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# Regioselective functionalisation of dibenzothiophenes through gold-catalysed intermolecular alkyne oxyarylation†

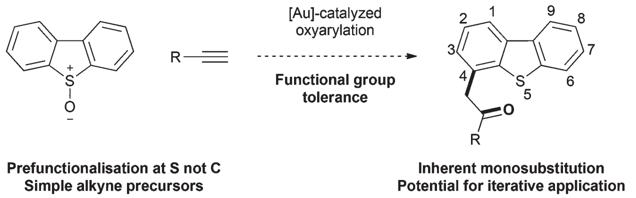
Matthew J. Barrett, Paul W. Davies* and Richard S. Grainger*

A protocol has been developed for direct $Csp^3$–$Csp^2$ bond formation at the 4- and 6-positions of dibenzothiophenes using a gold(I) catalyst with terminal alkynes and dibenzothiophene-*S*-oxides. The sulfoxide acts as a traceless directing group to avoid the need to prefunctionalise at carbon. The iterative use of this protocol is possible and has been employed in the preparation of novel macrocyclic structures. In addition, a cascade process shows how oxyarylations can be combined with other processes resulting in complex, highly efficient transformations.

## Introduction

Dibenzothiophenes are aromatic sulfur-containing heterocycles of broad utility. The optical, redox and conducting properties of dibenzothiophenes and their corresponding *S*,*S*-dioxides have led to applications in materials science.[1] *S*-Substituted dibenzothiophenes are used as precursors to triphenylenes[2] and as a platform for the transfer of reactive species such as $F_3C^+$ (Umemoto's reagent),[3] atomic oxygen (O(3P)),[4] nitrenes[5] and carbenes.[6] Biological and medicinal chemistry applications of dibenzothiophenes and their *S*-oxides have also been reported.[7]

Functionalised dibenzothiophenes are generally prepared through one of two main approaches. Late stage formation of the dibenzothiophene core has been achieved through intramolecular C–S[8] or C–C (biaryl)[9] bond formation and benzannulation of thiophenes or benzothiophenes.[10] Alternatively, dibenzothiophene undergoes regioselective bromination at the 2,8-positions[11] or the 3,7-positions of the corresponding *S*,*S*-dioxide.[12] Substitution at the 4- and 6-positions however requires stoichiometric metallation using organolithium or organoaluminium reagents.[13,14] Here we report a catalysis-based approach for direct carbon–carbon bond formation at the *unfunctionalised* 4- and 6-positions of dibenzothiophenes under mild and functional group tolerant conditions.



**Scheme 1** Proposed regiospecific functionalisation of dibenzothiophenes using the *S*-oxide as a traceless directing group.

Our interests in aromatic *S*-oxide chemistry[15] and π-acid catalysis[16] led us to investigate whether 4-substituted dibenzothiophenes could be accessed in an expedient fashion from dibenzothiophene *S*-oxides by a gold-catalysed alkyne oxyarylation.[17–19] This approach should be regiospecific, installing a $Csp^3$–$Csp^2$ bond with transfer of the oxygen atom to generate the synthetically versatile α-arylcarbonyl motif (Scheme 1).[20]

Following the introduction of alkyne oxyarylation with sulfoxides in gold-catalysed intramolecular cycloisomerisations by the groups of Toste[17a] and Zhang,[17b] the viability of an intermolecular process was shown by Ujaque, Asensio and co-workers (Scheme 2).[17c]

This and subsequent[17d,e] studies established that such processes are regiospecific by virtue of proceeding *via* a [3,3]-sigmatropic rearrangement of the vinyl gold carbenoid **B** formed on attack of the sulfoxide to the gold–alkyne complex (Scheme 2, **A** → **C**).[21]

Despite sulfoxide-based alkyne oxyarylation offering substantial potential for atom-economic, functional group tolerant and direct intermolecular aryl C–H functionalisation routes into challenging aromatic substitution patterns, they have

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*School of Chemistry, University of Birmingham, Haworth Building, Edgbaston, Birmingham, B15 2TT, UK. E-mail: p.w.davies@bham.ac.uk, r.s.grainger@bham.ac.uk*

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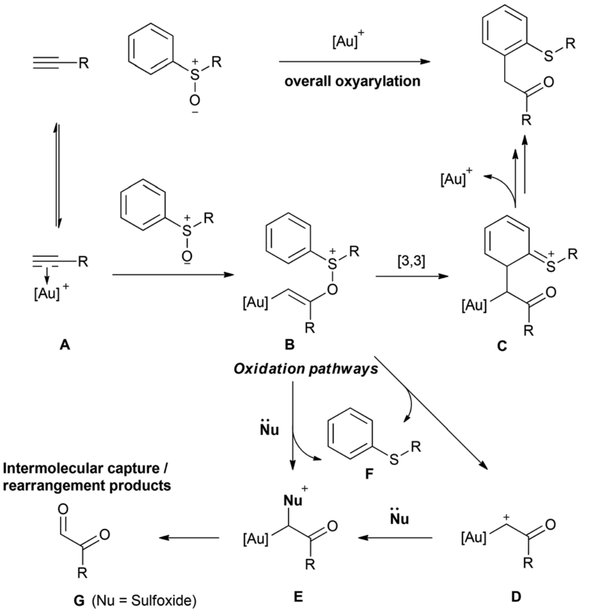


Scheme 2 General schematic for gold-catalysed oxyarylation reaction of alkynes with sulfoxides.

been rarely employed in synthesis. In large part this can be assigned to the challenges of ensuring that the key aromaticity-disrupting [3,3]-sigmatropic rearrangement (**B** → **C**) is favoured over elimination of a sulfide nucleofuge (**B** → **D**), or competing inter- or intra-molecular attack of a nucleophile (**B** → **E**).[17,22,23]

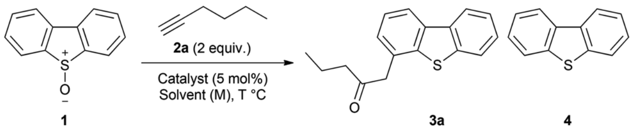
In addition, structural elaboration of the sulfoxide must not prevent it from being sufficiently nucleophilic to intercept the alkyne–gold complex **A**, yet not force further reaction at **B** to afford the biscarbonyl **G** alongside two equivalents of sulfide.[24,25]

## Results and discussion

The viability of selective elaboration of a dibenzothiophene through an alkyne oxyarylation approach was investigated using dibenzothiophene-*S*-oxide **1** and hex-1-yne **2a**. Applying the combination of $Ph_3PAuCl/AgSbF_6$ in superheated $CH_2Cl_2$ from Asensio's work[17c] generated a mixture of dibenzothiophenes **3a** and **4** in high yield with the desired oxyarylation product **3a** as the minor component (Table 1, entry 1).

An investigation of the reaction conditions was undertaken to explore the factors favouring the rearrangement pathway over those leading to S–O bond cleavage and formation of **4** (Table 1). The most significant factors identified in this study proved to be the use of electron-deficient rather than electron-rich ligands on gold (compare entries 7 and 10 *vs.* 4, 8 and 9) and the use of lower reaction temperatures (compare entries 13 and 14 *vs.* 11 and 1), which differ substantially from those conditions previously reported for the intermolecular oxyarylation reaction with sulfoxides.[17c,d] These observations are in keeping with higher temperature and electron-density at the gold centre being likely to increase the rate of elimination of the sulfide nucleofuge (Scheme 2, **B** → **D**).[26,27]

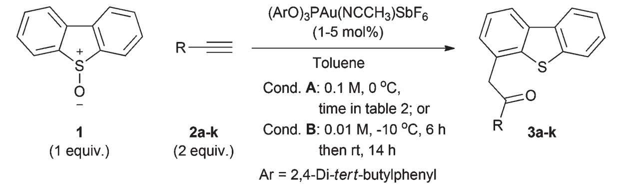
Table 1 Study of the reaction conditions for oxyarylation using dibenzothiophene-*S*-oxide[a]



