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Preparation and synthetic utility of 3-(benzotriazol-1-ylmethyl)areno- and -hetareno[*b*]thiophenes

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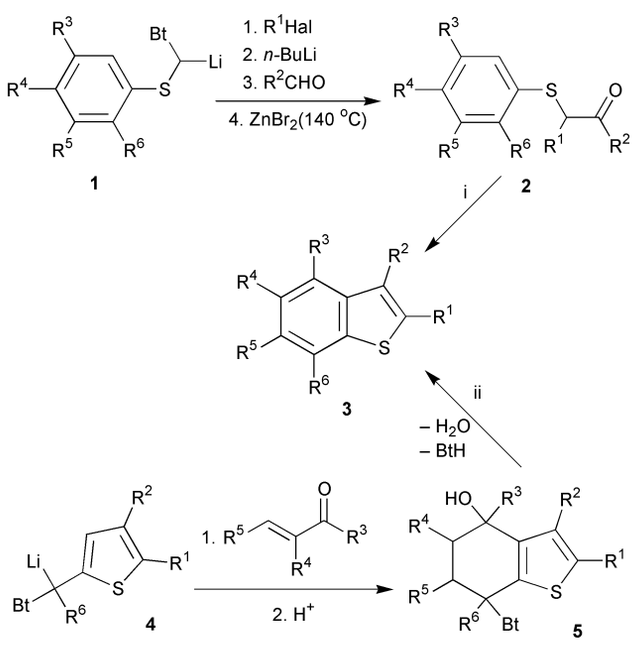
3-(Functionalized-methyl)- and 3-alkenylareno(hetareno)[*b*]thiophenes **13**–**16** are prepared *via* the side chain elaboration of 3-(benzotriazol-1-ylmethyl)thiophenes **10d**–**f**,**h**, readily available from the condensation of 1-benzotriazolyl-3-chloroacetone **7** with aromatic or heteroaromatic thiols followed by dehydrative cyclization of 1-(benzotriazol-1-yl)-3-[aryl(hetaryl)thio]acetones **9d**–**f**,**h**.

Introduction

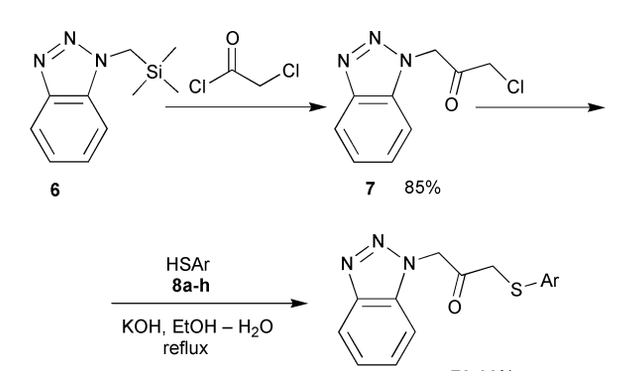
The development of new, efficient and general synthetic methods for the preparation of derivatives of fused thiophenes (benzo-, naphtho-, thieno- [*b*]thiophenes) is justified by the well-established practical importance of these compounds.[1] For example, *N*-[1-(1-benzothiophen-2-yl)ethyl]-*N*-hydroxyurea or zileton (Zyflo) was the first selective 5-lipoxygenase inhibitor to receive FDA (Food and Drug Administration) approval for the treatment of asthma.[2,3] 1-(Benzo[*b*]thienyl)-2-(thienyl)ethenes are anti-inflammatory agents,[4] 2-(1-benzothiophen-3-ylmethyl)-4,5-dihydro-1*H*-imidazole (Metizoline) is a adrenergic vasoconstrictor,[5] and other benzo- and thienothiophenes are used as urokinase inhibitors,[6] as components of liquid crystal compositions,[7] and as dyes.[8] Naphthothiophenes are claimed as pharmaceuticals,[9] components of compositions for the aqueous cold-bleaching of textiles,[10] and as photographic materials.[11]

Fused thiophenes **3** are available by two general routes: (i) the formation of a thiophene moiety beginning with *S*-substituted derivatives of aromatic or heteroaromatic thiols, *e.g. via* arylthio derivatives of type **2**, which are usually prepared by means of condensation of thiophenols and α-halogenoalkyl ketones in the presence of bases[12] and (ii) the construction of a fused aromatic (heteroaromatic) ring onto initial 2-substituted thiophenes. Benzotriazole-mediated strategy has been recently used in both of these two approaches **1** ⟶ **2** ⟶ **3**[13] and **4** ⟶ **5** ⟶ **3**[14] (Scheme 1).

