A Journal of the Gesellschaft Deutscher Chemiker

Angewandte International Edition GDCh Chemie

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Accepted Article

Title: 5-(Cyano)dibenzothiophenium Triflate: A Sulfur–Based Reagent for Electrophilic Cyanation and Cyanocyclizations

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To be cited as: *Angew. Chem. Int. Ed.* 10.1002/anie.201904557
Angew. Chem. 10.1002/ange.201904557

Link to VoR: http://dx.doi.org/10.1002/anie.201904557
http://dx.doi.org/10.1002/ange.201904557

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10.1002/anie.201904557

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5-(Cyano)dibenzothiophenium Triflate: A Sulfur–Based Reagent for Electrophilic Cyanation and Cyanocyclizations

Xiangdong Li, Christopher Golz and Manuel Alcarazo*[a]

Dedicated to Prof. Armin de Meijere on the occasion of his 80th birthday

Abstract: The synthesis of 5-(cyano)dibenzothiophenium triflate **9**, prepared by activation of dibenzo[b,d]thiophene-5-oxide with Tf_2O and subsequent reaction with TMSCN is reported, and its reactivity as electrophilic cyanation reagent evaluated. The scalable preparation, easy handling and broad substrate scope of the electrophilic cyanation promoted by **9**, which includes amines, thiols, silyl enol ethers, alkenes, electron rich (hetero)arenes and polyaromatic hydrocarbons, illustrate the synthetic potential of this reagent. Importantly, Lewis acid activation of the reagent is not required for the transfer process. We additionally report herein biomimetic cyanocyclization cascade reactions, which are not promoted by typical electrophilic cyanation reagents, demonstrating the superior ability of **9** to trigger challenging transformations.

The synthetic versatility of the cyano group, which is a privileged precursor of amines, amides, aldehydes, carboxylic acids and *N*-containing heterocycles;[1] as well as the prevalence of nitriles in natural products,[2] pharmaceuticals,[3] agrochemicals,[4] dyes[5] and high performance materials and polymers[6] has stimulated the development of efficient methodologies for the selective incorporation of –CN substituents at specific positions of elaborated organic scaffolds.[7] Despite of the sophistication achieved in this area,[8] most of the protocols described still use the inherent nucleophilicity of the cyanide anion to promote the C-*CN* bond forming event and hence, they are reminiscent to the classical Sandmeyer[9] and Rosenmund–von Braun reactions for the preparation of aromatic nitriles,[10] or the Kolbe nitrile synthesis for aliphatic ones.[11] Disconnection strategies based on the umpolung of the CN moiety are comparatively scarce and their synthetic potential has still not been fully exploited mainly due to the disadvantages associated with the use of the available electrophilic cyanide sources.[12] Namely, the extreme toxicity and volatility of pseudo halogens **1-3**,[13] or the considerably lower reactivity of *N*-cyano sulfonamides **4**, *N*-cyanobenzotriazole **5** and *N*-cyanobenzoimidazole **6**, which require the use of strong C-nucleophiles such as organometallic reagents or enolates to transfer the formal $[CN]^+$ unit.[14] It was not until the introduction of cyanobenziodoxone **7** by Zhdankin,[15] and its intensive use by Waser[16] and others[17] that metal-free electrophilic cyanation at unfunctionalized C-H positions of electron rich organic substrates could be efficiently achieved (Figure 1). We recently contributed to this area with the introduction of imidazolium thiocyanate **8**; it depicts a reactivity profile similar to the one of **7**, but is not based on thermally unstable hypervalent I(III) platforms.[18]

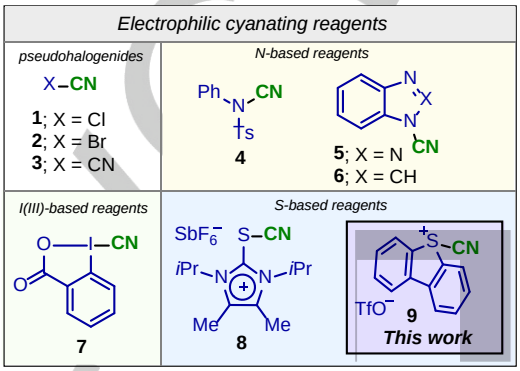

Figure 1. Representative electrophilic cyanation reagents.

