ACADEMIA ROMÂNĂ
Revue Roumaine de Chimie
https://www.icf.ro/rrch/

Rev. Roum. Chim.,
2024, *69*(5–6), 255–262
DOI: 10.33224/rrch.2024.69.5-6.03

*Dedicated to Professor Vasile P**â**rvulescu*
on the occasion of his 70th anniversary

SUZUKI-MIYAURA, SONOGASHIRA CROSS-COUPLING AND CuAAC REACTIONS SUITE FOR THE ACCESS TO A LARGE MACROCYCLE WITH *m,m'*-TERPHENYL MOTIF

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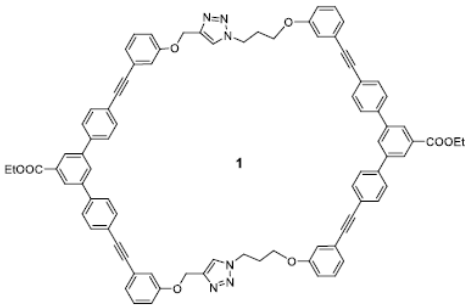
Received December 5, 2023

The access to a large semirigid macrocycle exhibiting two *m,m'*-terphenyl units was carried out by a suite of Suzuki-Miyaura, Sonogashira cross-coupling and CuAAC ("click") reactions. The target macrocycle exhibits two triazole and two ester protected carboxyl units of great use for the development of further applications.



INTRODUCTION

Supramolecular chemistry, introduced by Jean-Marie Lehn as the chemistry behind the molecules, or as the chemistry of secondary interactions, revealed unexpected and exciting properties of molecular assemblies formed by the connections of molecules[1a] and its development in the last years is spectacular.[1]

The self-assembled supramolecular aggregates, a main topic in supramolecular chemistry, are built up by weak contacts between molecules, which taken individually are not significant, but, multiplied at the level of the contacts between the molecules of the entire system, they enable the construction of highly sophisticated entities which fulfil many and various functionalities.[1] The most investigated secondary contacts between molecules are based on hydrogen bonds,[2] charge assisted hydrogen bonds [CAHB (salt-bridges)],[3] halogen bonding,[4] hydrophobic interactions,[5] interactions between aromatic units[6] or molecules and ions (*e.g.* anions[7]). Another important area of interest in which the involvement of secondary contacts is crucial, is represented by the host-guest supramolecular assemblies (*e.g.* having macrocycles, cyclophanes or cryptands (cages) as hosts).[8]

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Literature data reveal the versatility of *m,m'*-terphenyl building blocks which were successfully used for the obtaining of spectacular helical supramolecular aggregates (Yashima[9]), impressive large size, rigid macrocycles (*e.g.* the large oligophenylene hexagon reported by Schlüter[10]), switchable (by *cis-trans* isomerization) macrocycles (with azobenzene units[11]) and rigid macrocycles exhibiting *cis*-configurated C=C units (stilbenophanes[12]).

Continuing our previous works in which we reported exciting macrocycles,[13] cyclophanes[14] and cryptands[15] embedding various aromatic units we considered of interest to elaborate the design and to carry out the synthesis of a larger macrocycle (**1**) exhibiting *m,m'*-terphenyl aromatic building blocks connected via 1,4-disubstituted-1,2,3-triazole units. (Fig. 1).

