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[2+2+2] CYCLOADDITION OF SULFANYLBENZENE-TETHERED DIYNES WITH ALKYNES FOR THE SYNTHESIS OF MULTI-SUBSTITUTED DIBENZOTHIOPHENE DERIVATIVES

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Dedicated to Professor Isao Kuwajima on the occasion of his 77th birthday

Abstract – An intermolecular [2+2+2] cycloaddition of sulfanyl- and sulfonylbenzene-tethered 1,6-diynes with alkynes using rhodium catalysts gave dibenzothiophene derivatives in moderate to excellent yields. The consecutive reaction of tetraynes with an alkyne gave an axially chiral 1,1'-bi(dibenzothiophenyl) and its tetraoxide with up to excellent ee.

INTRODUCTION

The dibenzothiophene (DBT) skeleton is found in a lot of biologically active molecules, such as a potent inhibitor of DNA-dependent protein kinase[1] and a selective estrogen receptor antagonist.[2] In addition, DBT-containing derivatives have attracted much attention as organic electronics and materials in recent years, because they showed optoelectronic and redox properties, and electrochemical characteristics such as organic light-emitting diodes (OLED).[3]

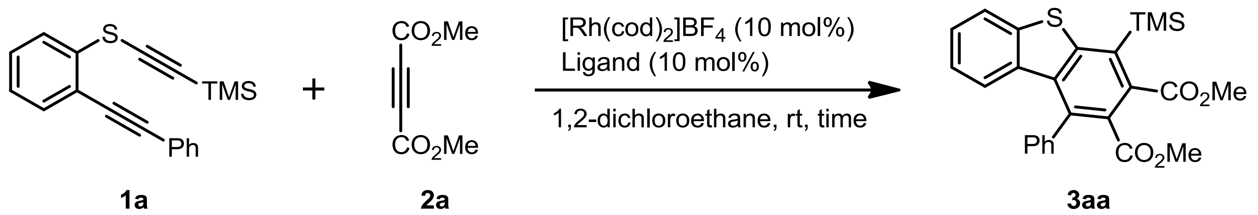
In spite of the wide applicability of DBT derivatives, there is some limitations in the synthesis of DBT, especially in catalytic synthetic approaches to multi-substituted DBT derivatives. There are many methods for the synthesis of DBT skeleton; intramolecular cyclization,[4] anionic cyclization,[5] radical cyclization,[6] photocyclization[7] and C-S bond formations[8] were successful examples. As for catalytic approaches, the protocols using cross-coupling,[9] C-H bond activation,[10] ring-closing metathesis[11] and C-S bond formations[12] were recently disclosed. Some of these reactions required harsh reaction conditions, such as high temperature, and/or basic or acidic condition, therefore, alternative efficient approaches, which can realize the milder reaction conditions, are strongly desired.

In contrast, transition-metal-catalyzed [2+2+2] cycloaddition is a reliable and atom-economical protocol for the construction of multicyclic six-membered ring systems.[13] It was already used for the syntheses of dibenzoheteroles, such as carbazoles,[14] dibenzofurans,[15] and dibenzosiloles.[16] However, to the best of our knowledge, it has never been used for the construction of DBT skeleton. We have comprehensively studied [2+2+2] cycloaddition of various substrates with alkyne motifs,[17] and considered that [2+2+2] cycloaddition of sulfanylbenzene-tethered 1,6-diynes with alkynes can be a new approach to the synthesis of multi-substituted DBT derivatives.

RESULTS AND DISCUSSION

We chose 1,6-diyne **1a** and dimethyl acetylenedicarboxylate (DMAD) (**2a**) as a model diyne and alkyne, and examined an intermolecular [2+2+2] cycloaddition using $[Rh(cod)_2]BF_4$ with several phosphine ligands. The desired reaction proceeded at room temperature, and tetra-substituted DBT **3aa** was obtained (Table 1). Triphenylphosphine gave a poor result, but alkylene-tethered diphosphine, 1,3-bis(diphenylphosphino)propane (DPPP) achieved moderate yield (Entries 1 and 2). We further examined diphosphines possessing a biaryl scaffold, and BIPHEP gave the best results (Entry 4).[18,19]

Table 1. Effect of ligands on the [2+2+2] cycloaddition of diyne **1a** with **2a**



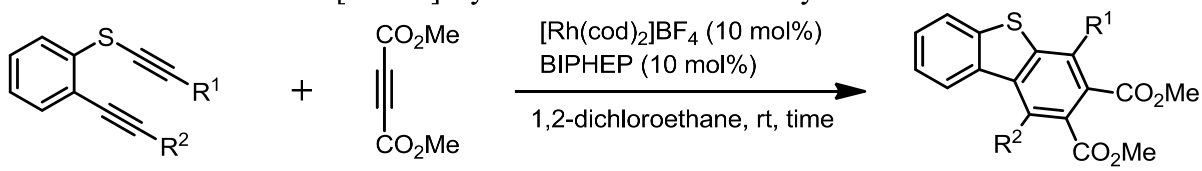
Entry [a]	Ligand	Time (h)	Yield (%)
1	$2PPh_3$	8	27
2	DPPP	8	61
3	*rac*-BINAP	1	84
4	BIPHEP	1	92

[a] Diyne/alkyne was 1/3.

Under the optimum conditions, various diynes were subjected to the intermolecular [2+2+2] cycloaddition (Table 2). The reaction of diyne **1b**, which has phenyl groups on its alkyne termini (R^1, R^2), proceeded to give cycloadduct **3ba** in moderate yield (Entry 1). The reaction of diynes **1c** and **1d**, which have an alkyl group and phenyl group on its alkyne termini, proceeded sluggishly, and a higher reaction temperature was needed (Entries 2 and 3). Diynes **1e** and **1f**, which have pentyl-substituted and unsubstituted alkyne terminus (R^1), respectively, were very reactive, and the slow addition of the diynes to a dichloroethane solution of DMAD over 30 min by syringe pump was needed (Entries 4 and 5). These yields of the cross-cycloadducts **3ea** and **3fa** were still low due to the formation of self-cycloadducts of diynes **1e** and **1f**. The reaction of diynes **1g** and **1h**, which have bulky trimethylsilyl group on its alkyne terminus (R^2), proceeded to give cycloadduct **3ga** and **3ha** in improved yields, due to the suppression of homo-cycloaddition of the diynes (Entries 6 and 7).[20] While the reactivity of diynes **1i** and **1j**, which have trimethylsilyl groups and *tert*-butyl groups, respectively, on both of alkyne termini was poor, no reaction proceeded (Entries 8 and 9). Diynes **1k** and **1l** with unsubstituted alkyne terminus(i) were too reactive, and self-cycloadducts were major products (Entries 10 and 11). On the other hand, diynes **1m** and **1n**, which have phenyl- and pentyl-substituted terminus (R^1), respectively, along with unsubstituted alkyne terminus, were good substrates (Entries 12 and 13). In particular, diyne **1n** realized the best yield of 94%.

Next, we examined the reaction of diyne **1a** with symmetrical or unsymmetrical alkynes **2b**-**2e** (Table 3). Unprotected diol **2b** could be used as a coupling partner and the corresponding DBT derivative **3ab** was obtained in good yield (Entry 1). Diarylacetyelene was less reactive and the poly-arylated DBT **3ac** was obtained, yet in low yield even at a higher temperature (Entry 2). The cycloaddition of unsymmetrical

Table 2. [2+2+2] Cycloaddition of various diynes **1** with **2a**



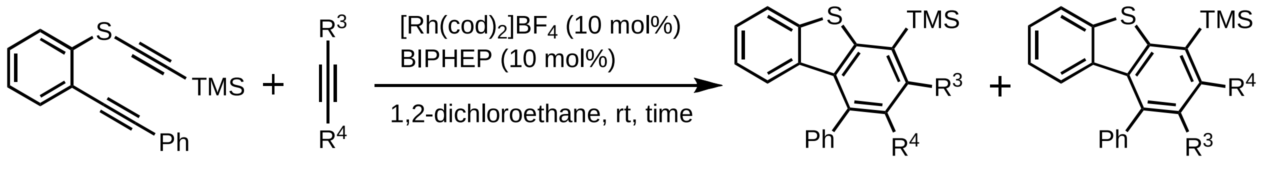
1 **2a** **3**

Entry [a]	**1** (R^1, R^2)	Time (h)	Yield (%)
1	**1b** (Ph, Ph)	1	52 (**3ba**)
2 [b]	**1c** (Me, Ph)	1	30 (**3ca**)
3 [b]	**1d** (*t*-Bu, Ph)	6	47 (**3da**)
4 [c]	**1e** (*n*-C_5H_{11}, Ph)	0.5	28 (**3ea**)
5 [c]	**1f** (H, Ph)	0.5	33 (**3fa**)
6 [c]	**1g** (*n*-C_5H_{11}, TMS)	0.5	67 (**3ga**)
7	**1h** (Ph, TMS)	1	89 (**3ha**)
8 [b]	**1i** (TMS, TMS)	3	NR [d]
9 [b]	**1j** (*t*-Bu, *t*-Bu)	3	NR [d]
10 [c]	**1k** (H, H)	0.5	38 (**3ka**)
11	**1l** (TMS, H)	1	24 (**3la**)
12	**1m** (Ph, H)	1	61 (**3ma**)
13 [c]	**1n** (*n*-C_5H_{11}, H)	0.5	94 (**3na**)

