JOC The Journal of Organic Chemistry

Article

pubs.acs.org/joc

Transition-Metal Free Mechanochemical Approach to Polyyne Substituted Pyrroles

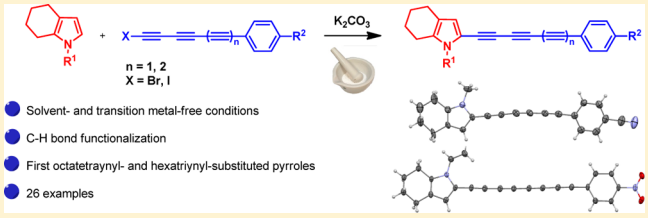
Bartłomiej Pigulski,[†] Agata Arendt,[†] Denis N. Tomilin,[‡] Lyubov N. Sobenina,[‡] Boris A. Trofimov,[‡] and Sławomir Szafert*[,†]

[†]Department of Chemistry, University of Wrocław, 14 F. Joliot-Curie, 50-383 Wrocław, Poland

[‡]A. E. Favorsky Irkutsk Institute of Chemistry, Siberian Branch, Russian Academy of Sciences, 1 Favorsky, 664033 Irkutsk, Russian Federation

Supporting Information

ABSTRACT: In this contribution, the synthesis of long chain hexatriynyl- and octatetraynyl-substituted pyrroles in one step from 1-halopolyyne precursors is reported. The products were obtained via a mechanochemical approach by simple grinding of 1-haloalkynes with *N*-substituted pyrroles and potassium carbonate which played a role of heterogeneous catalyst and this solvent- and transition metal-free approach is unprecedent in the synthesis of new, organic, long chain polyynes. Additionally, an extensive X-ray single crystal study of pyrrole end-capped polyynes is presented. Such compounds are possible substrates for different oligoheterocycles and have a significant application potential such as for instance molecular wires.



INTRODUCTION

Polyynes have been attracting constant interest from the scientific community for more than half a century and a variety of diverse compounds possessing such an unsaturated motif has been synthesized to date.[1] One of the major motivations for investigation of these linear carbon rods is that they can be regarded as model compounds of yet unknown, hypothetical, allotropic form of carbon, carbyne. Moreover polyynes possess considerable application potential. Such molecules have been explored as molecular wires and switches in nanoelectronics,[2] as materials for optoelectronics due to their strong, nonlinear optical response,[3] or as precursors for conducting polymers.[4] It is also noteworthy that polyyne motifs have been oftentimes recognized in the interstellar matter.[5]

Polyynes which contain pyrrole end-groups are a very scanty class of compounds. To the best of our knowledge, only butadiynes are known to date, among which there are porphyrinoids with butadiyne chains incorporated into a macrocycle skeleton[6] or modified bilirubins.[7] For instance, Vogel[6a] and Panda[6b] published the synthesis of a very physicochemically interesting 26π–β-octasubstituted diacetylene-cumulene porphycene from butadiyne-bridged bipyrroledialdehydes. It is noteworthy that the precursor for this molecule was obtained in seven synthetic steps.[6c] Other interesting examples of diacetylene porphyrinoids are dimeric and trimeric BODIPY based macrocycles obtained in the CuCl catalyzed homocoupling reaction shown by Shinokubo.[6d] Finally, a little different synthetic approach to pyrrole butadiyne compounds was presented by Fiandanese where the target molecule was obtained via heterocyclization from aminoaryl tetrayne.[6e]

Despite the synthetic inaccessibility of longer analogues, hexatriynyl- and octatetraynyl-substituted pyrroles were investigated with the use of computational methods.[8] Moreover, such heterocyclic-long conjugated systems may be used as very useful substrates for the synthesis of oligoheterocycles.[9]

Recently, we have reported the cross-coupling reaction between the conjugated 1-halobutadiynes and substituted pyrroles.[10] The reaction needed a short grinding of substrates with K_2CO_3 in a mortar and was insensitive to moisture and air. The scope covered mostly substrates with strongly electron withdrawing end-groups directly attached to the butadiyne moiety which was in accordance with the earlier data that showed effective coupling of 1-haloacetylenes possessing ester or ketone end-groups with substituted pyrroles.[11] In our work, however, we have surprisingly noticed that aryl substituted 1-halobutadiynes also undergo such coupling reactions. Reaction times were longer, but it was possible to obtain products with good yields. Encouraged by those findings, we decided to expand the scope of this reaction to longer aryl-substituted polyynes and to use this convenient mechanochemical approach for the synthesis of much longer pyrrole end-capped carbon rods.

Herein, we report the cross-coupling reaction between 1-halopolyynes with the carbon chain up to octatetrayne with a series of tetrahydroindoles giving a new class of pyrrole end-capped polyynes.

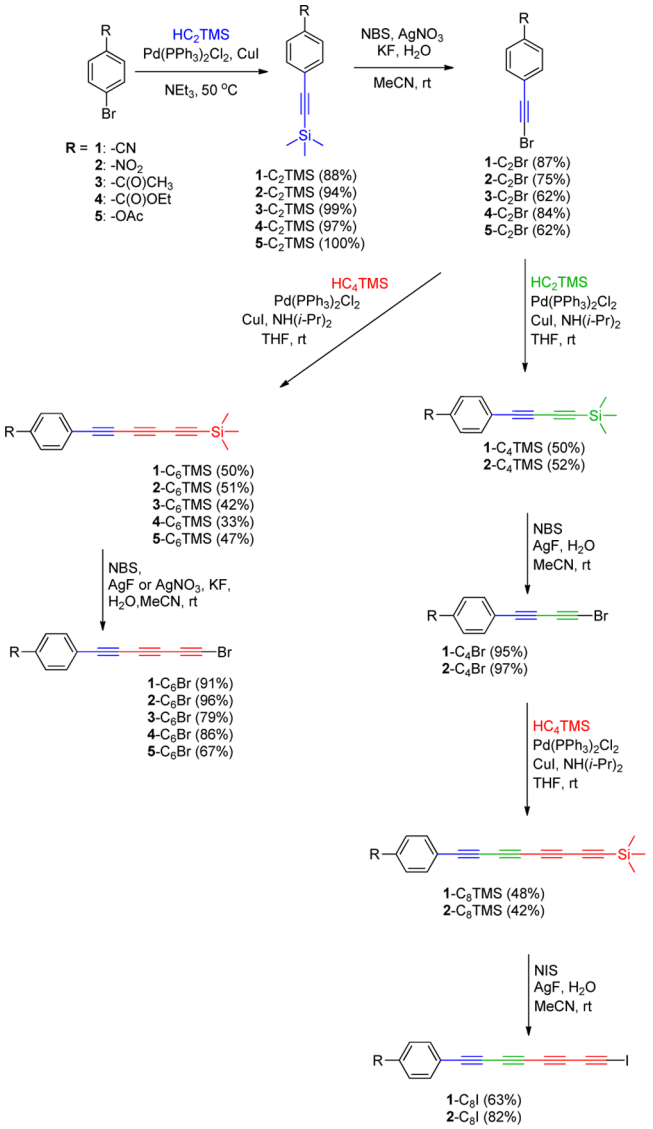
Received: July 20, 2016
Published: August 26, 2016

DOI: 10.1021/acs.joc.6b01732
J. Org. Chem. 2016, 81, 9188–9198

RESULTS AND DISCUSSION

Synthesis of Polyynyl-Substituted Pyrroles. In the initial thrust, a series of 1-haloacetylenes **1**-**5**-C_2Br was obtained as shown in Scheme 1. Next, through C_2 and C_4 chain elongation protocols based on Cadiot−Chodkiewicz cross-coupling a group of hexatriynes **1**-**5**-C_6TMS and two butadiynes **1**-**2**-C_4TMS were synthesized. All of the compounds were transformed to the corresponding bromides via desilylative halogenation, and the **1**-**2**-C_4Br were next used to obtain first **1**-**2**-C_8TMS and then target **1**-**2**-C_8I. The synthesis of the presented 1-iodooctatetraynes and 1-bromohexatriyne **1**-C_6Br were published in our earlier works.[12] New 1-bromohextariynes **2**-**5**-C_6Br were obtained in 67−96% yield and were reasonably stable (for days) in the solid state and when kept in the dark. Although, we have previously noticed that the coupling reaction of pyrroles with 1-haloalkynes is much faster for bromides than for iodides, unfortunately, we also discovered that longer 1-bromoalkynes are much less stable than the iodo derivatives. Hence, for 1-halooctatetraynes only iodo derivatives appeared available.

Scheme 1. Synthesis of 1-Halopolyynes



The ones with *N*-substituted tetrahydroindoles worked well, and the products were obtained with yields up to 97% (**2**-C_6THI-Bn), and the reaction times were between 3 and 24 h. Only the reaction of **4**-C_6Br and **5**-C_6Br with *N*-vinyl-substituted tetrahydroindole gave the product with lower yield (19%). Generally, the reactions with unsubstituted tetrahydroindole gave products with a little lower yield (8−52%), and also the reaction times were longer (19−72 h). Nevertheless, we were able to isolate pure products for all of the five hexatriynes (20 examples). Importantly, the reaction scope includes electron withdrawing substituents on a phenyl ring (**1**-**4**-C_6Br) as well as

All of the new compounds were characterized by ^{1}H and ^{13}C NMR spectroscopy and gave the HRMS mass signals supporting appropriate molecular structures. The ^{13}C NMR spectra, although routine, revealed signals for all carbons from the polyyne chains. As usual, the signal of the carbon adjacent to a halogen atom was the most upfield shifted and appeared between 42.9 and 45.1 ppm.

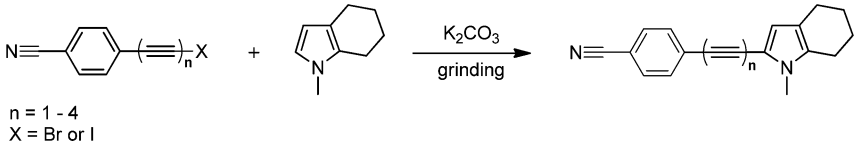
With all of the starting materials in hand, we performed initial test reactions using 4,5,6,7-tetrahydroindoles and utilizing the known, mechanochemical procedure.[10,13] Our choice of alkyl-substituted pyrroles eventuated from the fact that they are very convenient model substrates due to their synthetic availability, and moreover, tetrahydroindoles were previously used in similar couplings.

In order to optimize the reaction, we have first investigated a relationship between carbon chain length and the reaction rate (see Scheme 2). As the test compounds, we have selected the benzonitrile derivatives **1**-C_2Br, **1**-C_4Br, **1**-C_6Br, and *N*-methyl-4,5,6,7-tetrahydroindole. The reaction with **1**-C_2Br was very slow, and after several days, only traces of product were observed in the ^{1}H NMR spectrum. **1**-C_4Br reacted faster, but the reaction was not completed even after a few days. Surprisingly, the reaction for **1**-C_6Br was already completed after 3 h, which clearly shows that the longer chain provided a shorter reaction time.

As said already, iodides are generally less reactive than bromides,[10] but we have decided anyway to check a difference in reaction times between **1**-C_6I and **1**-C_8I. The results showed that the reaction between **1**-C_6I and *N*-methyl-4,5,6,7-tetrahydroindole was not completed even after a few days unlike **1**-C_8I which gave the desired product after 24 h. With all that in mind, we approached the syntheses of hexatriynyl-substituted pyrroles using 1-bromohexatriynes and octatetraynyl-substituted pyrroles using 1-iodooctatetraynes.

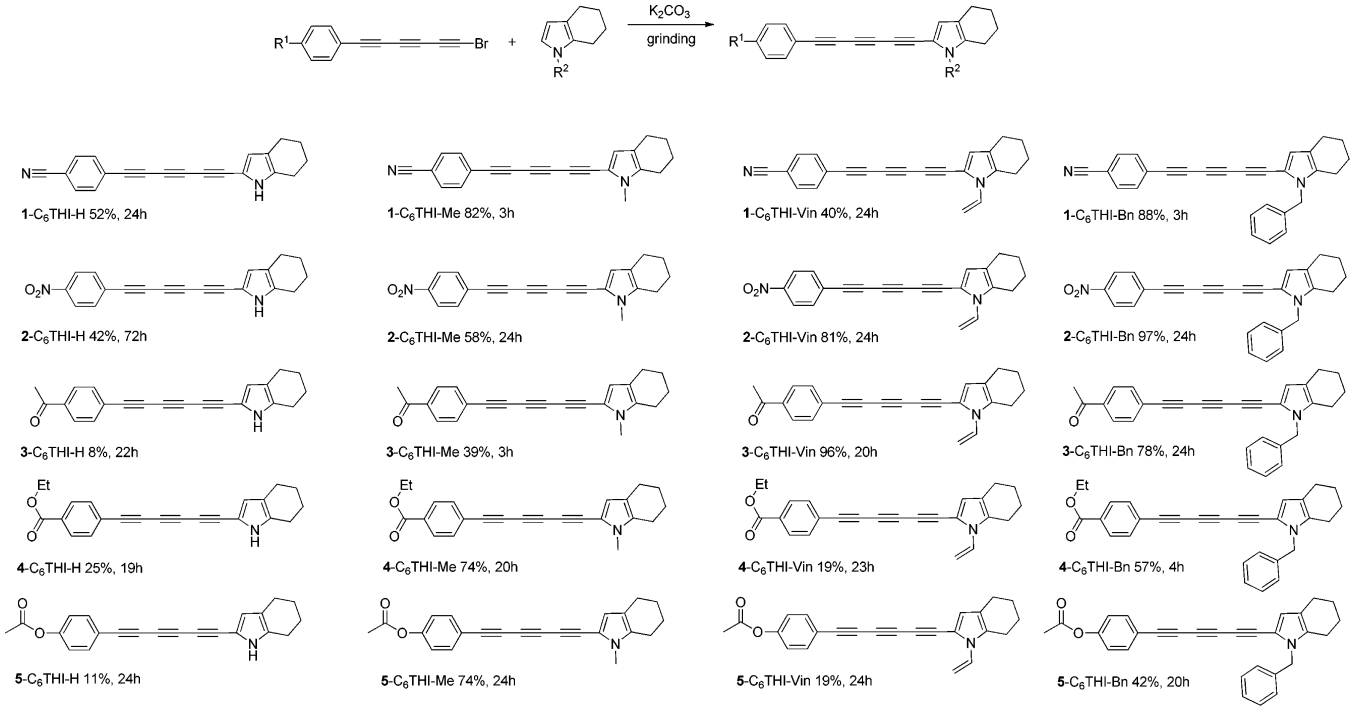
Reactions between 1-bromohexatriynes **1**-**5**-C_6Br and tetrahydroindoles were first performed (see Scheme 3). The

