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Supporting Information

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Creating a Reactive Enediyne Using Visible Light: Photocontrol of the Bergman Cyclization

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Experimental

General. All solvents used for synthesis and characterization were dried and degassed by passing them under nitrogen through steel columns containing activated alumina using an MBraun solvent purification system. Solvents for NMR analysis (Cambridge Isotope Laboratories) were used as received. Flash chromatography was performed using silica get 60 (230–400 mesh) from Silicycle Inc. Centrifugal chromatography was performed using a Harrison Research Inc. Chromatotron, model 8924 using TLC grade 7749 silica gel from Merck. All reagents were purchased from Aldrich with the exception of (trimethylsilyl)acetylene, which was purchased from Alfa Aesar, and $Pd(PPh_3)_4$ and Cp_2ZrCl_2 which were purchased from Strem. The starting materials, 3,5-dibromo-2-methylthiophene[1] and 1-(2-bromoethynyl)benzene[2] were prepared according to the literature procedures.

Techniques. ^{1}H NMR and ^{13}C NMR characterizations were performed on a Bruker AMX 400 instrument with a 5 mm inverse probe operating at 400.13 MHz for ^{1}H NMR and 100.6 MHz for ^{13}C NMR, a Varian 400 MercuryPlus instrument with a 5 mm ATB probe equipped with a shielded gradient operating at 400.10 MHz for ^{1}H NMR and 100.60 MHz for ^{13}C NMR, a Varian Inova 500 instrument with a 5 mm inverse probe equipped with a shielded gradient operating at 499.8 MHz for ^{1}H NMR and 125.7 MHz for ^{13}C NMR or a Bruker Avance II 600 with a 5 mm QNP cryoprobe operating at 150.90 MHz for ^{13}C NMR. Chemical shifts (δ) are reported in parts per million relative to tetramethylsilane using the residual solvent peak as a reference standard. Coupling constants (J) are reported in Hertz. FT-IR spectroscopy was performed using a Nicolet Nexus 670 instrument. UV-VIS absorption spectroscopy was performed using a Varian

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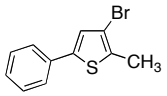
[1] L. N. Lucas, J. van Esch, R. M. Kellogg, B. L. Feringa, *Tetrahedron Lett.* **1999**, *40*, 1775–1778.

[2] M. X. W. Jiang, M. Rawat, W. D. Wulff, *J. Am. Chem. Soc.* **2004**, *126*, 5970–5971.

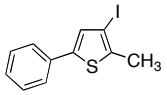
Cary 300 Bio spectrophotometer. Low resolution mass spectrometry (LRMS) measurements were performed using a HP5935 mass spectrometer, a Varian 4000 GC/MS/MS with electron impact operating at 10 mamp as the ionization source or chemical ionization (CI) with methanol or a PerSeptive Biosystems Voyager-DE Biospectrometry Workstation MALDI spectrometer. Melting points were measured using a Fisher-Johns melting point apparatus.

Photochemistry. Standard hand-held lamps used for visualizing TLC plates (Spectroline E-series, 470 mW/cm^2)[3] were used to carry out the ring-closing reactions at 365 nm. The ring-opening reactions were carried out using the light of a 150-W tungsten source that was passed through a 490 nm cutoff filter to eliminate higher energy light.



Synthesis of 3-bromo-2-methyl-5-phenylthiophene (2).[4] A two-phase mixture containing toluene (100 mL), aqueous Na_2CO_3 (100 mL, 2 M) and 3,5-dibromo-2-methylthiophene (15.0 g, 58.6 mmol) was deoxygenated by bubbling N_2 through it for 60 min. This mixture was treated with a solution of phenylboronic acid (7.15 g, 58.6 mmol) in EtOH (50 mL) and the reaction was bubbled with N_2 for an additional 30 min, at which time $Pd(PPh_3)_4$ (0.6 g, 0.5 mmol) was added in one portion. The reaction was heated at reflux for 16 h under an N_2 atmosphere. The heat source was removed and the reaction was allowed to cool to room temperature. The mixture was extracted with Et_2O (3 × 100 mL). The combined organic layers were extracted with brine (100 mL), dried using Na_2SO_4, filtered and evaporated to dryness *in vacuo*. Purification by flash chromatography (SiO_2, hexanes) yielded 11.1 g (75%) of 3-bromo-2-methyl-5-phenylthiophene (**2**) as a white solid.

