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

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ABSTRACT: A novel, highly modular synthetic method with high functional group tolerance was developed for the construction of chromenoquinoline derivatives from arylpropynoxy-bzonitriles and diaryliodonium triflates via 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 last few years, triple bond activation via the intermediacy of Cu(III) species2,3 using diaryliodonium salts4 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 of nucleophilic functional groups. For example, Gaunt and coworkers\textsuperscript{2f} developed several copper catalyzed transformations for the synthesis of dihydronaphthalene, chromene and dihydroquinoline derivatives from functionalized 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\textsuperscript{3a,3c}, quinazolines\textsuperscript{3b} and tetrahydroacridines\textsuperscript{3a} through the formation of iminium cations were 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\textsuperscript{5a}, iminobenzoxazine\textsuperscript{5b} and dihydrooxazole\textsuperscript{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 both with nitrile and alkyne functional groups.

**Scheme 1. Utilization of arylation-ring closure strategy**

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 through two sequential cyclization paths (Scheme 2).

**Scheme 2.** Highly modular synthesis of chromenoquinolines via arylation-ring closure

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, 6H-chromeno[4,3-b]quinolines act as estrogen receptor β–selective ligands, and they can be used also for bioimaging due to their fluorescent properties. Moreover, the spiro analogues of benzothiazolylchromeno derivatives have shown cytotoxic activity against MCF-7 (breast cancer) and HeLa (cervical cancer) cell lines.

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 arylation agent, while the oxidative coupling was performed at 75 °C for 1 h. Examination of the solvent effect on the conversion showed that the reaction is slow in DMF, CH₂Cl₂, THF, PhMe and 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)$_4$Cu(OTf) were used (entries 11-14). No reaction was observed in the absence of catalyst (entry 15).

Table 1. Optimization studies$^a$

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$^a$ 2-((3-phenylprop-2-yn-1-yl)oxy)benzonitrile (0.125 mmol), mesitylphenyliodonium 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 3a was
obtained in 78% yield (Scheme 3). When a methyl substituent was present in the \textit{ortho} position of the phenyl group of the iodonium salt, the reaction was slower (5 h reaction time was needed) and the desired product (3b) was isolated in 32% yield. In contrast, when the methyl group was \textit{meta} or \textit{para} to the iodonium salt, the reaction was fast, and the desired compounds (3c and 3d) were obtained in 65% and 50% yields, respectively. When the aryl part of the iodonium salt contained a halogen atom (F, Cl or Br) \textit{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 \textit{meta} or \textit{para} positions, 1a was transformed to the appropriate chromenoquinoline derivatives (3e-3i) in 47-65% yield. Diaryliodonium salt bearing a \textit{para} COOEt group provided the desired product (3j) in 70% yield. In the case of meta substituted iodonium salts, chromenoquinolines 3c, 3f and 3h were obtained as 1:1 mixtures of possible regioisomers.

\textbf{Scheme 3. Synthesis of chromeno[4,3-b]quinolines 1.}^a

\begin{center}
\includegraphics[width=0.9\textwidth]{scheme3.png}
\end{center}
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

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 phenylmesityliodonium triflate (2a) to prepare the desired chromenoquinoline derivatives (3k-3u). Two more examples (3v and 3w) are given where the applicability of the ring closure reaction is demonstrated with 4-ethoxycarbonyl-phenylmesityliodonium triflate (2m). When the arylpropynyloxybenzonitrile contained a thiophenyl group (1b), the appropriate product (3k) 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 compounds (3l and 3m) 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 (3n-3r) 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 (3s and 3t) in 72% and 48% yields. In the presence of an ester group on the aromatic ring of the arylpropynyloxybenzonitrile derivative (1l), we could isolate product 3u 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 (3v and 3w) 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 (3x) and bromo (3y and 3z) 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 (3aa) 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 cyclization in which the amide moiety is involved, providing benzoxazines through acetylene activation as we demonstrated earlier. 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 (3bb) 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.

**Scheme 5. Ring closure of trifunctional substrate**

![Scheme 5. Ring closure of trifunctional substrate](image)

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

![Figure 1. Molecular structure ORTEP representation of compound 3a.](image)

**Figure 1.** Molecular structure ORTEP representation of compound 3a.\(^8^9\) Displacement ellipsoids are drawn at the 50% probability level.
Regarding a possible mechanism for the transformation, on the basis of the literature reports\textsuperscript{2,3,5} we suppose that diaryliodonium salts generate highly electrophilic arylcopper(III) species (2) in the presence of the copper catalyst (Scheme 6). This copper(III)-intermediate interacts with the nitrile function (3) and forms a cationic species (4) and Cu(I). The arylnitrilium intermediate 4 can be readily attacked in an intermolecular fashion by the acetylene moiety resulting the formation of the chromene ring with exo vinyl cation (5). The resulting intermediate 5 can undergo an intramolecular cyclization via electrophilic aromatic substitution, providing the chromenoquinoline product (6).

