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FULL PAPER

Modular Synthesis of Diverse Multi-Functionalized Oligoarenes and Heteroarenes: Tailor to Desire – Molecules for Functional Materials

Sylvain Grosjean,[a] Zahid Hassan,[b,c] Christof Wöll,[c] and Stefan Bräse*[a,b,d]

Abstract: The modular synthesis of multi-functionalized biphenyl, terphenyl and higher linear oligophenylene dicarboxylic acids and pyridine-terminated oligoarenes by stepwise palladium–catalyzed borylation / Suzuki–Miyaura cross-coupling reactions is described. The presence of several distinct functional groups such as azide, hydroxy, and alkyne, as well as coordinative functional end-groups (carboxylic acid or pyridine) combined together in a single oligoarene-molecular unit at strategic positions, having an advantageous dual-utility. First, these compounds can serve as useful molecular bricks (ditopic organic linkers) in the construction of complex porous crystalline materials. Second, after the assembly into the crystalline coordination networks, orthogonal functional sites within the linker-backbone offers tremendous potential from application perspectives as they can be modified via a wide range of post-synthetic modifications including azide–alkyne click-chemistry, which allow further tailoring of the supramolecular assemblies to yield novel multifunctional materials.

Introduction

1,4-Benzenedicarboxylates (BDC), the simplest terephthalates, and their higher structural analogues (oligoarenedicarboxylates) are important building blocks that are of crucial importance for the assembly of a wide range of functional materials such as metal-organic frameworks (MOFs), covalent-organic frameworks (COFs), polymer gels and other related porous structures.[1] Carboxylate-functionalized (oligo)arenes (as organic ligands or linkers) can coordinate metal ions and clusters to form self-assembled nanostructured porous materials. For instance, isoreticular metal-organic frameworks (IRMOFs) series of materials,[2] are among few that possess (oligo)arene organic components and hence open the possibility of employing the vast range of transformations at organic cores. Modulating oligoarene dicarboxylates as organic linkers by; 1) introducing functional and reactive moieties as side-groups,[3] 2) varying the length of their backbones,[4] and 3) varying their geometries, allow an easy tuning of both structure and properties of the materials for diverse applications.[5] Proceeding the holistic approach of functional molecules to functional materials, we have been involved in the design and fabrication of different types of three-dimensionally structured materials *via* organic linker design. For instance, we previously reported the synthesis of a family of ditopic organic linkers (dicarboxylic acids) of different length for the growth of a series of isoreticular surface-mounted metal-organic frameworks (SURMOFs), where the choice of the linker's length determines the pore size of the material (Figure).[6]

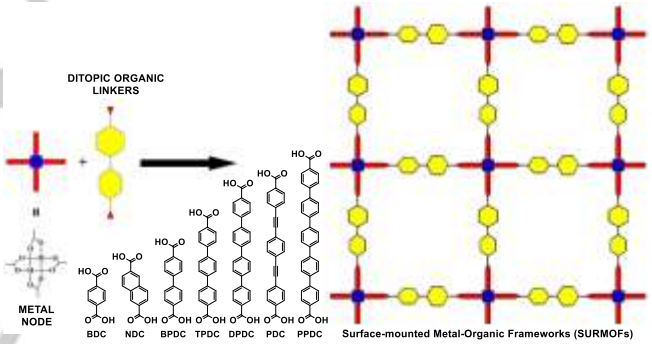

Figure 1. Structure and schematic representation of diverse ditopic organic linkers (dicarboxylic acids) used as molecular bricks for the growth of a series of novel isoreticular SURMOFs. Reproduced with permission from our work ref.[9] copyright 2012, Nature Publishing Group.

The surface-supported growth process, coupled with the organic structure variety brought *via* the linker design, offer a number of opportunities to construct functional materials, such as switchable molecular devices[7] or nanomembranes for separation.[8] Materials containing azide functional groups enable a wide range of post-synthetic modifications including azide–alkyne click chemistry to prepare novel structures. Such materials have the capacity to enable a controlled uptake-and-release of guest molecules for imaging and bio-applications,[9] provide for instance a pH-sensitive selective drug-release platform, which is a practical demonstration for the design of bio-materials with potential medical applications.[10] Herein, we describe a general and high yielding protocol for the generation of a library of diverse multi-functionalized oligoarene-dicarboxylic acids and pyridine-ended oligoarenes by Pd-catalyzed stepwise borylation / Suzuki–Miyaura cross-coupling reactions. In addition, synthetic protocols were also developed to access model polyarenes bearing azide, alkyne, or hydroxy side-groups that have enormous potential

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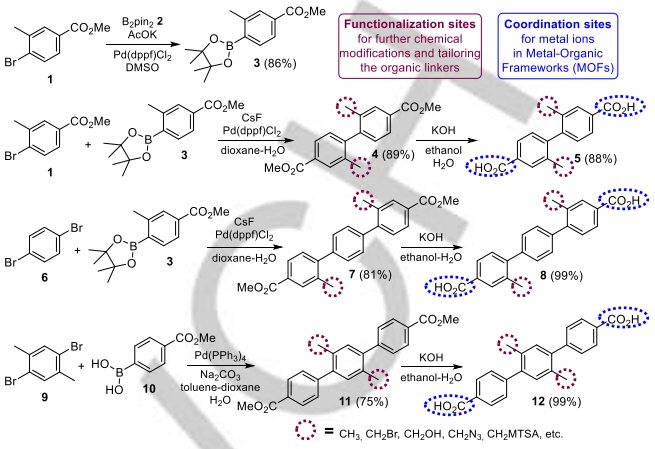
applications as building blocks and cross-linking ligands with different guest molecules to prepare next-generation functional materials.

Results and Discussion

Relying on our background and expertise in methods and design of materials, we focused first on the modular synthesis and selective modifications of the key substrate class, i.e. symmetrical biphenyls and terphenyls, which bear multiple, tunable functional groups at the desired specific positions at inner and/or outer benzene core. For the construction of the aryl-aryl bonds, the Suzuki-Miyaura cross-coupling reaction was chosen as it offers several advantages – including mild reaction conditions compatible with functional groups, simple procedures, high yields, low cost and bench-stable starting materials. All this contributes to the versatility of this reaction, which overcomes many of the limitations associated with other cross-coupling procedures.[11-14] While several strategies for the preparation of biphenyls and terphenyls have been reported,[15] the modulation of synthetic methods for introducing multiple tunable functional groups within a single molecular unit which can be reacted on demand, still remains a challenging task but of great importance in material design.

Employing the preeminent Pd-catalyzed step-wise borylation/Suzuki-Miyaura reaction, we aimed at the synthesis of biphenyl and terphenyl coupling products, and further install specific tunable functionalities at the required positions within the final building blocks (organic linker). The scheme below (Scheme 1) shows the synthesis of methyl-functionalized biphenyl- and terphenyl- dicarboxylic acid linkers. The carboxylic acid functional groups at the terminal positions of the oligoarenes are required as coordination sites with metal ions/clusters for the growth of networks; the methyl groups at benzylic positions can be further transformed into more useful azide or alkyne functional groups, make the resulting building blocks (please see the Scheme 6) suitable for post-synthetic modification *via* click-chemistry, once reticulated into the networks.

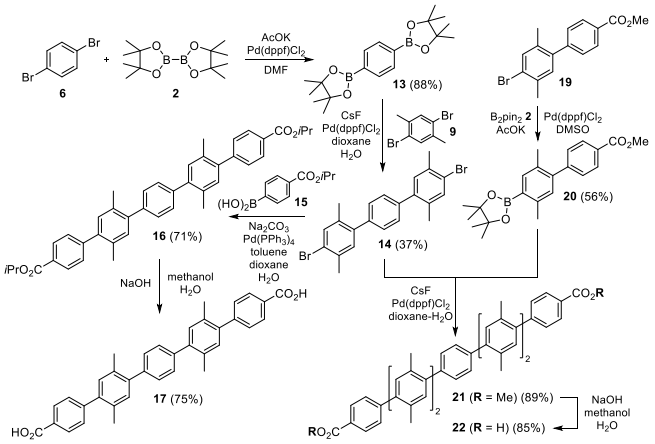
The bromoarene **1** reacted first under borylation reaction conditions with bis(pinacolato)diboron (B_2pin_2) **2** to give the boronic ester **3**, which is one of the key intermediates for the next steps of the synthetic strategy. Bromoarene **1**, and *para*-dibromoarenes **6** and **9** were reacted to obtain the corresponding ester-protected linker precursors **4**, **7** and **11**. Reactions involving the boronic ester **3** as coupling partner were performed using [1,1′-bis(diphenylphosphino)ferrocene]dichloropalladium(II) ($Pd(dppf)Cl_2$) as catalyst and cesium fluoride (CsF) as effective base in a refluxing dioxane-water mixture as an optimized standard protocol. The sterically hindered boronic ester **3** coupled cleanly with both the electron-poor bromoarene **1** and the relatively electron-rich dibromoarene **6**. For the synthesis coupling product **11**, involving the boronic acid **10** as coupling partner, the use of tetrakis(triphenylphosphine)palladium(0) ($Pd(PPh_3)_4$) as catalyst and sodium carbonate (Na_2CO_3) as a base in a refluxing toluene-dioxane-water mixture gave higher yields than the previous optimized catalyst/base/solvent system.



Scheme 1. Synthesis of methyl-functionalized biphenyl and terphenyl dicarboxylic acid linkers **5**, **8**, and **12**. Blue dashed areas: coordination sites for network growth. Purple dashed areas: anchor sites for further chemical functionalization.

The linker precursors **4**, **7** and **11** were hydrolyzed following standard procedure, by treatment with potassium hydroxide (KOH) aqueous solution followed by addition of hydrochloric acid, to give the corresponding dicarboxylic acid linkers **5**, **8** and **12** in good overall yields (from 67% to 74% over 2 or 3 steps).

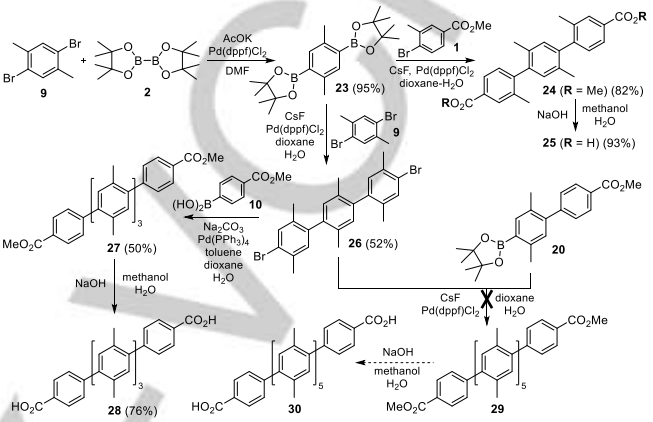
Boronic acids and, to a lesser extent, boronate esters as coupling partners in Suzuki–Miyaura reaction have been extensively utilized. However, for preparing higher oligoarenes with multiple valuable groups, the purification and characterization of products have been problematic and remain challenging tasks.[16] As depicted on the following scheme (Scheme 2), the boronic esters **13** and **20** were readily prepared by reacting both the bromoarenes **6** and **19**, separately, with B_2pin_2 **2**. Standard reaction conditions were applied for the borylation reaction, using $Pd(dppf)Cl_2$ as catalyst and potassium acetate (AcOK) as a base, in either dimethylformamide (DMF) or dimethylsulfoxide (DMSO). The boronic esters **13** and **20** are crucial key intermediates for the stepwise synthesis of longer oligoarene linkers; the bis-boronate **13** is especially important as it constitutes the central aromatic ring of the linkers, from which the whole synthetic process begins.



Scheme 2. Sequential borylation / Suzuki–Miyaura cross-coupling reactions for the synthesis of terphenyl building block **14** and oligoaryl-linkers **17** and **22**.

In the Suzuki–Miyaura coupling reaction involving symmetrical dibromoxylene **9** and benzenediboronic ester **13**, the formation of the mono-functionalization product was achieved under strict control of stoichiometry and after careful optimization of the reaction parameters (including solvents, temperature, base and reaction time). The reaction led to the dibromoterphenyl derivative **14** in a moderate yield (37%). Two-fold Suzuki–Miyaura cross-coupling reactions of the dibromoterphenyl **14** with the arylboronic acid **15** or the biarylboronic ester **20** resulted into the corresponding ester-protected linker precursors **16** and **21**. These precursors were subsequently hydrolyzed under basic conditions to obtain the linear polyaryl-dicarboxylic acids **17** (5 consecutive aromatic rings) and **22** (7 aromatic rings) in respectively 53% and 76% yield over 2 steps from dibromoterphenyl **14**.

Based on the same synthetic pathway, but employing the dibromoarene **9** as starting material, we explored a sterically hindered class of homologous compounds based on extended *para*-xylene (= *para*-dimethylbenzene) consecutive aromatic units (Scheme 3). Coupling sterically hindered components causes variations in electronic and conformational properties due to consequential twist between the planes of adjacent aromatic units.[17] As the solubility of the linear polyaromatic linkers drops when their length increases, methyl or longer alkyl- groups are often introduced to increase the solubility of the oligoarenes. Diborylation reaction of dibromoarene **9** with B_2pin_2 **2** provided the bis-boronate intermediate **23** in 95% yield. The latter was reacted with bromoarene **1**, giving access to the tetramethyl-terphenyl linker precursor **24**, which was subsequently hydrolyzed under basic conditions to give the terphenyl linker **25** in 72% over 3 steps. To reach longer molecules, the bis-coupling product intermediate **23** was involved in a Suzuki–Miyaura coupling reaction with dibromoxylene **9** to obtain the dibromoterphenyl derivative **26** in 52% yield. Two-fold Suzuki–Miyaura cross-coupling reaction of **26** with boronic acid **10**, followed by hydrolysis of the ester groups under basic conditions resulted in the corresponding linear oligoxylene dicarboxylic acid **28** (5 consecutive aromatic rings). Contrary to the previous synthetic pathway, the reaction between the terphenyl **26** and the boronic ester **20** never led to the expected ester-protected linker precursor **29**, and therefore the longest linker **30** (7 aromatic rings) was not obtained. In most cases, such long oligophenylenes are functionalized with higher molecular weight long-chain alkyl moieties to overcome the problem of solubility.[17] In our case, in spite of our efforts, we encounter solubility problems, and purification remained challenging and in particular, we obtained mostly homo-coupling products of the corresponding organoborane reaction partners.



Scheme 3. Sequential borylation / Suzuki–Miyaura cross-coupling reactions for the synthesis of terphenyl building block **26** and oligoaryl-linkers **28** and **30**.

We further demonstrated the synthetic utility of our modular protocol by studying an important class of heterocyclic linkers, pyridine-ended polyarenes. Pyridine, as an aromatic nitrogen-containing heterocycle, can coordinate with most transition metals, form complexes and different coordination networks.[18] The 4,4'-bipyridines, as nitrogen-donor ditopic ligands, can strongly bind/coordinate with metals, and therefore constitute efficient building units for the construction of a series of pillar-layer nanostructured materials with manifold applications. Based on the coordination properties of such pyridine-based linkers together with dicarboxylic acid linkers of different length, we have recently grown MOF thin-films and demonstrated adsorption of chiral guest molecules, like limonene.[19] This latter work shows that enantioselective adsorption properties of a chiral MOF depend not only on the chiral center, but also on the pore size (Figure 2).

