Supporting Information for:

Synthesis of 3,4-bis(benzylidene)cyclobutenes

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Experimental:

Materials: All reactions were carried out under argon using standard Schlenk techniques unless otherwise noted. All solvents were of ACS reagent grade or better unless otherwise noted. Anhydrous tetrahydrofuran (THF) and diethyl ether (Et₂O) were obtained from J. T. Baker and dried on a solvent column purification system. Silica gel (40 µm) was purchased from SiliCycle Inc. Pd(PPh₃)₄ and (PPh₃)₂PdCl₂ were purchased from Strem Chemicals. All other reagent grade materials were purchased from Alfa Aesar or Sigma-Aldrich and used without further purification. Compound 2 was prepared by a Glaser coupling (copper(I) chloride, N,N,N’,N’-tetramethylethylenediamine, air, in acetone) as described by Adlington et al.¹ The ¹H NMR data was consistent with that reported in the literature.²

NMR Spectroscopy: ¹H and ¹³C NMR spectra for all compounds were acquired in CDCl₃ on a Bruker Avance Spectrometer operating at (400 MHz and 100 MHz, respectively), or on a Varian Inova Spectrometer (500 MHz or 125 MHz, respectively). Chemical shifts ( δ) are reported in parts per million (ppm) and referenced with residual CHCl₃.

Mass Spectrometry: High-resolution mass spectra (HRMS) were obtained at the MIT Department of Chemistry Instrumentation Facility employing either electron impact (EI), electrospray (ESI), or Direct Analysis in Real Time (DART) as the ionization technique. Gas chromatography/mass spectrometry (GC/MS) was performed on an Agilent 5973N (GC/MS) using EI as the ionization technique.

Infrared (IR) spectroscopy: IR spectra were recorded on a Perkin-Elmer Model 2000 FT-IR spectrophotometer at the MIT Department of Chemistry Instrumentation Facility. Peaks are reported as strong (s), medium (m) or weak (w).

Absorption and Emission Spectroscopy: Ultraviolet-visible absorption spectra were measured with an Agilent 8453 diode array spectrophotometer and corrected for background signal with a solvent-filled cuvette. Fluorescence spectra were measured on a SPEX Fluorolog- 3 fluorimeter (model FL-321, 450 W Xenon lamp) using right-angle detection. Fluorescence quantum yields in Chloroform (CHCl₃) were determined relative to perylene in ethanol (EtOH) and are corrected for solvent refractive index and absorption differences at the excitation wavelength. Fluorescence lifetimes were measured via frequency modulation using a Horiba-Jobin-Yvon MF2 lifetime spectrometer equipped with a 365 nm laser diode and using the modulation of POPOP (1,4-bis(5-phenyloxazol-2-yl)benzene) as a calibration reference.

1,6-dibromo-1,6-diphenylhexa-2,4-diyne (6). A solution of 1,6-diphenylhexa-2,4-diyne-1,6-diol (10.000g, 38.1 mmol) in anhydrous Et₂O (200 mL) was cooled to -10 °C in a brine/ice bath and flushed with argon for 10 minutes. Phosphorus tribromide (PBr₃) (2.36 mL, 25.2 mmol) was added to the solution dropwise and the reaction mixture was allowed to warm to room temperature over 2 hours. The reaction mixture was poured over ice and neutralized with a saturated solution of sodium bicarbonate (NaHCO₃). The two layers were separated, then the aqueous phase was extracted with Et₂O (2 x 100 mL). The combined organics were washed with brine (100 mL), and dried over anhydrous magnesium sulfate (MgSO₄). The solvent was removed under reduce pressure to give 13.715g of 6 (93%) as a mixture of stereoisomers which was used in the next step without further purification.

**¹H NMR** (400 MHz, CDCl₃): 7.57 (dd, J=8.0 Hz, J=1.4 Hz, 2H), 7.38 (m, 3H), 5.78 (s, 1H)

1,2-dibromo-3,4-bis(benzylidene)cyclobutene (in,out)/(in,in)/(out,out) (7): To a solution of 1,6-dibromo-1,6-diphenylhexa-2,4-diyne (5.743g, 14.8 mmols) in anhydrous THF (100 mL) was added catalytic copper(I) bromide (CuBr) (106 mg, 0.7 mmols). The reaction mixture was flushed with Argon for 10 minutes then heated to 40 °C for 4 hours. After cooling to room temperature, the reaction mixture was diluted with dichloromethane (CH₂Cl₂) (200 mL) and washed with saturated aqueous ammonium chloride (NH₄Cl) (100 mL). The layers were separated and the organic layer was dried over anhydrous sodium sulfate (Na₂SO₄) and concentrated under reduced pressure to a dark red residue. Flash column chromatography of the residue (SiO₂, hexanes) yielded 3.707 g of an isomeric mixture of 7 (64% yield). Analytically pure samples of each isomer were obtained by flash column chromatography in hexanes (SiO₂, hexanes) followed by recrystallization from hot methanol (MeOH).