[a] Diyne/alkyne was 1/3. [b] The reactions was examined at 80 °C.
[c] Diyne was added to a 1,2-dichloroethane solution of DMAD over 30 min by using syringe pump.
[d] No Reaction.

alkynes also proceeded under the same reaction conditions. While the reaction of phenylacetylene (**2d**) gave a regioisomeric mixture of cycloadducts **3ad** and **4ad**, the reaction of methyl phenylpropiolate **2e** regioselectively proceeded to give **3ae** as a sole cycloadduct (Entries 3 and 4).

Table 3. Cycloaddition of diyne **1a** and various alkynes

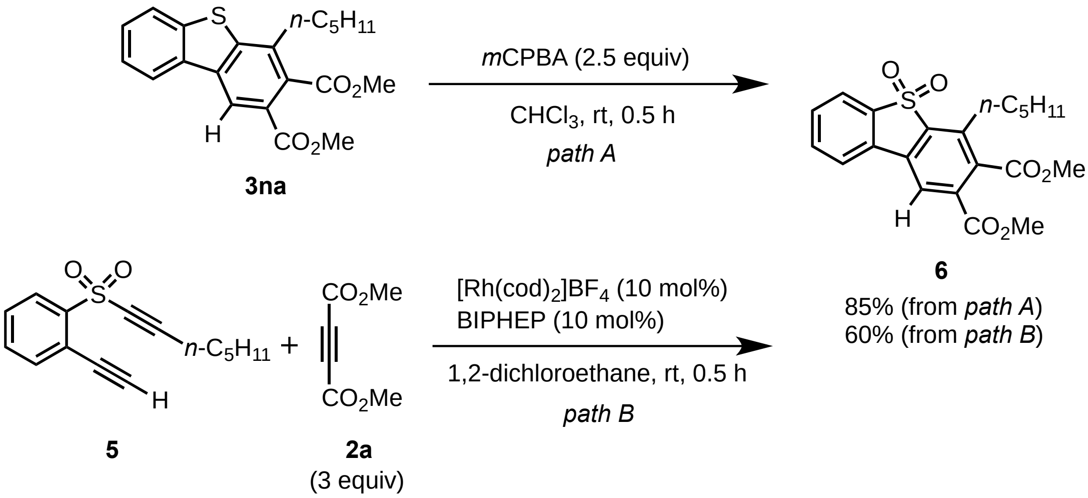


1a **2** **3** **4**

Entry[a]	**1** (R^3, R^4)	Time (h)	Yield (%)
1	**2b** (CH_2OH, CH_2OH)	1	75 (**3ab**)
2[b]	**2c** (C_6H_4(*p*-OMe), C_6H_4(*p*-OMe))	3	23 (**3ac**)
3	**2d** (H, Ph)	12	56 (**3ad**) /39 (**4ad**)
4	**2e** (Ph, CO_2Me)	1	80 (**3ae**)

[a] Diyne/alkyne was 1/3. [b] The reactions was examined at 80 °C.

We next focused on the synthesis of dibenzothiophene-5,5-dioxides (DBT-dioxides), because they have attracted attention as electronic materials.[21] For example, high binding affinities and selectivity to α 7-nicotinic acetylcholine receptors (α 7-nAChRs) was known.[22] Two methods were examined for the preparation of DBT-dioxide (Scheme 1). Oxidation of the obtained DBT **3na** readily proceeded using *m*CPBA at room temperature to give DBT-dioxide **6** (*path A*). As a more direct protocol, [2+2+2] cycloaddition of sulfonylbenzene-tethered diyne **5** with **2a** was examined. The reaction smoothly proceeded under the same conditions as sulfanylbenzene-tethered diyne **1n**, and DBT-dioxides **6** was obtained in moderate yield (*path B*).

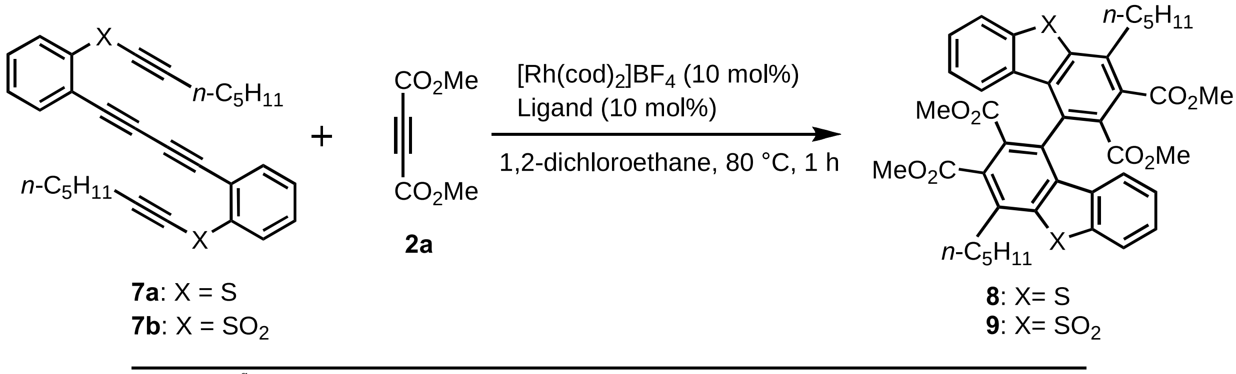


Scheme 1. Synthesis of dibenzothiophene-5,5-dioxide **6** by two methods

We further examined consecutive [2+2+2] cycloaddition using tetraynes **7** possessing a 1,3-diyne moiety and chose tetrayne **7a**, which has two sulfanylbenzene moieties, as a model substrate and submitted to the Rh-catalyzed reaction with **2a** (Table 4). When an achiral diphosphine ligand, 2,2'-bis(diphenylphosphino)-1,1'-biphenyl (BIPHEP) was used, doubly-cyclized product **8** was obtained, yet in low yield (Entry 1). The generation of axial chirality in **8** was ascertained by the HPLC analysis using a chiral column. We next screened several chiral diphosphine ligands (Entries 2-5). BINAP and its derivatives achieved good enantioselectivity, but the yield was miserable, because many unidentified by-products were formed. When Me-DUPHOS was used, the yield was significantly improved, but ee was low (Entry 5). In contrast, the reaction of sulfonylbenzene-tethered tetrayne **7b** using Rh-Me-DUPHOS catalyst realized excellent ee along with moderate yield (Entry 6). We ascertained the structural details of 1,1'-bi(dibenzothiophenyl)-5,5,5',5'-tetraoxide **9** by X-ray crystallographic analysis and its absolute configuration was determined to be *R* (Figure 1).

We measured the UV-vis spectra of the obtained DBT derivatives **3na** and **8**, and the DBT-dioxide derivatives **6** and **9** (Table 5). The λ_{max} of these compounds were observed at 294.5-330.5 nm. The DBT-dioxide derivatives were red-shifted compared with the DBT derivatives as expected (Entry 1 vs Entry 2 and Entry 3 vs Entry 4). In the case of DBT-dioxide derivatives, significant blue-shift of bi-DBT-dioxide was unexpectedly observed compared with mono-DBT-dioxide (Entry 2 vs Entry 4).

Table 4. Screening of chiral ligands in the enantioselective cycloaddition of tetraynes **7** with **2a**



Entry [a]	7	Ligand	Yield (%)	Ee (%)
1	**7a**	BIPHEP	19	-
2	**7a**	(*R*)-BINAP	5	78
3	**7a**	(*S*)-Tol-BINAP	7	73
4	**7a**	(*S*)-H_8-BINAP	16	82
5	**7a**	(*S,S*)-Me-DUPHOS	49	21
6 [b]	**7b**	(*S,S*)-Me-DUPHOS	65	97

[a] Tetrayne/alkyne was 1/6. [b] The reaction time was 8 h.

