JOC The Journal of Organic Chemistry
Cite This: J. Org. Chem. XXXX, XXX, XXX−XXX
Article
pubs.acs.org/joc

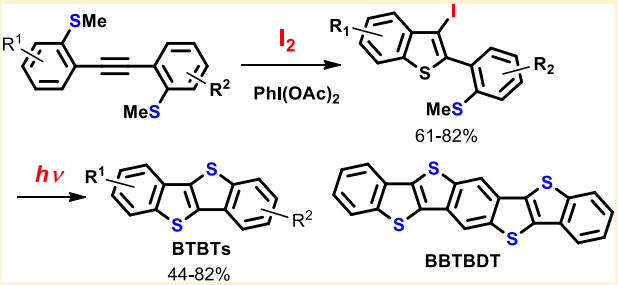
Synthesis of [1]Benzothieno[3,2-*b*][1]benzothiophene Derivatives via Successive Iodocyclization/Photocyclization of Alkynes

Tsugio Kitamura,* Kazuhiro Morita, Haruka Nakamori, and Juzo Oyamada

Department of Chemistry and Applied Chemistry, Saga University, Honjo-machi, Saga 840-8502, Japan

Supporting Information

ABSTRACT: A new synthetic method for [1]benzothieno[3,2-*b*][1]benzothiophene derivatives (BTBTs) was developed. The present method consists of iodocyclization of 1,2-bis(2-methylthiophenyl)ethynes and photolysis of 3-iodo-(2-methylthiophenyl)benzo[*b*]thiophenes. With 1,2-bis(2-methylthiophenyl)ethynes treated with I_2/PhI(OAc)$_2$ in CH_2Cl_2 at room temperature, selective cyclization at sulfur took place to give 3-iodo-(2-methylthiophenyl)benzo[*b*]-thiophenes in good yields. Irradiation of the iodinated benzo-[*b*]thiophenes with a high-pressure Hg lamp (>290 nm) provided BTBTs in good yields. Furthermore, the present method was applied to the synthesis of bis[1]benzothieno[2,3-*d*;2′,3′-*d*′]benzo[1,2-*b*;4,5-*b*′]dithiophene (BBTBDT).

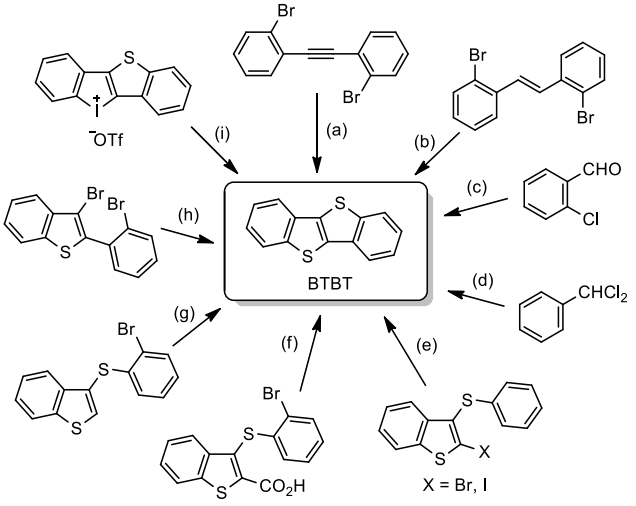


INTRODUCTION

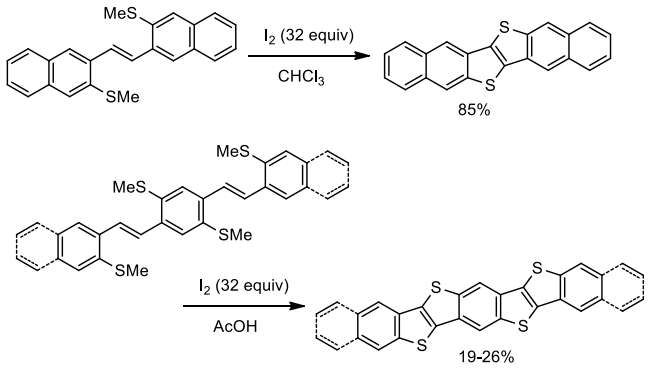
Recently, π-conjugated thiophene-based compounds such as [1]benzothieno[3,2-*b*][1]benzothiophene (BTBT) have attracted great attention as high-performance organic compounds because they are applicable to organic field-effect transistors (OFETs) and organic photovoltaics (OPVs).[1] Therefore, studies on the synthetic method of BTBT and its derivatives is very important in the development of organic electronic devices. As shown in Scheme 1, several methods preparing BTBT derivatives have been studied using readily available materials, such as 1,2-bis(2-bromophenyl)ethyne (path a),[2] 1,2-bis(2-bromophenyl)ethene (path b),[3] 2-chlorobenzaldehyde (path c),[4] and (dichloromethyl)benzene (path d).[5] These methods involve the reactions with NaSH, Na_2S, and elemental sulfur. Recently, the BTBT derivatives were prepared via Pd-catalyzed reactions in good to high yields from benzothiophene-based molecules such as 2-halo-3-(phenylthio)benzothiophene (path e),[6] 3-(2-bromophenylthio)benzothiophene-2-carboxylic acid (path f),[7] and 3-(2-bromophenylthio)benzothiophene (path g).[8] Other methods using 3-bromo-2-(2-bromophenyl)benzothiophene (path h)[9] and a cyclic diaryliodonium triflate (path i)[10] were reported.

On the other hand, our attention has been paid to iodine-promoted cyclization of methylthio-substituted diarylalkenes for the synthesis of a π-extended BTBT[11] and π-extended thienoacenes,[12] as described in Scheme 2. The iodine-promoted cyclization is a very convenient one-pot process.

Scheme 1. Previous Methods for BTBT Synthesis



Scheme 2. Iodine-Promoted Cyclization



Received: January 21, 2019

Downloaded from pubs.acs.org by EAST CAROLINA UNIV on 03/07/19. For personal use only.
J. Org. Chem.

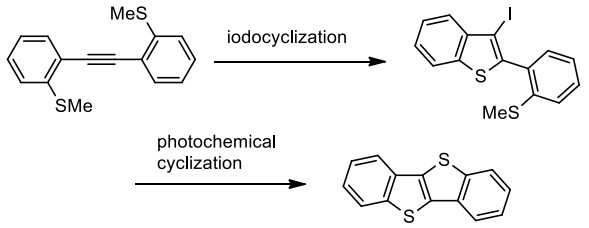
© XXXX American Chemical Society

DOI: 10.1021/acs.joc.9b00213
J. Org. Chem. XXXX, XXX, XXX−XXX

Although the yield of the π-extended BTBT is high, those of the π-extended thienoacenes are low (19−26%). In addition, a large amount of iodine (32 equiv) is required for this iodine-promoted cyclization. To improve these issues, we envisaged a procedure utilizing methylthio-substituted diarylalkyne derivatives.

Here, we report a new method for BTBT synthesis, which involves iodocyclization of a 1,2-bis(2-methylthiophenyl)ethyne and photochemical reaction of a 3-iodo-2-(2-methylthiophenyl)benzo[*b*]thiophene (Scheme 3). Since the

Scheme 3. This Work

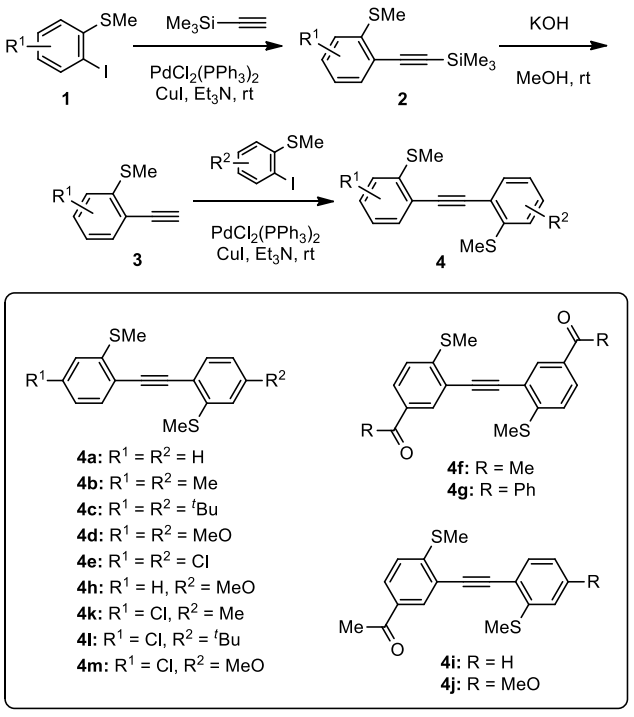


starting materials (i.e., 1,2-bis(2-methylthiophenyl)ethynes) can be prepared by the Sonogashira coupling reactions of readily available 1-iodo-2-(methylthio)arenes, this method may be useful rather than the synthesis of π-extended stilbene-type derivatives bearing a methylthio group shown in Scheme 2.

RESULTS AND DISCUSSION

First, we prepared 1,2-bis(2-methylthiophenyl)ethynes. The outline of the synthetic method is drawn in Scheme 4. 1-Ethynyl-2-(methylthio)arenes **3** were prepared by the Sonogashira coupling reaction of 1-iodo-2-(methylthio)benzenes **1** with trimethylsilylacetylene, followed by desilylation. The second Sonogashira coupling reaction of **3** with **1** afforded

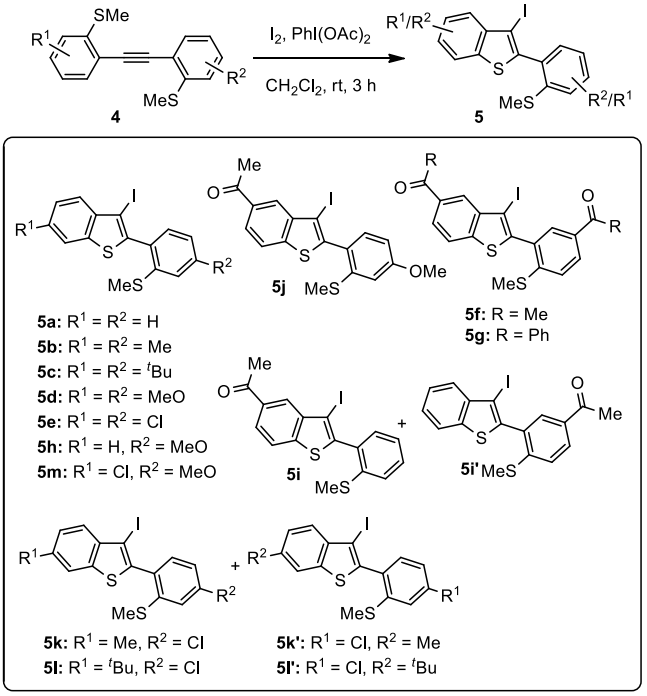
Scheme 4. Synthesis of 1,2-Bis(2-methylthiophenyl)ethynes 4



1,2-bis(2-methylthiophenyl)ethyne derivatives **4** in good yields. Since these reactions employed in the present procedure are reliable and established methods, they can be applied to various substituted diarylacetylenes.

