Synthesis of 3-Alkynyl-2-(methylsulfanyl)benzo[*b*]furans via Sonogashira Cross-Coupling of 3-Iodo-2-(methylsulfanyl)benzo[*b*]furans with Terminal Alkynes

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Abstract: 3-Alkynyl-2-(methylsulfanyl)benzo[*b*]furans were readily prepared under mild reaction conditions by palladium-catalyzed cross-coupling of 3-iodo-2-(methylsulfanyl)benzo[*b*]furans with a variety of terminal alkynes. The reaction was performed with propargyl alcohols, protected propargyl alcohols, as well as alkyl and aryl terminal alkynes. In addition, the 3-alkynylbenzo[*b*]furans obtained were readily transformed into more complex products using the hydrotelluration reaction, which furnished the desired vinylic tellurides in good yields. Moreover, using a copper-catalyzed homocoupling reaction, we were able to convert a 3-alkynylbenzo[*b*]furan into a symmetric diyne in good yield.

Key words: palladium, Sonogashira cross-coupling, furans, alkynes, catalysis

Heterocycles containing oxygen exhibit a broad range of biological activities, such as anticancer,[1] antiviral,[2] antioxidative,[3] insecticidal,[4] anti-inflammatory,[5] and antifungal[6] activity. The synthesis of heterocycles, particularly the benzo[*b*]furan nucleus, from a simple synthon and with a high degree of selectivity has been a major challenge to organic chemists. The characteristic structure of these compounds involves the presence of substituent groups at the C2 and C3 positions of the benzofuran skeleton. We were interested in studying the structure–activity relationship of benzofurans with a chalcogen atom at the 2-position and an alkyne group at the 3-position, in order to evaluate the pharmacological activity of these compounds. To the best of our knowledge, there are no reports in the literature dealing with the preparation of these 2,3-disubstituted benzofurans. In particular, the lack of an effective method for the introduction of an alkyne substituent at the C3 position of the skeleton has been an obstacle to the synthesis of these compounds.

In an attempt to develop an easy, versatile, and efficient methodology for such compounds, we chose a palladium cross-coupling reaction between 3-iodo-2-chalcogenobenzo[*b*]furans and terminal alkynes. The palladium-catalyzed cross-coupling reaction of hetaryl halides with terminal alkynes, commonly referred to as the Sonogashira reaction, is a powerful, versatile, and popular tool for the selective construction of new carbon–carbon bonds.[7]

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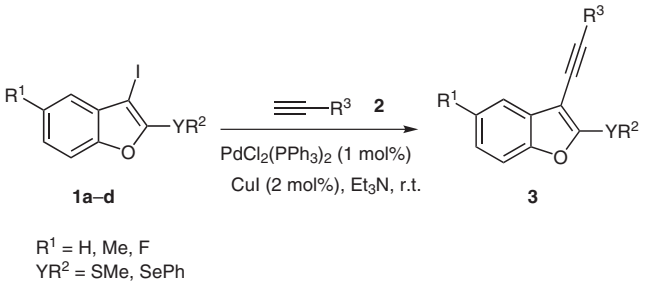
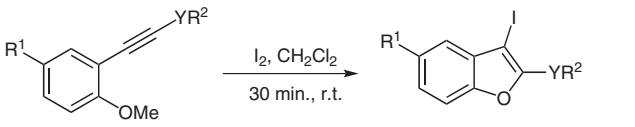
This reaction is generally cocatalyzed by copper salts, and an amine as base and a phosphine as a ligand for palladium are also typically employed. Recent advances in Sonogashira reactions, including the use of metals other than palladium[8] and a copper-free protocol,[9] have also been reported.

Our continuing interest in the synthesis[10] and applications[11] of organochalcogenides in organic synthesis prompted us to examine and expand the scope of the Sonogashira reaction of 3-iodo-2-(methylsulfanyl)benzo[*b*]furans **1a–d** with different terminal alkynes **2a–o** to provide 3-alkynylbenzo[*b*]furans **3a–v** (Scheme 1).



