Regioselective Synthesis of Dihydropyridocoumarin and Phenanthrolinone Derivatives via Iron(III) Chloride Mediated Intramolecular Cyclization

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Abstract: Potentially bioactive angular dihydropyridocoumarin and phenanthrolinone derivatives are synthesized in good to excellent yields using readily available iron(III) chloride ($FeCl_3$) as the catalyst. The process is very simple, straightforward and inexpensive, and provides a diverse range of pyranoquinolone or phenanthrolinone derivatives, via a 6-*endo*-dig mode of cyclization, starting from simple and easily available 6-(*N*-propargyl)aminocoumarin and -quinolone derivatives.

Key words: pyranoquinolone, phenanthrolinone, iron(III) chloride, Sonogashira coupling, 6-*endo*-dig cyclization

Naturally occurring quinoline derivatives are among some of the earliest discovered compounds found to possess remarkable biological activities,[1] and they have been utilized for the treatment of a various diseases. Compounds containing a quinoline motif are widely used as structural frameworks in a large number of biologically active natural products and pharmaceuticals.[2] They have also found application as antimalarials,[3] antibacterials,[4] antifungals[5] and anticancer agents.[6] Moreover, quinoline derivatives are used in materials science,[7] bioorganometallic processes,[8] and for the syntheses of fungicides, virucides, biocides, alkaloids, rubber chemicals and flavoring agents. Due to their potential biological activities,[9] coumarins fused with heterocycles have received increasing attention and are common structural motifs in many natural products.[10] Helietidine, dutadrupine, and geibalansine[11] are examples of natural products containing the pyranoquinoline core structure. Moreover, pyrano[3,2-*f*]quinolines, which are a combination of both a quinoline ring and a pyran moiety demonstrate unique biological activities, including psychotropic,[12] anti-allergic,[13] anti-inflammatory[14] and estrogenic,[15] and are used as potential pharmaceuticals.[16] 4,7-Phenanthroline derivatives and their analogues exhibit high antibacterial activity and are used for the treatment of gastrointestinal diseases.[17–22]

The toxicity and prohibitive prices of catalysts derived from heavy or rare metals constitute severe drawbacks in their use in large-scale applications in organic chemistry. Iron is one of the most abundant metals on earth, and is inexpensive and environmentally friendly.[23] Moreover, iron salts and complexes are commercially available.[24] The development of sustainable, environmentally friendly and low-cost C–C and C–X bond forming protocols have attracted significant attention from the synthetic organic chemistry community. Therefore, it is not surprising that iron salts have received much attention as alternative and promising catalysts for many selective organic transformations.[25] Among various iron salts, iron(III) chloride has been used as a Lewis acid to catalyze the Friedel–Crafts reaction,[26] the synthesis of esters and acetals,[27] the α-glycosidation of peracetylated sugars[28] and the cyclization of 2-(trimethylsilylmethyl)pentadienal.[29] In continuation of our work on the development of efficient protocols for the synthesis of pharmacologically important and potentially bioactive heterocyclic systems,[30] we decided to investigate whether iron(III) chloride could be used to catalyze the cyclization of various 6-(*N*-propargyl)aminocoumarin and -quinolone derivatives. Herein we report the results of our studies.

We previously observed[30n,31] two different results from the iron(III) chloride mediated reactions of *N*-aryl-*N*-(2-alkynyl)toluenesulfonamides **1** and *N*-(1,3-dimethyl-2,4-dioxo-1,2,3,4-tetrahydropyrimidin-5-yl)-4-methyl-*N*-(3-phenylprop-2-ynyl)benzenesulfonamide (**3**). As compound **1** gave the substituted quinoline derivatives **2** via iron(III) chloride mediated cyclization,[21] we hypothesized that compound **3** might also undergo a similar type of reaction to give the corresponding cyclized product. However, in practice, the reaction of **3** with iron(III) chloride furnished different results. This unexpected outcome prompted us to investigate a similar reaction of alkyne **7a** with iron(III) chloride (1 equiv) in 1,2-dichloroethane for 24 hours. The expected detosylated aromatized product **10** was not obtained. However, the reaction afforded a mixture of cyclized tosylated product **9a** in good yield (72%), along with coumarin **8** as a decomposition side product (Scheme 1). The structure of product **9a** was established from its elemental analysis and spectral data.

The precursors **7** for the present investigation were accessed according to our earlier published procedure, as shown in Scheme 2.[32] The optimized conditions for the iron(III) chloride mediated cyclization to give compounds **9** were established by screening different parameters.

The investigation was initiated using compound **7a** as a model substrate and the results are summarized in Table 1. Alkyne **7a** was initially treated with iron(III) chloride (1 equiv) in 1,2-dichloroethane at room temperature, but no reaction occurred (Table 1, entry 1).

