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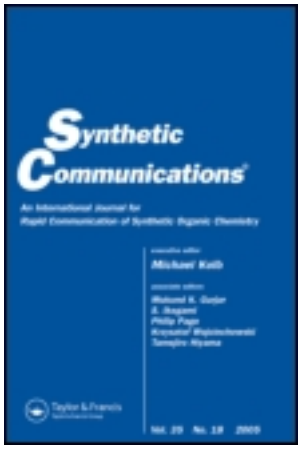

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Synthesis and Structural Analysis of Some Podands with C_3 Symmetry

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SYNTHESIS AND STRUCTURAL ANALYSIS OF SOME PODANDS WITH C_3 SYMMETRY

Adrian Woiczechowski-Pop, Ioana L. Dobra, Gheorghe D. Roiban, Anamaria Terec, and Ion Grosu

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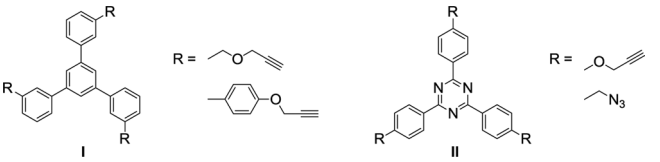
GRAPHICAL ABSTRACT



Abstract *The multistep syntheses of C_3-symmetrical tripodands with terminal triple bonds or azide groups exhibiting 1,3,5-triarylbenzene and 2,4,6-triaryl-1,3,5-triazine cores are reported herein. The structures of the newly synthesized compounds are supported by NMR investigations.*

Keywords Click reactions; cryptands; triarylbenzene; triaryltriazine; tripodands

INTRODUCTION

Three-dimensionally bridged cage molecules have proven a high capacity to act as molecular hosts and represent a challenging target for investigations in supramolecular chemistry.[1] The structurally well-defined cryptands cavities ensure highly specific interactions with anionic, cationic, or neutral guests and support the formation of regio- and stereoselective supramolecular host–guest entities.[2] In addition, the exciting properties of these supramolecular devices having various sized cavities can be exploited in applications such as storage, delivery, molecular recognition, and catalysis.[3] Therefore, the preparation of these molecules and of their intermediates is of high importance. In particular, we were interested in developing synthetic procedures for tripodands with C_3 symmetry and either triple bonds or azide groups at the ends of their chains, which are suitable for ring closure using the click reaction strategy.[4] In recent years interest has increased in the copper(I)-catalyzed azido-alkyne cycloaddition (click reaction), and many applications of this reaction

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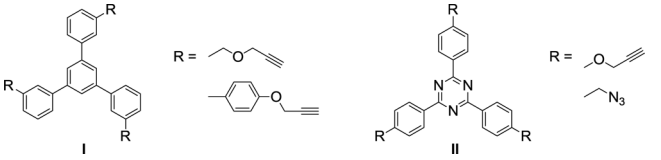

Chart 1.

for the obtaining of host macrocycles were reported.[5] Despite the high interest for the applications of the click reaction, the first synthesis of a cryptand using this reaction was reported in 2008[6] and was followed by only a few other publications on this subject.[7] The synthesis of new intermediates would therefore broaden the range of available substrates and open the way for new interesting macrocyles. We considered developing synthetic methodologies to obtain the access to new podands (**I** and **II**, Chart 1) exhibiting central benzene or triazine units and bearing terminal alkyne or azide groups in the arms.

RESULTS AND DISCUSSION

The synthesis of podands bearing terminal triple bonds with tris(phenyl)-benzene and tris(phenyl)triazine cores was carried out in several steps starting from *m*-bromoacetophenone and *p*-hydroxybenzonitrile. The general synthetic strategy for the preparation of podands with central phenyl units is depicted in Scheme 1 and follows two pathways.

