Synthesis of functionalized 1,2-diphenylacetylene derivatives

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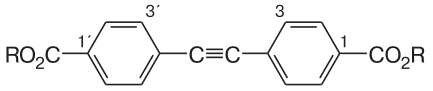
A series of new functionalized 1,2-diphenylacetylene derivatives, including those containing L-prolinamide substituents at the aromatic nuclei, was synthesized using the Sonogashira coupling at the key step.

Key words: 1,2-diphenylacetylenes, Sonogashira coupling, proline derivatives.

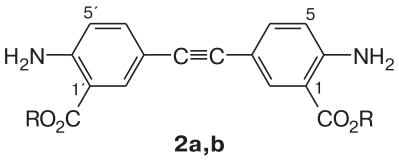
Derivatives of 1,2-diphenylacetylene attract an attention as the valuable intermediates in the synthesis of functionalized indoles[1—4] and benzofurans, including those among natural products.[5—8] The application prospect of such compounds has been shown for the obtaining of organic ferromagnetic materials[9] and electrode components of lithium-ion batteries.[10] Derivatives of 1,2-diphenylacetylene bearing carboxyl groups at the each of aromatic nuclei have been utilized as the so-called "dicarboxylate linkers" in Metal-Organic Frameworks (MOFs) that proved to be efficient in heterogeneous catalysis[11,12] and promising as materials for hydrogen storage.[13] A number of examples of their application for these purposes is still small and mostly limited to the usage of frame structures based on their simplest representative, 1,2-bis(4-carboxyphenyl)acetylene.

Most popular approaches for the production of 1,2-diphenylacetylene derivatives are the various embodiments of halogenoarene alkynylation *via* the Sonogashira coupling (e.g., see Ref. 14). In particular, acetylene by itself[15—17] or its synthetic equivalent (CaC_2/H_2O system)[18] used in combination with various aryl iodides as the starting compounds allow one to obtain symmetric 1,2-diarylacetylenes in good yields *via* the two successive alkylation processes.

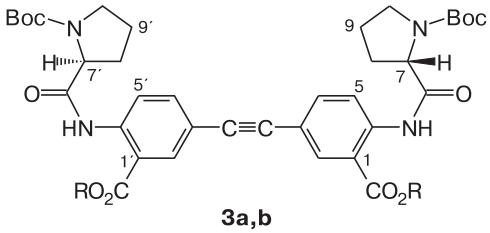
In order to enhance the number of available 1,2-diphenylacetylene derivatives that are promising for applications in the above mentioned areas, the present work reports on the synthesis of series of symmetrically substituted acetylenes **1—3** bearing methoxycarbonyl and carboxyl groups in aromatic cycles, including non-racemic chiral derivatives **3a**,**b**. Asymmetrically substituted diarylacetylenes **4a**,**b** were also obtained.*



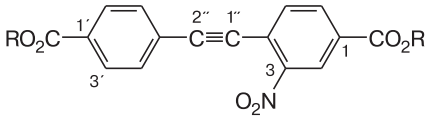
1a,b



2a,b



3a,b



4a,b

1—4: R = Me (**a**), H (**b**)

The Sonogashira coupling of methyl 4-iodobenzoate (**5**) with acetylene gave symmetric diarylacetylene **1a** in a good yield (Scheme 1). In the case of aryl iodide **6**, the process in wet acetonitrile using calcium carbide as the *in situ* source of acetylene was efficient, which provided new diarylacetylene **2a**. Compound **3a** has been for the

* Atom numbering on structures **1—4** and **8** corresponds to that given in the NMR spectra descriptions.

