

Supplementary Information:

Bottom-up Assembly of Nanoporous Graphene with Emergent Electronic States

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1.	Figure S1. STM scans showing the on-surface synthesis with methyl-bearing precursor 1 and fluorene-bearing precursor 2 .	S2
2.	Figure S2. Isomeric C-NPG structures.	S3
3.	Figure S3. Hybridization of 1D GNR edge-states into 2D C-NPG interface states.	S4
4.	Figure S4. Observation of isolated 1D GNRs.	S5
5.	Materials and General Methods	S6
6.	Synthetic Procedures	S7
7.	Figure S5. ¹ H NMR (600 MHz, CDCl ₃) spectrum of 6,11-dibromo-2-(6-methyl-[1,1'-biphenyl]-2-yl)-1,4-diphenyltriphenylene (1).	S10
8.	Figure S6. ¹³ C { ¹ H} NMR (151 MHz, CDCl ₃) spectrum of 6,11-dibromo-2-(6-methyl-[1,1'-biphenyl]-2-yl)-1,4-diphenyltriphenylene (1).	S11
9.	Figure S7. ¹ H NMR (600 MHz, CDCl ₃) spectrum of 2-ethynyl-6-methyl-1,1'-biphenyl (6).	S12
10.	Figure S8. ¹³ C { ¹ H} NMR (151 MHz, CDCl ₃) spectrum of 2-ethynyl-6-methyl-1,1'-biphenyl (6).	S13
11.	Figure S9. ¹ H NMR (600 MHz, CDCl ₃) spectrum of 6-bromo-[1,1'-biphenyl]-2-carbaldehyde (4).	S14
12.	Figure S10. ¹³ C { ¹ H} NMR (151 MHz, CDCl ₃) spectrum of 6-bromo-[1,1'-biphenyl]-2-carbaldehyde (4).	S15
13.	Figure S11. ¹ H NMR (600 MHz, CDCl ₃) spectrum of 6,11-dibromo-2-(9H-fluorene-4-yl)-1,4-diphenyltriphenylene (2).	S16
14.	Figure S12. ¹³ C { ¹ H} NMR (151 MHz, CDCl ₃) spectrum of 6,11-dibromo-2-(9H-fluorene-4-yl)-1,4-diphenyltriphenylene (2).	S17
15.	References	S18

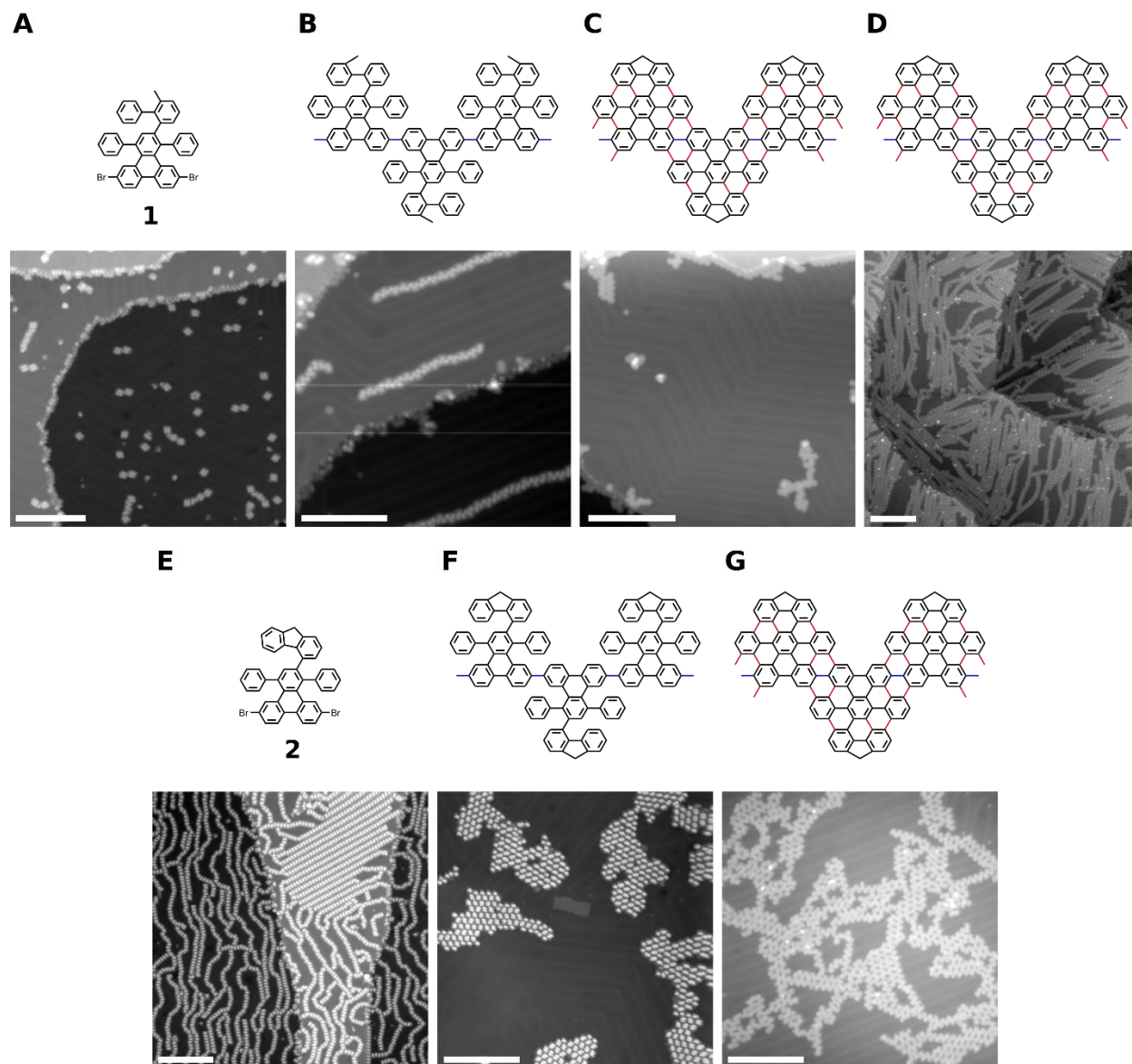


Figure S1. STM scans showing on-surface synthesis with methyl-bearing precursor **1** and fluorene-bearing precursor **2**. (A) **1**, as deposited on Au(111) at 24 °C ($V = 1.6$ V). (B) **1**, deposited on Au(111) and annealed to $T_1 = 200$ °C ($V = -1.6$ V). (C) **1**, deposited at 24 °C and annealed to $T_1 = 200$ °C and subsequently $T_2 = 400$ °C ($V = 2$ V). (D) **1**, deposited onto Au(111) held at $T_1 = 180$ °C followed by annealing to $T_2 = 400$ °C ($V = 2$ V). (E) **2**, as deposited on Au(111) at 24 °C ($V = 1.2$ V). (F) **2**, deposited on Au(111) and annealed to $T_1 = 200$ °C ($V = 1.2$ V). (G) **2**, deposited at 24 °C, annealed to $T_1 = 200$ °C and subsequently to $T_2 = 400$ °C ($V = 1.2$ V). $I = 50$ pA and scale bars = 20 nm for all images.