**¹H NMR** (500 MHz, CDCl₃): 7.49 (d, J=7.6 Hz, 2H), 7.44 (d, J=7.4 Hz, 2H), 7.40 (dd, J= 7.4 Hz, 2H), 7.34 (qt, J= 6.0 Hz, 2H), 7.32-7.27 (m, 2H), 6.57 (s, 1H), 6.23 (s, 1H)

**¹³C NMR** (125 MHz, CDCl₃): 141.0, 138.7, 134.9, 134.6, 134.1, 129.9, 129.5, 128.6, 128.3, 128.2, 127.80, 127.78, 116.1, 113.6

**HRMS** (EI): calc for C₁₈H₁₂Br₂ 385.9300, found 385.9288

**Melting point:** 84-88 °C (from MeOH)
7\text{(in,in)}

$^1$H NMR (500 MHz, CDCl$_3$): 6.94 (ψt, J=7.4 Hz, 1H), 6.90 (d, J=7.0 Hz, 2H), 6.79 (ψt, J= 7.7 Hz, 2H), 6.26 (s, 1H)

$^{13}$C NMR (125 MHz CDCl$_3$): 139.6, 134.9, 130.7, 129.5, 127.4, 127.3, 114.5

HRMS (DART): calc for C$_{18}$H$_{12}$Br$_2$ [M+H]$^+$ 388.9366, found 388.9380.

Melting point: 74-77 °C (from MeOH)

$^1$H NMR (400 MHz, CDCl$_3$): 7.61 (d, J=7.4 Hz, 2H), 7.39 (ψt, J=7.7 Hz, 2H), 7.32 (ψt, J= 7.3 Hz, 1H), 6.43 (s, 1H)

$^{13}$C NMR (100 MHz, CDCl$_3$): 139.6, 134.2, 132.0, 129.8, 128.5, 127.9, 110.6

HRMS (DART): calc for C$_{18}$H$_{12}$Br$_2$ [M+H]$^+$ 388.9366, found 388.9380.

Melting point: 138-140 °C (from MeOH)
3,4-bis(benzylidene)cyclobutene \((\text{in, out})/(\text{in, in})/(\text{out, out})\) (8), representative procedure: A reaction tube was charged with 7(\text{in, in}) (100 mg, 0.26 mmols), zinc dust (35 mg, 0.54 mmols), and acetic acid (AcOH) (1.3 mL). The suspension was flushed with argon for 10 minutes than heated to 120 °C for 30 minutes. After cooling to room temperature, the reaction mixture was diluted with H\(_2\)O (5 mL). The precipitate was collected by filtration and washed with methanol to give 57 mg (95%) of 8(\text{in, in}).

\[7(\text{in, out}) \rightarrow 8(\text{in, out})\]

\(^1\text{H NMR}\) (400 MHz, CDCl\(_3\)):
- 7.49 (d, \(J=7.4\) Hz, 2H), 7.40-7.28 (m, 8H), 7.22 (\(\psi t\), \(J=7.1\) Hz, 1H), 7.12 (d, \(J=2.6\) Hz, 1H), 6.30 (s, 1H), 6.24 (s, 1H)

\(^{13}\text{C NMR}\) (100 MHz, CDCl\(_3\)):
- 147.9, 144.6, 144.1, 142.7, 137.5, 136.6, 129.4, 128.7, 128.4, 128.0, 127.04, 127.01, 115.2, 115.1

\(\text{IR } \nu_{\text{max}}\) (cm\(^{-1}\), KBr):
- 517 (m), 694 (s), 748 (s), 913 (s), 1028 (m), 1077 (m), 1179 (w), 1448 (m), 1493 (m), 1598 (m), 1685 (w), 2926 (w), 3024 (m), 3058 (w)

\[7(\text{in, in}) \rightarrow 8(\text{in, in})\]

\(^1\text{H NMR}\) (400 MHz, CDCl\(_3\)):
- 7.03 (s, 1H), 6.91 (d, \(J=7.2\) Hz, 2H), 6.88 (\(\psi t\), \(J=7.4\) Hz, 1H), 6.77 (\(\psi t\), \(J=7.6\) Hz, 2H), 6.24 (s, 1H)

\(^{13}\text{C NMR}\) (100 MHz, CDCl\(_3\)):
- 146.0, 143.4, 136.6, 129.4, 127.2, 126.5, 115.8

\(\text{IR } \nu_{\text{max}}\) (cm\(^{-1}\), KBr):
- 694 (s), 748 (s), 913 (s), 1027 (w), 1076 (w), 1155 (w), 1179 (w), 1446 (m), 1493 (m), 1596 (w), 1736 (w), 2927 (w), 3023 (m), 3055 (w)
$7 \text{(out, out)} \rightarrow 8 \text{(out, out)}$