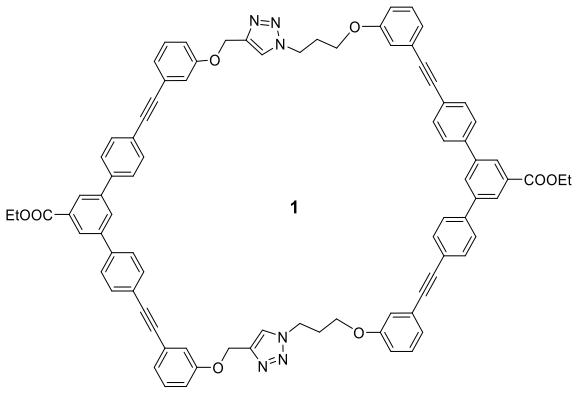


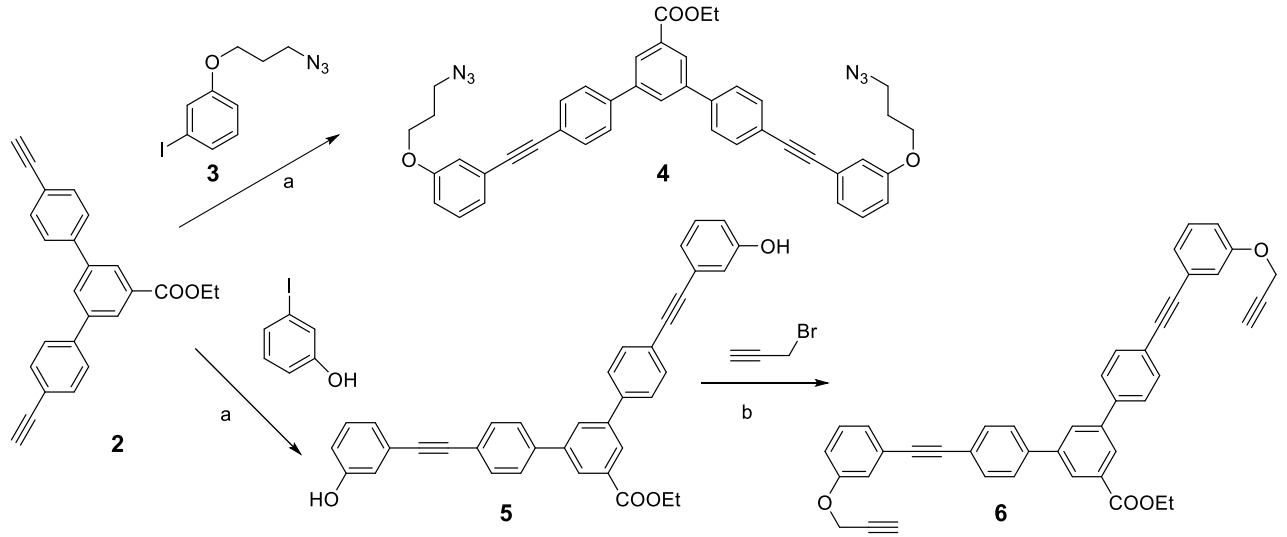
Fig. 1 – Target macrocycle (**1**) with *m,m'*-terphenyl units.