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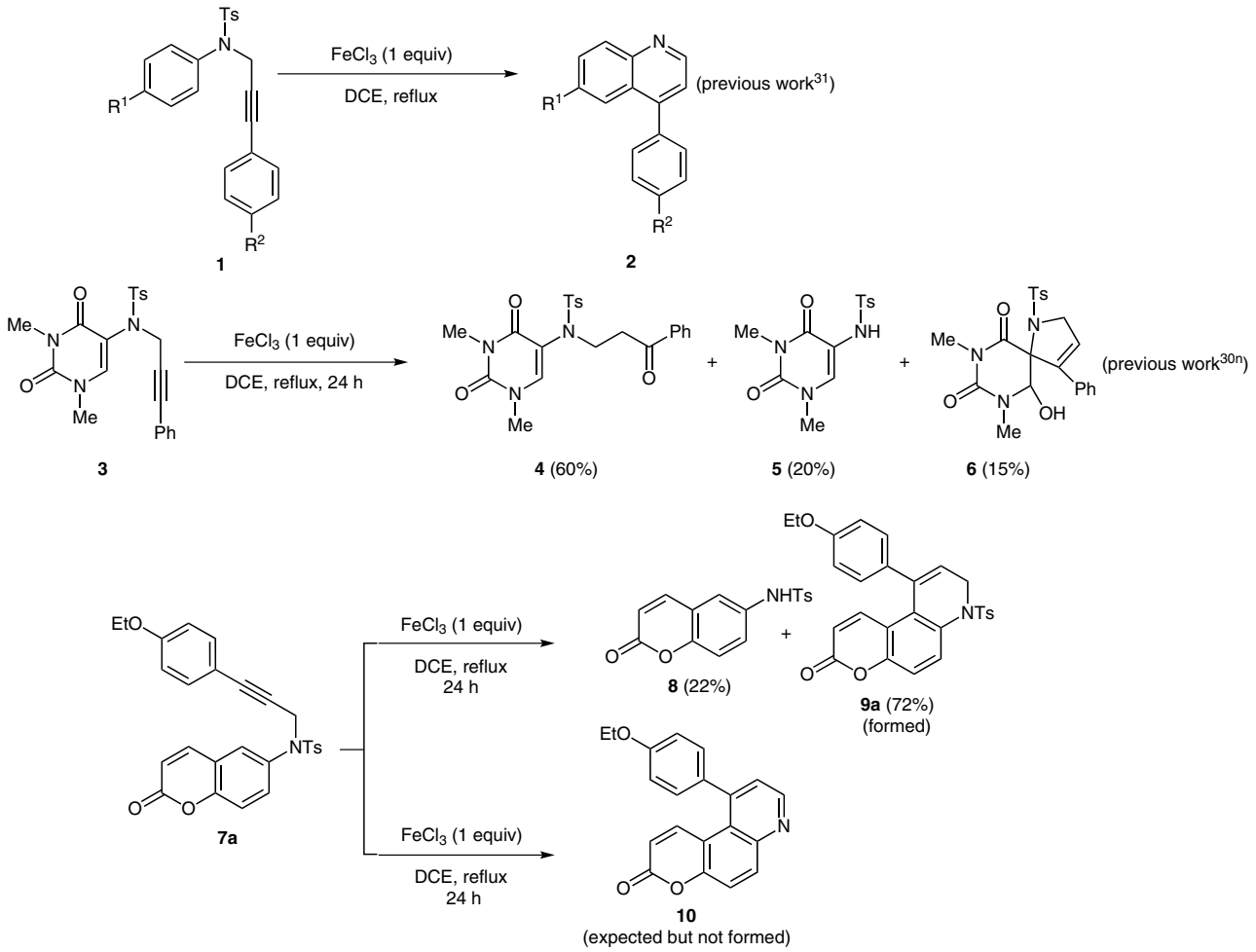
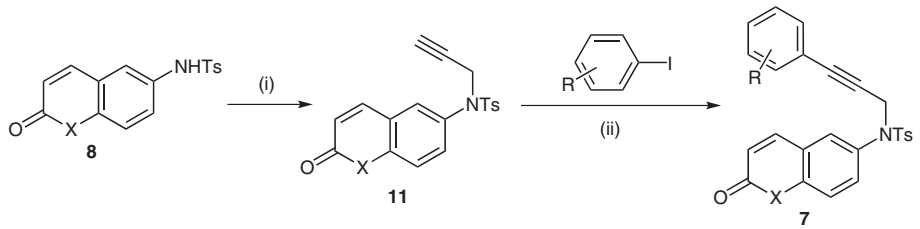


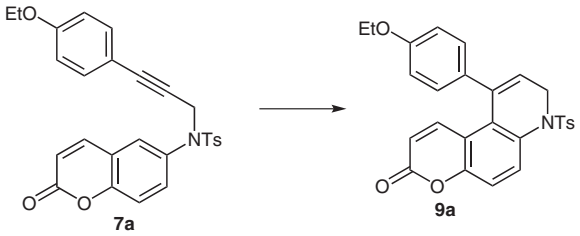
Scheme 1 Iron(III) chloride mediated reactions of substrates **1**, **3** and **7a**

We then attempted the same reaction by heating at reflux temperature in the presence of iron(III) chloride (0.1 equiv), and this reaction gave the cyclized product **9a**, but in only 15% yield (Table 1, entry 2). The number of equivalents of iron(III) chloride was then gradually increased from 0.1–2.0 equivalents. It was found that one equivalent of iron(III) chloride gave the best yield of the cyclized product **9a** (Table 1, entries 3–6). Pleasingly, reducing the reaction time from 24 hours to 12 hours resulted in the same yield of the product **9a** (Table 1, entry 7). However, a reaction time of less than 12 hours resulted in incomplete conversion, and consequently, a lower yield of the product **9a** (Table 1, entry 8). Next the effect of different solvents (EtOH, $CHCl_3$, CH_2Cl_2, THF, MeCN) on the yield of pyranoquinoline derivative **9a** was studied (Table 1, entries 9–13). Among these solvents, acetonitrile was found to give the highest yield (76%) of the product (Table 1, entry 13). The same reaction was also performed in the presence of iron(III) chloride for 10 hours (Table 1, entry 14), but a lower yield was obtained. Thus the optimized conditions for this transformation are as follows: iron(III) chloride (1 equiv) as the catalyst, acetonitrile as the solvent, reflux, 12 hours.



Scheme 2 *Reagents and conditions*: (i) progargyl bromide, anhydrous K_2CO_3, NaI, anhydrous acetone, reflux, 6 h; (ii) $Pd(PPh_3)_2Cl_2$, CuI (3 mol%), Et_3N, DMF, r.t., 2 h.

Table 1 Optimization of the Reaction Conditions

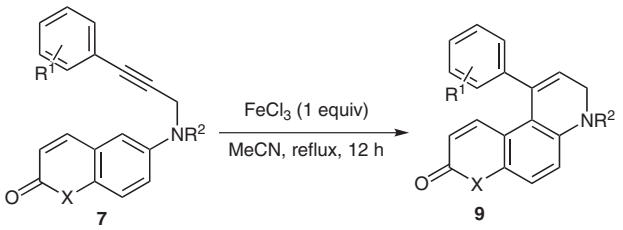


Entry	Catalyst (equiv)	Solvent	Temp	Time (h)	Yield (%)[a]
1	$FeCl_3$ (1.0)	DCE	r.t.	24	0
2	$FeCl_3$ (0.1)	DCE	reflux	24	15
3	$FeCl_3$ (0.2)	DCE	reflux	24	41
4	$FeCl_3$ (0.5)	DCE	reflux	24	63
5	$FeCl_3$ (2.0)	DCE	reflux	24	72
6	$FeCl_3$ (1.0)	DCE	reflux	24	72
7	$FeCl_3$ (1.0)	DCE	reflux	12	72
8	$FeCl_3$ (1.0)	DCE	reflux	6	53
9	$FeCl_3$ (1.0)	EtOH	reflux	12	34
10	$FeCl_3$ (1.0)	$CHCl_3$	reflux	12	24
11	$FeCl_3$ (1.0)	CH_2Cl_2	reflux	12	19
12	$FeCl_3$ (1.0)	THF	reflux	12	21
13	**$FeCl_3$ (1.0)**	**MeCN**	**reflux**	**12**	**76**
14	$FeCl_3$ (1.0)	MeCN	reflux	10	71

[a] Yield of isolated product.