| Entry | Gold catalyst | Solvent | Time/h | Temp/°C | Conc. M | Yield **1**[b]/% | Yield **3a**[b]/% | Yield **4**[b]/% | Ratio **3a** : **4** |
|---|---|---|---|---|---|---|---|---|---|
| 1[b] | $Ph_3PAuCl/AgSbF_6$[c] | $CH_2Cl_2$ | 16 | 70 | 1.0 | 0 | 37 | 61 | 1 : 1.6 |
| 2 | $Ph_3PAuCl/AgSbF_6$[c] | $ClCH_2CH_2Cl$ | 16 | 70 | 1.0 | 10[d] | 20 | 30[d] | — |
| 3 | $Ph_3PAuCl/AgSbF_6$[c] | $CH_3NO_2$ | 16 | 70 | 1.0 | 0 | 39 | 36 | 1.1 : 1 |
| 4 | $Ph_3PAuCl/AgOTs$[c] | $CH_3NO_2$ | 16 | 70 | 1.0 | 12 | 41 | 31 | 1.3 : 1 |
| 5 | AuCl | $CH_3NO_2$ | 16 | 70 | 1.0 | 52 | 4 | 22 | 1 : 5.5 |
| 6 | $AuPicolinateCl_2$ | $CH_3NO_2$ | 16 | 70 | 1.0 | 36 | 4 | 24 | 1 : 6.0 |
| 7 | $(p\text{-}F_3CC_6H_4)_3PAuCl/AgOTs$[c] | $CH_3NO_2$ | 16 | 70 | 1.0 | 5 | 42 | 24 | 1.8 : 1 |
| 8 | XPhosAuCl/AgOTs[c] | $CH_3NO_2$ | 16 | 70 | 1.0 | 51 | 10 | 24 | 1 : 2.4 |
| 9 | JohnPhosAuCl/AgOTs[c] | $CH_3NO_2$ | 16 | 70 | 1.0 | 52 | 8 | 24 | 1 : 3.0 |
| 10 | $(ArO)_3PAuCl/AgOTs$[c] | $CH_3NO_2$ | 16 | 70 | 1.0 | <5 | 47 | 17 | 2.8 : 1 |
| 11 | $(ArO)_3PAu(NCCH_3)SbF_6$ | $CH_3NO_2$ | 16 | 70 | 1.0 | <5 | 48 | 16 | 3.0 : 1 |
| 12 | $(ArO)_3PAu(NCCH_3)SbF_6$ | $CH_3NO_2$ | 3 | 70 | 0.1 | <5 | 44 | 20 | 2.2 : 1 |
| 13 | $(ArO)_3PAu(NCCH_3)SbF_6$ | $CH_3NO_2$ | 3 | RT | 0.1 | 8 | 67 | 10 | 6.7 : 1 |
| 14 | $(ArO)_3PAu(NCCH_3)SbF_6$ | $CH_2Cl_2$ | 3 | RT | 0.1 | <5 | 54 | 14 | 3.9 : 1 |
| 15 | $(ArO)_3PAu(NCCH_3)SbF_6$ | $CH_3CN$ | 3 | RT | 0.1 | 29 | 17 | 5 | 3.4 : 1 |
| 16 | $(ArO)_3PAu(NCCH_3)SbF_6$ | Toluene | 3 | RT | 0.1 | 0 | 84 | 8 | 10.5 : 1 |
| 17 | $(ArO)_3PAu(NCCH_3)SbF_6$ | Toluene | 3 | 0 | 0.1 | 0 | 91 | 8 | 11.4 : 1 |

[a] **1** (0.10 mmol), **2a** (0.20 mmol). [b] Yields calculated by $^1H$-NMR spectroscopy against a known quantity of internal standard (1,2,4,5-tetramethylbenzene). [c] Catalyst prepared by *in situ* combination of equimolar quantity of the (Ligand)AuCl with the appropriate Ag(counterion) salt. [d] Due to overlap with unidentified resonances estimated yields were determined. XPhos = 2-dicyclohexylphosphino-2,4,6-triisopropylbiphenyl; JohnPhos = (2-biphenyl)di-*tert*-butylphosphine; Ar = (2,4-di-*tert*-butylphenyl).

**Table 2** Selective formation of C-4 substituted dibenzothiophenes using different alkynes



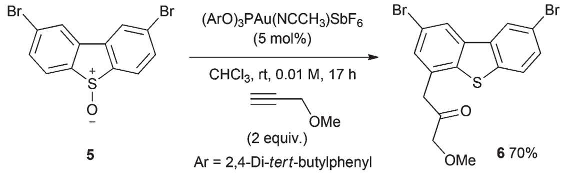
| Entry | R | Cond. | Mmol | Cat./mol% | Time/h | Yield[a]/% |
|---|---|---|---|---|---|---|
| 1 | $^n$Bu | A | 0.2 | 5 | 0.75 | 87 **3a** |
| 2 | $(CH_2)_3Cl$ | A | 0.2 | 5 | 0.75 | 79 **3b** |
| 3 | $(CH_2)_2Ph$ | A | 0.2 | 5 | 0.75 | 65 **3c** |
| 4 | $CH_2OMe$ | A | 0.2 | 5 | 0.75 | 87 **3d** |
| 5 | $CH_2OMe$ | A | 2.0 | 1 | 2 | 84 **3d** |
| 6 | $(CH_2)_4OTBDPS$ | A | 0.5 | 1 | 2 | 82 **3e** |
| 7 | $CH_2NPhth$ | A | 2.0 | 5 | 20[b] | 52 **3f** |
| 8 | $CH(OH)^nC_7H_{15}$ | A | 0.2 | 5 | 20[b] | 76 **3g** |
| 9 | Ph | A | 0.1 | 5 | 1.5 | 48[c] **3h** |
| 10 | Ph | B | 0.3 | 5 | 20 | 58 **3h** |
| 11 | $2\text{-}BrC_6H_4$ | B | 0.2 | 5 | 20 | 40 **3i** |
| 12 | $4\text{-}MeOC_6H_4$ | B | 0.2 | 5 | 20 | 42 **3j** |
| 13 | 2-Thienyl | B | 0.2 | 5 | 20 | 62 **3k** |

[a] Yields of isolated material after flash chromatography. [b] Reactions stirred for 4 h at 0 °C then warmed to rt over 16 hours. [c] Yield calculated by $^1$H-NMR spectroscopy against a known quantity of internal standard (1,2,4,5-tetramethylbenzene).

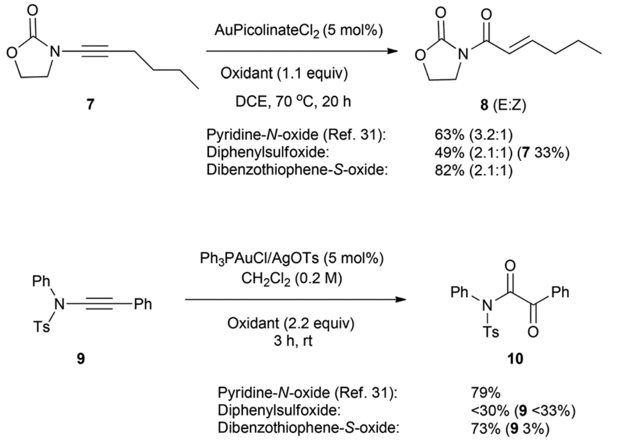
Little counterion effect was observed and similar results were obtained with the single component catalyst system (entries 10 and 11). Re-evaluating the solvent showed $CH_2Cl_2$ to be poor and that excellent selectivity was ultimately obtained in toluene at 0 °C using (2,4-di-*tert*-$BuC_6H_3O)_3PAu(NCCH_3)SbF_6$,[16d,28] affording **3a** in high yield (entry 17).

The use of dibenzothiophene-*S*-oxide **1** with different terminal alkynes **2b–k** was then studied in the oxyarylation reaction: chloro, aryl, vinyl and phthalimide substituents were well-tolerated as were the methyl and silyl-ethers, affording products **3b–k** in generally good yields (Table 2, entries 2–7).[29] The α-hydroxyketone oxyarylation product **3g** was also formed in high yield (entry 8) despite the potential for oxetan-3-one formation by intramolecular capture of the vinylgold intermediate by the propargylic alcohol, as reported using cationic gold(I) catalysts and pyridine-*N*-oxides.[30] This protocol proved to be robust: a very similar yield was obtained even when the reaction was run open to the air and using non-dried toluene with only 1 mol% catalyst loading on larger scale (entries 4 and 5).

The use of phenyl acetylene gave lower yields and led to formation of significant quantities of dibenzothiophene **4** under the standard conditions (Table 2, entry 9). Further reducing the temperature, which in-turn necessitated a higher dilution to maintain solubility of **1**, gave improved yields which were also seen with other aryl alkynes, including thiophene and *o*-bromobenzene (entries 10–13).



**Scheme 3** Use of substituted dibenzothiophene *S*-oxide.

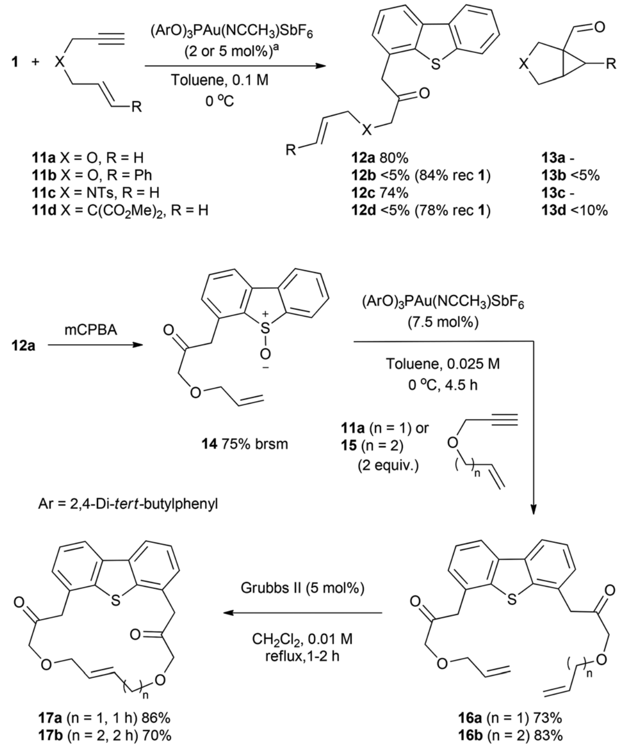


**Scheme 4** Comparison of reactivity in oxidative transformation of ynamides. Yield of known compounds **8** and **10** determined by $^1$H NMR against an internal standard.