Cyclization of ketones of the general type **2** (Scheme 1) is considered to be the best way to prepare 3-monosubstituted or symmetrical 2,3-disubstituted benzo- **3** ($R^1 = R^2 =$ Alk, H) and naphtho[*b*]thiophenes. When unsymmetrically substituted ketones **2** ($R^1 \neq R^2 \neq$ H) are employed, mixtures of regioisomers (*cf.* **3**) are usually obtained.[13] We have now extended benzotriazole methodology to the synthesis of 3-(functionalized)-areno(hetareno)[*b*]thiophenes.



Scheme 1



9a Ar = Ph; **9b** Ar = 4-Me-C_6H_4; **9c** Ar = 4-Cl-C_6H_4; **9d** Ar =1-naphthyl; **9e** Ar = 2-naphthyl; **9f** Ar = 2-thienyl; **9g** Ar = 2-benzofuryl; **9h** Ar = 2-benzothienyl

Scheme 2

Results and discussion

Acylation of easily available 1-[(trimethylsilyl)methyl]-1*H*-[1,2,3]benzotriazole **6**[15] with chloroacetyl chloride leads to 1-(1*H*-[1,2,3]benzotriazol-1-yl)-3-chloroacetone **7** – a promising synthon for heterocyclizations.[16] Chloroacetone **7** reacts with aromatic(heteroaromatic) thiols **8a**–**h** to give acetones **9a**–**h** bearing an ArS moiety (Scheme 2).

Cyclization of thioacetones **9a**–**h** to thiophenes **10** was carried out by treatment with $ZnCl_2$ in boiling benzene for 3 h. 1- And 2-naphthylthio derivatives **9d**,**e** both formed readily the desired naphthothiophenes **10d**,**e** in 76 and 86% yields respectively. The synthesis of compound **10d** could have been

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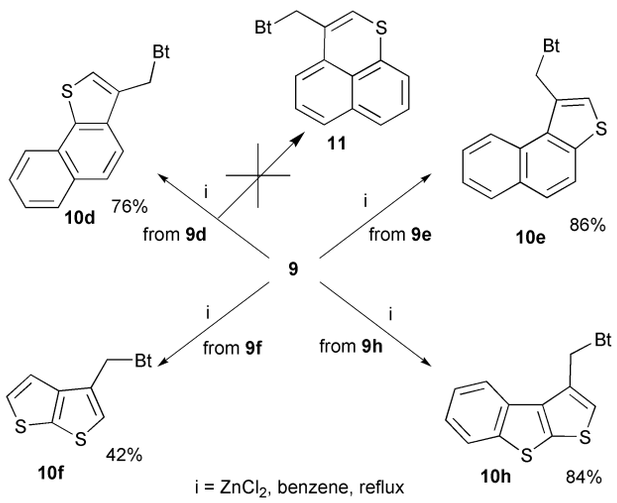
accompanied with benzo[*de*]thiochromene **11** formation. Nevertheless, compound **11** was not detected in the reaction mixture. This is in agreement with the results observed for the analogous cyclization of 1-(1-naphthylthio)acetone.[12] A strong tendency to cyclization is demonstrated by the benzothiophene derivative **9h** (yield of the cyclic product **10h** 84%). In contrast, the benzofuran analog **9g** was only resinified under the same conditions. Cyclization of 3-(2-thienylthio)acetone **9f** requires a longer reaction time (12 h) and gave the corresponding thienothiophene **10f** in 42% yield (Scheme 3). Compounds **10d**–**f**,**h** were previously unknown and were characterized by NMR spectroscopy and elemental analyses.



