Novel Synthesis of Bridged Phenylthienylethenes and Dithienylethenes via Pd-catalyzed Double Cyclization Reactions of Diarylhexadienynes

S. M. Abdur Rahman, Motohiro Sonoda, Miyako Ono, Koji Miki, and Yoshito Tobe*

Division of Frontier Materials Science, Graduate School of Engineering Science, Osaka University, and CREST, Japan Science and Technology Agency (JST),1-3 Machikaneyama, Toyonaka, Osaka 560-8531, Japan

E-mail:tobe@chem.es.osaka-u.ac.jp

Supporting Information

Contents S1	l -2
1. General	S 3
2. Synthesis of Bromoalkenes and Arylenynes as Precursors of Hexadienynes S3	3-4
• (Z)-1-Bromo-2-(2-thienyl)ethene (4a)	
• (Z)-1-Bromo-2-(3-thienyl)ethene (4b)	
• (Z)-1-(3-Bromo-2-thienyl)-1-buten-3-yne (5)	
• (Z)-1-Bromo-2-(2-bromo-3-thienyl)ethene (7)	
• (Z)-1-(3-Thienyl)-1-buten-3-yne (8)	
3. Synthesis of Phenylthienylhexadienynes and Dithienylhexadienynes (2a-e) and their Spect	ral
Data S5	5-7
• (Z,Z)-1-(2-Bromophenyl)-6-(2-thienyl)-1,5-hexadien-3-yne (2a)	
• (Z,Z)-1-(2-Bromophenyl)-6-(3-thienyl)-1,5-hexadien-3-yne (2b)	
• (Z,Z)-1-(3-Bromo-2-thienyl)-6-(2-thienyl)-1,5-hexadien-3-yne (2c)	
• (Z,Z)-1-(3-Bromo-2-thienyl)-6-(3-thienyl)-1,5-hexadien-3-yne (2d)	
• (Z,Z)-1-(2-Bromo-3-thienyl)-6-(3-thienyl)-1,5-hexadien-3-yne (2e)	
4. General Procedure for the Synthesis of Bridged Phenylthienylethenes and Dithienylether	nes
via Tandem Cyclization Reaction S7	1-9
 4-Indenylidene-4H-cyclopenta[b]thiophene (9a) 	
• 6-Indenylidene-6 <i>H</i> -cyclopenta[<i>b</i>]thiophene (9b)	

- Bi(4*H*-cyclopenta[*b*]thienylidene) (9c)
- 4-(6*H*-cyclopenta[*b*]thienylidene)-4*H*-cyclopenta[*b*]thiophene (9d)
- (Z)-Bi(6H-cyclopenta[b]thienylidene) ((Z)-9e)

6. General Procedure for the Photoinduced Isomerization of Bridged Phenylthienylethenes and		
Dithienylethenes	S9-10	
• (E)-Bi(cyclopenta[b]thienylidene) ((E)-9e)		
7. References	S10	
8. UV-visible Spectra of 9a-e (Figure S1)	S11	
9. ¹ H NMR and ¹³ C NMR Spectra of New Compounds		
(TMS-protected 5, 5, 7, TMS-protected 8, 8, 2a-2e, 9a-9e)	S12–S51	

5. General Procedure for the Pd-catalyzed Isomerization of Bridged Phenylthienylethenes S9

1. General: All reactions were carried out in a well-dried glassware under an argon or nitrogen atmosphere. Dichloromethane, toluene, *N*,*N*-dimethylformamide and diethylamine were distilled from CaH₂ under an Ar atmosphere. ¹H NMR (400, 300, or 270 MHz) and ¹³C NMR (100.4, 75.5, or 67.8 MHz) spectra were recorded in CDCl₃ or THF-*d*₈ at 30 °C. Chemical shifts are reported in parts per million downfield from internal tetramethylsilane for ¹H NMR spectra or CHCl₃ (δ = 77.0) for ¹³C NMR spectra. IR spectra were recorded as a neat film or as a KBr pellet. Recyclable preparative GPC separation was carried out with 600-mm × 20-mm GPC columns and CHCl₃ as an eluent.

2. Synthesis of Bromoalkenes and Arylenynes as Precursors of Hexadienynes:

(Z)-1-Bromo-2-(2-thienyl)ethane (4a) and (Z)-1-Bromo-2-(3-thienyl)ethane (4b): 2- and 3-Thiophenecarboxaldehydes were converted to the corresponding (Z)-bromoalkenes¹ (4a and 4b), respectively, by the Corey-Fuchs dibromomethylenation followed by selective reduction of the *E*-bromine atom according to a method similar to that reported by Uenishi *et al.*²

(Z)-1-(3-Bromo-2-thienyl)-1-buten-3-yne (5): A solution of ethynyltrimethylsilane (0.7 mL, 4.7 mmol) in Et₂NH (2.0 mL) was added dropwise over 20 min to a deoxygenated suspension of (Z)-1-bromo-2-(3-bromo-2-thienvl)ethene^{3,4} (1.15 g, 4.29 mmol), PdCl₂(PPh₃)₂ (30.2 mg, 0.043 mmol), and CuI (8.2 mg, 0.043 mmol) in Et₂NH (5.5 mL) under N₂. After stirring for 10 min at rt, the reaction mixture was diluted with water with then 10% aqueous HCl, and the resulting aqueous solution was extracted with ether. The extract was washed with brine and dried over anhydrous MgSO₄. After removal of the solvent in vacuo, the product was purified by column chromatography (hexane) on SiO₂ to afford 967 mg (79%)of (Z)-1-(3-bromo-2-thienyl)-4-(trimethylsilyl)-1-buten-3-yne as a yellow oil: ¹H NMR (270 MHz, $CDCl_3$) δ 7.31 (dd, J = 5.4, 0.9 Hz, 1H), 7.01 (dd, J = 11.9, 0.9 Hz, 1H), 6.99 (d, J = 5.4 Hz, 1H), 5.68 (d, J = 11.9 Hz, 1H), 0.28 (s, 9H); ¹³C NMR (75.5 MHz, CDCl₃) δ 134.7, 131.1, 129.3, 126.4, 113.9, 107.0, 106.4, 103.1, -0.3; IR (neat) 2959, 2898, 2136, 1488, 1434, 1376, 1342, 1250, 1162, 1014, 995, 844, 760, 706 cm⁻¹; MS (EI) m/z 286, 284 (M⁺). HRMS (EI) calcd for C₁₁H₁₃BrSSi: 285.9670, 283.9691. Found: 285.9672, 283.9686.

