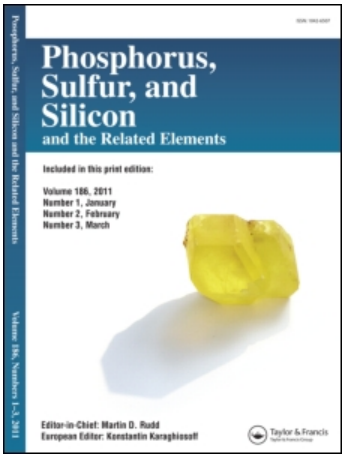

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PREPARATION OF 3,4-DISUBSTITUTED BENZO[*B*]THIOPHENES FOR USE IN THIA-ERGOLINE SYNTHESIS

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Synthetic methods for the preparation of 3,4-disubstituted benzo[*b*]thiophenes of potential use in the synthesis of thia-ergolines are described. Substituents were introduced at C-4 by reaction of the triflate derivative of 4-hydroxybenzo[*b*]thiophene with 1,1-dimethylbut-3-enol and but-3-enone using Heck-type methodology. Reaction sequences were developed to introduce a 3-(ethylnitro) side chain into the 4-triflate derivative and to apply the Heck methodology on the product to prepare 4-(4′-(3′-(2″-nitroethyl)-benzo[*b*]thienyl))2-methyl-3-buten-2-ol **4**, a compound appropriately substituted at the 3- and 4- positions for elaboration into a thia-ergoline derivative. Cyclization of **4** did not give the expected tricyclic product but treatment of **4** with Et_3N in either Ac_2O or PhNCO lead to (9b,9aa-H)-4,6,9,9a-tetrahydro-9-(1′-hydroxy-1′methylethyl)benzo[*b*]-thiopheno[4,3-ef][2,1]benziso-xaline, **10**.

Keywords: Benzo[*b*]thiophene; synthesis; Heck reactions

INTRODUCTION

Several studies have been published[1] in which the overall goal was to synthesize sulfur analogues (**1a**) of ergoline alkaloids (**1b**). A variety of strategies have been employed starting from either benzothiophene or naphthalene derivatives but none have achieved the target tetracyclic structure. Very few attempts have utilized naphthalene derivatives as the correctly substituted compounds are difficult to obtain. In addition, selective saturation of one of the naphthalene rings is required at some stage of the synthesis. Most attempts have utilized ben-

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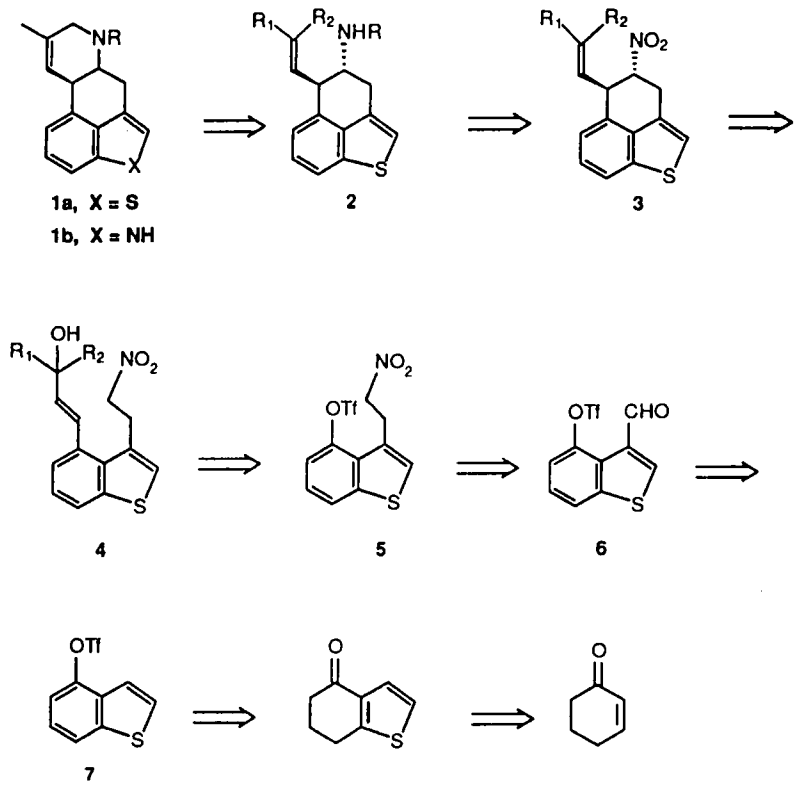
zothiophene derivatives, in spite of the fact that the required 3,4-disubstituted derivatives cannot be prepared by standard substitution reactions on the parent nucleus. Recently, we have re-examined some earlier studies on bromination of benzothiophene derivatives to determine if modified conditions could lead to appropriately substituted compounds. Although interesting, these studies did not lead to derivatives useful for the synthesis of thia-ergolines and are detailed elsewhere.[2] In this paper, we report the synthesis of 3,4-disubstituted compounds using Heck-type coupling reactions to introduce desired functional groups at C-4. These reactions add to the few examples of successful Pd-mediated coupling reactions reported with organosulfur compounds.[3] Although this approach has its limitations, we have succeeded in making several new 3,4-disubstituted benzothiophenes and in elaborating some of these derivatives to tetracyclic compounds, which, although are not completely analogous to ergolines, have interesting structures in relation to these biologically active molecules.

RESULTS AND DISCUSSION

Our general approach to thia-ergolines is illustrated in Scheme 1. Two key aspects of this scheme are the introduction of a formyl group at C-3 and Heck-type coupling to introduce appropriate substituents into C-4 substituted benzothiophenes. Previous studies indicate that it should be possible to introduce a formyl group at C-3 when a bulky electron donating substituent is already in place at C-4.[4] With less bulky electron donating substituents at C-4, electrophilic substitution normally occurs at C-5.[5] A key aspect of this scheme is utilization of Heck reactions with organosulfur compounds. At present, there are few examples of the use of such chemistry with sulfur compounds.[3] Consequently, conditions for carrying out these transformations had to be established along with the order of introduction of the formyl group at C-3 and elaboration of that substituent. Our initial thrust was to determine the general applicability of the Pd- catalyzed insertion of alkenes into 4-substituted benzothiophenes.