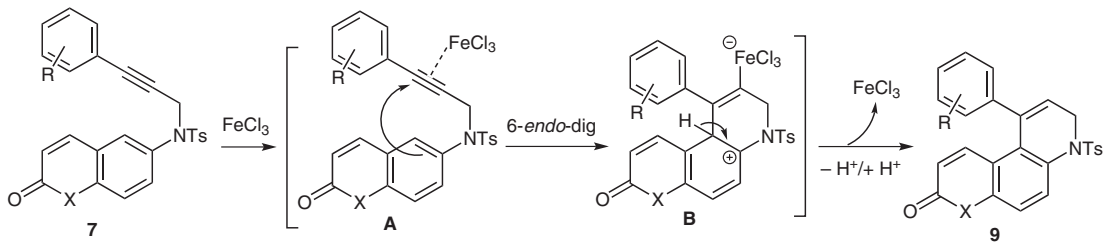
To test the scope and generality of this process, substrates **7b–j** were subjected to this transformation under the optimized reaction conditions, and the results are summarized in Table 2. The reactions of alkynes **7a–f** (R^1 = OEt, OMe, O*i*-Pr, OBn or $OCH_2CH{=}CH_2$) gave the corresponding cyclized adducts **9a–f** in yields of 66–76% (Table 2, entries 1–6). However, the reaction failed in the case of the substrate **7g** (R^1 = H; Table 2, entry 7), and full recovery of the starting material was possible, even after 12 hours. The same outcomes were obtained (recovery of the starting materials) in the cases of substrates **7h**,**i** (R^1 = Me or Ac; Table 2, entries 8 and 9). The reaction also failed when the tosyl group (R^2) was replaced by an ethyl group (substrate **7j**; Table 2, entry 10). From these results, it can be concluded that for the alkynes **7** (where X = O), the reaction is only successful with substrates containing a tosyl group and strong electron-donating groups at positions 2 or 4 of the aromatic ring adjacent to the alkyne moiety. Encouraged by these results, substrates **7k–n** (X = NMe or NEt) were reacted under the optimized conditions, and pleasingly, the expected substituted phenanthrolinone derivatives **9g–j** were obtained in 63–75% yields (Table 2, entries 11–14). However, similar reactions of substrates **7o–q** (where R^1 = Me or H) completely failed to give any cyclized product (Table 2, entries 15–17). These reactions also follow the same pattern as discussed earlier.

Table 2 Synthesis of Various Pyridocoumarins and Pyridoquinolones



Entry	Substrate	X	R^1	R^2	Product	Yield
1	**7a**	O	4-OEt	Ts	**9a**	76
2	**7b**	O	2-OEt	Ts	**9b**	71
3	**7c**	O	4-O*i*-Pr	Ts	**9c**	76
4	**7d**	O	2-OMe	Ts	**9d**	74
5	**7e**	O	4-OBn	Ts	**9e**	72
6	**7f**	O	4-$OCH_2CH{=}CH_2$	Ts	**9f**	66
7	**7g**	O	H	Ts	–	0
8	**7h**	O	4-Me	Ts	–	0
9	**7i**	O	4-Ac	Ts	–	0
10	**7j**	O	4-OMe	Et	–	0
11	**7k**	NMe	4-O*i*-Pr	Ts	**9g**	75
12	**7l**	NMe	4-OEt	Ts	**9h**	69
13	**7m**	NMe	4-OMe	Ts	**9i**	63
14	**7n**	NEt	4-OEt	Ts	**9j**	68
15	**7o**	NMe	4-Me	Ts	–	0
16	**7p**	NEt	4-Me	Ts	–	0
17	**7q**	NMe	H	Ts	–	0

A plausible reaction mechanism for the iron(III) chloride mediated formation of substituted quinoline derivatives is depicted in Scheme 3. Initially, the alkyne moiety is activated by iron(III) chloride to generate the π-complex **A**, which on subsequent intramolecular 6-*endo*-dig cyclization can produce the charged species **B**. Intermediate **B**, on simultaneous deprotonation and loss of iron(III) chloride (protodemetalation) produces the final product **9**. The reason behind the failure of the reaction in the absence of a tosyl group may be due to the fact that the lone pair of the nitrogen atom in the *N*-ethyl group captured the iron(III) chloride, and thus prevented the cyclization step taking place. Moreover, the reaction only occurs when a



Scheme 3 Proposed mechanism for the iron(III) chloride mediated synthesis

strong electron-donating group is present at the 2 and/or 4 position of the aromatic ring adjacent to the alkyne moiety. This is because the strong electron-donating group is able to activate the alkyne moiety such that it can form the π-complex **A**, which subsequently cyclizes to give the desired product. In other words, the availability of the nitrogen lone pair is reduced by the presence of the tosyl group. As a result, iron(III) chloride is free to form the aforementioned π-complex and thereby facilitates the 6-*endo*-dig cyclization to yield the product.

To summarize, we have successfully developed a simple, straightforward, inexpensive and efficient methodology for the synthesis of potentially bioactive pyranoquinoline and phenanthrolinone derivatives. The process utilizes readily available starting materials and involves an iron(III) chloride catalyzed intramolecular 6-*endo*-dig mode of cyclization.

Silica gel [Rankem (India), 60–120 or 230–400 mesh] was used for chromatographic separation. Silica gel-G [CDH (India)] was used for TLC. Petroleum-ether (PE) refers to the fraction boiling between 60–80 °C. Melting points were determined in open capillaries using a metal bath apparatus [Sunbeam (India)] and are uncorrected. IR spectra were run as KBr discs on a Perkin-Elmer 120-000A apparatus. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DPX-400 instrument as solutions in $CDCl_3$, with TMS as the internal standard. Mass spectra were recorded on a Qtof Micro instrument. CHN analyses were obtained using a Perkin Elmer 2400 series II CHN analyzer.

Compounds **7g**,**h**,**m**,**o**,**q** were prepared according to a previously published procedure.[32]

Alkynes 7; General Procedure

To a stirred solution of compound **11** (500 mg, 1 equiv), the appropriate iodobenzene (1.2 equiv) and anhydrous Et_3N (2 mL) in anhydrous DMF (8 mL) were added the catalysts $Pd(PPh_3)_2Cl_2$ (0.05 equiv) and CuI (0.05 equiv). The reaction mixture was stirred at room temperature for 1 h. After completion, the reaction mixture was poured into H_2O (20 mL) and extracted with CH_2Cl_2 (3 × 20 mL). The organic layer was successively washed with H_2O (5 × 20 mL), brine (20 mL) and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure to give a crude mass which was chromatographed over silica gel (60–120 mesh) using EtOAc–PE (1:9) as eluent to afford the product **7**.

***N*-[3-(4-Ethoxyphenyl)prop-2-yn-1-yl]-4-methyl-*N*-(2-oxo-2*H*-chromen-6-yl)benzenesulfonamide (7a)**

Yield: 576 mg (86%); pale grey solid; mp 144–146 °C.

