Synthesis A. Bontemps et al. Feature

Silver-Catalyzed Domino Hydroarylation/Cycloisomerization Reactions of 2-Alkynylquinoline-3-carbaldehydes: Access to (Hetero)arylpyranoquinolines

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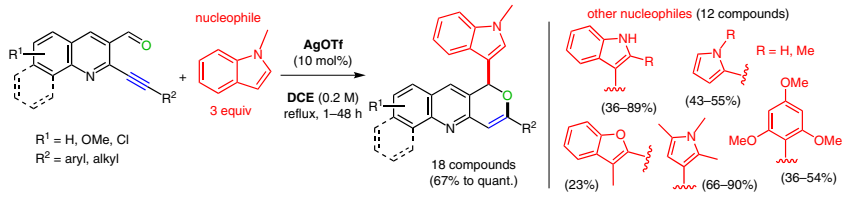

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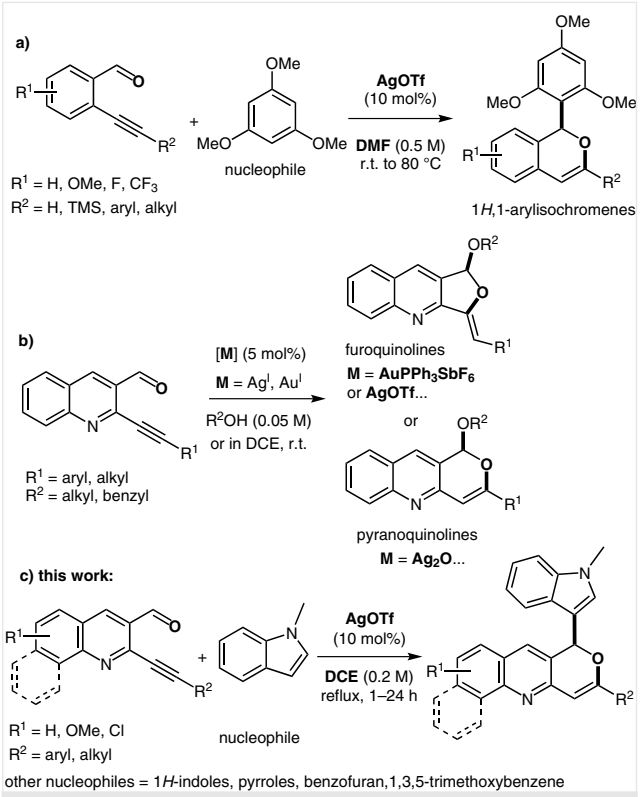
Received: 18.04.2016
Accepted: 21.04.2016
Published online: 07.06.2016
DOI: 10.1055/s-0035-1562234; Art ID: ss-2016-z0264-fa

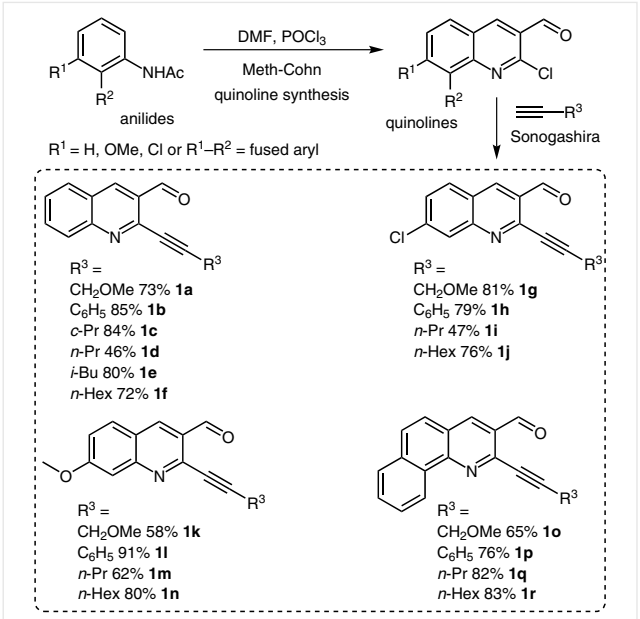
Abstract A silver trifluoromethanesulfonate catalyzed efficient access to the indolylpyranoquinoline scaffold is reported. Starting from 2-alkynylquinoline-3-carbaldehyde units with various substitution patterns on the quinoline and alkynyl parts, the use of silver trifluoromethanesulfonate (10 mol%) in 1,2-dichloroethane allowed a domino hydroarylation/cycloisomerization reaction, generating (hetero)aryl-functionalized pyranoquinolines. The heteroarenes that were used are *N*-methylindole (18 compounds, 67–100%), indole, and 2-methylindole (4 compounds, 36–89%), and the reaction was also compatible to a lesser extent with arenes such as pyrroles (5 compounds, 43–90%), 1,3,5-trimethoxybenzene, and 3-methylbenzofuran.
Key words, hydroarylation, silver, cycloisomerization, indolylpyranoquinolines, domino reaction, cyclofunctionalization

Quinolines and indoles are ubiquitous heterocycles exhibiting a large array of biological properties.[1] In order to develop new pharmacophores according to a diversity-oriented synthesis (DOS) strategy,[2] some efforts have been oriented towards the formation of mixed indolylquinoline moieties, with various linking features, allowing the discovery of new bioactive derivatives.[3] Among all the strategies to reach indolylquinoline derivatives, we chose to focus on straightforward and atom-economical metal-catalyzed cycloisomerization reactions, due to our continuing interest in enyne,[4] aniline-yne,[5] alkynylsilylenol ether,[6] enamine-yne,[7] and carbonyl-yne[8] cycloisomerization and domino reactions. We and others investigated cyclofunctionalization reactions on carbonyl-yne units with various nucleophilic species (alcohols,[8,9] terminal alkynes,[10] phosphites,[11] nitrogen derivatives,[12] activated methylenes,[13] allyl trialkylsilanes,[14] hydride,[15] and aromatics[16]). Particularly, we recently focused on nucleophiles such as aromatics, since they still remain underexplored (Scheme 1, a).[16d] Indeed, domino hydroarylation/cycloisomerization reactions have attracted our attention and we recently reported the reactivity of aromatics as nucleophiles on *o*-alkynylbenzaldehydes to form 1-aryl-1*H*-isochromenes (Scheme 1, a). Among these, one example with *N*-methylindole as a nucleophile triggered our interest to form indolylquinoline derivatives, since we already reported the formation of furo- and pyranoquinoline under silver or gold catalysis with alcohol groups as nucleophiles (Scheme 1, b).[8] Therefore, we intended to develop this chemistry on 2-alkynylquinoline-3-carbaldehydes to access mixed indole/quinoline moieties, using as a link a dihydropyran unit, providing the original indolylpyranoquinoline scaffold (Scheme 1, c) via a selective 6-*endo*-*dig* cyclization process.[8a]

First of all, to reach the desired 2-alkynyl(benzo)quinoline-3-carbaldehyde precursors (Scheme 2), we used the classical Meth-Cohn quinoline synthesis methodology[17] to obtain a wide array of 2-chloro(benzo)quinoline-3-carbaldehydes, which underwent Sonogashira coupling reactions to yield known (**1a**–**c**, **1k**, **1l**)[8a] or new (**1d**–**j**, **1m**–**r**) functionalized derivatives. For the Sonogashira reaction we needed to choose between four methods including a chloro–iodo exchange (see experimental part).[18] We also synthesized four alkynyl derivatives bearing aromatic substitutions (**1b**, **1h**, **1l**, **1p**, 76–91%) and focused on alkynyl derivatives bearing aliphatic substitutions (46–84% yield), which are less known in comparison with their aromatic counterparts (Scheme 2).



Scheme 1 Previous work from our group (a, b), and this work (c)



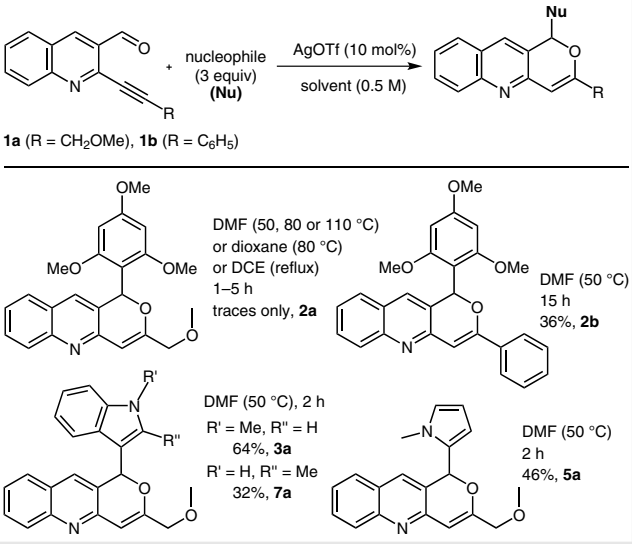
Scheme 2 Synthesis of precursors

With these polycyclic precursors in hand, and based on our previous optimized reaction conditions (Scheme 1, a), we investigated the addition of *N*-methylindole and also other nucleophiles (Scheme 3), for the tandem hydroaryla-

Biographical Sketches

Véronique Michelet completed her graduate studies at the Ecole Nationale Supérieure de Chimie de Paris (ChimieParisTech, France) in 1993 and received her PhD degree in 1996 from the University P. et M. Curie in the group of Prof. J.-P. Genêt. After two years of post-doctoral research in the groups of Prof. J. D. Winkler (University of Pennsylvania, USA) and Prof. A. G. M. Barrett (Imperial College, UK), she was appointed at ChimieParisTech as CNRS Associate Researcher in 1998 and promoted to Director of Research in 2007. Her research interests combine basic and applied aspects of catalysis for the development of new synthetic methodologies for carbon–carbon and carbon–heteroatom bond formation. This involves asymmetric catalysis, metallo-organocatalysis, and the development of novel catalytic systems for atom- and step-economical reactions such as cycloisomerization reactions and domino processes. The synthesis of fluorescent complexing agents is also developed in her group for the detection of polluting metal ions.

Philippe Belmont was born in Paris in 1970, grew up in the French Caribbean, and in 1990 moved to Grenoble (France) to study at the University Joseph Fourier, where, in 1996, he obtained his PhD degree in organic chemistry under the guidance of Dr. M. Demeunynck and Prof. J. Lhomme. He then moved for three years of post-doctoral research to Case Western Reserve University (Prof. A. J. Pearson, Cleveland, USA) and to the Collège de France (Prof. J.-M. Lehn and Dr. J.-P. Vigneron, Paris, France). In 2000 he joined the group of Prof. M. A. Ciufolini (University of Lyon, France) as a researcher for the CNRS. In 2004 he obtained his habilitation diploma and since then has managed a research group investigating organometallic chemistry (Rh, Au, Ag, Co) for the synthesis of nitrogen- and oxygen-containing heterocyclic compounds, with an interest in their biological properties. In 2009 he arrived at the Institut Curie in Paris (2009–2014) and since 2011 has been a Full Professor of Organic Chemistry at the School of Pharmacy (University Paris Descartes).



Scheme 3 First optimization

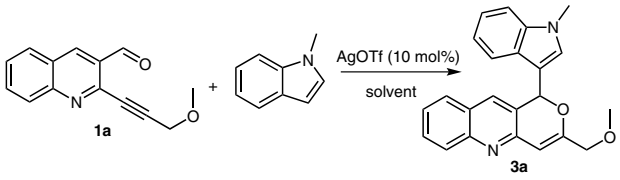
tion/cycloisomerization reaction. Of note, we chose a model substrate bearing an alkyl side chain (CH_2OMe) on the alkynyl unit, most of all because alkyl-substituted alkynes are more challenging and less studied substrates due to their instability and lower reactivity compared to the aryl-substituted ones.

Using 1,3,5-trimethoxybenzene as a nucleophile on substrate **1a** was inefficient, regardless of the reaction solvent (DMF, dioxane, DCE) or temperature (50–110 °C) chosen, and only traces of **2a** were detected (Scheme 3). This was in sharp contrast with our previous optimized conditions to construct isochromenes.[16d] Using the phenylalkynyl-functionalized quinoline substrate **1b** with 1,3,5-trimethoxybenzene as a nucleophile led to a low yield (36%) of the desired pyranoquinoline product **2b**.

Therefore, other nucleophiles were tested on **1a**. The use of *N*-methylindole gave the best results, with (*N*-methylindolyl)pyranoquinoline **3a** (Scheme 3) obtained in 64% yield in only two hours, but the temperature had to be lowered to 50 °C to control the amount of side products formed. Finally, the results with the unsubstituted indole as a nucleophile on substrate **1a** was disappointing (**7a**, 32%, Scheme 3) and *N*-methylpyrrole gave fair results (**5a**, 46%, Scheme 3).