Nature often uses carbocationic cascade cyclisations to produce complex molecular architectures from simple precursors, and chemists have been quite successful transferring this strategy into routine synthesis planning.[19] Initiation of such cyclisations is often triggered by elimination of a leaving group, the activation of olefins by π-acid catalysts, or the reaction of carbon-carbon double bonds with electrophiles.[20] However, we are not aware of the use of neither **7** nor **8** as promoters for the metal-free cyanofunctionalization of olefins, presumably due to the moderate electrophilic character of the cyano moieties in these two $[CN]^+$ synthons.[21]

Given the synthetic potential that such cyano-functionalization may have, we were encouraged to develop a new electrophilic cyanation reagent able to trigger these transformations. At that stage we envisioned that the dibenzothiophenium unit, which has been previously used for the preparation of electrophilic trifluoromethylation and alkynylation reagents might be an adequate platform to achieve a more efficient umpolung of the CN-group.[22] Herein, we report the synthesis of 5-(cyano)dibenzothiophenium triflate **9**, and preliminarily evaluate its reactivity on the cyanation of typical organic nucleophiles, and the cyanofunctionalization of a variety of indole derivatives.

The desired 5-(cyano)dibenzothiophenium salt **9** has been obtained in a one pot synthesis from sulfoxide **10** by activation with one equivalent of triflic acid anhydride at -50 °C and quenching of the *in situ* generated bistriflate with TMSCN. Compound **9** precipitates from the reaction mixture and is isolated as a beige solid. This synthetic route has been scaled up to ten grams with a reproducible 60% yield (Scheme 1). Diagnostic spectroscopic features of compound **9** are the ^{13}C-NMR signal for the carbon atom of the cyano moiety (δ = 103.8 ppm.), which is upfield shifted if compared with that of arylsulfonyl cyanides (δ = 110-119 ppm.), and the stretching frequency of the C≡N moiety at $\tilde{\nu}_{(CN)}$= 2191.7 cm^{-1}.

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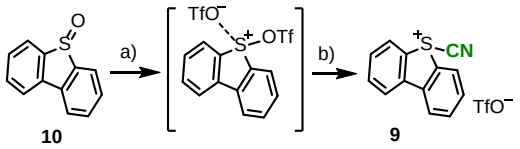
10.1002/anie.201904557



Scheme 1. Synthesis of 5-(cyano)dibenzothiophenium triflate. Reagents and conditions: a) Tf_2O (1 equiv.), -50°C, 1h, (not isolated); c) TMSCN (1 equiv.), CH_2Cl_2, -50°C, 8h, 60%.

X-ray diffraction analysis of monocrystals of **9** confirmed the expected connectivity (Figure 2). In the cationic part the sulfur atom remains at the plane defined by the dibenzothiophene skeleton; however, the C-S bond distances within the aromatic moiety, 1.7911(8) Å for S1-C2 and 1.7991(8) Å for S1-C13 are significantly longer than in dibenzothiophene (1.740 Å). This probably results from the reduction of aromaticity at the thiophene platform after coordination of the cyano moiety. In addition, the central sulfur atom adopts a trigonal-pyramidal coordination environment, being the sum of the bond angles around S1 286.6°(4); thus, there is a stereochemically relevant electron pair at this atom. Also of particular relevance is the short contact S1-O3 (2.6085(7) Å), which is significantly shorter than the sum of the van der Waals radii of the corresponding elements (3.32 Å). This interaction evidences some Lewis acidity at S1 and suggests that the initial step of the cyano transfer using **9** might imply the approach of the incoming nucleophile to the electron poor sulfur atom, followed by a reductive elimination type process. An analogous mechanism has been proposed for cyanation reactions promoted by reagent **7**.[23]

