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Use of stable amine-capped polyynes in the regioselective synthesis of push-pull thiophenes

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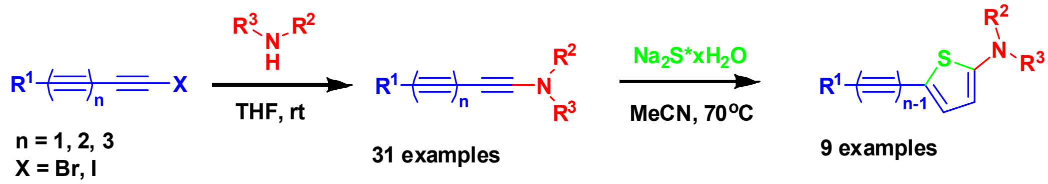


Abstract

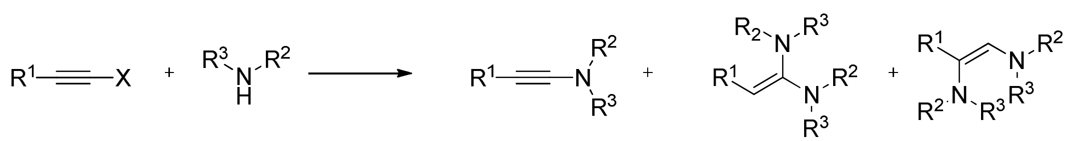
The reactions of a series of 1-halopolyynes with secondary amines led to novel amine end-capped polyynes exhibiting surprisingly high stability towards moisture. The new compounds were characterized by NMR spectroscopy, ESI-MS spectrometry, and x-ray single-crystal diffractometry. The use of amine end-capped polyynes as precursors to substituted push-pull thiophenes was next presented. The results show the first - to the best of our knowledge - transformation of ynamine to thiophene and the first regioselective transformation of a longer polyynes to butadiyne-substituted thiophene. Photophysical studies of the resulting compounds show that some of the substituted thiophenes have high quantum yield photoluminescence upon UV light irradiation.

Introduction

Polyynes and cumulenes have attracted an undiminished interest from the scientific community for more than half a century and a plethora of diverse compounds of this type have been synthesized to date.[1] These linear carbon rods are regarded as model compounds of hypothetical allotropic form of carbon – carbyne and they have significant application potential. Such molecules have been explored as molecular wires and switches in nanoelectronics,[2] as materials for optoelectronics (due to their nonlinear optical response),[3] or as precursors for conducting polymers.[4] Furthermore, polyynes exist in interstellar matter.[5]

Although ynamides are widely used as building blocks in organic synthesis,[6] ynamines remain much less explored due to problems with their handling and purification[6-7] owing to their high moisture sensitivity. In the literature, the hydrolytic instability of ynamines has even been described as follows: ‘it makes ynamine chemistry inaccessible’.[7c] However, *in situ* generated, they are useful tools in organic synthesis and are used for instance in amide,[8] thioamide,[9] and substituted naphthalene[10] syntheses.

Ynamines may be prepared *via* three general routes: elimination, substitution or isomerization.[7a] While the synthesis of ynamines *via* the reaction of 1-haloalkynes with secondary amines is known, the method has hardly been used and to date, the scope of the reaction has not been explored. A most probable reason for the low interest in this reaction was that it can give up to three types of unstable products: ynamines, 1,1-diaminoethenes, and 1,2-diaminoethenes (see Scheme 1) where the final structure of the main compound is strongly correlated with the electronic properties of an alkyne, steric bulkiness of an amine and, of course, reaction conditions.[7a,11]



Scheme 1. Possible products of a reaction of 1-haloalkynes with secondary amines.

Ynamines or ynamides containing $(C{\equiv}C)_2$ or a longer polyyne fragment directly bound to nitrogen are very rare. Some older works reporting the synthesis of butadiyne,[12] hexatriyne,[13] and octatetrayneamines[14] with the use of perchlorobutenyne precursors and *n*-butyllithium are known, but usually harsh reaction conditions were needed and characterization of the final products was very poor. Nevertheless, some butadiyne-substituted amines were tested in 1,*n*-topochemical polymerization[15] or were used for cyclization reactions.[16] Moreover, interesting push-pull ynamide polyynes with up to four acetylenic units are known.[17]

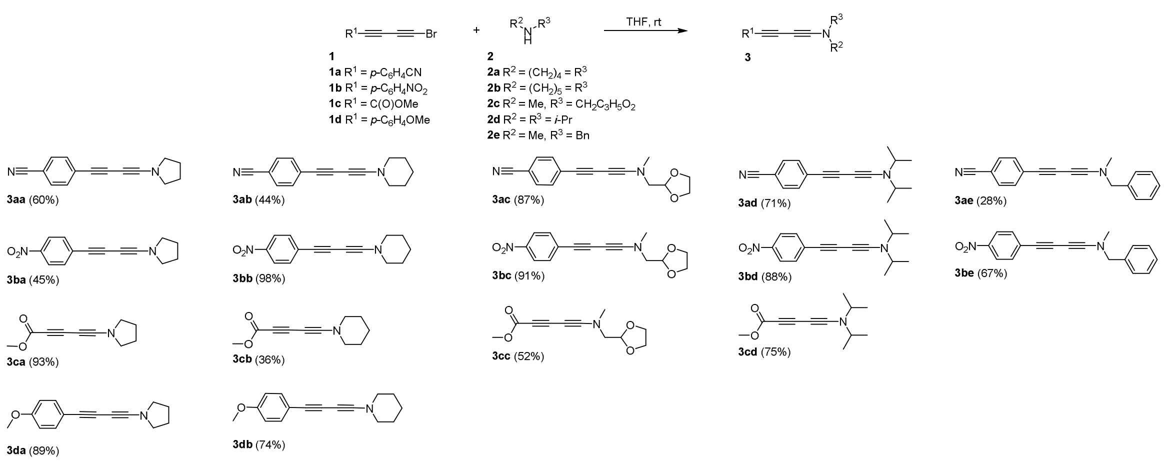
As reported above, the structures of products of a reaction between 1-halopolyynes and secondary amines were not obvious. Some of the older results suggested that 1-bromobutadiynes react with secondary amines giving products of multiple amination.[18] However, Guillemin and coworkers[19] accidentally synthesized a butadiynyl-substituted amine *via* a similar reaction and proved that products of a simple substitution are possible. Nevertheless, there is no detailed investigation on the reactivity of 1-halopolyynes with secondary amines and the ultimate goal of this work was to fill this gap.

Our recent research interests have focused on the synthesis and reactivity of 1-halopolyynes.[20] To date, we have explored their reactivity in the synthesis of organometallic polyynes[21] or in the mechanochemical synthesis of pyrrole end-capped polyynes.[22] Herein, we present a simple and versatile procedure that leads from 1-halopolyynes to the isolable and surprisingly stable amine end-capped polyynes. Moreover, the use of the resulting rod-like amines as substrates for regioselective synthesis of push-pull thiophenes is presented.

Results and Discussion

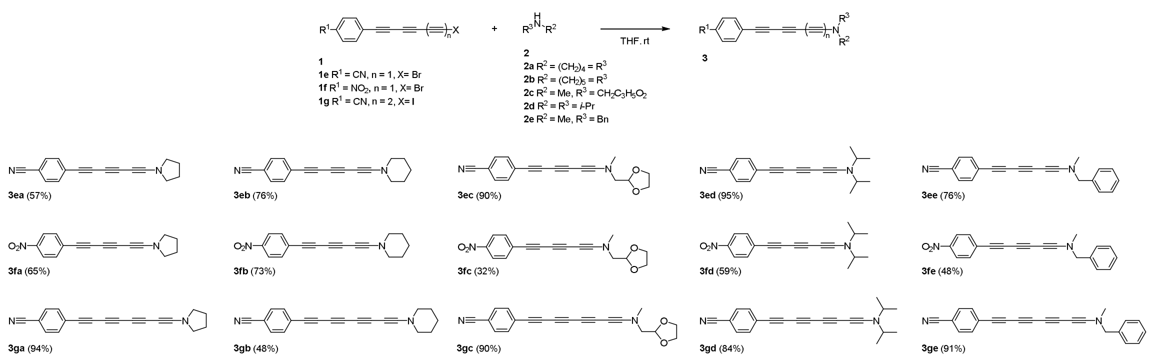
Synthesis of amine end-capped polyynes

Starting 1-halopolyynes were obtained according to the procedures previously developed in our group[21b,22a] with only 1-bromobutadiyne **1d** being newly synthesized (see the Supporting Information). Literature reports[23] and initial studies supported that the reaction of simple aryl 1-haloacetylenes with an excess of secondary amines gives diamination products. Therefore, we expected analogous products for 1-halopolyynes. Unexpectedly, test reactions of 1-bromobutadiynes **1a-b** and analogous iodides with pyrrolidine and piperidine gave only pure butadiynamines instead of diaminoenynes. As such, we performed reactions using a series of 1-halopolyynes with a variety of secondary amines. Firstly, we observed that the reaction times are shorter for bromides than iodides, therefore, for further reactions we used mostly bromides (if it was accessible). Secondly, we usually used THF as a solvent, but MeCN, CH_2Cl_2 and *n*-Bu_2O also gave analogous results. Thirdly, the reactions performed at elevated temperatures always gave the same ynamine product as those carried out at room temperature. Fourthly, an excess of amine did not affect the outcome of the reaction (we tested amounts from 2.0 to 8.0 equivalents with identical result). In conclusion, we did not find any conditions that gave products of multiple amination instead of ynamine. With the above in mind, we performed reactions for a series of 1-halopolyynes to obtain the relevant amine end-capped polyynes.



Scheme 2. Reaction of 1-bromobutadiynes with secondary amines.

In the first thrust, we performed the reactions for 1-bromobutadiynes (Scheme 2). We noticed that the reactions with electron withdrawing endgroups (**1a**-**c**) were faster than those for electron-rich anisole derivative (**1d**; see Experimental Section). Moreover, **1d** did not react with the less nucleophilic amines (**2c**-**e**) so the products were obtained only for pyrrolidine and piperidine. We tested a series of secondary amines in this transformation and it was clear that the reaction time strongly depended on nucleophilicity of an amine. The most nucleophilic ones (pyrrolidine **2a** and piperidine **2b**) gave products within minutes. Reactions for *N*-methylbenzylamine (**2e**) and 1-(1,3-dioxolan-2-yl)-*N*-methylmethaneamine (**2c**) were slower and usually took several hours, while reactions with diisopropylamine (**2d**) typically needed 24 h for completion. We also tested *N*-methylaniline and indoline, but no reaction was observed. For the working reactions the yields were from 28 to 98%, but in some cases the yields were further reduced by the purification process. Typically, products were dissolved in hexanes or a mixture of hexanes and CH_2Cl_2 and amine hydrobromide was filtered off, therefore, in case of low soluble products the yields might have been lowered.



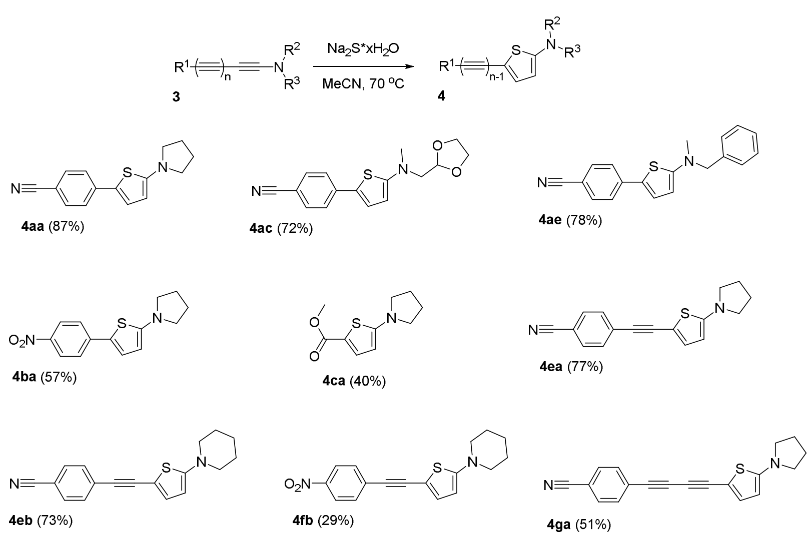
Scheme 3. Synthesis of amine end-capped hexatriynes and octatetraynes.

