RSC Advances

PAPER

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Cite this: *RSC Adv.*, 2014, **4**, 48547

Metal-free *n*-Et_4NBr-catalyzed radical cyclization of disulfides and alkynes leading to benzothiophenes under mild conditions†

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Received 7th August 2014
Accepted 10th September 2014

DOI: 10.1039/c4ra08260e

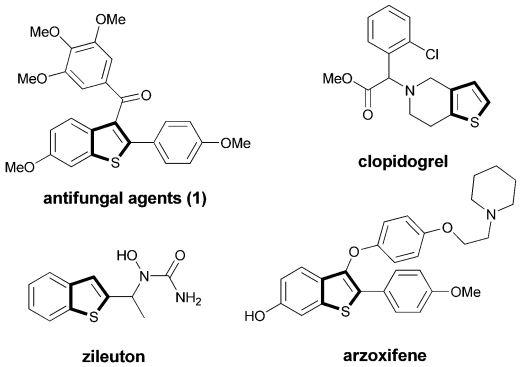
www.rsc.org/advances

A novel *n*-Et_4NBr-catalyzed method for the synthesis of benzothiophene derivatives *via* cascade reactions of substituted disulfides with alkynes through S–S bond cleavage and alkenyl radical cyclization reactions has been developed. The reaction has a high functional-group tolerance. The new method is environmental and practical, and the starting materials are readily available. These advantages, relative to previous methods, provide an opportunity for the construction of diverse and useful benzothiophene motifs.

Introduction

Heterocycles widely occur in natural products and biologically active molecules. Especially, they have often been assigned as privileged structures in drug development. Consequently, developing new, versatile and efficient approaches for the synthesis of heterocycles is of high ongoing interest. Benzothiophene derivatives are important heterocycles which have attracted much attention for their frequent occurrence in natural products and their wide range of biological and physiological activities[1] and are also widespread in material chemistry.[2] For example, they are often used as antimitotic,[3] antifungal agents (**1**)[4] and they are also found in numerous clinically important drugs, such as clopidogrel,[5] zileuton,[6] arzoxifene[7] and raloxifene[8] (Scheme 1). Thus, development of novel and efficient methods for the synthesis of these compounds will be valuable for the screening of novel biologically active molecules. However, investigations on the synthetic methods for the formation of benzothiophene motifs are rather limited.[9] The conventional methods for the synthesis of these important compounds typically involve two approaches. One is the electrophilic cyclization of *o*-alkynyl thioanisole.[10] The second approach mainly involves transition-metal catalyzed or strong base enhanced cyclization of *o*-haloalkynylbenzenes with various thiol surrogates.[11] Despite some great advantages of these reactions, there are still certain limitations including harsh reaction conditions, the uneasily available precursors and metal salt catalytic conditions. In 1973, Undheim and Lie attempted the direct conversion of thiophenols and alkynes to benzothiophene motifs under metal-free conditions, unfortunately, long time (5–22 days) were required, and the resulting yields were low.[12] Very recently, Li and co-workers developed an elegant work for the synthesis of benzothiophenes *via* intermolecular oxidative cyclization between thiophenols and alkynes using $Mn(OAc)_2$ as the catalyst.[13]

Disulfides are very stable in air and easily prepared from readily available thiols.[14] Recently, using disulfides as the starting materials to construct sulfur-based compounds *via* S–S bond cleavage have caught considerable attention.[15] Moreover, there are increasing demands for metal-free reactions owing to trace-metal impurities can be avoided in the end products.[16] In particular, direct and straightforward formation of various functional groups from inert C–H bonds meets the requirement of atom-economy and has emerged as a powerful tool for organic synthesis.[17] In this respect, lots of examples of direct sp^2 C–H functionalization *via* the radical pathway for the synthesis of heterocycles have been significantly disclosed by us[18] and



Scheme 1 Popular drugs containing the benzothiophene motif.

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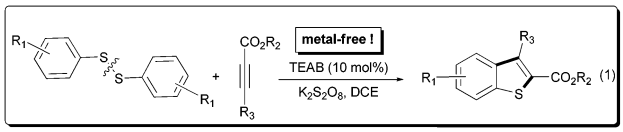
† Electronic supplementary information (ESI) available. CCDC 1010819. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c4ra08260e

other research groups.[19] Herein, we report a simple and practical metal-free approach to benzothiophenes *via* alkenyl radical cyclization reactions under mild conditions (eqn (1)).