Scheme 2. Test Reaction of 1-C_nX Polyynes with *N*-Methyl-4,5,6,7-tetrahydroindole

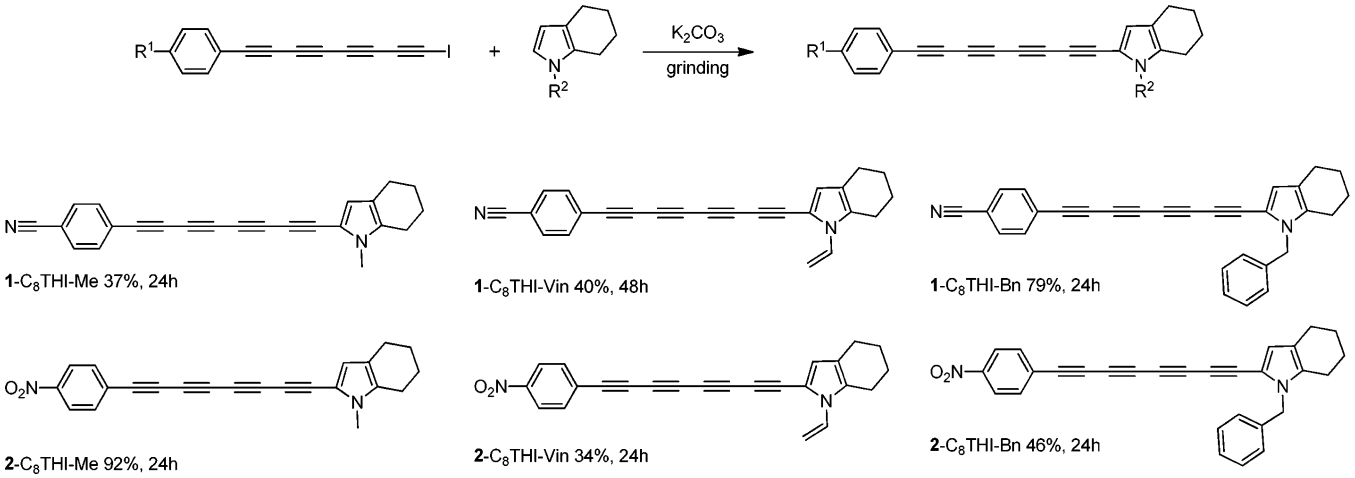


DOI: 10.1021/acs.joc.6b01732
J. Org. Chem. 2016, 81, 9188−9198

Scheme 3. Synthesis of Hexatriynyl-Substituted Tetrahydroindoles



Scheme 4. Synthesis of Octatetraynyl-Substituted Tetrahydroindoles



weakly electron donating -OC(O)Me group (**5**-C_6Br). Additionally, we have tested two 1-bromohexatriynes (**1**-C_6Br, **2**-C_6Br) in the reaction with 2-phenylpyrrole, but we were not able to isolate any coupling products (only substrates were retrieved). We are fully aware that the scope on the pyrrole side is a little narrow, but in our opinion, the finding itself (meaning, that a pyrrole may undergo such an unusual transformation with long 1-halopolyynes) is already a very important result.

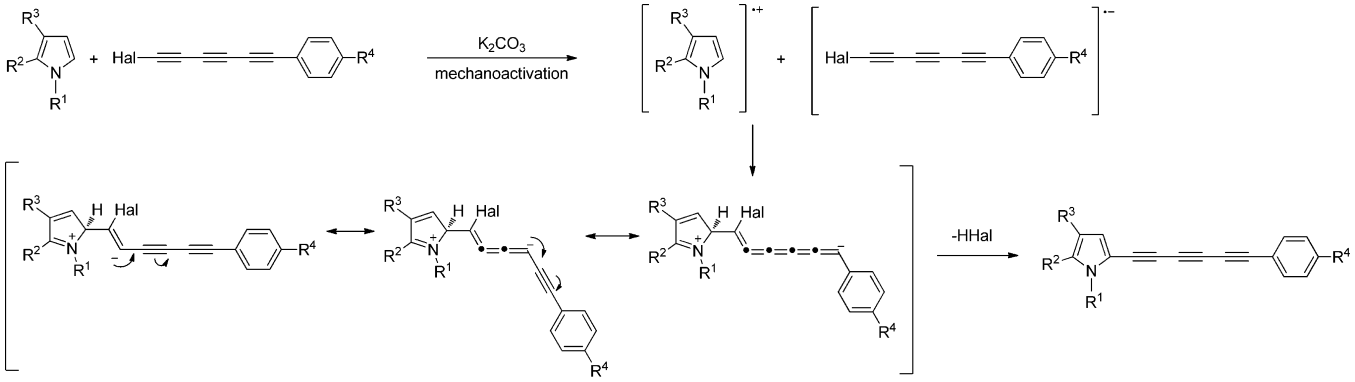
Reaction with 1-iodotetraynes presented a greater challenge. Reaction times were longer (24−48 h) than those for the corresponding 1-bromohexatriynes (3−24 h); however, products were obtained with yields ranging from 34% up to 92% (see Scheme 4). Unfortunately, reactions with unsubstituted tetrahydroindole were too slow, and we were unable to obtain the expected products.

Looking at the previously obtained aryl-substituted butadiynes,[10] it should be noticed that the yields obtained for the reaction of analogous tetrahydroindoles with 4-EtOC(O)C_6H_4C≡CC≡CBr (36−58%) were in general lower and the reaction times (24 h to 5 days) much longer. This implies that the use of longer conjugate systems C_6 and C_8 contribute to a better reaction performance.

A reaction mechanism for this inverse Sonogashira coupling has already been proposed,[14] and the ESR studies confirmed that the first step is the formation of an ion-radicals pair via a single electron transfer. A fine grinding of the reactants is intended to mix the substrates as evenly and finely as possible, which corresponds to a distribution of substrates in a solvent. In this case, the crystalline lattice plays a role of a highly ionized medium, resembling an ionic liquid. The NMR monitoring unambiguously proves that during "the resting delay" the reaction proceeds and that the given reaction time is experimentally determined. Thus, it is also an experimental fact that during "the resting delay" (actually, the reaction time)

DOI: 10.1021/acs.joc.6b01732
J. Org. Chem. 2016, 81, 9188−9198

Scheme 5. Proposed Mechanism of Long Chain Stabilization of a Radical Intermediate Product



the reaction proceeds. It is clear that migration/diffusion of the reactants in the solid state should be very slow. Apparently, the reactants contact each other already in the process of grinding to form charge transfer complexes and then ion radical pairs, and their further transformation to the final products is not immediate and takes some time. It is understood that the detailed mechanism of this reaction is still far from being entirely clarified and deserves an in-depth investigation, in particular, we should not ignore the mechanochemical contribution (formation of crystalline lattice defects) to the triggering of the coupling reaction.

On the basis of that, we may conclude that the longer chain gives better stabilization at the initial step (the formation of ion-radical pair) spawning the better yield and shorter reaction time as shown in Scheme 5. Moreover, less electron-rich bromides probably are more likely to form cation-radicals at the first step than more electron-rich iodides.

Coupling products presented in this contribution are new and exceptional from the structural point of view. To our best knowledge, pyrroles with -$(C{\equiv}C)_3R$ or -$(C{\equiv}C)_4R$ substituents are not known in the literature. Polyynes with heteroaromatic end-groups are generally rare, and to date, only symmetric octatetraynes with thiophene,[15] quinoline,[16] and pyridine[17] groups have been described.

X-ray Crystallography. Single crystals appropriate for X-ray analysis were in most cases obtained by liquid phase diffusion (CH_2Cl_2/*n*-hexane) or by slow evaporation of a solvent at low temperature. Coupling products crystallized rather well, and six X-ray solid state structures were solved, which are shown in Figure 1. The presented compounds are the first examples of hexatriynyl- and octatetraynyl-substituted pyrroles to date.

In all cases, a tetrahydroindole moiety, a polyyne chain, and a phenyl ring are coplanar except for **4**-C_6THI-Bn where the planes of pyrrole and phenyl rings are twisted by 81° most probably due to packing forces. The carbon−carbon chain bond lengths are given in Table 1, and it can be noticed that the triple bonds are usually slightly longer, while the single bonds are slightly longer than typical values for polyynes with carbon chains of that length.[18]

Contraction coefficients of polyyne chains are given in Table 2. Compounds **2**-C_6THI-Vin, **3**-C_6THI-Vin, and **2**-C_8THI-Vin are nearly linear with very low contraction coefficients (C1-Cn = 0.00−0.04%; C_{py}-C_{Ph} = 0.00−0.03%).

Since polyynes hold great potential for 1,*n*-topochemical polymerization,[4,19] we have analyzed packing arrangements of the polyynyl-substituted pyrroles. In four cases (**1**-C_6THI-Me, **2**-C_6THI-Vin, **3**-C_6THI-Vin, and **2**-C_8THI-Vin), molecules form in the solid state "head-to-tail" chains with strong $\pi\cdots\pi$ interactions between carbon chains which makes them good candidates for topochemical process. Next, the closest chain−chain separation was analyzed, which is understood as the closest carbon−carbon distance from two neighboring carbon chains. As revealed by thorough analysis, the closest distances between two carbon atoms of parallel chains are 3.702 Å for **1**-C_6THI-Me, 3.509 Å for **2**-C_6THI-Vin, 3.565 Å for **3**-C_6THI-Vin, and 3.422 Å for **2**-C_8THI-Vin, which is slightly above the sum of the van der Waals radii (3.4 Å).[20] Example of the packing diagram for **2**-C_8THI-Vin is given in Figure 2.

CONCLUSIONS

In summary, we have shown an effective and convenient way to novel pyrrole end-capped polyynes. For the first time, hexatriynyl- and ocatatetraynyl-pyrroles were obtained in reasonable to high yields, and the coupling reaction required only simple grinding of substrates with potassium carbonate under solvent- and transition metal-free conditions. Products were characterized using ^{1}H and ^{13}C NMR and ESI-MS techniques. Further, the first solid state structures of long polyynyl-substituded pyrroles were obtained, and their packing analysis revealed that four of them are promising candidates for 1,*n*-topochemical polymerization. We believe, that such a simple mechanochemical approach may lead to new synthetic protocols for novel carbon rods.

EXPERIMENTAL SECTION

General. All moisture- and air-sensitive reactions were conducted under N_2 with the use of standard Schlenk techniques. Inverse Sonogashira coupling reactions were carried out in the presence of air and moisture. Glassware was predried at 120 °C. Solvents were treated as follows: THF was distilled from Na/benzophenone, and CH_3CN (HPLC grade), hexane (HPLC grade), DCM (pure per analysis), and diethyl ether (pure per analysis) were used as received. CuI (99%), *N*-bromosuccinimide (99%), NH(*i*-Pr)$_2$ (99.5%), $Pd(PPh_3)_2Cl_2$ (99.5%), and K_2CO_3 (pure per analysis) were used as received. **1**-C_6Br, **1**-C_8I, **2**-C_6TMS, **2**-C_8I, **3**-C_2Br, **4**-C_2Br, **5**-C_2Br, butadiynyltrimethylsilane, and all pyrroles were obtained according to the known procedures.[12c,d,21]

^{1}H and ^{13}C{^{1}H}NMR spectra were recorded on 300 and 500 MHz spectrometers with an inverse broadband probe. For the ^{1}H NMR spectra, chemical shifts in chloroform-*d* were reported in the scale relative to the solvent residual peak (7.26 ppm for $CDCl_3$). For the ^{13}C{^{1}H}NMR spectra, chemical shifts were reported in the scale relative to $CDCl_3$ (77.16 ppm). 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. IR spectra were recorded with the use of an FTIR spectrometer, and the

DOI: 10.1021/acs.joc.6b01732
J. Org. Chem. 2016, 81, 9188−9198

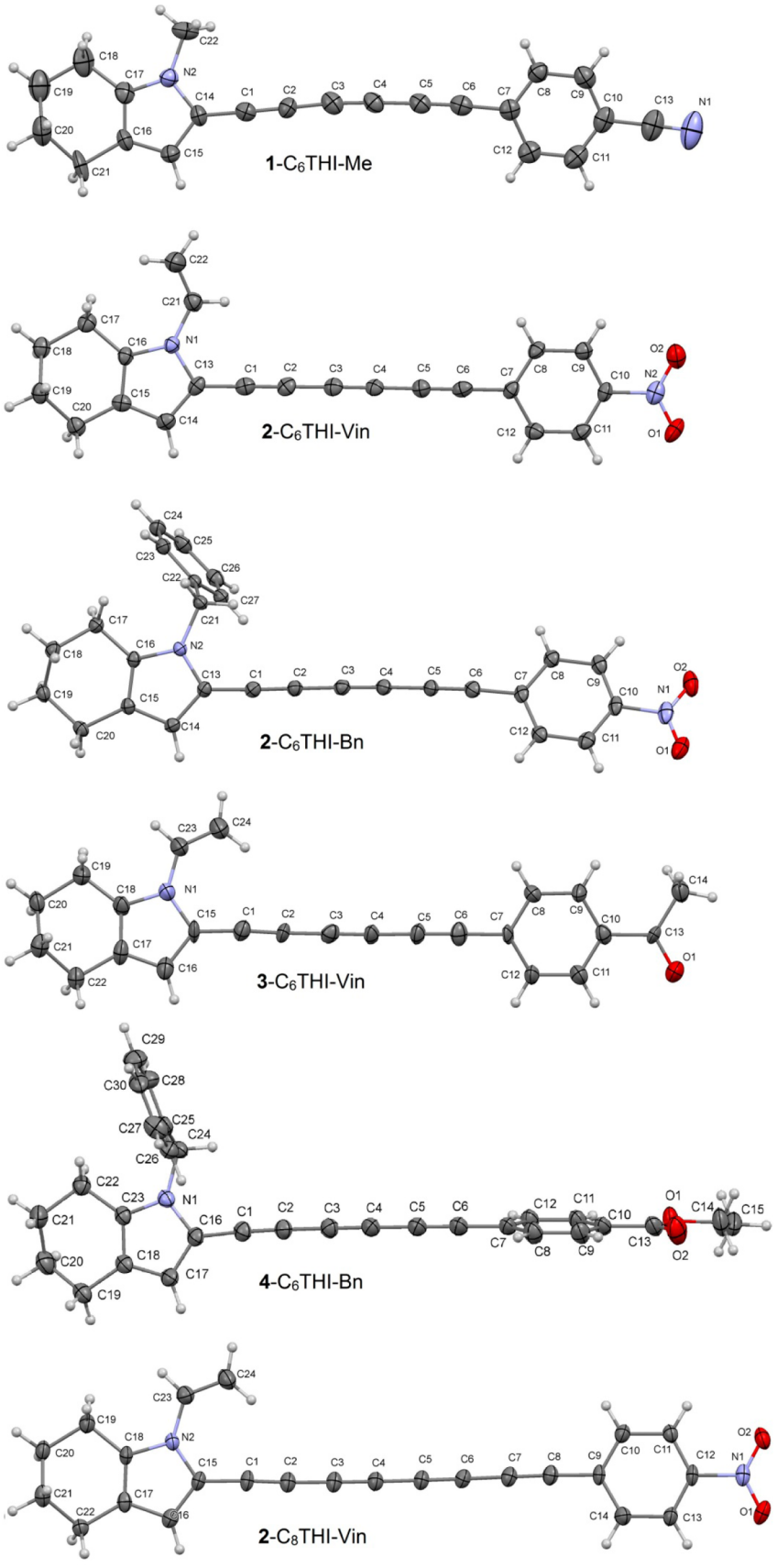


Figure 1. Molecular structures of coupling products. Thermal ellipsoids are given at 50% probability level. For **1**-C_6THI-Me and **4**-C_6THI-Bn, disorder is omitted for clarity.