RESULTS AND DISCUSSION

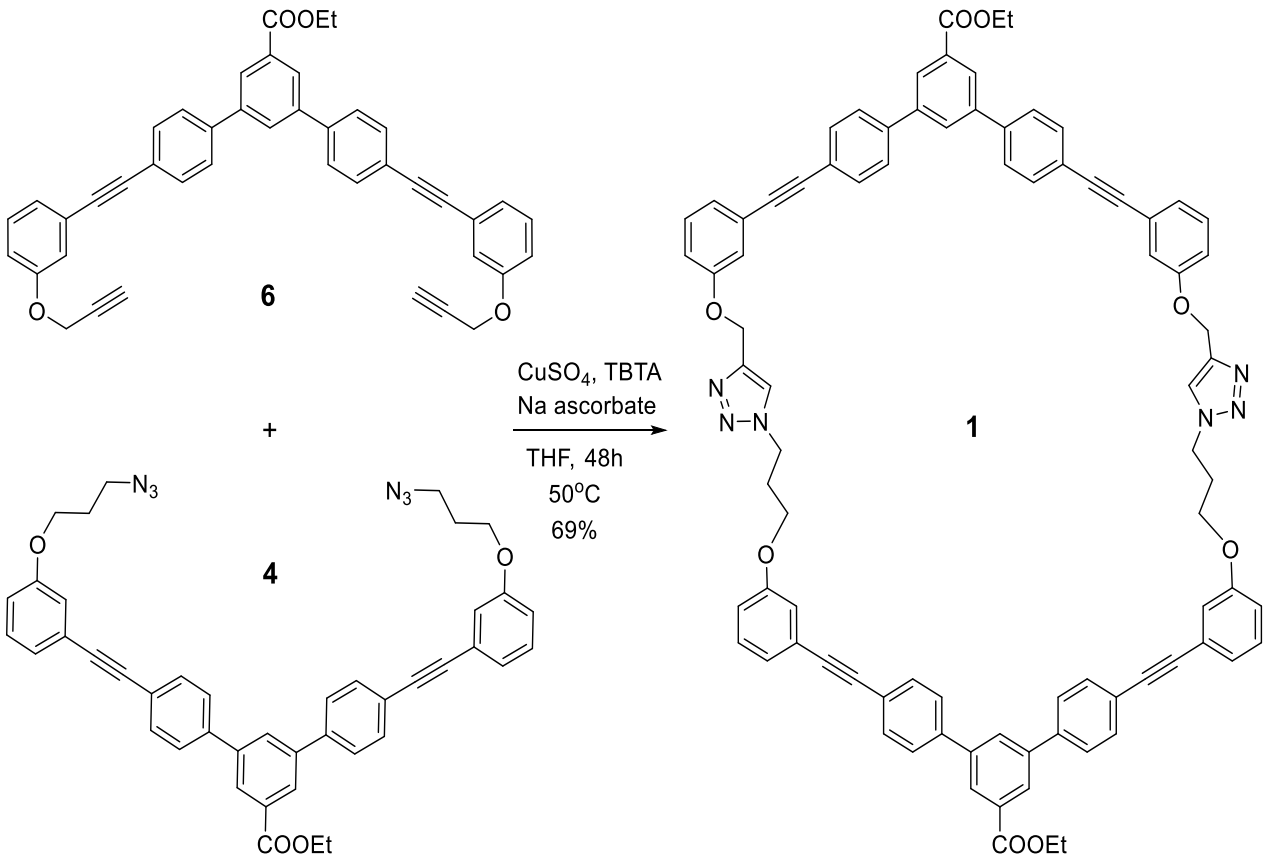
Macrocycle **1** was synthetized starting from the di-yne **2**. The Sonogashira cross-coupling reaction of **2** with the iodinated derivative **3** or *m*-iodophenol gave the diazide **4** and diphenol **5**, respectively in good yield (Scheme 1; [47% (**4**), 62% (**5**)]. The nucleophilic substitution reaction of **5** with propargylbromide afforded di-yne **6** (74% yield%). The CuAAC ("click") reaction of complementary dipodands **4** (diazide) and **6** (di-yne) lead to the formation of the target macrocycle **1** in very good yield (69%) (Scheme 2).

The starting di-yne **2** was prepared by a Suzuki-Miyaura cross-coupling reaction (PEPPSI (*1,3-Bis(2,6-diisopropylphenyl)-imidazol-2-ylidene](3-chloropyridyl)palladium(II) dichloride*), Cs_2CO_3, THF) of the commercially available ethyl ester of *m,m'*-dibromo-benzoic acid and the pinacolate ester of TIPS protected *p*-ethynylphenyl-boronic acid (Scheme 3, 74%), reaction followed by the di-yne TIPS deprotection with TBAF in THF at *rt* (89% yield).

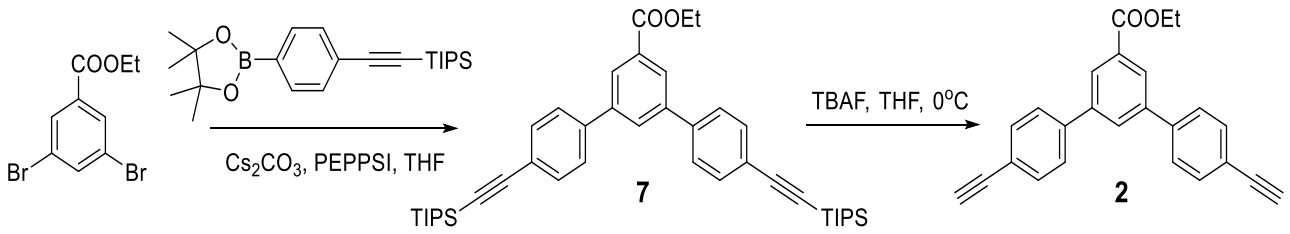
The structure of large dipodands **4**, **6** and macrocycle **1** was confirmed by NMR spectra (Figs. 2 and 3) and HRMS investigations (experimental part). Figures 2 and 3 also presents the assignment of the relevant signals in ^{1}H NMR spectra of these compounds. Macrocycle **1** as well as its dicationic derivative, to be obtained by an alkylation reaction (with CH_3I) at both triazole units, will be investigated in further works as host species in complexation reactions with aromatic or/and anionic guests.