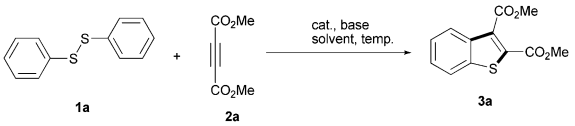


Results and discussion

We first chose 1,2-diphenyldisulfane **1a** and dimethyl but-2-ynedioate **2a** as the model substrates to optimize the catalysis conditions, which include oxidants, catalysts and solvents under nitrogen atmosphere. As shown in Table 1, several oxidants, $PhI(OAc)_2$, O_2, TBHP, H_2O_2 and $K_2S_2O_8$ (10 mol% catalytic amount relative to 1,2-diphenyldisulfane) were tested in DCE (entries 1–5) by using TEAB as the catalyst, and $K_2S_2O_8$ was the most effective oxidant. We attempted to use different catalysts, and TEAB was a suitable catalyst (entries 5–9 and 15). The effect of solvents (DCE, toluene, CH_3CN, 1,4-dioxane) was also investigated (entries 5, 10–12), DCE provided the highest yield. Reaction temperature was also investigated, and the yield of the target product reached maximum at 90 °C. After the optimization process for catalysts, oxidants, solvent and temperature, the following cyclization reactions were performed under our standard conditions: 10 mol% TEAB as the catalyst, 2.2 equiv. of $K_2S_2O_8$ as the oxidant and DCE as the solvent at 90 °C under nitrogen atmosphere.

The scope of TEAB-catalyzed cascade reactions of the substituted disulfides with alkynes was investigated under the optimized conditions. As shown in Table 2, the radical cyclization reactions could be performed for all the substrates examined, and the desired benzothiophene derivatives were obtained in good isolated yields. For substituted disulfides the substrates containing electron-donating groups exhibited higher reactivity than the others (products **3c**, **3d**, **3e**, **3f**, **3s**, **3t**, **3u** and **3v**). For different alkynes, including symmetric or unsymmetrical alkynes their reactivity did not show obviously difference (products **3a–3r**, **3s–3v**), unfortunately, terminal alkyne, 1,2-diarylethyne and 1,2-dialkylethyne were the poor substrates in this transformation (products **3w–3z**). As expected, *meta*-substituted substrates gave a mixture of two regioselective

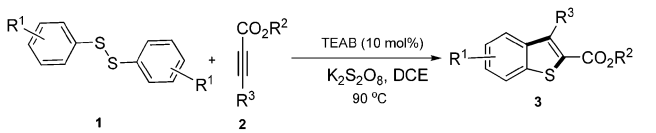
Table 1 Optimization of the reaction conditions[a]

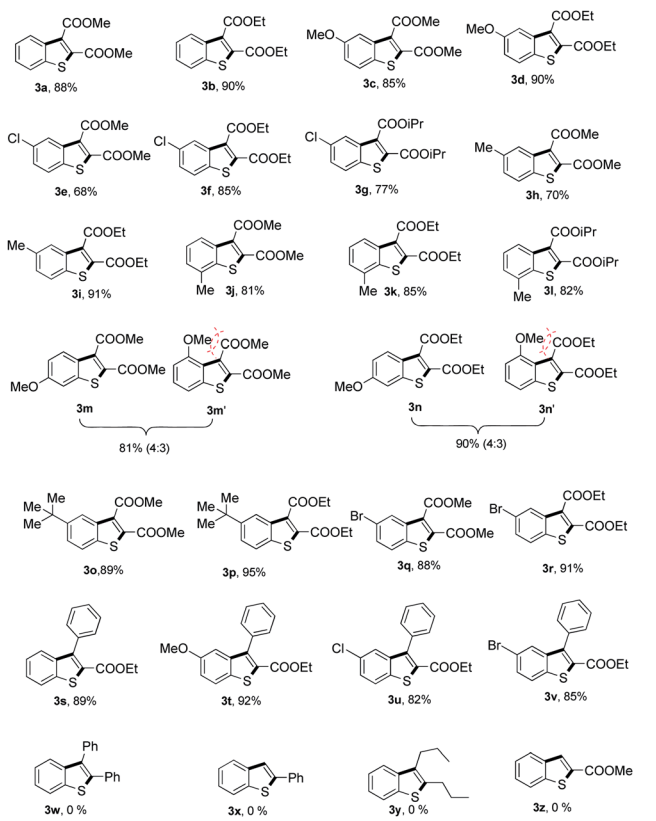


Entry	Catalyst	Oxidant	Solvent	Yield[b] (%)
1	TEAB	$PhI(OAc)_2$	DCE	15
2	TEAB	O_2	DCE	Trace
3	TEAB	TBHP	DCE	25
4	TEAB	H_2O_2	DCE	33
5	TEAB	$K_2S_2O_8$	DCE	88
6	TBAB	$K_2S_2O_8$	DCE	80
7	TBAI	$K_2S_2O_8$	DCE	58
8	TBAC	$K_2S_2O_8$	DCE	55
9	I_2	$K_2S_2O_8$	DCE	0
10	TEAB	$K_2S_2O_8$	CH_3CN	45
11	TEAB	$K_2S_2O_8$	Toluene	40
12	TEAB	$K_2S_2O_8$	1,4-Dioxane	38
13	TEAB	$K_2S_2O_8$	DCE	40[c]
14	TEAB	$K_2S_2O_8$	DCE	62[d]
15	TEAB	$K_2S_2O_8$	DCE	81[e]
16	None	$K_2S_2O_8$	DCE	Trace