DOI: 10.1021/acs.joc.6b01732
J. Org. Chem. 2016, 81, 9188−9198

Table 1. Bond Lengths in the Polyyne Chains [Å]

	Cpy-C1	C1−C2	C2−C3	C3−C4	C4−C5	C5−C6	C6−C7	C7−C8	CX-C_{Ph}
1-C_6THI-Me	1.381(4)	1.235(5)	1.311(4)	1.212(2)	1.361(3)	1.207(3)			1.430(3)
2-C_6THI-Vin	1.424(5)	1.207(5)	1.368(5)	1.209(5)	1.368(5)	1.205(5)			1.431(5)
2-C_6THI-Bn	1.419(2)	1.231(2)	1.386(2)	1.231(2)	1.398(2)	1.233(2)			1.458(2)
3-C_6THI-Vin	1.405(7)	1.208(7)	1.381(8)	1.208(7)	1.360(8)	1.212(8)			1.436(8)
4-C_6THI-Bn	1.404(2)	1.218(2)	1.354(2)	1.215(2)	1.357(2)	1.207(2)			1.430(2)
2-C_8THI-Vin	1.428(4)	1.201(4)	1.359(4)	1.219(4)	1.351(4)	1.218(4)	1.361(4)	1.212(4)	1.428(4)

Table 2. Contraction Coefficients for Polyyne Chains

	1-C_6THI-Me	**2**-C_6THI-Vin	**2**-C_6THI-Bn	**3**-C_6THI-Vin	**4**-C_6THI-Bn	**2**-C_8THI-Vin
C1-Cn[a]	0.21%	0.00%	0.12%	0.05%	0.16%	0.04%
C_{py}-C_{Ph}[b]	0.26%	0.00%	0.22%	0.03%	0.34%	0.03%

[a]Contraction C1−C*n* = (sum of C1−C*n* bond lengths − C1−C*n* distance)/sum of C1−C*n* bond lengths ×100%. [b]Contraction C_{py}-C_{Ph} = (sum of C_{py}-C_{Ph} bond lengths − C_{py}-C_{Ph} distance)/sum of C_{py}-C_{Ph} bond lengths ×100%.

samples were measured as fluorinated oil mulls. UV−vis spectra were recorded with the use of a one-beam spectrophometer.

Synthesis of New Trimethylsilyl-Protected Hexatriynes. *(**3**-C_6TMS) 1-(4-((Trimethylsilyl)hexatriynyl)phenyl)ethanone. General Procedure for the Cadiot−Chodkiewicz Cross-Coupling.* **3**-C_2Br (1.01 g, 4.53 mmol), butadiynyltrimethylsilane (0.667 g, 5.46 mmol), $Pd(PPh_3)_2Cl_2$ (0.064 g, 0.091 mmol), and CuI (0.035 g, 0.18 mmol) were dissolved in THF (20 mL) under N_2 atmosphere. The mixture was degassed three times with the use of a freeze−pump−thaw technique, and next, $NH(i\text{-}Pr)_2$ (1.61 mL, 11.5 mmol) was added. After 24 h, the solvent was removed under reduced pressure, and the product was purified by flash silica gel column chromatography (eluent: DCM/hexane, v/v, 1/3) to give 0.502 g (1.90 mmol) of yellow solid. Yield: 42%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92−7.90 (m, 2H, C_6H_4), 7.62−7.58 (m, 2H, C_6H_4), 2.60 (s, 3H, CH_3), 0.23 (s, 9H, $SiMe_3$). $^{13}C\{^1H\}$NMR (126 MHz, $CDCl_3$) δ 197.2 (C═O), 137.4 (C_{Ar}C═O), 133.3 (CH from C_6H_4), 128.4 (CH from C_6H_4), 125.8 (C_{Ar}C≡C), 90.3 (SiC≡C), 87.9 (C≡C), 77.4 (C_6H_4C≡C), 75.7 (C≡C), 68.5 (C≡C), 61.2 (C≡C), 26.8 (CH_3), −0.4 ($Si(CH_3)_3$). HRMS (ESI): *m*/*z* calcd for $C_{17}H_{17}OSi$, 265.1043 [M+H^+]; found, 265.1050.

*(**4**-C_6TMS) Ethyl 4-((trimethylsilyl)hexatriynyl)benzoate.* According to the general procedure for Cadiot−Chodkiewicz cross-coupling, **4**-C_2Br (0.265 g, 1.05 mmol), butadiynyltrimethylsilane (0.155 g, 1.27 mmol), $Pd(PPh_3)_2Cl_2$ (0.037 g, 0.053 mmol), CuI (0.010 g, 0.053 mmol), $NH(i\text{-}Pr)_2$ (0.34 mL, 2.4 mmol), and THF (15 mL) were used. Time, 4.5 h; purification, silica gel chromatography (hexane/DCM, v/v, 1/1); beige solid; yield, 33% (0.102 g, 0.346 mmol). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 (d, J_{HH} = 8.6 Hz, 2H, C_6H_4), 7.55 (d, J_{HH} = 8.6 Hz, 2H, C_6H_4), 4.37 (q, J_{HH} = 7.1 Hz, 2H, OCH_2), 1.38 (t, J_{HH} = 7.1 Hz, 3H, CH_3), 0.22 (s, 9H, $SiMe_3$). $^{13}C\{^1H\}$NMR (126 MHz, $CDCl_3$) δ 165.8 (C═O), 133.0 (CH from C_6H_4), 131.3 (C_{Ar}C═O), 129.6 (CH from C_6H_4), 125.4 (C_{Ar}C≡C), 90.1 (SiC≡C), 87.9 (C≡C), 76.9 (C_6H_4C≡C), 75.8 (C≡C), 68.2 (C≡C), 61.4 (OCH_2), 61.2 (C≡C), 14.4 (CH_3), −0.4 ($Si(CH_3)_3$). HRMS(ESI): *m*/*z* calcd for $C_{18}H_{18}O_2SiNa$, 317.0968 [M+Na^+]; found, 317.0963.

*(**5**-C_6TMS) 4-((Trimethylsilyl)hexatriynyl)phenyl Acetate.* According to the general procedure for Cadiot−Chodkiewicz cross-coupling, **5**-C_2Br (0.197 g, 0.824 mmol), butadiynyltrimethylsilane (0.121 g, 0.990 mmol), $Pd(PPh_3)_4$ (0.029 g, 0.041 mmol), CuI (0.0078 g, 0.041 mmol), $NH(i\text{-}Pr)_2$ (0.29 mL, 2.1 mmol), and THF (15 mL) were used. Time, 4.5 h; purification, silica gel chromatography (hexane/DCM, v/v, 1/1); beige solid; yield, 47% (0.108 g. 0.385 mmol). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 (d, J_{HH} = 8.8 Hz, 2H, C_6H_4), 7.07 (d, J_{HH} = 8.8 Hz, 2H, C_6H_4), 2.30 (s, 3H, CH_3), 0.22 (s, 9H, $SiMe_3$). $^{13}C\{^1H\}$NMR (126 MHz, $CDCl_3$) δ 169.0 (C═O), 151.8 (C_{Ar}O), 134.5 (CH from C_6H_4), 122.1 (CH from C_6H_4), 118.6 (C_{Ar}C≡C), 89.3 (SiC≡C), 88.1 (C≡C), 76.1 (C_6H_4C≡C), 74.6 (C≡C), 67.1 (C≡C), 61.6 (C≡C), 21.3 (CH_3), −0.4 ($Si(CH_3)_3$). HRMS(ESI): *m*/*z* calcd for $C_{17}H_{16}O_2SiNa$, 303.0812 [M+Na^+]; found, 303.0813.

Sythesis of New 1-Bromohexatriynes. *(**2**-C_6Br) 4-(Bromohexatriynyl)nitrobenzene. General Procedure for the Bromination of Trimethylsilyl-Protected Polyynes.* **2**-C_6TMS (0.124 g, 0.464 mmol) was dissolved in acetonitrile (10 mL). Next *N*-bromosuccinimide (0.100 g, 0.562 mmol), AgF (0.060 g, 0.47 mmol), and H_2O (17 μL) were added. The flask was wrapped with aluminum foil, and the mixture was stirred for 22 h. Next, the solvent was removed under reduced pressure, and the product was purified by passing through a short silica gel plug (DCM/hexane, v/v, 1/2) to give 0.122 g (0.445 mmol) of yellow, quickly darkening crystals. Yield:

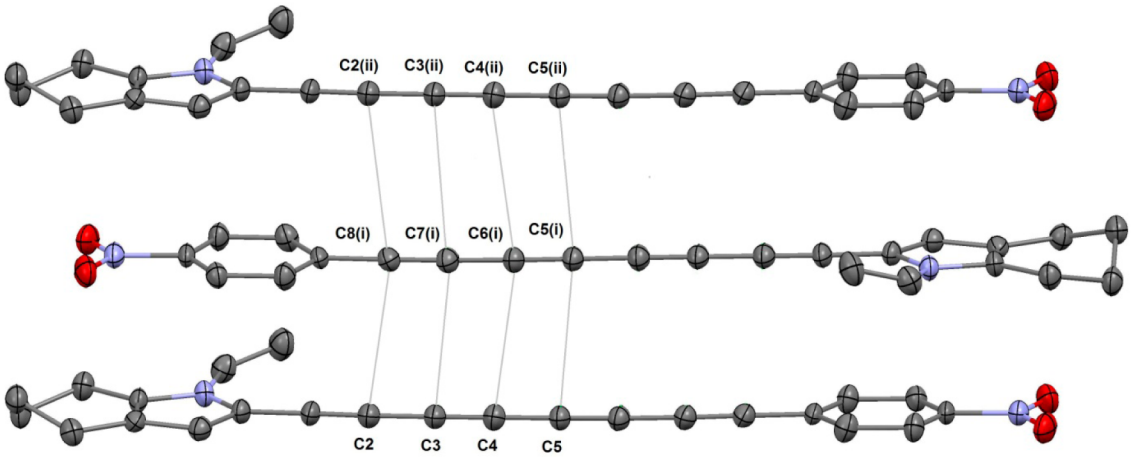


Figure 2. Packing motif for **2**-C_8THI-Vin. The closest intermolecular C−C distances [Å]: C2−C8(i)═C8(i)-C2(ii) 3.448, C3−C7(i)═C7(i)-C3(ii) 3.422, C4−C6(i)═C6(i)-C4(ii) 3.445, and C5−C5(i)═C5(i)-C5(ii) 3.466. Symmetry operations for related atoms are (i) −x, −1 + x, z; (ii) − x, −1/2 + y, 1/2−x.

DOI: 10.1021/acs.joc.6b01732
J. Org. Chem. 2016, 81, 9188−9198

96%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.23−8.18 (m, 2H, CH_{Ar}), 7.70−7.64 (m, 2H, CH_{Ar}). $^{13}C\{^1H\}$NMR (126 MHz, $CDCl_3$) δ 148.0 (CNO_2), 134.0 (CH_{Ar}), 127.8 ($C_{Ph}C{\equiv}C$), 123.9 (CH_{Ar}), 79.0 (C≡C), 73.2 (C≡C), 69.8 (C≡C), 65.9 (C≡C), 58.2 (C≡C), 45.1 (C≡CBr). HRMS(ESI): m/z calcd for $C_{12}H_5BrNO_2Na$, 273.9498 [M+Na$^+$]; found, 273.9493.

*(**3**-C$_6$Br) 1-(4-(Bromohexatriynyl)phenyl)ethanone.* According to the general procedure for bromination of trimethylsilyl-protected polyynes **3**-C$_6$TMS (0.077 g, 0.29 mmol), *N*-bromosuccinimide (0.062 g, 0.35 mmol), $AgNO_3$ (0.049 g, 0.29 mmol), KF (0.017 g, 0.29 mmol), H_2O (10 μL), and acetonitrile (10 mL) were used. Time, 6 h; purification, short silica gel plug (hexane/DCM, v/v, 1/1); yellow solid (which quickly changed to dark green or brown); yield, 79% (0.062 g, 0.23 mmol). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93−7.90 (m, 2H, C_6H_4), 7.62−7.59 (m, 2H, C_6H_4), 2.60 (s, 3H, CH_3). $^{13}C\{^1H\}$-NMR (126 MHz, $CDCl_3$) δ 197.1 (C=O), 137.5 ($C_{Ar}C$=O), 133.4 (CH from C_6H_4), 128.4 (CH from C_6H_4), 125.6 ($C_{Ar}C{\equiv}C$), 77.2 ($C_6H_4C{\equiv}C$), 74.7 (C≡C), 68.7 (C≡C), 66.1 (C≡C), 58.6 (C≡C), 44.1 (C≡CBr), 26.8 (CH_3). HRMS(ESI): m/z calcd for $C_{14}H_8BrO$, 270.9753 [M+H$^+$]; found, 270.9753.

