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1,3-Diethynylbicyclo[1.1.1]pentane, a Useful Molecular Building Block

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Dedicated to Professor Jaroslav Jonas on the occasion of his 75th birthday

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1,3-Diethynylbicyclo[1.1.1]pentane (DEBCP) has been found to be a valuable molecular building block mostly for the synthesis of extended, rigid, rod-like molecules. With its straightforward linear geometry, DEBCP can be used as a nonconjugated alternative to more frequently used π-conjugated, rod-like building blocks. Examples of reactions that introduce DEBCP into larger structures are (1) the reaction of DEBCP lithium acetylides with electrophiles such as TMSCl, CO_2, and Ph_2PCl, (2) Sonogashira–Hagihara cross-coupling reactions with aryl or heteroaryl iodides or bromides, and (3) umpolung reactions that afford the corresponding dibromo and diiodo derivatives of DEBCP, which then successfully react with *tert*-*C*-cuprates derived from *p*- and *m*-dicarbadodecaboranes or bicyclopentanes. These umpolung reactions afforded a new class of molecular rods that combine carborane or bicyclo[1.1.1]pentane cages with ethynylene linkers. Many of the DEBCP derivatives were studied by single-crystal X-ray diffraction. They form well-organized arrays of molecular rotors, the DEBCP units, and so can be considered as examples of artificial molecular-size machines.

Introduction

Various rigid, rod-like molecules are attracting increasing attention for a number of reasons, as addressed in the excellent review published by Schwab et al.[1] The most important of them are (1) the long-distance interaction phenomena such as electron and energy transfer and the magnetic coupling of transition-metal atoms, and (2) the molecular rods and connectors can be used for the construction of supramolecular assemblies and giant molecules for various purposes. Both of these factors play important roles in the design and preparation of functional devices on a molecular level, the straight rigid molecules being used as axles, wheel shafts, draw bars as well as conducting or insulating connecting rods. The rod-like molecules can also be useful in the construction of new functional materials by the so-called "bottom-up" approach in which one can take advantage of their defined geometry and stiffness in creating the void space in meso- and nanoporous materials. This is why there is a constant demand for new rigid, rod-like molecular building blocks that help to tailor the required properties of miscellaneous target substances. In addition to the entirely newly developed structures, there are some old ones, the synthetic potential and scope of which deserve further investigation. The 1,3-diethynylbicyclo[1.1.1]pentane (DEBCP, **1**) is an example. Since its preparation by Bunz and Szeimies,[2] who studied **1** as an interesting relay for π/σ conjugation,[3] it has attracted the attention of theoreticians.[4] However, it took a decade to find a significant synthetic application. Then Schwab et al. used DEBCP as a rod-like molecular building block for the preparation of extended trigonal and tetragonal connectors for a molecular construction set.[5] Only recently did we use DEBCP as a "line segment" in the construction of a molecular triangle.[6] We found this building block very interesting and decided to investigate its synthetic scope and limitations more thoroughly. We report our results herein.

Results and Discussion

The diyne **1** is relatively easily accessible from cheap pentaerythritol (**2**). Its synthesis follows the pathway shown in Scheme 1 and exploits already known procedures, the individual steps of which are well described in recent literature.[5–7] The crucial intermediates, the tetrahalide **3** and the diketone **4**, are stable enough to be stored in a refrigerator for a long time without change. (Note, both provided crystals suitable for X-ray diffraction.) Contrary to the originally used procedure,[7] we modified the first two steps of the synthesis, the preparation of the methallyl dichloride **5**,

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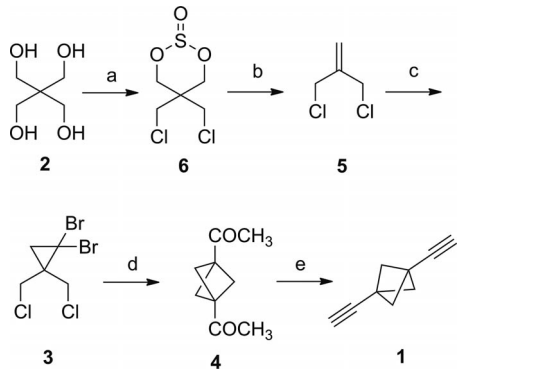
which is the precursor of **3**. Our approach combined the preparation of the cyclic sulfite **6**[8] with its vacuum flash pyrolysis,[9] thus avoiding a disagreeable oxidation with concentrated nitric acid, which can be a potential source of danger. The method suits preparations of **5** on the multigram scale, and so we were able to prepare a satisfactory amount of **1** in high purity. Fortunately, some of the concerns about the explosiveness of **1** conveyed by others did not come true[5] and we were able to sublime **1** and obtain a single crystal suitable for XRD analysis. Nevertheless, some caution in the handling of **1** is advisable as the diyne represents a kinetically stable, yet very strained molecule. In fact, the strain and resulting tendency of the bicyclopentane cage to rearrange were also the reasons why we decided to investigate carefully the scope and reactivity of **1**.

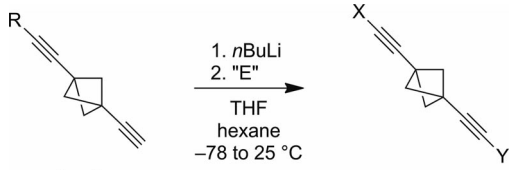


Scheme 1. Synthesis of the diyne **1** from pentaerythritol (**2**). Reagents and conditions: (a) $SOCl_2$, Py, 0–60 °C, 77%;[8] (b) 500 °C, 1 Torr, 65%;[9] (c) $HCBr_3$, KOH, 40 °C;[7] (d) (1) MeLi, diethyl ether, –40 to 0 °C, (2) biacetyl, *hv*, 0 °C;[7] (e) (1) hexachloroethane, PPh_3, 100 °C, (2) $NaNH_2$, liq. NH_3.[5,6]

Our reinvestigation of the reactivity of **1** first focused on simple modifications of the diyne termini in reactions of its lithium acetylides with electrophiles (Table 1). Recently, we have already performed one such reaction, silylation.[6] In addition to the disilylated derivative **7**, we were also able to prepare monosilylated **8**, which is of obvious synthetic importance (Table 1, Entry 1). Moreover, we have proven that **7** can be recycled to **1** in a deprotection reaction with aqueous ammonium fluoride in diethyl ether, if necessary. It increases the efficiency of the diyne exploitation remarkably. The less volatile disilyl derivative **7** can be stored (contrary to diyne **1**) in a refrigerator for months without any visible decomposition and then used as a convenient source of **1**.

Other electrophiles, carbon dioxide and chlorodiphenylphosphane, were chosen with a view to a possible coordination polymer investigation. A dilithium diacetylide of **1**, which was quantitatively formed by the addition of 2 equiv. of *n*BuLi (Table 1, Entries 2 and 3), afforded the dicarboxylic acid **9** and the bis(phosphane) **10**, respectively, in reasonable yields. When the monoprotected diyne **8** was used with 1 equiv. of *n*BuLi in similar reactions, the derivatives **11** and **12**, with different substituents at each terminus of the DEBCP unit, were prepared also in good yields (Table 1, Entries 4 and 5). For better purification and/or crystallization, the carboxylic acids **9** and **11** were methylated to their esters **13** and **14** by reaction with diazomethane to give excellent yields, 96 and 97%, respectively. The diester **13** then provided crystals suitable for XRD analysis.

Table 1. Reactions of lithium acetylides of **1** and **8** with electrophiles.

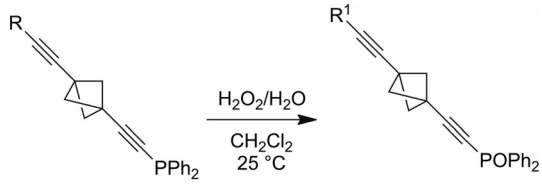


1 or **8** **7–12**

Entry	Starting compd. No.	R	Electrophile "E"	Product No.	X	Y	Yield [%][a]
1	**1**	H	TMSCl[b]	**7**	TMS	TMS	35
				8	H	TMS	45
2	**1**	H	CO_2	**9**	CO_2H	CO_2H	72[c]
3	**1**	H	PPh_2Cl	**10**	PPh_2	PPh_2	40
4	**8**	TMS	CO_2	**11**	TMS	CO_2H	78[d]
5	**8**	TMS	PPh_2Cl	**12**	TMS	PPh_2	63[e]

[a] Yields are given for the isolated and purified materials. [b] 1.25 equiv. of *n*BuLi and 1.5 equiv. of TMSCl were used in the reaction (see ref.[6]). [c] Reaction with an excess of ethereal diazomethane afforded the corresponding diester **13** (as **9**, X = Y = CO_2Me) in almost quantitative yield. [d] The product was isolated as the methyl ester **14** (as **11**, X = TMS, Y = CO_2Me) after reaction with an excess of diazomethane in diethyl ether. [e] Desilylation of **12** was carried out by reaction with TBAF in THF at 25 °C to yield 92% of **15**.

The phosphane **12** was desilylated by a standard procedure with TBAF in THF to yield phosphane **15**. The latter as well as the bis(phosphane) **10** were easily oxidized with 10% H_2O_2 to afford almost quantitative yields of the corresponding phosphane oxides **16** and **17** (Scheme 2). A two-phase reaction system (CH_2Cl_2/aqueous H_2O_2) in combination with a relatively short reaction time (ca. 40 min) prevented the formation of side-products and notably simplified the isolation of the desired compounds. These were obtained in high purity simply by evaporation of CH_2Cl_2 from the organic phase. The oxidation reaction modifies the coordination properties of the phosphanes, and the resulting phosphane oxides can be used to further extend the range of rod-like ligands for use in coordination polymers.



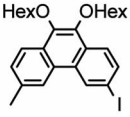
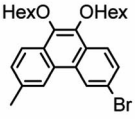
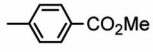
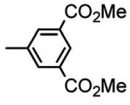
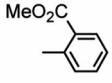
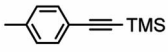
10: R = PPh_2
15: R = H
16: R^1 = $POPh_2$ 98 %
17: R^1 = H 98 %

Scheme 2. Oxidation of phosphanes to phosphane oxides.

The ability of the diyne **1** to undergo Sonogashira–Hagihara cross-coupling reactions has already been proven under standard[6] or copper-free[5] reaction conditions. Analogous reactivity has also been found in the case of its laterally substituted derivative.[10] In this study we synthesized a group of molecular rods **18**–**26**, mostly in high isolated yields (Table 2). The esters **23**–**25** are precursors of free acids with potential in the preparation of new metal–organic frameworks (MOFs).

Table 2. Sonogashira–Hagihara cross-coupling reactions of the diyne **1**.

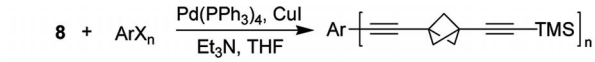
18 - 26

Entry	X[a]	Product	Ar	Yield [%][a]
1	I	**18**		86
2	I	**19**		88
3	I	**20**		74
4	I	**21**		41[b]
5	Br	**22**		41[b]
6	Br	**23**		68
7	Br	**24**		89
8	Br	**25**		65
9	Br	**26**		70

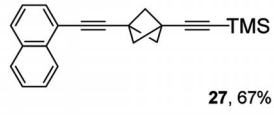
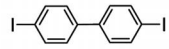
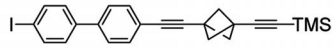
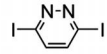
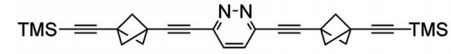
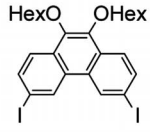
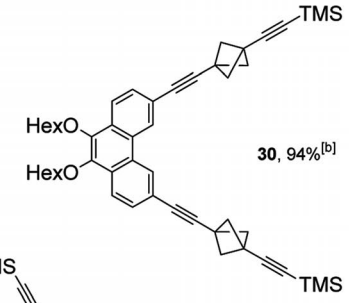
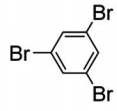
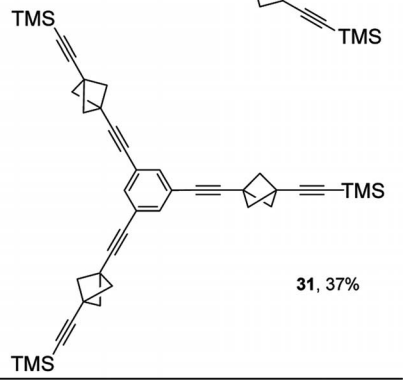
[a] Yields are given for isolated and purified material. [b] See ref.[6]

Sonogashira–Hagihara cross-coupling reactions of the monoprotected diyne **8** (Table 3) afforded acceptable yields of the rods **27** and **28**, which contain one DEBCP unit, the straight and V-shaped molecules **29** and **30** contain two DEBCP units, and the star-shaped molecule **31** has three DEBCP units in its structure. Desilylation of **27**–**31** can yield terminal alkyne derivatives that are useful molecular building blocks for the construction of larger covalent, "giant" molecules by suitable alkyne coupling reactions. Deprotection by a standard TBAF procedure was successfully demonstrated for compounds **12**, **27**, and **31**, which afforded good yields (92–95%) of the corresponding terminal alkynes. Only an obvious incompatibility of the ester group with the TBAF deprotection procedure reduced the yield of the terminal alkyne formed from the methyl ester **14** to 69%.

Table 3. Sonogashira cross-coupling reactions of the diyne **8**.



