Synthesis and Reactivity of 5-Bromopenta-2,4-diynenitrile (BrC 5 N) an Access to π-Conjugated Scaffolds

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This article is dedicated to François Diederich on the occasion of his retirement.

Abstract

The synthesis of 5-bromopenta-2,4-diynenitrile (BrC_5N) in 3 steps from commercially available compounds is reported. Reacting 5-bromopenta-2,4-diynenitrile with secondary amines led to the formation of stable butadiynamines or enynenitriles, depending on the nature of the amine reactant. The reaction of 5-bromopenta-2,4-diynenitrile with simple terminal alkynes in the presence of secondary amines, copper and palladium catalysts, provided a straightforward access to original polyfunctional carbon-rich scaffolds. In this work, different alkynes and secondary amines were tested, which allowed for the preparation of a family of substituted dienes. Given the high synthetic potential of 5-bromopenta-2,4-diynenitrile, we also prepared iodinated counterparts of this compound, *i.e.* 5-iodopenta-2,4-diynenitrile and its lower homologue 3-iodopropiolonitrile. The UV-visible spectrum of some relevant compounds was also recorded.

Keywords

Alkynes, dienes, enynes, ynamines

Acknowledgements

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Author Contribution Statement

J.-C. G. and Y. T. designed the project. J.-C. G., Y. T., N. K., R. L. and E. S. G. discussed the results and wrote the paper. N. K., R. L. and E. S. G. performed the experiments and analyzed the data. L. T. performed the X-ray crystallographic analyses. J.-P. G. performed additional characterization by NMR analyses.

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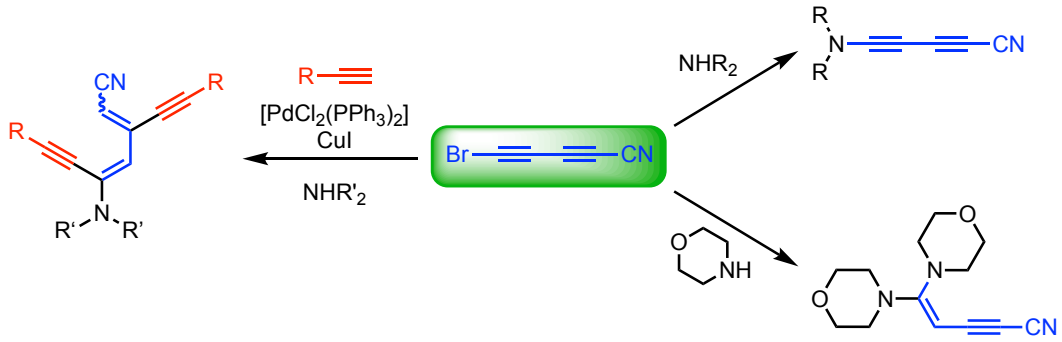
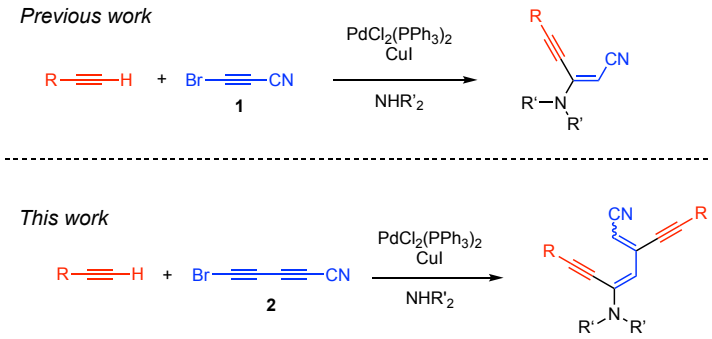


Hydrocarbon scaffolds:

The synthesis of 5-bromopenta-2,4-diynenitrile in 3 steps is reported. Its reaction with secondary amines led to the formation of stable butadiynamines or enynenitriles, depending on the nature of the amine. In Sonogashira conditions with terminal alkynes, a secondary amine, copper and palladium catalysts, this compound afforded original polyfunctional carbon-rich scaffolds. The UV-visible spectrum of some relevant compounds was also recorded.