*(**4**-C$_6$Br) Ethyl 4-(bromohexatriynyl)benzoate.* According to the general procedure for the bromination of trimethylsilyl-protected polyynes **4**-C$_6$TMS (0.102 g, 0.35 mmol), *N*-bromosuccinimide (0.074 g, 0.42 mmol), $AgNO_3$ (0.059 g, 0.346 mmol), KF (0.020 g, 0.35 mmol), H_2O (13 μL), and acetonitrile (10 mL) were used. Time, 2.5 h; purification, short silica gel plug (hexane/DCM, v/v, 1/1); yellow solid (which quickly changed to dark green or brown); yield, 86% (0.092 g. 0.30 mmol). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01−7.98 (m, 2H, C_6H_4), 7.58−7.55 (m, 2H, C_6H_4), 4.38 (q, J_{HH}= 7.1 Hz, 2H, OCH_2), 1.39 (t, J_{HH} = 7.1 Hz, CH_3). $^{13}C\{^1H\}$NMR (126 MHz, $CDCl_3$) δ 165.8 (C=O), 133.1 (CH from C_6H_4), 131.4 ($C_{Ar}C$=O), 129.7 (CH from C_6H_4), 125.3 ($C_{Ar}C{\equiv}C$), 76.8 ($C_6H_4C{\equiv}C$), 74.8 (C≡C), 68.5 (C≡C), 66.1 (C≡C), 61.5 (OCH_2), 58.7 (C≡C), 44.0 (C≡CBr), 14.4 (CH_3). HRMS(ESI): m/z calcd for $C_{15}H_9BrO_2Na$, 322.9678 [M+Na$^+$]; found, 322.9682.

*(**5**-C$_6$Br) 4-(Bromohexatriynyl)phenyl Acetate.* According to the general procedure for bromination of trimethylsilyl-protected polyynes **5**-C$_6$TMS (0.108 g, 0.357 mmol), *N*-bromosuccinimide (0.082 g, 0.46 mmol), $AgNO_3$ (0.065 g, 0.38 mmol), KF (0.022 g, 0.38 mmol), H_2O (14 μL), and acetonitrile (10 mL) were used. Time, 6 h; purification, short silica gel plug (hexane/DCM, v/v, 1/1); yellow solid (which quickly changed to dark green or brown); yield, 67% (0.070 g, 0.24 mmol). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55−7.52 (m, 2H, C_6H_4), 7.09−7.06 (m, 2H, C_6H_4), 2.30 (s, 3H, CH_3). $^{13}C\{^1H\}$NMR (126 MHz, $CDCl_3$) δ 168.8 (C=O), 151.7 ($C_{Ar}O$), 134.4 (CH from C_6H_4), 122.0 (CH from C_6H_4), 118.2 ($C_{Ar}C{\equiv}C$), 74.9 ($C_6H_4C{\equiv}C$), 74.3 (C≡C), 67.2 (C≡C), 66.0 (C≡C), 58.9 (C≡C), 42.9 (C≡CBr), 21.1 (CH_3). HRMS(ESI): m/z calcd for $C_{14}H_7BrO_2Na$, 308.9522 [M+Na$^+$]; found, 308.9514.

Synthesis of Polyynyl-Substituted Pyrroles. *(**1**-C$_6$THI-H), 4-((4,5,6,7-Tetrahydro-1H-indol-2-yl)hexatriynyl)benzonitrile. General Procedure for Inverse Sonogashira Coupling.* **1**-C$_6$Br (0.0080 g, 0.031 mmol), 4,5,6,7-tetrahydro-1*H*-indole (0.0080 g, 0.062 mmol), and K_2CO_3 (0.160 g) were placed in a mortar and ground for 10 min. After this time, the mixture was placed in a vial and left for 24 h. Then, the mixture was placed at the top of silica gel column, and the product was eluted with a mixture of hexane and dichloromethane (v/v; 1/1). Pure product was obtained as a yellow solid (0.0047 g, 0.016 mmol); yield, 52%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 (bs, 1H, N*H*), 7.64−7.56 (m, 4H, C_6H_4), 6.47 (d, J_{HH} = 2.3 Hz, 1H, pyrrole), 2.57 (t, J_{HH} = 6.2 Hz, 2H, CH_2), 2.47 (t, J_{HH} = 6.0 Hz, 2H, CH_2), 1.84−1.78 (m, 2H, CH_2), 1.78−1.69 (m, 2H, CH_2). $^{13}C\{^1H\}$NMR (126 MHz, $CDCl_3$) δ 133.3 ($NCCH_2$, pyrrole), 132.5 (CH, C_6H_4CN), 132.2 (CH, C_6H_4CN), 126.6 ($C_{Ar}C{\equiv}C$), 119.4 ($C_{THI}C{\equiv}C$), 119.3 (C≡N), 112.6 (CC≡N), 108.7 ($HCCH_2$, pyrrole), 79.0 (C≡C), 77.9 (C≡C), 77.8 (C≡C), 74.2 (C≡C), 69.7 (C≡C), 68.5 (C≡C), 23.5 (CH_2), 23.2 (CH_2), 23.0 (CH_2), 22.8 (CH_2). IR (fluorinated oil mull) 2224 (N≡C), 2140 (C≡C), 2092 (C≡C) cm^{-1}. HRMS(ESI): m/z calcd for $C_{21}H_{14}N_2$, 295.1230 [M+H$^+$]; found, 295.1230.

*(**1**-C$_6$THI-Me), 4-((1-Methyl-4,5,6,7-tetrahydro-1H-indol-2-yl)-hexatriynyl)benzonitrile.* According to the general procedure for inverse Sonogashira coupling, **1**-C$_6$Br (0.0084 g, 0.033 mmol), 1-methyl-4,5,6,7-tetrahydro-1*H*-indole (0.0089 g, 0.066 mmol), and K_2CO_3 (0.170 g) were used. Time, 3 h; purification, short silica gel plug (hexane/DCM, v/v, 1/1); yellow solid (0.0083 g, 0.027 mmol); yield, 82%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63−7.57 (m, 4H, C_6H_4), 6.46 (s, 1H, C*H*, pyrrole), 3.51 (s, 3H, CH_3), 2.52 (t, J_{HH} = 6.3 Hz, 2H, CH_2), 2.46 (t, J_{HH} = 6.1 Hz, 2H, CH_2), 1.86−1.80 (m, 2H, CH_2), 1.74−1.69 (m, 2H, CH_2). ^{13}C NMR (126 MHz, $CDCl_3$) δ 134.3 ($NCCH_2$, pyrrole), 133.3 (CH, C_6H_4CN), 132.2 (CH, C_6H_4CN), 126.7 ($C_{Ar}C{\equiv}C$), 118.8 ($C_{THI}C{\equiv}C$), 118.4 (C≡N), 118.2 (CH, pyrrole), 112.6 (CC≡N), 111.8 ($CHCCH_2$, pyrrole), 80.5 (C≡C), 79.1 (C≡C), 78.3 (C≡C), 73.9 (C≡C), 69.9 (C≡C), 69.3 (C≡C), 31.2 (CH_3), 23.4 (CH_2), 23.0 (CH_2), 23.0 (CH_2), 22.6 (CH_2). IR (fluorinated oil mull) 2222 (N≡C), 2147 (C≡C), 2095 (C≡C) cm^{-1}. HRMS(ESI): m/z calcd for $C_{22}H_{17}N_2$, 309.1386 [M+H$^+$]; found, 309.1364.

*(**1**-C$_6$THI-Vin), 4-((1-Vinyl-4,5,6,7-tetrahydro-1H-indol-2-yl)-hexatriynyl)benzonitrile.* According to the general procedure for inverse Sonogashira coupling, **1**-C$_6$Br (0.010 g, 0.040 mmol), 1-vinyl-4,5,6,7-tetrahydro-1*H*-indole (0.012 g, 0.080 mmol), and K_2CO_3 (0.220 g) were used. Time, 24 h; purification, short silica gel plug (hexane/DCM, v/v, 1/1); yellow solid (0.0051 g, 0.016 mmol); yield, 40%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63−7.56 (m, 4H, C_6H_4CN), 6.89 (dd, J_{HH} = 16.0, 9.3 Hz, 1H, C*H*=CH_2), 6.55 (s, 1H, pyrrole), 5.39 (dd, J_{HH} = 16.0, 1.2 Hz, 1H, CH=C*H*$_2$), 4.93 (dd, J_{HH} = 9.3, 1.2 Hz, 1H, CH=C*H*$_2$), 2.64 (t, J_{HH} = 6.2 Hz, 2H, CH_2), 2.47 (t, J = 6.1 Hz, 2H, CH_2), 1.86−1.79 (m, 2H, CH_2), 1.76−1.69 (m, 2H, CH_2). ^{13}C NMR (126 MHz, $CDCl_3$) δ 133.5 ($NCCH_2$, pyrrole), 133.3 (CH from C_6H_4CN), 132.2 (CH from C_6H_4CN), 130.0 (CH=CH_2), 126.5 ($C_{Ar}C{\equiv}C$), 121.1 (CH, pyrrole), 120.6 ($C_{THI}C{\equiv}C$), 118.3 (C≡N), 112.7 (CC≡N), 111.2 ($CHCCH_2$, pyrrole), 103.8 (CH=CH_2), 80.6 (C≡C), 78.9 (C≡C), 78.3 (C≡C), 73.4 (C≡C), 69.6 (C≡C), 69.3 (C≡C), 24.2 (CH_2), 23.1 (CH_2), 23.0 (CH_2), 23.0 (CH_2). IR (fluorinated oil mull) 2223 (N≡C), 2151 (C≡C), 2097 (C≡C) cm^{-1}. HRMS(ESI): m/z calcd for $C_{23}H_{16}N_2$, 321.1386 [M+H$^+$]; found, 321.1387.

*(**1**-C$_6$THI-Bn), 4-((1-Benzyl-4,5,6,7-tetrahydro-1H-indol-2-yl)-hexatriynyl)benzonitrile.* According to the general procedure for inverse Sonogashira coupling, **1**-C$_6$Br (0.0060 g, 0.024 mmol), 1-benzyl-4,5,6,7-tetrahydro-1*H*-indole (0.010 g, 0.048 mmol), and K_2CO_3 (0.160 g) were used. Time, 3 h; purification, short silica gel plug (hexane/DCM, v/v, 1/1); yellow solid (0.0079 g, 0.021 mmol); yield, 88%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62−7.54 (m, 4H, $C_6H_4C{\equiv}N$), 7.34−7.30 (m, 2H, C_6H_5), 7.29−7.24 (m, 1H, C_6H_5), 7.08−7.03 (m, 2H, C_6H_5), 6.54 (s, 1H, C*H*, pyrrole), 5.10 (s, 2H, CH_2Ph), 2.48 (t, J_{HH} = 6.0 Hz, 2H, CH_2), 2.40 (t, J_{HH} = 6.2 Hz, 2H, CH_2), 1.79−1.73 (m, 2H, CH_2), 1.73−1.65 (m, 2H, CH_2). ^{13}C NMR (126 MHz, $CDCl_3$) δ 137.6 (*ipso* from C_6H_5), 134.2 ($NCCH_2$, pyrrole), 133.2 (CH from C_5H_4CN), 132.2 (CH from C_5H_4CN), 128.9 (CH, C_6H_5), 127.6 (CH, *ortho* from C_6H_5), 126.8 (CH, C_6H_5), 126.6 ($C_{Ph}C{\equiv}C$), 119.4 (CH, pyrrole), 118.7 ($C_{THI}C{\equiv}C$), 118.3 (C≡N), 112.6 (CC≡N), 112.0 ($CHCCH_2$, pyrrole), 80.5 (C≡C), 79.0 (C≡C), 78.3 (C≡C), 73.8 (C≡C), 69.9 (C≡C), 69.3 (C≡C), 48.4 (CH_2Ph), 23.3 (CH_2), 23.1 (CH_2), 22.9 (CH_2), 22.8 (CH_2). IR (fluorinated oil mull) 2226 (N≡C), 2140 (C≡C), 2091 (C≡C) cm^{-1}. HRMS(ESI): m/z calcd for $C_{28}H_{21}N_2$, 385.1699 [M+H$^+$]; found, 385.1699.

*(**2**-C$_6$THI-H), 2-((4-Nitrophenyl)hexatriynyl)-4,5,6,7-tetrahydro-1H-indole.* According to the general procedure for inverse Sonogashira coupling, **2**-C$_6$Br (0.0090 g, 0.033 mmol), 4,5,6,7-tetrahydro-1*H*-indole (0.0080 g, 0.066 mmol), and K_2CO_3 (0.170 g) were used. Time, 3 d; purification, short silica gel plug (hexane/DCM, v/v, 1/1); red solid (0.0047 g, 0.014 mmol); yield, 42%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.15−8.07 (m, 2H, $C_6H_4NO_2$), 7.97 (s, 1H, N*H*), 7.61−7.54 (m, 2H, $C_6H_4NO_2$), 6.41 (d, J_{HH} = 2.3 Hz, 1H, C*H*, pyrrole), 2.50 (t, J_{HH} = 6.1 Hz, 2H, CH_2), 2.40 (t, J_{HH} = 6.0 Hz, 2H, CH_2), 1.78−1.71 (m, 2H, CH_2), 1.70−1.63 (m, 2H, CH_2). ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.7 (CNO_2), 133.6 ($NCCH_2$, pyrrole), 132.6 (CH from

DOI: 10.1021/acs.joc.6b01732
J. Org. Chem. 2016, 81, 9188−9198

C_6H_4), 128.6 ($C_{Ph}C{\equiv}C$), 123.9 (*C*H from C_6H_4), 119.4 (CH, pyrrole), 108.7 ($CHCCH_2$, pyrrole), 79.9 (*C*≡C), 77.8 (*C*≡C), 77.7 (*C*≡C), 74.5 (*C*≡C), 70.2 (*C*≡C), 68.5 (*C*≡C), 23.5 (CH_2), 23.2 (CH_2), 23.0 (CH_2), 22.8 (CH_2). IR (fluorinated oil mull) 2145 (C≡C), 2093 (C≡C) cm^{-1}. HRMS(ESI): *m*/*z* calcd for $C_{24}H_{17}N_2$, 315.1128 [M+H$^+$]; found, 315.1130.

