



# Alternative Sustainable Syntheses of 7-Substituted Anthra[2,3-*b*]thiophene Derivatives and Naphtho[2,3-*b*:6,7-*b'*]dithiophene

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## Introduction

Acene-cores terminating at one or both ends with thiophene units (Figure 1) are potentially attractive motifs for formation a wide range of semiconductor devices such as: bank cards, televisions, solar cells, medical devices, thermoelectric devices etc. These applications have become completely integrated into our daily lives with the advent of the ‘smart phone’ and similar technologies (Figure 2).

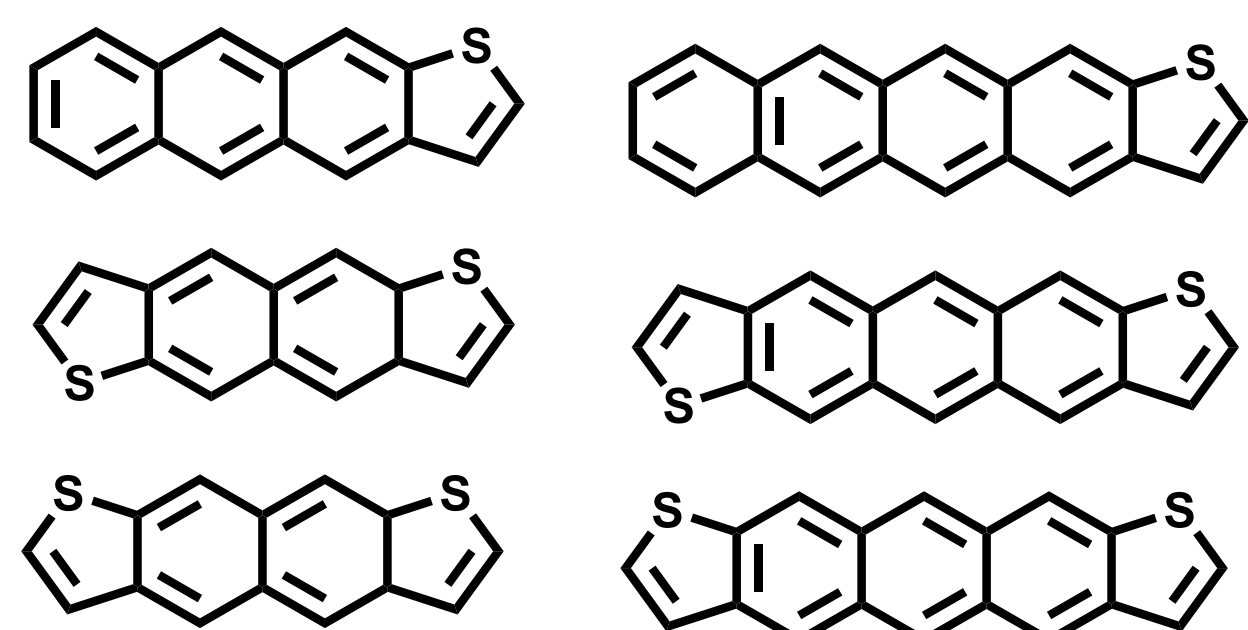


**Figure 1. Molecular structures of typical acenedithiophenes cores**

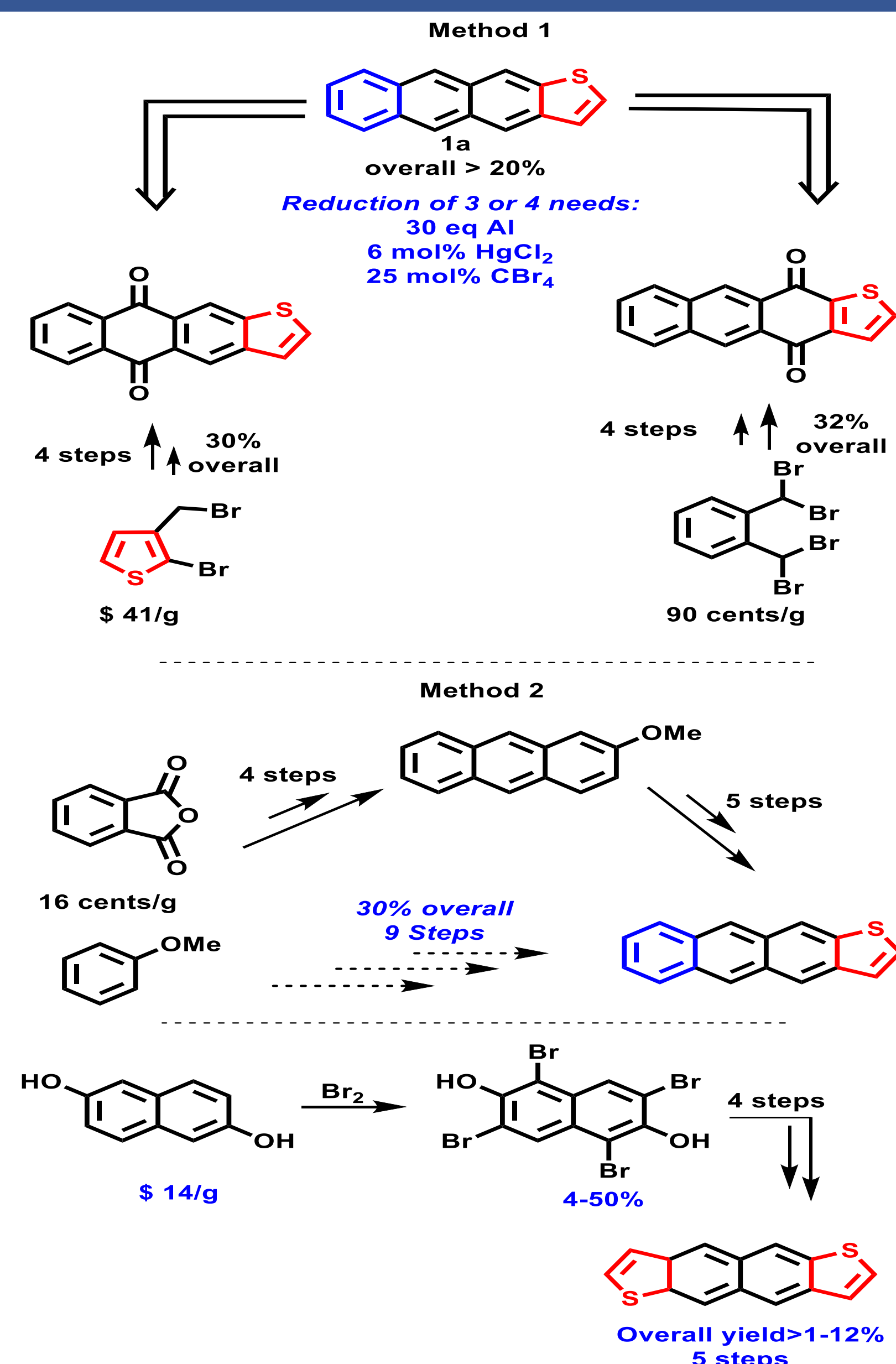


**Figure 2. Representative examples of device applications of organic electronic materials**

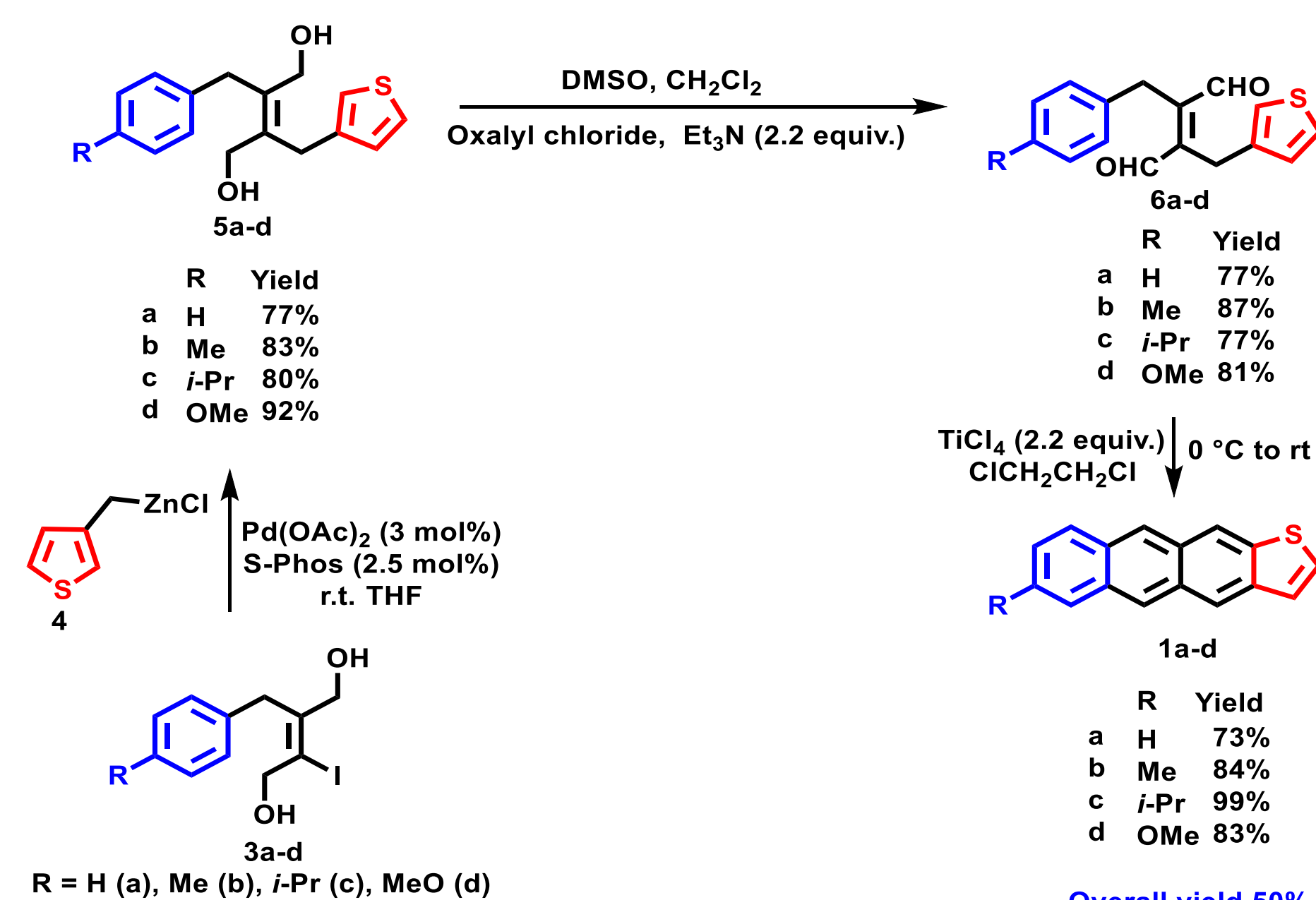
## Literature Methods

Various methodologies have been employed over the last 40 years for the preparation of the parent anthra[2,3-*b*]thiophene **1**. Multi-step syntheses using expensive (in either cost or time), or higher toxicity or environmentally less than desirable reagents, are the norm. Scheme 1 highlights all of the literature approaches to the synthesis of **1a** and **2**.

