A FACILE GENERAL SYNTHESIS OF 9-POSITION FUNCTIONALISED HETERONIUMANTHRACENE SALTS

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Abstract — Heteroniumanthracenes react selectively as the cations (**1a**) or as the corresponding carbinol bases (**9b,c**) with benzotriazole to give the corresponding 9*H*-(benzotriazol-1-yl)heterocycles (**10a-c**). As novel heterocyclic anion precursors, (**10a-c**) undergo smooth lithiations at the positions α to the benzotriazol-1-yl function, corresponding to the 9-position of the heterocycles (**1a**) and (**9b,c**). Subsequent trapping of the benzotriazolyl stabilised carbanions (**11a-c**) with various long chain alkyl halides forms intermediates of type (**12b**) which are converted by treatment with mineral acid, into the corresponding 9-functionalised heteroniumanthracene salts (**13-16**) (or their free bases (**17-19**)) in good to excellent yields.

INTRODUCTION

Readily available pyridinium, quinolinium or acridinium heteroaromatic cations, together with their oxygen or sulfur derivatives, play important roles in synthetic, physical-organic, and pharmaceutical chemistry,[1,2] and have found diverse high-tech applications.[3,4] As π-deficient electrophilic aromatic systems, heteroaromatic cations react with nucleophiles at the positions *alpha* or *gamma* to the heteroatom.[5] Formal loss of hydride can afford the substituted heterocyclic cations, but the synthetic potential of this method is limited to *Grignard* reagents,[6-8] activated aromatic systems,[9,10] cyanide anions

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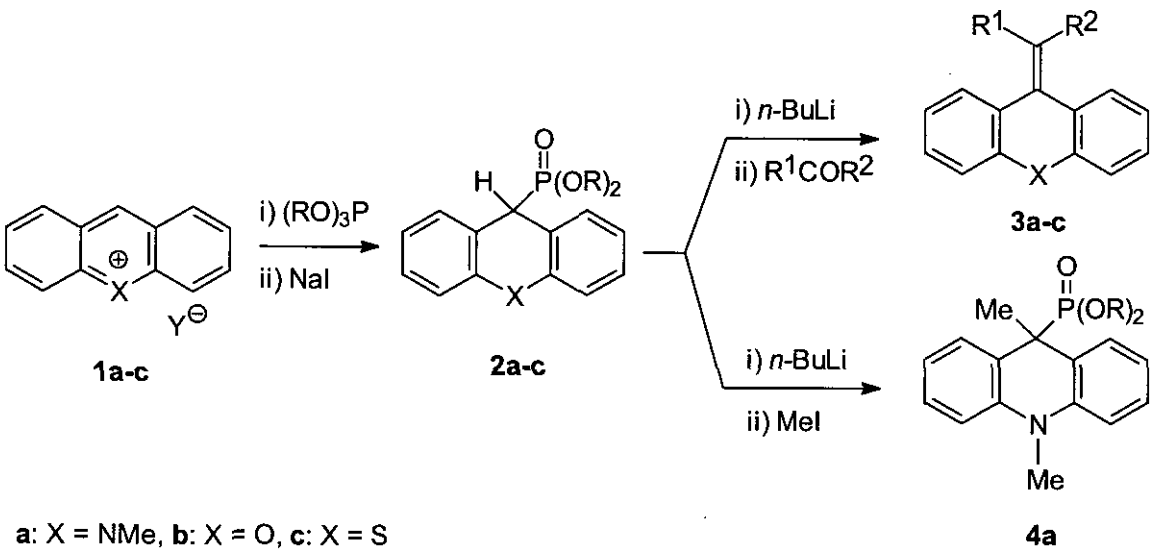
(*Reissert* compounds),[11,12] and a few others.[13] For example, this route has not been used for the synthesis of heteroaromatic cations containing long chain alkyl or ω-functionalised-alkyl substituents, compounds of considerable interest,[14] but which are relatively inaccessible. However, the preparation of such compounds, starting from alkyl halides, should be possible by using suitable heteroaromatic carbanion systems.[15]

Reactivity reversal in heteroaromatic cations ('Umpolung') has been achieved for some π-deficient heteroaromatic compounds by the application of appropriate *Wittig-Horner* reagents.[16] On treatment with a strong base, the phosphonates (**2**) (X: **a** = *N*-alkyl, **b** = O, and **c** = S) can be deprotonated to form antiaromatic eight π-systems *in situ*.[17] The addition of arylaldehydes or diaryl ketones leads to intramolecular redox reactions and consequent formation of exomethylene-containing heterocycles (**3**) in good yields (Scheme 1). However, the phosphonate carbanions derived from **2** do not react with enolisable carbonyl compounds, *e.g.* cycloalkanones and aliphatic aldehydes, to give compounds (**3**) (R^1 = R^2 = alkyl or R^1 = H, R^2 = alkyl).[17]

