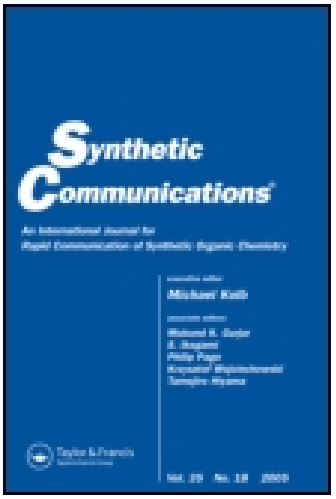

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EFFICIENT SYNTHESIS OF UNSYMMETRICAL DIBENZOTHIOPHENES BY ACID-MEDIATED INTRAMOLECULAR CYCLIZATION OF BIARYL METHYL SULFOXIDES

Vrajesh B. Pandya,[1,2] Mukul R. Jain,[1] Balaji V. Chaugule,[1] Jigar S. Patel,[1] Bhavesh M. Parmar,[1] Jignesh K. Joshi,[1] and Pankaj R. Patel[1]

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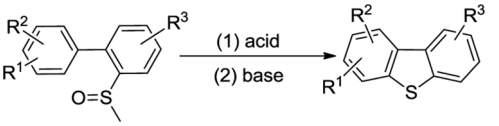
GRAPHICAL ABSTRACT



Abstract *A convenient and high-yielding synthesis of unsymmetrical dibenzothiophenes has been achieved by an acid-mediated ring closure of the biphenyl ring having a sulfoxide substituent at the* ortho *position. Various functional groups are well tolerated in this methodology.*

Keywords Cyclization; dibenzothiophene; intramolecular; sulfoxide

INTRODUCTION

Dibenzothiophenes **1** (Fig. 1) are biologically important because of their occurrence in a wide variety of natural products possessing useful biological activities.[1] Also, different substituted dibenzothiophene derivatives are reported to be anti-angiogenic agents,[2] antiobesity agents,[3] antiviral agents,[4] and agents for the treatment of *Pneucystis carinii* pneumonia.[5] The literature discloses different approaches for preparation of substituted dibenzothiophenes, such as disulfide ring closure,[6] photochemical cyclization of 2-(2′-methylthio)biphenyl radical,[7] sulfur insertion in biphenyl using $AlCl_3$,[8] fusion of 2,2′-dihydroxybiphenyl with P_2S_5,[9] ring contraction of thianthrene using copper bronze[10] and cyclization of biphenyl-2-sulfonyl chloride using $AlCl_3$ gives dibenzothiophene dioxide,[11] which upon deoxygenation gives dibenzothiophene.[12]

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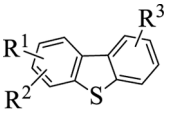
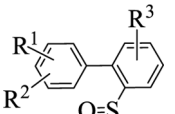


1

Figure 1. General structure of dibenzothiophenes.



2

Figure 2. General structure of sulfoxide.

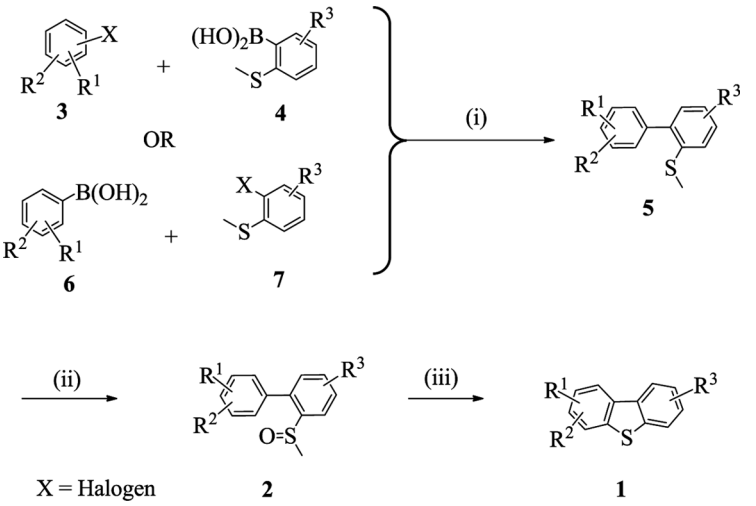
Sirringhaus et al. have reported synthesis of dibenzothienobisbenzothiophene by acid-mediated intermolecular cyclization of a sulfoxide derivative.[13] This literature report involved the use of expensive and hazardous chemicals such as trifluoromethanesulfonic acid and pyridine, and also the reaction took a long time and involved high temperature. The method does not have wider applicability in terms of functional group sensitivity. Recently, Sanz et al. have reported the synthesis of regioselectively functionalized dibenzothiophenes through anionic cyclization of benyne-tethered aryllithiums.[14]