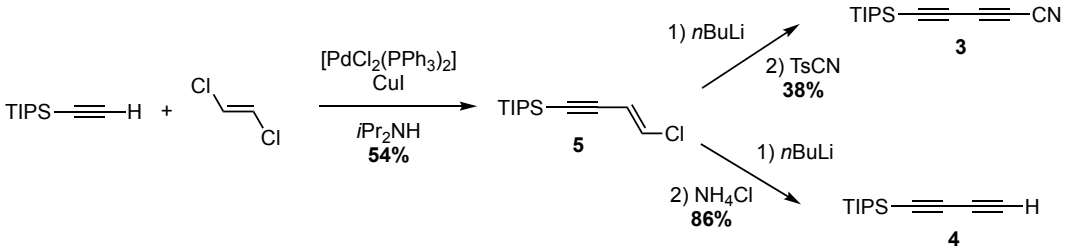
The reactivity of 1-halogenated alkynes is of particular interest in the field of organic synthesis.[1,2,3] The probably most popular reaction using such kind of species is the Cadiot-Chodkiewicz coupling consisting in a copper-catalyzed heterocoupling of alkynes.[4] C–N couplings may also be initiated in the presence of copper to form ynamides.[5] This property is essentially due to the ability of these compounds to undergo an oxidative addition with metals[6,7] and further react. This reactivity prompted us to evaluate the reactivity of bromopropynenitrile **1** (BrC_3N)[8] with terminal alkynes in the presence of CuI, [$PdCl_2(PPh_3)_2$] and a secondary amine in the context of space science (tentative synthesis of cyanobutadiynes[9,10]). Nevertheless, the targeted unsymmetrical diynes were not obtained but enynenitriles were isolated instead (scheme 1).[11] This peculiar reactivity relies on the presence of the secondary amine that most probably rapidly reacts with the electrophilic alkyne before the oxidative addition, deviating thus the usual synthetic reaction pathway. In a similar fashion, we have recently demonstrated that the 5-bromopenta-2,4-diynenitrile **2** (BrC_5N), which bears one more C≡C triple bond than BrC_3N, reacted in an original fashion with triisopropylsilylacetylene in the above-mentioned conditions.[12] As with BrC_3N, the unsymmetrical coupling product was not obtained. Instead, a conjugated dienynenitrile was isolated.

In the continuation of this work, we would now like to report on an alternative synthesis of BrC_5N and the further exploration of its reactivity with different alkynes and different amines in the same conditions. Its reactivity with secondary amines has also been investigated. The optical properties of the most relevant products are also reported in this paper.



Scheme 1. *Reactivity of BrC_3N* ***1*** *and BrC_5N* ***2*** *with alkynes, [$PdCl_2(PPh_3)_2$], CuI and a secondary amine.*

The synthesis of BrC_5N **2** has previously been described[12] following the brominative desilylation procedure of Kim and co-workers.[13] The synthesis of 5-(triisopropylsilyl)penta-2,4-diynenitrile **3** has already been achieved from the reaction of triisopropylsilylbutadiyne **4** (which was formed in two steps from commercially available compounds), *n*-butyllithium and tosyl cyanide. Alternatively, we developed a more straightforward synthetic way to compound **3**. Triisopropylsilylacetylene was reacted with (*E*)-1,2-dichloroethylene in the presence of CuI, $[PdCl_2(PPh_3)_2]$ and diisopropylamine to lead to enyne **5** in 54% yield, in a reaction fashion inspired by a precedent publication of the Negishi group.[14] The latter compound was subsequently reacted with *n*-butyllithium and tosyl cyanide to afford compound **3** in 38% yield. Only two steps are thus required and the synthesis was operated on the gram scale. This way also enabled the convenient synthesis of triisopropylsilylbutadiyne **4** by simply replacing tosyl cyanide by a saturated ammonium chloride solution (scheme 2).