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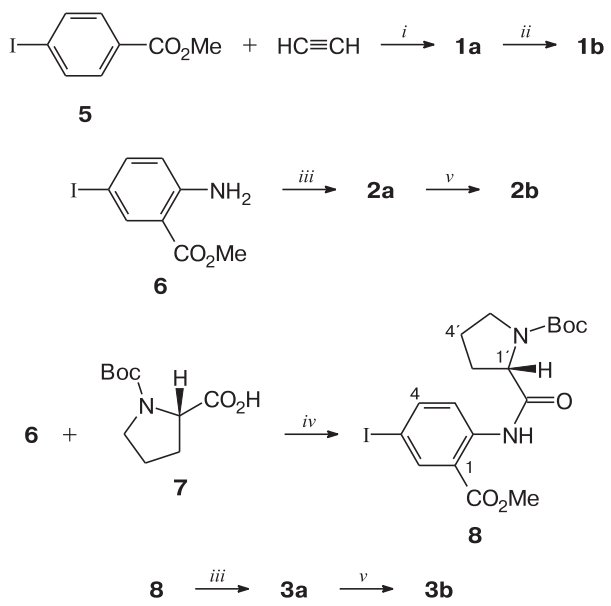
first time obtained (in the yield of 95%) in the similar way under these reaction conditions taking L-proline-containing aryl iodide **8**. The latter was synthesized *via* the condensation of anthranilic acid derivative **6** with *N*-Boc-L-proline **7**. The saponification of diesters **1a**, **2a**, and **3a** resulted in the corresponding dicarboxylic acids **1b**, **2b**, and **3b**.

Scheme 1



Reagents and conditions: *i*. $Pd(OAc)_2$, CuI, Ph_3P, Et_3N, MeCN, 20 °C; *ii*. 1) NaOH, EtOH, 20 °C, 2) conc. HCl; *iii*. CaC_2/H_2O, $Pd(OAc)_2$, CuI, Ph_3P, Et_3N, MeCN, 20 °C; *iv*. $POCl_3$, pyridine, −15—5 °C; *v*. 1) aq. NaOH, Me_2CO, 20 °C, 2) citric acid.

Known monoarylacetylene **9**[19] and bromo nitro arene **10**[20] were taken as the starting compounds for the synthesis of new asymmetric diarylacetylenes **4a**,**b** *via* the Sonogogashira coupling (Scheme 2).

The structure of new compounds **2**—**4** was confirmed by the dataset of spectral analysis. It is interesting that a double set of some signals was observed in the NMR spectra of L-proline-containing diphenylacetylenes **3a**,**b**, which was similar to that recorded previously[21] for their well-known precursor **8**. These spectral features are apparently due to the steric hindrances that can affect the state of conformational equilibrium of molecules in favor of two major "rotamers". It should be noted that we have not found any data on the synthesis of non-racemic 1,2-diphenylacetylene derivatives in the literature. The opportunity of their application, in particular, as the organic components for the design of new metal-organic framework structures will be the subject of our further researches.

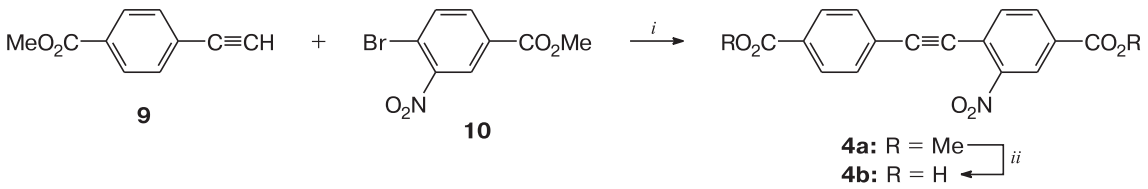
Experimental

Melting points were measured on a Kofler table. IR spectra were recorded on a Bruker ALPHA-T instrument. ^1H and ^{13}C NMR spectra of solutions in $CDCl_3$ (unless otherwise noted) were recorded on Bruker AC-200 and Bruker AM-300 spectrometers at 298 K relative to the solvent residual signals ($\delta_H = 7.27$ and $\delta_C = 77.0$ ppm, respectively). High-resolution mass spectra (HRMS) (ESI) were recorded on a Bruker micrOTOF II spectrometer at the capillary potential of 4.5 kV using a direct (syringe) injection of sample solution in methanol (3 μL min^{-1}) in the positive ions detection mode (mass range of 500—3000 Da), the main flow of nitrogen was 4 L min^{-1} (180 °C). The optical rotation was measured on a Jasco P-2000 polarimeter. Column chromatography was performed on a Silica gel 60 (0.04—0.06 mm, Fluka). The R_f values were measured on Silufol (Chemapol) and Kieselgel F254 (Fluka) plates possessing a fixed layer. Solvents, including light petroleum (LP) with b.p. 40—70 °C, were purified and dried according to the standard procedures.[22] For ultrasonic treatment of the reaction mixtures, a UZV-1/100-TN (Russia) bath was used.

