

A new approach for the synthesis of benzo[f]pyrrolo[1,2-a]-quinolines

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Dedicated to Prof. Alexandru T. Balaban on his 75th anniversary

(received 25 Jan 05; accepted 22 Mar 05; published on the web 07 Mar 05)

Abstract

For the first time, new benzo[f]pyrrolo[1,2-a]quinoline derivatives, structurally analogous to the steroid skeleton, were obtained in a simple way by 1,3-dipolar cycloaddition reactions of benzo[f]quinolinium-1-methylides, generated *in situ* from the corresponding quaternary salts, with electron-deficient alkynes.

Keywords: Benzo[f]quinoline, benzo[f]quinolinium quaternary salt, 1,3-dipolar cycloaddition reactions, benzo[f]pyrrolo[1,2-a]quinoline, benzo[f]quinolinium-1-methylides

Introduction

Benzo[f]pyrrolo[1,2-a]quinoline is an interesting N-bridgehead heterocyclic system, structurally analogous to the steroid skeleton.^{1,2} These compounds were obtained starting from 3-ethoxycarbonyl-1-hydroxy-8-methoxybenzo[f]quinoline *via* multi-step synthesis.^{1,2}

In order to continue our work³⁻⁶ on the synthesis of new N-bridgehead heterocyclic compounds with interesting chemical and biological properties, we extended our study to the synthesis of new benzo[f]pyrrolo[1,2-a]quinoline derivatives. It is well known that 1,3-dipolar cycloaddition reactions, conducted in a sequential manner, are efficient approaches for the synthesis of new interesting heterocyclic compounds.⁷⁻¹¹

Herein, we report new benzo[f]pyrrolo[1,2-a]quinoline derivatives obtained, for the first time, *via* 1,3-dipolar cycloaddition reactions of benzo[f]quinolinium-1-methylides with electron-deficient alkynes.

Results and Discussion

By the quaternization reaction of benzo[f]quinoline with α -halocarbonyl compounds such as (un)substituted phenacyl bromides, ω -bromo-2-acetyl thiophene or bromo-acetonaphthones, the corresponding benzo[f]quinolinium quaternary salts **1-13** were obtained (Scheme 1). Some of these quaternary salts were separated, purified and characterized (Compounds **1-4**, Table 1), others were used as crude products in the next step.

Table 1. Benzo[f]quinolinium salts 1-4

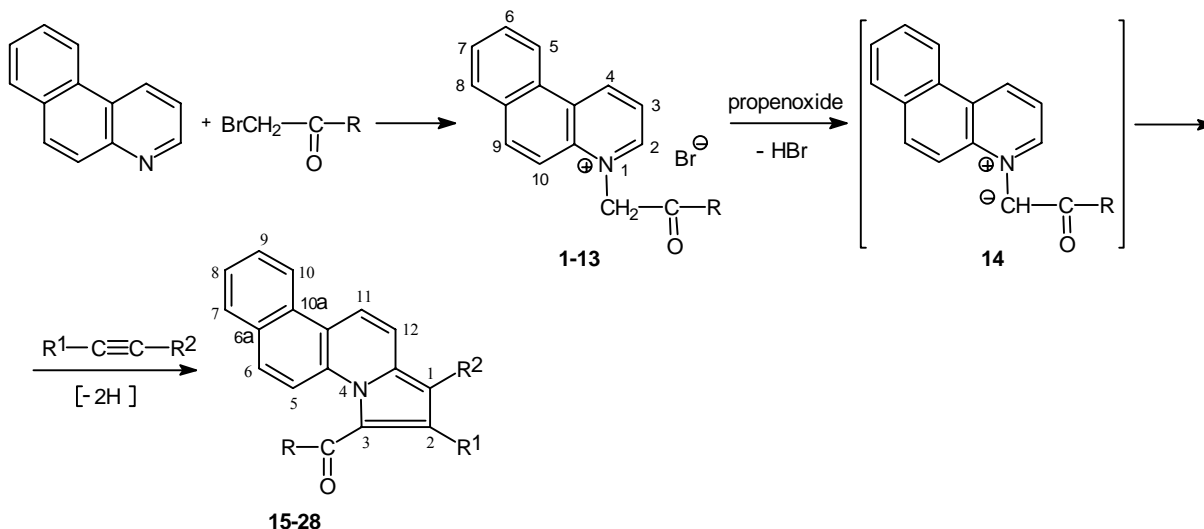
Compound	R	m.p.(°C)	yield(%)
1	3-BrC ₆ H ₄	242-244	87.5
2	4-MeOC ₆ H ₄	225-227	86.0
3	1-naphthyl	163.5-165	74.0
4	2-naphthyl	271-273	72.4

The direct reaction of these benzo[f]quinolinium quaternary salts with activated alkynes afforded new benzo[f]pyrrolo[1,2-*a*]quinoline derivatives **15-28** (Table 2) *via* benzo[f]quinolinium N-ylides **14**, generated *in situ* from the corresponding quaternary salts (Scheme 1).

Table 2. New benzo[f]pyrrolo[1,2-*a*]quinoline derivatives 15-28

Compound	R	R ¹	R ²	m.p.(°C)	yield (%)
15	Ph	H	CO ₂ Et	237.5-239	40.8
16	4-FC ₆ H ₄	CO ₂ Me	CO ₂ Me	237-238	40,0
17	4-ClC ₆ H ₄	H	CO ₂ Et	256-257	45.5
18	3-BrC ₆ H ₄	CO ₂ Me	CO ₂ Me	258,5-260	56.4
19	4-BrC ₆ H ₄	H	CO ₂ Et	259-260	55.8
20	3-NO ₂ C ₆ H ₄	H	CO ₂ Et	296-298	60.0
21	4-NO ₂ C ₆ H ₄	H	CO ₂ Et	291-293	60.5
22	4-MeOC ₆ H ₄	CO ₂ Me	CO ₂ Me	239-242	42.5
23	3,4-(MeO) ₂ C ₆ H ₃	CO ₂ Me	CO ₂ Me	249-251	46,6
24	4-PhC ₆ H ₄	CO ₂ Me	CO ₂ Me	228-229	48.0
25	2-thienyl	CO ₂ Me	CO ₂ Me	262-263.5	42.0
26	1-naphthyl	CO ₂ Me	CO ₂ Me	244-247	62.0
27	1-naphthyl	H	COC ₆ H ₅	233-235	60.0
28	2-naphthyl	CO ₂ Me	CO ₂ Me	239-240.5	60.8

These reactions took place in propene oxide as acid acceptor and reaction solvent. Ethyl propiolate, dimethyl acetylenedicarboxylate and phenylethyne ketone were used as activated alkynes.