Α suspension of K₂CO₃ (193 mg, 1.40 mmol) and (Z)-1-(3-bromo-2-thienyl)-4-(trimethylsilyl)-1-buten-3-yne (200 mg, 0.701 mmol) in MeOH (1.5 mL) was stirred at rt for 30 min. The reaction mixture was diluted with water and extracted with ether. The extract was washed with brine and dried over anhydrous MgSO₄. The solvent was removed in vacuo to give 148 mg (99%) of 5 as a yellow oil: ¹H NMR (270 MHz, CDCl₃) δ 7.32 (d, J = 5.4 Hz, 1H), 7.07 (d, J = 11.6 Hz, 1H), 7.01 (d, J = 5.4 Hz, 1H), 5.65 (dd, J = 11.6, 2.7 Hz, 1H), 3.60 (d, J = 2.7 Hz, 1H); ¹³C NMR (67.8 MHz, CDCl₃) δ 134.4, 132.0, 129.4, 126.5, 114.2, 105.4, 88.4, 81.7; IR (KBr) 2957, 2925, 2136, 1488, 1376, 1341, 1250, 1153, 1014, 845, 760, 705 cm⁻¹; MS (EI) m/z 214, 212 (M⁺). HRMS (EI) calcd for C₈H₅BrS: 213.9274, 211.9295. Found: 213.9247,

211.9294.

(Z)-1-Bromo-2-(2-bromo-3-thienyl)ethene (7): Tetrabromomethane (21.0 g, 63.0 mmol) was added to a solution of 2-bromo-3-thiophenecarboxaldehyde⁵ (5.00 g, 26.2 mmol) and triphenylphosphine (26.2 g, 100 mmol) in dichloromethane (250 mL) at 0 °C under N₂. After stirring for 10 min at rt, the reaction mixture was poured into a sat. NaHCO₃ solution. The organic layer was separated and the aqueous layer was extracted with dichloromethane. The combined organic solution was dried over anhydrous MgSO₄. After removal of the solvent in vacuo, the product was purified by 6.98 (77%) flash chromatography (hexane) SiO₂ to afford on g of 1,1-dibromo-2-(2-bromo-3-thienyl)ethene as a colorless oil.

A solution of Pd(OAc)₂ (224 mg, 1.00 mmol) and triphenylphosphine (1.05 g, 4.00 mmol) in toluene (100 mL) was stirred at rt for 1.5 h. A solution of 1,1-dibromo-2-(2-bromo-3-thienyl)ethene (6.98 g, 20.0 mmol) and tributyltin hydride (6.4 mL, 23.8 mmol) in toluene (5 mL) was slowly added to the above solution at rt. After strring at rt for 1 h, an 8% aqueous KF solution was added to the reaction mixture. After stirring for 2 h, the mixture was filtered through a pad of Celite. The organic phase was separated and the aqueous phase was extracted with ether. The combined organic solution was dried over anhydrous MgSO₄. After removal of the solvent in vacuo, the product was purified by flash chromatography (hexane) on SiO₂ to afford 3.20 g (60%) of (*Z*)-1-bromo-2-(2-bromo-3-thienyl)ethene (7) as a colorless oil: ¹H NMR (400 MHz, CDCl₃) δ 7.81 (d, *J* = 5.6 Hz, 1H), 7.29 (dd, *J* = 5.6, 0.4 Hz, 1H), 7.08 (dd, *J* = 8.0, 0.4 Hz, 1H), 6.45 (d, *J* = 8.0 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 135.3, 127.1, 125.7, 125.2, 114.8, 107.4; IR (neat) 3080, 2921, 1620, 1395, 1373, 1318, 1254, 1045, 997, 935, 876, 826, 765, 741, 695, 604 cm⁻¹; MS (EI) *m/z* 270, 268, 266 (M⁺). HRMS (EI) calcd for C₆H₄Br₂S: 269.8358, 267.8380, 265.8400. Found: 269.8364, 267.8394, 265.8380.