Commercially available methyl 4-iodobenzoate (**5**), 5-iodoanthranilic acid, *N*-Boc-L-proline (**7**), $POCl_3$, $Pd(OAc)_2$, CuI, Ph_3P, CaC_2, and pyridine (Acros Organics) were used. Methyl 4-ethynylbenzoate (**9**)[19] and methyl 4-bromo-3-nitrobenzoate (**10**)[20] were prepared according to the known procedures.

Dimethyl 4,4′-ethyne-1,2-diyldibenzoate (1a). A mixture of CuI (540 mg, 2.83 mmol), $Pd(OAc)_2$ (37 mg, 0.16 mmol), and Ph_3P (740 mg, 2.82 mmol) in MeCN (30 mL) deaerated by the ultrasonic treatment (UST) under argon atmosphere was stirred at 20 °C for 20 min. Aryl iodide **5** (1.95 g, 7.44 mmol) and Et_3N (410 mg, 40.42 mmol, 5.6 mL) were then added. The mixture was stirred under acetylene atmosphere for 5 h, left for 16 h, and then concentrated *in vacuo*. The residue was suspended in $CHCl_3$ and filtered through a short layer of SiO_2. The filtrate was evaporated; the residue was purified by chromatography on SiO_2 using benzene as the eluent. Diarylacetylene **1a** (0.80 g, 73%) was isolated as light brown crystals, R_f 0.34 (benzene), m.p. 218—221 °C. ^1H NMR ($CDCl_3$), δ: 3.94 (s, 6 H, 2 MeCO); 7.61

Scheme 2



Reagents and conditions: *i*. $Pd(PPh_3)_2Cl_2$, CuI, Et_3N, THF, 20 °C; *ii*. 1) aq. KOH, THF, 20 °C, 2) 1*N* aq. HCl.

(dd, 4 H, HC(3), HC(3′), HC(5), HC(5′), J = 8.6 Hz, J = 1.9 Hz); 8.05 (dd, 4 H, HC(2), HC(2′), HC(6), HC(6′), J = 8.6 Hz, J = 1.9 Hz); which is similar to that reported previously.[15]

4,4′-Ethyne-1,2-diyldibenzoic acid (1b). A mixture of diester **1a** (0.91 g, 3.09 mmol) and NaOH (0.72 g, 18 mmol) in EtOH (30 mL) was refluxed for 6 h, left for 16 h, and then concentrated *in vacuo*. The residue was dissolved in water and acidified with 10*M* HCl till pH 1. The precipitated product was filtered off, washed with water, and dried *in vacuo* (2 Torr) over P_2O_5. Dicarboxylic acid **1b** (0.83 g, 97%) was isolated as a brown powder, m.p. >200 °C (decomp.) ^{1}H NMR ($CDCl_3$), δ: 7.70 (br. d, 4 H, HC(3), HC(3′), HC(5), HC(5′), J = 8.0 Hz); 7.99 (br. d, 4 H, HC(2), HC(2′), HC(6), HC(6′), J = 8.0 Hz). ^{13}C NMR (DMSO-d_6), δ: 91.0 (C≡C); 126.0 (C(4), C(4′)); 129.6 (2 C(2), 2 C(2′)); 130.9 (2 C(1), 2 C(1′)); 131.7 (2 C(3), 2 C(3′)); 166.6 (2 CO); which is similar to that reported previously.[23]

