

On the Vilsmeier formylation of *N*-aryl-substituted 2-aminothiophenes - a simple route to new thieno[2,3-*b*]quinolinium salts

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Dedicated to Prof. Dr. Rainer Beckert on the occasion his 60th birthday

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Abstract

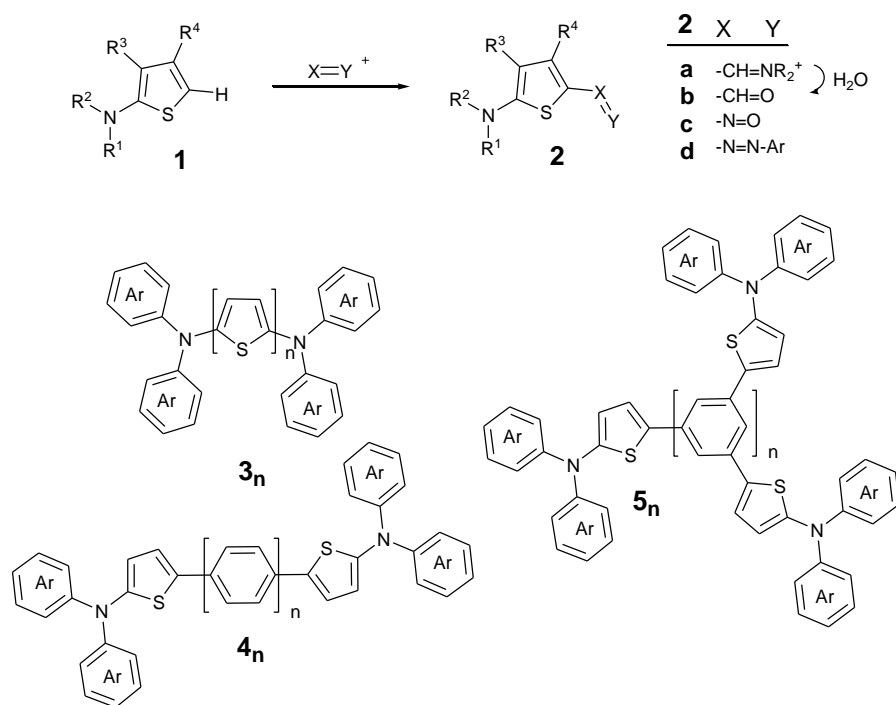
The Vilsmeier reaction of *N*-substituted 2-arylamino-thiophenes-5-carboxylic acid or their alkyl derivatives gives rise, depending on the substitution pattern at the thiophene moiety, to the formation of either *N*-substituted 2-arylamino-thiophene-5-carbaldehydes, corresponding imminium salt precursors, or novel thieno[2,3-*b*]quinolinium salts. These salts are highly reactive towards nucleophiles and can be easily transformed by reduction into the corresponding 4,9-dihydro derivatives.

Keywords: aromatic substitution, heterocycles, Vilsmeier formylation, reduction, 2-aminothiophenes, cations

Introduction

Similarly to *N,N*-disubstituted anilines the heterocyclic *N,N*-disubstituted 2-aminothiophene analogues **1** are highly reactive towards a large variety of electrophilic reagents. As far as the 5-position in these electron-rich heterocyclic compounds **1** is unsubstituted, 5-substituted 2-aminothiophene derivatives **2** are formed by reaction with these reagents. For instance, with the Vilsmeier reagent (VR),¹ with nitrous acid and its derivatives,² or with aryldiazonium salts³ the corresponding substitution products **2a**, **2c** and **2d**, respectively, are formed (Scheme 1). All these compounds received a lot of interest as versatile starting materials for deeply coloured methine, azamethine and azo dyes, some of which exhibit interested non-linear optical properties which enable to use these compounds for opto-electronic applications, eg. as NLO materials,⁴ as NIR dyes,⁵ or as sensors for estimating the solvent polarity.⁶

Furthermore, *N,N*-disubstituted 2-aminothiophenes **1** have been used, as far as they are *N*-aryl-substituted, as building blocks for a variety of oligomeric compounds of the general structure **3_n**,⁷ **4_n**,⁸ and **5_n**,⁸ useful e.g. as hole transport materials for manufacturing optoelectronic devices.¹⁰



Scheme 1

Obviously, a simple access to the *N,N*-disubstituted 2-aminothiophenes **1** was an important precondition for the preparation and application of the before-mentioned compounds. This access was found in a heavy-metal catalysed *C-N*-coupling of 2-halothiophenes **6** with secondary amines (Scheme 2).¹¹ This route allowed to prepare a large variety of *N,N*-disubstituted 2-aminothiophenes **7** but it gives in several cases only low yields of products.¹² Therefore, another synthetic route to the target compounds was an advantageous alternative. It was developed by us recently and consists in a heterocyclisation reaction starting from simple *N,N*-disubstituted acetamides **11**.¹³ These compounds can be simply transformed, *via* the corresponding *N,N'*-tetrasubstituted 1-amino-1-chloro-propeniminium salts **10**, into *N,N*-disubstituted 2-aminothiophene-carboxylic esters **9** and acids **8** from which the target compounds **7** are available by a simple decarboxylation reaction. This heterocyclisation route allows to prepare differently *N,N*-disubstituted 2-aminothiophenes in satisfactory yields mostly and opens the door for further synthetic transformations.¹⁴

Results and Discussion

Continuing our efforts for using *N,N*-disubstituted 2-aminothiophenes and their derivatives as starting materials for a variety of new compounds with interesting chemical and physical properties we studied the reaction of *N*-aryl-substituted 2-aminothiophenes **7** (R^1 and/or $R^2 =$ aryl) as well as their corresponding 5-carboxylic acids **8** and methyl carboxylates **9** towards the VR. In course of this study we found some interesting results which parallel, in general, with the reactivity of *N,N*-dialkyl-substituted 2-amino-thiophenes **7** ($R^1/R^2 =$ Alkyl) but differ in some cases from the one of the *N,N*-dialkyl-substituted compounds with this reagent. Thus, by starting from *N*-phenyl-substituted 5-aminothiophenes **7** ($R^1 =$ Aryl) as expected iminium salts **12** were obtained as primary reaction products.¹ The same type of salts **12** were obtained by starting with the *N,N*-dialkyl-substituted analogues and could be transformed by hydrolysis into the corresponding formyl derivatives **13**. Similar results have been obtained by starting from *N,N*-disubstituted 5-aminothiophene-2-carboxylic acids **8**. With the VR both the *N*-alkyl- as well as *N*-aryl-substituted compounds **8** were transformed into the iminium salts **12** or formyl derivatives **13** indicating that decarboxylation of the acids, used in course of the formylation reaction, had occurred.