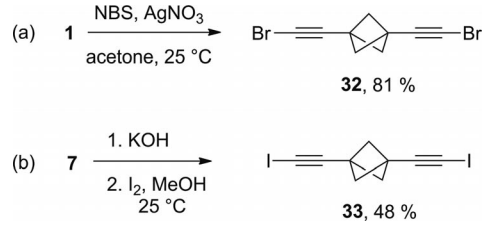
27 - 31

Entry	ArX_n	Product, yield[a]
1		 **27**, 67%
2		 **28**, 48%
3		 **29**, 65%
4		 **30**, 94%[b]
5		 **31**, 37%

[a] Yields are given for isolated and purified material. [b] See ref.[6]

The synthetic applicability of terminal alkynes can be extended by their umpolung to 1-haloalkynes.[11] It is well known from carborane chemistry that 1-bromoalkynes couple with *C*-cuprates derived from *p*-carboranes without any catalyst in high yields.[12] To prove the synthetic potential of **1** in similar reactions, we also tried its umpolung. The dibromodiyne **32** was prepared in high yield from **1** by using NBS in the presence of $AgNO_3$ in dry acetone[13] (Scheme 3a). The umpoled dibromodiyne **32** was found to be light-sensitive and highly reactive. The diiododiyne **33** was also synthesized. In this case, however, we started from the disilyl derivative **7** applying the procedure used probably for the first time by Jacobson and Carothers[14] and recently by others,[15] who treated the starting alkynes with potas-

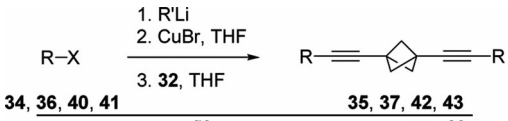
sium hydroxide and iodine in methanol. We used **7** in that procedure to accomplish the deprotection and subsequent iodination in a one-pot reaction (Scheme 3b). The intended advantage of such an approach, the use of cheap and heavy-metal-free reagents as well as **7** instead of the more volatile **1**, was, however, paid by the rather low yield of **33** (ca. 50%).



Scheme 3. Diyne umpolung: Synthesis of 1-haloalkynes **32** (a) and **33** (b).

The stability and reactivity of the dibromodiyne **32** under cross-coupling reaction conditions were tested in the reaction with a cuprate derived from 1-(trihexylsilyl)-1,12-dicarba-*closo*-dodecaborane (**34**; Table 4, Entry 1). An unoptimized coupling reaction gave a very encouraging 38% isolated yield of **35**. NMR analysis of the reaction mixture showed that the coupling reaction actually afforded more than 90% of **35**, but its unwillingness to crystallize together with further difficulties in separation, mostly due to the presence of two lipophilic trihexylsilyl groups, lowered the isolated amount of pure **35** to only 38%. These problems were eliminated in the next reaction, in which an excess of *m*-carborane **36** was used in place of **34**. No protecting groups were necessary, and the product **37** was isolated in 89% yield (Table 4, Entry 2). Together with the compounds prepared earlier,[16] **35** and **37** extend the family of molecular rods that combine carborane and bicyclopentane cages

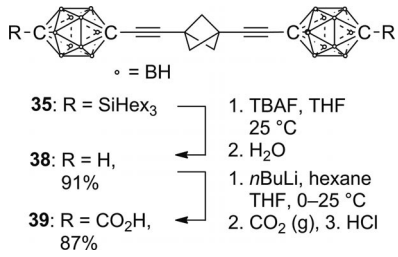
Table 4. Reactions of dibromodiyne **32** with cuprates.[a]



Entry	RX[b]	Product	Yield [%][c]
1	HC-C-SiHex$_3$ (**34**)	**35**	38
2	HC-CH (**36**)	**37**	89
3	I-CH$_2$Cl (**40**)	**42**	25
4	I-CH$_3$ (**41**)	**43**	12

[a] 1 equiv. of *n*BuLi in hexanes and 2 equiv. of *t*BuLi in pentane were used for lithiation of the carboranes and the iodo derivatives, respectively. [b] ◦ = BH. [c] Yields are given for isolated and purified material.

in their structures. The terminal carborane units offer opportunities for further modifications. As an example, the trihexylsilyl groups of **35** were removed by using TBAF in THF to yield **38**, and an even longer extended rod-like dicarboxylic acid **39** was prepared by lithiation and carboxylation (Scheme 4). It was interesting to compare the solubility of **39** with that of the dicarboxylic acid obtained by hydrolysis of the diester **23**, which has almost the same length. Although the latter, which has two *p*-phenylene groups in its structure, showed only negligible solubility, the two *p*-carborane units in molecule **39** led to a significant increase in solubility in common polar organic solvents.



Scheme 4. Preparation of the dicarboxylic acid **39**.

To the best of our knowledge, no successful C(sp^3)–C(sp) cross-coupling between the tertiary bridgehead carbon atom of a bicyclo[1.1.1]pentane cage and terminal alkynes has been published to date. The main reason for this is probably the insufficient reactivity of bicyclopentyl bridgehead halides in the crucial step of the coupling catalytic cycle, the oxidative addition of a transition-metal complex to a C–X bond at the bridgehead position due to the quite disadvantageous geometry of the reaction center, and the high strength of the C–X bond. It is therefore clear that for a successful coupling, an opposite arrangement, which would combine a suitable bridgehead organometal compound with a haloalkyne, could be more advantageous. Several unsuccessful attempts[17] indicated, however, that the choice of an appropriate metal at the bridgehead position would be of great importance. For example, the reaction of (3-butylbicyclo[1.1.1]pentyl)zinc chloride with 1-iodo-2-(trimethylsilyl)ethyne under [PdCl$_2$(dppf)] catalysis led only to an almost quantitative yield of a metal/halogen exchange product, the 1-butyl-3-iodobicyclo[1.1.1]pentane. Because the bicyclopentane bridgeheads have a geometry resembling that of the *closo*-carborane bridgehead carbon atoms, we were interested in whether the bicyclopentane bridgehead cuprates would be an appropriate choice for the cross-coupling reactions with haloalkynes such as **32** and **33**. Indeed, the reactions of the cuprates derived from 1-(chloromethyl)-6-iodotricyclo[3.2.0.0^{2,6}]heptane (**40**)[16,18] and 1-iodo-3-methylbicyclo[1.1.1]pentane (**41**)[17,19] with the dibromodiyne **32** were accomplished under the same reaction conditions as those used for the carboranes (Table 4, Entries 3 and 4). Even though the reactions gave rather low yields of **42** and **43**, it is the first time that molecular rods have been prepared that contain two bicyclopentane cages linked by an ethynylene bridge. The molecular structure of **42** was also confirmed by XRD analysis (Figure 1).

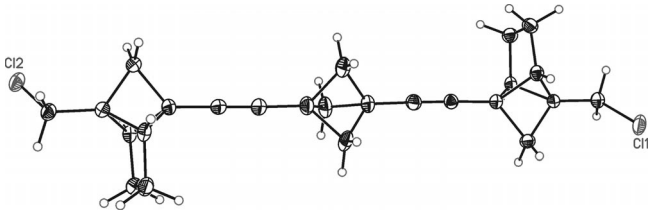


Figure 1. ORTEP representation of the molecular structure of the three-cage derivative **42**.

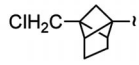
One of the common applications of terminal alkyne functionalities is in the formation of 1,2,3-triazole-1,4-diyl linkages by the Sharpless–Huisgen click reaction,[20] the 1,3-dipolar cycloaddition with organic azides. Clearly, we were interested in whether the alkyne **1** could take part in such click chemistry. However, our attempts to accomplish a model cycloaddition reaction of **1** with benzyl azide failed with or without a Cu catalyst. A poorly soluble white polymer was obtained instead, probably as a result of bicyclopentane cage opening, because no signals specific to the protons of the cage were detected by ^{1}H NMR analysis of the crude products. It has been proven several times that whenever in the course of a reaction a reactive site, such as an anion, cation, radical, or carbene, emerges at the atom next to the strained bicyclopentane cage, the cage tends to rearrange.[21] This might also be the reason for the rearrangement in this particular case.[22] Further investigations of cycloaddition reactions in the close proximity of the bicyclopentane cage should respect this fact in general and prospective reaction partners need to be carefully chosen to avoid the problem. We continue our investigations in this area.

Crystal Structure Analyses

The structures of many of the compounds presented in this paper were also determined by X-ray structure analysis. The corresponding CIF files have been deposited with the CCDC, and images of anisotropically refined structures can be found in the Supporting Information. Selected interatomic distances of the rod-like derivatives are presented in Table 5. Measurements of the DEBCP core, such as the intercage bridgehead-to-bridgehead distance (*ICD*), the length of the bridgehead exocyclic C–C bonds (D_{ex}), and the triple bond ($D_{C\equiv C}$), which may play an important role in the propagation of various long-range interactions through the DEBCP building block, are reported along with the "rod length" *D*, which is given as the distance of the two most distant non-hydrogen atoms located along the longitudinal axis of the molecule.

An interesting analogy was found between the crystal-packing characteristics of the diyne **1** and its bromo and iodo analogues **32** and **33**. The C–H···π interaction observed in crystals of **1** directs a "zig-zag" arrangement of the molecules. Similar "zig-zag" motifs were found in the haloalkynes **32** and **33**. These were directed, however, by C–Br···π and C–I···π intermolecular interactions, respectively.

Table 5. Selected interatomic distances [Å] in terminally substituted DEBCPs.

Compd.	R	*D*	*ICD*	D_{ex}	$D_{C\equiv C}$
1	H	7.133(2)	1.880(2)	1.448(2)	1.178(2)
7	TMS	10.922(6)	1.885(3)	1.459(3)	1.208(3)
10	PPh_2	10.7033(8)	1.885(2)	1.447(3)	1.200(3)
13	CO_2CH_3	10.065(3)	1.876(3)	1.448(3)	1.197(3)
16	$POPh_2$	10.6536(7)	1.873(4)	1.446(4)	1.191(4)
18	Ph	15.564(2)	1.882(2)	1.450(2)	1.194(2)
32	Br	10.62(1)	1.865(9)	1.418(9)	1.182(9)
33	I	11.180(3)	1.906(5)	1.447(6)	1.182(6)
38[a]		16.182(6) 16.202(6)	1.874(3) 1.884(3)	1.438(3) 1.453(3)	1.192(3) 1.192(3)
42		19.73(1)	1.880(3)	1.442(3)	1.185(3)

[a] The upper value is for the molecule involved in a C–H···π interaction.

The molecules of all three compounds are arranged in parquet-like ordered layers (Figure 2), but the mutual orientation of the parquet-like patterns in the neighboring layers is different. Although the "parquets" in the neighboring layers of **1** are more or less collinear, the ones in **32** and **33** are crossed. Because the C–H···π distance in **1** is much shorter than that of C–X···π, the molecules of **1** in the parquet layers are more tightly packed and thus leave less space for the lateral accommodation of the bulky bicyclopentane cages of the neighboring layers. They then favor the parallel arrangement. The longer C–X···π distance together with the bulkiness of the halogen atoms leave more space for the bicyclopentane cages. The crossed orientation then suits a close-packing of the neighboring layers much better.

In addition to the crystals of **1**, the packing forces in the crystals of two other compounds, the phosphorus derivatives **10** and **17**, bring their C≡C triple bonds into close contact with C–H bonds, which suggests weak C–H···π interactions. The hydrogen atoms in the phenyl rings of the phosphane or phosphane oxide moieties of these compounds, respectively, are involved. Particularly in the case of the phosphane oxide **17**, the packing is much closer due to additional C–H···O=P interactions and results in a C(sp)···H–C distance significantly shorter than the corresponding sum of the van der Waals radii of the atoms involved (Figure 3).

A different example of a C–H···π interaction was found in the crystals of *p*-carborane derivative **38**, which was successfully crystallized from toluene. The tabular crystals were stable in solution but collapsed upon drying or even after a few hours of standing at ambient temperature. Clearly, the solvent molecules are incorporated into the crystal lattice. Indeed, the bulky rods of **38** are arranged in columns surrounded by molecules of toluene. Some of the molecules of **38** are involved in the C–H···π interactions of their carborane C–H bonds with toluene molecules, which are located

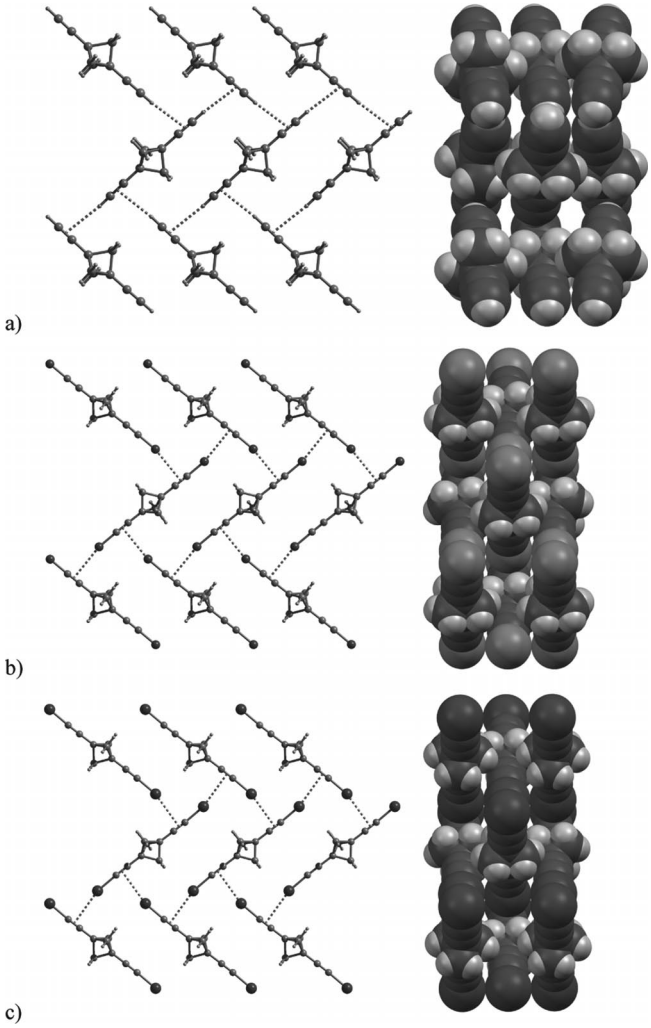


Figure 2. Comparison of the molecular packing in crystals of (a) the diyne **1** and (b) its bromo and (c) iodo analogues **32** and **33**, respectively. An arrangement of molecules in one layer is shown for each compound. The C–H···π and C–X···π interactions are shown as dashed lines (the H···C≡C, Br···C≡C, and I···C≡C distances are 2.710, 3.201, and 3.337 Å, respectively, measured to the center of the triple bond), the in-layer halogen···halogen contacts are slightly larger than the sum of the van der Waals radii (Br···Br and I···I distances are 3.953(4) and 4.096(1) Å, respectively). Space-filling models show different orientations of the parquet-like layers in **1** and its halo analogues **32** and **33**.