Overall, the first optimization attempts (Scheme 3) showed that, for the choice of the nucleophile, the reactivity of *N*-methylindole was superior to the other tested nucleophiles, although limited (**3a**, 64%). Therefore, we assumed that the presence of the nitrogen-containing quinoline could have an impact on the previously optimized reaction conditions,[16d] and we decided to further adjust the reaction conditions with *N*-methylindole as the nucleophile (Table 1).

Table 1 Reaction Conditions Optimization with *N*-Methylindole as the Nucleophile



Entry	Solvent	Temp (°C)	Conc n[a] (M)	Nu[equiv]	Time (h)	Yield[(%)]
1	DMF	50	0.5	3	2	64
2[b]	DMF	r.t.	0.5	3	24	–
3	DMF	80	0.2	3	2	68
4	dioxane	50	0.1	3	2	73
5	dioxane	50	0.2	3	1	76
6	dioxane	50	0.4	3	1	75
7	dioxane	80	0.2	3	1	80
8	dioxane	80	0.2	1.5	1	77
9	dioxane	80	0.2	10	1	86
10	DCE	50	0.2	3	2	75
11	**DCE**	**reflux**	**0.2**	**3**	**1**	**83**
12	DCE	reflux	0.2	10	1	80

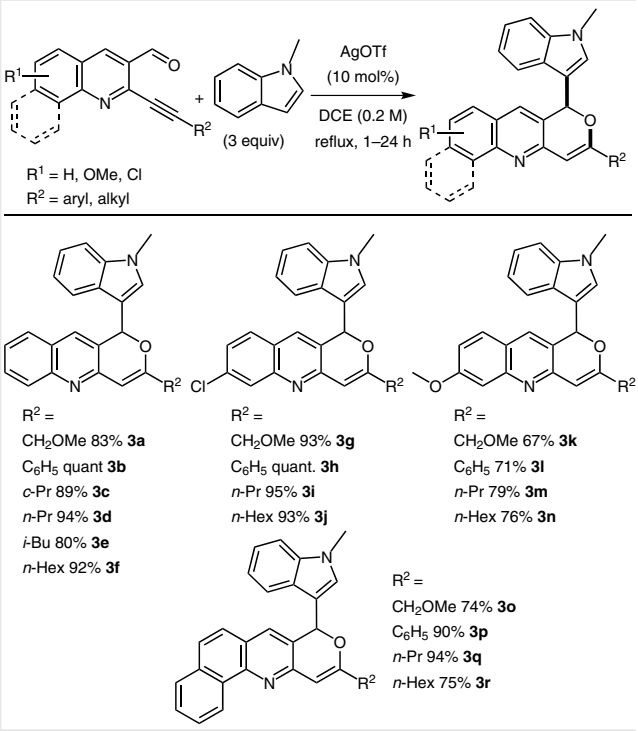
[a] *C* = concentration of the reaction mixture.
[b] Partial conversion.

Thus, we decided to have a look at the reactivity of *N*-methylindole as a heteroaromatic nucleophile under organometallic catalysis, since only few papers described some reactivity with gold,[16a] palladium,[16b] or silver.[16c,d] Using our optimized reaction conditions for obtaining isochromenes (Table 1, entry 1),[16d] we saw that performing the reaction at room temperature was ineffective even after 24 h (entry 2) and that indolylpyranoquinoline **3a** could be obtained, but only in 68% yield at 80 °C (entry 3), with a concentration of 0.2 M to avoid side-product formation.

Changing DMF for dioxane was slightly better, since the yields increased steadily from 73% to 86% (entries 4–9). Increasing the reaction medium concentration (entries 4 and 5, 0.1 to 0.2 M), did not have a major effect on the yields, but it permitted a reduction in the reaction time (1 h instead of 2 h). A higher concentration of the reaction medium did not give better results (entry 6, 0.4 M, 75%), but the factors influencing the yield improvement were the increase of the reaction temperature, from 50 to 80 °C, giving 80% of the desired derivative **3a** (entry 7), and also the amount of nucleophile used (from 3 to 10 equiv, entry 9) producing 86% of **3a**, whereas decreasing the amount (1.5 equiv, entry 8) had almost no effect (77%) compared with entry 7 (80%). Switching to DCE as the solvent (entries 10–12) was also promising, since with three equivalents of *N*-methylindole, at reflux for one hour at 0.2 M (entry 11), **3a**

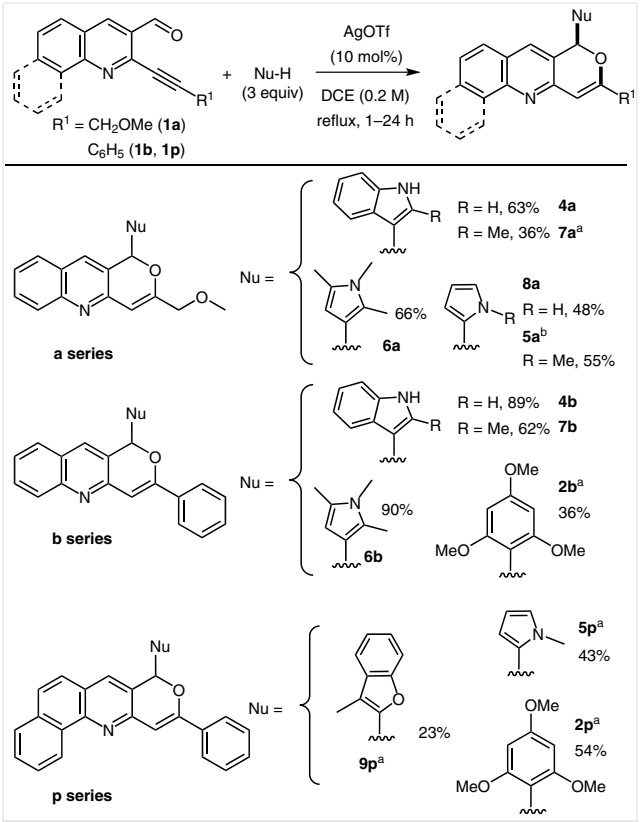
was produced efficiently (83%). This last result was about the same as for entry 7 performed in dioxane, but DCE was preferred due to easier reaction media treatment and better substrate solubilization, and was therefore chosen for the scope and limitations studies.

Therefore, starting from alkynylquinolines **1a–f** (Scheme 2), indolylpyranoquinolines **3a–f** (Scheme 4) were obtained efficiently, bearing a phenyl group substituent (**3b**, quant) or, more interestingly, a variety of alkyl chains: functionalized (**3a**, 83%), cyclic (**3c**, 89%), and possessing a linear or branched alkyl chain (**3d–f**, 80–94%). Then, the methodology was extended to indolylpyranoquinolines substituted on the quinoline core with an electron-withdrawing chloro atom (**3g–j**) or an electron-donating methoxy group (**3k–n**). The results were compared on the basis of the formation of four derivatives, in each case bearing a phenyl or alkyl substituent. We could observe that the presence of an electron-withdrawing chloro atom had a favorable impact on the reaction, since all the indolylpyranoquinolines were efficiently formed, whatever the substitution on the alkynyl unit (**3g–j**, 93–100%), whereas the presence of the electron-donating methoxy group (**3k–n**) caused a noticeable decrease in the product yields of 15–29%, the overall yields ranging from 67% to 79%. Finally, indolylpyranobenzoquinolines **3o–r** were successfully prepared when containing a CH_2OMe group (**3o**, 74%) and a hexyl chain (**3r**, 75%), and even more successfully prepared when containing a phenyl (**3p**, 90%) or a propyl group (**3q**, 94%).



Scheme 4 Scope and limitations with *N*-methylindole as the nucleophile

Then we examined the reactivity of various nucleophiles (NuH) with alkynylquinolines **1a**, **1b**, and **1p** (Scheme 5). Overall, the domino hydroarylation/cycloisomerization reactions were less efficient compared to when *N*-methylindole was used as the nucleophile, since the isolated yields were modest to good. Nevertheless, a large variation of the nucleophile was possible, as outlined in Scheme 5, leading to the 6-*endo-dig* cyclization products.



Scheme 5 Variation of the nucleophilic species. [a] Reaction performed in DMF. [b] 5-*exo-dig* product observed.

Interestingly, the reaction of indole or 1,2,5-trimethylpyrrole with compound **1a** yielded **4a** (63%) and **6a** (66%), respectively (Scheme 5). Using the more hindered 2-methylindole produced compound **7a** in lower yield (36%). In comparison with 1,2,5-trimethylpyrrole, the use of less nucleophilic pyrrole or *N*-methylpyrrole[19] respectively gave moderate yields of compounds **8a** (48%), accompanied with uncharacterized side products, and **5a** (55%) with some 5-*exo-dig* product. Gratifyingly, the reactions of alkynylquinoline **1b**, bearing a phenyl substituent on the alkynyl group, gave much better results with various nucleophiles such as indole (**4b**, 89%), 2-methylindole (**7b**, 62%), and 1,2,5-trimethylpyrrole (**6b**, 90%). Using the less nucleophilic 1,3,5-trimethoxybenzene generated arylpyranoquinoline **2b** in a modest 36% yield. Finally, the reactivity of alkynylbenzoquinoline **1p** followed a mixed nucleophilic/hin-

drance scale, with the yields depending on the nature of the nucleophile, increasing as follows: 3-methylbenzofuran (**9p**, 23%), *N*-methylpyrrole (**5p**, 43%), and 1,3,5-trimethoxybenzene (**2p**, 54%).

In conclusion, we have developed an efficient and versatile silver-catalyzed domino hydroarylation/cycloisomerization reaction of 2-alkynylquinoline-3-carbaldehyde scaffolds exhibiting a large variety of substitution on the alkynyl part (particularly the less studied aliphatic ones), on the quinoline core, or on the nucleophilic unit. Thanks to this straightforward AgOTf-catalyzed reaction, numerous aryl and heteroaryl substituents could be placed on the pyranoquinoline unit, efficiently generating 22 different indolylpyranoquinolines and 8 more compounds with a pyranoquinoline core bearing a pyrrole, a benzofuran, or a 1,3,5-trimethoxybenzene unit. This simple and efficient procedure opens new perspectives for the generation of key building blocks in medicinal chemistry.

All reactions were conducted under an inert atmosphere. Compounds **1a**, **1b**, **1c**, **1k**, and **1l** are known derivatives.[8a] Flash chromatography was performed by using 40–63 µm silica. Analytical TLC was carried out on Merck pre-coated GF 254 silica gel plates. Melting points were measured on a Stuart SMP3 melting point apparatus and are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AC 300 or AC 400 spectrometer by using $CDCl_3$ or DMSO-d_6 as both solvent and internal standard. Coupling constants (*J*) are given in Hz. IR spectra were obtained on a Perkin-Elmer 1600 spectrophotometer. HRMS was performed on a Q-TOF Waters spectrometer (UMR-8638, Paris, France) and on an ESI-MicrOTOFQ-II Bruker spectrometer (UMR-5246, Lyon, France).

2-Alkynylquinoline-3-carbaldehydes 1 by Sonogashira Coupling; General Procedures

Method A: Anhydrous DMF (1 mL) and Et_3N (0.56 mL, 4.00 mmol, 4 equiv), previously degassed with bubbling argon for 10 min, were added to a flask containing the appropriate chlorinated quinoline (1.00 mmol, 1 equiv), $[PdCl_2(PPh_3)_2]$ (35.1 mg, 0.050 mmol, 0.05 equiv), and CuI (9.5 mg, 0.050 mmol, 0.05 equiv) under an argon atmosphere. Finally, the appropriate alkyne derivative (1.20 mmol, 1.2 equiv) was added dropwise to the mixture, which was then stirred overnight at r.t. After completion of the reaction (attested by TLC analysis), the mixture was filtered through a short pad of silica and Celite and eluted with EtOAc. The crude was concentrated under reduced pressure and purified by column chromatography (silica gel, various solvent mixtures).

Method B: Anhydrous THF (15 mL) and Et_3N (0.21 mL, 1.50 mmol, 1.5 equiv), previously degassed with bubbling argon for 10 min, were added to a flask containing the appropriate iodinated quinoline (1.00 mmol, 1 equiv), $[PdCl_2(PPh_3)_2]$ (49.1 mg, 0.070 mmol, 0.07 equiv), and CuI (57.1 mg, 0.300 mmol, 0.3 equiv) under an argon atmosphere. Finally, the alkyne derivative (1.20 mmol, 1.2 equiv) was added dropwise to the mixture, which was then stirred overnight at r.t. After completion of the reaction (attested by TLC analysis), the mixture was filtered through a short pad of silica and Celite and eluted with EtOAc. The crude was concentrated under reduced pressure and purified by column chromatography (silica gel, various solvent mixtures).