Scheme 1 – Access to dipodand **6.**



Scheme 2 – Synthesis of macrocycle **1.**



Scheme 3 – Access to dipodand **2.**

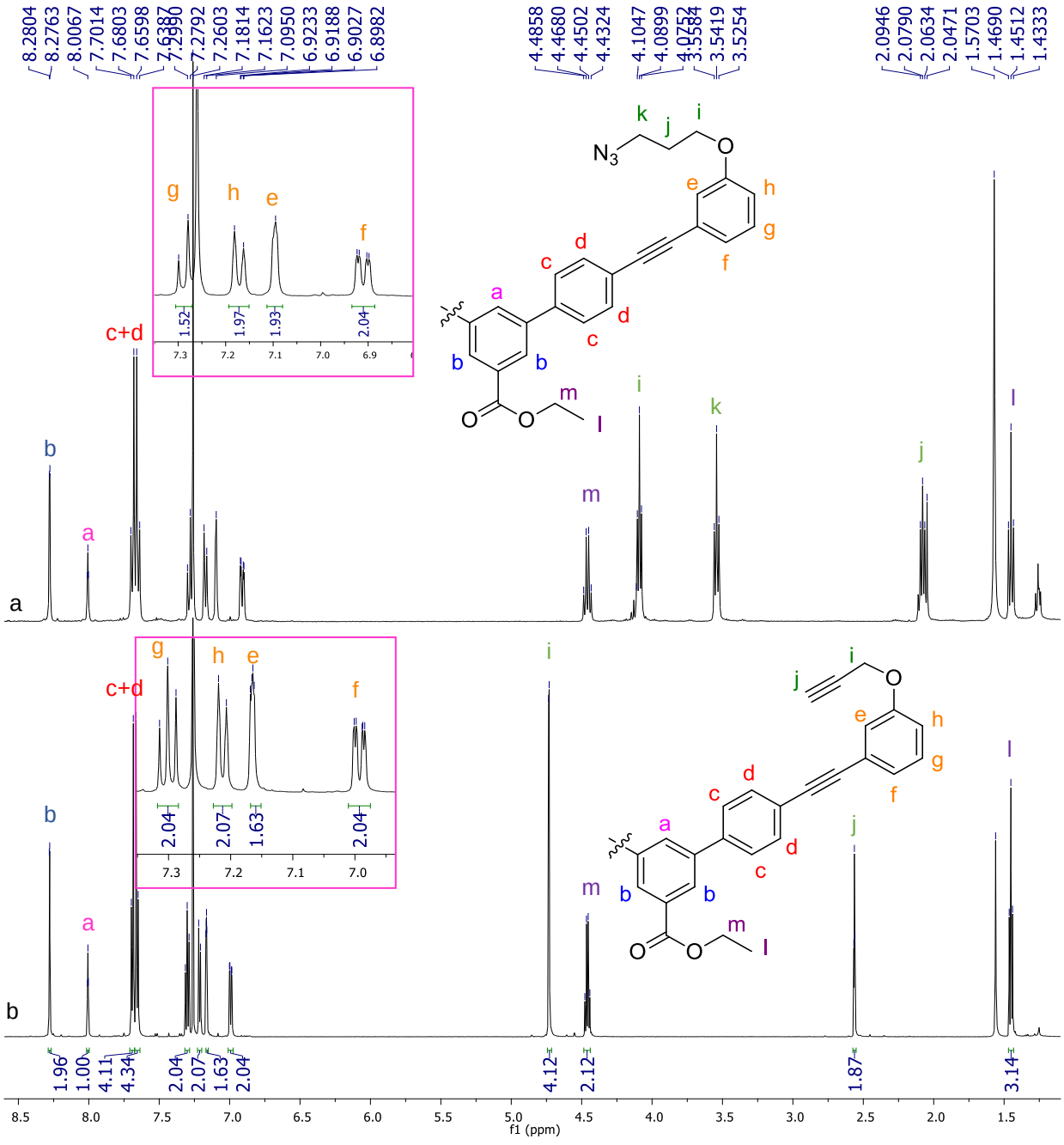


Fig. 2 – ^{1}H NMR spectra ($CDCl_3$, 600 MHz) of **4** (a) and **6** (b).

