Azaanthraquinone assembly from *N*-propargylamino quinone *via* iodine-induced 6-*endo-dig* electrophilic cyclization†

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An efficient methodology taking advantage of the excellent nucleophilicity of aminoquinone to assemble the azaanthraquinone framework was developed *via* an iodine-induced 6-*endo-dig* electrophilic cyclization. Therefore, starting from *N*-propargylaminoquinones, various 3-iodo-1-azaanthraquinones were obtained in yields ranging from 45% to 90%. The metal-free protocol features facile installation of an iodine atom on the azaanthraquinone ring and benign functional group compatibility.

Introduction

Considerable efforts have been devoted to the assembly of the 1-azaanthraquinone framework because naturally occurring alkaloids with this skeleton display diversified biological activities ranging from antimicrobial capacity to cytotoxicity.[1] Two kinds of synthetic approach based on Diels–Alder reaction have been applied extensively.[2,3] One involves pyridine annelation from aza-1,3-diene and 1,4-naphthoquinone (Fig. 1, route I), the other concerns benzene ring construction from 1,3-diene and 5,8-quinolinedione (Fig. 1, route II). However, these reactions suffered from low regioselectivity when asymmetric 1,3-dienes or quinone dienophiles were employed. Furthermore, the dimethylamine eliminated from the initial aza-Diels–Alder adduct is apt to react with the quinone dienophiles, significantly decreasing the reaction efficiency. Consequently, the development of new methodology for 1-azaanthraquinones is still highly desirable and challenging.

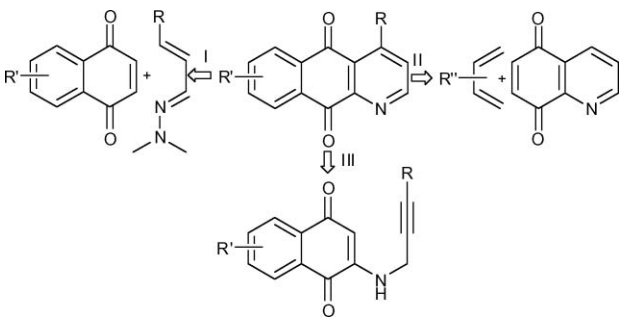
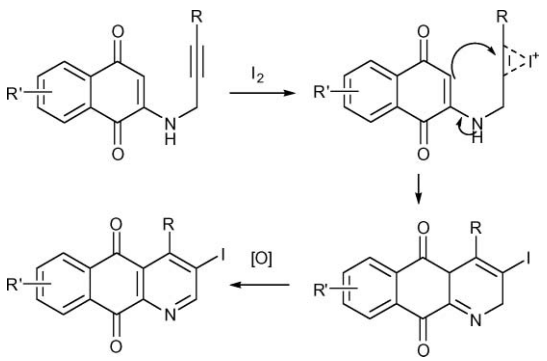


Fig. 1 Strategies for azaanthraquinone assembly.

Electrophilic cyclization has attracted much attention in recent decades and proven to be a powerful means to elaborate carbocycles and heterocycles.[4] Larock and Barluenga independently explored the electrophilic cyclization of alkynes by utilizing molecular iodine and bis(pyridine)iodonium tetrafluoroborate (IPy_2BF_4) as electrophiles.[5,6] The general mechanism includes activation of the C–C triple bond by iodine cation and subsequent nucleophilic attack by an intramolecular nucleophile. Thus, alkynes containing N, O, S functionalities undergo iodocyclization to afford heterocycles such as indoles,[5a,5b,6a,7a] isoindolinones,[5c] isoquinolines,[5d,5e,8] isocoumarins,[5g] isochromenes,[5h,6b,6c] furans,[5i,9] benzo[*b*]furans[5j] and benzo[*b*]thiophenes.[5l,5m,7b,7c] Besides N, O, S functionalities, arenes may also act as nucleophiles in electrophilic cyclization, furnishing quinolines[5f] and 2*H*-benzopyrans.[5k,6e] This metal-free methodology features robust conditions and facile installation of an iodine atom on the heterocycle ring.

Recently, we have developed an alternative route to attain azaanthraquinones from *N*-propargylaminoquinones by employing a Au(I)-catalyzed 6-*endo* cycloisomerization (Fig. 1, route III).[10] The nucleophilicity of aminoquinone in the metal-catalyzed cycloisomerization differs significantly from that of electron-rich double bonds such as enamide and enamine, as well as enaminone.[11] This finding prompted us to further investigate the reactivity of *N*-propargylaminoquinone in electrophilic cyclization and to explore the possibility of another strategy for the assembly of azaanthraquinones. As illustrated in Scheme 1, molecular iodine selectively coordinates with the C–C triple bond to form an iodonium ion, promoting nucleophilic attack from the double bond of the aminoquinone in a 6-*endo* manner. Then, the cyclized intermediate undergoes oxidative aromatization to afford the 1-azaanthraquinone.



Scheme 1 Proposed synthesis of 1-azaanthraquinone by iodine-induced 6-*endo-dig* electrophilic cyclization.

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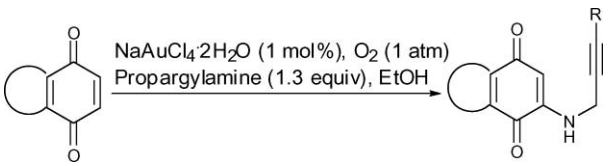
Results and discussion

Preparation of *N*-propargylaminoquinone by Au(III)-catalyzed sequential 1,4-nucleophilic addition–oxidation

Gold salts exhibit excellent Lewis acid properties in various chemical transformations involving the formation of C–C, C–O and C–N bonds.[12] As one of simplest salts, $NaAuCl_4 \cdot 2H_2O$ can selectively activate the carbonyl group in some condensation and addition reactions.[13,14] In our previous study, we developed a catalytic process to prepare aminoquinones by utilizing $NaAuCl_4 \cdot 2H_2O$ (Scheme 2).[15] The gold(III) catalyst not only promoted the 1,4-nucleophilic addition through activation the carbonyl group of the quinone but also accelerated the oxidation of the adduct amino-hydroquinone. Various aliphatic and aromatic amines underwent the sequential 1,4-nucleophilic addition–oxidation with quinones smoothly. However, what surprised us was the stability of the adduct derived from 2-butynylamine and 1,4-naphthoquinone in the reaction system, since Acradi reported that the enamines tethered by alkyne units proceeded through Au(III)-catalyzed cycloisomerization efficiently to afford pyridine derivatives.[11a] To further explore the nucleophilicity of *N*-propargylaminoquinones and screen the scope of the Au(III)-catalyzed sequential process, different quinones and propargylamines were examined. As shown in Table 1, 1,4-naphthoquinone reacted with various substituted aromatic propargylamines (*p*-Me, *p*-OMe, *p*-NO_2, *o*-NO_2, *o*-CO_2Me, *o*-Br), as well as 2-hexynylamine and 2-butynylamine, smoothly to afford corresponding *N*-propargylaminoquinones **1a–1i** in 60–78% yield (Table 1, entries 1–9). 2-Butynylamine reacted with different quinones including 8-methoxy-1,4-naphthoquinone, 8-hydroxy-1,4-naphthoquinone, 6,7-dimethoxy-1,4-naphthoquinone, 2,5,8-quinolinetrione and 5,8-quinolinedione regioselectively, the corresponding adducts **1j–1n** were obtained in yields ranging from 55% to 80% (Table 1, entries 10–14).