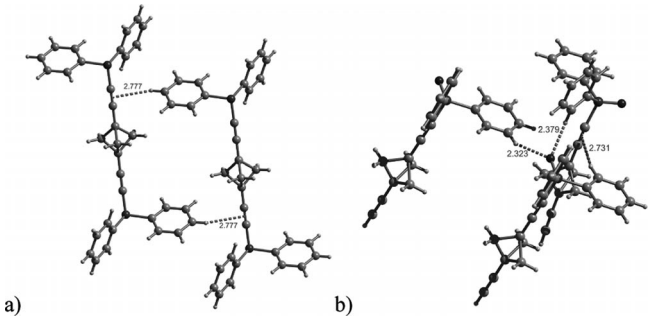


Figure 3. Crystal structures of (a) diphosphane **10** and (b) phosphane oxide **17**. The C–H···π distances depicted as dotted lines are 2.777(1) and 2.731(2) Å in **10** and **17**, respectively. The C–H···O=P distances drawn as dotted lines in the structure of **17** are 2.322(2) and 2.379(2) Å.

towards the ends of each of them and oriented almost perpendicular to their longitudinal axis at a distance of 2.356 Å, measured to the center of the toluene ring (Figure 4). Such a C–H···π interaction corresponds to the previously published examples found in crystals of *o*-carborane derivatives.[23] Interestingly, the packing forces slightly reduce the lengths of the rods in the interactions compared with the others (Table 5).

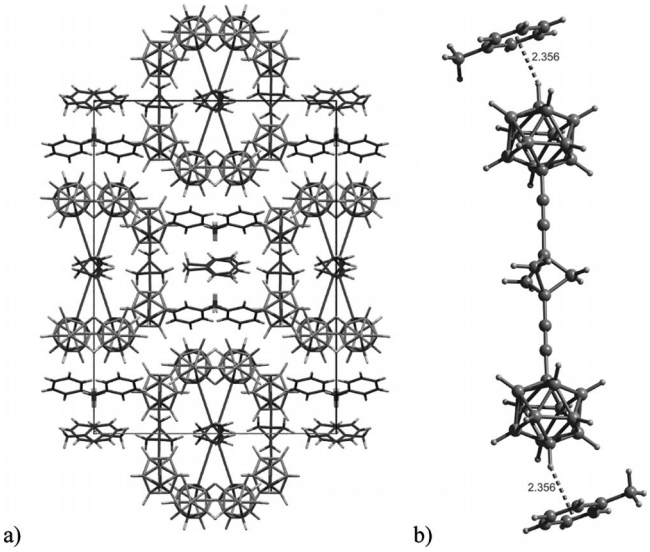


Figure 4. (a) Columnar organizations of the rod-like molecules in crystals of **38**. (b) C–H···π interactions between **38** and two molecules of toluene. The C–H···π distances, measured to the center of the phenyl ring and drawn as dotted lines, are 2.356(3) Å.

Well-organized arrays of molecular rotors are nowadays of great interest in materials science and nanotechnology research as well as being studied as examples of artificial molecular-sized machines.[24] From this point of view, the crystal structures of the DEBCP derivatives represent an interesting set of compounds in which one rotor, the bicyclo[1.1.1]pentane cage, is located in various kinds of crystal lattice environments. They differ not only in shape and immediate environment of the rotors, but also in the mutual orientation of their rotational axes in the crystal lattice, both given by the corresponding molecular crystal-packing patterns. It has already been shown that the parent diyne **1** and its halo analogues **32** and **33** prefer zig-zag arrangements of their molecules in their crystal lattices, although with different orientations of the parquet-ordered layers. Similarly, zig-zag motifs with cross-like oriented rotational axes of the bicyclopentane rotors were found in crystals of the diester **13** and the diphenyl derivative **18** (Figure 5a,b). In contrast, a more or less collinear, parallel orientation of the rotors was found in crystals of the diketone **4**, the disilyl derivative **7**, the bis(phosphane) **10**, the phosphane oxide **17**, and the "three-cage derivative" **42** (Figure 5c–g). In addition, "multidirectional" arrangements were found in crystals of the *p*-carborane derivative **38** (Figure 4) and diphosphane dioxide **16** (Figure 5h).

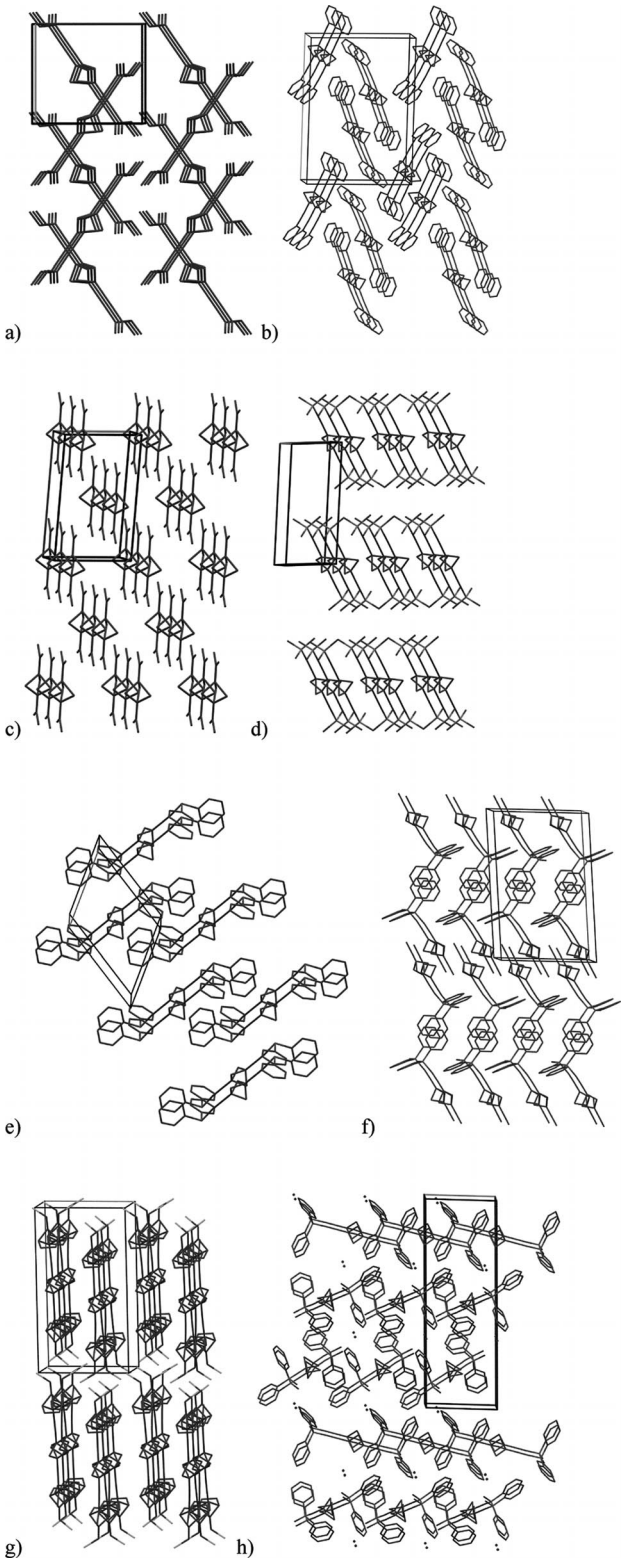


Figure 5. Molecular packing in crystals of the derivatives prepared. (a), (b) Cross-like orientation of the rotational axes of the BCP rotors in crystal lattices of the diester **13** and the diphenyl derivative **18**, respectively. (c)–(g) Parallel orientation of rotational axes of the rotors in molecules of (c) diketone **4**, (d) disilyl derivative **7**, (e) bis(phosphane) **10**, (f) phosphane oxide **17**, and (g) the three-cage derivative **42**. (h) In the diphosphane dioxide **16**, the rotational axes are oriented in three different directions. Hydrogen atoms have been omitted for clarity.

Conclusions

The linear DEBCP molecular rods can be considered as nonconjugated alternatives to more frequently used π-conjugated, rod-like molecular building blocks. Their acetylene termini are readily lithiated and react with electrophiles, such as TMSCl, CO_2, and Ph_2PCl, to afford rigid rod-like extended ligands. In addition to the simultaneous functionalization of both termini, the reaction of only one terminus or successive reactions of both termini with different reagents were possible when trimethylsilyl-protected DEBCP **8** was used. Sonogashira–Hagihara coupling reactions of DEBCP (**1**) with aryl or heteroaryl iodides or bromides afforded new extended molecules of rod-like or star-shape geometry. DEBCP (**1**) was successfully umpoled to its 1-iodo- and 1-bromoalkyne derivatives. Reactions of the latter with *tert*-*C*-cuprates, such as those derived from *p*- and *m*-dicarbadodecaboranes or bicyclopentanes, afforded a new class of molecular rods that combine carborane or bicyclo[1.1.1]pentane cages with ethynylene bridges.

As a part of the synthetic procedures presented herein, we have developed a simple method for the recovery of the parent DEBCP (**1**) from its bis(trimethylsilyl) derivative **7**, which remarkably increased the effectiveness of the preparation of monosilylated diyne **8**, in which **7** was formed as the main byproduct.

Crystals of some of the DEBCP derivatives were prepared and studied by single-crystal X-ray diffraction. In addition to multidirectional arrangements, parallel or zig-zag ordering of the DEBCP units was observed in the crystal lattices. The different molecular arrangements, the participation of molecules, particularly of their possibly rotating parts, in various crystal-packing interactions, and the effects of these interactions on the degree of rotational freedom of the DEBCP structural unit, as an example of a rigid molecular-size rotor, are our current interest.

Experimental Section

General: All reactions were carried out under argon with dry solvents, freshly distilled under anhydrous conditions unless otherwise noted. Standard Schlenk and vacuum techniques were used for all manipulations of air- or moisture-sensitive compounds. Yields refer to isolated chromatographically and spectroscopically homogeneous materials unless otherwise stated. [1.1.1]Propellane,[7] 1,3-diethynylbicyclo[1.1.1]pentane (**1**),[3,5] 1,3-bis(trimethylsilylethynyl)bicyclo[1.1.1]pentane (**7**),[6] [(3-ethynylbicyclo[1.1.1]pentyl)ethynyl]trimethylsilane (**8**),[6] 1-iodo-3-methylbicyclo[1.1.1]pentane (**41**),[17] 1-(chloromethyl)-6-iodotricyclo[3.2.0.$0^{2,6}$]heptane (**40**),[16,18] and an ethereal solution of diazomethane[25] were prepared according to previously published procedures. 1,12-Dicarba-*closo*-dodecaborane, 1,7-dicarba-*closo*-dodecaborane (**36**), CuBr, CuI, 1,4-diiodobenzene, 4,4′-diiodobiphenyl, 3,6-diiodopyridazine, chlorodiphenylphosphane, chlorotrihexylsilane, iodobenzene, iodomethane, 1-iodonaphthalene, methyl 4-bromobenzoate, methyl 2-bromobenzoate, [(4-bromophenyl)ethynyl]trimethylsilane, dimethyl 5-bromoisophthalate, $[Pd(PPh_3)_4]$, TBAF in THF, and 1,3,5-tribromobenzene were purchased and used without further purification. Triethylamine was distilled from CaH_2 under argon immediately prior to use. Acetone was dried with $CaCl_2$ and distilled from P_4O_{10} prior

to use. NBS was recrystallized from water and dried under vacuum prior to use. ^{1}H, ^{13}C, ^{11}B, and ^{31}P NMR spectra were acquired at 25 °C with 300, 400, and 500 MHz spectrometers. ^{1}H and ^{13}C NMR spectra are referenced to residual solvent peaks. GC–MS was performed with an instrument equipped with a fused silica capillary column (cross-linked 5% phenyl methyl silicone). Diffraction data were collected with a KUMA KM-4 κ-axis CCD diffractometer with Mo-K_α radiation (λ = 0.71073 Å). The structures were solved by direct methods and refined by standard methods using SHELXTL.[26] CCDC-871802 (for **1**), -871803 (for **3**), -871804 (for **4**), -871805 (for **7**), -871806 (for **10**), -871807 (for **13**), -871808 (for **16**), -871809 (for **17**), -871810 (for **18**), -871811 (for **32**), -871812 (for **33**), -871813 (for **38**), -871814 (for **41**), and -871815 (for **42**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

1,3-Diethynylbicyclo[1.1.1]pentane (1):[2,5,6] A solution of ammonium fluoride (900 mg, 24.3 mmol) in water (10 mL) was added to a solution of the disilyl derivative **7** (520 mg, 2 mmol) in diethyl ether (7 mL), and the resulting mixture was stirred at room temperature for 2 h. The ethereal layer was then separated and the aqueous layer extracted with diethyl ether (3 × 10 mL). The combined organic layers were dried with Na_2SO_4, filtered, and carefully concentrated at atmospheric pressure and 50 °C. The residue was sublimed by Kugelrohr distillation (50 °C, 400 Torr) into a flask cooled with liquid nitrogen. The diyne **1** was obtained as long white needles (212 mg, 91%). M.p. 63–65 °C (ref.[2] 65–67 °C).

