

SNAPSHOTS OF SOME TOPICS OF INTEREST OF RECENT NOTABLE ADVANCES IN CHEMISTRY

- Simple route for the preparation of sodium bicyclo[1.1.1]pentanesulfinate
- A facile protocol for the synthesis of indandione-terminated quinoids
- Synthesis of benzonaphthosilines
- Improvement of the discharge voltage of organic electrode materials by diluting the electron density in the π -conjugated skeleton

Table of contents

- 3 Snapshots of some topics of interest of recent notable advances in chemistry:
- 4 Simple route for the preparation of sodium bicyclo[1.1.1]pentanesulfinate
- 7 A facile protocol for the synthesis of indandione-terminated quinoids
- 9 Synthesis of benzonaphthosilines
- 11 Improvement of the discharge voltage of organic electrode materials by diluting the electron density in the π -conjugated skeleton

Snapshots of some topics of interest of recent notable advances in chemistry

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Simple Route for the Preparation of Sodium Bicyclo[1.1.1]pentanesulfinate

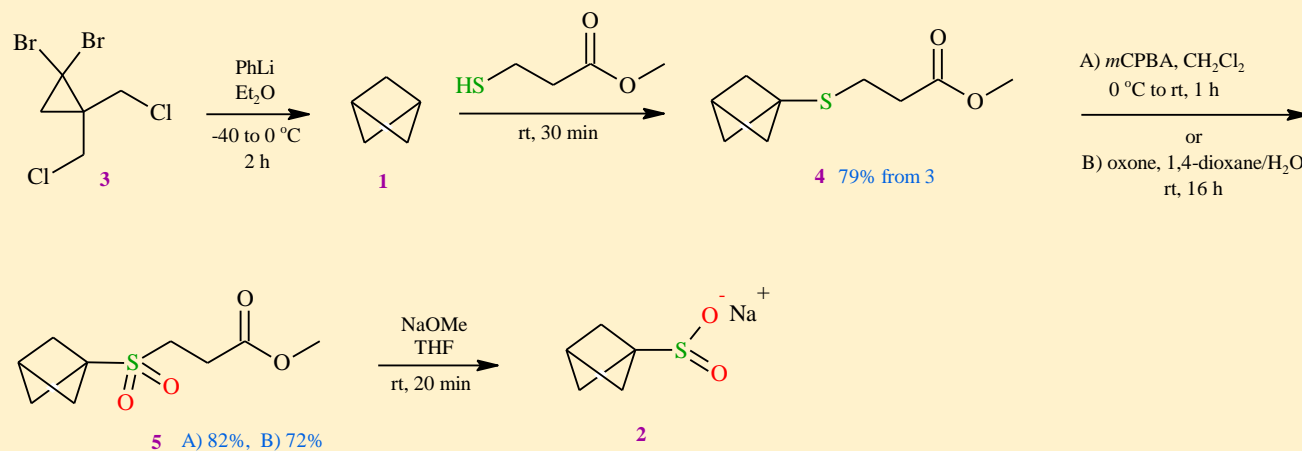
A four-step synthesis of sodium bicyclo[1.1.1]pentanesulfinate (BCP-SO₂Na) from commercially available precursors, 1,1-dibromo-2,2-bis(chloromethyl)cyclopropane, is described. The formed scalable building block was employed as a bench-stable precursor for the synthesis of bicyclo[1.1.1]pentylsulfones and bicycle-[1.1.1]pentanesulfonamides.

In the course of synthetic innovation of bioactive small molecules, the bioisosteric replacement of planar aromatic moieties by saturated hydrocarbons has shown a pharmacological improvement of therapeutics. Based on this strategy, a number of synthetic methods have employed the rigid bicyclo[1.1.1]-pentanes (BCPs) as a replacement of other motifs such as benzene, alkyne, and *tert*-butyl groups. The majority of BCPs reported thus far are accessed by radical or anionic reactions with the strained tricyclic motif [1.1.1]propellane **1**, which all of these reactions need the handling of this volatile precursor and the necessity of Schlenk techniques in the preparation. Furthermore, the limit accessibility of sulfur-based BCP motifs prohibited the broad application of this bioisostere.