The 2,8-dibromo substitution pattern, which is useful for further transformations in materials science applications,[1] was readily accommodated with *S*-oxide **5** reacting to afford the oxyarylation product **6** in good yield (Scheme 3).

The use of an ynamide under these reaction conditions did not lead cleanly to the oxyarylation products, though the complex mixture formed did indicate that **1** was functioning as an effective oxidant. In order to benchmark the potential suitability of dibenzothiophene-*S*-oxide as an oxidant in gold catalysis it was applied under the conditions previously reported by Davies and co-workers for the oxidative transformation of ynamides using pyridine *N*-oxides (Scheme 4).[31] Under those conditions **1** proved to be as, or more-, effective than the unsubstituted pyridine-*N*-oxide and substantially more effective than the diphenylsulfoxide in both the oxidative formation of α,β-unsaturated imide **8** and α-oxoimide **10.** Hence **1** may be considered as an alternative reagent to diphenylsulfoxide in gold-catalysed oxidative processes.[32,33]

Toste and co-workers had previously reported that the gold-catalysed reaction of 1,6-enynes in the presence of excess diphenylsulfoxide led to the formation of aldehydes by intramolecular cyclisation and capture of the intermediate cyclopropyl gold carbene with sulfoxide.[25] Given the higher reactivity observed of **1** compared to diphenylsulfoxide (Scheme 4), the reaction of enyne substrates **11** was studied to see whether **1** would be sufficiently nucleophilic to allow the intermolecular reaction of the sulfoxide at the gold–alkyne complex to compete with intramolecular cycloisomerisation.



**Scheme 5** The use of enynes in the oxyarylation process and application in an iterative approach to access 4,6-disubstituted dibenzothiophenes and subsequently macrocycles. [a] 2 mol% for **11a** and 5 mol% for **11b–d**.

Under our standard conditions the 1,6-enynes **11a** and **11c** reacted cleanly to give the oxyarylation products **12a/c** in high yield (Scheme 5). In contrast, the cinnamyl derivative **11b** and the malonate-derived enyne **11d** led to the aldehydes **13b/d** with low conversion. On this basis, the relatively high efficacy of dibenzothiophene *S*-oxide **1** as a nucleophile towards gold alkyne complexes allows it to compete with an intramolecular enyne cycloisomerisation so long as the latter pathway is not strongly biased toward cyclisation by reactive rotamer effects or use of more electron-rich alkenes. Products arising from capture of the vinyl gold carbenoid by the tethered alkene were not observed.[34]

Iterative application of the oxyarylation reaction was then tested to selectively functionalise both the 4- and 6-positions of dibenzothiophene (Scheme 5). The gold-catalysed reactions of **14**, from selective oxidation of **12a** using *m*CPBA,[35] with 1,6- and 1,7-enynes **11a** and **15** afforded high yields of the 4,6-disubstituted dibenzothiophenes **16a/b** respectively. A similar iterative process was also successfully applied to **3d** (see ESI† for details). While a higher catalyst loading and dilution were required for the second iteration, the compatibility of this approach with the flanking alkene and keto-functionality highlights the potential of using intermolecular oxyarylation approaches with substantially more-functionalised sulfoxides. Ring-closing metathesis of dienes **16a/b** furnished the new symmetrical and unsymmetrical macrocyclic products **17a/b** in good yield, isolated as *trans* double bond isomers. The double bond geometry in **17a** was determined to be trans through X-ray crystallography (Fig. 1).‡

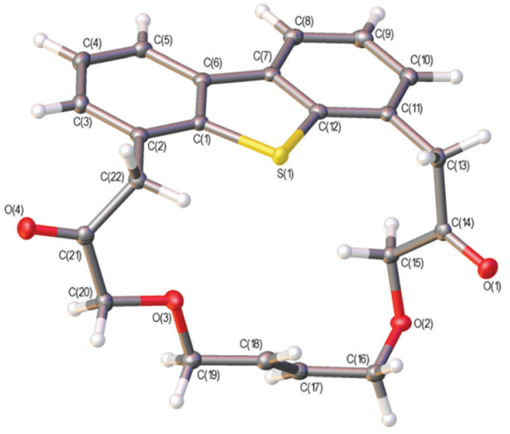
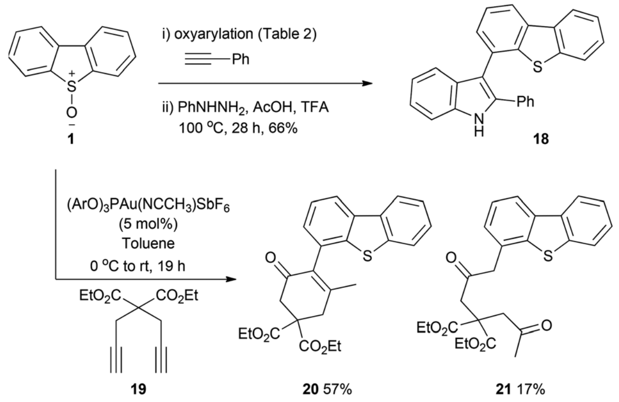


**Fig. 1** Crystal structure of macocycle **17a** with ellipsoids drawn at the 50% probability level.



**Scheme 6** Utilising the introduced ketomethylene group in (a) formation of a dibenzothienylindole as alternative to cross coupling, (b) cascade catalysis.

In addition to regiospecific formation of the $Csp^2$–$Csp^3$ bond the simultaneous installation of a methylenecarbonyl moiety introduces a potentially useful handle for elaboration. We explored this in two ways: first, a classical Fischer-indole synthesis from **3h** (yield unoptimised, Scheme 6) affords the 3-dibenzothiophene indole motif **18**.[7i] Thus an alternative is proffered to the standard cross-coupling strategies requiring prefunctionalisation of substrates for the formation of biaryl-

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‡ Crystal structure determination of **17a**. Crystal data for $C_{22}H_{20}O_4S$, $M = 380.44$, triclinic, space group $P\bar{1}$ (no. 2), $a = 9.0122(4)$ Å, $b = 10.2941(6)$ Å, $c = 10.6266(6)$ Å, $\alpha = 75.079(5)°$, $\beta = 73.655(4)°$, $\gamma = 75.040(5)°$, $V = 895.60(9)$ Å$^3$, $Z = 2$, $T = 100.00(10)$ K, $\mu(\text{CuK}\alpha) = 1.826$ mm$^{-1}$, $D_{calc} = 1.411$ g cm$^{-3}$, 4979 reflections measured ($8.85° \le 2\Theta \le 136.478°$), 3193 unique ($R_{int} = 0.0141$, $R_{sigma} = 0.0201$) which were used in all calculations. The final $R_1$ was 0.0290 ($I > 2\sigma(I)$) and $wR_2$ was 0.0733 (all data). CCDC 1405198.

linkages at the 4-position of dibenzothiophene. Second, a cascade process using 1,6-diyne **19** provides direct access into the α-arylated cyclohexenone **20** in a single step (Scheme 6). Gold-catalysed cycloisomerisation of the 1,5-ketoalkyne generated from intermolecular oxyarylation results in formation of five new bonds across the alkyne including three carbon–carbon bonds at one carbon. The formation of bisketone **21** as a side-product alongside the major product **20** is consistent with the hydration/aldol dehydration pathway Davies and Detty-Mambo previously reported in cycloisomerisation of alkynes tethered to unactivated, enolisable ketones in the presence of cationic gold(I) species.[36]

## Conclusions

Conditions have been developed for regioselective formation of Csp$^2$–Csp$^3$ bonds at the 4- and 6-positions of dibenzothiophenes without prior C-functionalisation. Selectivity for the oxyarylation pathway is favoured by lower temperature and electron-poor ligands on gold. The reactions allow for the introduction of a variety of functionality under robust, scalable conditions. Substantially more elaborate aryl sulfoxides can be used in the oxyarylation approach as demonstrated in an iterative application, which in conjunction with enyne substrates was used to access new macrocyclic structures. In addition, the use of the oxyarylation reaction as the basis for further cascade process development has been demonstrated.

## Experimental†

### General oxyarylation procedure 1 (GP1), Table 2, conditions A

The dibenzothiophene-*S*-oxide (1 eq.) and alkyne (2 eq.) were stirred in toluene (0.1 M) until dissolved. The mixture was then cooled in an ice bath at 0 °C and the catalyst, (2,4-di-*tert*-butyl$C_6H_3O)_3PAu(NCCH_3)SbF_6$ (1–5 mol%), was added. The reaction mixture was stirred until TLC showed consumption of dibenzothiophene-*S*-oxide, filtered through a pad of silica, washing with $CH_2Cl_2$ before being concentrated and the residue purified by column chromatography.