M.p. = 71–72 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.51 (d, J = 7.2 Hz, 2H), 7.37 (t, J = 7.6 Hz, 2H), 7.28–7.30 (m, 1H), 7.10 (s, 1H), 2.42 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 141.0, 133.5, 133.4, 128.9, 127.7, 125.4, 125.2, 109.8, 14.8.



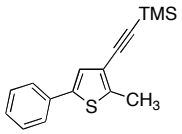
Synthesis of 3-iodo-2-methyl-5-phenylthiophene. A solution of 3-bromo-2-methyl-5-phenylthiophene (**2**) (2.0 g, 7.9 mmol) in anhydrous Et_2O (50 mL) was treated dropwise with *n*-butyllithium (3.79 mL, 2.5 M in hexanes, 9.5 mmol) over 5 min at –78 °C under an N_2 atmosphere. The resulting solution was stirred at this temperature for 30 min then quickly treated with a solution of I_2 (2.0 g, 8.7 mmol) in anhydrous Et_2O (20 mL) using a cannula. After stirring at this temperature for 1 h, the cooling bath was removed and the reaction was allowed to slowly warm to room temperature and stirred there for 18 h, at

[3] The power of the light source is given based on the specifications supplied by the company when the lamps were purchased. A light detector was not used to measure the intensity during the irradiation experiments.

[4] M. Irie, T. Lifka, S. Kobatake, N. Kato, *J. Am. Chem. Soc*. **2000**, *122*, 4871–4876.

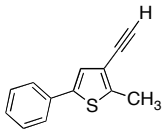
which time it was quenched with saturated aqueous solution of NH_4Cl (25 mL). The aqueous layer was separated and extracted with Et_2O (3 × 50 mL). The combined organic layers were then washed with 20% $Na_2S_2O_3$•$5H_2O$ (100 mL) and then brine (1 × 50 mL), dried over Na_2SO_4, filtered and evaporated to dryness *in vacuo*. Purification by flash chromatography (SiO_2, hexanes) yielded 1.7 g (72%) of 3-iodo-2-methyl-5-phenylthiophene as off-white crystals.

M.p. = 64–66 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.51 (d, J = 7.2 Hz, 2H), 7.36 (t, J = 7.2 Hz, 2H), 7.28 (d, J = 7.2 Hz, 1H), 7.16 (s, 1H) 2.44 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 142.7, 138.0, 133.4, 130.3, 128.9, 127.7, 125.4, 81.1, 18.0. FT-IR (KBr-cast): 1499, 1442, 1328, 1155, 1073, 1032, 1008, 830, 792, 758, 709, 689, 591, 463 cm^{-1}. LRMS (EI) m/z = 300 $[M]^+$. Anal. Calcd. For $C_{11}H_9SI$: C, 44.02; H, 3.02. Found: C, 44.33; H, 3.16.



Synthesis of trimethyl(2-(2-methyl-5-phenylthiophen-3-yl)ethynyl)silane (3). A solution of 3-iodo-2-methyl-5-phenylthiophene (0.70 g, 2.3 mmol) in anhydrous diisopropylamine (50 mL) was treated with dichlorobis(triphenylphosphine)palladium(II) (10 mg, 0.014 mmol), triphenylphosphine (4 mg, 0.015 mmol) and copper(I) iodide (3 mg, 0.016 mmol). The resulting solution was then treated with an excess of trimethylsilylacetylene (3.25 mL, 23.3 mmol) under an N_2 atmosphere and heated at 70 °C for 18 h, at which time it was filtered while hot and evaporated to dryness *in vacuo*. Purification by flash chromatography (SiO_2, hexanes) yielded 590 mg (93%) of trimethyl(2-(2-methyl-5-phenylthiophen-3-yl)ethynyl)silane (**3**) as an off white solid.

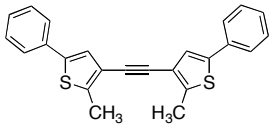
M.p. = 50–53 °C. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.51 (d, J = 8.0 Hz, 2H), 7.35 (d, J = 8.0 Hz, 2H), 7.26 (m, 1H), 2.53 (s, 3H), 0.26 (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 144.1, 139.9, 133.7, 128.7, 127.3, 125.4, 125.1, 120.7, 99.5, 96.4, 14.5, 0.0. FT-IR (KBr-cast): 2965, 2150, 1248, 1098, 897, 837, 751, 684 cm^{-1}. LRMS (EI) m/z = 270 $[M]^+$. Anal. Calcd. For $C_{16}H_{18}SSi$: C, 71.05; H, 6.71. Found: C, 71.04; H, 6.85.



