

Z. CAI, H. ZHANG, H. GENG, Z. LIU,* S. YANG, H. LUO, L. JIANG, Q. PENG, G. ZHANG, J. CHEN, Y. YI, W. HU, D. ZHANG* (BEIJING NATIONAL LABORATORY FOR MOLECULAR SCIENCES, P. R. CHINA)

Thiepin-Fused Heteroacenes: Simple Synthesis, Unusual Structure, and Semiconductors with Less Anisotropic Behavior

Chem. Eur. J. **2013**, *19*, 14573–14580.

Category

Synthesis of
Materials and
Unnatural Products

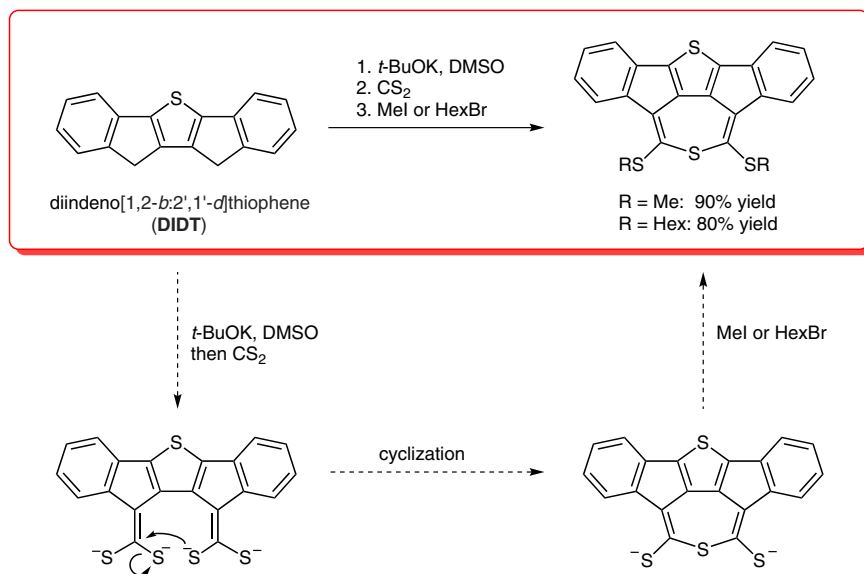
Key words

fused ring systems

thiepins

heteroacenes

One-Pot Synthesis of Thiepin-Fused Heteroacenes



Significance: Polycyclic aromatic hydrocarbons with heteroatom substitution are attractive materials for semiconductor applications. The authors present the efficient installation of a thiepin unit onto easily accessible DIDT (C.-H. Chen, Y.-J. Cheng, M. Dubosc, C.-H. Hsieh, C.-C. Chu, C.-S. Hsu *Chem. Asian J.* **2010**, *5*, 2483). In this one-pot synthesis, DIDT was deprotonated with potassium *tert*-butoxide, reacted with carbon disulfide, and quenched with methyl iodide or hexyl bromide. The fused thiepins were obtained in 90% and 80% yield.

Comment: HOMO and LUMO energies were determined by cyclic voltammetry (−5.35 eV and −3.26 eV, respectively, regardless of the alkyl chain). Both compounds exhibited typical p-type semiconducting behavior with hole mobilities up to $1.0 \times 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. Thin films were further characterized by AFM and XRD. Crystal structures were obtained for both compounds and showed multiple S⋯S contacts.

SYNFACTS Contributors: Timothy M. Swager, Georgios Markopoulos

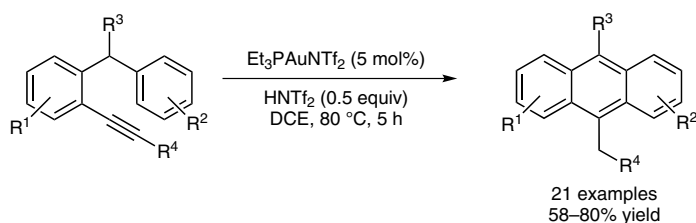
Synfacts 2014, 10(1), 0029 Published online: 13.12.2013

DOI: 10.1055/s-0033-1340393; Reg-No.: S14913SF

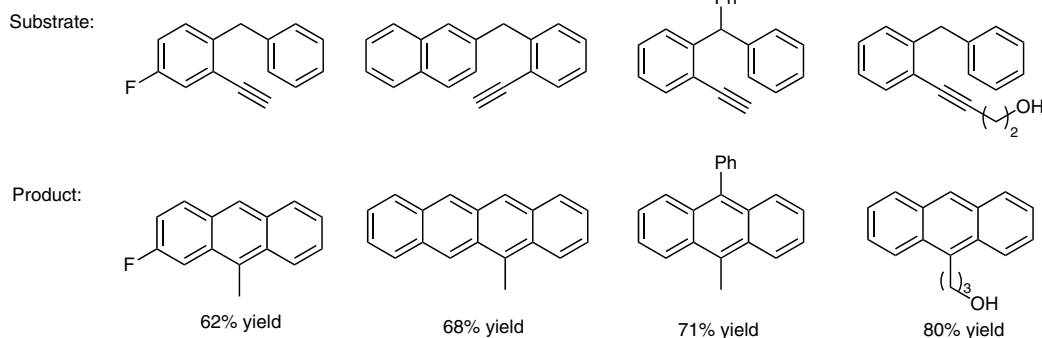
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C. SHU, C.-B. CHEN, W.-X. CHEN, L.-W. YE* (XIAMEN UNIVERSITY, P. R. OF CHINA)
Flexible and Practical Synthesis of Anthracenes through Gold-Catalyzed Cyclization of *o*-Alkynyldiarylmethanes
Org. Lett. **2013**, *15*, 5542–5545.