### General oxyarylation procedure 2 (GP2), Table 2, conditions B

The dibenzothiophene-*S*-oxide (1 eq.) and alkyne (2 eq.) were stirred in toluene (0.01 M) until dissolved. The mixture was then cooled in a (NaCl/ice) bath to −10 °C and the catalyst, (2,4-di-*tert*-butyl$C_6H_3O)_3PAu(NCCH_3)SbF_6$ (5 mol%) was added. The reaction mixture was stirred for 6 hours at this temperature and then allowed to warm to stir at rt for 14 hours, filtered through a pad of silica washing with $CH_2Cl_2$ before being concentrated and the residue purified by column chromatography.

Alkynes **11a**, 3-(prop-2-yn-1-yloxy)prop-1-ene (54 wt% in $Et_2O$), and **15**, 4-(prop-2-yn-1-yloxy)but-1-ene (77 wt% in $Et_2O$), were both used with a diethyl ether impurity.

### 1-(Dibenzo[*b*,*d*]thiophen-4-yl)hexan-2-one (3a)

Prepared according to **GP1** using dibenzothiophene-*S*-oxide **1** (40.0 mg, 0.2 mmol), 1-hexyne (23 μl, 0.4 mmol), toluene (2 mL) and catalyst (11.2 mg, 0.02 mmol, 5 mol%). The reaction was stirred for 45 minutes at 0 °C. Column chromatography (1 : 19 EtOAc : hexane) afforded **3a** (49 mg, 87%) as a white solid; $R_f$ 0.28 (1 : 19 EtOAc : hexane); mp: 43–45 °C; $^1$H-NMR (300 MHz, $CDCl_3$): $\delta$ = 8.20–8.13 (m, 1H), 8.10 (d, *J* 7.2, 1H), 7.92–7.82 (m, 1H), 7.51–7.43 (m, 3H), 7.32 (d, *J* 7.2, 1H), 3.96 (s, 2H), 2.51 (t, *J* 7.4, 2H), 1.63–1.50 (m, 2H), 1.33–1.19 (m, 2H), 0.85 (t, *J* 7.3, 3H); $^{13}$C-NMR (101 MHz, $CDCl_3$): $\delta$ = 207.5 (C), 140.0 (C), 139.1 (C), 136.1 (C), 136.0 (C), 129.2 (C), 128.0 (CH), 127.0 (CH), 125.2 (CH), 124.7 (CH), 123.0 (CH), 122.0 (CH), 120.6 (CH), 49.4 ($CH_2$), 42.0 ($CH_2$), 26.0 ($CH_2$), 22.3 ($CH_2$), 14.0 ($CH_3$); IR (neat): $\nu$ = 3057, 2957, 2930, 2872, 1708, 1584, 1404, 749; HR-MS (ES-TOF): *m*/*z*: calcd for $C_{18}H_{18}ONaS$: 305.0976, found 305.0978 [M + Na]$^+$.

### 6-Chloro-1-(dibenzo[*b*,*d*]thiophen-4-yl)hexan-2-one (3b)

Prepared according to **GP1** using dibenzothiophene-*S*-oxide **1** (40.0 mg, 0.2 mmol), 6-chloro-1-hexyne (48.5 μL, 0.4 mmol), toluene (2 mL) and catalyst (11.2 mg, 0.02 mmol, 5 mol%). The reaction was stirred for 45 minutes at 0 °C. Column chromatography (9 : 11 $CH_2Cl_2$ : hexane) afforded **3b** as a yellow oil (50 mg, 79%); $R_f$ 0.44 (9 : 11 $CH_2Cl_2$ : hexane); $^1$H-NMR (300 MHz, $CDCl_3$): $\delta$ = 8.18–8.12 (m, 1H), 8.09 (dd, *J* 7.9 and 0.9, 1H), 7.91–7.83 (m, 1H), 7.54–7.42 (m, 3H), 7.32 (d, *J* 7.2, 1H), 3.95 (s, 2H), 3.50–3.42 (m, 2H), 2.59–2.50 (m, 2H), 1.76–1.66 (m, 4H); $^{13}$C-NMR (101 MHz, $CDCl_3$): $\delta$ = 206.6 (C), 139.9 (C), 139.0 (C), 136.2 (C), 136.1 (C), 129.0 (C), 128.0 (CH), 127.0 (CH), 125.2 (CH), 124.8 (CH), 123.0 (CH), 122.0 (CH), 120.7 (CH), 49.4 ($CH_2$), 44.7 ($CH_2$), 41.1 ($CH_2$), 31.8 ($CH_2$), 21.1 ($CH_2$); IR (neat): $\nu$ = 3060, 2953, 1711, 1584, 1443, 1401, 749; HR-MS (ES-TOF): *m*/*z*: calcd for $C_{18}H_{17}ONaS^{35}Cl$: 339.0586, found 339.0574 [M + Na]$^+$.

### 1-(Dibenzo[*b*,*d*]thiophen-4-yl)-4-phenylbutan-2-one (3c)

Prepared according to **GP1** using dibenzothiophene-*S*-oxide **1** (40.0 mg, 0.2 mmol), 4-phenyl-1-butyne (56 μl, 0.4 mmol), toluene (2 mL) and catalyst (11.2 mg, 0.02 mmol, 5 mol%). The reaction was stirred for 45 minutes at 0 °C. Column chromatography (1 : 1 hexane : $CH_2Cl_2$) afforded **3c** (43 mg, 65%) as a white solid; $R_f$ 0.78 (3 : 7 EtOAc : hexane); mp: 102–104 °C; $^1$H-NMR (300 MHz, $CDCl_3$): $\delta$ = 8.04–7.96 (m, 1H), 7.93 (d, *J* 7.8, 1H), 7.74–7.66 (m, 1H), 7.38–7.26 (m, 3H), 7.15–6.93 (m, 6H), 3.78 (s, 2H), 2.79–2.63 (m, 4H); $^{13}$C-NMR (101 MHz, $CDCl_3$): $\delta$ = 206.3 (C), 140.9 (C), 140.0 (C), 139.0 (C), 136.2 (C), 136.1 (C), 128.9 (C), 128.6 (2CH), 128.5 (2CH), 128.0 (CH), 127.0 (CH), 126.2 (CH), 125.2 (CH), 124.7 (CH), 123.0 (CH), 122.0 (CH), 120.7 (CH), 49.6 ($CH_2$), 43.7 ($CH_2$), 29.9 ($CH_2$); IR (neat): $\nu$ = 3058, 3027, 2877, 1706, 1601, 1583, 1403, 1046, 746; HR-MS (ES-TOF): *m*/*z*: calcd for $C_{22}H_{18}ONaS$: 353.0976, found 353.0991 [M + Na]$^+$.

### 1-(Dibenzo[*b*,*d*]thiophen-4-yl)-3-methoxypropan-2-one (3d)

Prepared according to **GP1** using dibenzothiophene-*S*-oxide **1** (40.0 mg, 0.2 mmol), methyl propargyl ether (33.8 µl, 0.4 mmol), toluene (2 mL) and catalyst (11.2 mg, 0.02 mmol, 5 mol%). The reaction was stirred for 45 minutes at 0 °C. Column chromatography ($CH_2Cl_2$) afforded **3d** (47 mg, 87%) as a yellow solid; $R_f$ 0.31 (3 : 7 EtOAc : hexane); mp: 51–53 °C; $^1$H-NMR (300 MHz, $CDCl_3$): $\delta$ = 8.19–8.13 (m, 1H), 8.10 (d, *J* 7.7, 1H), 7.91–7.83 (m, 1H), 7.52–7.43 (m, 3H), 7.34 (d, *J* 7.2, 1H), 4.13 (s, 2H), 4.03 (s, 2H), 3.41 (s, 3H); $^{13}$C-NMR (101 MHz, $CDCl_3$): $\delta$ = 204.7 (C), 140.0 (C), 138.9 (C), 136.2 (C), 136.1 (C), 128.2 (C), 128.1 (CH), 127.1 (CH), 125.2 (CH), 124.7 (CH), 123.0 (CH), 122.0 (CH), 122.0 (CH), 77.3 ($CH_2$), 59.5 ($CH_3$), 45.5 ($CH_2$); IR (neat): $\nu$ = 2903, 1712, 1590, 1427, 1394, 1316, 1102, 759; HR-MS (ES-TOF): *m*/*z*: calcd for $C_{16}H_{14}O_2NaS$: 293.0612, found 293.0610 $[M + Na]^+$. **Open-flask protocol**: To a 25 mL RBF under an atmosphere of air was added dibenzothiophene-*S*-oxide **1** (401 mg, 2.0 mmol), methyl propargyl ether (338 µl, 4.0 mmol) and toluene (technical grade) (20 mL). The flask was placed in an ice bath and (2,4-di-*tert*-butyl$C_6H_3O)_3$PAu-($NCCH_3$)$SbF_6$ (22.4 mg, 0.002 mmol, 1 mol%) was added. The reaction was stirred at this temperature for 2 hours until TLC indicated reaction completion. Column chromatography ($CH_2Cl_2$) afforded **3d** (456 mg, 84%).