Method C: Anhydrous THF (15 mL) and Et_3N (0.21 mL, 1.50 mmol, 1.5 equiv), previously degassed with bubbling argon for 10 min, were added to a flask containing the appropriate chlorinated quinoline (1.00 mmol, 1 equiv), $[PdCl_2(PPh_3)_2]$ (49.1 mg, 0.070 mmol, 0.07 equiv), and CuI (57.1 mg, 0.300 mmol, 0.3 equiv) under an argon atmosphere. Finally, the alkyne derivative (1.20 mmol, 1.2 equiv) was added dropwise to the mixture, which was then stirred overnight at r.t. After completion of the reaction (attested by TLC analysis), the mixture was filtered through a short pad of silica and Celite and eluted with EtOAc. The crude was concentrated under reduced pressure and purified by column chromatography (silica gel, various solvent mixtures).

Method D: Anhydrous THF (12 mL) and Et_3N (7.0 mL, 12.0 mmol, 3 equiv), previously degassed with bubbling argon for 10 min, were added to a sealed tube containing the appropriate chlorinated quinoline (4.00 mmol, 1 equiv), $[PdCl_2(PPh_3)_2]$ (140 mg, 0.200 mmol, 0.05 equiv), and CuI (38.1 mg, 0.200 mmol, 0.05 equiv) under an argon atmosphere. Finally, the alkyne derivative (6.00 mmol, 1.5 equiv) was added dropwise to the mixture, which was then heated at 60 °C for 3 h under microwave irradiation. After completion of the reaction (attested by TLC analysis), the mixture was filtered through a short pad of basic alumina and Celite and eluted with CH_2Cl_2. The crude was concentrated under reduced pressure and purified by column chromatography (silica gel, various solvent mixtures).

2-(Pent-1-ynyl)quinoline-3-carbaldehyde (1d)

The crude product obtained by method A was purified by column chromatography (silica gel, cyclohexane–EtOAc (0.5% Et_3N), 1:0 to 8:2); this afforded a light yellow solid; yield: 88 mg (46%); mp 54–56 °C.

IR (neat): 3057, 2958, 2850, 2215, 1688, 1583, 1551, 1489, 1454, 1370, 1155, 1111, 917, 786, 754, 710 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.70 (s, 1 H), 8.70 (s, 1 H), 8.12 (d, *J* = 8.5 Hz, 1 H), 7.94 (d, *J* = 8.1 Hz, 1 H), 7.84 (ddd, *J* = 8.5, 6.9, 1.5 Hz, 1 H), 7.60 (ddd, *J* = 8.2, 6.8, 1.2 Hz, 1 H), 2.57 (t, *J* = 7.1 Hz, 2 H), 1.75 (sext, *J* = 7.3 Hz, 2 H), 1.11 (t, *J* = 7.4 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.4 (CH), 150.3 (C), 144.6 (C), 136.9 (CH), 133.0 (CH), 129.7 (CH), 129.4 (CH), 128.9 (C), 128.1 (CH), 126.4 (C), 98.1 (C), 77.8 (C), 21.9 (CH_2), 21.8 (CH_2), 13.9 (CH_3).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{15}H_{14}NO$: 224.1075; found: 224.1076.

2-(4-Methylpent-1-ynyl)quinoline-3-carbaldehyde (1e)

The crude product obtained by method A was purified by column chromatography (silica gel, cyclohexane–EtOAc, 9:1); this afforded a brown solid; yield: 189 mg (80%); mp 120–125 °C.

IR (neat): 3054, 2957, 2929, 2849, 2220, 1693, 1654, 1612, 1581, 1550, 1489, 1453, 1383, 1369, 1153, 1112, 915, 786, 760, 753, 712 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 10.70 (s, 1 H), 8.69 (s, 1 H), 8.12 (d, *J* = 8.6 Hz, 1 H), 7.93 (d, *J* = 7.9 Hz, 1 H), 7.83 (ddd, *J* = 8.6, 6.9, 1.2 Hz, 1 H), 7.59 (ddd, *J* = 7.9, 6.9, 0.7 Hz, 1 H), 2.49 (d, *J* = 6.6 Hz, 2 H), 2.12–1.98 (m, 1 H), 1.10 (d, *J* = 6.7 Hz, 6 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 191.4 (CH), 150.2 (C), 144.6 (C), 137.0 (CH), 133.0 (CH), 129.7 (CH), 129.3 (CH), 128.9 (C), 128.1 (CH), 126.4 (C), 97.3 (C), 78.5 (C), 29.0 (CH_2), 28.1 (CH), 22.4 (2 × CH_3).

HRMS (CI): *m*/*z* [M + H]$^+$ calcd for $C_{16}H_{16}NO$: 238.1226; found: 238.1236.

2-(Oct-1-ynyl)quinoline-3-carbaldehyde (1f)

The crude product obtained by method A was purified by column chromatography (silica gel, cyclohexane–EtOAc (0.5% Et_3N), 1:0 to 6:4); this afforded a light yellow solid; yield: 164 mg (72%); mp 50–52 °C.

IR (neat): 3073, 2930, 2854, 2234, 1691, 1584, 1552, 1491, 1469, 1452, 1372, 1157, 1112, 960, 915, 783, 745, 711 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 10.69 (s, 1 H), 8.69 (s, 1 H), 8.11 (d, *J* = 8.5 Hz, 1 H), 7.93 (d, *J* = 8.1 Hz, 1 H), 7.83 (ddd, *J* = 8.5, 7.0, 1.5 Hz, 1 H), 7.59 (ddd, *J* = 8.2, 6.8, 1.2 Hz, 1 H), 2.58 (t, *J* = 7.2 Hz, 2 H), 1.71 (quin, *J* = 7.3 Hz, 2 H), 1.55–1.45 (m, 2 H), 1.38–1.29 (m, 4 H), 0.90 (t, *J* = 6.8 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.4 (CH), 150.3 (C), 144.7 (C), 136.9 (CH), 133.0 (CH), 129.7 (CH), 129.3 (CH), 128.9 (C), 128.0 (CH), 126.4 (C), 98.4 (C), 77.6 (C), 31.5 (CH_2), 28.9 (CH_2), 28.3 (CH_2), 22.7 (CH_2), 19.8 (CH_2), 14.2 (CH_3).

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{18}H_{19}NONa$: 288.1364; found: 288.1363.

7-Chloro-2-(3-methoxyprop-1-ynyl)quinoline-3-carbaldehyde (1g)

The crude product obtained by method A was purified by column chromatography (silica gel, cyclohexane–EtOAc (0.5% Et_3N), 1:0 to 6:4); this afforded a beige solid; yield: 207 mg (81%); mp 127–129 °C.

IR (neat): 3049, 2949, 2853, 2233, 1693, 1608, 1583, 1548, 1479, 1365, 1095, 1069, 897, 846, 756 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 10.66 (s, 1 H), 8.70 (s, 1 H), 8.13 (s, 1 H), 7.90 (d, *J* = 8.7 Hz, 1 H), 7.59 (dd, *J* = 8.7, 1.9 Hz, 1 H), 4.48 (s, 2 H), 3.53 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 190.1 (CH), 150.2 (C), 144.2 (C), 139.4 (C), 136.9 (CH), 130.7 (CH), 129.5 (CH), 128.9 (C), 128.3 (CH), 124.9 (C), 92.4 (C), 82.3 (C), 60.3 (CH_2), 58.3 (CH_3).

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{14}H_{10}ClNO_2Na$: 282.0298; found: 282.0293.

7-Chloro-2-(phenylethynyl)quinoline-3-carbaldehyde (1h)

The crude product obtained by method C was purified by column chromatography (silica gel, cyclohexane–EtOAc (0.5% Et_3N), 1:0 to 9:1); this afforded a white solid; yield: 232 mg (79%); mp 178–180 °C.

IR (neat): 3049, 2860, 2207, 1692, 1609, 1585, 1545, 1480, 1382, 1370, 1289, 1146, 1065, 933, 881, 867, 806, 753, 744, 681 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 10.78 (s, 1 H), 8.72 (s, 1 H), 8.16 (s, 1 H), 7.90 (d, *J* = 8.7 Hz, 1 H), 7.70 (d, *J* = 7.4 Hz, 2 H), 7.58 (d, *J* = 8.7 Hz, 1 H), 7.52–7.38 (m, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 190.5 (CH), 150.6 (C), 145.1 (C), 139.5 (C), 137.0 (CH), 132.5 (2 × CH), 130.9 (CH), 130.2 (CH), 129.5 (CH), 129.1 (C), 128.8 (2 × CH), 128.5 (CH), 124.9 (C), 121.3 (C), 96.5 (C), 85.4 (C).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{18}H_{11}ClNO$: 292.0524; found: 292.0523.

7-Chloro-2-(pent-1-ynyl)quinoline-3-carbaldehyde (1i)

The crude product obtained by method A was purified by column chromatography (silica gel, cyclohexane–EtOAc (0.5% Et_3N), 1:0 to 8:2); this afforded a pale yellow solid; yield: 120 mg (47%); mp 109–110 °C.

IR (neat): 3050, 2965, 2860, 2216, 1686, 1608, 1583, 1547, 1482, 1467, 1368, 1066, 871, 845, 807, 754 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 10.65 (s, 1 H), 8.65 (s, 1 H), 8.10 (s, 1 H), 7.86 (d, *J* = 8.7 Hz, 1 H), 7.53 (d, *J* = 8.7 Hz, 1 H), 2.57 (t, *J* = 7.1 Hz, 2 H), 1.75 (sext, *J* = 7.2 Hz, 2 H), 1.10 (t, *J* = 7.4 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 190.9 (CH), 150.41 (C), 145.6 (C), 139.3 (C), 136.7 (CH), 130.8 (CH), 129.2 (CH), 129.0 (C), 128.3 (CH), 124.8 (C), 99.2 (C), 77.38 (C), 21.8 (CH_2), 21.8 (CH_2), 13.9 (CH_3).

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{15}H_{12}ClNONa$: 280.0505; found: 280.0509.

7-Chloro-2-(oct-1-ynyl)quinoline-3-carbaldehyde (1j)

The crude product obtained by method A was purified by column chromatography (silica gel, cyclohexane–EtOAc (0.5% Et_3N), 1:0 to 95:5); this afforded a pale yellow solid; yield: 226 mg (76%); mp 77–79 °C.

IR (neat): 3046, 2929, 2857, 2229, 1686, 1606, 1582, 1547, 1471, 1368, 1065, 932, 875, 847, 810, 756, 708 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 10.66 (s, 1 H), 8.66 (s, 1 H), 8.10 (s, 1 H), 7.87 (d, *J* = 8.7 Hz, 1 H), 7.54 (dd, *J* = 8.8, 2.1 Hz, 1 H), 2.59 (t, *J* = 7.1 Hz, 2 H), 1.72 (quin, *J* = 7.1 Hz, 2 H), 1.57–1.45 (m, 2 H), 1.41–1.29 (m, 4 H), 1.00–0.85 (m, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.0 (CH), 150.5 (C), 145.7 (C), 139.3 (C), 136.7 (CH), 130.9 (CH), 129.2 (CH), 129.0 (C), 128.3 (CH), 124.8 (C), 99.4 (C), 77.4 (C), 31.4 (CH_2), 28.9 (CH_2), 28.3 (CH_2), 22.7 (CH_2), 19.9 (CH_2), 14.2 (CH_3).

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{18}H_{18}ClNONa$: 322.0975; found: 322.0977.

7-Methoxy-2-(pent-1-ynyl)quinoline-3-carbaldehyde (1m)

The crude product obtained by method B was purified by column chromatography (silica gel, cyclohexane–EtOAc (0.5% Et_3N), 1:0 to 75:25); this afforded a yellow solid; yield: 89 mg (62%); mp 104–106 °C.

IR (neat): 3016, 2960, 2860, 2231, 1685, 1614, 1585, 1496, 1446, 1388, 1374, 1310, 1219, 1134, 1021, 917, 839, 827, 762, 706 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 10.63 (s, 1 H), 8.59 (s, 1 H), 7.79 (d, *J* = 9.0 Hz, 1 H), 7.41 (d, 1 H), 7.22 (dd, *J* = 9.0, 2.3 Hz, 1 H), 3.96 (s, 3 H), 2.55 (t, *J* = 7.1 Hz, 2 H), 1.74 (*sext*, *J* = 7.3 Hz, 2 H), 1.10 (t, *J* = 7.4 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.24 (CH), 163.7 (C), 152.4 (C), 145.3 (C), 136.2 (CH), 130.8 (CH), 127.4 (C), 121.8 (C), 121.7 (CH), 107.1 (CH), 97.8 (C), 77.8 (C), 55.9 (CH_3), 21.9 (CH_2), 21.8 (CH_2), 13.9 (CH_3).