Synthesis of 3-ethynyl-2-methyl-5-phenylthiophene. A solution of trimethyl(2-(2-methyl-5-phenylthiophen-3-yl)ethynyl)silane (**3**) (600 mg, 2.2 mmol) and K_2CO_3 (338 mg, 2.4 mmol) in methanol (25 mL) was stirred at room temperature for 1 h. The resulting suspension was evaporated to dryness *in vacuo*. The crude product was taken up in water (50 mL) and extracted with Et_2O (3 × 50 mL). The combined organic layers were dried with Na_2SO_4, filtered and evaporated to dryness *in vacuo*. Purification by flash chromatography (SiO_2, hexanes) yielded 387 mg (88%) of 3-ethynyl-2-methyl-5-phenylthiophene (**3**) as an off-white solid.

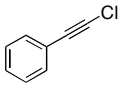
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.52 (d, J = 7.2 Hz, 2H), 7.36 (t, J = 7.2 Hz, 2H), 7.27-

7.29 (m, 1H), 7.19 (s, 3H) 3.20 (s, 1H), 2.55 (s, 3H). LRMS (EI) m/z = 198 $[M]^+$.



Synthesis of (Z)-1,2-bis(5-phenyl-2-methylthiophen-3-yl)acetylene (4). A solution of 3-iodo-2-methyl-5-phenylthiophene (395 mg, 1.3 mmol) in anhydrous diisopropylamine (50 mL), was treated with dichloro-bis(triphenylphosphine)palladium(II) (10 mg, 0.014 mmol), triphenylphosphine (4 mg, 0.015 mmol) and copper(I) iodide (3 mg, 0.016 mmol). The resulting solution was treated with 3-ethynyl-2-methyl-5-phenylthiophene (389 mg, 2.0 mmol) under an N_2 atmosphere and heated at 70 °C for 18 h, at which time it was evaporated to dryness *in vacuo*. Purification by flash chromatography (SiO_2, hexanes) yielded 380 mg (78%) of 2-methyl-3-(2-(2-methyl-5-phenylthiophen-3-yl)ethynyl)-5-phenylthiophene (**4**) as a pale yellow solid.

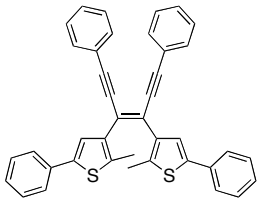
M.p. = 177–180 °C. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.56 (d, J = 7.5 Hz, 4H), 7.38 (t, J = 7.5 Hz, 4H), 7.29 (d, J = 6.5 Hz, 2H), 7.25 (s, 2H), 2.61 (s, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 142.5, 140.3, 133.8, 128.9, 127.5, 125.5, 125.1, 120.8, 86.2, 14.7. FT-IR (KBr-cast): 1499, 1426, 1092, 901, 832, 751, 685 cm^{-1}. LRMS (EI) m/z = 370 $[M]^+$. Anal. Calcd. For $C_{24}H_{18}S_2$: C, 77.80; H, 4.90. Found: C, 77.95; H, 4.85.



Synthesis of 1-(2-chloroethynyl)benzene.[5] A solution of phenylacetylene (2.0 g, 19.6 mmol) in THF (40 mL) was treated dropwise with *n*-butyllithium (8.0 mL, 2.5 M in hexanes, 21.5 mmol) over 5 min at –78 °C under an N_2 atmosphere. The resulting suspension was stirred at this temperature for 30 min, at which time a solution of *N*-chlorosuccinimide (2.87 g, 21.5 mmol) in THF (20 mL) was added in rapidly through a cannula. After stirring at this temperature for 1 h, the cooling bath was removed and the reaction was allowed to slowly warm to room temperature and stirred there for 18 h. The reaction was quenched with saturated NH_4Cl (25 mL), the aqueous layer was separated and extracted with Et_2O (3 × 50 mL). The combined organic layers were dried with Na_2SO_4, filtered and evaporated to dryness *in vacuo*. Purification by flash chromatography (SiO_2, hexanes) yielded 1.94 g (73%) of 1-(2-chloroethynyl)benzene as a clear oil.