Electrophile-induced cyclization of arylalkynes bearing sulfur at the ortho position is a highly efficient approach to benzothiophene derivatives.[13] We examined iodocyclization of methylthio-substituted diarylethynes **4**. Iodination of **4** with I_2/PhI(OAc)$_2$[14] in CH_2Cl_2 at room temperature proceeded efficiently to afford 3-iodo-2-arylbenzothiophenes **5** in good yields. The results are given in Table 1. Iodocyclization of

Table 1. Iodocyclization of 4[a]



entry	4	5	yield (%)[b]
1	**4a**: $R^1 = R^2$ = H	**5a**	64
2	**4b**: $R^1 = R^2$ = 4-Me	**5b**	61
3	**4c**: $R^1 = R^2$ = 4-^{t}Bu	**5c**	65
4	**4d**: $R^1 = R^2$ = 4-MeO	**5d**	67
5	**4e**: $R^1 = R^2$ = 4-Cl	**5e**	74
6	**4f**: $R^1 = R^2$ = 5-MeCO	**5f**	80
7	**4g**: $R^1 = R^2$ = 5-PhCO	**5g**	82
8	**4h**: R^1 = H, R^2 = 4-MeO	**5h**	75
9	**4i**: R^1 = H, R^2 = 5-MeCO	**5i** and **5i′** (1:2)[c]	74
10	**4j**: R^1 = 4-MeO, R^2 = 5-MeCO	**5j**	73
11	**4k**: R^1 = 4-Me, R^2 = 4-Cl	**5k** and **5k′** (2:3)[c]	76
12	**4l**: R^1 = 4-^{t}Bu, R^2 = 4-Cl	**5l** and **5l′** (1:1)[c]	70
13	**4m**: R^1 = 4-Cl, R^2 = 4-MeO	**5m**	76

[a]Conditions: **4** (1.0 mmol), I_2 (0.6 mmol), PhI(OAc)$_2$ (0.6 mmol), CH_2Cl_2 (1 mL), rt, 3 h. [b]Yields isolated by column chromatography. [c]Approximate ratios were determined by NMR.

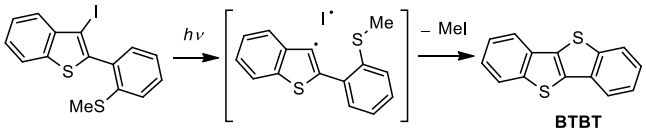
symmetrical diarylethynes **4a**−**4g** bearing electron-donating and -withdrawing groups gave single 3-iodo-2-arylbenzo[*b*]-thiophenes **5a**−**5g** in good to high yields (entries 1−7). In the case of unsymmetrical diarylethynes **4h**−**4m**; however, there is a possibility that the iodocyclization generates a regioisomeric mixture of 3-iodo-2-arylbenzo[*b*]thiophenes. Iodocyclization of diarylethynes **4i**, **4k**, and **4l** resulted in the formation of a

DOI: 10.1021/acs.joc.9b00213
J. Org. Chem. XXXX, XXX, XXX−XXX

regioisomeric mixture of **5** and **5′** (entries 9, 11, and 12), while the iodocyclization of methoxy-substituted diarylethynes **4h**, **4j**, and **4m** afforded one isomer of two possible benzo[*b*]-thiophenes **5** and **5′** (entries 8, 10, and 13). In the iodocyclization of methoxy-substituted diarylethynes **4h**, **4j**, and **4m**, it is considered that stabilized α-(4-methoxy-2-methylthiophenyl)vinyl cations are predominantly generated to give one kind of the regioisomers **5h**, **5j**, and **5m**, respectively.

Concerning cyclization of 3-iodo-2-(2-methylthiophenyl)-benzothiophene derivatives **5**, we have the experience that photolysis of β-(2-methylthiophenyl)vinyl bromides affords the corresponding vinyl radicals which exclusively cyclize at the sulfur to give benzothiophenes.[15] This knowledge reminds us to utilize photolysis for BTBT synthesis. As shown in Scheme 5, we expected that the (2-methylthiophenyl)benzothien-3-yl

Scheme 5. Photochemical Cyclization



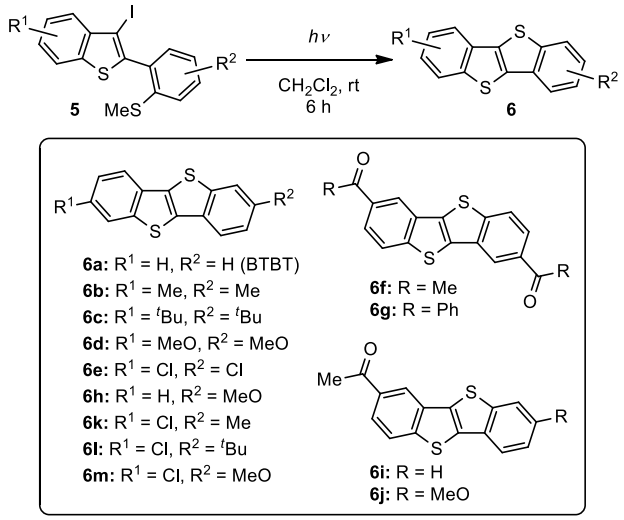
radical generated by photolysis of 3-iodo-2-(2-methylthiophenyl)benzothiophene might undergo the cyclization at the sulfur to form the BTBT structure.

Photolysis of 3-iodo-2-(2-methylthiophenyl)-benzothiophenes **5** in CH_2Cl_2 at room temperature for 6 h was conducted with a Pyrex-filtered high-pressure Hg lamp. The results are given in Table 2. As expected, irradiation of 3-iodo-2-phenylbenzothiophene (**5a**) gave BTBT (**6a**) in 72% yield without any byproducts (entry 1). Similar irradiation of other 3-iodo-2-arylbenzo[*b*]thiophenes **5** gave the corresponding BTBT derivatives **6** as the sole product. Interestingly, even in the mixture of the regioisomers **5** and **5′**, the photolysis of the mixture provided the same BTBT derivatives **6** (entries 9, 11, and 12). Although irradiation of the regioisomers **5** and **5′** generates the corresponding radical pairs, respectively, intramolecular cyclization of these radical pairs provides the same BTBT derivatives **6**. Therefore, the advantage of this methodology is that the synthesis of BTBT derivatives can be conducted without separation of the isomeric mixtures.

The iodocyclization/photocyclization methodology was found to be very useful in the synthesis of BTBT derivatives. The representative BTBT derivatives **6** bearing Me, *tert*-Bu, MeO, Cl, MeCO, and PhCO groups are conveniently prepared from easily available diarylethynes **4** composed of 7 symmetrical and 6 unsymmetrical alkynes. The BTBT derivatives **6f**, **6g**, **6i**, and **6j** bearing acetyl and benzoyl groups can be applied to further modifications by functional group transformations.

Finally, we challenged the synthesis of a π-extended thiophene-based heteroacene to enhance the utility of the present method because π-extended thienoacenes exhibited an excellent performance as organic field-effect transistors (OFETs).[6,12,16] The synthetic method is given in Scheme 6. With a readily available 1,4-dibromo-2,5-bis(butylthio)benzene (**7**),[17] the Sonogashira coupling of **7** with 1-ethynyl-2-(methylthio)benzene (**3a**) gave 2,5-bis(butylthio)-1,4-[2-(methylthio)phenylethynyl]benzene (**8**) in 94% yield. Iodocyclization of **8** with I_2/PhI(OAc)$_2$ afforded 5-(butylthio)-3-iodo-6-(3-iodobenzo[*b*]thiophen-2-yl)-2-[2-(methylthio)-

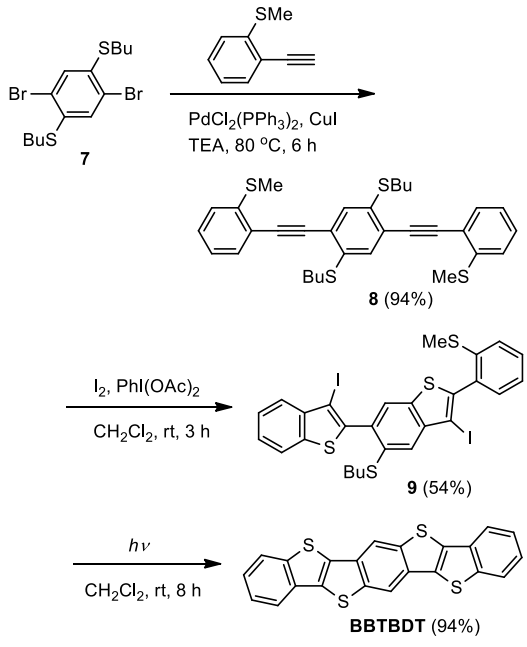
Table 2. Synthesis of BTBT Derivatives 6[a]



entry	5	6	yield (%)[b]
1	**5a**	**6a** (BTBT)	72
2	**5b**	**6b**	66
3	**5c**	**6c**	72
4	**5d**	**6d**	82
5	**5e**	**6e**	54
6	**5f**	**6f**	72
7	**5g**	**6g**	72
8	**5h**	**6h**	60
9	**5i** and **5i′**	**6i**	73
10	**5j**	**6j**	74
11	**5k** and **5k′**	**6k**	66
12	**5l** and **5l′**	**6l**	44
13	**5m**	**6m**	63

[a]Conditions: **5** (0.2 mmol), CH_2Cl_2 (20 mL), a high-pressure Hg lamp (400 W) (>290 nm), rt, 6 h. [b]Yields isolated by column chromatography.

Scheme 6. Synthesis of BBTBDT



DOI: 10.1021/acs.joc.9b00213
J. Org. Chem. XXXX, XXX, XXX−XXX

phenyl)benzo[*b*]thiophene (**9**) in 54% yield. Interestingly, we could not obtain other isomers although the reason was not clear. When a solution of **9** in CH_2Cl_2 was irradiated through a Prex-filter, a crystalline product, bis[1]benzothieno[2,3-*d*;2′,3′-*d*′]benzo[1,2-b;4,5-*b*′]dithiophene (BBTBDT), was obtained in 94% yield. Therefore, the present method is considered to be useful for the synthesis of π-extended thiophene-based heteroarenes.

CONCLUSION

In conclusion, we have developed a new methodology for synthesis of BTBT derivatives **6**. The present procedure includes iodocyclization of 1,2-bis(2-methylthiophenyl)-ethynes **4** with I_2/PhI(OAc)$_2$ and photolysis of 3-iodo-(2-methylthiophenyl)benzo[*b*]thiophenes **5**. These are convenient and clean reactions without any byproducts and are applicable in the synthesis of various substituted BTBT derivatives. 1,2-Bis(2-methylthiophenyl)ethynes **4** can be readily prepared by the reliable, established Sonogashira coupling reaction. Furthermore, the present procedure has been explained to be applicable to π-extended thienoacenes such as BBTBDT. Therefore, the present method utilizing iodocyclization/photocyclization is considered to be a useful approach for the synthesis of π-extended thienoacenes.