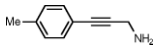
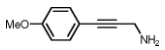
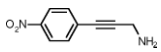
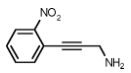
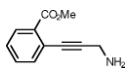
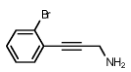
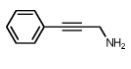
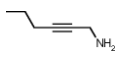
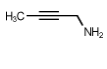
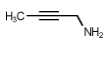
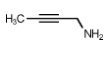
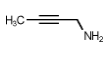
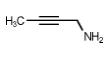
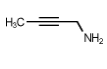


Scheme 2 Au(III)-catalyzed 1,4-nucleophilic addition–oxidation.

Assembly of azaanthraquinone by I_2-induced 6-*endo-dig* electrophilic cyclization

To examine the feasibility of the electrophilic cyclization, we initiated the study by choosing enyne **1a** as substrate (Scheme 3, Table 2). By treating compound **1a** with molecular iodine and $NaHCO_3$ in CH_2Cl_2 at room temperature for 12 h, the desired azaanthraquinone **2a** was achieved in 42% yield (Table 2, entry 1). A side-product **3** generated from 1,2-addition of iodine to the alkyne bond was also isolated. However, the amount of this 1,2-adduct can be reduced dramatically by raising the reaction temperature. When the cyclization was performed in 1,2-dichloroethane or acetonitrile at 80 °C, the yield of **2a** increased to 56% and 65%, respectively (Table 2, entries 2–3). To further raise the temperature to 100 °C, the solvent was switched to dioxane or nitromethane,

Table 1 Preparation of *N*-Propargylaminoquinone by Au(III)-catalyzed 1,4-nucleophilic addition-oxidation[a]

Entry	Quinone	Amine	Aminoquinone	Yield (%)
1			**1a**	65
2			**1b**	70
3			**1c**	65
4			**1d**	60
5			**1e**	72
6			**1f**	74
7			**1g**	60
8			**1h**	78
9			**1i**	70
10[b]			**1j**	60
11[b]			**1k**	80
12			**1l**	65
13[b]			**1m**	60
14[b]			**1n**	55

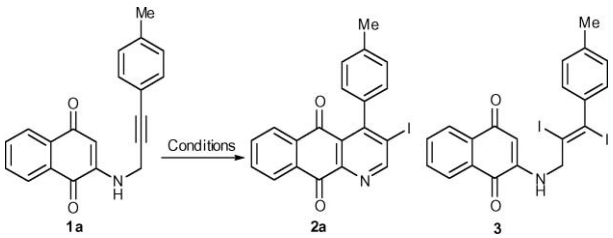
[a] 1 mol% $NaAuCl_4 \cdot 2H_2O$, 80 °C, 2 h. [b] 1 mol% $NaAuCl_4 \cdot 2H_2O$, rt, 4 h.

and we found that the electrophilic cyclization gave the best yield in nitromethane (Table 2, entries 4–5). Attempts to employ other additives such as Na_2CO_3, K_2CO_3 and K_3PO_4 resulted in inferior results (Table 2, entries 6–8). Although the transformation could be carried out by utilizing electrophiles NIS and ICl (Table 2, entries 9–10), the optimized condition was established to be a

Table 2 Optimization of reaction conditions

Entry	Electrophile[a]	Conditions[b]	Yield (%)[c]
1	I_2	$NaHCO_3$, CH_2Cl_2, rt, 12 h	42
2	I_2	$NaHCO_3$, $(ClCH_2)_2$, 80 °C, 12 h	56
3	I_2	$NaHCO_3$, CH_3CN, 80 °C, 12 h	65
4	I_2	$NaHCO_3$, dioxane, 100 °C, 12 h	40
5	I_2	$NaHCO_3$, CH_3NO_2, 100 °C, 4 h	77
6	I_2	Na_2CO_3, CH_3NO_2, 100 °C, 4 h	60
7	I_2	K_2CO_3, CH_3NO_2, 100 °C, 4 h	56
8	I_2	K_3PO_4, CH_3NO_2, 100 °C, 4 h	60
9	NIS	CH_3NO_2, 100 °C, 4 h	70
10	ICl	CH_3NO_2, 100 °C, 4 h	67

[a] 3.0 equivalents of electrophile was used. [b] The amount of additive is 2.0 equivalents. [c] Isolated yields.



Scheme 3 Azaanthraquinone assembly by electrophilic cyclization.

combination of iodine and nitromethane (Table 2, entry 5) after comparing the reaction efficiency and practicality.

The scope of the transformation was next investigated. As shown in Table 3, enyne substrates containing various aryl groups at the alkyne terminus underwent the iodine-induced 6-*endo*-*dig* electrophilic cyclization smoothly to afford the 4-aryl-1-azaanthraquinones with 53% to 77% yield (Table 3, entries 1–7). An electron-donating substituent (*p*-OMe) on the aryl ring facilitated the cyclization while electron-withdrawing substituents (*p*-NO_2, *o*-NO_2, *o*-CO_2Me, *o*-Br) hindered the conversion. For a Ph group, the yield was moderate. The structure of azaanthraquinone **2e** was further confirmed by X-ray crystallographic analysis (Fig. 2).[16] Different from the arylated 1-azaanthraquinones, alkyl-substituted 1-azaanthraquinone was obtained in higher yield (Table 3, entry 8). Considering that the alkaloid cleistopholine and its hydroxyl/methoxy derivatives feature a 4-methyl group on the 1-azaanthraquinone ring, we then turned our attention to the electrophilic cyclization of enynes derived from 2-butylnylamine and different 1,4-naphthoquinones. Enyne **1i** with a less sterically demanding methyl group converted to 3-iodocleistopholine **2i** in 90% yield (Table 3, entry 9). In a similar manner, 3-iodo-8-methoxycleistopholine **2j**, 5-hydroxy-3-iodocleistopholine **2k** and 6,7-dimethoxy-3-iodocleistopholine **2l** were prepared from enynes **1j–l** conveniently (Table 3, entries 10–12). Notably, the incorporation of an iodine atom on cleistopholine would definitely offer new opportunities for structure–activity relationship study and for further structural elaboration. In addition, enynes containing pyridone and pyridine moieties were well tolerated to afford 1,8-diazaanthraquinone **2m** and 1,5-diazaanthraquinone **2n** (Table 3, entries 13–14), demonstrating the synthetic versatility of the transformation.

