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

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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 work[3-6] 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

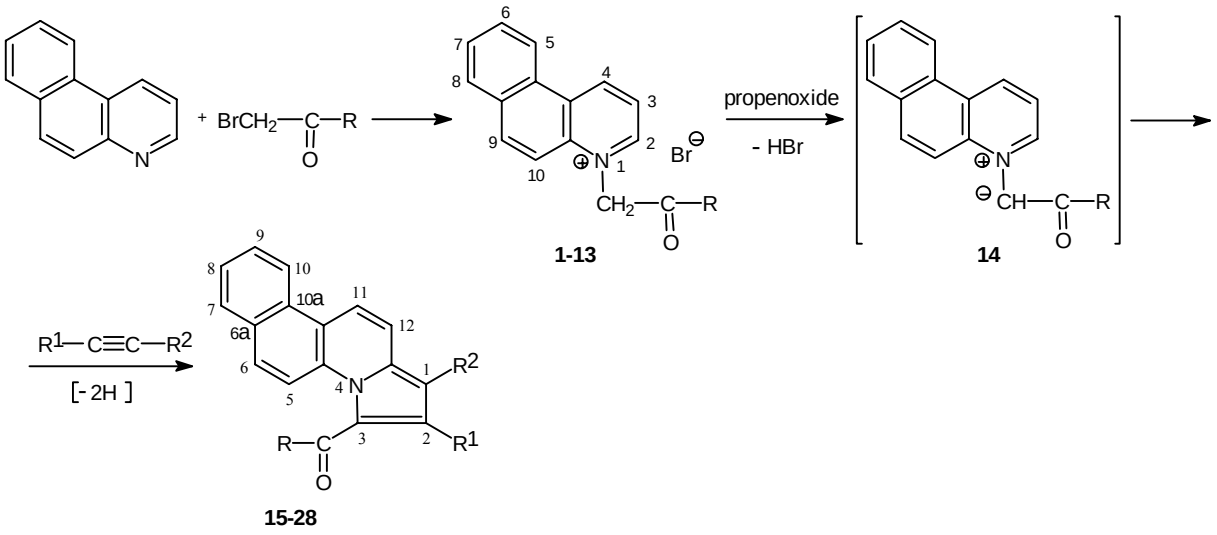
Compound	R	m.p.(°C)	yield(%)
1	3-BrC_6H_4	242-244	87.5
2	4-$MeOC_6H_4$	225-227	86.0
3	1-naphthyl	163.5-165	74.0
4	2-naphthyl	271-273	72.4

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_2Et	237.5-239	40.8
16	4-FC_6H_4	CO_2Me	CO_2Me	237-238	40,0
17	4-ClC_6H_4	H	CO_2Et	256-257	45.5
18	3-BrC_6H_4	CO_2Me	CO_2Me	258,5-260	56.4
19	4-BrC_6H_4	H	CO_2Et	259-260	55.8
20	3-$NO_2C_6H_4$	H	CO_2Et	296-298	60.0
21	4-$NO_2C_6H_4$	H	CO_2Et	291-293	60.5
22	4-$MeOC_6H_4$	CO_2Me	CO_2Me	239-242	42.5
23	3,4-$(MeO)_2C_6H_3$	CO_2Me	CO_2Me	249-251	46,6
24	4-PhC_6H_4	CO_2Me	CO_2Me	228-229	48.0
25	2-thienyl	CO_2Me	CO_2Me	262-263.5	42.0
26	1-naphthyl	CO_2Me	CO_2Me	244-247	62.0
27	1-naphthyl	H	COC_6H_5	233-235	60.0
28	2-naphthyl	CO_2Me	CO_2Me	239-240.5	60.8

These reactions took place in propene oxide as acid acceptor and reaction solvent. Ethyl propiolate, dimethyl acetylenedicarboxylate and phenylethynyl 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 1604-1641 cm^{-1} for the benzoyl or naphthoyl group, about 1692-1708 cm^{-1} for a carbethoxy group, and two carbonyl absorption bands at about 1728-1744 cm^{-1} and 1699-1710 cm^{-1} for the two carbomethoxy groups.

The ^{1}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 carbethoxy 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}H-NMR spectra of these compounds exhibit all the characteristic signals of the benzo[f]quinoline ring system.