EXPERIMENTAL SECTION

General Information. All solvents and starting materials were used as received without further purification unless otherwise indicated. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) were recorded in $CDCl_3$ solution. HRMS measurements were performed at the Institute for Materials Chemistry and Engineering, Kyushu University. Column chromatographic separations were carried out using silica gel as the stationary phase. 2-(Methylthio)aniline was purchased from Tokyo Chemical Industry. Other substituted 2-(methylthio)anilines such as 4-methyl-2-(methylthio)aniline, 4-*tert*-butyl-2-(methylthio)aniline, 4-methoxy-2-(methylthio)aniline, and 4-chloro-2-(methylthio)aniline were prepared according to the method described in the literature.[18]

General Procedure for the Synthesis of 1-Iodo-2-(methylthio)arenes 1a−1e. To a mixture of a 2-(methylthio)-aniline derivative (50 mmol) and aqueous H_2SO_4 solution (7 mL of H_2SO_4 and 70 mL of H_2O) was added dropwise an aqueous solution of $NaNO_2$ (3.48 g, 50.5 mmol) in H_2O (20 mL) at 0 °C. After the addition, the mixture was stirred for 30 min and then an aqueous solution of KI (15.0 g, 90.5 mmol) in H_2O (20 mL) was added dropwise. After the mixture was stirred for 2.5 h, the product was extracted with ether (20 mL × 3). The combined organic phase was washed with 10% HCl, saturated NaCl, and saturated $Na_2S_2O_3$, successively. After the product was dried over anhydrous Na_2SO_4, the solvent was evaporated by a rotary evaporator and the residue was submitted to column chromatography on silica gel. Elution with hexane/CH_2Cl_2 (4:1) gave the product.

*1-Iodo-2-(methylthio)benzene (**1a**).*[19] Pale yellow oil, 11.25 g (90%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.46 (s, 3H), 6.84 (t, J = 8.0 Hz, 1H), 7.10 (d, J = 8.0 Hz, 1H), 7.34 (t, J = 8.0 Hz, 1H), 7.78 (d, J = 8.0 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 17.0, 97.3, 124.9, 125.9, 128.7, 139.3, 143.1.

*1-Iodo-4-methyl-2-(methylthio)benzene (**1b**).* Pale yellow oil, 11.09 g (84%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.30 (s, 3H), 2.44 (s, 3H), 6.65 (d, J = 8.0 Hz, 1H), 6.91 (s, 1H), 7.62 (d, J = 8.0 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 16.6, 20.9, 93.0, 125.2, 126.6, 138.1, 138.4, 142.1. HRMS (EI-EB): m/z [M$^+$] calcd for C_8H_9IS, 263.9470; found, 263.9470.

*4-tert-Butyl-1-iodo-2-(methylthio)benzene (**1c**).* Pale yellow oil, 12.40 g (81%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.31 (s, 9H), 2.48 (s, 3H), 6.89 (dd, J = 2.4, 8.0 Hz, 1H), 7.15 (d, J = 2.4 Hz, 1H), 7.69 (d, J = 8.0 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 17.0, 31.0, 34.6, 94.0, 122.4, 123.6, 138.6, 141.9, 151.7. HRMS (EI-EB): m/z [M$^+$] calcd for $C_{11}H_{15}IS$, 305.9939; found, 305.9940.

*1-Iodo-4-methoxy-2-(methylthio)benzene (**1d**).* Pale yellow oil, 10.08 g (72%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.44 (s, 3H), 3.79 (s, 3H), 6.44 (dd, J = 2.8, 8.8 Hz, 1H), 6.67 (d, J = 2.8 Hz, 1H), 7.62 (d, J = 8.8 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 16.8, 35.3, 85.6, 111.2, 111.7, 139.4, 143.9, 160.2. HRMS (EI-EB): m/z [M$^+$] calcd for C_8H_9IOS, 279.9419; found, 279.9419.

*4-Chloro-1-iodo-2-(methylthio)benzene (**1e**).* Pale yellow oil, 8.68 g (61%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.46 (s, 3H), 6.83 (dd, J = 2.0, 8.0 Hz, 1H), 7.01 (d, J = 2.0 Hz, 1H), 7.66 (d, J = 8.0 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 16.9, 93.8, 124.2, 125.8, 135.1, 139.9, 145.3. HRMS (EI-EB): m/z [M$^+$] calcd for C_7H_6ClIS, 283.8923; found, 283.8924.

*Preparation of 1-Acyl-3-iodo-4-(methylthio)arenes (**1f** and **1g**).* To a solution of 1-iodo-2-(methylthio)benzene (**1a**, 5.00 g, 20 mmol) and acetyl chloride or benzoyl chloride (40 mmol) in CH_2Cl_2 (20 mL) was added anhydrous $AlCl_3$ (5.33 g, 40 mmol) in portions at 0 °C. The mixture was stirred for 3 h at room temperature and then poured into crushed ice (50 g) containing concentrated HCl (20 mL). The product was extracted with CH_2Cl_2 (20 mL × 3), washed with water, and dried over anhydrous Na_2SO_4. The solvent was evaporated by a rotary evaporator, and the residue was crystallized from EtOH. The product was filtered and washed with EtOH.

*4-Acetyl-2-iodo-1-(methylthio)benzene (**1f**).* Light purple solid, 4.15 g (71%). Mp: 108−111 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.52 (s, 3H), 2.56 (s, 3H), 7.11 (d, J = 8.4 Hz, 1H), 7.92 (dd, J = 2.0, 8.4 Hz, 1H), 8.34 (d, J = 2.0 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 16.7, 26.3, 95.9, 123.3, 128.2, 134.3, 139.0, 150.6, 195.8. HRMS (EI-EB): m/z [M$^+$] calcd for C_9H_9IOS, 291.9419; found, 291.9419.

*4-Benzoyl-2-iodo-1-(methylthio)benzene (**1g**).* White solid, 5.95 g (84%). Mp: 108−109 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.53 (s, 3H), 7.13 (d, J = 8.4 Hz, 1H), 7.49 (t, J = 8.0 Hz, 2H), 7.60 (t, J = 8.0 Hz, 1H), 7.75−7.80 (m, 3H), 8.23 (d, J = 2.0 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 16.7, 95.7, 123.1, 128.3, 129.7, 130.2, 132.4, 134.5, 137.2, 140.4, 149.5, 194.2. HRMS (EI-EB): m/z [M$^+$] calcd for $C_{14}H_{11}IOS$, 353.9575; found, 353.9575.

General Procedure for the Synthesis of 2-(Methylthio)-1-(trimethylsilylethynyl)arenes 2. To a solution of 1-iodo-2-(methylthio)arene (**1**) (15 mmol) and trimethylsilylacetylene (1.77g, 18 mmol) in triethylamine (60 mL) were added $PdCl_2(PPh_3)_2$ (0.211 g, 0.3 mmol) and CuI (0.029 g, 0.15 mmol), and the mixture was stirred at room temperature for 4 h. The reaction mixture was poured into water and extracted with CH_2Cl_2 (20 mL × 3). The CH_2Cl_2 solution was washed with saturated NH_4Cl, water, and brine, successively, and dried over anhydrous Na_2SO_4. After evaporation of the solvent, the product was purified by column chromatography on silica gel using hexane/CH_2Cl_2 (2:5) as an eluent.

*2-(Methylthio)-1-(trimethylsilylethynyl)benzene (**2a**).*[13d] Pale yellow oil, 3.24 g (98%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.28 (s, 9H), 2.47 (s, 3H), 7.05 (t, J = 7.6 Hz, 1H), 7.13 (d, J = 8.0 Hz, 1H), 7.25−7.29 (m, 1H), 7.42 (dd, J = 0.8, 7.6 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ −0.1, 14.9, 101.3, 102.1, 121.1, 123.9, 124.0, 128.9, 132.6, 142.0.

*4-Methyl-2-(methylthio)-1-(trimethylsilylethynyl)benzene (**2b**).* Pale yellow oil, 3.44 g (98%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.27 (s, 9H), 2.33 (s, 3H), 2.46 (s, 3H), 6.86 (d, J = 7.8 Hz, 1H), 6.92 (s, 1H), 7.30 (d, J = 7.8 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ −0.1, 14.8, 21.5, 100.1, 102.3, 118.2, 124.5, 124.9, 132.3, 139.0, 141.5. HRMS (EI-EB): m/z [M$^+$] calcd for $C_{13}H_{18}SSi$, 234.0898; found, 234.0899.

*4-tert-Butyl-2-(methylthio)-1-(trimethylsilylethynyl)benzene (**2c**).* Pale yellow oil, 3.86 g (93%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.26 (s, 9H), 1.30 (s, 9H), 2.50 (s, 3H), 7.09 (dd, J = 0.6, 8.0 Hz, 1H), 7.17 (d, J = 0.6 Hz, 1H), 7.35 (d, J = 8.0 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ −0.1, 15.1, 31.0, 35.0, 100.2, 102.3, 118.5, 121.4, 121.6, 132.3, 140.9, 152.1. HRMS (EI-EB): m/z [M$^+$] calcd for $C_{16}H_{24}SSi$, 276.1368; found, 276.1368.

DOI: 10.1021/acs.joc.9b00213
J. Org. Chem. XXXX, XXX, XXX−XXX

*4-Methoxy-2-(methylthio)-1-(trimethylsilylethynyl)benzene (**2d**).* Pale yellow oil, 3.64 g (97%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.27 (s, 9H), 2.46 (s, 3H), 3.82 (s, 3H), 6.58 (dd, J = 2.4, 8.4 Hz, 1H), 6.65 (d, J = 2.4 Hz, 1H), 7.36 (d, J = 8.4 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 0.0, 15.0, 55.3, 99.5, 102.1, 109.0, 110.4, 113.5, 133.9, 143.8, 160.1. HRMS (EI-EB): m/z [M$^+$] calcd for $C_{13}H_{18}OSSi$, 250.0848; found, 250.0848.

*4-Chloro-2-(methylthio)-1-(trimethylsilylethynyl)benzene (**2e**).* Pale yellow oil, 3.67 g (96%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.27 (s, 9H), 2.47 (s, 3H), 7.03 (dd, J = 1.6, 8.4 Hz, 1H), 7.06 (d, J = 1.6 Hz, 1H), 7.32 (d, J = 8.4 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ −0.2, 14.7, 100.9, 102.3, 119.1, 123.2, 124.0, 133.2, 134.9, 144.2. HRMS (EI-EB): m/z [M$^+$] calcd for $C_{12}H_{15}ClSSi$, 254.0352; found, 254.0352.

*4-Acetyl-1-(methylthio)-2-(trimethylsilylethynyl)benzene (**2f**).* Pale yellow solid, 3.31 g (84%). Mp: 111−112 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.30 (s, 9H), 2.52 (s, 3H), 2.57 (s, 3H), 7.17 (d, J = 8.2 Hz, 1H), 7.88 (d, J = 8.2 Hz, 1H), 7.98 (s, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ −0.2, 14.6, 26.4, 100.9, 102.8, 120.5, 122.8, 128.3, 132.5, 132.8, 149.0, 196.5. HRMS (EI-EB): m/z [M$^+$] calcd for $C_{14}H_{18}OSSi$, 262.0848; found, 262.0847.

