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

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10. General: All reactions were carried out in a well-dried glassware under an argon or nitrogen atmosphere. Dichloromethane, toluene, $\mathrm{N}, \mathrm{N}$-dimethylformamide and diethylamine were distilled from $\mathrm{CaH}_{2}$ under an Ar atmosphere. ${ }^{1} \mathrm{H}$ NMR (400, 300, or 270 MHz ) and ${ }^{13} \mathrm{C}$ NMR (100.4, 75.5 , or 67.8 MHz ) spectra were recorded in $\mathrm{CDCl}_{3}$ or $\mathrm{THF}-d_{8}$ at $30^{\circ} \mathrm{C}$. Chemical shifts are reported in parts per million downfield from internal tetramethylsilane for ${ }^{1} \mathrm{H}$ NMR spectra or $\mathrm{CHCl}_{3}(\delta=77.0)$ for ${ }^{13} \mathrm{C}$ NMR spectra. IR spectra were recorded as a neat film or as a KBr pellet. Recyclable preparative GPC separation was carried out with $600-\mathrm{mm} \times 20-\mathrm{mm}$ GPC columns and $\mathrm{CHCl}_{3}$ 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 ( $Z$ )-bromoalkenes ${ }^{1}$ ( $\mathbf{4 a}$ and $\mathbf{4 b}$ ), 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 ( $0.7 \mathrm{~mL}, 4.7$ mmol) in $\mathrm{Et}_{2} \mathrm{NH}(2.0 \mathrm{~mL})$ was added dropwise over 20 min to a deoxygenated suspension of (Z)-1-bromo-2-(3-bromo-2-thienyl)ethene ${ }^{3,4}(1.15 \mathrm{~g}, 4.29 \mathrm{mmol}), \mathrm{PdCl}_{2}\left(\mathrm{PPh}_{3}\right)_{2}(30.2 \mathrm{mg}, 0.043$ $\mathrm{mmol})$, and $\mathrm{CuI}(8.2 \mathrm{mg}, 0.043 \mathrm{mmol})$ in $\mathrm{Et}_{2} \mathrm{NH}(5.5 \mathrm{~mL})$ under $\mathrm{N}_{2}$. 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 $\mathrm{MgSO}_{4}$. After removal of the solvent in vacuo, the product was purified by column chromatography (hexane) on $\mathrm{SiO}_{2}$ to afford 967 mg (79\%) of (Z)-1-(3-bromo-2-thienyl)-4-(trimethylsilyl)-1-buten-3-yne as a yellow oil: ${ }^{1} \mathrm{H}$ NMR ( 270 MHz , $\left.\mathrm{CDCl}_{3}\right) \delta 7.31(\mathrm{dd}, J=5.4,0.9 \mathrm{~Hz}, 1 \mathrm{H}), 7.01(\mathrm{dd}, J=11.9,0.9 \mathrm{~Hz}, 1 \mathrm{H}), 6.99(\mathrm{~d}, J=5.4 \mathrm{~Hz}, 1 \mathrm{H})$, $5.68(\mathrm{~d}, J=11.9 \mathrm{~Hz}, 1 \mathrm{H}), 0.28(\mathrm{~s}, 9 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR $\left(75.5 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 134.7,131.1,129.3,126.4$, 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, $706 \mathrm{~cm}^{-1}$; MS (EI) $\mathrm{m} / \mathrm{z} 286,284\left(\mathrm{M}^{+}\right)$. HRMS (EI) calcd for $\mathrm{C}_{11} \mathrm{H}_{13} \mathrm{BrSSi}$ : 285.9670, 283.9691. Found: 285.9672, 283.9686.

A suspension of $\mathrm{K}_{2} \mathrm{CO}_{3} \quad(193 \quad \mathrm{mg}, \quad 1.40 \quad \mathrm{mmol})$ and (Z)-1-(3-bromo-2-thienyl)-4-(trimethylsilyl)-1-buten-3-yne ( $200 \mathrm{mg}, 0.701 \mathrm{mmol}$ ) 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 $\mathrm{MgSO}_{4}$. The solvent was removed in vacuo to give $148 \mathrm{mg}(99 \%)$ of 5 as a yellow oil: ${ }^{1} \mathrm{H}$ NMR $\left(270 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.32(\mathrm{~d}$, $J=5.4 \mathrm{~Hz}, 1 \mathrm{H}), 7.07(\mathrm{~d}, J=11.6 \mathrm{~Hz}, 1 \mathrm{H}), 7.01(\mathrm{~d}, J=5.4 \mathrm{~Hz}, 1 \mathrm{H}), 5.65(\mathrm{dd}, J=11.6,2.7 \mathrm{~Hz}, 1 \mathrm{H})$, $3.60(\mathrm{~d}, J=2.7 \mathrm{~Hz}, 1 \mathrm{H}){ }^{13} \mathrm{C} \operatorname{NMR}\left(67.8 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 134.4,132.0,129.4,126.5,114.2,105.4$, 88.4, 81.7; IR (KBr) 2957, 2925, 2136, 1488, 1376, 1341, 1250, 1153, 1014, 845, 760, $705 \mathrm{~cm}^{-1}$; MS (EI) $m / z$ 214, $212\left(\mathrm{M}^{+}\right)$. HRMS (EI) calcd for $\mathrm{C}_{8} \mathrm{H}_{5} \mathrm{BrS}: 213.9274$, 211.9295. Found: 213.9247,
211.9294.
(Z)-1-Bromo-2-(2-bromo-3-thienyl)ethene (7): Tetrabromomethane ( $21.0 \mathrm{~g}, 63.0 \mathrm{mmol}$ ) was added to a solution of 2-bromo-3-thiophenecarboxaldehyde ${ }^{5}(5.00 \mathrm{~g}, 26.2 \mathrm{mmol})$ and triphenylphosphine ( $26.2 \mathrm{~g}, 100 \mathrm{mmol}$ ) in dichloromethane ( 250 mL ) at $0^{\circ} \mathrm{C}$ under $\mathrm{N}_{2}$. After stirring for 10 min at rt , the reaction mixture was poured into a sat. $\mathrm{NaHCO}_{3}$ solution. The organic layer was separated and the aqueous layer was extracted with dichloromethane. The combined organic solution was dried over anhydrous $\mathrm{MgSO}_{4}$. After removal of the solvent in vacuo, the product was purified by flash chromatography (hexane) on $\mathrm{SiO}_{2}$ to afford $6.98 \quad \mathrm{~g} \quad$ (77\%) of 1,1-dibromo-2-(2-bromo-3-thienyl)ethene as a colorless oil.