Scheme 1

The starting materials **1a–d** are readily available in 87–95% yield by electrophilic cyclization[12] of (2-chalcogenoalkynyl)anisoles by treatment with iodine in dichloromethane (Scheme 2).[13]



1a R^1 = H, YR^2 = SMe 93%
1b R^1 = Me, YR^2 = SMe 95%
1c R^1 = F, YR^2 = SMe 87%
1d R^1 = H, YR^2 = SePh 90%

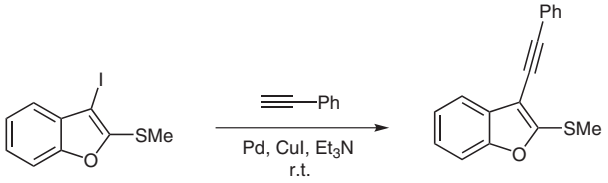
Scheme 2

For a preliminary optimization of the reaction conditions, we chose 3-iodo-2-(methylsulfanyl)benzo[*b*]furan (**1a**) and phenylacetylene (**2a**) as the substrates. Thus, a mixture of **1a** (0.5 mmol), alkyne **2a** (1.25 mmol), triethylamine (2 mL) as solvent, and copper(I) iodide (2 mol%)

were employed with a variety of palladium salts, at room temperature (Table 1).

According to Table 1, both palladium(0) and palladium(II) with the different ligands tested exhibited catalytic activity and $PdCl_2(PPh_3)_2$ (5 mol%) gave the desired product in excellent yield (entry 1). However, it is important to note that when the amount of catalyst was reduced from five to two or one mol%, an increase in the yield was observed (cf. entries 1, 2, and 8). The other palladium salts were less effective (entries 3, 5–7). When the reactions were carried out in the absence of palladium or copper, the desired coupling product was not obtained (entry 9).

Table 1 Study of Catalyst Effect on the Coupling Reaction[a]



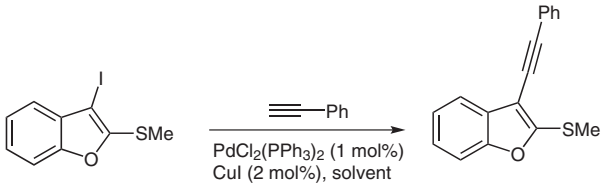
1a **3a**

Entry	Catalyst (mol%)	Yield **3a** (%)[b]
1	$PdCl_2(PPh_3)_2$ (5)	90
2	$PdCl_2(PPh_3)_2$ (2)	97
3	$Pd(OAc)_2$ (2)	trace
4	$Pd(PPh_3)_4$ (2)	85
5	$PdCl_2(NCPh)_2$ (2)	38
6	$PdCl_2$ (2)	34
7	$Pd(acac)_2$ (2)	40
8	$PdCl_2(PPh_3)_2$ (1)	99
9	–	n.r.[c]

[a] CuI (2 mol%) was used in all the reactions.
[b] Yields were determined by GC analysis.
[c] Reaction carried out in the absence of CuI (n.r. = no reaction).

An analysis of the influence of the solvent showed that the best results were obtained when dioxane was used (Table 2, entry 4). *N*,*N*-Dimethylformamide, methanol, 1,2-dimethoxyethane, toluene, and tetrahydrofuran gave moderate yields (entries 1–3, 5, and 6). However, when triethylamine was used as solvent and base, the Sonogashira product was obtained in 99% yield (entry 11). We also investigated other bases, and found that optimal results were achieved when organic bases such as pyrrolidine and triethylamine were used (entries 4, 9, and 11), while inorganic bases, such as potassium phosphate and potassium carbonate, gave the desired product in moderate yields (entries 7 and 8). When sodium hydroxide was used as the base, only traces of the desired product were detected (entry 10). Thus, a careful analysis revealed that the optimum conditions for this coupling involved the use of $PdCl_2(PPh_3)_2$ (1 mol%), triethylamine (2 mL), 3-iodo-

Table 2 Optimization of Reaction Conditions[a]



1a **3a**

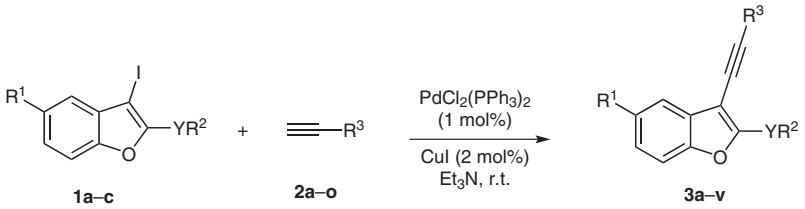
Entry	Solvent	Base	Yield (%)[b]
1	DMF	Et_3N	60
2	MeOH	Et_3N	45
3	DME	Et_3N	37
4	dioxane	Et_3N	92
5	toluene	Et_3N	56
6	THF	Et_3N	54
7	dioxane	K_3PO_4	67
8	dioxane	K_2CO_3	50
9	dioxane	pyrrolidine	87
10	dioxane	NaOH	trace
11	Et_3N	Et_3N	99

[a] CuI (2 mol%) was used in all the reactions.
[b] Yields were determined by GC analysis.