[a] Reaction conditions: under nitrogen atmosphere, **1a** (0.5 mmol), **2a** (1.7 mmol.), catalyst (0.05 mmol), oxidant (2.2 equiv.), solvent (1.5 mL), 90 °C and reaction time (24 h). TBAC = $(n\text{-Bu})_4NCl$; TBAB = $(n\text{-Bu})_4NBr$; TBAI = $(n\text{-Bu})_4NI$; TEAB = Et_4NBr; TBHP = *tert*-butyl hydroperoxide solution 5.5 M in decane; DCE = 1,2-dichloroethane. [b] Isolated yield (based on the amount of **1a**). [c] 50 °C. [d] 60 °C. [e] 80 °C.

Table 2 TEAB-catalyzed synthesis of benzothiophene derivatives *via* radical cyclization of disulfides with alkynes[a,b,c]





[a] Reaction conditions: under nitrogen atmosphere, substituted diphenyldisulfane (0.5 mmol), alkynes (1.7 mmol), TEAB (0.05 mmol), $K_2S_2O_8$ (1.1 mmol), DCE (1.5 mL). [b] Isolated yield (based on the amount of **1**). [c] Reaction time (24 h).

products (products **3m**/**3m′** and **3n**/**3n′**), which suggested that the existence of possible steric hindrance arising from the presence of a *meta*-substituent "COOMe" (see Table 2, **3m′** and **3m′**). Besides that, the more stability of intermediate **C** of **3m′** and **3n′** as shown in Scheme 5 can not be excluded. The metal-free TEAB-catalyzed radical cyclization reactions could tolerate some functional groups including esters (products **3a–3v**), ethers (products **3c**, **3d**, **3m**, **3o** and **3t**), C–Cl bond (products **3e**, **3f** and **3g**) and C–Br bond (products **3q** and **3r**), which could be used for further modifications at the substituted positions. The structure of **3b** was unambiguously confirmed by X-ray crystallographic analysis (Fig. 1) (see ESI for details†). Interestingly, treatment of benzenethiol (**4a**) with dimethyl but-2-ynedioate (**2a**) under the optimized conditions produced dimethyl benzo[*b*]thiophene-2,3-dicarboxylate (**3a**) in a moderate yield (Scheme 2).

Further, we explored the synthetic applicability of the method. As shown in Scheme 3, the gram-scale reaction was performed in the usual laboratory setup with a one-neck round-bottomed flask fitted with a nitrogen balloon, and the reaction afforded **3a** in 93% yield. This example clearly demonstrates the practical aspect of this newly developed method.

To understand the mechanism further, the reaction of **1a** was tested in the presence of TEMPO (2,2,6,6-tetramethylpiperidine 1-oxy, a well-known radical inhibitor) as a radical scavenger. The formation of **2a** was completely inhibited in the reactions (eqn (1), Scheme 4), demonstrating that a radical process may be involved in this reaction. Moreover, control experiments were conducted to elucidate the mechanism of this radical cyclization reaction. The intermolecular kinetic isotope effects (KIE) were investigated, and no kinetic isotope effect ($\kappa_H/\kappa_D = 1.0$) was observed, which indicates that C–H bond cleavage might not be the rate-determining step (eqn (2), Scheme 4).

On the basis of these preliminary results and reports in the literature,[20] a possible mechanism for TEAB-catalyzed radical cyclization reactions for the synthesis of benzothiophene derivatives is suggested in Scheme 5. Reaction of tetraethylammonium bromide with peroxydisulfate produced tetraethylammonium sulfate radical anions,[15g] then the tetraethylammonium sulfate radical reacts with the disulfides to form an thiyl radical **A**. The addition of thiyl radical **A** to alkyne **2a** affords the alkenyl radical intermediate **B**,[13] which further undergoes intramolecular radical substitution reaction to give intermediate **C**. Finally, hydrogen abstraction of radical intermediate **C** by tetraethylammonium sulfate radical anions leads to the benzothiophene derivatives. Further investigations on the more detailed mechanism are ongoing in our laboratory.