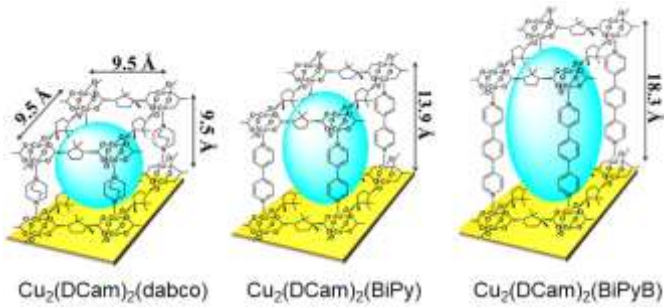
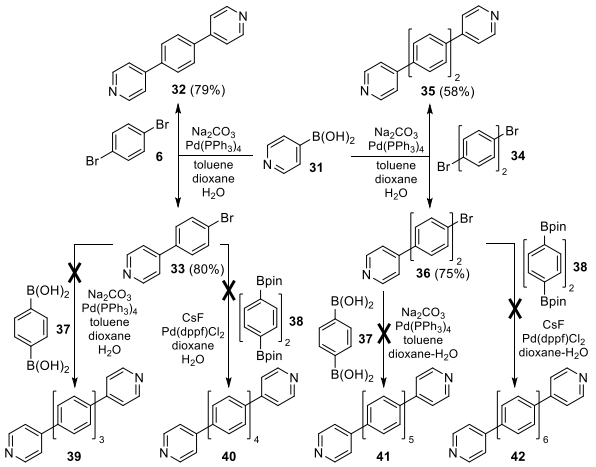


Figure 2. Structure and schematic representation of isoreticular chiral SURMOFs with tunable pore size. D-camphoric acid (DCam) as chiral center, and pyridine-based ditopic organic linkers (dabco, bipyridine and bipyridinebenzene) were used as molecular blocks for the growth of the network. Reproduced from our work from ref. ref.[19] copyright 2015, Royal Society of Chemistry.

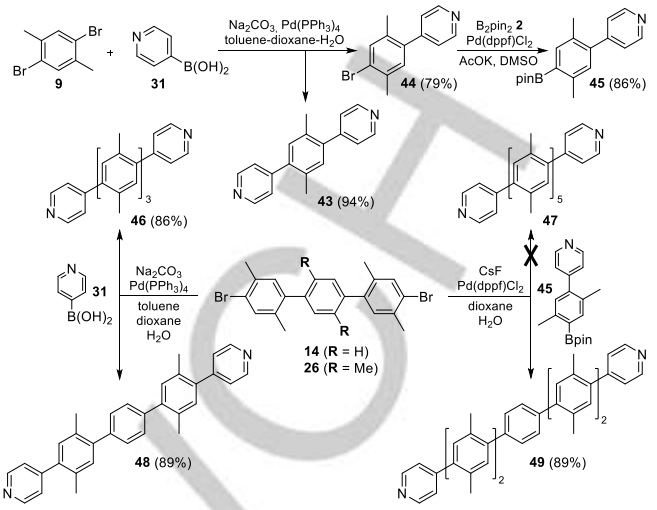
Using the previously established catalyst/base/solvent systems optimized for the Suzuki–Miyaura cross-coupling reactions, we aimed to synthesize a series of pyridine-ended polyarene model compounds with 1 to 6 consecutive aromatic rings in between the pyridine end-groups (Scheme 4).



Scheme 4. Suzuki-Miyaura based strategy for the synthesis of pyridine-ended oligoarene linkers.

Playing on the stoichiometry of the reactions, several mono- and di-substituted products were synthesized: dibromobenzene **6** and dibromobiphenyl **34** reacted with pyridylboronic acid **31** to give the corresponding bis-coupling products, respectively dipyridylbenzene **32** and dipyridylbiphenyl **35**. The mono-selective Suzuki–Miyaura cross-coupling reactions between the same partners (i.e. compound **31** with dibromoarenes **6** or **34**) afforded respectively the mono-coupling products pyridylphenylbromide **33** and pyridylbiphenylbromide **36** in rather good yields. Involved in cross-coupling reactions with aryldiboronic esters, the mono-coupling products **33** and **36** were aimed as intermediates for the stepwise selective oligomerization to the longer pyridine-terminated oligoarenes **39** (3 consecutive aromatic rings between pyridine end-groups), **40** (4 aromatic rings), **41** (5 aromatic rings), and **42** (6 aromatic rings). Unfortunately, none of the targeted pyridine-ended polyarene linkers **39**-**42** were obtained under the standard Suzuki-Miyaura reaction conditions. Although we assume the reactions failed for solubility reasons, all attempts using other solvent systems remained unfruitful and we moved forward to a more soluble family of linkers.

As for the previous section concerning the synthesis of oligoarene dicarboxylic acids, we attempted to prepare new *para*-xylene-based pyridine-terminated linkers with a xylene-core length of 1 to 5 units (Scheme 5). As mentioned earlier, the presence of methyl groups on aromatic cores may help to overcome the solubility problems we faced with benzene-based linkers. The shortest dipyridyl-linker **43** (1 xylene unit) and the formation of the mono-functionalization product **44** was obtained from dibromoxylene **9** and boronic acid **31** under our standard Suzuki-Miyaura bis-coupling protocol in very good yield (94%).

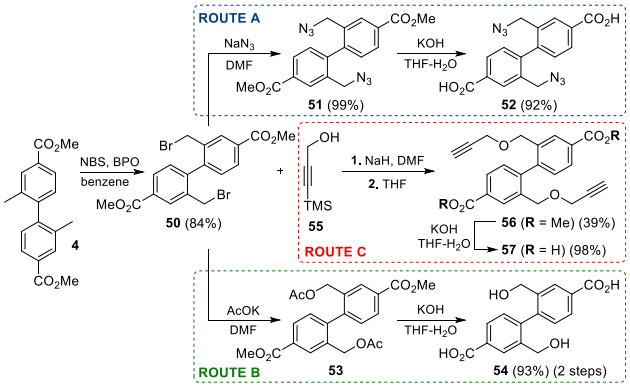


Scheme 5. Borylation / Suzuki-Miyaura based strategy for the synthesis of pyridine-ended oligoxylene linkers with 1, 3 and 5 consecutive aromatic rings.

The boronic ester **45**, as a key intermediate for the controlled increase of linker length, was synthesized in two steps from dibromoxylene **9** and 4-pyridylboronic acid **31**. Suzuki–Miyaura coupling reaction, followed by a borylation reaction with B_2pin_2 **2** led to the 4-pyridylxyleneboronic ester **45** in 68% overall yield. Comparably to our results with the dicarboxyilic acid linkers, the best results for boronic ester coupling were obtained with a $Pd(dppf)Cl_2$ / CsF system in a dioxane-water mixture, while boronic acid coupling partner reacted much better with a $Pd(PPh_3)_4$ / Na_2CO_3 system in a toluene-dioxane-water mixture. Starting from previously described dibromoterphenyls **14** and **26**, the dipyridyl-linkers **46**, **48** and **49** (with respectively 3, 5, and 7 consecutive aromatic rings) were obtained in good yields (86% to 89%), but the synthesis of the linker **47** (5 consecutive xylene rings) failed unexpectedly. In this latter case, we assume that the steric hindrance of the substrates forbids an efficient approach of the coupling partners; as for the dicarboxylic acid analogue **29**, we only obtained the homo-coupling product.

In the quest of building blocks, which combine several individual functions in a single molecular unit, we synthesized a series of functionalized model biphenyl linkers (Scheme 6) and their homologous terphenyl derivatives (Scheme 7). Organic azides, as energy-rich and versatile intermediates, have taken on an important position at the interface between chemistry,[20] biology,[21] and material science.[22] In recent last years, azide-alkyne “click modifications” have been extended to material and surface science.[23] The model oligoarenes we prepared have advantageous dual-functions: on the one hand the biaryl-dicarboxylic acids can coordinate with metals ions/clusters, and therefore be employed as building blocks for the construction of coordination polymeric networks material; on the other hand azide–alkyne click chemistry, as post-synthetic modification process, can be exploited for the fine tuning of the structural assembly properties, which we have demonstrated for the design of bio-materials.[10]

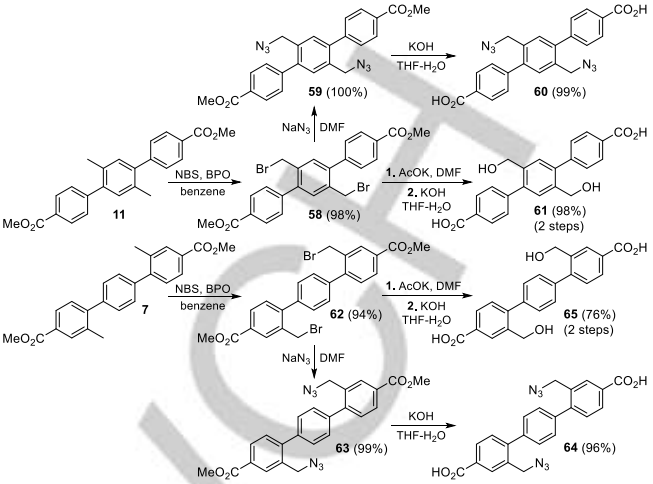
Starting from linker precursor **4**, which exhibits two methyl groups at reactive benzylic positions, free radical bromination conditions using *N*-bromosuccinimide (NBS) and dibenzoyl peroxide (BPO) in benzene were applied and the key intermediate bis(bromomethyl) derivative **50** was obtained in rather good yield (Scheme 6).



Scheme 6. Functionalization strategy from dimethyl-precursor **4**: synthesis of key intermediate bis(bromomethyl)biphenyl **50** and access to functionalized linkers **52** (azide, route **A**), **54** (hydroxy, route **B**), and **57** (alkyne, route **C**).

Taking advantage of the reactivity of such bromomethyl moieties – sensitive to nucleophilic substitutions – the intermediate **50** was engaged as starting material in three different synthetic pathways, leading to bis-functionalized linker precursors **51** (azide groups, route A), **53** (acetyl-protected hydroxy groups, route B), and **56** (alkyne groups, route C). In this latter case, the trimethylsilyl-propargyl alcohol **55** was transformed to its corresponding alcoholate by treatment with sodium hydride, before to react with the bis(bromomethyl) intermediate **50**. Using the standard potassium hydroxide hydrolysis protocol, the ester-protected compounds **51**, **53** and **56** were subsequently transformed into the corresponding dicarboxylic acid linkers **52** (azide), **54** (hydroxy) and **57** (alkyne).

We then applied a similar synthetic strategy to the isomeric dimethylterphenyl analogues **7** (outer-core methyl functionalities) and **11** (inner-core methyl functionalities) (Scheme 7). Following the same three-steps procedure (bromination at benzylic positions / nucleophilic substitution / ester hydrolysis), the dimethyl-functionalized terphenyl derivatives **7** and **11** were transformed into the corresponding hydroxy- and azido-functionalized terphenyldicarboxylic acids **60**, **61**, **64** and **65** in very good overall yields (71% to 97% over 3 steps).



Scheme 7. Synthesis of isomeric functionalized terphenyl-linkers **60** and **64** (azide groups), **61** and **65** (hydroxyl groups).

Conclusions

In this study, we presented a straightforward and efficient synthetic strategy for the preparation of linear ditopic organic linkers that are diversely functionalized. A modular synthesis of a series of diverse biphenyl, terphenyl and higher linear oligoaryldicarboxylic acids and pyridine-terminated oligoarenes by palladium–catalyzed borylation/Suzuki–Miyaura cross-coupling reactions was investigated. The described multi-step synthetic pathways allow an easy access to compounds with a length of 2 to 7 consecutive functionalized aromatic rings. Several individual functional groups were combined in single molecular units, which have an enormous potential in material engineering. In addition to serve as useful molecular bricks (ditopic linkers) in the construction of different types of complex porous materials, the synthesized molecules can also be modified *via* a wide range of post-synthetic modifications once reticulated, including azide–alkyne click-chemistry, which tailor the properties of the materials to fit with desired applications. Using this holistic concept of tailoring molecular backbones with distant moieties for the synthesis of functional materials, we are currently progressing on modular synthesis of short polymer molecules to be incorporated into three-dimensionally structured materials for our more ambitious application perspectives.

Experimental Section

General methods. All substrates, reagents and solvents employed here were commercially available and used as supplied without further purification. Thin-layer chromatography (TLC) were carried out on silica gel plates (Silica gel 60, F254, Merck) with detection by UV. Purifications were performed with preparative chromatography using normal-phase silica gel (Silica gel 60, 230-400 mesh, Merck). The compounds were characterized with nuclear magnetic resonance spectroscopy (NMR), high resolution mass spectrometry (HRMS), and infra-red spectroscopy (IR). NMR spectra were recorded on a Bruker AM 500 spectrometer (500 MHz for ^{1}H / 125 MHz for ^{13}C), as solutions in $CDCl_3$, or DMSO-d_6. Chemical shifts, δ, were quoted in parts per million (ppm) and were referenced to

solvent residual peak as internal standard. The following abbreviations were used to describe peak patterns when appropriate: s = singlet, d = doublet, t = triplet, q = quartet, sep = septet, m = multiplet, and br = broad. Coupling constants, *J*, are reported in Hertz unit (Hz). Mass spectra were recorded with a Finnigan MAT 95 (70 eV) spectrometer under electron impact (EI) conditions. The molecular fragments were quoted as the relation between mass and charge (*m/z*). The abbreviation [M^+] refers to the molecular ion. IR spectra were recorded with a FTIR Bruker IFS 88 spectrometer, using the attenuated total reflection technique (ATR). The absorption band positions are given in wave numbers, ν, in cm^{-1}.

General synthetic procedures:

(**A**) **Borylation reaction** (mono-coupling): Bromo derivative (1 equiv), bis(pinacolato)diboron (B_2pin_2) (**2**) (1.1 equiv), [1,1′-bis(diphenylphosphino)ferrocene]dichloropalladium(II) ($Pd(dppf)Cl_2$) (5 mol%), and potassium acetate (AcOK) (3 equiv) were dissolved in degassed anhydrous dimethylsulfoxide (DMSO) under argon atmosphere. The mixture was heated at 85°C for 18h to 72h. The reaction mixture was cooled down to room temperature, then added to water before being extracted with dichloromethane. Combined organic layers were washed with water and brine, then dried over magnesium sulfate and evaporated under reduced pressure. The crude product was purified by column chromatography (silica gel) to give the corresponding pinacolatoboronyl derivative.

(**B**) **Borylation reaction** (bis): *para*-dibromo derivative (1 equiv), bis(pinacolato)diboron (**2**) (3 equiv), [1,1′-bis(diphenylphosphino)ferrocene]dichloropalladium(II) (6 mol%), and potassium acetate (6 equiv) were dissolved in degassed dimethylformamide (DMF) under argon atmosphere. The mixture was heated at 85°C for 48h to 96h. The reaction mixture was cooled down to room temperature, then added to water before being extracted with dichloromethane. Combined organic layers were washed with water and brine, then dried over magnesium sulfate and evaporated under reduced pressure. The crude product was purified by column chromatography (silica gel) to give the corresponding *para*-bis(pinacolatoboronyl) derivative.

(**C**) **Suzuki-Miyaura cross-coupling reaction** (mono-coupling): boron derivative (boronic acid or pinacolatoboronyl) (1 equiv), bromo derivative (1-5 equiv), [1,1′-bis(diphenylphosphino)ferrocene]dichloropalladium(II) (5 mol%), and cesium fluoride (CsF) (3 equiv) were dissolved in a degassed dioxane-water mixture (2/1) under argon atmosphere. The mixture was refluxed for 24h to 72h. The reaction mixture was cooled down to room temperature, then added to water before being extracted with dichloromethane. Combined organic layers were washed with water and brine, then dried over magnesium sulfate and evaporated under reduced pressure. The crude product was purified by column chromatography (silica gel) to give the corresponding coupling product.

