4.76 (d, J = 2.4 Hz, 2H), 2.52 (t, J = 2.3 Hz, 1H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 158.5, 137.4, 136.4, 115.10, 115.07, 113.7, 104.7, 77.8, 77.1, 57.2; IR ν_{max}/cm^{-1} (solid): 2957, 1486, 1286, 1235, 1132, 1016; HRMS m/z [M − H] Calculated for $C_{10}H_5NOBr$: 233.9554; found 233.9565.

General Procedure 2 for the Synthesis of Arylpropynyloxy-benzonitriles. Arylpropynyloxy-benzonitriles were synthesized by Sonogashira reaction from the appropriate 2-(prop-2-yn-1-yloxy)-benzonitrile derivative and aryl iodide according to the modified procedure of Kotschy.[11] 2-(Prop-2-ynyloxy)benzonitrile (390 mg, 2.48 mmol), $PdCl_2(PPh_3)_2$ (43.5 mg, 0.060 mmol, 3 mol %), and copper(I)iodide (11.8 mg, 0.060 mmol, 3 mol %) were added to a 50 mL round-bottom flask fitted with a rubber septum; then, the system was charged with argon. DIPA (20 mL) was added under an argon atmosphere; then, the iodobenzene (422 mg, 2.07 mmol, 231 μL) was added dropwise. If the iodoarene was solid, it was added with

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the copper and palladium sources before the addition of DIPA. The resulting mixture was stirred at 30−45 °C for the appropriate time. The reaction mixure was diluted with dichloromethane (20 mL) and distilled water (20 mL), neutralized with 2 M HCl solution, and extracted with dichloromethane (4 × 20 mL). The combined organics were washed with distilled water (1 × 50 mL) and with brine (1 × 50 mL), dried over anhydrous magnesium sulfate, filtered, and evaporated. The crude residue was purified by column chromatography.

*2-(3-Phenylprop-2-ynyloxy)benzonitrile (**1a**).*[12] Prepared according to the general procedure from 2-(prop-2-yn-1-yloxy)benzonitrile and iodobenzene (422 mg, 2.07 mmol, 231 μL) at 40−45 °C for 1 h. Purification of the crude product by column chromatography on silica gel afforded the product as a drab solid (327 mg, 1.40 mmol, 68%). Mp 64−65 °C; R_f = 0.42 (hexane−ethyl acetate, 5:1). ^{1}H NMR (250 MHz,$CDCl_3$) δ 7.65−7.51 (m, 2H), 7.48−7.39 (m, 2H), 7.37−7.26 (m, 3H), 7.26−7.18 (m, 1H), 7.05 (t, *J* = 7.5 Hz, 1H), 5.06 (s, 2H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 159.7, 134.6, 134.3, 132.2, 129.4, 128.8, 122.2, 121.9, 116.8, 113.5, 102.9, 88.7, 82.9, 57.8; IR ν_{max}/cm^{-1} (solid): 2973, 2232, 1597, 1492, 1454, 1289, 1231, 1015, 758, 737, 694.

*2-((3-(Thiophen-2-yl)prop-2-yn-1-yl)oxy)benzonitrile (**1b**).*[10] Prepared according to the general procedure from 2-(prop-2-ynyloxy)-benzonitrile and 2-iodothiophene (434 mg, 228 μL, 2.07 mmol) for 40 min at 30−35 °C. Purification of the crude product by column chromatography on silica gel afforded the product as a browny solid (465 mg, 1.95 mmol, 94%). Mp 79−80 °C; R_f = 0.45 (hexane−ethyl acetate, 4:1). ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.56−7.42 (m, 2H), 7.19 (d, *J* = 5.2 Hz, 1H), 7.17−7.06 (m, 1H), 6.97 (t, *J* = 7.6 Hz, 1H), 6.88 (dd, *J* = 5.0, 3.8 Hz, 1H), 4.97 (s, 2H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 159.6, 134.6, 134.3, 133.6, 128.5, 127.5, 122.0, 116.7, 113.4, 102.9, 86.9, 82.1, 57.8; IR ν_{max}/cm^{-1} (solid): 2234, 1597, 1491, 1455, 1290, 1231, 1196, 1167, 1113, 1004, 849, 701.

*2-((3-(p-Tolyl)prop-2-yn-1-yl)oxy)benzonitrile (**1c**).*[10] Prepared in a one-pot synthesis. 2-Hydroxybenzonitrile (834 mg; 7.00 mmol) and potassium carbonate (1.94 g; 14.0 mmol) were added to a 100 mL round-botton flask fitted with a rubber septum; then, the system was charged with argon. Dimethylformamide (35 mL) was added under an argon atmosphere; then, propargyl bromide (80% toluene solution) (1.35 g; 9.10 mmol; 1.02 mL) was added dropwise. Then, the mixture was stirred at 50 °C for 16 h. After that, $PdCl_2(PPh_3)_2$ (123 mg; 0.175 mmol; 3 mol %) and copper(I)iodide (33.3 mg; 0.175 mmol; 3 mol %) dissolved in diisopropylamine (3 mL) were added under an argom atmosphere to the reaction mixture; then, 4-iodotoluene (1.27 g; 5.83 mmol) dissolved in diisopropylamine (1.5 mL) was added dropwise under an argom atmosphere. The resulting mixture was stirred at 40−45 °C for 3 h. The workup is according to the steps written in the general procedure. Purification of the crude product by column chromatography on silica gel afforded the product as a light brown solid (637 mg, 2.58 mmol, 44% for the two steps). Mp 37−38 °C; R_f = 0.32 (hexane−ethyl acetate, 7:1). ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.64−7.51 (m, 2H), 7.31 (d, *J* = 8.1 Hz, 2H), 7.22 (d, *J* = 8.7 Hz, 1H), 7.11 (d, *J* = 8.0 Hz, 2H), 7.04 (t, *J* = 7.6 Hz, 1H), 5.03 (s, 2H), 2.33 (s, 3H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 159.8, 139.6, 134.6, 134.2, 132.1, 129.5, 121.8, 119.1, 116.8, 113.5, 102.8, 88.9, 82.3, 57.8, 21.9; IR ν_{max}/cm^{-1} (solid): 2231, 1597, 1508, 1492, 1453, 1371, 1291, 1230, 1169, 1110, 1011, 820.

*2-((3-(4-Methoxyphenyl)prop-2-yn-1-yl)oxy)benzonitrile (**1d**).* Prepared according to the general procedure from 4-iodoanisole (484 mg, 2.07 mmol), for 45 min at 45 °C. Purification of the crude product by column chromatography on silica gel afforded the product as a reddish-brown solid (325 mg, 1.24 mmol, 60%). Mp 58−59 °C; R_f = 0.32 (hexane−ethyl acetate, 4:1). ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.56−7.37 (m, 2H), 7.25 (d, *J* = 8.7 Hz, 2H), 7.12 (d, *J* = 8.9 Hz, 1H), 6.93 (t, *J* = 7.6 Hz, 1H), 6.72 (d, *J* = 8.7 Hz, 2H), 4.92 (s, 2H), 3.68 (s, 3H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 160.5, 159.8, 134.6, 134.2, 133.8, 121.8, 116.8, 114.4, 114.2, 113.5, 102.8, 88.8, 81.6, 57.9, 55.7; IR ν_{max}/cm^{-1} (solid): 2232, 1605, 1510, 1492, 1291, 1249, 1231, 1175, 1034, 834; HRMS *m*/*z* [M + H]$^+$ Calculated for $C_{17}H_{14}NO_2$: 264.1025; found 264.1023.

*2-((3-(2-Chlorophenyl)prop-2-yn-1-yl)oxy)benzonitrile (**1e**).* Prepared according to the general procedure from 2-chloroiodobenzene (493 mg, 253 μL, 2.07 mmol) for 30 min at 40 °C. Purification of the crude product by column chromatography on silica gel afforded the product as a drab solid (344 mg, 1.29 mmol, 62%). Mp 82−83 °C; R_f = 0.30 (hexane−ethyl acetate, 4:1). ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.48 (t, *J* = 7.3 Hz, 2H), 7.37−7.06 (m, 5H), 6.96 (t, *J* = 7.5 Hz, 1H), 5.01 (s, 2H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 159.6, 136.6, 134.6, 134.2, 134.0, 130.5, 129.7, 126.9, 122.2, 122.0, 116.7, 113.7, 102.9, 88.0, 85.5, 57.7; IR ν_{max}/cm^{-1} (solid): 2232, 1600, 1492, 1475, 1455, 1290, 1231, 1015, 759, 739; HRMS *m*/*z* [M + H]$^+$ Calculated for $C_{16}H_{11}NOCl$: 268.0524; found 268.0529.

*2-((3-(4-Chlorophenyl)prop-2-yn-1-yl)oxy)benzonitrile (**1f**).* Prepared according to the general procedure from 4-chloroiodobenzene (493 mg, 2.07 mmol) for 30 min at 40 °C. Purification of the crude product by column chromatography on silica gel afforded the product as a drab solid (460 mg, 1.72 mmol, 83%). Mp 128−129 °C; R_f = 0.62 (hexane−ethyl acetate, 7:3). ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.49 (t, *J* = 8.0 Hz, 2H), 7.22 (q, *J* = 8.6 Hz, 4H), 7.11 (d, *J* = 8.3 Hz, 1H), 6.98 (t, *J* = 7.6 Hz, 1H), 4.95 (s, 2H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 159.6, 135.5, 134.6, 134.3, 133.4, 129.1, 122.0, 120.7, 116.7, 113.4, 102.9, 87.6, 83.9, 57.7; IR ν_{max}/cm^{-1} (solid): 2923, 2232, 1597, 1487, 1453, 1290, 1231, 1014, 827, 753; HRMS *m*/*z* [M + H]$^+$ Calculated for $C_{16}H_{11}NOCl$: 268.0529; found 268.0528.

*2-((3-(3-Bromophenyl)prop-2-yn-1-yl)oxy)benzonitrile (**1g**).* Prepared according to the general procedure from 3-bromoiodobenzene (585 mg, 264 μL, 2.07 mmol) for 30 min at 35 °C. Purification of the crude product by column chromatography on silica gel afforded the product as a drab solid (614 mg, 1.97 mmol, 95%). Mp 58−59 °C; R_f = 0.40 (hexane−ethyl acetate, 4:1). ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.66−7.52 (m, 3H), 7.46 (d, *J* = 8.0 Hz, 1H), 7.34 (d, *J* = 7.7 Hz, 1H), 7.25−7.13 (m, 2H), 7.07 (t, *J* = 7.6 Hz, 1H), 5.04 (s, 2H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 159.6, 134.9, 134.6, 134.3, 132.5, 130.8, 130.2, 124.1, 122.5, 122.0, 116.6, 113.3, 102.9, 87.1, 84.2, 57.6; IR ν_{max}/cm^{-1} (solid): 2236, 1600, 1558, 1490, 1474, 1455, 1289, 1231, 1019, 786, 739, 683; HRMS *m*/*z* [M + H]$^+$ Calculated for $C_{16}H_{11}NOBr$: 312.0024; found 312.0028.