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{16}H_{15}NO_2Na$: 276.1000; found: 276.0990.

7-Methoxy-2-(oct-1-ynyl)quinoline-3-carbaldehyde (1n)

The crude product obtained by method B was purified by column chromatography (silica gel, cyclohexane–EtOAc (0.5% Et_3N), 1:0 to 8:2); this afforded an ochre solid; yield: 135 mg (80%); mp 61–63 °C.

IR (neat): 2933, 2855, 2225, 1689, 1620, 1582, 1495, 1445, 1388, 1375, 1309, 1227, 1134, 1014, 875, 842, 814, 763, 708 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 10.63 (s, 1 H), 8.60 (s, 1 H), 7.80 (d, *J* = 9.0 Hz, 1 H), 7.42 (s, 1 H), 7.23 (d, *J* = 8.9 Hz, 1 H), 3.96 (s, 3 H), 2.57 (t, *J* = 7.1 Hz, 2 H), 1.71 (quin, *J* = 7.1 Hz, 2 H), 1.55–1.44 (m, 2 H), 1.39–1.29 (m, 4 H), 0.97–0.87 (m, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.3 (CH), 163.7 (C), 152.5 (C), 145.4 (C), 136.2 (CH), 130.8 (CH), 127.5 (C), 121.8 (C), 121.7 (CH), 107.2 (CH), 98.1 (C), 77.7 (C), 55.9 (CH_3), 31.5 (CH_2), 28.9 (CH_2), 28.4 (CH_2), 22.7 (CH_2), 19.8 (CH_2), 14.2 (CH_3).

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{19}H_{21}NO_2Na$: 318.1470; found: 318.1465.

2-(3-Methoxyprop-1-ynyl)benzo[*h*]quinoline-3-carbaldehyde (1o)

The crude product obtained by method D was purified by column chromatography on basic alumina gel (CH_2Cl_2–MeOH, 1:0 to 9:1); this afforded a light yellow solid; yield: 720 mg (65%); mp 147–149 °C.

IR (neat): 3056, 2930, 2823, 2223, 1687, 1578, 1558, 1488, 1442, 1402, 1382, 1363, 1328, 1132, 1096, 917, 897, 817, 803, 748 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.74 (s, 1 H), 9.40–9.29 (m, 1 H), 8.68 (s, 1 H), 7.96–7.89 (m, 1 H), 7.87 (d, *J* = 8.9 Hz, 1 H), 7.83–7.71 (m, 3 H), 4.53 (s, 2 H), 3.57 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 190.9 (CH), 149.6 (C), 142.55 (C), 135.7 (CH), 135.01 (C), 130.5 (C), 130.1 (CH), 129.9 (CH), 129.7 (C), 128.1 (CH), 127.9 (CH), 126.0 (CH), 125.6 (CH), 125.4 (C), 91.4 (C), 83.2 (C), 60.6 (CH_2), 58.4 (CH_3).

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{18}H_{13}NO_2Na$: 298.0844; found: 298.0830.

2-(Phenylethynyl)benzo[*h*]quinoline-3-carbaldehyde (1p)

The crude product obtained by method D was purified by column chromatography (silica gel, cyclohexane–EtOAc (1% Et_3N), 95:5 to 8:2); this afforded a light yellow solid; yield: 940 mg (76%); mp 121–123 °C.

IR (neat): 3056, 2850, 2209, 1686, 1578, 1556, 1493, 1443, 1381, 1334, 1168, 995, 925, 817, 802, 743, 680 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.84 (s, 1 H), 9.43–9.35 (m, 1 H), 8.69 (s, 1 H), 7.94–7.89 (m, 1 H), 7.86 (d, *J* = 8.9 Hz, 1 H), 7.82–7.69 (m, 5 H), 7.51–7.39 (m, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.2 (CH), 149.7 (C), 143.3 (C), 135.7 (CH), 135.0 (C), 132.4 (2 × CH), 130.6 (C), 130.1 (CH), 129.9 (CH), 129.8 (CH), 129.7 (C), 128.8 (2 × CH), 128.1 (CH), 127.9 (CH), 126.1 CH), 125.7 (CH), 125.2 (C), 121.8 (C), 95.4 (C), 86.2 (C).

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{22}H_{13}NONa$: 330.0895; found: 330.0889.

2-(Pent-1-ynyl)benzo[*h*]quinoline-3-carbaldehyde (1q)

The crude product obtained by method A was purified by column chromatography (silica gel, CH_2Cl_2–PE (0.5% Et_3N), 3:7 to 6:4); this afforded a beige solid; yield: 146 mg (82%); mp 105–107 °C.

IR (neat): 3051, 2960, 2847, 2230, 1686, 1580, 1558, 1499, 1486, 1402, 1377, 1327, 1136, 984, 934, 823, 800, 749, 739, 714 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.74 (s, 1 H), 9.39–9.30 (m, 1 H), 8.64 (s, 1 H), 7.92–7.86 (m, 1 H), 7.82 (d, *J* = 8.8 Hz, 1 H), 7.79–7.69 (m, 3 H), 2.61 (t, *J* = 7.0 Hz, 2 H), 1.79 (*sext*, *J* = 7.2, 6.6 Hz, 2 H), 1.14 (t, *J* = 7.3 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.6 (CH), 149.6 (C), 144.0 (C), 135.5 (CH), 135.0 (C), 130.6 (C), 130.0 (CH), 129.7 (C), 129.4 (CH), 128.0 (CH), 127.7 (CH), 126.0 (CH), 125.7 (CH), 125.0 (C), 97.8 (C), 78.2 (C), 22.0 (CH_2), 21.9 (CH_2), 13.9 (CH_3).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{19}H_{16}NO$: 274.1232; found: 274.1224.

2-(Oct-1-ynyl)benzo[*h*]quinoline-3-carbaldehyde (1r)

The crude product obtained by method A was purified by column chromatography (silica gel, cyclohexane–EtOAc (0.5% Et_3N), 1:0 to 95:5); this afforded a beige solid; yield: 171 mg (83%); mp 72–74 °C.

IR (neat): 3051, 2930, 2849, 2227, 1687, 1579, 1558, 1486, 1402, 1377, 1327, 1137, 993, 935, 823, 800, 749, 715 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.74 (s, 1 H), 9.39–9.30 (m, 1 H), 8.65 (s, 1 H), 7.93–7.87 (m, 1 H), 7.84 (d, *J* = 8.8 Hz, 1 H), 7.79–7.70 (m, 3 H), 2.63 (t, *J* = 7.1 Hz, 2 H), 1.75 (quin, *J* = 7.2 Hz, 2 H), 1.63–1.49 (m, 2 H), 1.37 (s, 4 H), 0.98–0.90 (m, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.7 (CH), 149.7 (C), 144.0 (C), 135.5 (CH), 135.0 (C), 130.6 (C), 130.0 (CH), 129.7 (C), 129.4 (CH), 128.1 (CH), 127.7 (CH), 126.0 (CH), 125.7 (CH), 125.0 (C), 98.1 (C), 78.0 (C), 31.5 (CH_2), 29.0 (CH_2), 28.5 (CH_2), 22.7 (CH_2), 20.0 (CH_2), 14.2 (CH_3).

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{22}H_{21}NONa$: 338.1521; found: 338.1515.

Silver-Catalyzed Domino Hydroarylation–Cycloisomerization; General Procedure

The nucleophilic moiety NuH (3 equiv) and AgOTf (10 mol%) were added to a 0.2 M solution or suspension of the appropriate *ortho*-alkynylquinolinecarbaldehyde (1 equiv) in anhyd distilled DCE (1 mL) under argon. The mixture was stirred at reflux temperature and the reaction was monitored by TLC analysis until completion (1–24 h). Then, the reaction mixture was filtered through a short pad of silica and Celite and eluted with a CH_2Cl_2–MeOH mixture (90:10). The crude was concentrated under reduced pressure and purified by column chromatography (silica gel, various solvent mixtures).

3-Phenyl-1-(2,4,6-trimethoxyphenyl)-1*H*-pyrano[4,3-*b*]quinoline (2b)

The reaction was carried out at 50 °C in DMF instead of DCE. The crude product was purified by column chromatography (silica gel, cyclohexane–EtOAc, 1:0 to 8:2); this afforded a yellow solid; yield: 31 mg (36%); mp 191–193 °C.

IR (neat): 2970, 2899, 1608, 1417, 1226, 1123 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.96 (d, *J* = 8.0 Hz, 1 H), 7.83–7.78 (m, 2 H), 7.61–7.51 (m, 2 H), 7.40–7.26 (m, 5 H), 7.10 (s, 1 H), 6.74 (s, 1 H), 6.25 (s, 2 H), 3.89 (s, 3 H), 3.71 (s, 6 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 162.1 (C), 160.7 (C), 160.4 (2 × C), 152.5 (C), 147.8 (C), 134.4 (C), 129.6 (CH), 129.2 (CH), 128.9 (CH), 128.3 (2 × CH), 128.2 (CH), 127.9 (C), 127.7 (C), 127.4 (CH), 125.8 (2 × CH), 124.8 (CH), 107.8 (C), 101.0 (CH), 91.2 (2 × CH), 72.9 (CH), 56.0 (2 × CH_3), 55.4 (CH_3).

HRMS (CI): *m*/*z* [M + H]$^+$ calcd for $C_{27}H_{24}NO_4$: 426.1700; found: 426.1689.

10-Phenyl-8-(2,4,6-trimethoxyphenyl)-8*H*-benzo[*h*]pyrano[4,3-*b*]quinoline (2p)

The reaction was carried out at 80 °C in DMF instead of DCE, and at 0.5 M reaction media concentration. The crude product was purified by column chromatography (silica gel, cyclohexane–EtOAc, 1:0 to 1:1); this afforded an orange solid; yield: 128 mg (54%); mp 227–229 °C.

IR (neat): 3048, 2940, 2841, 1592, 1490, 1451, 1419, 1407, 1215, 1201, 1156, 1150, 1121, 1040, 1025, 810, 767, 746, 687 cm^{-1}.

^{1}H NMR (400 MHz, DMSO-d_6): δ = 9.17 (d, J = 8.0 Hz, 1 H), 7.97 (d, J = 7.2 Hz, 1 H), 7.85–7.77 (m, 2 H), 7.78–7.65 (m, 4 H), 7.49–7.40 (m, 4 H), 7.06 (s, 1 H), 6.90 (s, 1 H), 6.41 (s, 2 H), 3.87 (s, 3 H), 3.69 (s, 6 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 162.1 (C), 160.0 (C), 159.1 (2 × C), 150.5 (C), 144.7 (C), 133.6 (C), 133.3 (C), 130.5 (C), 129.8 (CH), 129.3 (CH), 128.6 (2 × CH), 127.9 (CH), 127.8 (CH), 127.3 (C), 126.6 (CH), 125.8 (CH), 125.7 (CH), 125.3 (2 × CH), 124.7 (C), 123.8 (CH), 106.4 (C), 101.3 (CH), 91.7 (2 × CH), 72.5 (CH), 56.0 (2 × CH_3), 55.4 (CH_3).

HRMS (ESI): m/z [M + H]$^+$ calcd for $C_{31}H_{26}NO_4$: 476.1862; found: 476.1855.

3-(Methoxymethyl)-1-(1-methyl-1*H*-indol-3-yl)-1*H*-pyrano[4,3-*b*]quinoline (3a)

The crude product was purified by column chromatography (silica gel, cyclohexane–EtOAc, 8:2 to 6:4); this afforded an orange solid; yield: 59 mg (83%); mp 81–83 °C.

IR (neat): 3051, 2932, 2823, 1638, 1615, 1559, 1476, 1463, 1424, 1303, 1197, 1107, 993, 968, 818, 754, 736 cm^{-1}.

