

## Background

Organic semiconductors are growing in application for utilization in modern technology such as solar panels, electronic devices, and printers. The main interest in these organic compounds is their low cost (compared to silicon, a commercial semiconductor) and flexibility. Organic semiconductors are characterized by several integral traits [1] including, but not limited to:

- (1) extended **conjugation** throughout the molecule
- (2) **coplanarity** of the entire molecule so that all p-orbitals align
- (3) **narrow band gap** to significantly increase the electrical conduction from HOMO to LUMO

Bibenzothiophene (BBT) (4) is an example of an organic semiconductor. [2, 3] Different derivatives of BBT have been reported, including extending the conjugation of BBT by aromatic groups [2] and by introducing sulfonic acid groups to it to increase water solubility for the use as a fluorescent probe for quantifying caffeine in caffeine-containing beverages. [4]

## Research Question

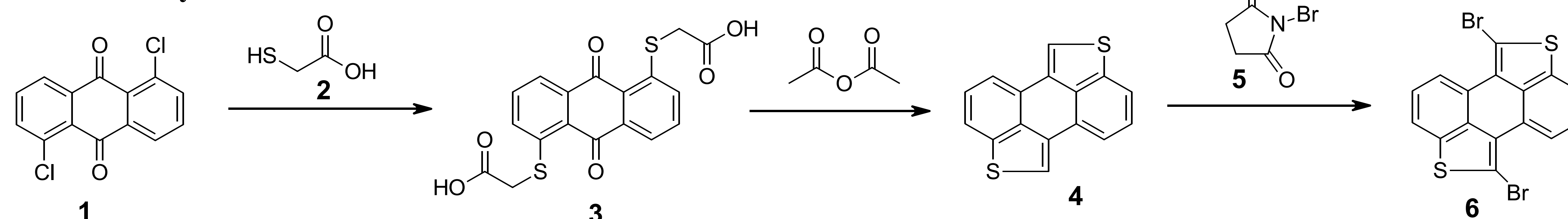
This research seeks to further synthesize, analyze and understand the effect of linking aromatic phenyl- and thienyl groups to the BBT core on band-gap energies. These groups will be linked in two ways to the BBT core: (a) via a single bond; (b) via a C,C-triple bond.

## Methods

**Synthesis:** our synthesis can be divided into two parts: **Part 1:** the synthesis of brominated BBT 6 (Scheme 1) following the basic protocol of [2]: reacting 1,5-dichloroanthraquinone 1 with thioglycolic acid 2 produced bis-2,2'-[(9,10-dihydro-9,10-dioxo-1,5-anthracenediyl)bis(thio)]acetic acid 3. Acetic anhydride refluxed with 3 produced BBT 4. N-bromosuccinimide 5 reacted with 4 produced brominated BBT 6. **Part 2** describes five carbon coupling reactions with 6: two Suzuki and three Sonogashira reactions (Scheme 2) following the general reaction protocol of [5] for the Suzuki coupling and [6] for the Sonogashira coupling. All coupling reactions used Pd(PPh<sub>3</sub>)<sub>4</sub> as the catalyst.