Scheme 1. The synthetic procedure.

The structures of all new benzo[*f*]pyrrolo[1,2-*a*]quinoline derivatives **15-28** were confirmed by chemical and spectral analysis.

The IR spectra of these compounds exhibit characteristic carbonyl absorption bands at about $1604\text{--}1641\text{ cm}^{-1}$ for the benzoyl or naphthoyl group, about $1692\text{--}1708\text{ cm}^{-1}$ for a carboxy group, and two carbonyl absorption bands at about $1728\text{--}1744\text{ cm}^{-1}$ and $1699\text{--}1710\text{ cm}^{-1}$ for the two carbomethoxy groups.

The $^1\text{H-NMR}$ spectra of compounds **15**, **17**, **19-21** and **27** reveal signals of the H-2 protons from the pyrrolo ring at δ 7.44-7.86 ppm as characteristic singlets. The characteristic signals for the ethyl protons of the carboxy group appear at δ 4.40-4.42 ppm (q) and δ 1.41-1.42 ppm (t), a normal chemical shift is observed for an α -unsubstituted ethyl ester and the two signals for the methyl protons of the 1- and 2-carbomethoxy groups appear at δ 2.98-3.53 ppm and at δ 3.84-3.98 ppm. The $^1\text{H-NMR}$ spectra of these compounds exhibit all the characteristic signals of the benzo[*f*]quinoline ring system.

The $^{13}\text{C-NMR}$ spectra of **15-28** show characteristic signals for the carbonyl carbons from benzoyl, thienoyl and naphthoyl groups at δ 180-188 ppm. The characteristic signals for the carbonyl carbon from the carboxy group (compounds **15**, **17**, **19-21** and **27**) appear at δ ~164 ppm and two signals for the carbonyl carbons from 1- and 2-carbomethoxy groups (compounds **16**, **18**, **22-26** and **28**) appear at δ 163-167 ppm.

In conclusion, new benzo[f]pyrrolo[1,2-*a*]quinoline derivatives, otherwise difficult to obtain, were obtained easily by 1,3-dipolar cycloaddition reactions of benzo[f]quinolinium-1-methylide, generated *in situ* from the corresponding quaternary salts, with activated alkynes.

Experimental Section

General Procedures. Melting points were determined on a Boetius apparatus and are uncorrected. The IR spectra were recorded on a Nicolet Impact 410 spectrometer, in KBr pellets. The ^1H NMR and ^{13}C NMR spectra were registered with a Varian Gemini 300BB instrument at ambient temperature using TMS as internal standard; for unambiguous assignment ^1H -decoupling COSY (^1H - ^1H) and COSY (^1H - ^{13}C) were used. The solvent used was CDCl_3 for the compounds **2**, **4**, **15-27**, **19**, **21**, **22-24**, **26** and **28**, or a mixture of 10:1 molar ratio CDCl_3 :TFA only for the compounds **1**, **3**, **18**, **20**, **25** and **27**. Satisfactory microanalyses for all new compounds were obtained: C \pm 0.20, H \pm 0.16, N \pm 0.26. Benzo[f]quinoline, (un)substituted phenacyl bromides, ω -bromo-2-acetyl thiophene and bromo-acetonaphthones were commercially available products (Aldrich) or were prepared by bromination of the corresponding carbonyl compounds.

General synthetic procedure for benzo[f]quinolinium salts

A mixture of a benzo[f]quinoline (3.6 g, 20 mmol) and the corresponding α -bromocarbonyl compound (20 mmol) in chloroform (50 mL) was heated at reflux for 20 hours. The mixture was cooled and left overnight at the room temperature. The solid product was filtered, washed with a mixture of methylene dichloride-diethyl ether (20 mL) and recrystallised from methanol/diethyl ether.

The yields and m. p. of separated benzo[f]quinolinium quaternary salts are shown in Table 1. The spectral data are given below.

1-(3-Bromophenacyl)benzo[f]quinolinium bromide (1). beige crystals; IR (cm^{-1}): 1689($\nu_{\text{C=O}}$); ^1H NMR (δ , ppm, *J*, Hz): 6.93 (s, 2H, CH_2), 7.48 (t, 1H, *J* = 8.0, H-5'), 7.75 (d, 1H, *J* = 9.6, H-9), 7.85 (ddd, 1H, *J* = 1.8, 2.0, 8.0, H-4'), 7.90-8.10 (m, 3H), 8.19 (ddd, 1H, *J* = 1.8, 8.0, 2.0, H-6'), 8.25 (dd, 1H, *J* = 8.6, 5.9, H-3), 8.26 (t, 1H, *J* = 1.8, H-2'), 8.40 (d, 1H, *J* = 9.6, H-10), 8.79 (d, 1H, *J* = 8.3, H-5), 9.31 (d, 1H, *J* = 5.9, H-4), 9.70 (d, 1H, *J* = 8.6, H-2); ^{13}C NMR (δ , ppm): 188.54 (CO), 147.39 (CH-2), 141.62 (CH), 140.41 (Cq), 139.80 (CH), 138.52 (CH), 134.47 (Cq), 131.48 (CH), 131.22 (Cq), 131.01 (CH), 130.79 (CH), 129.90 (CH), 129.15 (Cq), 128.03 (Cq), 127.47 (CH), 123.74 (Cq), 123.32 (CH), 122.52 (CH), 114.42 (2CH), 64.31 (CH_2). Anal. Calcd. for $\text{C}_{21}\text{H}_{15}\text{BrNO}$: C, 55.17; H, 3.31; N, 3.06. Found: C, 55.20; H, 3.30; N, 3.09.

