Claisen-Schmidt(C-S) Condensation Based Organic Semiconductor Polymers

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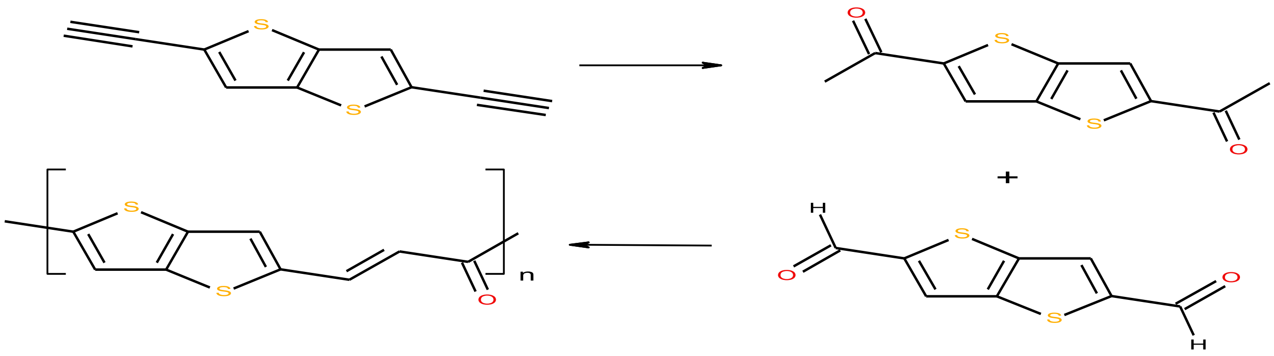
Chemistry:

The Sonogishira coupling reaction affords alkyne terminal aromatic derivatives. With it, the bromine derivatives of a wide variety of organic semiconductor intermediates can be readily converted to terminal alkynes. Such terminal alkynes can be converted to ketones in high yields. The Vilsmeir reaction of formamide and phosphorus oxychloride yields aldehyde terminal derivatives also of a wide variety of precursor intermediate aromatic organic semiconductors. The Claisen-Schmidt condensation between a methyl ketone and an aldehyde, would afford new unique semiconductor polymers. For example:

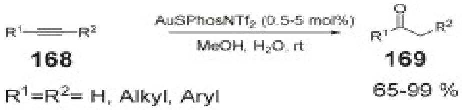


Scheme 1: This is a simple example of this idea. This polymerization can be applied to intermediates of DPP, Isoindigo, Pechman, Imide etc.. resulting in new unique polymers. Such donor polymers conjugated through the enol or enolate, would exhibit lumo's/homo's based on acidity or alkalinity.

Ketones :

Transformation of alkynes to ketones is a well known reaction. In the past Hg salts were used but modern low toxicity catalysts are now available.

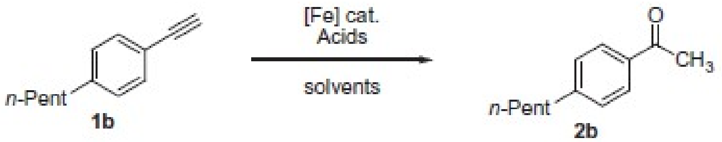
Scheme 67



Chinchilla, Rafael, and Carmen Nájera. "The Sonogashira reaction: a booming methodology in synthetic organic chemistry."*Chemical reviews",* 107.3 (2007): 874-922.

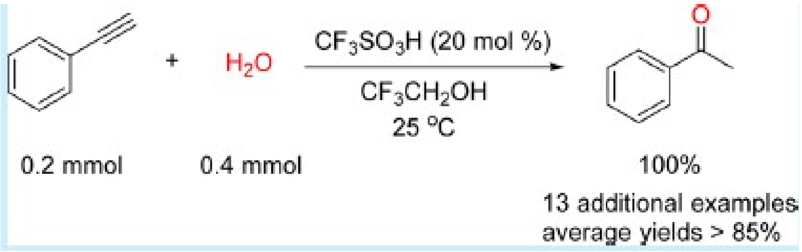
Chinchilla, Rafael, and Carmen Najera. "Chemicals from alkynes with palladium catalysts."*Chemical reviews",* 114.3 (2013): 1783-1826.

Xu, Yun, et al. "Hydration of alkynes at room temperature catalyzed by gold (I) isocyanide compounds."*Green Chemistry",* 17.1 (2015): 532-537.