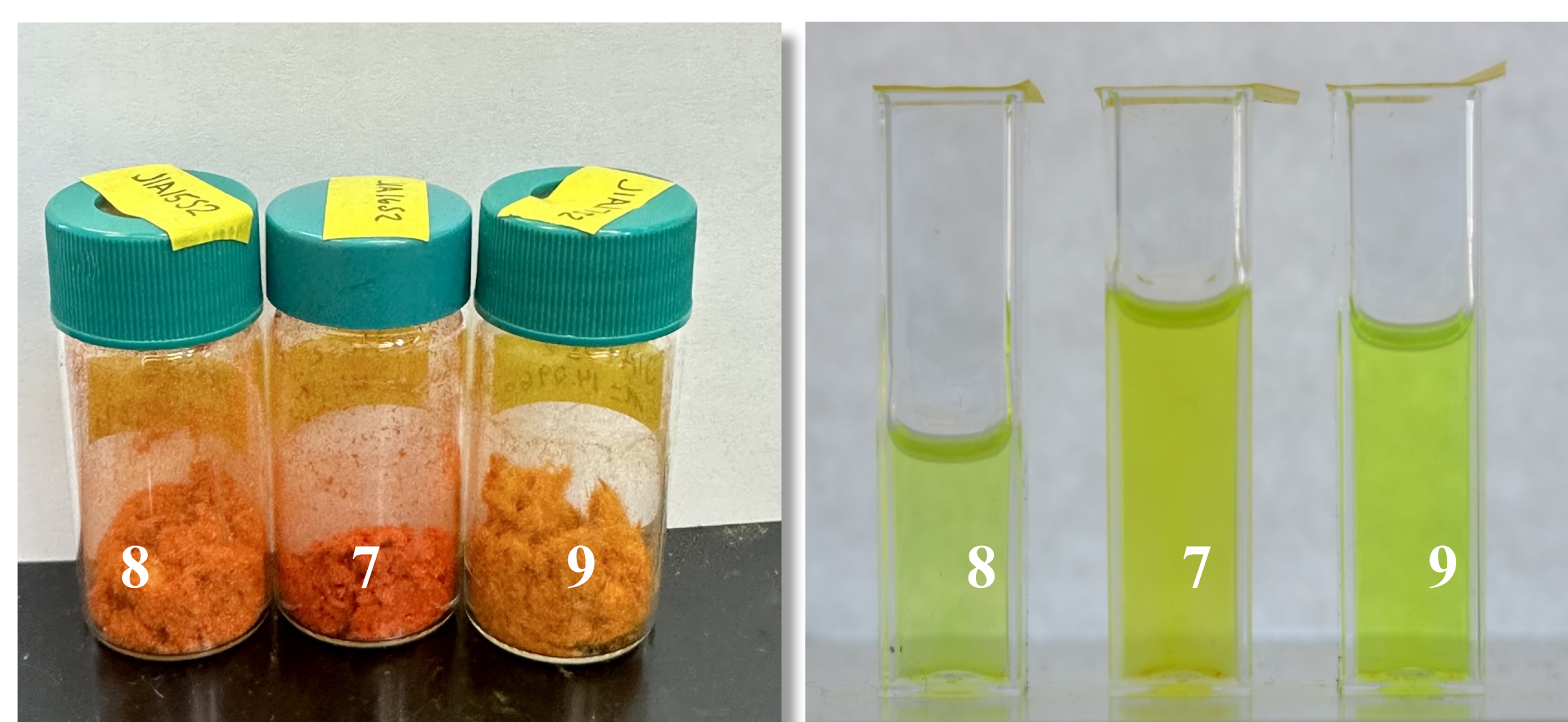
**Analysis:** The synthesized compounds were analyzed by TLC (SiO<sub>2</sub>, toluene as mobile phase), FTIR spectroscopy (Perkin Elmer UATR Spectrum 2, four scans), melting point analysis (Mettler Toledo MP90), and UVvis spectroscopy (Thermo Fisher Genesys 10S). The Suzuki and Sonogashira products were also analyzed via molecular modeling using Spartan 16 calculations, "Equilibrium Geometry" at "Ground" state in "Gas"; using different DFT functional with the 6-31G\* basis set.

## Scheme 1. Synthesis of Brominated BBT 6



**Table 1.** UV-vis and band gap energy data for BBT and BBT-based compounds.

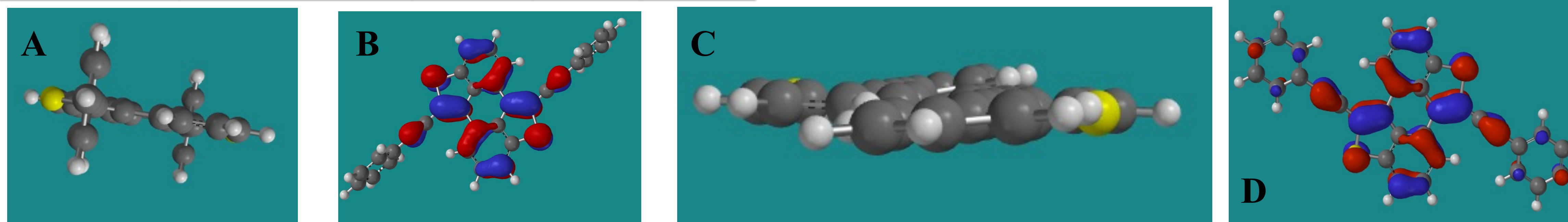
	$\lambda_{max}$	$E_g$ (eV)
Solid 4 (BBT)	348, 366, 380nm	3.56, 3.39, 3.26
Solid 8	442, 468 nm	2.81, 2.65
Solid 9	452, 476nm	2.74, 2.69
Solid 11	438, 464nm	2.83, 2.67



**Figure 2.** Color and appearance of the three Sonogashira-based solids 7-9 (left side) and their respective solutions (right side).