3,3′-(Bicyclo[1.1.1]pentane-1,3-diyl)diprop-2-ynoic Acid (9): A solution of *n*BuLi in hexane (2.5 M, 4.00 mL, 10.000 mmol) was added dropwise to a stirred solution of freshly sublimed diyne **1** (550 mg, 4.735 mmol) in THF (25 mL) at –78 °C. A white dense precipitate formed immediately. The suspension was stirred at –78 °C for 40 min, heated to room temperature, and then cooled back to –78 °C. Gaseous CO_2 was bubbled into the solution through a PTFE cannula at –78 °C for 20 min and at room temperature for 15 min. The white suspension was dissolved in 30% aqueous $NaHCO_3$ (50 mL) and the basic water phase was washed with diethyl ether (3 × 50 mL). The colorless water phase was then acidified with concentrated aqueous HCl (pH ≈ 1). The product was salted out with NaCl, extracted with diethyl ether (4 × 50 mL), and the combined organic phases were dried with Na_2SO_4. Solvents were removed under reduced pressure, and the remaining impurities were washed out from the resulting yellowish solid on a frit with ice-cold $CHCl_3$ (30 mL) and pentane (20 mL). Diacid **9** was isolated as a snow-white crystalline solid (700 mg, 72%). M.p. 243 °C (dec.). ^{1}H NMR (300 MHz, [D$_6$]acetone): δ = 2.51 (s, 6 H, CH_2), 10.75 (br. s, 2 H, OH) ppm. ^{13}C NMR (75 MHz, [D$_6$]acetone): δ = 30.6, 59.9, 74.1, 85.8, 154.9 ppm. IR (KBr): $\tilde{\nu}$ = 3065, 3004, 2977, 2925, 2886, 2606, 2518, 2238, 1676, 1509, 1408, 1283, 1223, 1131, 914, 859, 755, 657, 602 cm^{-1}. MS: *m*/*z* (%) = 203 (<1) $[M]^+$, 159 (5) $[M - COOH]^+$, 143 (6), 131 (13), 116 (10), 115 (100), 113 (6), 103 (27), 102 (10), 90 (8), 89 (21), 78 (17), 77 (25), 74 (6), 66 (6), 65 (15), 63 (27), 62 (13), 51 (39), 50 (33), 49 (8), 45 (10), 44 (62). HRMS (ESI): calcd. for $[C_{11}H_7O_4]^-$ 203.0350; found 203.0350.

***P*,*P*′-(Bicyclo[1.1.1]pentane-1,3-diyldiethynediyl)bis(diphenylphosphane) (10):** Freshly distilled diyne **1** (500 mg, 4.304 mmol) was dissolved in THF (25 mL), and the colorless solution was cooled to –78 °C. Subsequently, a solution of *n*BuLi in hexane (2.5 M, 4.00 mL, 10.0 mmol) was added, and a dense white precipitate formed. The suspension was stirred at –78 °C for 40 min, at room temperature for 10 min, and then cooled back to –78 °C. Ph_2PCl (1.97 mL, 11.0 mmol) was then added, and the reaction mixture turned yellow immediately. Cooling was interrupted after 40 min, and the yellow reaction mixture was stirred at room temperature for 10 h. A white precipitate slowly dissolved during this time leaving a clear yellow solution. The reaction mixture was diluted with diethyl ether (80 mL), washed with concentrated aqueous NH_4Cl (2 × 40 mL) and water (1 × 30 mL), and the yellow organic phase was dried with Na_2SO_4. Volatiles were removed under reduced pressure to leave a yellow oil. Column chromatography on silica gel (hexane/CH_2Cl_2, 2:1) yielded **10** as a white crystalline solid (824 mg, 40%). M.p. 128.9–132.4 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.52 (s, 6 H, CH_2), 7.38–7.40 (m, 12 H, Ar-H), 7.62–7.67 (m, 8 H, Ar-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 31.0, 59.2, 76.6, 107.3 (*J* = 2.61 Hz), 128.5 (*J* = 7.56 Hz), 129.0, 132.5 (*J* = 21.00 Hz), 136.1 (*J* = 6.38 Hz) ppm. ^{31}P NMR (121 MHz, $CDCl_3$): δ = –31.77 ppm. IR (KBr): $\tilde{\nu}$ = 3049, 2988, 2963, 2914, 2874, 2166, 1584, 1478, 1433, 1237, 1096, 1070, 1026, 998, 745, 695 cm^{-1}. MS: *m*/*z* (%) = 485 (45) $[M]^+$, 484 (39) $[M]^+$, 409 (27), 407 (100) $[M - Ph]^+$, 377 (30), 375 (86), 300 (13), 299 (65) $[M - PPh_2]^+$, 297 (10), 283 (13), 265 (18), 252 (11), 233 (10), 221 (22), 220 (21), 207 (12), 189 (8), 183 (50) $[PPh_2]^+$, 178 (10), 170 (8), 165 (18), 152 (11), 133 (12), 115 (19), 109 (20), 108 (47), 107 (69), 91 (21), 77 (58) $[Ph]^+$, 65 (12), 57 (12), 51 (41). HRMS (APCI): calcd. for $[C_{33}H_{26}P_2 + H]^+$ 485.1583; found 485.1574.

({3-[(Trimethylsilyl)ethynyl]bicyclo[1.1.1]pentyl}ethynyl)diphenylphosphane (12): A solution of *n*BuLi in hexane (2.5 M, 720 μL, 1.8 mmol) was added dropwise to a solution of silane **8** (310 mg, 1.6 mmol) in THF (12 mL) at –78 °C. The colorless reaction mixture was stirred at this temperature for 30 min, then at 0 °C for 10 min, and finally cooled back to –78 °C. Subsequently, Ph_2PCl (359 μL, 2.0 mmol) was added to the reaction mixture, which turned yellow immediately. Cooling was interrupted after 1 h, and the yellow reaction mixture was stirred at room temperature for an additional 10 h. The solution was diluted with diethyl ether (40 mL) and washed with concentrated aq. NH_4Cl (2 × 20 mL) and water (1 × 20 mL). The yellow organic phase was dried with Na_2SO_4. The solvents were removed under reduced pressure, and column chromatography on silica gel (hexane/CH_2Cl_2, 2:1) yielded **12** as white crystals (388 mg, 63%). M.p. 141.1–143.2 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.22 (s, 9 H, CH_3), 2.44 (s, 6 H, CH_2), 7.32–7.42 (m, 6 H, Ar-H), 7.59–7.65 (m, 4 H, Ar-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 0.02, 30.7, 59.1, 76.3 (*J* = 7.32 Hz), 84.8, 104.4, 107.5 (*J* = 2.72 Hz), 128.5 (*J* = 7.60 Hz), 128.9, 132.5 (*J* = 21.01 Hz), 136.1 (*J* = 6.48 Hz) ppm. ^{31}P NMR (121 MHz, $CDCl_3$): δ = –31.73 ppm. IR (KBr): $\tilde{\nu}$ = 3063, 2989, 2962, 2913, 2877, 2167, 1477, 1434, 1247, 1115, 847, 763, 744, 721, 695 cm^{-1}. GC–MS: *m*/*z* (%) = 371 (23) $[M]^+$, 357 (7) $[M - CH_3]^+$, 343 (1), 299 (18), 283 (5), 265 (8), 247 (4), 233 (7), 221 (22), 191 (4), 183 (15), 165 (5), 135 (30), 107 (13), 97 (6), 73 (100) $[TMS]^+$, 59 (14), 45 (8). HRMS (APCI): calcd. for $[C_{24}H_{25}PSi + H]^+$ 373.1536; found 373.1530.

[(3-Ethynylbicyclo[1.1.1]pentyl)ethynyl]diphenylphosphane (15): A solution of TBAF in THF (1.0 M, 1.00 mL, 1.0 mmol) was slowly added to a solution of silyl–phosphane **12** (240 mg, 0.6 mmol) in THF (5 mL) at room temperature, and the reddish reaction mixture was stirred for 50 min, then diluted with diethyl ether (50 mL), washed with water (3 × 20 mL), and dried with Na_2SO_4. Solvents were removed under reduced pressure, and the resulting reddish oil was purified by column chromatography on silica gel (hexane/CH_2Cl_2, 2:1) to yield the pure product **15** as a white crystalline solid (178 mg, 92%). M.p. 94.1–95.8 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.14 (s, 1 H, ≡CH), 2.45 (s, 6 H, CH_2), 7.34–7.42 (m, 6 H, Ar-H), 7.59–7.66 (m, 4 H, Ar-H) ppm. ^{13}C NMR (75 MHz,

$CDCl_3$): δ = 29.9, 30.8, 58.8, 68.4, 76.4 (*J* = 7.34 Hz), 82.3, 107.1 (*J* = 2.98 Hz), 128.5 (*J* = 7.65 Hz), 128.9, 132.4 (*J* = 21.00 Hz), 136.0 (*J* = 6.29 Hz) ppm. ^{31}P NMR (121 MHz, $CDCl_3$): δ = –31.83 ppm. IR (KBr): ṽ = 3275, 3056, 2991, 2967, 2913, 2877, 2156, 1476, 1432, 1311, 1291, 1234, 1087, 1023, 913, 740, 693, 653 cm^{-1}. GC–MS: *m*/*z* (%) = 299 (17) $[M]^+$, 283 (9), 265 (8), 252 (12), 233 (5), 221 (18), 207 (13), 191 (100), 178 (34), 165 (21), 133 (8), 107 (28), 91 (11), 77 (14) $[Ph]^+$, 65 (6), 51 (13). HRMS (APCI): calcd. for $[C_{21}H_{17}P + H]^+$ 301.1141; found 301.1141.

Dimethyl 3,3′-(Bicyclo[1.1.1]pentane-1,3-diyl)diprop-2-ynoate (13): An ethereal solution of CH_2N_2 was added dropwise to a solution of diacid **9** (41 mg, 0.2 mmol) in diethyl ether (4 mL) at room temperature until the reaction mixture turned yellow. The solution was stirred for 10 min, and then the volatiles were removed under reduced pressure. Column chromatography on silica gel (hexane/ethyl acetate, 2:1) yielded **13** as white crystals (45 mg, 96%). M.p. 165.3–166.9 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.44 (s, 6 H, CH_2), 3.74 (s, 6 H, OCH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 29.8, 52.7, 58.4, 71.9, 84.9, 153.6 ppm. IR (KBr): ṽ = 3008, 2963, 2922, 2886, 2235, 1710, 1436, 1283, 1218, 1121, 967, 855, 753 cm^{-1}. GC–MS: *m*/*z* (%) = 232 (69) $[M]^+$, 217 (100) $[M – CH_3]^+$, 201 (41) $[M – 2CH_3]^+$, 189 (22), 173 (67) $[M – CO_2CH_3]^+$, 157 (28) $[M – CO_2CH_3 + CH_3]^+$, 145 (73), 129 (24), 117 (15), 115 (94), 102 (42), 88 (37), 75 (18), 63 (43), 59 (40), 43 (21). HRMS (EI): calcd. for $[C_{13}H_{11}O_4]^+$ 231.0657; found 231.0659.

