Naphtho- and Benzo[*g*]quinoxalino-Fused Oxazocinoquinolinones and Their Diaryl and Alkynyl Analogues from Quinolin-8-ols: A Library of Novel Polynuclear Heteroaromatics

Rupankar Paira, Arindam Maity, Subhendu Naskar, Shyamal Mondal, Priyankar Paira, Abhijit Hazra, Krishnendu B. Sahu, Pritam Saha, Sukdeb Banerjee, Nirup B. Mondal*

Department of Chemistry, Indian Institute of Chemical Biology, Council of Scientific and Industrial Research, 4 Raja S. C. Mullick Road, Jadavpur, Kolkata 700032, India
Fax +91(33)24735197; E-mail: nirup@iicb.res.in

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Abstract: The efficient syntheses of 6,6,8,6,6-pentacyclic naphtho-fused oxazocinoquinolinones and 6,6,8,6,6,6-hexacyclic benzo[*g*]quinoxalino-fused oxazocinoquinolinones were achieved in one-pot sequences. The generation of libraries of their diaryl- and alkynyl-substituted analogues via Suzuki–Miyaura and Sonogashira cross-coupling reactions, respectively, were also achieved.

Key words: fused-ring systems, oxazocinoquinolinones, diarylations, alkynylations, cross-coupling

Nitrogen- and oxygen-containing heterocycles are omnipresent substructures in a myriad of biologically active natural products and small-molecule pharmaceuticals.[1,2] The compounds inhibit enzyme function by binding to the catalytic intermediate enzyme–DNA complex,[3–6] exhibit high binding affinity to the glycine site of the *N*-methyl-D-aspartate receptor, and are highly promising antagonists for the treatment of several central nervous system disorders.[7] The intercalative binding of these drugs to DNA is due to the presence of a linearly fused cyclic system.[8] Moreover, tri-, tetra-, penta-, and hexacyclic compounds containing one or two heterocyclic rings fused to a quinoline ring in a linear fashion, derived from natural sources or of synthetic origin, are reported to have antitumor and anticancer activities.[9] Because quinolinone-containing natural products express such a wide array of bioactivities, the synthesis and derivatization of this family of compounds are increasingly gaining importance. Great efforts, therefore, have been made to discover and optimize new reactions and methodologies to facilitate the construction of these heterocycles.[10] Phase-transfer catalysis has long been recognized as a versatile methodology for organic synthesis in industry, academia, and process chemistry.[11] As a part of our ongoing endeavor to use phase-transfer catalysis for the construction of structurally unique N-heteroaromatics,[12] we contemplated applying this tool to the syntheses of novel naphtho- and benzo[*g*]quinoxalino-fused oxazocinoquinolinones, containing a quinolinone moiety in their core structure, in one-pot sequences (Scheme 1).

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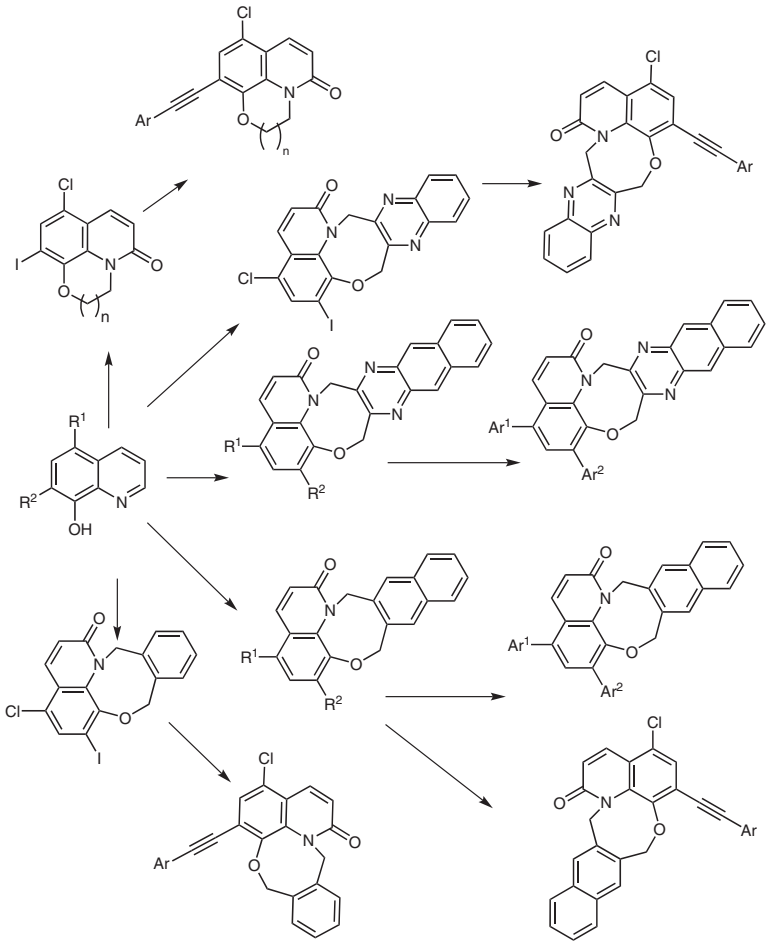
We were also interested in functionalizing the synthesized quinolinones by forming their diaryl- and alkynyl-substituted analogues because of the neuroprotective properties of diarylquinolinones,[13] the antiviral activity of alkynyluracil nucleosides,[14a] and the antiproliferative activity of 4-alkynylpyrones.[14b] Biaryl motifs also occur in a range of pharmaceuticals, herbicides, and natural products,[15] and alkynyl moieties exist in several bioactive compounds, e.g. β-D-4′-*C*-ethynyl-2′-3′-dideoxycytidine (a substrate for HIV reverse transcriptase),[16a] SKS-927 (inhibits Src kinase activity),[16b] and in a series of nonterpenoid C_{15}-metabolites known as lauroxanes[16c] and in several substituted flavones (3-alkynyl-substituted flavone)[16d] with anticancer potential. We, therefore, attempted to apply the two most versatile and widely used reactions, the Suzuki–Miyaura[17] and Sonogashira[18] cross-coupling reactions, for the selective incorporation of aryl and alkynyl groups onto the heteroaromatic compounds, i.e. polycyclic oxazocinoquinolinones that possess halo substituents ready to act as handles for aryl or alkynyl insertion (Scheme 1).

In this paper, we wish to report in detail the syntheses of novel penta- and hexacyclic heteroaromatics and their diarylated and alkynylated derivatives, along with a plausible pathway for their formation.

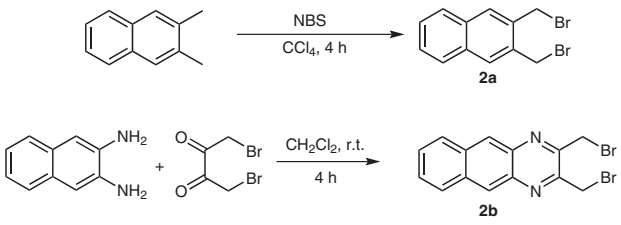
For the synthesis of our initial target compounds, naphtho- and benzo[*g*]quinoxalino-fused oxazocinoquinolinones, the reagents chosen as the key building blocks were well-known quinolin-8-ol derivatives and 2,3-bis(bromomethyl)naphthalene or 2,3-bis(bromomethyl)benzo[*g*]quinoxaline, both very easily synthesized from 2,3-dimethylnaphthalene or naphthalene-2,3-diamine, respectively (Scheme 2).

First, quinolin-8-ol (**1a**) and 2,3-bis(bromomethyl)naphthalene (**2a**) were reacted in a 1:3 molar ratio under phase transfer catalysis (PTC) conditions.[12a] During the reaction, thin-layer chromatography was performed every two hours to monitor progress and showed that complete conversion of alcohol **1a** into product **3a** occurred after 12 hours. Usual workup followed by chromatographic separation gave the product in 86% yield (Table 1, entry 1). The characterization of the product as a fused pentacyclic quinolinone was accomplished by spectral analysis. The success of the synthesis of unsubstituted derivative **3a** from alcohol **1a** and dibromo compound **2a** led to the syn-



Scheme 1

theses of a variety of naphtho-fused oxazocinoquinolinones by the cyclization of quinolin-8-ol derivatives **1b–e** with 2,3-bis(bromomethyl)naphthalene (**2a**); the corresponding quinolinones were isolated in excellent yields (78–88%) (entries 2–5, respectively).



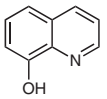
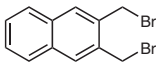
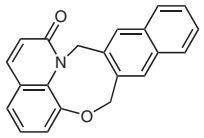
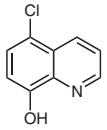
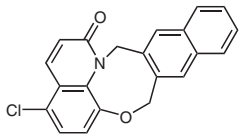
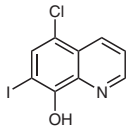
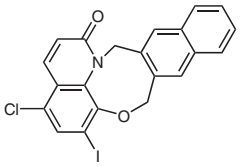
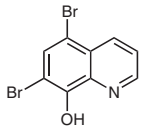
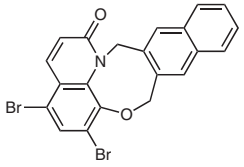
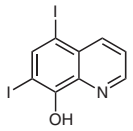
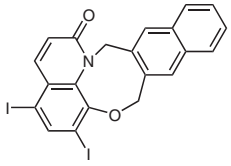
Scheme 2

To explore the scope of this methodology with a more complex ring system, dibromo compound **2a** was replaced with 2,3-bis(bromomethyl)benzo[*g*]quinoxaline (**2b**), which was allowed to react with quinolin-8-ol (**1a**) (Table 2, entry 1) and its substituted derivatives **1b–e** (entries 2–5, respectively) under similar reaction conditions to those above. The reactions appeared to be complete within 14 hours and the corresponding products **3f–j** were isolated in high yields (75–86%).

After the successful construction of the naphtho- and benzo[*g*]quinoxalino-fused oxazocinoquinolinones, attempts were made at the synthesis of their diarylated derivatives using the well-known Suzuki–Miyaura cross-coupling reaction. The journey to the target polycyclic diarylquinolinones began with the reaction of benzo[*g*]quinoxalino-fused dibromooxazocinoquinolinone **3i** and phenylboronic acid (**4a**) as model reaction partners. When the Suzuki–Miyaura cross-coupling reaction was carried out using Amberlite IRA 402(OH) resin mediated conditions in water,[12e] the corresponding product was obtained in only moderate yield (up to 51%, Table 3, entries 1–3), possibly because of the poor solubility of quinolinone **3i** in aqueous media. However, use of the *N*,*N*-dimethylformamide–water (2:3) solvent system removed the solubility problem, and carrying out the reaction at 100 °C for 8 hours using Amberlite IRA 402(OH) as the base and 0.5 mol% of tetrakis(triphenylphosphine)palladium(0) as the catalyst gave diarylated product **5a** in high yield (86%) (entry 5). A change in the ratio of the solvent system severely lowered the yield of the product (entries 4–6).