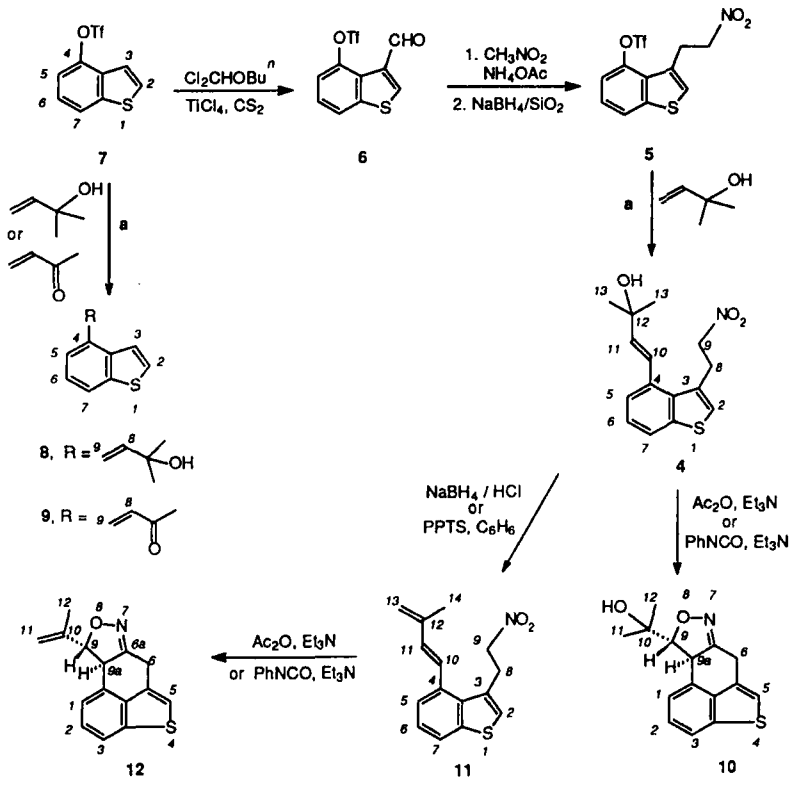
Both aromatic halides and triflates have been used successfully for Pd-catalyzed alkene insertion.[6] Since 4-halo-substituted benzothiophenes are available only by multi-step syntheses,[5] we opted to utilize the triflate **7**, which is made readily from 4-hydroxybenzothiophene, which itself, is reasonably accessible from cyclohex-2-enone.[7] Conversion of 4-hydroxybenzothiophene using Tf_2O and NaH gave only moderate yields (69%) of **7** but use of pyridine in place of NaH resulted in excellent (91%) isolated yields. Initial attempts to react **7**



SCHEME 1 Synthetic scheme for preparation of thia-ergolines.

with 2-methyl-3-buten-2-ol using either $Pd(PPh_3)_2Cl_2$ or $Pd(PPh_3)_4$ resulted in only very poor conversion to the desired product. However, use of $Pd(OAc)_2$ and tri-*o*-tolylphosphine as co-ligand resulted in **8** being formed in 21% isolated yield (Scheme 2). Use of LiCl (3 equivalents), which is thought to produce a reactive Pd-coordinated chloro-derivative by displacement of the triflate, increased the isolated yield of **8** to 98%. Using the same conditions, high conversion (82%) of the triflate to **9** by reaction with methyl vinyl ketone was achieved. NMR spectra of both **8** and **9** showed that the products contained the double bond in the *trans* arrangement (J = 16.0 and 16.1 Hz for **8** and **9** respectively).

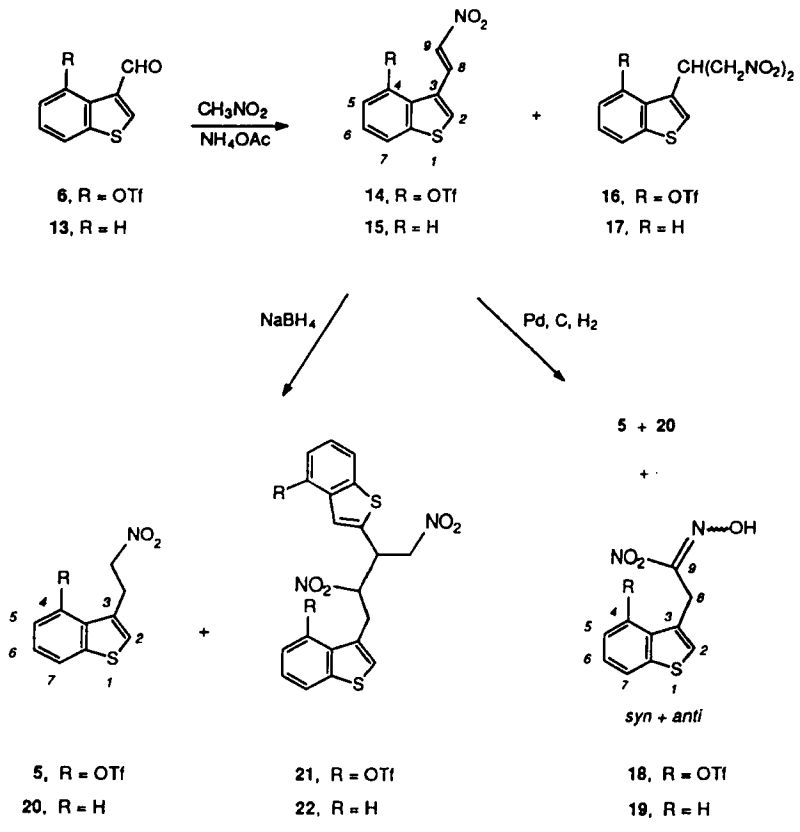
The next step in the overall synthesis was to confirm that formylation of 4-substituted benzothiophenes did occur at C-3. Rieche formylation of the triflate **7** in CS_2 did not proceed to completion, but reaction of **7** with excess dichloromethyl *n*-butyl ether and $TiCl_4$ (5 equivalents of each) resulted in the formation of one major product (>90%), **6**, along with traces of another formy-



a: $Pd(OAc)_2$, (*o*-tolyl)$_3$P, DMF, Et_3N, LiCl, 120°C, ca. 1h

SCHEME 2 Synthesis of tetracyclic benzothienyliso-oxazoles.

lated product (3%). Both products were isolated, but their NMR spectra did not prove conclusively whether the formyl group had entered the 2- or 3-position for the major product. However, reduction of the major product to the corresponding alcohol and comparison of its spectral data to literature values[4b),8] of the 2- and 3-methanol derivatives, both of which are known compounds, confirmed that formylation had occured at C-3. Nitro-aldol condensation of **6** gave the unsaturated nitro-compound **14** and small quantities of a by-product **16** arising from 1,4-addition of a second nitromethane anion (Scheme 3). Scale-up of this reaction proved troublesome, but careful monitoring of both the reaction time and use of 0.72 mol. equiv. of NH_4OAc enabled 81% of **14** to be obtained from



SCHEME 3 Nitroethylation of benzothiophenes.

a 5g scale reaction. Using an equivalent reaction sequence, benzothiophene was converted to the nitro-alkene **15**, along with **17** as a by-product. **15** was used to establish reaction conditions for the reduction of the double bond of **14**.

Our first attempt to synthesise the nitro-alkane **5** from **14** utilized standard hydrogenation conditions over a Pd/C catalyst. **5** was obtained in only low yield with the aldoxime **18** being formed as the major product. Analysis of the NMR spectra of **18** showed that both the *syn*- and *anti*-isomers were formed with the *anti*-isomer produced as the major product. Likewise, Pd/C catalysed hydogenation of the unsubstituted nitro-alkene **15** resulted in the *anti*-aldoxime **19** as the major product with the *syn*-isomer and the nitro-alkane **20** being formed as minor products. Reduction of the triflate-substituted nitro-alkene **14** with $NaBH_4$ in methanol gave low yields of the desired nitro-alkane **5** along with the dimer **21** as the major product. Similarly, the dimeric compound **22** was the major

product obtained from reduction of **15** under the same conditions. The dimeric products are not entirely unexpected as it is known that the intermediate nitronate salts of nitro-alkene reductions act as Michael donors and react with the nitro-alkene, a Michael acceptor. In some cases, this unwanted side-reaction can be eliminated by use of water as co-solvent which provides the necessary proton to favor nitro-alkane formation. However, use of water in this work, although improving the yield of **20** to 52%, did not limit dimer formation satisfactorily. A methanol/water co-solvent also improved conversion of **14** to **5** (54%) but did not eliminate dimer formation.