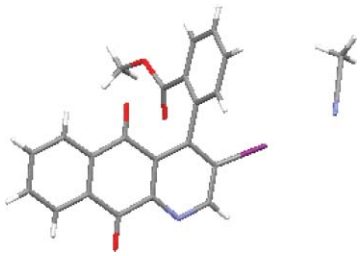


Fig. 2 X-Ray crystal structure of 1-azaanthraquinone **2e**·CH_3CN.

Conclusion

In conclusion, a methodology to assemble the azaanthraquinone and diazaanthraquinone skeletons from *N*-propargylaminoquinones was developed by utilizing an iodine-induced 6-*endo*-*dig* electrophilic cyclization. The excellent nucleophilicity of the double bond of aminoquinone was examined. Besides, the protocol features mild conditions and benign functional group compatibility. Application of the methodology in tricycloquinone alkaloid synthesis and structural modification will be pursued.

Experimental

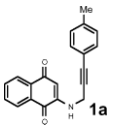
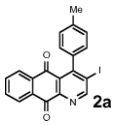
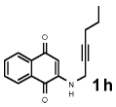
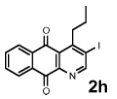
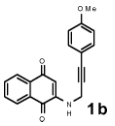
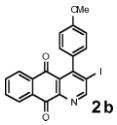
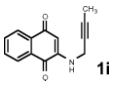
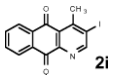
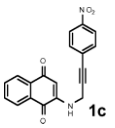
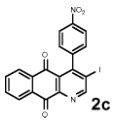
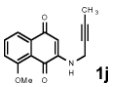
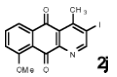
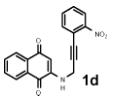
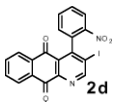
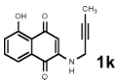
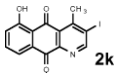
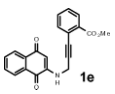
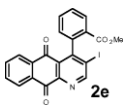
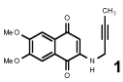
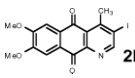
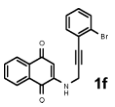
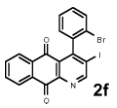
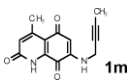
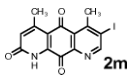
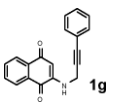
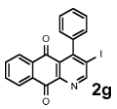
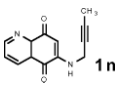
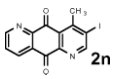
Melting points are uncorrected. IR spectra were recorded on a Nicolet FT-IR 5DX spectrometer as KBr pellets. NMR spectra were recorded on a Bruker ACF-300 spectrometer by using tetramethylsilane (TMS) or residue solvent as internal standards. The *J* values are given in Hz. Mass spectra were taken on a VG-ZAB-HS spectrometer in the electron impact ionization mode. Elemental analyses were performed with a Perkin–Elmer 240C analyzer.

General procedure for the preparation of aminoquinones by Au(III)-catalyzed sequential 1,4-nucleophilic addition–oxidation

Quinone (2.0 mmol) and $NaAuCl_4·2H_2O$ (8.0 mg, 0.02 mmol) were dissolved in ethanol (4.0 mL) under oxygen atmosphere. Then the amine (1.3 mmol) was added to the above solution. The resulting reaction mixture was heated at 80 °C or at room temperature for a certain time (monitored by TLC). After cooling, the mixture was poured into water (40 mL), and extracted with CH_2Cl_2 (30 mL × 3). The combined organic extracts were dried by anhydrous $MgSO_4$. After filtration, the solvent was removed by distillation. The remaining crude product was purified by flash chromatography to give the aminoquinone.

2-[3-(4-Methylphenyl)-2-propynylamino]-1,4-naphthoquinone (1a). Red brown solid, mp 188–190 °C (EtOH); IR (KBr) ν_{max} 3336, 1681, 1594, 1493, 812, 774, 725 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.08 (dd, J_1 = 16.5 Hz, J_2 = 7.8 Hz, 2H), 7.73 (t, J = 7.5 Hz, 1H), 7.63 (t, J = 7.5 Hz, 1H), 7.32 (d, J = 8.1 Hz, 2H), 7.11 (d, J = 7.5 Hz, 2H), 6.12 (br s, 1H), 5.90 (s, 1H), 4.20 (d, J = 5.4 Hz, 2H), 2.34 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 183.1, 181.5, 147.2, 138.9, 134.7, 133.3, 132.1, 131.6, 130.4, 129.1, 126.3, 126.2, 118.9, 102.3, 85.1, 81.6, 33.2, 21.4; MS (EI) *m*/*z* 302 (M+1, 3), 301 (M^+, 100), 300 (M-1, 28), 129(26). Anal. Calcd for $C_{20}H_{15}NO_2$: C, 79.72; H, 5.02; N, 4.65. Found: C, 79.67; H, 4.89; N, 4.69.

Table 3 Azaanthraquinone assembly by iodine-induced 6-*endo-dig* electrophilic cyclization[a]

Entry	Aminoquinone	Azaanthraquinone	Yield (%)[b]	Entry	Aminoquinone	Azaanthraquinone	Yield (%)[b]
1	 1a	 2a	77	8	 1h	 2h	84
2	 1b	 2b	72	9	 1i	 2i	90
3	 1c	 2c	58	10	 1j	 2j	75
4	 1d	 2d	53	11	 1k	 2k	60
5	 1e	 2e	56	12	 1l	 2l	87
6	 1f	 2f	54	13	 1m	 2m	84
7	 1g	 2g	62	14	 1n	 2n	45

[a] All reactions were performed in 0.05 M. [b] Isolated yield.