^{1}H NMR (400 MHz, DMSO-d_6): δ = 7.90 (d, J = 8.5 Hz, 1 H), 7.75 (d, J = 8.1 Hz, 1 H), 7.70 (s, 1 H), 7.65 (tt, J = 8.2, 1.5 Hz, 1 H), 7.51 (d, J = 8.0 Hz, 1 H), 7.47 (d, J = 8.2 Hz, 1 H), 7.40 (tt, J = 8.2, 1.4 Hz, 1 H), 7.25 (s, 1 H), 7.19 (t, J = 7.6 Hz, 1 H), 7.02 (t, J = 7.5 Hz, 1 H), 6.85 (s, 1 H), 6.22 (s, 1 H), 3.99 (d, J = 14.1 Hz, 1 H), 3.92 (d, J = 14.1 Hz, 1 H), 3.77 (s, 3 H), 3.24 (s, 3 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 160.5 (C), 150.6 (C), 147.5 (C), 137.1 (C), 131.3 (CH), 130.3 (CH), 129.5 (CH), 128.0 (CH), 127.9 (CH), 127.0 (C), 125.9 (C), 125.8 (C), 125.3 (CH), 121.6 (CH), 119.7 (CH), 119.3 (CH), 111.8 (C), 110.2 (CH), 103.2 (CH), 74.3 (CH), 70.7 (CH_2), 57.8 (CH_3), 32.5 (CH_3).

HRMS (ESI): m/z [M + Na]$^+$ calcd for $C_{23}H_{20}N_2O_2Na$: 379.1422; found: 379.1430.

1-(1-Methyl-1*H*-indol-3-yl)-3-phenyl-1*H*-pyrano[4,3-*b*]quinoline (3b)

The crude product was purified by column chromatography (silica gel, cyclohexane–EtOAc, 9:1 to 6:4); this afforded an orange oil (78 mg, quant).

IR (neat): 3057, 2932, 1675, 1609, 1576, 1553, 1492, 1468, 1448, 1364, 1235, 1221, 1047, 907, 729, 690 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.07 (d, J = 8.4 Hz, 1 H), 7.83–7.74 (m, 3 H), 7.70–7.56 (m, 3 H), 7.42–7.26 (m, 6 H), 7.17 (t, J = 7.6 Hz, 1 H), 6.93 (s, 1 H), 6.89 (s, 1 H), 6.85 (s, 1 H), 3.74 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 159.9 (C), 152.2 (C), 148.1 (C), 137.6 (C), 134.1 (C), 131.8 (CH), 130.0 (CH), 129.8 (CH), 129.8 (CH), 128.5 (2 × CH), 128.3 (CH), 127.9 (CH), 127.5 (C), 126.7 (C), 126.2 (C), 126.1 (2 × CH), 125.4 (CH), 122.4 (CH), 120.3 (CH), 120.0 (CH), 112.5 (C), 109.8 (CH), 102.1 (CH), 74.9 (CH), 33.0 (CH_3).

HRMS (ESI): m/z [M + H]$^+$ calcd for $C_{27}H_{21}N_2O$: 389.1654; found: 389.1667.

3-Cyclopropyl-1-(1-methyl-1*H*-indol-3-yl)-1*H*-pyrano[4,3-*b*]quinoline (3c)

The crude product was purified by column chromatography (silica gel, cyclohexane–EtOAc, 1:0 to 7:3); this afforded a pale yellow solid; yield: 62 mg (89%); mp 189–190 °C.

IR (neat): 3047, 2923, 2851, 1611, 1603, 1557, 1493, 1477, 1418, 1304, 1286, 1053, 1028, 965, 949, 809, 798, 752, 740 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.98 (d, J = 8.4 Hz, 1 H), 7.66 (d, J = 7.9 Hz, 1 H), 7.61 (t, J = 7.6 Hz, 1 H), 7.54 (d, J = 8.2 Hz, 1 H), 7.51 (s, 1 H), 7.34 (t, J = 6.2 Hz, 2 H), 7.31–7.26 (m, 1 H), 7.14 (t, J = 7.3 Hz, 1 H), 6.78 (s, 1 H), 6.60 (s, 1 H), 6.18 (s, 1 H), 3.73 (s, 3 H), 1.68–1.57 (m, 1 H), 1.01–0.91 (m, 1 H), 0.81–0.70 (m, 2 H), 0.70–0.59 (m, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.8 (C), 152.3 (C), 148.3 (C), 137.6 (C), 131.4 (CH), 129.5 (2 × CH), 128.4 (CH), 127.8 (CH), 127.2 (C), 126.7 (C), 125.6 (C), 124.8 (CH), 122.4 (CH), 120.2 (CH), 120.0 (CH), 112.9 (C), 109.7 (CH), 101.2 (CH), 74.7 (CH), 33.0 (CH_3), 14.8 (CH), 6.5 (2 × CH_2).

HRMS (ESI): m/z [M + H]$^+$ calcd for $C_{24}H_{21}N_2O$: 353.1654; found: 353.1642.

1-(1-Methyl-1*H*-indol-3-yl)-3-propyl-1*H*-pyrano[4,3-*b*]quinoline (3d)

The crude product was purified by column chromatography (silica gel, cyclohexane–EtOAc, 1:0 to 7:3); this afforded an orange oil; yield: 67 mg (94%).

IR (neat): 3058, 2961, 2931, 2873, 1612, 1557, 1465, 1424, 1371, 1152, 976, 907, 727 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.98 (d, J = 8.4 Hz, 1 H), 7.66 (d, J = 8.0 Hz, 1 H), 7.61 (ddd, J = 8.4, 6.8, 1.5 Hz, 1 H), 7.54 (d, J = 7.9 Hz, 1 H), 7.51 (s, 1 H), 7.38–7.27 (m, 3 H), 7.12 (t, J = 7.5 Hz, 1 H), 6.92 (s, 1 H), 6.64 (s, 1 H), 6.11 (s, 1 H), 3.77 (s, 3 H), 2.24 (t, J = 7.5 Hz, 2 H), 1.64–1.50 (m, 7.1 Hz, 2 H), 0.87 (t, J = 7.4 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.7 (C), 151.7 (C), 146.3 (C), 137.7 (C), 132.7 (CH), 130.2 (CH), 129.6 (CH), 127.8 (CH), 127.2 (CH), 127.1 (C) 126.6 (C), 125.7 (C), 125.5 (CH), 122.5 (CH), 120.4 (CH), 120.1 (CH), 112.4 (C), 109.8 (CH), 101.7 (CH), 74.9 (CH), 36.7 (CH_2), 33.1 (CH_3), 20.1 (CH_2), 13.7 (CH_3).

HRMS (ESI): m/z [M + H]$^+$ calcd for $C_{24}H_{23}N_2O$: 355.1810; found: 355.1809.

3-Isobutyl-1-(1-methyl-1*H*-indol-3-yl)-1*H*-pyrano[4,3-b]quinoline (3e)

The crude product was purified by column chromatography (silica gel, cyclohexane–EtOAc, 1:0 to 6:4); this afforded a yellow oil; yield: 59 mg (80%).

IR (neat): 3052, 2955, 2927, 2868, 1632, 1615, 1558, 1495, 1463, 1422, 1304, 1152, 980, 907, 852, 816, 803, 752, 739, 729 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.00 (d, J = 8.2 Hz, 1 H), 7.69–7.48 (m, 4 H), 7.40–7.27 (m, 3 H), 7.12 (t, J = 7.4 Hz, 1 H), 6.93 (s, 1 H), 6.63 (s, 1 H), 6.12 (s, 1 H), 3.77 (s, 3 H), 2.23–2.07 (m, 2 H), 2.00–1.85 (m, 1 H), 0.93 (d, J = 6.6 Hz, 3 H), 0.80 (d, J = 6.6 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 165.1 (C), 152.3 (C), 148.1 (C), 137.6 (C), 131.7 (CH), 129.6 (CH), 129.5 (CH), 128.3 (CH), 127.8 (CH), 127.4 (C), 126.6 (C), 125.7 (C), 125.0 (CH), 122.3 (CH), 120.5 (CH), 120.0 (CH), 112.6 (C), 109.7 (CH), 103.9 (CH), 74.8 (CH), 44.0 (CH_2), 33.0 (CH_3), 26.5 (CH), 22.6 (CH_3), 22.3 (CH_3).

HRMS (ESI): m/z [M + H]$^+$ calcd for $C_{25}H_{25}N_2O$: 369.1967; found: 369.1961.

3-Hexyl-1-(1-methyl-1*H*-indol-3-yl)-1*H*-pyrano[4,3-*b*]quinoline (3f)

The crude product was purified by column chromatography (silica gel, cyclohexane–EtOAc, 1:0 to 6:4); this afforded a brownish oil; yield: 73 mg (92%).

IR (neat): 3059, 2954, 2926, 2856, 1611, 1466, 1371, 1152, 1093, 980, 908, 730 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.01 (d, *J* = 8.4 Hz, 1 H), 7.68 (d, *J* = 7.9 Hz, 1 H), 7.62 (t, *J* = 7.7 Hz, 1 H), 7.57–7.52 (m, 2 H), 7.35 (t, *J* = 7.9 Hz, 2 H), 7.29 (d, *J* = 7.3 Hz, 1 H), 7.13 (t, *J* = 7.4 Hz, 1 H), 6.86 (s, 1 H), 6.65 (s, 1 H), 6.14 (s, 1 H), 3.75 (s, 3 H), 2.33–2.19 (m, 2 H), 1.50 (quin, *J* = 7.2 Hz, 2 H), 1.29–1.04 (m, 6 H), 0.82 (t, *J* = 6.8 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.3 (C), 152.1 (C), 147.7 (C), 137.7 (C), 131.9 (CH), 129.7 (CH), 129.6 (CH), 128.1 (CH), 127.8 (CH), 127.3 (C), 126.6 (C), 125.7 (C), 125.1 (CH), 122.4 (CH), 120.5 (CH), 120.0 (CH), 112.8 (C), 109.7 (CH), 102.6 (CH), 74.8 (CH), 34.6 (CH_2), 33.0 (CH_3), 31.6 (CH_2), 28.8 (CH_2), 26.6 (CH_2), 22.7 (CH_2), 14.2 (CH_3).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{27}H_{29}N_2O$: 397.2280; found: 397.2272.

7-Chloro-3-(methoxymethyl)-1-(1-methyl-1*H*-indol-3-yl)-1*H*-pyrano[4,3-*b*]quinoline (3g)

The crude product was purified by column chromatography (silica gel, cyclohexane–EtOAc, 1:0 to 75:25); this afforded a brownish oil; yield: 73 mg (93%).

IR (neat): 3057, 2915, 2805, 1641, 1610, 1596, 1558, 1479, 1466, 1374, 1107, 1067, 983, 927, 922, 807, 750, 738, 720 cm^{-1}.

^{1}H NMR (400 MHz $CDCl_3$): δ = 8.18 (s, 1 H), 7.64–7.54 (m, 2 H), 7.50 (d, *J* = 8.6 Hz, 1 H), 7.36 (t, *J* = 9.9 Hz, 2 H), 7.32–7.27 (m, 1 H), 7.12 (t, *J* = 7.5 Hz, 1 H), 7.00 (s, 1 H), 6.71 (s, 1 H), 6.56 (s, 1 H), 4.08 (d, *J* = 14.6 Hz, 1 H), 3.98 (d, *J* = 14.5 Hz, 1 H), 3.79 (s, 3 H), 3.37 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.2 (C), 151.3 (C), 145.3 (C), 137.7 (C), 137.0 (C), 133.8 (CH), 130.1 (CH), 129.1 (CH), 127.2 (CH), 126.2 (C), 126.0 (C), 125.6 (CH), 125.4 (C), 122.7 (CH), 120.3 (CH), 120.3 (CH), 111.2 (C), 109.9 (CH), 101.1 (CH), 75.4 (CH), 71.5 (CH_2), 59.1 (CH_3), 33.2 (CH_3).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{23}H_{20}ClN_2O_2$: 391.1208; found: 391.1198.

7-Chloro-1-(1-methyl-1*H*-indol-3-yl)-3-phenyl-1*H*-pyrano[4,3-*b*]quinoline (3h)

The crude product was purified by column chromatography (silica gel, cyclohexane–EtOAc, 1:0 to 85:15); this afforded an orange oil (83 mg, quant).

IR (neat): 3056, 2933, 1607, 1595, 1574, 1489, 1475, 1450, 1416, 1216, 1067, 1044, 1025, 942, 739, 688 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.08 (s, 1 H), 7.79–7.75 (m, 2 H), 7.74 (d, *J* = 8.0 Hz, 1 H), 7.57 (s, 1 H), 7.48 (d, *J* = 8.6 Hz, 1 H), 7.41–7.27 (m, 6 H), 7.16 (t, *J* = 7.4 Hz, 1 H), 6.94 (s, 2 H), 6.81 (s, 1 H), 3.75 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.2 (C), 152.9 (C), 147.7 (C), 137.6 (C), 135.8 (C), 133.7 (C), 132.0 (CH), 130.4 (CH), 129.8 (CH), 129.0 (CH), 128.6 (2 × CH), 126.8 (CH), 126.6 (C), 126.4 (C), 126.4 (CH), 126.3 (2 × CH), 125.7 (C), 122.5 (CH), 120.2 (CH), 120.2 (CH), 112.0 (C), 109.8 (CH), 101.2 (CH), 75.0 (CH), 33.0 (CH_3).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{27}H_{20}ClN_2O$: 423.1259; found: 423.1241.