Both synthetic methodologies required compound **2**, which was obtained in good yield by a trimerization reaction of *m*-bromoacetophenone in acidic conditions, according to literature data for similar intermediates.[8]

The first pathway is the synthesis of compound **5** in a multistep reaction methodology. Tris(biphenyl)benzene **3**, obtained from tribromosubstituted derivative **2** by a Suzuki coupling reaction,[9] was used in a demethylation transformation with pyridine hydrochloride at 200 °C to afford derivative **4** in 76% yields.[10]

The NMR spectroscopy confirmed the C_3 symmetry of compound **4**. The aromatic region of ^{1}H NMR spectrum of **4** exhibits the expected number and pattern of resonances, with the singlet recorded for the central 1,3,5-trisubstituted benzene ring and the AB system attributed to protons on the *p*-substituted phenyl rings being considered as key elements. The formation of the triphenolic form **4** was proven by the presence in NMR spectrum of the new singlet attributed to the three hydroxyl groups. Mass spectrometry (MALDI-TOF ES+) revealed the molecular peak at m/z 583.230.

The final step toward obtaining tripodand **5** was the phase-transfer reaction[11] of triphenol **4** with propargyl bromide at room temperature in dichloromethane, using 50% aqueous solution of NaOH and tributylammonium bromide. The propargyl group was inserted on all three sites in fair yields (17%). The symmetrical structure of **5** was confirmed by NMR spectra. The ^{1}H NMR spectrum exhibits in the aromatic region the characteristic singlet for the central trisubstituted benzene core,

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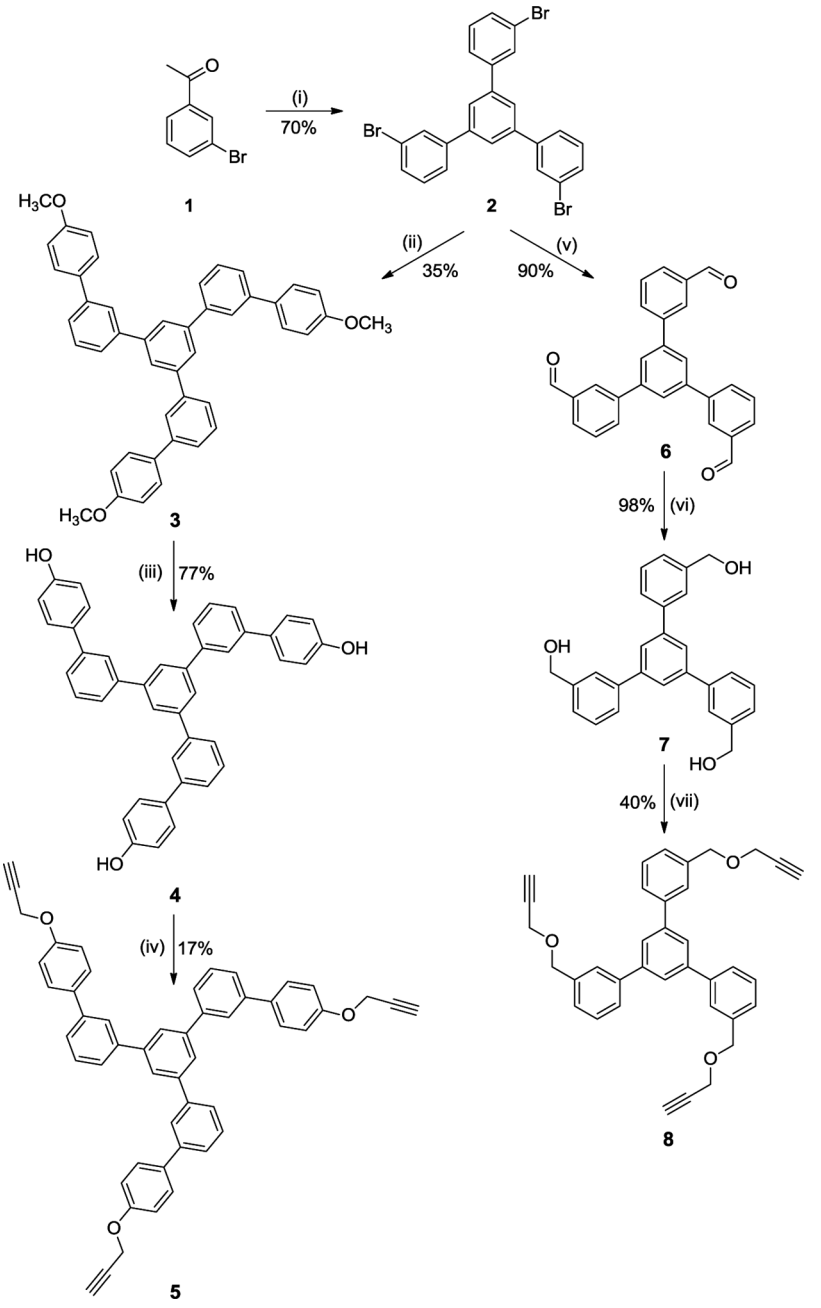