IR (KBr): 1569, 1732, 2238, 2922 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.41 (t, *J* = 7.2 Hz, 3 H), 2.39 (s, 3 H), 4.02 (q, *J* = 7.2 Hz, 2 H), 4.70 (s, 2 H), 6.46 (d, *J* = 9.6 Hz, 1 H), 6.79 (d, *J* = 8.8 Hz, 2 H), 7.10 (d, *J* = 8.8 Hz, 2 H), 7.22 (d, *J* = 8.0 Hz, 1 H), 7.25–7.27 (m, 2 H), 7.41 (dd, *J* = 2.4 Hz, 8.8 Hz, 1 H), 7.55–7.61 (m, 3 H), 7.65 (d, *J* = 9.6 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.7, 21.6, 42.1, 63.6, 81.5, 86.3, 113.8, 114.4, 117.3, 117.5, 119.1, 128.1, 128.4, 129.5, 131.5, 132.9, 135.4, 136.0, 143.0, 144.0, 153.2, 159.3, 160.3.

MS (ESI): *m*/*z* = 474.00 [M + H]$^+$ (100%).

Anal. Calcd for $C_{27}H_{23}NO_5S$: C, 68.48; H, 4.90; N, 2.96. Found: C, 68.30; H, 4.95; N, 3.00.

***N*-[3-(2-Ethoxyphenyl)prop-2-yn-1-yl]-4-methyl-*N*-(2-oxo-2*H*-chromen-6-yl)benzenesulfonamide (7b)**

Yield: 556 mg (83%); pale grey solid; mp 142–144 °C.

IR (KBr): 1596, 1733, 2242, 2978 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.25–1.33 (m, 3 H), 2.32 (s, 3 H), 4.00 (q, *J* = 6.8 Hz, 2 H), 4.72 (s, 2 H), 6.45 (d, *J* = 9.6 Hz, 1 H), 6.84 (q, *J* = 8.0 Hz, 2 H), 7.10–7.15 (m, 3 H), 7.23–7.27 (m, 2 H), 7.52–7.67 (m, 5 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.7, 21.5, 42.3, 64.0, 83.0, 86.7, 111.5, 111.7, 117.2, 117.4, 119.0, 120.2, 128.1, 128.5, 129.4, 130.1, 131.4, 133.5, 135.3, 136.1, 143.1, 143.9, 153.2, 159.5, 160.3.

MS (ESI): *m*/*z* = 474.00 [M + H]$^+$ (100%).

Anal. Calcd for $C_{27}H_{23}NO_5S$: C, 68.48; H, 4.90; N, 2.96. Found: C, 68.27; H, 4.94; N, 3.02.

***N*-[3-(4-Isopropoxyphenyl)prop-2-yn-1-yl]-4-methyl-*N*-(2-oxo-2*H*-chromen-6-yl)benzenesulfonamide (7c)**

Yield: 600 mg (87%); pale grey solid; mp 120–122 °C.

IR (KBr): 1594, 1730, 2240, 2972 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.33 (d, *J* = 6.0 Hz, 6 H), 2.38 (s, 3 H), 4.53 (m, 1 H), 4.65 (s, 2 H), 6.45 (d, *J* = 9.6 Hz, 1 H), 6.77 (d, *J* = 8.8 Hz, 2 H), 7.09 (d, *J* = 8.8 Hz, 2 H), 7.21–7.27 (m, 3 H), 7.41 (dd, *J* = 2.4 Hz, 8.8 Hz, 1 H), 7.54–7.58 (m, 3 H), 7.65 (d, *J* = 9.6 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.6, 21.9, 42.1, 69.9, 81.4, 86.3, 113.6, 115.6, 117.3, 117.4, 119.1, 128.1, 128.4, 129.5, 131.5, 133.0, 135.3, 135.9, 143.0, 144.0, 153.2, 158.3, 160.3.

MS (ESI): *m*/*z* = 488.12 [M + H]$^+$ (100%).

Anal. Calcd for $C_{28}H_{25}NO_5S$: C, 68.98; H, 5.17; N, 2.87. Found: C, 68.87; H, 5.14; N, 2.94.

***N*-[3-(2-Methoxyphenyl)prop-2-yn-1-yl]-4-methyl-*N*-(2-oxo-2*H*-chromen-6-yl)benzenesulfonamide (7d)**

Yield: 592 mg (91%); pale grey solid; mp 142–144 °C.

IR (KBr): 1696, 1732, 2236, 2923 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.33 (s, 3 H), 3.75 (s, 3 H), 4.72 (s, 2 H), 6.44 (d, *J* = 9.2 Hz, 1 H), 6.85 (q, *J* = 8.0 Hz, 2 H), 7.10 (d, *J* = 7.2 Hz, 1 H), 7.16 (d, *J* = 7.6 Hz, 2 H), 7.28 (q, *J* = 7.2 Hz, 2 H), 7.53–7.65 (m, 5 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.5, 42.3, 55.6, 82.9, 87.0, 110.5, 111.2, 117.2, 117.3, 119.0, 120.4, 128.1, 128.5, 129.4, 130.2, 131.8, 133.2, 135.3, 136.0, 143.1, 143.9, 153.2, 160.1, 160.3.

MS (ESI): *m*/*z* = 460.07 $[M + H]^+$ (100%).

Anal. Calcd for $C_{26}H_{21}NO_5S$: C, 67.96; H, 4.61; N, 3.05. Found: C, 68.07; H, 4.66; N, 3.08.

_N_-{3-[4-(Benzyloxy)phenyl]prop-2-yn-1-yl}-4-methyl-_N_-(2-oxo-2_H_-chromen-6-yl)benzenesulfonamide (7e)
Yield: 621 mg (82%); pale grey solid; mp 134–136 °C.

IR (KBr): 1693, 1732, 2228, 2991 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.38 (s, 3 H), 4.65 (s, 2 H), 5.06 (s, 2 H), 6.46 (d, *J* = 9.2 Hz, 1 H), 6.87 (d, *J* = 8.8 Hz, 2 H), 7.11 (d, *J* = 8.8 Hz, 2 H), 7.22 (d, *J* = 7.6 Hz, 2 H), 7.25–7.27 (m, 2 H), 7.34–7.40 (m, 5 H), 7.55–7.58 (m, 3 H), 7.65 (d, *J* = 9.6 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.6, 42.1, 70.0, 81.7, 86.1, 114.3, 114.8, 117.3, 117.5, 119.1, 127.4, 128.1, 128.2, 128.4, 128.7, 129.5, 131.4, 133.0, 135.4, 135.9, 136.4, 143.0, 144.0, 153.2, 159.0, 160.3.