With the optimal set of reaction conditions thus selected, the study was further extended by coupling dibromoquinolinones **3d** and **3i** with various aryl- and heteroarylboronic acids **4a–e**, and the corresponding diarylated products

Table 1 Construction of Naphtho-Fused Oxazocinoquinolinones **3a–e** from Quinolin-8-ol Derivatives[a]

Entry	Quinolin-8-ol derivative	Alkylating agent	Time (h)	Product	Yield[b] (%)
1	 **1a**	 **2a**	12	 **3a**	86
2	 **1b**	**2a**	12	 **3b**	81
3	 **1c**	**2a**	10	 **3c**	87
4	 **1d**	**2a**	12	 **3d**	88
5	 **1e**	**2a**	14	 **3e**	78

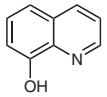
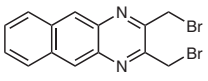
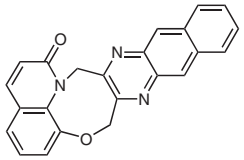
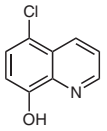
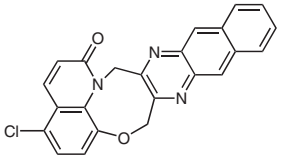
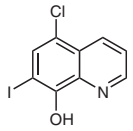
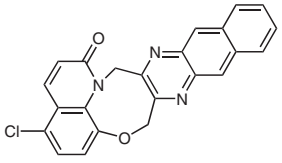
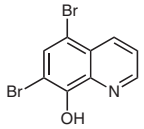
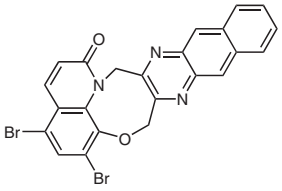
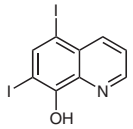
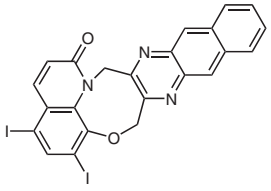
[a] All reactions were carried out using PTC under the conditions reported previously.[12a]
[b] Isolated yield.

5a–g were obtained in excellent yields (81–94%) (Table 4, entries 1–7). As expected, the rate-accelerating effect of a *para*-methoxy group relative to the boronic acid functionality, as in compound **4b**, was well indicated by the achieved yields (94%) of the corresponding products and shortest reaction time (4 h) required (entries 2 and 7) compared with the other examples. The reactions of two structural isomers, boronic acids **4c** and **4e**, demonstrated interesting results. Although both substrates produced the corresponding diarylated quinolinones **5e** and **5f** in high yields in the reaction with dibromo compound **3d** (entries 5 and 6, respectively), higher steric crowding in **5f** compared with that in **5e** decelerated the reaction. This meant the synthesis of the latter compound required a longer reaction time (entry 6).

Regarding the mechanistic course, it is expected that the reaction follows the same pathway as palladium-catalyzed Suzuki–Miyaura cross-coupling reactions using Amberlite resin as the base.[12e] The two arylation steps occur at different rates, and carrying out the reaction of compound **3d** and boronic acid **4b** for a shorter duration (1.5 h) gave monoarylated quinolinone **5h** along with some of diarylated product **5g** (entry 8). This evidence unambiguously proves that the diarylation protocol is actually the sum of two consecutive monoarylation reactions and not the result of two parallel monoarylations.

We next focused our attention towards the possibility of applying the Sonogashira cross-coupling reaction to polycyclic N,O-heterocycle-fused 5-chloro-7-iodoquinolinones, which contain an iodo substituent suitable for undergoing alkynyl substitution, for the synthesis of alkynylquinolinones. At the outset, we chose pentacyclic 5-chloro-7-iodoquinolinone **3c** and phenylacetylene (**6a**) as model reaction partners for the development of the optimum reaction conditions (Table 5). After thorough screening of palladium catalysts, solvents, bases, and reaction parameters (time and temperature), we found that carrying out the reaction at room temperature for six hours in *N*,*N*-dimethylformamide, using triethylamine as a base, 0.2 mol% of palladium(II) acetate as a catalyst, and 0.2 mol% of copper(I) iodide as co-catalyst, produced product **7a** in the best yield (78%) (entry 9). Alteration of any one

Table 2 Construction of Benzo[*g*]quinoxalino-Fused Oxazocinoquinolinones **3f–j** from Quinolin-8-ol Derivatives[a]

Entry	Quinolin-8-ol derivative	Alkylating agent	Time (h)	Product	Yield[b] (%)
1	 **1a**	 **2b**	14	 **3f**	80
2	 **1b**	**2b**	14	 **3g**	86
3	 **1c**	**2b**	12	 **3h**	82
4	 **1d**	**2b**	12	 **3i**	75
5	 **1e**	**2b**	14	 **3j**	79

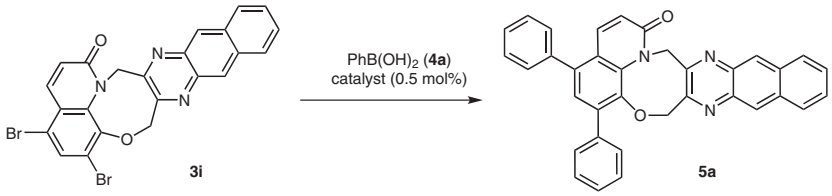
[a] All reactions were carried out using PTC under the conditions reported previously.[12a]
[b] Isolated yield.

of the above conditions decelerated the coupling and severely lowered the yield of the product (entries 1–8 and 10).

The scope of this methodology was investigated for the preparation of our target alkynylquinolinones by treating dihaloquinolinone **3c** with aryl- and heteroarylalkynes **6b–d** (Table 6, entries 2–4). In further pursuit of this objective, presynthesized tricyclic dihaloquinolinones **8a–c** were also treated with various aryl-, heteroaryl-, and cyclopropylalkynes under the optimal set of reaction conditions to synthesize the corresponding alkynylquinolinones (Table 7, entries 1–8). The results summarized in Tables 6 and 7 reveal that the reactions generally proceed with good to excellent yields. However, the presence of an electron-withdrawing group, such as 4-fluorophenyl or 2-pyridyl, marginally lowers the yield (e.g., Table 7, entries 2, 3, 5, and 8) and the cyclopropyl group drastically lowers it (e.g., entry 6). These results are attributed to the lower activity of the intermediate copper acetylide species because of the electron-withdrawing properties of the substituents. The study was further extended using presynthesized tetra- and pentacyclic quinolinones[12b–d] as substrates. A gradual decrease in the yields of the corresponding products **11** and **13** (entries 9–14), compared with those of compounds **9**, was observed which might be due to an increase in steric crowding and the structural complexity of the systems. Indeed, attempts to alkynylate hexacyclic 5-chloro-7-iodoquinolinone **3h** were unsuccessful. We presume that the greater structural complexity of fused 6,6,8,6,6,6-ring systems might be partly responsible for the reluctant nature of compound **3h** towards the Sonogashira reaction.

The mechanistic course of the alkynylation is expected to follow the usual profile of palladium-catalyzed Sonogashira cross-coupling reactions.[19] In all cases, the carbon–chloride bond remained intact and the coupling reaction only involved the carbon–iodide bond; thus, complete regioselectivity occurred in every case.

Table 3 Optimization of the Reaction Conditions for the Suzuki–Miyaura Cross-Coupling Reaction of Benzo[*g*]quinoxalino-Fused Dibromooxazocinoquinolinone **3i** and Phenylboronic Acid (**4a**)



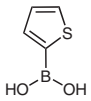
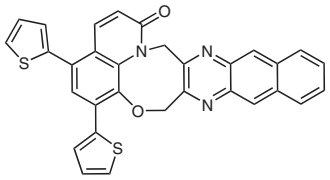
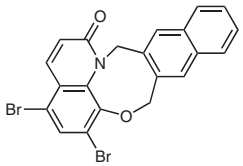
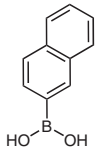
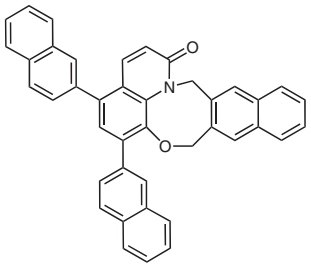
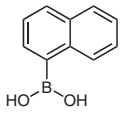
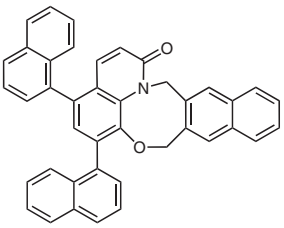
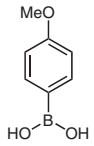
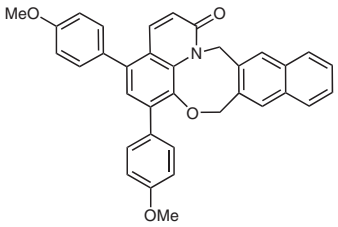
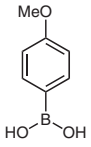
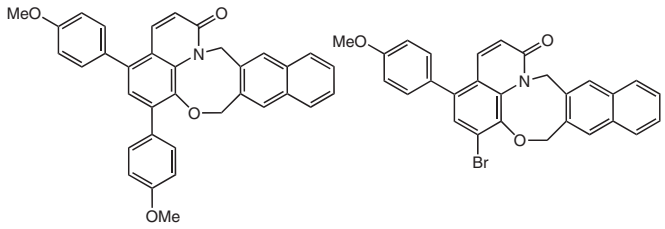
Entry	Solvent/base	Catalyst	Time (h)	Temp (°C)	Yield[a] (%)
1	H_2O/Amberlite resin	$PdCl_2/Ph_3P$	12	110	43
2	H_2O/Amberlite resin	$Pd(OAc)_2/Ph_3P$	14	110	37
3	H_2O/Amberlite resin	$Pd(PPh_3)_4$	12	110	51
4	DMF–H_2O (1:4)/Amberlite resin	$Pd(PPh_3)_4$	12	110	63
5	DMF–H_2O (2:3)/Amberlite resin	$Pd(PPh_3)_4$	8	100	86
6	DMF–H_2O (3:2)/Amberlite resin	$Pd(PPh_3)_4$	14	110	72
7	DMF–H_2O (2:3)/Amberlite resin	$Pd(PPh_3)_4$[b]	14	110	58

[a] Isolated yield.
[b] Using 0.1 mol% Pd catalyst.