2-(methylsulfanyl)benzo[*b*]furan (**1a**; 0.5 mmol), copper(I) iodide (2 mol%), and phenylacetylene (**2a**; 1.25 mmol), at room temperature for three hours.

To expand the applicability of our method, we applied these conditions to other halobenzo[*b*]furans **1a**–**d** and other terminal alkynes **2a**–**o**. The results, summarized in Table 3, show that the reaction worked well for a variety of propargyl alcohols, protected propargyl alcohols, and aryl- and alkyl-substituted alkynes. A detailed analysis revealed that the reaction was effective with alkynes containing both no substituted and substituted aryl groups (entries 1–4). Both hindered and nonhindered propargyl alcohols provided the coupling products in excellent yields (entries 5–8). We also tested a protected propargyl alcohol, and, although the reaction gave the product **3k** in 84% yield, it required a long reaction time, 24 hours (entry 11). We also found that the coupling reaction was not sensitive to steric effects on the terminal alkynes. For example, terminal alkynes containing a *tert*-butyl or *n*-butyl group gave the desired product in comparable yields (entries 12 and 13). The effect of the hydroxy position in the alkyne chain was also examined. Alkynols **2i** and **2j** (entries 9 and 10), with four and twelve carbons between the hydroxy group and the triple bond, respectively, produced the corresponding product in yields similar to those obtained with alkynes containing the hydroxy group at the propargyl position.

Table 3 Cross-Coupling Reactions between 3-Iodobenzo[*b*]furans **1a–c** and Alkynes **2a–o**



1a–c **2a–o** **3a–v**

R^1 = H, Me, F
YR^2 = SMe, SePh

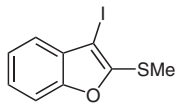
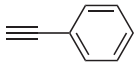
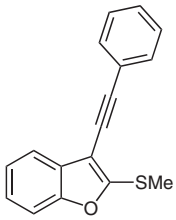
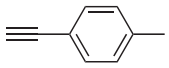
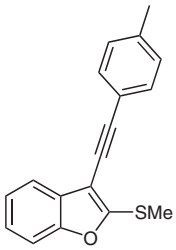
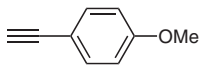
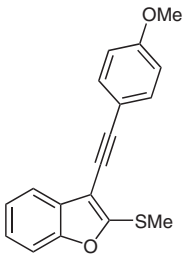
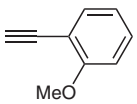
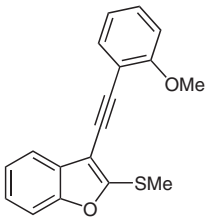
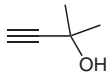
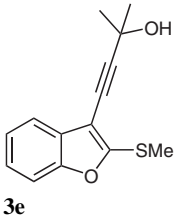
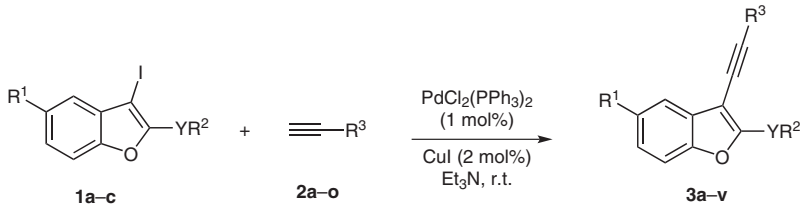
Entry	Substrate	Alkyne	Product	Yield (%)[a,b]
1	 **1a**	 **2a**	 **3a**	99
2	**1a**	 **2b**	 **3b**	96
3	**1a**	 **2c**	 **3c**	95
4	**1a**	 **2d**	 **3d**	85
5	**1a**	 **2e**	 **3e**	93

Table 3 Cross-Coupling Reactions between 3-Iodobenzo[*b*]furans **1a–c** and Alkynes **2a–o** (continued)