*2-((3-(4-Bromophenyl)prop-2-yn-1-yl)oxy)benzonitrile (**1h**).* Prepared according to the general procedure from 4-bromoiodobenzene (585 mg, 2.07 mmol) for 45 min at 45 °C. Purification of the crude product by column chromatography on silica gel afforded the product as a drab solid (598 mg, 1.92 mmol, 93%). Mp 108−109 °C; R_f = 0.40 (hexane−ethyl acetate, 4:1). ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.49 (t, *J* = 8.0 Hz, 2H), 7.35 (d, *J* = 7.9 Hz, 2H), 7.15 (dd, *J* = 18.8, 8.1 Hz, 3H), 6.98 (t, *J* = 7.4 Hz, 1H), 4.95 (s, 2H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 159.6, 134.6, 134.3, 133.6, 132.0, 123.7, 122.0, 121.1, 116.7, 113.4, 102.9, 87.6, 84.1, 57.7; IR ν_{max}/cm^{-1} (solid): 2233, 1601, 1487, 1458, 1290, 1231, 1015, 826, 738; HRMS *m*/*z* [M + H]$^+$ Calculated for $C_{16}H_{11}NOBr$: 312.0024; found 312.0027.

*2-((3-(4-Fluorophenyl)prop-2-yn-1-yl)oxy)benzonitrile (**1i**).* Prepared according to the general procedure from 4-fluoroiodobenzene (459 mg, 238 μL, 2.07 mmol) for 25 min at 30 °C. Purification of the crude product by column chromatography on silica gel afforded the product as a drab solid (378 mg, 1.51 mmol, 73%). Mp 64−65 °C; R_f = 0.63 (hexane−ethyl acetate, 7:3). ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.56−7.42 (m, 2H), 7.31 (dd, *J* = 8.7, 5.4 Hz, 2H), 7.12 (d, *J* = 8.8 Hz, 1H), 7.02−6.83 (m, 3H), 4.95 (s, 2H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 159.7, 134.6, 134.3, 134.1, 121.9, 118.30, 118.25, 116.7, 116.3, 115.9, 113.4, 102.9, 87.7, 82.7, 57.70; IR ν_{max}/cm^{-1} (solid): 2227, 1700, 1559, 1541, 1508, 1491, 1458, 1231, 1017, 838; HRMS *m*/*z* [M + H]$^+$ Calculated for $C_{16}H_{11}NOF$: 252.0825; found 252.0820.

*2-((3-(4-Acetylphenyl)prop-2-yn-1-yl)oxy)benzonitrile (**1j**).* Prepared according to the general procedure from 4-iodoacetophenone (509 mg, 2.07 mmol) for 30 min at 40 °C. Purification of the crude product by column chromatography on silica gel afforded the product as a drab solid (508 mg, 1.85 mmol, 89%). Mp 88−89 °C; R_f = 0.26 (hexane−ethyl acetate, 3:1). ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.80 (d, *J* = 7.4 Hz, 2H), 7.51 (d, *J* = 7.1 Hz, 2H), 7.41 (d, *J* = 7.3 Hz, 2H), 7.12 (d, *J* = 8.1 Hz, 1H), 6.99 (t, *J* = 6.8 Hz, 1H), 4.99 (s, 2H), 2.50 (s, 3H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 197.6, 159.6, 137.2, 134.6,

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134.3, 132.3, 128.6, 126.9, 122.1, 116.6, 113.4, 102.9, 87.8, 86.1, 57.6, 27.0; IR ν_{max}/cm^{-1} (solid): 2233, 1685, 1603, 1492, 1290, 1257, 1230, 1017, 844, 835, 734; HRMS m/z $[M + H]^+$ Calculated for $C_{18}H_{14}NO_2$: 276.1025; found 276.1018.

*4-(3-(2-Cyanophenoxy)prop-1-yn-1-yl)phenyl Acetate (**1k**).* Prepared according to the one-pot synthesis described for compound **1c** from 4-iodophenyl acetate (611 mg, 2.33 mmol) for 5 h at 45 °C. Purification of the crude product by column chromatography on silica gel afforded the product as a light brown solid (218 mg, 0.749 mmol, 32% for the two steps). Mp 102−103 °C; R_f = 0.32 (hexane−ethyl acetate, 7:3). ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.54−7.41 (m, 2H), 7.33 (d, J = 8.6 Hz, 2H), 7.11 (d, J = 8.4 Hz, 1H), 7.03−6.90 (m, 3H), 4.94 (s, 2H), 2.19 (s, 3H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 169.5, 159.7, 151.4, 134.6, 134.3, 133.4, 122.2, 121.9, 119.8, 116.7, 113.5, 102.8, 87.9, 83.0, 57.7, 21.5; IR ν_{max}/cm^{-1} (solid): 2234, 1769, 1599, 1506, 1492, 1229, 1198, 1016, 737; HRMS m/z $[M + Na]^+$ Calculated for $C_{18}H_{13}NO_3Na$: 314.0793; found 314.0791.

*Methyl 4-(3-(2-Cyanophenoxy)prop-1-yn-1-yl)benzoate (**1l**).* Prepared according to the general procedure from methyl-4-iodobenzoate (542 mg, 2.07 mmol) for 30 min at 35 °C. Purification of the crude product by column chromatography on silica gel afforded the product as a drab solid (531 mg, 1.82 mmol, 88%). Mp 94−95 °C; R_f = 0.50 (hexane−ethyl acetate, 7:3). ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.88 (d, J = 8.4 Hz, 2H), 7.49 (t, J = 7.7 Hz, 2H), 7.38 (d, J = 8.4 Hz, 2H), 7.12 (d, J = 8.5 Hz, 1H), 6.98 (t, J = 7.6 Hz, 1H), 4.98 (s, 2H), 3.82 (s, 3H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 166.7, 159.6, 134.6, 134.3, 132.1, 130.6, 129.8, 126.8, 122.0, 116.6, 113.4, 102.9, 87.8, 85.8, 57.6, 52.7; IR ν_{max}/cm^{-1} (solid): 2235, 1723, 1601, 1491, 1287, 1231, 1111, 1020, 860, 737.698; HRMS m/z $[M + H]^+$ Calculated for $C_{18}H_{14}NO_3$: 292.0974; found 292.0975.

*5-Chloro-2-(3-phenylprop-2-ynyloxy)benzonitrile (**1m**).* Prepared according to the general procedure from 5-chloro-2-(prop-2-ynyloxy)-benzonitrile (382 mg, 2.00 mmol) and iodobenzene (340 mg, 1.67 mmol, 186 μL) for 30 min at 30−35 °C. Purification of the crude product by column chromatography on silica gel afforded the product as a drab solid (236 mg, 0.884 mmol, 44%). Mp 79−80 °C; R_f = 0.38 (hexane−ethyl acetate, 7:1). ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.49−7.37 (m, 2H), 7.37−7.29 (m, 2H), 7.28−7.20 (m, 3H), 7.09 (dd, J = 8.2, 1.2 Hz, 1H), 4.95 (s, 2H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 158.4, 134.6, 133.5, 132.2, 129.5, 128.8, 126.8, 122.0, 115.4, 114.9, 104.3, 89.2, 82.4, 58.2; IR ν_{max}/cm^{-1} (solid): 2237, 1485, 1285, 1235, 1138, 1010, 1000, 817, 738, 694; HRMS m/z $[M + Na]^+$ Calculated for $C_{16}H_{10}NOClNa$: 290.0349; found 290.0359.

*5-Bromo-2-(3-phenylprop-2-ynyloxy)benzonitrile (**1n**).* Prepared according to the general procedure from 5-bromo-2-(prop-2-ynyloxy)-benzonitrile (354 mg, 1.50 mmol) and iodobenzene (255 mg, 1.25 mmol, 140 μL) for 30 min at 30−35 °C. Purification of the crude product by column chromatography on silica gel afforded the product as a white crystalline solid (225 mg, 0.723 mmol, 58%). Mp 86−87 °C; R_f = 0.33 (hexane−ethyl acetate, 5:1). ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.66−7.50 (m, 1H), 7.39−7.27 (m, 1H), 7.28−7.15 (m, 1H), 7.09−6.97 (m, 1H), 4.95 (s, 1H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 158.9, 137.4, 136.4, 132.2, 129.5, 128.8, 121.9, 115.3, 113.5, 104.7, 89.2, 82.3, 58.1; IR ν_{max}/cm^{-1} (solid): 2960, 2234, 1487, 1285, 1233, 1133, 1011, 813, 692; HRMS m/z $[M + Na]^+$ Calculated for $C_{16}H_{10}NOBrNa$: 333.9843; found 333.9856.

*4-Bromo-2-(3-phenylprop-2-ynyloxy)benzonitrile (**1o**).* Prepared according to the one-pot synthesis described for compound **1c** from 4-bromo-2-hydroxybenzonitrile (500 mg, 2.53 mmol) and iodobenzene (396 mg, 1.94 mmol, 217 μL) for 3 h at 45−50 °C. Purification of the crude product by column chromatography on silica gel afforded the product as a drab solid (112 mg, 0.360 mmol, 20%). Mp 114−115 °C; R_f = 0.36 (hexane−ethyl acetate, 5:1). ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.41−7.28 (m, 4H), 7.27−7.15 (m, 4H), 7.15−7.05 (m, 1H), 4.94 (s, 2H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 160.0, 134.9, 132.3, 129.6, 129.0, 128.8, 125.3, 121.9, 117.4, 116.0, 102.0, 89.5, 82.1, 58.2; IR ν_{max}/cm^{-1} (solid): 2234, 1587, 1484, 1230, 1012, 1000, 854, 815, 738, 693; HRMS m/z $[M + Na]^+$ Calculated for $C_{16}H_{10}NOBrNa$: 333.9843; found 333.9853.