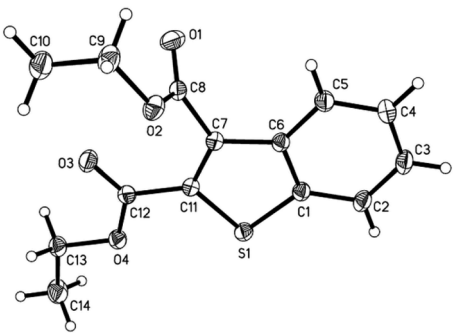
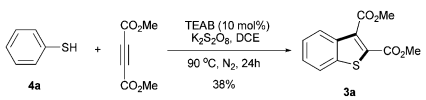
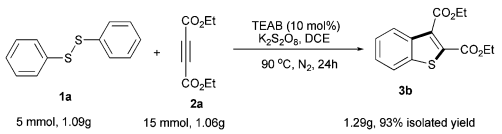


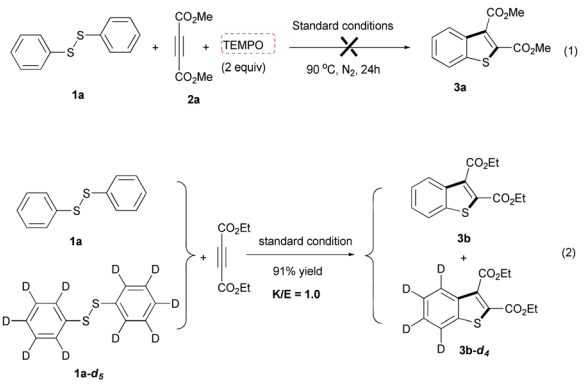
Fig. 1 X-ray crystal structure of compound **3b**.



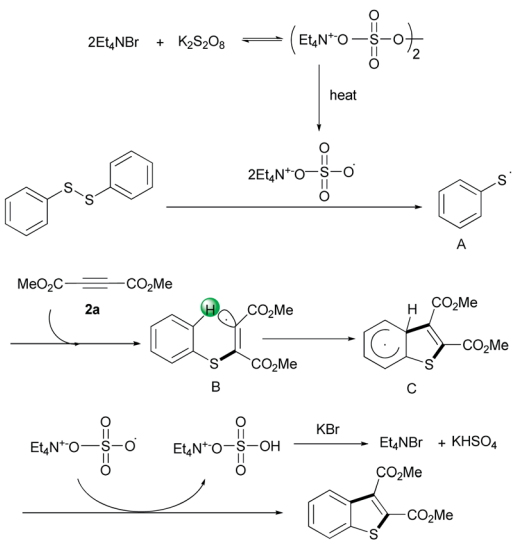
Scheme 2 Synthesis of **3a** using benzenethiol (**4a**) and dimethyl but-2-ynedioate (**2a**) as starting materials under standard conditions.



Scheme 3 Synthesis of **3b** on gram scale.



Scheme 4 Control experiments.



Scheme 5 A proposed mechanism for the direct transformation.

Experimental section

General experimental procedures

All reagents and solvents were obtained from commercial suppliers and used without further purification. Mass analyses and HRMS were obtained on a Finnigan-LCQDECA mass spectrometer. Flash chromatography was performed on silica gel (200–300 mesh). ^{1}H and ^{13}C NMR data were recorded at 400 and 100 MHz on a BRUKER 400 spectrometer. Chemical shifts (δ) are expressed in parts per million (ppm) coupling constants (J) are in Hz. Proton and carbon magnetic resonance spectra (^{1}H NMR and ^{13}C NMR) were recorded using tetramethylsilane (TMS) in the solvent of $CDCl_3$ as the internal standard (^{1}H NMR: TMS at 0.00 ppm, $CDCl_3$ at 7.28 ppm; ^{13}C NMR: $CDCl_3$ at 77.0 ppm).

General procedure for synthesis of substituted benzothiophenes. A 25 mL Schlenk tube equipped with a magnetic stirring bar was charged with TEAB (10.5 mg), potassium persulfate (1.1 mmol), substituted various disulfides (**1**) (0.5 mmol) and alkynes (**2**) (1.7 mmol). The tube was evacuated twice and backfilled with nitrogen, and DCE (1.5 mL) was added to the tube under nitrogen atmosphere. The tube was sealed with a balloon and then the mixture was allowed to stir under nitrogen atmosphere at 90 °C for 24 h. After completion of the reaction, the resulting solution was cooled to room temperature, and the solvent was removed with the aid of a rotary evaporator. The residue was purified by column chromatography on silica gel using petroleum ether–ethyl acetate as eluent to provide the desired product (**3**).

Dimethyl benzo[b]thiophene-2,3-dicarboxylate ***(3a)***.[20] Eluent petroleum ether–ethyl acetate (30 : 1). White solid, mp 83–84 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ 7.92 (d, 1H, J = 5.2 Hz), 7.84 (d, 1H, J = 5.6 Hz), 7.50–7.45 (m, 2H), 4.02 (s, 3H), 3.94 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ 164.9, 162.2, 140.3, 136.7, 133.2, 133.1, 127.5, 125.7, 124.5, 122.6, 53.0, 52.9. HRMS m/z calcd for $C_{12}H_{10}O_4S$ [M + Na]$^+$: 273.0197, found: 273.0191.