R^1 = H, Me, F
YR^2 = SMe, SePh

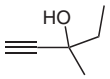
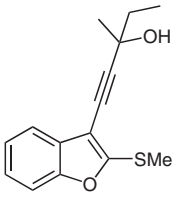
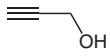
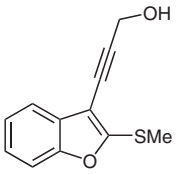
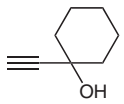
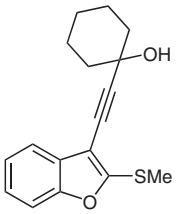
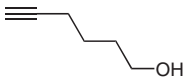
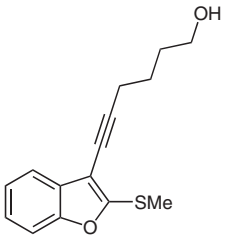
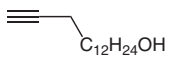
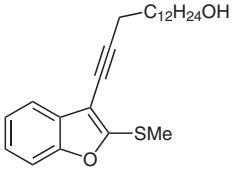
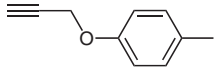
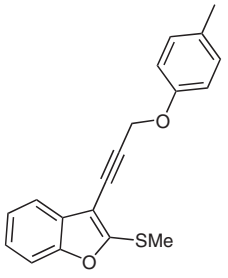
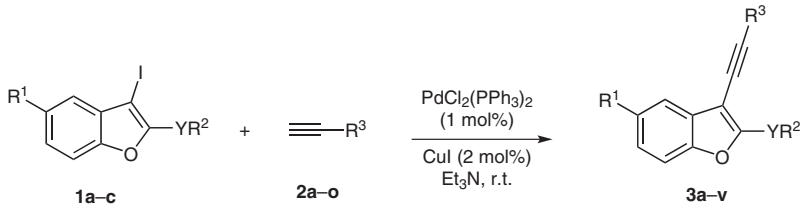
Entry	Substrate	Alkyne	Product	Yield (%)[a,b]
6	**1a**	 **2f**	 **3f**	80
7	**1a**	 **2g**	 **3g**	88
8	**1a**	 **2h**	 **3h**	86
9	**1a**	 **2i**	 **3i**	80
10	**1a**	 **2j**	 **3j**	78
11	**1a**	 **2k**	 **3k**	84[c]

Table 3 Cross-Coupling Reactions between 3-Iodobenzo[*b*]furans **1a–c** and Alkynes **2a–o** (continued)



1a–c **2a–o** **3a–v**

R^1 = H, Me, F
YR^2 = SMe, SePh

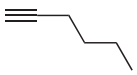
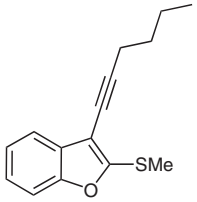
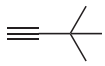
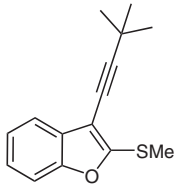
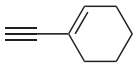
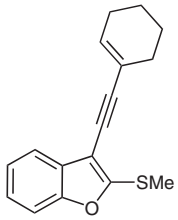
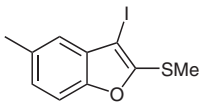
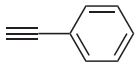
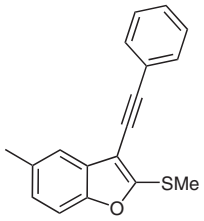
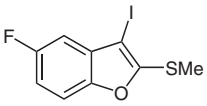
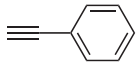
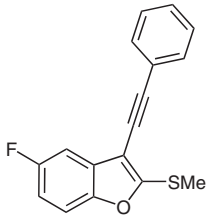
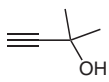
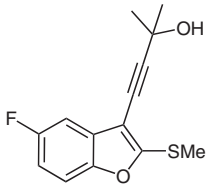
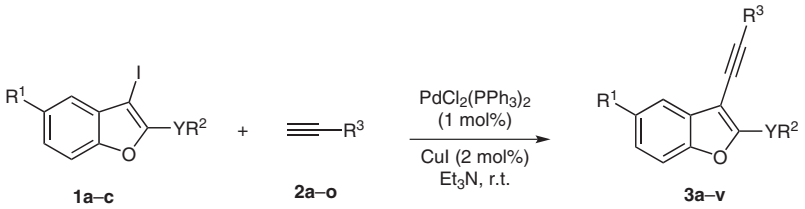
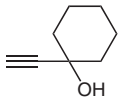
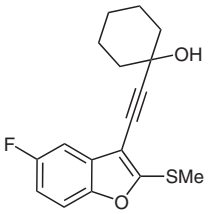
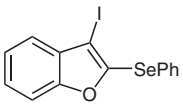
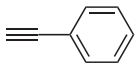
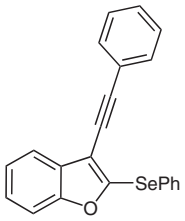
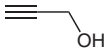
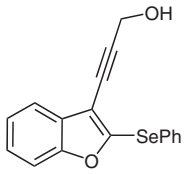
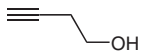
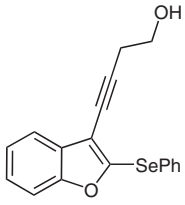
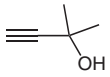
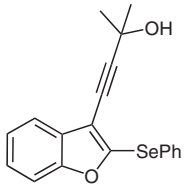
Entry	Substrate	Alkyne	Product	Yield (%)[a,b]
12	**1a**	 **2l**	 **3l**	89
13	**1a**	 **2m**	 **3m**	75
14	**1a**	 **2n**	 **3n**	45
15	 **1b**	 **2a**	 **3o**	75
16	 **1c**	 **2a**	 **3p**	72
17	**1c**	 **2e**	 **3q**	80