## Literature Methods



## Results and Discussion

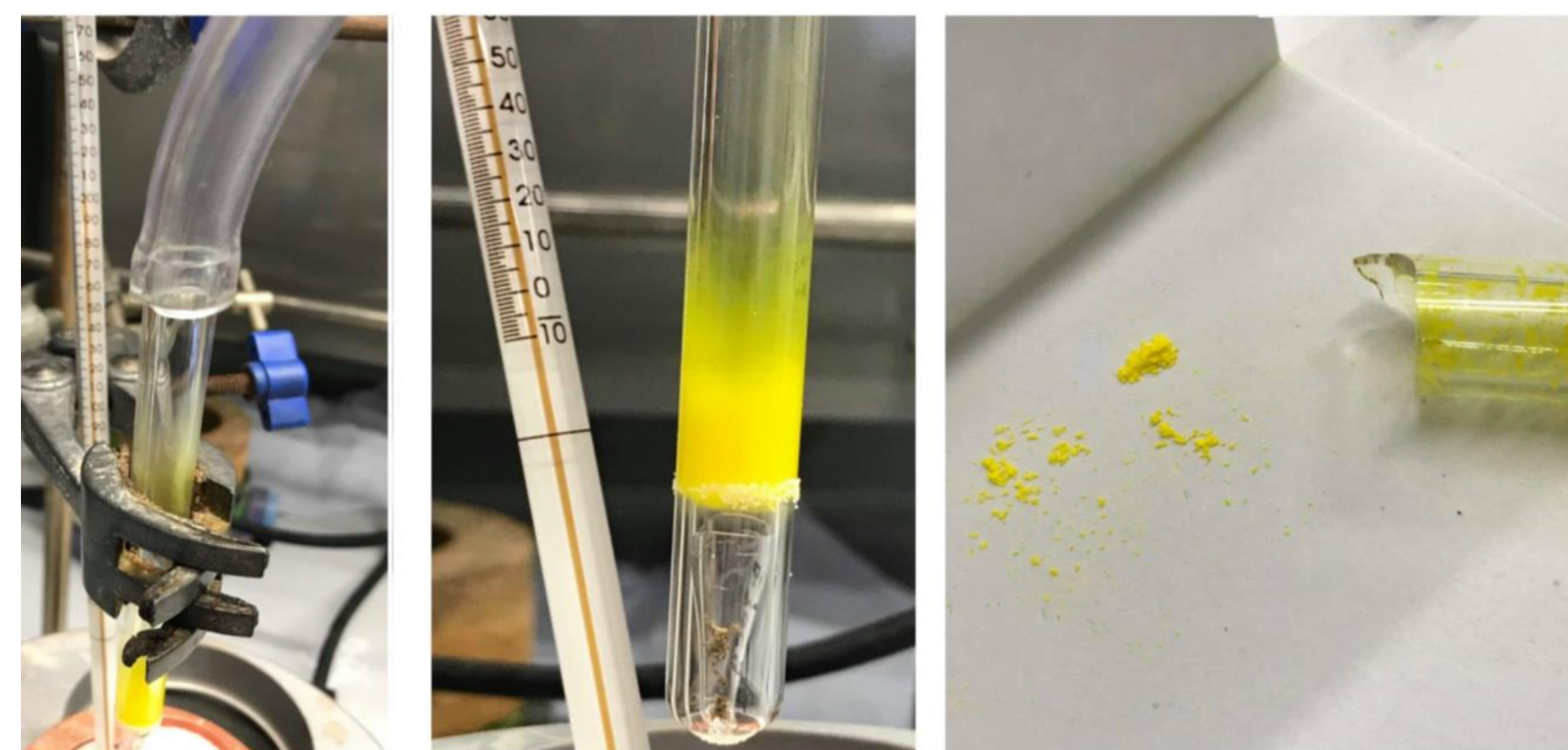


**Scheme 2. Methodology for synthesis of anthra[2,3-*b*]thiophenes 1a-d**

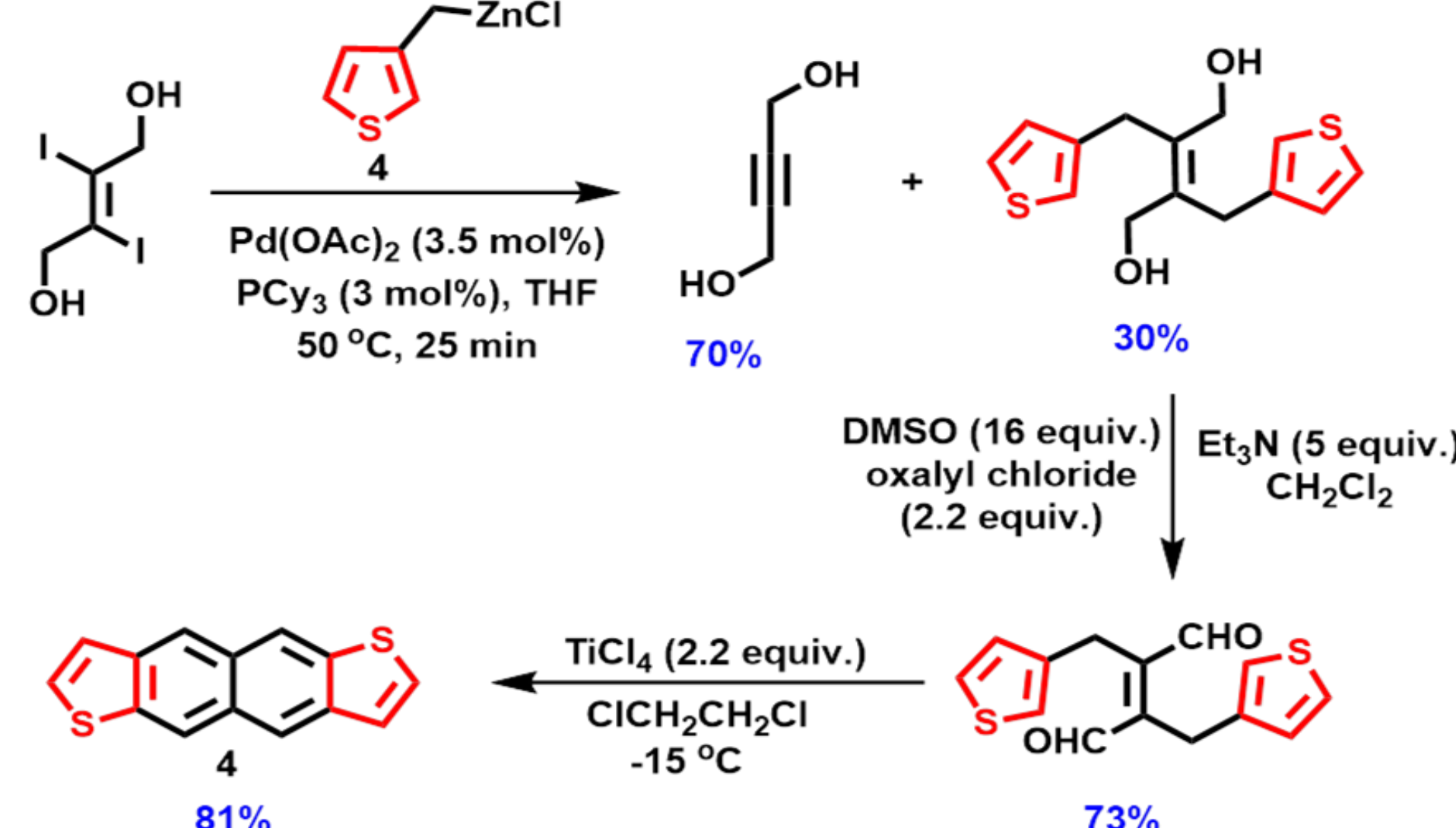
## Results and Discussion

Our approach to **1a–1d** (Scheme 3) begins with the cheap commercially available crystalline iodides **3a–d**. Alternatively, **3a–d** are easily prepared from 2-butyne-1,4-diol and benzylic chlorides, both of which are typically available at low cost (<5 pence mmol<sup>-1</sup>).