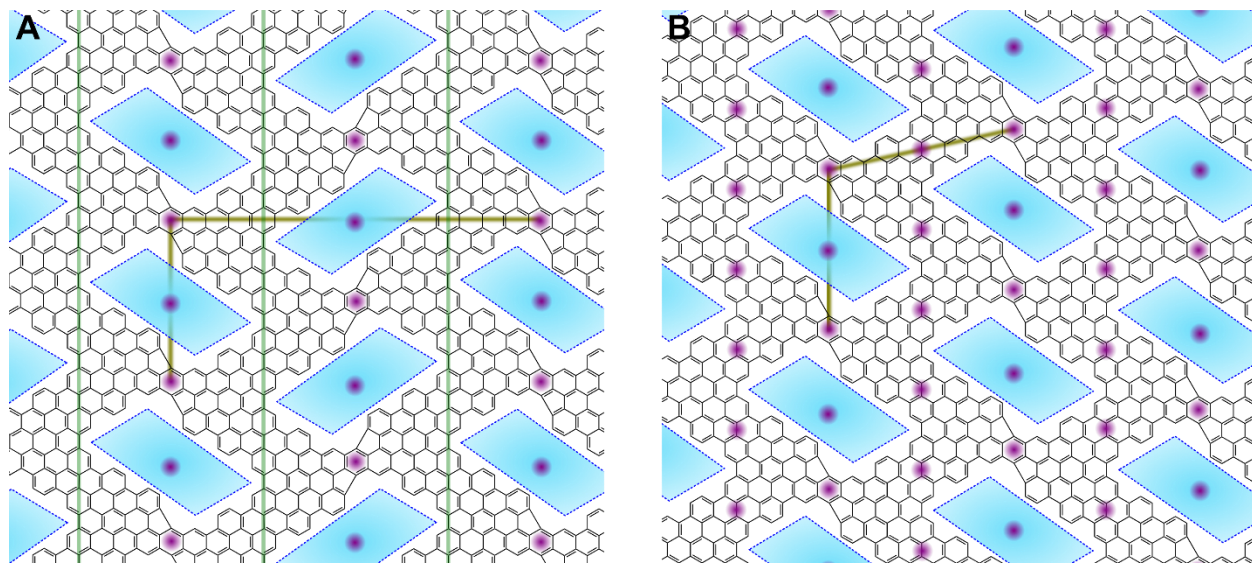


Figure S2. Isomeric C-NPG structures. (A) Type *anti* with anti-aligned pores highlighted in blue. (B) Type *syn* with aligned pores highlighted in blue. For both structures, the lattice vectors are indicated in brown, the local inversion symmetry points are shown in purple, and the screw axes are shown in green.

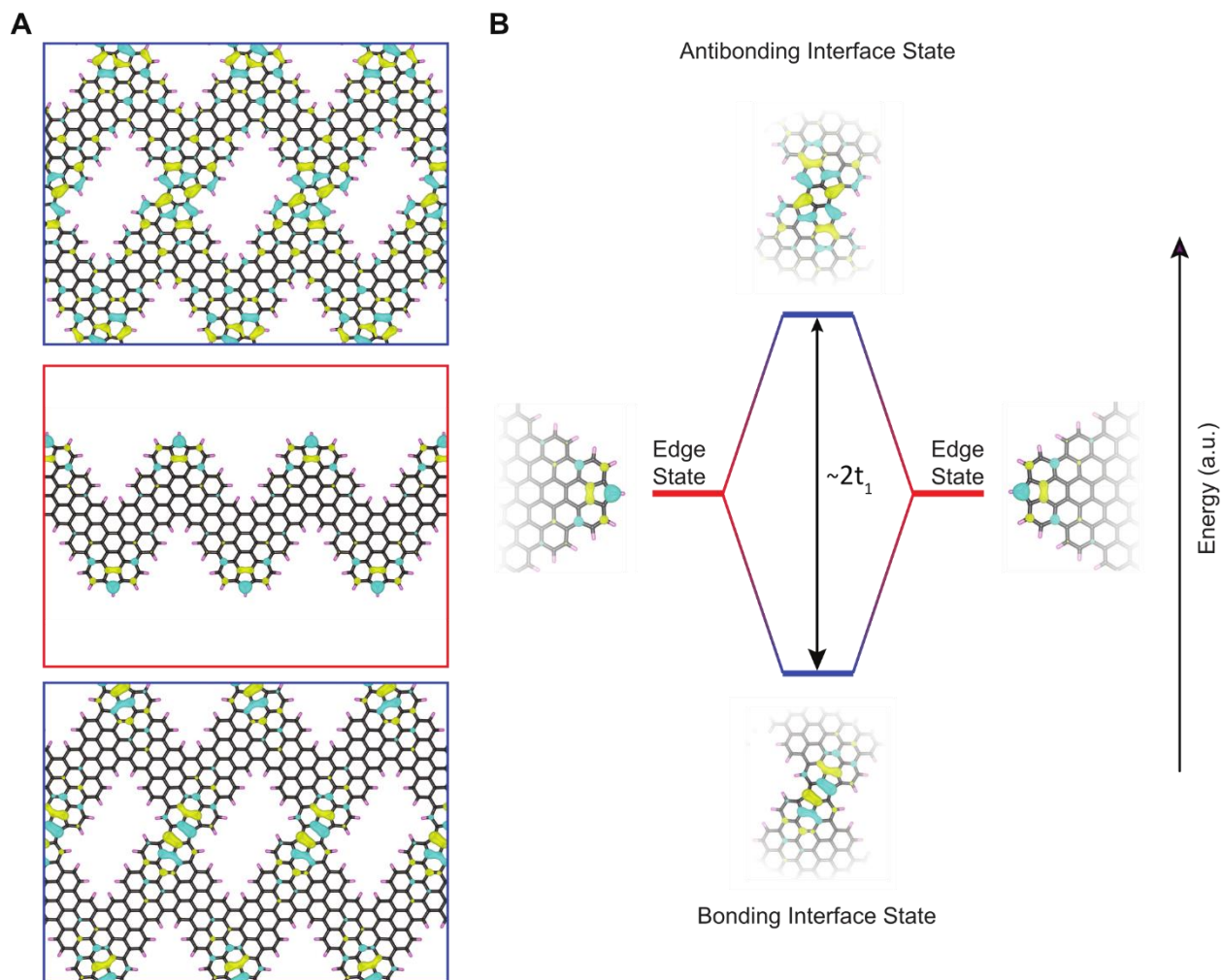


Figure S3. Hybridization of 1D GNR edge-states into 2D C-NPG interface states. (A) Crystal orbitals corresponding to bonding (bottom panel) and antibonding (top panel) interface states, as well as the edge state for a 1D fluorenyl-chevron GNR (middle panel). All crystal orbitals are calculated using DFT and drawn at the Γ -point. (B) Schematic process of hybridization of 1D edge band states from an initial energy (red horizontal lines) into energy-split 2D bonding and antibonding interface bands (blue horizontal lines). The hybridization/splitting is characterized by an effective tight-binding hopping parameter t_1 .