Next, the reaction of 1-bromohexatriynes and 1-iodooctatetraynes with a series of secondary amines was performed (Scheme 3). Since 1-bromooctatetraynes appeared not enough stable, so for longer chains we used more stable 1-iodooctatetraynes. Products were obtained with short reaction times (usually few hours), and only the reaction with less nucleophilic diisopropylamine was slightly slower. Yields obtained for hexatriynes (from 32 to 95%) and octatetraynes (from 48 to 90%) were acceptable.

In the literature ynamines are usually described as 'highly unstable' due to their moist-ure sensitivity but, ynamines with $(C{\equiv}C)_2$ or longer carbon chains appeared to be quite stable. This was tentatively attributed to the C-N carbon atom which is less electrophilic than in ana-logues with single triple bond because of a resonance effect of a polyyne system. The NMR spectra of the ynamines were measured in wet $CDCl_3$ and no decomposition was observed even after few days in solution. Compounds stored for few days in open vials however, showed new signals in the ^{1}H NMR spectra which originated from the corresponding amides. Only more electron rich **3da** and **3db** showed much faster decomposition in the presence of moisture and in these cases more careful handling was needed. In the literature ynamides are often mentioned as more convenient and easier to handle modification of ynamines. As such, the chemistry of ynamides is far richer than ynamines. Our results show that amine end-capped polyynes are far more stable than short chained N-ethynylamines and may play an important role as convenient building blocks in organic chemistry.

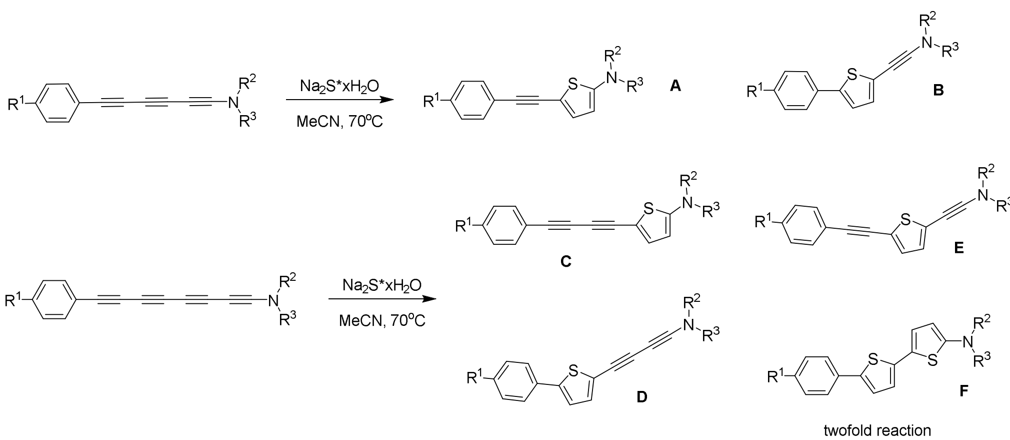
Synthesis of push-pull thiophenes

Next, we utilized the amine end-capped polyynes as substrates for the synthesis of functionalized thiophenes. Such a transformation for butadiynes is known,[24] but to the best our knowledge, the reaction for butadiynamine has no literature precedence. Moreover, in the known examples, the presence of a strong base is usually needed.



Scheme 4. Synthesis of substituted thiophenes.

We performed the reaction of nine amine end-capped polyynes with sodium sulfide in acetonitrile (no base added). Reactions at room temperature turned out to be very slow and were incomplete even after 24 h. The same reactions at 70 ^{o}C gave pure thiophenes already after few hours, proving that this simple procedure effectively produced push-pull 2-aminothiophenes (**4aa**, **4ac**, **4ae**, **4ba**, **4ca**) from the corresponding butadiynes under very mild conditions (see Scheme 4). Surprisingly, the reactions for hexatriynes (**3ea**, **3eb**, and **3fb**) were regioselective and the only observed products were 2-amino-5-(phenylethynyl)thiophene (**A** in Scheme 5) with no traces of 2-(aminoethynyl)-5-phenylthiophene (**B** in Scheme 5). When octatetrayne **3ga** was reacted with one equivalent of sodium sulfide the reaction was once again regioselective and the only product was **4ga** (**C** in Scheme 5) and no traces of **E**- and **D**-type products were observed. The structures of **4ea**, **4eb**, **4fb**, and **4ga** derivatives were confirmed with the use of HMQC and HMBC experiments. Yields were usually from moderate to good (29-87%).



Scheme 5. Possible products for the reaction of amine end-capped polyynes with Na_2S.

Interestingly, the reaction of **3ga** with excess sodium sulfide gave another product, which was probably the effect of its twofold reaction with Na_2S (**F** in Scheme 5). Carefully increasing an excess of Na_2S we observed diminishing amount of **4ga** and increasing amount of product with four doublets from two thiophene rings in ^{1}H NMR. However, the product decomposes very quickly in solution and in solid state, so it was impossible to record its clear ^{1}H and ^{13}C NMR spectrum. Moreover, decomposition of all the resulting thiophenes was observed during recording of the NMR spectra in $CDCl_3$, probably due to the presence of small amounts of HCl in a solvent. Thus, all the NMR spectra for the thiophenes were recorded in C_6D_6.

All the obtained thiophenes were stable in the solid state at room temperature for days but after longer exposure time we observed the decrease of doublets from thiophene moiety (J_{HH} = 4 Hz) in ^{1}H NMR spectra. Instead, new doublets with higher coupling constant (J_{HH} = 10 Hz) appeared. According to the literature, decomposition products are probably products of photo-oxidation.[25] So, all thiophenes were stored in refrigerator in the dark.

Substituted push-pull 2-aminothiophenes exhibit excellent properties for optoelectronic applications and play an important role in NLO (nonlinear optics) materials.[26] Compounds with 2-aminothiophene moiety exhibit also strong anti-AR (androgen receptor) potency,[27] are used as fluorescence biomarkers[28] or play an important role as fluorescent dyes.[25,29] For instance, DTM-2 and BAP-2 (Figure 1) are used for *in vivo* fluorescence imaging of β-amyloid (Aβ) plaques that is expected to be a new method for detecting Alzheimer's disease.[28b,28c] Substituted 2-amino-5-phenylethynylthiophenes or 2-amino-5-phenylthiophenes (G and H in Figure 1) have also an influence on A_1 adenosine receptor.[30] The approach presented so far to obtain these compounds was different from that shown in this work, so we believe, we have added a valuable contribution to the synthesis of such thiophenes with high application potential.

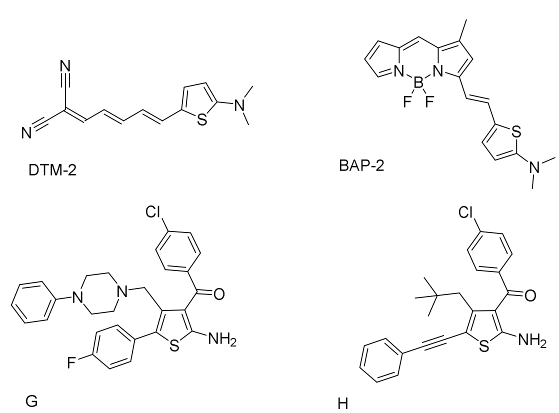


Figure 1. Examples of biologically active 2-aminothiophenes and fluorescent biomarkers with 2-aminothiophene moiety.

Recently, during the preparation of this manuscript, Witulski and coworkers published the first synthesis of 2-(tosylamido) and 2,5-bis(tosylamido)thiophenes from butadiyneamides and butadiyne-1,4-diamides under similar conditions.[31] Our work is the first synthesis of thiophenes from polyyneamines and may be considered as a complementary addition to Witulski's results and is the first synthesis of 2-amino-5-phenylthiophenes and 2-amino-5-phenylethynylthiophenes from butadiynes and hexatriynes. Reactions of polyynes higher than butadiynes with sodium sulfide are rare and usually mixtures of different products are obtained.[32]

Emission spectroscopy

Some of the presented thiophenes exhibit strong photoluminescence upon the UV irradiation, thus we recorded absorption and emission/excitation spectra for all the new thiophenes. Aryl-substituted thiophenes **4aa**, **4ac**, **4ae**, and **4ba** exhibited the strongest fluorescence in visible range, whereas for carbonyl **4ca**, ethynyl **4ea**, **4eb**, **4fb** and butadiynyl-substituted **4ga** compounds no emission was observed. Absorption and emission spectra of all samples were recorded in a variety of solvents (see the Supporting Information). Stokes shifts and emission quantum yields of the best emitting samples are summarized in Table 1. Emission and excitation spectra in Et_2O are shown in Figure 2 (for spectra in other solvents see the Supporting Information). Compounds **4aa**, **4ca**, and **4ea** exhibited very similar spectroscopic properties with nearly identical blue fluorescence. The highest value of QY was recorded for **4aa** (74%), but compounds **4ac** and **4ae** exhibited comparable values (67 and 69%, respectively). The presence of a nitro substituent instead of a nitrile (compound **4ba**) led to a lower QY (6%) and the maximum of the emission band shifted from 444 to 579 nm (orange emission). Moreover, **4ba** did not exhibit significant emission in CH_2Cl_2 and DMF. Nitro-group-containing fluorophores are known to have generally low photoluminescence quantum yield due to decrease in the radiative rate and the increase in the internal conversion rate of an exited state.[33]

Table 1. Emission parameters of substituted thiophenes. All spectra recorded in Et_2O.

	Em_{max} [nm]	Ex_{max} [nm]	Stokes shift [cm^{-1}]	Reference sample	QY [%]

4aa	444	397	2670	Quinine sulfate in 0.1 M H_2SO_4	74
4ac	443	393	2870	Quinine sulfate in 0.1 M H_2SO_4	67
4ae	442	391	2950	Quinine sulfate in 0.1 M H_2SO_4	69
4ba	579	453	4800	Rhodamine B in ethanol	6

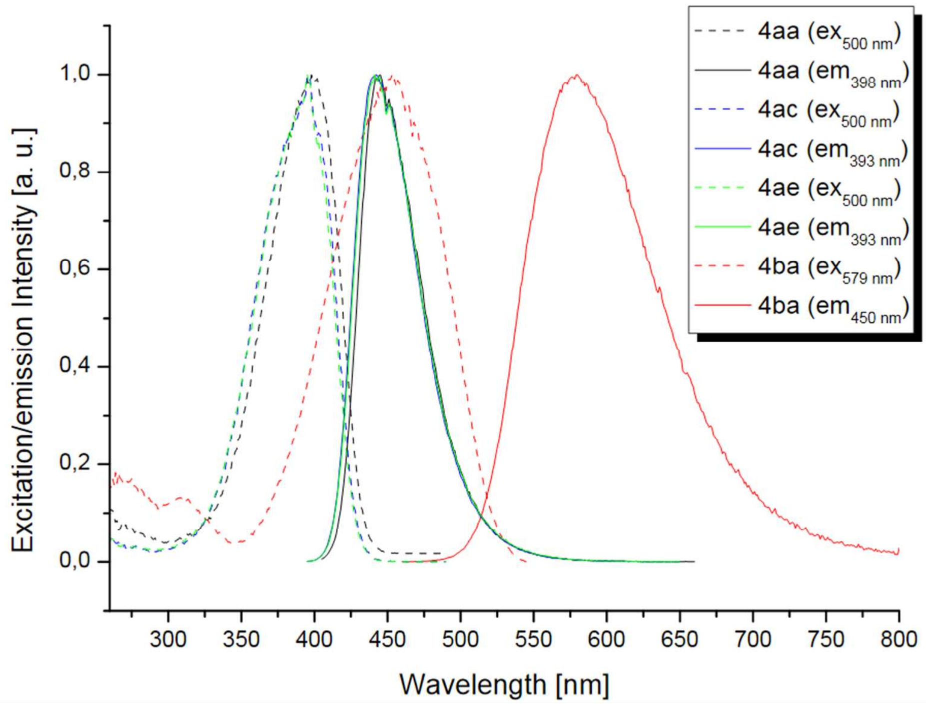


Figure 2. Emission and excitation spectra in Et_2O.