In this regard, a scalable sodium bicyclo[1.1.1]pentanesulfinate (BCP-SO₂Na) **2** was synthesized by Bär and co-workers as a bench-stable salt.

- *Synthetic route*

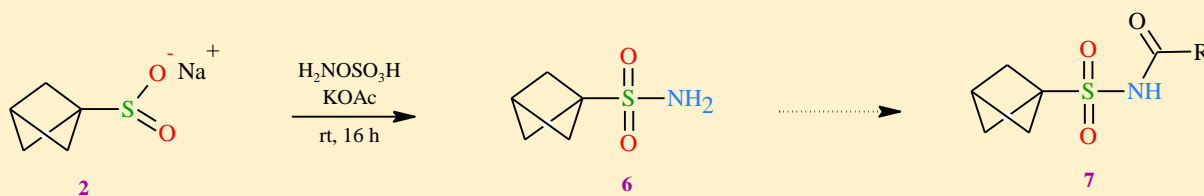
A four-step synthetic procedure was accomplished to obtain BCP-SO₂Na in good yield and purity without need of purification or crystallization. The [1.1.1]propellane **1** was prepared from commercially available precursor **3** with phenyllithium in diethyl ether followed by the addition of methyl 3-mercaptopropionate to produce the sulfide **4** (Scheme 1). After washing with NaOH solution and removal of the solvent, sulfide **4** was oxidized with either 3-chloroperoxybenzoic acid (*m*CPBA) or oxone to yield compound **5** in 82% (A) or 72% (B) yield, respectively. Finally, the sulfone **5** was converted to the respective sulfinate **2** in a retro-Michael reaction initiated by sodium methoxide.



Scheme 1. Preparation of BCP-SO₂Na. Oxone: 2KHSO₅·KHSO₄·K₂SO₄.

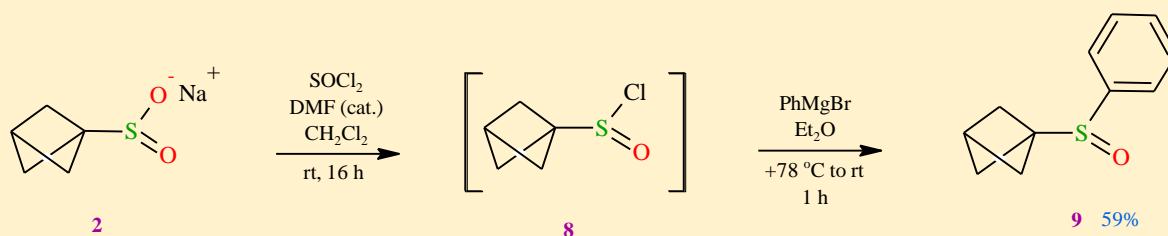
- *Application of sulfinate (BCP-SO₂Na)*

The primary BCP sulfonamide **6** was obtained from BCP-SO₂Na **2** in the presence of hydroxylamine-*O*-sulfonic acid, which provides easy access to *N*-alkyl sulfonamides **7** (Scheme 2).



Scheme 2. Synthesis of primary sulfonamide.

Chlorination of BCP-SO₂Na **2** provided sulfinyl chloride **8**, which further reacted with phenylmagnesium bromide *in situ* to form sulfoxide **9** (Scheme 3).



Scheme 3. Chlorination of BCP-SO₂Na followed by reaction with phenylmagnesium bromide to form sulfoxide **9**.

The building block BCP-SO₂Na has shown a range of applications including sulfones and sulfonamides, which could lead to further useful applications in medicinal chemistry.

Review

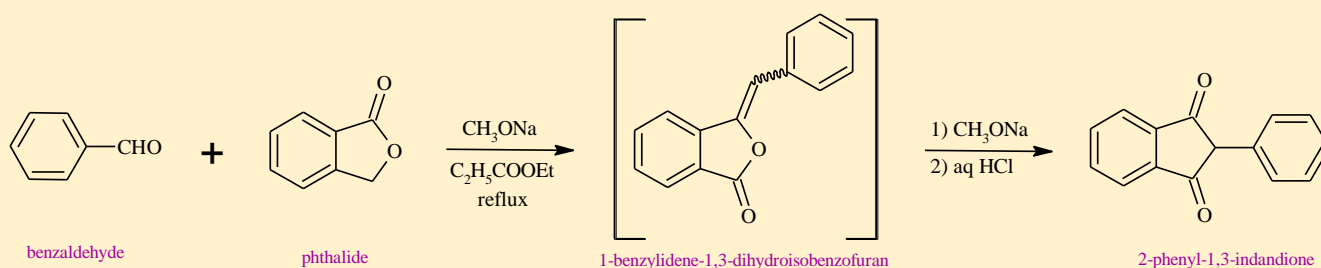
R. M. Bär, P. J. Gross, M. Nieger, S. Bräse, *Chem. Eur. J.*, **2020**, *26*, 4242 – 4245.