The ^{13}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 carbethoxy 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 ^{1}H 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 ^{1}H-decoupling COSY (^{1}H-^{1}H) and COSY (^{1}H-^{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 ± 0.20, H ± 0.16, N ± 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($\upsilon_{C=O}$); ^{1}H NMR (δ, ppm, *J*, Hz): 6.93 (s, 2H, C*H*$_2$), 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 (*C*O), 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 (*C*H$_2$). Anal. Calcd. for $C_{21}H_{15}BrNO$: 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($\upsilon_{C=O}$); ^{1}H NMR (δ, ppm, *J*, Hz): 3.89 (s, 3H, 4-OC*H*$_3$), 6.89 (s, 2H, C*H*$_2$), 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 (*C*O), 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 (*C*H_2). Anal. Calcd. for $C_{22}H_{18}BrNO_2$: 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($\upsilon_{C=O}$); ^{1}H NMR (δ, ppm, *J*, Hz): 7.00 (s, 2H, CH_2), 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 $C_{25}H_{18}BrNO$: 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($\upsilon_{C=O}$); ^{1}H NMR (δ, ppm, *J*, Hz): 7.04 (s, 2H, CH_2), 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 (*C*O), 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 (*C*H_2). Anal. Calcd. for $C_{25}H_{18}BrNO$: 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($\upsilon_{C=O\ ester}$), 1626($\upsilon_{C=O\ ketone}$); ^{1}H NMR (δ, ppm, *J*, Hz): 1.41 (t, 3H, *J* = 7.1, 3.4, CH_2CH_3), 4.40 (q, 2H, *J* = 7.1, CH_2CH_3), 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 (*C*O), 164.08 (*C*OOC_2H_5), 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 (*C*H_2CH$_3$), 14.55 (CH$_2$*C*H$_3$). Anal. Calcd. for $C_{26}H_{19}NO_3$: 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($\upsilon_{C=O\ ester}$), 1699($\upsilon_{C=O\ ester}$), 1630($\upsilon_{C=O\ ketone}$); ^{1}H NMR (δ, ppm, *J*, Hz): 3.52 (s, 3H, 1-COO*CH$_3$*), 3.92 (s, 3H, 2-COO*CH$_3$*), 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); ^{13}C NMR (δ, ppm): 185.41 (*C*O), 166.11 (d, *J* = 256, Cq-35), 165.38 (2-*C*OOCH$_3$), 164.00 (1-*C*OOCH$_3$), 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-COO*CH$_3$*), 51.68 (1-COO*CH$_3$*). Anal. Calcd. for $C_{27}H_{18}FNO_5$: C, 71.21; H, 3.98; N, 3.07. Found: C, 71.23; H, 4.00; N, 3.02.

1-Carbethoxy-3-(4-chlorobenzoyl)-benzo[*f*]pyrrolo[1,2-*a*]quinoline (17). yellow crystals; IR (cm^{-1}): 1705($\upsilon_{C=O\ ester}$), 1635($\upsilon_{C=O\ ketone}$); ^{1}H NMR (δ, ppm, *J*, Hz): 1.42 (t, 3H, *J* = 7.1, 3.4, CH$_2$*CH$_3$*), 4.41 (q, 2H, *J* = 7.1, *CH$_2$*CH$_3$), 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); ^{13}C NMR (δ, ppm): 182.87 (CO), 163.97 (*CO*OC$_2$H$_5$), 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 (*CH$_2$*CH$_3$), 14.51 (CH$_2$*CH$_3$*). Anal. Calcd. for $C_{26}H_{19}NO_3$: 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($\upsilon_{C=O\ ester}$), 1708($\upsilon_{C=O\ ester}$), 1641($\upsilon_{C=O\ ketone}$); ^{1}H NMR (δ, ppm, *J*, Hz): 3.56 (s, 3H, 1-COO*CH$_3$*), 3,98 (s, 3H, 2-COO*CH$_3$*), 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); ^{13}C NMR (δ, ppm): 186.14 (*C*O), 167.13 (2-*C*OOCH$_3$), 164.83 (1-*C*OOCH$_3$), 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-COO*C*H$_3$), 52.72 (1-COO*C*H$_3$). Anal. Calcd. for $C_{27}H_{18}BrNO_5$: C, 62.81; H, 3.51; N, 2.71. Found: C, 62.80; H, 3.56; N, 2.70.