Methyl 2-amino-5-iodobenzoate (6). Concentrated H_2SO_4 (3.7 mL) was added dropwise at 20 °C under argon atmosphere to a stirred solution of 5-iodoanthranilic acid (5.0 g, 19 mmol) in MeOH (20 mL), and the mixture was refluxed for 7 h. The mixture was then concentrated *in vacuo* to the volume of 10 mL, poured into a vigorously stirred saturated solution of $NaHCO_3$ (80 mL), and extracted with EtOAc. The organic layer was washed with a brine solution, dried over Na_2SO_4, and concentrated *in vacuo*; the residue was purified by chromatography on SiO_2 (eluent was benzene). Ester **6** (3.68 g) was isolated as yellow crystals, m.p. 80—82 °C (LP). ^{1}H NMR ($CDCl_3$), δ: 3.87 (s, 3 H, MeO); 5.76 (br.s, 2 H, H_2N); 6.46 (d, 1 H, HC(3), J = 8.7 Hz); 7.48 (dd, 1 H, HC(4), J = 8.7 Hz, J = 2.2 Hz); 8.14 (d, 1 H, 2 HC(6), J = 2.2 Hz); which is similar to that reported previously.[24]

Dimethyl 3,3′-ethyne-1,2-diylbis(6-aminobenzoate) (2a). A mixture of CuI (110 mg, 0.58 mmol), $Pd(OAc)_2$ (60 mg, 0.27 mmol), and Ph_3P (130 mg, 0.49 mmol) in MeCN (30 mL) deaerated (UST) under argon atmosphere was stirred at 20 °C for 20 min. Iodide **5** (1.39 g, 5.0 mmol), Et_3N (1.53 g, 15.11 mmol, 2.1 mL), H_2O (0.15 g, 8.33 mmol), and finely ground CaC_2 (1.0 g, 15.60 mmol) were then added. The reaction mixture was stirred for 7 h and concentrated *in vacuo*; the residue was extracted with hot EtOAc. The extract was filtered and concentrated *in vacuo*, the residue was purified by chromatography on SiO_2 using gradient elution of PhH → PhH/EtOAc (4 : 1). Diarylalkyne **2a** (0.57 g, 70%) was isolated as yellow crystals, m.p. 245—249 °C. HRMS (ESI), found *m/z*: 325.1179, 347.0997; $C_{18}H_{16}N_2O_4$; calculated 325.1183 $[M + H]^+$, 347.1002 $[M + Na]^+$. IR (KBr), ν/cm^{-1}: 788, 834, 985, 1103, 1162, 1235, 1300, 1430, 1506—1663, 1688, 2342, 2361, 2838—3033, 3367, 3464. ^{1}H NMR (DMSO-d_6), δ: 3.82 (s, 6 H, 2 MeO); 6.75 (d, 2 H, HC(5), HC(5′), J = 8.6 Hz); 7.26 (dd, 2 H, HC(4), HC(4′), J = 8.6 Hz, J = 1.9 Hz); 7.83 (d, 2 H, HC(2), HC(2′), J = 1.9 Hz). ^{13}C NMR (DMSO-d_6), δ: 51.3 (Me, Me′); 86.9 (C□C); 108,8 (C(5), C(5′)); 109.0 (C(3), C(3′)); 116.9 (C(1), C(1′)); 133.9 (C(2), C(2′)); 136.0 (C(4), C(4′)); 150.8 (C(6), C(6′)); 167.1 (CO, C′O).

3,3′-Ethyne-1,2-diyilbis(6-aminobenzoic acid) (2b). Sodium hydroxide solution (15 mL, 5%) was added to a solution of diester **2a** (0.45 g, 1.39 mmol) in acetone (25 mL) stirred at 20 °C under argon atmosphere. The mixture was stirred at 20 °C for 10 h, concentrated *in vacuo* to the volume of ~15 mL, and acidified with citric acid till pH ~4. The formed precipitate was filtered off, washed with water and then EtOAc, and dried *in vacuo* (2 Torr) till the constant weight. Dicarboxylic acid **2b** (0.40 g, 97%) was isolated as a yellow powder, m.p. >200 °C (decomp.). HRMS (ESI), found *m/z*: 297.0866; $C_{16}H_{12}N_2O_4$; calculated 297.0870 $[M + H]^+$. IR (KBr), ν/cm^{-1}: 683, 827, 905, 1169, 1228, 1287, 1326, 1421, 1552, 1625, 1667, 2520—2886, 3384, 3496. ^{1}H NMR (DMSO-d_6), δ: 6.75 (d, 2 H, HC(5), HC(5′), J = 8.6 Hz); 7.24 (dd, 2 H, HC(4), HC(4′), J = 8.6 Hz, J = 1.8 Hz); 7.80 (d, 2 H, HC(2), HC(2′), J = 1.8 Hz). ^{13}C NMR (DMSO-d_6), δ: 87.9 (C≡C); 109,0 (C(5), C(5′)); 109.9 (C(1), C(1′)); 116.8 (C(3), C(3′)); 134.0 (C(2), C(2′)); 135.9 (C(4), C(4′)); 151.1 (C(6), C(6′)); 169.0 (CO, C′O).