*4-Benzoyl-1-(methylthio)-2-(trimethylsilylethynyl)benzene (**2g**).* Light brown oil, 4.82 g (99%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.28 (s, 9H), 2.54 (s, 3H), 7.20 (d, J = 8.4 Hz, 1H), 7.50 (t, J = 7.2 Hz, 2H), 7.60 (t, J = 7.2 Hz, 1H), 7.75−7.77 (m, 3H), 7.84 (s, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ −0.2, 14.7, 100.9, 102.9, 120.4, 122.6, 128.3, 129.8, 130.2, 132.3, 133.0, 134.0, 137.5, 148.4, 195.1. HRMS (EI-EB): m/z [M$^+$] calcd for $C_{19}H_{20}OSSi$, 324.1004; found, 324.1004.

General Procedure for the Synthesis of 1-Ethynyl-2-(methylthio)benzenes 3. To a solution of KOH (0.842 g, 15 mmol) in MeOH (40 mL) was added 2-(methylthio)-1-(trimethylsilylethynyl)benzene (**2**, 10 mmol) at room temperature, and the mixture was stirred for 2 h. The reaction mixture was poured into water and extracted with ether (15 mL × 3). The combined organic phase was washed with water and brine and dried over anhydrous Na_2SO_4. After evaporation of the solvent, the residue was submitted to column chromatography on silica gel. Elution with hexane/CH_2Cl_2 (2:1) gave the desired product.

*1-Ethynyl-2-(methylthio)benzene (**3a**).*[20] Pale yellow oil, 1.13 g (76%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.49 (s, 3H), 3.47 (s, 1H), 7.09 (t, J = 8.0 Hz, 1H), 7.17 (d, J = 8.0 Hz, 1H), 7.32 (t, J = 8.0 Hz, 1H), 7.46 (d, J = 8.0 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 15.0, 81.0, 83.4, 120.2, 124.20, 124.24, 129.2, 133.1, 141.8.

*1-Ethynyl-4-methyl-2-(methylthio)benzene (**3b**).* Pale yellow oil, 1.31 g (81%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.35 (s, 3H), 2.49 (s, 3H), 3.42 (s, 1H), 6.90 (d, J = 8.0 Hz, 1H), 6.97 (s, 1H), 7.35 (d, J = 8.0 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 14.9, 21.4, 81.0, 82.6, 117.1, 124.8, 125.0, 132.7, 139.3, 141.3. HRMS (EI-EB): m/z [M$^+$] calcd for $C_{10}H_{10}S$, 162.0503; found, 162.0503.

*4-tert-Butyl-1-ethynyl-2-(methylthio)benzene (**3c**).* Pale yellow oil, 1.84 g (90%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.32 (s, 9H), 2.52 (s, 3H), 3.41 (s, 1H), 7.13 (dd, J = 1.6, 8.0 Hz, 1H), 7.22 (d, J = 1.6 Hz, 1H), 7.40 (d, J = 8.0 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 15.4, 31.0, 35.0, 81.2, 82.5, 117.8, 121.9, 122.0, 132.8, 140.8, 152.5. HRMS (EI-EB): m/z [M$^+$] calcd for $C_{13}H_{16}S$, 204.0973; found, 204.0972.

*1-Ethynyl-4-methoxy-2-(methylthio)benzene (**3d**).* Pale yellow oil, 1.75 g (98%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.48 (s, 3H), 3.39 (s, 1H), 3.82 (s, 3H), 6.61 (dd, J = 2.4, 8.4 Hz, 1H), 6.69 (d, J = 2.4 Hz, 1H), 7.39 (d, J = 8.4 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 14.9, 55.2, 80.9, 81.9, 109.1, 110.4, 112.2, 134.2, 143.4, 160.4. HRMS (EI-EB): m/z [M$^+$] calcd for $C_{10}H_{10}OS$, 178.0452; found, 178.0452.

*4-Chloro-1-ethynyl-2-(methylthio)benzene (**3e**).* Pale yellow oil, 0.932 g (51%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.49 (s, 3H), 3.49 (s, 1H), 7.06 (dd, J = 2.0, 8.4 Hz, 1H), 7.10 (d, J = 2.0 Hz, 1H), 7.37 (d, J = 8.4 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 14.8, 79.8, 84.4, 117.9, 123.3, 124.1,133.8, 135.3, 144.0. HRMS (EI-EB): m/z [M$^+$] calcd for C_9H_7ClS, 181.9957; found, 181.9955.

*4-Acetyl-2-ethynyl-1-(methylthio)benzene (**3f**).* Light brown solid, 1.86 g (99%). Mp: 76−77 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.54 (s, 3H), 2.58 (s, 3H), 3.55 (s, 1H), 7.19 (d, J = 8.0 Hz, 1H), 7.91 (d, J = 8.0 Hz, 1H), 8.02 (s, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 14.5, 26.3, 79.9, 84.6, 119.4, 122.8, 128.6, 132.77, 132.80, 148.8, 196.2. HRMS (EI-EB): m/z [M$^+$] calcd for $C_{11}H_{10}OS$, 190.0452; found, 190.0452.

*4-Benzoyl-2-ethynyl-1-(methylthio)benzene (**3g**).* Light brown solid, 2.52 g (100%). Mp: 71−72 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.55 (s, 3H), 3.52 (s, 1H), 7.23 (d, J = 8.4 Hz, 1H), 7.49 (t, J = 7.6 Hz, 2H), 7.60 (t, J = 7.6 Hz, 1H), 7.75−7.82 (m, 3H), 7.80 (d, J = 8.4 Hz, 1H), 7.90 (d, J = 2.0 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 14.7, 80.0, 84.7, 119.4, 122.9, 128.4, 129.8, 130.6, 132.4, 133.2, 134.6, 137.4, 148.3, 195.0. HRMS (EI-EB): m/z [M$^+$] calcd for $C_{16}H_{12}OS$, 252.0609; found, 252.0608.

General Procedure for the Synthesis of 1-Aryl-2-[2-(methylthio)phenyl]ethynes 4. To a solution of 1-iodo-2-(methylthio)benzene (**1**, 3 mmol) and 1-ethynyl-2-(methylthio)arene (**3**, 3.6 mmol) in trimethylamine (12 mL) were added $PdCl_2(PPh_3)_2$ (42 mg, 0.06 mmol) and CuI (6 mg, 0.03 mmol), and the mixture was stirred at room temperature for 3 h. The reaction mixture was poured into water and extracted with CH_2Cl_2 (15 mL × 3). The CH_2Cl_2 solution was washed with saturated NH_4Cl, water, and brine, successively, and dried over anhydrous Na_2SO_4. Evaporation of the solvent gave the crude product, which was purified by column chromatography on silica gel. Elution with hexane/CH_2Cl_2 gave the product.

*1,2-Bis[2-(methylthio)phenyl]ethyne (**4a**).*[21] Pale yellow solid, 0.657 g (81%). Mp: 124−126 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.52 (s, 6H), 7.12 (t, J = 8.0 Hz, 2H), 7.19 (d, J = 8.0 Hz, 2H), 7.31 (t, J = 8.0 Hz, 2H), 7.55 (d, J = 8.0 Hz, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 15.1, 93.1, 121.2, 124.0, 124.1, 128.8, 132.5, 141.5.

*1,2-Bis(4-methyl-2-(methylthio)phenyl)ethyne (**4b**).* Pale yellow solid, 0.706 g (79%). Mp: 124−126 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.37 (s, 6H), 2.51 (s, 6H), 6.92 (d, J = 8.0 Hz, 2H), 6.98 (s, 2H), 7.42 (d, J = 8.0 Hz, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 15.1, 21.5, 92.5, 118.6, 124.8, 125.1, 132.2, 138.7, 140.9. HRMS (EI-EB): m/z [M$^+$] calcd for $C_{18}H_{18}S_2$, 298.0850; found, 298.0851.

*1,2-Bis[4-(tert-butylphenyl)-2-(methylthio)phenyl]ethyne (**4c**).* Pale yellow solid, 1.147 g (100%). Mp: 81−83 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.33 (s, 18H), 2.54 (s, 6H), 7.15 (d, J = 8.0 Hz, 2H), 7.24 (s, 2H), 7.47 (d, J = 8.0 Hz, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 15.5, 31.0, 35.0, 92.5, 119.0, 121.79, 121.81, 132.2, 140.5, 151.9. HRMS (EI-EB): m/z [M$^+$] calcd for $C_{24}H_{30}S_2$, 382.1789; found, 382.1790.

*1,2-Bis[4-methoxy-2-(methylthio)phenyl]ethyne (**4d**).* Pale yellow solid, 0.981 g (99%). Mp: 137−140 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.50 (s, 6H), 3.80 (s, 6H), 6.64 (dd, J = 2.4, 8.4 Hz, 2H), 6.70 (d, J = 2.4 Hz, 2H), 7.45 (d, J = 8.4 Hz, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 15.2, 55.3, 91.6, 109.2, 110.5, 114.0, 133.6, 143.0, 159.9. HRMS (EI-EB): m/z [M$^+$] calcd for $C_{18}H_{18}O_2S_2$, 330.0748; found, 330.0748.

*1,2-Bis[4-chloro-2-(methylthio)phenyl]ethyne (**4e**).* Pale yellow solid, 0.831 g (82%). Mp: 131−132 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.51 (s, 6H), 7.08 (d, J = 8.0 Hz, 2H), 7.12 (s, 2H), 7.43 (d, J = 8.0 Hz, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 15.0, 92.9, 119.1, 123.6, 124.2, 133.3, 135.0, 143.8. HRMS (EI-EB): m/z [M$^+$] calcd for $C_{16}H_{12}Cl_2S$, 337.9757; found, 337.9758.

*1,2-Bis[5-acetyl-2-(methylthio)phenyl]ethyne (**4f**).* Pale yellow solid, 0.808 g (76%). Mp: 196−197 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.58 (s, 6H), 2.61 (s, 6H), 7.23 (d, J = 8.2 Hz, 2H), 7.92 (d, J = 8.2 Hz, 2H), 8.11 (s, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 14.7, 26.4, 93.0, 120.1, 122.9, 128.5, 132.4, 132.9, 148.7, 196.5. HRMS (EI-EB): m/z [M$^+$] calcd for $C_{20}H_{18}O_2S_2$, 354.0748; found, 354.0747.

*1,2-Bis[5-benzoyl-2-(methylthio)phenyl]ethyne (**4g**).* Pale yellow solid, 1.091 g (76%). Mp: 212−213 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.58 (s, 6H), 7.26 (d, J = 8.0 Hz, 2H), 7.50 (t, J = 7.4 Hz, 4H), 7.60 (t, J = 7.4 Hz, 2H), 7.78−7.80 (m, 6H), 7.96 (d, J = 1.6 Hz, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 14.9, 93.1, 120.1, 122.8,

DOI: 10.1021/acs.joc.9b00213
J. Org. Chem. XXXX, XXX, XXX−XXX

128.4, 129.8, 130.5, 132.4, 133.3, 134.1, 137.5, 148.2, 195.1. HRMS (EI-EB): m/z [M^+] calcd for $C_{30}H_{22}O_2S_2$, 478.1061; found, 478.1062.