7-Chloro-1-(1-methyl-1*H*-indol-3-yl)-3-propyl-1*H*-pyrano[4,3-*b*]quinoline (3i)

The crude product was purified by column chromatography (silica gel, cyclohexane–EtOAc, 1:0 to 9:1); this afforded a yellow solid; yield: 70 mg (95%); mp 164–166 °C.

IR (neat): 3048, 2959, 2929, 2869, 1630, 1614, 1596, 1557, 1478, 1464, 1336, 1066, 970, 919, 891, 809, 741, 720 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.03 (s, 1 H), 7.61 (d, *J* = 8.0 Hz, 1 H), 7.48 (s, 1 H), 7.45 (d, *J* = 8.7 Hz, 1 H), 7.37 (d, *J* = 8.3 Hz, 1 H), 7.31–7.27 (m, 2 H), 7.12 (t, *J* = 7.5 Hz, 1 H), 6.96 (s, 1 H), 6.61 (s, 1 H), 6.18 (s, 1 H), 3.79 (s, 3 H), 2.27 (t, *J* = 7.5 Hz, 2 H), 1.58 (*sext*, *J* = 7.1 Hz, 2 H), 0.88 (t, *J* = 7.4 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.3 (C), 152.6 (C), 146.9 (C), 137.7 (C), 136.0 (C), 132.4 (CH), 129.7 (CH), 129.0 (CH), 126.4 (C), 126.3 (2 × CH), 125.9 (C), 125.5 (C), 122.5 (CH), 120.4 (CH), 120.1 (CH), 112.0 (C), 109.8 (CH), 101.6 (CH), 75.0 (CH), 36.7 (CH_2), 33.1 (CH_3), 20.1 (CH_2), 13.7 (CH_3).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{24}H_{22}ClN_2O$: 389.1415; found: 389.1409.

7-Chloro-3-hexyl-1-(1-methyl-1*H*-indol-3-yl)-1*H*-pyrano[4,3-*b*]quinoline (3j)

The crude product was purified by column chromatography (silica gel, cyclohexane–EtOAc, 1:0 to 9:1); this afforded a white solid; yield: 80 mg (93%); mp 116–118 °C.

IR (neat): 3052, 2949, 2927, 2860, 1615, 1596, 1545, 1464, 1442, 1413, 1369, 1334, 1234, 1069, 1000, 987, 929, 893, 805, 772, 735 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.94 (s, 1 H), 7.61 (d, *J* = 8.0 Hz, 1 H), 7.45–7.39 (m, 2 H), 7.32 (d, *J* = 8.3 Hz, 1 H), 7.23 (d, *J* = 8.3 Hz, 2 H), 7.09 (t, *J* = 7.5 Hz, 1 H), 6.85 (s, 1 H), 6.58 (s, 1 H), 6.05 (s, 1 H), 3.73 (s, 3 H), 2.30–2.16 (m, 2 H), 1.47 (quin, *J* = 7.1 Hz, 2 H), 1.27–1.08 (m, 6 H), 0.79 (t, *J* = 6.7 Hz, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 166.9 (C), 153.2 (C), 148.5 (C), 137.7 (C), 135.3 (C), 131.4 (CH), 129.5 (CH), 128.9 (CH), 127.4 (CH), 126.6 (C), 125.9 (CH), 125.9 (C), 125.7 (C), 122.5 (CH), 120.4 (CH), 120.0 (CH), 112.6 (C), 109.7 (CH), 102.6 (CH), 74.8 (CH), 34.7 (CH_2), 33.0 (CH_3), 31.6 (CH_2), 28.8 (CH_2), 26.6 (CH_2), 22.6 (CH_2), 14.1 (CH_3).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{27}H_{28}ClN_2O$: 431.1885; found: 431.1872.

7-Methoxy-3-(methoxymethyl)-1-(1-methyl-1*H*-indol-3-yl)-1*H*-pyrano[4,3-*b*]quinoline (3k)

The crude product was purified by column chromatography (silica gel, cyclohexane–EtOAc, 8:2 to 4:6); this afforded a light yellow solid; yield: 81 mg (67%); mp 68–70 °C.

IR (neat): 3075, 2932, 2826, 1645, 1615, 1553, 1504, 1476, 1445, 1364, 1235, 1218, 1193, 1130, 1111, 1027, 840, 811, 744, 721 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.65 (d, *J* = 7.9 Hz, 1 H), 7.46 (s, 1 H), 7.44–7.36 (m, 2 H), 7.33 (d, *J* = 8.2 Hz, 1 H), 7.30–7.23 (m, 1 H), 7.10 (t, *J* = 7.4 Hz, 1 H), 7.01 (d, *J* = 9.0 Hz, 1 H), 6.89 (s, 1 H), 6.66 (s, 1 H), 6.35 (s, 1 H), 4.05 (d, *J* = 14.2 Hz, 1 H), 3.99–3.88 (m, 4 H), 3.72 (s, 3 H), 3.36 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.9 (C), 160.5 (C), 151.5 (C), 149.7 (C), 137.6 (C), 131.6 (CH), 129.7 (CH), 128.7 (CH), 126.5 (C), 123.5 (C), 122.5 (C), 122.3 (CH), 120.4 (CH), 119.9 (CH), 118.1 (CH), 112.5 (C), 109.6 (CH), 107.0 (CH), 103.9 (CH), 75.2 (CH), 71.7 (CH_2), 58.7 (CH_3), 55.5 (CH_3), 32.9 (CH_3).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{24}H_{23}N_2O_3$: 387.1703; found: 387.1697.

7-Methoxy-1-(1-methyl-1*H*-indol-3-yl)-3-phenyl-1*H*-pyrano[4,3-*b*]quinoline (3l)

The crude product was purified by column chromatography (silica gel, cyclohexane–EtOAc, 9:1 to 1:1); this afforded an orange oil; yield: 60 mg (71%).

IR (neat): 3057, 2929, 2850, 1605, 1575, 1542, 1501, 1447, 1421, 1377, 1344, 1234, 1207, 1152, 1130, 1044, 1024, 811, 739, 691 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.83–7.71 (m, 3 H), 7.60 (s, 1 H), 7.54 (s, 1 H), 7.49 (d, *J* = 8.9 Hz, 1 H), 7.41–7.27 (m, 5 H), 7.16 (t, *J* = 7.4 Hz, 1 H), 7.06 (dd, *J* = 8.9, 2.4 Hz, 1 H), 7.02 (s, 1 H), 6.92 (s, 1 H), 6.84 (s, 1 H), 3.97 (s, 3 H), 3.76 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.1 (C), 159.6 (C), 152.4 (C), 149.9 (C), 137.6 (C), 134.3 (C), 131.5 (CH), 129.8 (CH), 129.7 (CH), 128.8 (CH), 128.5 (2 × CH), 126.9 (C), 126.1 (2 × CH), 123.9 (C), 122.5 (C), 122.4 (CH), 120.3 (CH), 120.0 (CH), 118.2 (CH), 113.0 (C), 109.7 (CH), 107.0 (CH), 102.2 (CH), 75.0 (CH), 55.6 (CH_3), 33.0 (CH_3).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{28}H_{23}N_2O_2$: 419.1754; found: 419.1739.

7-Methoxy-1-(1-methyl-1*H*-indol-3-yl)-3-propyl-1*H*-pyrano[4,3-*b*]quinoline (3m)

The crude product was purified by column chromatography (silica gel, cyclohexane–EtOAc, 1:0 to 6:4); this afforded an orange oil; yield: 61 mg (79%).

IR (neat): 3055, 3006, 2960, 2932, 2872, 2831, 1611, 1558, 1503, 1465, 1447, 1237, 1218, 1140, 1028, 983, 810, 739 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.66 (d, *J* = 7.9 Hz, 1 H), 7.42–7.30 (m, 4 H), 7.29–7.22 (m, 1 H), 7.11 (t, *J* = 7.4 Hz, 1 H), 6.98 (dd, *J* = 8.8, 1.9 Hz, 1 H), 6.87 (s, 1 H), 6.58 (s, 1 H), 6.11 (s, 1 H), 3.92 (s, 3 H), 3.70 (s, 3 H), 2.25 (t, *J* = 7.5 Hz, 2 H), 1.66–1.49 (m, 2 H), 0.88 (t, *J* = 7.4 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.5 (C), 160.8 (C), 152.3 (C), 149.6 (C), 137.5 (C), 131.3 (CH), 129.4 (CH), 128.6 (CH), 126.5 (C), 123.2 (C), 122.2 (CH), 120.4 (CH), 119.7 (CH), 117.5 (CH), 112.7 (C), 109.5 (CH), 106.8 (CH), 102.6 (CH), 74.8 (CH), 55.4 (CH_3), 36.4 (CH_2), 32.8 (CH_3), 19.9 (CH_2), 13.6 (CH_3).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{25}H_{25}N_2O_2$: 385.1911; found: 385.1896.

3-Hexyl-7-methoxy-1-(1-methyl-1*H*-indol-3-yl)-1*H*-pyrano[4,3-*b*]quinoline (3n)

The crude product was purified by column chromatography (silica gel, cyclohexane–EtOAc, 1:0 to 7:3); this afforded an orange oil; yield: 65 mg (76%).

IR (neat): 3059, 3007, 2953, 2928, 2856, 1612, 1557, 1504, 1465, 1446, 1235, 1216, 1140, 1027, 810, 738 cm^{-1}.

1 H NMR (400 MHz, $CDCl_3$): δ = 7.67 (d, *J* = 7.9 Hz, 1 H), 7.50–7.40 (m, 2 H), 7.41–7.31 (m, 2 H), 7.32–7.23 (m, 1 H), 7.11 (t, *J* = 7.4 Hz, 1 H), 6.99 (d, *J* = 8.8 Hz, 1 H), 6.84 (s, 1 H), 6.61 (s, 1 H), 6.08 (s, 1 H), 3.92 (s, 3 H), 3.73 (s, 3 H), 2.25 (sept, *J* = 7.3 Hz, 2 H), 1.49 (quin, *J* = 7.3 Hz, 2 H), 1.33–1.01 (m, 6 H), 0.82 (t, *J* = 6.4 Hz, 3 H).

13C NMR (100 MHz, $CDCl_3$): δ = 165.9 (C), 160.9 (C), 152.3 (C), 149.5 (C), 137.6 (C), 131.5 (CH), 129.5 (CH), 128.7 (CH), 126.6 (C), 123.1 (C), 122.3 (CH), 122.2 (C), 120.5 (CH), 119.9 (CH), 117.7 (CH), 113.0 (C), 109.6 (CH), 106.7 (CH), 102.5 (CH), 74.7 (CH), 55.6 (CH_3), 34.6 (CH_2), 32.9 (CH_3), 31.6 (CH_2), 28.8 (CH_2), 26.6 (CH_2), 22.6 (CH_2), 14.1 (CH_3).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{28}H_{31}N_2O_2$: 427.2380; found: 427.2368.

10-(Methoxymethyl)-8-(1-methyl-1*H*-indol-3-yl)-8*H*-benzo[*h*]pyrano[4,3-*b*]quinoline (3o)

The crude product was purified by column chromatography (silica gel, cyclohexane–EtOAc, 1:0 to 8:2); this afforded a light yellow solid; yield: 60 mg (74%); mp 170–172 °C.

IR (neat): 3073, 2929, 2850, 1652, 1600, 1560, 1476, 1446, 1399, 1388, 1202, 1115, 997, 818, 804, 753, 741 cm^{-1}.