**Scheme 6. Plausible mechanism for the arylation-cyclization reaction.**

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 arylpropynloxybenzonitriles 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

\(^1\)H-NMR and \(^{13}\)C-NMR spectra were recorded on a Bruker Avance-250 spectrometer operating at 250 MHz 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 Bruker Alpha spectrometer on a single-reflection diamond ATR spectrometer as solids or thin films. In the IR spectra only the strongest/structurally most important peaks (\(n, \text{cm}^{-1}\)) are listed. HRMS were measured on an Agilent Technologies 6210 Time of Flight mass spectrometer. Melting points were recorded on Buchi 501 apparatus and are reported uncorrected. All solvents used were distilled using standard methods. Ethyl acetate was distilled from calcium hydride. All mixed solvent systems are reported as v/v solutions. All reactions were monitored by TLC using Merck DC pre coated TLC plates with 0.25 mm Kieselgel 60 F\(_{254}\). Visualization was performed with a 254 nm UV lamp. \(m\)CPBA was dried under high vacuum at room temperature and was stored under argon. All other chemicals were used as received without further purification.

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 bottom flask fitted with a rubber septum then the system was charged with argon. Dimethyl formamide (60 ml) was added under 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 x 50 ml), the combined organics were washed with saturated LiCl solution (5 x 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’)

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%). M. p. 77-78 °C; $R_f = 0.35$ (hexane-ethyl acetate, 5:1). $^1$H NMR (250 MHz, CDCl$_3$): $\delta = 7.49$ (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$_3$): $\delta = 159.43$, 134.61, 134.26, 122.05, 116.55, 113.35, 102.86, 78.01, 77.59, 56.91; IR $\nu_{\text{max}}$/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%). M. p. 125-126 °C; $R_f = 0.60$ (hexane-ethyl acetate, 4:1). $^1$H NMR (250 MHz, CDCl$_3$) $\delta = 7.51$ (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$_3$) $\delta = 158.06$, 134.57, 133.51, 126.99, 115.21, 114.78, 104.25, 77.74, 77.12, 57.28; IR $\nu_{\text{max}}$/cm$^{-1}$ (solid): 2930, 1488, 1285, 1266, 1234, 1135, 1018; HRMS m/z [M-H] Calculated for C$_{10}$H$_5$NOCl: 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 (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%). M. p. 125-126 °C; $R_f = 0.60$ (hexane-ethyl acetate, 4:1). $^1$H NMR (250 MHz, CDCl$_3$) $\delta = 7.51$ (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$_3$) $\delta = 158.06$, 134.57, 133.51, 126.99, 115.21, 114.78, 104.25, 77.74, 77.12, 57.28; IR $\nu_{\text{max}}$/cm$^{-1}$ (solid): 2930, 1488, 1285, 1266, 1234, 1135, 1018; HRMS m/z [M-H] Calculated for C$_{10}$H$_5$NOCl: 190.0060; found 190.0069.
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%). M. p. 128-129 °C; \( R_f = 0.32 \) (hexane-ethyl acetate, 5:1). \(^1\)H NMR (250 MHz, CDCl\(_3\)) \( \delta \) 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\(_3\)) \( \delta \) 158.54, 137.44, 136.37, 115.10, 115.07, 113.72, 104.74, 77.77, 77.06, 57.21; IR \( \nu \)max/cm\(^{-1}\) (solid): 2957, 1486, 1286, 1235, 1132, 1016; HRMS m/z [M-H] Calculated for C\(_{10}\)H\(_5\)NOBr: 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 argon atmosphere then the iodoarene (422 mg, 2.07 mmol, 231 µl) was added dropwise. If the iodoarene was solid, it was added with the copper and palladium sources before the addition of DIPA. The resulted mixture was stirred at 30-45 °C for the appropriate time. The reaction mixture was diluted with dichloromethane (20 ml) and distilled water (20 ml), neutralized with 2 M HCl solution, extracted with dichloromethane (4 x 20 ml). The combined organics were washed with distilled water (1 x 50 ml), with brine (1 x 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 iodoarene (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%). M. p. 64-65 °C; \( R_f = 0.42 \) (hexane-ethyl acetate, 5:1). \(^1\)H NMR (250 MHz, CDCl\(_3\)) \( \delta \) 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\(_3\)) \( \delta \) 159.72, 134.59, 134.28, 132.20, 129.37, 128.75, 122.18, 121.86, 116.75, 113.45, 102.86, 88.74, 82.88, 57.76; IR \( \nu_{\text{max}} / \text{cm}^{-1} \) (solid): 2973, 2232, 1597, 1492, 1454, 1289, 1231, 758, 737, 694.