*1-[4-Methoxy-2-(methylthio)phenyl]-2-[2-(methylthio)phenyl]-ethyne (**4h**).* Pale yellow solid, 0.784 g (87%). Mp: 58−60 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.51 (s, 3H), 2.52 (s, 3H), 3.84 (s, 3H), 6.65 (dd, J = 2.4, 8.0 Hz, 1H), 6.72 (d, J = 2.4 Hz, 1H), 7.11 (t, J = 8.0 Hz, 1H), 7.18 (d, J = 8.0 Hz, 1H), 7.28 (t, J = 8.0 Hz,1H), 7.47 (d, J = 8.0 Hz, 1H), 7.52 (d, J = 8.0 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 15.1 (two peaks overlapped), 55.3, 91.7, 93.1, 109.2, 110.5, 113.5, 121.5, 124.1, 128.5, 132.3, 133.8, 141.2, 143.3, 160.1. HRMS (EI-EB): m/z [M^+] calcd for $C_{17}H_{16}OS_2$, 300.0643; found, 300.0642.

*1-[5-Acetyl-2-(methylthio)phenyl]-2-[2-(methylthio)phenyl]-ethyne (**4i**).* Pale yellow solid, 0.703 g (75%). Mp: 110−111 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.54 (s, 3H), 2.56 (s, 3H), 2.60 (s, 3H), 7.14 (t, J = 7.6 Hz, 1H), 7.19−7.23 (m, 2H), 7.34 (t, J = 8.0 Hz, 1H), 7.56 (dd, J = 1.2, 7.6 Hz, 1H), 8.90 (dd, J = 2.0, 8.4 Hz, 1H), 8.09 (d, J = 2.0 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 14.8, 15.1, 26.4, 92.0, 94.1, 120.5, 120.6, 122.8, 124.0, 124.2, 128.2, 129.2, 132.3, 132.7, 133.8, 141.8, 148.7, 196.7. HRMS (EI-EB): m/z [M^+] calcd for $C_{18}H_{16}OS_2$, 312.0643; found, 312.0644.

*1-[5-Acetyl-2-(methylthio)phenyl]-2-[4-methoxy-2-(methylthio)-phenyl]ethyne (**4j**).* Pale yellow solid, 1.02 g (99%). Mp: 100−101 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.51 (s, 3H), 2.53 (s, 3H), 2.58 (s, 3H), 3.84 (s, 3H), 6.65 (dd, J = 2.4, 8.4 Hz, 1H), 6.70 (d, J = 2.4 Hz, 1H), 7.18 (d, J = 8.4 Hz, 1H), 7.48 (d, J = 8.4 Hz, 1H), 7.85 (dd, J = 2.0, 8.4 Hz, 1H), 8.05 (d, J = 2.0 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 14.7, 15.0, 26.4, 55.3, 90.6, 94.2, 109.2, 110.4, 112.8, 120.8, 122.6, 127.8, 131.9, 132.7, 133.9, 143.5, 148.3, 160.3, 196.7. HRMS (EI-EB): m/z [M^+] calcd for $C_{19}H_{18}O_2S_2$, 342.0748; found, 342.0747.

*1-[4-Chloro-2-(methylthio)phenyl]-2-[4-methyl-2-(methylthio)-phenyl]ethyne (**4k**).* Pale yellow solid, 0.832 g (87%). Mp: 111−113 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.37 (s, 3H), 2.506 (s, 3H), 2.510 (s, 3H), 6.93 (d, J = 7.6 Hz, 1H), 6.99 (s, 1H), 7.07 (dd, J = 1.6, 8.0 Hz, 1H), 7.11 (d, J = 1.6 Hz, 1H), 7.41−7.44 (m, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 15.1, 15.2, 21.7, 91.4, 94.3, 118.1, 119.7, 123.6, 124.3, 124.9, 125.3, 132.5, 133.3, 134.7, 139.4, 141.3, 143.7. HRMS (EI-EB): m/z [M^+] calcd for $C_{17}H_{15}ClS_2$, 318.0304; found, 318.0304.

*1-[4-Chloro-2-(methylthio)phenyl]-2-[4-tert-butyl-2-(methylthio)phenyl]ethyne (**4l**).* Pale yellow solid, 0.920 g (85%). Mp: 52−54 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.33 (s, 9H), 2.50 (s, 3H), 2.54 (s, 3H), 7.07 (d, J = 8.0 Hz, 1H), 7.11 (s, 1H), 7.15 (d, J = 8.4 Hz, 1H), 7.23 (s, 1H), 7.44 (d, J = 8.0 Hz, 1H), 7.46 (d, J = 8.4 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 14.8, 15.2, 30.9, 34.8, 91.1, 94.2, 118.3, 119.3, 121.5, 121.6, 123.2, 123.9, 132.2, 133.0, 134.4, 140.6, 143.6, 152.1. HRMS (EI-EB): m/z [M^+] calcd for $C_{20}H_{21}ClS_2$, 360.0773; found, 360.0772.

*1-[4-Chloro-2-(methylthio)phenyl]-2-[4-methoxy-2-(methylthio)-phenyl]ethyne (**4m**).* Pale yellow solid, 0.733 g (73%). Mp: 110−112 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.505 (s, 3H), 2.509 (s, 3H), 3.85 (s 3H), 6.66 (dd, J = 2.0, 8.4 Hz, 1H), 6.71 (s, 1H), 7.07 (dd, J = 2.0, 8.4 Hz, 1H), 7.10 (d, J = 2.0 Hz, 1H), 7.42 (d, J = 8.0 Hz, 1H), 7.46 (d, J = 8.4 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 15.07, 15.14, 55.4, 90.7, 94.1, 109.3, 110.5, 113.2, 119.7, 123.5, 124.2, 133.1, 133.9, 134.5, 143.4, 160.3 (one peak overlapped). HRMS (EI-EB): m/z [M^+] calcd for $C_{17}H_{15}ClOS_2$, 334.0253; found, 334.0253.

*3-Iodobenzothiophenes **5** by Iodination of 1-Aryl-2-[2-(methylthio)phenyl]ethynes **4**.* To a solution of 1-aryl-2-[2-(methylthio)phenyl]ethyne **4** (1.0 mmol) in CH_2Cl_2 (1 mL) were added $PhI(OAc)_2$ (0.193 g, 0.6 mmol) and I_2 (0.152 g, 0.6 mmol), and the mixture was stirred at room temperature for 3 h. The reaction mixture was quenched with aqueous $Na_2S_2O_3$ and extracted with CH_2Cl_2 (10 mL × 3). The organic phase was washed with water and dried over anhydrous Na_2SO_4. The solvent was evaporated by a rotary evaporation, and the residue was submitted to column chromatography on silica gel. Elution with CH_2Cl_2/hexane (1:3) gave the desired product.

*3-Iodo-2-[2-(methylthio)phenyl]benzo[b]thiophene (**5a**).* White solid, 0.245 g (64%). Mp: 113−114 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.42 (s, 3H), 7.24−7.34 (m, 3H), 7.40−7.47 (m, 3H), 7.80 (d, J = 8.0 Hz, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 15.9, 83.8, 122.3, 124.6, 125.3, 125.4, 125.6, 126.0, 129.9, 131.4, 133.3, 139.6, 139.7, 141.0 (one peak overlapped). HRMS (EI-EB): m/z [M^+] calcd for $C_{15}H_{11}IS_2$, 381.9347; found, 381.9347.

*3-Iodo-6-methyl-2-[4-methyl-2-(methylthio)phenyl]benzo[b]-thiophene (**5b**).* White solid, 0.250 g (61%). Mp: 104−106 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.41 (s, 3H), 2.44 (s, 3H), 2.51 (s, 3H), 7.05 (d, J = 7.4 Hz, 1H), 7.13 (s, 1H), 7.18 (d, J = 7.4 Hz, 1H), 7.27 (d, J = 8.0 Hz, 1H), 7.59 (s, 1H), 7.66 (d, J = 8.0 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 15.9, 21.5, 21.6, 83.4, 122.0, 125.52, 125.55, 126.2, 126.9, 130.6, 131.3, 135.6, 138.9, 139.3, 139.80, 139.85 (one peak overlapped). HRMS (EI-EB): m/z [M^+] calcd for $C_{17}H_{15}IS_2$, 409.9660; found, 409.9659.

*3-Iodo-6-tert-butyl-2-[4-tert-butyl-2-(methylthio)phenyl]benzo-[b]thioophene (**5c**).* White solid, 0.321 g (65%). Mp: 125−127 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.38 (s, 9H), 1.40 (s, 9H), 2.42 (s, 3H), 7.22 (d, J = 8.0 Hz, 1H), 7.26 (d, J = 8.0 Hz, 1H), 7.36 (s, 1H), 7.52 (d, J = 8.4 Hz, 1H), 7.71 (d, J = 8.4 Hz, 1H), 7.80 (s, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 16.2, 31.3, 31.5, 35.0, 35.1, 83.1, 118.3, 122.1, 123.0, 123.5, 125.3, 130.8, 131.6, 138.5, 138.7, 139.6, 140.4, 148.9, 152.8. HRMS (FAB-EB): m/z [M^+ + H] calcd for $C_{23}H_{28}IS_2$, 495.0677; found, 495.0677.

*3-Iodo-6-methoxy-2-[4-methoxy-2-(methylthio)phenyl]benzo-[b]thiophene (**5d**).* White solid, 0.296 g (67%). Mp: 114−117 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.41 (s, 3H), 3.89 (s, 3H), 3.90 (s, 3H), 6.76 (dd, J = 2.0, 8.4 Hz, 1H), 6.84 (s, 1H), 7.07 (dd, J = 2.0, 8.8 Hz, 1H), 7.22 (d, J = 8.4 Hz, 1H), 7.28 (s, 1H), 7.66 (d, J = 8.8 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 15.7, 55.4, 55.7, 83.4, 104.6, 109.2, 111.4, 115.2, 125.4, 126.5, 132.6, 135.0, 138.0, 140.7, 141.3, 158.3, 160.6. HRMS (EI-EB): m/z [M^+] calcd for $C_{17}H_{15}IO_2S_2$, 441.9558; found, 441.9557.

*6-Chloro-2-[4-chloro-2-(methylthio)phenyl]-3-iodobenzo[b]-thiophene (**5e**).* White solid, 0.334 g (74%). Mp: 170−171 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.44 (s, 3H), 7.21−7.22 (m, 2H), 7.26 (s, 1H), 7.43 (dd, J = 2.0, 8.8 Hz, 1H), 7.71 (d, J = 8.8 Hz, 1H), 7.81 (d, J = 2.0 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 15.7, 83.5, 121.8, 124.7, 124.8, 126.2, 126.9, 130.8, 132.0, 132.4, 136.3, 139.5, 140.2, 140.4, 142.1. HRMS (EI-EB): m/z [M^+] calcd for $C_{15}H_9Cl_2IS_2$, 449.8567; found, 449.8568.