MS (ESI): *m*/*z* = 536.11 $[M + H]^+$ (100%).

Anal. Calcd for $C_{32}H_{25}NO_5S$: C, 71.76; H, 4.70; N, 2.62. Found: C, 71.90; H, 4.75; N, 2.70.

_N_-{3-[4-(Allyloxy)phenyl]prop-2-yn-1-yl}-4-methyl-_N_-(2-oxo-2_H_-chromen-6-yl)benzenesulfonamide (7f)
Yield: 577 mg (84%); pale grey solid; mp 120–122 °C.

IR (KBr): 1692, 1731, 2230, 2997 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.38 (s, 3 H), 4.52 (dd, *J* = 1.2 Hz, 4.0 Hz, 2 H), 4.65 (s, 2 H), 5.30 (dd, *J* = 1.2 Hz, 10.4 Hz, 1 H), 5.41 (dd, *J* = 1.2 Hz, 9.2 Hz, 1 H), 5.98–6.05 (m, 1 H), 6.45 (d, *J* = 9.6 Hz, 1 H), 6.81 (d, *J* = 8.8 Hz, 2 H), 7.10 (dd, *J* = 2.0 Hz, 9.2 Hz, 2 H), 7.20–7.28 (m, 3 H), 7.41 (dd, *J* = 2.4 Hz, 8.8 Hz, 1 H), 7.54–7.58 (m, 3 H), 7.66 (d, *J* = 9.6 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.6, 42.1, 68.8, 81.6, 86.1, 114.1, 114.7, 117.2, 117.5, 118.0, 119.1, 128.0, 128.4, 129.5, 131.5, 132.7, 132.9, 135.3, 135.9, 143.1, 144.1, 153.2, 158.9, 160.3.

MS (ESI): *m*/*z* = 486.21 $[M + H]^+$ (100%).

Anal. Calcd for $C_{28}H_{23}NO_5S$: C, 69.26; H, 4.77; N, 2.88. Found: C, 69.10; H, 4.81; N, 2.81.

_N_-[3-(4-Acetylphenyl)prop-2-yn-1-yl]-4-methyl-_N_-(2-oxo-2_H_-chromen-6-yl)benzenesulfonamide (7i)
Yield: 547 mg (82%); pale grey solid; mp 126–128 °C.

IR (KBr): 1686, 1729, 2228, 2969 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.40 (s, 3 H), 2.59 (s, 3 H), 4.70 (s, 2 H), 6.47 (d, *J* = 9.6 Hz, 1 H), 7.23–7.28 (m, 5 H), 7.39 (dd, *J* = 2.4 Hz, 8.8 Hz, 1 H), 7.54–7.58 (m, 3 H), 7.64 (d, *J* = 9.6 Hz, 1 H), 7.87 (d, *J* = 8.4 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.6, 26.6, 42.0, 85.3, 86.4, 117.3, 117.5, 119.2, 126.7, 128.0, 128.2, 128.3, 129.6, 131.3, 131.6, 135.2, 135.7, 136.6, 143.0, 144.3, 153.3, 160.2, 197.2.

MS (ESI): *m*/*z* = 472.09 $[M + H]^+$ (100%).

Anal. Calcd for $C_{27}H_{21}NO_5S$: C, 68.77; H, 4.49; N, 2.97. Found: C, 68.90; H, 4.51; N, 2.91.

6-{Ethyl[3-(4-methoxyphenyl)prop-2-yn-1-yl]amino}-2_H_-chromen-2-one (7j)
Yield: 668 mg (91%); yellow gum.

IR (KBr): 1569, 1679, 1720, 2969 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.26 (t, *J* = 7.2 Hz, 3 H), 3.51 (q, *J* = 7.2 Hz, 2 H), 3.78 (s, 3 H), 4.23 (s, 2 H), 6.40 (d, *J* = 9.6 Hz, 1 H), 6.81 (d, *J* = 8.4 Hz, 2 H), 6.88 (d, *J* = 2.8 Hz, 1 H), 7.12 (dd, *J* = 2.8 Hz, 9.2 Hz, 1 H), 7.24–7.39 (m, 3 H), 7.67 (d, *J* = 9.2 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 12.4, 41.0, 46.1, 55.3, 83.5, 84.1, 111.2, 113.7, 113.9, 114.8, 116.7, 117.4, 119.0, 119.3, 132.3, 133.1, 143.9, 145.1, 146.8, 159.6, 161.5.

MS (ESI): *m*/*z* = 334.14 $[M + H]^+$ (100%).

Anal. Calcd for $C_{21}H_{19}NO_3$: 75.66; H, 5.74; N, 4.20. Found: C, 75.46; H, 5.81; N, 4.29.

_N_-[3-(4-Isopropoxyphenyl)prop-2-yn-1-yl]-4-methyl-_N_-(1-methyl-2-oxo-1,2-dihydroquinolin-6-yl)benzenesulfonamide (7k)
Yield: 581 mg (85%); pale grey solid; mp 110–112 °C.

IR (KBr): 1681, 1702, 2222, 2951 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.33 (d, *J* = 6.0 Hz, 6 H), 2.38 (s, 3 H), 3.69 (s, 3 H), 4.53 (t, *J* = 6.0 Hz, 1 H), 4.67 (s, 2 H), 6.71 (d, *J* = 8.8 Hz, 1 H), 6.77 (d, *J* = 8.4 Hz, 1 H), 7.09 (d, *J* = 8.4 Hz, 2 H), 7.22 (d, *J* = 8.0 Hz, 2 H), 7.31 (d, *J* = 8.8 Hz, 1 H), 7.46–7.69 (m, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.6, 21.9, 29.6, 42.2, 69.9, 81.7, 86.1, 113.7, 114.8, 115.5, 120.8, 122.4, 128.1, 128.5, 128.6, 129.4, 130.8, 131.9, 132.0, 132.1, 133.0, 133.9, 135.6, 138.7, 139.5, 143.8, 158.2, 160.2.

MS (ESI): *m*/*z* = 501.19 $[M + H]^+$ (100%).

Anal. Calcd for $C_{29}H_{28}N_2O_4S$: C, 69.58; H, 5.64; N, 5.60. Found: C, 69.77; H, 5.67; N, 5.48.

_N_-[3-(4-Ethoxyphenyl)prop-2-yn-1-yl]-4-methyl-_N_-(1-methyl-2-oxo-1,2-dihydroquinolin-6-yl)benzenesulfonamide (7l)
Yield: 611 mg (92%); pale grey solid; mp 144–146 °C.

