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A New Synthesis of Benzo[*b*]acridones

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Abstract: A novel and efficient route for the synthesis of new benzo[*b*]acridones has been described. It involves the Diels–Alder reaction of N-substituted-4-quinolone-3-carbaldehyde with *ortho*-benzoquinodimethanes giving benzo[*b*]-1,6,6a,12a-tetrahydroacridones, which are the result of a cycloaddition reaction followed by an in situ deformylation. The oxidation of these tetrahydroacridones in dimethyl sulfoxide using a catalytic amount of iodine gives the new benzo[*b*]acridone derivatives. It was demonstrated that the cycloaddition reaction is only efficient if an electron-withdrawing N-protecting group is present.

Key words: 4-quinolone-3-carbaldehydes, benzo[*b*]acridones, Diels–Alder reactions, oxidation, N-protecting groups.

Acridones are a group of naturally occurring nitrogen heterocyclic compounds found exclusively in plants belonging to the Rutaceae family.[1] Both natural and synthetic acridone derivatives exhibit a variety of important biological activities. They are known to present important antiparasitic activity, against leishmania and malaria, and antifungal activities.[2,3] Certain derivatives are important anticancer,[4,5] and antiviral compounds,[6–8] some of them being selective inhibitors of human immunodeficiency virus type-1 (HIV-1) replication in chronically HIV-1 infected cells. Another important potential applications of acridones is their possible use as fluorescent agents,[9] such as labels for fluorescence detection of target biological materials and as fluorescent anion receptors and sensors.

There are only a few examples of benzo[*b*]acridones described in the literature where an additional aromatic ring is linearly fused to the acridone moiety.[10] The most common derivatives of this type of compounds are the benzo[*b*]acronycines which present potent antitumour activity,[10–13] being found to be more active than acronycine,[10] a natural pyranoacridone alkaloid that exhibits promising activity against a broad spectrum of tumors.[14] *cis*-1,2-Diacetoxy-1,2-dihydrobenzo[*b*]acronycine has also shown an impressive broad spectra of antitumor activities, and it is currently in phase II clinical trials.[12]

Acridones and their benzo[*b*]derivatives are usually prepared by the Ullmann condensation of anilines with *ortho*-halogen-substituted benzoic or naphthoic acids followed by the acid induced ring closure of the *N*-phenyl anthranilic acids,[3,5,7,13,15] or by the condensation of 3-amino-2-naphthalenecarboxylic acid with phloroglucinol.[8,10] Besides these classical syntheses, other methods involve the intermolecular nucleophilic coupling of arynes with 2-aminobenzoates and subsequent intramolecular nucleophilic cyclization,[16] and the anionic *N*-Fries rearrangement of *N*-carbamoyl diarylamines to anthranilamides followed by smoothly cyclization with tryflic anhydride.[17] Benzo[*b*]acridones have also been obtained by the Friedel–Crafts reaction of 3,5-dimethoxyacetanilide with 2-methoxy-1-naphthoyl chloride followed by base-catalyzed cyclization.[11]

The variety of important potential applications of acridones and their benzo[*b*]acridone derivatives highlight these compounds as targets for the preparation of new derivatives or/and to develop new strategies for their synthesis. In the present communication we describe a new method for the synthesis of novel benzo[*b*]acridones by Diels–Alder reaction of N-substituted-4-quinolone-3-carbaldehyde, acting as a dienophile, with the highly reactive dienes *ortho*-benzoquinodimethanes, followed by oxidation of the obtained intermediates.

Initial experiments considered the Diels–Alder reaction of 1-methyl-4-quinolone-3-carbaldehyde (**1**)[18] with *ortho*-benzoquinodimethane (**3a**), formed in situ by thermal extrusion of sulfur dioxide from 1,3-dihydrobenzo[*c*]thiophene 2,2-dioxide (**2a**).[19] This reaction afforded a diastereomeric mixture of benzo[*b*]-1,6,6a,12a-tetrahydroacridone derivatives **4** and **5** and benzo[*b*]acridone **6** (Scheme 1, Table 1).[20] Tetrahydroacridones **4**[21] and **5**[22] are the result of the predicted cycloaddition reaction followed by deformylation of the expected cycloadduct, a β-ketoaldehyde **7**, under the experimental conditions.[23] Benzo[*b*]acridone **6**[24] is presumably obtained by the in situ oxidation of tetrahydroacridones **4** and **5**.[25] However, even after several attempts using different experimental conditions (varying amounts of diene, catalysts, reaction time, and heating conditions) low overall yields were obtained in the formation of compounds **4**, **5**, and **6**.[20]