2-((3-(thiophen-2-yl)prop-2-yn-1-yl)oxy)benzonitrile (1b)

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 brown solid (465 mg, 1.95 mmol, 94%). M. p. 79-80 °C; \( R_f = 0.45 \) (hexane-ethyl acetate, 4:1). \(^1\)H NMR (250 MHz, CDCl\(_3\)) \( \delta \) 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\(_3\)) \( \delta \) 159.63, 134.63, 134.29, 133.56, 128.51, 127.45, 121.95, 116.67, 113.38, 102.87, 86.87, 82.12, 57.78; IR \( \nu_{\text{max}} / \text{cm}^{-1} \) (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)

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 bottom flask fitted with a rubber septum then the system was charged with argon. Dimethyl formamide (35 ml) was added under 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 argon atmosphere to the reaction mixture then 4-iodotoluene (1.27 g; 5.83 mmol) dissolved in diisopropylamine (1.5
ml) was added dropwise under argon atmosphere. The resulted 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). M. p. 37-38 °C; \( R_f = 0.32 \) (hexane-ethyl acetate, 7:1). \(^1\)H NMR (250 MHz, CDCl\(_3\)) \( \delta \) 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\(_3\)) \( \delta \) 159.76, 139.62, 134.63, 134.23, 132.11, 129.52, 121.82, 119.10, 116.81, 113.47, 102.77, 88.93, 82.26, 57.83, 21.93; IR \( \nu_{\text{max}}/\text{cm}^{-1} \) (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%). M. p. 58-59 °C; \( R_f = 0.32 \) (hexane-ethyl acetate, 4:1). \(^1\)H NMR (250 MHz, CDCl\(_3\)) \( \delta \) 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\(_3\)) \( \delta \) 160.49, 159.79, 134.60, 134.21, 133.75, 121.79, 116.79, 114.38, 114.20, 113.50, 102.77, 88.78, 81.62, 57.90, 55.70; IR \( \nu_{\text{max}}/\text{cm}^{-1} \) (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%). M. p. 82-83 °C; \( R_f = 0.30 \) (hexane-ethyl acetate, 4:1). \(^1\)H NMR (250 MHz, CDCl\(_3\)) \( \delta \) 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\(_3\)) \( \delta \) 159.59,
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%). M. p. 128-129 °C; \( R_f = 0.62 \) (hexane-ethyl acetate, 7:3). \(^1\)H NMR (250 MHz, CDCl\(_3\)) \( \delta \) 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\(_3\)) \( \delta \) 159.64, 135.47, 134.59, 134.31, 133.43, 129.10, 121.97, 120.66, 116.65, 113.37, 102.94, 87.58, 83.87, 57.68; IR \( \nu_{\max} \)/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 268.0529.