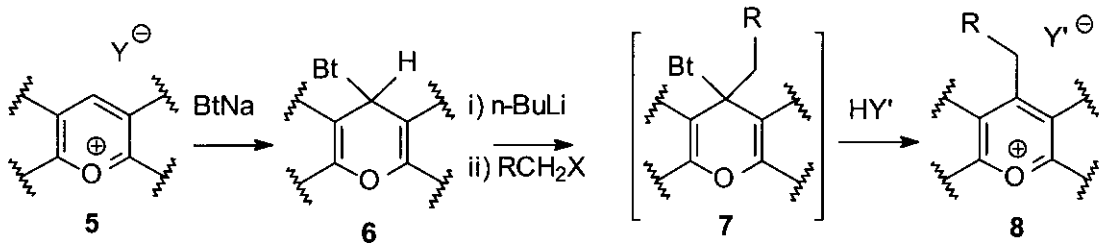


Scheme 1

Considerable effort has been devoted to applying this route to synthesise 4-(long chain alkyl) substituted derivatives of pyridines[18] and quinolines[19] by electrophilic substitution using alkyl halides, but the final elimination of the phosphonate group is difficult and gives only moderate yields. Although the carbanion of phosphonate (**2a**) (X = NMe) was alkylated with methyl iodide to give 9,10-dimethyl-9,10-dihydroacridine-9-phosphonate (**4a**), hydrolysis to remove the phosphonate group was not reported.[20] No

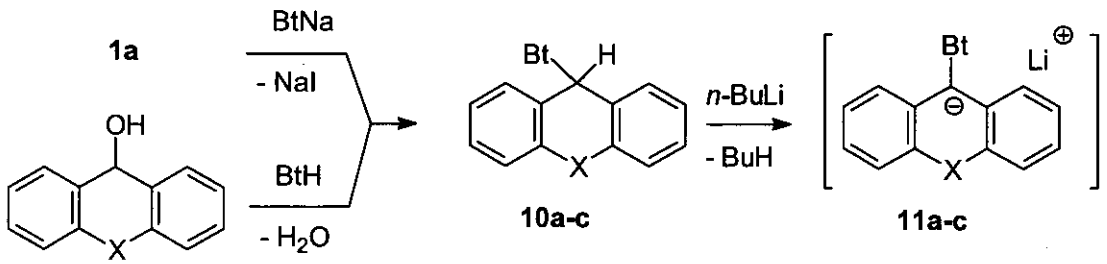
other general method is available which enables overall electrophilic substitution *gamma* to the heteroatom in such heteroaromatic system.

Recently we showed that various *O*-heteronium cations (*e.g.* bridged pyrylium, benzo[*b*]pyrylium and xanthylium salts (**5**) react with benzotriazole to give addition products of type (**6**) (Scheme 2).[21] As novel anion precursors, **6** undergo smooth lithiations at the position α to the benzotriazol-1-yl function, *i.e.* at the *gamma* position of the *O*-heterocycle. Subsequent trapping with various electrophiles then forms intermediates (**7**). Treatment of **7** with a mineral acid, reforms the new pyrylium, benzo[*b*]pyrylium and xanthylium salts (**8**), functionalised in the *gamma* position, in good to excellent yields by simple recrystallisation from the reaction mixture.