9	$FeCl_2 \cdot 4H_2O$	MsOH	DCE	60	1	92

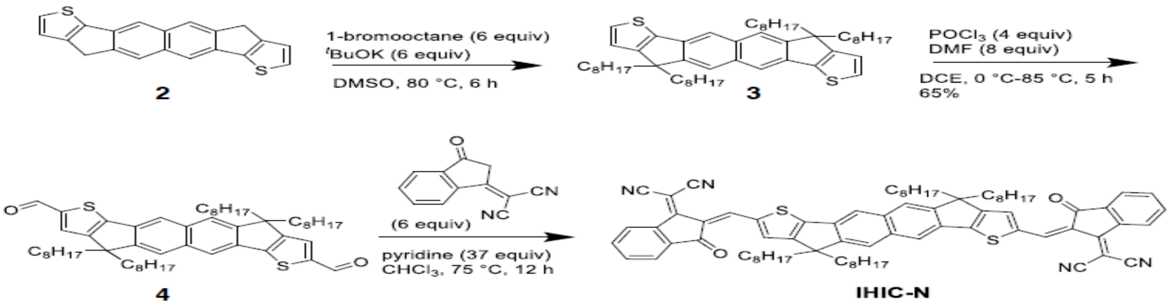
Park, Jungmin, et al. "Iron-catalyzed indirect hydration of alkynes in presence of methanesulfonic acid."*Tetrahedron Letters",* 54.33 (2013): 4414-4417.



Liu, Wenbo, Haining Wang, and Chao-Jun Li. "Metal-free Markovnikov-type alkyne hydration under mild conditions."*Organic letters",* 18.9 (2016): 2184-2187.

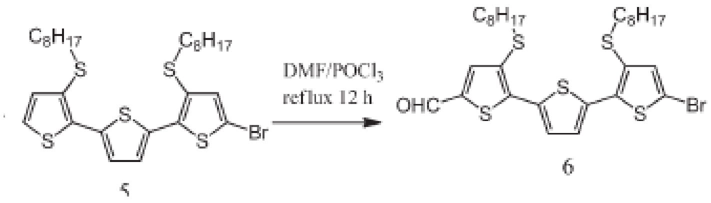
Aldehyde derivatives:

The Vilsmeier Haack (V-H) reaction is typically employed to add a terminal aldehyde to electron donor sections of non-Fullerene acceptors (NFA). The reaction is with POCl3 and DMF. For example conversion of 3 to 4 below is a typical example.

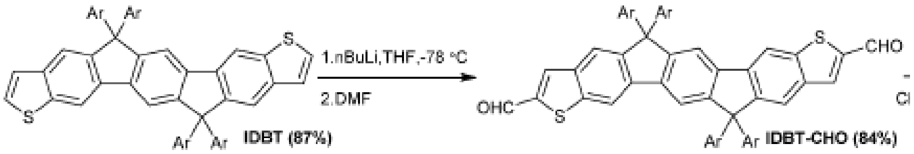


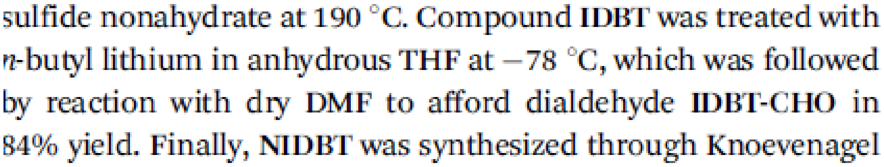
Scheme S1. Synthesis of IHIC-N from **2**

Zhang, Junxiang, et al. "Panchromatic Ternary Photovoltaic Cells Using a Nonfullerene Acceptor Synthesized Using C–H Functionalization."*Chemistry of Materials",* (2018).

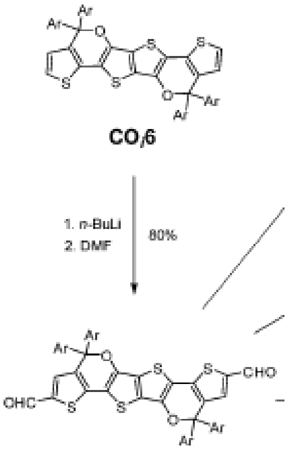


Zou, Yan, et al. "The effect of alkylthio side chains in oligothiophene-based donor materials for organic solar cells."*Molecular Systems Design & Engineering",* (2018).