Methyl 3-{3-[(Trimethylsilyl)ethynyl]bicyclo[1.1.1]pentyl}prop-2-ynoate (14): A flame-dried Schlenk flask was charged with a solution of monosilylated diyne **8** (411 mg, 2.2 mmol) in dry THF (15 mL), and *n*BuLi (2.5 M, 920 μL, 2.3 mmol) was added at –78 °C. The colorless solution was stirred at –78 °C for 60 min, then heated to 0 °C and cooled back to –78 °C. Gaseous CO_2 was bubbled into the solution through a PTFE cannula at –78 °C for 15 min and at room temperature for an additional 15 min. A white solid precipitated during this time. The reaction mixture was diluted with water (30 mL) and washed with $CHCl_3$ (2 × 20 mL). The water phase was acidified with concentrated HCl (pH ≈ 1), and the product was salted out with NaCl and extracted with diethyl ether (4 × 20 mL). The combined ethereal phases were dried with Na_2SO_4. Evaporation of the solvents under reduced pressure provided crude **11** as a white solid (475 mg), which was dissolved in diethyl ether (10 mL). An ethereal solution of diazomethane was then added at room temperature, and the yellow solution was stirred for an additional 10 min. The volatiles were removed under reduced pressure. Column chromatography on silica gel (hexane/$CHCl_3$, 1:1) afforded the product **14** as white needles (421 mg, 78%). M.p. 90.3–91.9 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.13 (s, 9 H, CH_3), 2.37 (s, 6 H, CH_2), 3.74 (s, 3 H, OCH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = –0.2, 28.9, 31.1, 52.5, 58.6, 71.5, 85.1, 85.8, 103.5, 153.5 ppm. IR (KBr): ṽ = 2995, 2960, 2916, 2881, 2229, 2162, 1712, 1437, 1336, 1259, 1213, 1115, 980, 849, 758, 719 cm^{-1}. GC–MS: *m*/*z* (%) = 245 (2) $[M]^+$, 231 (41) $[M – CH_3]^+$, 215 (13), 201 (35), 187 (12) $[M – COOCH_3]^+$, 173 (48) $[M – TMS]^+$, 157 (18), 145 (59), 129 (30), 115 (18), 107 (21), 97 (26), 89 (89), 73 (78) $[TMS]^+$, 59 (100), 43 (35). HRMS (EI): calcd. for $[C_{14}H_{18}O_2Si + Na]^+$ 269.0968; found 269.0968.

Methyl 3-(3-Ethynylbicyclo[1.1.1]pentyl)prop-2-ynoate: The ester **14** (180 mg, 0.73 mmol) was desilylated in THF (8 mL) according to the procedure previously used for **15**; however, only a small excess of TBAF solution in THF (1.0 M, 850 μL, 0.85 mmol) and a lower temperature (–15 °C) were used. Column chromatography on silica gel (hexane/CH_2Cl_2, 1:1) afforded the pure product as a white crystalline solid (88 mg, 69%). M.p. 84.4–85.5 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.07 (s, 1 H, ≡CH), 2.37 (s, 6 H, CH_2), 3.73 (s, 3 H, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 29.1, 30.4, 52.7, 58.4, 68.6, 71.5, 81.6, 85.7, 153.7 ppm. IR (KBr): ṽ = 3271, 2996, 2963, 2918, 2880, 2851, 2231, 1709, 1436, 1334, 1259, 1218, 1101, 1022, 803, 747, 682 cm^{-1}. GC–MS: *m*/*z* (%) = 173 (2) $[M]^+$, 159 (4) $[M – CH_3]^+$, 143 (13) $[M – OCH_3]^+$, 131 (9), 128 (4), 115 (100) $[M – COOCH_3]^=$, 103 (34), 89 (36), 77 (44), 75 (9), 63 (33), 51 (29). HRMS (EI): calcd. for $[C_{11}H_9O_2]^+$ 173.0603; found 173.0604.

***P,P′*-(Bicyclo[1.1.1]pentane-1,3-diyldiethynediyl)bis(diphenylphosphane oxide) (16):** A solution of bis(phosphane) **10** (500 mg, 1.0 mmol) in CH_2Cl_2 (15 mL) was mixed with 10% aqueous H_2O_2 (20 mL), and the resulting two-phase system was rapidly stirred at room temperature for 45 min. Subsequently, an additional portion of CH_2Cl_2 (80 mL) was added, and the aqueous phase was separated. The colorless organic phase was washed with water (3 × 30 mL) and dried with Na_2SO_4. Complete evaporation of CH_2Cl_2 provided the pure product **16** as white crystals (525 mg, 98%). M.p. 233.8–235.1 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.53 (s, 6 H, CH_2), 7.45–7.50 (m, 8 H, Ar-H), 7.53–7.57 (m, 4 H, Ar-H), 7.76–7.81 (m, 8 H, Ar-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 30.2 (*J* = 3.35 Hz), 58.7, 74.8 (*J* = 165.75 Hz), 103.9 (*J* = 28.39 Hz), 128.4 (*J* = 13.44 Hz), 130.7 (*J* = 11.19 Hz), 132.1 (*J* = 2.30 Hz), 132.4 (*J* = 122.04 Hz) ppm. ^{31}P NMR (121 MHz, $CDCl_3$): δ = 9.05 ppm. IR (KBr): ṽ = 3052, 3000, 2919, 2882, 2184, 1482, 1439, 1233, 1202, 1121, 1070, 997, 751, 726, 697 cm^{-1}. MS: *m*/*z* (%) = 517 (46), 515 (100) $[M]^+$, 488 (9), 487 (19), 440 (9), 439 (32) $[M – Ph]^+$, 425 (8), 411 (9), 391 (8), 331 (19), 315 (14) $[M – POPh_2]^+$, 265 (10), 202 (10), 201 (39) $[POPh_2]^+$, 189 (7), 185 (7), 183 (33), 78 (15), 77 (74) $[Ph]^+$, 65 (7), 51 (55), 50 (15), 47 (49). HRMS (APCI): calcd. for $[C_{33}H_{26}O_2P_2 + H]^+$ 517.1481; found 517.1472. $C_{33}H_{26}O_2P_2 + H_2O$: calcd. C 74.15, H 5.28, P 11.59; found C 74.43, H 5.11, P 11.73.

[(3-Ethynylbicyclo[1.1.1]pentyl)ethynyl]diphenylphosphane Oxide (17): Oxidation of the phosphane **15** (155 mg, 0.5 mmol) according to the previous procedure afforded the pure product **17** as a colorless oil that slowly crystallized (161 mg, 98%). M.p. 156.3–157.9 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.06 (s, 1 H, ≡CH), 2.36 (s, 6 H, CH_2), 7.37–7.46 (m, 6 H, Ar-H), 7.71–7.78 (m, 4 H, Ar-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 29.5 (*J* = 3.56 Hz), 30.3, 58.5, 68.7, 74.2 (*J* = 167.61 Hz), 81.4, 104.7 (*J* = 28.86 Hz), 128.4 (*J* = 13.42 Hz), 130.6 (*J* = 11.35 Hz), 132.0 (*J* = 2.94 Hz), 132.6 (*J* = 121.85 Hz) ppm. ^{31}P NMR (121 MHz, $CDCl_3$): δ = 8.89 ppm. IR (KBr): ṽ = 3273, 3070, 3003, 2972, 2920, 2885, 2172, 1437, 1230, 1196, 1117, 924, 775, 750, 723, 692, 648 cm^{-1}. GC–MS: *m*/*z* (%) = 316 (98) $[M]^+$, 287 (23), 271 (11), 253 (26), 239 (33), 220 (12), 201 (42), 191 (97), 183 (74), 165 (60), 152 (35), 127 (31), 115 (52), 107 (22), 91 (33), 77 (100) $[Ph]^+$, 63 (23), 51 (54). HRMS (APCI): calcd. for $[C_{21}H_{17}OP + H]^+$ 317.1090; found 317.1085.

General Procedure for the Sonogashira–Hagihara Cross-Coupling Reaction (GP): A flame-dried Schlenk flask was charged with a haloarene (3 equiv.), $[Pd(PPh_3)_4]$ (8 mol-%), and CuI (6 mol-%). After three successive vacuum/argon cycles, dry and degassed THF (2.50 mL) and triethylamine (2.50 mL) were added through a syringe. Finally, a solution of freshly sublimed diyne **1** (1 equiv.) in THF (2.50 mL) was added to the reaction mixture. The yellow solution was stirred at room temperature (in the case of iodoarenes) or at 55 °C (in the case of bromoarenes) for 16 h. A white solid precipitated. The yellow reaction mixture was cooled to room temperature, diluted with diethyl ether or CH_2Cl_2 (100–150 mL), and washed with saturated aqueous NH_4Cl (3 × 30 mL) and water (1 × 20 mL). The yellow organic phase was dried with Na_2SO_4. After evaporation of the volatiles, the pure products were isolated by column chromatography on silica gel or recrystallized.

1,3-Bis(phenylethynyl)bicyclo[1.1.1]pentane (18): Compound **18** was prepared according to the GP from iodobenzene (1.282 g, 6.3 mmol, 703 μL) and the diyne **1** (243 mg, 2.1 mmol). Pure **18** (485 mg, 86%) was isolated as a white solid by column chromatography on silica gel (hexane/CH_2Cl_2, 4:1). M.p. 173.4–174.8 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.49 (s, 6 H, CH_2), 7.29–7.30 (m, 6 H, Ar-H), 7.42–7.44 (m, 4 H, Ar-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 30.8, 59.0, 80.1, 88.2, 122.9, 128.1, 128.2, 131.8 ppm. IR (KBr): $\tilde{\nu}$ = 3080, 3060, 3049, 3033, 2993, 2983, 2963, 2910, 2874, 2230, 1597, 1571, 1490, 1442, 1302, 1205, 1177, 1070, 1027, 914, 841, 755, 691 cm^{-1}. MS: *m*/*z* (%) = 268 (49) $[M]^+$, 267 (52), 265 (50), 253 (38), 252 (100), 239 (17), 226 (12), 215 (9), 202 (5), 189 (21), 176 (4), 165 (18), 152 (11), 139 (14), 127 (30), 115 (19), 101 (7), 89 (6), 77 (20), 63 (8), 51 (9). HRMS (EI): calcd. for $[C_{21}H_{16}]^+$ 268.1252; found 268.1249. $C_{21}H_{16}$ (268.36): calcd. C 93.99, H 6.01; found C 93.90, H 5.84.

1,3-Bis(1-naphthylethynyl)bicyclo[1.1.1]pentane (19): Compound **19** was prepared from 1-iodonaphthalene (283 μL, 1.9 mmol) and the diyne **1** (90 mg, 0.8 mmol) according to the GP. The reaction mixture was stirred at 45 °C for 6 h. Column chromatography on silica gel (hexane/CH_2Cl_2, 4:1) provided the hydrocarbon **19** as a white solid (252 mg, 88%). M.p. 185.4–186.8 °C (dec.). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.68 (s, 6 H, CH_2), 7.43 (dd, J_1 = 7.21, J_2 = 8.21 Hz, 2 H, Ar-H), 7.54 (ddd, J_1 = 1.25, J_2 = 6.89, J_3 = 8.06 Hz, 2 H, Ar-H), 7.61 (ddd, J_1 = 1.32, J_2 = 6.86, J_3 = 8.30 Hz, 2 H, Ar-H), 7.70 (dd, J_1 = 1.07, J_2 = 7.14 Hz, 2 H, Ar-H), 7.83 (dd, J_1 = 1.79, J_2 = 8.29 Hz, 2 H, Ar-H), 7.86 (ddd, J_1 = 0.82, J_2 = 2.07, J_3 = 8.06 Hz, 2 H, Ar-H), 8.34 (ddd, J_1 = 1.02, J_2 = 1.85, J_3 = 8.46 Hz, 2 H, Ar-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 31.2, 59.4, 78.3, 93.2, 120.6, 125.2, 126.1, 126.3, 126.7, 128.3, 128.6, 130.6, 133.2, 133.5 ppm. IR (KBr): $\tilde{\nu}$ = 3086, 3055, 3045, 2990, 2967, 2914, 2876, 2214, 1585, 1532, 1505, 1480, 1460, 1435, 1397, 1375, 1334, 1297, 1253, 1219, 1178, 1156, 1119, 1017, 949, 902, 861, 796, 771, 745, 696, 633, 610, 567, 543, 457 cm^{-1}. MS: *m*/*z* (%) = 368.2 (14) $[M]^+$, 352.1 (11), 339.1 (8), 326.1 (5), 277.1 (72), 262.1 (100), 239.1 (4), 215.1 (6), 199.0 (13), 183.0 (67), 152.1 (16), 141.0 (7), 108.0 (21), 77.0 (11), 51.0 (9). HRMS (EI): calcd. for $[C_{29}H_{20}]^+$ 368.1565; found 368.1563. $C_{29}H_{20}$ (368.48): calcd. C 94.53, H 5.47; found C 94.20, H 5.46.

1,3-Bis[(4-iodophenyl)ethynyl]bicyclo[1.1.1]pentane (20): Compound **20** was prepared from 1,4-diiodobenzene (7.100 g, 21.5 mmol) and the diyne **1** (500 mg, 4.3 mmol) according to the GP. Recrystallization from $CHCl_3$ yielded pure **20** as white crystals (1.648 g, 74%). M.p. >235 °C (dec.). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.46 (s, 6 H, CH_2), 7.10–7.14 (m, 4 H, Ar-H), 7.60–7.65 (m, 4 H, Ar-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 30.8, 58.9, 79.3, 89.6, 94.0, 122.4, 133.3, 137.4 ppm. IR (KBr): $\tilde{\nu}$ = 2989, 2910, 2873, 1900, 1479, 1387, 1296, 1107, 1055, 1003, 818, 779, 700 cm^{-1}. MS: *m*/*z* (%) = 520 (20) $[M]^+$, 393 (4) $[M - I]^+$, 265 (98) $[M - 2I]^+$, 239 (9), 213 (6), 169 (14), 139 (15), 126 (41) $[I]^+$, 112 (14), 97 (21), 83 (26), 72 (67), 59 (100). HRMS (APCI): calcd. for $[C_{21}H_{14}I_2 + H]^+$ 520.9258; found 520.9253.