The stereochemistry of diastereomers **4** and **5** was assigned as *cis* and *trans*, respectively, based on the NOESY studies. In the NOESY spectrum of isomer **4** there is a NOE cross peak between signals of H-12a (multiplet, δ_H = 3.31–3.36) and H-6a (double triplet, δ_H = 3.95), due to their spatial proximity, while in the spectrum of isomer **5** the NOE cross peak was not present (H-12a, multiplet, δ_H = 2.80–2.90; H-6a, multiplet, δ_H = 3.57–3.63). The main ^{1}H NMR features to support the structure of acridone **6** is the absence of aliphatic signals and the three singlets at δ_H = 3.95 (N-Me), 7.77 (H-6), and 9.13 (H-1). The

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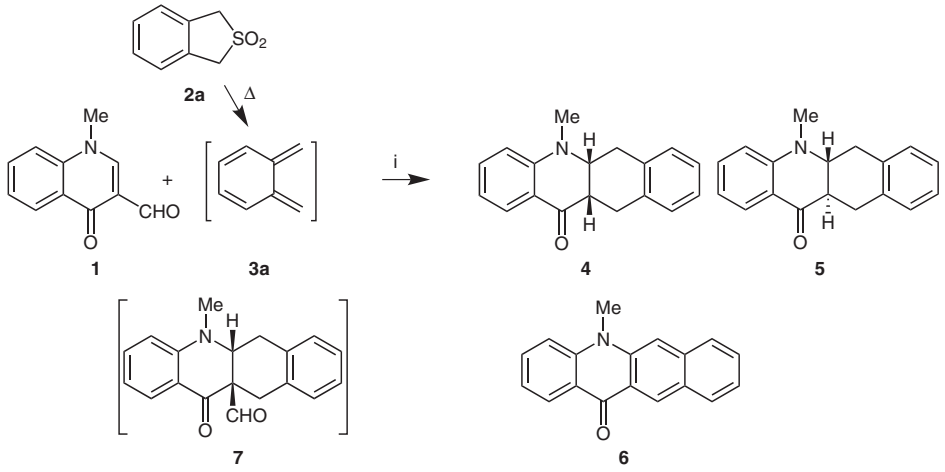


Scheme 1 *Reagents and conditions*: (i) 1,2,4-trichlorobenzene, reflux.

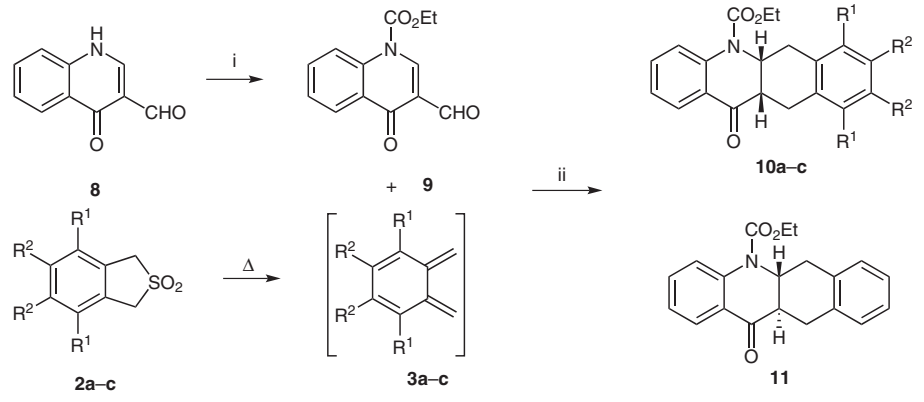
Table 1 Reaction Conditions for the Syntheses of Compounds **4**–**6**

Entry	Time (h)	Sulfone **2a** (equiv)	Conditions	Catalyst	Yield (%)		
					4 + **5**[a]	**6**	**1**[b]
1	7	2	TCB, reflux N_2	–	7	<5	59
2	16	2	TCB, reflux N_2	–	9	6	51
3	16	5	TCB, reflux N_2	–	14	8	40
4	24	10	TCB, reflux N_2	–	14	11	27
5	24	10	TCB, reflux	–	13	15	21
6	20	10	TCB, reflux N_2	$AlCl_3$	0	5	0
7	26	10	TCB, reflux N_2	$La(OTf)_3$	4	3	6

[a] Although we present the combined yield, these compounds were isolated as pure compounds (in a 4:1 proportion of **4/5**) by preparative TLC.
[b] Recovered starting material.

high frequency of the latter signal is due to the anisotropic and mesomeric deshielding effects of the carbonyl group.