*(**2**-C_6THI-Me), 1-Methyl-2-((4-nitrophenyl)hexatriynyl)-4,5,6,7-tetrahydro-1H-indole.* According to the general procedure for inverse Sonogashira coupling, **2**-C_6Br (0.0176 g, 0.064 mmol), 1-methyl-4,5,6,7-tetrahydro-1*H*-indole (0.0174 g, 0.064 mmol), and K_2CO_3 (0.170 g) were used. Time, 24 h; purification, short silica gel plug (hexane/DCM, v/v, 1/2); red solid (0.0122 g, 0.037 mmol); yield, 58%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.22−8.18 (m, 2H, $C_6H_4NO_2$), 7.67−7.63 (m, 2H, $C_6H_4NO_2$), 6.47 (s, 1H, pyrrole), 3.52 (s, 3H, CH_3), 2.52 (t, J_{HH} = 6.3 Hz, 2H, CH_2), 2.46 (t, J_{HH} = 6.1 Hz, 2H, CH_2), 1.87−1.80 (m, 2H, CH_2), 1.75−1.69 (m, 2H, CH_2). ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.6 (CNO_2), 134.4 ($NCCH_2$, pyrrole), 133.6 (*C*H from C_6H_4), 128.7 ($C_{Ph}C{\equiv}C$), 123.8 (*C*H from C_6H_4), 118.9 ($C_{THI}C{\equiv}C$), 118.3 (CH, pyrrole), 111.8 ($CHCCH_2$, pyrrole), 80.6 (*C*≡C), 79.9 (*C*≡C), 78.1 (*C*≡C), 74.2 (*C*≡C), 70.4 (*C*≡C), 69.4 (*C*≡C), 31.3 (CH_3), 23.4 (CH_2), 23.1 (CH_2), 23.0 (CH_2), 22.6 (CH_2). IR (fluorinated oil mull) 2144 (C≡C), 2096 (C≡C) cm^{-1}. HRMS(ESI): *m*/*z* calcd for $C_{21}H_{16}N_2O_2Na$, 351.1103 [M+Na$^+$]; found, 351.1107.

*(**2**-C_6THI-Vin), 2-((4-Nitrophenyl)hexatriynyl)-1-vinyl-4,5,6,7-tetrahydro-1H-indole.* According to the general procedure for inverse Sonogashira coupling, **2**-C_6Br (0.0115 g, 0.042 mmol), 1-vinyl-4,5,6,7-tetrahydro-1*H*-indole (0.0124 g, 0.084 mmol), and K_2CO_3 (0.240 g) were used. Time, 24 h; purification, short silica gel plug (hexane/DCM, v/v, 1/2); red solid (0.0116 g, 0.034 mmol); yield, 81%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.22−8.17 (m, 2H, $C_6H_4NO_2$), 7.67−7.62 (m, 2H, $C_6H_4NO_2$), 6.89 (dd, J_{HH} = 16.0, 9.3 Hz, 1H, $CH{=}CH_2$), 6.56 (s, 1H, pyrrole), 5.40 (dd, J_{HH} = 16.0, 1.2 Hz, 1H, $CH{=}CH_2$), 4.93 (dd, J_{HH} = 9.3, 1.2 Hz, 1H, $CH{=}CH_2$), 2.64 (t, J_{HH} = 6.2 Hz, 2H, CH_2), 2.47 (t, J_{HH} = 6.1 Hz, 2H, CH_2), 1.86−1.80 (m, 2H, CH_2), 1.76−1.70 (m, 2H, CH_2). ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.7 (CNO_2), 133.6 (*C*H from C_6H_4), 130.0 ($C_{Ar}C{\equiv}C$), 128.4 (*C*H from C_6H_4), 123.8 (*C*H of C_6H_4), 121.2 (CH, pyrrole), 120.6 ($C_{THI}C{\equiv}C$), 111.2 ($CHCCH_2$, pyrrole), 103.9 ($HC{=}CH_2$), 80.7 (*C*≡C), 79.8 (*C*≡C), 78.0 (*C*≡C), 73.7 (*C*≡C), 70.1 (*C*≡C), 69.3 (*C*≡C), 24.2 (CH_2), 23.1 (CH_2), 23.0 (CH_2), 23.0 (CH_2). IR (fluorinated oil mull) 2147 (C≡C), 2096 (C≡C) cm^{-1}. HRMS(ESI): *m*/*z* calcd for $C_{22}H_{17}N_2O_2$, 341.1286 [M+H$^+$]; found, 341.1293.

*(**2**-C_6THI-Bn) 1-Benzyl-2-((4-nitrophenyl)hexatriynyl)-4,5,6,7-tetrahydro-1H-indole.* According to the general procedure for inverse Sonogashira coupling **2**-C_6Br (0.0155 g, 0.0566 mmol), 1-benzyl-4,5,6,7-tetrahydro-1*H*-indole (0.024 g, 0.132 mmol), and K_2CO_3 (0.390 g) were used. Time, 24 h; purification, short silica gel plug (hexane/DCM, v/v, 1/1); red solid (0.0224 g, 0.055 mmol); yield, 97%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.21−8.17 (m, 2H, C_6H_4), 7.65−7.60 (m, 2H, C_6H_4), 7.35−7.30 (m, 2H, C_6H_5), 7.29−7.25 (m, 1H, C_6H_5), 7.08−7.04 (m, 2H, C_6H_5), 6.55 (s, 1H, CH, pyrrole), 5.10 (s, 2H, CH_2Ph), 2.48 (t, J_{HH} = 5.9 Hz, 2H, CH_2), 2.40 (t, J_{HH} = 6.1 Hz, 2H, CH_2), 1.79−1.73 (m, 2H, CH_2), 1.72−1.66 (m, 2H, CH_2). ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.6 (CNO_2), 137.6 (*ipso* from C_6H_5), 134.3 ($NCCH_2$, pyrrole), 133.6 (*C*H from C_6H_4), 128.9 (CH, C_6H_5), 128.6 ($C_{Ar}C{\equiv}C$), 127.6 (CH, *ortho* from C_6H_5), 126.8 (CH, C_6H_5), 123.8 (CH from C_6H_4), 119.5 ($C_{THI}C{\equiv}C$), 118.9 (CH, pyrrole), 112.0 ($CHCCH_2$, pyrrole), 79.9 (*C*≡C), 78.1 (*C*≡C), 74.2 (*C*≡C), 70.4 (*C*≡C), 69.4 (*C*≡C), 48.5 (CH_3), 23.3 (CH_2), 23.1 (CH_2), 22.9 (CH_2), 22.8 (CH_2). HRMS(ESI): *m*/*z* calcd for $C_{27}H_{21}N_2O_2$, 405.1598 [M+H$^+$]; found, 405.1596.

*(**3**-C_6THI-H), 1-(4-((4,5,6,7-Tetrahydro-1H-indol-2-yl)hexatriynyl)-phenyl)ethanone.* According to the general procedure for inverse Sonogashira coupling, **3**-C_6Br (0.0140 g, 0.0516 mmol), 4,5,6,7-tetrahydro-1*H*-indole (0.0125 g, 0.104 mmol), and K_2CO_3 (0.265 g) were used. Time, 22 h; purification, short silica gel plug (hexane/DCM, v/v, 1/1); yellow solid (0.0013 g, 0.0042 mmol); yield, 8%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (s, 1H, N*H*), 7.93−7.89 (m, 2H, C_6H_4), 7.61−7.57 (m, 2H, C_6H_4), 6.46 (d, J_{HH} = 2.4 Hz, 1H, pyrrole), 2.60 (s, 3H, $C(O)CH_3$), 2.57 (t, J_{HH} = 6.2 Hz, 2H, CH_2), 2.47 (t, J_{HH} = 6.0 Hz, 2H, CH_2), 1.84−1.78 (m, 2H, CH_2), 1.76−1.71 (m, 2H, CH_2). ^{13}C NMR (75 MHz, $CDCl_3$) δ 197.2 (C=O), 137.1 ($NCCH_2$, pyrrole), 133.1 (*C*H from C_6H_4), 132.3 ($C_{Ar}C{=}O$), 128.4 (*C*H from C_6H_4), 126.4 ($C_{Ar}C{\equiv}C$), 119.3 (CH, pyrrole), 119.1 ($C_{THI}C{\equiv}C$), 108.8 ($CHCCH_2$, pyrrole), 78.9 (*C*≡C), 77.4 (*C*≡C), 73.7 (*C*≡C), 69.0 (*C*≡C), 68.8 (*C*≡C), 26.8 ($C(O)CH_3$), 23.5 (CH_2), 23.2 (CH_2), 23.1 (CH_2), 22.8 (CH_2), one acetylene signal under solvent. HRMS(ESI): *m*/*z* calcd for $C_{22}H_{16}NO$, 310.1237 [M−H$^-$]; found, 310.1243.

*(**3**-C_6THI-Me), 1-(4-((1-Methyl-4,5,6,7-tetrahydro-1H-indol-2-yl)-hexatriynyl)phenyl)ethanone.* According to the general procedure for inverse Sonogashira coupling, **3**-C_6Br (0.0550 g, 0.203 mmol), 1-methyl-4,5,6,7-tetrahydro-1*H*-indole (0.025 g, 0.185 mmol), and K_2CO_3 (0.800 g) were used. Time, 3 h; purification, short silica gel plug (hexane/DCM, v/v, 1/1); yellow solid (0.026 g, 0.080 mmol); yield, 39%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 (d, J_{HH} = 8.6 Hz, 2H, C_6H_4), 7.59 (d, J_{HH} = 8.6 Hz, 2H, C_6H_4), 6.45 (s, 1H, pyrrole), 3.51 (s, 3H, NCH_3), 2.60 (s, 3H, $C(O)CH_3$), 2.52 (t, J_{HH} = 6.3 Hz, 2H, CH_2), 2.46 (t, J_{HH} = 6.1 Hz, 2H, CH_2), 1.86−1.80 (m, 2H, CH_2), 1.74−1.69 (m, 2H, CH_2). ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.2 (C=O), 137.1 ($NCCH_2$, pyrrole), 133.4 ($C_{Ar}C{=}O$), 133.0 (*C*H from C_6H_4), 128.4 (*C*H from C_6H_4), 126.5 ($C_{Ar}C{\equiv}C$), 118.7 ($C_{THI}C{\equiv}C$), 117.9 (CH, pyrrole), 111.9 ($CHCCH_2$, pyrrole), 80.5 (*C*≡C), 79.4 (*C*≡C), 78.0 (*C*≡C), 73.3 (*C*≡C), 69.6 (*C*≡C), 69.2 (*C*≡C), 31.2 (NCH_3), 26.8 ($C(O)CH_3$), 23.4 (CH_2), 23.05 (CH_2), 23.0 (CH_2), 22.6 (CH_2). IR (fluorinated oil mull) 2145 (C≡C), 2095 (C≡C) cm^{-1}. HRMS-(ESI): *m*/*z* calcd for $C_{23}H_{20}NO$, 326.1539 [M+H$^+$]; found, 326.1535.

*(**3**-C_6THI-Vin), 1-(4-((1-Vinyl-4,5,6,7-tetrahydro-1H-indol-2-yl)-hexatriynyl)phenyl)ethanone.* According to the general procedure for inverse Sonogashira coupling, **3**-C_6Br (0.0130 g, 0.0480 mmol), 1-vinyl-4,5,6,7-tetrahydro-1*H*-indole (0.0141 g, 0.0958 mmol), and K_2CO_3 (0.271 g) were used. Time, 20 h; purification, short silica gel plug (hexane/DCM, v/v, 1/1); yellow solid (0.0155 g, 0.0459 mmol); yield, 96%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93−7.90 (m, 2H, C_6H_4), 7.62−7.57 (m, 2H, C_6H_4), 6.90 (dd, J_{HH} = 16.0, 9.3 Hz, 1H, $CH{=}CH_2$), 6.53 (s, 1H, pyrrole), 5.39 (dd, J_{HH} = 16.0, 1.2 Hz, 1H, $CH{=}CH_2$), 4.92 (dd, J_{HH} = 9.3, 1.1 Hz, 1H, $CH{=}CH_2$), 2.64 (t, J_{HH} = 6.2 Hz, 2H, CH_2), 2.60 (s, 3H, $C(O)CH_3$), 2.47 (t, J_{HH}= 6.1 Hz, 2H, CH_2), 1.82 (ddd, J_{HH} = 8.4, 7.7, 4.2 Hz, 2H, CH_2), 1.75−1.69 (m, 2H, CH_2). ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.2 (C=O), 137.1 ($NCCH_2$, pyrrole), 133.3 ($C_{Ar}C{=}O$), 133.1 (*C*H from C_6H_4), 130.1 ($CH{=}CH_2$), 128.4 (*C*H from C_6H_4), 126.3 ($C_{Ar}C{\equiv}C$), 120.9 (CH, pyrrole), 120.5 ($C_{THI}C{\equiv}C$), 111.4 ($CHCCH_2$, pyrrole), 103.7 ($CH{=}CH_2$), 80.7 (*C*≡C), 79.3 (*C*≡C), 77.8 ($C_6H_4C{\equiv}C$), 72.9 ($C_{THI}C{\equiv}C$), 69.6 (*C*≡C), 68.9 (*C*≡C), 26.8 ($C(O)CH_3$), 24.2 (CH_2), 23.2 (CH_2), 23.0 (CH_2), 23.0 (CH_2). HRMS(ESI): *m*/*z* calcd for $C_{24}H_{20}NO$, 338.1539 [M+H$^+$]; found, 338.1538.

*(**3**-C_6THI-Bn), 1-(4-((1-Benzyl-4,5,6,7-tetrahydro-1H-indol-2-yl)-hexatriynyl)phenyl)ethanone.* According to the general procedure for inverse Sonogashira coupling, **3**-C_6Br (0.0088 g, 0.032 mmol), 1-benzyl-4,5,6,7-tetrahydro-1*H*-indole (0.0137 g, 0.064 mmol), and K_2CO_3 (0.225 g) were used. Time, 24 h; purification, short silica gel plug (hexane/DCM, v/v, 1/1); yellow solid (0.0100 g, 0.025 mmol); yield, 78%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92−7.89 (m, 2H, C_6H_4), 7.59−7.56 (m, 2H, C_6H_4), 7.35−7.30 (m, 2H, C_6H_5), 7.27 (d, J_{HH} = 1.2 Hz, 1H, C_6H_5), 7.06 (dd, J_{HH} = 9.4, 2.4 Hz, 2H, C_6H_5), 6.53 (s, 1H, CH, pyrrole), 5.10 (s, 2H, CH_2Ph), 2.60 (s, 3H, $C(O)CH_3$), 2.48 (t, J_{HH} = 5.9 Hz, 2H, CH_2), 2.40 (t, J_{HH} = 6.1 Hz, 2H, CH_2), 1.80−1.71 (m, 2H, CH_2), 1.72−1.66 (m, 2H, CH_2). ^{13}C NMR (75 MHz, $CDCl_3$) δ 197.2 (C=O), 137.6 (*ipso* from C_6H_5), 137.0 ($C_{Ph}C{=}O$), 134.0 ($NCCH_2$, pyrrole), 133.0 (*C*H from C_6H_4), 128.9 (CH, *ortho* from C_6H_5), 128.4 (CH from C_6H_4), 127.6 (CH from C_6H_5), 126.8 (CH from C_6H_5), 126.4 ($C_{Ar}C{\equiv}C$), 119.4 ($C_{THI}C{\equiv}C$), 118.5 (CH, pyrrole), 112.1 ($CHCCH_2$, pyrrole), 80.5 (*C*≡C), 79.4 (*C*≡C), 77.9 ($C_6H_4C{\equiv}C$), 73.3 ($C_{THI}C{\equiv}C$), 69.6 (*C*≡C), 69.1 (*C*≡C), 48.4 (CH_2Ph), 26.8 ($C(O)CH_3$), 23.3 (CH_2), 23.1 (CH_2), 22.9 (CH_2), 22.8 (CH_2). HRMS(ESI): *m*/*z* calcd for $C_{29}H_{24}NO$, 402.1852 [M+H$^+$]; found, 402.1854.