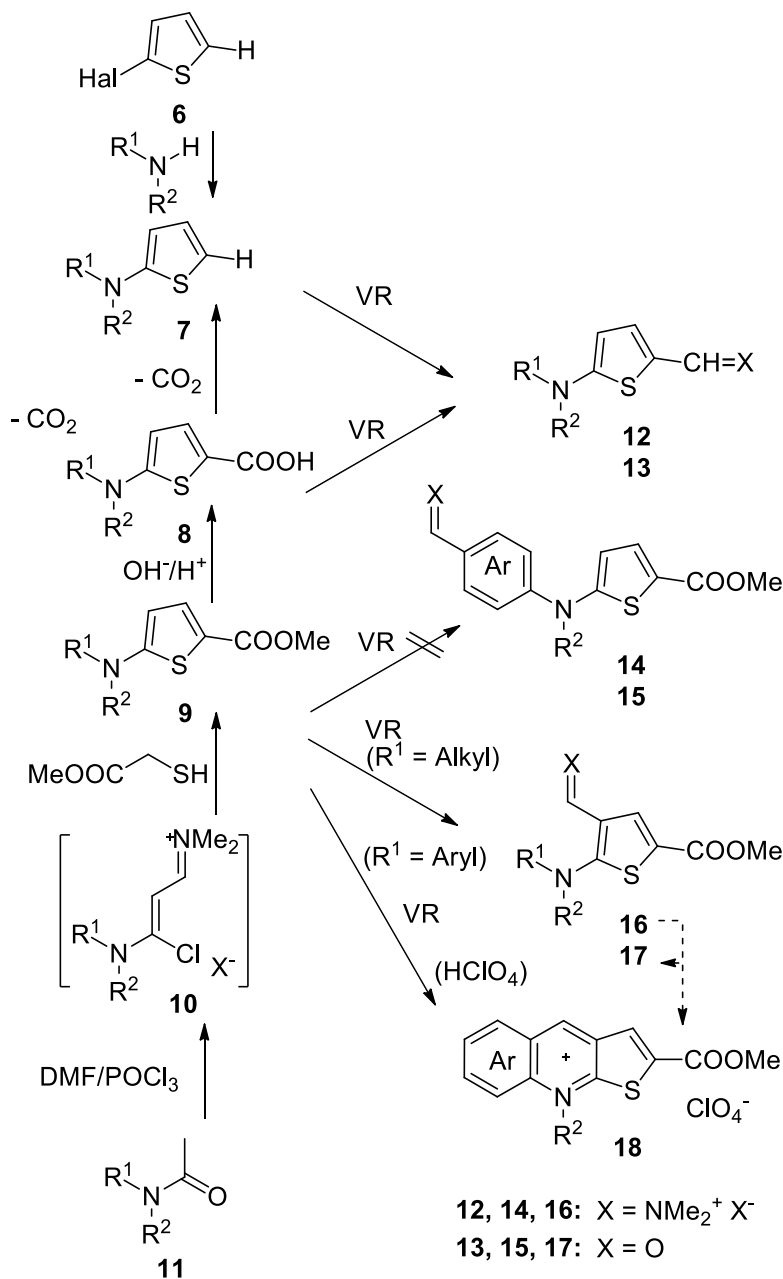
The appropriate iminium salts **12** could be easily isolated, e.g. as perchlorates, after quenching the reaction mixture with methanol by addition of perchloric acid and the formyl derivatives **13** were obtained by neutralisation of the reaction mixture with aqueous sodium hydroxide.

By starting with *N*-aryl-substituted 5-aminothiophene-2-carboxylic esters **9**, however, neither corresponding 4-formyl-derivatives **17** or the iminium salt precursors **16** nor corresponding 4'-formyl derivatives **15** or iminium salts **14** bearing the CH=X group at the aryl moiety of the starting esters were formed. Instead, 2-methoxycarbonyl-substituted thieno[2,3-*b*]quinolinium salts **18** were obtained. These salts could be conveniently isolated in satisfactory yields as pale yellow coloured perchlorates after addition of perchloric acid to the reaction mixture quenched with methanol. Obviously, the starting *N*-aryl-substituted methyl carboxylates **9** were transformed in the first step into the corresponding iminium salts **16** which cyclize subsequently under the reaction conditions applied to yield the heterocyclic products **18**.

The heterocyclisation reaction found has some analogies, as would be worth mentioning, in the reaction of *N*-substituted 2-(*N*-phenyl)-naphthylamines with the VR which transform the starting compounds into appropriate benz[*a*] acridinium salts.¹⁵

The structures of **12**, **13**, **16** and **17**, as well as of the thieno[2,3-*b*]quinolinium perchlorates **18** prepared follow unambiguously from their analytic data recorded. Thus, in the ¹H NMR spectra of the iminium salts **12a**, **12b** and **12e**, prepared as examples from the corresponding *N,N*-disubstituted 2-aminothiophene derivatives **7** and **8**, characteristic singlets between 7.8 - 8.7 ppm and a couple of singlets at 3.3 and 3.5 ppm were recorded in addition to a series of multiplets. The singlets can be attributed to the protons at the iminium moieties and *N*-methyl groups, respectively, whereas the multiplets can be attributed to the protons at the aryl moieties. In the ¹H

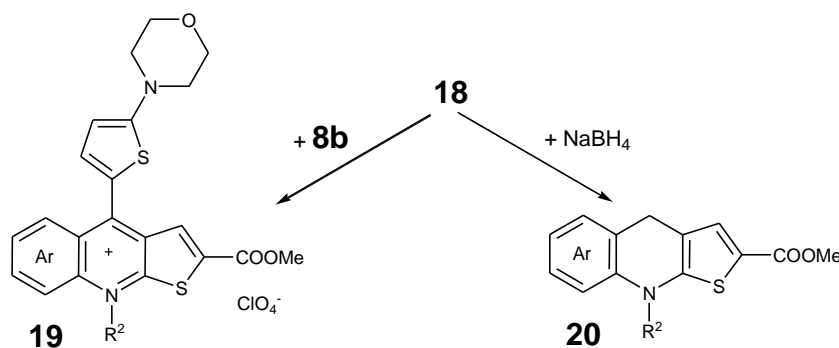
NMR spectra of the formyl derivatives **13a**, **13b**, **17a**, and **17b**, prepared from the corresponding iminium salt precursors **12** or directly from the *N,N*-disubstituted methyl 2-aminothiophene carboxylates **9**, respectively, characteristic singlets between 8.7 and 9.5 ppm originated from the protons at the formyl groups and at about 7.9 ppm originated from the protons at the thiophene moieties in the compounds **17a** and **17b** were recorded. Additionally, characteristic doublets in the ^1H NMR spectra of the iminium salts **12** at about 6.4 ppm and between 7.5 – 7.9 ppm with coupling constants of 4.3 – 4.8 Hz originated from the protons at the thiophene moieties were observed.



Scheme 2

In the ^1H NMR spectra of the thieno[2,3-*b*]quinolinium salts **18**, besides several multiplets between 7.0 and 9.5 ppm corresponding to the protons of the aryl moieties, characteristic singlets at about 4.0, 8.7 and 10.0 ppm were recorded. These signals can be attributed to the methyl group at the carboxylate moieties and to the protons at the 3- and 4-positions of the heterocyclic thieno[2,3-*b*]quinolinium moieties, respectively.

