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"Acetylene Zipper" Reactions and Pd–Cu-Catalyzed Cross-coupling in the Synthesis of Vicinal 1,3-Alkadiynylarylamines and Aminopyridines

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Abstract—A preparative method was developed for vicinal-substituted 1,3-alkadiynylarylamines and aminopyridines involving a successive application of "acetylene zipper" reaction to synthesize 1,3-alkadiynes followed by Sonogashira reaction.

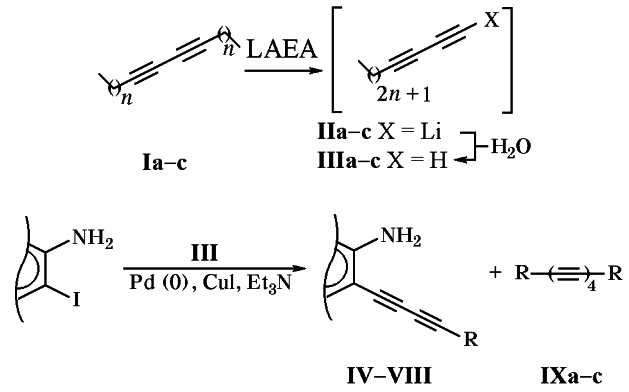
Acetylene compounds isomerization catalyzed by bases that had been discovered by A. E. Faworsky [1] found versatile application in the organic synthesis [2–4]. For instance, in [5] was developed a convenient method for preparation of *N*-allenylpyrroles by N-propargylation of pyrroles in the presence of KOH in DMSO; the reaction was accompanied by isomerization furnishing an allene derivative.

In a multiposition prototropic isomerization ("acetylene zipper" reaction) the transfer of a triple bond along an unbranched carbon chain occurs under treatment with diamine amides. The reaction is applied to preparation of acetylenes [6] and diacetylenes [7] with terminal triple bonds and often it is an indispensable synthetic procedure for designing molecules including long chains of polymethylene units [8]. We showed formerly [9] that the "acetylene zipper" reaction of diacetylene hydrocarbons followed by cross-coupling of terminal diynes with aryl iodides can be successfully used for preparation aryl-substituted diacetylenes.

Since Castro studies [10] functionalized arylacetylenes are used as convenient synthons in building up various fused heterocycles. Derivatives with an amine function can undergo intramolecular cyclization by nucleophilic addition of the amino group to the triple bond, and also by electrophilic addition of the diazonium ion in the case of amino group diazotization (Richter reaction) [11]. Unlike monoacetylenes, diacetylenes were seldom involved into such reactions [12] due to the difficulties arising in preparation of the diacetylene derivatives. The main preparation method for functionalized arylacetylenes is nowadays the cross-coupling reaction of appropriate aryl halides with terminal acetylenes (Sonogashira reaction [13]). The lesser accessibility and mainly the low stability of terminal diynes limited their application to the synthesis.

The use of "acetylene zipper" reaction for preparation of 1,3-alkadiynes combined with Sonogashira reaction resulted in development of a preparative synthesis of functionalized 1-aryl-1,3-alkadiynes [9]. In the present study this synthetic approach was applied to preparation of vicinal-substituted 1,3-alkadiynylarylamines and aminopyridines (see the scheme).

Scheme.



R = $CH_3(CH_2)_{2n+1}$, n = 2 (**a**), 3 (**b**), 5 (**c**).

1,3-Alkadiynes **III** were obtained from the corresponding disubstituted isomers **I** by treating with

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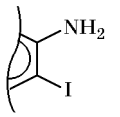
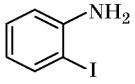
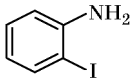
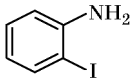
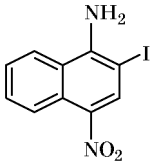
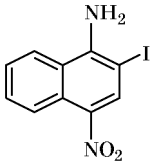
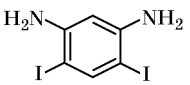
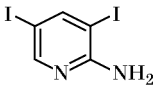
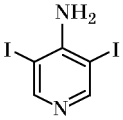
Run no.		Compd. no.	Yield[a], %	Catalyst
1		**IVa**	87 (74)*	$Pd(OAc)_2$
2		**IVb**	95 (88)*	$Pd(OAc)_2$
3		**IVc**	67	$Pd(OAc)_2$
4		**Va**	88	$Pd(OAc)_2$
5		**Vb**	92	$Pd(OAc)_2$
6		**VIa**	46	$PdCl_2(PPh_3)_2$
7		**VIIa**	66	$PdCl_2(PPh_3)_2$
8		**VIIIb**	86	$PdCl_2(PPh_3)_2$

[a] The values in parentheses correspond to the respective hydrochlorides.