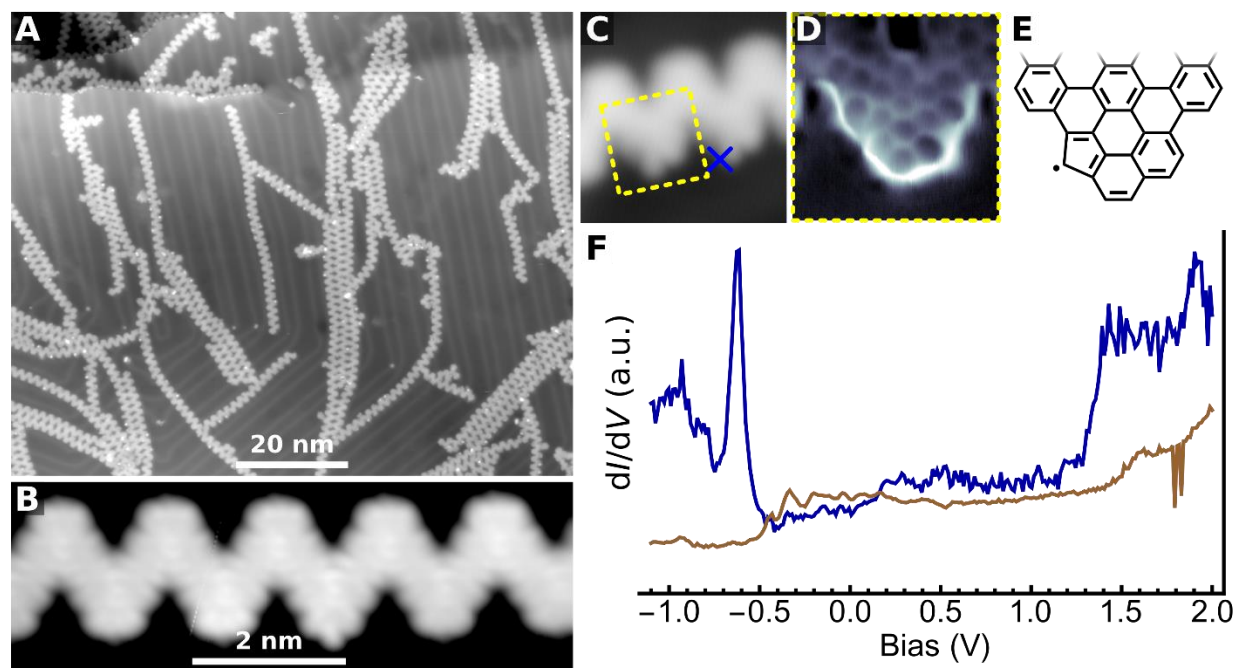
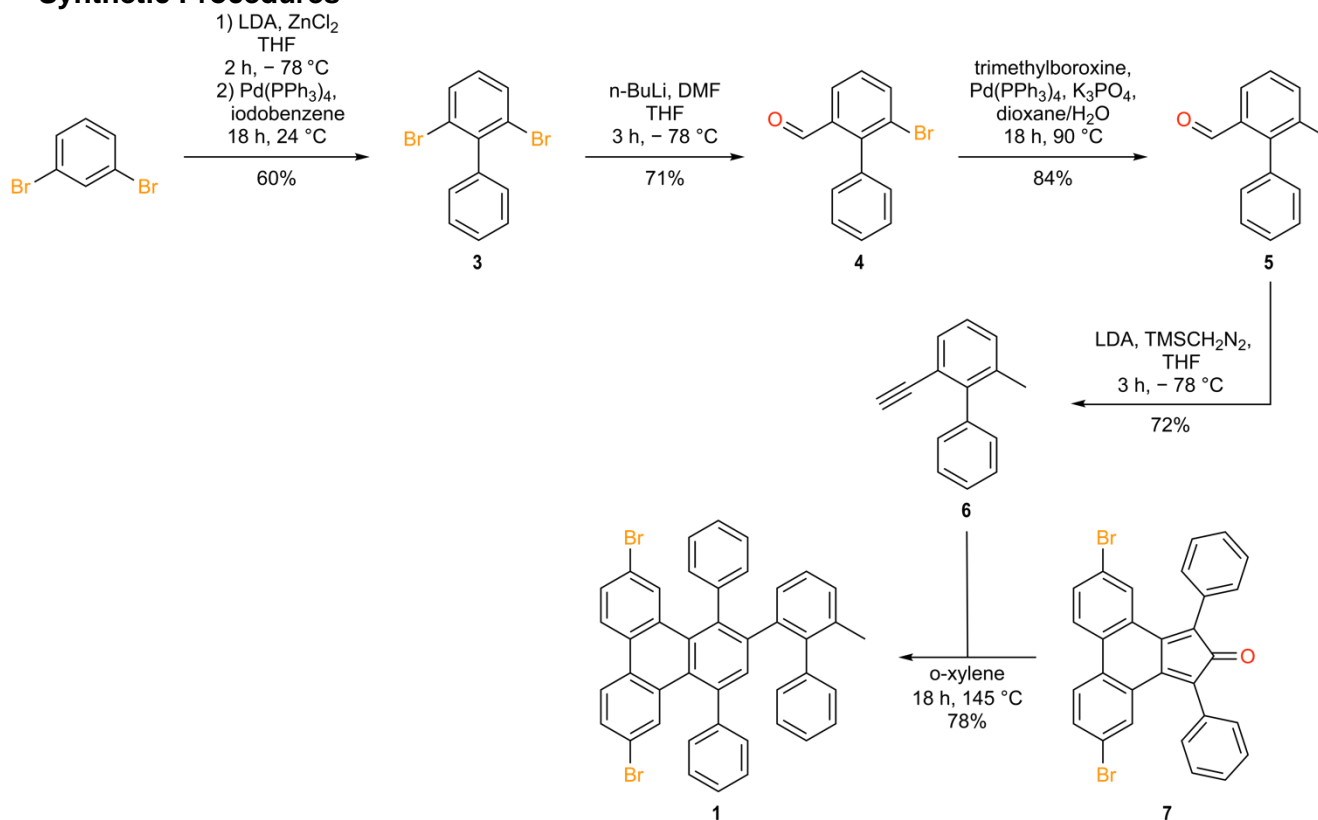


Figure S4. Observation of isolated 1D GNRs. (A) STM image of a low-coverage sample of GNRs from monomer **1** ($V = -1.2$ V, $I = 50$ pA). (B) STM image of a single, isolated GNR ($V = -700$ mV, $I = 100$ pA). (C) STM image of a ribbon with an alternative edge structure (yellow box) ($V = -800$ mV, $I = 50$ pA). (D) BRSTM image of the boxed segment of the ribbon shown in panel C that exhibits an alternative edge-structure ($V = -50$ mV, $I = 180$ pA, $V_{\text{osc}} = 20$ mV). (E) Structural model of the alternative edge structure. (F) dI/dV spectra recorded on the alternative edge structure (blue) and on the bare Au(111) surface (gold) ($f = 620$ Hz, $V_{\text{osc}} = 4$ mV).

Materials and General Methods. Unless otherwise stated, all manipulations of air and/or moisture sensitive compounds were carried out in oven-dried glassware, under an atmosphere of Ar. All solvents and reagents were purchased from Alfa Aesar, Spectrum Chemicals, Acros Organics, TCI America, and Sigma-Aldrich and were used as received unless otherwise noted. Organic solvents were dried by passing through a column of Al_2O_3 and were degassed by vigorous bubbling of N_2 or Ar through the solvent for 20 min. Flash column chromatography was performed on SiliCycle silica gel (particle size 40–63 μm). Thin layer chromatography was carried out using SiliCycle silica gel 60 Å F-254 precoated plates (0.25 mm thick) and visualized by UV absorption. All ^1H and ^{13}C $\{^1\text{H}\}$ NMR spectra were recorded on Bruker AV-600, and AV-500 MHz spectrometers, and are referenced to residual solvent peaks (CDCl_3 ^1H NMR δ = 7.26 ppm, ^{13}C NMR δ = 77.16 ppm; CD_2Cl_2 ^1H NMR δ = 5.32 ppm, ^{13}C NMR δ = 53.84 ppm). ESI mass spectrometry was performed on a Finnigan LTQFT (Thermo) spectrometer. Compounds **7** and **8** were prepared according to literature procedures.^{1,2}

Synthetic Procedures



Scheme S1. Synthesis of Monomer 1.