^1H NMR (400 MHz, DMSO-d_6): δ = 9.18 (d, *J* = 7.5 Hz, 1 H), 7.97 (d, *J* = 7.2 Hz, 1 H), 7.81–7.64 (m, 5 H), 7.56 (d, *J* = 7.9 Hz, 1 H), 7.46 (d, *J* = 8.2 Hz, 1 H), 7.23 (s, 1 H), 7.19 (t, *J* = 7.6 Hz, 1 H), 7.03 (t, *J* = 7.5 Hz, 1 H), 6.92 (s, 1 H), 6.37 (s, 1 H), 4.01 (d, *J* = 14.1 Hz, 1 H), 3.95 (d, *J* = 14.1 Hz, 1 H), 3.75 (s, 3 H), 3.25 (s, 3 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 159.8 (C), 149.4 (C), 145.0 (C), 137.1 (C), 133.3 (C), 131.6 (CH), 130.5 (C), 130.2 (CH), 127.9 (CH), 127.8 (CH), 126.6 (CH), 125.9 (CH), 125.9 (C), 125.7 (C), 125.5 (CH), 124.7 (C), 123.8 (CH), 121.6 (CH), 119.6 (CH), 119.3 (CH), 112.1 (C), 110.0 (CH), 103.4 (CH), 74.1 (CH), 70.7 (CH_2), 57.8 (CH_3), 32.4 (CH_3).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{27}H_{23}N_2O_2$: 407.1754; found: 407.1740.

8-(1-Methyl-1*H*-indol-3-yl)-10-phenyl-8*H*-benzo[*h*]pyrano[4,3-*b*]quinoline (3p)

The crude product was purified by column chromatography (silica gel, cyclohexane–EtOAc, 1:0 to 9:1); this afforded a light brown solid; yield: 79 mg (90%); mp 118–120 °C.

IR (neat): 3049, 2930, 1615, 1598, 1575, 1490, 1450, 1427, 1392, 1334, 1258, 1045, 1025, 813, 766, 739, 688 cm^{-1}.

^1H NMR (400 MHz, DMSO-d_6): δ = 9.24 (d, *J* = 7.8 Hz, 1 H), 8.01 (d, *J* = 7.6 Hz, 1 H), 7.95 (s, 1 H), 7.85–7.71 (m, 7 H), 7.46 (d, *J* = 8.2 Hz, 1 H), 7.43–7.36 (m, 3 H), 7.20 (t, *J* = 7.7 Hz, 1 H), 7.16 (s, 1 H), 7.12–7.07 (m, 2 H), 7.05 (s, 1 H), 3.72 (s, 3 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 157.4 (C), 150.1 (C), 145.4 (C), 137.1 (C), 133.6 (C), 133.4 (C), 131.7 (CH), 130.5 (C), 130.3 (CH), 129.8 (CH), 128.5 (2 × CH), 128.1 (CH), 127.9 (CH), 126.8 (CH), 126.1 (C), 126.1 (CH), 125.8 (C), 125.7 (CH), 125.4 (2 × CH), 124.8 (C), 123.9 (CH), 121.7 (CH), 119.5 (CH), 119.5 (CH), 112.4 (C), 110.2 (CH), 102.2 (CH), 73.8 (CH), 32.4 (CH_3).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{31}H_{23}N_2O$: 439.1810; found: 439.1794.

8-(1-Methyl-1*H*-indol-3-yl)-10-propyl-8*H*-benzo[*h*]pyrano[4,3-*b*]quinoline (3q)

The crude product was purified by column chromatography (silica gel, cyclohexane–EtOAc, 1:0 to 95:5); this afforded an orange solid; yield: 76 mg (94%); mp 138–140 °C.

IR (neat): 3056, 2957, 2928, 2871, 1638, 1603, 1557, 1478, 1464, 1446, 1393, 1374, 1335, 1301, 1141, 1067, 975, 816, 804, 753, 741 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 9.31 (d, *J* = 7.7 Hz, 1 H), 7.86 (d, *J* = 7.3 Hz, 1 H), 7.75–7.60 (m, 4 H), 7.56 (s, 1 H), 7.46 (d, *J* = 8.8 Hz, 1 H), 7.36 (d, *J* = 8.2 Hz, 1 H), 7.32–7.26 (m, 1 H), 7.13 (ddd, *J* = 8.0, 6.9, 1.2 Hz, 1 H), 6.90 (s, 1 H), 6.72 (s, 1 H), 6.24 (s, 1 H), 3.76 (s, 3 H), 2.26 (dd, *J* = 8.4, 6.6 Hz, 2 H), 1.65–1.51 (m, 2 H), 0.87 (t, *J* = 7.3 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.7 (C), 151.0 (C), 146.1 (C), 137.7 (C), 134.0 (C), 131.7 (CH), 129.7 (C+CH), 127.9 (2 × CH), 126.9 (CH), 126.6 (C), 126.1 (CH), 125.4 (C+CH), 124.9 (C), 124.7 (CH), 122.4 (CH), 120.5 (CH), 120.0 (CH), 112.9 (C), 109.7 (CH), 103.3 (CH), 74.7 (CH), 36.6 (CH_2), 33.0 (CH_3), 20.1 (CH_2), 13.7 (CH_3).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{28}H_{25}N_2O$: 405.1961; found: 405.1949.

10-Hexyl-8-(1-methyl-1*H*-indol-3-yl)-8*H*-benzo[*h*]pyrano[4,3-*b*]quinoline (3r)

The crude product was purified by column chromatography (silica gel, cyclohexane–EtOAc, 1:0 to 98:2); this afforded a light yellow solid; yield: 67 mg (75%); mp 134–136 °C.

IR (neat): 3047, 2954, 2924, 2889, 2855, 1634, 1600, 1543, 1476, 1446, 1424, 1388, 1375, 1334, 1237, 1153, 978, 959, 899, 813, 786, 747, 678 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 9.32 (d, *J* = 7.9 Hz, 1 H), 7.86 (dd, *J* = 7.8, 1.2 Hz, 1 H), 7.76–7.61 (m, 4 H), 7.57 (s, 1 H), 7.47 (d, *J* = 8.8 Hz, 1 H), 7.35 (d, *J* = 8.2 Hz, 1 H), 7.31–7.26 (m, 1 H), 7.14 (ddd, *J* = 8.0, 6.9, 1.2 Hz, 1 H), 6.83 (s, 1 H), 6.74 (s, 1 H), 6.23 (s, 1 H), 3.74 (s, 3 H), 2.39–2.17 (m, 2 H), 1.51 (quin, *J* = 7.2 Hz, 2 H), 1.25–1.00 (m, 6 H), 0.83 (t, *J* = 6.9 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 164.7 (C), 151.1 (C), 146.2 (C), 137.7 (C), 133.9 (C), 131.7 (CH), 131.4 (C), 129.6 (CH), 127.9 (CH), 127.8 (CH), 126.8 (CH), 126.7 (C), 125.9 (CH), 125.6 (CH), 125.2 (C), 124.9 (C), 124.6 (CH), 122.3 (CH), 120.5 (CH), 119.9 (CH), 113.3 (C), 109.6 (CH), 103.3 (CH), 74.6 (CH), 34.6 (CH_2), 33.0 (CH_3), 31.7 (CH_2), 28.9 (CH_2), 26.7 (CH_2), 22.7 (CH_2), 14.2 (CH_3).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{31}H_{31}N_2O$: 447.2431; found: 447.2413.

1-(1*H*-Indol-3-yl)-3-(methoxymethyl)-1*H*-pyrano[4,3-*b*]quinoline (4a)

The crude product was purified by column chromatography (silica gel, cyclohexane–EtOAc, 8:2 to 6:4); this afforded an orange solid; yield: 43 mg (63%); mp 117–119 °C.

IR (neat): 3145, 3060, 2920, 2850, 1644, 1614, 1550, 1496, 1457, 1426, 1354, 1199, 1108, 973, 901, 824, 743 cm^{-1}.

^1H NMR (400 MHz, DMSO-d_6): δ = 11.32 (s, 1 H), 7.94 (d, *J* = 8.4 Hz, 1 H), 7.79 (d, *J* = 8.1 Hz, 1 H), 7.75 (s, 1 H), 7.70 (ddd, *J* = 8.5, 6.9, 1.5 Hz, 1 H), 7.48–7.41 (m, 3 H), 7.37 (d, *J* = 2.5 Hz, 1 H), 7.12 (ddd, *J* = 8.3, 7.0, 1.2 Hz, 1 H), 6.97 (t, *J* = 7.6 Hz, 1 H), 6.88 (s, 1 H), 6.30 (s, 1 H), 4.05 (d, *J* = 14.7 Hz, 1 H), 3.96 (d, *J* = 14.5 Hz, 1 H), 3.27 (s, 3 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 162.6 (C), 150.0 (C), 145.4 (C), 136.7 (C), 132.6 (CH), 130.1 (CH), 128.0 (CH), 126.9 (C), 126.3 (2 × CH), 125.9 (C), 125.6 (CH), 125.4 (C), 121.5 (CH), 119.4 (CH), 119.1 (CH), 112.1 (C), 111.8 (CH), 101.3 (CH), 74.7 (CH), 70.6 (CH_2), 57.9 (CH_3).

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{22}H_{18}N_2O_2Na$: 365.1266; found: 365.1265.

1-(1*H*-Indol-3-yl)-3-phenyl-1*H*-pyrano[4,3-*b*]quinoline (4b)

The crude product was purified by column chromatography (silica gel, cyclohexane–EtOAc, 1:0 to 7:3); this afforded a light yellow solid; yield: 67 mg (89%); mp 200–202 °C.

IR (neat): 3134, 3057, 2981, 2918, 2855, 1606, 1577, 1553, 1493, 1457, 1445, 1420, 1340, 1319, 1250, 1052, 906, 739, 683 cm^{-1}.

^1H NMR (400 MHz, DMSO-d_6): δ = 11.26 (s, 1 H), 7.95 (d, *J* = 8.3 Hz, 1 H), 7.84–7.74 (m, 4 H), 7.71–7.61 (m, 2 H), 7.47–7.35 (m, 5 H), 7.21 (s, 1 H), 7.13 (t, *J* = 7.6 Hz, 1 H), 7.06–6.98 (m, 2 H), 6.97 (s, 1 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 158.3 (C), 151.4 (C), 147.7 (C), 136.7 (C), 133.6 (C), 131.2 (CH), 129.9 (CH), 129.5 (CH), 128.5 (2 × CH), 128.0 (CH), 128.0 (CH), 127.0 (C), 126.3 (CH), 126.1 (C), 125.7 (C), 125.5 (2 × CH), 125.3 (CH), 121.6 (CH), 119.5 (CH), 119.3 (CH), 112.8 (C), 112.0 (CH), 101.9 (CH), 74.5 (CH).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{26}H_{19}N_2O$: 375.1497; found: 375.1501.

3-(Methoxymethyl)-1-(1-methyl-1*H*-pyrrol-2-yl)-1*H*-pyrano[4,3-*b*]quinoline (5a)

The crude product was purified by column chromatography (silica gel, cyclohexane–EtOAc, 1:0 to 75:25); this afforded a beige solid; yield: 67 mg (55%); mp 101–103 °C.

IR (neat): 3037, 3000, 2933, 2878, 2812, 1648, 1637, 1620, 1611, 1494, 1401, 1293, 1204, 1115, 1016, 1003, 944, 902, 848, 818, 751, 723 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 8.00 (d, *J* = 8.7 Hz, 1 H), 7.68–7.60 (m, 2 H), 7.51 (s, 1 H), 7.40 (ddd, *J* = 8.0, 6.9, 1.2 Hz, 1 H), 6.72 (dd, *J* = 2.6, 1.8 Hz, 1 H), 6.51 (s, 1 H), 6.32 (s, 1 H), 6.05 (dd, *J* = 3.7, 2.6 Hz, 1 H), 5.91 (dd, *J* = 3.7, 1.8 Hz, 1 H), 4.04 (d, *J* = 13.9 Hz, 1 H), 3.99 (d, *J* = 13.9 Hz, 1 H), 3.69 (s, 3 H), 3.28 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.2 (C), 150.9 (C), 148.3 (C), 131.8 (CH), 129.8 (CH), 128.7 (CH), 128.6 (C), 127.8 (CH), 127.5 (C), 125.7 (CH), 125.0 (CH), 124.8 (C), 112.3 (CH), 106.9 (CH), 105.0 (CH), 74.1 (CH), 71.7 (CH_2), 58.3 (CH_3), 35.0 (CH_3).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{19}H_{19}N_2O_2$: 307.1441; found: 307.1429.

8-(1-Methyl-1*H*-pyrrol-2-yl)-10-phenyl-8*H*-benzo[*h*]pyrano[4,3-*b*]quinoline (5p)

The reaction was carried out at 80 °C in DMF instead of DCE, and at 0.5 M reaction media concentration. The crude product was purified by column chromatography (silica gel, cyclohexane–EtOAc, 1:0 to 9:1); this afforded an ochre solid; yield: 83 mg (43%); mp 209–211 °C.