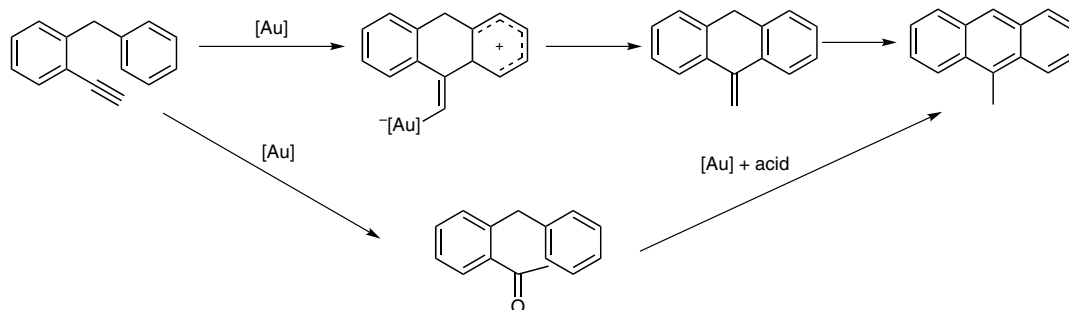
Gold-Catalyzed Synthesis of Anthracenes



Selected examples:



Proposed mechanistic pathways:



Significance: The gold-catalyzed synthesis of anthracene derivatives from their corresponding *o*-alkynyldiarylmethanes is reported. Compared to previously reported syntheses, the presented method is a mild and atom-economic approach that enables access to functionalized anthracenes from a wide substrate scope in good yields.

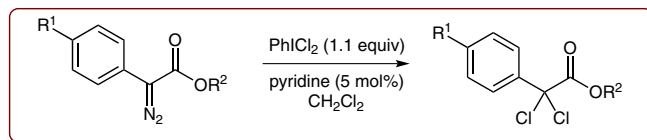
Comment: In addition to anthracenes, the authors report the synthesis of a tetracene derivative (see above) from a naphthalene-containing substrate, thus demonstrating the potential of this synthetic strategy in the synthesis of functionalized extended acenes.

SYNFACTS Contributors: Timothy M. Swager, Gregory D. Gutierrez
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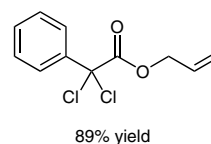
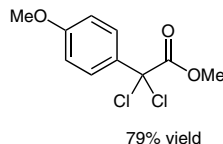
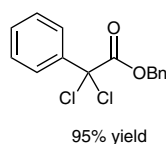
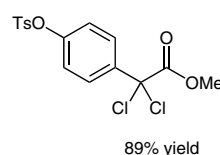
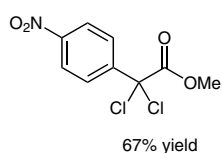
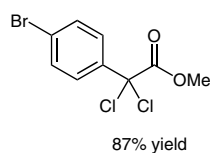
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Hypervalent Iodine for α,α -Dihalogenation

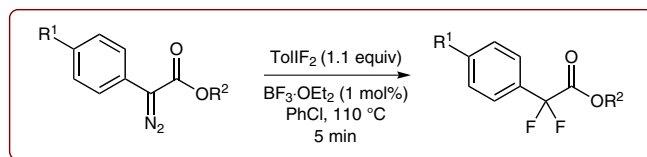
Chlorination:



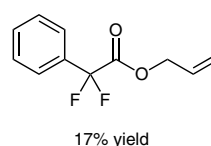
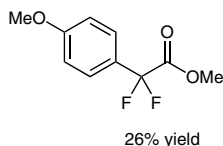
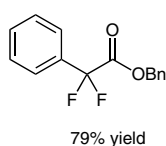
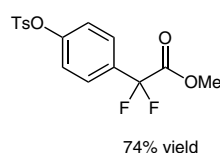
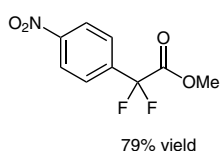
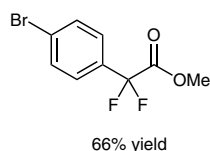
Selected examples:



Fluorination:



Selected examples:



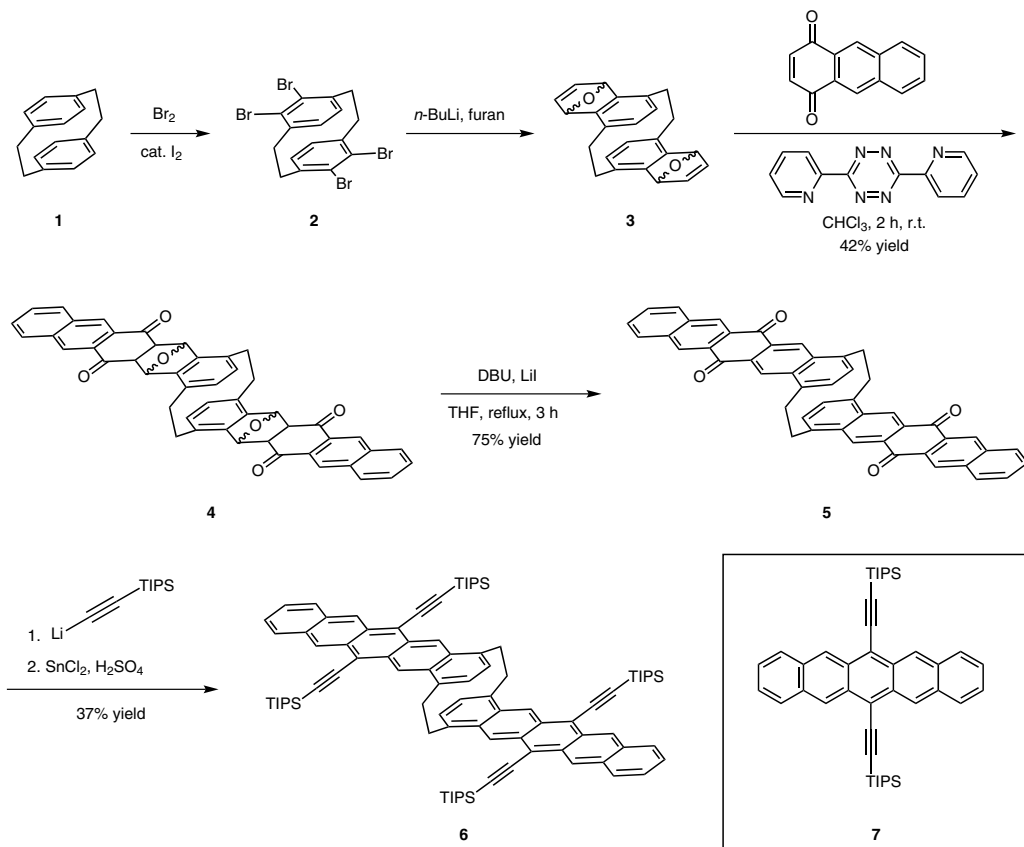
Significance: Functionalization at the α -position of carbonyls represents one of the most versatile and useful types of transformations in organic chemistry. In this paper, the authors describe the use of a hypervalent iodine species to doubly halogenate the α -position of esters with either chlorine or fluorine.