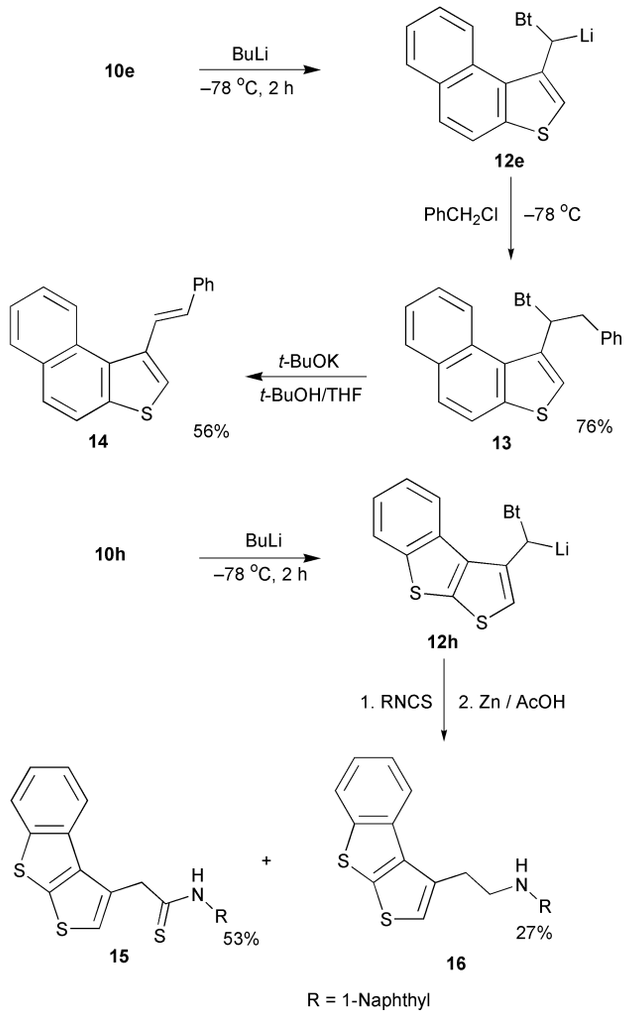
Scheme 3

All our attempts to involve phenylthioacetones **9a**–**c** into the same cyclization failed (Scheme 3). Increasing the reaction temperature (refluxing in toluene) and (or) reaction time up to 24 h leads only to the transformation of these derivatives into the respective diaryl disulfides.

Replacement of the Bt-moiety with nucleophiles was attempted for naphthothiophene **10e**. However, this compound was inert to reagents such as KOH–EtOH (reflux, 72 h), PhSK–EtOH (reflux, 48 h), $NaBH_4$–EtOH (reflux, 12 h), $LiAlH_4$–THF (reflux, 12 h), 1-methylindole–$ZnCl_2$ (toluene, 12 h, reflux), MeMgI (Et_2O, 12 h, reflux) and cyclopentylmagnesium chloride (Et_2O, 12 h, reflux).

Side-chain metalation of thiophene derivatives is normally difficult to achieve because a competing ring metalation predominates.[17] However, due to the electron-withdrawing ability of the benzotriazolyl group, compounds **10** can easily be deprotonated exclusively at the side-chain CH_2 alpha to the benzotriazolyl group. Accordingly, treatment of **10e**,**h** with *n*-butyllithium at −78 °C under argon in tetrahydrofuran furnished deep-blue solutions of the lithio derivatives **12e**,**h** (Scheme 4). Reactions of the anion **12e** with benzyl chloride gave the corresponding product **13** in 76% yield. Refluxing the benzyl derivative **13** with *t*-BuOK–*t*-BuOH–THF leads to removal of the Bt-moiety with formation of stilbene **14** (yield 56%). Reaction of the lithio derivative **12h** with 1-naphthyl isothiocyanate followed by reduction with Zn–AcOH leads to formation of thioamide **15** (yield 53%) and amine **16** (yield 27%).

In conclusion, novel routes to 3-(functionalized-methyl)- and 3-alkenylareno-(hetareno)[*b*]thiophenes have been developed which should be of general applicability.