A solution of $\mathrm{Pd}(\mathrm{OAc})_{2}(224 \mathrm{mg}, 1.00 \mathrm{mmol})$ and triphenylphosphine $(1.05 \mathrm{~g}, 4.00 \mathrm{mmol})$ in toluene ( 100 mL ) was stirred at rt for 1.5 h . A solution of 1,1-dibromo-2-(2-bromo-3-thienyl)ethene $(6.98 \mathrm{~g}, 20.0 \mathrm{mmol})$ and tributyltin hydride $(6.4 \mathrm{~mL}, 23.8 \mathrm{mmol})$ in toluene $(5 \mathrm{~mL})$ 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 $\mathrm{MgSO}_{4}$. After removal of the solvent in vacuo, the product was purified by flash chromatography (hexane) on $\mathrm{SiO}_{2}$ to afford 3.20 g (60\%) of (Z)-1-bromo-2-(2-bromo-3-thienyl)ethene (7) as a colorless oil: ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 7.81$ $(\mathrm{d}, J=5.6 \mathrm{~Hz}, 1 \mathrm{H}), 7.29(\mathrm{dd}, J=5.6,0.4 \mathrm{~Hz}, 1 \mathrm{H}), 7.08(\mathrm{dd}, J=8.0,0.4 \mathrm{~Hz}, 1 \mathrm{H}), 6.45(\mathrm{~d}, J=8.0 \mathrm{~Hz}$, $1 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 135.3$, 127.1, 125.7, 125.2, 114.8, 107.4; IR (neat) 3080, 2921, $1620,1395,1373,1318,1254,1045,997,935,876,826,765,741,695,604 \mathrm{~cm}^{-1}$; MS (EI) $\mathrm{m} / \mathrm{z} 270$, 268, $266\left(\mathrm{M}^{+}\right)$. HRMS (EI) calcd for $\mathrm{C}_{6} \mathrm{H}_{4} \mathrm{Br}_{2} \mathrm{~S}$ : 269.8358, 267.8380, 265.8400. Found: 269.8364, 267.8394, 265.8380.
(Z)-1-(3-Thienyl)-1-buten-3-yne ${ }^{6}$ (8): To a solution of ethynyltrimethylsilane ( $0.34 \mathrm{~mL}, 2.4$ mmol), bromoalkene $\mathbf{4 b}(378 \mathrm{mg}, 2.0 \mathrm{mmol})$, and $\mathrm{Et}_{2} \mathrm{NH}(1.0 \mathrm{~mL}, 9.7 \mathrm{mmol})$ in toluene ( 5.0 mL ) was added $\mathrm{CuI}(29.0 \mathrm{mg}, 0.015 \mathrm{mmol}, 7.5 \mathrm{~mol} \%)$, followed by $\operatorname{Pd}\left(\mathrm{PPh}_{3}\right)_{4}(58.0 \mathrm{mg}, 0.050 \mathrm{mmol}, 2.5$ $\mathrm{mol} \%$ ) under $\mathrm{N}_{2}$. After stirring at rt for 5 min , the reaction mixture was poured into a saturated aqueous $\mathrm{NH}_{4} \mathrm{Cl}$ solution. The organic layer was separated and the aqueous solution was extracted with ether. The combined organic solution was dried over anhydrous $\mathrm{MgSO}_{4}$. After removal of the solvent in vacuo, the product was purified by flash chromatography (hexane) on $\mathrm{SiO}_{2}$ to afford 410 $\mathrm{mg}(99 \%)$ of (Z)-1-(3-thienyl)-4-trimethylsilyl-1-buten-3-yne as a colorless oil: ${ }^{1} \mathrm{H}$ NMR ( 400 MHz , $\left.\mathrm{CDCl}_{3}\right) \delta 7.82(\mathrm{~d}, J=2.8 \mathrm{~Hz}, 1 \mathrm{H}), 7.68(\mathrm{dd}, J=5.2,1.2 \mathrm{~Hz}, 1 \mathrm{H}), 7.29(\mathrm{dd}, J=5.2,2.8 \mathrm{~Hz}, 1 \mathrm{H})$, $6.69(\mathrm{~d}, J=12.0 \mathrm{~Hz}, 1 \mathrm{H}), 5.61(\mathrm{~d}, J=12.0 \mathrm{~Hz}, 1 \mathrm{H}), 0.27(\mathrm{~s}, 9 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 138.6,133.6,127.9,125.8,124.9,105.9,104.2,102.0,-0.2$; IR (neat) 3096, 3025, 2959, 2898, $2138,1600,1421,1251,1148,1020,844,797,760,698,635 \mathrm{~cm}^{-1}$; MS (EI) $\mathrm{m} / \mathrm{z} 206\left(\mathrm{M}^{+}\right)$. HRMS (EI) calcd for $\mathrm{C}_{11} \mathrm{H}_{14} \mathrm{SSi}: 206.0586$. Found: 206.0589.

A suspension of $\mathrm{K}_{2} \mathrm{CO}_{3} \quad(550 \quad \mathrm{mg}, \quad 3.98$ mmol) and (Z)-1-(3-thienyl)-4-(trimethylsilyl)-1-buten-3-yne ( $400 \mathrm{mg}, 1.94 \mathrm{mmol}$ ) in $\mathrm{MeOH}(4.0 \mathrm{~mL}$ ) 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 $\mathrm{MgSO}_{4}$. The solvent was removed in vacuo to give $259 \mathrm{mg}(99 \%)$ of $\mathbf{8}$ as a pale yellow oil: ${ }^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, \mathrm{CDCl}_{3}, 30{ }^{\circ} \mathrm{C}$ ) $\delta$ $7.82-7.80(\mathrm{~m}, 1 \mathrm{H}), 7.67(\mathrm{dd}, J=5.1,0.6 \mathrm{~Hz}, 1 \mathrm{H}), 7.29(\mathrm{dd}, J=5.1,3.3 \mathrm{~Hz}, 1 \mathrm{H}), 6.75(\mathrm{~d}, J=12.0$, $1 \mathrm{H}), 5.58(\mathrm{dd}, J=12.0,2.7 \mathrm{~Hz}, 1 \mathrm{H}), 3.38(\mathrm{~d}, J=2.7 \mathrm{~Hz}, 1 \mathrm{H}) ;{ }^{13} \mathrm{C} \mathrm{NMR}\left(75.5 \mathrm{MHz}, \mathrm{CDCl}_{3}, 30^{\circ} \mathrm{C}\right)$ $\delta 138.2,134.3,127.8,125.9,125.1,104.9,84.1,82.5$; IR (neat) $3287,3095,3027,2089,1603,1418$, 1349, 1260, 1146, 1082, 873, 832, 797, 750, 692, $618 \mathrm{~cm}^{-1}$; MS (EI) $m / z 134$ (M ${ }^{+}$). HRMS (EI) calcd for $\mathrm{C}_{8} \mathrm{H}_{6} \mathrm{~S}: 134.0190$. Found: 134.0176.