(Z)-1-(3-Thienyl)-1-buten-3-yne⁶ (8): To a solution of ethynyltrimethylsilane (0.34 mL, 2.4 mmol), bromoalkene **4b** (378 mg, 2.0 mmol), and Et₂NH (1.0 mL, 9.7 mmol) in toluene (5.0 mL) was added CuI (29.0 mg, 0.015 mmol, 7.5 mol%), followed by Pd(PPh₃)₄ (58.0 mg, 0.050 mmol, 2.5 mol%) under N₂. After stirring at rt for 5 min, the reaction mixture was poured into a saturated aqueous NH₄Cl solution. The organic layer was separated and the aqueous solution was extracted with ether. The combined organic solution was dried over anhydrous MgSO₄. After removal of the solvent in vacuo, the product was purified by flash chromatography (hexane) on SiO₂ to afford 410 mg (99%) of (*Z*)-1-(3-thienyl)-4-trimethylsilyl-1-buten-3-yne as a colorless oil: ¹H NMR (400 MHz, CDCl₃) δ 7.82 (d, *J* = 2.8 Hz, 1H), 7.68 (dd, *J* = 5.2, 1.2 Hz, 1H), 7.29 (dd, *J* = 5.2, 2.8 Hz, 1H), 6.69 (d, *J* = 12.0 Hz, 1H), 5.61 (d, *J* = 12.0 Hz, 1H), 0.27 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ 138.6, 133.6, 127.9, 125.8, 124.9, 105.9, 104.2, 102.0, -0.2; IR (neat) 3096, 3025, 2959, 2898, 2138, 1600, 1421, 1251, 1148, 1020, 844, 797, 760, 698, 635 cm⁻¹; MS (EI) *m*/z 206 (M⁺). HRMS (EI) calcd for C₁₁H₁₄SSi: 206.0586. Found: 206.0589.

Α K₂CO₃ (550 3.98 suspension of mg, mmol) and (Z)-1-(3-thienyl)-4-(trimethylsilyl)-1-buten-3-yne (400 mg, 1.94 mmol) in MeOH (4.0 mL) was stirred at rt for 5 min. The reaction mixture was diluted with water and extracted with ethyl acetate. The extract was washed with brine and dried over anhydrous MgSO₄. The solvent was removed in vacuo to give 259 mg (99%) of 8 as a pale yellow oil: ¹H NMR (300 MHz, CDCl₃, 30 °C) δ 7.82–7.80 (m, 1H), 7.67 (dd, J = 5.1, 0.6 Hz, 1H), 7.29 (dd, J = 5.1, 3.3 Hz, 1H), 6.75 (d, J = 12.0, 1H), 5.58 (dd, J = 12.0, 2.7 Hz, 1H), 3.38 (d, J = 2.7 Hz, 1H); ¹³C NMR (75.5 MHz, CDCl₃, 30 °C) δ 138.2, 134.3, 127.8, 125.9, 125.1, 104.9, 84.1, 82.5; IR (neat) 3287, 3095, 3027, 2089, 1603, 1418, 1349, 1260, 1146, 1082, 873, 832, 797, 750, 692, 618 cm⁻¹; MS (EI) *m/z* 134 (M⁺). HRMS (EI) calcd for C₈H₆S: 134.0190. Found: 134.0176.

3. General Procedure for the Synthesis of Hexadienynes (2a-e):

The Sonogashira-Hagihara coupling reactions of 4a, 4b, or 8 with enynes 3, ⁷ 7, or 5 gave the corresponding hexadienynes 2a-e in 55–93% yields. As a typical procedure, the preparation of hexadienyne 2a is described below:

(Z,Z)-1-(2-Bromophenyl)-6-(2-thienyl)-1,5-hexadien-3-yne (2a): A solution of enyne 3 (380 mg, 1.83 mmol) in Et₂NH (5.0 mL) was added dropwise slowly to a deoxygenated suspension of (Z)-bromoalkene 4a (310 mg, 1.7 mmol), PdCl₂(PPh₃)₂ (15 mg, 0.021 mmol, 10 mol%), and CuI (8 mg, 0.04 mmol, 20 mol%) in Et₂NH (10 mL) under N₂. After stirring at rt for 30 min, the reaction mixture was diluted with water then with 10% aqueous HCl, and the resulting aqueous solution was extracted with ether. The extract was washed with brine and dried over anhydrous MgSO₄. After removal of the solvent in vacuo, the product was purified by column chromatography (hexane) on SiO_2 to afford 283 mg (55%) of **2a** (ZZ/EZ = 98/2) as a yellowish oil. The ZZ/EZ ratio of the products was determined by comparison of the integration of the vinyl proton signals adjacent to the acetylenic carbon in the ¹H NMR spectrum. Pure (Z,Z)-isomer was obtained by subjection of the isomeric mixtures to a recyclable preparative GPC: ¹H NMR (270 MHz, CDCl₃) δ 8.34 (dd, J = 7.8, 1.6 Hz, 1H), 7.59 (d, J = 7.8 Hz, 1H), 7.35–7.24 (m, 3H), 7.13 (td, J = 7.8, 1.6 Hz, 1H), 7.01 (d, J = 11.6 Hz, 1H), 7.01–6.98 (m, 1H), 6.90 (d, J = 11.1 Hz, 1H), 6.13 (dd, J = 11.6, 3.0 Hz, 1H), 5.71 (dd, J = 11.1, 3.0 Hz, 1H); relatively small vinyl proton signals were assigned to the (*E*,*Z*)-isomer: δ 7.45 (d, J = 16.2 Hz, 1H), 6.96 (d, J = 11.3 Hz, 1H), 6.43 (dd, J = 16.2, 2.7 Hz, 1H), 5.73 (dd, J = 11.3, 10.2 Hz)2.7 Hz, 1H); ¹³C NMR (67.8 MHz, CDCl₃) δ 140.4, 137.0, 135.8, 132.6, 132.4, 129.7, 129.6, 129.4, 127.1, 127.0, 126.5, 124.1, 109.9, 104.5, 96.7, 94.8; IR (neat) 3053, 3021, 2923, 2162, 1587, 1557, 1467, 1434, 1213, 1023, 947, 831, 795, 768, 748, 702 cm⁻¹; MS (EI) *m/z* 316, 314 (M⁺). HRMS (EI) calcd for $C_{16}H_{11}BrS$: 315.9745, 313.9765. Found: 315.9734, 313.9775.

