

Supporting Information

Breakdown of Interference Rules in Azulene, a Non-Alternant Hydrocarbon

Jianlong Xia,^{1,‡} Brian Capozzi,^{2,‡} Sujun Wei,¹ Mikkel Strange,³ Arunabh Batra,²
Jose R. Moreno,¹ Roey J. Amir,⁴ Elizabeth Amir,⁵ Gemma C. Solomon,³
Latha Venkataraman,^{*,2} Luis M. Campos.^{*,1}

¹ *Department of Chemistry, Columbia University, New York, NY 10027, USA,*

² *Department of Applied Physics and Applied Mathematics, Columbia University,
New York, NY 10027, USA,*

³ *Nano-Science Center and Department of Chemistry, University of Copenhagen,
Copenhagen 2100, Denmark*

⁴ *School of Chemistry, Tel-Aviv University, Tel-Aviv 69978, Israel.*

⁵ *The Pernick Faculty of Engineering, Shenkar College of Engineering and Design,
Ramat-Gan 52526, Israel.*

‡ These authors contributed equally.

* Corresponding Author Email: lv2117@columbia.edu, lcampos@columbia.edu

Contents

- 1) Additional Figures
 - a) Figure S1: Two-dimensional conductance histograms
 - b) Figure S2: Conductance data for 1,3PyAz
 - c) Figure S3: UV-vis data for 1,3PyAz
- 2) Theoretical Methods
 - a) Figure S4: Tight-binding transmission calculation
- 3) Synthetic Methods
 - a) General Methods
 - b) Synthetic Procedures
- 4) References
- 5) NMR Spectra

1) Additional Figures:

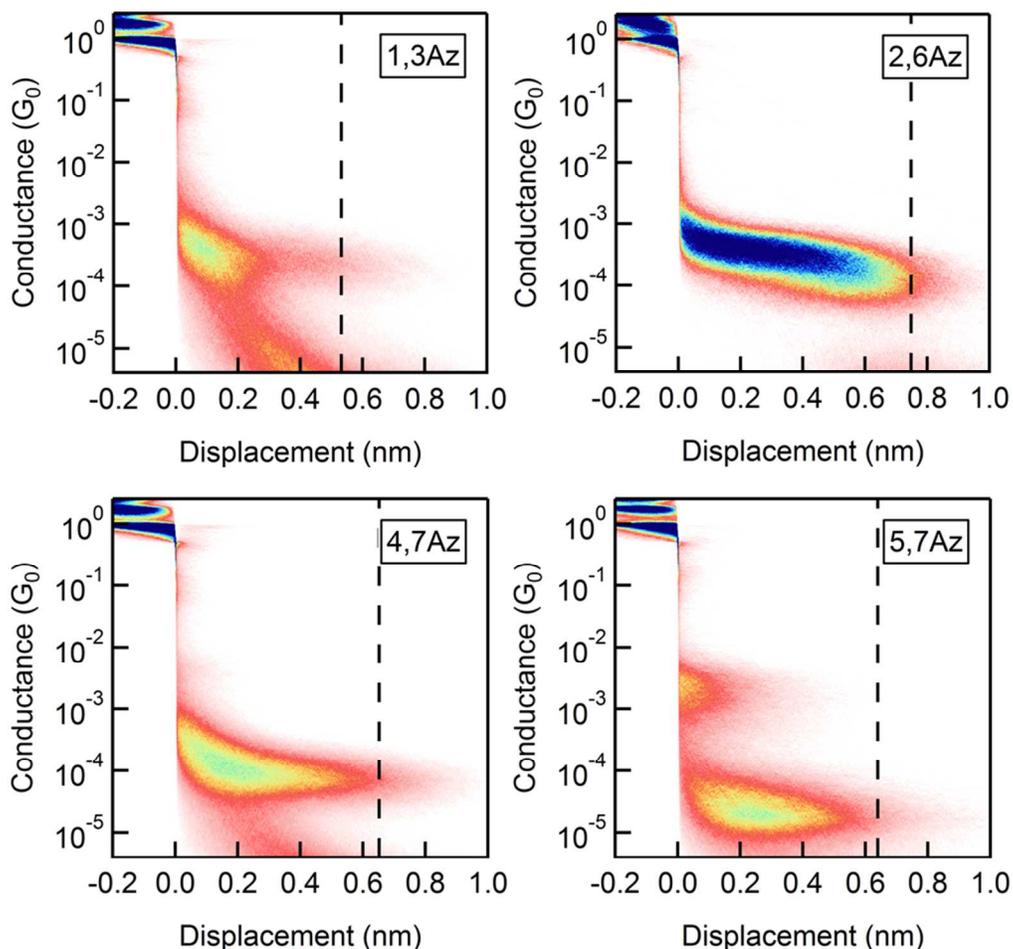


Figure S1: Two-dimensional conductance vs displacement histograms for 1,3Az; 2,6Az; 4,7Az; and 5,7Az. Histograms were constructed by aligning each individual conductance vs displacement trace at the end of the $1G_0$ plateau and then overlaying all traces. Dashed lines indicate the step-lengths obtained from the 2D histograms. Step-lengths are computed by integrating all counts in the conductance feature, and creating a 1D line profile. The step-length is then obtained by finding where the line profile falls to 20% of its peak value.

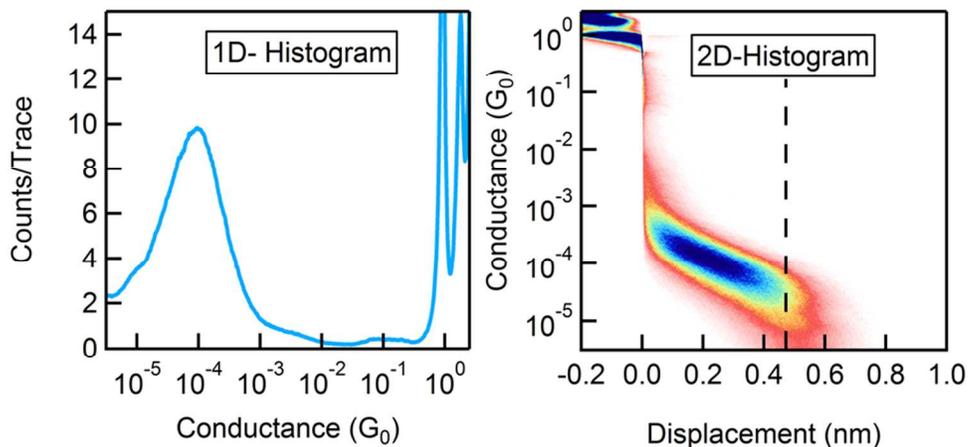


Figure S2: (a) One-dimensional, logarithmically binned conductance histogram, and (b) 2-dimensional conductance vs. displacement histogram for 1,3PyAz. We find that 1,3PyAz has a calculated length of 1.03nm (structure optimized using density functional theory, B3LYP/6-31G*), a 2D histogram step length of 0.56nm, and a most probable conductance of $9 \times 10^{-5} G_0$ (from log-binned histogram). The dashed line indicates the measured step-length as determined by the method described in the caption of Figure S1.

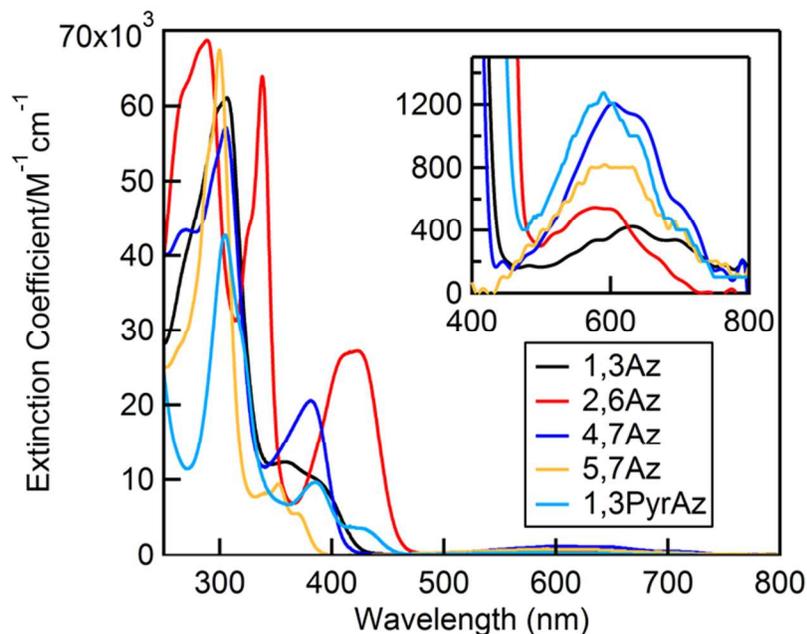


Figure S3: UV-vis spectra of pyridine-linked azulene molecule along with the four methyl-sulfide linked derivatives. Inset: magnification of the region between 400 and 800 nm (S_0 - S_1 transition). All solutions are at a concentration of $10 \mu\text{M}$.