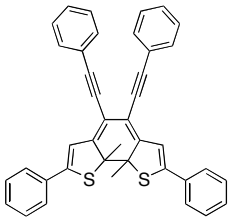
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.44 (dd, J = 6.0, 1.2 Hz, 2H), 7.30-7.34 (m, 3H).

[5] Y. H. Liu, Z. Q. Zhong, K. Nakajima, T. Takahashi, *J. Org. Chem.* **2002**, *67*, 7451–7456.



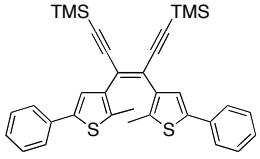
Synthesis of (Z)-1,6-bis(phenyl)-3,4-bis(5'-phenyl-2'-methylthiophen-3'-yl)hex-3-en-1,5-diyne (6). A solution of Cp_2ZrCl_2 (494 mg, 1.69 mmol) in THF (12.5 mL) was treated with EtMgCl (1.69 mL, 2.0 M THF solution, 3.37 mmol) at –78 °C. The reaction mixture was stirred for 1 h at the same temperature, at which time, (Z)-1,2-bis(5-phenyl-2-methylthiophen-3-yl)acetylene (**4**) (500 mg, 1.35 mmol) was added. After warming to 0 °C and stirring at this temperature for 90 min, 1-(2-chloroethynyl)benzene (184 mg, 1.35 mmol) was added. The reaction was allowed to warm to room temperature and stirred there for 30 min followed by heating at 50 °C for 2 h. The reaction mixture was treated with 1-(2-bromoethynyl)benzene (326 mg, 1.69 mmol) and CuCl (13 mg, 0.13 mmol) stirred at 50 °C for 18 h. The reaction mixture was evaporated to dryness *in vacuo* and purification by flash chromatography (SiO_2, 10% CH_2Cl_2 in hexanes) yielding 300 mg (39%) of compound **6** as a green crystalline solid.

M.p. = 70–75 °C. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.58-7.55 (m, 4H), 7.44 (d, J = 7.0 Hz, 4H), 7.38-7.36 (m, 6H), 7.32 (t, J = 7.0 Hz, 4H), 7.23 (t, J = 7.5 Hz, 2H), 7.01 (s, 2H), 2.33 (s, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 139.9, 137.5, 135.0, 134.2, 131.7, 128.8, 128.6, 128.4, 127.2, 125.6, 125.0, 124.8, 123.4, 96.9, 90.5, 14.5. FT-IR (KBr-cast): 1597, 1486, 1441, 1069, 1027, 947, 911, 841, 758, 688, 530, 489, 466 cm^{-1}. LRMS: (MALDI) m/z = 573 $[M+1]^+$. Anal. Calcd. For $C_{40}H_{28}S_2$: C, 83.88; H, 4.93. Found: C, 83.79; H, 5.03.



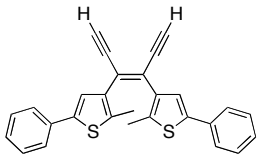
Photochemical synthesis of the ring-closed isomer of (Z)-1,6-bis(phenyl)-3,4-bis(5'-phenyl-2'-methylthiophen-3'-yl)hex-3-en-1,5-diyne (6). A solution of compound **6** (2 mg, 0.003 mmol) in C_6D_6 (0.8 mL) was placed in a 5-mm NMR tube and irradiated with 365 nm light for 5 min yielding a solution of the photostationary state containing 92% of the ring-closed isomer according to the ^{1}H NMR spectrum. The remaining 8% was assigned to the ring-open isomer **6**. The ring-closed isomer was not purified.

^{1}H NMR (C_6D_6, 500 MHz) δ 7.62 (d, J = 7.5 Hz, 4 H), 7.39-7.41 (m, 4 H), 7.07 (s, 2 H), 6.93-7.02 (m, 12 H), 2.38 (s, 6 H).