### 6-((*tert*-Butyldiphenylsilyl)oxy)-1-(dibenzo[*b*,*d*]thiophen-4-yl)-hexan-2-one (3e)

Prepared according to **GP1** using dibenzothiophene-*S*-oxide **1** (100 mg, 0.5 mmol), *tert*-butyl(hex-5-yn-1-yloxy)diphenylsilane (336 mg, 1.0 mmol), toluene (5 mL) and catalyst (11.2 mg, 2 mol%). The reaction was stirred for 2 hours at 0 °C. Column chromatography (3 : 2 hexane : $CH_2Cl_2$) afforded **3e** (222 mg, 82%) as a viscous oil; $R_f$ 0.31 (3 : 2 hexane : $CH_2Cl_2$); $^1$H-NMR (300 MHz, $CDCl_3$): $\delta$ = 8.20–8.13 (m, 1H), 8.09 (dd, *J* 7.9 and 0.9, 1H), 7.88–7.82 (m, 1H), 7.67–7.59 (m, 4H), 7.51–7.32 (m, 9H), 7.30 (d, *J* 7.3, 1H), 3.93 (s, 2H), 3.60 (t, *J* 6.2, 2H), 2.51 (t, *J* 7.3, 2H), 1.77–1.60 (m, 2H), 1.53–1.40 (m, 2H), 1.01 (s, 9H); $^{13}$C-NMR (101 MHz, $CDCl_3$): $\delta$ = 207.2 (C), 140.0 (C), 139.1 (C), 136.2 (C), 136.1 (C), 135.7 (4CH), 134.1 (2C), 129.7 (2CH), 129.2 (C), 128.0 (CH), 127.7 (4CH), 127.0 (CH), 125.2 (CH), 124.7 (CH), 123.0 (CH), 122.0 (CH), 120.6 (CH), 63.6 ($CH_2$), 49.4 ($CH_2$), 42.0 ($CH_2$), 32.0 ($CH_2$), 27.0 ($3CH_3$), 20.4 ($CH_2$), 19.4 (C); IR (neat): $\nu$ = 2930, 2856, 1713, 1588, 1427, 1105; HR-MS (ES-TOF): *m*/*z*: calcd for $C_{34}H_{36}O_2NaSiS$: 559.2103, found 559.2102 $[M + Na]^+$.

### 2-(3-(Dibenzo[*b*,*d*]thiophen-4-yl)-2-oxopropyl)isoindoline-1,3-dione (3f)

Prepared according to **GP1** using dibenzothiophene-*S*-oxide **1** (200 mg, 1.0 mmol), *N*-propargyl phthalimide (370 mg, 2.0 mmol) and catalyst (22.4 mg, 0.04 mmol, 2 mol%) for 4 hours at 0 °C and stirring for a further 16 hours at rt. The precipitate formed was washed with toluene and then recrystallized from hot EtOH affording **3f** as yellow crystals (201 mg, 52%); $R_f$ 0.65 (3 : 7 EtOAc : hexane); mp: 190–192 °C (EtOH); $^1$H-NMR (300 MHz, $CDCl_3$): $\delta$ = 8.20–8.15 (m, 1H), 8.13 (dd, *J* 7.9 and 1.0, 1H), 7.90–7.85 (m, 1H), 7.85–7.78 (m, 2H), 7.75–7.67 (m, 2H), 7.54–7.44 (m, 3H), 7.40 (d, *J* 7.3, 1H), 4.56 (s, 2H), 4.11 (s, 2H); $^{13}$C-NMR (101 MHz, $CDCl_3$): $\delta$ = 199.0 (C), 167.7 (2C), 140.0 (C), 139.0 (C), 136.5 (C), 136.1 (C), 134.2 (2CH), 132.1 (2C), 128.0 (CH), 127.5 (C), 127.2 (CH), 125.4 (CH), 124.8 (CH), 123.6 (2CH), 123.1 (CH), 122.0 (CH), 121.1 (CH), 46.7 ($CH_2$), 46.3 ($CH_2$); IR (neat): $\nu$ = 2970, 1769, 1735, 1698, 1470, 1409, 1067; HR-MS (ES-TOF): *m*/*z*: calcd for $C_{23}H_{15}NO_3NaS$: 408.0670, found 408.0667 $[M + Na]^+$.

### 1-(Dibenzo[*b*,*d*]thiophen-4-yl)-3-hydroxydecan-2-one (3g)

Prepared according to **GP1** using dibenzothiophene-*S*-oxide **1** (40 mg, 0.2 mmol), dec-1-yn-3-ol (64 µl, 0.4 mmol), toluene (2 mL) and catalyst (11.2 mg, 5 mol%) for 4 hours at 0 °C and stirring for a further 16 hours at rt. Purification of the reaction mixture with column chromatography (9 : 1 hexane : EtOAc), followed by recrystallization from hot MeOH afforded **3g** (54 mg, 76%); $R_f$ 0.25 (9 : 1 hexane : EtOAc); mp: 52–54 °C; $^1$H-NMR (300 MHz, $CDCl_3$): $\delta$ = 8.21–8.14 (m, 1H), 8.11 (d, *J* 7.9, 1H), 7.91–7.82 (m, 1H), 7.54–7.43 (m, 3H), 7.33 (d, *J* 7.2, 1H), 4.38 (dd, *J* 7.4 and 3.6, 1H), 4.07 (s, 2H), 3.33 (s, 1H), 2.02–1.88 (m, 1H), 1.75–1.62 (m, 1H), 1.59–1.16 (m, 10H), 0.88 (t, *J* 6.6, 3H); $^{13}$C-NMR (101 MHz, $CDCl_3$): $\delta$ = 208.9 (C), 139.9 (C), 138.9 (C), 136.3 (C), 136.1 (C), 128.1 (CH), 127.9 (C), 127.1 (CH), 125.2 (CH), 124.8 (CH), 123.0 (CH), 122.0 (CH), 121.0 (CH), 76.4 (CH), 44.3 ($CH_2$), 34.0 ($CH_2$), 31.9 ($CH_2$), 29.5 ($CH_2$), 29.2 ($CH_2$), 24.9 ($CH_2$), 22.8 ($CH_2$), 14.2($CH_3$); IR (neat): $\nu$ = 3446, 2924, 2854, 1714, 1585, 1443, 1402, 1047, 749; HR-MS (ES-TOF): *m*/*z*: calcd for $C_{22}H_{26}O_2NaS$: 377.1551, found 377.1565 $[M + Na]^+$.

### 2-(Dibenzo[*b*,*d*]thiophen-4-yl)-1-phenylethanone (3h)

Prepared according to **GP2** using dibenzothiophene-*S*-oxide **1** (60.0 mg, 0.3 mmol), phenylacetylene (65 µl, 0.6 mmol), toluene (0.01 M, 30 mL) and catalyst (16.8 mg, 0.03 mmol, 5 mol%). Column chromatography (19 : 1 hexane : EtOAc), followed by recrystallization from hot EtOAc afforded **3h** (53 mg, 58%) as a white solid; $R_f$ 0.33 (19 : 1 hexane : EtOAc); mp: 127–129 °C; $^1$H-NMR (300 MHz, $CDCl_3$): $\delta$ = 8.19–8.12 (m, 1H), 8.12–8.05 (m, 3H), 7.89–7.82 (m, 1H), 7.63–7.54 (m, 1H), 7.52–7.40 (m, 5H), 7.34 (d, *J* 6.9, 1H), 4.55 (s, 2H); $^{13}$C-NMR (101 MHz, $CDCl_3$): $\delta$ = 196.4 (C), 139.9 (C), 139.1 (C), 136.7 (C), 136.2 (2C), 133.5 (CH), 129.5 (C), 128.9 (2CH), 128.7 (2CH), 127.9 (CH), 127.0 (CH), 125.1 (CH), 124.7 (CH), 123.0 (CH), 122.0 (CH), 120.6 (CH), 44.7 ($CH_2$); IR (neat): $\nu$ = 3056, 2924, 2856, 1685, 1580, 1440, 1206, 908; HR-MS (ES-TOF): *m*/*z*: calcd for $C_{20}H_{14}ONaS$: 325.0663, found 325.0660 $[M + Na]^+$.

### 1-(2-Bromophenyl)-2-(dibenzo[*b*,*d*]thiophen-4-yl)ethanone (3i)

Prepared according to **GP2** using dibenzothiophene-*S*-oxide **1** (40.0 mg, 0.2 mmol), 1-bromo-2-ethynylbenzene (50 µL, 0.4 mmol), toluene (20 mL, 0.01 mmol) and catalyst (11.2 mg, 0.02 mmol, 5 mol%). Column chromatography (19 : 1 hexane : EtOAc) followed by recrystallization from hot EtOH afforded **3i** (30.5 mg, 40%) as white needles; $R_f$ 0.20 (19 : 1 hexane : EtOAc);

mp: 93–95 °C; $^1$H-NMR (300 MHz, $CDCl_3$): $\delta$ = 8.18–8.12 (m, 1H), 8.09 (dd, *J* 7.7 and 1.1, 1H), 7.89–7.82 (m, 1H), 7.64–7.59 (m, 1H), 7.51–7.42 (m, 3H), 7.41–7.35 (m, 2H), 7.35–7.24 (m, 2H), 4.53 (s, 2H); $^{13}$C-NMR (101 MHz, $CDCl_3$): $\delta$ = 200.2 (C), 141.4 (C), 140.2 (C), 139.1 (C), 136.2 (C), 136.1 (2C), 133.7 (CH), 131.8 (CH), 128.8 (CH), 128.3 (CH), 127.6 (CH), 127.0 (CH), 125.1 (CH), 124.7 (CH), 123.0 (CH), 122.0 (CH), 120.8 (CH), 118.8(C), 48.7 ($CH_2$); IR (neat): $\nu$ = 3054, 2940, 1703, 1591, 1441, 1332, 989, 742; HR-MS (ES-TOF): *m*/*z*: calcd for $C_{20}H_{14}OS^{79}Br$: 380.9949, found 380.9948 $[M + H]^+$.