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

The Sonogashira-Hagihara coupling reactions of $\mathbf{4 a}, \mathbf{4 b}$, or $\mathbf{8}$ with enynes $\mathbf{3},{ }^{7} \mathbf{7}$, or $\mathbf{5}$ gave the corresponding hexadienynes 2a-e in $55-93 \%$ yields. As a typical procedure, the preparation of hexadienyne $\mathbf{2 a}$ is described below:
(Z,Z)-1-(2-Bromophenyl)-6-(2-thienyl)-1,5-hexadien-3-yne (2a): A solution of enyne $\mathbf{3}$ (380 mg, $1.83 \mathrm{mmol})$ in $\mathrm{Et}_{2} \mathrm{NH}(5.0 \mathrm{~mL})$ was added dropwise slowly to a deoxygenated suspension of ( $Z$ )-bromoalkene $4 \mathbf{4 a}(310 \mathrm{mg}, 1.7 \mathrm{mmol}), \mathrm{PdCl}_{2}\left(\mathrm{PPh}_{3}\right)_{2}(15 \mathrm{mg}, 0.021 \mathrm{mmol}, 10 \mathrm{~mol} \%)$, and $\mathrm{CuI}(8$ $\mathrm{mg}, 0.04 \mathrm{mmol}, 20 \mathrm{~mol} \%)$ in $\mathrm{Et}_{2} \mathrm{NH}(10 \mathrm{~mL})$ under $\mathrm{N}_{2}$. 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 $\mathrm{MgSO}_{4}$. After removal of the solvent in vacuo, the product was purified by column chromatography (hexane) on $\mathrm{SiO}_{2}$ to afford $283 \mathrm{mg}(55 \%)$ of $\mathbf{2 a}(Z Z / E Z=98 / 2)$ as a yellowish oil. The $Z Z / E Z$ ratio of the products was determined by comparison of the integration of the vinyl proton signals adjacent to the acetylenic carbon in the ${ }^{1} \mathrm{H}$ NMR spectrum. Pure $(Z, Z)$-isomer was obtained by subjection of the isomeric mixtures to a recyclable preparative GPC: ${ }^{1} \mathrm{H}$ NMR ( $270 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 8.34$ (dd, $J=7.8$, $1.6 \mathrm{~Hz}, 1 \mathrm{H}), 7.59(\mathrm{~d}, J=7.8 \mathrm{~Hz}, 1 \mathrm{H}), 7.35-7.24(\mathrm{~m}, 3 \mathrm{H}), 7.13(\mathrm{td}, J=7.8,1.6 \mathrm{~Hz}, 1 \mathrm{H}), 7.01(\mathrm{~d}, J=$ $11.6 \mathrm{~Hz}, 1 \mathrm{H}), 7.01-6.98(\mathrm{~m}, 1 \mathrm{H}), 6.90(\mathrm{~d}, J=11.1 \mathrm{~Hz}, 1 \mathrm{H}), 6.13(\mathrm{dd}, J=11.6,3.0 \mathrm{~Hz}, 1 \mathrm{H}), 5.71(\mathrm{dd}$, $J=11.1,3.0 \mathrm{~Hz}, 1 \mathrm{H})$; relatively small vinyl proton signals were assigned to the $(E, Z)$-isomer: $\delta 7.45$ (d, $J=16.2 \mathrm{~Hz}, 1 \mathrm{H}), 6.96(\mathrm{~d}, J=11.3 \mathrm{~Hz}, 1 \mathrm{H}), 6.43(\mathrm{dd}, J=16.2,2.7 \mathrm{~Hz}, 1 \mathrm{H}), 5.73(\mathrm{dd}, J=11.3$, $2.7 \mathrm{~Hz}, 1 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $67.8 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 140.4,137.0,135.8,132.6,132.4,129.7,129.6,129.4$, $127.1,127.0,126.5,124.1,109.9,104.5,96.7,94.8$; IR (neat) $3053,3021,2923,2162,1587,1557$, 1467, 1434, 1213, 1023, 947, 831, 795, 768, 748, $702 \mathrm{~cm}^{-1}$; MS (EI) $\mathrm{m} / \mathrm{z} 316,314\left(\mathrm{M}^{+}\right)$. HRMS (EI) calcd for $\mathrm{C}_{16} \mathrm{H}_{11} \mathrm{BrS}: 315.9745,313.9765$. Found: 315.9734, 313.9775.