1-(4-Methoxyphenacyl)benzo[f]quinolinium bromide (2). yellow-mustard crystals; IR (cm^{-1}): 1675($\nu_{\text{C=O}}$); ^1H NMR (δ , ppm, *J*, Hz): 3.89 (s, 3H, 4- OCH_3), 6.89 (s, 2H, CH_2), 7.03 (d, 2H, *J* = 8.9, H-3', -5'), 7.75 (d, 1H, *J* = 9.6, H-9), 7.84 (td, 1H, *J* = 1.1, 7.8, H-7/6), 7.92 (td, 1H, *J* = 1.5,

7.8, H-6/7), 8.01 (dd, 1H, $J = 7.8, 1.5$, H-8), 8.16 (d, 2H, $J = 8.9$, H-2', -6'), 8.19 (dd, 1H, $J = 8.6, 5.9$, H-3), 8.31 (d, 1H, $J = 9.6$, H-10), 8.71 (dl, 1H, $J = 7.8$, H-5), 9.33 (d, 1H, $J = 5.9$, H-4), 9.71 (d, 1H, $J = 8.6$, H-2); ^{13}C NMR (δ , ppm): 187.724 (CO), 165.52 (Cq-10b), 141.30 (CH), 140.26 (Cq), 139.24 (CH), 131.20 (2CH-2', -6'), 130.71 (CH), 130.52 (CH), 129.66 (CH), 128.78 (CH), 127.85 (Cq), 126.63 (Cq), 125.63 (Cq), 123.23 (CH), 122.38 (CH-3), 114.64 (2CH-2', -6'), 64.00 (CH₂). Anal. Calcd. for C₂₂H₁₈BrNO₂: C, 64.72; H, 4.44; N, 3.43. Found: C, 64.71; H, 4.46; N, 3.44.

1-(1-Naphthoyl)benzo[f]quinolinium bromide (3). yellow-mustard crystals; IR (cm⁻¹): 1689($\nu_{\text{C=O}}$); ^1H NMR (δ , ppm, J , Hz): 7.00 (s, 2H, CH₂), 7.52-7.56 (m, 2H, H-6, -7), 7.82 (d, 1H, $J = 9.5$, H-9), 7.88-8.20 (m, 6H), 8.24 (dd, 1H, $J = 8.4, 5.9$, H-3),), 8.38 (d, 1H, $J = 9.5$, H-10), 8.51 (dl, 1H, $J = 7.2$, naphthyl H-8'/2'), 8.70 (dd, 1H, $J = 7.4, 8.5$, naphthyl H-3'), 8.82 (dl, 1H, $J = 8.5$, naphthyl H-2'/8'), 9.37 (d, 1H, $J = 5.9$, H-4), 9.80 (d, 1H, $J = 8.4$, H-2). Anal. Calcd. for C₂₅H₁₈BrNO: C, 70.10; H, 4.24; N, 3.27. Found: C, 70.12; H, 4.23; N, 3.29.

1-(2-Naphthoyl)benzo[f]quinolinium bromide (4). beige crystals; IR (cm⁻¹): 1667($\nu_{\text{C=O}}$); ^1H NMR (δ , ppm, J , Hz): 7.04 (s, 2H, CH₂), 7.59 (td, 1H, $J = 8.0$, H-6/7), 7.65 (td, 1H, $J = 8.0$, H-7/6), 7.80 (d, 1H, $J = 9.6$, H-9), 7.86-8.15 (m, 7H), 8.21 (dd, 1H, $J = 8.5, 5.9$, H-3), 8.37 (d, 1H, $J = 9.6$, H-10), 8.79 (dl, 1H, $J = 8.0$, H-5), 8.90 (d, 1H, $J = 0.6$, H-1'), 9.30 (d, 1H, $J = 5.9$, H-4), 9.76 (d, 1H, $J = 8.5$, H-2); ^{13}C NMR (δ , ppm): 189.95 (CO), 147.38 (Cq), 141.40 (CH), 140.43 (Cq), 139.77 (CH), 136.79 (CH), 132.42 (Cq), 131.96 (CH), 131.92 (CH), 131.22 (Cq), 130.99 (CH), 130.77 (CH), 130.21 (CH), 131.00 (CH), 129.90 (CH), 129.58 (Cq), 129.16 (CH), 128.03 (Cq), 127.94 (CH), 127.69 (CH), 123.29 (CH), 122.93 (2CH), 114.45 (CH), 108.70 (Cq), 64.40 (CH₂). Anal. Calcd. for C₂₅H₁₈BrNO: C, 70.10; H, 4.24; N, 3.27. Found: C, 70.10; H, 4.24; N, 3.26.

General procedure for benzo[f]pyrrolo[1,2-*a*]quinolines

A mixture of benzo[f]quinolinium quaternary salt (10 mmol) and alkyne (11 mmol) in propene oxide (50 mL) was stirred at room temperature for 10-12 days and then was concentrated under reduced pressure. The residue was treated with methanol (10 mL) and left overnight at room temperature. The solid was filtered, washed with cold methanol and then with diethyl ether. All crude products were recrystallised from chloroform/diethyl ether.

The yields and m. p. for benzo[f]pyrrolo[1,2-*c*]quinolines are shown in Table 2. The spectral data are given below.

