Convenient one-pot method for the preparation of polysubstituted benzo[*b*]- and naphtho[1,2-*b*]-furans and -thiophenes

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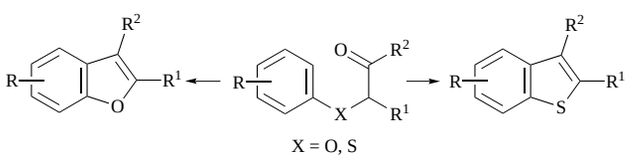
***N*-(Phenoxymethyl)- and *N*-(phenylthiomethyl)-benzotriazoles are versatile substrates for the preparation of benzofurans and benzothiophenes by insertion reactions of their anions into alkyl and aryl aldehydes and *in situ* cyclization of the α-aryloxy and α-arylthio ketones thus formed. *N*-(Naphthyloxy)- and *N*-(naphthylthio)-benzotriazoles are similarly efficient precursors for naphthofurans and naphthothiophenes.**

Introduction

The constant and growing interest in the development of new efficient and general synthetic methods for the preparation of fused heterocyclic systems involving furan and thiophene subunits is justified by their well-established valuable physiological and pharmacological properties.[1–4] In addition, recent technical applications of polysubstituted benzofurans and benzothiophenes, including numerous fluorescent dyes used as retrograde tracers, and Ca^{2+} and Mg^{2+} fluorescent indicator conjugates, *etc.*[4,5] increase their significance.

Benzo[*b*]furans **A** and benzo[*b*]thiophenes **C** (Scheme 1) are



Scheme 1

each available by two general routes: (i) the construction of a fused benzene ring starting from 2-substituted furans[6a] or thiophenes,[6b–d] and (ii) the formation of a furan[6e–l] or thiophene[6l–n] moiety beginning with S(O)-substituted derivatives of (thio)phenols. The extensive literature devoted to such methods has been summarized.[1,7–9]

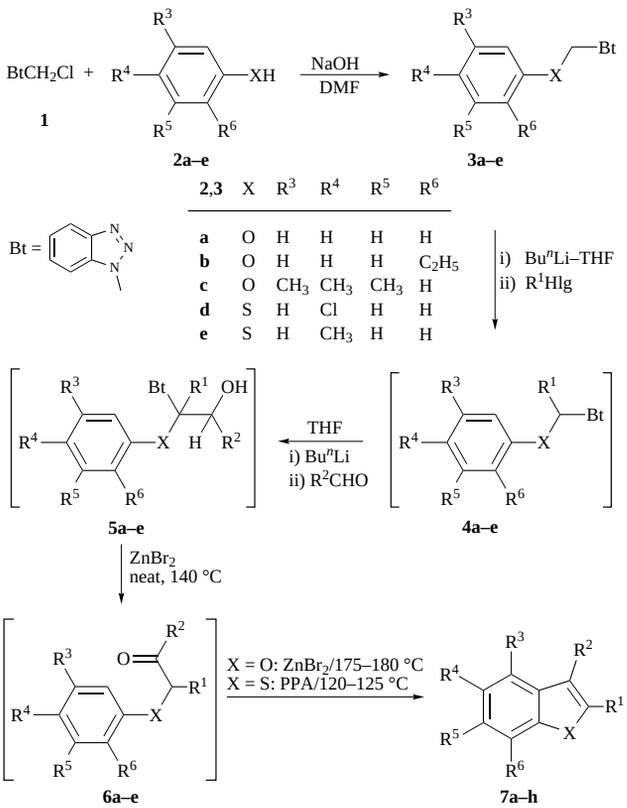
Among the known methods, both benzo[*b*]furans **A** and benzo[*b*]thiophenes **C** have most frequently been obtained by acid-catalyzed cyclizations of α-substituted aryl(thio)oxycarbonyl compounds of general type **B**,[1,9] a route which has proven to be of great value for the synthesis of a wide variety of **A** and **C**. The assembling of a benzene ring from derivatized furans or thiophenes has been of lesser synthetic importance (annulation of a benzene ring;[2] the scope and limitations of this method for the benzothiophene series were recently given[6d]). Aryl(thio)oxy keto-derivatives of type **B** are often prepared by means of condensation of (thio)phenols and α-halogeno-β-keto esters in the presence of bases (for an example, see ref. 10). The analogous α-aryl(thio)oxy aldehydes are frequently used in a protected (acetal) form, and are prepared from (thio)phenols and α-halo acetals.[11–13] Known methods for the preparation of both benzo[*b*]furans and benzo[*b*]thiophenes are briefly compared later in this paper, but no existing method is completely general. The preparations of aryl(thio)oxy ketones of type **B** also possess certain limitations, especially as far as varieties of R^1 and R^2 substituent are concerned. Hence, novel general routes for both benzo[*b*]furans and benzo[*b*]thiophenes retain synthetic importance.

We recently developed an efficient method for carbon insertion, which allowed the preparation of several new α-aryl(thio)oxy ketones in moderate to good yields (53–86%).[14] We have now extended this methodology to provide convenient one-pot procedures to prepare polysubstituted benzo[*b*]furans and benzo[*b*]thiophenes.

Results and discussion

1-(Aryloxymethyl)benzotriazoles **3a**–**c** were prepared by reactions of 1-chloromethylbenzotriazole **1** with polysubstituted phenols **2a**–**c** (Scheme 2). Lithiation of phenyl ethers **3a**–**c** with Bu^{n}Li, followed by quenching with an appropriate electrophile, afforded the substituted benzotriazole derivatives **4a**–**f**. Alkyl intermediates **4** could be isolated, and this was done for the cases of **4a** and **4b**. In general, **4a**–**f** were used directly in the next step. Treatment of **4a**–**f** with an additional equivalent of Bu^{n}Li, and subsequently with an aldehyde formed intermediates **5a**–**f**. Once again, derivatives **5** could be isolated and characterized, and this was done in the case of **5b**. However, in general, **5a**–**f** were treated directly without isolation with $ZnBr_2$ (neat mixture of 140 °C), to afford the corresponding α-aryloxy ketones **6a**–**f** as a result of pinacol-type rearrangement (*cf.* ref. 14). Here also, **6a**–**f** were generally not isolated; the resulting mixture was heated at 175–180 °C for 10–24 h, to give the desired polysubstituted benzo[*b*]furans **7a**–**f** in good overall yields (49–80% for four steps). Several α-aryloxy ketones **6a**–**e** were isolated in the course of the reactions in order to prove the reaction sequence; on further treatment with $ZnBr_2$ at elevated temperature, **6a**–**e** each gave the corresponding benzofuran **7a**–**e**, respectively.

Following a similar protocol, various substituted benzo[*b*]-thiophenes **7g** and **7h** (Scheme 2) were prepared in one-pot procedures from 1-(arylthiomethyl)benzotriazoles **3d** and **3e** *via* the corresponding alkylated analogs **4**, and arylthio ketones **6**. Just as for the sequence leading to the analogous benzofurans, intermediates (**4h** and **6h**) were isolated during the course of these similar transformations in the benzo[*b*]-thiophene series. Cyclization of ketones **6g** and **6h** occurred smoothly in hot (120–125 °C) polyphosphoric acid, leading to the expected benzo[*b*]thiophenes **7g** and **7h** in good overall yields (75–78%). Polyphosphoric acid is the reagent/solvent of choice for the benzo[*b*]thiophene series: when the ketone **6h** was treated with zinc bromide at elevated temperature under conditions similar to the preparation of the benzo[*b*]furan series, only a low yield (*ca.* 5%, according to the GC–MS data) of the desired product **7h** was obtained after 40 h of heating; instead, di-*p*-tolyl disulfide (15%) and 1,4-di-*p*-toluoylbutane (35%) were isolated from the reaction mixture by column chromatography together with unreacted starting ketone **6h**. This may be explained by the thermal instability of ketones **6g**, **6h** derived from thiophenol: the structures of the by-products clearly indicate a radical cleavage of the *tert*-C–S bond. The linear structure of 1,4-di-*p*-toluoylbutane was formed