Scheme 2

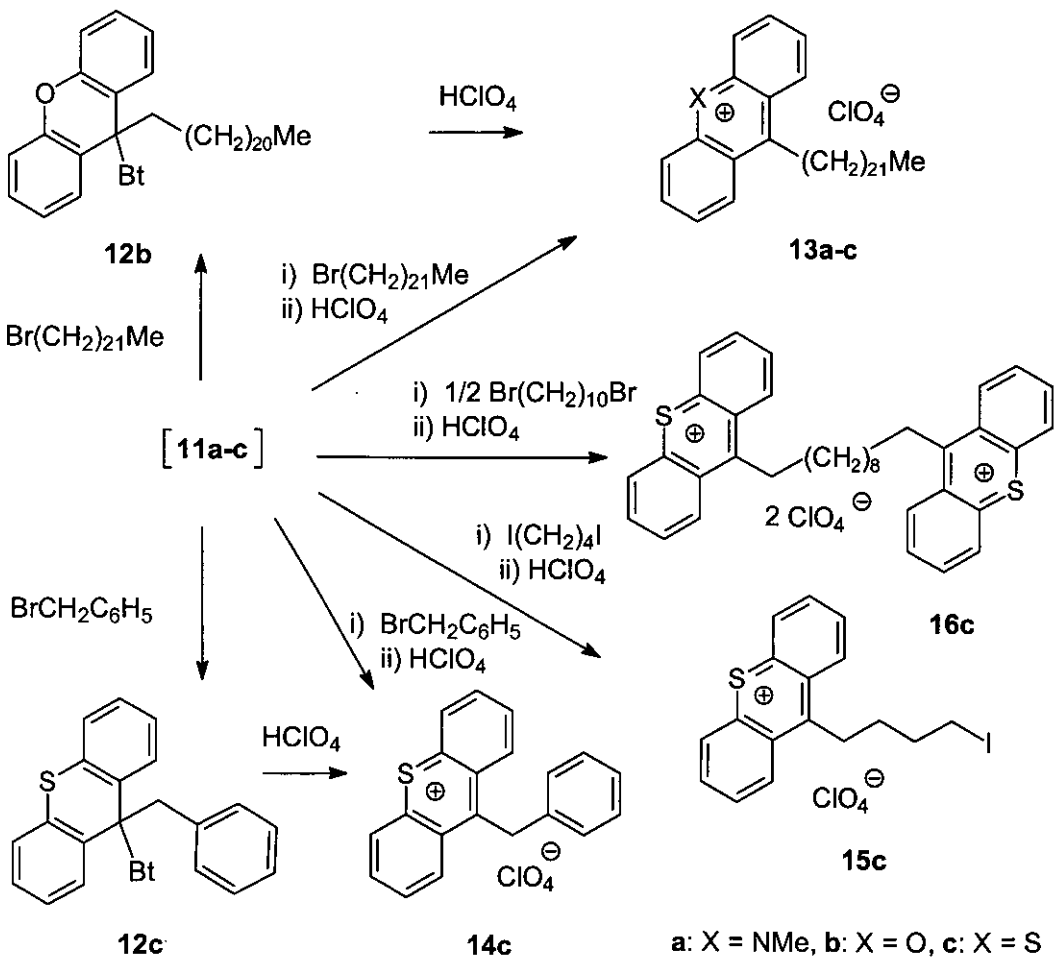
Benzotriazole has been applied extensively as a useful synthetic auxiliary.[22,23] A chemical chameleon, benzotriazole can act initially as a nucleophile, further as an anion stabilising group, and finally as a good leaving group. Analogously to intermediate (**7**), it was expected that benzotriazolyl addition products corresponding to the heteroaromatic cations (**1a**) or the carbinol bases (**9b,c**) would be versatile intermediates for the synthesis of new heteronium salts functionalised in the 9-position. The aim of the present research is to synthesise new heterocyclic cations with long aliphatic chains, which are not easily available by classical methods. Due to their amphiphilic nature, compounds of this type should lead to new applications, *e.g.* in the areas of *Langmuir-Blodgett* films, and analytical chemistry, as pH sensors and membrane probes.[5] We now report that the readily available *N*-methylacridinium salt (**1a**)[24] indeed undergoes facile nucleophilic addition at 20 °C in the 9 position of the benzotriazolate anion to give **10a**[25] in quantitative yield (Scheme 3), in a similar manner to xanthylium salts of type (**5**).[21] The analogous 9*H*-benzotriazolylxanthene (**10b**) and -thioxanthene derivatives (**10c**) were synthesised[25] by dehydration of the carbinol derivatives, 9*H*-10-oxaanthracen-9-ol (**9b**) and 9*H*-10-thioanthracen-9-ol (**9c**)[26] respectively, in the presence of catalytic amounts of acid. The colorless, crystalline 9*H*-benzotriazolyl heteroniaanthracenes (**10a-c**) were all easily purified by recrystallisation and are stable to neutral and basic conditions, but upon treatment with even weak acids they eliminate benzotriazole to regenerate salts of type (**1**).