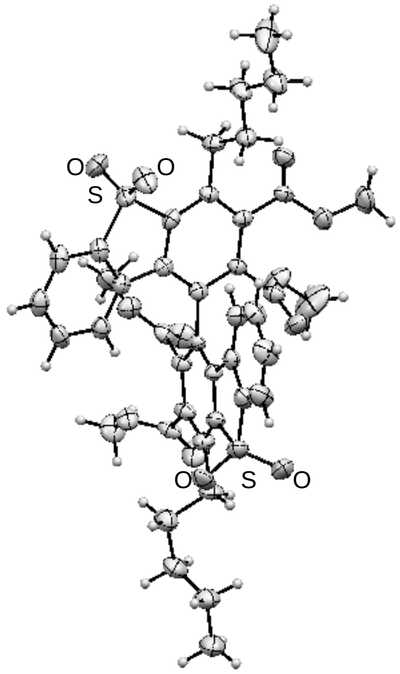
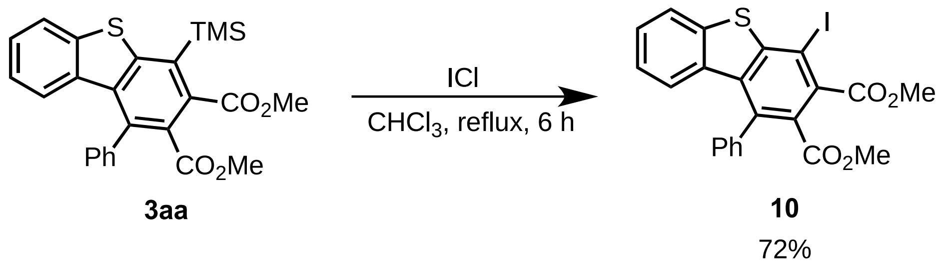


Figure 1. ORTEP diagram of cycloadduct **9**

Table 5. UV-vis data of **3na**, **6**, **8** and **9**

Entry	Compound	UV-vis λ_{max} (nm) / log ε
1	**3na**	294.5 / 3.84
2	**6**	330.5 / 3.57
3	**8**	297.5 / 4.03
4	**9**	304.0 / 4.07

In addition, we examined the synthetic transformation of cycloadduct **3aa** by iodine monochloride and obtained 4-iode-DBT **10** in good yield (Scheme 2).



Scheme 2. Synthetic transformation of cycloadduct **3aa**

In conclusion, we developed Rh-catalyzed [2+2+2] cycloaddition of sulfanylbenzene- and sulfonylbenzene-tethered 1,6-diynes with alkynes. The present reaction provides a new protocol for the synthesis of multi-substituted DBT derivatives. We will further synthesize various DBT derivatives and evaluate them as organic electronics and materials.

EXPERIMENTAL

General. All reactions were examined under an argon atmosphere in oven-dried glassware with a magnetic stirring bar. A hexane solution of *n*-butyllithium (1.58 M) was purchased from Kanto Chemical Co., Inc. Dehydrated dichloromethane and 1,2-dichloroethane were purchased from Wako Pure Chemical Industries Ltd. (Wako) and degassed by argon bubbling before use. Other reagents were purchased from Wako, Kanto, TCI, or Aldrich and were used without further purification. Flash column chromatography was performed with silica gel (Kanto Chemical Co., Inc. 60N). Preparative thin-layer chromatography (PTLC) was performed with silica gel-precoated glass plates (Merck 60 GF254) prepared in our laboratory. IR spectra were recorded with Horiba FT730 spectrophotometer. NMR spectra were measured with JEOL AL-400 (400 MHz), JEOL ECS400 (400 MHz), JEOL ECX500 (500 MHz), or JEOL Lambda 500 (500 MHz) using TMS as an internal standard and $CDCl_3$ was used as a solvent. High-resolution mass spectra (HRMS) were measured on a JEOL JMS-SX102A with FAB (Fast Atomic Bombardment) method or JMS-T100CS with ESI (Electro Spray Ionization) method. Optical rotations were measured with Jasco DIP-1000 polarimeter. 2,3-Bis(methoxycarbonyl)dibenzothiophene **(3ka)** was a known compound and its spectra was accorded with those in the literature.[23] Diynes **1** were prepared by Sonogashira coupling of the corresponding alkynes and (hept-1-ynyl)(2-iodophenyl)sulfane or (2-iodophenyl)(trimethylsilylethynyl)sulfane, which was prepared by the literature protocols.[24,25] Tetrayne **7a** was prepared by CuCl-TMEDA-mediated oxidative coupling[26] of (2-ethynylphenyl)(hept-1-ynyl)sulfane (**1n**). The following oxidation using *m*CPBA[27] gave tetrayne tetraoxide **7b**.

[2-(Phenylethynyl)phenyl](trimethylsilylethynyl)sulfane (1a): a pale brown solid; mp 43 °C; IR (CH_2Cl_2) 2892, 2097, 879, 843, 753 cm^{-1}; ^{1}H NMR δ 0.27 (s, 9H), 7.20 (ddd, *J* = 1.1, 7.6, 7.6 Hz, 1H), 7.34-7.39 (m, 4H), 7.47 (dd, *J* = 1.3, 7.6 Hz, 1H), 7.55-7.57 (m, 2H), 7.73 (dd, *J* = 0.6, 8.0 Hz, 1H); ^{13}C NMR δ -0.1, 85.4, 89.8, 96.8, 107.8, 120.3, 122.7, 125.4, 126.0, 128.4, 128.7, 129.2, 131.6, 132.0, 135.9; HRMS (ESI positive) *m/z* calcd for $C_{19}H_{19}SSi$ ($[M+H]^+$): 307.0971. Found: 307.0971.

(Phenylethynyl)[2-(phenylethynyl)phenyl]sulfane (1b): a brown oil; IR (CH_2Cl_2) 2850, 2170, 752, 688 cm^{-1}; ^{1}H NMR δ 7.20 (ddd, *J* = 1.1, 7.5, 7.5 Hz, 1H), 7.34-7.39 (m, 7H), 7.49 (dd, *J* = 1.2, 7.7 Hz, 1H), 7.53-7.55 (m, 2H), 7.58-7.60 (m, 2H), 7.77 (dd, *J* = 0.6, 8.1 Hz, 1H); ^{13}C NMR δ 70.5, 85.5, 96.9, 99.3, 120.3, 122.7, 122.8, 125.5, 125.9, 128.4, 128.4, 128.7, 128.8, 129.2, 131.7, 131.9, 132.1, 136.5; HRMS

(ESI positive) *m/z* calcd for $C_{22}H_{15}S$ ($[M+H]^+$): 311.0889. Found: 311.0889.

[2-(Phenylethynyl)phenyl](prop-1-ynyl)sulfane (1c):. a brown oil; IR (CH_2Cl_2) 2913, 1057, 752, 689 cm^{-1}; ^{1}H NMR δ 2.14 (s, 3H), 7.17 (ddd, *J* = 1.1, 7.5, 7.5 Hz, 1H), 7.32-7.36 (m, 4H), 7.45 (dd, *J* = 1.3, 7.7 Hz, 1H), 7.56-7.57 (m, 2H), 7.70 (d, *J* = 8.1 Hz, 1H); ^{13}C NMR δ 5.3, 63.5, 85.6, 96.6, 96.8, 119.9, 122.8, 125.2, 125.5, 128.4, 128.6, 129.0, 131.6, 131.9, 137.3; HRMS (ESI positive) *m/z* calcd for $C_{17}H_{13}S$ ($[M+H]^+$): 249.0732. Found: 249.0773.

(3,3-Dimethylbut-1-ynyl)[2-(phenylethynyl)phenyl]sulfane (1d): a pale yellow oil; IR (CH_2Cl_2) 2865, 2215, 1058, 754, 689 cm^{-1}; ^{1}H NMR δ 1.35 (s, 9H), 7.16 (ddd, *J* = 1.2, 7.6, 7.6 Hz, 1H), 7.34-7.37 (m, 4H), 7.45 (dd, *J* = 1.3, 7.7 Hz, 1H), 7.55-7.57 (m, 2H), 7.66 (dd, *J* = 0.9, 8.1 Hz, 1H); ^{13}C NMR δ 29.1, 30.9, 65.2, 85.6, 96.6, 109.2, 119.8, 122.8, 124.8, 125.4, 128.3, 128.6, 129.0, 131.6, 131.8, 137.5; HRMS (ESI positive) *m/z* calcd for $C_{20}H_{19}S$ ($[M+H]^+$): 291.1202. Found: 291.1202.