(*Z*,*Z*)-1-(2-Bromophenyl)-6-(3-thienyl)-1,5-hexadien-3-yne (2b): A yellowish colorless oil (93%, ZZ/EZ = 91/9). The *ZZ/EZ* ratio of the products was determined by comparison of the integration of

the vinyl proton signals adjacent to the acetylenic carbon in the ¹H NMR spectrum: ¹H NMR (270 MHz, CDCl₃) δ 8.27 (dd, J = 7.8, 1.6 Hz, 1H), 7.69 (d, J = 1.6 Hz, 1H), 7.60 (dd, J = 7.8, 1.6 Hz, 1H), 7.53 (dd, J = 4.9, 1.6 Hz, 1H), 7.28 (td, J = 7.8, 1.6 Hz, 1H), 7.20 (dd, J = 4.9, 3.0 Hz, 1H), 7.15 (td, J = 7.8, 1.6 Hz, 1H), 6.97 (d, J = 11.9 Hz, 1H), 6.67 (d, J = 11.9 Hz, 1H), 6.06 (dd, J = 11.9, 3.0 Hz, 1H); relatively small vinyl proton signals were assigned to the (*E*,*Z*)-isomer: δ 7.36 (d, J = 16.2 Hz, 1H), 6.73 (d, J = 11.9 Hz, 1H), 6.38 (dd, J = 16.2, 3.0 Hz, 1H), 5.78 (dd, J = 11.9, 3.0 Hz, 1H); ¹³C NMR (67.8 MHz, CDCl₃) δ 138.3, 137.2, 135.9, 132.71, 132.67, 129.65, 129.60, 127.7, 127.2, 125.5, 125.19, 125.17, 124.0, 109.9, 105.8, 93.7; IR (neat) 3094, 3052, 3021, 2161, 1587, 1557, 1467, 1434, 1349, 1260, 1149, 1023, 948, 871, 795, 768, 740, 634 cm⁻¹; MS (EI) *m*/*z* 316, 314 (M⁺). HRMS (EI) calcd for C₁₆H₁₁BrS: 315.9745, 313.9765. Found: 315.9743, 313.9778.

(Z,Z)-1-(3-Bromo-2-thienyl)-6-(2-thienyl)-1,5-hexadien-3-yne (2c): A dark red solid (92%, ZZ/EZ/EE = 90/7/3). The ZZ/EZ/EE ratio of the products was determined by comparison of the integration of the vinyl proton signals adjacent to the acetylenic carbons in the ¹H NMR spectrum; mp 68–70 °C; ¹H NMR (270 MHz, CDCl₃) δ 7.33 (d, *J* = 5.4 Hz, 1H), 7.30 (d, *J* = 1.6 Hz, 1H), 7.29 (d, *J* = 5.4 Hz, 1H), 7.07 (d, *J* = 11.3 Hz, 1H), 7.03 (d, *J* = 5.4 Hz, 1H), 7.01 (dd, *J* = 5.4, 1.6 Hz, 1H), 6.97 (d, *J* = 11.3 Hz, 1H), 6.00 (dd, *J* = 11.3, 2.7 Hz, 1H), 5.85 (dd, *J* = 11.3, 2.7 Hz, 1H); other six doublet of doublets signals at δ 6.32, 6.25, 6.19, 6.14, 5.84, and 5.71 ppm were assigned to the vinyl proton signals adjacent to the acetylenic carbon of the two (*E*,*Z*)-isomers and (*E*,*E*)-isomer, two (*E*,*Z*)-isomers: δ 6.32 (dd, *J* = 16.0, 3.0 Hz, 1H), 6.25 (dd, *J* = 16.0, 3.0 Hz, 1H), 5.84 (dd, *J* = 11.2, 3.0 Hz, 1H); (*E*,*E*)-isomer: δ 6.19 (dd, *J* = 16.0, 2.8 Hz, 1H), 6.14 (dd, *J* = 16.0, 2.8 Hz, 1H); ¹³C NMR (67.8 MHz, CDCl₃) δ 140.5, 134.9, 132.4, 130.0, 129.6, 129.4, 127.2, 126.5, 113.7, 106.6, 104.5, 99.4, 97.5; IR (neat) 3103, 3087, 2153, 1597, 1443, 1437, 1374, 1339, 1261, 1145, 1080, 880, 870, 795, 750, 714, 634 cm⁻¹; MS (EI) *m*/z 322, 320 (M⁺). HRMS (EI) calcd for C₁₄H₉BrS₂: 321.9308, 319.9329. Found: 321.9292, 319.9332.

(*Z*,*Z*)-1-(3-Bromo-2-thienyl)-6-(3-thienyl)-1,5-hexadien-3-yne (2d): A pale yellow solid (83%, *ZZ/EZ* = 99/1). The *ZZ/EZ* ratio of the products was determined by comparison of the integration of the vinyl proton signals adjacent to the acetylenic carbon in the ¹H NMR spectrum; mp 72–73 °C; ¹H NMR (270 MHz, CDCl₃) δ 7.78 (d, *J* = 2.7 Hz, 1H), 7.66 (dd, *J* = 4.9. 0.5 Hz, 1H), 7.28 (d, *J* = 5.1 Hz, 1H), 7.27 (d, *J* = 4.9 Hz, 1H), 7.05 (d, *J* = 11.1 Hz, 1H), 7.01 (d, *J* = 5.1 Hz, 1H), 6.75 (d, *J* = 11.3 Hz, 1H), 5.94 (dd, *J* = 11.1, 3.0 Hz, 1H), 5.89 (dd, *J* = 11.3, 3.0 Hz, 1H); other two doublet of doublets signals at δ 6.27 and 5.85 ppm were assigned to the vinyl proton signals adjacent to the acetylenic carbon of (*E*,*Z*)-isomer: δ 6.27 (dd, *J* = 16.0, 3.0 Hz, 1H), 5.85 (dd, *J* = 16.0, 3.0 Hz, 1H); ¹³C NMR (67.8 MHz, CDCl₃) δ 138.4, 134.8, 132.8, 130.1, 129.4, 127.7, 126.4, 125.8, 125.3, 113.7, 106.4, 105.8, 99.6, 94.5; IR (neat) 3103, 2156, 1578, 1543, 1443, 1438, 1396, 1375, 1339, 1255, 1213, 1148, 1041, 883, 830, 754, 704 cm⁻¹; MS (EI) *m/z* 322, 320 (M⁺). HRMS (EI) calcd for