Compounds **4aa**, **4ac**, **4ae**, and **4ba** exhibited moderate solvatochromism and could be taken into consideration as solvent polarity probes. Stockes shifts for spectra recorded in solvents more polar than Et_2O were significantly higher (see the Table S1 in the Supporting Information). Correlation of absorption and emission maxima with solvents π* values[34] for compound **4aa** was examined (see Figures S5 and S6 in the Supporting Information). Correlation parameters were calculated using the equation:

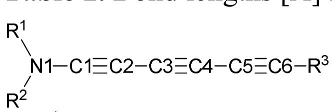
$$\nu_{\max} = \nu_0 + s\pi^*$$

where ν_{max} is the absorption/emission maximum, ν_0 shows the absorption/emission maximum of the compound in non-polar solvent (π*=0), s describes quantitatively the sensitivity of the dye to solvent polarity change. In case of compound **4aa** the value was -1200 cm^{-1}, which is rather low in comparison to the best known solvent polarity probes which are pyridinium betaines, which are about 8 times more sensitive to solvent polarity changes.[35] As the emission is much slower process than absorption, a larger solvatochromic shifts of emission bands are expected. Solvent sensitivity index *s* was much higher in case of emission spectra and its value was -2800 cm^{-1} for **4aa**. The thorough spectroscopic experiments including quantum yields measurements in different solvents, the synthesis of larger series of substituted thiophenes and the theoretical calculations are now under study and will be the topic of our next publication. Herein, we present preliminary data to indicate possible application of this group of compounds.

X-ray Crystallography

According to the literature, a few crystal structures of butadiynamines are known,[15,36] and the only crystal structure of nitrogen end-capped hexatriyne is the structure of hexatriynamide.[17] We obtained monocrystals of five ynamines appropriate for single crystal x-ray analysis. Monocrystals were obtained from the mixture of CH_2Cl_2 and hexanes. Compounds **3ad**, **3ac**, and **3fd** crystallize in monoclinic system, $P2_1/c$ space group, whereas **3ec** and **3fe** crystallize in triclinic system, *P*-1 space group (for further details on the structures see the Supporting Information). Molecular views of the two butadiynes **3ad** and **3ca** and three hexatriynes **3ec**, **3fd**, and **3fe** are presented in the Figure 3. The bond lengths in polyyne chains and the contraction coefficients are presented in the Table 2. All hexatriynes (**3ec**, **3fd**, **3fe**) possess nearly linear polyyne chains whereas butadiynes were slightly more distorted due to packing forces. The N1 nitrogen atom in all cases exhibited a typical flat sp^2 geometry and the N1-C1 bond length was from 1.311 Å (for **3ca**) to 1.322 Å (for **3ad**).

Table 2. Bond lengths [Å] in polyyne chains and contraction coefficients.



	N1-C1	C1-C2	C2-C3	C3-C4	C4-C5	C5-C6	C6-C7	C1-Cx^a	N1-Cx+1^b
3ad	1.322(3)	1.221(3)	1.362(3)	1.214(3)	1.420(3)	-	-	0.29%	0.35%
3ca	1.311(3)	1.216(3)	1.356(3)	1.217(3)	1.438(3)	-	-	0.05%	0.31%

3ec	1.319(2)	1.204(3)	1.364(3)	1.212(3)	1.371(3)	1.204(3)	1.432(3)	0.06%	0.08%
3fd	1.321(2)	1.217(2)	1.358(2)	1.217(2)	1.368(2)	1.208(2)	1.432(2)	0.02%	0.03%
3fe	1.321(3)	1.206(3)	1.360(3)	1.210(3)	1.370(3)	1.197(3)	1.436(3)	0.00%	0.03%

[a]Contraction C1-Cx = (C1-Cx sum of bond lengths − C1-Cx distance)/C1-Cx sum of bond lengths x 100%. [b]Contraction N1-Cx+1 = (N1-Cx+1 sum of bond lengths - N1-Cx+1 distance)/N1-Cx+1 sum of bond lengths x 100%.

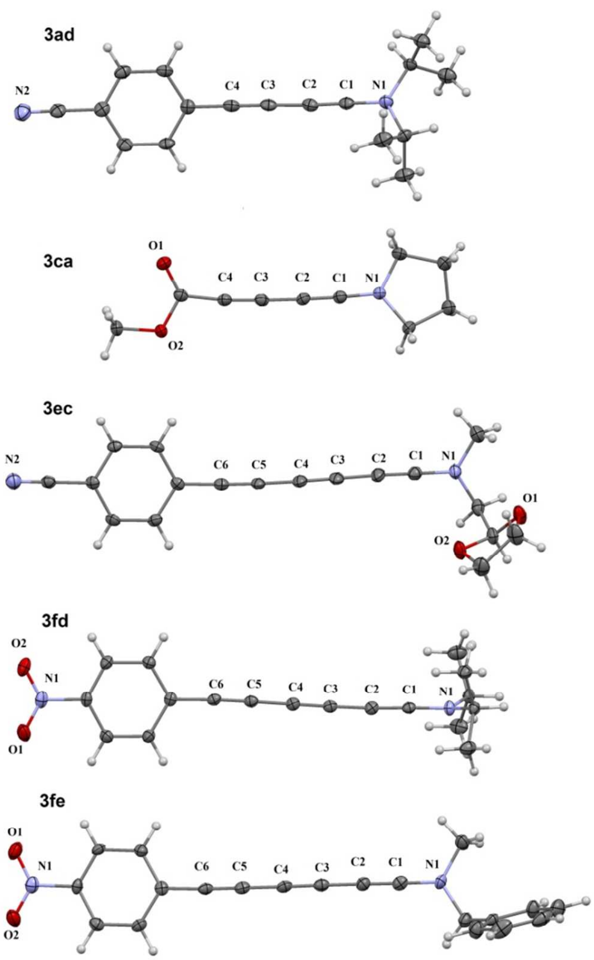


Figure 3. Molecular structures of amine end-capped polyynes. Thermal ellipsoids are drawn at 50% probability level.

Since aminobutadiynes and diaminobutadiynes are used in topochemical crystal-to-crystal polymerization,[15,36] we analyzed the packing motifs of the presented compounds in detail. The closest chain-chain separation was scrutinized for each structure, which was understood as the closest carbon–carbon distance from two neighboring polyyne carbon chains. We found two possible candidates for 1,*n*-topochemical polymerization: **3ca** and **3ec**. In the other cases, the carbon-carbon contacts were not short enough. In case of **3ad** and **3fd** bulky diisopropylamine group prevented from close chain-chain contacts.

The closest C-C contact in **3ca** (3.513 Å) was slightly above the sum of the van der Waals radii for two carbon atoms (3.4 Å), making it a promising candidate for topochemical polymerization (see Figure 4). The closest carbon-carbon contact in **3ec** was longer (3.965 Å) but still the polymerization could be possible.

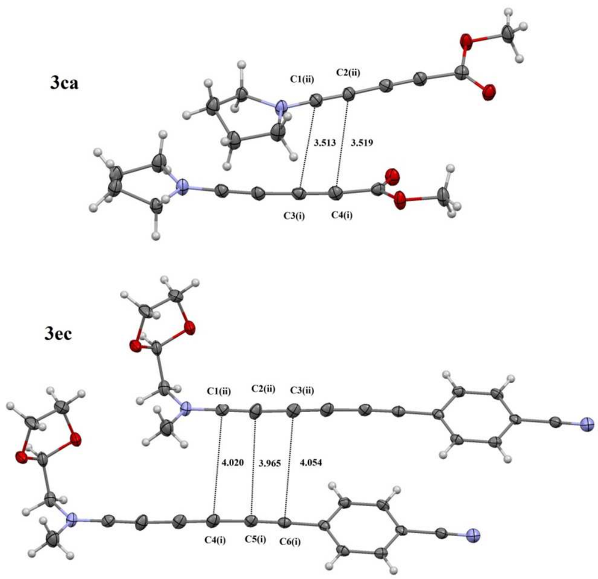


Figure 4. Packing motifs for **3ca** (top) and **3ec** (bottom). Distances in Å. Symmetry operations for related atoms are: **3ca** (i) = x, y, z; (ii) = x, 1.5-y, 0.5+z; **3ec** (i) = x, y, z; (ii) = -1 +x, y, z.

Moreover, an x-ray solid state structure of substituted thiophene **4aa** was obtained. Its molecular view is presented in the Figure 5. The whole molecule adopts a nearly planar geometry, except slightly distorted pyrrolidine moiety. The C1-N1 bond was short (1.351 Å) and the N1 nitrogen atom adopted a nearly planar sp^2 geometry which was similar to the known structures of 2-amine-5-arylthiophenes.[37]

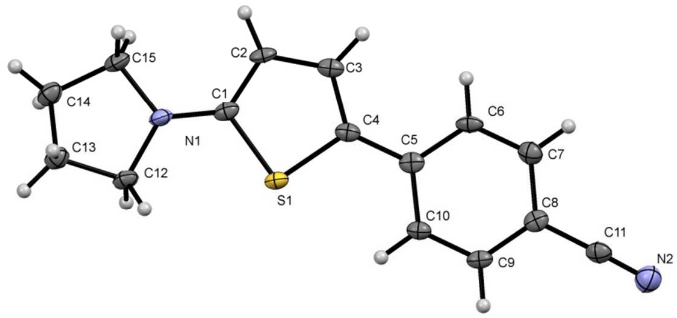


Figure 5. Molecular structure of **4aa**. Thermal ellipsoids are drawn at 50 % probability level. Selected bond lengths and angles: C1-N1 = 1.351(4) Å; C15-N1 = 1.465(4) Å; C12-N1 = 1.457(4) Å; C1-S1 = 1.746(3) Å; C4-S1 = 1.759(3) Å; C1-C2 = 1.379(5); C3-C4 = 1.371(4) Å; C2-C3 = 1.407(5) Å; C4-C5 = 1.448(4) Å; <(C1-N1-C15) = 121.9(3)˚; <(C1-N1-C12) =125.0(3)˚; <(C12-N1-C15) = 112.6(2)˚.

Conclusions

We showed that the reaction of 1-halopolyynes with secondary amines is a very convenient synthetic way to amine end-capped polyynes. The reaction gives products under very mild conditions and with good yields and selectivity. The resulting N-capped polyynes are far more stable towards moisture than short N-ethynylamines and may be regarded, similarly to the ynamides, as a convenient substrate in synthetic organic chemistry. Moreover, single x-ray diffraction structures for five amine end-capped polyynes were obtained and the structural analysis was presented. The reaction of amine end-capped polyynes with sodium sulfide yielded a series of novel, substituted push-pull thiophenes and, according to our knowledge, it is the first known direct transformation of ynamines to thiophenes. Moreover, the reaction of hexatriynes and octatetraynes with sodium sulfide is the first regioselective example of such transformation. Some of the obtained thiophenes exhibit strong fluorescence with high quantum yields and may be regarded as solvent polarity probes.

Experimental Section

General

All reactions were conducted under N_2 by using standard Schlenk techniques. Glassware was pre-dried at 120 °C. Solvents were treated as follows: hexane was distilled from Na, THF was distilled from Na/benzophenone, CH_2Cl_2 and CH_3CN were distilled from P_2O_5, Et_2O (pure for analysis) was used as received. 1-Halopolyynes and ((4-methoxyphenyl)buta-1,3-diyn-1-yl)trimethylsilane were obtained according to the known procedures.[21, 38] Pyrrolidine (98%), piperidine (puriss p.a.), diisopropylamine (99.5%), *N*-methylbenzylamine (97%), 2-methylaminomethyl-1,3-dioxolane (98%), $Pd(PPh_3)_2Cl_2$ (99 %), *N*-bromosuccinimide (99 %), sodium sulfide hydrate (≥60% of Na_2S), $AgNO_3$ (puriss p.a.), KF (puriss p.a.) were used as received.

^{1}H and ^{13}C NMR spectra were recorded with a 500 MHz spectrometer with an inverse broadband probe. For all the ^{1}H NMR spectra, the chemical shifts are given in ppm relative to the solvent residual peaks ($CDCl_3$, ^{1}H: 7.26 ppm, ^{13}C: 77.16 ppm; C_6D_6, ^{1}H: 7.16 ppm, ^{13}C: 128.06 ppm; $CD_3C(O)CD_3$, ^{1}H: 2.05 ppm, ^{13}C: 29.84 ppm). Coupling constants are given in Hz. HMBC and HMQC techniques were used for peak assignment. HRMS spectra were recorded using a spectrometer with a TOF mass analyzer and an ESI ion source. Fluorescence emission and excitation spectra were recorded using an spectrophotometer equipped with a 450 W Xe lamp. Absorption spectra were recorded on a one-beam spectrometer. Quantum yields were recorded using comparative method of Williams *et al.*[39] in accordance with the Jobin Yvon Horiba guide.[40] Quinine sulfate in 0.1 M H_2SO_4 and rhodamine B in ethanol were used as standard samples with quantum yields of 0.54 and 0.49 QY, respectively.[41]

Details of X-ray data collection and reduction

X-Ray diffraction data were collected with the use of ω scan technique. The space groups were determined from systematic absences and subsequent least-squares refinement. Lorentz and polarization corrections were applied. The structures were solved by direct methods and refined by full-matrix, least-squares on F^2 by use of the SHELXTL Package.[42] Non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atom positions were calculated and added to the structure factor calculations, but were not refined.