(Hept-1-ynyl)[2-(phenylethynyl)phenyl]sulfane (1e): a pale brown oil; IR (CH_2Cl_2) 2859, 2215, 1491, 753, 689 cm^{-1}; ^{1}H NMR δ 0.92 (t, *J* = 7.3 Hz, 3H), 1.32-1.47 (m, 4H), 1.63 (tt, *J* = 7.1, 7.1 Hz, 2H), 2.03 (t, *J* = 7.1 Hz, 2H), 7.16 (ddd, *J* = 1.1, 7.5, 7.5 Hz, 1H), 7.33-7.37 (m, 4H), 7.45 (dd, *J* = 1.1, 7.7 Hz, 1H), 7.56-7.57 (m, 2H), 7.70 (dd, *J* = 0.7, 8.1 Hz, 1H); ^{13}C NMR δ 14.0, 20.3, 22.2, 28.3, 31.1, 64.2, 85.6, 96.6, 101.5, 119.8, 122.8, 125.1, 125.5, 128.4, 128.6, 129.0, 131.6, 131.9, 137.5; HRMS (ESI positive) *m/z* calcd for $C_{21}H_{21}S$ ($[M+H]^+$): 305.1358. Found: 305.1358.

Ethynyl[2-(phenylethynyl)phenyl]sulfane (1f): a pale brown oil; IR (CH_2Cl_2) 3287, 3057, 2219, 753, 688 cm^{-1}; ^{1}H NMR δ 3.35 (s, 1H), 7.20 (ddd, *J* = 1.0, 7.6, 7.6 Hz, 1H), 7.35-7.38 (m, 4H), 7.48 (dd, *J* = 1.1, 7.6 Hz, 1H), 7.56-7.57 (m, 2H), 7.73 (d, *J* = 8.1 Hz, 1H); ^{13}C NMR δ 70.5, 85.3, 88.5, 96.9, 120.5, 122.6, 125.6, 126.1, 128.4, 128.8, 129.2, 131.6, 132.0, 135.0; HRMS (ESI positive) *m/z* calcd for $C_{16}H_{11}S$ ($[M+H]^+$): 235.0576. Found: 235.0578.

(Hept-1-ynyl)[2-(trimethylsilylethynyl)phenyl]sulfane (1g): pale yellow oil; IR (CH_2Cl_2) 2860, 2157, 1250, 864, 753 cm^{-1}; ^{1}H NMR δ 0.27 (s, 9H), 0.91 (t, *J* = 7.3 Hz, 3H), 1.33-1.45 (m, 4H), 1.62 (tt, *J* = 7.2, 7.2 Hz, 2H), 2.47 (t, *J* = 7.1 Hz, 2H), 7.10 (ddd, *J* = 1.1, 7.5, 7.5 Hz, 1H), 7.32 (ddd, *J* = 1.3, 7.6, 7.6 Hz, 1H), 7.38 (dd, *J* = 1.2, 7.6 Hz, 1H), 7.66 (dd, *J* = 0.7, 8.1 Hz, 1H); ^{13}C NMR δ -0.2, 14.0, 20.3, 22.2, 28.3, 31.1, 64.3, 100.7, 101.6, 102.5, 119.6, 124.8, 125.2, 129.2, 132.2, 137.9; HRMS (ESI positive) *m/z* calcd for $C_{18}H_{25}SSi$ ($[M+H]^+$): 301.1441. Found: 301.1426.

Phenylethynyl[2-(trimethylsilylethynyl)phenyl]sulfane (1h): a yellow solid; mp 67 °C; IR (CH_2Cl_2) 2854, 2157, 862, 844 cm^{-1}; ^{1}H NMR δ 0.29 (s, 9H), 7.15 (ddd, *J* = 0.9, 7.5, 7.5 Hz, 1H), 7.33-7.36 (m, 4H), 7.41 (dd, *J* = 1.1, 7.6 Hz, 1H), 7.52-7.54 (m, 2H), 7.73 (d, *J* = 8.1 Hz, 1H); ^{13}C NMR δ 0.9, 76.1, 100.4, 101.7, 103.8, 121.0, 123.9, 126.3, 126.8, 129.5, 129.8, 130.4, 132.8, 133.4, 138.0; HRMS (ESI positive) *m/z* calcd for $C_{19}H_{18}NaSSi$ ($[M+Na]^+$): 329.0791. Found: 329.0793.

(Trimethylsilylethynyl)[2-(trimethylsilylethynyl)phenyl]sulfane (1i): a pale brown oil; IR (CH_2Cl_2) 2898, 2098, 863, 842, 756 cm^{-1}; ^1H NMR δ 0.32 (s, 9H), 0.33 (s, 9H), 7.19 (ddd, J = 1.0, 7.5, 7.5 Hz, 1H), 7.41 (ddd, J = 1.3, 7.5, 7.5 Hz, 1H), 7.45 (dd, J = 1.0, 7.6 Hz, 1H), 7.71 (d, J = 8.1 Hz, 1H); ^{13}C NMR δ -0.2, -0.1, 89.3, 100.6, 102.7, 107.9, 120.0, 125.1, 125.7, 129.3, 132.2, 136.3; HRMS (ESI positive) *m/z* calcd for $C_{16}H_{23}SSi_2$ ($[M+H]^+$): 303.1054. Found: 303.1054.

(3,3-Dimethylbut-1-ynyl)[2-(3,3-dimethylbut-1-ynyl)phenyl]sulfane (1j): a yellow oil; IR (CH_2Cl_2) 2863, 2240, 1033, 752 cm^{-1}; ^1H NMR δ 1.34 (s, 18H), 7.09 (ddd, J = 1.1, 7.5, 7.5 Hz, 1H), 7.27-7.30 (m, 2H), 7.59 (d, J = 8.1 Hz, 1H); ^{13}C NMR δ 28.3, 29.1, 30.9, 30.9, 63.5, 75.5, 106.4, 109.0, 120.5, 124.4, 125.2, 128.2, 131.5, 137.2; HRMS (ESI positive) *m/z* calcd for $C_{18}H_{23}S$ ($[M+H]^+$): 271.1515. Found: 271.1515.

Ethynyl(2-ethynylphenyl)sulfane (1k): a brown oil; IR (CH_2Cl_2) 3288, 3059, 754 cm^{-1}; ^1H NMR δ 3.35 (s, 1H), 3.48 (s, 1H), 7.18 (ddd, J = 1.1, 7.6, 7.6 Hz, 1H), 7.38 (ddd, J = 1.4, 7.7, 7.7 Hz, 1H), 7.45 (dd, J = 1.3, 7.7 Hz, 1H), 7.71 (dd, J = 0.8, 8.1 Hz, 1H); ^{13}C NMR δ 70.2, 79.5, 84.8, 88.7, 119.3, 125.8, 126.1, 129.8, 133.0, 135.4; HRMS (ESI positive) *m/z* calcd for $C_{10}H_7S$ ($[M+H]^+$): 159.0263. Found: 159.0264.

(2-Ethynylphenyl)(trimethylsilylethynyl)sulfane (1l): a brown oil; IR (CH_2Cl_2) 3291, 2898, 2097, 862, 754 cm^{-1}; ^1H NMR δ 0.27 (s, 9H), 3.47 (s, 1H), 7.17 (ddd, J = 1.1, 7.6, 7.6 Hz, 1H), 7.39 (ddd, J = 1.4, 7.6, 7.6 Hz, 1H), 7.45 (dd, J = 1.2, 7.8 Hz, 1H), 7.67 (dd, J = 0.6, 8.1 Hz, 1H); ^{13}C NMR δ 0.9, 80.6, 85.6, 90.4, 109.1, 120.1, 126.5, 126.9, 130.8, 134.0, 137.3; HRMS (ESI positive) *m/z* calcd for $C_{13}H_{15}SSi$ ($[M+H]^+$): 231.0658. Found: 231.0656.