Table 4 Construction of Polycyclic Diarylquinolinones **5a–g** Using the Suzuki–Miyaura Cross-Coupling Reaction[a]

Entry	Quinolinone derivative	Boronic acid	Time (h)	Product	Yield[b] (%)
1	**3i**	**4a**	8	**5a**	86
2	**3i**	**4b**	4	**5b**	94
3	**3i**	**4c**	9	**5c**	81

Table 4 Construction of Polycyclic Diarylquinolinones **5a–g** Using the Suzuki–Miyaura Cross-Coupling Reaction[a] (continued)

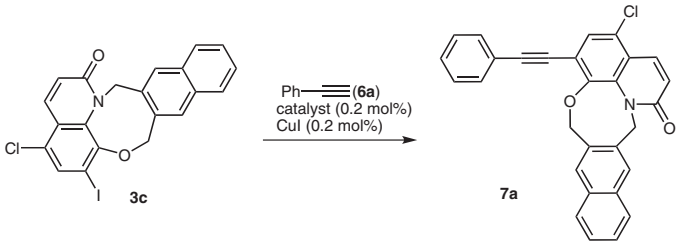
Entry	Quinolinone derivative	Boronic acid	Time (h)	Product	Yield[b] (%)
4	**3i**	 **4d**	10	 **5d**	83
5	 **3d**	 **4c**	9	 **5e**	87
6	**3d**	 **4e**	12	 **5f**	84
7	**3d**	 **4b**	4	 **5g**	94
8	**3d**	 **4b**	1.5	 **5g + 5h**	31 + 43

[a] All reactions were carried out under the optimal set of reaction conditions (see above).
[b] Isolated yield.

All the products were characterized by NMR spectroscopy and mass spectrometry. Single-crystal X-ray crystallographic analysis of quinolinone **3a**[20] and alkynyl derivative **11a**[21] was carried out for the unambiguous determination of their structures (Figure 1 and Figure 2, respectively).

In summary, we have demonstrated the efficient one-pot synthesis of a novel class of penta- and hexacyclic heteroaromatics containing a fused oxazocinoquinolinone ring system. The application of these molecules for the construction of novel diaryl- and alkynyl-substituted polynuclear heteroaromatics using Suzuki–Miyaura and Sonogashira cross-coupling reactions, respectively, has also been disclosed. The novelty of these versatile methodologies lies in their operational simplicity, mild reaction conditions, and use of readily available starting materials. We presume that the structural similarities of these molecules to several natural and synthetic bioactive compounds may lead to the identification of new biologically active molecules.

Table 5 Optimization of the Reaction Conditions for the Sonogashira Cross-Coupling Reaction Using Pentacyclic 5-Chloro-7-iodoquinolinone **3c** and Phenylacetylene (**6a**)



Entry	Solvent, base	Catalyst[a]	Time (h)	Temp (°C)	Yield[a] (%)
1	MeCN, K_2CO_3	$PdCl_2/Ph_3P/CuI$	14	r.t.	25
2	MeCN, Et_3N	$PdCl_2/Ph_3P/CuI$	14	r.t.	38
3	toluene, Cs_2CO_3	$Pd(PPh_3)_4/CuI$	8	r.t.	20
4	toluene, Et_3N	$Pd(OAc)_2/Ph_3P/CuI$	6	r.t.	27
5	DMSO, Et_3N	$Pd(OAc)_2/Ph_3P/CuI$	12	r.t.	35
6	DMSO, Et_3N	$Pd(OAc)_2/Ph_3P/CuI$	12	80	35
7	DMF, Na_2CO_3	$PdCl_2/Ph_3P/CuI$	8	r.t.	43
8	DMF, Et_3N	$PdCl_2/Ph_3P/CuI$	8	r.t.	58
9	DMF, Et_3N	$Pd(OAc)_2/Ph_3P/CuI$	6	r.t.	78
10	DMF, Et_3N	$Pd(OAc)_2/Ph_3P/CuI$	10	80	62[b]

[a] Isolated yield.
[b] Using 0.1 mol% Pd catalyst and 0.1 mol% CuI.

Table 6 Construction of Naphtho-Fused Alkynyloxazocinoquinolinones **7a–d** Using the Sonogashira Cross-Coupling Reaction[a]

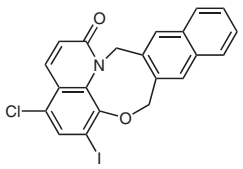
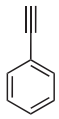
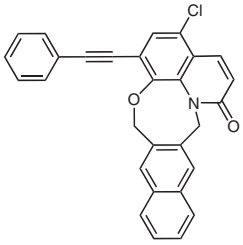
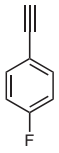
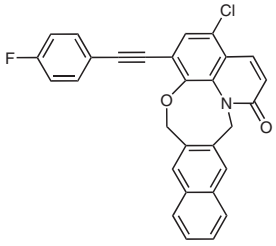
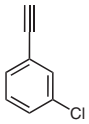
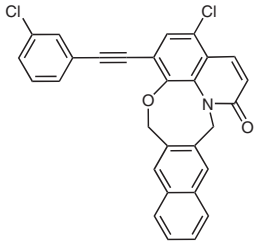
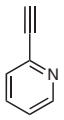
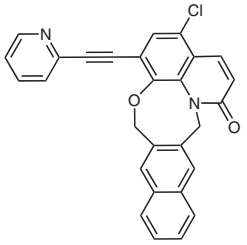
Entry	Quinolinone derivative	Arylacetylene	Time (h)	Product	Yield[b] (%)
1	 **3c**	 **6a**	6	 **7a**	78
2	**3c**	 **6b**	8	 **7b**	73

Table 6 Construction of Naphtho-Fused Alkynyloxazocinoquinolinones **7a–d** Using the Sonogashira Cross-Coupling Reaction[a] (continued)

Entry	Quinolinone derivative	Arylacetylene	Time (h)	Product	Yield[b] (%)
3	**3c**	 **6c**	8	 **7c**	74
4	**3c**	 **6d**	8	 **7d**	70

[a] All reactions were carried out under the optimal set of reaction conditions (see above).
[b] Isolated yield.

Table 7 Construction of Tri-, Tetra-, and Other Pentacyclic N,O-Heterocycle-Fused Alkynylquinolinones Using the Sonogashira Cross-Coupling Reaction[a]

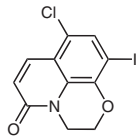
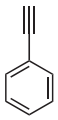
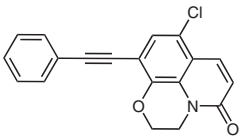
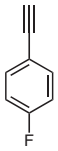
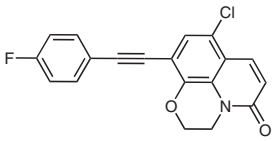
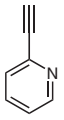
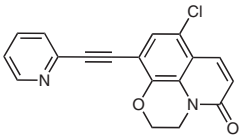
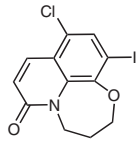
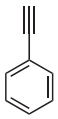
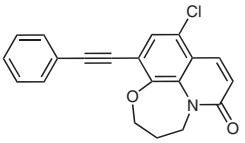
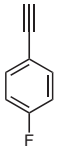
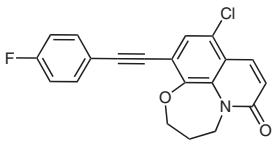
Entry	Quinolinone derivative	Arylacetylene	Time (h)	Product	Yield[b] (%)
1	 **8a**	 **6a**	6	 **9a**	93
2	**8a**	 **6b**	8	 **9b**	88
3	**8a**	 **6d**	8	 **9c**	86
4	 **8**	 **6a**	6	 **9d**	91
5	**8b**	 **6b**	8	 **9e**	88

Table 7 Construction of Tri-, Tetra-, and Other Pentacyclic N,O-Heterocycle-Fused Alkynylquinolinones Using the Sonogashira Cross-Coupling Reaction[a] (continued)

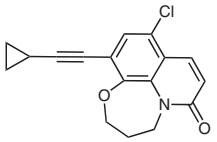
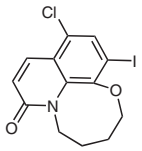
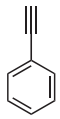
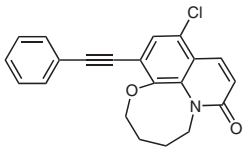
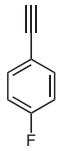
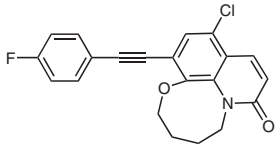
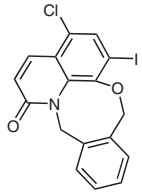
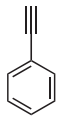
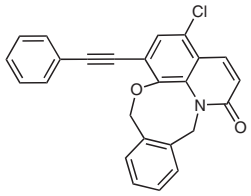
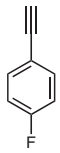
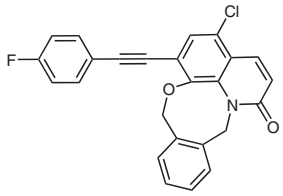
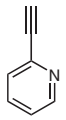
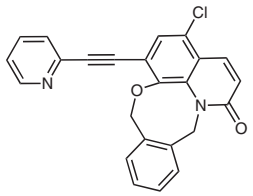
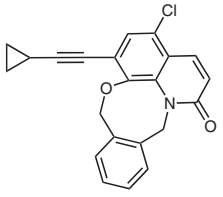
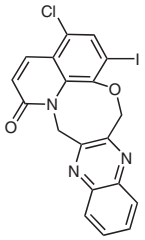
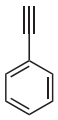
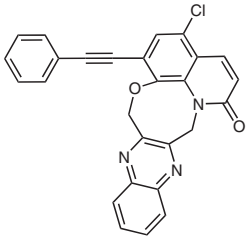
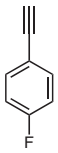
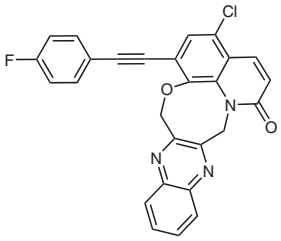
Entry	Quinolinone derivative	Arylacetylene	Time (h)	Product	Yield[b] (%)
6	**8b**	 **6e**	11	 **9f**	47
7	 **8c**	 **6a**	6	 **9g**	92
8	**8c**	 **6b**	8	 **9h**	85
9	 **10**	 **6a**	6	 **11a**	87
10	**10**	 **6b**	8	 **11b**	83
11	**10**	 **6d**	8	 **11c**	67
12	**10**	 **6e**	12	 **11d**	52

Table 7 Construction of Tri-, Tetra-, and Other Pentacyclic N,O-Heterocycle-Fused Alkynylquinolinones Using the Sonogashira Cross-Coupling Reaction[a] (continued)

Entry	Quinolinone derivative	Arylacetylene	Time (h)	Product	Yield[b] (%)
13	 **12**	 **6a**	8	 **13a**	86
14	**12**	 **6b**	8	 **13b**	80

[a] All reactions were carried out under the optimal set of reaction conditions (see above).
[b] Isolated yield.