*4-((3-Phenylprop-2-yn-1-yl)oxy)-[1,1′-biphenyl]-3-carbonitrile (**1p**).* 5-Bromo-2-(3-phenylprop-2-ynyloxy)benzonitrile (156 mg, 0.5 mmol), phenylboronic acid (183 mg, 0.75 mmol), palladium acetate (5.61 mg, 0.025 mmol, 5 mol %) and tri-*tert*-butylphosphonium tetrafluoroborate (7.25 mmol, 0.025 mmol, 5 mol %) and potassium carbonate (138 mg, 1.00 mmol) were added to a 20 mL round-bottom flask, and the system was charged with argon. Tetrahydrofuran (2.50 mL) and distilled water (2.50 mL) were added dropwise under an argon atmosphere; then, the reaction mixture was stirred at 50 °C for 1.5 h. The reaction mixure was diluted with distilled water (10 mL) and extracted with ethyl acetate (4 × 10 mL). The combined organics were washed with brine (1 × 30 mL), dried over anhydrous magnesium sulfate, filtered, and evaporated. Purification of the crude product by column chromatography on silica gel afforded the product as a drab oil (135 mg, 0.438 mmol, 86%). R_f = 0.35 (hexane−ethyl acetate, 5:1). ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.70−7.61 (m, 2H), 7.43−7.37 (m, 2H), 7.40−7.25 (m, 4H), 7.29−7.15 (m, 5H), 4.97 (s, 2H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 159.0, 138.9, 135.3, 133.1, 132.6, 132.2, 129.5, 129.4, 128.8, 128.2, 127.1, 122.2, 116.7, 113.9, 103.3, 88.9, 82.9, 58.0; IR ν_{max}/cm^{-1} (solid): 2231, 1487, 1282, 1236, 1129, 1013, 999, 763, 738, 692; HRMS m/z $[M + Na]^+$ Calculated for $C_{22}H_{15}NONa$: 332.1051; found 332.1059.

*N-(2-(3-(2-Cyanophenoxy)prop-1-yn-1-yl)phenyl)acetamide (**1q**).* Prepared according to the general procedure from *N*-(2-iodophenyl)-acetamide (362 mg, 2.30 mmol) for 2 h at 30−35 °C. Purification of the crude product by column chromatography on silica gel afforded the product as a drab solid (400 mg, 1.38 mmol, 60%). Mp 119−120 °C; R_f = 0.35 (hexane−ethyl acetate, 3:2); ^{1}H NMR (250 MHz, $CDCl_3$) δ 8.24 (d, J = 8.3 Hz, 1H), 7.64 (s, 1H), 7.57−7.46 (m, 2H), 7.33−7.20 (m, 2H), 7.11 (d, J = 8.4 Hz, 1H), 6.97 (dt, J = 16.3, 7.5 Hz, 2H), 5.05 (s, 2H), 1.99 (s, 3H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 168.8, 159.4, 139.6, 134.7, 134.5, 132.3, 130.7, 123.8, 122.3, 120.1, 116.5, 113.2, 110.9, 103.0, 89.8, 84.2, 57.7, 25.1; IR ν_{max}/cm^{-1} (solid); 2233, 1699, 1600, 1581, 1517, 1492, 1446, 1301, 1231, 1016761, 740; HRMS m/z $[M + Na]^+$ Calculated for $C_{18}H_{14}N_2O_2Na$: 313.0953; found 313.0940.

General Procedure 3 for the One-Pot Synthesis of Arylmesityliodonium Triflates. Arylmesityliodonium triflates (**2a−2m**) were synthesized in a one-pot procedure from the appropriate iodoarene and mesitylene according to the modified procedure[5a] of Olofsson.[13] *m*-Chloroperbenzoic acid (65% active oxidant, 1.32 g, 5.00 mmol) and the appropriate iodoarene (4.50 mmol) were dissolved in dichloromethane (20 mL). Mesitylene (696 μL, 5.00 mmol) was added, and the solution was cooled to 0 °C. Trifluoromethanesulfonic acid (825 mg, 486 μL, 5.50 mmol) was added dropwise in 5 min, and the resulting reaction mixture was allowed to warm to room temperature over 2 h. The volatile components were removed under reduced pressure, and the resulting material was suspended in diethyl ether (40 mL). The suspension was stored at −20 °C for 2 h. The resulting crystals were filtered off and were washed with ether to give the appropriate arylmesityliodonium triflate as a solid, which was dried at 100 °C under vacuum.

*Mesityl(phenyl)iodonium Trifluoromethanesulfonate (**2a**).*[5a] Prepared according to the general procedure from iodobenzene. The product was obtained as a white solid (1.71 g, 3.62 mmol, 80%). Mp 147−148 °C; ^{1}H NMR (250 MHz, DMSO-d_6) δ 7.99 (d, 2H, J = 7.7 Hz), 7.64 (t, 1H, J = 7.3 Hz), 7.50 (t, 2H, J = 7.4 Hz), 7.22 (s, 2H), 2.60 (s, 6H), 2.29 (s, 3H); ^{13}C NMR (62.5 MHz, DMSO-d_6) δ 143.1, 141.5, 134.5, 131.8, 131.7, 129.7, 122.5, 114.5, 26.2, 20.5; IR ν_{max}/cm^{-1} (solid): 1443, 1246, 1157, 1025, 856, 742, 632, 572, 515, 454; HRMS m/z $[M - OTf]^+$ Calculated for $C_{15}H_{16}I$: 323.0291; found 323.0289.

*2-Methylphenyl(mesityl)iodonium Trifluoromethanesulfonate (**2b**).*[5a] Prepared according to the general procedure from 2-iodotoluene. The product was obtained as a white solid (2.02 g, 4.16 mmol, 93%). Mp 166−167 °C; ^{1}H NMR (250 MHz, DMSO-d_6) δ 7.97 (d, 1H, J = 7.9 Hz), 7.55 (d, 2H, J = 4.4 Hz), 7.26 (m, 1H, J = 4.3 Hz), 7.21 (s, 2H), 2.57 (s, 9H), 2.29 (s, 3H); ^{13}C NMR (62.5 MHz, DMSO-d_6) δ 142.9, 141.6, 140.7, 136.7, 132.4, 131.8, 129.9, 129.3, 121.8, 118.5, 26.1, 24.4, 20.4; IR ν_{max}/cm^{-1} (solid): 1467, 1245,

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1156, 1027, 855, 759, 634, 516; HRMS m/z [M − OTf]$^+$ Calculated for $C_{16}H_{18}I$: 337.0448; found 337.0443.

*3-Methylphenyl(mesityl)iodonium Trifluoromethanesulfonate (**2c**).*[5a] Prepared according to the general procedure from 3-iodotoluene. The product was obtained as a white solid (1.59 g, 3.26 mmol, 73%). Mp 171−172 °C; ^{1}H NMR (250 MHz, DMSO-d_6): δ 7.87 (s, 1H), 7.78 (d, 1H, J = 7.6 Hz), 7.45 (d, 1H, J = 7.6 Hz), 7.38 (t, 1H, J = 7.7 Hz), 7.21 (s, 2H), 2.61 (s, 6H), 2.32 (s, 3H), 2.29 (s, 3H); ^{13}C NMR (62.5 MHz, DMSO-d_6): δ 143.0, 141.9, 141.5, 134.6, 132.5, 131.6, 131.5, 129.7, 122.4, 114.3, 26.3, 20.7, 20.4; IR ν_{max}/cm^{-1} (solid): 1455, 1275, 1245, 1156, 1025, 634, 516; HRMS m/z [M − OTf]$^+$ Calculated for $C_{16}H_{18}I$: 337.0448; found 337.0440.

*4-Methylphenyl(mesityl)iodonium Trifluoromethanesulfonate (**2d**).*[5a] Prepared according to the general procedure from 4-iodotoluene. The product was obtained as a white solid (2.07 g, 4.26 mmol, 95%). Mp 183−184 °C; ^{1}H NMR (250 MHz, DMSO-d_6) δ 7.88 (d, 2H, J = 8.4 Hz), 7.30 (d, 2H, J = 8.2 Hz), 7.20 (s, 2H), 2.60 (s, 6H), 2.32 (s, 3H), 2.28 (s, 3H); ^{13}C NMR (62.5 MHz, DMSO-d_6) δ 142.9, 142.2, 141.4, 134.5, 132.4, 129.7, 122.7, 110.8, 26.2, 20.7, 20.4; IR ν_{max}/cm^{-1} (solid): 1452, 1246, 1157, 1024, 804, 632, 481; HRMS m/z [M − OTf]$^+$ Calculated for $C_{16}H_{18}I$: 337.0448; found 337.0444.

*(2-Chlorophenyl)(mesityl)iodonium Trifluoromethanesulfonate (**2e**).*[5a] Prepared according to the general procedure from 1-chloro-2-iodobenzene. The product was obtained as an off-white solid (1.41 g, 2.78 mmol, 62%). Mp 167−168 °C; ^{1}H NMR (250 MHz, DMSO-d_6) δ 8.27 (dd, 1H, J = 8.1 and 1.3 Hz), 7.82 (dd, 1H, J = 8.1 and 1.4 Hz), 7.68 (td, 1H, J = 7.9 and 1.4 Hz), 7.45 (td, 1H, J = 7.9 and 1.4 Hz), 7.21 (s, 2H), 2.62 (s, 6H), 2.28 (s, 3H); ^{13}C NMR (62.5 MHz, DMSO-d_6) δ 143.2, 141.8, 138.9, 135.7, 134.3, 130.7, 130.0 (d, J = 7.8 Hz), 122.6, 116.4, 26.1, 20.4; IR ν_{max}/cm^{-1} (solid): 1449, 1276, 1239, 1160, 1024, 759, 631, 516,432; HRMS m/z [M − OTf]$^+$ Calculated for $C_{15}H_{15}ClI$: 356.9901; found 356.9899.

*(4-Chlorophenyl)(mesityl)iodonium Trifluoromethanesulfonate (**2f**).*[5a] Prepared according to the general procedure from 1-chloro-4-iodobenzene. The product was obtained as a white solid (1.37 g, 2.70 mmol, 60%). Mp 177−178 °C; ^{1}H NMR (250 MHz, DMSO-d_6) δ 7.98 (d, 2H, J = 8.7 Hz), 7.57 (d, 2H, J = 8.7 Hz), 7.23 (s, 2H), 2.59 (s, 6H), 2.29 (s, 3H); ^{13}C NMR (62.5 MHz, DMSO-d_6) δ 143.2, 141.5, 136.9, 136.2, 131.7, 129.8, 122.7, 112.2, 26.2, 20.4; IR ν_{max}/cm^{-1} (solid): 1473, 1245, 1163, 1024, 807, 631, 516; HRMS m/z [M − OTf]$^+$ Calculated for $C_{15}H_{15}ClI$: 356.9901; found 356.9901.