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%). M. p. 58-59 °C; \( R_f = 0.40 \) (hexane-ethyl acetate, 4:1). \(^1\)H NMR (250 MHz, CDCl\(_3\)) \( \delta \) 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\(_3\)) \( \delta \) 159.59, 134.85, 134.62, 134.33, 132.53, 130.78, 130.21, 124.13, 122.51, 122.02, 116.63, 113.34, 102.94, 87.10, 84.21, 57.58; IR \( \nu_{\max} \)/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 (525 mg, 318 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 (524 mg, 1.93 mmol, 94%). M. p. 142-143 °C; \( R_f = 0.35 \) (hexane-ethyl acetate, 4:1). \(^1\)H NMR (250 MHz, CDCl\(_3\)) \( \delta \) 7.57 – 7.41 (m, 3H), 7.40 (d, \( J = 8.0 \) Hz, 2H), 7.32 (d, \( J = 7.7 \) Hz, 1H), 7.20 – 7.11 (m, 2H), 7.11 (t, \( J = 7.6 \) Hz, 1H), 5.01 (s, 2H); \(^13\)C NMR (62.5 MHz, CDCl\(_3\)) \( \delta \) 159.72, 134.84, 134.62, 134.33, 132.53, 130.78, 130.21, 124.13, 122.51, 122.02, 116.63, 113.34, 102.94, 87.10, 84.21, 57.58; IR \( \nu_{\max} \)/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.
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%). M. p. 108-109 °C; R_{f} = 0.40 (hexane-ethyl acetate, 4:1). \( ^{1} \text{H NMR} \) (250 MHz, CDCl\(_{3} \)) \( \delta \) 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); \( ^{13} \text{C NMR} \) (62.5 MHz, CDCl\(_{3} \)) \( \delta \) 159.63, 134.60, 134.32, 133.62, 132.03, 123.73, 121.98, 121.12, 116.65, 113.37, 102.94, 87.64, 84.06, 57.70; IR \( \nu_{\text{max}}/\text{cm}^{-1} \) (solid): 2233, 1601, 1487, 1458, 1290, 738; HRMS m/z \([\text{M}+\text{H}]^{+}\) 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%). M. p. 64-65 °C; R_{f} = 0.63 (hexane-ethyl acetate, 7:3). \( ^{1} \text{H NMR} \) (250 MHz, CDCl\(_{3} \)) \( \delta \) 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); \( ^{13} \text{C NMR} \) (62.5 MHz, CDCl\(_{3} \)) \( \delta \) 159.68, 134.60, 134.28, 134.14, 121.92, 118.30, 118.25, 116.70, 116.25, 115.90, 113.38, 102.88, 87.66, 82.66, 57.70; IR \( \nu_{\text{max}}/\text{cm}^{-1} \) (solid): 2227, 1700, 1559, 1541, 1508, 1491, 1458, 1231, 1017, 838; HRMS m/z \([\text{M}+\text{H}]^{+}\) 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%). M. p. 88-89 °C; R_{f} = 0.26 (hexane-ethyl acetate, 3:1). \( ^{1} \text{H NMR} \) (250 MHz, CDCl\(_{3} \)) \( \delta \) 7.80 (d, \( J = 7.4 \) Hz, 2H), 7.46 (dd, \( J = 26.1, 7.2 \) Hz, 4H), 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 197.60, 159.57, 137.18, 134.64, 134.33, 132.31, 128.58, 126.91, 122.06, 116.62, 113.36, 102.93, 87.78, 86.06, 57.64, 27.03; IR $\nu_{\text{max}}$/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). M. p. 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 169.50, 159.67, 151.36, 134.64, 134.26, 133.41, 122.18, 121.93, 119.81, 116.71, 113.46, 102.80, 87.91, 83.04, 57.72, 21.50; IR $\nu_{\text{max}}$/cm$^{-1}$ (solid): 2234, 1769, 1599, 1506, 1492, 1229, 1198, 1016, 737; HRMS m/z [M+Na]$^+$ Calculated for C$_{18}$H$_{13}$NO$_3$Na: 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%). M. p. 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 166.67, 159.57, 134.63, 134.32, 132.09, 130.58, 129.84, 126.75, 122.04, 116.61, 113.35, 102.93, 87.82, 85.75, 57.63, 52.67; IR $\nu_{\text{max}}$/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%). M. p. 79-80 °C; Rf = 0.38 (hexane-ethyl acetate, 7:1). ¹H NMR (250 MHz, CDCl₃) 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); ¹³C NMR (62.5 MHz, CDCl₃) δ 158.38, 134.55, 133.50, 132.20, 129.51, 128.79, 126.81, 121.95, 115.38, 114.91, 104.28, 89.20, 82.36, 58.16; IR νmax/cm⁻¹ (solid): 2237, 1485, 1285, 1235, 1138, 1010, 1000, 817, 738, 694; HRMS m/z [M+Na]+ Calculated for C₁₆H₁₀NOClNa: 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%). M. p. 86-87 °C; Rf = 0.33 (hexane-ethyl acetate, 5:1). ¹H NMR (250 MHz, CDCl₃) 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); ¹³C NMR (62.5 MHz, CDCl₃) δ 158.85, 137.44, 136.35, 132.21, 129.53, 128.80, 121.94, 115.25, 113.53, 104.73, 89.24, 82.31, 58.11; IR νmax/cm⁻¹ (solid): 2960, 2234, 1487, 1285, 1235, 1138, 1010, 1000, 813, 692; HRMS m/z [M+Na]+ Calculated for C₁₆H₁₀NOBrNa: 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%). M. p. 114-115 °C; Rf = 0.36 (hexane-ethyl acetate, 5:1). ¹H NMR (250 MHz, CDCl₃) δ 7.41 – 7.28 (m, 4H), 7.27 – 7.15 (m, 1H).
(m, 4H), 7.15 – 7.05 (m, 1H), 4.94 (s, 2H); $^{13}$C NMR (62.5 MHz, CDCl$_3$) δ 159.95, 134.92, 132.29, 129.57, 128.97, 128.82, 125.31, 121.93, 117.38, 116.01, 101.95, 89.49, 82.13, 58.22; IR $\nu_{\text{max}}$/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 argon atmosphere then the reaction mixture was stirred at 50 °C for 1.5 h. The reaction mixture was diluted with distilled water (10 ml) and extracted with ethyl acetate (4 x 10 ml). The combined organics were washed with brine (1 x 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 159.03, 138.94, 135.34, 133.14, 132.57, 132.23, 129.45, 129.41, 128.78, 128.19, 127.09, 122.19, 116.70, 113.93, 103.32, 88.92, 82.92, 57.99; IR $\nu_{\text{max}}$/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%). M. p. 119-120 °C;
\( R_f = 0.35 \) (hexane-ethyl acetate, 3:2); \(^1\)H NMR (250 MHz, CDCl\(_3\)) \( \delta \) 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\(_3\)) \( \delta \) 168.77, 159.39, 139.64, 134.74, 134.49, 132.29, 130.73, 123.79, 122.29, 120.10, 116.53, 113.19, 110.91, 103.03, 89.82, 84.20, 57.70, 25.11; IR \( \nu_{\text{max}}/\text{cm}^{-1} \) (solid); 2233, 1699, 1600, 1581, 1517, 1492, 1446, 1301, 1231, 106761, 740; HRMS m/z [M+Na]⁺ Calculated for C\(_{18}\)H\(_{14}\)N\(_2\)O\(_2\)Na: 313.0953; found 313.0940.