DOI: 10.1021/acs.joc.6b01732
J. Org. Chem. 2016, 81, 9188−9198

(4-C_6THI-H), Ethyl 4-((4,5,6,7-Tetrahydro-1H-indol-2-yl)-hexatriynyl)benzoate. According to the general procedure for inverse Sonogashira coupling, **4**-C_6Br (0.0130 g, 0.0432 mmol), 4,5,6,7-tetrahydro-1*H*-indole (0.0105 g, 0.0873 mmol), and K_2CO_3 (0.235 g) were used. Time, 19 h; purification, short silica gel plug (hexane/DCM, v/v, 1/1); yellow solid (0.0038 g, 0.011 mmol); yield, 25%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (s, 1H, N*H*), 8.02−7.98 (m, 2H, C_6H_4), 7.59−7.55 (m, 2H, C_6H_4), 6.45 (d, J_{HH} = 2.3 Hz, 1H, pyrrole), 4.38 (q, J_{HH} = 7.1 Hz, 2H, OCH_2), 2.57 (t, J_{HH}= 6.2 Hz, 2H, CH_2), 2.47 (t, J_{HH} = 6.0 Hz, 2H, CH_2), 1.40 (t, J_{HH} = 7.1 Hz, 3H, CH_3). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.9 (*C*═O), 132.8 (*C*H from C_6H_4), 132.2 ($NCCH_2$, pyrrole), 131.0 (C_{Ar}C═O), 129.7 (*C*H from C_6H_4), 126.1 (C_{Ar}C≡C), 119.3 (*C*H, pyrrole), 119.0 (C_{THI}C≡C), 108.9 ($CHCCH_2$, pyrrole), 79.1 (*C*≡C), 77.8 (C≡*C*), 77.5 (C_6H_4C≡C), 73.5 (*C*≡C), 68.8 (*C*≡C), 68.7 (C≡*C*), 61.4 (OCH_2), 23.6 (CH_2), 23.2 (CH_2), 23.1 (CH_2), 22.8 (CH_2), 14.4 (CH_3). HRMS(ESI): *m*/*z* calcd for $C_{23}H_{18}NO_2$, 340.1343 [M−H$^-$]; found, 340.1350.

(4-C_6THI-Me), Ethyl 4-((1-Methyl-4,5,6,7-tetrahydro-1H-indol-2-yl)hexatriynyl)benzoate. According to the general procedure for inverse Sonogashira coupling, **4**-C_6Br (0.0106 g, 0.035 mmol), 1-methyl-4,5,6,7-tetrahydro-1*H*-indole (0.0095 g, 0.070 mmol), and K_2CO_3 (0.201 g) were used. Time, 20 h; purification, short silica gel plug (hexane/DCM, v/v, 1/1); yellow solid (0.0094 g, 0.026 mmol); yield, 74%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02−7.98 (m, 2H, C_6H_4), 7.58−7.55 (m, 2H, C_6H_4), 6.44 (s, 1H, pyrrole), 4.38 (q, J_{HH}= 7.1 Hz, 2H, OCH_2), 3.51 (s, 3H, CH_3), 2.52 (t, J_{HH} = 6.3 Hz, 2H, CH_2), 2.46 (t, J_{HH} = 6.1 Hz, 2H, CH_2), 1.86−1.80 (m, 2H, CH_2), 1.74−1.69 (m, 2H, CH_2), 1.40 (t, J_{HH} = 7.1 Hz, 3H, CH_3). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.9 (*C*═O), 134.0 ($NCCH_2$, pyrrole), 132.8 (*C*H from C_6H_4), 131.0 (C_{Ar}C═O), 129.6 (*C*H from C_6H_4), 126.2 (C_{Ar}C≡C), 118.9 (C_{THI}C≡C), 117.9 (2C, *C*H, pyrrole, $CHCCH_2$, pyrrole), 80.5 (*C*≡C), 79.5 (*C*≡C), 77.6 (C_6H_4C≡C), 73.2 (*C*≡C), 69.6 (C≡*C*), 68.9 (*C*≡C), 61.4 (OCH_2), 31.2 (CH_3), 23.4 (CH_2), 23.1 (CH_2), 23.0 (CH_2), 22.6 (CH_2), 14.4 (CH_3). IR (fluorinated oil mull) 2148 (C≡C), 2096 (C≡C) cm^{-1}. HRMS(ESI): *m*/*z* calcd for $C_{24}H_{22}NO_2$, 356.1645 [M+H$^+$]; found, 356.1645.

(4-C_6THI-Vin), Ethyl 4-((1-Vinyl-4,5,6,7-tetrahydro-1H-indol-2-yl)-hexatriynyl)benzoate. According to the general procedure for inverse Sonogashira coupling, **4**-C_6Br (0.0095 g, 0.032 mmol), 1-vinyl-4,5,6,7-tetrahydro-1*H*-indole (0.0093 g, 0.063 mmol), and K_2CO_3 (0.188 g) were used. Time, 23 h; purification, short silica gel plug (hexane/DCM, v/v, 1/1); yellow solid (0.0022 g, 0.0060 mmol); yield, 19%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02−7.99 (m, 2H, C_6H_4), 7.58−7.55 (m, 2H, C_6H_4), 6.90 (dd, J_{HH} = 16.0, 9.3 Hz, 1H, C*H*═CH_2), 6.53 (s, 1H, pyrrole), 5.39 (dd, J_{HH} = 16.0, 1.2 Hz, 1H, C*H*═CH_2), 4.92 (dd, J_{HH} = 9.3, 1.2 Hz, 1H, C*H*═CH_2), 4.38 (q, J_{HH} = 7.1 Hz, 2H, OCH_2), 2.64 (t, J_{HH} = 6.2 Hz, 2H, CH_2), 2.47 (t, J_{HH} = 6., 1 Hz, 2H, CH_2), 1.86−1.80 (m, 2H, CH_2), 1.76−1.70 (m, 2H, CH_2), 1.40(t, J_{HH} = 7.1 3H, CH_3). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.9 (*C*═O), 133.3 ($NCCH_2$, pyrrole), 132.8 (*C*H from C_6H_4), 131.0 (C_{Ar}C═O), 130.1 CH═CH_2), 129.7 (*C*H from C_6H_4), 126.0 (C_{Ar}C≡C), 120.8 (*C*H, pyrrole), 120.5 (C_{THI}C≡C), 111.4 ($CHCCH_2$, pyrrole), 103.6 (CH═CH_2), 80.7 (*C*≡C), 79.4 (*C*≡C), 72.7 (C≡*C*), 69.6 (*C*≡C), 68.6 (C≡*C*), 61.4 (OCH_2), 24.2 (CH_2), 23.2 (CH_2, 23.0 (CH_2), 23.0 (CH_2), 14.4 (CH_3), one acetylene signal under solvent. HRMS(ESI): *m*/*z* calcd for $C_{25}H_{22}NO_2$, 368.1645 [M+H$^+$]; found, 368.1644.

(4-C_6THI-Bn), Ethyl 4-((1-Benzyl-4,5,6,7-tetrahydro-1H-indol-2-yl)hexatriynyl)benzoate. According to the general procedure for inverse Sonogashira coupling, **4**-C_6Br (0.0190 g, 0.0631 mmol), 1-benzyl-4,5,6,7-tetrahydro-1*H*-indole (0.0200 g, 0.095 mmol), and K_2CO_3 (0.390 g) were used. Time, 4 h; purification, short silica gel plug (hexane/DCM, v/v, 1/1); yellow solid (0.0156 g, 0.0362 mmol); yield, 57%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02−7.97 (m, 2H, C_6H_4), 7.56−7.53 (m, 2H, C_6H_4), 7.38−7.27 (m, 3H, C_6H_5), 7.09−7.05 (m, 2H, C_6H_5), 6.53 (s, 1H, *C*H, pyrrole), 5.10 (s, 2H, CH_2Ph), 4.38 (q, J_{HH} = 7.1 Hz, 2H, OCH_2), 2.48 (t, J_{HH} = 5.9 Hz, 2H, CH_2), 2.40 (t, J_{HH} = 6.1 Hz, 2H, CH_2), 1.78−1.73 (m, 2H, CH_2), 1.72−1.67 (m, 2H, CH_2), 1.40 (t, J_{HH} = 7.1 Hz, 3H, CH_3). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.9 (C═O), 137.6 (*ipso* from C_6H_5), 133.9 ($NCCH_2$, pyrrole), 132.7 (*C*H from C_6H_4), 130.9 (C_{Ar}C═O), 129.6 (*C*H from C_6H_4), 128.9 (CH, *ortho* from C_6H_5), 127.6 (*C*H from C_6H_5), 126.8 (CH from C_6H_5), 126.1 (C_{Ar}C≡C), 119.3 (C_{THI}C≡C), 118.4 (CH, pyrrole), 112.1 (C_{THI}C≡C), 80.5 (*C*≡C), 79.5 (*C*≡C), 77.5 C_6H_4C≡C), 73.1 (*C*≡C), 69.6 (C≡*C*), 68.9 (*C*≡C), 61.4 (OCH_2), 48.4 (CH_2Ph), 23.3 (CH_2), 23.1 (CH_2), 22.9 (CH_2), 22.8 (CH_2), 14.4 (CH_3). HRMS(ESI): *m*/*z* calcd for $C_{30}H_{26}NO_2$, 432.1958 [M+H$^+$]; found, 432.1956.

(5-C_6THI-H), 4-((4,5,6,7-Tetrahydro-1H-indol-2-yl)hexatriynyl)-phenyl Acetate. According to the general procedure for inverse Sonogashira coupling, **5**-C_6Br (0.0112 g, 0.0390 mmol), 4,5,6,7-tetrahydro-1*H*-indole (0.0095 g, 0.078 mmol), and K_2CO_3 (0.207 g) were used. Time, 24 h; purification, short silica gel plug (hexane/DCM, v/v, 1/1); yellow solid (0.0014 g, 0.0043 mmol); yield, 11%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 (s, 1H, N*H*), 7.55−7.50 (m, 2H, C_6H_4), 7.09−7.06 (m, 2H, C_6H_4), 6.44 (d, J_{HH} = 2.4 Hz, 1H, pyrrole), 2.56 (t, J_{HH} = 6.2 Hz, 2H, CH_2), 2.47 (t, J_{HH} = 6.0 Hz, 2H, CH_2), 2.30 (s, 3H, CH_3), 1.84−1.78 (m, 2H, CH_2), 1.74 (dt, J_{HH} = 5.0, 4.5 Hz, 2H, CH_2). ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.1 (*C*═O), 151.5 (C_{Ar}O), 134.2 (*C*H from C_6H_4), 132.0 ($NCCH_2$, pyrrole), 122.1 (*C*H from C_6H_4), 119.2 (C_{Ar}C≡C), 119.1 (C_{THI}C≡C), 118.8 (CH, pyrrole), 109.0 ($CHCCH_2$, pyrrole), 79.2 (*C*≡C), 77.4 (C_6H_4C≡C), 75.0 (*C*≡C), 72.7 (C≡*C*), 69.0 (*C*≡C), 67.4 (C≡*C*), 23.6 (CH_2), 23.2 (CH_2), 23.1 (CH_2), 22.8 (CH_2), 21.3 (CH_3). HRMS(ESI): *m*/*z* calcd for $C_{22}H_{16}NO_2$, 326.1186 [M−H$^-$]; found, 326.1187.

(5-C_6THI-Me), 4-((1-Methyl-4,5,6,7-tetrahydro-1H-indol-2-yl)-hexatriynyl)phenyl Acetate. According to the general procedure for inverse Sonogashira coupling, **5**-C_6Br (0.0101 g, 0.0352 mmol), 1-methyl-4,5,6,7-tetrahydro-1*H*-indole (0.0095 g, 0.070 mmol), and K_2CO_3 (0.196 g) were used. Time, 24 h; purification, short silica gel plug (hexane/DCM, v/v, 1/1); yellow solid (0.0090 g, 0.026 mmol); yield, 74%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54−7.51 (m, 2H, C_6H_4), 7.09−7.05 (m, 2H, C_6H_4), 6.43 (s, 1H, pyrrole), 3.51 (s, 3H, CH_3), 2.51 (t, J_{HH} = 6.3 Hz, 2H, CH_2), 2.46 (t, J_{HH} = 6.1 Hz, 2H, CH_2), 2.30 (s, 3H, CH_3), 1.82 (ddd, J_{HH} = 8.6, 7.7, 4.3 Hz, 2H, CH_2), 1.71 (ddd, J_{HH} = 15.3, 7.5, 4.2 Hz, 2H, CH_2). ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.1 (*C*═O), 151.5 (C_{Ar}O), 134.2 (*C*H from C_6H_4), 133.7 ($NCCH_2$, pyrrole), 122.1 (CH from C_6H_4), 119.2 (C_{Ar}C≡C), 118.6 (C_{THI}C≡C), 117.6 (CH, pyrrole), 112.1 ($CHCCH_2$, pyrrole), 80.4 (*C*≡C), 79.6 (*C*≡C), 75.0 (C_6H_4C≡C), 72.3 (C≡*C*), 69.7 (*C*≡C), 67.5 (*C*≡C), 31.2 (CH_3), 23.4 (CH_2), 23.0 (CH_2), 23.0 (CH_2), 22.6 (CH_2), 21.3 (CH_3). HRMS(ESI): *m*/*z* calcd for $C_{23}H_{20}NO_2$, 342.1489 [M+H$^+$]; found, 342.1487.