*2-Bromophenyl(mesityl)iodonium Trifluoromethanesulfonate (**2g**).*[5a] Prepared according to the general procedure from 2-bromoiodobenzene. The product was obtained as an off-white solid (1.65 g, 2.98 mmol, 66%). Mp 167−168 °C; ^{1}H NMR (250 MHz, DMSO-d_6) δ 8.18 (dd, 1H, J = 7.9 and 1.4 Hz), 7.95 (dd, 1H, J = 7.9 and 1.4 Hz), 7.59 (td, 1H, J = 7.9 and 1.4 Hz), 7.47 (td, 1H, J = 7.9 and 1.4 Hz), 7.22 (s, 2H) 2.62 (s, 6H), 2.29 (s, 3H); ^{13}C NMR (62.5 MHz, DMSO-d_6) δ 143.2, 141.8, 139.0, 134.1, 130.4, 130.0, 126.5, 119.4, 26.3, 20.4; IR ν_{max}/cm^{-1} (solid): 1442, 1276, 1241, 1160, 1025, 757, 631, 516; HRMS m/z [M − OTf]$^+$ Calculated for $C_{15}H_{15}BrI$: 400.9396; found 400.9386.

*3-Bromophenyl(mesityl)iodonium Trifluoromethanesulfonate (**2h**).*[5a] Prepared according to the general procedure from 3-bromoiodobenzene. The product was obtained as an off-white solid (1.35 g, 2.45 mmol, 55%). Mp 173−174 °C; ^{1}H NMR (250 MHz, DMSO-d_6) δ 8.29 (s, 1H), 7.90 (d, 1H, J = 8.1 Hz), 7.84 (d, 1H, J = 7.4 Hz), 7.44 (t, 1H, J = 7.9), 7.23 (s, 2H), 2.60 (s, 6H), 2.30 (s, 3H); ^{13}C NMR (62.5 MHz, DMSO-d_6) δ 144.0, 143.3, 141.7, 136.1, 134.7, 133.5, 133.1, 129.8, 123.4, 122.6, 114.9, 26.3, 20.5; IR ν_{max}/cm^{-1} (solid): 1454, 1222, 1024, 797, 634, 516; HRMS m/z [M − OTf]$^+$ Calculated for $C_{15}H_{15}BrI$: 400.9396; found: 400.9402.

*4-Bromophenyl(mesityl)iodonium Trifluoromethanesulfonate (**2i**).*[5a] Prepared according to the general procedure from 4-bromoiodobenzene. The product was obtained as a white solid (1.69 g, 3.07 mmol, 68%). Mp 179−180 °C; ^{1}H NMR (250 MHz, DMSO-d_6) δ 7.90 (d, 2H, J = 8.5 Hz), 7.70 (d, 2H, J = 8.5 Hz), 7.22 (s, 2H), 2.60 (s, 6H), 2.29 (s, 3H); ^{13}C NMR (62.5 MHz, DMSO-d_6) δ 143.2, 141.5, 136.3, 134.6, 129.8, 125.7, 122.7, 113.0, 26.2, 20.5; IR ν_{max}/cm^{-1} (solid): 1473, 1245, 1232, 1024, 807, 631, 518, 475; HRMS m/z [M − OTf]$^+$ Calculated for $C_{15}H_{15}BrI$: 400.9396; found: 400.9399.

*2-Fluorophenyl(mesityl)iodonium Trifluoromethanesulfonate (**2j**).*[5a] Prepared according to the general procedure from 2-fluoroiodobenzene. The product was obtained as an off-white solid (1.04 g, 2.12 mmol, 47%). Mp 161−162 °C; ^{1}H NMR (250 MHz, DMSO-d_6) δ 8.27 (m, 1H), 7.72 (m, 1H), 7.56 (td, 1H, J = 8.8 and 1.3 Hz), 7.35 (td, 1H, J = 7.9 and 1.3 Hz), 7.20 (s, 2H), 2.62 (s, 6H), 2.27 (s, 3H); ^{13}C NMR (62.5 MHz, DMSO-d_6) δ 143.2, 141.5, 137.4, 135.3 (d, J = 8.3 Hz), 129.8, 127.5 (d, J = 2.6 Hz), 122.7, 117.3, 116.9, 101.6, 101.3, 26.0, 20.4; IR ν_{max}/cm^{-1} (solid): 1476, 1279, 1236, 1161, 1027, 770, 635, 515; HRMS m/z [M − OTf]$^+$ Calculated for $C_{15}H_{15}FI$: 341.0197; found: 341.0194.

*3-Fluorophenyl(mesityl)iodonium Trifluoromethanesulfonate (**2k**).* Prepared according to the general procedure from 3-fluoroiodobenzene. The product was obtained as an off-white solid (1.31 g, 2.67 mmol, 59%). Mp 177−178 °C; ^{1}H NMR (250 MHz, DMSO-d_6) δ 7.97 (d, J = 8.0 Hz, 1H), 7.75 (d, J = 7.5 Hz, 1H), 7.53 (t, J = 9.6 Hz, 2H), 7.22 (s, 2H), 2.60 (s, 6H), 2.29 (s, 3H); ^{13}C NMR (62.5 MHz, DMSO-d_6) δ 143.70, 142.05, 133.87, 133.75, 130.94, 130.90, 130.19, 123.05, 122.17, 121.77, 119.67, 119.33, 114.16, 26.65, 20.83; IR ν_{max}/cm^{-1} (solid): 2045, 1592, 1582, 1471, 1286, 1239, 1225, 1168, 1025, 839, 735, 668; HRMS m/z [M − OTf]$^+$ Calculated for $C_{15}H_{15}FI$: 341.0203; found 341.0217.

*4-Fluorophenyl(mesityl)iodonium Trifluoromethanesulfonate (**2l**).*[5a] Prepared according to the general procedure from 4-fluoroiodobenzene. The product was obtained as an off-white solid (1.63 g, 3.33 mmol, 74%). Mp 178−179 °C; ^{1}H NMR (250 MHz, DMSO-d_6) δ 7.37 (t, 2H, J = 8.7 Hz), 7.22 (s, 2H), 2.60 (s, 6H), 2.29 (s, 3H); ^{13}C NMR (62.5 MHz, DMSO-d_6) δ 143.1, 141.5, 137.4, 137.2, 129.7, 119.4, 119.0, 26.2, 20.5; IR ν_{max}/cm^{-1} (solid): 1575, 1483, 1224, 1168, 1024, 849, 632, 508; HRMS m/z [M − OTf]$^+$ Calculated for $C_{15}H_{15}FI$: 341.0203; found: 341.0195.

*(4-(Ethoxycarbonyl)phenyl)(mesityl)iodonium Trifluoromethanesulfonate (**2m**).*[5a] Prepared according to the general procedure from ethyl 4-iodobenzoate with the exception that 3-chloroperoxybenzoic acid, mesitylene, and the aryl iodide were stirred together at room temperature for 4 h before the addition of the trifluoromethanesulfonic acid. The product was obtained as a white solid (1.159 g, 47%). Mp 174−175 °C; ^{1}H NMR (250 MHz, DMSO-d_6): δ 8.09 (d, 2H, J = 8.4 Hz), 7.99 (d, 2H, J = 8.4 Hz), 7.24 (s, 2H), 4.31 (q, 2H, J = 6.9 Hz), 2.59 (s, 2H), 2.30 (s, 1H), 1.29 (t, 3H, J = 7.0 Hz); ^{13}C NMR (62.5 MHz, DMSO-d_6): δ 164.5, 143.4, 141.7, 134.7, 132.7, 131.9, 129.9, 122.6, 119.3, 61.4, 26.3, 20.5, 14.0; IR ν_{max}/cm^{-1} (solid): 1723, 1584, 1458, 1395, 1272, 1238, 1161, 1103, 1025, 849, 753, 634, 516; HRMS m/z [M − OTf]$^+$ Calculated for $C_{18}H_{20}IO_2$: 395.0502; found: 395.0504.

General Procedure 4 for the Synthesis of 7-Aryl-6*H*-chromeno[4,3-*b*]quinolines. 2-(3-Phenylprop-2-ynyloxy)-benzonitrile (**1a**) (117 mg, 0.500 mmol), diaryl iodonium salt (0.600 mmol, 1.2 equiv), and copper(I)chloride (4.96 mg; 0.050 mmol, 10 mol %) were added to a 4 mL vial; then, the system was charged with argon. Ethyl acetate (1 mL) was added under an argon atmosphere; then, the reaction mixture was stirred at 75 °C for the appropriate time. Saturated sodium hydrogen carbonate solution (10 mL) was added to the mixture, the aqueous layer was extracted with dichloromethane (4 × 10 mL), and the combined organics were washed with brine (1 × 25 mL), dried over anhydrous magnesium sulfate, filtered, and evaporated. The crude residue was purified by column chromatography.

*7-Phenyl-6H-chromeno[4,3-b]quinoline (**3aa**).*[14] Prepared according to the general procedure from 2-(3-phenylprop-2-ynyloxy)-benzonitrile and phenyl(mesityl)iodonium trifluoromethanesulfonate (283 mg, 0.600 mmol) for 1 h. Purification of the crude product by column chromatography on silica gel afforded the product as a drab solid (120 mg, 0.388 mmol, 78%). Mp 159−160 °C; R_f = 0.45 (hexane−ethyl acetate, 10:1). ^{1}H NMR (250 MHz, $CDCl_3$) δ 8.42 (d, J = 6.7 Hz, 1H), 8.05 (d, J = 7.8 Hz, 1H), 7.62−7.48 (m, 1H), 7.46−7.29 (m, 4H), 7.30−7.11 (m, 4H), 7.09−6.97 (m, 1H), 6.84 (d, J = 7.4 Hz, 1H), 4.96 (s, 2H).; ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 157.7, 149.1,

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148.4, 144.1, 135.3, 132.3, 130.0, 129.73, 129.65, 129.2, 128.9, 127.5, 126.6, 126.5, 126.21, 123.9, 123.2, 122.9, 117.6, 67.1; IR ν_{max}/cm^{-1} (solid): 2927, 2910, 1583, 1560, 1506, 1490, 1465, 1222, 1044, 769, 737, 700; HRMS m/z $[M + H]^+$ Calculated for $C_{22}H_{16}NO$: 310.1232; found 310.1236.

*11-Methyl-7-phenyl-6H-chromeno[4,3-b]quinoline (**3ab**).* Prepared according to the general procedure from 2-(3-phenylprop-2-ynyloxy)benzonitrile and 2-methylphenyl(mesityl)iodonium trifluoromethanesulfonate (292 mg, 0.600 mmol) for 5 h. Purification of the crude product by column chromatography on silica gel afforded the product as a drab solid (52.0 mg, 0.161 mmol, 32%). Mp 124−125 °C; R_f = 0.30 (hexane−ethyl acetate, 30:1). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 8.48 (dd, J = 7.7, 1.3 Hz, 1H), 7.39 (d, J = 5.6 Hz, 4H), 7.30−6.98 (m, 7H), 6.84 (d, J = 8.1 Hz, 1H), 4.96 (s, 2H), 2.81 (s, 3H); ^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 157.6, 147.6, 147.3, 144.2, 137.9, 135.8, 132.0, 129.9, 129.7, 129.1, 128.8, 127.4, 126.3, 126.2, 124.5, 124.3, 122.8, 122.7, 117.5, 67.2, 18.6; IR ν_{max}/cm^{-1} (solid): 2928, 2365, 1588, 1489, 1394, 1369, 1222, 1040, 769, 741; HRMS m/z $[M + H]^+$ Calculated for $C_{23}H_{18}NO$: 324.1388; found 324.1392.