(Z,Z)-1-(2-Bromophenyl)-6-(3-thienyl)-1,5-hexadien-3-yne (2b): A yellowish colorless oil (93\%, $Z Z / E Z=91 / 9)$. The $Z Z / E Z$ ratio of the products was determined by comparison of the integration of
the vinyl proton signals adjacent to the acetylenic carbon in the ${ }^{1} \mathrm{H}$ NMR spectrum: ${ }^{1} \mathrm{H}$ NMR (270 $\left.\mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 8.27(\mathrm{dd}, J=7.8,1.6 \mathrm{~Hz}, 1 \mathrm{H}), 7.69(\mathrm{~d}, J=1.6 \mathrm{~Hz}, 1 \mathrm{H}), 7.60(\mathrm{dd}, J=7.8,1.6 \mathrm{~Hz}$, $1 \mathrm{H}), 7.53(\mathrm{dd}, J=4.9,1.6 \mathrm{~Hz}, 1 \mathrm{H}), 7.28(\mathrm{td}, J=7.8,1.6 \mathrm{~Hz}, 1 \mathrm{H}), 7.20(\mathrm{dd}, J=4.9,3.0 \mathrm{~Hz}, 1 \mathrm{H})$, $7.15(\mathrm{td}, J=7.8,1.6 \mathrm{~Hz}, 1 \mathrm{H}), 6.97(\mathrm{~d}, J=11.9 \mathrm{~Hz}, 1 \mathrm{H}), 6.67(\mathrm{~d}, J=11.9 \mathrm{~Hz}, 1 \mathrm{H}), 6.06(\mathrm{dd}, J=11.9$, $3.0 \mathrm{~Hz}, 1 \mathrm{H}), 5.75(\mathrm{dd}, J=11.9,3.0 \mathrm{~Hz}, 1 \mathrm{H})$; relatively small vinyl proton signals were assigned to the $(E, Z)$-isomer: $\delta 7.36(\mathrm{~d}, J=16.2 \mathrm{~Hz}, 1 \mathrm{H}), 6.73(\mathrm{~d}, J=11.9 \mathrm{~Hz}, 1 \mathrm{H}), 6.38(\mathrm{dd}, J=16.2,3.0 \mathrm{~Hz}$, $1 \mathrm{H}), 5.78(\mathrm{dd}, J=11.9,3.0 \mathrm{~Hz}, 1 \mathrm{H}) ;{ }^{13} \mathrm{C} \operatorname{NMR}\left(67.8 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 138.3,137.2,135.9,132.71$, 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, $634 \mathrm{~cm}^{-1}$; MS (EI) $\mathrm{m} / \mathrm{z} 316,314\left(\mathrm{M}^{+}\right)$. HRMS (EI) calcd for $\mathrm{C}_{16} \mathrm{H}_{11} \mathrm{BrS}: 315.9745,313.9765$. 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 ${ }^{1} \mathrm{H}$ NMR spectrum; $\mathrm{mp} 68-70{ }^{\circ} \mathrm{C} ;{ }^{1} \mathrm{H}$ NMR $\left(270 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.33(\mathrm{~d}, J=5.4 \mathrm{~Hz}, 1 \mathrm{H}), 7.30(\mathrm{~d}, J=1.6 \mathrm{~Hz}, 1 \mathrm{H}), 7.29$ $(\mathrm{d}, J=5.4 \mathrm{~Hz}, 1 \mathrm{H}), 7.07(\mathrm{~d}, J=11.3 \mathrm{~Hz}, 1 \mathrm{H}), 7.03(\mathrm{~d}, J=5.4 \mathrm{~Hz}, 1 \mathrm{H}), 7.01(\mathrm{dd}, J=5.4,1.6 \mathrm{~Hz}, 1 \mathrm{H})$, $6.97(\mathrm{~d}, J=11.3 \mathrm{~Hz}, 1 \mathrm{H}), 6.00(\mathrm{dd}, J=11.3,2.7 \mathrm{~Hz}, 1 \mathrm{H}), 5.85(\mathrm{dd}, J=11.3,2.7 \mathrm{~Hz}, 1 \mathrm{H})$; other six doublet of doublets signals at $\delta 6.32,6.25,6.19,6.14,5.84$, 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: $\delta 6.32(\mathrm{dd}, J=16.0,3.0 \mathrm{~Hz}, 1 \mathrm{H}), 6.25(\mathrm{dd}, J=16.0,3.0 \mathrm{~Hz}, 1 \mathrm{H}), 5.84(\mathrm{dd}, J=11.2$, $3.0 \mathrm{~Hz}, 1 \mathrm{H}), 5.71(\mathrm{dd}, J=11.2,3.0 \mathrm{~Hz}, 1 \mathrm{H}) ;(E, E)$-isomer: $\delta 6.19(\mathrm{dd}, J=16.0,2.8 \mathrm{~Hz}, 1 \mathrm{H}), 6.14$ $(\mathrm{dd}, J=16.0,2.8 \mathrm{~Hz}, 1 \mathrm{H}) ;{ }^{13} \mathrm{C} \operatorname{NMR}\left(67.8 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 140.5,134.9,132.4,130.0,129.6,129.4$, $127.2,126.5,113.7,106.6,104.5,99.4,97.5$; IR (neat) 3103, 3087, 2153, 1597, 1443, 1437, 1374, 1339, 1261, 1145, 1080, 880, 870, 795, 750, 714, $634 \mathrm{~cm}^{-1}$; MS (EI) $\mathrm{m} / \mathrm{z} 322,320\left(\mathrm{M}^{+}\right)$. HRMS (EI) calcd for $\mathrm{C}_{14} \mathrm{H}_{9} \mathrm{BrS}_{2}$ : 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\%, $Z Z / E Z=99 / 1)$. The $Z Z / E Z$ ratio of the products was determined by comparison of the integration of the vinyl proton signals adjacent to the acetylenic carbon in the ${ }^{1} \mathrm{H}$ NMR spectrum; mp $72-73{ }^{\circ} \mathrm{C}$; ${ }^{1} \mathrm{H}$ NMR ( $270 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 7.78(\mathrm{~d}, J=2.7 \mathrm{~Hz}, 1 \mathrm{H}), 7.66(\mathrm{dd}, J=4.9 .0 .5 \mathrm{~Hz}, 1 \mathrm{H}), 7.28(\mathrm{~d}, J=5.1$ $\mathrm{Hz}, 1 \mathrm{H}), 7.27(\mathrm{~d}, J=4.9 \mathrm{~Hz}, 1 \mathrm{H}), 7.05(\mathrm{~d}, J=11.1 \mathrm{~Hz}, 1 \mathrm{H}), 7.01(\mathrm{~d}, J=5.1 \mathrm{~Hz}, 1 \mathrm{H}), 6.75(\mathrm{~d}, J=$ $11.3 \mathrm{~Hz}, 1 \mathrm{H}), 5.94(\mathrm{dd}, J=11.1,3.0 \mathrm{~Hz}, 1 \mathrm{H}), 5.89(\mathrm{dd}, J=11.3,3.0 \mathrm{~Hz}, 1 \mathrm{H})$; other two doublet of doublets signals at $\delta 6.27$ and 5.85 ppm were assigned to the vinyl proton signals adjacent to the acetylenic carbon of ( $E, Z$ )-isomer: $\delta 6.27(\mathrm{dd}, J=16.0,3.0 \mathrm{~Hz}, 1 \mathrm{H}), 5.85(\mathrm{dd}, J=16.0,3.0 \mathrm{~Hz}, 1 \mathrm{H})$; ${ }^{13} \mathrm{C}$ NMR ( $67.8 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 138.4,134.8,132.8,130.1,129.4,127.7,126.4,125.8,125.3,113.7$, 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, $704 \mathrm{~cm}^{-1}$; MS (EI) $m / z 322,320\left(\mathrm{M}^{+}\right)$. HRMS (EI) calcd for