2-[3-(4-Methoxyphenyl)-2-propynylamino]-1,4-naphthoquinone (1b). Red brown solid, mp 172–175 °C (EtOH); IR (KBr) ν_{max} 3351, 1679, 1595, 1566, 1492, 1355, 834, 725 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.10 (d, J = 7.5 Hz, 1H), 8.05 (d, J = 7.5 Hz, 1H), 7.72 (t, J = 7.5 Hz, 1H), 7.61 (t, J = 7.2 Hz, 1H), 7.36 (d, J = 8.7 Hz, 2H), 6.82 (d, J = 9.0 Hz, 2H), 6.10 (br s, 1H), 5.89 (s, 1H), 4.18 (d, J = 5.7 Hz, 2H), 3.79 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 183.1, 181.6, 159.9, 147.2, 134.7, 133.4, 133.2, 132.1, 130.4, 126.23, 126.18, 114.0, 113.9, 102.3, 84.9, 81.0, 55.2, 33.2; MS (EI) m/z 318 (M+1, 2), 317 (M$^+$, 24), 315 (M-2, 63), 173 (44), 145 (100). Anal. Calcd for $C_{20}H_{15}NO_3$: C, 75.70; H, 4.76; N, 4.41. Found: C, 75.87; H, 4.87; N, 4.61.

2-[3-(4-Nitrophenyl)-2-propynylamino]-1,4-naphthoquinone (1c). Red brown solid, mp 228–230 °C (HOAc); IR (KBr) ν_{max} 3349, 1682, 1601, 1567, 1523, 1493, 1341, 856, 726 cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.21–8.18 (m, 2H), 8.01–7.94 (m, 2H), 7.84 (td, J_1 = 7.5 Hz, J_2 = 1.5 Hz, 1H), 7.75 (td, J_1 = 7.5 Hz, J_2 = 1.5 Hz, 1H), 7.70–7.66 (m, 2H), 5.89 (s, 1H), 4.38 (d, J = 5.7 Hz, 2H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 181.2, 180.9, 147.4, 146.4, 134.3, 132.3, 132.1, 131.9, 129.9, 128.2, 125.4, 124.9, 123.3, 100.9, 89.8, 81.0, 31.5; MS (EI) m/z 332 (M$^+$, 11), 331 (M-1, 8), 330 (M-2, 67), 102 (100). Anal. Calcd for $C_{19}H_{12}N_2O_4$: C, 68.67; H, 3.64; N, 8.43. Found: C, 68.69; H, 3.74; N, 8.47.

2-[3-(2-Nitrophenyl)-2-propynylamino]-1,4-naphthoquinone (1d). Red brown solid, mp 195–197 °C (EtOH); IR (KBr) ν_{max} 3350, 1680, 1600, 1568, 1522, 1493, 1341, 744, 726 cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.06 (d, J = 7.8 Hz, 1H), 7.99 (dd, J_1 = 7.5 Hz, J_2 = 1.2 Hz, 1H), 7.95 (dd, J_1 = 7.5 Hz, J_2 = 1.2 Hz, 1H), 7.90 (t, J = 6.0 Hz, 1H), 7.83 (td, J_1 = 7.5 Hz, J_2 = 1.5 Hz, 1H), 7.76–7.68 (m, 3H), 7.64–7.59 (m, 1H), 5.89 (s, 1H), 4.37 (d, J = 6.3 Hz, 2H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 181.2, 181.0, 149.1, 147.4, 134.4, 134.1, 133.1, 132.3, 131.9, 129.9, 129.3, 125.4, 124.9, 124.0, 115.9, 101.2, 91.9, 77.7, 31.6; MS (EI) m/z 332 (M$^+$, 0.1), 315 (19), 224 (19), 130 (37), 104 (82), 76 (100). Anal. Calcd for $C_{19}H_{12}N_2O_4$: C, 68.67; H, 3.64; N, 8.43. Found: C, 68.54; H, 3.66; N, 8.46.

2-[3-(2-Methoxycarbonylphenyl)-2-propynylamino]-1,4-naphthoquinone (1e). Red brown solid, mp 188–190 °C (EtOH); IR

(KBr) ν_{max} 3384, 1722, 1610, 1496, 1260, 751, 725 cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d$_6$) δ 8.00–7.80 (m, 5H), 7.73 (t, J = 7.2 Hz, 1H), 7.57–7.45 (m, 3H), 5.89 (s, 1H), 4.33 (d, J = 5.7 Hz, 2H), 3.78 (s, 3H); ^{13}C NMR (75 MHz, DMSO-d$_6$) δ 181.2, 181.0, 147.5, 134.4, 133.3, 132.4, 131.9, 131.7, 131.6, 129.8, 129.4, 128.2, 125.4, 124.9, 121.2, 101.0, 89.0, 81.0, 51.7, 31.7; MS (EI) m/z 345 (M$^+$, 2), 343 (M-2, 10), 330 (12), 284 (100). Anal. Calcd for $C_{21}H_{15}NO_4$: C, 73.03; H, 4.38; N, 4.06. Found: C, 72.98; H, 4.39; N, 4.01.

2-[3-(2-Bromophenyl)-2-propynylamino]-1,4-naphthoquinone (1f). Red–brown solid, mp 180–182 °C (EtOH); IR (KBr) ν_{max} 3446, 1678, 1599, 1570, 1494, 750, 724 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$) δ 8.11 (dd, J_1 = 7.8 Hz, J_2 = 1.2 Hz, 1H), 8.06 (dd, J_1 = 7.8 Hz, J_2 = 1.2 Hz, 1H), 7.73 (td, J_1 = 7.5 Hz, J_2 = 1.2 Hz, 1H), 7.63 (td, J_1 = 7.8 Hz, J_2 = 1.5 Hz, 1H), 7.56 (dd, J_1 = 7.8 Hz, J_2 = 1.2 Hz, 1H), 7.45 (dd, J_1 = 7.5 Hz, J_2 = 1.8 Hz, 1H), 7.25 (td, J_1 = 7.5 Hz, J_2 = 1.2 Hz, 1H), 7.17 (td, J_1 = 7.8 Hz, J_2 = 1.8 Hz, 1H), 6.16 (br, s, 1H), 5.97 (s, 1H), 4.28 (d, J = 5.7 Hz, 2H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 183.0, 181.5, 147.1, 134.7, 133.6, 133.3, 132.4, 132.1, 130.4, 129.9, 127.0, 126.24, 126.21, 125.6, 124.2, 102.8, 87.0, 83.5, 33.1; MS (EI) m/z 367 (M+2, 4), 366 (M+1, 2), 365 (M$^+$, 7), 286 (100). Anal. Calcd for $C_{19}H_{12}BrNO_2$: C, 62.32; H, 3.30; N, 3.82. Found: C, 62.27; H, 3.37; N, 3.72.