2) Theoretical methods:

We use a model molecular system with the azulene and naphthalene backbone connected to linkers consisting of an ethynyl group for the calculations carried out here. We minimize the geometry for these model systems using density functional theory. We then describe exchange and correlation effects in the GW approximation,¹ attach the molecules to featureless, wideband leads and calculate the transmission using the Landauer-Büttiker formula.² More details about the GW method can be found in the work of Thygesen and Rubio³, but in brief we represent all Green's functions and self-energies on a energy grid on the real axis and perform a self-consistent calculation for a central region coupled to non-interacting leads. We use an energy grid extending from -100eV to 100eV with a grid spacing of 0.0025eV and a numerical value for the imaginary "infinitesimal" used in the retarded Green's function of twice the energy grid spacing (0.005eV). For these calculations, we only consider the π system of the molecule which is modeled using a Hamiltonian of the Pariser-Parr-Pople (PPP)⁴ type consisting of a simple nearest neighbor tight-binding part $h = t \sum_{\langle ij \rangle \sigma} c_{i\sigma}^{\dagger} c_{j\sigma}$ and a part describing the electron-electron interactions $V_{int} = \sum_i V_{ii} n_{i\uparrow} n_{i\downarrow} + \frac{1}{2} \sum_{i \neq j} V_{ij} (n_i - 1)(n_j - 1)$, where $c_{i\sigma}^{\dagger}$ ($c_{j\sigma}$) creates (annihilates) an electron with spin σ in a p_z orbital on the i 'th atom and $n_i = \sum_{\sigma} c_{i\sigma}^{\dagger} c_{j\sigma}$. For simplicity, we use a distance independent hopping parameter of $t=-2.5\text{eV}$ and Ohno's parameterization⁵ for the interactions described by an onsite repulsion $U=10\text{eV}$ ($V_{ij} = U/\sqrt{1 + 0.6117r_{ij}^2}$, where r_{ij} is distance between atom i and j in Angstrom). The onsite energy of the p_z orbitals is set to zero. We mention that despite the simplicity of the PPP Hamiltonian, the trends in the experimentally measured optical excitations for azulene and naphthalene are well captured. We have diagonalized the Hamiltonian for the molecules in gas phase (without linkers) exactly, which for azulene yields an S_0 - S_1 and S_0 - S_2 excitation energy of 1.6eV and 3.1eV. The calculated charge excitation gap of azulene is 6.4eV. For naphthalene we find a considerably larger S_0 - S_1 excitation energy of 3.9eV while the charge excitation gap is 8.2eV. This is in good qualitative agreement with experiments considering that the linker groups were not included. Further, the trend in the shift of the excitation energy with substitution pattern

using a simple 2-atom linker is captured. We therefore believe that the PPP Hamiltonian captures the essential features of the naphthalene and azulene molecules.

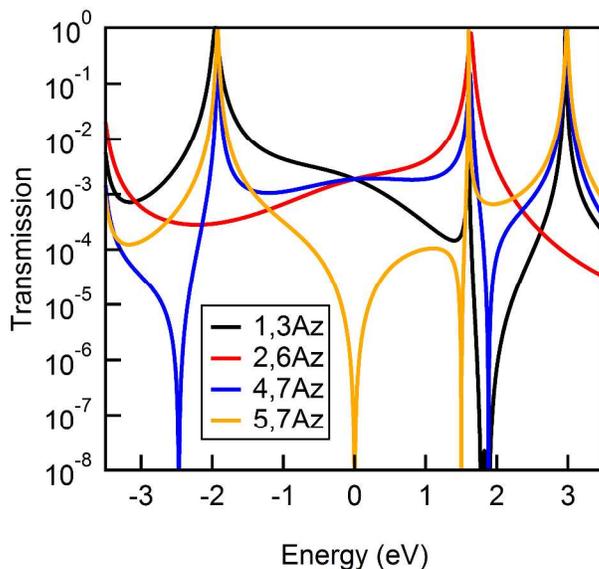


Figure S4: Transmission spectra for an azulene without linkers attached to wide-band electrodes at different points as indicated. The tight-binding model treats each atom with an on-site energy, ϵ , and is coupled to its nearest neighbors by an energy τ . Linking atoms are coupled to leads using an imaginary self-energy, $-i\Gamma/2$. The parameters used for this calculations are: on-site energy $\epsilon=0$, inter-atom coupling $\tau=4$ and electrode coupling $\Gamma=-3$.

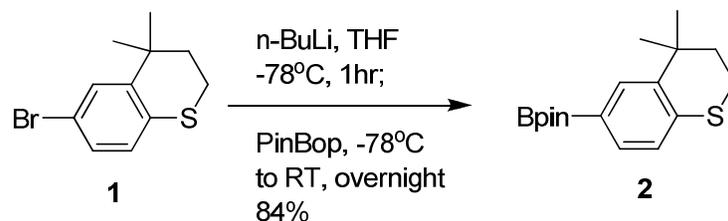
3) Synthetic Methods

General Methods:

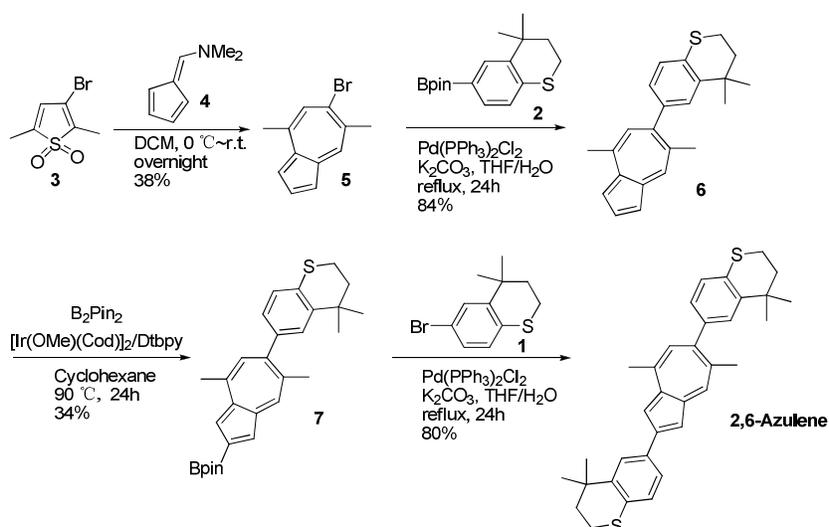
Chemicals were purchased from Sigma-Aldrich and used as received, unless otherwise noted. All reactions were performed in oven-dried round bottom flasks, unless otherwise noted. ^1H and ^{13}C nuclear magnetic resonance spectra were recorded at 300 K on a *Bruker* DRX300 (300MHz) or *Bruker* DRX400 (400MHz) FT NMR spectrometer. High-resolution mass spectra were from a *JMS-HX110 HF* mass spectrometer (ionization mode: FAB+). Uv-vis absorption spectra were taken on a Shimadzu UV-1800 spectrophotometer.

Synthetic Procedures:

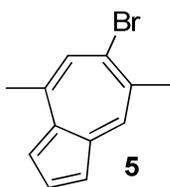
6-bromo-4,4-dimethylthiochroman,⁶ 2,5-dimethyl-3-bromothiophene-*S,S*-dioxide **3**,^{7,8} 1,3-dibromoazulene,⁹ 4,7-dibromoazulene¹⁰ and 2,4-Dibromo-3-methylthiophene (**10**)¹¹ were prepared as reported.