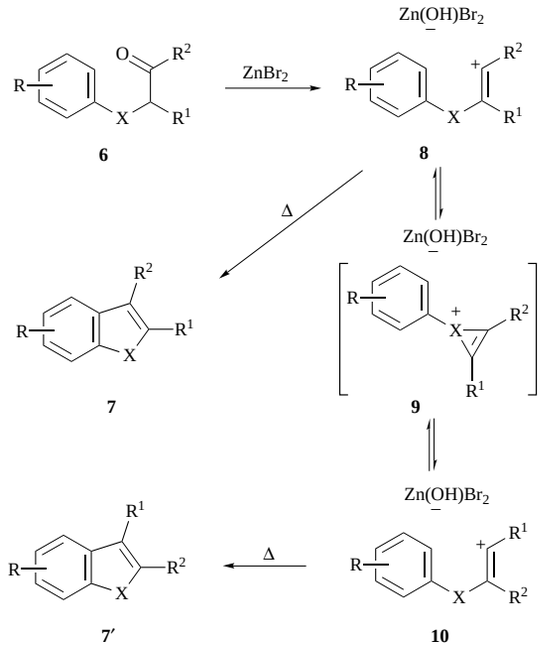
2,3	X	R^3	R^4	R^5	R^6
a	O	H	H	H	H
b	O	H	H	H	C_2H_5
c	O	CH_3	CH_3	CH_3	H
d	S	H	Cl	H	H
e	S	H	CH_3	H	H

4–7	X	R^1	R^2	R^3	R^4	R^5	R^6
a	O	$C_6H_5CH_2$	$C_6H_5(CH_2)_2$	H	H	H	H
b	O	*n*-C_8H_{17}	4-$CH_3C_6H_4$	H	H	H	H
c	O	CH_3	4-$CH_3C_6H_4$	H	H	H	H
d	O	*n*-C_4H_9	2,4-$Cl_2C_6H_3$	H	H	H	H
e	O	*n*-C_3H_7	C_6H_5	H	H	H	C_2H_5
f	O	*n*-C_6H_{13}	4-ClC_6H_4	CH_3	CH_3	CH_3	H
g	S	$C_6H_5CH_2$	$C_6H_5(CH_2)_2$	H	Cl	H	H
h	S	CH_3	4-$CH_3C_6H_4$	H	CH_3	H	H

Scheme 2

via migration of the unpaired electron to the methyl carbon atom followed by the recombination of two radical species.

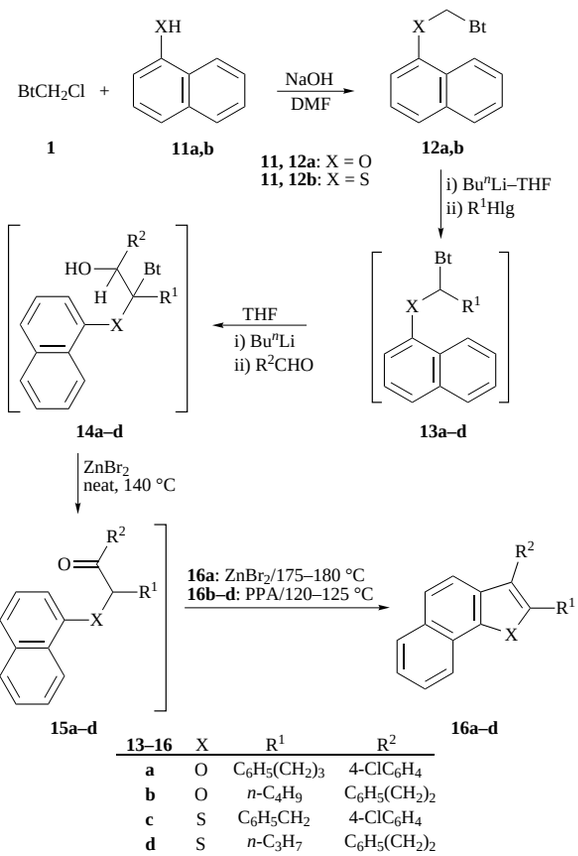
Cyclization of ketones of general type **6** (Scheme 3) is considered to be the best way to prepare symmetrical 2,3-*dialkylsubstituted* benzo[*b*]furans and benzo[*b*]thiophenes.[1] When the corresponding unsymmetrically substituted ketones ($R^1 \neq R^2 \neq H$) are employed, mixtures of regioisomers with substituents partly exchanged at the C(2) and C(3) positions were usually obtained.[1,15] The isomer ratio has been shown to depend greatly on the reaction temperature in the benzofuran series, and, accordingly, in order to obtain benzofurans or benzothiophenes free from the corresponding regioisomers, special reagents/methods need to be used.[1] In our reactions involving the use of both zinc bromide and polyphosphoric acid, the formation of alternative isomers was largely suppressed, leading to predominant isolation of products **7a**–**h** with the expected unrearranged structure. However, in the ^1H NMR spectra of some products, *i.e.* **7a**, a second weak set of signals for the corresponding positional isomer was observed. The GC–MS spectra of initially isolated **7a** and **7b** also show existence of a second peak of the same molecular weight, but with different fragmentation. The ratio of 'regular' **7** and 'reversed' **7′** products, according to the GC–MS data, was *ca.* 13 : 1 in the case of **7a** and 20 : 1 in the case of **7b**. Cyclodehydration reactions leading to the formation of benzofurans and benzothiophenes with substituents swapped at the C(2) and C(3) positions, probably, involve cations of type **8**, which exist in equilibrium with the corresponding 3-membered heterocyclic cations **9**: depending



Scheme 3

on the lability of the X–C–R^2 and X–C–R^1 bonds, either **10**, or **8** can be formed, and thus variously substituted benzofurans or benzothiophenes can result (Scheme 3).

Naphthofurans **16a** and **16b** and naphthothiophenes **16c** and **16d** with various substituents at the C(2) and C(3) positions were prepared (Scheme 4) in overall yields of 71–83%, by a route similar to that for the benzo-furan and -thiophene series described above. The (benzotriazol-1-yl)methyl 1-naphthyl (thio)ethers **12a** and **12b** were isolated (95% yield in both cases), but all the subsequent transformations were performed in one-pot sequences: lithiation and addition of alkyl halide afforded substituted (thio)naphthols **13a**–**d**, which were treated *in situ*



13–16	X	R^1	R^2
a	O	$C_6H_5(CH_2)_3$	4-ClC_6H_4
b	O	*n*-C_4H_9	$C_6H_5(CH_2)_2$
c	S	$C_6H_5CH_2$	4-ClC_6H_4
d	S	*n*-C_3H_7	$C_6H_5(CH_2)_2$

Scheme 4

with more Bu″Li and various aldehydes to form the appropriate alcohols **14a–d**. The Lewis acid ($ZnBr_2$) induced carbon insertion and formed the corresponding ketones **15a–d**. For the preparation of naphthofuran **16a** the temperature was raised to 175–180 °C, while for the preparation of **16b** and naphthothiophenes **16c** and **16d** polyphosphoric acid was added, followed by an increase in temperature to 120–125 °C. The high temperature (neat) cyclization of the intermediate **15b** gave a mixture of desired benzophenone **16b** and a by-product whose structure appears to include a naphthopyran ring (according to NMR spectra of the crude reaction mixture). However, all attempts to separate **16b** and the by-product failed. Therefore we used PPA-catalyzed cyclization for the preparation of **16b**. The reactions were monitored by TLC and GC–MS of the reaction mixtures; after they were complete, simple work-up afforded the desired naphthofurans **16a** and **16b** and naphthothiophenes **16c** and **16d**. As in the benzothiophene preparations, the use of $ZnBr_2$ for cyclization of naphthothio ketone **15c** after 20 h of heating at 175–180 °C did not give a substantial amount of **16c**, but led instead to the formation of di(1-naphthyl) disulfide (15%) and 1,4-bis(4-chlorobenzoyl)-2,3-diphenylbutane (16%). As in the case of **6h**, the last named product was a result of consecutive rearrangement–recombination of the radical formed after thermal decomposition of ketone **15c**. Intermediates **13** and **15** could be isolated, as we demonstrated for the cases of **13a** and **15a**, **15b** and **15d**, and then could be converted smoothly into the corresponding naphtho-furans and -thiophenes **16**, as shown for the cases of **15a** and **15d** (see Experimental), which increases the synthetic utility of the new process.