Dimethyl 4,4′-(Bicyclo[1.1.1]pentane-1,3-diyldiethynediyl)dibenzoate (23): Compound **23** was prepared from methyl 4-bromobenzoate (2.777 g, 12.9 mmol) and the diyne **1** (500 mg, 4.3 mmol) according to the GP. The reaction mixture was stirred at 55 °C for 18 h. After general workup, column chromatography on silica gel (hexane/CH_2Cl_2, 1:20) followed by recrystallization from $CHCl_3$ provided the diester **23** as a white solid (1.126 g, 68%). M.p. 244.9–246.8 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.50 (s, 6 H, CH_2), 3.91 (s, 6 H, OCH_3), 7.46 (d, J = 8.27 Hz, 4 H, Ar-H), 7.96 (d, J = 8.28 Hz, 4 H, Ar-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 30.9, 52.2, 59.0, 79.6, 91.1, 127.6, 129.4, 129.5, 131.7, 166.5 ppm. IR (KBr): $\tilde{\nu}$ = 2991, 2947, 2914, 2877, 2848, 2225, 1716, 1603, 1437, 1404, 1281, 1194, 1173, 1111, 1014, 964, 854, 769 cm^{-1}. MS: *m*/*z* (%) = 384 (33) $[M]^+$, 369 (3) $[M - CH_3]^+$, 353 (12) $[M - OCH_3]^+$, 325 (27) $[M - CO_2CH_3]^+$, 310 (7) $[M - CO_2CH_3 - CH_3]^+$, 293 (9), 265 (100) $[M - 2CO_2CH_3]^+$, 239 (8), 189 (9), 185 (8), 161 (16), 139 (15), 126 (20), 115 (11), 97 (9), 83 (13), 69 (11), 59 (34) $[CO_2CH_3]^+$. HRMS (APCI): calcd. for $[C_{25}H_{20}O_4 + H]^+$ 385.1434; found 385.1434.

4,4′-(Bicyclo[1.1.1]pentane-1,3-diyldiethynediyl)dibenzoic Acid: The diester **23** (60 mg, 0.16 mmol) was suspended in a solution of KOH (330 mg, 5.88 mmol) in MeOH (15 mL) and water (10 mL). The suspension was stirred at 60 °C for 14 h. During this time, the suspension slowly disappeared leaving a clear solution. The reaction mixture was cooled to room temperature and acidified with concentrated HCl (pH ≈ 1). A white precipitate was filtered off and washed with water (2 × 10 mL), $CHCl_3$ (2 × 15 mL), and diethyl ether (2 × 10 mL). The diacid was isolated as grayish crystals (36 mg, 64%). M.p. >260 °C (dec.). ^{1}H and ^{13}C NMR spectra were not recorded due to the poor solubility of in common solvents. IR (KBr): $\tilde{\nu}$ = 3072, 2987, 2910, 2879, 2818, 2669, 2549, 2224, 1684, 1603, 1556, 1421, 1313, 1290, 1174, 1109, 1014, 858, 768 cm^{-1}. MS: *m*/*z* (%) = 356 (43) $[M]^+$, 311 (40) $[M - COOH]^+$, 265 (100) $[M - 2COOH]^+$, 252 (67), 239 (11), 189 (18), 165 (18), 152 (8), 127 (12), 115 (11), 77 (9). HRMS (EI): calcd. for $[C_{23}H_{16}O_4]^+$ 356.1049; found 356.1052.

Tetramethyl 5,5′-(Bicyclo[1.1.1]pentane-1,3-diyldiethynediyl)diisophthalate (24): Compound **24** was prepared from dimethyl 5-bromoisophthalate (487 mg, 1.8 mmol) and the diyne **1** (90 mg, 0.8 mmol) according to the GP. Column chromatography of the crude product on silica gel (CH_2Cl_2) provided the tetraester **24** as a white solid (346 mg, 89%). M.p. >170 °C (dec.). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.50 (s, 6 H, CH_2), 3.94 (s, 12 H, OCH_3), 8.25 (dd, J_1 = 0.61, J_2 = 1.61 Hz, 4 H, Ar-H), 8.58 (dt, J_1 = 0.82, J_2 = 1.60 Hz, 2 H, Ar-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 30.7, 52.5, 58.9, 78.4, 90.0, 123.9, 130.0, 130.8, 136.6, 165.5 ppm. IR (KBr): $\tilde{\nu}$ = 3098, 3074, 2998, 2979, 2953, 2919, 2879, 2850, 2227, 1722, 1597, 1454, 1444, 1434, 1343, 1306, 1264, 1248, 1206, 1127, 1108, 1086, 1004, 977, 957, 921, 875, 784, 757, 722, 676, 564 cm^{-1}. MS, (ESI): *m*/*z* (%) = 501 (10) $[M + H]^+$, 523 (100) $[M + Na]^+$. HRMS (ESI): calcd. for $[C_{29}H_{24}O_8 + H]^+$ 501.15439; found 501.15411. $C_{29}H_{24}O_8$ (500.50): calcd. C 69.59, H 4.83; found C 69.68, H 4.71.

Dimethyl 2,2′-(Bicyclo[1.1.1]pentane-1,3-diyldiethynediyl)dibenzoate (25): Compound **25** was prepared from methyl 2-bromobenzoate (465 μL, 3.3 mmol) and the diyne **1** (150 mg, 1.3 mmol) according to the GP. The reaction mixture was stirred at 55 °C for 18 h. Column chromatography of the crude product on silica gel (CH_2Cl_2) provided the diester **25** as a white solid (322 mg, 65%). M.p. 134.6–135.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.53 (s, 6 H, CH_2), 3.92 (s, 6 H, OCH_3), 7.34 (ddd, J_1 = 1.38, J_2 = 7.70, J_3 = 7.65 Hz, 2 H, Ar-H), 7.43 (ddd, J_1 = 1.42, J_2 = 7.58, J_3 = 7.70 Hz, 2 H, Ar-H), 7.53 (dd, J_1 = 0.97, J_2 = 7.75 Hz, 2 H, Ar-H), 7.91 (dd, J_1 = 1.03, J_2 = 7.86 Hz, 2 H, Ar-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 31.2, 52.0, 59.1, 78.8, 93.4, 123.4, 127.8, 130.3, 131.5, 132.3, 134.3, 166.7 ppm. IR (KBr): $\tilde{\nu}$ = 3069, 3030, 2990, 2967, 2931, 2876, 2841, 2228, 1736, 1717, 1595, 1567, 1485, 1445, 1434, 1425, 1294, 1271, 1253, 1193, 1164, 1134, 1079, 1058, 1043, 961, 830, 800, 780, 760, 705, 664 cm^{-1}. MS: *m*/*z* (%) = 384 (8) $[M]^+$, 369 (55) $[M - CH_3]^+$, 354 (14) $[M - OCH_3]^+$, 337 (100) $[M - OCH_3 - CH_3]^+$, 325 (9) $[M - CO_2CH_3]^+$, 309 (31) $[M - CO_2CH_3 - CH_3]^+$, 293 (13), 281 (34), 265 (23) $[M - 2CO_2CH_3]^+$, 252 (37), 239 (11), 226 (6), 209 (5), 165 (7), 126 (6), 114 (9). HRMS (EI): calcd. for

$[C_{25}H_{20}O_4]^+$ 384.1362; found 384.1363. $C_{25}H_{20}O_4$ (384.43): calcd. C 78.11, H 5.24; found C 77.86, H 5.18.

1,3-Bis({4-[(trimethylsilyl)ethynyl]phenyl}ethynyl)bicyclo[1.1.1]pentane (26): Compound **26** was prepared from [(4-bromophenyl)ethynyl]trimethylsilane (633 mg, 2.5 mmol) and the diyne **1** (112 mg, 1.0 mmol) according to the GP. The reaction mixture was stirred at 55 °C for 18 h. The product precipitated from the reaction mixture. Consecutive washing with saturated aqueous NH_4Cl (2 × 15 mL), water (2 × 20 mL), diethyl ether (3 × 10 mL), and hexane (3 × 10 mL) and drying in vacuo afforded **26** in satisfactory purity as a white solid (310 mg, 70%). M.p. >265 °C (dec.). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.24 (s, 18 H, CH_3), 2.46 (s, 6 H, CH_2), 7.33 (d, J = 8.58 Hz, 4 H, Ar-H), 7.38 (d, J = 8.57 Hz, 4 H, Ar-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = –0.1, 30.9, 59.0, 79.9, 90.1, 96.2, 104.6, 122.8, 123.0, 131.5, 131.8 ppm. IR (KBr): $\tilde{\nu}$ = 3087, 3047, 2985, 2960, 2908, 2873, 2223, 2154, 1602, 1507, 1497, 1412, 1405, 1298, 1254, 1245, 1224, 1175, 1103, 1014, 865, 847, 835, 760, 699, 641, 551 cm^{-1}. MS: *m*/*z* (%) = 460 (100) $[M]^+$, 445 (49) $[M - CH_3]^+$, 387 (9) $[M - TMS]^+$, 371 (13), 357 (27), 215 (18), 207 (16), 73 (49) $[TMS]^+$. HRMS (EI): calcd. for $[C_{31}H_{32}Si_2]^+$ 460.2043; found 460.2050. $C_{31}H_{32}Si_2$ (460.77): calcd. C 80.81, H 7.00; found C 80.56, H 6.89.

Trimethyl{[3-(1-naphthylethynyl)bicyclo[1.1.1]pentyl]ethynyl}silane (27): Compound **27** was prepared from 1-iodonaphthalene (263 μL, 1.8 mmol) and the monosilylated diyne **8** (320 mg, 1.7 mmol) according to the GP. Column chromatography of the crude product on silica gel (hexane/CH_2Cl_2, 4:1) provided the silyl derivative **27** as a white crystalline solid (358 mg, 67%). M.p. 128.3–129.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.20 (s, 9 H, CH_3), 2.51 (s, 6 H, CH_2), 7.40 (dd, J_1 = 7.20, J_2 = 8.24 Hz, 1 H, Ar-H), 7.51 (ddd, J_1 = 1.33, J_2 = 6.88, J_3 = 8.09 Hz, 1 H, Ar-H), 7.58 (ddd, J_1 = 1.40, J_2 = 6.86, J_3 = 8.32 Hz, 1 H, Ar-H), 7.65 (dd, J_1 = 1.16, J_2 = 7.16 Hz, 1 H, Ar-H), 7.83 (ddd, J_1 = 4.51, J_2 = 7.68, J_3 = 14.70 Hz, 2 H, Ar-H), 8.29 (ddd, J_1 = 1.12, J_2 = 2.19, J_3 = 8.28 Hz, 1 H, Ar-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 0.04, 30.7, 30.8, 59.2, 78.0, 84.8, 93.2, 104.6, 120.5, 125.1, 126.1, 126.3, 126.7, 128.2, 128.5, 130.5, 133.1, 133.4 ppm. IR (KBr): $\tilde{\nu}$ = 3088, 3059, 3047, 2986, 2963, 2913, 2877, 2163, 1633, 1586, 1507, 1461, 1448, 1401, 1334, 1270, 1250, 1218, 1173, 1157, 1142, 1116, 1010, 966, 950, 918, 863, 847, 796, 772, 760, 724, 712, 700, 623, 601, 567, 514, 458, 437, 421 cm^{-1}. MS: *m*/*z* (%) = 314.1 (59) $[M]^+$, 299.1 (63) $[M - CH_3]^+$, 283.1 (33), 269.1 (21), 255.1 (20), 239.1 (92), 226.1 (30), 215.1 (36), 202.1 (24), 189.1 (29), 176.1 (58), 165.1 (21), 151.1 (23), 121.0 (6), 107.0 (11), 97.0 (16), 83.0 (12), 73.0 (100) $[TMS]^+$, 59.0 (20), 43.0 (8). HRMS (EI): calcd. for $[C_{22}H_{22}Si]^+$ 314.1491; found 314.1484. $C_{22}H_{22}Si$ (314.50): calcd. C 84.02, H 7.05; found C 83.81, H 7.13.

1-Ethynyl-3-(1-naphthylethynyl)bicyclo[1.1.1]pentane: The silyl derivative **27** (159 mg, 0.5 mmol) was desilylated according to the procedure previously used for compound **15** with TBAF in THF (1.0 M, 800 μL, 0.8 mmol) at room temperature. Column chromatography on silica gel (hexane/CH_2Cl_2, 4:1) afforded the pure product as a white solid (116 mg, 95%). M.p. 85.6–87.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.15 (s, 1 H, ≡CH), 2.52 (s, 6 H, CH_2), 7.40 (dd, J_1 = 7.38, J_2 = 8.06 Hz, 1 H, Ar-H), 7.52 (ddd, J_1 = 1.19, J_2 = 6.87, J_3 = 7.98 Hz, 1 H, Ar-H), 7.58 (ddd, J_1 = 1.27, J_2 = 6.90, J_3 = 8.29 Hz, 1 H, Ar-H), 7.65 (dd, J_1 = 0.77, J_2 = 7.11 Hz, 1 H, Ar-H), 7.82 (ddd, J_1 = 4.55, J_2 = 7.23, J_3 = 8.19 Hz, 2 H, Ar-H), 8.28 (ddd, J_1 = 0.75, J_2 = 1.66, J_3 = 8.32 Hz, 1 H, Ar-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 30.1, 30.9, 58.9, 68.2, 78.1, 82.6, 92.9, 120.5, 125.1, 126.1, 126.3, 126.7, 128.2, 128.6, 130.5, 133.1, 133.4 ppm. IR (KBr): $\tilde{\nu}$ = 3286, 3088, 3059, 3045, 3033, 2990, 2968, 2914, 2878, 2223, 2112, 1619, 1585, 1570, 1505, 1447, 1400, 1334, 1325, 1292, 1266, 1247, 1217, 1170, 1158, 1105, 1019, 969, 955, 865, 799, 775, 740, 662, 652, 603, 564, 540, 505, 463, 451, 428 cm^{-1}. MS: *m*/*z* (%) = 242.1 (36) $[M]^+$, 241.1 (100) $[M - H]^+$, 239.1 (87), 226.1 (70), 215.1 (23), 202.1 (11), 189.1 (12), 176.1 (69), 165.1 (16), 151.1 (29), 126.0 (8), 119.5 (7), 101.4 (4), 87.0 (5), 75.0 (5), 63.0 (6), 51.0 (5). HRMS (EI): calcd. for $[C_{19}H_{14}]^+$ 242.1096; found 242.1084. $C_{19}H_{14}$ (242.32): calcd. C 94.18, H 5.82; found C 93.94, H 5.96.