The aforementioned literature methods involve high-temperature reactions using sulfur or sulfur-containing reagents or organolithium reagents. Also, some of these methods suffer from poor yields. Direct introduction of functional groups in dibenzothiophene nucleus also has limitations of regioselectivity. Literature methods for synthesis of 4-substituted dibenzothiophene ring involve metallation reactions in dibenzothiophene ring at the 4-position followed by the addition of appropriate electrophile.[15] Electrophilic substitution reaction on dibenzothiophene ring goes at the 2-position. Hence the synthesis of 1- and 3-substituted dibenzothiophene derivatives is relatively difficult and involves multiple steps.

In continuation of our interest in synthesizing dibenzothiophenes with a variety of substituents, herein we report a simple, cost-effective, and industrially applicable synthesis of unsymmetrical dibenzothiophenes by acidic ring closure of sulfoxide **2** (Fig. 2) using inorganic reagents, sulfuric acid, and potassium carbonate.

RESULTS AND DISCUSSION

To access sulfoxide **2**, the synthetic strategy depicted in Scheme 1 is adapted. Several methods are reported to make the biphenyl ring system. For the sake of simplicity and easy availability of substituted boronic acids, we adapted the Suzuki coupling[16] reaction. Thus, the coupling of substituted phenylboronic acid with substituted halobenzene gave the biphenyl ring, which upon oxidation with hydrogen peroxide[17] produced desired sulfoxide **2** in excellent yield.

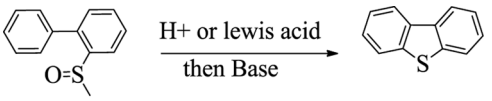


Scheme 1. Reagents and conditions: (i) $Pd(OAc)_2$, Na_2CO_3, MeOH, 70–95%; (ii) H_2O_2 (50%), Cat. V_2O_5, MeCN, 80–90%; (iii) conc.H_2SO_4, 0–75 °C, then aq. K_2CO_3, rt.

Once sulfoxide **2** was in hand, we set forth to screen the best acidic reagent to achieve ring closure and thereby produce dibenzothiophene. Sulfuric acid was found to give the best result in terms of yield and purity of dibenzothiophene as compared to the other Lewis or mineral acids screened. It was also found that the cyclization worked excellently when neat sulfuric acid was used. Sulfuric acid in solvent took a longer time to bring the desired cyclization and also the isolated yield was less (Table 1).

To extend the application of this reaction for the synthesis of substituted dibenzothiophenes, sulfoxide **2** with various substituents has been synthesized and subjected to cyclization in neat sulfuric acid (Table 2). It was observed that sulfoxide **2** containing electron-releasing groups produced greater yield of the corresponding dibenzothiophenes (**2a, 2b**, and **2c**). Electron withdrawing group such as nitro (**2e**)

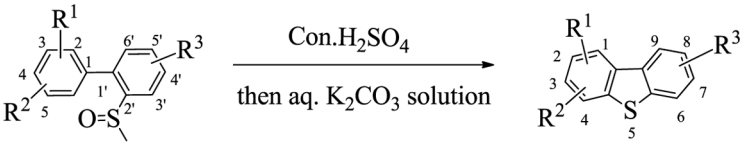
Table 1. Screening of acidic reagents for cyclization



2 1

No.	Cyclization reagent	Solvent	Reaction time (h)	Temperature (°C)	Yield (%)
1	H_2SO_4 (3v/w)	Neat	0.25	0–25	94
2	I_2 (2 equiv.)	Toluene	20	70	No reaction
3	$AlCl_3$ (2 equiv.)	Toluene	20	70	No reaction
4	TFA (3v/w)	Neat	20	0–25	10
5	H_2SO_4 (3v/w)	Chloroform	15	0–25	50