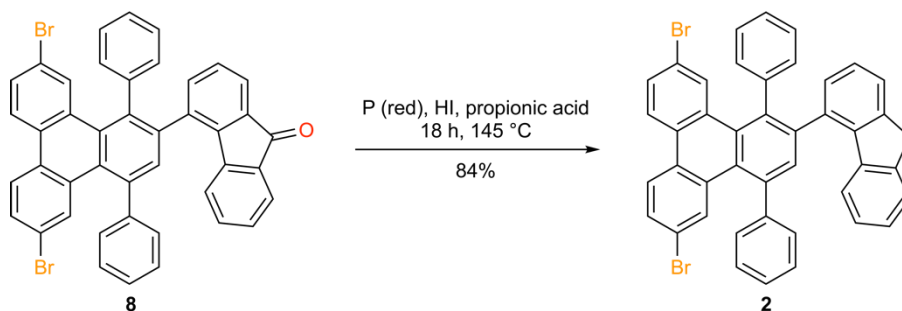
6,11-dibromo-2-(6-methyl-[1,1'-biphenyl]-2-yl)-1,4-diphenyltriphenylene (1) A 5 mL Schlenk tube was charged under N₂ with **7** (0.184 g, 0.34 mmol) and **6** (0.065 g, 0.34 mmol) in degassed o-xylene (2 mL). The reaction mixture was sealed under N₂ and stirred for 18 h at 145 °C. The reaction mixture was cooled to 24 °C and concentrated on a rotary evaporator. Column chromatography (SiO₂; 3:1 hexane/CH₂Cl₂) yielded **1** (0.186 g, 0.26 mmol, 78%) as a colorless crystalline solid. ¹H NMR (600 MHz, CDCl₃) δ = 8.19 (dd, *J* = 14.5, 8.7 Hz, 2H), 7.78 (d, *J* = 2.0 Hz, 1H), 7.59 (m, 2H), 7.53–7.27 (m, 13H), 7.09 (m, 2H), 7.03–6.99 (m, 3H), 6.43 (s, 1H), 6.34 (s, 1H), 2.07 (s, 3H) ppm; ¹³C {¹H} NMR (151 MHz, CDCl₃) δ = 143.7, 141.5, 141.0, 140.9, 140.4, 139.3, 137.8, 137.3, 136.4, 134.8, 133.4, 133.1, 132.8, 132.8, 131.9, 131.6, 131.1, 130.6, 130.3, 129.8, 129.7, 129.6, 129.6, 129.5, 129.5, 129.5, 129.5, 129.4, 129.0, 128.6, 128.3, 127.8, 127.6, 127.4, 127.2, 126.7, 126.5, 124.7, 124.6, 120.2, 120.0, 21.4 ppm; HRMS (EI-TOF) *m/z*: [C₄₃H₂₈Br₂]⁺ calcd. [C₄₃H₂₈Br₂] 702.0558; found 702.0559.

2-ethynyl-6-methyl-1,1'-biphenyl (6) A 25 mL Schlenk flask was charged under N₂ with lithium diisopropylamide (0.8 mL, 1.6 mmol, 2 M in THF/heptane/ethylbenzene) in dry THF (0.7 mL). The reaction mixture was cooled to –78 °C. (Trimethylsilyl)diazomethane (0.8 mL, 1.6 mmol, 2M in Et₂O) was added dropwise and the reaction mixture stirred for 30 min at –78 °C. **5** (0.250 g, 1.3 mmol) in dry THF (2.0 mL) was added dropwise and the reaction mixture stirred for 5 h at 24 °C. The reaction mixture was quenched with AcOH (10 mL), diluted with H₂O (50 mL), and extracted with CH₂Cl₂ (100 mL). The combined organic phases were washed with saturated aqueous NaCl (50 mL), dried over MgSO₄, and concentrated on a rotary evaporator. Column chromatography (SiO₂; 19:1 hexane/CH₂Cl₂) yielded **6** (0.184 g, 0.94 mmol, 72%) as a colorless oil. ¹H NMR (600 MHz, CDCl₃) δ = 7.53 (m, 1H), 7.51–7.48 (m, 2H), 7.44–7.42 (m, 1H), 7.35–7.32 (m, 3H), 7.29–

7.27 (m, 1H) 2.92 (s, 1H), 2.18 (s, 3H) ppm; ^{13}C { ^1H } NMR (151 MHz, CDCl_3) δ = 144.7, 140.0, 136.2, 130.7, 129.5, 128.1, 127.3, 127.1, 122.0, 83.3, 80.1, 20.9 ppm; HRMS (EI-TOF) m/z : [$\text{C}_{15}\text{H}_{12}$] $^+$ calcd. [$\text{C}_{15}\text{H}_{12}$] 192.0939; found 192.0935.

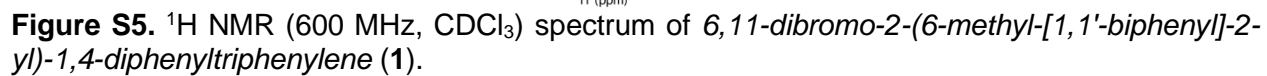
6-methyl-[1,1'-biphenyl]-2-carbaldehyde (5) A 100 mL Schlenk tube was charged under N_2 with **4** (0.500 g, 1.92 mmol), potassium phosphate (1.63 g, 7.66 mmol), and trimethylboroxine (2.4 g, 19.2 mmol) in 1,4-dioxane (19 mL) and H_2O (2 mL). The reaction mixture was degassed via freeze-pump-thaw, three cycles. [1,1'-Bis(diphenylphosphino)ferrocene]dichloropalladium(II) (0.140 g, 0.192 mmol) was added under N_2 . The reaction mixture was sealed under N_2 and stirred for 18 h at 80 °C. The reaction mixture was diluted with H_2O (50 mL) and extracted with CH_2Cl_2 (150 mL). The combined organic phases were washed with H_2O (50 mL), 1 M HCl (50 mL), saturated aqueous NaCl (50 mL), dried over MgSO_4 , and concentrated on a rotary evaporator. Column chromatography (SiO_2 ; CH_2Cl_2) yielded **5** (0.314 g, 1.60 mmol, 84%) as a colorless oil. ^1H NMR (500 MHz, CD_2Cl_2) δ = 9.67 (s, 1H), 7.81 (d, J = 7.8 Hz, 1H), 7.53 (d, J = 7.5 Hz, 1H), 7.50–7.38 (m, 4H), 7.28–7.22 (m, 2H), 2.13 (s, 3H) ppm; LRMS (EI+) m/z : [$\text{C}_{14}\text{H}_{12}\text{O}$] $^+$ calcd. [$\text{C}_{14}\text{H}_{12}\text{O}$] 196.09; found 196.10. (Analysis matches reported values)³

6-bromo-[1,1'-biphenyl]-2-carbaldehyde (4) A 100 mL Schlenk flask was charged under N_2 with **3** (0.936 g, 3.00 mmol) in dry THF (19 mL). The reaction mixture was cooled to –78 °C. $n\text{-BuLi}$ (1.2 mL, 3.0 mmol, 2.5 M in hexanes) was added dropwise over 10 min and the reaction mixture stirred for an additional 15 min at –78 °C. A solution of DMF (0.526 g, 7.20 mmol) in dry THF (3.8 mL) was added dropwise and the reaction mixture stirred for 18 h at 24 °C. The reaction mixture was quenched with saturated aqueous ammonium chloride (100 mL) and extracted with CH_2Cl_2 (200 mL). The combined organic phases were washed with H_2O (100 mL), dried over MgSO_4 and concentrated on a rotary evaporator. Column chromatography (SiO_2 ; 19:1 hexane/ EtOAc) yielded **4** (0.554 g, 2.12 mmol, 71%) as a colorless solid. ^1H NMR (600 MHz, CDCl_3) δ = 9.65 (s, 1H), 7.98 (d, J = 7.8 Hz, 1H), 7.92 (d, J = 7.8 Hz, 1H), 7.49 (m, 3H), 7.40 (t, J = 7.9 Hz, 1H), 7.30–7.28 (m, 2H) ppm; ^{13}C { ^1H } NMR (151 MHz, CDCl_3) δ = 191.7, 146.0, 138.0, 136.4, 130.3, 129.4, 128.7, 128.4, 126.4, 125.3 ppm; HRMS (EI-TOF) m/z : [$\text{C}_{13}\text{H}_9\text{BrO}$] $^+$ calcd. [$\text{C}_{13}\text{H}_9\text{BrO}$] 259.9837; found 259.9843.