$\mathrm{C}_{14} \mathrm{H}_{9} \mathrm{BrS}_{2}$ : $321.9308,319.9329$. 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 $\mathbf{8}$ (188 mg, $1.4 \mathrm{mmol})$, bromoalkene $7(406 \mathrm{mg}, 1.5 \mathrm{mmol})$, and $\mathrm{Et}_{2} \mathrm{NH}(1.1 \mathrm{~mL}, 10 \mathrm{mmol})$ in toluene ( 5.0 mL ) was added $\mathrm{CuI}(28.0 \mathrm{mg}, 0.015 \mathrm{mmol}, 10 \mathrm{~mol} \%)$, followed by $\mathrm{Pd}\left(\mathrm{PPh}_{3}\right)_{4}(58.0 \mathrm{mg}, 0.050 \mathrm{mmol}, 3.5$ $\mathrm{mol} \%$ ) under $\mathrm{N}_{2}$. After stirring at rt for 5 min , the reaction mixture was poured into saturated aqueous $\mathrm{NH}_{4} \mathrm{Cl}$ solution. The organic layer was separated and the aqueous layer was extracted with ether. The combined organic solution was dried over anhydrous $\mathrm{MgSO}_{4}$. After removal of the solvent in vacuo, the product was purified by flash chromatography (hexane) on $\mathrm{SiO}_{2}$ to afford 333 mg (74\%) of 2e as a pale yellow solid: mp $54-56{ }^{\circ} \mathrm{C} ;{ }^{1} \mathrm{H} \mathrm{NMR}\left(300 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 8.00$ (dd, $J=5.7$, $0.4 \mathrm{~Hz}, 1 \mathrm{H}), 7.75-7.77(\mathrm{~m}, 1 \mathrm{H}), 7.61(\mathrm{ddd}, J=5.4,0.6,0.6 \mathrm{~Hz}, 1 \mathrm{H}), 7.28(\mathrm{ddd}, J=5.4,2.1,0.3 \mathrm{~Hz}$, $1 \mathrm{H}), 7.22(\mathrm{dd}, J=5.7,0.6 \mathrm{~Hz}, 1 \mathrm{H}), 6.73(\mathrm{~d}, J=11.7 \mathrm{~Hz}, 1 \mathrm{H}), 6.72(\mathrm{~d}, J=11.7 \mathrm{~Hz}, 1 \mathrm{H}), 5.97$ (ddd, $J$ $=11.7,2.7,0.6 \mathrm{~Hz}, 1 \mathrm{H}), 5.82(\mathrm{dd}, J=11.7,2.7 \mathrm{~Hz}, 1 \mathrm{H}){ }^{13} \mathrm{C} \operatorname{NMR}\left(75.5 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 138.4$, $137.1,132.7,130.2,127.7,126.6,125.6,125.4,125.3,114.6,107.9,105.9,96.0,94.2$; IR (KBr) 3093, 2157, 1603, 1429, 1263, 994, 871, 822, 796, 769, 716, 635, $624 \mathrm{~cm}^{-1}$; MS (EI) $\mathrm{m} / \mathrm{z} 322,320$ $\left(\mathrm{M}^{+}\right)$. Anal. Calcd for $\mathrm{C}_{14} \mathrm{H}_{9} \mathrm{BrS}_{2}$ : 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 ( 0.01 M ) of a hexadienynes $2 \mathbf{a}, \mathbf{b}, \mathbf{c}, \mathbf{d}$, or $\mathbf{e}$ in DMF was added to a mixture of $\operatorname{Pd}(\mathrm{OAc})_{2}(20 \mathrm{~mol} \%)$, triphenylphosphine ( $40 \mathrm{~mol} \%$ ), anhydrous potassium carbonate (3 eqiuv), and tetrabutylammonium bromide ( 1.1 equiv) and stirred. The resulting mixture was heated and stirried at $80^{\circ} \mathrm{C}$. 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 $\mathrm{MgSO}_{4}$. After removal of the solvent in vacuo, the residue was chromatographed on $\mathrm{SiO}_{2}$ (hexane) to afford the corresponding product as a mixture of Z - and $E$-isomers. In all case, $Z$-isomers were major products.

4-Indenylidene-4H-cyclopenta[b]thiophene ( $\boldsymbol{Z}$ )-9a and ( $\boldsymbol{E}$ )-9a) ( $85 \%$ yield, $Z / E=75 / 25$ determined by ${ }^{1} \mathrm{H}$ NMR spectrum). The proportion of $E$-isomer increased with increasing reaction time after consumption of the starting dienyne $\mathbf{2 a}(54 \%, Z / E=35 / 65)$. These isomers were separated by preparative HPLC. Dark unknown materials, which were insoluble in $\mathrm{CHCl}_{3}$, were formed gradually on standing a solution of $(Z)-\mathbf{9 a}$ in $\mathrm{CHCl}_{3}$ (or $\mathrm{CDCl}_{3}$ ). It was not possible therefore to measure the absorption spectrum of (Z)-9a accurately. (Z)-9a: a reddish solid; dec. $>300{ }^{\circ} \mathrm{C} ;{ }^{1} \mathrm{H}$ NMR (270 MHz, $\left.