IR (neat): 3095, 2923, 2854, 1618, 1597, 1575, 1489, 1450, 1442, 1428, 1409, 1394, 1318, 1255, 1055, 1050, 998, 816, 770, 757, 731, 689 cm^{-1}.

^1H NMR (400 MHz, DMSO-d_6): δ = 9.23 (dd, *J* = 7.3, 2.1 Hz, 1 H), 8.02 (dd, *J* = 7.6, 1.7 Hz, 1 H), 7.98 (s, 1 H), 7.85 (dd, *J* = 8.2, 2.3 Hz, 3 H), 7.82–7.71 (m, 3 H), 7.49–7.42 (m, 3 H), 7.05 (s, 1 H), 7.03 (s, 1 H), 6.86 (t, *J* = 2.2 Hz, 1 H), 5.86 (t, *J* = 3.1 Hz, 1 H), 5.55 (dd, *J* = 3.7, 1.8 Hz, 1 H), 3.86 (s, 3 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 156.2 (C), 149.9 (C), 145.5 (C), 133.5 (2 × C), 132.0 (CH), 130.6 (C), 130.0 (CH), 129.5 (C), 128.8 (2 × CH), 128.3 (CH), 128.1 (CH), 126.9 (CH), 126.3 (CH), 125.7 (CH), 125.2 (2 × CH), 124.8 (C), 124.7 (CH), 124.6 (C), 123.9 (CH), 111.2 (CH), 106.4 (CH), 102.4 (CH), 71.9 (CH), 34.2 (CH_3).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{27}H_{21}N_2O$: 389.1654; found: 389.1646.

3-(Methoxymethyl)-1-(1,2,5-trimethyl-1*H*-pyrrol-3-yl)-1*H*-pyrano[4,3-*b*]quinoline (6a)

The crude product was purified by column chromatography (silica gel, cyclohexane–EtOAc, 8:2 to 5:5); this afforded a light yellow solid; yield: 59 mg (66%); mp 48–50 °C.

IR (neat): 3057, 2916, 2818, 1642, 1616, 1495, 1427, 1398, 1382, 1311, 1115, 1096, 986, 823, 745, 716, 661 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.98 (d, *J* = 8.4 Hz, 1 H), 7.66–7.53 (m, 3 H), 7.36 (t, *J* = 7.5 Hz, 1 H), 6.33 (s, 1 H), 6.28 (s, 1 H), 5.83 (s, 1 H), 4.12 (d, *J* = 14.3 Hz, 1 H), 3.98 (d, *J* = 14.3 Hz, 1 H), 3.44 (s, 3 H), 3.43 (s, 3 H), 2.24 (s, 3 H), 2.21 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 161.5 (C), 151.9 (C), 147.9 (C), 132.0 (CH), 129.4 (CH), 128.5 (CH), 128.2 (C), 127.8 (CH), 127.7 (C), 127.6 (C), 127.3 (C), 125.2 (CH), 115.1 (C), 105.6 (CH), 103.6 (CH), 75.9 (CH), 71.7 (CH_2), 58.9 (CH_3), 30.4 (CH_3), 12.7 (CH_3), 10.8 (CH_3).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{21}H_{23}N_2O_2$: 335.1754; found: 335.1751.

3-Phenyl-1-(1,2,5-trimethyl-1*H*-pyrrol-3-yl)-1*H*-pyrano[4,3-*b*]quinoline (6b)

The crude product was purified by column chromatography (silica gel, cyclohexane–EtOAc, 9:1 to 85:15); this afforded an ochre solid; yield: 66 mg (90%); mp 122–124 °C.

IR (neat): 3055, 2912, 2851, 1606, 1575, 1536, 1492, 1415, 1396, 1312, 1042, 1024, 929, 903, 755, 725, 717, 689 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.02 (d, *J* = 8.3 Hz, 1 H), 7.88–7.79 (m, 2 H), 7.68–7.58 (m, 3 H), 7.43–7.34 (m, 4 H), 6.88 (s, 1 H), 6.42 (s, 1 H), 5.83 (s, 1 H), 3.46 (s, 3 H), 2.31 (s, 3 H), 2.21 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.5 (C), 152.7 (C), 147.9 (C), 134.2 (C), 131.9 (CH), 129.9 (CH), 129.5 (CH), 128.5 (2 × CH), 128.2 (CH), 127.9 (C+CH), 127.7 (C), 127.6 (C), 127.4 (C), 126.1 (2 × CH), 125.2 (CH), 115.4 (C), 105.9 (CH), 102.1 (CH), 75.9 (CH), 30.4 (CH_3), 12.7 (CH_3), 10.8 (CH_3).

HRMS (CI): *m*/*z* [M + H]$^+$ calcd for $C_{25}H_{23}N_2O$: 367.1810; found: 367.1805.

3-(Methoxymethyl)-1-(2-methyl-1*H*-indol-3-yl)-1*H*-pyrano[4,3-*b*]quinoline (7a)

The reaction was carried out at 50 °C in DMF instead of DCE. The crude product was purified by column chromatography (silica gel, cyclohexane–EtOAc, 8:2 to 1:1); this afforded a light yellow solid; yield: 85 mg (36%); mp 226–228 °C.

IR (neat): 3142, 3034, 2920, 2841, 2759, 1645, 1617, 1566, 1496, 1464, 1426, 1397, 1311, 1198, 1105, 1010, 904, 816, 753, 740 cm^{-1}.

^{1}H NMR (400 MHz, DMSO-d_6): δ = 11.29 (s, 1 H), 7.89 (d, *J* = 8.4 Hz, 1 H), 7.66 (d, *J* = 8.1 Hz, 1 H), 7.62 (t, *J* = 7.8 Hz, 1 H), 7.40 (s, 1 H), 7.38–7.32 (m, 2 H), 7.15 (d, *J* = 7.9 Hz, 1 H), 7.02 (t, *J* = 7.4 Hz, 1 H), 6.84 (t, *J* = 7.4 Hz, 1 H), 6.76 (s, 1 H), 6.26 (s, 1 H), 4.09 (d, *J* = 14.1 Hz, 1 H), 3.98 (d, *J* = 14.1 Hz, 1 H), 3.34 (s, 3 H), 2.44 (s, 3 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 161.7 (C), 151.2 (C), 147.4 (C), 136.0 (C), 135.6 (C), 131.1 (CH), 129.4 (CH), 127.9 (CH), 127.9 (CH), 127.1 (C), 126.7 (C), 126.4 (C), 125.2 (CH), 120.5 (CH), 118.9 (CH), 118.9 (CH), 110.9 (CH), 107.4 (C), 103.0 (CH), 74.6 (CH), 70.7 (CH_2), 57.9 (CH_3), 11.6 (CH_3).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{23}H_{21}N_2O_2$: 357.1598; found: 357.1589.

1-(2-Methyl-1*H*-indol-3-yl)-3-phenyl-1*H*-pyrano[4,3-*b*]quinoline (7b)

The crude product was purified by column chromatography (silica gel, cyclohexane–EtOAc, 1:0 to 0:1) and then washed with EtOAc; this afforded a yellow solid; yield: 42 mg (62%); mp 246–248 °C.

IR (neat): 3143, 3056, 2920, 2843, 2758, 1607, 1576, 1494, 1460, 1444, 1419, 1339, 1049, 1028, 904, 753, 741, 685 cm^{-1}.

^{1}H NMR (300 MHz, DMSO-d_6): δ = 11.33 (s, 1 H), 7.92 (d, *J* = 8.3 Hz, 1 H), 7.84–7.77 (m, 2 H), 7.69 (d, *J* = 8.0 Hz, 1 H), 7.64 (t, *J* = 7.3 Hz, 1 H), 7.47 (s, 1 H), 7.46–7.32 (m, 5 H), 7.17 (d, *J* = 7.9 Hz, 1 H), 7.05–6.96 (m, 2 H), 6.91 (s, 1 H), 6.82 (t, *J* = 7.5 Hz, 1 H), 2.46 (s, 3 H).

^{13}C NMR (75 MHz, DMSO-d_6): δ = 159.7 (C), 152.1 (C), 147.6 (C), 136.2 (C), 135.7 (C), 133.5 (C), 131.0 (CH), 130.0 (CH), 129.5 (CH), 128.6 (2 × CH), 128.0 (CH), 127.9 (CH), 127.2 (C), 126.9 (C), 126.7 (C), 125.5 (2 × CH), 125.3 (CH), 120.6 (CH), 119.0 (2 × CH), 111.0 (CH), 107.3 (C), 101.9 (CH), 74.8 (CH), 11.7 (CH_3).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{27}H_{21}N_2O$: 389.1648; found: 389.1636.

3-(Methoxymethyl)-1-(1*H*-pyrrol-2-yl)-1*H*-pyrano[4,3-*b*]quinoline (8a)

The crude product was purified by column chromatography (silica gel, cyclohexane–EtOAc, 1:0 to 1:9); this afforded a white solid; yield: 28 mg (48%); mp 180–182 °C.

IR (neat): 3174, 3131, 3090, 2997, 2924, 2871, 2815, 1654, 1614, 1604, 1564, 1497, 1429, 1400, 1311, 1286, 1207, 1154, 1117, 1095, 1015, 941, 813, 756, 718 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.79 (s, 1 H), 7.98 (d, *J* = 8.2 Hz, 1 H), 7.71–7.56 (m, 3 H), 7.42 (td, *J* = 7.3, 1.2 Hz, 1 H), 6.87 (td, *J* = 2.6, 1.4 Hz, 1 H), 6.47 (s, 1 H), 6.28 (s, 1 H), 6.18 (q, *J* = 2.9 Hz, 1 H), 6.07 (s, 1 H), 4.04 (d, *J* = 13.7 Hz, 1 H), 3.98 (d, *J* = 13.7 Hz, 1 H), 3.35 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.4 (C), 150.4 (C), 148.2 (C), 132.0 (CH), 129.9 (CH), 128.8 (C), 128.6 (CH), 127.9 (CH), 127.5 (C), 125.8 (CH), 125.1 (C), 119.5 (CH), 109.8 (CH), 108.5 (CH), 104.9 (CH), 74.9 (CH), 71.8 (CH_2), 58.7 (CH_3).

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{18}H_{16}N_2O_2Na$: 315.1109; found: 315.1103.

8-(3-Methylbenzofuran-2-yl)-10-phenyl-8*H*-benzo[*h*]pyrano[4,3-*b*]quinoline (9p)

The reaction was carried out at 80 °C in DMF instead of DCE, and at 0.5 M reaction media concentration. The crude product was purified by column chromatography (silica gel, cyclohexane–EtOAc, 1:0 to 9:1); this afforded a yellow solid; yield: 51 mg (23%); mp 227–229 °C.

IR (neat): 3061, 2920, 1618, 1599, 1574, 1492, 1450, 1318, 1257, 1196, 1051, 1005, 911, 811, 765, 748, 689 cm^{-1}.

^{1}H NMR (400 MHz, DMSO-d_6): δ = 9.23 (d, *J* = 7.7 Hz, 1 H), 8.00 (d, *J* = 7.4 Hz, 1 H), 7.93–7.71 (m, 7 H), 7.68 (d, *J* = 7.5 Hz, 1 H), 7.50 (d, *J* = 7.9 Hz, 1 H), 7.48–7.43 (m, 3 H), 7.36–7.27 (m, 2 H), 7.26 (s, 1 H), 7.10 (s, 1 H), 2.35 (s, 3 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 157.6 (C), 153.7 (C), 149.7 (C), 148.8 (C), 145.5 (C), 133.5 (C), 133.1 (C), 131.8 (CH), 130.3 (C), 130.0 (CH), 128.9 (C), 128.6 (2 × CH), 128.2 (CH), 127.9 (CH), 126.8 (CH), 126.4 (CH), 125.5 (CH), 125.4 (2 × CH), 125.4 (CH), 124.9 (C), 123.9 (CH), 123.3 (C), 122.7 (CH), 120.2 (CH), 115.6 (C), 111.3 (CH), 102.3 (CH), 71.9 (CH), 7.6 (CH_3).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{31}H_{22}NO_2$: 440.1651; found: 440.1644.

Acknowledgment

This work was supported by the CNRS, ATIP CNRS-INCa, and Institut Curie. A. B. and G. M. are respectively grateful to the French Ministry of Research and the Fondation Pierre-Gilles de Gennes for financial support. We thank A. Berlioz-Barbier and C. Duchamp, from the Centre Commun de Spectrométrie de Masse (CCSM) of Université Lyon 1, for the assistance and access to the mass spectrometry facility.

Supporting Information

Supporting information for this article is available online at http://dx.doi.org/10.1055/s-0035-1562234.

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