(1d) 1-(Bromobutadiynyl)-4-methoxybenzene

((4-Methoxyphenyl)butadiynyl)trimethylsilane (391 mg, 2.22 mmol) was dissolved in acetonitrile and next NBS (474 mg, 2.66 mmol), $AgNO_3$ (377 mg, 2.22 mmol), KF (129 mg, 2.22 mmol), and H_2O (75 μL, 4.4 mmol) were added. The flask was wrapped with aluminum foil and the mixture was stirred for 24 h at room temperature under N_2 atmosphere. Next, the solvent was evaporated, the solid dissolved in eluent and filtrated through the silica gel plug (eluent: hexanes/chloroform; v/v; 1:1). Solvent was evaporated under reduced pressure yielding yellow solid, yield: 28% (0.150 g, 0.638 mmol). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 – 7.43 (m, 2H, H_{Ar}), 6.85 – 6.82 (m, 2H, H_{Ar}), 3.82 (s, 3H, CH_3). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.9 (C_{Ar}O), 134.8 (C_{Ar}H), 114.5 (C_{Ar}C≡C), 113.3 (C_{Ar}H), 74.7 (*C*≡C), 73.5 (*C*≡C), 66.0 (*C*≡C) 55.7 (*C*H_3), 44.0 (*C*≡C). HRMS(ESI): *m/z* calcd for $C_{11}H_8BrO$: 234.9759 [M+H$^+$]; found: 234.9753.

Synthesis of amine end-capped polyynes

(3aa) 4-(Pyrrolidin-1-ylbutadiynyl)benzonitrile

4-(Bromobutadiynyl)benzonitrile (**1a**, 12 mg, 0.052 mmol) was dissolved in a dry and oxygen-free THF (10 mL) under N_2 atmosphere. Next, pyrrolidine (26 μL, 0.32 mmol) was added and the mixture was stirred for 1 h at room temperature. After this time the solvent was evaporated, product was dissolved in hexanes, filtrated with the use of the Schlenk technique and dried under reduced pressure. Product was obtained as a red solid, yield: 60% (6.9 mg, 0.031 mmol). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 – 7.53 (m, 2H, H_{Ar}), 7.46 – 7.42 (m, 2H, H_{Ar}), 3.38 – 3.34 (m, 4H, NCH_2), 1.90 – 1.87 (m, 4H, CH_2). ^{13}C{^{1}H}NMR (126 MHz, $CDCl_3$) δ 132.0 (*C*H_{Ar}), 131.8 (*C*H_{Ar}), 129.2 (*C*C≡N), 118.9 (*C*≡N), 110.4 (C_{Ar}C≡C), 91.1 (*C*≡C), 81.3 (*C*≡C), 79.2 (*C*≡C), 52.1 (*C*H_2N), 51.7 (*C*≡C), 25.9 (*C*H_2). HRMS(ESI): *m/z* calcd for $C_{15}H_{13}N_2$: 221.1073 [M+H$^+$]; found: 221.1072.

(3ab) 4-(Piperidin-1-ylbutadiynyl)benzonitrile

4-(Bromobutadiynyl)benzonitrile (**1a**, 10 mg, 0.043 mmol), piperidine (26 μL, 0.26 mmol), and THF (10 mL) were reacted according to the procedure for **3aa**. Reaction time: 1 h, orange solid, yield 44% (4.5 mg, 0.019 mmol). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 – 7.53 (m, 2H, H_{Ar}), 7.46 – 7.43 (m, 2H, H_{Ar}), 3.18 – 3.14 (m, 4H, NCH_2), 1.66 – 1.61 (m, 4H, CH_2), 1.57 – 1.53 (m, 2H, CH_2). ^{13}C{^{1}H}NMR (126 MHz, $CDCl_3$) δ 132.1 (*C*H_{Ar}), 131.9 (*C*H_{Ar}), 129.0 (*C*C≡N), 118.9 (*C*≡N), 110.6 (C_{Ar}C≡C), 92.4 (*C*≡C), 81.0 (*C*≡C), 78.8 (*C*≡C), 52.6 (*C*H_2N), 50.7 (*C*≡C), 25.1 (*C*H_2), 23.5 (*C*H_2). HRMS(ESI): *m/z* calcd for $C_{16}H_{15}N_2$: 235.1230 [M+H$^+$]; found: 235.1230.

(3ac) 4-((((1,3-Dioxolan-2-yl)methyl)(methyl)amino)butadiynyl)benzonitrile

4-(Bromorobutadiynyl)benzonitrile (**1a**, 12 mg, 0.052 mmol), 1-(1,3-dioxolan-2-yl)-*N*-methylmethanamine (17 μL, 0.15 mmol) and THF (10 mL) were reacted according to the procedure for **3aa**. Reaction time: 3 h, orange solid, yield: 87% (12 mg, 0.045 mmol). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 – 7.52 (m, 2H, H_{Ar}), 7.46 – 7.43 (m, 2H, H_{Ar}), 5.11 (t, *J* = 4.0 Hz, 1H, OCH_2O), 4.05 – 3.97 (m, 2H, OCH_2), 3.97 – 3.88 (m, 2H, OCH_2), 3.17 (d, *J* = 4.0 Hz, 2H, OC*H*O), 3.00 (s, 3H, CH_3). ^{13}C{^{1}H}NMR (126 MHz, $CDCl_3$) δ 132.1 (CH_{Ar}), 131.9 (CH_{Ar}), 129.0 (*C*C≡N), 118.9 (*C*≡N), 110.6 (C_{Ar}C≡C), 102.6 (O*C*HO), 92.2 (*C*≡C), 81.0 (*C*≡C), 79.0 (*C*≡C), 65.4 (OCH_2), 57.5 (NCH_2), 50.6 (*C*≡C), 42.5 (CH_3). HRMS(ESI): *m/z* calcd for $C_{16}H_{15}N_2O_2$: 267.1128 [M+H$^+$]; found: 267.1123.

(3ad) 4-((Diisopropylamino)butadiynyl)benzonitrile

1-(Bromobutadiynyl)-4-nitrobenzene (**1a**, 18 mg, 0.078 mmol), *N,N*-diisopropylamine (66 μL, 0.47 mmol) and THF (10 mL) were reacted according to the procedure for **3aa**. Reaction time: 24 h, orange solid, yield: 71% (13.8 mg, 0.055 mmol). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 – 7.52 (m, 2H, H_{Ar}), 7.46 – 7.44 (m, 2H, H_{Ar}), 3.19 (hept, *J* = 6.6 Hz, 2H, C*H*), 1.24 (d, *J* = 6.6 Hz, 12H, CH_3). ^{13}C{^{1}H}NMR (126 MHz, $CDCl_3$) δ 132.0 (CH_{Ar}), 131.7 (CH_{Ar}), 129.4 (*C*C≡N), 119.0 (*C*≡N), 110.1 (C_{Ar}C≡C), 88.3 (*C*≡C), 82.1 (*C*≡C), 79.0 (*C*≡C), 57.2 (*C*≡C), 53.0 (N*C*H), 21.7 (CH_3). HRMS(ESI): *m/z* calcd for $C_{17}H_{19}N_2$: 251.1543 [M+H$^+$]; found: 251.1539.

(3ae) 4-((Benzyl(methyl)amino)butadiynyl)benzonitrile

4-(Bromobutadiynyl)benzonitrile (**1a**, 7.4 mg, 0.032 mmol), *N*-methylbenzylamine (13 μL, 0.096 mmol) and THF 10 mL) were reacted according to the procedure for **3aa**. Reaction time: 1 h, orange solid, yield: 28% (2.4 mg, 0.0089 mmol). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 – 7.53 (m, 2H, $H_{benzonitrile}$), 7.47 – 7.44 (m, 2H, $H_{benzonitrile}$), 7.41 – 7.36 (m, 2H, H_{Ph}), 7.36 – 7.32 (m, 3H, H_{Ph}), 4.19 (s, 2H, CH_3), 2.82 (s, 3H, CH_3). ^{13}C{^{1}H}NMR (126 MHz, $CDCl_3$) δ 135.8 (C_{Ph}), 132.1 ($CH_{benzonitrile}$), 131.9 ($CH_{benzonitrile}$), 129.0 (*C*C≡N), 128.9 (CH_{Ph}), 128.4 (CH_{Ph}), 128.3 (CH_{Ph}), 118.9 (*C*≡N), 110.6 (C_{Ar}C≡C), 92.7 (*C*≡C), 80.9 (*C*≡C), 79.1 (*C*≡C), 59.6 (*C*≡C), 51.2 (s), 40.3 (*C*≡C). HRMS(ESI): *m/z* calcd for $C_{19}H_{15}N_2$: 271.1229 [M+H$^+$]; found: 271.1225.

(3ba) 1-((4-Nitrophenyl)butadiynyl)pyrrolidine

1-(Bromobutadiynyl)-4-nitrobenzene (**1b**, 16 mg, 0.064 mmol), pyrrolidine (27 µL, 0.33 mmol) and THF (10 mL) were reacted according to the procedure for **3aa**. Reaction time: 24 h, red solid, yield 45% (7.0 mg, 0.029 mmol). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.16 – 8.12 (m, 2H, CH_{Ar}), 7.52 – 7.45 (m, 2H, CH_{Ar}), 3.40 – 3.36 (m, 4H, NCH_2), 1.92 – 1.87 (m, 4H, CH_2). ^{13}C{^{1}H}NMR (126 MHz, $CDCl_3$) δ 146.2 (*C*NO_2), 131.8 (C_{Ar}H), 131.4 (C_{Ar}C≡C), 123.8 (C_{Ar}H), 92.0 (*C*≡C), 82.7 (*C*≡C), 79.4 (*C*≡C), 52.2 (NCH_2), 52.1 (*C*≡C), 26.0 (CH_2). HRMS(ESI): *m/z* calcd for $C_{14}H_{13}N_2O_2$: 241.0971 [M+H$^+$]; found: 241.0973.

(3bb) 1-((4-Nitrophenyl)butadiynyl)piperidine

1-(Bromobutadiynyl)-4-nitrobenzene (**1b**, 12 mg, 0.048 mmol), piperidine (29 µL, 0.26 mmol) and THF (10 mL) were reacted according to the procedure for **3aa**. Reaction time: 18 h, orange solid, yield 98% (12 mg, 0.047 mmol). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.16 – 8.12 (m, 2H, CH_{Ar}), 7.51 – 7.48 (m, 2H, CH_{Ar}), 3.20 – 3.15 (m, 4H, NCH_2), 1.67 – 1.61 (m, 4H, CH_2), 1.59 – 1.51 (m, 2H, CH_2). ^{13}C{^{1}H}NMR (126 MHz, $CDCl_3$) δ 146.3 (*C*NO_2), 131.9 (*C*H_A), 131.2 (C_{Ar}C≡C), 123.8 (*C*H_A), 93.2 (*C*≡C), 82.3 (*C*≡C), 79.1 (*C*≡C), 52.6 (NCH_2), 51.1 (*C*≡C), 25.1 (*C*H_2), 23.5 (*C*H_2). HRMS(ESI): *m/z* calcd for $C_{15}H_{15}N_2O_2$: 255.1128 [M+H$^+$]; found: 255.1124.