A Facile Protocol for the Synthesis of Indandione-Terminated Quinoids

A new three-steps approach for the synthesis of 1,3-indandione-terminated π -conjugated quinoids is described. The strategy is based on alkoxide-mediated rearrangement reaction of the alkene precursors, followed by air oxidation. The optoelectronic properties of the resulting quinoids can be modulated by tuning the central cores and the aryl termini. The incorporation of these quinoids in organic thin-film transistors exhibited n-channel characteristics with electron mobility of up to $0.38 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$.

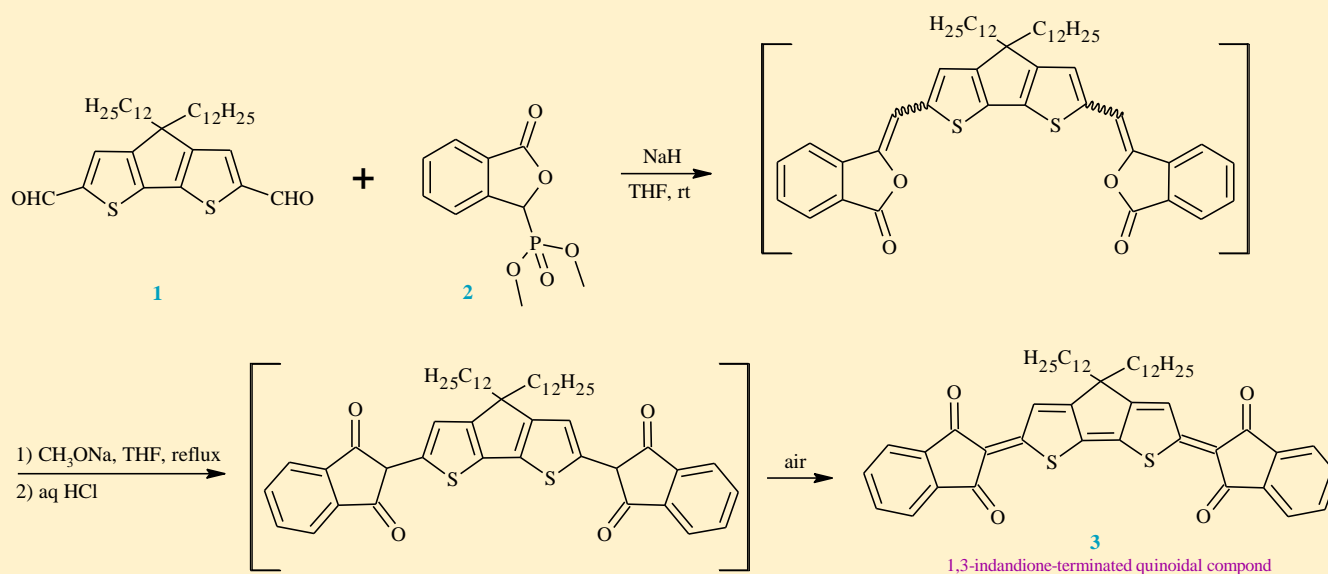
Quinoidal compounds have emerged as an extraordinary class of compounds with their electronic, optical, and magnetic properties. However, the available compounds suffer from many drawbacks due to synthetic challenges, such as difficult functionalization of their end groups, limited central core units, poor stability, and a high LUMO energy levels as a result of the lack of strong electron-withdrawing end groups.