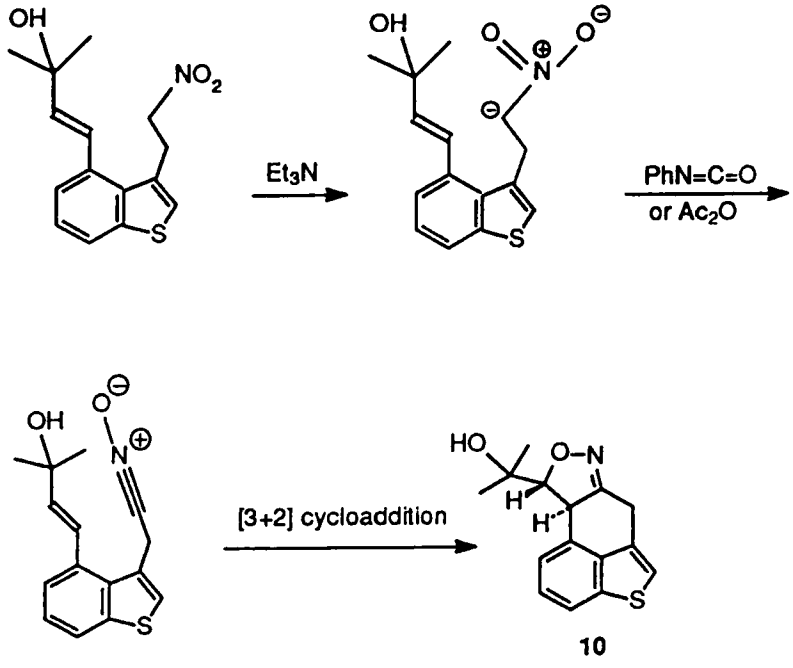
Borchardt and co-workers[9] utilized silica gel in $NaBH_4$ mediated nitro-alkene reductions with the rationale that the reduction would occur at the surface and that SiOH groups would transfer a proton to the intermediate nitronate salts thus preventing dimer formation. Application of this method was very successful in this work as it enabled conversion of **15** and **14** to the corresponding nitro-alkanes, **20** and **5**, in 76 and 95% respectively when silica was used with a chloroform/2-propanol solvent mixture.

Palladium catalyzed insertion of 2-methyl-3-buten-2-ol into compound **5** using the conditions established earlier afforded the nitroalkenol **4** in high yield (84%). This compound contains all of the necessary functional groups for cyclization to thia-ergoline derivatives. Using methodology developed by Somei and co-workers for cyclization of an analogous indole derivative,[10] compound **4** was treated sequentially with $NaBH_4$ and 2N HCl. Instead of obtaining the required tricyclic nitro-alkene **3** (Scheme 1), the diene **11** was recovered in good yield (85%) (Scheme 2). Alternatively, when a catalytic amount of HCl was used after $NaBH_4$ treatment, the methyl-ether of **4** was obtained, presumably by reaction of the intermediate carbocation with the solvent. Application of other bases in place of $NaBH_4$ also failed to produce the tricyclic product **3**.

An interesting reaction occurred on treatment of the nitro-alkenol **4** with Ac_2O and Et_3N. It was hoped that protection of the alcohol as the acetate would enhance the formation of the necessary anion adjacent to the $-NO_2$ substitutent and thus facilitate cyclization. However, these reagents converted the nitro-alkenol **4** to the isoxazoline derivative **10** in a high yielding (91%), clean reaction. The identity of this compound was established from its spectral data. In the IR spectrum, bands were seen for the $-OH$ group (3322 cm^{-1}) and for the C=N bond (1644 cm^{-1}) but bands for the $-NO_2$ group were absent. A variety of couplings, confirmed by irradiation experiments, were noted in the ^1H NMR spectrum. These included geminal coupling (J = 17.2 Hz) between H-6a and H-6b, allylic coupling of H-6a to H-5 and a W-J^4 coupling of H-6a to H-9a (J = 1.5 Hz). The resonance for H-6b showed only the geminal coupling. The coupling between H-9a and H-9b was somewhat smaller than expected (J = 7.9

Hz), but these hydrogens are concluded to be *trans* to one another based on the W-J^4 coupling of H-9a to H-6a. Mass spectra and microanalytical data were consistent with the proposed structure of **10**.

Very few examples of a cyclization of this type using Ac_2O have been reported[11,12], but similar cyclizations have been reported by reaction of nitro-alkenes with phenylisocyanate and Et_3N.[13] Treatment of the nitro-alkenol **4** with these reagents resulted in the same isoxazoline derivative **10** in yields very similar to those obtained using Ac_2O. Likewise, treatment of the nitro-diene **11** with phenylisocyanate resulted in conversion to the isoxazoline derivate **12** in 94% isolated yield. **12** could also be obtained by treatment of **11** with Ac_2O although in somewhat lower yield (69%). The phenylisocyanate and Ac_2O mediated cyclizations likely proceed by similar mechanisms. In one case, the "electrophilic carbonyl carbon" of the isocyanate reacts with the anion, whereas with Ac_2O, reaction occurs at the anhydride C=O with loss of acetate. Subsequent intramolecular cycloaddition to the double bond, either stepwise as shown in Scheme 4, or, perhaps *via* an intermediate nitrile-oxide, results in the isoxazoline.



SCHEME 4 Possible mechanistic pathway to benzothienyliso-oxazoles.

To date, further attempts to utilize derivatives such as **4** or the isoxazolines **10** and **12** for the synthesis of thia-ergoline derivatives have met with no success. However, the introduction of complex substituents at the 3,4-positions of the benzothiophene system using Heck-type methodology give some hope that this strategy will lead to interesting and useful compounds.

EXPERIMENTAL SECTION

Reagents, Materials and General Methods

Organic, inorganic reagents and solvents were purchased from standard chemical suppliers and were used as received if purities were >99%. In experiments requiring anhydrous, high purity solvents, these materials were prepared according to the methods described by Perrin and Amarego.[14]

Nmr spectra were obtained on either a Bruker ACE-200 or Bruker AM-400 spectrometer in $CDCl_3$ solution unless stated otherwise. Numbering sequences used for description of coupling information are given in the Schemes. Mass spectra were obtained using a Kratos MS-80 RFA instrument. IR spectra were recorded using a Nicolet 5DX instrument as thin films (neat) or as KBr pellets. Microanalytical data were obtained by Mrs D. Fox in the chemical analytical laboratories of The University of Calgary. Flash column chromatography was performed using grade 60 (230–400 mesh) silica gel (Aldrich Chemical Company) and preparative thin layer chromatography was conducted using commercial plates (Analtech and Sigma Chemical Company). Ethyl acetate 10% in hexanes was used as eluent unless stated otherwise.