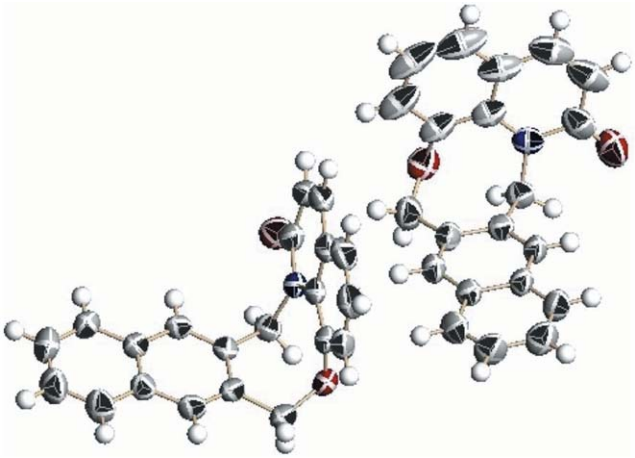


Figure 1 ORTEP representation of compound **3a** (not labeled for simplification); the displacement ellipsoid is drawn at a probability of 50%

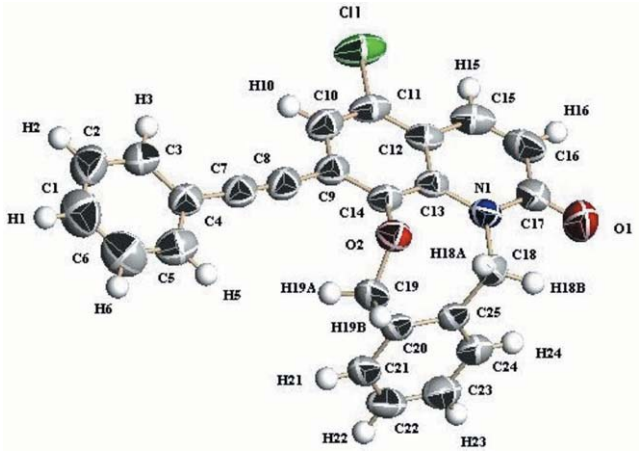


Figure 2 ORTEP representation of compound **11a**, the displacement ellipsoid is drawn at a probability of 50%

Melting points were determined with a capillary melting point apparatus and are uncorrected. Mass spectrometry (ESI, positive) was conducted using an LC-ESI-Q-TOF micro mass spectrometer. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker 300/600 MHz DPX spectrometer using TMS as an internal standard. The quinolin-8-ol and naphthalene derivatives, 1,4-dibromobutane-2,3-dione, NBS, boronic acids, alkynes, catalysts, and PTC (TBAB) were purchased from Aldrich Chemical Company Ltd (USA). The organic solvents used for the chemical syntheses and chromatography were acquired from E. Merck (India) and were of analytical grade. All chromatographic purification was performed using silica gel (100–200 mesh) obtained from SRL (India). Thin-layer chromatography was performed on precoated silica gel 60 F254 aluminum sheets (E. Merck, Germany) and the spots were developed using Liebermann–Burchard solution.

Penta- and Hexacyclic Quinolinones 3a–j; General Procedure

Polycyclic oxazocinoquinolinones **3a–j** were synthesized using the same protocol reported previously by us.[12a]

8,15-Dihydronaphtho[2′,3′:6,7][1,4]oxazocino[2,3,4-*ij*]quinolin-1-one (3a)

Yellow needles. Yield: 86%; mp 236–238 °C; R_f = 0.35 (30% EtOAc–petroleum ether).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 5.33 (d, J = 14.4 Hz, 1 H), 5.97 (m, 2 H), 6.55 (d, J = 13.8 Hz, 1 H), 6.70 (d, J = 9.0 Hz, 1 H), 7.12 (t, J = 7.8 Hz, 1 H), 7.23 (m, 1 H), 7.40 (m, 3 H), 7.50 (m, 2 H), 7.68 (m, 1 H), 7.79 (m, 1 H), 8.05 (s, 1 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 45.5 (CH_2), 78.5 (CH_2), 122.1 (CH), 123.0 (CH), 123.2 (C), 125.1 (CH), 125.2 (CH), 125.5 (CH), 126.2 (CH), 126.7 (CH), 127.1 (CH), 128.0 (CH), 131.7 (CH),

132.6 (C), 133.1 (2 C), 133.6 (2 C), 138.8 (CH), 146.5 (C), 162.6 (C).

HRMS (ESI): *m/z* [M + Na]$^+$ calcd for $C_{21}H_{15}NO_2Na$: 336.0995; found: 336.1006.

4-Chloro-8,15-dihydronaphtho[2′,3′:6,7][1,4]oxazocino[2,3,4-*ij*]quinolin-1-one (3b)
Yellow needles. Yield: 81%; mp 242–246 °C; R_f = 0.33 (30% EtOAc–petroleum ether).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.30 (d, *J* = 14.7 Hz, 1 H), 5.95 (m, 2 H), 6.54 (d, *J* = 13.5 Hz, 1 H), 6.78 (d, *J* = 9.9 Hz, 1 H), 7.17 (d, *J* = 8.4 Hz, 1 H), 7.29 (m, 1 H), 7.43 (m, 2 H), 7.50 (s, 1 H), 7.68 (m, 1 H), 7.78 (m, 1 H), 7.99 (m, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 45.8 (CH_2), 78.4 (CH_2), 120.4 (C), 123.0 (CH), 123.5 (CH), 125.2 (CH), 125.3 (CH), 126.3 (CH), 126.8 (CH), 127.1 (CH), 128.0 (CH), 128.8 (C), 131.8 (CH), 132.7 (2 C), 133.2 (C), 134.9 (CH), 135.0 (2 C), 145.4 (C), 162.1 (C).

HRMS (ESI): *m/z* [M + Na]$^+$ calcd for $C_{21}H_{14}ClNO_2Na$: 370.0605; found: 370.0632.

4-Chloro-6-iodo-8,15-dihydronaphtho[2′,3′:6,7][1,4]oxazocino[2,3,4-*ij*]quinolin-1-one (3c)
Brown needles. Yield: 87%; mp 250–252 °C; R_f = 0.25 (25% EtOAc–petroleum ether).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.53 (d, *J* = 14.7 Hz, 1 H), 5.87 (m, 2 H), 6.37 (d, *J* = 13.5 Hz, 1 H), 6.78 (d, *J* = 9.6 Hz, 1 H), 7.45 (m, 2 H), 7.57 (s, 1 H), 7.68 (s, 1 H), 7.72 (m, 1 H), 7.82 (m, 1 H), 7.95 (d, *J* = 9.9 Hz, 1 H), 8.08 (s, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 46.8 (CH_2), 77.0 (CH_2), 95.2 (C), 120.5 (C), 123.3 (CH), 125.2 (CH), 126.4 (CH), 126.8 (CH), 127.2 (CH), 128.0 (CH), 129.2 (C), 131.5 (CH), 132.4 (C), 132.5 (C), 132.6 (CH), 132.7 (C), 133.2 (C), 134.8 (CH), 135.0 (C), 145.2 (C), 162.1 (C).

HRMS (ESI): *m/z* [M + Na]$^+$ calcd for $C_{21}H_{13}ClINO_2Na$: 495.9572; found: 495.9561.

4,6-Dibromo-8,15-dihydronaphtho[2′,3′:6,7][1,4]oxazocino[2,3,4-*ij*]quinolin-1-one (3d)
Brown needles. Yield: 88%; mp 238–240 °C; R_f = 0.23 (25% EtOAc–petroleum ether).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.63 (d, *J* = 14.8 Hz, 1 H), 5.88 (m, 2 H), 6.51 (d, *J* = 13.5 Hz, 1 H), 6.77 (d, *J* = 9.6 Hz, 1 H), 7.44 (m, 2 H), 7.57 (s, 1 H), 7.63 (s, 1 H), 7.71 (m, 1 H), 7.80 (m, 1 H), 7.91 (d, *J* = 9.6 Hz, 1 H), 8.02 (s, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 46.2 (CH_2), 76.0 (CH_2), 118.9 (C), 121.0 (C), 121.1 (C), 123.2 (CH), 125.4 (CH), 126.4 (CH), 126.9 (CH), 127.2 (CH), 127.9 (CH), 130.2 (CH), 131.4 (CH), 132.5 (C), 132.6 (2 C), 133.2 (C), 136.2 (C), 137.4 (CH), 142.7 (C), 162.1 (C).

HRMS (ESI): *m/z* [M + Na]$^+$ calcd for $C_{21}H_{13}Br_2NO_2Na$: 491.9205; found: 491.9202.

4,6-Diiodo-8,15-dihydronaphtho[2′,3′:6,7][1,4]oxazocino[2,3,4-*ij*]quinolin-1-one (3e)
Yellow needles. Yield: 78%; mp 246–248 °C; R_f = 0.30 (25% EtOAc–petroleum ether).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.51 (d, *J* = 14.4 Hz, 1 H), 5.87 (m, 2 H), 6.32 (d, *J* = 13.8 Hz, 1 H), 6.73 (d, *J* = 9.9 Hz, 1 H), 7.47 (m, 2 H), 7.57 (s, 1 H), 7.68 (m, 1 H), 7.81 (m, 2 H), 8.00 (m, 1 H), 8.06 (s, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 47.4 (CH_2), 76.8 (CH_2), 94.8 (C), 96.3 (C), 123.9 (CH), 124.4 (C), 125.2 (CH), 126.4 (CH), 126.9 (CH), 127.3 (CH), 128.0 (CH), 131.5 (CH), 131.8 (C), 132.4 (C), 132.7 (C), 133.2 (C), 134.1 (C), 142.3 (CH), 142.7 (CH), 147.1 (C), 162.3 (C).

HRMS (ESI): *m/z* [M + Na]$^+$ calcd for $C_{21}H_{13}I_2NO_2Na$: 587.8928; found: 587.8917.

8,17-Dihydrobenzo[*g*]quinazolino[8′,8a′,1′:2,3,4][1,4]oxazocino[6,7-*b*]quinoxalin-1-one (3f)
Yellow solid. Yield: 80%; mp 221–223 °C; R_f = 0.35 (40% EtOAc–petroleum ether).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 5.39 (d, *J* = 16.2 Hz, 1 H), 5.93 (d, *J* = 16.2 Hz, 1 H), 6.17 (d, *J* = 13.8 Hz, 1 H), 6.64 (d, *J* = 13.2 Hz, 1 H), 6.75 (d, *J* = 9.0 Hz, 1 H), 7.20 (m, 1 H), 7.30 (m, 1 H), 7.48 (m, 1 H), 7.58 (m, 2 H), 8.11 (m, 2 H), 8.52 (s, 1 H), 8.64 (s, 1 H), 8.78 (s, 1 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 49.1 (CH_2), 79.0 (CH_2), 122.6 (C), 123.4 (CH), 125.0 (C), 125.7 (C), 126.6 (C), 126.9 (C), 127.0 (CH), 127.2 (CH), 127.5 (CH), 128.4 (C), 128.5 (2 CH), 128.7 (CH), 134.0 (CH), 137.4 (CH), 137.6 (CH), 139.0 (CH), 150.5 (C), 152.6 (2 C), 162.7 (C).

HRMS (ESI): *m/z* [M + Na]$^+$ calcd for $C_{23}H_{15}N_3O_2Na$: 388.1056; found: 388.1039.

4-Chloro-8,17-dihydrobenzo[*g*]quinazolino[8′,8a′,1′:2,3,4][1,4]oxazocino[6,7-*b*]quinoxalin-1-one (3g)
Yellow solid. Yield: 86%; mp 236–238 °C; R_f = 0.35 (30% EtOAc–petroleum ether).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.31 (d, *J* = 16.5 Hz, 1 H), 5.89 (d, *J* = 16.5 Hz, 1 H), 6.04 (d, *J* = 14.4 Hz, 1 H), 6.36 (d, *J* = 13.8 Hz, 1 H), 6.83 (d, *J* = 9.6 Hz, 1 H), 7.61 (m, 3 H), 7.77 (s, 1 H), 8.06 (m, 3 H), 8.56 (s, 1 H), 8.82 (s, 1 H).