Diethyl benzo[b]thiophene-2,3-dicarboxylate ***(3b)***. Eluent petroleum ether–ethyl acetate (30 : 1). White solid, mp 62–64 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ 7.95 (d, 1H, J = 6.0 Hz), 7.84 (d, 1H, J = 6.0 Hz), 7.48–7.45 (m, 2H), 4.52 (q, 2H, J = 7.2 Hz), 4.42 (q, 2H, J = 7.2 Hz), 1.45 (t, 3H, J = 8.0 Hz), 1.41 (t, 3H, J = 8.0 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ 164.5, 161.8, 140.3, 136.9, 133.5, 133.3, 127.3, 125.6, 124.4, 122.5, 62.1, 14.17, 14.16. HRMS m/z calcd for $C_{14}H_{14}O_4S$ [M + Na]$^+$: 301.0510, found: 301.0511.

Dimethyl 5-methoxybenzo[b]thiophene-2,3-dicarboxylate ***(3c)***.[13] Eluent petroleum ether–ethyl acetate (30 : 1). White solid, mp 98–100 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ 7.71 (d, 1H, J = 8.8 Hz), 7.37 (s, 1H), 7.15 (d, 1H, J = 9.2 Hz), 4.10 (s, 3H), 3.95 (s, 3H), 3.89 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ 164.9, 162.8, 158.4, 137.9, 134.5, 132.9, 132.3, 123.2, 118.8, 105.3, 55.6, 53.0, 52.8. HRMS m/z calcd for $C_{13}H_{12}O_5S$ [M + Na]$^+$: 303.0303, found: 303.0303.

Diethyl 5-methoxybenzo[b]thiophene-2,3-dicarboxylate ***(3d)***. Eluent petroleum ether–ethyl acetate (30 : 1). White solid, mp 59–61 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ 7.69 (d, 1H, J = 9.2 Hz), 7.38 (s, 1H), 7.13 (d, 1H, J = 9.2 Hz), 4.50 (q, 2H, J = 8.0 Hz), 4.41 (q, 2H, J = 8.0 Hz), 3.88 (s, 3H), 1.45 (t, 3H, J = 4.0 Hz), 1.40 (t, 3H, J = 4.0 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ 164.5, 161.9, 158.3, 138.0, 134.9, 132.9, 132.3, 123.2, 118.6, 105.3, 62.1, 61.8, 55.5, 14.2, 14.1. HRMS m/z calcd for $C_{15}H_{16}O_5S$ [M + Na]$^+$: 331.0616, found: 331.0610.

Dimethyl 5-chlorobenzo[b]thiophene-2,3-dicarboxylate ***(3e)***. Eluent petroleum ether–ethyl acetate (30 : 1). White solid, mp 105–107 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ 7.79 (s, 1H), 7.78 (d, 1H, J = 8.0 Hz), 7.45 (d, 1H, J = 8.0 Hz), 4.03 (s, 3H), 3.96 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ 164.2, 161.9, 138.2, 137.8, 135.6, 132.3, 131.9, 128.1, 124.2, 123.6, 53.2, 53.0. HRMS m/z calcd for $C_{12}H_9ClO_4S$ [M + Na]$^+$: 306.9808, found: 306.9815.

Diethyl 5-chlorobenzo[b]thiophene-2,3-dicarboxylate ***(3f)***. Eluent petroleum ether–ethyl acetate (30 : 1). White solid, mp 81–83 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ 7.98 (s, 1H), 7.78 (d, 1H, J = 8.0 Hz), 7.45 (d, 1H, J = 8.0 Hz), 4.51 (q, 2H, J = 8.0 Hz), 4.41 (q, 2H, J = 8.0 Hz), 1.48–1.40 (m, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ 163.8, 161.5, 138.2, 137.9, 135.9, 132.1, 131.9, 127.9, 124.1, 123.6, 62.4, 62.1, 14.1. HRMS m/z calcd for $C_{14}H_{13}ClO_4S$ [M + Na]$^+$: 335.0121, found: 335.0126.

Diisopropyl 5-chlorobenzo[b]thiophene-2,3-dicarboxylate ***(3g)***. Eluent petroleum ether–ethyl acetate (30 : 1). yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ 7.93 (s, 1H), 7.75 (d, 1H, J = 8.8 Hz), 7.44 (d, 1H, J = 8.4 Hz), 5.43–5.37 (m, 1H), 5.30–5.24 (m, 1H), 1.46 (d, 6H, J = 8.4), 1.40 (d, 6H, J = 8.4). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ 163.4, 160.9, 138.2, 137.9, 136.0, 132.3, 132.0, 127.8, 123.9, 123.6, 70.4, 70.0, 21.8, 21.7. HRMS m/z calcd for $C_{16}H_{17}ClO_4S$ [M + Na]$^+$: 363.0434, found: 363.0440.