Scheme 1. Reagents and conditions: (i) F_3CSO_3H, toluene, reflux, 30 h; (ii) $H_3COPhB(OH)_2$, $Pd(PPh_3)_4$, aqueous Na_2CO_3, THF–toluene 1:1, 90 °C, Ar; (iii) HCl, pyridine, reflux, water, rt; (iv) 50% NaOH, TBAB, propargyl bromide, rt; (v) *n* BuLi 1.6 M, dry THF, −78 °C, dry DMF; (vi) $NaBH_4$, H_2O, THF, rt; and (vii) 50% NaOH, TBAB, propargyl bromide, rt.

and in the aliphatic region two signals are revealed, a doublet assigned for OCH_2 protons and a triplet corresponding to CH protons from the propargyl groups.

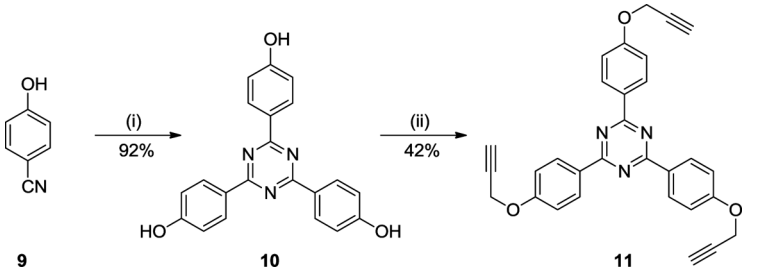
In the second strategy, alcohols are used as precursors in the synthesis of alkyne ligands. To this goal the synthesis of trisaldehyde **6** was performed, with the chosen synthetic methodology representing an improved (90% yield) and less toxic route (*n*-BuLi and dimethylformamide) than those found in literature[12] for the synthesis of trisubstituted compounds with formyl group. Reduction of aldehyde **6** in (tetrahydrofurane) with solution of $NaBH_4$ in H_2O[13] led to the formation of trisalcohol **7** in quantitative yields (98%). The advantages of this synthetic route are the short reaction time and simple purification method. Compound **7** was subjected to a similar reaction presented for the synthesis of **5**. The greater yield of **8** (40%) compared to **5** can be explained by the greater reactivity of the anion of hydroxymethyl groups compared to the anions of phenol ones.