HRMS (ESI): *m/z* [M + Na]$^+$ calcd for $C_{23}H_{14}ClN_3O_2Na$: 422.0667; found: 422.0679.

4-Chloro-6-iodo-8,17-dihydrobenzo[*g*]quinazolino[8′,8a′,1′:2,3,4][1,4]oxazocino[6,7-*b*]quinoxalin-1-one (3h)
Yellow solid. Yield: 82%; mp 245–247 °C; R_f = 0.35 (30% EtOAc–petroleum ether).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.32 (m, 1 H), 5.89 (d, *J* = 16.2 Hz, 1 H), 6.04 (d, *J* = 14.1 Hz, 1 H), 6.36 (d, *J* = 14.1 Hz, 1 H), 6.83 (d, *J* = 9.9 Hz, 1 H), 7.60 (m, 2 H), 7.77 (s, 1 H), 8.06 (m, 3 H), 8.60 (m, 1 H), 8.82 (s, 1 H).

HRMS (ESI): *m/z* [M + Na]$^+$ calcd for $C_{23}H_{13}ClIN_3O_2Na$: 547.9633; found: 547.9668.

4,6-Dibromo-8,17-dihydrobenzo[*g*]quinazolino[8′,8a′,1′:2,3,4][1,4]oxazocino[6,7-*b*]quinoxalin-1-one (3i)
Yellow solid. Yield: 75%; mp 242–244 °C; R_f = 0.33 (30% EtOAc–petroleum ether).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.49 (d, *J* = 16.2 Hz, 1 H), 5.91 (d, *J* = 16.2 Hz, 1 H), 6.09 (d, *J* = 13.5 Hz, 1 H), 6.54 (d, *J* = 13.5 Hz, 1 H), 6.82 (d, *J* = 9.9 Hz, 1 H), 7.59 (m, 2 H), 7.74 (s, 1 H), 7.99 (d, *J* = 9.9 Hz, 1 H), 8.05 (m, 2 H), 8.56 (s, 1 H), 8.80 (s, 1 H).

HRMS (ESI): *m/z* [M + Na]$^+$ calcd for $C_{23}H_{13}Br_2N_3O_2Na$: 543.9267; found: 543.9285.

4,6-Diiodo-8,17-dihydrobenzo[*g*]quinazolino[8′,8a′,1′:2,3,4][1,4]oxazocino[6,7-*b*]quinoxalin-1-one (3j)
Yellow solid. Yield: 79%; mp 247–249 °C; R_f = 0.30 (30% EtOAc–petroleum ether).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.25 (d, *J* = 16.9 Hz, 1 H), 5.92 (m, 2 H), 6.27 (d, *J* = 14.1 Hz, 1 H), 6.76 (d, *J* = 9.6 Hz, 1 H), 7.59 (m, 2 H), 7.87 (d, *J* = 9.6 Hz, 1 H), 8.09 (m, 2 H), 8.23 (s, 1 H), 8.55 (s, 1 H), 8.80 (s, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 51.7 (CH_2), 78.0 (CH_2), 94.8 (C), 95.9 (C), 124.2 (CH), 124.7 (C), 126.8 (CH), 127.0 (CH), 127.2 (CH), 128.4 (2 CH), 128.7 (CH), 134.0 (C), 134.3 (C), 134.4 (C), 137.4 (C), 137.9 (C), 142.4 (CH), 143.0 (CH), 149.7 (2 C), 150.9 (C), 162.7 (C).

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{23}H_{13}I_2N_3O_2Na$: 639.8989; found: 639.8972.

Penta- and Hexacyclic Diarylquinolinones 5a–g; General Procedure

Dibromoquinolinone **3d** or **3i** (0.5 mmol) was taken up in DMF–H_2O (2:3, 20 mL) in a 100-mL round-bottomed flask under an inert atmosphere. Amberlite IRA 402(OH) (400 mg) was added, and the mixture was stirred at 45–50 °C until the substrate had dissolved. Then, 0.5 mol% $Pd(PPh_3)_4$ and one of the aryl- or heteroarylboronic acids **4a**–**f** (1.1 mmol) were added to the solution and the stirring was continued for the appropriate time period, as given in Table 4, at 100 °C. After completion of the reaction, the resin was recovered by simple filtration, thoroughly washed with EtOH (20 mL) followed by NaOH soln (20 mL), and then dried at 80 °C under reduced pressure for use in subsequent runs. The filtrate was transferred to a separating funnel and extracted with EtOAc (75 mL). The organic layer was washed thoroughly with H_2O until free from alkali, dried (anhyd Na_2SO_4), and evaporated to dryness in a rotary evaporator under reduced pressure. The residue was purified by chromatography (silica gel, EtOAc–petroleum ether) to give the corresponding fused diarylquinolinone.

4,6-Diphenyl-8,17-dihydrobenzo[*g*]quinazolino[8′,8a′,1′:2,3,4][1,4]oxazocino[6,7-*b*]quinoxalin-1-one (5a)

Yellow solid. Yield: 86%; mp 250–252 °C; R_f = 0.30 (30% EtOAc–petroleum ether).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 5.01 (d, *J* = 16.2 Hz, 1 H), 5.54 (d, *J* = 15.6 Hz, 1 H), 6.15 (d, *J* = 14.4 Hz, 1 H), 6.48 (d, *J* = 14.4 Hz, 1 H), 6.67 (d, *J* = 9.6 Hz, 1 H), 7.24 (s, 1 H), 7.36 (m, 2 H), 7.44 (m, 4 H), 7.55 (m, 4 H), 7.70 (m, 3 H), 8.09 (m, 2 H), 8.49 (s, 1 H), 8.80 (s, 1 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 38.7 (CH_2), 68.1 (CH_2), 121.9 (CH), 126.6 (CH), 126.8 (CH), 127.1 (CH), 127.2 (CH), 128.1 (CH), 128.3 (CH), 128.4 (CH), 128. 5 (2 CH), 128.6 (CH), 128.7 (CH), 128.8 (2 CH), 129.3 (CH), 129.9 (CH), 130.9 (2 CH), 132.4 (2 C), 133.9 (C), 134.2 (C), 134.9 (C), 137.0 (C), 137.1 (C), 137.3 (CH), 137.5 (C), 138.2 (C), 138.6 (C), 144.2 (C), 150.8 (C), 152.2 (C), 163.3 (C).

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{35}H_{23}N_3O_2Na$: 540.1682; found: 540.1693.

4,6-Bis(4-methoxyphenyl)-8,17-dihydrobenzo[*g*]quinazolino[8′,8a′,1′:2,3,4][1,4]oxazocino[6,7-*b*]quinoxalin-1-one (5b)

Yellow solid. Yield: 94%; mp 248–250 °C; R_f = 0.25 (30% EtOAc–petroleum ether).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 3.86 (s, 3 H), 3.90 (s, 3 H), 5.00 (d, *J* = 16.2 Hz, 1 H), 5.53 (d, *J* = 16.2 Hz, 1 H), 6.15 (d, *J* = 13.8 Hz, 1 H), 6.47 (d, *J* = 13.8 Hz, 1 H), 6.65 (d, *J* = 10.2 Hz, 1 H), 6.98 (m, 2 H), 7.05 (m, 2 H), 7.21 (s, 1 H), 7.28 (m, 2 H), 7.56 (m, 2 H), 7.65 (m, 2 H), 7.70 (m, 1 H), 8.07 (m, 2 H), 8.49 (s, 1 H), 8.80 (s, 1 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 51.3 (CH_2), 55.4 (2 CH_3), 77.4 (CH_2), 113.9 (2 CH), 114.0 (2 CH), 120.3 (C), 121.4 (CH), 126.5 (CH), 126.6 (CH), 126.8 (CH), 127.1 (CH), 128.3 (2 CH), 128.7 (CH), 129.2 (C), 130.7 (2 CH), 130.9 (C), 131.0 (2 CH), 133.9 (C), 134.1 (C), 134.9 (C), 136.8 (C), 137.5 (CH), 137.5 (C), 137.7 (C), 138.1 (C), 143.9 (C), 150.9 (C), 152.3 (C), 159.4 (C), 159.6 (C), 163.5 (C).

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{37}H_{27}N_3O_4Na$: 600.1894; found: 600.1902.

4,6-Di-2-naphthyl-8,17-dihydrobenzo[*g*]quinazolino[8′,8a′,1′:2,3,4][1,4]oxazocino[6,7-*b*]quinoxalin-1-one (5c)

Brown solid. Yield: 81%; mp 254–256 °C; R_f = 0.28 (30% EtOAc–petroleum ether).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 5.02 (d, *J* = 16.2 Hz, 1 H), 5.53 (d, *J* = 15.6 Hz, 1 H), 6.21 (d, *J* = 13.8 Hz, 1 H), 6.55 (d, *J* = 13.8 Hz, 1 H), 6.69 (d, *J* = 9.6 Hz, 1 H), 7.45 (s, 1 H), 7.49 (m, 1 H), 7.54 (m, 7 H), 7.74 (m, 1 H), 7.87 (m, 2 H), 7.91 (m, 1 H), 7.93 (m, 3 H), 7.99 (m, 1 H), 8.02 (m, 1 H), 8.08 (m, 1 H), 8.16 (s, 1 H), 8.46 (s, 1 H), 8.78 (s, 1 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 51.1 (CH_2), 77.5 (CH_2), 120.7 (C), 122.0 (CH), 126.3 (CH), 126.5 (CH), 126.6 (3 CH), 126.7 (CH), 126.9 (CH), 127.1 (2 CH), 127.3 (CH), 127.7 (CH), 127.8 (CH), 128.0 (CH), 128.1 (CH), 128.2 (CH), 128.3 (2 CH), 128.4 (CH), 128.6 (CH), 128.7 (CH), 129.0 (CH), 132.7 (C), 132.9 (C), 133.1 (C), 133.4 (C), 133.9 (C), 134.1 (C), 134.5 (C), 134.9 (C), 136.0 (C), 137.2 (C), 137.4 (CH), 137.5 (C), 138.1 (C), 138.2 (C), 144.3 (C), 150.8 (C), 152.2 (C), 163.3 (C).

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{43}H_{27}N_3O_2Na$: 640.1995; found: 640.1978.

4,6-Di-2-thienyl-8,17-dihydrobenzo[*g*]quinazolino[8′,8a′,1′:2,3,4][1,4]oxazocino[6,7-*b*]quinoxalin-1-one (5d)

Yellow solid. Yield: 83%; mp 240–242 °C; R_f = 0.25 (30% EtOAc–petroleum ether).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 5.07 (m, 1 H), 5.64 (m, 1 H), 6.14 (m, 1 H), 6.45 (m, 1 H), 6.68 (d, *J* = 9.6 Hz, 1 H), 7.40 (s, 1 H), 7.47 (m, 2 H), 7.56 (m, 4 H), 7.77 (m, 1 H), 7.81 (m, 1 H), 8.11 (m, 2 H), 8.51 (s, 1 H), 8.64 (s, 1 H), 8.81 (s, 1 H).