3-fold excess of lithium 2-aminoethylamide (LAEA) in a mixture benzene–hexane–THF. The presence in the solvent of nonpolar components favors formation of lithium acetylides of terminal isomers **II**. The isomerization of disubstituted diacetylenes is fast (5–10 min) and occurs under mild conditions (16–18°C). The preparative yield of terminal isomers reached 90%. However the Pd–Cu catalyzed cross-coupling did not require isolation of unstable terminal diacetylenes, and the synthesis might be performed as one-pot process. On completing the isomerization the lithium acetylides were quenched by adding a little water, and the cross-coupling with iodoamino derivatives was carried out catalyzed by $PdCl_2(PPh_3)_2$ or $Pd(OAc)_2$ and CuI as cocatalyst in the presence of PPh_3 and Et_3N. The reaction products were isolated by chromatography, the set of iododerivatives and yields of products are given in the table. The aniline derivatives **IVa, b** were also prepared as hydrochlorides. In this case the chromatographic separation was not necessary, and the products were more stable at storage. At testing the influence of the length of alkyl substituent of the diacetylene hydrocarbon on the result of the reaction we established that reaction proceeded with high yield with diacetylene hydrocarbons **Ia, b**. To obtain full conversion of iodide diyne **I** should be used in "acetylene zipper" reaction in a 25% excess for the cross-coupling is accompanied with side process of terminal diyne dehydrodimerization resulting in the corresponding tetraynes. The yields of tetraynes **IXa, b** amounted to 2–4% with respect to the hydrocarbon brought into the reaction.

Taking into consideration that with growing length of the alkyl substituent the stability of the corresponding terminal diynes diminished and their tendency to oxidative coupling grew we used a 1.5-fold excess of hexadeca-7,9-diyne (**1c**) with respect to 2-iodoaniline. Regardless of these measures the yield of the target product was reduced: the reaction mixture suffered strong tarring, and 2-(hexa-1,3-decadiynyl)aniline **IVc** was isolated in 67% yield; therewith the yield of dotriaconta-13,15,17,19-tetrayne (**IXc**) was 16% (see table, run no. *3*). The insignificant effect of the chain length of the alkyl substituent on the product yield was observed in reaction with 1-naphthylamine derivative (see table, runs nos. *4, 5*). We also compared the reactivity of 2-amino-3,5-diiodopyridine with that of 4-amino-3,5-diiodopyridine and found that both compounds reacted under mild conditions and afforded bisdiynyl derivatives **VIIa, VIIIb** (see Table, runs nos. *7, 8*) in 66 and 79% yield respectively. The presence of two electron-donor substituents in 1,3-diamino-2,4-diiodobenzene resulted in reduction of the compound reactivity in the cross-coupling and in lower yield of the target product (see table, run no. *6*). A 1.5-fold excess of deca-4,6-diyne (**Ia**) was brought into the "acetylene zipper" reaction. After the iodide conversion was complete from the reaction mixture alongside compound **VIa** was isolated also in 12% yield a product of monosubstitution, 1,3-diamino-4-(1,3-decadiynyl)-5-iodobenzene. It should be noted that under the reaction conditions the vicinal 1,3-alkadiynylarylamines did not undergo cyclization in spite of the presence of copper and palladium salts.

We established that the bromo derivatives are inactive under the given conditions. 2-Bromo-4-nitroaniline and 4-amino-4-bromopyridine were not involved into the reaction even when the reaction mixture was heated at reflux for several days.

The method developed provides a possibility to prepare versatile alkadiynyl-substituted aryl(hetaryl)amines from accessible initial compounds.

EXPERIMENTAL

IR spectra were recorded on spectrophotometer Specord IR75 in the range 4000–400 cm^{-1} and on UR-20 spectrophotometer from 2% solutions of compounds in CCl_4 and CH_2Cl_2.