Table 3 Cross-Coupling Reactions between 3-Iodobenzo[*b*]furans **1a–c** and Alkynes **2a–o** (continued)



1a–c **2a–o** **3a–v**

R^1 = H, Me, F
YR^2 = SMe, SePh

Entry	Substrate	Alkyne	Product	Yield (%)[a,b]
18	**1c**	 **2h**	 **3r**	91
19	 **1d**	 **2a**	 **3s**	50[d]
20	**1d**	 **2g**	 **3t**	40[d]
21	**1d**	 **2o**	 **3u**	55[d]
22	**1d**	 **2e**	 **3v**	45[d]

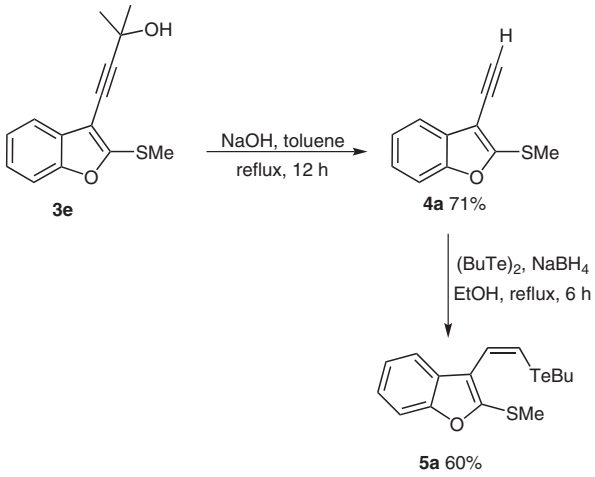
[a] Isolated yields.
[b] The reactions were carried out for 2–6 h at r.t.
[c] The reaction was carried out for 24 h at r.t.
[d] The reactions were carried out for 16 h at 60 °C.

Finally, we explored the possibility of expanding our methodology to other 3-iodobenzo[*b*]furans **1b**,**c** with a methyl and fluorine in the aromatic ring. It was found that the reaction worked well, affording the 3-alkynylbenzo[*b*]furan derivatives **3o–r** in good to excellent yields,

under the same reaction conditions (Table 3, entries 15–18).

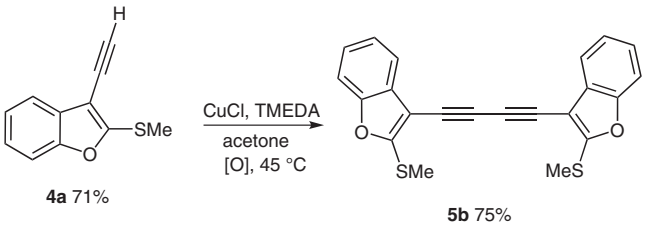
In an attempt to broaden the scope of our methodology, the possibility of performing the reaction with an organoselenium group on the 3-iodobenzofurans was also investigated. Substrate **1d**, which has a phenylselanyl group on the 2-position, was cross-coupled efficiently with alkynes (Table 3, entries 19–22).