Conclusion

One-carbon homologation reaction of benzotriazole-containing (thio)alkoxy derivatives **4**, **13** afforded a new series of α-(thio)alkoxy-substituted ketones **6a–h** and **15a–d**, which were subsequently cyclized to give a wide range of various substituted benzo[*b*]furans **7a–f** and benzo[*b*]thiophenes **7g**,**h**. Several compounds, fused benzo derivatives, were also prepared, *i.e.* naphtho[1,2-*b*]furans **16a**,**b** and naphtho[1,2-*b*]thiophenes **16c**,**d**. The overall yields of compounds **7a–h** were in the range of 49–80%, while **16a–d** yields were 71–83%. The reaction sequence was performed in a one-pot manner, starting from the corresponding (benzotriazol-1-yl)methyl aryl (thio)ethers **3a–e** and **12a**,**b**. The procedure is simple, efficient, and more general than most of the previously used methods, thus adding a valuable alternative to the known reactions for the preparation of benzo[*b*]furans and benzo[*b*]thiophenes.

Experimental

General

Melting points were determined with a hot-stage apparatus and are uncorrected. NMR spectra were taken in $CDCl_3$ with tetramethylsilane as the internal standard for ^1H (300 MHz) or solvent as the internal standard for ^{13}C (75 MHz). *J* Values are given in Hz. Tetrahydrofuran (THF) was distilled under nitrogen immediately prior to use from sodium–benzophenone. All reactions with air-sensitive compounds were carried out under an argon atmosphere. Column chromatography was conducted with silica gel 230–400 mesh.

General procedure for the preparation of 1-(aryloxymethyl)-benzotriazoles 3a–c, 1-(arylthiomethyl)benzotriazoles 3d and 3e, 1-(1-naphthyloxymethyl)benzotriazole 12a, and 1-(1-naphthylthiomethyl)benzotriazole 12b

To a stirred solution of the corresponding (thio)phenol **2a–e** or (thio)naphthol **11a**,**b** (15 mmol) in ethanol (50 cm^3), NaOH (15 mmol, 0.60 g) was added at room temperature. After 1 h, ethanol was evaporated *in vacuo*, and a solution of 1-chloromethylbenzotriazole **1** (15 mmol, 2.51 g) in DMF (50 cm^3) was added to the resulting solid. The reaction mixture was heated at 65–70 °C for 15 h. On cooling, the mixture was poured into ice–water to give crystals, which were filtered, washed with water (100 cm^3) and dried to afford the pure products **3a–e** and **12a**,**b**.

1-(Phenoxymethyl)benzotriazole 3a. Isolated as a white solid (3.24 g, 96%), mp 64–65 °C (lit.,[16] 64 °C); δ_H(300 MHz; $CDCl_3$) 6.56 (2 H, s), 7.03 (1 H, t, *J* 7.2), 7.09 (2 H, d, *J* 8.2), 7.28 (2 H, d, *J* 7.2), 7.41 (1 H, t, *J* 8.0), 7.53 (1 H, t, *J* 8.0), 7.70 (1 H, d, *J* 8.3), 8.08 (1 H, d, *J* 8.31); δ_C(75 MHz; $CDCl_3$) 75.0, 109.9, 116.4, 120.1, 123.1, 124.4, 128.1, 129.7, 132.8, 146.3 and 156.2.

1-(2-Ethylphenoxymethyl)benzotriazole 3b. Isolated as a white solid (2.88 g, 76%), mp 54–55 °C (Found: N, 16.76. Calc. for $C_{15}H_{15}N_3O$: N, 16.60%); δ_H(300 MHz; $CDCl_3$) 1.10 (3 H, t, *J* 7.4), 2.54 (2 H, q, *J* 7.4), 6.59 (2 H, s), 6.96–7.01 (1 H, m), 7.14–7.19 (3 H, m), 7.42 (1 H, t, *J* 7.5), 7.54 (1 H, t, *J* 7.5), 7.66 (1 H, d, *J* 8.2), 8.09 (1 H, d, *J* 8.2); δ_C(75 MHz; $CDCl_3$) 14.2, 22.9, 75.0, 109.7, 114.0, 120.0, 123.0, 124.3, 127.0, 128.0, 129.5, 132.8, 133.9, 146.2 and 154.0.

1-(3,4,5-Trimethylphenoxymethylbenzotriazole 3c. Isolated as a white solid (3.65 g, 91%), mp 98–99 °C (Found: C, 71.86; H, 6.75; N, 16.10. Calc. for $C_{16}H_{17}N_3O$: C, 71.99; H, 6.41; N, 15.72%); δ_H(300 MHz; $CDCl_3$) 2.07 (3 H, s), 2.21 (6 H, s), 6.50 (2 H, s), 6.73 (2 H, s), 7.40 (1 H, t, *J* 7.5), 7.53 (1 H, t, *J* 7.5), 7.70 (1 H, d, *J* 8.2), 8.07 (1 H, d, *J* 8.2); δ_C(75 MHz; $CDCl_3$) 14.6, 20.7, 75.3, 110.0, 115.4, 120.1, 124.4, 128.0, 129.8, 132.9, 137.9, 146.4 and 153.6.

1-[(4-Chlorophenyl)thiomethyl]benzotriazole 3d. Isolated as a white solid (4.00 g, 97%), mp 105–106 °C (Found: C, 56.72; H, 3.57; N, 15.33. Calc. for $C_{13}H_{10}N_3ClS$: C, 56.72; H, 3.66; N, 15.27%); δ_H(300 MHz; $CDCl_3$) 5.93 (2 H, s), 7.16–7.23 (4 H, m), 7.38–7.51 (3 H, m), 8.07 (1 H, d, *J* 8.2); δ_C(75 MHz; $CDCl_3$) 52.6, 110.0, 120.3, 124.3, 127.6, 129.5, 130.3, 132.1, 134.4, 135.3 and 146.5.

1-[(4-Methylphenyl)thiomethyl]benzotriazole 3e. Isolated as a white solid (3.56 g, 93%), mp 104–105 °C (Found: N, 16.91. Calc. for $C_{14}H_{13}N_3S$: N, 16.47%); δ_H(300 MHz; $CDCl_3$) 2.30 (3 H, s), 5.89 (2 H, s), 7.03 (2 H, d, *J* 8.0), 7.12 (2 H, d, *J* 8.0), 7.35–7.46 (3 H, m), 8.08 (1 H, d, *J* 8.3); δ_C(75 MHz; $CDCl_3$) 21.1, 53.2, 110.2, 120.1, 124.1, 127.3, 128.2, 130.1, 132.2, 133.5, 139.1 and 146.4.