One of the advantages of Scheme 2 is the greater solubility of the 7-alkyl derivatives **1b–1d**, allowing routine acquisition of fully assigned <sup>13</sup>C NMR spectra, while **1b–1d** are also easier to process in subsequent further functionalization or device preparations (Figures 3-4).

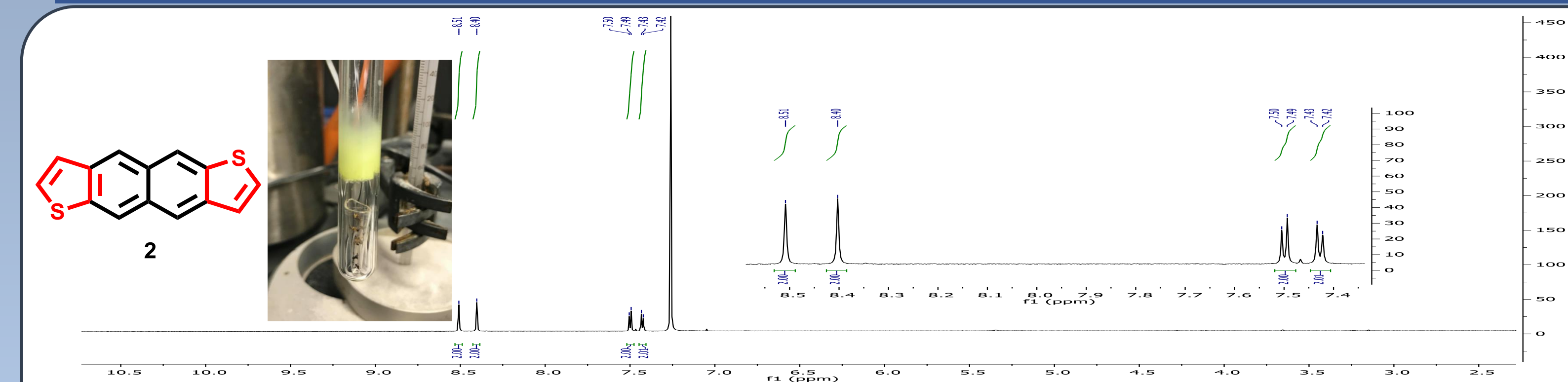


In contrast to the literature synthesis of naphtho[2,3-*b*:6,7-*b'*]dithiophene **2**, as shown in Scheme 1, which use expensive (toxic) starting materials and provided low overall yield, we have made naphtho[2,3-*b*:6,7-*b'*]dithiophene **2** using cheap and straightforward method (Scheme 3).