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{31}H_{19}N_3O_2S_2Na$: 552.0811; found: 552.0816.

4,6-Di-2-naphthyl-8,15-dihydronaphtho[2′,3′:6,7][1,4]oxazocino[2,3,4-*ij*]quinolin-1-one (5e)

Brown solid. Yield: 87%; mp 244–246 °C; R_f = 0.21 (25% EtOAc–petroleum ether).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 4.77 (d, *J* = 14.4 Hz, 1 H), 5.48 (d, *J* = 14.4 Hz, 1 H), 6.09 (d, *J* = 13.8 Hz, 1 H), 6.61 (d, *J* = 13.8 Hz, 1 H), 6.65 (d, *J* = 10.2 Hz, 1 H), 7.28 (s, 1 H), 7.32 (s, 1 H), 7.43 (m, 2 H), 7.45 (m, 1 H), 7.51 (m, 2 H), 7.57 (m, 2 H), 7.64 (m, 2 H), 7.81 (m, 3 H), 7.89 (m, 3 H), 7.95 (m, 2 H), 8.01 (m, 1 H), 8.06 (s, 1 H), 8.14 (s, 1 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 46.8 (CH_2), 75.8 (CH_2), 120.6 (C), 121.7 (CH), 125.0 (CH), 126.2 (CH), 126.4 (2 CH), 126.5 (CH), 126.6 (2 CH), 127.0 (CH), 127.2 (CH), 127.4 (CH), 127.7 (CH), 127.8 (CH), 127.9 (CH), 128.0 (4 CH), 128.3 (2 CH), 128.9 (CH), 131.5 (CH), 132.6 (C), 132.7 (C), 132.8 (C), 133.1 (C), 133.2 (C), 133.4 (2 C), 133.9 (C), 134.9 (C), 135.3 (C), 136.4 (C), 136.9 (CH), 137.3 (C), 137.8 (C), 143.0 (C), 163.0 (C).

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{41}H_{27}NO_2Na$: 588.1934; found: 588.1923.

4,6-Di-1-naphthyl-8,15-dihydronaphtho[2′,3′:6,7][1,4]oxazocino[2,3,4-*ij*]quinolin-1-one (5f)

Brown solid. Yield: 84%; mp 248–250 °C; R_f = 0.23 (25% EtOAc–petroleum ether).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.75 (m, 1 H), 5.28 (d, *J* = 14.1 Hz, 1 H), 6.03 (m, 2 H), 6.59 (m, 2 H), 7.36 (m, 3 H), 7.45 (m, 5 H), 7.60 (m, 5 H), 7.71 (m, 1 H), 7.84 (m, 4 H), 7.97 (m, 2 H), 8.09 (m, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 46.3 (CH_2), 78.4 (CH_2), 121.7 (C), 121.8 (CH), 125.1 (CH), 125.4 (CH), 125.9 (CH), 126.0 (CH), 126.2 (CH), 126.5 (2 CH), 126.7 (CH), 127.2 (CH), 127.8 (CH), 127.9 (CH), 128.0 (2 CH), 128.1 (CH), 128.2 (2 CH), 128.3 (2 CH), 128.4 (2 CH), 131.3 (CH), 131.9 (C), 132.7 (C), 133.1 (C), 133.4 (C), 133.5 (C), 133.8 (2 C), 134.1 (C), 134.4 (C), 135.2 (C), 136.2 (C), 136.5 (C), 137.0 (C), 137.1 (CH), 143.0 (C), 162.9 (C).

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{41}H_{27}NO_2Na$: 588.1934; found: 588.1931.

4,6-Bis(4-methoxyphenyl)-8,15-dihydronaphtho[2′,3′:6,7][1,4]oxazocino[2,3,4-*ij*]quinolin-1-one (5g)
Yellow solid. Yield: 94%; mp 243–245 °C; R_f = 0.18 (25% EtOAc–petroleum ether).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 3.85 (s, 3 H), 3.92 (s, 3 H), 4.78 (d, *J* = 14.4 Hz, 1 H), 5.48 (d, *J* = 15.0 Hz, 1 H), 6.03 (d, *J* = 13.2 Hz, 1 H), 6.53 (d, *J* = 13.8 Hz, 1 H), 6.62 (d, *J* = 9.6 Hz, 1 H), 6.94 (m, 2 H), 7.07 (m, 3 H), 7.22 (m, 2 H), 7.33 (s, 1 H), 7.42 (m, 2 H), 7.60 (s, 1 H), 7.62 (m, 2 H), 7.66 (m, 1 H), 7.81 (m, 1 H), 8.04 (s, 1 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 46.9 (CH_2), 55.3 (2 CH_3), 75.6 (CH_2), 113.8 (2 CH), 113.9 (2 CH), 120.1 (C), 121.1 (CH), 125.0 (CH), 126.1 (CH), 126.5 (CH), 126.6 (CH), 127.1 (CH), 128.0 (CH), 129.9 (C), 130.5 (2 CH), 131.0 (2 CH), 131.3 (C), 131.4 (CH), 132.6 (C), 133.1 (C), 133.4 (C), 134.0 (C), 134.8 (C), 136.9 (C), 137.0 (CH), 137.4 (C), 142.5 (C), 159.2 (C), 159.3 (C), 163.1 (C).

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{35}H_{27}NO_4Na$: 548.1832; found: 548.1811.

6-Bromo-4-(4-methoxyphenyl)-8,15-dihydronaphtho[2′,3′:6,7][1,4]oxazocino[2,3,4-*ij*]quinolin-1-one (5h)
Yellow solid. Yield: 43%; mp 241–243 °C; R_f = 0.20 (25% EtOAc–petroleum ether).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 3.92 (s, 3 H), 4.69 (d, *J* = 14.4 Hz, 1 H), 5.43 (d, *J* = 14.4 Hz, 1 H), 5.97 (d, *J* = 13.8 Hz, 1 H), 6.48 (d, *J* = 13.8 Hz, 1 H), 6.77 (d, *J* = 9.6 Hz, 1 H), 7.06 (m, 2 H), 7.20 (s, 1 H), 7.29 (s, 1 H), 7.41 (m, 2 H), 7.58 (m, 2 H), 7.63 (m, 1 H), 7.78 (m, 1 H), 7.98 (m, 2 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 30.9 (CH_3), 46.8 (CH_2), 75.6 (CH_2), 114.1 (2 CH), 119.3 (C), 122.5 (CH), 125.0 (CH), 125.3 (CH), 126.2 (CH), 126.6 (CH), 127.1 (CH), 127.9 (CH), 128.3 (C), 128.8 (C), 130.4 (2 CH), 131.4 (CH), 132.6 (C), 132.9 (C), 133.1 (C), 133.4 (C), 134.9 (CH), 135.7 (C), 138.0 (C), 142.2 (C), 159.6 (C), 162.8 (C).

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{28}H_{20}BrNO_3Na$: 520.0519; found: 520.0554.

Polycyclic Alkynylquinolinones 7a–d, 9a–h, 11a–d, 13a, and 13b; General Procedure
One of the arylacetylenes **6a–e** (1.1 mmol), Et_3N (1.1 mmol), and CuI (0.2 mmol) were added to DMF (10 mL) in a 25-mL round-bottom flask, and the mixture was stirred for 30 min at r.t. under an argon atmosphere. The fused dihaloquinolinone **3c**, **8a–c**, **10** or **12** (1.0 mmol), $Pd(OAc)_2$ (0.2 mol%) and Ph_3P (1 mol%) were then added to the mixture and the stirring was continued for the appropriate time period, as given in Tables 6 and 7; TLC was performed every 2 h to monitor the progress of the reaction. After completion of the reaction, the mixture was extracted with EtOAc (3 × 50 mL). The organic layers were combined, washed thoroughly with brine (25 mL), dried (Na_2SO_4), and evaporated to dryness in a rotary evaporator under reduced pressure. The residue was purified by chromatography (silica gel, EtOAc–petroleum ether) to give the corresponding fused alkynylquinolinone.

4-Chloro-6-(phenylethynyl)-8,15-dihydronaphtho[2′,3′:6,7][1,4]oxazocino[2,3,4-*ij*]quinolin-1-one (7a)
Brown crystalline solid. Yield: 78%; mp 263–265 °C; R_f = 0.23 (25% EtOAc–petroleum ether).

IR (KBr): 3455, 1653, 1587 cm^{-1}.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 5.83 (d, *J* = 14.4 Hz, 1 H), 5.97 (m, 2 H), 6.62 (d, *J* = 13.8 Hz, 1 H), 6.78 (d, *J* = 9.6 Hz, 1 H), 7.36 (s, 1 H), 7.42 (m, 2 H), 7.45 (m, 3 H), 7.57 (s, 1 H), 7.68 (m, 3 H), 7.78 (m, 1 H), 7.95 (m, 1 H), 8.01 (s, 1 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 45.8 (CH_2), 76.1 (CH_2), 84.3 (C), 97.2 (C), 120.4 (C), 121.3 (C), 122.4 (C), 123.2 (CH), 125.4 (CH), 126.4 (CH), 126.6 (CH), 126.8 (CH), 127.2 (CH), 128.0 (CH), 128.5 (C), 128.6 (2 CH), 129.2 (CH), 131.6 (CH), 131.8 (2 CH), 132.7 (C), 132.8 (C), 133.2 (2 C), 134.7 (CH), 135.3 (C), 145.5 (C), 162.2 (C).

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{29}H_{18}ClNO_2Na$: 470.0918; found: 470.0941.

4-Chloro-6-[(4-fluorophenyl)ethynyl]-8,15-dihydronaphtho[2′,3′:6,7][1,4]oxazocino[2,3,4-*ij*]quinolin-1-one (7b)
Gray crystalline solid. Yield: 73%; mp 256–258 °C; R_f = 0.21 (25% EtOAc–petroleum ether).

IR (KBr): 3450, 1668, 1586 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.79 (d, *J* = 14.7 Hz, 1 H), 5.97 (m, 2 H), 6.61 (d, *J* = 13.5 Hz, 1 H), 6.79 (d, *J* = 9.9 Hz, 1 H), 7.15 (m, 2 H), 7.35 (m, 1 H), 7.43 (m, 2 H), 7.57 (s, 1 H), 7.67 (m, 3 H), 7.79 (m, 1 H), 7.95 (m, 1 H), 8.02 (s, 1 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 45.9 (CH_2), 76.2 (CH_2), 84.0 (C), 96.0 (C), 115.9 (CH), 116.1 (CH), 118.5 (C), 118.6 (C), 120.4 (C), 121.1 (C), 123.2 (CH), 125.4 (CH), 126.4 (CH), 126.6 (CH), 126.9 (CH), 127.2 (CH), 128.0 (CH), 128.5 (C), 131.6 (CH), 132.7 (C), 132.8 (C), 133.1 (C), 133.2 (C), 133.7 (CH), 133.8 (CH), 134.7 (CH), 135.3 (C), 145.6 (C), 162.1 (C), 162.2 (C).