Symmetrical (C_3) 1,3,5-triazine derivatives are playing an important role in chemically selective processes and in supramolecular chemistry. They exhibit a high ability to form hydrogen bonds, favor π–π contacts, and can be involved in different anion–π interactions. Therefore the synthesis of some 1,3,5-tris(phenyl)-2,4,6-triazine derivatives is of interest.[14,15b]

One of the target compounds, tripodand **11** (Scheme 2) was prepared in a two-step reaction. First triphenol **10**[15] was synthesized by a trimerization reaction from commercially available *p*-hydroxybenzonitrile **9** and then the phenol was transformed in trialkyne **11**. Initially, a phase-transfer reaction was performed at room temperature, using propargyl bromide in dichloromethane, 50% aqueous solution of NaOH, and tributylammonium bromide. This reaction proved to be inefficient, considering the poor yield obtained after workup (8%). The yield of the reaction was substantially improved (42%) by an alternative reaction (K_2CO_3 in acetone at reflux).[16]

^{1}H NMR spectrum of **11** is in concordance with the proposed symmetric structure, the two types of protons of the *p*-disubstituted phenyl ring being assigned as an AB system. The protons corresponding to propargyl groups are exhibited in aliphatic region of the spectrum as a doublet signal for methylene group and a more shielded triplet signal for protons of the terminal triple bonds.

The synthesis of **13** was achieved by a trimerization reaction of compound **12** under argon, at room temperature using triflic acid in excess as solvent (90%) by a similar procedure to that used in the case of triazine derivative **10**. The triazide **14**



Scheme 2. Reagents and conditions: (i) F_3CSO_3H, dry $CHCl_3$, 0 °C (2 h), rt (12 h); and (ii) propargyl bromide, K_2CO_3, acetone, reflux.

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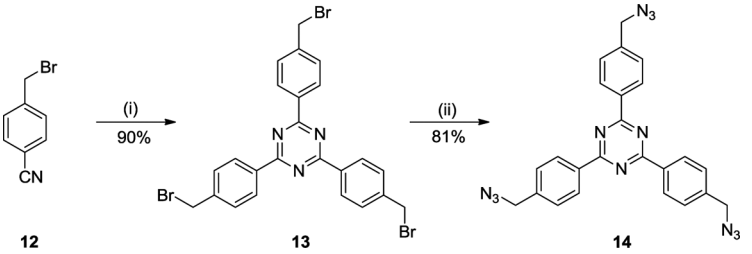

Scheme 3. Reagents and conditions: (i) F_3CSO_3H, 0 °C, rt (24 h) and (ii) NaN_3, DMSO, rt.

was obtained in good yields (81%) by the reaction of **13** with NaN_3 in dimethylsulfoxide, following a typical procedure (Scheme 3).[17]

The ^1H NMR spectrum shows in the aromatic region an AB system for protons of the *p*-disubstituted ring and a singlet signal in aliphatic region corresponding to protons of the methylene groups.

CONCLUSIONS

In summary, we have synthesized and structurally characterized several podands with C_3 symmetry by combining different synthetic methodologies. The advantage of these building blocks is conferred by the extended aromatic units, which assure rigidity to the cage molecules and are suitable for the formation of π-stacking interactions with other aromatic derivatives. The structure of the compounds was determined using NMR spectroscopy, mass spectrometry, and elemental analysis.

EXPERIMENTAL

Solvents were dried and distilled under argon using standard procedures before use. Chemicals of commercial grade were used without further purification.

^1H NMR, ^{13}C NMR, correlation spectroscopy (COSY) and heteronuclear multiple quantum correlation (HMQC) spectra were recorded at room temperature using $CDCl_3$ and dimethylsulfoxide (DMSO-d_6) as solvents in 5-mm tubes on Brucker 250 (operating at 250 MHz for protons and 60 MHz for carbon atoms), Bruker Avance 300 (operating at 300 MHz for protons and 75 MHz for carbon atoms), and Brucker AM 400 (operating at 400 MHz for protons and 100 MHz for carbon atoms) instruments. Electrospray ionization instruments. (ESI+) mass spectra were recorded using an Esquire 3000 ion-trap mass spectrometer (Bruker Daltonic GmbH) equipped with a standard ESI/APCI source, and an Agilent 6320 ionic trap mass spectrometer equipped with a ESI/APCI source: The mass spectra (MALDI+) were recorded from $CHCl_3$ solutions on a MALDI-TOF Microflex (Bruker) spectrometer [2-[(2E)-3(4-tert-butylphenyl)-2-methylprop-2-enylidene]malononitrile (DCTB) as matrix]. Thin-layer chromatography (TLC) was carried out on aluminum sheets coated with silica gel 60 F_{254} using ultraviolet (UV) visualization. Preparative column chromatography was performed using PharmPrep 60 CC (40–63 μm) silica gel purchased from Merck. Elemental analyses were carried out on a Perkin-Elmer 2400-B microanalyzer.