(**D**) **Suzuki-Miyaura cross-coupling reaction** (bis-coupling): *para*-dibromo derivative (1 equiv), boronic acid derivative (3 equiv), tetrakis(triphenylphosphine)palladium(0) ($Pd(PPh_3)_4$) (5 mol%) and sodium carbonate (Na_2CO_3) (8 equiv) were added in a degassed mixture of toluene-dioxane-water mixture (2/2/1) under argon. The mixture was heated at 85°C for 72h to 96h under argon. The reaction mixture was cooled down to room temperature, organic solvents were removed under reduced pressure. The resulting aqueous mixture was extracted several times with dichloromethane. Combined organic layers were washed with water and brine, then dried over magnesium sulfate and evaporated under reduced pressure. The crude product was purified by column chromatography (silica gel) to give the corresponding bis-coupling product.

(**E**) **Suzuki-Miyaura cross-coupling reaction** (bis-coupling): *para*-dibromo derivative (1 equiv), pinacolatoboronyl derivative (3-5 equiv), [1,1′-bis(diphenylphosphino)ferrocene]dichloropalladium(II) (10 mol%), and cesium fluoride (6 equiv) were dissolved in a degassed dioxane-water mixture (2/1) under argon atmosphere. The mixture was refluxed for 24h to 60h. The reaction mixture was cooled down to room temperature, then added to water before being extracted with dichloromethane. Combined organic layers were washed with water and brine, then dried over magnesium sulfate and evaporated under reduced pressure. The crude product was purified by column chromatography (silica gel) to give the corresponding bis-coupling product.

(**F**) **Suzuki-Miyaura cross-coupling reaction** (bis-coupling): *para*-bis(pinacolatoboronyl) derivative (1 equiv), bromo derivative (2.2 equiv), [1,1′-bis(diphenylphosphino)ferrocene]dichloropalladium(II) (10 mol%), and cesium fluoride (6 equiv) were dissolved in a degassed dioxane-water mixture (2/1) under argon atmosphere. The mixture was refluxed for 24h to 72h. The reaction mixture was cooled down to room temperature, then added to water before being extracted with dichloromethane. Combined organic layers were washed with water and brine, then dried over magnesium sulfate and evaporated under reduced pressure. The crude product was purified by column chromatography (silica gel) to give the corresponding bis-coupling product.

(**G**) **Bromination reaction**: Dimethyl dicarboxylate derivative (1 equiv) and *N*-bromosuccinimide (NBS) (2.2 equiv) were dissolved in benzene. After degassing (bubbling with argon) for 30 minutes dibenzoyl peroxide (BPO) (2 mol%) was added and the mixture was refluxed for 24h under argon. The reaction mixture was cooled to room temperature, then concentrated under reduced pressure. The crude product was either purified by column chromatography, or treated with methanol and filtrated, then washed with a small amount of methanol to give the corresponding bis(bromomethyl) derivative.

(**H**) **Azidation reaction**: Bis(bromomethyl) derivative (1 equiv) and sodium azide (2.1 equiv) were dissolved in dry dimethylformamide and the mixture was stirred at 60°C for 4h to 18h (under argon). The reaction mixture was cooled to room temperature, then added to water before being extracted with ethyl acetate. Combined organic layers were washed with water and brine, then dried over magnesium sulfate and evaporated under reduced pressure to give the corresponding bis(azidomethyl) derivative.

(**I**) **Acylation reaction**: Bis(bromomethyl) derivative (1 equiv) and potassium acetate (6 equiv) were dissolved in dry dimethylformamide and the mixture was stirred at 80°C for 24h (under argon). The reaction mixture was cooled to room temperature, then added to water before being extracted with dichloromethane. Combined organic layers were washed with water and brine, then dried over magnesium sulfate and evaporated under reduced pressure to give the corresponding bis(acetyloxymethyl) derivative.

(**J**) **Ester hydrolysis (alkyl substituted linkers)**: Dialkyl dicarboxylate derivative (1 equiv) was dissolved in methanol or ethanol. An aqueous solution of potassium or sodium hydroxide (KOH or NaOH) (10-60 equiv) was added and the reaction was refluxed for 3h to 24h. The solution was cooled down in ice, and concentrated hydrochloric acid was added until pH = 2. The aqueous suspension was filtrated; the solid was washed extensively with water, and dried under vacuum at 40°C to give the corresponding dicarboxylic acid.

(**K**) **Ester hydrolysis (functional group substituted linkers)**: Dialkyl dicarboxylate derivative (1 equiv) was dissolved in tetrahydrofuran (THF). An aqueous solution of potassium hydroxide (10-30 equiv) was added and

the reaction mixture was stirred at room temperature for 24h to 72h. The organic solvent was evaporated under reduced pressure, then concentrated hydrochloric acid was added until pH = 2. The aqueous suspension was filtrated; the solid was washed extensively with water, and dried under vacuum at 40°C to give the corresponding dicarboxylic acid.

Methyl 3-methyl-4-(pinacolatoboronyl)benzoate (**3**): Methyl 4-bromo-3-methylbenzoate (**1**) (4.500 g, 19.64 mmol, 1 equiv), B_2pin_2 (**2**) (5.487 g, 21.61 mmol, 1.1 equiv), $Pd(dppf)Cl_2$ (0.802 g, 0.98 mmol, 0.05 equiv), and AcOK (5.783 g, 58.93 mmol, 3 equiv) were reacted in DMSO (75 mL) for 72h according to **general procedure A**. The crude product was purified by column chromatography (20 to 80 % dichloromethane in *n*-hexane) to give (**3**) (4.642 g, 86 %) as a slight green oil. ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 7.82 (s, 1H, CH_{Ar}), 7.80 (s, 2H, CH_{Ar}), 3.90 (s, 3H, CO_2CH_3), 2.57 (s, 3H, ArCH_3), 1.35 (s, 12H, $CH_{3(Bpin)}$) ppm. ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 167.5 (CO_2CH_3), 145.0 (C^{IV}), 135.9 (CH_{Ar}), 131.9 (C^{IV}), 130.6 (CH_{Ar}), 125.7 (CH_{Ar}), 84.0 (C^{IV}), 52.2 (CO_2CH_3), 25.0 ($CH_{3(Bpin)}$), 22.2 (ArCH_3) ppm. IR (ATR): ν = 2979, 1720, 1560, 1496, 1402, 1372, 1318, 1289, 1196 cm^{-1}. MS (EI): *m/z* = 276 (18) [M$^+$], 261 (26) [M$^+$-CH_3], 245 (5) [M$^+$-OCH_3]. HRMS (EI): *m/z* $C_{15}H_{21}BO_4$, calcd.: 276.1533, found: 276.1527.

Dimethyl 2,2'-dimethyl-[1,1'-biphenyl]-4,4'-dicarboxylate (**4**): Methyl 3-methyl-4-(pinacolatoboronyl)benzoate (**3**) (1.457 g, 5.28 mmol, 1 equiv), methyl 4-bromo-3-methylbenzoate (**1**) (1.209 g, 5.28 mmol, 1 equiv), $Pd(dppf)Cl_2$ (215 mg, 0.26 mmol, 0.05 equiv) and CsF (2.404 g, 15.83 mmol, 3 equiv) were reacted in dioxane-water mixture (2/1, 195 mL) for 24h according to **general procedure C**. The crude product was purified by column chromatography (0 to 15 % ethyl acetate in *n*-hexane) to give dimethyl 2,2'-dimethyl-[1,1'-biphenyl]-4,4'-dicarboxylate (**4**) (1.401 g, 89 %) as a white solid. ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 7.96 (s, 2H, CH_{Ar}), 7.90 (d, 2H, *J* = 7.5 Hz, CH_{Ar}), 7.15 (d, 2H, *J* = 7.5 Hz, CH_{Ar}), 3.93 (s, 6H, CO_2CH_3), 2.07 (s, 6H, ArCH_3) ppm. ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 167.2 (CO_2CH_3), 145.6 (C^{IV}), 136.0 (C^{IV}), 131.3 (CH_{Ar}), 129.6 (C^{IV}), 129.1 (CH_{Ar}), 127.1 (CH_{Ar}), 52.3 (CO_2CH_3), 19.8 (ArCH_3) ppm. IR (ATR): ν = 2950, 1710, 1606, 1434, 1402, 1282, 1197 cm^{-1}. MS (EI): *m/z* = 298 (100) [M$^+$], 267 (83) [M$^+$-OCH_3]. HRMS (EI): *m/z* $C_{18}H_{18}O_4$, calcd.: 298.1205, found: 298.1197.

2,2'-dimethyl-[1,1'-biphenyl]-4,4'-dicarboxylic acid (**5**): Dimethyl 2,2'-dimethyl-[1,1'-biphenyl]-4,4'-dicarboxylate (**4**) (0.429 g, 1.44 mmol, 1 equiv) and KOH (1.614 g, 28.76 mmol, 20 equiv) were reacted in EtOH-H_2O (1/1, 30 mL) for 3h according to **general procedure J** to give (**5**) (0.341 g, 88 %) as a white solid. ^{1}H-NMR (500 MHz, DMSO): δ = 12.97 (b-s, 2H, CO_2H), 7.91 (s, 2H, CH_{Ar}), 7.82 (d, 2H, *J* = 7.5 Hz, CH_{Ar}), 7.20 (d, 2H, *J* = 7.5 Hz, CH_{Ar}), 2.04 (s, 6H, ArCH_3) ppm. ^{13}C-NMR (125 MHz, DMSO): δ = 167.2 (CO_2H), 144.7 (C^{IV}), 135.5 (C^{IV}), 130.9 (CH_{Ar}), 130.1 (C^{IV}), 129.0 (CH_{Ar}), 126.8 (CH_{Ar}), 19.4 (ArCH_3) ppm. IR (ATR): ν = 2954, 1677, 1603, 1426, 1286, 1266, 1122 cm^{-1}. MS (EI): *m/z* = 270 (100) [M$^+$], 255 (8), 181 (26), 165 (49). HRMS (EI): *m/z* $C_{16}H_{14}O_4$, calcd.: 270.0892, found: 270.0888.

Dimethyl 2,2''-dimethyl-[1,1':4',1''-terphenyl]-4,4''-dicarboxylate (**7**): Methyl 3-methyl-4-pinacolatoboronylbenzoate (**3**) (1.247 g, 4.52 mmol, 2.5 equiv), 1,4-dibromobenzene (**6**) (0.426 g, 1.81 mmol, 1 equiv), $Pd(dppf)Cl_2$ (147 mg, 0.18 mmol, 0.1 equiv) and CsF (1.646 g, 10.84 mmol, 6 equiv) were reacted in dioxane-water mixture (2/1, 120 mL) for 24h according to **general procedure C**. The crude product was purified by column chromatography (35 to 100 % dichloromethane in *n*-hexane) to give dimethyl 2,2''-dimethyl-[1,1':4',1''-terphenyl]-4,4''-dicarboxylate (**7**) (0.548 g, 81 %) as a white solid. ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 7.99 (d, 2H, *J* = 1.5 Hz, CH_{Ar}), 7.93 (dd, 2H, *J* = 8.0 Hz, *J* = 1.5 Hz, CH_{Ar}), 7.39 (s, 4H, CH_{Ar}), 7.36 (d, 2H, *J* = 8.0 Hz, CH_{Ar}), 3.95 (s, 6H, CO_2CH_3), 2.38 (s, 6H, ArCH_3) ppm. ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 167.3 (CO_2CH_3), 146.2 (C^{IV}), 140.1 (C^{IV}), 135.8 (C^{IV}), 131.7 (CH_{Ar}), 130.1 (CH_{Ar}), 129.2 (C^{IV}), 128.9 (CH_{Ar}), 127.2 (CH_{Ar}), 52.3 (CO_2CH_3), 20.7 (ArCH_3) ppm. IR (ATR): ν = 3052, 2948, 1717, 1606, 1484, 1295, 1281, 1194 cm^{-1}. MS (EI): *m/z* = 374 [M$^+$], 343 [M$^+$-OCH_3]. HRMS (EI): *m/z* $C_{24}H_{22}O_4$, calcd.: 374.1518, found: 374.1511.

2,2''-dimethyl-[1,1':4',1''-terphenyl]-4,4''-dicarboxylic acid (**8**): (**7**) (0.600 g, 1.60 mmol, 1 equiv) and KOH (1.797 g, 32.03 mmol, 20 equiv) were reacted in EtOH-H_2O (1/1, 30 mL) for 3h according to **general procedure J** to give (**8**) (0.547 g, 99 %) as a white solid. ^{1}H-NMR (500 MHz, DMSO): δ = 12.95 (b-s, 2H, CO_2H), 7.91 (s, 2H, CH_{Ar}), 7.84 (d, 2H, *J* = 7.0 Hz, CH_{Ar}), 7.48 (s, 4H, CH_{Ar}), 7.40 (d, 2H, *J* = 7.0 Hz, CH_{Ar}), 2.35 (s, 6H, ArCH_3) ppm. ^{13}C-NMR (125 MHz, DMSO): δ = 167.2 (CO_2H), 145.1 (C^{IV}), 139.4 (C^{IV}), 135.3 (C^{IV}), 131.3 (CH_{Ar}), 129.9 (CH_{Ar}), 129.7 (C^{IV}), 128.8 (CH_{Ar}), 127.0 (CH_{Ar}), 20.2 (ArCH_3) ppm. IR (ATR): ν = 2967, 1679, 1607, 1566, 1426, 1310, 1260, 1132 cm^{-1}. MS (EI): *m/z* = 346 [M$^+$]. HRMS (EI): *m/z* $C_{22}H_{18}O_4$, calcd.: 346.1205, found: 346.1199.

Dimethyl 2',5'-dimethyl-[1,1':4',1''-terphenyl]-4,4''-dicarboxylate (**11**): 2,5-dibromo-*p*-xylene (**9**) (3.000 g, 11.37 mmol, 1 equiv), 4-methoxycarbonylphenylboronic acid (**10**) (6.135 g, 34.10 mmol, 3 equiv), $Pd(PPh_3)_4$ (657 mg, 0.57 mmol, 0.05 equiv) and Na_2CO_3 (9.639 g, 90.92 mmol, 8 equiv) were reacted in toluene-dioxane-water mixture (2/2/1, 450 mL) for 96h according to **general procedure D**. The crude product was purified by column chromatography (30 to 60 % dichloromethane in *n*-hexane) to give dimethyl 2',5'-dimethyl-[1,1':4',1''-terphenyl]-4,4''-dicarboxylate (**11**) (3.192 g, 75 %) as a white solid. ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 8.11 (d, 4H, *J* = 8.5 Hz, CH_{Ar}), 7.45 (d, 4H, *J* = 8.5 Hz, CH_{Ar}), 7.16 (s, 2H, CH_{Ar}), 3.96 (s, 6H, CO_2CH_3), 2.27 (s, 6H, ArCH_3) ppm. ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 167.2 (CO_2CH_3), 146.4 (C^{IV}_{Ar}), 140.5 (C^{IV}_{Ar}), 132.8 (C^{IV}_{Ar}), 131.9 (CH_{Ar}), 129.6 and 129.4 (CH_{Ar}), 128.8 (C^{IV}_{Ar}), 52.3 (CO_2CH_3), 20.0 (ArCH_3) ppm. IR (ATR): ν = 2944, 1713, 1608, 1519, 1491, 1436, 1385, 1277 cm^{-1}. MS (EI): *m/z* = 374 (100) [M$^+$], 343 (23) [M$^+$-OCH_3], 239 (12) [M$^+$-$C_6H_4CO_2CH_3$]. HRMS (EI): *m/z* $C_{24}H_{22}O_4$, calcd.: 374.1518, found: 374.1520.