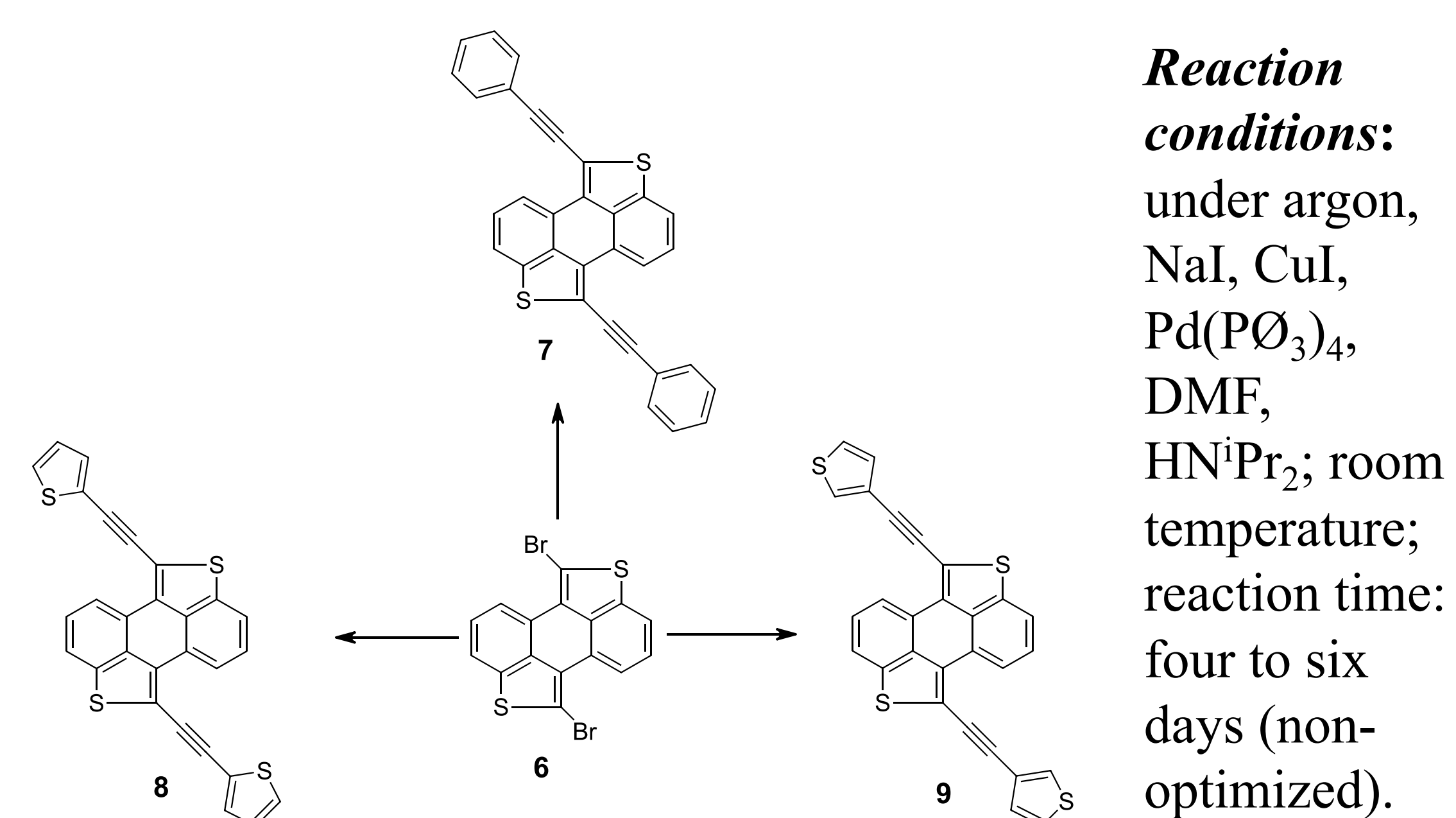
**Table 3.** HOMO/LUMO energies computed for 7 using various DFT functionals.