Scheme 4

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 the 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. Heteroaromatic thiols **8d**–**h** were prepared according to the known procedure.[18]

1-(1*H*-[1,2,3]Benzotriazol-1-yl)-3-chloroacetone (7)

To a solution of 1-[(trimethylsilyl)methyl]-1*H*-[1,2,3]benzotriazole **6** (8 g, 39 mmol) in dry diethyl ether (40 cm^3), chloroacetyl chloride (4.41 g, 39 mmol) was added and the reaction mixture was kept overnight at room temperature. The precipitate formed was filtered off, washed with cold Et_2O and dried *in vacuo* to give the chloroacetone **7** (6.55 g, 85%) as yellow needles, mp 161–162 °C (Found: C, 51.68; H, 3.65; N, 20.01. $C_9H_8ClN_3O$ requires C, 51.56; H, 3.85; N, 20.05%); δ_H (300 MHz; $CDCl_3$–DMSO-d_6 5 : 1) 4.50 (2 H, s), 5.88 (2 H, s), 7.41 (1 H, t, *J* 8.8), 7.52 (1 H, t, *J* 8.4), 7.60 (1 H, d, *J* 9.2), 8.04 (1 H, d, *J* 9.2); δ_C (75 MHz; $CDCl_3$–DMSO-d_6 5 : 1) 45.6, 53.3, 109.1, 118.7, 123.2, 126.9, 132.8, 144.8, 194.2.

General procedure for the preparation of 1-([1,2,3]benzotriazol-1-yl)-3-[aryl(hetaryl)thio]acetones (9a–h)

An appropriate thiol (2 mmol) and KOH (115 mg, 2 mmol) were dissolved in 15 cm^3 of 60% EtOH at 20 °C. 1-Chloro-3-(1*H*-[1,2,3]benzotriazol-1-yl)acetone (**7**) (420 mg, 2 mmol) was added in one portion. The reaction mixture was refluxed

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overnight. Crystals of the corresponding compounds **9a**–**h** were filtered off, washed with EtOH and dried *in vacuo*.

1-([1,2,3]Benzotriazol-1-yl)-3-(phenylthio)acetone (9a). White prisms, 87%, mp 129 °C (Found: C, 63.66; H, 4.71; N, 14.87. $C_{15}H_{13}N_3OS$ requires C, 63.58; H, 4.63; N, 14.83%); δ_H(300 MHz, $CDCl_3$) 4.00 (2 H, s), 5.85 (2 H, s), 7.25–7.43 (8H, m), 8.00 (1 H, d, *J* 8.1); δ_C(75 MHz, $CDCl_3$) 40.1, 53.4, 108.8, 118.5, 122.9, 126.3, 126.6, 128.3, 128.8, 132.5, 132.8, 144.6, 196.1.

1-([1,2,3]Benzotriazol-1-yl)-3-[(4-methylphenyl)thio]acetone (9b). White prisms, 76%, mp 133 °C (Found: N, 13.72. $C_{16}H_{15}N_3OS$ requires N, 14.13%); δ_H(300 MHz, $CDCl_3$) 2.33 (3 H, s), 3.74 (2 H, s), 5.65 (2 H, s), 7.14 (3 H, d, *J* 7.9), 7.32 (2 H, d, *J* 7.9), 7.35–7.42 (2 H, m), 8.06 (1 H, d, *J* 8.1); δ_C(75 MHz, $CDCl_3$) 21.1, 42.0, 54.3, 109.2, 120.1, 124.0, 127.8, 129.4, 130.3, 131.0, 133.4, 138.2, 145.9, 196.5.

1-([1,2,3]Benzotriazol-1-yl)-3-[(4-chlorophenyl)thio]acetone (9c). White prisms, 77%, mp 135.5 °C (Found: C, 56.46; H, 3.81; N, 13.11. $C_{15}H_{12}ClN_3OS$ requires C, 56.69; H, 3.81; N, 13.23%); δ_H(300 MHz, $CDCl_3$) 3.76 (2 H, s), 5.65 (2 H, s), 7.18 (1 H, d, *J* 8.2), 7.26–7.51 (6 H, m), 8.08 (1 H, d, *J* 8.2); δ_C(75 MHz, $CDCl_3$) 41.4, 54.2, 109.0, 120.2, 124.2, 128.0, 129.6, 131.6, 131.7, 133.4, 134.0, 145.9, 196.2.