2',5'-dimethyl-[1,1':4',1''-terphenyl]-4,4''-dicarboxylic acid (**12**): (**11**) (0.535 g, 1.43 mmol, 1 equiv) and KOH (2.004 g, 35.72 mmol, 25 equiv) were reacted in EtOH-H_2O (1/1, 60 mL) for 24h according to **general procedure J** to give (**12**) (0.492 g, 99 %) as a white solid. ^{1}H-NMR (500 MHz, DMSO): δ = 8.03 (d, 4H, *J* = 8.0 Hz, CH_{Ar}), 7.52 (d, 4H, *J* = 8.0 Hz, CH_{Ar}), 7.20 (s, 2H, CH_{Ar}), 2.24 (s, 6H, ArCH_3) ppm. ^{13}C-NMR (125 MHz, DMSO): δ = 167.2 (CO_2H), 145.4 (C^{IV}_{Ar}), 139.8 (C^{IV}_{Ar}), 132.4 (C^{IV}_{Ar}), 131.6 (CH_{Ar}), 129.4 (C^{IV}_{Ar}), 129.3 and 129.2 (CH_{Ar}), 19.6 (ArCH_3) ppm. IR (ATR): ν = 2986, 1685, 1605, 1565, 1423, 1385, 1284, 1173 cm^{-1}. MS (EI): *m/z* = 430 [M$^+$]. HRMS (EI): *m/z* $C_{22}H_{18}O_4$, calcd.: 430.2144, found: 430.2143.

1,4-bis(pinacolatoboronyl)benzene (**13**): 1,4-dibromobenzene (**6**) (2.36 g, 10.00 mmol, 1 equiv), B_2pin_2 (**2**) (7.62 g, 30.00 mmol, 3 equiv), $Pd(dppf)Cl_2$ (0.49 g, 0.60 mmol, 0.06 equiv), and AcOK (5.89 g, 60.00 mmol, 6 equiv) were reacted in DMF (70 mL) for 96h according to **general procedure B**. The crude product was purified by column chromatography (0% to 10% ethyl acetate in *n*-hexane) to give (**13**) (2.89 g, 88 %) as a pale-green solid. ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 7.80 (s, 4H, CH_{Ar}), 1.35 (s, 24H, C$H_{3(Bpin)}$) ppm. ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 134.0 (CH_{Ar}), 84.0 (C^{IV}), 83.6 (C^{IV}), 25.2 ($CH_{3(Bpin)}$) ppm. IR (ATR): ν = 2977, 1522, 1466, 1392, 1328, 1277, 1172 cm^{-1}. MS (EI): *m/z* = 330 (100) [M$^+$], 315 (73) [M$^+$-CH_3], 244 (95) [MH$^+$-$OC(CH_3)_2C(CH_3)_2$]. HRMS (EI): *m/z* $C_{18}H_{28}B_2O_4$, calcd.: 330.2174, found: 330.2174.

4,4''-dibromo-2,2'',5,5''-tetramethyl-1,1':4',1''-terphenyl (**14**): 1,4-bis(pinacolatoboronyl)benzene (**13**) (2.000 g, 6.06 mmol, 1 equiv), 2,5-dibromo-*p*-xylene (**9**) (7.998 g, 30.30 mmol, 5 equiv), $Pd(dppf)Cl_2$ (0.495 g, 0.61 mmol, 0.1 equiv), and CsF (5.523 g, 36.36 mmol, 6 equiv) were

reacted in dioxane-water mixture (2/1, 60 mL) for 72h according to **general procedure F**. The crude product was purified by column chromatography (*n*-hexane) to give (**14**) (0.994 g, 37 %) as a white solid. ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 7.47 (s, 2H, C*H*$_{Ar}$), 7.32 (s, 4H, C*H*$_{Ar}$), 7.15 (s, 2H, C*H*$_{Ar}$), 2.41 (s, 6H, ArC*H*$_3$), 2.27 (s, 6H, ArC*H*$_3$) ppm. ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 140.9 (*C*^{IV}), 139.8 (*C*^{IV}), 135.2 (*C*^{IV}), 134.8 (*C*^{IV}), 134.0 (CH$_{Ar}$), 132.2 (CH$_{Ar}$), 129.0 (CH$_{Ar}$), 123.7 (*C*^{IV}), 22.4 (Ar*C*H$_3$), 19.9 (Ar*C*H$_3$) ppm. IR (ATR): ν = 2954, 2919, 2855, 1475, 1442, 1373, 1357, 1177, 1113 cm^{-1}. MS (EI): *m/z* = 446 (4) – 444 (9) – 442 (4) [M$^+$]. HRMS (EI): *m/z* $C_{22}H_{20}Br_2$, calcd.: 441.9932, found: 441.9930.

Diisopropyl 2',2''',5',5'''-tetramethyl-[1,1':4',1'':4'',1''':4''',1''''-quinquephenyl]-4,4''''-dicarboxylate (**16**): 4,4''-dibromo-2,2'',5,5''-tetramethyl-1,1':4',1''-terphenyl (**14**) (0.300 g, 0.68 mmol, 1 equiv), 4-isopropoxycarbonylphenylboronic acid (**15**) (0.843 g, 4.05 mmol, 6 equiv), $Pd(PPh_3)_4$ (78 mg, 0.07 mmol, 0.1 equiv) and Na_2CO_3 (1.002 g, 9.46 mmol, 14 equiv) were reacted in toluene-dioxane-water mixture (2/2/1, 100 mL) for 72h according to **general procedure D**. The crude product was purified by column chromatography (40 to 70 % dichloromethane in *n*-hexane) to give (**16**) (0.294 g, 71 %) as a white solid. ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 8.12 (d, 4H, *J* = 8.0 Hz, C*H*$_{Ar}$), 7.47 (d, 4H, *J* = 8.0 Hz, C*H*$_{Ar}$), 7.44 (s, 4H, C*H*$_{Ar}$), 7.25 (s, 2H, C*H*$_{Ar}$), 7.18 (s, 2H, C*H*$_{Ar}$), 5.30 (sep, 2H, *J* = 6.5 Hz, C*H*(CH$_3$)$_2$), 2.37 (s, 6H, ArC*H*$_3$), 2.30 (s, 6H, ArC*H*$_3$), 1.41 (d, 12H, *J* = 6.5 Hz, CH(C*H*$_3$)$_2$) ppm. ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 166.2 (*C*O$_2$*i*Pr), 146.4 (*C*^{IV}), 141.3 (*C*^{IV}), 140.2 (*C*^{IV}), 140.1 (*C*^{IV}), 133.0 (*C*^{IV}), 132.7 (*C*^{IV}), 132.2 (*C*H$_{Ar}$), 131.8 (*C*H$_{Ar}$), 129.5 (*C*H$_{Ar}$), 129.4 (*C*H$_{Ar}$), 129.1 (*C*H$_{Ar}$), 68.5 (*C*H(CH$_3$)$_2$), 22.2 (CH(*C*H$_3$)$_2$), 20.2 (Ar*C*H$_3$), 20.0 (Ar*C*H$_3$) ppm. IR (ATR): ν = 2984, 1710, 1608, 1485, 1376, 1272, 1177 cm^{-1}. MS (EI): *m/z* = 610 (54) [M$^+$]. HRMS (EI): *m/z* $C_{42}H_{42}O_4$, calcd.: 610.3083, found: 610.3080. EA ($C_{42}H_{42}O_4$): Calcd.: C, 82.59 %; H, 6.93 %, found: C, 82.19 %; H, 6.85 %.

2',2''',5',5'''-tetramethyl-[1,1':4',1'':4'',1''':4''',1''''-quinquephenyl]-4,4''''-dicarboxylic acid (**17**): Diisopropyl 2',2''',5',5'''-tetramethyl-[1,1':4',1'':4'',1''':4''',1''''-quinquephenyl]-4,4''''-dicarboxylate (**16**) (0.200 g, 0.33 mmol, 1 equiv) and NaOH (0.786 g, 19.65 mmol, 60 equiv) were reacted in MeOH-H_2O (10/1, 33 mL) for 24h according to **general procedure J** to give (**17**) (0.150 g, 87 %) as a white solid. ^{1}H-NMR (600 MHz, DMSO): δ = 8.02 (b-d, 6H, *J* = 6.6 Hz, C*H*$_{Ar}$ and CO$_2$*H*), 7.82 (d, 2H, *J* = 6.6 Hz, C*H*$_{Ar}$), 7.51 (d, 2H, *J* = 6.6 Hz, C*H*$_{Ar}$), 7.49 (s, 4H, C*H*$_{Ar}$), 7.25 (s, 2H, C*H*$_{Ar}$), 7.21 (s, 2H, C*H*$_{Ar}$), 2.32 (s, 6H, ArC*H*$_3$), 2.27 (s, 6H, ArC*H*$_3$) ppm. ^{13}C-NMR (150 MHz, DMSO): δ = 161.3, 142.8, 140.3, 139.5, 132.3, 132.1, 131.7, 131.4, 129.9, 129.1, 129.0, 128.8, 126.8, 19.6, 19.5 ppm. MS (EI): *m/z* = 526 (100) [M$^+$]. HRMS (EI): *m/z* $C_{36}H_{30}O_4$, calcd.: 526.2144, found: 526.2142.

Methyl 4-(pinacolatoboronyl)benzoate (**18**): Methyl 4-bromobenzoate (0.500 g, 2.33 mmol, 1 equiv), B_2pin_2 (**2**) (0.649 g, 2.56 mmol, 1.1 equiv), $Pd(dppf)Cl_2$ (0.095 g, 0.12 mmol, 0.05 equiv), and AcOK (0.685 g, 6.98 mmol, 3 equiv) were reacted in DMSO (15 mL) for 72h according to **general procedure A**. The crude product was purified by column chromatography (0 to 5% ethyl acetate in *n*-hexane) to give (**18**) (0.505 g, 83 %) as a pale grey solid. ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 8.02 (d, 2H, *J* = 8.0 Hz, C*H*$_{Ar}$), 7.87 (d, 2H, *J* = 8.0 Hz, C*H*$_{Ar}$), 3.92 (s, 3H, CO$_2$C*H*$_3$), 1.35 (s, 12H, C*H*$_{3(Bpin)}$) ppm. ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 167.3 (*C*O$_2$Me), 134.8 (*C*H$_{Ar}$), 132.4 (*C*^{IV}), 128.7 (*C*H$_{Ar}$), 84.3 (*C*$^{IV}_{(Bpin)}$), 52.3 (CO$_2$C*H*$_3$), 25.0 (*C*H$_{3(Bpin)}$) ppm. IR (ATR): ν = 2985, 2924, 1720, 1614, 1561, 1508, 1434, 1397, 1326, 1190 cm^{-1}. MS (EI): *m/z* = 262 (38) [M$^+$], 247 (67) [M$^+$-CH$_3$]. HRMS (EI): *m/z* $C_{14}H_{19}BO_4$, calcd.: 262.1376, found: 262.1376.

Methyl 4'-bromo-2',5'-dimethyl-[1,1'-biphenyl]-4-carboxylate (**19**): Methyl 4-(pinacolatoboronyl)benzoate (**18**) (1.000 g, 3.82 mmol, 1 equiv), 2,5-dibromo-*p*-xylene (**9**) (5.035 g, 19.08 mmol, 5 equiv), $Pd(dppf)Cl_2$ (156 mg, 0.19 mmol, 0.05 equiv), and CsF (1.739 g, 11.45 mmol, 3 equiv) were reacted in dioxane-water mixture (2/1, 60 mL) for 72h according to **general procedure C**. The crude product was purified by column chromatography (30 to 50 % dichloromethane in *n*-hexane) to give (**19**) (0.919 g, 75 %) as a pale yellow solid. ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 8.08 (d, 2H, *J* = 8.5 Hz, C*H*$_{Ar}$), 7.46 (s, 1H, C*H*$_{Ar}$), 7.36 (d, 2H, *J* = 8.5 Hz, C*H*$_{Ar}$), 7.08 (s, 1H, C*H*$_{Ar}$), 3.95 (s, 3H, CO$_2$C*H*$_3$), 2.39 (s, 3H, ArC*H*$_3$), 2.20 (s, 3H, ArC*H*$_3$) ppm. ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 167.1 (*C*O$_2$CH$_3$), 145.8 (*C*$^{IV}_{Ar}$), 140.1 (*C*$^{IV}_{Ar}$), 135.4 (*C*$^{IV}_{Ar}$), 134.6 (*C*$^{IV}_{Ar}$), 134.1 (*C*H$_{Ar}$), 131.8 (*C*H$_{Ar}$), 129.6 (*C*H$_{Ar}$), 129.2 (*C*H$_{Ar}$), 124.3 (*C*$^{IV}_{Ar}$), 52.3 (CO$_2$*C*H$_3$), 22.4 (Ar*C*H$_3$), 19.8 (Ar*C*H$_3$) ppm. IR (ATR): ν = 2949, 1717, 1602, 1484, 1433, 1382, 1271 cm^{-1}. MS (EI): *m/z* = 320 (100) – 318 (83) [M$^+$], 289 (40) – 287 (37) [M$^+$-OCH$_3$], 240 (56) [M$^+$-Br]. HRMS (EI): *m/z* $C_{16}H_{15}BrO_2$, calcd.: 318.0255, found: 318.0258.

Methyl 2',5'-dimethyl-4'-(pinacolatoboronyl)-[1,1'-biphenyl]-4-carboxylate (**20**): Methyl 4'-bromo-2',5'-dimethyl-[1,1'-biphenyl]-4-carboxylate (**19**) (0.900 g, 2.82 mmol, 1 equiv), B_2pin_2 (**2**) (0.788 g, 3.10 mmol, 1.1 equiv), $Pd(dppf)Cl_2$ (115 mg, 0.14 mmol, 0.05 equiv), and AcOK (0.830 g, 8.46 mmol, 3 equiv) were reacted in DMSO (30 mL) for 18h according to **general procedure A**. The crude product was purified by column chromatography (30 to 70 % dichloromethane in *n*-hexane) to give (**20**) (0.575 g, 56 %) as a pale yellow solid. ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 8.07 (d, 2H, *J* = 8.0 Hz, C*H*$_{Ar}$), 7.68 (s, 1H, C*H*$_{Ar}$), 7.39 (d, 2H, *J* = 8.0 Hz, C*H*$_{Ar}$), 7.05 (s, 1H, C*H*$_{Ar}$), 3.94 (s, 3H, CO$_2$C*H*$_3$), 2.54 and 2.23 (2 s, 6H, ArC*H*$_3$), 1.36 (s, 12H, C*H*$_{3(Bpin)}$). ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 167.2 (*C*O$_2$CH$_3$), 146.9 (*C*^{IV}), 143.3 (*C*^{IV}), 142.5 (*C*^{IV}), 138.2 (*C*H$_{Ar}$), 131.4 (*C*^{IV}), 131.1 (*C*H$_{Ar}$), 129.5 and 129.3 (*C*H$_{Ar}$), 83.6 (*C*$^{IV}_{(Bpin)}$), 52.3 (CO$_2$*C*H$_3$), 25.0 (*C*H$_{3(Bpin)}$), 21.8 and 19.7 (Ar*C*H$_3$) ppm. IR (ATR): ν = 2977, 2927, 1720, 1606, 1437, 1410, 1390, 1377, 1279, 1178 cm^{-1}. MS (EI): *m/z* = 366 (100) [M$^+$], 351 (10) [M$^+$-CH$_3$]. HRMS (EI): *m/z* $C_{22}H_{27}BO_4$, calcd.: 366.2002, found: 366.2001.