First attempts to transform the new thieno[2,3-*b*]quinolinium salts **18** into certain consecutive products demonstrate that these salts are able to react with a variety of nucleophiles, such as with aliphatic amines, sulfides or with *N,N*-disubstituted aromatic or heteroaromatic amines. Furthermore, they are able to react with usual reducing agents. For instance, by heating the thieno[2,3-*b*]quinolinium perchlorate **18** with 2-morpholino-thiophene-5-carboxylic acid **8j** in acetic anhydride a deeply coloured condensation product of structure **19** was obtained (Scheme 3). In accordance with the analytical data of the product we assume the corresponding addition products is formed first and then subsequently transformed by hydride abstraction into the target products **19** by air oxygen or by using a second equivalent of the starting thieno[2,3-*b*]quinolinium salt **18**.



Scheme 3

By allowing to react the thieno[2,3-*b*]quinolinium perchlorates **18** with sodium borotetrahydride in methanol or DMF the corresponding 4,9-dihydro-thieno[2,3-*b*]quinolines **20** were formed. In contrast to the salts **19**, these compounds exhibit in their ^1H NMR spectra characteristic signals at about 4.6 ppm for the protons at the CH_2 group. The 4,9-dihydro-thieno[2,3-*b*]quinolines **20** are nearly colourless compounds and exhibit intense fluorescence in the blue spectral region. With strong electron accepting compounds the 4,9-dihydro-thieno[2,3-*b*]quinolines **20** can act as hydride donors. Detailed information on this characteristic property will be reported shortly.

Experimental Section

General. ^1H NMR and ^{13}C NMR spectra were recorded with a Bruker DRX 500 P instrument at 500.13 and 125.76 MHz, respectively. Elemental analyses were performed with a Eurovektor Hekatech EA-3000 elemental analyzer. The mass spectra were recorded with a Bruker Esquire-LC 00084 instrument and the melting points with a Boetius heating-table microscope.

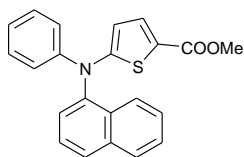
The *N,N*-disubstituted 2-aminothiophenes **7** as well as the *N,N*-disubstituted 5-aminothiophene-2-carboxylic acids **8** and their methyl derivatives **9** used as starting materials were prepared accordingly to the literature.^{13a, 16} The following starting materials not described in detail hitherto were prepared according to the literature by reaction of the corresponding 1-chloro-propene-3-(*N,N*-dimethyl)-iminium salt with methyl thioglycolate.¹³

General procedure for preparation of *N*-disubstituted methyl 2-aminothiophene-5-carboxylates (**9**)

(a) Preparation of *N,N'*-tetrasubstituted 1-amino-1-chloro-propeniminium salts (10**).** To a solution of *N,N*-disubstituted acetamide (0.1 mol) in DMF (25 mL) POCl_3 (30.0 g, 0.2 mol) was added under stirring and cooling. The resulting mixture was left standing over night at room temperature and then poured in ice water (250 mL). After addition of perchloric acid (70 %, 25 mL) the aqueous solution was extracted with dichloromethane (2x 200 mL) and the organic phase was evaporated after drying with MgSO_4 . The residues crystallised after some standing and have been used without further purification for the next step.

(b) Preparation of *N,N*-disubstituted methyl 2-aminothiophene-5-carboxylates (9**).** To a mixture of a *N,N'*-tetrasubstituted 1-amino-1-chloro-propeniminium perchlorate **10** (0.1 mol) and methyl thioglycolate (12.0 g, 0.11 mol) in acetonitrile (100 mL) sodium methanolate was added under stirring at room temperature until the mixture attains a pH > 9. After some standing, the resulting mixture was diluted with water (500 mL) until the products start to crystallise. They were isolated by suction and recrystallised for purification from toluene.

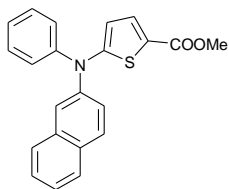
The following *N,N*-disubstituted methyl 2-aminothiophene-5-carboxylates **9** not described in the literature hitherto were so obtained:



Methyl 5-[(*N*-(1-naphthyl)-*N*-phenyl)amino]thiophene-2-carboxylate (9b**)** from *N*-(1-naphthyl)-*N*-phenyl-acetamide¹⁷ (**11b**) via the corresponding 1-chloro-3-dimethylamino-1-*N*-(1-naphthyl)-*N*-phenyl-propeniminium perchlorate (**10b**) in a yield of 85 % and a m.p. of 90 - 91°C. ^1H NMR (500 MHz, CDCl_3): δ = 3.79 (s, 3H, OCH_3), 6.35 (d, J =

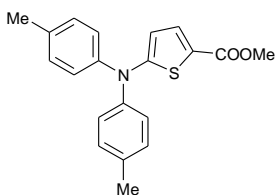
5.6 Hz, CH_{th}), 7.05 – 7.09 (m, 1 arom. H), 7.26 – 7.28 (m, 4 arom. H), 7.45 – 7.53 (m, 5 arom. H), 7.54 (d, J = 5.6 Hz, CH_{th}), 7.86 – 8.00 (m, 2 arom. H); ^{13}C NMR (125.76 MHz, CDCl_3): δ = 51.46, 115.46, 121.39, 121.52, 123.70, 124.58, 125.01, 125.50, 126.60, 127.33, 127.63, 129.44, 129.60, 130.93, 133.81, 134.03, 144.28, 145.80, 159.66, 162.83.

Anal. Calcd for $\text{C}_{22}\text{H}_{17}\text{NO}_2\text{S}$ (359.44): C 73.51, H 4.77, N 3.90; found C 73.66, H 4.71, N 3.83.



Methyl 5-[(N-(2-naphthyl)-N-phenyl)amino]-thiophene-2-carboxylate (9c), from *N*-(2-naphthyl)-*N*-phenyl-acetamide¹⁷ (**11c**) via the corresponding 1-chloro-3-dimethylamino-1-*N*-(2-naphthyl)-*N*-phenyl-propeniminium perchlorate (**10c**) in a yield of 85 % and a m.p. of 117 – 118 °C. ¹H NMR (500 MHz, CDCl₃): δ = 3.82 (s, 3H, OCH₃), 6.50 (d, *J* = 5.6 Hz, 1H, CH_{th}), 7.17 (m, 1 arom. H), 7.26 (t, *J* = 2.0 Hz, 1 arom. H), 7.28 (t, *J* = 2.0 Hz, 1 arom. H), 7.32 – 7.37 (m, 3 arom. H), 7.40 – 7.48 (m, 2 arom. H), 7.59 (d, *J* = 5.6 Hz, 1H, CH_{th}), 7.63 – 7.69 (m, 2 arom. H), 7.78 – 7.80 (m, 2 arom. H); ¹³C NMR (125.76 MHz, CDCl₃): δ = 51.79, 112.79, 119.90, 121.62, 123.26, 123.74, 126.19, 126.50, 126.80, 127.08, 128.20, 128.54, 129.35, 130.47, 134.00, 135.21, 142.33, 147.38, 160.60, 162.27.