Preparations of 6,7-dihydro-5H-benzo[b]thiophen-4-one and 4-Hydroxybenzo[b]-thiophene. These compounds were prepared from cyclohex-2-enone in an overall 50% yield using procedures similar to those reported by Napier and coworkers.[7]

4-Trifluoromethylsulphonyloxybenzo[b]thiophene (7). Trifluoromethanesulphonic anhydride (7.20 mL, 42.8 mmol) was added by syringe to a stirred solution of the phenol (5.13 g, 34.1 mmol) in freshly distilled pyridine (140 mL) under Ar at −20°C. After 10 minutes, the pink coloured solution was allowed to warm to room temperature and was stirred for an additional 1.5 hours. The organic solution was added to ether (600 mL) and was extracted with 5% aqueous HCl (8 × 50 mL), 5% NaOH (3 × 50 mL), brine (1 × 100 mL) and dried ($MgSO_4$). The solvent was evaporated *in vacuo* and the residue was distilled to give a clear

liquid 7, 8.78g (91%), b.p. 75°–78°C/0.03 torr. IR (neat) cm^{-1} 3113(CH), 1321 (SO_2), 1211 (CF_3), 1140 (SO_2); ^1H NMR (400 MHz) 7.90 (ddd, 1H, $J_{7,6}$ = 8.0 Hz, $J_{7,5}$ = 0.8 Hz, $J_{7,3}$ = 0.5 Hz, H-7), 7.60 (br.d, 1H, $J_{2,3}$ = 5.7 Hz, H-2), 7.48 (dd, 1H, $J_{3,2}$ = 5.7 Hz, $J_{3,7}$ = 0.5 Hz, H-3), 7.40 (dd, 1H, $J_{6,5}$ = 7.9 Hz, Hz, $J_{6,7}$ = 8.0 Hz, H-6), and 7.33 (dd, 1H, $J_{5,6}$ = 7.9 Hz, $J_{5,7}$ = 0.8 Hz, H-5); ^{13}C NMR (50 MHz) 144.1 (Cq), 142.6 (Cq) and 132.7 (Cq), 128.9 (CH), 124.7 (CH), 122.6 (CH), 119.2 (CH), 118.8 (q, $J_{C\text{-}F}$ = 320 Hz, CF_3), and 116.4 (CH); MS m/e 282 (37, $M^{\cdot+}$), 149 (100, M-[SO_2 CF_3]); Analysis calcd. for $C_9H_5F_3O_3S_2$: C 38.30, H 1.79, S 22.72%; found: C 38.06, H 1.72, S 22.60%.

Alternatively, a solution of the phenol (0.30 g, 2.0 mmol) in anhydrous ether (4 mL) was added dropwise to a stirred suspension of sodium hydride (0.048 g, 2.0 mmol) in ether at 0°C under Ar. After 10 minutes, trifluoromethanesulphonic anhydride (0.592 g,·2.1 mmol) in anhydrous ether (5 mL) was added slowly by syringe. The mixture was then heated at reflux for 1 hour. Water (15 mL) was added and the organic layer was separated. The aqueous phase was extracted with ether (2 × 5 mL) and the combined organic extracts were washed with 5% NaOH (2 × 5 mL), water (1 × 10 mL), brine (1 × 15 mL) and dried ($MgSO_4$). After filtration of the reaction mixture, the solvent was evaporated *in vacuo* and the residue was purified by distillation to give 0.39 g (69%) of the triflate **7**, b.p. 75°–78°C/0.03 torr. Re-acidification of the basic extracts with the usual work up afforded 0.88 g (29%) of unreacted phenol.

3-Carboxaldehydebenzo[b]thiophene (13). **13** was prepared using a modification of the procedure reported by Buu-Hoi.[4c] Dichloromethyl *n*-butyl ether[4a] (12.40 g, 77 mmol) was added dropwise over 30 minutes to an ice cold solution of benzo[*b*]thiophene (10.80 g, 80 mmol) and titanium tetrachloride (30 mL, 274 mmol) in anhydrous carbon disulphide (200 mL) under Ar. After 2 hours, concentrated HCl (10 mL) was added and the mixture taken up into chloroform (150 mL). The organic solution was washed with water (2 × 100 mL), saturated $NaHCO_3$ (2 × 30 mL), brine (1 × 100 mL) and was dried ($MgSO_4$). The solvent was evaporated *in vacuo* and the residue was purified by flash chromatography to give 6.86 g (55%) of aldehyde **13**. Crystallization of the crude product from hexanes (charcoal) yielded a white solid, m.p. 56°–57°C [Lit. 58°C[4c]]. IR (neat) cm^{-1} 1684 (C═O); ^1H NMR (200 MHz) 10.15 (s, 1H, H-8), 8.67 (m, 1H, H-7), 8.32 (s, 1H, H-2), 7.87 (m, 1H, H-4), and 7.49 (m, 2H, H-5, H-6).

4-(4'-Benzo[b]thienyl)-2-methyl-3-buten-2-ol (8). To a solution of the triflate **7** (56.5mg, 0.2 mmol) in DMF (4 mL) under Ar at room temperature were added, sequentially, triethylamine (84 μL, 0.6 mmol), 2-methyl-3-buten-2-ol (146 μL,

1.4 mmol), tri-*o*-tolylphosphine (6.1 mg, 0.02 mmol), lithium chloride (25.4 mg, 0.6 mmol) and $Pd(OAc)_2$ (3.6 mg, 0.016 mmol). The resulting solution was stirred at 120°C for 45 minutes and then was cooled to room temperature. Dichloromethane (25 mL) was added and the resulting mixture was washed with 5% aqueous HCl (1 × 10 mL), water (1 × 15 mL) and brine (1 × 25 mL), and was dried ($MgSO_4$). The solvent was evaporated *in vacuo* and the residue was purified by flash chromatography (20% EtOAc in hexanes) to afford 43 mg (98%) of the alcohol **8**. The crude product was recrystallized from hexanes to yield a pale yellow solid, m.p. 85°–86°C. IR (neat) cm^{-1} 3387 (OH); ^1H NMR (400 MHz) 7.79 (br.d, 1H, $J_{7,6}$ = 8.0 Hz, H-7), 7.58 (dd, 1H, $J_{3,2}$ = 5.6 Hz, $J_{3,7}$ = 0.6 Hz, H-3), 7.49 (d, 1H, $J_{5,6}$ = 7.4 Hz, H-5), 7.48 (d, 1H, $J_{2,3}$ = 5.6 Hz, H-2), 7.33 (dd, 1H, $J_{6,7}$ = 8.0 Hz, $J_{6,5}$ = 7.4 Hz, H-6), 7.12 (d, 1H, $J_{8,9}$ = 16.0 Hz, H-8), 6.47 (d, 1H, $J_{8,9}$ = 16.0 Hz, H-9), 1.60 (br.s, 1H, OH), and 1.50 (s, 6H, 2 × CH_3); ^{13}C NMR (50 MHz) 139.8 (CH =), 137.8 (Cq), 132.5 (Cq), 126.3 (CH), 124.3 (CH), 123.7 (CH), 121.6 (CH), 121.5 (CH), 120.9 (CH), 120.9 (Cq), 71.3 (C-OH), and 30.0 (2 × CH_3); MS m/e 218 (61, $M^{\cdot+}$), 203 (52, M-[H_2O]); Analysis calcd. for $C_{13}H_{14}OS$: C 71.52, H 6.46%; found: C 71.22, H 6.09%.