Dimethyl 2',2'',2''',2'''',5',5'',5''',5''''-octamethyl-[1,1':4',1'':4'',1''':4''',1'''':4''',1''''':4''''',1''''''-septephenyl]-4,4''''''-dicarboxylate (**21**): 4,4''-dibromo-2,2'',5,5''-tetramethyl-1,1':4',1''-terphenyl (**14**) (0.300 g, 0.68 mmol, 1 equiv), methyl 2',5'-dimethyl-4'-(pinacolatoboronyl)-[1,1'-biphenyl]-4-carboxylate (**20**) (0.742 g, 2.03 mmol, 3 equiv), $Pd(dppf)Cl_2$ (55 mg, 0.07 mmol, 0.1 equiv), and CsF (0.616 g, 4.05 mmol, 6 equiv) were reacted in dioxane-water mixture (2/1, 60 mL) for 60h according to **general procedure E**. The crude product was purified by column chromatography (0 to 70 % dichloromethane in *n*-hexane) to give (**21**) (0.456 g, 89 %) as a white solid. ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 8.12 (d, 4H, *J* = 8.0 Hz, C*H*$_{Ar}$), 7.49 (d, 4H, *J* = 8.0 Hz, C*H*$_{Ar}$), 7.47 (s, 4H, C*H*$_{Ar}$), 7.24 (s, 2H, C*H*$_{Ar}$), 7.16 (s, 2H, C*H*$_{Ar}$), 7.11 (s, 2H, C*H*$_{Ar}$), 7.09 (s, 2H, C*H*$_{Ar}$), 3.96 (s, 6H, CO$_2$C*H*$_3$), 2.37 and 2.28 (2 s, 12H, ArC*H*$_3$), 2.16 (s, 12H, ArC*H*$_3$) ppm. ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 167.3 (*C*O$_2$), 146.9 (*C*^{IV}), 141.2 (*C*^{IV}), 140.6 (*C*^{IV}), 140.4 (*C*^{IV}), 140.3 (*C*^{IV}), 139.7 (*C*^{IV}), 133.6 (*C*^{IV}), 133.3 (*C*^{IV}), 132.5 (*C*^{IV}), 132.3 (*C*^{IV}), 131.8 (*C*H$_{Ar}$), 131.6 (*C*H$_{Ar}$), 131.5 (*C*H$_{Ar}$), 131.1 (*C*H$_{Ar}$), 129.6 (*C*H$_{Ar}$), 129.5 (*C*H$_{Ar}$), 129.1 (*C*H$_{Ar}$), 128.6 (*C*^{IV}), 52.3 (CO$_2$*C*H$_3$), 20.3 (Ar*C*H$_3$), 20.1 (Ar*C*H$_3$), 19.6 (Ar*C*H$_3$) ppm. IR (ATR): ν = 3006, 2951, 2918, 1723, 1608, 1483, 1437, 1275, 1178, 1114 cm^{-1}. MS (EI): *m/z* = 762 (74) [M$^+$]. HRMS (EI): *m/z* $C_{54}H_{50}O_4$, calcd.: 762.3709, found: 762.3707.

2',2'',2''',2'''',5',5'',5''',5''''-octamethyl-[1,1':4',1'':4'',1''':4''',1'''':4''',1''''':4''''',1''''''-septephenyl]-4,4''''''-dicarboxylic acid (**22**): Dimethyl 2',2'',2''',2'''',5',5'',5''',5''''-octamethyl-[1,1':4',1'':4'',1''':4''',1'''':4''',1''''':4''''',1''''''-septephenyl]-4,4''''''-dicarboxylate (**21**) (0.250 g, 0.33 mmol, 1 equiv) and NaOH (0.786 g, 19.66 mmol, 60 equiv) were reacted in MeOH-H_2O (10/1, 33 mL) for 24h according to **general procedure J** to give (**22**) (0.205 g, 85 %) as a white solid. ^{1}H-NMR (500 MHz, DMSO): δ = 12.96 (br-s, 2H, CO$_2$*H*), 8.03 (br-s, 4H, C*H*$_{Ar}$), 7.55 (br-s, 4H, C*H*$_{Ar}$), 7.51 (s, 4H, C*H*$_{Ar}$), 7.25 (s, 2H, C*H*$_{Ar}$), 7.21 (s, 2H, C*H*$_{Ar}$), 7. 09 (s, 4H, C*H*$_{Ar}$), 2.32 and 2.25 (2 s, 12H, ArC*H*$_3$), 2.10 (s, 12H, ArC*H*$_3$) ppm. MS (EI): *m/z* = 734 (23) [M$^+$].

1,4-bis(pinacolatoboronyl)-2,5-dimethylbenzene (**23**): 2,5-dibromo-*p*-xylene (**9**) (1.060 g, 4.02 mmol, 1 equiv), B_2pin_2 (**2**) (3.059 g, 12.05 mmol, 3 equiv), $Pd(dppf)Cl_2$ (0.196 g, 0.24 mmol, 0.06 equiv), and AcOK (2.365 g, 24.10 mmol, 6 equiv) were reacted in DMF (40 mL) for 48h according to **general procedure B**. The crude product was purified by column chromatography (50 to 70% dichloromethane in *n*-hexane) to give (**23**) (1.450 g, 95%) as a white solid. ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 7.54 (s, 2H, CH_{Ar}), 2.49 (s, 6H, ArCH_3), 1.34 (s, 24H, C$H_{3(Bpin)}$) ppm. ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 140.7 (C^{IV}), 137.0 (CH_{Ar}), 83.5 (C^{IV}), 25.0 (C$H_{3(Bpin)}$), 21.6 (ArCH_3) ppm. IR (ATR): ν = 2975, 2928, 1501, 1460, 1406, 1370, 1321, 1285, 1166 cm^{-1}. MS (EI): *m/z* = 358 (22) [M$^+$], 343 (31) [M$^+$-CH_3]. HRMS (EI): *m/z* $C_{18}H_{28}B_2O_4$, calcd.: 358.2487, found: 358.2489.

Dimethyl 2,2',2'',5'-tetramethyl-[1,1':4',1''-terphenyl]-4,4''-dicarboxylate (**24**): 1,4-bis(pinacolatoboronyl)-2,5-dimethylbenzene (**23**) (0.653 g, 1.82 mmol, 1 equiv), methyl 4-bromo-3-methylbenzoate (**1**) (0.919 g, 4.01 mmol, 2.2 equiv), $Pd(dppf)Cl_2$ (149 mg, 0.18 mmol, 0.10 equiv), and CsF (1.662 g, 10.94 mmol, 6 equiv) were reacted in dioxane-water mixture (2/1, 120 mL) for 48h according to **general procedure F**. The crude product was purified by column chromatography (30 to 70% dichloromethane in *n*-hexane) to give (**24**) (0.600 g, 82 %) as a white solid. ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 7.98 (s, 2H, CH_{Ar}), 7.91 (d, 2H, *J* = 8.0 Hz, CH_{Ar}), 7.25 (dd, 2H, *J* = 8.0 Hz, *J* = 1.5 Hz, CH_{Ar}), 6.98 (d, 2H, *J* = 8.0 Hz, CH_{Ar}), 3.94 (s, 6H, CO_2CH_3), 2.17 (s, 3H, ArCH_3), 2.16 (s, 3H, ArCH_3), 2.01 (s, 6H, ArCH_3) ppm. ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 167.4 (CO_2CH_3), 146.5 (C^{IV}), 140.0 (C^{IV}), 136.5 (C^{IV}), 132.7 (C^{IV}), 131.2 (CH_{Ar}), 130.4 (CH_{Ar}), 129.7 (CH_{Ar}), 129.1 (C^{IV}), 127.0 (CH_{Ar}), 52.2 (CO_2CH_3), 20.0 (ArCH_3), 19.9 (ArCH_3), 19.3 (ArCH_3) ppm. IR (ATR): ν = 3004, 2950, 1714, 1437, 1404, 1285, 1258, 1198 cm^{-1}. MS (EI): *m/z* = 402 (100) [M$^+$], 387 (15) [M$^+$-CH_3], 371 (23) [M$^+$-OCH_3]. HRMS (EI): *m/z* $C_{26}H_{26}O_4$, calcd.: 402.1831, found: 402.1827.

2,2',2'',5'-tetramethyl-[1,1':4',1''-terphenyl]-4,4''-dicarboxylic acid (**25**): Dimethyl 2,2',2'',5'-tetramethyl-[1,1':4',1''-terphenyl]-4,4''-dicarboxylate (**24**) (0.403 g, 1.00 mmol, 1 equiv) and KOH (1.124 g, 20.03 mmol, 20 equiv) were reacted in EtOH-H_2O (1/1, 20 mL) for 3h according to **general procedure J** to give (**25**) (0.348 g, 93 %) as a white solid. ^{1}H-NMR (500 MHz, DMSO): δ = 12.93 (b-s, 2H, CO_2H), 7.90 (s, 2H, CH_{Ar}), 7.82 (d, 2H, *J* = 7.5 Hz, CH_{Ar}), 7.25 (d, 2H, *J* = 7.5 Hz, CH_{Ar}), 7.04 (s, 2H, CH_{Ar}), 2.11 (s, 6H, ArCH_3), 1.98 (s, 6H, ArCH_3) ppm. ^{13}C-NMR (125 MHz, DMSO): δ = 167.3 (CO_2H), 145.5 (C^{IV}), 139.5 (C^{IV}), 135.9 (C^{IV}), 132.2 (C^{IV}), 130.7 (CH_{Ar}), 130.1 (CH_{Ar}), 129.8 (C^{IV}), 129.5 (CH_{Ar}), 126.8 (CH_{Ar}), 19.6 (ArCH_3), 19.4 (ArCH_3), 18.9 (ArCH_3) ppm. IR (ATR): ν = 2917, 1678, 1607, 1565, 1422, 1286, 1264, 1124 cm^{-1}. MS (EI): *m/z* = 374 (31) [M$^+$], 91 (100), 69 (41). HRMS (EI): *m/z* $C_{24}H_{22}O_4$, calcd.: 374.1518, found: 374.1513.

4,4''-dibromo-2,2',2'',5,5',5''-hexamethyl-1,1':4',1''-terphenyl (**26**): 1,4-bis(pinacolatoboronyl)-2,5-dimethylbenzene (**23**) (2.890 g, 8.07 mmol, 1 equiv), 2,5-dibromo-*p*-xylene (**9**) (10.652 g, 40.35 mmol, 5 equiv), $Pd(dppf)Cl_2$ (0.659 g, 0.81 mmol, 0.1 equiv), and CsF (7.356 g, 48.42 mmol, 6 equiv) were reacted in dioxane-water mixture (2/1, 45 mL) for 48h according to **general procedure F**. The crude product was purified by column chromatography (*n*-hexane) to give (**26**) (1.977 g, 52 %) as a white solid. ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 7.45 (s, 2H, CH_{Ar}), 7.03 (m, 2H, CH_{Ar}), 6.94 (m, 2H, CH_{Ar}), 2.39 (s, 6H, ArCH_3), 2.05 (m, 6H, ArCH_3), 2.02 (s, 6H, ArCH_3) ppm. ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 140.8 (C^{IV}), 140.7 (C^{IV}), 139.7 (C^{IV}), 139.6 (C^{IV}), 135.5 (C^{IV}), 134.9 (C^{IV}), 134.8 (C^{IV}), 133.4 (CH_{Ar}), 132.8 (CH_{Ar}), 131.8 (CH_{Ar}), 130.7 (CH_{Ar}), 123.4 (C^{IV}), 22.5 (ArCH_3), 19.4 (ArCH_3), 19.2 (ArCH_3) ppm. IR (ATR): ν = 3021, 2917, 2854, 1477, 1445, 1392, 1268, 1177 cm^{-1}. MS (EI): *m/z* = 474 (47) – 472 (100) – 470 (47) [M$^+$]. HRMS (EI): *m/z* $C_{24}H_{24}Br_2$, calcd.: 470.0244, found: 470.0245.

Dimethyl 2',2'',2''',5',5'',5'''-hexamethyl-[1,1':4',1'':4'',1''':4''',1'''':4'''',1''''-quinquephenyl]-4,4''''-dicarboxylate (**27**): 4,4''-dibromo-2,2',2'',5,5',5''-hexamethyl-1,1':4',1''-terphenyl (**26**) (0.473 g, 1.00 mmol, 1 equiv), 4-methoxycarbonylphenylboronic acid (**10**) (0.900 g, 5.00 mmol, 5 equiv), $Pd(PPh_3)_4$ (116 mg, 0.10 mmol, 0.1 equiv) and Na_2CO_3 (1.272 g, 12.00 mmol, 12 equiv) were reacted in toluene-dioxane-water mixture (2/2/1, 30 mL) for 72h according to **general procedure D**. The crude product was purified by column chromatography (30 to 60 % dichloromethane in *n*-hexane) to give (**27**) (0.291 g, 50 %) as a white solid. ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 8.12 (d, 4H, *J* = 8.5 Hz, CH_{Ar}), 7.49 (d, 4H, *J* = 8.5 Hz, CH_{Ar}), 7.16 (s, 2H, CH_{Ar}), 7.12 (m, 2H, CH_{Ar}), 7.06 (m, 2H, CH_{Ar}), 3.96 (s, 3H, C$H(CH_3)_2$), 2.28 (s, 6H, ArCH_3), 2.13 (m, 12H, ArCH_3), 1.40 (d, 12H, *J* = 6.5 Hz, CO_2CH_3) ppm. ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 167.3, 146.9, 141.4, 140.2, 139.6, 133.6, 132.9, 132.2, 131.7, 131.1, 130.8, 129.5, 128.6, 52.3, 20.1, 20.0, 19.6, 19.4 ppm. IR (ATR): ν = 2980, 1709, 1608, 1484, 1373, 1273, 1176 cm^{-1}. MS (EI): *m/z* = 582 (100) [M$^+$]. HRMS (EI): *m/z* $C_{40}H_{38}O_4$, calcd.: 582.2770, found: 582.2766.

2',2'',2''',5',5'',5'''-hexamethyl-[1,1':4',1'':4'',1''':4''',1'''':4'''',1''''-quinquephenyl]-4,4''''-dicarboxylic acid (**28**): Dimethyl 2',2'',2''',5',5'',5'''-hexamethyl-[1,1':4',1'':4'',1''':4''',1'''':4'''',1''''-quinquephenyl]-4,4''''-dicarboxylate (**27**) (0.109 g, 0.19 mmol, 1 equiv) and NaOH (0.450 g, 11.27 mmol, 60 equiv) were reacted in MeOH-H_2O (6/1, 21 mL) for 24h according to **general procedure J** to give (**28**) (0.079 g, 76 %) as a white solid. ^{1}H-NMR (500 MHz, DMSO): δ = 12.96 (b-s, 2H, CO_2H), 8.03 (d, 4H, *J* = 8.5 Hz, CH_{Ar}), 7.55 (d, 4H, *J* = 8.5 Hz, CH_{Ar}), 7.20 (s, 2H, CH_{Ar}), 7.11 (m, 2H, CH_{Ar}), 7.07 (m, 2H, CH_{Ar}), 2.26 (s, 6H, ArCH_3), 2.08 (s, 6H, ArCH_3), 2.07 (s, 6H, ArCH_3) ppm. ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 167.2, 145.7, 139.6, 133.0, 132.9, 132.3, 131.9, 131.8, 131.5, 131.3, 130.8, 129.3, 129.3, 19.7, 19.6, 19.2 ppm. IR (ATR): ν = 2918, 1677, 1606, 1483, 1416, 1311, 1271, 1176 cm^{-1}. MS (EI): *m/z* = 554 (2) [M$^+$]. HRMS (EI): *m/z* $C_{44}H_{46}O_4$, calcd.: 554.2457, found: 554.2455.