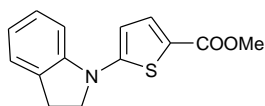
Anal. Calcd for C₂₂H₁₇NO₂S (359.44): C 73.51, H 4.77, N 3.90; found C 73.38, H 4.81, N 4.02



Methyl 5-(di-4-tolyl-amino)-thiophene-2-carboxylate (9d), from *N,N*-bis-(4-tolyl)-acetamide (**11d**) [18] via the corresponding 1-chloro-1-[bis-(4-tolyl)amino]-propene-3-dimethylmethiniminium perchlorate (**10d**) in a yield of 60 % and a m.p. of 111 °C. ¹H NMR (500 MHz, CDCl₃): δ = 2.33 (s, 6H, CH₃), 3.78 (s, 3H, OCH₃), 6.30 (d, *J* = 4.1 Hz, 1 H, CH_{th}), 7.12 (s, 8 arom. H), 7.51 (d, *J* = 4.3 Hz,

1H, CH_{th}).

Anal. Calcd for C₂₀H₁₉NO₂S (337.44): C 71.19, H 5.68, N 4.15; found C 71.37, H 5.60, N 4.28.



Methyl 5-(2,3-dihydro-indol-1-yl)-thiophene-2-carboxylate (9e), from *N*-acetyl-2,3-1*H*-dihydro-indol (**11e**) [19] via the corresponding 1-chloro-1-(*N*-(2,3-dihydro-1*H*-indolyl)-dimethylpropeniminium perchlorate (**10f**) in a yield of 56 % and a m.p. of 95 – 97 °C. ¹H NMR

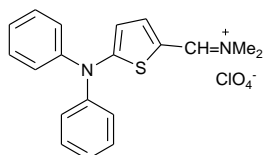
(500 MHz, CDCl₃): δ = 3.27 (t, *J* = 11.5 Hz, 2H, CH₂), 3.87 (s, 3H, OCH₃), 4.05 (t, *J* = 11.5 Hz, 2H, CH₂), 6.33 (d, *J* = 6.0 Hz, 1H, CH_{th}), 6.91 (t, *J* = 8.0 Hz, 1 arom. H), 7.22 (t, *J* = 10.4 Hz, 2 arom. H), 7.37 (d, *J* = 10.4 Hz, 1 arom. H), 7.66 (d, *J* = 5.7 Hz, 1H, CH_{th}); ¹³C NMR (125.76 MHz, CDCl₃): δ = 27.74, 51.77, 53.53, 108.66, 109.33, 120.77, 121.23, 125.25, 127.56, 131.58, 136.47, 144.45, 157.42, 164.37.

Anal. Calcd for C₁₄H₁₃NO₂S (259.32): C 64.84, H 5.05, N 5.40; found C 64.81, H 5.12, N 5.44.

General procedure for preparation of *N,N*-disubstituted 2-amino-thiophene-5-*N',N'*-dimethylmethiniminium perchlorates (**12**)

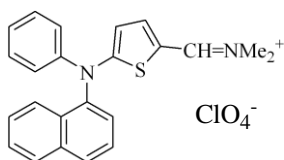
To a mixture of a *N,N*-disubstituted 2-aminothiophene (**7**, 0.01 mol) or a corresponding *N,N*-disubstituted 2-aminothiophene-5-carboxylic acid (**8**, 0.01 mol) in DMF (25 mL) POCl₃ (3.0 g, 0.02 mol) was added under stirring and cooling. The resulting mixture was heated at 60 °C for 20 min and mixed after cooling with methanol (25 mL) and perchloric acid (70 %, 3 mL). The product precipitated after adding some diethyl ether was isolated by suction, dried in air, and recrystallised from acetic acid.

The following *N,N*-disubstituted 2-amino-thiophene-5-*N',N'*-dimethylmethiniminium perchlorates **12** were so obtained:

2-Diphenylamino-thiophene-5-dimethylmethiniminium perchlorate (12a),

from 2-diphenylamino-thiophene (**7a**) in a yield of 80 % or from 2-diphenylamino-thiophene-5-carboxylic acid (**8a**) [16] a yield of 70 % and a m.p. of 197 - 198 °C. ¹H NMR (500 MHz, CF₃COOH): δ = 3.32 (s, 3H, NCH₃), 3.50 (s, 3H, NCH₃), 6.48 (d, *J* = 4.8 Hz, 1H, CH_{th}), 7.41 - 7.45 (m, 2 arom H), 7.52 - 7.56 (m, 8 arom. H), 7.94 (d, *J* = 4.8 Hz, 1H, CH_{th}), 8.70 (s, 1H, CH=N); ¹³C NMR (125.76 MHz, CDCl₃): δ = 43.37, 115.31, 117.51, 119.83, 122.09, 129.82, 132.69, 134.18, 148.06, 163.81.

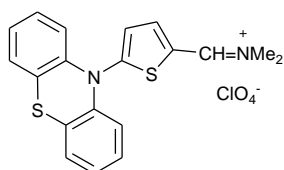
Anal. Calcd for C₁₉H₁₉ClN₂O₄S (406.88): C 56.09, H 4.71, N 6.88; found C 55.97, H 4.75, N 6.69.

5-[(*N*-(1-Naphtyl)-*N*-phenyl]amino-thiophene-2-dimethylmethiniminium perchlorate (12b),

from 2-[(*N*-(1-naphtyl)-*N*-phenyl]amino-thiophene-5-carboxylic acid (**8b**) via the corresponding methyl 2-[(*N*-(1-naphtyl)-phenyl] amino-thiophene-5-carboxylate (**9b**) in a yield of 62 % and a m.p. of 197 °C. ¹H NMR (500 MHz, CF₃COOH): δ = 3.17 (s, 3H, NCH₃), 3.35 (s, 3H, NCH₃), 6.37 (s, br, 1H, CH_{th}), 7.23 (m, 1 arom. H), 7.31 (t, *J* = 7.6

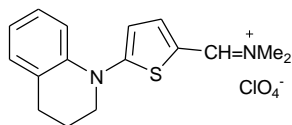
Hz, 1 arom. H), 7.40 - 7.46 (m, 6 arom. H), 7.60 (d, *J* = 4.3 Hz, 1H, CH_{th}), 7.82 (s, 1H, CH=N), 7.84 - 7.88 (m, 4 arom. H).

Anal. Calcd for C₂₃H₂₁ClN₂O₄S (456.94): C 60.46, H 4.63, N 6.13; found C 60.73, H 4.49, N 6.27.

2-Phenothiazin-10-yl-thiophene-2-dimethylmethiniminium perchlorate (12e),

from 10-(2-thienyl)-10*H*-phenothiazine (**7e**) [16] in a yield of 80 % and a m.p. of 198 °C. ¹H NMR (500 MHz, CF₃COOH): δ = 2.92 (s, 3H, NCH₃), 3.33 (s, 3H, NCH₃), 5.68 (d, *J* = 11.0 Hz, 1H, CH_{th}), 7.22 (t, 2 arom. H), 7.30 (t, 2 arom. H), 7.45 (dq, 4 arom. H), 7.66 (s, 1H, CH=N), 8.10 (d, *J* = 4.0 Hz, 1H, CH_{th}).

Anal. Calcd for C₁₉H₁₇ClN₂O₄S₂ (436.93): C 52.23, H 3.92, N 6.41; found C 52.44, H 3.96, N 6.53.