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{29}H_{17}ClFNO_2Na$: 488.0824; found: 488.0859.

4-Chloro-6-[(3-chlorophenyl)ethynyl]-8,15-dihydronaphtho[2′,3′:6,7][1,4]oxazocino[2,3,4-*ij*]quinolin-1-one (7c)
Brown crystalline solid. Yield: 74%; mp 258–260 °C; R_f = 0.24 (25% EtOAc–petroleum ether).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.77 (d, *J* = 14.4 Hz, 1 H), 5.97 (m, 2 H), 6.61 (d, *J* = 13.8 Hz, 1 H), 6.80 (d, *J* = 9.6 Hz, 1 H), 7.35 (s, 1 H), 7.42 (m, 4 H), 7.56 (m, 2 H), 7.65 (s, 1 H), 7.70 (m, 1 H), 7.79 (m, 1 H), 7.96 (m, 1 H), 8.02 (s, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 45.9 (CH_2), 76.3 (CH_2), 85.4 (C), 95.4 (C), 120.6 (C), 120.7 (C), 123.4 (CH), 124.2 (C), 125.4 (CH), 126.4 (CH), 126.6 (CH), 126.9 (CH), 127.2 (CH), 128.0 (CH), 128.5 (C), 129.5 (CH), 129.9 (2 CH), 131.6 (CH), 131.7 (CH), 132.7 (2 C), 133.1 (C), 133.3 (C), 134.5 (C), 134.6 (CH), 135.4 (C), 145.8 (C), 162.1 (C).

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{29}H_{17}Cl_2NO_2Na$: 504.0529; found: 504.0498.

4-Chloro-6-(2-pyridylethynyl)-8,15-dihydronaphtho[2′,3′:6,7][1,4]oxazocino[2,3,4-*ij*]quinolin-1-one (7d)
Yellowish crystalline solid. Yield: 70%; mp 248–250 °C; R_f = 0.21 (25% EtOAc–petroleum ether).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.84 (d, *J* = 14.4 Hz, 1 H), 5.99 (m, 2 H), 6.61 (d, *J* = 13.5 Hz, 1 H), 6.81 (d, *J* = 9.6 Hz, 1 H), 7.36 (m, 1 H), 7.44 (m, 3 H), 7.60 (s, 1 H), 7.69 (m, 2 H), 7.79 (m, 2 H), 7.97 (m, 1 H), 8.01 (s, 1 H), 8.73 (m, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 45.9 (CH_2), 76.4 (CH_2), 83.7 (C), 95.8 (C), 120.3 (C), 120.9 (C), 123.5 (CH), 123.6 (CH), 125.5 (CH), 126.4 (CH), 126.8 (CH), 126.9 (CH), 127.2 (CH), 127.6 (CH), 127.9 (CH), 128.5 (C), 131.5 (CH), 132.7 (2 C), 133.1 (C), 133.2 (C), 134.6 (CH), 135.3 (C), 136.4 (CH), 142.7 (C), 146.2 (C), 150.4 (CH), 162.0 (C).

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{28}H_{17}ClN_2O_2Na$: 471.0871; found: 471.0883.

8-Chloro-10-(phenylethynyl)-2,3-dihydro[1,4]oxazino[2,3,4-*ij*]quinolin-5-one (9a)

Yellowish crystalline solid. Yield: 93%; mp 163–164 °C; R_f = 0.55 (40% EtOAc–petroleum ether).

IR (KBr): 3460, 1663, 1590 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.30 (m, 2 H), 4.49 (m, 2 H), 6.79 (d, *J* = 9.9 Hz, 1 H), 7.38 (m, 4 H), 7.67 (m, 2 H), 8.09 (d, *J* = 9.6 Hz, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 39.8 (CH_2), 64.1 (CH_2), 83.6 (C), 96.9 (C), 112.9 (C), 118.2 (C), 122.5 (C), 122.6 (CH), 123.8 (C), 126.0 (CH), 127.8 (C), 128.4 (2 CH), 128.9 (CH), 131.8 (2 CH), 135.4 (CH), 142.9 (C), 159.6 (CO).

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{19}H_{12}ClNO_2Na$: 344.0449; found: 344.0461.

8-Chloro-10-[(4-fluorophenyl)ethynyl]-2,3-dihydro[1,4]oxazino[2,3,4-*ij*]quinolin-5-one (9b)

White crystalline solid. Yield: 88%; mp 151–153 °C; R_f = 0.50 (40% EtOAc–petroleum ether).

IR (KBr): 3460, 1669, 1588 cm^{-1}.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 4.29 (m, 2 H), 4.49 (m, 2 H), 6.78 (d, *J* = 10.2 Hz, 1 H), 7.07 (m, 2 H), 7.35 (s, 1 H), 7.56 (m, 2 H), 8.08 (d, *J* = 10.2 Hz, 1 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 39.8 (CH_2), 64.2 (CH_2), 83.3 (C), 95.8 (C), 112.7 (C), 115.7 (CH), 115.9 (CH), 118.3 (C), 118.6 (C), 122.6 (CH), 123.9 (C), 125.9 (CH), 127.8 (C), 133.7 (CH), 133.8 (CH), 135.4 (CH), 142.8 (C), 159.6 (CO), 162.0 (C), 163.7 (C).

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{19}H_{11}ClFNO_2Na$: 362.0355; found: 362.0343

8-Chloro-10-(2-pyridylethynyl)-2,3-dihydro[1,4]oxazino[2,3,4-*ij*]quinolin-5-one (9c)

White crystalline solid. Yield: 86%; mp 199–200 °C; R_f = 0.14 (40% EtOAc–petroleum ether).

IR (KBr): 3455, 1663, 1590 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.30 (m, 2 H), 4.50 (t, *J* = 4.5 Hz, 2 H), 6.80 (d, *J* = 9.9 Hz, 1 H), 7.29 (m, 1 H), 7.43 (s, 1 H), 7.58 (d, *J* = 4.8 Hz, 1 H), 7.73 (m, 1 H), 8.09 (d, *J* = 9.9 Hz, 1 H), 8.66 (d, *J* = 4.2 Hz, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 39.7 (CH_2), 64.2 (CH_2), 83.1 (C), 95.6 (C), 111.8 (C), 118.7 (C), 122.9 (CH), 123.2 (CH), 123.8 (C), 126.1 (CH), 127.4 (CH), 127.8 (C), 135.3 (CH), 136.2 (CH), 142.7 (C), 143.5 (C), 150.2 (CH), 159.5 (CO).

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{18}H_{11}ClN_2O_2Na$: 345.0407; found: 345.0407

9-Chloro-11-(phenylethynyl)-3,4-dihydro[1,4]oxazepino[2,3,4-*ij*]quinolin-6(2*H*)-one (9d)

White crystalline solid. Yield: 91%; mp 171–173 °C; R_f = 0.62 (40% EtOAc–petroleum ether).

IR (KBr): 3448, 1661, 1580 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.36 (m, 2 H), 4.43 (m, 2 H), 4.63 (m, 2 H), 6.75 (d, *J* = 9.6 Hz, 1 H), 7.37 (m, 4 H), 7.56 (m, 2 H), 8.03 (d, *J* = 9.9 Hz, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 27.6 (CH_2), 42.3 (CH_2), 71.4 (CH_2), 84.2 (C), 96.4 (C), 118.1 (C), 120.1 (C), 122.6 (C), 123.0 (CH), 126.1 (C), 126.6 (CH), 128.4 (2 CH), 128.9 (CH), 131.8 (2 CH), 134.9 (C), 135.2 (CH), 148.6 (C), 162.0 (CO).

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{20}H_{14}ClNO_2Na$: 358.0605; found: 358.0618.

9-Chloro-11-[(4-fluorophenyl)ethynyl]-3,4-dihydro[1,4]oxazepino[2,3,4-*ij*]quinolin-6(2*H*)-one (9e)

Brown crystalline solid. Yield: 88%; mp 177–178 °C; R_f = 0.55 (40% EtOAc–petroleum ether).

IR (KBr): 3440, 1673, 1585 cm^{-1}

^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.36 (m, 2 H), 4.21 (m, 2 H), 4.62 (m, 2 H), 6.75 (d, *J* = 9.8 Hz, 1 H), 7.06 (m, 2 H), 7.34 (s, 1 H), 7.54 (m, 2 H), 8.02 (d, *J* = 9.8 Hz, 1 H).

^{13}C NMR (400 MHz, $CDCl_3$): δ = 27.6 (CH_2), 42.3 (CH_2), 71.5 (CH_2), 83.9 (C), 95.2 (C), 115.6 (CH), 116.0 (CH), 117.9 (C), 118.8 (C), 120.2 (C), 123.1 (CH), 126.2 (CH), 128.8 (C), 133.7 (CH), 133.9 (CH), 135.0 (C), 135.2 (CH), 148.6 (C), 160.5 (C), 162.0 (C).

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{20}H_{13}ClFNO_2Na$: 376.0517; found: 376.0561.

9-Chloro-11-(cyclopropylethynyl)-3,4-dihydro[1,4]oxazepino[2,3,4-*ij*]quinolin-6(2*H*)-one (9f)

Yellowish crystalline solid. Yield: 47%; mp 183–185 °C; R_f = 0.61 (40% EtOAc–petroleum ether).

IR (KBr): 3467, 1651, 1564 cm^{-1}

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.91 (m, 4 H), 1.53 (m, 1 H), 2.33 (m, 2 H), 4.32 (m, 2 H), 4.59 (m, 2 H), 6.71 (d, *J* = 9.3 Hz, 1 H), 7.20 (s, 1 H), 7.98 (d, *J* = 9.9 Hz, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 0.6 (CH), 9.1 (2 CH_2), 27.7 (CH_2), 42.1 (CH_2), 70.7 (C), 71.2 (CH_2), 101.4 (C), 118.8 (C), 119.5 (C), 122.6 (CH), 125.9 (C), 126.9 (CH), 134.8 (C), 135.2 (CH), 148.7 (C), 162.1 (CO).

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{17}H_{14}ClNO_2Na$: 322.0605; found: 322.0590.

10-Chloro-12-(phenylethynyl)-2,3,4,5-tetrahydro[1,4]oxazocino[2,3,4-*ij*]quinolin-7-one (9g)

Yellow crystalline solid. Yield: 92%; mp 119–120 °C; R_f = 0.75 (40% EtOAc–petroleum ether).

IR (KBr): 3457, 1667, 1577 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.63 (m, 2 H), 2.07 (m, 2 H), 4.45 (m, 2 H), 4.95 (m, 2 H), 6.79 (d, *J* = 9.6 Hz, 1 H), 7.39 (m, 4 H), 7.55 (m, 2 H), 8.12 (d, *J* = 9.6 Hz, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 22.2 (CH_2), 26.8 (CH_2), 44.1 (CH_2), 76.2 (CH_2), 84.3 (C), 96.2 (C), 119.4 (C), 122.0 (C), 122.5 (C), 123.0 (CH), 126.4 (CH), 128.2 (C), 128.4 (2 CH), 128.9 (CH), 131.7 (2 CH), 135.1 (CH), 138.0 (C), 144.5 (C), 162.2 (CO).