**General procedure 3 for the one-pot synthesis of aryl-mesityliodonium 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 aryl-mesityliodonium triflate as a solid, which was dried at 100 °C under vacuum.

For characterization and spectral data of iodonium salts 2a-2m see Supporting Information.

**General procedure 4 for the synthesis of 7-aryl-6H-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 eq.) 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 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 x 10 ml) the combined organics were washed with brine (1 x 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 (3a)

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%). M. p. 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 157.69, 149.09, 148.42, 144.11, 135.28, 132.25, 130.00, 129.73, 129.65, 129.17, 128.94, 127.46, 126.58, 126.52, 126.21, 123.92, 123.19, 122.90, 117.57, 67.13; IR $\nu_{\text{max}}$/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 (3b)

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%). M. p. 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= 157.63, 147.61, 147.31, 144.23, 142.43, 137.93, 135.76, 132.02, 129.86, 129.67, 129.10, 128.80, 127.38, 126.25, 126.22, 124.48, 124.33, 122.77, 122.68,
117.51, 67.20, 18.59; IR \( \nu_{\text{max}} / \text{cm}^{-1} \) (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 (3c)

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%). M. p. 99-100 °C; \( R_f = 0.35 \) (hexane-ethyl acetate, 25:1). \(^1\)H NMR (250 MHz, CDCl\(_3\)) \( \delta \) 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\(_3\)) \( \delta \) 157.67, 157.56, 149.62, 149.01, 148.61, 147.89, 144.33, 143.96, 139.99, 139.36, 136.12, 135.47, 132.12, 130.29, 129.66, 129.48, 129.32, 129.19, 129.13, 129.06, 128.91, 128.87, 128.83, 128.62, 126.19, 126.12, 126.03, 125.49, 124.37, 124.02, 123.62, 122.83, 122.35, 117.53, 117.41, 67.16, 67.11, 24.54, 22.08; IR \( \nu_{\text{max}} / \text{cm}^{-1} \) (solid): 2928, 2366, 2340, 1701, 1577, 1558, 1539, 1506, 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 (3d)

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 20 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%). M. p. 193-194 °C; \( R_f = 0.35 \) (hexane-ethyl acetate, 15:1). \(^1\)H NMR (250 MHz, CDCl\(_3\)) \( \delta \) 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\(_3\)) \( \delta \) 157.56, 148.19, 146.93, 143.51, 136.57, 135.49,
132.00, 129.65, 129.17, 128.87, 127.40, 126.09, 125.35, 123.97, 123.19, 122.85, 117.51, 67.17, 22.17; IR $\nu_{\text{max}}$/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 (3e)$^{16}$

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%). M. p. 174-175 °C; $R_f = 0.38$ (hexane-ethyl acetate, 20:1). $^1$H NMR (250 MHz, CDCl$_3$) $\delta$ 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$_3$) $\delta$ 157.64, 149.34, 146.79, 143.27, 134.57, 132.47, 132.40, 131.57, 130.58, 129.54, 129.38, 129.25, 128.14, 126.14, 125.31, 124.03, 123.54, 122.94, 117.60, 67.00; IR $\nu_{\text{max}}$/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 (3f)