Comment: While the chlorination procedure was shown to be broadly functional group tolerant, the need for $BF_3 \cdot OEt_2$ in the case of fluorination limits the possible functionality in the starting material. The authors report that substrates with labile moieties such as OMe or $NHAc$ decompose upon heating with $BF_3 \cdot OEt_2$.

R. BULA, M. FINGERLE, A. RUFF, B. SPEISER, C. MAICHLE-MÖSSMER, H. F. BETTINGER*
(UNIVERSITÄT TÜBINGEN AND UNIVERSITÄT STUTTGART, GERMANY)
Anti-[2.2](1,4)pentacenophane: A Covalently Coupled Pentacene Dimer
Angew. Chem. Int. Ed. **2013**, 52, 11647–11650.

Pentacenes Communicate Through Space

Synthesis of *anti*-[2.2](1,4)pentacenophane 6:



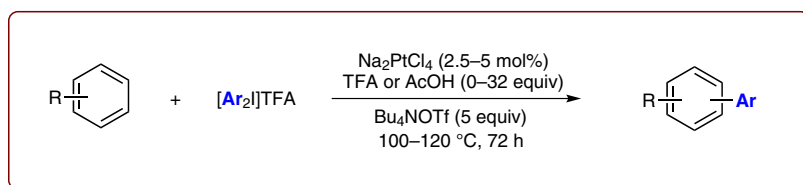
Significance: Due to their demonstrated utility in optoelectronic devices, polyacenes continue to garner attention as fascinating systems for studying the fundamental properties that are responsible for their observed behavior. The authors contribute to the study of charge-transfer communication between pentacenes by creatively expanding on the concept of covalently coupled anthracenes developed by the Misumi group in the 1970s (*Tetrahedron Lett.* **1972**, 13, 1731). Preliminary characterization of **6** via UV/Vis spectroscopy, DFT modeling, and cyclic voltammetry provides a useful benchmark for future studies of this class of compounds.

Comment: Applying de Meijere's method (*Chem. Ber.* **1993**, 126, 2531) of accessing *pseudo-para* tetrabromide **2** and cycloadducts **3** is a clever approach to constructing *anti*-[2.2]pentacenophane **6**, a blue solid that is moderately soluble in organic solvents. The bathochromic shift (~20 nm) of **6**, compared to pentacene monomer **7**, is attributed to coupling between the pentacene subunits. It would be interesting to build off of this result by comparing the device performance of **6** and related pentacenophanes to their respective pentacene monomers.

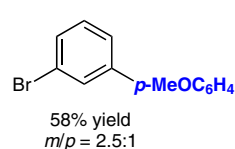
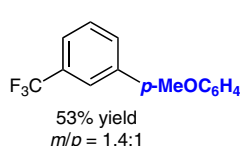
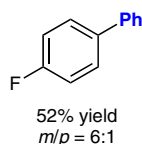
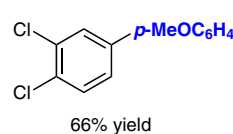
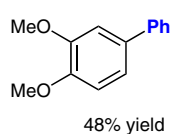
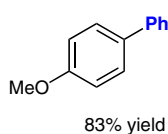
SYNFACTS Contributors: Timothy M. Swager, Joseph M. Azzarelli
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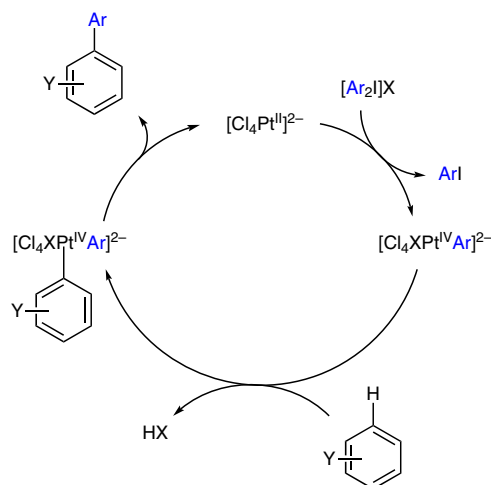
C–H Arylation with Platinum



Selected examples:



Proposed mechanism:



Significance: C–H activation in aryl systems finds broad applicability in the construction of conjugated organic materials. This paper reports the use of a platinum catalyst to couple aryl groups pendant on hypervalent iodine to simple arenes via a C–H activation pathway.