*5-Acetyl-2-[5-acetyl-2-(methylthio)phenyl]-3-iodobenzo[b]-thiophene (**5f**).* White solid, 0.373 g (80%). Mp: 185−187 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.50 (s, 3H), 2.62 (s, 3H), 2.76 (s, 3H), 7.37 (d, J = 8.4 Hz, 1H), 7.88 (d, J = 2.0 Hz, 1H), 7.91 (d, J = 8.8 Hz, 1H), 8.03−8.07 (m, 2H), 8.38 (d, J = 1.2 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 15.5, 27.0, 27.2, 85.5, 123.0, 124.3, 125.4, 127.2, 130.0, 131.5, 132.3, 133.6, 135.2, 141.3, 141.5, 144.6, 147.3, 196.9, 197.8. HRMS (FAB-EB): m/z [M^+ + H] calcd for $C_{19}H_{16}IO_2S_2$, 466.9636; found, 466.9635.

*5-Benzoyl-2-[5-benzoyl-2-(methylthio)phenyl]-3-iodobenzo[b]-thiophene (**5g**).* White solid, 0.484 g (82%). Mp: 199−200 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.53 (s, 3H), 7.41 (d, J = 8.4 Hz, 1H), 7.47−7.65 (m, 6H), 7.74 (d, J = 2.0 Hz, 1H), 7.83−7.94 (m, 6H), 7.97 (dd, J = 2.0, 8.0 Hz, 1H), 8.22 (s, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 15.7, 85.4, 122.8, 124.3, 127.3, 128.8, 128.9, 130.3, 130.5, 132.0, 132.2, 132.8, 132.9, 133.5, 133.8, 135.5, 137.9, 138.0, 141.1, 141.6, 144.1, 146.7, 195.5, 196.5 (one peak overlapped). HRMS (EI-EB): m/z [M^+] calcd for $C_{29}H_{20}IO_2S_2$, 590.9949; found, 590.9947.

*3-Iodo-2-[4-methoxy-2-(methylthio)phenyl]benzo[b]thiophene (**5h**).* White solid, 0.309 g (75%). Mp: 133−134 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.42 (s, 3H), 3.89 (s, 3H), 6.78 (dd, J = 2.4, 8.6 Hz, 1H), 6.86 (d, J = 2.4 Hz, 1H), 7.22 (d, J = 8.6 Hz, 1H), 7.38−7.48 (m, 2H), 7.79 (d, J = 8.4 Hz, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 15.7, 55.4, 84.3, 109.3, 111.4, 122.2, 125.2, 125.3, 125.5, 125.9, 132.4, 139.7, 140.88, 140.90, 141.1, 160.7. HRMS (EI-EB): m/z [M^+] calcd for $C_{16}H_{13}IOS_2$, 411.9452; found, 411.9452.

DOI: 10.1021/acs.joc.9b00213
J. Org. Chem. XXXX, XXX, XXX−XXX

*2-[5-Acetyl-2-(methylthio)phenyl]-3-iodobenzo[b]thiophene and 5-Acetyl-3-iodo-2-[2-(methylthio)phenyl]benzo[b]thiophene (**5i** and **5i′**, 1:1 Mixture).* White solid, 0.314 g (74%). Mp: 57−59 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.44 (s), 2.49 (s), 2.60 (s), 2.75 (s), 7.26−7.52 (m), 7.80−7.89 (m), 8.01−8.06 (m), 8.37 (d, J = 1.2 Hz). ^{13}C NMR (400 MHz, $CDCl_3$): δ 15.1, 15.7, 26.4, 26.7, 84.2, 84.5, 122.2, 122.4, 123.7, 124.58, 124.60, 125.4, 125.8, 126.0, 126.6, 129.3, 130.0, 131.15, 131.20, 132.3, 132.5, 133.0, 134.5, 139.39, 139.45, 139.5, 140.76, 140.86, 142.5, 144.2, 146.9, 196.5, 197.4. HRMS (EI-EB): m/z [M$^+$] calcd for $C_{17}H_{13}IOS_2$, 423.9452; found, 423.9454.

*5-Acetyl-3-iodo-2-[4-methoxy-2-(methylthio)phenyl]benzo[b]thiophene (**5j**).* White solid, 0.332 g (73%). Mp: 158−200 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.41 (s, 3H), 2.74 (s, 3H), 3.88 (s, 3H), 6.78 (d, J = 8.0 Hz, 1H), 6.85 (s, 1H), 7.22 (d, J = 8.0 Hz, 1H), 7.85 (d, J = 8.0 Hz, 1H), 7.99 (d, J = 8.0 Hz, 1H), 8.34 (s, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 16.1, 27.2, 55.7, 85.5, 109.7, 111.9, 122.8, 125.0, 125.1, 127.0, 132.7, 134.9, 141.2, 141.4, 142.9, 144.8, 161.2, 197.9. HRMS (EI-EB): m/z [M$^+$] calcd for $C_{18}H_{15}IO_2S_2$, 453.9558; found, 453.9557.

*6-Chloro-3-iodo-2-[2-(methylthio)-4-methylphenyl]benzo[b]thiophene and 2-[4-Chloro-2-(methylthio)phenyl]-3-iodo-6-methylbenzo[b]thiophene (**5k** and **5k′**, 2:3 Mixture).* White solid, 0.327 g (76%). Mp: 131−132 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.41 (s, 3H), 2.43 (s, 3H), 2.50 (s, 3H), 7.05 (d, J = 8.0 Hz, 1H), 7.13 (s, 1H), 7.16 (d, J = 7.6 Hz, 1H), 7.19 (s, 2H), 7.23 (s, 1H), 7.27 (d, J = 8.4 Hz, 1H), 7.40 (d, J = 8.8 Hz, 1H), 7.59 (s, 1H), 7.65 (d, J = 8.0 Hz, 1H), 7.69 (d, J = 8.4 Hz, 1H), 7.77 (s, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 15.6, 15.9, 21.5, 21.6, 83.2, 83.8, 121.7, 122.0, 124.49, 125.52, 124.6, 125.6, 126.0, 126.1, 126.8, 127.1, 129.9, 131.2, 131.3, 131.7, 132.5, 135.9, 136.0, 138.2, 138.8, 139.2, 139.6, 139.7, 140.2, 140.4, 141.7, 142.1. HRMS (FAB-EB): m/z [M$^+$ + H] calcd for $C_{16}H_{13}ClIS_2$, 430.9192; found, 430.9192.

*2-[4-tert-Butyl-2-(methylthio)phenyl]-6-chloro-3-iodobenzo[b]thiophene and 6-tert-Butyl-2-[4-chloro-2-(methylthio)phenyl]-3-iodobenzo[b]thiophene (**5l** and **5l′**, 1:1 Mixture).* White solid, 0.331 g (70%). Mp: 86−87 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.39 (s), 1.41 (s), 2.43 (s), 2.44 (s), 7.20−7.27 (m), 7.37−7.43 (m), 7.55 (d, J = 1.6 Hz), 7.71 (d, J = 8.8 Hz), 7.80−7.81 (m). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 15.6, 16.2, 31.2, 31.5, 34..9, 35.0, 83.0, 83.6, 118.3, 121.6, 122.2, 123.0, 123.7, 124.42, 124.45, 125.4, 125.9, 126.7, 130.2, 131.0, 131.3, 131.6, 132.4, 135.8, 138.5, 138.60, 138.63, 139.5, 139.6, 140.3, 141.8, 142.1, 149.2, 153.0. HRMS (EI-EB): m/z [M$^+$] calcd for $C_{19}H_{18}ClIS_2$, 471.9583; found, 471.9583.

*6-Chloro-3-iodo-2-[4-methoxy-2-(methylthio)phenyl]benzo[b]thiophene (**5m**).* White solid, 0.339 g (76%). Mp: 128−129 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.42 (s, 3H), 3.89 (s, 3H), 6.78 (dd, J = 2.4, 8.4 Hz, 1H), 6.85 (d, J = 2.4 Hz, 1H), 7.21 (d, J = 8.4 Hz, 1H), 7.42 (dd, J = 2.0, 8.4 Hz, 1H), 7.70 (d, J = 8.4 Hz, 1H), 7.79 (d, J = 2.0 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 15.8, 55.4, 83.6, 109.4, 111.6, 121.7, 124.9, 126.0, 126.8, 131.7 132.4, 139.4, 140.4, 141.1, 141.5, 160.8. HRMS (EI-EB): m/z [M$^+$] calcd for $C_{16}H_{12}ClIOS_2$, 445.9063; found, 445.9063.

*Synthesis of [1]Benzothieno[3,2-b][1]benzothiophene Derivatives **6**.* The CH_2Cl_2 solution (0.01 M, 20 mL) of **5** (0.2 mmol) was placed in a Pyrex tube and irradiated at room temperature by a high-pressure Hg lamp (400 W) using a merry-go-round apparatus. After 6 h of irradiation, the evaporation of the solvent gave the product as a solid. The product was obtained by filtration and washed with hexane.

*[1]Benzothieno[3,2-b][1]benzothiophene (BTBT, **6a**).*[2a] White solid, 34.6 mg (72%). Mp: 191−200 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39−7.49 (m, 4H), 7.89−7.94 (m, 4H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 121.6, 124.0, 124.9, 125.0, 133.1, 133.4, 142.2.

*2,7-Dimethyl[1]benzothieno[3,2-b][1]benzothiophene (**6b**).* White solid, 35.4 mg (66%). Mp: 193−200 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.51 (s, 6H), 7.25 (d, J = 8.0 Hz, 2H), 7.69 (s, 2H), 7.73 (d, J = 8.0 Hz, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 21.6, 121.0, 123.8, 126.4, 130.9, 134.8, 142.4. HRMS (EI-EB): m/z [M$^+$] calcd for $C_{16}H_{12}S_2$, 268.0380; found, 268.0381.

*2,7-Di-tert-butyl[1]benzothieno[3,2-b][1]benzothiophene (**6c**).* White solid, 50.8 mg (72%). Mp: 250−260 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.42 (s, 18H), 7.51 (d, J = 8.8 Hz, 2H), 7.81 (d, J = 8.8 Hz, 2H), 7.90 (s, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 31.5, 35.1, 120.2, 120.9, 123.0, 130.9, 132.7, 142.4, 148.3. HRMS (EI-EB): m/z [M$^+$] calcd for $C_{22}H_{24}S_2$, 352.1319; found, 352.1320.

*2,7-Dimethoxy[1]benzothieno[3,2-b][1]benzothiophene (**6d**).* White solid, 49.3 mg (82%). Mp: 116−119 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.91 (s, 6H), 7.05 (dd, J = 2.0, 8.8 Hz, 2H), 7.38 (d, J = 2.0 Hz, 2H), 7.70 (d, J = 8.8 Hz, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 55.7, 107.1, 114.2, 121.7, 127.4, 131.1, 143.4, 157.5. HRMS (EI-EB): m/z [M$^+$] calcd for $C_{16}H_{12}O_2S_2$, 300.0279; found, 300.0276.