Since the yields obtained were not satisfactory we decided to reduce the electronic density of the C2=C3 double bound of 4-quinolone-3-carbaldehyde (**8**) by introducing an electron-withdrawing ethoxycarbonyl N-protecting group. It was found that the 1-ethoxycarbonyl-4-quinolone-3-carbaldehyde (**9**) was not stable on silica gel since a partial hydrolysis of the carbamate occurred during purification by column chromatography. However, after several attempts with different reaction conditions; changing the base (Et_3N, PS-TBD, NaH), the solvent (THF, $CHCl_3$),



Scheme 2 *Reagents and conditions*: (i) K_2CO_3, $ClCO_2Et$, acetone, r.t.; (ii) 1,2,4-trichlorobenzene, reflux.

and the reaction temperature (r.t. to 60 °C), we found the optimal method (1.5 equiv of ethyl chloroformate, K_2CO_3 as base, acetone as solvent, and r.t.) to isolation of 1-ethoxycarbonyl-4-quinolone-3-carbaldehyde (**9**) in good yield (96%) without need for purification (Scheme 2).

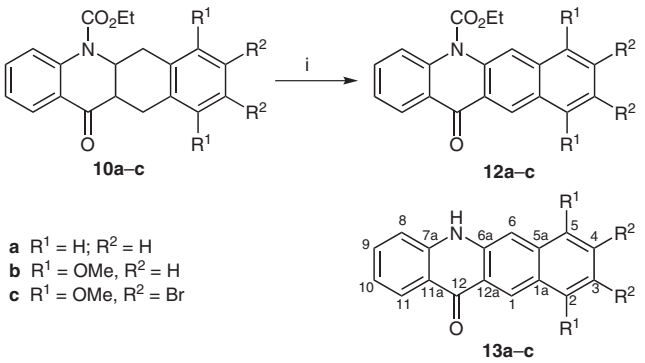
After several attempts, we found that the Diels–Alder reaction of 1-ethoxycarbonyl-4-quinolone-3-carbaldehyde (**9**) with *ortho*-benzoquinodimethane (**3a**) in refluxing 1,2,4-trichlorobenzene afforded the *cis*-benzo[*b*]tetrahydroacridone **10a** (Table 2, entries 1–4). A better yield (71%) was obtained when using two molar equivalents of sulfone **2a** and 9 hours reaction time. Traces of the *trans*-diastereomer **11** were found when the reaction proceeded for 16 hours (Table 2, entry 2). Applying these optimized conditions to the cycloaddition might give rise to the expected adduct **13**, a β-ketoaldehyde which was prone to deformylation under the reactions conditions, yielding the mixture of diastereomers **8** and **9**, which could be separated by thin-layer chromatography (TLC). This type of deformylation was already reported by Wallace conditions to the cycloaddition reactions of **9** with substituted *ortho*-benzoquinodimethanes **3b**,**c**,[26] the corresponding benzo[*b*]-1,6,6a,12a-tetrahydroacridones **10b**,**c** were obtained in good yields (84% and 81%, Table 2, entries 5 and 6).

Table 2 Reaction Conditions and Yields in the Diels–Alder Reaction of 1-Ethoxycarbonyl-4-quinolone-3-carbaldehyde **9** with *ortho*-Benzoquinodimethanes **3a–c**

Entry	Time (h)	Sulfone **2a–c** (equiv)	R^1	R^2	Yield (%)	
					10a–c	**11**
1	4	**2a** 5	H	H	49	–
2	16	**2a** 5	H	H	57	1
3	9	**2a** 5	H	H	64	–
4	9	**2a** 2	H	H	71	–
5	9	**2b** 2	OMe	H	84	–
6	9	**2c** 2	OMe	Br	81	–

The stereochemistry of compounds **10a–c** was established as *cis* based on the presence of a NOE cross peak between the signals of H-12a (multiplet, δ_H = 3.33–3.42) and H-6a (multiplets, δ_H = 5.25–5.34) in their NOESY spectrum.