4-(4'-Benzo[b]thienyl)-3-buten-2-one (9). To a solution of the triflate **7** (254 mg, 0.9 mmol) in DMF (20 mL) under Ar at room temperature were added, sequentially, triethylamine (376 μL, 2.7 mmol), methyl vinyl ketone (449 μL, 5.4 mmol), tri-*o*-tolylphosphine (27.2 mg, 0.072 mmol), lithium chloride (114 mg, 2.7 mmol) and $Pd(OAc)_2$ (16.2 mg, 0.09 mmol). The resulting solution was stirred at 120°C for 1 hour and then was cooled to room temperature. Dichloromethane (100 mL) was added and the resulting mixture was washed with 5% aqueous HCl (1 × 20 mL), water (1 × 50 mL) and with brine (1 × 50 mL), and was dried ($MgSO_4$). The solvent was evaporated *in vacuo* and the residue was purified by flash chromatography (20% EtOAc in hexanes) to afford 149 mg, (82%) of the methyl ketone **9**. The product was recrystallized from hexanes to yield a pale yellow solid, m.p. 77°–78°C. IR (neat) cm^{-1} 3104 (CH), 1667 (C═O), 1607 (C═C); ^1H NMR (400 MHz) 8.07 (d, 1H, $J_{8,9}$ = 16.1 Hz, H-8), 7.94 (br.dd, 1H, $J_{7,6}$ = 8.1 Hz, $J_{5,7}$ = 1.0 Hz, H-7), 7.67 (dd, 1H, $J_{5,6}$ = 7.5 Hz, $J_{5,7}$ = 1.0 Hz, H-5), 7.66 (dd, 1H, $J_{3,2}$ = 5.5 Hz, $J_{3,7}$ = 0.8 Hz, H-3), 7.60 (d, 1H, $J_{2,3}$ = 5.5 Hz, H-2), 7.39 (dd, 1H, $J_{6,7}$ = 8.1 Hz, $J_{6,5}$ = 7.5 Hz, H-6), 6.87 (d, 1H, $J_{9,8}$=16.1 Hz, H-9), and 2.45 (s, 3H, CH_3); ^{13}C NMR (100 MHz) 198.0 (C═0), 140.8 (Cq), 140.3 (CH), 138.8 (Cq), 129.6 (Cq), 128.2 (CH), 128.0 (CH), 124.5 (CH), 124.3 (CH), 122.7 (CH), 121.2 (CH), and 28.0 (CH_3); MS m/e 202 (75, $M^{\cdot+}$), 187 (100, M-[CH_3]); Analysis calcd. for $C_{12}H_{10}OS$: C71.26, H 4.98%; C 71.20, H 4.82%.

3-Carboxaldehyde-4-trifluoromethylsulphonyloxybenzo[b]thiophene (6). Dichloromethyl *n*-butyl ether (11.96 g, 76.2 mmol) was added dropwise over 5 minutes to an ice-cooled stirred solution of the triflate **7** (4.30 g, 15.2 mmol) and titanium tetrachloride (8.35 mL, 76.2 mmol) in CH_2Cl_2 (150 mL) under Ar. After 10 minutes, the mixture was allowed to warm to room temperature and was stirred for an additional 1.5 hours. A mixture of ice (50 g) and concentreated HCl (20 mL) was added and the resultant mixture was stirred vigorously for 15 minutes. The organic layer was washed with saturated $NaHCO_3$ (2 × 30 mL), water (3 × 60 mL) and brine (1 × 100 mL), and was dried ($MgSO_4$). After filtration of the reaction mixture, the solvent was evaporated *in vacuo* and the residue was purified by flash chromatography to yield 0.09 g (2%) of recovered starting material **7**, 0.14 g (3%) of the 2-aldehyde and 4.25 g (94%) of the 3-aldehyde **6**.

The 2-isomer was recrystallized from hexanes (charcoal) to afford colourless plates, m.p. 89°–90°C. IR (neat) cm^{-1} 1673 (C═O), 1131 (SO_2); ^1H NMR (400 MHz) 10.16 (s, 1H, CHO), 8.12 (d, 1H, $J_{3,7}$ = 0.5 Hz, H-3), 7.93 (d, $J_{7,6}$ = 8.2 Hz, H-7), 7.59 (dd, 1H, $J_{6,7}$ = 8.2 Hz, $J_{6,5}$ = 7.9 Hz, H-6), and 7.40 (d, 1H, $J_{5,6}$ = 7.9 Hz, H-5); ^{13}C NMR (50 MHz) 183.3 (CHO), 144.5 (Cq), 143.8 (Cq), 139.5 (CH), 135.4 (Cq), 128.3 (Cq), 125.9 (CH), 123.3(CH), 118.6 (q, J_{C-F}═321 Hz, CF_3), and 118.6 (CH); MS m/e 310 (40, $M^{\cdot+}$), 177 (100, M-[SO_2CF_3]); Analysis calcd. for $C_{10}H_5F_3O_4S$: C 38.71, H 1.62%; found C 38.89, H 1.29%; Exact mass calcd. for $C_{10}H_5F_3O_4S$: 309.9581; found: 309.9568.

The 3-isomer **6** was recrystallized from hexanes (charcoal) to afford colourless plates, m.p. 63.5°–64.5°C. IR (neat) cm^{-1} 1694 (C═O), 1319 and 1138 (SO_2); ^1H NMR (400 MHz) 10.41 (s, 1H, CHO), 8.57 (s, 1H, H-2), 7.96 (dd, 1H, $J_{7,6}$ = 7.1 Hz, $J_{7,5}$ = 1.9 Hz, H-7), and 7.53 (m, 2H, H-5, H-6); ^{13}C NMR (50 MHz) 184.0 (CHO), 145.3 (Cq), 145.2 (Cq), 144.7 (Cq), 132.1 (Cq), 128.6 (CH), 128.5 (CH), 123.5 (CH), 118.7 (q, J_{C-F} = 321 Hz, CF_3), and 117.4 (CH); MS m/e 310 (44, $M^{\cdot+}$), 177 (100, M-[SO_2CF_3]); Analysis: C 38.71, H 1.62%; found: C 38.89, H 1.29%; Exact mass calcd. for $C_{10}H_5F_3O_4S$: 309.9581; found: 309.9570.

3-Hydroxymethyl-4-hydroxybenzo[b]thiophene. A solution of the 3-aldehyde **6** (78 mg, 0.025 mmol) in anhydrous ether (2 mL) was added dropwise over 5 minutes to a stirred suspension of lithium aluminum hydride (19 mg, 0.5 mmol) in anhydrous ether (4 mL) under Ar at room temperature. After 15 minutes, water was added carefully and the pH of the solution was adjusted to 8 with 5% aqueous NaOH. The organic layer was separated and the aqueous phase was extracted with ether (3 × 5 mL). The combined organic extracts were washed with water (2 × 5 mL), brine (1 × 10 mL) and were dried ($MgSO_4$). After

filtration of the reaction mixture, the solvent was evaporated *in vacuo* and the residue was purified by preparative thin layer chromatography (25% EtOAc in hexanes) yielding 41mg (91%) of 3-hydroxymethyl-4-hydroxybenzo[b]thiophene. Recrystallization from acetone/chloroform to afforded a white solid, m.p. 118–122°C [Lit. 121°–122°C[4(b)]]. IR (neat) 3443 (OH); ^{1}H NMR (200 MHz) CD_3OH, 7.31 (dd, 1H, $J_{7,6}$ = 8.1 Hz, $J_{7,5}$ = 0.8 Hz, H-7), 7.24 (br.s, 1H, H-2), 7.15 (dd, 1H, $J_{6,7}$ = 8.1 Hz, $J_{6,5}$ = 7.8 Hz, H-6), 6.73 (dd, 1H, $J_{5,6}$ = 7.8 Hz, $J_{5,7}$ = 0.8 Hz, H-5), and 4.91 (br.s, 2H, H-8).