2-(3,4-Dihydro-2*H*-quinolin-1-yl)-thiophene-5-dimethyl-methiniminium perchlorate (12f),

from 2-(3,4-dihydro-2*H*-quinolin-1-yl)-thiophene-5-carboxylic acid (**8f**), prepared from the corresponding methyl 2-(3,4-dihydro-2*H*-quinolin-1-yl)-thiophene-5-carboxylate^[13a] (**9g**) in a yield of 85 % and a m.p. of 204 - 211 °C. ¹H NMR (500 MHz, CF₃COOH): δ = 2.01 (q, *J* = 6.3 Hz, 2H, CH₂), 2.67 (t, *J* = 6.2 Hz, 2H, CH₂), 3.34 (s, 3H, NCH₃) 3.38 (s, 3H, NCH₃), 3.76 (t, *J* = 6.4 Hz, 2H, CH₂), 6.80 (d, *J* = 5.0 Hz, 1H, CH_{th}), 7.08 (m, 1 arom. H), 7.16 (m, 2 arom. H), 7.46, d, *J* = 8.0 Hz, 1 arom. H), 7.66, d, *J* = 5.1 HZ, 1H, CH_{th}), 7.88 (s, 1H, CH=N).

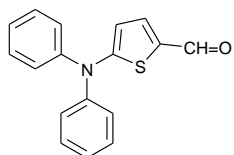
Anal. Calcd for C₁₆H₁₉ClN₂O₄S (370.85) C 51.82, H 5.16, N 7.55; found C 51.65, H 5.22, N 7.50.

General procedure for preparation of *N,N*-disubstituted methyl 2-amino-5-formyl-thiophene-5-carboxylates (**13**) or 2-amino-3-formyl-thiophene-5-carboxylates (**17**)

To a solution of a *N,N*-disubstituted 2-aminothiophene **7**, a *N,N*-disubstituted 2-aminothiophene-5-carboxylic acid **8**, or a *N,N*-disubstituted methyl 2-aminothiophene-5-carboxylate **9** (0.01 mol, each) in DMF (25 mL) POCl₃ (3.0 g, 0.02 mol) was added under stirring and cooling. The resulting mixture was left standing at room temperature or heated at 60 °C for 20 min and mixed after cooling with methanol (25 mL) and water (50 mL). After addition of aqueous sodium hydroxide until weak basic reaction the products precipitated after some standing at room temperature and were isolated by suction, dried in air and recrystallised from cyclohexane or toluene.

The following *N,N*-disubstituted 2-amino-thiophene-5-carbaldehydes **13** and 2-amino-thiophene-3-carbaldehydes **17** were so obtained:

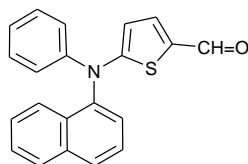
2-Diphenylamino-thiophene-5-carbaldehyde (**13a**),



from 2-diphenylaminothiophene (**7a**) [16] in a yield of 85 % or from 2-diphenylamino-thiophene-5-carboxylic acid (**8a**) [16] in a yield of 76% with a m.p. 92 °C. ¹H NMR (500 MHz, CDCl₃): δ = 6.38 (d, *J* = 4.4 Hz, 1H, CH_{th}), 7.22 (t, *J* = 7.3 Hz, 2 arom. H), 7.27 – 7.28 (m, 4 arom. H), 7.34 – 7.37 (m, 4 arom. H), 7.46 (d, *J* = 4.4 Hz, 1H, CH_{th}), 9.56 (s, 1H, CH=O); ¹³C NMR (125.76 MHz, CF₃COOH): δ = 112.40, 125.48, 126.36, 129.62, 129.84, 139.22, 145.75, 165.25, 180.73.

Anal. Calcd for C₁₇H₁₃NOS (279.36): C 73.09, H 4.69, N 5.01; found C 73.16, H 4.60, N 4.93.

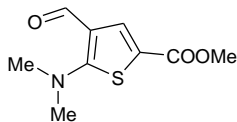
2-[(*N*-(1-Naphtyl)-*N*-phenyl)amino]-thiophene-5-carbaldehyde (**13b**),



from 2-[(*N*-(1-naphtyl)-*N*-phenyl)amino]-thiophene-5-carboxylic acid (**8b**) via the corresponding methyl 2-[(*N*-(1-naphtyl)-*N*-phenyl)amino]-thiophene-5-carboxylate (**9b**) in a yield of 62 % as pale yellow oil. ¹H NMR (500 MHz, CDCl₃): δ = 6.28 (s, br, 1H, CH_{th}), 7.17 – 7.18 (m, 1 arom. H), 7.32 – 7.38 (m, 4 arom. H), 7.46 – 7.54 (m, 5 arom. H), 7.90 – 7.94 (m, 2 arom. H., 1 heterom. H), 9.39 (s, br, 1H, CHO).

Anal. Calcd for C₂₁H₁₅NOS (329.61): C 76.57, H 4.59, N 4.25, O 4.86, S 9.73; found C 76.76, H 4.64, N 4.51.

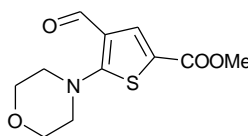
Methyl 2-dimethylamino-3-formyl-thiophene-5-carboxylate (**17a**),



from methyl 2-dimethylamino-thiophene-5-carboxylate^{13a} (**9h**) in a yield of 60 % and a m.p. of 110 °C. ¹H NMR (500 MHz, CDCl₃): δ = 3.42 (s, 3H, OCH₃) 3.51 (s, 3H, NCH₃), 3.90 (s, 3H, NCH₃), 7.97 (s, 1H, CH_{th}), 8.87 (s, 1H, CHO).

Anal. Calcd for C₉H₁₁NO₃S (213.05): C 50.69, H 5.20, N 6.57; found C 50.73, H 5.22, N 6.49.

Methyl 2-(4-morpholinyl)-3-formyl-thiophene-3-carboxylate (**17b**),



from methyl 2-(4-morpholinyl)-thiophene-5-carboxylate^{13a} (**9j**) in a yield of 72 % and a m.p. of 118 °C. ¹H NMR (500 MHz, CDCl₃): δ = 3.68 (t,

$J = 4.8$ Hz, 4H, CH₂), 3.90 (s, 3H, OCH₃), 4.08 (t, $J = 4.8$ Hz, 4H, CH₂), 7.99 (s, 1H, CH_{th}), 9.32 (s, 1H, CHO); ¹³C NMR (125.76 MHz, CDCl₃): $\delta = 45.94, 51.99, 115.30, 129.82, 137.41, 162.35, 169.72, 182.09$.

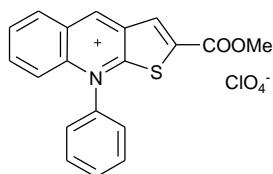
Anal. Calcd for C₁₁H₁₃NO₄S (255.29): C 51.75, H 5.13, N 5.49; found C 51.63, H 5.22, N 5.58.