(3bc) *N*-((1,3-dioxolan-2-yl)methyl)-*N*-methyl-4-(4-nitrophenyl)butadiynamine

1-(Bromobutadiynyl)-4-nitrobenzene (**1b**, 8.0 mg, 0.032 mmol), 1-(1,3-dioxolan-2-yl)-*N*-methylmethanamine (22 µL, 0.19 mmol) and THF (10 mL) were reacted according to the procedure for **3aa**. Reaction time: 2 h, yellow solid, yield 91% (8.1 mg, 0.029 mmol). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.15 – 8.11 (m, 2H, CH_{Ar}), 7.51 – 7.47 (m, 2H, CH_{Ar}), 5.11 (t, J = 4.0 Hz, 1H, OC*H*O), 4.04 – 4.01 (m, 2H, OCH_2), 3.93 – 3.90 (m, 2H, OCH_2), 3.18 (d, J = 4.0 Hz, 2H, NCH_2), 3.01 (s, 3H, CH_3). ^{13}C{^{1}H}NMR (126 MHz, $CDCl_3$) δ 146.4 (*C*NO_2), 131.9 (*C*H_{Ar}), 131.1 (C_{Ar}C≡C), 123.7 (*C*H_{Ar}), 102.5 (O*C*HO), 93.0 (*C*≡C), 82.3 (*C*≡C), 79.2 (*C*≡C), 65.4 (O*C*H_2), 57.5 (NCH_2), 50.9 (*C*≡C), 42.6 (*C*H_3). HRMS(ESI): *m/z* calcd for $C_{15}H_{15}N_2O_4$: 287.1026 [M+H$^+$]; found: 287.1024.

(3bd) *N*,*N*-diisopropyl-4-(4-nitrophenyl)butadiynamine

1-(Bromobutadiynyl)-4-nitrobenzene (**1b**, 10 mg, 0.040 mmol), diisopropylamine (17 μL, 0.12 mmol) and THF (10 mL) were reacted according to the procedure for **3aa**. Reaction time: 24 h, yellow solid, yield 88% (9.8 mg, 0.035 mmol). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.16 – 8.10 (m, 2H), 7.51 – 7.48 (m, 2H), 3.21 (hept, *J* = 6.6 Hz, 2H), 1.25 (d, *J* = 6.6 Hz, 12H). ^{13}C{^{1}H}NMR (126 MHz, $CDCl_3$) δ 146.0 (*C*NO_2), 131.7 (*C*H_{Ar}), 131.6 (C_{Ar}C≡C), 123.7 (*C*H_{Ar}), 89.2 (*C*≡C), 83.5 (*C*≡C), 79.4 (*C*≡C), 57.6 (*C*≡C), 53.1 (*C*H), 21.7 (*C*H_3). HRMS(ESI): *m/z* calcd for $C_{16}H_{19}N_2O_2$: 271.1441 [M+H$^+$]; found: 271.1442.

(3be) *N*-benzyl-*N*-methyl-4-(4-nitrophenyl)butadiynamine

1-(Bromobutadiynyl)-4-nitrobenzene (**1b**, 12 mg, 0.048 mmol), *N*-methylbenzylamine (19 μL, 0.14 mmol) and THF (10 mL) were reacted according to the procedure for **3aa**. Reaction time: 4 h, yellow solid, yield 67% (9.3 mg, 0.032 mmol). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.16 – 8.12 (m, 2H, $C_6H_4NO_2$), 7.52 – 7.49 (m, 2H, $C_6H_4NO_2$), 7.41 – 7.37 (m, 2H, C_6H_5), 7.36 – 7.32 (m, 3H, C_6H_5), 4.20 (s, 2H, C*H_2*), 2.83 (s, 3H, C*H_3*). ^{13}C{^{1}H}NMR (126 MHz, $CDCl_3$) δ 146.3 (*C*NO_2), 135.6 (C_{Ph}), 131.8 (*C*$H_{nitrobenzene}$), 131.0 ($C_{nitrobenzene}$), 128.8 (*C*H_{Ph}), 128.2 (two overlapped signals, *C*H_{Ph}), 123.6 (*C*$H_{nitrobenzene}$), 93.4 (*C*≡C), 82.1 (*C*≡C), 79.2 (*C*≡C), 59.5 (*C*H_2), 51.4 (*C*≡C), 40.1 (*C*H_3). HRMS(ESI): *m/z* calcd for $C_{18}H_{14}N_2O_2Na$: 313.0947 [M+Na$^+$]; found: 313.0950.

(3ca) Methyl 5-(pyrrolidin-1-yl)penta-2,4-diynoate

Methyl 5-bromopenta-2,4-diynoate (**1c**, 27 mg, 0.14 mmol), pyrrolidine (36 μL, 0.42 mmol) and THF (10 mL) were reacted according to the procedure for **3aa**. Reaction time: 1 h, yellow solid, yield 93% (23 mg, 0.13 mmol). ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.75 (s, 3H, C*H_3*), 3.40 – 3.36 (m, 4H, NC*H_2*), 1.90 – 1.85 (m, 4H, C*H_2*). ^{13}C{^{1}H}NMR (126 MHz, $CDCl_3$) δ 154.8 (*C*=O), 92.5 (*C*≡C), 77.7 (*C*≡C), 75.0 (*C*≡C), 54.0 (*C*≡C), 52.5 (*C*H_3), 52.0 (N*C*H_2), 25.9 (*C*H_2). HRMS(ESI): *m/z* calcd for $C_{10}H_{12}NO_2$: 178.0863 [M+H$^+$]; found: 178.0867.

(3cb) Methyl 5-(piperidin-1-yl)penta-2,4-diynoate

Methyl 5-bromopenta-2,4-diynoate (**1c**, 27 mg, 0.144 mmol), piperidine (25 μL, 0.26 mmol) and THF (10 mL) were reacted according to the procedure for **3aa**. Reaction time: 1 h, yellow solid, yield 36% (10 mg, 0.052 mmol). ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.75 (s, 3H, C*H_3*), 3.21 – 3.14 (m, 4H, NC*H_2*), 1.66 – 1.60 (m, 4H, C*H_2*), 1.51 – 1.57 (m, 2H, C*H_2*). ^{13}C{^{1}H}NMR

(126 MHz, $CDCl_3$) δ 154.8 (*C*=O), 93.7 (*C*≡C), 77.4 (*C*≡C), 74.8 (*C*≡C), 52.9 (*C*≡C), 52.5 (*C*H_3), 52.3 (N*C*H_2), 25.1 (*C*H_2), 23.3 (*C*H_2). HRMS(ESI): *m/z* calcd for $C_{11}H_{14}NO_2$: 192.1019 [M+H$^+$]; found: 192.1023.

(3cc) Methyl 5-(((1,3-dioxolan-2-yl)methyl)(methyl)amino)penta-2,4-diynoate

Methyl 5-bromopenta-2,4-diynoate (**1c**, 16 mg, 0.086 mmol), 1-(1,3-dioxolan-2-yl)-*N*-methylmethanamine (29 μL, 0.25 mmol) and THF (5 mL) were reacted according to the procedure for **3aa**. Reaction time: 1 h, yellow solid, yield: 53% (10 mg, 0.045 mmol). ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.08 (t, *J* = 3.9 Hz, 1H, OC*H_2*O), 4.01 – 3.99 (m, 2H, OC*H_2*), 3.92 – 3.89 (m, 2H, OC*H_2*), 3.75 (s, 3H, C*H_3*), 3.16 (d, *J* = 3.9 Hz, 2H, OC*H*O), 3.00 (s, 3H, C*H_3*). ^{13}C{^{1}H}NMR (126 MHz, $CDCl_3$) δ 154.7 (*C*=O), 102.3 (O*C*HO), 93.6 (*C*≡C), 77.1 (*C*≡C), 74.6 (*C*≡C), 65.4 (O*C*H_2), 57.2 (N*C*H_2), 52.5 (O*C*H_3), 52.4 (*C*≡C), 42.4 (*C*H_3). HRMS(ESI): *m/z* calcd for $C_{11}H_{14}NO_4$: 224.0917 [M+H$^+$]; found: 224.0915.

(3cd) Methyl 5-(diisopropylamino)penta-2,4-diynoate

Methyl 5-bromopenta-2,4-diynoate (**1c**, 9.9 mg, 0.052 mmol), *N,N*-diisopropylamine (23 μL, 0.15 mmol) and THF (5 mL) were reacted according to the procedure for **3aa**. Reaction time: 2.5 h, yellow solid, yield: 75% (8.2 mg, 0.39 mmol). ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.76 (s, 3H, C*H_3*), 3.19 (hept, *J* = 13.1, 6.6 Hz, 2H, C*H*), 1.22 (d, *J* = 6.5 Hz, 12H, C*H_3*). ^{13}C{^{1}H}NMR (126 MHz, $CDCl_3$) δ 155.0 (*C*=O), 90.4 (*C*≡C), 78.8 (*C*≡C), 75.3 (*C*≡C), 59.7 (*C*≡C), 53.3 (O*C*H_3), 52.4 (N*C*H), 21.6 (*C*H_3). HRMS(ESI): *m/z* calcd for $C_{12}H_{17}NO_2Na$: 230.1151 [M+Na$^+$]; found: 230.1149.

(3da) 1-((4-Methoxyphenyl)butadiynyl)pyrrolidine

1-(Bromobutadiynyl)-4-methoxybenzene (**1d**, 9.6 mg, 0.041 mmol), pyrrolidine (10 μL, 0.12 mmol) and THF (10 mL) were reacted according to the procedure for **3aa**. Reaction time: 4 h, yellow solid, yield: 89% (8.9 mg, 0.037 mmol). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 – 7.36 (m, 2H, H_{Ar}), 6.81 – 6.80 (m, 2H, H_{Ar}), 3.79 (s, 3H, C*H_3*), 3.32 (t, *J* = 6.8 Hz, 4H, NC*H_2*), 1.88 – 1.82 (m, 4H, C*H_2*). ^{13}C{^{1}H}NMR (126 MHz, $CDCl_3$) δ 159.5 (OC_{Ar}), 133.7 (*C*H_{Ar}), 115.9 (C_{Ar}C≡C), 114.1 (*C*H_{Ar}), 87.5 (*C*≡C), 79.7 (*C*≡C), 74.3 (*C*≡C), 55.4 (O*C*H_3), 52.2 (N*C*H_2), 50.7 (C≡C), 25.9 (*C*H_2). HRMS(ESI): *m/z* calcd for $C_{15}H_{17}NNaO_2$: 266.1151 [M+H_2O+Na$^+$]; found: 266.1163.

(3db) 1-((4-Methoxyphenyl)butadiynyl)piperidine

1-(Bromobutadiynyl)-4-methoxybenzene (**1d**, 12 mg, 0.051 mmol), piperydine (15 μL, 0.15 mmol) and THF (5 mL) were reacted according to the procedure for **3aa.** Reaction time: 4 h, yellow solid, yield: 74% (9.1 mg, 0.038 mmol). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 – 7.37 (m, 2H, H_{Ar}), 6.81 – 6.80 (m, 2H, H_{Ar}), 3.80 (s, 3H, CH_3), 3.13 – 3.11 (m, 4H, NCH_2), 1.64 – 1.59 (m, 4H, CH_2), 1.55 – 1.51 (m, 2H, CH_2). ^{13}C{^{1}H}NMR (126 MHz, $CDCl_3$) δ 159.6 (C_{Ar}O), 133.7 (CH_{Ar}), 115.7 (CH_{Ar}), 114.1 (C_{Ar}C≡C), 88.8 (*C*≡C), 79.4 (*C*≡C), 74.0 (*C*≡C), 55.4 (CH_3), 52.8 (NCH_2), 49.9 (*C*≡C), 25.1 (CH_2), 23.6 (CH_2). HRMS(ESI): *m/z* calcd for $C_{16}H_{18}NO$: 240.1343 [M+H$^+$]; found: 240.1352.

(3ea) 4-(Pyrrolidin-1-ylhexatriynyl)benzonitrile

4-(Bromohexatriynyl)benzonitrile (**1e**, 9.0 mg, 0.035 mmol), pyrrolidine (22 μL, 0.21 mmol) and THF (10 mL) were reacted according to the procedure for **3aa**. Reaction time: 1 h, red solid, yield 57% (5.0 mg, 0.020 mmol). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 – 7.56 (m, 2H, H_{Ar}), 7.54 – 7.51 (m, 2H, H_{Ar}), 3.38 (ddd, J = 6.7, 4.3, 2.6 Hz, 4H, NCH_2), 1.90 – 1.85 (m, 4H, CH_2). ^{13}C{^{1}H}NMR (126 MHz, $CDCl_3$) δ 133.1 (CH_{Ar}), 132.2 (CH_{Ar}), 127.7 (*C*C≡N), 118.7 (*C*≡N), 111.9 (C_{Ar}C≡C), 86.9 (*C*≡C), 80.5 (*C*≡C), 76.8 (*C*≡C), 72.2 (*C*≡C), 66.4 (*C*≡C), 54.6 (*C*≡C), 52.1 (NCH_2), 26.0 (CH_2). HRMS(ESI): *m/z* calcd for $C_{17}H_{13}N_2$: 245.1073 [M+H$^+$]; found: 245.1076.