1-Carbethoxy-3-benzoyl-benzo[f]pyrrolo[1,2-*a*]quinoline (15). yellow crystals; IR (cm⁻¹): 1692($\nu_{\text{C=O}}$ ester), 1626($\nu_{\text{C=O}}$ ketone); ^1H NMR (δ , ppm, J , Hz): 1.41 (t, 3H, $J = 7.1, 3.4$, CH₂CH₃), 4.40 (q, 2H, $J = 7.1$, CH₂CH₃), 7.58 (ddd, 2H, $J = 7.8, 8.5$, H-3', -5'), 7.59-7.70 (m, 3H, H-8, -9, -4'), 7.73 (s, 1H, H-2), 7.92 (d, 1H, $J = 9.5$, H-12), 7.94 (dd, 1H, $J = 7.8$, H-7), 7.99 (d, 1H, $J = 9.5$, H-11), 8.14 (dd, 2H, $J = 1.5, 8.5$, H-2', -6'), 8.50 (d, 1H, $J = 9.6$, H-6), 8.56 (d, 1H, $J = 9.6$, H-5), 8.58 (dd, 1H, $J = 1.4, 8.4$, H-10); ^{13}C NMR (δ , ppm): 184.31 (CO), 164.08 (COOC₂H₅), 140.21 (Cq), 139.00 (Cq), 132.81 (CH), 131.95 (Cq), 130.74 (Cq), 130.19 (CH), 130.09 (CH),

129.71 (Cq), 129.45 (CH), 128.76 (CH), 128.53 (2CH), 127.68 (Cq), 127.62 (CH), 126.58 (CH), 123.69 (CH), 122.82 (CH), 120.83 (Cq), 119.67 (CH), 117.59 (CH), 107.06 (Cq), 60.17 (CH₂CH₃), 14.55 (CH₂CH₃). Anal. Calcd. for C₂₆H₁₉NO₃: C, 79.37; H, 3.56; N, 4.87. Found: C, 79.32; H, 3.47; N, 4.88.

1,2-Dicarbomethoxy-3-(4-fluorobenzoyl)-benzo[f]pyrrolo[1,2-a]quinoline (16). yellow crystals; IR (cm⁻¹): 1743($\nu_{\text{C=O}}$ ester), 1699($\nu_{\text{C=O}}$ ester), 1630($\nu_{\text{C=O}}$ ketone); ¹H NMR (δ , ppm, *J*, Hz): 3.52 (s, 3H, 1-COOCH₃), 3.92 (s, 3H, 2-COOCH₃), 7.17 (t, 2H, *J* = 8.7, H-3', -5'), 7.59 (t, 1H, *J* = 7.9, H-8), 7.60 (d, 1H, *J* = 9.3, H-12), 7.70 (ddd, 1H, *J* = 1.3, 8.4, 7.9, H-9), 7.82 (d, 1H, *J* = 9.3, H-11), 7.88 (dl, 1H, *J* = 7.9, H-7), 8.03 (dd, 2H, *J* = 5.4, 8.7, H-2', -6'), 8.41 (d, 1H, *J* = 9.7, H-6), 8.49 (d, 1H, *J* = 9.7, H-5), 8.54 (d, 1H, *J* = 8.4, H-10); ¹³C NMR (δ , ppm): 185.41 (CO), 166.11 (d, *J* = 256, Cq-35), 165.38 (2-COOCH₃), 164.00 (1-COOCH₃), 137.42 (Cq), 132.51 (d, *J* = 9.3, C-2', -6'), 130.99 (Cq), 130.61 (Cq), 129.97 (CH-11), 129.60 (d, *J* = 5.32, Cq-1'), 128.75 (CH-7), 127.95 (CH), 126.84 (CH-8), 125.26 (Cq), 123.10 (CH-6), 122.80 (CH-10), 121.08 (Cq), 118.25 (CH-8), 117.88 (CH-5), 115.70 (d, *J* = 22, CH-3', -5'), 104.67 (Cq-1), 52.39 (2-COOCH₃), 51.68 (1-COOCH₃). Anal. Calcd. for C₂₇H₁₈FNO₅: C, 71.21; H, 3.98; N, 3.07. Found: C, 71.23; H, 4.00; N, 3.02.

1-Carbomethoxy-3-(4-chlorobenzoyl)-benzo[f]pyrrolo[1,2-a]quinoline (17). yellow crystals; IR (cm⁻¹): 1705($\nu_{\text{C=O}}$ ester), 1635($\nu_{\text{C=O}}$ ketone); ¹H NMR (δ , ppm, *J*, Hz): 1.42 (t, 3H, *J* = 7.1, 3.4, CH₂CH₃), 4.41 (q, 2H, *J* = 7.1, CH₂CH₃), 7.56 (d, 2H, *J* = 8.5, H-3', -5'), 7.62 (ddd, 1H, *J* = 1.1, 7.0, 7.6, H-8), 7.72 (s, 1H, H-2), 7.72 (ddd, 1H, *J* = 1.5, 9.1, 7.6, H-9), 7.95 (s, 2H, H-11, -12), 7.96 (dd, 1H, *J* = 1.5, 7.0, H-7), 8.07 (d, 2H, *J* = 8.5, H-2', -6'), 8.50 (d, 1H, *J* = 9.5, H-6), 8.58 (d, 1H, *J* = 9.5, H-5), 8.58 (dl, 1H, *J* = 9.1, H-10); ¹³C NMR (δ , ppm): 182.87 (CO), 163.97 (COOC₂H₅), 140.39 (Cq), 139.22 (Cq), 130.27 (CH), 129.67 (Cq), 129.58 (CH), 128.86 (2CH), 128.79 (CH), 127.72 (CH), 127.20 (Cq), 126.69 (CH), 123.98 (CH), 122.82 (CH), 120.90 (Cq), 119.52 (CH), 117.55 (CH), 107.20 (Cq), 60.26 (CH₂CH₃), 14.51 (CH₂CH₃). Anal. Calcd. for C₂₆H₁₉NO₃: C, 72.98; H, 4.24; N, 3.27. Found: C, 73.02; H, 4.27; N, 3.28.