C₁₄H₉BrS₂: 321.9308, 319.9329. Found: 321.9314, 319.9341.

(*Z*,*Z*)-1-(2-Bromo-3-thienyl)-6-(3-thienyl)-1,5-hexadien-3-yne (2e): To a solution of 8 (188 mg, 1.4 mmol), bromoalkene 7 (406 mg, 1.5 mmol), and Et₂NH (1.1 mL, 10 mmol) in toluene (5.0 mL) was added CuI (28.0 mg, 0.015 mmol, 10 mol%), followed by Pd(PPh₃)₄ (58.0 mg, 0.050 mmol, 3.5 mol%) under N₂. After stirring at rt for 5 min, the reaction mixture was poured into saturated aqueous NH₄Cl solution. The organic layer was separated and the aqueous layer was extracted with ether. The combined organic solution was dried over anhydrous MgSO₄. After removal of the solvent in vacuo, the product was purified by flash chromatography (hexane) on SiO₂ to afford 333 mg (74%) of **2e** as a pale yellow solid: mp 54–56 °C; ¹H NMR (300 MHz, CDCl₃) δ 8.00 (dd, *J* = 5.7, 0.4 Hz, 1H), 7.75–7.77 (m, 1H), 7.61 (ddd, *J* = 5.4, 0.6, 0.6 Hz, 1H), 7.28 (ddd, *J* = 5.4, 2.1, 0.3 Hz, 1H), 7.22 (dd, *J* = 5.7, 0.6 Hz, 1H), 6.73 (d, *J* = 11.7 Hz, 1H), 6.72 (d, *J* = 11.7 Hz, 1H), 5.97 (ddd, *J* = 11.7, 2.7, 0.6 Hz, 1H), 5.82 (dd, *J* = 11.7, 2.7 Hz, 1H); ¹³C NMR (75.5 MHz, CDCl₃) δ 138.4, 137.1, 132.7, 130.2, 127.7, 126.6, 125.6, 125.4, 125.3, 114.6, 107.9, 105.9, 96.0, 94.2; IR (KBr) 3093, 2157, 1603, 1429, 1263, 994, 871, 822, 796, 769, 716, 635, 624 cm⁻¹; MS (EI) *m/z* 322, 320 (M⁺). Anal. Calcd for C₁₄H₉BrS₂: C, 52.34; H, 2.82. Found: C, 52.53; H, 2.78.

4. General Procedure for the Synthesis of Bridged Phenylthienylethenes and Dithienylethenes via Tandem Cyclization Reaction:

A solution (0.01M) of a hexadienynes **2a**, **b**, **c**, **d**, or **e** in DMF was added to a mixture of $Pd(OAc)_2$ (20 mol%), triphenylphosphine (40 mol%), anhydrous potassium carbonate (3 eqiuv), and tetrabutylammonium bromide (1.1 equiv) and stirred. The resulting mixture was heated and stirried at 80 °C. After cooled to rt, the reaction mixture was diluted with water and the resulting aqueous solution solution was extracted with ether. The combined organic layer was washed with brine and dried over anhydrous MgSO₄. After removal of the solvent in vacuo, the residue was chromatographed on SiO₂ (hexane) to afford the corresponding product as a mixture of *Z*- and *E*-isomers. In all case, *Z*-isomers were major products.

4-Indenylidene-4*H***-cyclopenta[***b***]thiophene ((***Z***)-9a and (***E***)-9a) (85% yield, Z/E = 75/25 determined by ¹H NMR spectrum). The proportion of** *E***-isomer increased with increasing reaction time after consumption of the starting dienyne 2a** (54%, Z/E = 35/65). These isomers were separated by preparative HPLC. Dark unknown materials, which were insoluble in CHCl₃, were formed gradually on standing a solution of (*Z*)-9a in CHCl₃ (or CDCl₃). It was not possible therefore to measure the absorption spectrum of (*Z*)-9a accurately. (*Z*)-9a: a reddish solid; dec. > 300 °C; ¹H NMR (270 MHz, CDCl₃) δ 8.23 (d, *J* = 7.0 Hz, 1H), 7.71 (d, *J* = 4.9 Hz, 1H), 7.31–7.27 (m, 2H), 7.24–7.16 (m, 1H), 7.19 (d, *J* = 4.9 Hz, 1H), 6.95 (d, *J* = 5.4 Hz, 1H), 6.91 (d, *J* = 5.4 Hz, 1H), 6.80 (d, *J* = 5.4 Hz, 1H), 6.77 (d, *J* = 5.4 Hz, 1H); ¹³C NMR (67.8 MHz, CDCl₃) δ 149.5, 144.9, 142.8, 137.6, 136.7, 134.9, 134.2, 129.6, 129.1, 128.8, 126.6, 125.6, 125.3, 125.0, 123.9, 121.8; IR (KBr)