$^1H$ NMR (400 MHz, CDCl$_3$): 7.50 (s, 1H), 7.46 (d, $J=7.4$ Hz, 2H), 7.37 (q, $J=7.4$ Hz, 2H), 7.24 (q, $J=7.4$ Hz, 1H), 6.24 (s, 1H)

$^{13}C$ NMR (100 MHz, CDCl$_3$): 146.0, 143.4, 137.2, 128.8, 127.9, 127.0, 110.3

IR $\nu_{\mathrm{max}}$ (cm$^{-1}$, KBr): 525 (m) 688 (s), 741 (m), 769 (s), 866 (w), 910 (m), 1027 (w), 1074 (w), 1259 (w), 1448 (m), 1493 (w), 1736 (w), 2928 (w), 3022 (w), 3050 (w), 3082 (w)

Figure S1. Comparison of $^1H$ NMR spectra of compounds 7 and 8. Deshielding of $H_b$ is evident in the spectra of $8 \text{(in, in)}$ and $8 \text{(out, out)}$. 
1,2-bis(3-thiophene)-3,4-bis(benzylidene)cyclobutene (10) (89%). To a solution of 7 (482 mg, 1.2 mmols) in toluene (PhCH$_3$) (11 mL) was added 3-thiopheneboronic acid (350 mg, 2.7 mmols), EtOH (3 mL), and H$_2$O (3 mL). The system was bubbled with argon for 60 minutes before adding Pd(PPh$_3$)$_4$ (80 mg, 2.5%) followed by flushing with argon for an additional 10 minutes. The reaction mixture was heated to reflux overnight. After cooling to room temperature, the reaction was diluted with CH$_2$Cl$_2$ (50 mL) and filtered through celite. The solvent was removed under reduced pressure to give a pale brown solid. The crude material was purified by flash column chromatography (SiO$_2$, 1:9 benzene:hexanes) to give 436 mg (89%) of pure 10 as a pale yellow solid.

$^1$H NMR (400 MHz, CDCl$_3$): 7.65 (dd, $J$=2.8 Hz, 1.2 Hz, 1H), 7.57 (d, $J$=7.4 Hz, 2H), 7.40 ($\psi t$, $J$=7.8 Hz, 2H), 7.36 (dd, $J$= 5.0 Hz, 3.4 Hz, 1H), 7.30 (d, $J$=5.2 Hz, 2H), 7.17 (dd, $J$=4.9 Hz, 2.9 Hz, 1H), 7.05 (m, 3H), 7.01 (m, 2H), 6.87 (m, 2H), 6.65 (s, 1H), 6.60 (s, 1H)

$^{13}$C NMR (100 MHz, CDCl$_3$): 146.3, 144.5, 142.7, 141.4, 136.8, 136.2, 133.9, 133.1, 129.7, 129.6, 128.3, 128.0, 127.7, 127.0, 126.9, 126.7, 126.0, 125.4, 125.0, 124.9, 116.1, 113.3

HRMS (ESI): [M+H] calc for 395.0923, found 395.0936

Melting point: 124-130 °C
1,2-bis(phenylethynyl)-3,4-bis(benzylidene)cyclobutene(out,out) (11(out,out)). Compound 7(out,out) (50 mg, 0.13 mmols), phenylacetylene (50 µL, 0.31 mmols), (PPh₃)₂PdCl₂ (5 mg, 6 µmols), and copper(I) iodide (CuI) (2 mg, 12 µmols) were suspended in triethylamine (Et₃N) (1.5 mL) that had been degassed using the freeze-pump-thaw method. Argon was bubbled through the suspension for 30 minutes. The reaction mixture was heated to 35 °C overnight. After cooling to room temperature, the reaction mixture was diluted with CH₂Cl₂ (25 mL) and filtered through a pad of celite. The solvent was removed under reduced pressure. The crude residue was flushed through a silica plug (1:3 CH₂Cl₂:hexanes) then recrystallized from hot CH₂Cl₂/MeOH to give 33 mg (59%) of 11(out,out) as yellow crystals.

**¹H NMR** (500 MHz, CDCl₃): 7.83 (d, J = 7.5 Hz, 2H), 7.56 (2H, m), 7.42-7.39 (5H, m), 7.31 (ψt, J = 7.5 Hz, 1H), 6.51 (s, 1H)

**¹³C NMR** (125 MHz, CDCl₃): 141.0, 138.7, 135.9, 132.0, 129.6, 129.5, 128.7, 128.5, 127.6, 122.7, 113.9, 105.6, 84.3

**HRMS (DART):** calc for C₃₄H₂₂ [M+H]+ 431.1794, found 431.1797

**Melting point:** 160-163 °C with decomposition (from CH₂Cl₂/MeOH)

**Absorbance** (in CHCl₃): λ_max = 304 nm, 402 nm

**Emission** (in CHCl₃): λ_em = 485 nm, Φ_em = 0.63, t = 5.77 ns