Table 2. Synthesis of substituted dibenzothiophenes

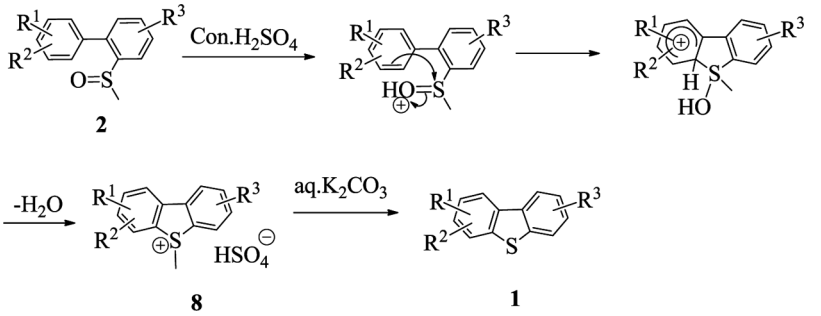


2 **1**

No.	Substituent on 2	Substituent on 1	Temperature (°C)	Time (h)	Yield (%)
a	$R^1 = R^2 = R^3 = H$	$R^1 = R^2 = R^3 = H$	0–25	0.5	94
b	$R^1 = R^3 = H$, $R^2 = 4$-F	$R^1 = R^3 = H$, $R^2 = 3$-F	0–25	0.5	92
c	$R^1 = R^3 = H$, $R^2 = 2$-CH_3	$R^1 = R^3 = H$, $R^2 = 1$-CH_3	0–25	0.5	97
d	$R^1 = R^3 = H$, $R^2 = 4$-$COOCH_3$	$R^1 = R^3 = H$, $R^2 = 3$-$COOCH_3$	0–25	1	75
e	$R^1 = R^3 = H$, $R^2 = 4$-NO_2	$R^1 = R^3 = H$, $R^2 = 3$-NO_2	0–75	2	49
f	$R^1 = 3$-OCH_3, $R^2 = 4$-$COOCH_3$, $R^3 = H$	$R^1 = 2$-OCH_3, $R^2 = 3$-$COOCH_3$ $R^3 = H$	0–25	1	74
g	$R^1 = 2$-CH_3, $R^2 = H$, $R^3 = 5'$-$COCH_3$	$R^1 = 1$-CH_3, $R^2 = H$, $R^3 = 8$-$COCH_3$	0–25	0.25	82
h	$R^1 = 2$-CH_3, $R^2 = H$, $R^3 = 5'$-CH_2CH_3	$R^1 = 1$-CH_3, $R^2 = H$, $R^3 = 8$-CH_2CH_3	0–25	0.25	85
i	$R^1 = 3$-$COCH_3$, $R^2 = R^3 = H$	$R^1 = 2$-$COCH_3$, $R^2 = R^3 = H$	0–25	0.25	70
j	$R^1 = 2$-$COOCH_3$, $R^2 = R^3 = H$	$R^1 = 1$-$COOCH_3$, $R^2 = R^3 = H$	0–25	1	55

and ester (**2d**) resist cyclization and hence gave relatively lesser yields. Most of the reactions were completed at 25 °C within 30 min, except for reactions with ring systems bearing electron-withdrawing groups (**2d, 2e**, and **2f**). The 1-substituted dibenzothiophenes have been effectively synthesized, as can be seen from examples **2c** and **2j**. Substituents on both rings are possible through this methodology (**2 h** and **2 g**).

The proposed mechanism of the reaction is shown in Scheme 2. The first step involves protonation of sulfoxide followed by nucleophilic attack of neighboring aromatic ring. Dehydration eventually led to aromatization, furnishing salt **8**. The demethylation of salt using base gives the desired dibenzothiophene derivatives. This mechanism correlates with our experimental observation of poor yield and more reaction time for electron-withdrawing group substituted sulfoxide as it destabilizes the positively charged transition state. Nenaidenko et al. have reviewed the synthetic capabilities of sulfonium salts with mechanistic aspects.[18] Nucleofugality of the group attached to the *S* atom is one of the main factors that determines direction of nucleophilic attack on sulfonium salt. In our case, biaryl sulfide is a good leaving group compared to methyl in sulfonium salt **8** and also methyl group provides an



Scheme 2. Proposed mechanism for cyclization.

electrophilic center for the nucleophile, that is, hydroxide ion generated from aqueous potassium carbonate.