3060, 2892, 1543, 1445, 1364, 1259, 1020, 831, 748 (br) cm⁻¹; MS (EI) *m/z* 234 (M⁺). HRMS (EI) calcd for C₁₆H₁₀S: 234.0503. Found: 234.0488. (*E*)-**9a**: a dark red solid; dec. > 300 °C; ¹H NMR (270 MHz, CDCl₃) δ 7.89 (d, *J* = 7.3 Hz, 1H), 7.33 (d, *J* = 5.1 Hz, 1H), 7.30-7.16 (m, 3H), 7.16 (d, *J* = 5.4 Hz, 1H), 7.16 (d, *J* = 5.4 Hz, 1H), 7.02 (d, *J* = 5.1 Hz, 1H), 6.87 (d, *J* = 5.4 Hz, 1H); ¹³C NMR (67.8 MHz, CDCl₃) δ 146.0, 144.1, 141.4, 140.7, 136.7, 136.2, 136.1, 129.5, 128.7, 128.0, 125.9, 125.8, 124.9, 124.9, 122.7, 121.9; IR (KBr) 3080, 3006, 1470, 1446, 1358, 1221, 1124, 873, 766, 749, 720, 691, 667 cm⁻¹; UV (25 °C, CHCl₃, 1.5 × 10⁻⁵ M) λ_{max} (log ε) 394 (4.48), 374 (4.46), 360 (4.25, sh) nm; MS (EI) *m/z* 234 (M⁺). HRMS (EI) calcd for C₁₆H₁₀S: 234.0503. Found: 234.0494.

6-Indenylidene-6*H***-cyclopenta**[*b*]**thiophene** ((*Z*)-9**b** and (*E*)-9**b**) (89%, *Z*/*E* = 89/11 determined by ¹H NMR spectrum). These isomers were separated by preparative HPLC. (*Z*)-9**b** (*Z*/*E* = 89/11): a reddish brown solid; dec. > 300 °C; ¹H NMR (270 MHz, CDCl₃) δ 8.33–8.29 (m, 1H), 7.47 (d, *J* = 4.7 Hz, 1H), 7.36–7.30 (m, 3H), 7.03 (d, *J* = 4.7 Hz, 1H), 6.96 (s, 2H), 6.85 (s, 2H); ¹³C NMR (100.4 MHz, CDCl₃) δ 153.1, 144.6, 141.8, 135.8, 134.6, 133.9, 131.3, 130.6, 129.8, 129.2, 129.1, 127.9, 126.9, 124.6, 121.8, 120.5; IR (KBr) 3090, 2925, 1474, 1448, 1370, 1325, 990, 865, 837, 764, 749, 644 cm⁻¹; UV (25 °C, CHCl₃, 1.3 × 10⁻⁵ M) (*Z*/*E* = 89/11) λ_{max} 400, 381 nm; MS (EI) *m*/*z* 234 (M⁺). HRMS (EI) calcd for C₁₆H₁₀S: 234.0503. Found: 234.0497. (*E*)-9**b** (*Z*/*E* = 6/94): a reddish brown solid; dec. > 300 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.86 (d, *J* = 7.3 Hz, 1H), 7.33 (dd, *J* = 4.8, 0.7 Hz, 1H), 7.27-7.25 (m, 1H), 7.23 (td, *J* = 7.3, 1.3 Hz, 1H), 7.17 (td, *J* = 7.3, 1.7 Hz, 1H), 7.11 (dd, *J* = 5.6, 0.7 Hz, 1H), 7.01 (d, *J* = 5.6 Hz, 1H), 6.99 (d, *J* = 5.6 Hz, 1H), 6.93 (d, *J* = 4.8 Hz, 1H), 6.88 (d, *J* = 5.6 Hz, 1H); ¹³C NMR (100.4 MHz, CDCl₃) δ 149.7, 144.3, 140.4, 136.7, 136.5, 135.8, 135.3, 131.1, 130.1, 128.6, 128.4, 125.8, 125.6, 124.6, 121.9, 120.1; IR (KBr) 3063, 3012, 1522, 1471, 1450, 1370, 1322, 1186, 761, 721, 643 cm⁻¹; UV (25 °C, CHCl₃, 1.7 × 10⁻⁵ M) (*Z*/*E* = 6/94) λ_{max} 412, 391 nm; MS (EI) *m*/*z* 234 (M⁺). HRMS (EI) calcd for C₁₆H₁₀S: 234.0503. Found: 234.0503. Found: 234.0503. Found: 234.0503.

Bi(*4H*-cyclopenta[*b*]thienylidene) ((*Z*)-9c and (*E*)-9c) (38% yield, *Z*/*E* = 77/23): (*Z*)-9c (*Z*/*E* = 77/23): a brown solid; dec. > 245 °C; ¹H NMR (400 MHz, THF-*d*₈) δ 7.65 (d, *J* = 4.8 Hz, 2H), 7.29 (dd, *J* = 4.8, 1.2 Hz, 2H), 6.84 (d, *J* = 5.6 Hz, 2H), 6.80 (dd, *J* = 5.6, 1.2 Hz, 2H); ¹³C NMR (100.4 MHz, THF-*d*₈) δ 138.9, 137.7, 128.8, 128.0, 126.4, 125.8, 123.7; IR (KBr) 3091, 2923, 1657, 1608, 1467, 1350, 1243, 1206, 1129, 1040, 868, 827, 688 cm⁻¹; UV (25 °C, CHCl₃, 5.7 × 10⁻⁶ M) (*Z*/*E* = 85/15) λ_{max} 381, 364, 348 (sh) nm; MS (EI) *m*/*z* 240 (M⁺). (*E*)-9c (*Z*/*E* = 3/97): a brown solid; ¹H NMR (400 MHz, THF-*d*₈) δ 7.41 (d, *J* = 4.8 Hz, 2H), 7.23 (dd, *J* = 4.8, 1.3 Hz, 2H), 7.01 (dd, *J* = 5.5, 1.3 Hz, 2H), 6.90 (d, *J* = 5.5 Hz, 2H); ¹³C NMR (100.4 MHz, THF-*d*₈) δ 147.9, 140.9, 137.5, 130.1, 126.8, 126.6, 123.2. UV (25 °C, CHCl₃, 1.3 × 10⁻⁵ M) (*Z*/*E* = 3/97) λ_{max} 387, 368, 350 (sh) nm; MS (EI) *m*/*z* 240 (M⁺). HRMS (EI) Calcd for C₁₄H₁₈S₂: 240.0067. Found: 240.0051.