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%). M. p. 120-121 °C; $R_f = 0.40$ (hexane-ethyl acetate, 20:1). $^1$H NMR (250 MHz, CDCl$_3$) $\delta$ 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$_3$) $\delta$ 157.72, 157.64, 150.01, 149.94, 148.99, 148.81, 144.19, 144.19, 136.84, 134.70, 134.27, 134.20, 132.68, 132.65, 132.15,
9-bromo-7-phenyl-6H-chromeno[4,3-b]quinoline (3g)

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%). M. p. 199-200 °C; R_f = 0.38 (hexane-ethyl acetate, 20:1). 1H NMR (250 MHz, CDCl₃) δ 8.38 (d, J = 7.4 Hz, 1H), 7.91 (d, J = 8.9 Hz, 1H), 7.60 (dd, J₁ = 7.5 Hz, J₂ = 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); 13C NMR (62.5 MHz, CDCl₃) δ 157.67, 149.43, 146.92, 143.27, 134.51, 133.18, 132.55, 131.64, 129.52, 129.39, 129.27, 128.63, 128.59, 126.19, 124.04, 123.46, 122.95, 120.69, 117.61, 66.98; IR ν_max/cm⁻¹ (solid): 2365, 2343, 1580, 1560, 1489, 1223, 832, 737; HRMS m/z [M+H]^+ Calculated for C₂₂H₁₅NOBr: 388.0337; found 388.0339.

8-fluoro-7-phenyl-6H-chromeno[4,3-b]quinoline and 10-fluoro-7-phenyl-6H-chromeno[4,3-b]quinoline (3h)

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%). M. p. 141-142 °C; R_f = 0.36 (hexane-ethyl acetate, 15:1). 1H NMR (250 MHz, CDCl₃) 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, 1H), 7.64 – 6.83 (m, 10H), 5.09 (s, 1H), 5.01 (s, 1H); 13C NMR (62.5 MHz, CDCl₃) δ 165.41, 157.77, 157.74, 150.16, 149.67, 144.26, 141.41,
9-fluoro-7-phenyl-6H-chromeno[4,3-b]quinolone (3i)

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%). M. p. 140-141 °C; \( R_f = 0.35 \) (hexane-ethyl acetate, 15:1). \(^1\)H NMR (250 MHz, CDCl\(_3\)) \( \delta \) 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\(_3\)) \( \delta \) 162.77, 158.84, 157.54, 148.55, 148.51, 145.44, 143.60, 143.51, 134.78, 132.42, 132.27, 129.50, 129.36, 129.20, 128.31, 128.16, 126.02, 123.90, 123.64, 122.93, 120.00, 119.59, 117.59, 110.19, 109.82, 67.05; IR \( \nu_{\text{max}}/\text{cm}^{-1} \) (solid): 2367, 2339, 1558, 1489, 1222, 1044, 833, 769; HRMS m/z [M+H]\(^+\) Calculated for C\(_{23}\)H\(_{15}\)NOF: 328.1138; found 328.1139.

7-phenyl-6H-chromeno[4,3-b]quinoline-9-carboxylate (3j)

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%). M. p. 146-147 °C; \( R_f = 0.30 \) (hexane-ethyl acetate, 10:1). \(^1\)H NMR (250 MHz, CDCl\(_3\)) \( \delta \) 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), 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\(_3\)) \( \delta \)
166.62, 157.91, 150.97, 150.22, 145.45, 134.44, 132.89, 130.08, 129.62, 129.33, 129.27, 128.19, 126.67, 126.42, 123.89, 123.45, 122.98, 117.65, 67.01, 61.63, 14.70; IR ν\text{max}/\text{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 (3k)

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%). M. p. 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 157.63, 148.97, 148.30, 136.95, 134.59, 132.34, 129.99, 129.92, 129.34, 128.22, 127.98, 127.90, 126.92, 126.28, 126.20, 125.17, 123.73, 122.94, 117.59, 67.19; IR ν\text{max}/\text{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 (3l)

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%). M. p. 137-138 °C; R_f = 0.30 (hexane-ethyl acetate, 15:1). \(^1\)H NMR (250 MHz, CDCl_3) δ 8.60 (dd, J1 = 7.68 Hz, J2 = 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,
8.0 Hz, 1H), 5.14 (s, 2H), 2.50 (s, 3H); $^{13}$C NMR (62.5 MHz, CDCl$_3$) $\delta$ 157.71, 149.08, 148.41, 144.31, 138.76, 132.21, 132.20, 129.97, 129.86, 129.68, 129.58, 127.65, 126.61, 126.51, 126.23, 123.96, 123.29, 122.87, 117.57, 67.19, 21.82; IR $\nu_{\text{max}}$/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 (3m)
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%). M. p. 164-165 °C; $R_f = 0.29$ (hexane-ethyl acetate, 10:1). $^1$H NMR (250 MHz, CDCl$_3$) $\delta$ 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$_3$) $\delta$ 160.11, 157.67, 149.09, 148.42, 144.02, 132.19, 130.94, 129.96, 129.65, 127.80, 127.21, 126.57, 126.50, 126.19, 123.97, 123.47, 122.87, 117.53, 114.58, 67.20, 55.78; IR $\nu_{\text{max}}$/cm$^{-1}$ (solid): 2908, 2368, 2341, 1519, 1499, 1248, 1042, 737; HRMS m/z [M+H]$^+$ Calculated for C$_{23}$H$_{18}$NO$: 340.1388; found 340.1336.