General procedure for preparation of *N*-substituted 2-methoxycarbonyl-thieno[2,3-*b*]quinolinium perchlorates (18)

To a solution of a *N*-substituted methyl *N*-aryl-2-aminothiophene-5-carboxylate (**9**, 0.01 mol) in DMF (25 mL) POCl₃ (3.0 g, 0.02 mol) was added under stirring and cooling. The resulting mixture was heated at 60 °C for 20 min and mixed after cooling with methanol (25 mL) and perchloric acid (70 %, 3 mL). The product precipitated after addition of some diethyl ether was isolated by suction, dried at air, and recrystallised from acetic acid.

The following *N*-substituted 2-methoxycarbonyl-thieno[2,3-*b*]quinolinium perchlorates (**18**) were so obtained:

2-Methoxycarbonyl-9-phenyl-thieno[2,3-*b*]quinolinium perchlorate (18a),

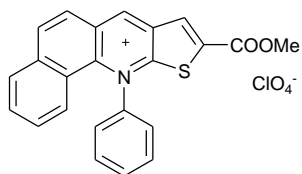


from methyl 2-(*N,N*-diphenylamino)-thiophene-5-carboxylate^{13a} (**9a**) in a yield of 90 % and a m.p. of 293 – 295 °C. ¹H NMR (500 MHz, DMSO-*D*₆): $\delta = 3.96$ (s, 3H, CH₃O), 7.63 (d, $J = 12.0$ Hz, 1 arom H), 7.95 – 7.98 (m, 5 arom. H), 8.10 (m, 1 arom. H), 8.27 (m, 1 arom. H), 8.76 (s, 1H, CH_{th}), 8.78 (s, 1 arom H), 10.05 (s, 1 arom. H).

MS (ESI, 70 eV): $m/z = 320.0$; calcd for C₁₉H₁₄NO₂S⁺ = 320.38; ¹³C NMR (125.76 MHz, CF₃COOH): $\delta = 53.13, 112.01, 124.66, 126.44, 128.48, 129.67, 130.71, 131.09, 132.36, 132.38, 134.34, 137.27, 137.37, 140.26, 144.65, 161.73, 162.53$.

Anal. Calcd for C₁₉H₁₄ClNO₆S (419.84): C 54.36, H 3.36, N 3.34; found C 54.55, H 3.28, N 3.46.

9-Methoxycarbonyl-11-phenyl-benzo[*h*]thieno[2,3-*b*]quinolinium perchlorate (18b),

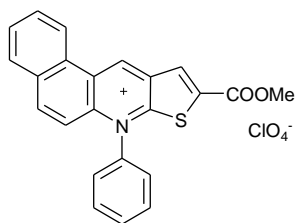


from methyl 2-[*N*-phenyl-*N*-(1-naphthyl)]-amino-thiophene-5-carboxylate (**9b**) in a yield of 88 % and a m.p. of 300 - 301 °C. ¹H NMR (500 MHz, DMSO-*D*₆): $\delta = 3.90$ (s, 3H, CH₃O), 7.18 (d, $J = 10.8$ Hz, 1 arom. H), 7.47 – 7.52 (m, 2 arom. H), 7.76 (t, $J = 10.0$ Hz, 1 arom. H), 8.01 (t, $J = 10.4$ Hz, 1 arom. H), 8.10 – 8.23 (m, 4

arom. H), 8.33 (d, $J = 10.8$ Hz, 1 arom. H), 8.56 (d, $J = 10.8$ Hz, 1 arom. H), 8.81 (s, 1 arom. H), 8.86 (dd, $J = 10.8$ and 2.2 Hz, 2 arom. H), 10.18 (s, 1 arom. H); ¹³C NMR (125.76 MHz, CF₃COOH): $\delta = 53.12, 117.19, 119.20, 124.89, 124.30, 125.49, 126.42, 127.56, 128.58, 128.69, 128.86, 129.67, 130.94, 132.56, 133.05, 133.29, 134.46, 134.66, 137.59, 140.57, 145.11, 162.44, 162.78$.

MS (ESI, 70 eV): $m/z = 370.0$; calcd for C₂₃H₁₆NO₂S⁺ = 370.44.

Anal. Calcd for C₂₃H₁₆ClNO₆S (469.89): C 58.79, H 3.43, N 2.98; found C 58.55, H 3.13, N 3.10.

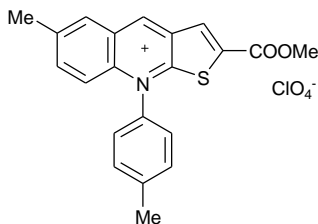
9-Methoxycarbonyl-7-phenyl-benzo[f]thieno[2,3-b]quinolinium perchlorate (18c),

from methyl 2-[*N*-phenyl-*N*-(2-naphthyl)-amino-thiophene-5-carboxylate (**9c**) in a yield of 92 % and a m.p. of 330 - 332 °C. ¹H NMR (500 MHz, DMSO-D₆): δ = 3.98 (s, 3H, CH₃O), 7.54 (d, *J* = 12.4 Hz, 1 arom. H), 7.89 – 8.00 (m, 5 arom H), 8.03 (t, 1 arom H), 8.15 (t, 1 arom. H), 8.35 (d, *J* = 10.4 Hz, 1 arom. H), 8.65 (d, *J* = 12.8 Hz, 1 arom. H), 8.69 (s, 1 arom. H), 9.20 (d, *J* =

11.2 Hz, 1 arom. H), 10.87 (s, 1 arom H); ¹³C NMR (125.76 MHz, CF₃COOH): δ = 53.13, 113.89, 122.00, 124.74, 125.42, 127.68, 129.26, 129.44, 130.00, 130.08, 130.62, 131.14, 132.13, 132.39, 134.36, 137.87, 140.82, 141.93, 158.40, 162.83.

MS (ESI, 70 eV): *m/z* = 370.0; calcd for C₂₃H₁₆NO₂S⁺ = 370.44.

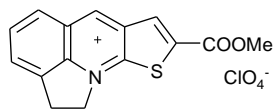
Anal. Calcd for C₂₃H₁₆ClNO₆S (469.89): C 58.79, H 3.43, N 2.98; found C 59.02, H 3.25, N 3.07.

2-Methoxycarbonyl-6-methyl-9-(4-tolyl)-thieno[2,3-b]quinolinium perchlorate (18d),

from methyl 2-(*N,N*-(4-tolyl)]-aminothiophene-5-carboxylate (**9d**) in a yield of 60 % and a m.p. of 313 - 315 °C. ¹H NMR (500 MHz, DMSO-D₆): δ = 2.52 (s, 3H, CH₃), 2.65 (s, 3H, CH₃), 3.95 (s, 3H, CH₃O), 7.14 (d, *J* = 11.6 Hz, 1 arom. H) 7.72 – 7.80 (m, 4 arom H), 7.56 (dd, *J* = 12.0 and 2.0 Hz, 1 arom. H), 8.51 (s, 1 arom. H), 8.71 (s, 1 arom. H), 9.91 (s, 1 arom. H).

MS (ESI, 70 eV): *m/z* = 348.1; calcd for C₂₁H₁₈NO₂S⁺ = 348.44.