Comment: The authors have previously reported a similar process using a palladium catalyst (*ACS Catal.* **2011**, *1*, 170). However, with the exception of some examples in which the reaction resulted in mixed isomers, the use of a platinum catalyst produced materials with different selectivity than the palladium catalyst, providing two processes with complementary reactivity.

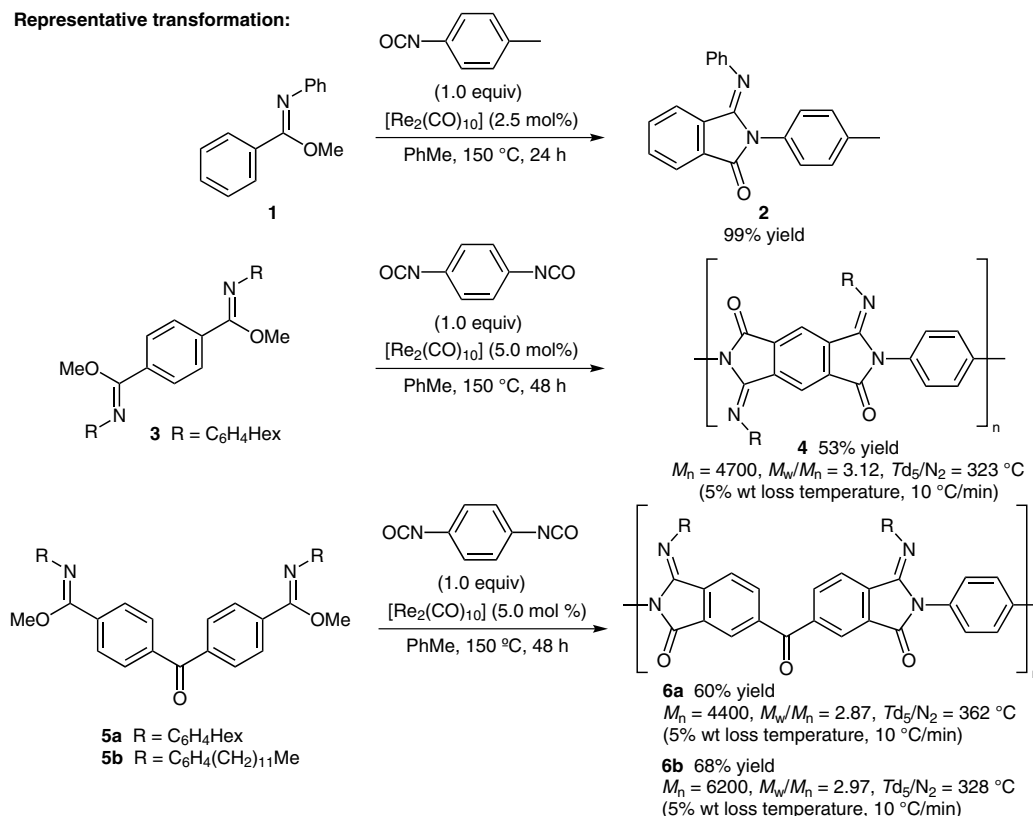
S. SUEKI, Y. GUO, M. KANAI, Y. KUNINOBU* (THE UNIVERSITY OF TOKYO AND CREST SCIENCE AND TECHNOLOGY AGENCY, TOKYO, JAPAN)

Rhenium-Catalyzed Synthesis of 3-Imino-1-isindolinones by C–H Bond Activation: Application to the Synthesis of Polyimide Derivatives

Angew. Chem. Int. Ed **2013**, *52*, 11879–11883.

Insert, Cyclize, Eliminate: Polyimides from Imidates and Isocyanates

Representative transformation:



Significance: Polyimides find application in aerospace engineering and electronic materials because of their inherent rigidity, strength, heat-resistance, and electrical non-conductance. However, their low solubility in organic solvents limits processability. The authors hypothesized that the solubility could be improved by switching the carbonyl group into an imino group functionalized with pendant alkyl chains. They confirmed their hypothesis by developing a mild, atom-economical rhenium-catalyzed transformation that involves sequential C–H activation, intramolecular nucleophilic cyclization, and elimination of methanol.

Comment: The key step in the reported methodology is the restoration of the C=N double bond by elimination of a small molecule (methanol). The efficacy of this tactic is evidenced by the good yields obtained throughout a diverse substrate scope and on a gram-scale reaction (80% yield). This is the first example of polyimide derivatives having imino groups; the polymers obtained are highly soluble in toluene, tetrahydrofuran, dichloromethane, and chloroform. It will be important to explore the mechanical properties of this new class of polyimides to determine how they compare to their less soluble, carbonyl-containing counterparts.