1-([1,2,3]Benzotriazol-1-yl)-3-(1-naphthylthio)acetone (9d). White prisms, 88%, mp 162 °C (Found: C, 68.11; H, 4.46; N, 12.58. $C_{19}H_{15}N_3OS$ requires C, 68.44; H, 4.54; N, 12.61%); δ_H(300 MHz, $CDCl_3$) 3.82 (2 H, s), 5.59 (2 H, s), 6.99 (1 H, d, *J* 8.2), 7.30–7.35 (2 H, m), 7.41 (1 H, t, *J* 7.9), 7.55–7.61 (2 H, m), 7.59 (1 H, d, *J* 10.4), 7.66 (1 H, d, *J* 7.1), 7.82 (1 H, d, *J* 8.2), 8.04 (1 H, d, *J* 7.2), 8.39 (1 H, d, *J* 8.2); δ_C(75 MHz, $CDCl_3$) 41.5, 54.4, 109.0, 120.1, 124.0, 124.5, 125.7, 126.7, 127.2, 127.8, 128.9, 129.3, 130.1, 130.6, 132.8, 133.4, 134.2, 145.9, 196.4.

1-([1,2,3]Benzotriazol-1-yl)-3-(2-naphthylthio)acetone (9e). White prisms, 93%, mp 126.5 °C (Found: C, 68.31; H, 4.49; N, 12.62. $C_{19}H_{15}N_3OS$ requires C, 68.44; H, 4.54; N, 12.61%); δ_H(300 MHz, $CDCl_3$) 3.88 (2 H, s), 5.67 (2 H, s), 6.99 (1 H, d, *J* 7.9), 7.22–7.34 (2 H, m), 7.41–7.52 (3 H, m), 7.72–7.83 (3 H, m), 7.85 (1 H, s), 8.02 (1 H, d, *J* 8.0); δ_C(75 MHz, $CDCl_3$) 41.3, 54.4, 109.1, 120.1, 124.1, 126.6, 127.0, 127.3, 127.4, 127.8, 127.8, 129.0, 129.3, 130.5, 132.4, 133.3, 133.6, 145.9, 196.6.

1-([1,2,3]Benzotriazol-1-yl)-3-(2-thienylthio)acetone (9f). Off-white prisms, 73%, mp 117 °C (Found: C, 53.90; H, 3.82. $C_{13}H_{11}N_3OS_2$ requires C, 53.95; H, 3.84%); δ_H(300 MHz, $CDCl_3$) 3.64 (2 H, s), 5.65 (2 H, s), 6.97–6.99 (1 H, m), 7.21 (1 H, s), 7.33–7.41 (3 H, m), 7.46–7.49 (1 H, m), 8.07 (1 H, d, *J* 8.2); δ_C(75 MHz, $CDCl_3$) 45.5, 54.4, 109.5, 120.0, 124.0, 128.0, 131.0, 131.2, 134.0, 136.0, 146.0, 196.0.

1-(Benzofuran-2-ylthio)-3-([1,2,3]benzotriazol-1-yl)acetone (9g). White prisms, 80% mp 129 °C (Found: C, 62.85; H, 4.12; N, 12.66. $C_{17}H_{13}N_3O_2S$ requires C, 63.14; H, 4.06; N, 13.00%); δ_H(300 MHz, $CDCl_3$) 3.77 (2 H, s), 5.76 (2 H, s), 6.92 (1 H, s), 7.21–7.51 (7H, m), 8.05 (1 H, d, *J* 8.2); δ_C(75 MHz, $CDCl_3$) 41.3, 54.4, 109.2, 111.0, 111.1, 113.3, 120.1, 121.0, 123.3, 124.1, 125.4, 127.9, 133.4, 145.9, 146.7, 156.5, 196.1.