### 2-(Dibenzo[*b*,*d*]thiophen-4-yl)-1-(4-methoxyphenyl)ethanone (3j)

Prepared according to **GP2** using dibenzothiophene-*S*-oxide **1** (40.0 mg, 0.2 mmol), 1-ethynyl-4-methoxybenzene (52 µl, 0.4 mmol), toluene (20 mL) and catalyst (11.2 mg, 0.02 mmol, 5 mol%). Column chromatography (19 : 1 hexane : EtOAc) afforded **3j** (28 mg, 42%) as a white solid; $R_f$ 0.18 (19 : 1 hexane : EtOAc); mp: 113–115 °C; $^1$H-NMR (300 MHz, $CDCl_3$): $\delta$ = 8.19–8.12 (m, 1H), 8.11–8.01 (m, 3H), 7.90–7.82 (m, 1H), 7.51–7.39 (m, 3H), 7.34 (d, *J* 7.2, 1H), 6.98–6.89 (m, 2H), 4.49 (s, 2H), 3.86 (s, 3H); $^{13}$C-NMR (101 MHz, $CDCl_3$): $\delta$ = 195.0 (C), 163.8 (C), 139.8 (C), 139.1 (C), 136.3 (C), 136.2 (C), 131.0 (2CH), 129.9 (C), 129.7 (C), 127.8 (CH), 126.9 (CH), 125.1 (CH), 124.7 (CH), 123.0 (CH), 122.0 (CH), 120.4 (CH), 114.0 (2CH), 55.6 ($CH_3$), 44.4 ($CH_2$); IR (neat): $\nu$ = 2910, 1717, 1593, 1508, 1400, 1167, 751; HR-MS (ES-TOF): *m*/*z*: calcd for $C_{21}H_{17}O_2NS$: 333.0949, found 333.0950 $[M + H]^+$.

### 2-(Dibenzo[*b*,*d*]thiophen-4-yl)-1-(thiophen-2-yl)ethanone (3k)

Prepared according to **GP2** using dibenzothiophene-*S*-oxide **1** (40 mg, 0.2 mmol), 2-ethynylthiophene (44 µl, 0.4 mmol), toluene (20 mL, 0.01 mmol) and catalyst (11.2 mg, 0.02 mmol, 5 mol%). Purification of the reaction mixture by column chromatography (9 : 1 hexane : EtOAc) afforded **3k** (38 mg, 62%) as an orange oil; $R_f$ 0.65 (9 : 1 hexane : EtOAc); $^1$H-NMR (300 MHz, $CDCl_3$): $\delta$ = 8.19–8.11 (m, 1H), 8.09 (dd, *J* 7.5 and 1.2, 1H), 7.90–7.82 (m, 2H), 7.65 (dd, *J* 4.9 and 0.7, 1H), 7.51–7.38 (m, 4H), 7.11 (dd, *J* 4.9 and 4.0, 1H), 4.46 (s, 2H); $^{13}$C-NMR (101 MHz, $CDCl_3$): $\delta$ = 189.2 (C), 143.9 (C), 139.9 (C), 138.9 (C), 136.2 (C), 136.2 (C), 134.4 (CH), 132.9 (CH), 129.2 (C), 128.4 (CH), 127.8 (CH), 127.0 (CH), 125.1 (CH), 124.7 (CH), 123.0 (CH), 122.0 (CH), 120.7 (CH), 45.5 ($CH_2$); IR (neat): $\nu$ = 3092, 3074, 1641, 1410, 1276, 1057, 750; HR-MS (EI-TOF): *m*/*z*: calcd for $C_{18}H_{13}OS_2$: 308.0330, found 308.0329 $[M + H]^+$.

### 1-(2,8-Dibromodibenzo[*b*,*d*]thiophen-4-yl)-3-methoxypropan-2-one (6)

Sulfoxide **5** (71.6 mg, 0.2 mmol) was added to a 50 mL RBF with methyl propargyl ether (34 µl, 0.4 mmol) and $CHCl_3$ (30 mL). catalyst (11.2 mg, 0.01 mmol, 5 mol%) was added and the mixture was stirred at rt for 17 hours. Purification by column chromatography ($CH_2Cl_2$) afforded **6** (58 mg, 70%) as a white solid; $R_f$ 0.07 (19 : 1 hexane : EtOAc); mp: 139–141 °C; $^1$H-NMR (300 MHz, $CDCl_3$): $\delta$ = 8.18 (s, 1H), 8.12 (s, 1H), 7.68 (d, *J* 8.5, 1H), 7.56 (dd, *J* 8.5 and 1.3, 1H), 7.46 (s, 1H), 4.12 (s, 2H), 4.00 (s, 2H), 3.45 (s, 3H); $^{13}$C-NMR (101 MHz, $CDCl_3$): $\delta$ = 204.1 (C), 139.4 (C), 138.0 (C), 136.6 (C), 136.4 (C), 131.5 (CH), 130.6 (CH), 130.0 (C), 125.0 (CH), 124.3 (CH), 123.8 (CH), 119.1 (C), 119.0 (C), 77.6 ($CH_2$), 59.6 ($CH_3$), 44.8 ($CH_2$); IR (neat): $\nu$ = 3067, 2901, 1723, 1567, 1410, 1319, 1072, 1042, 746; HR-MS (ES-TOF): *m*/*z*: calcd for $C_{16}H_{12}O_2NaS^{79}Br^{81}Br$: 450.8802, found 450.8801 $[M + Na]^+$.

### 1-(Allyloxy)-3-(dibenzo[*b*,*d*]thiophen-4-yl)propan-2-one (12a)

Prepared according to **GP1** using dibenzothiophene-*S*-oxide **1** (100 mg, 0.5 mmol), 3-(prop-2-yn-1-yloxy)prop-1-ene **11a** (54 wt% in $Et_2O$, 177 mg, 1.0 mmol), and catalyst (11.2 mg, 0.02 mmol, 2 mol%). The reaction mixture was stirred for 4 hours at 0 °C and left to warm to rt for a further 16 hours. Column chromatography ($CH_2Cl_2$) afforded **12a** (119 mg, 80%) as a yellow oil; $R_f$ 0.34 ($CH_2Cl_2$); $^1$H-NMR (300 MHz, $CDCl_3$): $\delta$ = 8.19–8.14 (m, 1H), 8.10 (dd, *J* 7.9 and 1.0, 1H), 7.90–7.83 (m, 1H), 7.52–7.43 (m, 3H), 7.35 (d, *J* 7.2, 1H), 5.89 (ddt, *J* 17.2, 10.4 and 5.8, 1H), 5.27 (dd, *J* 17.2 and 1.5, 1H), 5.21 (dd, *J* 10.4 and 1.5, 1H), 4.18 (s, 2H), 4.06 (s, 2H), 4.06–4.02 (m, 2H); $^{13}$C-NMR (101 MHz, $CDCl_3$): $\delta$ = 205.0 (C), 140.0 (C), 139.0 (C), 136.2 (C), 136.1 (C), 133.8 (CH), 128.3 (C), 128.1 (CH), 127.0 (CH), 125.2 (CH), 124.7 (CH), 123.0 (CH), 122.0 (CH), 120.8 (CH), 118.3 ($CH_2$), 74.8 ($CH_2$), 72.6 ($CH_2$), 45.6 ($CH_2$); IR (neat): $\nu$ = 2901, 1726, 1554, 1443, 1402, 1096, 912; HR-MS (ES-TOF): *m*/*z*: calcd for $C_{18}H_{16}O_2SNa$: 319.0769, found 319.0775 $[M + Na]^+$.