The last step of our procedure considered the oxidation of benzo[*b*]-1,6,6a,12a-tetrahydroacridones **10a–c** in order to obtain the corresponding benzo[*b*]acridones **12a–c**. Firstly, we studied oxidation of benzo[*b*]-1,6,6a,12a-tetrahydroacridone **10a** with a large excess of chloranil in refluxing dry 1,4-dioxane; however, after 26 hours there was no reaction. In a second attempt, we used a large excess of 2,3-dichloro-5,6-dicyano-*p*-benzoquinone in refluxing dry 1,4-dioxane with the result that a small quantity of the desired 7-ethoxycarbonylbenzo[*b*]acridone **12a** was obtained accompanied by much decomposition. However, oxidation of benzo[*b*]-1,6,6a,12a-tetrahydroacridone **10a** with dimethyl sulfoxide using a catalytic amount of iodine,[27,28] did give the expected acridone derivatives (Scheme 3). When the reaction was performed at 170–180 °C mixtures of the expected 7-ethoxycarbonylbenzo[*b*]acridone derivatives **12a–c**[29] and the unprotected benzo[*b*]acridone derivatives **13a–c**[30] were isolated in good overall yields (62–86%), the latter being slightly more abundant. When the temperature was increased to 190–200 °C the reaction was more selective, and we obtained mainly the unprotected benzo[*b*]acridone derivatives **13a–c**, in good yields (59–82%), and a very small amount of the 7-ethoxycarbonylbenzo[*b*]acridone derivatives **12a–c** (2–4%).



Scheme 3 *Reagents and conditions*: (i) I_2, DMSO.

The main features in the ^{1}H NMR of **12a–c** and **13a–c** that allow us to differentiate them are: i) the signals of the ethyl group of **12a–c** at δ_H = 1.42–1.44 (CH_3) and δ_H = 4.47–4.50 (CH_2); and ii) the signals of the NH proton of **13a–c** at δ_H = 11.75–12.05. Both compounds present two singlets at high frequency due to the resonances of H-1 (δ_H = 8.85–9.22 for **12a–c**; δ_H = 8.94–9.11 for **13a–c**) and H-6 (δ_H = 8.37–8.63 for **12a–c**; δ_H = 7.96–8.21 for **13a–c**).

In conclusion, a new methodology for the synthesis of benzo[*b*]acridones has been developed. This synthetic route comprises three steps, the synthesis of 4-quinolone-3-carbaldehyde, followed by their reaction with *ortho*-benzoquinodimethanes, and then oxidation of the obtained products. The cycloaddition reaction is only efficient if an electron-withdrawing N-protecting group is present.

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(18) 1-Methyl-4-quinolone-3-carbaldehyde(**1**) was prepared by a Vilsmeier reaction of 2′-aminoacetophenone, followed by acidic hydrolysis of the resultant 4-chloroquinoline-3-carbaldehyde to form 4-quinolone-3-carbaldehyde (**8**), which was then N-methylated to avoid undesirable side reactions of the amino group. The following procedure was used: Coelho, A.; El-Maatougui, A.; Ravina, E.; Cavaleiro, J. A. S.; Silva, A. M. S. *Synlett* **2006**, 3324.

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(20) **Optimized Experimental Procedure**
A mixture of 1-methyl-4-quinolone-3-carbaldehyde (**1**, 121.7 mg, 0.65 mmol) and 1,3-dihydrobenzo[*c*]thiophene 2,2-dioxide (**2a**) in 1,2,4-trichlorobenzene (TCB, 6 mL) was refluxed under a variety of reaction conditions (see Table 1). After cooling to r.t., the reaction mixture was purified by silica gel column chromatography; the TCB solvent was removed using light PE as eluent, and then the cycloadducts were eluted with a mixture of light PE–EtOAc (4:1). The solvent was evaporated to dryness and the mixture of diastereomers was separated by preparative thin-layer chromatography using a mixture of light PE–EtOAc (9:1). The 7-methylbenzo[*b*]-1,6,6a,12a-tetrahydroacridones **4** and **5** and the benzo[*b*]acridone(**6**) were obtained as yellow compounds.