4-(6*H*-cyclopenta[*b*]thienylidene)-4*H*-cyclopenta[*b*]thiophene ((*Z*)-9d and (*E*)-9d) (49% yield, Z/E = 83/17). (*Z*)-9d (Z/E = 83/17): a brown solid; dec. > 250 °C; ¹H NMR (400 MHz, THF- d_8) δ 7.78 (d, J = 5.1 Hz, 1H), 7.60 (dd, J = 4.7, 0.9 Hz, 1H), 7.34 (dd, J = 5.1, 1.3 Hz, 1H), 7.03 (d, J = 4.7 Hz, 1H), 6.86 (d, J = 5.6 Hz, 1H), 6.85 (d, J = 5.6 Hz, 1H), 6.83 (dd, J = 5.6, 0.9 Hz, 1H), 6.81 (dd, J = 5.6, 1.3 Hz, 1H); ¹³C NMR (100.4 MHz, THF- d_8) δ 154.0, 149.7, 138.8, 137.0, 136.9, 132.8, 132.2, 129.7, 129.6, 128.1, 127.9, 126.7, 123.0, 121.0; IR (KBr) 3087, 2921, 1614, 1470, 1357, 1271, 1212, 1121, 995, 869, 831, 758, 654 cm⁻¹; UV (25 °C, CHCl₃, 5.5×10^{-6} M) (Z/E = 83/17) λ_{max} 399, 380, 362 (sh) nm; MS (EI) m/z 240 (M⁺). HRMS (EI) Calcd for $C_{14}H_{18}S_2$: 240.0067. Found: 240.0066. (*E*)-**9d** (Z/E = 39/61): a brown solid; ¹H NMR (400 MHz, THF- d_8) δ 7.46 (dd, J = 5.0, 0.6 Hz, 1H), 7.38 (d, J = 5.2 Hz, 1H), 7.23 (dd, J = 5.2, 1.3 Hz, 1H), 6.96 (dd, J = 5.6, 0.6 Hz, 1H), 6.93 (d, J = 5.0 Hz, 1H), 6.89 (d, J = 5.7 Hz, 1H), 6.87 (d, J = 5.6 Hz, 1H), 6.74 (dd, J = 5.7, 1.3 Hz, 1H); ¹³C NMR (100.4 MHz, THF- d_8) δ 152.3, 148.0, 140.7, 137.5, 136.7, 134.9, 131.8, 130.6, 127.6, 127.1, 126.4, 123.0, 120.8, 112.8; UV (25 °C, CHCl₃, 1.6 × 10⁻⁵ M) (Z/E = 39/61) λ_{max} 404, 386, 370 (sh) nm; MS (EI) m/z 240 (M⁺).

(Z)-Bi(6*H*-cyclopenta[*b*]thienylidene) ((Z)-9e) (87% yield): a deep red crylstal; dec. > 250 °C; ¹H NMR (270 MHz, THF-*d*₈) δ 7.66 (dd, *J* = 4.8 Hz, 2H), 7.08 (d, *J* = 4.8 Hz, 2H), 6.91 (d, *J* = 5.7 Hz, 2H), 6.87 (dd, *J* = 5.7 Hz, 2H); ¹³C NMR (100.4 MHz, THF-*d*₈) δ 153.3, 136.2, 132.3, 132.2, 129.6, 128.9, 121.0; IR (KBr) 3092, 1522, 1460, 1339, 1321, 1297, 1220, 1092, 990, 876, 838, 756, 706, 639 cm⁻¹; UV (25 °C, CHCl₃, 5.1 × 10⁻⁶ M) λ_{max} (log ε) 410 (4.63), 389 (4.57), 368 (4.28, sh) nm; MS (EI) *m*/*z* 240 (M⁺). HRMS (EI) calcd for C₁₄H₈S₂: 240.0067. Found: 240.0062. In this case, the reaction proceeded even with a smaller amount of the catalyst and the additive (Pd(OAc)₂ (5 mol%), PPh₃ (10 mol%)) to give (*Z*)-**9e** in 83% yield.

5. General Procedure for the Pd-catalyzed Isomerization of Bridged Phenylthienylethenes and Dithienylethenes:

Pd-catalyzed Isomerization of 9a,b, and e:

A dilute solution (0.01 M) of the bridged phenylthienylethenes **9a**, **b**, or **e** in DMF was added to a mixture of $Pd(OAc)_2$ (20 mol%) and triphenylphosphine (40 mol%). The resulting mixture was heated at 80 °C. The progress of the isomerization reaction was monitored by ¹H NMR spectroscopy of aliquats taken from the reaction mixture and worked up as usual. The diastereoisomer ratios were determined based on the integrations of the diagnostic peaks of the *Z*- and *E*-isomers.