Dimethyl 5-methylbenzo[b]thiophene-2,3-dicarboxylate ***(3h)***. Eluent petroleum ether–ethyl acetate (30 : 1). White solid, mp 83.7–85.2 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ 7.75–7.72 (m, 2H), 7.33 (d, 1H, J = 8.0 Hz), 4.05 (s, 3H), 3.95 (s, 3H), 2.49 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ 165.4, 162.3, 137.7, 137.1, 135.7, 133.0, 129.5, 124.1, 122.2, 52.9, 52.8, 21.5. HRMS m/z calcd for $C_{13}H_{12}O_4S$ [M + Na]$^+$: 287.0354, found: 287.0359.

Diethyl 5-methylbenzo[b]thiophene-2,3-dicarboxylate ***(3i)***. Eluent petroleum ether–ethyl acetate (30 : 1). Pale yellow viscous liquid. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ 7.93 (s, 1H), 7.45–7.73 (m, 2H), 7.33 (d, 1H, J = 8.0 Hz), 4.52 (q, 2H, J = 7.2 Hz), 4.41 (q, 2H, J = 7.2 Hz), 2.50 (s, 3H), 1.46 (t, 3H, J = 8.0), 1.42 (t, 3H, J = 8.0). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ 164.8, 161.9, 137.7, 137.2, 135.6, 133.3, 133.0, 129.3, 124.0, 122.1, 62.0, 61.9, 21.5, 14.17, 14.16. HRMS m/z calcd for $C_{15}H_{16}O_4S$ [M + Na]$^+$: 315.0667, found: 315.0663.

Dimethyl 7-methylbenzo[b]thiophene-2,3-dicarboxylate ***(3j)***. Eluent petroleum ether–ethyl acetate (30 : 1). White solid, mp 74–75 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ 7.79 (d, 1H, J = 8.4 Hz), 7.41 (t, 1H, J = 7.2 Hz), 7.29 (d, 1H, J = 7.2 Hz), 4.04 (s, 3H), 3.97 (s, 3H), 2.58 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ 165.0, 162.3, 140.8, 136.7, 134.0, 132.5, 132.2, 127.5, 126.2, 122.1, 52.9, 52.8, 20.0. HRMS m/z calcd for $C_{13}H_{12}O_4S$ [M + Na]$^+$: 287.0354, found: 287.0359.

Diethyl 7-methylbenzo[b]thiophene-2,3-dicarboxylate ***(3k)***. Eluent petroleum ether–ethyl acetate (30 : 1). White solid, mp 76–77 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ 7.78 (d, 1H, J = 8.0 Hz), 7.38 (t, 1H, J = 7.2 Hz), 7.28 (d, 1H, J = 7.2 Hz), 4.51 (q, 2H, J

= 7.2 Hz), 4.42 (q, 2H, J = 7.2 Hz), 2.56 (s, 3H), 1.47–1.40 (m, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ 164.7, 161.8, 140.7, 136.8, 134.1, 132.7, 132.1, 127.4, 125.1, 122.0, 62.0, 61.9, 20.0, 14.2. HRMS m/z calcd for $C_{15}H_{16}O_4S$ $[M + Na]^+$: 315.0667, found: 315.0663.

*Diisopropyl 7-methylbenzo[b]thiophene-2,3-dicarboxylate (**3l**).* Eluent petroleum ether–ethyl acetate (30 : 1). Pale yellow viscous liquid. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ 7.74 (d, 1H, J = 8.0 Hz), 7.39 (t, 1H, J = 8.0 Hz), 7.28 (d, 1H, J = 7.2 Hz), 5.42 (m, 1H), 5.28 (m, 1H), 2.57 (s, 3H), 1.46 (d, 6H, J = 4.0 Hz), 1.41 (d, 6H, J = 8.0 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ 164.4, 161.3, 140.7, 136.8, 134.6, 132.6, 132.2, 127.3, 126.0, 121.8, 71.4, 70.0, 69.7, 21.9, 21.5, 20.4. HRMS m/z calcd for $C_{17}H_{20}O_4S$ $[M + Na]^+$: 343.0980, found: 343.0979.

*Dimethyl 6-methoxybenzo[b]thiophene-2,3-dicarboxylate (**3m**).* Eluent petroleum ether–ethyl acetate (40 : 1). White solid, mp 83–85 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ 7.78 (d, 1H, J = 9.2 Hz), 7.27 (s, 1H), 7.88 (d, 1H, J = 9.2 Hz), 4.03 (s, 3H), 3.94 (s, 3H), 3.90 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ 165.1, 162.1, 159.8, 142.5, 133.4, 130.8, 129.8, 125.3, 116.6, 104.0, 55.6, 52.9, 52.8. HRMS m/z calcd for $C_{13}H_{12}O_5S$ $[M + Na]^+$: 303.0303, found: 303.0307.