1-(3'-Benzo[b]thienyl)-2-nitroethene (15). **15** was prepared using a modification of the procedure reported by Campaigne and co-workers[15]. A solution of the 3-aldehyde **13** (0.75 g, 4.62 mmol) and ammonium acetate (0.34 g, 4.62 mmol) in freshly distilled nitromethane (15 mL) was heated at reflux for 1 hour under Ar. The solvent was evaporated *in vacuo*. The yellow-orange residue was triturated with warm absolute alcohol forming yellow crystals of compound **15**, 0.84 g (88%), m.p. 110°–112°C [Lit. 112°C–113°C[15]]. IR (neat) cm^{-1} 1510 and 1327; ^{1}H NMR (200 MHz) 8.31 (dd, 1H, $J_{8,9}$ = 13.7 Hz, $J_{8,2}$ = 0.5 Hz, H-8), 7.99–7.91 (m, 2H, H-4, H-7), 7.96 (s, 1H, H-2), 7.35(d, 1H, $J_{9,8}$ = 13.7 Hz, H-9), and 7.51 (m, 2H, H-5, H-6); ^{13}C NMR (50 MHz) 140.5 (Cq), 136.7 (CH), 136.4 (Cq), 132.8 (CH), 131.0 (CH), 122.1 (Cq), 125.7 (2CH), 123.3 (CH), and 122.0 (CH); MS m/e 205 ($M^{\cdot+}$).

1-(3'-(4'-Trifluoromethylsulphonyloxybenzo[b]thienyl))-2-nitroethene (14). A solution of the triflate-aldehyde **6** (1.84 g, 5.93 mmol) and ammonium acetate (0.33 g, 4.28 mmol) in freshly distilled nitromethane (35 mL) was heated at reflux for 45 min under Ar. The solvent was evaporated *in vacuo*. The yellow-orange residue was triturated with warm absolute alcohol forming yellow crystals of compound **14**, 1.70 g (81%), m.p. 116°–117°C. IR (neat) cm^{-1} 3112 (CH), 1520 and 1331 (NO_2); ^{1}H NMR (400 MHz) 8.56 (dd, 1H, $J_{8,9}$ = 13.5 Hz, $J_{8,2}$ = 0.8 Hz, H-8), 7.93 (dd, 1H, $J_{7,6}$ = 7.1 Hz, $J_{7,5}$ = 1.8 Hz, H-7), 7.92 (br.s, 1H, H-2), 7.55 (d, 1H, $J_{9,8}$ = 13.5 Hz, H-9), and 7.49 (m, 2H, H-5, H-6); ^{13}C NMR (50 MHz) 144.1 (Cq), 143.4 (Cq), 138.8 (CH), 131.5 (CH), 130.6(CH), 129.2 (Cq), 126.1 (CH), 125.6 (Cq), 123.4 (CH), 118.5 (q, $J_{C\text{-}F}$ = 320 Hz, CF_3), and 118.3 (CH); MS m/e 353 (23, $M^{\cdot+}$), 220 (5, M-[SO_2 CF_3]), 174 (100, 220-[NO_2]); Analysis calcd. for $C_{11}H_6F_3NO_5S_2$: C 37.40, H 1.71, N 3.96%; found: C 37.29, H 1.41, N 3.65%.

1-(3'-Benzo[b]thienyl)-2-nitroethane (20). Sodium borohydride (0.076 g, 2.0 mmol) was added over 10 minutes to a vigorously stirred mixture of **15** (0.103 g, 0.5 mmol), silica gel (1g), chloroform (8 mL) and propan-2-ol (1.5 mL) at room temperature. The reaction mixture was stirred for 1.5 hours, the mixture

was filtered and the filter pad was washed with CH_2Cl_2 (50 mL). The combined filtrates were washed with 5% HCl (1 × 10 mL), brine (1 × 30 mL) and were dried ($MgSO_4$). The solvent was evaporated *in vacuo* and the residue was purified by flash chromatography to give 0.079 g (76%) of the saturated nitro compound **20** as an oil. IR (neat) cm^{-1} 1550 and 1376(NO_2); ^1H NMR (400 MHz) 7.89 (ddd, 1H, $J_{4,5}$ = 6.9 Hz, $J_{4,6}$ = 1.2 Hz, $J_{4,7}$ = 0.8 Hz, H-7), 7.75 (ddd, 1H, $J_{7,6}$ = 7.5 Hz, $J_{7,5}$ = 1.4 Hz, $J_{7,4}$ = 0.8 Hz, H-4), 7.43 (m, 2H, H-5, H-6), 7.24 (br.s, 1H, H-2), 4.73 (t, 2H, $J_{9,8}$ = 7.3 Hz, H-9), and 3.60 (dt, 2H, $J_{8,9}$ = 7.3 Hz, $J_{8,2}$ = 0.9 Hz, H-8); ^{13}C NMR (100 MHz) 140.4 (Cq), 137.8 (Cq), 128.8 (Cq), 124.6 (CH), 124.3 (CH), 123.8 (CH), 123.1 (CH), 120.9 (CH), 74.3 (CH_2NO_2), and 26.2 (CH_2); MS m/e 207 (72, $M^{\cdot+}$), 161 (59, M-[NO_2]), 160 (100, M-[HNO_2]); Analysis calcd. for $C_{10}H_9NO_2S$: C 57.95, H 4.38, N 6.76%; found: C 57.79, H 4.05, N 6.63%.

1-(3'-(4'-Trifluoromethylsulphonyloxybenzo[b]thienyl))-2-nitroethane (5). Sodium borohydride (0.076 g, 2.0 mmol) was added over 10 minutes to a vigorously stirred mixture of **14** (0.177 g, 0.5 mmol), silica gel (1g), chloroform (8 mL) and propan-2-ol (1.5 mL) at room temperature. The reaction mixture was stirred for 45 minutes, the mixture was filtered and the filter pad was washed with CH_2Cl_2 (50 mL). The combined filtrates were washed with 5% HCl (1 × 10 mL), brine (1 × 30 mL) and were dried ($MgSO_4$). The solvent was evaporated *in vacuo* to give a pale yellow solid **5**, 0.165 g (95%). Compound **5** was recrystallized from hexanes (charcoal) to yield a pale yellow solid, m.p. 83°–85°C. IR (neat) cm^{-1} 1544 and 1382 (NO_2); ^1H NMR (400 MHz) 7.88 (dd, 1H, $J_{7,6}$ = 7.8 Hz, $J_{7,5}$ = 1.2 Hz, H-7), 7.43 (t, 1H, $J_{6,7}$ = $J_{6,5}$ = 7.8 Hz, H-6), 7.38 (dd, 1H, $J_{5,6}$ = 7.8 Hz, $J_{5,7}$ = 1.2 Hz, H-5), 7.37 (br.s, 1H, H-2), 4.75 (t, 2H, $J_{9,8}$ = 6.6 Hz, H-9), and 3.76 (dt, 2H, $J_{8,9}$ = 6.6 Hz, $J_{8,2}$ = 0.7 Hz, H-8); ^{13}C NMR (50 MHz) 144.1 (Cq), 140.4 (Cq), 129.6 (Cq), 128.6 (Cq), 127.5 (CH), 125.1 (CH), 123.4 (CH), 118.5 (q, $J_{C\text{-}F}$ = 320 Hz, CF_3), 116.8 (CH), 76.4 (CH_2NO_2), and 27.8 (CH_2); MS m/e 355 (25, $M^{\cdot+}$), 222 (17, M-[SO_2CF_3]), 176 (100, 222-[NO_2]); Analysis calcd. for $C_{11}H_8F_3N_5O_2S$: C 37.18, H 2.27, N 3.94%; found C 37.14, H 2.02, N 3.82%.