1,2-Dicarbomethoxy-3-(3-bromobenzoyl)-benzo[f]pyrrolo[1,2-a]quinoline (18). yellow crystals; IR (cm⁻¹): 1740($\nu_{\text{C=O}}$ ester), 1708($\nu_{\text{C=O}}$ ester), 1641($\nu_{\text{C=O}}$ ketone); ¹H NMR (δ , ppm, *J*, Hz): 3.56 (s, 3H, 1-COOCH₃), 3.98 (s, 3H, 2-COOCH₃), 7.41 (t, 1H, *J* = 7.9, H-5'), 7.45 (dl, 1H, *J* = 8.2, H-6'), 7.55 (d, 1H, *J* = 9.3, H-12), 7.63 (td, 1H, *J* = 1.0, 7.7, H-8/9), 7.72 (ddd, 1H, *J* = 1.5, 7.1, 7.7, H-9/8), 7.82 (ddd, 1H, *J* = 1.0, 1.9, 9.0, H-4'), 7.87 (d, 1H, *J* = 9.3, H-11), 7.92 (dl, 1H, *J* = 7.7, H-7), 8.19 (t, 1H, *J* = 1.8, H-2'), 8.35 (d, 1H, *J* = 9.6, H-6), 8.52 (dl, 1H, *J* = 8.5, H-10), 8.60 (d, 1H, *J* = 9.6, H-5); ¹³C NMR (δ , ppm): 186.14 (CO), 167.13 (2-COOCH₃), 164.83 (1-COOCH₃), 138.85 (Cq), 138.68 (Cq), 137.31 (CH), 132.96 (CH), 130.99 (Cq), 130.85 (CH), 130.79 (Cq), 130.53 (CH), 129.51 (Cq), 128.93 (CH), 128.66 (CH), 128.36 (CH), 127.34 (CH), 125.10 (CH), 124.89 (Cq), 123.04 (Cq), 122.83 (CH), 121.65 (Cq), 118.17 (CH), 117.35 (CH), 53.48 (2-COOCH₃), 52.72 (1-COOCH₃). Anal. Calcd. for C₂₇H₁₈BrNO₅: C, 62.81; H, 3.51; N, 2.71. Found: C, 62.80; H, 3.56; N, 2.70.

1-Carbomethoxy-3-(4-bromobenzoyl)-benzo[f]pyrrolo[1,2-a]quinoline (19). yellow crystals; IR (cm⁻¹): 1708($\nu_{\text{C=O}}$ ester), 1637($\nu_{\text{C=O}}$ ketone); ¹H NMR (δ , ppm, *J*, Hz): 1.42 (t, 3H, *J* = 7.1, 3.4, CH₂CH₃), 4.40 (q, 2H, *J*

= 7.1, CH_2CH_3), 7.62 (ddd, 1H, $J = 1.0, 7.0, 7.4$, H-8), 7.69 (s, 1H, H-2), 7.71 (ddd, 1H, $J = 1.5, 8.8, 7.0$, H-9), 7.72 (d, 2H, $J = 8.6$, H-3', -5'), 7.94 (s, 2H, H-11, -12), 7.95 (dd, 1H, $J = 1.5, 8.0$, H-7), 8.01 (d, 2H, $J = 8.6$, H-2', -6'), 8.50 (d, 1H, $J = 9.6$, H-6), 8.57 (dl, 1H, $J = 8.8$, H-10), 8.58 (dl, 1H, $J = 9.6$, H-5); ^{13}C NMR (δ , ppm): 182.97 (CO), 163.95 ($COOC_2H_5$), 140.41 (Cq), 137.18 (Cq), 131.83 (2CH), 131.53 (2CH), 130.74 (Cq), 129.67 (Cq), 126.69 (CH), 124.00 (CH), 122.82 (CH), 120.92 (Cq), 119.52 (CH), 117.54 (CH), 107.22 (Cq), 60.26 (CH_2CH_3), 14.53 (CH_2CH_3). Anal. Calcd. for $C_{26}H_{18}BrNO_3$: C, 66.12; H, 3.84; N, 2.96. Found: C, 66.13; H, 3.87; N, 3.00.

1-Carbethoxy-3-(3-nitrobenzoyl)-benzo[f]pyrrolo[1,2-a]quinoline (20). yellow-chlorine crystals; IR (cm^{-1}): 1703($\nu_{C=O}$ ester), 1638($\nu_{C=O}$ ketone); 1H NMR (δ , ppm, J , Hz): 1.46 (t, 3H, $J = 7.1, 3.4$, CH_2CH_3), 4.47 (q, 2H, $J = 7.1$, CH_2CH_3), 7.70 (ddd, 1H, $J = 1.0, 7.7, 8.0$, H-8), 7.77 (ddd, 1H, $J = 1.5, 8.0, 7.7$, H-9), 7.84 (t, 1H, $J = 7.7$, H-5'), 7.86 (s, 1H, H-2), 7.94 (d, 1H, $J = 9.5$, H-12), 8.01 (dd, 1H, $J = 1.5, 7.7$, H-7), 8.04 (d, 1H, $J = 9.5$, H-11), 8.45 (dt, 1H, $J = 7.7, 1.1$, H-6'), 8.50 (d, 1H, $J = 9.3$, H-6), 8.57 (ddd, 1H, $J = 1.1, 2.3, 7.7$, H-4'), 8.65 (dl, 1H, $J = 8.0$, H-10), 8.79 (d, 1H, $J = 9.3$, H-5), 8.93 (t, 1H, $J = 1.9$, H-2'); ^{13}C NMR (δ , ppm): 182.27 (CO), 165.58 ($COOC_2H_5$), 148.25 (Cq), 141.69 (Cq), 139.33 (Cq), 135.73 (CH), 133.12 (CH), 131.96 (Cq), 130.89 (Cq), 130.62 (CH), 130.14 (CH), 129.54 (Cq), 128.93 (CH), 128.31 (CH), 127.54 (CH), 127.33 (CH), 126.66 (Cq), 126.14 (CH), 124.75 (CH), 122.85 (CH), 121.44 (CH), 119.17 (CH), 117.20 (CH), 107.80 (Cq), 61.78 (CH_2CH_3), 13.97 (CH_2CH_3). Anal. Calcd. for $C_{26}H_{18}N_2O_5$: C, 71.23; H, 4.14; N, 6.39. Found: C, 71.20; H, 4.14; N, 6.40.