*8-Methyl-7-phenyl-6H-chromeno[4,3-b]quinoline and 10-Methyl-7-phenyl-6H-chromeno[4,3-b]quinoline (**3ac**).* Prepared according to the general procedure from 2-(3-phenylprop-2-ynyloxy)benzonitrile and 3-methylphenyl(mesityl)iodonium trifluoromethanesulfonate (292 mg, 0.600 mmol) for 20 min. Purification of the crude product by column chromatography on silica gel afforded the product as a drab solid (105 mg, 0.325 mmol, 65%). Mp 99−100 °C; R_f = 0.35 (hexane−ethyl acetate, 25:1). ^{1}H NMR (250 MHz, $CDCl_3$) δ 8.52−8.28 (m, 1H), 7.94 (d, J = 8.3 Hz, 0.5H), 7.84 (s, 0.5H), 7.50−6.94 (m, 9H), 6.82 (t, J = 7.6 Hz, 1H), 4.94 (s, 1H), 4.77 (s, 1H), 2.40 (s, 1.5H), 1.77 (s, 1.5H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 157.7, 157.6, 149.6, 149.0, 148.6, 147.9, 144.3, 144.0, 140.0, 139.4, 136.1, 135.5, 132.1, 130.3, 129.7, 129.5, 129.3, 129.2, 129.13, 129.06, 128.91, 128.87, 128.8, 128.6, 126.2, 126.1, 126.0, 125.5, 124.4, 124.0, 123.6, 122.83, 122.78, 122.4, 117.5, 117.4, 67.2, 67.1, 24.5, 22.1; IR ν_{max}/cm^{-1} (solid): 2928, 2366, 2340, 1701, 1577, 1558, 1539, 1506, 1487, 1219, 1042, 738; HRMS m/z $[M + H]^+$ Calculated for $C_{23}H_{18}NO$: 324.1388; found 324.1392.

*9-Methyl-7-phenyl-6H-chromeno[4,3-b]quinoline (**3ad**).*[15] Prepared according to the general procedure from 2-(3-phenylprop-2-ynyloxy)benzonitrile and 4-methylphenyl(mesityl)iodonium trifluoromethanesulfonate (292 mg, 0.600 mmol) for 30 min. Purification of the crude product by column chromatography on silica gel afforded the product as a drab solid (81.5 mg, 0.252 mmol, 50%). Mp 193−194 °C; R_f = 0.35 (hexane−ethyl acetate, 15:1). ^{1}H NMR (250 MHz, $CDCl_3$) δ 8.41 (d, J = 7.3 Hz, 1H), 7.96 (d, J = 8.5 Hz, 1H), 7.53−7.29 (m, 4H), 7.28−6.96 (m, 5H), 6.84 (d, J = 8.0 Hz, 1H), 4.94 (s, 2H), 2.26 (s, 3H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 157.6, 148.2, 146.9, 143.5, 136.6, 135.5, 132.0, 129.7, 129.2, 128.9, 127.4, 126.1, 125.4, 124.0, 123.2, 122.9, 117.5, 67.2, 22.2; IR ν_{max}/cm^{-1} (solid): 2924, 2367, 2340, 1585, 1495, 1467, 1221, 1049, 1000, 831, 737; HRMS m/z $[M + H]^+$ Calculated for $C_{23}H_{18}NO$: 324.1388; found 324.1390.

*9-Chloro-7-phenyl-6H-chromeno[4,3-b]quinoline (**3af**).*[16] Prepared according to the general procedure from 2-(3-phenylprop-2-ynyloxy)benzonitrile and (4-chlorophenyl)(mesityl)iodonium trifluoromethanesulfonate (302 mg, 0.600 mmol) for 2 h. Purification of the crude product by column chromatography on silica gel afforded the product as a white solid (95.0 mg, 0.277 mmol, 55%). Mp 174−175 °C; R_f = 0.38 (hexane−ethyl acetate, 20:1). ^{1}H NMR (250 MHz, $CDCl_3$) δ 8.47−8.25 (m, 1H), 7.95 (d, J = 8.9 Hz, 1H), 7.54−7.36 (m, 4H), 7.30 (d, J = 2.1 Hz, 1H), 7.28−7.20 (m, 1H), 7.19−7.10 (m, 2H), 7.03 (t, J = 7.4 Hz, 1H), 6.84 (d, J = 8.1 Hz, 1H), 4.94 (s, 2H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 157.6, 149.3, 146.8, 143.3, 134.6, 132.5, 132.4, 131.6, 130.6, 129.5, 129.4, 129.3, 128.1, 126.1, 125.3, 124.0, 123.5, 122.9, 117.6, 67.0; IR ν_{max}/cm^{-1} (solid): 2369, 1585, 1489, 1373, 1223, 1047, 833, 737; HRMS m/z $[M + H]^+$ Calculated for $C_{22}H_{15}NOCl$: 344.0842; found 344.0844.

*8-Bromo-7-phenyl-6H-chromeno[4,3-b]quinoline and 10-Bromo-7-phenyl-6H-chromeno[4,3-b]quinoline (**3ah**).* Prepared according to the general procedure from 2-(3-phenylprop-2-ynyloxy)benzonitrile and 3-bromophenyl(mesityl)iodonium trifluoromethanesulfonate (331 mg, 0.600 mmol) for 3 h. Purification of the crude product by column chromatography on silica gel afforded the product as a drab solid (94.0 mg, 0.243 mmol, 49%). Mp 120−121 °C; R_f = 0.40 (hexane−ethyl acetate, 20:1). ^{1}H NMR (250 MHz, $CDCl_3$) δ 8.49 (d, J = 7.7 Hz, 1H), 8.36 (s, 0.4H), 8.17 (d, J = 8.0 Hz, 0.6H), 7.72 (d, J = 7.5 Hz, 1H), 7.63−7.09 (m, 8H), 7.05−6.87 (m, 1H), 5.07 (s, 1H), 4.94 (s, 1H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 157.7, 157.6, 150.0, 149.9, 149.0, 148.8, 144.19, 144.19, 136.8, 134.7, 134.3, 134.2, 132.68, 132.65, 132.2, 131.0, 129.94, 129.90, 129.8, 129.6, 129.3, 129.2, 128.79, 128.75, 128.0, 126.3, 126.2, 125.8, 125.5, 125.1, 124.0, 123.5, 123.1, 123.0, 122.9, 119.5, 117.6, 117.5, 67.3, 67.0; IR ν_{max}/cm^{-1} (solid): 2366, 2342, 1584, 1570, 1487, 1245, 1221, 1043, 737; HRMS m/z $[M + H]^+$ Calculated for $C_{22}H_{15}NOBr$: 388.0337; found 388.0339.

*9-Bromo-7-phenyl-6H-chromeno[4,3-b]quinoline (**3ai**).* Prepared according to the general procedure from 2-(3-phenylprop-2-ynyloxy)-benzonitrile and (4-bromophenyl)(mesityl)iodonium trifluoromethanesulfonate (331 mg, 0.600 mmol) for 1 h. Purification of the crude product by column chromatography on silica gel afforded the product as a white solid (90.0 mg, 0.232 mmol, 47%). Mp 199−200 °C; R_f = 0.38 (hexane−ethyl acetate, 20:1). ^{1}H NMR (250 MHz, $CDCl_3$) δ 8.38 (d, J = 7.4 Hz, 1H), 7.91 (d, J = 8.9 Hz, 1H), 7.60 (dd, J_1 = 7.5 Hz, J_2 = 2.5 Hz, 1H), 7.52−7.34 (m, 4H), 7.25 (t, J = 7.6 Hz, 1H), 7.20−7.10 (m, 2H), 7.04 (t, J = 7.4 Hz, 1H), 6.84 (d, J = 8.1 Hz, 1H), 4.95 (s, 2H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 157.7, 149.4, 146.9, 143.3, 134.5, 133.2, 132.6, 131.6, 129.5, 129.4, 129.3, 128.63, 128.59, 126.2, 124.0, 123.5, 123.0, 120.7, 117.6, 67.0; IR ν_{max}/cm^{-1} (solid): 2365, 2343, 1580, 1560, 1489, 1223, 1044, 832, 737; HRMS m/z $[M + H]^+$ Calculated for $C_{22}H_{15}NOBr$: 388.0337; found 388.0342.

*8-Fluoro-7-phenyl-6H-chromeno[4,3-b]quinoline and 10-Fluoro-7-phenyl-6H-chromeno[4,3-b]quinoline (**3ak**).* Prepared according to the general procedure from 2-(3-phenylprop-2-ynyloxy)benzonitrile and 3-fluorophenyl(mesityl)iodonium trifluoromethanesulfonate (294 mg, 0.600 mmol) for 1 h. Purification of the crude product by column chromatography on silica gel afforded the product as a drab solid (106 mg, 0.324 mmol, 65%). Mp 141−142 °C; R_f = 0.36 (hexane−ethyl acetate, 15:1). ^{1}H NMR (250 MHz, $CDCl_3$) δ 8.52 (d, J = 7.7 Hz, 1H), 8.00 (d, J = 8.5 Hz, 0.4H), 7.81 (dd, J = 10.2, 2.7 Hz, 0.6H), 7.64−6.83 (m, 10H), 5.09 (s, 1H), 5.01 (s, 1H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 165.4, 157.8, 157.7, 150.2, 149.7, 144.3, 141.4, 137.7, 137.6, 135.0, 132.7, 132.6, 129.54, 129.47, 129.32, 129.26, 129.1, 128.8, 128.7, 128.5, 128.21, 128.15, 126.4, 126.33, 126.28, 124.8, 124.5, 123.6, 123.3, 122.9, 122.53, 122.50, 117.6, 116.9, 116.5, 113.6, 113.3, 112.1, 111.7, 67.0, 66.7; IR ν_{max}/cm^{-1} (solid): 2366, 2342, 1583, 1487, 1468, 1222, 1137, 1043, 738; HRMS m/z $[M + H]^+$ Calculated for $C_{22}H_{15}NOF$: 328.1138; found 328.1139.