Anti- and *syn*-3-(2'-(hydroxyimino)ethyl)benzo[*b*]thiophene (**19**). A mixture of **15** (0.51 g, 2.5 mmol) and 10% palladium on carbon (0.26 g, 5% by weight) in ethyl acetate (40 mL) was stirred under a hydrogen atmosphere at 20°C for 1.5 hours. The catalyst was removed by filtration through celite and the solvent was evaporated *in vacuo*. The residue was purified by flash chromatography (20% EtOAc in hexanes) to yield 0.09 g (17%) of the saturated nitro compound **20** and 0.28 g (59%) of the aldoxime **19** as an inseparable mixture of *anti-* and *syn-*

isomers (79:21). The aldoxime mixture **19** was recrystallized from hexanes to afford a pale yellow solid, m.p. 131°–138°C. IR (neat) cm^{-1} 3231 (OH), 1657 (C═N); ^1H NMR (400 MHz) 8.36^{anti} (br.s, 1H, OH), 7.90–7.76 (m, 2H, H-4, H-7), 7.75^{syn} (br.s, 1H, OH), 7.63^{syn} (t, 1H, $J_{9,8}$ = 6.2 Hz, H-9), 7.40 (m, 2H, H-5, H-6), 7.25^{anti} (br.s, 1H, H-2), 7.23^{syn} (br.s, 1H, H-2), 6.96^{anti} (t, 1H, $J_{9,8}$ = 5.2 Hz, H-9), 3.98^{anti} (dd, 2H, $J_{8,9}$ = 5.2 Hz, $J_{8,2}$ = 0.8 Hz, H-8), and 3.78^{syn} (dd, 2H, $J_{8,9}$ = 6.2 Hz, $J_{8,2}$ = 0.9 Hz, H-8); MS m/e 191 (60, $M^{\cdot+}$), 173 (77, M-[H_2O]), 147 (100, M-[CH═NOH]); Analysis calcd. for $C_{10}H_9NOS$: C 62.80, H 4.74, N 7.32%; found: C 62.86, H 4.70, N 7.15%.

Preparation of anti- and syn-4-trifluoromethylsulphonyloxy-3-(3-(2'-(hydroxyimino)ethyl)benzo[b]thiophene (18). A mixture of **14** (0.247 g, 0.7 mmol) and 10% palladium on carbon (0.124 g, 5% by weight) in ethyl acetate (15 mL) was stirred under a hydrogen atmosphere at 20°C for 30 minutes. The catalyst was removed by filtration through celite and the solvent was evaporated *in vacuo*. The residue was purified by flash chromatography (20% EtOAc in hexanes) to yield 0.017 g of an unknown compound, 0.027 g (11%) of the saturated nitro compound **5** and 0.144 g (61%) of the aldoxime **18** as an inseparable mixture of *anti*- and *syn*-isomers (87:13). The aldoxime mixture **18** was recrystallized from hexanes to afford a pale yellow solid, m.p. 108°–109°C. IR (neat) cm^{-1} 3229 (OH), 1270 and 1131 (SO_2); ^1H NMR (400 MHz) 7.87 (m, 1H, H-7), 7.71^{syn} (t, 1H, $J_{9,8}$ = 5.7 Hz, H-9), 7.45^{anti} (br.s, 1H, OH), 7.38 (m, 2H, H-6, H-5), 7.34^{anti} (br.s, 1H, H-2), 7.30^{syn} (br.s, 1H, H-2), 7.10^{syn} (br.s, 1H, OH), 7.03^{anti} (t, 1H, $J_{9,8}$ = 5.3 Hz, H-9), 4.13^{anti} (dd, 2H, $J_{8,9}$ = 5.3 Hz, $J_{8,2}$ = 1.0 Hz, H-8), and 3.96^{syn} (dd, 2H, $J_{8,9}$ = 5.7 Hz, $J_{8,2}$ = 1.1 Hz, H-8); MS m/e 339 (39, $M^{\cdot+}$), 206 (10, M-[SO_2CF_3]), 189 (100, 206-[OH]); Analysis calcd. for $C_{11}H_8F_3NO_4S_2$: C 38.94, H 2.38, N 4.13%; found: C 38.55, H 2.18, N 4.09%.

4-(4'-(3'-(2''-Nitroethyl)benzo[b]thienyl))-2-methyl-3-buten-2-ol (4). To a solution of the triflate **5** (80 mg, 0.225 mmol) in DMF (5 mL) under Ar at room temperature were added sequentially triethylamine (94 mL, 0.675 mmol), 2-methyl-3-buten-2-ol(141 mL, 1.35 mmol), tri-*o*-tolylphosphine (6.8 mg, 0.0225 mmol), lithium chloride (28.6 mg, 0.675 mmol) and $Pd(OAc)_2$ (4.1 mg, 0.018 mmol). The solution was stirred at 120°C for 45 minutes and then was cooled to room temperature. Dichloromethane (25 mL) was added and the resulting mixture was washed with water (1 × 15 mL), brine (1 × 25 mL) and was dried ($MgSO_4$). The solvent was evaporated *in vacuo* and the residue was purified by flash chromatography (30% EtOAc in hexanes) to afford 55 mg (84%) of the nitro-alcohol **4**. The product was recrystallized from chloroform/hexanes to yield a pale yellow solid, m.p. 63°–66°C. IR (neat) cm^{-1} 3415 (OH),

1551 and 1379 (NO_2); ^{1}H NMR (400 MHz) benzene d^6, 7.45 (dd, 1H, $J_{7,6}$ = 8.0 Hz, $J_{7,5}$ = 0.9 Hz, H-7), 7.12 (dt, 1H, $J_{5,6}$ = 7.3 Hz, $J_{5,7}$ = $J_{5,10}$ = 0.9 Hz, H-5), 7.11 (br.d, 1H, $J_{10,11}$ = 15.6 Hz, H-10), 7.01 (dd, 1H, $J_{6,7}$ = 8.0 Hz, $J_{6,5}$ = 7.3 Hz, H-6), 6.44 (br.s, 1H, H-2), 5.87 (d, 1H, $J_{11,10}$ = 15.6 Hz, H-11), 3.85 (t, 2H, $J_{9,8}$ = 7.9 Hz, H-9), 3.15 (dt, 2H, $J_{8,9}$ = 7.9 Hz, $J_{8,2}$ = 0.9 Hz, H-8), 1.30 (br.s, 1H, OH), and 1.21 (s, 6H, H-13); ^{13}C NMR (100 MHz) benzene d^6, 142.4 (C-11), 141.9 (Cq), 135.5 (Cq), 135.1 (Cq), 131.3 (Cq), 125.1 (C-5), 125.0 (C-2), 124.8 (C-6), 124.7 (C-10), 122.5 (C-7), 74.8 (C-9), 70.5 (C-12), 29.9 (C-13), and 29.4(C-8); MS m/e 291 (38, $M^{\cdot+}$), 171 (82, M-[CH_2NO_2][$HC(CH_3)_2OH$]); Analysis calcd. for $C_{15}H_{17}NO_3S$: C 61.83, H 5.88, N 4.81%; found: C 61.96, H 5.81, N 4.70%.

