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Electrophilic Cyanative Alkenylation of Arenes

Mingyue Zhao, Alejandro G. Barrado, Kristin Sprenger, Christopher Golz, Ricardo A. Mata, and Manuel Alcarazo*

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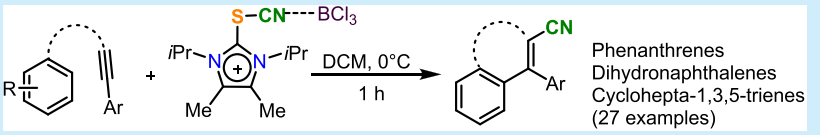
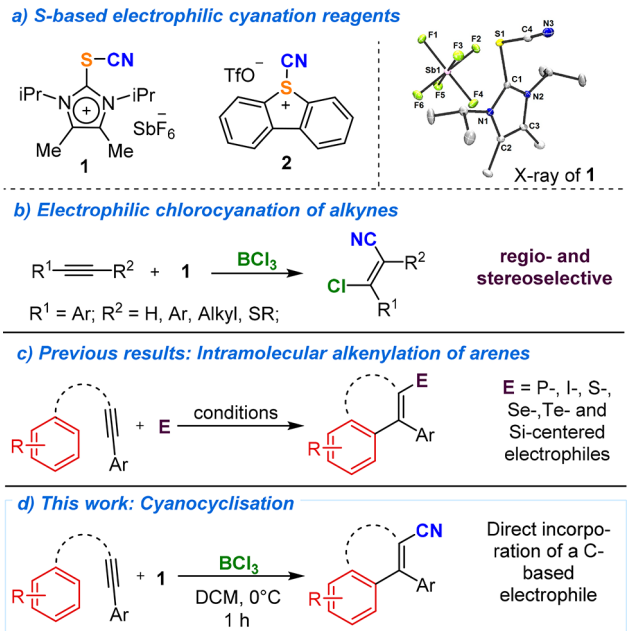


ABSTRACT: A variety of appropriately substituted internal alkynes were transformed into the corresponding cyano-substituted phenanthrenes, dihydronaphthalenes, and cyclohepta-1,3,5-trienes in moderate to excellent yields by treatment with imidazolium thiocyanate **1**, which serves as an easy to handle $[CN]^+$ precursor, in the presence of BCl_3. The synthetic value of the method is additionally demonstrated by the transformation of the primarily obtained products into heavily substituted quinolines. Additionally, the dynamic properties of the prepared dibenzocyclohepta-1,3,5-trienes have been investigated.

The proton-promoted cascade cyclization of polyprenoid chains into complex polycyclic scaffolds is widely recognized as an iconic example of biosynthesis and also as one of the most efficient methods ever transferred from nature to the laboratory for the construction of complexity.[1] In fact, there are many examples of synthetic campaigns that have been designed to make use of such a strategy.[2] Whereas most of these cation-π cyclization cascades are triggered by the elimination of a leaving group or the activation of olefins by protons or π-acid catalysts, synthetic chemists have also been keen in expanding the scope of these transformations to additional electrophiles.[3] Hence, the ring closure event(s) can be combined with the incorporation of an exocyclic functionality into the final polycycle, making the obtained products synthetically more appealing. Remarkable examples of advances in this direction are the cyclization-cascade-promoted halonium,[4] selenenium,[5] and sulfenium cations;[6] however, limitations still remain. For example, the utilization of carbon-based electrophiles as cascade initiators is comparatively underdeveloped, despite the fact that these transformations ideally combine the cyclization step with the formation of exocyclic C−C bonds.