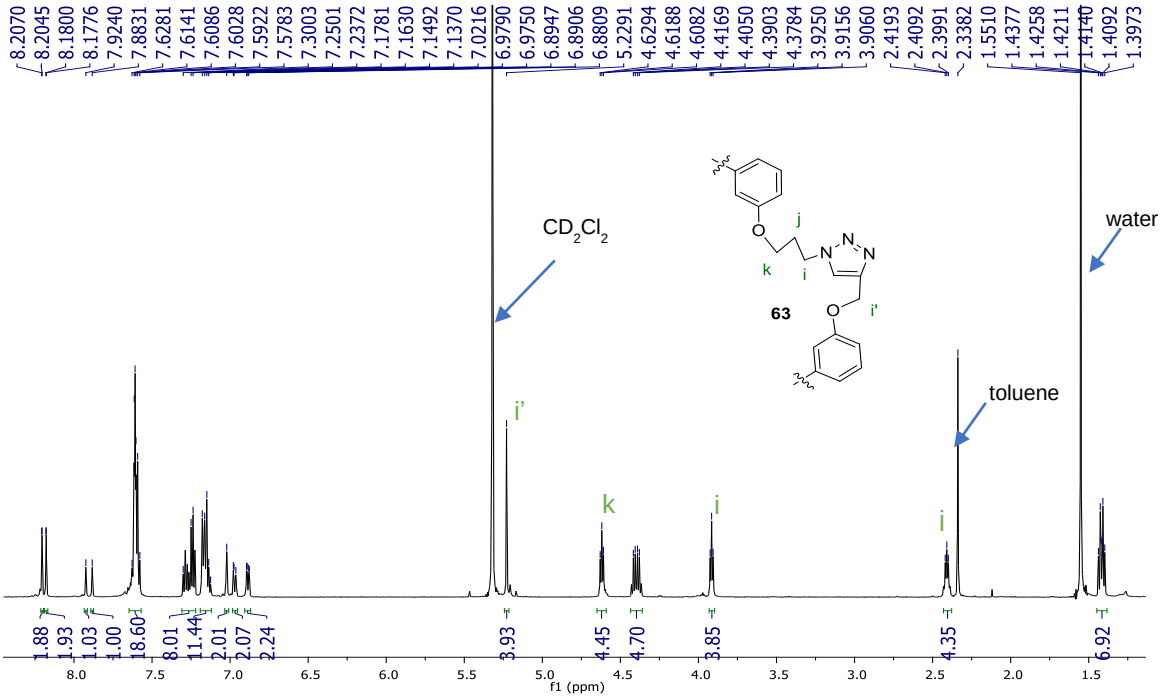


Fig. 3 – ^{1}H NMR spectrum (CD_2Cl_2, 600 MHz) of macrocycle **1.**

EXPERIMENTAL

General data

^{1}H NMR (600 MHz) and ^{13}C NMR (150 MHz) were recorded at *rt* in appropriate solvents [$CDCl_3$, CD_2Cl_2, $(CD_3)_2CO$]. Thin layer chromatography (TLC) was conducted on Silicagel 60 F_{254} TLC plates. TLC were visualized by UV irradiation at 254 and 365 nm and if needed with staining solution ($KMnO_4$). Column chromatography was conducted with 40-63 μm silica gel. HRMS were recorded using an LTQ XL OBITRAP mass spectrometer equipped with ESI/APCI sources. Melting points were recorded with open capillary tubes in an electric Apotec apparatus.

Chemicals were purchased from Sigma Aldrich, Alfa Aesar, TCI chemicals or Merck and were used without further purification. Solvents were dried and distilled under Ar using standard procedures.