(3eb) 4-(Piperidin-1-ylhexatriynyl)benzonitrile

4-(Bromohexatriynyl)benzonitrile (**1e**, 13 mg, 0.051 mmol), piperidine (30 μL, 0.30 mmol) and THF (5 mL) were reacted according to the procedure for **3aa**. Reaction time: 2 h, yellow solid, yield 76% (10 mg, 0.039 mmol). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 – 7.56 (m, 2H, H_{Ar}), 7.53 (d, J = 8.5 Hz, 2H, H_{Ar}), 3.20 – 3.15 (m, 4H, NCH_2), 1.66 – 1.60 (m, 4H, CH_2), 1.56 – 1.51 (m, 2H, CH_2). ^{13}C{^{1}H}NMR (126 MHz, $CDCl_3$) δ 133.0 (CH_{Ar}), 132.1 (CH_{Ar}), 127.6 (*C*C≡N), 118.6 (*C*≡N), 111.8 (C_{Ar}C≡C), 88.1 (*C*≡C), 80.3 (*C*≡C), 76.6 (*C*≡C), 71.9 (*C*≡C), 66.1 (*C*≡C), 53.3 (*C*≡C), 52.4 (NCH_2), 25.1 (CH_2), 23.4 (CH_2). HRMS(ESI): *m/z* calcd for $C_{18}H_{15}N_2$: 259.1230 [M+H$^+$]; found: 259.1225.

(3ec) 4-((((1,3-Dioxolan-2-yl)methyl)(methyl)amino)hexatriynyl)benzonitrile

4-(Bromohexatriynyl)benzonitrile (**1e**, 5.0 mg, 0.020 mmol), 1-(1,3-dioxolan-2-yl)-*N*-methylmethanamine (7 μL, 0.06 mmol) and THF (5 mL) were reacted according to the procedure for **3aa**. Reaction time: 1.5 h, yellow solid, yield 90% (5.1 mg, 0.018 mmol). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 – 7.56 (m, 2H, H_{Ar}), 7.54 – 7.51 (m, 2H, H_{Ar}), 5.10 (t, *J* = 3.9 Hz, 1H, OC*H*O), 4.05 – 3.98 (m, 2H, OCH_2), 3.95 – 3.88 (m, 2H, OCH_2), 3.16 (d, *J* = 3.9 Hz, 2H, NCH_2), 3.00 (s, 3H, CH_3). ^{13}C{^{1}H}NMR (126 MHz, $CDCl_3$) δ 133.0 (CH_{Ar}), 132.1 (CH_{Ar}), 127.5 (*C*C≡N), 118.6 (*C*≡N), 111.9 (C_{Ar}C≡C), 102.5 (O*C*HO), 88.0 (*C*≡C), 80.2 (*C*≡C), 76.5 (*C*≡C), 71.7 (*C*≡C), 66.1 (*C*≡C), 65.4 (CH_3), 57.3 (NCH_2), 53.1 (*C*≡C), 42.4 (CH_3). HRMS(ESI): *m/z* calcd for $C_{18}H_{15}N_2O_2$: 291.1128 [M+H$^+$]; found: 291.1119.

(3ed) 4-((Diisopropylamino)hexatriynyl)benzonitrile

4-(Bromohexatriynyl)benzonitrile (**1e**, 24 mg, 0.088 mmol), diisopropylamine (37 μL, 0.26 mmol) and THF (10 mL) were reacted according to the procedure for **3aa**. Reaction time: 24 h, yellow solid, yield 95% (23 mg, 0.084 mmol). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 – 7.56 (m, 2H), 7.53 – 7.50 (m, 2H), 3.17 (hept, *J* = 6.6 Hz, 2H), 1.23 (d, *J* = 6.6 Hz, 12H). ^{13}C{^{1}H}NMR (126 MHz, $CDCl_3$) δ 132.8 (CH_{Ar}), 132.1 (CH_{Ar}), 127.8 (*C*C≡N), 118.6 (*C*≡N), 111.6 (C_{Ar}C≡C), 84.4 (*C*≡C), 80.6 (*C*≡C), 77.1 (*C*≡C), 72.8 (*C*≡C), 66.5 (*C*≡C), 59.9 (*C*≡C), 53.1 (*C*H), 21.6 (CH_3). HRMS(ESI): *m/z* calcd for $C_{19}H_{19}N_2$:275.1543 [M+H$^+$]; found: 275.1541.

(3ee) 4-((Benzyl(methyl)amino)hexatriynyl)benzonitrile

4-(Bromohexatriynyl)benzonitrile (**1e**, 18 mg, 0.071 mmol), *N*-methylbenzylamine (23 μL, 0.17 mmol) and THF (10 mL) were reacted according to the procedure for **3aa**. Reaction time: 24 h, yellow solid, yield 76% (16 mg, 0.054 mmol). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.6 Hz, 2H, C_6H_4CN), 7.53 (d, *J* = 8.6 Hz, 2H, C_6H_4CN), 7.41 – 7.34 (m, 3H, C_6H_5), 7.33 – 7.30 (m, 2H, C_6H_5), 4.18 (s, 2H, CH_2), 2.82 (s, 3H, CH_3). ^{13}C{^{1}H}NMR (126 MHz, $CDCl_3$) δ 135.4 (C_{Ph}), 133.0 ($CH_{benzonitrile}$), 132.1 ($CH_{benzonitrile}$), 129.0 (CH_{Ph}), 128.4 (CH_{Ph}), 128.4 (CH_{Ph}), 127.5 (*C*C≡N), 118.5 (*C*≡N), 111.9 (C_{Ar}C≡C), 88.5 (*C*≡C), 80.2 (*C*≡C), 76.7 (*C*≡C), 71.7 (*C*≡C), 66.3 (*C*≡C), 59.4 (CH_2), 53.8 (*C*≡C), 40.1 (CH_3). HRMS(ESI): *m/z* calcd for $C_{21}H_{15}N_2$: 295.1230 [M+H$^+$]; found: 295.1232.

(3fa) 1-((4-Nitrophenyl)hexatriynyl)pyrrolidine

1-(Bromohexatriynyl)-4-nitrobenzene (**1f**, 7.0 mg, 0.026 mmol), pyrrolidine (4 μL, 0.052 mmol) and THF (5 mL) were reacted according to the procedure for **3aa**. Reaction time: 1 h, orange solid, yield 65% (4.4 mg, 0.017 mmol). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.16 (d, *J* = 9.0 Hz, 2H, H_{Ar}), 7.59 (d, *J* = 9.0 Hz, 2H, H_{Ar}), 3.40 – 3.37 (m, 4H, NCH_2), 1.91 – 1.84 (m, 4H, CH_2). $^{13}C\{^{1}H\}$NMR (126 MHz, $CDCl_3$) δ 147.1 (CNO_2), 133.2 (CH_{Ar}), 129.7 (C_{Ar}C≡C), 123.8 (CH_{Ar}), 87.2 (*C*≡C), 81.4 (*C*≡C), 76.7 (*C*≡C), 72.8 (*C*≡C), 66.5 (*C*≡C), 54.6 (*C*≡C), 52.0 (NCH_2), 25.9 (CH_2). HRMS(ESI): *m/z* calcd for $C_{16}H_{13}N_2O_2$: 265.0972 [$M+H^+$]; found: 265.0968.

(3fb) 1-((4-Nitrophenyl)hexatriynyl)piperidine

1-(Bromohexatriynyl)-4-nitrobenzene (**1f**, 6.0 mg, 0.022 mmol), piperidine (13 μL, 0.13 mmol) and THF (5 mL) were reacted according to the procedure for **3aa**. Reaction time: 1.5 h, orange solid, yield: 73% (4.4 mg, 0.016 mmol). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.19 – 8.15 (m, 2H, H_{Ar}), 7.61 – 7.57 (m, 2H, H_{Ar}), 3.23 – 3.13 (m, 4H, NCH_2), 1.67 – 1.61 (m, 4H, CH_2), 1.58 – 1.52 (m, 2H, CH_2). $^{13}C\{^{1}H\}$NMR (126 MHz, $CDCl_3$) δ 147.2 (CNO_2), 133.2 (CH_{Ar}), 129.7 (C_{Ar}C≡C), 123.8 (CH_{Ar}), 88.5 (*C*≡C), 81.3 (*C*≡C), 76.5 (*C*≡C), 72.5 (*C*≡C), 66.2 (*C*≡C), 53.5 (*C*≡C), 52.4 (NCH_2), 25.1 (CH_2), 23.4 (CH_2). HRMS(ESI): *m/z* calcd for $C_{17}H_{15}N_2O_2$: 279.1128 [$M+H^+$]; found: 279.1126.

(3fc) *N*-((1,3-dioxolan-2-yl)methyl)-*N*-methyl-6-(4-nitrophenyl)hexatriynamine

1-(Bromohexatriynyl)-4-nitrobenzene (**1f**, 28.0 mg, 0.10 mmol), 1-(1,3-dioxolan-2-yl)-*N*-methylmethanamine (35 μL, 0.31 mmol) and THF (5 mL) were reacted according to the procedure for **3aa**. Reaction time: 1.5 h, orange solid, yield: 32% (9.9 mg, 0.032 mmol). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.17 – 8.15 (m, 2H, H_{Ar}), 7.60 – 7.58 (m, 2H, H_{Ar}), 5.10 (t, *J* = 3.9 Hz, 1H), 4.02 (dd, *J* = 8.8, 5.2 Hz, 2H), 3.92 (dd, *J* = 4.4, 2.3 Hz, 2H), 3.17 (d, *J* = 3.9 Hz, 2H), 3.00 (s, 3H, CH_3). $^{13}C\{^{1}H\}$NMR (126 MHz, $CDCl_3$) δ 147.2 (CNO_2), 133.2 (CH_{Ar}), 129.6 (C_{Ar}C≡C), 123.8 (CH_{Ar}), 102.4 (O*C*HO), 88.4 (*C*≡C), 81.2 (*C*≡C), 76.4 (*C*≡C), 72.3 (*C*≡C), 66.2 (*C*≡C), 65.4 (OCH_2), 57.3 (*C*≡C), 53.2 (NCH_2), 42.4 (CH_3). HRMS(ESI): *m/z* calcd for $C_{17}H_{15}N_2O_4$: 311.1026 [$M+H^+$]; found: 311.1021.

(3fd) *N*,*N*-diisopropyl-6-(4-nitrophenyl)hexatriynamine

1-(Bromohexatriynyl)-4-nitrobenzene (**1f**, 12 mg, 0.041 mmol), *N,N*-diisopropylamine (18 μL, 0.13 mmol) and THF (5 mL) were reacted according to the procedure for **3aa**. Reaction time: 4 h, orange solid, yield: 59% (7.0 mg, 0.024 mmol). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.17 – 8.15 (m, 2H, H_{Ar}), 7.58 – 7.56 (m, 2H, H_{Ar}), 3.18 (hept, J = 6.6 Hz, 2H, CH), 1.24 (d, J = 6.5 Hz, 12H, CH_3). ^{13}C{^{1}H}NMR (126 MHz, $CDCl_3$) δ 147.0 (CNO$_2$), 133.0 (CH$_{Ar}$), 129.9 (C_{Ar}C≡C), 123.8 (CH$_{Ar}$), 84.8 (C≡C), 81.7 (C≡C), 77.0 (C≡C), 73.5 (C≡C), 66.6 (C≡C), 60.2 (C≡C), 53.2 (NCH), 21.7 (CH$_3$). HRMS(ESI): *m/z* calcd for $C_{18}H_{19}N_2O_2$: 295.1441 [M+H$^+$]; found: 295.1446.