GC-MS measurements were carried out on Agilent 68-90 instrument at ionizing electrons energy 70 eV, ionization by electron impact, detector Agilent 5973, and on Finnigan INCOS 50 instrument at ionizing electrons energy 70 eV.

^1H and ^{13}C NMR spectra were registered on spectrometer Bruker at operating frequencies 300 and 75 MHz respectively from solutions in $CDCl_3$ or $(CD_3)_2CO$.

Elemental analyses were performed on Hewlett-Packard 185 B analyzer.

The initial iodides were prepared by known procedures [14]. Disubstituted diacetylene hydrocarbons **Ia–c** were obtained by Glase–Hey reaction [15]. The dimerization products of terminal diynes **IIIa–c**, tetraynes **IXa–c** were characterized previously [16] and were separated from the reaction mixtures by chromatography in 2–16% yield.

General procedure. To a mixture of anhydrous ethylenediamine (7.5 mmol, 0.6 ml) and THF (1.8 ml) in an argon flow was added lithium (7.5 mmol, 53 mg) by small portions. On lithium dissolution the mixture turned dark-blue and self-heated; on completion of lithium dissolution the color changed to light-yellow. To the obtained suspension in THF of lithium 2-aminoethylamide was added anhydrous benzene (1.8 ml) and anhydrous hexane (1.8 ml). The reaction mixture was cooled to 16°C, and diacetylene hydrocarbon **I** (2.5 mmol) was added thereto. Within several seconds the mixture turned dark-brown. The reaction mixture was stirred at 16–18°C for 15 min, and then 1 ml of water was added. After the hydrolysis of lithium acetylide **II** into the reaction mixture was added in succession aryl iodide (2 mmol), Pd(II) (0.2 mmol), PPh_3 (52.5 mg, 0.2 mmol), Et_3N (5 ml), and CuI (57 mg, 0.3 mmol). On the complete consumption of the initial iodide (TLC monitoring) the reaction mixture was poured into water, the organic layer was separated, and the water layer was extracted with dichloromethane (2×5 ml). The combined organic solution was washed with NH_4Cl solution till neutral washings, and the washings were extracted with dichloromethane (1×5 ml). The combined organic solution was dried over $MgSO_4$. The solvent was removed in a vacuum, the residue was subjected to chromatography or the products were isolated as hydrochlorides. To this end the residue was dissolved in anhydrous hexane, and a flow of dry HCl was passed through the solution for 30 min. The salt was filtered off and dried.

2-(1,3-Decadiynyl)aniline (IVa) was obtained from 4,6-decadiyne (335 mg, 2.5 mmol) and 2-iodoaniline (438 mg, 2 mmol) in 87% yield (435 mg, 1.74 mmol). Dark-yellow oily substance. R_f 0.27 (hexane–CH_2Cl_2, 4:1). IR spectrum (CCl_4), ν_{max}, cm^{-1}: 3480 s, 3390 s (NH_2), 3070 m (H–C^2_{sp}), 2960 s, 2930 s, 2860 s (H–C^3_{sp}), 2230 w, 2140 m (C≡C), 1620 s (C=C), 1470 s, 1400 s, 1255 s, 840 s. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 0.90 t (3H, CH_3, *J* 7 Hz), 1.18–1.32 m [8H, $(CH_2)_4$], 2.35 t (2H, ≡CCH_2, *J* 7 Hz), 4.44 s (2H, NH_2), 6.65–6.72 m (2H), 7.11 t (1H, *J* 7 Hz), 7.27 t (1H, *J* 7 Hz) (H arom). ^{13}C NMR spectrum, ($CDCl_3$), δ, ppm: 14.32, 23.07, 28.69, 29.50, 32.25 (C^3_{sp}), 19.98 ($\underline{C}H_2C$≡), 65.65, 71.69, 80.03, 86.34 (C_{sp}), 107.18, 114.53, 118.00, 130.37, 133.26, 149.28 (C arom). Mass spectrum, *m/z* (I_{rel}, %): 225 (100), 226 (20), 196 (30), 186 (40), 182 (30), 154 (70), 144 (10), 130 (33), 117 (33), 106 (5), 101 (5), 93 (5). Found, %: C 85.02, 85.29; H 8.42, 8.45; N 6.03, 5.96. $C_{16}H_{19}N$. Calculated, %: C 85.28; H 8.50; N 6.22.