(2-Ethynylphenyl)(phenylethynyl)sulfane (1m): a pale brown oil; IR (CH_2Cl_2) 3287, 3020, 2170, 752, 688 cm^{-1}; ^1H NMR δ 3.51 (s, 1H), 7.18 (ddd, J = 1.1, 7.6, 7.6 Hz, 1H), 7.33-7.37 (m, 4H), 7.39 (ddd, J = 1.5, 7.6, 7.6 Hz, 1H), 7.52-7.55 (m, 2H), 7.76 (dd, J = 0.7, 8.1 Hz, 1H); ^{13}C NMR δ 75.6, 80.7, 85.7, 100.5, 120.1, 123.8, 126.6, 126.9, 129.5, 129.9, 130.8, 132.9, 134.1, 137.9; HRMS (ESI positive) *m/z* calcd for $C_{16}H_{10}S$ ($[M]^+$): 234.0498. Found: 234.0498.

(2-Ethynylphenyl)(hept-1-ynyl)sulfane (1n): pale brown oil; IR (CH_2Cl_2) 3290, 2859, 1461, 753 cm^{-1}; ^1H NMR δ 0.92 (t, J = 7.2 Hz, 3H), 1.31-1.46 (m, 4H), 1.62 (tt, J = 7.1, 7.1 Hz, 2H), 2.47 (t, J = 7.1 Hz, 2H), 3.46 (s, 1H), 7.14 (ddd, J = 1.1, 7.6, 7.6 Hz, 1H), 7.36 (ddd, J = 1.4, 7.7, 7.7 Hz, 1H), 7.42 (dd, J = 1.2, 7.6 Hz, 1H), 7.68 (dd, J = 0.8, 8.1 Hz, 1H); ^{13}C NMR δ 13.9, 20.3, 22.2, 28.3, 31.1, 63.4, 79.7, 84.4, 101.8, 118.6, 125.2, 125.4, 129.5, 132.8, 137.8; HRMS (ESI positive) *m/z* calcd for $C_{15}H_{17}S$ ($[M+H]^+$): 229.1046. Found: 229.1045.

(2-Ethynylphenyl)(hept-1-ynyl)sulfone (5): a brown oil; IR (CH_2Cl_2) 3267, 2200, 1163, 1126, 792 cm^{-1}; ^1H NMR δ 0.87 (t, J = 7.2 Hz, 3H), 1.25-1.38 (m, 4H), 1.55-1.61 (m, 2H), 2.40 (t, J = 7.1 Hz, 2H), 3.66 (s, 1H), 7.54 (ddd, J = 1.3, 7.8, 7.8 Hz, 1H), 7.61 (ddd, J = 1.3, 7.8, 7.8 Hz, 1H), 7.72 (dd, J = 1.2, 7.6 Hz, 1H), 8.10 (dd, *J* = 1.1, 7.9 Hz, 1H); ^{13}C NMR δ 14.8, 20.0, 23.0, 27.7, 31.9, 78.2, 79.9, 88.3, 98.7, 122.3, 129.2, 130.0, 134.3, 136.6, 143.7; HRMS (ESI positive) *m/z* calcd for $C_{15}H_{16}NaO_2S$ ($[M+Na]^+$): 283.0763. Found: 283.0762.

1,4-Bis[2-(hept-1-ynylsulfanyl)phenyl]buta-1,3-diyne (7a): a brown solid; mp 35 °C; IR (CH_2Cl_2) 2858, 2359, 1434, 752 cm^{-1}; ^{1}H NMR δ 0.92 (t, *J* = 7.4 Hz, 6H), 1.32-1.46 (m, 8H), 1.62 (tt, *J* = 7.3, 7.3 Hz, 4H), 2.48 (t, *J* = 7.0 Hz, 4H), 7.15 (ddd, *J* = 1.0, 7.4, 7.4 Hz, 2H), 7.38 (ddd, *J* = 1.1, 7.7, 7.7 Hz, 2H), 7.47 (dd, *J* = 1.3, 7.8 Hz, 2H), 7.68 (d, *J* = 8.2 Hz, 2H); ^{13}C NMR δ 13.9, 20.3, 22.1, 28.2, 31.0, 63.6, 79.6, 80.3, 101.9, 118.2, 125.3, 125.5, 129.9, 133.3, 139.1; HRMS (ESI positive) *m/z* calcd for $C_{30}H_{30}NaS_2$ ($[M+Na]^+$): 477.1681. Found: 477.1682.

1,4-Bis[2-(hept-1-ynylsulfonyl)phenyl]buta-1,3-diyne (7b): a brown solid; mp 115 °C; IR (CH_2Cl_2) 2198, 1331, 1160, 766 cm^{-1}; ^{1}H NMR δ 0.83 (t, *J* = 7.3 Hz, 6H), 1.24-1.38 (m, 8H), 1.64 (tt, *J* = 7.1, 7.1 Hz, 4H), 2.52 (t, *J* = 7.2 Hz, 4H), 7.57 (ddd, *J* = 1.3, 7.8, 7.8 Hz, 2H), 7.64 (ddd, *J* = 1.3, 7.6, 7.6 Hz, 2H), 7.76 (dd, *J* = 1.0, 7.7 Hz, 2H), 8.12 (dd, *J* = 1.0, 7.9 Hz, 2H); ^{13}C NMR δ 14.8, 20.0, 23.0, 27.8, 32.0, 77.9, 80.3, 83.8, 99.9, 121.7, 129.3, 130.5, 134.3, 136.7, 144.5; HRMS (ESI positive) *m/z* calcd for $C_{30}H_{30}NaO_4S_2$ ($[M+Na]^+$): 541.1478. Found: 541.1478.

Typical Procedure for the Rh-catalyzed cycloaddition: $[Rh(cod)_2]BF_4$ (2.0 mg, 0.005 mmol) and BIPHEP (2.6 mg, 0.005 mmol) were placed in Schlenk tube, which was then evacuated and backfilled with argon (3 ×). To the reaction vessel was added CH_2Cl_2 (1.0 mL). Then it was filled with H_2, and the mixture was stirred at r.t. for 30 min under H_2. After removal of the solvent and H_2 under reduced pressure, the reaction vessel was filled with argon. 1,2-Dichloroethane (0.2 mL) was added to the flask and the mixture was stirred to give a reddish solution. Then, a 1,2-dichloroethane solution (0.3 mL) of diyne (0.05 mmol) and DMAD (21.3 mg, 0.15 mmol) was added and the mixture was stirred at room temperature for 1 h. The volatiles were removed under reduced pressure, and the crude products were purified by PTLC.

2,3-Bis(methoxycarbonyl)-1-phenyl-4-(trimethylsilyl)dibenzothiophene (3aa): a brown solid; mp 135 °C; IR (CH_2Cl_2) 2849, 1734, 885, 841, 701 cm^{-1}; ^{1}H NMR δ 0.56 (s, 9H), 3.47 (s, 3H), 3.88 (s, 3H), 6.67 (d, *J* =8.4 Hz, 1H), 7.02 (ddd, *J* =1.0, 8.3, 8.3 Hz, 1H), 7.33-7.37 (m, 3H), 7.50-7.51 (m, 3H), 7.81 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR δ 0.8, 52.0, 52.6, 121.9, 124.0, 125.4, 126.9, 128.3, 128.7, 129.0, 129.9, 132.2, 133.5, 134.3, 135.4, 137.3, 137.8, 140.1, 148.0, 168.9, 169.8; HRMS (ESI positive) *m/z* calcd for $C_{25}H_{24}NaO_4SSi$ ($[M+Na]^+$): 471.1057. Found: 471.1055.

2,3-Bis(methoxycarbonyl)-1,4-diphenyldibenzothiophene (3ba): a yellow solid; mp 178 °C; IR (CH_2Cl_2) 2849, 1739, 744, 701 cm^{-1}; ^{1}H NMR δ 3.52 (s, 3H), 3.56 (s, 3H), 6.72 (d, 8.4 Hz, 1H), 7.05 (ddd, *J* =1.1, 7.8, 7.8 Hz, 1H), 7.33 (ddd, *J* =1.1, 7.3, 7.3 Hz, 1H) 7.42-7.54 (m, 10H), 7.72 (d, *J* = 7.9 Hz, 1H);

^{13}C NMR δ 52.2, 52.3, 122.5, 124.3, 125.6, 127.1, 128.4, 128.5, 128.6, 128.6, 128.7, 128.7, 129.3, 130.6, 134.7, 135.3, 135.4, 136.4, 137.6, 138.4, 141.2, 143.2, 168.1, 168.4; HRMS (ESI positive) *m/z* calcd for $C_{28}H_{20}NaO_4S$ ($[M+Na]^+$): 475.0975. Found: 475.0974.