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Synthesis of 4

Concentrated hydrochloric acid (55 mL) was added with vigorous stirring to pyridine (60 mL), cooled to 0 °C. After the addition was complete, the mixture was heated and water distilled off until the internal temperature reached 200 °C (around 30 mL). The resulting pyridinium chloride was cooled to 140 °C, and **3** (0.60 g, 0.96 mmol) was added in one portion. An immediate color change to red occurred and heating to reflux was resumed for 4 h. The mixture was then allowed to cool to 100 °C, when water (100 mL) was added, and the mixture stirred for 12 h at room temperature. The brown precipitate that resulted was collected by filtration, washed with plenty of water and chloroform, and dried under vacuum to give **4** as a brown solid (0.43 g, 77%). ^{1}H NMR (300 MHz, DMSO-d_6) δ ppm: 9.57 (s, 3H, OH), 8.03 (s, 3H, H_2), 8.00 (s, 3H, H_2'), 7.79 (d, 3H, H_6', $^3J = 7.5$ Hz), 7.65–7.61 (overlapped signals, 9H, H_2'', H_4', H_6''), 7.54 (t, 3H, H_5', $^3J = 7.5$ Hz), 6.86 (d, 6H, H_3'', H_5'', $^3J = 7.8$ Hz). ^{13}C NMR (75 MHz, DMSO-d_6) δ ppm: 157.25, 141.95, 140.95, 130.92, 129.41, 128.16, 125.56, 125.02, 115.70. MS (MALDI-TOF ES+) $[M + H]^+$ m/z 583.230. Anal. calcd. for $C_{42}H_{30}O_3$ (582.69): C, 86.57; H, 5.19. Found: C, 86.76; H, 5.34.

Synthesis of 5

A 50% aqueous solution of NaOH (0.248 g, 36 equiv., 6.18 mmol) was added to a solution of **4** (0.100 g, 1 equiv., 0.172 mmol) in 6 mL dichloromethane. After cooling to 0 °C, TBAB (0.042 g, 0.75 equiv., 0.128 mmol) was added. The mixture was stirred for half an hour at this temperature, and then propargyl bromide 80% in toluene (0.092 g, 3.6 equiv., 0.618 mmol) was added. The mixture was allowed to stir overnight at room temperature. The resulted suspension was extracted with dichloromethane (DCM). Combined organic phases were washed with water and brine, dried over Na_2SO_4, and filtered, and the solvent was removed under reduced pressure. The crude product was purified by column chromatography on silica gel (eluent AcOEt–pentane 1:3) to obtain compound **5** (0.020 g, 17%). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 7.89 (s, 3H, H_2), 7.87 (s, 3H, H_2'), 7.67–7.52 (overlapped signals, 15H, H_{arom}), 7.08 (d, 6H, $^3J = 8.4$ Hz, H_3''), 4.75 (d, 6H, $^4J = 2.4$ Hz, OCH_2), 2.55 (t, 3H, $^4J = 2.4$ Hz, C ≡ CH). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm: 157.21, 142.48, 141.62, 141.36, 134.50, 129.90, 128.33, 126.10, 125.97, 125.91, 125.45, 115.24, 78.48, 75.64, 55.88. Anal. calcd. for $C_{51}H_{36}O_3$ (696.83): C, 87.90; H, 5.21. Found: C, 88.08; H, 5.32.