During the past few years, we have been actively involved in the development of sulfur-based platforms able to efficiently promote the umpolung of typical organic building blocks, such as the cyano group. That research crystallized in the identification of imidazolium thiocyanate **1** and 5-(cyano) dibenzothiazolium triflate **2** as effective sources of $[CN]^+$ synthons (Scheme 1a).[7] Both reagents efficiently transfer the cyano unit to typical S-, N-, and C-nucleophiles under metal-free conditions. Moreover, an equimolar mixture of **1**/BCl_3 is able to promote the chlorocyanation of alkynes with exquisite levels of regio- and stereoselection (Scheme 1b).[8]

Scheme 1. Structure and Reactivity of Representative S-based Electrophilic Cyanation Reagents



Being aware of the multitude of reports available describing the intramolecular, metal-free, elementoarylation of alkynes[9]

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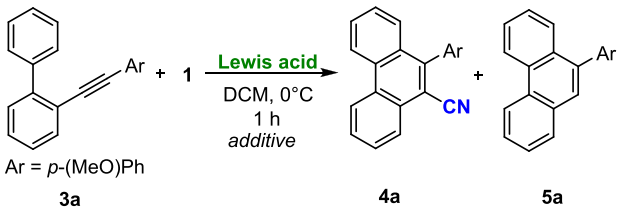
Org. Lett. XXXX, XXX, XXX−XXX

promoted by I-,[10] Br-,[11] S-,[16] Se-,[12] B-,[13] and Si-based electrophiles (Scheme 1c);[14] we envisaged that by design of the alkyne substrates, the annulative cyanoarylation of the carbon−carbon triple bond might be favored at the expense of the chlorocyanation (Scheme 1d). In this Letter, the feasibility of this hypothesis is demonstrated, and the application of the newly developed method to the synthesis of cyano-substituted phenanthrenes, dihydronaphthalenes, and dibenzocyclohepta-1,3,5-trienes of different substitution patterns is described. The prevalence of the nitrile moiety in natural products,[15] pharmaceuticals,[16] agrochemicals,[17] dyes,[18] and high-performance materials[19] anticipates a broad range of applications for the protocol described herein.

Employing biphenyl **3a** as the model substrate, its reaction with thioimidazolium salt **1** in the presence of a range of Lewis acids was evaluated. Only starting material was recovered when $AlCl_3$ was used as the promoter, whereas $Al(TfO)_3$, $Yb(TfO)_3$, and $BF_3{\cdot}OEt_3$ induced the formation of phenanthrene product **5a** with excellent conversion (Table 1, entries 1−4).

Table 1. Reaction Optimization



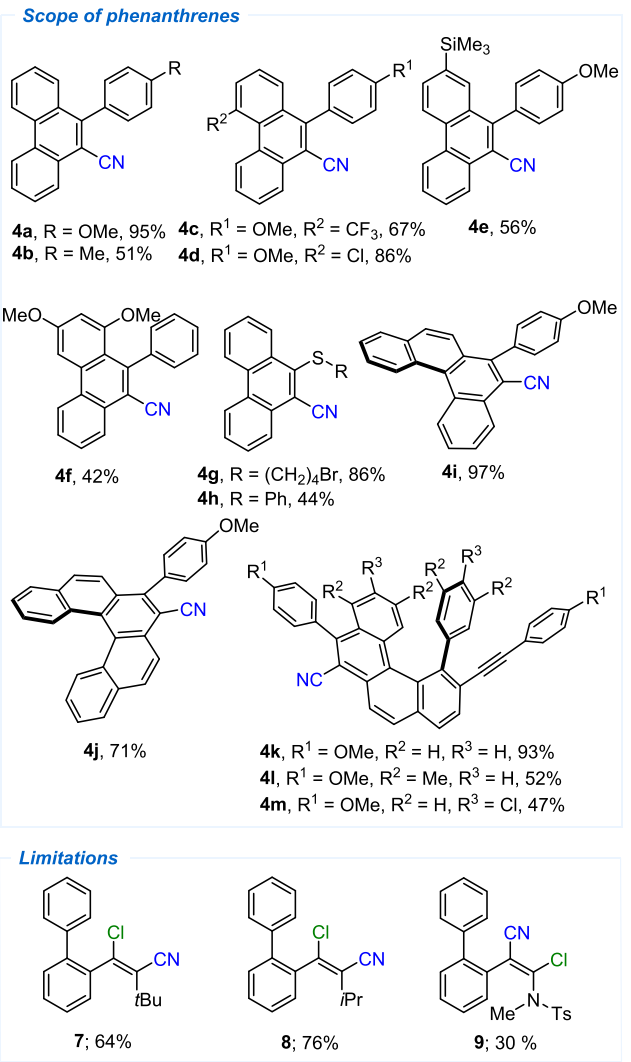
entry	Lewis acid (equiv)	conv. (%)[a]	additive	4a/5a
1	$AlCl_3$ (1.0)	n.r.		
2	$Al(TfO)_3$ (1.0)	>95		only **5a**
3	$Yb(TfO)_3$ (1.0)	>95		only **5a**
4	$BF_3{\cdot}OEt_3$ (1.0)	>95		only **5a**
5	BCl_3 (1.0)	>95		1:1
6	$B(C_6F_5)_3$ (1.0)	>95		1:1
7	BCl_3 (1.0)	n.r.	DIPEA[b]	
8	BCl_3 (1.0)	78	**6**[b]	only **4a**
9	BCl_3 (1.2)	95[c]	**6**[b,d]	only **4a**