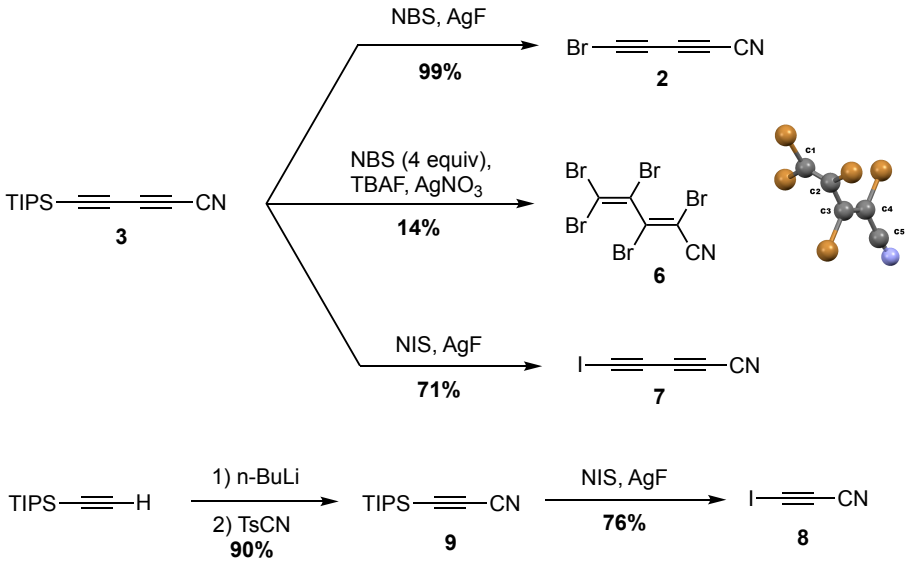
Scheme 2. Synthesis of 5-triisopropylsilylpenta-2,4-diynenitrile **3** and triisopropylsilylbutadiyne **4.**

Compound **3** was then reacted with *N*-bromosuccinimide (NBS) and AgF in acetonitrile in the dark, affording **2** in 99% yield after sublimation of the residue. Kim and co-workers also described different conditions in order to carry out the desilylative bromination.[13] When **3** was reacted with 4 equivalents of NBS, 1 equivalent of tetrabutylammonium fluoride (TBAF) and a catalytic amount of $AgNO_3$ in dimethylformamide (DMF), **2** was not obtained. Instead, (*E*)-2,3,4,5,5-pentabromopenta-2,4-dienenitrile **6** was isolated as the major product of the reaction in 14% yield. The unexpected formation of **6** arises, most likely, from the polybromination of **3**, in a similar manner as the reported bromination of 1,4-dibromobuta-1,3-diyne.[15]

By replacing NBS by *N*-iodosuccinimide (NIS) in the first conditions, the iodinated analogue 5-iodopenta-2,4-diynenitrile **7** was conveniently prepared and obtained in 71%

yield as a pale yellow solid, after purification by column chromatography over neutral alumina. The latter seems to be thermally more stable than **2**, which must be stored at –20°C to be preserved from degradation. In the case of **7**, no apparent decomposition could be observed after several days at room temperature. Given the easy synthesis of compound **7**, we also prepared the lower homologue, 3-iodopropiolonitrile **8**, following the same procedure. Thus, triisopropylsilylacetylene was reacted with *n*-butyllithium and tosyl cyanide to afford 3-(triisopropylsilyl)propiolonitrile **9** (90% yield), which was then subjected to a desilylative iodination in the presence of NIS and AgF. 3-Iodopropiolonitrile **8** was obtained in 76% yield. The synthesis of **8** has already been reported by Kloster-Jensen, but only in 60% yield and required first the preparation of cyanoacetylene in two extra steps (scheme 3).[16]

The structure of **6** could unambiguously be confirmed by single-crystal X-ray diffraction.[1] The most remarkable feature of this molecule is the dihedral angle of 92(1)° between the two double bonds of the butadiene moiety, which is probably due to the steric hindrance induced by bromine atoms. As a consequence, despite the presence of the nitrile group, π-electrons are mostly localized as evidenced by the carbon–carbon double bonds lengths which are close to the length of the double bond of ethylene (*ca* 1.34 Å): 1.31(1) Å for C1–C2 and 1.28(1) Å for C3–C4.[17] This observation means that the π-system is not delocalized, despite the presence of the nitrile group.