SYNFACTS Contributors: Timothy M. Swager, Joseph. M. Azzarelli

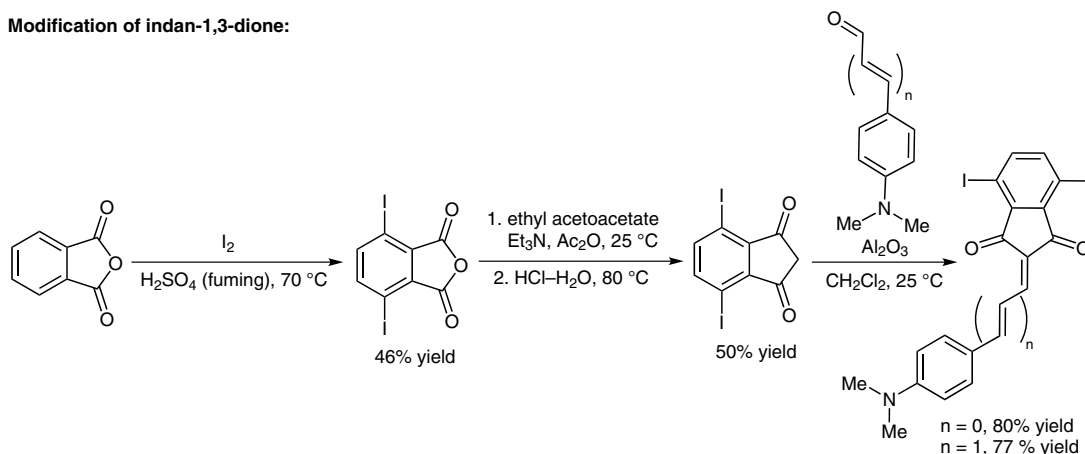
Synfacts 2014, 10(1), 0034 Published online:

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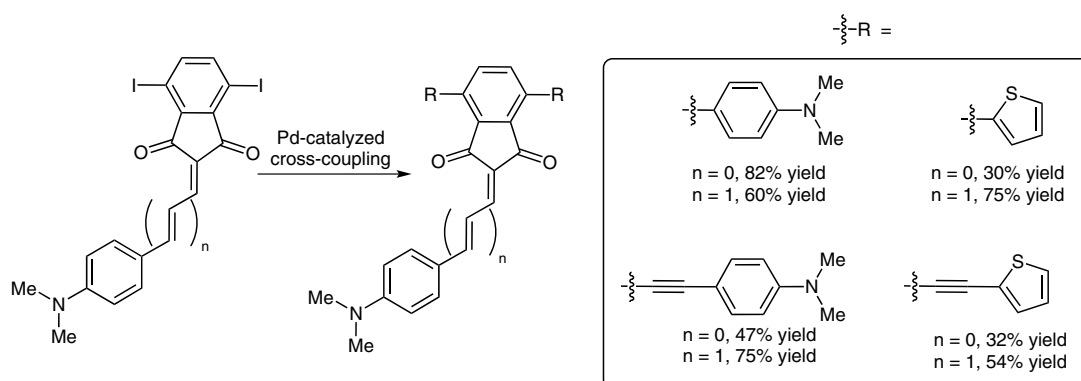
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Push–Pull Chromophores from Indan-1,3-dione

Modification of indan-1,3-dione:



T-Shaped chromophore synthesis:



Significance: The synthesis of T-shaped push–pull chromophores based on indan-1,3-dione as an electron acceptor is presented. The two donor moieties that comprise the T-shaped architecture are installed via the Knoevenagel condensation of 4,7-diiodoindan-1,3-dione with an aryl aldehyde, followed by palladium-catalyzed cross-coupling of the iodides with *N,N*-dimethylaniline or thiophene-containing substituents.

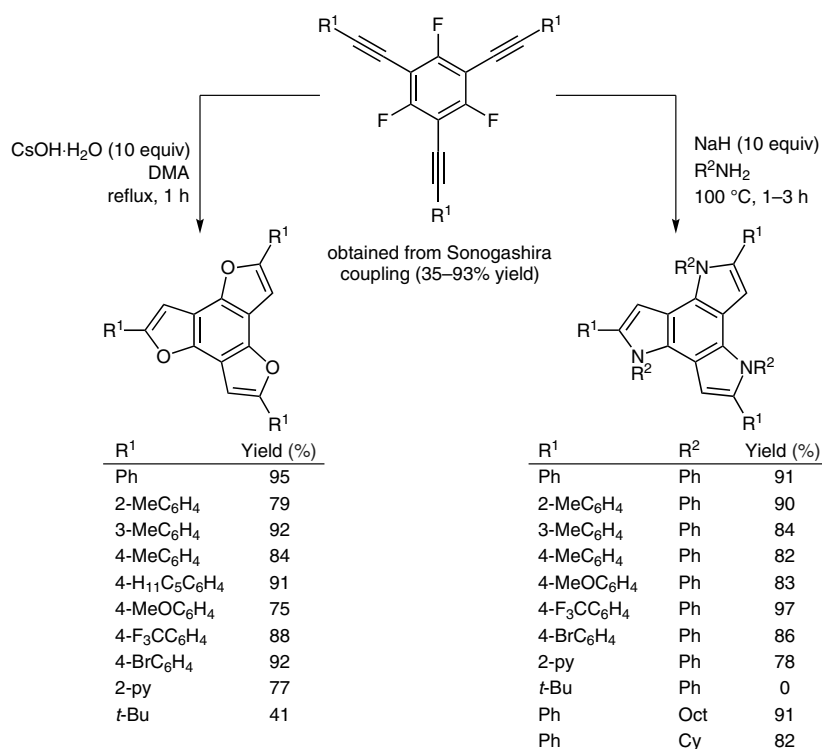
Comment: The optical and electronic properties of the synthesized T-shaped chromophores are extensively studied by UV/Vis absorption spectroscopy and calculations. Their non-linear optical properties are also examined through theoretical calculations.

H. TSUJI,* G. CANTAGREL, Y. UEDA, T. CHEN, L.-J. WAN,* E. NAKAMURA* (THE UNIVERSITY OF TOKYO AND JST-PRESTO, SAITAMA, JAPAN; BEIJING NATIONAL LABORATORY FOR MOLECULAR SCIENCES AND INSTITUTE OF CHEMISTRY, BEIJING, P. R. OF CHINA)

Synthesis of Benzotrifuran and Benzotripyrrole Derivatives and Molecular Orientations on the Surface and in the Solid State

Chem. Asian J. **2013**, *8*, 2377–2382.