2-(1,3-Dodecadiynyl)aniline (IVb) was obtained from 5,7-dodecadiyne (450 mg, 2.5 mmol) and 2-iodoaniline (438 mg, 2 mmol) in 95% yield (481 mg, 1.9 mmol). Dark-yellow oily substance. R_f 0.22 (hexane–CH_2Cl_2, 4:1). IR spectrum (CCl_4), ν_{max}, cm^{-1}: 3500 m, 3400 m (NH_2), 3080 w, 3030 w (H–C^2_{sp}), 2925 s, 2850 s (H–C^3_{sp}), 2240 w, 2150 m (C≡C), 1610 s (C=C), 1470 s, 1400 s, 1255 s, 840 s. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 0.89 t (3H, CH_3, *J* 7 Hz), 1.21–1.42 s [10H, $(CH_2)_5$], 1.57 q (2H, ≡$CCH_2\underline{C}H_2$, *J* 7 Hz), 2.39 t (2H, ≡CCH_2, *J* 7 Hz), 4.29 s (2H, NH_2), 6.66–6.71 m (2H), 7.14 t (1H, *J* 7 Hz), 7.31 t (1H, *J* 7 Hz) (H arom). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 14.53, 23.07, 28.69, 29.33, 29.50, 29.57, 32.25 (C^3_{sp}), 20.07 ($\underline{C}H_2C$≡), 65.44, 71.99, 80.00, 86.40 (C_{sp}), 107.08, 114.84,

118.40, 130.57, 133.51, 149.62 (C arom). Found, %: C 85.16, 85.32; H 9.10, 9.15; N 5.62, 5.65. $C_{18}H_{23}N$. Calculated, %: C 85.32; H 9.15; N 5.53.

2-(1,3-Hexadecadiynyl)aniline (IVc) was obtained from 7,9-hexadecadiyne (654 mg, 3 mmol) and 2-iodoaniline (438 mg, 2 mmol) in 67% yield (409 mg, 1.34 mmol), mp 31°C (from petroleum ether, bp 40–70°C). R_f 0.24 (hexane–CH_2Cl_2, 4:1). IR spectrum (CCl_4), ν, cm^{-1}: 3505 m, 3405 m (NH_2), 3080 s, 3030 s (H–C^2_{sp}), 2950 s, 2850 s (H–C^3_{sp}), 2230 s, 2150 s (C≡C), 1600 s (C=C), 1480 s, 1445 s, 1300 s, 1240 s, 1140 m, 900 s. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.91 t (3H, CH_3, *J* 7 Hz), 1.21–1.67 m [20H, $(CH_2)_{10}$], 2.39 t (2H, ≡CCH_2, *J* 7 Hz), 4.28 s (2H, NH_2), 6.65–6.69 m (2H), 7.14 t (1H, *J* 7 Hz), 7.28 t (1H, *J* 7 Hz) (H arom). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 14.55, 23.11, 28.70, 29.33, 29.54, 29.78, 29.92, 30.04, 30.07, 30.09, 32.34 (C^3_{sp}), 20.08 ($\underline{C}H_2C$≡), 65.47, 72.05, 79.95, 86.33 (C_{sp}), 106.94, 114.68, 118.26, 130.57, 133.50, 149.88 (C arom). Mass spectrum, *m/z* (I_{rel}, %): 309 (100), 224 (11), 210 (14) 196 (26), 182 (23), 168 (23), 167 (22), 156 (57), 154 (51), 130 (34), 117 (26), 106 (37), 93 (8), 91 (8), 79 (12), 77 (14), 67 (8), 55 (16), 43 (37), 41 (37). Found, %: C 85.14, 85.23; H 10.09, 10.02; N 4.59, 4.57. $C_{22}H_{31}N$. Calculated, %: C 85.38; H 10.10; N 4.53.