2-(3-Phenyl-2-propynylamino)-1,4-naphthoquinone (1g). Brown solid, mp 175–177 °C (EtOH); IR (KBr) ν_{max} 3330, 1683, 1594, 1564, 1494, 1355, 753 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$) δ 8.10 (d, J = 7.5 Hz, 1H), 8.05 (d, J = 7.5 Hz, 1H), 7.72 (t, J = 7.3 Hz, 1H), 7.62 (t, J = 7.5 Hz, 1H), 7.43–7.41 (m, 2H), 7.31–7.29 (m, 3H), 6.12 (br s, 1H), 5.90 (s, 1H), 4.21 (d, J = 5.4 Hz, 2H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 183.1, 181.5, 147.2, 134.7, 133.3, 132.1, 131.8, 130.4, 128.7, 128.3, 126.3, 126.2, 122.0, 102.4, 85.0, 82.4, 33.1; MS (EI) m/z 287 (M$^+$, 15), 285 (M-2, 43), 230 (12), 115 (100). Anal. Calcd for $C_{19}H_{13}NO_2$: C, 79.43; H, 4.56; N, 4.88. Found: C, 79.47; H, 4.65; N, 4.86.

2-(2-Hexynylamino)-1,4-naphthoquinone (1h). Orange solids, mp 138–139 °C (EtOH); IR (KBr) ν_{max} 3342, 1681, 1609, 1594, 1563, 1495, 1356, 725 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$) δ 8.09 (dd, J_1 = 7.5 Hz, J_2 = 0.9 Hz, 1H), 8.04 (dd, J_1 = 7.5 Hz, J_2 = 0.9 Hz, 1H), 7.72 (td, J_1 = 7.5 Hz, J_2 = 1.5 Hz, 1H), 7.62 (td, J_1 = 7.5 Hz, J_2 = 0.9 Hz, 1H), 5.98 (br s, 1H), 5.81 (s, 1H), 3.97–3.94 (m, 2H), 2.19–2.13 (m, 2H), 1.52 (h, J = 7.5 Hz, 2H), 0.96 (t, J = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 183.0, 181.6, 147.2, 134.7, 133.4, 132.1, 130.4, 126.23, 126.18, 102.1, 85.8, 73.4, 32.8, 21.9, 20.6, 13.4; MS (EI) m/z 253 (M$^+$, 1), 252 (M-1, 13), 224 (100). Anal. Calcd for $C_{16}H_{15}NO_2$: C, 75.87; H, 5.97; N, 5.53. Found: C, 75.63; H, 6.03; N, 5.66.

2-(2-Butynylamino)-1,4-naphthoquinone (1i). Orange solids, mp 189–192 °C (EtOH); IR (KBr) ν_{max} 3281, 1677, 1609, 1573, 1499, 1357, 1335, 828, 777, 722 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$) δ 8.10 (dd, J_1 = 7.5 Hz, J_2 = 0.6 Hz, 1H), 8.04 (dd, J_1 = 7.5 Hz, J_2 = 0.6 Hz, 1H), 7.73 (td, J_1 = 7.5 Hz, J_2 = 1.2 Hz, 1H), 7.62 (td, J_1 = 7.5 Hz, J_2 = 1.2 Hz, 1H), 6.02 (br s, 1H), 5.81 (s, 1H), 3.91 (q, J = 2.4 Hz, 2H), 1.83 (t, J = 2.4 Hz, 3H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 183.0, 181.5, 147.2, 134.6, 133.4, 132.0, 130.4, 126.19, 126.15, 102.1, 81.2, 72.5, 32.7, 3.4; MS (EI) m/z 225 (M$^+$, 41), 224 (M-1, 90), 183 (100), 182 (92). Anal. Calcd for $C_{14}H_{11}NO_2$: C, 74.65; H, 4.92; N, 6.22. Found: C, 74.78; H, 4.91; N, 6.31.

2-(2-Butynylamino)-8-methoxy-1,4-naphthoquinone (1j).. Yellow solid, mp 232 °C (EtOH); IR (KBr) ν_{max} 3338, 1669, 1612, 1586, 1509, 1357, 1298, 818, 795, 738 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.78 (dd, J_1 = 7.8 Hz, J_2 = 1.2 Hz, 1H), 7.66 (t, J = 8.4 Hz, 1H), 7.18 (dd, J_1 = 7.8 Hz, J_2 = 0.9 Hz, 1H), 6.09 (br s, 1H), 5.75 (s, 1H), 4.00 (s, 3H), 3.93–3.89 (m, 2H), 1.82 (t, J = 2.4 Hz, 3H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 182.6, 179.8, 160.0, 148.2, 135.9, 135.8, 119..0, 118.2, 116.0, 100.5, 81.1, 72.6, 56.4, 32.7, 3.4; MS (EI) m/z 256 (M+1, 1), 255 (M$^+$, 46), 254 (M-1, 30), 240 (52), 228 (76), 212 (100). Anal. Calcd for $C_{15}H_{13}NO_3$: C, 70.58; H, 5.13; N, 5.49. Found: C, 70.48; H, 5.04; N, 5.38.

2-(2-Butynylamino)-5-hydroxy-1,4-naphthoquinone (1k). Red brown solid, mp 172–174 °C (EtOH); IR (KBr) ν_{max} 3357, 1625, 1601, 1512, 1468, 1247, 829, 775 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$) δ 12.96 (s, 1H), 7.61–7.58 (m, 1H), 7.48 (t, J = 8.1 Hz, 1H), 7.26–7.23 (m, 1H), 6.15 (br, s, 1H), 5.71 (s, 1H), 3.96–3.92 (m, 2H), 1.84 (t, J = 2.7 Hz, 3H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 189.1, 180.8, 161.1, 147.9, 134.0, 130.4, 125.9, 119.1, 114.8, 101.1, 81.6, 72.1, 32.8, 3.5; MS (EI) m/z 242 (M+1, 2), 241 (M$^+$, 71), 240 (M-1, 79), 199 (71), 198 (100). Anal. Calcd for $C_{14}H_{11}NO_3$: C, 69.70; H, 4.60; N, 5.81. Found: C, 69.71; H, 4.70; N, 5.84.