*9-Fluoro-7-phenyl-6H-chromeno[4,3-b]quinolone (**3al**).* Prepared according to the general procedure from 2-(3-phenylprop-2-ynyloxy)-benzonitrile and (4-fluorophenyl)(mesityl)iodonium trifluoromethanesulfonate (294 mg, 0.600 mmol) for 1 h. Purification of the crude product by column chromatography on silica gel afforded the product as a light yellow solid (90.0 mg, 0.274 mmol, 55%). Mp 140−141 °C; R_f = 0.35 (hexane−ethyl acetate, 15:1). ^{1}H NMR (250 MHz, $CDCl_3$) δ 8.35 (d, J = 7.6 Hz, 1H), 8.00 (dd, J = 9.1, 5.6 Hz, 1H), 7.50−7.34 (m, 3H), 7.32−7.07 (m, 4H), 7.02 (t, J = 7.5 Hz, 1H), 6.94 (dd, J = 10.0, 2.5 Hz, 1H), 6.82 (d, J = 8.1 Hz, 1H), 4.93 (s, 2H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 162.8, 158.8, 157.5, 148.6, 148.5, 145.4, 143.6, 143.5, 134.8, 132.4, 132.3, 129.5, 129.4, 129.2, 128.3, 128.2, 126.0, 123.9, 123.6, 122.9, 120.0, 119.6, 117.6, 110.2, 109.8, 67.1; IR ν_{max}/cm^{-1} (solid): 2367, 2339, 1558, 1489, 1222, 1044, 833, 769; HRMS m/z $[M + H]^+$ Calculated for $C_{22}H_{15}NOF$: 328.1138; found 328.1144.

*7-Phenyl-6H-chromeno[4,3-b]quinoline-9-carboxylate (**3am**).* Prepared according to the general procedure from 2-(3-phenylprop-2-ynyloxy)benzonitrile and 4-ethoxycarbonyl(mesityl)iodonium trifluoromethanesulfonate (327 mg, 0.600 mmol) for 1 h. Purification of the crude product by column chromatography on silica gel afforded the product as a drab solid (133 mg, 0.341 mmol, 70%). Mp 146−147 °C; R_f = 0.30 (hexane−ethyl acetate, 10:1). ^{1}H NMR (250 MHz, $CDCl_3$) δ 8.40 (d, J = 7.8 Hz, 1H), 8.22−7.95 (m, 3H), 7.44 (s, 3H), 7.31−7.10 (m, 3H), 7.04 (t, J = 7.1 Hz, 1H), 6.84 (d, J = 7.8 Hz, 1H),

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4.98 (s, 2H), 4.22 (q, J = 7.1 Hz, 2H), 1.24 (t, J = 7.1 Hz, 3H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 166.6, 157.9, 151.0, 150.2, 145.5, 134.4, 132.9, 130.1, 129.6, 129.33, 129.27, 128.2, 126.7, 126.4, 123.9, 123.5, 123.0, 117.7, 67.0, 61.6, 14.7; IR ν_{max}/cm^{-1} (solid): 2928, 2370, 1715, 1586, 1467, 1293, 1251, 1226, 1103, 1048, 848, 737; HRMS m/z [M + H]$^+$ Calculated for $C_{25}H_{20}NO_3$: 382.1443; found 382.1444.

*7-(Thiophen-2-yl)-6H-chromeno[4,3-b]quinoline (**3ba**).* Prepared according to the general procedure from 2-((3-(thiophen-2-yl)prop-2-yn-1-yl)oxy)benzonitrile (120 mg, 0.500 mmol) and phenyl(mesityl)-iodonium trifluoromethanesulfonate (283 mg, 0.600 mmol) for 40 min. Purification of the crude product by column chromatography on silica gel afforded the product as a yellow solid (75.0 mg, 0.238 mmol, 48%). Mp 147−148 °C; R_f = 0.35 (hexane−ethyl acetate, 15:1). ^{1}H NMR (250 MHz, $CDCl_3$) δ 8.40 (dd, J = 7.8, 1.7 Hz, 1H), 8.05 (d, J = 8.4 Hz, 1H), 7.66−7.49 (m, 2H), 7.44 (d, J = 5.1 Hz, 1H), 7.37−7.17 (m, 2H), 7.18−7.09 (m, 1H), 7.05 (t, J = 7.5 Hz, 1H), 6.97 (d, J = 2.8 Hz, 1H), 6.86 (d, J = 8.1 Hz, 1H), 5.09 (s, 2H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 157.6, 149.0, 148.3, 137.0, 134.6, 132.3, 130.0, 129.9, 129.3, 128.2, 128.0, 127.9, 126.9, 126.3, 126.2, 125.2, 123.7, 122.9, 117.6, 67.2; IR ν_{max}/cm^{-1} (solid): 2927, 2367, 2341, 1586, 1558, 1496, 1465, 1215, 1042, 768, 704; HRMS m/z [M + H]$^+$ Calculated for $C_{20}H_{14}NOS$: 316.0796; found 316.0800.

*7-(p-Tolyl)-6H-chromeno[4,3-b]quinoline (**3ca**).* Prepared according to the general procedure from 2-((3-(*p*-tolyl)prop-2-yn-1-yl)oxy)-benzonitrile (124 mg, 0.500 mmol) and phenyl(mesityl)iodonium trifluoromethanesulfonate (283 mg, 0.600 mmol) for 35 min. Purification of the crude product by column chromatography on silica gel afforded the product as a yellow solid (115 mg, 0.356 mmol, 71%). Mp 137−138 °C; R_f = 0.30 (hexane−ethyl acetate, 15:1). ^{1}H NMR (250 MHz, $CDCl_3$) δ 8.60 (dd, J_1 = 7.68 Hz, J_2 = 1.25 Hz 1H), 8.22 (d, J = 8.4 Hz, 1H), 7.68 (t, J = 7.1 Hz, 1H), 7.55 (d, J = 8.1 Hz, 1H), 7.46−7.31 (m, 4H), 7.27−7.13 (m, 3H), 7.01 (d, J = 8.0 Hz, 1H), 5.14 (s, 2H), 2.50 (s, 3H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 157.7, 149.1, 148.4, 144.3, 138.8, 132.21, 132.20, 130.0, 129.9, 129.7, 129.6, 127.7, 126.6, 126.5, 126.2, 124.0, 123.3, 122.9, 117.6, 67.2, 21.8; IR ν_{max}/cm^{-1} (solid): 2927, 2363, 2342, 1587, 1495, 1465, 1223, 1043, 769, 745; HRMS m/z [M + H]$^+$ Calculated for $C_{23}H_{18}NO$: 324.1388; found 324.1395.

*7-(4-Methoxyphenyl)-6H-chromeno[4,3-b]quinoline (**3da**).* Prepared according to the general procedure from 2-((3-(4-methoxyphenyl)prop-2-yn-1-yl)oxy)benzonitrile (132 mg, 0.500 mmol) and phenyl(mesityl)iodonium trifluoromethanesulfonate (283 mg, 0.600 mmol) for 40 min. Purification of the crude product by column chromatography on silica gel afforded the product as a yellow solid (59 mg, 0.172 mmol, 34%). Mp 164−165 °C; R_f = 0.29 (hexane−ethyl acetate, 10:1). ^{1}H NMR (250 MHz, $CDCl_3$) δ 8.42 (d, J = 7.7 Hz, 1H), 8.06 (d, J = 8.4 Hz, 1H), 7.54 (t, J = 7.6 Hz, 1H), 7.42 (d, J = 8.3 Hz, 1H), 7.27 (t, J = 8.9 Hz, 2H), 7.16−6.98 (m, 3H), 6.95 (d, J = 7.6 Hz, 2H), 6.86 (d, J = 7.8 Hz, 1H), 5.01 (s, 2H), 3.78 (s, 3H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 160.1, 157.7, 149.1, 148.4, 144.0, 132.2, 130.9, 130.0, 129.7, 127.8, 127.2, 126.6, 126.5, 126.2, 124.0, 123.5, 122.9, 117.5, 114.6, 67.2, 55.8; IR ν_{max}/cm^{-1} (solid): 2908, 2368, 2341, 1519, 1499, 1248, 1042, 737; HRMS m/z [M + H]$^+$ Calculated for $C_{23}H_{18}NO_2$: 340.1338; found 340.1336.

*7-(2-Chlorophenyl)-6H-chromeno[4,3-b]quinoline (**3ea**).* Prepared according to the general procedure from 2-((3-(2-chlorophenyl)prop-2-yn-1-yl)oxy)benzonitrile (134 mg, 0.500 mmol) and phenyl(mesityl)iodonium trifluoromethanesulfonate (283 mg, 0.600 mmol) for 1 h. Purification of the crude product by column chromatography on silica gel afforded the product as a yellow solid (125 mg, 0.364 mmol, 73%). Mp 112−113 °C; R_f = 0.29 (hexane−ethyl acetate, 15:1). ^{1}H NMR (250 MHz, $CDCl_3$) δ 8.61 (d, J = 7.7 Hz, 1H), 8.24 (d, J = 8.4 Hz, 1H), 7.71 (t, J = 7.6 Hz, 1H), 7.61 (d, J = 7.4 Hz, 1H), 7.54−7.26 (m, 6H), 7.21 (t, J = 7.6 Hz, 1H), 7.02 (d, J = 8.1 Hz, 1H), 5.09 (q, J = 14.1 Hz, 2H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 157.7, 149.1, 148.5, 141.0, 134.2, 134.1, 132.3, 131.3, 130.6, 130.4, 130.2, 129.9, 127.6, 127.0, 126.9, 126.2, 126.0, 123.8, 122.9, 117.7, 67.0; IR ν_{max}/cm^{-1} (solid): 2927, 2366, 2339, 1585, 1473, 1221, 1042, 769, 741; HRMS m/z [M + H]$^+$ Calculated for $C_{22}H_{15}NOCl$: 344.0842; found 344.0845.

*7-(4-Chlorophenyl)-6H-chromeno[4,3-b]quinoline (**3fa**).* Prepared according to the general procedure from 2-((3-(4-chlorophenyl)prop-2-yn-1-yl)oxy)benzonitrile (130 mg, 0.489 mmol) and phenyl-(mesityl)iodonium trifluoromethanesulfonate (277 mg, 0.587 mmol) for 1 h. Purification of the crude product by column chromatography on silica gel afforded the product as a drab solid (121 mg, 0.353 mmol, 75%). Mp 202−203 °C; R_f = 0.38 (hexane−ethyl acetate, 15:1). ^{1}H NMR (250 MHz, $CDCl_3$) δ 8.54 (d, J = 6.9 Hz, 1H), 8.19 (d, J = 7.9 Hz, 1H), 7.81−7.63 (m, 1H), 7.55 (d, J = 7.1 Hz, 2H), 7.49−7.32 (m, 3H), 7.31−7.12 (m, 3H), 6.99 (d, J = 7.5 Hz, 1H), 5.09 (s, 2H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 157.6, 149.1, 148.3, 142.8, 135.2, 133.6, 132.4, 131.1, 130.1, 129.9, 129.5, 127.2, 126.8, 126.2, 123.7, 123.2, 123.0, 117.6, 67.0; IR ν_{max}/cm^{-1} (solid):2973, 2370, 2341, 1588, 1488, 1221, 1090, 1044, 837, 770; HRMS m/z [M + H]$^+$ Calculated for $C_{22}H_{15}NOCl$: 344.0842; found 344.0844.