\mathrm{CDCl}_{3}\right) \delta 8.23(\mathrm{~d}, J=7.0 \mathrm{~Hz}, 1 \mathrm{H}), 7.71(\mathrm{~d}, J=4.9 \mathrm{~Hz}, 1 \mathrm{H}), 7.31-7.27(\mathrm{~m}, 2 \mathrm{H})$, $7.24-7.16(\mathrm{~m}, 1 \mathrm{H}), 7.19(\mathrm{~d}, J=4.9 \mathrm{~Hz}, 1 \mathrm{H}), 6.95(\mathrm{~d}, J=5.4 \mathrm{~Hz}, 1 \mathrm{H}), 6.91(\mathrm{~d}, J=5.4 \mathrm{~Hz}, 1 \mathrm{H}), 6.80$ $(\mathrm{d}, J=5.4 \mathrm{~Hz}, 1 \mathrm{H}), 6.77(\mathrm{~d}, J=5.4 \mathrm{~Hz}, 1 \mathrm{H}) ;{ }^{13} \mathrm{C} \operatorname{NMR}\left(67.8 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 149.5,144.9,142.8$, 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) $\mathrm{cm}^{-1}$; MS (EI) $\mathrm{m} / \mathrm{z} 234$ ( $\mathrm{M}^{+}$). HRMS (EI) calcd for $\mathrm{C}_{16} \mathrm{H}_{10} \mathrm{~S}: 234.0503$. Found: 234.0488. (E)-9a: a dark red solid; dec. > $300{ }^{\circ} \mathrm{C} ;{ }^{1} \mathrm{H}$ NMR ( $270 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 7.89(\mathrm{~d}, J=7.3 \mathrm{~Hz}, 1 \mathrm{H}), 7.33(\mathrm{~d}, J=5.1 \mathrm{~Hz}, 1 \mathrm{H}), 7.30-7.16(\mathrm{~m}, 3 \mathrm{H}), 7.16(\mathrm{~d}, J$ $=5.4 \mathrm{~Hz}, 1 \mathrm{H}), 7.16(\mathrm{~d}, J=5.4 \mathrm{~Hz}, 1 \mathrm{H}), 7.16(\mathrm{~d}, J=5.4 \mathrm{~Hz}, 1 \mathrm{H}), 7.02(\mathrm{~d}, J=5.1 \mathrm{~Hz}, 1 \mathrm{H}), 6.87(\mathrm{~d}, J$ $=5.4 \mathrm{~Hz}, 1 \mathrm{H}) ;{ }^{13} \mathrm{C} \mathrm{NMR}\left(67.8 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 146.0,144.1,141.4,140.7,136.7,136.2,136.1$, 129.5, 128.7, 128.0, 125.9, 125.8, 124.9, 124.9, 122.7, 121.9; IR (KBr) 3080, 3006, 1470, 1446, $1358,1221,1124,873,766,749,720,691,667 \mathrm{~cm}^{-1}$; UV $\left(25^{\circ} \mathrm{C}, \mathrm{CHCl}_{3}, 1.5 \times 10^{-5} \mathrm{M}\right) \lambda_{\max }(\log \varepsilon)$ 394 (4.48), 374 (4.46), 360 (4.25, sh) nm; MS (EI) $m / z 234$ ( $\mathrm{M}^{+}$). HRMS (EI) calcd for $\mathrm{C}_{16} \mathrm{H}_{10} \mathrm{~S}$ : 234.0503. Found: 234.0494.

6-Indenylidene-6 $\boldsymbol{H}$-cyclopenta[b]thiophene $((\boldsymbol{Z})-\mathbf{9 b}$ and $(\boldsymbol{E})-\mathbf{9 b})(89 \%, Z / E=89 / 11$ determined by ${ }^{1} \mathrm{H}$ NMR spectrum). These isomers were separated by preparative HPLC. $(Z)-9 \mathbf{b}(Z / E=89 / 11)$ : a reddish brown solid; dec. $>300{ }^{\circ} \mathrm{C} ;{ }^{1} \mathrm{H} \operatorname{NMR}\left(270 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 8.33-8.29(\mathrm{~m}, 1 \mathrm{H}), 7.47(\mathrm{~d}, J=$ $4.7 \mathrm{~Hz}, 1 \mathrm{H}), 7.36-7.30(\mathrm{~m}, 3 \mathrm{H}), 7.03(\mathrm{~d}, J=4.7 \mathrm{~Hz}, 1 \mathrm{H}), 6.96(\mathrm{~s}, 2 \mathrm{H}), 6.85(\mathrm{~s}, 2 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR (100.4 $\mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 153.1,144.6,141.8,135.8,134.6,133.9,131.3,130.6,129.8,129.2,129.1,127.9$, 126.9, 124.6, 121.8, 120.5; IR (KBr) 3090, 2925, 1474, 1448, 1370, 1325, 990, 865, 837, 764, 749, $644 \mathrm{~cm}^{-1} ; \mathrm{UV}\left(25{ }^{\circ} \mathrm{C}, \mathrm{CHCl}_{3}, 1.3 \times 10^{-5} \mathrm{M}\right)(\mathrm{Z} / E=89 / 11) \lambda_{\text {max }} 400,381 \mathrm{~nm} ; \mathrm{MS}(\mathrm{EI}) \mathrm{m} / \mathrm{z} 234\left(\mathrm{M}^{+}\right)$. HRMS (EI) calcd for $\mathrm{C}_{16} \mathrm{H}_{10} \mathrm{~S}$ : 234.0503. Found: 234.0497. $(E)-9 b(Z / E=6 / 94)$ : a reddish brown solid; dec. $>300{ }^{\circ} \mathrm{C}$; ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 7.86(\mathrm{~d}, J=7.3 \mathrm{~Hz}, 1 \mathrm{H}$ ), $7.33(\mathrm{dd}, J=4.8,0.7$ $\mathrm{Hz}, 1 \mathrm{H}), 7.27-7.25(\mathrm{~m}, 1 \mathrm{H}), 7.23(\mathrm{td}, J=7.3,1.3 \mathrm{~Hz}, 1 \mathrm{H}), 7.17(\mathrm{td}, J=7.3,1.7 \mathrm{~Hz}, 1 \mathrm{H}), 7.11(\mathrm{dd}, J$ $=5.6,0.7 \mathrm{~Hz}, 1 \mathrm{H}), 7.01(\mathrm{~d}, J=5.6 \mathrm{~Hz}, 1 \mathrm{H}), 6.99(\mathrm{~d}, J=5.6 \mathrm{~Hz}, 1 \mathrm{H}), 6.93(\mathrm{~d}, J=4.8 \mathrm{~Hz}, 1 \mathrm{H}), 6.88$ $(\mathrm{d}, J=5.6 \mathrm{~Hz}, 1 \mathrm{H}) ;{ }^{13} \mathrm{C} \operatorname{NMR}\left(100.4 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 149.7,144.3,140.4,136.7,136.5,135.8,135.3$, 131.1, 130.1, 128.6, 128.4, 125.8, 125.6, 124.6, 121.9, 120.1; IR (KBr) 3063, 3012, 1522, 1471, $1450,1370,1322,1186,761,721,643 \mathrm{~cm}^{-1}$; UV $\left(25{ }^{\circ} \mathrm{C}, \mathrm{CHCl}_{3}, 1.7 \times 10^{-5} \mathrm{M}\right)(Z / E=6 / 94) \lambda_{\max } 412$, 391 nm ; MS (EI) $m / z 234\left(\mathrm{M}^{+}\right)$. HRMS (EI) calcd for $\mathrm{C}_{16} \mathrm{H}_{10} \mathrm{~S}: 234.0503$. Found: 234.0513.