Scheme S2. Synthesis of Monomer **2**.

6,11-dibromo-2-(9H-fluoren-4-yl)-1,4-diphenyltriphenylene (2) A 10 mL Schlenk flask was charged with **8** (71.6 mg, 0.10 mmol), red phosphorous (21.1 mg, 0.68 mmol) and HI (0.28 mL, 57 wt.%) in propionic acid (2 mL). The suspension was heated to 145 °C under N₂ for 18 h. The suspension was cooled to 24 °C and quenched with saturated K₂CO₃ solution. The suspension was washed three times with CH₂Cl₂ and the combined organic phases were washed with saturated aqueous NaCl solution, dried over MgSO₄, and concentrated on a rotary evaporator. Column chromatography (SiO₂; 1:1 CH₂Cl₂/hexanes) yielded **2** (59.2 mg, 0.084 mmol, 84%) as a colorless solid. ¹H NMR (600 MHz, CDCl₃) δ = 8.28 (dd, *J* = 8.8, 3.7 Hz, 2H), 7.88 (d, *J* = 2.0 Hz, 1H), 7.71 (m, 2H), 7.58 (dd, *J* = 8.7, 2.0 Hz, 1H), 7.53–7.41 (m, 8H), 7.20–7.10 (m, 5H), 7.02–6.96 (m, 4H), 6.88 (d, *J* = 2.0 Hz, 1H), 3.91 (s, 2H) ppm; ¹³C {¹H} NMR (151 MHz, CDCl₃) δ = 143.6, 143.4, 143.2, 141.6, 140.9, 140.3, 139.4, 139.0, 137.6, 136.0, 133.0, 132.7, 132.7, 132.4, 131.7, 131.4, 131.1, 130.7, 129.8, 129.6, 129.5, 129.5, 129.3, 129.2, 129.1, 128.4, 128.2, 127.6, 127.0, 126.5, 126.3, 125.7, 124.7, 124.6, 124.5, 123.4, 122.6, 120.1, 120.0, 36.8 ppm; HRMS (ESI-TOF) *m/z*: [C₄₃H₂₅Br₂]⁺ calcd. [C₄₃H₂₅Br₂] 699.0328; found 699.0325 ppm.



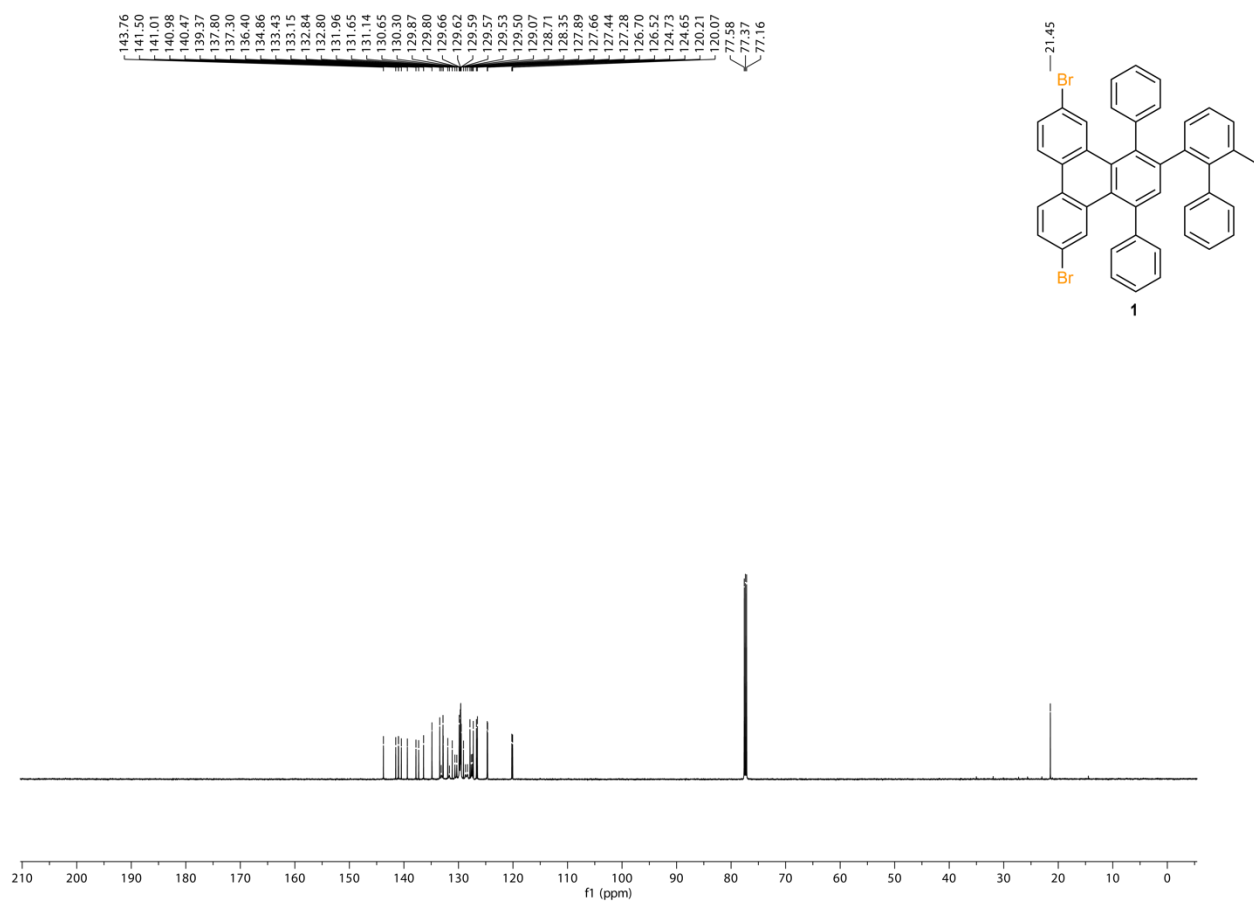


Figure S6. ¹³C {¹H} NMR (151 MHz, CDCl₃) spectrum of 6,11-dibromo-2-(6-methyl-[1,1'-biphenyl]-2-yl)-1,4-diphenyltriphenylene (**1**).