a: X = NMe, **b**: X = O, **c**: X = S

Scheme 3

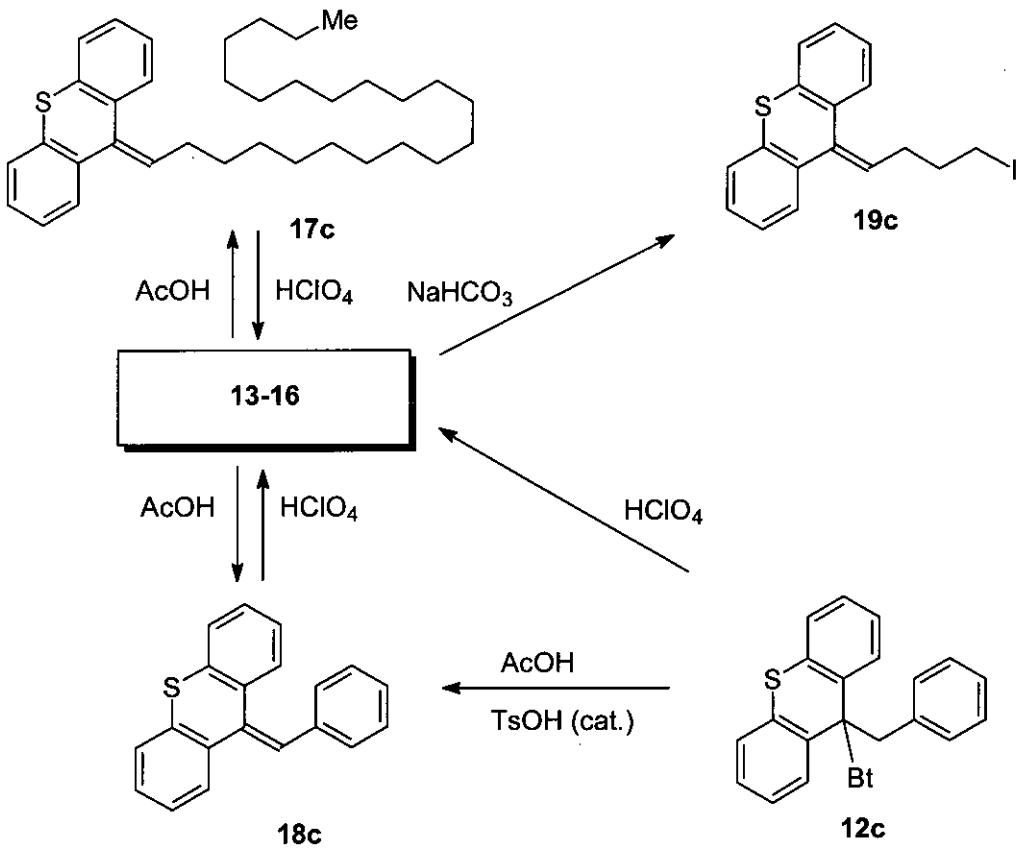
We have already applied this general synthetic method to a variety of medium and long chain derivatised pyrylium, benzo[*b*]pyrylium and xanthylium salts: by using 1-bromodocosane, one of the longest carbon-chain electrophile commercially available, we prepared *O*-heterocycles with a docosanyl moiety at the position *gamma* to the heteroatom.[27]



a: X = NMe, **b**: X = O, **c**: X = S

Scheme 4

We have now extended this technique to acridinium, xanthylium, and thioxanthylium salts. As expected, the derivatives (**10a-c**) were easily deprotonated by a strong base (*n*-BuLi) in dry THF at -78 °C to give lithiated heterocycles (**11a-c**) *in situ*. Intermediates (**11a-c**) undergo regioselective reaction with the electrophile in the 9-position. These additions and the subsequent eliminations of benzotriazole anion are outlined in Scheme 4 and they provide a convenient alternative to the sequence of Scheme 1 for the effective electrophilic substitution of π-deficient heterocycles.