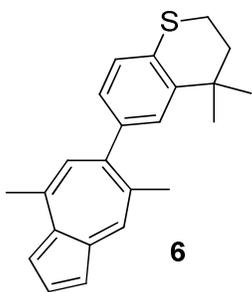
To a stirred solution of 6-bromo-4,4-dimethylthiochroman **1**¹¹ (2.0g, 7.8mmol) in 40ml dry THF was slowly added 2.3M n-BuLi (3.7ml, 8.6mmol) at -78°C under Ar. The resulting mixture was stirred at the same temperature for another hour, and then PinBop (3.2ml, 15.6mmol) was added via syringe. The reaction flask was allowed to warm up to room temperature and left to stir overnight. The mixture was quenched with methanol and water (40ml); then it was extracted with dichloromethane (3 x 50ml). The combined organic solvents were washed with brine, dried over Mg₂SO₄. After removing the solvent, the residue was purified by flash chromatography (ethyl acetate/hexane = 1:10) to give a yellowish white solid **2** (2g, 84% yield). ¹H NMR (400MHz, CDCl₃, ppm): δ 7.77 (d, *J* = 0.8 Hz, 1H), 7.45 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.09 (d, *J* = 8.0 Hz, 1H), 3.03 (m, 2H), 1.95 (m, 2H), 1.35 (s, 6H), 1.33 (s, 12H). ¹³C NMR (100MHz, CDCl₃, ppm): δ 141.2, 136.2, 132.7, 132.2, 126.0, 83.6, 37.7, 32.9, 30.1, 24.9, 23.3. HR-MS (FAB) *m/z* calcd for C₁₇H₂₅O₂SB: 304.1672, found: 304.1676.



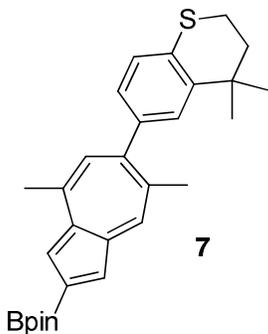
Scheme S1. Synthetic route of 2,6-Azulene.



2, 5-dimethyl-3-bromothiophene-*S*, *S*-dioxide **3**^{7,8} (1.72 g, 7.71 mmol) was dissolved in 150 mL dichloromethane under argon. The solution was cooled down to 0 °C, then a solution of dimethylaminofulvene **4** (9.33 g, 7.71 mmol) in 12 mL dichloromethane was added over a period of 1 hour. The mixture was stirred at 0 °C for 6 h before the addition of another 0.5 equivalents of dimethylaminofulvene **4** (dissolved in 5 mL dichloromethane). Then the reaction mixture was warmed up to room temperature and stirred over night. Water (50 mL) was added, the mixture was extracted with dichloromethane (3 × 30 mL), the combined organic phases was washed with water (3 × 50 mL) and dried with sodium sulfate. After removing the solvent, the crude product was purified by chromatography (ethyl acetate/hexane = 1:10) using alumina to give 4,7-dimethyl-6-bromoazulene **5** as a dark solid (692 mg, yield: 38%). ¹H NMR (400 MHz, CDCl₃, ppm): δ 8.30 (s, 1H), 7.82 (t, *J* = 3.6 Hz, 1H), 7.75 (s, 1H), 7.31 (d, *J* = 3.6 Hz, 1H), 7.26 (d, *J* = 4.4 Hz, 1H), 2.83 (s, 3H), 2.75 (s, 3H). ¹³C NMR (100 MHz, CDCl₃, ppm): δ 142.6, 138.6, 137.1, 136.3, 136.0, 135.2, 130.1, 130.0, 119.3, 116.1, 30.3, 24.1. HR-MS (FAB) *m/z* calcd for C₁₂H₁₁Br: 235.1237, Found (isotopic pattern): 234.0044, 235.1237, 236.0022.



4,7-dimethyl-6-bromoazulene **5** (235 mg, 1mmol), compound **2** (335 mg, 1.1 mmol), Pd(PPh₃)₂Cl₂ (70 mg, 0.1 mmol) and K₂CO₃ (276 mg, 2 mmol) were charged in a 25 mL Schlenk flask under argon, then 11 mL degassed THF/H₂O (10:1) was added. The result mixture was heated to 70 °C and stirred for 24 h. After cooled down to room temperature, water (10 mL) was added, the reaction mixture was extracted with dichloromethane (3 × 10 mL), the combined organic phase was washed with water (3 × 15 mL) and dried over sodium sulfate. After removing the solvent under reduced pressure, the crude mixture was purified by silica column chromatography (ethyl acetate/hexane = 1:10) to give compound **6** as a dark blue solid (284 mg, 84%). ¹H NMR (400 MHz, CDCl₃, ppm): δ 8.40 (s, 1H), 7.82 (d, , *J* = 4 Hz, 1H), 7.31-7.34 (m, 2H), 7.29 (d, *J* = 4 Hz, 1H), 7.15-7.19 (m, 2H), 7.02 (d, *J* = 8 Hz, 1H), 3.10 (t, *J* = 6 Hz, 2H), 2.39 (s, 3H), 2.88 (s, 3H), 2.04 (t, *J* = 6 Hz, 2H), 1.38 (s, 6H). ¹³C NMR (100 MHz, CDCl₃, ppm): δ 150.3, 143.4, 142.2, 141.7, 139.8, 139.0, 135.9, 135.3, 130.5, 128.9, 128.7, 126.7, 126.3, 125.9, 118.0, 114.6, 37.7, 33.1, 30.3, 26.1, 24.6, 23.1. HR-MS (FAB) *m/z* calcd for C₂₃H₂₄S: 332.1599, Found: 332.1607.

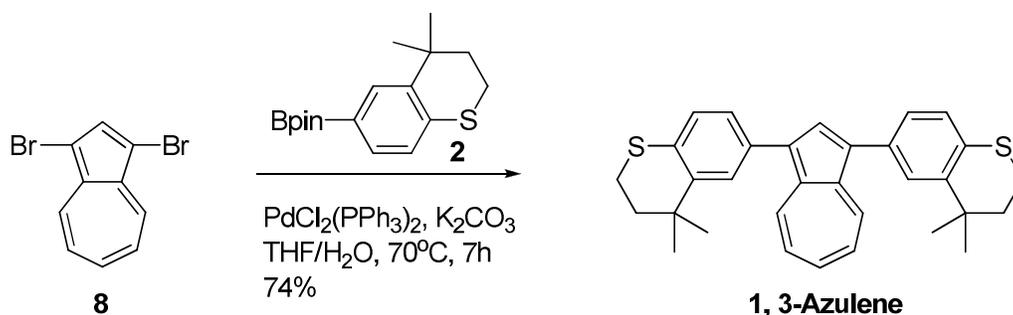


Compound **6** (200 mg, 0.6 mmol), Bis(pinacolato)diboron (B₂Pin₂, 76 mg, 0.3 mmol), [Ir(OMe)(Cod)]₂ (20 mg, 0.03 mmol) and 4,4'-di-tert-butyl-2,2'-bipyridyl (dtbpy, 32 mg, 0.12