IR (KBr): 1646, 1702, 2220, 2991 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.40 (t, *J* = 7.2 Hz, 3 H), 2.38 (s, 3 H), 3.69 (s, 3 H), 4.02 (q, *J* = 6.8 Hz, 2 H), 4.67 (s, 2 H), 6.72 (d, *J* = 9.2 Hz, 1 H), 6.78 (d, *J* = 8.4 Hz, 2 H), 7.10 (d, *J* = 8.4 Hz, 2 H), 7.22 (d, *J* = 8.0 Hz, 2 H), 7.31 (d, *J* = 8.8 Hz, 1 H), 7.49–7.59 (m, 5 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.7, 21.6, 29.6, 42.2, 63.5, 81.8, 86.0, 113.9, 114.4, 114.8, 120.8, 122.4, 128.1, 128.6, 129.4, 130.8, 132.9, 133.9, 135.6, 138.7, 139.5, 143.8, 159.2, 162.2.

MS (ESI): *m*/*z* = 487.24 $[M + H]^+$ (100%).

Anal. Calcd for $C_{28}H_{26}N_2O_4S$: C, 69.11; H, 5.39; N, 5.76. Found: C, 68.90; H, 5.44; N, 5.70.

_N_-[3-(4-Ethoxyphenyl)prop-2-yn-1-yl]-_N_-(1-ethyl-2-oxo-1,2-dihydroquinolin-6-yl)-4-methylbenzenesulfonamide (7n)
Yield: 553 mg (84%); pale grey solid; mp 128–130 °C.

IR (KBr): 1642, 1702, 2217, 2981 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.35 (t, *J* = 7.2 Hz, 3 H), 1.41 (t, *J* = 7.2 Hz, 3 H), 2.39 (s, 3 H), 4.02 (t, *J* = 6.8 Hz, 2 H), 4.34 (d, *J* = 7.2 Hz, 2 H), 4.67 (s, 2 H), 6.71 (d, *J* = 9.6 Hz, 1 H), 6.78 (d, *J* = 8.8 Hz, 2 H), 7.10 (d, *J* = 8.8 Hz, 2 H), 7.22 (d, *J* = 8.0 Hz, 2 H), 7.33 (d, *J* = 8.8 Hz, 1 H), 7.50–7.56 (m, 3 H), 7.61 (d, *J* = 8.4 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 12.7, 14.7, 21.6, 37.5, 42.3, 63.5, 81.8, 86.0, 114.0, 114.4, 114.7, 121.1, 122.5, 128.1, 128.8, 129.4, 130.9, 132.9, 133.7, 135.8, 138.5, 138.6, 143.8, 159.2, 161.7.

MS (ESI): *m*/*z* = 501.14 $[M + H]^+$ (100%).

Anal. Calcd for $C_{29}H_{28}N_2O_4S$: C, 69.58; H, 5.64; N, 5.60. Found: C, 69.70; H, 5.58; N, 5.70.

_N_-(1-Ethyl-2-oxo-1,2-dihydroquinolin-6-yl)-4-methyl-_N_-(3-_p_-tolylprop-2-yn-1-yl)benzenesulfonamide (7p)
Yield: 532 mg (86%); pale grey solid; mp 130–132 °C.

IR (KBr): 1509, 1590, 1645, 1656, 2973 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 1.34 (t, *J* = 7.2 Hz, 3 H), 2.33 (s, 3 H), 2.38 (s, 3 H), 4.33 (q, *J* = 6.8 Hz, 2 H), 4.68 (s, 2 H), 6.70 (d, *J* = 9.6 Hz, 1 H), 7.06 (m, 4 H), 7.22 (d, *J* = 8.0 Hz, 2 H), 7.33 (d, *J* = 8.8 Hz, 1 H), 7.50–7.56 (m, 3 H), 7.61 (d, *J* = 8.0 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 12.8, 21.5, 21.6, 37.6, 42.3, 82.7, 86.1, 114.7, 119.0, 121.1, 122.5, 128.1, 128.9, 129.0, 129.4, 130.9, 131.3, 133.6, 135.7, 138.6, 138.7, 138.9, 143.8, 161.7.

MS (ESI): *m*/*z* = 471.09 $[M + H]^+$ (100%).

Anal. Calcd for $C_{28}H_{26}N_2O_3S$: C, 71.46; H, 5.57; N, 5.95. Found: C, 71.60; H, 5.48; N, 5.90.

Pyranoquinoline and Phenanthrolinone Derivatives; General Procedure

Alkyne **7** (100 mg) was added to a vigorously stirred solution of $FeCl_3$ (1 equiv) in MeCN (2 mL) at r.t., and the resulting mixture was stirred at 80 °C under an N_2 atmosphere for 12 h. After completion of the reaction (monitored by TLC), the mixture was cooled and extracted with CH_2Cl_2 (3 × 25 mL). The combined organic extract was washed with brine (25 mL) and dried over Na_2SO_4. The solvent was removed by distillation and the resulting crude residue was purified by filtration through a pad of silica gel (230–400 mesh, PE–EtOAc) to give the pure cyclized product **9**.

9-(4-Ethoxyphenyl)-7-tosyl-7,8-dihydro-3*H*-pyrano[3,2-*f*]quinolin-3-one (9a)

Yield: 76 mg (76%); pale yellow solid; mp 176–178 °C.

IR (KBr): 1510, 1609, 1734, 2970 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 1.43 (t, *J* = 6.8 Hz, 3 H), 2.19 (s, 3 H), 4.02 (q, *J* = 6.8 Hz, 2 H), 4.47 (s, 2 H), 5.76 (t, *J* = 4.8 Hz, 1 H), 5.95 (d, *J* = 10.0 Hz, 1 H), 6.49 (s, 2 H), 6.72 (d, *J* = 7.6 Hz, 2 H), 6.96 (t, *J* = 6.8 Hz, 3 H), 7.35 (d, *J* = 8.0 Hz, 3 H), 8.08 (d, *J* = 8.8 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.8, 21.4, 45.2, 63.5, 114.4, 114.6, 115.3, 117.2, 125.0, 127.5, 128.2, 129.0, 129.3, 130.7, 132.1, 133.7, 136.0, 136.7, 141.4, 143.7, 153.6, 158.7, 160.0.

MS (ESI): *m*/*z* = 474.00 $[M + H]^+$ (100%), 496.00 $[M + Na]^+$ (66%).

Anal. Calcd for $C_{27}H_{23}NO_5S$: C, 68.48; H, 4.90; N, 2.96. Found: C, 68.61; H, 4.94; N, 3.02.

9-(2-Ethoxyphenyl)-7-tosyl-7,8-dihydro-3*H*-pyrano[3,2-*f*]quinolin-3-one (9b)

Yield: 71 mg (71%); pale yellow solid; mp 178–180 °C.