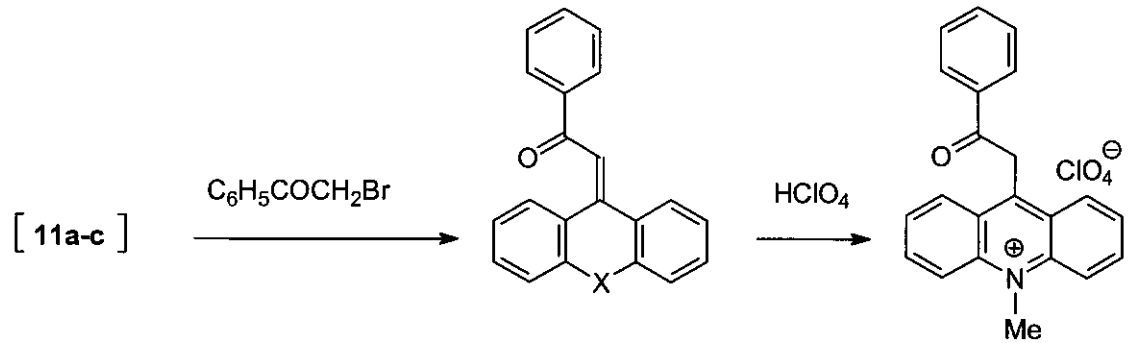
Scheme 5

Depending of the electrophiles used, a variety of compounds (**13-15**) substituted in the 9 position by long chain alkyl, ω-arylalkyl or ω-halogenoalkyl heterocycles, and a symmetrical bifunctional system (**16c**) connected by an aliphatic chain, were isolated in each of the nitrogen, oxygen and sulfur series of anionic starting compounds (**11a-c**) (Scheme 4). Using the lithiated 9*H*-benzotriazolylxanthene (**11b**) or 9*H*-benzotriazolylthioxanthene (**11c**) as a nucleophile and 1-bromodocosane or benzyl bromide as an electrophile, the intermediate 9-substituted 9-benzotriazol-1-yl derivatives (**12b**) and (**12c**), could be

isolated. Treatment of **12b,c** with perchloric acid gives corresponding perchlorates (**13b**) and (**14c**), respectively. Compounds of type (**13-16**) could also be prepared directly, without isolation of intermediates of type (**12**), by addition of perchloric acid to the reaction mixture (Scheme 4).

Protons of the alkyl substituents in position α to the heteroaromatic cations in **13c-16c** are remarkably acidic. By using a weaker acid, such as acetic acid as solvent for recrystallization of salts (**13c**) and (**14c**) the corresponding free bases (**17c**) and (**18c**) were obtained and characterised (Scheme 5). Compound (**19c**) was obtained by treatment of salt (**15c**) with sodium bicarbonate. This tendency to deprotonation is so strong that analytically pure samples of salts (**13a-c**) show in the ^{1}H-NMR spectra significant amounts of the signals of the corresponding free bases, thus addition of CF_3CO_2D was necessary to obtaining spectra of the cations only. Further evidence for easy deprotonation is that samples of salts (**13a-c**) exchanged the protons in α position against deuterium during few days in solution $CDCl_3/CF_3CO_2D$.

The methodology described above has also been successful applied (as described else where[25]) to the synthesis of chalcone derivatives (**20a-c**) and the corresponding salt (**21a**) (Scheme 6). It clearly possesses considerable potential for the synthesis of other functionalised heterocycles.



Scheme 6

In summary, benzotriazole methodology has enabled the preparation of a series of stable, novel heteroniumanthracenes substituted in the 9-position with alkyl, ω-arylalkyl, ω-halogenoalkyl or phenacyl groups, and the corresponding symmetrical bifunctional systems connected by an aliphatic chain. This represents the first generally applicable method for the indirect derivatisation by electrophilic attack of *N*-alkylacridinium, xanthylium and thioxanthylium cations.

EXPERIMENTAL

General. *Melting points* were determined on a Koefler hot stage apparatus and are uncorrected. ^{1}H- and ^{13}C-NMR spectra were recorded at 300 MHz and 75 MHz respectively on a Varian XL 300 spectrometer in $CDCl_3$ or $CDCl_3/CF_3CO_2D$ referenced to Me_4Si for the proton spectra and the solvent for the carbon spectra. Elemental analyses (C, H, N) were performed on a Carlo Erba 1106 elemental analyzer. Tetrahydrofuran (THF) was distilled under nitrogen from sodium-benzophenone immediately before use. All reactions with water-sensitive compounds were carried out under dry nitrogen atmospheres. 9*H*-9-(1*H*-Benzotriazol-1-yl) derivatives (**10a-c**) were prepared according to literature procedure.[25]

Preparation of the 9-Substituted 9-(1*H*-Benzotriazol-1-yl) Derivatives 12b and 12c; General Procedure. To a solution of the 9*H*-(1*H*-benzotriazol-1-yl) derivatives (**10b,c**) (1.25 mmol) in dry THF (30 mL), at -78 °C, was added *n*-BuLi (0.78 mL, 1.25 mmol, 1.6 M in hexane). The solution was stirred at -78 °C for 30 min, before addition of electrophile (1.25 mmol) as a solution in dry THF (10 mL). The reaction mixture was stirred overnight and allowed to warm to rt, before being quenched with saturated aqueous NH_4Cl solution (40 mL), and extracted with ether (2 x 30 mL). The combined organic extracts were washed with brine, water, and dried with $MgSO_4$. The solvent was removed *in vacuo* and the resulting precipitate was recrystallised.