Methyl 2-[(*N*-*tert*-butoxycarbonyl-L-prolinoyl)amino]-5-iodobenzoate (8). Phosphorus oxychloride (1.47 g, 9.6 mmol, 0.9 mL) was added dropwise at −10 °C to a stirred pyridine (40 mL) solution of *N*-Boc-L-proline **7** (1.74 g, 8.08 mmol) and arylamine **6** (2.24 g, 8.08 mmol) under argon atmosphere. The reaction mixture was stirred for 30 min (−10—5 °C), then poured into water (200 mL) containing ice, and extracted with EtOAc. The aqueous layer was additionally extracted with EtOAc. The extract was washed with water, saturated $NaHCO_3$ solution, dried over Na_2SO_4, and concentrated *in vacuo*. The residue was purified by chromatography on silica gel using $CHCl_3$ as the eluent. The isolated product with R_f 0.56 (EtOAc/LP, 1 : 2) was crystallized from petroleum ether to give amide **8** (2.8 g, 74%) as light brown crystals, m.p. 92—95 °C, $[\alpha]^{23}_D$ −103.96 (c = 1.0, $CHCl_3$). ^{1}H NMR ($CDCl_3$), δ: 1.35 and 1.49 (both br.s, integral ratio of 5/4, 9 H, Me_3C); 1.74—2.42 (m, 4 H, HC(4′), HC(5′)); 3.39—3.80 (m, 2 H, HC(3′)); 3.91 (s, 3 H, MeO); 4.27 and 4.41 (both m, integral ratio of 5/4, 1 H, HC(1′)); 7.81 (br.d, 1 H, HC(3), J = 8.2 Hz); 8.34 (br.s, 1 H, HC(4)); 8.57 (br.d, 1 H, HC(6), J = = 8.2 Hz); 11.43 (m, 1 H, HN) (mixture of rotamers, see Ref. 21).

Dimethyl 3,3′-ethyne-1,2-diylbis[6-(*N*-*tert*-butoxycarbonyl-L-prolinoylamino)benzoate] (3a). A mixture of CuI (114 mg, 0.60 mmol), $Pd(OAc)_2$ (67 mg, 0.30 mmol), and Ph_3P (160 mg, 0.61 mmol) in MeCN (50 mL) deaerated under argon atmosphere was stirred at 20 °C for 20 min. Solution of iodoarene **8** (2.8 g, 5.9 mmol) in MeCN (5 mL), Et_3N (1.82 g, 18 mmol, 2.5 mL), H_2O (0.22 g, 12.2 mmol), and finely grounded CaC_2 (1.15 g, 17.9 mmol) were then added. The mixture was stirred for 5 h and then concentrated *in vacuo* (30—40 °C, 2 Torr). The residue was pounded with Bu^tOMe and filtered. The filtrate was evaporated to dryness *in vacuo*, and the residue was purified by chromatography on SiO_2 using a LP—EtOAc gradient till 40% of the latter. Product **3a** (2.02 g, 95%) was isolated as light brown crystals, m.p. 126—130 °C (Bu^tOMe—LP), $[\alpha]^{23}_D$ −152.63 (c = 1.0, $CHCl_3$). HRMS (ESI), found *m/z*: 719.3279, 741.3101, 757.2836; $C_{38}H_{46}N_4O_{10}$; calculated 719.3287 $[M + H]^+$, 741.3106 $[M + Na]^+$, 757.2846 $[M + K]^+$. IR (KBr), ν/cm^{-1}: 769, 855, 1082, 1159, 1240, 1291, 1379, 1460, 1512, 1580, 1698, 2876, 2958, 2975, 3250. ^{1}H NMR ($CDCl_3$), δ: 1.21 and 1.35 (both br.s, integral ratio of ~3/2, 18 H, 2 Me_3C); 1.96 (m, 4 H, HC(9), HC(9′)); 2.23 (m, 4 H, HC(8), HC(8′)); 3.44—3.79 (m, 4 H, HC(10), HC(10′)); 3.94 (s, 6 H, MeO, Me′O); 4.31 and 4.45 (both m, integral ratio of ~3/2, 2 H, HC(7), HC(7′)); 7.69 (br.d, 2 H, HC(4), HC(4′), J = 8.5 Hz); 8.23 (br.s, 2 H, HC(2), HC(2′)); 8.80 (br.d, 2 H, HC(5), HC(5′), J = 8.5 Hz); 11.57 (m, 2 H, HN, HN′) (mixture of rotamers).