CONCLUSION

In summary, a convenient and efficient method for the synthesis of unsymmetrical dibenzothiophene derivatives has been reported. The advantage of the described methodology over the reported ones is incorporation of substituents in the dibenzothiophene core with ease and good yields. The present method utilizes inexpensive and environmentally friendly reagents. Further, the duration of the reaction is very short and also reactions are accomplished at low temperature. This method gives access to a substituent at every position of dibenzothiophene. 1-Subsituted dibenzothiophene, which is difficult to make by direct substitution reaction on dibenzothiophene, can be easily prepared by this method. This methodology has potential applications for the synthesis of sulfur-containing fused heterocycles.

EXPERIMENTAL

Melting points were recorded with a Thomas–Hoover capillary melting-point apparatus and are uncorrected. Infrared (IR) spectra were recorded with an Fourier transform (FT-IR) instrument as a thin film or using KBr pellets, and are expressed in centimeters^{-1}. ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra were recorded using dimethylsulfoxide (DMSO) as a solvent. Ultra performance liquid chromatography (UPLC) purity were recorded in 0.05% TFA in water–ACN as a mobile phase and BEH C18, 2.1 × 100 mm column as a stationary phase. Elemental analyses were carried out with a C, Hanalyzer. Thin-layer chromatography (TLC) was performed on precoated plates (0.25 mm, silica gel 60 F254). Column chromatography was carried out with silica gel (100–200 mesh). The reactions were carried out in oven-dried glassware under dry N_2. MeOH and ACN were purified and dried before use. Distilled n-hexane and EtOAc were used for column chromatography.

General Procedure for Suzuki Coupling

Sodium carbonate (2 mmol) was added to a mixture of substituted halobenzene (**3** or **7**) (1 mmol) in dry methanol (10 v/w) placed in a round-bottomed flask

attached with condenser followed by palladium acetate (2 mol%). Substituted phenylboronic acid (**4** or **6**) (1 mmol) was added in one lot, and the reaction mixture was subjected to reflux. After 5 h, the reaction mixture was cooled to 25–30 °C. Methanol (3 v/w) was added, and the mixture was vacuum filtered through a sintered glass funnel using celite as a filter aid to furnish a residue. The residue obtained was purified by flash chromatography using 100 to 200-mesh silica gel as a stationary phase and *n*-hexane–ethyl acetate as a mobile phase (yield 70–90%).

General Procedure for Oxidation

A solution of biphenyl compound (**5**) (1 mmol) and V_2O_5 (0.1 mmol) in acetonitrile (5 mL) was cooled at 0 °C by keeping a round-bottomed flask in an ice bath under a nitrogen environment. Aqueous hydrogen peroxide (1.2 mmol, 50%) was added to the reaction mixture and it was stirred at 10 °C for 1 h. After 1 h, the reaction mixture was diluted with water (15 mL) and extracted with ethyl acetate (25 mL). The organic layer was dried over anhydrous sodium sulfate, filtered, and evaporated to offer the corresponding sulfoxide (yield = 80–90%).

General Procedure for Cyclization

Sulfoxide compound (**2**) (0.5 g) was added in portions to stirred concentrated H_2SO_4 (1.5 mL, 3 v/w) in a one-necked, round-bottomed flask containing a guard tube at 0–5 °C. The reaction mixture was stirred at 25 °C for 0.5–2 h. The reaction mixture was poured on ice-cold water (10 mL) and then made basic with aqueous potassium carbonate solution (pH 8). The aqueous layer was extracted with ethyl acetate (2 × 15 mL). The organic layer was dried over anhydrous sodium sulfate, filtered, and evaporated to give the titled compound (yield = 49–97%).

Spectral Data of Synthesized Compounds

Dibenzo[*b,d*]thiophene (1a). White solid, mp: 98 °C, IR (KBr): ν_{max} 3051, 1583, 1415, 1307, 1230, 1130, 1066, 929, 734, 495 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ 7.47–7.53 (m, 4H), 7.99–8.04 (m, 2H), 8.34–8.38 (m, 2H); ^1H NMR (400 MHz, $CDCl_3$): δ 7.43–7.47 (m, 4H), 7.83–7.87 (m, 2H), 8.13–8.18 (m, 2H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 122.0, 123.0, 124.7, 127.0, 135.0, 138.5. CHNS: Calculated for $C_{12}H_8S$: C, 78.22; H, 4.38; S, 17.40. Found: C, 78.32; H, 4.34; S,17.20.