Compound	DFT Functional	HOMO (eV)	LUMO (eV)	$E_g$ (eV)
4	B3LYP			3.51
7	B3LYP	-5.03	-2.02	3.01
7	$\omega$ B97X-D	-6.7	-0.71	5.99
7	EDF2	-4.85	-2.35	2.50
7	B3LYP(start at dihedral = 45°)	-5.03	-2.02	3.01

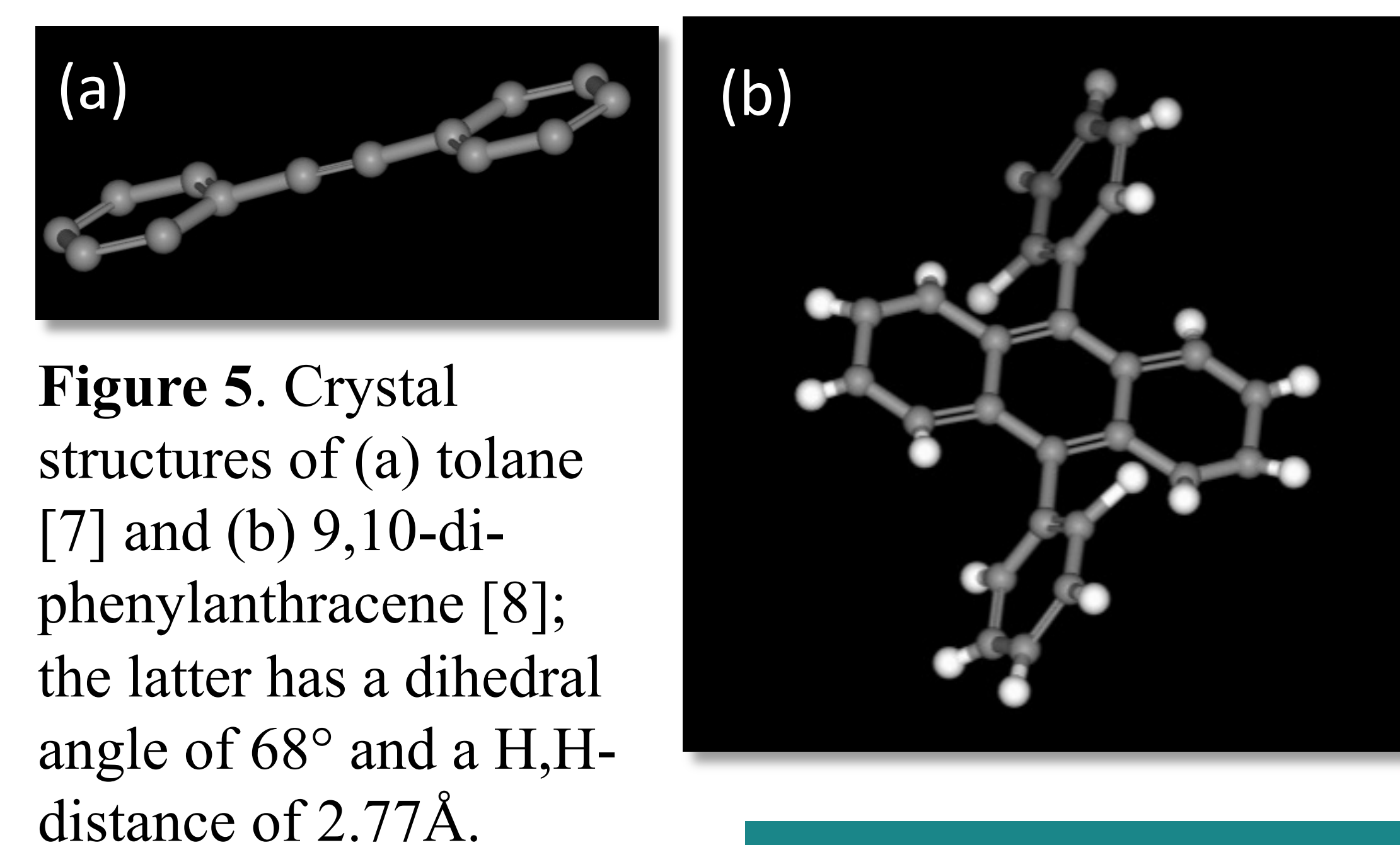
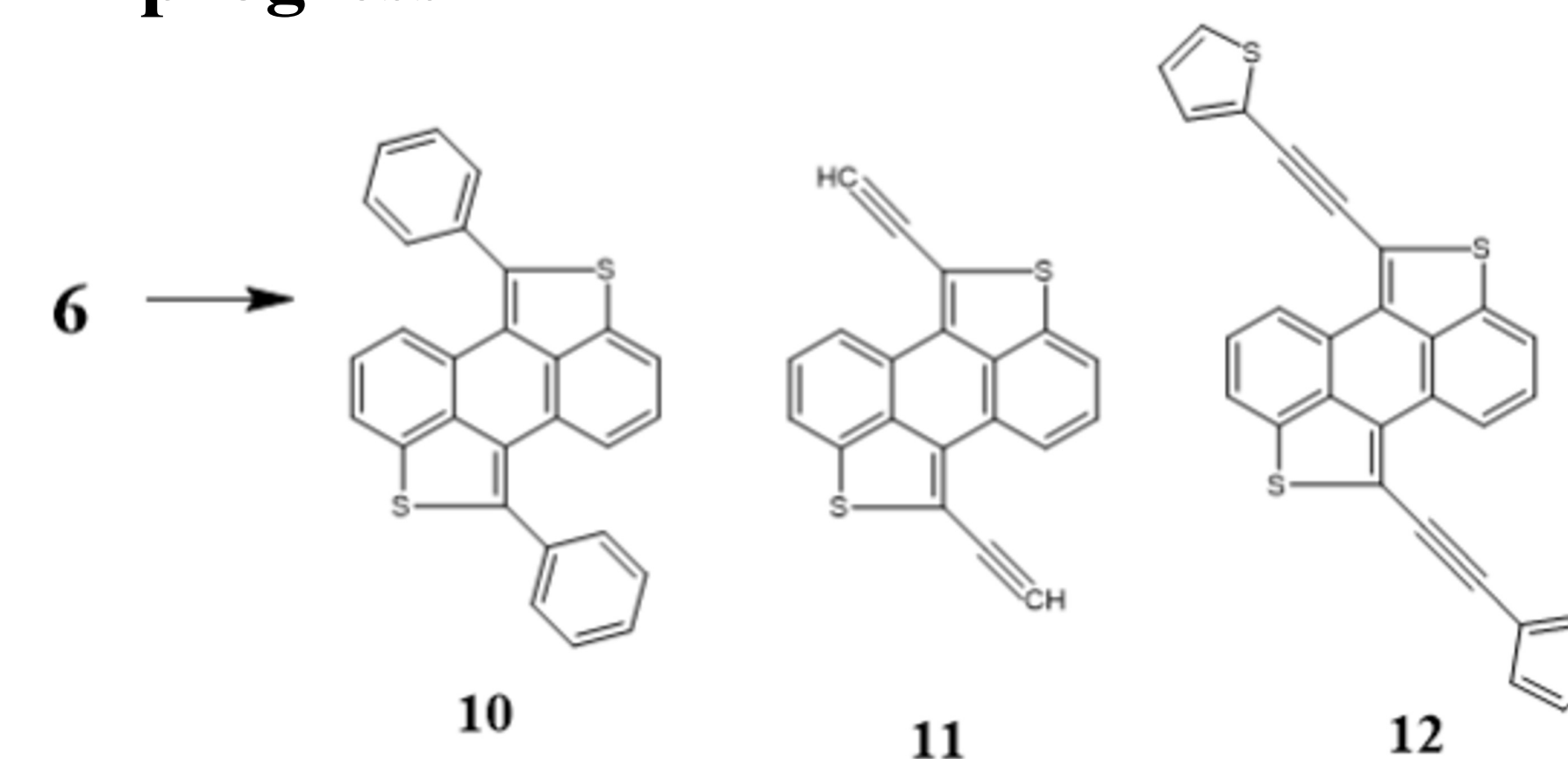