In addition, the 3-alkynylbenzo[*b*]furans obtained by this method appear to be promising intermediates for the preparation of more highly substituted benzo[*b*]furans. We therefore investigated the synthesis of vinylic telluride **5a** using compound **4a** as starting material. For this purpose, 3-alkynylbenzo[*b*]furan **3e** was subjected to a retro-Favorskii reaction,[14] in which a propargylic monoacetylenic alcohol reacted with sodium hydroxide in toluene under reflux for twelve hours, affording the terminal alkyne **4a** in 71% yield (Scheme 3). Then, compound **4a** reacted with dibutyl ditelluride and sodium borohydride in ethanol under reflux for six hours, by the hydrotelluration reaction,[15] affording the corresponding vinylic telluride **5a**, in 60% yield. Many classes of organotellurium compounds have been prepared and studied to date, and vinylic tellurides are certainly the most useful and promising of these compounds in view of their usefulness in organic syntheses, including in the synthesis of natural products.[16]



Scheme 3

The terminal alkyne **4a** thus obtained was readily transformed into a diyne system via an oxidative homocoupling reaction catalyzed by a copper salt (Scheme 4). Diynes are important structural units for biologically active organic compounds, including anticancer antibiotics,[17] and other natural products,[18] as well as for new functional materials.[19] In view of this, we carried out the reaction of the terminal alkyne **4a** with copper(I) chloride (5 mol%) and *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (5 mol%) in acetone under heating ***and an oxygen atmosphere*** for four hours; this gave the symmetric diyne **5b** in 75% yield (Scheme 4).[20]



Scheme 4

In summary, we have described the Sonogashira cross-coupling reaction of 3-iodo-2-(methylsulfanyl)benzo[*b*]furan with a variety of terminal alkynes in the presence of a catalytic amount of $PdCl_2(PPh_3)_2$, copper(I) iodide as cocatalyst, and triethylamine as solvent and base, under mild reaction conditions. In addition, the 3-alkynylbenzo[*b*]furans obtained were readily transformed into more complex products by the hydrotelluration reaction, furnishing the desired vinylic telluride in good yields. Similarly, using copper-catalyzed homocoupling reactions, we were able to convert 3-alkynylbenzo[*b*]furan into symmetric diynes in good yields. The studies of the structure–activity relationship and pharmacological activity of these compounds are in progress and will appear in a specialized journal soon.

^{1}H NMR were obtained at 400 MHz of samples dissolved in $CDCl_3$. Chemical shifts are reported in ppm, referenced to the solvent peak of $CDCl_3$ or tetramethylsilane (TMS) as the external reference. ^{13}C NMR were obtained at 100 MHz of samples dissolved in $CDCl_3$. Chemical shifts are reported in ppm, referenced to the solvent peak of $CDCl_3$. High-resolution mass spectra were recorded on a double focusing magnetic sector mass spectrometer using EI at 70 eV. GC-MS analyses were performed using Shimadzu QP2010PLUS GC/MS combination. Column chromatography was performed using silica gel (230–400 mesh) following the methods described by Still. Thin-layer chromatography (TLC) was performed using silica gel GF254, 0.25 mm thickness. For visualization, TLC plates were either placed under ultraviolet light, or stained with iodine vapor or acidic vanillin. The following solvents were dried and purified by distillation from the reagents indicated: tetrahydrofuran from sodium with a benzophenone ketyl indicator. All other solvents were ACS or HPLC grade unless otherwise noted. Air- and moisture-sensitive reactions were conducted in flame-dried or oven-dried glassware equipped with tightly fitted rubber septa and under a positive atmosphere of dry nitrogen or argon. Reagents and solvents were handled using standard syringe techniques. Temperatures above room temperature were maintained by use of a mineral oil bath with an electrically heated coil connected to a controller.

Cross-Coupling Reaction; General Procedure

The appropriate benzofuran **1a–c** (0.5 mmol) was added to a Schlenk tube containing $PdCl_2(PPh_3)_2$ (0.0035 g, 1 mol%) and Et_3N (2 mL) under an argon atmosphere. To the resulting soln was added CuI (0.0019 g, 2 mol%). The reaction mixture was stirred for 15 min at r.t. Then a soln of the appropriate terminal alkyne **2** (1.25 mmol) in Et_3N (1 mL) was added dropwise, and the reaction mixture was stirred at r.t. Subsequently, the mixture was diluted with CH_2Cl_2 (20 mL) and washed with brine (3 × 20 mL). The organic phase was separated, dried ($MgSO_4$), and concentrated under vacuum. The residue was purified by flash chromatography (silica gel, EtOAc–hexane). Selected spectral and analytical data are given below.