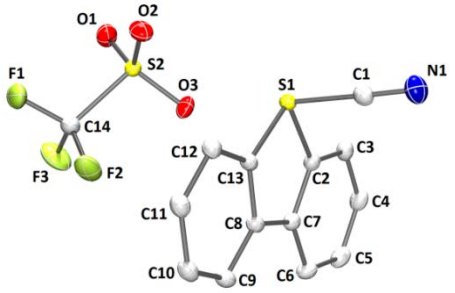
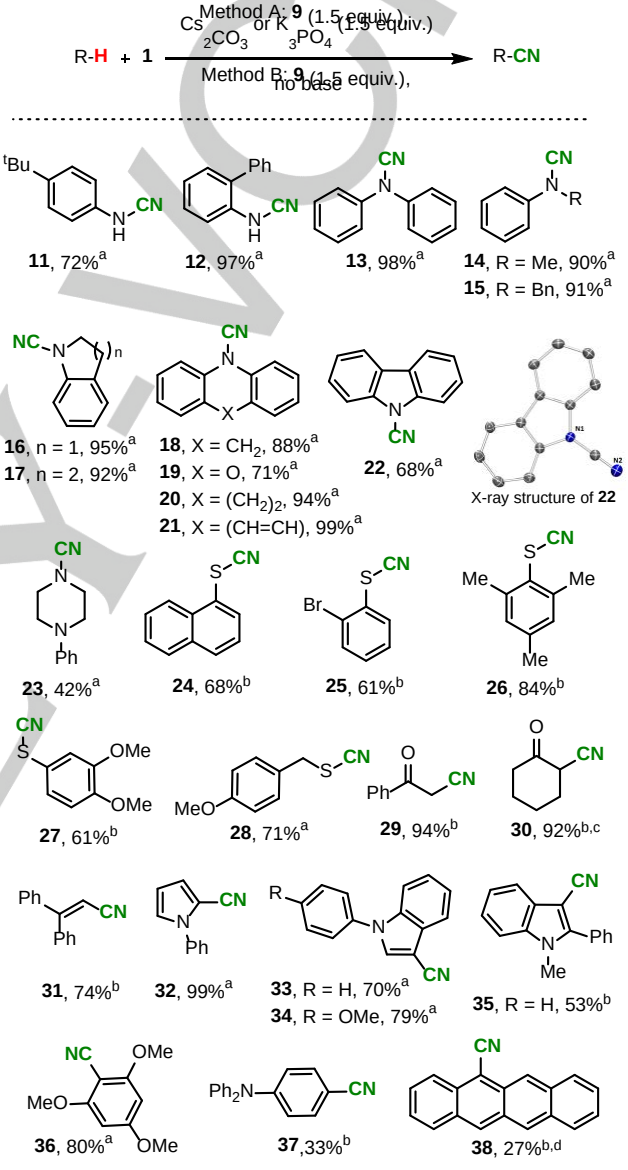


Figure 2. Molecular structure of compound **9** in the solid state. Anisotropic displacement shown at 50% probability level and hydrogen atoms omitted for clarity. Selected bond lengths [Å] and angles [deg]: S1-C1, 1.7404(9); S1-C2, 1.7911(8); S1-C13, 1.7991(8); S1-O3, 2.6085(7); O3-S1-C1, 176.07(3); C2-S1-C1, 96.06(4); C13-S1-C1, 98.92(4).[24]

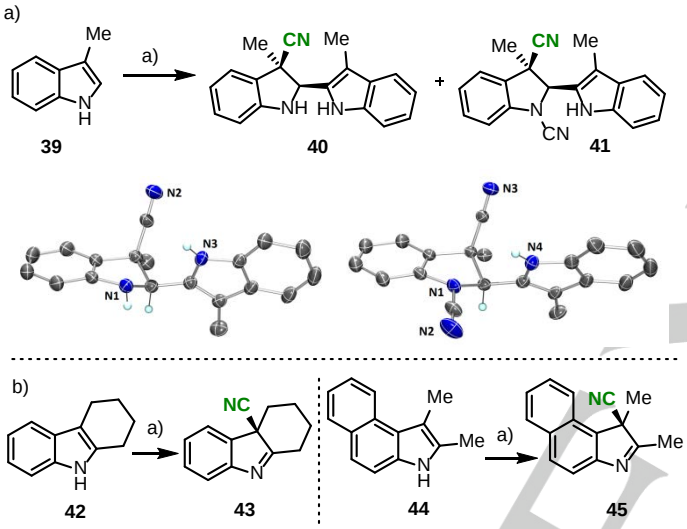
Once compound **9** was completely characterized, we started our investigation by subjecting benchmark N-, S- and C-based nucleophiles to its action. Optimization of the reaction conditions using anilines revealed Cs_2CO_3 as the optimal base (Scheme 2, Method A). Under these conditions cyanamides **11-23** can be obtained in moderate to excellent yields. Aromatic thiols do not require the addition of base to afford thiocyanates **24-27** (Method B), while for aliphatic ones Cs_2CO_3 is again necessary to obtain acceptable results, **28**. Silyl enol ethers and terminal olefins, as well as electron rich homo-, hetero-, and polycyclic aromatics were also transformed into the desired nitriles **29-38** under similar conditions.[25] While the profile of **8** and **9** regarding substrate scope is quite similar, all cyano transfer reactions shown in Scheme 2 took place at relatively low temperatures (-50°C→50°C), and without activation of the transfer reagent with $BF_3{\cdot}OEt_2$. This suggests inherently higher electrophilicity at the CN moiety of **9**.