1-(1-Naphthyloxymethyl)benzotriazole 12a. Isolated as a white solid (3.92 g, 95%), mp 102–103 °C (Found: C, 74.11; H, 4.76; N, 15.36. Calc. for $C_{17}H_{13}N_3O$: C, 74.17; H, 4.76; N, 15.26%); δ_H(300 MHz; $CDCl_3$) 6.65 (2 H, s), 7.16 (1 H, d, *J* 7.5), 7.31 (2 H, t, *J* 8.0), 7.37–7.48 (4 H, m), 7.63 (1 H, d, *J* 8.0), 7.74 (1 H, d, *J* 7.4), 8.03 (1 H, d, *J* 8.2), 8.11 (1 H, d, *J* 8.5); δ_C(75 MHz; $CDCl_3$) 74.8, 108.0, 109.6, 119.9, 121.3, 122.6, 124.3, 125.4, 125.6, 125.7, 126.5, 127.5, 128.1, 132.7, 134.5, 146.2 and 151.7.

1-(1-Naphthylthiomethyl)benzotriazole 12b. Isolated as white crystals (4.15 g, 95%), mp 103–104 °C (Found: C, 69.76; H, 4.57; N, 14.29. Calc. for $C_{17}H_{13}N_3S$: C, 70.08; H, 4.50; N, 14.42%); δ_H(300 MHz; $CDCl_3$) 6.01 (2 H, s), 7.30–7.46 (6 H, m), 7.61–7.78 (4 H, m), 8.02 (1 H, d, *J* 7.6); δ_C(75 MHz; $CDCl_3$) 52.6, 110.1, 120.1, 124.1, 126.7, 126.8, 127.4, 127.6, 127.7, 129.1, 129.2, 129.3, 132.2, 132.4, 132.9, 133.5 and 146.4.

General procedure for the preparation of 1-(benzotriazol-1-yl)-1-phenoxy 1-substituted methanes 4a,b, 1-(benzotriazol-1-yl)-1-(4-methylphenylthio)ethane 4h, and 1-(1-naphthyloxy)-1-(benzotriazol-1-yl)-4-phenylbutane 13a

To a stirred solution of the corresponding 1-(aryloxymethyl)-benzotriazoles **3a**,**b**, 1-[(4-methylphenyl)thiomethyl]benzotriazole **3e**, or 1-(1-naphthyloxymethyl)benzotriazole **12a** (5 mmol) in dry THF (50 cm^3) at −78 °C under argon Bu″Li (1.6 M, 3.8 cm^3, 5.5 mmol) was added. After 1 h, the appropriate electrophile (5.5 mmol) [benzyl bromide (0.94 g) for **4a**, *n*-octyl iodide (1.32 g) for **4b**, methyl iodide (0.78 g) for **4h**, or 1-phenyl-3-bromopropane (1.00 g) for **13a**] in THF (5 cm^3) was added. The mixture was stirred at −78 °C for an additional 3 h and then at room temperature overnight. After being quenched with water (50 cm^3), the mixture was extracted with Et_2O (3 × 50 cm^3) and the combined organic layer was dried (Na_2SO_4). The

solvent was evaporated *in vacuo* and the residue purified either by recrystallization or by column chromatography to give the corresponding pure product **4a**, **4b**, **4h** or **13a**.

1-(Benzotriazol-1-yl)-1-phenoxy-2-phenylethane 4a. Purified by recrystallization from CH_2Cl_2–hexane to give a white solid (1.50 g, 95%), mp 89–90 °C (Found: C, 76.17; H, 5.47; N, 13.56. Calc. for $C_{20}H_{17}N_3O$: C, 76.17; H, 5.43; N, 13.32%); δ_H(300 MHz; $CDCl_3$) 3.55 (1 H, dd, *J* 6.0, 14.0), 3.79 (1 H, dd, *J* 6.0, 14.0), 6.85–7.00 (4 H, m), 7.09–7.17 (3 H, m), 7.19–7.23 (2 H, m), 7.32 (1 H, t, *J* 8.0), 7.43 (1 H, t, *J* 8.0), 7.76 (1 H, d, *J* 8.3), 8.01 (1 H, d, *J* 8.3); δ_C(75 MHz; $CDCl_3$) 41.4, 89.0, 111.0, 116.4, 120.2, 123.1, 124.2, 127.4, 127.7, 128.6, 129.4, 129.6, 131.7, 134.5, 146.6 and 156.1.

1-(Benzotriazol-1-yl)-1-phenoxynonane 4b. Purified by column chromatography (hexane–EtOAc = 8 : 1) to give a colourless oil (1.48 g, 88%) (Found: C, 74.98; H, 8.46; N, 12.41. Calc. for $C_{21}H_{27}N_3O$: C, 74.74; H, 8.06; N, 12.45%); δ_H(300 MHz; $CDCl_3$) 0.87 (3 H, t, *J* 6.5), 1.13–1.61 (12 H, m), 2.25–2.40 (1 H, m), 2.43–2.58 (1 H, m), 6.84–6.93 (2 H, m), 6.98 (2 H, d, *J* 7.9), 7.15 (2 H, t, *J* 7.9), 7.30 (1 H, t, *J* 7.6), 7.42 (1 H, t, *J* 7.6), 7.82 (1 H, d, *J* 8.4), 8.02 (1 H, d, *J* 8.4); δ_C(75 MHz; $CDCl_3$) 13.8, 22.4, 24.5, 28.7, 28.8, 29.0, 31.5, 34.6, 88.2, 111.0, 116.1, 119.9, 122.7, 124.0, 127.4, 129.4, 131.0, 146.6 and 156.1.

1-(Benzotriazol-1-yl)-1-(4-methylphenylthio)ethane 4h. Purified by column chromatography (hexane–EtOAc = 8 : 1) to give a colourless oil (1.21 g, 90%) (Found: C, 66.75; H, 5.98; N, 15.74. Calc. for $C_{15}H_{15}N_3S$: C, 66.89; H, 5.62; N, 15.61%); δ_H(300 MHz; $CDCl_3$) 2.09 (3 H, d, *J* 7.1), 2.22 (3 H, s), 6.25 (1 H, q, *J* 7.1), 6.88–6.95 (4 H, m), 7.35 (1 H, t, *J* 7.3), 7.44 (1 H, t, *J* 7.3), 7.68 (1 H, d, *J* 8.3), 8.03 (1 H, d, *J* 8.3); δ_C(75 MHz; $CDCl_3$) 20.6, 21.0, 63.1, 111.1, 120.0, 123.8, 126.9, 127.2, 129.7, 131.4, 134.2, 139.2 and 146.5.

1-(1-Naphthyloxy)-1-(benzotriazol-1-yl)-4-phenylbutane 13a. Purified by column chromatography (hexane–EtOAc = 8 : 1) to give a colourless oil (1.75 g, 89%); *m/z* (FAB) 394.1913 (M + 1). $C_{26}H_{23}N_3O$ requires 394.1919; δ_H(300 MHz; $CDCl_3$) 1.60–1.75 (1 H, m), 1.88–2.03 (1 H, m), 2.42–2.54 (1 H, m), 2.60–2.79 (3 H, m), 6.91 (1 H, d, *J* 7.7), 7.03–7.52 (12 H, m), 7.72 (2 H, d, *J* 8.0), 8.01 (1 H, d, *J* 8.2), 8.31 (1 H, d, *J* 8.0); δ_C(75 MHz; $CDCl_3$) 26.2, 34.2, 34.9, 87.7, 107.7, 111.0, 120.1, 121.3, 122.4, 124.3, 125.5, 125.6, 125.7, 126.0, 126.5, 127.7, 127.8, 128.3, 128.4, 131.1, 134.5, 141.0, 146.6 and 151.6.