3-Fluorodibenzo[*b,d*]thiophene (1b). White solid, mp: 101 °C; IR (KBr): ν_{max} 3387, 1604, 1440, 1396, 1315, 1240, 891, 840, 758, 732 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ 7.32–7.37 (m, 1H), 7.46–7.51 (m, 2H), 7.92–7.95 (m, 1H), 7.98–8.02 (m, 1H), 8.30–8.32 (m, 1H), 8.33– 8.38 (m, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 109.3, 112.8, 121.8, 122.9, 123.4, 124.9, 126.6, 131.7, 134.2, 138.50, 140.0; ESI-MS: m/z: 225.4 $(M + Na)^+$. CHNS: Calculated for $C_{12}H_7FS$: C, 71.26; H, 3.49; S, 15.85. Found: C, 70.90; H, 3.36; S, 15.98.

1-Methyldibenzo[*b,d*]thiophene (1c). White solid; mp: 74 °C; IR (KBr): ν_{max} 3387, 3059, 2949, 1905, 1438, 1307, 1028, 773, 738, 729, 707 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ 2.87 (s, 3H), 7.30 (d, $J = 8$ Hz, 1H), 7.38–7.42 (m, 1H),

7.49–7.54 (m, 2H), 7.87 (d, $J = 8$ Hz, 1H), 8.02–8.06 (m, 1H), 8.37–8.41 (m, 1H);^{13}C NMR (100 MHz, DMSO-d_6): δ 22.1, 120.6, 122.9, 124.6, 125.0, 126.1, 126.4, 127.1, 133.0, 134.6, 135.8, 138.7, 138.9. CHNS: Calculated for $C_{13}H_{10}S$: C, 78.75; H, 5.08; S, 16.17. Found: C, 78.30; H, 5.05; S, 16.11.

Methyldibenzo[*b,d*]thiophene-3-carboxylate (1d). White solid, mp: 138 °C; IR (KBr): ν_{max} 2939, 1712, 1597, 1442, 1388, 1288, 1253, 1112, 974, 848, 754 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ 3.90 (s, 3H), 7.55–7.60 (m, 2H), 8.04–8.10 (m, 2H), 8.44–8.47 (m, 1H), 8.51 (d, $J = 8.4$ Hz, 1H), 8.67 (d, $J = 1.6$ Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 52.3, 122.0, 122.9, 123.0, 124.0, 125.0, 125.1, 127.9, 128.1, 134.0, 138.1, 138.7, 140.2, 165.9. CHNS: Calculated for $C_{14}H_{10}O_2S$: C, 69.40; H, 4.16; S, 13.23. Found: C, 69.48; H, 4.17; S, 13.41.

3-Nitrodibenzo[*b,d*]thiophene (1e). Yellow solid; mp: 150 °C; IR (KBr): ν_{max} 2962, 1604, 1518, 1448, 1330, 1261, 1103, 1022, 879, 771, 738 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.61–7.66 (m, 2H), 8.14 (d, $J = 8$ Hz, 1H), 8.32 (dd, $J = 8.8$ Hz, 2 Hz, 1H), 8.52 (d, $J = 8$ Hz, 1H), 8.60 (d, $J = 8.8$ Hz, 1H), 9.08 (d, $J = 2$ Hz, 1H);^{13}C NMR (100 MHz, DMSO-d_6): δ 118.5, 119.6, 122.5, 123.3, 123.5, 125.3, 128.8, 133.2, 139.1, 140.0, 141.3, 145.8; ESI-MS: m/z: 230 $(M + H)^+$, CHNS: Calculated for $C_{12}H_7NO_2S$: C, 62.87; H, 3.08; N, 6.11; S, 13.99. Found: C, 62.86; H, 3.10; N, 6.10; S, 13.95.

Methyl 2-methoxydibenzo[*b,d*]thiophene-3-carboxylate (1f). White solid, mp: 128 °C; IR (KBr): ν_{max} 3347, 1610, 1450, 1366, 1345, 1250, 891, 840, 760, 740 cm^{-1};^{1}H NMR (400 MHz, DMSO-d_6): δ 3.82 (s, 3H), 3.96 (s, 3H), 7.51–7.57 (m, 2H), 8.03 (d, $J = 8.4$ Hz, 1H), 8.10 (s, 1H), 8.29 (s, 1H), 8.49 (d, $J = 8.4$ Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 52.0, 56.3, 105.3, 120, 123.0, 23.1, 124.6, 125.2, 127.9, 129.5, 134.4, 139.0, 140.8, 156.1, 165.9; ESI-MS: m/z: 273 $(M + H)^+$. CHNS: Calculated for $C_{15}H_{12}O_3S$: C, 66.16; H, 4.44; S, 11.77. Found: C, 66.15; H, 4.51; S, 11.65.