2-(1,3-Decadiynyl)-4-nitro-1-naphthylamine (Va) was obtained from 4,6-decadiyne (335 mg, 2.5 mmol) and 2-iodo-4-nitro-1-naphthylamine (628 mg, 2 mmol) in 88% yield (554 mg, 1.76 mmol), mp 134–136°C (CH_2Cl_2). R_f 0.56 (hexane–CH_2Cl_2, 1:1). IR spectrum (CCl_4), ν_{max}, cm^{-1}: 3535 m, 3480 m, 3425 s (NH_2), 2290 w, 2260 w, 2150 w (C≡C), 1630 s (C=C), 1370 s. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.89 t (3H, CH_3, *J* 7 Hz); 1.22–1.38 m [6H, $(CH_2)_3$], 1.57 q (2H, ≡$CCH_2C\underline{H}_2$, *J* 7 Hz), 2.47 t (2H, ≡CCH_2, *J* 7 Hz), 5.86 s (2H, NH_2), 7.62 t (1H, *J* 8 Hz), 7.77 t (1H, *J* 8 Hz), 7.89 d (1H, *J* 8 Hz), 8.39 s (1H), 8.89 d (1H, *J* 8 Hz) (H arom). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 14.11, 23.06, 29.29, 29.52, 32.20 (C^3_{sp}), 20.06 ($\underline{C}H_2C$≡), 66.04, 70.03, 81.34, 87.87 (C_{sp}), 116.92, 121.33, 122.18, 124.77, 126.88, 127.43, 130.14, 130.92, 136.11, 153.07 (C arom). Found, %: C 74.72, 74.72; H 6.28, 6.38; N 8.51, 8.86. $C_{20}H_{20}N_2O$. Calculated, %: C 74.98; H 6.29; N 8.74.

2-(1,3-Dodecadiynyl)-4-nitro-1-naphthylamine (Vb) was obtained from 5,7-dodecadiyne (450 mg, 2.5 mmol) and 2-iodo-4-nitro-1-naphthylamine (628 mg, 2 mmol) in 92% yield (640 mg, 1.84 mmol), mp 112–114°C (CH_2Cl_2). R_f 0.59 (hexane–CH_2Cl_2, 1:1). IR spectrum (CH_2Cl_2), ν_{max}, cm^{-1}: 3520 m, 3405 m (NH_2), 2230 m, 2140 m (C≡C), 1600 s (C=C). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.92 t (3H, CH_3, *J* 7 Hz), 1.21–1.46 m [10H, $(CH_2)_5$], 1.63 m (2H, ≡$CCH_2C\underline{H}_2$, *J* 7 Hz), 2.45 t (2H, ≡CCH_2, *J* 7 Hz), 5.90 s (2H, NH_2), 7.61 t (1H, *J* 8 Hz), 7.76 t (1H, *J* 8 Hz), 7.91 d (1H, *J* 8 Hz), 8.42 s (1H), 8.83 d (1H, *J* 8 Hz) (H arom). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 14.22, 23.02, 28.60, 29.29, 29.41, 29.52, 32.20 (C^2_{sp}), 19.96 ($\underline{C}H_2C$≡), 66.03, 69.99, 81.40, 87.85 (C_{sp}), 116.95, 121.34, 122.08, 124.87, 126.91, 127.46, 130.24, 130.97, 136.14, 153.09 (C arom). Mass spectrum, *m/z* (I_{rel}, %): 348 (5), 314 (7), 291 (3), 184 (4), 168 (8), 251 (5), 217 (6), 201 (4), 167 (4), 140 (4), 97 (100).

4,6-Bis(1,3-decadiynyl)-1,3-diaminobenzene (VIa) was obtained from 4,6-decadiyne (670 mg, 5 mmol) and 1,3-diamine-4,6-diiodobenzene (719 mg, 2 mmol) in 46% yield (343 mg, 0.96 mmol), mp 76–78°C (from petroleum ether, bp 40–70°C). R_f 0.62 (acetone–petroleum ether, bp 40–70°C, 1:1). IR spectrum (CCl_4), ν_{max}, cm^{-1}: 3520 m, 3410 s (NH_2), 2965 s, 2940 s, 2855 m (H–C^3_{sp}), 2225 w, 2150 m (C≡C), 1610 s (C=C), 1445 m, 1355 m, 1325 m, 890 w. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.92 t (6H, CH_3, *J* 7 Hz), 1.24–1.77 m (16H, CH_2), 2.37 t (4H, CH_2C≡, *J* 7 Hz), 4.36 s (4H, NH_2), 5.91 s (1H), 7.30 s (1H) (H arom). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 14.44 (CH_3), 20.08, 22.91, 28.70, 28.97, 31.70 (CH_2), 65.62, 71.67, 78.38, 85.79 (C_{sp}), 97.94, 98.28, 138.84, 151.55 (C arom). Mass spectrum (of hydrochloride), *m/z* (I_{rel}, %): 410 (4), 408 (11), 373 (32), 372 (100), 343 (6), 303 (6), 301 (15), 294 (15), 230 (12), 185 (10), 183 (11). Found (for hydrochloride),%: C 76.46, 76.17; H 8.17, 8.20; N 6.38, 6.42. $C_{26}H_{33}N_2Cl$. Calculated, %: C 76.35; H 8.13; N 6.85.