6. General Procedure for the Photoinduced Isomerization of Bridged Phenylthienylethenes and Dithienylethenes:

Photochemical Reactions of 9a,b:

A solution of **9a** or **b** (0.01 mmol, a mixture of isomers) in THF (0.75 mL) in a Pyrex tube was degassed by bubbling Ar for 5 min. While bubbling Ar, the tube was protected from the room light by shielding with an aluminum foil. The solution was irradiated with a high-pressure mercury lamp

in a tap water. The progress of the photochemical reaction was monitored using HPLC by injecting a fixed volume of the solution at appropriate intervals and yields were determined by comparing the integrations of the peaks of the (Z)- and (E)-isomers.

Photochemical Reactions of 9c-e:

A solution of **9c**, **d**, or **e** (0.01mmol) and anhydrous 1,4-dioxane (1.0 mg, as an internal standard) in THF- d_8 (0.75 mL) in a NMR tube was degassed by bubbling Ar for 5 min. While bubbling Ar, the tube was protected from the room light by shielding with an aluminum foil. The solution was irradiated with a high-pressure mercury lamp in a tap water. The progress of the photochemical reaction was monitored by ¹H NMR spectroscopy. The diastereoisomer ratios were determined by comparing with integrations of the diagnostic peaks of the (*Z*)- and (*E*)-isomers.

(*E*)-**Bi**(cyclopenta[*b*]thienylidene) ((*E*)-9e): Preparative scale photolysis was conducted as follows: A solution of (*Z*)-9e (10 mg, 0.042 mmol) in 1.5 mL of THF, placed in a Pyrex test tube, was degassed by bubbling argon for 5 min. While bubbling Ar, the tube was protected from the room light by shielding with an aluminum foil. The solution was irradiated with a high-pressure mercury lamp in a tap water at room temperature for 8 h. After removal of the solvent in vacuo, the product was purified by flash chromatography (hexane) on SiO₂ to give a 3.0 mg of (*E*)-9e (30%) as a deep red solid together with 3.0 mg of unreacted (*Z*)-9e; dec. > 250 °C; ¹H NMR (400 MHz, THF-*d*₈) δ 7.44 (d, *J* = 4.8 Hz, 2H), 6.92 (d, *J* = 4.8 Hz, 2H), 6.85 (d, *J* = 5.6 Hz, 2H), 6.69 (d, *J* = 5.6 Hz, 2H); ¹³C NMR (100.4 MHz, THF-*d*₈) δ 152.4, 136.7, 134.6, 132.2, 131.9, 127.5, 121.0; IR (KBr) 3081, 2924, 2853, 1518, 1465, 1447, 1325, 1218, 1103, 1037, 994, 875, 830, 755, 717, 659, 614, 593, 570, 524 cm⁻¹; UV (25 °C, CHCl₃, 5.0 × 10⁻⁶ M) (*Z*/*E*=5/95) λ_{max} 422, 398, 378 (sh) nm; MS (EI) *m/z* 240 (M⁺). HRMS (EI) calcd for C₁₄H₈S₂: 240.0067. Found: 240.0062.

7. References:

- (a) Herz, H. -G.; Queiroz, M. J. R. P.; Maas, G. Synthesis 1999, 1013–1016. (b) Rossi, R.; Carpita, A.; Lippolis, V. Synth. Commun. 1991, 21, 2119. (c) Rossi, R.; Carpita, A.; Lippolis, V. Synth. Commun. 1991, 21, 333–349.
- 2. Uenishi, J.; Kawahama, R.; Yonemitsu, O.; Tsuji, J. J. Org. Chem. 1998, 63, 8965–8975.
- 3. Tietze, L. F.; Lücke, L. P.; Major, F.; Müller, P. Aust. J. Chem. 2004, 57, 635-640.
- 4. Fuller, L. S.; Iddon, B.; Smith, K. A. J. Chem. Soc., Perkin Trans 1 1997, 3465–3470.
- Christophersen, C.; Begtrup, M.; Ebdrup, S.; Petersen, H.; Vedsø, P. J. Org. Chem. 2003, 68, 9513–9516.
- Fossatelli, M.; Van der Kerk, A. C. T. H. M.; Vasilevsky, S. F.; Brandsma, L. *Tetrahedron Lett.* 1992, *33*, 4229–4232.
- 7. Sonoda, M.; Itahashi, K.; Tobe, Y. Tetrahedron Lett. 2002, 43, 5269-5272.

8. UV-visible Spectra of 9a-e



Figure S1. UV-visible spectra of (a) bridged phenylthienylethenes **9a-b** and (b) dithienylethenes **9c-e** in CHCl₃. Concentration: $[(E)-1] = 1.5 \times 10^{-5}$ M; $[(E)-9a] = 1.5 \times 10^{-5}$ M; $[9b (Z/E = 89/11)] = 1.3 \times 10^{-5}$ M; $[9b (Z/E = 6/94)] = 1.7 \times 10^{-5}$ M; $[9c (Z/E = 85/15)] = 5.7 \times 10^{-6}$ M; $[9c (Z/E = 3/97)] = 1.3 \times 10^{-5}$ M; $[9d (Z/E = 83/17)] = 5.5 \times 10^{-6}$ M; $[9d (Z/E = 39/61)] = 1.6 \times 10^{-5}$ M; $[(Z)-9e] = 5.0 \times 10^{-6}$ M; $[9e (Z/E = 5/95)] = 5.1 \times 10^{-6}$ M.







S13



5 Br

















S22

























S30













(E)-9a















































(E)-9e