1-Carbethoxy-3-(4-nitrobenzoyl)-benzo[f]pyrrolo[1,2-a]quinoline (21). orange crystals; IR (cm^{-1}): 1706($\nu_{C=O}$ ester), 1640($\nu_{C=O}$ ketone); 1H NMR (δ , ppm, J , Hz): 1.42 (t, 3H, $J = 7.1, 3.4$, CH_2CH_3), 4.40 (q, 2H, $J = 7.1$, CH_2CH_3), 7.66 (ddd, 1H, $J = 1.2, 8.2, 7.0$, H-8), 7.71 (s, 1H, H-2), 7.75 (ddd, 1H, $J = 1.5, 7.0, 8.2$, H-9), 7.98 (dd, 1H, $J = 1.5, 8.2$, H-7), 8.00 (s, 2H, H-11, -12), 8.25 (d, 2H, $J = 8.9$, H-2', -6'), 8.44 (d, 2H, $J = 8.9$, H-3', -5'), 8.54 (d, 1H, $J = 9.6$, H-6), 8.62 (dl, 1H, $J = 8.2$, H-10), 8.67 (d, 1H, $J = 9.6$, H-5); ^{13}C NMR (δ , ppm): 181.39 (CO), 163.69 ($COOC_2H_5$), 150.15 (Cq-4'), 143.91 (Cq-3), 140.99 (Cq-12), 132.01 (Cq-4a), 131.24 (CH-9), 130.28 (2CH-2', 6'), 129.82 (CH-11), 129.66 (Cq-10a), 128.86 (CH-7), 127.91 (CH-2), 126.98 (Cq-6a), 126.92 (CH-8), 124.76 (CH-5), 123.71 (2CH-3', 5'), 122.87 (CH-10), 121.78 (Cq-11a), 119.52 (CH-12), 117.52 (CH-6), 107.86 (Cq-1), 60.39 (CH_2CH_3), 14.52 (CH_2CH_3). Anal. Calcd. for $C_{26}H_{18}N_2O_5$: C, 71.23; H, 4.14; N, 6.39. Found: C, 71.24; H, 4.18; N, 6.36.

1,2-Dicarbomethoxy-3-(4-methoxybenzoyl)-benzo[f]pyrrolo[1,2-a]quinoline (22). yellow crystals; IR (cm^{-1}): 1736($\nu_{C=O}$ ester), 1710 ($\nu_{C=O}$ ester), 1635($\nu_{C=O}$ ketone); 1H NMR (δ , ppm, J , Hz): 3.53 (s, 3H, OCH_3), 3.89 (s, 3H, 1- $COOCH_3$), 3.93 (s, 3H, 2- $COOCH_3$), 6.97 (d, 2H, $J = 9.2$, H-3', -5'), 7.68 (d, 1H, $J = 9.2$, H-11), 7.55-7.75 (m, 2H, H-8, -9), 7.81 (d, 1H, $J = 9.2$, H-12), 7.88 (dd, 1H, $J = 1.5, 8.1$, H-7), 7.99 (d, 2H, $J = 9.2$, H-2', -6'), 8.43 (d, 1H, $J = 8.8$, H-6), 8.48 (d, 1H, $J = 8.8$, H-5), 8.56 (d, 1H, $J = 8.6$, H-10); ^{13}C NMR (δ , ppm): 186.10 (CO), 165.44 (2- $COOCH_3$), 164.27 (1- $COOCH_3$), 163.70 (Cq-4'), 136.95 (Cq), 132.39 (CH), 131.45 (CH), 131.07 (Cq), 130.60 (CH), 130.52 (CH), 129.84 (Cq), 129.70 (Cq), 128.73 (Cq), 128.67 (Cq), 128.33 (CH), 128.22 (Cq), 127.93 (CH), 122.90 (Cq), 122.63 (CH), 120.94 (Cq), 118.23 (CH), 117.89 (CH), 113.92 (2CH-3', -5'), 104.54 (Cq), 55.65 (2- $COOCH_3$), 52.50 (1- $COOCH_3$), 52.34

(OCH₃). Anal. Calcd. for C₂₈H₂₁NO₆: C, 71.94; H, 4.53; N, 2.99. Found: C, 72.00; H, 4.50; N, 3.00.