9-(1*H*-Benzotriazol-1-yl)-9-docosanylxanthene (**12b**): Yield 0.58 g (76%), mp 90-91 °C (hexane). ^{1}H-NMR ($CDCl_3$): δ: 8.06 (d, J = 8.2 Hz, 1H), 7.40-7.15 (m, 5H), 7.10-6.70 (m, 5H), 6.52 (d, J = 8.3 Hz, 1H), 3.20-3.00 (m, 2H), 1.60-0.80 (m, 43H). ^{13}C-NMR ($CDCl_3$) δ: 150.3 (2C), 146.9, 132.4, 129.6 (2C), 126.7, 126.7 (4C), 124.0 (2C), 123.7, 121.7, 119.7, 116.4 (2C), 111.5, 63.9, 44.8, 31.9, 29.7 (10C), 29.6 (2C), 29.5, 29.3 (2C), 29.2, 23.5, 22.6, 14.1. *Anal.* Calcd for $C_{41}H_{57}N_3O$: C, 81.00; H, 9.47; N, 6.91. Found: C, 80.93; H, 9.54; N, 6.97.

9-(1*H*-Benzotriazol-1-yl)-9-benzylthioxanthene (**12c**): Yield 0.45 g (90%), mp 190-191 °C (EtOAc). ^{1}H-NMR ($CDCl_3$): δ: 8.09 (d, J = 8.2 Hz, 1H), 7.24-6.86 (m, 11H), 6.58-6.48 (m, 3H), 6.44 (d, J = 8.3 Hz, 2H), 4.45 (s, 2H). ^{13}C-NMR ($CDCl_3$) δ: 147.1, 134.0, 132.7, 132.6, 131.2 (2C), 130.7, 128.1 (2C), 127.7 (2C), 127.3 (2C), 126.9, 126.6, 126.4 (2C), 125.0, 123.9, 119.8, 112.6, 70.1, 49.5. *Anal.* Calcd for $C_{26}H_{19}N_3S$: C, 77.00; H, 4.73; N, 10.36. Found: C, 76.94; H, 4.86; N, 10.42.

Preparation of the Salts (13-16); General Procedure. To a solution of the corresponding 9*H*-(1*H*-benzotriazol-1-yl) derivatives (**10a-c**) (1.25 mmol) in dry THF (30 mL), at -78 °C, was added *n*-BuLi (0.78 mL, 1.25 mmol, 1.6 M in hexane). The solution was stirred at -78 °C for 30 min, before addition the

electrophile (1.25 mmol, in case of **16c** 0.63 mmol) as a solution in dry THF (10 mL). The reaction mixture was stirred overnight and allowed to warm to rt, before being quenched with saturated aqueous NH_4Cl solution (40 mL), and extracted with ether (2 x 30 mL). The combined organic extracts were washed with brine, water, dried with $MgSO_4$. The solvent was removed *in vacuo*. Acetic acid (20 mL) and $HClO_4$ (0.4 mL, 70%) were added to the resulting residue. The precipitate was collected by filtration and recrystallised or washed with glacial acetic acid.

9-Docosanyl-10-methylacridinium perchlorate (**13a**): Yield 0.55 g (73%), mp 113-115 °C. ^{1}H-NMR ($CDCl_3/CF_3CO_2D$) δ: 8.65 (d, J = 8.8 Hz, 2H), 8.62 (d, J = 7.9 Hz, 2H), 8.36 (dd, J = 8.5 Hz, J = 7.5 Hz, 2H), 7.95 (dd, J = 8.2 Hz, J = 7.2 Hz, 2H), 4.88 (s, 3H), 3.86 (dd, J = 8.0 Hz, J = 7.9 Hz, 2H), 1.94-1.75 (m, 2H), 1.75-1.55 (m, 2H), 1.50-1.00 (m, 36H), 0.88 (t, J = 6.7 Hz, 3H). ^{13}C-NMR ($CDCl_3/CF_3CO_2D$) δ: 164.1 (2C), 140.9, 138.9 (2C), 128.0 (2C), 127.1 (2C), 125.2 (2C), 119.2 (2C), 39.0 (CH_3), 32.6, 31.8, 30.3, 29.9, 29.6 (13C), 29.4, 29.3 (2C), 22.6, 14.0 (CH_3). *Anal.* Calcd for $C_{36}H_{56}NO_4Cl$: C, 71.78; H, 9.39; N, 2.33. Found: C, 71.85; H, 9.67; N, 2.36.