*2,7-Dichloro[1]benzothieno[3,2-b][1]benzothiophene (**6e**).* White solid, 33.4 mg (54%). Mp: 247−253 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43 (dd, J = 1.6, 8.4 Hz, 2H), 7.77 (d, J = 8.4 Hz, 2H), 7.89 (d, J = 1.6 Hz, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 122.3, 123.7, 125.8, 131.2, 131.4, 133.2, 143.3. HRMS (EI-EB): m/z [M$^+$] calcd for $C_{14}H_6Cl_2S_2$, 307.9288; found, 307.9287.

*3,8-Diacetyl[1]benzothieno[3,2-b][1]benzothiophene (**6f**).* White solid, 46.7 mg (72%). Mp: 252−253 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.75 (s, 6H), 8.03 (s, 4H), 8.50 (s,2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 27.2, 122.3, 124.6, 125.2, 133.1, 134.8, 135.2, 147.4, 197.8. HRMS (EI-EB): m/z [M$^+$] calcd for $C_{18}H_{12}O_2S_2$, 324.0279; found, 324.0278.

*3,8-Dibenzoyl[1]benzothieno[3,2-b][1]benzothiophene (**6g**).* White solid, 64.6 mg (72%). Mp: 287 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 (t, J = 7.6 Hz, 4H), 7.66 (t, J = 7.6 Hz, 2H), 7.87−7.89 (m, 6H), 8.05 (d, J = 8.8 Hz, 2H), 8.38 (s, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 123.7, 123.9, 126.3, 126.7, 128.5, 130.0, 130.1, 132..6, 134.8, 137.7, 146.5, 196.2. HRMS (EI-EB): m/z [M$^+$] calcd for $C_{28}H_{16}O_2S_2$, 448.0592; found, 448.0594.

*2-Methoxy[1]benzothieno[3,2-b][1]benzothiophene (**6h**).* White solid, 32.4 mg (60%). Mp: 177−179 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.93 (s, 3H), 7.07 (dd, J = 2.0, 8.4 Hz, 1H), 7.36−7.47 (m, 3H), 7.77 (d, J = 8.4 Hz, 1H), 7.84 (d, J = 8.0 Hz, 1H), 7.91 (d, J = 8.0 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 55.7, 106.9, 114.3, 121.1, 122.2, 123.9, 124.4, 124.8, 127.0, 131.2, 133.2, 133.3 141.7, 143.9, 157.8. HRMS (EI-EB): m/z [M$^+$] calcd for $C_{15}H_{10}OS_2$, 270.0173; found, 270.0175.

*2-Acetyl[1]benzothieno[3,2-b][1]benzothiophene (**6i**).* White solid, 41.2 mg (73%). Mp: 153−155 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.74 (s, 3H), 7.44−7.49 (m, 2H), 7.89−7.99 (m, 4H), 8.47 (s, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 26.8, 121.6, 121.8, 123.9, 124.0, 124.2, 125.0, 125.4, 132.6, 132.9, 133.6, 134.0, 134.3, 142.3, 146.8, 197.6. HRMS (EI-EB): m/z [M$^+$] calcd for $C_{16}H_{10}OS_2$, 282.0173; found, 282.0173.

*2-Acetyl-7-methoxy[1]benzothieno[3,2-b][1]benzothiophene (**6j**).* White solid, 46.2 mg (74%). Mp: 187−188 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.74 (s, 3H), 3.93 (s, 3H), 7.10 (dd, J = 2.4, 8.4 Hz, 1H), 7.43 (d, J = 2.4 Hz, 1H), 7.78 (d, J = 8.4 Hz, 1H), 7.97 (s, 2H), 8.43 (s, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 26.9, 55.7, 106.8, 114.7, 121.3, 122.3, 123.8, 123.9, 126.6, 131.5, 133.5, 134.1, 134.3, 144.1, 146.5, 158.2, 197.7. HRMS (EI-EB): m/z [M$^+$] calcd for $C_{17}H_{12}O_2S_2$, 312.0279; found, 312.0278.

*2-Chloro-7-methyl[1]benzothieno[3,2-b][1]benzothiophene (**6k**).* White solid, 38.1 mg (66%). Mp: 200−207 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.51 (s, 3H), 7.27 (d, J = 8.8 Hz, 1H), 7.40 (d, J = 8.8 Hz, 1H), 7.70 (s, 1H), 7.74 (d, J = 8.8 Hz, 2H), 7.87 (s, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 21.7, 121.2, 122.0, 123.5, 123.9, 125.6, 126.6, 130.56, 130.61, 131.7, 132.0, 133.7, 135.5, 142.6, 143.1. HRMS (EI-EB): m/z [M$^+$] calcd for $C_{15}H_9ClS_2$, 287.9834; found, 287.9835.

*2-tert-Butyl-7-chloro[1]benzothieno[3,2-b][1]benzothiophene (**6l**).* White solid, 29.1 mg (44%). Mp: 260−267 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.42 (s, 9H), 7.42 (dd, J = 2.0, 8.4 Hz, 1H), 7.53 (dd, J = 1.6, 8.4 Hz, 1H), 7.77−7.82 (m, 2H), 7.89−7.91 (m, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 31.5, 35.1, 120.3, 121.1, 122.1, 123.3, 123.6, 125.6, 130.55, 130.60, 131.8, 132.3, 133.6, 142.6, 143.2, 149.0. HRMS (EI-EB): m/z [M$^+$] calcd for $C_{18}H_{15}ClS_2$, 330.0304; found, 330.0302.

DOI: 10.1021/acs.joc.9b00213
J. Org. Chem. XXXX, XXX, XXX−XXX

*2-Chloro-7-methoxy[1]benzothieno[3,2-b][1]benzothiophene (**6m**).* White solid, 38.4 mg (63%). Mp: 189−199 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.92 (s, 3H), 7.08 (d, J = 8.8 Hz, 1H), 7.40−7.42 (m, 2H), 7.73−7.76 (m, 2H), 7.89 (s, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 55.7, 106.9, 114.5, 121.7, 122.2, 123.5, 125.5, 126.8, 130.2, 130.7, 131.8, 133.6, 142.8, 144.0, 158.0. HRMS (EI-EB): m/z [M$^+$] calcd for $C_{15}H_9ClOS_2$, 303.9783; found, 303.9784.

*Synthesis of 2,5-Bis(butylthio)-1,4-bis[(2-methylthiophenyl)-ethynyl]benzene (**8**).* To a solution of 1,4-dibromo-2,5-bis-(butylthio)benzene (**7**)[17] (412 mg, 1 mmol) and 1-ethynyl-2-(methylthio)benzene (**3a**) (356 mg, 2.4 mmol) in trimethylamine (10 mL) were added $PdCl_2(PPh_3)_2$ (28 mg, 0.04 mmol) and CuI (4 mg, 0.02 mmol), and the mixture was stirred at 80 °C for 6 h. The reaction mixture was poured into water and extracted with toluene (15 mL × 3). The organic phase was washed with saturated NH_4Cl, water, and brine, successively, and dried over anhydrous Na_2SO_4. Evaporation of the solvent gave the crude product, which was purified by column chromatography on silica gel. Elution with hexane/EtOAc (2:1) gave the product **8** in 94% yield (514 mg), as a yellow solid. Mp: 106 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.95 (t, J = 7.6 Hz, 6H), 1.45−1.55 (m, 4H), 1.67−1.74 (m, 4H), 2.53 (s, 6H), 3.01 (t, J = 7.6 Hz, 4H), 7.13 (t, J = 7.6 Hz, 2H), 7.20 (d, J = 7.6 Hz, 2H), 7.32 (t, J = 7.6 Hz, 2H), 7.48 (s, 2H), 7.55 (d, J = 7.6 Hz, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 13.7, 15.2, 22.1, 30.9, 32.6, 93.4, 94.3, 121.0, 123.4, 124.1, 124.2, 129.1, 131.2, 132.6, 136.6, 141.8. HRMS (EI-EB): m/z [M$^+$] calcd for $C_{32}H_{34}S_4$, 546.1543; found, 546.1542.

*Synthesis of 5-(Butylthio)-3-iodo-6-(3-iodobenzo[b]thiophen-2-yl)-2-[2-(methylthio)phenyl)benzo[b]thiophene (**9**).* To a solution of $PhI(OAc)_2$ (97 mg, 0.30 mmol) and I_2 (76 mg, 0.30 mmol) in CH_2Cl_2 (2 mL) was added bisethynylbenzene **8** (37 mg, 0.25 mmol), and the mixture was stirred at room temperature for 3 h. The reaction mixture was quenched with aqueous $Na_2S_2O_3$ and extracted with CH_2Cl_2 (10 mL × 3). The organic phase was washed with water and dried over anhydrous Na_2SO_4. The solvent was evaporated by a rotary evaporation, and the residue was submitted to column chromatography on silica gel. Elution with CH_2Cl_2/hexane (1:1) gave the desired product **9** in 52% yield (95 mg), as a yellow solid. Mp: 142−144 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.91 (t, J = 7.6 Hz, 3H), 1.41−1.46 (m, 2H), 1.62−1.68 (m, 2H), 2.47 (s, 3H), 2.97 (t, J = 7.6 Hz, 2H), 7.26−7.51 (m, 6H), 7.77 (s, 1H), 7.82−7.84 (m, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 13.7, 16.0, 22.1, 30.8, 33.5, 83.1, 84.4, 122.3, 124.7, 125.1, 125.4 (two peaks overlapped), 125.5, 125.7, 126.1, 130.1, 131.3, 132.6, 133.0, 136.0, 136.3, 139.6, 139.7, 140.8, 140.9, 142.2, 143.3. HRMS (FAB-EB): m/z [M$^+$ + H] calcd for $C_{27}H_{23}I_2S_4$, 728.8766; found, 728.8770.

Synthesis of Bis[1]benzothieno[2,3-d;2′,3′-d′]benzo[1,2-b;4,5-b′]dithiophene (BBTBDT)..[12,16] A CH_2Cl_2 solution (0.01 M, 5 mL) of **9** (36 mg, 0.05 mmol) was placed in a Pyrex tube and irradiated at 15−20 °C by a high-pressure Hg lamp (400 W) using a merry-go-round apparatus. After 8 h of irradiation, the evaporation of the solvent gave an almost pure crystalline BBTBDT. Filtration and washing with hexane and EtOH gave BBTBDT in 94% yield (19 mg) as a yellow solid. Mp: >300 °C (lit.[12] mp > 300 °C, lit.[16] mp > 380 °C). HRMS (EI-EB): m/z [M$^+$] calcd for $C_{22}H_{10}S_4$, 401.9665; found, 401.9666. Although BBTBDT was not soluble in $CDCl_3$, no impurities were not observed in ^{1}H and ^{13}C NMR spectra.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.9b00213.

^{1}H and ^{13}C NMR spectra of compounds **1**−**6** and **8**−**9** (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: kitamura@cc.saga-u.ac.jp.