[a]Conversions were determined by NMR. [b]**6** = 2,6-di-*tert*-butylpyridine, 1.0 equiv. [c]Isolated yield. [d]1.2 equiv.

Interestingly, both BCl_3 and $B(C_6F_5)_3$ were able to enroll **1** in the desired cyclization, and cyano-substituted phenanthrene **4a** could be obtained for the first time, albeit as an equimolar mixture with **5a** (Table 1, entries 5 and 6). Because the annulation from **3a** to **4a** generates stoichiometric amounts of protons and acids are known to catalyze the formation of **5a** from **3a**, organic bases were incorporated in the reaction mixture in an attempt to quench that reaction pathway.[20] Interestingly, whereas DIPEA completely suppresses any cyclization, much bulkier 2,6-di-*tert*-butylpyridine seems not to interfere with the Lewis acid promoter, allowing the conversion of **3a** toward **4a** in a selective manner (Table 1, entries 7 and 8). Finally, increasing the amount of BCl_3 up to 1.2 equiv substantially improved the conversion; the isolation of **4a** with an excellent (95%) yield was possible under these conditions (Table 1, entry 9).

Having identified the optimal reaction conditions, the scope and limitations of the new transformation were explored. As expected from a cyclization proceeding through a carbocationic intermediate, electron-rich substituents at the alkyne termini, such as *p*-anisyl **3a,c−e,i** or thioalkyl/aryl **3g,h**, facilitate the regioselective attack of the $[CN]^+$ unit and seem to be critical for obtaining high yields of the corresponding phenanthrenes (Scheme 2). In fact, the reaction fails when the akyne moieties

Scheme 2. Scope of the Electrophilic Cyanation of 1-(Aryl)-2-etynylbenzenes toward Phenanthrenes[a]



[a]Standard conditions were used in all cases: **3a−n** (1 equiv), **1** (1.2 equiv), 2,6-di-*tert*-butylpyridine (1.2 equiv), DCM, rt, 1 h.

are alkyl- or −NTs-substituted. In these cases, products of alkyne chlorocyanation such as **7−9** are obtained. Contrarily, there is relative tolerance regarding the substitution pattern at the arene undergoing substitution. Even substrate **3c**, decorated with a strong electron-withdrawing $-CF_3$ group, affords the desired phenanthrene **4c** in acceptable yield. The cyclization has been successfully extended to substrates bearing condensed arene moieties affording cyano-substituted [4]- and [5]helicenes **4i−m**. In all cases the use of 2,6-di-*tert*-butylpyridine is essential to suppress the noncyanative cyclization.

The connectivity of phenanthrene derivatives **4i** and **4k** and chloroacrylonitrile **9** was confirmed by the X-ray analysis; their structures are depicted in Figure 1 (for **4i** and **9**) and the Supporting Information (for **4k**).