2-(2-Butynylamino)-6,7-dimethoxy-1,4-naphthoquinone (1l). Red brown solid, mp 240–242 °C (EtOH); IR (KBr) ν_{max} 3295, 1675, 1604, 1567, 1505, 1344, 792 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.54 (s, 1H), 7.46 (s, 1H), 5.95 (br s, 1H), 5.68 (s, 1H), 4.02 (s, 3H), 3.99 (s, 3H), 1.83 (s, 3H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 183.0, 180.7, 154.3, 151.9, 147.4, 128.8, 124.5, 108.2, 107.9, 101.0, 81.2, 72.6, 56.5, 56.4, 32.8, 3.5; MS (EI) m/z 286 (M+1, 7), 285 (M$^+$, 100), 284 (M-1, 35), 242 (94). Anal. Calcd for $C_{16}H_{15}NO_4$: C, 67.36; H, 5.30; N, 4.91. Found: C, 67.27; H, 5.17; N, 4.89.

7-(2-Butynylamino)-4-methyl-2,5,8-quinolinetrione (1m). Red solid, mp 201–203 °C (EtOH); IR (KBr) ν_{max} 3239, 1654, 1592, 1509, 852 cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d$_6$) δ 11.30 (br s, 1H), 8.16 (br s, 1H), 6.36 (d, J = 0.9 Hz, 1H), 5.60 (s, 1H), 4.00 (q, J = 2.7 Hz, 2H), 2.45 (d, J = 0.6 Hz, 3H), 1.78 (t, J = 2.4 Hz, 3H); ^{13}C NMR (75 MHz, DMSO-d$_6$) δ 178.6, 174.5, 160.0, 149.8, 148.5, 142.2, 122.4, 110.6, 95.5, 79.3, 73.2, 31.2, 21.1, 2.5; MS (EI) m/z 257 (M+1, 1), 256 (M$^+$, 100), 255 (M-1, 12), 229 (15). Anal. Calcd for $C_{14}H_{12}N_2O_3$: C, 65.62; H, 4.72; N, 10.93. Found: C, 65.63; H, 4.78; N, 11.04.

6-(2-Butynylamino)-5,8-quinolinedione (1n). Orange solid, mp 198 °C dec. (EtOH); IR (KBr) ν_{max} 3207, 1679, 1605, 1568, 1333, 793 cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d$_6$) δ 8.96 (dd, J_1 = 4.8 Hz, J_2 = 1.6 Hz, 1H), 8.33 (dd, J_1 = 7.8 Hz, J_2 = 1.8 Hz, 1H), 7.84 (t, J = 6.0 Hz, 1H), 7.73 (dd, J_1 = 7.8 Hz, J_2 = 4.5 Hz, 1H), 5.86 (s, 1H), 4.00 (q, J = 2.70 Hz, 2H), 1.79 (t, J = 2.2 Hz, 3H); ^{13}C NMR (75 MHz, DMSO-d$_6$) δ 181.5, 180.2, 154.5 148.4, 147.5, 133.9, 127.5, 126.6, 102.2, 79.6, 74.0, 31.5, 3.0; MS (EI) m/z 227 (M+1, 1), 226 (M$^+$, 71), 225 (M-1, 32), 224 (M-2, 95), 103(100). Anal. Calcd for $C_{13}H_{10}N_2O_2$: C, 69.02; H, 4.46; N, 12.38. Found: C, 69.27; H, 4.76; N, 12.35.

General procedure for the preparation of azaanthraquinones by molecular iodine-induced 6-*endo-dig* electrophilic cyclization of *N*-propargylaminoquinones

Molecular iodine (230 mg, 0.9 mmol) was added in portions to a stirred solution containing *N*-propargylaminoquinone (0.3 mmol) and $NaHCO_3$ (44 mg, 0.6 mmol) in nitromethane (6.0 mL) at room temperature. Then the reaction was heated at 100 °C for 4 h. After cooling to room temperature, the reaction mixture was diluted with chloroform (30 mL). The resulting solution was washed successively by saturated $Na_2S_2O_3$ solution (15 mL) and brine (15 mL). The organic phase was dried with anhydrous $MgSO_4$, filtered and concentrated. The residue was purified by flash chromatography to give pure product.

3-Iodo-4-(4-methylphenyl)-benzo[g]quinoline-5,10-dione (2a). Yellow solids, mp 200–202 °C (THF); IR (KBr) ν_{max} 1677, 1606, 1571, 730 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 9.48 (s, 1H), 8.38–8.35 (m, 1H), 8.10–8.07 (m, 1H), 7.84–7.75 (m, 2H), 7.36 (d, J = 7.8 Hz, 2H), 6.99 (d, J = 8.1 Hz, 2H), 2.49 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 182.0, 181.5, 161.3, 155.7, 149.0, 139.1, 138.2, 134.8, 134.4, 133.2, 132.5, 129.4, 129.1, 127.5, 127.3, 126.7, 110.2, 21.6; MS (EI) m/z 425 (M^+, 34), 424 (M-1, 9), 410 (100). Anal. Calcd for $C_{20}H_{12}INO_2$: C, 56.49; H, 2.84; N, 3.29. Found: C, 56.50; H, 2.69; N, 3.10.

3-Iodo-4-(4-methoxyphenyl)-benzo[g]quinoline-5,10-dione (2b). Yellow solids, mp 265–267 °C (THF); IR (KBr) ν_{max} 1681, 1586, 1511, 960, 723 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6) δ 9.45 (s, 1H), 8.19–8.16 (m, 1H), 7.95–7.86 (m, 3H), 7.05 (s, 4H), 3.85 (s, 3H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 182.0, 181.1, 160.3, 158.8, 154.1, 148.8, 134.6, 134.5, 134.3, 133.3, 132.4, 129.5, 128.7, 126.7, 126.3, 113.6, 110.9, 55.1; MS (EI) m/z 441 (M^+, 100), 440 (M-1, 19), 410 (20). Anal. Calcd for $C_{20}H_{12}INO_3$: C, 54.44; H, 2.74; N, 3.17. Found: C, 54.27; H, 3.00; N, 3.23.