### *N*-Allyl-*N*-(3-(dibenzo[*b*,*d*]thiophen-4-yl)-2-oxopropyl)-4-methylbenzenesulfonamide (12c)

Prepared according to **GP1** using dibenzothiophene-*S*-oxide **1** (40 mg, 0.2 mmol), *N*-allyl-4-methyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide **11c** (96 mg, 0.4 mmol), and catalyst (11.2 mg, 0.02 mmol, 5 mol%). The reaction mixture was stirred for 2.5 hours at 0 °C. Column chromatography (9 : 1 hexane : EtOAc) followed by recrystallization from hot MeOH afforded **12c** (66 mg, 74%) as a white solid; $R_f$ 0.31 (9 : 1 hexane : EtOAc); mp: 104–106 °C; $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 8.21–8.14 (m, 1H), 8.11 (dd, *J* 8.1, 0.9, 1H), 7.91–7.82 (m, 1H), 7.65 (d, *J* 8.3, 2H), 7.53–7.43 (m, 3H), 7.32 (d, *J* 7.2, 1H), 7.21 (d, *J* 8.1, 2H), 5.58 (ddt, *J* 16.9, 10.1 and 6.8, 1H), 5.03 (dd, *J* 10.1, 1.1, 1H), 4.96 (dd, *J* 16.9, 1.1, 1H) 4.10 (s, 2H), 4.01 (s, 2H), 3.78 (d, *J* 6.7, 2H), 2.36 (s, 3H); $^{13}$C-NMR (101 MHz, $CDCl_3$): $\delta$ = 201.9 (C), 143.7 (C), 140.0 (C), 139.0 (C), 136.3 (C), 136.2 (C), 136.0 (C), 132.1 (CH), 129.8 (2CH), 128.2 (CH), 128.0 (C), 127.6 (2CH), 127.1 (CH), 125.3 (CH), 124.8 (CH), 123.0 (CH), 122.0 (CH), 120.9 (CH), 120.5 ($CH_2$) 54.4 ($CH_2$), 51.4 ($CH_2$), 46.4 ($CH_2$), 21.6 ($CH_3$); IR (neat): $\nu$ = 1731, 1443, 1397, 1153, 1045, 924, 752; HR-MS (ES-TOF): *m*/*z*: calcd for $C_{25}H_{24}NO_3S_2$: 450.1198, found 450.1180 $[M + H]^+$.

### 1-(Allyloxy)-3-(5-oxidodibenzo[*b*,*d*]thiophen-4-yl)propan-2-one (14)

*m*CPBA (72.3 mg, 0.42 mmol, 1.1 equiv.) was added in 5 portions over 10 minutes to a solution of **12a** (113 mg, 0.38 mmol) in $CH_2Cl_2$ (10 mL) at 0 °C. The reaction was allowed to warm to rt over 2 hours, washed with $NaHCO_3$ (4 × 10 mL), extracted with $CH_2Cl_2$ (4 × 10 mL), dried over $Na_2SO_4$, filtered and concentrated under reduced pressure. Purification by column chromatography (4 : 1 hexane : EtOAc to EtOAc) afforded firstly **12a** (25 mg, 22%) and then **14** (74 mg, 62%) as a white solid; $R_f$ 0.37 (3 : 7 hexane : EtOAc); mp: 98–100 °C; $^1$H-NMR (300 MHz, $CDCl_3$): $\delta$ = 7.96 (d, *J* 7.5, 1H), 7.80 (d, *J* 7.6, 1H), 7.74 (d, *J* 7.5, 1H), 7.64–7.53 (m, 2H), 7.50 (td, *J* 7.5 and 0.9, 1H), 7.29 (d, *J* 7.6, 1H), 5.94 (ddt, *J* 17.2, 10.5 and 5.7, 1H), 5.32 (dd, *J* 17.2 and 1.5, 1H), 5.24 (dd, *J* 10.5 and 1.2, 1H), 4.38–4.17 (m, 4H), 4.11 (d, *J* 5.8, 2H); $^{13}$C-NMR (101 MHz, $CDCl_3$): $\delta$ = 204.6 (C), 144.7 (C), 144.0 (C), 137.7 (C), 137.3 (C), 135.0 (C), 133.9 (CH), 132.7 (CH), 132.7 (CH), 131.7 (CH), 129.7 (CH), 127.5 (CH), 122.2 (CH), 121.0 (CH), 118.3 ($CH_2$), 75.1 ($CH_2$), 72.7 ($CH_2$), 42.5 ($CH_2$); IR (neat): $\nu$ = 3050, 2857, 1725, 1551, 1485, 1424, 1321, 1161, 1145, 1070, 1045, 1012, 762; HR-MS (ES-TOF): *m*/*z*: calcd for $C_{18}H_{17}O_3S$: 313.0898, found 313.0906 $[M + H]^+$.

### 3,3′-(Dibenzo[*b*,*d*]thiophene-4,6-diyl)bis(1-(allyloxy)propan-2-one) (16a)

Sulfoxide **14** (68 mg, 0.22 mmol) and enyne **11a** (54 wt% in $Et_2O$, 78.3 mg, 0.44 mmol) were dissolved in toluene (8.8 mL, 0.025 M). After stirring for 20 minutes the reaction mixture was transferred to an ice bath at 0 °C. (2,4-Di-*tert*-butyl$C_6H_3O)_3$-PAu($NCCH_3$)$SbF_6$ (12.3 mg, 0.011 mmol, 5 mol%) was added with a further portion (6.1 mg, 5.5 μmol, 2.5 mol%) added after 3 hours with the reaction mixture then stirred for a further 1 hour at 0 °C. The reaction mixture was filtered through a plug of silica and washed with $CH_2Cl_2$ (10 mL). The reaction mixture was concentrated under reduced pressure and purified by column chromatography (4 : 1 hexane : EtOAc) providing **16a** (65 mg, 73%) as a white solid; $R_f$ 0.58 (1 : 1 hexane : EtOAc); mp: 77–80 °C; $^1$H-NMR (300 MHz, $CDCl_3$): $\delta$ = 8.08 (d, *J* 7.7, 2H), 7.47 (app t, *J* 7.6, 2H), 7.34 (d, *J* 7.2, 2H), 5.90 (ddt, *J* 17.2, 10.4 and 5.7, 2H), 5.27 (app d, *J* 17.2, 2H), 5.21 (app d, *J* 10.4, 2H) 4.17 (s, 4H), 4.11–4.01 (m, 8H); $^{13}$C-NMR (101 MHz, $CDCl_3$): $\delta$ = 204.8 (2C), 139.5 (2C), 136.6 (2C), 133.8 (2CH), 128.3 (2CH), 128.3 (2C), 125.4 (2CH), 121.0 (2CH), 118.3 ($2CH_2$), 74.8 ($2CH_2$), 72.6 ($2CH_2$), 45.6 ($2CH_2$); IR (neat): $\nu$ = 2855, 1722, 1574, 1426, 1390, 1331, 1164, 1060, 1045; HR-MS (ES-TOF): *m*/*z*: calcd for $C_{24}H_{24}O_4NaS$: 431.1293, found 431.1288 $[M + Na]^+$.

### 1-(Allyloxy)-3-(6-(3-(but-3-en-1-yloxy)-2-oxopropyl)dibenzo[*b*,*d*]-thiophen-4-yl)propan-2-one (16b)

Sulfoxide **14** (60 mg, 0.192 mmol) and enyne **15** (77 wt% in $Et_2O$, 50 mg, 0.348 mmol) were dissolved in toluene (0.025 M, 10 mL). After stirring for 20 minutes at rt the reaction was transferred to an ice bath at 0 °C and (2,4-di-*tert*-butyl$C_6H_3O)_3$-PAu($NCCH_3$)$SbF_6$ (7.5 mol%) was added. The reaction was stirred for 4 hours filtered through a pad of silica washing with $CH_2Cl_2$, concentrated and purified by column chromatography (4 : 1 hexane : EtOAc) to afford **16b** (68 mg, 83%) as an off white solid; $R_f$ 0.81 (1 : 1 hexane : EtOAc); mp: 57–59 °C; $^1$H-NMR (300 MHz, $CDCl_3$): $\delta$ = 8.02 (dd, *J* 7.9 and 0.8, 2H), 7.40 (app t, *J* 7.6, 2H), 7.28 (d, *J* 7.3, 2H), 5.91–5.68 (m, 2H), 5.21 (dd, *J* 17.2 and 1.6, 1H), 5.15 (dd, *J* 10.2 and 1.6, 1H), 5.04 (dd, *J* 17.2 and 1.6, 1H), 4.97 (dd, *J* 10.2 and 1.6, 1H), 4.10 (s, 4H), 4.02–3.96 (m, 6H), 3.48 (t, *J* 6.7, 2H), 2.37–2.27 (m, 2H); $^{13}$C-NMR (101 MHz, $CDCl_3$): $\delta$ = 205.1 (C), 204.9 (C), 139.6 (2C), 136.7 (2C), 134.9 (CH), 133.8 (CH), 128.3 (2CH), 128.2 (2C), 125.4 (2CH), 121.0 (2CH), 118.3 ($CH_2$), 117.0 ($CH_2$), 75.9 ($CH_2$), 74.8 ($CH_2$), 72.6 ($CH_2$), 71.3 ($CH_2$), 45.6 ($2CH_2$), 34.2 ($CH_2$); IR (neat): $\nu$ = 2860, 1721, 1644, 1575, 1476, 143, 1061, 913, 776; HR-MS (ES-TOF): *m*/*z*: calcd for $C_{25}H_{26}O_4NaS$: 445.1450, found 445.1429 $[M + Na]^+$.