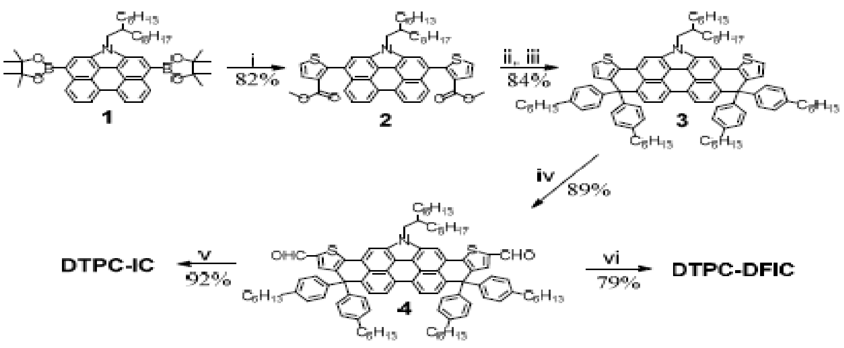

sulfide nonahydrate at 190 °C. Compound **IDBT** was treated with *n*-butyl lithium in anhydrous THF at −78 °C, which was followed by reaction with dry DMF to afford dialdehyde **IDBT-CHO** in 84% yield. Finally, **NIDBT** was synthesized through Knoevenagel

Wang, Pengfei, et al. "A large-band gap small-molecule electron acceptor utilizing a new indacenodibenzothiophene core for organic solar cells."*Materials Chemistry Frontiers",* 2.1 (2018): 136-142.



Li, Ting, et al. "A carbon–oxygen-bridged hexacyclic ladder-type building block for low-band gap nonfullerene acceptors."*Materials Chemistry Frontiers",* 2.4 (2018): 700-703.

The above two references are not V-H reactions but similar and they do afford high aldehyde yields.



A typical V-H procedure:

In a dry round-bottom flask were added 3 (395 mg, 0.30 mmol) and 30 mL anhydrous DCE. Then DMF (0.17 mL, 2.11 mmol) and POCl3 (0.10 mL, 1.00 mmol) were added and the reaction solution was stirred at reflux for 6 h. Saturated sodium acetate aqueous solution (10 mL) was added and the mixture was stirred for another 2 h. Then the mixture was extracted into dichloromethane, and the organic layer was washed with water and dried over anhydrous sodium sulfate. After removing solvent under reduced pressure, the residue was purified by column chromatography (DCM) on silica gel to yield a red oil as the desired product 4 (367 mg, 89% yield).

Yao, Zhaoyang, et al. "Dithienopicenocarbazole-Based Acceptors for Efficient Organic Solar Cells with Optoelectronic Response Over 1000 nm and an Extremely Low Energy Loss."*Journal of the American Chemical Society",* 140.6 (2018): 2054-2057.

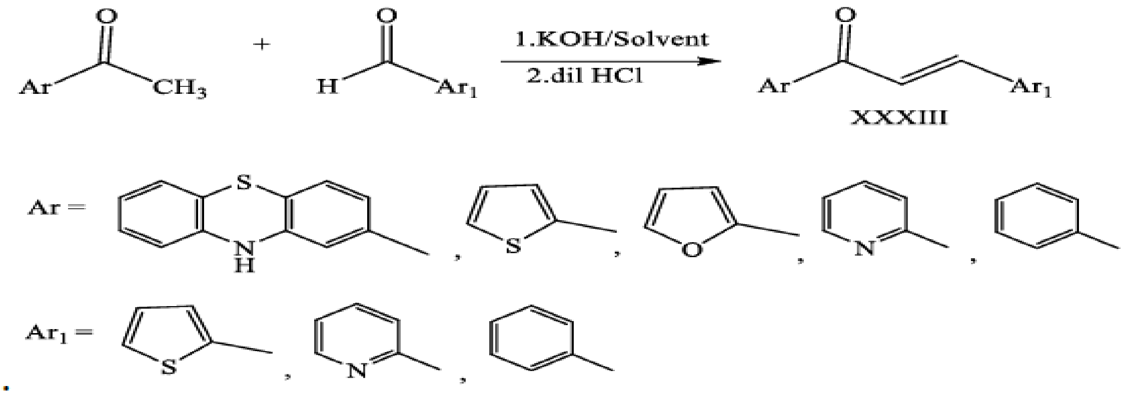
In this case, they obtained an 89% yield with a classic V-H synthesis.

By far the best review I have found of the Vilsmeier-Haack or simply the Vilsmeier reaction is in the book; Synthetic Methods in Organic Electronic Materials by Parker and Marder (RSC, 2015) pp 111-114. I refer the reader to this excellent book!