3,3′-Ethyne-1,2-diylbis[6-(*N*-*tert*-butoxycarbonyl-L-prolinoylamino)benzoic acid] (3b). Sodium hydroxide solution (10 mL, 5%) was added to a solution of diester **3a** (0.76 g, 1.06 mmol) in acetone (20 mL) stirred at 20 °C under argon atmosphere. The mixture was stirred at 20 °C for 4 h, then acidified with citric acid till pH ~4, concentrated *in vacuo* to the volume of 10 mL, and

extracted with EtOAc. The extract was washed with water and then brine, dried over Na_2SO_4, and concentrated *in vacuo*. The residue was purified by chromatography on SiO_2 using a LP →Bu^{t}OMe gradient. Compound **6** (0.9 g, 72%) was isolated as light brown crystals, m.p. (THF—Bu^{t}OMe) >200 °C (decomp.), $[\alpha]^{23}_D$ −153.77 (*c* = 1.0, MeOH). HRMS (ESI), found *m/z*: 691.2966, 713.2787, 729.2528; $C_{36}H_{42}N_4O_{10}$; calculated 691.2974 $[M + H]^+$, 713.2793 $[M + Na]^+$, 729.2533 $[M + K]^+$. IR (KBr), ν/cm^{-1}: 844, 1089, 1161, 1292, 1397, 1410, 1515, 1581, 1654, 1699, 2886, 2977, 3436. ^{1}H NMR (DMSO-d$_6$), δ: 1.29 and 1.43 (both br.s, integral ratio of ~2/1, 18 H, 2 Me$_3$C); 1.81—2.39 (m, 8 H, HC(8), HC(8′), HC(9), HC(9′)); 3.51 (m, 4 H, HC(10), HC(10′)); 4.18 (m, 2 H, HC(7), HC(7′)); 7.68 (dd, 2 H, HC(4), HC(4′), *J* = 8.7 Hz, *J* = 1.9 Hz); 8.16 (br.d, 2 H, HC(2), HC(2′), *J* = 1.9 Hz); 8.68 (br.d, 2 H, HC(5), HC(5′), *J* = 8.7 Hz); 11.79 and 11.85 (both br.s, integral ratio of ~2/1, 2 H, HN, HN′) (mixture of rotamers). ^{13}C NMR ($CDCl_3$/CD_3OD), δ: 23.9, 24.4 (C(9), C(9′)); 27.0, 28.3 (2 C<u>Me</u>$_3$); 31.6 (C(8), C(8′)); 46.9 (C(10), C(10′)); 62.2, 62.8 (C(7), C(7′)); 80.4 (<u>C</u>Me$_3$); 88.4 (C□C); 116.0 (C(1), C(1′)); 117,7 (C(3), C(3′)); 134.9 (C(5), C(5′)); 137.3 (C(2), C(2′), C(4), C(4′)); 140.5 (C(6), C(6′)); 154.9 (C(7), C(7′)); 172.3 (CO, C′O).