Procedure for the synthesis of macrocycle 1

Dialkyne **6** (40 mg, 0.065 mmol) and diazide **4** (46 mg, 0.065 mmol) were dissolved in 28 mL THF. To this solution, $CuSO_4 \times 5H_2O$ (5 mg, 0.021 mmol), TBTA (11 mg, 0.020 mmol), sodium ascorbate (13 mg, 0.065 mmol) and water (5 mL) were added. The reaction mixture was stirred at 50℃ for 48 h. The mixture was afterwards extracted with dichloromethane (2×30 mL), and the separated organic layer was washed with aqueous ammonium chloride (1M, 2×20 mL) and water (3×15 mL) and dried over anhydrous $MgSO_4$. After the evaporation of the solvents, crude **1** was purified on column chromatography using chloroform: methanol = 40:1 as eluent.

Yield 69%, white solid, mp = 154–155ºC, R_f = 0.51 (chloroform: methanol = 40:1),

^{1}H NMR (600 MHz, CD_2Cl_2) δ (ppm): 8.20 (d, 2H, *J*=1.4 Hz), 8.18 (d, 2H, *J*=1.4 Hz), 7.92 (s, 1H), 7.88 (s, 1H), 7.61-7.57 (overlapped peaks, 16H), 7.30-7.22 (overlapped peaks, 4H), 7.17-7.12 (overlapped peaks, 8H), 7.02 (s, 2H), 6.97 (dd, 2H, *J*=8.2 Hz, *J*=2.3 Hz), 6.88 (dd, 2H, *J*=8.2 Hz, *J*=2.4 Hz), 5.2 (s, 4H), 4.46 (t, 4H, *J*=6.3 Hz), 4.40 (q, 4H, *J*=7.1 Hz), 3.91 (t, 4H, *J*=5.6 Hz), 2.40 (cv., 4H, *J*=6.1 Hz), 1.45-1 (overlapped peaks, 6H).

^{13}C NMR (150 MHz, CD_2Cl_2) δ (ppm): 166.60, 166.54, 158.96, 158.63, 144.23, 141.629, 141.624, 140.33, 140.31, 132.69, 162.69, 130.51, 130.50, 130.21, 130.16, 130.12, 130.08, 129.54, 128.73, 127.72, 127.70, 127.62, 127.59, 125.81, 125.18, 125.06, 124.84, 124.80, 124.19, 123.26, 118.58, 117.62, 115.97, 115.88, 90.71, 90.69, 89.58, 64.63, 62.69, 61.86, 47.53, 30.17, 14.73, 14.72.

HRMS (APCI+) *m/z*, calculated for $C_{86}H_{67}N_6O_8^+$ = 1311.5015, found $[M+H]^+$ = 1311.4960

Procedure for the synthesis of compound 2

To a cooled solution of **7** (9 mmol) in THF (100 mL), TBAF (27 mL, 1 M in THF, 27 mmol) was added and the mixture was stirred at 0ºC for 10 min, then for 2 h at *rt*. At the end, the solvent was removed by rotary evaporation and the residue was dissolved in 30 mL $CHCl_3$ and sequentially washed with 10% aq HCl (3x10 mL) and brine (3x10 mL). The organic layer was dried over $MgSO_4$, filtered to remove $MgSO_4$, and the solvent was evaporated under vacuum. The crude product **2** was purified by recrystallization from acetonitrile.

***Ethyl-4,4"-diethynyl-[1,1':3',1"-terphenyl]-5'-carboxylate* (2)**

Yield 89%, white solid, mp.=147–148ºC

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 8.24 (d, 2H, *J* = 1.6 Hz), 7.95 (t, 1H, *J* = 1.6 Hz), 7.64 (d, 4H, *J* = 8.4 Hz), 7.60 (d, 4H, *J*=8.4 Hz).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 166.39, 141.41, 140.48, 132.88, 132.02, 130.04, 127.51, 127.30, 121.92, 83.45, 78.35, 61.51, 14.54

HRMS (APCI+) *m/z* calculated for $C_{25}H_{19}O_2^+$: 351.1380; found: $[M+H]^+$351.1371

General procedure for Sonogashira cross coupling reaction (access to dipodands 4 and 5)