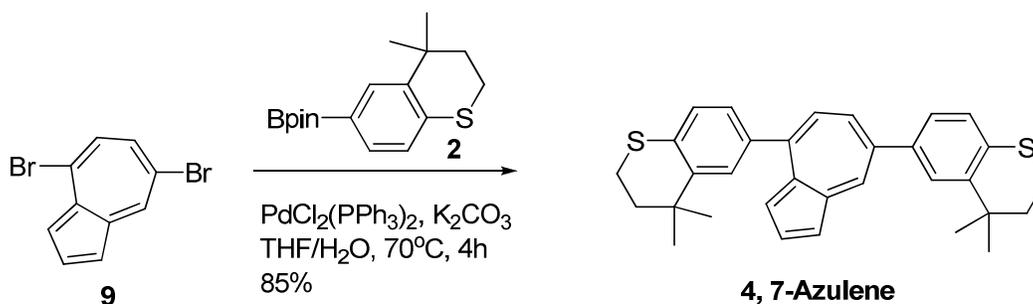
mmol) were charged in a 25-mL reaction vial under argon, then 10 mL of cyclohexane was added. The resulting mixture was heated to 90 °C and stirred for 24 h. After cooled down to room temperature, the solvent was removed under reduced pressure, and the dark residue was purified by silica column chromatography (ethyl acetate/hexane = 1:10) to give compound **7** as a purple solid (94 mg, 34%). ¹H NMR (400 MHz, CDCl₃, ppm): δ 8.35 (s, 1H), 7.66 (s, 1H), 7.63 (s, 1H), 7.28 (d, *J* = 2 Hz, 1H), 7.15 (d, *J* = 8 Hz, 1H), 7.06 (s, 1H), 6.97 (dd, *J*₁ = 6.4, 2 Hz, 1H), 3.08 (t, *J* = 6 Hz, 2H), 2.85 (s, 3H), 2.33 (s, 3H), 2.02 (t, *J* = 6 Hz, 2H), 1.42 (s, 12H), 1.35 (s, 6H). ¹³C NMR (100 MHz, CDCl₃, ppm): δ 151.9, 145.3, 142.2, 141.7, 141.4, 139.6, 136.3, 130.6, 128.8, 128.7, 126.6, 126.3, 125.8, 121.2, 83.6, 37.7, 33.1, 30.3, 29.7, 26.1, 24.9, 24.7, 23.1. HR-MS (FAB) *m/z* calcd for C₂₉H₃₅BO₂S: 458.2451, Found: 458.2456.



Compound **7** (90 mg, 0.2 mmol), compound **1** (51 mg, 0.2 mmol), Pd(PPh₃)₂Cl₂ (14 mg, 0.02 mmol) and K₂CO₃ (55 mg, 0.4 mmol) were charged 25-mL reaction vial under argon, then 3.5 mL degassed THF/H₂O (6:1) was added. The result mixture was heated to 70 °C and stirred for 24 h. After cooled down to room temperature, the solvent was removed under reduced pressure, and the dark residue was purified by silica column chromatography (ethyl acetate/hexane = 1:10) to give compound **2,6-Azulene** as a yellow-blue solid (80 mg, 80%). ¹H NMR (400 MHz, CDCl₃, ppm): δ 8.28 (s, 1H), 7.98 (d, *J* = 2 Hz, 1H), 7.67 (dd, *J*₁ = 6.4 Hz, *J*₂ = 2 Hz, 1H), 7.53 (d, *J* = 2 Hz, 1H), 7.49 (d, *J* = 2 Hz, 1H), 7.31 (d, *J* = 2 Hz, 1H), 7.15-7.20 (m, 2H), 7.11 (s, 1H), 7.01 (dd, *J*₁ = 6, 2 Hz, 1H), 3.09 (m, 4H), 2.88 (s, 3H), 2.36 (s, 3H), 2.04 (m, 4H), 1.46 (s, 6H), 1.37 (s, 6H). ¹³C NMR (100 MHz, CDCl₃, ppm): δ 149.1, 148.3, 142.3, 142.2, 142.1, 141.7, 140.2, 138.6, 137.2, 132.8, 132.0, 130.4, 129.8, 129.6, 127.0, 126.8, 126.2, 126.0, 125.3, 125.1, 113.7, 111.0, 37.8, 37.7, 33.1, 30.3, 30.2, 26.2, 24.6, 23.2, 23.1. HR-MS (FAB) *m/z* calcd for C₃₄H₃₆S₂: 508.2258, Found: 508.2265.

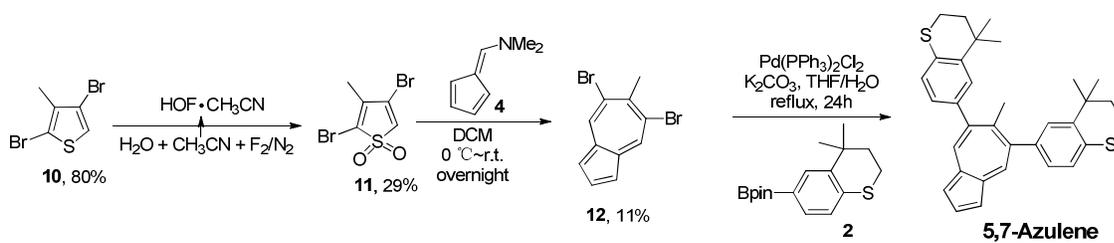


1,3-dibromoazulene **8**⁹ (33mg, 0.12mmol), compound **2** (140mg, 0.46mmol), Pd(PPh₃)₂Cl₂ (4mg, 0.006mmol) and K₂CO₃ (64 mg, 0.46 mmol) were charged in a 10ml 2-neck round bottom flask under argon, and then 3ml of degassed THF/H₂O (4/1) was added via a syringe. The reaction was heated at 70°C for 7hr and then cooled down to room temperature. Water (10ml) was added, the resulting green solution was extracted with dichloromethane (10ml x 3). The combined organic solvents were washed with brine and dried over Mg₂SO₄. After removing solvents, the residue was purified by flash chromatography (hexane/dichloromethane=2:1) to give **1,3-Azulene** as a green solid (41mg, 74%). ¹H NMR (400MHz, CDCl₃, ppm): δ 8.46 (d, *J* = 9.6 Hz, 2H), 8.04 (s, 1H), 7.62 (d, *J* = 1.6 Hz, 2H), 7.55 (t, *J* = 10 Hz, 1H), 7.33 (dd, *J* = 8.0, 1.6 Hz, 2H), 7.22 (d, *J* = 8.0 Hz, 2H), 7.08 (t, *J* = 10 Hz, 2H), 3.10 (m, 4H), 2.05 (m, 4H), 1.41 (s, 12H). ¹³C NMR (100MHz, CDCl₃, ppm): δ 142.4, 139.1, 136.8, 136.6, 136.3, 133.1, 130.7, 130.3, 128.3, 127.6, 127.0, 123.4, 38.0, 33.4, 30.5, 23.4. HR-MS *m/z* calcd for C₃₂H₃₂S₂: 480.1945, found: 480.1935.

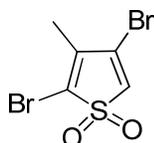


4,7-dibromoazulene **9**¹⁰ (25mg, 0.09mmol), compound **2** (106mg, 0.36mmol), Pd(PPh₃)₂Cl₂ (3mg, 0.004mmol) and K₂CO₃ (50mg, 0.36 mmol) were charged in a 10ml 2-neck round bottom flask under argon, and then 3ml of degassed THF/H₂O (4/1) was added via a syringe. The reaction was heated at 70°C for 4hr and then cooled down to room temperature. Water (10ml) was added, the resulting blue solution was extracted with DCM (10ml x 3). The combined

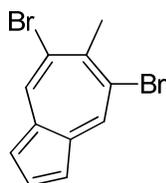
organic solvents were washed with brine and dried over Mg_2SO_4 . After removing solvents, the residue was purified by flash chromatography (hexane/dichloromethane=2:1) to give **4**, **7-Azulene** as a blue solid (35mg, 85%). ^1H NMR (400MHz, CDCl_3 , ppm): δ 8.63 (d, $J = 1.6$ Hz, 1H), 7.86 (t, $J = 3.6$ Hz, 1H), 7.82 (dd, $J = 10.8, 2.0$ Hz, 1H), 7.68 (d, $J = 2.0$ Hz, 1H), 7.64 (d, $J = 2.0$ Hz, 1H), 7.49 (d, $J = 3.6$ Hz, 1H), 7.35 (dt, $J = 8.0, 2.0$ Hz, 2H), 7.24 (s, 1H), 7.22 (d, $J = 1.6$ Hz, 1H), 7.20 (s, 1H), 3.10 (m, 4H), 2.04 (m, 4H), 1.43 (s, 6H), 1.39 (s, 6H). ^{13}C NMR (100MHz, CDCl_3 , ppm): δ 149.3, 142.6, 140.6, 137.7, 136.9, 136.3, 128.0, 127.2, 126.5, 126.4, 125.9, 125.6, 120.4, 118.5, 37.9, 33.4, 33.3, 30.5, 23.4, 23.3. HR-MS m/z calcd for $\text{C}_{32}\text{H}_{32}\text{S}_2$: 480.1945, found: 480.1948.