1,2-Dicarbomethoxy-3-(3,4-dimethoxybenzoyl)-benzo[f]pyrrolo[1,2-a]quinoline (23). yellow crystals; IR (cm⁻¹): 1730($\nu_{\text{C=O}}$ ester), 1708($\nu_{\text{C=O}}$ ester), 1636($\nu_{\text{C=O}}$ ketone); ¹H NMR (δ , ppm, *J*, Hz): 3.45 (s, 3H, 1-COOCH₃), 3.84 (s, 3H, 2-COOCH₃), 3.88 (s, 3H, 3'-OCH₃), 3.89 (s, 3H, 4'-OCH₃), 6.81 (d, 1H, *J* = 8.5, H-5'), 7.45-7.60 (m, 5H, H-2', -6', -8, -9, -12), 7.72 (d, 1H, *J* = 9.4, H-11), 7.76 (dl, 1H, *J* = 8.4, H-10), 7.78 (dl, 1H, *J* = 7.7, H-7), 8.29 (d, 1H, *J* = 9.8, H-6), 8.35 (d, 1H, *J* = 9.8, H-5); ¹³C NMR (δ , ppm): 185.92 (CO), 165.50 (2-COOCH₃), 163.64 (1-COOCH₃), 154.07 (Cq-4'), 149.15 (Cq-3'), 131.00 (Cq), 130.99 (CH), 130.53 (Cq), 130.01 (Cq), 129.82 (CH), 129.63 (Cq), 128.37 (Cq), 127.81 (CH), 125.71 (Cq), 125.38 (CH), 122.76 (CH), 122.51 (CH), 120.89 (Cq), 118.22 (CH), 117.90 (CH), 112.33 (CH), 110.02 (CH-5'), 104.37 (Cq), 56.22 (2-COOCH₃), 56.08 (1-COOCH₃), 52.36 (4'-OCH₃), 51.56 (3'-OCH₃). Anal. Calcd. for C₂₉H₂₃NO₇: C, 70.01; H, 4.66; N, 2.81. Found: C, 70.00; H, 4.62; N, 2.80.

1,2-Dicarbomethoxy-3-(4-phenylbenzoyl)-benzo[f]pyrrolo[1,2-a]quinoline (24). yellow-orange crystals; IR (cm⁻¹): 1740($\nu_{\text{C=O}}$ ester), 1705($\nu_{\text{C=O}}$ ester), 1629($\nu_{\text{C=O}}$ ketone); ¹H NMR (δ , ppm, *J*, Hz): 3.49 (s, 3H, 1-COOCH₃), 3.92 (s, 3H, 2-COOCH₃), 7.38-7.51 (m, 5H, H-2''-6''), 7.57 (ddd, 1H, *J* = 1.8, 8.0, 7.8, H-8), 7.61-7.70 (m, 2H, H-9, -12), 7.73 (d, 2H, *J* = 8.5, H-3', -5'), 7.81 (d, 1H, *J* = 9.3, H-11), 7.86 (dd, 1H, *J* = 1.3, 8.0, H-7), 8.08 (d, 2H, *J* = 8.5, H-2', -6'), 8.39 (d, 1H, *J* = 9.7, H-6), 8.46 (d, 1H, *J* = 9.7, H-5), 8.51 (dl, 1H, *J* = 8.0, H-10); ¹³C NMR (δ , ppm): 186.65 (CO), 165.47 (2-COOCH₃), 163.64 (1-COOCH₃), 146.46 (Cq), 139.69 (Cq), 137.39 (Cq), 136.52 (Cq), 131.13 (Cq), 130.67 (Cq), 130.54 (2CH-2', -6'), 129.97 (CH-10), 129.72 (Cq), 129.43 (Cq), 129.07 (CH), 126.79 (CH-7), 128.50 (CH), 127.94 (CH), 127.33 (CH), 127.27 (CH), 126.82 (CH), 125.87 (Cq), 122.98 (CH), 122.86 (CH), 121.10 (Cq), 118.47 (CH), 117.95 (CH), 104.67 (Cq), 52.42 (2-COOCH₃), 51.72 (1-COOCH₃). Anal. Calcd. for C₃₃H₂₃NO₅: C, 74.49; H, 4.69; N, 3.10. Found: C, 74.45; H, 4.64; N, 3.09.

1,2-Dicarbomethoxy-3-(2-thenoyl)-benzo[f]pyrrolo[1,2-a]quinoline (25). orange crystals; IR (cm⁻¹): 1728($\nu_{\text{C=O}}$ ester), 1701($\nu_{\text{C=O}}$ ester), 1614($\nu_{\text{C=O}}$ ketone); ¹H NMR (δ , ppm, *J*, Hz): 3.63 (s, 3H, 1-COOCH₃), 3.98 (s, 3H, 2-COOCH₃), 7.19 (dd, 1H, *J* = 4.0, 3.2, H-4'), 7.60-7.95 (m, 7H, H-7, -8, -9, -11, -12, -3', 5'), 8.42 (d, 1H, *J* = 9.6, H-6), 8.58 (d, 1H, *J* = 9.6, H-5), 8.59 (dl, 1H, *J* = 8.8, H-10); ¹³C NMR (δ , ppm): 179.79 (CO), 166.49 (2-COOCH₃), 164.42 (1-COOCH₃), 143.54 (Cq), 137.55 (Cq), 136.93 (CH), 136.25 (CH), 130.96 (Cq), 130.71 (Cq), 130.54 (CH), 129.63 (Cq), 128.83 (CH-4'), 128.47 (CH), 128.29 (CH), 123.67 (CH), 122.82 (CH), 121.19 (Cq), 117.84 (Cq), 117.73 (CH), 104.41 (Cq), 103.36 (Cq), 52.92 (2-COOCH₃), 52.17 (1-COOCH₃). Anal. Calcd. for C₂₅H₁₇NO₅S: C, 67.71; H, 3.86; N, 3.16. Found: C, 67.72; H, 3.89; N, 3.20.