(21) **Physical Data for *cis*-7-Methylbenzo[*b*]-1,6,6a,12a-tetrahydroacridone (4)**
^{1}H NMR (300.1 MHz, $CDCl_3$): δ = 2.80–3.02 (m, 3 H, 1 × H-1, 2 × H-6), 3.11 (s, 3 H, NCH_3), 3.31–3.36 (m, 1 H, H-12a), 3.81 (dd, 1 H, *J* = 1.6, 17.3 Hz, H-1), 3.95 (dt, 1 H, *J* = 5.5, 11.0 Hz, H-6a), 6.69 (d, 1 H, *J* = 8.6 Hz, H-8), 6.71 (ddd, 1 H, *J* = 0.9, 7.3, 7.6 Hz, H-10), 6.96 (d, 1 H, *J* = 7.4 Hz, H-5), 7.06 (dt, 1 H, *J* = 1.5, 7.4 Hz, H-4), 7.13 (dt, 1 H, *J* = 1.3, 7.4 Hz, H-3), 7.20 (d, 1 H, *J* = 7.4 Hz, H-2), 7.41 (ddd, 1 H, *J* = 1.7, 7.3, 8.6 Hz, H-9), 7.86 (dd, 1 H, *J* = 1.7, 7.6 Hz, H-11). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 26.1 and 26.6 (C-1 and C-6), 37.6 (NCH_3), 45.1 (C-12a), 60.4 (C-6a), 113.1 (C-8), 116.6 (C-10), 118.8 (C-11a), 125.8 (C-4), 126.4 (C-3), 127.9 (C-11), 129.1 and 129.2 (C-2 and C-5), 133.0 (C-5a), 133.8 (C-1a), 135.6 (C-9), 150.0 (C-7a), 194.1 (C-12). ESI$^+$-MS: *m/z* (%) = 264 (100) $[M + H]^+$, 286 (93) $[M + Na]^+$, 302 (8) $[M + K]^+$, 549 (47) $[2 M + Na]^+$. HRMS (EI, 70 eV): *m/z* calcd for $C_{18}H_{17}NO$: 263.1310; found: 263.1309.

(22) **Physical Data for *trans*-7-Methylbenzo[*b*]-1,6,6a,12a-tetrahydroacridone (5)**
^{1}H NMR (300.1 MHz, $CDCl_3$): δ = 2.80–2.90 (m, 1 H, H-12a), 2.91–3.01 (m, 1 H, H-1), 3.07 (s, 3 H, NCH_3), 3.11–3.16 (m, 1 H, H-6), 3.49–3.56 (m, 2 H, H-1, H-6), 3.57–3.63 (m, 1 H, H-6a), 6.81 (ddd, 1 H, *J* = 0.9, 7.3, 7.6 Hz, H-10), 6.90 (d, 1 H, *J* = 8.7 Hz, H-8), 7.18–7.25 (m, 4 H, H-2 to

H-5), 7.46 (ddd, 1 H, *J* = 1.8, 7.3, 8.7 Hz, H-9), 7.96 (dd, 1 H, *J* = 1.8, 7.6 Hz, H-11).
^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 29.1 (C-1), 34.1 (NCH_3), 36.6 (C-6), 46.8 (C-12a), 59.0 (C-6a), 113.9 (C-8), 117.5 (C-10), 119.6 (C-11a), 126.2 and 126.6 (C-3 and C-4), 127.9 (C-1), 128.9 and 129.0 (C-2 and C-5), 132.9 (C-5a), 134.4 (C-1a), 135.7 (C-9), 152.7 (C-7a), 194.6 (C-12). ESI$^+$-MS: *m/z* (%) = 264 (100) [M + H]$^+$, 286 (25) [M + Na]$^+$, 549 (19) [2 M + Na]$^+$. HRMS (EI, 70 eV): *m/z* calcd for $C_{18}H_{17}NO$: 263.1310; found: 263.1312.