Scheme 3. Synthetic schemes of **2**, **6–9** and X-ray structure of compound **6**.

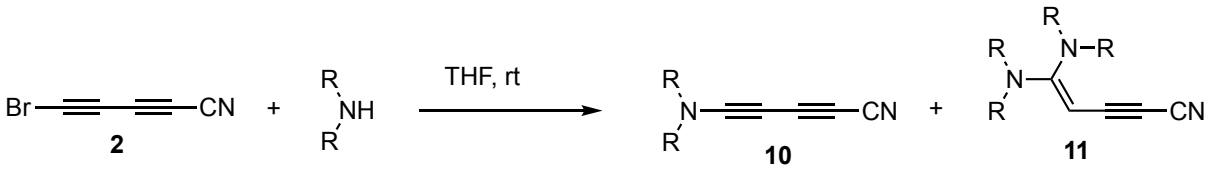
[1] CCDC-995341 (**6**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

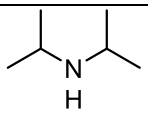
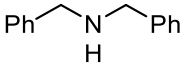
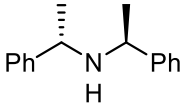
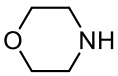
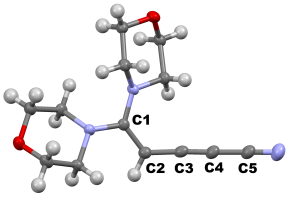
The formation of ynamines by reacting 1-bromobutadiynes and secondary amines has recently been described by Szafert and co-workers.[18] We also investigated the reactivity of BrC_5N with diverse secondary amines (3 equivalents) in THF at room temperature (Table 1). Even though this research group showed the sole formation of ynamines (even in the presence of an excess of amine), they had envisioned the potential formation of diamination products. When we performed the reaction, we have also taken this into account. When diisopropylamine was used, the corresponding ynamine **10a** was obtained in 90% yield (entry 1). Dibenzylamine and (−)-bis[(*S*)-1-phenylethyl]amine allowed for the formation of the corresponding ynamines **10b** and **10c** in 55 and 45% respectively (entries 2 and 3). The difference of yields obtained for **10b**,**c** compared to **10a** might be attributed to a less important steric hindrance of the amino groups, which, in the case of **10a**, contributes more importantly in stabilizing the ynamine and let it tolerate purification by chromatography. When **2** was reacted with morpholine, the expected ynamine **10d** was not obtained. Instead, the product of double addition **11d** was isolated in 48% yield (entry 4). Morpholine is probably less hindered than the other amines tested. Moreover, due to its rigid conformation, it is also more nucleophilic. These two reasons could explain the absence of formation of the related ynamine.

X-ray quality crystals were obtained for compound **11d**[2] that confirmed the structure determined on the basis of ^{1}H and ^{13}C NMR spectroscopy. The compound crystallized as a dimer in the unit cell (See Supporting Information, Figure SI-2), but only one molecule is represented in Table 1. The π-system of compound **11d** is mostly planar, and the two morpholine 6-membered rings adopt a chair conformation. Delocalization of electrons from the nitrogen atom of the morpholine moieties toward the cyano group can be evidenced by carbon–carbon bond lengths. The double bond length C1–C2 is 1.372(2) Å, which is slightly longer than a usual C=C double bond (*ca* 1.34 Å). Single bonds C2–C3 and C4–C5 are rather short, with bond lengths of 1.398(2) and 1.375(3) Å respectively, which can be compared to an average non-conjugated single bond length of 1.54 Å. Triple bond C3–C4 is less affected with a bond length of 1.205(2) Å, which is in agreement with the length of a usual C≡C triple bond (about 1.19 Å).