Scheme 2. Substrate scope of the electrophilic cyanation using 5-(cyano) dibenzothiophenium triflate **9**. All yields are isolated unless otherwise stated. [a]Method A was applied. [b]Method B was applied. [c]NMR yield. The identity of **30** was confirmed by its derivatization with $TsNH\text{-}NH_2$ and isolation of the corresponding 3-aminopyrazole. [d]Two equivalents of **9** were employed.

In an attempt to further evaluate the utility of **9** in more complex transformations, we tested its reactivity towards indole **39**, in which the most reactive position 3 is blocked with a methyl

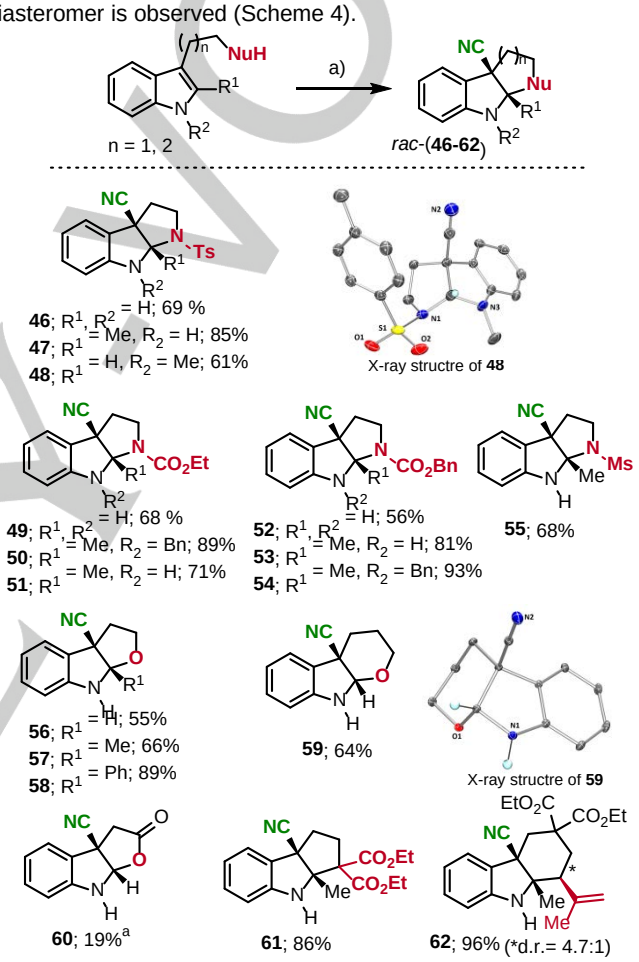
substituent. A mixture of two products **40** and **41** was obtained under these conditions. The connectivity of **40**, which could be assessed by X-ray analysis, corresponds to a dimeric structure originated from the initial attack of the $[CN]^+$ moiety at position 3 of indole **39** and subsequent trapping of the in situ generated iminium salt with a second equivalent of **39**. Compound **41** is the product of additional cyanation at the most nucleophilic amino group of **40** (Scheme 3a). Only the diasteromer coming from the *syn*-attack of both groups to the carbon-carbon double bond was detected. Simultaneous decoration of the indole substrate with two alkyl-substituents in positions 2- and 3-, as is the case of **42** and **44**, quenches the dimerization pathway. In these cases, after the initial electrophilic cyanation step deprotonation of the N-atom takes place affording indolenines **43** and **45** (See the SI for the X-ray structure of **43**).



Scheme 3. a)Reaction of **9** with 3-methylindole **39**. Reagents, conditions and isolated yields: a) **9** (1.5 equiv.), Cs_2CO_3 (1.0 equiv.) 0°C, DCM, 2h, **40** (50%), **41** (30 %). Molecular structures of compounds **40** and **41** in the solid state. Anisotropic displacement shown at 30% probability level. Only selected hydrogen atoms are shown.[24] b) Reaction of **9** with **42** and **44**. Reagents, conditions and isolated yields: a) **9** (1.5 equiv.), CH_3CN, r.t., 15 min., **43** (76%), **44** (86 %).