2-(Methylsulfanyl)-3-(phenylethynyl)benzofuran (3a)
Yield: 0.130 g (99%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.63–7.56 (m, 3 H), 7.43–7.32 (m, 4 H), 7.28–7.26 (m, 2 H), 2.67 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.9, 131.5, 128.9, 128.3, 124.7, 123.4, 123.2, 119.6, 110.8, 104.8, 97.1, 79.0, 16.1.

MS (EI, 70 eV): *m*/*z* (%) = 264 (3), 261 (100), 246 (56), 218 (20), 202 (22), 149 (14).

3-[(2-Methoxyphenyl)ethynyl]-2-(methylsulfanyl)benzofuran (3d)
Yield: 0.124 g (85%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.66–7.64 (m, 1 H), 7.53 (dd, *J* = 5.8, 1.7 Hz, 1 H), 7.41–7.39 (m, 1 H), 7.31–7.24 (m, 3 H), 6.96–6.86 (m, 2 H), 3.91 (s, 3 H), 2.69 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.8, 154.7, 134.0, 133.1, 129.7, 124.6, 123.3, 120.4, 119.7, 112.4, 110.6, 105.2, 93.5, 82.9, 81.0, 55.7, 16.1.

MS (EI, 70 eV): *m*/*z* (%) = 293 (6), 290 (100), 275 (48), 261 (45), 244 (19), 215 (23), 186 (16).

2-Methyl-4-[2-(methylsulfanyl)benzofuran-3-yl]but-3-yn-2-ol (3e)
Yield: 0.114 g (93%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.52–7.49 (m, 1 H), 7.38–7.36 (m, 1 H), 7.25–7.20 (m, 2 H), 2.76 (s, 1 H), 2.60 (s, 3 H), 1.68 (s, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.8, 154.7, 128.8, 124.5, 123.2, 119.3, 110.6, 104.1, 101.8, 71.8, 65.7, 31.5, 15.9.

MS (EI, 70 eV): *m*/*z* (%) = 246 (2), 243 (89), 228 (55), 186 (17), 143 (28), 42 (100).

HRMS (EI): *m*/*z* calcd for $C_{14}H_{14}O_2S$: 246.0715; found: 246.0717.

1-[2-(Methylsulfanyl)benzofuran-3-yl)ethynyl]cyclohexanol (3h)
Yield: 0.122 g (86%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.53–7.50 (m, 1 H), 7.40–7.38 (m, 1 H), 7.28–7.22 (m, 2 H), 2.62 (s, 3 H), 2.33 (s, 1 H), 2.10–2.00 (m, 2 H), 1.70–1.59 (m, 7 H), 1.34–1.25 (m, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.9, 153.8, 128.9, 124.6, 123.3, 119.5, 110.7, 104.3, 100.8, 74.1, 69.4, 40.1, 25.2, 23.5, 16.0.

MS (EI, 70 eV): *m*/*z* (%) = 282 (100), 267 (13), 236 (61), 185 (34), 163 (12), 143 (26).

2-(Methylsulfanyl)-3-[3-(*p*-tolyloxy)prop-1-ynyl]benzofuran (3k)
Yield: 0.129 g (84%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.47–7.45 (m, 1 H), 7.38–7.36 (m, 1 H), 7.26–7.20 (m, 2 H), 7.10 (d, *J* = 8.5 Hz, 2 H), 6.97 (d, *J* = 8.5 Hz, 2 H), 4.96 (s, 2 H), 2.58 (s, 3 H), 2.29 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.8, 155.6, 154.8, 130.7, 129.9, 129.8, 124.7, 123.4, 119.6, 115.0, 114.7, 110.7, 103.8, 92.1, 56.9, 20.5, 16.0.

MS (EI, 70 eV): *m*/*z* (%) = 304 (16), 230 (14), 198 (100), 166 (16).

3-(3,3-Dimethylbut-1-ynyl)-2-(methylsulfanyl)benzofuran (3m)
Yield: 0.091 g (75%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.52–7.50 (m, 1 H), 7.39–7.34 (m, 1 H), 7.26–7.21 (m, 2 H), 2.62 (s, 3 H), 1.37 (s, 9 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.8, 153.6, 129.3, 124.5, 123.0, 119.5, 110.6, 106.7, 105.6, 68.3, 31.0, 28.4, 16.1.

MS (EI, 70 eV): *m*/*z* (%) = 244 (2), 241 (100), 226 (89), 211 (26), 179 (20), 151 (20).