2-Amino-3,5-bis(1,3-decadiynyl)pyridine (VIIa) was obtained from 4,6-decadiyne (670 mg, 5 mmol) and 2-amino-3,5-diiodopyridine (691 mg, 2 mmol) in 66% yield (473 mg, 1.32 mmol), mp 84–86°C (from benzene). R_f 0.7 (ettyl acetate–petroleum ether, bp 40–70°C, 3:7). IR spectrum (CCl_4), ν_{max}, cm^{-1}: 3535 m, 3485 m, 3410 m (NH_2), 3295 m, 3225 m, 3150 m (H–C^2_{sp}), 2925 s, 2850 s (H–C^3_{sp}), 2240 m, 2150 m (C≡C), 1590 s (C=C), 1450 s, 1400 s, 1225 s, 900 s. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.90 t (6H, CH_3, *J* 7 Hz), 1.20–1.67 m (20H, CH_2), 2.37 m (4H, CH_2C≡), 5.52 s (2H, NH_2), 7.60 s (1H, $H^{6\text{-}Py}$), 8.14 s (1H, $H^{4\text{-}Py}$). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 14.43 (CH_3); 19.99, 20.04, 22.91, 28.50, 28.63, 28.96, 28.97, 31.67, 31.69 (CH_2), 64.97,

65.39, 69.09, 71.83, 75.62, 81.33, 85.38, 87.76 (C_{sp}), 102.11, 108.81, 144.23, 152.77, 159.57 (C arom). Found, %: C 83.46, 83.70; H 8.44, 8.57; N 7.57, 7.80. $C_{25}H_{30}N_2$. Calculated, %: C 83.75; H 8.43; N 7.81.

4-Amino-3,5-bis(1,3-dodecadiynyl)pyridine (VIIIb) was obtained from 5,7-dodecadiyne (810 mg, 5 mmol) and 4-amino-3,5-diiodopyridine (691 mg, 2 mmol) in 86% yield (616 mg, 1.72 mmol), mp 78–80°C (from benzene). R_f 0.52 (CH_2Cl_2–petroleum ether, bp 40–70°C, 3:1). IR spectrum (CCl_4), ν_{max}, cm^{-1}: 3535 m, 3420 m (NH_2), 2975 s, 2940 s, 2865 s (H–C^3_{sp}), 2240 m, 2150 w (C≡C), 1605 m (C=C), 1470 m, 1255 s, 1090 s, 1000 s, 860 m. ^{1}H NMR spectrum [$(CD_3)_2CO$], δ, ppm: 0.89 t (6H, CH_3, *J* 7 Hz), 1.28–1.47 m (20H, CH_2), 2.59 m (4H, CH_2), 2.45 t (4H, CH_2C≡), 6.46 s (2H, NH_2), 8.26 s (2H, H^{Py}). ^{13}C NMR spectrum [$(CD_3)_2CO$], δ, ppm: 13.86 (CH_3), 19.34, 22.81, 28.42, 28.60, 28.83, 29.09, 28.35, 29.61, 29.85, 30.11, 32.07 (CH_2), 65.09, 68.25, 82.21, 87.19 (C_{sp}), 102.86, 153.28, 156.96 (C^{Py}). Mass spectrum, *m/z* (I_{rel}, %): 414 (100), 399 (5), 385 (10), 371 (12), 357 (20), 315 (10), 262 (80), 183 (58), 108 (40).

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