To a mixture of CuI (4 mg, 0.022 mmol), $Pd(PPh_3)_2Cl_2$ (44 mg, 0.06 mmol), and 3-iodophenol or iodoether **3** (0.62 mmol), Et_3N (4 mL) and dry THF (6 mL) were added. The mixture was stirred for 10 min at *rt* under Ar. After addition of the terphenyl di-yne **2** (0.285 mmol), the mixture was stirred for 6 h at 50ºC. Afterwards, the solvent was evaporated, the residue was dissolved in CH_2Cl_2 (50 mL), filtered through a pad of Celite, and washed with brine (2x20 mL). The organic layer was dried over $MgSO_4$ and then evaporated. The crude product was purified by silicagel column chromatography to give the desired pure product.

***Ethyl-4,4''-bis((3-(3-azidopropoxy)phenyl)ethynyl)-[1,1':3',1''-terphenyl]-5'-carboxylate* (4)**

Yield 47%, yellow thick oil, R_f= 0.28 (pentane: ethyl acetate = 4:1)

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 8.27 (d, 2H, *J* = 1.7 Hz), 8.00 (t, 1H, *J* = 1.7 Hz), 7.69 (d, 4H, *J* = 8.4 Hz), 7.65 (d, 4H, *J* = 8.4 Hz), 7.27 (m, 2H), 7.17 (d, 2H, *J* = 7.6 Hz), 7.09 (m, 2H), 6.91 (dd, 2H, *J*=8.3 Hz,*J*=2.5 Hz), 4.46 (q, 2H, *J* = 7.1 Hz), 4.09 (t, 4H, *J* = 5.9 Hz), 3.53 (t, 4H, *J* = 6.6 Hz), 2.07 (m, 4H), 1.45 (t, 3H, *J*=7.1 Hz).

HRMS (APCI+) *m/z* calculated for $C_{43}H_{37}N_6O_4^+$:701.2871; found:$[M+H]^+$701.2864

***Ethyl-4,4''-bis((3-hydroxyphenyl)ethynyl)-[1,1':3',1''-terphenyl]-5'-carboxylate* (5)**

Yield 62 %, yellow solid, mp = 79–80ºC , R_f = 0.48 (dichloromethane : methanol=40:1)

^{1}H NMR (600 MHz, $(CD_3)_2CO$) δ (ppm): 8.65 (s, 2H, -OH), 8.31 (d, 2H, *J* = 1.4 Hz) 8.27 (s, 1H), 7.90 (d, 4H, *J* = 8.2 Hz), 7.70 (d, 4H, *J* = 8.2 Hz), 7.26 (t, 2H, *J* = 7.8 Hz), 7.06 (overlapped peaks, 4H), 6.90 (dd, 2H, *J* = 8.0 Hz, *J* = 1.7 Hz) 4.44 (q, 2H), 1.43 (t, 3H)

^{13}C NMR (150 MHz, $(CD_3)_2CO$) δ (ppm): 342.89, 334.76, 318.60, 317.00, 309.52, 309.45, 307.08, 306.99, 304.70, 304.11, 301.32, 300.25, 300.20, 295.29, 293.49, 267.66, 265.66, 238.32, 191.05.

HRMS (APCI+)*m/z* calculated for $C_{37}H_{26}O_4$ 534.1826, found 534.1863,

Procedure for the synthesis of compound 6

K_2CO_3 (3 mmol) was added to a solution of **5** (0.5 mmol) in 20 mL dry acetonitrile. The mixture was refluxed for 30 minutes under argon atmosphere then cooled to *rt*. Propargyl bromide (80 wt. % in toluene, 1.1 mmol) was added and the mixture was refluxed (under stirring) overnight. The solution was then concentrated to dryness, water (40 mL) was added and the product was extracted with ethyl acetate (4×20 mL). The combined organic layer was washed with brine (2×20 mL), concentrated under vacuum and crude **6** was purified by column chromatography.