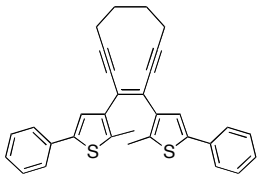
Synthesis of (Z)-1,6-bis(trimethysilyl)-3,4-bis(5'-phenyl-2'-methylthiophen-3'-yl)hex-3-en-1,5-diyne (5). A solution of Cp_2ZrCl_2 (494 mg, 1.69 mmol) in THF (25 mL) was treated with EtMgCl (1.69 mL, 2.0 M THF solution, 3.37 mmol) at –78 ºC. After stirring for 90 min at the same temperature, the reaction mixture was treated with (Z)-1,2-bis(5-phenyl-2-methylthiophen-3-yl)acetylene (**4**) (500 mg, 1.35 mmol) and warmed to 0 °C. After stirring for 2 h, the reaction was treated with 1-(2-bromoethynyl)benzene[2] (250 mg, 1.42 mmol) and stirred at room temperature for 30 min, followed by heating at 50 °C for 1 h. The reaction was treated with 1-(2-bromoethynyl)benzene (250 mg, 1.42 mmol) and CuCl (13 mg, 0.13 mmol) and stirred at 50 °C for 3 h. The heating source was removed, reaction was allowed to cool to room temperature and stirred there for 16 h, at which time it was quenched with NH_4Cl (25 mL) and extracted with EtOAc (3 × 50 mL). The combined organic layers were dried with Na_2SO_4, filtered and evaporated to dryness *in vacuo*. Purification by flash chromatography (SiO_2, 10–50% CH_2Cl_2 in hexanes) followed by centrifugal chromatography (SiO_2, 10% CH_2Cl_2 in hexanes) and crystallization from MeOH/CH_2Cl_2 yielded 340 mg (45%) of compound (**5**) as colourless needles.

M.p. = 178–180 °C. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.37 (d, J = 7.5 Hz, 4H), 7.30 (t, J = 7.5 Hz, 4H), 7.23-7.20 (m, 2H), 6.83 (s, 2H), 2.23 (s, 6H), 0.27 (s, 18H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 139.6, 137.6, 134.5, 134.1, 128.8, 127.2, 125.7, 125.5, 124.7, 104.6, 102.5, 14.4, 0.0. FT-IR (KBr-cast): 3448, 2958, 2143, 1249, 847, 756, 691 cm^{-1}. LRMS (EI) m/z = 565 $[M]^+$. Anal. Calcd. For $C_{34}H_{36}S_2Si_2$: C, 72.28; H, 6.42. Found: C, 72.19; H, 6.55.



Synthesis of (Z)-3,4-bis(5'-phenyl-2'-methylthiophen-3'-yl)hex-3-en-1,5-diyne. A solution of compound **5** (250 mg, 0.44 mmol) and potassium carbonate (306 mg, 2.21 mmol) in methanol (50 mL) and THF (50 mL) was stirred at room temperature for 1 h. The resulting suspension was evaporated to dryness *in vacuo*. Purification by flash chromatography (SiO_2, 25% CH_2Cl_2 in hexanes) yielded (Z)-3,4-bis(5'-phenyl-2'-methylthiophen-3'-yl)hex-3-en-1,5-diyne which was used directly in the next reaction.

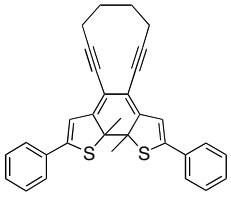
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.41 (d, J = 8.0 Hz, 4H), 7.31 (t, J = 7.4 Hz, 4H), 7.20-7.25 (m, 2H), 6.93 (s, 2H), 3.57 (s, 2H), 2.20 (s, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 140.1, 137.6, 134.1, 133.9, 128.8, 127.3, 125.5, 125.4, 124.3, 84.4, 83.4, 14.4.



Synthesis of (Z)-3,4-bis(5'-phenyl-2'-methylthiophen-3'-yl)cyclodeca-3-en-1,5-diyne (1o). A solution of (Z)-3,4-bis(5'-phenyl-2'-methylthiophen-3'-yl)hex-3-en-1,5-diyne (0.44 mmol) in anhydrous THF (50 mL) was treated dropwise with *n*-butyllithium (3.79

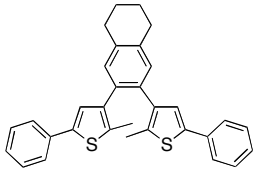
mL, 2.5 M in hexanes, 9.48 mmol) over a 5-min period at –78 °C under an N_2 atmosphere. After stirring at this temperature for 30 min, HMPA (2 mL) was added and the resulting suspension was stirred for 30 min, at which time 1,4-diiodobutane (124 mg, 0.40 mmol) was added dropwise. The cooling bath and the reaction was allowed to slowly warm to room temperature and the reaction was stirred there for 16 h. The crude reaction mixture was evaporated to dryness *in vacuo*. Purification by flash chromatography (SiO_2, 10% CH_2Cl_2 in hexanes) afforded 40 mg (19% for two steps) of compound **1o**.