4-(4'-(3'-(2"-Nitroethyl)-benzo[b]thienyl))-3-methyl-1,3-butadiene (11). A mixture of **4** (87.9 mg, 0.3 mmol) and pyridinium- *p*-toluenesulphonate (7.6 mg, 0.03 mmol) in benzene (5 mL) was stirred at reflux under Ar for 30 minutes. After cooling, the organic solution was washed with 5% aqueous NaOH (1 × 1 mL), brine (1 × 5 mL) and was dried ($MgSO_4$). The solvent was evaporated *in vacuo* and the residue was filtered through a silica plug (20% EtOAc in hexanes) to afford 82 mg (100%) of the unstable diene. Compound **11** was recrystallized from hexanes to yield a white solid, m.p. 71°–72°C. IR (neat) cm^{-1} 3086 (CH), 2971 (CH), 1553 and 1379 (NO_2); ^{1}H NMR (400 MHz) 7.78 (dd, 1H, $J_{7,6}$ = 7.9 Hz, $J_{7,5}$ = 1.0 Hz, H-7), 7.41 (dd, 1H, $J_{5,6}$ = 7.4 Hz, $J_{5,7}$ = 1.0 Hz, H-5), 7.34 (dd, 1H, $J_{6,7}$ = 7.9 Hz, $J_{6,5}$ = 7.4 Hz, H-6), 7.24 (br.s, 1H, H-2), 7.23 (d, 1H, $J_{10,11}$ = 15.7 Hz, H-10), 6.75 (d, 1H, $J_{11,10}$ = 15.7 Hz, H-11), 5.17 (d, 2H, J_{gem} = 6.5 Hz, H-13), 4.68 (t, 2H, $J_{9,8}$ = 7.7 Hz, H-9), 3.77 (dt, 2H, $J_{8,9}$ = 7.7 Hz, $J_{8,2}$ = 0.7 Hz, H-8), and 2.04 (s, 3H, CH_3, H-14); ^{13}C NMR (100 MHz) 141.7 (Cq), 141.6(Cq), 136.1 (C-11), 134.9 (Cq), 134.8 (Cq), 130.8 (Cq), 126.5 (C-2), 125.2 (C-10), 124.6 (C-6), 124.2 (C-5), 122.4 (C-7), 118.5 (C-13), 75.0 (C-9), 29.7 (C-8), and 18.5 (C-14); MS m/e 273 (38, $M^{\cdot+}$); Analysis calcd. for $C_{15}H_{15}NO_2S$: C 65.91, H 5.53, N 5.12%; found: C 65.94, H 5.44, N 5.06%.

(9b,9aa-H)-4,6,9,9a-Tetrahydro-9-(1'-hydroxy-1'-methylethyl)benzo[b-]thiopheno-[4,3-ef][2,1]benzisoxazole (10). Acetic anhydride (0.25 mL, 2.60 mmol) was added to a solution of **4** (0.189 g, 0.65 mmol) and triethylamine (0.14 mL, 0.975 mmol) in dichloromethane (10 mL). The reaction mixture was stirred at reflux under Ar for 40 hours. After cooling, the solution was washed with 5% aqueous HCl (1 × 3 mL), water (1 × 5 mL), brine (1 × 10 mL) and was dried ($MgSO_4$). The solvent was removed *in vacuo* and the residue was filtered through a silica plug (30% EtOAc in hexanes). Evaporation of the solvent yielded a solid, which was recrystallized from hexanes/chloroform to give

10 (0.161 g, 91%) as a white solid, m.p. 148°–149°C. IR (neat) cm^{-1} 3322 (OH), 2928 (CH), 1644 (C═N), 768; ^1H NMR (400 MHz) 7.78 (dd, 1H, $J_{3,2}$ = 8.1 Hz, $J_{3,1}$ = 0.9 Hz, H-3), 7.39 (dd, 1H, $J_{2,1}$ = 7.4 Hz, $J_{2,3}$ = 8.1 Hz, H-2), 7.19 (br.s, 1H, H-5), 7.13 (dd, 1H, $J_{1,2}$ = 7.4 Hz, $J_{1,3}$ = 0.9 Hz, H-1), 4.74 (br.d, 1H, $J_{9a,9}$ = 7.9 Hz, H-9a), 4.62 (d, 1H, $J_{9,9a}$ = 7.9 Hz, H-9), 4.15 (d, 1H, $J_{6B,6A}$ = 17.2 Hz, H-6b), 3.79 (ddd, 1H, $J_{6A,6B}$ = 17.2 Hz, $J_{6A,5}$ = 2.0 Hz, $J_{6A,9a}$ = 1.5 Hz, H-6a), 2.09 (br.s, 1H, OH), 1.50 (s, 3H, H-11), and 1.45 (s, 3H, H-12); ^{13}C NMR (100 MHz) 156.6 (C-6a), 139.0 (Cq), 136.5 (Cq), 133.7 (Cq), 129.1 (Cq), 125.6 (C-2), 121.4 (C-3), 120.5 (C-5), 119.9 (C-1), 91.9 (C-9), 71.2 (C-10), 50.7 (C-9a), 26.7 (C-11), 26.2 (C-6), and 25.4 (C-12); MS m/e 273 (12, $M^{\cdot+}$), 59 (100, $[HO\text{-}C^+(CH_3)_2]$; Analysis calcd. For $C_{15}H_{15}NO_2S$: C 65.91, H 5.53, N 5.12%; found: C 65.36, H 5.32, N 5.03%; Exact mass calcd. for $C_{15}H_{15}NO_2S$: 273.0823; found: 273.0811.

(9b,9aa-H)-4,6,9,9a-Tetrahydro-9-(1'-methylethenyl)benzo[b]thiopheno[4,3-ef]-[2,1]benzisoxazole (12). Phenyl isocyanate (0.37 mL, 3.40 mmol) was added to a solution of **11** (0.155 g, 0.567 mmol) and triethylamine (15.8 mL, 0.113 mmol) in benzene (8 mL). The reaction mixture was stirred at room temperature under Ar for 4 days. The precipitated urea side product was removed by filtration, and the filtrate was concentrated *in vacuo*. Purification of the residue by flash chromatography (10% EtOAc in hexanes) gave **12** as a solid (0.135 g, 94%) which was recrystallized from hexanes to yield a pale yellow solid, mp. 101°–104°C. IR (KBr) cm^{-1} 2918 (CH), 1645 (C═N), 763; ^1H NMR (400 MHz) 7.77 (dd, 1H, $J_{3,2}$ = 7.9 Hz, $J_{3,1}$ = 0.8 Hz, H-3), 7.36 (dd, 1H, $J_{2,1}$ = 7.4 Hz, $J_{2,3}$ = 7.9 Hz, H-2), 7.18 (br.s, 1H, H-5), 7.14 (dd, 1H, $J_{1,2}$ = 7.4 Hz, $J_{1,3}$ = 0.8 Hz, H-1), 5.37 (br.s, 1H, H-11), 5.24 (m, 1H, H-11), 4.98 (d, 1H, $J_{9,9a}$ = 11.5 Hz, H-9), 4.66 (br.d, 1H, $J_{9a,9}$ = 11.5 Hz, H-9a), 4.17 (d, 1H, $J_{6B,6A}$ = 17.9 Hz, H-6b), 3.79 (ddd, 1H, $J_{6A,6B}$ = 17.9 Hz, $J_{6A,5}$ = 2.0 Hz, $J_{6A,9a}$ = 1.8 Hz, H-6a), and 2.01 (br.s, 3H, H-12); ^{13}C NMR (100 MHz) 157.2 (C-6a), 141.9 (Cq), 136.4 (Cq), 132.4 (cq), 128.1 (Cq), 125.6 (C-6), 121.5 (C-7), 120.5 (C-2), 119.9 (C-5), 116.6 (C-11), 90.5 (C-9), 50.9 (C-9a), 26.1 (C-6), and 17.1 (C-12); MS m/e 255 (5, $M^{\cdot+}$), 185 (100, M-[CH_2 = $C(CH_3)$-CHO]); Exact mass calcd. for $C_{15}H_{13}NOS$: 255.0718; found: 255.0728.

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