(3fe) *N*-benzyl-*N*-methyl-6-(4-nitrophenyl)hexatriynamine

1-(Bromohexatriynyl)-4-nitrobenzene (**1f**, 22 mg, 0.080 mmol), *N*-methylbenzylamine (31 μL, 0.24 mmol) and THF (5 mL) were reacted according to the procedure for **3aa**. Reaction time: 1.5 h, orange solid, yield: 48% (12 mg, 0.038 mmol). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.18 – 8.16 (m, 2H, $C_6H_4NO_2$), 7.60 – 7.58 (m, 2H, $C_6H_4NO_2$), 7.40 – 7.31 (m, 5H, C_6H_5), 4.19 (s, 2H, CH_2), 2.82 (s, 3H, CH_3). ^{13}C{^{1}H}NMR (126 MHz, $CDCl_3$) δ 147.2 (CNO$_2$), 135.4 (C_{Ph}), 133.2 (CH$_{nitrobenzene}$), 129.6 ($C_{nitrobenzene}$C≡C), 129.0 (CH$_{Ph}$), 128.4 (CH$_{Ph}$), 128.5 (CH$_{Ph}$), 123.8 (CH$_{nitrobenzene}$) 88.1 (C≡C), 81.2 (C≡C), 76.6 (C≡C), 72.3 (C≡C), 66.4 (C≡C), 59.5 (CH$_2$), 53.9 (C≡C), 40.1 (CH$_3$). HRMS(ESI): *m/z* calcd for $C_{20}H_{15}N_2O_2$: 315.1128 [M+H$^+$]; found: 315.1132.

(3ga) 4-(Pyrrolidin-1-yloctatetraynyl)benzonitrile

4-(Iodooctatetrayl)benzonitrile (**1g**, 31 mg, 0.095 mmol), pyrrolidine (24 μL, 0.29 mmol) and THF (10 mL) were reacted according to the procedure for **3aa**. Reaction time: 2 h, red solid, yield 94% (24 mg, 0.089 mmol). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 – 7.55 (m, 4H, H_{Ar}), 3.39 (ddd, J = 6.8, 4.3, 2.6 Hz, 4H, NCH_2), 1.90 – 1.86 (m, 4H), CH_2). ^{13}C{^{1}H}NMR (126 MHz, $CDCl_3$) δ 133.4 (CH$_{Ar}$), 132.2 (CH$_{Ar}$), 126.7 (CC≡N), 118.4 (C≡N), 112.5 (C_{Ar}C≡C), 85.4 (C≡C), 79.6 (C≡C), 75.7 (C≡C), 71.3 (C≡C), 68.7 (C≡C), 68.3 (C≡C), 63.9 (C≡C), 55.8 (C≡C), 52.0 (NCH$_2$), 25.9 (CH$_2$). HRMS(ESI): *m/z* calcd for $C_{19}H_{13}N_2$: 269.1073 [M+H$^+$]; found: 269.1073.

(3gb) 4-(Piperidin-1-yloctatetraynyl)benzonitrile

4-(Iodooctatetraynyl)benzonitrile (**1g**, 10 mg, 0.031 mmol), piperidine (11 µL, 0.11 mmol) and THF (10 mL) were reacted according to the procedure for **3aa**. Reaction time: 1.5 h, red solid, yield: 48% (4.3 mg, 0.015 mmol). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 – 7.54 (m, 4H, H_{Ar}), 3.20 – 3.16 (m, 2H, NCH_2), 1.66 – 1.60 (m, 4H, CH_2), 1.57 – 1.50 (m, 2H, CH_2). ^{13}C{^{1}H}NMR (126 MHz, $CDCl_3$) δ 133.4 (CH$_{Ar}$), 132.2 (CH$_{Ar}$), 126.7 (CC≡N), 118.4 (C≡N), 112.5 (C_{Ar}C≡C), 86.6 (C≡C), 79.5 (C≡C), 75.6 (C≡C), 71.2 (C≡C), 68.5 (C≡C), 68.1 (C≡C), 63.7 (C≡C), 54.6 (C≡C), 52.3 (NCH$_2$), 25.1 (CH$_2$), 23.3 (CH$_2$). HRMS(ESI): *m/z* calcd for $C_{20}H_{15}N_2$: 283.1230 [M+H$^+$]; found: 283.1231.

(3gc) 4-((((1,3-Dioxolan-2-yl)methyl)(methyl)amino)octatetraynyl)benzonitrile

4-(Iodooctatetraynyl)benzonitrile (**1g**, 10 mg, 0.031 mmol), 1-(1,3-dioxolan-2-yl)-*N*-methylmethanamine (11 µL, 0.095 mmol) and THF (5 mL) were reacted according to the procedure for **3aa**. Reaction time: 5 h, red solid, yield: 90% (8.9 mg, 0.028 mmol). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 – 7.59 (m, 2H, H_{Ar}), 7.57 – 7.56 (m, 2H, H_{Ar}), 5.09 (t, *J* = 3.9 Hz, 1H, OCH_2O), 4.01 (dd, *J* = 4.4, 2.3 Hz, 2H, OCH_2), 3.92 (dd, *J* = 4.4, 2.3 Hz, 2H, OCH_2O), 3.16 (d, *J* = 3.9 Hz, 2H, OCHO), 3.00 (s, 3H, CH_3). ^{13}C{^{1}H}NMR (126 MHz, $CDCl_3$) δ 133.4 (CH$_{Ar}$), 132.2 (CH$_{Ar}$), 126.6 (CC≡N), 118.4 (C≡N), 112.6 (C_{Ar}C≡C), 102.4 (OCHO), 86.6 (C≡C), 79.4 (C≡C), 75.6 (C≡C), 71.1 (C≡C), 68.4 (C≡C), 67.9 (C≡C), 65.4 (OCH$_2$), 63.6 (C≡C), 57.2 (NCH$_2$), 54.2 (C≡C), 42.4 (CH$_3$). HRMS(ESI): *m/z* calcd for $C_{20}H_{14}N_2O_2Na$: 337.0947 [M+Na$^+$]; found: 337.0946.

(3gd) 4-((Diisopropylamino)octatetraynyl)benzonitrile

4-(Iodooctatetrayl)benzonitrile (**1g**, 10 mg, 0.031 mmol), diisopropylamine (14 µL, 0.10 mmol) and THF (10 mL) were reacted according to the procedure for **3aa**. Reaction time: 24 h, red solid, yield 84% (7.7 mg, 0.026 mmol). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 – 7.54 (m, 4H, CH_{Ar}), 3.17 (hept, *J* = 6.5 Hz, 2H, CH), 1.23 (d, *J* = 6.6 Hz, 12H, CH_3). ^{13}C{^{1}H}NMR (126 MHz, $CDCl_3$) δ 133.3 (CH$_{Ar}$), 132.2 (CH$_{Ar}$), 126.8 (CC≡N), 118.4 (C≡N), 112.4 (C_{Ar}C≡C), 82.9 (C≡C), 79.7 (C≡C), 75.9 (C≡C), 71.5 (C≡C), 69.0 (C≡C), 68.9 (C≡C), 64.3 (C≡C), 61.3 (C≡C), 53.2 (CH), 21.7 (CH$_3$). HRMS(ESI): *m/z* calcd for $C_{21}H_{19}N_2$: 299.1543 [M+H$^+$]; found: 299.1546.

(3ge) 4-((Benzyl(methyl)amino)octatetraynyl)benzonitrile

4-(Iodooctatetrayl)benzonitrile (**1g**, 7.0 mg, 0.022 mmol), *N*-methylbenzylamine (9 μL, 0.072 mmol) and THF (10 mL) were reacted according to the procedure for **3aa**. Reaction time: 24 h, red solid, yield: 91% (6.4 mg, 0.020 mmol). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 – 7.55 (m, 4H, C_6H_4CN), 7.41 – 7.28 (m, 5H, C_6H_5), 4.18 (s, 2H. CH_2), 2.82 (s, 3H, CH_3). ^{13}C{^{1}H}NMR (126 MHz, $CDCl_3$) δ 135.1 (C_{Ph}), 133.3 ($CH_{benzonitrile}$), 132.1 ($CH_{benzonitrile}$), 128.9 (CH_{Ph}), 128.4 (CH_{Ph}), 128.2 (CH_{Ph}), 126.5 (*C*C≡N), 118.2 (*C*≡N), 112.4 (C_{Ar}C≡C), 86.9 (*C*≡C), 79.3 (*C*≡C), 75.6 (*C*≡C), 71.0 (*C*≡C), 68.5 (*C*≡C), 67.8 (*C*≡C), 63.7 (*C*≡C), 59.3 (CH_2), 54.8 (*C*≡C), 39.9 (CH_3). HRMS(ESI): *m/z* calcd for $C_{23}H_{15}N_2$: 319.1230 [M+H$^+$]; found: 319.1243.

Synthesis of push-pull thiophenes

(4aa) 4-(5-(Pyrrolidin-1-yl)thiophen-2-yl)benzonitrile

4-(Pyrrolidin-1-ylbutadiynyl)benzonitrile (**3aa**, 19 mg, 0.086 mmol) was dissolved in MeCN (10 mL) and the mixture was heated to 70 °C under N_2 atmosphere. Next, Na_2S•xH_2O (60% of Na_2S, 0.10 mmol) was added and the mixture was stirred for 2.5 h. After this time water (100 mL) was added and the product was extracted with Et_2O (3 x 30 mL). Combined organic layers were washed twice with H_2O (2 x 20 mL), dried over $MgSO_4$, filtered and the solvent was evaporated under reduced pressure yielding 19 mg (0.075 mmol) of yellow solid. Yield: 87%. ^{1}H NMR (500 MHz, C_6D_6) δ 7.10 – 7.07 (m, 2H, $H_{benzonitrile}$), 7.05 – 7.02 (m, 2H, $H_{benzonitrile}$), 6.97 (d, *J* = 4.0 Hz, 1H, $H_{thiophene}$), 5.58 (d, *J* = 4.0 Hz, 1H, $H_{thiophene}$), 2.86 – 2.81 (m, 4H, NCH_2), 1.38 – 1.33 (m, 4H, CH_2). ^{13}C{^{1}H}NMR (126 MHz, C_6D_6) δ 157.2 ($C_{thiophene}$N), 139.8 ($C_{benzonitrile}$), 132.6 ($CH_{benzonitrile}$), 126.4 ($CH_{thiophene}$), 124.0 ($C_{thiophene}$), 123.5 ($CH_{benzonitrile}$), 119.5 (*C*≡N), 108.0 (*C*C≡N), 101.7 ($CH_{thiophene}$), 50.4 (NCH_2), 25.7 (CH_2). HRMS(ESI): *m/z* calcd for $C_{15}H_{15}N_2S$: 255.0950 [M+H$^+$]; found: 255.0949.

(4ac) 4-(5-(((1,3-Dioxolan-2-yl)methyl)(methyl)amino)thiophen-2-yl)benzonitrile

4-((((1,3-Dioxolan-2-yl)methyl)(methyl)amino)butadiynyl)benzonitrile (**3ac**, 0.083 mmol), Na_2S•xH_2O (60% of Na_2S, 12 mg, 0.10 mmol) and MeCN (10 mL) were reacted according to the procedure for **4aa**. Yellow solid (18 mg, 0.060 mmol), yield: 72% ^{1}H NMR (500 MHz, C_6D_6) δ 7.01 (s, 4H, $H_{benzonitrile}$), 6.86 (d, *J* = 4.1 Hz, 1H, $H_{thiophene}$), 5.73 (d, *J* = 4.1 Hz, 1H, $H_{thiophene}$), 4.89 (t, *J* = 3.9 Hz, 1H, OC*H*), 3.44 – 3.37 (m, 2H, OCH_2), 3.28 – 3.20 (m, 4H, OCH_2, NCH_2), 2.74 (s, 3H, CH_3). $^{13}C\{^1H\}$NMR (126 MHz, C_6D_6) δ 160.1 ($C_{thiophene}$N), 139.5 ($C_{benzonitrile}$), 132.6 ($CH_{benzonitrile}$), 126.2 ($CH_{thiophene}$), 124.9 ($C_{thiophene}$), 123.7 ($CH_{benzonitrile}$), 119.4 (C≡N), 108.4 (CC≡N), 103.1 (OCHO), 102.4 ($CH_{thiophene}$), 65.0 (OCH_2), 58.2 (NCH_2), 41.0 (CH_3). HRMS(ESI): *m/z* calcd for $C_{16}H_{17}N_2O_2S$: 301.1005 [M+H$^+$]; found: 301.1010.