In this context, Du and co-workers reported an operationally simple synthetic approach with a wide substrate scope. The outcome of the synthetic route showed promising features in terms of stability and semiconducting properties. The strategy is based on the preparation of aromatic moieties bearing a tertiary carbon center at each end. The cornerstone of the synthetic route takes advantage of the reaction between benzaldehyde and phthalide in the presence of CH_3ONa that forms 2-phenyl-1,3-indandione by the rearrangement of a 1-benzylidene-1,3-dihydroisobenzofuran intermediate (Scheme 1).



Scheme 1. Synthesis of 2-phenyl-1,3-indandione.

The synthetic pathway was carried out in three steps: condensation, alkoxide-mediated rearrangement, and oxidation. The procedure was accomplished by Wittig-Horner reaction between 4,4-didodecyl-4H-cyclopenta[2,1-*b*:3,4-*b'*]dithiophene-2,6-dicarboxaldehyde **1** with phthalide-3-phosphonate **2** using NaH as a base, followed by rearrangement reaction in the presence of CH_3ONa . Subsequent air oxidation gave the desired product 1,3-indandione-terminated quinoidal compound **3** in 70% yield (Scheme 2).



Scheme 2. Synthesis of 1,3-indandione-terminated quinoidal compounds.

The UV-vis-NIR absorption spectra of the prepared compounds showed red-shifted spectra with absorption maxima $\lambda_{\text{max}} = 610\text{-}835\text{ nm}$, and high molar extinction coefficients (ϵ) of up to $2.4 \times 10^5\text{ Lmol}^{-1}\text{cm}^{-1}$.

Their electrochemical properties showed low-lying LUMO levels of less than -4.0 eV . The optoelectronic properties of these quinoids could be finely tuned by engineering of the central core and termini. Additionally, organic thin-film transistors (OTFTs) based on these quinoids showed n-channel characteristics with the highest electron mobility (μ_e) of up to $0.38\text{ cm}^2\text{V}^{-1}\text{s}^{-1}$.

This novel synthetic protocol provides a new class of organic semiconductors as well as new building blocks for organic semiconductors.

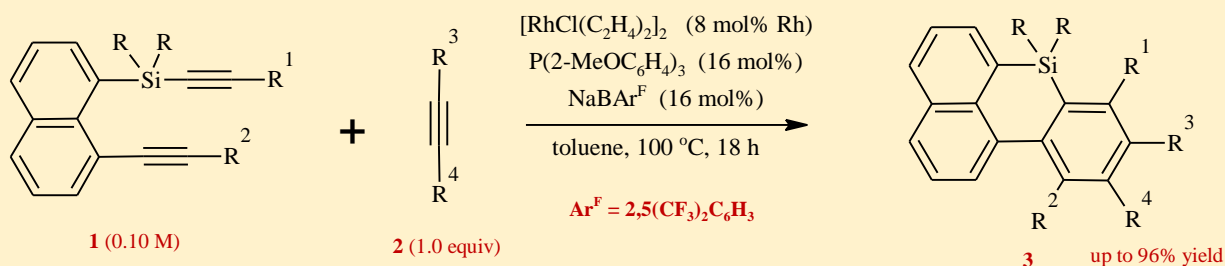
Review

T. Du, R. Gao, Y. Deng, C. Wang, Q. Zhou, Y. Geng, *Angew. Chem. Int. Ed.*, **2020**, *59*, 221–225.

Synthesis of Benzonaphthosilines

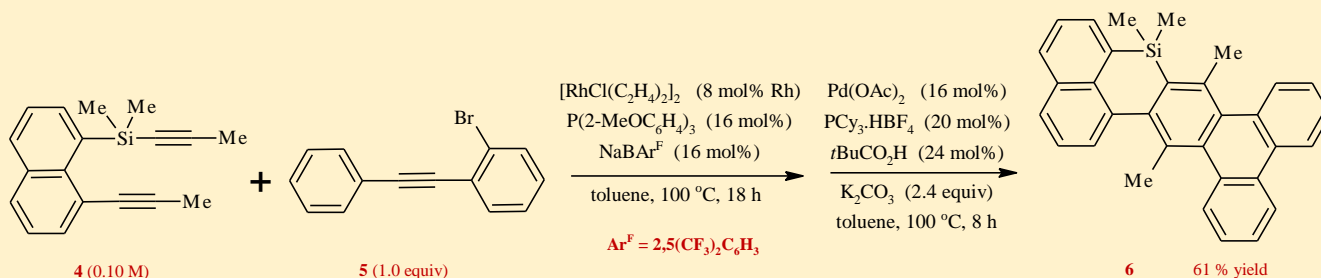
A synthetic procedure for 7*H*-benzo[*e*]naphtho[1,8-*bc*]silines is described that accomplished by a rhodium-mediated [2+2+2]cycloaddition of alkynyl(8-alkynyl-1-naphthyl)silanes with internal alkynes through the use of P(2-MeOC₆H₄)₃ as a ligand for rhodium. In addition, an enantioselective variant for the construction of a silicon stereogenic center is highlighted.