Anal. Calcd for C₂₁H₁₈ClNO₆S (447.89): C 56.31, H 4.05, N 3.13 found C 56.18, H 4.25, N 3.00.

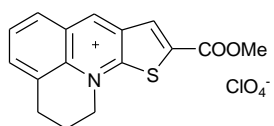
1,2-Dihydro-7-methoxycarbonyl-cyclopenta[1,2-*i,j*]quinolinium perchlorate (18e),

from methyl 2-(2,3-dihydro-indol-1-yl)-thiophene-5-carboxylate (**9e**) in a yield of 60 % and a m.p. of 250 - 251 °C. ¹H NMR (500 MHz, DMSO-D₆): δ = 3.97 (t, *J* = 9.2 Hz, 2H, CH₂), 4.03 (s, H, OCH₃), 5.36 (t, *J* = 9.6 Hz, 2H, CH₂), 7.99 (t, *J* = 10.6 Hz, 1 arom H), 8.15 (d, *J* =

9.6 Hz, 1 arom. H), 8.37 (d, *J* = 11.2 Hz, 1 arom. H), 8.71 (s, 1 arom. H), 9.74 (s, 1 arom. H).

MS (ESI, 70 eV): *m/z* = 269.9; calcd for C₁₅H₁₂NO₂S⁺ = 270.33; ¹³C NMR (125.76 MHz, CF₃COOH): δ = .

Anal. Calcd for C₁₅H₁₂ClNO₆S (369.8): C 48.72, H 3.27, N 3.79; found C 48.48, H 3.33, N 3.57.

2,3-Dihydro-1*H*-7-methoxycarbonyl-benzo[1,2-*i,j*]quinolinium perchlorate (18f),

from methyl 2-(3,4-dihydro-2*H*-quinolin-1-yl)-thiophene-5-carboxylate^{13a} (**9f**) in a yield of 74 % and a m.p. of 278 - 279 °C. ¹H NMR (500 MHz, CF₃COOH): δ = 3.03 (q, 2H, CH₂), 3.82 (t, *J* = 8.0 Hz, 2H, CH₂), 4.53 (s, 3H, OCH₃), 5.35 (t, *J* = 8.0 Hz, 2H, CH₂), 8.29

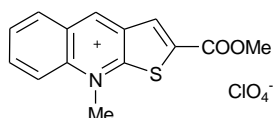
(t, *J* = 10.8 Hz, 1 arom. H), 8.45 (d, *J* = 9.6 Hz, 1 arom. H), 8.65 (t, *J* = 10.8 Hz, 1 arom. H), 8.92 (s, 1 arom. H), 9.82 (s, 1 arom. H); ¹³C NMR (125.76 MHz, CF₃COOH): δ = 19.14, 24.86, 53.24,

54.65, 126.80, 127.57, 128.08, 128.95, 130.05, 132.14, 133.21, 134.73, 135.54, 143.33, 157.96, 162.63.

MS (ESI, 70 eV): $m/z = 284.0$; calcd for $C_{16}H_{14}NO_2S^+ = 284.35$.

Anal. Calcd for $C_{16}H_{14}ClNO_6S$ (383.80): C 50.07, H 3.68, N 3.65; found C 49.88, H 3.58, N 3.46.

2-Methoxycarbonyl-9-methyl-thieno[2,3-b]quinolinium perchlorate (**18h**),

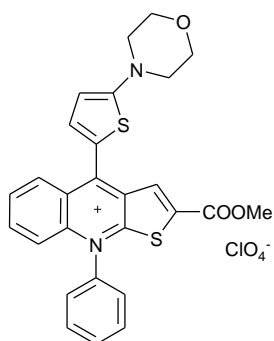


from methyl *N*-methyl-*N*-phenyl-2-amino-thiophene-5-carboxylate^{13a} (**9h**) in a yield of 70 % and a m.p. of 265 – 268 °C. ¹H NMR (500 MHz, DMSO-*D*₆): $\delta = 4.53$ (s, 3H, NCH₃), 5.17 (s, 3H, OCH₃), 8.42 (t, $J = 9.6$ Hz, 1 arom. H), 8.47 – 8.85 (m, 3 arom H), 8.91 (s, 1 arom. H), 9.90 (s, 1 arom H); ¹³C NMR (125.76 MHz, CF₃COOH): $\delta = 41.50, 53.25, 115.50, 126.45, 128.40, 130.11, 131.30, 132.50, 133.12, 137.52, 130.28, 143.84, 162.44$.

MS (ESI, 70 eV): $m/z = 257.9$; Calcd for $C_{14}H_{12}NO_2S^+ = 258.32$.

Anal. Calcd for $C_{14}H_{12}ClNO_6S$ (357.77): C 47.00, H 3.38, N 3.92; found C 47.22, H 3.30, Cl 10.12, N 4.02, S 9.16.

2-Methoxycarbonyl-4-[5-(*N*-morpholinyl)-2-thienyl]-9-phenyl-thieno[2,3-b]quinolinium perchlorate (**19**)



A mixture of 2-methoxycarbonyl-9-phenyl-thieno[2,3-b]quinolinium perchlorate (**18b**, 0.01 mol) and 2-morpholinothiophene-5-carboxylic acid **8j** (0.02 mol) in acetic anhydride (20 mL) was refluxed for 4 h. After cooling the reaction mixture and adding some diethyl ether the product formed crystals and it was isolated by suction in a yield of 42 % and a m.p. of 234 – 237 °C. ¹H NMR (500 MHz, DMSO-*D*₆): 3.68 (t, $J = 4.8$ Hz, 4H, CH₂), 3.84 (t, $J = 4.8$ Hz, 4H, CH₂), 3.88 (s, 3H, OCH₃), 7.02 (d, $J = 4.9$ Hz, 1H, CH_{th}), 7.27 (d, $J = 8.7$ Hz, 1 arom. H), 7.84 – 7.90 (m, 5 arom. H), 8.00 (dt, 2 arom. H), 8.11 (d, $J = 4.8$ Hz, 1H CH_{th}), 8.57 (s, 1H, CH_{th}), 8.67 (d, $J = 8.6$ Hz, 1 arom. H).

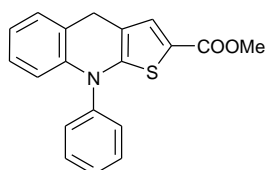
Anal. Calcd for $C_{27}H_{23}ClN_2O_7S_2$ (587.06): C 55.24, H 3.95, N 4.77; found C 55.67, H 4.12, N 4.69.

General procedure for preparation of methyl 4,9-dihydro-thieno[2,3-b]quinoline-carboxylates (**20**)

To a mixture of a thieno[2,3-b]quinolinium salt **18** (0.01 mol) in methanol (25 mL) or DMF (25 mL) sodium borotetrahydride (0.8 g, 0.02 mol) was added under stirring at room temperature. After finishing the gas evolution the reaction mixture was diluted with water (100 mL) and the precipitate formed isolated by suction.

The following 4,9-dihydro-thieno[2,3-b]quinoline-carboxylates **20** were so prepared.