(5-C_6THI-Vin), 4-((1-Vinyl-4,5,6,7-tetrahydro-1H-indol-2-yl)-hexatriynyl)phenyl Acetate. According to the general procedure for inverse Sonogashira coupling, **5**-C_6Br (0.0169 g, 0.0589 mmol), 1-vinyl-4,5,6,7-tetrahydro-1*H*-indole (0.0173 g, 0.118 mmol), and K_2CO_3 (0.342 g) were used. Time, 24 h; purification, short silica gel plug (hexane/DCM, v/v, 1/1); yellow solid (0.0026 g, 0.011 mmol); yield, 19%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54−7.51 (m, 2H, C_6H_4), 7.09−7.06 (m, 2H, C_6H_4), 6.90 (dd, J_{HH} = 16.0, 9.3 Hz, 1H, C*H*═CH_2), 6.52 (s, 1H, pyrrole), 5.39 (dd, J_{HH} = 16.0, 1.2 Hz, 1H, C*H*═CH_2), 4.91 (dd, J_{HH} = 9.3, 1.1 Hz, 1H), 2.64 (t, J_{HH} = 6.2 Hz, 2H, CH_2), 2.46 (t, J_{HH} = 6.1 Hz, 2H, CH_2), 2.30 (s, 3H, CH_3), 1.82 (ddd, J_{HH}= 8.4, 7.7, 4.2 Hz, 2H, CH_2), 1.72 (ddd, J_{HH} = 12.5, 6.1, 2.7 Hz, 2H, CH_2). ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.1 (*C*═O), 151.6 (C_{Ar}O), 134.2 (*C*H from C_6H_4), 133.0 ($NCCH_2$, pyrrole), 130.1 (CH═CH_2), 122.1 (CH from C_6H_4), 120.6 (CH, pyrrole), 120.4 (C_{THI}C≡C), 119.0 (C_{Ar}C≡C), 111.5 ($CHCCH_2$, pyrrole), 103.5 (CH═CH_2), 80.7 (*C*≡C), 79.6 (*C*≡C), 74.9 (C_6H_4C≡C), 71.9 (*C*≡C), 69.8 (C≡*C*), 67.3 (*C*≡C), 24.2 (CH_2), 23.2 (CH_2), 23.0 (CH_2), 23.0 (CH_2), 21.3 (CH_3). IR (fluorinated oil mull) 2147 (C≡C), 2104 (C≡C) cm^{-1}. HRMS(ESI): *m*/*z* calcd for $C_{24}H_{20}NO_2$, 354.1486 [M+H$^+$]; found, 354.1486.

(5-C_6THI-Bn), 4-((1-Benzyl-4,5,6,7-tetrahydro-1H-indol-2-yl)-hexatriynyl)phenyl Acetate. According to the general procedure for inverse Sonogashira coupling, **5**-C_6Br (0.0123 g, 0.0428 mmol), 1-benzyl-4,5,6,7-tetrahydro-1*H*-indole (0.0181 g, 0.0857 mmol), and K_2CO_3 (0.304 g) were used. Time, 20 h; purification, short silica gel plug (hexane/DCM, v/v, 1/1); yellow solid (0.0074 g, 0.018 mmol); yield, 42%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53−7.48 (m, 2H, C_6H_4),

DOI: 10.1021/acs.joc.6b01732
J. Org. Chem. 2016, 81, 9188−9198

7.38−7.27 (m, 3H, C_6H_5), 7.09−7.04 (m, 2H from C_6H_4 and 2H from C_6H_5), 6.51 (s, 1H, C*H*, pyrrole), 5.10 (s, 2H, CH_2Ph), 2.48 (t, J_{HH} = 6.0 Hz, 2H, CH_2), 2.40 (t, J_{HH} = 6.1 Hz, 2H, CH_2), 2.30 (s, 3H, CH_3), 1.78−1.74 (m, 2H, CH_2), 1.71−1.67 (m, 2H, CH_2). ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.1 (C═O), 151.5 (C_{Ar}O), 137.7 (*ipso* from C_6H_5), 134.2 (*C*H from C_6H_4), 133.7 (NCCH$_2$, pyrrole), 128.9 (*C*H, *ortho* from C_6H_5), 127.6 (CH from C_6H_5), 126.8 (CH from C_6H_5), 122.1 (*C*H from C_6H_4), 119.2 (C_{Ar}C≡C), 119.1 (C_{THI}C≡C), 118.2 (*C*H, pyrrole), 112.3 (CHC*C*H$_2$, pyrrole), 80.5 (*C*≡C), 79.6 (*C*≡C), 75.0 (C_6H_4C≡*C*), 72.3 (*C*≡C), 69.7 (*C*≡C), 67.5 (*C*≡C), 48.4 (CH_2Ph), 23.4 (CH_2), 23.1 (CH_2), 23.0 (CH_2), 22.8 (CH_2), 21.3 (CH_3). HRMS(ESI): *m*/*z* calcd for $C_{29}H_{24}NO_2$, 418.1802 [M+H$^+$]; found, 418.1800.

*(**1**-C_8THI-Me), 4-((1-Methyl-4,5,6,7-tetrahydro-1H-indol-2-yl)-octatetraynyl)benzonitrile.* According to the general procedure for inverse Sonogashira coupling, **1**-C_8I (0.0105 g, 0.0323 mmol), 1-methyl-4,5,6,7-tetrahydro-1*H*-indole (0.0080 g, 0.064 mmol), and K_2CO_3 (0.140 g) were used. Time, 24 h; purification, short silica gel plug (hexane/DCM, v/v, 1/1); yellow solid (0.0041 g, 0.012 mmol); yield, 37%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64−7.58 (m, 4H, C_6H_4), 6.48 (s, 1H, pyrrole), 3.50 (s, 3H, CH_3), 2.51 (t, J_{HH} = 6.3 Hz, 2H, CH_2), 2.45 (t, J_{HH} = 6.1 Hz, 2H, CH_2), 1.86−1.80 (m, 2H, CH_2), 1.74−1.68 (m, 2H, CH_2). ^{13}C NMR (126 MHz, $CDCl_3$) δ 134.7 (NCCH$_2$, pyrrole), 133.6 (*C*H, C_6H_4CN), 132.3 (*C*H, C_6H_4CN), 126.1 (C_{Ar}C≡C), 119.0 (C_{THI}C≡C), 118.9 (*C*H, pyrrole), 118.2 (*C*≡N), 113.0 (*C*C≡N), 111.6 (CHC*C*H$_2$, pyrrole), 81.2 (*C*≡C), 78.8 (*C*≡C), 76.5 (C_6H_4C≡*C*), 72.5 (*C*≡C), 71.2 (*C*≡C), 70.0 (*C*≡C), 66.1 (*C*≡C), 65.3 (*C*≡C), 31.3 (CH_3), 23.4 (CH_2), 23.0 (CH_2), 22.9 (CH_2), 22.7 (CH_2). IR (fluorinated oil mull) 2223 (N≡C), 2188 (C≡C), 2153 (C≡C), 2102 (C≡C) cm^{-1}. HRMS(ESI): *m*/*z* calcd for $C_{24}H_{17}N_2$, 333.1386 [M+H$^+$]; found, 333.1391.

*(**1**-C_8THI-Vin), 4-((1-Vinyl-4,5,6,7-tetrahydro-1H-indol-2-yl)-octatetraynyl)benzonitrile.* According to the general procedure for inverse Sonogashira coupling, **1**-C_8I (0.0114 g, 0.0351 mmol), 1-vinyl-4,5,6,7-tetrahydro-1*H*-indole (0.0103 g, 0.070 mmol), and K_2CO_3 (0.210 g) were used. Time, 2 d; purification, short silica gel plug (hexane/DCM, v/v, 1/1); yellow solid (0.0047 g, 0.014 mmol); yield, 40%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64−7.58 (m, 4H, C_6H_4CN), 6.88 (dd, J_{HH} = 16.0, 9.3 Hz, 1H, C*H*═CH_2), 6.57 (s, 1H, pyrrole), 5.39 (dd, J_{HH} = 16.0, 1.2 Hz, 1H, CH═C*H*$_2$), 4.94 (dd, J_{HH} = 9.3, 1.2 Hz, 1H, CH═C*H*$_2$), 2.63 (t, J_{HH} = 6.2 Hz, 2H, CH_2), 2.46 (t, J_{HH} = 6.1 Hz, 2H, CH_2), 1.86−1.79 (m, 2H, CH_2), 1.75−1.69 (m, 2H, CH_2). ^{13}C NMR (126 MHz, $CDCl_3$) δ 134.0 (NCCH$_2$, pyrrole), 133.6 (*C*H from C_5H_4CN), 132.3 (CH from C_5H_4CN), 130.0 (CH═CH_2), 126.0 (C_{Ar}C≡C), 121.9 (*C*H, pyrrole), 120.7 (C_{THI}C≡C), 118.2 (C≡N), 113.1 (*C*C≡N), 111.0 (CHC*C*H$_2$, pyrrole), 104.1 (CH═*C*H$_2$), 81.2 (*C*≡C), 78.8 (*C*≡C), 76.4 (C_6H_4C≡*C*), 71.2 (C_{THI}C≡*C*), 71.0 (*C*≡C), 69.8 (*C*≡C), 65.8 (*C*≡C), 65.1 (*C*≡C), 24.2 (CH_2), 23.1 (CH_2), 23.0 (CH_2), 23.0 (CH_2). HRMS(ESI): *m*/*z* calcd for $C_{25}H_{17}N_2$, 345.1386 [M+H$^+$]; found, 345.1391.

*(**1**-C_8THI-Bn), 4-((1-Benzyl-4,5,6,7-tetrahydro-1H-indol-2-yl)-octatetraynyl)benzonitrile.* According to the general procedure for inverse Sonogashira coupling, **1**-C_8I (0.0140 g, 0.043 mmol), 1-benzyl-4,5,6,7-tetrahydro-1*H*-indole (0.0182 g, 0.086 mmol), and K_2CO_3 (0.320 g) were used. Time, 1 d; purification, short silica gel plug (hexane/DCM, v/v, 1/1); yellow solid (0.0140 g, 0.034 mmol); yield, 79%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63−7.57 (m, 4H, C_6H_4C≡N), 7.34−7.30 (m, H, 2H, C_6H_5), 7.28−7.24 (m, 1H, C_6H_5), 7.07−7.02 (m, H, 2H, C_6H_5), 6.56 (s, 1H, C*H*, pyrrole), 5.09 (s, 2H, C*H*$_2$Ph), 2.47 (t, J_{HH} = 6.0 Hz, 2H, CH_2), 2.39 (t, J_{HH} = 6.2 Hz, 2H CH_2), 1.78−1.72 (m, 2H CH_2), 1.72−1.65 (m, 2H, CH_2). ^{13}C NMR (126 MHz, $CDCl_3$) δ 137.5 (*ipso* from C_6H_5), 134.7 (NCCH$_2$, pyrrole), 133.6 (*C*H from C_5H_4CN), 132.3 (CH from C_5H_4CN), 128.9 (*C*H, C_6H_5), 127.7 (*C*H, *ortho* from C_6H_5), 126.8 (*C*H, C_6H_5), 126.1 (C_{Ar}C≡C), 119.6 (C_{THI}C≡C), 119.5 (*C*H, pyrrole), 118.2 (C≡N), 113.0 (*C*C≡N), 111.9 (CHC*C*H$_2$, pyrrole), 81.2 (*C*≡C), 78.8 (*C*≡C), 76.5 (*C*≡C), 72.4 (*C*≡C), 71.2 (*C*≡C), 69.9 (*C*≡C), 66.1 (*C*≡C), 65.3 (*C*≡C), 48.5 (CH_2Ph), 23.3 (CH_2), 23.1 (CH_2), 22.9 (CH_2), 22.8 (CH_2). HRMS(ESI): *m*/*z* calcd for $C_{30}H_{21}N_2$, 409.1699 [M+H$^+$]; found, 409.1705.

*(**2**-C_8THI-Me), 1-Methyl-2-((4-nitrophenyl)octatetraynyl)-4,5,6,7-tetrahydro-1H-indole.* According to the general procedure for inverse Sonogashira coupling, **2**-C_8I (0.0085 g, 0.025 mmol), 1-methyl-4,5,6,7-tetrahydro-1*H*-indole (0.0067 g, 0.050 mmol), and K_2CO_3 (0.150 g) were used. Time, 1 d; purification, short silica gel plug (hexane/DCM, v/v, 1/1); yellow solid (0.0080 g, 0.023 mmol); yield, 92%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.23−8.18 (m, 2H, $C_6H_4NO_2$), 7.69−7.64 (m, 2H, $C_6H_4NO_2$), 6.49 (s, 1H, pyrrole), 3.51 (s, 3H, CH_3), 2.52 (t, J_{HH} = 6.3 Hz, 2H), 2.46 (t, J_{HH} = 6.1 Hz, 2H), 1.86−1.80 (m, 2H), 1.75−1.68 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.9 (CNO_2), 134.8 (NCCH$_2$, pyrrole), 133.9 (*C*H from C_6H_4), 128.1 (C_{Ar}C≡C), 123.9 (*C*H from C_6H_4), 119.1 (C_{THI}C≡C), 119.0 (*C*H, pyrrole), 111.6 (CHC*C*H$_2$, pyrrole), 81.3 (*C*≡C), 79.6 (*C*≡C), 76.3 (C_6H_4C≡*C*), 72.7 (C_{THI}C≡*C*), 71.2 (*C*≡C), 70.4 (*C*≡C), 66.4 (*C*≡C), 65.3 (*C*≡C), 31.3 (CH_3), 23.4 (CH_2), 23.0 (CH_2), 22.9 (CH_2), 22.7 (CH_2). HRMS(ESI): *m*/*z* calcd for $C_{23}H_{17}N_2O_2$, 353.1285 [M+H$^+$]; found, 353.1282.