Preparation of 1-(4-methylphenyl)-2-(benzotriazol-1-yl)-2-phenoxydecanol 5b

To a stirred solution of **4b** (5 mmol) in dry THF (50 cm^3) at −78 °C under argon Bu″Li (1.6 M, 3.8 cm^3, 5.5 mmol) was added. After 2 min, 4-methylbenzaldehyde (5.5 mmol, 0.66 g) in THF (5 cm^3) was added. The mixture was stirred at −78 °C for an additional 3 h and then at room temperature overnight. After being quenched with water (50 cm^3), the mixture was extracted with Et_2O (3 × 50 cm^3) and the combined organic layer was dried (Na_2SO_4). The solvent was evaporated *in vacuo* and the residue purified by column chromatography (hexane–EtOAc = 8 : 1) to give product **5b** as a mixture of diastereomers; a colourless oil (1.26 g, isolated yield 55%) (Found: N, 9.39. Calc. for $C_{29}H_{35}N_3O_2$: N, 9.18%); δ_H(300 MHz; $CDCl_3$) (data in square brackets are given for minor isomer, the ratio of the products, according to the GC–MS data, is 2 : 1) 0.85 (3 H, t, *J* 5.3), 0.98–1.26 (10 H, m), 1.42–1.54 (2 H, m), 2.26 (3 H, s) [2.20 (3 H, s)], 2.62–2.69 (2 H, m), 3.62 (1 H, br s), [3.42 (1 H, br s)], 5.57 (1 H, s), [5.43 (1 H, s)], 6.51–6.55 (2 H, m), 6.72 (2 H, d, *J* 8.1) [6.65 (2 H, d, *J* 8.1)], [6.84 (2 H, d, *J* 7.8)], 6.91–6.97 (2 H, m), 7.02–7.11 (3 H, m), 7.27–7.30 (2 H, m), 7.87–7.90 (1 H, m), 7.97–8.03 (1 H, m); δ_C(75 MHz; $CDCl_3$) 14.0, 21.1 [20.9], 22.5 [22.4], 22.9, 28.8, 28.9, 29.4, 31.6, 32.8, 78.1 [77.3], 98.98 [99.0], 114.5 [113.3], 119.1 [119.2], 119.4 [119.3], 123.2 [123.4], 123.9 [123.7], 127.1 [127.06], 127.4, 128.6 [128.4], 129.4 [129.3], 134.1 [134.0], 134.2, 138.3 [138.2], 146.0 [145.9] and 153.9 [153.8].

General procedure for the preparation of α-aryl(thio)oxy ketones 6a–e, 6h and α-naphthyl(thio)oxy ketones 15a, 15b and 15d

To a stirred solution of the corresponding 1-(aryloxymethyl)benzotriazoles **3a**,**c**, 1-[(4-methylphenyl)thiomethyl]-benzotriazole **3e**, 1-(1-naphthyloxymethyl)benzotriazole **12a**, or 1-(1-naphthylthiomethyl)benzotriazole **12b** (5 mmol) in dry THF (50 cm^3) at −78 °C under argon, Bu″Li (1.6 M, 3.8 cm^3, 5.5 mmol) was added. After 1 h, the appropriate electrophile (5.5 mmol) [benzyl bromide (0.94 g) for **6a**, *n*-octyl iodide (1.32 g) for **6b**, methyl iodide (0.78 g) for **6c** and **6h**, *n*-butyl bromide (0.75 g) for **6d** and **15b**, 1-phenyl-3-bromopropane (1.00 g) for **15a**, or *n*-propyl iodide (0.93 g) for **6e** and **15d**] in THF (5 cm^3) was added. The mixture was stirred at −78 °C for an additional 3 h and then at room temperature overnight. The solution formed was cooled again to −78 °C, and another equivalent of Bu″Li (1.6 M, 3.8 cm^3, 5.5 mmol) was added. After 2 min, the appropriate aldehyde (5.5 mmol) [hydrocinnamaldehyde (0.74 g) for **6a**, **15b** and **15d**, 4-methylbenzaldehyde (0.66 g) for **6b**, **6c** and **6h**, 2,4-dichlorobenzaldehyde (0.96 g) for **6d**, benzaldehyde (0.58 g) for **6e**, or 4-chlorobenzaldehyde (0.77 g) for **15a**], in THF (5 cm^3) was added. The mixture was stirred at −78 °C for an additional 3 h and then at room temperature overnight. A solution of $ZnBr_2$ (12 mmol, 2.7 g) in THF (10 cm^3) was added, the solvent was distilled off, and the oily residue was heated at 140 °C for 10 h. Upon cooling, crude product was dissolved in Et_2O, filtered, quenched with water (50 cm^3) and extracted with Et_2O (3 × 50 cm^3). The combined organic layer was dried (Na_2SO_4). The solvent was evaporated *in vacuo* and the residue purified by column chromatography to give the corresponding pure products **6** or **15**.

1,5-Diphenyl-2-phenoxypentan-3-one 6a. Purified by column chromatography (hexane–EtOAc = 20 : 1) to give a colourless oil (1.02 g, 62%) (Found: C, 83.61; H, 6.64. Calc. for $C_{23}H_{22}O_2$: C, 83.60; H, 6.71%); δ_H(300 MHz, $CDCl_3$) 2.66–2.82 (4 H, m), 3.09 (2 H, d, *J* 6.2), 4.73 (1 H, t, *J* 6.2), 6.76 (2 H, d, *J* 8.2), 6.94 (1 H, t, *J* 7.5), 7.05 (2 H, d, *J* 7.7), 7.13–7.31 (10 H, m); δ_C(75 MHz; $CDCl_3$) 28.9, 38.4, 39.9, 83.7, 115.0, 121.6, 126.0, 126.8, 128.3, 129.5, 129.7, 136.2, 140.8 157.6 and 210.7.

1-(4-Methylphenyl)-2-phenoxydecan-1-one 6b. Purified by column chromatography (hexane–EtOAc = 40 : 1) to give a colourless oil (1.28 g, 76%) (Found: C, 81.31; H, 9.21. Calc. for $C_{23}H_{30}O_2$: C, 81.60; H, 8.94%); δ_H(300 MHz, $CDCl_3$) 0.87 (3 H, t, *J* 4.7), 1.20–1.41 (10 H, m), 1.42–1.71 (2 H, m), 1.84–2.21 (2 H, m), 2.36 (3 H, s), 5.26 (1 H, dd, *J* 4.7, 8.1), 6.82–6.91 (3 H, m), 7.14–7.25 (4 H, m), 7.99 (2 H, d, *J* 8.3); δ_C(75 MHz; $CDCl_3$) 14.0, 21.5, 22.5, 25.7, 29.1, 29.2, 29.3, 31.7, 33.4, 81.3, 115.1, 121.1, 128.8, 129.3, 129.4, 131.9, 144.3, 157.9 and 198.5.

1-(4-Methylphenyl)-2-phenoxypropan-1-one 6c. Purified by column chromatography (hexane–EtOAc = 8 : 1) to give white crystals (1.00 g, 84%), mp 74–75 °C (Found: C, 80.21; H, 6.96. Calc. for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71%); δ_H(300 MHz; $CDCl_3$) 1.68 (3 H, d, *J* 6.8), 2.37 (3 H, s), 5.45 (1 H, q, *J* 6.8), 6.83–6.93 (3 H, m), 7.17–7.26 (4 H, m), 7.98 (2 H, d, *J* 8.3); δ_C(75 MHz; $CDCl_3$) 18.7, 21.6, 76.5, 115.1, 121.3, 128.9, 129.4, 129.5, 131.6, 144.5, 157.4 and 198.4.

1-(2,4-Dichlorophenyl)-2-phenoxyhexan-1-one 6d. Purified by column chromatography (hexane–EtOAc = 8 : 1) to give a colourless oil (1.10 g, 66%) (Found: C, 63.89; H, 5.55. Calc. for $C_{18}H_{18}Cl_2O_2$: C, 64.11; H, 5.38%); δ_H(300 MHz; $CDCl_3$) 0.89 (3 H, t, *J* 7.2), 1.25–1.42 (2 H, m), 1.45–1.61 (2 H, m), 1.92–1.99 (2 H, m), 5.28 (1 H, t, *J* 6.2), 6.86 (2 H, d, *J* 8.0), 6.93 (1 H, t, *J* 7.3), 7.19–7.27 (3 H, m), 7.39 (1 H, s), 7.47 (1 H, d, *J* 8.4); δ_C(75 MHz; $CDCl_3$) 13.7, 22.3, 27.5, 31.8, 82.3, 115.4, 121.6, 126.9, 129.5, 130.2, 130.3, 132.3, 137.4, 157.8 and 200.5.