1-(9-Methyldibenzo[b,d]thiophen-2-yl)ethanone (1g). White solid, mp: 125 °C; IR (KBr): ν_{max} 1678, 1356, 1313, 1244, 879, 840, 767 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ 2.72 (s, 3H), 2.94 (s, 3H), 7.38 (d, $J = 7.2$ Hz, 1H), 7.49 (t, $J = 7.6$ Hz, 1H), 7.95 (d, $J = 8$ Hz, 1H), 8.11 (dd, $J = 8.4$, 1.6 Hz, 1H), 8.21 (d, $J = 8.4$ Hz, 1H), 8.90 (d, $J = 1.6$ Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 21.8, 26.7, 120.8, 121.9, 124.6, 125.5, 127, 127.5, 132.5, 133.3, 134.9, 135.6, 139.3, 143.8, 197.3; ESI-MS: m/z: 240.8 $(M + H)^+$; CHNS. Calculated for $C_{15}H_{12}OS$: C, 74.97; H, 5.03; S, 13.34. Found: C, 74.90; H, 4.99; S, 13.10.

8-Ethyl-1-methyldibenzo[b,d]thiophene (1h). Semisolid, IR (KBr): ν_{max} 2999, 1460, 1217, 1033, 758 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ 1.30 (t, 3H), 2.83 (q, 2H), 7.29 (d, $J = 7.6$ Hz, 1H), 7.38 (d, $J = 7.6$ Hz, 1H), 7.40 (d, $J = 8.4$ Hz, 1H), 7.85 (d, $J = 7.6$ Hz, 1H), 7.94 (d, $J = 8.4$ Hz, 1H), 8.20 (d, $J = 0.8$ Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 16.0, 22.2, 28.4, 120.6, 122.6, 124.0, 126.2, 126.4, 127.0, 133.0, 134.6, 135.9, 136.0, 139.2, 140.2. CHNS: Calculated for $C_{15}H_{14}S$: C, 79.60; H, 6.23; S, 14.17; Found. C, 79.37; H, 6.33; S, 14.32.

1-(Dibenzo[b,d]thiophen-2-yl)ethanone (1i). White solid, mp: 125 °C; IR (KBr): ν_{max} 1664, 1446, 1354, 1269, 964, 754, 603 cm^{-1}; ^{1}H NMR (400 MHz,

DMSO-d_6): δ 2.77 (s, 3H), 7.51–7.58 (m, 2H), 7.74 (t, 1H), 8.05–8.09 (m, 1H), 8.36 (d, $J = 8$ Hz, 1H), 8.42–8.46 (m, 1H), 8.70 (d, $J = 8$ Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 26.5, 122.0, 122.8, 124.8, 124.8, 126.7, 127.4, 130.1, 130.3, 133.4, 136.6, 137.5, 141.1, 197.7. CHNS: Calculated for $C_{14}H_{10}OS$: C, 74.31; H, 4.45; S, 14.17. Found: C, 74.38; H, 4.43; S, 14.27.

Methyldibenzo[b,d]thiophene-1-carboxylate (1j). White solid, mp: 88 °C; IR (KBr): ν_{max} 1664, 1446, 1354, 1269, 964, 754, 603 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ 4.02 (s, 3H), 7.47–7.51 (m, 1H), 7.54–7.57 (m, 1H), 7.59–7.61 (m, 1H), 7.72 (dd, $J = 8$, 4 Hz, 1H), 8.10 (d, $J = 8$ Hz, 1H), 8.21 (d, $J = 8$ Hz, 1H), 8.26 (dd, $J = 8$, 4 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 52.8, 123.2, 124.6, 124.7, 125.5, 126.1, 126.2, 127.5, 128.4, 131.0, 132.9, 139.2, 139.9, 168.7; ESI-MS: m/z: 265.16 $(M+Na)^+$. CHNS: Calculated for $C_{14}H_{10}O_2S$: C, 69.40; H, 4.16; S, 13.21. Found: C, 69.47; H, 4.28; S, 13.15.