1-(Benzothiophen-2-ylthio)-3-([1,2,3]benzotriazol-1-yl)-acetone (9h). White prisms, 98%, mp 165 °C (Found: C, 59.98; H, 3.63; N, 12.30. $C_{17}H_{13}N_3OS_2$ requires C, 60.16; H, 3.87; N, 12.38%); δ_H(300 MHz, $CDCl_3$) 3.78 (2 H, s), 5.65 (2 H, s), 7.21–7.27 (1 H, m), 7.31–7.40 (4 H, m), 7.42 (1 H, s), 7.68–7.77 (2 H, m), 8.06 (1 H, d, *J* 7.6); δ_C(75 MHz, $CDCl_3$) 44.1, 54.7, 109.1, 120.2, 122.0, 123.7, 124.2, 124.9, 125.4, 128.0, 130.9, 133.1, 133.4, 139.3, 142.0, 145.9, 196.0.

General procedure for the preparation of (3-thiophen-1-ylmethyl)-1-benzotriazoles (10d,e,f,h)

An appropriate 1-[areno(hetareno)-2-ylthio]-3-(benzotriazol-1-yl)acetone **9d**,**e**,**f**,**h** (1 mmol) was dissolved in hot benzene (70 cm^3) and $ZnCl_2$ (1 g) was added. The vigorously stirred reaction mixture was refluxed for 3 h (12 h for the compound **10f**), then H_2O (50 cm^3) was added and the mixture was refluxed overnight until complete dissolution of solid materials. The organic layer was separated, dried over $MgSO_4$ and filtered. Crude material obtained after removal of toluene was purified by column chromatography (SiO_2, $CHCl_3$).

1-(Naphtho[1,2-*b*]thiophen-3-ylmethyl)-1*H*-[1,2,3]benzotriazole (10d). White prisms, 76%, mp 197 °C (Found: N, 12.96. $C_{19}H_{13}N_3S$ requires N, 13.33%); δ_H(300 MHz, $CDCl_3$) 6.11 (2 H, s), 7.24–7.39 (3 H, m), 7.41 (1 H, s), 7.45–7.57 (2 H, m), 7.68 (1 H, d, *J* 8.7), 7.79 (1 H, d, *J* 8.7), 7.86 (1 H, d, *J* 7.5), 8.04 (2 H, t, *J* 8.4); δ_C(75 MHz, $CDCl_3$) 46.8, 109.7, 115.9, 119.5, 120.0, 123.3, 123.9, 124.4, 126.0, 126.1, 126.8, 127.4, 128.8, 130.4, 130.8, 132.7, 134.9, 138.6, 146.3.

2-(Naphtho[2,1-*b*]thiophen-1-ylmethyl)-1*H*-[1,2,3]benzotriazole (10e). White prisms, 86%, mp 140 °C (Found: C, 72.02; H, 4.16; N, 13.06. $C_{19}H_{13}N_3S$ requires C, 72.35; H, 4.16; N, 13.33%); δ_H(300 MHz, $CDCl_3$) 6.49 (2 H, s), 6.83 (1 H, s), 7.22–7.28 (1 H, m), 7.30–7.36 (2 H, m), 7.49–7.64 (2 H, m), 7.74 (1 H, d, *J* 8.7), 7.83 (1 H, d, *J* 8.7), 7.95 (1 H, dd, *J* 7.8, 1.2), 8.05–8.11 (1 H, m), 8.39 (1 H, d, *J* 8.4); δ_C(75 MHz, $CDCl_3$) 50.3, 109.8, 120.1, 121.0, 123.3, 124.0, 124.4, 125.3, 126.2, 126.8, 127.6, 129.2, 129.6, 131.9, 132.1, 133.1, 140.0, 146.2.

1-(Thieno[2,3-*b*]thiophen-3-ylmethyl)-1*H*-[1,2,3]benzotriazole (10f). White prisms, 42%, mp 108 °C (Found: C, 57.71; H, 3.16; N, 15.08. $C_{13}H_9N_3S_2$ requires C, 57.54; H, 3.35; N, 15.49%); δ_H(300 MHz, $CDCl_3$) 5.99 (2 H, d, *J* 0.8), 7.07 (1 H, d, *J* 5.3), 7.25–7.45 (5 H, m), 8.05 (1 H, dt, *J* 8.0, 0.9); δ_C(75 MHz, $CDCl_3$) 47.2, 109.6, 118.5, 120.1, 124.0, 126.6, 127.1, 127.5, 129.0, 132.7, 138.3, 145.0, 146.2.