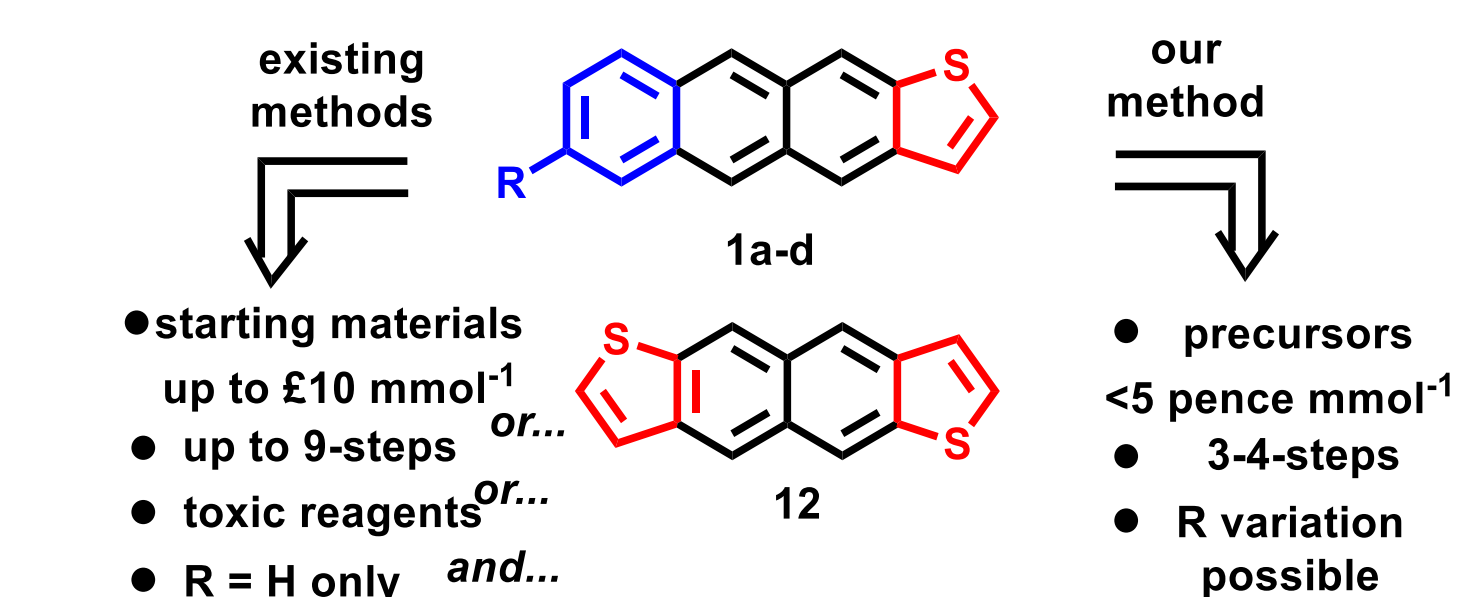
**Scheme 3. Straightforward Synthesis of Naphtho[2,3-*b*:6,7-*b'*]dithiophene 2**

## Representative Spectra



## Conclusion

- Efficient synthesis of 7-substituted compounds **1a–d** and **2**
- The methods employed are simple
- Use of low cost starting materials
- Chromatography free approaches
- The procedure are scalable
- Compounds **1a–d** are prepared in three steps in overall yields of >50%.



**Scheme 4. Comparative between our approach and the literature**

## References

1. **Mustafa A. Al-jumaili**, Simon Woodward “Syntheses of 7-Substituted Anthra[2,3-*b*]thiophene Derivatives and Naphtho[2,3-*b*:6,7-*b'*]dithiophene” *J. Org. Chem.* **2018**, *83*, 11437–11445.
2. **Mustafa A-jabbar Al-jumaili**, Simon Woodward, “Efficient Synthesis of 2,5-Dicarbonyl Derivatives of 3,4-Ethylenedithiophene (EDTT) via Addition- Elimination Reaction” *Tetrahedron* **2017**, *73*, 5847–5852.
3. **Takimiya et al.** *J. Am. Chem. Soc.* **2011**, *133*, 5024–5035.

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