2,3-Bis(methoxycarbonyl)-4-methyl-1-phenyldibenzothiophene (3ca): a yellow solid; mp 150 °C; IR (CH_2Cl_2) 2850, 1732, 1216, 742, 701 cm^{-1}; ^{1}H NMR δ 2.74 (s, 3H), 3.50 (s, 3H), 3.93 (s, 3H), 6.68 (d, *J* = 8.3 Hz, 1H), 7.06 (ddd, *J* =1.1, 7.8, 7.8 Hz, 1H), 7.35-7.39 (m, 3H), 7.50-7.52 (m, 3H), 7.85 (d, *J* = 7.9 Hz, 1H); ^{13}C NMR δ 19.9, 53.1, 53.7, 123.7, 125.4, 126.6, 128.0, 129.0, 129.3, 129.7, 130.4, 131.6, 131.9, 135.4, 136.2, 136.8, 138.8, 141.3, 143.9, 169.3, 169.7; HRMS (ESI positive) *m/z* calcd for $C_{23}H_{18}NaO_4SSi$ ($[M+Na]^+$): 413.0818. Found: 413.0818.

4-(1,1-Dimethylethyl)-2,3-bis(methoxycarbonyl)-1-phenyldibenzothiophene (3da): a yellow solid; mp 170 °C; IR (CH_2Cl_2) 2951, 1734, 1216, 750, 708 cm^{-1}; ^{1}H NMR δ 1.30 (s, 9H), 3.91 (s, 3H), 4.04 (s, 3H), 5.74 (d, *J* = 8.5 Hz, 1H), 6.90 (ddd, *J* =1.2, 7.8, 7.8 Hz, 1H), 7.28 (ddd, *J* =1.1, 7.6, 7.6 Hz, 1H), 7.35-7.36 (m, 2H), 7.50-7.56 (m, 3H), 7.74 (d, *J* = 7.9 Hz, 1H); ^{13}C NMR δ 35.1, 40.1, 53.7, 53.9, 123.1, 124.8, 125.8, 127.0, 127.6, 129.4, 129.8, 131.8, 134.2, 136.4, 138.0, 138.8, 142.0, 142.7, 143.4, 144.5, 168.8, 172.1; HRMS (ESI positive) *m/z* calcd for $C_{26}H_{24}NaO_4SSi$ ($[M+Na]^+$): 455.1288. Found: 455.1285.

2,3-Bis(methoxycarbonyl)-4-pentyl-1-phenyldibenzothiophene (3ea): a yellow oil; IR (CH_2Cl_2) 2853, 1101, 741, 701 cm^{-1}; ^{1}H NMR δ 0.94 (t, *J* = 7.1 Hz, 3H), 1.39-1.50 (m, 4H), 1.79-1.86 (m, 2H), 2.89 (t, *J* = 8.1 Hz, 2H), 3.49 (s, 3H), 3.91 (s, 3H), 6.67 (d, *J* = 8.4 Hz, 1H), 7.04 (ddd, *J* =1.0, 8.3, 8.3 Hz, 1H), 7.35-7.38 (m, 3H), 7.50-7.51 (m, 3H), 7.83 (d, *J* = 7.9 Hz, 1H); ^{13}C NMR δ 13.9, 22.3, 29.2, 32.1, 33.5, 52.0, 52.5, 122.5, 124.2, 125.4, 126.9, 127.7, 128.2, 128.5, 129.3, 130.6, 134.5, 135.2, 135.6, 135.7, 137.8, 140.1, 142.4, 168.3, 168.6; HRMS (ESI positive) *m/z* calcd for $C_{27}H_{26}NaO_4S$ ($[M+Na]^+$): 469.1444. Found: 469.1443.

2,3-Bis(methoxycarbonyl)-1-phenyldibenzothiophene (3fa): a brown solid; mp 175 °C; IR (CH_2Cl_2) 2851, 1726, 770, 701 cm^{-1}; ^{1}H NMR δ 3.57 (s, 3H), 3.95 (s, 3H), 6.60 (d, *J* = 8.3 Hz, 1H), 7.70 (ddd, *J* =0.9, 7.7, 7.7 Hz, 1H), 7.37-7.40 (m, 3H), 7.51-7.53 (m, 3H), 7.83 (d, *J* = 8.0 Hz, 1H), 8.57 (s, 1H); ^{13}C NMR δ 52.0, 52.6, 122.6, 124.1, 124.3, 124.6, 125.6, 127.4, 128.5, 128.6, 129.4, 132.5, 134.6, 136.5, 136.7, 136.8, 140.1, 141.3, 165.7, 168.8; HRMS (ESI positive) *m/z* calcd for $C_{22}H_{16}NaO_4S$ ($[M+Na]^+$): 399.0662. Found: 399.0660.

2,3-Bis(methoxycarbonyl)-4-pentyl-1-(trimethylsilyl)dibenzothiophene (3ga): a yellow oil; IR (CH_2Cl_2) 2859, 1726, 1436, 842, 763 cm^{-1}; ^{1}H NMR δ 0.46 (s, 9H), 0.92 (t, *J* = 7.2 Hz, 3H), 1.36-1.47 (m, 4H), 1.72-1.79 (m, 2H), 2.94 (t, *J* = 8.2 Hz, 2H), 3.89 (s, 3H), 3.91 (s, 3H), 7.41 (ddd, *J* =1.1, 7.1, 7.1 Hz, 1H), 7.45 (ddd, *J* =1.1, 7.2, 7.2 Hz, 1H), 7.84 (d, *J* = 7.5 Hz, 1H), 8.32 (d, *J* = 7.6 Hz, 1H); ^{13}C NMR δ

2.2, 14.0, 22.3, 29.1, 32.1, 33.6, 52.5, 52.5, 122.7, 123.3, 127.0, 127.3, 129.3, 134.8, 135.8, 136.5, 136.6, 140.0, 142.3, 142.4, 169.4, 170.0; HRMS (ESI positive) *m/z* calcd for $C_{24}H_{30}NaO_4SSi$ ($[M+Na]^+$): 465.1526. Found: 465.1527.

2,3-Bis(methoxycarbonyl)-4-phenyl-1-(trimethylsilyl)dibenzothiophene (3ha): a white solid; mp 171 °C; IR (CH_2Cl_2) 2899, 1730, 882, 850, 847 cm^{-1}; ^1H NMR δ 0.52 (s, 9H), 3.58 (s, 3H), 3.91 (s, 3H), 7.43-7.50 (m, 7H), 7.75-7.77 (m, 1H), 8.36-8.38 (m, 1H); ^{13}C NMR δ 2.1, 52.3, 52.6, 122.6, 123.4, 127.1, 127.4, 128.6, 128.6, 128.7, 129.7, 135.7, 136.2, 136.3, 136.4, 138.0, 141.1, 142.3, 143.2, 169.0, 169.8; HRMS (ESI positive) *m/z* calcd for $C_{25}H_{24}NaO_4SSi$ ($[M+Na]^+$): 471.1057. Found: 471.1056.

2,3-Bis(methoxycarbonyl)-4-(trimethylsilyl)dibenzothiophene (3la): a brown oil; IR (CH_2Cl_2) 2850, 1727, 861, 843 cm^{-1}; ^1H NMR δ 0.53 (s, 9H), 3.96 (s, 3H), 3.96 (s, 3H), 7.49-7.54 (m, 2H), 7.88 (dd, J = 1.7, 7.7 Hz, 1H), 8.23 (dd, J = 1.7, 5.8 Hz, 1H), 8.78 (s, 1H); ^{13}C NMR δ 0.0, 52.1, 52.1, 121.4, 121.8, 123.7, 123.8, 124.4, 127.2, 131.6, 133.6, 134.7, 138.2, 139.3, 149.7, 166.2, 170.0; HRMS (ESI positive) *m/z* calcd for $C_{19}H_{20}NaO_4SSi$ ($[M+Na]^+$): 395.0744. Found: 395.0745.