(23) This type of deformylation reaction has been previously reported for similar compounds, see: (a) Cremins, P. J.; Saengchantara, S. T.; Wallace, T. W. *Tetrahedron* **1987**, *43*, 3075. (b) Sandulache, A.; Silva, A. M. S.; Cavaleiro, J. A. S. *Tetrahedron* **2002**, *58*, 105.

(24) **Physical Data for 7-Methylbenzo[*b*]acridone (6)**
^{1}H NMR (300.1 MHz, $CDCl_3$): δ = 3.95 (s, 1 H, NCH_3), 7.26 (ddd, 1 H, *J* = 0.8, 6.8, 7.9 Hz, H-10), 7.43 (ddd, 1 H, *J* = 1.2, 6.7, 8.1 Hz, H-3), 7.50 (d, 1 H, *J* = 8.6 Hz, H-8), 7.57 (ddd, 1 H, *J* = 1.3, 6.7, 8.2 Hz, H-4), 7.74 (ddd, 1 H, *J* = 1.7, 6.8, 8.6 Hz, H-9), 7.81 (s, 1 H, H-6), 7.90 (d, 1 H, *J* = 8.2 Hz, H-5), 8.05 (d, 1 H, *J* = 8.1 Hz, H-2), 8.57 (dd, 1 H, *J* = 1.7, 7.9 Hz, H-11), 9.13 (s, 1 H, H-1). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 33.8 (NCH_3), 110.5 (C-6), 114.4 (C-8), 120.5 (C-10), 121.3 (C11a), 122.6 (C-12a), 124.5 (C-3), 126.9 (C-5), 127.9 (C-1a), 128.0 (C-11), 128.7 (C-4), 129.0 (C-1), 129.5 (C-2), 134.4 (C-9), 136.4 (C-5a), 139.7 (C-6a), 143.6 (C-7a), 179.4 (C-12). ESI$^+$-MS: *m/z* (%) = 260 (100) [M + H]$^+$, 282 (33) [M + Na]$^+$, 541 (54) [2 M + Na]$^+$. HRMS (EI, 70 eV): *m/z* calcd for $C_{18}H_{13}NO$: 259.0997; found: 259.0999.

(25) Although the cycloaddition reactions were carried out under nitrogen to avoid moisture, the reaction medium was not deoxygenated, the residual oxygen presumably being the oxidant.

(26) 4,7-Dimethoxy-1,3-dihydrobenzo[*c*]thiophene 2,2-dioxides **2b**,**c** were prepared according to the following literature procedure: Sandulache, A.; Silva, A. M. S.; Cavaleiro, J. A. S. *Monatsh. Chem.* **2003**, *134*, 551.

(27) A reagent system used by our group in the cyclodehydrogenation of 2′-hydroxychalcones and dehydrogenation of tetrahydroxanthones, see: (a) Silva, A. M. S.; Pinto, D.; Tavares, H. R.; Cavaleiro, J. A. S.; Jimeno, M. L.; Elguero, J. *Eur. J. Org. Chem.* **1998**, 2031. (b) Barros, A.; Silva, A. M. S. *Magn. Reson. Chem.* **2006**, *44*, 1122. (c) Barros, A.; Silva, A. M. S. *Monatsh. Chem.* **2006**, *137*, 1505.

(28) **Optimized Experimental Procedure**
Iodine (4%) was added to a solution of the appropriate 7-ethoxycarbonylbenzo[*b*]-1,6,6a,12a-tetrahydroacridones **10a–c** (0.16 mmol) in DMSO (3 mL). The solution was heated at 170–180 °C or at reflux, for 50 min. After cooling to r.t., the reaction mixture was poured onto ice (10 g) and H_2O (10 mL), a small amount of $Na_2S_2O_3$ was added to eliminate the remaining traces of iodine, and the reaction mixture was stirred for some minutes. The yellow solid obtained was filtered off, washed with H_2O (2 × 20 mL), dissolved in EtOAc (20 mL), and washed with H_2O (2 × 20 mL). The solvent was evaporated to dryness and the residue was purified by silica gel column with a mixture of light PE–EtOAc (4:1 to 2:1). The 7-ethoxycarbonylbenzo[*b*]acridones **12a–c** were obtained as yellow solids and the benzo[*b*]acridones **13a–c** were obtained as orange solids. When the reactions were carried out 170–180 °C; the results were as follows: **12a**, 37%; **13a**, 49%; **12b**, 25%; **13b**, 37%; **12c**, 25%; **13c**, 45%. When the reactions were carried in refluxing DMSO, the yields were: **12a**, 2%; **13a**, 59%; **12b**, 2%; **13b**, 59%; **12c**, 4%; **13c**, 82%.