***Ethyl-4,4''-bis((3-(prop-2-yn-1-yloxy)phenyl)ethynyl)-[1,1':3',1''-terphenyl]-5'-carboxylate* (6)**

Yield: 74%, white solid. R_f=0.32 (ethyl acetate : pentane = 1:6), m. p. = 114 – 115 °C

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 8.27 (d, 2H, *J* = 1.7 Hz) 8.00(t, 1H, *J* = 1.7 Hz), 7.68 (d, 4H, *J* = 8.4 Hz), 7.65 (d, 4H, *J* = 8.4 Hz), 7.30 (m, 2H), 7.21 (d, 2H, *J* = 7.6 Hz), 7.16 (m, 2H), 6.98 (dd, 2H, *J* = 8.3 Hz, *J* = 2.5 Hz), 4.73 (d, 4H, *J* = 2.3 Hz), 4.46 (q, 2H, *J* = 7.1 Hz), 2.56 (t, 2H, *J* = 2.3 Hz), 1.45 (t, 3H, *J* = 7.1 Hz).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 166.47, 157.50, 141.45, 139.99, 132.38, 131.97, 129.99, 129.66, 127.41, 127.33, 125.27, 124.40, 122.92, 117.63, 115.98, 90.34, 89.28, 78.41, 75.95, 61.51, 56.04, 14.56.

HRMS (APCI+) *m/z* found 610.2090, calculated for $C_{43}H_{30}O_4$ 610.2139

Procedure for the synthesis of compound 7

In a dry two-neck flask, endowed with cooling system, the ethyl ester of 3,5-dibromobenzoic acid (0.1 mmol), triisopropyl((4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethynyl)silane (0.4 mmol), Cs_2CO_3 (0.5 mmol) were dissolved in 10 mL dry THF. The solution was degassed for 10 minutes, then [1,3-bis(2,6-diisopropylphenyl)-imidazol-2-ylidene](3-chloropyridyl)palladium(II) dichloride (PEPPSI) (0.0055 mmol) was added and the mixture was stirred at 60ºC for 12 h. The reaction mixture was then cooled to *rt*, filtered through celite, and THF was evaporated. The crude product was solved in 50 mL DCM and washed with water (2x20 mL) and brine (20 mL). The organic phase was dried over magnesium sulfate, and after filtration the solvent was evaporated under low pressure. The raw product was purified by column chromatography on silicagel using petroleum ether (PE) and diethyl ether (EE) 20 /1 as elution system.

***Ethyl-4,4''-bis((triisopropylsilyl)ethynyl)-[1,1':3',1''-terphenyl]-5'-carboxylate* (7)**

Yield 74%, white solid, R_f = 0.4 (PE:EE = 20:1)

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 8.23 (d, 2H, *J* = 1.7 Hz), 7.93 (t, 1H, *J* = 1.7 Hz), 7.61 (d, 4H, *J* = 8.5 Hz), 7.58 (d, 4H, *J* = 8.5 Hz), 4.45 (q, 2H, *J* = 7.1 Hz), 1.43 (t, 3H, *J* = 7.1 Hz), 1.15 (s, 42H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 166.49, 141.52, 139.96, 132.76, 131.91, 130.00, 127.36, 127.16, 123.33, 106.82, 92.02, 61.49, 25.00, 18.83, 14.53, 11.47.

CONCLUSIONS

The synthesis of macrocycle **1** was carried out successfully starting from the commercially available ethyl ester of *m,m'*-dibromobenzoic acid. The terphenyl skeleton decorated with two ethynyl groups was built up in good yields by Suzuki-Miyaura cross-coupling reactions, while its

decoration with the requested complementary groups (-N_3 and -C≡CH, respectively) relied on Sonogashira cross-coupling reactions with appropriately substituted *m*-iodophenol reagents, followed by a subsequent reaction with propargyl bromide in the case of the alkyne-terminated podand. The final step for the access to macrocycle **1** consisted of the CuAAC reaction of **4** and **6**. This last reaction underwent regioselectively (only the 1,4-substituted triazole was formed) and in very good yields (69%) due to the high steric complementarity of the two *m,m'*-terphenyl building blocks (**4** and **6**).

Acknowledgments. The financial support by Roumanian National Authority for Scientific Research and Innovation, CNCS-UEFISCDI, projects PN-III-P4-ID-PCCF-2016-0088 and PN-III-P4-PCE-2021-1812, is gratefully acknowledged.

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