1-Phenyl-2-(2-ethylphenoxy)pentan-1-one 6e. Purified by column chromatography (hexane–EtOAc = 40 : 1) to give white crystals (0.95 g, 72%), mp 56–57 °C (Found: C, 80.58; H, 8.02. Calc. for $C_{19}H_{22}O_2$: C, 80.82; H, 7.85%); δ_H(300 MHz; $CDCl_3$)

0.99 (3 H, t, *J* 7.4), 1.25 (3 H, t, *J* 7.5), 1.57–1.67 (2 H, m), 1.98–2.12 (2 H, m), 2.75 (2 H, q, *J* 7.1), 5.30 (1 H, dd, *J* 4.7, 8.3), 6.60 (1 H, d, *J* 8.0), 6.84 (1 H, t, *J* 7.3), 7.00 (1 H, t, *J* 7.3), 7.13 (1 H, d, *J* 7.2), 7.43 (2 H, t, *J* 7.6), 7.54 (1 H, t, *J* 7.4), 8.09 (2 H, d, *J* 7.2); δ_C(75 MHz; $CDCl_3$) 13.8, 14.2, 19.1, 23.3, 35.4, 80.8, 111.4, 121.0, 126.6, 128.6, 128.7, 129.2, 132.8, 133.4, 134.5, 155.4 and 199.3.

1-(4-Methylphenyl)-2-(4-methylphenylthio)propan-1-one 6h. Purified by column chromatography (hexane–EtOAc = 20 : 1) to give a colourless oil (1.09 g, 81%) (Found: C, 75.32; H, 6.90. Calc. for $C_{17}H_{18}OS$: C, 75.52; H, 6.71%); δ_H(300 MHz; $CDCl_3$) 1.51 (3 H, d, *J* 6.9), 2.35 (3 H, s), 2.44 (3 H, s), 4.56 (1 H, q, *J* 6.8), 7.10 (2 H, d, *J* 8.0), 7.24–7.29 (4 H, m), 7.89 (2 H, d, *J* 8.2); δ_C(75 MHz; $CDCl_3$) 16.9, 21.2, 21.6, 46.2, 128.1, 128.8, 129.3, 129.7, 133.2, 135.1, 138.9, 143.8 and 195.9.

1-(4-Chlorophenyl)-2-(1-naphthyloxy)-5-phenylpentan-1-one 15a. Purified by column chromatography (hexane–EtOAc = 20 : 1) to give a colourless oil (1.53 g, 74%) (Found: C, 78.18; H, 5.94. Calc. for $C_{27}H_{23}O_2Cl$: C, 78.23; H, 5.60%); δ_H(300 MHz; $CDCl_3$) 1.90–2.35 (4 H, m), 2.73 (2 H, t, *J* 7.4), 5.33 (1 H, dd, *J* 4.1, 8.2), 6.57 (1 H, d, *J* 7.8), 7.16–7.51 (11 H, m), 7.75–7.78 (1 H, m), 8.03 (2 H, d, *J* 8.7), 8.35–8.38 (1 H, m); δ_C(75 MHz; $CDCl_3$) 27.2, 32.7, 35.3, 82.0, 105.6, 121.2, 121.9, 125.5, 125.6, 125.7, 126.0, 126.6, 127.6, 128.4, 129.0, 130.2, 132.5, 134.7, 140.1, 141.4, 153.3 and 198.1.

1-Phenyl-4-(1-naphthyloxy)octan-3-one 15b. Purified by column chromatography (hexane–EtOAc = 20 : 1) to give a colourless oil (1.39 g, 80%) (Found: C, 83.22; H, 7.76. Calc. for $C_{24}H_{26}O_2$: C, 83.20; H, 7.56%); δ_H(300 MHz; $CDCl_3$) 0.89 (3 H, t, *J* 7.1), 1.28–1.56 (4 H, m), 1.75–1.87 (1 H, m), 1.89–2.02 (1 H, m), 2.67–3.05 (4 H, m), 4.66 (1 H, dd, *J* 4.9, 8.2), 6.52 (1 H, d, *J* 7.5), 7.05 (2 H, d, *J* 6.6), 7.10–7.29 (5 H, m), 7.43 (1 H, d, *J* 8.1), 7.48–7.52 (2 H, m), 7.79–7.82 (1 H, m), 8.32–8.35 (1 H, m); δ_C(75 MHz; $CDCl_3$) 13.8, 22.4, 27.5, 29.0, 32.0, 38.5, 83.4, 105.2, 121.1, 122.0, 125.5, 125.6, 125.7, 126.0, 126.6, 127.6, 128.4, 134.7, 140.8, 153.5 and 211.5.

1-Phenyl-4-(1-naphthylthio)heptan-3-one 15d. Purified by column chromatography (hexane–EtOAc = 8 : 1) to give a semi crystalline solid (1.62 g, 93%) (Found: C, 79.04; H, 7.00. Calc. for $C_{23}H_{24}OS$: C, 79.27; H, 6.94%); δ_H(300 MHz; $CDCl_3$) 0.90 (3 H, t, *J* 7.3), 1.30–1.56 (2 H, m), 1.64–1.87 (2 H, m), 2.83–2.95 (4 H, m), 3.71 (1 H, t, *J* 7.5), 7.11–7.25 (6 H, m), 7.33 (1 H, d, *J* 8.5), 7.42–7.49 (2 H, m), 7.70–7.77 (4 H, m); δ_C(75 MHz; $CDCl_3$) 13.7, 20.5, 30.0, 32.4, 40.9, 56.9, 126.0, 126.2, 126.4, 126.6, 127.5, 127.7, 128.4, 128.6, 129.3, 131.2, 132.5, 133.6, 140.9 and 206.4.

General procedure for the preparation of polysubstituted benzo[*b*]furans 7a–d and 2-(3-phenylpropyl)-3-(4-chlorophenyl)-naphtho[1,2-*b*]furan 16a. A mixture of the corresponding α-aryloxy ketone **6** or 1-(4-chlorophenyl)-2-(1-naphthyloxy)-5-phenylpentan-1-one **15a** (5 mmol) and $ZnBr_2$ (10 mmol, 2.3 g) was heated at 175–180 °C for 10–24 h. On cooling, the oily residue was dissolved in Et_2O, filtered, quenched with water (50 cm^3) and extracted with Et_2O (3 × 50 cm^3). The combined organic layers were dried (Na_2SO_4), and the solvent was evaporated *in vacuo*. The crude product was purified by column chromatography to give the corresponding products **7** or **16a**.

2-Benzyl-3-(2-phenylethyl)benzo[*b*]furan 7a. Purified by column chromatography (hexane–EtOAc = 40 : 1) to give a colourless oil (1.25 g, 80%) (Found: C, 88.93; H, 6.72. Calc. for $C_{23}H_{20}O$: C, 88.43; H, 6.45%); δ_H(300 MHz; $CDCl_3$) {data in square brackets are given for the regioisomer, 2-(2-phenylethyl)-3-benzylbenzo[*b*]furan; the ratio of the products, according to the GC–MS data, was 13 : 1} 2.90–3.06 (4 H, m), [3.84 (2 H, s)], 3.88 (2 H, s), 7.07–7.30 (14 H, m), [7.37–7.53 (14 H, m)]; δ_C(75 MHz; $CDCl_3$) 26.1, 32.5, 36.0, 111.0, 114.6, 119.0, 122.1, 123.4, 126.1, 126.5, 128.3, 128.4, 128.5, 137.8, 141.6, 152.7 and 154.3.