Silicon-bridged π -conjugated compounds represent an important class of materials in optoelectronics. Among this class is 5*H*-dibenzo[*b,d*]siloles (dibenzosiloles) which have been prepared by different methods. In contrast, the synthetic routes of a structurally related compound, 7*H*-benzo[*e*]naphtho[1,8-*bc*]silines (benzonaphthosilines), featuring a 6-membered silacycle have been less explored. In this regard, Maesato and Shintani reported an efficient procedure for preparation of benzonaphthosilines **3** by a rhodium-catalyzed [2 + 2 + 2] cycloaddition of alkynyl-(8-alkynyl-1-naphthyl)silanes **1** with internal alkynes **2** using P(2-MeOC₆H₄)₃ as a ligand for rhodium (Scheme 1).



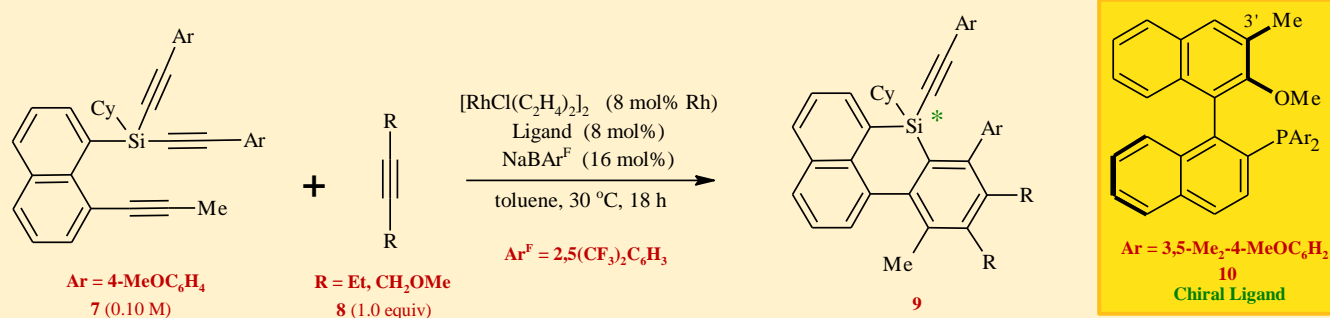
Scheme 1. Synthesis of benzonaphthosilines.

The reaction of **4** with 1-bromo-2-(phenylethynyl)benzene **5** followed by palladium-catalyzed intramolecular C-H arylation gave a new silicon-bridged π -conjugated compound, naphthotriphenylenosilene **6** (Scheme 2).



Scheme 2. Preparation of naphthotriphenylenosilene.

An asymmetric variant of the process was accomplished through the reaction of prochiral **7** with 3-hexyne **8** using a chiral ligand, 3'-methylated (*R*)-MeO-mop **10**, at 30 °C which produced silicon-stereogenic benzonaphthol-silene **9** in up to 87% yield and 81% ee (Scheme 3).



Scheme 3. Asymmetric synthesis of silicon-stereogenic dibenzosiloles.

The asymmetric silicon-stereogenic dibenzosiloles were relatively high enantioselectivity.