3-Iodo-4-(4-nitrophenyl)-benzo[g]quinoline-5,10-dione (2c). Yellow solids, mp > 300 °C (THF); IR (KBr) ν_{max} 1682, 1583, 1509, 1282, 958, 729 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6) δ 9.53 (s, 1H), 8.40 (dd, J_1 = 6.6 Hz, J_2 = 1.8 Hz, 2H), 8.23–8.20 (m, 1H), 7.89 (m, 3H), 7.48 (dd, J_1 = 6.9 Hz, J_2 = 1.8 Hz, 2H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 181.9, 180.9, 160.6, 152.0, 149.6, 148.7, 147.0, 134.7, 134.6, 132.9, 132.5, 129.0, 126.8, 126.5, 123.6, 108.5; MS (EI) m/z 456 (M^+, 100), 455 (M-1, 13), 439 (12), 409 (24). Anal. Calcd for $C_{19}H_9IN_2O_4$: C, 50.02; H, 1.99; N, 6.14. Found: C, 50.43; H, 1.99; N 5.97.

3-Iodo-4-(2-nitrophenyl)-benzo[g]quinoline-5,10-dione (2d). Yellow solids, mp 275–278 °C (CH_3CN); IR (KBr) ν_{max} 1678, 1585, 1521, 1350, 1284, 960, 727 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6) δ 9.50 (s, 1H), 8.43 (dd, J_1 = 8.4 Hz, J_2 = 0.9 Hz, 1H), 8.21–8.18 (m, 1H), 7.98–7.79 (m, 5H), 7.31 (dd, J_1 = 7.8 Hz, J_2 = 1.2 Hz, 1H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 182.3, 180.8, 160.6, 152.4, 148.5, 145.8, 138.0, 135.3, 134.8, 134.7, 132.7 132.5, 129.8, 128.4, 126.8, 126.7, 124.5, 107.6; MS (EI) m/z: 410 (100), 255 (17). Anal. Calcd for $C_{19}H_9IN_2O_4$: C, 50.02; H, 1.99; N, 6.14. Found: C, 49.91; H, 2.07; N, 6.08.

3-Iodo-4-(2-methoxycarbonylphenyl)-benzo[g]quinoline-5,10-dione (2e). Orange solids, mp 239–241 °C (CH_3CN); IR (KBr) ν_{max} 1708, 1680, 1288, 1273, 958, 731 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 9.43 (s, 1H), 8.35 (dd, J_1 = 8.1 Hz, J_2 = 1.8 Hz, 1H), 8.25 (dd, J_1 = 7.8 Hz, J_2 = 1.2 Hz, 1H), 8.02 (dd, J_1 = 7.5 Hz, J_2 = 1.2 Hz, 1H), 7.82–7.68 (m, 3H), 7.61 (td, J_1 = 7.5 Hz, J_2 = 1.2 Hz, 1H), 7.00 (d, J = 7.5 Hz, 1H), 3.67 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 182.1, 181.6, 165.9, 161.2, 159.6, 148.7, 144.3, 134.6, 134.4, 133.2, 132.9, 132.7, 130.7, 128.6, 128.5, 127.8, 127.6, 127.4, 127.3, 107.7, 52.1; MS (EI) m/z: 410 (24), 342 (100), 255 (24). Anal. Calcd for $C_{21}H_{12}INO_4$: C, 53.75; H, 2.58; N, 2.99. Found: C, 53.65; H, 2.71; N, 3.06.

3-Iodo-4-(2-bromophenyl)-benzo[g]quinoline-5,10-dione (2f).. Brown solids, mp 288–290 °C (CH_3CN); IR (KBr) ν_{max} 1685, 1672, 1287, 960, 760 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6) δ 9.55 (s, 1H), 8.23–8.20 (m, 1H), 8.00–7.89 (m, 3H), 7.78 (dd, J_1 = 7.8 Hz, J_2 = 0.9 Hz, 1H), 7.53 (td, J_1 = 7.2 Hz, J_2 = 1.2 Hz, 1H), 7.42 (td, J_1 = 7.8 Hz, J_2 = 1.5 Hz, 1H), 7.16 (dd, J_1 = 7.5 Hz, J_2 = 1.8 Hz, 1H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 181.6, 180.8, 161.0, 152.8, 148.7, 142.9, 134.8, 134.7, 132.6, 132.2, 129.8, 128.8, 128.0, 126.8, 126.6, 120.8, 109.9; MS (EI) m/z: 410 (100), 255 (12). Anal. Calcd for $C_{19}H_9BrINO_2$: C, 46.56; H, 1.85; N, 2.86. Found: C, 46.47; H, 1.92; N, 2.76.

3-Iodo-4-phenyl-benzo[g]quinoline-5,10-dione (2g). Yellow solids, mp 263–265 °C (THF); IR (KBr) ν_{max} 1683, 1587, 1284, 960, 723 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 9.50 (s, 1H), 8.39–8.36 (m, 1H), 8.09–8.06 (m, 1H), 7.84–7.77 (m, 2H), 7.58–7.54 (m, 3H), 7.12–7.09 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 181.9, 181.5, 161.4, 155.5, 149.0, 142.1, 134.8, 134.4, 133.1, 132.5, 128.7, 128.4, 127.6, 127.3, 126.8, 109.8; MS (EI) m/z 411 (M^+, 74), 410 (M-1, 100), 284 (71). Anal. Calcd for $C_{19}H_{10}INO_2$: C, 55.50; H, 2.45; N, 3.41. Found: C, 55.34; H, 2.49; N, 3.57.

3-Iodo-4-propyl-benzo[g]quinoline-5,10-dione (2h). Yellow solids, mp 190–192 °C (THF); IR (KBr) ν_{max} 1681, 1592, 1284, 988, 725 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 9.27 (s, 1H), 8.28–8.25 (m, 1H), 8.20–8.17 (m, 1H), 7.82–7.76 (m, 2H), 3.34 (t, J = 7.8 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 183.7, 181.5, 161.6, 157.1, 149.5, 134.7, 134.2, 133.6, 132.1, 129.3, 127.4, 127.1, 109.9, 40.7, 22.2, 14.5; MS (EI) m/z: 377 (M^+, 100), 360 (50). Anal. Calcd for $C_{16}H_{12}INO_2$: C, 50.95; H, 3.21; N, 3.71. Found: C, 50.97; H, 3.20; N, 3.81.

3-Iodo-4-methyl-benzo[g]quinoline-5,10-dione (2i). Yellow solids, mp 233–235 °C (THF); IR (KBr) ν_{max} 1682, 1664, 1589, 1281, 977, 721 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 9.30 (s, 1H), 8.32–8.19 (m, 1H), 8.22–8.19 (m, 1H), 7.82–7.79 (m, 2H), 3.02 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 184.2, 181.5, 161.2, 153.6, 149.2, 134.7, 133.7, 132.3, 129.9, 127.4, 127.2, 110.5, 27.3; MS (EI) m/z: 349 (M^+, 100), 321 (5). Anal. Calcd for $C_{14}H_8INO_2$: C, 48.16; H, 2.31; N, 4.01. Found: C, 48.09; H, 2.49; N, 3.95.