Facile Access to Heteroaromatic Triphenylene Analogues



Significance: Planar disc-shaped molecules have attractive properties for applications in materials science, particularly when they exhibit three-fold symmetry. In the present work, the authors demonstrate a versatile approach to the synthesis of benzotrifurans and benzotripyrroles. The C_{3h}-symmetric target molecules are obtained in a triple cyclization with excellent yields over a wide range of substrates (75–97%). The authors also study the 2-D molecular arrangement of the phenyl-substituted benzotrifuran via scanning tunneling microscopy and compare it to its 3-D arrangement in the crystalline state.

Comment: The starting 1,3,5-triethynylbenzenes are prepared by Sonogashira coupling with 1,3,5-trifluoro-2,4,6-triiodobenzene. Reaction with cesium hydroxide in *N,N*-dimethylacetamide (DMA) or with a sodium amide in an amine solvent induces the triple cyclization. For alkynes with *tert*-butyl substitution, the reaction hardly proceeds beyond the second ring closure. Crystal structures were obtained for four benzotrifurans and one benzotripyrrol, and the authors analyze their emission spectra in the solid state and in solution.

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M. GHOLAMI, S. RAMSAYWACK, M. N. CHAUR, A. H. MURRAY, R. MCDONALD, M. J. FERGUSON, L. ECHEGOYEN, R. R. TYKWINSKI* (UNIVERSITY OF ERLANGEN-NUREMBERG, GERMANY; UNIVERSITY OF ALBERTA, EDMONTON, CANADA; UNIVERSIDAD DEL VALLE, SANTIAGO DE CALI, COLOMBIA; UNIVERSITY OF TEXAS AT EL PASO, USA)

Synthesis and Derivatization of Expanded $[n]$ Radialenes ($n = 3, 4$)

Chem. Eur. J. **2013**, *19*, 15120–15132.

Category

Synthesis of
Materials and
Unnatural Products

Key words

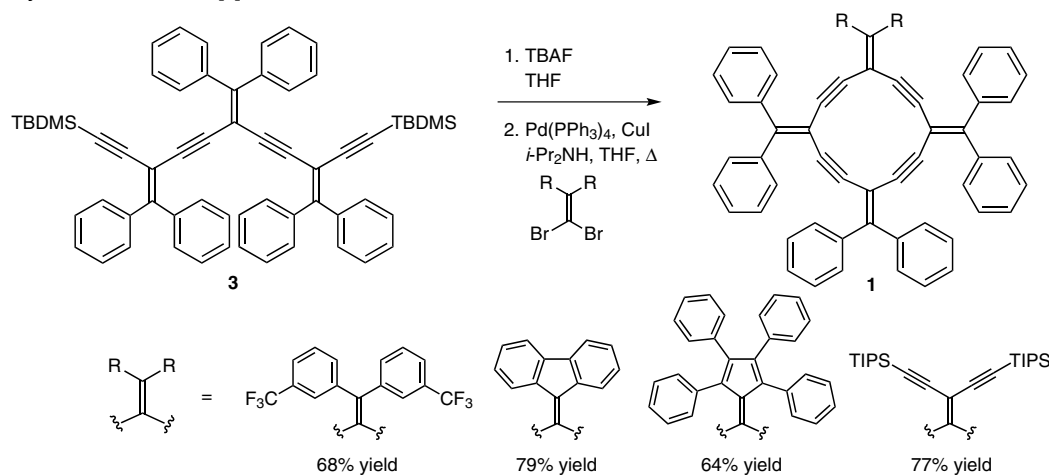
expanded
radialenes

strained
macrocycles

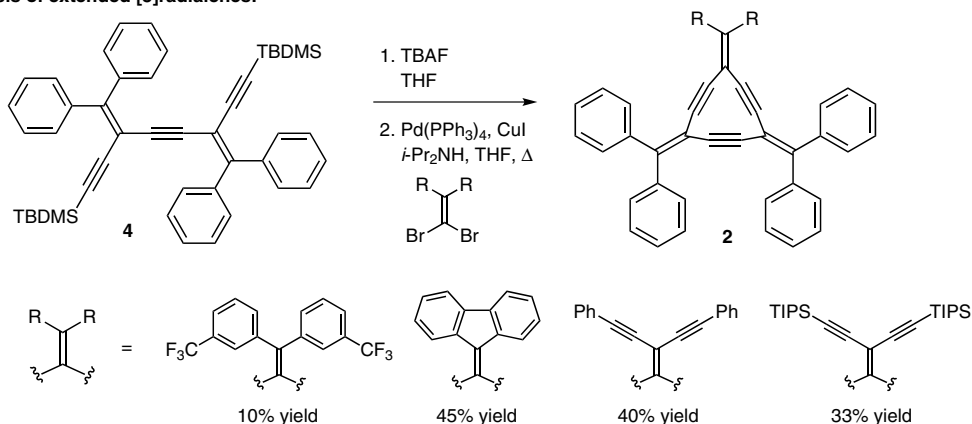
carbon-rich
molecules

Expanded $[n]$ Radialenes: Unusual Carbon-Rich Molecules

Synthesis of extended $[4]$ radialenes:



Synthesis of extended $[3]$ radialenes:



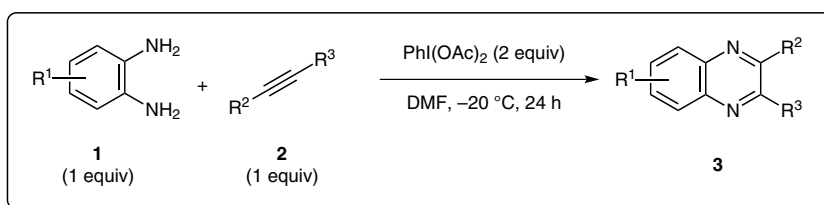
Significance: Conjugated macrocycles belong to a class of carbon-rich molecules that exhibit unusual structures and fascinating electronic and optical properties. Here, Tykwinski and co-workers report synthetic approaches to extended $[4]$ radialenes **1** and $[3]$ radialenes **2**.