*7-(3-Bromophenyl)-6H-chromeno[4,3-b]quinoline (**3ga**).* Prepared according to the general procedure from 2-((3-(3-bromophenyl)prop-2-yn-1-yl)oxy)benzonitrile (156 mg, 0.500 mmol) and phenyl(mesityl)iodonium trifluoromethanesulfonate (283 mg, 0.600 mmol) for 30 min. Purification of the crude product by column chromatography on silica gel afforded the product as a drab solid (129 mg, 0.333 mmol, 67%). Mp 162−163 °C; R_f = 0.33 (hexane−ethyl acetate, 15:1). ^{1}H NMR (250 MHz, $CDCl_3$) δ 8.54 (d, J = 7.5 Hz, 1H), 8.19 (d, J = 8.3 Hz, 1H), 7.68 (d, J = 7.3 Hz, 2H), 7.58−7.33 (m, 5H), 7.31−7.13 (m, 2H), 6.99 (d, J = 8.0 Hz, 1H), 5.09 (s, 2H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 157.6, 149.1, 148.3, 142.3, 137.4, 132.5, 132.4, 132.1, 130.8, 130.1, 129.9, 128.3, 127.0, 126.9, 126.18, 126.15, 123.7, 123.4, 123.2, 123.0, 117.6, 66.9; IR ν_{max}/cm^{-1} (solid): 2928, 2368, 2341, 1584, 1560, 1472, 1223, 1044, 770, 701; HRMS m/z [M + H]$^+$ Calculated for $C_{22}H_{15}NOBr$: 388.0337; found 388.0342.

*7-(4-Bromophenyl)-6H-chromeno[4,3-b]quinoline (**3ha**).* Prepared according to the general procedure from 2-((3-(4-bromophenyl)prop-2-yn-1-yl)oxy)benzonitrile (156 mg, 0.500 mmol) and phenyl(mesityl)iodonium trifluoromethanesulfonate (283 mg, 0.600 mmol) for 1 h. Purification of the crude product by column chromatography on silica gel afforded the product as a drab solid (140 mg, 0.362 mmol, 72%). Mp 183−184 °C; R_f = 0.33 (hexane−ethyl acetate, 15:1). ^{1}H NMR (250 MHz, $CDCl_3$) δ 8.54 (d, J = 7.4 Hz, 1H), 8.19 (d, J = 8.3 Hz, 1H), 7.70 (d, J = 7.7 Hz, 3H), 7.52−7.30 (m, 3H), 7.20 (d, J = 7.5 Hz, 3H), 6.99 (d, J = 8.0 Hz, 1H), 5.09 (s, 2H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 157.6, 149.1, 148.3, 142.8, 134.1, 132.5, 132.4, 131.3, 130.1, 129.9, 127.1, 126.8, 126.18, 126.16, 123.7, 123.3, 123.2, 123.0, 117.6, 67.0; IR ν_{max}/cm^{-1} (solid): 2928, 2366, 2341, 1487, 1222, 1043, 1014, 835, 771, 701; HRMS m/z [M + H]$^+$ Calculated for $C_{22}H_{15}NOBr$: 388.0337; found 388.0338.

*7-(4-Fluorophenyl)-6H-chromeno[4,3-b]quinoline (**3ia**).* Prepared according to the general procedure from 2-((3-(4-fluorophenyl)prop-2-yn-1-yl)oxy)benzonitrile (81.0 mg, 0.323 mmol) and phenyl-(mesityl)iodonium trifluoromethanesulfonate (183 mg, 0.387 mmol) for 1 h. Purification of the crude product by column chromatography on silica gel afforded the product as a yellow solid (63.0 mg, 0.193 mmol, 60%). Mp 181−182 °C; R_f = 0.28 (hexane−ethyl acetate, 15:1). ^{1}H NMR (250 MHz, $CDCl_3$) δ 8.55 (d, J = 6.8 Hz, 1H), 8.19 (d, J = 7.8 Hz, 1H), 7.79−7.60 (m, 1H), 7.53−7.15 (m, 8H), 6.99 (d, J = 7.6 Hz, 1H), 5.09 (s, 2H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 157.6, 149.1, 148.3, 143.0, 132.4, 131.5, 131.4, 131.1, 131.0, 130.0, 129.8, 127.4, 126.7, 126.2, 123.8, 123.4, 123.0, 117.6, 116.5, 116.2, 67.0; IR ν_{max}/cm^{-1} (solid): 2932, 2365, 2342, 1496, 1221, 1044, 847, 769, 735; HRMS m/z [M + H]$^+$ Calculated for $C_{22}H_{15}NOF$: 328.1138; found 328.1139.

*1-(4-(6H-Chromeno[4,3-b]quinolin-7-yl)phenyl)ethan-1-one (**3ja**).* Prepared according to the general procedure from 2-((3-(4-acetylphenyl)prop-2-yn-1-yl)oxy)benzonitrile (176 mg, 0.500 mmol) and phenyl(mesityl)iodonium trifluoromethanesulfonate (283 mg, 0.600 mmol) for 75 min. Purification of the crude product by column chromatography on silica gel afforded the product as a yellow solid (126 mg, 0.359 mmol, 72%). Mp 185−186 °C; R_f = 0.31 (hexane−ethyl acetate, 5:1). ^{1}H NMR (250 MHz, $CDCl_3$) δ 8.53 (d, J = 7.7 Hz, 1H), 8.27−8.04 (m, 3H), 7.67 (dt, J = 8.5, 4.2 Hz, 1H), 7.51−7.30 (m,

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5H), 7.17 (t, J = 7.5 Hz, 1H), 6.96 (d, J = 8.1 Hz, 1H), 5.05 (s, 2H), 2.70 (s, 3H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 197.9, 157.6, 149.0, 148.3, 142.8, 140.2, 137.5, 132.4, 130.1, 130.0, 129.1, 126.9, 126.8, 126.2, 126.1, 123.7, 122.99, 122.96, 117.6, 66.9, 27.2; IR ν_{max}/cm^{-1} (solid): 2928, 2364, 2341, 1685, 1586, 1468, 1359, 1222, 1045, 769; HRMS m/z [M + H]$^+$ Calculated for $C_{24}H_{18}NO_2$: 352.1338; found 352.1342.

*4-(6H-Chromeno[4,3-b]quinolin-7-yl)phenyl Acetate (**3ka**).* Prepared according to the general procedure from 4-(3-(2-cyanophenoxy)prop-1-yn-1-yl)phenyl acetate (146 mg, 0.500 mmol) and phenyl(mesityl)iodonium trifluoromethanesulfonate (283 mg, 0.600 mmol) for 2 h. Purification of the crude product by column chromatography on silica gel afforded the product as a yellow solid (88.0 mg, 0.240 mmol, 48%). Mp 124−125 °C; R_f = 0.32 (hexane−ethyl acetate, 5:1). ^{1}H NMR (250 MHz, $CDCl_3$) δ 8.42 (dd, J = 7.7, 1.4 Hz, 1H), 8.06 (d, J = 8.4 Hz, 1H), 7.61−7.48 (m, 1H), 7.37 (d, J = 8.2 Hz, 1H), 7.32−7.15 (m, 6H), 7.05 (t, J = 7.5 Hz, 1H), 6.86 (d, J = 8.1 Hz, 1H), 4.98 (s, 2H), 2.24 (s, 3H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 169.7, 157.7, 151.2, 149.1, 148.4, 143.1, 132.7, 132.3, 130.8, 130.0, 129.8, 127.4, 126.7, 126.4, 126.2, 123.9, 123.4, 122.9, 122.5, 117.6, 67.1, 21.6; IR ν_{max}/cm^{-1} (solid): 2365, 1771, 1751, 1495, 1200, 1045, 771, 730; HRMS m/z [M + H]$^+$ Calculated for $C_{24}H_{18}NO_3$: 368.1287; found 368.1271.

*Methyl 4-(6H-Chromeno[4,3-b]quinolin-7-yl)benzoate (**3la**).* Prepared according to the general procedure from methyl 4-(3-(2-cyanophenoxy)prop-1-yn-1-yl)benzoate (146 mg, 0.500 mmol) and phenyl(mesityl)iodonium trifluoromethanesulfonate (283 mg, 0.600 mmol) for 1.5 h. Purification of the crude product by column chromatography on silica gel afforded the product as a yellow solid (146 mg, 0.398 mmol, 80%). Mp 188−189 °C; R_f = 0.44 (hexane−ethyl acetate, 5:1). ^{1}H NMR (250 MHz, $CDCl_3$) δ 8.54 (d, J = 7.6 Hz, 1H), 8.32−8.12 (m, 3H), 7.77−7.61 (m, 1H), 7.47−7.31 (m, 5H), 7.17 (t, J = 7.5 Hz, 1H), 6.97 (d, J = 8.1 Hz, 1H), 5.06 (s, 2H), 3.99 (s, 3H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 167.0, 157.6, 149.0, 148.3, 142.9, 140.1, 132.4, 130.8, 130.4, 130.1, 129.9, 129.8, 126.9, 126.8, 126.2, 126.1, 123.7, 123.0, 117.6, 66.9, 52.8; IR ν_{max}/cm^{-1} (solid): 2926, 2368, 1725, 1588, 1286, 1104, 1043, 769; HRMS m/z [M + H]$^+$ Calculated for $C_{24}H_{18}NO_3$: 368.1287; found 368.1291.

*Ethyl 7-(4-Fluorophenyl)-6H-chromeno[4,3-b]quinoline-9-carboxylate (**3im**).* Prepared according to the general procedure from 2-((3-(4-fluorophenyl)prop-2-yn-1-yl)oxy)benzonitrile (126 mg, 0.500 mmol) and 4-ethoxycarbonyl-phenyl(mesityl)iodonium trifluoromethanesulfonate (327 mg, 0.600 mmol) for 1 h. Purification of the crude product by column chromatography on silica gel afforded the product as a drab solid (101 mg, 0.253 mmol, 51%). Mp 202−203 °C; R_f = 0.20 (hexane−ethyl acetate, 15:1). ^{1}H NMR (250 MHz, $CDCl_3$) δ 8.42 (d, J = 7.1 Hz, 1H), 8.24−7.98 (m, 3H), 7.30 (t, J = 7.9 Hz, 1H), 7.20 (d, J = 7.0 Hz, 4H), 7.08 (t, J = 7.6 Hz, 1H), 6.88 (d, J = 8.1 Hz, 1H), 5.00 (s, 2H), 4.27 (q, J = 7.2 Hz, 2H), 1.28 (t, J = 7.2 Hz, 3H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 166.5, 157.9, 151.0, 150.3, 144.3, 132.9, 131.6, 131.4, 130.2, 129.3, 129.2, 128.4, 126.7, 126.4, 124.1, 123.4, 123.0, 117.6, 116.7, 116.4, 66.9, 61.7, 14.7; IR ν_{max}/cm^{-1} (solid): 2926, 2362, 2341; 1716, 1293, 1275, 1252, 1224, 1102, 1048, 851, 734; HRMS m/z [M + H]$^+$ Calculated for $C_{25}H_{19}NO_3F$: 400.1349; found 400.1350.