$\operatorname{Bi}(4 H$-cyclopenta[b]thienylidene) $((Z)-9 \mathbf{c}$ and $(E)-9 \mathbf{c})(38 \%$ yield, $Z / E=77 / 23):(Z)-9 \mathbf{c}(Z / E=$ $77 / 23$ ): a brown solid; dec. $>245{ }^{\circ} \mathrm{C}$; ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{THF}-d_{8}$ ) $\delta 7.65(\mathrm{~d}, J=4.8 \mathrm{~Hz}, 2 \mathrm{H}), 7.29$ (dd, $J=4.8,1.2 \mathrm{~Hz}, 2 \mathrm{H}), 6.84(\mathrm{~d}, J=5.6 \mathrm{~Hz}, 2 \mathrm{H}), 6.80(\mathrm{dd}, J=5.6,1.2 \mathrm{~Hz}, 2 \mathrm{H}),{ }^{13} \mathrm{C}$ NMR (100.4 $\left.\mathrm{MHz}, \mathrm{THF}-d_{8}\right) \delta 138.9,137.7,128.8,128.0,126.4,125.8,123.7$; IR (KBr) 3091, 2923, 1657, 1608, $1467,1350,1243,1206,1129,1040,868,827,688 \mathrm{~cm}^{-1}$; UV $\left(25^{\circ} \mathrm{C}, \mathrm{CHCl}_{3}, 5.7 \times 10^{-6} \mathrm{M}\right)(Z / E=$ 85/15) $\lambda_{\max } 381,364,348(\mathrm{sh}) \mathrm{nm}$; MS (EI) $m / z 240\left(\mathrm{M}^{+}\right) .(E)-9 \mathrm{c}(Z / E=3 / 97)$ : a brown solid; ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{THF}-d_{8}$ ) $\delta 7.41(\mathrm{~d}, J=4.8 \mathrm{~Hz}, 2 \mathrm{H}), 7.23(\mathrm{dd}, J=4.8,1.3 \mathrm{~Hz}, 2 \mathrm{H}), 7.01(\mathrm{dd}, J=$ $5.5,1.3 \mathrm{~Hz}, 2 \mathrm{H}), 6.90(\mathrm{~d}, J=5.5 \mathrm{~Hz}, 2 \mathrm{H}){ }^{13} \mathrm{C}$ NMR (100.4 MHz, THF-d $)^{\text {}}$ ) $147.9,140.9,137.5$, 130.1, 126.8, 126.6, 123.2. UV ( $25^{\circ} \mathrm{C}, \mathrm{CHCl}_{3}, 1.3 \times 10^{-5} \mathrm{M}$ ) $(Z / E=3 / 97) \lambda_{\max } 387,368,350(\mathrm{sh})$ $\mathrm{nm} ; \mathrm{MS}(\mathrm{EI}) \mathrm{m} / \mathrm{z} 240\left(\mathrm{M}^{+}\right)$. HRMS (EI) Calcd for $\mathrm{C}_{14} \mathrm{H}_{18} \mathrm{~S}_{2}$ : 240.0067. Found: 240.0051.

4-( $\mathbf{6 H} \boldsymbol{H}$-cyclopenta $[\boldsymbol{b}]$ thienylidene)-4 $\boldsymbol{H}$-cyclopenta $[\boldsymbol{b}]$ thiophene ( $(\boldsymbol{Z})$-9d and (E)-9d) (49\% yield, $Z / E=83 / 17) .(Z)-9 d(Z / E=83 / 17):$ a brown solid; dec. $>250{ }^{\circ} \mathrm{C} ;{ }^{1} \mathrm{H}$ NMR $\left(400 \mathrm{MHz}, \mathrm{THF}-d_{8}\right) \delta$
$7.78(\mathrm{~d}, J=5.1 \mathrm{~Hz}, 1 \mathrm{H}), 7.60(\mathrm{dd}, J=4.7,0.9 \mathrm{~Hz}, 1 \mathrm{H}), 7.34(\mathrm{dd}, J=5.1,1.3 \mathrm{~Hz}, 1 \mathrm{H}), 7.03(\mathrm{~d}, J=$ $4.7 \mathrm{~Hz}, 1 \mathrm{H}), 6.86(\mathrm{~d}, J=5.6 \mathrm{~Hz}, 1 \mathrm{H}), 6.85(\mathrm{~d}, J=5.6 \mathrm{~Hz}, 1 \mathrm{H}), 6.83(\mathrm{dd}, J=5.6,0.9 \mathrm{~Hz}, 1 \mathrm{H}), 6.81$ $(\mathrm{dd}, J=5.6,1.3 \mathrm{~Hz}, 1 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR (100.4 MHz, THF- $d_{8}$ ) $\delta 154.0,149.7,138.8,137.0,136.9,132.8$, 132.2, 129.7, 129.6, 128.1, 127.9, 126.7, 123.0, 121.0; IR (KBr) 3087, 2921, 1614, 1470, 1357, 1271, $1212,1121,995,869,831,758,654 \mathrm{~cm}^{-1}$; UV $\left(25^{\circ} \mathrm{C}, \mathrm{CHCl}_{3}, 5.5 \times 10^{-6} \mathrm{M}\right)(Z / E=83 / 17) \lambda_{\max } 399$, 380, 362 (sh) nm; MS (EI) m/z $240\left(\mathrm{M}^{+}\right)$. HRMS (EI) Calcd for $\mathrm{C}_{14} \mathrm{H}_{18} \mathrm{~S}_{2}$ : 240.0067. Found: 240.0066. $(E)-9 d(Z / E=39 / 61)$ : a brown solid; ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{THF}-d_{8}$ ) $\delta 7.46(\mathrm{dd}, J=5.0,0.6$ $\mathrm{Hz}, 1 \mathrm{H}), 7.38(\mathrm{~d}, J=5.2 \mathrm{~Hz}, 1 \mathrm{H}), 7.23(\mathrm{dd}, J=5.2,1.3 \mathrm{~Hz}, 1 \mathrm{H}), 6.96(\mathrm{dd}, J=5.6,0.6 \mathrm{~Hz}, 1 \mathrm{H}), 6.93$ $(\mathrm{d}, J=5.0 \mathrm{~Hz}, 1 \mathrm{H}), 6.89(\mathrm{~d}, J=5.7 \mathrm{~Hz}, 1 \mathrm{H}), 6.87(\mathrm{~d}, J=5.6 \mathrm{~Hz}, 1 \mathrm{H}), 6.74(\mathrm{dd}, J=5.7,1.3 \mathrm{~Hz}$, $1 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR (100.4 MHz, THF- $d_{8}$ ) $\delta 152.3,148.0,140.7,137.5,136.7,134.9,131.8,130.6,127.6$, 127.1, 126.4, 123.0, 120.8, 112.8; UV ( $25{ }^{\circ} \mathrm{C}, \mathrm{CHCl}_{3}, 1.6 \times 10^{-5} \mathrm{M}$ ) $(Z / E=39 / 61) \lambda_{\max } 404,386$, 370 (sh) nm; MS (EI) m/z $240\left(\mathrm{M}^{+}\right)$.