In order to explore the generality and synthetic relevance of these cyanation reactions, we first decided to equip a series of indoles with an internal nucleophilic group and explore intramolecular cyanofunctionalizations. Hence, a series of N-protected tryptamine derivatives were initially subjected to the action of **9**. All substrates tested, regardless of the nature of the N-protecting group, smoothly delivered the corresponding tricyclic pyrroloindolines in good chemical yields **46**-**55** (Scheme 4). The length of the tether connecting the olefin and amino functionalities explains that only the diasteromer derived from the *anti*-cyanoamination is observed. The pyrroloindoline core is found in a number of alkaloids,[26] and has classically been synthesized by treatment of *N*-protected tryptophan esters with electrophilic reagents such as halonium, selenonium or even sulfonium ions.[27] Promotion of this kind of cyclization by electrophilic cyano moieties is to the best of our knowledge unprecedented, and renders cyano-pyrroloindolines of potential synthetic and/or pharmacological interest.

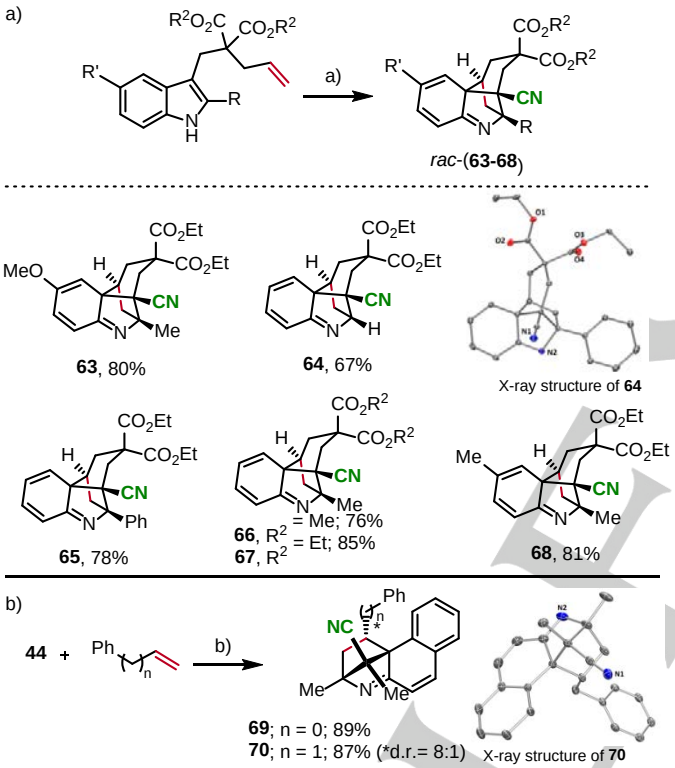
The superiority of **9** as $[CN]^+$ synthon when compared with **7** or **8** can be inferred from these cyanoaminations; under identical reaction conditions neither **7** nor **8** are capable to promote the cyanoamination of the simplest substrate of the series, N-tosyl tryptamine, to afford **46** (See the Supporting Information). Moreover, the scope of this reaction can be likewise extended to indole substrates tethered with O- or even C-nucleophiles. Exception made of compound **62**, where an additional chiral center is formed; in all other cases only one diasteromer is observed (Scheme 4).



Scheme 4. Reaction scope of the cyano-cyclisation of triptamine and triptophol derivatives. Reagents, conditions: a) **9** (1.5 equiv.), r.t., CH_3CN, 2h, unless otherwise stated. [a]CH_2Cl_2 was used as solvent. Molecular structures of compounds **47** and **59** in the solid state. Anisotropic displacement shown at 50% probability level. Only selected hydrogen atoms are shown.[24]

Finally, having established conditions for the effective cyanation of 2,3-disubstituted indoles towards cyano-substituted indolenines **43** and **45**, we evaluated the possible involvement of these substrates into a subsequent [4+2] Povarov-type cyclization. Such cascade process is not easy because it requires the consecutive dearomatization of both rings of the original indole; however, a couple single precedents found in the literature for cousin structures indicated that the transformation

might be possible.[28] Hence, allyl substituted indoles were prepared and submitted to reaction with **9.** To our delight, the desired products **63-68** containing a pentacyclic skeleton were smoothly delivered with excellent diasteroselectivities (Scheme 5a). Note that despite four consecutive chiral centres being formed, three of them on quaternary carbon atoms, only the diasteromer shown is formed. The slightly lower chemical yield obtained for **64** is explained by the concurrent direct cyanation at position 2- of the indole core. The depicted transformation also takes place intermolecularly; in that case, liberated from the constrains exerted by the malonate tether, the incoming olefin preferentially attacks the azadiene intermediate from its less sterically hindered face, that is the one occupied by the cyano substituent (Scheme 5b). This explains the reverse facial selectivity observed in **69** and **70**.