1,4-di(pyridin-4-yl)benzene (**32**): 1,4-dibromobenzene (**6**) (1.416 g, 6.00 mmol, 1 equiv), 4-pyridylboronic acid (**31**) (2.582 g, 21.01 mmol, 3.5 equiv), $Pd(PPh_3)_4$ (490 mg, 0.60 mmol, 0.1 equiv) and Na_2CO_3 (5.088 g, 48.04 mmol, 8 equiv) were reacted in toluene-dioxane-water mixture (2/2/1, 50 mL) for 72h according to **general procedure D**. The crude product was purified by column chromatography (0 to 25 % acetone in dichloromethane) to give (**32**) (1.105 g, 79 %) as a white solid. ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 8.71 (d, 4H, *J* = 6.0 Hz, CH_{Py}), 7.78 (s, 4H, CH_{Ar}), 7.57 (d, 4H, *J* = 6.0 Hz, CH_{Py}) ppm. ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 150.4 (CH_{Py}), 147.7 (C$^{IV}{}_{Py}$), 139.0 (C$^{IV}{}_{Ar}$-Py), 127.9 (CH_{Py}), 121.7 (CH_{Ar}) ppm. IR (ATR): ν = 1584, 1548, 1478, 1403, 1226, 1040 cm^{-1}. MS (EI): *m/z* = 232 (100) [M$^+$], 156 (8) [M$^+$-C_5H_4N]. HRMS (EI): *m/z* $C_{16}H_{12}N_2$, calcd.: 232.1000, found: 232.0994.

4-(4-bromophenyl)pyridine (**33**): 4-pyridylboronic acid (**31**) (1.500 g, 12.20 mmol, 1 equiv), 1,4-dibromobenzene (**6**) (8.636 g, 36.61 mmol, 3 equiv), $Pd(PPh_3)_4$ (705 mg, 0.61 mmol, 0.05 equiv) and Na_2CO_3 (5.174 g, 48.81 mmol, 4 equiv) were reacted in toluene-dioxane-water mixture (2/2/1, 200 mL) for 48h according to **general procedure C**. The crude product was purified by column chromatography (0 to 40 % ethyl acetate in dichloromethane) to give (**33**) (2.278 g, 80 %) as a pale yellow solid. ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 8.67 (d, 2H, *J* = 6.0 Hz, CH_{Py}), 7.62 (d, 2H, *J* = 8.5 Hz, CH_{Ar}), 7.50 (d, 2H, *J* = 8.5 Hz, CH_{Ar}), 7.46 (d, 2H, *J* = 6.0 Hz, CH_{Py}) ppm. ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 150.5 (CH_{Py}), 147.3 (C^{IV}), 137.2 (C^{IV}), 132.4 (CH_{Ar}), 128.7 (CH_{Ar}), 123.7 (C^{IV}), 121.5 (CH_{Py}) ppm. IR (ATR): ν = 3022, 2917, 1714, 1591, 1537, 1475, 1391, 1269, 1180 cm^{-1}. MS (EI): *m/z* = 235 (90) – 233 (100) [M$^+$]. HRMS (EI): *m/z* $C_{11}H_8BrN$, calcd.: 232.9840, found: 232.9839.

4,4'-di(pyridin-4-yl)-1,1'-biphenyl (**35**): 4-pyridylboronic acid (**31**) (1.182 g, 9.62 mmol, 3 equiv), 4,4'-dibromobiphenyl (**34**) (1.000 g,

3.21 mmol, 1 equiv), $Pd(PPh_3)_4$ (185 mg, 0.16 mmol, 0.05 equiv) and Na_2CO_3 (2.718 g, 25.64 mmol, 8 equiv) were reacted in toluene-dioxane-water mixture (2/2/1, 60 mL) for 48h according to **general procedure D**. The crude product was purified by column chromatography (30 to 100 % ethyl acetate in dichloromethane) to give (**35**) (0.573 g, 58 %) as a white solid. ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 8.70 (d, 4H, J = 6.0 Hz, CH_{Py}), 7.77 (m, 8H, CH_{Ar}), 7.57 (d, 4H, J = 6.0 Hz, CH_{Py}) ppm. ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 150.5 (CH_{Py}), 147.8 (C$^{IV}_{Py}$), 141.1 (C$^{IV}_{Ar}$-Py), 137.6 (C$^{IV}_{Ar}$-Py), 127.9 (CH_{Py}), 121.6 (CH_{Ar}) ppm. IR (ATR): ν = 1581, 1552, 1475, 1401, 1226, 1039 cm^{-1}. MS (EI): *m/z* = 308 (100) [M$^+$]. HRMS (EI): *m/z* $C_{22}H_{16}N_2$, calcd.: 308.1313, found: 308.1311.

4-(4'-bromo-[1,1'-biphenyl]-4-yl)pyridine (**36**): 4-pyridylboronic acid (**31**) (1.000 g, 8.14 mmol, 1 equiv), 4,4'-dibromobiphenyl (**34**) (7.615 g, 24.41 mmol, 3 equiv), $Pd(PPh_3)_4$ (470 mg, 0.41 mmol, 0.05 equiv) and Na_2CO_3 (3.450 g, 32.54 mmol, 4 equiv) were reacted in toluene-dioxane-water mixture (2/2/1, 125 mL) for 48h according to **general procedure C**. The crude product was purified by column chromatography (0 to 40 % ethyl acetate in dichloromethane) to give (**36**) (1.887 g, 75 %) as a yellow solid. ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 8.68 (d, 2H, J = 6.0 Hz, CH_{Py}), 7.73 (d, 2H, J = 8.5 Hz, CH_{Ar}), 7.68 (d, 2H, J = 8.5 Hz, CH_{Ar}), 7.60 (d, 2H, J = 8.5 Hz, CH_{Ar}), 7.55 (d, 2H, J = 6.0 Hz, CH_{Py}), 7.50 (d, 2H, J = 8.5 Hz, CH_{Ar}) ppm.

1,4-di(pyridin-4-yl)-2,5-dimethylbenzene (**43**): 2,5-dibromo-*p*-xylene (**9**) (2.112 g, 8.00 mmol, 1 equiv), 4-pyridylboronic acid (**31**) (2.951 g, 24.00 mmol, 3 equiv), $Pd(PPh_3)_4$ (462 mg, 0.40 mmol, 0.05 equiv) and Na_2CO_3 (0.848 g, 8.00 mmol, 8 equiv) were reacted in toluene-dioxane-water mixture (2/2/1, 400 mL) for 72h according to **general procedure D**. The crude product was purified by column chromatography (50 to 85 % ethyl acetate in dichloromethane) to give (**43**) (1.960 g, 94 %) as a white solid. ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 8.68 (d, 4H, J = 6.0 Hz, CH_{Py}), 7.31 (d, 4H, J = 6.0 Hz, CH_{Py}), 7.15 (s, 2H, CH_{Ar}), 2.29 (s, 6H, ArCH_3) ppm. ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 149.7 (CH_{Py}), 149.4 (C$^{IV}_{Py}$), 139.3 (C$^{IV}_{Ar}$-Py), 132.9 (C$^{IV}_{Ar}$-CH$_3$), 131.7 (CH_{Py}), 124.3 (CH_{Ar}), 19.9 (ArCH_3) ppm. IR (ATR): ν = 3023, 2921, 1593, 1543, 1481, 1414, 1387, 1216, 1183 cm^{-1}. MS (EI): *m/z* = 260 (100) [M$^+$], 245 (17) [M$^+$-CH$_3$], 182 (4) [M$^+$-C$_5$H$_4$N]. HRMS (EI): *m/z* $C_{18}H_{16}N_2$, calcd.: 260.1313, found: 260.1312.

4-(4-bromo-2,5-dimethylphenyl)pyridine (**44**): 4-pyridylboronic acid (**31**) (0.100 g, 0.81 mmol, 1 equiv), 2,5-dibromo-*p*-xylene (**9**) (1.074 g, 4.07 mmol, 5 equiv), $Pd(PPh_3)_4$ (47 mg, 0.04 mmol, 0.05 equiv) and Na_2CO_3 (0.259 g, 2.44 mmol, 3 equiv) were reacted in toluene-dioxane-water mixture (2/2/1, 25 mL) for 24h according to **general procedure C**. The crude product was purified by column chromatography (0 to 20 % ethyl acetate in dichloromethane) to give (**44**) (0.169 g, 79 %) as a yellow oil. ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 8.64 (d, 2H, J = 6.0 Hz, CH_{Py}), 7.47 (s, 1H, CH_{Ar}), 7.22 (d, 2H, J = 6.0 Hz, CH_{Py}), 7.06 (s, 1H, CH_{Ar}), 2.39 and 2.21 (2 s, 6H, ArCH_3) ppm. ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 149.9 (CH_{Py}), 148.9 (C$^{IV}_{Py}$), 138.3 (C$^{IV}_{Ar}$-CH$_3$), 135.7 (C$^{IV}_{Ar}$-CH$_3$), 134.4 (C$^{IV}_{Ar}$-Py), 134.3 (CH_{Ar}), 131.5 (CH_{Ar}), 124.9 (C$^{IV}_{Ar}$-Br), 124.2 (CH_{Py}), 22.4 and 19.6 (ArCH_3) ppm. IR (ATR): ν = 3021, 2920, 1594, 1475, 1383, 1215, 1182 cm^{-1}. MS (EI): *m/z* = 263 (100) – 261 (100) [M$^+$]. HRMS (EI): *m/z* $C_{13}H_{12}BrN$, calcd.: 261.0153, found: 261.0155.

4-(2,5-dimethyl-4-(pinacolatoboronyl)phenyl)pyridine (**45**): 4-(4-bromo-2,5-dimethylphenyl)pyridine (**44**) (0.840 g, 3.20 mmol, 1 equiv), B_2pin_2 (**2**) (0.895 g, 3.53 mmol, 1.1 equiv), $Pd(dppf)Cl_2$ (0.131 g, 0.16 mmol, 0.05 equiv), and AcOK (0.943 g, 9.61 mmol, 3 equiv) were reacted in DMSO (25 mL) for 48h according to **general procedure A**. The crude product was purified by column chromatography (dichloromethane) to give (**45**) (0.849 g, 86 %) as a yellow oil. ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 8.65 (d, 2H, J = 6.0 Hz, CH_{Py}), 7.69 (s, 1H, CH_{Ar}), 7.31 (d, 2H, J = 6.0 Hz, CH_{Py}), 7.03 (s, 1H, CH_{Ar}), 2.54 and 2.24 (2 s, 6H, ArCH_3), 1.36 (s, 12H, C$H_{3(Bpin)}$) ppm. ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 149.2 (CH_{Py}), 142.8 (C^{IV}), 141.2 (C^{IV}), 138.4 (CH_{Ar}), 131.2 (C^{IV}), 130.8 (CH_{Ar}), 124.4 (CH_{Py}), 83.8 (C$^{IV}_{(Bpin)}$), 25.0 (C$H_{3(Bpin)}$), 21.8 and 19.6 (ArCH_3) ppm. IR (ATR): ν = 2976, 2927, 1595, 1447, 1372, 1312, 1265, 1180 cm^{-1}. MS (EI): *m/z* = 309 (62) [M$^+$]. HRMS (EI): *m/z* $C_{19}H_{24}BNO_2$, calcd.: 309.1900, found: 309.1899.

4,4'-(2,2',2'',5,5',5''-hexamethyl-[1,1':4',1''-terphenyl]-4,4''-diyl)dipyridine (**46**): 4,4''-dibromo-2,2',2'',5,5',5''-hexamethyl-1,1':4',1''-terphenyl (**26**) (0.200 g, 0.42 mmol, 1 equiv), 4-pyridylboronic acid (**31**) (0.312 g, 2.54 mmol, 6 equiv), $Pd(PPh_3)_4$ (48 mg, 0.042 mmol, 0.1 equiv) and Na_2CO_3 (0.356 g, 3.36 mmol, 8 equiv) for 72h were reacted in toluene-dioxane-water mixture (2/2/1, 30 mL) according to **general procedure D**. The crude product was purified by column chromatography (0 to 10 % ethyl acetate in dichloromethane) to give (**46**) (0.170 g, 86 %) as a white solid. ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 8.68 (d, 4H, J = 5.0 Hz, CH_{Py}), 7.36 (d, 4H, J = 5.0 Hz, CH_{Py}), 7.14 (s, 2H, CH_{Ar}), 7.13 (m, 2H, CH_{Ar}), 7.05 (m, 2H, CH_{Ar}), 2.30 (s, 6H, ArCH_3), 2.14 (m, 6H, ArCH_3), 2.11 (s, 6H, ArCH_3) ppm. ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 149.9 (C$^{IV}_{Py}$), 149.8 (CH_{Py}), 142.0 (C^{IV}), 141.9 (C^{IV}), 140.1 (C^{IV}), 140.0 (C^{IV}), 137.9 (C^{IV}), 137.9 (C^{IV}), 133.9 (C^{IV}), 133.9 (C^{IV}), 133.0 (C^{IV}), 132.9 (C^{IV}), 132.1 (C^{IV}), 132.0 (CH_{Ar}), 131.9 (CH_{Ar}), 130.9 (CH_{Ar}), 130.8 (CH_{Ar}), 124.5 (CH_{Py}), 20.0 (CH_3), 19.9 (CH_3), 19.6 (CH_3), 19.4 (CH_3) ppm. IR (ATR): ν = 2921, 2854, 1595, 1534, 1481, 1411, 1385, 1222, 1188 cm^{-1}. MS (EI): *m/z* = 468 (100) [M$^+$]. HRMS (EI): *m/z* $C_{34}H_{32}N$, calcd.: 468.2565, found: 468.2565.

4,4'-(2,2'',5,5''-tetramethyl-[1,1':4',1''-terphenyl]-4,4''-diyl)dipyridine (**48**): 4,4''-dibromo-2,2'',5,5''-tetramethyl-1,1':4',1''-terphenyl (**14**) (0.188 g, 0.42 mmol, 1 equiv), 4-pyridylboronic acid (**31**) (0.312 g, 2.54 mmol, 6 equiv), $Pd(PPh_3)_4$ (48 mg, 0.042 mmol, 0.1 equiv) and Na_2CO_3 (0.358 g, 3.36 mmol, 8 equiv) were reacted in toluene-dioxane-water mixture (2/2/1, 50 mL) for 72h according to **general procedure D**. The crude product was purified by column chromatography (70 to 80 % ethyl acetate in dichloromethane) to give (**48**) (0.165 g, 89 %) as a white solid. ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 8.69 (d, 4H, J = 6.0 Hz, CH_{Py}), 7.44 (s, 4H, CH_{Ar}), 7.40 (d, 4H, J = 6.0 Hz, CH_{Py}), 7.27 (s, 2H, CH_{Ar}), 7.18 (s, 2H, CH_{Ar}), 2.37 (s, 6H, ArCH_3), 2.33 (s, 6H, ArCH_3) ppm. ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 150.8 (C$^{IV}_{Py}$), 148.8 (CH_{Py}), 142.1 (C^{IV}), 140.1 (C^{IV}), 137.8 (C^{IV}), 133.5 (C^{IV}), 132.5 (C^{IV}), 132.5 (CH_{Ar}), 131.6 (CH_{Ar}), 129.1 (CH_{Ar}), 124.7 (CH_{Py}), 20.2 (ArCH_3), 19.9 (ArCH_3) ppm. IR (ATR): ν = 3021, 2920, 2855, 1595, 1481, 1403, 1383, 1206, 1185 cm^{-1}. MS (EI): *m/z* = 440 (100) [M$^+$]. HRMS (EI): *m/z* $C_{32}H_{28}N_2$, calcd.: 440.2252, found: 440.2251.