Methyl 4-(4-methoxycarbonylphenylethynyl)-3-nitrobenzoate (4a). Complex $Pd(PPh_3)_2Cl_2$ (44 mg, 0.063 mmol) and salt CuI (5.7 mg, 0.03 mmol) were added to a stirred solution of methyl 4-ethynylbenzoate **9** (200 mg, 1.25 mmol), bromide **10** (390 mg, 1.5 mmol), and triethylamine (1 mL) in THF (10 mL) under argon atmosphere. Once the reaction was completed (2 h, TLC monitoring), the mixture was evaporated *in vacuo*, and the residue was purified by column chromatography on SiO_2. The gradient elution with benzene—ethyl acetate till 10% of the latter gave product **4a** (250 mg, 59%) as light yellow crystals, m.p. 102 °C (sublimate). HRMS (ESI), found *m/z*: 340.0823; $C_{18}H_{13}NO_6$; calculated 340.0816 $[M + H]^+$. IR (KBr), ν/cm^{-1}: 767, 978, 1016, 1104, 1176, 1232, 1274, 1288, 1353, 1403, 1436, 1535, 1602, 1616, 1720, 2967, 3064, 3422. ^{1}H NMR ($CDCl_3$), δ: 3.96 (s, 3 H, CH_3—O—C(4′)); 4.01 (s, 3 H, CH_3—O—C(1)); 7.68 (d, 2 H, HC(2′), HC(6′), *J* = 8.4 Hz); 7.82 (d, 1 H, HC(5), *J* = 8 Hz); 8.08 (d, 2 H, HC(3′), HC(5′), *J* = 8.4 Hz); 8.27 (dd, 1 H, HC(6), *J* = 8 Hz, *J* = 1.6 Hz); 8.75 (d, 1 H, HC(2), *J* = 1.6 Hz). ^{13}C NMR ($CDCl_3$), δ: 52.3 (<u>Me</u>O_2CC(1)); 52.9 (<u>Me</u>O_2CC(4′)); 86.8 (<u>C</u>(1″)≡C(2″)); 99.0 (C(1″)≡<u>C</u>(2″)); 122.1 (C(2)); 125.9 (C(4));126.4 (C(1′)); 129.6 (C(2′), C(6′)); 132.1 (C(3′), C(5′)); 133.2 (C(6)); 134.9 (C(5)); 149.5 (C(3)); 164.4 (CO_2—C(4′)); 166.2 (CO_2—C(1)).

4-(4-Carboxyphenylethynyl)-3-nitrobenzoic acid (4b). An aqueous solution of KOH (25 mL, 0.006%) was added to a solution of diester **4a** (0.2 g, 0.64 mmol) in THF (20 mL). The mixture was stirred for 4 h and then evaporated to dryness. The residue was dissolved in water (20 mL), and the resulting solution was acidified with 1*M* HCl till pH 2. The formed precipitate was filtered off and dried *in vacuo*. Acid **4b** (0.12 g, 55%) was isolated as dark red crystals, m.p. >200 °C (decomp.). HRMS (ESI), found *m/z*: 334.0318, 350.0058; $C_{16}H_9NO_6$; calculated 334.0322 $[M + Na]^+$, 350.0061 $[M + K]^+$. IR (KBr), ν/cm^{-1}: 758, 770, 858, 917, 1016, 1122, 1242, 1280, 1310, 1342, 1421, 1534, 1558, 1615, 1691, 1616, 2826, 2880, 2990, 3082, 3434. ^{1}H NMR ($CDCl_3$), δ: 7.73 (d, 2 H, HC(2′), HC(6′), *J* = 8.3 Hz); 7.98—8.06 (m, 3 H, HC(5), HC(3′), HC(5′)); 8.08 (d, 2 H, HC(3′), HC(5′), *J* = 8.4 Hz); 8.27 (dd, 1 H, HC(6), *J* = 8.1 Hz, *J* = 1.6 Hz); 8.58 (d, 1 H, HC(2), *J* = 1.6 Hz).

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