[2] CCDC-994731 (**11d**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table 1. Reactivity of BrC_5N (**2**) with secondary amines.[a]



Entry	R_2NH	**10** (yield in %)[b]	**11** (yield in %)[b]
1		**10a** (90)	**11b** (0)
2		**10b** (55)	**11b** (0)
3		**10c** (57)	**11c** (0)
4		**10d** (0)	**11d** (48) 

a) **2** (1 equiv.), amine (3 equiv.).
b) Isolated yields.

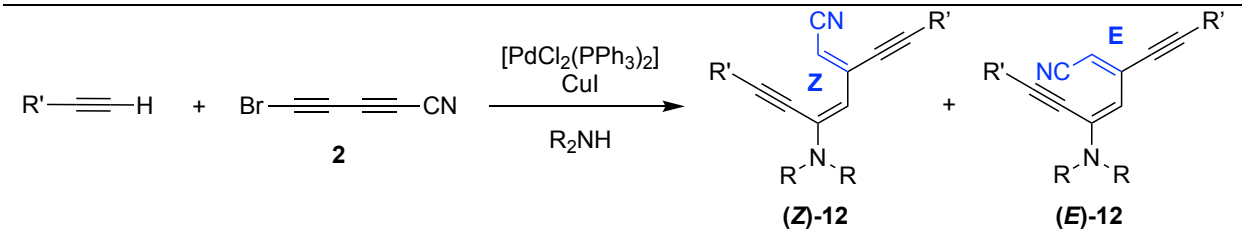
Since we recently showed that ynamides readily react with tetracyanoethylene (TCNE) to yield 1,1,4,4-tetracyanobutadienes (TCBDs),[19] compound **10a** was also mixed with 1 equivalent of TCNE. It resulted in the formation of many strongly colored products (according to TLC analysis) that we were not able to isolate. The same kind of results was observed when reacting compound **11d** with TCNE. It confirms that *N*-alkylynamines, contrary to *N*-arylynamines,[20,21] are not able to afford TCBDs by reaction with TCNE in these conditions.

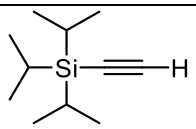
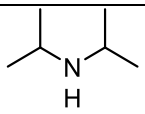
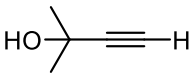
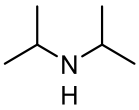
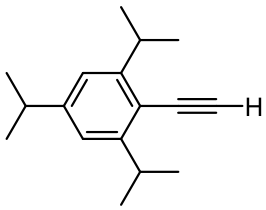
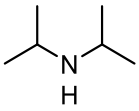
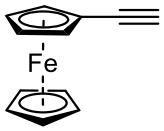
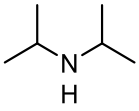
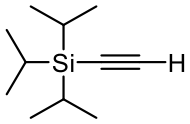
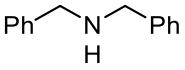
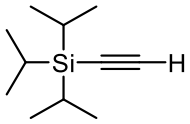
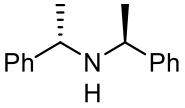
As explained in the introduction, we have recently described that BrC_5N did not react in Cadiot-Chodkiewicz coupling fashion with triisopropylsilylacetylene, palladium and copper co-catalysts in the presence of diisopropylamine. Instead, a diene was obtained, involving the reaction of the amine and two equivalents of triisopropylsilylacetylene.[12] Therefore, we wanted to investigate the scope of this multi-component reaction by using different terminal alkynes and different secondary amines. In each case, CuI and $[PdCl_2(PPh_3)_2]$ were used as co-catalysts in THF at room temperature (Table 2). When triisopropylsilylacetylene was used along with diisopropylamine, diene **12a** was obtained in 54% yield (entry 1). When using 2-

methylbut-3-yn-2-ol, a mixture of the *Z* and *E* isomers of compound **12b** was isolated in 36% yield (entry 2). The *Z*-isomer remained the major product with a *Z*/*E*-ratio of 77/23. The fact that *E* isomer could be formed in this case can be explained by the use of a less hindered alkyne than the previously described triisopropylsilylacetylene derivative **12a**. Therefore, the cyano group is able to find some room to point towards the other direction. Nevertheless, this steric hindrance is probably the origin of the selectivity in favor of the *Z* isomer. Similar results were obtained with 2-ethynyl-1,3,5-triisopropylbenzene and ferrocenylacetylene (entries 3 and 4). They led to the corresponding dienes **12c** and **12d** in 68 and 65 % yields respectively (*Z*/*E*-ratio: 86/14 and 74/26 respectively).