(Z)-Bi( $\mathbf{6 H}$-cyclopenta[b]thienylidene) ( $(\boldsymbol{Z})-\mathbf{9 e})\left(87 \%\right.$ yield): a deep red crylstal; dec. $>250{ }^{\circ} \mathrm{C}$; ${ }^{1} \mathrm{H}$ NMR ( $270 \mathrm{MHz}, \mathrm{THF}-d_{8}$ ) $\delta 7.66(\mathrm{dd}, J=4.8 \mathrm{~Hz}, 2 \mathrm{H}), 7.08(\mathrm{~d}, J=4.8 \mathrm{~Hz}, 2 \mathrm{H}), 6.91(\mathrm{~d}, J=5.7$ $\mathrm{Hz}, 2 \mathrm{H}), 6.87(\mathrm{dd}, J=5.7 \mathrm{~Hz}, 2 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR (100.4 MHz, THF- $d_{8}$ ) $\delta 153.3,136.2,132.3,132.2$, 129.6, 128.9, 121.0; IR (KBr) 3092, 1522, 1460, 1339, 1321, 1297, 1220, 1092, 990, 876, 838, 756, $706,639 \mathrm{~cm}^{-1}$; UV $\left(25^{\circ} \mathrm{C}, \mathrm{CHCl}_{3}, 5.1 \times 10^{-6} \mathrm{M}\right) \lambda_{\text {max }}(\log \varepsilon) 410(4.63), 389(4.57), 368(4.28, \mathrm{sh})$ $\mathrm{nm} ; \mathrm{MS}(\mathrm{EI}) m / z 240\left(\mathrm{M}^{+}\right)$. HRMS (EI) calcd for $\mathrm{C}_{14} \mathrm{H}_{8} \mathrm{~S}_{2}: 240.0067$. Found: 240.0062. In this case, the reaction proceeded even with a smaller amount of the catalyst and the additive $\left(\operatorname{Pd}(\mathrm{OAc})_{2}(5\right.$ $\mathrm{mol} \%), \mathrm{PPh}_{3}(10 \mathrm{~mol} \%)$ ) 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 $(0.01 \mathrm{M})$ of the bridged phenylthienylethenes $\mathbf{9 a}, \mathbf{b}$, or $\mathbf{e}$ in DMF was added to a mixture of $\mathrm{Pd}(\mathrm{OAc})_{2}$ ( $20 \mathrm{~mol} \%$ ) and triphenylphosphine ( $40 \mathrm{~mol} \%$ ). The resulting mixture was heated at $80{ }^{\circ} \mathrm{C}$. The progress of the isomerization reaction was monitored by ${ }^{1} \mathrm{H}$ 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 $9 \mathbf{a}$ or $\mathbf{b}$ ( 0.01 mmol , a mixture of isomers) in THF $(0.75 \mathrm{~mL})$ 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 $9 \mathbf{c}, \mathbf{d}$, or $\mathbf{e}(0.01 \mathrm{mmol})$ and anhydrous 1,4 -dioxane ( 1.0 mg , as an internal standard) in THF- $d_{8}(0.75 \mathrm{~mL})$ 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 ${ }^{1} \mathrm{H}$ NMR spectroscopy. The diastereoisomer ratios were determined by comparing with integrations of the diagnostic peaks of the $(Z)$ - and $(E)$-isomers.
( $\boldsymbol{E})$ - $\mathbf{B i}($ cyclopenta $[\boldsymbol{b}]$ thienylidene) ( $(\boldsymbol{E})-\mathbf{9 e})$ : Preparative scale photolysis was conducted as follows: A solution of $(Z)-9 \mathbf{e}(10 \mathrm{mg}, 0.042 \mathrm{mmol})$ 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 $\mathrm{SiO}_{2}$ to give a 3.0 mg of $(E)-9 \mathbf{e}(30 \%)$ as a deep red solid together with 3.0 mg of unreacted (Z)-9e; dec. $>250{ }^{\circ} \mathrm{C} ;{ }^{1} \mathrm{H}$ NMR $\left(400 \mathrm{MHz}, \mathrm{THF}-d_{8}\right) \delta$ $7.44(\mathrm{~d}, J=4.8 \mathrm{~Hz}, 2 \mathrm{H}), 6.92(\mathrm{~d}, J=4.8 \mathrm{~Hz}, 2 \mathrm{H}), 6.85(\mathrm{~d}, J=5.6 \mathrm{~Hz}, 2 \mathrm{H}), 6.69(\mathrm{~d}, J=5.6 \mathrm{~Hz}, 2 \mathrm{H})$; ${ }^{13} \mathrm{C}$ NMR (100.4 MHz, THF- $d_{8}$ ) $\delta 152.4,136.7,134.6,132.2,131.9,127.5,121.0$; IR (KBr) 3081, 2924, 2853, 1518, 1465, 1447, 1325, 1218, 1103, 1037, 994, 875, 830, 755, 717, 659, 614, 593, 570, $524 \mathrm{~cm}^{-1} ; \mathrm{UV}\left(25{ }^{\circ} \mathrm{C}, \mathrm{CHCl}_{3}, 5.0 \times 10^{-6} \mathrm{M}\right)(Z / E=5 / 95) \lambda_{\max } 422,398,378(\mathrm{sh}) \mathrm{nm} ; \mathrm{MS}(\mathrm{EI}) \mathrm{m} / \mathrm{z}$ $240\left(\mathrm{M}^{+}\right)$. HRMS (EI) calcd for $\mathrm{C}_{14} \mathrm{H}_{8} \mathrm{~S}_{2}: 240.0067$. Found: 240.0062.

## 7. References:

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


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