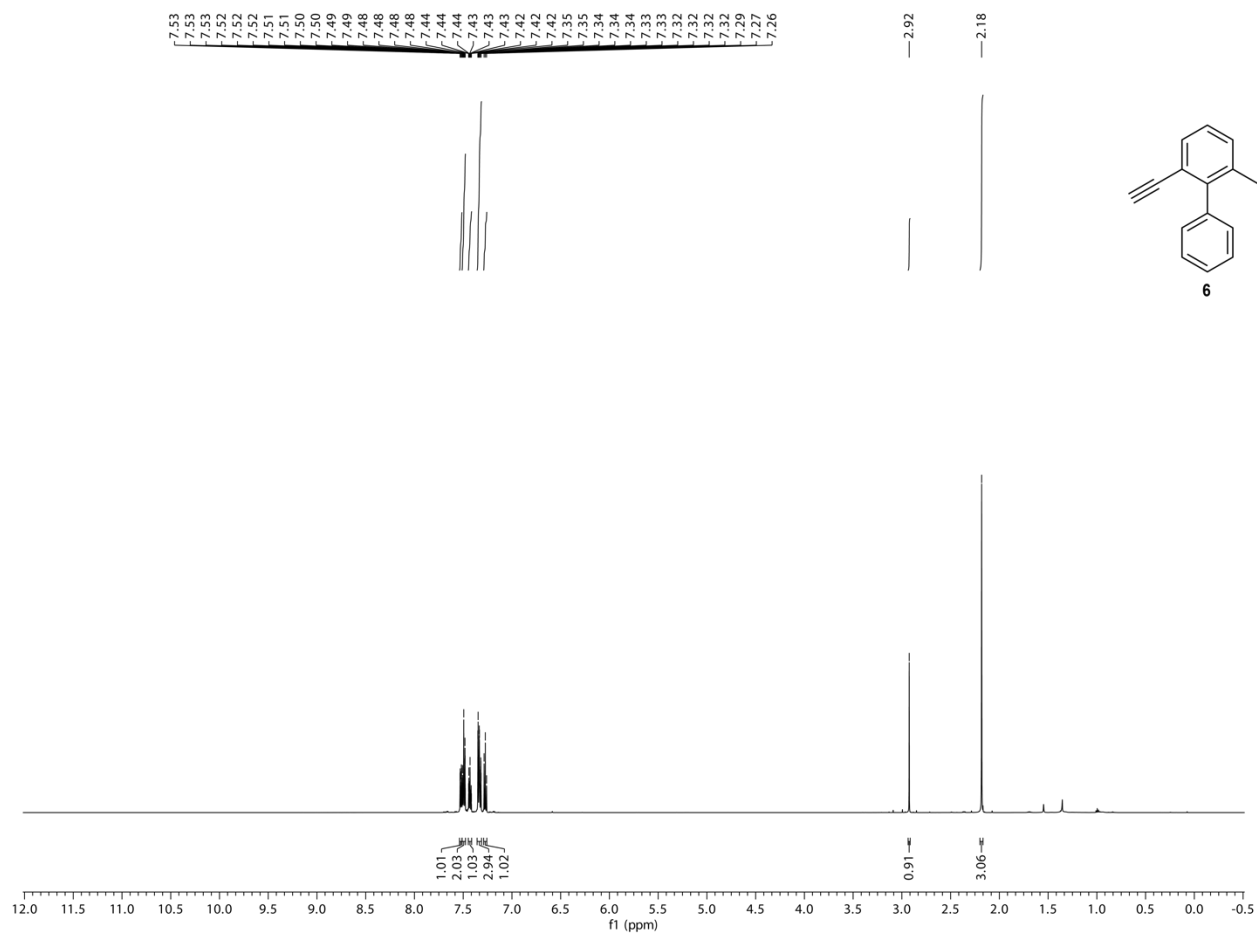


Figure S7. ^1H NMR (600 MHz, CDCl_3) spectrum of 2-ethynyl-6-methyl-1,1'-biphenyl (**6**).

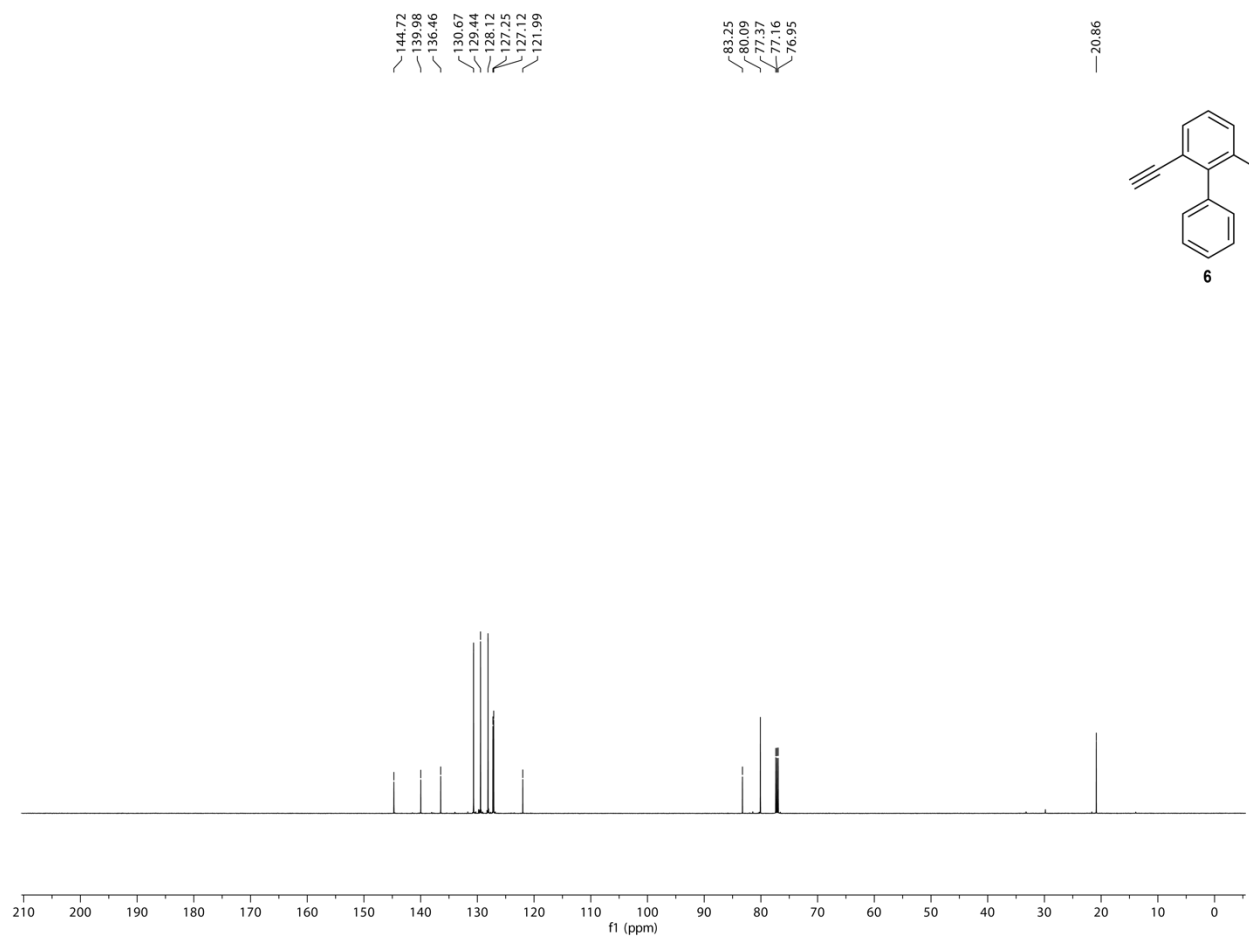


Figure S8. ^{13}C $\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) spectrum of 2-ethynyl-6-methyl-1,1'-biphenyl (**6**).