(29) **Physical Data for 7-Ethoxycarbonylbenzo[*b*]-acridone (12a)**
Mp 118–120 °C. ^{1}H NMR (300.1 MHz, $CDCl_3$): δ = 1.42 (t, 3 H, *J* = 7.1 Hz, $NCO_2CH_2CH_3$), 4.47 (q, 2 H, *J* = 7.1 Hz, $NCO_2CH_2CH_3$), 7.39 (ddd, 1 H, *J* = 1.1, 7.4, 7.7 Hz, H-10), 7.52 (ddd, 1 H, *J* = 1.2, 6.8, 8.1 Hz, H-3), 7.62 (ddd, 1 H, *J* = 1.3, 6.8, 8.2 Hz, H-4), 7.66 (ddd, 1 H, *J* = 1.7, 7.4, 8.4 Hz, H-9), 7.86 (d, 1 H, *J* = 8.4 Hz, H-8), 7.92 (d, 1 H, *J* = 8.2 Hz, H-5), 8.04 (d, 1 H, *J* = 8.1 Hz, H-2), 8.31 (dd, 1 H, *J* = 1.7, 7.7 Hz, H-11), 8.37 (s, 1 H, H-6), 8.85 (s, 1 H, H-1). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 14.1 ($NCO_2CH_2CH_3$), 64.2 ($NCO_2CH_2CH_3$), 119.8 (C-6), 122.6 (C-8), 124.6 (C-10), 125.4 (C-12a), 125.8 (C-11a), 126.1 (C-3), 126.8 (C-11), 127.7 (C-5), 128.0 (C-1), 128.9 (C-4), 129.5 (C-2), 129.9 (C-1a), 133.0 (C-9), 135.2 (C-5a), 135.9 (C-6a), 140.8 (C-7a), 153.8 ($NCO_2CH_2CH_3$), 181.0 (C-12). ESI$^+$-MS: *m/z* (%) = 318 (75) [M + H]$^+$, 340 (31) [M + Na]$^+$, 356 (11) [M + K]$^+$, 657 (100) [2 M + Na]$^+$, 974 (30) [3 M + Na]$^+$. HRMS (EI, 70 eV): *m/z* calcd for $C_{20}H_{15}NO_3$: 317.1052; found: 317.1053.

(30) **Physical Data for Benzo[*b*]acridone (13a)**
Mp >300 °C. ^{1}H NMR (300.1 MHz, $CDCl_3$): δ = 7.22 (ddd, 1 H, *J* = 0.8, 6.9, 8.0 Hz, H-10), 7.44 (ddd, 1 H, *J* = 0.9, 7.1, 7.9 Hz, H-3), 7.55 (d, 1 H, *J* = 8.4 Hz, H-8), 7.60 (ddd, 1 H, *J* = 1.1, 7.1, 8.2 Hz, H-4), 7.76 (ddd, 1 H, *J* = 1.5, 6.9, 8.4 Hz, H-9), 7.96 (s, 1 H, H-6), 8.01 (d, 1 H, *J* = 8.2 Hz, H-5), 8.17 (d, 1 H, *J* = 7.9 Hz, H-2), 8.26 (dd, 1 H, *J* = 1.5, 8.0 Hz, H-11), 8.94 (s, 1 H, H-1), 11.75 (s, 1 H, NH). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 112.0 (C-6), 117.0 (C-8), 118.9 (C-11a), 120.2 (C-10), 121.2 (C-12a), 124.1 (C-3), 126.4 (C-11), 126.5 (C-5), 127.3 (C-1), 127.7 (C-1a), 128.5 (C-4), 129.7 (C-2), 134.3 (C-9), 135.9 (C-5a), 137.9 (C-6a), 142.1 (C-7a), 178.2 (C-12). ESI$^+$-MS: *m/z* (%) = 246 (100) [M + H]$^+$. HRMS (EI, 70 eV): *m/z* calcd for $C_{17}H_{11}NO$: 245.0841; found: 245.0842.