### Macrocycle 17a

[1,3-Bis-(2,4,6-trimethylphenyl)-2-imidazolidinylidene]dichloro-(phenylmethylene)(tricyclohexylphosphine)ruthenium (10.4 mg, 0.012 mmol) was added to a solution of **16a** (100 mg, 0.245 mmol) in $CH_2Cl_2$ (25 mL). The reaction mixture was heated to reflux for 1 hour, allowed to cool, concentrated and purified by column chromatography (3 : 7 hexane : EtOAc) to afford **17a** (80 mg, 86%) as a white solid; $R_f$ 0.58 (1 : 1 hexane : EtOAc); mp: 165–167 °C; $^1$H-NMR (300 MHz, $CDCl_3$): $\delta$ = 8.08 (d, *J* 7.2, 2H), 7.48 (app t, *J* 7.6, 2H), 7.39 (d, *J* 7.0, 2H), 5.74–5.60 (m, 2H), 4.19 (s, 4H), 4.02 (s, 4H), 3.96 (dd, *J* 3.0 and 1.3, 4H); $^{13}$C-NMR (101 MHz, $CDCl_3$): $\delta$ = 205.0 (2C), 139.2 (2C), 136.7 (2C), 130.2 (2CH), 128.1 (2CH), 128.1 (2C), 125.7 (2CH), 121.1 (2CH), 74.3 ($2CH_2$), 71.1 ($2CH_2$), 45.6 ($2CH_2$); IR (neat): $\nu$ = 2855, 1722, 1574, 1426, 1390, 1331, 1144, 1060, 1045, 919, 776, 731; HR-MS (ES-TOF): *m*/*z*: calcd for $C_{22}H_{20}O_4NaS$: 403.0980, found 403.0996 $[M + Na]^+$.

### Macrocycle 17b

[1,3-Bis-(2,4,6-trimethylphenyl)-2-imidazolidinylidene]dichloro-(phenylmethylene)(tricyclohexylphosphine)ruthenium (5.0 mg, 0.006 mmol) was added to a solution of **16b** (50 mg, 0.118 mmol) in $CH_2Cl_2$ (25 mL). The reaction mixture was heated to reflux for 2 hours, concentrated and purified by column chromatography (3 : 7 hexane : EtOAc) to afford **17b** (35 mg, 70%) as a white solid; $R_f$ 0.48 (1 : 1 hexane : EtOAc); mp: 138–139 °C; $^1$H-NMR (300 MHz, $CDCl_3$): $\delta$ = 8.07 (d, *J* 7.8, 2H), 7.48 (td, *J* 7.6 and 3.1, 2H), 7.37 (d, *J* 5.1, 2H), 6.11–5.95 (m, 1H), 5.69 (dt, *J* 15.0 and 5.6, 1H), 4.18 (s, 4H), 4.15–4.05 (m, 6H), 3.64 (t, *J* 5.8, 2H), 2.42 (dd, *J* 11.6 and 5.6, 2H); $^{13}$C-NMR (101 MHz, $CDCl_3$): $\delta$ = 206.6 (C), 205.8 (C), 139.2 (C), 139.1 (C), 136.7 (C), 136.6 (C), 132.0 (CH), 128.7 (CH), 128.7 (CH), 128.4 (C), 128.4 (C) 127.4 (CH), 125.4 (2CH), 121.0 (CH), 120.9 (CH), 76.3 ($CH_2$), 74.4 ($CH_2$), 71.7 ($CH_2$), 71.2 ($CH_2$), 44.7 ($CH_2$), 44.2 ($CH_2$), 32.8 ($CH_2$); IR (neat): $\nu$ = 2861, 1720, 1644, 1575, 1426, 1143, 1062, 914, 775; HR-MS (ES-TOF): *m*/*z*: calcd for $C_{23}H_{22}O_4NaS$: 417.1137, found 417.1136 $[M + Na]^+$.

### 3-(Dibenzo[*b*,*d*]thiophen-4-yl)-2-phenyl-1*H*-indole (18)

To **3h** (55 mg, 0.183 mmol, 1.0 eq.) was added AcOH (0.80 ml), TFA (0.28 ml) and phenylhydrazine (45 μL, 0.46 mmol, 2.5 eq.) in a sealed (Ace) tube. The reaction was stirred at 100 °C for 28 hours at which point reaction completion was observed by TLC. The mixture was added to ice/water (10 mL), the mixture was extracted with $CH_2Cl_2$ (10 mL × 3) and the organic portions were washed with HCl (1 M, 5 mL), water (5 mL), dried over $Na_2SO_4$, concentrated and purified by column chromatography (9 : 1 hexane : EtOAc) to afford **18** (45.6 mg, 66%) as a viscous orange oil; $R_f$ 0.31 (9 : 1 hexane : EtOAc); $^1$H-NMR (300 MHz, $CDCl_3$): $\delta$ = 8.46 (s, 1H), 8.21 (ddd, *J* 7.6, 5.6 and 1.4, 2H), 7.77–7.70 (m, 1H), 7.59–7.48 (m, 3H), 7.48–7.41 (m, 3H), 7.40–7.34 (m, 2H), 7.33–7.20 (m, 4H), 7.13 (td, *J* 7.6 and 0.9, 1H); $^{13}$C-NMR (101 MHz, $CDCl_3$): $\delta$ = 141.4 (C), 140.1 (C), 136.1 (C), 136.0 (2C), 134.8 (C), 132.5 (C), 130.5 (C), 129.3 (CH), 128.9 (2CH), 128.8 (C), 127.9 (CH), 127.3 (2CH), 126.7 (CH), 125.0 (CH), 124.3 (CH), 123.0 (CH), 122.9 (CH), 121.8 (CH), 120.4 (CH), 120.4 (CH), 120.3 (CH), 113.5 (C), 111.1 (CH); IR (neat): $\nu$ = 3408, 3057, 1578, 1487, 1442, 1384, 1253, 905, 742, 693; HR-MS (ES-TOF): *m*/*z*: calcd for $C_{26}H_{18}NS$: 376.1160, found 376.1170 $[M + H]^+$.

### Diethyl 4-(dibenzo[*b*,*d*]thiophen-4-yl)-3-methyl-5-oxocyclohex-3-ene-1,1-dicarboxylate (20) and diethyl 2-(3-(dibenzo[*b*,*d*]-thiophen-4-yl)-2-oxopropyl)-2-(2-oxopropyl)malonate (21)

Prepared according to **GP1** using dibenzothiophene-*S*-oxide **1** (40 mg, 0.2 mmol), diyne **19** (48.6 mg, 0.4 mmol), toluene (2 mL) and catalyst (11.2 mg, 5 mol%). The reaction was stirred for 2 hours at 0 °C before allowing to warm to rt for 17 hours. Column chromatography (3 : 7 hexane : $CH_2Cl_2$ to $CH_2Cl_2$) afforded **20** (49 mg, 57%) as a colourless oil and **21** (15 mg, 17%) as a colourless oil.

**20** $R_f$ 0.48 (3 : 7 hexane : EtOAc); $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 8.13 (ddd, *J* 12.9, 5.7 and 2.4, 2H), 7.83–7.75 (m, 1H), 7.55–7.37 (m, 3H), 7.11 (dd, *J* 7.2 and 1.0, 1H), 4.44–4.21 (m, 4H), 3.32–2.94 (m, 4H), 1.85 (s, 3H), 1.32 (t, *J* 7.1, 3H), 1.31 (t, *J* 7.1, 3H),; $^{13}$C NMR (101 MHz, $CDCl_3$): $\delta$ = 192.4 (C), 169.9 (C), 169.8 (C) 156.3 (C), 156.3 (C), 140.1 (C), 139.4 (C), 136.1 (C), 136.1 (C) 135.8 (C), 128.2 (CH), 126.8 (CH), 124.7 (CH), 124.5 (CH), 122.8 (CH), 121.8 (CH), 121.0 (CH), 62.6 ($CH_2$), 62.4 ($CH_2$), 55.0 (C), 42.6 ($CH_2$), 37.5 ($CH_2$), 22.7 ($CH_3$), 14.2 ($2CH_3$); IR (neat): $\nu$ = 2982, 1729, 1673, 1302, 1250, 1167, 752; HR-MS (ES-TOF): *m*/*z*: calcd for $C_{25}H_{24}O_5NaS$: 459.1242, found 459.1229 $[M + Na]^+$.

**21** $R_f$ 0.42 (7 : 3 hexane : EtOAc); $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 8.18–8.12 (m, 1H), 8.09 (dd, *J* 7.9 and 0.9, 1H), 7.87–7.81 (m, 1H), 7.50–7.42 (m, 3H), 7.31 (d, *J* 7.0, 1H), 4.13 (q, *J* 7.1, 2H), 4.12 (q, *J* 7.1, 2H), 3.97 (s, 2H), 3.50 (s, 2H), 3.31 (s, 2H), 1.99 (s, 3H), 1.17 (t, *J* 7.0, 6H); $^{13}$C NMR (101 MHz, $CDCl_3$): $\delta$ = 206.0 (C), 204.6 (C), 169.5 (2C), 139.9 (C), 139.1 (C), 136.3 (C), 136.0 (C), 128.4 (CH), 128.2 (C), 127.1 (CH), 125.3 (CH), 124.8 (C), 122.9 (C), 122.0 (CH), 120.8 (CH), 62.1 ($2CH_2$), 53.2 (C), 49.4 ($CH_2$), 45.8 ($CH_2$), 44.9 ($CH_2$), 30.2 ($CH_3$), 14.0 ($2CH_3$); IR (neat): $\nu$ = 2982, 2930, 1719, 1444, 1403, 1364, 1201, 1096, 754; HR-MS (ES-TOF): *m*/*z*: calcd for $C_{25}H_{26}O_6SNa$: 477.1348, found 477.1339 $[M + Na]^+$.

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