2-Octyl-3-(4-methylphenyl)benzo[*b*]furan 7b. Purified by column chromatography (hexane–EtOAc = 40 : 1) to give a colourless oil (1.26 g, 79%) (Found: C, 86.34; H, 8.76. Calc. for $C_{23}H_{28}O$: C, 86.20; H, 8.81%); δ_H(300 MHz; $CDCl_3$) 0.87 (3 H, t, *J* 6.7), 1.18–1.40 (10 H, m), 1.72–1.81 (2 H, m), 2.43 (3 H, s), 2.84 (2 H, t, *J* 7.7), 7.18–7.30 (4 H, m), 7.38 (2 H, d, *J* 8.0), 7.45 (1 H, d, *J* 7.4), 7.54 (1 H, d, *J* 8.2); δ_C(75 MHz; $CDCl_3$) 14.1, 21.3, 22.7, 26.8, 28.4, 29.2, 29.3, 29.4, 31.9, 110.8, 116.6, 119.5, 122.5, 123.4, 129.0, 129.1, 129.4, 129.9, 136.7, 154.0 and 155.2.

2-Methyl-3-(4-methylphenyl)benzo[*b*]furan 7c. Purified by column chromatography (hexane–EtOAc = 20 : 1) to give a colourless oil (0.88 g, 80%); *m*/*z* (EI) 222.1055 (M^+). $C_{16}H_{14}O$ requires 222.1045; δ_H(300 MHz; $CDCl_3$) 2.45 (3 H, s), 2.55 (3 H, s), 7.20–7.33 (4 H, m), 7.41–7.48 (3 H, m), 7.59 (1 H, d, *J* 7.1); δ_C(75 MHz; $CDCl_3$) 12.8, 21.2, 110.7, 116.8, 119.4, 122.5, 123.4, 128.8, 129.4, 129.8, 130.0, 136.6, 151.0 and 154.1.

2-Butyl-3-(2,4-dichlorophenyl)benzo[*b*]furan 7d. Purified by column chromatography (hexane–EtOAc = 40 : 1) to give a colourless oil (0.94 g, 59%) (Found: C, 68.28; H, 5.54. Calc. for $C_{18}H_{16}Cl_2O$: C, 67.91; H, 5.07%); δ_H(300 MHz; $CDCl_3$) 0.88 (3 H, t, *J* 7.3), 1.28–1.40 (2 H, m), 1.64–1.82 (2 H, m), 2.58–2.80 (2 H, m), 7.18–7.37 (5 H, m), 7.49 (1 H, d, *J* 8.0), 7.58 (1 H, s); δ_C(75 MHz; $CDCl_3$) 13.7, 22.3, 26.8, 29.9, 110.9, 113.8, 119.7, 122.6, 123.6, 127.2, 128.8, 129.8, 130.4, 133.0, 134.3, 135.4, 153.9 and 156.4.

2-(3-Phenylpropyl)-3-(4-chlorophenyl)naphtho[1,2-*b*]furan 16a. Purified by column chromatography (hexane–EtOAc = 40 : 1) to give a colourless oil (1.41 g, 71%); *m*/*z* (EI) 396.1298 (M^+). $C_{27}H_{21}ClO$ requires 396.1281; δ_H(300 MHz; $CDCl_3$) 2.13–2.23 (2 H, m), 2.71 (2 H, t, *J* 7.4), 2.96 (2 H, t, *J* 7.4), 7.14–7.29 (6 H, m), 7.38–7.50 (4 H, m), 7.57–7.68 (3 H, m), 7.93 (1 H, d, *J* 8.2), 8.32 (1 H, d, *J* 8.2); δ_C(75 MHz; $CDCl_3$) 26.3, 30.1, 35.3, 117.4, 118.1, 119.9, 121.2, 123.4, 123.7, 124.9, 125.9, 126.3, 128.4, 128.5, 129.0, 130.4, 131.3, 131.4, 133.0, 141.5, 149.4 and 154.2.

Preparation of 2-methyl-3-(4-methylphenyl)-5-methylbenzo[*b*]-thiophene 7h and 2-propyl-3-(2-phenylethyl)naphtho[1,2-*b*]-thiophene 16d

To the corresponding 1-(4-methylphenyl)-2-(4-methylphenylthio)propan-1-one **6h** (5 mmol, 1.28 g) or 1-phenyl-4-(1-naphthylthio)heptan-3-one **15d** (5 mmol, 1.74 g) polyphosphoric acid (10 g) was added at room temperature and the reaction mixture was heated at 120–125 °C for 20 h. Upon cooling, the oily residue was dissolved in Et_2O, poured into ice–water (100 cm^3) and extracted with Et_2O (3 × 50 cm^3). The combined organic layer was dried (Na_2SO_4) and the solvent was evaporated *in vacuo*. The residue was purified by column chromatography to give the corresponding product **7h** or **16d**.

2-Methyl-3-(4-methylphenyl)-5-methylbenzo[*b*]thiophene 7h. Purified by column chromatography (hexane–EtOAc = 40 : 1) to give a colourless oil (1.02 g, 81%) (Found: C, 80.98; H, 6.48. Calc. for $C_{17}H_{16}S$: C, 80.91; H, 6.39%); δ_H(300 MHz; $CDCl_3$) 2.36 (3 H, s), 2.42 (3 H, s), 2.45 (3 H, s), 7.06–7.10 (2 H, m), 7.24–7.30 (4 H, m), 7.63 (1 H, d, *J* 8.2); δ_C(75 MHz; $CDCl_3$) 14.5, 21.3, 21.4, 121.6, 122.5, 125.4, 129.2, 129.9, 132.5, 133.5, 133.8, 135.3, 136.0 and 136.8.

2-Propyl-3-(2-phenylethyl)naphtho[1,2-*b*]thiophene 16d. Purified by column chromatography (hexane–EtOAc = 40 : 1) to give white crystals (2.74 g, 83%), mp 78–79 °C (Found: C, 83.36; H, 6.53. Calc. for $C_{23}H_{22}S$: C, 83.60; H, 6.72%); δ_H(300 MHz; $CDCl_3$) 1.03 (3 H, t, *J* 7.3), 1.67–1.79 (2 H, m), 2.78 (2 H, t, *J* 7.7), 3.09 (2 H, t, *J* 8.1), 3.55 (2 H, t, *J* 8.1), 7.27–7.39 (5 H, m), 7.55 (1 H, t, *J* 7.2), 7.65 (1 H, t, *J* 8.3), 7.71 (1 H, d, *J* 8.7), 7.84 (1 H, d, *J* 8.7), 7.99 (1 H, d, *J* 8.2), 8.72 (1 H, d, *J* 8.3); δ_C(75 MHz; $CDCl_3$) 14.0, 24.9, 30.6, 31.1, 35.8, 120.9, 123.2, 124.5, 126.0, 126.2, 128.5, 129.3, 129.9, 132.2, 133.2, 133.8, 136.7, 141.0 and 141.6.