*Dimethyl 4-methoxybenzo[b]thiophene-2,3-dicarboxylate (**3m′**).* Eluent petroleum ether–ethyl acetate (40 : 1). White solid, mp 118–119 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ 7.45–7.40 (m, 2H), 6.78 (d, 2H, J = 6.0 Hz), 4.03 (s, 3H), 3.93 (s, 3H), 3.92 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ 166.7, 161.9, 156.0, 142.6, 131.1, 129.1, 128.2, 127.2, 114.9, 105.1, 56.1, 52.9, 52.8. HRMS m/z calcd for $C_{13}H_{12}O_5S$ $[M + Na]^+$: 303.0303, found: 303.0307.

*Diethyl 6-methoxybenzo[b]thiophene-2,3-dicarboxylate (**3n**).* Eluent petroleum ether–ethyl acetate (40 : 1). White solid, mp 115–116 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ 7.79 (d, 1H, J = 8.8 Hz), 7.24 (s, 1H), 7.08 (d, 1H, J = 8.8 Hz), 4.50 (q, 2H, J = 7.2 Hz), 4.40 (q, 2H, J = 7.2 Hz), 3.90 (s, 3H), 1.47–1.28 (m, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ 164.7, 161.7, 159.7, 142.4, 133.5, 131.0, 130.2, 125.2, 116.5, 104.1, 61.9, 61.8, 55.6, 14.19, 14.16. HRMS m/z calcd for $C_{15}H_{16}O_5S$ $[M + Na]^+$: 331.0616, found: 331.0615.

*Diethyl 4-methoxybenzo[b]thiophene-2,3-dicarboxylate (**3n′**).* Eluent petroleum ether–ethyl acetate (40 : 1). White solid, mp 68–69 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ 7.42–7.41 (m, 2H), 6.78 (d, 1H, J = 5.6 Hz), 4.50 (q, 2H, J = 7.2 Hz), 4.39 (q, 2H, J = 7.2 Hz), 3.93 (s, 3H), 1.48–1.38 (m, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ 166.2, 161.6, 156.0, 142.6, 134.1, 128.9, 128.8, 127.3, 114.8, 105.1, 61.9, 61.8, 55.8, 14.2, 14.1. HRMS m/z calcd for $C_{15}H_{16}O_5S$ $[M + Na]^+$: 331.0616, found: 331.0615.

*Dimethyl 5-tert-butylbenzo[b]thiophene-2,3-dicarboxylate (**3o**).* Eluent petroleum ether–ethyl acetate (30 : 1). Pale yellow viscous liquid. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ 7.77 (s, 1H), 7.67 (d, 1H, J = 8.8 Hz), 7.48 (d, 1H, J = 8.8 Hz), 3.95 (s, 3H), 3.84 (s, 3H), 1.28 (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ 165.2, 162.3, 149.1, 137.8, 136.8, 133.5, 132.8, 126.3, 122.1, 120.1, 52.9, 52.8, 34.9, 31.4. HRMS m/z calcd for $C_{16}H_{18}O_4S$ $[M + Na]^+$: 329.0825, found: 329.0823.

*Diethyl 5-tert-butylbenzo[b]thiophene-2,3-dicarboxylate (**3p**).* Eluent petroleum ether–ethyl acetate (30 : 1). Pale yellow viscous liquid. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ 7.78 (s, 1H), 7.66 (d, 1H, J = 8.4 Hz), 7.46 (d, 1H, J = 8.8 Hz), 4.42 (q, 2H, J = 7.2 Hz), 4.30 (q, 2H, J = 7.2 Hz), 1.37–1.12 (m, 15H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ 164.7, 161.9, 149.0, 137.7, 136.9, 133.5, 133.3, 123.1, 122.1, 120.1, 62.0, 61.8, 31.3, 14.2. HRMS m/z calcd for $C_{18}H_{22}O_4S$ $[M + Na]^+$: 357.1136, found: 357.1137.

*Dimethyl 5-bromobenzo[b]thiophene-2,3-dicarboxylate (**3q**).* Eluent petroleum ether–ethyl acetate (30 : 1). White solid, mp 98–100 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ 8.12 (s, 1H), 7.69 (d, 1H, J = 8.0 Hz), 7.56 (d, 1H, J = 8.0 Hz), 4.03 (s, 3H), 3.96 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ 164.1, 161.8, 138.6, 138.1, 135.4, 131.7, 130.6, 127.2, 123.8, 119.9, 53.1, 52.9. HRMS m/z calcd for $C_{12}H_9BrO_4S$ $[M + Na]^+$: 350.9303, found: 350.9302, 352.9275.

*Diethyl 5-bromobenzo[b]thiophene-2,3-dicarboxylate (**3r**).* Eluent petroleum ether–ethyl acetate (30 : 1). White solid, mp 96–97 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ 8.14 (s, 1H), 7.72 (d, 1H, J = 8.0 Hz), 7.58 (d, 1H, J = 8.0 Hz), 4.51 (q, 2H, J = 8.0 Hz), 4.43 (q, 2H, J = 8.0 Hz), 1.47–1.40 (m, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ 163.7, 161.4, 138.6, 138.3, 135.7, 131.8, 130.5, 127.2, 123.8, 119.8, 62.4, 62.1, 14.1 HRMS m/z calcd for $C_{14}H_{13}BrO_4S$ $[M + Na]^+$: 378.9616, found: 378.9615, 380.9588.