7-(2-chlorophenyl)-6H-chromeno[4,3-b]quinoline (3n)
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%). M. p. 112-113 °C; $R_f = 0.29$ (hexane-ethyl acetate, 15:1). $^1$H NMR (250 MHz, CDCl$_3$) $\delta$ 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 157.74, 149.12, 148.53, 141.04, 134.23, 134.06, 132.33, 131.31, 130.64, 130.43, 130.19, 129.90, 127.59, 126.98, 126.88, 126.19, 125.95, 123.80, 122.94, 117.66, 66.95; IR ν\(_{\text{max}}/\text{cm}^{-1}\) (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 (3o)

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%). M. p. 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 157.60, 149.07, 148.32, 142.79, 135.15, 133.64, 132.39, 131.06, 130.06, 129.90, 129.52, 127.18, 126.80, 126.17, 123.72, 123.23, 122.98, 117.58, 66.96. IR ν\(_{\text{max}}/\text{cm}^{-1}\) (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 (3p)

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%). M. p. 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 157.60, 149.07, 148.33, 142.31, 137.38, 132.49, 132.40, 132.14, 130.80, 130.08, 129.93, 128.34, 127.03, 126.87, 126.18, 126.15, 123.71, 123.39, 123.19, 122.98, 117.59, 66.94; IR $\nu_{\text{max}}$/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 (3q)
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%). M. p. 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, $J = 7.9$ 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 157.60, 149.07, 148.32, 142.77, 134.13, 132.47, 132.40, 131.34, 130.06, 129.91, 127.09, 126.81, 126.18, 126.16, 123.71, 123.33, 123.16, 122.99, 117.59, 66.95; IR $\nu_{\text{max}}$/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 (3r)
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%). M. p. 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 157.61,
1-(4-(6H-chromeno[4,3-b]quinolin-7-yl)phenyl)ethan-1-one (3s)
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). Purification of the crude product by column chromatography on silica gel afforded the product as a yellow solid (126 mg, 0.359 mmol, 72%). M. p. 185-186 °C; R_f = 0.31 (hexane-ethyl acetate, 5:1). 1H 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, 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); 13C NMR (62.5 MHz, CDCl_3) δ 197.91, 157.57, 149.03, 148.31, 142.82, 140.24, 137.48, 132.41, 130.07, 129.95, 129.14, 126.87, 126.83, 126.18, 126.07, 123.67, 122.99, 122.96, 117.58, 66.89, 27.18; IR ν_max/cm⁻¹ (solid): 2928, 2364, 2341, 1685, 1586, 1468, 1359, 1222, 1045, 769; HRMS m/z [M+H]^+ Calculated for C_{22}H_{15}NOF: 328.1138; found 328.1139.

4-(6H-chromeno[4,3-b]quinolin-7-yl)phenyl acetate (3t)
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%). M. p. 124-125 °C; R_f = 0.32 (hexane-ethyl acetate, 5:1). 1H 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); 13C NMR (62.5 MHz, CDCl_3) δ 169.65, 157.65, 151.23, 149.09,
methyl 4-(6H-chromeno[4,3-b]quinolin-7-yl)benzoate (3u)

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%). M. p. 188–189 °C; \( R_f = 0.44 \) (hexane-ethyl acetate, 5:1). \(^1\)H NMR (250 MHz, CDCl\(_3\)) \( \delta \) 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\(_3\)) \( \delta \) 166.96, 157.59, 149.03, 148.30, 142.92, 140.09, 132.39, 130.82, 130.42, 130.08, 129.92, 129.84, 126.87, 126.84, 126.18, 126.09, 123.67, 122.97, 117.57, 66.89, 52.79; IR \( \nu_{\text{max}}/\text{cm}^{-1} \) (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 (3v)

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%). M. p. 202-203 °C; \( R_f = 0.20 \) (hexane-ethyl acetate, 15:1). \(^1\)H NMR (250 MHz, CDCl\(_3\)) \( \delta \) 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\(_3\)) \( \delta \) 166.54, 157.86, 151.01,
150.28, 144.26, 132.93, 131.55, 131.42, 130.21, 129.33, 129.22, 128.35, 126.65, 126.41, 124.10, 123.40, 123.01, 117.64, 116.73, 116.38, 66.90, 61.66, 14.68; 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_{3}F: 400.1349; found 400.1350.