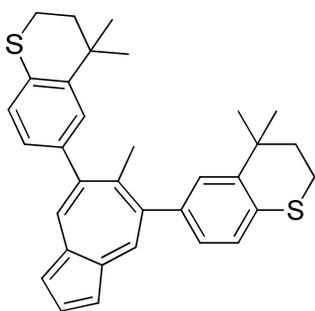
Scheme S2. Synthetic route of 5,7-Azulene.



2,4-Dibromo-3-methylthiophene **10** (942 mg, 3.68 mmol) was dissolved in 15 mL CH_2Cl_2 and cooled down to $0\text{ }^\circ\text{C}$, $\text{HOF}\cdot\text{CH}_3\text{CN}$ solution (0.23 M) was slowly added to the reaction mixture and the reaction was stopped after 2h by adding a saturated solution of NaHCO_3 . The organic material was extracted with CH_2Cl_2 , washed with water and dried over Na_2SO_4 . The crude product was purified by recrystallization from hot hexanes to afford 2,4-Dibromo-3-methylthiophene-*S*, *S*-dioxide (**11**) as a white solid (310 mg, yield: 29%). ^1H NMR (400 MHz, CDCl_3 , ppm): 7.01 (s, 1H), 2.12 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3 , ppm): δ 136.7, 131.1, 128.7, 118.4, 15.5. HR-MS (FAB) m/z calcd for $\text{C}_5\text{H}_4\text{Br}_2\text{O}_2\text{S}$: 288.9675, Found: 288.9651.

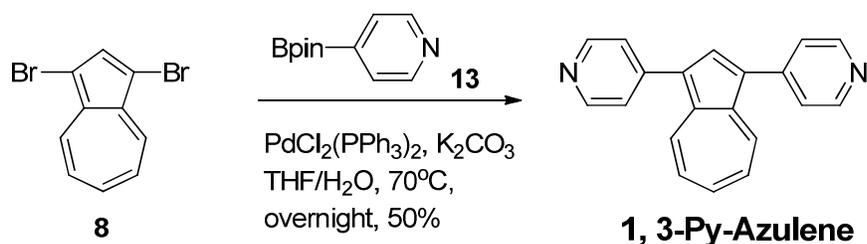


2,4-Dibromo-3-methylthiophene-*S,S*-dioxide **11** (310 mg, 1.07 mmol) was dissolved in 15 mL dichloromethane under argon. The solution was cooled down to 0 °C, then a solution of dimethylaminofulvene **4** (130 mg, 1.07 mmol) in 2 mL dichloromethane was added over a period of 30 min. The mixture was stirred at 0 °C for 6 h before the addition of another 0.5 equivalent of dimethylaminofulvene (dissolved in 2 mL dichloromethane). Then the reaction mixture was warmed up to room temperature and stirred overnight. After removing the solvent, the crude product was purified by chromatography (hexanes) using alumina to give 5,7-Dibromo-6-methylazulene **12** as a blue solid (36 mg, yield: 11%). ¹H NMR (400 MHz, CDCl₃, ppm): 8.80 (s, 2H), 7.88 (t, *J* = 4 Hz, 1H), 7.32 (d, *J* = 4 Hz, 2H), 3.08 (s, 3H). ¹³C NMR (100 MHz, CDCl₃, ppm): δ 145.1, 139.6, 139.4, 136.3, 120.2, 119.0, 35.9. HR-MS (FAB) *m/z* calcd for C₁₁H₈Br₂: 299.9925, Found: 299.8973.



5,7-Azulene

5,7-Dibromo-6-methylazulene **12** (35 mg, 0.117 mmol), compound **2** (89 mg, 0.292 mmol), Pd(PPh₃)₂Cl₂ (8 mg, 0.011 mmol) and K₂CO₃ (65 mg, 0.47 mmol) were charged in a reaction vial under argon, then 2.1 mL degassed THF/H₂O (20:1) was added. The result mixture was heated to 70 °C and stirred for 24 h. After cooled down to room temperature, the solvent was removed under high vacuum, and the crude mixture was purified by chromatography (dichloromethane/hexanes = 1:3) to give **5,7-Azulene** as a dark blue solid (45 mg, 78 %). ¹H NMR (400 MHz, CDCl₃, ppm): 8.34 (s, 2H), 7.86 (t, *J* = 3.6 Hz, 1H), 7.36 (d, *J* = 1.2 Hz, 2 H), 7.29 (d, *J* = 3.6 Hz, 2H), 7.16 (d, *J* = 8.4 Hz, 2H), 7.06 (dd, *J* = 1.6 Hz, 2H), 3.07-3.10 (m, 4H), 2.12 (s, 3H), 2.01-2.04 (m, 4H), 1.37 (s, 12H). ¹³C NMR (100 MHz, CDCl₃, ppm): δ 145.3, 142.7, 142.0, 138.2, 137.8, 137.2, 137.0, 129.9, 127.4, 126.8, 126.4, 117.7, 37.9, 32.9, 30.4, 27.8, 23.1. HR-MS (FAB) *m/z* calcd for C₃₃H₃₄S₂: 494.7650, Found: 494.7642.

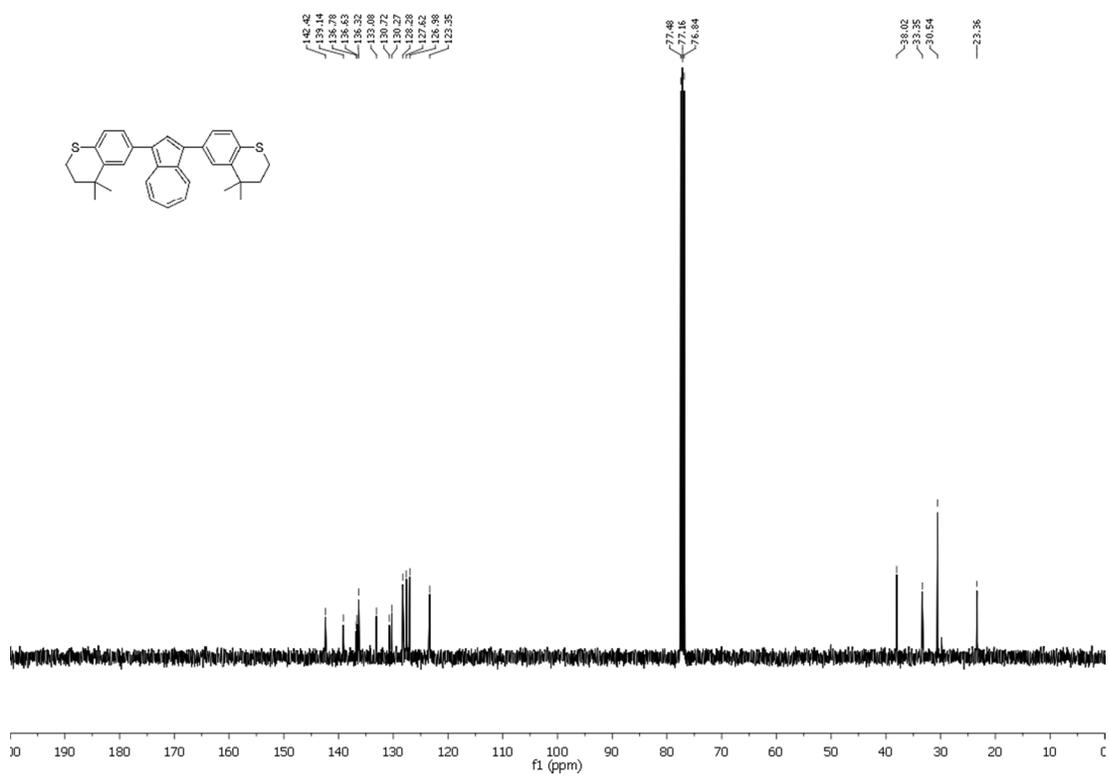
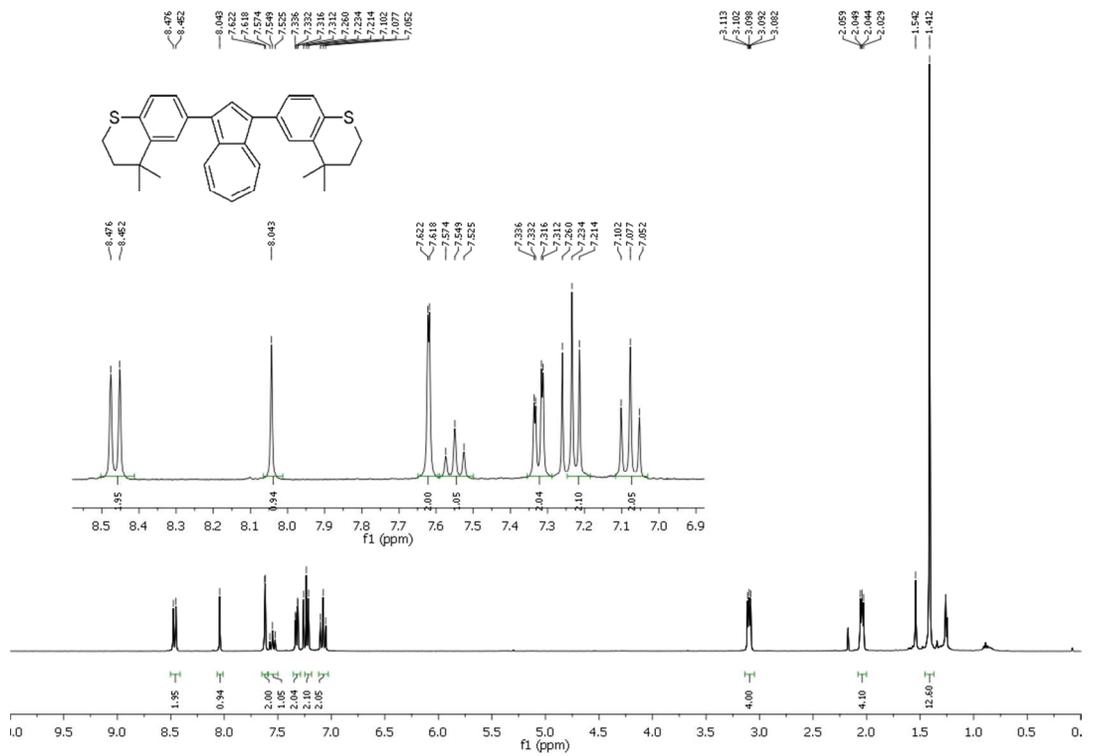