Other secondary amines were also tested, namely dibenzylamine and (-)-bis[(*S*)-1-phenylethyl]amine with triisopropylsilylacetylene (entries 5 and 6). Surprisingly, with dibenzylamine, no diene could be obtained, and with (-)-bis[(*S*)-1-phenylethyl]amine, the corresponding diene **12f** was obtained in only 8% yield. Diisopropylamine is, by far, the best amine that was used. Such a difference is hard to explain. One explanation could be found in the formation of the ynamine that we proved to be the first step of the mechanism. With diisopropylamine, we could isolate the ynamine in 90% yield as previously mentioned (table 1) whereas with (-)-bis[(*S*)-1-phenylethyl]amine and dibenzylamine, the yields are significantly lower. Therefore, the less efficient formation of the ynamine could explain finally the low formation of the corresponding diene.

Table 2. Syntheses of dienes **12** using different amines and different alkynes.[a]

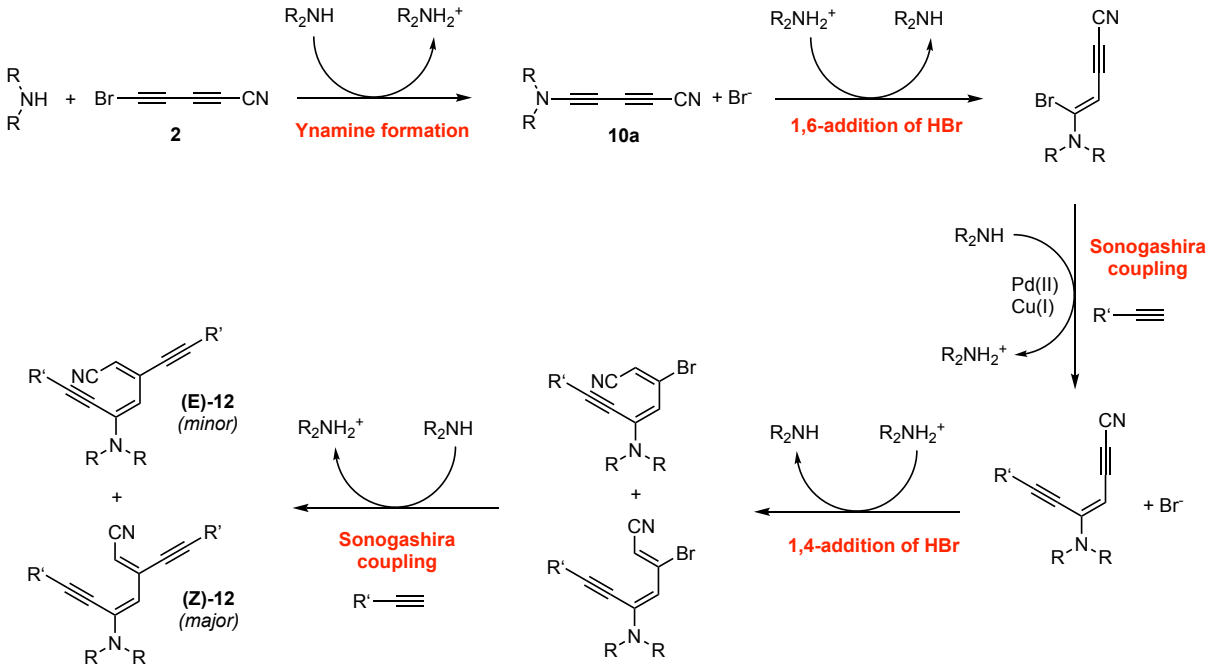


Entry	Alkyne	Amine	Yield of **12** (*Z*/E-ratio)
1			**12a**: 54% (100/0)
2			**12b**: 36% (77/23)
3			**12c**: 68% (86/14)
4			**12d**: 65% (74/26)
5			**12e**: 0%
6			**12f**: 8% (100/0)

a) **2** (1 equiv.), alkyne (2 equiv.), amine (5 equiv.), $[PdCl_2(PPh_3)_2]$ (10 mol%), CuI (10 mol%).