IR (KBr): 1575, 1732, 2980 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 1.01 (t, *J* = 6.8 Hz, 3 H), 2.21 (s, 3 H), 3.72 (q, *J* = 7.6 Hz, 1 H), 3.87 (q, *J* = 7.6 Hz, 1 H), 4.49 (d, *J* = 4.0 Hz, 2 H), 5.93 (t, *J* = 4.8 Hz, 2 H), 6.40 (d, *J* = 6.8 Hz, 1 H), 6.76–6.79 (m, 2 H), 6.99–7.06 (m, 3 H), 7.21–7.30 (m, 2 H), 7.49 (d, *J* = 7.6 Hz, 2 H), 8.06 (d, *J* = 9.2 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.4, 21.4, 45.0, 63.3, 111.8, 114.6, 115.6, 116.5, 120.6, 127.6, 127.8, 128.2, 129.2, 129.3, 129.4, 129.5, 130.2, 133.2, 133.5, 136.8, 141.0, 143.6, 152.9, 155.0, 160.1.

MS (ESI): *m*/*z* = 474.00 $[M + H]^+$ (100%), 496.00 $[M + Na]^+$ (66%).

Anal. Calcd for $C_{27}H_{23}NO_5S$: C, 68.48; H, 4.90; N, 2.96. Found: C, 68.64; H, 4.85; N, 3.03.

9-(4-Isopropoxyphenyl)-7-tosyl-7,8-dihydro-3*H*-pyrano[3,2-*f*]quinolin-3-one (9c)

Yield: 76 mg (76%); pale yellow solid; mp 160–162 °C.

IR (KBr): 1579, 1732, 2992 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 1.35 (d, *J* = 6.0 Hz, 6 H), 2.18 (s, 3 H), 4.46 (d, *J* = 3.6 Hz, 2 H), 4.54 (quin, *J* = 6.0 Hz, 1 H), 5.76 (t, *J* = 4.8 Hz, 1 H), 5.95 (t, *J* = 9.6 Hz, 1 H), 6.49 (d, *J* = 7.2 Hz, 2 H), 6.71 (d, *J* = 8.4 Hz, 2 H), 6.95–7.00 (m, 3 H), 7.32–7.35 (m, 3 H), 8.08 (d, *J* = 8.8 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.3, 22.0, 45.2, 70.0, 114.5, 115.3, 115.8, 117.1, 124.9, 127.5, 128.2, 129.0, 129.3, 130.7, 131.9, 133.7, 136.1, 136.7, 141.4, 143.7, 153.6, 157.7, 159.9.

MS (ESI): *m*/*z* = 488.19 $[M + H]^+$ (100%).

Anal. Calcd for $C_{28}H_{25}NO_5S$: C, 68.98; H, 5.17; N, 2.87. Found: C, 68.84; H, 5.15; N, 2.83.

9-(2-Methoxyphenyl)-7-tosyl-7,8-dihydro-3*H*-pyrano[3,2-*f*]quinolin-3-one (9d)

Yield: 74 mg (74%); pale yellow solid; mp 162–164 °C.

IR (KBr): 1575, 1595, 1729, 2920 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 2.23 (s, 3 H), 3.56 (s, 3 H), 4.44 (dd, *J* = 4.8 Hz, 17.2 Hz, 1 H), 4.62 (dd, *J* = 5.2 Hz, 17.2 Hz, 1 H), 5.92 (t, *J* = 10.0 Hz, 1 H), 5.97 (t, *J* = 4.8 Hz, 1 H), 6.24 (d, *J* = 7.2 Hz, 1 H), 6.76 (t, *J* = 7.2 Hz, 1 H), 6.84 (d, *J* = 8.0 Hz, 1 H), 6.96–7.02 (m, 3 H), 7.23–7.29 (m, 2 H), 7.45 (d, *J* = 7.6 Hz, 2 H), 8.07 (d, *J* = 8.8 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.4, 45.1, 55.2, 111.0, 114.7, 115.3, 116.6, 120.7, 127.6, 128.0, 128.1, 128.3, 129.2, 129.3, 129.5, 130.3, 133.0, 133.1, 136.6, 140.9, 143.6, 153.1, 155.6, 160.0.

MS (ESI): *m*/*z* = 460.06 $[M + H]^+$ (100%).

Anal. Calcd for $C_{26}H_{21}NO_5S$: C, 67.96; H, 4.61; N, 3.05. Found: C, 67.79; H, 4.65; N, 3.11.

9-[4-(Benzyloxy)phenyl]-7-tosyl-7,8-dihydro-3*H*-pyrano[3,2-*f*]quinolin-3-one (9e)

Yield: 72 mg (72%); pale yellow solid; mp 184–186 °C.

IR (KBr): 1571, 1592, 1731, 2952 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 2.12 (s, 3 H), 4.46 (s, 2 H), 5.06 (s, 2 H), 5.76 (s, 1 H), 5.94 (t, *J* = 10.0 Hz, 1 H), 6.50 (s, 2 H), 6.75–6.80 (m, 2 H), 6.92–6.97 (m, 3 H), 7.21–7.42 (m, 8 H), 8.07 (d, *J* = 8.8 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.3, 45.2, 70.0, 114.6, 115.0, 115.3, 117.2, 125.1, 127.5, 128.2, 128.7, 128.9, 129.3, 130.7, 132.5, 133.7, 136.0, 136.5, 136.6, 141.3, 143.7, 153.6, 158.5, 159.9.

MS (ESI): *m*/*z* = 536.08 $[M + H]^+$ (100%).

Anal. Calcd for $C_{32}H_{25}NO_5S$: C, 71.76; H, 4.70; N, 2.62. Found: C, 71.98; H, 4.65; N, 2.58.

9-[4-(Allyloxy)phenyl]-7-tosyl-7,8-dihydro-3*H*-pyrano[3,2-*f*]quinolin-3-one (9f)

Yield: 66 mg (66%); pale yellow solid; mp 120–122 °C.

IR (KBr): 1508, 1567, 1724, 2919 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 2.19 (s, 3 H), 4.47 (d, *J* = 4.8 Hz, 2 H), 4.53 (d, *J* = 4.8 Hz, 2 H), 5.33 (dd, *J* = 1.2 Hz, 10.4 Hz, 1 H), 5.44 (dd, *J* = 1.2 Hz, 16.8 Hz, 1 H), 5.77 (t, *J* = 4.8 Hz, 1 H), 5.95 (d, *J* = 10.0 Hz, 1 H), 6.02–6.06 (m, 1 H), 6.50 (d, *J* = 7.6 Hz, 2 H), 6.75 (d, *J* = 8.8 Hz, 2 H), 6.94–6.97 (m, 3 H), 7.30–7.35 (m, 3 H), 8.08 (d, *J* = 8.8 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.4, 45.2, 68.8, 114.6, 114.7, 115.3, 117.2, 118.1, 125.1, 127.4, 127.5, 128.2, 129.4, 130.1, 130.7, 132.3, 132.9, 133.7, 136.0, 136.6, 141.4, 143.8, 153.6, 158.3, 160.0.