Also see Strategic Applications of Named Reactions in Organic Synthesis by Kurti and Czako (Elsevier, 2005).

Claisen-Schmidt Condensation:

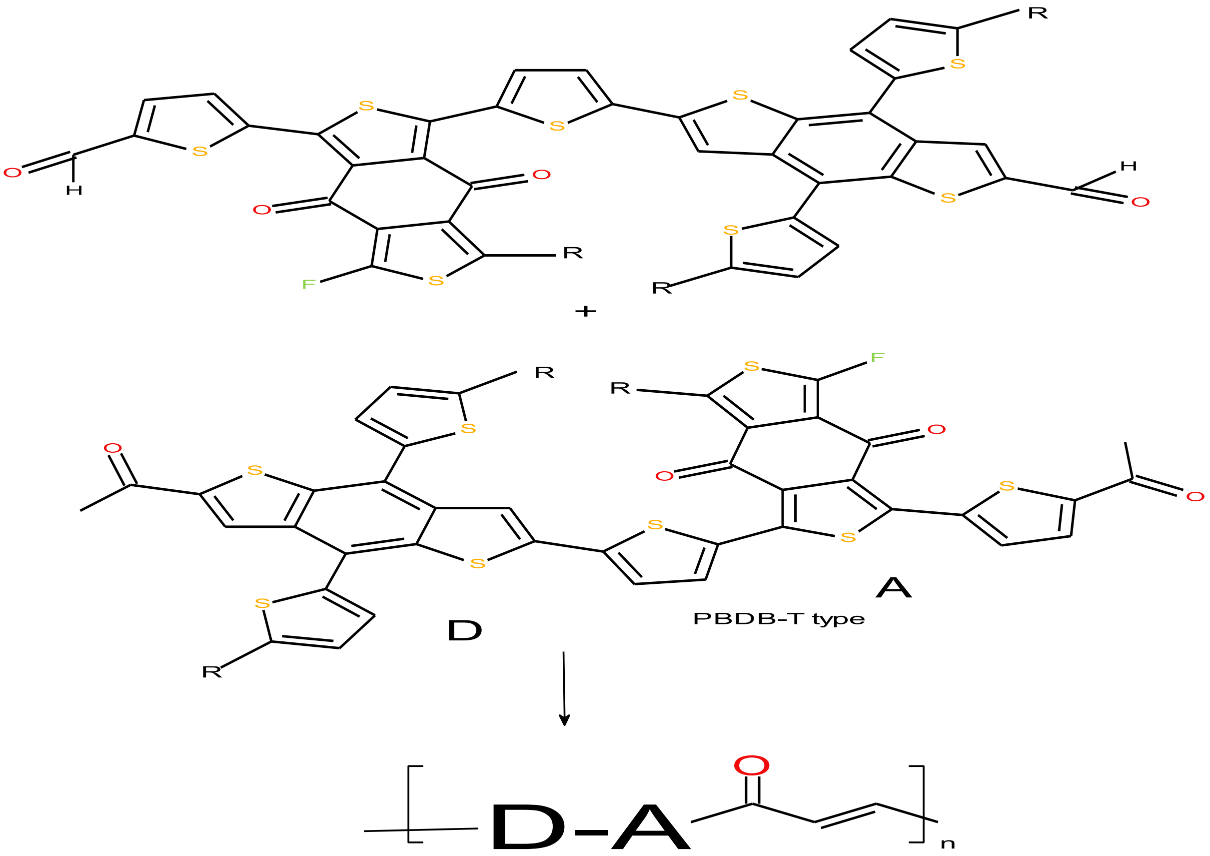
A detailed review of this reaction can also be found in Strategic Applications of Named Reactions in Organic Synthesis by Kurti and Czako (Elsevier, 2005). More recent examples are:



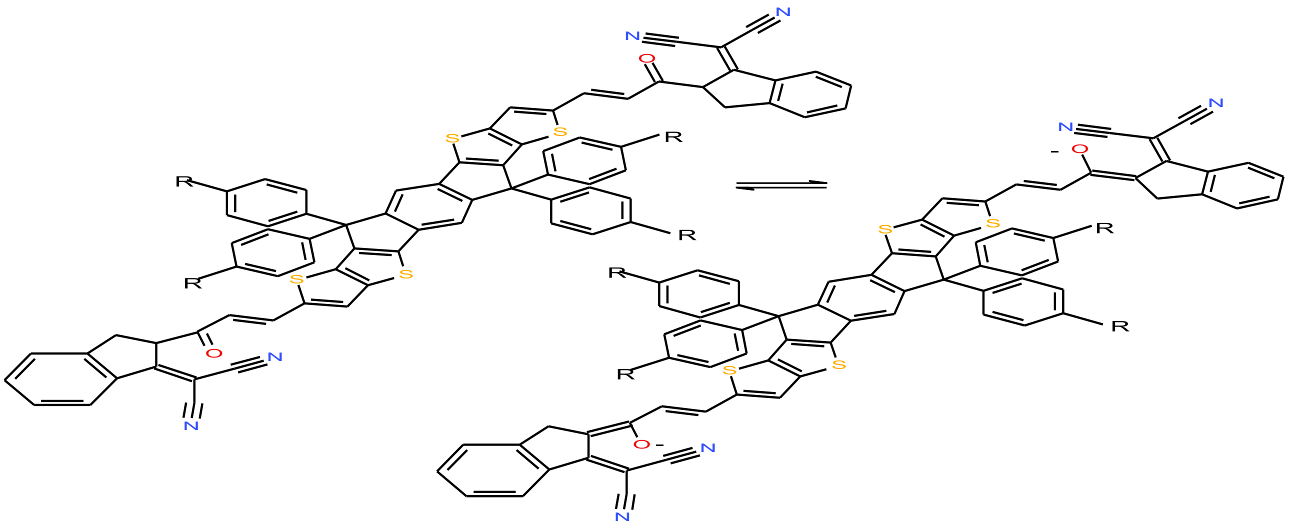
Verma, Shipra, Alok Kumar Srivastava, and O. P. Pandey. "A Review on Chalcones Synthesis and their Biological Activity."*PharmaTutor",* 6.2 (2018): 22-39.

Chavan, B. B., et al. "Synthesis & Medicinal Significance of Chalcones-A Review."*Asian Journal of Biomedical and Pharmaceutical Sciences",* 6.56 (2016): 01.

Therefore applying this idea to organic semiconductors especially organic solar cells results in the following typical structures:



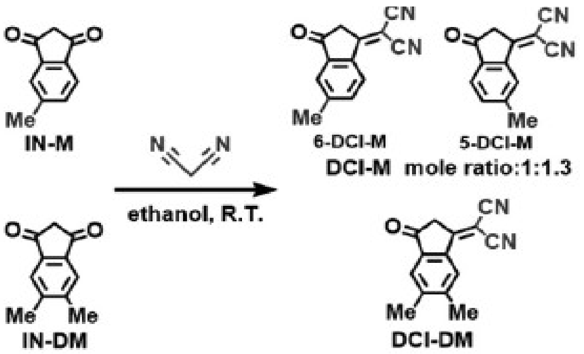
Scheme 2: Typical Donor polymer (simplified structure since the unsaturated ketone can also be shown reversed). This is an example of a Claisen-Schmidt condensation.



Scheme 3: Typical Acceptor based on the above ideas. Because a resonance structure is possible, it might perfrom as a pH indicator that would change color. Conjugation would require the enol or enolate form which then links all the unsaturation.
(See scheme 4 for a possible synthesis.)

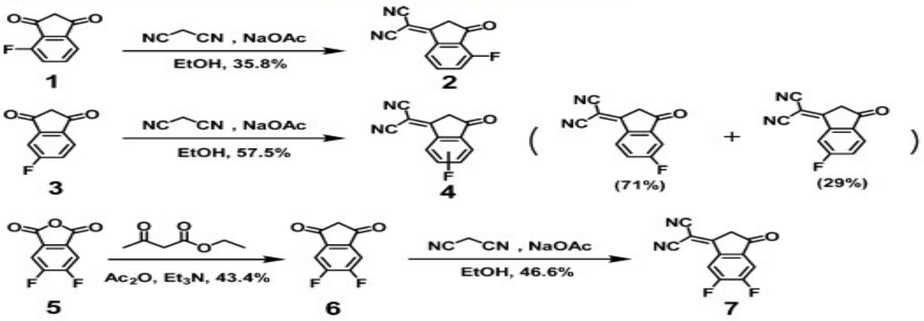
Examples of Acceptor End Groups:

I present these examples to give the reader a feel for this chemistry.