2-Methoxycarbonyl-9-phenyl-4,9-dihydrothieno[2,3-b]quinoline (**20a**),

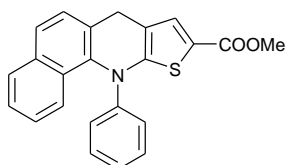


from 2-methoxycarbonyl-9-phenyl-thieno[2,3-b]quinolinium perchlorate **18a** in a yield of 68 % and a m.p. of 233 °C. ¹H NMR (500 MHz,

CDCl₃): δ = 3.75 (s, 3H, OCH₃), 4.23 (s, 2H, CH₂), 7.50 (dd, J = 8.3, 1.0 Hz, 1 arom. H), 6.26 (d, J = 8.3 Hz, 1 arom. H), 6.90 (t, 1 arom. H), 6.97 (t, 1 arom. H), 7.38 – 7.39 (m, 2 arom. H) 7.46 (s, 1H, CH_{th}), 7.48 – 7.51 (m, 1 arom. H), 7.56 – 7.59 (m, 2 arom. H); ¹³C NMR (125.76 MHz, CCl₄): δ = 27.40, 50.06, 112.10, 118.73, 122.05, 125.95, 126.30, 125.46, 126.30, 127.21, 127.42, 128.80, 128.89, 132.62, 151.25, 160.45.

Anal. Calcd for C₁₉H₁₅NO₂S (321.39): C 71.00, H 4.70, N 4.36; found C 71.18, H 4.72, N 4.61.

9-Methoxycarbonyl-11-phenyl-4,9-dihydro-benzo[h]thieno [2,3-b]quinoline (20b),

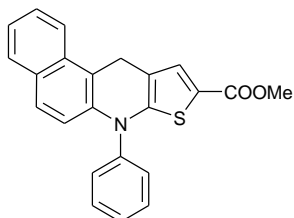


from 9-methoxycarbonyl-11-phenyl-benzo[h]thieno[2,3-b]quinolinium perchlorate **18b** in a yield of 75 % and a m.p. of 186 – 192 °C. ¹H NMR (500 MHz, CDCl₃): δ = 3.69 (s, 3H, OCH₃), 4.36 (s, 2H, CH₂), 6.07 (d, J = 9.1 Hz, 1 arom. H), 6.86 - 6.91 (m, 2 arom. H), 7.18 (d, J = 7.9 Hz, 1 arom. H), 7.42 – 7.43 (m, 1 arom. H), 7.50 –

7.54 (m, 2 arom. H), 7.58 – 7.64 (m, 2 arom. H), 7.77 (d, J = 8.5 Hz, 1 arom. H), 8.01 (d, J = 8.0 Hz, 1 arom. H), 8.16 (d, J = 8.3 Hz, 1 arom. H); ¹³C NMR (125.76 MHz, CCl₄): δ = 27.42, 50.08, 112.10, 113.52, 117.33, 118.74, 121.14, 122.30, 123.39, 126.59, 127.78, 128.81, 128.91, 129.77, 132.62, 134.44, 136.78, 139.78, 151.26, 160.45.

Anal. Calcd for C₂₃H₁₇NO₂S (371.45): C 74.37, H 4.61, N 3.77; found C 74.74, H 4.68, N 3.72.

9-Methoxycarbonyl-7-phenyl-4,9-dihydrobenzo[f]thieno[2,3-b]quinoline (20c),

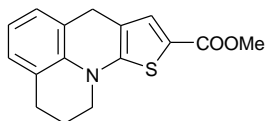


from 9-methoxycarbonyl-7-phenyl-benzo[f]thieno[2,3-b]quinolinium perchlorate **18c** in a yield of 84 % and a m.p. of 265 – 272 °C. ¹H NMR (500 MHz, CDCl₃): δ = 3.78 (s, 3H, OCH₃), 4.57 (s, 2H, CH₂), 6.62 (d, J = 9.1 Hz, 1 arom. H), 7.23 – 7.43 (m 3 arom. H), 7.50 – 7.54 (m, 2 arom. H), 7.56 – 7.63 (m, 4 arom. H), 7.74 (d, J = 8.0 Hz, 1 arom. H), 7.812 (d, J = 8.5 Hz, 1 arom. H); ¹³C NMR (125.76 MHz, CD₂Cl₂): δ = 25.91, 51.92, 112.05, 114.56, 115.24, 116.24, 118.17,

122.55, 124.12, 124.53, 127.93, 128.48, 129.94, 130.04, 131.25, 137.51, 141.16, 142.04, 153.20, 163.15.

Anal. Calcd for C₂₃H₁₇NO₂S (371.45): C 74.37, H 4.61, N 3.77; found C 74.31, H 4.28, N 3.58.

9-Methoxycarbonyl-2,3-dihydro-1*H*,7*H*-pyrido[3,2,1-*ij*]thieno[2,3-*b*]quinoline (20f),

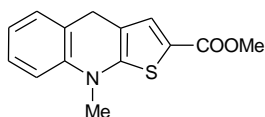


from 2,3-dihydro-1*H*-7-methoxycarbonyl-benzo[1,2-*ij*]quinolinium perchlorate **18f** in a yield of 50 % and a m.p. of 138 – 141 °C. ¹H NMR (500 MHz, CDCl₃): δ = 2.12 (q, 2H, CH₂), 2.81 (t, J = 6.2 Hz, 2H, CH₂), 3.58 (t, J = 5.8 Hz, 2H, CH₂), 3.82 (s, 3H, OCH₃), 4.05 (s, 2H, CH₂),

6.81 (t, J = 7.4 Hz, 2 arom. H), 6.90 (t, J = 6.4 Hz, 1 arom. H), 7.45 (s, 1H, CH_{th}).

Anal. Calcd for C₁₆H₁₅NO₂S (285.36): C 67.34, H 5.30, N 4.91; found C 67.48, H 5.12, N 5.08.

2-Methoxycarbonyl-9-methyl-4,9-dihydro-thieno[2,3-*b*]quinoline (20h),



from 2-methoxycarbonyl-9-methyl-thieno[2,3-*b*]quinolinium perchlorate **18h** in a yield of 70 % and a m.p. of 115- 120 °C. ¹H NMR (500 MHz, CDCl₃): δ = 3.33 (s, 3H, NCH₃), 3.82 (s, 3H, OCH₃), 4.05 (s, 2H, CH₂), 6.81 (d, J = 8.1 Hz, 1 arom. H), 6.92 (m, 1 arom. H), 7.08 (dd, J = 7.4

Hz, 1.0 Hz, 1 arom. H), 7.16 (t, $J = 8.2$ Hz, 1 arom, H), 7.43 (s, 1H CH_{th}); ¹³C NMR (125.76 MHz, CD₂Cl₂): $\delta = 28.50, 36.80, 51.84, 112.16, 114.77, 120.34, 127.50, 129.84, 131.40, 133.27, 134.50, 140.26, 153.34, 162.28$.

Anal. Calcd for C₁₄H₁₃NO₂S (259.32): C 64.84, H 5.05, N 5.40; found C 64.48, H 5.01, N 5.67.

Acknowledgements

The author thanks Prof. Dr. Karl Leo, Director of the Institut für Angewandte Photophysik, TU Dresden, for his interest and generous technical support.

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