2,3-Bis(methoxycarbonyl)-4-phenyldibenzothiophene (3ma): a yellow solid; mp 128 °C; IR (CH_2Cl_2) 2851, 1727, 741, 701 cm^{-1}; ^1H NMR δ 3.66 (s, 3H), 3.99 (s, 3H), 7.46-7.54 (m, 7H), 7.80 (dd, J = 2.6, 8.3 Hz, 1H), 8.27 (dd, J = 1.9, 6.1 Hz, 1H), 8.80 (s, 1H); ^{13}C NMR δ 52.4, 52.7, 122.7, 122.5, 122.8, 124.8, 125.1, 127.8, 128.7, 128.8, 128.9, 132.4, 135.1, 135.2, 135.8, 137.2, 140.6, 145.5, 166.4, 168.9; HRMS (ESI positive) *m/z* calcd for $C_{22}H_{16}NaO_4S$ ($[M+Na]^+$): 399.0662. Found: 399.0662.

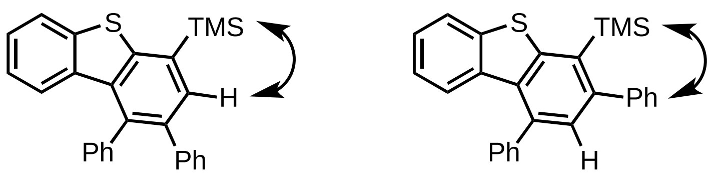
2,3-Bis(methoxycarbonyl)-4-pentyldibenzothiophene (3na): a yellow oil; IR (CH_2Cl_2) 2860, 1725, 1110, 741 cm^{-1}; ^1H NMR δ 0.92 (t, J = 7.1 Hz, 3H), 1.36-1.45 (m, 4H), 1.74-1.80 (m, 2H), 2.89 (t, J = 8.3 Hz, 2H), 3.97 (s, 3H), 3.99 (s, 3H), 7.50-7.54 (m, 2H), 7.88-7.90 (m, 1H), 8.21-8.23 (m, 1H), 8.66 (s, 1H); ^{13}C NMR δ 13.9, 22.2, 28.8, 32.0, 33.3, 52.5, 52.5, 121.3, 122.2, 122.8, 124.7, 124.9, 127.6, 131.9, 134.9, 135.2, 135.7, 139.7, 144.4, 166.4, 169.6; HRMS (ESI positive) *m/z* calcd for $C_{21}H_{22}NaO_4S$ ($[M+Na]^+$): 393.1131. Found: 393.1131.

2,3-Bis(hydroxymethyl)-1-phenyl-4-(trimethylsilyl)dibenzothiophene (3ab): a white solid; mp 181 °C; IR (CH_2Cl_2) 3341, 2853, 840, 736, 703 cm^{-1}; ^1H NMR δ 0.67 (s, 9H), 2.96 (brs, 1H), 3.44 (brs, 1H), 4.65 (s, 2H), 5.08 (s, 2H), 6.39 (d, J = 8.3 Hz, 1H), 6.96 (ddd, J =1.1, 7.8, 7.8 Hz, 1H), 7.29 (ddd, J =1.1, 7.5, 7.5 Hz, 1H), 7.32-7.34 (m, 2H), 7.55-7.56 (m, 3H), 7.78 (d, J = 7.7 Hz, 1H); ^{13}C NMR δ 3.1, 60.0, 62.8, 121.8, 123.6, 124.8, 125.9, 128.0, 129.1, 129.2, 132.8, 133.8, 134.8, 134.8, 139.4, 139.7, 140.6, 144.2, 146.4; HRMS (ESI positive) *m/z* calcd for $C_{23}H_{24}NaO_2SSi$ ($[M+Na]^+$): 415.1158. Found: 415.1157.

2,3-Bis(4-methoxyphenyl)-1-phenyl-4-(trimethylsilyl)dibenzothiophene (3ac): a brown solid; mp 210 °C; IR (CH_2Cl_2) 2853, 1245, 756, 734 cm^{-1}; ^1H NMR δ 0.18 (s, 9H), 3.61 (s, 3H), 3.74 (s, 3H), 6.39 (d, J = 8.2 Hz, 2H), 6.49 (d, J = 8.2 Hz, 1H), 6.63 (ddd, J =0.6, 8.9, 8.9 Hz, 1H), 6.92 (d, J = 8.7 Hz, 2H), 6.96 (ddd, J =1.1, 7.2, 7.2 Hz, 1H), 7.12 (dd, J = 1.7, 7.9 Hz, 2H), 7.22-7.26 (m, 3H), 7.29 (ddd, J =0.9, 7.6, 7.6 Hz, 1H), 7.82 (d, J = 7.7 Hz, 1H); ^{13}C NMR δ 2.6, 55.9, 56.2, 113.0, 113.4, 122.8, 124.5, 126.0, 126.7, 127.8, 129.3, 131.0, 133.0, 133.2, 133.3, 133.4, 136.4, 136.7, 139.6, 140.0, 140.7, 141.3, 146.4, 147.9, 157.9, 159.2 (a pair of peaks at the aromatic region was overlapped); HRMS (ESI positive) *m/z* calcd for $C_{35}H_{32}NaO_2SSi$ ($[M+Na]^+$): 567.1784. Found: 567.1785.

1,2-Diphenyl-4-(trimethylsilyl)dibenzothiophene (3ad): NOESY correlation was observed between TMS and C-H on dibenzothiophene ring (Figure 2) (its NOESY spectrum was listed in supporting information); a white solid; mp 160 °C; IR (CH_2Cl_2) 2853, 884, 839, 743, 699 cm^{-1}; ^{1}H NMR δ 0.53 (s, 9H), 6.67 (d, J = 8.3 Hz, 1H), 6.99 (ddd, J =1.1, 7.7, 7.7 Hz, 1H), 7.13-7.18 (m, 5H), 7.21-7.23 (m, 2H), 7.29-7.34 (m, 4H) 7.60 (s, 1H), 7.82 (d, J =7.9 Hz, 1H); ^{13}C NMR δ 0.0, 123.3, 124.7, 126.3, 126.9, 127.2, 128.4, 128.5, 129.5, 131.3, 133.7, 133.8, 135.3, 136.7, 138.9, 139.2, 140.6, 141.0, 142.6, 145.7 (a pair of peaks at the aromatic region was overlapped); HRMS (ESI positive) *m/z* calcd for $C_{27}H_{24}NaSSi$ ($[M+Na]^+$): 431.1260. Found: 431.1262.

1,3-Diphenyl-4-(trimethylsilyl)dibenzothiophene (4ad): NOESY correlation was observed between TMS and C-H on benzene ring (Figure 2) (its NOESY spectrum was listed in supporting information); a white solid; mp 214 °C; IR (CH_2Cl_2) 2850, 839, 742, 701, 699 cm^{-1}; ^{1}H NMR δ 0.21 (s, 9H), 7.05 (ddd, J =1.1, 7.6, 7.6 Hz, 1H), 7.14-7.16 (m, 2H), 7.32 (ddd, J =1.1, 7.6, 7.6 Hz, 1H), 7.33-7.37 (m, 5H), 7.48-7.49 (m, 5H), 7.83 (d, J = 7.9 Hz, 1H); ^{13}C NMR δ 1.4, 121.9, 123.5, 124.8, 125.9, 127.2, 127.7, 128.6, 129.0, 129.4, 129.6, 130.6, 131.0, 134.7, 139.0, 139.4, 141.1, 144.5, 147.1, 147.5 (a pair of peaks at the aromatic region was overlapped); HRMS (ESI positive) *m/z* calcd for $C_{27}H_{25}SSi$ ($[M+H]^+$): 409.1441. Found: 409.1438.

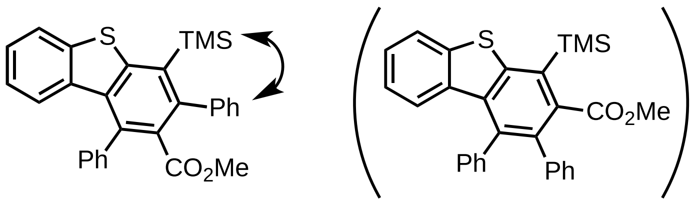


3ad **4ad**

Figure 2. NOESY experiment on **3ad** and **4ad**

2-(Methoxycarbonyl)-1,3-diphenyl-4-(trimethylsilyl)dibenzothiophene (3ae): NOESY correlation was observed between TMS and C-H on benzene ring, which is not observed in regioisomer **4ae** (Figure 3) (its NOESY spectrum was listed in supporting information); a white solid; mp 174 °C; IR (CH_2Cl_2) 2852, 1733, 884, 840, 763, 701 cm^{-1}; ^{1}H NMR δ 0.17 (s, 9H), 3.09 (s, 3H), 6.60 (d, J = 8.3 Hz, 1H), 7.02 (ddd, J =1.1, 7.7, 7.7 Hz, 1H), 7.32-7.34 (m, 6H), 7.41-7.43 (m, 2H), 7.47-7.49 (m, 3H) 7.82 (d, J = 7.9 Hz, 1H); ^{13}C NMR δ 1.2, 51.2, 121.9, 123.7, 124.9, 126.2, 127.4, 127.7, 128.2, 128.6, 129.3, 130.3, 131.3, 132.1, 133.3, 134.7, 135.7, 138.1, 139.6, 141.0, 143.3, 147.2, 169.3; HRMS (ESI positive) *m/z* calcd for

$C_{29}H_{26}NaO_2SSi$ ($[M+Na]^+$): 489.1315. Found: 489.1316.