M.p. = 65–70 °C. ^{1}H NMR (C_6D_6, 500 MHz) δ 7.39 (d, J = 7.0 Hz), 7.22 (s, 2H), 6.99 (t, J = 7.5 Hz, 4H), 6.92 (m, 2H), 2.15-2.20 (m, 10H), 1.59-1.65 (m, 4H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 140.0, 137.2, 134.5, 134.4, 129.0, 127.3, 125.7, 124.7, 101.1, 85.5, 29.2, 22.0, 14.7 (13 of 14 found). FT-IR (KBr-cast): 3446, 3059, 2918, 2854, 2195, 1600, 1502, 1444, 1073, 756, 691, 483 cm^{-1}. LRMS: (MALDI) m/z = 474 [M]$^+$.



Synthesis of the ring-closed isomer 1c. A solution of (Z)-3,4-bis(5'-phenyl-2'-methylthiophen-3'-yl)cyclodeca-3-en-1,5-diyne **(1o)** (8.0 mg, 0.017 mmol) in C_6D_6 (0.8 mL) was placed in a 5-mm NMR tube and irradiated with 365-nm light for 50 min yielding a solution of the photostationary state containing 82% of the ring-closed isomer **1c** according to the ^{1}H NMR spectrum. The remaining 18% was assigned to the ring-open isomer **1o**. This mixture was heated at 75 °C for 23 h using an oil bath to thermally decompose the remaining ring-open isomer **1o**. The solution was evaporated to dryness *in vacuo* and purified by centrifugal chromatography (SiO_2, 5% CH_2Cl_2 in hexanes) yielding 3.5 mg of **1c** (44%).

M.p. = 130 °C (dec.). ^{1}H NMR (C_6D_6, 500 MHz) δ 7.31 (dd, J = 4.0, 5.5 Hz, 4H), 6.96-7.01 (m, 6H), 6.91 (s, 2H), 2.31 (s, 6H), 2.11-2.22 (m, 4H), 1.55 (br s, 4H). ^{13}C NMR (C_6D_6, 600 MHz) δ 150.7, 149.9, 134.2, 129.1, 128.7, 126.8, 117.9, 115.5, 101.4, 81.4, 65.1, 28.4, 27.0, 21.9. FT-IR (KBr-cast): 3420, 2923, 2854, 1638, 1486, 1444, 1075, 756, 687, 469 cm^{-1}. LRMS: (MALDI) m/z = 474 [M]$^+$.



Synthesis of (Z)-1,2-bis(5'-phenyl-2'-methylthiophen-3'-yl)-5,6,7,8-tetrahydronaphthalene (7). A solution of (Z)-3,4-bis(5'-phenyl-2'-methylthiophen-3'-yl)cyclodeca-3-en-1,5-diyne (**1o**) (10 mg, 21 mmol) in C_6D_6 (5 mL) in a Wheaton vial was treated with (199 μl) 1,4-cyclohexadiene. The solution was heated with constant stirring in an oil bath at 75 °C for 19 h. The crude reaction mixture was evaporated to

dryness *in vacuo*. Purification by flash chromatography (SiO_2, 25% CH_2Cl_2 in hexanes) afforded 3 mg (30%) of compound **7** as a light yellow solid.

M.p. = 75–80ºC. ^{1}H NMR (C_6D_6, 500 MHz) δ 7.51 (d, J = 7.5 Hz, 4H), 7.13 (s, 2H), 7.11 (s, 2H), 7.06 (t, J = 7.5 Hz, 4H), 6.95-6.99 (m, 2H), 2.68 (br s, 4H), 2.06 (s, 6H), 1.64 (br s, 4H). ^{13}C NMR (C_6D_6, 600 MHz) δ 140.0, 139.8, 136.3, 135.1, 134.9, 133.8, 131.5129.1, 127.2, 126.6, 125.8, 29.4, 23.6, 14.0. FT-IR (KBr-cast): 3446, 2955, 2917, 2849, 1634, 1473, 1463, 1389, 1366, 1230, 730, 719, 478 cm^{-1}. LRMS: (EI) m/z = 476 $[M]^+$.