Synthesis of 6

1,3,5-Tris-(3-bromophenyl)benzene (**2**) (1.80 g, 1 equiv., 3.31 mmol) was dissolved in anhydrous tetrahydrofuran (THF) in a two-necked round bottom flask under argon atmosphere. After cooling to −78 °C, *n*BuLi 1.6 M (10.36 mL, 5 equiv., 16.57 mmol) was added dropwise with a syringe. The lithiated intermediate was kept approximately 30 min at −78 °C and anhydrous DMF (2.58 mL, 10 equiv., 33.14 mmol) was added dropwise to the solution. The mixture was left to reach room temperature and then HCl 0.1 M and H_2O were added until the solution clarified.

The solution was concentrated until the THF was removed. The precipitate was filtered and recrystallized from acetone to afford **6** as a white solid (1.16 g, 90%). ^{1}H NMR (300 MHz, $CDCl_3$) δ ppm: 10.14 (s, 3H, CHO), 8.23 (pseudotriplet, 3H, H_2', $^4J = {}^4J' = 1.5$ Hz), 7.99 (overlapped dd, 3H, H_4', $^3J = 7.5$ Hz, $^4J = {}^4J' = 1.8$ Hz), 7.94 (overlapped dd, 3H, H_6', $^3J = 7.5$ Hz, $^4J = {}^4J' = 1.2$ Hz), 7.89 (s, 3H, H_2), 7.70 (t, 3H, H_5', $^3J = 7.5$ Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm: 192.29, 141.59, 137.14, 133.38, 129.86, 129.59, 128.19, 125.83. Anal. calcd. for $C_{27}H_{18}O_3$ (390.43): C, 83.06; H, 4.65. Found: C, 82.88; H, 4.80.

Synthesis of 7

A solution of sodium borohydride (0.39 g, 15 equiv., 10.37 mmol) in 2.50 mL water was added dropwise to **6** (0.27 g, 1 equiv., 0.69 mmol) dissolved in 10 mL THF. The mixture was allowed to stir at room temperature for 1 h and then washed with ethyl acetate. The organic layer was dried over Na_2SO_4 and evaporated under vacuum to afford compound **7** as white powder (0.27 g, 98%). ^{1}H NMR (300 MHz, DMSO-d_6) δ ppm: 7.87 (s, 3H, H_2), 7.78 (s, 3H, H_2'), 7.73 (d, 3H, H_4', $^3J = 7.2$ Hz), 7.48 (t, 3H, H_5', $^3J = 7.5$ Hz), 7.38 (d, 3H, H_6', $^3J = 7.5$ Hz), 5.28 (t, 3H, OH, $^3J = 5.7$ Hz), 4.61 (d, 6H, CH_2, $^3J = 5.7$ Hz). ^{13}C NMR (75 MHz, DMSO-d_6) δ ppm: 143.18, 141.64, 139.74, 128.62, 125.75, 125.36, 125.02, 124.13, 62.76. MS (APCI+) $m/z = 418.895$ $[M + Na]^+$, $m/z = 815.814$ $[2M + Na]^+$. Anal. calcd. for $C_{27}H_{24}O_3$ (396.48): C, 81.79; H, 6.10. Found: C, 81.63; H, 5.89.