ORCID

Tsugio Kitamura: 0000-0001-5592-5228

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by JSPS KAKENHI (16K05703).

■ REFERENCES

(1) (a) Wang, C.; Dong, H.; Hu, W.; Liu, Y.; Zhu, D. Semiconducting π-Conjugated Systems in Field-Effect Transistors: A Material Odyssey of Organic Electronics. *Chem. Rev.* **2012**, *112*, 2208−2267. (b) Murphy, A. R.; Frechet, J. M. J. Organic Semiconducting Oligomers for Use in Thin Film Transistors. *Chem. Rev.* **2007**, *107*, 1066−1096. (c) Takimiya, K.; Nakano, M.; Kang, M. J.; Miyazaki, E.; Osaka, I. Thienannulation: Efficient Synthesis of π-Extended Thienoacenes Applicable to Organic Semiconductors. *Eur. J. Org. Chem.* **2013**, *2013*, 217−227. (d) Takimiya, K.; Osaka, I.; Mori, T.; Nakano, M. Organic Semiconductors Based on [1]-Benzothieno[3,2-b][1]benzothiophene Substructure. *Acc. Chem. Res.* **2014**, *47*, 1493−1502. (e) Larik, F. A.; Faisal, M.; Saeed, A.; Abbas, Q.; Kazi, M. A.; Abbas, N.; Thebo, A. A.; Khan, D. M.; Channar, P. A. Thiophene-Based Molecular and Polymeric Semiconductors for Organic Field Effect Transistors and Organic Thin Film Transistors. *J. Mater. Sci.: Mater. Electron.* **2018**, *29*, 17975−18010. (f) Nakano, M.; Takimiya, K. Sodium Sulfide-Promoted Thiophene-Annulations: Powerful Tools for Elaborating Organic Semiconducting Materials. *Chem. Mater.* **2017**, *29*, 256−264. (g) Takimiya, K.; Shinamura, S.; Osaka, I.; Miyazaki, E. Thienoacene-Based Organic Semiconductors. *Adv. Mater.* **2011**, *23*, 4347−4370.

(2) (a) Sashida, H.; Yasuike, S. Studies on Tellurium-Containing Heterocycles. 7. A Simple One-Pot Synthesis of [1]Benzotelluro[3,2-b][1]benzotellurophenes and its Selenium and Sulfur Analogs from 2,2′-Dibromodiphenylacetylene. *J. Heterocycl. Chem.* **1998**, *35*, 725−726. (b) Li, Y.; Nie, C.; Wang, H.; Li, X.; Verpoort, F.; Duan, C. A Highly Efficient Method for the Copper-Catalyzed Selective Synthesis of Diryl Chalcogenides from Easily Available Chalcogen Sources. *Eur. J. Org. Chem.* **2011**, *2011*, 7331−7338.

(3) Saito, M.; Yamamoto, T.; Osaka, I.; Miyazaki, E.; Takimiya, K.; Kuwabara, H.; Ikeda, M. Facile Synthesis of [1]Bezothieno[3,2-b]benzothiophene from *o*-Dihalostilbenes. *Tetrahedron Lett.* **2010**, *51*, 5277−5280.

(4) Saito, M.; Osaka, I.; Miyazaki, E.; Takimiya, K.; Kuwabara, H.; Ikeda, M. One-Step Synthesis of [1]Benzothieno[3,2-b][1]-benzothiophene from *o*-Chlorobenzaldehyde. *Tetrahedron Lett.* **2011**, *52*, 285−288.

(5) (a) Amin, A.; Khassanov, A.; Reuter, K.; Meyer-Friedrichsen, T.; Halik, M. Low-Voltage Organic Field Effect Transistors with a 2-Tridecyl[1]benzothieno[3,2-b][1]benzothiophene Semiconductor Layer. *J. Am. Chem. Soc.* **2012**, *134*, 16548−16550. (b) Košata, B.; Kozmik, V.; Svoboda, J. Reactivity of [1]Benzothieno[3,2-b][1]-benzothiophene - Electrophilic and Metalation Reactions. *Collect. Czech. Chem. Commun.* **2002**, *67*, 645−664.

(6) Mori, T.; Nishimura, T.; Yamamoto, T.; Doi, I.; Miyazaki, E.; Osaka, I.; Takimiya, K. Consecutive Thiophene-Annulation Approach to p-Extended Thienoacene-Based Organic Semiconductors with [1]Benzothieno[3,2-b][1]benzothiophene (BTBT) Substructure. *J. Am. Chem. Soc.* **2013**, *135*, 13900−13913.

(7) Minami, S.; Hirano, K.; Satoh, T.; Miura, M. Synthesis of [1]Benzothieno[3,2-b]benzothiophene (BTBT) and its Higher Homologs through Palladium-Catalyzed Intramolecular Decarboxylative Arylation. *Tetrahedron Lett.* **2014**, *55*, 4175−4177.

(8) Vásquez-Céspedes, S.; Ferry, A.; Candish, L.; Glorius, F. Heterogeneously Catalyzed Direct C-H Thiolation of Heteroarenes. *Angew. Chem., Int. Ed.* **2015**, *54*, 5772−5776.

(9) Matsumura, M.; Muranaka, A.; Kurihara, R.; Kanai, M.; Yoshida, K.; Kakusawa, N.; Hashizume, D.; Uchiyama, M.; Yasuike, S. General Synthesis, Structure, and Optical Properties of Benzothiophene-Fused

DOI: 10.1021/acs.joc.9b00213
J. Org. Chem. XXXX, XXX, XXX−XXX

Benzoheteroles Containing Group 15 and 16 Elements. *Tetrahedron* **2016**, *72*, 8085−8090.
(10) (a) Wang, M.; Fan, Q.; Jiang, X. Transition-Metal-Free Diarylannulated Sulfide and Selenide Construction via Radical/Anion-Mediated Sulfur-Iodine and Selenium-Iodine Exchange. *Org. Lett.* **2016**, *18*, 5756−5759. (b) Wang, M.; Wei, J.; Fan, Q.; Jiang, X. Cu(II)-Catalyzed Sulfide Construction: Both Aryl Groups Utilization of Intermolecular and Intramolecular Diaryliodonium Salt. *Chem. Commun.* **2017**, *53*, 2918−2921.
(11) Yamamoto, T.; Takimiya, K. Facile Synthesis of Highly π-Extended Heteroarenes, Dinaphto[2,3-b:2′,3′-f]chalcogenopheno-[3,2-b]chalcogenophenes, and Their Application to Field-Effect Transistors. *J. Am. Chem. Soc.* **2007**, *129*, 2224−2225.
(12) Yamamoto, T.; Nishimura, T.; Mori, T.; Miyazaki, E.; Osaka, I.; Takimiya, K. Largely π-Extended Thienoacenes with Internal Thieno[3,2-b]thiophene Substructures: Synthesis, Characterization, and Organic Field-Effect Transistor Applications. *Org. Lett.* **2012**, *14*, 4914−4917.
(13) (a) Kitamura, T.; Takachi, T.; Miyaji, M.; Kawasato, H.; Kobayashi, S.; Taniguchi, H. Electrophilic Addition to *o*-ArY-Substituted Phenylalkynes. A Highly Selective Cyclization Controlled by Heteroatoms. *Tetrahedron Lett.* **1989**, *30*, 7445−7446. (b) Kitamura, T.; Takachi, T.; Miyaji, M.; Kawasato, H.; Taniguchi, H. Intramolecular Cyclization to 1-Phenyl-1-benzothiophenium Salts by Electrophilic Addition of *o*-(Phenylsulfanyl)phenylalkynes. *J. Chem. Soc., Perkin Trans. 1* **1994**, 1907−1911. (c) Larock, R. C.; Yue, D. Synthesis of Benzo[*b*]thiophenes by Electrophilic Cyclization. *Tetrahedron Lett.* **2001**, *42*, 6011−6013. (d) Yue, D.; Larock, R. C. Synthesis of 2,3-Disubstituted Benzo[*b*]thiophenes via Palladium-Catalyzed Coupling and Electrophilic Cyclization of Terminal Acetylenes. *J. Org. Chem.* **2002**, *67*, 1905−1909.
(14) (a) Aoki, K.; Ogata, Y. Reaction of Propylene with a Mixture of Iodine and Iodosobenzene or Phenyl Iodine Diacetate. *Bull. Chem. Soc. Jpn.* **1968**, *41*, 1476−1477. (b) Ogata, Y.; Aoki, K. Iodination of Aromatic Compounds with a Mixture of Iodine and Peracetic Acid. III. Autocatalysis and Relative Rates. *J. Am. Chem. Soc.* **1968**, *90*, 6187−6191.
(15) (a) Kitamura, T.; Kawasato, H.; Kobayashi, S.; Taniguchi, H. Exclusive Cyclization at Sulfur in Photolysis of β-[(o-Arylthio)-phenyl]vinyl Bromides. *Chem. Lett.* **1986**, *15*, 839−842. (b) Kitamura, T.; Kobayashi, S.; Taniguchi, H. Photolysis of β-(o-Methylthiophenyl)vinyl Bromides. A Versatile Synthesis of Benzo-[*b*]thiophenes. *Chem. Lett.* **1988**, *17*, 1637−1638.
(16) Yang, Y. S.; Yasuda, T.; Adachi, C. Organic Single-Crystal Transistors Based on π-Extended Heteroheptacene Microribbons. *Bull. Chem. Soc. Jpn.* **2012**, *85*, 1186−1191.
(17) Wang, C.; Nishida, J.-i.; Bryce, M. R.; Yamashita, Y. Synthesis, Characterization, and OFET and OLED Properties of π-Extended Ladder-Type Heteroacenes Based on Indolodibenzothiophene. *Bull. Chem. Soc. Jpn.* **2012**, *85*, 136−143.
(18) Hari, D. P.; Hering, T.; König, B. Visible Light Photocatalytic Synthesis of Benzothiophenes. *Org. Lett.* **2012**, *14*, 5334−5337.
(19) Kim, J. S.; Reibenspies, J. H.; Darensbourg, M. Y. Characteristics of Nickel(0), Nickel(I), and Nickel(II) in Phosphino Thioether Complexes: Molecular Structure and *S*-Dealkylation of $(Ph_2P(o\text{-}C_6H_4)SCH_3)_2Ni^0$. *J. Am. Chem. Soc.* **1996**, *118*, 4115−4123.
(20) Mehta, S.; Waldo, J. P.; Larock, R. C. Competition Studies in Alkyne Electrophilic Cyclization Reactions. *J. Org. Chem.* **2009**, *74*, 1141−1147.
(21) Kowalik, J.; Tolbert, L. M. Diphenylacetylene and the LICKOR Superbase: *oo*′-Dimetalation and Reaction with Electrophiles. A Convenient Synthesis of *oo*′-Disubstituted Diphenylacetylenes. *J. Org. Chem.* **2001**, *66*, 3229−3231.

DOI: 10.1021/acs.joc.9b00213
J. Org. Chem. XXXX, XXX, XXX−XXX