({3-[(4′-Iodobiphenyl-4-yl)ethynyl]bicyclo[1.1.1]pentyl}ethynyl)trimethylsilane (28): Compound **28** was prepared from 4,4′-diiodobiphenyl (2.910 g, 7.2 mmol) and the monosilylated diyne **8** (450 mg, 2.4 mmol) according to the GP. Slow-elution column chromatography on silica gel (hexane/$CHCl_3$, 4:1) provided the iodo derivative **28** as a white solid (531 mg, 48%). M.p. 257.2–258.1 °C (dec.). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.16 (s, 9 H, CH_3), 2.41 (s, 6 H, CH_2), 7.29–7.31 (m, 2 H, Ar-H), 7.45–7.46 (m, 4 H, Ar-H), 7.75–7.76 (m, 2 H, Ar-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 0.01, 30.6, 30.8, 59.1, 79.7, 84.8, 89.3, 93.4, 104.6, 122.3, 126.6, 128.8, 132.3, 137.9, 139.6, 139.8 ppm. IR (KBr): $\tilde{\nu}$ = 3038, 2988, 2963, 2912, 2876, 2221, 2163, 1585, 1557, 1518, 1480, 1448, 1411, 1387, 1307, 1263, 1250, 1213, 1191, 1120, 1102, 1085, 1064, 1000, 920, 861, 852, 843, 814, 761, 728, 718, 701, 623, 558, 519, 507, 497 cm^{-1}. MS: *m*/*z* (%) = 466.1 (42) $[M]^+$, 451.0 (72) $[M - CH_3]^+$, 435.0 (15), 423.0 (12), 407.0 (11), 393.0 (13) $[M - TMS]^+$, 361.0 (13), 339.2 (17) $[M - I]^+$, 324.1 (11), 309.1 (23), 279.1 (11), 265.1 (23), 239.1 (10), 215.1 (12), 200.1 (24), 189.1 (14), 127.9 (34) $[I]^+$, 97.0 (15), 73.0 (100) $[TMS]^+$, 59.0 (18), 44.0 (11). HRMS (EI): calcd. for $[C_{24}H_{23}ISi]^+$ 466.0614; found 466.0606. UV/Vis (CH_2Cl_2): λ_{max} (ε) = 290 (44.7 × 10^3 M^{-1} cm^{-1}) nm. $C_{24}H_{23}ISi$ (466.44): calcd. C 61.80, H 4.97; found C 61.59, H 4.93.

3,6-Bis({3-[(trimethylsilyl)ethynyl]bicyclo[1.1.1]pentyl}ethynyl)pyridazine (29): Compound **29** was prepared from 3,6-diiodopyridazine (111 mg, 0.335 mmol) and the monosilylated diyne **8** (140 mg, 0.7 mmol) according to the GP. Column chromatography on silica gel (CH_2Cl_2) provided the pyridazine derivative **29** as a white crystalline solid (99 mg, 0.219 mmol, 65%). M.p. >160 °C (dec.). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.15 (s, 18 H, CH_3), 2.43 (s, 12 H, CH_2), 7.40 (s, 2 H, Ar-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = –0.1, 30.0, 31.2, 58.9, 76.7, 85.2, 94.7, 104.0, 128.7, 145.5 ppm. IR (KBr): $\tilde{\nu}$ = 2991, 2965, 2915, 2900, 2879, 2229, 2165, 1570, 1557, 1531, 1507, 1486, 1449, 1408, 1336, 1269, 1251, 1120, 1101, 920, 857, 846, 760, 720, 701, 621 cm^{-1}. MS: *m*/*z* (%) = 452.2 (31) $[M]^+$, 437.2 (100) $[M - CH_3]^+$, 421.2 (42), 407.1 (9), 379.2 (29) $[M - TMS]^+$, 363.1 (38), 349.1 (53), 337.1 (10), 307.1 (14), 277.1 (13), 255.1 (7), 240.1 (8), 226.1 (9), 202.1 (5), 189.1 (6), 138.1 (3), 123.1 (11). HRMS (EI): calcd. for $[C_{28}H_{32}N_2Si_2]^+$ 452.2104; found 452.2099. $C_{28}H_{32}N_2Si_2$ (452.75): calcd. C 74.28, H 7.12, N 6.19; found C 74.46, H 7.38, N 6.11.

1,3,5-Tris({3-[(trimethylsilyl)ethynyl]bicyclo[1.1.1]pentyl}ethynyl)benzene (31): A flame-dried Schlenk flask was charged with the silyldiyne **8** (130 mg, 0.690 mmol), 1,3,5-tribromobenzene (72 mg, 0.215 mmol), $[Pd(PPh_3)_4]$ (32 mg, 0.028 mmol, 4 mol-%), and CuI (4 mg, 0.021 mmol, 3 mol-%). After three successive vacuum/argon cycles, dry and degassed THF (4 mL) and triethylamine (2 mL) were added through syringe. The dark solution was stirred at 55 °C for 96 h. A white solid precipitated. The reaction mixture was cooled to room temperature, diluted with toluene (50 mL), and washed with water (3 × 20 mL). The dark organic phase was dried with Na_2SO_4. After evaporation of the volatiles, the pure product **31** was isolated by column chromatography on silica gel (hexane/$CHCl_3$, 2:1) as white crystals (53 mg, 37%). M.p. >230 °C (dec.).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.15 (s, 27 H, CH_3), 2.35 (s, 18 H, CH_2), 7.32 (s, 3 H, Ar-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 0.01, 30.3, 30.8, 59.0, 78.5, 84.8, 89.3, 104.4, 123.4, 134.3 ppm. IR (KBr): $\tilde{\nu}$ = 2987, 2964, 2916, 2879, 2164, 1583, 1417, 1252, 1095, 856, 760, 723 cm^{-1}. MS: *m*/*z* (%) = 636 (1) $[M]^+$, 621 (1) $[M - CH_3]^+$, 563 (<1) $[M - TMS]^+$, 547 (<1) $[M - TMS - CH_3]^+$, 533 (1), 517 (1), 503 (1), 490 (1) $[M - 2TMS]^+$, 473 (2), 459 (3), 449 (1), 431 (2), 417 (2) $[M - 3TMS]^+$, 401 (2), 357 (1), 303 (<1), 155 (2), 97 (8), 73 (100) $[TMS]^+$, 59 (4). HRMS (EI): calcd. for $[C_{42}H_{48}Si_3]^+$ 636.3064; found 636.3077.

1,3,5-Tris[(3-ethynylbicyclo[1.1.1]pentyl)ethynyl]benzene: Compound **31a** was prepared from trisilylated derivative **31** (38 mg, 0.06 mmol) in THF (3.50 mL) and a solution of TBAF in THF (1.0 M, 240 μL, 0.24 mmol) according to the procedure described for compound **27a**. Column chromatography on silica gel (hexane/$CHCl_3$, 2:1) afforded the product as white crystals (23 mg, 92%). M.p. >202 °C (dec.). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.09 (s, 3 H, ≡CH), 2.36 (s, 18 H, CH_2), 7.33 (s, 3 H, Ar-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 30.0, 30.5, 58.7, 68.3, 78.4, 82.4, 89.0, 123.4, 134.3 ppm. IR (KBr): $\tilde{\nu}$ = 3300, 2987, 2914, 2877, 2224, 2112, 1583, 1450, 1417, 1246, 877, 758 cm^{-1}. MS: *m*/*z* (%) = 415 (14) $[M - 2H_2]^+$, 401 (72), 387 (100), 374 (57), 363 (59), 350 (84), 337 (99), 324 (48), 313 (57), 300 (63), 287 (56), 274 (29), 263 (27), 261 (26), 250 (26), 237 (24), 224 (16), 211 (10), 200 (13), 187 (19), 175 (12), 162 (12), 150 (13), 115 (14), 89 (9), 65 (12), 51 (25). HRMS (APCI): calcd. for $[C_{33}H_{24} + H]^+$ 421.1951; found 421.1943.

1,3-Bis(bromoethynyl)bicyclo[1.1.1]pentane (32): Freshly recrystallized NBS (1.388 g, 7.8 mmol) and $AgNO_3$ (340 mg, 2.0 mmol) were added to a solution of freshly sublimed diyne **1** (405 mg, 3.5 mmol) in acetone (10 mL). The yellowish solution was stirred at room temperature in the dark for 2.5 h. A white solid precipitated. The reaction mixture was diluted with CH_2Cl_2 (25 mL) and washed with water (2 × 20 mL). The clear colorless organic phase was dried with Na_2SO_4. Solvents were removed under reduced pressure, and the residue was purified by flash column chromatography on silica gel (hexane/CH_2Cl_2, 3:1) to give **32** as white crystals (778 mg, 81%). M.p. 118 °C (subl.), 182 °C (dec.). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.31 (s, 6 H, CH_2) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 30.7, 39.9, 58.6, 78.5 ppm. IR (KBr): $\tilde{\nu}$ = 2993, 2970, 2914, 2877, 2557, 2198, 1506, 1446, 1236, 1119, 719 cm^{-1}. GC–MS: *m*/*z* (%) = 273 (1) $[M]^+$, 193 (3) $[M - Br]^+$, 167 (1), 143 (1), 129 (4), 114 (100), 88 (16), 74 (4), 63 (15), 50 (21). HRMS (EI): calcd. for $[C_9H_5Br_2]^+$ 270.8758; found 270.8769. $C_9H_6Br_2$ (273.95): calcd. C 39.46, H 2.21, Br 58.33; found C 39.60, H 2.25, Br 58.11.

1,3-Bis(iodoethynyl)bicyclo[1.1.1]pentane (33): A solution of KOH (337 mg, 6.0 mmol) in water (1.50 mL) was added to a suspension of the silylated diyne **7** (150 mg, 0.6 mmol) in a mixture of MeOH (5 mL) and THF (2 mL) at room temperature. Freshly sublimed I_2 (584 mg, 2.3 mmol) was added to the cloudy reaction mixture after 15 min. The yellowish solution was stirred at room temperature for 2.5 h, and a dense white precipitate formed. The reaction mixture was then diluted with water (25 mL) and extracted with CH_2Cl_2 (2 × 25 mL). The combined organic phases were dried with Na_2SO_4. Solvents were removed under reduced pressure, and the product was isolated by column chromatography on silica gel (pentane) in a purity of around 95%. The remaining impurities were sublimed by Kugelrohr distillation (100 °C, 360 mTorr). The desired diiododiyne **33** was obtained as a white crystalline solid (102 mg, 48%). M.p. 196 °C (dec.). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.32 (s, 6 H, CH_2) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = –3.8, 31.3, 59.2, 92.7 ppm. IR (KBr): $\tilde{\nu}$ = 2989, 2962, 2910, 2873, 1502, 1443, 1230, 1097, 802 cm^{-1}. GC–MS: *m*/*z* (%) = 368 (1) $[M]^+$, 241 (11) $[M - I]^+$, 177 (7), 165 (3), 127 (4) $[I]^+$, 114 (100), 88 (24), 74 (6), 63 (16), 50 (23). HRMS (EI): calcd. for $[C_9H_6I_2]^+$ 367.8559; found 367.8560.

1,3-Bis{[12-(trihexylsilyl)-1,12-dicarba-*closo*-dodecaboran-1-yl]ethynyl}bicyclo[1.1.1]pentane (35): A flame-dried Schlenk flask was charged with trihexylsilyl-*p*-carborane **34** (970 mg, 2.3 mmol) in dry THF (10 mL). The solution was cooled to –78 °C, and a solution of *n*BuLi in hexane (2.5 M, 940 μL, 2.350 mmol) was added dropwise. After 15 min, the cooling was interrupted, and the reaction mixture was heated to room temperature and stirred for 60 min. The colorless solution was cooled to –78 °C, and CuBr (344 mg, 2.4 mmol) was added. The reaction mixture was stirred at that temperature for 15 min, then heated up to room temperature and vigorously stirred for an additional 90 min. The reaction mixture turned from bright to dark green during this time. A solution of dibromodiyne **32** (301 mg, 1.1 mmol) in dry THF (5 mL) was added, and the mixture was stirred at 45 °C for 60 h. The crude reaction mixture was cooled to room temperature, diluted with CH_2Cl_2 (150 mL), washed with water (3 × 40 mL), and the clear green organic phase was dried with Na_2SO_4. Solvents were evaporated under reduced pressure, and most of the impurities were removed by repeated (3 ×) column chromatography on silica gel (hexane). The crude product obtained as colorless oil was dissolved in THF and precipitated by MeOH to yield pure **35** as a white crystalline solid (406 mg, 38%). M.p. 154.2–155.8 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.45–0.56 (m, 12 H, CH_2), 0.91 (t, *J* = 6.25 Hz, 18 H, CH_3), 1.12–1.41 (m, 48 H, CH_2), 2.06 (s, 6 H, CH_2), 1.30–3.10 (m, 20 H, BH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 12.8, 14.1, 22.6, 23.4, 29.7, 31.4, 33.4, 58.4, 70.3, 72.7, 76.4, 77.9 ppm. ^{11}B NMR (96 MHz, $CDCl_3$): δ = –10.4 (d, *J* = 182 Hz), –13.2 (d, *J* = 176 Hz) ppm. IR (KBr): $\tilde{\nu}$ = 2956, 2926, 2856, 2613, 1693, 1626, 1464, 1408, 1298, 1188, 1090, 993, 962, 870, 768, 737 cm^{-1}. MS (MALDI-TOF): *m*/*z* (center of isotope cluster) = 968.4 $[M + H]^+$, 685.7 $[M - SiHex_3 + H]^+$. HRMS (APCI): calcd. for $[C_{49}H_{104}B_{20}Si_2 + H]^+$ 969.9610; found 969.9652.