5-Methyl-2-(methylsulfanyl)-3-(phenylethynyl)benzofuran (3o)
Yield: 0.104 g (75%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.59–7.57 (m, 2 H), 7.40–7.27 (m, 5 H), 7.09–7.06 (m, 1 H), 2.65 (s, 3 H), 2.45 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.8, 153.5, 133.0, 131.4, 128.9, 128.3, 128.2, 125.9, 119.4, 110.3, 96.9, 79.2, 21.2, 16.1.

MS (EI, 70 eV): *m*/*z* (%) = 274 (100), 260 (70), 231 (16), 216 (16), 199 (11), 137 (10).

5-Fluoro-2-(methylsulfanyl)-3-(phenylethynyl)benzofuran (3p)
Yield: 0.101 g (72%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.57–7.55 (m, 2 H), 7.35–7.33 (m, 3 H), 7.32–7.25 (m, 2 H), 6.97 (td, *J* = 6.4, 3.0 Hz, 1 H), 2.67 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.8, 158.4, 156.9, 151.1, 131.4, 128.5, 128.3, 122.9, 122.1 (d, *J* = 26.3 Hz), 111.4 (d, *J* = 9.5 Hz), 105.3 (d, *J* = 25.6 Hz), 97.4, 78.3, 15.7.

MS (EI, 70 eV): *m*/*z* (%) = 280 (26), 278 (100), 264 (84), 236 (28), 220 (39), 191 (23), 139 (9).

3-Ethynyl-2-(methylsulfanyl)benzofuran (4a) by Retro-Favorskii Reaction
Powdered NaOH (0.120 g, 3 mmol) was added to a two-necked round-bottomed flask equipped with a reflux condenser, containing a soln of **3e** (0.246 g, 1.0 mmol) in toluene (10 mL) under an argon atmosphere. The mixture was slowly heated to reach reflux temperature, during which time the reaction mixture became dark brown, and was refluxed for 12 h. After this, the mixture was diluted with CH_2Cl_2 (20 mL), and washed with brine (3 × 20 mL). The organic phase was separated, dried ($MgSO_4$), and concentrated under vacuum. The residue was purified by flash chromatography (silica gel, EtOAc–hexane).

Yield: 0.133 g (71%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.57–7.53 (m, 1 H), 7.43–7.38 (m, 1 H), 7.29–7.24 (m, 2 H), 3.52 (s, 1 H), 2.64 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.2, 154.8, 128.9, 124.7, 123.5, 119.5, 110.8, 103.7, 85.0, 73.7, 16.0.

MS (EI, 70 eV): *m*/*z* (%) = 188 (2), 185 (100), 171 (84), 143 (62), 127 (15), 100 (17).

(*Z*)-3-[2-(Butyltellanyl)vinyl]-2-(methylsulfanyl)benzofuran (5a)
$NaBH_4$ (0.095 g, 2.5 mmol) was added in small portions to a soln of **4a** (0.188 g, 1 mmol) in THF (5 mL) and the $(BuTe)_2$ (0.184 g, 0.5 mmol) in EtOH (10 mL) at r.t. under argon. Towards the end of the addition, when the red color of the soln had disappeared, the mixture was refluxed for 12 h. After this, the mixture was diluted with EtOAc (20 mL) and washed with brine (3 × 20 mL). The organic phase was separated, dried ($MgSO_4$), and concentrated under vacuum. The residue was purified by flash chromatography (silica gel, EtOAc–hexane).

Yield: 0.223 g (60%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.50–7.47 (m, 1 H), 7.42–7.39 (m, 1 H), 7.34 (d, *J* = 10 Hz, 1 H), 7.28 (d, *J* = 10 Hz, 1 H), 7.27–7.19 (m, 2 H), 2.67 (t, *J* = 7.6 Hz, 2 H), 2.54 (s, 3 H), 1.78 (quin, *J* = 7.4 Hz, 2 H), 1.37 (sext, *J* = 7.3 Hz, 2 H), 0.90 (t, *J* = 7.3 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.3, 146.9, 127.7, 127.5, 124.5, 122.6, 121.7, 119.9, 110.7, 110.3, 99.9, 33.9, 24.9, 17.2, 13.3, 8.1.

MS (EI, 70 eV): *m*/*z* (%) = 371 (42), 315 (25), 300 (22), 268 (21), 186 (43), 172 (100), 143 (30), 113 (23).

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