Comment: Synthesis of the extended radialenes **1** and **2** is accomplished by a one-pot deprotection and palladium-catalyzed cross-coupling reaction of common intermediates **3** and **4**, respectively. Increased bond-angle strain appears to reduce yields in the synthesis of **2** compared to **1**. A modified synthesis that leads to C_2 -symmetric expanded $[4]$ radialenes is also presented in this work.

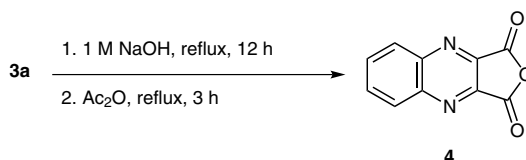
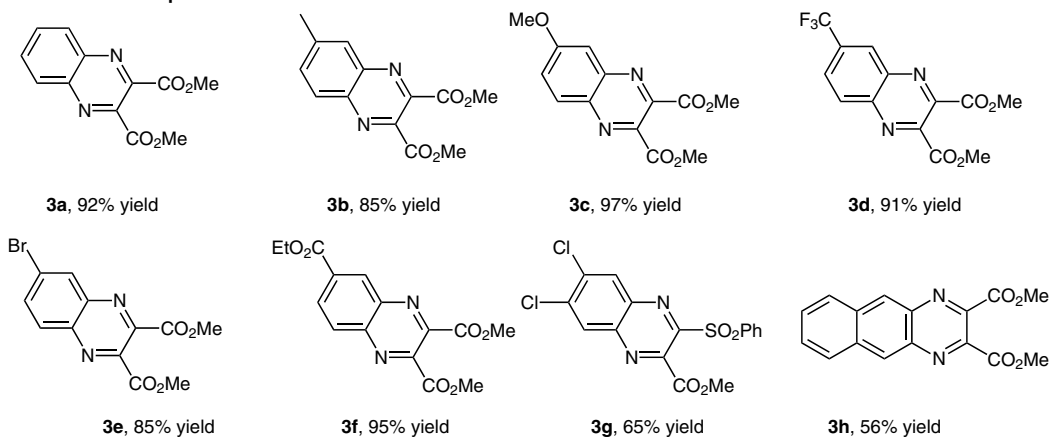
SYNFACTS Contributors: Timothy M. Swager, Derik K. Frantz
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S. OKUMURA, Y. TAKEDA,* K. KIYOKAWA, S. MINAKATA* (OSAKA UNIVERSITY, JAPAN)
Hypervalent Iodine(III)-Induced Oxidative [4+2] Annulation of *o*-Phenylenediamines and Electron-Deficient Alkynes: Direct Synthesis of Quinoxalines from Alkyne Substrates under Metal-Free Conditions
Chem. Commun. **2013**, 49, 9266–9268.

Quinoxalines Directly from Electron-Deficient Alkynes



Selected examples:



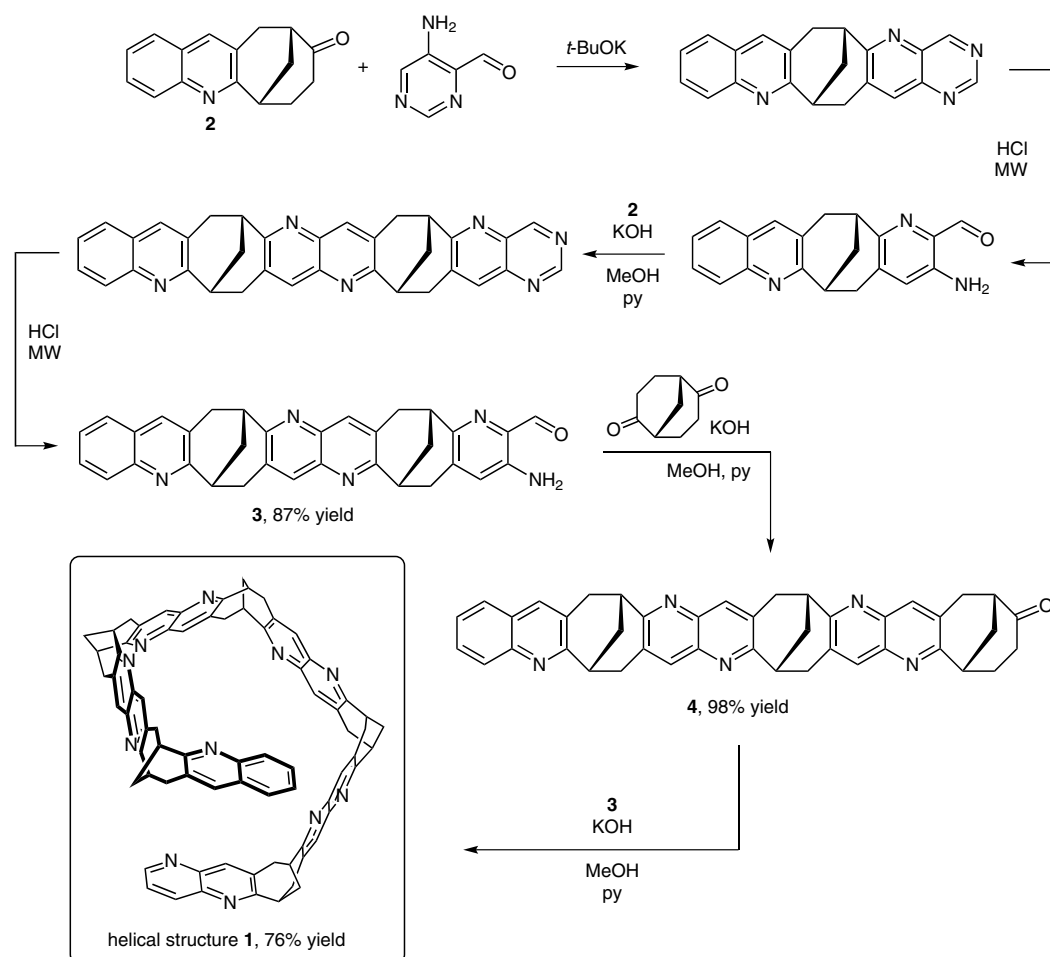
Significance: The authors report the metal-free oxidative [4+2] annulation of electron-deficient alkynes and *ortho*-phenylenediamines to synthesize quinoxalines, which are most commonly prepared by condensing diamines with α -diketones. The reactions with electron-rich, -neutral, and -poor substrates all proceed with high yield. The synthesis of anhydride **4** demonstrates the utility of this method, as such electron-deficient quinoxalines are challenging to prepare by traditional methods.