1-(Thieno[2,3-*b*]benzothiophen-3-ylmethyl)-1*H*-[1,2,3]benzotriazole (10h). White prisms, 84%, mp 169.5 °C (Found: C, 63.76; H, 3.27; N, 13.06. $C_{17}H_{11}N_3S_2$ requires C, 63.52; H, 3.46; N, 13.08%); δ_H(300 MHz, $CDCl_3$) 6.24 (2 H, s), 7.06 (1 H, s), 7.30–7.42 (5 H, m), 7.79 (1 H, d, *J* 7.7), 8.05 (2 H, d, *J* 7.1); δ_C(75 MHz, $CDCl_3$) 47.7, 109.8, 120.1, 121.5, 123.3, 124.0, 124.3, 124.9, 126.2, 127.5, 128.8, 132.1, 132.9, 138.9, 139.6, 143.9, 146.4.

1-(1-Naphtho[2,1-*b*]thiophen-1-yl-2-phenylethyl)-1*H*-[1,2,3]-benzotriazole (13)

To a stirred solution of naphthothiophene **10e** (315 mg, **1** mmol) in THF (20 cm^3) *n*-BuLi (1.5 M, 0.66 cm^3, **1** mmol) was added under argon at −78 °C. After 2 h, benzyl chloride (126 mg, 1 mmol) was added. The mixture was stirred at −78 °C for an additional 3 h and was allowed to warm to rt overnight. After removal of the solvent, Et_2O (100 cm^3) was added and the mixture was washed with H_2O (2 × 10 cm^3), dried over $MgSO_4$ and filtered. The residue formed after removal of Et_2O was separated on a column (SiO_2, $CHCl_3$) to give compound **13b** (308 mg, 76%) as white prisms, mp 186 °C (Found: N, 9.97. $C_{26}H_{19}N_3S$ requires N, 10.36%); δ_H(300 MHz, $CDCl_3$) 3.93 (1 H, dd, *J* 3.8, 14.5), 4.24 (1 H, dd, *J* 10.7, 14.5), 7.06–7.32 (9H, m), 7.51 (1 H, s), 7.55 (1 H, d, *J* 7.6), 7.63 (1 H, t, *J* 7.9), 7.76 (1 H, d, *J* 8.6), 7.86 (1 H, d, *J* 8.6), 7.94–8.05 (2 H, m), 8.62 (1 H, d, *J* 8.35); δ_C(75 MHz, $CDCl_3$) 40.9, 61.6, 109.7, 120.0, 121.2, 123.3, 123.9, 124.7, 125.2, 126.2, 126.8, 127.0, 127.3, 128.6, 128.8, 129.3, 129.5, 131.6, 132.1, 133.1, 136.6, 136.9, 140.0, 146.1.

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1-[(*E*)-2-Phenylethenyl]naphtho[2,1-*b*]thiophene (14)

To a stirred solution of naphthothiophene **10e** (315 mg, 1 mmol) in THF (20 cm^3) *n*-BuLi (1.5 M, 0.66 cm^3, 1 mmol) was added under argon at −78 °C. After 2 h, benzyl chloride (126 mg, 1 mmol) was added. The mixture was stirred at −78 °C for an additional 3 h and allowed to warm to rt overnight. Then, *t*-BuOH (20 cm^3) and *t*-BuOK (1 g) were added and the mixture was refluxed for 48 h. After removal of solvents *in vacuo*, Et_2O (100 cm^3) was added and the mixture was washed with H_2O (2 × 10 cm^3), dried over $MgSO_4$ and filtered. The residue formed after removal of Et_2O was purified on a column (SiO_2, ethyl acetate–hexanes = 1 : 7) to give pure compound **14** (160 mg, 56%) as slowly solidified brown oil, mp 72 °C (Found: C, 83.50; H, 4.70. $C_{20}H_{14}S$ requires C, 83.87; H, 4.94%); δ_H(300 MHz, $CDCl_3$) 7.02 (1 H, d, *J* 15.7), 7.30–7.37 (2 H, m), 7.43 (2 H, t, *J* 7.2), 7.51 (1 H, s), 7.75 (1 H, dd, *J* 1.7, 6.4), 7.61 (2 H, d, *J* 7.8), 7.72 (1 H, s), 7.76 (1 H, d, *J* 5.1), 7.85 (1 H, d, *J* 8.8), 7.92–7.97 (1 H, m), 8.62 (1 H, d, *J* 8.2); δ_C(75 MHz, $CDCl_3$) 121.0, 122.8, 124.1, 125.1, 125.3, 125.6, 126.3, 126.6, 127.9, 128.7, 128.8, 130.3, 131.7, 131.9, 132.7, 137.2, 138.0, 138.9.