MS (ESI): *m*/*z* = 486.09 $[M + H]^+$ (100%).

Anal. Calcd for $C_{28}H_{23}NO_5S$: C, 69.26; H, 4.77; N, 2.88. Found: C, 69.40; H, 4.71; N, 2.91.

9-(4-Isopropoxyphenyl)-4-methyl-7-tosyl-7,8-dihydro-4,7-phenanthrolin-3(4*H*)-one (9g)

Yield: 75 mg (75%); pale yellow solid; mp 174–176 °C.

IR (KBr): 1508, 1563, 1660, 2973 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.34 (d, *J* = 6.0 Hz, 6 H), 2.14 (s, 3 H), 3.75 (s, 3 H), 4.45 (s, 2 H), 4.51 (quin, *J* = 6.0 Hz, 1 H), 5.75 (t, *J* = 5.2 Hz, 1 H), 6.24 (d, *J* = 10.0 Hz, 1 H), 6.47 (br s, 2 H), 6.67 (d, *J* = 8.0 Hz, 2 H), 6.92 (d, *J* = 8.0 Hz, 2 H), 7.06 (d, *J* = 10.0 Hz, 1 H), 7.35 (d, *J* = 8.0 Hz, 2 H), 7.43 (d, *J* = 9.2 Hz, 1 H), 8.13 (d, *J* = 8.8 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.3, 22.0, 29.9, 45.3, 70.0, 114.7, 115.6, 117.0, 119.8, 124.7, 127.4, 128.1, 129.0, 129.28, 129.33, 132.2, 132.5, 136.1, 137.1, 137.2, 139.8, 143.5, 157.4, 161.6.

MS (ESI): *m*/*z* = 501.20 $[M + H]^+$ (100%), 523.17 $[M + Na]^+$ (33%).

Anal. Calcd for $C_{29}H_{28}N_2O_4S$: C, 69.58; H, 5.64; N, 5.60. Found: C, 69.74; H, 5.65; N, 5.63.

9-(4-Ethoxyphenyl)-4-methyl-7-tosyl-7,8-dihydro-4,7-phenanthrolin-3(4*H*)-one (9h)
Yield: 69 mg (69%); pale yellow gummy solid.

IR (KBr): 1510, 1606, 1651, 2249, 2982 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.42 (t, *J* = 6.8 Hz, 3 H), 2.15 (s, 3 H), 3.75 (s, 3 H), 4.01 (q, *J* = 6.8 Hz, 2 H), 4.44 (d, *J* = 5.2 Hz, 2 H), 5.76 (t, *J* = 5.2 Hz, 1 H), 6.23 (d, *J* = 10.0 Hz, 1 H), 6.48 (br s, 1 H), 6.68 (d, *J* = 8.0 Hz, 2 H), 6.92 (d, *J* = 8.0 Hz, 1 H), 7.05 (d, *J* = 10.0 Hz, 1 H), 7.35 (d, *J* = 8.0 Hz, 2 H), 7.43 (d, *J* = 9.2 Hz, 1 H), 7.47–7.51 (m, 1 H), 7.55 (t, *J* = 8.0 Hz, 1 H), 8.13 (d, *J* = 9.2 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.8, 21.4, 29.9, 45.3, 63.5, 114.2, 114.7, 116.9, 119.8, 124.7, 127.4, 128.1, 129.0, 129.3, 132.2, 132.7, 136.1, 137.0, 137.2, 139.8, 143.5, 158.5, 161.5.

MS (ESI): *m*/*z* = 487.12 $[M + H]^+$ (100%).

Anal. Calcd for $C_{28}H_{26}N_2O_4S$: C, 69.11; H, 5.39; N, 5.76. Found: C, 69.28; H, 5.45; N, 5.67.

9-(4-Methoxyphenyl)-4-methyl-7-tosyl-7,8-dihydro-4,7-phenanthrolin-3(4*H*)-one (9i)
Yield: 63 mg (63%); pale yellow gummy solid.

IR (KBr): 1507, 1556, 1662, 2968 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.15 (s, 3 H), 3.75 (s, 3 H), 3.80 (s, 3 H), 4.45 (s, 2 H), 5.76 (s, 1 H), 6.23 (d, *J* = 9.6 Hz, 1 H), 6.49 (br s, 2 H), 6.69 (d, *J* = 7.2 Hz, 2 H), 6.92 (d, *J* = 7.2 Hz, 2 H), 7.05 (d, *J* = 8.8 Hz, 1 H), 7.35 (d, *J* = 7.2 Hz, 2 H), 7.43 (d, *J* = 8.4 Hz, 1 H), 8.13 (d, *J* = 8.4 Hz, 1 H).

MS (ESI): *m*/*z* = 473.19 $[M + H]^+$ (100%).

Anal. Calcd for $C_{27}H_{24}N_2O_4S$: C, 68.62; H, 5.12; N, 5.93. Found: C, 68.48; H, 5.15; N, 5.99.

9-(4-Ethoxyphenyl)-4-ethyl-7-tosyl-7,8-dihydro-4,7-phenanthrolin-3(4*H*)-one (9j)
Yield: 68 mg (68%); pale yellow gummy solid.

IR (KBr): 1510, 1552, 1660, 2973 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.21–1.31 (m, 3 H), 1.42 (t, *J* = 7.2 Hz, 3 H), 2.15 (s, 3 H), 4.01 (d, *J* = 6.4 Hz, 2 H), 4.38 (d, *J* = 6.8 Hz, 2 H), 4.44 (s, 2 H), 5.74 (s, 1 H), 6.22 (d, *J* = 9.6 Hz, 1 H), 6.49 (br s, 2 H), 6.68 (d, *J* = 7.2 Hz, 2 H), 6.92 (d, *J* = 7.2 Hz, 2 H), 7.06 (d, *J* = 10.0 Hz, 1 H), 7.34 (t, *J* = 7.2 Hz, 2 H), 7.43 (d, *J* = 8.8 Hz, 1 H), 8.13 (d, *J* = 8.8 Hz, 1 H).

MS (ESI): *m*/*z* = 501.09 $[M + H]^+$ (100%).

Anal. Calcd for $C_{29}H_{28}N_2O_4S$: C, 69.58; H, 5.64; N, 5.60. Found: C, 69.78; H, 5.69; N, 5.69.

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Supporting Information for this article is available online at http://www.thieme-connect.com/ejournals/toc/synthesis.

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