9-Docosanylxanthylium perchlorate (**13b**): Yield 0.45 g (61% with isolation of intermediate compound **12b**), mp 139-141 °C. ^{1}H-NMR ($CDCl_3$/TFA) δ: 8.69 (d, J = 8.5 Hz, 2H), 8.56 (dd, J = 7.4 Hz, J = 8.7 Hz, 2H), 8.34 (d, J = 8.7 Hz, 2H), 8.09 (dd, J = 7.4 Hz, J = 8.5 Hz, 2H), 4.02 (t, J = 8.0 Hz, 2H), 2.08-1.86 (m, 2H), 1.78-1.60 (m, 2H), 1.60-1.10 (m, 36H), 0.89 (t, J = 6.6 Hz, 3H). ^{13}C-NMR ($CDCl_3$/TFA) δ: 181.9 (2C), 157.4, 144.5 (2C), 129.7 (2C), 128.4 (2C), 123.4 (2C), 120.4 (2C), 34.1, 32.0, 31.5, 30.7, 29.7 (12C), 29.6 (2C), 29.4, 29.3, 22.7, 14.0. HRMS: Calcd for $C_{35}H_{53}O$: 489.4096. Found: 489.4018.

9-Docosanylthioxanthylium perchlorate (**13c**): Was observed by NMR monitoring of crude reaction mixture which by recrystallization from EtOAc gave **17c**. Pure **13c** was obtained by treating **17c** with acetic acid and $HClO_4$ (70%), mp 118-122 °C. ^{1}H-NMR ($CDCl_3$) δ: 9.05 (d, J = 8.8 Hz, 2H), 8.73 (d, J = 8.5 Hz, 2H), 8.35 (dd, J = 8.8 Hz, J = 7.4 Hz, 2H), 8.22 (dd, J = 8.5 Hz, J = 7.2 Hz, 2H), 4.17 (m, 2H), 2.08-1.92 (m, 2H), 1.84-1.64 (m, 2H, overlapped with H_2O signal), 1.56-1.00 (m, 36H), 0.89 (t, J = 6.8 Hz, 3H). ^{13}C-NMR ($CDCl_3$/TFA) δ: 175.9 (2C), 146.9, 137.5 (2C),131.9 (2C), 131.7 (2C), 129.7 (2C), 128.3 (2C), 33.9, 33.4, 31.9, 30.6, 29.7 (12C), 29.5, 29.4, 29.3 (2C), 22.6, 14.0. HRMS: Calcd for $C_{35}H_{53}S$: 505.3868. Found: 505.3862.

9-Benzylthioxanthylium perchlorate (**14c**): Yield 0.38 g (78%), mp 195 °C (decomp). ^{1}H-NMR ($CDCl_3$/TFA) δ: 9.04 (d, J = 8.8 Hz, 2H), 8.69 (d, J = 8.2 Hz, 2H), 8.34 (dd, J = 7.4 Hz, J = 7.8 Hz, 2H), 8.16 (dd, J = 7.4 Hz, J = 8.2 Hz, 2H), 7.40-7.20 (m, 3H), 7.10 (d, J = 6.6 Hz, 2H), 5.53 (s, 2H). ^{13}C-NMR ($CDCl_3$/TFA) δ: 171.5 (2C), 147.5, 137.6, 137.3 (2C), 132.8 (2C), 132.0 (2C), 130.7 (2C), 129.6 (2C), 128.2 (2C), 128.1 (2C), 127.9, 38.1. HRMS: Calcd for $C_{20}H_{14}S$: 286.0816. Found: 286.0799.

9-(1-Iodobut-4-yl)thioxanthylium perchlorate (**15c**): Yield 0.38 g (63%), mp 168-169 °C. ^{1}H-NMR ($CDCl_3$/TFA) δ: 9.13 (d, *J* = 8.8 Hz, 2H), 8.65 (d, *J* = 8.5 Hz, 2H), 8.37 (dd, *J* = 7.4 Hz, *J* = 7.8 Hz, 2H), 8.26 (dd, *J* = 8.5 Hz, *J* = 7.1 Hz, 2H), 4.17 (dd, *J* = 8.4 Hz, *J* = 7.7 Hz, 2H), 3.38 (t, *J* = 6.1 Hz, 2H), 2.45-2.0 (m, 4H). ^{13}C-NMR ($CDCl_3$/TFA) δ: 175.0 (2C), 146.9, 137.7 (2C), 132.0 (2C), 131.9 (2C), 129.7 (2C), 128.2 (2C), 33.7, 33.0, 31.9, 5.5. *Anal.* Calcd for $C_{17}H_{16}O_4ClIS$: C, 42.65; H, 3.38. Found: C, 42.54; H, 3.23.