1,2-Dicarbomethoxy-3-(1-naphthoyl)-benzo[f]pyrrolo[1,2-a]quinoline (26). yellow crystals; IR (cm⁻¹): 1744($\nu_{\text{C=O}}$ ester), 1705($\nu_{\text{C=O}}$ ester), 1630($\nu_{\text{C=O}}$ ketone); ¹H NMR (δ , ppm, *J*, Hz): 2.98 (s, 3H, 1-COOCH₃), 3.88 (s, 3H, 2-COOCH₃), 7.48 (dd, 1H, *J* = 7.4, 8.2, H-3'), 7.56-7.68 (m, 5H, H-7, -8, -10, -6', 7'), 7.72 (ddd, 1H, *J* = 1.3, 7.0, 7.3, H-9), 7.82 (d, 1H, *J* = 9.5, H-12), 7.87 (d, 1H, *J* = 9.5, H-11), 7.89 (dd, 1H, *J* = 1.3, 8.1, H-5'), 8.04 (dd, 1H, *J* = 1.3, 7.4, H-4'), 8.49 (d, 1H, *J* = 9.6, H-6), 8.57 (d, 1H, *J* = 9.6, H-5), 8.59 (dl, 1H, *J* = 8.3, H-10), 8.67 (dd, 1H, *J* = 1.3,

7.4, H-8'); ^{13}C NMR (δ , ppm): 186.79 (CO), 165.29 (2-COOCH₃), 163.45 (1-COOCH₃), 138.12 (Cq), 135.00 (Cq), 133.86 (Cq), 133.70 (CH), 131.43 (Cq), 131.12 (Cq), 130.98 (CH), 130.77 (Cq), 129.90 (CH), 129.69 (Cq), 128.79 (CH), 128.40 (CH), 128.30 (CH), 127.89 (CH), 127.22 (Cq), 126.83 (2CH), 125.73 (CH), 124.10 (CH), 123.74 (CH), 122.84 (CH), 121.21 (Cq), 118.83 (CH), 117.83 (CH), 104.38 (Cq), 51.99 (2-COOCH₃), 51.67 (1-COOCH₃). Anal. Calcd. for C₃₁H₂₁NO₅: C, 76.37; H, 4.34; N, 5.75. Found: C, 76.39; H, 4.34; N, 5.76.

1-Benzoyl-3-(1-naphthoyl)-benzo[*f*]pyrrolo[1,2-*a*]quinoline (27). yellow crystals; IR (cm⁻¹): 1621($\nu_{\text{C=O}}$), 1604($\nu_{\text{C=O}}$); ^1H NMR (δ , ppm, *J*, Hz): 7.36 (t, 2H, *J* = 7.8, phenyl H-3'', -5''), 7.45 (s, 1H, H-2), 7.64 (dd, 2H, *J* = 7.8, 1.5, phenyl H-2'', -6''), 7.68 (d, 1H, *J* = 7.4, H-12), 7.30-8.10 (m, 11H, H-7, -8, -9, -11, 2'-7', -4''), 8.28 (m, 1H, naphthyl H-8'), 8.64 (d, 1H, *J* = 8.1, H-10), 8.70 (d, 1H, *J* = 9.5, H-6), 8.93 (d, 1H, *J* = 9.5, H-5); ^{13}C NMR (δ , ppm): 194.49 (phenacyl-CO), 184.74 (naphthoyl-CO), 143.41 (Cq), 137.61 (Cq), 136.75 (CH), 134.29 (CH), 134.11 (CH), 133.35 (CH), 132.34 (Cq), 131.75 (CH), 131.34 (Cq), 131.18 (Cq), 131.18 (Cq), 130.53 (CH), 130.13 (CH), 129.47 (Cq), 129.38 (2CH), 129.18 (CH), 128.90 (2CH), 128.72 (CH), 128.38 (CH), 127.87 (CH), 127.22 (CH), 125.05 (CH), 124.39 (CH), 123.07 (CH), 122.77 (Cq), 119.14 (CH), 117.94 (CH), 114.65 (Cq), 104.32 (Cq-1). Anal. Calcd. for C₃₄H₂₁NO₂: C, 85.87; H, 4.45; N, 2.94. Found: C, 85.90; H, 4.44; N, 2.90.

1,2-Dicarbomethoxy-3-(2-naphthoyl)-benzo[*f*]pyrrolo[1,2-*a*]quinoline (28). yellow-orange crystals; IR (cm⁻¹): 1739($\nu_{\text{C=O}}$ ester), 1707($\nu_{\text{C=O}}$ ester), 1627($\nu_{\text{C=O}}$ ketone); ^1H NMR (δ , ppm, *J*, Hz): 3.26 (s, 3H, 1-COOCH₃), 3.98 (s, 3H, 2-COOCH₃), 7.59 (ddd, 1H, *J* = 1.4, 7.0, 8.3, H-8), 7.60-7.71 (m, 3H, H-7, -5', -6'), 7.72 (d, 1H, *J* = 9.4, H-12), 7.77 (ddd 1H, *J* = 1.4, 7.0, 8.3, H-9), 7.88 (d, 1H, *J* = 9.4, H-11), 8.00 (d, 1H, *J* = 8.7, H-5'), 8.06 (d, 1H, *J* = 8.7, H-4'), 8.07 (dd, 1H, *J* = 1.6, 8.7, H-8'), 8.39 (d, 1H, *J* = 8.7, H-3'), 8.47 (d, 1H, *J* = 9.6, H-6), 8.58 (d, 1H, *J* = 1.6, H-1'), 8.60 (dl, 1H, *J* = 8.3, H-10), 8.65 (d, 1H, *J* = 9.6, H-5); ^{13}C NMR (δ , ppm): 188.09 (CO), 167.14 (2-COOCH₃), 164.81 (1-COOCH₃), 138.43 (Cq), 136.21 (Cq), 134.27 (Cq), 133.45 (CH), 132.03 (Cq), 131.09 (Cq), 130.77 (CH), 130.36 (Cq), 129.80 (CH), 129.61 (CH), 129.29 (CH), 128.93 (CH), 128.26 (CH), 127.96 (CH), 127.48 (CH), 127.20 (CH), 125.65 (Cq), 124.65 (CH), 124.39 (CH), 122.86 (CH), 121.45 (Cq), 118.23 (CH), 117.56 (CH), 104.43 (Cq), 53.23 (2-COOCH₃), 52.58 (1-COOCH₃). Anal. Calcd. for C₃₁H₂₁NO₅: C, 76.37; H, 4.34; N, 5.75. Found: C, 76.35; H, 4.32; N, 5.73.

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