One-pot procedure for the preparation of polysubstituted benzo[*b*]furans 7a–f, benzo[*b*]thiophenes 7g, 7h, naphtho[1,2-*b*]-furans 16a, 16b, and naphtho[1,2-*b*]thiophenes 16c, 16d

To a stirred solution of the corresponding 1-[aryloxy(thio)-

methyl]benzotriazoles **3a**–**3e** or 1-[naphthyloxy(thio)methyl]-benzotriazoles **12a**,**b** (5 mmol) in dry THF (50 cm^3) at −78 °C under argon, Bu″Li (1.6 M, 3.8 cm^3, 5.5 mmol) was added. After 1 h, the appropriate electrophile (5.5 mmol) [benzyl bromide (0.94 g) for **7a**,**g** and **16c**, *n*-octyl iodide (1.32 g) for **7b**, methyl iodide (0.78 g) for **7c**,**h**, *n*-butyl bromide (0.75 g) for **7d** and **16b**, *n*-propyl iodide (0.93 g) for **7e** and **16d**, *n*-hexyl bromide (0.91 g) for **7f**, and 1-bromo-3-phenylpropane (1.10 g) for **16a**] in THF (5 cm^3) was added. The mixture was stirred at −78 °C for an additional 3 h and then at room temperature overnight. The reaction solution was cooled down to −78 °C and a second equivalent of Bu″Li (1.6 M, 3.8 cm^3, 5.5 mmol) was added. After 2 min, the appropriate aldehyde (5.5 mmol) [hydrocinnamaldehyde (0.74 g) for **7a**,**g** and **16b**,**d**, 4-methylbenzaldehyde (0.66 g) for **7b**,**c**,**h**, 2,4-dichlorobenzaldehyde (0.96 g) for **7d**, benzaldehyde (0.58 g) for **7e**, and 4-chlorobenzaldehyde (0.77 g) for **7f** and **16a**,**c**] in THF (5 cm^3) was added. The mixture was stirred at −78 °C for an additional 3 h and then at room temperature overnight. A solution of $ZnBr_2$ (12 mmol, 2.7 g) in THF (10 cm^3) was added, and the oily residue was heated at 140 °C for 10 h.

Method A: preparation of benzo[*b*]furans 7a–f and naphtho-[1,2-*b*]furan 16a

The reaction mixture was heated at 175–180 °C for 10–24 h. Upon cooling, the oily residue was dissolved in Et_2O, filtered, quenched with water (50 cm^3), and extracted with Et_2O (3 × 50 cm^3). The combined organic layers were dried (Na_2SO_4), and solvent was evaporated *in vacuo*. The residue was purified by column chromatography to give the corresponding compounds **7a**–**f** or **16a**.

Method B: preparation of benzo[*b*]thiophenes 7g, 7h, naphtho-[1,2-*b*]furan 16b and naphtho[1,2-*b*]thiophenes 16c,d

To the crude oily residue polyphosphoric acid (10 g) was added at room temperature, and the reaction mixture was heated at 120–125 °C for 20 h. Upon cooling, the oily residue was dissolved in Et_2O, poured into ice–water (100 cm^3) and extracted with Et_2O (3 × 50 cm^3). The combined organic layer was dried (Na_2SO_4) and the solvent was evaporated *in vacuo*. The crude product was purified by column chromatography to give the corresponding products **7g**, **7h** or **16b**–**d**. The appearance and NMR spectral data for compounds **7a**–**d**, **7h** and **16a**, **16d** were identical to those described above (cyclization of **6** into **7** and **15** into **16**).

2-Propyl-3-phenyl-7-ethylbenzo[*b*]furan 7e. Purified by column chromatography (hexane–EtOAc = 40 : 1) to give a colourless oil (0.95 g, 72%); *m*/*z* (EI) 264.1511 (M^+). $C_{19}H_{20}O$ requires 264.1514; δ_H(300 MHz; $CDCl_3$) 0.99 (3 H, t, *J* 7.3), 1.38 (3 H, t, *J* 7.6), 1.75–1.87 (2 H, m), 2.84 (2 H, t, *J* 7.4), 2.96 (2 H, q, *J* 7.6), 7.07–7.17 (2 H, m), 7.33–7.39 (2 H, m), 7.44–7.48 (4 H, m); δ_C(75 MHz; $CDCl_3$) 13.9, 14.2, 21.9, 23.0, 28.8, 117.0, 122.7, 122.8, 126.9, 127.4, 128.5, 128.7, 129.2, 133.2, 152.5 and 154.7.

2-Hexyl-3-(4-chlorophenyl)-4,5,6-trimethylbenzo[*b*]furan 7f. Purified by column chromatography (hexane–EtOAc = 40 : 1) to give a colourless oil (1.12 g, 64%) (Found: C, 78.19; H, 8.08. Calc. for $C_{23}H_{27}ClO$: C, 77.93; H, 7.68%); δ_H(300 MHz; $CDCl_3$) 0.87 (3 H, t, *J* 6.0), 1.19–1.36 (6 H, m), 1.61–1.70 (2 H, m), 2.04 (3 H, s), 2.21 (3 H, s), 2.41 (3 H, s), 2.57 (2 H, t, *J* 4.9), 7.17 (1 H, s), 7.28 (2 H, d, *J* 8.5), 7.41 (2 H, d, *J* 7.8); δ_C(75 MHz; $CDCl_3$) 14.0, 15.0, 16.1, 22.5, 26.3, 28.3, 28.8, 31.5, 109.4, 116.3, 125.6, 128.3, 128.5, 129.4, 132.1, 132.6, 133.2, 133.5, 152.2 and 154.9.

2-Benzyl-3-(2-phenylethyl)-5-chlorobenzo[*b*]thiophene 7g. Purified by column chromatography (hexane–EtOAc = 40 : 1) to give a colourless oil (1.41 g, 78%) (Found: C, 76.50; H, 5.56. Calc. for $C_{23}H_{19}ClS$: C, 76.12; H, 5.28%); δ_H(300 MHz; $CDCl_3$) 2.85 (2 H, t, *J* 7.7), 3.09 (2 H, t, *J* 7.7), 3.90 (2 H, s), 7.09–7.16 (4 H, m), 7.21–7.32 (7 H, m), 7.63–7.66 (2 H m); δ_C(75 MHz; $CDCl_3$) 28.9, 34.3, 35.8, 121.1, 123.3, 124.0, 126.2, 126.7, 128.5, 128.6, 130.3, 130.7, 137.0, 139.4, 141.2, 141.3 and 141.5.

2-Butyl-3-(2-phenylethyl)naphtho[1,2-*b*]furan 16b. Purified by column chromatography (hexane–EtOAc = 40 : 1) to give a colourless oil (1.20 g, 73%) (Found: C, 87.65; H, 7.74. Calc. for $C_{24}H_{24}O$: C, 87.76; H, 7.36%); δ_H(300 MHz; $CDCl_3$) 0.92 (3 H, t, *J* 7.3), 1.28–1.40 (2 H, m), 1.58 (2 H, quintet, *J* 7.4), 2.61 (2 H, t, *J* 7.4), 2.94–2.98 (4 H, m), 7.13–7.28 (5 H, m), 7.43 (1 H, t, *J* 7.0), 7.52–7.63 (3 H, m), 7.91 (1 H, d, *J* 8.2), 8.26 (1 H, d, *J* 8.2); δ_C(75 MHz; $CDCl_3$) 13.8, 22.4, 26.1, 30.7, 36.5, 114.4, 118.1, 119.8, 121.3, 122.5, 124.4, 124.8, 125.96, 126.0, 128.3, 128.4, 128.6, 130.9, 141.7, 149.1 and 154.5.

2-Benzyl-3-(4-chlorophenyl)naphtho[1,2-*b*]thiophene 16c. Purified by column chromatography (hexane–EtOAc = 40 : 1) to give white crystals (1.49 g, 78%), mp 123–124 °C (Found: C, 78.21; H, 4.50. Calc. for $C_{25}H_{17}ClS$: C, 78.11; H, 4.46%); δ_H(300 MHz; $CDCl_3$) 4.03 (2 H, s), 7.14 (2 H, d, *J* 6.9), 7.20–7.35 (6 H, m), 7.40 (1 H, t, *J* 7.4), 7.48–7.53 (3 H, m), 7.69 (1 H, d, *J* 8.8), 7.79 (1 H, d, *J* 8.8), 7.88 (1 H, d, *J* 8.0); δ_C(75 MHz; $CDCl_3$) 34.8, 120.5, 123.4, 124.8, 125.2, 125.7, 126.5, 128.5, 128.6, 129.3, 129.6, 131.7, 132.0, 133.7, 133.9, 135.1, 136.7, 136.8, 140.0 and 141.2.

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