1,3-Bis[(1,7-dicarba-*closo*-dodecaboran-1-yl)ethynyl]bicyclo[1.1.1]pentane (37): A flame-dried Schlenk flask was charged with *m*-carborane **36** (548 mg, 3.8 mmol) in THF (15 mL), and a solution of *n*BuLi in cyclohexane (2.0 M, 950 μL, 1.9 mmol) was added to the colorless solution at –78 °C. After 15 min, cooling was interrupted, and the yellowish reaction mixture was stirred at room temperature for 60 min, then cooled to –78 °C, and CuBr (287 mg, 2.0 mmol) was added. The yellow-green reaction mixture was stirred at this temperature for 15 min, then heated up to room temperature, and vigorously stirred for an additional 90 min. The reaction mixture turned from bright to dark green during this time. A solution of dibromodiyne **32** (130 mg, 1.1 mmol) in dry THF (5 mL) was added, and the mixture was stirred at 45 °C for 24 h. The crude reaction mixture was cooled to room temperature, diluted with diethyl ether (150 mL), washed with saturated aqueous NH_4Cl (3 × 40 mL) and water (1 × 40 mL), and the clear green organic phase was dried with $MgSO_4$. Solvents were removed under reduced pressure, and the unreacted starting carborane **36** (330 mg, 2.3 mmol) was sublimed off from the crude reaction mixture by Kugelrohr distillation (115 °C, 500 mTorr). Column chromatography on silica gel (hexane) afforded the carborane **37** as a white crystalline solid (170 mg, 0.424 mmol, 89%). M.p. 235 °C (subl.), 272–274 °C (dec.). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.40–3.70 (br. s, 20 H, BH), 2.20 (s, 6 H, CH_2), 2.93 (br. s, 2 H, CH) ppm. ^{1}H{^{11}B} NMR (400 MHz, $CDCl_3$): δ = 2.10 (br. s, 4 H, BH), 2.17 (br. s, 6 H, BH), 2.20 (s, 6 H, CH_2), 2.40 (br. s, 4 H, BH), 2.52 (br. s, 2 H, BH), 2.86 (br. s, 4 H, BH), 2.93 (br. s, 2 H, CH) ppm. ^{13}C NMR

(100 MHz, $CDCl_3$): δ = 29.6, 54.8, 58.5, 61.1, 75.2, 76.3 ppm. $^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$): δ = –3.17 (br. s, 2 B), –8.30 (br. s, 2 B), –9.85 (br. s, 4 B), –11.01 (br. s, 4 B), –13.86 (br. s, 4 B), –14.59 (br. s, 4 B) ppm. IR (KBr): $\tilde{\nu}$ = 3071, 2991, 2973, 2916, 2880, 2608, 2253, 1449, 1306, 1209, 1135, 1081, 1052, 1008, 994, 971, 922, 906, 824, 783, 728 cm^{-1}. MS: *m*/*z* (center of isotope cluster) (%) = 399.4 (100) $[M]^+$, 384.4 (46), 365.3 (7), 257.2 (72) $[M - C_2H_{11}B_{10}]^+$, 195.2 (31). HRMS (EI): calcd. for $[C_{13}H_{28}{}^{10}B_2{}^{11}B_{18}]^+$ 402.4125; found 402.4138. $C_{13}H_{28}B_{20}$ (400.56): calcd. C 38.98, H 7.05; found C 39.25, H 7.06.

1,3-Bis[(1,12-dicarba-*closo*-dodecaboran-1-yl)ethynyl]bicyclo[1.1.1]-pentane (38): A solution of TBAF in THF (1.0 M, 4.50 mL, 4.500 mmol) was added to a stirred solution of silylated carborane **35** (200 mg, 0.2 mmol) in THF (5 mL) at room temperature. The yellowish reaction mixture was stirred at this temperature for 2 h. The mixture was then diluted with diethyl ether (60 mL), washed with water (3 × 20 mL), and the organic phase was dried with Na_2SO_4. Solvents were removed under reduced pressure, and column chromatography on silica gel (hexane) afforded the pure carborane **38** as white crystals (76 mg, 91%). M.p. 164 °C (subl.), >272 °C (dec.). ^1H NMR (300 MHz, $CDCl_3$): δ = 1.20–3.40 (m, 20 H, BH), 2.08 (s, 6 H, CH_2), 2.61 (br. s, 2 H, CH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 29.6, 58.4, 59.7, 69.3, 76.3, 77.9 ppm. ^{11}B NMR (96 MHz, $CDCl_3$): δ = –11.7 (d, *J* = 172 Hz), –15.4 (d, *J* = 169 Hz) ppm. IR (KBr): $\tilde{\nu}$ = 3064, 2989, 2916, 2879, 2613, 2247, 1304, 1207, 1144, 1084, 1045, 1005, 939, 820, 731 cm^{-1}. GC–MS: *m*/*z* (center of isotope clusters) (%) = 400 (100) $[M]^+$, 385 (62), 368 (6), 353 (3), 342 (2), 257 (77), 231 (8), 217 (2), 196 (5), 180 (2), 167 (3). HRMS (APCI): calcd. for $[C_{13}H_{28}B_{20} + H]^+$ 405.4125; found 405.4119.

12,12′-(Bicyclo[1.1.1]pentane-1,3-diyldiethynediyl)bis(1,12-dicarba-*closo*-dodecaborane-1-carboxylic acid) (39): A solution of *n*BuLi in hexane (2.5 M, 140 µL, 0.35 mmol) was added to a solution of carborane **38** (60 mg, 0.15 mmol) in THF (8 mL) at 0 °C. The clear, slightly yellowish reaction mixture was stirred at room temperature for 60 min. Subsequently, gaseous CO_2 was bubbled into the reaction mixture through a PTFE cannula for 30 min. A dense white precipitate was formed during this time. The reaction mixture was diluted with 20% aqueous $NaHCO_3$ (30 mL), then washed with CH_2Cl_2 (2 × 20 mL), and finally acidified with concentrated HCl (pH ≈ 1). The product was salted out with NaCl and extracted with diethyl ether (4 × 20 mL). The combined colorless organic phases were dried with Na_2SO_4. Solvents were removed under reduced pressure, and impurities were washed off with ice-cold CH_2Cl_2. The pure diacid **39** was obtained as white crystals (64 mg, 0.131 mmol, 87%). M.p. >280 °C (dec.). ^1H NMR (300 MHz, [D$_6$]acetone): δ = 1.50–3.40 (m, 20 H, BH), 2.15 (s, 6 H, CH_2), 9.41 (br. s, 2 H, COOH) ppm. ^{13}C NMR (75 MHz, [D$_6$]acetone): δ = 31.1, 59.8, 69.7, 77.2, 78.7, 81.6, 163.9 ppm. ^{11}B NMR (96 MHz, [D$_6$]acetone): δ = –12.2 (d, *J* = 162 Hz), –13.9 (d, *J* = 164 Hz) ppm. IR (KBr): $\tilde{\nu}$ = 3500, 3421, 3373, 3238, 2993, 2918, 2881, 2621, 2249, 1724, 1616, 1412, 1275, 1128, 987, 906, 791, 731 cm^{-1}. MS (MALDI-TOF): *m*/*z* (center of isotope cluster) = 489.7 $[M + H]^+$, 444.6 $[M - COO + H]^+$. HRMS (EI): calcd. for $[C_{15}H_{28}B_{20}O_4]^+$ 492.3849; found 492.3837.

1,3-Bis{[6-(chloromethyl)tricyclo[3.2.0.0^{2,6}]heptyl]ethynyl}bicyclo-[1.1.1]pentane (42): A solution of *t*BuLi in pentane (1.7 M, 2.0 mL, 3.4 mmol) was added dropwise to a solution of 1-(chloromethyl)-6-iodotricyclo[3.2.0.0^{2,6}]heptane (**40**; 453 mg, 1.7 mmol) in THF (10 mL) in a flame-dried Schlenk flask at –78 °C. The reaction mixture turned yellow immediately, and the clear solution was stirred for 15 min. CuBr (258 mg, 1.8 mmol) was then added, and the green solution was stirred at the same temperature for 15 min, then slowly warmed to room temperature and cooled again to –78 °C. A solution of dibromodiyne **32** (210 mg, 0.8 mmol) in THF (5 mL) was added to the dark solution of cuprate at –78 °C. The cooling source was then removed, and the solution was stirred at room temperature for 24 h and at 45 °C for an additional 24 h. The reaction mixture was diluted with $CHCl_3$ (75 mL), washed with concentrated aqueous NH_4Cl (2 × 20 mL) and water (1 × 20 mL), and the brownish organic phase was dried with Na_2SO_4. Evaporation of the solvents provided the crude product **42**, which was purified by column chromatography on silica gel (hexane/$CHCl_3$, 3:1) and obtained as a white crystalline solid (75 mg, 25%). M.p. >255 °C (dec.). ^1H NMR (300 MHz, $CDCl_3$): δ = 1.66–1.83 (m, 8 H, CH_2), 2.18 (s, 4 H, CH_2), 2.21 (s, 6 H, CH_2), 2.73 (s, 4 H, CH), 3.35 (s, 4 H, CH_2Cl) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 25.2, 30.1, 34.0, 41.0, 44.5, 45.4, 58.9, 65.9, 76.2, 80.7 ppm. IR (KBr): $\tilde{\nu}$ = 2964, 2908, 2870, 1460, 1437, 1306, 1282, 1259, 1227, 1142, 1074, 1016, 804, 715 cm^{-1}. MS: *m*/*z* (%) = 395 (<1) $[M]^+$, 345 (<1), 333 (2), 305 (3), 281 (13), 269 (20), 255 (23), 243 (16), 229 (30), 215 (39), 203 (50), 191 (29), 179 (33), 165 (45), 153 (23), 141 (24), 129 (25), 115 (37), 103 (8), 91 (24), 79 (100), 67 (8), 59 (8). HRMS (APCI): calcd. for $[C_{25}H_{26}Cl_2 + H]^+$ 397.1484; found 397.1475.

1,3-Bis[(3-methylbicyclo[1.1.1]pentyl)ethynyl]bicyclo[1.1.1]pentane (43): Compound **43** was prepared according to the previous general procedure used for compound **42** from 1-iodo-3-methylbicyclo[1.1.1]pentane (**41**; 687 mg, 3.3 mmol), *t*BuLi in pentane (1.7 M, 3.88 mL, 6.6 mmol), CuBr (488 mg, 3.4 mmol), and dibromodiyne **32** (380 mg, 1.387 mmol) in THF (14 mL). Product **43** was purified by column chromatography on silica gel (hexane/CH_2Cl_2, 3:1, then hexane/CH_2Cl_2, 4:1) and isolated as a white crystalline solid (47 mg, 12%). M.p. 143.8–145.0 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.10 (s, 6 H, CH_3), 1.87 (s, 12 H, CH_2), 2.23 (s, 6 H, CH_2) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 17.7, 27.9, 30.1, 38.8, 56.4, 58.9, 78.1, 79.4 ppm. IR (KBr): $\tilde{\nu}$ = 2966, 2910, 2870, 1444, 1377, 1342, 1277, 1134, 1051, 806 cm^{-1}. MS: *m*/*z* (%) = 277 (<1) $[M]^+$, 259 (2), 245 (7), 231 (18), 217 (25), 203 (48), 191 (47), 178 (53), 165 (100), 152 (40), 141 (37), 128 (53), 115 (68), 105 (20), 91 (55), 77 (50), 65 (26), 55 (37). HRMS (APCI): calcd. for $[C_{21}H_{24} + H]^+$ 277.1951; found 277.1946.

Supporting Information (see footnote on the first page of this article): ^1H, ^{11}B, and ^{13}C NMR spectra of all new compounds and ORTEP diagrams of anisotropically refined structures of the compounds studied by XRD.

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1,3-Diethynylbicyclo[1.1.1]pentane has been investigated to prove its usefulness as a versatile rod-like molecular building block that can be considered a nonconjugated analogue of the more frequently used diethynylarylenes. Standard terminal alkyne chemistry worked well, including umpolung reaction to 1-haloalkynes and subsequent cross-coupling with carboranyl or bicyclopentyl bridgehead cuprates.

Keywords: Alkynes / Cross coupling / Umpolung / Small ring systems / Rod-like molecules