Encouraged by the results obtained in the synthesis of phenanthrenes from *o*-alkynyl biaryls, the cyclization of 1,4-

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Org. Lett. XXXX, XXX, XXX−XXX

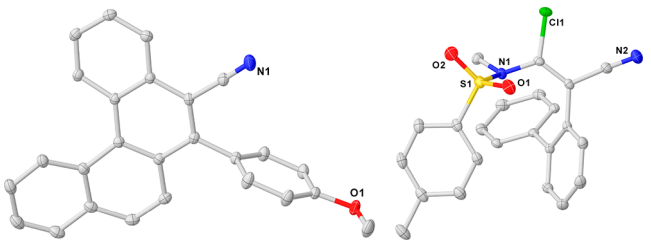
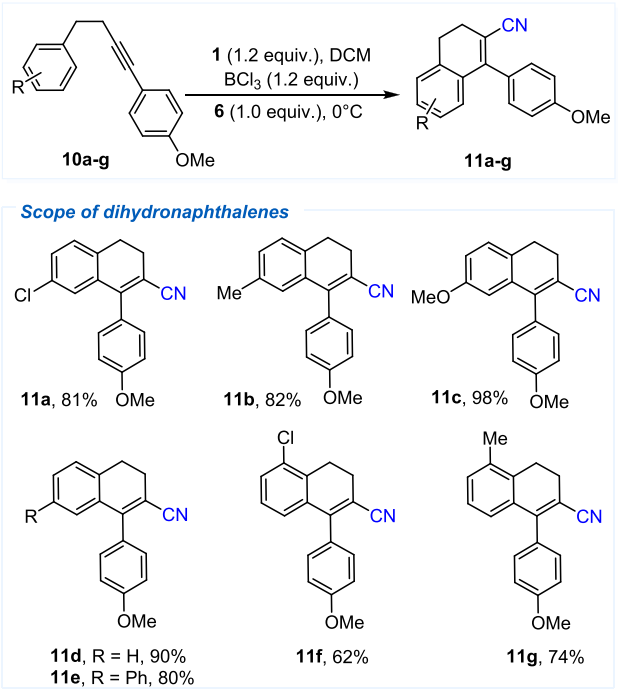


Figure 1. Molecular diagram of the X-ray structure of **4j** (left) and **9** (right). H atoms are removed for clarity, and ellipsoids are drawn at 50% probability.

diaryl-1-butynes **10a–g** into the corresponding dihydronaphthalenes **11a–g** was subsequently investigated. For this transformation, the presence of a *p*-(methoxy)phenyl substituent directly attached to the alkyne moiety proved to be essential. Once this condition was satisfied, the reaction proceeded in moderate to good yield for a range of substrates. Electron-donating, neutral or even moderate electron-withdrawing substituents on the arene undergoing alkenylation are tolerated (Scheme 3).

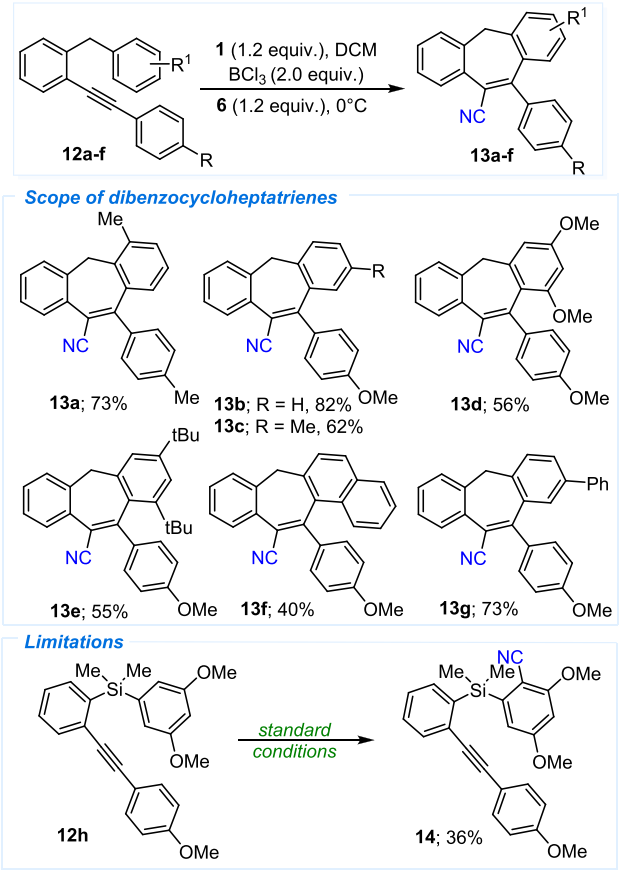
Scheme 3. Cyclization of 1,4-Diphenyl-1-butynes into Dihydrophenanthrenes