4,4'-(2,2',2''',2''',5,5',5''',5''''-octamethyl-[1,1':4',1'':4'',1''':4''',1''''-quinquephenyl]-4,4''''-diyl)dipyridine (**49**): 4,4''-dibromo-2,2'',5,5''-tetramethyl-1,1':4',1''-terphenyl (**14**) (0.300 g, 0.68 mmol, 1 equiv), 4-(2,5-dimethyl-4-(pinacolatoboronyl)phenyl)pyridine (**45**) (0.626 g, 2.03 mmol, 3 equiv), $Pd(dppf)Cl_2$ (55 mg, 0.07 mmol, 0.1 equiv), and CsF (0.616 g, 4.05 mmol, 6 equiv) were reacted in a dioxane-water mixture (60 mL) for 60h according to **general procedure E**. The crude product was purified by column chromatography (10 to 100 % ethyl acetate in dichloromethane) to give (**49**) (0.389 g, 89 %) as a white solid. ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 8.68 (d, 4H, J = 6.0 Hz, CH_{Py}), 7.47 (s, 4H, CH_{Ar}), 7.35 (d, 4H, J = 6.0 Hz, CH_{Py}), 7.25 (s, 2H, CH_{Ar}), 7.15 (s, 2H, CH_{Ar}), 7.13 (s, 2H, CH_{Ar}), 7.08 (s, 2H, CH_{Ar}), 2.36 and 2.30 (2 s, 12H, ArCH_3), 2.16 and 2.15 (2 s, 12H, ArCH_3) ppm. ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 149.9 (C^{IV}), 149.7 (CH_{Py}), 141.8 (C^{IV}), 141.4 (C^{IV}), 140.7 (C^{IV}), 140.3 (C^{IV}), 140.1 (C^{IV}), 138.1 (C^{IV}), 137.9 (C^{IV}), 133.9 (C^{IV}), 133.7 (C^{IV}), 133.2 (C^{IV}), 132.5 (C^{IV}), 132.2 (C^{IV}), 132.1 (C^{IV}), 132.0 (CH_{Ar}), 131.8 (CH_{Ar}), 131.6 (CH_{Ar}), 131.5 (CH_{Ar}), 129.1 (CH_{Ar}), 124.5 (CH_{Py}), 20.2 (ArCH_3), 19.9 (ArCH_3), 19.6 (ArCH_3), 19.5 (ArCH_3) ppm. MS (EI): *m/z* = 648 (100) [M$^+$]. HRMS (EI): *m/z* $C_{48}H_{44}N_2$, calcd.: 648.3504, found: 648.3502.

Dimethyl 2,2'-bis(bromomethyl)-[1,1'-biphenyl]-4,4'-dicarboxylate (**50**): Dimethyl 2,2'-dimethyl-[1,1'-biphenyl]-4,4'-dicarboxylate (**4**) (0.600 g,

2.01 mmol, 1 equiv), NBS (0.787 g, 4.43 mmol, 2.2 equiv) and BPO (10 mg, 0.04 mmol, 0.02 equiv) were reacted in benzene (30 mL) for 24h according to **general procedure G**. The crude product was purified by column chromatography (40 to 70 % dichloromethane in *n*-hexane) to give (**50**) (0.772 g, 84 %) as a white wax. ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 8.24 (d, 2H, *J* = 1.5 Hz, C*H*$_{Ar}$), 8.06 (dd, 2H, *J* = 8.0 Hz, *J* = 1.5 Hz, C*H*$_{Ar}$), 7.36 (d, 2H, *J* = 8.0 Hz, C*H*$_{Ar}$), 4.33 and 4.17 (2 d, 4H, *J* = 10.5 Hz, Ar*CH*$_2$Br), 3.97 (s, 6H, CO_2CH_3) ppm. ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 166.3 (CO_2CH_3), 143.2 (C^{IV}_{Ar}), 136.4 (C^{IV}_{Ar}), 132.2 (*C*H$_{Ar}$), 131.2 (C^{IV}_{Ar}), 130.2 (*C*H$_{Ar}$), 129.6 (*C*H$_{Ar}$), 52.6 (CO_2CH_3), 30.7 (CH_2Br) ppm. IR (ATR): ν = 2950, 1716, 1606, 1434, 1407, 1288, 1194, 1142 cm^{-1}. MS (EI): *m/z* = 458 (3) – 456 (6) – 454 (3) [M$^+$], 377 (54) [M$^+$-Br], 298 (20) [M$^+$-2Br], 237 (100). HRMS (EI): *m/z* $C_{18}H_{16}Br_2O_4$, calcd.: 453.9415, found: 453.9409.

Dimethyl 2,2'-bis(azidomethyl)-[1,1'-biphenyl]-4,4'-dicarboxylate (**51**): Dimethyl 2,2'-bis(bromomethyl)-[1,1'-biphenyl]-4,4'-dicarboxylate (**50**) (1.600 g, 3.35 mmol, 1 equiv) and sodium azide (0.458 g, 7.04 mmol, 2.1 equiv) were reacted in DMF (35 mL) for 18h according to **general procedure H** to give (**51**) (1.265 g, 99 %) as a yellow oil. ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 8.17 (d, 2H, *J* = 1.5 Hz, C*H*$_{Ar}$), 8.09 (dd, 2H, *J* = 8.0 Hz, *J* = 1.5 Hz, C*H*$_{Ar}$), 7.29 (d, 2H, *J* = 8.0 Hz, C*H*$_{Ar}$), 4.14 (AB system, 4H, Ar*CH*$_2$N$_3$), 3.97 (s, 6H, CO_2CH_3) ppm. ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 166.4 (CO_2CH_3), 143.4 (C^{IV}_{Ar}), 134.2 (C^{IV}_{Ar}), 130.9 (C^{IV}_{Ar}), 130.7 (*C*H$_{Ar}$), 130.1 (*C*H$_{Ar}$), 129.6 (*C*H$_{Ar}$), 52.6 (CO_2CH_3), 52.4 (CH_2N_3) ppm. IR (ATR): ν = 2951, 2093, 1717, 1675, 1606, 1434, 1344 cm^{-1}. MS (EI): *m/z* = 349 (10) [M$^+$-OCH$_3$], 310 (51) [M$^+$-N$_3$-N$_2$], 296 (100) [M$^+$-N$_3$-N$_3$]. HRMS (EI): *m/z* $C_{18}H_{17}N_6O_4$, calcd.: 381.1306, found: 381.1306.

2,2'-bis(azidomethyl)-[1,1'-biphenyl]-4,4'-dicarboxylic acid (**52**): Dimethyl 2,2'-bis(azidomethyl)-[1,1'-biphenyl]-4,4'-dicarboxylate (**51**) (1.275 g, 3.35 mmol, 1 equiv) and KOH (3.762 g, 67.04 mmol, 20 equiv) were reacted in a THF-water mixture (50 mL) for 48h according to **general procedure K** to give (**52**) (1.088 g, 92 %) as a white solid. ^{1}H-NMR (500 MHz, DMSO): δ = 13.23 (b-s, 2H, CO_2H), 8.13 (d, 2H, *J* = 1.5 Hz, C*H*$_{Ar}$), 8.00 (dd, 2H, *J* = 8.0 Hz, *J* = 1.5 Hz, C*H*$_{Ar}$), 7.37 (d, 2H, *J* = 8.0 Hz, C*H*$_{Ar}$), 4.27 (AB system, 4H, *J* = 14.0 Hz, C*H*$_2$N$_3$) ppm. ^{13}C-NMR (125 MHz, DMSO): δ = 166.8 (CO_2H), 142.9 (C^{IV}_{Ar}), 134.1 (C^{IV}_{Ar}), 131.0 (C^{IV}_{Ar}), 130.2 (*C*H$_{Ar}$), 130.1 (*C*H$_{Ar}$), 129.0 (*C*H$_{Ar}$), 51.4 (*C*H$_2$N$_3$) ppm. IR (ATR): ν = 2860, 2097, 1683, 1605, 1424, 1290, 1257 cm^{-1}. MS (FAB): *m/z* = 353 [MH$^+$], 282 [M$^+$-N$_3$-N$_2$], 268 [M$^+$-N$_3$-N$_3$]. HRMS (FAB): *m/z* $C_{16}H_{13}N_6O_4$, calcd.: 353.0998, found: 353.0994.

2,2'-bis(hydroxymethyl)-[1,1'-biphenyl]-4,4'-dicarboxylic acid (**54**): Dimethyl 2,2'-bis(bromomethyl)-[1,1'-biphenyl]-4,4'-dicarboxylate (**50**) (0.580 g, 1.27 mmol, 1 equiv) and AcOK (0.499 g, 5.09 mmol, 4 equiv) were reacted in DMF (5 mL) for 24h according to **general procedure I**. The residue and KOH (0.713 g, 12.72 mmol, 10 equiv) were reacted in a THF-water mixture (20 mL) for 48h according to **general procedure K** to give (**54**) (0.359 g, 93 %) as a white solid. ^{1}H-NMR (500 MHz, DMSO): δ = 12.99 (b-s, 2H, CO_2H), 8.19 (s, 2H, C*H*$_{Ar}$), 7.87 (d, 2H, *J* = 7.5 Hz, C*H*$_{Ar}$), 7.20 (d, 2H, *J* = 7.5 Hz, C*H*$_{Ar}$), 5.25 (b-t, 2H, *J* = 3.0 Hz, CH_2OH), 4.17 (qd, 4H, *J* = 9.0 Hz, *J* = 3.0 Hz, CH_2OH) ppm. ^{13}C-NMR (125 MHz, DMSO): δ = 167.3 (CO_2H), 141.7 (C^{IV}), 140.1 (C^{IV}), 130.2 (C^{IV}), 129.0 (*C*H$_{Ar}$), 128.0 (*C*H$_{Ar}$), 127.4 (*C*H$_{Ar}$), 60.3 (CH_2OH) ppm. IR (ATR): ν = 1679, 1605, 1582, 1404, 1254, 1197 cm^{-1}.

Dimethyl 2,2'-bis((prop-2-yn-1-yloxy)methyl)-[1,1'-biphenyl]-4,4'-dicarboxylate (**56**): 3-(Trimethylsilyl)propargyl alcohol (**55**) (0.559 g, 4.36 mmol, 2.6 equiv) in DMF (5 mL) was added to a suspension of sodium hydride (201 mg, 5.03 mmol, 3 equiv) in DMF (10 mL) at 0°C under argon, and the mixture was stirred at 0°C for 30 minutes. This mixture was added dropwise at 0°C to a solution of dimethyl 2,2'-bis(bromomethyl)-[1,1'-biphenyl]-4,4'-dicarboxylate (**50**) (0.765 g, 1.68 mmol, 1 equiv) in THF (30 mL) and the mixture was stirred at 0°C for 1h, then at room temperature for 24h. The reaction was filtered through a pad of celite, which was washed with dichloromethane. The filtrate was evaporated under reduced pressure and the crude product was purified by column chromatography (60 to 100 % dichloromethane in *n*-hexane) to give (**56**) (0.261 g, 38 %) as a colorless oil. ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 8.22 (d, 2H, *J* = 1.5 Hz, C*H*$_{Ar}$), 8.02 (dd, 1H, *J* = 8.0 Hz, *J* = 1.5 Hz, C*H*$_{Ar}$), 7.26 (d, 2H, *J* = 8.0 Hz, C*H*$_{Ar}$), 4.29 (AB system, 4H, Ar*CH*$_2$O), 4.02 (d, 4H, *J* = 2.5 Hz, O*CH*$_2$C≡CH), 3.95 (s, 6H, CO_2CH_3), 2.33 (t, 2H, *J* = 2.5 Hz, OCH$_2$C≡C*H*) ppm. ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 166.9 (CO_2CH_3), 143.8 (C^{IV}_{Ar}), 136.0 (C^{IV}_{Ar}), 130.3 (*C*H$_{Ar}$), 130.2 (C^{IV}_{Ar}), 129.7 (*C*H$_{Ar}$), 128.9 (*C*H$_{Ar}$), 79.3 (OCH$_2$C≡CH), 75.0 (OCH$_2$C≡CH), 69.1 (ArCH_2O), 57.9 (OCH$_2$C≡CH), 52.4 (CO_2CH_3) ppm. IR (ATR): ν = 1172 cm^{-1}. MS (FAB): *m/z* = 407 [MH$^+$], 375 [M$^+$-OCH$_3$], 351 [M$^+$-OCH$_2$C≡CH]. HRMS (FAB): *m/z* $C_{24}H_{23}O_6$, calcd.: 407.1495, found: 407.1491.

2,2'-bis((prop-2-yn-1-yloxy)methyl)-[1,1'-biphenyl]-4,4'-dicarboxylic acid (**57**): Dimethyl 2,2'-bis((prop-2-yn-1-yloxy)methyl)-[1,1'-biphenyl]-4,4'-dicarboxylate (**56**) (0.203 g, 0.50 mmol, 1 equiv) and KOH (0.841 g, 14.98 mmol, 30 equiv) were reacted in a THF-water mixture (20 mL) for 72h according to **general procedure K** to give (**57**) (0.185 g, 98 %) as a white solid. ^{1}H-NMR (500 MHz, DMSO): δ = 13.11 (b-s, 2H, CO_2H), 8.09 (d, 2H, *J* = 1.5 Hz, C*H*$_{Ar}$), 7.93 (dd, 2H, *J* = 8.0 Hz, *J* = 1.5 Hz, C*H*$_{Ar}$), 7.29 (d, 2H, *J* = 8.0 Hz, C*H*$_{Ar}$), 4.24 (AB system, 4H, Ar*CH*$_2$O), 4.06 (d, 4H, *J* = 2.0 Hz, O*CH*$_2$C≡CH), 3.36 (t, 2H, *J* = 2.0 Hz, OCH$_2$C≡C*H*) ppm. ^{13}C-NMR (125 MHz, DMSO): δ = 167.0 (CO_2H), 142.6 (C^{IV}_{Ar}-CO_2H), 135.9 (C^{IV}_{Ar}), 130.5 (C^{IV}_{Ar}), 129.6 (*C*H$_{Ar}$), 129.2 (*C*H$_{Ar}$), 128.3 (*C*H$_{Ar}$), 79.8 (OCH$_2$C≡CH), 77.5 (OCH$_2$C≡*C*H), 68.1 (ArCH_2O), 57.2 (O*CH*$_2$C≡CH) ppm. IR (ATR): ν = cm^{-1}. MS (EI): *m/z* = 378 (56) [M$^+$], 69 (100) [$CH_2OCH_2C{\equiv}CH$]. HRMS (EI): *m/z* $C_{22}H_{18}O_6$, calcd.: 378.1103, found: 378.1095.