Reaction kinetics of the Bergman cyclization of (Z)-3,4-bis(5'-phenyl-2'-methylthiophen-3'-yl)cyclodeca-3-en-1,5-diyne (1o). A benzene solution of ring-open isomer **1o** (8.43×10^{-3} M) was prepared by dissolving **1o** (20.0 mg, 4.22×10^{-2} mmol) in C_6D_6 in a 5 mL volumetric flask. Similarly, a 1.85×10^{-2} M solution of an internal standard was prepared by dissolving *p*-nitroanisole (28.4 mg, 1.85×10^{-1} mmol) in a 10 mL volumetric flask. Both flasks were filled to the line with C_6D_6. Using *p*-nitroanisole as an internal standard (0.3 mL, 5.55 x 10^{-3} mmol), a solution of **1o** (0.3 mL, 2.53 x 10^{-3} mmol) in an NMR tube was treated with 1,4-cyclohexadiene (26 μL, 2.78×10^{-1} mmol), after which the solution was frozen with liquid N_2 and degassed under high vacuum. The reaction mixture was heated to 75 °C and the reaction progress was monitored using a Varian Inova 500 instrument working at 499.8 MHz over a 14-h period.

The integration areas of starting materials and products were normalized against *p*-nitroanisole as an internal standard and values were corrected to the number of protons integrated and the initial concentrations. Concentrations of the starting materials and products were plotted against time. The data were fitted to a single-exponential-decay rate equation by Microsoft Excel program.

Reaction kinetics for the consumption of 1o and formation of 7 (data processing). The area under the peaks observed in the ^{1}H NMR spectrum corresponding to ring-open isomer **1o** and product **7** were integrated and their values were normalized against those for the internal standard (*p*-nitroanisole). These values were converted to concentration by setting time t = 0 sec to the initial concentration of **1o.** Apparent reaction rates were determined by fitting the data, assuming pseudo-first order kinetic conditions. To plot the data of **1o** presented in Figure 2 of the manuscript, the values of $\ln(C_0)$ were subtracted from each data point. The effective rate of formation[6] of **7** was calculated by fitting the data to $\ln[P_{inf}/(P_{inf}–C)]$ where P_{inf} is the concentration of compound **7** when the reaction is completed.

Reaction kinetics of the Bergman cyclisation of the ring-closed isomer 1c. A benzene solution of isomer **1c** (3.16×10^{-3} M) was prepared by dissolving **1c** (3.0 mg, 6.32×10^{-3} mmol) in C_6D_6 in a 2 mL volumetric flask. The internal standard solution, *p*-nitronaisole 1.85×10^{-2} M in C_6D_6 (the same one as described above) was added. The flask was filled to the line with C_6D_6. Using *p*-nitroanisole as an internal standard (0.15 mL, 2.73×10^{-3}

[6] T. A. Zeidan, S. V. Kovalenko, M. Manoharan, I. V. Alabugin, *J. Org. Chem.* **2006**, *71*, 962–975.

mmol), a solution of **1c** (0.50 mL, 1.58×10^{-3} mmol). The NMR tube was placed in a preheated oil bath at 75 °C and removed at different time intervals for ^{1}H NMR analysis. After 7 h, 1,4-cyclohexadiene (26 μL, 2.78×10^{-2} mmol) was added and the NMR tube was further heated and removed at intervals for ^{1}H NMR analysis until a total time of 13 h was reached.

Reaction kinetics for the consumption of 1c. As described above for **1o**, the area under the peaks in the ^{1}H NMR spectrum corresponding to ring-closed isomer **1c** were integrated and their value were normalized against those for the *p*-nitroanisole internal standard. These values were converted to concentration by setting time $t = 0$ sec to the initial concentration of **1c**. Apparent reaction rates were determined by fitting the data, assuming pseudo-first order kinetic coinditions. To plot the data of **1c** presented in Figure 2 of the manuscript, $\ln(C_0)$ was subtracted from each data point.