In all cases studied, the 6-*endo*-dig cyclization took place exclusively over the alternative 5-*exo* pathway to afford dihydrophenanthrenes; no trace of dihydrofulvene-type products was observed. However, careful analysis of the crude reaction mixtures allowed the detection of two groups of minor side products. Namely, those derived from the chlorocyanation of the triple bond in **10a–g** and those originated from the BCl_3-promoted demethylation of the MeO groups in **11a–g**. The X-ray structures of **11a,c–e** are reported in the Supporting Information.

In a final effort to further expand the scope of this cyanoannulation, the possibility of generating dibenzocyclohepta-1,3,5-trienes from 1-benzyl-2-etynylbenzenes was evaluated. This cyclization toward seven-membered rings proved to be more difficult than the ones already studied, and the use of 2.0 equiv of BCl_3 was required to accelerate the transformation. Under these conditions, the model structure **12a** smoothly underwent the desired cyclization to afford **13a** in a remarkable 73% isolated yield. However, products of demethylation are observed in variable amounts for substrates **12b–f**, all decorated with MeO groups, causing a systematic drop in the yields of the desired cycloheptatrienes (Scheme 4).

Scheme 4. Cyclization of 1-Benzyl-2-etynylbenzenes into Dibenzocyclohepta-1,3,5-trienes



For substrates containing exceptionally electron-rich aromatic moieties, as in the case of **12h**, the electrophilic cyanation at the ring becomes a competitive reaction pathway (Scheme 4).

The X-ray structures of **13b,e–g** indicate that the central seven-membered ring adopts a boat-like conformation, and, as consequence, these molecules are chiral, and if the inversion barrier between the two possible boats is high enough, then the resolution of the racemic mixture should be possible. (See the Supporting Information for the X-ray structures of **13b,e–g**.)[21] In fact, from all cyclohepta-1,3,5-trienes prepared, only the more sterically demanding **13e** and **13f** could be resolved into the corresponding enantiomers by chiral stationary phase chromatography (IG-u, Hex/*i*PrOH 99:1, 298 K for **13e**; and IG-u, Hex/*i*PrOH 97:3, 288 K for **13f**). Moreover, for **13e**, which hardly racemizes at room temperature, the circular dichroism spectra of both isolated fractions were measured. (See the Supporting Information). As expected for enantiomers, they display perfect mirror symmetry.

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Org. Lett. XXXX, XXX, XXX−XXX

Density functional theory (DFT) calculations at the B3LYP-D3/def2-TZVP level (with Becke–Johnson damping) additionally confirm that this is actually the case for compounds **13e** and **13f**.[22] All calculations were carried out with the Gaussian16 program package for the reaction pathway optimization,[23] applying the local quadratic approximation.[24] The rate-determining step for the interconversion of the enantiomers in both compounds is the flipping of the $-CH_2-$ group in the cycloheptatriene ring. Surprisingly, the rotation of the gear assembly formed by the naphthyl and *p*-(methoxy)-phenyl moieties, or even the *t*Bu- and *p*-(methoxy)phenyl ones (in **13f** and **13e**, respectively), is not high enough to peak on the calculated potential energy surface (Figure 2). The