3ae **4ae**

Figure 3. NOESY experiment on **3ae** and the structure of regioisomer **4ae**

2,3-Bis(methoxycarbonyl)-4-pentyldibenzothiophene-5,5-dioxide (6): a white solid; mp 140 °C; IR (CH_2Cl_2) 1733, 1151, 1101, 819 cm^{-1}; ^1H NMR δ 0.93 (t, J = 7.2 Hz, 3H), 1.36-1.49 (m, 4H), 1.76-1.82 (m, 2H), 3.00 (t, J = 8.5 Hz, 2H), 3.96 (s, 3H), 3.97 (s, 3H), 7.57 (dd, J = 7.6, 7.6 Hz, 1H), 7.66 (dd, J = 7.5, 7.5 Hz, 1H), 7.81 (d, J = 7.8 Hz, 1H), 7.83 (d, J = 7.9 Hz, 1H), 8.19 (s, 1H); ^{13}C NMR δ 14.9, 23.2, 30.9, 32.0, 33.2, 53.9, 54.2, 121.6, 123.1, 123.1, 130.8, 132.2, 133.8, 134.3, 135.2, 138.5, 139.1, 140.4, 140.6, 165.9, 168.7; HRMS (ESI positive) m/z calcd for $C_{21}H_{22}NaO_6S$ ($[M+Na]^+$): 425.1029. Found: 425.1028.

2,2',3,3'-Tetrakis(methoxycarbonyl)-4,4'-dipentyl-1,1'-bidibenzothiophene (8): a brown solid; mp 115 ℃; IR (CH_2Cl_2) 2857, 1736, 1116, 739 cm^{-1}; ^1H NMR δ 0.97 (t, J = 7.2 Hz, 6H), 1.43-1.54 (m, 8H), 1.87-1.96 (m, 4H), 3.09-3.15 (m, 2H), 3.21-3.27 (m, 2H), 3.39 (s, 6H), 3.88 (s, 6H), 6.30 (d, J = 8.3 Hz, 2H), 6.88 (ddd, J =1.1, 7.8, 7.8 Hz, 2H), 7.25 (ddd, J =1.1, 7.6, 7.6 Hz, 2H), 7.75 (d, J = 7.9 Hz, 2H); ^{13}C NMR δ 14.0, 22.4, 29.3, 31.9, 33.6, 52.0, 52.5, 122.4, 124.4, 124.8, 127.0, 129.2, 129.4, 131.5, 135.0, 135.2, 136.5, 139.9, 143.3, 167.2, 168.2; HRMS (ESI positive) m/z calcd for $C_{42}H_{42}NaO_8S_2$ ($[M+Na]^+$): 761.2213. Found: 761.2205. $[\alpha]^{26}_D$ 6.3 (c 0.18, $CHCl_3$, 82% ee). Ee was determined by HPLC analysis using a chiral column (Daicel Chiralpak IA: 4 x 250 mm, 254 nm UV detector, rt, eluent: 1% 2-propanol in hexane, flow rate: 1.0 mL/min, retention time: 26.3 min for major isomer and 22.1 min for minor isomer).

2,2',3,3'-Tetrakis(methoxycarbonyl)-4,4'-dipentyl-1,1'-bidibenzothiophene-5,5,5',5'-tetraoxide (9): a brown solid; mp 204 °C; IR (CH_2Cl_2) 1739, 1310, 1162, 739 cm^{-1}; ^1H NMR δ 0.96 (t, J = 7.2 Hz, 6H), 1.39-1.53 (m, 8H), 1.82-1.87 (m, 4H), 3.22-3.31 (m, 2H), 3.33-3.37 (m, 2H), 3.51 (s, 6H), 3.89 (s, 6H), 6.42 (d, J = 8.1 Hz, 2H), 7.31 (ddd, J =1.2, 7.8, 7.8 Hz, 2H), 7.64 (ddd, J =0.8, 7.6, 7.6 Hz, 2H), 7.79 (d, J = 7.1 Hz, 2H); ^{13}C NMR δ 15.0, 23.3, 30.8, 32.3, 33.1, 53.9, 54.1, 123.2, 125.1, 130.1, 130.2, 132.3, 133.9, 135.7, 136.2, 139.1, 139.2, 140.1, 142.7, 166.4, 167.1; HRMS (ESI positive) m/z calcd for $C_{42}H_{42}NaO_{12}S_2$ ($[M+Na]^+$): 825.2010. Found: 825.2002. $[\alpha]^{26}_D$ -52.1 (c 0.49, $CHCl_3$, 97% ee). Ee was determined by HPLC analysis using a chiral column (Daicel Chiralpak IA: 4 x 250 mm, 254 nm UV detector, rt, eluent: 10% 2-propanol in hexane, flow rate: 1.0 mL/min, retention time: 17.7 min for major isomer and 21.7 min for minor isomer). The crystal data of **9**: $C_{42}H_{42}O_{12}S_2$, M=802.91, triclinic, space group P1 (#1), a = 9.4846(3) Å, b = 11.7163(3) Å, c = 18.1232(5) Å, α = 82.456(2) °, β = 80.977(2) °, γ = 85.287(2) °, V = 1967.89(9) Å^3, T=173 K, Z=2, μ(Cu Kα) 17.688 cm^{-1}; number of reflections measured: total 23163 and unique 11998, $R1$=0.0552, $wR2$=0.1385, Flack parameter (Friedel pairs = 4945) 0.030(13). CCDC 1010885.

4-Iodo-2,3-bis(methoxycarbonyl)-1-phenyldibenzothiophene (10): a solution of 2,3-bis(methoxycarbonyl)-1-phenyl-4-(trimethylsilyl)dibenzothiophene (**3aa**) (22.4 mg, 0.05 mmol) and ICl (9.0 mg, 0.06 mmol) in $CHCl_3$ (0.25 mL) was stirred under reflux for 6 h. The resulting mixture was concentrated under reduced pressure. Et_2O was added and the solution was treated with sat. $Na_2S_2O_3$. The almost colourless organic phase was separated. The solvent was removed in vacuo to afford crude products, which were purified by flash column chromatography on silica gel to give 4-iodo-2,3-bis(methoxycarbonyl)-1-phenyldibenzothiophene (**10**) (18 mg, 72%): a white solid; mp 172 °C; IR (CH_2Cl_2) 2850, 1735, 1206, 701 cm^{-1}; ^{1}H NMR δ 3.49 (s, 3H), 3.97 (s, 3H), 6.61 (d, J = 8.4 Hz, 1H), 7.07 (ddd, J =1.0, 7.7, 7.7 Hz, 1H), 7.34-7.36 (m, 2H), 7.40 (ddd, J =0.8, 7.2, 7.2 Hz, 1H), 7.49-7.55 (m, 3H), 7.84 (d, J = 8.0 Hz, 1H); ^{13}C NMR δ 51.8, 52.5, 86.7, 122.0, 124.1, 125.8, 126.9, 128.1, 128.3, 128.5, 129.7, 133.2, 134.6, 135.8, 136.7, 137.0, 139.3, 149.4, 166.6, 167.3; HRMS (ESI positive) m/z calcd for $C_{22}H_{15}INaO_4S$ ($[M+Na]^+$): 524.9628. Found: 524.9628.

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18. When $[Rh(cod)Cl]_2$ (5 mol%) was used in place of $[Rh(cod)_2]BF_4$ (10 mol%), most of diyne **1a** remained even at 80 °C for 3 h, and the yield of cycloadduct **3aa** was below 5%.
19. When di-*tert*-butyl acetylenedicarboxylate was used in place of DMAD, the yield was not changed (92%).
20. The effect of a molar ratio of diyne **1g** to DMAD was examined (1/2: 34%, 1/3: 67%, 1/5: 68%).
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