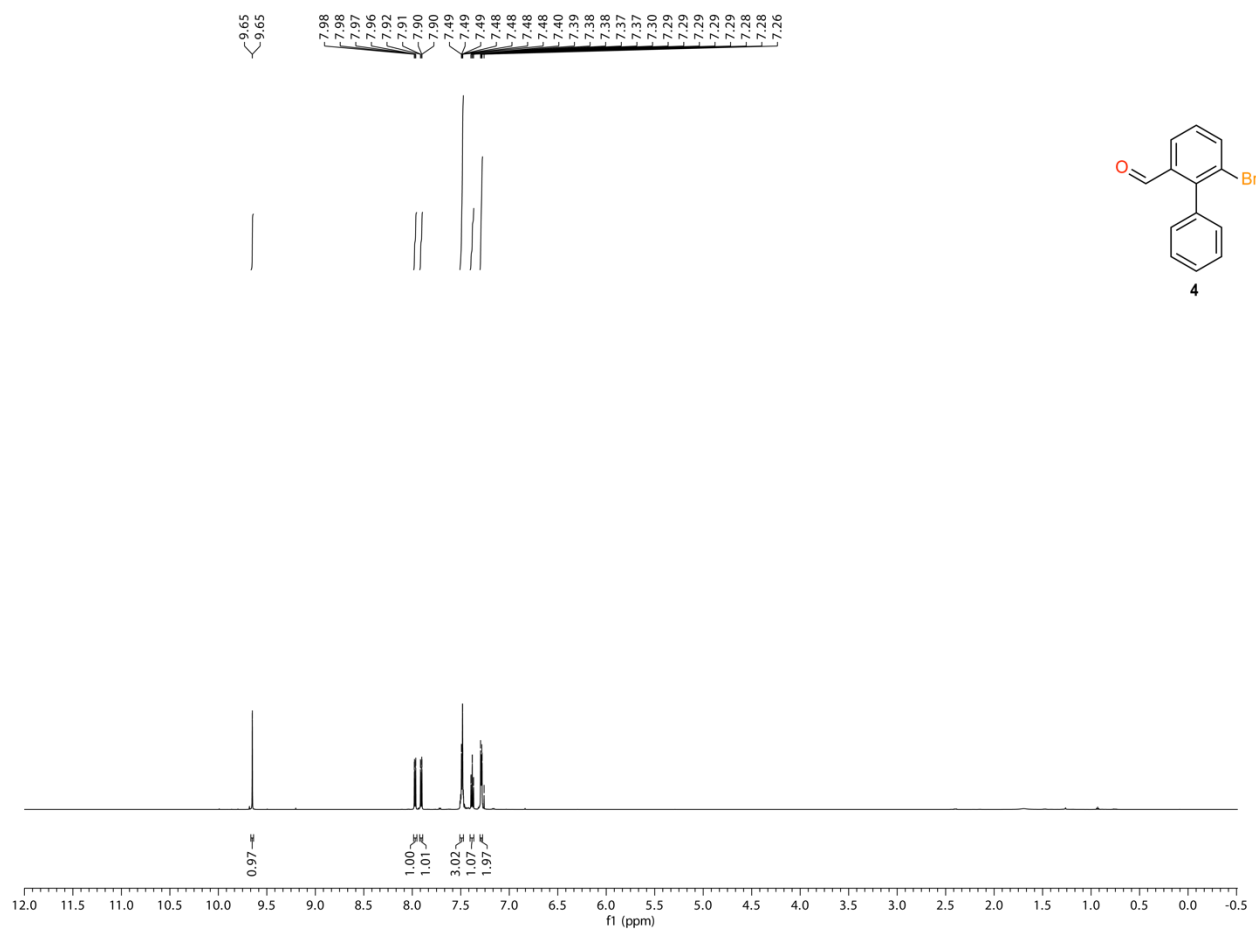


Figure S9. ^1H NMR (600 MHz, CDCl_3) spectrum of 6-bromo-[1,1'-biphenyl]-2-carbaldehyde (**4**).

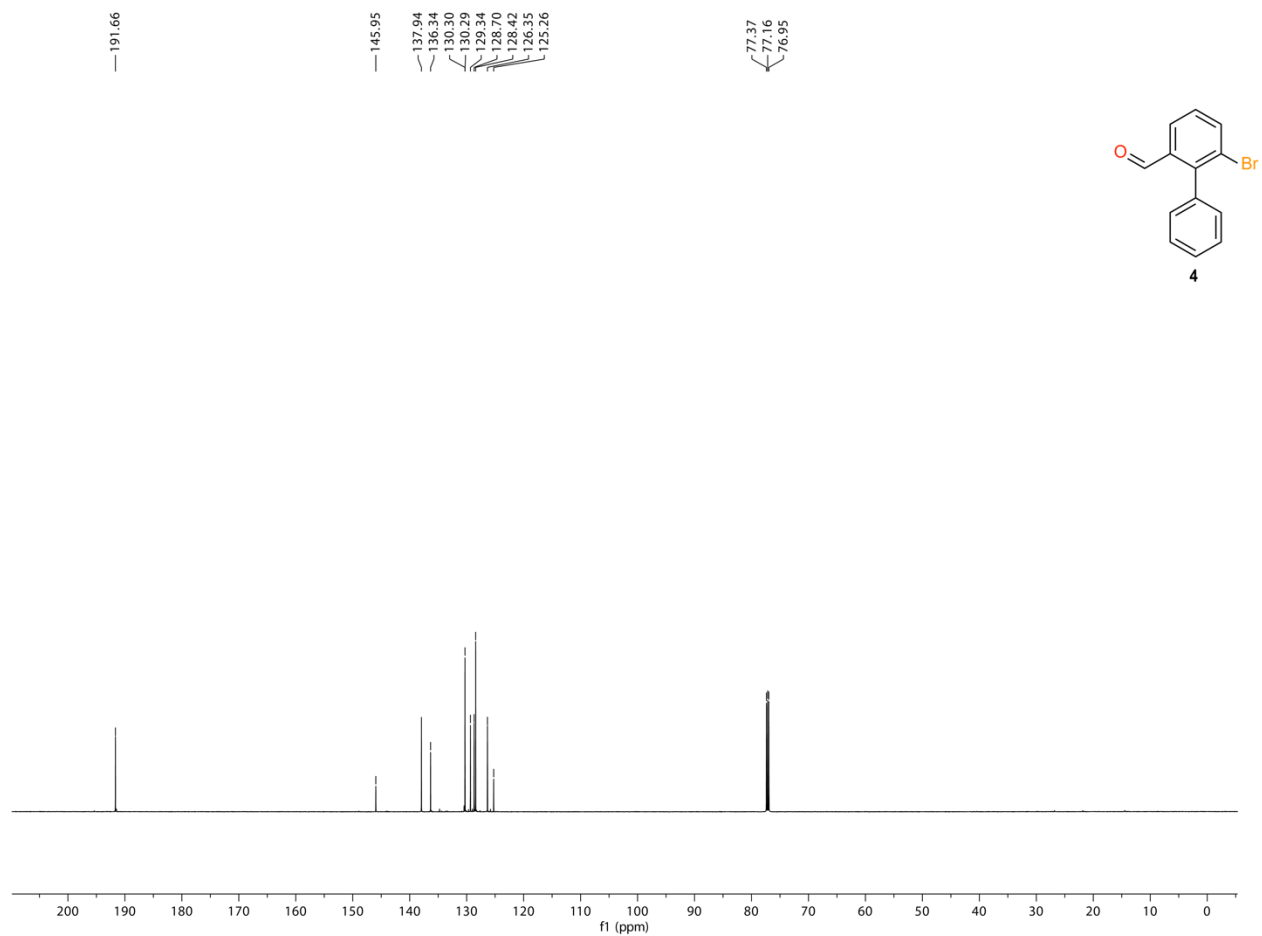


Figure S10. ^{13}C $\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) spectrum of 6-bromo-[1,1'-biphenyl]-2-carbaldehyde (4).