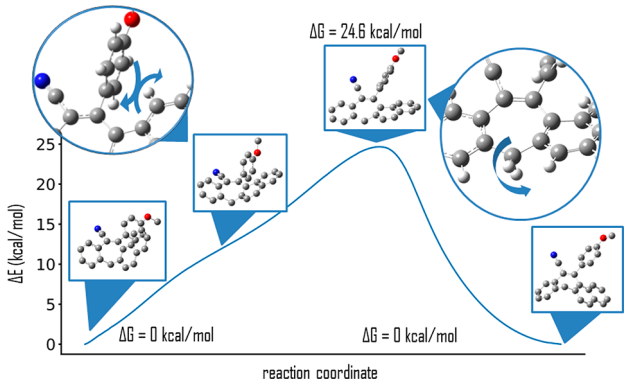
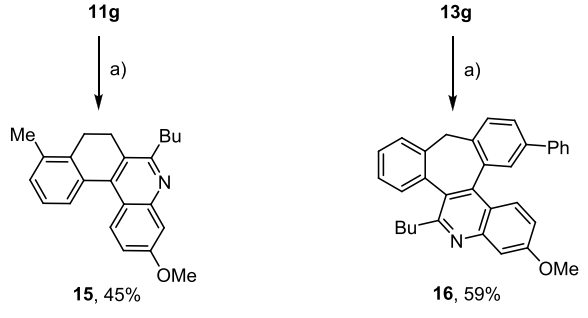


Figure 2. Reaction path profile for the inversion of **13f** under the local quadratic approximation calculated with B3LYP-D3/6-31+G(d).[24] The Gibbs free energies (with the electronic energy recomputed at the B3LYP-D3/def2-TZVP level of theory) are provided.

transition state and the minima were converged, and the free energies were computed by applying the double-harmonic approximation. The free energies of activation for these inversions ($\Delta G^{\#}$) are 24.6 (**13f**) and 28.2 kcal/mol (**13e**), which means that their half lives at 25 °C are approximately 34 h and 1.7 years, respectively.

Finally, the synthetic utility of the building blocks obtained is showcased by the transformation of dihydrophenanthrene **11g** and cycloheptatriene **13g** into quinoline derivatives **15** and **16**, respectively, following an already described methodology that consists of the addition of BuLi to the nitrile unit, the in situ generation of a N-centered iminyl radical by treatment with iodine, and the subsequent oxidative cyclization into the desired quinoline (Scheme 5).[25]

Scheme 5. Transformation of Aryl Acrylonitriles into Polysubstituted Quinolines[a]



[a]Reagents and conditions: (a) *n*BuLi, THF, 0 °C; then, I_2, 60°C.

In conclusion, an efficient method has been developed for the cyanative cyclization of conveniently substituted alkynes into phenanthrenes, dihydronaphthalenes, and dibenzocycloheptatrienes of different substitution patterns employing imidazolium thiocyanate **1** as a $[CN]^+$ synthon. Substituents such as MeO–, Cl–, Br–, Me_3Si–, RS–, or CF_3– are tolerated, and the acrylonitriles obtained can be elaborated into more complex materials by employing the rich chemistry of the nitrile group.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.0c01204.

General experimental procedures, characterization data, and ^1H and ^{13}C NMR spectra of new compounds (PDF)

Accession Codes

CCDC 1979429–1979440 and 1980636 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

■ AUTHOR INFORMATION

Corresponding Author

Manuel Alcarazo – *Institut für Organische und Biomolekulare Chemie, Georg August Universität Göttingen, 37077 Göttingen, Germany;* orcid.org/0000-0002-5491-5682; Email: manuel.alcarazo@chemie.uni-goettingen.de

Authors

Mingyue Zhao – *Institut für Organische und Biomolekulare Chemie, Georg August Universität Göttingen, 37077 Göttingen, Germany*

Alejandro G. Barrado – *Institut für Organische und Biomolekulare Chemie, Georg August Universität Göttingen, 37077 Göttingen, Germany*

Kristin Sprenger – *Institut für Organische und Biomolekulare Chemie, Georg August Universität Göttingen, 37077 Göttingen, Germany*

Christopher Golz – *Institut für Organische und Biomolekulare Chemie, Georg August Universität Göttingen, 37077 Göttingen, Germany*

Ricardo A. Mata – *Institut für Physikalische Chemie, Georg August Universität Göttingen, 37077 Göttingen, Germany*

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.orglett.0c01204

Notes

The authors declare no competing financial interest.

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