Scheme 5. Reaction scope of the electrophilic cyanation-Povarov cascade. Reagents, conditions: a) **9** (1.0-1.5 equiv.), r.t., CH_2Cl_2, 3-36h; b) **9** (1.5 equiv.), r.t., CH_2Cl_2, 11-36h. [a]Diasteromeric mixture (8:1 ratio); the second diasteromer only differs in the configuration of the carbon marked (*). Molecular structures of compounds **64** and **70** in the solid state. Anisotropic displacement shown at 50% probability level. Only selected hydrogen atoms are shown.[24]

In summary, in 5-(cyano)dibenzothiophenium triflate **9**, whose synthesis is described along this paper, the umpolung of the cyano moiety is so efficient that this moiety can not only be transferred to typical organic nucleophiles, but also is capable to promote electrophilic cyanocyclization cascades in appropriately designed substrates. The development of asymmetric versions of the reaction sequences herein described, and the applications of structurally related sulfonium salts in other chemical transformations are currently under investigation in our laboratory.

Experimental Section

Synthesis of 5-(cyano)dibenzothiophenium triflate (9): Tf_2O (25 mmol, 1 equiv, 4.205 mL) was added dropwise within 5 minutes to a solution of dibenzo[b,d]thiophene 5-oxide (1.00 equiv., 25 mmol, 5.007 g) in dry dichloromethane (350 mL) at -50°C. After stirring the resulting mixture for 1 hour, TMSCN (25 mmol, 1 equiv, 3.353 mL) was added dropwise and the mixture was further stirred at -50°C for 8 additional hours. Then, the cooling system was removed, and the formed suspension allowed reaching room temperature. Filtration of the solvents afforded **9** as a white/beige solid, which was further washed with dichloromethane (2 x 50 mL), and finally dried under vacuum (5.39 g.; 60%).

Acknowledgements

Support from the European Research Council (ERC CoG 771295), the Deutsche Forschungsgemeinschaft (INST 186/1237-1) and the University of Göttingen is gratefully acknowledged. We also thank B. Waldecker and F. Kraft for preliminary experimental contributions towards the synthesis of **9** and Dr. M. John for assistance with NMR analysis.

Conflict of interest

A patent regarding reagent **9** and its synthetic applications has been filed by the University of Göttingen (application number DE102018211606.7).

Keywords: electrophilic cyanation • transfer reagents • sulfonium salts • metal-free functionalizations • umpolung

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[25] Noteworthy, the nitrile formation takes place for these more challenging substrates without the necessity of activation of the cyanation reagent with a Lewis acid catalyst.

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10.1002/anie.201904557

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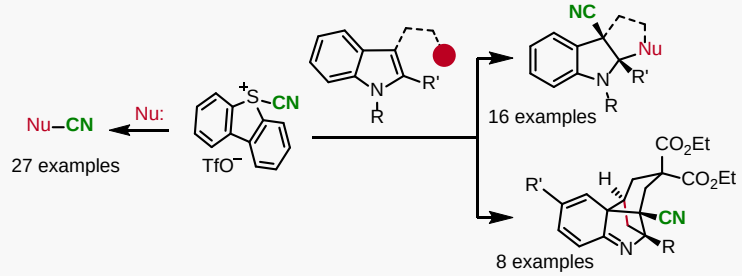

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5-(Cyano)dibenzothiophenium Triflate: A Sulfur–Based Reagent for Electrophilic Cyanation and Cyanocyclizations

Perfidious to its nature: The synthesis of 5-(cyano)dibenzothiophenium triflate is reported. In this compound the umpolung of the cyano moiety is so efficient that this group can not only be transferred to typical organic nucleophiles, but it is also capable to initiate cationic cyanocyclization cascades in appropriately designed substrates.