*Ethyl 3-phenylbenzo[b]thiophene-2-carboxylate (**3s**).* Eluent petroleum ether–ethyl acetate (30 : 1). Pale yellow viscous liquid ^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ 7.92 (d, 1H, J = 8.0 Hz), 7.58 (d, 1H, J = 8.0 Hz), 7.54–7.49 (m, 3H), 7.44 (d, 2H, J = 8.0 Hz), 7.38 (t, 1H, J = 8.0 Hz), 4.27 (q, 2H, J = 8.0 Hz), 1.24 (t, 3H, J = 8.0 Hz) (the ^{1}H NMR spectrum is in agreement with that of compound **3a** in ref. 21). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ 162.7, 143.8, 140.5, 140.2, 134.8, 129.7, 128.8, 128.0, 127.1, 125.3, 124.8, 122.5, 61.3, 14.0. HRMS m/z calcd for $C_{17}H_{14}O_2S$ $[M + Na]^+$: 305.0612, found: 305.0623.

*Ethyl 5-methoxy-3-phenylbenzo[b]thiophene-2-carboxylate (**3t**).* Eluent petroleum ether–ethyl acetate (25 : 1). Pale yellow viscous liquid ^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ 7.77 (d, 1H, J = 8.0 Hz), 7.54–7.47 (m, 3H), 7.43–7.40 (m, 2H), 7.16 (dd, 1H, J = 8.0 Hz), 6.95 (d, 1H, J = 4.0 Hz), 4.24 (q, 2H, J = 8.0 Hz), 3.78 (s, 3H), 1.21 (t, 3H, J = 8.0 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ 162.6, 158.1, 143.4, 141.2, 134.8, 132.9, 130.1, 129.5, 128.1, 123.4, 118.4, 106.5, 60.9, 55.4, 13.5. HRMS m/z calcd for $C_{18}H_{16}O_3S$ $[M + Na]^+$: 335.0718, found: 335.0721.

*Ethyl 5-chloro-3-phenylbenzo[b]thiophene-2-carboxylate (**3u**).* Eluent petroleum ether–ethyl acetate (25 : 1). White solid, mp 86–88 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ 7.82 (d, 1H, J = 8.0 Hz), 7.52–7.50 (m, 4H), 7.46 (dd, 1H, J = 8.0 Hz), 7.41–7.38 (m, 2H), 4.25 (q, 2H, J = 8.0 Hz), 1.21 (t, 3H, J = 8.0 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ 162.3, 142.9, 141.4, 138.4, 134.1, 131.3, 130.6, 129.6, 128.3, 128.2, 127.7, 124.6, 123.6, 61.4, 13.9. HRMS m/z calcd for $C_{17}H_{13}ClO_2S$ $[M + Na]^+$: 339.0222, found: 339.0220.

*Ethyl 5-bromo-3-phenylbenzo[b]thiophene-2-carboxylate (**3v**).* Eluent petroleum ether–ethyl acetate (30 : 1). White solid, mp 79–81 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ 7.78 (d, 1H, J = 8.0 Hz), 7.68 (d, 1H, J = 4.0 Hz), 7.59 (d, 1H, J = 8.0 Hz), 7.53–7.49 (m, 3H), 7.40 (dd, 2H, J = 8.0 Hz), 4.25 (q, 2H, J = 8.0 Hz), 1.21 (t, 3H, J = 8.0 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ 162.2, 142.8, 141.8, 138.9, 134.1, 130.5, 130.3, 129.6, 128.3, 128.2, 127.7,

123.9, 119.0, 61.4, 13.9. HRMS *m*/*z* calcd for $C_{17}H_{13}BrO_2S$ [M + Na]$^+$: 382.9717, found: 382.9715, 384.9726.

Conclusions

In conclusion, we have developed a simple, green and efficient strategy for the synthesis of benzothiophene derivatives by metal-free intermolecular radical cyclization between readily available disulfides and alkynes through direct aryl C(sp^2)–H functionalization. The process is of tolerance towards various functional groups in the substrates, and the synthesis of these compounds will attract much attention in academic and industrial research because of their wide applications in numerous pharmaceuticals, biologically active compounds as well as functional materials.

Acknowledgements

The authors gratefully acknowledge the financial support from the National Natural Science Foundation of China (no. 21302110, 21302109 and21375075), the Taishan Scholar Foundation of Shandong Province, the Natural Science Foundation of Shandong Province (ZR2013BQ017 and ZR2013BM007), the Project of Shandong Province Higher Educational Science and Technology Program (J13LD14), and the Scientific Research Foundation of Qufu Normal University (BSQD 2012021).

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