**Figure 4.** (A) non-coplanar geometry for 7 using the B3LYP functional; (B) respective HOMO; (C) coplanar geometry for 7 using the EDF2 functional; (D) respective HOMO. The H,H-distance in D is 2.77 Å (orange dashed line).

## Scheme 2. Successful carbon-carbon coupling reactions



## Scheme 3. Carbon-carbon coupling reactions in progress



**Figure 5.** Crystal structures of (a) toluene [7] and (b) 9,10-diphenylanthracene [8]; the latter has a dihedral angle of 68° and a H,H-distance of 2.77 Å.

## Results and Conclusions

1. Compounds 6-9 were synthesized in about 80% yield. Two Suzuki reactions were attempted but were unsuccessful.
2. The yellow-orange colors of 7, 8 and 9 (Figure 2) and  $\lambda_{max}$  values of about 450nm translate into bandgap energies of about 2.75eV which places them in the range of bandgap values for semiconductors which is 2-3 eV.
3. Depending on the computational method used, the phenyl ring will align either coplanar with the core or will rotate out of plane. (Figure 4).
4. Known single crystal X-ray structures can serve as a predictor of geometries as they show coplanarity for two phenyl rings connected by a triple bond (Figure 5a) and a non-coplanar geometry for a phenyl ring directly attached to an anthracene core (Figure 5b).

## Future Work

1. Further analysis of the three Sonogashira products (NMR and X-ray analysis).
2. Resynthesis of the desired Suzuki compounds.

## References and Acknowledgments

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