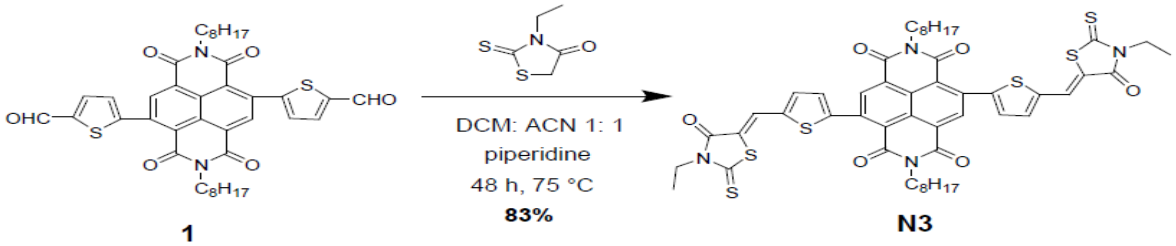


Li, Sunsun, et al. "Energy-Level Modulation of Small-Molecule Electron Acceptors to Achieve over 12% Efficiency in Polymer Solar Cells."*Advanced Materials",* 28.42 (2016): 9423-9429.

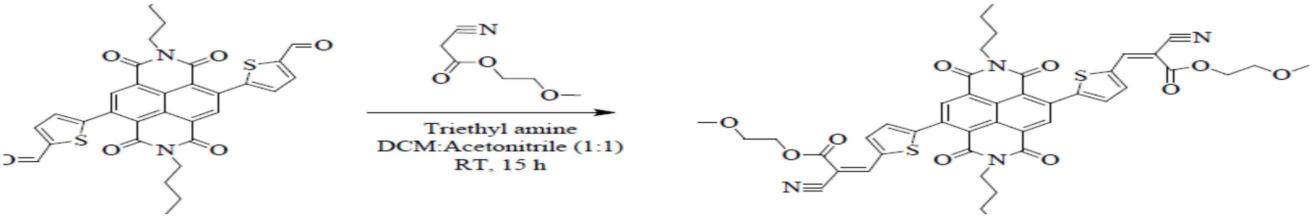
Scheme 1. Synthetic Routes for INIC, INIC1, INIC2, and INIC3

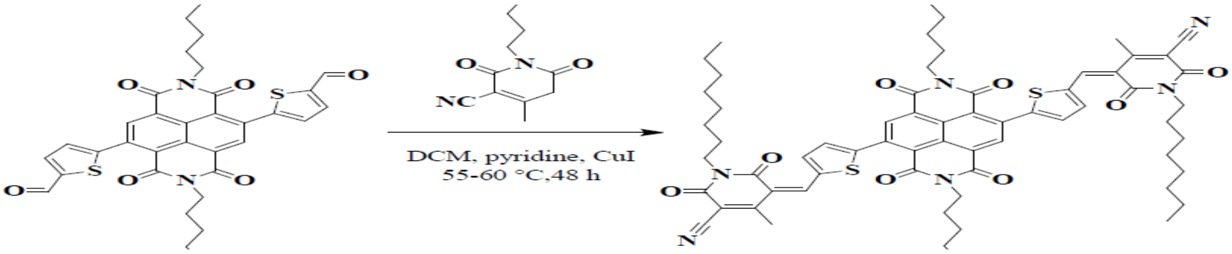


Dai, Shuixing, et al. "Fused nonacyclic electron acceptors for efficient polymer solar cells."*Journal of the American Chemical Society",* 139.3 (2017): 1336-1343.



Srivani, Doli, et al. "Non-fullerene acceptors based on central naphthalene diimide flanked by rhodanine or 1, 3-indanedione."*Chemical Communications",* 53.52 (2017): 7080-7083.