The first step being the formation of ynamine,[12] the fact that copper and palladium co-catalysts were necessary to the reaction let us think that Sonogashira couplings occurred. Moreover, we proved that the presence of halogenides (coming from BrC_5N for instance) was mandatory for the success of the reaction. Thus, we deduced that the mechanism was a combination of two Sonogashira couplings and two halogenide additions[22] after the ynamine was formed. In a previous paper, we showed that 1,6-addition on a similar structure (*i.e.* Me–C≡C–C≡C–CN) was largely favored over 1,4-addition in THF.[23] Therefore,

in this case, we also suggest that 1,6-addition of halogenide on the intermediate ynamine happens before the 1,4-addition. It could thus explain the selectivity observed in favor of **(*Z*)-12** versus **(*E*)-12**, as indicated in Scheme 4.



Scheme 4. Proposed mechanism for the formation of compound **12**.

The optical properties of compounds **10a**,**b**, **11d** and **12a** were investigated by means of UV/Vis absorption spectroscopy. All spectra were recorded in CH_2Cl_2 at 293 K. Absorption spectra of ynamines **10a** and **10b** are very similar (Figure 1). Their absorption spectra exhibit five absorption maxima between 250 and 350 nm with absorption coefficients ranging from 1.5 to 8.0 x 10^3 M^{-1} cm^{-1}. Their most intense transition lie at higher energy, with a maximum between 230 and 240 nm, and reach more than 6.0 x 10^4 M^{-1} cm^{-1}. No absorption could be observed in the visible region.

The absorption spectrum of **11d** is significantly different from **10a,b** and shows an intense absorption band at 334 nm (ε = 2.3 x 10^4 M^{-1} cm^{-1}) with a shoulder at about 317 nm (Figure 4). One less intense band is visible at 264 nm (ε = 6.8 x 10^3 M^{-1} cm^{-1}). Importantly, this compound significantly absorbs in the visible region up to 500 nm.

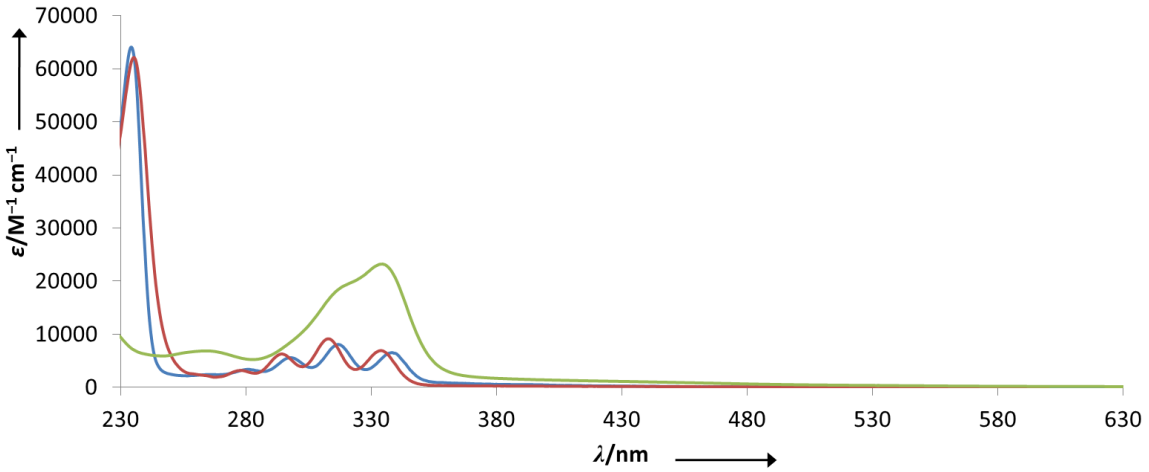


Figure 3. Absorption spectra of ynamines **10a** (blue line), **10b** (red line) and **11d** (green line) recorded in CH_2Cl_2.