Comment: Initial results with *tert*-butyl hypoiodite predominately yielded the dearomatized *cis,cis*-mucononitrile. Phenyliodine diacetate (PIDA) proved to be crucial, despite attempts with several other hypervalent iodine reagents. The reaction is also highly solvent-dependent, proceeding more effectively with increasing solvent polarity.

SYNFACTS Contributors: Timothy M. Swager, Jonathan G. Weis
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A Tubular Structural Analogue of Helicene

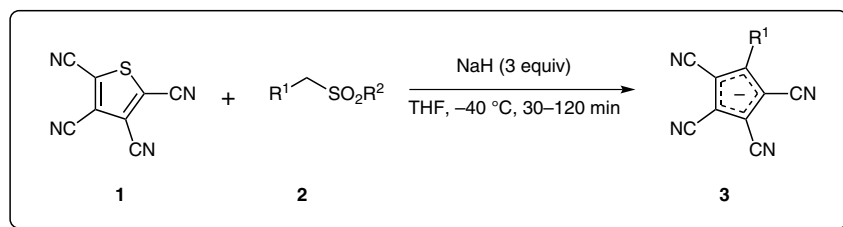


Significance: Helical molecular systems, both natural and unnatural, continue to capture the interests of chemists. Using an enantiomerically pure bicyclic moiety to appropriately place kinks into the system, Wärnmark and co-workers report the synthesis of helical structure **1**, an orthogonal topological analogue of helicene.

Comment: The synthesis of **1** is accomplished by repeated employment of a two-step set of reactions consisting of (1) ring-opening hydrolysis in acid and (2) Friedländer condensation with a chiral bicyclic ketone. By this strategy, monomer **2** is converted into ring-opened trimer **3**, which is converted into trimeric ketone **4**. Condensation of **4** and **3** affords the helical target **1**.

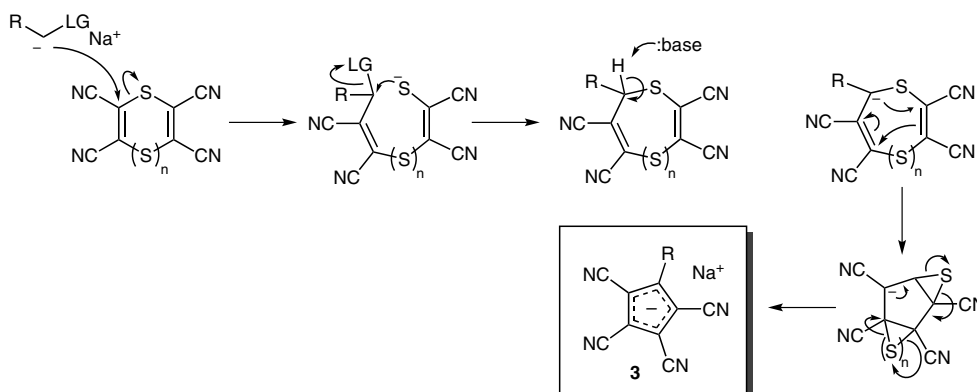
T. SAKAI,* S. SEO, J. MATSUOKA, Y. MORI* (MEIJO UNIVERSITY, NAGOYA, JAPAN)
 Synthesis of Functionalized Tetracyanocyclopentadienides from Tetracyanothiophene and Sulfones
J. Org. Chem. **2013**, *78*, 10978–10985.

Superacid Anions from Tetracyanothiophene



Entry	R ¹	R ²	Product	Yield (%)
1	CO ₂ Me	Ph	3a	59
2	CN	Tol	3b	96
3	CONMe(OMe)	Tol	3c	86
4	Ph	Ph	3d	15
5	Ph	CF ₃	3e	71
6	CH ₂ CH ₂ OBn	CF ₃	3f	61

Proposed mechanism:



Significance: The authors report an improved synthesis of tetracyanocyclopentadienyl anions, a class of superacid anions with functional handles. By including the leaving group on the nucleophile, product **3** is accessed more directly from thiophene **1** and sulfone **2**. The researchers demonstrate the reaction's utility with a variety of sulfones and successful exchange of cations.

Comment: Optimization of the reaction conditions revealed a strong dependence on base, with NaH outperforming alkoxide, silazide, and non-ionic nitrogen bases. Using phenylsulfones as the leaving groups proved more facile than using halides. Ketones could not be directly synthesized with this method but can be obtained from the Weinreb amide derivative **3c**.

SYNFACTS Contributors: Timothy M. Swager, Jonathan G. Weis
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