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REFERENCES

1. Andrews, M. D. Product class 6: Dibenzothiophenes. *Sci. Synth.* **2001**, *10*, 211.
2. Salvati, M. E.; Eudy, N. H.; Hallett, W. A.; Powell, D. W. Substituted dibenzothiophenes having antiangiogenic activity. U.S. Patent 6,022,307, 2000. *Chem. Abstr.* **2000**, *132*, 137278.
3. Block, M. H.; Donald, C. S.; Foote, K. M.; Brittain, D. R. Amino substituted dibenzothiophene derivatives for the treatment of disorders mediated by the NP Y5 receptor. Patent WO 01/85714, 2001. *Chem. Abstr.* **2001**, *135*, 371628.
4. Albrecht, W. L.; Fleming R. W.; Horgan, S. W.; Mayer, G. D. Bis-basic-substituted polycyclic aromatic compounds: A new class of antiviral agents, 8: Bis-basic derivatives of carbazole, dibenzofuran, and dibenzothiophene. *J. Med. Chem.* **1977**, *20*, 364.
5. Tidwell, R. R.; Hall, J. E. Dicationic dibenzofuran and dibenzothiophene compounds and methods of use thereof. U.S. Patent 6,172,104, 2001. *Chem. Abstr.* **2000**, *132*, 180475.
6. Campaigne, E.; Ergener, L.; Heaton, B. G. Formation of dibenzothiophene by a disulfide ring closure. *J. Org. Chem.* **1962**, *27*, 4111.
7. Kampmeier, J. A.; Geer, R. P.; Meskin, A. J.; D'Silva, R. M. Radical reactions of organic sulfides, II: Behavior of the 2-(2′-methylthio)biphenylyl radical. *J. Am. Chem. Soc.* **1966**, *88*, 4096.
8. Gilman, H.; Jacoby, A. L. Dibenzothiophene: Orientation and derivatives. *J. Org. Chem.* **1938**, *3* (2), 108.
9. Cullinane, N. M.; Davies, C. G.; Davies, G. I. Substitution derivatives of diphenylene sulphide and diphenylenesulphone. *J. Chem. Soc.* **1936**, 1435.
10. Cullinane, M.; Morgan, N. M. E.; Plummer, C. A. J. Synthesis of some heterocycles. *Rec. Trav. Chim.* **1937**, *56*, 627; *Chem. Abstra.* **1937**, *31*, 6238.
11. Chaix, M. The ultraviolet absorption of substances containing two benzene nuclei. *Bull. Soc. Chim. Fr.* **1933**, *53*, 700.
12. Bordwell, F. G.; McKellin, W. H. The reduction of sulfones to sulfides. *J. Am. Chem. Soc.* **1951**, *73*, 2251.

13. Sirringhaus, H.; Friend, R. H.; Wang, C.; Leuninger, J.; Müllen, K. Dibenzothienobisbenzothiophene—A novel fused-ring oligomer with high field-effect mobility. *J. Mat. Chem.* **1999**, *9*, 2095.
14. Sanz, R.; Fernández, Y.; Castroviejo, M. P.; Pérez, A.; Fañanás, F. J. A route to regioselectively functionalized carbazoles dibenzofurans, and dibenzothiophenes through anionic cyclization of benzyne-tethered aryllithiums. *J. Org. Chem.* **2006**, *71*, 6291.
15. Katritzky, A. R.; Perumal, S. Synthesis of some 4-substituted and 4,6-disubstituted dibenzothiophenes. *J. Heterocycl. Chem.* **1990**, *27*, 1737.
16. Lee, J. H.; Park, E. S.; Yoon, C. M. Suzuki coupling reaction of 6-ido- or 6,8-diidospiropyran: Synthesis of spiropyran analogs. *Tetrahedron Lett.* **2001**, *42*, 8311.
17. Maciuca, A. L.; Ciocan, C. E.; Dumitriu, E.; Fajula, F.; Hulea, V. V-, Mo-, and W-containing layered double hydroxides as effective catalysts for mild oxidation of thioethers and thiophenes with H_2O_2. *Catal. Today.* **2008**, *138*, 33.
18. Nenaidenko, V. G.; Balenkova, E. S. New synthetic capabilities of sulfonium salts. *Russ. J. Org. Chem.* **2003**, *39* (3), 291.