The absorption spectrum of **12a** shows two bands with absorption maxima being reached at 266 nm (ε = 1.8 x 10^4 M^{-1} cm^{-1}) and 421 (ε = 1.3 x 10^4 M^{-1} cm^{-1}) (Figure 4, blue line). The latter is most probably a consequence of a charge transfer between the amino and the cyano groups. In order to evidence this push-pull character, which is responsible for a low-lying energy band in the visible region of the absorption spectrum, we added trifluoroacetic acid (TFA) to a solution of **12a** in CH_2Cl_2, protonating thus the amino group and preventing the delocalization of the lone pair of the nitrogen atom toward the cyano group. The most significant consequence of this protonation in the spectrum was the disappearance of the band of lowest energy, previously situated at 421 nm (Figure 4, red line). No absorption in the visible range could thus be observed anymore.

Addition of triethylamine (NEt_3) to the latter solution regenerated the initial absorption spectrum of **12a**, the only exception being the area higher in energy than 300 nm, due to the absorption caused by the excess of NEt_3 added (Figure 4, green line). These observations evidence the charge transfer occurring on compound **12a** and the reversibility of the protonation-deprotonation sequence. Indeed, this indicates that no degradation was observed upon addition of TFA in the experiment timescale, despite the extended π-system that could potentially have induced unexpected by-reactions intra- or intermolecularly.

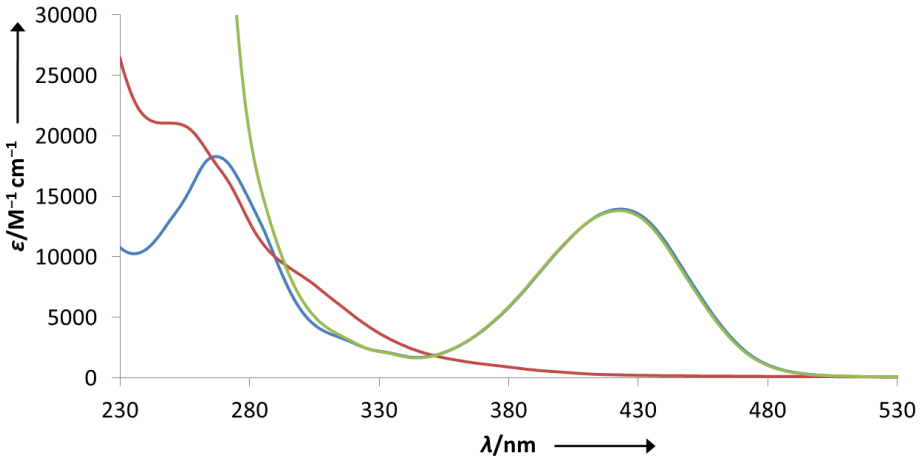


Figure 4. Absorption spectra of compound **12a** (blue line), compound **12a** and TFA (red line), diene **12a** plus TFA and NEt_3 (green line), recorded in CH_2Cl_2.

In conclusion, the reactivity of 5-bromopenta-2,4-diynenitrile (BrC_5N, **2**) was explored in different conditions and revealed its ability to form π-extended systems. In particular, a series of dienes was synthesized in variable yields, far from the Cadiot-Chodkiewicz products that were initially targeted. This unprecedented reactivity shows this molecule has a very high synthetic potential and paves the way to the synthesis of other original carbon-rich scaffolds. In the continuation of this work, we are now working on the synthesis of its ethynylogue 7-bromohepta-2,4,6-triynenitrile (BrC_7N) that promises to exhibit an exceptional synthetic potential if it reacts the same way as BrC_5N. It could also be used as a potential precursor of C_7N^- anion like BrC_5N served as a precursor of C_5N^- anion in the gas phase for interstellar simulations.[24]

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