7-(4-[(methoxycarbonyl)phenyl]-6H-chromeno[4,3-b]quinoline-9-carboxylate (3w)

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%). M. p. 204-205 °C; R_f = 0.25 (hexane-ethyl acetate, 7:1). \textsuperscript{1}H NMR (250 MHz, CDCl\textsubscript{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); \textsuperscript{13}C NMR (62.5 MHz, CDCl\textsubscript{3}) δ 166.90, 166.44, 157.86, 150.98, 150.19, 144.18, 139.27, 133.02, 131.14, 130.57, 130.24, 129.81, 129.47, 129.03, 128.50, 126.42, 126.12, 123.73, 123.29, 123.05, 117.66, 66.80, 61.67, 52.81, 14.69; 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 (3x)

Prepared according to the general procedure from 5-chloro-2-(3-phenylprop-2-ynyl)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%). M. p. 164-165 °C; R_f = 0.43 (hexane-ethyl acetate, 10:1). \textsuperscript{1}H NMR (250 MHz, CDCl\textsubscript{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); \textsuperscript{13}C NMR
(62.5 MHz, CDCl₃) δ 156.07, 148.29, 147.81, 144.38, 135.05, 131.90, 130.01, 129.94, 129.57, 129.21, 129.05, 128.09, 127.60, 126.94, 126.52, 125.76, 125.10, 122.72, 119.03, 67.20; IR νmax/cm⁻¹ (solid): 2956, 2365, 2341, 1584, 1492, 1437, 1250, 1002, 824, 768, ; HRMS m/z [M+H]+ Calculated for C₂₂H₁₅NOCl: 344.0842; found 344.0849.

2-bromo-7-phenyl-6H-chromeno[4,3-b]quinoline (3y)
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%). M. p. 179-180 °C; Rf = 0.34 (hexane-ethyl acetate, 15:1). ¹H NMR (250 MHz, CDCl₃) 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); ¹³C NMR (62.5 MHz, CDCl₃) δ 156.56, 148.29, 147.67, 144.41, 135.03, 134.77, 130.02, 129.96, 129.56, 129.22, 129.05, 128.73, 127.61, 126.95, 126.52, 125.57, 122.67, 119.45, 115.48, 67.18; IR νmax/cm⁻¹ (solid): 2957, 2857, 2364, 2342, 1581, 1491, 1480, 1435, 1248, 1002, 824, 767, 702; HRMS m/z [M+H]+ Calculated for C₂₂H₁₅NOBr: 388.0337; found 388.0345.

3-bromo-7-phenyl-6H-chromeno[4,3-b]quinoline (3z)
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%). M. p. 184-185 °C; Rf = 0.33 (hexane-ethyl acetate, 15:1). ¹H NMR (250 MHz, CDCl₃) 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); ¹³C NMR (62.5 MHz, CDCl₃) δ 158.07, 148.38, 148.17, 144.28, 135.06, 129.97, 129.89, 129.57,
2,7-diphenyl-6H-chromeno[4,3-b]quinoline (3aa)
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%). M. p. 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 157.19, 148.96, 148.40, 144.22, 141.07, 136.00, 135.28, 130.95, 130.01, 129.77, 129.63, 129.18, 129.12, 128.96, 127.51, 127.37, 126.64, 126.51, 124.61, 123.99, 123.13, 117.96, 67.25; IR $v_{max}$/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$_{22}$H$_{15}$NOBr: 388.0337; found 388.0351.

N-(2-(6H-chromeno[4,3-b]quinolin-7-yl)phenyl)acetamide (3bb)
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%). M. p. 83-84 °C; $R_f = 0.32$ (hexane-ethyl 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 168.97, 157.78, 149.52, 148.57, 139.56, 135.82, 132.56, 130.28, 127.27, 126.85, 126.07, 125.87, 125.33, 125.26, 124.53, 123.57, 123.33, 123.00, 117.72, 66.93, 24.56; IR $\nu_{\text{max}}$/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$_2$O$_2$: 367.1447; found 367.1431.

ASSOCIATED CONTENT

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Author Contributions

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

Supporting Information

Experimental procedures, characterization data, and NMR spectra for all compounds, as well as single crystal X-ray structural description of 3a. This material is available free of charge via the Internet at http://pubs.acs.org.

REFERENCES


(8) For details see Supporting Information.

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