Synthesis of 8

A 50% aqueous solution of NaOH (0.671 g, 36 equiv., 16.8 mmol) was added to a solution of **7** (0.185 g, 1 equiv., 0.466 mmol) in 6 mL CH_2Cl_2. After cooling to 0 °C, TBAB (0.113 g, 0.75 equiv., 0.350 mmol) was added. The mixture was stirred for half an hour at this temperature and then propargyl bromide 80% in toluene (0.25 g, 3.6 equiv., 1.68 mmol) was added. The mixture was allowed to stir overnight at room temperature. The resulting suspension was extracted with CH_2Cl_2. Combined organic phases were washed with water and brine, dried over Na_2SO_4, and filtered, and the solvent was removed under reduced pressure. The crude product was purified by column chromatography on silica gel (eluent AcOEt–pentane 1:3) to obtain the pure compound **8** (0.094 g, 40%). ^{1}H NMR (250 MHz, $CDCl_3$) δ ppm: 7.79 (s, 3H, H_2), 7.70 (s, 3H, H_2'), 7.64 (d, 3H, H_4', $^3J = 7.5$ Hz), 7.48 (t, 3H, H_5', $^3J = 7.5$ Hz), 7.39 (d, 3H, H_6', $^3J = 7.5$ Hz), 4.71 (s, 6H, CH_2O), 4.25 (d, 6H, OCH_2, $^3J = 2.5$ Hz), 2.50 (t, 3H, CH, $^3J = 2.5$ Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm: 142.09, 141.26, 137.91, 128.97, 127.29, 127.05, 126.94, 125.27, 79.57, 74.79, 71.50, 57.23. Anal. calcd. for $C_{36}H_{30}O_3$ (510.62): C, 84.68; H, 5.92. Found: C, 84.84; H, 5.68.

Synthesis of 11

Compound **10** (0.100 g, 1 equiv., 0.28 mmol) and propargyl bromide 80% in toluene (0.15 g, 3.6 equiv., 1.01 mmol) were allowed to reflux overnight in acetone in the presence of K_2CO_3(0.58 g, 15 equiv., 4.20 mmol). The mixture was partitioned

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between water and ethyl acetate. Combined organic fractions were dried over $MgSO_4$, and the solvent was removed. Purification by column chromatography (eluent AcOEt–pentane 1:5) furnished compound **11** as a white solid (0.055 g, 42%). ^{1}H NMR (250 MHz, $CDCl_3$) δ ppm: 8.72 (d, 6H, H_2', H_6', $^3J = 7.5$ Hz), 7.14 (d, 6H, H_3', H_5', $^3J = 7.5$ Hz), 4.82 (d, 6H, OCH_2, $^3J = 2.5$ Hz), 2.58 (t, 3H, C≡CH, $^3J = 2.5$ Hz). ^{13}C NMR (125 MHz, *CDCl*$_3$) δ ppm: 170.79, 161.11, 130.82, 129.98, 114.87, 78.24, 76.10, 56.01. MS (ESI+) $m/z = 472.2$ $[M + H]^+$. Anal. calcd. for $C_{30}H_{21}N_3O_3$ (471.51): C, 76.42; H, 4.49; N, 8.91. Found: C, 76.68; H, 4.71; N, 8.82.

Synthesis of 14

NaN_3 (0,080 g, 3.6 equiv., 1.22 mmol) was added to a stirred solution of compound **13** (0.2 g, 1 equiv., 0.34 mmol) in DMSO (10 mL). The solution was allowed to stir at room temperature overnight. The mixture was washed with ethyl acetate (3×25 mL). The reunited organic phases were dried over Na_2SO_4, and the solvent was evaporated in vacuo. The purification by column chromatography on silica gel (eluent CH_2Cl_2–pentane 1:2) gave the pure compound **14** as a straw-colored oil, which solidifies in the refrigerator (0.130 g, 81%). ^{1}H NMR (250 MHz, $CDCl_3$) δ ppm: 8.54 (d, 6H, H_2', H_6', $^3J = 7.5$ Hz), 7.36 (d, 6H, H_3', H_5', $^3J = 7.5$ Hz), 4.34 (s, 6H, CH_2N_3). ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm: 140.63, 132.25, 128.25, 118.22, 111.62, 53.60. Anal. calcd. for $C_{24}H_{18}N_{12}$ (474.48): C, 60.75; H, 3.82; N, 35.42. Found: C, 60.49; H, 3.89; N, 35.21.

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