1-Carbethoxy-3-(4-bromobenzoyl)-benzo[*f*]pyrrolo[1,2-*a*]quinoline (19). yellow crystals; IR (cm^{-1}): 1708($\upsilon_{C=O\ ester}$), 1637($\upsilon_{C=O\ ketone}$); ^{1}H NMR (δ, ppm, *J*, Hz): 1.42 (t, 3H, *J* = 7.1, 3.4, CH$_2$*CH$_3$*), 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 (*C*O), 163.95 (*C*OOC_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($\upsilon_{C=O\ ester}$), 1638($\upsilon_{C=O\ ketone}$); ^{1}H 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 (*C*O), 165.58 (*C*OOC_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($\upsilon_{C=O\ ester}$), 1640($\upsilon_{C=O\ ketone}$); ^{1}H 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 (*C*O), 163.69 (*C*OOC_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($\upsilon_{C=O\ ester}$), 1710 ($\upsilon_{C=O\ ester}$), 1635($\upsilon_{C=O\ ketone}$); ^{1}H 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 (*C*O), 165.44 (2-*C*$OOCH_3$), 164.27 (1-*C*$OOCH_3$), 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

(O*C*H$_3$). Anal. Calcd. for $C_{28}H_{21}NO_6$: 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($\upsilon_{C=O\ ester}$), 1708($\upsilon_{C=O\ ester}$), 1636($\upsilon_{C=O\ ketone}$); ^{1}H NMR (δ, ppm, *J*, Hz): 3.45 (s, 3H, 1-COO*CH$_3$*), 3.84 (s, 3H, 2-COO*CH$_3$*), 3.88 (s, 3H, 3′-OCH$_3$), 3.89 (s, 3H, 4′-OCH$_3$), 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); ^{13}C NMR (δ, ppm): 185.92 (*C*O), 165.50 (2-*C*OOCH$_3$), 163.64 (1-*C*OOCH$_3$), 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-COO*C*H$_3$), 56.08 (1-COO*C*H$_3$), 52.36 (4′-O*C*H$_3$), 51.56 (3′-O*C*H$_3$). Anal. Calcd. for $C_{29}H_{23}NO_7$: 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($\upsilon_{C=O\ ester}$), 1705($\upsilon_{C=O\ ester}$), 1629($\upsilon_{C=O\ ketone}$); ^{1}H NMR (δ, ppm, *J*, Hz): 3.49 (s, 3H, 1-COO*CH$_3$*), 3.92 (s, 3H, 2-COO*CH$_3$*), 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); ^{13}C NMR (δ, ppm): 186.65 (*C*O), 165.47 (2-*C*OOCH$_3$), 163.64 (1-*C*OOCH$_3$), 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-COO*C*H$_3$), 51.72 (1-COO*C*H$_3$). Anal. Calcd. for $C_{33}H_{23}NO_5$: 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($\upsilon_{C=O\ ester}$), 1701($\upsilon_{C=O\ ester}$), 1614($\upsilon_{C=O\ ketone}$); ^{1}H NMR (δ, ppm, *J*, Hz): 3.63 (s, 3H, 1-COO*CH$_3$*), 3.98 (s, 3H, 2-COO*CH$_3$*), 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); ^{13}C NMR (δ, ppm): 179.79 (*C*O), 166.49 (2-*C*OOCH$_3$), 164.42 (1-*C*OOCH$_3$), 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-COO*C*H$_3$), 52.17 (1-COO*C*H$_3$). Anal. Calcd. for $C_{25}H_{17}NO_5S$: 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($\upsilon_{C=O\ ester}$), 1705($\upsilon_{C=O\ ester}$), 1630($\upsilon_{C=O\ ketone}$); ^{1}H NMR (δ, ppm, *J*, Hz): 2.98 (s, 3H, 1-COO*CH$_3$*), 3.88 (s, 3H, 2-COO*CH$_3$*), 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 (*C*O), 165.29 (2-*C*OOCH$_3$), 163.45 (1-*C*OOCH$_3$), 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-COO*C*H$_3$), 51.67 (1-COO*C*H$_3$). Anal. Calcd. for $C_{31}H_{21}NO_5$: 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(υ$_{C=O}$), 1604(υ$_{C=O}$); ^{1}H 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-*C*O), 184.74 (naphthoyl-*C*O), 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 $C_{34}H_{21}NO_2$: 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(υ$_{C=O\ ester}$), 1707(υ$_{C=O\ ester}$), 1627(υ$_{C=O\ ketone}$); ^{1}H NMR (δ, ppm, *J*, Hz): 3.26 (s, 3H, 1-COO*CH$_3$*), 3.98 (s, 3H, 2-COO*CH$_3$*), 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 (*C*O), 167.14 (2-*C*OOCH$_3$), 164.81 (1-*C*OOCH$_3$), 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-COO*CH$_3$*), 52.58 (1-COO*C*H$_3$). Anal. Calcd. for $C_{31}H_{21}NO_5$: C, 76.37; H, 4.34; N, 5.75. Found: C, 76.35; H, 4.32; N, 5.73.

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