(4ae) 4-(5-(Benzyl(methyl)amino)thiophen-2-yl)benzonitrile

4-((Benzyl(methyl)amino)butadiynyl)benzonitrile (**3ae**, 15 mg, 0.055 mmol), Na_2S•xH_2O (60% of Na_2S, 6.4 mg, 0.08 mmol) and MeCN (10 mL) were reacted according to the procedure for **4aa**. Yellow solid (13 mg 0.043 mmol), yield: 78% ^{1}H NMR (500 MHz, C_6D_6) δ 7.13 – 7.09 (m, 2H, C_6H_5), 7.07 – 7.01 (m, 3H, C_6H_5), 7.00 (s, 4H, C_6H_4CN), 6.83 (d, J = 4.1 Hz, 1H, $H_{thiophene}$), 5.66 (d, J = 4.1 Hz, 1H, $H_{thiophene}$), 4.02 (s, 2H, CH_2), 2.47 (s, 3H, CH_3). $^{13}C\{^1H\}$NMR (126 MHz, C_6D_6) δ 160.3 ($C_{thiophene}$N), 139.4 ($C_{benzonitrile}$), 137.4 (C_{Ph}), 132.6 ($CH_{benzonitrile}$), 129.0 (CH_{Ph}), 127.8 (CH_{Ph}), 127.5 (CH_{Ph}), 126.2 ($CH_{thiophene}$), 125.2 ($C_{thiophene}$), 123.8 ($CH_{benzonitrile}$), 119.4 (C≡N), 108.5 (CC≡N), 103.5 ($CH_{thiophene}$), 59.1 (CH_2), 39.5 (CH_3). HRMS(ESI): *m/z* calcd for $C_{19}H_{16}N_2NaS$: 327.0930 [M+Na$^+$]; found: 327.0931.

(4ba) 1-(5-(4-Nitrophenyl)thiophen-2-yl)pyrrolidine

1-((4-Nitrophenyl)butadiynyl)pyrrolidine (**3ba**, 14 mg, 0.058 mmol), Na_2S•xH_2O (60% of Na_2S, 14 mg, 0.12 mmol) and MeCN (10 mL) were reacted according to the procedure for **4aa**. Yellow solid (9.0 mg, 0.033 mmol), yield: 57% ^{1}H NMR (500 MHz, C_6D_6) δ 7.95 – 7.90 (m, 2H, $H_{nitrobenzene}$), 7.09 – 7.05 (m, 2H, $H_{nitrobenzene}$), 6.99 (d, J = 4.1 Hz, 1H, $H_{thiophene}$), 5.58 (d, J = 4.1 Hz, 1H, $H_{thiophene}$), 2.84 – 2.80 (m, 4H, NCH_2), 1.37 – 1.32 (m, 4H, CH_2). $^{13}C\{^1H\}$NMR (126 MHz, C_6D_6) δ 157.9 ($C_{thiophene}$N), 144.8 (CNO$_2$), 141.9 ($C_{nitrobenzene}$), 127.5 ($CH_{thiophene}$), 124.7 ($CH_{nitrobenzene}$), 123.5 ($C_{thiophene}$), 122.9 ($CH_{nitrobenzene}$), 102.1 ($CH_{thiophene}$), 50.4 (*NCH*$_2$), 25.7 (CH_2). HRMS(ESI): *m/z* calcd for $C_{14}H_{15}N_2O_2S$: 275.0849 [M+H$^+$]; found: 275.0850.

(4ca) Methyl 5-(pyrrolidin-1-yl)thiophene-2-carboxylate

Methyl 5-(pyrrolidin-1-yl)penta-2,4-diynoate (**3ca**, 14.7 mg, 0.083 mmol), Na_2S•xH_2O (60% of Na_2S, 9.7 mg, 0.12 mmol) and MeCN (10 mL) were reacted according to the procedure for **4aa**. Yellow solid (6.9 mg, 0.033 mmol), yield: 40% ^{1}H NMR (500 MHz, C_6D_6) δ 7.85 (d, J = 4.2 Hz, 1H, $H_{thiophene}$), 5.44 (d, J = 4.2 Hz, 1H, $H_{thiophene}$), 3.58 (s, 3H, CH_3), 2.65 (t, 4H, NCH_2), 1.21 – 1.19 (m, 4H, CH_2). ^{1}H NMR (500 MHz, Acetone) δ 7.48 (d, J = 4.2 Hz, 1H, 1H, $H_{thiophene}$), 5.79 (d, J = 4.3 Hz, 1H, 1H, $H_{thiophene}$), 3.72 (s, 3H, CH_3), 3.34 – 3.30 (m, 4H NCH_2), 2.09 – 2.07 (m, 4H CH_2). ^{13}C{^{1}H}NMR (126 MHz, C_6D_6) δ 163.2 (*C*=O), 161.2 ($C_{thiophene}$N), 135.8 ($CH_{thiophene}$), 101.5 ($CH_{thiophene}$), 51.1 (CH_3), 50.1 (NCH_2), 25.5 (CH_2) (one signal under solvent). ^{13}C{^{1}H}NMR (126 MHz, Acetone-d_6) δ 163.4 (*C*=O),), 162.2 ($C_{thiophene}$N), 136.3 ($CH_{thiophene}$), 126.1 ($CH_{thiophene}$), 101.9 ($CH_{thiophene}$), 51.3 (CH_3), 51.2 (NCH_2), 26.4 (CH_2). HRMS(ESI): *m/z* calcd for $C_{10}H_{14}NO_2S$: 212.0740 [M+H$^+$]; found: 212.0751.

(4ea) 4-((5-(Pyrrolidin-1-yl)thiophen-2-yl)ethynyl)benzonitrile

4-(Pyrrolidin-1-ylhexatriynyl)benzonitrile (**3ea**, 17 mg, 0.070 mmol), Na_2S•xH_2O (60% of Na_2S, 12 mg, 0.10 mmol) and MeCN (10 mL) were reacted according to the procedure for **4aa**. Yellow solid (15 mg, 0.054 mmol), yield: 77% ^{1}H NMR (500 MHz, C_6D_6) δ 7.20 (d, J = 4.0 Hz, 1H, $H_{thiophene}$), 7.00 – 6.97 (m, 2H, $H_{benzonitrile}$), 6.80 – 6.77 (m, 2H, $H_{benzonitrile}$), 5.42 (d, J = 4.0 Hz, 1H, $H_{thiophene}$), 2.72 – 2.68 (m, 4H, NCH_2), 1.28 – 1.24 (m, 4H, CH_2). ^{13}C{^{1}H}NMR (126 MHz, C_6D_6) δ 157.9 ($C_{thiophene}$N), 135.2 ($CH_{thiophene}$), 132.0 ($CH_{benzonitrile}$), 130.8 ($CH_{benzonitrile}$), 128.8 (*C*C≡N), 118.8 (*C*≡N), 110.6 ($C_{benzonitrile}$C≡C), 104.3 ($C_{thiophene}$), 100.7 ($CH_{thiophene}$), 91.4 (*C*≡C), 90.7 (*C*≡C), 50.3 (NCH_2), 25.6 (CH_2). HRMS(ESI): *m/z* calcd for $C_{17}H_{15}N_2S$: 279.0950 [M+H$^+$]; found: 279.0953.

(4eb) 4-((5-(Piperidin-1-yl)thiophen-2-yl)ethynyl)benzonitrile

4-(Piperidin-1-ylhexatriynyl)benzonitrile (**3eb**, 14 mg, 0.052 mmol), Na_2S•xH_2O (60% of Na_2S, 7.0 mg, 0.059 mmol) and MeCN were reacted according to the procedure for **4aa**. Yellow solid (11 mg, 0.038 mmol), yield: 73% ^{1}H NMR (500 MHz, C_6D_6) δ 7.12 (d, J = 4.1 Hz, 1H, $H_{thiophene}$), 6.97 – 6.94 (m, 2H, $H_{benzonitrile}$), 6.79 – 6.76 (m, 2H, $H_{benzonitrile}$), 5.67 (d, J = 4.1 Hz, 1H, $H_{thiophene}$), 2.77 – 2.73 (m, 4H, NCH_2), 1.23 – 1.17 (m, 4H, CH_2), 1.10 – 1.04 (m, 2H, CH_2). ^{13}C{^{1}H}NMR (126 MHz, C_6D_6) δ 162.4 ($C_{thiophene}$N), 134.5 ($CH_{thiophene}$), 131.9 ($CH_{benzonitrile}$), 131.0 ($CH_{benzonitrile}$), 128.4 (*C*C≡N), 118.7 (*C*≡N), 111.0 ($C_{benzonitrile}$C≡C), 106.8 ($C_{thiophene}$), 104.1 ($CH_{thiophene}$), 91.4 (*C*≡C), 89.8 (*C*≡C), 51.5 (NCH_2), 25.1 (CH_2), 23.6 (CH_2). HRMS(ESI): *m/z* calcd for $C_{18}H_{16}N_2NaS$: 315.0926 [M+Na$^+$]; found: 315.0925.

(4fb) 1-(5-((4-Nitrophenyl)ethynyl)thiophen-2-yl)piperidine

1-((4-Nitrophenyl)hexatriynyl)piperidine (**3fb** 19 mg, 0.068 mmol), Na_2S•xH_2O (60% of Na_2S, 8.6 mg, 0.10 mmol) and MeCN (10 mL) were reacted according to the procedure for **4aa**. Yellow solid (5.7 mg, 0.020 mmol), yield: 29% ^{1}H NMR (500 MHz, C_6D_6) δ 7.67 – 7.64 (m, 2H, $H_{benzonitrile}$), 7.14 (d, J = 4.1 Hz, 1H, $H_{thiophene}$), 7.01 – 6.98 (m, 2H, $H_{benzonitrile}$), 5.67 (d, J = 4.1 Hz, 1H, $H_{thiophene}$), 2.78 – 2.73 (m, 4H, NCH_2), 1.23 – 1.17 (m, 4H, CH_2). ^{13}C{^{1}H}NMR (126 MHz, C_6D_6) δ 162.6 ($C_{thiophene}$N), 146.6 (CNO$_2$), 134.9 (CH$_{thiophene}$), 131.0 (CH$_{nitrobenzene}$), 130.5 ($C_{nitrobenzene}$C≡C), 123.7 (CH$_{nitrobenzene}$), 106.6 ($C_{thiophene}$C≡C), 104.1 (CH$_{thiophene}$), 91.5 (C≡C), 91.0 (C≡C), 51.5 (NCH$_2$), 25.0 (CH$_2$). HRMS(ESI): *m/z* calcd for $C_{17}H_{17}N_2O_2S$: 313.1005 [M+H$^+$]; found: 313.1007.

(4ga) 4-((5-(Pyrrolidin-1-yl)thiophen-2-yl)butadiynyl)benzonitrile

4-(Pyrrolidin-1-yloctatetraynyl)benzonitrile (**3ga**, 14 mg, 0.043 mmol), Na_2S•xH_2O (60% of Na_2S, 5.4 mg, 0.046 mmol) and MeCN (10 mL) were reacted according to the procedure for **4aa**. Yellow solid (6.8 mg, 0.022 mmol), yield: 51% ^{1}H NMR (500 MHz, C_6D_6) δ 7.15 (d, J = 4.2 Hz, 1H, $H_{thiophene}$), 6.85 – 6.82 (m, 2H, $H_{benzonitrile}$), 6.69 – 6.67 (m, 2H, $H_{benzonitrile}$), 5.26 (d, J = 4.1 Hz, 1H, $H_{thiophene}$), 2.63 – 2.58 (m, 4H, NCH_2), 1.23 – 1.19 (m, 4H, CH_2). ^{13}C{^{1}H}NMR (126 MHz, C_6D_6) δ 158.4 ($C_{thiophene}$N), 137.7 (CH$_{thiophene}$), 132.3 (CH$_{benzonitrile}$), 131.8 (CH$_{benzonitrile}$), 127.1 (CC≡N), 118.4 (C≡N), 112.0 ($C_{benzonitrile}$C≡C), 103.2 ($C_{thiophene}$), 100.7 (CH$_{thiophene}$), 82.9 (C$_{benzonitrile}$$C$≡C), 81.3 (C$_{thiophene}$$C$≡C), 80.1 ($C$≡C), 78.0 ($C$≡C), 50.2 ($NCH_2$), 25.5 ($CH_2$). HRMS(ESI): *m/z* calcd for $C_{19}H_{17}N_2OS$: 321.1056 [M+H$_3$O$^+$]; found: 321.1057.

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Notes

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Associated Content

Supporting Information

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CIF files for **3ad** (CCDC-1500869), **3ca** (CCDC-1500872), **3ec** (CCDC-1500871), **3fd** (CCDC-1500873), **3fe** (CCDC-1500870), and **4aa** (CCDC-1500868) (CIF), ^{1}H and ^{13}C NMR spectra, emission spectroscopy details, X-ray crystallography details (PDF).

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