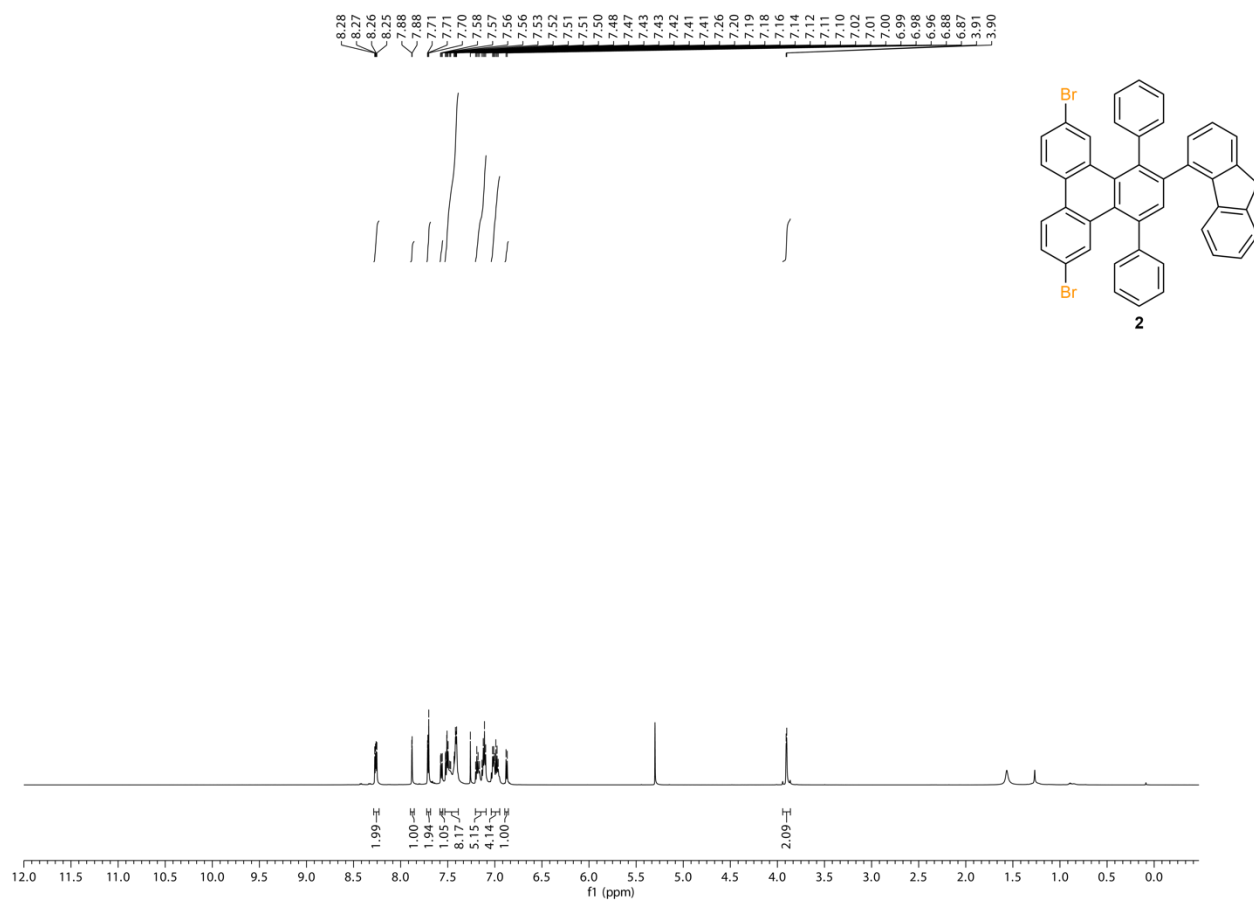


Figure S11. ¹H NMR (600 MHz, CDCl₃) spectrum of 6,11-dibromo-2-(9H-fluoren-4-yl)-1,4-diphenyltriphenylene (2).

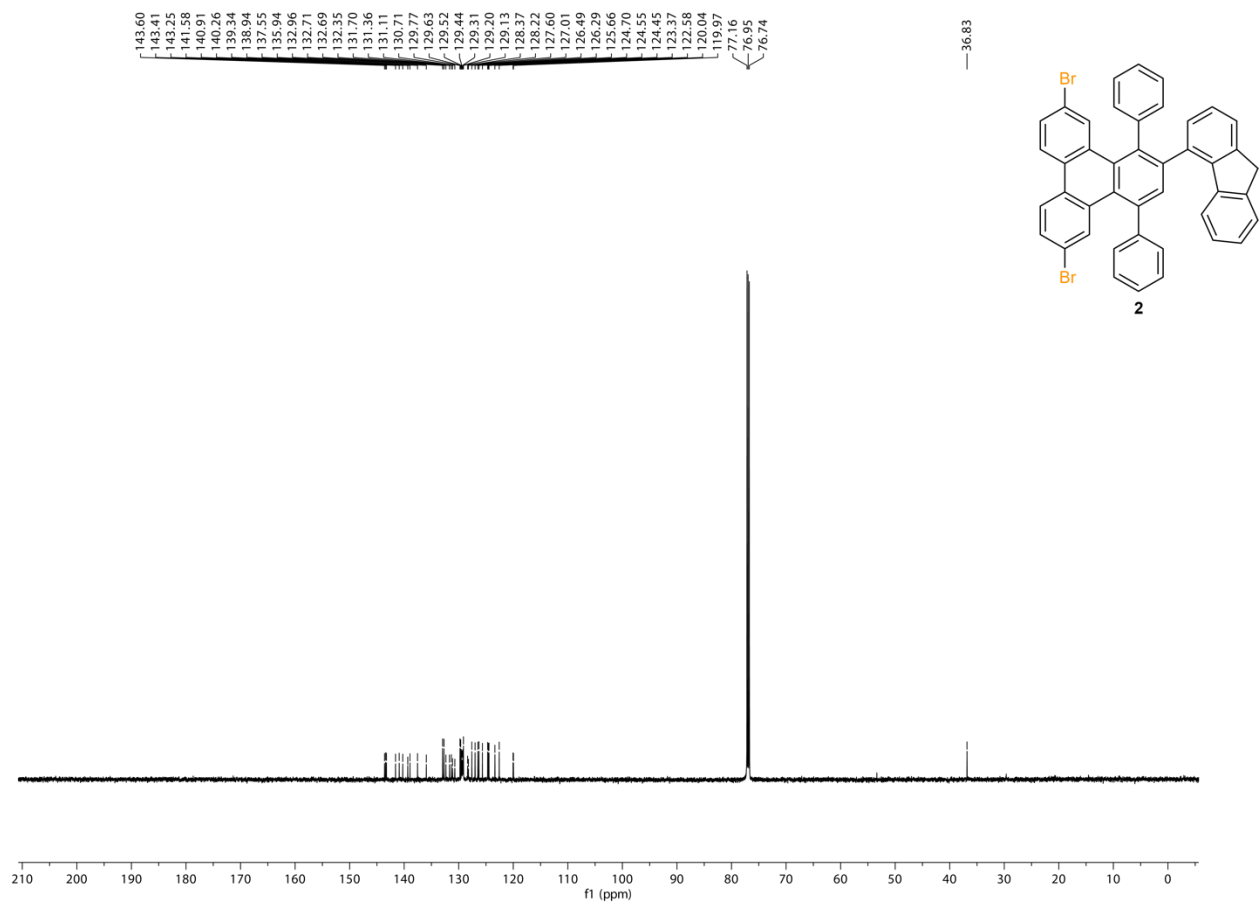


Figure S12. ¹³C {¹H} NMR (151 MHz, CDCl₃) spectrum of 6,11-dibromo-2-(9H-fluoren-4-yl)-1,4-diphenyltriphenylene (**2**).

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