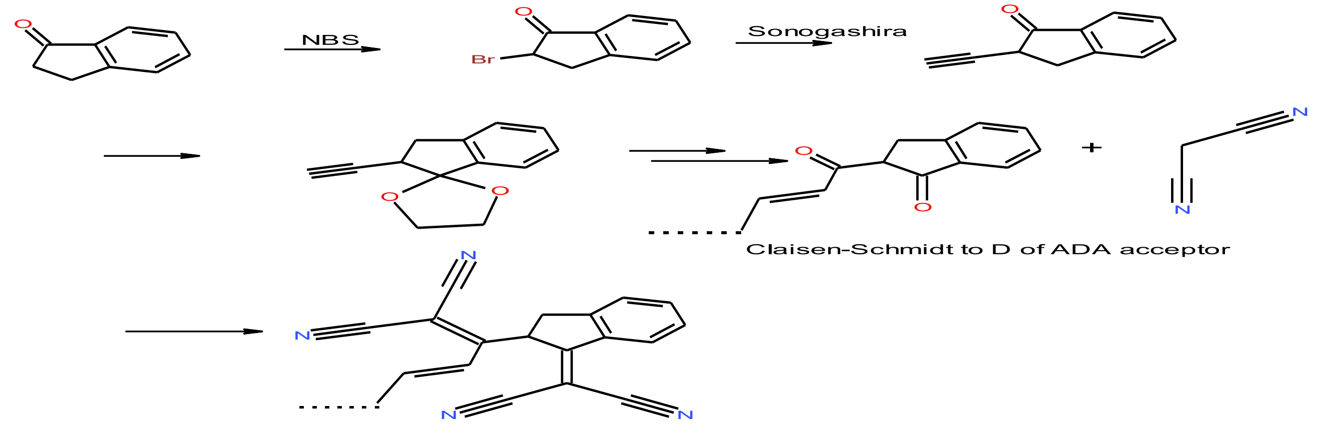


Srivani, Doli, et al. "Naphthalene diimide-based non-fullerene acceptors flanked by open-ended and aromatizable acceptor functionalities."*Chemical Communications",* 53.81 (2017): 11157-11160.

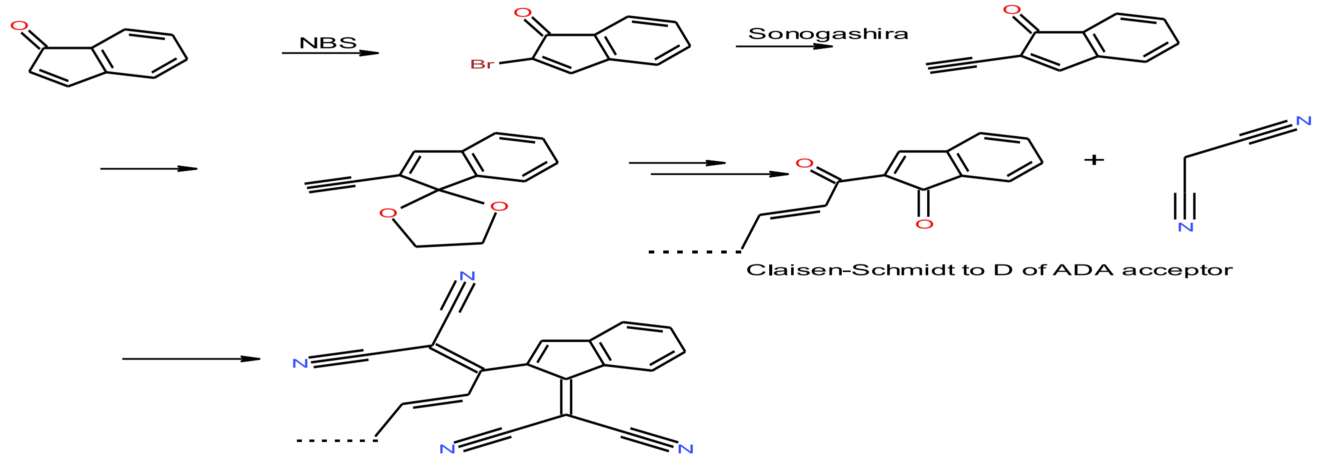
The above examples form the NF acceptor by the Kovenagle condensation.

See: Organic Reactions V15 (Wiley, 1967) or previously mentioned more recent book by Parker and Marder.

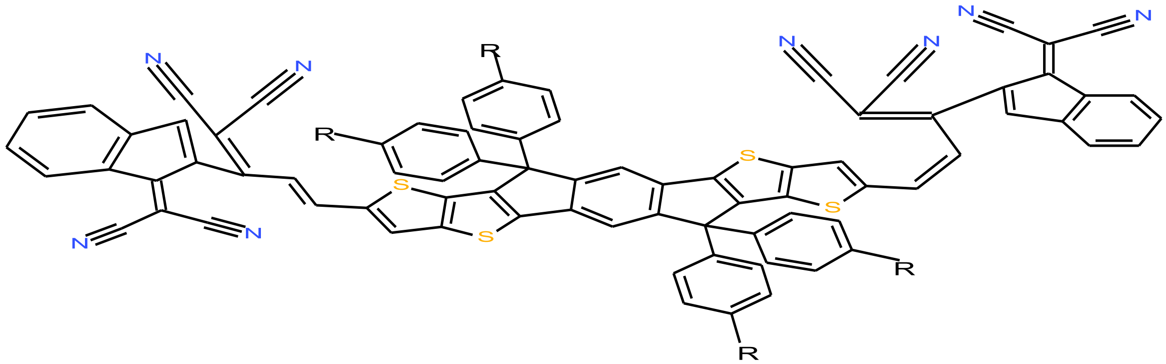
Examples of proposed Acceptor end group synthesis:



This example might not work because the indanone 2 proton would be abstracted as it is more acidic, if the ketal is hydrolyzed; therefore, if that's the problem then the ketal should be hydrolyzed last after the C-S condensation. However the indenone version would not have this problem. Also another problem might be that the malononitrile might also attack the unsaruration in a Michael reaction? See House, Herbert O., and William C. McDaniel. "Perhydroindan derivatives. 18. The use of indenone ketals as dienophiles."*The Journal of Organic Chemistry",* 42.12 (1977): 2155-2160. For similar problems.

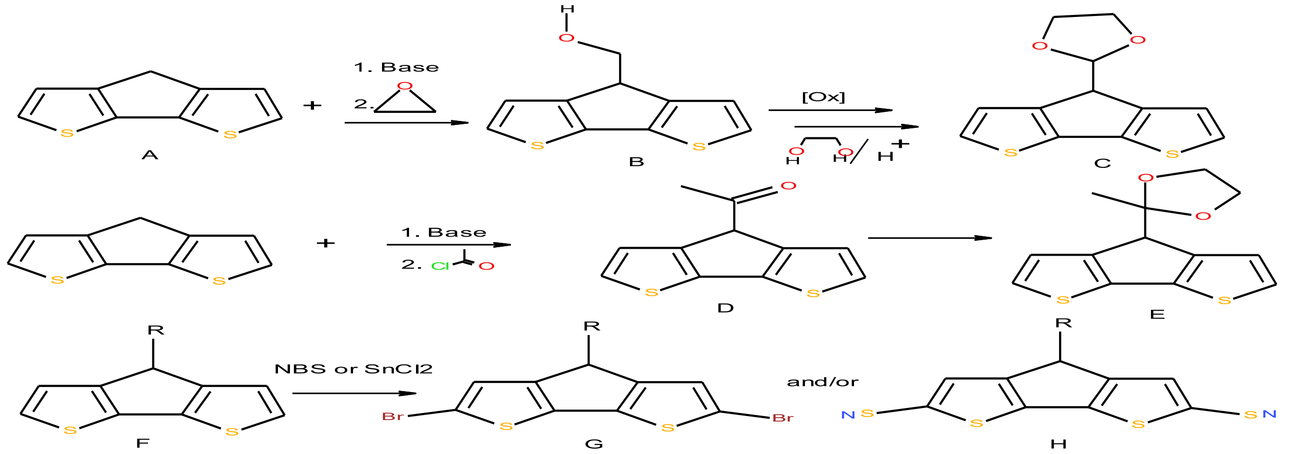


Scheme 4: Potential synthesis of acceptor terminals. In this case, the indenone double bond eliminates the 2-proton. Obviously experimentation is required to see if any of this actually works.

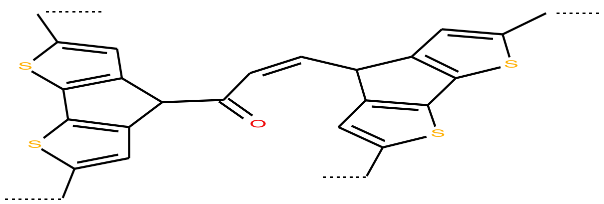


Scheme 5: This is an example of scheme 4. If the malononitrile would react twice then the electron withdrawal would be greater and would effect the lumo-homo levels.

It is also possible for this C-S condensation to be employed as a **crosslinking reaction**.



R=aldehyde or ketone that reacts by the Claisen-Schmidt reaction to generate a crosslink of the following structure



Scheme 6: This illustrates the idea of employing the Claisen-Schmidt condensation to afford crosslinks. Compounds G and/or H can be placed in Donor polymers or in A-D-A acceptors by the Stille reaction. Hydrolysis of the ketals would reveal the ketone and aldehyde which can then form the crosslink.

Thank you for reading this proposal.

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