1,10-Bis-(9-thioxanthylium)decane bis-perchlorate (**16c**): Yield 0.56 g (76%), mp 209-210 °C. ^{1}H-NMR ($CDCl_3$/TFA) δ: 9.08 (d, *J* = 8.8 Hz, 4H), 8.60 (d, *J* = 8.7 Hz, 4H), 8.35 (t, *J* = 7.7 Hz, 4H), 8.24 (t, *J* = 7.7 Hz, 4H), 4.21-4.10 (m, 4H), 2.15-1.90 (m, 4H), 1.85-1.65 (m, 4H), 1.60-1.30 (m, 8H). ^{13}C-NMR ($CDCl_3$/TFA) δ: 176.4 (4C), 146.8 (2C), 137.6 (4C), 132.2 (4C), 131.8 (4C), 129.8 (4C), 128.0 (4C), 33.9 (2C), 33.5 (2C), 30.5 (2C), 29.0 (4C). *Anal.* Calcd for $C_{36}H_{36}O_8Cl_2S_2$: C, 59.09; H, 4.97. Found: C, 58.82; H, 5.11.

Preparation of 9*H*-9-Docosanylidenethioxanthene (**17c**). Obtained by general procedure for the preparation of the salts (**13-16**) followed by recrystallisation from EtOAc. Yield 0.45 g (71%), mp 55-57 °C. ^{1}H-NMR ($CDCl_3$) δ: 7.50-7.33 (m, 4H), 7.33-7.14 (m, 4H), 5.90 (t, *J* = 7.4 Hz, 1H), 2.43 (q, *J* = 7.4 Hz, 2H), 1.60-1.40 (m, 2H), 1.45-1.05 (m, 36H), 0.90 (t, *J* = 6.5 Hz, 3H). ^{13}C-NMR ($CDCl_3$) δ: 138.9, 135.4, 134.0, 133.7, 133.0, 131.8, 128.7, 126.8 (2C), 126.7, 126.5, 125.8, 125.7, 125.6, 31.9, 30.2, 29.7 (12C), 29.6 (2C), 29.5, 29.4, 29.3, 22.7, 14.1. *Anal.* Calcd for $C_{35}H_{52}S$: C, 83.26; H, 10.40. Found: C, 82.63; H, 10.39.

Preparation of 9*H*-9-Benzylidenethioxanthene (18c). Obtained by recrystallisation of 9-benzylthioxanthylium perchlorate (**14c,** 0.19 g, 0.49 mmol) from AcOH. Yield 0.09 g (65%), mp 118-119 °C. ^{1}H-NMR ($CDCl_3$) δ: 7.71 (d, *J* = 7.3 Hz, 1H), 7.47 (d, *J* = 7.7 Hz, 1H), 7.43 (d, *J* = 6.7 Hz, 1H), 7.32 (t, *J* = 7.6 Hz, 1H), 7.28-7.10 (m, 8H), 6.98 (t, *J* = 6.8 Hz, 1H), 6.88 (s, 1H). ^{13}C-NMR ($CDCl_3$) δ: 138.0, 136.9, 136.1, 133.9, 133.4, 132.3, 129.8, 129.6, 129.2 (2C), 128.1 (2C), 127.4, 127.1 (2C), 127.0 (2C), 126.1, 125.9, 125.2. 83.64 *Anal.* Calcd for $C_{20}H_{14}S$: C, 83.87; H, 4.94. Found: C, 83.64; H, 5.09.

Preparation of 9*H*-9-(1-Iodobut-4-ylidene)thioxanthene (19c). A suspension of 9-(1-iodobut-4-yl)-*thioxanthylium perchlorate* (**15c**, *0.20 g, 0.42 mmol*) *in* CH_2Cl_2 *(10 mL) was stirred with saturated* $NaHCO_3$ solution (2 mL) for 10 min at rt, the organic layer was separated, dried over $MgSO_4$, and for 12 h over molecular sieves, concentrated under reduced pressure to give colorless oil. Yield 0.14 g (86%). ^{1}H-NMR ($CDCl_3$) δ: 7.55-7.35 (m, 4H), 7.34-7.14 (m, 4H), 5.81 (t, *J* = 7.4 Hz, 1H), 3.18 (t, *J* = 6.9 Hz,

2H), 2.60-2.45 (m, 2H), 2.00 (pentet, J = 7.1 Hz, 2H). ^{13}C-NMR ($CDCl_3$) δ: 138.4, 136.8, 133.7, 133.5, 131.8, 129.9, 128.6, 127.1, 126.9, 126.8 (2C), 125.9, 125.8, 125.5, 33.7, 30.4, 5.8. HRMS: Calcd for $C_{17}H_{15}IS$: 377.9939. Found: 377.9930.

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