Dimethyl 2',5'-bis(bromomethyl)-[1,1':4',1''-terphenyl]-4,4''-dicarboxylate (**58**): Dimethyl 2',5'-dimethyl-[1,1':4',1''-terphenyl]-4,4''-dicarboxylate (**11**) (0.600 g, 1.60 mmol, 1 equiv), NBS (0.627 g, 3.53 mmol, 2.2 equiv) and BPO (8 mg, 0.03 mmol, 0.02 equiv) were reacted in benzene (15 mL) for 24h according to **general procedure G**. The crude product was treated with methanol and filtrated, then washed with a small amount of methanol to give (**58**) (0.853 g, 98 %) as a white solid. ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 8.16 (d, 4H, *J* = 8.0 Hz, C*H*$_{Ar}$), 7.58 (d, 4H, *J* = 8.0 Hz, C*H*$_{Ar}$), 7.44 (s, 2H, C*H*$_{Ar}$), 4.42 (s, 4H, C*H*$_2$Br), 3.97 (s, 6H, CO_2CH_3) ppm. ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 166.9 (CO_2CH_3), 143.9 (C^{IV}_{Ar}), 141.4 (C^{IV}_{Ar}), 135.8 (C^{IV}_{Ar}), 133.0 (*C*H$_{Ar}$), 129.9 (*C*H$_{Ar}$), 129.8 (C^{IV}_{Ar}-CO_2Me), 129.2 (*C*H$_{Ar}$), 52.4 (CO_2CH_3), 30.9 (CH_2Br) ppm. IR (ATR): ν = 2985, 2947, 1710, 1609, 1490, 1413, 1276, 1191 cm^{-1}. MS (EI): *m/z* = 534 (28) – 532 (54) – 530 (28) [M$^+$], 501 (13) [M$^+$-OMe], 453 (99) – 451 (100) [M$^+$-Br]. HRMS (EI): *m/z* $C_{24}H_{20}Br_2O_4$, calcd.: 529.9728, found: 529.9727.

Dimethyl 2',5'-bis(azidomethyl)-[1,1':4',1''-terphenyl]-4,4''-dicarboxylate (**59**): Dimethyl 2',5'-bis(bromomethyl)-[1,1':4',1''-terphenyl]-4,4''-dicarboxylate (**58**) (0.375 g, 0.71 mmol, 1 equiv) and sodium azide (0.096 g, 1.48 mmol, 2.1 equiv) were reacted in DMF (15 mL) for 4h according to **general procedure H** to give (**59**) (0.321 g, 100 %) as a white solid. ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 8.15 (d, 4H, *J* = 8.5 Hz, C*H*$_{Ar}$), 7.49 (d, 4H, *J* = 8.5 Hz, C*H*$_{Ar}$), 7.43 (s, 2H, C*H*$_{Ar}$), 4.33 (s, 4H, C*H*$_2$N$_3$), 3.97 (s, 6H, CO_2CH_3) ppm. ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 166.9 (CO_2CH_3), 144.0 (C^{IV}_{Ar}), 141.2 (C^{IV}_{Ar}), 133.3 (C^{IV}_{Ar}), 131.6 (*C*H$_{Ar}$), 130.0 (*C*H$_{Ar}$), 129.9 (C^{IV}_{Ar}-CO_2Me), 129.4 (*C*H$_{Ar}$), 52.4 (CO_2CH_3), 52.3 (CH_2N_3) ppm. IR (ATR): ν = 2953, 2088, 1716, 1607, 1436, 1338, 1272, 1180 cm^{-1}. MS (EI): *m/z* = 456 (1) [M$^+$], 428 (63) [M$^+$-N$_2$]. HRMS (EI): *m/z* $C_{24}H_{20}N_6O_4$, calcd.: 456.1546, found: 456.1548.

2',5'-bis(azidomethyl)-[1,1':4',1''-terphenyl]-4,4''-dicarboxylic acid (**60**): Dimethyl 2',5'-bis(azidomethyl)-[1,1':4',1''-terphenyl]-4,4''-dicarboxylate (**59**) (0.913 g, 2.00 mmol, 1 equiv) and KOH (3.367 g,

60.01 mmol, 30 equiv) were reacted in a THF-water mixture (60 mL) for 24h according to **general procedure K** to give (**60**) (0.846 g, 99 %) as a white solid. ^{1}H-NMR (500 MHz, DMSO): δ = 13.09 (b-s, 2H, CO_2H), 8.06 (d, 4H, J = 8.0 Hz, CH_{Ar}), 7.57 (d, 4H, J = 8.0 Hz, CH_{Ar}), 7.55 (s, 2H, CH_{Ar}), 4.50 (s, 4H, ArCH_2N_3) ppm. ^{13}C-NMR (125 MHz, DMSO): δ = 167.1 (CO_2H), 143.4 (C^{IV}-CO_2H), 140.4 (C^{IV}), 133.2 (C^{IV}-CH_2N_3), 131.8 (CH$_{Ar}$), 130.1 (C^{IV}), 129.5 (CH$_{Ar}$), 129.2 (CH$_{Ar}$), 51.3 (ArCH_2N_3) ppm. IR (ATR): ν = 2874, 2092, 1682, 1607, 1417, 1279 cm^{-1}. MS (EI): *m/z* = 428 (45) [M$^+$], 368 (100) [M$^+$-H-OH-N$_3$]. HRMS (EI): *m/z* $C_{22}H_{16}N_6O_4$, calcd.: 428.1233, found: 428.1235.

2',5'-bis(hydroxymethyl)-[1,1':4',1''-terphenyl]-4,4''-dicarboxylic acid (**61**): Dimethyl 2',5'-bis(bromomethyl)-[1,1':4',1''-terphenyl]-4,4''-dicarboxylate (**58**) (0.300 g, 0.56 mmol, 1 equiv) and AcOK (0.221 g, 2.26 mmol, 4 equiv) were reacted in DMF (5 mL) for 24h according to **general procedure I**. The residue and KOH (0.316 g, 5.64 mmol, 10 equiv) were reacted in a THF-water mixture (16 mL) for 48h according to **general procedure K** to give (**61**) (0.208 g, 98 %) as a white solid. ^{1}H-NMR (500 MHz, DMSO): δ = 8.03 (d, 4H, J = 8.0 Hz, CH_{Ar}), 7.58 (d, 4H, J = 8.0 Hz, CH_{Ar}), 7.48 (s, 2H, CH_{Ar}), 4.45 (s, 4H, $CH_3CO_2CH_2$) ppm. ^{13}C-NMR (125 MHz, DMSO): δ = 167.2 (CO_2H), 144.6 (C^{IV}), 138.6 (C^{IV}), 138.0 (C^{IV}), 129.6 (C^{IV}), 129.5 (CH$_{Ar}$), 129.4 (CH$_{Ar}$), 129.3 (CH$_{Ar}$), 129.2 (CH$_{Ar}$), 60.5 (CH_2OH) ppm.

Dimethyl 2,2''-bis(bromomethyl)-[1,1':4',1''-terphenyl]-4,4''-dicarboxylate (**62**): Dimethyl 2,2''-dimethyl-[1,1':4',1''-terphenyl]-4,4''-dicarboxylate (**7**) (0.575 g, 1.54 mmol, 1 equiv), NBS (0.601 g, 3.38 mmol, 2.2 equiv) and BPO (7 mg, 0.031 mmol, 0.02 equiv) were reacted in benzene (15 mL) for 24h according to **general procedure G**. The crude product was treated with methanol and filtrated, then washed with a small amount of methanol to give (**62**) (0.767 g, 94 %) as a white solid. ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 8.25 (d, 2H, J = 1.5 Hz, CH_{Ar}), 8.04 (dd, 2H, J = 8.0 Hz, J = 1.5 Hz, CH_{Ar}), 7.58 (s, 4H, CH_{Ar}), 7.41 (d, 2H, J = 8.0 Hz, CH_{Ar}), 4.53 (s, 4H, ArCH_2Br), 3.97 (s, 6H, CO_2CH_3) ppm. ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 166.5 (CO_2CH_3), 145.9 (C^{IV}_{Ar}), 139.2 (C^{IV}_{Ar}), 135.9 (C^{IV}_{Ar}), 132.5 (CH$_{Ar}$), 130.9 (CH$_{Ar}$), 130.2 (C^{IV}_{Ar}), 129.7 (CH$_{Ar}$), 129.0 (CH$_{Ar}$), 52.5 (CO_2CH_3), 31.4 (CH_2Br) ppm. IR (ATR): ν = 2950, 1712, 1607, 1484, 1433, 1392, 1284, 1244 cm^{-1}. MS (EI): *m/z* = 534 (23) – 532 (54) – 530 (24) [M$^+$], 371 (100) [M$^+$-2Br]. HRMS (EI): *m/z* $C_{22}H_{22}O_4{}^{79}Br_2$, calcd.: 531.9879, found: 531.9877.

Dimethyl 2,2''-bis(azidomethyl)-[1,1':4',1''-terphenyl]-4,4''-dicarboxylate (**63**): Dimethyl 2,2''-bis(bromomethyl)-[1,1':4',1''-terphenyl]-4,4''-dicarboxylate (**62**) (0.590 g, 1.11 mmol, 1 equiv) and sodium azide (0.151 g, 2.33 mmol, 2.1 equiv) were reacted in DMF (20 mL) for 4h according to **general procedure H** to give (**63**) (0.505 g, 99 %) as a white solid. ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 8.16 (d, 2H, J = 1.5 Hz, CH_{Ar}), 8.09 (dd, 2H, J = 8.0 Hz, J = 1.5 Hz, CH_{Ar}), 7.46 (d, 2H, J = 8.0 Hz, CH_{Ar}), 7.45 (s, 4H, CH_{Ar}), 4.41 (s, 4H, ArCH_2N_3), 3.97 (s, 6H, CO_2CH_3) ppm. ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 166.6 (CO_2CH_3), 146.1 (C^{IV}_{Ar}), 139.2 (C^{IV}_{Ar}), 133.5 (C^{IV}_{Ar}), 131.1 (CH$_{Ar}$), 130.8 (CH$_{Ar}$), 130.0 (C^{IV}_{Ar}), 129.7 (CH$_{Ar}$), 129.2 (CH$_{Ar}$), 52.6 (CH_2N_3), 52.5 (CO_2CH_3) ppm. IR (ATR): ν = 2951, 2084, 1714, 1605, 1434, 1272, 1177 cm^{-1}. MS (FAB): *m/z* = 457 [MH$^+$], 456 [M$^+$-OCH$_3$], 310 [M$^+$-N$_3$-N$_2$], 296 [M$^+$-N$_3$-N$_3$]. HRMS (EI): *m/z* $C_{24}H_{21}N_6O_4$, calcd.: 457.1619, found: 457.1623.

2,2''-bis(azidomethyl)-[1,1':4',1''-terphenyl]-4,4''-dicarboxylic acid (**64**): Dimethyl 2,2''-bis(azidomethyl)-[1,1':4',1''-terphenyl]-4,4''-dicarboxylate (**63**) (0.457 g, 1.00 mmol, 1 equiv) and KOH (1.683 g, 30.00 mmol, 30 equiv) were reacted in a THF-water mixture (30 mL) for 72h according to **general procedure K** to give (**64**) (0.413 g, 96 %) as a white solid. ^{1}H-NMR (500 MHz, DMSO): δ = 13.17 (b-s, 2H, CO_2H), 8.13 (s, 2H, CH_{Ar}), 8.01 (d, 2H, J = 8.0 Hz, CH_{Ar}), 7.54 (s, 4H, CH_{Ar}), 7.52 (d, 2H, J = 8.0 Hz, CH_{Ar}), 4.56 (s, 4H, CH_2N_3) ppm. ^{13}C-NMR (125 MHz, DMSO): δ = 166.9 (CO_2H), 145.2 (C^{IV}), 138.6 (C^{IV}), 133.6 (C^{IV}), 130.7 (CH$_{Ar}$), 130.7 (CH$_{Ar}$), 130.3 (C^{IV}), 129.3 (CH$_{Ar}$), 129.0 (CH$_{Ar}$), 51.6 (CH_2N_3) ppm. IR (ATR): ν = 2924, 2095, 1685, 1602, 1419, 1278 cm^{-1}. MS (EI): *m/z* = 428 (45) [M$^+$]. HRMS (EI): *m/z* $C_{22}H_{16}N_6O_4$, calcd.: 428.1233, found: 428.1232.

2,2''-bis(hydroxymethyl)-[1,1':4',1''-terphenyl]-4,4''-dicarboxylic acid (**65**): Dimethyl 2,2''-bis(bromomethyl)-[1,1':4',1''-terphenyl]-4,4''-dicarboxylate (**62**) (0.230 g, 0.43 mmol, 1 equiv) and AcOK (0.255 g, 2.60 mmol, 4 equiv) were reacted in DMF (5 mL) for 24h according to **general procedure I**. The residue and KOH (0.242 g, 4.32 mmol, 10 equiv) were reacted in a THF-water mixture (16 mL) for 48h according to **general procedure K** to give (**65**) (0.125 g, 76 %) as a white solid. ^{1}H-NMR (500 MHz, DMSO): δ = 8.23 (s, 2H, CH_{Ar}), 7.91 (d, 2H, J = 7.5 Hz, CH_{Ar}), 7.51 (s, 4H, CH_{Ar}), 7.43 (d, 2H, J = 7.5 Hz, CH_{Ar}), 4.51 (s, 4H, CH_2OH) ppm. ^{13}C-NMR (125 MHz, DMSO): δ = 167.3 (CO_2H), 143.8 (C^{IV}), 139.9 (C^{IV}), 138.8 (C^{IV}), 130.0 (C^{IV}), 129.8 (CH$_{Ar}$), 129.1 (CH$_{Ar}$), 128.8 (CH$_{Ar}$), 127.8 (CH$_{Ar}$), 60.6 (CH_2OH) ppm.

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Conflict of interest

The authors declare no conflict of interest.

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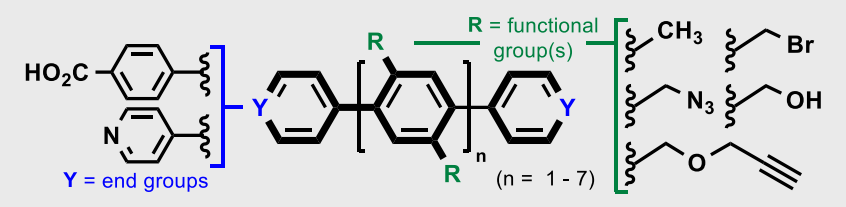
Modular Synthesis- Molecules for Functional Materials

FULL PAPER



Multi-functional, tunable molecular-bricks for functional materials: The Modular multi-step synthesis of diversely functionalized biphenyl, terphenyl and higher linear oligoarene dicarboxylic acids and pyridine-ended oligoarenes by palladium–catalyzed borylation / Suzuki–Miyaura cross-coupling reactions is described. The synthesized ditopic organic linkers constitute material of choice for the growth of different types of porous crystalline materials, including MOFs, SURMOFs, SURGELs and related structures. Once reticulated into the crystalline coordination networks, the functional groups (azide, alkyne) suitable for further Post-Synthetic Modification including azide–alkyne click-chemistry, which allow further tailoring of the properties to yield novel functional materials.

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Modular Synthesis of Diverse Multi-Functionalized Oligoarenes and Heteroarenes: Tailor to Desire – Molecules for Functional Materials