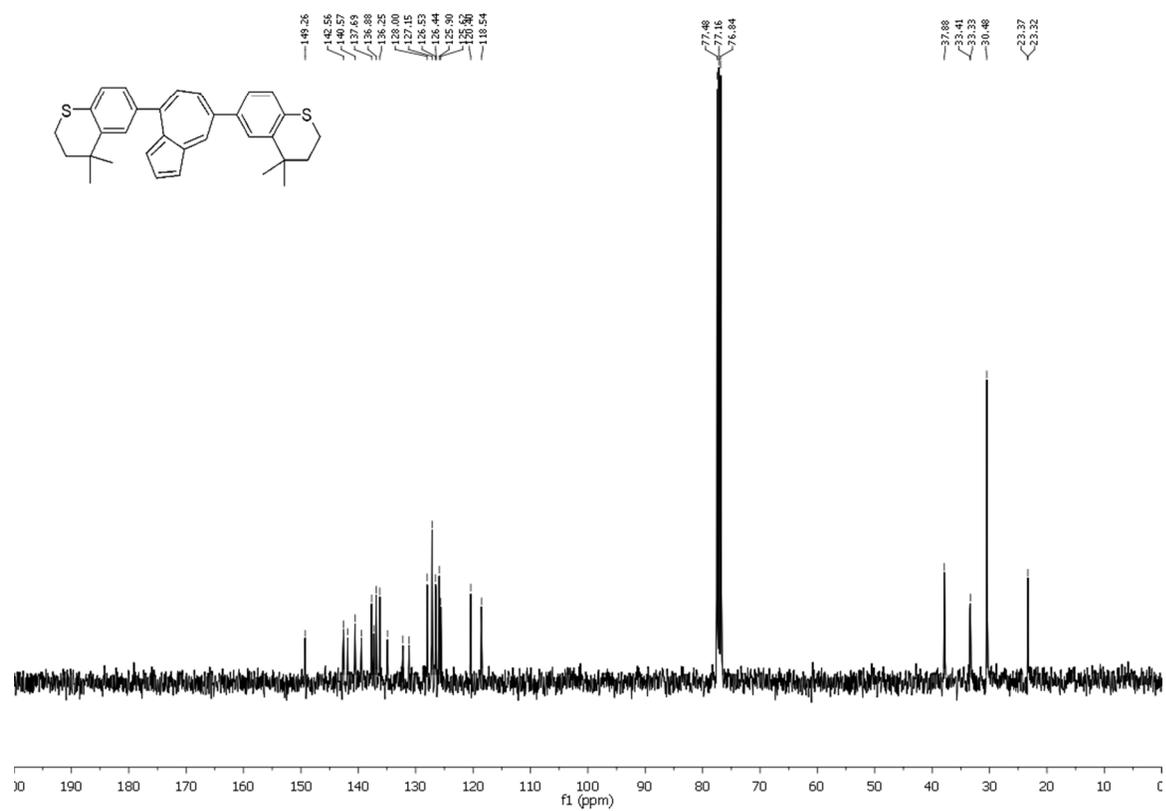
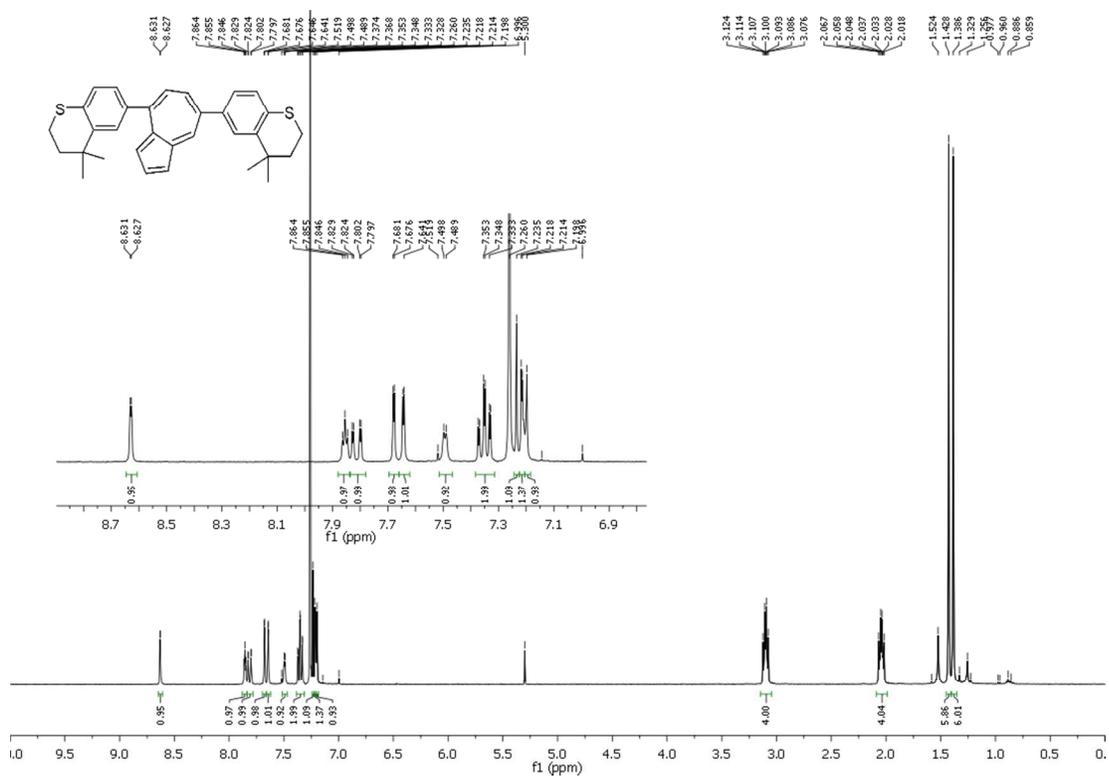
1,3-dibromoazulene **8** (100 mg, 0.35 mmol), Pyridine-4-boronic acid **13** (90%, 172 mg, 1.4 mmol), Pd(PPh₃)₂Cl₂ (12 mg, 0.017 mmol) and K₂CO₃ (193 mg, 1.4 mmol) were charged in a 20-mL reaction vial under argon, and then 6 ml of degassed THF/H₂O (5/1) was added via a syringe. The reaction was heated at 70°C for overnight and then cooled down to room temperature. Water (10ml) was added, the resulting green solution was extracted with dichloromethane (10ml x 3). The combined organic solvents were washed with brine and dried over Na₂SO₄. After removing solvents, the residue was purified by flash chromatography (hexane/dichloromethane=2:1) to give **1, 3-Py-Azulene** as a green solid (50 mg, 50%) ¹H NMR (400MHz, CDCl₃, ppm): δ 7.34 (t, *J* = 10 Hz, 2H), 7.56 (m, 4H), 7.76 (t, *J* = 10 Hz, 1H), 8.19 (s, 1H), 8.65 (d, *J* = 9.6 Hz, 2H), 8.73 (m, 4H). ¹³C NMR (100 MHz, CDCl₃, ppm): δ 124.07, 125.55, 127.54, 136.14, 136.74, 137.70, 139.91, 144.14, 149.96.