***N*-(1-Naphthyl)-2-thieno[2,3-*b*][1]benzothiophen-3-ylethanethioamide (15)**

To a stirred solution of benzothiophene **10h** (321 mg, 1 mmol) in THF (20 cm^3), *n*-BuLi (1.5 M, 0.66 cm^3, 1 mmol) was added under argon at −78 °C. After 2 h, 1-naphthyl isothiocyanate (185 mg, 1 mmol) was added. The mixture was stirred at −78 °C for an additional 3 h and was allowed to warm to rt overnight. To the mixture AcOH (10 cm^3) and Zn powder (1 g) were added and the mixture was refluxed for 72 h. Then, Et_2O (100 cm^3) was added and the mixture was washed with H_2O (2 × 10 cm^3) and 10% $NaHCO_3$ (6 × 10 cm^3), dried over $MgSO_4$ and filtered. The residue formed after removal of Et_2O was purified on a column (SiO_2, ethyl acetate–hexanes = 1 : 5) to give 207 mg (53%) of pure compound **15**, yellow prisms, mp 223 °C (Found: C, 68.10; H, 3.68, N, 3.59. $C_{22}H_{15}NS_3$ requires C, 67.83; H, 3.88, N 3.60%); δ_H(300 MHz, $CDCl_3$) 4.45 (2 H, s), 7.10–7.34 (6 H, m), 7.38 (1 H, s), 7.54 (1 H, d, *J* 8.2), 7.64 (1 H, d, *J* 7.9), 7.70 (1 H, d, *J* 8.2), 7.76 (1 H, d, *J* 7.9), 8.03 (1 H, d, *J* 7.9), 11.64 (1 H, br s); δ_C(75 MHz, $CDCl_3$) 45.4, 121.7, 122.8, 123.6, 124.1, 124.2, 124.6, 125.1, 125.7, 126.4, 126.4, 127.2, 127.7, 128.3, 128.8, 131.0, 132.5, 133.8, 135.9, 137.8, 140.0, 143.6, 202.7 and compound **16** (see below).

***N*-(2-Thieno[2,3-*b*][1]benzothiophen-3-ylethyl)naphthalen-1-amine (16)**

Yield 97 mg (27%), yellow oil; δ_H(300 MHz, $CDCl_3$) 3.49 (2 H, t, *J* 6.7), 3.72 (2 H, t, *J* 6.7), 4.49 (1 H, br s), 6.66 (1 H, d, *J* 7.6), 7.10 (1 H, s), 7.23 (1 H, d, *J* 9.3), 7.29–7.46 (5 H, m), 7.66 (1 H, d, *J* 8.3), 7.79 (1 H, d, *J* 8.7), 7.82 (1 H, d, *J* 7.8), 8.04 (1 H, d, *J* 7.8); δ_C(75 MHz, $CDCl_3$) 29.4, 43.1, 104.5, 117.6, 119.8, 121.0, 123.4, 123.6, 124.0, 124.6, 124.6, 124.7, 125.7, 126.5, 128.6, 132.9, 133.4, 134.2, 138.8, 140.0, 143.0, 144.1; *m*/*z* (EI) 360.0850 (M^+). $C_{22}H_{18}NS_2$ requires 360.0881.

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