Review

T. Maesato, R. Shintani, *Chem. Lett.*, **2020**, *49*, 344–346.

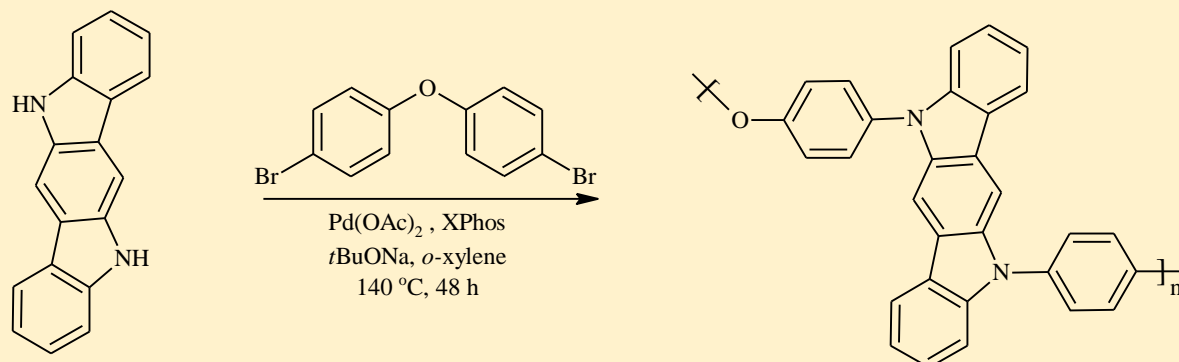
Improvement of the Discharge Voltage of Organic Electrode Materials by Diluting the Electron Density in the π -Conjugated Skeleton

An approach is reported to enhance the discharge voltage of battery cells through dilution of the electron density of N-based redox centers in conjugated organic materials. The electron-rich heterocyclic compounds with pentatomic rings showed a lower electron density compared with conventional electron active counterparts with hexatomic rings. Additionally, they exhibited a high atomic-dipole-moment-corrected Hirshfeld charge population, which led to a significant increase in the oxidation potential.

Organic electrode materials have significant advantages compared with commercial Li-ion battery cathodes in terms of sustainability resources, environmental benign, adjustment of their redox properties through tuning their structures, economic viability, and compatibility with various cations or anions. These features make them promising candidates as battery materials.

In fact, the redox potential of the electrode materials constitutes a key property of cathode materials. The redox potential of p-type N-heterocyclic-ring-based organics, which have a higher discharge voltage than n-type materials, is determined by their HOMO level. Thus, upshifting the HOMO level by functionalization of the compound with appropriate strong electron-withdrawing groups near the redox center represents an important step toward improving the efficiency of organic cathode materials. Based on frontier molecular orbital theory, the structure of N-containing heterocyclic-ring-based organic compounds influences their electron distribution and delocalization. Accordingly, the planarity of the pentatomic-ring framework represents a good molecular skeleton due to the fact that the lone-pair electrons of the nitrogen atom would participate in conjugation and delocalization to the whole skeleton, resulting in simultaneously weaken the activity of the single-electron free radical in the intermediate and reducing the electron density of the nitrogen redox center. Hence, both of the functionalization and rearrangement of the molecular skeleton could play an effective role to regulate redox potential of organic electrode materials.

In view of this strategy, Dai and colleagues reported an organic polymer serving as a cathode material for organic batteries. This polymer based on redox-active 5,11-diphenyl-5,11-dihydroindolo[3,2-*b*]carbazole (DPICZ) with an ether linkage (p-DPICZ-O), which contained a pentatomic N-ring as the redox center (Scheme). It had a lower electron density compared with those of conventional hexatomic-heterocyclic rings. Furthermore, this material showed a higher atomic-dipole-moment-corrected Hirshfeld (ADCH) charge population. ADCH defines as the ability/strength of an atom to gain or lose electrons.



Scheme . The preparation of p-DPICZ-O was accomplished through the Buchwald-Hartwig copolymerization of indolo[3,2-b]carbazole with bis(4-bromophenyl)ether in anhydrous *o*-xylene using palladium acetate as a precatalyst.

The outcome was a sharp increase of the discharge voltage to 3.7-4.3 V vs Li⁺/Li with good cycling stability. The study demonstrated that N-containing heterocyclic-ring compounds with the pentatomic π -conjugation showed high performance in both strengthening the delocalization and stabilizing the free radical electrons in the conjugation during the electrochemical processes leading to improve the discharge voltage of cathode materials for organic batteries.

Review

G. Dai, Y. Gao, Z. Niu, P. He, X. Zhang, Y. Zhao, H. Zhou, *ChemSusChem*, **2020**, *13*, 2264 – 2270.