*7-(4-(Methoxycarbonyl)phenyl)-6H-chromeno[4,3-b]quinoline-9-carboxylate (**3lm**).* Prepared according to the general procedure from methyl 4-(3-(2-cyanophenoxy)prop-1-yn-1-yl)benzoate (146 mg, 0.500 mmol) and 4-ethoxycarbonyl-phenyl(mesityl)iodonium trifluoromethanesulfonate (327 mg, 0.600 mmol) for 2.5 h. Purification of the crude product by column chromatography on silica gel afforded the product as a yellow solid (148 mg, 0.337 mmol, 67%). Mp 204−205 °C; R_f = 0.25 (hexane−ethyl acetate, 7:1). ^{1}H NMR (250 MHz, $CDCl_3$) δ 8.51 (d, J = 7.5 Hz, 1H), 8.34−8.09 (m, 5H), 7.48−7.33 (m, 3H), 7.17 (t, J = 7.1 Hz, 1H), 6.97 (d, J = 8.0 Hz, 1H), 5.07 (s, 2H), 4.34 (q, J = 6.6 Hz, 2H), 4.01 (s, 3H), 1.35 (t, J = 6.8 Hz, 3H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 166.9, 166.4, 157.9, 151.0, 150.2, 144.2, 139.3, 133.0, 131.1, 130.6, 130.2, 129.8, 129.5, 129.0, 128.5, 126.4, 126.1, 123.7, 123.3, 123.1, 117.7, 66.8, 61.7, 52.8, 14.7; IR ν_{max}/cm^{-1} (solid): 2930, 2365, 2342, 1720, 1290, 1252, 1104, 1047, 734; HRMS m/z [M + H]$^+$ Calculated for $C_{27}H_{22}NO_5$: 440.1498; found 440.1496.

*2-Chloro-7-phenyl-6H-chromeno[4,3-b]quinoline (**3ma**).* Prepared according to the general procedure from 5-chloro-2-(3-phenylprop-2-ynyloxy)benzonitrile (134 mg, 0.500 mmol) and phenyl(mesityl)iodonium trifluoromethanesulfonate (283 mg, 0.600 mmol) for 30 min. Purification of the crude product by column chromatography on silica gel afforded the product as a drab solid (133 mg, 0.388 mmol, 78%). Mp 164−165 °C; R_f = 0.43 (hexane−ethyl acetate, 10:1). ^{1}H NMR (250 MHz, $CDCl_3$) δ 8.52 (s, 1H), 8.18 (d, J = 8.3 Hz, 1H), 7.69 (t, J = 7.2 Hz, 1H), 7.63−7.45 (m, 4H), 7.45−7.36 (m, 1H), 7.29 (d, J = 5.8 Hz, 3H), 6.91 (d, J = 8.6 Hz, 1H), 5.10 (s, 2H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 156.1, 148.3, 147.8, 144.4, 135.1, 131.9, 130.0, 129.9, 129.6, 129.2, 129.1, 128.1, 127.6, 127.0, 126.5, 125.8, 125.1, 122.7, 119.0, 67.2; IR ν_{max}/cm^{-1} (solid): 2956, 2365, 2341, 1584, 1492, 1437, 1250, 1002, 824, 768; HRMS m/z [M + H]$^+$ Calculated for $C_{22}H_{15}NOCl$: 344.0842; found 344.0849.

*2-Bromo-7-phenyl-6H-chromeno[4,3-b]quinoline (**3na**).* Prepared according to the general procedure from 5-bromo-2-(3-phenylprop-2-ynyloxy)benzonitrile (156 mg, 0.500 mmol) and phenyl(mesityl)-iodonium trifluoromethanesulfonate (283 mg, 0.600 mmol) for 1 h. Purification of the crude product by column chromatography on silica gel afforded the product as a drab solid (154 mg, 0.398 mmol, 80%). Mp 179−180 °C; R_f = 0.34 (hexane−ethyl acetate, 15:1). ^{1}H NMR (250 MHz, $CDCl_3$) δ 8.55 (d, J = 2.5 Hz, 1H), 8.07 (d, J = 8.4 Hz, 1H), 7.64−7.53 (m, 1H), 7.51−7.36 (m, 4H), 7.36−7.25 (m, 2H), 7.23−7.14 (m, 2H), 6.75 (d, J = 8.7 Hz, 1H), 4.99 (s, 2H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 156.6, 148.3, 147.7, 144.4, 135.0, 134.8, 130.02, 129.96, 129.6, 129.2, 129.1, 128.7, 127.6, 127.0, 126.5, 125.6, 122.7, 119.5, 115.5, 67.2; IR ν_{max}/cm^{-1} (solid): 2957, 2857, 2364, 2342, 1581, 1491, 1480, 1435, 1248, 1002, 824, 767, 702; HRMS m/z [M + H]$^+$ Calculated for $C_{22}H_{15}NOBr$: 388.0337; found 388.0345.

*3-Bromo-7-phenyl-6H-chromeno[4,3-b]quinoline (**3oa**).* Prepared according to the general procedure from 4-bromo-2-(3-phenylprop-2-ynyloxy)benzonitrile (78 mg, 0.250 mmol) and phenyl(mesityl)-iodonium trifluoromethanesulfonate (142 mg, 0.300 mmol) for 1 h. Purification of the crude product by column chromatography on silica gel afforded the product as a drab solid (65.0 mg, 0.168 mmol, 67%). Mp 184−185 °C; R_f = 0.33 (hexane−ethyl acetate, 15:1). ^{1}H NMR (250 MHz, $CDCl_3$) δ 8.26 (d, J = 8.4 Hz, 1H), 8.02 (d, J = 8.4 Hz, 1H), 7.55 (t, J = 7.6 Hz, 1H), 7.48−7.31 (m, 4H), 7.30−7.21 (m, 1H), 7.16 (d, J = 6.8 Hz, 3H), 7.03 (s, 1H), 4.97 (s, 2H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 158.1, 148.4, 148.2, 144.3, 135.1, 130.0, 129.9, 129.6, 129.2, 129.0, 127.5, 127.4, 126.8, 126.5, 126.1, 125.6, 122.9, 122.6, 120.8, 67.4; IR ν_{max}/cm^{-1} (solid): 2963, 2935, 2909, 2364, 2342, 2328, 1582, 1488, 1423, 1217, 1041, 873, 769, 704; HRMS m/z [M + H]$^+$ Calculated for $C_{22}H_{15}NOBr$: 388.0337; found 388.0351.

*2,7-Diphenyl-6H-chromeno[4,3-b]quinoline (**3pa**).* Prepared according to the general procedure from 4-((3-phenylprop-2-yn-1-yl)oxy)-[1,1′-biphenyl]-3-carbonitrile (77.3 mg, 0.250 mmol) and phenyl(mesityl)iodonium trifluoromethanesulfonate (142 mg, 0.300 mmol) for 30 min. Purification of the crude product by column chromatography on silica gel afforded the product as a green solid (67.5 mg, 0.175 mmol, 70%). Mp 194−195 °C; R_f = 0.30 (hexane−ethyl acetate, 15:1). ^{1}H NMR (250 MHz, $CDCl_3$) δ 8.72 (s, 1H), 8.12 (d, J = 8.4 Hz, 1H), 7.69−7.50 (m, 4H), 7.50−7.32 (m, 6H), 7.32−7.14 (m, 4H), 6.97 (d, J = 8.4 Hz, 1H), 5.06 (s, 2H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 157.2, 149.0, 148.4, 144.2, 141.1, 136.0, 135.3, 131.0, 130.0, 129.8, 129.6, 129.2, 129.1, 129.0, 127.5, 127.4, 126.6, 126.5, 124.6, 124.0, 123.1, 118.0, 67.3; IR ν_{max}/cm^{-1} (solid): 2962, 2363, 2342, 1560, 1506, 1488, 1460, 1251, 1227, 1047, 1003, 767, 737, 700; HRMS m/z [M + H]$^+$ Calculated for $C_{28}H_{20}NO$: 386.1545; found 386.1552.

*N-(2-(6H-Chromeno[4,3-b]quinolin-7-yl)phenyl)acetamide (**3qa**).* Prepared according to the general procedure from 4-(3-(2-cyanophenoxy)prop-1-yn-1-yl)phenyl acetate (145 mg, 0.500 mmol) and phenyl(mesityl)iodonium trifluoromethanesulfonate (283 mg, 0.600 mmol) for 1.5 h. Purification of the crude product by column chromatography on silica gel afforded the product as a yellow solid (84.0 mg, 0.230 mmol, 46%). Mp 83−84 °C; R_f = 0.32 (hexane−ethyl

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acetate, 2:1). ^{1}H NMR (250 MHz, $CDCl_3$) δ 8.51 (d, J = 7.8 Hz, 1H), 8.20 (dd, J = 15.8, 8.3 Hz, 2H), 7.70 (t, J = 7.3 Hz, 1H), 7.57−7.22 (m, 5H), 7.14 (d, J = 7.3 Hz, 2H), 7.02−6.82 (m, 2H), 5.15−4.82 (m, 2H), 1.69 (s, 3H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 169.0, 157.8, 149.5, 148.6, 139.6, 135.8, 132.6, 130.3, 127.3, 126.9, 126.1, 125.9, 125.33, 125.26, 124.5, 123.6, 123.3, 123.0, 117.7, 66.9, 24.6; IR ν_{max}/cm^{-1} (solid): 1700, 1582, 1519, 1449, 1300, 1230, 1044, 1004, 768, 731; HRMS m/z [M + H]$^+$ Calculated for $C_{24}H_{19}N_2O_2$: 367.1447; found 367.1431.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b02490.

Details of optimization studies and NMR spectra for all compounds, as well as single crystal X-ray structural description of **3aa** (PDF)

X-ray crystallographic data for **3aa** (CIF)

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Notes

The authors declare no competing financial interest.

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(8) For details, see the Supporting Information.

(9) Crystallographic data for the crystal structure of **3aa** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 1430075.

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