*(**2**-C_8THI-Vin), 2-((4-Nitrophenyl)octatetraynyl)-1-vinyl-4,5,6,7-tetrahydro-1H-indole.* According to the general procedure for inverse Sonogashira coupling, **2**-C_8I (0.0074 g, 0.021 mmol), 1-vinyl-4,5,6,7-tetrahydro-1*H*-indole (0.0063 g, 0.042 mmol), and K_2CO_3 (0.140 g) were used. Time, 1 d; purification, short silica gel plug (hexane/DCM, v/v, 1/1); yellow solid (0.0026 g, 0.0071 mmol); yield, 34%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.22−8.19 (m, 2H), 7.69−7.65 (m, 2H), 6.88 (dd, J_{HH} = 16.0, 9.3 Hz, 1H), 6.58 (s, 1H), 5.40 (dd, J_{HH} = 16.0, 1.2 Hz, 1H), 4.94 (dd, J_{HH} = 9.3, 1.2 Hz, 1H), 2.64 (t, J_{HH} = 6.2 Hz, 2H), 2.47 (t, J_{HH} = 6.1 Hz, 2H), 1.86−1.79 (m, 2H), 1.77−1.69 (m, 2H) ^{13}C NMR (151 MHz, $CDCl_3$) δ 147.9 (CNO_2), 134.2 (NCCH$_2$ of pyrrole), 133.9 (CH of C_6H_4), 130.0 (HC═CH_2), 128.0 (C_{Ar}C≡C), 123.9 (CH of C_6H_4), 121.9 (CH of pyrrole), 120.7 (CC≡C of pyrrole), 111.0 (CHCCH$_2$ of pyrrole), 104.1 (HC═*C*H$_2$), 81.2 (*C*≡C), 79.5 (*C*≡C), 76.2 (C_6H_4C≡*C*), 72.2 (pyrroleC≡*C*), 71.0 (*C*≡C), 70.3 (*C*≡C), 66.1 (*C*≡C), 65.1 (*C*≡C), 24.2 (CH_2), 23.1 (CH_2), 23.0 (CH_2), 23.0 (CH_2). HRMS(ESI): *m*/*z* calcd for $C_{24}H_{17}N_2O_2$, 365.1285 [M+H$^+$]; found, 365.1279.

*(**2**-C_8THI-Bn), 1-Benzyl-2-((4-nitrophenyl)octatetraynyl)-4,5,6,7-tetrahydro-1H-indole.* According to the general procedure for inverse Sonogashira coupling, **2**-C_8I (0.0095 g, 0.028 mmol), 1-benzyl-4,5,6,7-tetrahydro-1*H*-indole (0.012 g, 0.056 mmol), and K_2CO_3 (0.220 g) were used. Time, 1 d; purification, short silica gel plug (hexane/DCM, v/v, 1/1); red solid (0.0055 g, 0.013 mmol); yield, 46%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.21−8.18 (m, 2H, C_6H_4), 7.67−7.64 (m, 2H, C_6H_4), 7.34−7.30 (m, 2H, C_6H_5), 7.29−7.24 (m, 1H, C_6H_5), 7.07−7.24 (m, 2H, C_6H_5), 6.57 (s, 1H, C*H*, pyrrole), 5.09 (s, 2H, C*H*$_2$Ph), 2.48 (t, J_{HH} = 6.0 Hz, 2H, CH_2), 2.40 (t, J_{HH} = 6.1 Hz, 2H, CH_2), 1.78−1.72 (m, 2H, CH_2), 1.72−1.65 (m, 2H, CH_2). ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.9 (CNO_2), 137.5 (*ipso* from C_6H_5), 134.8 (NCCH$_2$, pyrrole), 133.9 (*C*H from C_6H_4), 128.9 (*C*H, C_6H_5), 128.1 (C_{Ar}C≡C), 127.7 (*C*H, C_6H_5), 126.8 (*C*H, C_6H_5), 123.9 (*C*H from C_6H_4), 119.7 (C_{THI}C≡C), 119.6 (*C*H, pyrrole), 111.8 (CHC*C*H$_2$, pyrrole), 81.2 (*C*≡C), 79.6 (*C*≡C), 76.3 (C_6H_4C≡*C*), 72.6 (C_{THI}C≡*C*), 71.2 (*C*≡C), 70.4 (*C*≡C), 66.3 (*C*≡C), 65.2 (*C*≡C), 48.5 (CH_2Ph), 23.3 (CH_2), 23.1 (CH_2), 22.9 (CH_2), 22.8 (CH_2). HRMS(ESI): *m*/*z* calcd for $C_{29}H_{21}N_2O_2$, 429.1598 [M+H$^+$]; found, 429.1602.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b01732.

CIF files for **1**-C_6THI-Me, **2**-C_6THI-Vin, **2**-C_6THI-Bn, **3**-C_6THI-Vin, **4**-C_6THI-Bn, and **2**-C_8THI-Vin (CIF)

^{1}H and ^{13}C NMR spectra for all new compounds and UV−vis spectra (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: slawomir.szafert@chem.uni.wroc.pl.

DOI: 10.1021/acs.joc.6b01732
J. Org. Chem. 2016, 81, 9188−9198

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The work was supported by the National Science Centre Poland (UMO-2013/08/M/ST5/00942).

■ REFERENCES

(1) (a) Haley, M. M.; Tykwinski, R. R. *From Molecules to Materials*; Wiley-VCH: Weinheim, Germany, 2005. (b) Cataldo, F. E. *Polyynes: Synthesis Proprties and Applications*; CRC Press Taylor & Francis Group: Boca Raton, FL, 2006. (c) Chalifoux, W. A.; Tykwinski, R. R. *C. R. Chim.* **2009**, *12*, 341−358. (d) Chalifoux, W. A.; Tykwinski, R. R. *Nat. Chem.* **2010**, *2*, 967−971.

(2) (a) Moreno-García, P.; Gulcur, M.; Manrique, D. Z.; Pope, T.; Hong, W.; Kaliginedi, V.; Huang, C.; Batsanov, A. S.; Bryce, M. R.; Lambert, C.; Wandlowski, T. *J. Am. Chem. Soc.* **2013**, *135*, 12228−12240. (b) Gulcur, M.; Moreno-García, P.; Zhao, X.; Baghernejad, M.; Batsanov, A. S.; Hong, W.; Bryce, M. R.; Wandlowski, T. *Chem. - Eur. J.* **2014**, *20*, 4653−4660. (c) Schwarz, F.; Kastlunger, G.; Lissel, F.; Riel, H.; Venkatesan, K.; Berke, H.; Stadler, R.; Lörtcher, E. *Nano Lett.* **2014**, *14*, 5932−5940. (d) Lissel, F.; Schwarz, F.; Blaque, O.; Riel, H.; Lörtscher, E.; Venkatesan, K.; Berke, H. *J. Am. Chem. Soc.* **2014**, *136*, 14560−14569.

(3) (a) Slepkov, A. D.; Hegmann, F. A.; Eisler, S.; Elliot, E.; Tykwinski, R. R. *J. Chem. Phys.* **2004**, *120*, 6807−6810. (b) Eisler, S.; Slepkov, A. D.; Elliot, E.; Luu, T.; McDonald, R.; Hegmann, F. A.; Tykwinski, R. R. *J. Am. Chem. Soc.* **2005**, *127*, 2666−2676. (c) Xu, G.-L.; Wang, C.-Y.; Ni, Y.-H.; Goodson, T. G.; Ren, T. *Organometallics* **2005**, *24*, 3247−3254. (d) Samoc, M.; Dalton, G. T.; Gladysz, J. A.; Zheng, Q.; Velkov, Y.; Agren, H.; Norman, P.; Humphrey, M. G. *Inorg. Chem.* **2008**, *47*, 9946−9957. (e) Fazio, E.; D'Urso, L.; Consiglio, G.; Giuffrida, A.; Compagnini, G.; Puglisi, O.; Patanè, S.; Neri, F.; Forte, G. *J. Phys. Chem. C* **2014**, *118*, 28812−28819.

(4) (a) Xu, G. L.; Zou, G.; Ni, Y.-H.; DeRosa, M. C.; Crutchley, R. J.; Ren, T. *J. Am. Chem. Soc.* **2003**, *125*, 10057−10065. (b) Sun, A.; Lauher, J. W.; Goroff, N. S. *Science* **2006**, *312*, 1030−1034. (c) Cao, Z.; Xi, B.; Jodoin, D. S.; Zhang, L.; Cummings, S. P.; Gao, Y.; Tyler, S.; Fanwick, P. E.; Crutchley, R. J.; Ren, T. *J. Am. Chem. Soc.* **2014**, *136*, 12174−12183.

(5) (a) Cernicharo, J.; Guelin, M. *Astron. Astroph.* **1996**, *309*, L27−L30. (b) Bell, M. B.; Feldman, P. A.; Travers, M. J.; McCarthy, M. C.; Gottlieb, C. A.; Thaddeus, P. *Astrophys. J.* **1997**, *483*, L61−L64. (c) Bell, M. B.; Watson, J. K. G.; Feldman, P. A.; Travers, M. J. *Astrophys. J.* **1998**, *508*, 286−290. (d) McCarthy, M. C.; Gottlieb, C. A.; Gupta, H.; Thaddeus, P. *Astrophys. J.* **2006**, *652*, L141−L144. (e) Brunken, S.; Gupta, H.; Gottlieb, C. A.; McCarthy, M. C.; Thaddeus, P. *Astrophys. J.* **2007**, *664*, L43−L46.

(6) (a) Martire, D. O.; Jux, N.; Aramendia, P. F.; Negri, R. M.; Lex, J.; Braslavsky, S. E.; Schaffner, K.; Vogel, E. *J. Am. Chem. Soc.* **1992**, *114*, 9969−9978. (b) Rana, A.; Lee, S.; Kim, D.; Panda, P. K. *Chem. - Eur. J.* **2015**, *21*, 12129−12135. (c) Cho, D. H.; Lee, J. H.; Kim, B. H. *J. Org. Chem.* **1999**, *64*, 8048−8050. (d) Sakida, T.; Yamaguchi, S.; Shinokubo, H. *Angew. Chem., Int. Ed.* **2011**, *50*, 2280−2283. (e) Fiandanese, V.; Bottalico, D.; Marchese, G.; Punzi, A. *Tetrahedron* **2008**, *64*, 53−60.

(7) (a) Tu, B.; Lightner, D. A. *J. Heterocycl. Chem.* **2003**, *40*, 707−711. (b) McDonagh, A. F.; Lightner, D. A. *J. Med. Chem.* **2007**, *50*, 480−488. (c) Pfeiffer, W. P.; Lightner, D. A. *Monatsh. Chem.* **2014**, *145*, 1777−1801.

(8) (a) Yao, S.; Zhou, C.; Wu, J.; Li, J.; Han, B.; Cheng, H. *Int. J. Quantum Chem.* **2008**, *108*, 1565−1571. (b) Rao, J. L. *Centr. Eur. J. Chem.* **2007**, *5*, 793−812. (c) Hwang, T.-S.; Juan, N.; Chen, H.-Y.; Chen, C. C.; Lo, S.-J.; Chao, I. *Chem. - Eur. J.* **2004**, *10*, 1616−1624.

(9) Kilickiran, P.; Hopf, H.; Dix, I.; Jones, P. G. *Eur. J. Org. Chem.* **2010**, *2010*, 4035−4045.

(10) Tomilin, D. N.; Pigulski, B.; Gulia, N.; Arendt, A.; Sobenina, L. N.; Mikhaleva, A. I.; Szafert, S.; Trofimov, B. A. *RSC Adv.* **2015**, *5*, 73241−73248.

(11) Sobenina, L. N.; Tomilin, D. N.; Trofimov, B. A. *Russ. Chem. Rev.* **2014**, *83*, 475−501.

(12) (a) Gulia, N.; Osowska, K.; Pigulski, B.; Lis, T.; Galewski, Z.; Szafert, S. *Eur. J. Org. Chem.* **2012**, *2012*, 4819−4830. (b) Gulia, N.; Pigulski, B.; Charewicz, M.; Szafert, S. *Chem. - Eur. J.* **2014**, *20*, 2746−2749. (c) Gulia, N.; Pigulski, B.; Szafert, S. *Organometallics* **2015**, *34*, 673−682. (d) Pigulski, B.; Gulia, N.; Szafert, S. *Chem. - Eur. J.* **2015**, *21*, 17769−17778.

(13) Sobenina, L. N.; Tomilin, D. N.; Petrova, O. V.; Gulia, N.; Osowska, K.; Szafert, S.; Mikhaleva, A. I.; Trofimov, B. A. *Russ. J. Org. Chem.* **2010**, *46*, 1373−1377.

(14) Trofimov, B. A.; Sobenina, L. N.; Stepanova, Z. V.; Vakul'skaya, T. I.; Kazheva, O. N.; Aleksandrov, G. G.; Dyachenko, O. A.; Mikhaleva, A. I. *Tetrahedron* **2008**, *64*, 5541−5544.

(15) (a) Heuft, M. A.; Collins, S. K.; Yap, G. P. A.; Fallis, A. G. *Org. Lett.* **2001**, *3*, 2883−2886. (b) Eisler, S.; Chahal, N.; McDonald, R.; Tykwinski, R. R. *Chem. - Eur. J.* **2003**, *9*, 2542−2550.

(16) Sarkar, A.; Okada, S.; Komatsu, K.; Nakanishi, H.; Matsuda, H. *Macromolecules* **1998**, *31*, 5624−5630.

(17) Wang, C.; Batsanov, A. S.; Bryce, M. R.; Martin, S.; Nichols, R. J.; Higgins, S. J.; Garcia-Suarez, V. M.; Lambert, C. J. *J. Am. Chem. Soc.* **2009**, *131*, 15647−15654.

(18) (a) Szafert, S.; Gladysz, J. A. *Chem. Rev.* **2003**, *103*, 4175−4206. (b) Szafert, S.; Gladysz, J. A. *Chem. Rev.* **2006**, *106*, PR1−PR33.

(19) (a) Deschamps, J.; Balog, M.; Boury, B.; Ben Yahia, M.; Filhol, J. S.; van der Lee, A.; Al Choueiry, A.; Barisien, T.; Legrand, L.; Schott, M.; Dutremez, S. G. *Chem. Mater.* **2010**, *22*, 3961−3982. (b) Biradha, K.; Santra, R. *Chem. Soc. Rev.* **2013**, *42*, 950−967.

(20) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441−451.

(21) (a) Bartik, B.; Dembinski, R.; Bartik, T.; Arif, A. M.; Gladysz, J. A. *New J. Chem.* **1997**, *21*, 739−750. (b) Trofimov, B. A.; Mikhaleva, A. I.; Schmidt, E. Y.; Sobenina, L. N. *Chemistry of Pyrroles*; CRC Press: Boca Raton, FL, 2014. (c) Arendt, A.; Kołkowski, R.; Samoc, M.; Szafert, S. *Phys. Chem. Chem. Phys.* **2015**, *17*, 13680−13688.

DOI: 10.1021/acs.joc.6b01732
J. Org. Chem. 2016, 81, 9188−9198