3-Iodo-9-methoxyl-4-methyl-benzo[g]quinoline-5,10-dione (2j). Yellow solids, mp 181–183 °C (THF); IR (KBr) ν_{max} 1669, 1587, 1264, 977, 765 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 9.26 (s, 1H), 7.77 (dd, J_1 = 7.8 Hz, J_2 = 1.2 Hz, 1H), 7.69 (t, J = 8.1 Hz, 1H), 7.30 (dd, J_1 = 8.1 Hz, J_2 = 0.9 Hz, 1H), 4.01 (s, 3H), 2.94 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 184.5, 180.2, 161.2, 160.0, 152.7, 136.0, 135.4, 128.8, 120.8, 119.6, 117.8, 109.2, 56.6, 26.9; MS (EI) m/z: 379 (M^+, 100), 350 (7). Anal. Calcd for $C_{15}H_{10}INO_3$: C, 47.52; H, 2.66; N, 3.69. Found: C, 47.43; H, 2.79; N, 3.52.

6-Hydroxy-3-iodo-4-methyl-benzo[g]quinoline-5,10-dione (2k). Orange solids, mp 190–192 °C (THF); IR (KBr) ν_{max} 1676, 1623,

1260, 788 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 12.36 (s, 1H), 9.32 (s, 1H), 7.85 (dd, $J_1 = 7.5$ Hz, $J_2 = 1.2$ Hz, 1H), 7.68 (t, $J = 8.1$ Hz, 1H), 7.33 (dd, $J_1 = 8.7$ Hz, $J_2 = 1.2$ Hz, 1H), 3.06 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 189.8, 180.8, 162.4, 161.8, 153.8, 149.3, 136.9, 132.2, 129.5, 125.2, 119.8, 116.0, 110.8, 27.9; MS (EI) *m/z*: 365 (M^+, 100). Anal. Calcd for $C_{14}H_8INO_3$: C, 46.05; H, 2.21; N, 3.84. Found: C, 46.17; H, 2.41; N, 3.80.

7,8-Dimethoxy-3-iodo-4-methyl-benzo[g]quinoline-5,10-dione (2l). Yellow solids, mp 263–265 °C (THF); IR (KBr) ν_{max} 1670, 1579, 1513, 1322, 1007, 778 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 9.28 (s, 1H), 7.69 (s, 1H), 7.60 (s, 1H), 4.07 (s, 3H), 4.05 (s, 3H), 3.02 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 183.4, 180.7, 160.8, 154.4, 154.0, 153.2, 149.5, 129.8, 128.6, 127.2, 110.3, 108.4, 108.1, 56.7, 56.5, 27.3; MS (EI) *m/z*: 409 (M^+, 100), 378 (2). Anal. Calcd for $C_{16}H_{12}INO_4$: C, 46.97; H, 2.96; N, 3.42. Found: C, 46.91; H, 2.94; N, 3.52.

4,6-Dimethyl-3-iodo-pyrido[3,2-g]quinoline-2,5,10(1H)-trione (2m). Yellow solids, mp 285–287 °C (CH_3OH–$CHCl_3$); IR (KBr) ν_{max} 1646, 1552, 1296, 703 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$ and CF_3CO_2H) δ 9.49 (s, 1H), 7.02 (s, 1H), 3.20 (s, 3H), 2.80 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$ and CF_3CO_2H) δ 176.0, 157.6, 155.8, 144.0, 139.6, 127.0, 125.6, 120.0, 116.2, 112.4, 110.0, 108.7, 27.6, 22.5; MS (EI) *m/z*: 381 (M+1, 1), 380 (M^+, 100), 352 (3). Anal. Calcd for $C_{14}H_9IN_2O_3$: C, 44.23; H, 2.39; N, 7.37. Found: C, 44.51; H, 2.22; N, 7.38.

3-Iodo-4-methyl-pyrido[2,3-g]quinoline-5,10-dione (2n). Brown solids, mp 220–222 °C (THF); IR (KBr) ν_{max} 2923, 1682, 1582, 1285, 980, 722 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 9.37 (s, 1H), 9.14 (dd, $J_1 = 4.5$ Hz, $J_2 = 1.5$ Hz, 1H), 8.67 (dd, $J_1 = 7.8$ Hz, $J_2 = 1.5$ Hz, 1H), 7.77 (dd, $J_1 = 8.1$ Hz, $J_2 = 4.8$ Hz, 1H), 3.07 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 182.5, 181.2, 161.7, 155.7, 154.3, 148.7, 148.6, 135.5, 130.1, 129.2, 128.2, 111.1, 27.4; MS (EI) *m/z*: 352 (M+2, 15), 350 (M^+, 100). Anal. Calcd for $C_{13}H_7IN_2O_2$: C, 44.60; H, 2.02; N, 8.00. Found: C, 44.67; H, 2.08; N, 7.81.

2-[2,3-Diiodo-3-(4-methylphenyl)-2-propen-1-ylamino]-1,4-naphthalenedione (3). Brown solids, mp 155–157 °C (EtOAc); IR (KBr) ν_{max} 1687, 1676, 1284, 726 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.13 (dd, $J_1 = 7.5$ Hz, $J_2 = 0.9$ Hz, 1H), 8.09 (dd, $J_1 = 7.5$ Hz, $J_2 = 1.2$ Hz, 1H), 7.75 (td, $J_1 = 7.5$ Hz, $J_2 = 1.2$ Hz, 1H), 7.65 (td, $J_1 = 7.5$ Hz, $J_2 = 1.2$ Hz, 1H), 7.19–7.10 (m, 4H), 6.32 (t, $J = 6.0$ Hz, 1H), 5.90 (s, 1H), 4.40 (d, $J = 6.3$ Hz, 2H), 2.36 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 183.1, 181.6, 147.0, 144.3, 138.9, 134.8, 133.4, 132.2, 130.4, 129.2, 127.9, 126.34, 126.27, 103.2, 99.6, 99.0, 59.0, 21.4; MS (EI) *m/z* 301 (54), 129 (100). Anal. Calcd for $C_{20}H_{15}I_2NO_2$: C, 43.27; H, 2.72; N, 5.76. Found: C, 43.20; H, 2.69; N, 5.90.

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16 CCDC 748375 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via*www.ccdc.cam.ac.uk/data_request/cif†.