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{21}H_{16}ClNO_2Na$: 372.0767; found: 372.0804.

10-Chloro-12-[(4-fluorophenyl)ethynyl]-2,3,4,5-tetrahydro[1,4]oxazocino[2,3,4-*ij*]quinolin-7-one (9h)

Brown crystalline solid. Yield: 85%; mp 139–140 °C; R_f = 0.69 (40% EtOAc–petroleum ether).

IR (KBr): 3450, 1663, 1584 cm^{-1}

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.61 (m, 2 H), 2.08 (m, 2 H), 4.42 (m, 2 H), 4.92 (m, 2 H), 6.79 (d, *J* = 9.3 Hz, 1 H), 7.08 (m, 2 H), 7.41 (s, 1 H), 7.55 (m, 2 H), 8.12 (d, *J* = 9.6 Hz, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 22.3 (CH_2), 26.8 (CH_2), 44.1 (CH_2), 76.3 (CH_2), 84.1 (C), 95.0 (C), 115.7 (CH), 116.0 (CH), 118.7 (C), 119.5 (C), 121.8 (C), 123.1 (CH), 126.3 (CH), 128.2 (C), 133.7 (CH), 133.8 (CH), 135.1 (CH), 138.0 (C), 144.5 (C), 161.2 (CO), 162.2 (C), 164.5 (C).

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{21}H_{15}ClFNO_2Na$: 390.0673; found: 390.0721.

4-Chloro-6-(phenylethynyl)-8,13-dihydrobenzo[1′,2′:6,7][1,4]oxazocino[2,3,4-*ij*]quinolin-1-one (11a)
Yellowish crystalline solid. Yield: 87%; mp 202–204 °C; R_f = 0.83 (40% EtOAc–petroleum ether).

IR (KBr): 3453, 1655, 1579 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.58 (d, *J* = 14.7 Hz, 1 H), 5.87 (m, 2 H), 6.39 (d, *J* = 13.5 Hz, 1 H), 6.77 (d, *J* = 9.9 Hz, 1 H), 7.06 (m, 1 H), 7.23 (m, 2 H), 7.38 (s, 1 H), 7.43 (m, 3 H), 7.53 (m, 1 H), 7.63 (m, 2 H), 7.97 (d, *J* = 9.6 Hz, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 45.2 (CH_2), 76.5 (CH_2), 84.2 (C), 97.1 (C), 120.3 (C), 121.3 (C), 122.4 (C), 123.0 (CH), 126.0 (CH), 126.6 (CH), 128.4 (CH), 128.51 (CH), 128.53 (C), 128.6 (2 CH), 129.2 (CH), 131.8 (2 CH), 132.5 (CH), 134.5 (C), 134.6 (CH), 135.1 (C), 136.0 (C), 145.8 (C), 162.0 (CO).

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{25}H_{16}ClNO_2Na$: 420.0767; found: 420.0804.

4-Chloro-6-[(4-fluorophenyl)ethynyl]-8,13-dihydrobenzo[1′,2′:6,7][1,4]oxazocino[2,3,4-*ij*]quinolin-1-one (11b)
Yellowish crystalline solid. Yield: 83%; mp 249 °C; R_f = 0.81 (40% EtOAc–petroleum ether).

IR (KBr): 3427, 1660, 1581 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.55 (d, *J* = 14.7 Hz, 1 H), 5.87 (m, 2 H), 6.38 (d, *J* = 13.5 Hz, 1 H), 6.77 (d, *J* = 9.6 Hz, 1 H), 7.12 (m, 3 H), 7.24 (m, 2 H), 7.37 (s, 1 H), 7.53 (m, 1 H), 7.62 (m, 2 H), 7.98 (d, *J* = 9.6 Hz, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 45.2 (CH_2), 76.5 (CH_2), 84.0 (C), 95.9 (C), 115.8 (CH), 116.1 (CH), 118.5 (C), 118.6 (C), 120.4 (C), 121.1 (C), 123.1 (CH), 125.9 (CH), 126.5 (CH), 128.4 (CH), 128.5 (CH), 132.5 (CH), 133.7 (CH), 133.8 (CH), 134.5 (C), 134.6 (CH), 135.1 (C), 135.8 (C), 145.8 (C), 161.3 (C), 162.0 (C), 164.7 (CO).

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{25}H_{15}ClFNO_2Na$: 438.0668; found: 438.0665.

4-Chloro-6-(2-pyridylethynyl)-8,13-dihydrobenzo[1′,2′:6,7][1,4]oxazocino[2,3,4-*ij*]quinolin-1-one (11c)
Brown crystalline solid. Yield: 67%; mp 109–110 °C; R_f = 0.36 (40% EtOAc–petroleum ether).

IR (KBr): 3408, 1659, 1581 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 5.57 (d, *J* = 15.0 Hz, 1 H), 5.84 (m, 2 H), 6.34 (d, *J* = 13.6 Hz, 1 H), 6.75 (d, *J* = 9.8 Hz, 1 H), 7.08 (m, 1 H), 7.23 (m, 3 H), 7.40 (s, 1 H), 7.49 (m, 1 H), 7.66 (m, 2 H), 7.94 (d, *J* = 9.8 Hz, 1 H), 8.59 (d, *J* = 4.8 Hz, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 45.3 (CH_2), 76.9 (CH_2), 83.8 (C), 95.8 (C), 120.4 (C), 120.9 (C), 123.5 (CH), 123.8 (CH), 126.1 (C), 127.6 (CH), 128.4 (CH), 128.5 (CH), 130.9 (C), 132.5 (CH), 134.5 (C), 134.6 (C), 135.9 (CH), 136.2 (CH), 136.4 (CH), 142.7 (C), 146.6 (C), 150.4 (CH), 161.9 (CO).

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{24}H_{15}ClN_2O_2Na$: 421.0714; found: 421.0720.

4-Chloro-6-(cyclopropylethynyl)-8,13-dihydrobenzo[1′,2′:6,7][1,4]oxazocino[2,3,4-*ij*]quinolin-1-one (11d)
Yellowish crystalline solid. Yield: 52%; mp 216–218 °C; R_f = 0.77 (40% EtOAc–petroleum ether).

IR (KBr): 3463, 1656, 1567 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.94 (m, 4 H), 1.66 (m, 1 H), 5.46 (d, *J* = 15.0 Hz, 1 H), 5.81 (m, 2 H), 6.34 (m, 1 H), 6.75 (m, 1 H), 7.03 (m, 1 H), 7.24 (m, 3 H), 7.51 (m, 1 H), 7.96 (m, 1 H).

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{22}H_{16}ClNO_2Na$: 384.0762; found: 384.0744.

4-Chloro-6-(phenylethynyl)-8,15-dihydroquinazolino[8′,8a′,1′:2,3,4][1,4]oxazocino[6,7-*b*]quinoxalin-1-one (13a)
Brown crystalline solid. Yield: 86%; mp 259–260 °C; R_f = 0.63 (40% EtOAc–petroleum ether).

IR (KBr): 3453, 1667, 1580 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.79 (d, *J* = 16.2 Hz, 1 H), 5.97 (d, *J* = 16.2 Hz, 1 H), 6.19 (d, *J* = 13.2 Hz, 1 H), 6.73 (d, *J* = 13.5 Hz, 1 H), 6.83 (d, *J* = 9.9 Hz, 1 H), 7.43 (m, 4 H), 7.65 (m, 2 H), 7.74 (m, 2 H), 7.99 (m, 2 H), 8.16 (m, 1 H).

^{13}C NMR (300 MHz, $CDCl_3$): δ = 48.5 (CH_2), 76.8 (CH_2), 83.7 (C), 98.1 (C), 120.4 (C), 121.3 (C), 122.2 (C), 123.5 (CH), 127.0 (CH), 128.3 (CH), 128.6 (2 CH), 129.0 (C), 129.3 (CH), 129.8 (CH), 130.1 (CH), 130.8 (CH), 131.7 (C), 131.9 (2 CH), 134.9 (CH), 141.1 (C), 141.9 (C), 145.9 (C), 149.3 (C), 151.4 (C), 162.0 (CO).

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{27}H_{16}ClN_3O_2Na$: 472.0823; found: 472.0830.

4-Chloro-6-[(4-fluorophenyl)ethynyl]-8,15-dihydroquinazolino[8′,8a′,1′:2,3,4][1,4]oxazocino[6,7-*b*]quinoxalin-1-one (13b)
White crystalline solid. Yield: 80%; mp 257–258 °C; R_f = 0.67 (40% EtOAc–petroleum ether).

IR (KBr): 3438, 1673, 1580 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.75 (d, *J* = 16.2 Hz, 1 H), 5.96 (d, *J* = 16.2 Hz, 1 H), 6.17 (d, *J* = 16.2 Hz, 1 H), 6.72 (d, *J* = 13.5 Hz, 1 H), 6.83 (d, *J* = 12.6 Hz, 1 H), 7.13 (m, 2 H), 7.40 (s, 1 H), 7.64 (m, 2 H), 7.75 (m, 2 H), 7.99 (m, 2 H), 8.17 (m, 1 H).

^{13}C NMR (300 MHz, $CDCl_3$): δ = 48.5 (CH_2), 76.9 (CH_2), 83.5 (C), 96.9 (C), 115.8 (CH), 116.1 (CH), 118.3 (C), 120.4 (C), 121.0 (C), 123.6 (CH), 126.9 (CH), 128.2 (CH), 129.0 (C), 129.8 (CH), 130.2 (CH), 130.9 (CH), 133.8 (CH), 133.9 (CH), 134.8 (CH), 134.9 (C), 141.1 (C), 141.9 (C), 145.9 (C), 149.3 (C), 151.3 (C), 161.4 (CO), 161.9 (C), 164.8 (C).

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{27}H_{15}ClFN_3O_2Na$: 490.0729; found: 490.0737.

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(20) For the single-crystal X-ray crystallographic analysis of compound **3a** ($C_{21}H_{15}NO_2$), yellowish needle-shaped crystals were grown from $CHCl_3$–MeCN (7:3); monoclinic, space group *P*2(1)/*n*; unit cell parameters: a = 14.102(5), b = 15.073(5), c = 15.994(6). Diffraction data were measured with MoKα (0.71073 Å) radiation at 296 K using a Kappa Apex 2 instrument. The structure was solved by direct methods using the SHELX-97 program. Refinements of F^2 were carried out against all reflections using SHELX-97.

(21) For the single-crystal X-ray crystallographic analysis of compound **11a** ($C_{25}H_{16}ClNO_2$), yellowish block-shaped crystals were grown from $CHCl_3$–MeCN (9:1); triclinic, space group *P*1; unit cell parameters: a = 9.1980(7), b = 10.0460(8), c = 10.9903(9), α = 70.913(3), β = 87.778(3), γ = 79.707(2). Diffraction data were measured with MoKα (0.71073 Å) radiation at 296 K using a Kappa Apex 2 instrument. The structure was solved by direct methods using the SHELX-97 program. Refinements of F^2 were carried out against all reflections using SHELX-97.