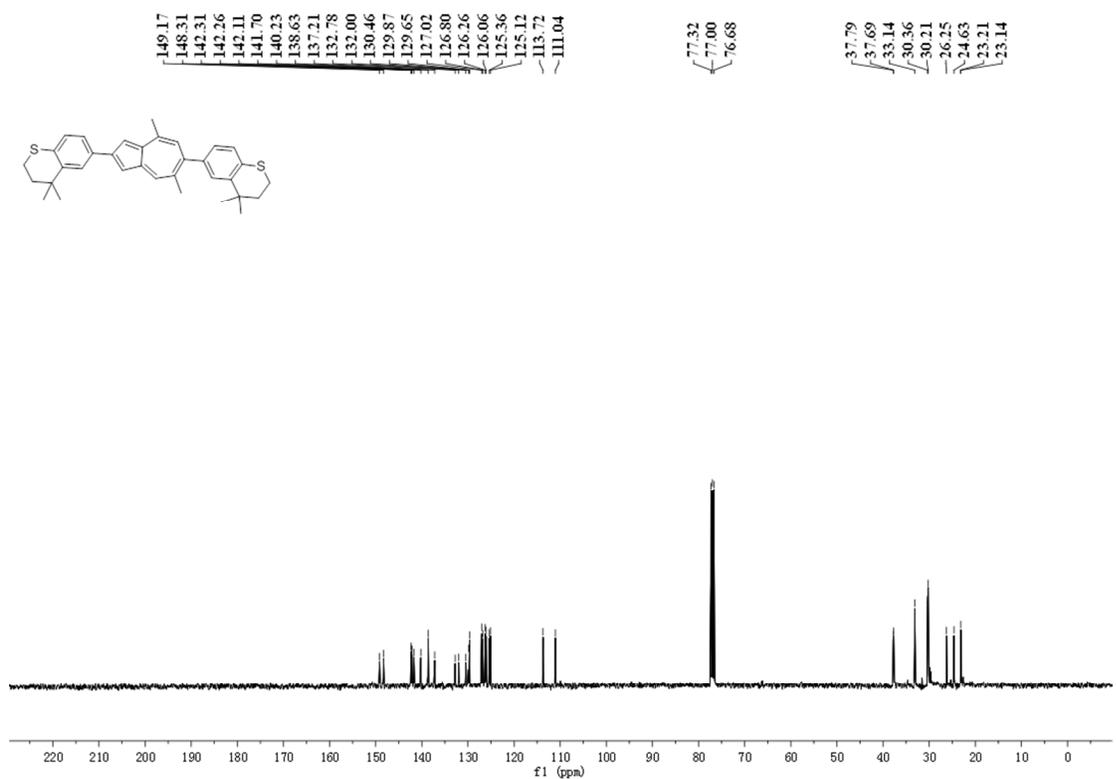
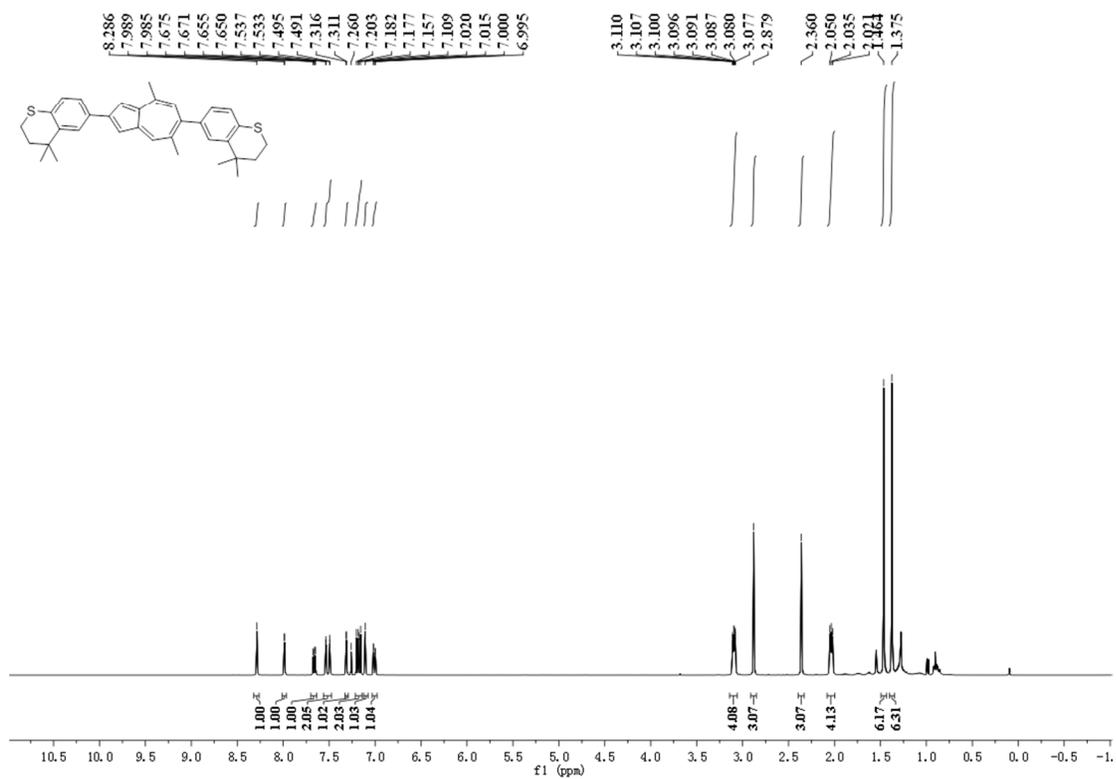
4) References:

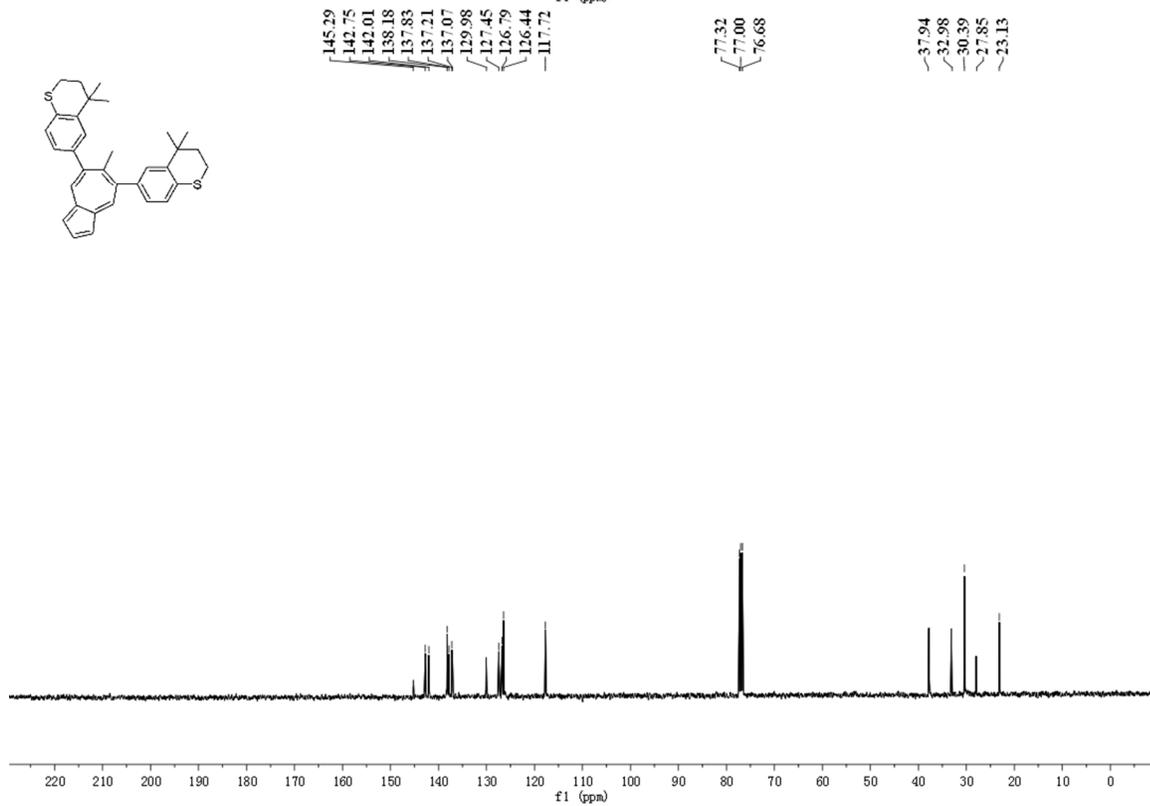
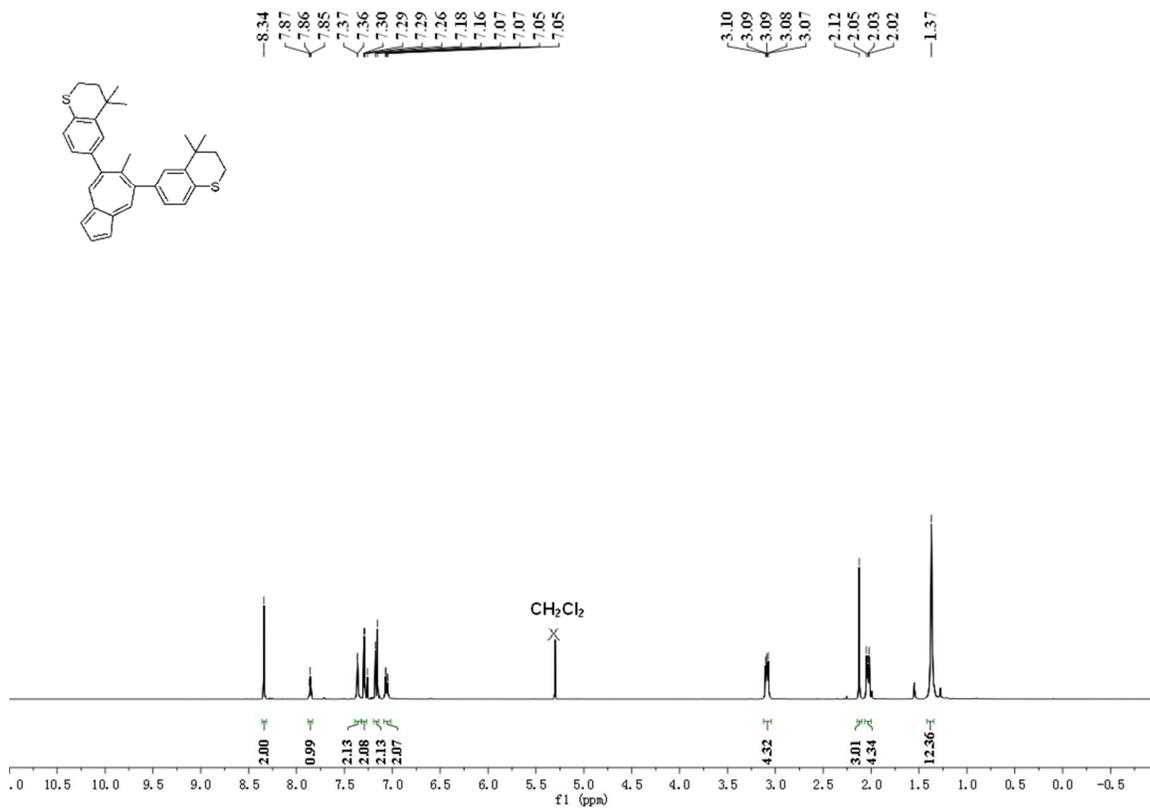
- (1) Hedin, L. *Phys. Rev.*, **1965**, 139, (3A), A796-A823.
- (2) Büttiker, M.; Imry, Y.; Landauer, R.; Pinhas, S. *Phys. Rev. B*, **1985**, 31, (10), 6207-6215.
- (3) Thygesen, K. S.; Rubio, A. *Phys. Rev. B*, **2008**, 77, (11), 115333.
- (4) Pariser, R.; Parr, R. G. *The Journal of Chemical Physics*, **1953**, 21, (3), 466-471.
- (5) Ohno, K. *Theoretica chimica acta*, **1964**, 2, (3), 219-227.
- (6) Meisner, J. S.; Sedbrook, D. F.; Krikorian, M.; Chen, J.; Sattler, A.; Carnes, M. E.; Murray, C. B.; Steigerwald, M.; Nuckolls, C. *Chemical Science*, **2012**, 3, (4), 1007-1014.
- (7) Ko, C.-C.; Kwok, W.-M.; Yam, V. W.-W.; Phillips, D. L. *Chemistry – A European Journal*, **2006**, 12, (22), 5840-5848.
- (8) Tsirk, A.; Gronowitz, S.; Hörnfeldt, A.-B. *Tetrahedron*, **1995**, 51, (25), 7035-7044.
- (9) Mitchell, R. H.; Chen, Y.; Zhang, J. *Organic Preparations and Procedures International*, **1997**, 29, (6), 715-719.
- (10) Amir, E.; Amir, R. J.; Campos, L. M.; Hawker, C. J. *J. Am. Chem. Soc.*, **2011**, 133, (26), 10046-10049.
- (11) Mitchell, R. H.; Iyer, V. S. *J. Am. Chem. Soc.*, **1996**, 118, (4), 722-726.

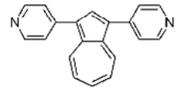
5) NMR Spectra



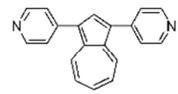
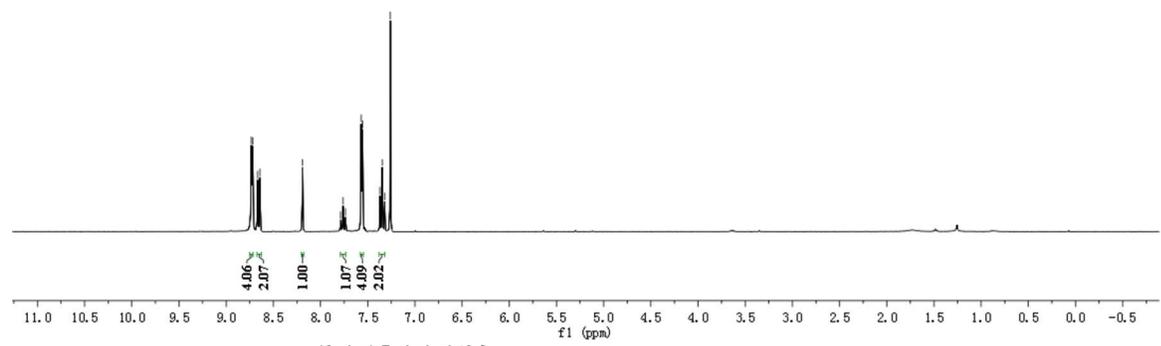








8.73
8.72
8.67
8.64
8.19
7.79
7.76
7.74
7.57
7.56
7.56
7.37
7.35
7.32
7.26



149.96
144.14
139.91
137.70
136.74
136.14
127.54
125.55
124.07

77.32
77.00
76.68

